Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

for

THF-Enabled $PtBr_2$-Catalyzed Desymmetric Hydrogenative [3 + 2] Cycloaddition of 2-Alkynylbenzaldehyde-Tethered Cyclohexadienones

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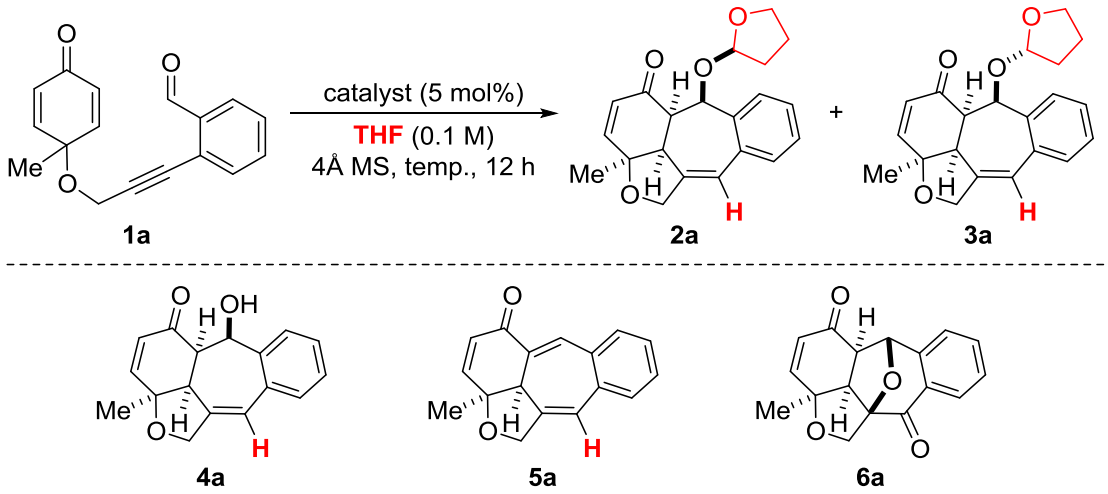
1. General Information

Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. THF was dried using Na/benzophenone. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (petroleum ether: EtOAc as eluent). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with either a 400 or 600 MHz spectrometer. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets), dt (doublet of triplet) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. High resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

2. Complete Screening and Optimization of the [3+2] Cycloaddition Reaction

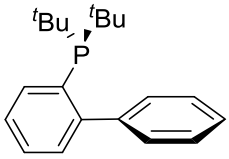
Table S1. Catalyst, Temperature and Concentration Optimization



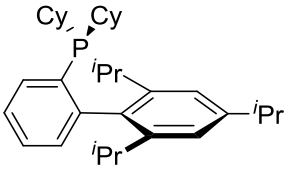
entry	catalyst	*T* (℃)	Concentration (M)	yield (%)[b]				
				2a	**3a**	**4a**	**5a**	**6a**
1	$PtCl_2$	70	0.1	42	37	-	-	-
2	**$PtBr_2$**	**70**	**0.1**	**49**	**40**	**-**	**-**	**-**
3[c]	$PtBr_2$	70	0.1	-[d]	-	-	-	-
4[e]	$PtBr_2$	70	0.1	-	-	35	46	-
5[f]	$PtBr_2$	25	0.1	28	25	-	-	-
6	PtI_2	70	0.1	8	10	-	-	-
7	$(Ph_3P)_2PtCl_2$	70	0.1	25	27	-	-	-
8	$Pt(COD)Cl_2$	70	0.1	19	17	-	-	-
9	$PtCl_4$	70	0.1	25	23	-	-	-
10	PtI_4	70	0.1	8	10	-	-	-
11	PtO_2	70	0.1	-[g]	-	-	-	-
12	$PtBr_2$	70	0.2	46	38	-	-	-
13	$PtBr_2$	70	0.05	35	31	-	-	-

Table S1. (continued)

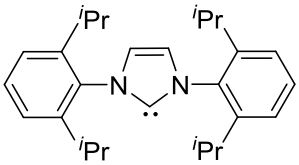
entry	catalyst	*T* (℃)	Concentration (M)	yield (%)[b]				
				2a	**3a**	**4a**	**5a**	**6a**
14	JohnPhosAuNTf$_2$	25	0.1	-[g]	-	-	-	-
15	JohnPhosAuNTf$_2$	70	0.1	-[g]	-	-	-	-
16	XPhosAuNTf$_2$	70	0.1	-[g]	-	-	-	-
17	IPrAuNTf$_2$	70	0.1	-[g]	-	-	-	-
18	[Rh(COD)Cl]$_2$	70	0.1	-	-	-	-	32
19	[Rh(COD)$_2$]BF$_4$	70	0.1	-	-	-	-	19
20	Pd(dppf)Cl$_2$	70	0.1	-[g]	-	-	-	-
21	AgSbF$_6$	70	0.1	-[g]	-	-	-	-



JohnPhos



XPhos

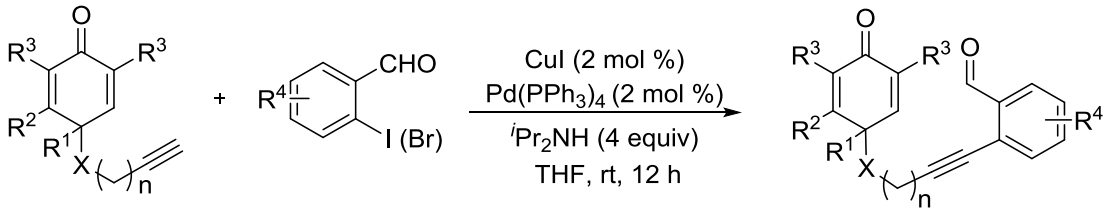


IPr

[a]All reactions were performed at the 0.2 mmol scale with 5 mol % of catalyst and 4 Å MS (100 mg) in THF (0.1 M) at 70 ℃ for 12 h. [b]Isolated product yield. [c]Reaction performed with 1,4-dioxane in place of THF as the solvent. [d]Reaction gave unknown decomposition products based on TLC analysis and ^{1}H NMR measurements of the crude reaction mixture. [e]Reaction performed in the absence of 4 Å MS. [f]Reaction performed at 25 ℃ for 30 h. [g]No reaction based on TLC analysis and ^{1}H NMR measurements of the crude reaction mixture.

3. Preparation of the Substrates 1 and 7

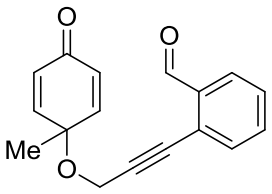
General Procedure for the Preparation of *O*- and *N*-Tethered Cyclohexadienones 1 and 7.



According to the corresponding literature procedures,[S1] to a solution of the *O*-tethered- or *N*-tethered alkynes **S1**[S2–S5] and **S2**[S6–S7] (2.0 mmol), 2-iodo(bromo)-benzaldehyde **S3** (2.2 mmol, 1.1 equiv), $Pd(PPh_3)_4$ (46.2 mg, 0.02 equiv) and CuI (7.6 mg, 0.02 equiv) in anhydrous THF (0.2 M, 10 mL) was added $^{i}Pr_2NH$ (8 mmol, 4 equiv) under an argon atmosphere. The resulting reaction mixture was stirred at room temperature for 8–24 h until full consumption of the starting material, as indicated by TLC analysis. The reaction mixture was quenched with the addition of saturated NH_4Cl solution (10 mL), followed by extraction with EtOAc (15 mL x 2). The combined organic extracts were then washed with saturated brine (15 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford *O*-tethered cyclohexadienones **1a**–**z** and **7a**–**f** and *NTs*-tethered cyclohexadienones **1aa**–**ad** in good to excellent yields.

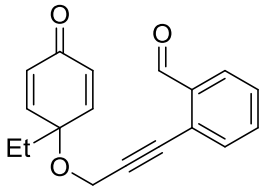
Substrates **1a, 1b, 1c, 1e, 1g, 1h, 1l, 1n, 1s, 1aa, 1ab, 7a, 7c** and **7e** were synthesized following literature procedures.[S1]

2-(3-((1-Methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1a)[S1]



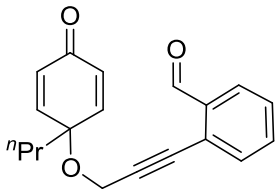
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1a** in 81% yield (1.079 g, 5 mmol scale) as a yellow solid; mp 82–84 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.57–7.53 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 6.91–6.87 (m, 2H), 6.37–6.34 (m, 2H), 4.29 (s, 2H), 1.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.3, 184.9, 150.6, 136.1, 133.7, 133.4, 130.6, 129.0, 127.3, 125.8, 92.8, 82.3, 73.4, 54.3, 26.3.

2-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1b)[S1]



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1b** in 78% yield (437 mg) as a pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.93–7.89 (m, 1H), 7.57–7.51 (m, 2H), 7.48–7.43 (m, 1H), 6.83 (d, *J* = 10.2 Hz, 2H), 6.41 (d, *J* = 10.2 Hz, 2H), 4.31 (s, 2H), 1.86 (q, *J* = 7.6 Hz, 2H), 0.87 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.2, 185.1, 149.7, 136.0, 133.6, 133.3, 131.7, 128.9, 127.2, 125.8, 92.9, 82.2, 77.0, 54.2, 32.2, 7.7.

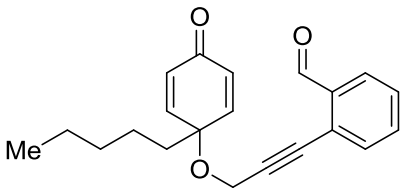
2-(3-((4-Oxo-1-propylcyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1c)[S1]



Column chromatography (eluent: petroleum ether/EtOAc = 25:1 to 10:1) to afford **1c** in 78% yield (1.377 g, 6 mmol scale) as a pale-yellow solid; mp 74–76 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.56–7.51 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 10.2 Hz, 2H), 6.40 (d, *J* = 10.2 Hz, 2H), 4.30 (s, 2H), 1.81–1.75 (m, 2H), 1.34–1.26 (m, 2H), 0.90 (t, *J* = 7.4H); ^{13}C NMR (150 MHz,

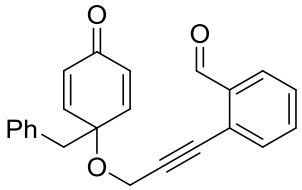
$CDCl_3$) δ 191.3, 185.2, 150.0, 136.1, 133.7, 133.4, 131.5, 128.9, 127.3, 125.8, 93.0, 82.2, 76.5, 54.1, 41.5, 16.9, 14.2.

2-(3-((4-Oxo-1-pentylcyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1d)



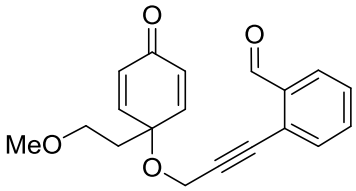
Column chromatography (eluent: petroleum ether/EtOAc = 25:1 to 15:1) to afford **1d** in 67% yield (432 mg) as a pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.58–7.52 (m, 2H), 7.47–7.44 (m, 1H), 6.84 (d, *J* = 10.2 Hz, 2H), 6.39 (d, *J* = 10.2 Hz, 2H), 4.30 (s, 2H), 1.82–1.79 (m, 2H), 1.30–1.26 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 185.3, 150.1, 136.2, 133.7, 133.4, 131.6, 129.0, 127.3, 125.9, 93.0, 82.2, 76.6, 54.1, 39.3, 31.8, 23.1, 22.4, 13.9; HRMS (ESI) calcd for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1642, found: 323.1651.

2-(3-((1-Benzyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1e)[S1]



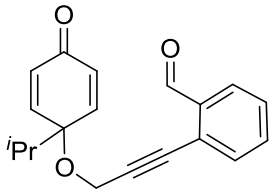
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1e** in 91% yield (623 mg) as a pale-yellow solid; mp 64–66 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.28–7.22 (m, 3H), 7.18 (d, *J* = 6.7 Hz, 2H), 6.85 (d, *J* = 10.2 Hz, 2H), 6.32 (d, *J* = 10.2 Hz, 2H), 4.30 (s, 2H), 3.09 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.3, 184.9, 149.4, 136.1, 134.3, 133.7, 133.3, 131.4, 130.7, 129.0, 128.1, 127.3, 127.2, 125.8, 92.9, 82.4, 76.3, 54.4, 46.2.

2-(3-((1-(2-Methoxyethyl)-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benz aldehyde (1f)



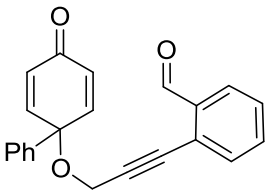
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 8:1) to afford **1f** in 69% yield (428 mg) as a pale-yellow solid; mp 90–92 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.57–7.53 (m, 2H), 7.46 (t, *J* = 7.1 Hz, 1H), 6.90 (d, *J* = 10.2 Hz, 2H), 6.38 (d, *J* = 10.2 Hz, 2H), 4.30 (s, 2H), 3.46 (t, *J* = 6.2 Hz, 2H), 3.27 (s, 3H), 2.08 (t, *J* = 6.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 185.1, 149.7, 136.2, 133.7, 133.4, 131.1, 129.0, 127.4, 125. 8, 92.9, 82.4, 75.1, 67.2, 58.5, 54.0, 39.5; HRMS (ESI) calcd for $C_{19}H_{19}O_4$ $[M+H]^+$: 311.1278, found: 311.1284.

2-(3-((1-Isopropyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyd e (1g)[S1]



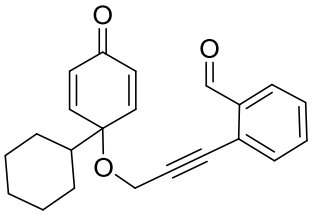
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1g** in 70% yield (412 mg) as a colorless solid; mp 60–62 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H),7.57–7.52 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 10.3 Hz, 2H), 6.44 (d, *J* = 10.3 Hz, 2H), 4.30 (s, 2H), 2.09 (dt, *J* = 13.8, 6.9 Hz, 1H), 0.98 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 191.5, 150.7, 144.3, 134.5, 132.3, 128.9, 128.2, 127.5, 124.6, 99.2, 89.1, 83.6, 68.7, 52.0, 51.6, 37.4, 17.3, 16.8.

2-(3-((4-Oxo-[1,1'-biphenyl]-1(4*H*)-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1h)[S1]



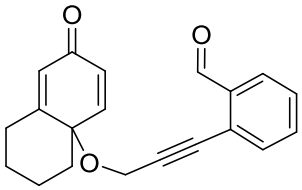
Column chromatography (eluent: petroleum ether/EtOAc = 25:1 to 12:1) to afford **1h** in 78% yield (525 mg) as a colorless solid; mp 120–122 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.58–7.55 (m, 2H), 7.52–7.45 (m, 3H), 7.40–7.37 (m, 2H), 7.35–7.31 (m, 1H), 6.94 (d, *J* = 10.1 Hz, 2H), 6.44 (d, *J* = 10.1 Hz, 2H), 4.54 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.3, 185.3, 149.4, 137.52 136.2, 133.8, 133.4, 130.1, 129.1, 128.9, 128.6, 127.4, 125.8, 125.7, 92.8, 82.6, 77.1, 54.1.

2-(3-((4-Oxo-[1,1'-bi(cyclohexane)]-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1i)



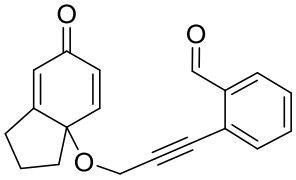
Column chromatography (eluent: petroleum ether/EtOAc = 25:1 to 12:1) to afford **1i** in 68% yield (455 mg) as a yellow solid; mp 100–102 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.45 (d, *J* = 0.7 Hz, 1H), 7.88 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.54–7.49 (m, 2H), 7.44–7.41 (m, 1H), 6.82 (d, *J* = 10.3 Hz, 2H), 6.40 (d, *J* = 10.3 Hz, 2H), 4.26 (s, 2H), 1.90 (d, *J* = 11.9 Hz, 2H), 1.76–1.72 (m, 3H), 1.64 (d, *J* = 12.9 Hz, 1H), 1.23–1.16 (m, 2H), 1.11–1.05 (m, 1H), 0.95 (dd, *J* = 12.7, 3.3 Hz, 1H), 0.91 (dd, *J* = 12.7, 3.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.3, 185.4, 149.4, 136.1, 133.7, 133.3, 132.1, 128.9, 127.2, 125.9, 93.2, 82.0, 78.7, 53.9, 46.5, 27.3, 26.3, 26.3; HRMS (ESI) calcd for $C_{22}H_{23}O_3$ $[M+H]^+$: 335.1642, found: 335.1649.

2-(3-((7-Oxo-1,3,4,7-tetrahydronaphthalen-4a(2*H*)-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1j)



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford 1j in 50% yield (306 mg) as a yellow solid; mp 74–76 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.91 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.57–7.52 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 10.0 Hz, 1H), 6.36–6.35 (m, 1H), 6.25 (s, 1H), 4.14 (d, *J* = 15.6 Hz, 1H), 4.11 (d, *J* = 15.6 Hz, 1H), 2.61–2.52 (m, 1H), 2.38 (d, *J* = 12.6 Hz, 1H), 2.24 (d, *J* = 13.8 Hz, 1H), 2.07–1.97 (m, 2H), 1.65 (d, *J* = 11.7 Hz, 1H), 1.43–1.36 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 185.9, 162.0, 150.2, 136.2, 133.7, 133.4, 131.0, 129.0, 127.2, 126.9, 125.9, 92.6, 82.0, 74.5, 53.3, 39.4, 32.6, 28.1, 20.3; HRMS (ESI) calcd for $C_{20}H_{19}O_3$ $[M+H]^+$: 307.1329, found: 307.1338.

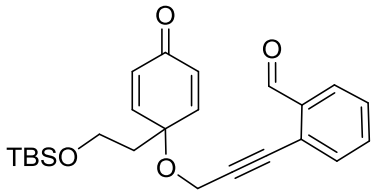
2-(3-((6-Oxo-1,2,3,6-tetrahydro-3a*H*-inden-3a-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1k)



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford 1k in 89% yield (520 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.55–7.51 (m, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 9.9 Hz, 1H), 6.35 (dd, *J* = 9.9, 1.6 Hz, 1H), 6.23 (s, 1H), 4.19 (d, *J* = 15.8 Hz, 1H), 4.12 (d, *J* = 15.8 Hz, 1H), 2.85–2.78 (m, 1H), 2.54–2.46 (m, 1H), 2.33–2.24 (m, 1H), 2.20 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.00–1.90 (m, 1H), 1.70–1.65 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 185.9, 165.9, 144.4, 136.1, 133.7, 133.4, 132.1, 128.9, 127.2,

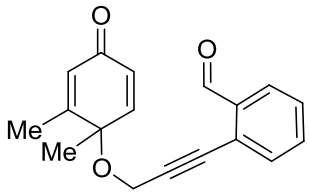
126.0, 125.6, 92.7, 81.7, 79.3, 52.9, 35.7, 28.8, 21.6; HRMS (ESI) calcd for $C_{19}H_{17}O_3$ $[M+H]^+$: 293.1172, found: 293.1180.

2-(3-((1-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-4-oxocyclohexa-2,5-dien-1-yl)oxy) prop-1-yn-1-yl)benzaldehyde (1l)[S1]



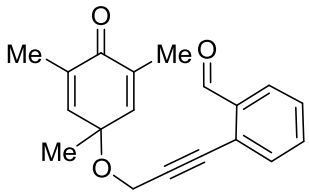
Column chromatography (eluent: petroleum ether/EtOAc = 40:1 to 25:1) to afford **1l** in 74% yield (608 mg) as a yellow solid; mp 60–62 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.57–7.51 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 10.2 Hz, 2H), 6.36 (d, *J* = 10.1 Hz, 2H), 4.29 (s, 2H), 3.72 (t, *J* = 6.0 Hz, 2H), 2.03 (t, *J* = 6.0 Hz, 2H), 0.86 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.3, 185.3, 150.0, 136.2, 133.7, 133.4, 130.9, 129.0, 127.3, 125.9, 92.9, 82.3, 75.2, 57.8, 53.9, 42.9, 25.8, 18.1, -5.5.

2-(3-((1,2-Dimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1m)



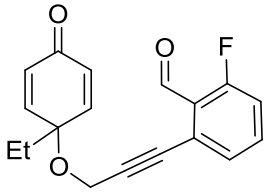
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1m** in 86% yield (482 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.57–7.52 (m, 2H), 7.45 (t, *J* = 7.1 Hz, 1H), 6.87 (d, *J* = 10.0 Hz, 1H), 6.33 (d, *J* = 10.0 Hz, 1H), 6.23 (s, 1H), 4.18 (d, *J* = 15.5 Hz, 2H), 4.10 (d, *J* = 15.5 Hz, 2H), 2.07 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.3, 185.2, 159.4, 150.9, 136.1, 133.7, 133.4, 130.3, 129.4, 129.0, 127.3, 125. 8, 92.2, 82.1, 75.2, 53.9, 25.5, 18.1; HRMS (ESI) calcd for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172, found: 281.1181.

2-(3-((1,3,5-Trimethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzalde hyde (1n)[S1]



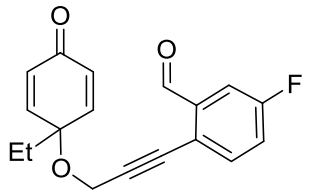
Column chromatography (eluent: petroleum ether/EtOAc = 25:1 to 15:1) to afford 1n in 79% yield (465 mg) as a pale-yellow solid; mp 74–76 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.53–7.49 (m, 2H), 7.43–7.39 (m, 1H), 6.58 (s, 2H), 4.21 (s, 2H), 1.90 (s, 6H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.3, 186.2, 145.5, 136.9, 136.0, 133.6, 133.4, 128.8, 127.1, 126.0, 93.4, 81.7, 73.3, 53.7, 26.5, 15.9.

2-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)-6-fluorobenzald ehyde (1o)



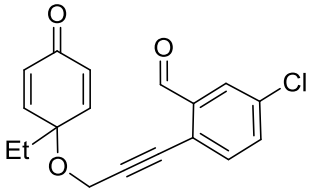
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1o** in 80% yield (477 mg) as a pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.49 (td, *J* = 8.1, 5.4 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.14–7.10 (m, 1H), 6.84 (d, *J* = 10.2 Hz, 2H), 6.39 (d, *J* = 10.2 Hz, 2H), 4.29 (s, 2H), 1.85 (d, *J* = 7.6 Hz, 2H), 0.85 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8 (d, *J* = 3.5 Hz), 185.2, 162.7 (d, *J* = 262.3 Hz), 149.8, 134.8 (d, *J* = 10.5 Hz), 131.8, 129.8, 129.7 (d, *J* = 3.6 Hz), 125.9 (d, *J* = 3.4 Hz), 124.4 (d, *J* = 8.1 Hz), 117.2 (d, *J* = 8.1 Hz), 93.6, 82.4 (d, *J* = 4.2 Hz), 77.2, 54.2, 32.2, 7.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.40 (dd, *J* = 10.4, 5.5 Hz); HRMS (ESI) calcd for $C_{18}H_{16}FO_3$ $[M+H]^+$: 299.1078, found: 299.1083.

2-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)-5-fluorobenzald ehyde (1p)



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1p** in 40% yield (239 mg; from 2-bromo-5-fluorobenzaldehyde) as a pale-pink solid; mp 72–74 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.40 (d, *J* = 3.1 Hz, 1H), 7.55 (dd, *J* = 8.5, 2.8 Hz, 1H), 7.52 (dd, *J* = 8.5, 5.1 Hz, 1H), 7.24 (td, *J* = 8.2, 2.4 Hz, 1H), 6.80 (d, *J* = 10.2 Hz, 2H), 6.39 (d, *J* = 10.2 Hz, 2H), 4.29 (s, 2H), 1.84 (q, *J* = 7.6 Hz, 2H), 0.85 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.1, 185.1, 162.5 (d, *J* = 253.2 Hz), 161.7, 149.6, 138.2 (d, *J* = 6.7 Hz), 135.5 (d, *J* = 7.7 Hz), 131.8, 121.9 (d, *J* = 3.5 Hz), 121.3 (d, *J* = 22.8 Hz), 113.8 (d, *J* = 23.0 Hz), 92.7 (d, *J* = 1.4 Hz), 81.1, 77.1, 54.1, 32.2, 7.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.19 – -108.30 (m); HRMS (ESI) calcd for $C_{18}H_{16}FO_3$ $[M+H]^+$: 299.1078, found: 299.1087.

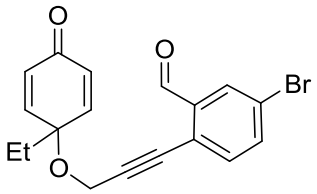
5-Chloro-2-(3-((1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzald ehyde (1q)



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1q** in 73% yield (460 mg) as a pale-yellow solid; mp 71–73 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.83 (d, *J* = 2.2 Hz, 1H), 7.49 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 10.2 Hz, 2H), 6.39 (d, *J* = 10.2 Hz, 2H), 4.28 (s, 2H), 1.84 (q, *J* = 7.6 Hz, 2H), 0.84 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.9, 185.1, 149.6, 137.2, 135.5, 134.6, 133.7, 131.8, 127.2, 124.0, 93.9, 81.2, 77.1,

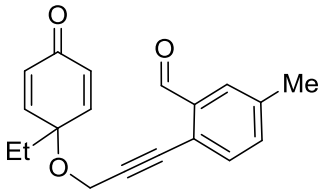
54.1, 32.2, 7.8; HRMS (ESI) calcd for $C_{18}H_{16}ClO_3$ $[M+H]^+$: 315.0782, found: 315.0789.

5-Bromo-2-(3-((1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1r)



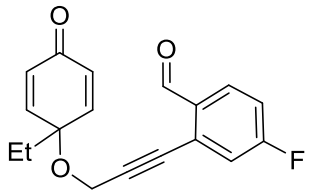
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1r** in 87% yield (625 mg) as a pale-yellow solid; mp 74–76 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.02 (d, *J* = 1.9 Hz, 1H), 7.66 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 10.2 Hz, 2H), 6.41 (d, *J* = 10.2 Hz, 2H), 4.29 (s, 2H), 1.85 (q, *J* = 7.6 Hz, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.9, 185.1, 149.6, 137.2, 136.6 134.7, 131.8, 130.3, 124.5, 123.5, 94.1, 81.3, 77.1, 54.1, 32.5, 7.8; HRMS (ESI) calcd for $C_{18}H_{16}BrO_3$ $[M+H]^+$: 359.0277, found: 395.0276.

2-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)-5-methylbenzaldehyde (1s)[S1]



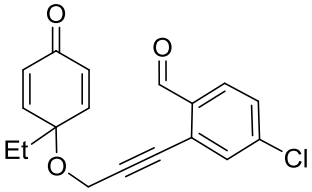
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1s** in 84% yield (494 mg) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.66 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.79 (d, *J* = 10.2 Hz, 2H), 6.37 (d, *J* = 10.2 Hz, 2H), 4.26 (s, 2H), 2.35 (s, 3H), 1.82 (q, *J* = 7.6 Hz, 2H), 0.82 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 185.1, 149.7, 139.3, 135.9, 134.5, 133.2, 131.7, 127.5, 122.9, 92.1, 82.3, 77.0, 54.2, 32.1, 21.2, 7.7;

2-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)-4-fluorobenzaldehyde (1t)



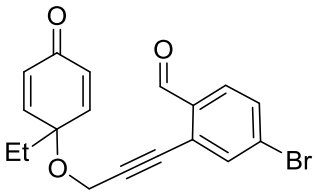
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1t** in 34% yield (203 mg; from 2-bromo-4-fluorobenzaldehyde) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.92 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.14 (td, *J* = 8.5, 2.3 Hz, 1H), 6.80 (d, *J* = 10.1 Hz, 2H), 6.41 (d, *J* = 10.2 Hz, 2H), 4.30 (s, 2H), 1.85 (q, *J* = 7.5 Hz, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.7, 185.1, 165.5 (d, *J* = 257.0 Hz), 149.6, 132.9 (d, *J* = 2.8 Hz), 131.9, 130.2 (d, *J* = 10.2 Hz), 128.3 (d, *J* = 11.0 Hz), 120.0 (d, *J* = 23.6 Hz), 116.9 (d, *J* = 22.1 Hz), 94.1, 81.0 (d, *J* = 2.8 Hz), 77.2, 54.1, 32.2, 7.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ –103.02 - –103.25 (m); HRMS (ESI) calcd for $C_{18}H_{16}FO_3$ $[M+H]^+$: 299.1078, found: 299.1078.

4-Chloro-2-(3-((1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1u)



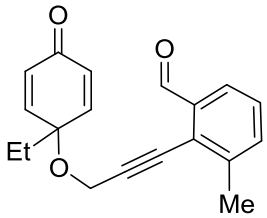
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 9:1) to afford **1u** in 38% yield (239 mg; from 2-bromo-4-chlorobenzaldehyde) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 10.1 Hz, 2H), 6.39 (d, *J* = 10.1 Hz, 2H), 4.28 (s, 2H), 1.84 (q, *J* = 7.5 Hz, 2H), 0.84 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.0, 185.1, 149.5, 140.1, 134.4, 133.0, 131.9, 129.4, 128.6, 127.2, 94.2, 80.8, 77.1, 54.0, 32.2, 7.8; HRMS (ESI) calcd for $C_{18}H_{16}ClO_3$ $[M+H]^+$: 315.0782, found: 315.0782.

4-Bromo-2-(3-((1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1v)



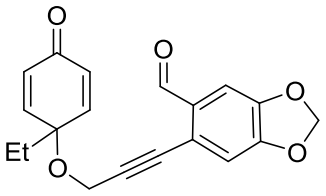
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 9:1) to afford **1v** in 69% yield (496 mg) as a pale-yellow solid; mp 67–69 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.58–7.56 (m, 1H), 6.80 (d, *J* = 10.2 Hz, 2H), 6.40 (d, *J* = 10.2 Hz, 2H), 4.29 (s, 2H), 1.85 (q, *J* = 7.6 Hz, 2H), 0.85 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.2, 185.1, 149.5, 136.0, 134.8, 132.4, 131.9, 128.7, 128.6, 127.2, 94.3, 80.7, 77.1, 54.1, 32.2, 7.8; HRMS (ESI) calcd for $C_{18}H_{16}BrO_3$ $[M+H]^+$: 359.0277, found: 359.0277.

2-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)-3-methylbenzaldehyde (1w)



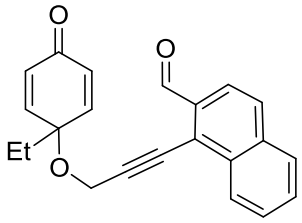
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1w** in 64% yield (377 mg) as a pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 10.0 Hz, 2H), 6.41 (d, *J* = 10.0 Hz, 2H), 4.35 (s, 2H), 2.47 (s, 3H), 1.86 (q, *J* = 7.6 Hz, 2H), 0.87 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.0, 185.2, 149.8, 141.8, 136.5, 134.9, 131.8, 128.4, 125.6, 124.7, 97.5, 80.8, 77.1, 54.3, 32.3, 20.4, 7.8; HRMS (ESI) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329, found: 295.1329.

6-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)benzo[d][1,3]dioxole-5-carbaldehyde (1x)



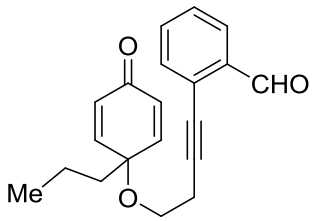
Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 8:1) to afford **1x** in 45% yield (292 mg; from 6-Bromopiperonal) as a pale-yellow solid; mp 61–63 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.32 (s, 1H), 6.90 (s, 1H), 6.80 (d, *J* = 10.2 Hz, 2H), 6.41 (d, *J* = 10.1 Hz, 2H), 6.07 (s, 2H), 4.28 (s, 2H), 1.85 (q, *J* = 7.6 Hz, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.7, 185.2, 152.3, 149.8, 148.9, 132.6, 131.8, 122.5, 112.2, 106.0, 102.4, 91.7, 82.0, 77.1, 54.2, 32.2, 7.8; HRMS (ESI) calcd for $C_{19}H_{17}O_5$ $[M+H]^+$: 325.1071, found: 325.1070.

1-(3-((1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)prop-1-yn-1-yl)-2-naphthaldehyde (1y)



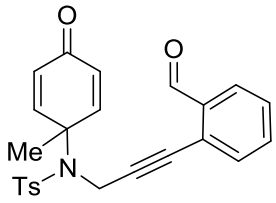
Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 8:1) to afford **1y** in 39% yield (258 mg; from 1-bromo-2-naphthaldehyde) as a colorless solid; mp 105–107 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.45–8.41 (m, 1H), 7.95 (dd, *J* = 8.6, 3.2 Hz, 1H), 7.88 (dd, *J* = 8.5, 3.5 Hz, 2H), 7.67–7.64 (m, 2H), 6.87 (d, *J* = 10.1 Hz, 2H), 6.44 (d, *J* = 10.1 Hz, 2H), 4.48 (s, 2H), 1.90 (q, *J* = 7.6 Hz, 2H), 0.89 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 185.2, 149.8, 135.7, 134.8, 133.2, 131.9, 129.4, 129.3, 128.5, 127.8, 127.0, 126.4, 121.9, 99.0, 80.1, 77.2, 54.4, 32.3, 7.8; HRMS (ESI) calcd for $C_{22}H_{18}NaO_3$ $[M+Na]^+$: 353.1148, found: 353.1148.

2-(4-((4-Oxo-1-propylcyclohexa-2,5-dien-1-yl)oxy)but-1-yn-1-yl)benzaldehyde (1z)



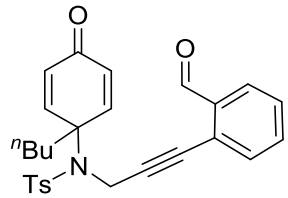
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 10:1) to afford **1z** in 71% yield (438 mg) as a pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.86 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.51–7.46 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 6.78–6.74 (m, 2H), 6.35–6.30 (m, 2H), 3.51 (t, *J* = 6.7 Hz, 2H), 2.69 (t, *J* = 6.7 Hz, 2H), 1.74–1.69 (m, 2H), 1.30–1.22 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 185.3, 150.8, 136.0, 133.6, 133.1, 131.1, 128.1, 127.1, 126.9, 94.2, 77.3, 75.7, 63.3, 41.5, 21.6, 16.7, 14.1; HRMS (ESI) calcd for $C_{26}H_{26}NO_4S$ $[M+H]^+$: 309.1485, found: 309.1484.

***N*-(3-(2-Formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)benzenesulfonamide (1aa)[S1]**



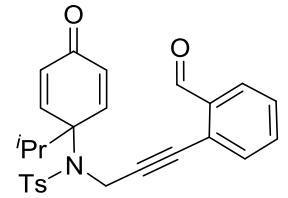
Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 5:1) to afford **1aa** in 60% yield (503 mg) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.91 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.57 (dt, *J* = 7.6, 3.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.09–7.06 (m, 2H), 6.23–6.20 (m, 2H), 4.54 (s, 2H), 2.41 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 184.2, 151.0, 144.1, 138.4, 136.1, 133.7, 133.4, 129.6, 129.1, 128.0, 127.8, 127.5, 125.0, 92.4, 81.1, 60.2, 37.2, 25.8, 21.4.

***N*-(1-Butyl-4-oxocyclohexa-2,5-dien-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1ab)**[S1]



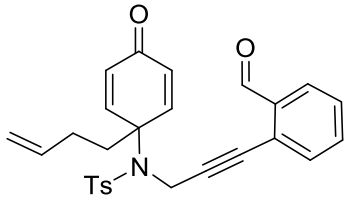
Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 4:1) to afford **1ab** in 86% yield (794 mg) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.25 (s, 2H), 7.00 (d, *J* = 10.2 Hz, 2H), 6.26 (d, *J* = 10.1 Hz, 2H), 4.56 (s, 2H), 2.39 (s, 3H), 2.06–2.00 (m, 2H), 1.252–1.18 (m, 2H), 1.12–1.05 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 184.8, 149.3, 144.2, 138.6, 136.3, 133.8, 133.5, 129.6, 129.1, 127.9, 127.7, 125.2, 92.6, 81.1, 64.2, 37.0, 36.4, 26.1, 22.6, 21.5, 13.7.

***N*-(3-(2-Formylphenyl)prop-2-yn-1-yl)-*N*-(1-isopropyl-4-oxocyclohexa-2,5-dien-1-yl)-4-methylbenzenesulfonamide (1ac)**



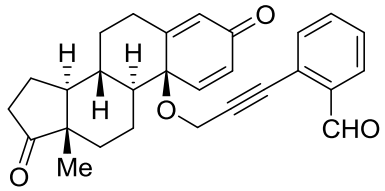
Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 4:1) to afford **1ac** in 92% yield (824 mg) as a colorless solid; mp 114–116 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.90 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.56 (td, *J* = 7.6, 1.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 10.4 Hz, 2H), 6.25 (d, *J* = 10.4 Hz, 2H), 4.61 (s, 2H), 2.76–2.71 (m, 1H), 2.36 (s, 3H), 0.93 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 184.8, 146.8, 144.3, 137.3, 136.2, 133.8, 133.4, 130.1, 129.5, 129.1, 128.1, 127.8, 125.1, 92.1, 81.3, 66.9, 36.8, 33.6, 21.5, 17.4; HRMS (ESI) calcd for $C_{26}H_{26}NO_4S$ $[M+H]^+$: 448.1577, found: 448.1577.

***N*-(1-(But-3-en-1-yl)-4-oxocyclohexa-2,5-dien-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1ad)**



Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 6:1) to afford 1ad in 84% yield (772 mg) as a pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.91 (d, *J* = 7.0 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.57 (td, *J* = 7.6, 1.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 10.2 Hz, 2H), 6.29 (d, *J* = 10.2 Hz, 2H), 5.68–5.62 (m, 1H), 4.95–4.90 (m, 2H), 4.56 (s, 2H), 2.40 (s, 3H), 2.20–2.13 (m, 2H), 1.91–1.87 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 184.5, 148.8, 144.1, 138.4, 136.1, 136.1, 133.7, 133.4, 129.7, 129.6, 129.0, 127.9, 127.6, 125.0, 115.7, 92.4, 81.1, 63.8, 36.9, 35.4, 28.0, 21.4; HRMS **(ESI)** calcd for $C_{27}H_{26}NO_4S$ $[M+H]^+$: 460.1577, found: 460.1577.

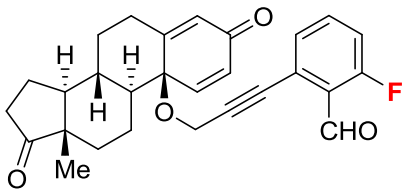
2-(3-(((8*S*,9*S*,10*S*,13*S*,14*S*)-13-Methyl-3,17-dioxo-3,6,7,8,9,11,12,13,14,15,16,17-dodecahydro-10*H*-cyclopenta[*a*]phenanthren-10-yl)oxy)prop-1-yn-1-yl)benzaldehyde (7a)[S1]



Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 4:1) to afford **7a** in 68% yield (583 mg) as a colorless solid; mp 189–191 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.54 (td, *J* = 7.2, 1.1 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 10.3 Hz, 1H), 6.38 (dd, *J* = 10.3, 1.9 Hz, 1H), 6.22 (s, 1H), 4.15 (s, 2H), 2.66 (td, *J* = 12.7, 4.6 Hz, 1H), 2.47–2.39 (m, 2H), 2.21 (qd, *J* = 11.4, 3.7 Hz, 1H), 2.12–2.08 (m, 3H), 1.97–1.91 (m, 1H), 1.88–1.83 (m, 1H), 1.81–1.76 (m, 1H), 1.64–1.57 (m, 1H), 1.27–1.13 (m, 4H), 0.97 (s,

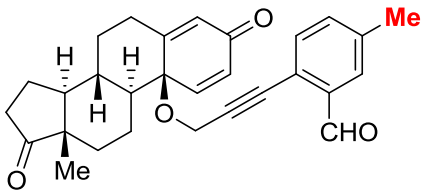
3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 191.3, 184.9, 163.2, 149.2, 136.1, 133.7, 133.3, 131.6, 128.9, 127.3, 126.6, 125.8, 92.7, 82.1, 76.4, 55.3, 53.4, 50.1, 47.7, 35.6, 34.6, 32.5, 32.2, 31.0, 22.1, 21.9, 13.8.

2-Fluoro-6-(3-(((8*S*,9*S*,10*S*,13*S*,14*S*)-13-methyl-3,17-dioxo-3,6,7,8,9,11,12,13,14,15,16,17-dodecahydro-10*H*-cyclopenta[*a*]phenanthren-10-yl)oxy)prop-1-yn-1-yl)benzaldehyde (7b)



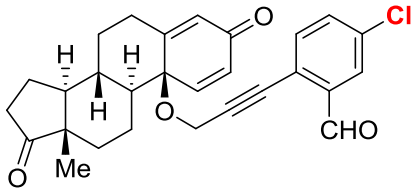
Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 4:1) to afford **7b** in 53% yield (473 mg) as a pale-yellow solid; mp 180–182 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.49 (td, *J* = 8.0, 5.5 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.14–7.09 (m, 2H), 6.36 (dd, *J* = 10.3, 1.8 Hz, 1H), 6.19 (s, 1H), 4.14 (d, *J* = 12.1 Hz, 1H), 4.12 (d, *J* = 12.1 Hz, 1H), 2.64 (td, *J* = 12.8, 4.7 Hz, 1H), 2.43 (dd, *J* = 19.4, 8.9 Hz, 1H), 2.39–2.38 (m, 1H), 2.20 (ddd, *J* = 22.6, 11.4, 3.6 Hz, 1H), 2.11–2.01 (m, 3H), 1.95–1.89 (m, 1H), 1.86–1.82 (m, 1H), 1.81–1.76 (m, 1H), 1.63–1.55 (m, 1H), 1.25–1.18 (m, 4H), 0.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 187.7 (d, *J* = 3.2 Hz), 185.0, 163.2, 162.6 (d, *J* = 262.6 Hz), 149.4, 134.8 (d, *J* = 10.5 Hz), 131.5, 129.6 (d, *J* = 3.6 Hz), 126.5, 125.9 (d, *J* = 3.4 Hz), 124.4 (d, *J* = 8.2 Hz), 117.1 (d, *J* = 21.5 Hz), 93.2, 82.2 (d, *J* = 4.3 Hz), 76.4, 55.2, 53.4, 50.1, 47.7, 35.5, 34.5, 32.4, 32.1, 31.0, 22.1, 21.9, 13.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ –116.31; HRMS (ESI) calcd for $C_{28}H_{28}FO_4$ $[M+H]^+$: 447.1966, found: 447.1972.

5-Methyl-2-(3-(((8*S*,9*S*,10*S*,13*S*,14*S*)-13-methyl-3,17-dioxo-3,6,7,8,9,11,12,13,14,15,16,17-dodecahydro-10*H*-cyclopenta[*a*]phenanthren-10-yl)oxy)prop-1-yn-1-yl)benzaldehyde (7c)[S1]



Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 4:1) to afford **5c** in 60% yield (531 mg) as a colorless solid; mp 230–232 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.70 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 10.3 Hz, 1H), 6.37 (dd, *J* = 10.3, 1.7 Hz, 1H), 6.21 (s, 1H), 4.14 (s, 2H), 2.66 (td, *J* = 12.7, 4.7 Hz, 1H), 2.47–2.41 (m, 2H), 2.39 (s, 3H), 2.24–2.17 (m, 1H), 2.10–2.01 (m, 3H), 1.96–1.90 (m, 1H), 1.86–1.77 (m, 2H), 1.64–1.56 (m, 1H), 1.27–1.11 (m, 4H), 0.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.5, 185.0, 163.3, 149.3, 139.4, 136.0, 134.6, 133.2, 131.5, 127.6, 126.5, 123.0, 91.9, 82.2, 76.4, 55.3, 53.5, 50.1, 47.7, 35.6, 34.6, 32.5, 32.2, 31.0, 22.1, 21.9, 21.3, 13.8;

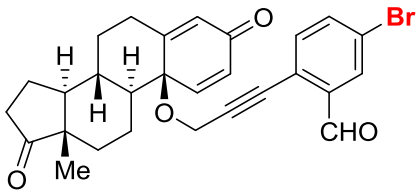
5-Chloro-2-(3-(((8*S*,9*S*,10*S*,13*S*,14*S*)-13-methyl-3,17-dioxo-3,6,7,8,9,11,12,13,14,15,16,17-dodecahydro-10*H*-cyclopenta[*a*]phenanthren-10-yl)oxy)prop-1-yn-1-yl)benzaldehyde (7d)



Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 4:1) to afford 5d in 46% yield (426 mg) as a pale-yellow solid; mp 192–194 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.51 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 10.3 Hz, 1H), 6.39 (dd, *J* = 10.3, 2.0 Hz, 1H), 6.22 (s, 1H), 4.15 (d, *J* = 1.3 Hz, 2H), 2.64 (ddd, *J* = 12.8, 5.2, 3.8 Hz, 1H), 2.46 (dd, *J* = 19.5, 8.8 Hz, 1H), 2.43–2.39 (m, 1H), 2.20 (qd, *J* = 11.4, 3.7 Hz, 1H), 2.13–2.06 (m, 3H),

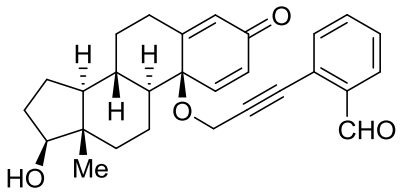
1.97–1.92 (m, 1H), 1.88–1.85 (m, 1H), 1.81–1.77 (m, 1H), 1.64–1.57 (m, 1H), 1.28–1.13 (m, 4H), 0.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 190.0, 184.9, 163.0, 149.1, 137.2, 135.6, 134.5, 133.8, 131.7, 127.3, 126.7, 124.1, 93.6, 81.1, 76.5, 55.3, 53.4, 50.1, 47.7, 35.6, 34.6, 32.5, 32.2, 31.1, 22.1, 21.9, 13.8; HRMS (ESI) calcd for $C_{28}H_{28}ClO_4$ $[M+H]^+$: 463.1671, found: 463.1671.

5-Bromo-2-(3-(((8*S*,9*S*,10*S*,13*S*,14*S*)-13-methyl-3,17-dioxo-3,6,7,8,9,11,12,13,14,15,16,17-dodecahydro-10*H*-cyclopenta[*a*]phenanthren-10-yl)oxy)prop-1-yn-1-yl)benzaldehyde (7e)[S1]



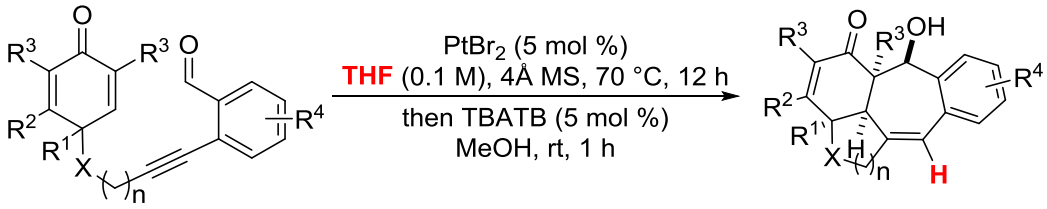
Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 4:1) to afford **5e** in 69% yield (700 mg) as a colorless solid; mp 183–185 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.02 (d, *J* = 2.1 Hz, 1H), 7.67 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 10.3 Hz, 1H), 6.39 (dd, *J* = 10.3, 1.9 Hz, 1H), 6.22 (s, 1H), 4.14 (s, 2H), 2.64 (ddd, *J* = 12.7, 5.2, 4.1 Hz, 1H), 2.46 (dd, *J* = 19.4, 8.8 Hz, 1H), 2.43–2.39 (m, 1H), 2.21 (qd, *J* = 11.4, 3.7 Hz, 1H), 2.12–2.03 (m, 3H), 1.97–1.92 (m, 1H), 1.89–1.77 (m, 2H), 1.64–1.57 (m, 1H), 1.28–1.12 (m, 4H), 0.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 189.9, 184.9, 163.0, 149.1, 137.3, 136.7, 134.6, 131.7, 130.3, 126.7, 124.5, 123.6, 93.8, 81.2, 76.5, 55.3, 53.4, 50.1, 47.7, 35.6, 34.6, 32.8, 32.2, 31.1, 22.1, 21.9, 13.8; HRMS (ESI) calcd for $C_{28}H_{28}BrO_4$ $[M+H]^+$: 507.1165, found: 507.1167.

2-(3-(((8*S*,9*S*,10*S*,13*S*,14*S*,17*S*)-17-Hydroxy-13-methyl-3-oxo-3,6,7,8,9,11,12,13,14,15,16,17-dodecahydro-10*H*-cyclopenta[a]phenanthren-10-yl)oxy)prop-1-yn-1-yl) benzaldehyde (7f)



Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 3:1) to afford **5f** in 53% yield (456 mg) as a colorless solid; mp 171–173 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.91 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.58–7.42 (m, 3H), 7.12 (d, *J* = 10.3 Hz, 1H), 6.37 (dd, *J* = 10.3, 2.0 Hz, 1H), 6.23–6.15 (m, 1H), 4.15 (s, 2H), 3.62 (t, *J* = 8.4 Hz, 1H), 2.62 (ddd, *J* = 12.5, 5.1, 3.8 Hz, 1H), 2.40–2.31 (m, 1H), 2.14–1.95 (m, 4H), 1.90–1.82 (m, 1H), 1.74–1.55 (m, 3H), 1.50–1.31 (m, 2H), 1.19–0.89 (m, 4H), 0.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 185.2, 164.1, 149.9, 136.1, 133.7, 133.3, 131.4, 128.9, 127.3, 126.3, 126.0, 92.9, 82.0, 81.5, 55.7, 53.4, 49.9, 43.1, 36.3, 35.1, 33.4, 32.5, 30.4, 23.6, 22.6, 11.0; HRMS (ESI) calcd for $C_{26}H_{26}NO_4S$ $[M+H]^+$: 431.2217, found: 431.2214.

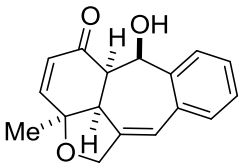
4. General Procedure for the THF-enabled $PtBr_2$-Catalyzed Desymmetric Hydrogenative [3 + 2] Cycloaddition and TBATB-Mediated Deacetalization



To an oven-dried round-bottom flask (10 mL) equipped with a magnetic stir bar were added *O- or NTs*-tethered cyclohexadienones **1** or **7** (0.2 mmol), 4Å MS (100 mg) and $PtBr_2$ (3.5 mg, 0.01 mmol). The reaction vessel was capped and charged with an argon atmosphere through three cycles of the vacuum-argon-backfill method over 5 min. Anhydrous THF (2 mL) was then added and the resulting reaction mixture was stirred at 70 ^{o}C for 24 h. Upon completion, the reaction mixture was cooled to room

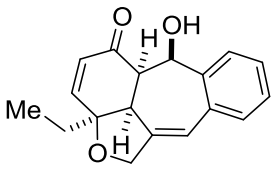
temperature, tetrabutylammonium tribromide (TBATB) (4.8 mg, 0.01mmol) and MeOH (2 mL) were added. The resulting reaction mixture was stirred at room temperature for 1 h (monitored by TLC), filtered through a pad of Celite and rinsed with EtOAc. The filtrate was washed with saturated $NaHCO_3$ (10 mL) and extracted with EtOAc (10 mL x 2). The combined organic phases are washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the desired product **4** or **8**.

(2a*S*,2a^1*S***,5a*R***,6*R***)-2a-Ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cycloheptа[1,2,3-*cd*]benzofuran-5(1*H*)-one (4a)**



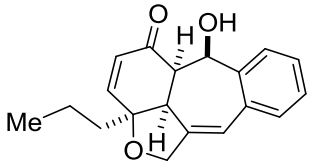
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4a** in 75% yield (40 mg); colorless solid, mp 182–184 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.56 (dd, *J* = 10.1, 1.8 Hz, 1H), 6.20 (d, *J* = 2.3 Hz, 1H), 5.78 (d, *J* = 10.1 Hz, 1H), 4.92 (dd, *J* = 11.8, 2.6 Hz, 1H), 4.66 (d, *J* = 13.3 Hz, 1H), 4.28 (d, *J* = 13.3 Hz, 1H), 3.55 (d, *J* = 11.9 Hz, 1H), 3.44 (dd, *J* = 4.9, 3.1 Hz, 1H), 3.39–3.34 (m, 1H), 1.62 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.1, 152.0, 140.0, 139.6, 132.2, 130.2, 127.6, 127.5, 127.3, 123.8, 82.2, 72.8, 71.0, 50.5, 49.4, 22.8; HRMS (ESI) calcd for $C_{17}H_{17}O_3$ $[M+H]^+$: 269.1172, found: 269.1170.

(2aS*,2a^1*S***,5a*R***,6*R***)-2a-Ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cycloheptа[1,2,3-*cd*]benzofuran-5(1*H*)-one (4b)**



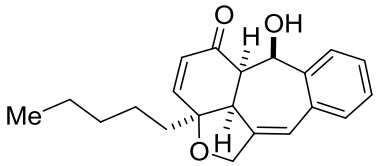
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4b** in 93% yield (53 mg); colorless solid, mp 99–101 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 10.2 Hz, 1H), 6.21 (s, 1H), 5.81 (d, *J* = 10.2 Hz, 1H), 4.91 (d, *J* = 11.3 Hz, 1H), 4.64 (d, *J* = 13.1 Hz, 1H), 4.29 (d, *J* = 13.1 Hz, 1H), 3.58 (d, *J* = 11.7 Hz, 1H), 3.42 (s, 2H), 2.02–1.96 (m, 1H), 1.89–1.83 (m, 1H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 151.8, 140.3, 139.6, 132.2, 130.3, 128.0, 127.6, 127.5, 127.3, 123.8, 84.4, 72.9, 71.1, 49.6, 47.9, 29.4, 8.0; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1329, found: 283.1326.

(2a*S,2a^{1}*S**,5a*R**,6*R**)-6-Hydroxy-2a-propyl-2a,2a^{1},5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4c)**



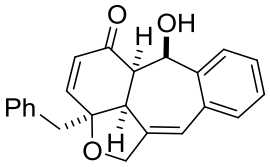
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4c** in 97% yield (58 mg); colorless solid, mp 138–140 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.30–7.26 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.61 (dd, *J* = 10.2, 1.7 Hz, 1H), 6.20 (d, *J* = 2.1 Hz, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 4.91 (dd, *J* = 11.8, 2.4 Hz, 1H), 4.64 (dt, *J* = 13.2, 1.7 Hz, 1H), 4.28 (dt, *J* = 13.2, 1.8 Hz, 1H), 3.57 (d, *J* = 11.8 Hz, 1H), 3.44 (dd, *J* = 5.1, 2.9 Hz, 1H), 3.43–3.40 (m, 1H), 1.93 (ddd, *J* = 14.1, 10.7, 6.1 Hz, 1H), 1.80 (ddd, *J* = 14.1, 11.0, 5.7 Hz, 1H), 1.62–1.54 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 151.8, 140.2, 139.6, 132.2, 130.3, 127.8, 127.5, 127.5, 127.3, 123.8, 84.4, 72.9, 71.1, 49.5, 48.5, 38.9, 17.1, 14.5; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1483.

(2a*S,2a^1*S**,5a*R**,6*R**)-6-Hydroxy-2a-pentyl-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4d)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 5:1) to give the product **4d** in 92% yield (60 mg); colorless solid, mp 198–200 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.61 (dd, *J* = 10.2, 1.3 Hz, 1H), 6.20 (d, *J* = 1.8 Hz, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 13.2 Hz, 1H), 4.28 (d, *J* = 13.2 Hz, 1H), 3.58 (d, *J* = 11.8 Hz, 1H), 3.45–3.41 (m, 2H), 1.94 (ddd, *J* = 14.1, 10.9, 5.9 Hz, 1H), 1.80 (ddd, *J* = 14.1, 11.2, 5.6 Hz, 1H), 1.59–1.50 (m, 2H), 1.39–1.32 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 151.9, 140.2, 139.6, 132.2, 130.3, 127.8, 127.6, 127.5, 127.4, 123.8, 84.4, 73.0, 71.1, 49.5, 48.5, 36.7, 32.2, 23.4, 22.5, 14.0; HRMS (ESI) calcd for $C_{21}H_{25}O_3$ $[M+H]^+$: 325.1798, found: 325.1791.

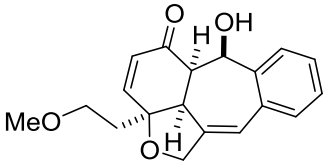
(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Benzyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4e)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4e** in 57% yield (40 mg); colorless solid, mp 196–198 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.37–7.29 (m, 5H), 7.29–7.26 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.51 (dd, *J* = 10.2, 1.0 Hz, 1H), 6.18 (d, *J* = 1.6 Hz, 1H), 5.82 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 11.8 Hz, 1H), 4.59 (d, *J* = 13.1 Hz, 1H), 4.26 (d, *J* = 13.1 Hz, 1H), 3.55 (d, *J* = 11.8 Hz, 1H), 3.38–3.32 (m, 2H), 3.25 (d,

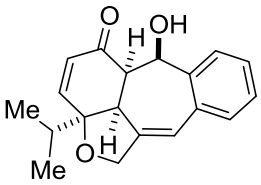
J = 14.1 Hz, 1H), 3.10 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.2, 151.3, 139.7, 139.6, 135.3, 132.2, 130.4, 130.2, 128.4, 127.9, 127.6, 127.5, 127.3, 127.2, 123.9, 84.2, 72.8, 71.1, 49.4, 48.0, 42.7; HRMS (ESI) calcd for $C_{23}H_{20}NaO_3$ $[M+Na]^+$: 367.1305, found: 367.1304.

(2a*S,2a^1*S**,5a*R**,6*R**)-6-Hydroxy-2a-(2-methoxyethyl)-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4f)**



Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 2:1) to give the product **4f** in 83% yield (52 mg); colorless solid, mp 126–127 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.58 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.19 (d, *J* = 1.9 Hz, 1H), 5.79 (d, *J* = 10.2 Hz, 1H), 4.89 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.65 (d, *J* = 13.2 Hz, 1H), 4.28 (d, *J* = 13.1 Hz, 1H), 3.67 (ddd, *J* = 9.9, 6.7, 5.1 Hz, 1H), 3.62–3.57 (m, 2H), 3.55–3.50 (m, 2H), 3.35 (s, 3H), 2.19 (ddd, *J* = 14.7, 6.9, 5.0 Hz, 1H), 2.10 (ddd, *J* = 14.8, 6.7, 5.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.5, 151.3, 140.0, 139.8, 132.1, 130.3, 127.8, 127.5, 127.5, 127.3, 123.7, 83.5, 72.9, 71.1, 67.7, 58.6, 49.2, 48.8, 36.4; HRMS (ESI) calcd for $C_{19}H_{21}O_4$ $[M+H]^+$: 313.1434, found: 313.1433.

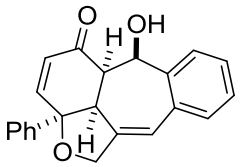
(2a*S,2a^1*S**,5a*R**,6*R**)-6-Hydroxy-2a-isopropyl-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4g)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 5:1) to give the product **4g** in 59% yield (35 mg); colorless solid, mp 107–109 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.4 Hz,

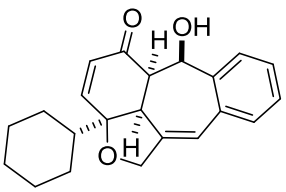
1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.65 (dd, *J* = 10.3, 1.7 Hz, 1H), 6.24 (d, *J* = 1.9 Hz, 1H), 5.88 (d, *J* = 10.3 Hz, 1H), 4.94 (dd, *J* = 11.5, 2.6 Hz, 1H), 4.61 (d, *J* = 12.9 Hz, 1H), 4.29 (d, *J* = 12.9 Hz, 1H), 3.55–3.48 (m, 3H), 2.15 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.13 (dd, *J* = 6.9, 3.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 151.6, 141.0, 139.6, 132.0, 130.6, 128.5, 127.5, 127.5, 127.4, 123.7, 86.3, 73.2, 71.2, 50.5, 45.9, 34.5, 17.6, 17.4; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1486.

(2a*S,2a^1*S**,5a*R**,6*R**)-6-Hydroxy-2a-phenyl-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4h)**



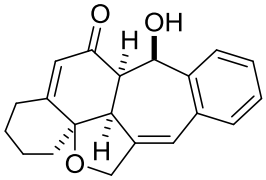
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 4:1) to give the product **4h** in 90% yield (60 mg); colorless solid, mp 145–147 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.57–7.54 (m, 2H), 7.46–7.44 (m, 2H), 7.42–7.38 (m, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.70 (dd, *J* = 10.1, 1.8 Hz, 1H), 6.25 (d, *J* = 2.1 Hz, 1H), 6.09 (d, *J* = 10.1 Hz, 1H), 4.96 (d, *J* = 13.1 Hz, 1H), 4.76 (dd, *J* = 11.8, 2.5 Hz, 1H), 4.51 (dt, *J* = 13.2, 1.8 Hz, 1H), 3.53–3.50 (m, 1H), 3.48 (d, *J* = 11.8 Hz, 1H), 3.41 (dd, *J* = 4.8, 3.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.5, 149.2, 139.8, 139.7, 139.0, 132.4, 130.2, 129.3, 128.9, 128.7, 127.7, 127.5, 127.4, 125.5, 123.7, 86.0, 72.7, 71.8, 53.1, 48.4; HRMS **(ESI)** calcd for $C_{22}H_{18}NaO_3$ $[M+Na]^+$: 353.1148, found: 353.1145.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Cyclohexyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4i)**



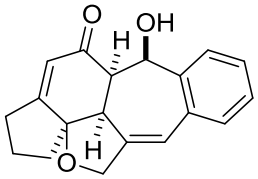
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 5:1) to give the product **4i** in 78% yield (52 mg); colorless solid, mp 126–128 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 10.3, 1.6 Hz, 1H), 6.22 (d, *J* = 1.9 Hz, 1H), 5.85 (d, *J* = 10.3 Hz, 1H), 4.93 (dd, *J* = 11.5, 2.6 Hz, 1H), 4.59 (d, *J* = 12.9 Hz, 1H), 4.28 (d, *J* = 12.9 Hz, 1H), 3.54 (d, *J* = 11.6 Hz, 2H), 3.51 (dd, *J* = 5.4, 3.1 Hz, 1H), 1.95 (d, *J* = 8.2 Hz, 1H), 1.88 (d, *J* = 12.1 Hz, 1H), 1.85 (d, *J* = 11.4 Hz, 2H), 1.80 (ddd, *J* = 11.6, 7.4, 3.0 Hz, 1H), 1.74–1.68 (m, 1H), 1.34–1.25 (m, 4H), 1.24–1.16 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 191.3, 184.9, 163.2, 149.2, 136.1, 133.7, 133.3, 131.6, 128.9, 127.3, 126.6, 125.8, 92.7, 82.1, 76.4, 55.3, 53.4, 50.1, 47.7, 35.6, 34.6, 32.5, 32.2, 31.0, 22.1, 21.9, 13.8; HRMS (ESI) calcd for $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798, found: 337.1793.

(6a*R,6a^1*S**,14*R**,14a*R**)-14-Hydroxy-3,4,5,6,6a^1,8,14,14a-octahydro-1*H*-benzo[*h*]benzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-1-one (4j)**



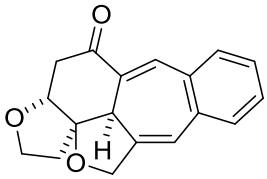
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4j** in 74% yield (46 mg); colorless solid, mp 214–216 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.29–7.26 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.19 (d, *J* = 1.8 Hz, 1H), 5.68 (s, 1H), 4.90 (dd, *J* = 11.8, 2.5 Hz, 1H), 4.60 (d, *J* = 13.3 Hz, 1H), 4.20 (d, *J* = 13.3 Hz, 1H), 3.61 (d, *J* = 11.8 Hz, 1H), 3.39 (dd, *J* = 4.6, 3.3 Hz, 1H), 3.19 (d, *J* = 2.1 Hz, 1H), 2.67 (td, *J* = 12.2, 4.2 Hz, 1H), 2.19 (d, *J* = 11.8 Hz, 1H), 2.08–2.04 (m, 1H), 2.04–1.99 (m, 1H), 1.99–1.91 (m, 2H), 1.80–1.73 (m, 1H), 1.40–1.31 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.1, 165.0, 140.2, 139.9, 132.1, 130.3, 127.7, 127.5, 127.3, 123.8, 122.7, 84.2, 72.5, 70.2, 49.9, 49.4, 36.6, 32.0, 28.5, 21.9; HRMS (ESI) calcd for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1485, found: 309.1486.

(5a*R*,5a^1*S***,13*R***,13a*R***)-13-Hydroxy-4,5,5a^1,7,13,13a-hexahydrobenzo[5,6]cycloheptа[1,2,3-*cd*]cyclopenta[*h*]benzofuran-1(3*H*)-one (4k)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 4:1) to give the product **4k** in 68% yield (40 mg); pale-yellow solid, mp 176–178 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.28 (s, 1H), 5.86 (d, *J* = 1.3 Hz, 1H), 5.04 (s, 1H), 4.55 (d, *J* = 13.1 Hz, 1H), 4.26 (d, *J* = 13.1 Hz, 1H), 3.51 (d, *J* = 7.2 Hz, 1H), 3.43 (s, 1H), 3.31 (dd, *J* = 5.8, 3.7 Hz, 1H), 2.83–2.74 (m, 1H), 2.35 (dt, *J* = 16.7, 6.5 Hz, 1H), 2.22–2.11 (m, 1H), 2.04 (dd, *J* = 17.7, 9.3 Hz, 1H), 1.91–1.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 166.5, 141.6, 139.9, 132.1, 131.5, 128.5, 127.5, 127.4, 123.0, 122.6, 89.0, 72.5, 69.6, 53.2, 41.9, 32.2, 27.9, 20.9; HRMS (ESI) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329, found: 295.1328.

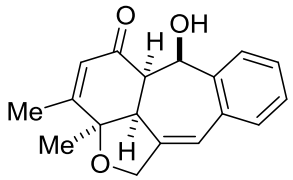
2a,3,4,5,5a^1,7-Hexahydrobenzo[5,6]cyclohepta[1,2,3-*cd*][1,3]dioxole[*h*]benzofuran-1(2*H*)-one (4l)



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4l** in 48% yield (27 mg); pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.41–7.31 (m, 3H), 6.61 (s, 1H), 4.76–4.67 (m, 2H), 4.30 (dd, *J* = 6.4, 4.5 Hz, 1H), 4.08 (td, *J* = 8.7, 6.0 Hz, 1H), 3.93 (dd, *J* = 15.1, 8.2 Hz, 1H), 3.10 (s, 1H), 2.84 (dd, *J* = 16.6, 4.3 Hz, 1H), 2.74 (dd, *J* = 16.6, 6.5 Hz, 1H), 2.27 (ddd, *J* = 12.5, 8.4, 6.8 Hz, 1H), 2.13–2.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 145.3, 137.0, 135.9, 133.5, 133.3, 131.2, 129.9, 128.8, 126.6, 119.5, 88.2,

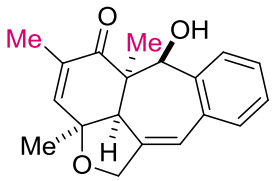
77.6, 70.3, 65.8, 45.7, 40.8, 37.7; HRMS (ESI) calcd for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172, found: 281.1172.

(2a*R,2a^1*S**,5a*R**,6*R**)-6-Hydroxy-2a,3-dimethyl-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4m)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4m** in 66% yield (37 mg); colorless solid, mp 170–1726 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 2.1 Hz, 1H), 5.65 (d, *J* = 1.1 Hz, 1H), 4.90 (dd, *J* = 11.7, 2.3 Hz, 1H), 4.62 (d, *J* = 13.3 Hz, 1H), 4.15 (dt, *J* = 13.4, 1.8 Hz, 1H), 3.71 (d, *J* = 11.8 Hz, 1H), 3.45 (dd, *J* = 5.1, 3.1 Hz, 1H), 3.35 (dd, *J* = 4.8, 2.4 Hz, 1H), 1.94 (d, *J* = 1.2 Hz, 3H), 1.61 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.7, 163.0, 139.9, 139.8, 132.1, 130.2, 127.5, 127.4, 127.2, 125.9, 123.7, 84.0, 72.7, 70.5, 51.5, 49.4, 22.2, 17.6; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1329, found: 283.1331.

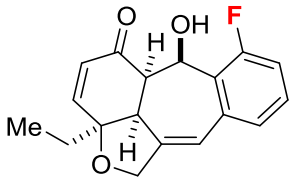
(2a*S,2a^1*R**,5a*R**,6*S**)-6-Hydroxy-2a,4,5a-trimethyl-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4n)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4n** in 84% yield (50 mg); colorless solid, mp 126–128 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.4, 1.3 Hz, 1H), 7.25 (d, *J* = 6.9 Hz, 1H), 7.20 (td, *J* = 7.4, 0.8 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 1.4 Hz, 1H), 6.42 (s, 1H), 4.81 (d, *J* = 6.8 Hz, 1H), 4.38 (s, 2H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.59 (s, 1H), 1.88 (d, *J* =

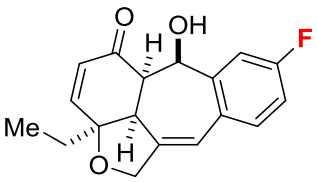
1.1 Hz, 3H), 1.48 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.8, 147.0, 145.6, 138.2, 136.5, 135.7, 130.8, 129.6, 128.2, 126.8, 121.8, 81.8, 79.2, 70.0, 62.2, 53.6, 27.7, 26.4, 16.1; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1492.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Ethyl-7-fluoro-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4o)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4o** in 55% yield (33 mg); pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (td, *J* = 8.0, 5.7 Hz, 1H), 6.97–6.89 (m, 2H), 6.63 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.54 (s, 1H), 6.24 (d, *J* = 10.4 Hz, 1H), 5.81 (dd, *J* = 7.2, 4.5 Hz, 1H), 4.44 (dd, *J* = 13.1, 1.1 Hz, 1H), 4.38 (dt, *J* = 13.1, 2.1 Hz, 1H), 3.47 (dd, *J* = 9.1, 4.5 Hz, 1H), 3.19 (d, *J* = 7.6 Hz, 1H), 3.04 (d, *J* = 8.2 Hz, 1H), 1.83–1.76 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.4, 160.2 (d, *J* = 246.9 Hz), 151.3, 146.1, 138.1, 131.6, 129.1 (d, *J* = 9.4 Hz), 126.6 (d, *J* = 13.6 Hz), 125.5 (d, *J* = 3.0 Hz), 121.7 (d, *J* = 2.6 Hz), 114.1 (d, *J* = 23.9 Hz), 82.7, 70.2, 65.3 (d, *J* = 6.94 Hz), 58.6, 45.1, 32.1, 8.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ –117.19 (dd, *J* = 9.7, 5.5 Hz); HRMS (ESI) calcd for $C_{18}H_{18}FO_3$ $[M+H]^+$: 301.1234, found: 301.1234.

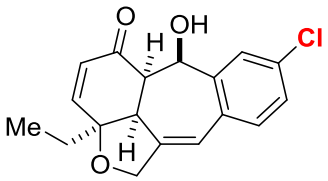
(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Ethyl-8-fluoro-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4p)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 43:1) to give the product **4p** in 77% yield (46 mg); colorless solid, mp 145–147 ℃; ^{1}H NMR (600

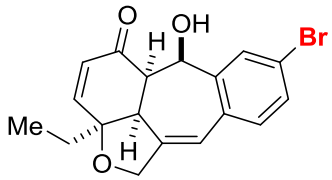
MHz, $CDCl_3$) δ 7.64 (dd, *J* = 10.9, 1.5 Hz, 1H), 6.97 (dd, *J* = 8.2, 6.1 Hz, 1H), 6.85 (td, *J* = 8.0, 2.4 Hz, 1H), 6.62 (d, *J* = 10.2 Hz, 1H), 6.16 (s, 1H), 5.81 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 9.3 Hz, 1H), 4.62 (d, *J* = 13.1 Hz, 1H), 4.26 (d, *J* = 13.1 Hz, 1H), 3.61 (d, *J* = 11.2 Hz, 1H), 3.41 (s, 2H), 2.00–1.95 (m, 1H), 1.89–1.83 (m, 1H), 1.11 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.2, 162.2 (d, *J* = 247.2 Hz), 152.00, 142.5 (d, *J* = 6.9 Hz), 139.2 (d, *J* = 2.9 Hz), 134.0 (d, *J* = 8.0 Hz), 133.9, 127.8, 126.5 (d, *J* = 3.4 Hz), 122.7, 114.9 (d, *J* = 21.4 Hz), 114.1 (d, *J* = 21.4 Hz), 84.5, 72.5, 71.1, 49.2, 48.0, 29.3, 7.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ –113.58 to –113.72 (m); HRMS (ESI) calcd for $C_{18}H_{18}FO_3$ $[M+H]^+$: 301.1234, found: 301.1232.

(2a*S,2a^1*S**,5a*R**,6*R**)-8-Chloro-2a-ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4q)**



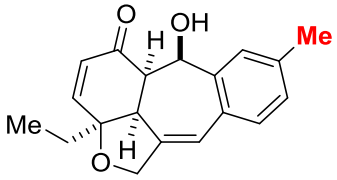
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 4:1) to give the product **4q** in 82% yield (52 mg); colorless solid, mp 190–192 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.13 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 10.2 Hz, 1H), 6.14 (s, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.62 (d, *J* = 13.1 Hz, 1H), 4.26 (d, *J* = 13.2 Hz, 1H), 3.62 (d, *J* = 11.8 Hz, 1H), 3.41 (s, 2H), 2.03–1.96 (m, 1H), 1.89–1.83 (m, 1H), 1.11 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.1, 151.9, 141.5, 140.8, 133.5, 133.4, 128.8, 127.8, 127.8, 127.3, 122.7, 84.5, 72.4, 71.0, 49.1, 48.0, 29.2, 7.9; HRMS (ESI) calcd for $C_{18}H_{18}ClO_3$ $[M+H]^+$: 317.0939, found: 317.0940.

(2a*S,2a^1*S**,5a*R**,6*R**)-8-Bromo-2a-ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4r)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4r** in 80% yield (72 mg); colorless solid, mp 207–209 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.30 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.63 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.14 (d, *J* = 1.9 Hz, 1H), 5.82 (d, *J* = 10.2 Hz, 1H), 4.85 (d, *J* = 11.3 Hz, 1H), 4.63 (d, *J* = 13.5 Hz, 1H), 4.26 (dd, *J* = 13.5, 1.8 Hz, 1H), 3.56 (d, *J* = 11.9 Hz, 1H), 3.44–3.38 (m, 2H), 2.03–1.96 (m, 1H), 1.89–1.83 (m, 1H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.1, 151.9, 141.7, 141.1, 133.6, 130.8, 130.4, 129.3, 127.8, 122.8, 121.9, 84.5, 72.4, 71.1, 49.1, 48.0, 29.2, 7.9; HRMS (ESI) calcd for $C_{18}H_{18}BrO_3$ $[M+H]^+$: 361.0434, found: 361.0442.

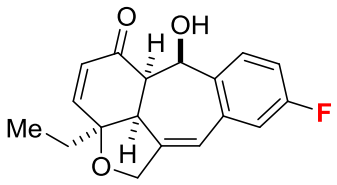
(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Ethyl-6-hydroxy-8-methyl-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4s)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4s** in 84% yield (50 mg); colorless solid, mp 176–178 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 10.2 Hz, 1H), 6.17 (s, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.9 Hz, 1H), 4.27 (d, *J* = 12.9 Hz, 1H), 3.59 (d, *J* = 11.8 Hz, 1H), 3.40 (s, 2H), 2.35 (s, 3H), 1.97 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.85 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.11 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 151.7, 139.3, 138.9,

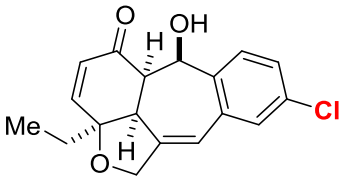
137.3, 132.3, 128.2, 128.0, 127.9, 127.6, 123.6, 84.3, 72.9, 71.1, 49.6, 47.9, 29.3, 21.3, 7.9; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1493.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Ethyl-9-fluoro-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4t)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 4:1) to give the product **4t** in 79% yield (48 mg); colorless solid, mp 106–108 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.3, 6.3 Hz, 1H), 6.95 (td, *J* = 8.4, 2.7 Hz, 1H), 6.71 (dd, *J* = 9.8, 2.7 Hz, 1H), 6.62 (dd, *J* = 10.2, 1.6 Hz, 1H), 6.13 (d, *J* = 2.0 Hz, 1H), 5.82 (d, *J* = 10.2 Hz, 1H), 4.86 (d, *J* = 11.2 Hz, 1H), 4.64 (d, *J* = 13.5 Hz, 1H), 4.28 (dd, *J* = 13.5, 1.8 Hz, 1H), 3.59 (d, *J* = 11.8 Hz, 1H), 3.44–3.38 (m, 2H), 1.99 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.86 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.3, 161.7 (d, *J* = 245.0 Hz), 151.8, 142.0, 135.4 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 7.4 Hz), 129.6 (d, *J* = 8.0 Hz), 128.0, 122. 9, 122.9, 118.2 (d, *J* = 21.9 Hz), 114.1 (d, *J* = 20.5 Hz), 84.5, 72.6, 71.0, 49.3, 48.0, 29.3, 7.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ –117.12 (dd, *J* = 15.7, 7.6 Hz); HRMS (ESI) calcd for $C_{18}H_{18}FO_3$ $[M+H]^+$: 301.1234, found: 301.1227.

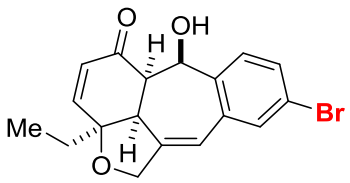
(2a*S,2a^1*S**,5a*R**,6*R**)-9-Chloro-2a-ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4u)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 4:1) to give the product **4u** in 85% yield (54 mg); colorless solid, mp 112–114 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.99 (d, *J* =

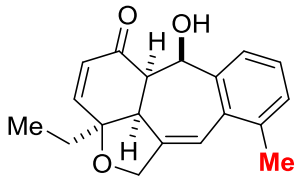
2.0 Hz, 1H), 6.62 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.12 (d, *J* = 1.9 Hz, 1H), 5.81 (d, *J* = 10.2 Hz, 1H), 4.85 (d, *J* = 10.4 Hz, 1H), 4.64 (d, *J* = 13.5 Hz, 1H), 4.28 (d, *J* = 13.5 Hz, 1H), 3.57 (d, *J* = 11.7 Hz, 1H), 3.45–3.38 (m, 2H), 1.99 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.86 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.2, 151.9, 142.1, 138.1, 132.9, 132.0, 131.6, 129.2, 127.9, 127.3, 122.7, 84.5, 72.6, 71.1, 49.2, 48.0, 29.3, 8.0; HRMS (ESI) calcd for $C_{18}H_{18}ClO_3$ $[M+H]^+$: 317.0939, found: 317.0940.

(2a*S,2a^1*S**,5a*R**,6*R**)-9-Bromo-2a-ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4v)**



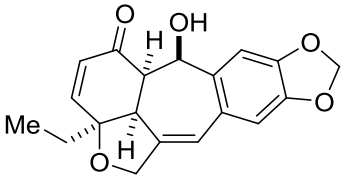
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4v** in 96% yield (69 mg); colorless solid, mp 117–119 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.13 (d, *J* = 1.6 Hz, 1H), 6.61 (dd, *J* = 10.2, 1.1 Hz, 1H), 6.09 (d, *J* = 1.6 Hz, 1H), 5.79 (d, *J* = 10.2 Hz, 1H), 4.80 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 13.5 Hz, 1H), 4.26 (d, *J* = 13.5 Hz, 1H), 3.61 (d, *J* = 11.8 Hz, 1H), 3.43–3.36 (m, 2H), 1.97 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.84 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.1, 151.8, 142.2, 138.7, 134.3, 132.3, 130.2, 129.4, 127.8, 122.5, 120.9, 84.5, 72.5, 71.0, 49.1, 48.0, 29.2, 7.9; HRMS (ESI) calcd for $C_{18}H_{17}BrNaO_3$ $[M+Na]^+$: 383.0253, found: 383.0251.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Ethyl-6-hydroxy-10-methyl-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4w)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 4:1) to give the product **4w** in 79% yield (47 mg); colorless solid, mp 91–93 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 1H), 7.14 (dt, *J* = 14.1, 7.2 Hz, 2H), 6.66–6.60 (m, 2H), 6.07 (d, *J* = 10.3 Hz, 1H), 5.11 (dd, *J* = 8.9, 3.3 Hz, 1H), 4.58 (d, *J* = 12.9 Hz, 1H), 4.39 (d, *J* = 12.8 Hz, 1H), 3.45 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.23 (d, *J* = 7.9 Hz, 1H), 3.20 (d, *J* = 9.3 Hz, 1H), 2.32 (s, 3H), 1.90–1.78 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 151.7, 143.3, 139.9, 137.0, 131.4, 130.2, 130.2, 127.3, 126.4, 119.2, 83.3, 74.6, 71.0, 55.9, 45.9, 31.5, 20.6, 8.1; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1488.

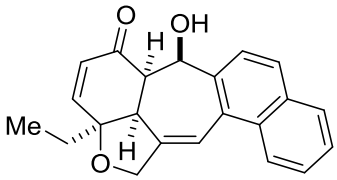
(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydro-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4x)**



Column chromatography (eluent: petroleum ether/EtOAc = 150:1 to 3:1) to give the product **4x** in 59% yield (39 mg); pale-yellow solid, mp 192–194 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (s, 1H), 6.63 (d, *J* = 10.2 Hz, 1H), 6.51 (s, 1H), 6.08 (s, 1H), 5.96 (d, *J* = 9.9 Hz, 2H), 5.85 (d, *J* = 10.2 Hz, 1H), 4.86 (d, *J* = 11.7 Hz, 1H), 4.63 (d, *J* = 13.0 Hz, 1H), 4.27 (d, *J* = 13.0 Hz, 1H), 3.59 (d, *J* = 11.8 Hz, 1H), 3.44–3.39 (m, 2H), 1.99 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.87 (dq, *J* = 14.8, 7.5 Hz, 1H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.5, 151.9, 147.3, 146.5, 138.4, 134.5,

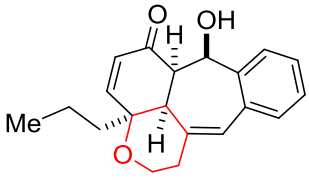
127.9, 124.3, 123.3, 111.7, 108.3, 101.2, 84.4, 72.8, 71.1, 49.7, 47.7, 29.5, 8.0; HRMS (ESI) calcd for $C_{19}H_{18}NaO_5$ $[M+Na]^+$: 349.1046, found: 349.1047.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Ethyl-6-hydroxy-2a,2a^1,5a,6-tetrahydronaphtho[2',1':5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (4y)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4y** in 64% yield (43 mg); pale-yellow solid, mp 188–190 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.55–7.47 (m, 2H), 7.27 (s, 1H), 6.66 (d, *J* = 10.3 Hz, 1H), 6.18 (d, *J* = 10.3 Hz, 1H), 5.36 (dd, *J* = 8.5, 3.7 Hz, 1H), 4.66 (d, *J* = 12.9 Hz, 1H), 4.51 (d, *J* = 12.9 Hz, 1H), 3.57 (dd, *J* = 9.0, 3.8 Hz, 1H), 3.25 (d, *J* = 8.6 Hz, 1H), 3.20 (d, *J* = 8.8 Hz, 1H), 1.81 (dt, *J* = 8.7, 6.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.7, 151.7, 146.2, 137.8, 133.3, 131.9, 130.9, 129.6, 128.5, 127.9, 126.7, 126.4, 125.9, 123.6, 117.9, 83.0, 75.1, 70.9, 58.5, 45.4, 32.1, 8.1; HRMS (ESI) calcd for $C_{22}H_{20}NaO_3$ $[M+Na]^+$: 355.1305, found: 355.1303.

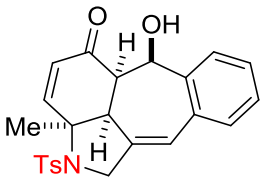
(3a*S,3a^1*S**,6a*R**,7*R**)-7-Hydroxy-3a-propyl-1,2,3a,3a^1,6a,7-hexahydro-6H-benzo[5,6]cyclohepta[1,2,3-*de*]chromen-6-one (4z)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4z** in 56% yield (35 mg); colorless solid, mp 140–142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.72 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.35 (s, 1H), 5.76 (d, *J* = 10.3 Hz, 1H), 4.77 (d, *J* = 11.8 Hz, 1H), 4.01 (dd, *J* = 11.2, 4.0 Hz, 1H), 3.64–3.55

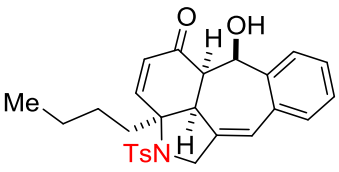
(m, 1H), 3.54 (dd, *J* = 5.8, 1.3 Hz, 1H), 3.41 (d, *J* = 11.9 Hz, 1H), 3.37 (d, *J* = 4.9 Hz, 1H), 2.56 (td, *J* = 13.1, 5.1 Hz, 1H), 2.24 (d, *J* = 13.6 Hz, 1H), 1.96–1.86 (m, 1H), 1.85–1.75 (m, 1H), 1.74–1.61 (m, 1H), 1.56–1.46 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 156.2, 140.1, 135.1, 131.6, 130.2, 129.4, 128.6, 127.0, 126.9, 125.4, 78.7, 73.5, 64.9, 55.9, 49.2, 43.0, 39.2, 17.2, 14.4; HRMS (ESI) calcd for $C_{20}H_{23}O_3$ $[M+H]^+$: 311.1642, found: 311.1649.

(2a*S,2a^1*S**,5a*R**,6*R**)-6-Hydroxy-2a-methyl-2-tosyl-1,2,2a,2a^1,5a,6-hexahydro-5*H*-benzo[5,6]cyclohepta[1,2,3-*cd*]indol-5-one (4aa)**



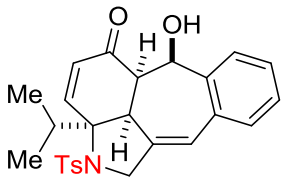
Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 2:1) to give the product **4aa** in 55% yield (36 mg); colorless solid, mp 154–156 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04–7.02 (m, 1H), 7.01 (s, 1H), 6.29 (s, 1H), 5.70 (d, *J* = 10.2 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.24 (d, *J* = 13.3 Hz, 1H), 4.17 (d, *J* = 13.3 Hz, 1H), 3.46 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 1H), 3.39 (dd, *J* = 5.4, 2.4 Hz, 1H), 2.45 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 150.9, 143.7, 139.7, 138.5, 133.1, 132.5, 129.8, 129.5, 128.0, 127.4, 126.9, 126.6, 126.1, 72.7, 67.8, 53.8, 52.7, 49.5, 22.8, 21.5; HRMS (ESI) calcd for $C_{24}H_{24}NO_4S$ $[M+H]^+$: 422.1421, found: 422.1421.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Butyl-6-hydroxy-2-tosyl-1,2,2a,2a^1,5a,6-hexahydro-5*H*-benzo[5,6]cyclohepta[1,2,3-*cd*]indol-5-one (4ab)**



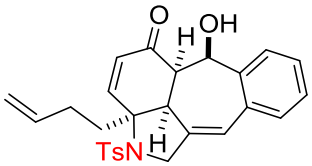
Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 2:1) to give the product **4ab** in 60% yield (56 mg); colorless solid, mp 167–169 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 10.3, 1.6 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.27 (s, 1H), 5.70 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.12 (dd, *J* = 34.1, 13.2 Hz, 2H), 3.65 (s, 1H), 3.50 (d, *J* = 11.9 Hz, 1H), 3.34 (dd, *J* = 5.5, 2.5 Hz, 1H), 2.52 (ddd, *J* = 18.3, 9.8, 4.7 Hz, 1H), 2.45 (s, 3H), 1.81–1.75 (m, 1H), 1.44–1.31 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.2, 150.8, 143.8, 139.6, 137.7, 133.4, 132.3, 129.7, 129.6, 127.9, 127.3, 127.1, 126.8, 126.4, 126.3, 72.8, 71.9, 54.1, 49.5, 47.7, 33.8, 26.3, 22.8, 21.5, 14.0; HRMS (ESI) calcd for $C_{27}H_{30}NO_4S$ $[M+H]^+$: 464.1890, found: 464.1888.

(2a*S,2a^{1}*S**,5a*R**,6*R**)-6-Hydroxy-2a-isopropyl-2-tosyl-1,2,2a,2a^{1},5a,6-hexahydro-5*H*-benzo[5,6]cyclohepta[1,2,3-*cd*]indol-5-one (4ac)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4ac** in 38% yield (34 mg); colorless solid, mp 187–189 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 10.4, 0.8 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.29 (s, 1H), 5.87 (d, *J* = 10.4 Hz, 1H), 4.89 (d, *J* = 11.2 Hz, 1H), 4.10 (d, *J* = 12.6 Hz, 1H), 4.01 (d, *J* = 12.5 Hz, 1H), 3.74 (d, *J* = 5.6 Hz, 1H), 3.49 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.32 (d, *J* = 11.4 Hz, 1H), 3.07 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.44 (s, 3H), 1.13–1.07 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.2, 149.4, 143.6, 139.8, 137.6, 134.0, 132.0, 129.7, 128.0, 127.3, 127.3, 127.0, 126.6, 126.4, 75.6, 72.6, 54.9, 52.2, 44.5, 33.7, 21.5, 18.6, 17.5; HRMS (ESI) calcd for $C_{26}H_{28}NO_4S$ $[M+H]^+$: 450.1734, found: 450.1728.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-(But-3-en-1-yl)-6-hydroxy-2-tosyl-1,2,2a,2a^1,5a,6-hexahydro-5*H*-benzo[5,6]cyclohepta[1,2,3-*cd*]indol-5-one (4ad)**



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to give the product **4ad** in 55% yield (51 mg); colorless solid, mp 181–183 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 10.2 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.27 (s, 1H), 5.83 (tt, *J* = 10.3, 6.5 Hz, 1H), 5.72 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.10 (dd, *J* = 36.4, 13.2 Hz, 2H), 3.67 (s, 1H), 3.47 (d, *J* = 11.9 Hz, 1H), 3.36 (d, *J* = 3.0 Hz, 1H), 2.75–2.64 (m, 1H), 2.45 (s, 3H), 2.37–2.28 (m, 1H), 2.19 (dt, *J* = 18.6, 9.3 Hz, 1H), 1.91–1.83 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.1, 150.2, 144.0, 139.6, 137.4, 136.9, 133.1, 132.3, 129.9, 129.5, 128.0, 127.4, 127.2, 126.9, 126.6, 126.6, 115.8, 72.8, 71.8, 54.0, 49.5, 47.5, 32.9, 28.2, 21.6; HRMS (ESI) calcd for $C_{27}H_{28}NO_4S$ $[M+H]^+$: 462.1734, found: 462.1734.

(2*aS,2*a1R**)-2a-methyl-2a,2a1-dihydrobenzo[5,6]cyclohepta[1,2,3-cd]benzofuran-5(1H)-one (5a)**

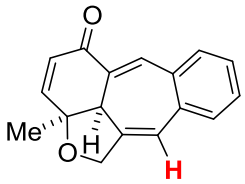


Table S1, entry 4: Column chromatography (eluent: petroleum ether/EtOAc = 30:1 to 10:1) to give the product **5a** in 46% yield (23 mg); pale-yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.41–7.33 (m, 3H), 6.80 (d, *J* = 10.4 Hz, 1H), 6.59 (d, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 10.4 Hz, 1H), 4.64 (dd, *J* = 13.5, 1.2 Hz, 1H), 4.40 (dt, *J* = 13.5, 1.8 Hz, 1H), 2.83 (d, *J* = 1.2 Hz, 1H), 1.48 (s, 3H); ^{13}C

NMR (150 MHz, $CDCl_3$) δ 184.2, 150.4, 146.2, 136.6, 135.7, 133.9, 132.8, 130.3, 130.2, 129.2, 128.4, 126.4, 118.8, 79.0, 70.0, 47.0, 28.1; HRMS (ESI) calcd for $C_{17}H_{15}O_2$ $[M+H]^+$: 251.1067, found: 251.1072.

(*2aS*,2a1R*,5aR*,6R*,11aR)-2a-methyl-2a,2a1,5a,6-tetrahydro-1*H*-6,11a-epoxybenzo[5,6]cyclohepta[1,2,3-cd]benzofuran-5,11-dione (6a)**[S1]

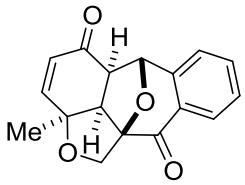
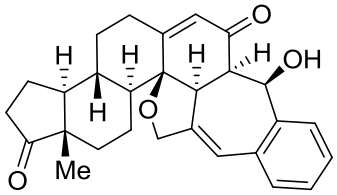


Table S1, entry 18: Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 5:1) to afford **6a** in 32% yield (18 mg); yellow solid, mp 199–201 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 10.3 Hz, 1H), 6.25 (d, *J* = 10.3 Hz, 1H), 5.66 (s, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 3.86 (d, *J* = 10.4 Hz, 1H), 3.00 (d, *J* = 8.9 Hz, 1H), 2.98 (d, *J* = 8.9 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.2, 191.5, 152.9, 144.3, 134.5, 130.0, 128.9, 128.2, 127.4, 124.5, 99.5, 88.6, 77.6, 68.4, 54.0, 51.4, 27.8.

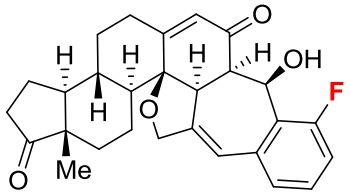
(3a*S*,3b*S*,7a*R*,7a^1*S*,8*R*,15a*R*,15b*S*,17a*S*)-8-Hydroxy-17a-methyl-2,3,3a,3b,4,5,7a,7a^1,8,14,15b,16,17,17a-tetradecahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]cyclopenta[5,6]naphtho[2,1-*h*]benzofuran-1,7-dione (8a)



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 2:1) to give the product **8a** in 80% yield (697 mg); colorless solid, mp 140–142 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.27–7.24 (m, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.18 (d, *J* = 2.0 Hz, 1H), 5.66 (s, 1H), 4.89 (dd, *J* = 11.8, 2.3

Hz, 1H), 4.58 (d, *J* = 13.3 Hz, 1H), 4.21 (d, *J* = 13.2 Hz, 1H), 3.62 (d, *J* = 11.9 Hz, 1H), 3.59–3.58 (m, 1H), 3.33 (t, *J* = 3.9 Hz, 1H), 2.75–2.70 (m, 1H), 2.48 (dd, *J* = 19.5, 8.7 Hz, 1H), 2.26–2.21 (m, 1H), 2.16–2.04 (m, 3H), 1.98–1.78 (m, 4H), 1.63–1.55 (m, 1H), 1.50 (td, *J* = 11.4, 4.4 Hz, 1H), 1.38–1.30 (m, 2H), 1.15–1.08 (m, 1H), 0.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.3, 155.7, 140.2, 134.7, 131.7, 130.2, 129.4, 128.7, 127.1, 126.9, 125.4, 76.7, 73.4, 65.0, 56.3, 51.7, 39.1, 27.5; HRMS (ESI) calcd for $C_{28}H_{31}O_4$ $[M+H]^+$: 431.2217, found: 431.2216.

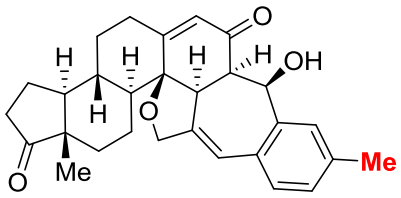
(3a*S*,3b*S*,7a*R*,7a^1*S*,8*R*,15a*R*,15b*S*,17a*S*)-9-Fluoro-8-hydroxy-17a-methyl-2,3,3a,3b,4,5,7a,7a^1,8,14,15b,16,17,17a-tetradecahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]cyclopenta[5,6]naphtho[2,1-*h*]benzofuran-1,7-dione (8b)



Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 2:1) to give the product **8b** in 53% yield (48 mg); colorless solid, mp 260–262 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (td, *J* = 7.9, 5.5 Hz, 1H), 6.93 (dd, *J* = 9.8, 8.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 5.95 (d, *J* = 1.1 Hz, 1H), 5.61 (dd, *J* = 7.4, 4.9 Hz, 1H), 4.42 (d, *J* = 13.9 Hz, 1H), 4.22 (dt, *J* = 13.2, 2.0 Hz, 1H), 3.79 (d, *J* = 8.0 Hz, 1H), 3.43 (dd, *J* = 6.7, 4.8 Hz, 1H), 3.37–3.34 (m, 1H), 2.76 (ddd, *J* = 12.4, 4.8, 3.6 Hz, 1H), 2.46 (dd, *J* = 19.5, 8.7 Hz, 1H), 2.31–2.26 (m, 1H), 2.13–2.09 (m, 1H), 2.08–2.04 (m, 2H), 1.98–1.91 (m, 1H), 1.84–1.80 (m, 1H), 1.75–1.69 (m, 1H), 1.67–1.63 (m, 1H), 1.57 (ddd, *J* = 18.4, 10.8, 6.2 Hz, 1H), 1.42 (td, *J* = 11.8, 4.2 Hz, 1H), 1.33–1.27 (m, 2H), 1.19–1.11 (m, 1H), 0.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 197.9, 164.4, 161.6 (d, *J* = 248.0 Hz), 144.3, 136.6 (d, *J* = 3.4 Hz), 128.9 (d, *J* = 9.9 Hz), 126.9 (d, *J* = 11.9 Hz), 126.3 (d, *J* = 2.7 Hz), 125.5, 122.1 (d, *J* = 2.1 Hz), 114.6, (d, *J* = 24.4 Hz), 84.7, 69.5, 66.5 (d, *J* = 4.4 Hz), 54.8, 50.6, 49.1, 47.8, 42.3, 36.1, 35.7, 31.7, 31.7, 30.9, 21.7, 20.8, 13.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ –113.71 (dd, *J*

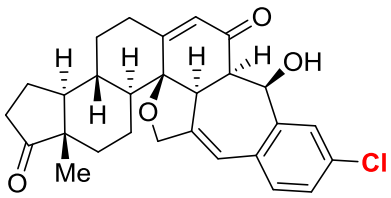
= 10.0, 5.1 Hz); HRMS (ESI) calcd for $C_{28}H_{30}FO_4$ $[M+H]^+$: 449.2123, found: 449.2117.

(3a*S*,3b*S*,7a*R*,7a^1*S*,8*R*,15a*R*,15b*S*,17a*S*)-8-Hydroxy-10,17a-dimethyl-2,3,3a,3b,4,5,7a,7a^1,8,14,15b,16,17,17a-tetradecahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]cyclopenta[5,6]naphtho[2,1-*h*]benzofuran-1,7-dione (8c)



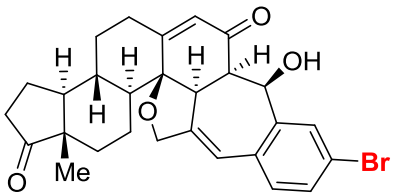
Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 24:1) to give the product **8c** in 81% yield (72 mg); colorless solid, mp 213–215 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.15 (s, 1H), 5.66 (s, 1H), 4.86 (d, *J* = 10.4 Hz, 1H), 4.57 (d, *J* = 13.1 Hz, 1H), 4.19 (d, *J* = 13.1 Hz, 1H), 3.60 (d, *J* = 12.0 Hz, 1H), 3.58 (d, *J* = 1.5 Hz, 1H), 3.33–3.28 (m, 1H), 2.72 (td, *J* = 12.5, 4.7 Hz, 1H), 2.48 (dd, *J* = 19.4, 8.8 Hz, 1H), 2.35 (s, 3H), 2.23 (dd, *J* = 9.2, 2.7 Hz, 1H), 2.16–2.04 (m, 3H), 1.99–1.94 (m, 1H), 1.92 (dd, *J* = 11.6, 4.8 Hz, 1H), 1.89–1.77 (m, 2H), 1.59 (dq, *J* = 12.4, 9.2 Hz, 1H), 1.49 (td, *J* = 11.1, 4.4 Hz, 1H), 1.34 (ddd, *J* = 17.6, 12.7, 5.4 Hz, 2H), 1.11 (qd, *J* = 12.9, 4.1 Hz, 1H), 0.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 197.9, 165.8, 139.5, 138.7, 137.3, 132.3, 128.4, 128.0, 127.5, 123.6, 122.7, 85.6, 72.7, 70.2, 50.7, 49.1, 48.5, 47.9, 44.5, 35.9, 35.7, 32.4, 31.4, 30.9, 21.8, 21.3, 21.2, 13.8; HRMS (ESI) calcd for $C_{29}H_{33}O_4$ $[M+H]^+$: 445.2373, found: 445.2378.

(3a*S*,3b*S*,7a*R*,7a^1*S*,8*R*,15a*R*,15b*S*,17a*S*)-10-Chloro-8-hydroxy-17a-methyl-2,3,3a,3b,4,5,7a,7a^1,8,14,15b,16,17,17a-tetradecahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]cyclopenta[5,6]naphtho[2,1-*h*]benzofuran-1,7-dione (8d)



Column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 2:1) to give the product **8d** in 88% yield (82 mg); colorless solid, mp 241–243 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.12 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.13 (d, *J* = 2.1 Hz, 1H), 5.66 (d, *J* = 1.0 Hz, 1H), 4.82 (dd, *J* = 11.9, 2.5 Hz, 1H), 4.57 (d, *J* = 13.4 Hz, 1H), 4.19 (dt, *J* = 13.6, 1.9 Hz, 1H), 3.62 (d, *J* = 11.9 Hz, 1H), 3.58 (d, *J* = 2.1 Hz, 1H), 3.32 (dd, *J* = 4.6, 3.1 Hz, 1H), 2.76–2.68 (m, 1H), 2.48 (dd, *J* = 19.5, 8.6 Hz, 1H), 2.26–2.22 (m, 1H), 2.15–2.05 (m, 3H), 1.98–1.90 (m, 2H), 1.89–1.83 (m, 1H), 1.82–1.76 (m, 1H), 1.59 (tt, *J* = 12.4, 9.2 Hz, 1H), 1.50 (td, *J* = 11.5, 4.4 Hz, 1H), 1.38–1.30 (m, 2H), 1.15–1.07 (m, 1H), 0.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.1, 197.5, 166.0, 141.7, 140.8, 133.5, 133.4, 128.8, 128.0, 127.3, 122.7, 122.6, 85.7, 72.3, 70.2, 50.7, 48.8, 48.5, 47.8, 44.6, 35.9, 35.7, 32.3, 31.5, 30.9, 21.8, 21.2, 13.8; HRMS (ESI) calcd for $C_{28}H_{30}ClO_4$ $[M+H]^+$: 465.1827, found: 465.1830.

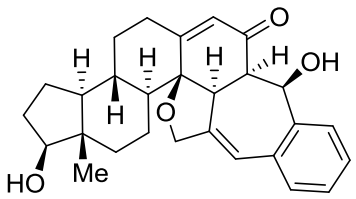
(3a*S*,3b*S*,7a*R*,7a^{1}*S*,8*R*,15a*R*,15b*S*,17a*S*)-10-Bromo-8-hydroxy-17a-methyl-2,3,3a,3b,4,5,7a,7a^{1},8,14,15b,16,17,17a-tetradecahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]cyclopenta[5,6]naphtho[2,1-*h*]benzofuran-1,7-dione (8e)



Column chromatography (eluent: petroleum ether/EtOAc = 15:1 to 2:1) to give the product **8e** in 96% yield (98 mg); colorless solid, mp 250–252 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.27 (d, *J* = 1.3 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.11 (s, 1H), 5.65 (s, 1H), 4.81 (d, *J* = 11.4 Hz, 1H), 4.55 (d, *J* = 13.5 Hz, 1H), 4.18 (d, *J* = 13.4 Hz, 1H), 3.63 (d, *J* = 11.9 Hz, 1H), 3.55 (d, *J* = 1.4 Hz, 1H), 3.35–3.27 (m, 1H), 2.71 (td, *J* = 12.5, 4.5 Hz, 1H), 2.47 (dd, *J* = 19.4, 8.8 Hz, 1H), 2.23 (d, *J* = 12.0 Hz, 1H), 2.14–2.03 (m, 3H), 1.97–1.82 (m, 3H), 1.80–1.74 (m, 1H), 1.62–1.54 (m, 1H), 1.49 (td, *J* = 11.4, 4.2 Hz, 1H), 1.33 (qd, *J* = 12.9, 5.4 Hz, 2H), 1.10 (qd, *J* = 12.8, 3.8 Hz, 1H), 0.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.0, 197.5, 166.0, 141.9, 141.1, 133.5, 130.8, 130.3, 129.2, 122.7, 122.5, 121.8, 85.6, 72.2, 70.2, 50.6, 48.7,

48.4, 47.8, 44.6, 35.8, 35.7, 32.3, 31.4, 30.9, 21.8, 21.2, 13.8; HRMS (ESI) calcd for $C_{28}H_{30}BrO_4$ $[M+H]^+$: 509.1322, found: 509.1336.

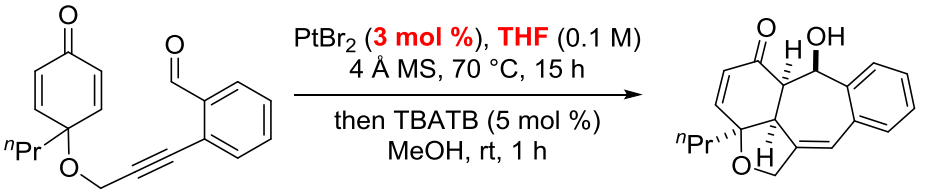
(1*S*,3a*S*,3b*S*,7a*R*,7a^1*S*,8*R*,15a*R*,15b*S*,17a*S*)-1,8-Dihydroxy-17a-methyl-2,3,3a,3b,4,5,7a,7a^1,8,14,15b,16,17,17a-tetradecahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]cyclopenta[5,6]naphtho[2,1-*h*]benzofuran-7(1H)-one (8f)



Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 2:1) to give the product **8f** in 86% yield (74 mg); colorless solid, mp 154–156 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 6.7 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.18 (s, 1H), 5.64 (s, 1H), 4.88 (d, *J* = 10.9 Hz, 1H), 4.58 (d, *J* = 13.3 Hz, 1H), 4.20 (d, *J* = 13.3 Hz, 1H), 3.67 (t, *J* = 8.8 Hz, 2H), 3.59 (s, 1H), 3.36–3.29 (m, 1H), 2.68 (td, *J* = 12.6, 4.3 Hz, 1H), 2.18 (d, *J* = 11.7 Hz, 1H), 2.14–2.04 (m, 1H), 1.94 (dd, *J* = 20.9, 11.1 Hz, 3H), 1.88–1.78 (m, 1H), 1.78–1.57 (m, 3H), 1.47 (td, *J* = 16.0, 6.0 Hz, 2H), 1.34 (ddd, *J* = 18.4, 12.0, 6.0 Hz, 1H), 1.16 (dd, *J* = 14.6, 10.7 Hz, 1H), 1.07–0.94 (m, 2H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 166.6, 140.5, 139.8, 132.2, 130.3, 127.6, 127.4, 127.3, 123.6, 122.4, 85.8, 81.5, 72.7, 70.2, 50.4, 49.0, 48.6, 44.5, 43.2, 36.4, 36.1, 33.2, 31. 7, 30.5, 23.3, 21.6, 11.1; HRMS (ESI) calcd for $C_{28}H_{33}O_4$ $[M+H]^+$: 433.2373, found: 433.2372.

5. Gram-Scale Synthesis of 4c and Selective Transformations

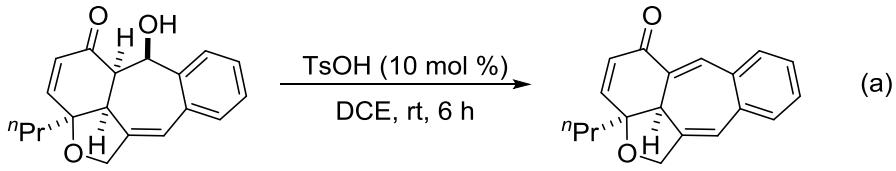
5.1. Scale-Up Experiment



1c (1.03 g, 3.5 mmol) **4c** (1.01 g, 97% yield)

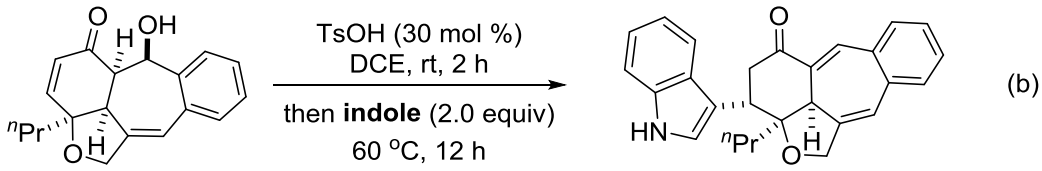
To an oven-dried round-bottom flask (100 mL) equipped with a magnetic stir bar were added *O*-tethered cyclohexadienones **1c** (1.03 mg, 3.5 mmol), 4Å MS (1.75 g) and $PtBr_2$ (36.2 mg, 0.105 mmol). The reaction vessel was capped and charged with an argon atmosphere through three cycles of the vacuum-argon-backfill method over 10 min. Anhydrous THF (35 mL) was then added and the resulting reaction mixture was stirred at 70 ^{o}C for 15 h. Upon completion, the reaction mixture was cooled to room temperature, tetrabutylammonium tribromide (TBATB) (84.4 mg, 0.175 mmol) and MeOH (35 mL) were added. The resulting reaction mixture was stirred at room temperature for 1 h (monitored by TLC), filtered through a pad of Celite and rinsed with EtOAc. The filtrate was washed with saturated $NaHCO_3$ (50 mL) and extracted with EtOAc (50 mL x 3). The combined organic phases are washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the desired product **4c** (1.01 g, 97 % yield).

5.2. Selective transformations



4c **9** (99%)

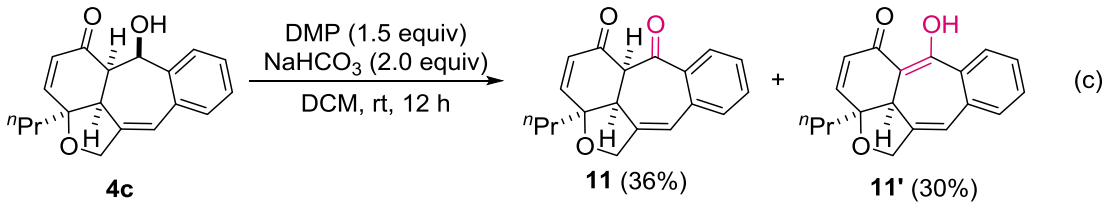
To a solution of **4c** (0.2 mmol, 59.3 mg) in 1,2-dichloroethane (2 mL) at room temperature was added TsOH (10 mol %). The resulting reaction mixture was stirred at room temperature for 6 h until full consumption of the starting material, as indicated by TLC analysis. Upon completion, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1 to 6:1) to afford the desired product **9** in 99% yield (55 mg) as a pale-yellow solid, mp 90–92 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 5.7 Hz, 2H), 7.37–7.32 (m, 1H), 6.73 (d, *J* = 10.4 Hz, 1H), 6.58 (d, *J* = 1.1 Hz, 1H), 6.36 (d, *J* = 10.4 Hz, 1H), 4.67–4.58 (m, 1H), 4.38 (d, *J* = 13.5 Hz, 1H), 2.79 (s, 1H), 1.79–1.71 (m, 1H), 1.69–1.61 (m, 1H), 1.35–1.28 (m, 1H), 1.23–1.17 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.5, 149.7, 146.1, 136.5, 135.2, 133.9, 132.8, 131.4, 130.2, 129.4, 128.3, 126.3, 118.7, 81.9, 69.9, 45.4, 42.9, 17.2, 14.2; HRMS (ESI) calcd for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1380, found: 279.1376.



4c **10** (71%)

To a solution of **4c** (0.2 mmol, 59.3 mg) in 1,2-dichloroethane (2 mL) at room temperature was added TsOH (30 mol %). The resulting reaction mixture was stirred at room temperature for 2 h until full consumption of the starting material. Upon completion, indole (0.4 mmol, 2.0 equiv) was added to the reaction mixture and stirred at 60 °C for 12 h (monitored by TLC analysis). Upon completion, the reaction

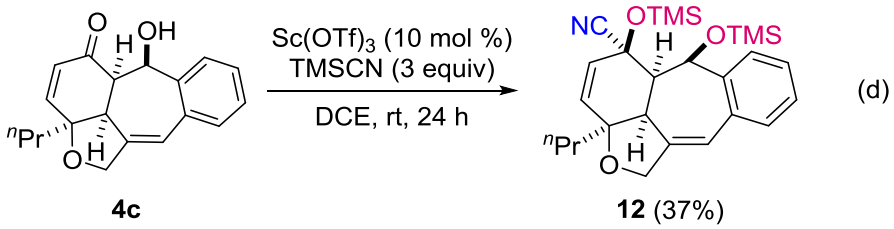
mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 25:1 to 10:1) to give the product **10** in 71% yield (56 mg) as a pale-yellow solid, mp 241–243 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.84–7.82 (m, 1H), 7.66–7.63 (m, 1H), 7.63–7.61 (m, 1H), 7.46–7.33 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.64 (d, *J* = 1.5 Hz, 1H), 4.84 (d, *J* = 14.1 Hz, 1H), 4.75 (d, *J* = 14.3 Hz, 1H), 4.12 (t, *J* = 4.3 Hz, 1H), 3.34 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.71 (s, 1H), 2.68 (dd, *J* = 16.5, 3.5 Hz, 1H), 1.57–1.46 (m, 4H), 0.70 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 148.0, 137.8, 135.7, 134.3, 133.8, 132.8, 132.5, 129.7, 128.3, 127.4, 126.1, 122.3, 120.9, 119.6, 118.6, 118.3, 115.2, 111.1, 86.4, 68.4, 47.7, 41.8, 36.9, 35.2, 16.1, 14.3; HRMS (ESI) calcd for $C_{27}H_{26}NO_2$ $[M+H]^+$: 396.1958, found: 396.1956.



To a solution of **4c** (0.2 mmol, 59.3 mg) in dichloromethane (4 mL) at room temperature was added $NaHCO_3$ (0.4 mmol, 2.0 equiv) and Dess-Martin periodinane (DMP, 0.3 mmol, 1.5 equiv). The resulting reaction mixture was stirred at room temperature for 12 h until full consumption of the starting material, as indicated by TLC analysis. Upon completion, the reaction mixture was quenched by adding saturated sodium thiosulfate (2 mL) and saturated aqueous $NaHCO_3$ (2 mL), extracted with EtOAc (10 mL × 2). The combined organic phases are washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 30:1 to 15:1) to afford the diketone product **11** (21 mg) and its enol isomer **11′** (18 mg) in 36 and 30% yield, respectively.

Product **11:** white solid, mp 125–127 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 10.5 Hz, 1H), 6.31 (s, 1H), 6.04 (d, *J* = 10.5 Hz, 1H), 5.32 (s, 1H), 4.64 (d, *J* = 14.2 Hz, 1H), 4.45 (d, *J* = 14.1 Hz, 1H), 3.32 (s, 1H), 2.19–2.11 (m, 1H), 2.10–2.03 (m, 1H), 1.63–1.53 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.8, 192.8, 151.1, 142.2, 135.3, 134.4, 131.9, 131.7, 130.9, 127.9, 127.5, 122.8, 85.8, 78.7, 70.7, 50.6, 39.7, 16.8, 14.5; HRMS (ESI) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329, found: 295.1328.

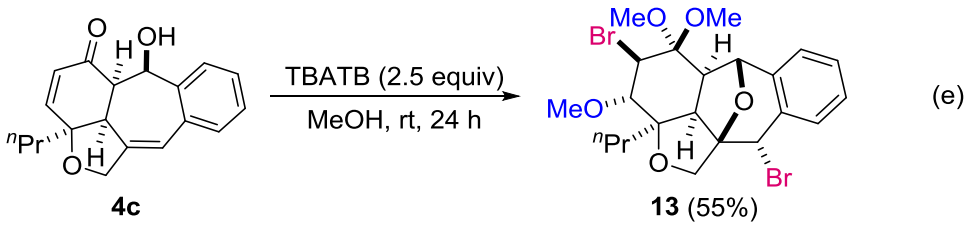
Product **11′**: white solid, mp 111–113 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 15.91 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 6.45 (d, *J* = 9.9 Hz, 2H), 6.29 (d, *J* = 10.2 Hz, 1H), 4.59 (d, *J* = 13.5 Hz, 1H), 4.30 (d, *J* = 13.4 Hz, 1H), 2.90 (s, 1H), 1.71 (td, *J* = 12.9, 4.8 Hz, 1H), 1.64–1.58 (m, 1H), 1.31–1.22 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.6, 176.5, 150.7, 146.0, 137.0, 133.7, 130.8, 129.8, 129.6, 129.1, 126.7, 117.2, 106.6, 82.7, 69.1, 43.5, 42.4, 16.9, 14.2; HRMS (ESI) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329, found: 295.1325.



4c **12** (37%)

To a solution of **4c** (0.2 mmol, 59.3 mg) and $Sc(OTf)_3$ (10 mol %) in 1,2-dichloroethane (2 mL) was added TMSCN (0.6 mmol, 3 equiv). The resulting reaction mixture was stirred at room temperature for 24 h. Upon completion, the solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1 to 8:1) to afford the desired product **12** in 37% yield (34.6 mg) as a colorless solid, mp 114–116 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.19 (td, *J* = 7.2, 0.9 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.10 (d, *J* = 2.6 Hz, 1H), 5.78 (dd, *J*

= 10.1, 0.9 Hz, 1H), 5.74 (d, *J* = 10.1 Hz, 1H), 5.18 (d, *J* = 3.7 Hz, 1H), 4.54 (d, *J* = 13.6 Hz, 1H), 4.28 (dt, *J* = 13.6, 2.4 Hz, 1H), 3.06 (d, *J* = 1.2 Hz, 1H), 2.75 (t, *J* = 4.2 Hz, 1H), 1.75 (ddd, *J* = 13.8, 10.7, 6.1 Hz, 1H), 1.63 (ddd, *J* = 14.0, 11.2, 5.4 Hz, 1H), 1.56–1.47 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.30 (s, 9H), -0.23 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.7, 139.6, 133.6, 132.7, 131.8, 128.2, 126.7, 126.7, 126.2, 123.4, 122.0, 83.9, 74.3, 70.3, 65.3, 45.9, 43.8, 40.2, 17.1, 14.6, 0.5, -0.3; HRMS (ESI) calcd for $C_{26}H_{38}NO_3Si_2$ $[M+H]^+$: 468.2385; found: 468.2378.

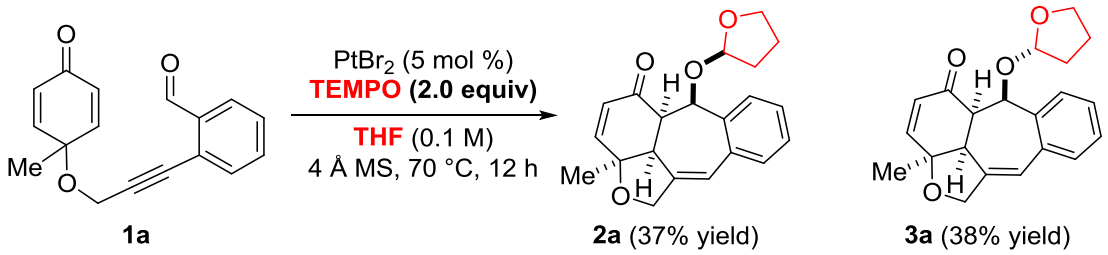


4c **13** (55%) (e)

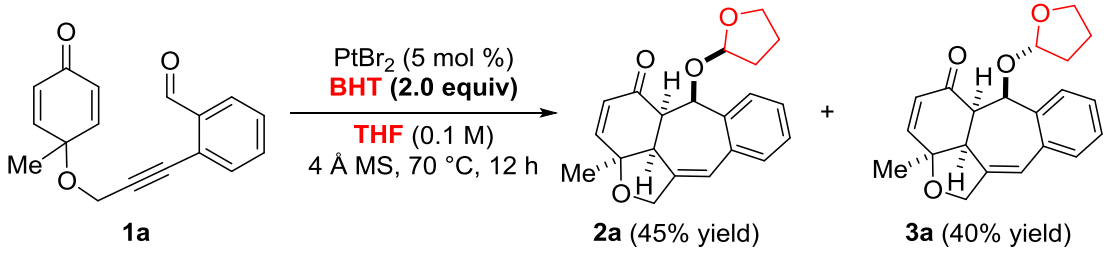
To a solution of **4c** (0.2 mmol, 59.3 mg) in MeOH (2 mL) was added tetrabutylammonium tribromide (TBATB) (0.5 mmol, 2.5 equiv). The resulting reaction mixture was stirred at room temperature for 24 h until full consumption of the starting material, as indicated by TLC analysis. Upon completion, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1 to 7:1) to afford the product **13** in 55% yield (59 mg) as a colorless solid, mp 189–191 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 5.62 (s, 1H), 5.54 (s, 1H), 4.47 (d, *J* = 6.8 Hz, 1H), 4.21 (d, *J* = 10.4 Hz, 1H), 4.16 (d, *J* = 10.4 Hz, 1H), 3.98 (d, *J* = 6.1 Hz, 1H), 3.69 (s, 3H), 3.67 (d, *J* = 9.6 Hz, 1H), 3.29 (s, 3H), 3.14 (s, 3H), 2.89 (d, *J* = 9.2 Hz, 1H), 1.90–1.81 (m, 1H), 1.75–1.67 (m, 1H), 1.56–1.48 (m, 1H), 1.40 (td, *J* = 11.9, 6.1 Hz, 1H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 131.8, 131.3, 128.2, 128.1, 123.0, 98.8, 97.8, 89.6, 87.7, 80.1, 71.6, 61.5, 55.0, 53.5, 50.9, 49.8, 48.6, 48.1, 33.2, 16.5, 14.7; HRMS (ESI) calcd for $C_{22}H_{28}Br_2NaO_5$ $[M+Na]^+$: 553.0196; found: 553.0195.

6. Control Experiments with 1a

6.1. Probing a H• Atom or Hydride Shift Pathway

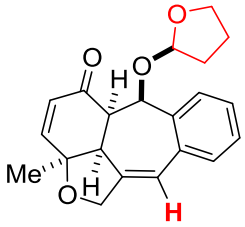


A 10 mL round-bottom flask was charged with **1a** (0.2 mmol, 53.3 mg), 4 Å MS (100 mg), $PtBr_2$ (0.01 mmol, 5 mol %), TEMPO (0.4 mmol, 2.0 equiv) and anhydrous THF (0.1 M, 2 mL) under an argon atmosphere, and the reaction mixture was stirred at 70 ^{o}C for 12 h. Upon completion, the reaction mixture cooled to room temperature and filtered through a pad of Celite and rinsed with EtOAc. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1 to 6:1) to afford the desired products **2a** (25 mg, 37% yield) and **3a** (25.7 mg, 38% yield).



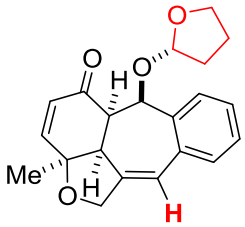
A 10 mL round-bottom flask was charged with **1a** (0.2 mmol, 53.3 mg), 4 Å MS (100 mg), $PtBr_2$ (0.01 mmol, 5 mol %), BHT (0.4 mmol, 2.0 equiv) and anhydrous THF (0.1 M, 2 mL) under an argon atmosphere, and the reaction mixture was stirred at 70 ^{o}C for 12 h. Upon completion, the reaction mixture cooled to room temperature and filtered through a pad of Celite, rinsed with EtOAc. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1 to 6:1) to afford the desired product **2a** (31 mg, 45% yield) and **3a** (27 mg, 40% yield).

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Methyl-6-(((*R**)-tetrahydrofuran-2-yl)oxy)-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (2a)**



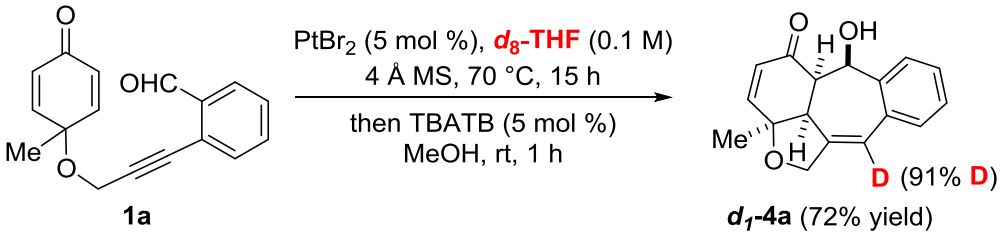
Colorless solid; mp 139–141 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 6.1 Hz, 1H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.46 (s, 1H), 6.24 (s, 1H), 5.71 (s, 1H), 5.27 (s, 1H), 5.02–4.85 (m, 1H), 4.66 (d, *J* = 13.0 Hz, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 3.99–3.87 (m, 2H), 3.45 (s, 1H), 2.35–1.92 (m, 3H), 1.87 (s, 1H), 1.69 (s, 1H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 150.3, 137.6, 127.3, 127.0, 78.4, 71.2, 67.1, 32.3, 23.6; HRMS (ESI) calcd for $C_{21}H_{23}O_4$ $[M+H]^+$: 339.1591, found: 339.1585.

(2a*S,2a^1*S**,5a*R**,6*R**)-2a-Methyl-6-(((*S**)-tetrahydrofuran-2-yl)oxy)-2a,2a^1,5a,6-tetrahydrobenzo[5,6]cyclohepta[1,2,3-*cd*]benzofuran-5(1*H*)-one (3a)**



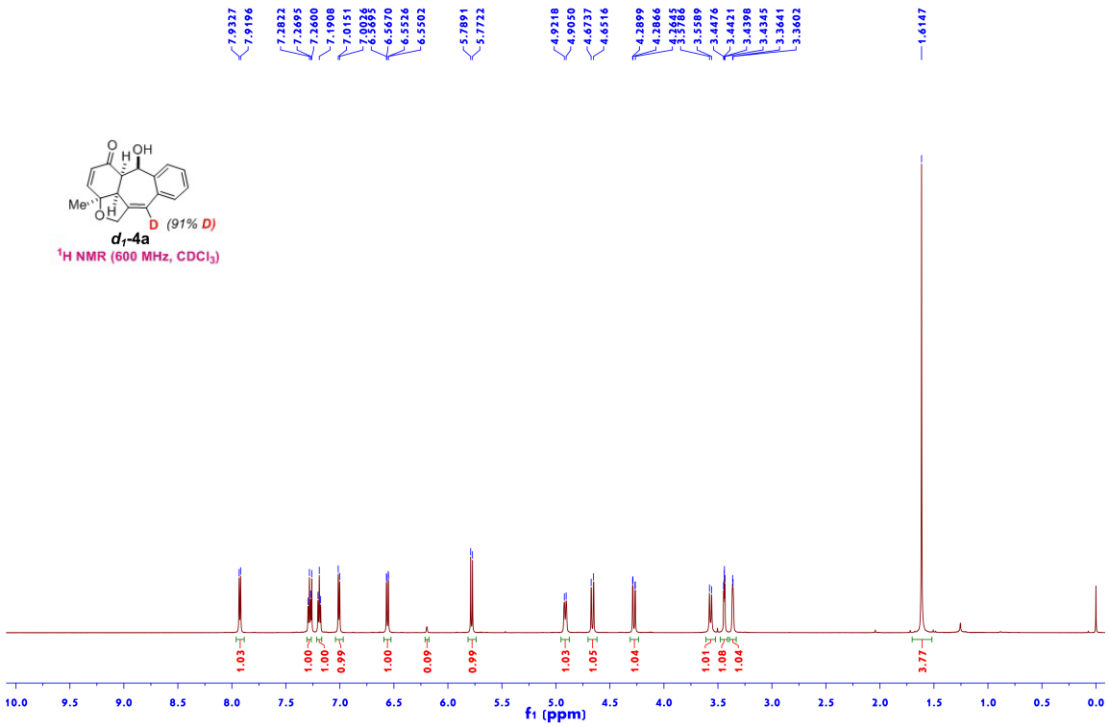
Colorless solid; mp 139–141 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.46 (d, *J* = 10.1 Hz, 1H), 6.24 (s, 1H), 5.74 (d, *J* = 9.3 Hz, 1H), 5.41 (s, 1H), 5.04 (s, 1H), 4.65 (d, *J* = 12.8 Hz, 1H), 4.27 (d, *J* = 12.9 Hz, 1H), 3.84 (s, 2H), 3.37 (s, 1H), 3.34 (s, 1H), 2.17 (s, 2H), 1.99 (s, 1H), 1.91 (s, 1H), 1.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.0, 150.3, 137.6, 131.7, 127.3, 127.0, 123.4, 105.8, 81.6, 78.4, 71.2, 67.1, 32.3, 23.5; HRMS (ESI) calcd for $C_{21}H_{23}O_4$ $[M+H]^+$: 339.1591; found: 339.1588.

6.2. Deuterium-Labeling Experiments

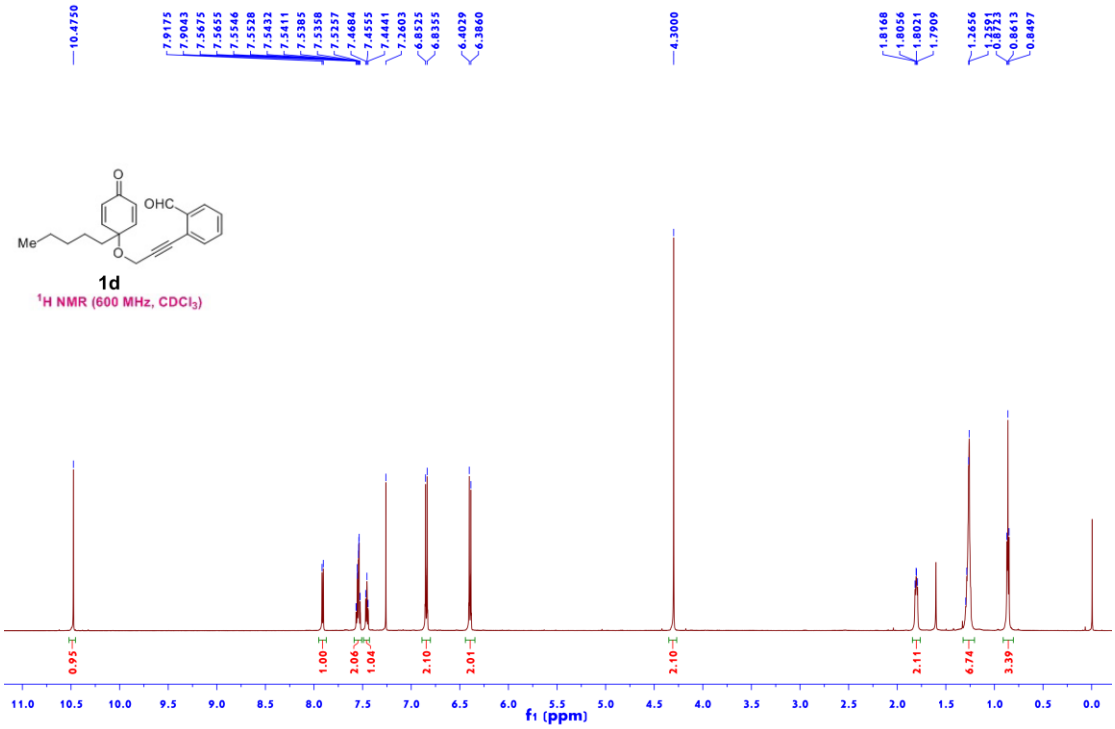


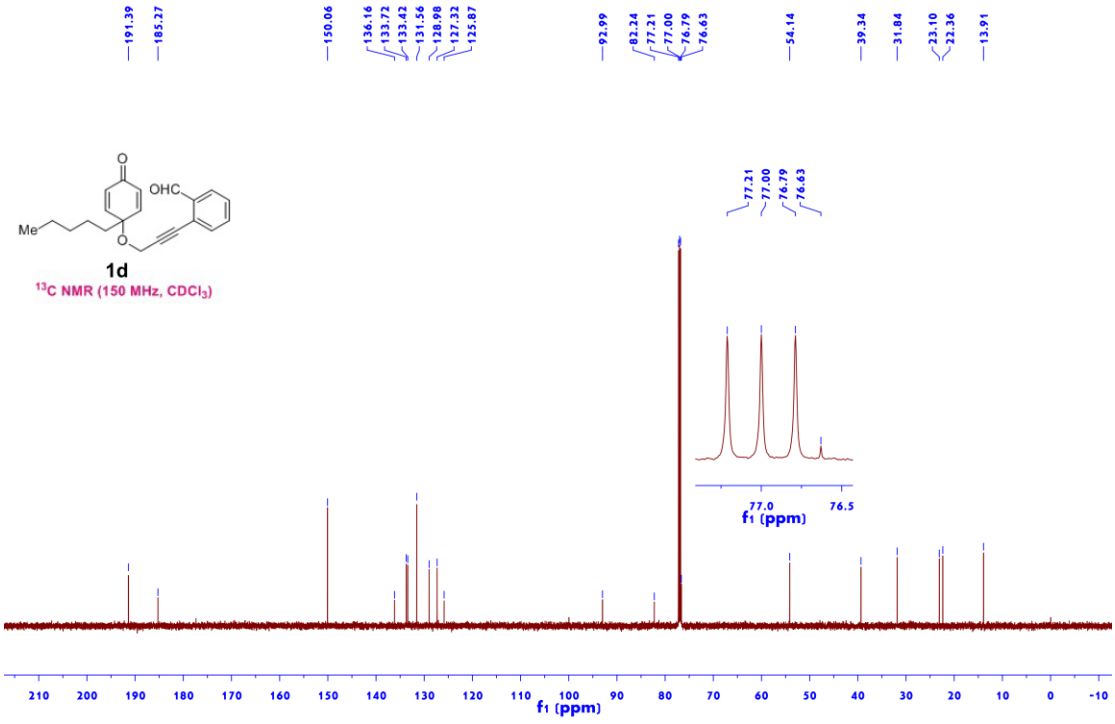
A 10 mL round-bottom flask was charged with **1a** (0.2 mmol, 53.3 mg, 1.0 equiv), 4 Å MS (100 mg), $PtBr_2$ (0.01 mmol, 3.5 mg, 5 mol %) and anhydrous d_8-THF (0.1 M, 2 mL) under an argon atmosphere, and the reaction mixture was stirred at 70 ^oC for 12 h. Upon completion, the reaction mixture was cooled to room temperature and tetrabutylammonium tribromide (TBATB) (0.01 mmol, 4.8 mg, 5 mol%) and MeOH (2 mL) were added. The resulting reaction mixture was stirred at room temperature for 1 h (monitored by TLC analysis), filtered through a pad of Celite and rinsed with EtOAc. The filtrate was washed with saturated $NaHCO_3$ (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phases are washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1 to 3:1) to afford the desired product ***d*$_1$-4a** (39 mg) in 72% yield.

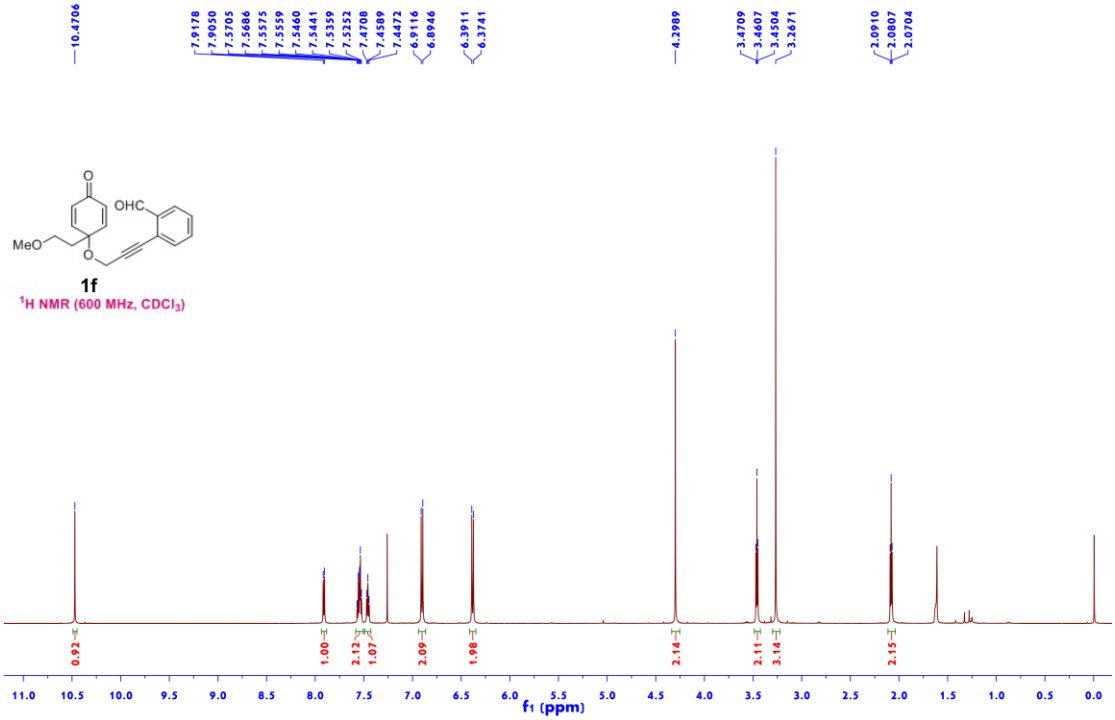
Colorless solid; mp 180–182 ℃; ^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.56 (dd, *J* = 10.1, 1.5 Hz, 1H), 6.20 (s, 1H), 5.78 (d, *J* = 10.1 Hz, 1H), 4.91 (d, *J* = 10.1 Hz, 1H), 4.66 (d, *J* = 13.3 Hz, 1H), 4.28 (dd, *J* = 13.3, 2.0 Hz, 1H), 3.57 (d, *J* = 11.8 Hz, 1H), 3.44 (dd, *J* = 4.6, 3.2 Hz, 1H), 3.36 (d, *J* = 2.3 Hz, 1H), 1.61 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.2, 152.0, 139.9, 139.6, 132.2, 130.2, 127.6, 127.6, 127.5, 127.4, 82.3, 72.8, 71.0, 50.5, 49.5, 22.9; HRMS (ESI) calcd for $C_{17}H_{15}DNaO_3$ $[M+Na]^+$: 292.1054; found: 292.1051.

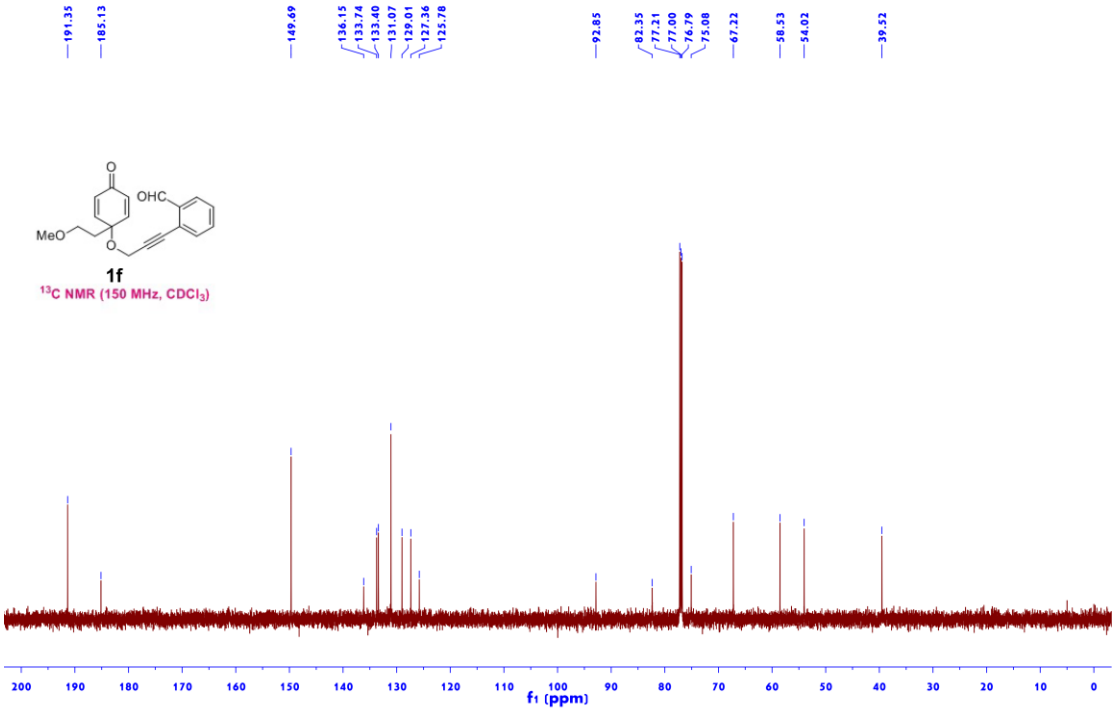

7.9327
7.9196
7.2822
7.2695
7.2600
7.1908
7.0151
7.0026
6.9885
6.5670
6.5526
6.5502
5.7891
5.7722
4.9218
4.9050
4.6737
4.6516
4.2899
4.2866
3.5589
3.4476
3.4421
3.4398
3.4345
3.3641
3.3602
1.6147
O
H
OH
Me
O
H
D (91% D)
d1-4a
1H NMR (600 MHz, CDCl3)
1.03
1.00
1.00
0.99
1.00
0.09
0.99
1.03
1.05
1.04
1.01
1.08
1.04
3.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

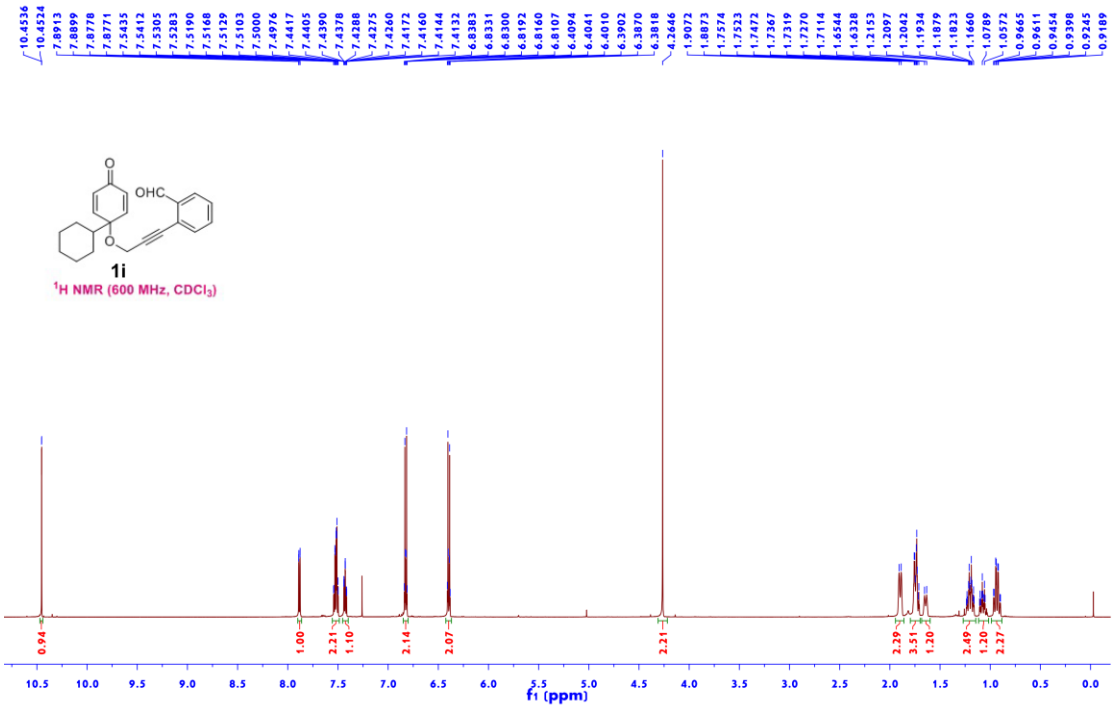
7. ^{1}H, ^{13}C and ^{19}F NMR Spectra for All New Compounds

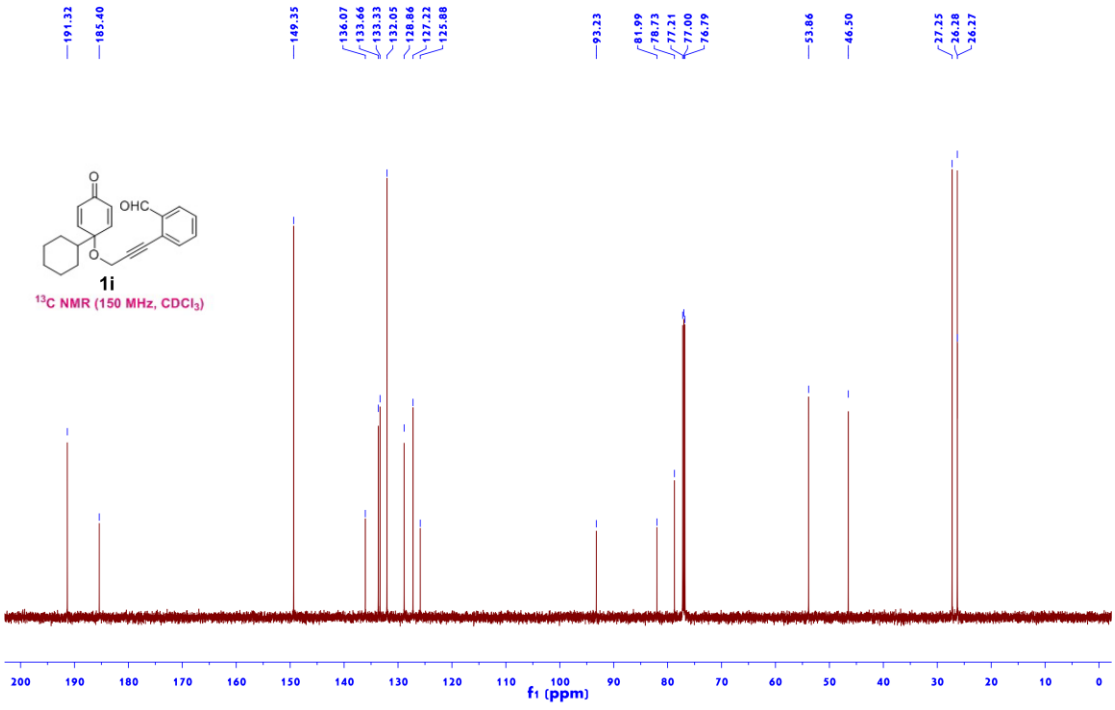


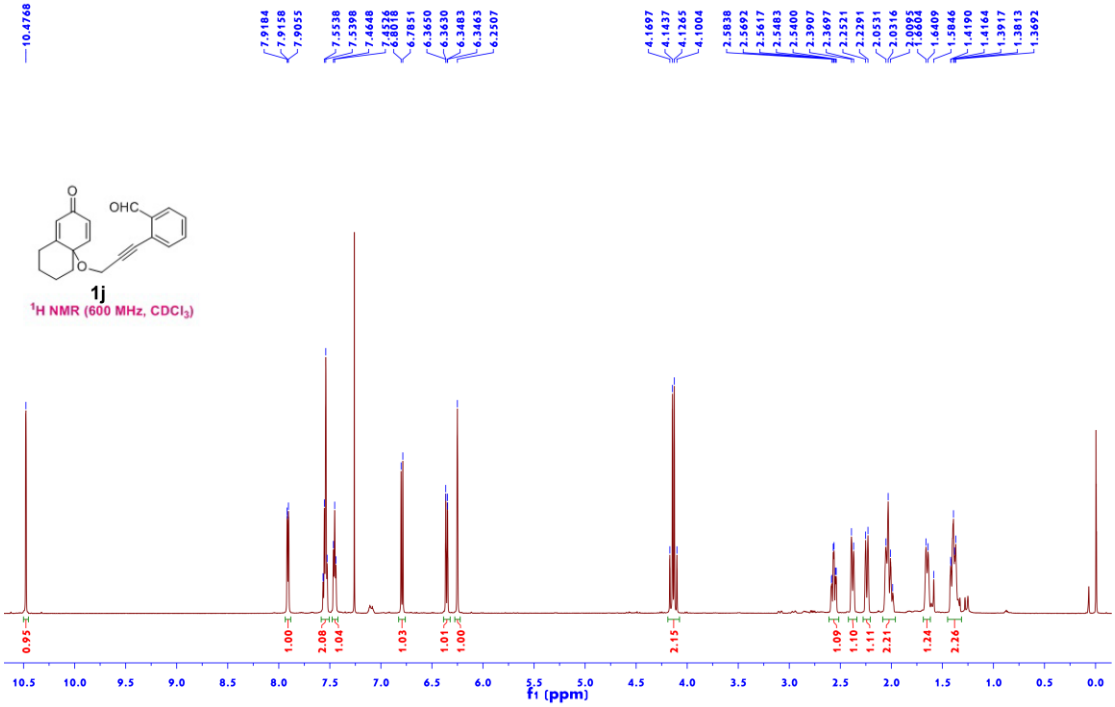


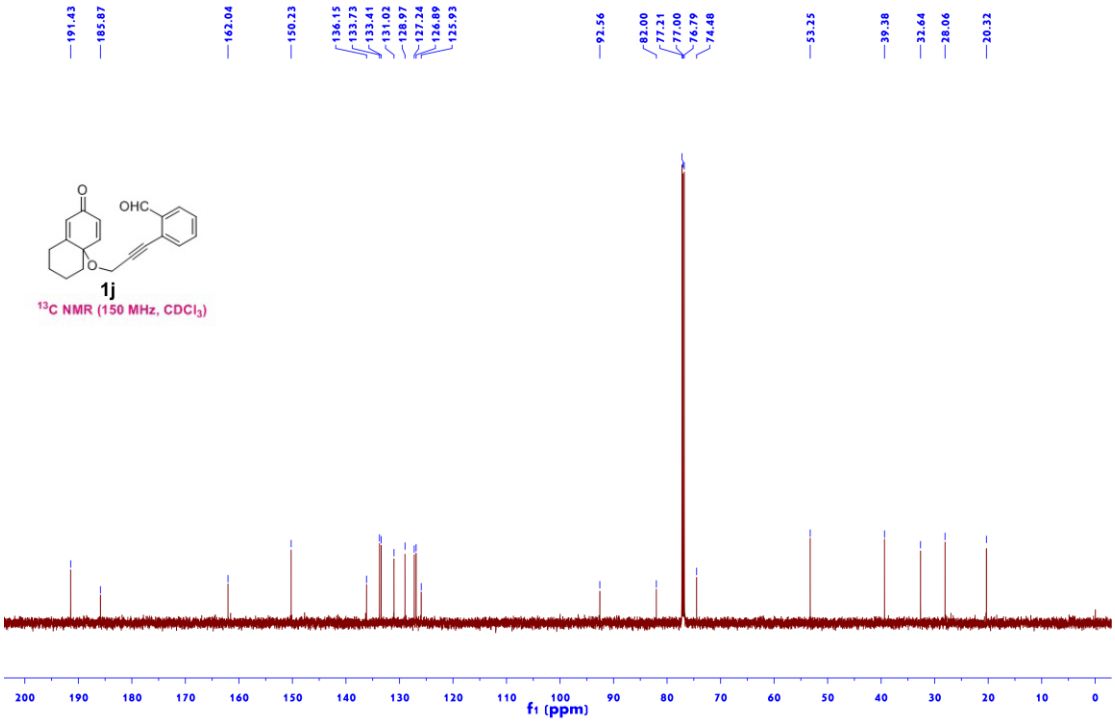

10.4706
7.9178
7.9050
7.5705
7.5686
7.5575
7.5559
7.5460
7.5441
7.5359
7.5252
7.4708
7.4589
7.4472
6.9116
6.8946
6.3911
6.3741
4.2989
3.4709
3.4607
3.4504
3.2671
2.0910
2.0807
2.0704
O
OHC
MeO
O
1f
1H NMR (600 MHz, CDCl3)
0.92
1.00
2.12
1.07
2.09
1.98
2.14
2.11
3.14
2.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

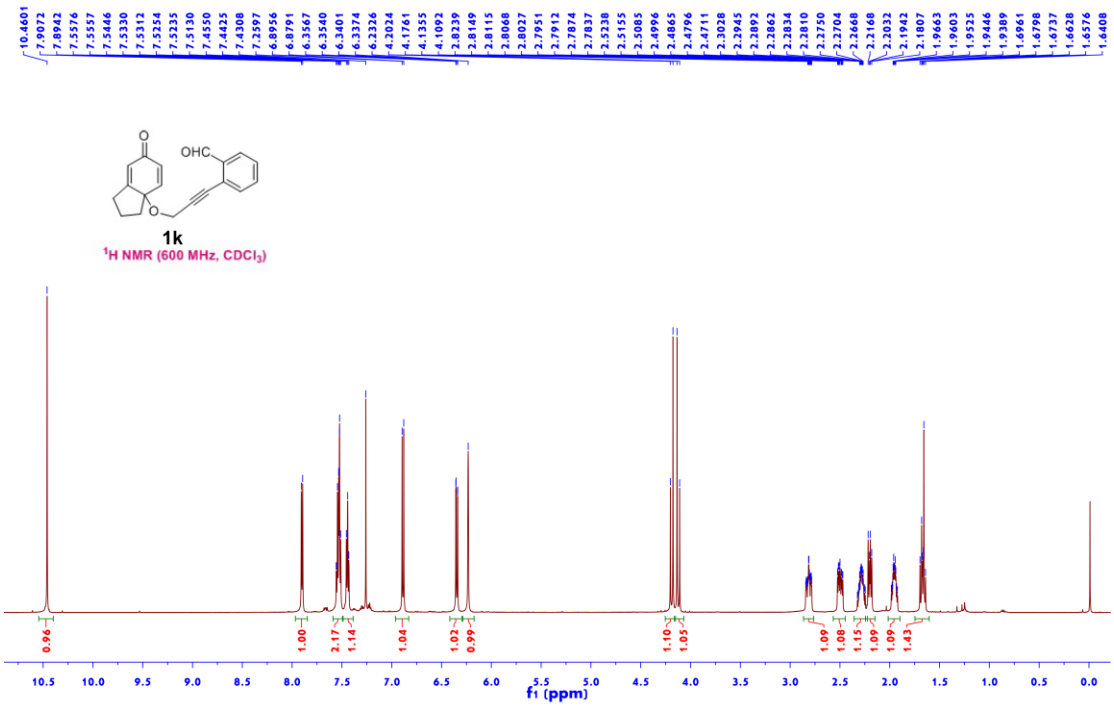

191.35
165.13
149.69
136.15
133.74
133.40
131.07
129.01
127.36
125.78
92.85
82.35
77.21
77.00
76.79
75.08
67.22
58.53
54.02
39.52
O
OHC
MeO
O
1f
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

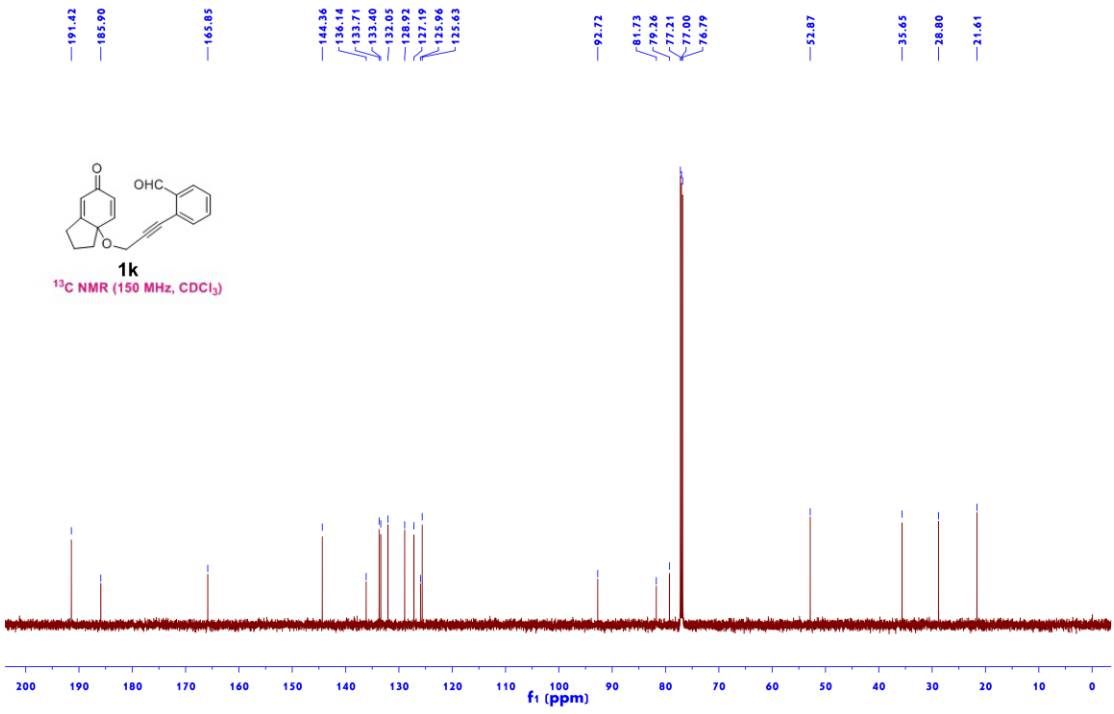

OHC
O
O
1i
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)

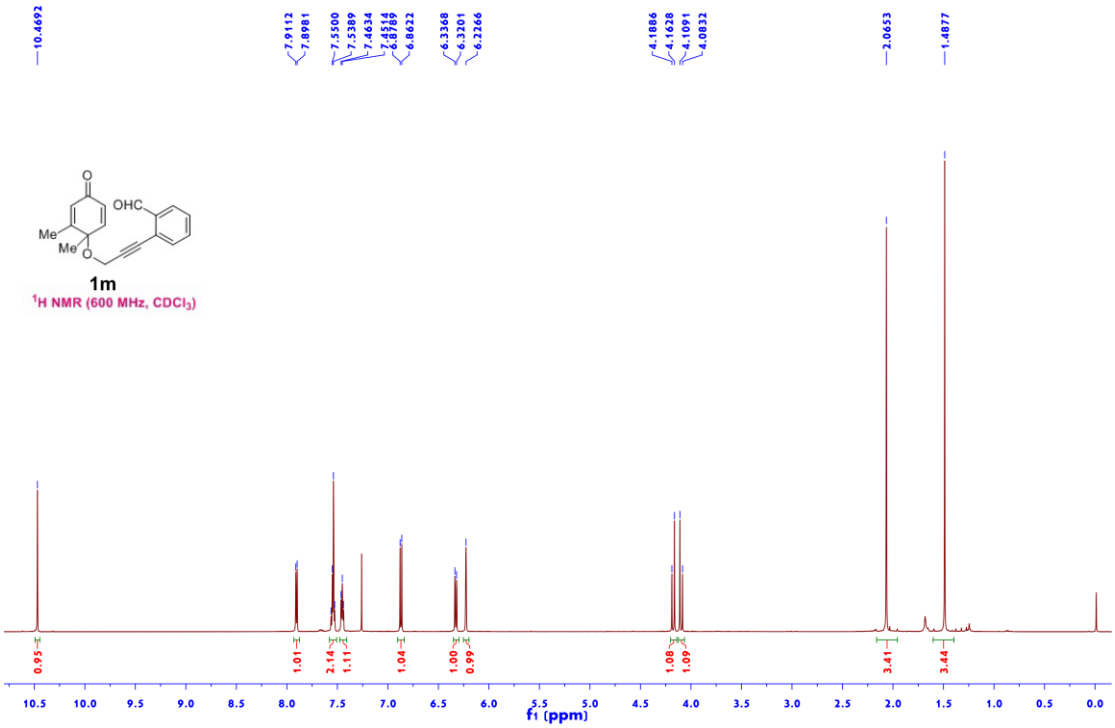

OHC
O
O
1i
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)

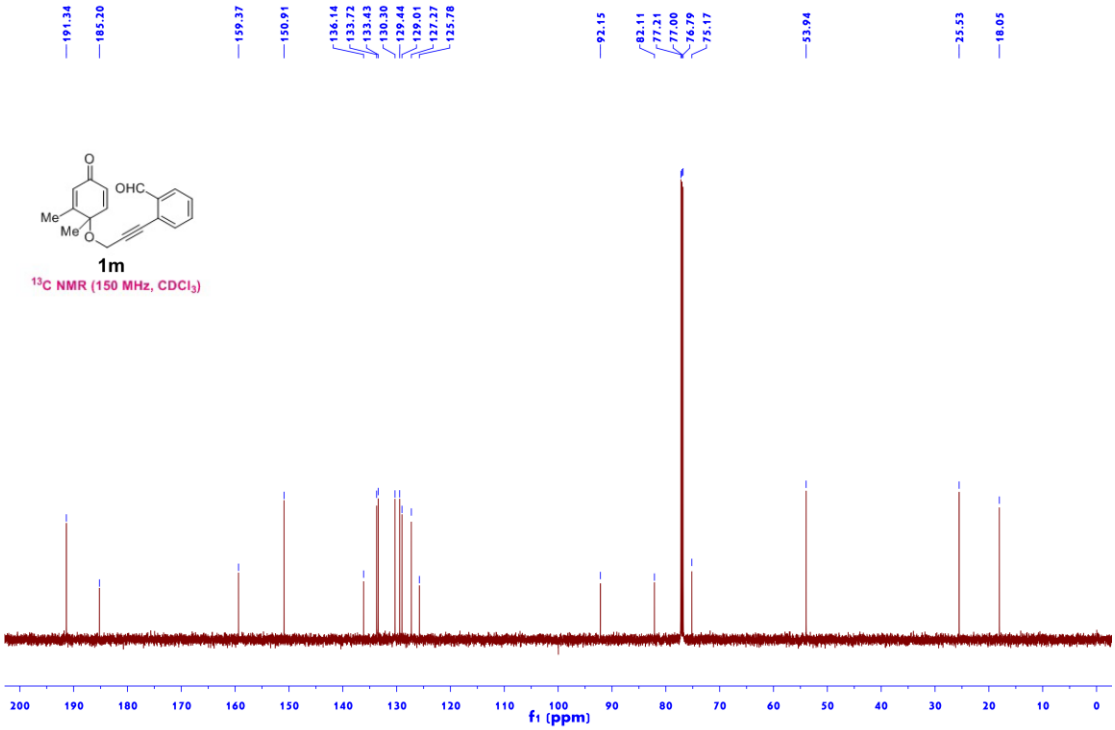

10.4768
7.9184
7.9158
7.9055
7.5538
7.5398
7.4648
6.8018
6.7851
6.3650
6.3630
6.3483
6.3463
6.2307
4.1697
4.1437
4.1265
4.1004
2.5838
2.5692
2.5617
2.5483
2.5400
2.3907
2.3697
2.2521
2.2291
2.0531
2.0316
1.6409
1.5846
1.4190
1.4164
1.3917
1.3813
1.3692
OHC
1j
1H NMR (600 MHz, CDCl3)
0.95
1.00
2.08
1.04
1.03
1.01
1.00
2.15
1.09
1.10
1.11
2.21
1.24
2.26
f1 (ppm)

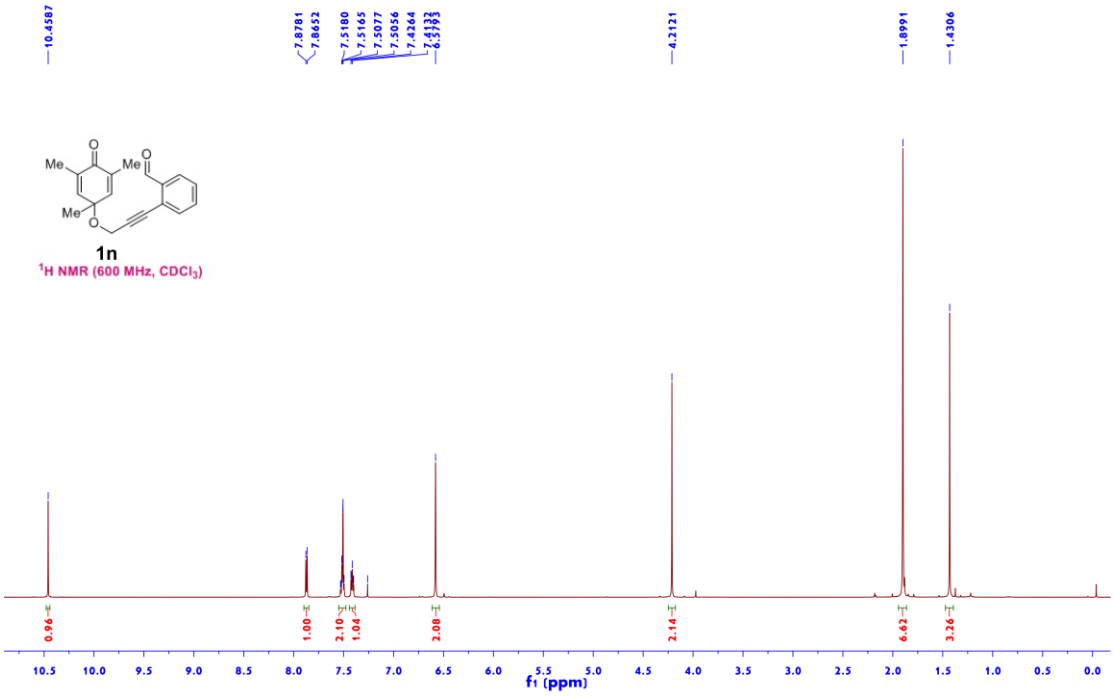

191.43
185.87
162.04
150.23
136.15
133.73
133.41
131.02
128.97
127.24
126.89
125.93
92.56
82.00
77.21
77.00
76.79
74.48
53.25
39.38
32.64
28.06
20.32
OHC
1j
13C NMR (150 MHz, CDCl3)
f1 (ppm)

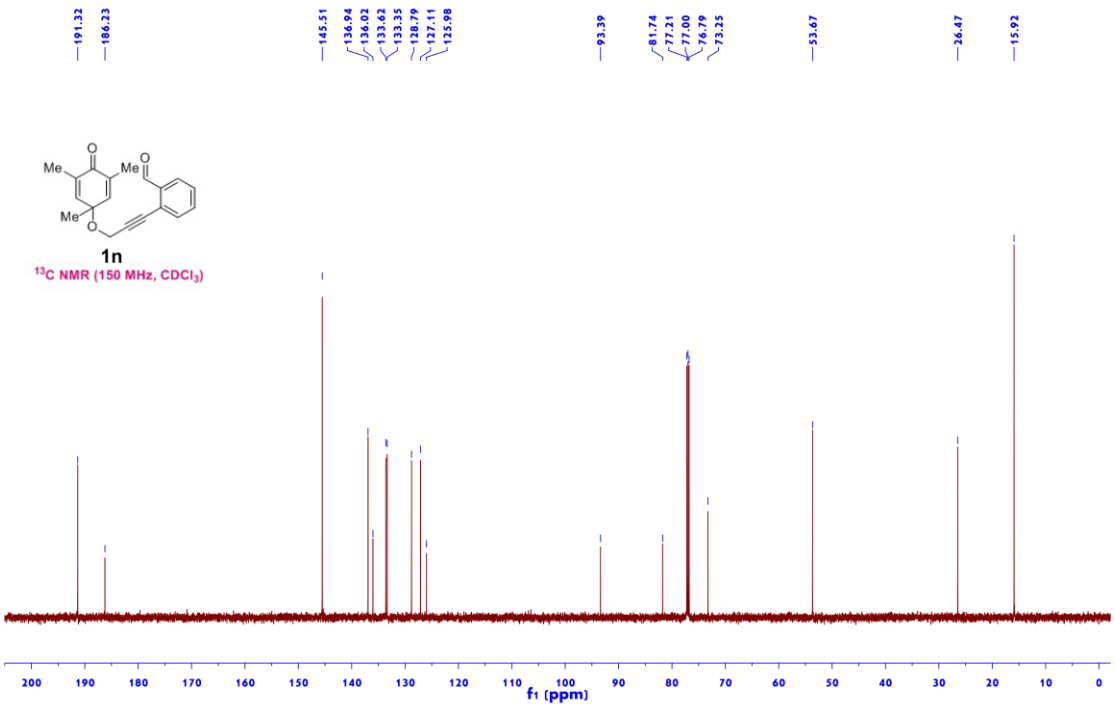

OHC
1k
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)

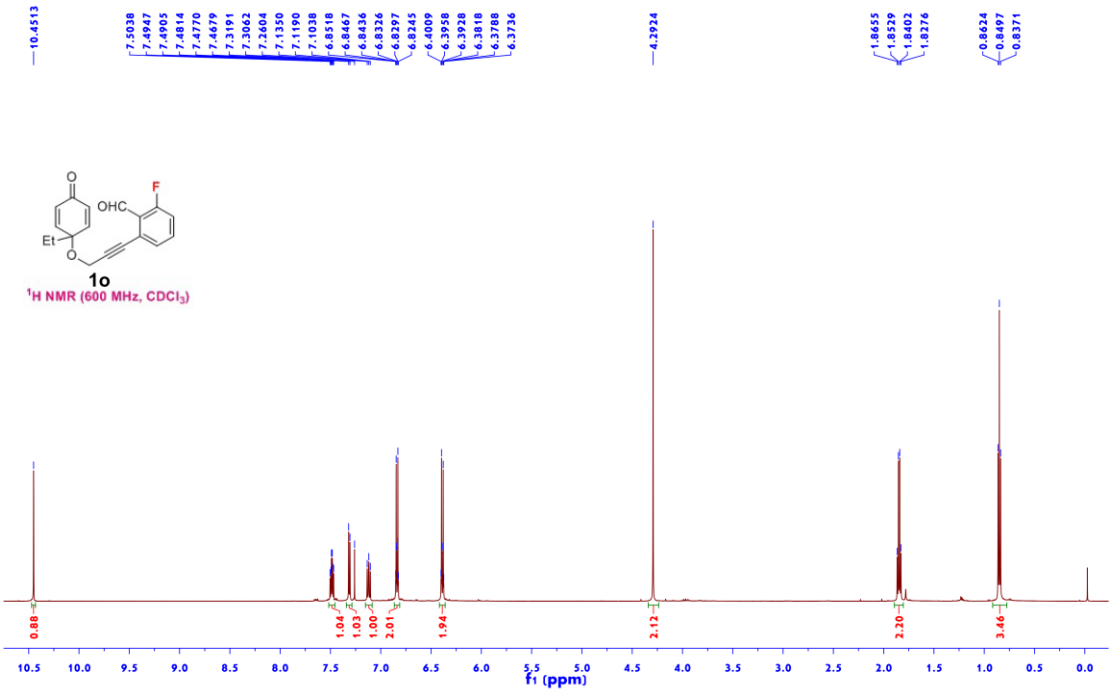

OHC
1k
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)

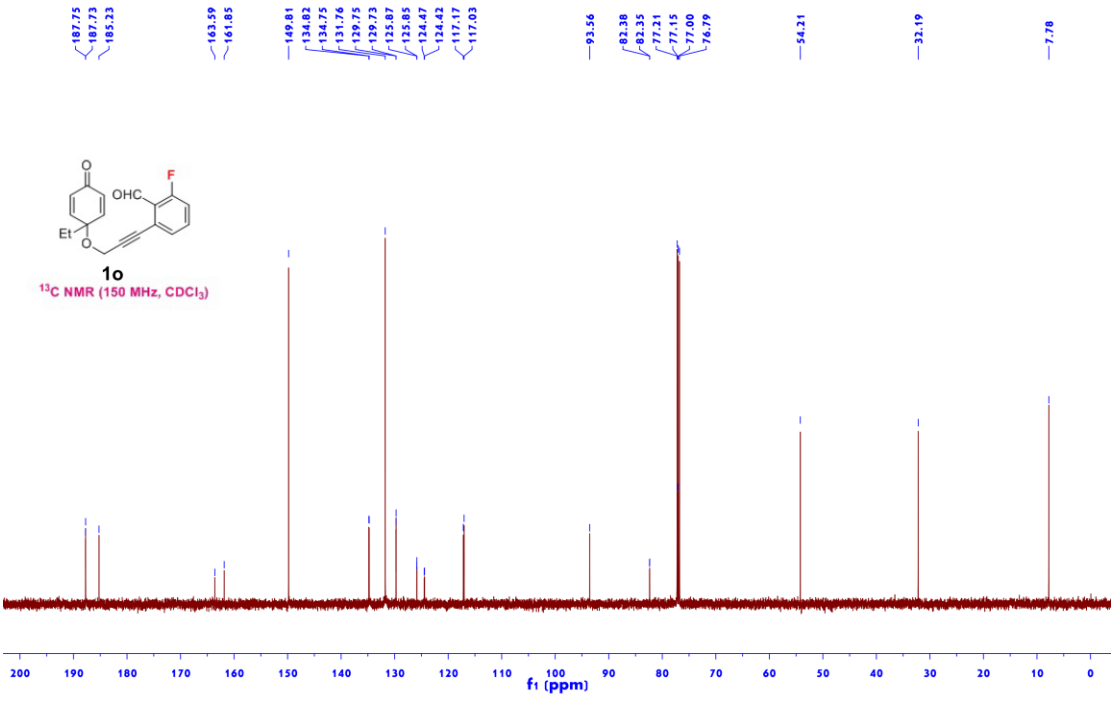

10.4692
7.9112
7.8981
7.5500
7.5389
7.4634
7.4514
6.8709
6.8622
6.3368
6.3201
6.2266
4.1686
4.1628
4.1091
4.0832
2.0653
1.4877
OHC
Me
Me
O
1m
1H NMR (600 MHz, CDCl3)
0.95
1.01
2.14
1.11
1.04
1.00
0.99
1.08
1.09
3.41
3.44
f1 (ppm)

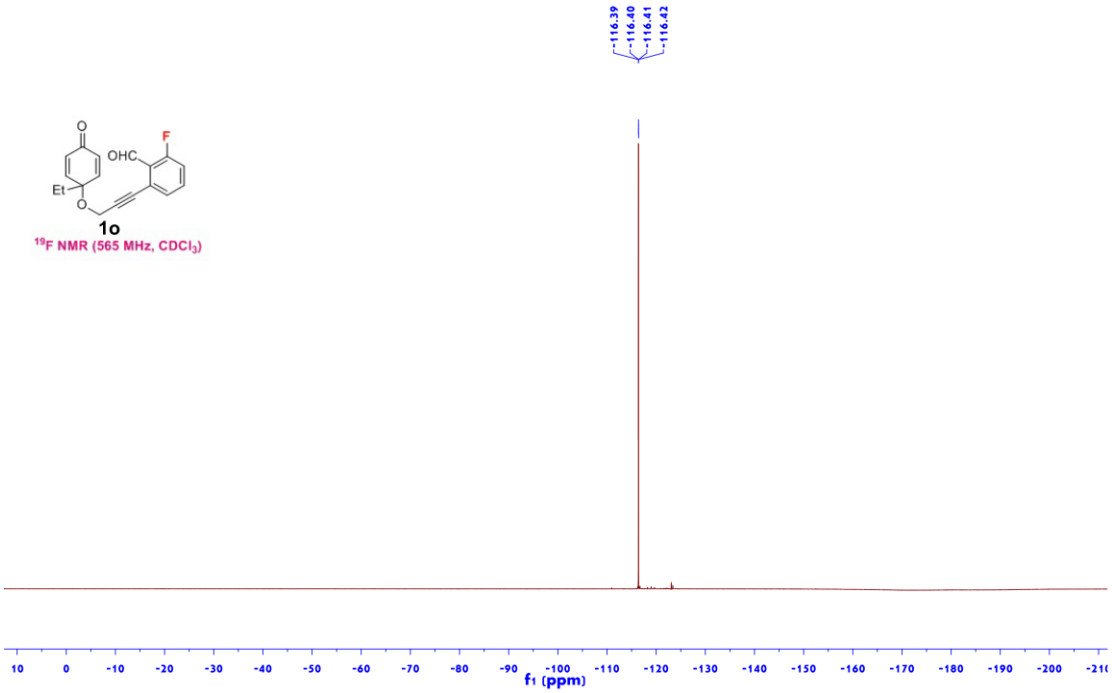

191.34
185.20
159.37
150.91
136.14
133.72
133.43
130.30
129.44
129.01
127.27
125.78
92.15
82.11
77.21
77.00
76.79
75.17
53.94
25.53
18.05
OHC
Me
Me
O
1m
13C NMR (150 MHz, CDCl3)
f1 (ppm)

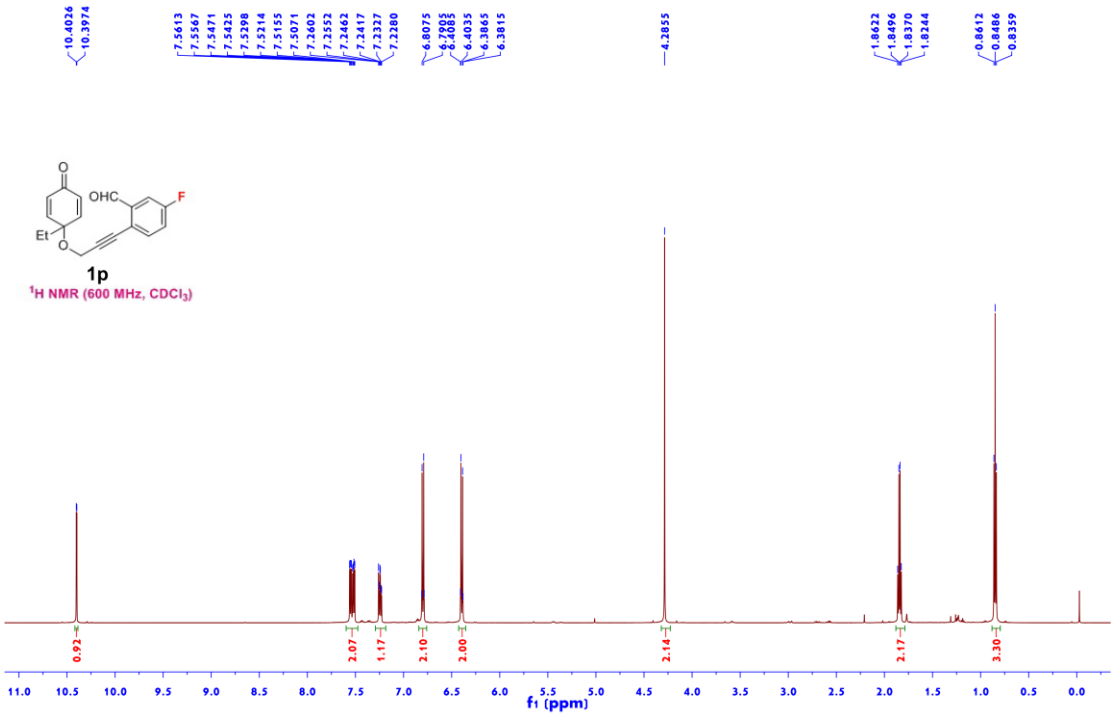

10.4587
7.8781
7.8652
7.5180
7.5165
7.5077
7.5056
7.4264
6.5393
4.2121
1.8991
1.4306
Me
Me
Me
O
O
O
1n
1H NMR (600 MHz, CDCl3)
0.96
1.00
2.10
1.04
2.08
2.14
6.62
3.26
f1 (ppm)

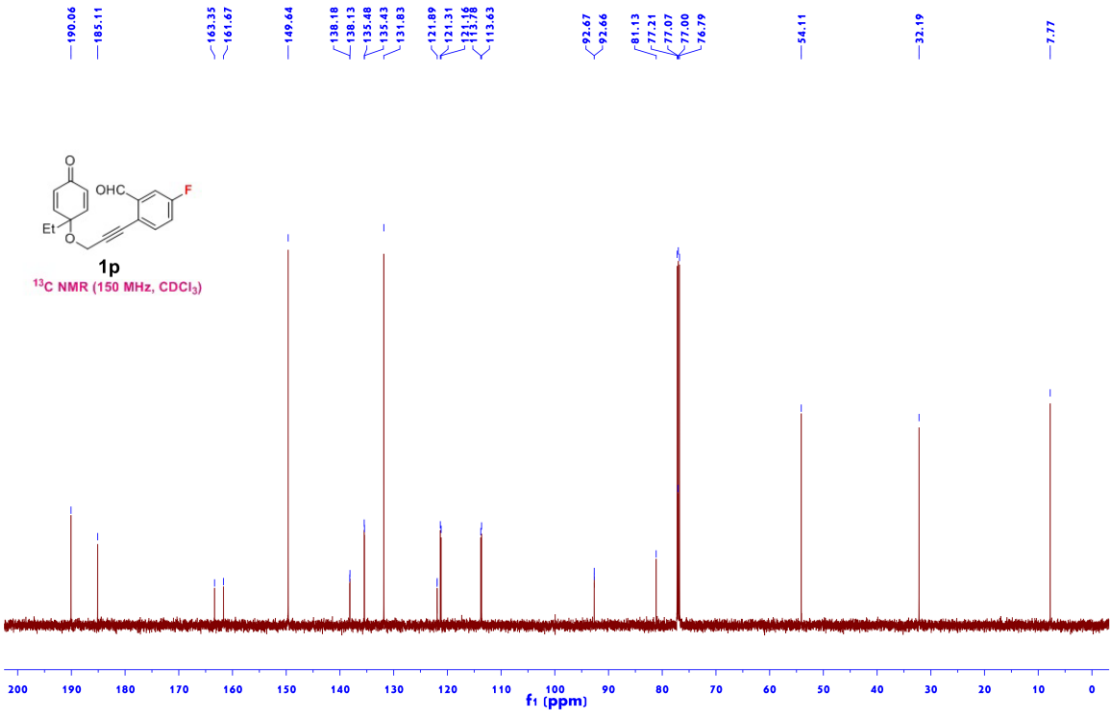

191.32
186.23
145.51
136.94
136.02
133.62
133.35
128.79
127.11
125.98
93.39
81.74
77.21
77.00
76.79
73.25
53.67
26.47
15.92
Me
Me
Me
O
O
O
1n
13C NMR (150 MHz, CDCl3)
f1 (ppm)

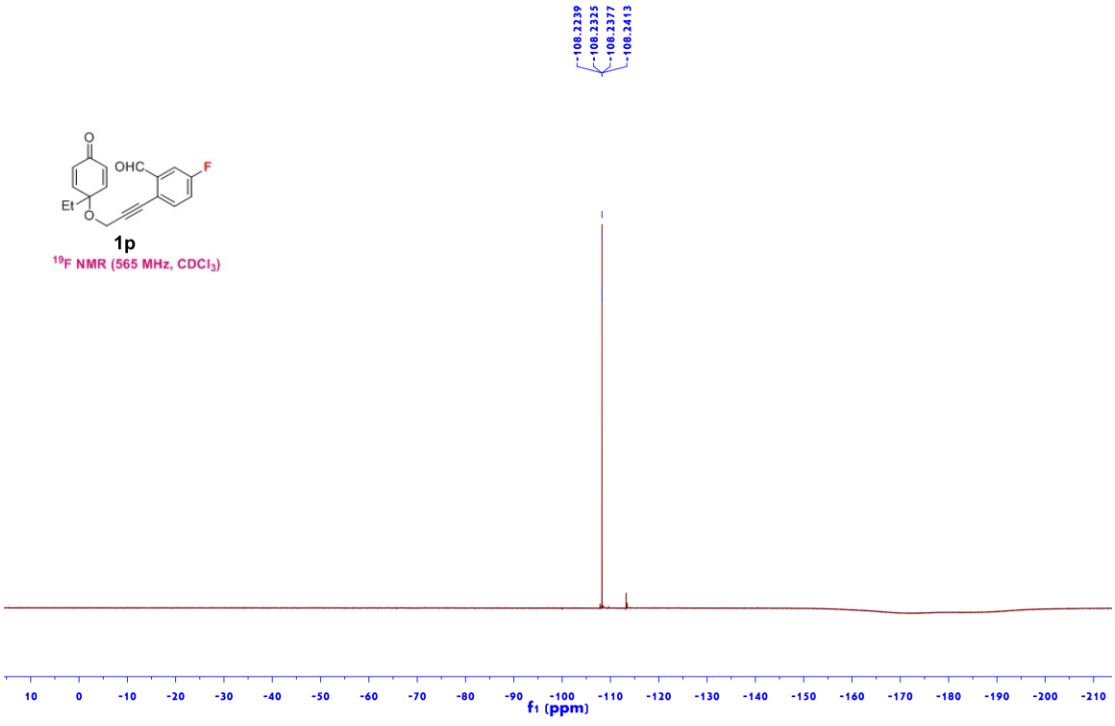

10.4513
7.5038
7.4947
7.4905
7.4814
7.4770
7.4679
7.3191
7.3062
7.2604
7.1350
7.1190
7.1038
6.8518
6.8467
6.8436
6.8326
6.8297
6.8245
6.4009
6.3958
6.3928
6.3818
6.3788
6.3736
4.2924
1.8655
1.8529
1.8402
1.8276
0.8624
0.8497
0.8371
O
OHC
F
Et
O
1o
1H NMR (600 MHz, CDCl3)
0.88
1.04
1.03
1.00
2.01
1.94
2.12
2.20
3.46
f1 (ppm)

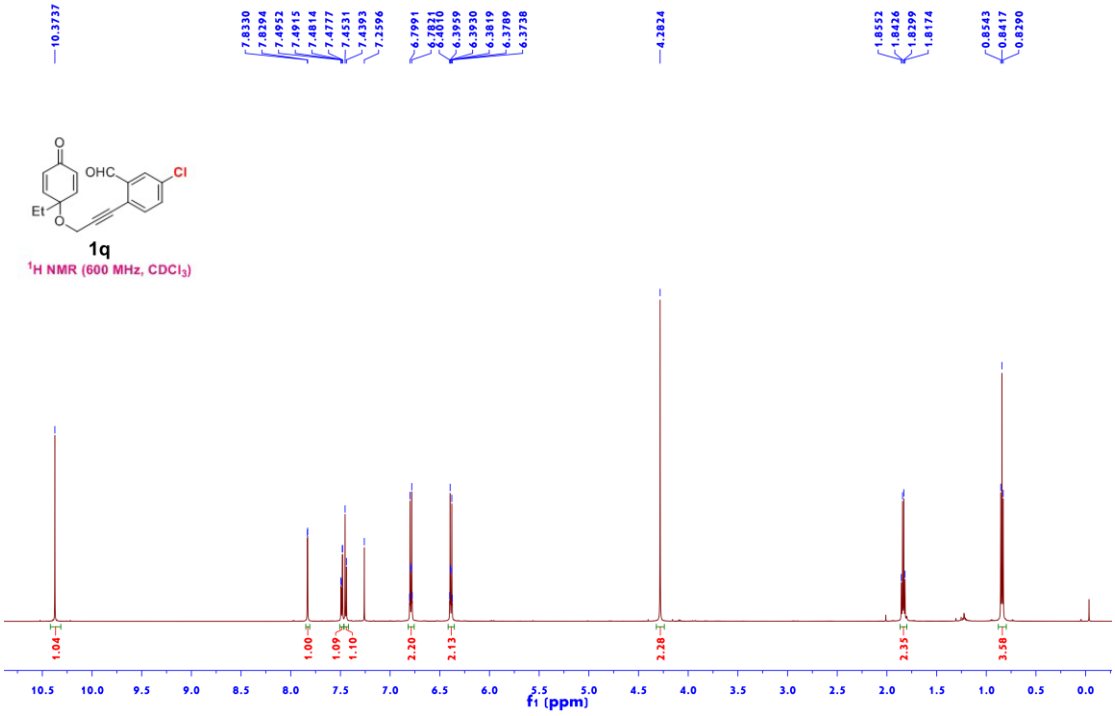

187.75
187.73
185.23
163.59
161.85
149.81
134.82
134.75
131.76
129.75
129.73
125.87
125.85
124.47
124.42
117.17
117.03
93.56
82.38
82.35
77.21
77.15
77.00
76.79
54.21
32.19
7.78
O
OHC
F
Et
O
1o
13C NMR (150 MHz, CDCl3)
f1 (ppm)

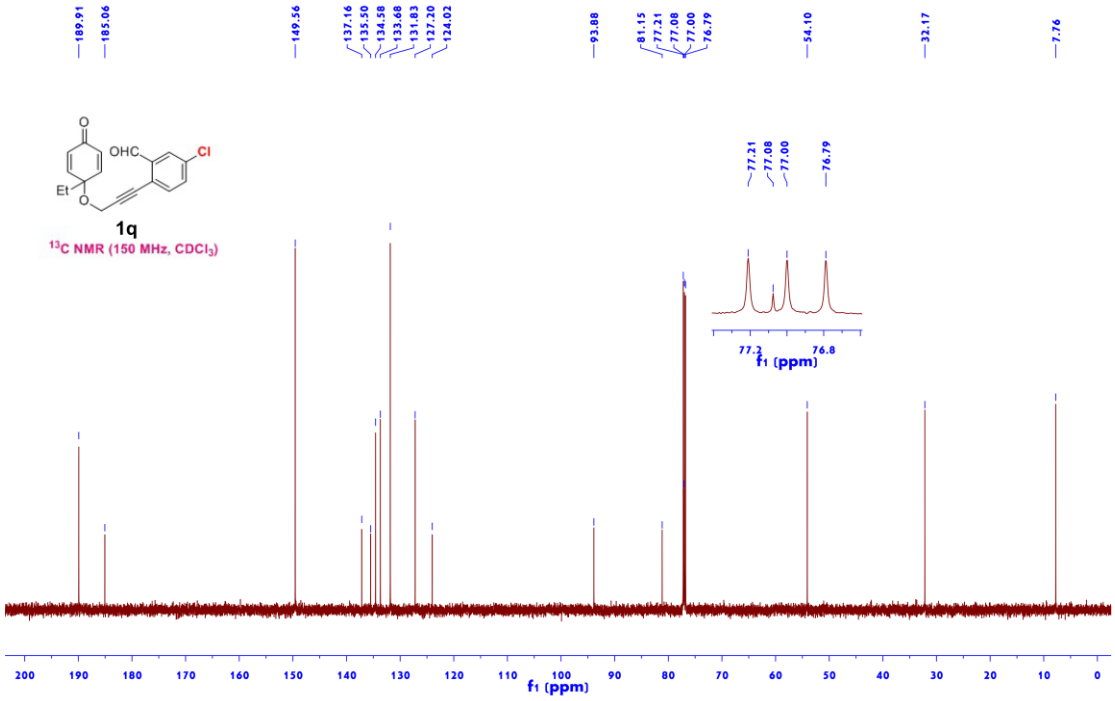

-116.39
-116.40
-116.41
-116.42
O
OHC
F
Et
O
1o
^{19}F NMR (565 MHz, CDCl$_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f$_1$ (ppm)

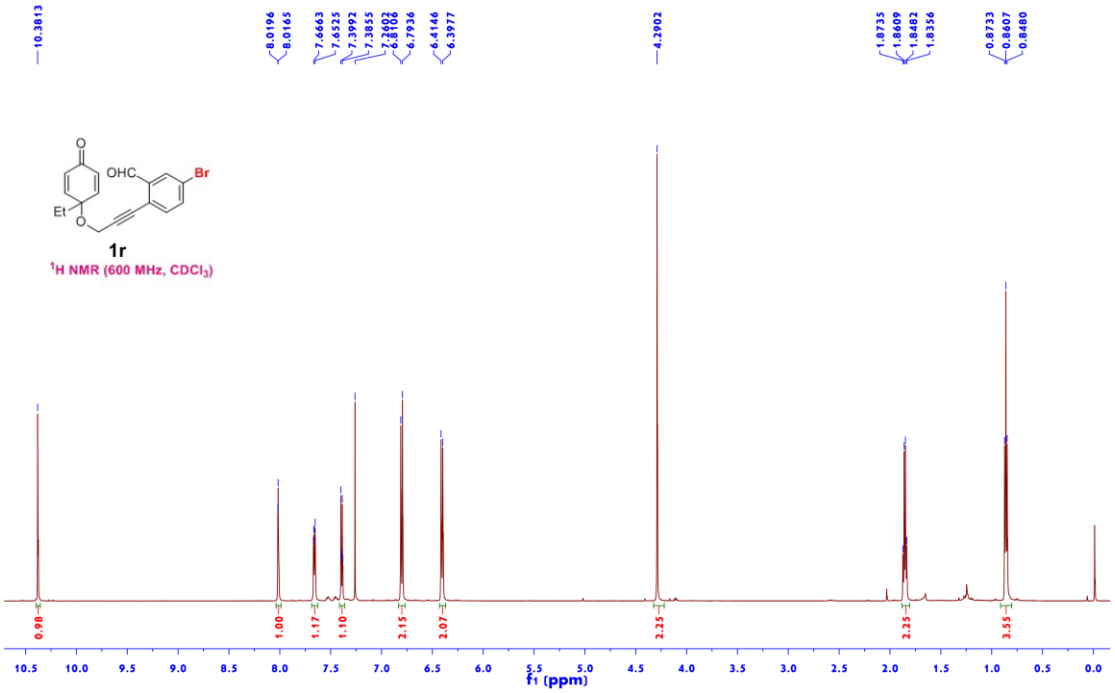

10.4026
10.3974
7.5613
7.5567
7.5471
7.5425
7.5298
7.5214
7.5155
7.5071
7.2602
7.2552
7.2462
7.2417
7.2327
7.2280
6.8075
6.7805
6.4085
6.4035
6.3865
6.3815
4.2855
1.8622
1.8496
1.8370
1.8244
0.8612
0.8486
0.8359
O
OHC
F
Et
O
1p
^{1}H NMR (600 MHz, CDCl$_3$)
0.92
2.07
1.17
2.10
2.00
2.14
2.17
3.30
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f$_1$ (ppm)

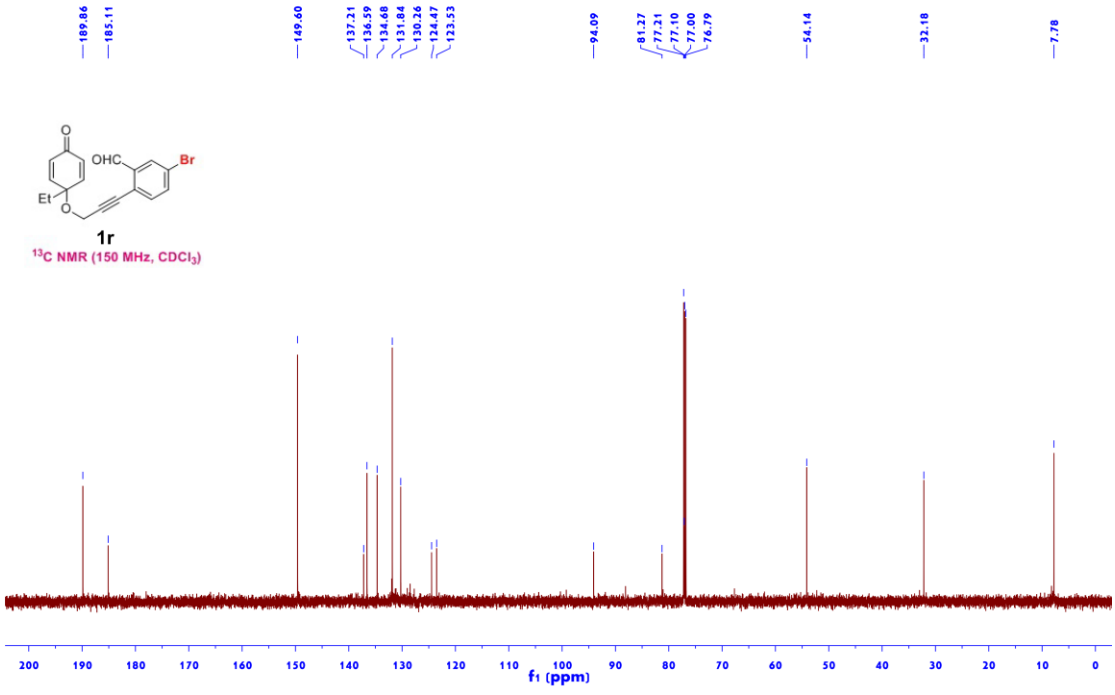

190.06
185.11
163.35
161.67
149.64
138.18
138.13
135.48
135.43
131.83
121.89
121.31
113.63
92.67
92.66
81.13
77.21
77.07
77.00
76.79
54.11
32.19
7.77
OHC
F
Et
O
1p
13C NMR (150 MHz, CDCl3)
f1 (ppm)

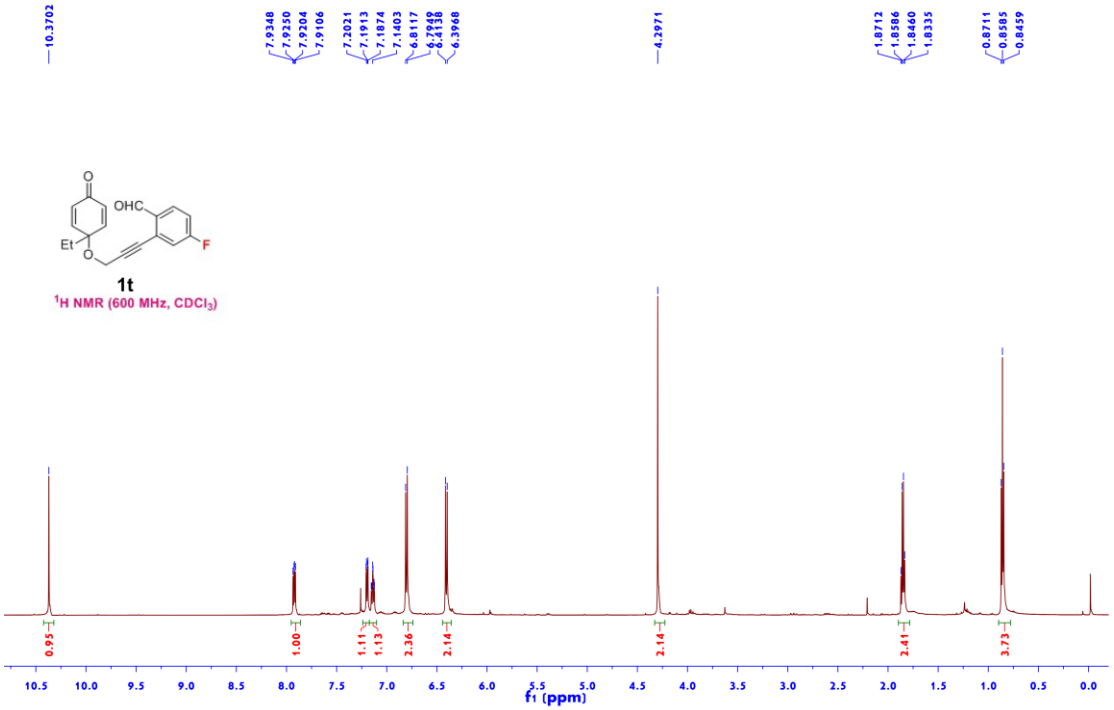

-108.2239
-108.2325
-108.2377
-108.2413
OHC
F
Et
O
1p
19F NMR (565 MHz, CDCl3)
f1 (ppm)

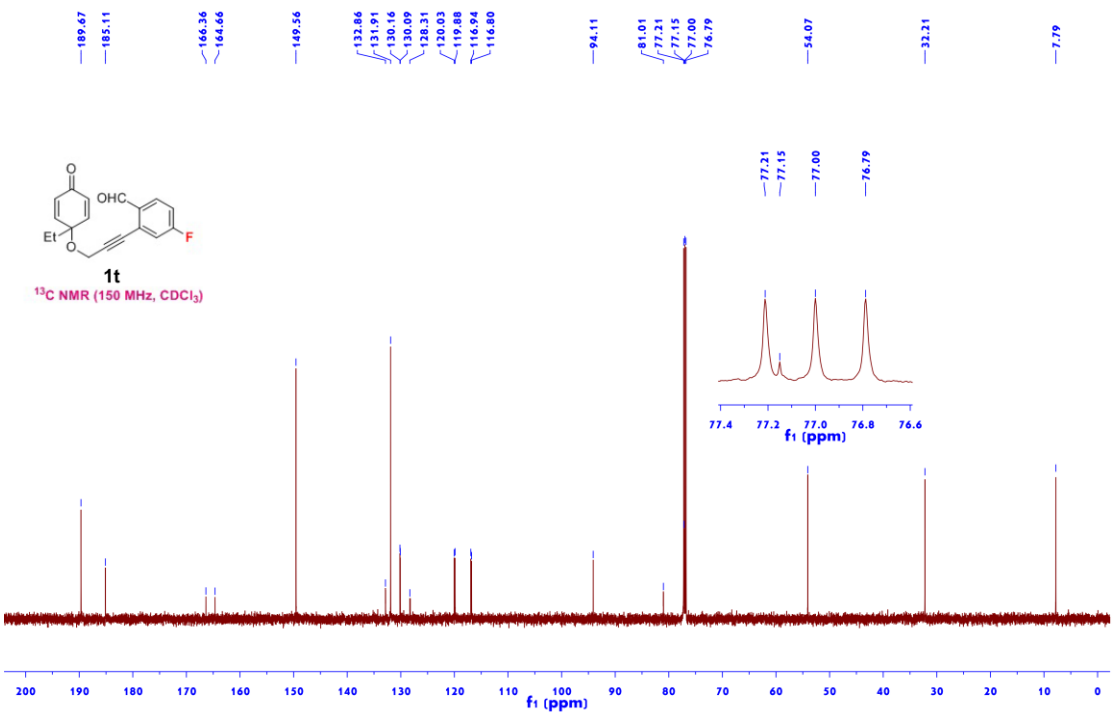

10.3737
7.8330
7.8294
7.4952
7.4915
7.4814
7.4777
7.4531
7.4393
7.3596
6.7991
6.7831
6.4010
6.3959
6.3930
6.3819
6.3789
6.3738
4.2824
1.8552
1.8426
1.8299
1.8174
0.8543
0.8417
0.8290
OHC
Cl
Et
O
1q
^{1}H NMR (600 MHz, CDCl$_3$)
1.04
1.00
1.09
1.10
2.20
2.13
2.28
2.35
3.58
f1 (ppm)

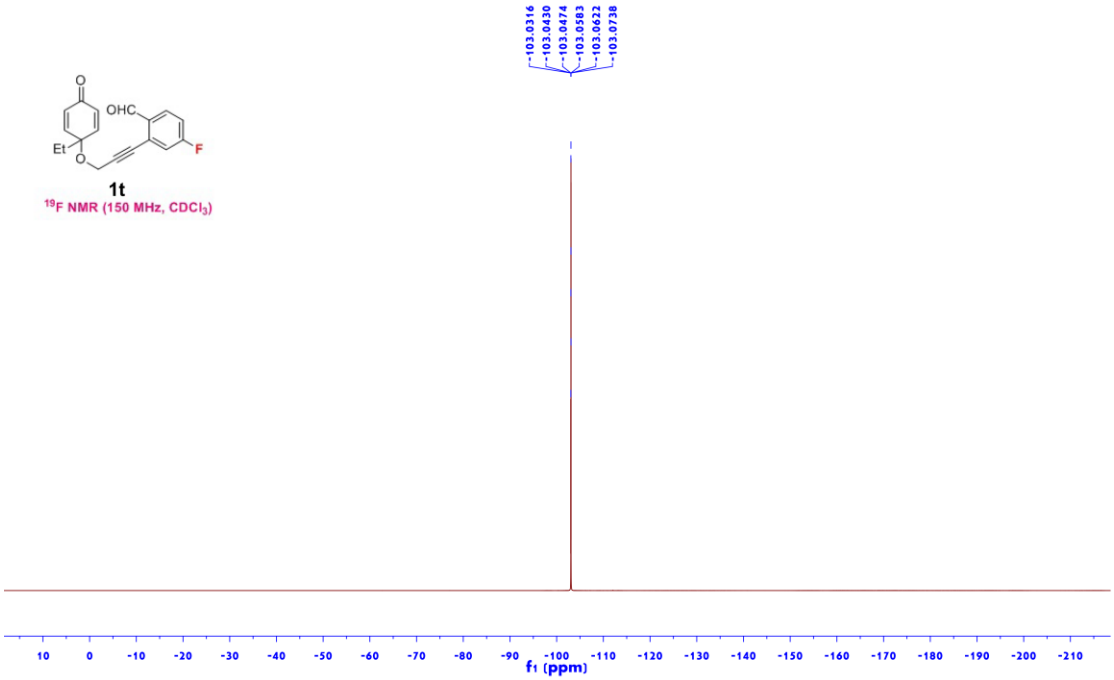

189.91
185.06
149.56
137.16
135.50
134.58
133.68
131.83
127.20
124.02
93.88
81.15
77.21
77.08
77.00
76.79
54.10
32.17
7.76
OHC
Cl
Et
O
1q
^{13}C NMR (150 MHz, CDCl$_3$)
77.21
77.08
77.00
76.79
77.2
76.8
f1 (ppm)
f1 (ppm)

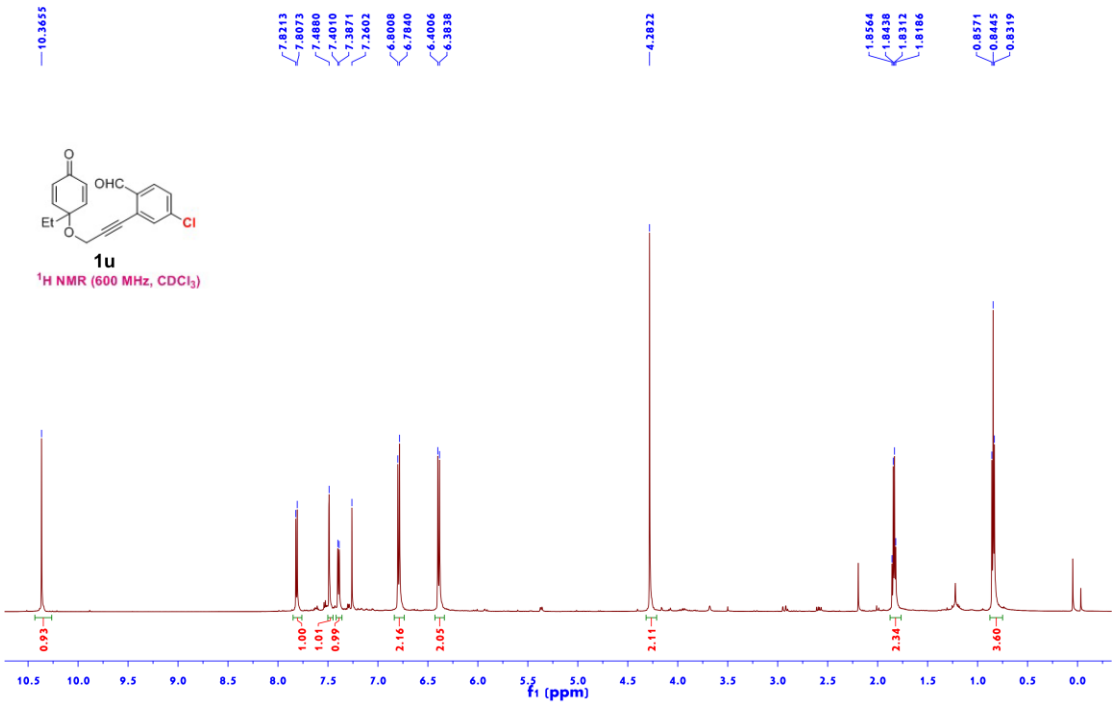

10.3813
8.0196
8.0165
7.6663
7.6525
7.3992
7.3855
7.3602
7.3108
6.7936
6.4146
6.3977
4.2902
1.8735
1.8609
1.8482
1.8356
0.8733
0.8607
0.8480
O
OHC
Br
Et
O
1r
^{1}H NMR (600 MHz, CDCl$_3$)
0.98
1.00
1.17
1.10
2.15
2.07
2.25
2.25
3.55
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

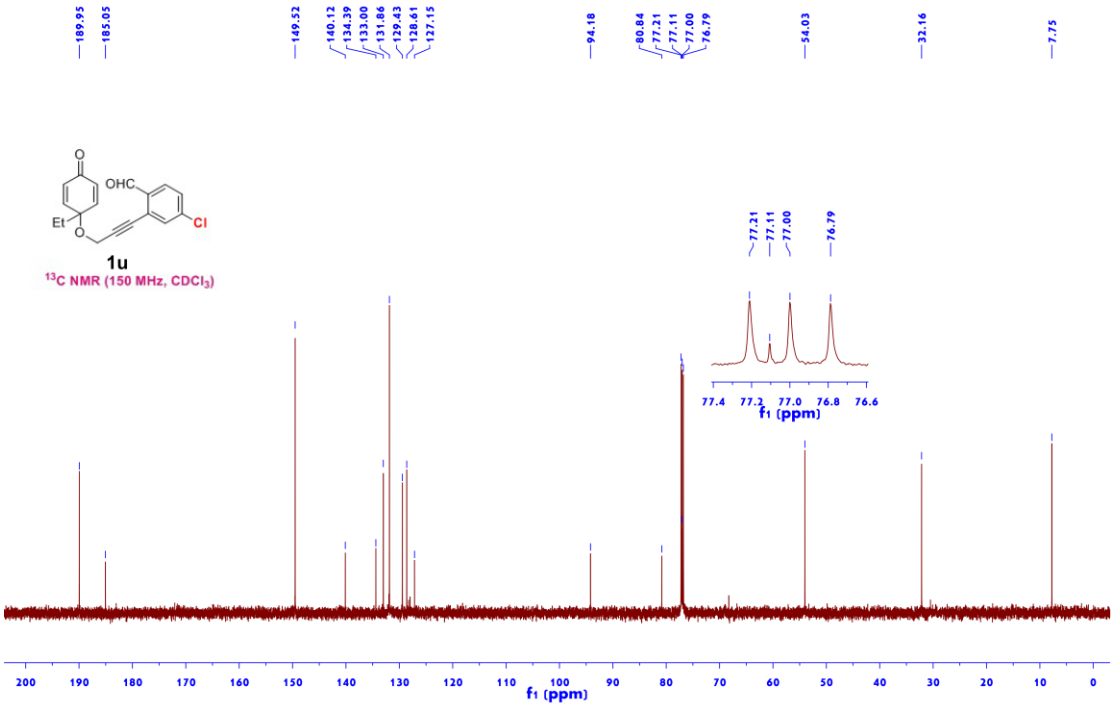

189.86
185.11
149.60
137.21
136.59
134.68
131.84
130.26
124.47
123.53
94.09
81.27
77.21
77.10
77.00
76.79
54.14
32.18
7.78
O
OHC
Br
Et
O
1r
^{13}C NMR (150 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

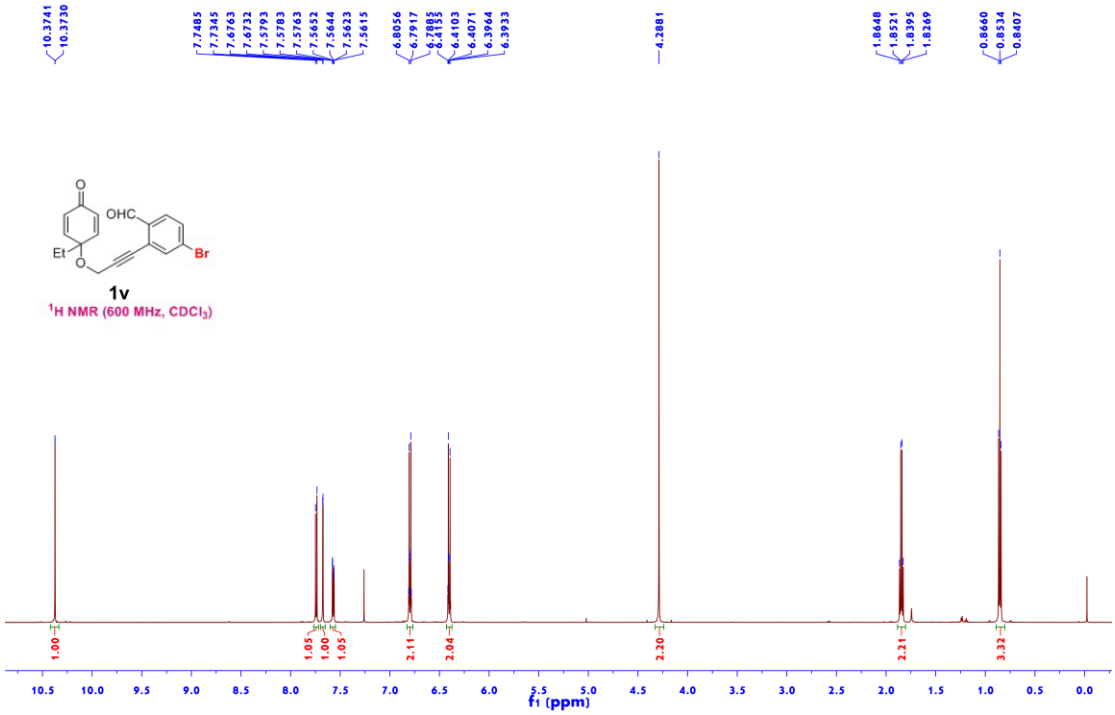

10.3702
7.9348
7.9250
7.9204
7.9106
7.2021
7.1913
7.1874
7.1403
6.8117
6.7949
6.4138
6.3968
4.2971
1.8712
1.8586
1.8460
1.8335
0.8711
0.8585
0.8459
OHC
Et
O
F
1t
1H NMR (600 MHz, CDCl3)
0.95
1.00
1.11
1.13
2.36
2.14
2.14
2.41
3.73
f1 (ppm)

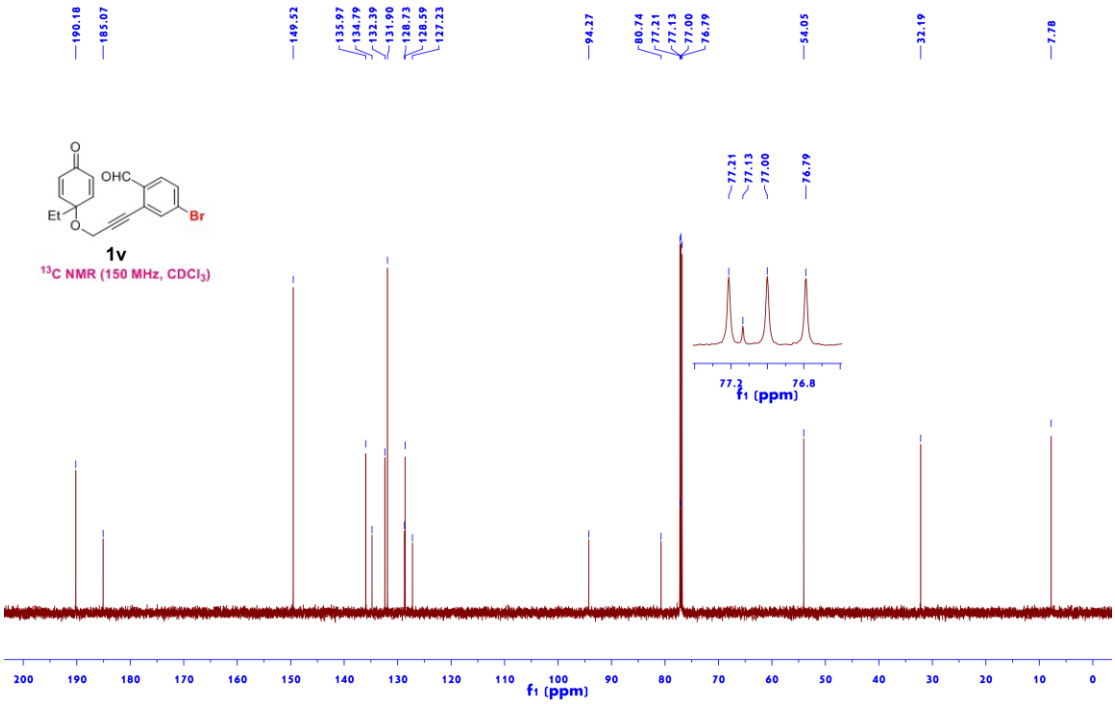

189.67
185.11
166.36
164.46
149.56
132.86
131.91
130.16
130.09
128.31
120.03
119.88
116.94
116.80
94.11
81.01
77.21
77.15
77.00
76.79
54.07
32.21
7.79
OHC
Et
O
F
1t
13C NMR (150 MHz, CDCl3)
77.21
77.15
77.00
76.79
77.4
77.2
77.0
76.8
76.6
f1 (ppm)
f1 (ppm)

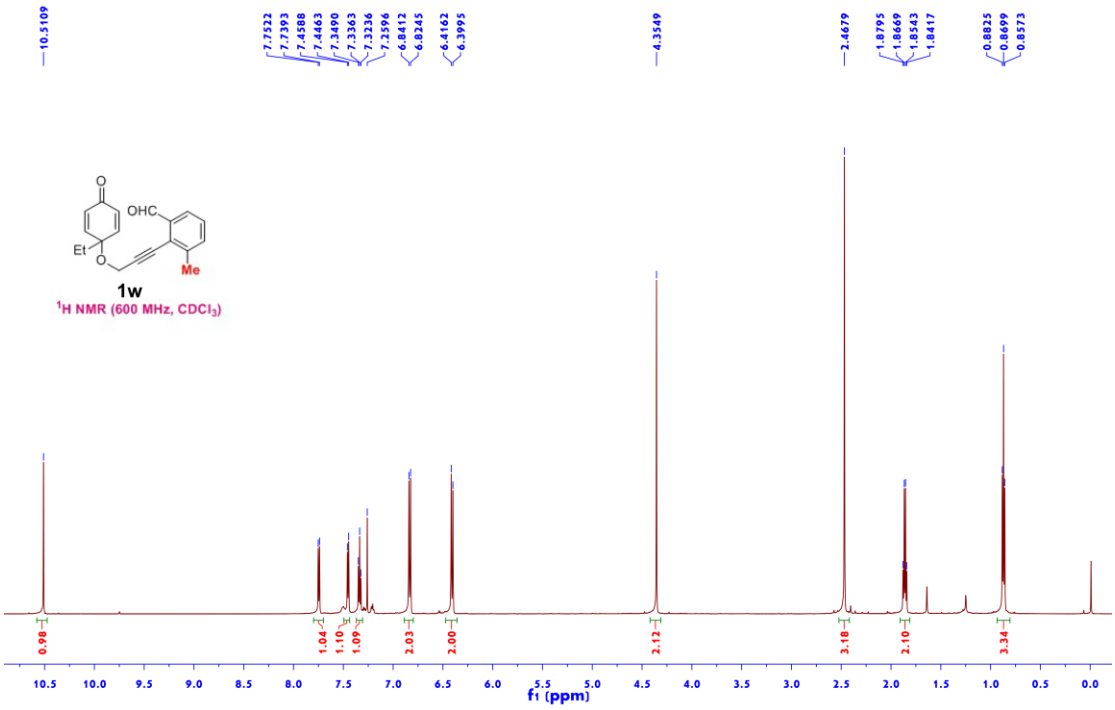

-103.0316
-103.0430
-103.0474
-103.0583
-103.0622
-103.0738
OHC
Et
O
F
1t
^{19}F NMR (150 MHz, $CDCl_3$)
f1 (ppm)

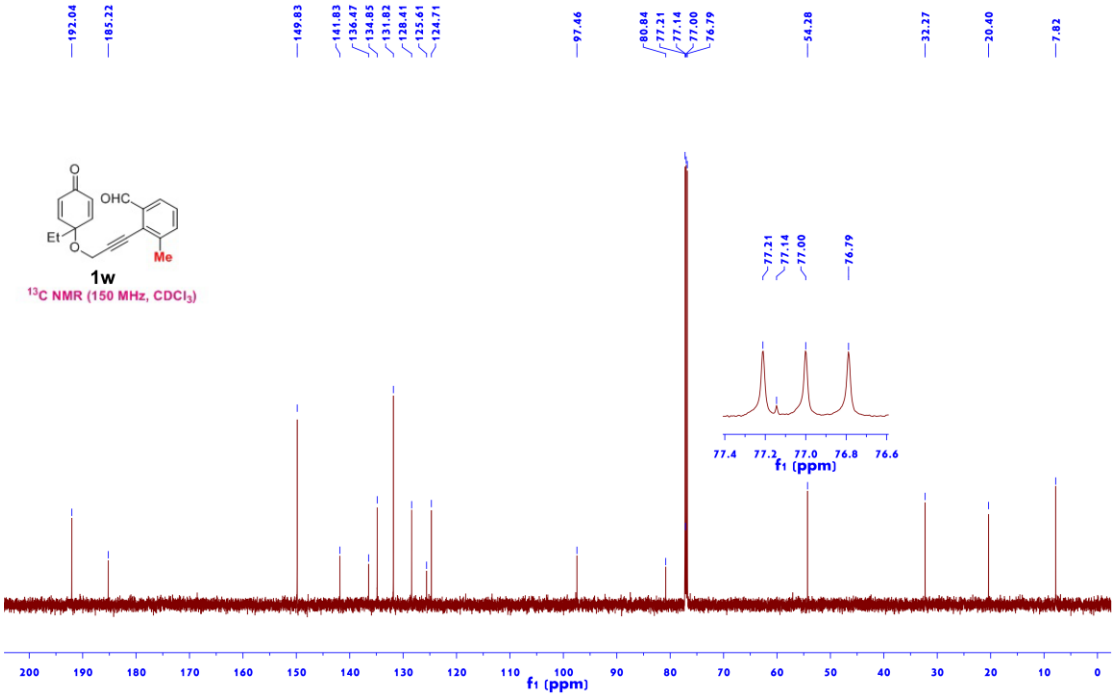

10.3655
7.8213
7.8073
7.4880
7.4010
7.3871
7.2602
6.8008
6.7840
6.4006
6.3838
4.2822
1.8564
1.8438
1.8312
1.8186
0.8571
0.8445
0.8319
OHC
Et
O
Cl
1u
^{1}H NMR (600 MHz, $CDCl_3$)
0.93
1.00
1.01
0.99
2.16
2.05
2.11
2.34
3.60
f1 (ppm)

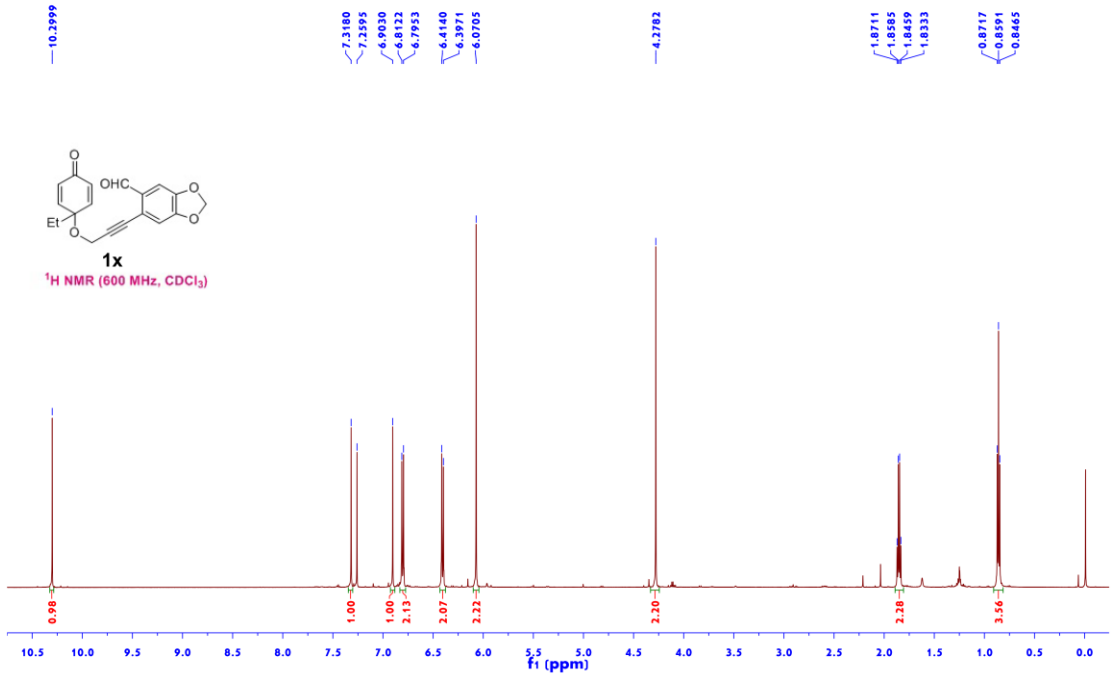

189.95
185.05
149.52
140.12
134.39
133.00
131.86
129.43
128.61
127.15
94.18
80.84
77.21
77.11
77.00
76.79
54.03
32.16
7.75
O
OHC
Et
O
Cl
1u
13C NMR (150 MHz, CDCl3)
77.21
77.11
77.00
76.79
77.4 77.2 77.0 76.8 76.6
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

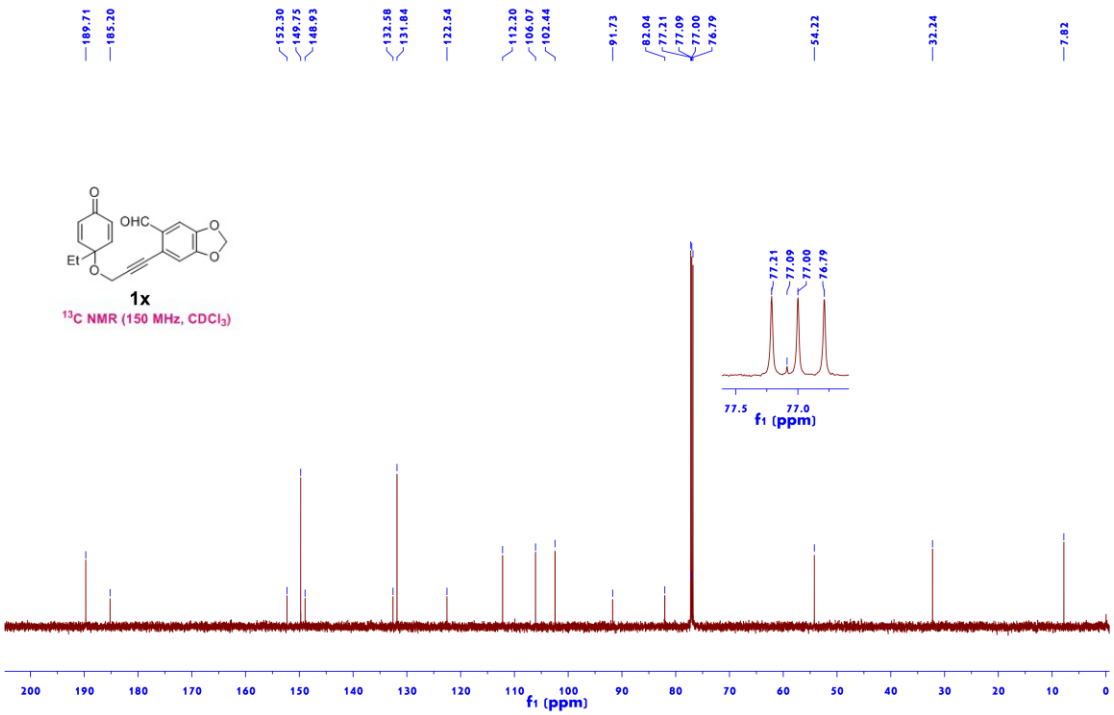

10.3741
10.3730
7.7485
7.7345
7.6763
7.6732
7.5793
7.5783
7.5763
7.5652
7.5644
7.5623
7.5615
6.8056
6.7917
6.7885
6.4155
6.4103
6.4071
6.3964
6.3933
4.2881
1.8648
1.8521
1.8395
1.8269
0.8660
0.8534
0.8407
O
OHC
Et
O
Br
1v
1H NMR (600 MHz, CDCl3)
1.00
1.05
1.00
1.05
2.11
2.04
2.20
2.21
3.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

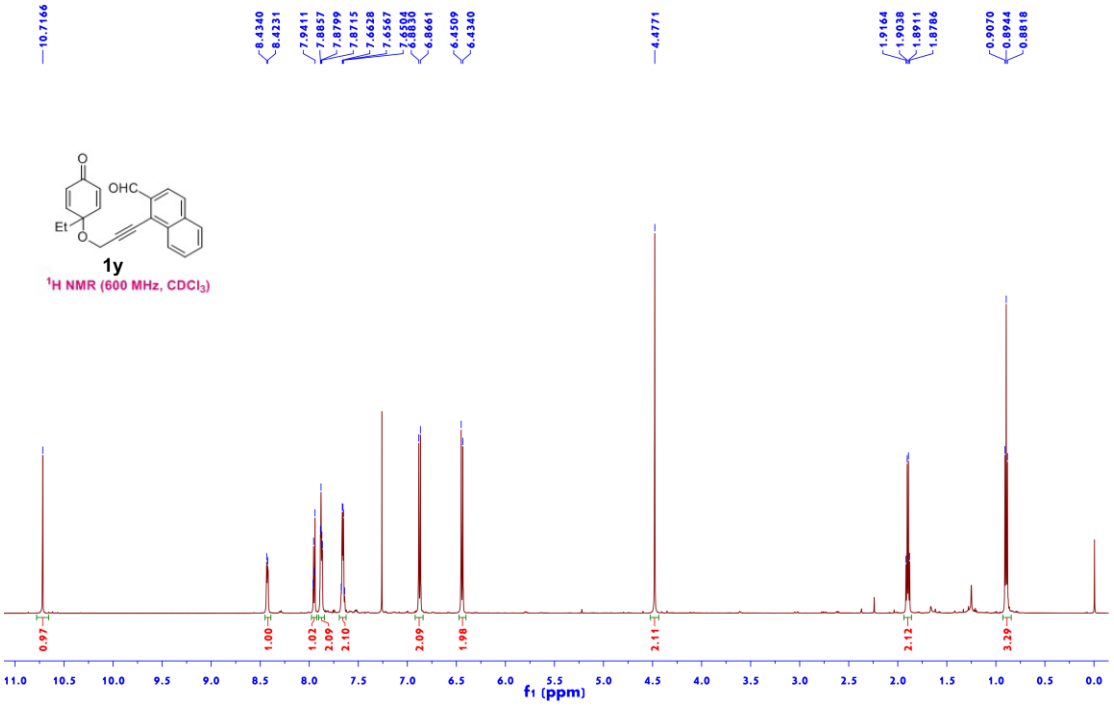

190.18
185.07
149.52
135.97
134.79
132.39
131.90
128.73
128.59
127.23
94.27
80.74
77.21
77.13
77.00
76.79
54.05
32.19
7.78
O
OHC
Et
O
Br
1v
13C NMR (150 MHz, CDCl3)
77.21
77.13
77.00
76.79
77.2
76.8
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

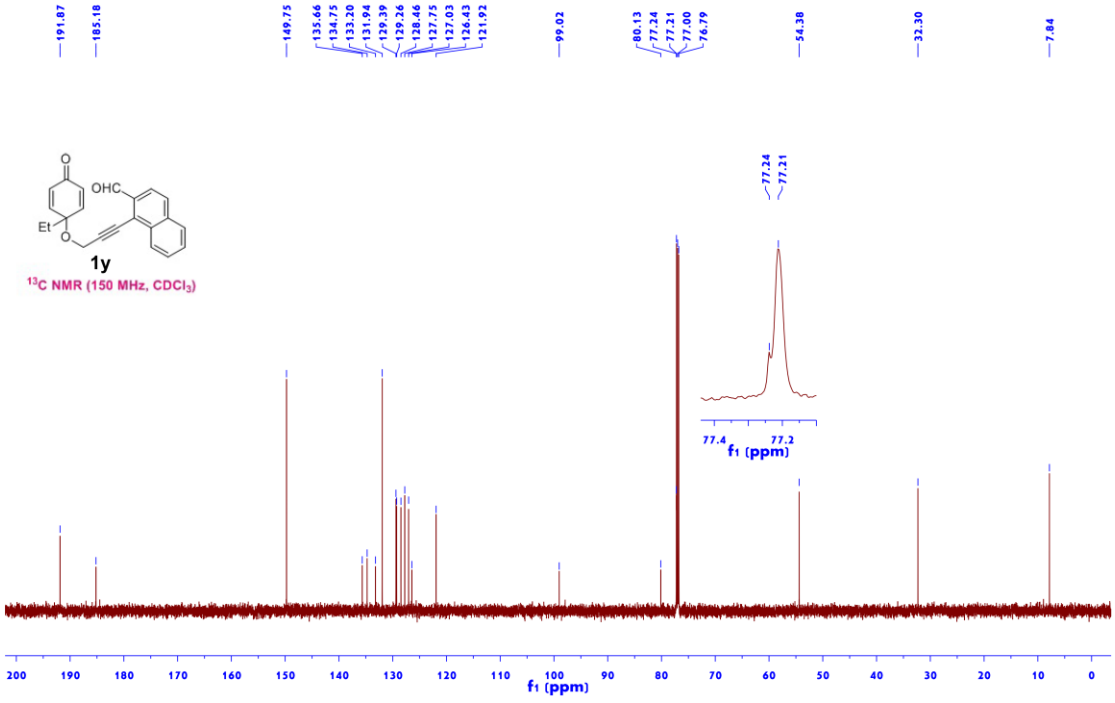

10.5109
7.7522
7.7393
7.4588
7.4463
7.3490
7.3363
7.3236
7.2596
6.8412
6.8245
6.4162
6.3995
4.3549
2.4679
1.8795
1.8669
1.8543
1.8417
0.8825
0.8699
0.8573
O
OHC
Et
O
Me
1w
1H NMR (600 MHz, CDCl3)
0.98
1.04
1.10
1.09
2.03
2.00
2.12
3.18
2.10
3.34
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

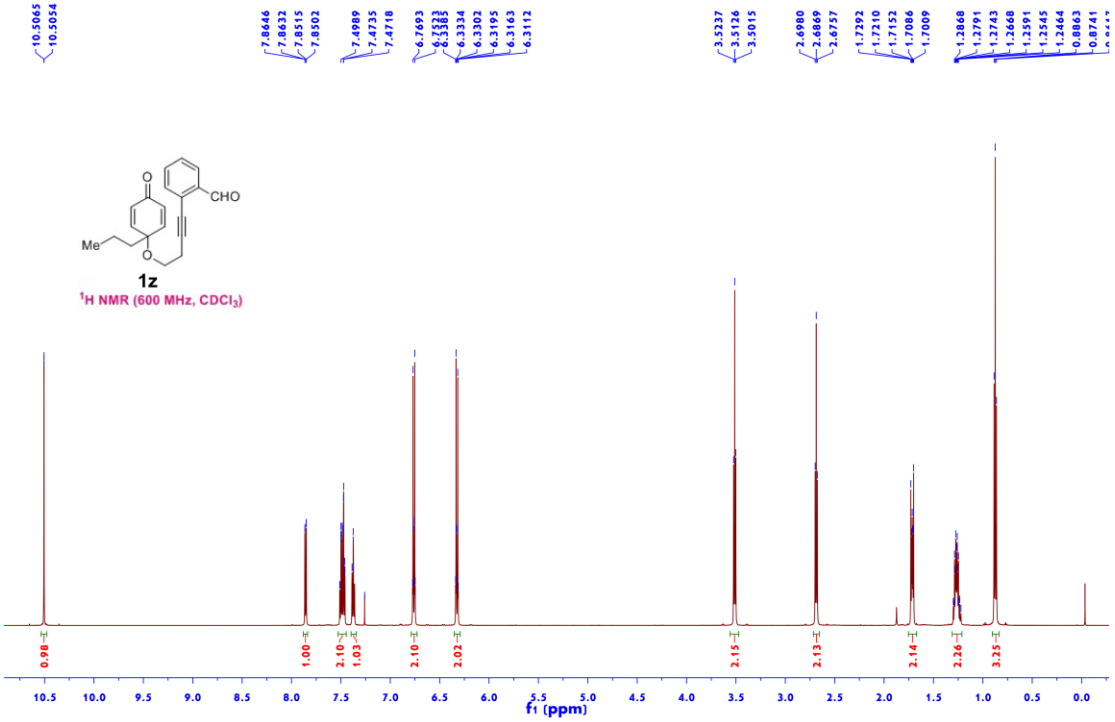

192.04
185.22
149.83
141.83
136.47
134.85
131.82
128.41
125.61
124.71
97.46
80.84
77.21
77.14
77.00
76.79
54.28
32.27
20.40
7.82
OHC
Et
O
Me
1w
13C NMR (150 MHz, CDCl3)
77.21
77.14
77.00
76.79
77.4
77.2
77.0
76.8
76.6
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

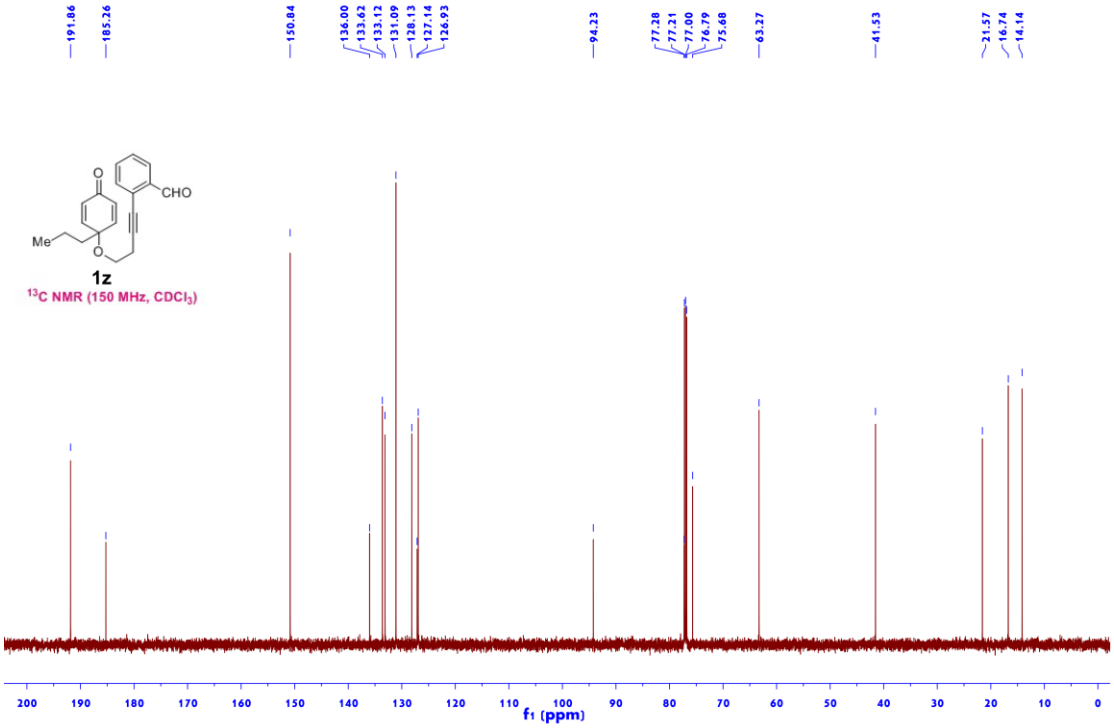

10.2999
7.3180
7.2595
6.9030
6.8122
6.7953
6.4140
6.3971
6.0705
4.2782
1.8711
1.8585
1.8459
1.8333
0.8717
0.8591
0.8465
OHC
Et
O
O
O
1x
1H NMR (600 MHz, CDCl3)
0.98
1.00
1.00
2.13
2.07
2.22
2.20
2.28
3.56
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

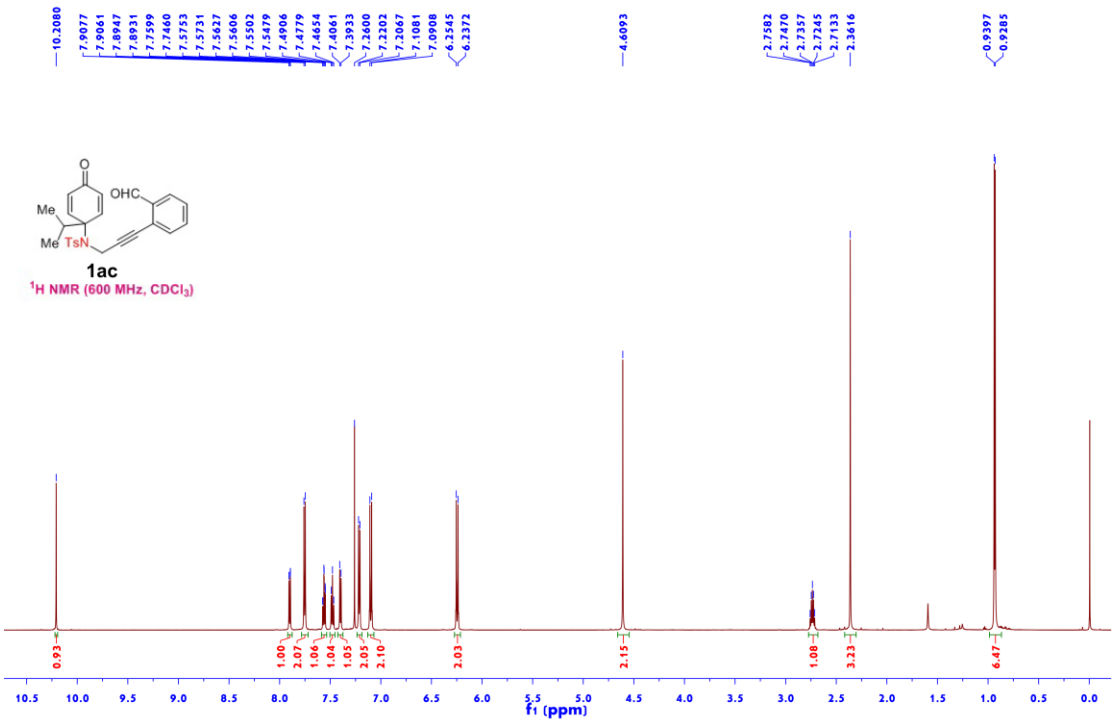

189.71
185.20
152.30
149.75
148.93
132.58
131.84
122.54
112.20
106.07
102.44
91.73
82.04
77.21
77.09
77.00
76.79
54.22
32.24
7.82
OHC
Et
O
1x
13C NMR (150 MHz, CDCl3)
77.21
77.09
77.00
76.79
77.5
77.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

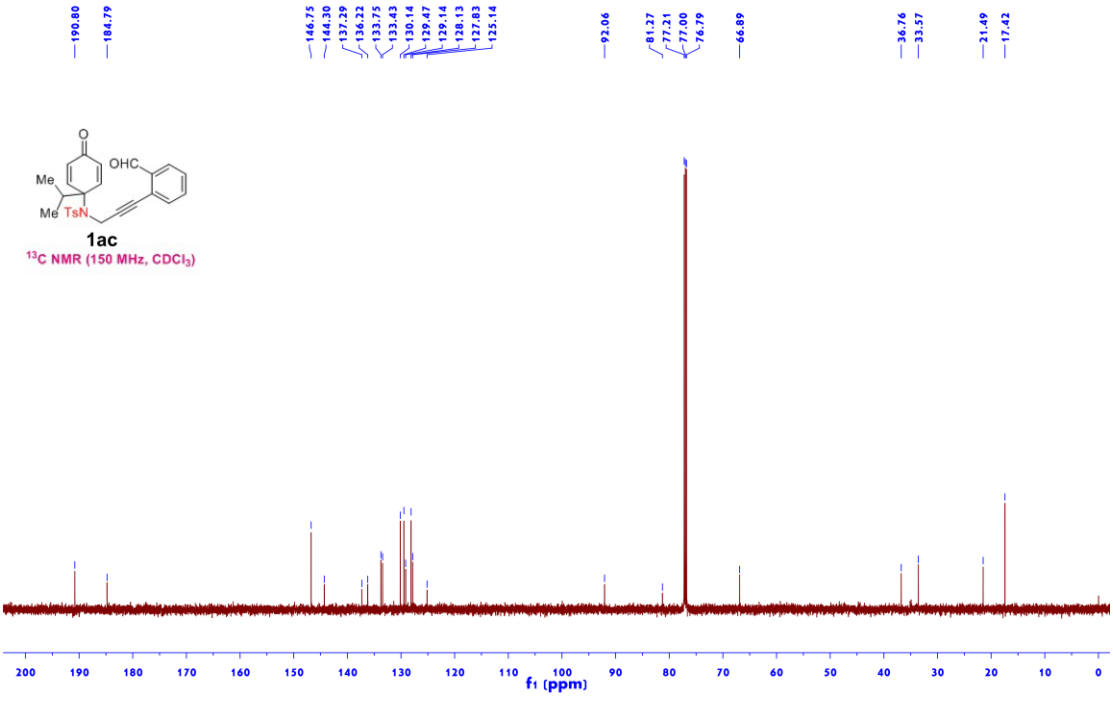

10.7166
8.4340
8.4231
7.9411
7.8857
7.8799
7.8715
7.6628
7.6567
7.6504
6.8830
6.8661
6.4509
6.4340
4.4771
1.9164
1.9038
1.8911
1.8786
0.9070
0.8944
0.8818
OHC
Et
O
1y
1H NMR (600 MHz, CDCl3)
0.97
1.00
1.02
2.09
2.10
2.09
1.98
2.11
2.12
3.29
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

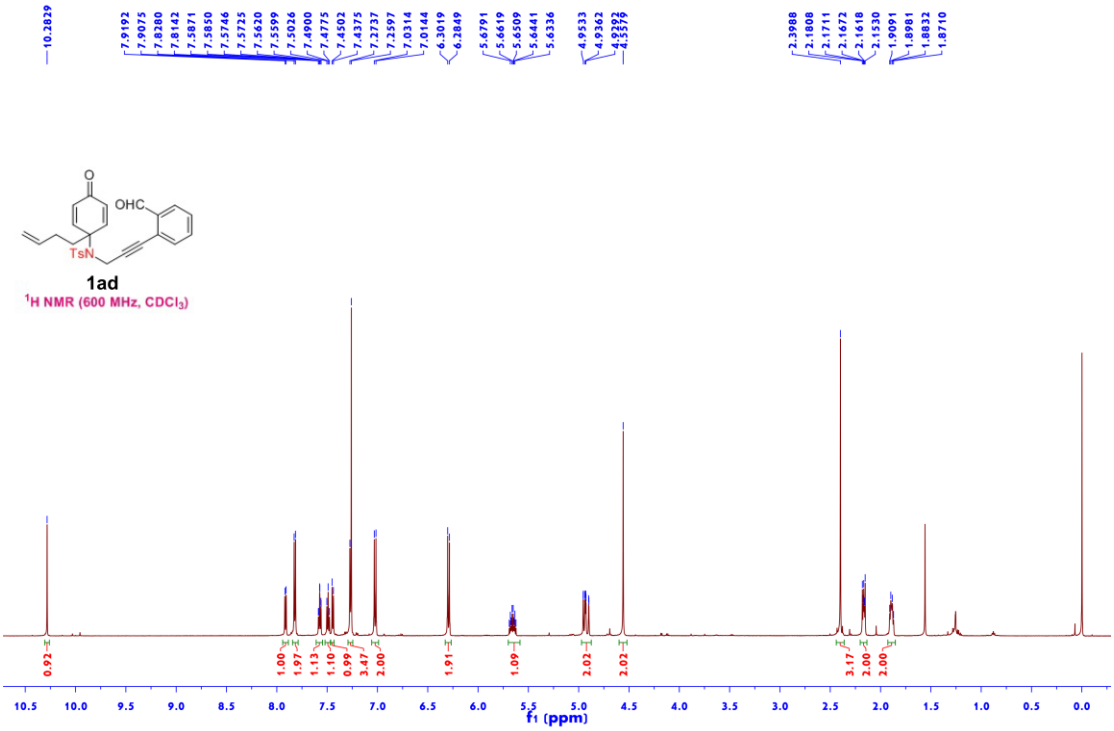

OHC
Et
O
1y
13C NMR (150 MHz, CDCl3)
f1 (ppm)

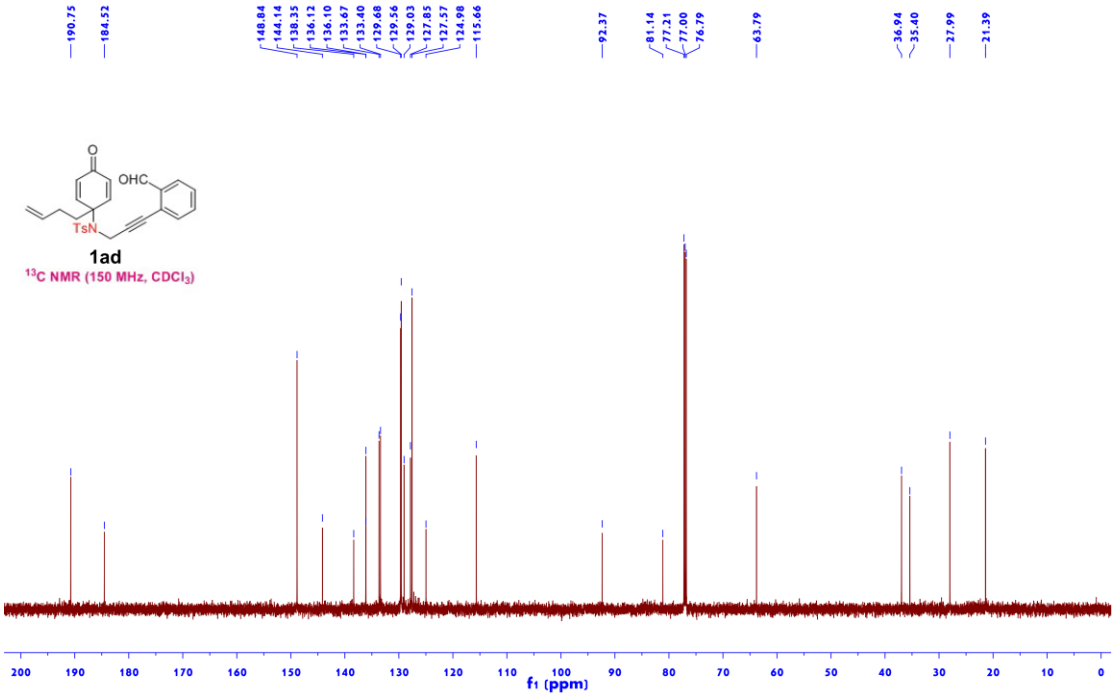

CHO
Me
O
1z
1H NMR (600 MHz, CDCl3)
f1 (ppm)

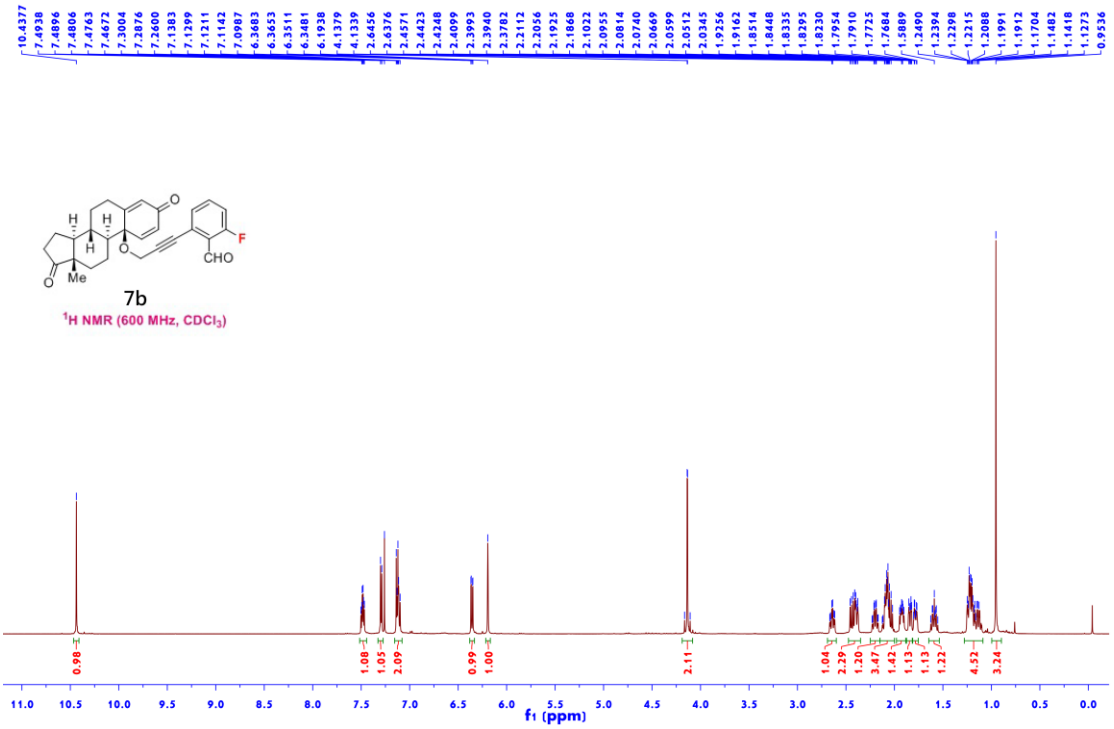

191.86
185.26
150.84
136.00
133.62
133.12
131.09
128.13
127.14
126.93
94.23
77.28
77.21
77.00
76.79
75.68
63.27
41.53
21.57
16.74
14.14
O
CHO
Me
O
1z
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

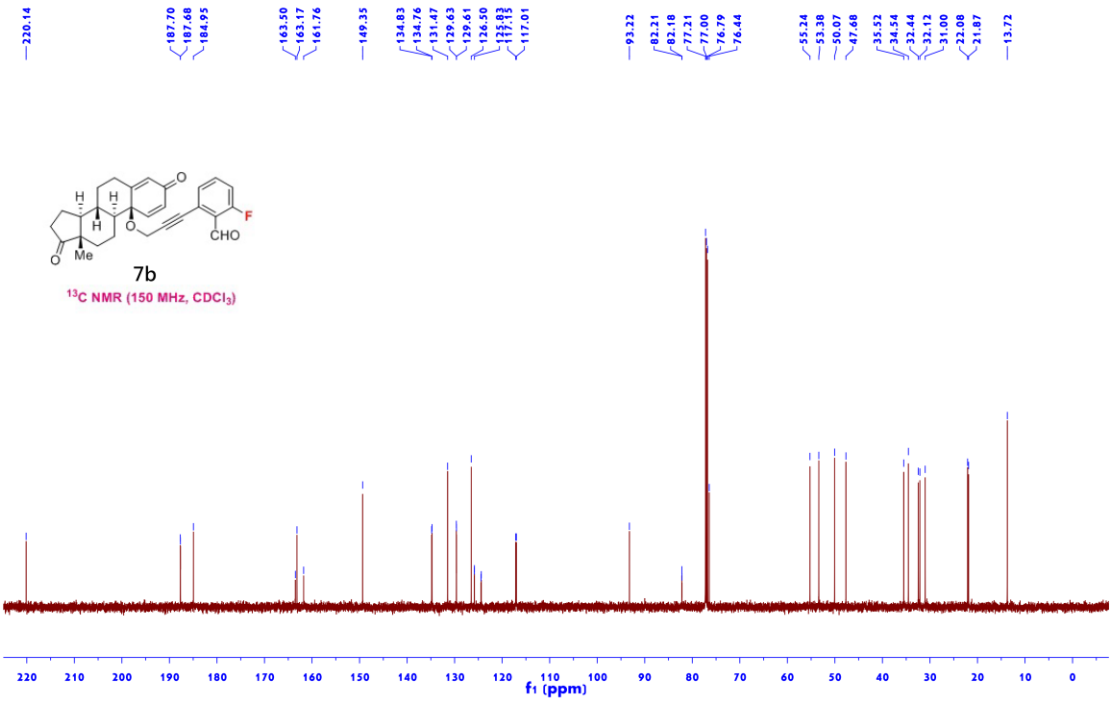

10.2080
7.9077
7.9061
7.8947
7.8931
7.7599
7.7460
7.5753
7.5731
7.5627
7.5606
7.5502
7.5479
7.4906
7.4779
7.4654
7.4061
7.3933
7.2600
7.2202
7.2067
7.1081
7.0908
6.2545
6.2372
4.6093
2.7582
2.7470
2.7357
2.7245
2.7133
2.3616
0.9397
0.9285
O
OHC
Me
Me
TsN
1ac
1H NMR (600 MHz, CDCl3)
0.93
1.00
2.07
1.06
1.04
1.05
2.05
2.10
2.03
2.15
1.08
3.23
6.47
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

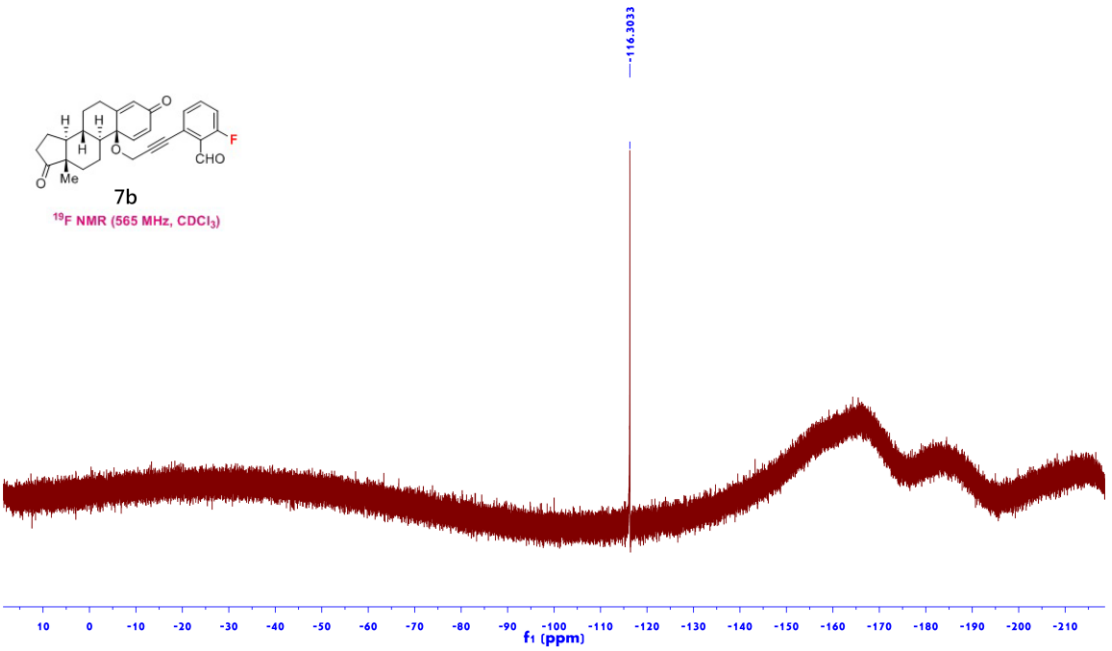

190.80
184.79
146.75
144.30
137.29
136.22
133.75
133.43
130.14
129.47
129.14
128.13
127.83
125.14
92.06
81.27
77.21
77.00
76.79
66.89
36.76
33.57
21.49
17.42
O
OHC
Me
Me
TsN
1ac
13C NMR (150 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

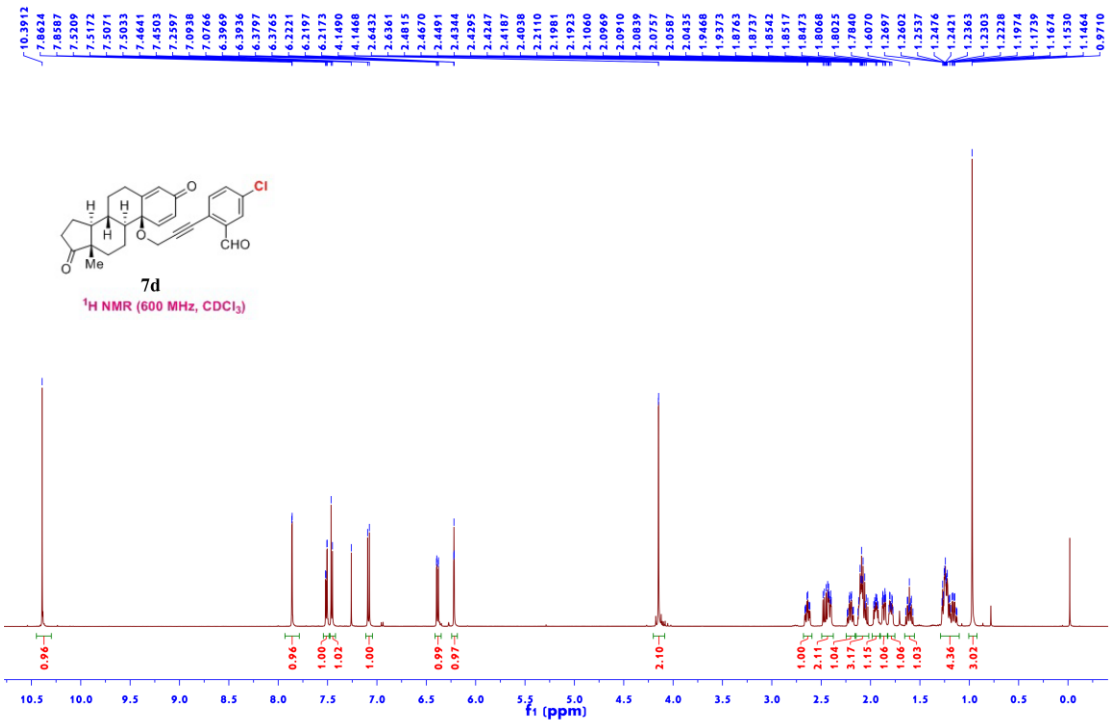

10.2829
7.9192
7.9075
7.8280
7.8142
7.5871
7.5850
7.5746
7.5725
7.5620
7.5599
7.5026
7.4900
7.4775
7.4502
7.4375
7.2737
7.2597
7.0314
7.0144
6.3019
6.2849
5.6791
5.6619
5.6509
5.6441
5.6336
4.9533
4.9362
4.8282
4.5579
2.3988
2.1808
2.1711
2.1672
2.1618
2.1530
1.9091
1.8981
1.8832
1.8710
O
OHC
TsN
1ad
1H NMR (600 MHz, CDCl3)
0.92
1.00
1.97
1.13
1.10
0.99
3.47
2.00
1.91
1.09
2.02
2.02
3.17
2.00
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

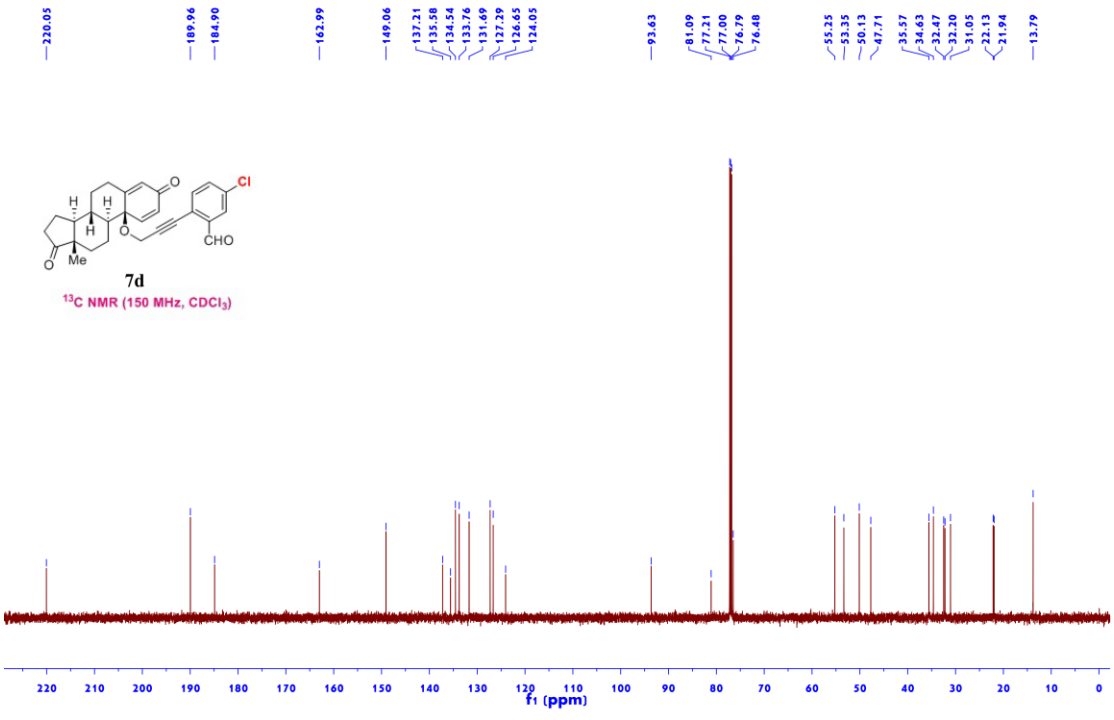

190.75
184.52
148.84
144.14
138.35
136.12
136.10
133.67
133.40
129.68
129.56
129.03
127.85
127.57
124.98
115.66
92.37
81.14
77.21
77.00
76.79
63.79
36.94
35.40
27.99
21.39
O
OHC
TsN
1ad
13C NMR (150 MHz, CDCl3)
f1 (ppm)

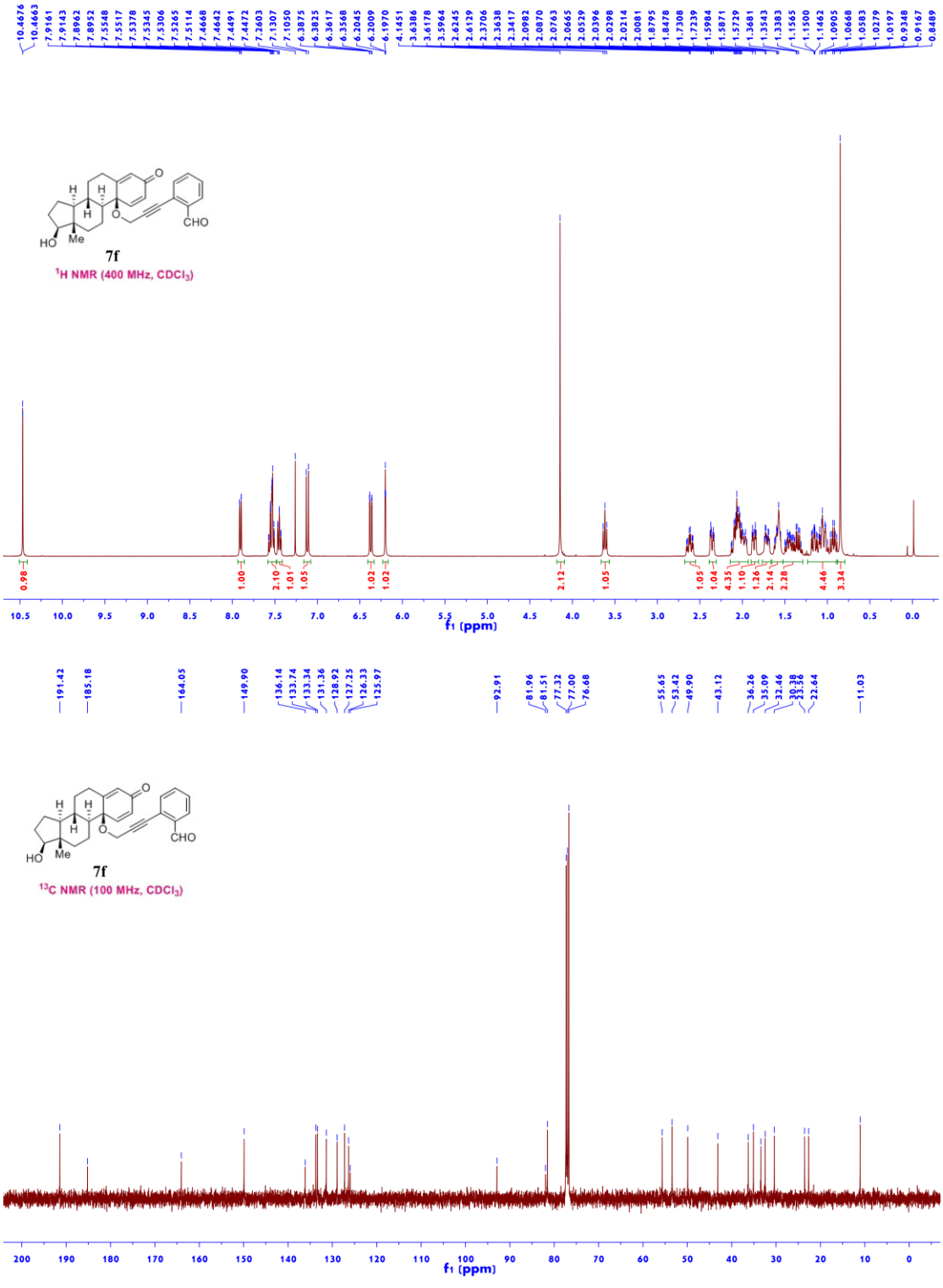

10.4377
7.4938
7.4896
7.4806
7.4763
7.4672
7.3004
7.2876
7.2600
7.1383
7.1299
7.1211
7.1142
7.0987
6.3683
6.3653
6.3511
6.3481
6.1938
4.1379
4.1339
2.6456
2.6376
2.4571
2.4423
2.4248
2.4099
2.3993
2.3940
2.3782
2.2112
2.2056
2.1925
2.1868
2.1022
2.0955
2.0814
2.0740
2.0669
2.0599
2.0512
2.0345
1.9256
1.9162
1.8514
1.8448
1.8335
1.8295
1.8230
1.7954
1.7910
1.7725
1.7684
1.5889
1.2490
1.2394
1.2298
1.2215
1.2088
1.1991
1.1912
1.1704
1.1482
1.1418
1.1273
0.9536
O
H
H
H
O
F
CHO
O
Me
7b
1H NMR (600 MHz, CDCl3)
0.98
1.08
1.05
2.09
0.99
1.00
2.11
1.04
2.29
1.20
3.47
1.42
1.13
1.13
1.22
4.52
3.24
f1 (ppm)

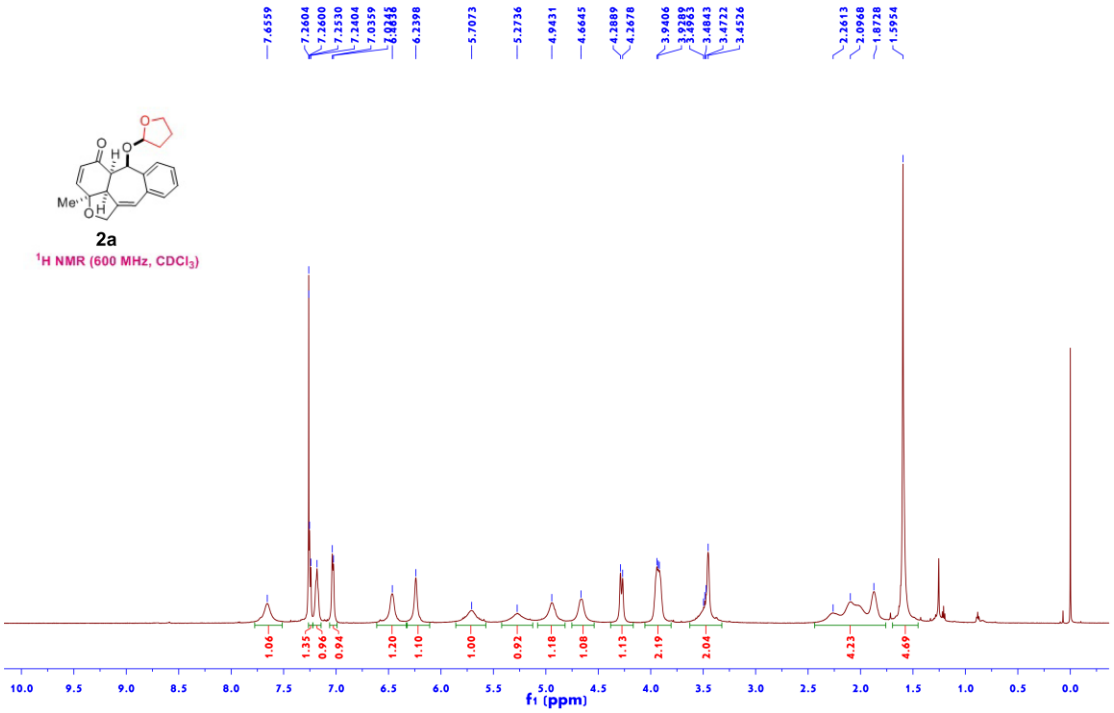

220.14
187.70
187.68
184.95
163.50
163.17
161.76
149.35
134.83
134.76
131.47
129.63
129.61
126.50
93.22
82.21
82.18
77.21
77.00
76.79
76.44
55.24
53.38
50.07
47.68
35.52
34.54
32.44
32.12
31.00
22.08
21.87
13.72
O
H
H
H
O
F
CHO
Me
O
7b
13C NMR (150 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

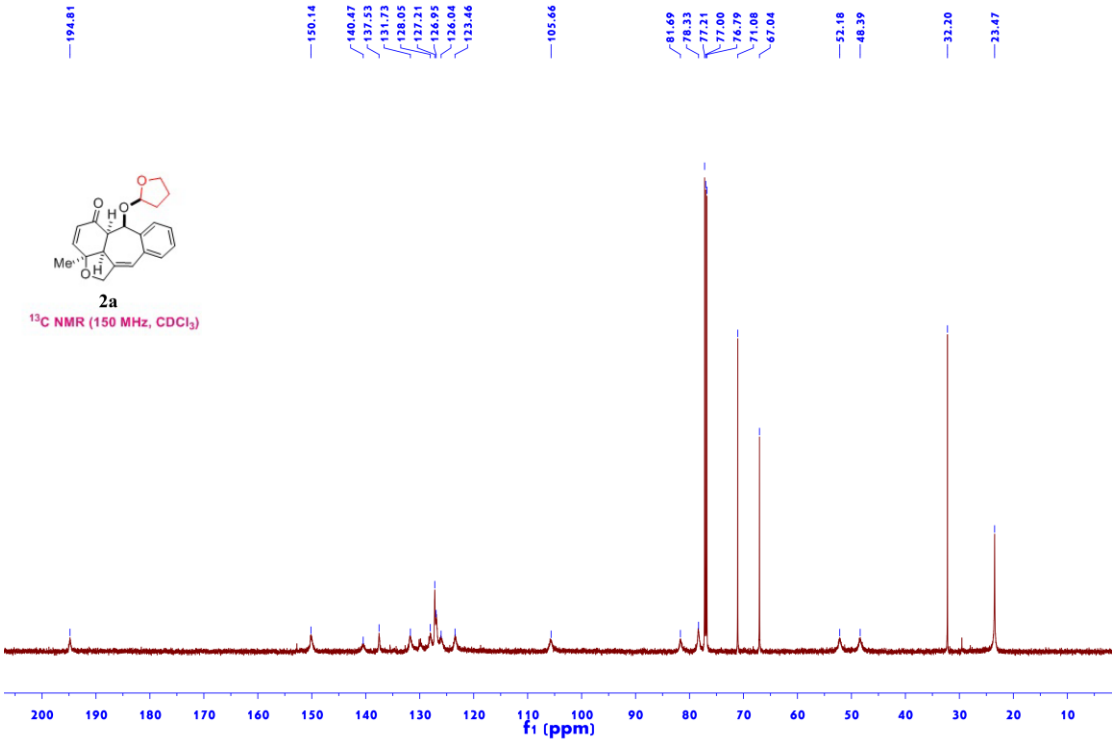

-116.3033
O
H
H
H
O
F
CHO
Me
O
7b
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

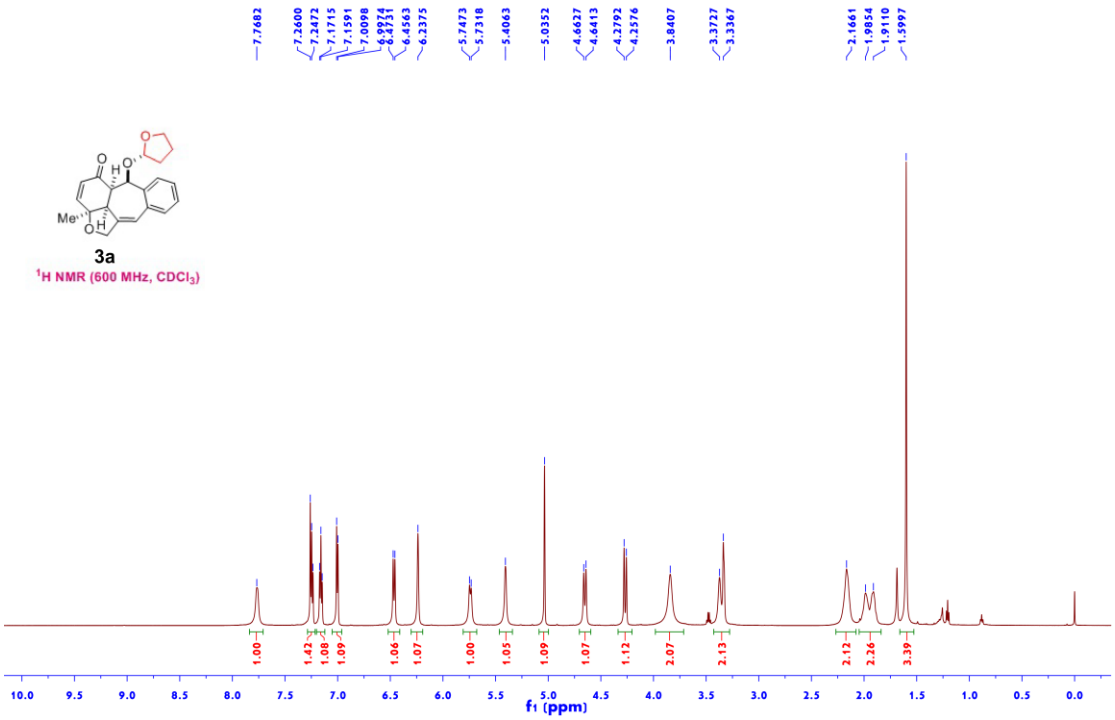

10.3912
7.8624
7.8587
7.5209
7.5172
7.5071
7.5033
7.4641
7.4503
7.2597
7.0938
7.0766
6.3969
6.3936
6.3797
6.3765
6.2221
6.2197
6.2173
4.1490
4.1468
2.6432
2.6361
2.4815
2.4670
2.4491
2.4344
2.4295
2.4247
2.4187
2.4038
2.2110
2.1981
2.1923
2.1060
2.0969
2.0910
2.0839
2.0757
2.0587
2.0435
1.9468
1.9373
1.8763
1.8737
1.8542
1.8517
1.8473
1.8068
1.8025
1.7840
1.6070
1.2697
1.2602
1.2537
1.2476
1.2421
1.2363
1.2303
1.2228
1.1974
1.1739
1.1674
1.1530
1.1464
0.9710
Cl
O
H
H
H
O
Me
O
CHO
7d
1H NMR (600 MHz, CDCl3)
0.94
0.96
1.00
1.02
1.00
0.99
0.97
2.10
1.00
2.11
1.04
3.17
1.15
1.06
1.06
1.03
4.36
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


220.05
189.96
184.90
162.99
149.06
137.21
135.58
134.54
133.76
131.69
127.29
126.65
124.05
93.63
81.09
77.21
77.00
76.79
76.48
55.25
53.35
50.13
47.71
35.57
34.63
32.47
32.20
31.05
22.13
21.94
13.79
Cl
O
H
H
H
O
Me
O
CHO
7d
13C NMR (150 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7f
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
7f
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

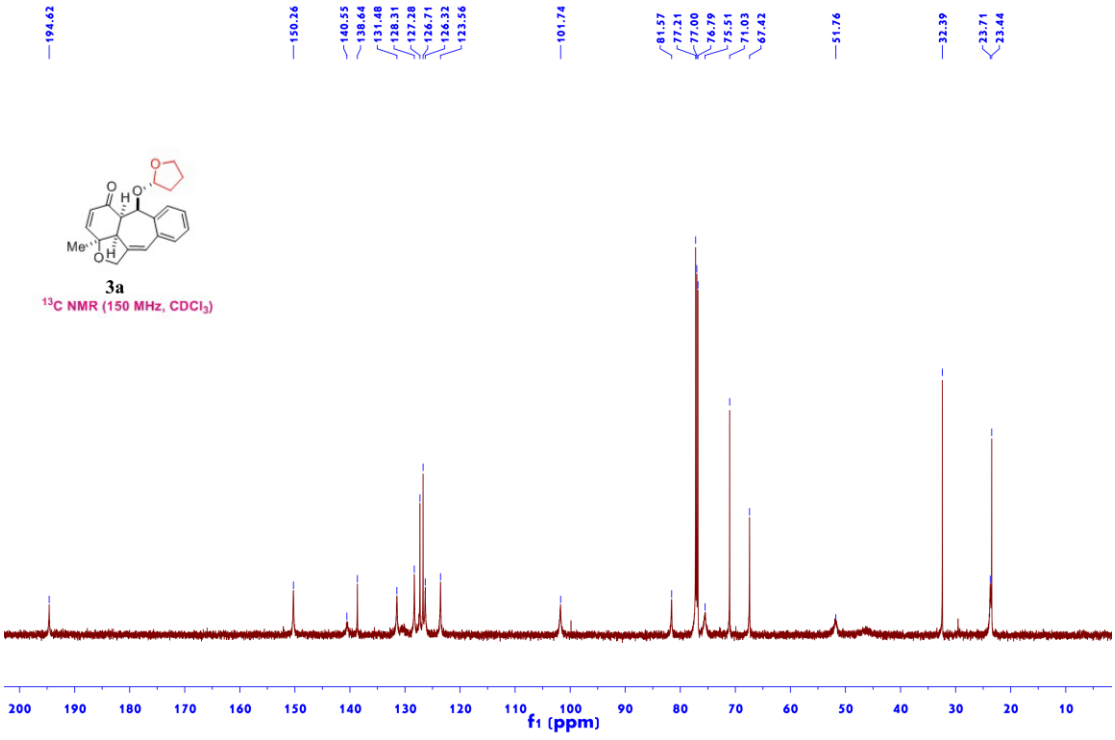

2a
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)


2a
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)



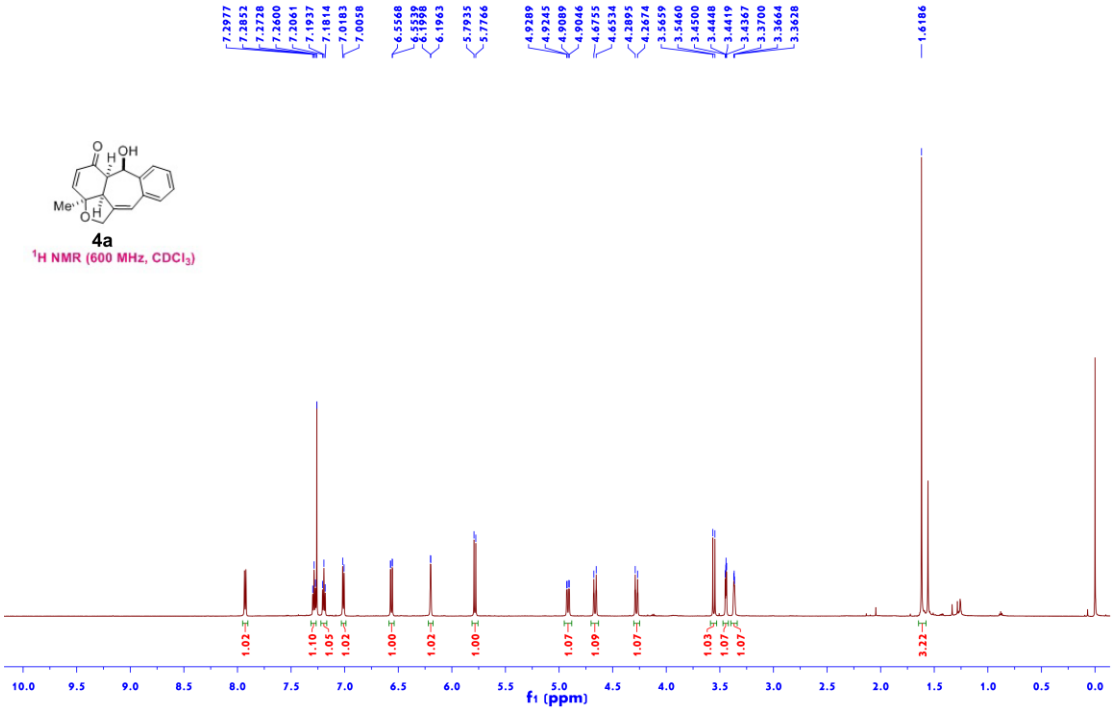
3a

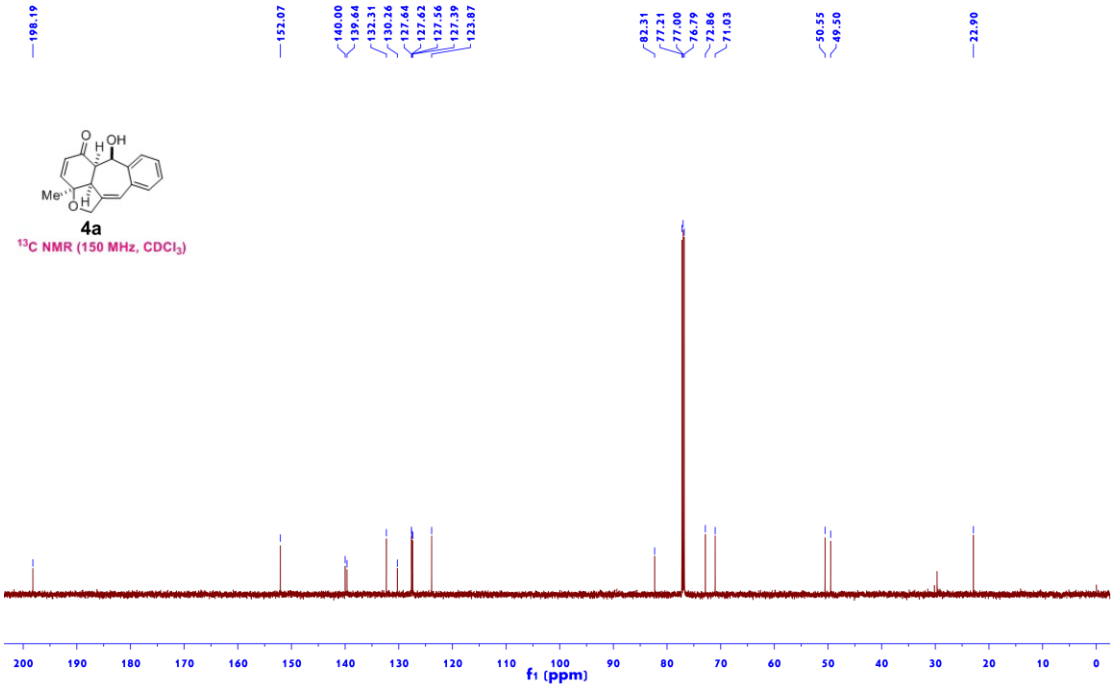
^{1}H NMR (600 MHz, $CDCl_3$)

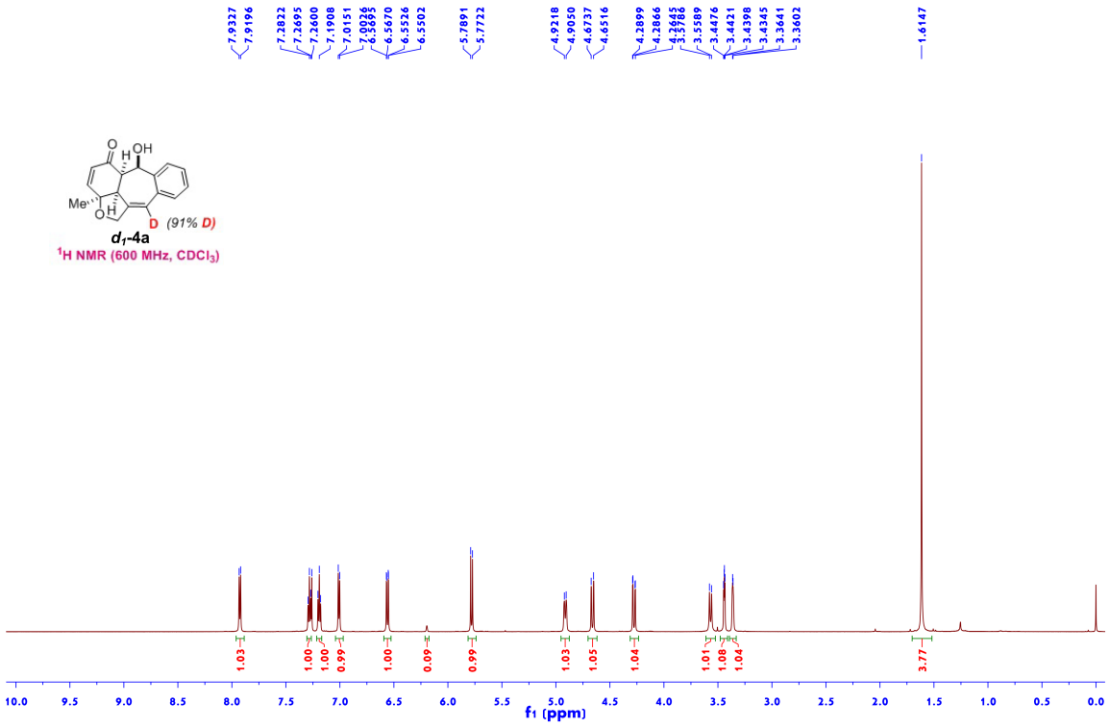


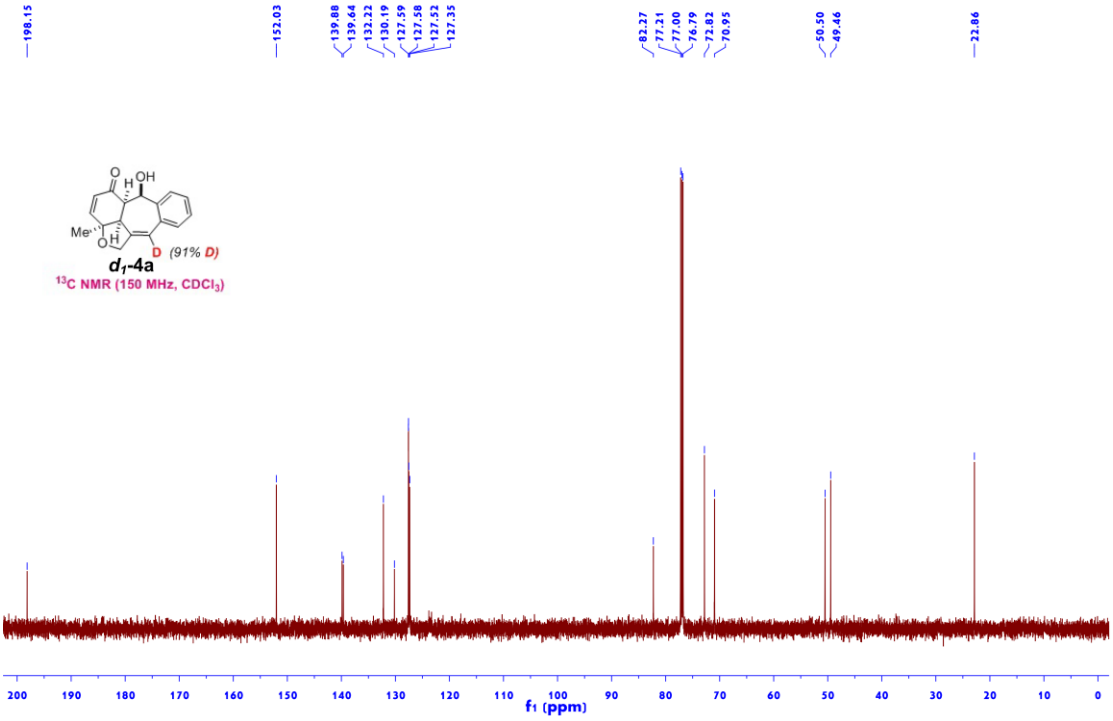
3a

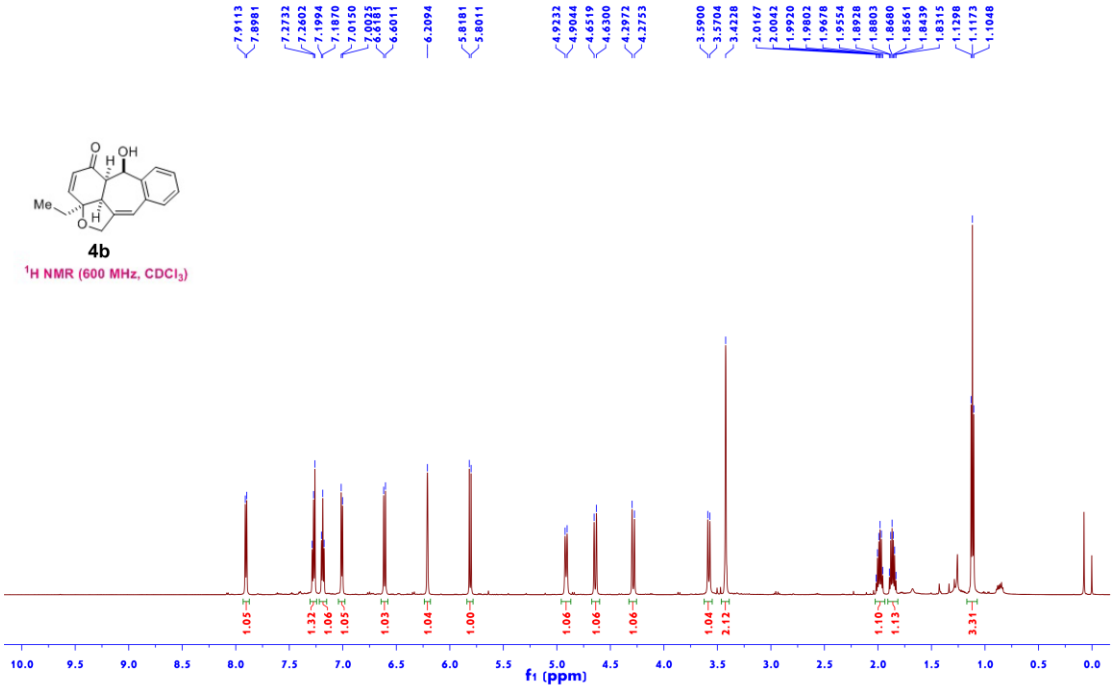
^{13}C NMR (150 MHz, $CDCl_3$)

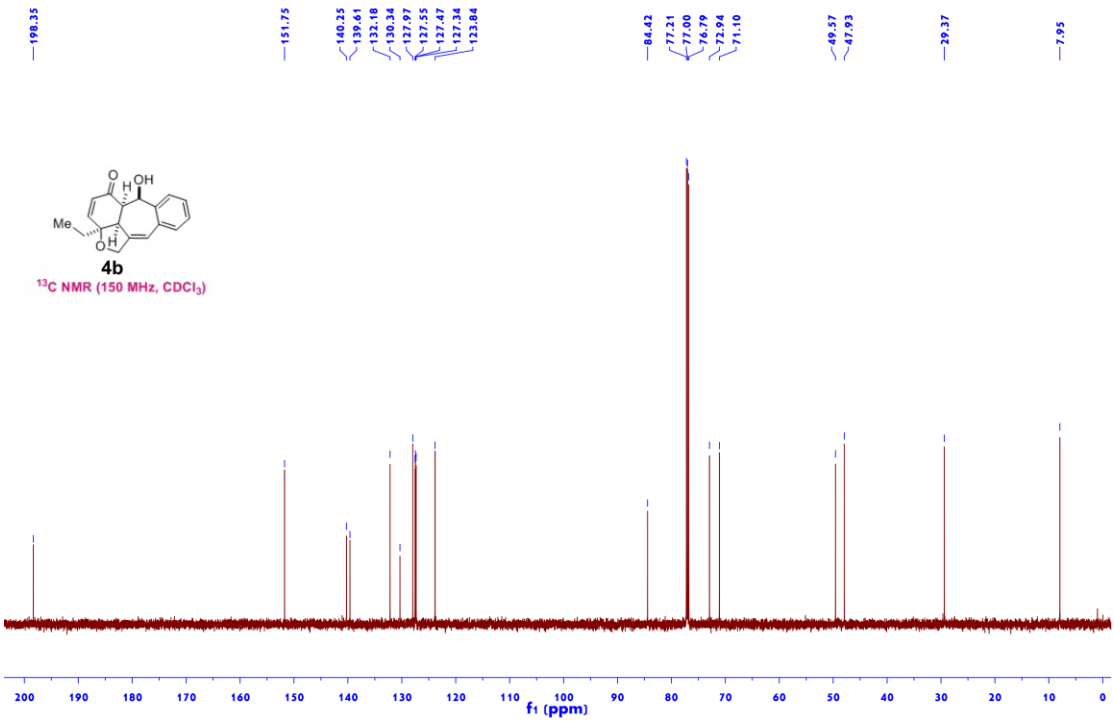

7.2977
7.2852
7.2728
7.2600
7.2061
7.1937
7.1814
7.0183
7.0058
6.5568
6.5538
6.1998
6.1963
5.7935
5.7766
4.9289
4.9245
4.9089
4.9046
4.6755
4.6534
4.2895
4.2674
3.5659
3.5460
3.4500
3.4448
3.4419
3.4367
3.3700
3.3664
3.3628
1.6186
O
H
OH
Me
O
H
4a
1H NMR (600 MHz, CDCl3)
1.02
1.10
1.05
1.02
1.00
1.02
1.00
1.07
1.09
1.07
1.03
1.07
1.07
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

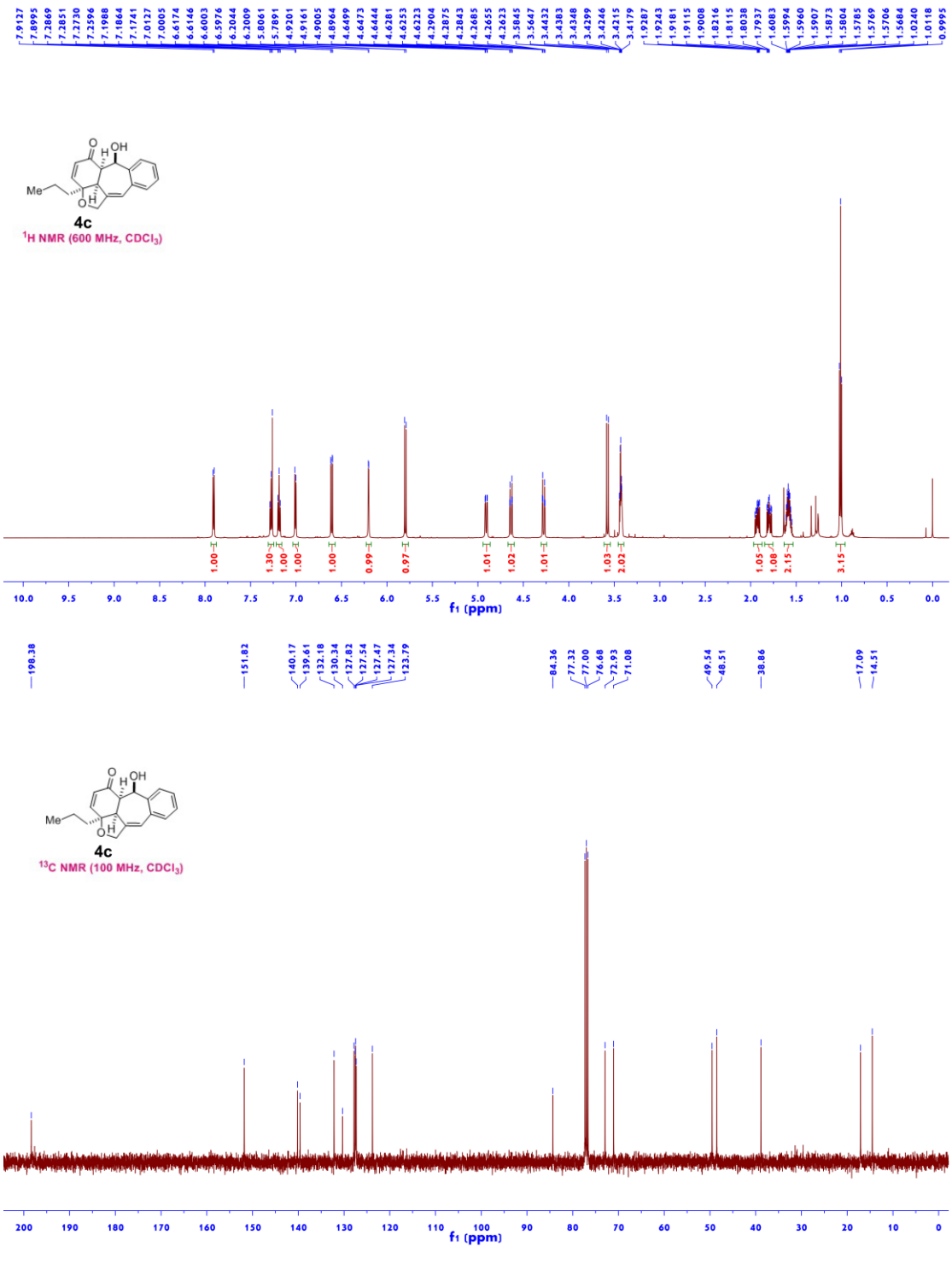

198.19
152.07
140.00
139.64
132.31
130.26
127.64
127.62
127.56
127.39
123.87
82.31
77.21
77.00
76.79
72.86
71.03
50.55
49.50
22.90
O
H
OH
Me
O
H
4a
13C NMR (150 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

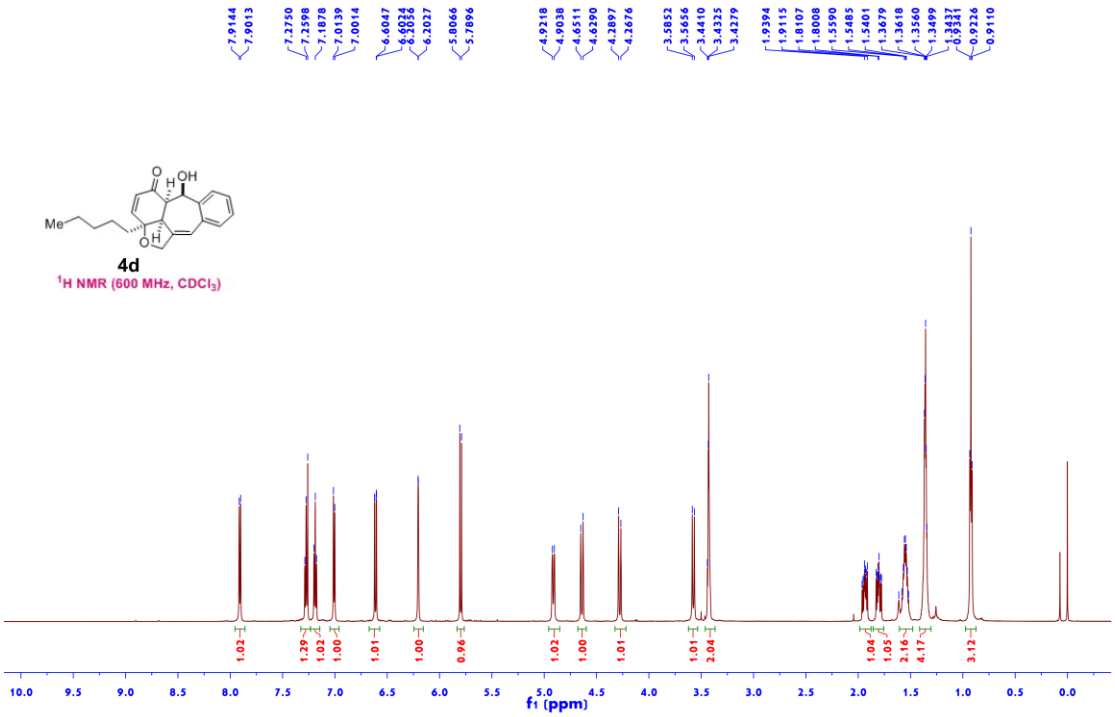

7.9327
7.9196
7.2822
7.2695
7.2600
7.1908
7.0151
6.5670
6.5526
6.5502
5.7891
5.7722
4.9218
4.9050
4.6737
4.6516
4.2899
4.2866
3.5589
3.4476
3.4421
3.4398
3.4345
3.3641
3.3602
1.6147
O
H
OH
Me
OH
H
D
(91% D)
d1-4a
1H NMR (600 MHz, CDCl3)
1.03
1.00
1.00
0.99
1.00
0.09
0.99
1.03
1.05
1.04
1.01
1.08
1.04
3.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

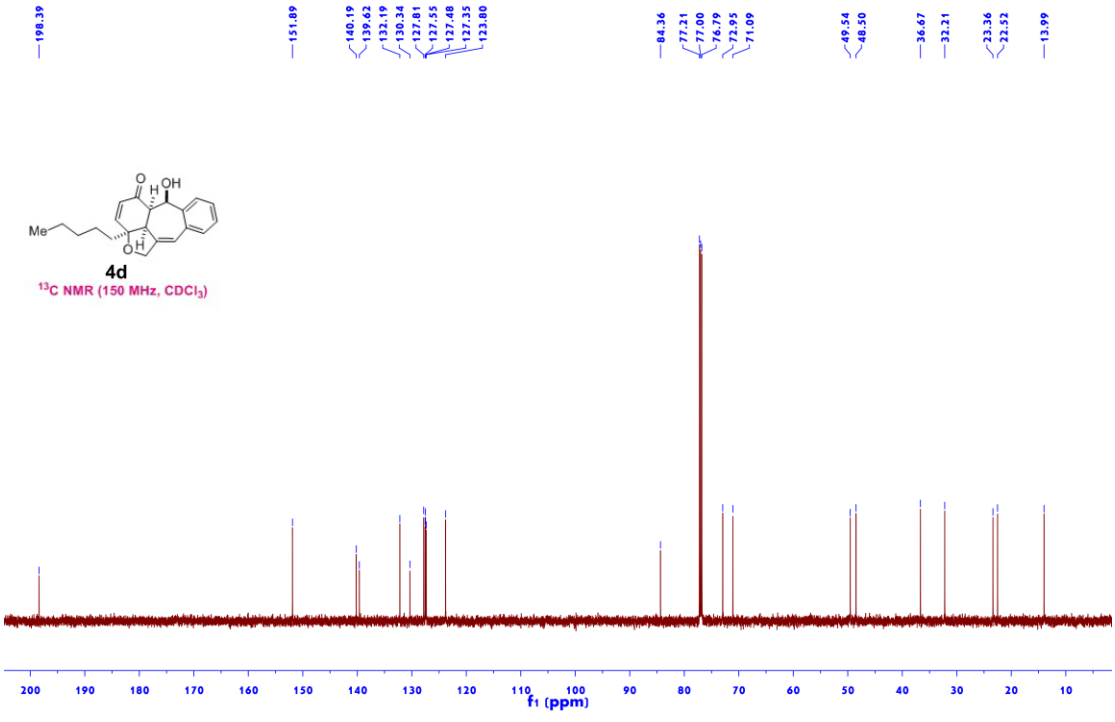

198.15
152.03
139.88
139.64
132.22
130.19
127.59
127.58
127.52
127.35
82.27
77.21
77.00
76.79
72.82
70.95
50.50
49.46
22.86
O
H
OH
Me
OH
H
D
(91% D)
d1-4a
13C NMR (150 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

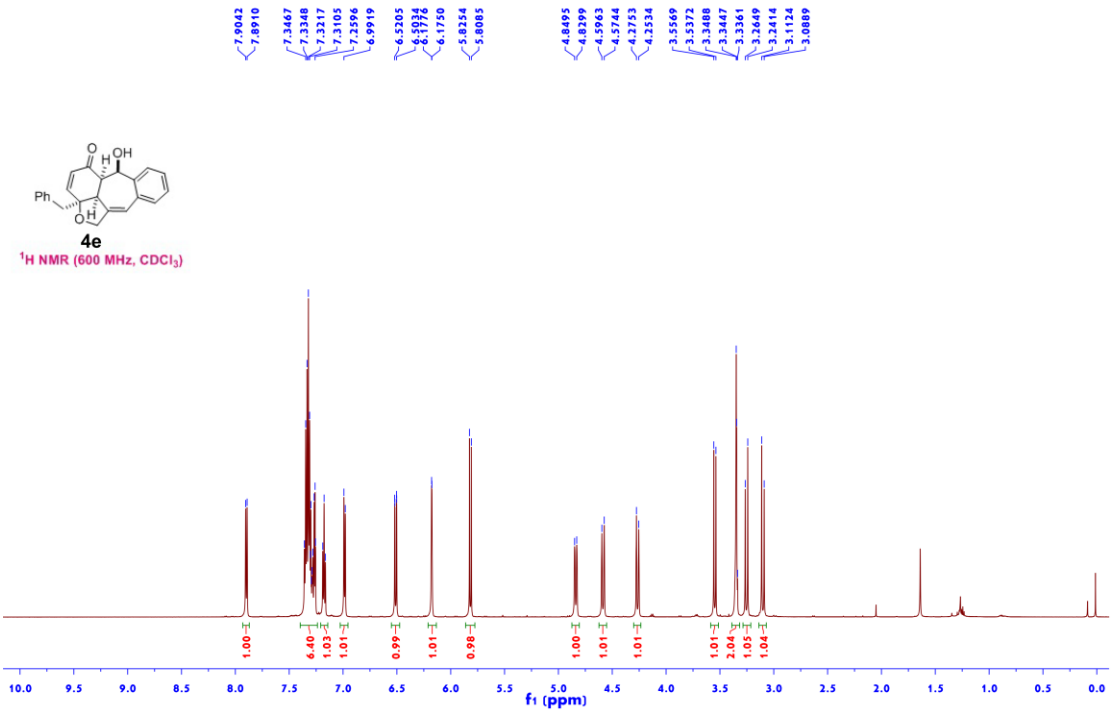

4b
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)


4b
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)


4c
1H NMR (600 MHz, CDCl3)
4c
13C NMR (100 MHz, CDCl3)
f1 (ppm)


4d
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


4d
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)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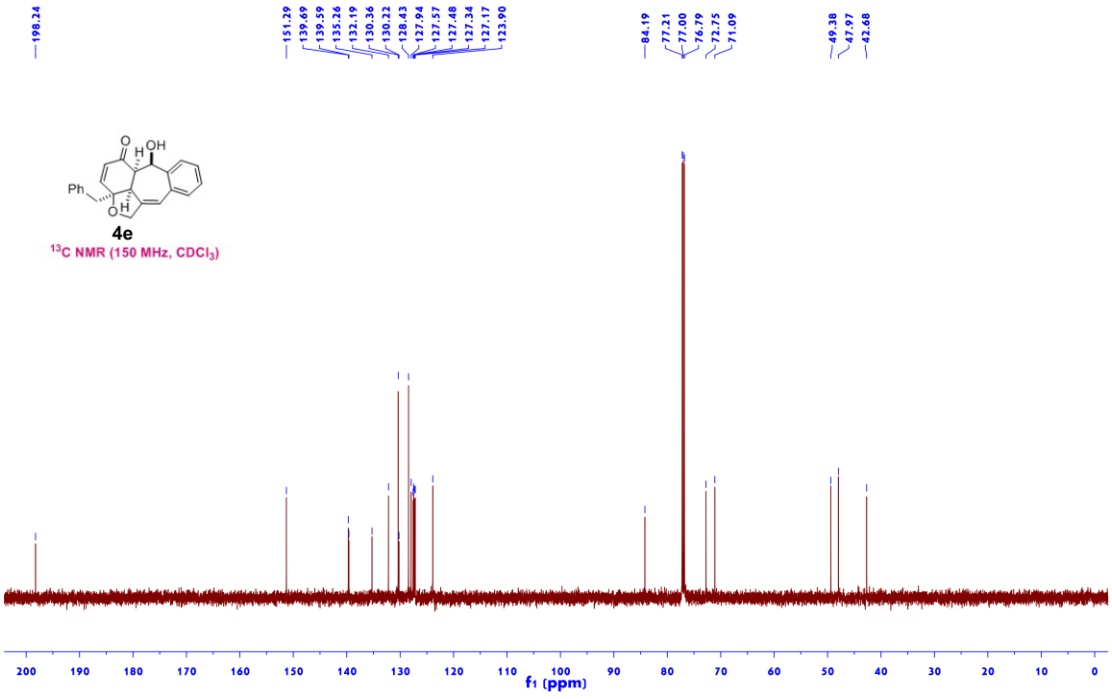
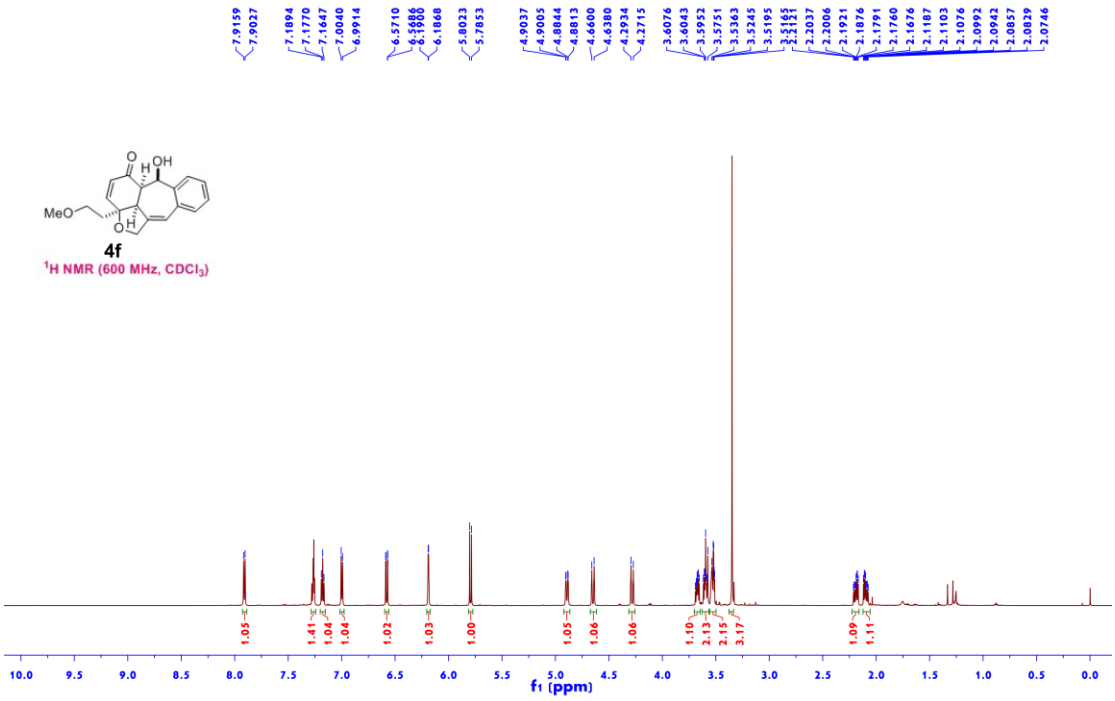
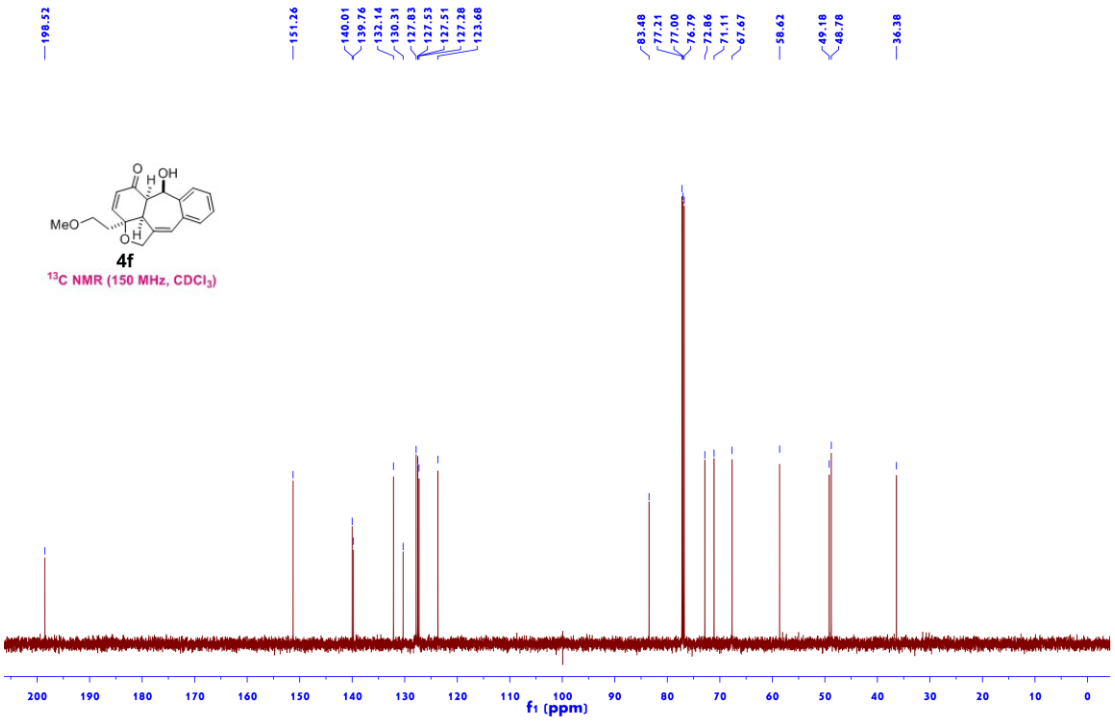
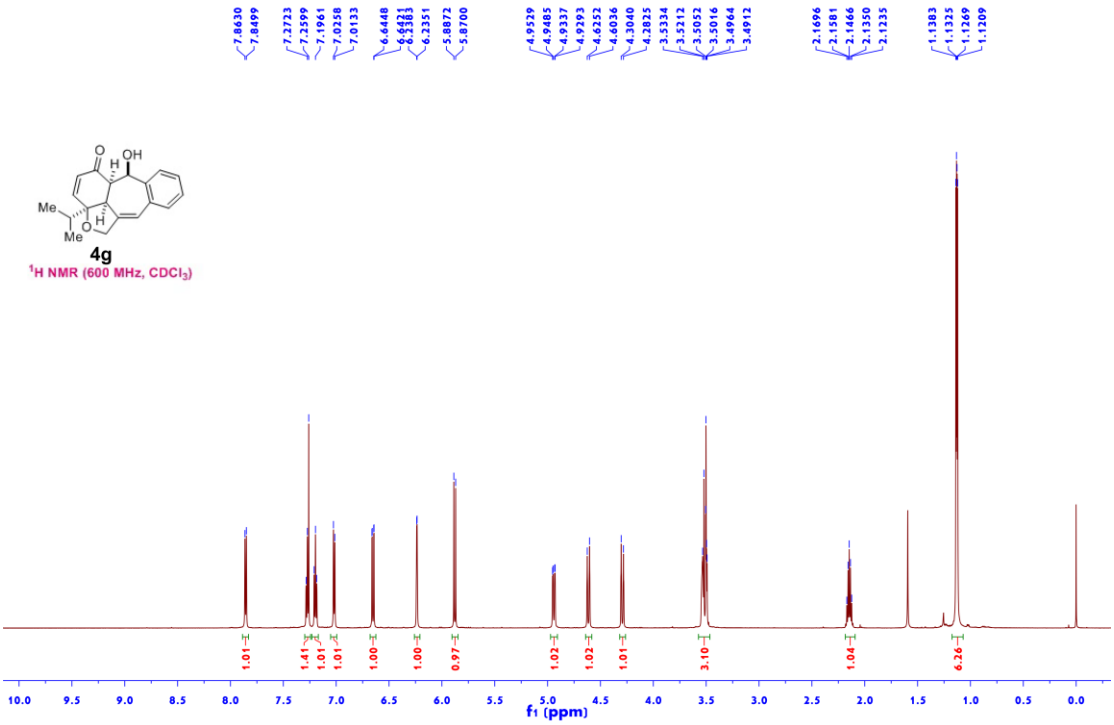
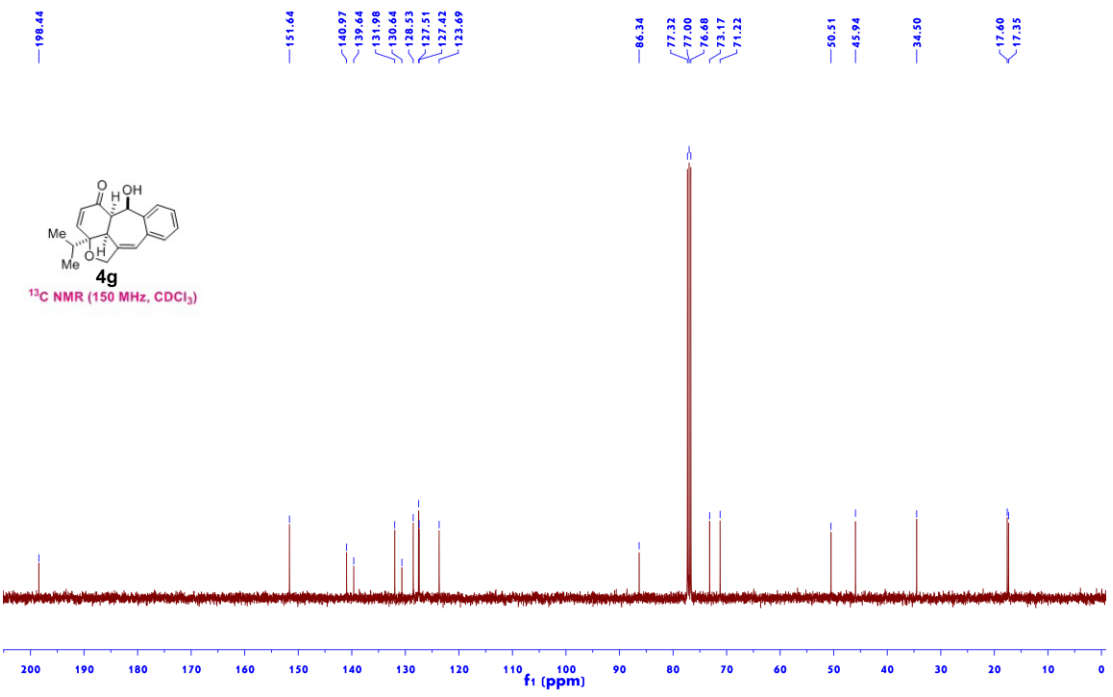
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)

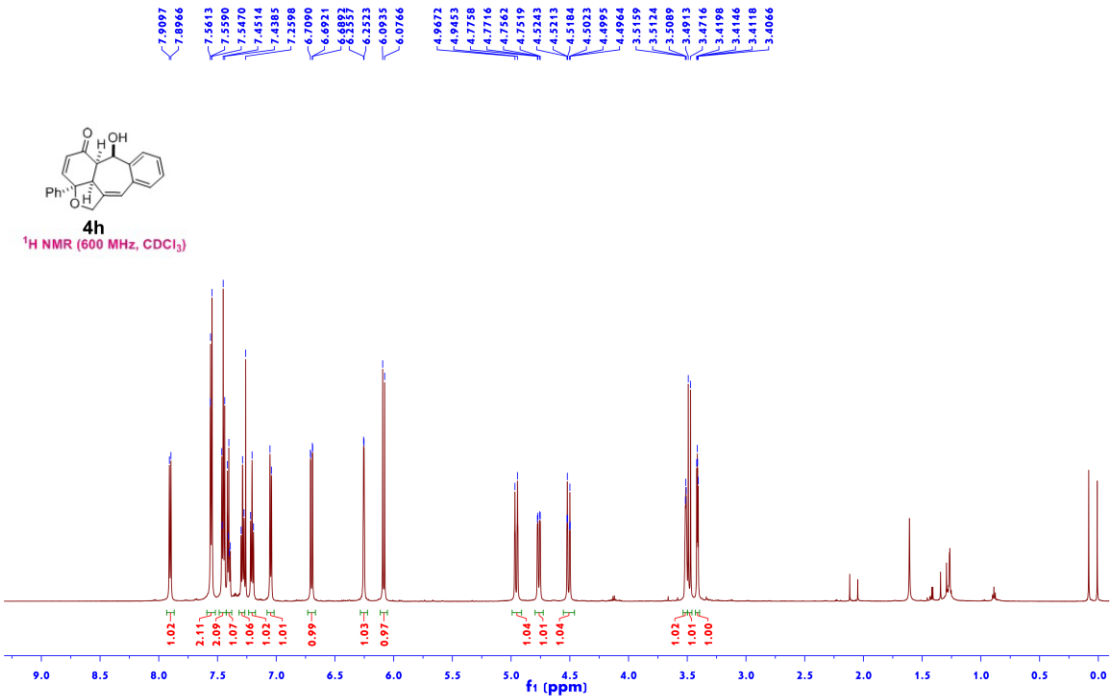

4e
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)

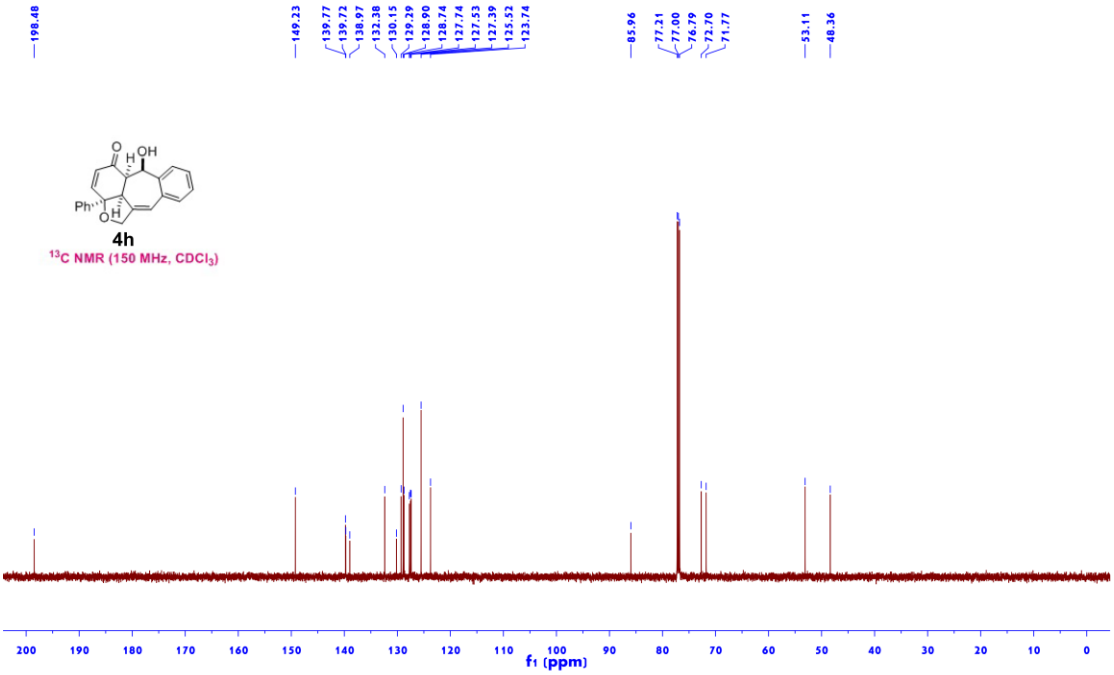

4f
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)

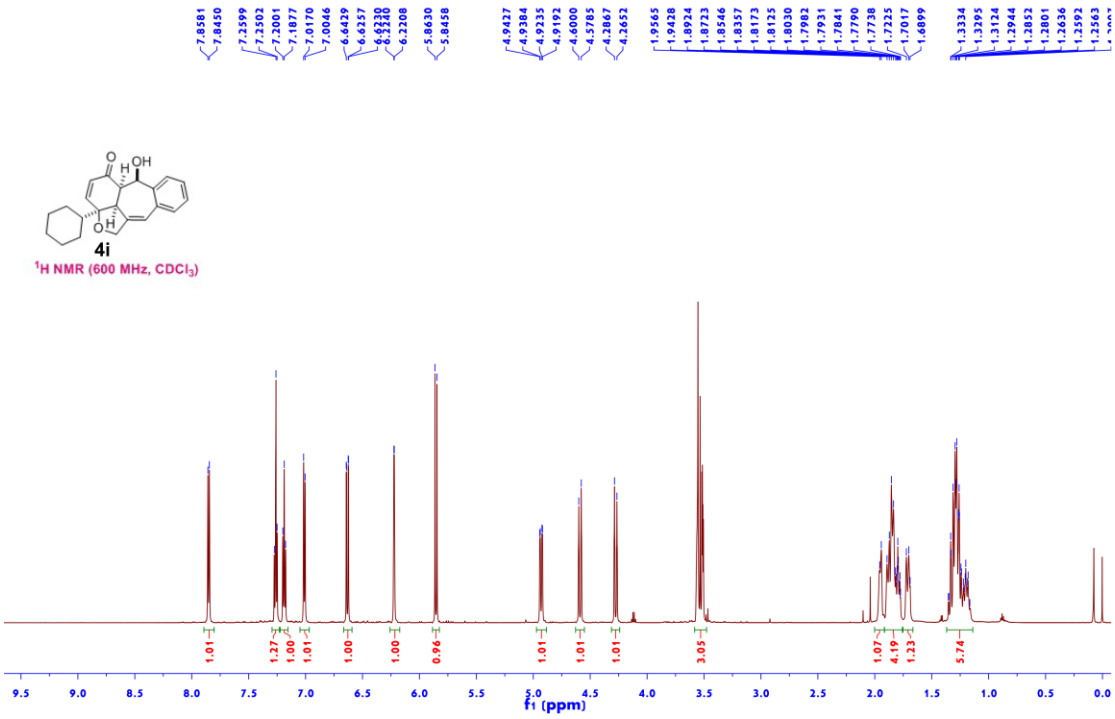

4f
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)

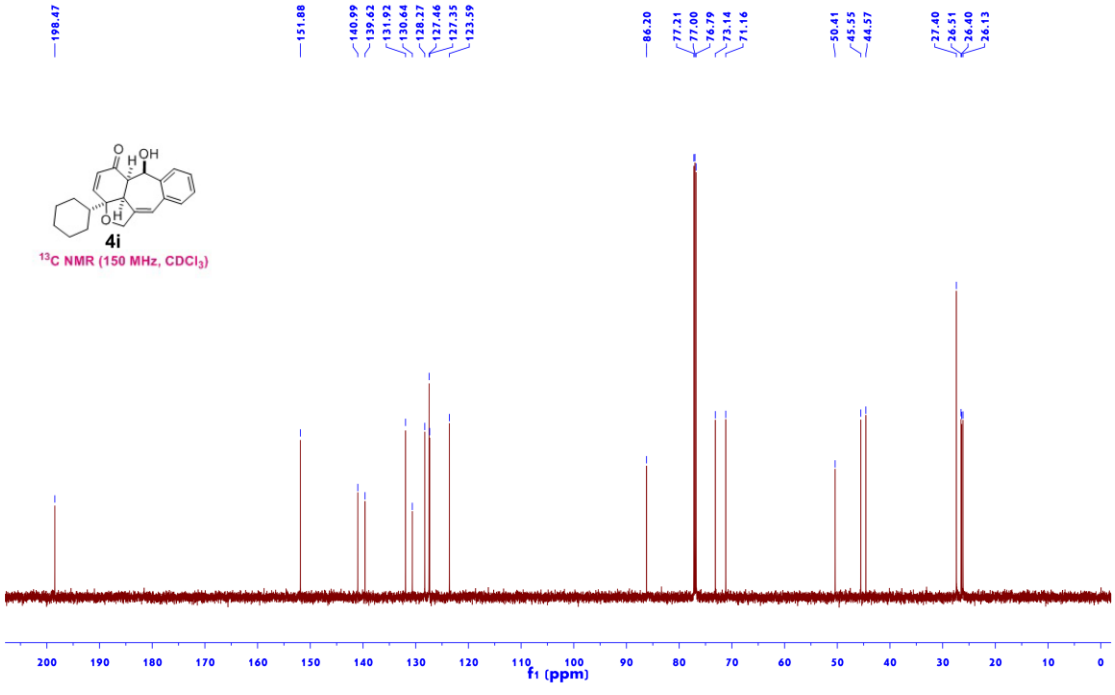

4g
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

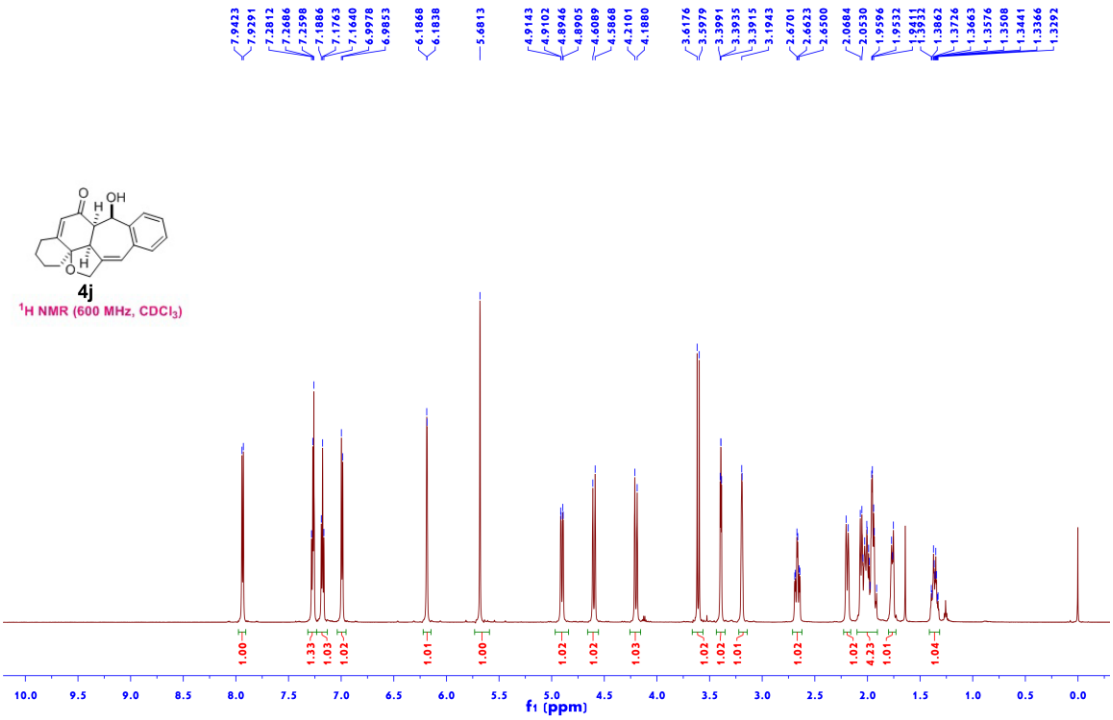

4g
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)

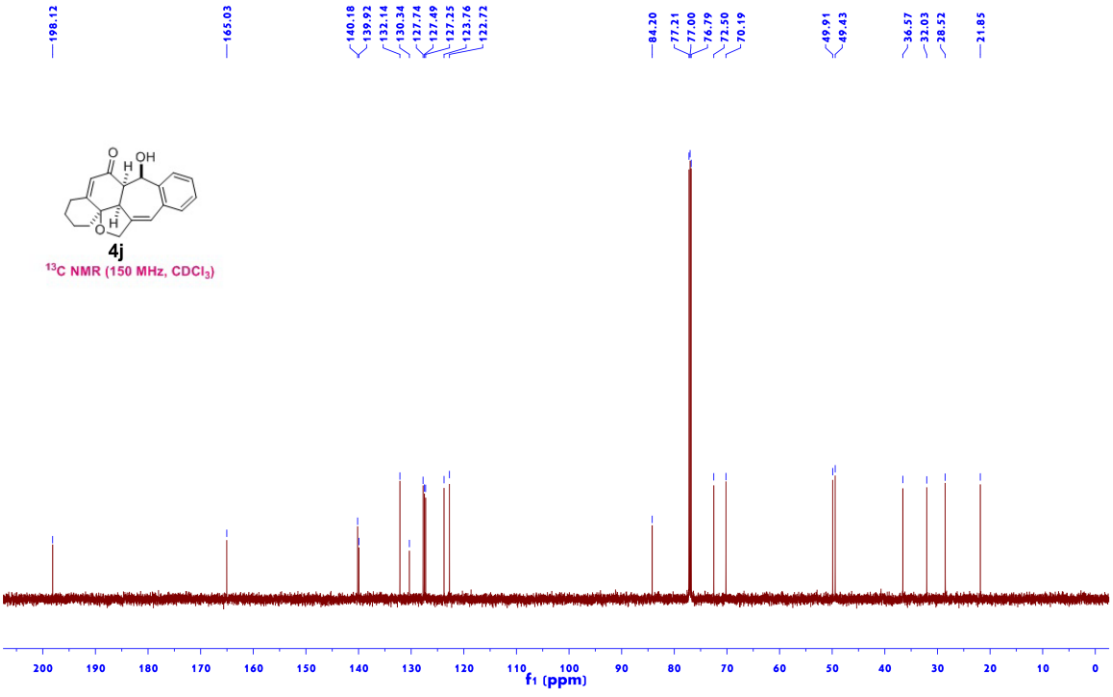

4h
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)

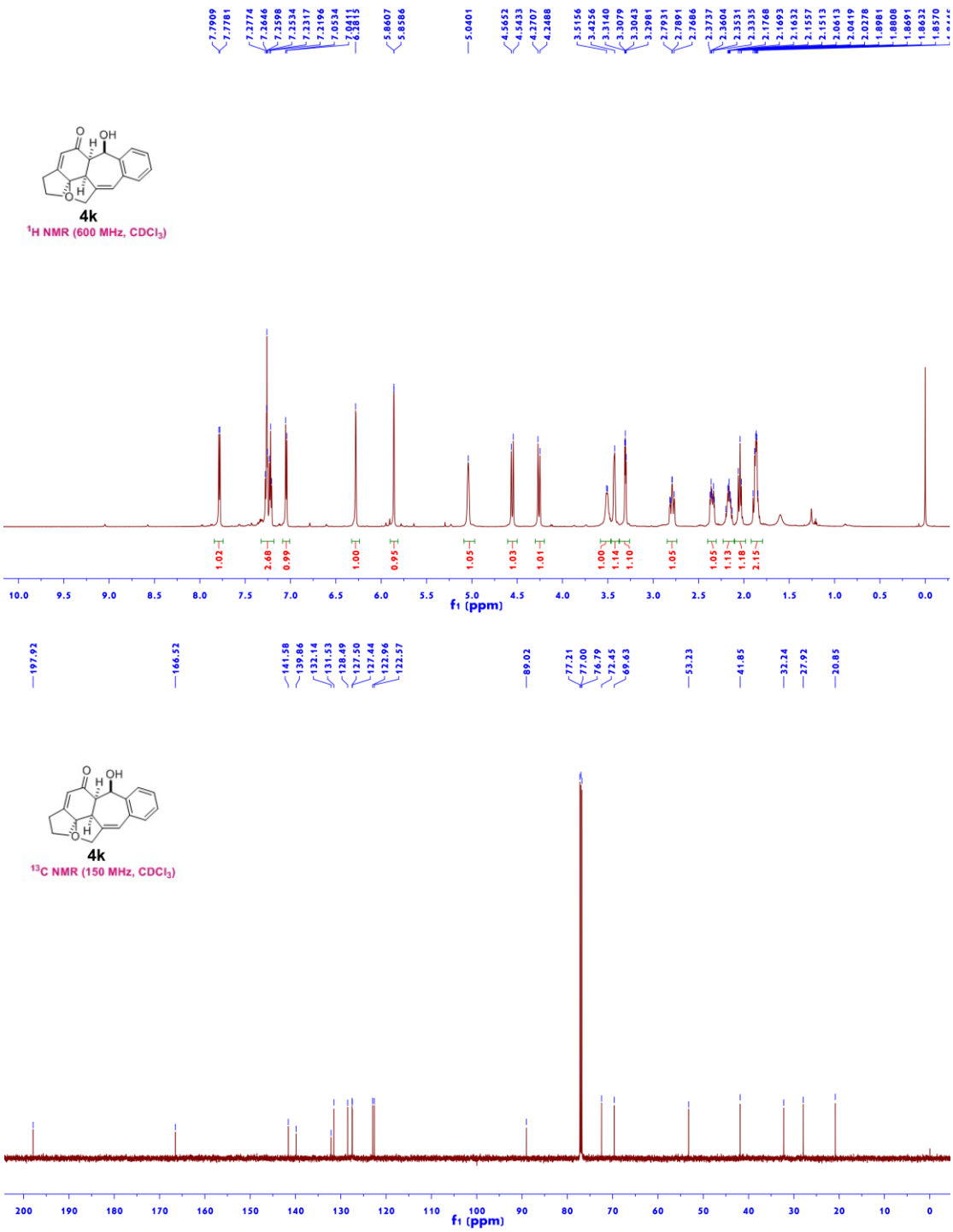

4h
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)

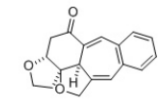

4i
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


4i
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)


4j
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

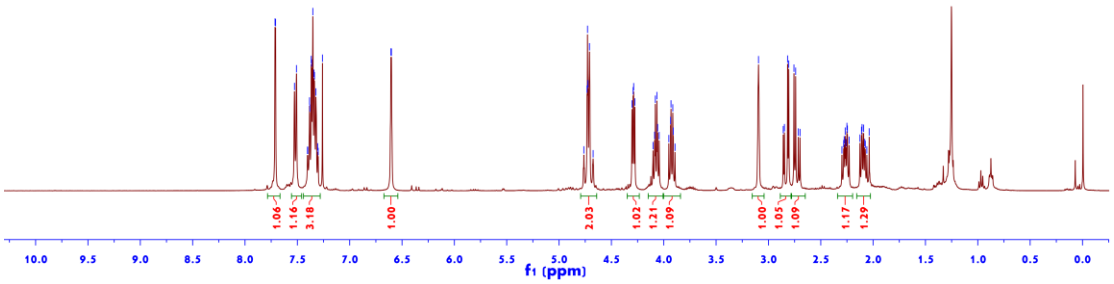

4j
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)

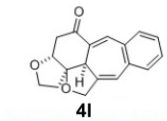

4k
1H NMR (600 MHz, CDCl3)
4k
13C NMR (150 MHz, CDCl3)
f1 (ppm)



4l

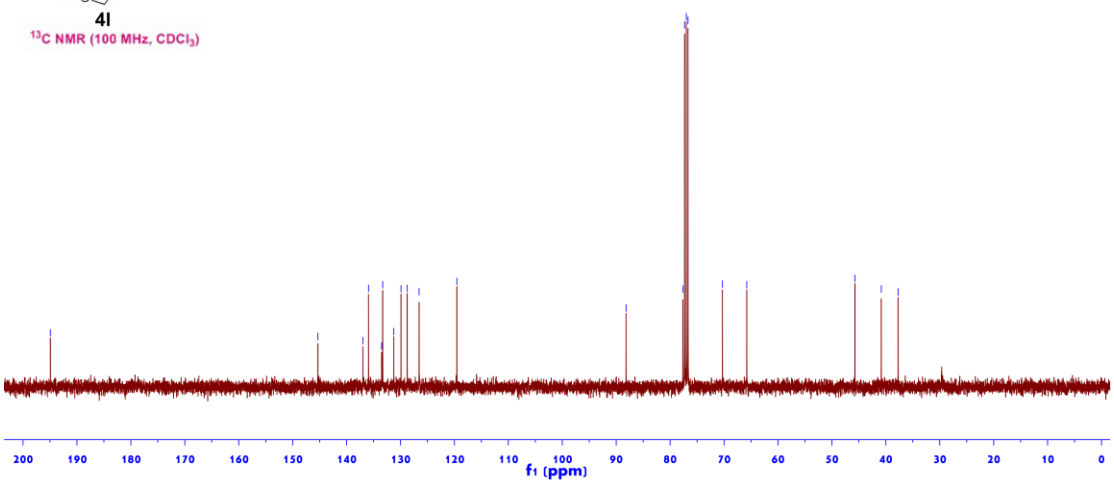
^{1}H NMR (400 MHz, $CDCl_3$)

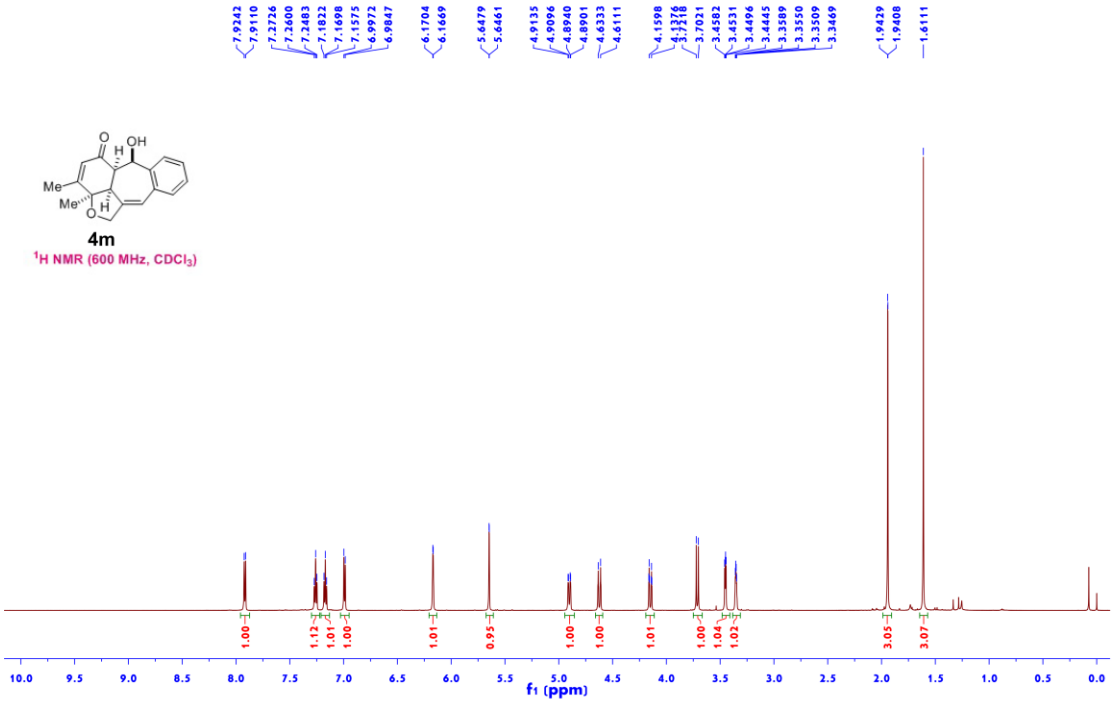


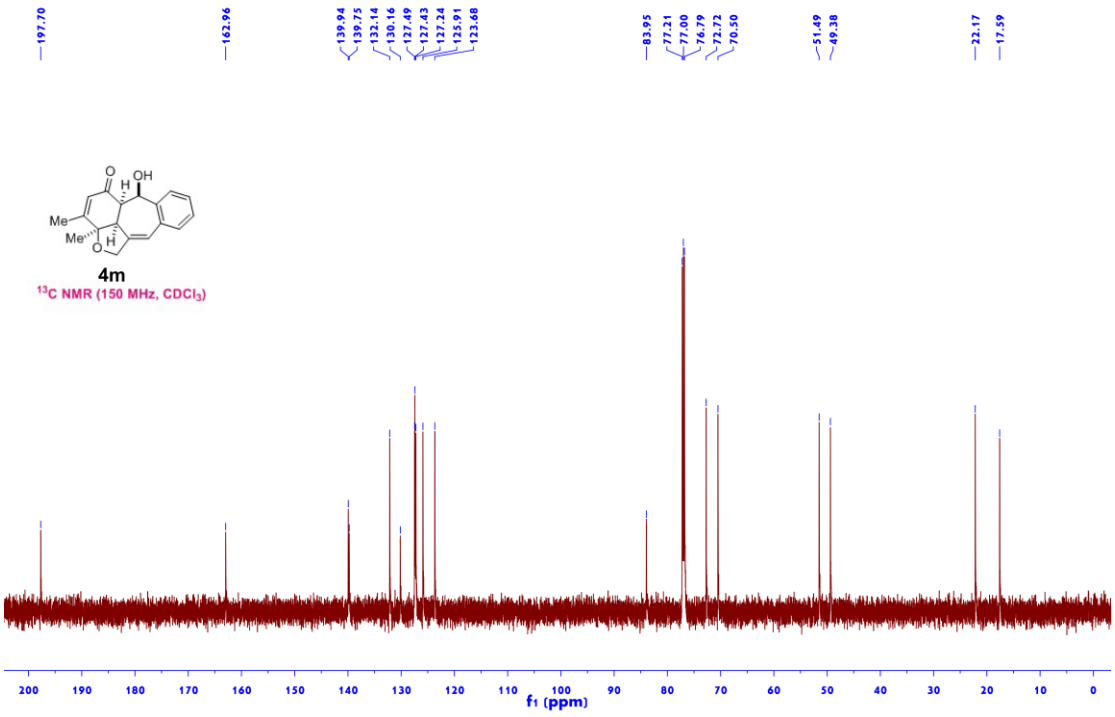


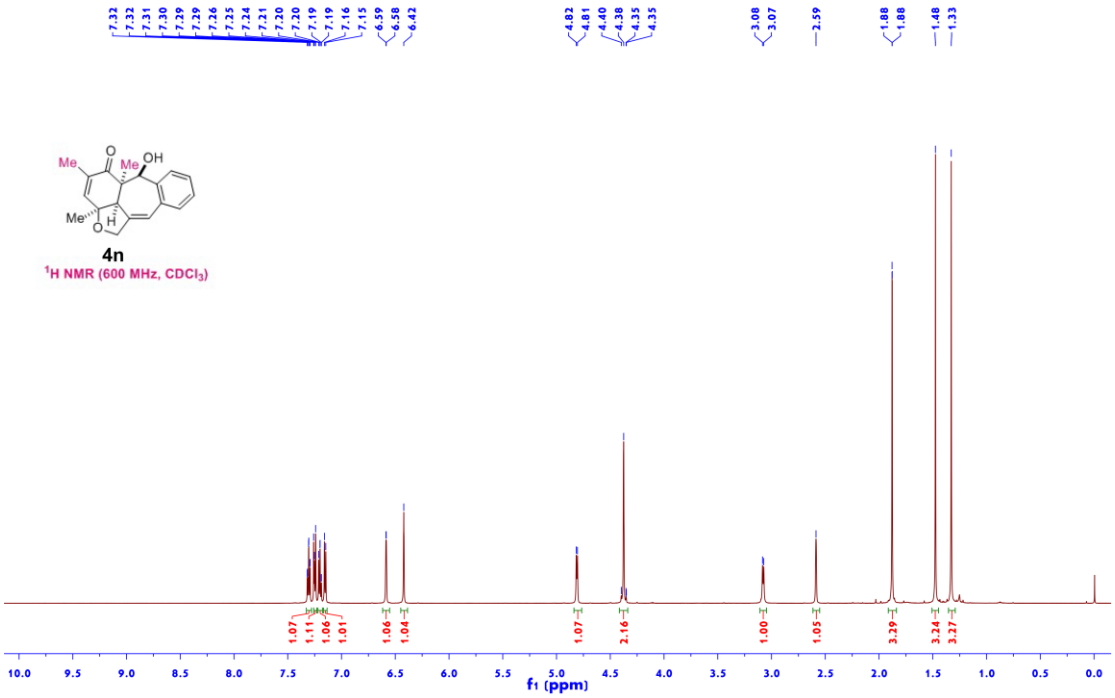
4l

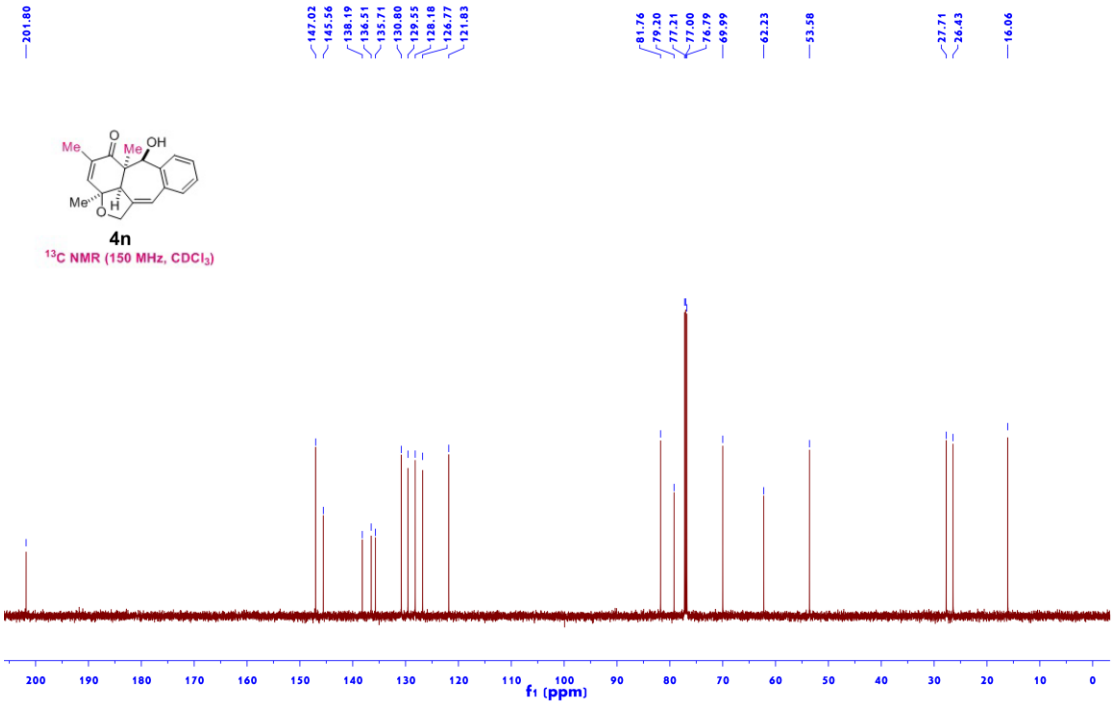
^{13}C NMR (100 MHz, $CDCl_3$)

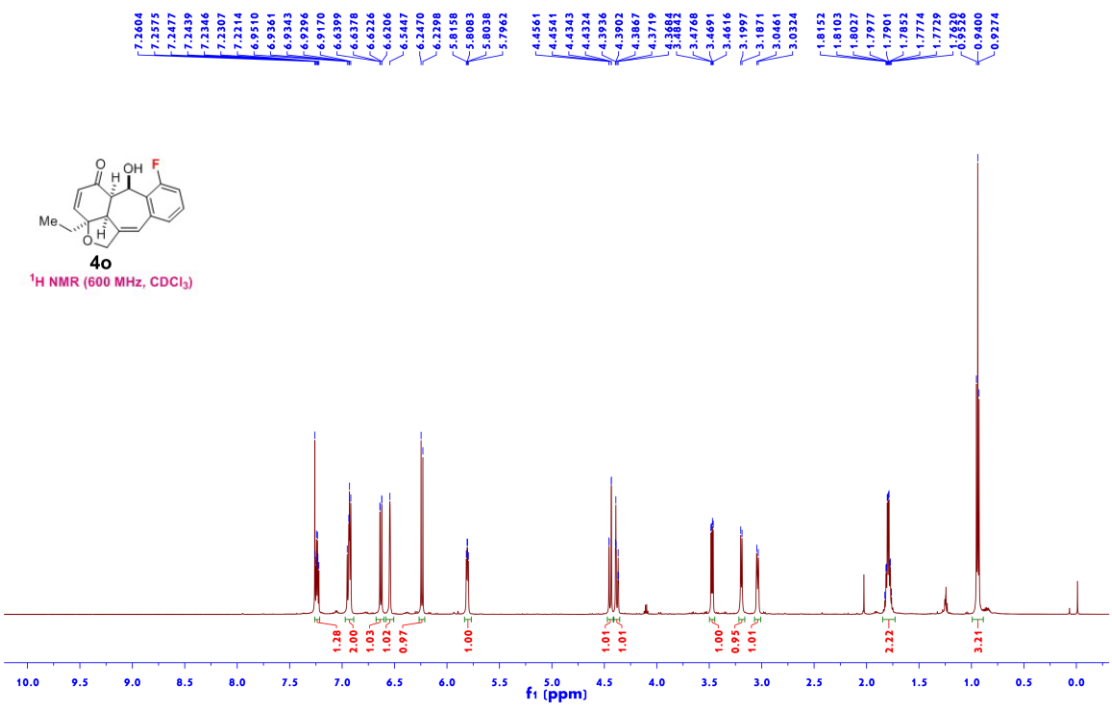


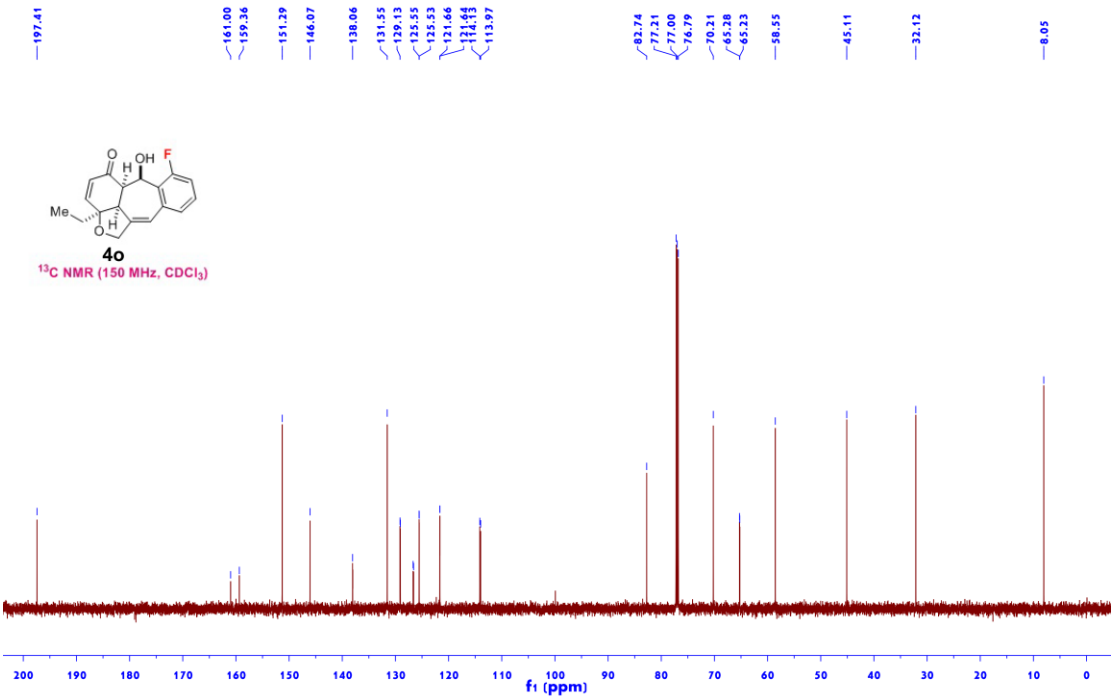

4m
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)

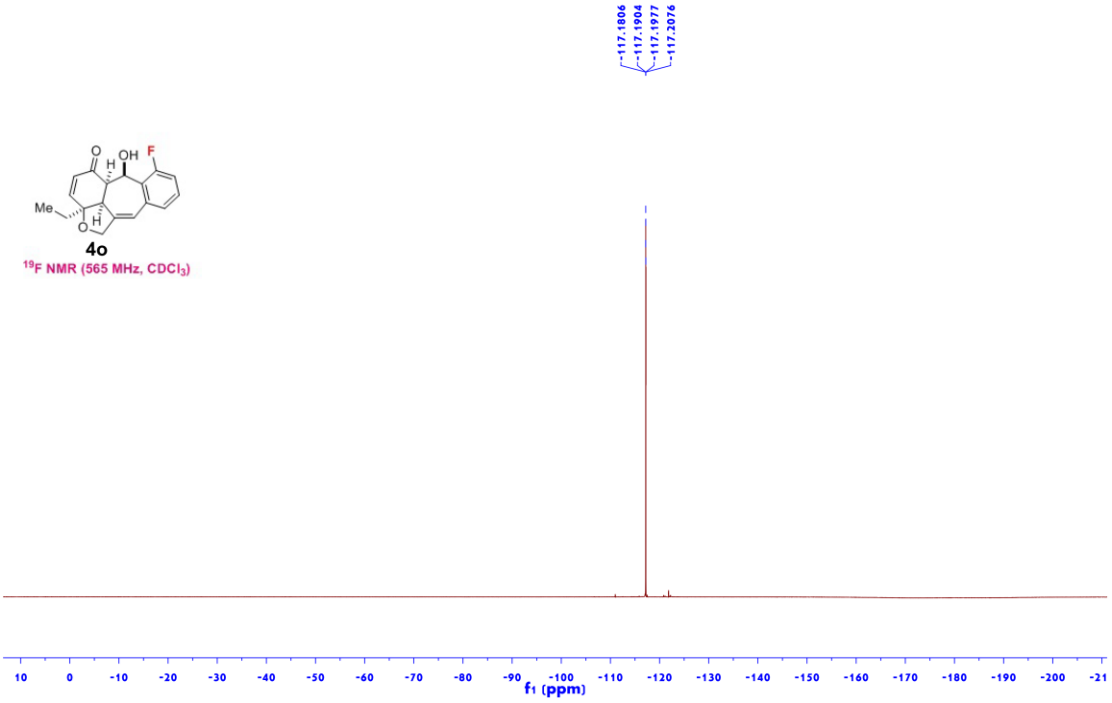

4m
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)

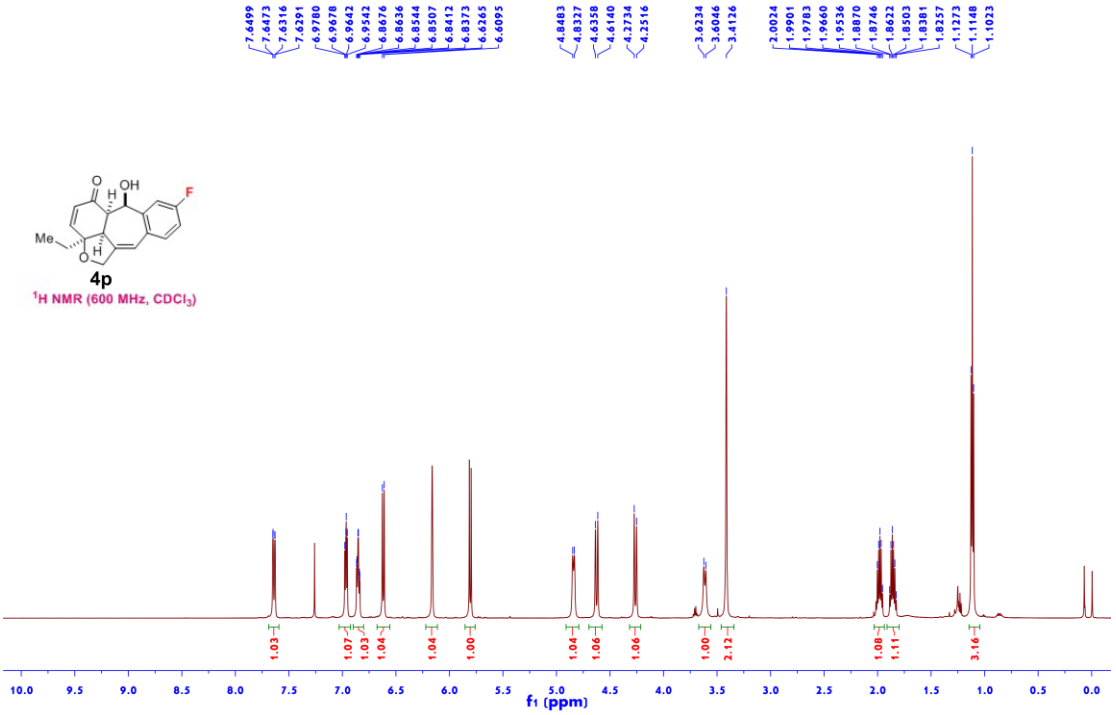

4n
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)

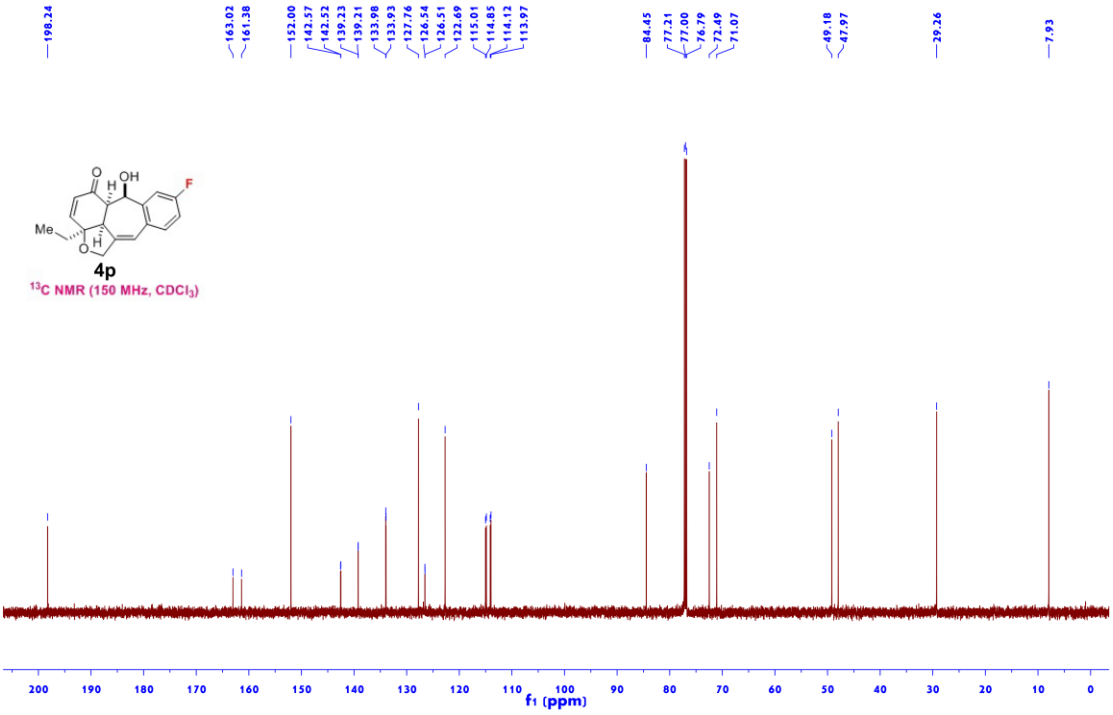

4n
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)

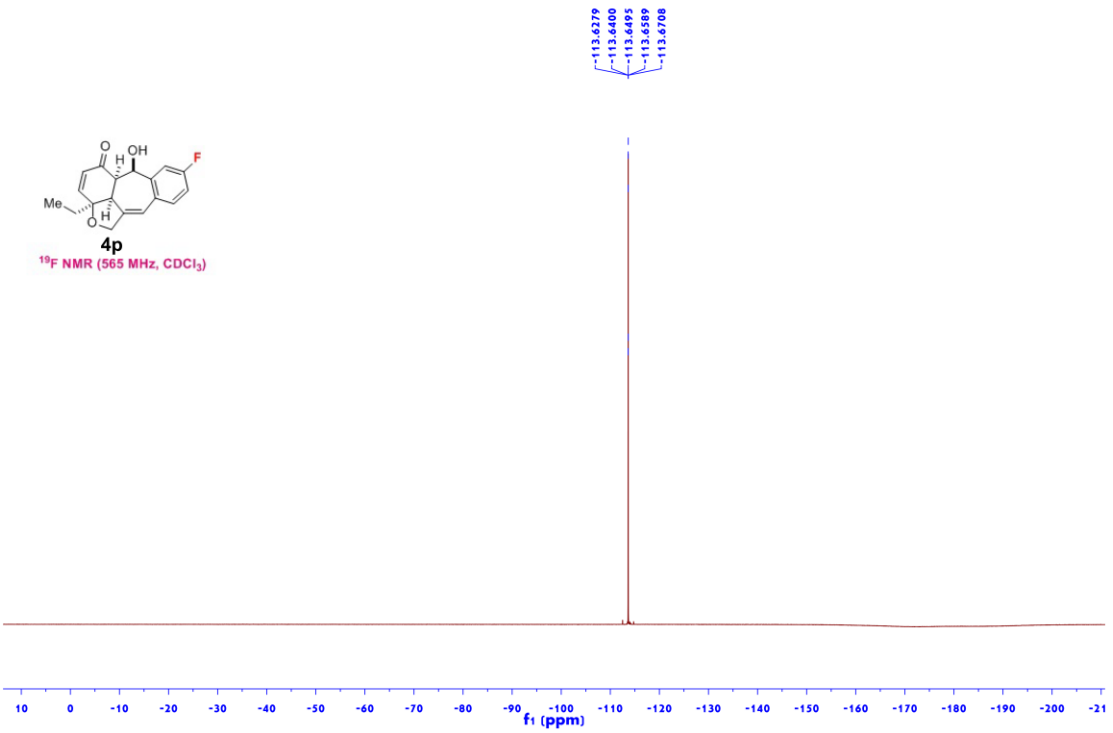

4o
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)

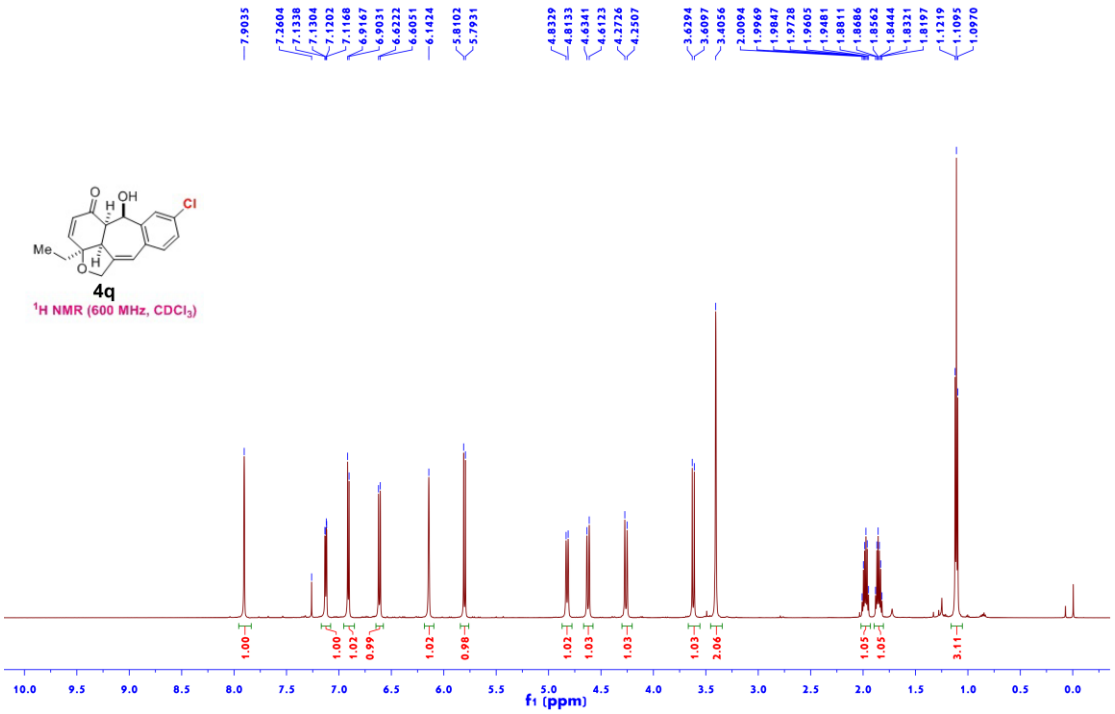

4o
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)

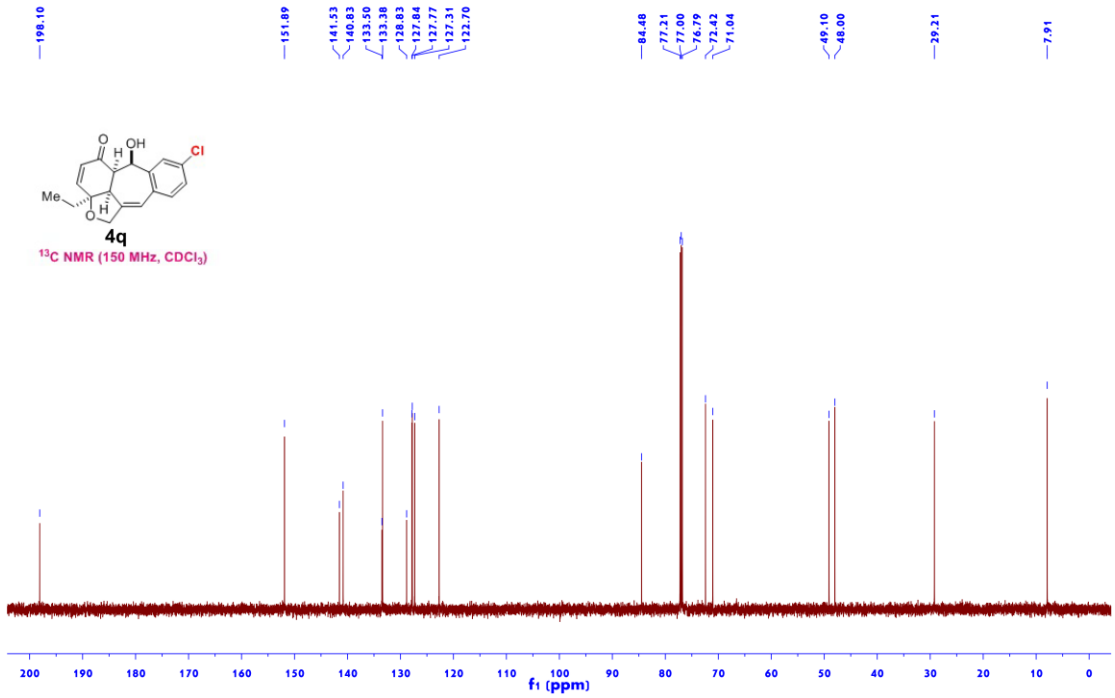

-117.1806
-117.1904
-117.1977
-117.2076
4o
^{19}F NMR (565 MHz, CDCl$_3$)
f1 (ppm)

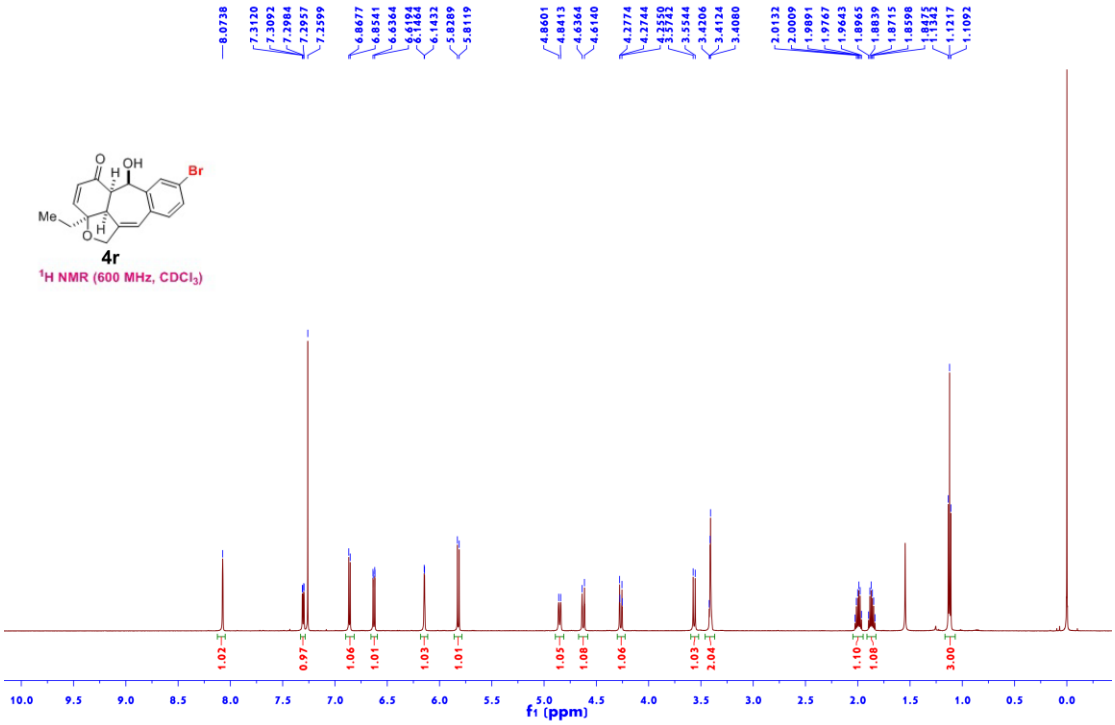

4p
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

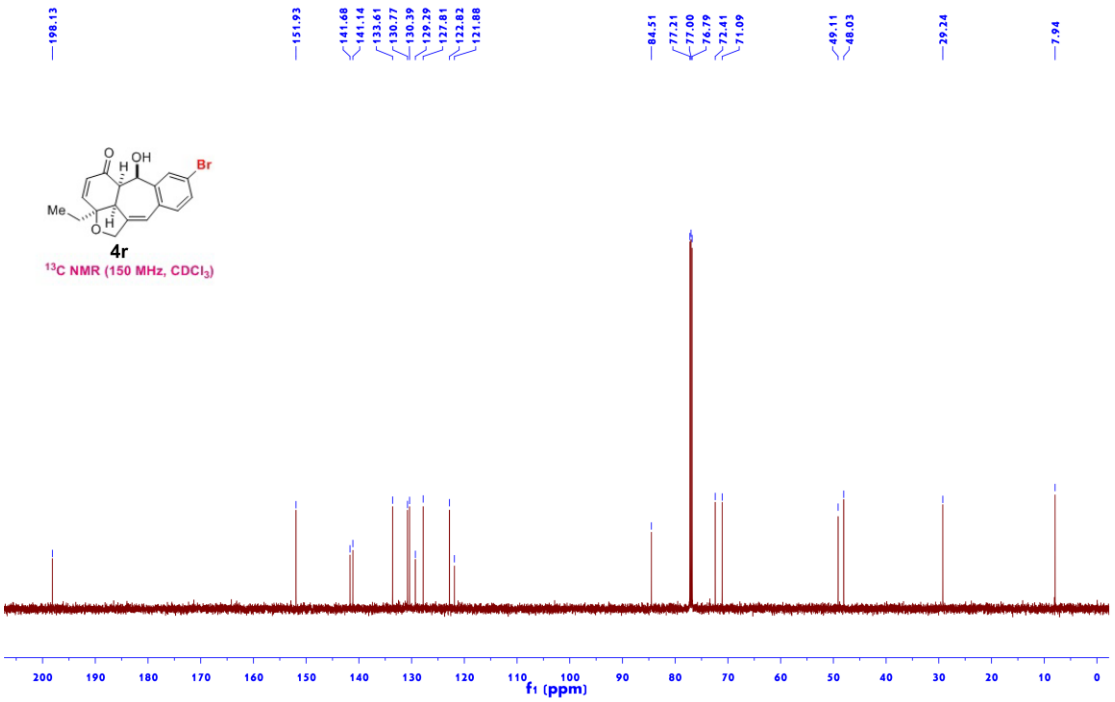

198.24
163.02
161.38
152.00
142.57
142.52
139.23
139.21
133.98
133.93
127.76
126.54
126.51
122.69
115.01
114.85
114.12
113.97
84.45
77.21
77.00
76.79
72.49
71.07
49.18
47.97
29.26
7.93
O
OH
H
F
Me
O
H
4p
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

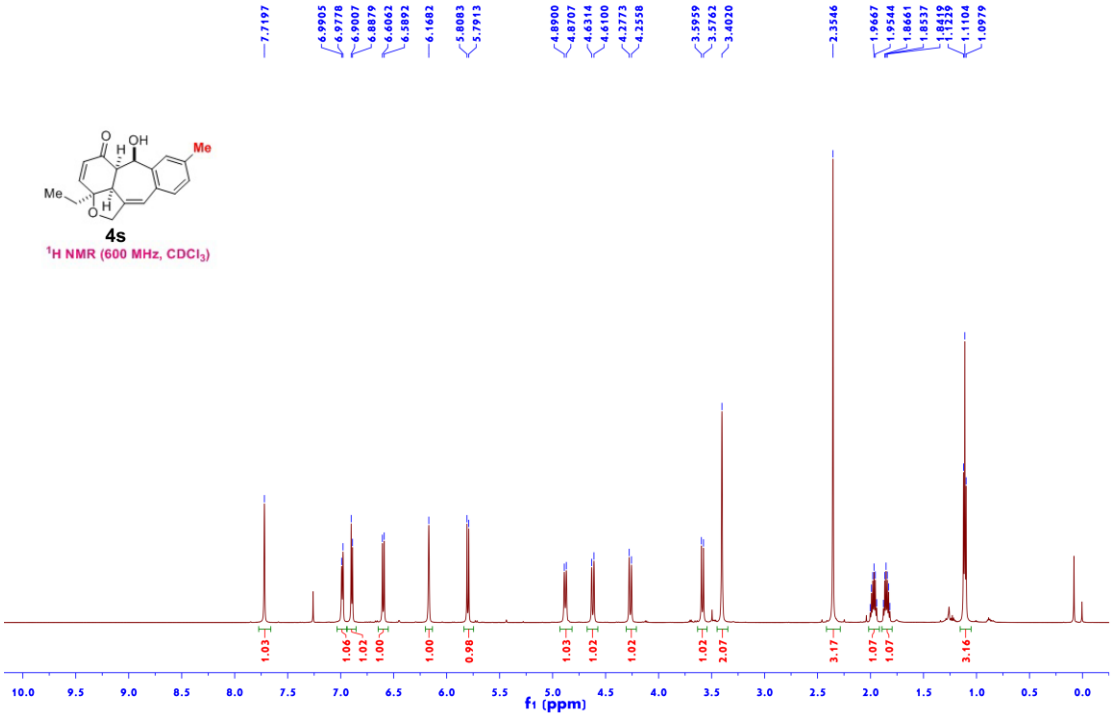

-113.6279
-113.6400
-113.6495
-113.6589
-113.6708
O
OH
H
F
Me
O
H
4p
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -21
f1 (ppm)


4q
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


4q
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)


4r
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


4r
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)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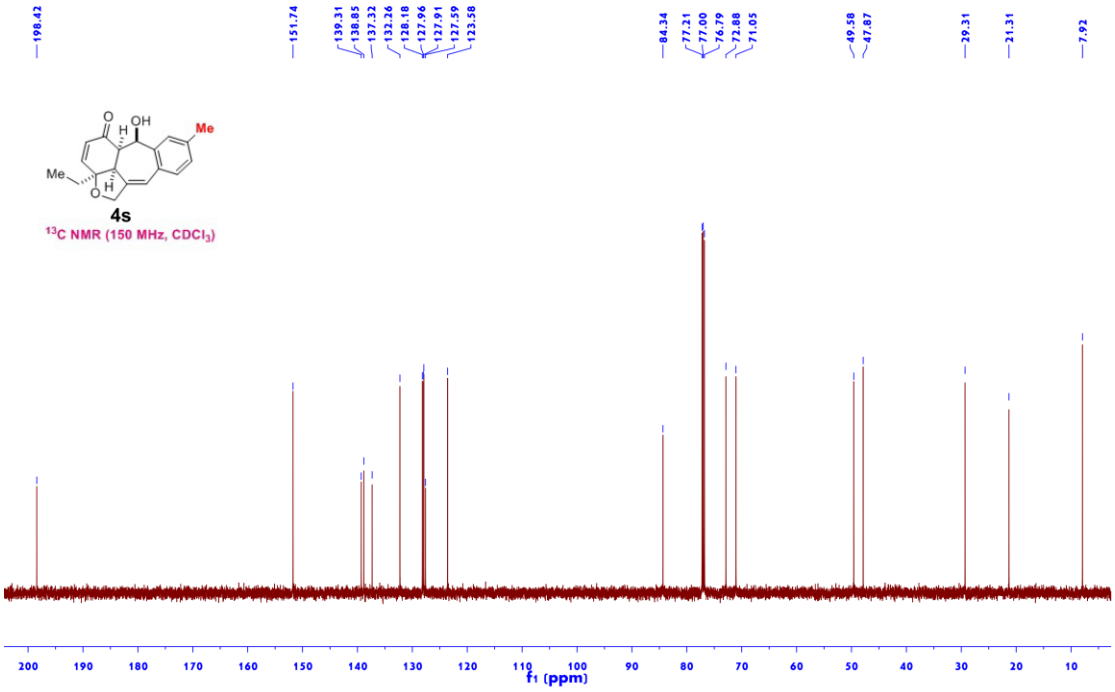
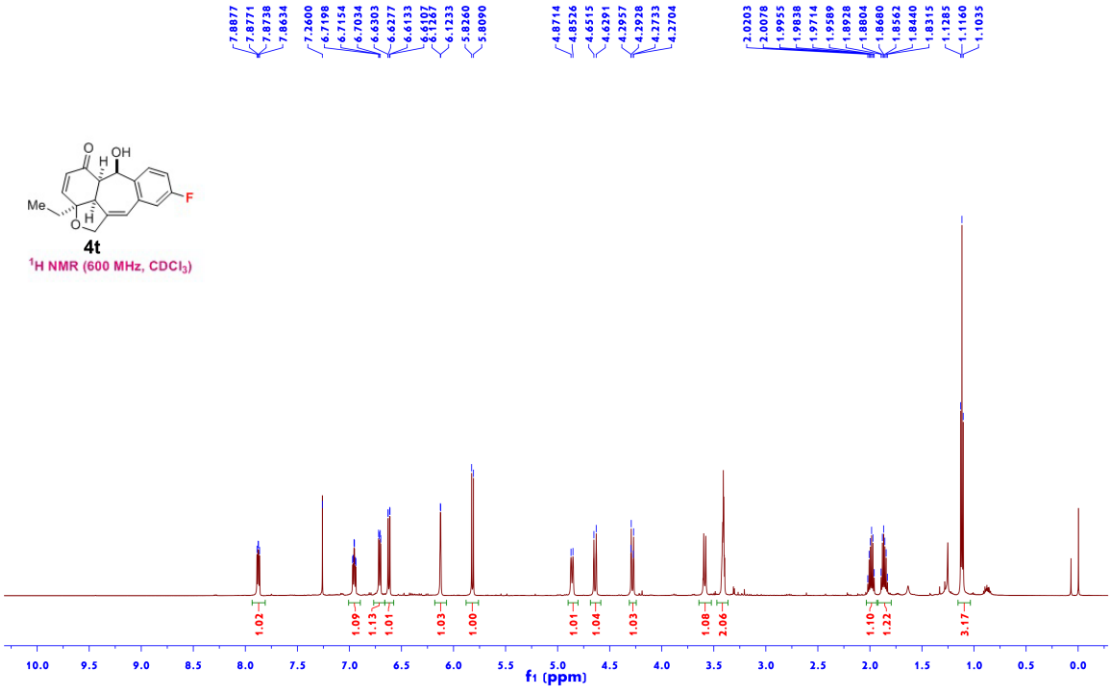
6.9905
6.9778
6.9007
6.8879
6.6062
6.5892
6.1682
5.8083
5.7913
4.8900
4.8707
4.6314
4.6100
4.2773
4.2558
3.5959
3.5762
3.4020
2.3546
1.9667
1.9544
1.8661
1.8537
1.1104
1.0979
Me
OH
H
O
Me
H
4s
1H NMR (600 MHz, CDCl3)
1.03
1.06
1.02
1.00
1.00
0.98
1.03
1.02
1.02
1.02
2.07
3.17
1.07
1.07
3.16
f1 (ppm)


198.42
151.74
139.31
138.85
137.32
132.26
128.18
127.96
127.91
127.59
123.58
84.34
77.21
77.00
76.79
72.88
71.05
49.58
47.87
29.31
21.31
7.92
Me
OH
H
O
Me
H
4s
13C NMR (150 MHz, CDCl3)
f1 (ppm)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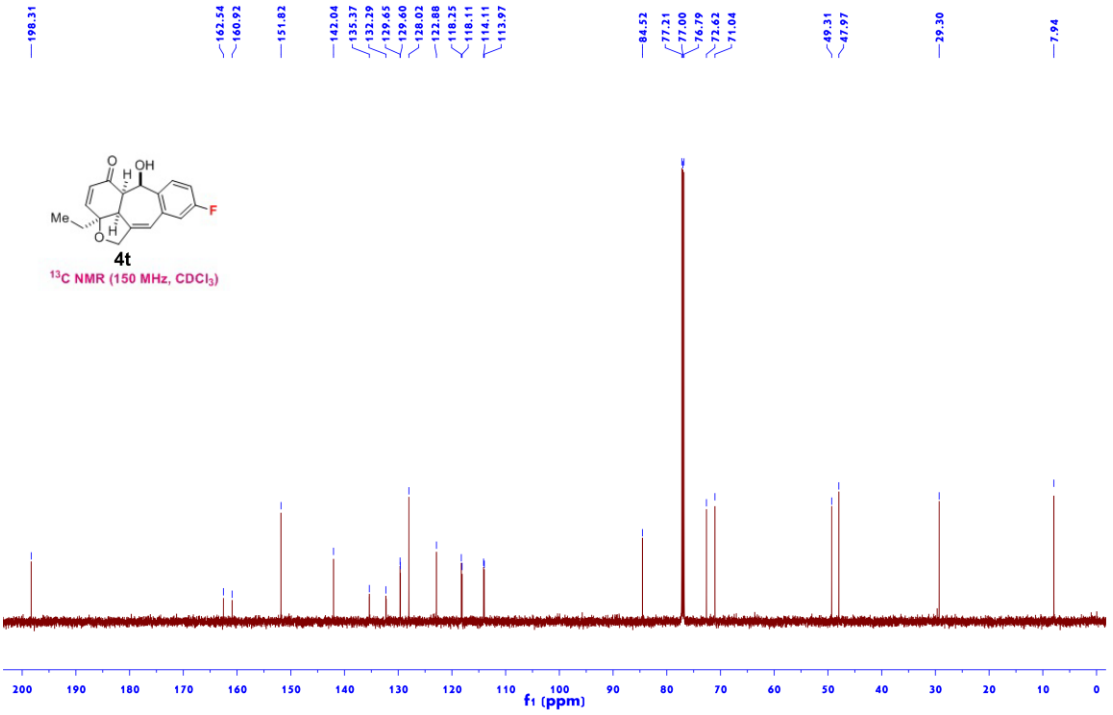
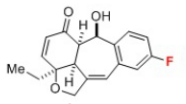
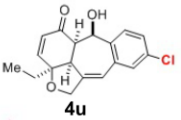
7.8871
7.8738
7.8634
7.2600
6.7198
6.7154
6.7034
6.6303
6.6277
6.6133
6.1233
5.8260
5.8090
4.8714
4.8526
4.6515
4.6291
4.2957
4.2928
4.2733
4.2704
2.0203
2.0078
1.9955
1.9838
1.9714
1.9589
1.8928
1.8804
1.8680
1.8562
1.8440
1.8315
1.1285
1.1160
1.1035
O
H
OH
Me
O
H
F
4t
1H NMR (600 MHz, CDCl3)
1.02
1.09
1.13
1.01
1.03
1.00
1.01
1.04
1.03
1.08
2.06
1.10
1.22
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.31
162.54
160.92
151.82
142.04
135.37
132.29
129.65
129.60
128.02
122.88
118.25
110.11
114.11
113.97
84.52
77.21
77.00
76.79
72.62
71.04
49.31
47.97
29.30
7.94
O
H
OH
Me
O
H
F
4t
13C NMR (150 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



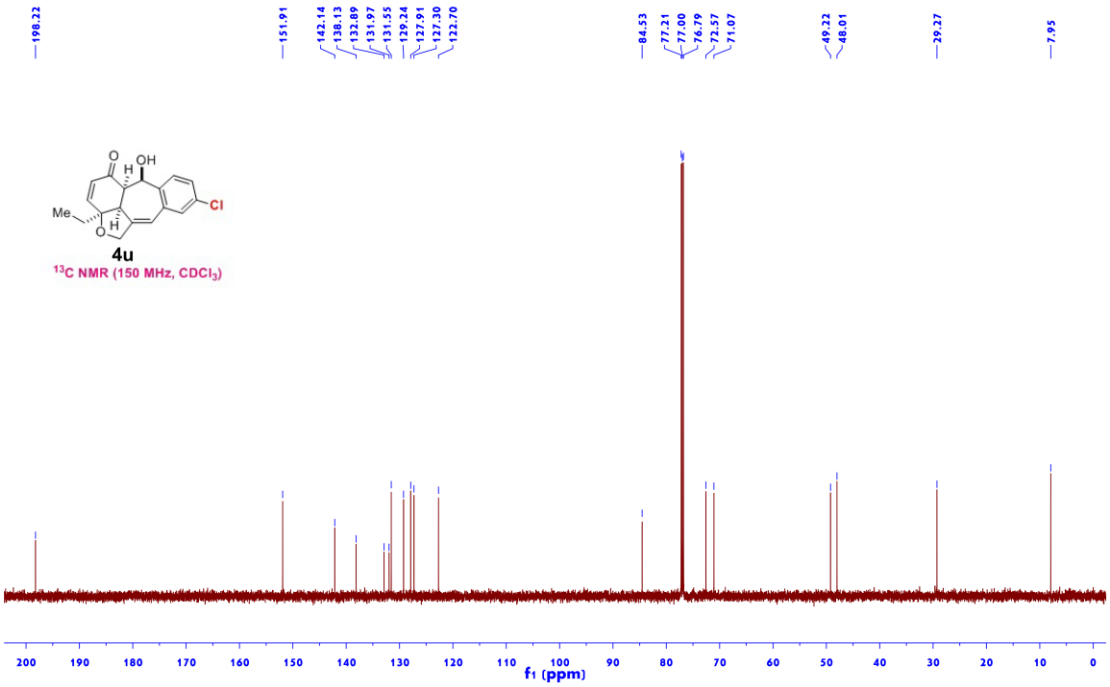
4t

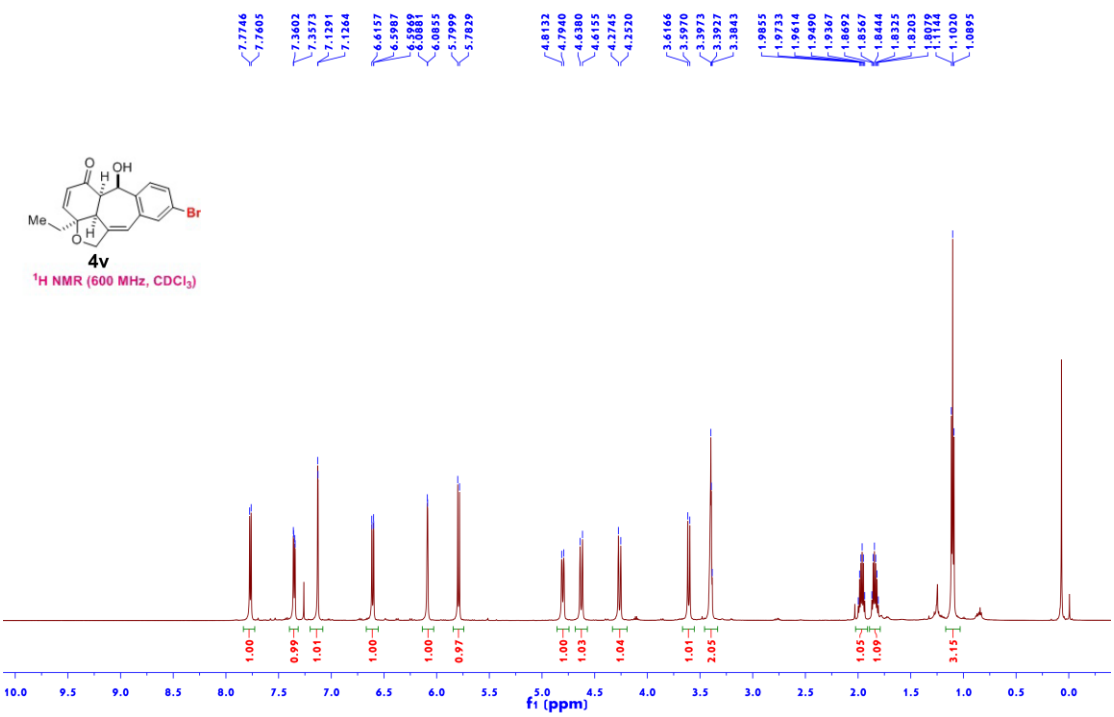
^{19}F NMR (565 MHz, $CDCl_3$)

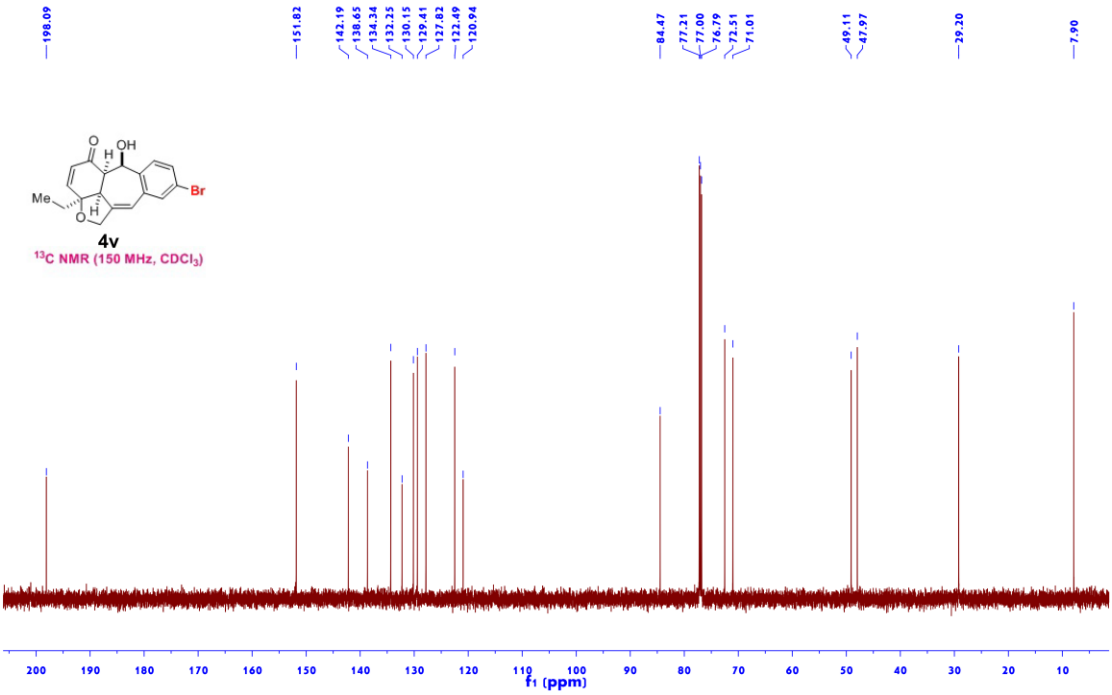


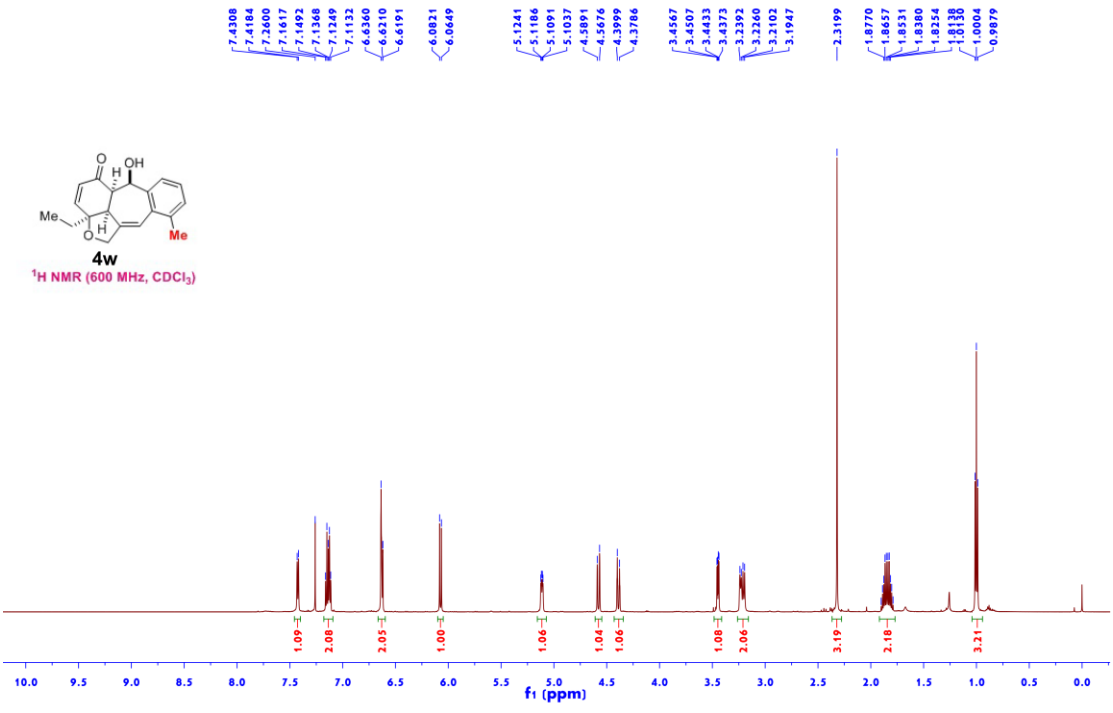
4u

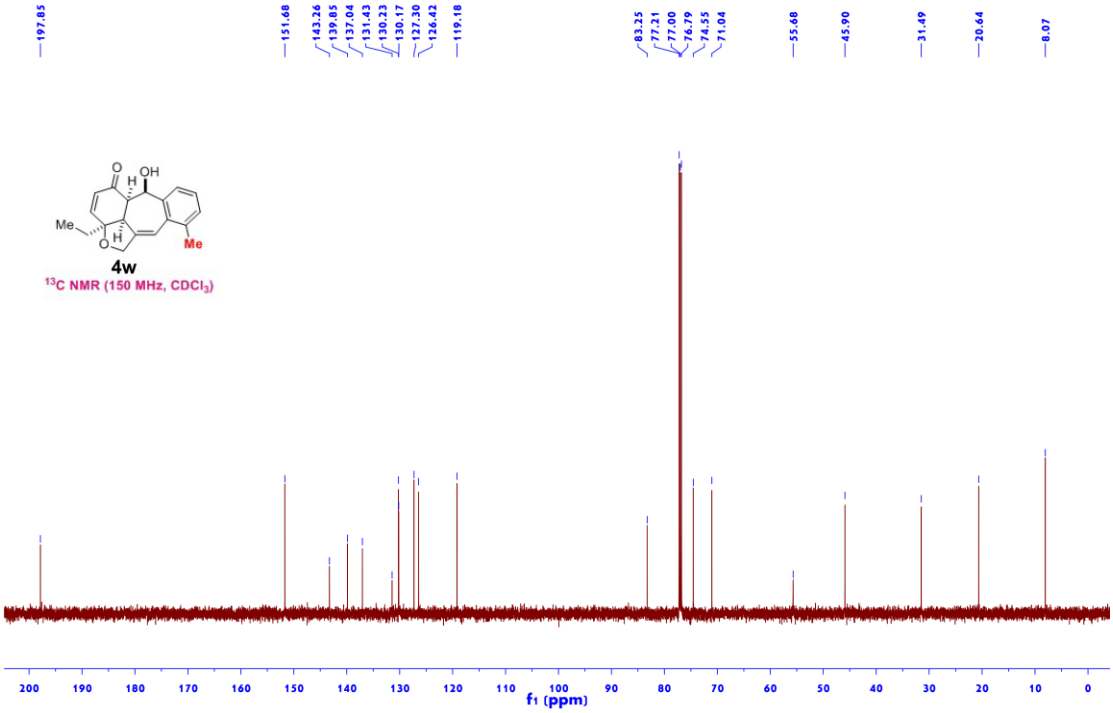
^{1}H NMR (600 MHz, $CDCl_3$)

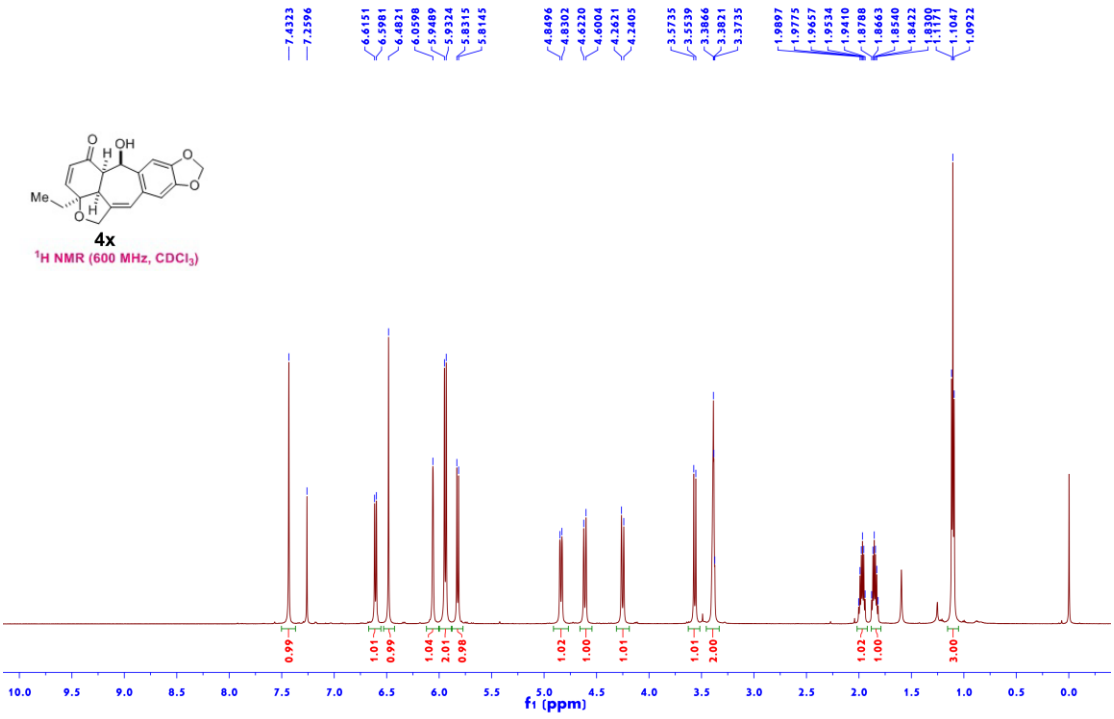

198.22
151.91
142.14
138.13
132.89
131.97
131.55
129.24
127.91
127.30
122.70
84.53
77.21
77.00
76.79
72.57
71.07
49.22
48.01
29.27
7.95
O
H
OH
Me
O
H
Cl
4u
13C NMR (150 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.7746
7.7605
7.3602
7.3573
7.1391
7.1264
6.6157
6.5987
6.0855
5.7999
5.7829
4.8132
4.7940
4.6380
4.6155
4.2745
4.2520
3.6166
3.5970
3.3973
3.3927
3.3843
1.9855
1.9733
1.9614
1.9490
1.9367
1.8692
1.8567
1.8444
1.8325
1.8203
1.1020
1.0895
O
H
OH
Me
O
H
Br
4v
1H NMR (600 MHz, CDCl3)
1.00
0.99
1.01
1.00
1.00
0.97
1.00
1.03
1.04
1.01
2.05
1.05
1.09
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.09
151.82
142.19
138.65
134.34
132.25
130.15
129.41
127.82
122.49
120.94
84.47
77.21
77.00
76.79
72.51
71.01
49.11
47.97
29.20
7.90
O
OH
H
Me
O
H
Br
4v
13C NMR (150 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.4308
7.4184
7.2600
7.1617
7.1492
7.1368
7.1249
7.1132
6.6360
6.6210
6.6191
6.0821
6.0649
5.1241
5.1186
5.1091
5.1037
4.5891
4.5676
4.3999
4.3786
3.4567
3.4507
3.4433
3.4373
3.2392
3.2260
3.2102
3.1947
2.3199
1.8770
1.8657
1.8531
1.8380
1.8254
1.8138
1.8130
1.0004
0.9879
O
OH
H
Me
O
H
Me
4w
1H NMR (600 MHz, CDCl3)
1.09
2.08
2.05
1.00
1.06
1.04
1.06
1.08
2.06
3.19
2.18
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.85
151.68
143.26
139.85
137.04
131.43
130.23
130.17
127.30
126.42
119.18
83.25
77.21
77.00
76.79
74.55
71.04
55.68
45.90
31.49
20.64
8.07
O
OH
H
Me
O
H
Me
4w
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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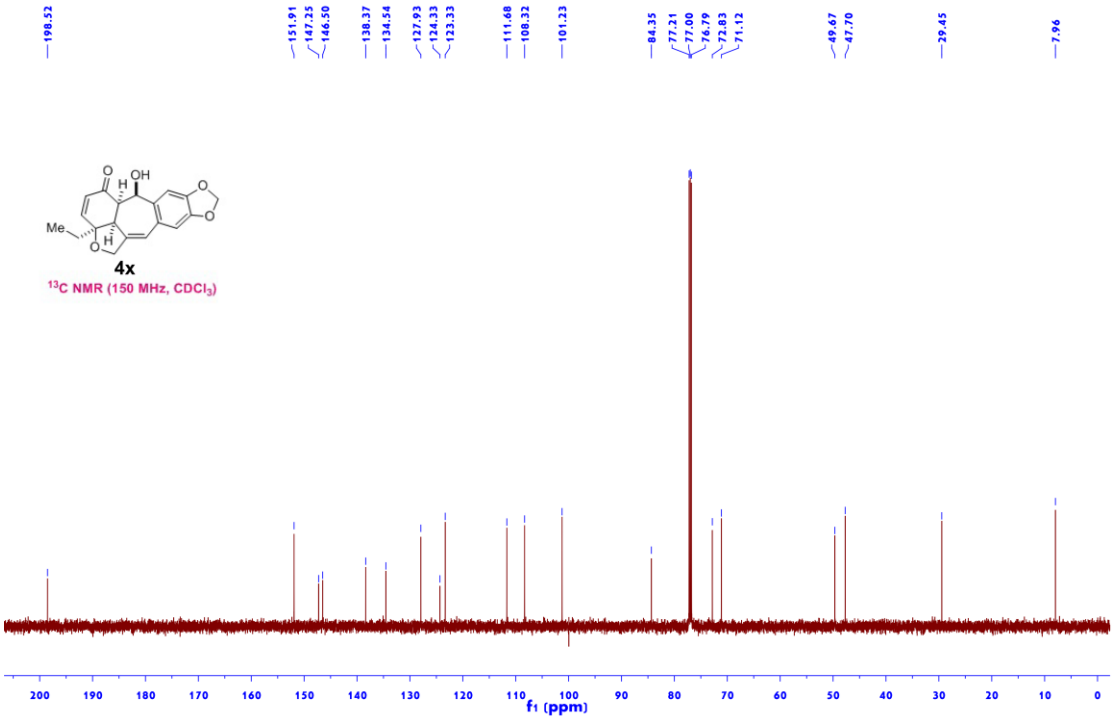
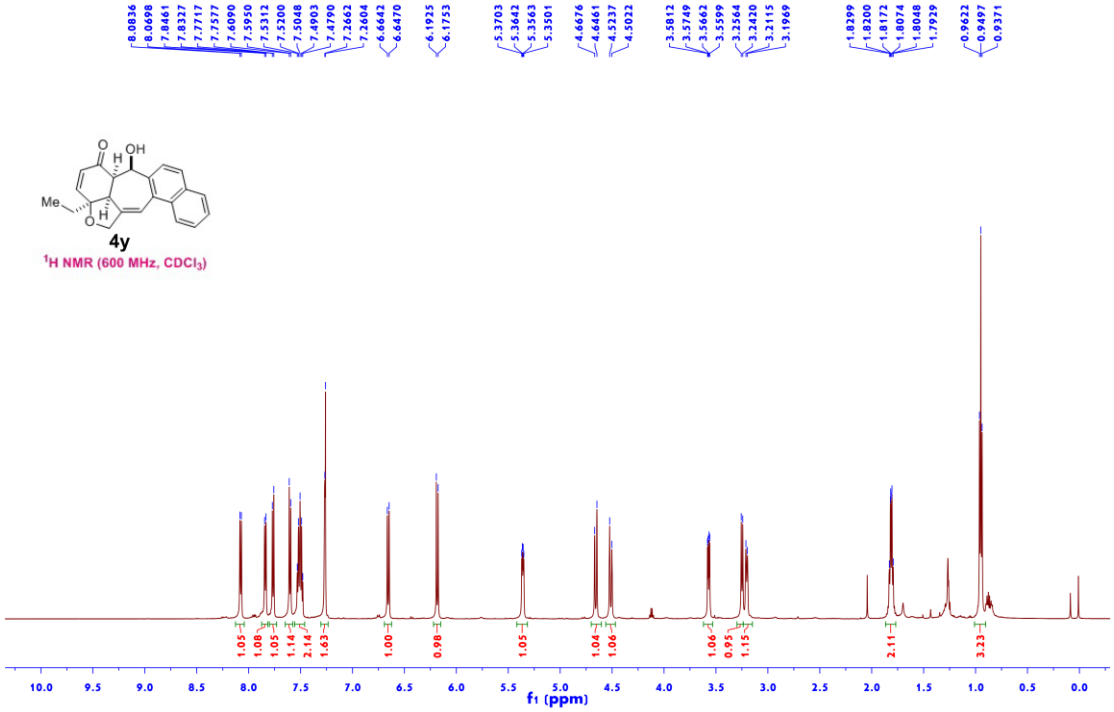
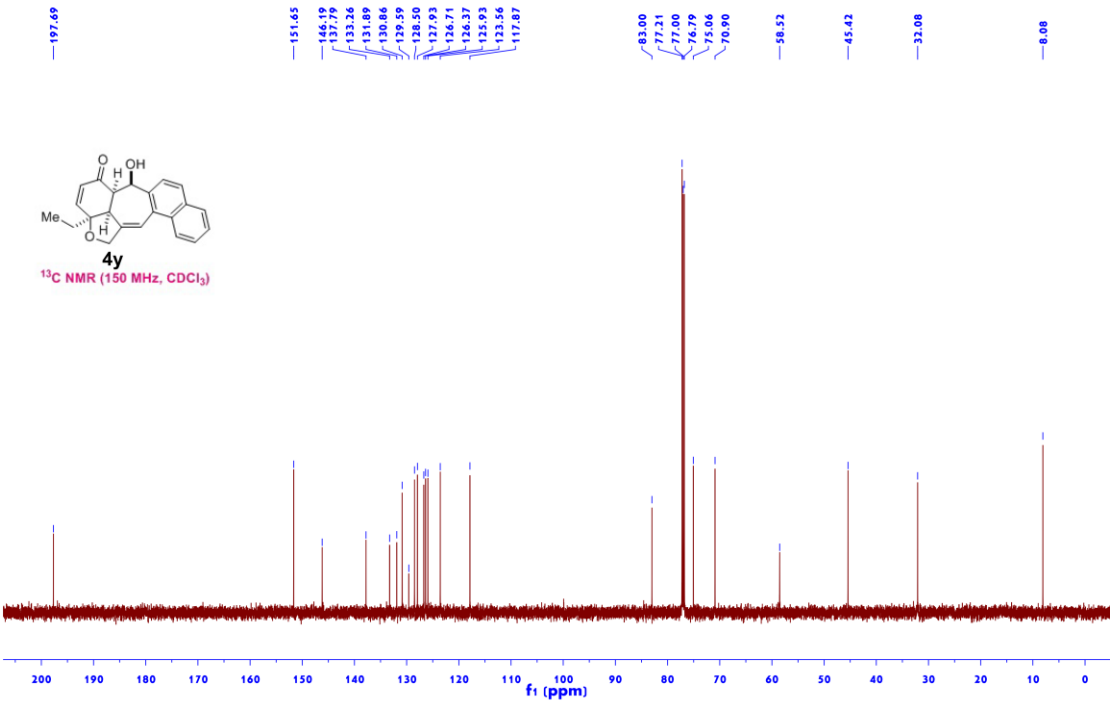
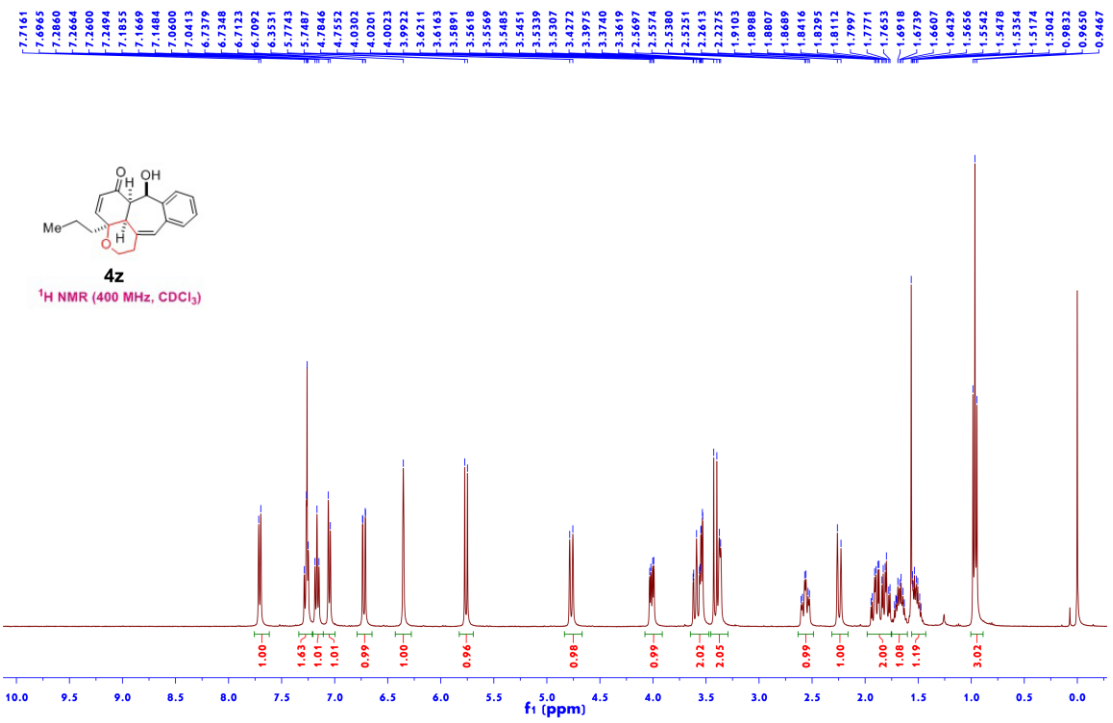
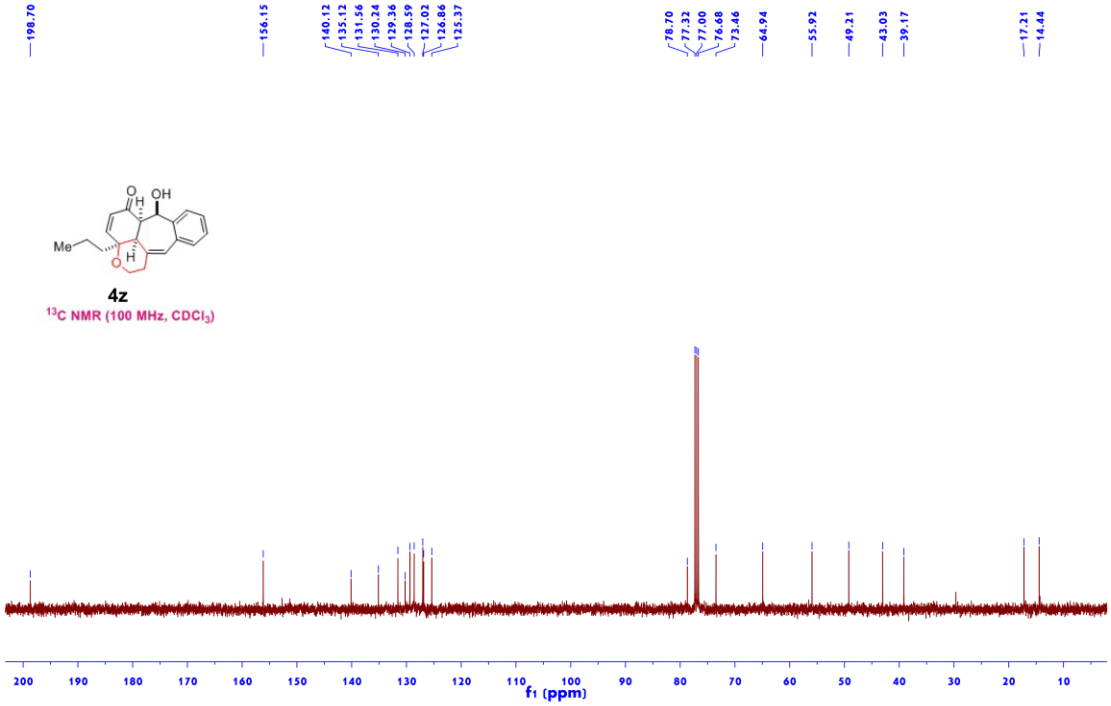
7.2596
6.6151
6.5981
6.4821
6.0598
5.9489
5.9324
5.8315
5.8145
4.8496
4.8302
4.6220
4.6004
4.2621
4.2405
3.5735
3.5539
3.3866
3.3821
3.3735
1.9897
1.9775
1.9657
1.9534
1.9410
1.8788
1.8663
1.8540
1.8422
1.1317
1.1047
1.0922
O
OH
H
O
O
Me
O
H
4x
1H NMR (600 MHz, CDCl3)
0.99
1.01
0.99
1.04
2.01
0.98
1.02
1.00
1.01
1.01
2.00
1.02
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

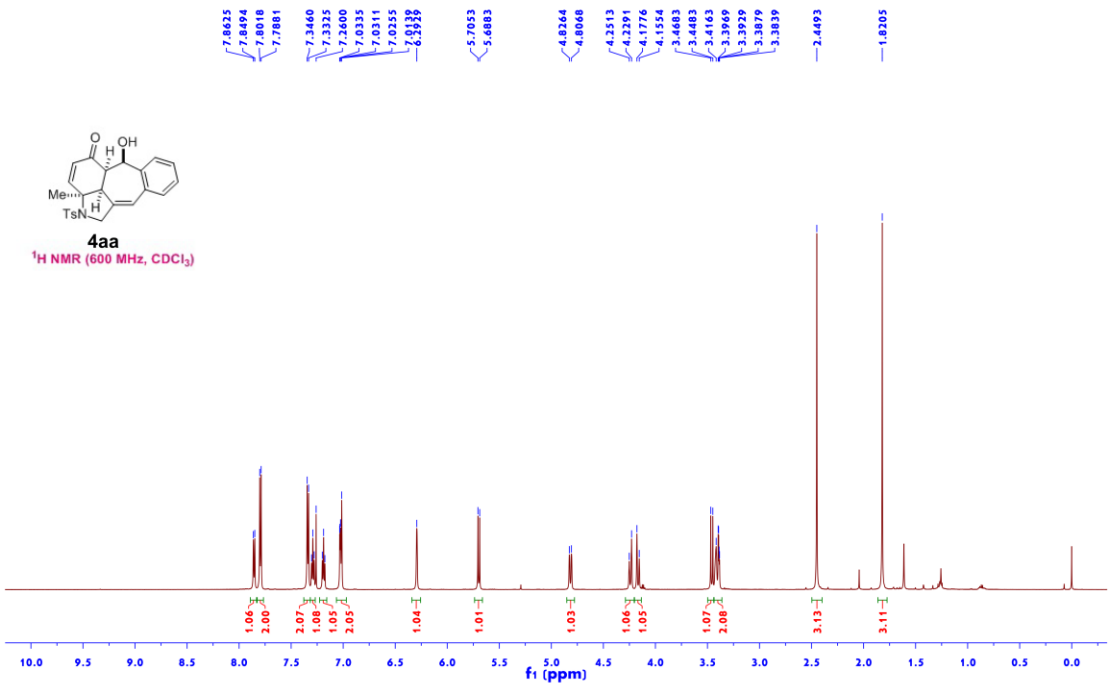

198.52
151.91
147.25
146.50
138.37
134.54
127.93
124.33
123.33
111.68
108.32
101.23
84.35
77.21
77.00
76.79
72.83
71.12
49.67
47.70
29.45
7.96
4x
13C NMR (150 MHz, CDCl3)
f1 (ppm)

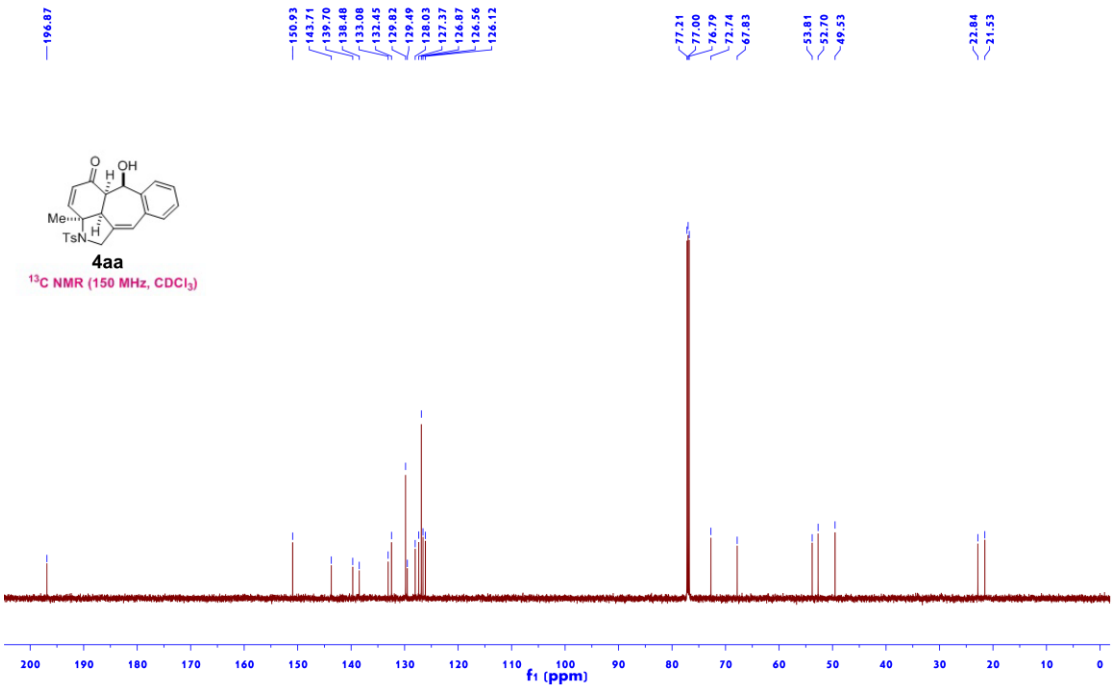

8.0836
8.0698
7.8461
7.8327
7.7717
7.7577
7.6090
7.5950
7.5312
7.5200
7.5048
7.4903
7.4790
7.2662
7.2604
6.6642
6.6470
6.1925
6.1753
5.3703
5.3642
5.3563
5.3501
4.6676
4.6461
4.5237
4.5022
3.5812
3.5749
3.5662
3.5599
3.2564
3.2420
3.2115
3.1969
1.8299
1.8200
1.8172
1.8074
1.8048
1.7929
0.9622
0.9497
0.9371
4y
1H NMR (600 MHz, CDCl3)
1.05
1.08
1.05
1.14
2.14
1.63
1.00
0.98
1.05
1.04
1.06
1.06
0.95
1.15
2.11
3.23
f1 (ppm)

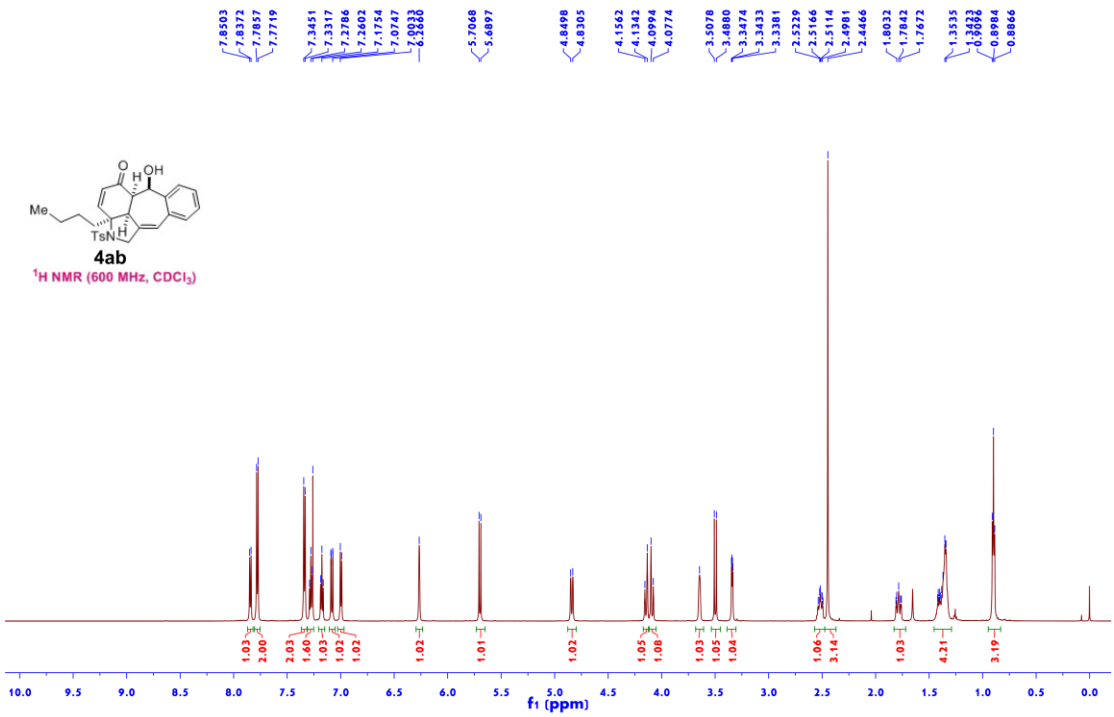

197.69
151.65
146.19
137.79
133.26
131.89
130.86
129.59
128.50
127.93
127.71
126.37
125.93
123.56
117.87
83.00
77.21
77.00
76.79
75.06
70.90
58.52
45.42
32.08
8.08
Me
4y
13C NMR (150 MHz, CDCl3)
f1 (ppm)

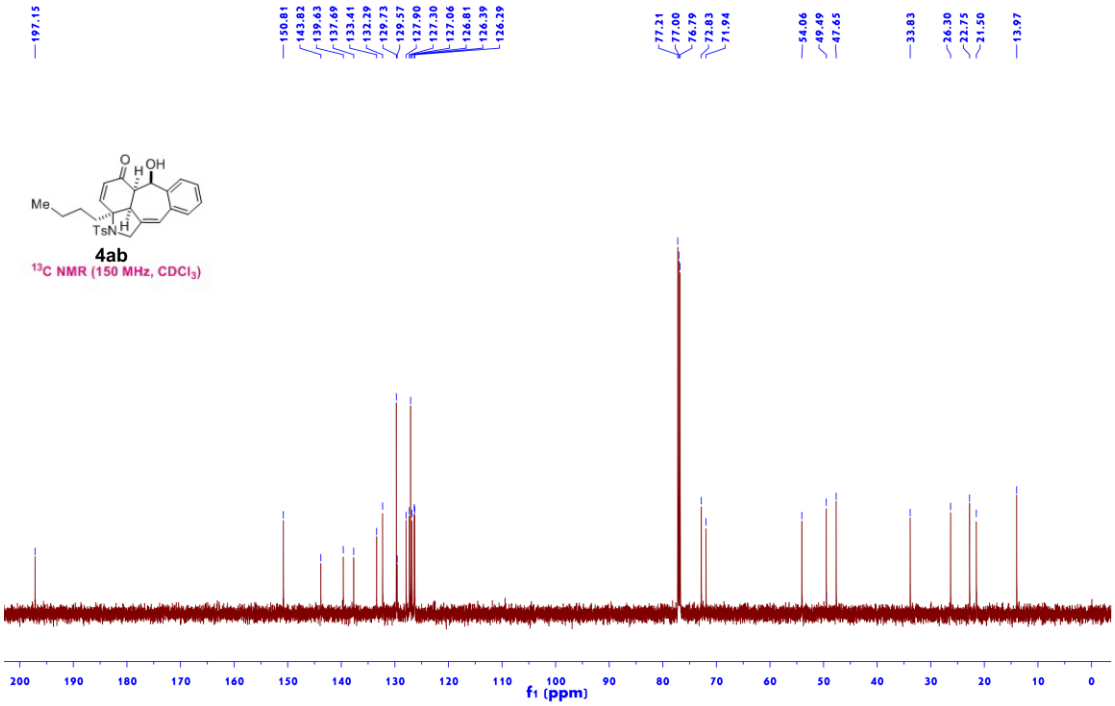

Me
4z
1H NMR (400 MHz, CDCl3)
f1 (ppm)

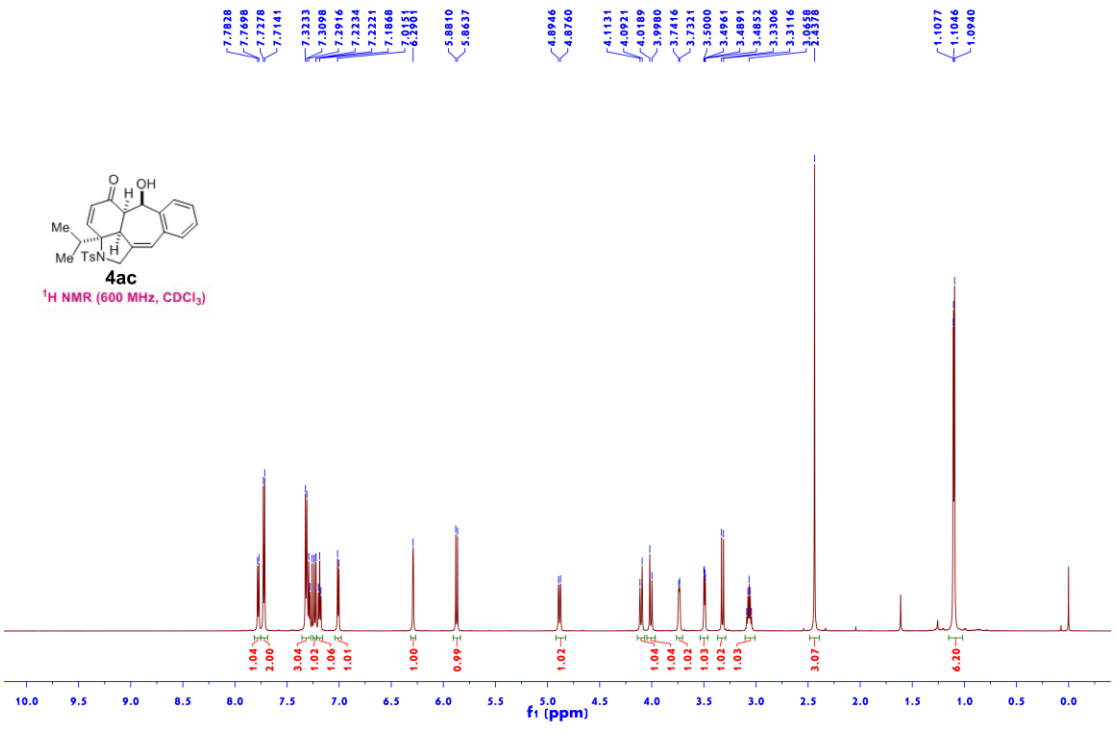

198.70
156.15
140.12
135.12
131.56
130.24
129.36
128.59
127.02
126.86
125.37
78.70
77.32
77.00
76.68
73.46
64.94
55.92
49.21
43.03
39.17
17.21
14.44
O
H
OH
Me
O
H
4z
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

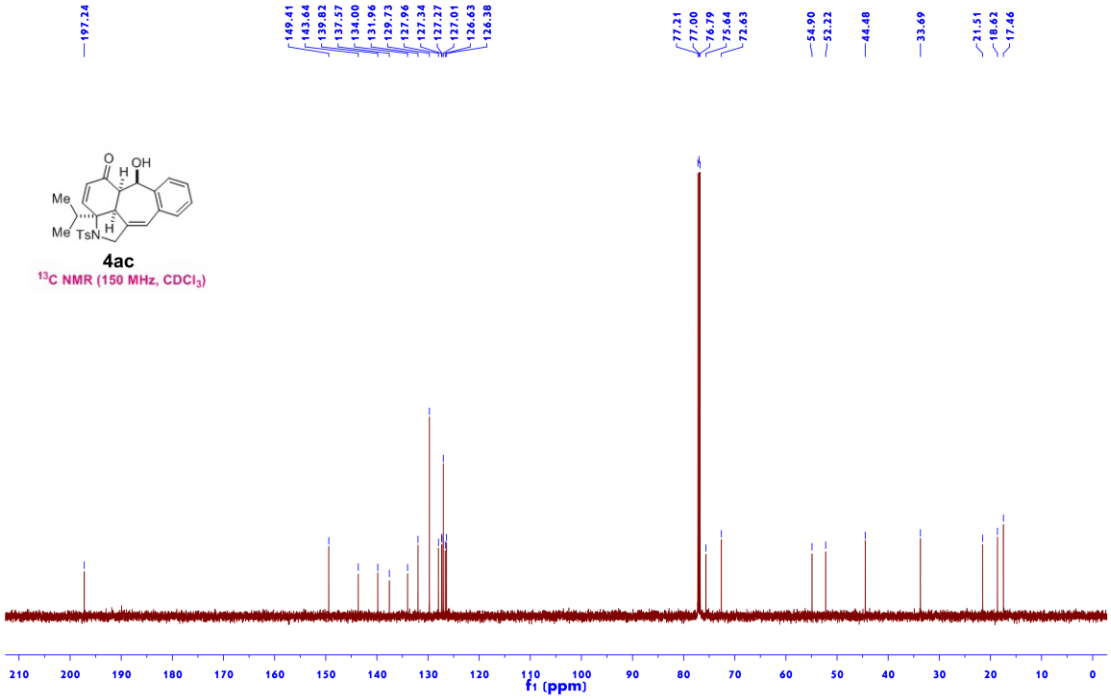

7.8625
7.8494
7.8018
7.7881
7.3460
7.3325
7.2600
7.0335
7.0311
7.0255
7.0139
6.9959
5.7053
5.6883
4.8264
4.8068
4.2513
4.2291
4.1776
4.1554
3.4683
3.4483
3.4163
3.3969
3.3929
3.3879
3.3839
2.4493
1.8205
O
H
OH
Me
TsN
H
4aa
1H NMR (600 MHz, CDCl3)
1.06
2.00
2.07
1.08
1.05
2.05
1.04
1.01
1.03
1.06
1.05
1.07
2.08
3.13
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

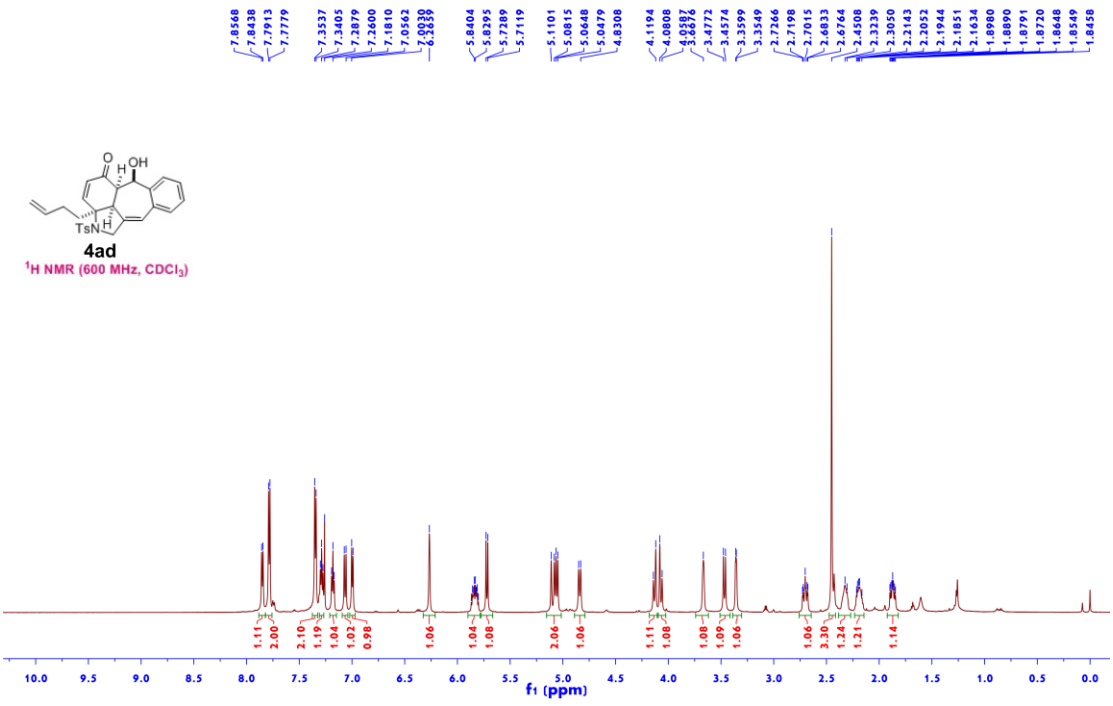

196.87
150.93
143.71
139.70
138.48
133.08
132.45
129.82
129.49
128.03
127.37
126.87
126.56
126.12
77.21
77.00
76.79
73.74
67.83
53.81
52.70
49.53
22.84
21.53
O
H
OH
Me
TsN
H
4aa
13C NMR (150 MHz, CDCl3)
f1 (ppm)

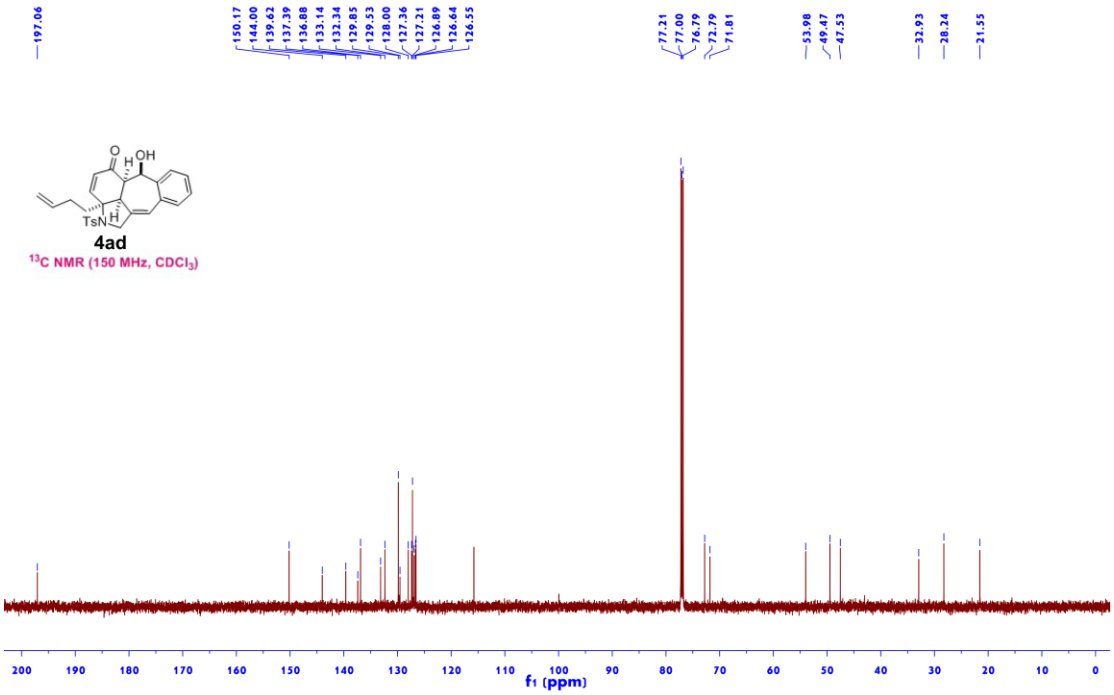

7.8503
7.8372
7.7857
7.7719
7.3451
7.3317
7.2786
7.2602
7.1754
7.0747
5.7068
5.6897
4.8498
4.8305
4.1562
4.1342
4.0994
4.0774
3.5078
3.4880
3.3474
3.3433
3.3381
2.5229
2.5166
2.5114
2.4981
2.4466
1.8032
1.7842
1.7672
1.3535
0.8984
0.8866
O
H
OH
Me
TsN
H
4ab
1H NMR (600 MHz, CDCl3)
f1 (ppm)

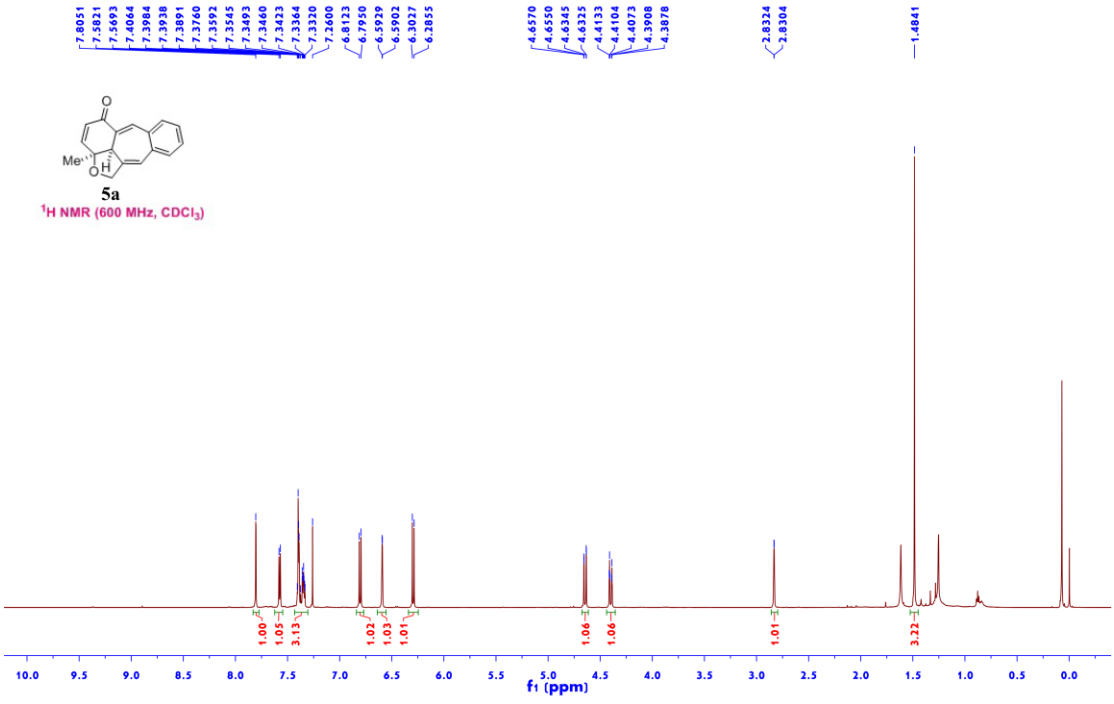

197.15
150.81
143.62
139.63
137.69
133.41
132.29
129.73
129.57
127.90
127.30
127.06
126.81
126.39
126.29
77.21
77.00
76.79
72.83
71.94
54.06
49.49
47.65
33.83
26.30
22.75
21.50
13.97
O
H
OH
Me
TsN
H
4ab
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

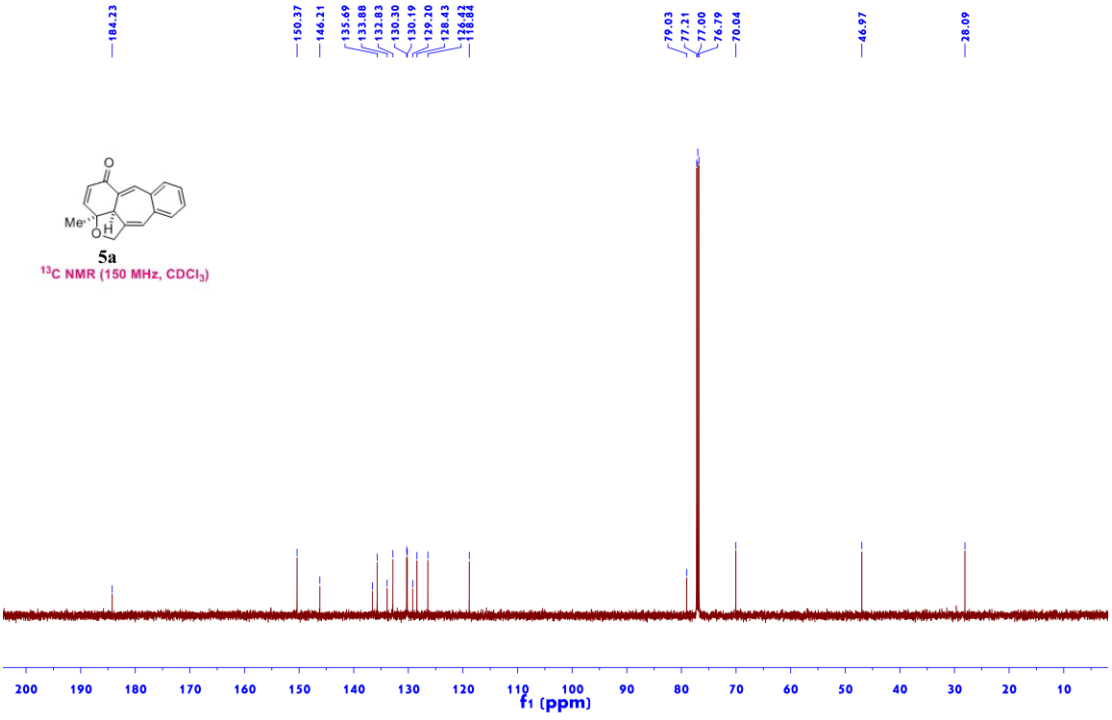

7.7828
7.7698
7.7278
7.7141
7.3233
7.3098
7.2916
7.2234
7.2221
7.1868
7.0151
6.9901
5.8810
5.8637
4.8946
4.8760
4.1131
4.0921
4.0189
3.9980
3.7416
3.7321
3.5000
3.4961
3.4891
3.4852
3.3306
3.3116
3.0658
2.4378
1.1077
1.1046
1.0940
O
H
OH
Me
Me
TsN
H
4ac
1H NMR (600 MHz, CDCl3)
1.04
2.00
3.04
1.02
1.06
1.01
1.00
0.99
1.02
1.04
1.04
1.02
1.03
1.02
1.03
3.07
6.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

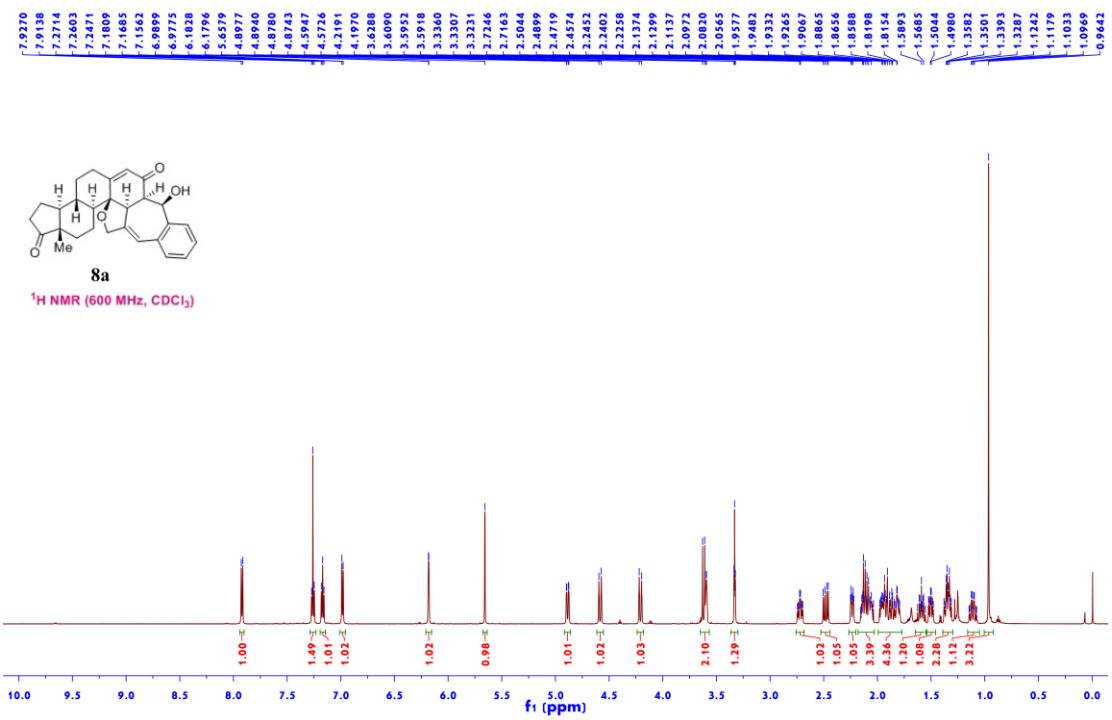

197.24
149.41
143.64
139.82
137.57
134.00
131.96
129.73
127.96
127.34
127.27
127.01
126.63
126.38
77.21
77.00
76.79
75.64
72.63
54.90
52.22
44.48
33.69
21.51
18.62
17.46
O
OH
H
Me
Me
TsN
H
4ac
13C NMR (150 MHz, CDCl3)
f1 (ppm)

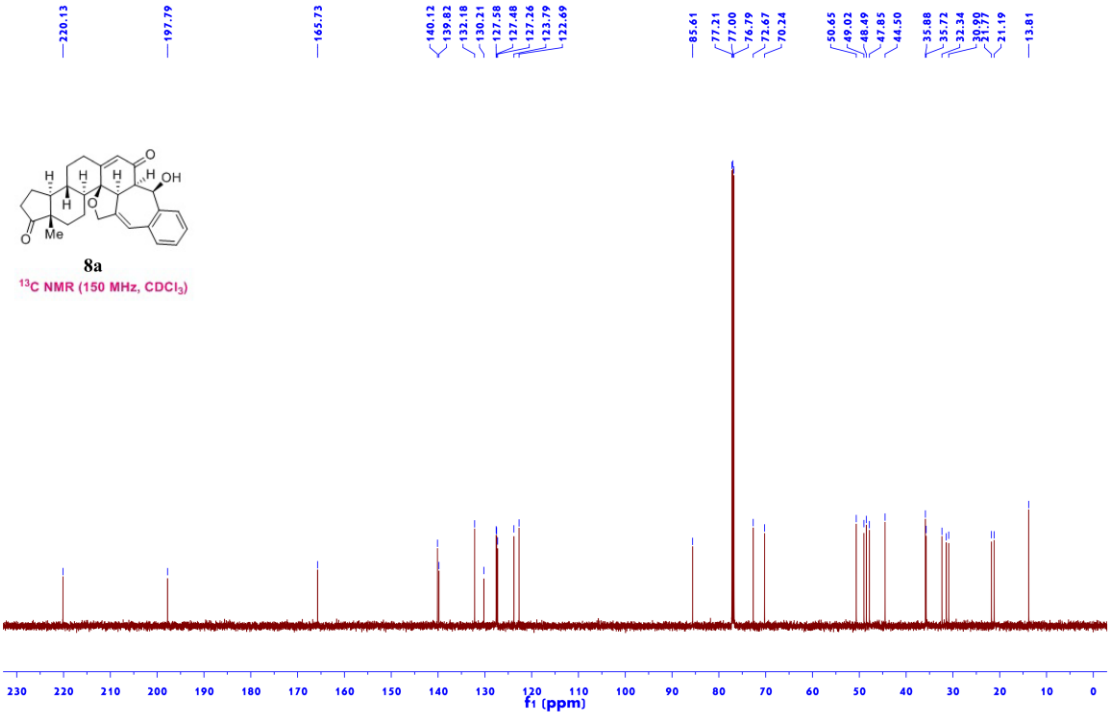

7.8568
7.8438
7.7913
7.7779
7.3537
7.3405
7.2879
7.2600
7.1810
7.0562
5.8404
5.8295
5.7389
5.7119
5.1101
5.0815
5.0648
5.0479
4.8308
4.1194
4.0808
3.6676
3.4772
3.4574
3.3599
3.3549
2.7266
2.7198
2.7015
2.6833
2.6764
2.4508
2.3239
2.3050
2.2143
2.2052
2.1944
2.1851
2.1634
1.8980
1.8890
1.8791
1.8720
1.8648
1.8549
1.8458
O
OH
H
TsN
H
4ad
1H NMR (600 MHz, CDCl3)
1.11
2.00
2.10
1.19
1.04
1.02
0.98
1.06
1.04
1.08
2.06
1.06
1.11
1.08
1.08
1.09
1.06
1.06
3.30
1.24
1.21
1.14
f1 (ppm)


197.06
150.17
144.00
139.62
137.39
136.88
133.14
132.34
129.85
129.53
128.00
127.36
127.21
126.89
126.64
126.55
77.21
77.00
76.79
72.79
71.81
53.98
49.47
47.53
32.93
28.24
21.55
O
H
OH
TsN
H
4ad
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.8051
7.5821
7.5693
7.4064
7.3984
7.3938
7.3891
7.3760
7.3592
7.3545
7.3493
7.3460
7.3423
7.3364
7.3320
7.2600
6.8123
6.7950
6.5929
6.5902
6.3027
6.2855
4.6570
4.6550
4.6345
4.6325
4.4133
4.4104
4.4073
4.3908
4.3878
2.8324
2.8304
1.4841
O
Me
O
H
5a
1H NMR (600 MHz, CDCl3)
1.00
1.05
3.13
1.02
1.03
1.01
1.06
1.06
1.01
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

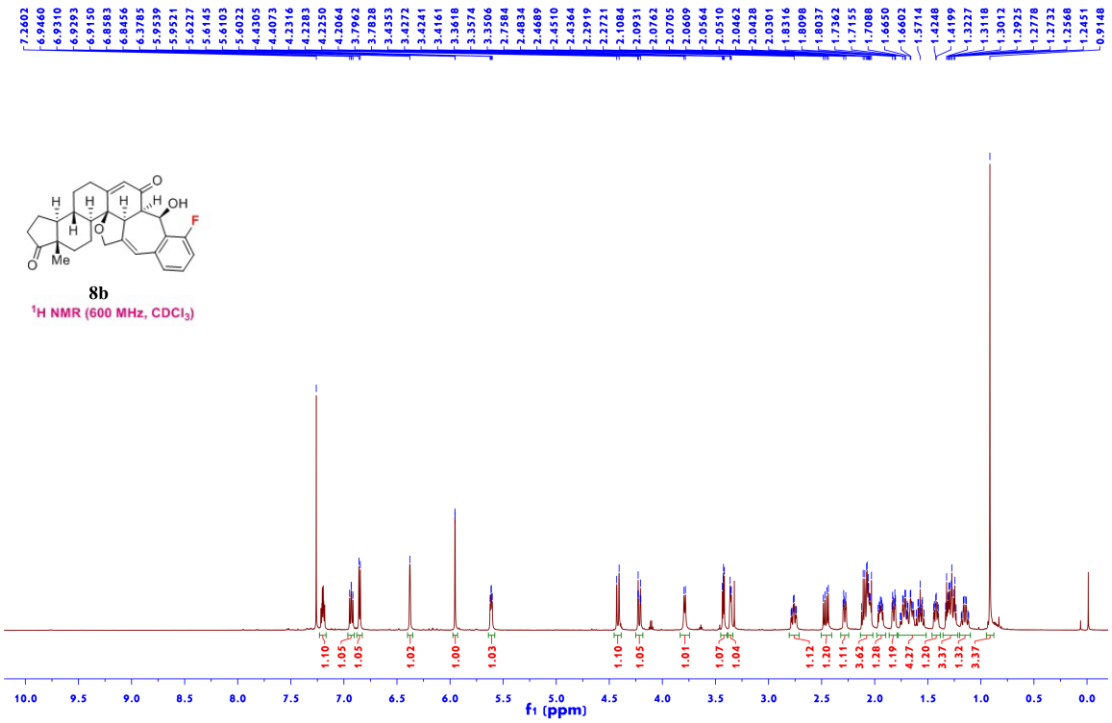

184.23
150.37
146.21
135.69
133.88
132.83
130.30
130.19
129.20
128.43
126.42
126.04
79.03
77.21
77.00
76.79
70.04
46.97
28.09
Me
O
H
O
5a
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.9270
7.9138
7.2714
7.2603
7.2471
7.1809
7.1685
7.1562
6.9899
6.9775
6.1828
6.1796
5.6579
4.8977
4.8940
4.8780
4.8743
4.5947
4.5726
4.2191
4.1970
3.6288
3.6090
3.5952
3.5918
3.3360
3.3307
3.3231
2.7246
2.7163
2.5044
2.4899
2.4719
2.4574
2.2452
2.2402
2.2258
2.1374
2.1299
2.1137
2.0972
2.0820
2.0565
1.9577
1.9482
1.9332
1.9265
1.9067
1.8865
1.8656
1.8588
1.8198
1.8154
1.5893
1.5685
1.5044
1.4980
1.3582
1.3501
1.3393
1.3287
1.1242
1.1179
1.1033
1.0969
0.9642
H
H
H
H
OH
O
O
H
O
Me
8a
1H NMR (600 MHz, CDCl3)
1.00
1.49
1.01
1.02
1.02
0.98
1.01
1.02
1.03
2.10
1.29
1.02
1.05
1.05
3.39
4.36
1.20
1.08
2.28
1.12
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



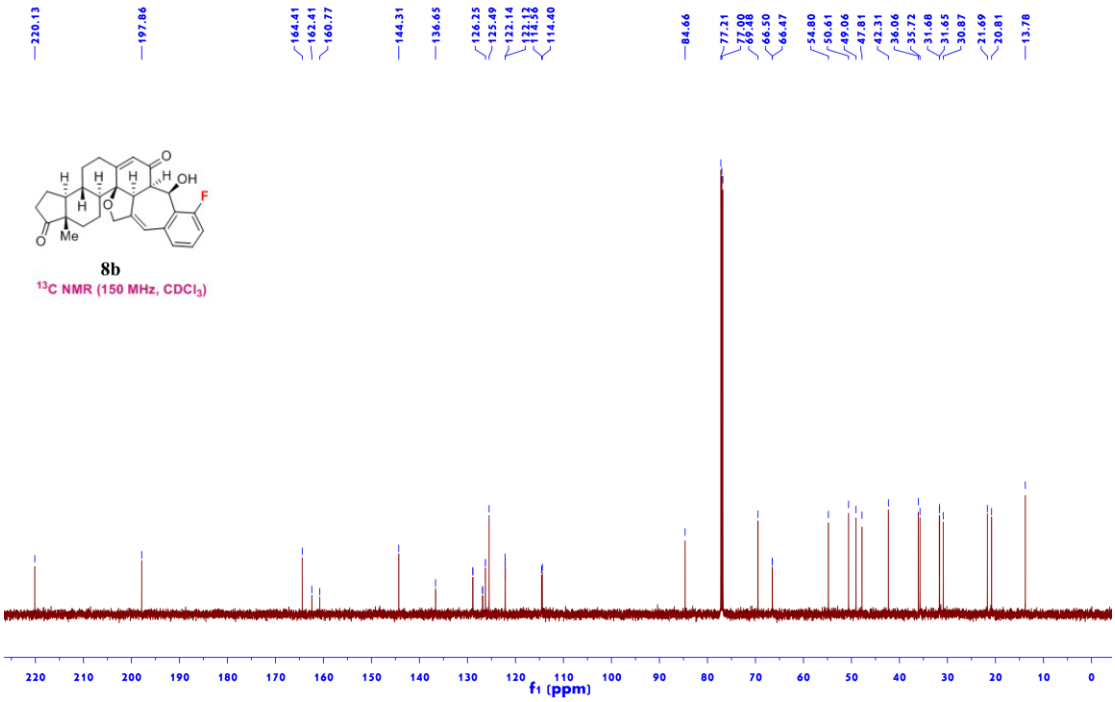
8a

^{13}C NMR (150 MHz, $CDCl_3$)



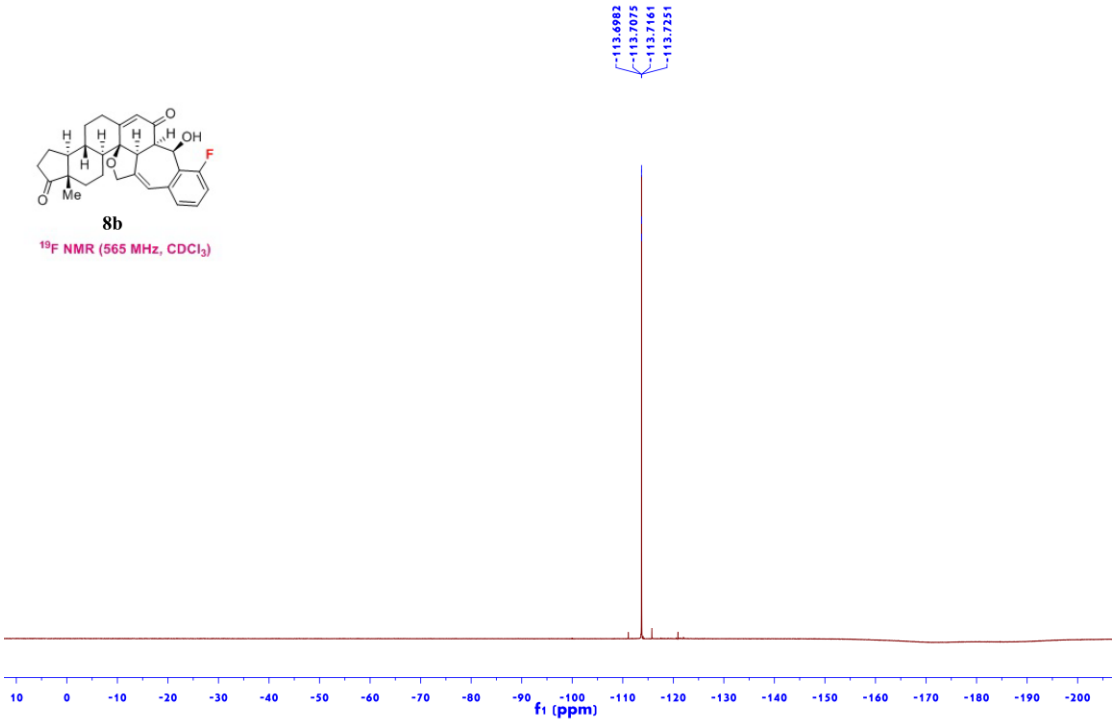
8b

^{1}H NMR (600 MHz, $CDCl_3$)



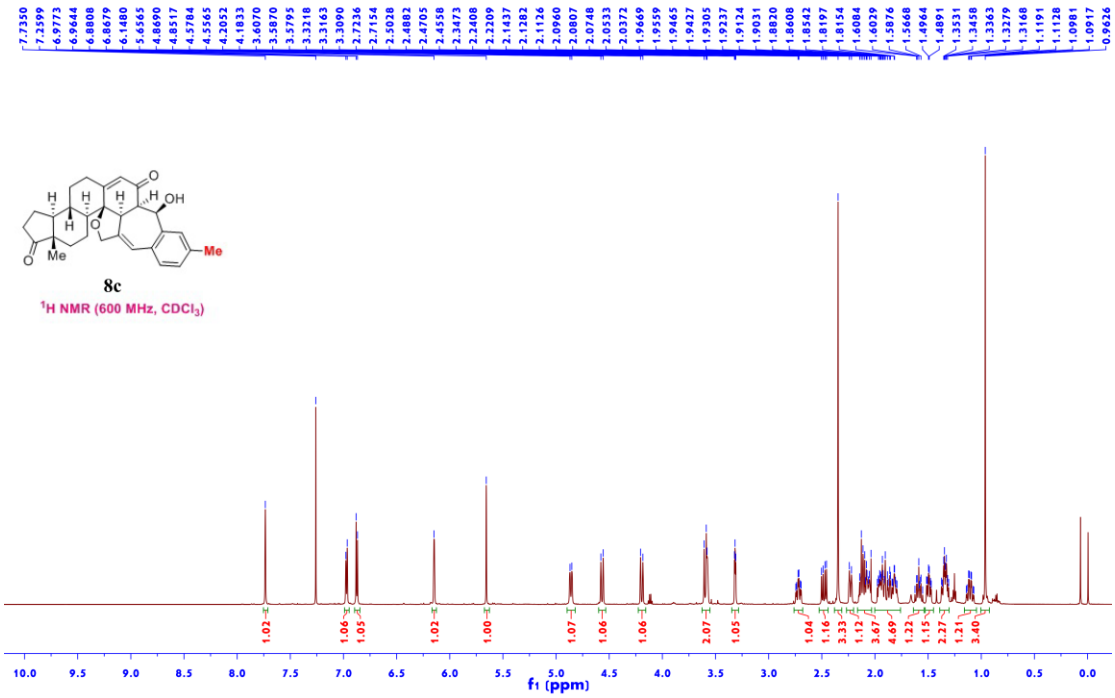
8b

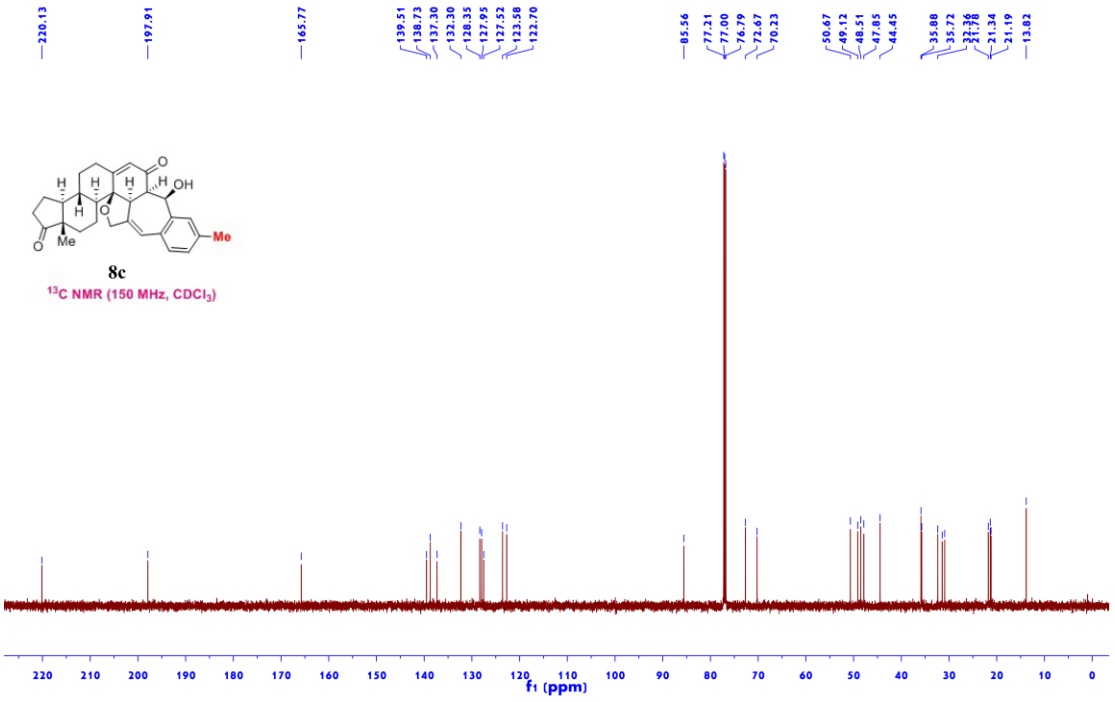
^{13}C NMR (150 MHz, $CDCl_3$)

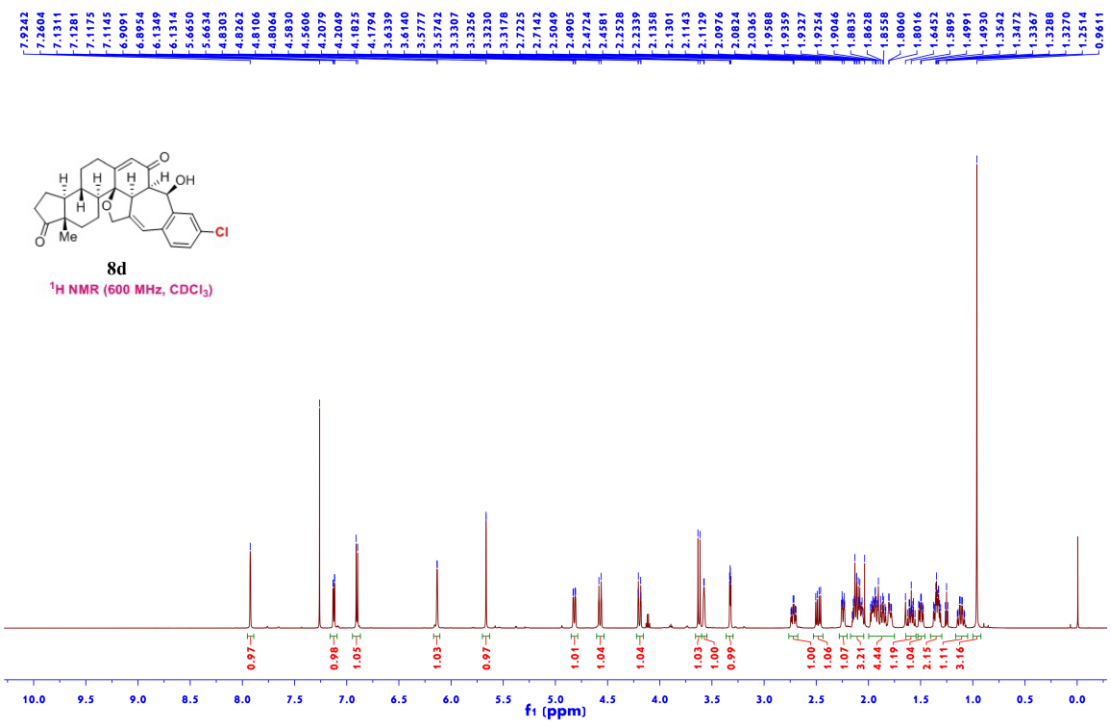


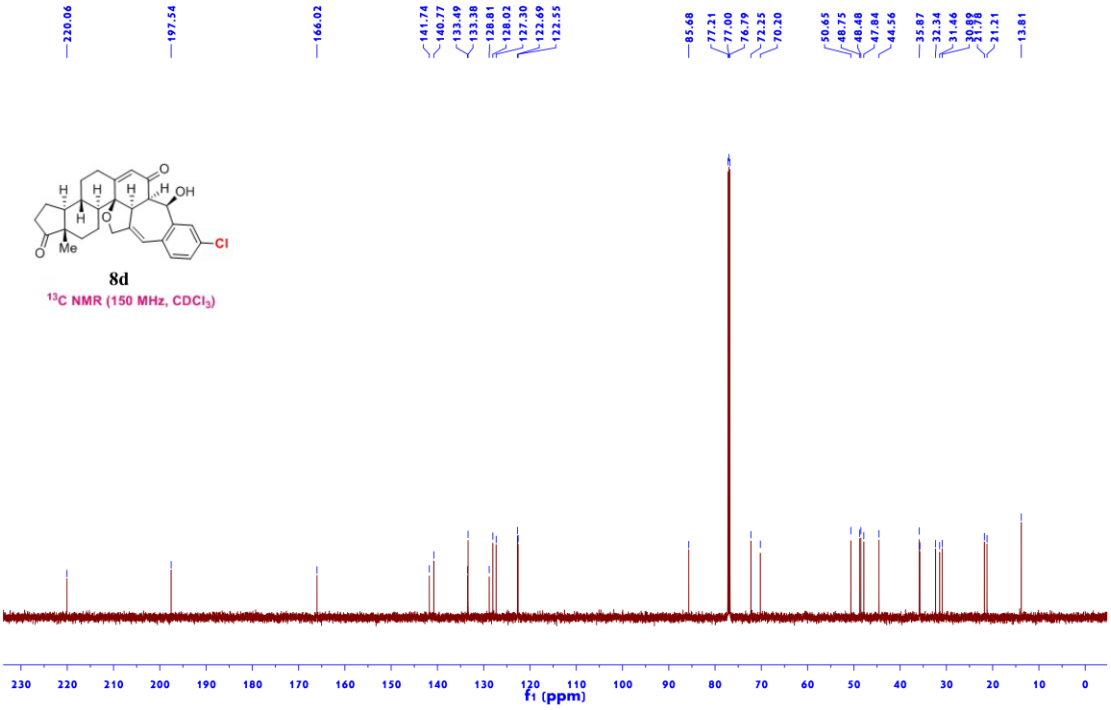
8b

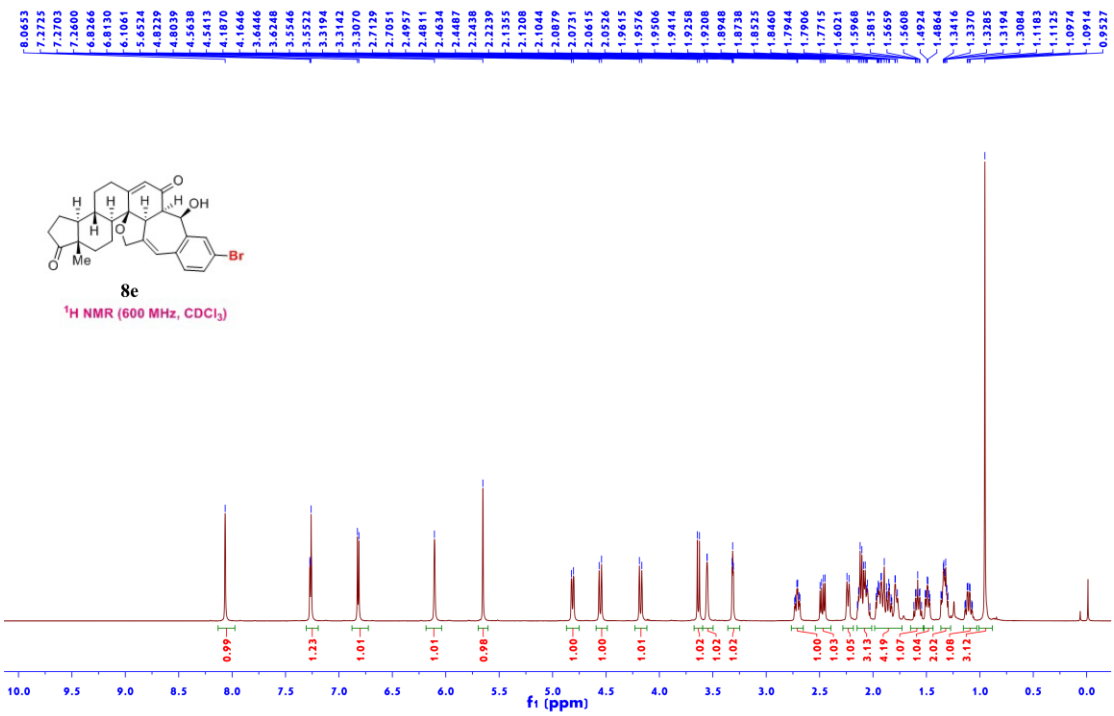
^{19}F NMR (565 MHz, $CDCl_3$)


8c
^{1}H NMR (600 MHz, CDCl$_3$)
f$_1$ (ppm)


8c
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)


8d
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


8d
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)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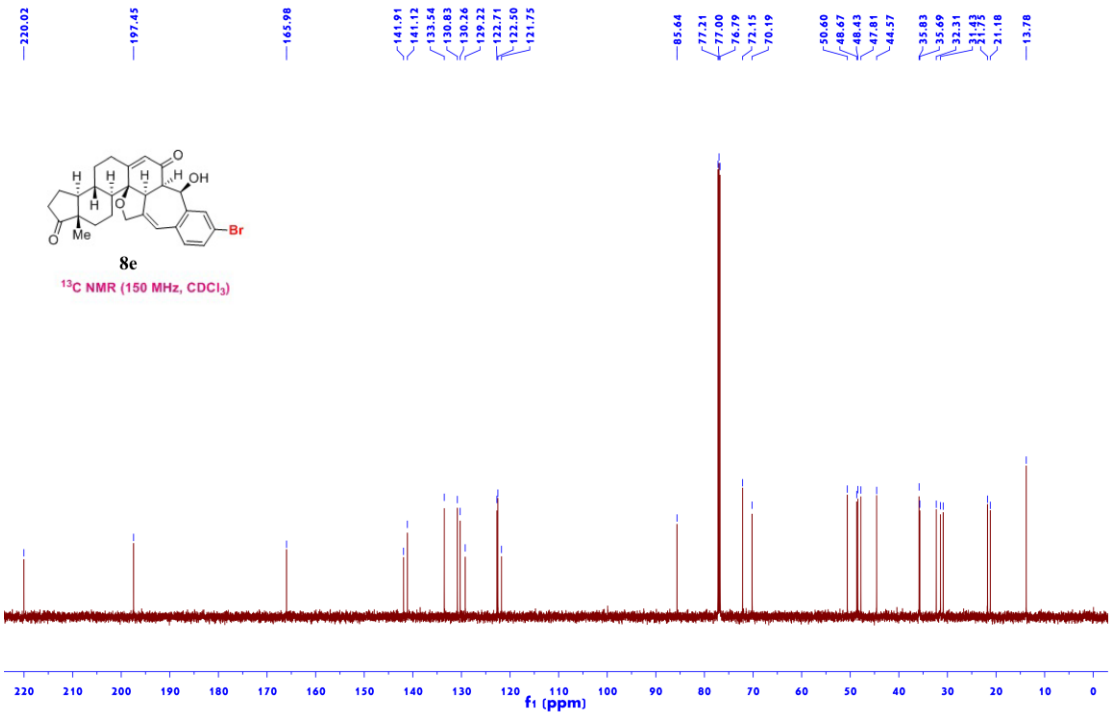
4.5413
4.1870
4.1646
3.6446
3.6248
3.5546
3.5522
3.3194
3.3142
3.3070
2.7129
2.7051
2.4957
2.4811
2.4634
2.4487
2.2438
2.2239
2.1355
2.1208
2.1044
2.0879
2.0731
2.0615
2.0526
1.9615
1.9576
1.9506
1.9414
1.9258
1.9208
1.8948
1.8738
1.8525
1.8460
1.7944
1.7906
1.7715
1.6021
1.5968
1.5815
1.5659
1.5608
1.4924
1.4864
1.3416
1.3370
1.3285
1.3194
1.3084
1.1183
1.1125
1.0974
1.0914
0.9527
8e
1H NMR (600 MHz, CDCl3)
0.99
1.23
1.01
1.01
0.98
1.00
1.00
1.01
1.02
1.02
1.02
1.00
1.03
1.05
3.13
4.19
1.07
1.04
2.02
1.08
3.12
f1 (ppm)


220.02
197.45
165.98
141.91
141.12
133.54
130.83
130.26
129.22
122.71
122.50
121.75
85.64
77.21
77.00
76.79
72.15
70.19
50.60
48.67
48.43
47.81
44.57
35.83
35.69
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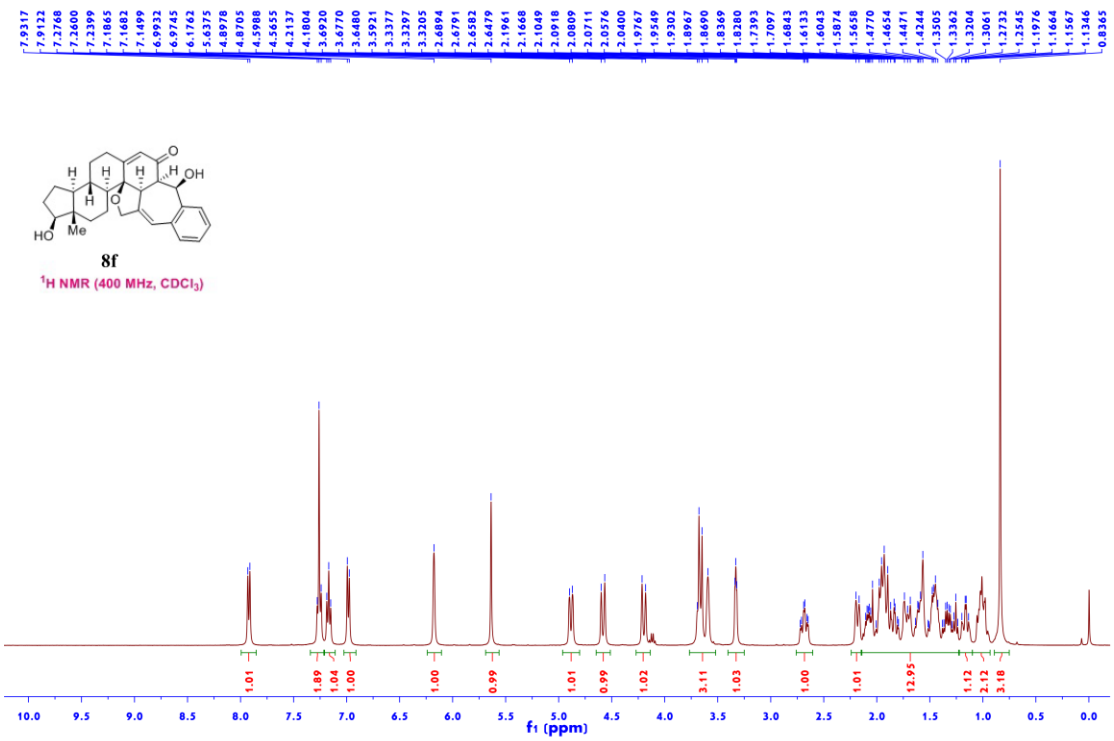
31.13
21.18
13.78
8e
13C NMR (150 MHz, CDCl3)
f1 (ppm)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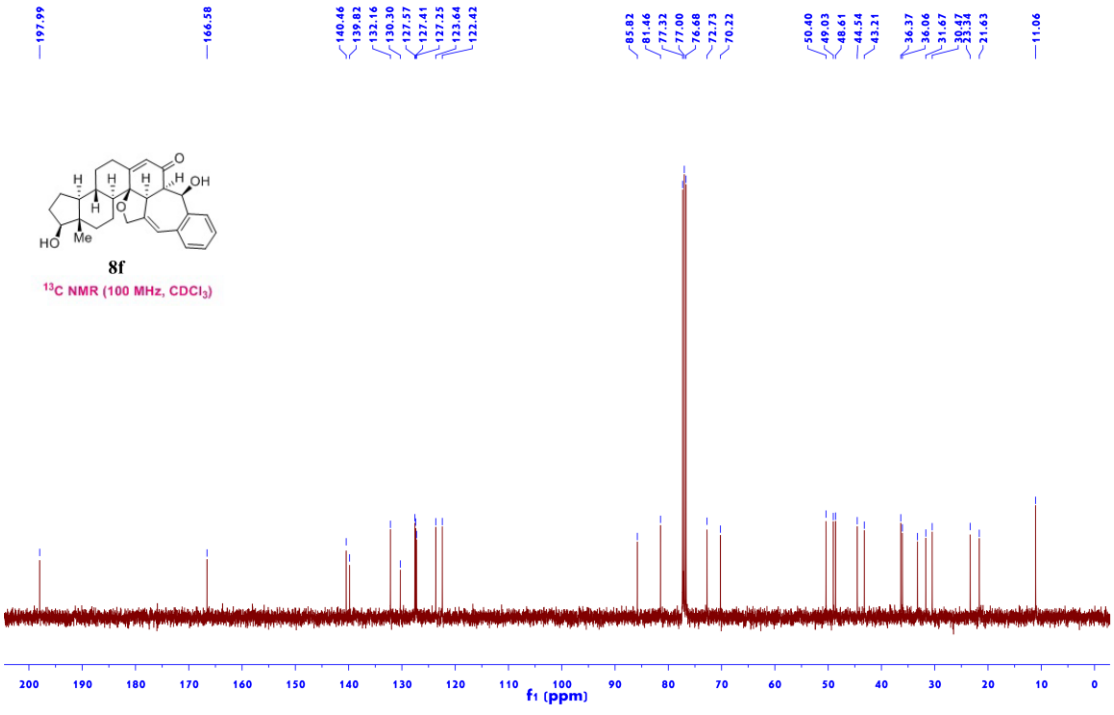
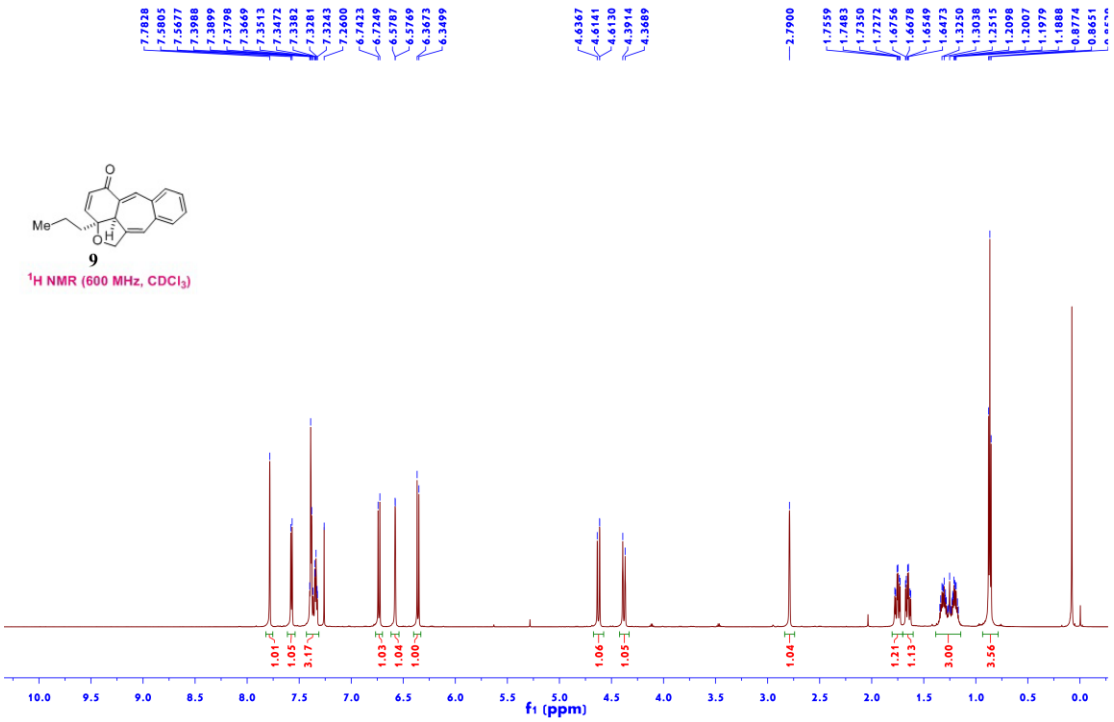
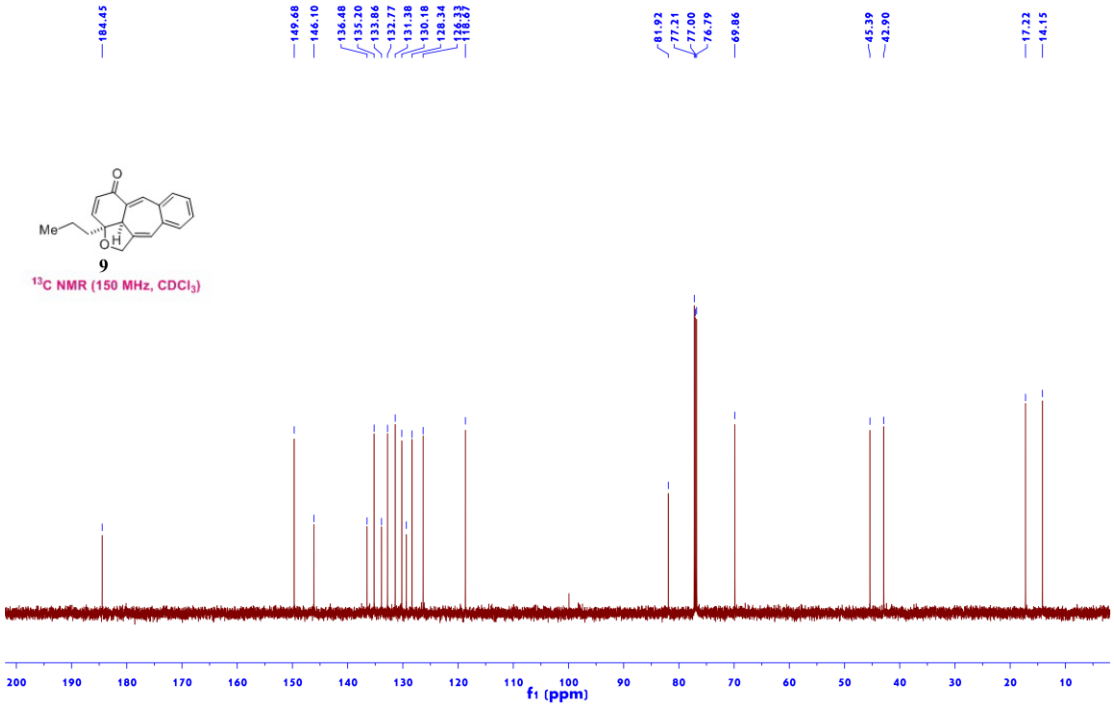
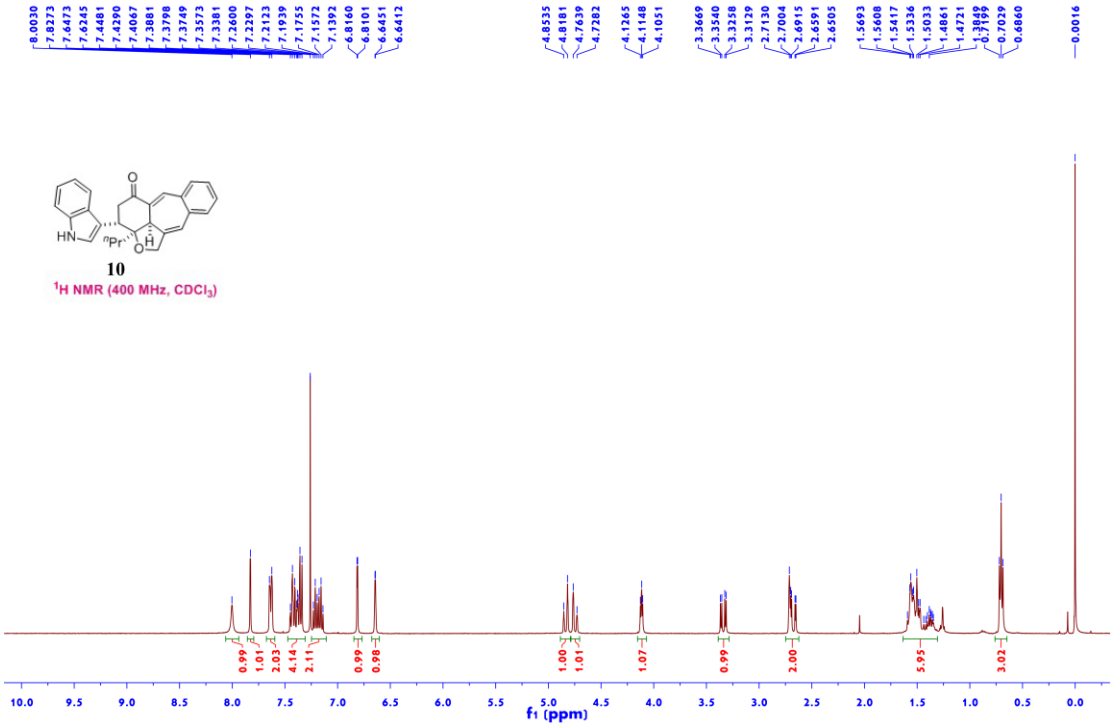
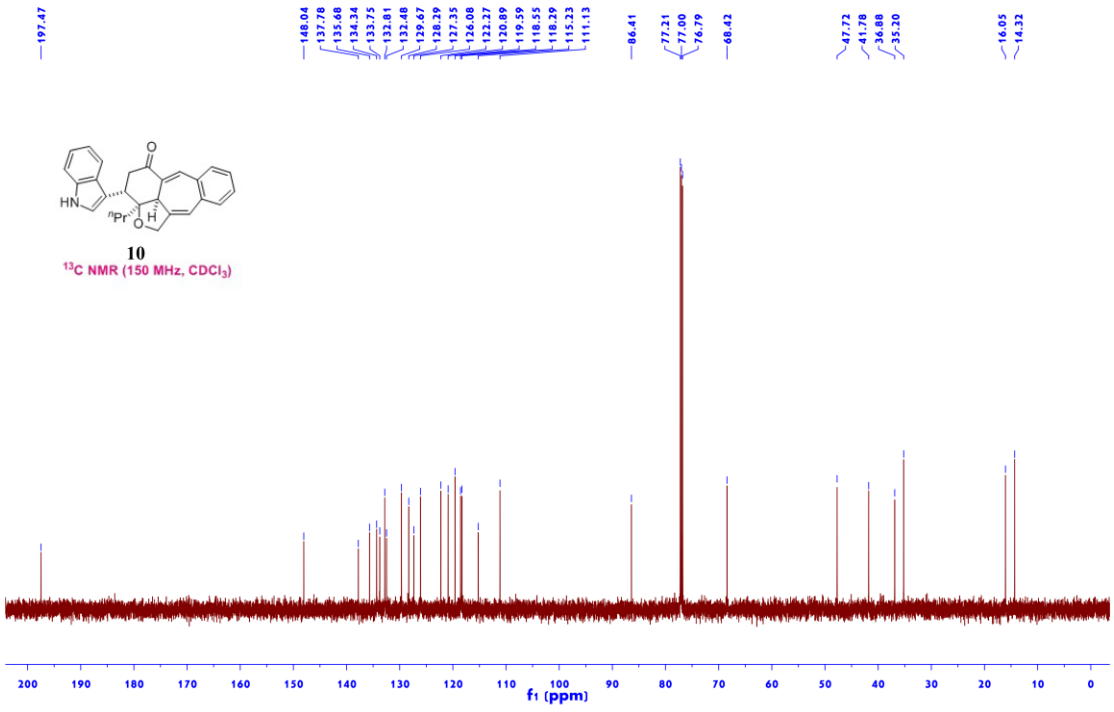
7.9122
7.2768
7.2600
7.2399
7.1865
7.1682
7.1499
6.9932
6.9745
6.1762
5.6375
4.8978
4.8705
4.5988
4.5655
4.2137
4.1804
3.6920
3.6770
3.6480
3.5921
3.3337
3.3297
3.3205
2.6894
2.6791
2.6582
2.6479
2.1961
2.1668
2.1049
2.0918
2.0809
2.0711
2.0576
2.0400
1.9767
1.9549
1.9302
1.8967
1.8690
1.8369
1.8280
1.7393
1.7097
1.6843
1.6133
1.6043
1.5874
1.5658
1.4770
1.4654
1.4471
1.4244
1.3505
1.3362
1.3204
1.3061
1.2732
1.2545
1.1976
1.1664
1.1567
1.1346
0.8365
8f
1H NMR (400 MHz, CDCl3)
1.01
1.89
1.04
1.00
1.00
0.99
1.01
0.99
1.02
3.11
1.03
1.00
1.01
12.95
1.12
2.12
3.18
f1 (ppm)

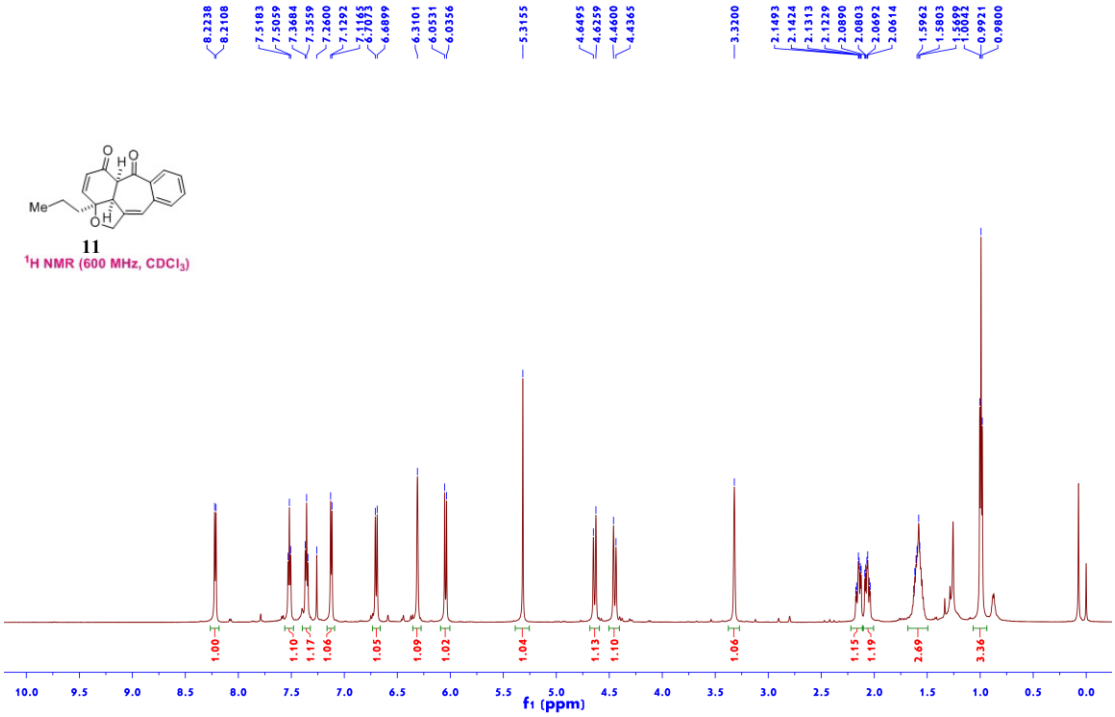

197.99
166.58
140.46
139.82
132.16
130.30
127.57
127.41
127.25
123.64
122.42
85.82
81.46
77.32
77.00
76.68
72.73
70.22
50.40
49.03
48.61
44.54
43.21
36.37
36.06
31.67
30.47
23.34
21.63
11.06
8f
13C NMR (100 MHz, CDCl3)
f1 (ppm)

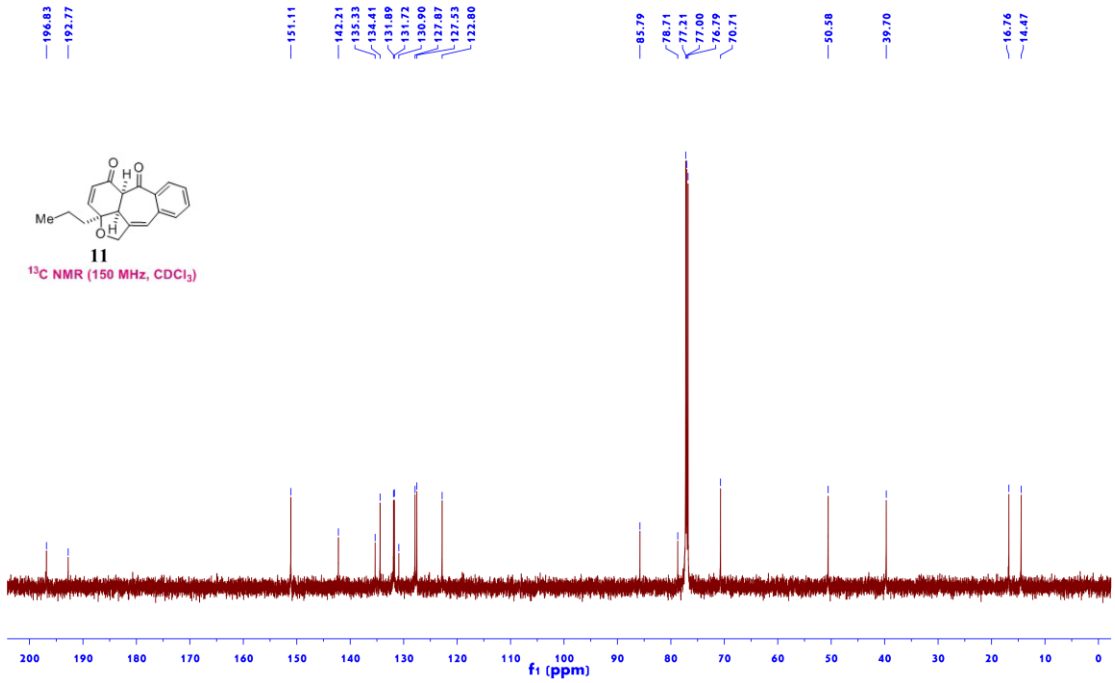

Me
O
H
9
1H NMR (600 MHz, CDCl3)
f1 (ppm)

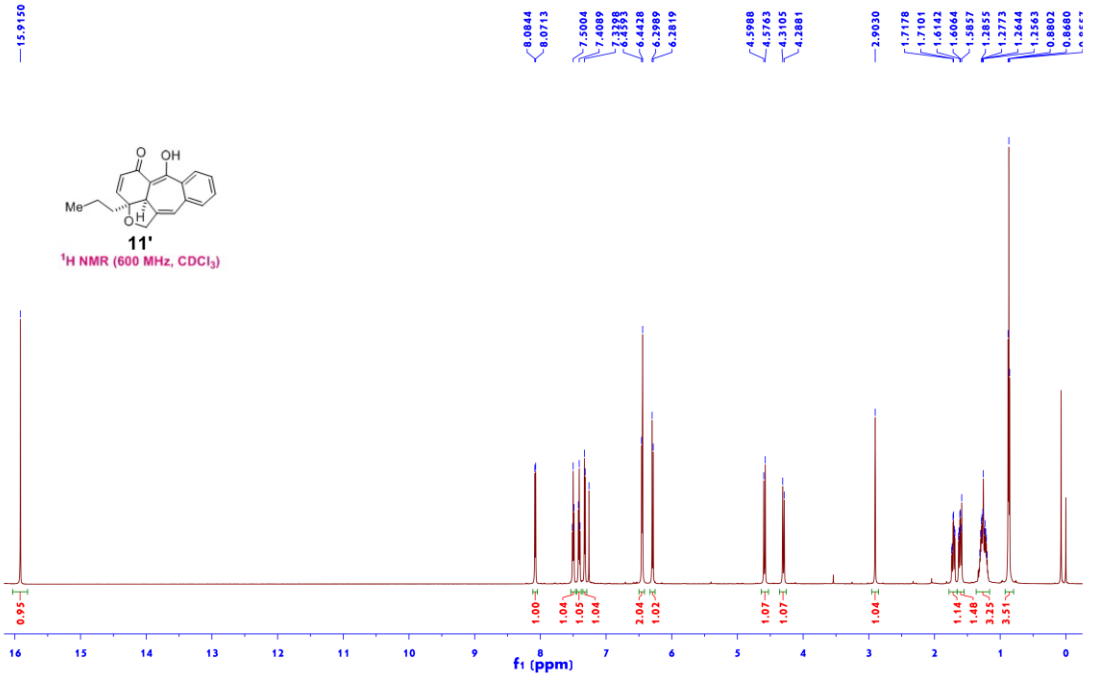

Me
O
H
9
13C NMR (150 MHz, CDCl3)
f1 (ppm)

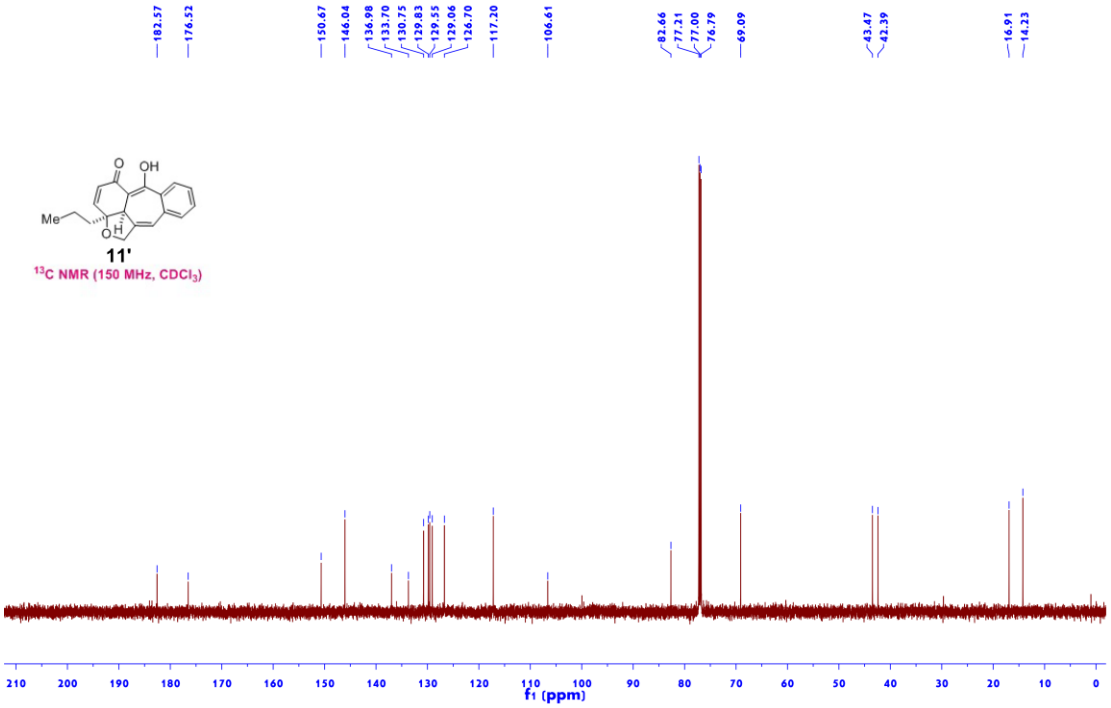

10
^{1}H NMR (400 MHz, CDCl$_3$)
f$_1$ (ppm)

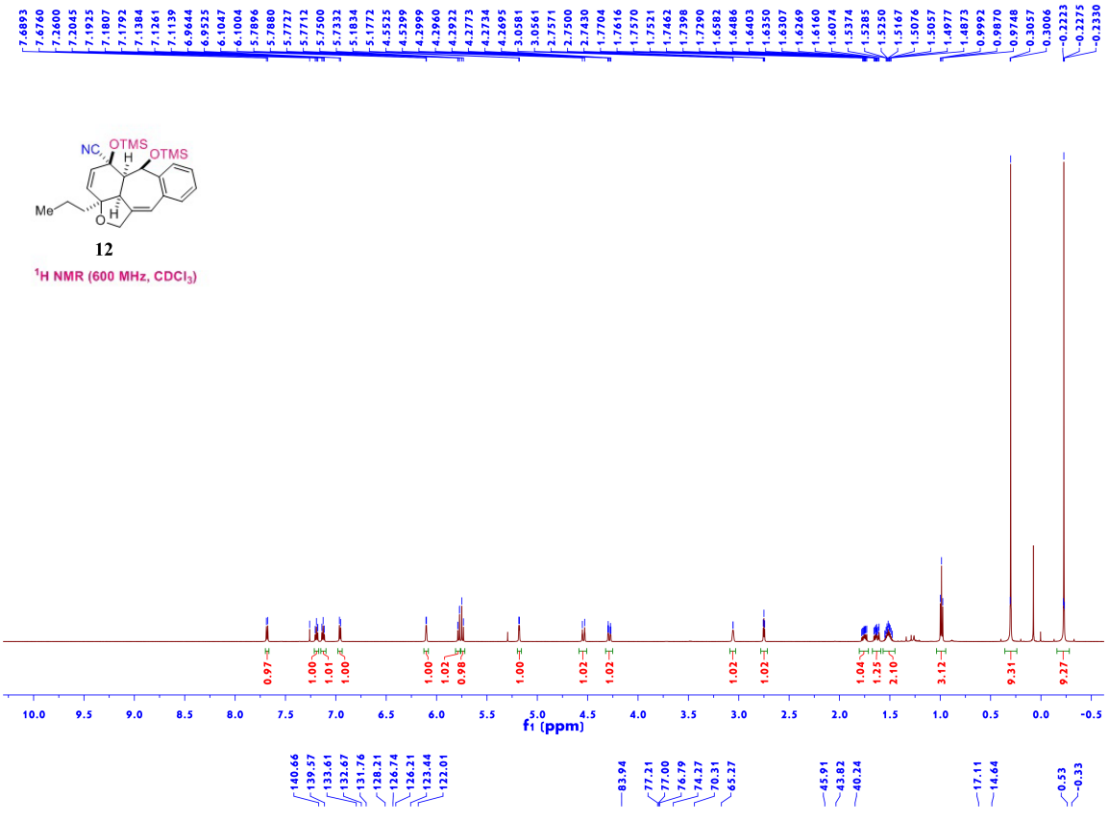

10
^{13}C NMR (150 MHz, CDCl$_3$)
f$_1$ (ppm)

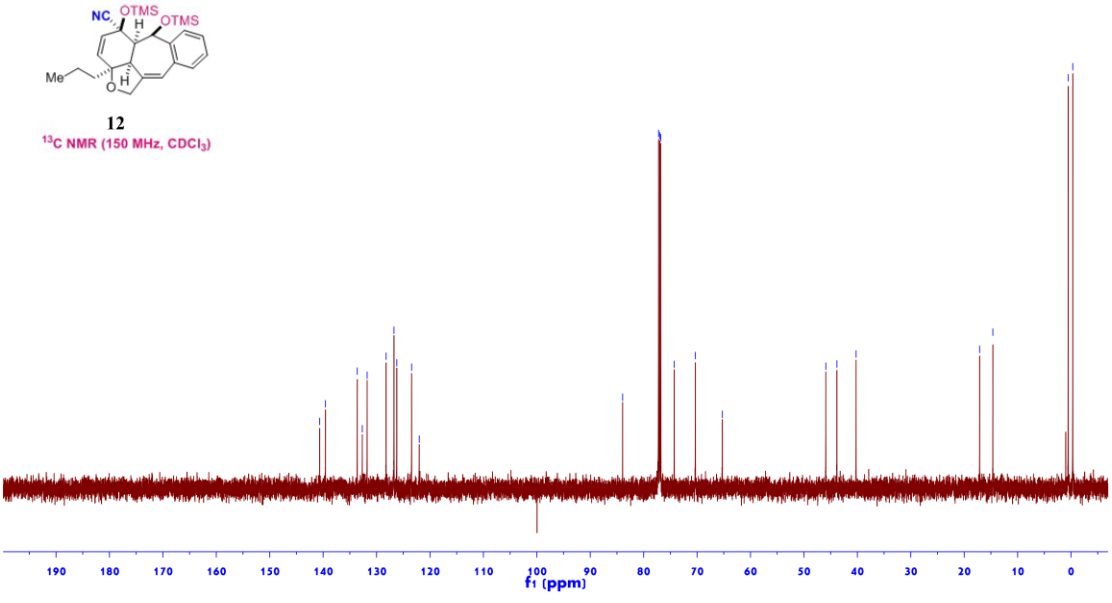

11
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

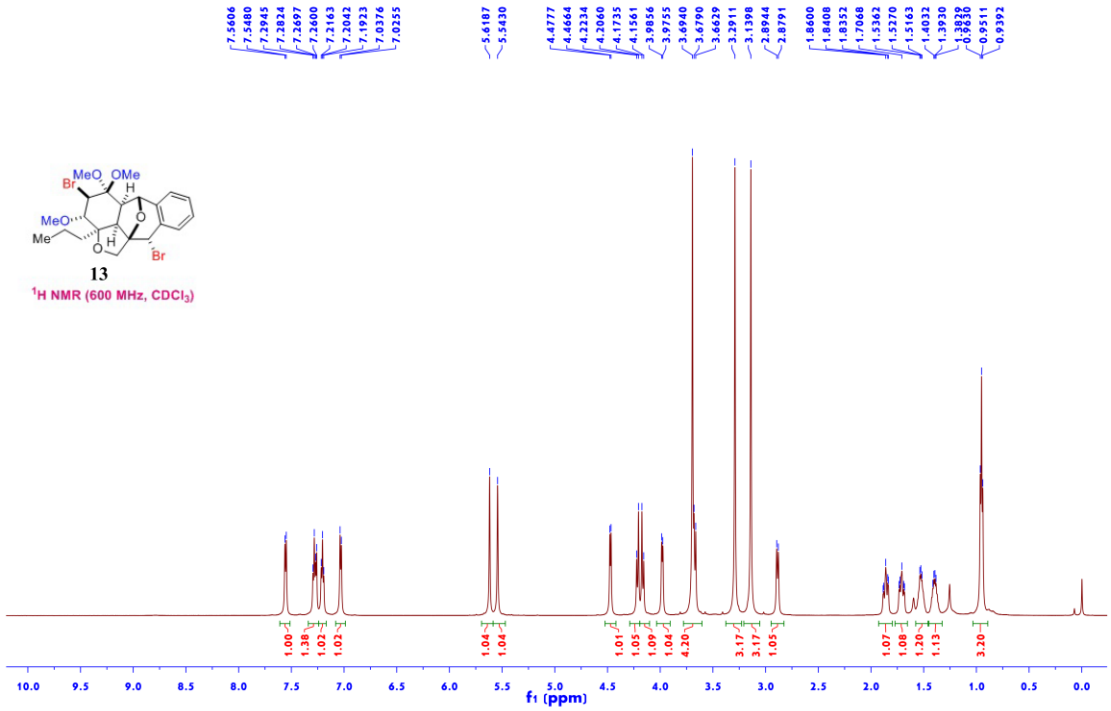

11
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)

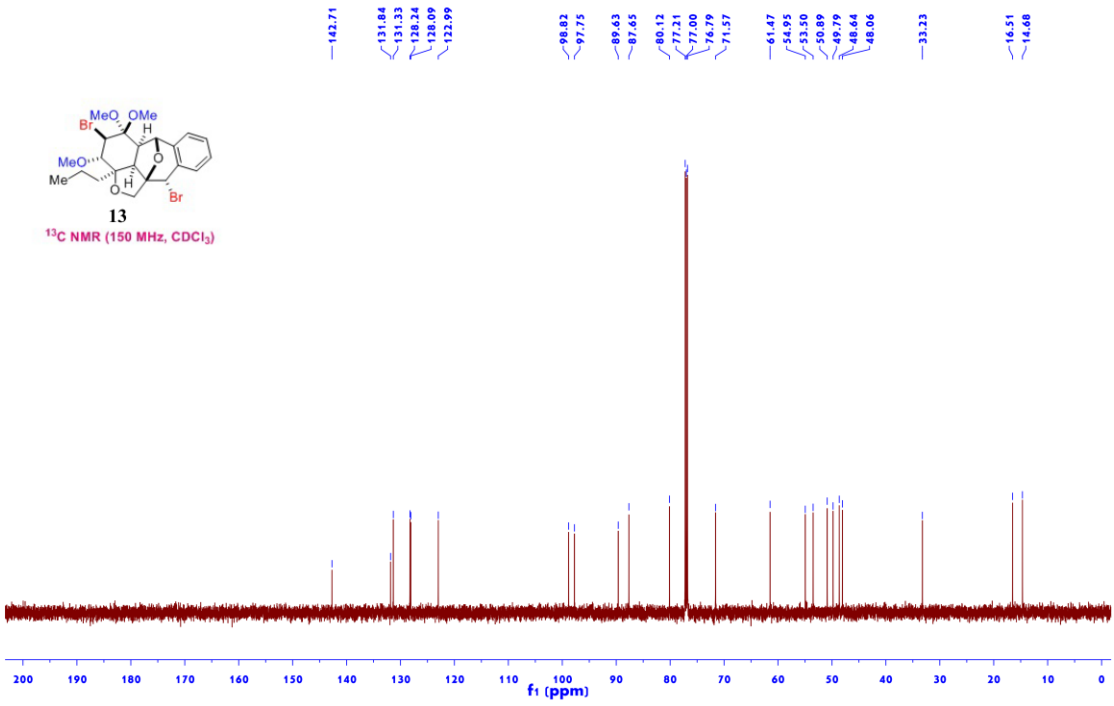

11'
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


11'
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)


NC
OTMS
H
OTMS
Me
O
H
12
1H NMR (600 MHz, CDCl3)
f1 (ppm)


NC
OTMS
H
OTMS
Me
O
H
12
13C NMR (150 MHz, CDCl3)
f1 (ppm)


13
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


13
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)

8. X-ray Crystal Structures of 2a, 4a, 8d and 13

Crystal preparation: Compound **2a** (30 mg) was dissolved in hexane/EtOAc = 9:1 (10 mL) in a 25 mL round-bottom flask while compounds **4a**, **8d** or **13** (30 mg) were dissolved in hexane/EtOAc/CH_2Cl_2 = 8:1:1 (5 mL) in a 25 mL round-bottom flask and the resultant solution was allowed to slowly evaporate at room temperature to give crystals suitable for X-ray diffraction analysis. The intensity data were collected at 100 K or 150 K on a single crystal X-ray diffractometer. More information on crystal structures can also be obtained from the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers 2150312 (**2a**), 2150313 (**4a**), 2150314 (**8d**) and 2150315 (**13**), respectively.

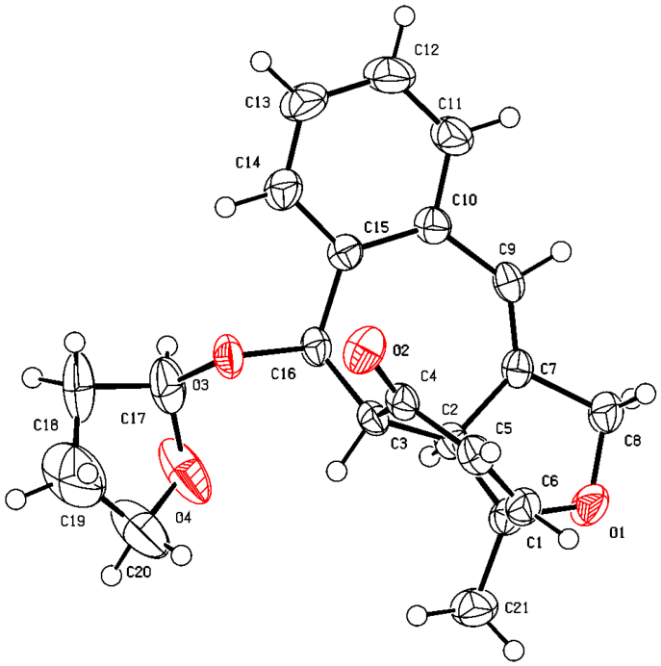


Figure S1. ORTEP drawing of **2a** with thermal ellipsoids at 30% probability levels.

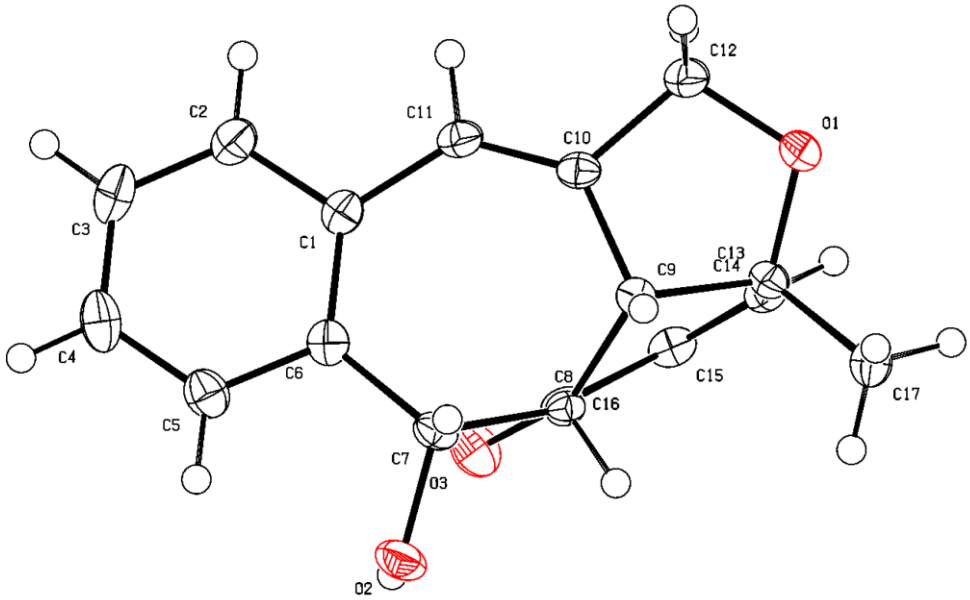


Figure S2. ORTEP drawing of **4a** with thermal ellipsoids at 30% probability levels.

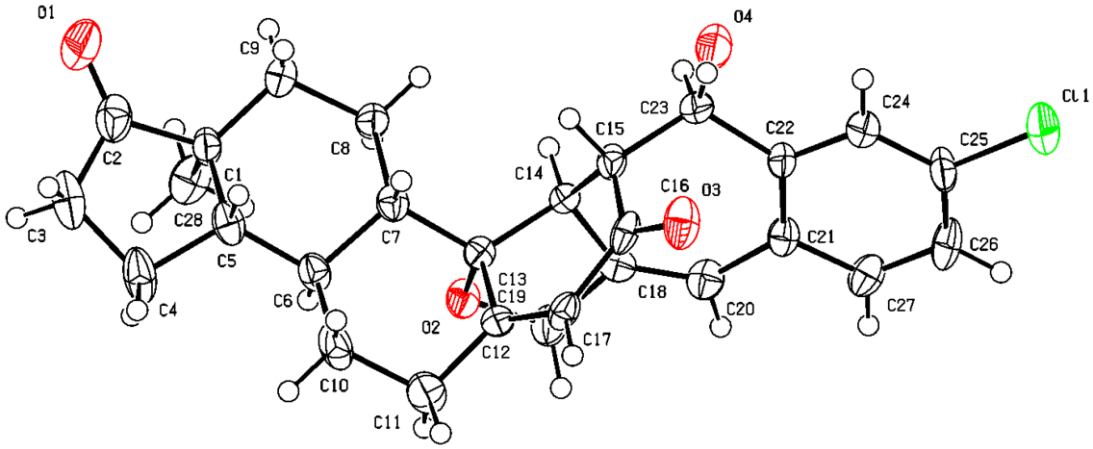


Figure S3. ORTEP drawing of **8d** with thermal ellipsoids at 30% probability levels.

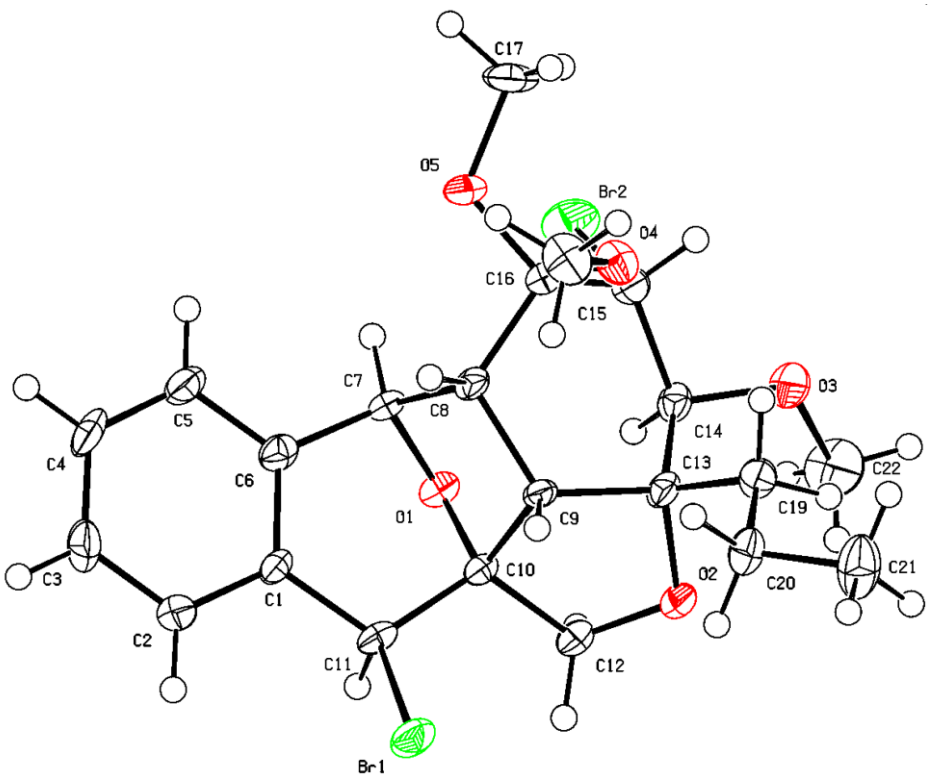


Figure S4. ORTEP drawing of **13** with thermal ellipsoids at 30% probability levels.

9. References

S1. K. K. Gollapelli, V. B. Patil, A. Vinaykumar and R. Chegondi, Rh(I)-Catalyzed Stereoselective Desymmetrization of Prochiral Cyclohexadienones *via* Highly *exo*-Selective Huisgen-type [3 + 2] Cycloaddition, *Chem. Sci.*, 2021, **12**, 1544-1550.

S2. J. K. Hexum, R. Tello-Aburto, N. B. Struntz, A. M. Harned and D. A. Harki, Bicyclic Cyclohexenones as Inhibitors of NF-κB Signaling, *ACS Med. Chem. Lett.*, 2012, **3**, 459-464.

S3. Y. Fukui, P. Liu, Q. Liu, Z.-T. He, N.-Y. Wu, P. Tian and G.-Q. Lin, Tunable Arylative Cyclization of 1,6-Enynes Triggered by Rhodium (III)-Catalyzed C-H Activation, *J. Am. Chem. Soc.*, 2014, **136**, 15607-15614.

S4. Z.-T. He, X.-Q. Tang, L.-B. Xie, M. Cheng, P. Tian and G.-Q. Lin, Efficient Access to Bicyclo[4.3.0]nonanes: Copper-Catalyzed Asymmetric Silylative Cyclization of Cyclohexadienone-Tethered Allenes, *Angew. Chem. Int. Ed.*, 2015, **54**, 14815-14818.

S5. D. Gao, X.-Y. Liu, H. Xu, Y.-X. Tan, Q. Liao, Q.-H. Li, X. Yang and G.-Q. Lin, P. Tian, One-Pot Preparation of 9,10-Dihydrophenanthrenes Initiated by Rhodium(III)-Catalyzed C-H Activation and Relay Diels-Alder Reaction, *Org. Lett.*, 2020, **22**, 4300-4305.

S6. H. Jin, Q. Zhang, E. Li, P. Jia and N. Li, Y. Huang, Phosphine-Catalyzed Intramolecular Rauhut-Currier Reaction: Enantioselective Synthesis of Hydro-2h-indole Derivatives, *Org. Biomol. Chem.*, 2017, **15**, 7097-7101.

S7. D. Xu, Y. Zhao, D. Song, Z. Zhong, S. Feng, X. Xie, X. Wang and X. She, (3 +2)-Annulation of *p*-Quinamine and Aryne: A Strategy To Construct the Multisubstituted Hydrocarbazoles, *Org. Lett.*, 2017, **9**, 3600-3603.