Supplementary Information

AgOTf-catalyzed cascade annulation of 5-hexyn-1-ols and aldehydes: Enabling the diastereoselective synthesis of [6,6,6]-trioxa-fused ketals and hexahydro-2*H*-chromenes

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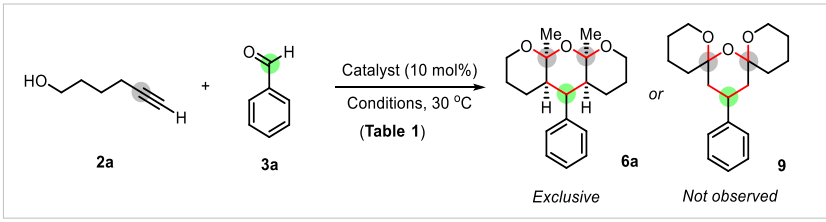
1) *General Information*:

All reactions were performed under argon atmosphere with oven (80 ºC) or flame-dried glassware with a septum seal. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under the argon atmosphere immediately before use. Anhydrous dichloromethane, dichloroethane, methanol and fluorobenzene were purchased from commercial sources and used without any further treatment. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel, and 30 °C corresponds to the room temperature of the laboratory when the experiments were carried out. Analytical thin-layer chromatography (TLC) was performed on TLC Silica gel 60 F254. Visualization was accomplished with short wave UV light, anisaldehyde or $KMnO_4$ staining solutions followed by heating. Chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 200, 400, and 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm), the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; td, triplet doublet; and br, broad. . HRMS data were recorded on Q Exactive HybridTM Quadrupole-OrbitrapTM mass spectrometer (Thermo Scientific, TM Accela 1250 pump). Experimental procedures for all new compounds and known compounds without published experimental procedures are described below. Compounds that are not presented in the main text of the manuscript are numbered starting from **S1**.

2) Table S1. Reaction optimization studies[a]



entry	catalyst	Solvent, time	Temp.	yield (**6a**%)[b]
1.	$Sc(OTf)_3$	CH_2Cl_2, 24 h	rt	-[d]
2.	$Ni(OTf)_2$	CH_2Cl_2, 24 h	rt	-[d]
3.	$Zn(OTf)_2$	CH_2Cl_2, 24 h	rt	-[d]
4.	$Bi(OTf)_3$	CH_2Cl_2, 24 h	rt	-[d]
5.	$Hg(OTf)_2$	CH_3CN:H_2O(9:1), 24 h	rt	-[d]
6.	$Yb(OTf)_2$	CH_3CN	rt	-[d]
7.	$Ln(OTf)_3$	CH_2Cl_2, 24 h	rt	-[d]
8.	$In(OTf)_3$	CH_2Cl_2, 24 h	rt	-[d]
9.	*p*-TSA	CH_2Cl_2, 24 h	rt	-[d]
	Solvent screening			
10.	AgOTf	CH_3CN , 24 h	rt	15
11.	AgOTf	$(CH_2)_2Cl_2$, 5 h	rt	65
12.	AgOTf	$(CH_2)_2Cl_2$, 3 h	80° C	73
13.	AgOTf	PhF, 24 h	rt	49
14.	AgOTf	PhF, 24 h	80° C	70
	Catalyst load screening			
15.	AgOTf (5 mol%)	CH_2Cl_2, 24 h	rt	49
16.	AgOTf (2 mol%)	CH_2Cl_2, 24 h	rt	30

[a]Unless otherwise noted, all reaction were carried out with **2a** (1.17 mmol), **3a** (0.47 mmol) and catalyst (10 mol %), in the indicated solvent (anhydrous, 2 mL) at 30 °C. [b]Isolated yields of **6a**. [c]**2a** (0.47 mmol) and **3a** (0.47 mmol) were used. [d]No reaction observed. Tf = triflate (CF_3SO_2).

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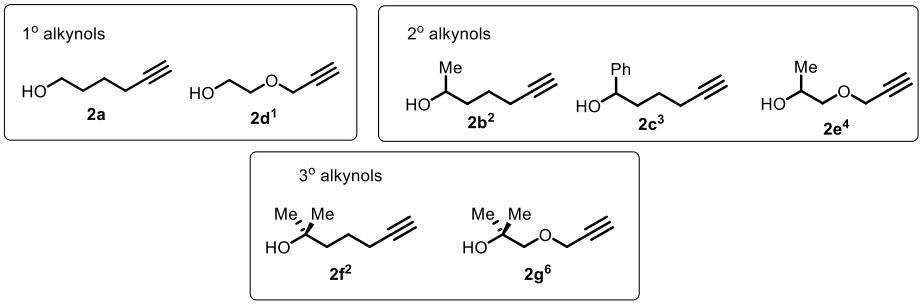
3) Synthesis of 5-hexyn-1-ols (2):

Alkynol **2a** was purchased from commercial sources, and alkynols (**2b**-**2g**) were synthesised by using known literature reports (see below details of chemical structures with related references.[1,2,3,4,5,6]

[1] (a)Thorat, S. S.; Kataria, P.; Kontham, R. *Org. Lett.* **2018**, 20, 872−875. (b) Ashwini K. N.; Madhukar S. P.; Ravindar K. *Org. Biomol. Chem*., **2018**, *16*, 3229-3240.

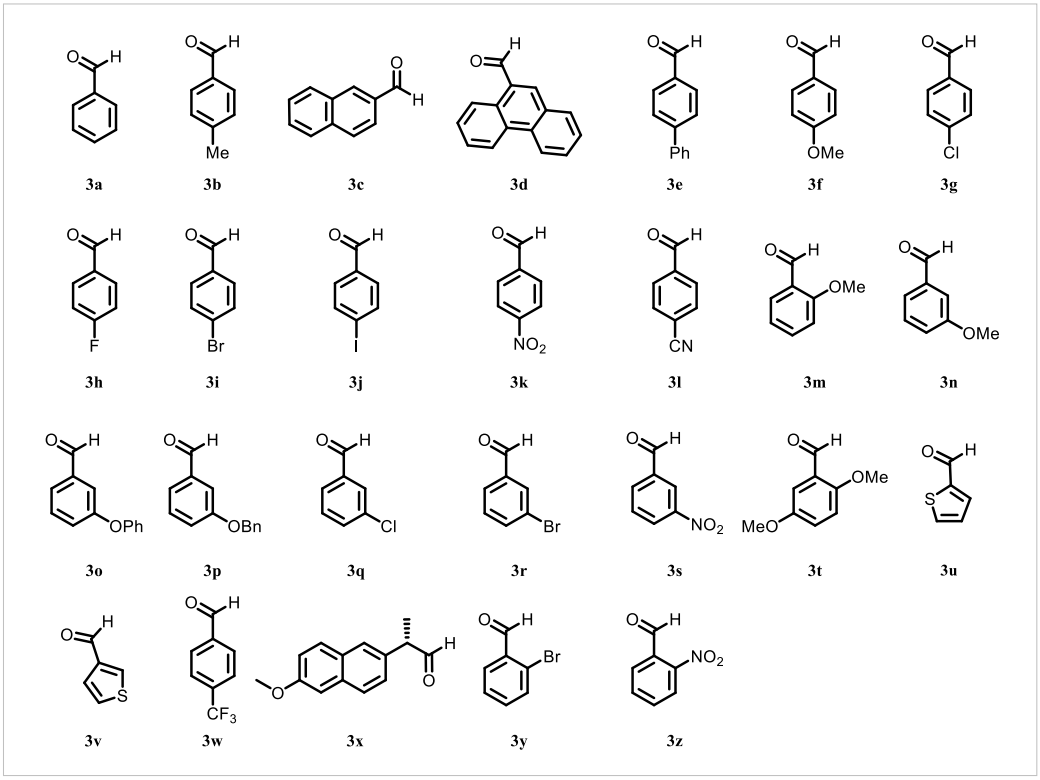
[2] Nakate, A. K.; Thorat, S. S.;Jain, S.; Gamidi, R. K.; Kumar, V.; Kontham, R. *Org. Chem. Front*, **2022**, 9, 802–809.

[3] Rizk, T.; Bilodeau, E. J. F.; Beauchemin, A. M. Angew. Chemie - Int. Ed. 2009, 48 (44), 8325-8327.

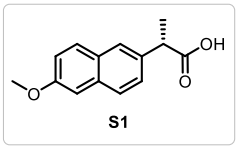


4) General Information on aldehydes (3)

All aldehydes (**3a-3r'**) were purchased from commercial sources.



(*S*)-2-(6-Methoxynaphthalen-2-yl)propanoic acid (S1):



(*S*)-Naproxen tablets were crushed and partitioned between ethyl acetate and 1.0 M HCl to neutral pH and extracted with 100 mL of EtOAc (10 mL X 3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.62 (m, 3H), 7.41 (dd, *J* =

[4] Harada, T.; Muramatsu, K.; Mizunashi, K.; Kitano, C.; Imaoka, D.; Fujiwara, T.; Kataoka, H. *J. Org. Chem.*, **2008**, *73*, 249–258.

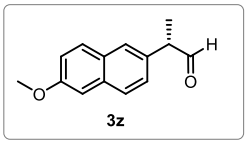
[5] Hamasaka, G.; Uozumi, Y. *Chem comm*. **2014**, 50 (93) 14516-14518;

[6] Singh, U. S.; Court, C. PCT. **2013**, No. 12. (WO 2013/086397 Al).

[7]Bellotti, P.; Huang, H. M.; Faber, T.; Laskar, R.; Glorius, F. Catalytic Defluorinative Ketyl-Olefin Coupling by Halogen-Atom Transfer. *Chem. Sci.* **2022**, *13* (26), 7855–7862.

1.8, 8.4 Hz, 1H), 7.19-7.05 (m, 2H), 3.97-3.80 (m, 4H), 1.59 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.4, 157.7, 134.9, 133.8, 129.3, 128.9, 127.2, 126.2, 126.2, 119.1, 105.6, 55.3, 45.2, 18.2.

(*S*)-2-(6-Methoxynaphthalen-2-yl)propanal (3z):



In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, naproxen (**S1**) (691 mg, 3.00 mmol, 1.00 equiv.) was dissolved in dry THF (15 mL), then the solution was cooled to 0 °C and $LiAlH_4$ (342 mg, 9.00 mmol, 3.00 equiv.) was added portion wise, then the reaction was warmed at room temperature and stirred overnight. The reaction was diluted with Et_2O (20 mL), cooled to 0 °C and carefully quenched with water (400 µL), NaOH (2M, 400 µL), and water (1.2 mL). After warming to room temperature, $MgSO_4$ was added and the suspension was filtered over a short pad Celite®, rinsing thoroughly with Et_2O and the solvent was removed in vacuo. The intermediate alcohol was dissolved in CH_2Cl_2 (20 mL) and pyridinium chlorochromate (1.29 g, 6.00 mmol, 2.00 equiv.) was added portion wise. The reaction was stirred for 90 minutes, the diluted with Et_2O (40 mL) and filtered over a pad of Celite, thoroughly rinsing with Et_2O. The volatiles were removed in vacuo, then the residue was purified by flash column chromatography (SiO_2, 25% EtOAc /hexanes) to afford (**3z**) (0. 47 g, 74%) as a white solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.38 Hz, 1H), 7.75-7.70 (m, 2H), 7.59 (s, 1H), 7.32-7.22 (m, 1H), 7.21-7.10 (m, 2H), 3.91 (s, 3H), 3.75 (q, *J* = 7.70, 13.63 Hz, 1H), 1.51 (d, *J* = 7.00 Hz, 3H); ^{13}C NMR (101MHz, $CDCl_3$) δ 201.3, 158.0, 134.0, 132.8, 129.3, 129.3, 127.8, 127.1, 126.8, 119.4, 105.7, 55.4, 53.0, 14.8. The experimental data are known in the literature report[7].

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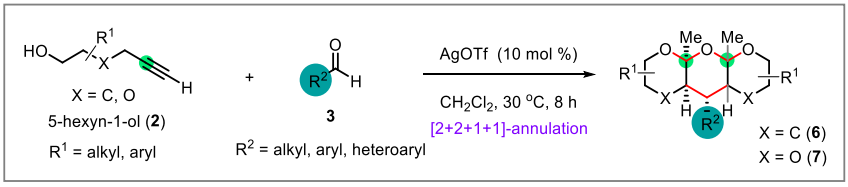
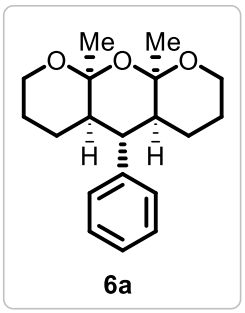
5) *General Procedure A* for the Synthesis and characterization of [6,6,6]-bis-pyrano pyrans (6&7) from alkynols (2) and aldehydes (3):



Alkynol **2 (**1.17 mmol, 2.5 equiv) and aldehyde **3** (0.47 mmol, 1.0 equiv) was taken into a single neck 10 mL round bottom flask equipped with positive argon flow, then dissolved in 2 mL of anhydrous CH_2Cl_2. Catalyst (AgOTf, 0.047 mmol, 0.1 equiv) was added under an argon atmosphere at 30 °C. The resulting reaction mixture was stirred at 30 °C. After

completion of the reaction (monitored by TLC, visualized using UV, anisaldehyde, and $KMnO_4$ staining solutions), quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2x5 mL), then washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered through a sintered glass funnel. The filtrate was concentrated under reduced pressure and purified using silica-gel column chromatography (SiO_2, 100-200 mesh) to afford the corresponding bis-pyrano pyran **6** and **7.**

9a,10a-Dimethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6a):



6a

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.115 g, 0.99 mmol, 2.5 equiv) and benzaldehyde (**3a**) (0.05 g, 1.17 mmol, 1.0 equiv, 0.1 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.012g, 0.047 mmol) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6a**) (0.261 g, 92%) as a colourless liquid (single diastereomer). The **6a** was confirmed by ^1H, ^{13}C, DEPT, HRMS and X-ray analysis; M.P (Melting Point) = 185-188 ^oC; TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.01 (dd, *J* = 4.8, 11.7 Hz, 2H), 3.70-3.62 (m, 3H), 1.84-1.79 (m, 3H), 1.65-1.57 (m, 3H), 1.52 (s, 6H), 1.25-1.19 (m, 2H), 1.11 (d, *J* = 13.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.6, 128.9, 128.0, 126.6, 99.6, 64.5, 43.7, 36.9, 24.0, 23.8, 20.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{27}O_3$ 303.1995; Found 303.1951.

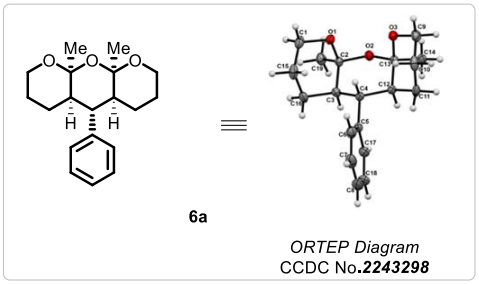
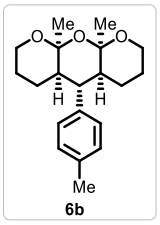


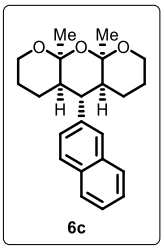
Figure 1. ORTEP diagram of compound **6a**.

9a,10a-Dimethyl-5-(p-tolyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6b):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol(**2a**) (0.204 g, 2.08 mmol, 2.5 equiv) and 4-methylbenzaldehyde (**3b**) (0.1 g, 0.83 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.021 g, 0.083 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(p-tolyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6b**) (0.223 g, 85%) as a colourless liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.13 (d, *J* = 7.88 Hz, 2H), 7.06 (dd, *J* = 8.0 Hz, 2H), 4.00 (dd, *J* = 5.6, 11.9 Hz, 2H), 3.70-3.58 (m, 3H), 2.33 (s, 3H), 1.84-1.77 (m, 3H), 1.65-1.60 (m, 3H), 1.51 (s, 6H), 1.25-1.19 (m, 2H), 1.14-1.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.4, 136.1, 129.6, 127.8, 99.6, 64.5, 43.7, 36.5, 24.0, 23.8, 21.2, 20.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{20}H_{29}O_3$ 317.4410; Found 317.4405.

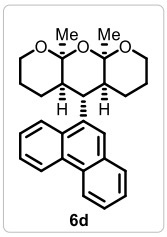
9a,10a-Dimethyl-5-(naphthalen-2-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6c):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.163 g, 1.66 mmol, 2.5 equiv) and 2-naphthaldehyde (**3c**) (0.1 g, 0.66 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0169 g, 0.066 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(naphthalen-2-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6c**) 0.168 g, 75%) as a colourless liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.79 (m, 3H), 7.66 (s, 1H), 7.49-7.43 (m, 2H), 7.31 (dd, *J* = 1.6, 8.4 Hz, 1H), 4.04 (dd, *J* = 5.6, 11.9 Hz, 2H), 3.84 (t, *J* = 11.8 Hz, 1H), 3.69 (dt, *J* = 2.8, 12.5 Hz, 2H), 1.96-1.88 (m, 3H), 1.62 (s, 1H), 1.60 (s, 2H), 1.55 (s, 6H), 1.25-1.19 (m,

2H), 1.11 (d, *J* = 12.13 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.9, 133.7, 132.6, 128.8, 127.8, 127.6, 126.2, 125.6, 99.6, 64.6, 43.5, 37.1, 24.0, 23.9, 20.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{23}H_{29}O_3$ 353.2111; Found 353.2110.

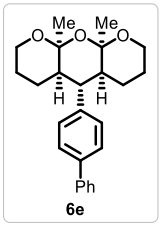
9a,10a-Dimethyl-5-(phenanthren-9-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6d):



6d

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.118 g, 1.20 mmol, 2.5 equiv) and phenanthrene-9-carbaldehyde (**3d**) (0.1 g, 0.48 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0122 g, 0.048 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(phenanthren-9-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6d**) 0.157 g, 81%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.75-8.73 (m, 2H), 8.34-8.31 (m, 1H), 8.13-8.11 (m, 1H), 7.66-7.63 (m, 4H), 6.90 (d, *J* = 2.0 Hz, 1H), 4.16-4.07 (dt, *J* = 2.25, 12.38 Hz, 2H), 4.01-3.94 (m, 2H), 2.92-2.90 (m**,** 2H), 2.70-2.65 (m, 2H), 2.01-1.94 (m, 2H), 1.79-1.72 (m, 2H), 1.70 (s, 6H) 1.26 (s, 1H), 1.21 (m, 1H), 1.00-0.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.4, 141.7, 136.6, 131.2, 129.4, 128.1, 127.5, 126.9, 126.5, 126.3, 125.1, 124.9, 124.7, 123.5, 123.4, 118.5, 85.2, 62.3, 29.2, 25.1, 19.4; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{27}H_{31}O_3$ 403.5340; Found 403.5339.

5-([1,1'-Biphenyl]-4-yl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6e):

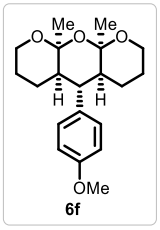


6e

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.134 g, 1.37 mmol, 2.5 equiv) and [1,1'-biphenyl]-4-carbaldehyde (**2e**) (0.1 g, 0.54 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0138 g, 0.054 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction,

quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-([1,1'-biphenyl]-4-yl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6e**) (0.155 g, 75%) as a colourless liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.55 (m, 4H), 7.46-7.42 (m, 2H), 7.36-7.31 (m, 1H), 7.26-7.23 (m, 2H), 4.03 (dd, *J* = 5.4, 11.9 Hz, 2H), 3.73-3.65 (m, 3H), 1.87-1.83 (m, 3H), 1.68-1.62 (m, 3H), 1.54 (s, 6H), 1.33-1.28 (m, 2H), 1.14 (d, *J* = 14.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, δ 141.7, 140.9, 139.4, 128.9, 128.8, 128.3, 127.5, 127.3, 127.1, 127.0, 99.6, 64.5, 43.7, 36.6, 24.0, 23.9, 20.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{25}H_{31}O_3$ 379.2268; Found 379.2263.

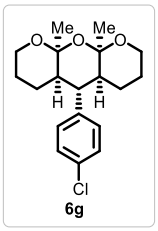
5-(4-Methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6f):



6f

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.180 g, 1.83 mmol, 2.5 equiv) and 4-methoxybenzaldehyde (**3f**) (0.1 g, 0.73 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0187 g, 0.073 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(3-methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6f**) (0.195 g, 80%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.00 (dd, *J* = 5.4, 11.9 Hz, 2H), 3.80 (s, 3H), 3.69-3.56 (m, 3H), 1.82-1.74 (m, 3H), 1.64-156 (m, 3H), 1.51 (s, 6H), 1.27-1.23 (m, 2H), 1.13-1.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.3, 134.5, 128.7, 114.3, 99.6, 64.5, 55.4, 43.9, 36.1, 24.0, 23.8, 20.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{20}H_{29}O_4$ 333.4123; Found 333.4117.

5-(4-Chlorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6g):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol(**2a**) (0.174 g, 1.77 mmol, 2.5 equiv) and 4-chlorobenzaldehyde (**3g**) (0.1 g, 0.57 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0146 g, 0.057 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(4-chlorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6g**) (0.179 g, 75%) %) as a light yellow colour liquid (single diastereomer). The **6g** was confirmed by ^1H, ^{13}C, DEPT, HRMS and X-ray analysis; TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$,400 MHz): δ 7.32-7.27 (m, 2H), 7.14-7.09 (m, 2H), 4.00 (dd, *J* = 5.4, 12.0 Hz, 2H), 3.71-3.60 (m, 3H), 1.79-1.75 (m, 3H), 1.63 (tt, *J* = 4.2, 13.9 Hz, 3H), 1.51 (s, 6H), 1.23-1.17 (m, 2H), 1.12 (dd, *J* = 3.0, 13.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.1, 132.2, 129.2, 129.1, 99.5, 64.5, 43.7, 36.5, 29.8, 23.9, 23.7, 19.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}ClO_3$ 337.8447; Found 337.8443.

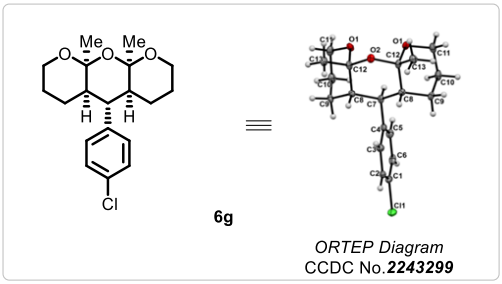
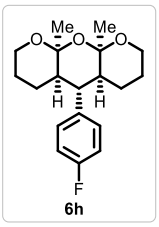


Figure 2. ORTEP diagram of compound **6g**.

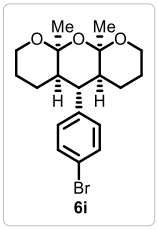
5-(4-Fluorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6h):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.193 g, 2.00 mmol, 2.5 equiv) and 4-flourobenzaldehyde (**3h**) (0.1 g, 0.80 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.020 g, 0.080 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture

was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(4-fluorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6h**) (0.193 g 75%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06-7.19 (m, 2H), 6.95-7.05 (m, 2H), 4.00 (dd, *J* = 11.9, 5.4 Hz, 2H), 3.60-3.71 (m, 3H), 1.74-1.80 (m, 3H), 1.54-1.70 (m, 3H), 1.51 (s, 6H), 1.16-1.23 (m, 2H), 1.07-1.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ,161.57 (d, J_{CF} = 244.14 Hz), 138.12 (d, J_{CF} = 3.05 Hz), 129.2, 115.71 (d, J_{CF} = 21.36 Hz), 99.5, 64.5, 43.8, 36.3, 23.9, 23.7, 19.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.4; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}FO_3$ 321.4044; Found 321.4039.

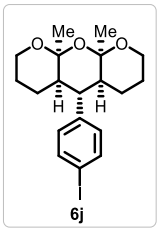
5-(4-Bromophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6i):



6i

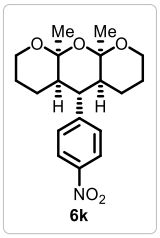
Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.132 g, 1.35 mmol, 2.5 equiv) and 4-bromobenzaldehyde (**3i**) (0.1 g, 0.50 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0128 g, 0.050 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(4-bromophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6i**) (0.144 g, 72%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.39 (m, 2H), 7.09-7.02 (m, 2H), 4.00 (dd, *J* = 5.3, 11.9 Hz, 2H), 3.71-3.60 (m, 3H), 1.80-1.74 (m, 3H), 1.68-1.60 (m, 3H), 1.51 (s, 6H), 1.23-1.16 (m, 2H), 1.12 (dd, *J* = 2.9, 13.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.6, 132.1, 129.7, 120.2, 99.5, 64.5, 43.7, 36.6, 23.9, 23.8, 19.9, 14.3;HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}BrO_3$ 382.1060; Found 382.1057.

5-(4-Iodophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6j):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.107 g, 1.00 mmol, 2.5 equiv) and 4-iodobenzaldehyde (**3j**) (0.1 g, 0.43 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0110 g, 0.043 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(4-iodophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6j**) (0.152 g, 83%) as a colourless liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.00 (dd, *J* = 5.4, 11.9 Hz, 2H), 3.71-3.60 (m, 3H), 1.79-1.73 (m, 3H), 1.63-1.59 (m, 3H), 1.51 (s, 6H), 1.24-1.17 (m, 2H), 1.12 (dd, *J* = 2.9, 13.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.3, 138.0, 130.0, 99.5, 91.6, 64.5, 43.6, 36.7, 29.8, 23.9, 23.8, 19.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}IO_3$ 429.0921; Found 429.0924.

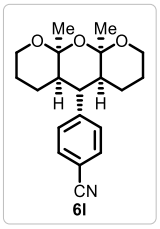
9a,10a-Dimethyl-5-(4-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6k):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.162 g, 1.65 mmol, 2.5 equiv) and 4-nitrobenzaldehyde (**3k**) (0.1 g, 0.66 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0159 g, 0.066 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(4-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6k**) (0.164 g, 72%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.24-8.18 (m, 2H), 7.41-7.34 (m, 2H), 4.02

(dd, *J* = 5.2, 11.9 Hz, 2H), 3.85 (t, *J* = 11.7 Hz, 1H), 3.68 (dt, *J* = 2.7, 12.4 Hz, 2H), 1.86-1.64 (m, 6H), 1.53 (s, 6H), 1.20-1.04 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.9, 146.9, 128.8, 124.3, 99.3, 64.4, 43.6, 37.4, 23.8, 23.8, 19.8; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}NO_5$ 348.1805; Found 348.1802.

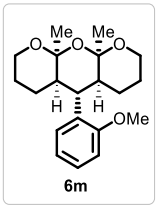
9a,10a-Dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran-5-yl)benzonitrile(6l):



6l

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.187 g, 1.90 mmol, 2.5 equiv) and 4-formylbenzonitrile (**3l**) (0.1 g, 0.76 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0194 g, 0.076 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran-5-yl)benzonitrile (**6l**) (0.174 g, 70%) as a colourless liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.26 Hz, 2H), 4.01 (dd, *J* = 4.13, 12.38 Hz, 2H), 3.77 (t, *J* = 11.7 Hz, 1H), 3.71-3.63 (m, 2H), 1.83-1.62 (m, 6H), 1.52 (s, 6H), 1.19-1.06 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 148.7, 132.8, 128.8, 118.9, 110.6, 99.3, 64.4, 43.5, 37.5, 23.9, 23.8, 19.8; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{26}NO_3$ 328.1907; Found 328.1901.

5-(2-Methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6m):

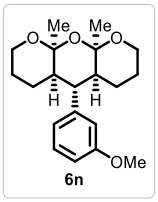


6m

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.180 g, 1.83 mmol, 2.5 equiv) and 2-methoxybenzaldehyde (**3m**) (0.1 g, 0.73 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0187g, 0.073 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through

sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(2-methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6m**) (0.185 g, 76%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 6.6 Hz, 1H), 6.99-6.90 (m, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 4.34 (t, *J* = 11.8 Hz, 1H), 3.99 (dd, *J* = 5.0, 11.3 Hz, 2H), 3.84 (s, 3H), 3.68-3.60 (m, 2H), 2.03-1.93 (m, 2H), 1.79-1.69 (m, 2H), 1.60-1.57 (m, 2H), 1.51 (s, 6H), 1.22-1.15 (m, 2H), 1.07 (d, *J* = 12.88 Hz, 2H); ^{13}C NMR ($CDCl_3$,101 MHz): δ 127.0, 126.4, 121.2, 110.4, 99.6, 64.7, 55.5, 44.0, 29.8, 27.6, 24.3, 24.1, 20.3; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{20}H_{29}O_4$ 333.4400; Found 333.4389.

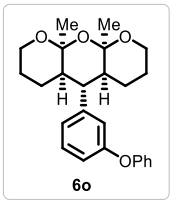
5-(3-Methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6n):



6n

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.180 g, 1.83 mmol, 2.5 equiv) and 3-methoxybenzaldehyde (**3n**) (0.1 g, 0.73 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.173g, 0.073 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(3-methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6n**) (0.195 g, 80%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.21 (m, 1H), 6.81-6.70 (m, 3H), 4.01 (dd, *J* = 4.8, 11.3 Hz, 2H), 3.81 (s, 3H), 3.69-3.62 (m, 3H), 1.80-1.75 (m, 3H), 1.64-1.59 (m, 3H), 1.52 (s, 6H), 1.12 (d, *J* = 12.6 Hz, 2H), 1.00-0.7 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.1, 144.3, 129.8, 111.2, 99.6, 64.5, 55.3, 43.6, 37.0, 29.8, 24.0, 23.8, 20.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{20}H_{29}O_4$ 333.4213; Found 333.4209.

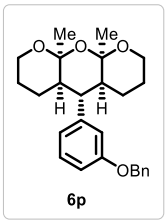
9a,10a-Dimethyl-5-(3-phenoxyphenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6o):



6o

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.123 g, 1.26 mmol, 2.5 equiv) and 3-phenoxybenzaldehyde (**3o**) (0.1 g, 0.73 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0128 g, 0.040 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(3-phenoxyphenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6o**) (0.153 g, 77%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.28 (m, 3H), 7.13-7.07 (m, 1H), 7.00-6.92 (m, 3H), 6.89-6.85 (m, 2H), 3.99 (dd, *J* = 5.2, 11.8 Hz, 2H), 3.69-3.61 (m, 3H), 1.80-1.75 (m, 3H), 1.72-1.58 (m, 3H), 1.51 (s, 6H), 1.32-1.26 (m, 2H), 1.15-1.09 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 z): δ 157.6, 157.5, 144.8, 130.1, 129.9, 123.3, 118.6, 117.1, 99.5, 64.5, 43.6, 37.0, 23.9, 23.8, 19.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{25}H_{31}O_4$ 395.5110; Found 395.5106.

5-(3-(Benzyloxy)phenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6p)

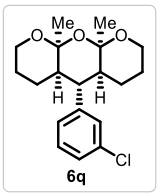


6p

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.115 g, 1.17 mmol, 2.5 equiv) and 3-(benzyloxy)benzaldehyde (**3p**) (0.1 g, 0.47 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0120 g, 0.047 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(3-(benzyloxy)phenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6p** (0.143 g, 74%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.18 (m, 7H), 6.88-

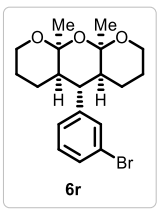
6.82 (m, 1H), 6.81-6.74 (m, 2H), 5.06 (s, 2H), 4.04-3.97 (m, 2H), 3.69-3.59 (m, 3H), 1.80-1.75 (m, 3H), 1.61-1.59 (m, 3H), 1.51 (s, 6H), 1.25-1.19 (m, 2H), 1.14-1.06 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.3, 144.3, 137.1, 129.8, 128.7, 128.1, 127.7, 112.5, 99.5, 70.1, 64.5, 43.6, 24.0, 23.8, 20.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{26}H_{33}O_4$ 409.2373; Found 409.2369.

5-(3-Chlorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6q):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.174 g, 1.77 mmol, 2.5 equiv) and 3-chlorobenzaldehyde (**3q**) (0.1 g, 0.57 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0146 g, 0.057 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(3-chlorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6q**) (0.162 g, 68%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.34 (m, 1H), 7.33-7.08 (m, 1H), 7.19 (t, *J* = 7.75 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.00 (dd, *J* = 4.5, 11.8 Hz, 2H), 3.73-3.59 (m, 3H), 1.82-1.76 (m, 3H), 1.71-1.59 (m, 3H), 1.52 (s, 6H), 1.24-1.18 (m, 2H), 1.14 (d, *J* = 11.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.2, 130.5, 129.9, 123.2, 99.5, 64.5, 43.6, 37.0, 23.9, 23.8, 19.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}ClO_3$ 337.8560; Found 337.8556.

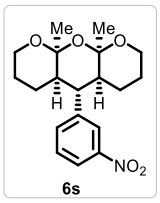
5-(3-Bromophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6r):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.132 g, 1.35 mmol, 2.5 equiv) and 3-bromobenzaldehyde (**3r**) (0.1 g, 0.50 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0128 g, 0.050 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10

mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(3-bromophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6r**) (0.144 g, 70%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (d, *J* = 7.88 Hz, 1H), 7.32 (s, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.00 (dd, *J* = 4.7, 11.8 Hz, 2H), 3.73-3.59 (m, 3H), 1.82-1.76 (m, 3H), 1.71-1.59 (m, 3H), 1.52 (s, 6H), 1.24-1.18 (m, 2H), 1.14 (d, *J* = 13.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.2, 130.5, 129.9, 123.2, 99.5, 64.5, 43.6, 37.0, 23.9, 23.8, 19.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}BrO_3$ 382.1060; Found 382.1057.

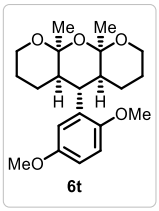
9a,10a-Dimethyl-5-(3-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6s):



6s

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.162 g, 1.65 mmol, 2.5 equiv) and 3-nitrobenzaldehyde (**3s**) (0.1 g, 0.66 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0169 g, 0.066 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(3-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6s**) (0.160 g, 70%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (td, *J* = 1.9, 7.5 Hz, 1H), 8.06-8.02 (m, 1H), 7.57-7.47 (m, 2H), 4.02 (dd, *J* = 4.38, 12.3 Hz, 2H), 3.84 (t, *J* = 11.8 Hz, 1H), 3.68 (dt, *J* = 2.6, 12.3 Hz, 2H), 1.88-1.66 (m, 6H), 1.53 (s, 6H), 1.21-1.07 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 149.0, 145.1, 129.9, 121.9, 99.4, 64.4, 43.6, 37.2, 23.9, 23.8, 19.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{19}H_{26}NO_5$ 348.1727; Found 348.1830.

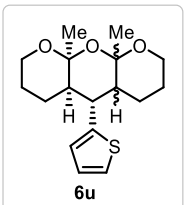
5-(2,5-Dimethoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6t):



6t

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.147 g, 1.50 mmol, 2.5 equiv) and 2,5-dimethoxybenzaldehyde (**3t**) (0.1 g, 0.60 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0153 g, 0.060 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(2,5-dimethoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6t)** (0.152 g, 70%) as a colourless liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81 (d, *J* = 8.8 Hz, 1H), 6.70 (dd, *J* = 2.9, 8.8 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 4.30 (t, *J* = 11.9 Hz, 1H), 3.98 (dd, *J* = 5.4, 11.5 Hz, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 3.67-3.62 (m, 2H), 2.00-1.94 (m, 2H), 1.72 (d, *J* = 12.1 Hz, 2H), 1.59 (s, 2H), 1.51 (s, 6H), 1.21 (d, *J* = 13.6 Hz, 2H), 1.08 (d, *J* = 13.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.2, 153.4, 133.1, 112.9, 111.2, 110.8, 99.6, 64.7, 56.0, 55.8, 44.1, 28.0, 24.3, 24.1, 20.3; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{21}H_{31}O_5$ 363.2088; Found 363.2238.

9a,10a-Dimethyl-5-(thiophen-2-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6u):

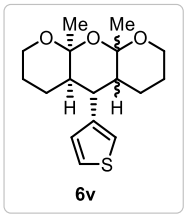


6u

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol(**2a**) (0.218 g, 2.20 mmol, 2.5 equiv) and thiophene-2-carbaldehyde (**3u**) (0.1 g, 0.89 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.022 g, 0.089 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(thiophen-2-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran

(**6u**) 0.178 g, 65%) as a light yellow colour liquid with *dr* 1:1. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (dd, *J* = 1.0, 5.0 Hz, 1H), 6.98-6.95 (m, 3H), 6.00-6.67 (m, 1H), 6.24 (d, *J* = 3.5 Hz, 1H), 4.01 (d, *J* = 9.0 Hz, 2H), 3.98-3.95 (m, 1H), 3.81-3.70 (m, 3H), 3.42 (dd, *J* = 3.6, 11.8 Hz, 1H), 2.60-2.54 (m, 1H), 2.47-2.40 (m, 2H), 2.36 2.24 (m, 2H), 2.17-2.10 (m, 1H), 2.10-2.01 (m, 2H), 1.97-1.85 (m, 3H), 1.84-1.72 (m, 6H), 1.71-1.61 (m, 4H), 1.59-1.56 (br. s., 4H), 1.42-1.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.2, 142.9, 127.6, 127.0, 126.4, 126.1, 124.6, 103.9, 97.6, 63.2, 62.8, 44.6, 43.4, 43.0, 40.6, 38.8, 27.5, 27.0, 24.6, 22.4, 21.3; HRMS (ESI) *m/z*[M+H]$^+$ Calcd for $C_{17}H_{25}O_3S$ 309.1519; Found 309.1918.

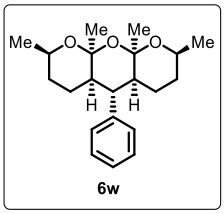
9a,10a-Dimethyl-5-(thiophen-3-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6v):



6v

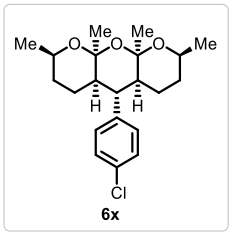
Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.218 g, 2.20 mmol, 2.5 equiv) and thiophene-3-carbaldehyde (**3v**) (0.1 g, 0.89 mmol, 1.0 equiv, 0.1 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.022 g, 0.089 mmol) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-5-(thiophen-3-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-*e*]pyran (**6v**) 0.192 g, 70%) as a light yellow colour liquid with *dr* 1:1. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (dd, *J* = 3.0, 5.0 Hz, 1H), 7.24-7.23 (m, 1H), 7.21-7.19 (m, 2H), 7.01-7.00 (m, 1H), 6.74 (dd, *J* = 1.3, 5.0 Hz, 1H), 4.11-4.02 (m, 1H), 3.93 (dd, *J* = 6.0, 12.0 Hz, 1H), 3.84-3.79 (m, 2H), 3.78-3.74 (m, 1H), 3.59 (dt, *J* = 3.0, 12.6 Hz, 1H), 2.57-2.51 (m, 1H), 2.26-2.20 (m, 1H), 2.10-2.04 (m, 1H), 1.94-1.86 (m, 1H), 1.80-1.75 (m, 2H), 1.58-1.53 (m, 3H), 1.51 (s, 3H), 1.34 (d, *J* = 5.3 Hz, 1H), 1.30-127 (m, 2H), 1.27-1.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.7, 140.8, 130.0, 128.6, 125.6, 124.5, 123.0, 122.5, 103.1, 97.3, 63.1, 62.5, 44.1, 43.7, 43.0, 38.9, 34.5, 29.8, 26.6, 26.1, 24.8, 24.5, 21.3; HRMS (ESI) *m/z:* [M+H]$^+$ Calcd for $C_{17}H_{25}O_3S$ 309.4360; Found 309.4357.

2,8,9a,10a-Tetramethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6w):



Following the *General Procedure A*, to the mixture of hept-6-yn-2-ol (**2b**) (0.263 g, 2.35 mmol, 2.5 equiv) and benzaldehyde (**3a**) (0.1 g, 0.94 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.024 g, 0.094 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 2,8,9a,10a-tetramethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6w**) 0.202 g, 65%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes);^{1}H NMR ($CDCl_3$, 400 MHz): 7.33 - 7.39 (m, 3H) 7.16 - 7.21 (m, 2H) 3.56 - 3.69 (m, 1H) 3.17 - 3.24 (m, 1H) 2.88 - 3.03 (m, 1H) 2.29 - 2.41 (m, 1H) 2.05 - 2.14 (m, 3H) 1.71 - 1.83 (m, 2H) 1.57 (s, 6H) 1.22 - 1.30 (m, 6H) 0.80 - 0.83 (m, 2H) 0.71 - 0.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 149.7, 131.8, 126.1, 124.7, 123.7, 101.5, 101.2, 70.2, 68.4, 49.3, 44.7, 42.8, 34.0, 27.9, 25.1, 24.2, 23.6, 22.6, 22.4, 19.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{21}H_{31}O_3$ 331.4242; Found 331.4240.

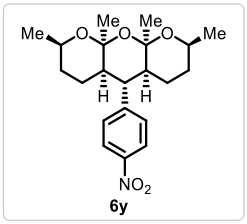
2,8,9a,10a-Tetramethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6x):



Following the *General Procedure A*, to the mixture of hept-6-yn-2-ol (**2b**) (0.199 g, 1.77 mmol, 2.5 equiv) and 4-chlorobenzaldehyde (**3g**) (0.1 g, 0.71 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0181 g, 0.071 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 2,8,9a,10a-tetramethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6x**) 0.176 g, 68%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2,

40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (dd, *J* = 1.7, 8.1 Hz, 1H), 7.58 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.28 (d, *J* = 1.4 Hz, 1H), 7.21 (dd, *J* = 1.6, 7.8 Hz, 1H), 3.92-3.83 (m, 1H), 3.79-3.69 (m, 1H), 2.90 (t, *J* = 11.7 Hz, 1H), 1.96-191 (m, 1H), 1.85-1.75 (m, 1H), 1.69 (m, 3H), 1.59 (s, 3H), 1.58-1.49 (m, 2H), 1.33-1.08 (m, 12H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 147.5, 133.2, 132.3, 131.8, 126.1, 118.9, 110.8, 101.5, 101.2, 70.2, 68.3, 49.2, 44.6, 43.0, 34.0, 29.8, 27.9, 25.1, 24.2, 23.6, 22.6, 22.4, 19.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{21}H_{30}O_3Cl$ 365.1800; Found 365.1905.

2,8,9a,10a-Tetramethyl-5-(4-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6y):

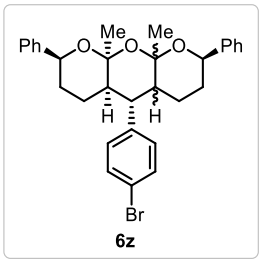


6y

Following the *General Procedure A*, to the mixture of hept-6-yn-2-ol (**2b**) (0.226 g, 1.98 mmol, 2.5 equiv) and 4-nitrobenzaldehyde (**3k**) (0.1 g, 0.79 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.020 g, 0.079 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 2,8,9a,10a-tetramethyl-5-(4-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6y**) 0.161 g, 65%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31-8.09 (m, 2H), 7.42-7.26 (m, 2H), 3.98-3.63 (m, 2H), 2.98 (t, *J* = 11.7 Hz, 1H), 2.05-1.74 (m, 3H), 1.70 (s, 3H), 1.60 (s, 3H), 1.33-1.07 (m, 13H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 149.7, 147.0, 131.8, 126.1, 124.7, 123.7, 101.5, 101.2, 70.2, 68.4, 49.3, 44.7, 42.8, 34.0, 27.9, 25.1, 24.2, 23.6, 22.6, 22.4, 19.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{21}H_{30}NO_5$ 376.4165; Found 376.4160.

5-(4-Bromophenyl)-9a,10a-dimethyl-2,8-diphenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6z):

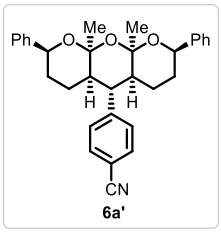
Following the *General Procedure A*, to the mixture of 1-phenylhex-5-yn-1-ol (**2c**) (0.234 g, 1.35 mmol, 2.5 equiv) and 4-bromobenzaldehyde (**3i**) (0.1 g, 0.54 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0138 g, 0.054 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of



6z

reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5-(4-bromophenyl)-9a,10a-dimethyl-2,8-diphenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6z**) 0.181 g, 63%) as a light yellow colour liquid in *dr* 2:1. TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (dd, *J* = 2.3, 8.4 Hz, 1H), 7.43-7.28 (m, 11H), 7.11 (dd, *J* = 2.13, 8.4 Hz, 2H), 6.98 (dd, *J* = 2.25, 8.00 Hz, 1H), 4.84 (dd, *J* = 2.8, 11.9 Hz, 1H), 4.76 (dd, *J* = 3.1, 10.9 Hz, 1H), 2.96 (t, *J* = 11.8 Hz, 1H), 2.10-1.97 (m, 2H), 1.94 (s, 3H), 1.89-1.82 (m, 2H), 1.74 (s, 3H), 1.71-1.68 (m, 1H), 1.60-1.56 (m, 1H), 1.55-1.40 (m, 2H), 1.35-1.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.2, 143.0, 142.3, 140.2, 132.8, 132.6, 131.5, 128.7, 128.6, 128.4, 128.3, 128.1, 127.4, 127.3, 127.2, 126.8, 126.4, 126.4, 126.1, 125.7, 125.5, 120.6, 102.1, 102.1, 100.5, 76.2, 76.1, 74.4, 49.4, 45.0, 43.0, 42.3, 36.7, 34.1, 28.6, 27.9, 25.1, 24.6, 24.4, 24.2, 23.9, 19.6; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{31}H_{34}BrO_3$ 534.2686; Found 534.2696.

9a,10a-Dimethyl-2,8-diphenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran-5-yl)benzonitrile (6a'):

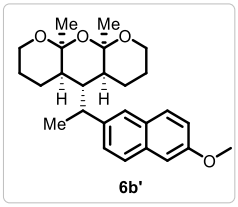


6a'

Following the *General Procedure A*, to the mixture of 1-phenylhex-5-yn-1-ol (**2c**) (0.331 g, 1.90 mmol, 2.5 equiv) and 4-formylbenzonitrile (**3l**) (0.1 g, 0.76 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.015g, 0.076 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 9a,10a-dimethyl-2,8-diphenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran-5-yl)benzonitrile (**6a'**) 0.219 g, 60%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.27- 7.10 (m, 12H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.0 Hz, 1H), 2.94 (t, *J* = 11.6 Hz, 1H), 2.00-1.84 (m, 3H), 1.81 (br. s., 3H), 1.73 (d, *J* = 13.9

Hz, 2H), 1.61 (br. s., 3H), 1.46 (br. s., 2H), 1.24-0.99 (m., 2H), 1.01 (d, *J* = 13.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 147.1, 143.0, 142.1, 133.3, 132.4, 131.9, 128.5, 128.3, 127.5, 127.4, 126.4, 126.1, 125.5, 118.8, 111.0, 102.0, 76.1, 74.4, 49.3, 44.8, 43.1, 34.0, 28.5, 25.0, 24.4, 24.0, 19.6; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{32}H_{34}NO_3$ 480.2531; Found 480.2524.

(*S*)-1-(6-methoxynaphthalen-2-yl)ethyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6b'):

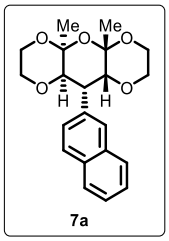


6b'

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.916 g, 0.933 mmol, 2.5 equiv) and 2-(6-methoxynaphthalen-2-yl)propanal (**3x**) (0.1 g, 0.466 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.022 g, 0.046 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford (*S*)-1-(6-methoxynaphthalen-2-yl)ethyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (**6b'**) 0.124 g, 65%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.77-7.70 (m, 2H), 7.63 (s, 1H), 7.37 (dd, *J* = 1.63, 8.38 Hz, 1H), 7.18- 7.13 (m, 2H), 3.93 (s, 3H), 3.87-3.63 (m, 4H), 3.37 (t, *J* = 5.63 Hz, 2H), 2.81 (d, *J* = 2.25 Hz, 1H), 2.58 (s, 1H), 2.25 (s, 3H), 1.69 (m, 2H), 1.65 (m, 2H), 1.54 (m, 4H), 1.30 (s, 3H), 1.25 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 147.0, 146.3, 133.3, 130.1, 129.4, 129.1, 128.3, 127.7, 126.9, 120.7, 119.1, 105.8, 77.5, 77.4, 76.8, 74.3, 61.9, 61.3, 55.5, 38.2, 35.3, 31.9, 29.8, 26.0, 22.3, 20.0, 19.6, 12.4, 0.1; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{26}H_{35}O_4$ $[M+H]^+$ 411.5755; Found 411.5759.

4a,5a-Dimethyl-10-(naphthalen-2-yl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) (7a):

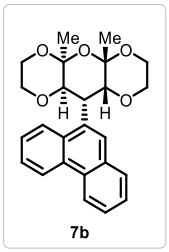
Following the *General Procedure A*, to the mixture of 2-(prop-2-yn-1-yloxy)ethan-1-ol (**2d**) (0.160 g, 1.60 mmol, 2.5 equiv) and 2-naphthaldehyde (**3c**) (0.1 g, 0.64 mmol, 1.0 equiv) in



7a

anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.015g, 0.064 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 4a,5a-dimethyl-10-(naphthalen-2-yl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) **(7a)** 0.171 g, 75%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.84 (m, 1H), 7.83 (s, 2H), 7.71 (dd, *J* = 3.3, 5.8 Hz, 1H), 7.55-7.52 (m, 1H), 7.48-7.44 (m, 2H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.24 - 4.17 (m, 2H), 4.10 (dt, *J* = 2.1, 17.7 Hz, 2H), 4.02 (dd, *J* = 3.6, 12.3 Hz, 1H), 3.83 (dd, *J* = 3.4, 12.2 Hz, 1H), 3.73-3.69 (m, 2H), 3.51-3.45 (m, 2H), 3.21 (dd, *J* = 3.5, 12.1 Hz, 1H), 1.78 (s, 3H), 1.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 135.6, 133.6, 132.9, 131.0, 129.0, 128.3, 128.0, 127.9, 127.8, 127.3, 126.1, 125.8, 97.7, 96.1, 80.3, 71.5, 68.3, 66.1, 64.1, 60.4, 57.8, 39.7, 38.9, 30.5, 29.1, 25.9, 23.9, 23.1, 22.7, 14.2, 11.1; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{21}H_{25}O_5$ 357.4214; Found 357.4208.

4a,5a-Dimethyl-10-(phenanthren-9-yl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) (7b) :



7b

Following the *General Procedure A*, to the mixture of 2-(prop-2-yn-1-yloxy)ethan-1-ol (**2d**) (0.120 g, 1.20 mmol, 2.5 equiv) and phenanthrene-9-carbaldehyde (**3d**) (0.1 g, 0.48 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.012 g, 0.048 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 4a,5a-dimethyl-10-(phenanthren-9-yl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) **(7b**) 0.157 g, 80%) as a light yellow colour liquid (single diastereomer). The **7b** was confirmed by ^1H, ^{13}C, DEPT, HRMS and X-ray analysis; M.P (Melting Point) = 202-204 ^oC; TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ

8.85-8.82 (m, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.15-8.12 (m, 1H), 7.93-7.91 (m, 1H), 7.80 (s, 1H), 7.70-7.86 (m, 1H), 7.64-7.59 (m, 2H), 7.53-7.52 (m, 1H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.22-4.20 (m, 1H), 4.19-4.17 (m, 1H), 4.09-4.03 (m, 1H), 3.86-3.80 (m, 2H), 3.67 (dd, *J* = 2.6, 11.7 Hz, 1H), 3.52-3.46 (m, 1H), 3.43-3.38 (m, 1H), 3.19 (dd, *J* = 3.5, 12.3 Hz, 1H), 1.88 (s, 3H), 1.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 167.9, 132.6, 131.5, 131.4, 131.0, 129.8, 129.1, 129.0, 128.5, 127.1, 126.9, 126.7, 126.1, 124.1, 122.5, 122.2, 98.0, 96.3, 78.0, 70.7, 68.3, 66.2, 64.2, 60.4, 58.2, 38.9, 33.4, 30.5, 29.9, 29.1, 26.0, 23.9, 23.1, 22.8, 14.3, 14.2, 11.1; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{25}H_{27}O_5$ 407.4780; Found 407.4775.

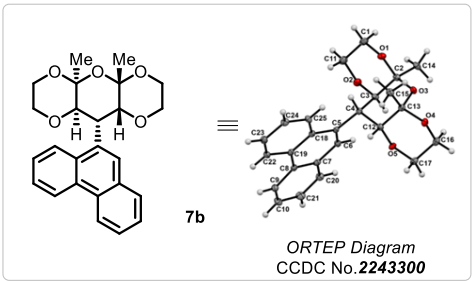
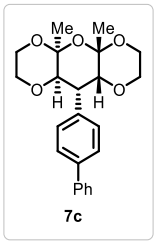


Figure 3. ORTEP diagram of compound **7b**.

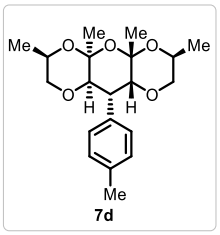
10-([1,1'-Biphenyl]-4-yl)-4a,5a-dimethyloctahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) (7c):



Following the *General Procedure A*, to the mixture of 2-(prop-2-yn-1-yloxy)ethan-1-ol (**2d**) (0.137 g, 1.37 mmol, 2.5 equiv) and [1,1'-biphenyl]-4-carbaldehyde (**3e**) (0.1 g, 0.54 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0138 g, 0.054 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 10-([1,1'-biphenyl]-4-yl)-4a,5a-dimethyloctahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) (**7c**) 0.167 g, 80%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (dd, *J* = 3.3, 5.8 Hz, 1H), 7.61-7.57 (m, 3H), 7.54-7.52 (m, 1H), 7.46-7.41 (m, 3H), 7.36-7.32 (m, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.23-4.18 (m, 2H), 4.04-3.93 (m, 2H), 3.85-3.73 (m, 2H), 3.68 -

3.66 (m, 1H), 3.58-3.51 (m, 1H), 3.47 (dd, *J* = 2.4, 11.3 Hz, 1H), 3.27 (dd, *J* = 3.4, 12.1 Hz, 1H), 1.76 (s, 3H), 1.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 167.9, 141.1, 140.1, 137.1, 132.6, 131.0, 129.7, 129.0, 128.9, 127.2, 97.6, 96.1, 80.1, 77.4, 71.6, 68.3, 66.1, 64.0, 60.4, 57.8, 39.3, 38.9, 30.5, 29.9, 29.1, 25.9, 23.9, 23.1, 22.7, 14.2, 11.1;HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{23}H_{27}O_5$ 383.1853; Found 383.1857.

3,4a,5a,7-Tetramethyl-10-(p-tolyl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) (7d):

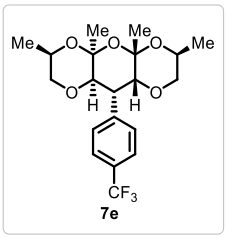


7d

Following the *General Procedure A*, to the mixture of 1-(prop-2-yn-1-yloxy)propan-2-ol (**2e**) (0.238 g, 2.00 mmol, 2.5 equiv) and 4-methylbenzaldehyde (**3b**) (0.1 g, 0.83 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.021 g, 0.083 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 3,4a,5a,7-tetramethyl-10-(p-tolyl)octahydro-10H-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) (**7d**) 0.179 g, 62%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.27 (m, 1H), 7.22-7.11 (m, 3H), 4.34-4.30 (m, 1H), 4.20-4.15 (m, 1H), 4.05-.98 (m, 1H), 3.84-3.79 (m, 1H), 3.69 (dd, *J* = 2.6, 11.4 Hz, 1H), 3.64-3.56 (m, 1H), 3.65-3.60 (m, 1H), 3.23-3.17 (m, 1H), 3.03 (t, *J* = 11.0 Hz, 1H), 2.34 (s, 3 H), 2.33 (s, 1H), 1.70 (s, 3H), 1.64 (s, 2H), 1.47 (d, *J* = 6.88 Hz, 3H), 1.28-1.24 (m, 3H), 1.14-1.08 (m, 4H), 1.07-1.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.4, 129.7, 125.4, 125.4, 97.7, 96.4, 79.1, 71.6, 70.4, 68.7, 64.6, 63.7, 39.4, 29.9, 25.9, 23.3, 17.5, 16.5; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{20}H_{29}O_5$ 349.4391; Found 349.4385.

3,4a,5a,7-Tetramethyl-10-(4-(trifluoromethyl)phenyl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) (7e):

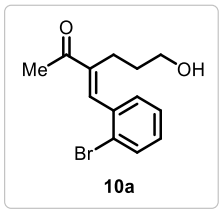
Following the *General Procedure A*, to the mixture of 1-(prop-2-yn-1-yloxy)propan-2-ol (**2e**) (0.163 g, 1.43 mmol, 2.5 equiv) and 4-(trifluoromethyl)benzaldehyde (**3w**) (0.1 g, 0.57 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0146 g, 0.057 mmol, 0.1 equiv)



7e

under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 3,4a,5a,7-tetramethyl-10-(4-(trifluoromethyl)phenyl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine) **(7e**) 0.154 g, 67%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): 7.60 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 4.35 (d, *J* = 11.88 Hz, 2H), 4.24-4.19 (m, 1H), 4.08-4.01 (m, 1H), 3.91 (dd, *J* = 2.0, 11.8 Hz, 1H), 3.69 (dd, *J* = 2.7, 11.4 Hz, 1H), 3.50 (d, *J* = 2.0 Hz, 1H), 3.27-3.21 (m, 1H), 3.17-3.10 (m, 1H), 3.07-3.00 (m, 1H), 1.71 (s, 3H), 1.65 (s, 3H), 1.15-1.10 (m, 4H) 1.07-1.05 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.4, 129.7, 125.4 (d, J_{CF} = 3.81 Hz), 97.7, 96.4, 79.1, 77.4, 71.6, 70.4, 68.7, 64.6, 63.7, 39.4, 29.9, 25.9, 23.3, 17.5, 16.5: ^{19}F NMR ($CDCl_3$, 376 MHz): δ –62.44; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{20}H_{26}F_3O_5$ 403.4102; Found 403.4100.

(*E*)-3-(2-Bromobenzylidene)-6-hydroxyhexan-2-one (10a):

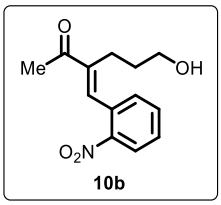


10a

Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.132 g, 1.35 mmol, 2.5 equiv) and 2-bromobenzaldehyde (**3y**) (0.1 g, 0.50 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0128 g, 0.050 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford (*E*)-3-(2-bromobenzylidene)-6-hydroxyhexan-2-one (**10a**) 0.130 g, 85%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.57 (s, 1H), 7.37-7.32 (m, 2H), 7.25-7.20 (m, 1H), 3.52 (t, *J* = 6.2 Hz, 2H), 2.51 (s, 3H), 2.46 (t, *J* = 7.5 Hz, 2H), 1.63-1.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 200.8, 143.1, 140.4, 136.2, 133.0, 130.1, 130.0, 127.6, 123.9, 62.0,

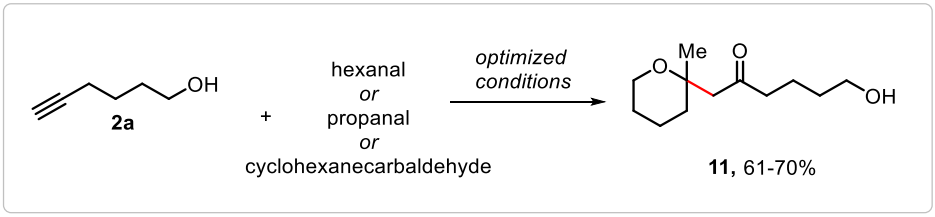
32.1, 26.3, 22.1; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{13}H_{16}BrO_2$ 284.0328; Found 284.0275.

(*E*)-6-Hydroxy-3-(2-nitrobenzylidene)hexan-2-one (10b):



Following the *General Procedure A*, to the mixture of hex-5-yn-1-ol (**2a**) (0.162 g, 1.65 mmol, 2.5 equiv) and 2-nitrobenzaldehyde (**3z**) (0.1 g, 0.66 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0169 g, 0.066 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 6-hydroxy-3-(2-nitrobenzylidene)hexan-2-one (**10b**) 0.145 g, 89%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.19 (dd, *J* = 1.1, 8.3 Hz, 1H), 7.83 (s, 1H), 7.73-7.66 (m, 1H), 7.58-7.52 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 3.47 (t, *J* = 6.1 Hz, 2H), 2.52 (s, 3H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.62 (br. s., 1H), 1.54-1.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 200.4, 142.6, 138.0, 133.9, 132.0, 130.9, 129.5, 125.2, 61.8, 32.1, 26.3, 22.4; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{13}H_{16}NO_4$ 250.2621; Found 250.2618.

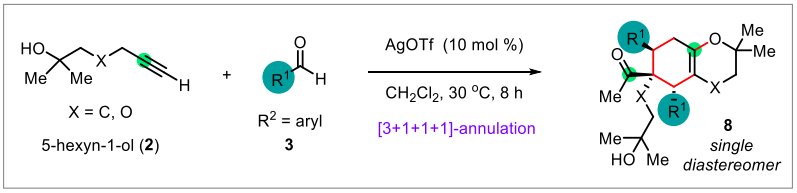
6-Hydroxy-1-(2-methyltetrahydro-2H-pyran-2-yl)hexan-2-one (11):



Following the *General Procedure*, to the mixture of hex-5-yn-1-ol (**2a**) (0.284 g, 0.99 mmol, 2.5 equiv) and hexanal (or) propanal (or) cyclohexanecarbaldehydee (**6**) (1.16 mmol, 1 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.029 g, 0.116 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over

anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) 6-hydroxy-1-(2-methyltetrahydro-2H-pyran-2-yl)hexan-2-one (**11**) 0.152 g, 61%, with hexanal). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.70 - 3.66 (m, 2H), 3.62 (t, *J* = 6.3 Hz, 2H), 2.68 - 2.60 (m, 1H), 2.60 - 2.50 (m, 3H), 1.66 - 1.60 (m, 6H), 1.56 - 1.49 (m, 5H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 210.4, 77.4, 73.0, 62.5, 61.8, 52.9, 44.6, 35.3, 32.2, 29.8, 25.9, 23.1, 19.5, 19.4; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{12}H_{23}O_3$ 215.3050; found 215.2687.

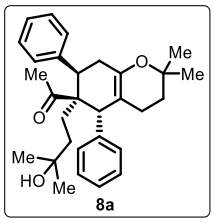
6) *General Procedure B* for the Synthesis and characterization of hexahydro-2*H*-chromens (8) from alkynols (2) and aldehydes (3):



Alkynol **2 (**1.17 mmol, 2.5 equiv) and aldehyde **3** (0.47 mmol, 1.0 equiv) was taken into a single neck 10 mL round bottom flask equipped with positive argon flow, then dissolved in 2 mL of anhydrous DCM. Catalyst (AgOTf, 0.047 mmol, 0.1 equiv) was added under an argon atmosphere at 30 ^{o}C. The resulting reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of the reaction (monitored by TLC, visualized using UV, anisaldehyde, and $KMnO_4$ staining solutions), quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2x5 mL), then washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered through a sintered glass funnel. The filtrate was concentrated under reduced pressure and purified using silica-gel column chromatography (SiO_2, 100-200 mesh) to afford the corresponding hexahydro-2*H*-chromens **8.**

6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-5,7-diphenyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8a):

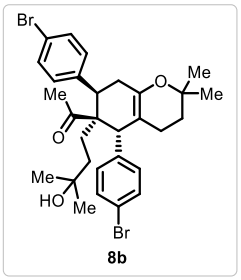
Following the *General Procedure B*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.294 g, 2.33 mmol, 2.5 equiv) and benzaldehyde (**3a**) (0.1 g, 0.93 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.023g, 0.093 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction,



8a

quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-5,7-diphenyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (**8a**) 0.285 g, 68%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.30 (m, 7H), 7.22-7.13 (m, 3H), 3.63 (s, 1 H), 3.21 (dd, *J* = 5.5, 12.3 Hz, 1H), 2.98-2.86 (m, 1H), 2.40-2.29 (m, 1H), 2.14 (s, 3H), 1.87-1.77 (m, 1H), 1.66-1.49 (m, 5H), 1.25 (s, 3H), 1.19 (s, 3H), 1.17-1.05 (m, 1H), 0.96-0.90 (m, 1H), 0.84 (s, 3H), 0.79 (s, 3H), 0.27-0.14 (m, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 209.9, 147.7, 141.6, 140.4, 131.2, 130.7, 128.2, 127.8, 127.3, 126.8, 104.4, 73.4, 70.4, 57.7, 53.7, 43.4, 38.2, 33.4, 33.2, 30.2, 29.2, 28.6, 27.9, 27.6, 25.3, 22.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{30}H_{39}O_3$ 447.2894; Found 447.2889.

5,7-Bis(4-bromophenyl)-6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8b):

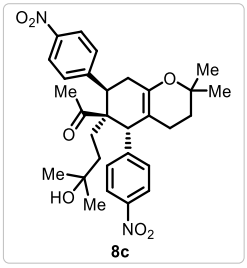


8b

Following the *General Procedure B*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.222 g, 1.77 mmol, 2.5 equiv) and 4-bromobenzaldehyde (**3i**) (0.1 g, 0.71 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.018 g, 0.071 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 5,7-Bis(4-bromophenyl)-6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (**8b**) 0.205 g, 63%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, *J* = 8.63, 2H), 8.06 (d, *J* = 8.76, 2H), 7.60-7.50 (m, 4H), 3.81 (s, 1H), 3.15 (dd, *J* = 5.6, 12.13 Hz, 1H), 2.97-2.90(m, 1H), 2.40-2.33 (m, 1H), 2.21 (s, 3 H), 1.88-1.75 (m, 1H), 1.66-1.48 (m, 5H), 1.27-1.25 (m,

3H), 1.20 (s, 3H), 1.06-1.01 (m, 1H), 0.95-0.89 (m, 1H), 0.88 (s, 3H), 0.80 (s, 3H), 0.22 (dt, *J* = 3.8, 13.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 208.9, 148.8, 148.2, 147.7, 147.4, 146.8, 131.8, 131.3, 123.3, 122.8, 103.2, 73.8, 70.0, 57.6, 53.4, 43.7, 37.9, 33.0, 32.8, 30.3, 29.9, 29.6, 28.5, 27.7, 27.3, 25.1, 22.8; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{30}H_{37}Br_2O_3$ 605.4215; found 605.4209.

6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-5,7-bis(4-nitrophenyl)-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8c):

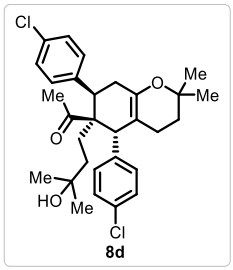


8c

Following the *General Procedure B*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.250 g, 1.98 mmol, 2.5 equiv) and 4-nitrobenzaldehyde (**3k**) (0.12 g, 0.79 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.020 g, 0.079 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-5,7-bis(4-nitrophenyl)-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (**8c**) 0.213 g, 60%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, *J* = 8.6 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.62-7.49 (m, 4H), 3.81 (s, 1H), 3.15 (dd, *J* = 5.8, 12.0 Hz, 1H), 2.94 (t, *J* = 14.5 Hz, 1H), 2.41-2.32 (m, 1H), 2.21 (s, 3H), 1.90-1.75 (m, 1H), 1.68-1.55 (m, 5H), 1.25 (br. s., 3H), 1.20 (s, 3H), 1.05-1.01 (m, 1H), 0.97-0.91 (m, 1H), 0.88 (s, 3H), 0.80 (s, 3H), 0.27-0.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 209.1, 149.0, 148.4, 147.9, 147.6, 147.0, 132.0, 131.5, 123.5, 123.0, 103.4, 74.0, 70.2, 57.8, 53.6, 43.9, 38.2, 33.2, 33.0, 30.5, 30.1, 29.9, 28.7, 27.9, 27.6, 25.3, 23.0; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{30}H_{37}N_2O_7$ 537.6250; found 537.6248.

7-bis(4-chlorophenyl)-6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8d):

Following the *General Procedure B*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.222 g, 1.77 mmol, 2.5 equiv) and 4-chlorobenzaldehyde (**3g**) (0.1 g, 0.71 mmol, 1.0 equiv) in



anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.018 g, 0.071 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) 7-bis(4-chlorophenyl)-6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (**8d**) 0.237 g, 65%) as a light yellow colour liquid (single diastereomer). The **8d** was confirmed by ^1H, ^{13}C, DEPT, HRMS and X-ray analysis; TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.27 (m, 6H), 7.17 (d, *J* = 8.8 Hz, 2H), 3.61 (s, 1H), 3.06 (dd, *J* = 5.8, 12.3 Hz, 1H), 2.90-2.79 (m, 1H), 2.32-2.24 (m, 1H), 2.14 (s, 3 H), 1.88-1.75 (m, 1H), 1.66-1.48 (m, 5H), 1.24 (s, 3H), 1.18 (s, 3H), 1.06 (dt, *J* = 3.88, 13.5 Hz, 1H), 0.95-0.89 (m, 1H), 0.88 (s, 3H), 0.83 (s, 3H), 0.26 (dt, *J* = 3.8, 13.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 209.7, 147.8, 139.9, 138.8, 133.3, 132.7, 132.5, 131.9, 128.4, 127.9, 104.1, 73.6, 70.4, 57.6, 53.1, 43.0, 38.2, 33.3, 33.2, 30.4, 29.3, 28.9, 27.9, 27.6, 25.3, 22.9; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{30}H_{37}Cl_2O_3$ 516.5150; Found 516.5144.

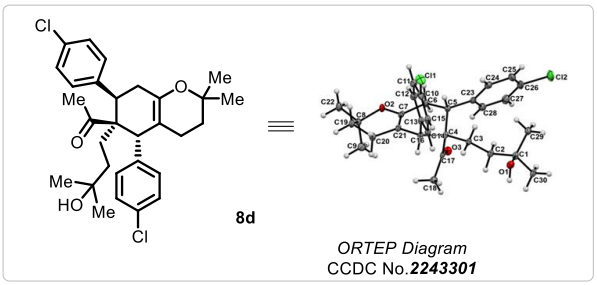
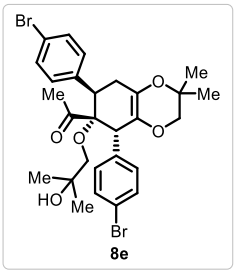


Figure 4. ORTEP diagram of compound **8d**.

7-bis(4-bromophenyl)-6-(2-hydroxy-2-methylpropoxy)-2,2-dimethyl-2,3,5,6,7,8-hexahydrobenzo[b][1,4]dioxin-6-yl)ethan-1-one (8e):

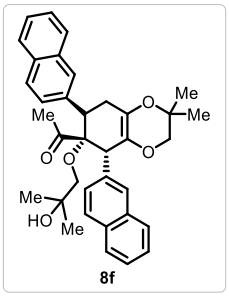
Following the *General Procedure B*, to the mixture of 2-methyl-1-(prop-2-yn-1-yloxy)propan-2-ol (**2g**) (0.173 g, 1.35 mmol, 2.5 equiv) and 4-bromobenzaldehyde (**3i**) (0.1 g, 0.54 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0138 g, 0.054 mmol, 0.1 equiv) under argon atmosphere at 30 ^oC and reaction mixture was stirred at 30 ^oC for 8 h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution,



8e

then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 7-bis(4-bromophenyl)-6-(2-hydroxy-2-methylpropoxy)-2,2-dimethyl-2,3,5,6,7,8-hexahydrobenzo[b][1,4]dioxin-6-yl)ethan-1-one (**8e**) 0.229 g, 70%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.36-7.32 (m, 2H), 7.26-7.24 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.11 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 1H), 3.73-3.63 (m, 2H), 3.56-3.48 (m, 2H), 2.67-2.58 (m, 1H), 2.46-2.40 (m, 1H), 1.57 (s, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 209.8, 139.6, 137.3, 132.2, 131.7, 131.2, 131.0, 130.9, 125.2, 122.1, 121.3, 87.8, 74.0, 72.8, 72.5, 70.8, 47.6, 42.6, 33.1, 29.9, 29.4, 27.0, 26.6, 24.0, 22.8; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{28}H_{33}Br_2O_5$ 609.3670; Found 609.3666.

6-(2-hydroxy-2-methylpropoxy)-2,2-dimethyl-5,7-di(naphthalen-2-yl)-2,3,5,6,7,8-hexahydrobenzo[b][1,4]dioxin-6-yl)ethan-1-one (8f):



8f

Following the *General Procedure B*, to the mixture of 2-methyl-1-(prop-2-yn-1-yloxy)propan-2-ol (**2g**) (0.205 g, 1.60 mmol, 2.5 equiv) and 2-naphthaldehyde (**3c**) (0.1 g, 0.64 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added AgOTf (0.0163 g, 0.064 mmol, 0.1 equiv) under argon atmosphere at 30 ^{o}C and reaction mixture was stirred at 30 ^{o}C for 8h. After completion of reaction, quenched with saturated aqueous $NaHCO_3$ solution, then extracted with CH_2Cl_2 (2 x 5 mL) and washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc /hexanes) to afford 6-(2-hydroxy-2-methylpropoxy)-2,2-dimethyl-5,7-di(naphthalen-2-yl)-2,3,5,6,7,8-hexahydrobenzo[b][1,4]dioxin-6-yl)ethan-1-one (**8f**) 0.228 g, 65%) as a light yellow colour liquid (single diastereomer). TLC: R_f = 0.3 (SiO_2, 40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92-7.82 (m, 5H), 7.76-7.69 (m, 3H), 7.56-7.48 (m, 4H), 7.42-7.39 (m, 2H), 4.37-4.29 (m, 1H), 3.93 (dd, *J* = 5.8, 11.5 Hz, 1H), 3.86 (d, *J* = 8.4 Hz, 1H), 3.71 (d, *J* = 10.8 Hz, 1H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.03 (br. s.,

1H), 2.88-2.76 (m, 1H), 2.63 (dd, *J* = 5.8, 16.2 Hz, 1H), 1.61 (br. s., 1H), 1.46 (s, 3H), 1.43 (s, 3H), 1.33 (d, *J* = 1.8 Hz, 6H), 0.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 210.6, 138.4, 135.7, 133.7, 133.5, 133.1, 132.5, 131.0, 128.9, 128.8, 128.2, 128.1, 128.1, 128.0, 127.9, 127.6, 127.4, 127.3, 126.6, 126.4, 126.1, 125.9, 125.7, 88.3, 74.1, 72.8, 72.5, 70.9, 48.5, 43.3, 33.6, 29.9, 29.4, 27.1, 26.7, 24.1, 22.8; HRMS (ESI) *m/z:* $[M+H]^+$ Calcd for $C_{36}H_{39}O_5$ 551.2792; Found 551.2801.

7) X-ray crystallography data:

SC-XRD: The single crystal X-ray diffraction measurements were performed to determine the crystal structure of compounds **6a, 6g, 7b** and **8d** at 100 K using APEX3 (Bruker, 2016; Bruker D8 VENTURE Kappa Duo PHOTON II CPAD) diffractometer having graphite-monochromatized (MoKα (0.71073)). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5^{o} steps φ/ω. The data were collected with a time frame of 10 sec by setting the sample to detector distance fixed at 40 cm. All the data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2008) was used for structure solution, and full-matrix least-squares refinement on F^{2}.[1, 2] the molecular graphics of ORTEP diagrams were performed by Mercury software. The crystal symmetry of the components was cross-checked by running the cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed. The Encifer software was used to correct the cif files. Four compounds **6a, 6g, and 7b** and **8d** were crystallized by the slow evaporation method using a solvent system of 20% EtOAc/Hexane.

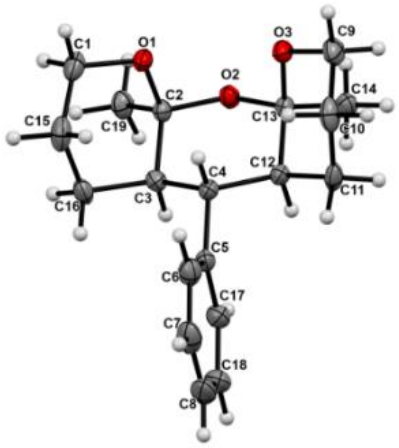


Figure 1. ORTEP diagram of compound **6a**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

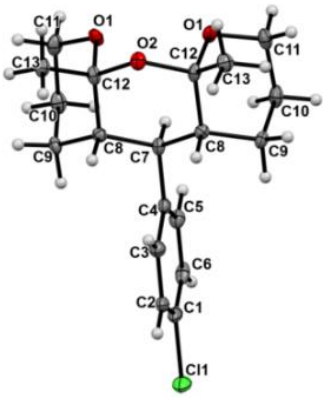


Figure 2. ORTEP diagram of compound **6g**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

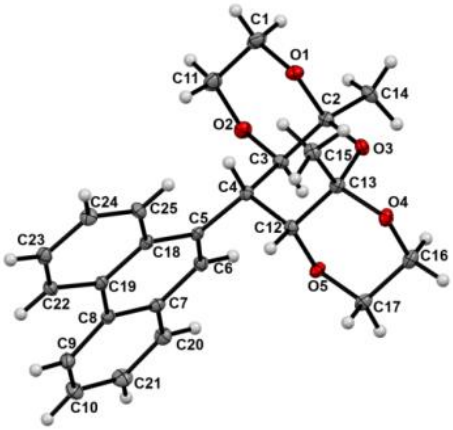


Figure 3. ORTEP diagram of compound **7b**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

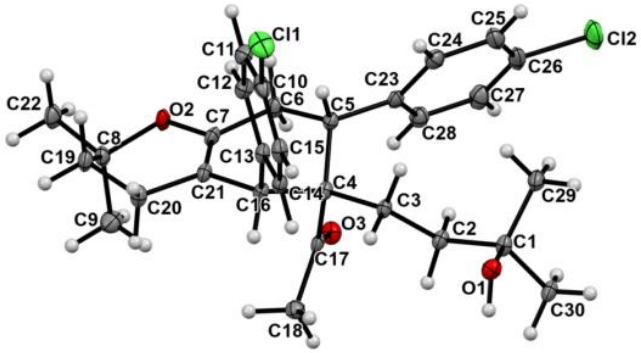


Figure 4. ORTEP diagram of compound **8d**, the asymmetric unit, contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

Table 2. Crystallographic information details of compounds **6a**, **6g**, **7b** and **8d**.

Crystal data	Compound **6a**	Compound **6g**	Compound **7b**	Compound **8d**
Chemical formula	$C_{19}H_{26}O_3$	$C_{19}H_{25}ClO_3$	$C_{25}H_{26}O_5$	$C_{30}H_{36}Cl_2O_3$
Formula weight (M_r)	302.40	336.84	406.46	515.49
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	*T*riclinic
Space group	*Pna2₁*	*Pnma*	*Pna2₁*	*P-1*
Temperature T (K)	100	100	100	100
a (Å)	8.7312 (11)	14.719 (3)	8.7057 (10)	10.1704 (10)
b (Å)	16.422 (2)	12.729 (2)	18.724 (2)	12.2125 (13)
c (Å)	11.2564 (15)	8.8925 (17)	12.0239 (12)	12.2391 (13)
α (°)	90	90	90	66.671 (4)
β (°)	90	90	90	78.351 (4)
γ (°)	90	90	90	87.561 (4)
Z	4	4	4	2
Volume ($Å^3$)	1614.0 (4)	1666.1 (5)	1959.9 (4)	1366.0 (2)
Source of radiation	Mo*K*α (0.71073)	Mo*K*α (0.71073)	MoKα (0.71073)	MoKα (0.71073)
D_{calc} (g cm^{-3})	1.244	1.343	1.377	1.253
Crystal size (mm)	0.19 ×0.1×0.09	0.19×0.1×0.08	0.23×0.12×0.1	0.19x0.12x0.1
μ (mm^{-1})	0.08	0.24	0.10	0.27
Data collection				
Diffractometer	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)
No. of measured, independent and observed [I > 2σ(I)] reflections	65854, 3515, 3313	54108, 1885, 1612	100962, 4255, 4164	67475, 5946, 4719
Theta range (°)	2.19−27.28	2.79− 26.77	2.58− 27.38	2.47− 26.84
R_{int}	0.069	0.161	0.063	0.098
Refinement				
R[F^2 > 2σ (F^2)], wR(F^2)	0.045, 0.126	0.090, 0.214	0.031, 0.085	0.045, 0.118
GOF on F^2	1.11	1.15	1.12	1.08
No. of independent reflections	3515	1885	4255	5946
No. of parameters	201	119	274	325
F_000	656	720	864	548
No. of restraints	1	0	1	0
H-atom treatment	Constr	Constr	Constr	Constr
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e A^{-3})	0.36, −0.19	1.95, −0.51	0.30, −0.22	0.32, −0.27

CCDC number	2243298	2243299	2243300	2243301

Table 3. Hydrogen-bond geometry (A˚, °) of compounds **6g**, **7b** and **8d** are given as below.

Name of the compound	*D*–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
Compound **6g**	C2−H2···O1	0.9500	2.5100	3.342(6)	146
	C2−H2···O1	0.9500	2.5100	3.342(6)	146
Compound **7b**	C3−H3···O5	0.9800	2.4200	2.8124(3)	103
	C4−H4···O1	0.9800	2.5500	2.9412(3)	104
	C15−H15B···O1	0.9600	2.4700	3.0721(4)	121
	C24−H24···O4	0.9300	2.5200	3.3447(4)	148
Compound **8d**	O1−H1···O2	0.8500	2.0300	2.8686(3)	167
	C6−H18···O3	0.9700	2.4400	2.9259(3)	111
	C28−H2···O3	0.9300	2.3800	3.0125(3)	126

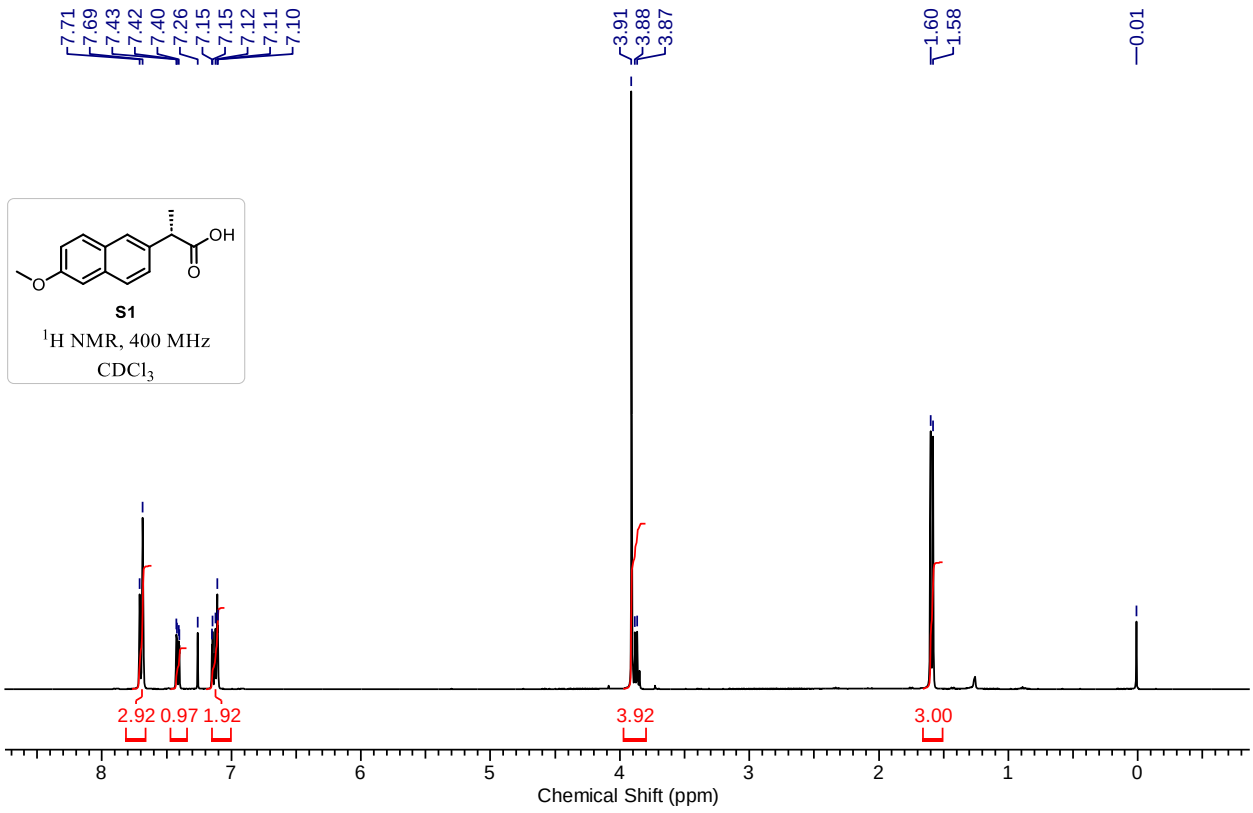
References

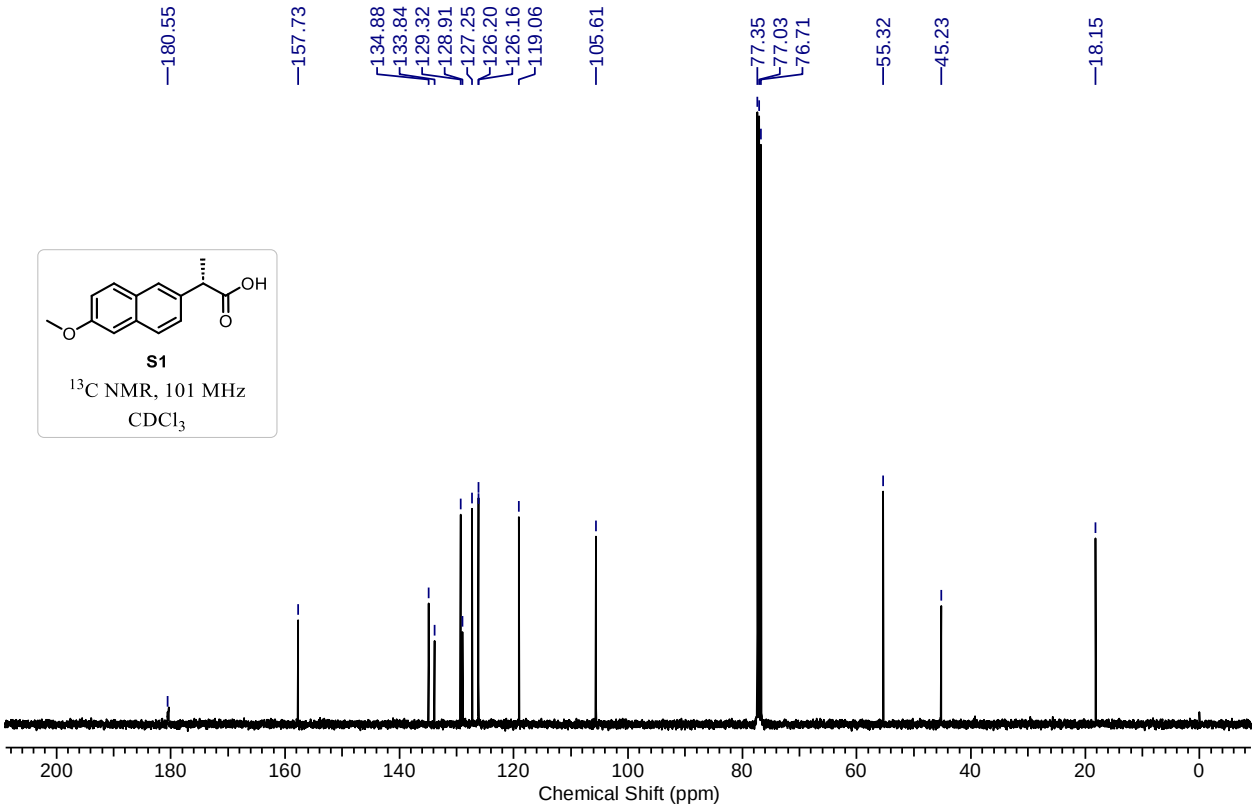
1. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst*. (2015). C71, 3–8.

2. G. M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Cryst*. (2015). A71, 3–8.

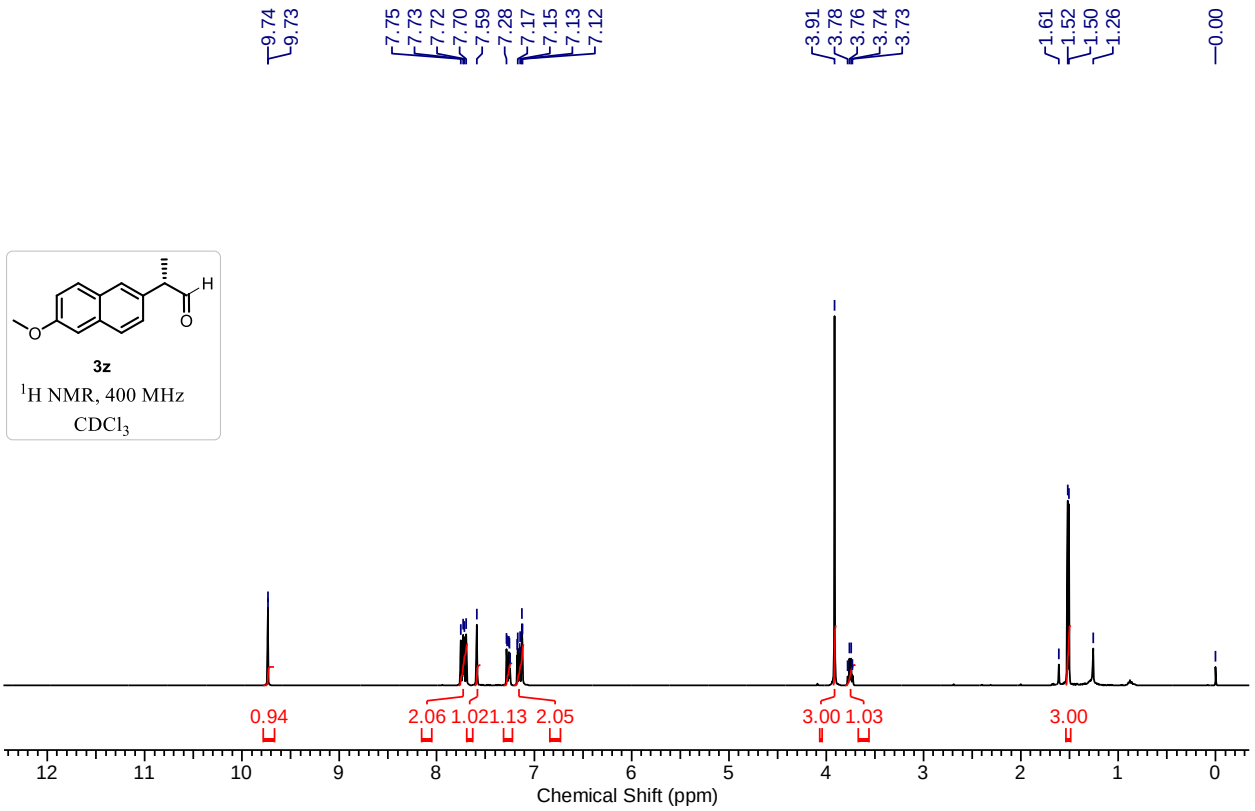
8) ^{1}H, ^{13}C NMR Spectra

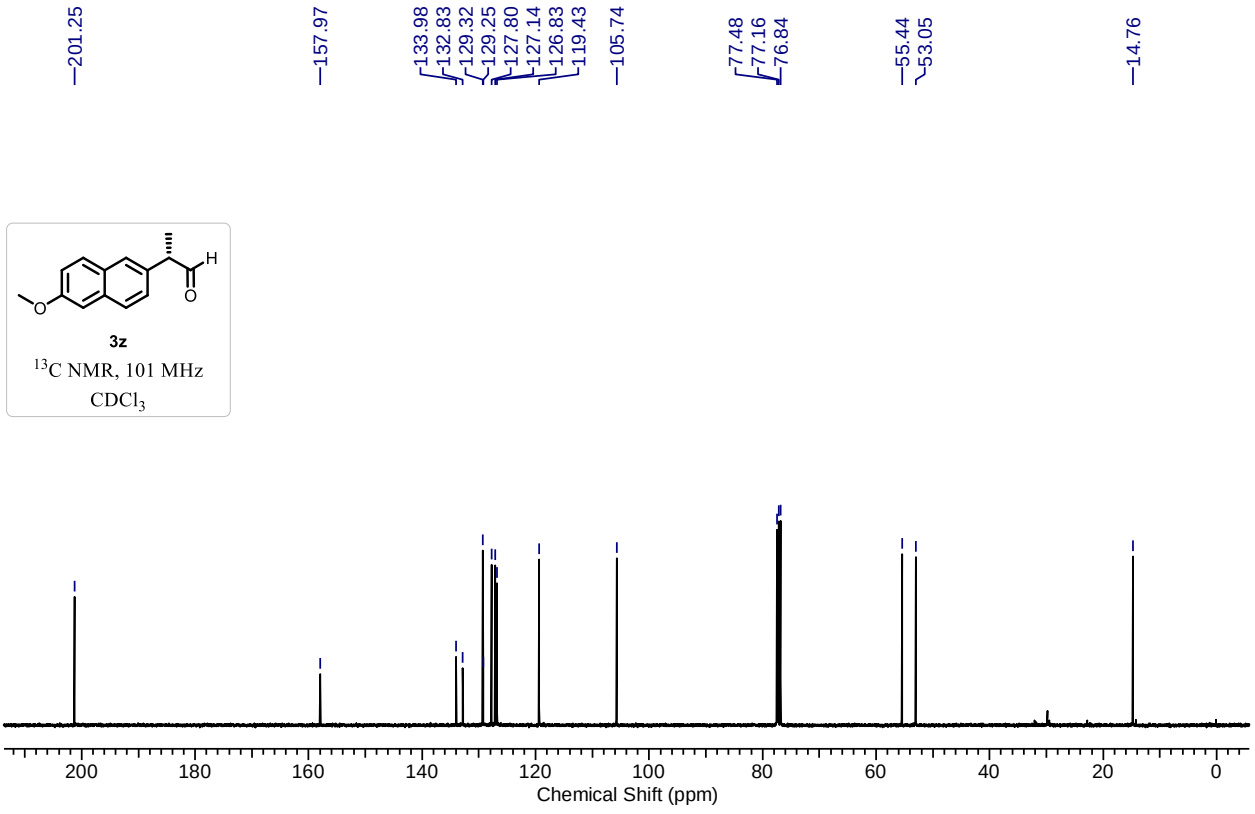
(*S*)-2-(6-Methoxynaphthalen-2-yl)propanoic acid (S1):



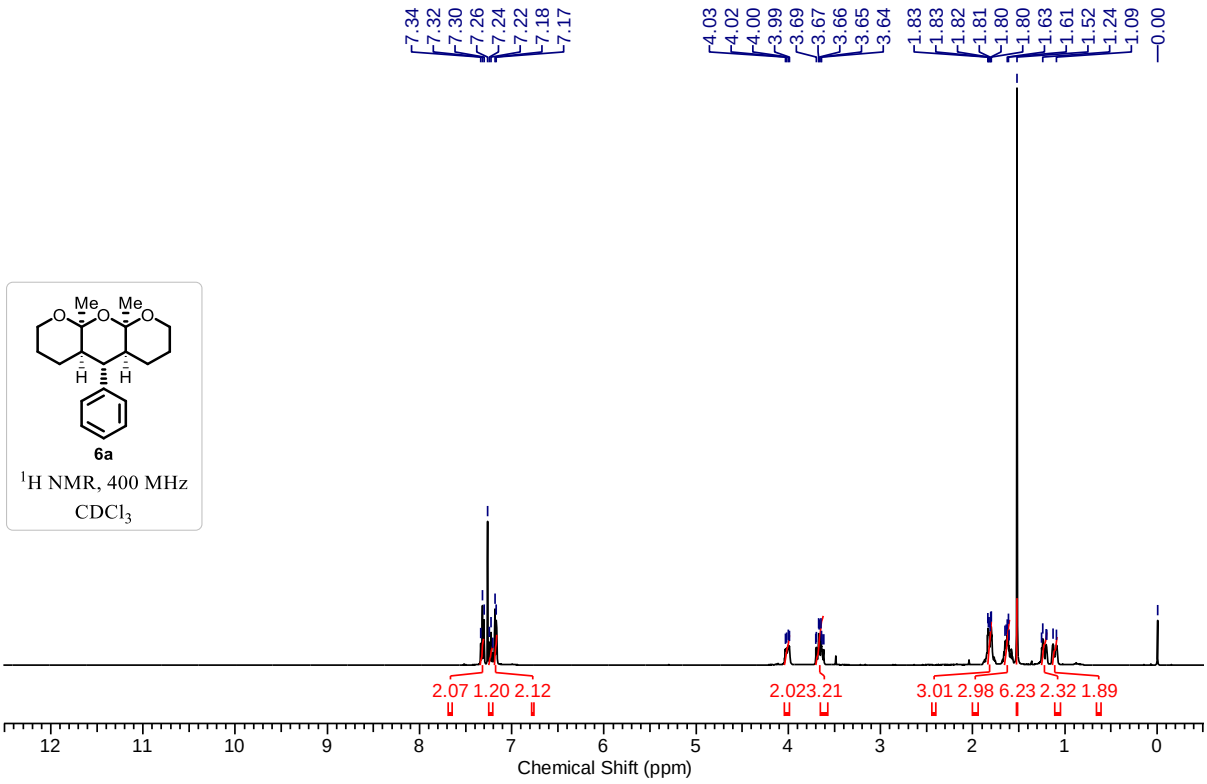


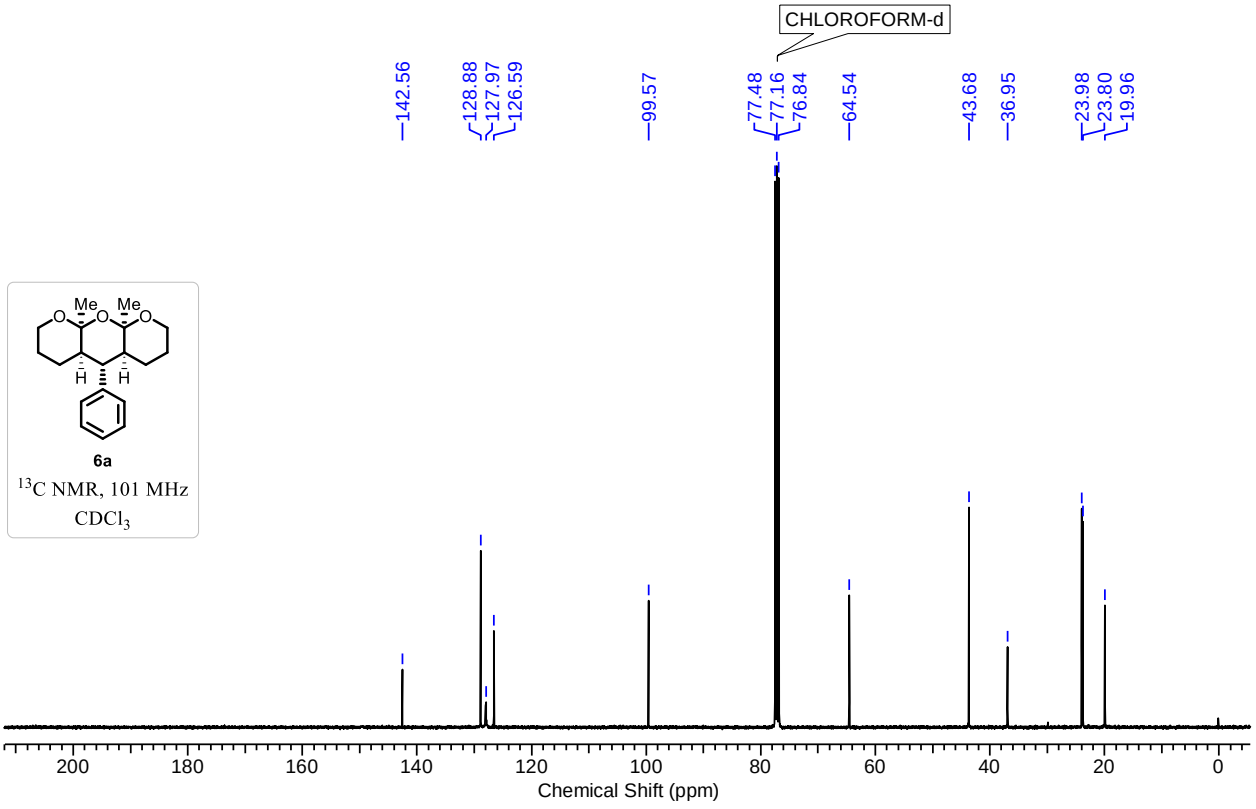
(*S*)-2-(6-Methoxynaphthalen-2-yl)propanal (3z):



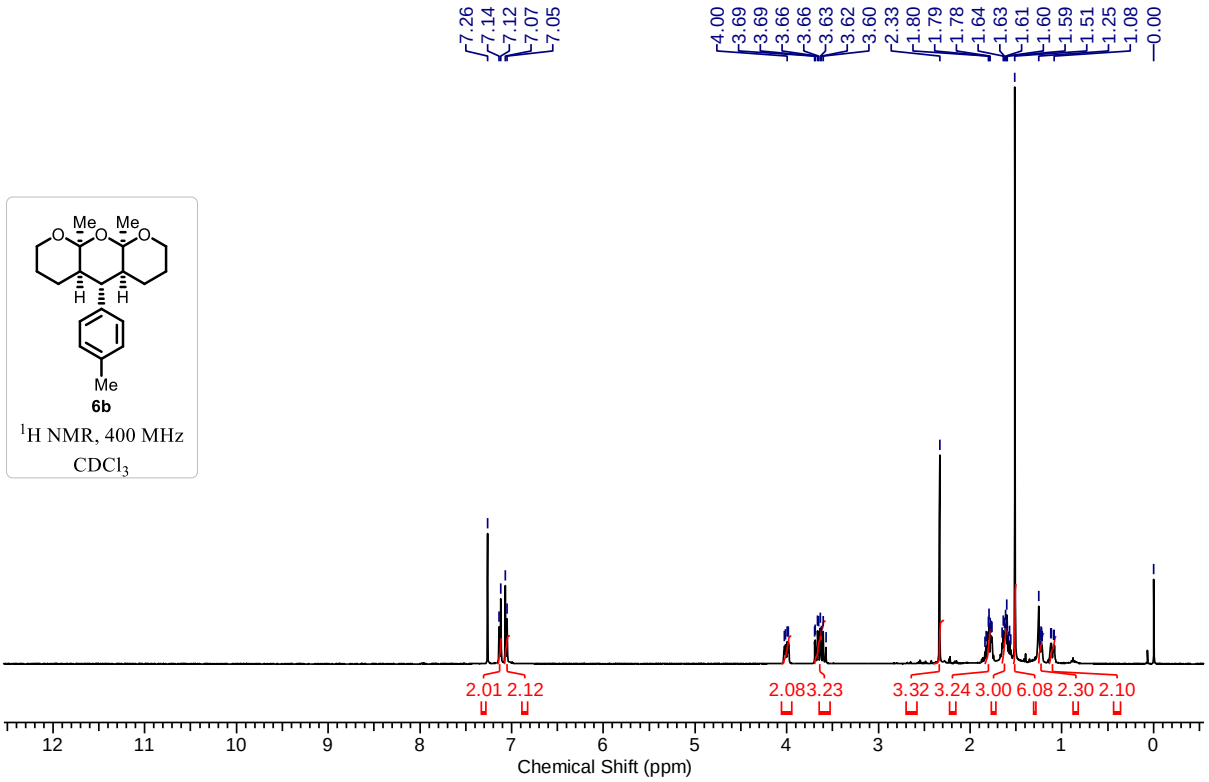


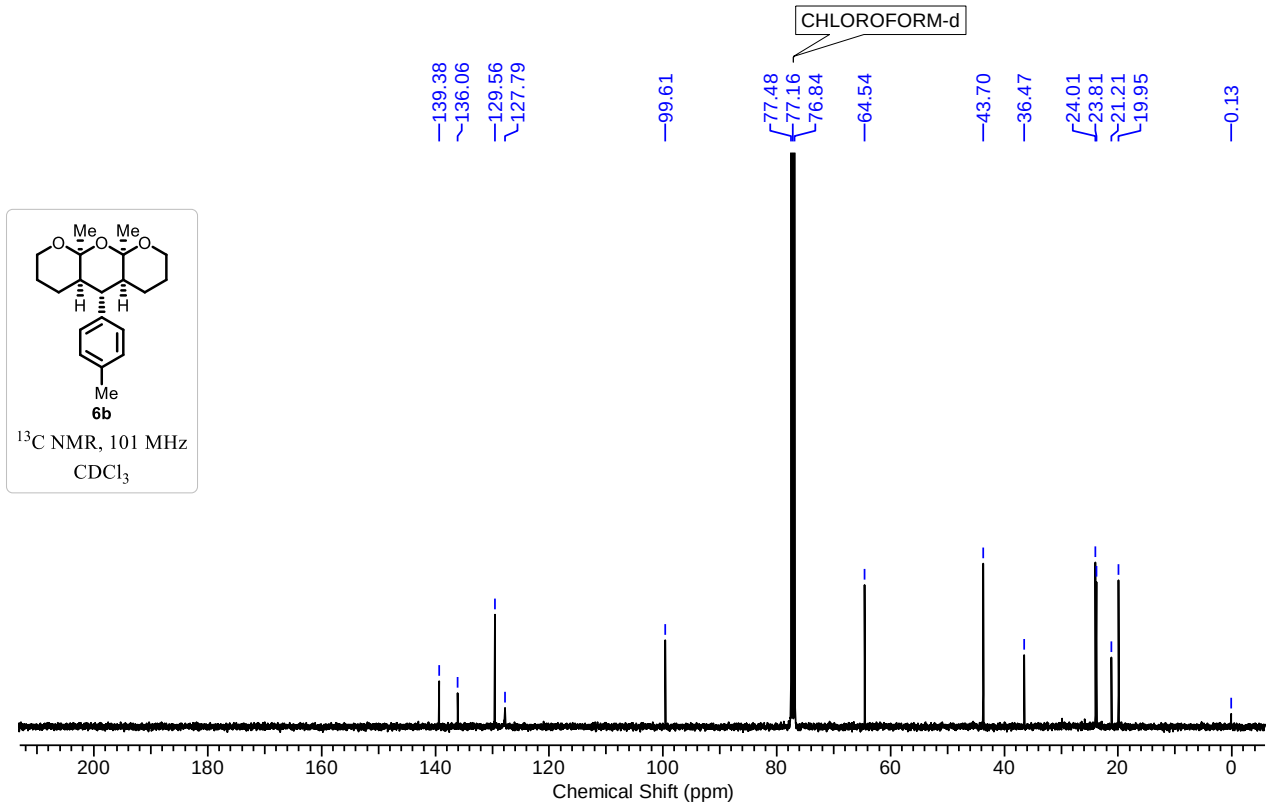
9a,10a-Dimethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6a):



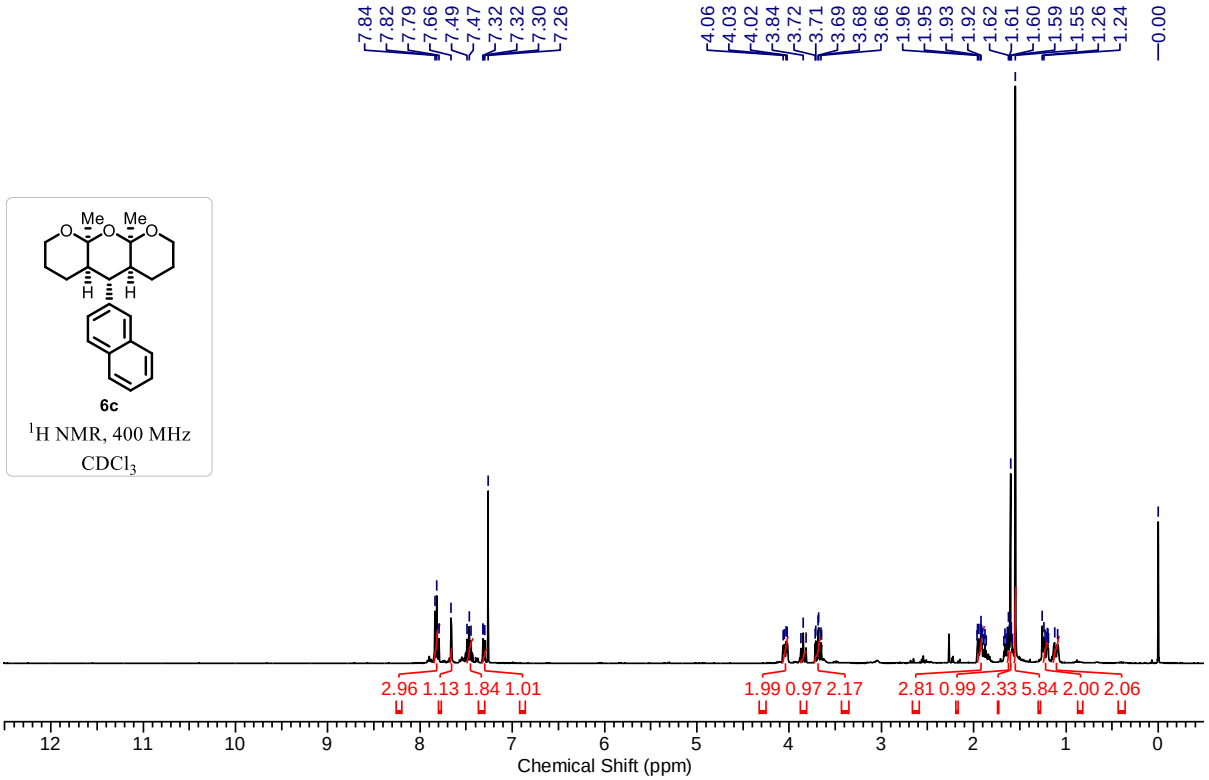


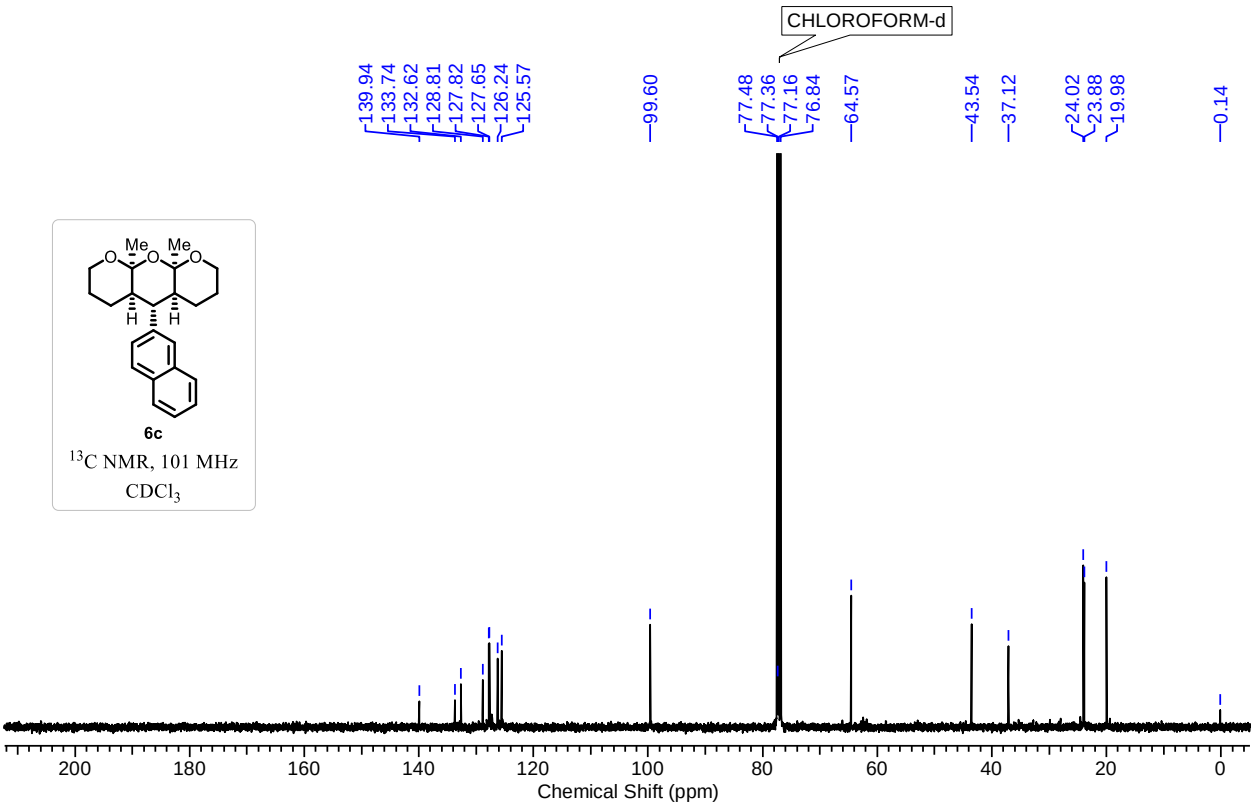
9a,10a-Dimethyl-5-(p-tolyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6b):



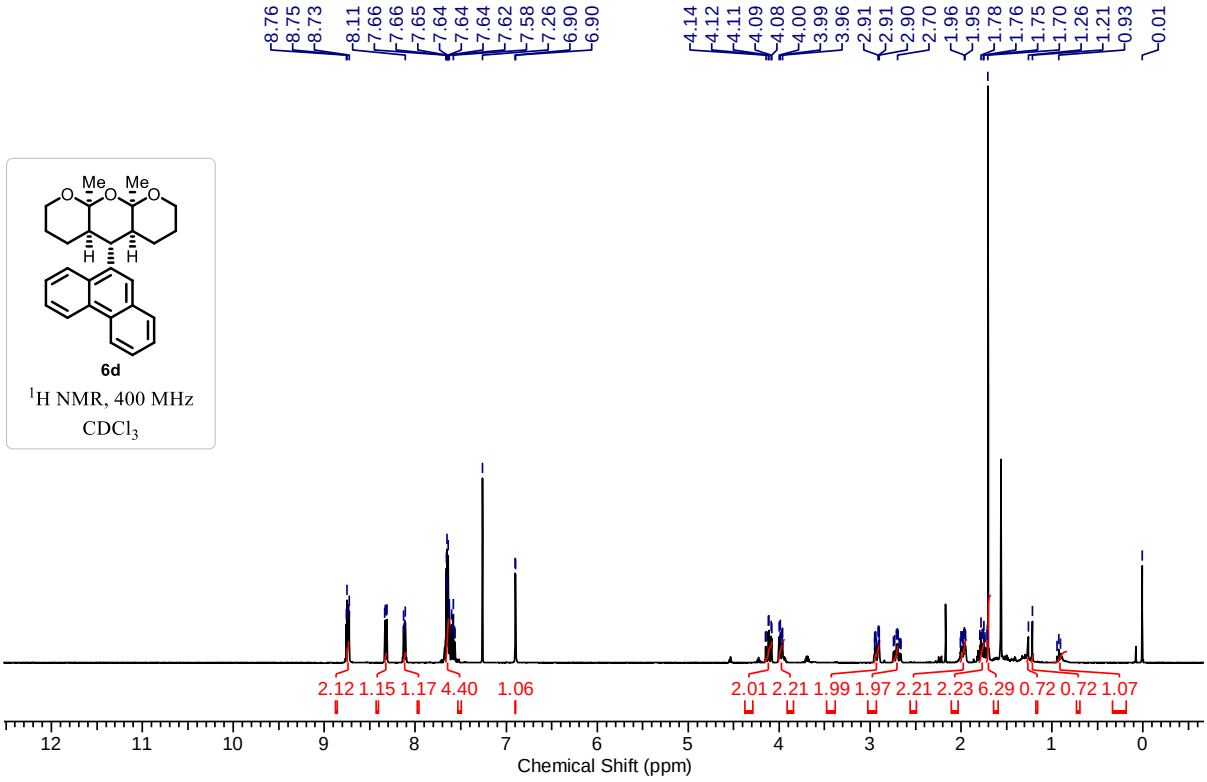


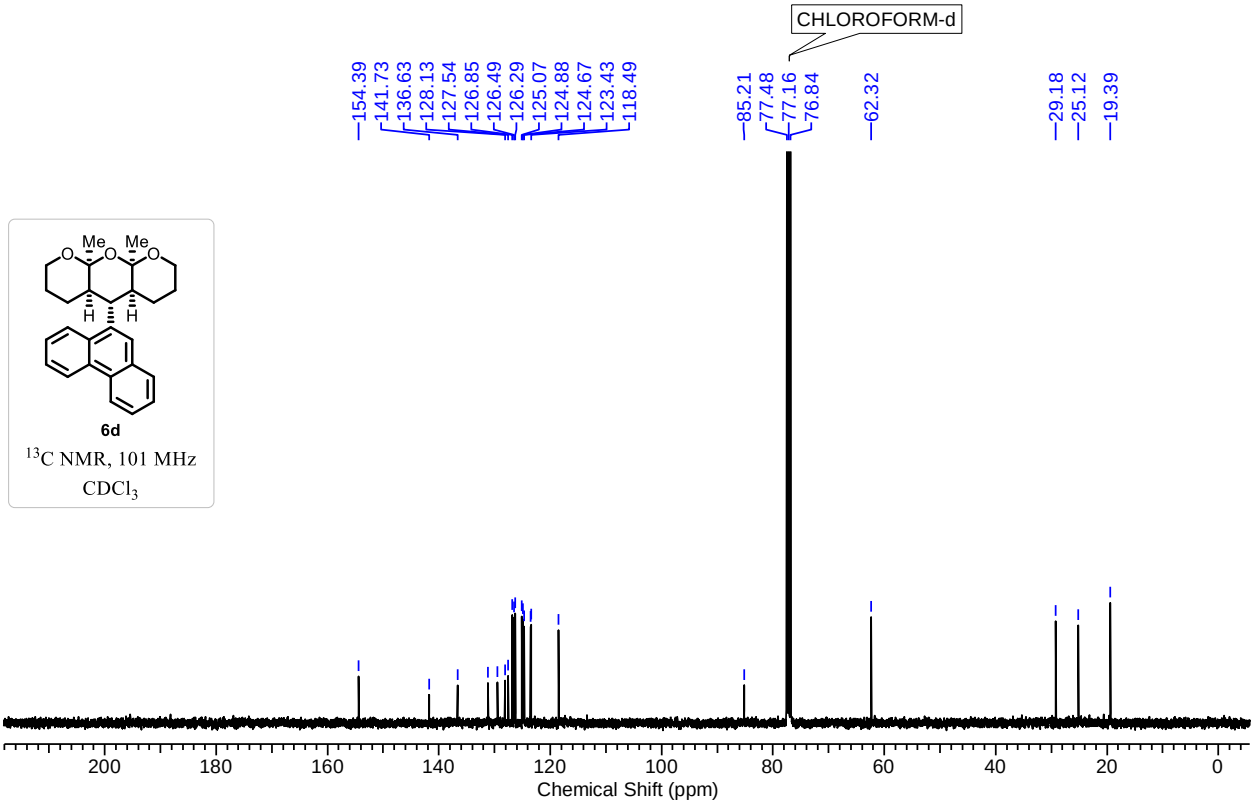
9a,10a-Dimethyl-5-(naphthalen-2-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6c):



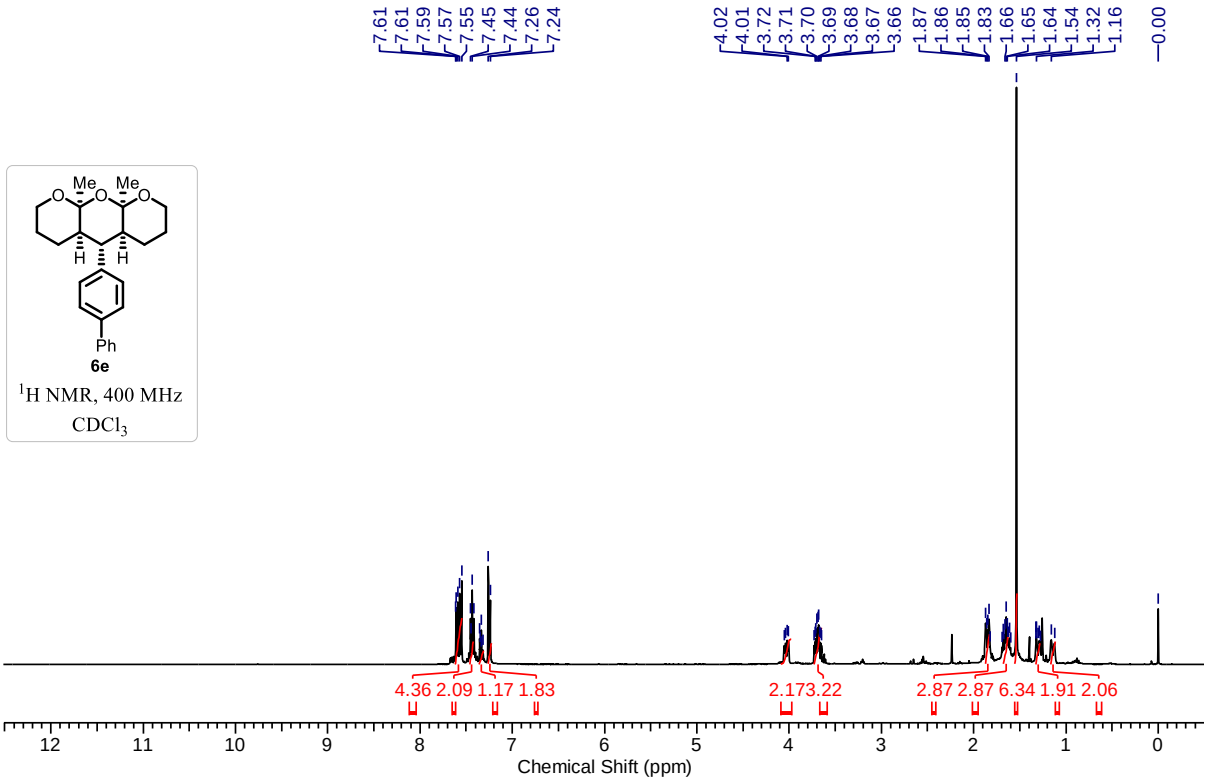


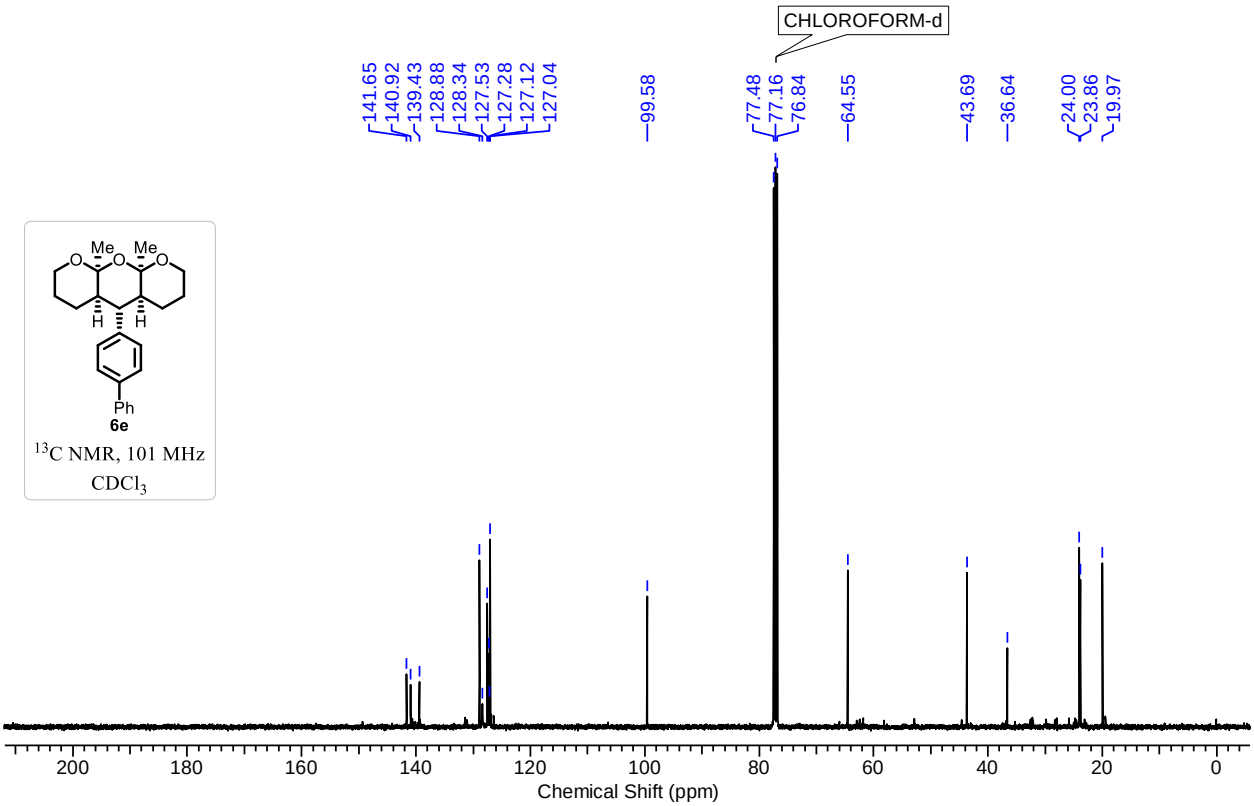
9a,10a-Dimethyl-5-(phenanthren-9-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6d):



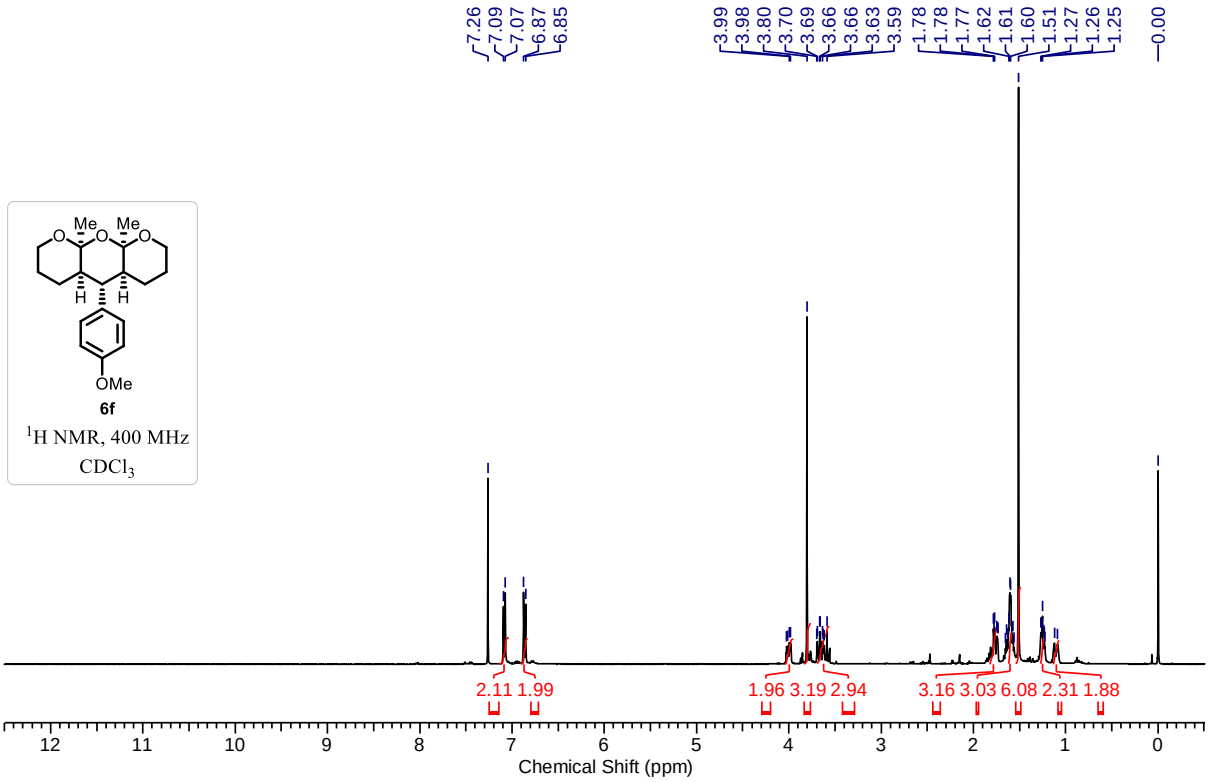


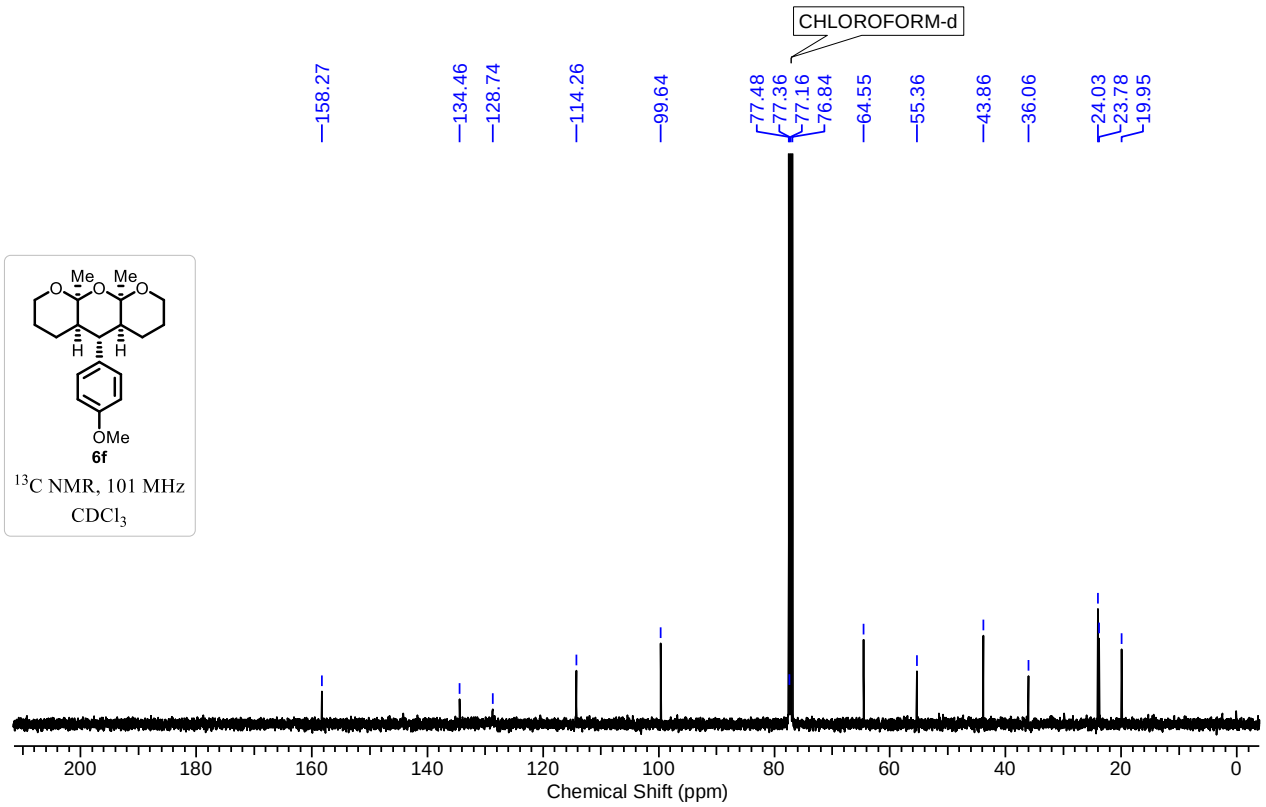
5-([1,1'-Biphenyl]-4-yl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6e):



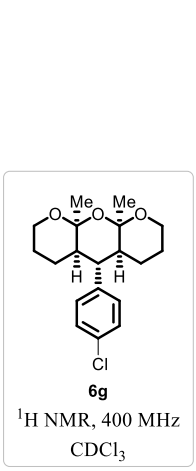


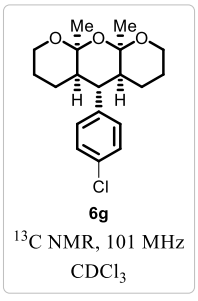
5-(4-Methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6f):



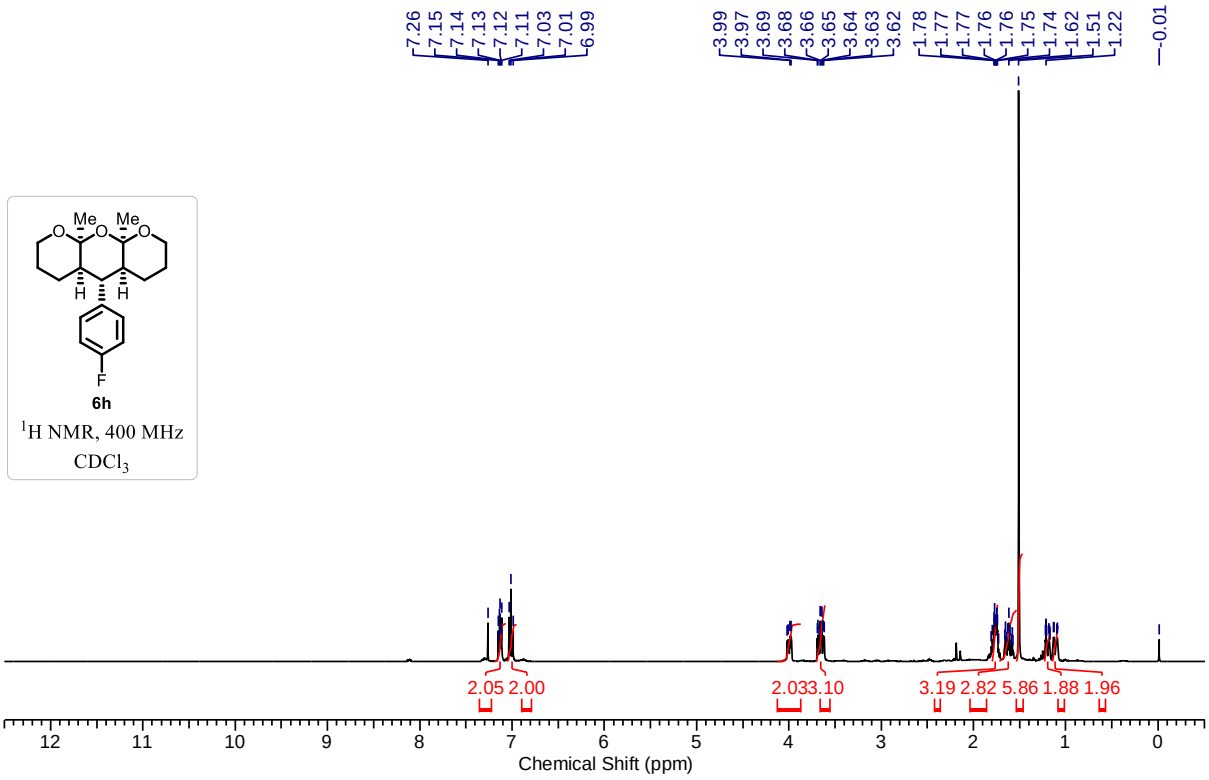


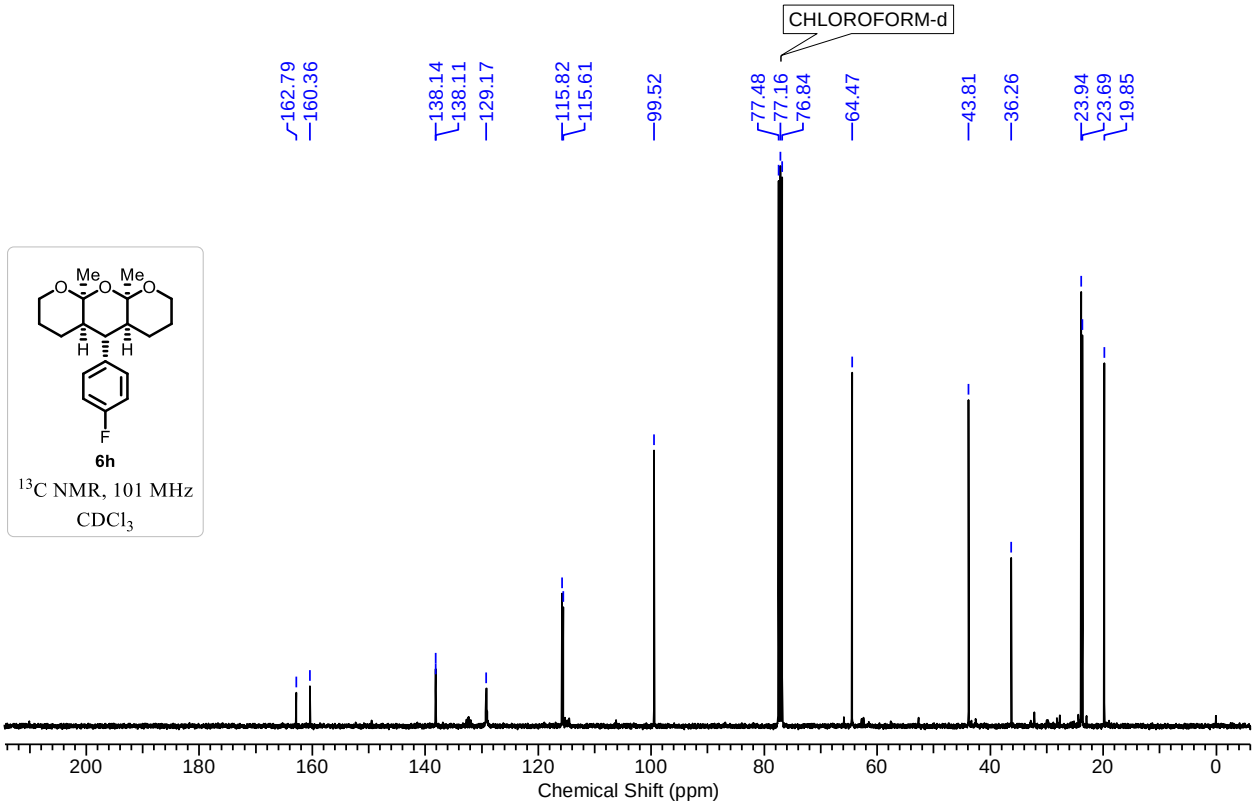
5-(4-Chlorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6g):



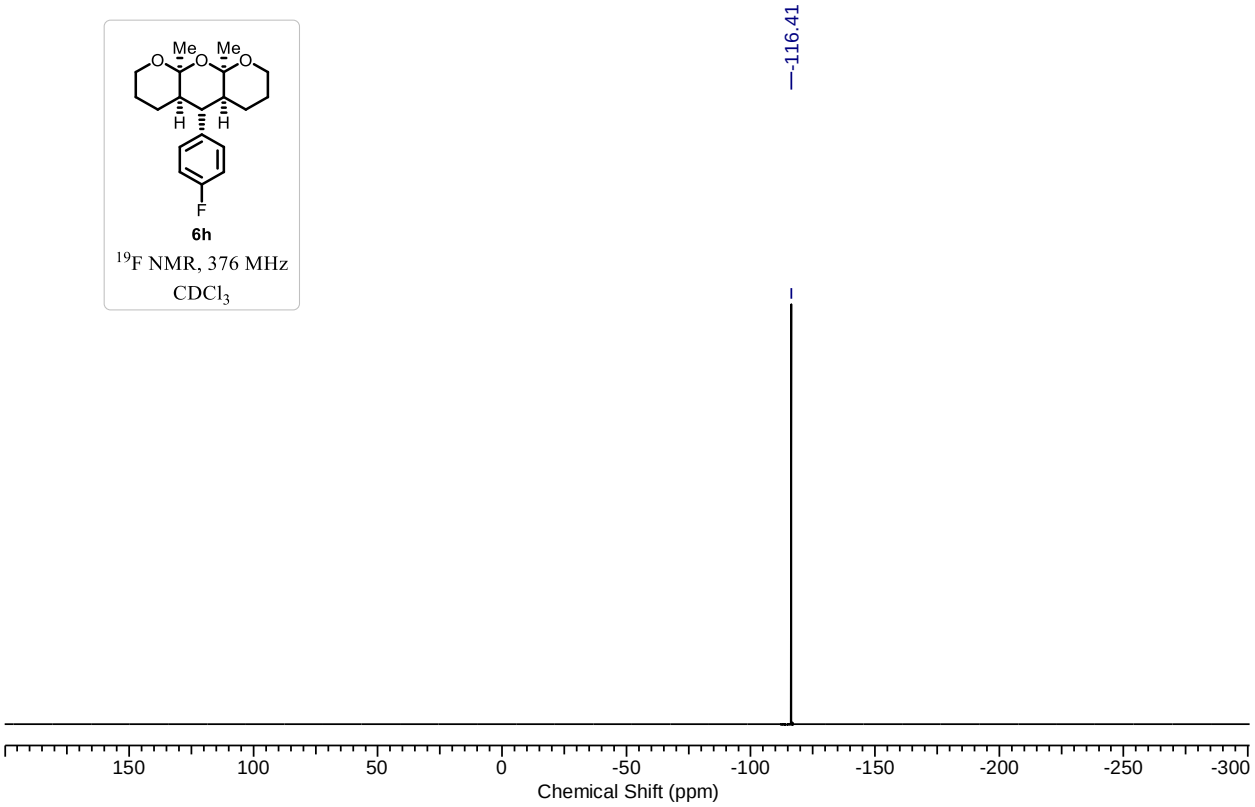


5-(4-Fluorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6h):

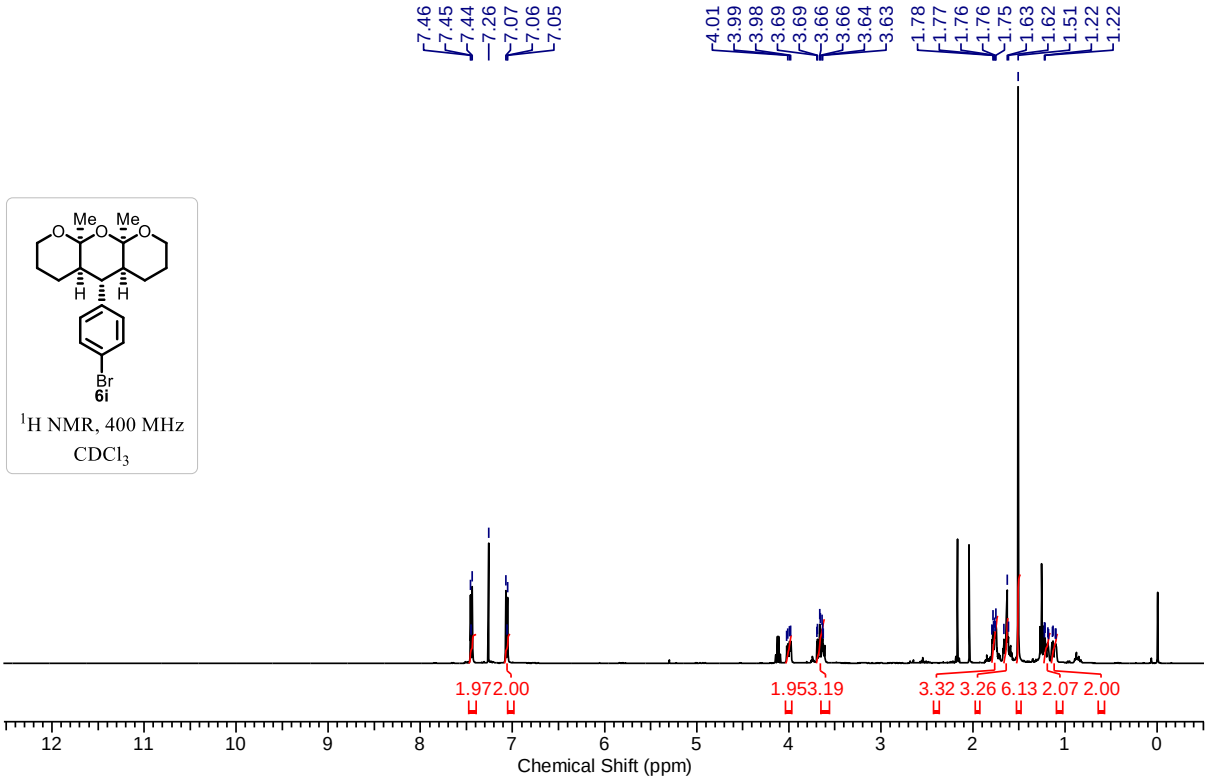


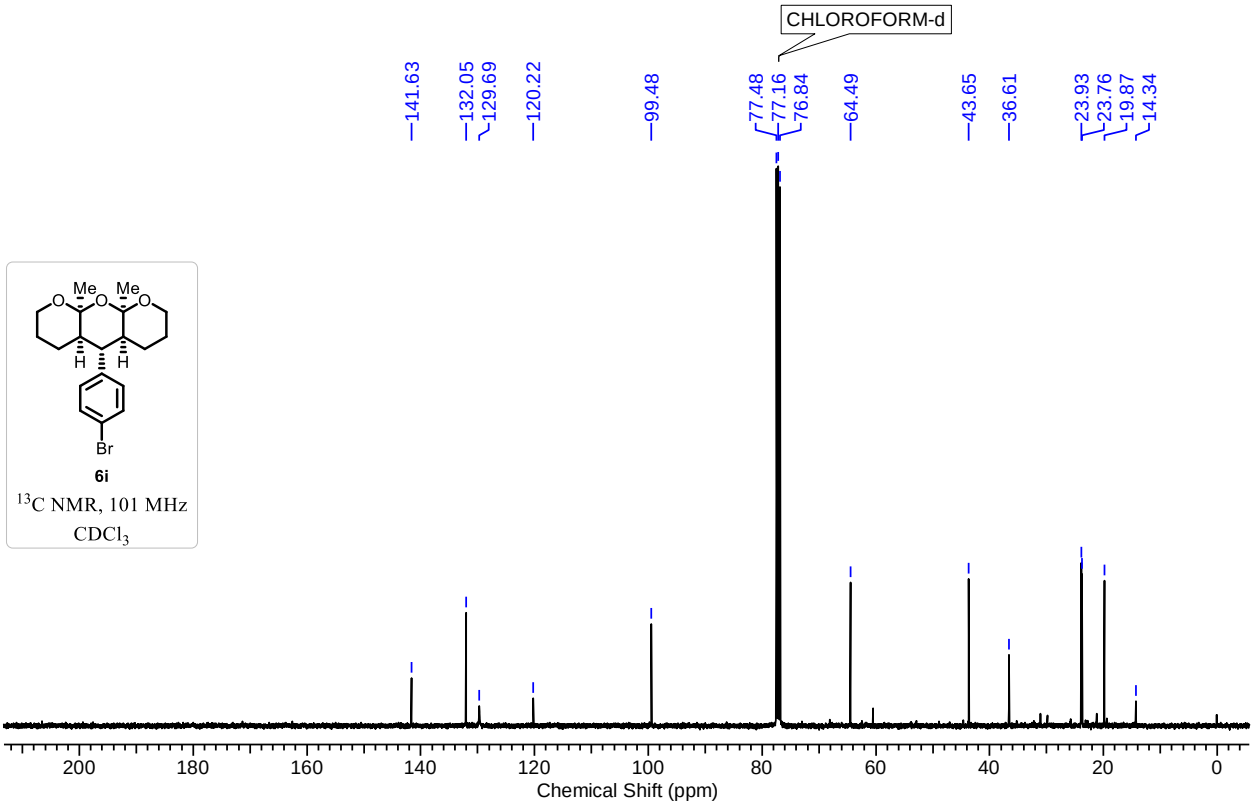


5-(4-Fluorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6h):

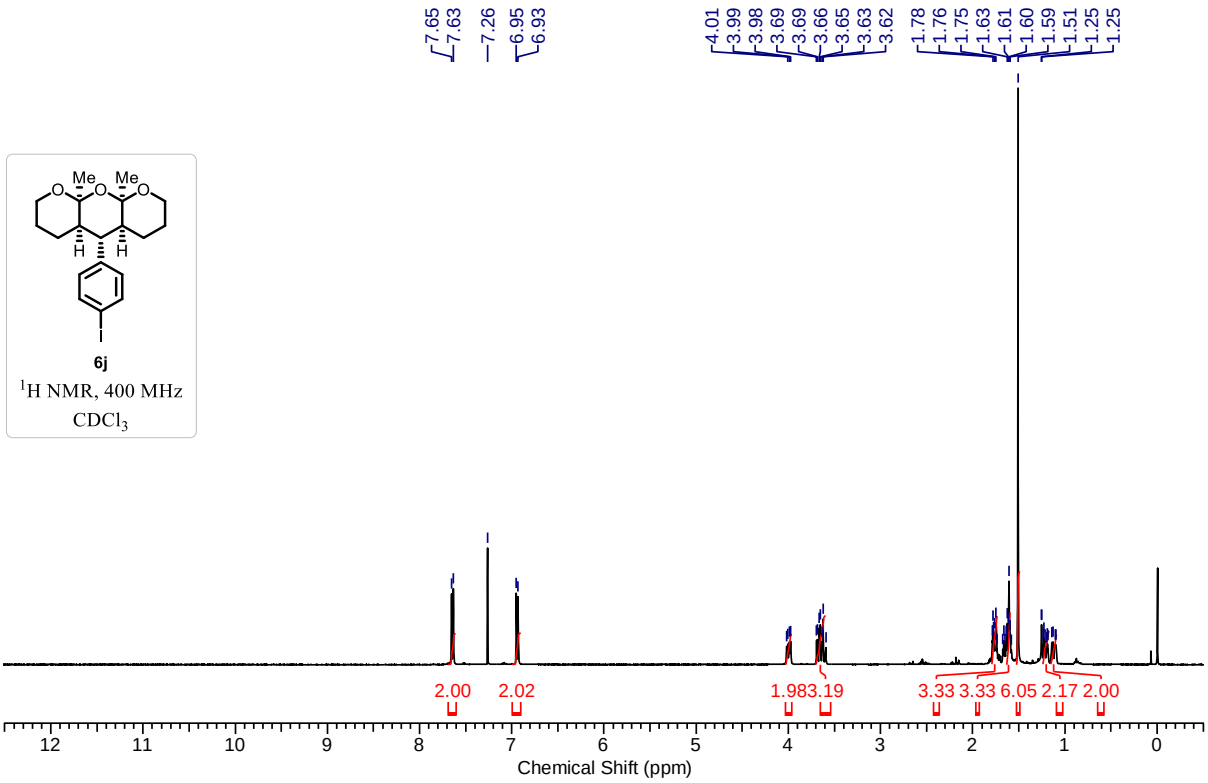


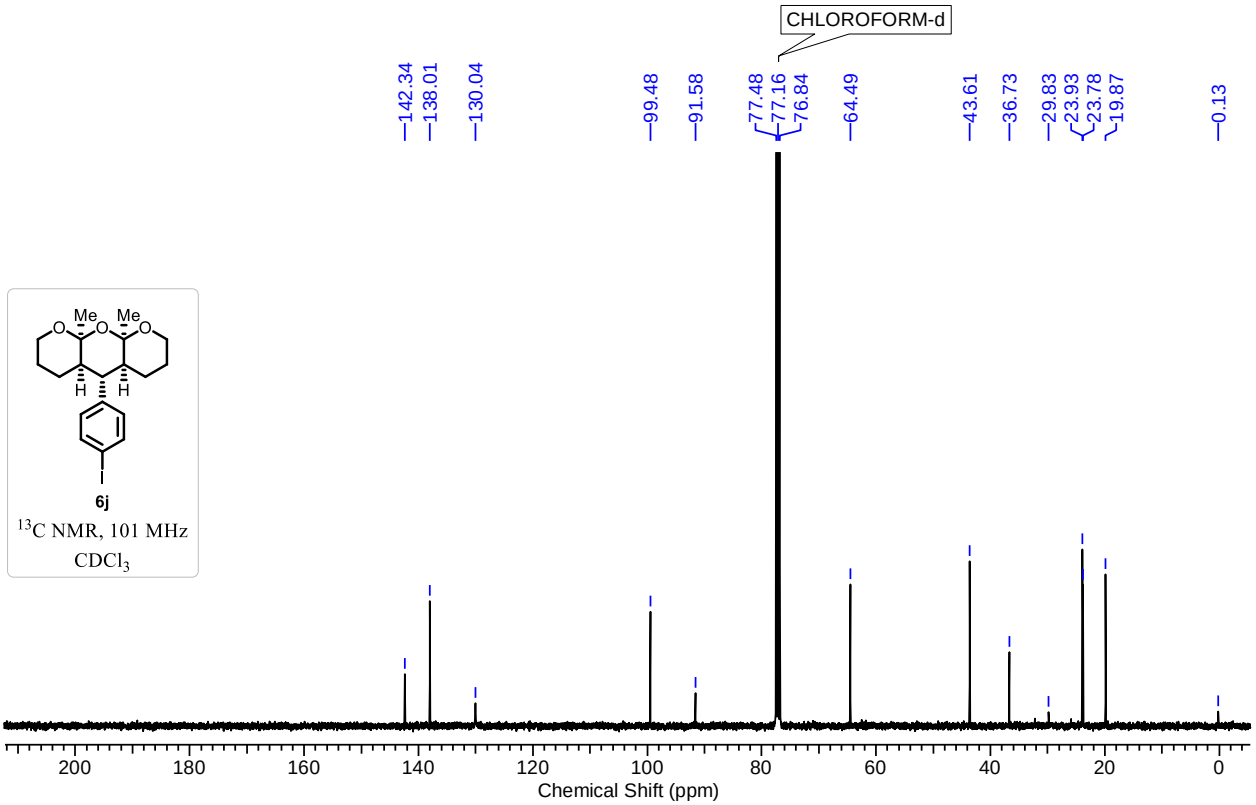
5-(4-Bromophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6i):



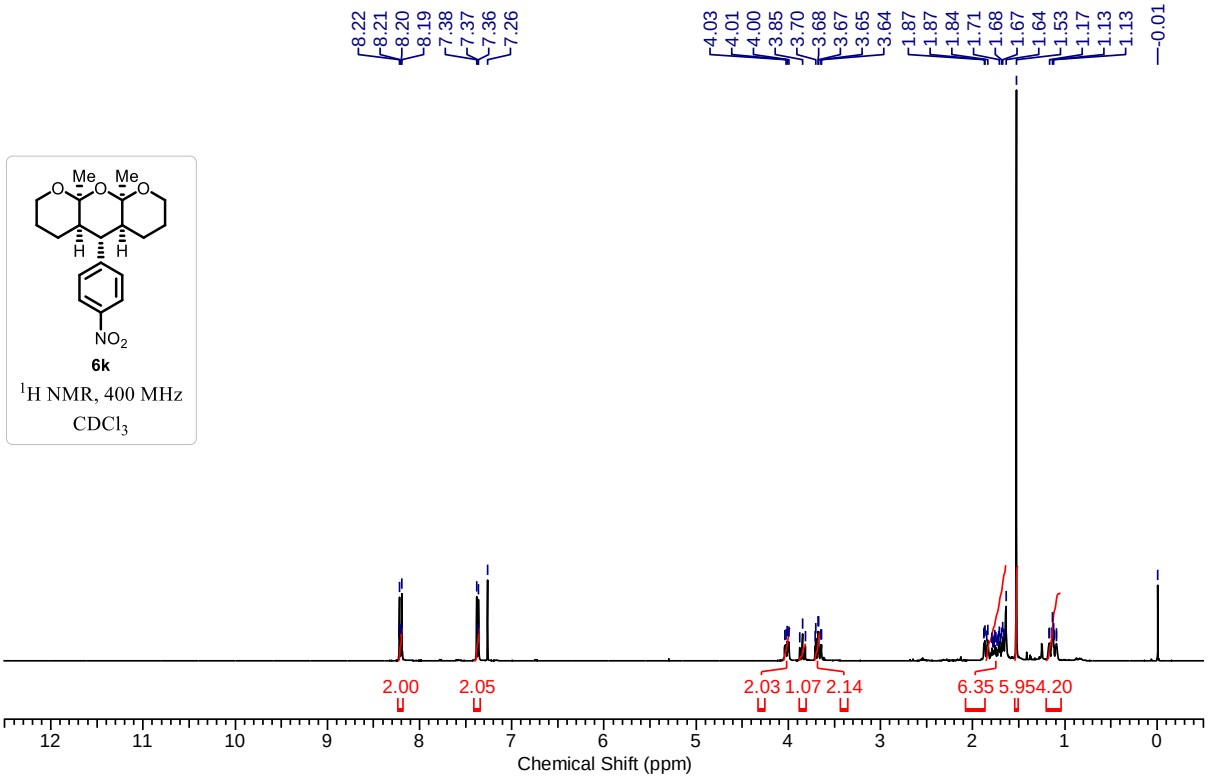


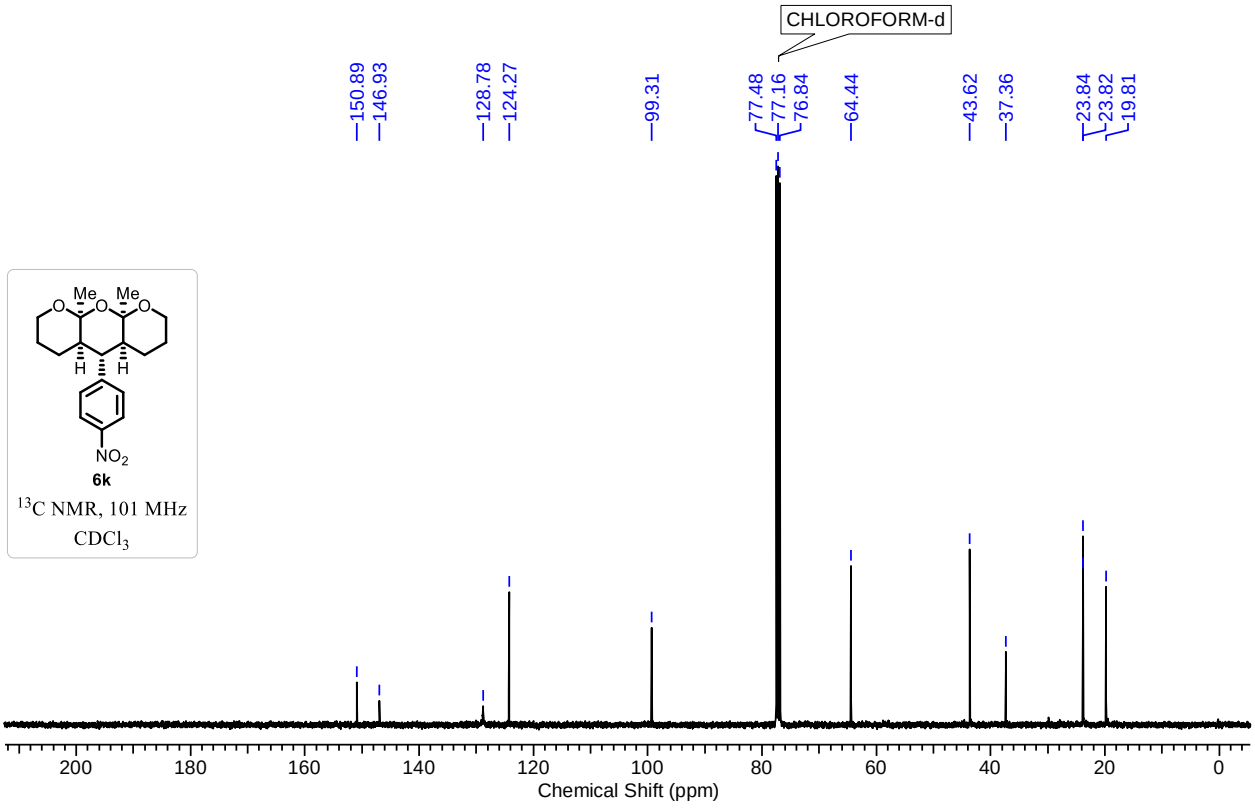
5-(4-Iodophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6j):



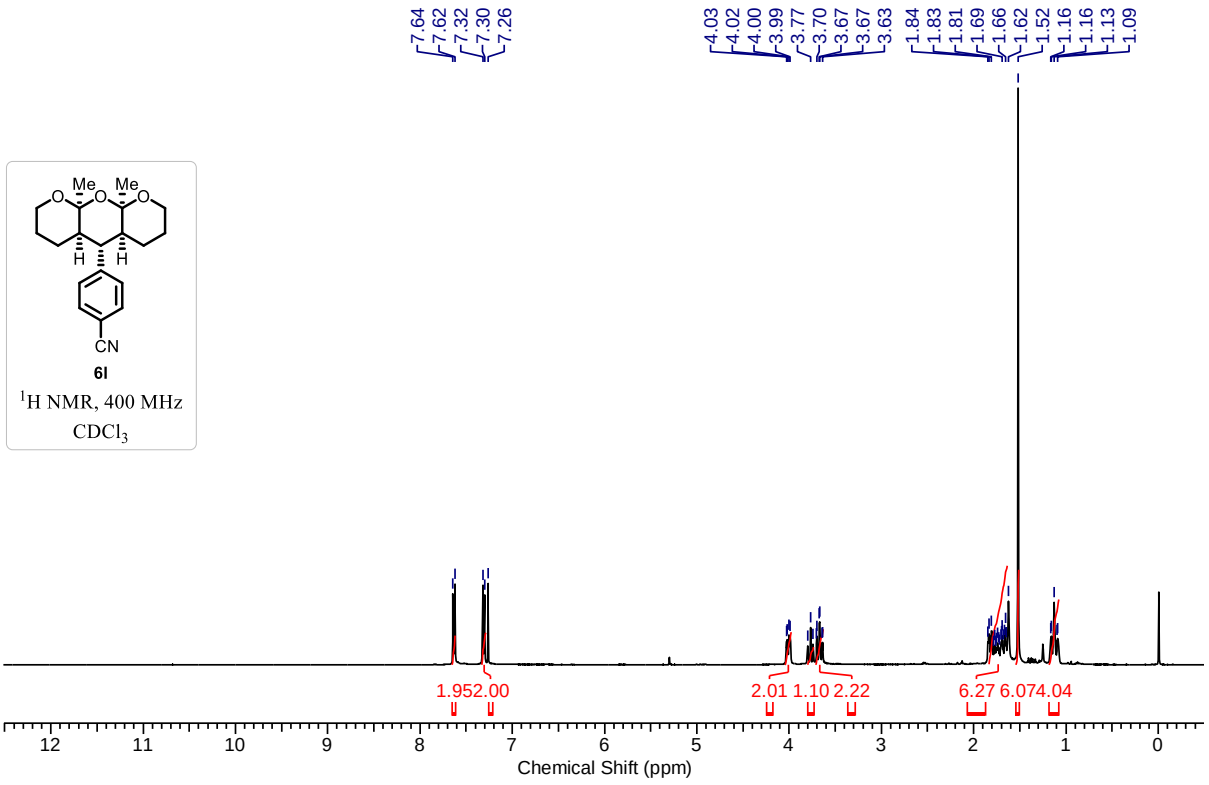


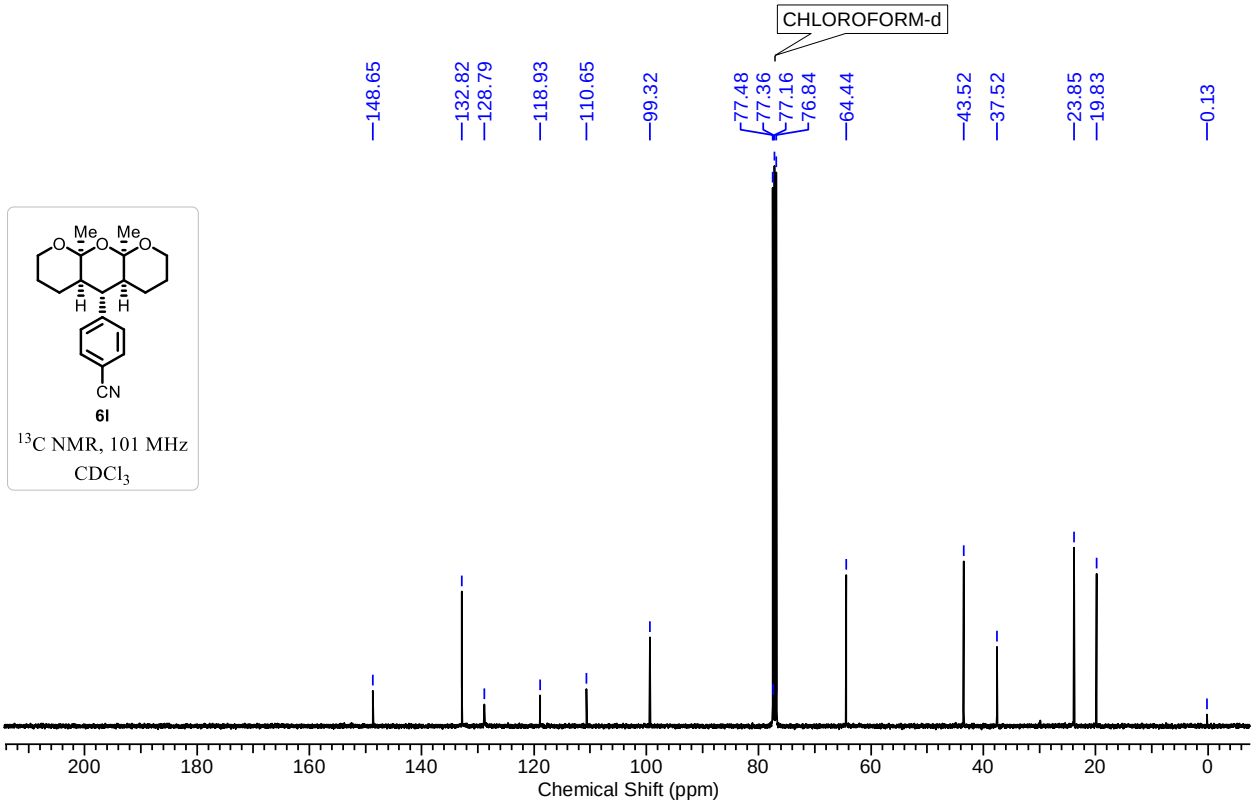
9a,10a-Dimethyl-5-(4-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6k):



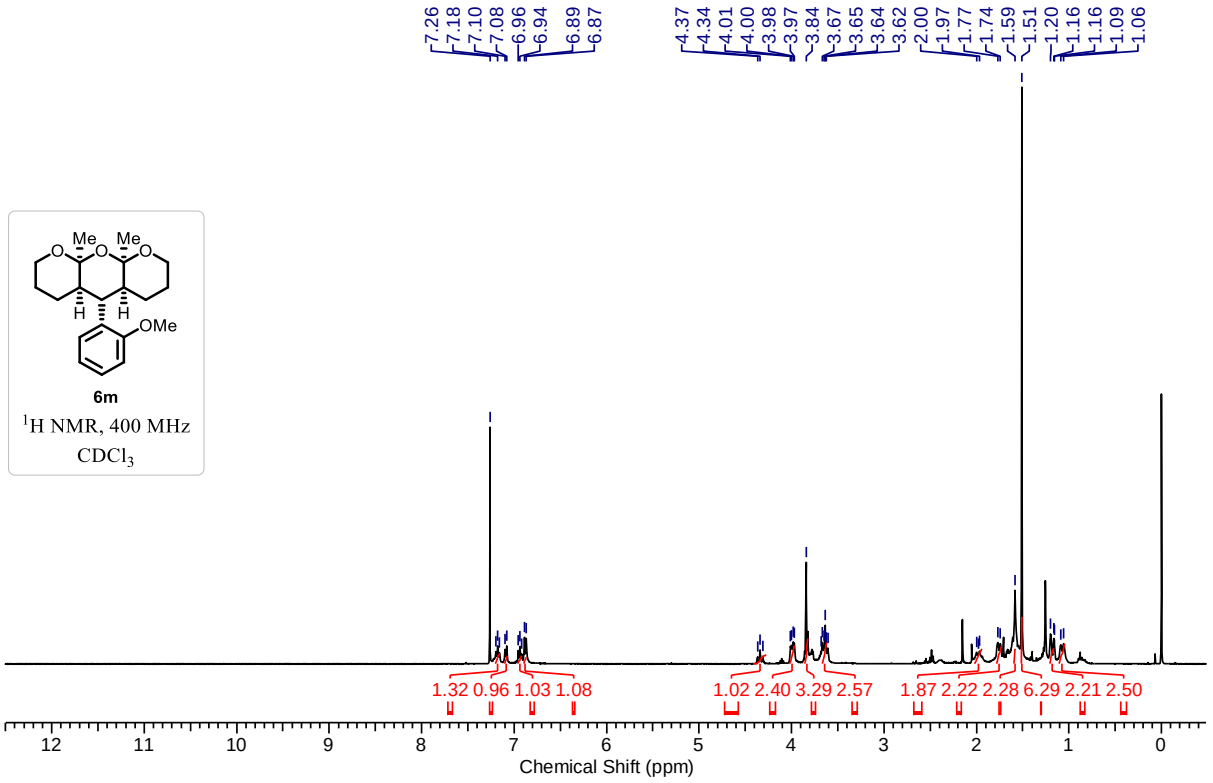


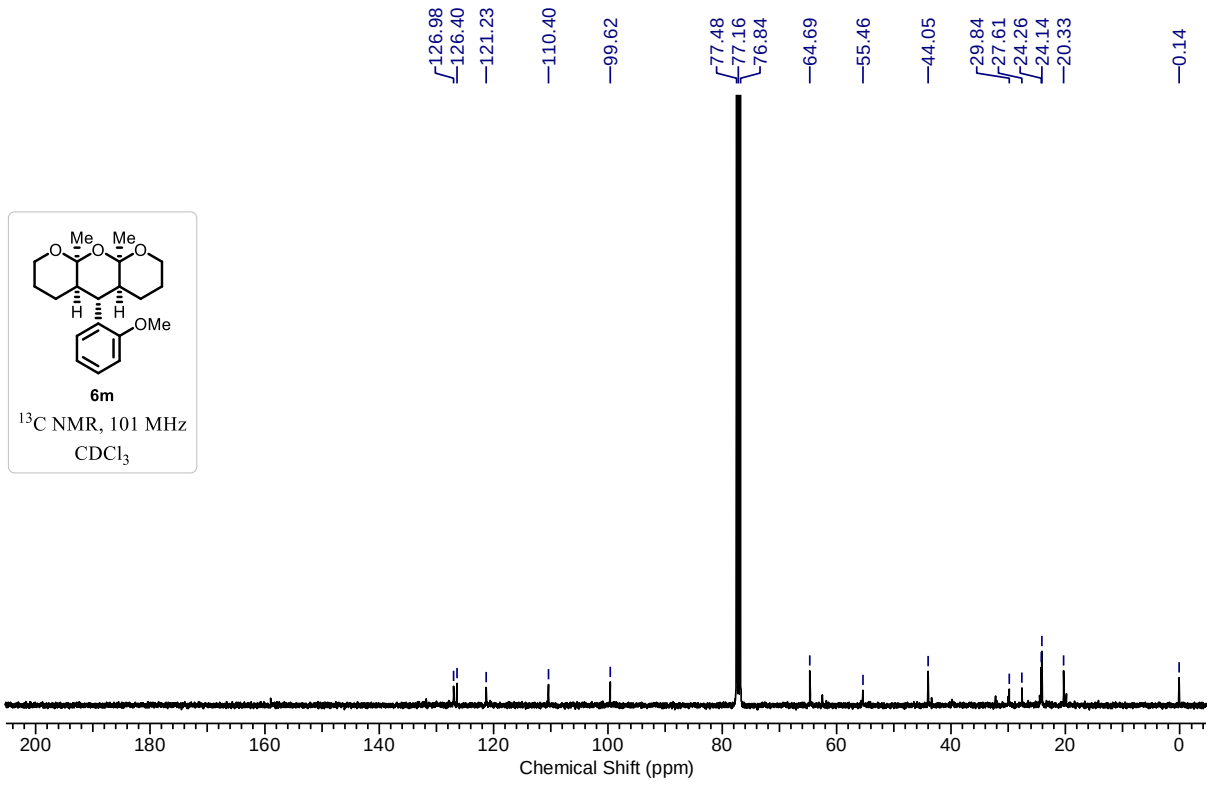
9a,10a-Dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran-5-yl)benzonitrile(6l):



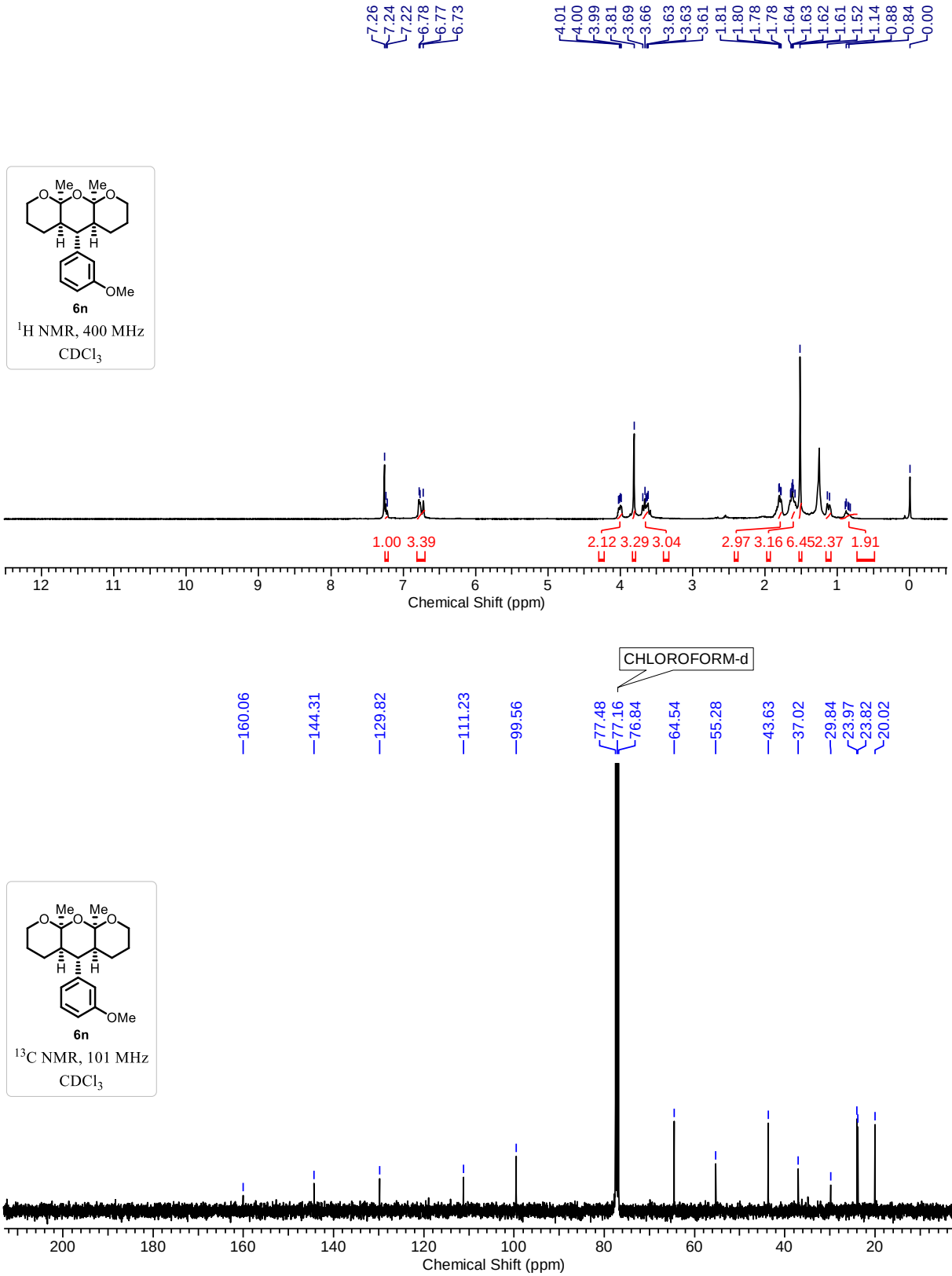


5-(2-Methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6m):

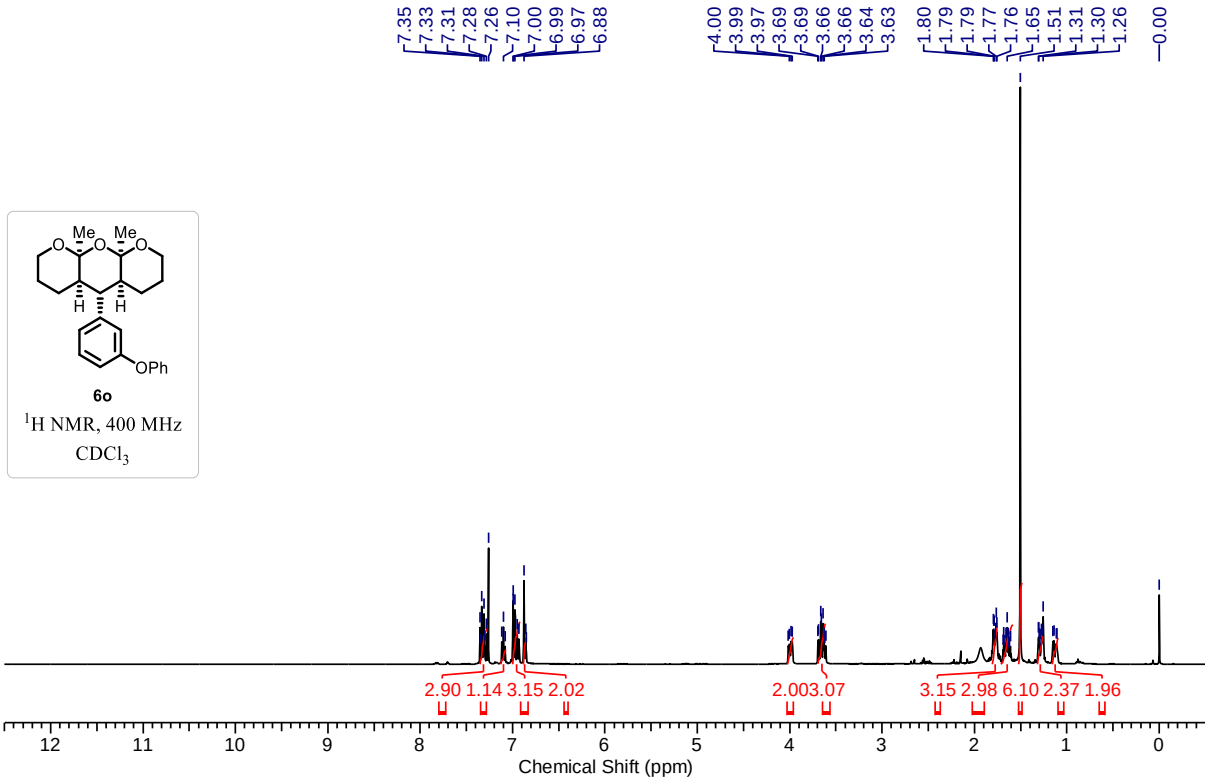


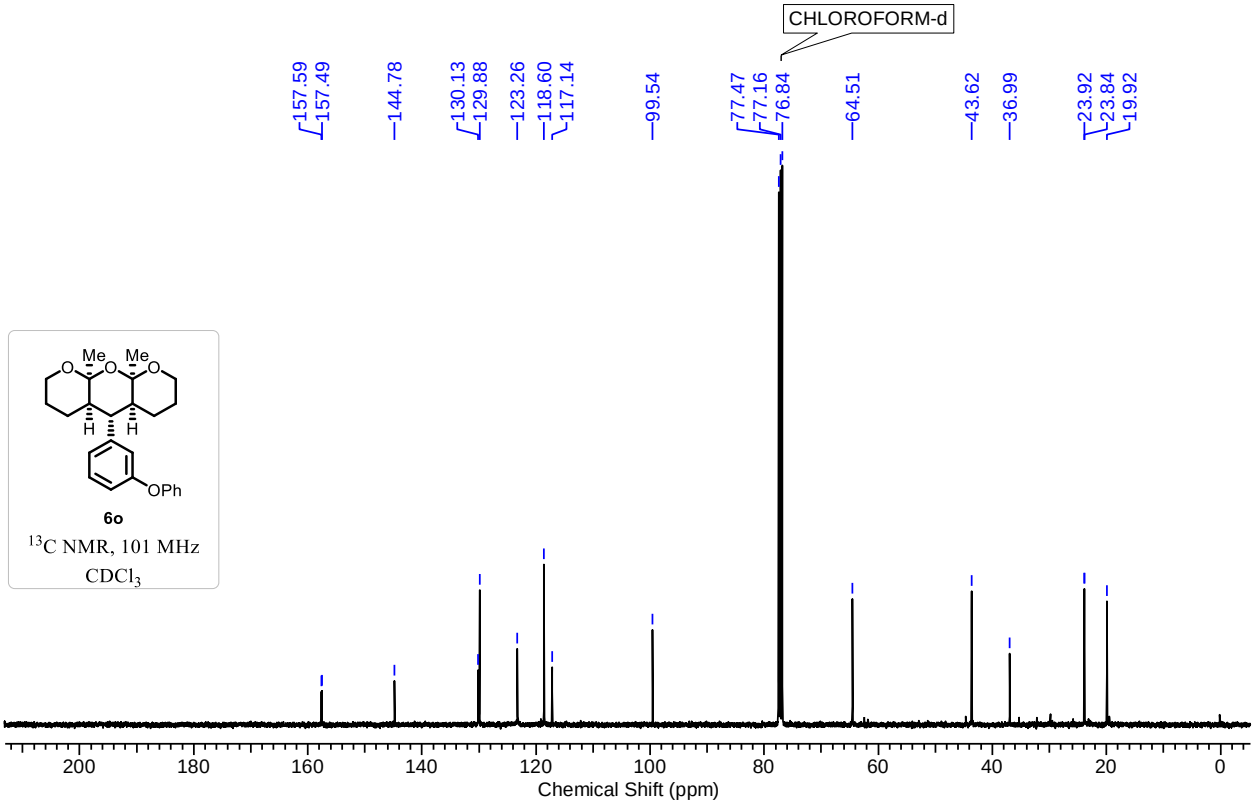


5-(3-Methoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6n):

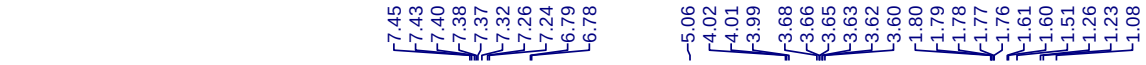


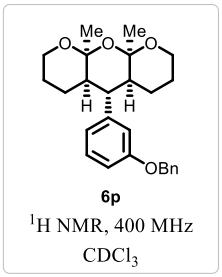
9a,10a-Dimethyl-5-(3-phenoxyphenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6o):





5-(3-(Benzyloxy)phenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6p)

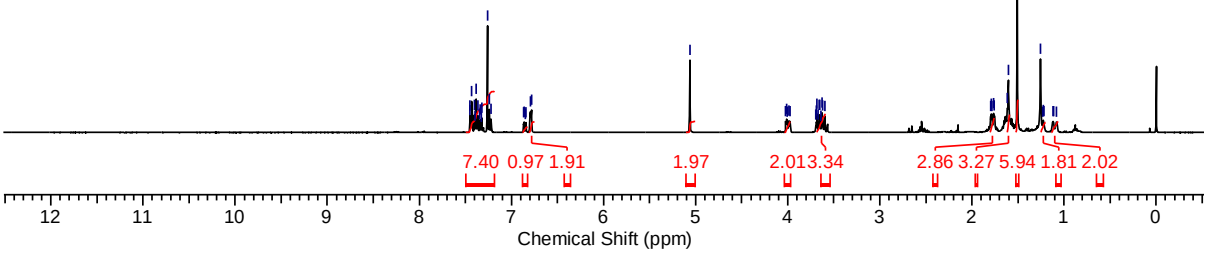


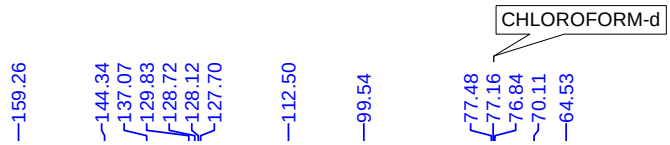


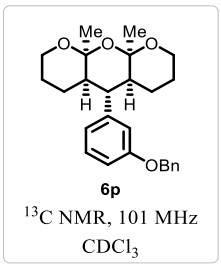
6p

^{1}H NMR, 400 MHz

$CDCl_3$



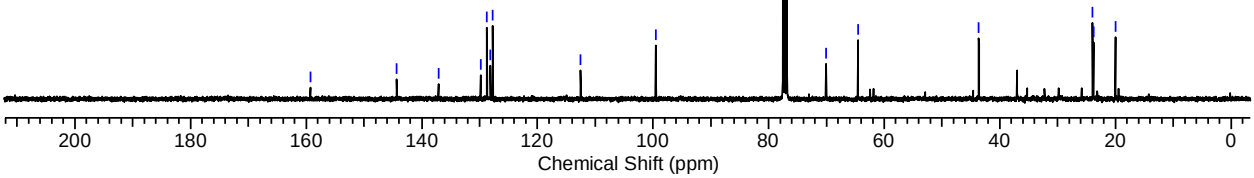




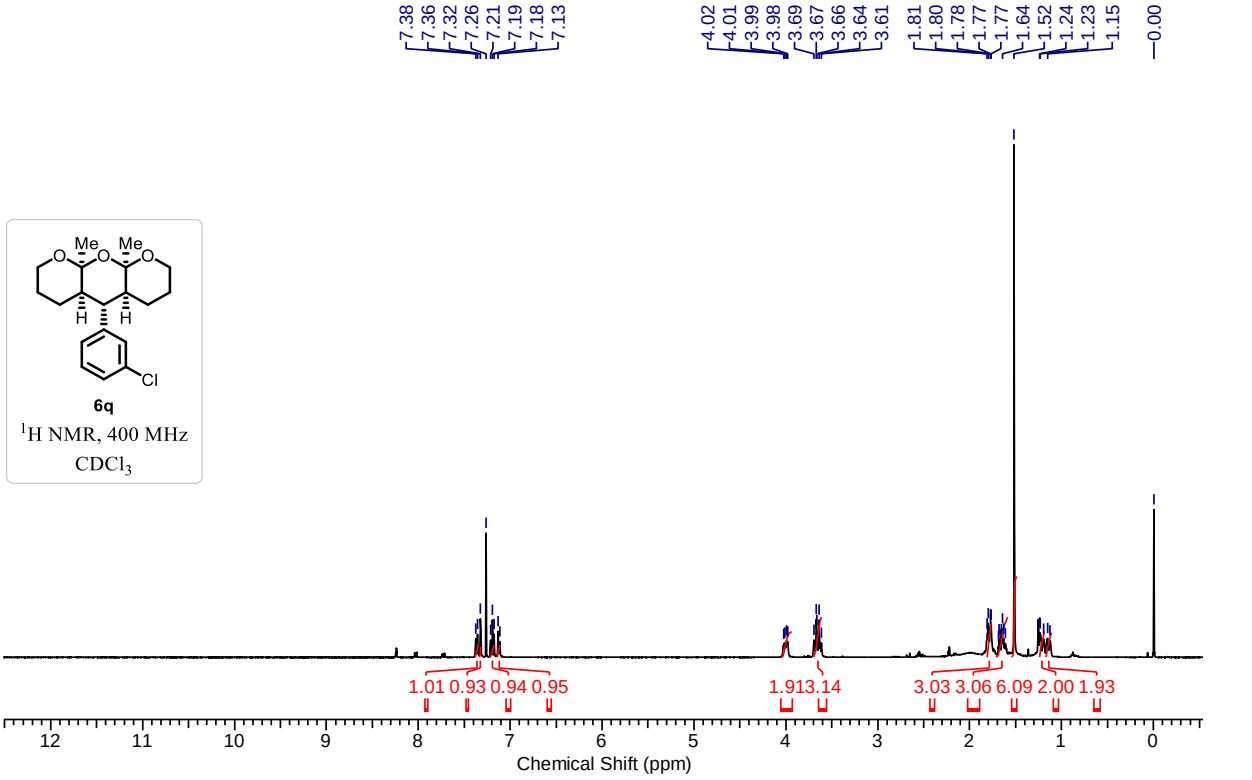
6p

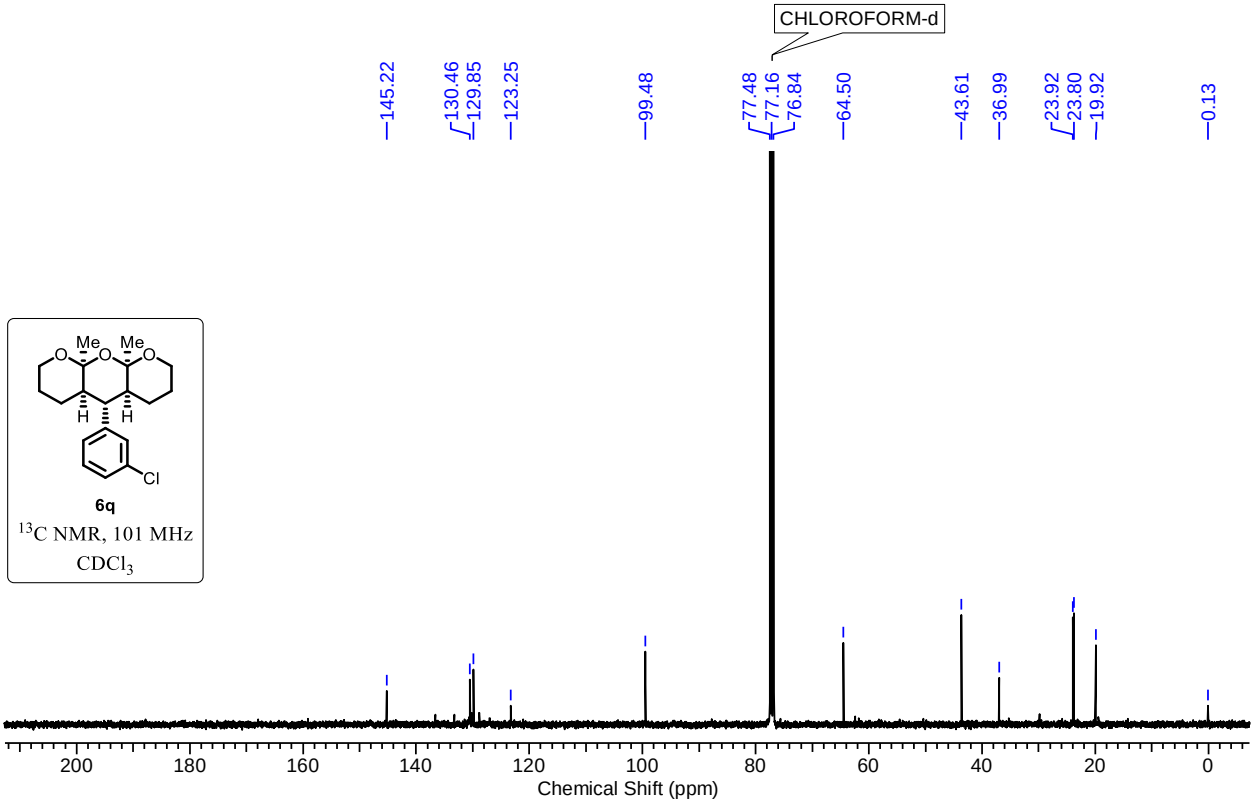
^{13}C NMR, 101 MHz

$CDCl_3$

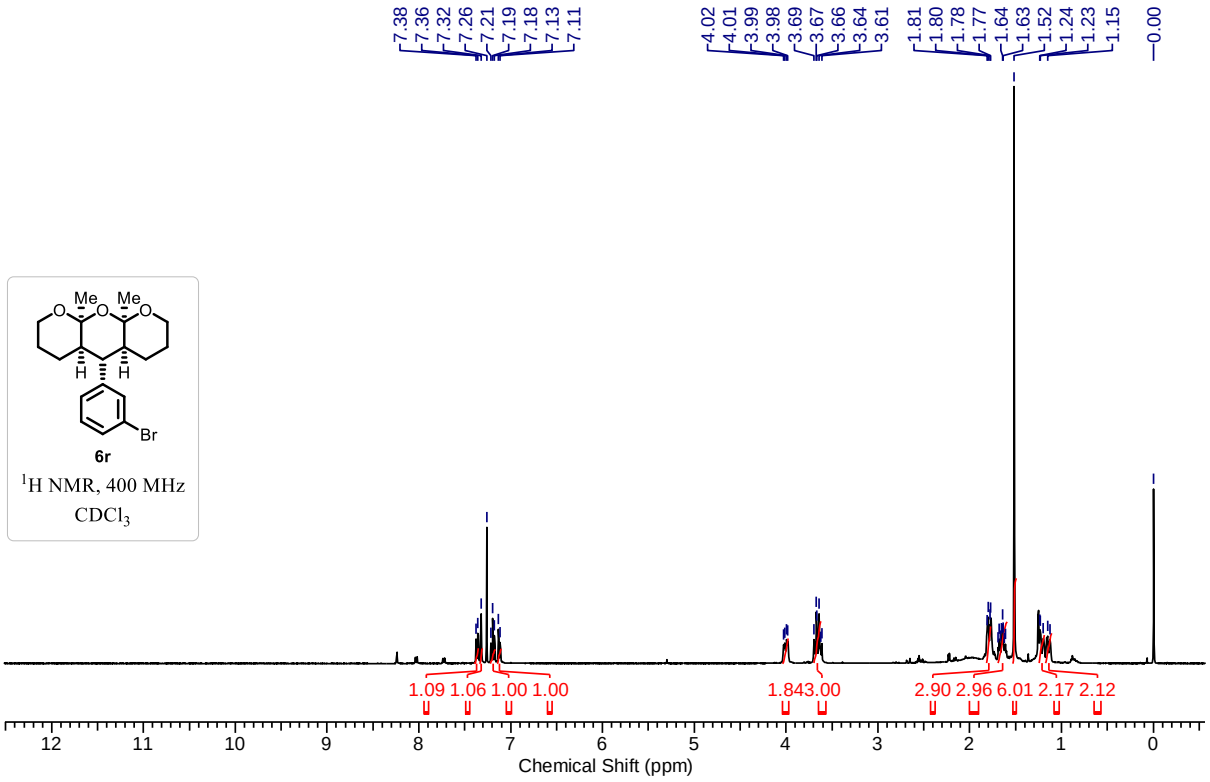


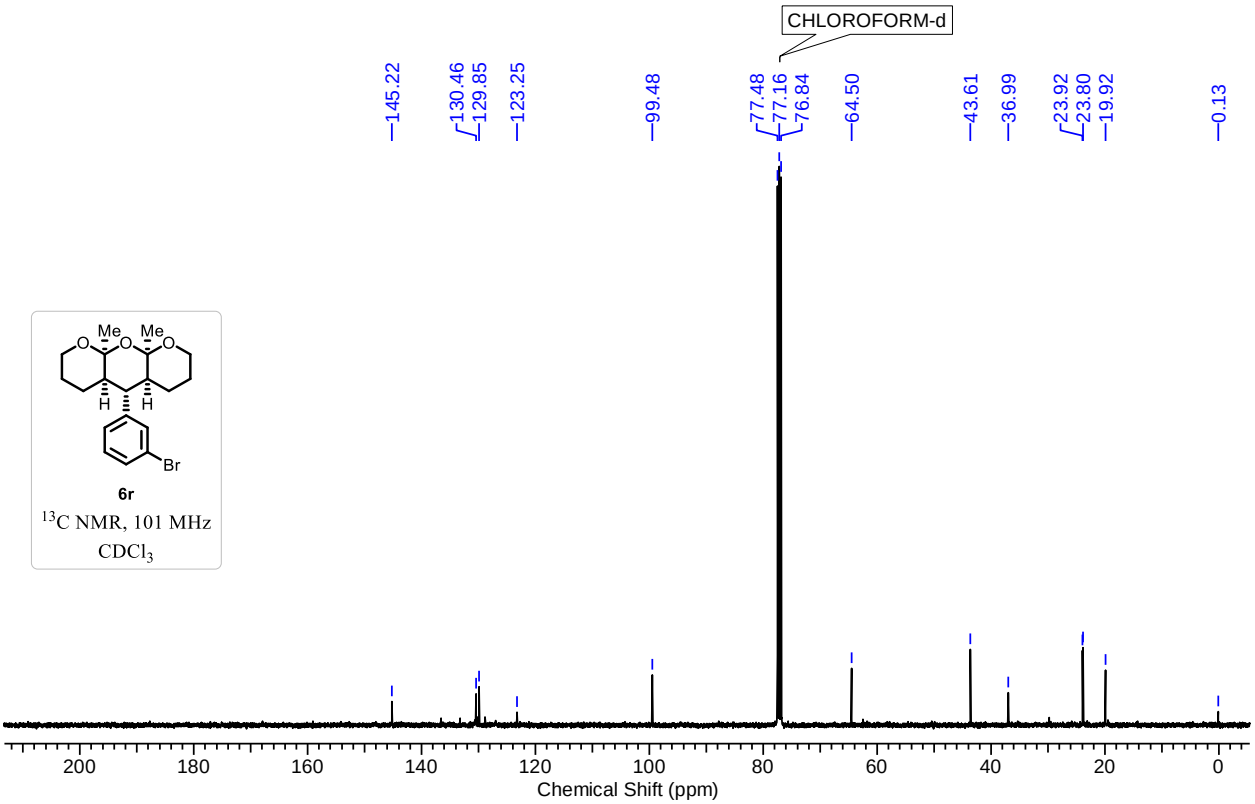
5-(3-Chlorophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6q):



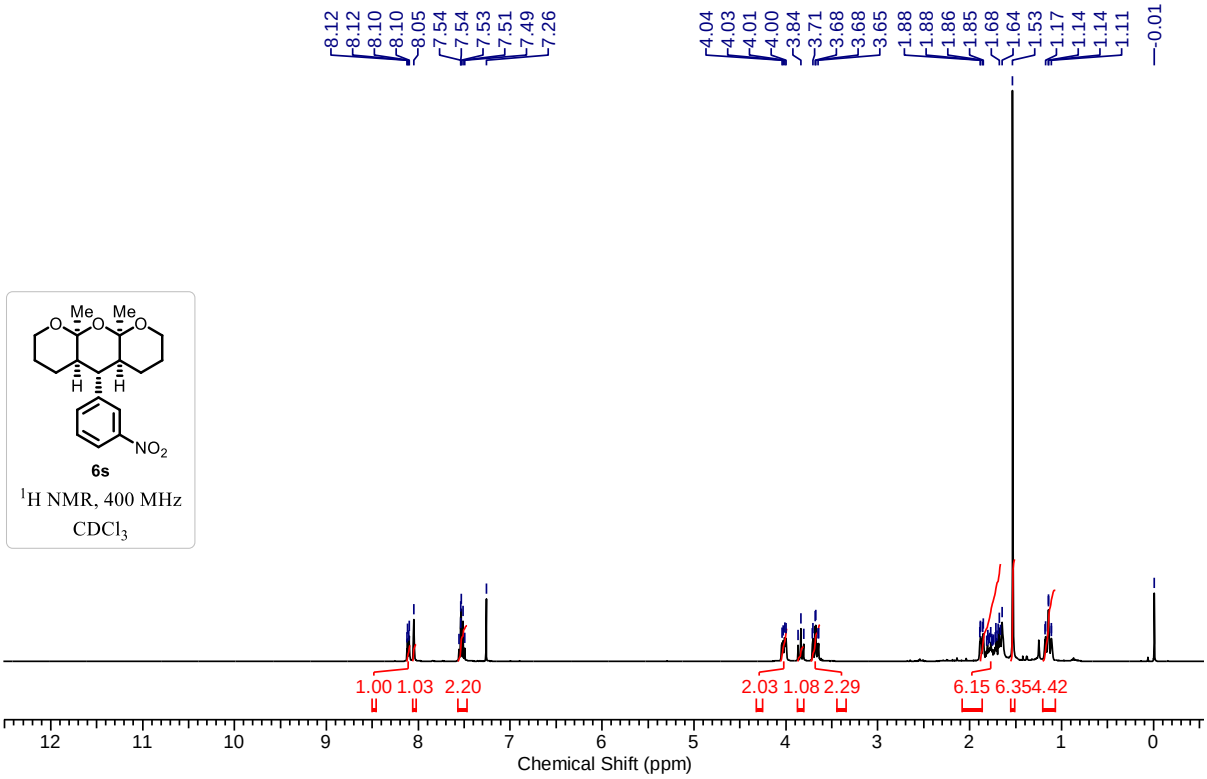


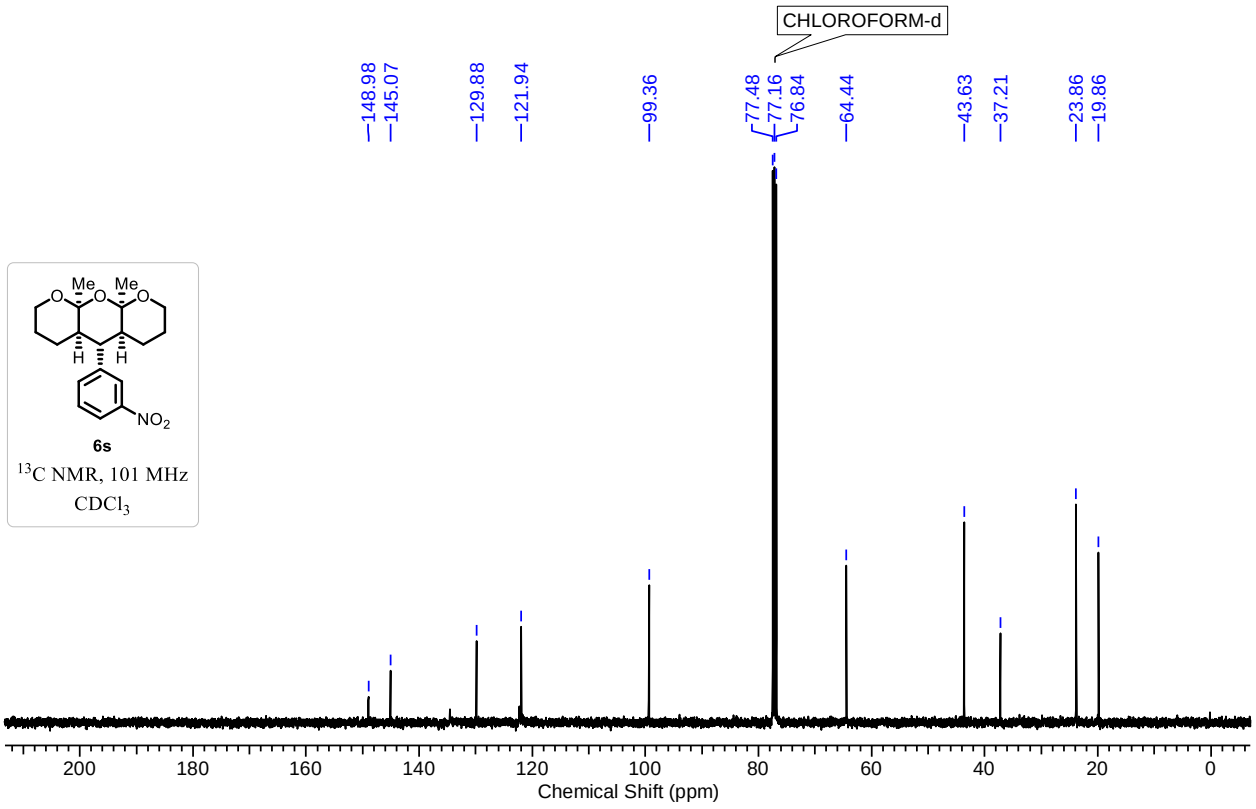
5-(3-Bromophenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6r):



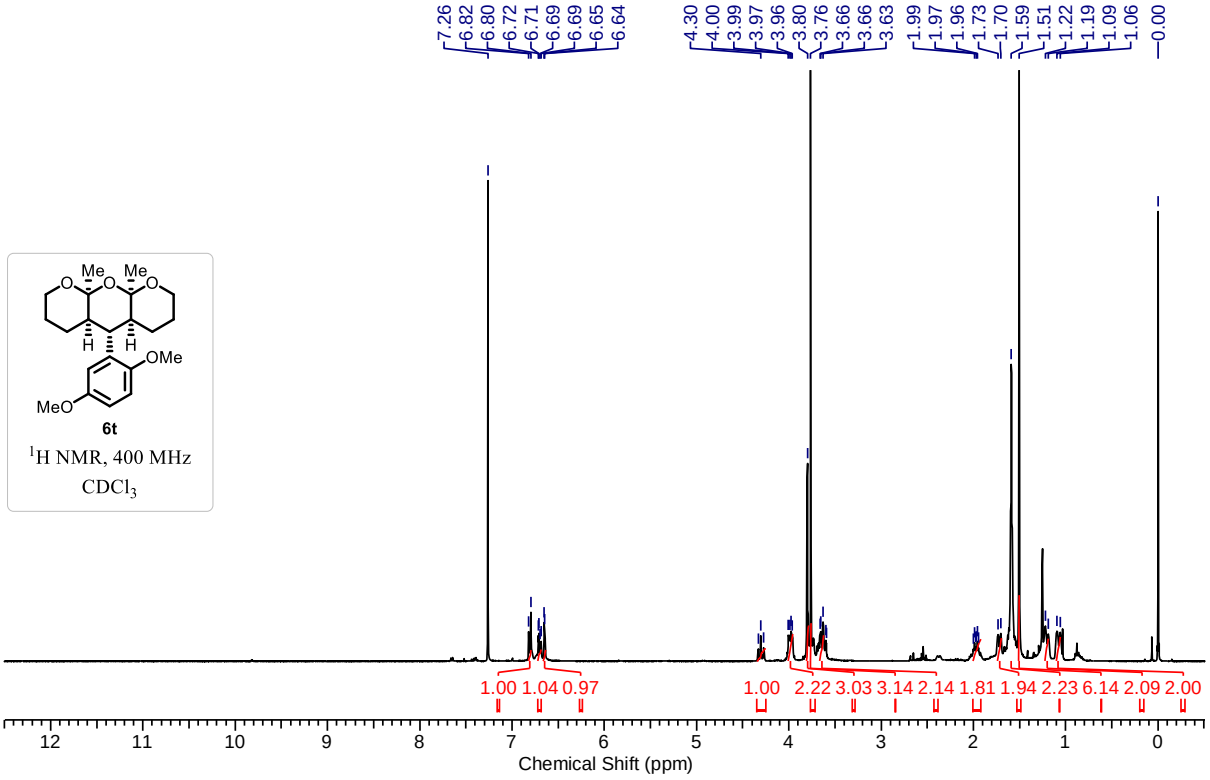


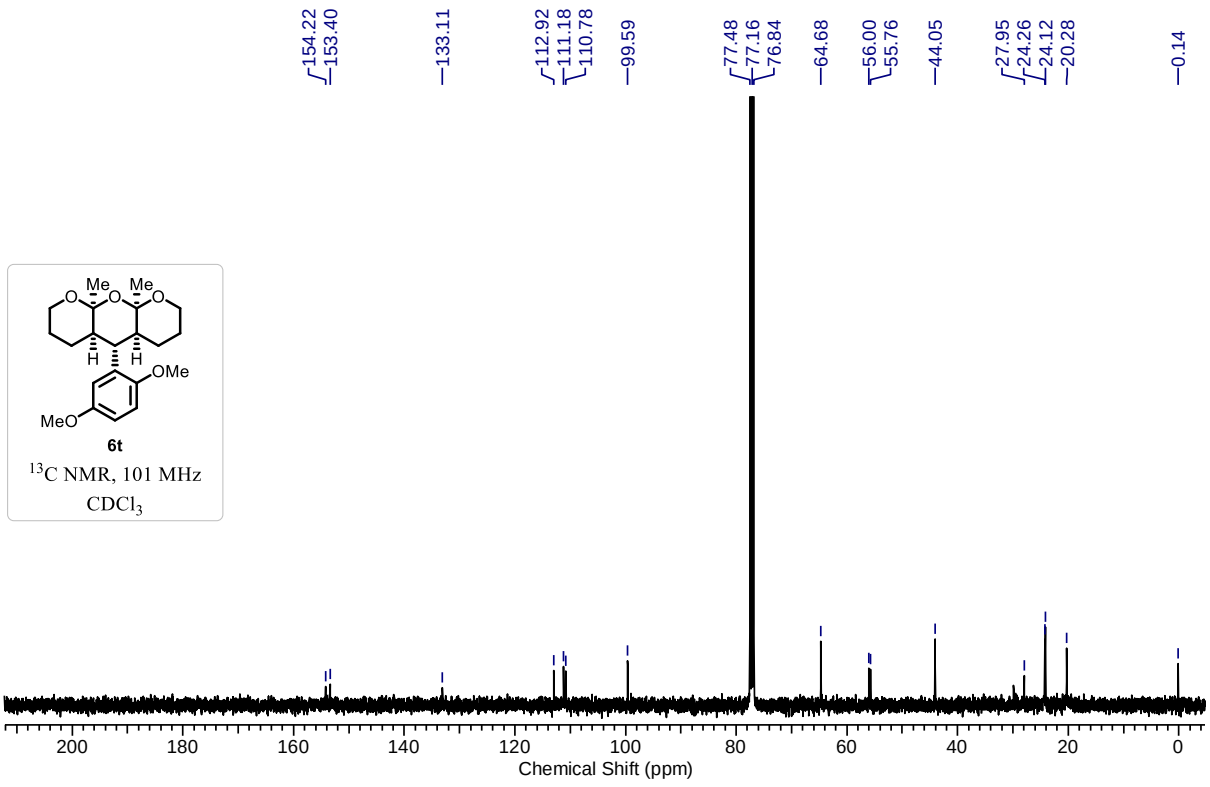
9a,10a-Dimethyl-5-(3-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6s):



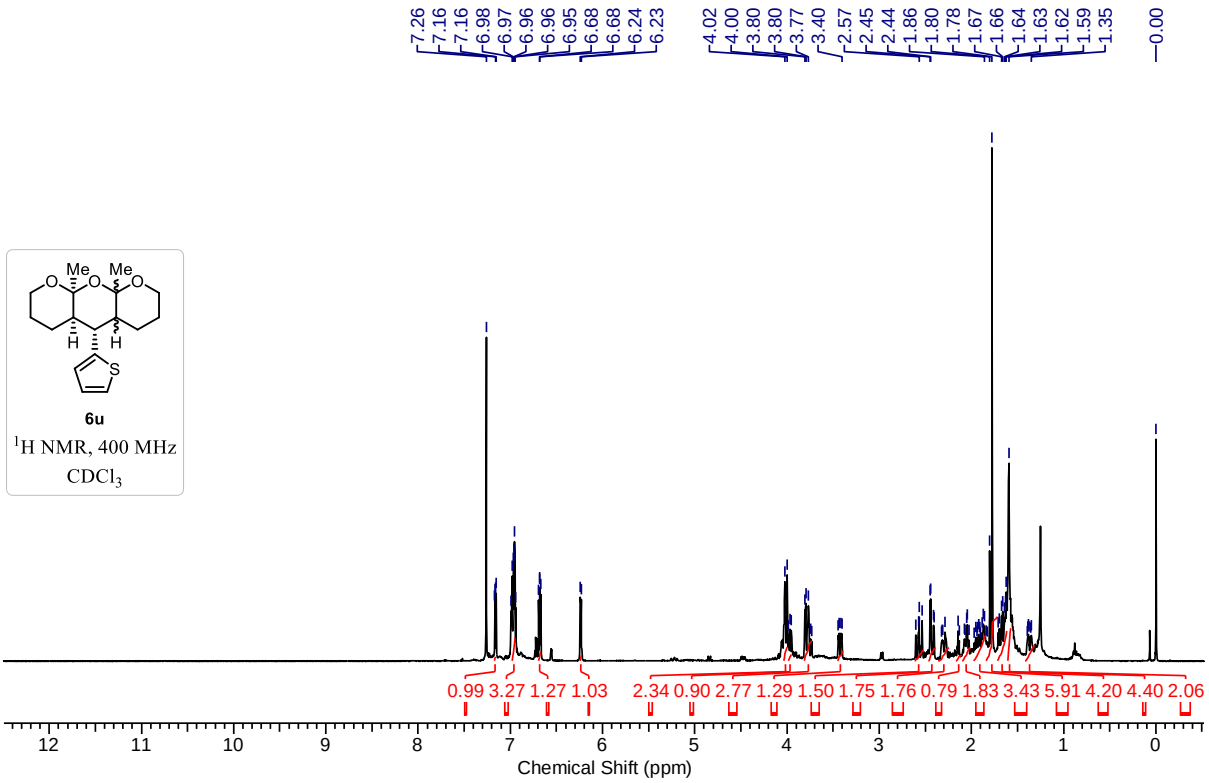


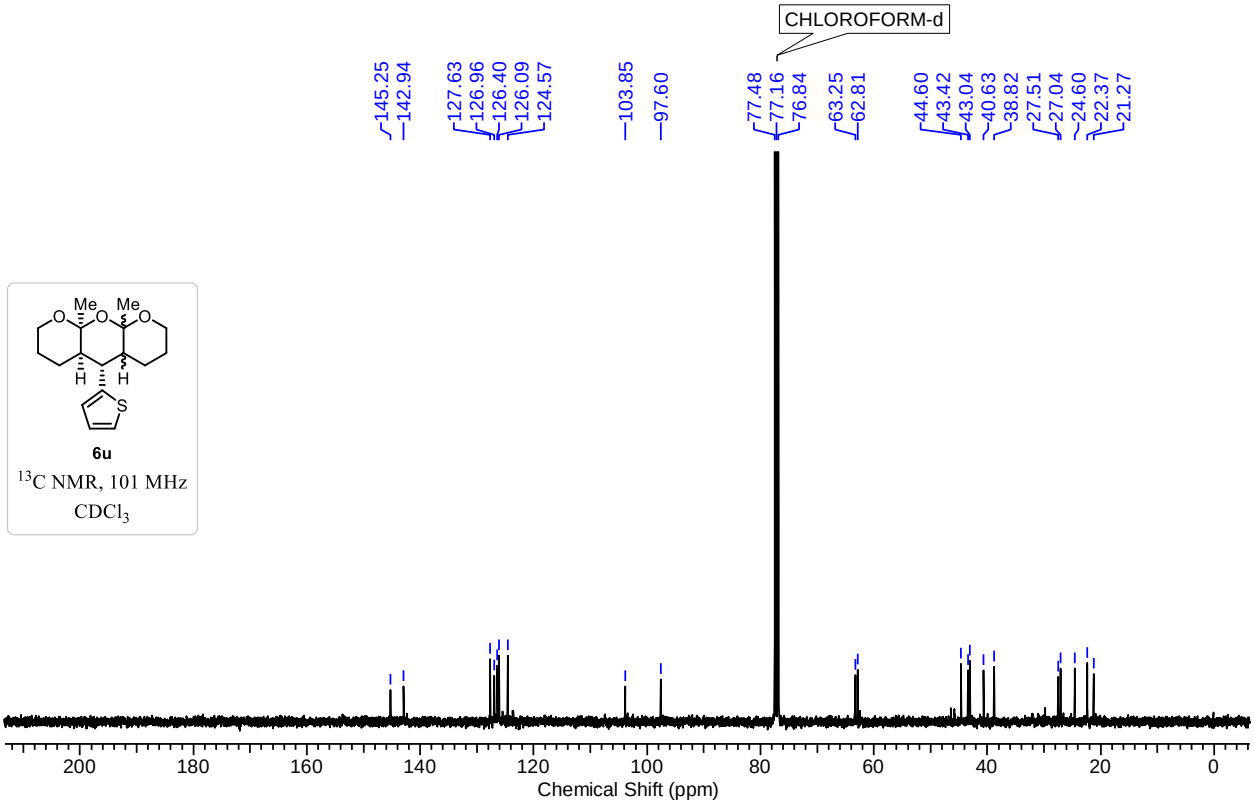
5-(2,5-Dimethoxyphenyl)-9a,10a-dimethyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6t):



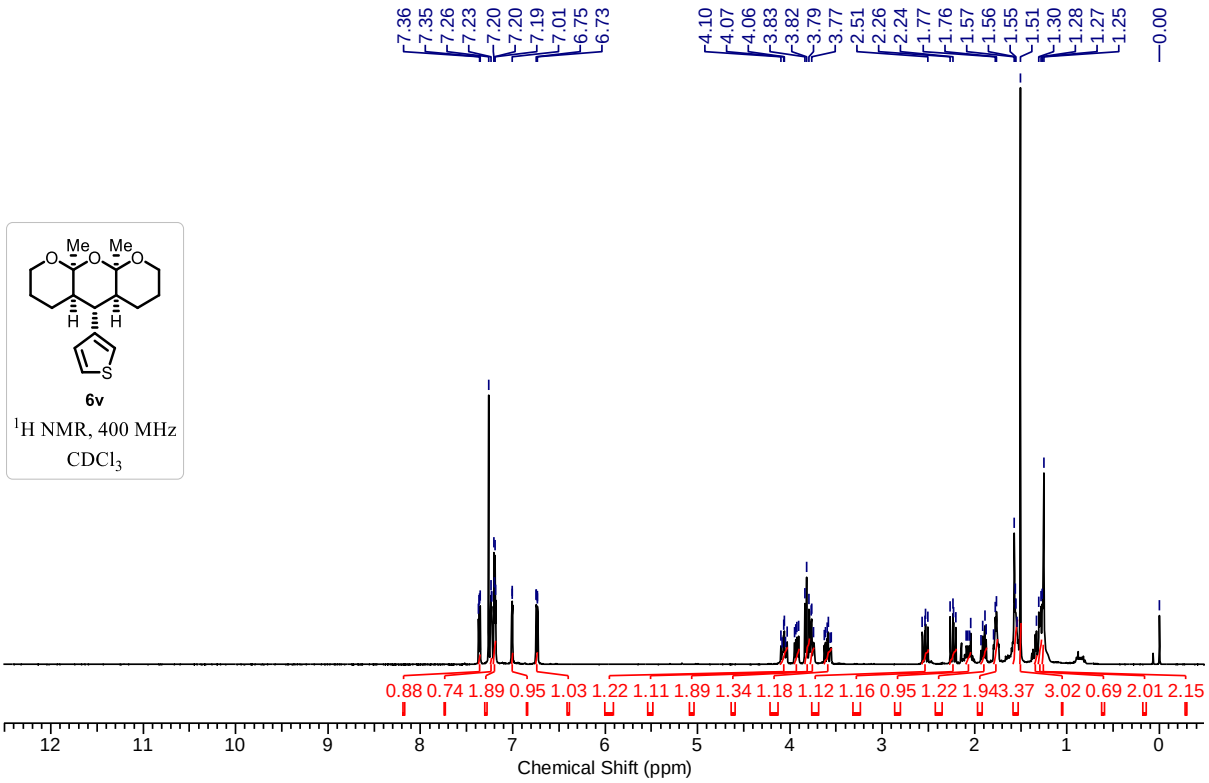


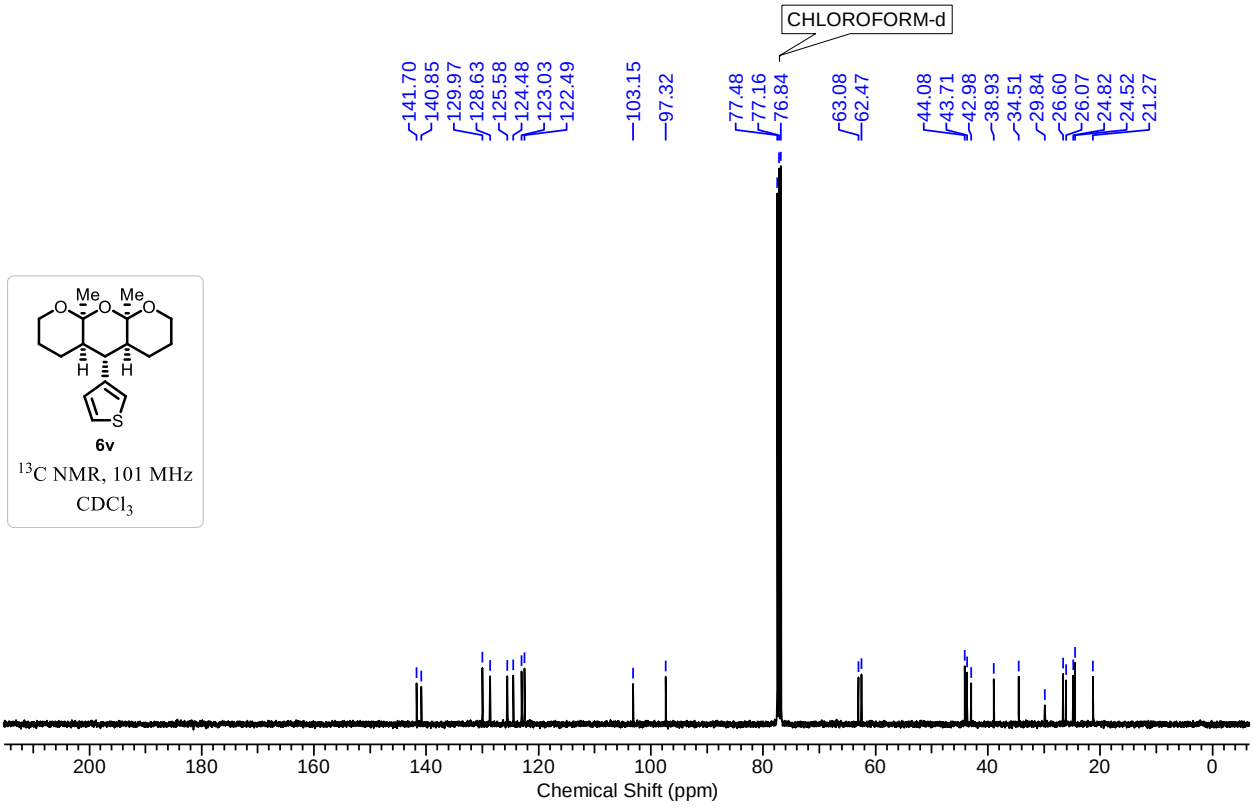
9a,10a-Dimethyl-5-(thiophen-2-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6u):



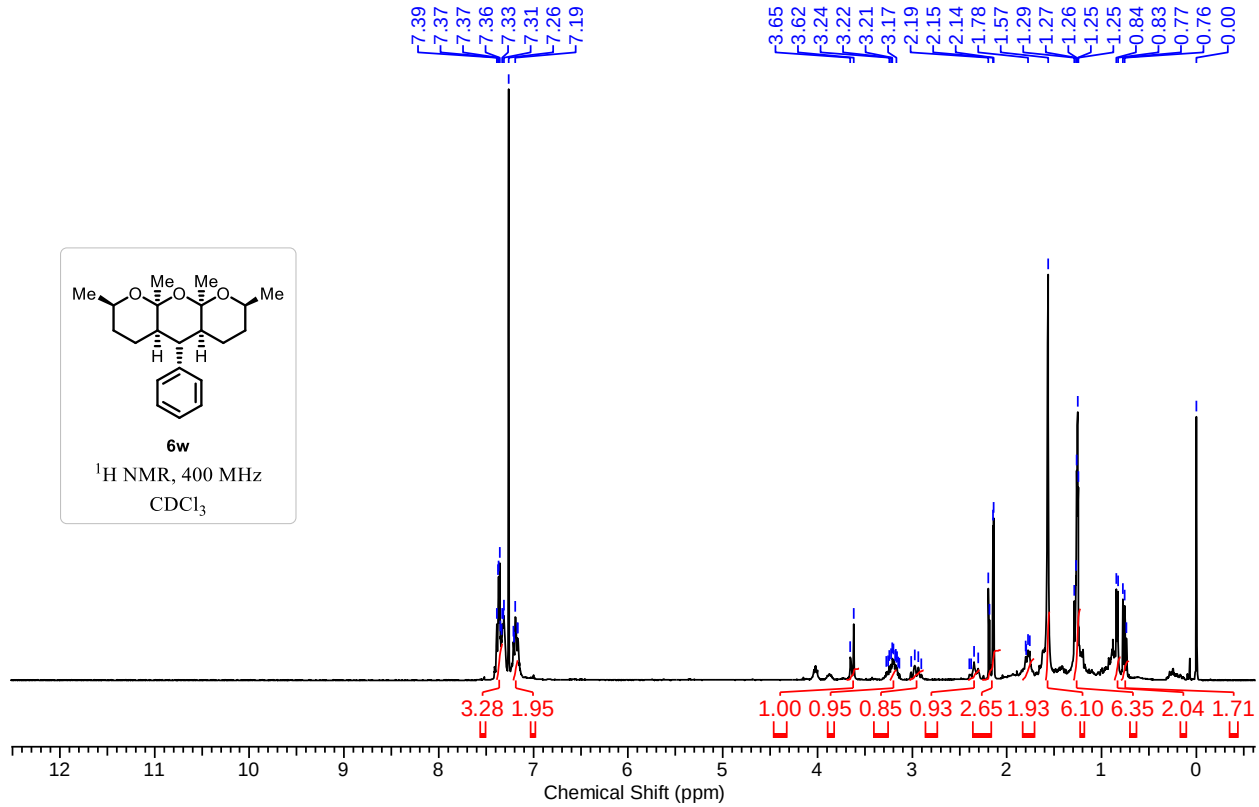


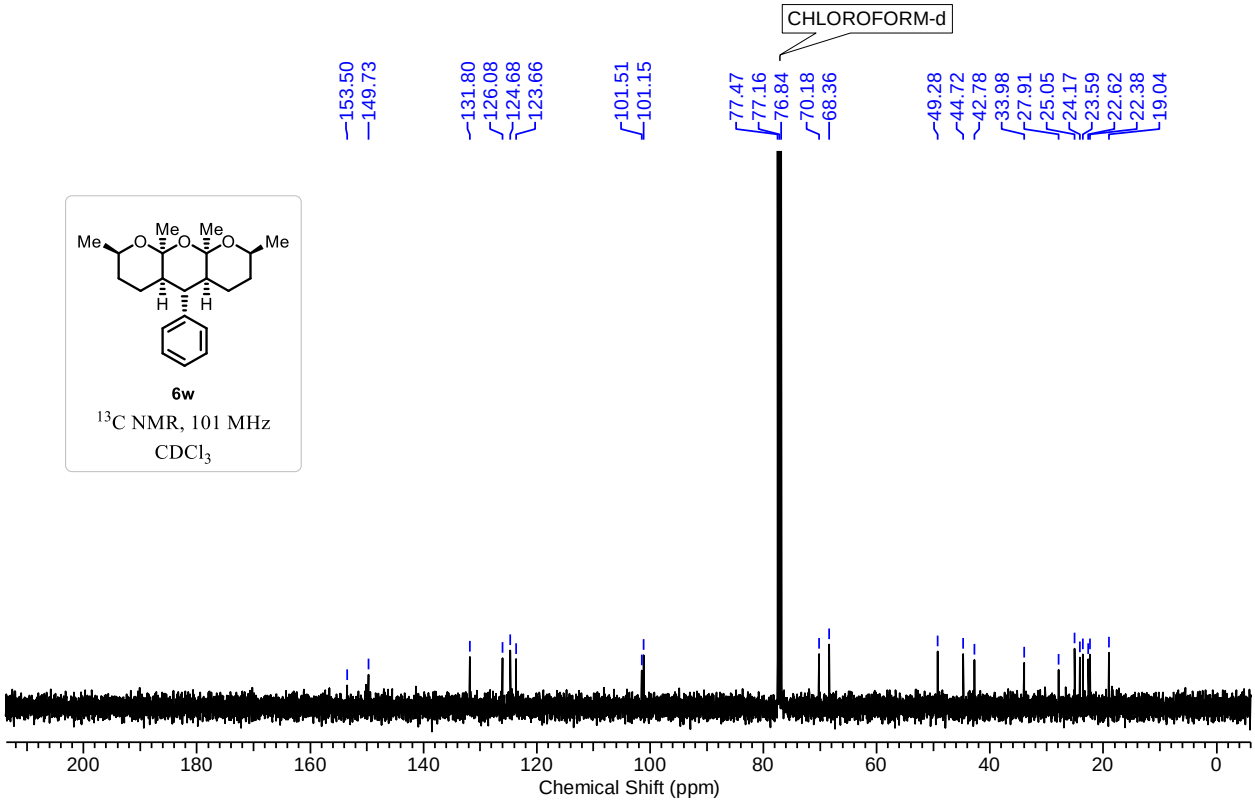
9a,10a-Dimethyl-5-(thiophen-3-yl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6v):



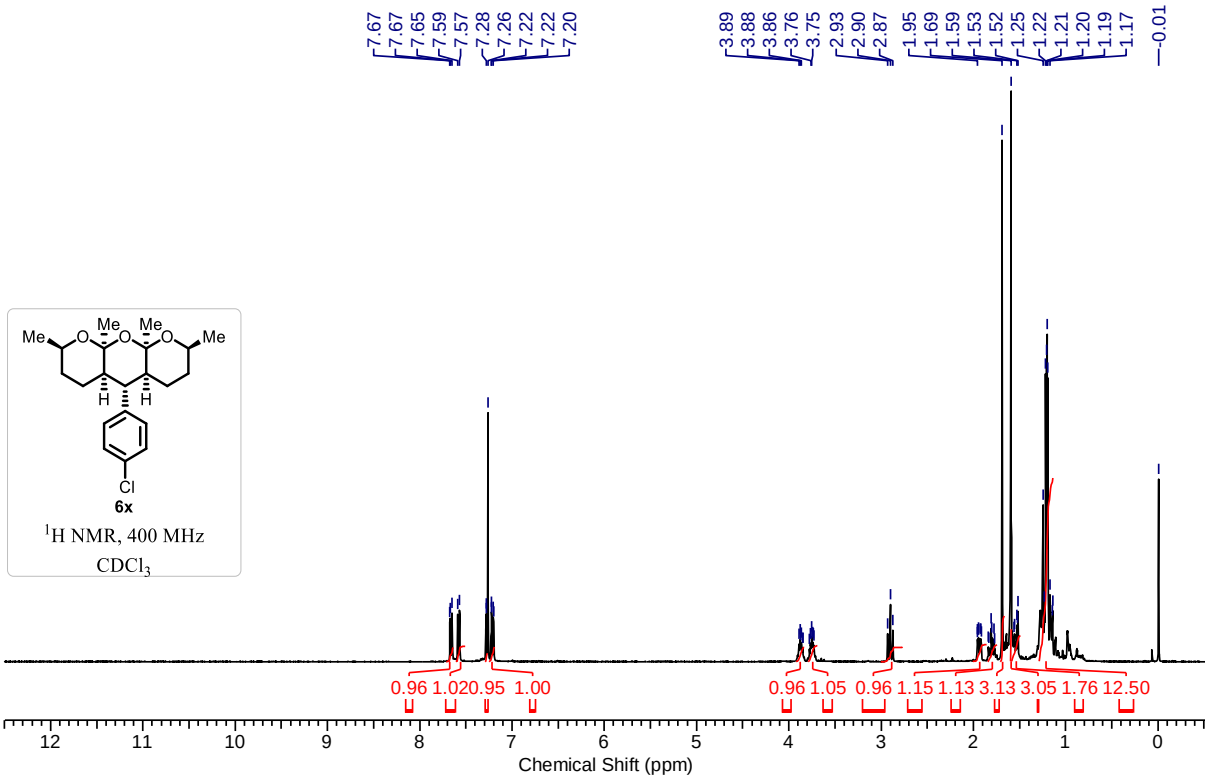


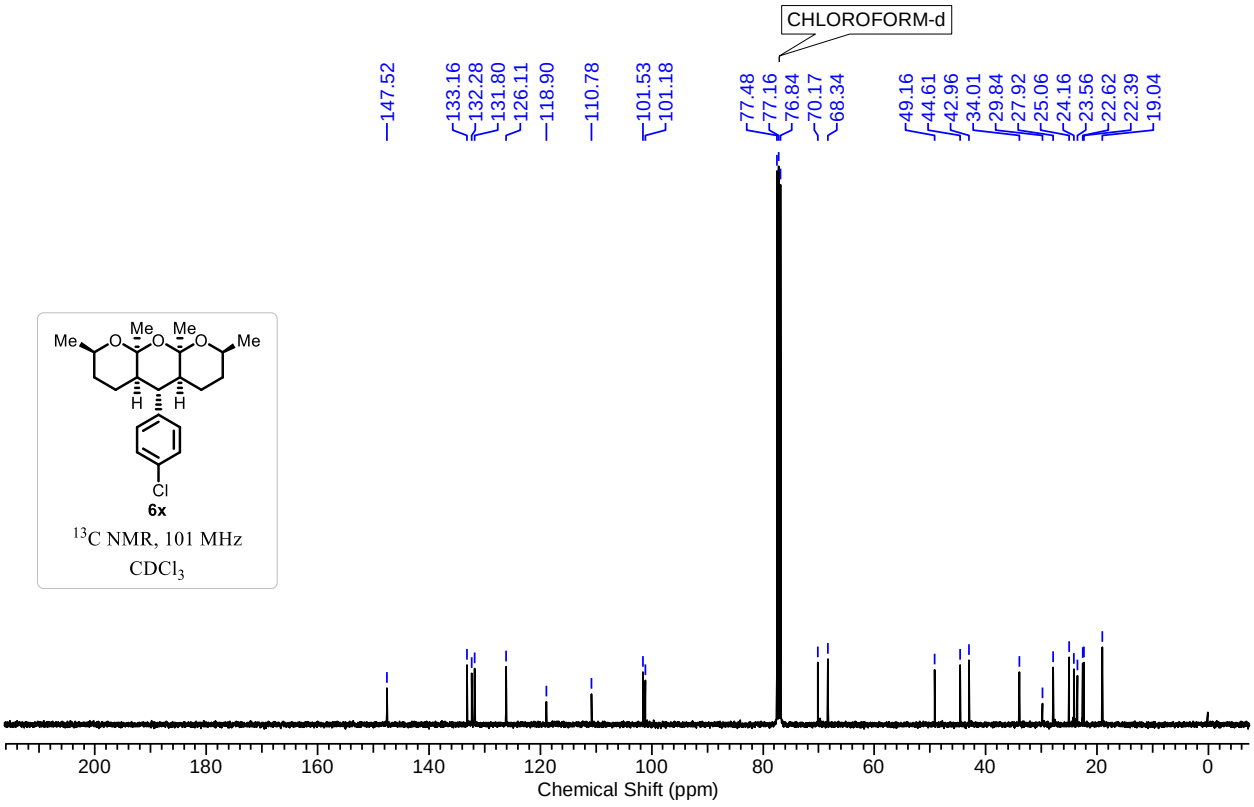
2,8,9a,10a-Tetramethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6w):



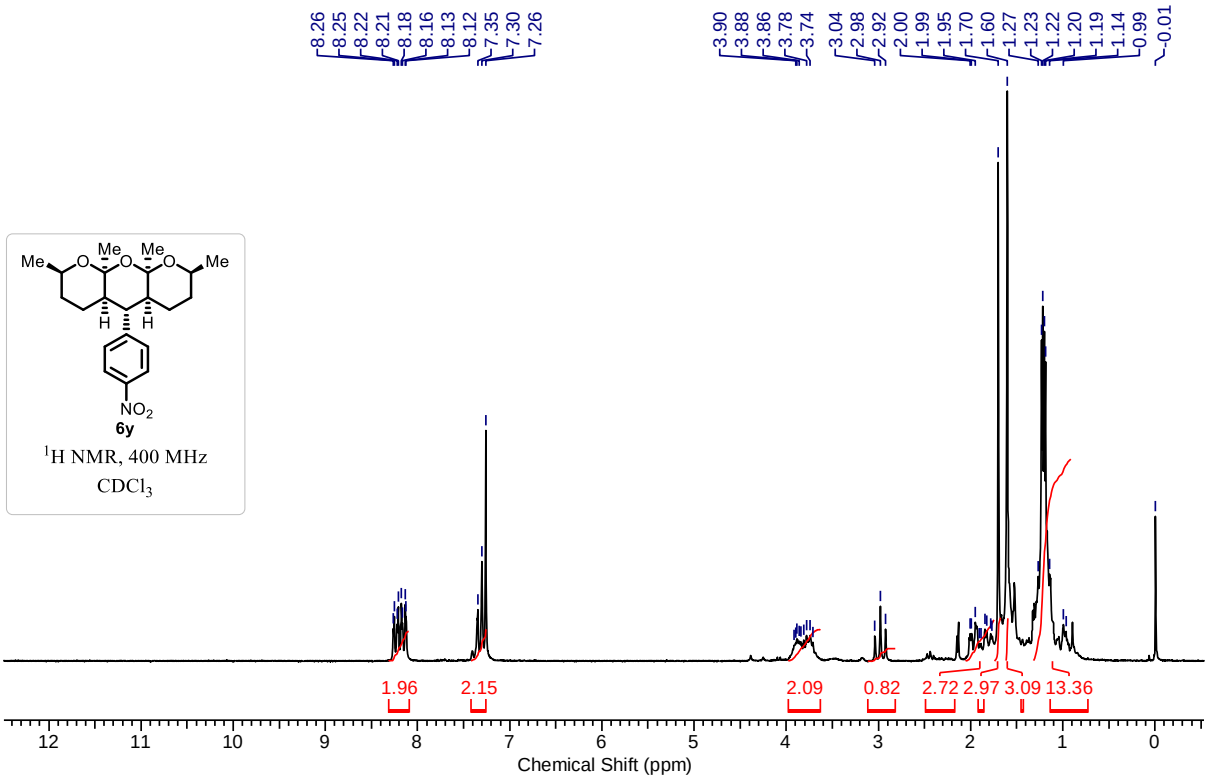


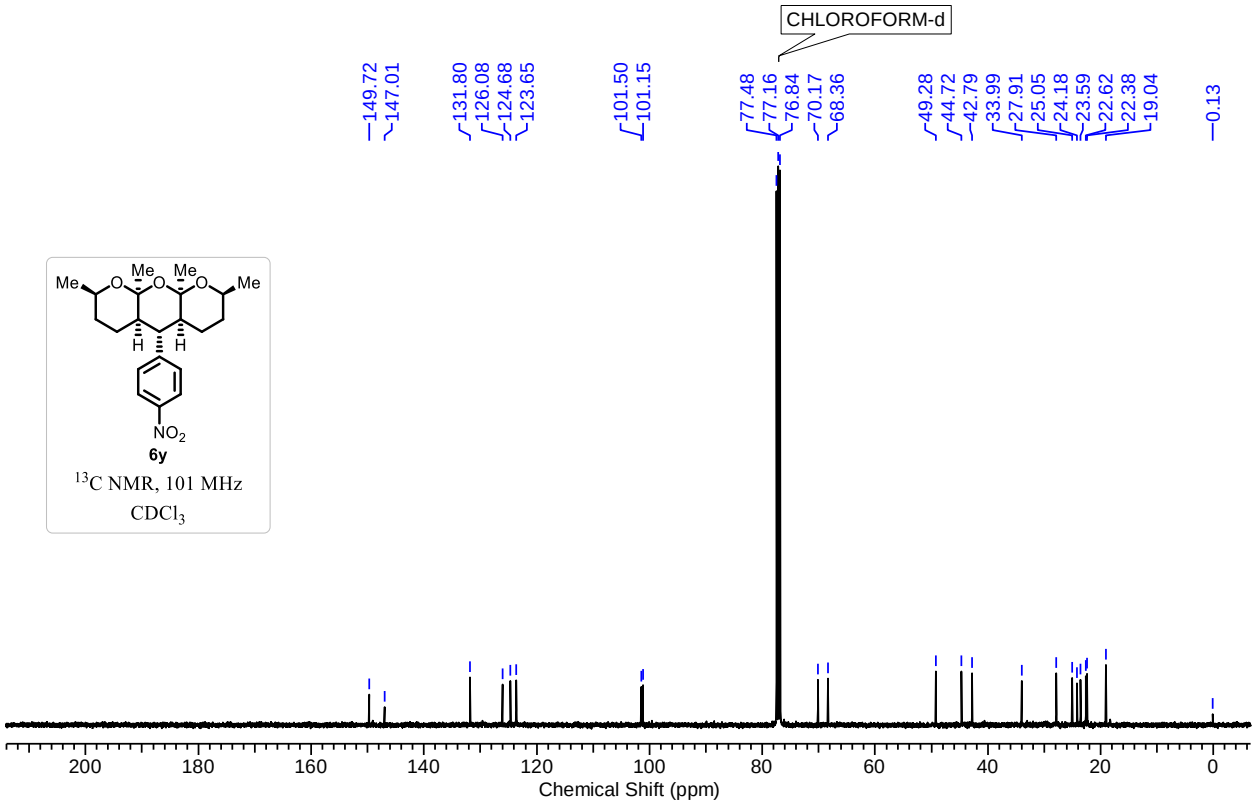
2,8,9a,10a-Tetramethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6x):



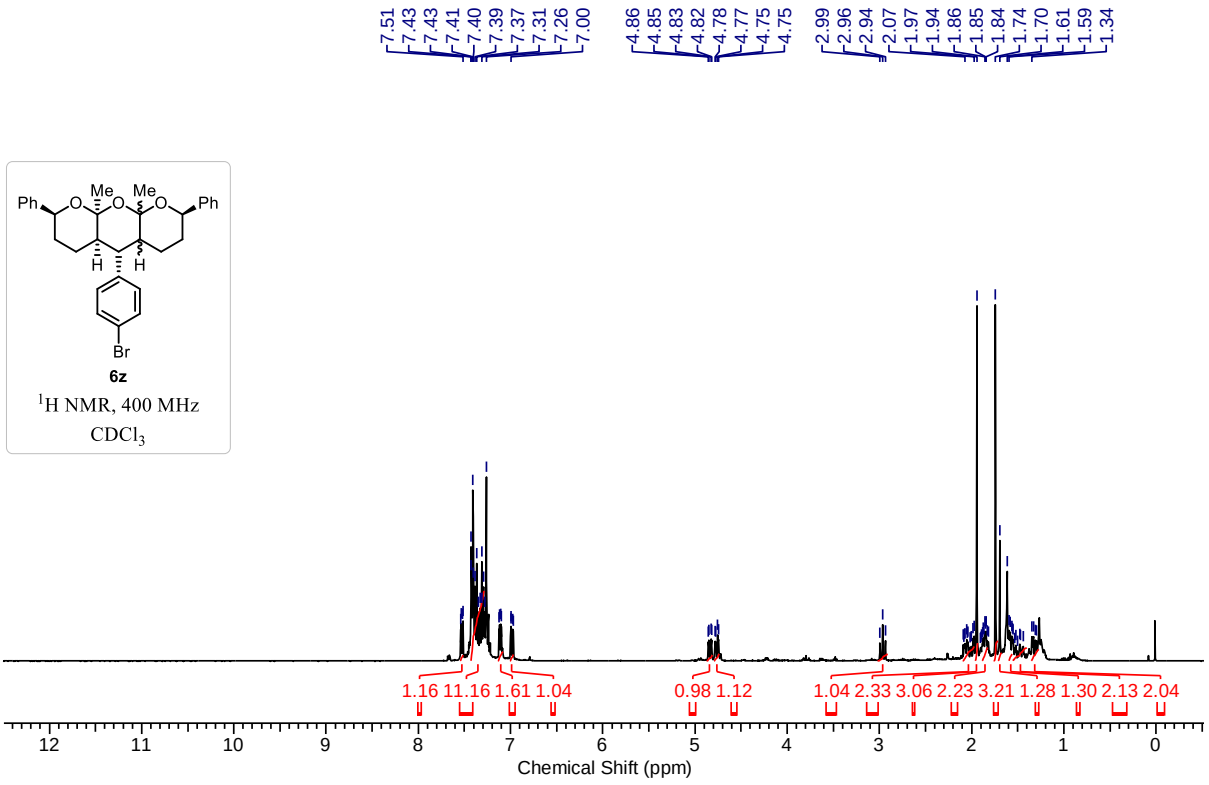


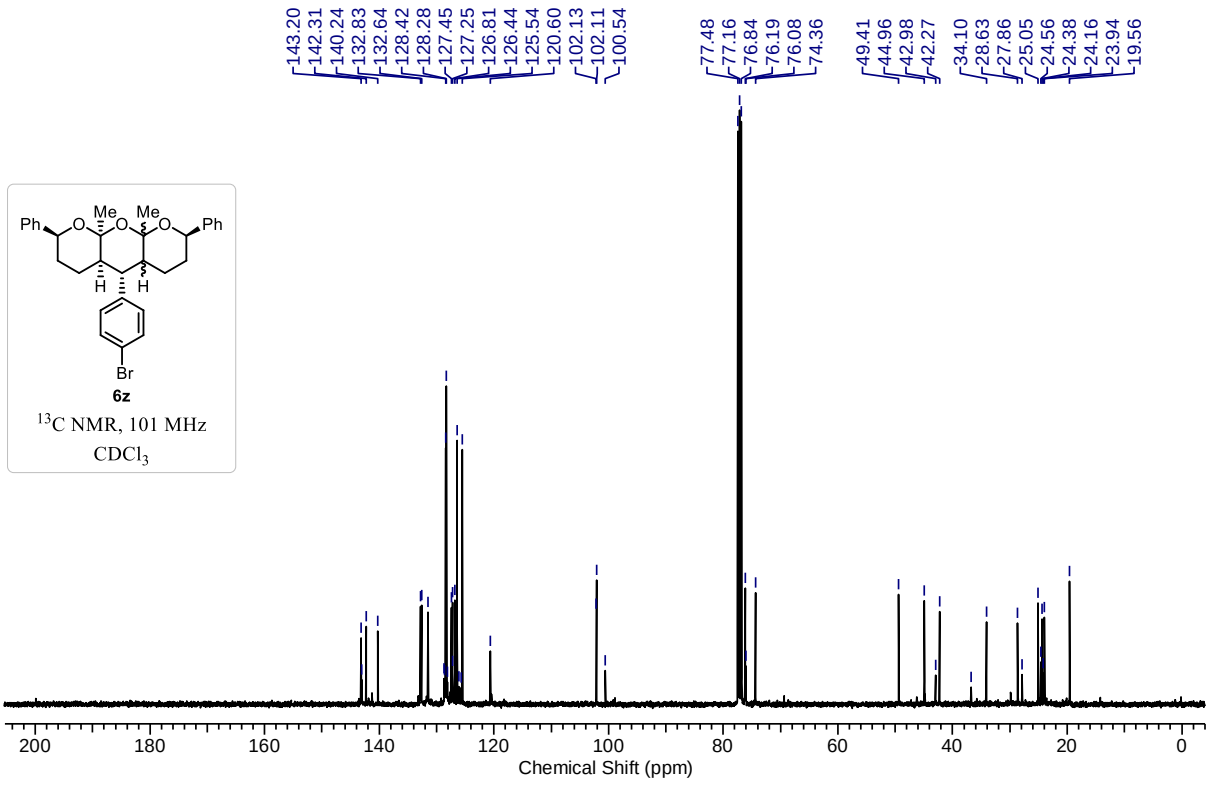
2,8,9a,10a-Tetramethyl-5-(4-nitrophenyl)octahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (6y):



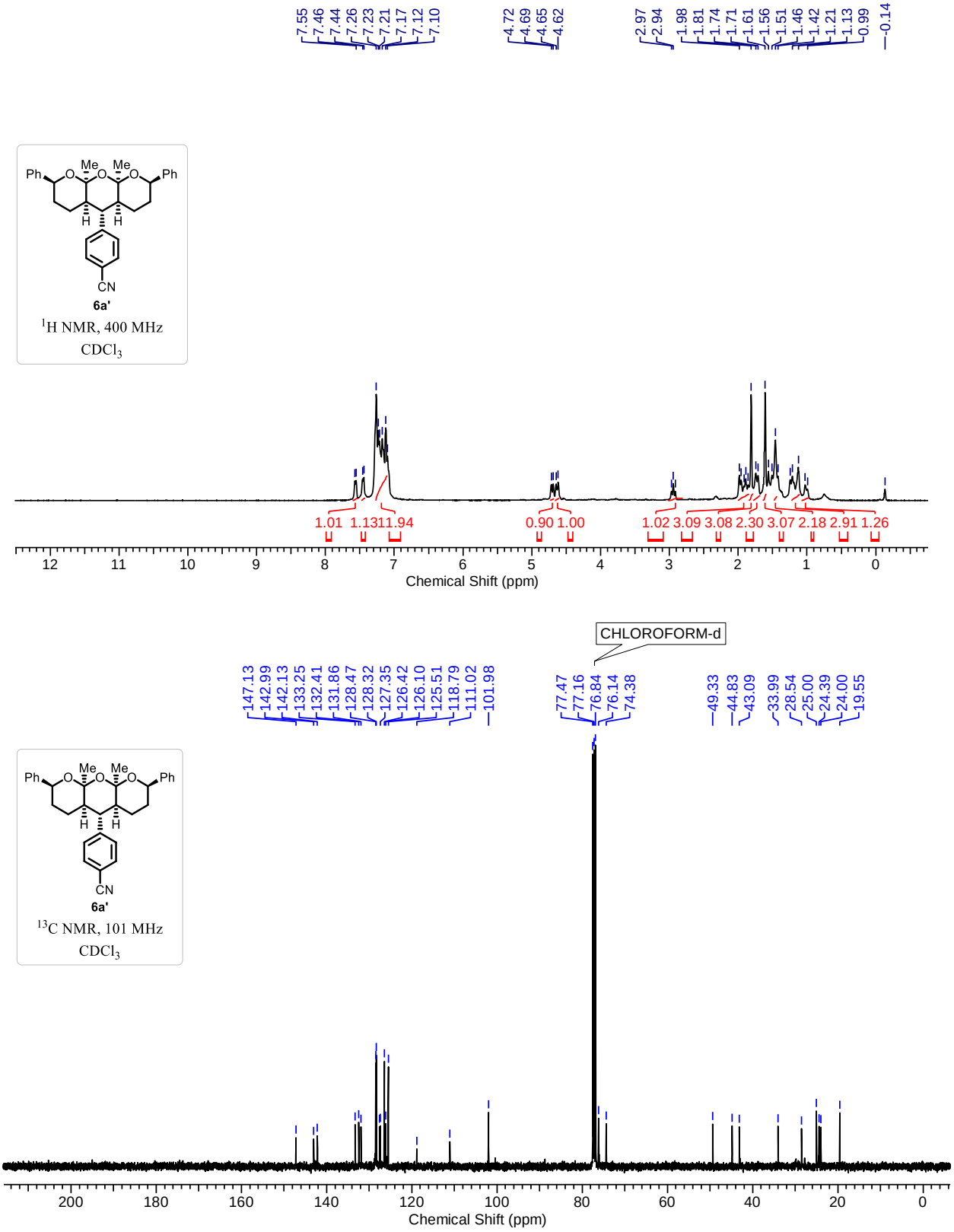


5-(4-Bromophenyl)-9a,10a-dimethyl-2,8-diphenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran(6z):

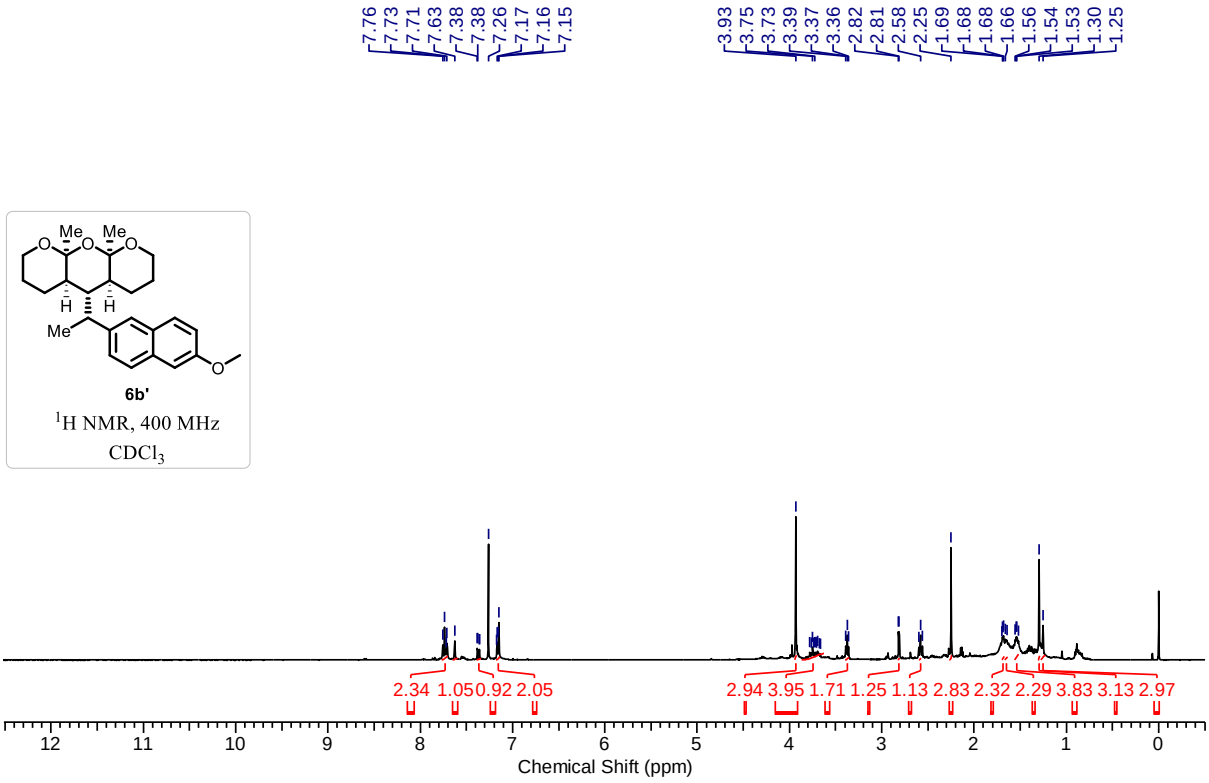


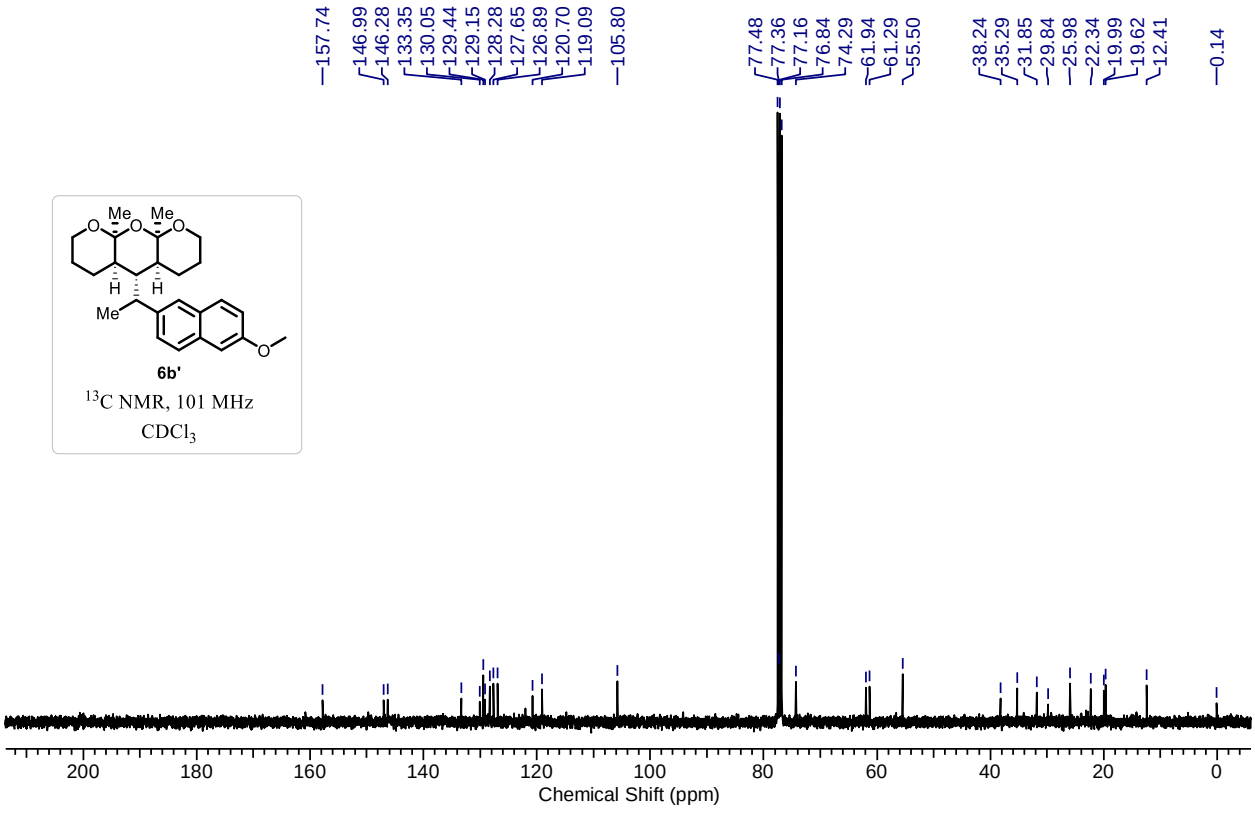


9a,10a-Dimethyl-2,8-diphenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran-5-yl)benzonitrile(6a'):

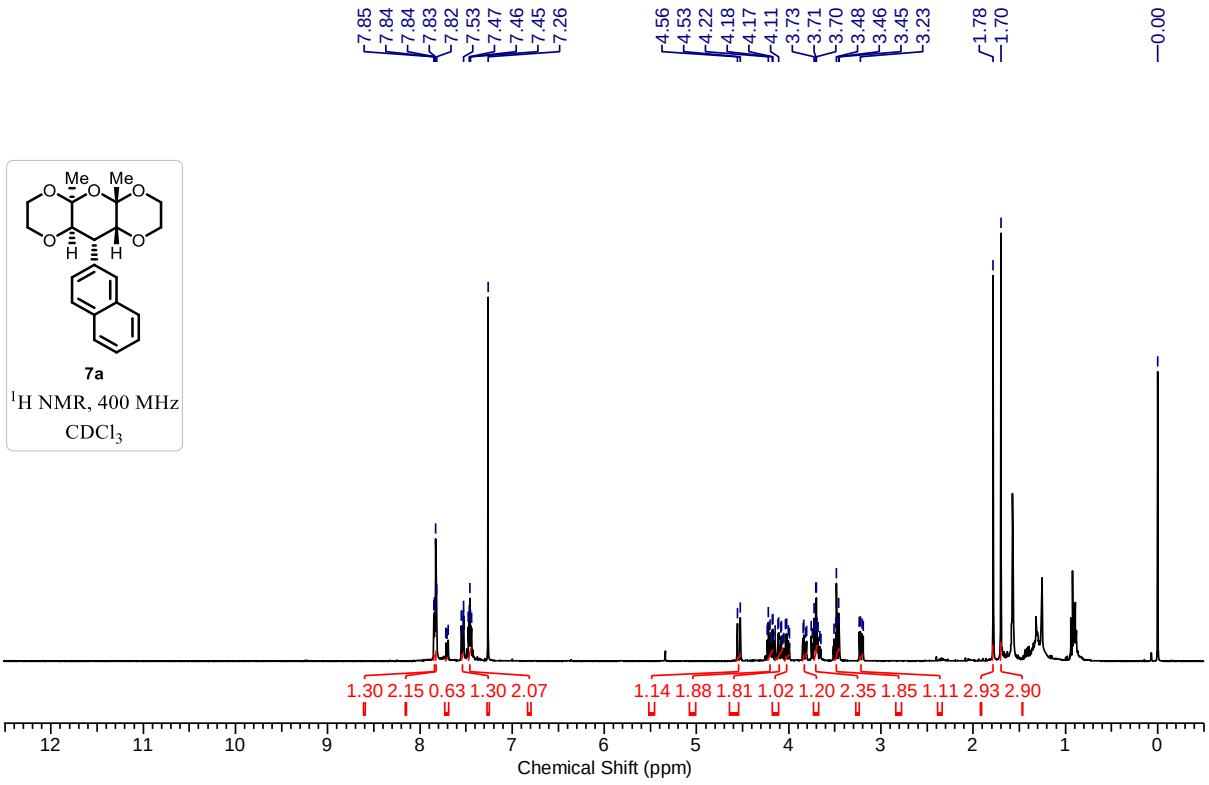


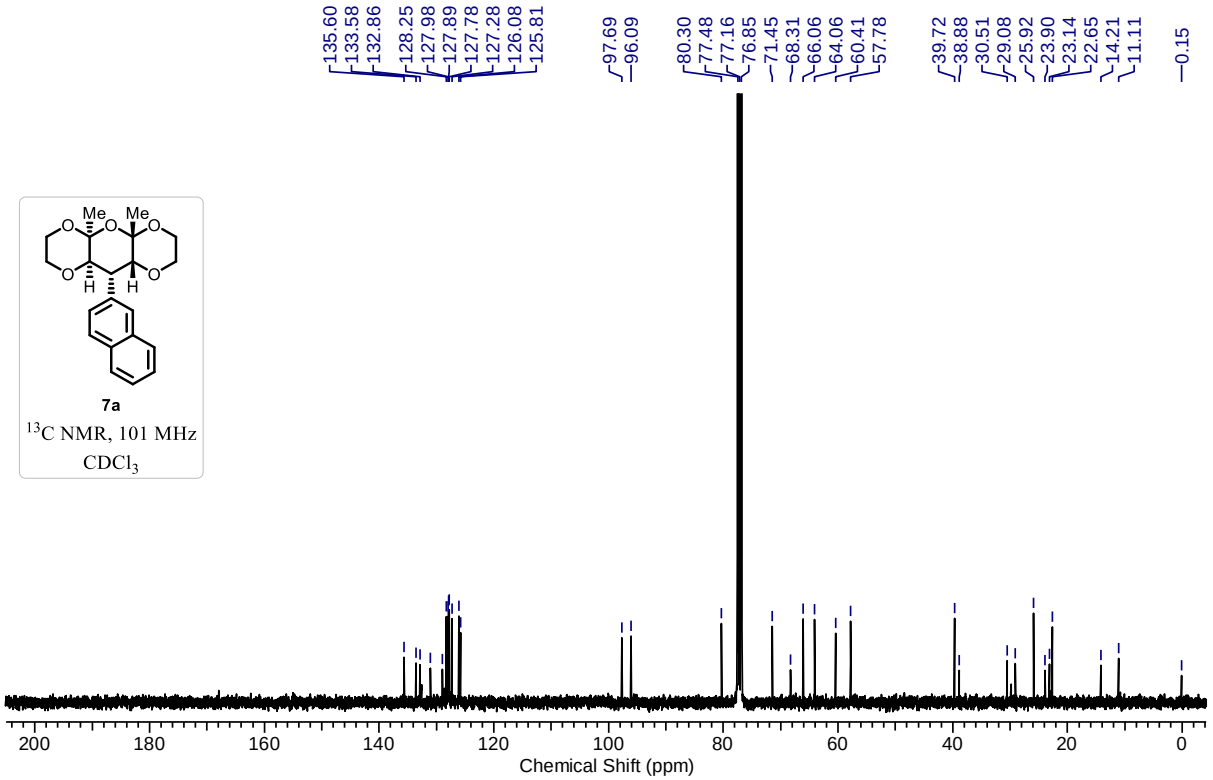
(*S*)-1-(6-Methoxynaphthalen-2-yl)ethyl)-9a,10a-dimethyloctahydro-2H,5H,6H-dipyrano[2,3-b:3',2'-e]pyran (6b'):



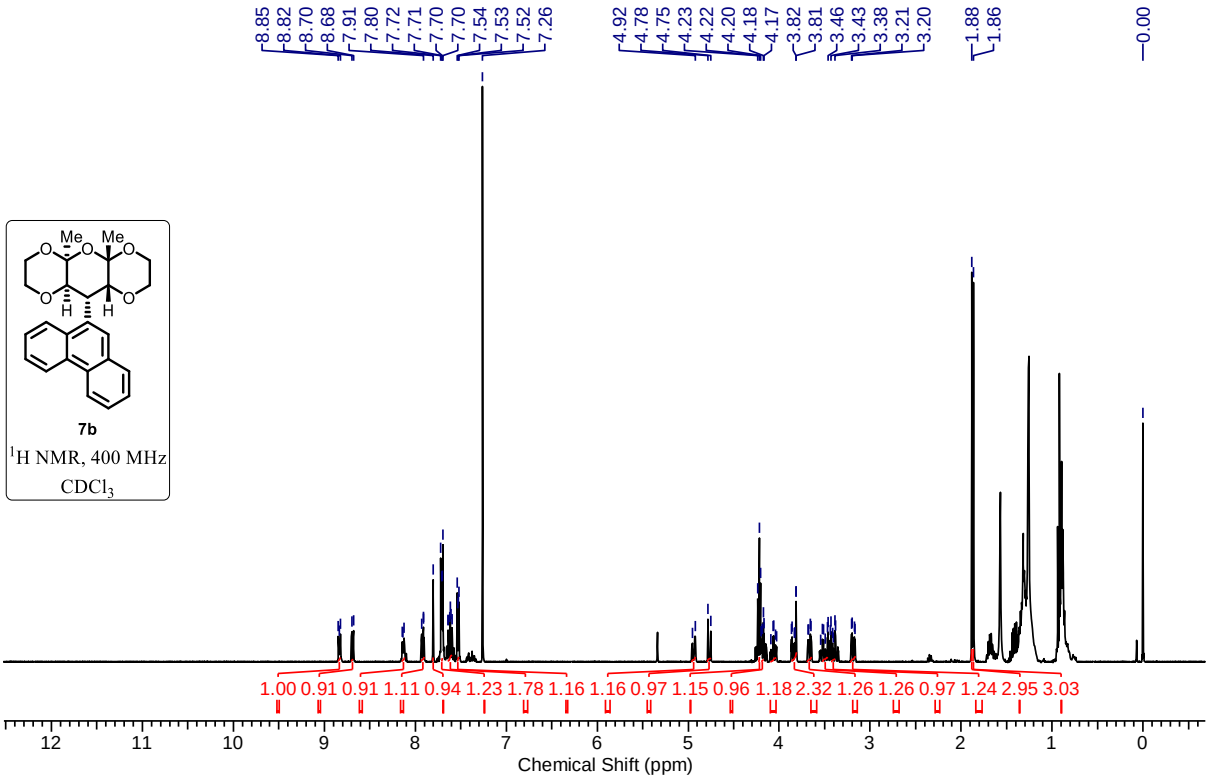


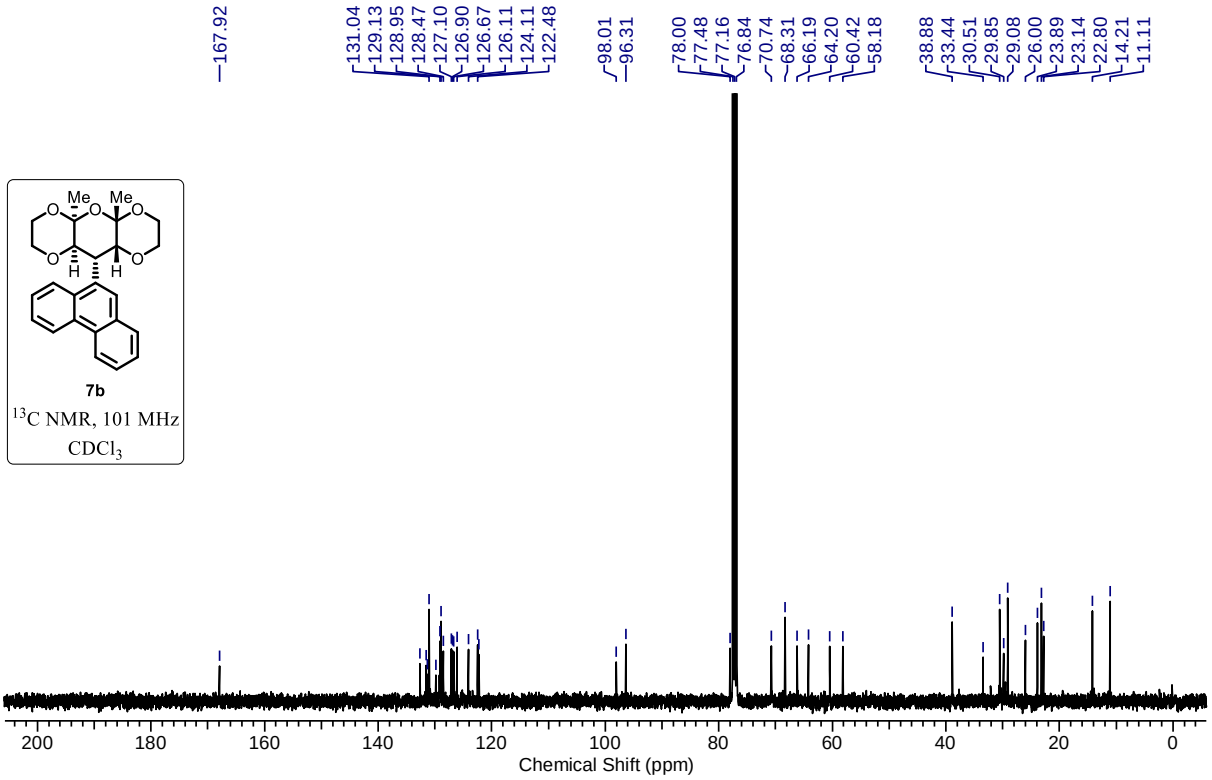
4a,5a-Dimethyl-10-(naphthalen-2-yl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine)(7a):



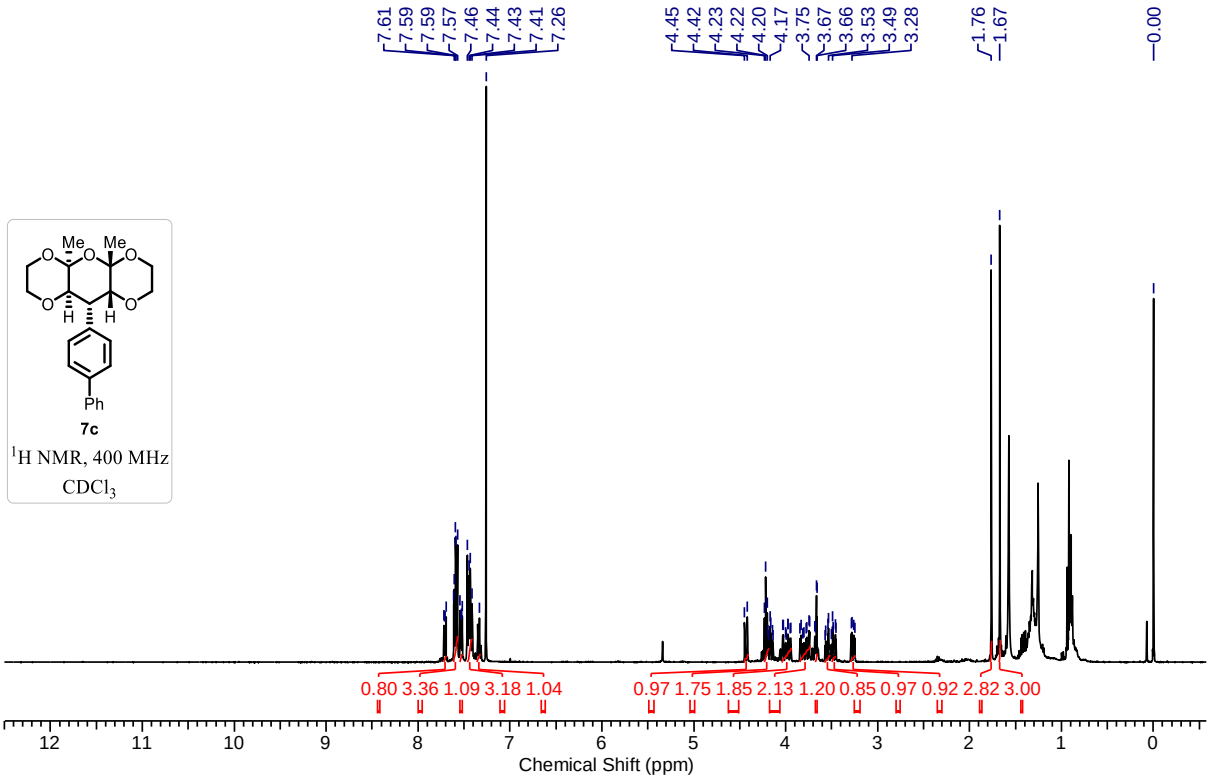


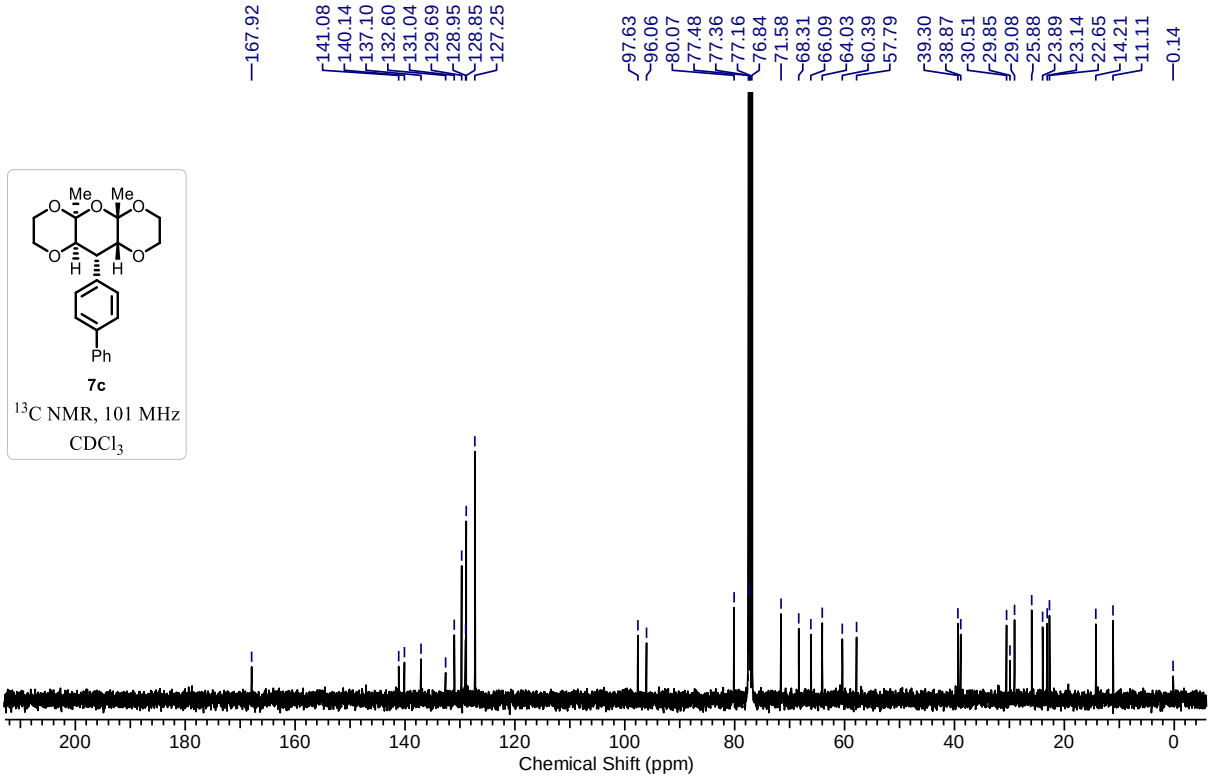
4a,5a-Dimethyl-10-(phenanthren-9-yl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine)(7b) :



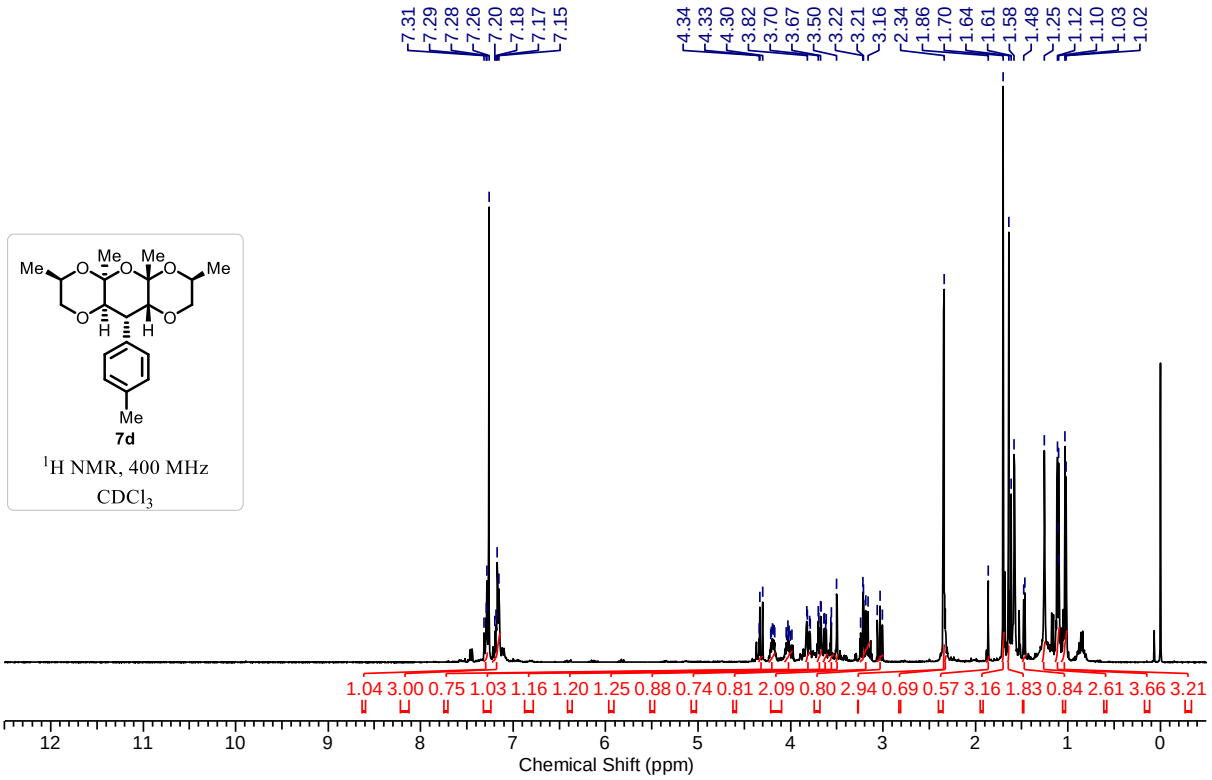


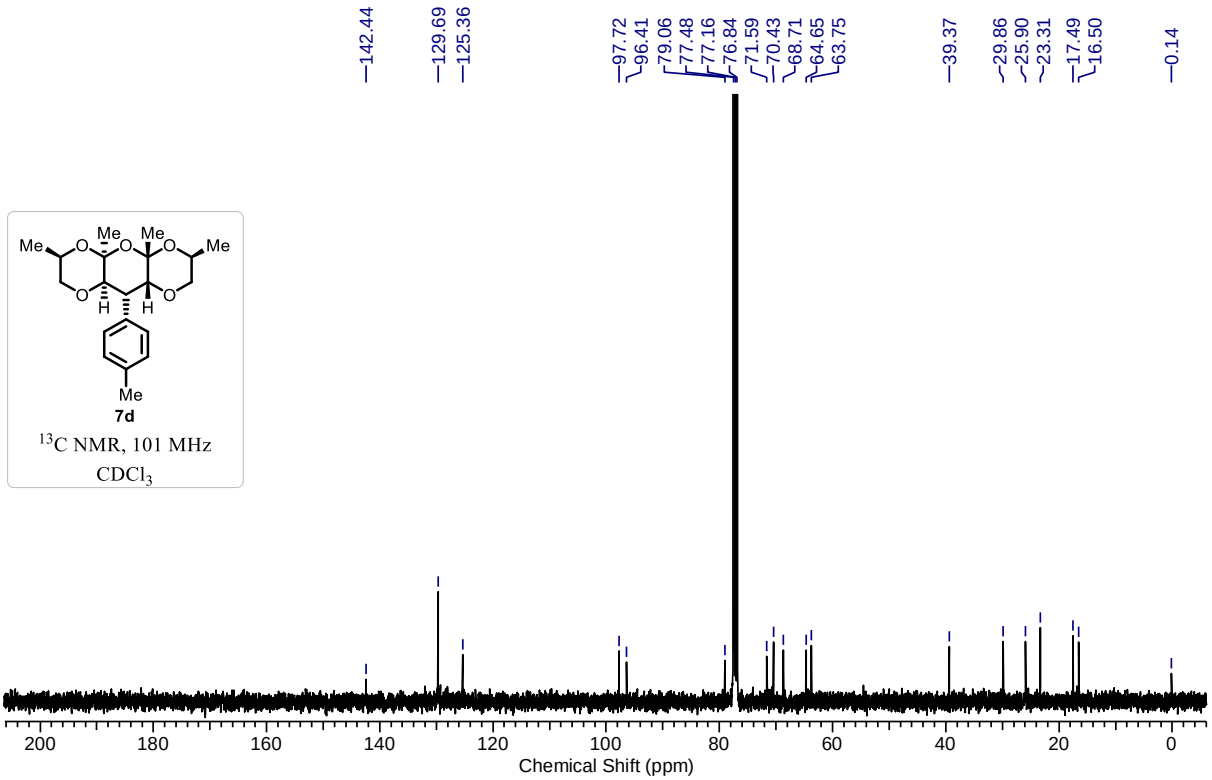
10-([1,1'-Biphenyl]-4-yl)-4a,5a-dimethyloctahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine)(7c):



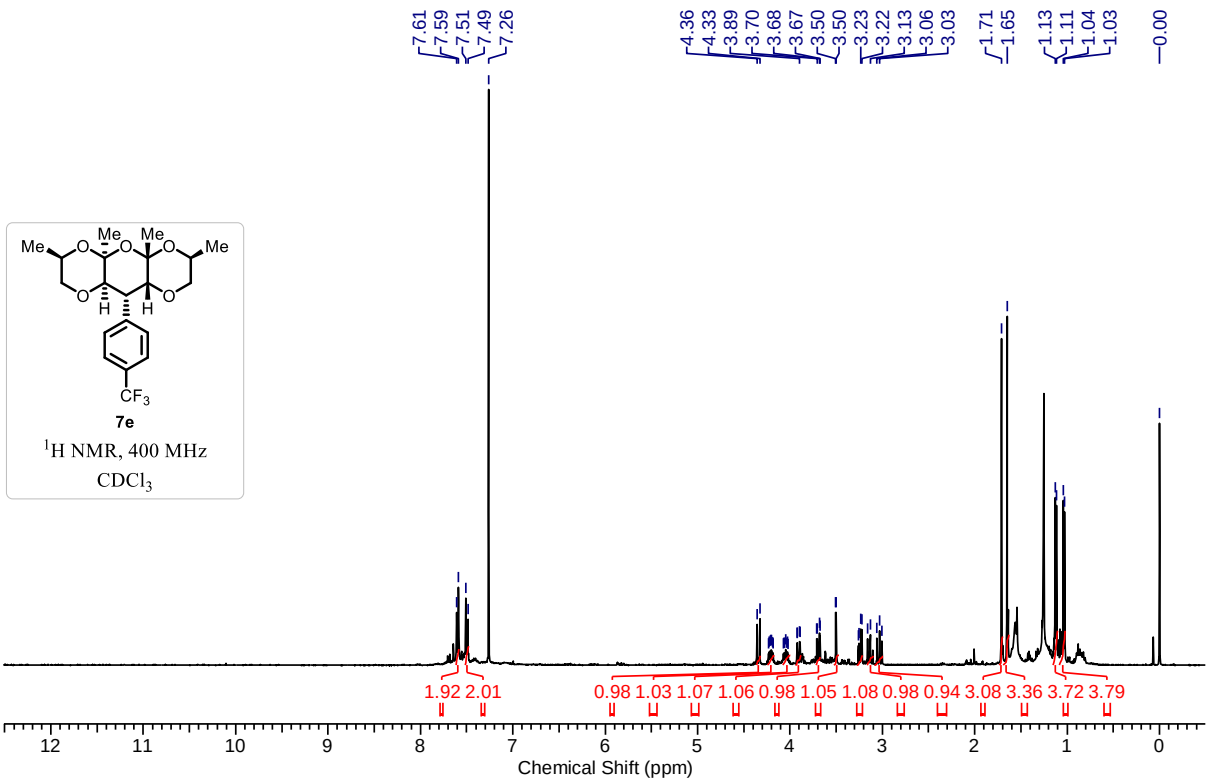


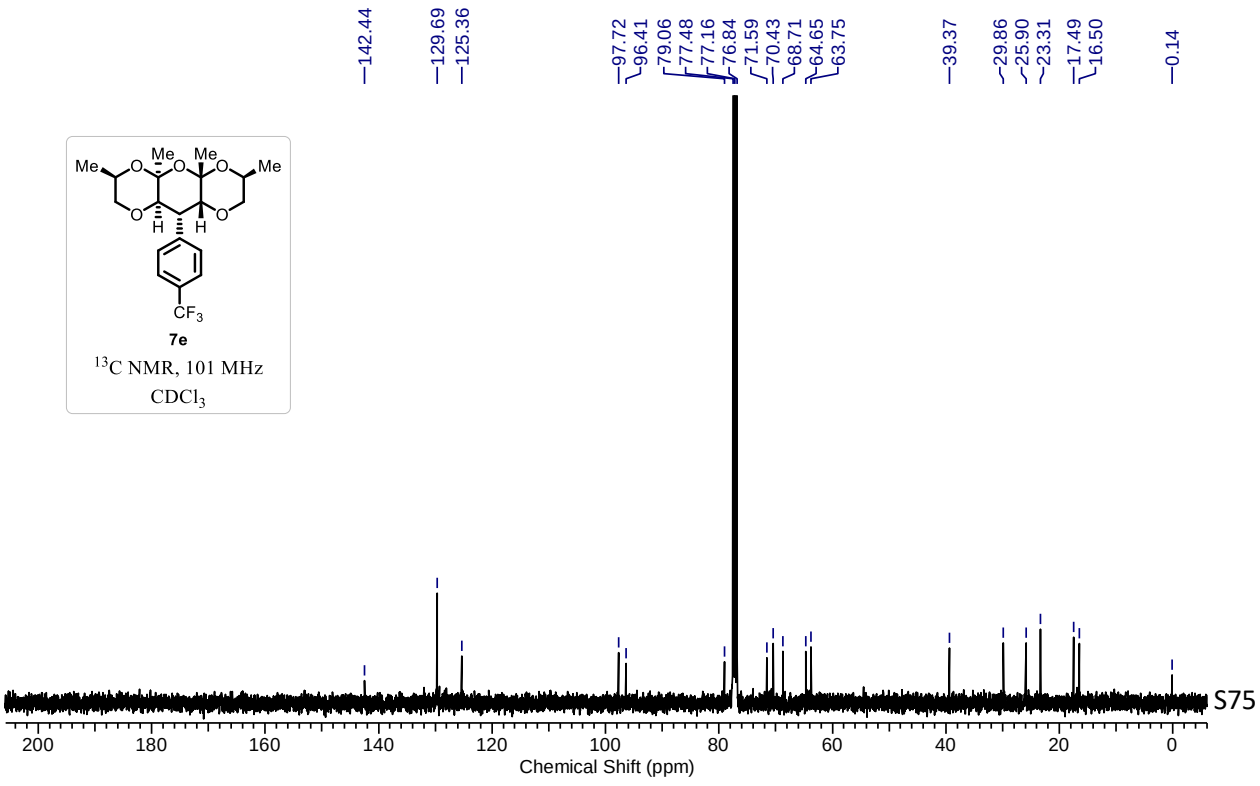
3,4a,5a,7-Tetramethyl-10-(p-tolyl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine)(7d):



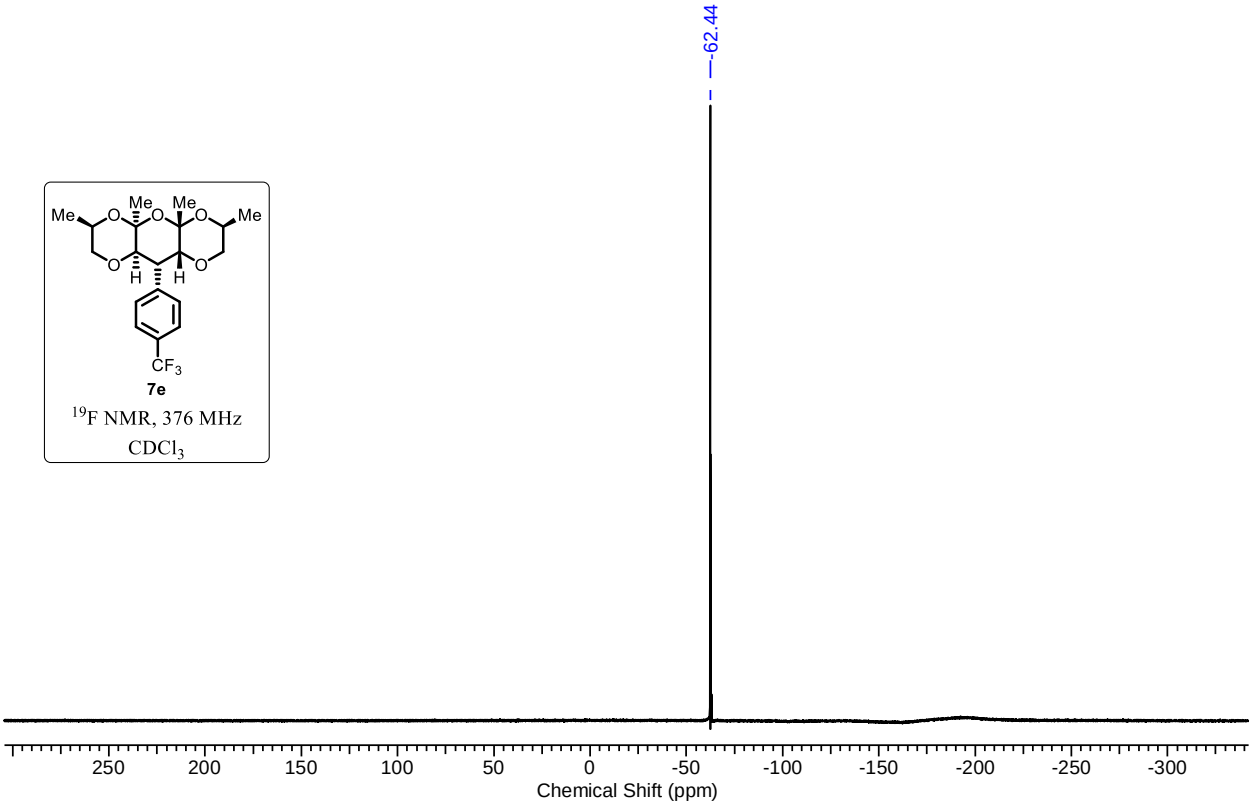


3,4a,5a,7-Tetramethyl-10-(4-(trifluoromethyl)phenyl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine)(7e):

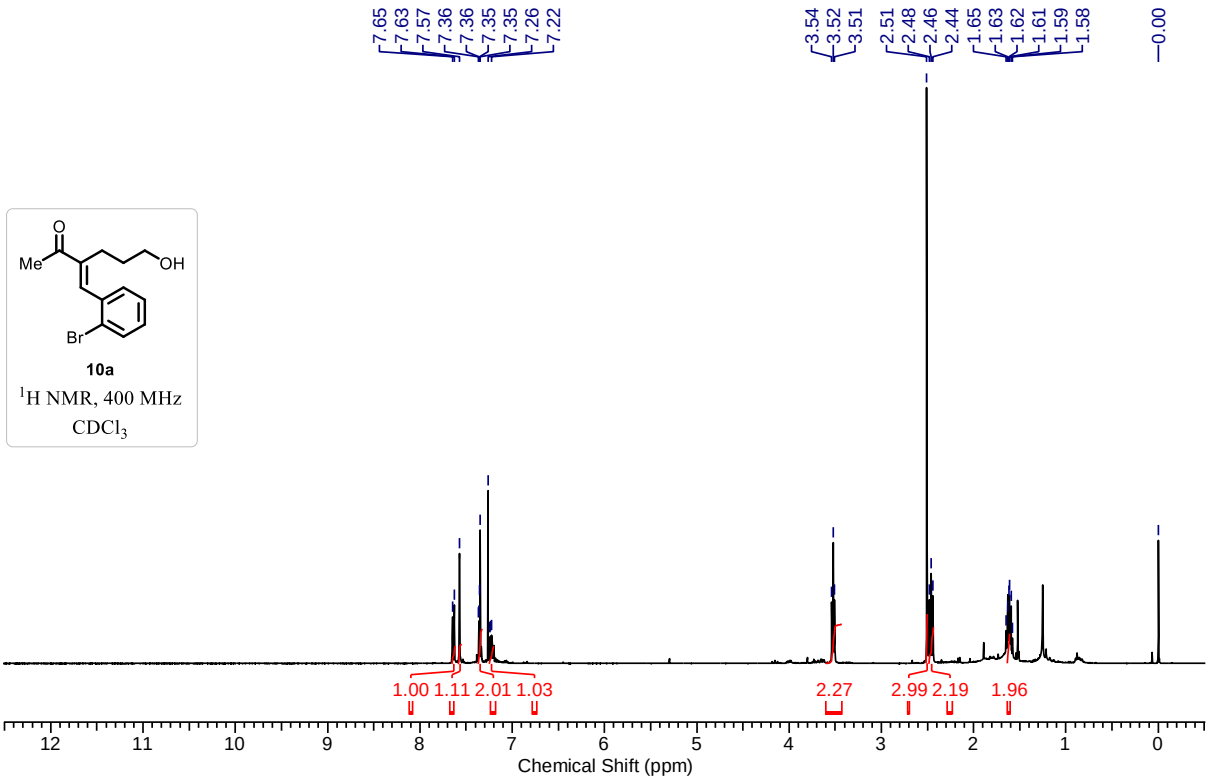


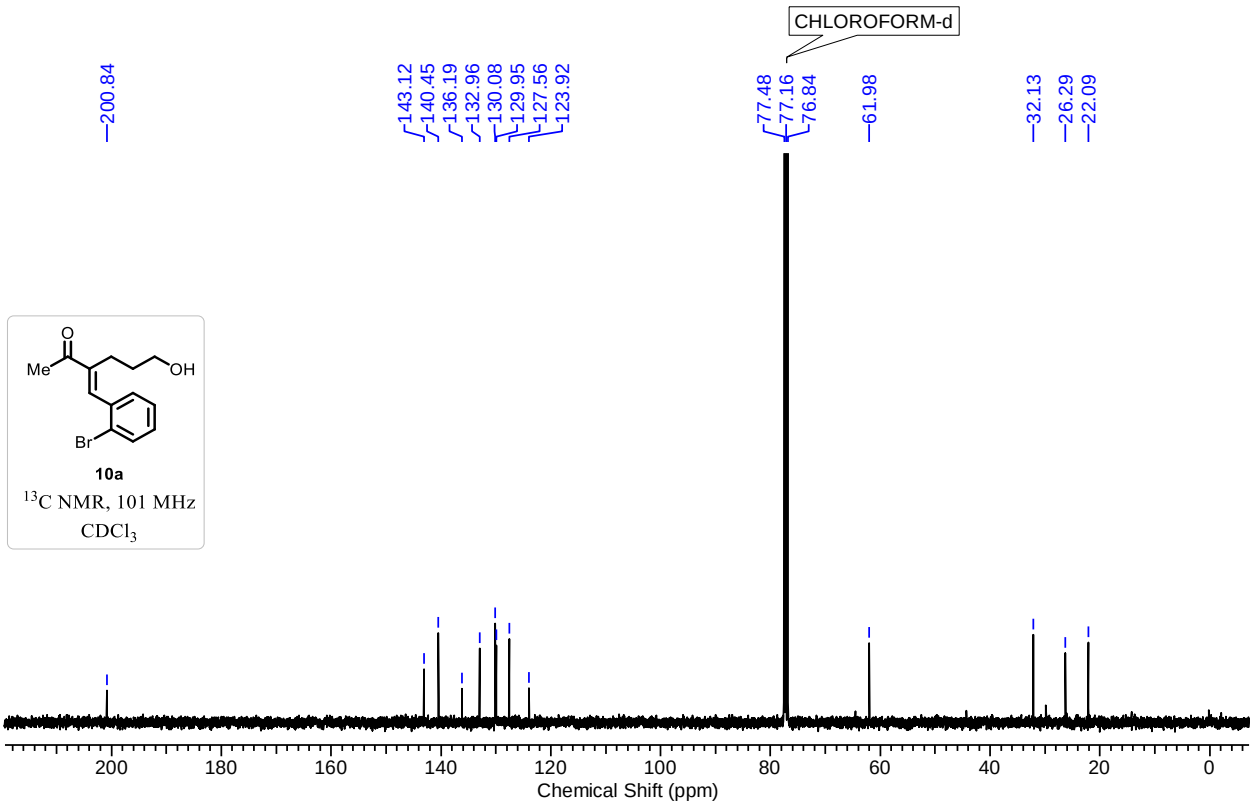


3,4a,5a,7-Tetramethyl-10-(4-(trifluoromethyl)phenyl)octahydro-10*H*-pyrano[2,3-b:5,6-b']bis([1,4]dioxine)(7e):

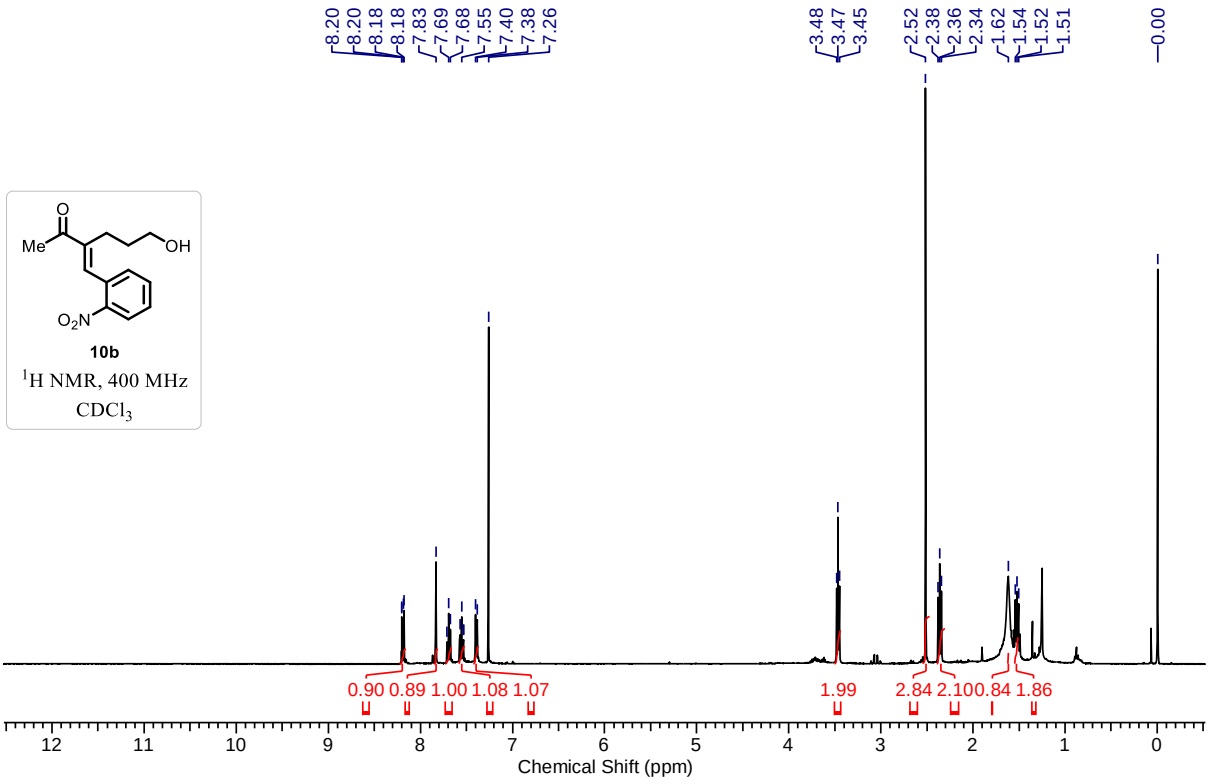


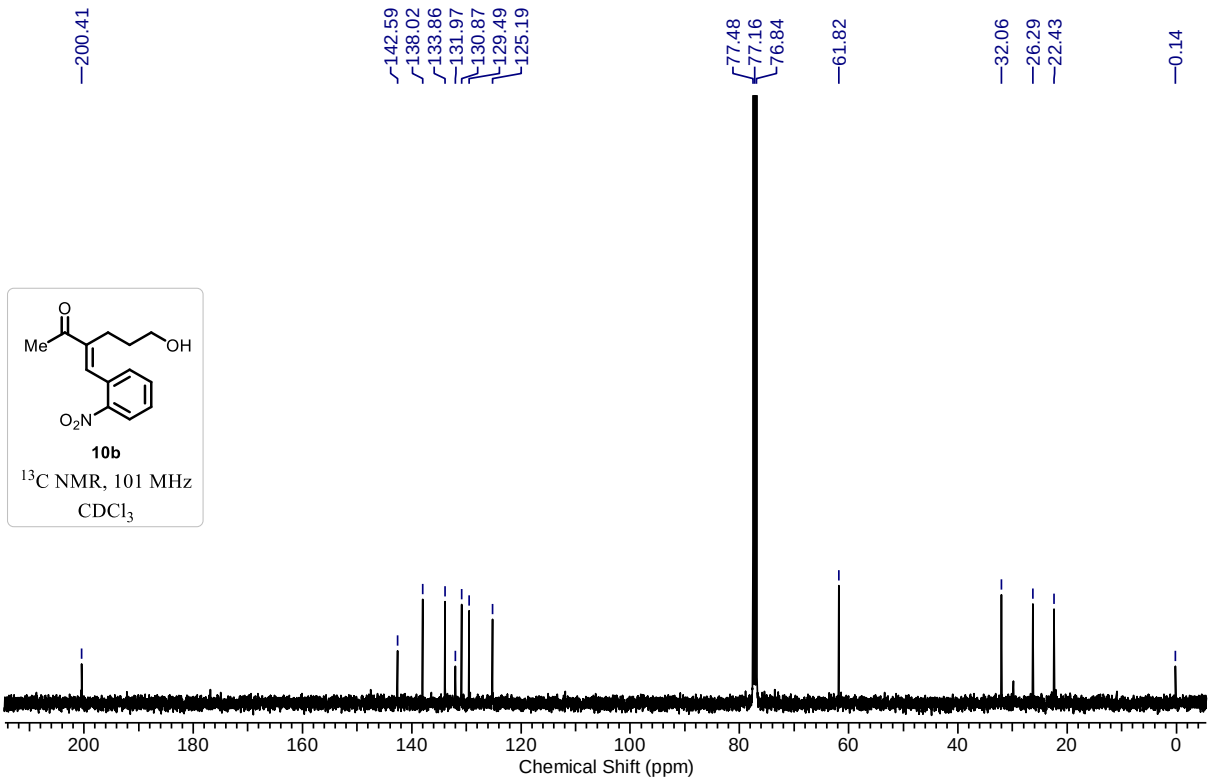
(*E*)-3-(2-Bromobenzylidene)-6-hydroxyhexan-2-one (10a):



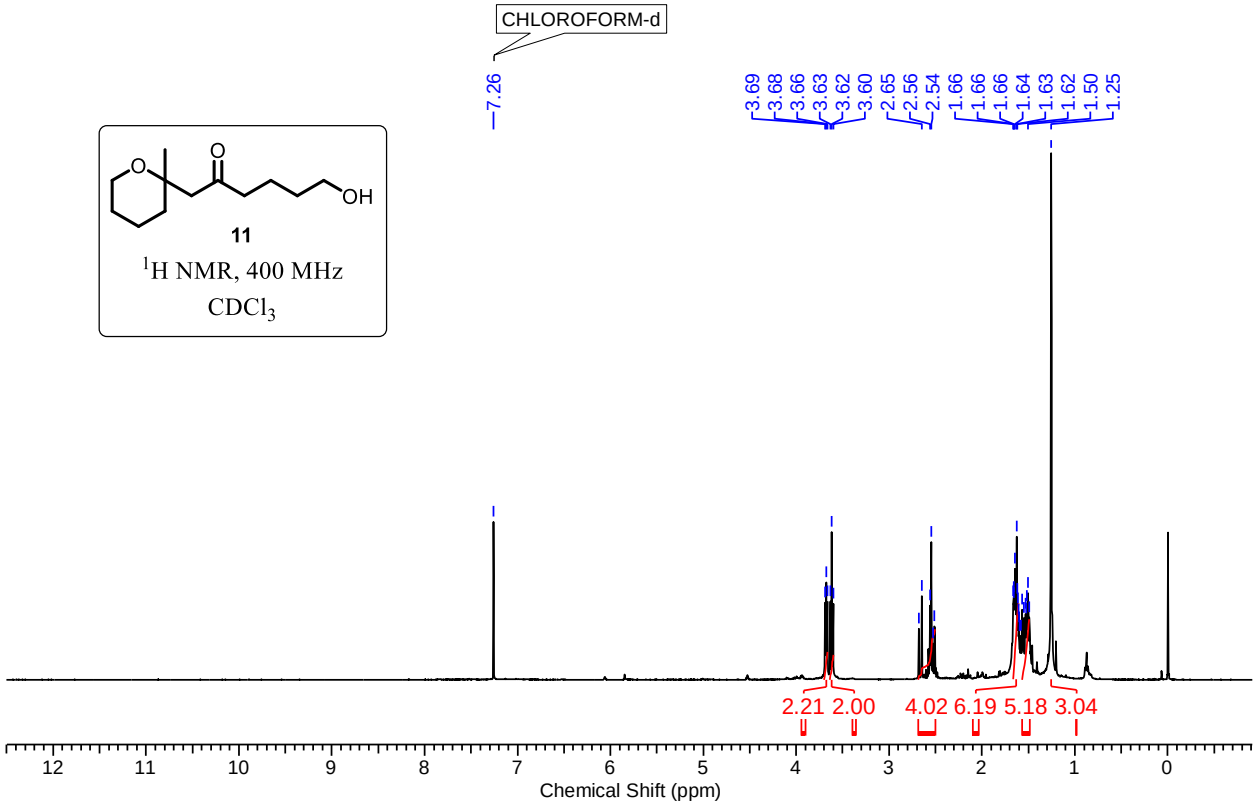


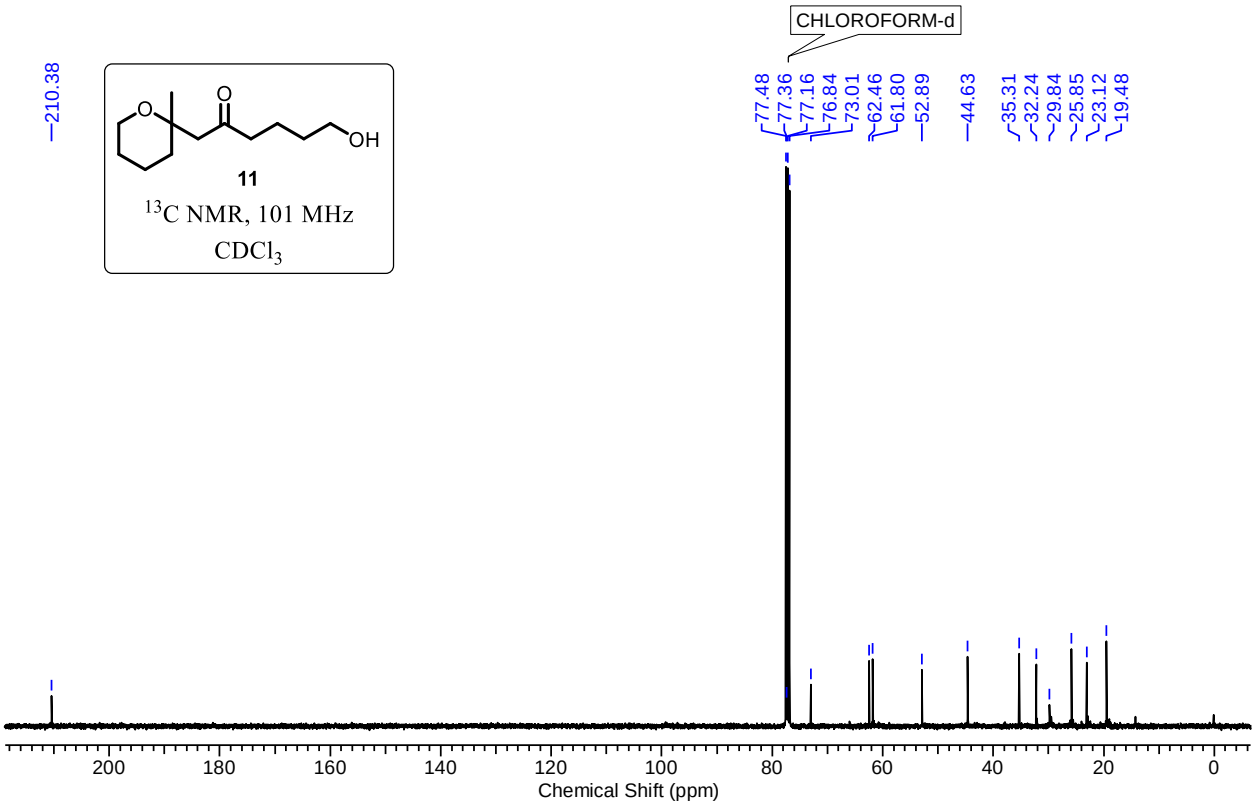
(*E*)-6-Hydroxy-3-(2-nitrobenzylidene)hexan-2-one (10b):



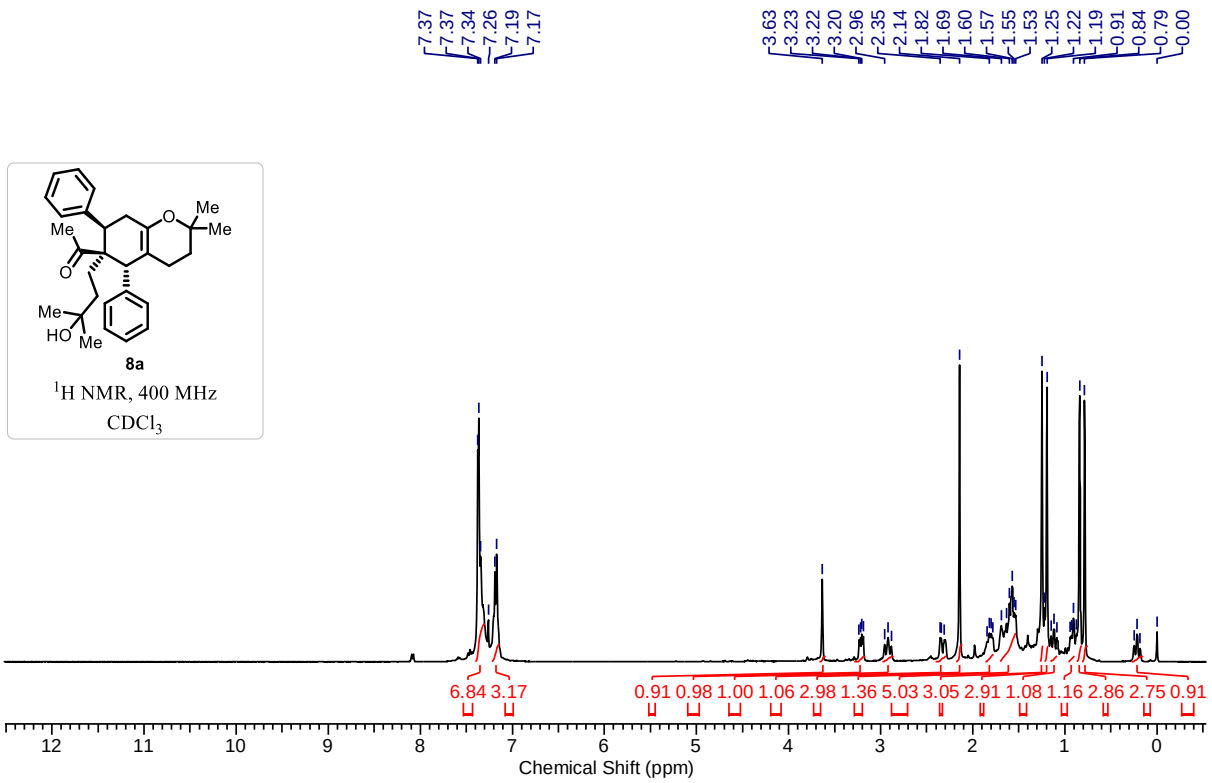


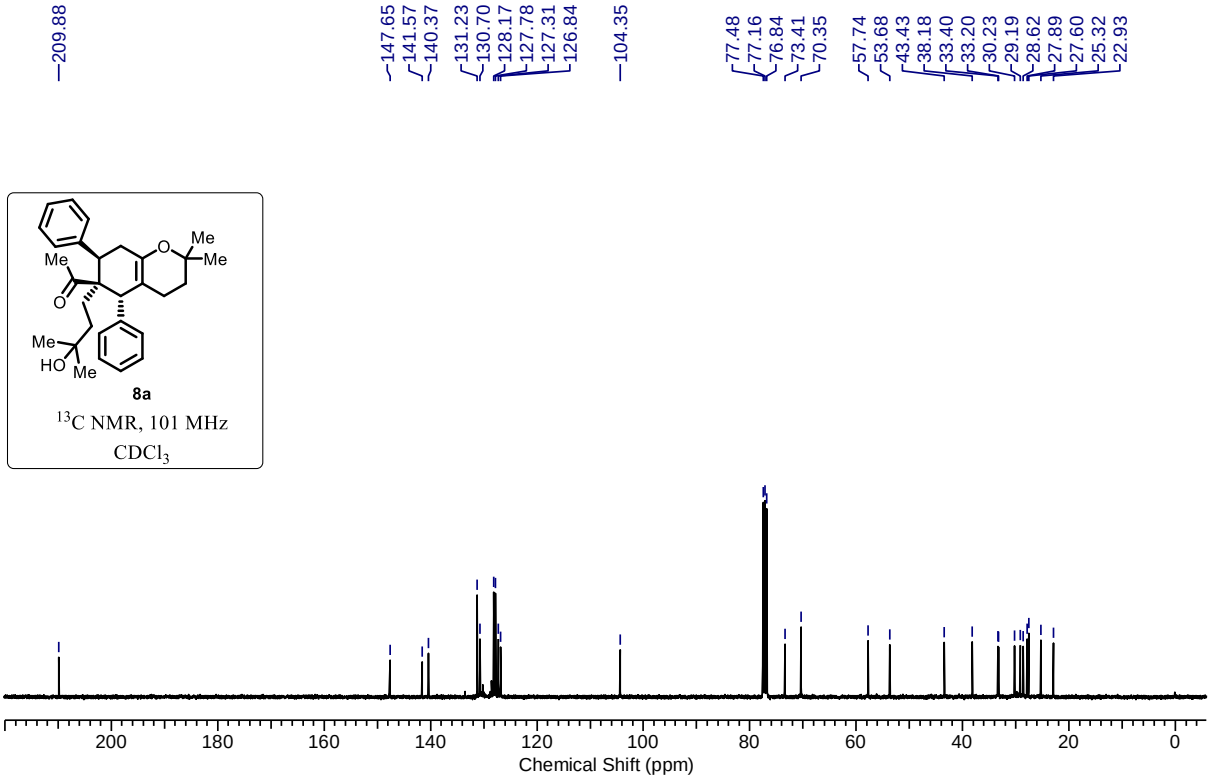
6-Hydroxy-1-(2-methyltetrahydro-2*H*-pyran-2-yl)hexan-2-one (11)



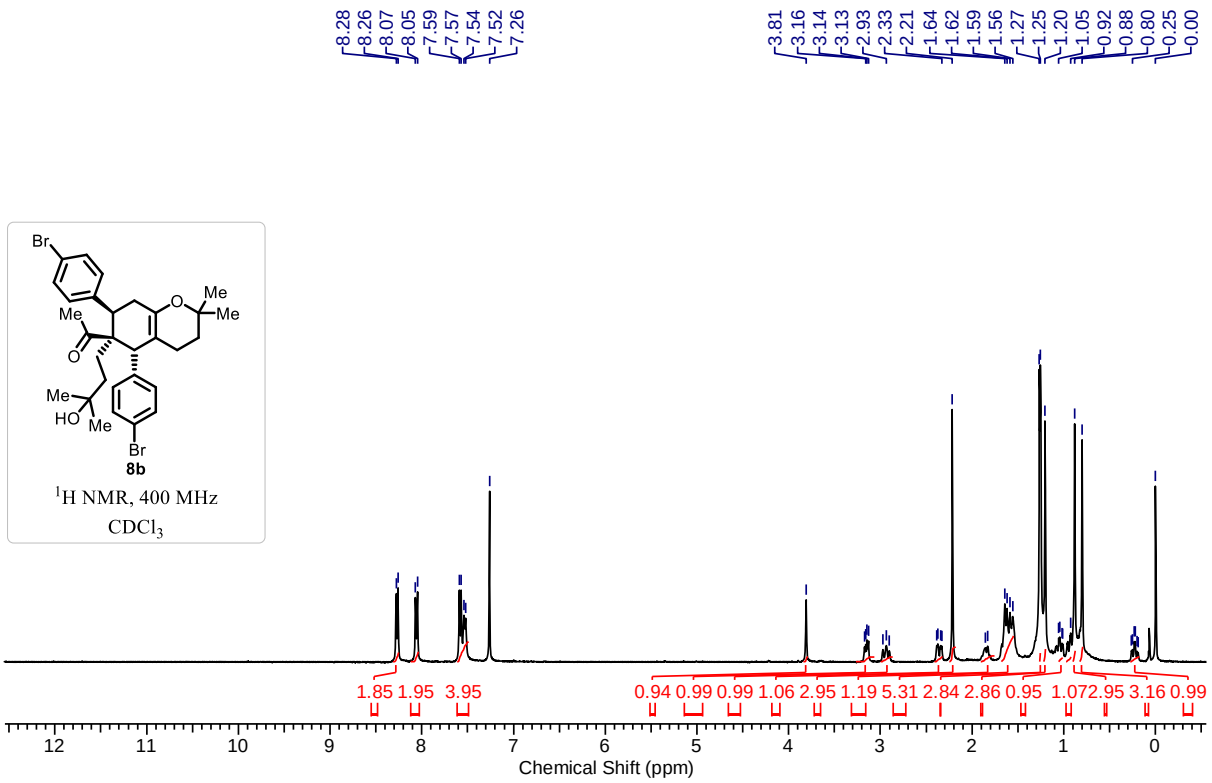


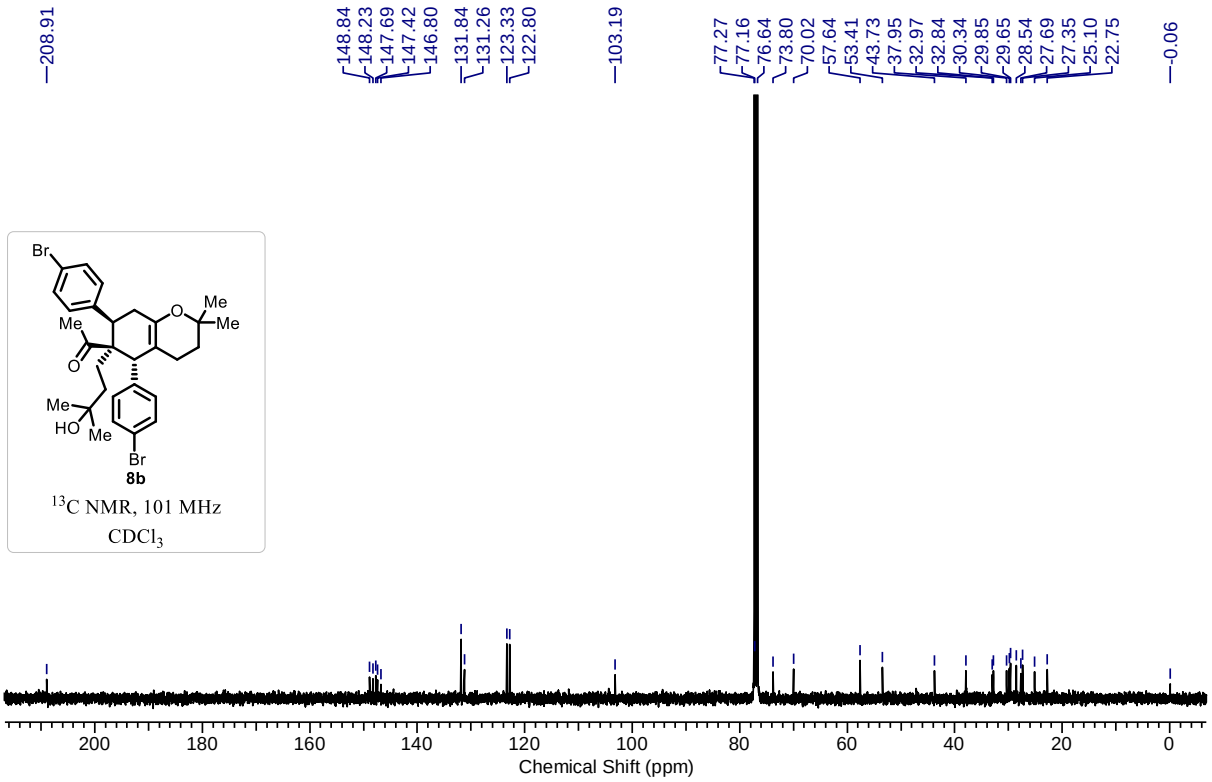
6-(3-Hydroxy-3-methylbutyl)-2,2-dimethyl-5,7-diphenyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8a):



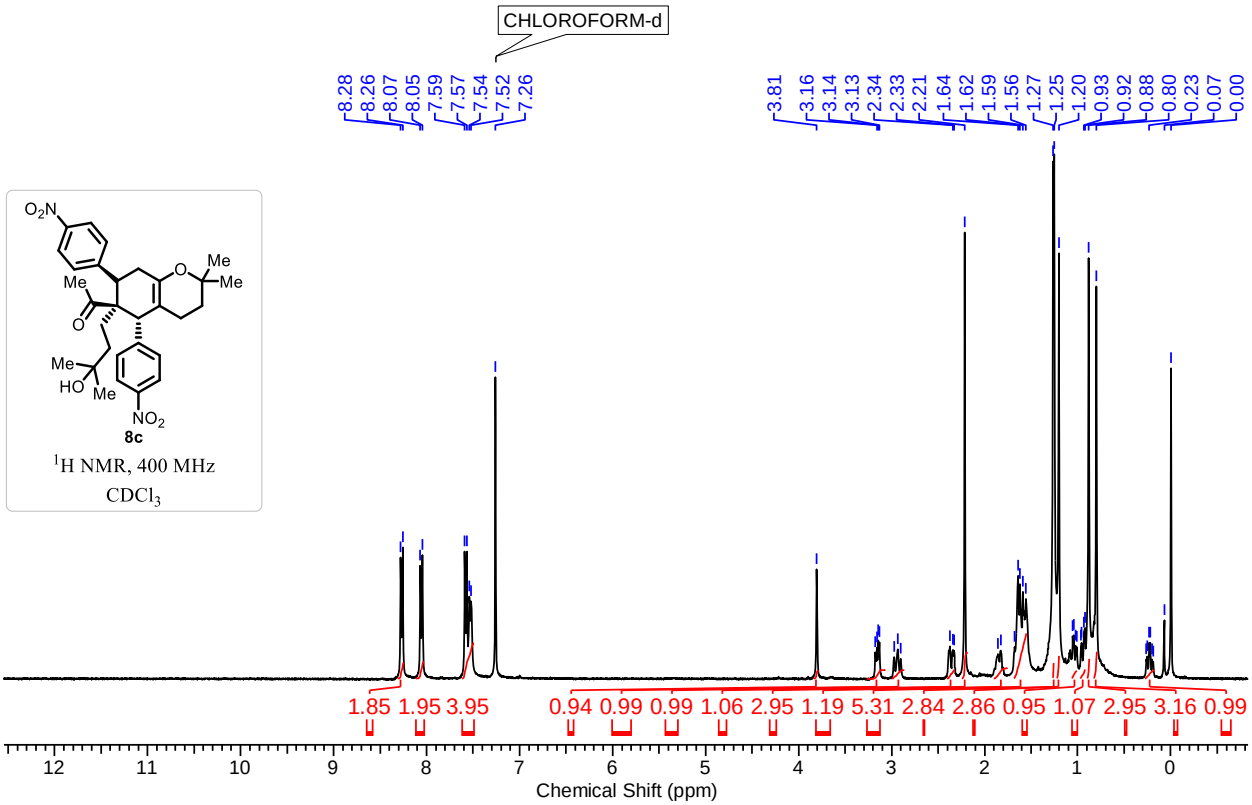


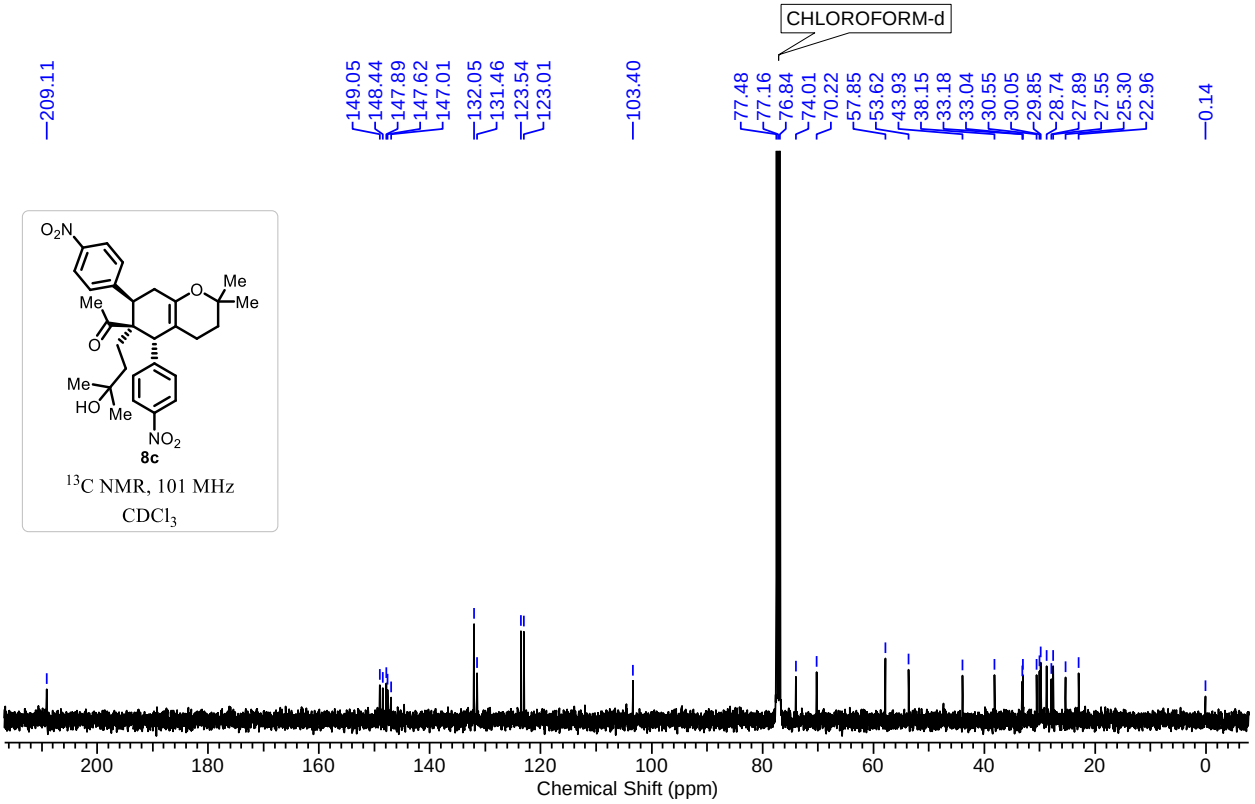
5,7-Bis(4-bromophenyl)-6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8b):



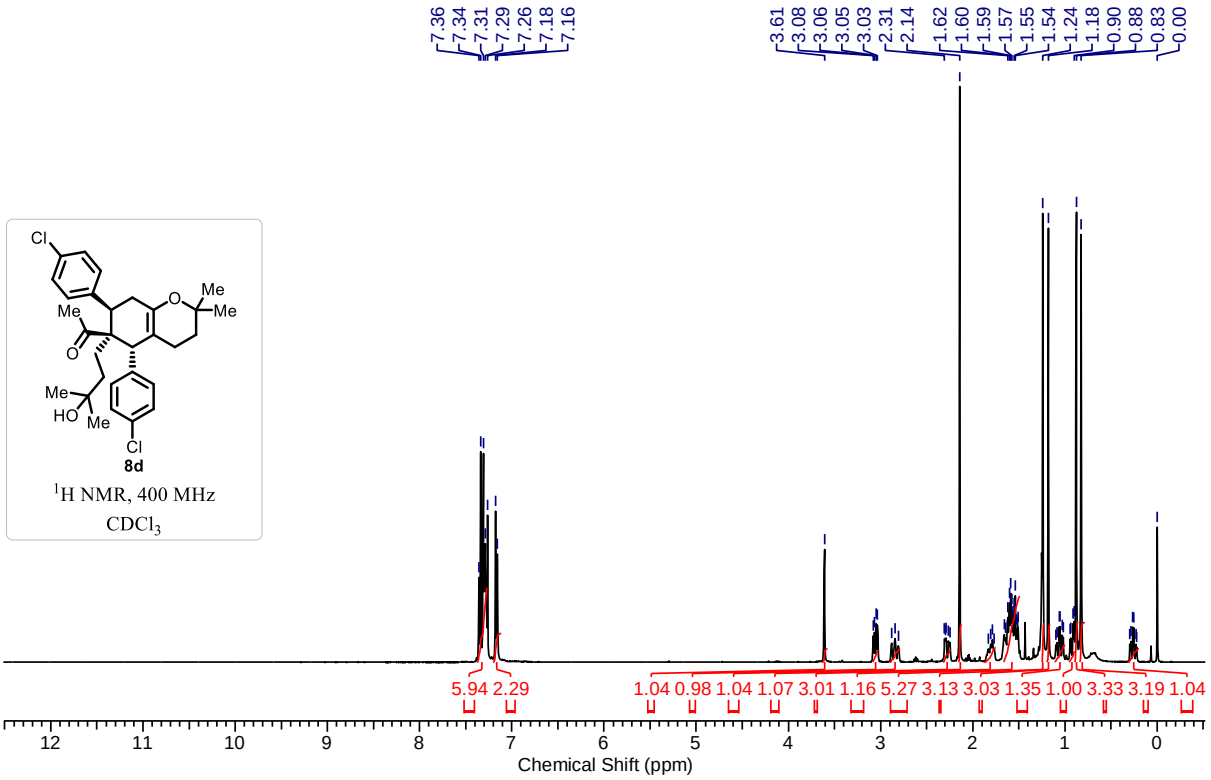


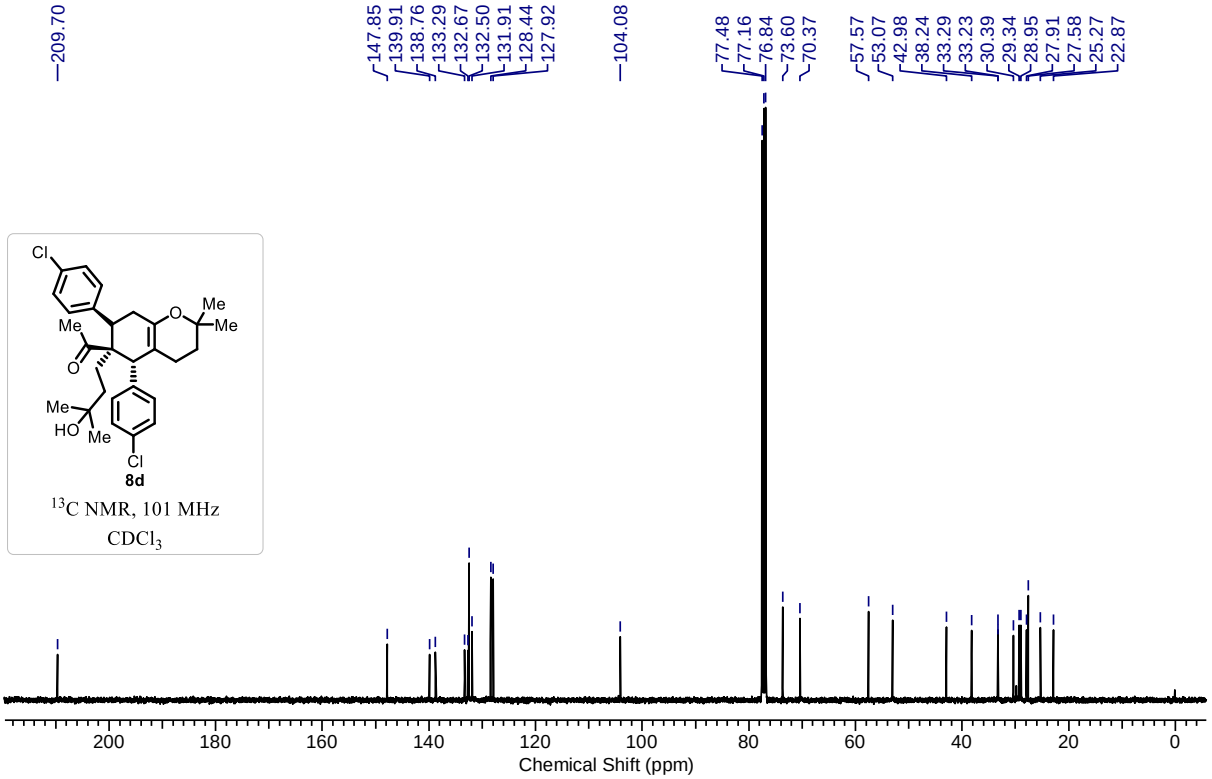
6-(3-Hydroxy-3-methylbutyl)-2,2-dimethyl-5,7-bis(4-nitrophenyl)-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8c):



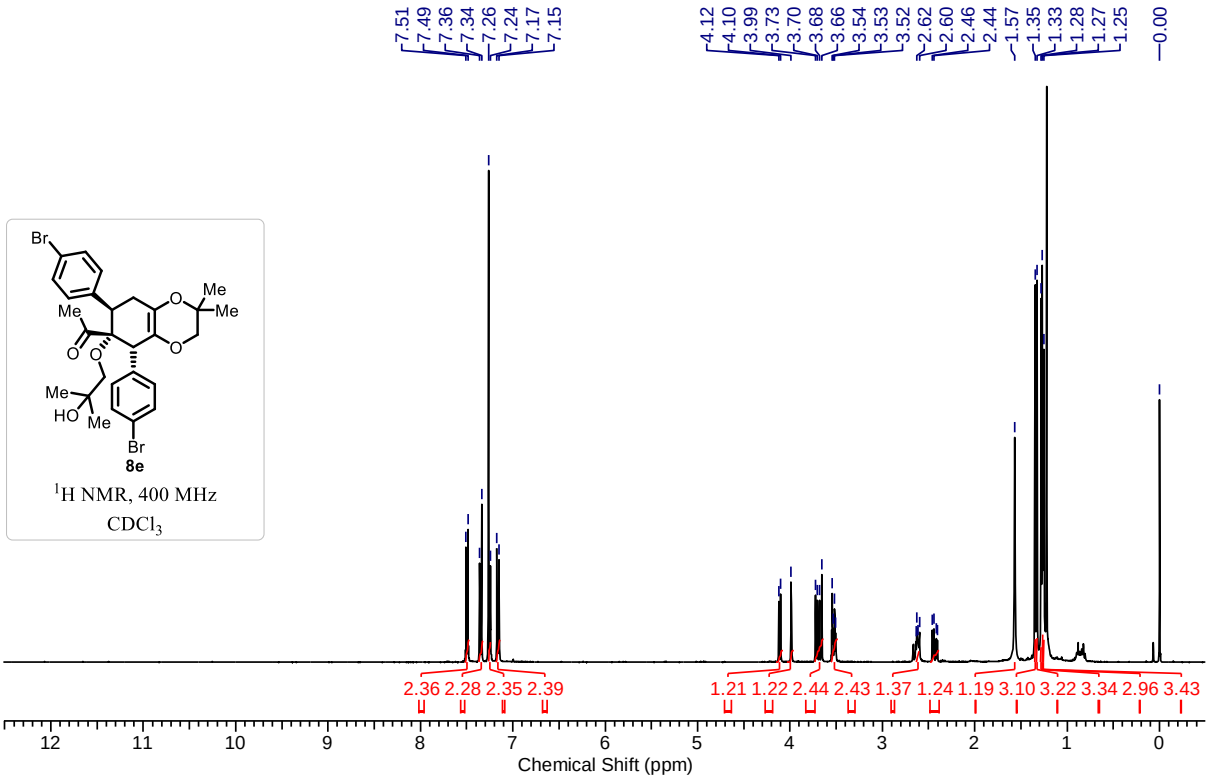


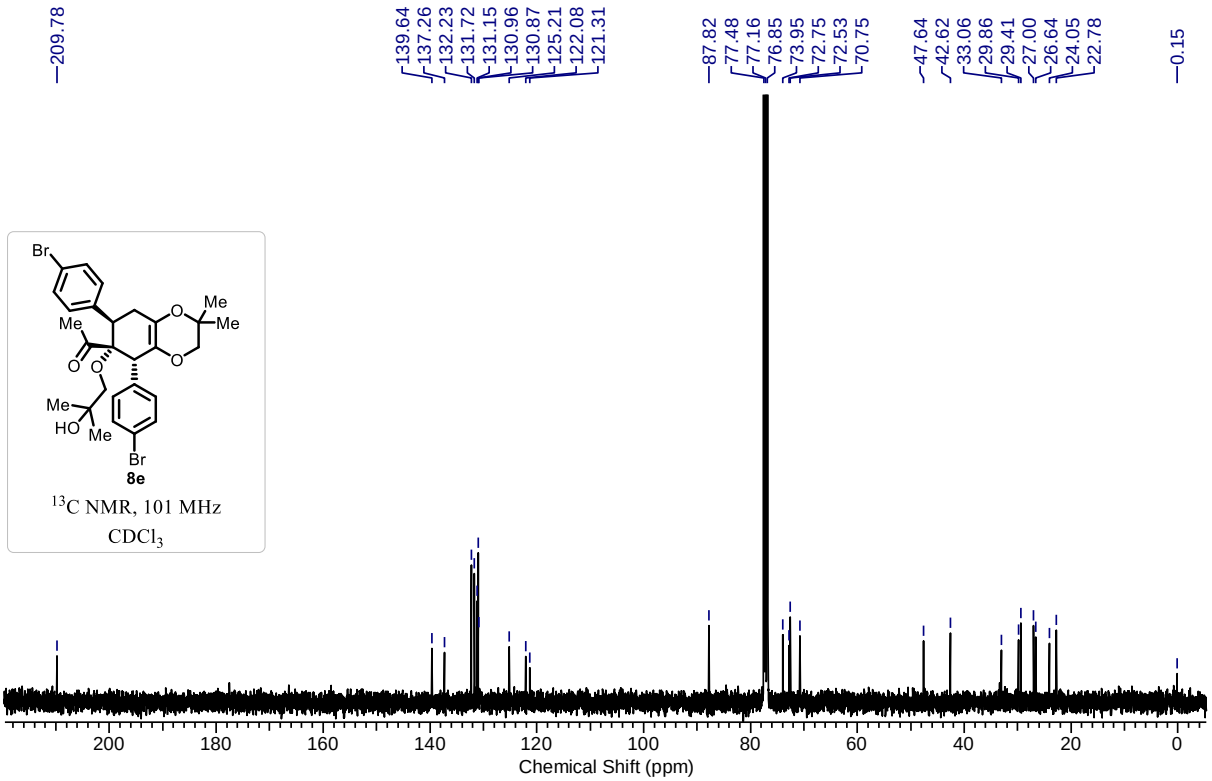
5,7-Bis(4-chlorophenyl)-6-(3-hydroxy-3-methylbutyl)-2,2-dimethyl-3,4,5,6,7,8-hexahydro-2*H*-chromen-6-yl)ethan-1-one (8d):



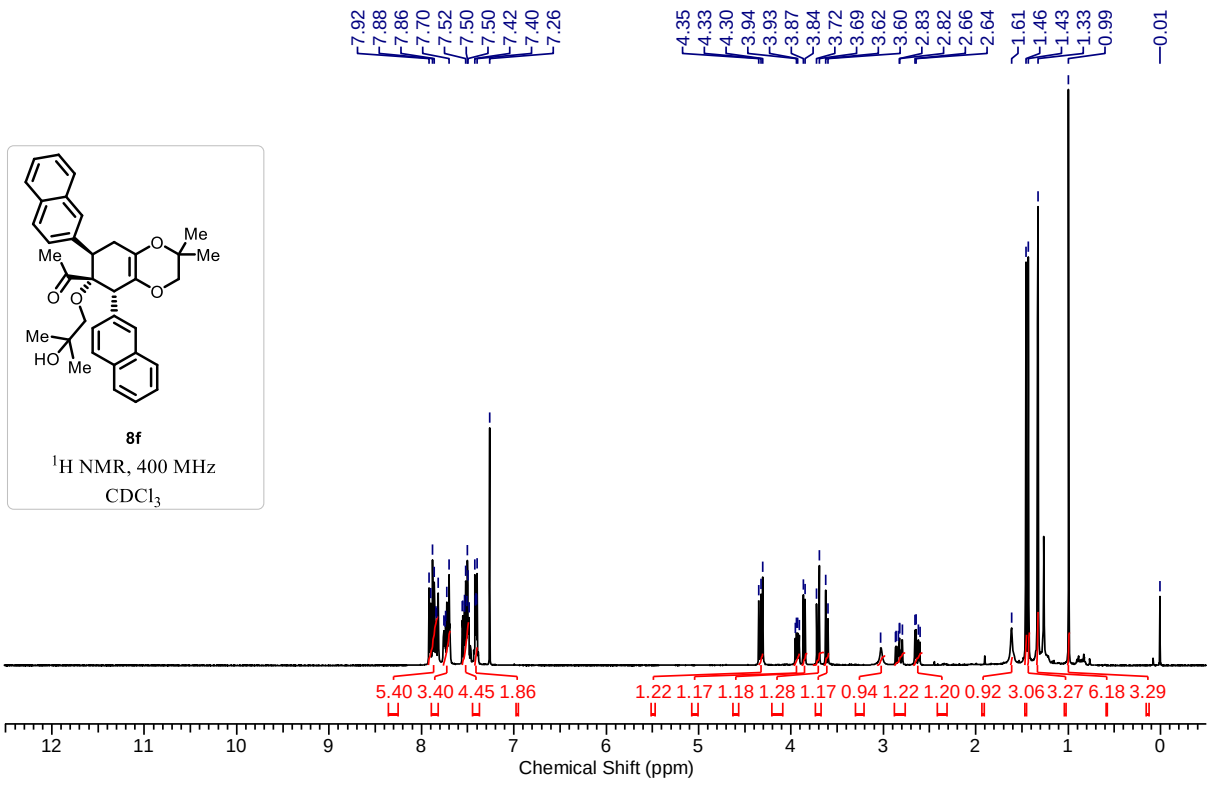


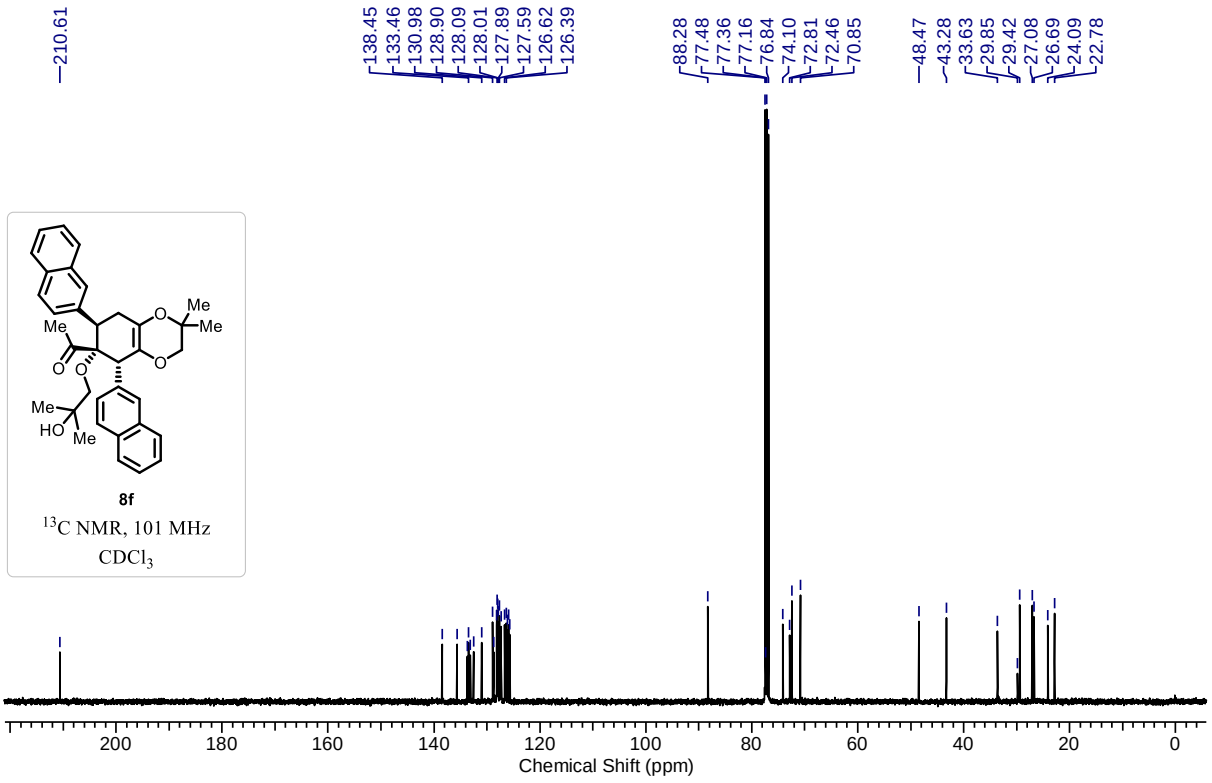
5,7-Bis(4-bromophenyl)-6-(2-hydroxy-2-methylpropoxy)-2,2-dimethyl-2,3,5,6,7,8-hexahydrobenzo[b][1,4]dioxin-6-yl)ethan-1-one (8e):



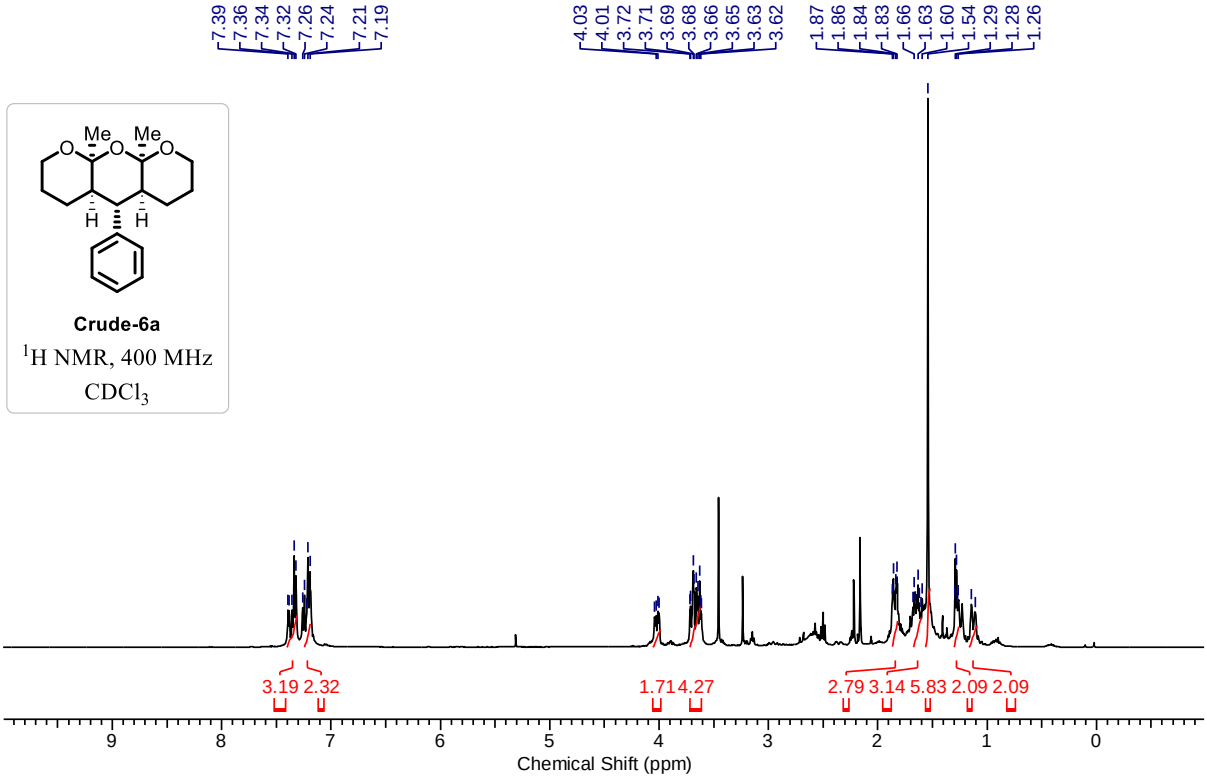


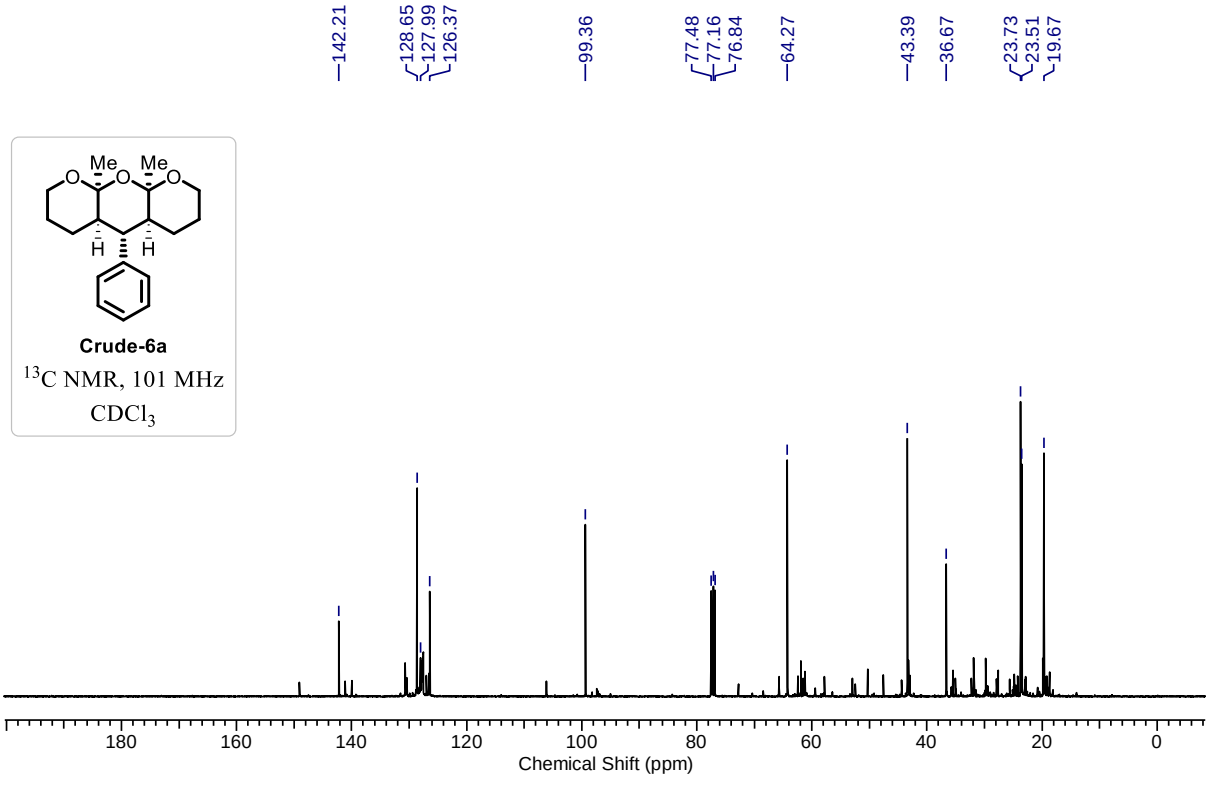
6-(2-Hydroxy-2-methylpropoxy)-2,2-dimethyl-5,7-di(naphthalen-2-yl)-2,3,5,6,7,8-hexahydrobenzo[b][1,4]dioxin-6-yl)ethan-1-one (8f):



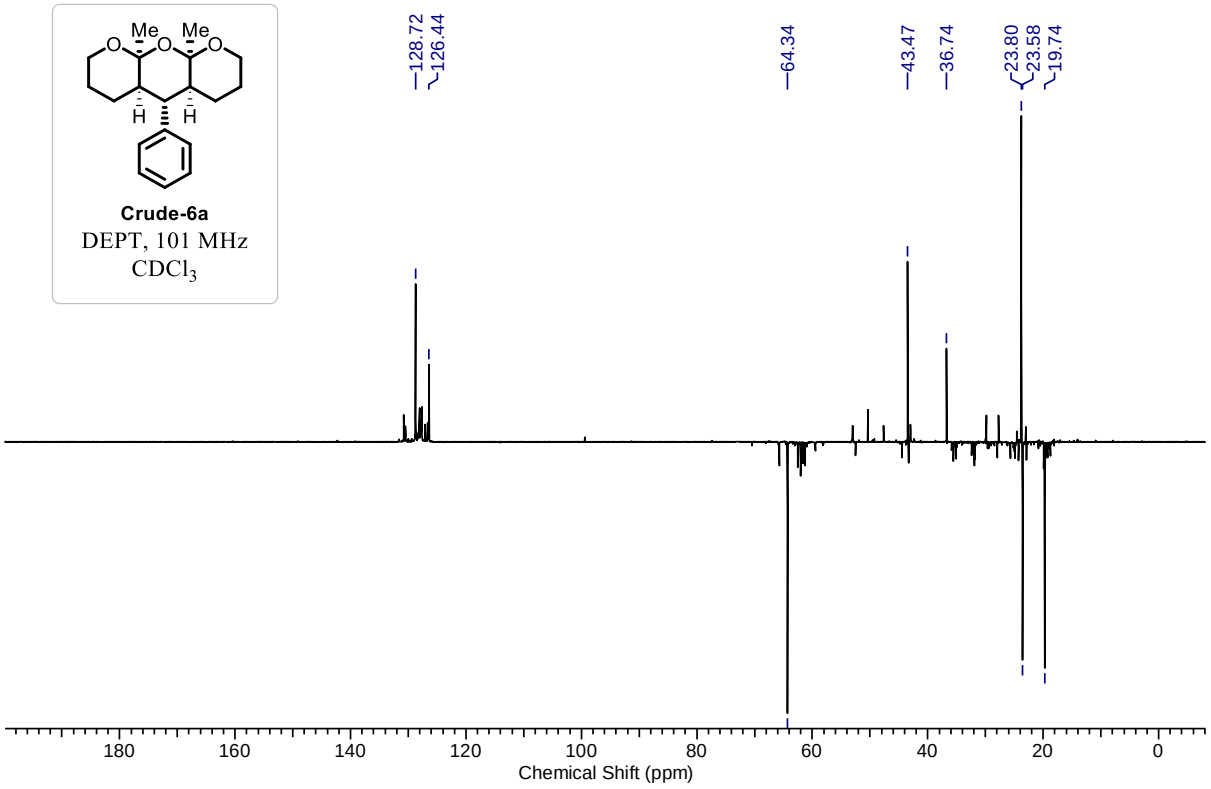


9a,10a-Dimethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (Crude-6a)





9a,10a-Dimethyl-5-phenyloctahydro-2*H*,5*H*,6*H*-dipyrano[2,3-b:3',2'-e]pyran (Crude-6a)



THE END