Electronic Supplementary Information

for

PtI_4-Catalyzed Oxidative and Hydrogenative Dearomative [3 + 2] Cycloadditions of 1*H*-Indole *N*-Tethered *o*-Alkynylbenzaldehydes

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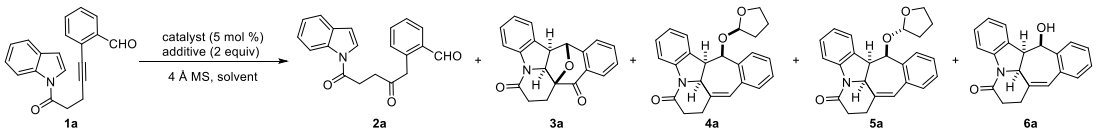
Table of Contents

1. General information

All commercial chemicals were used without additional purification, unless otherwise stated. All catalysts were purchased from Energy Chemical and Sigma-Aldrich. THF and Toluene were dried using Na/benzophenone, DCE was dried using CaH_2. 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 NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded with either a Bruker AVQ-600 or 400 spectrometer instrument in $CDCl_3$. 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 Finnigan MAT95XP LC/HRMS TOF spectrometer using simultaneous electrospray (ESI). Melting points were determined using a digital melting point apparatus (MPA-100).

2. Complete Screening and Optimization of [3+2] cycloaddition

Table S1. Optimization of the Reaction Conditions[a]



entry	catalyst	additive	solvent	T [°C]/*t* [h]	yield[b] (%)				
					2a	**3a**	**4a**	**5a**	**6a**
1[c]	$[Rh(COD)Cl]_2$	-	H_2O	80/48	28				
2[c]	$[Rh(COD)Cl]_2$	H_2O	toluene	80/18		21			
3	$[Rh(COD)Cl]_2$	DMSO	toluene	80/16		31			
4	$[Rh(COD)Cl]_2$	DPSO	toluene	80/12		39			
5	$[Rh(COD)Cl]_2$	PMSO	toluene	80/12		44			
6	$AuBr_3$	PMSO	toluene	80/12		69			
7	$Me_2S.AuCl$	PMSO	toluene	80/12		56			

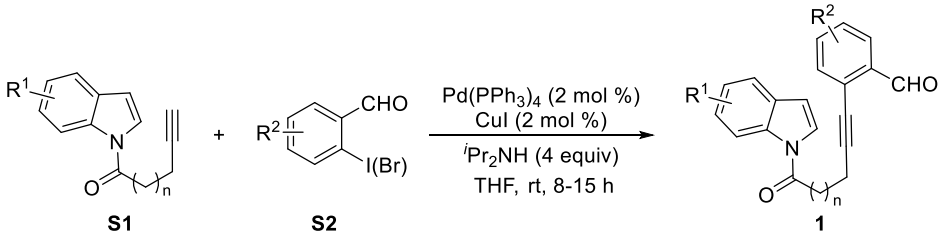
Table S1. (continued)

8	JohnPhosAuNTf$_2$	PMSO	toluene	800/48	9	36			
9	XPhosAuNTf$_2$	PMSO	toluene	80/48	6	25			
10	IPrAuNTf$_2$	PMSO	toluene	80/48	20	19			
11	PtCl$_2$	PMSO	toluene	80/12		47			
12	Pt(COD)Cl$_2$	PMSO	toluene	80/12		78			
13	PtBr$_2$	PMSO	toluene	80/12		85			
14	PtI$_2$	PMSO	toluene	80/12		73			
15	PtCl$_4$	PMSO	toluene	80/12		50			
16	PtBr$_4$	PMSO	toluene	80/12		60			
17	PtI$_4$	PMSO	toluene	80/12		99			
18	PtI$_4$ (1 mol%)	PMSO	toluene	80/12		99			
19	PtI$_4$	PMSO	DCE	80/12		98			
20	PtI$_4$	PMSO	THF	80/12		78			
21	PtI$_4$ (1 mol%)	PMSO	toluene	25/72		97			
22	PtI$_4$	-	THF	80/12			36	25	29
23	PtBr$_4$	-	THF	80/12			33	23	20
24	PtCl$_2$	-	THF	80/12			28	25	21
25	PtBr$_2$	-	THF	80/12			31	27	24

[a] All reactions were performed with **1a** (0.2 mmol), catalyst (5 mol %), additive (0.4 mmol), and 4 Å MS (200 mg) in solvent (2 mL) at 80 °C. [b] Isolated product yields. [c] Reaction was performed in the absence of 4 Å MS. DPSO = diphenylsulfoxide; PMSO = phenylmethylsulfoxide; JohnPhos = 2-(di-*tert*-butylphosphino)biphenyl; Xphos = 2-(dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl; IPr = 1,3-bis(diisopropylphenyl) imidazole-2ylidene).

3. Preparation and characterization of starting materials

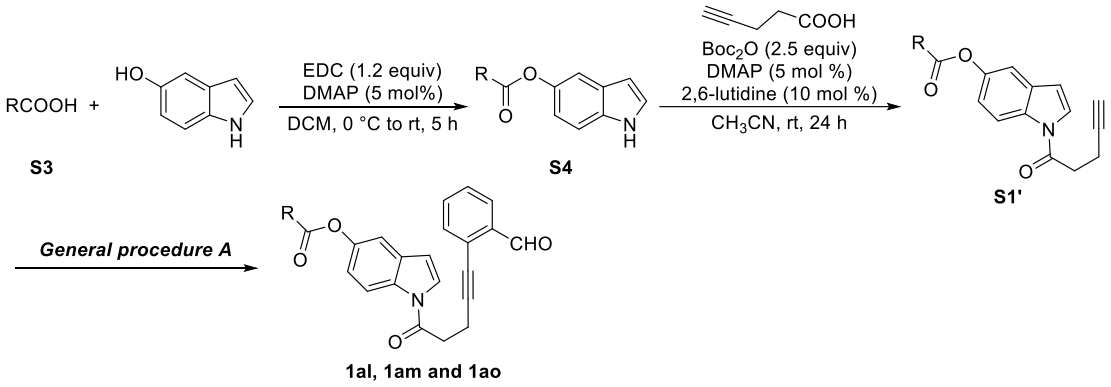
3.1. General procedure A



To a solution of **S1** (2.0 mmol), 2-iodo(bromo)-benzaldehydes **S2** (2.2 mmol, 1.1 equiv), Pd(PPh$_3$)$_4$ (46.2 mg, 0.04 mmol) and CuI (7.6 mg, 0.04 mmol) in anhydrous THF (10

mL) was added *i*Pr$_2$NH (8 mmol, 4 equiv) under an argon atmosphere.[S1] The resulting reaction mixture was stirred at room temperature for 8-15 h until full consumption of the starting material (as indicated by TLC). The reaction mixture was quenched with saturated NH_4Cl solution (15 mL), extracted with EtOAc (2 × 15 mL). The combined organic layers were washed with saturated brine (10 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 **1**.

3.2. General procedure B for the synthesis of 1al, 1am and 1ao



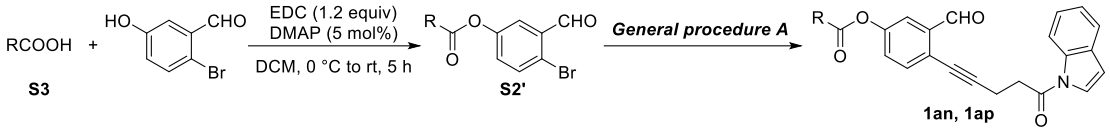
Step 1: Following slightly modified literature procedure, to a solution of 5-hydroxyindole (1.332 g, 10.0 mmol), acid derivative (10.0 mmol) and DMAP (61 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of EDC (*N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride, 2.3 g, 12 mmol) in CH_2Cl_2 (10 mL) at 0 ℃ under an argon atmosphere.[S2] The reaction was stirred at room temperature for 5 h. Upon completion (monitored by TLC), the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (2 × 20 mL), the combined organic layers were washed with brine, 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 **S4**.

Step 2: Following literature procedure, to a solution of 4-pentynoic acid (1.0 equiv), **S4** (2.5 equiv), DMAP (5 mol %), and 2,6-lutidine (5 mol %) in CH_3CN (0.4 M) was added Boc_2O (2.5 equiv) at room temperature.[S1] The resulting reaction mixture was stirred at room temperature for 24 h. The resulting reaction mixture was concentrated

under reduced pressure to give a crude oil, which was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to give **S1′**.

Step 3: Following general procedure A, substrates **1al**, **1am** and **1ao** were obtained from **S1′** as pale-yellow solids in respective overall yields of 73%, 70% and 66% over 3 steps.

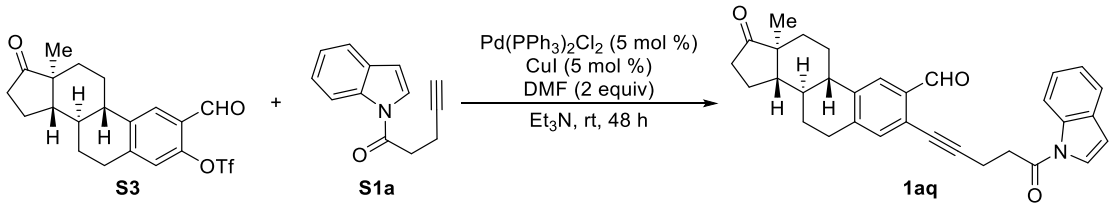
3.3. General procedure C for the synthesis of 1an and 1ap



Step 1: Following slightly modified literature procedure, to a solution of 2-bromo-5-hydroxybenzaldehyde (402 mg, 2.0 mmol), acid derivative (2.0 mmol) and DMAP (12.2 mg, 0.1 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of EDC (2.4 mmol) in CH_2Cl_2 (5 mL) at 0 ℃ under an argon atmosphere.[S2] The reaction was stirred at room temperature for 5 h. Upon completion (monitored by TLC), the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (2 × 10 mL), the combined organic layers were 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 provide **S2′**.

Step 2: Following general procedure A, substrate **1an** and **1ap** were prepared from **S2′** as pale-yellow solids in respective overall yields of 75% and 72% over 2 steps.

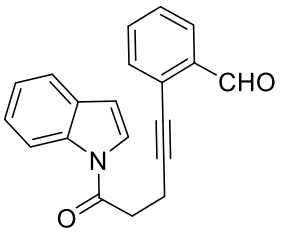
3.4. General procedure D for the synthesis of 1aq



To a solution of **S1a** (4.32 mmol, 1.5 equiv) and **S3** (2.88 mmol) in anhydrous Et_3N (12 mL) were added $Pd(PPh_3)_2Cl_2$ (101 mg, 0.144 mmol), CuI (27.4 mg, 0.144 mmol) and DMF (5.76 mmol, 2 equiv) under an argon atmosphere.[S1,S3] The resulting reaction

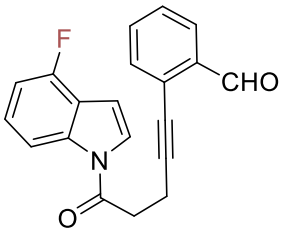
mixture was stirred at room temperature for 48 h. The reaction mixture was quenched with saturated NH_4Cl solution (15 mL) and extracted with EtOAc (2 × 15 mL). The combined organic layers were washed with saturated brine (15 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 15:1 to 5:1) to give **1aq** as a pale-yellow solid in 45% yield (619 mg).

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1a)



The title compound was prepared following general procedure A in 87% yield (524 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 147–149 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.52 (s, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.54–7.45 (m, 3H), 7.43–7.34 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 3.6 Hz, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.1, 136.0, 135.5, 133.6, 133.3, 130.3, 128.2, 127.1, 126.9, 125.3, 124.2, 123.8, 120.9, 116.5, 109.6, 95.4, 77.3, 34.7, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{16}NO_2$ $[M+H]^+$: 302.1176; found: 302.1180.

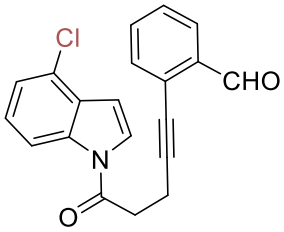
2-(5-(4-fluoro-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1b)



The title compound was prepared following general procedure A in 69% yield (441 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 161–163 ℃; **^{1}H NMR**

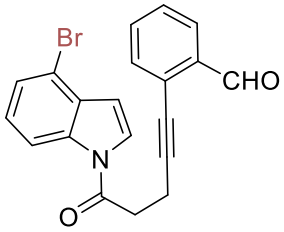
(600 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.55–7.48 (m, 2H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.30 (td, *J* = 8.2, 5.5 Hz, 1H), 6.97 (t, *J* = 9 Hz, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 3.30 (t, *J* = 7.3 Hz, 2H), 3.04 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.2, 155.6 (d, *J* = 248.3 Hz), 137.6 (d, *J* = 9.0 Hz), 136.1, 133.7, 133.4, 128.3, 127.2, 126.9, 126.2 (d, *J* = 7.2 Hz), 124.1, 119.1 (d, *J* = 21.8 Hz), 112.6 (d, *J* =3.4 Hz), 109.2 (d, *J* = 18.5 Hz), 105.2, 95.1, 77.5, 34.8, 15.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –121.68 – –121.70 (m); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_2$ $[M+H]^+$: 320.1081; found: 320.1078.

2-(5-(4-chloro-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1c)



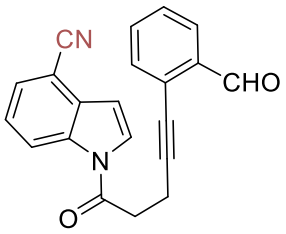
The title compound was prepared following general procedure A in 71% yield (477 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 148–150 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 8.40–8.36 (m, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.55–7.47 (m, 3H), 7.40 (td, *J* = 7.6, 1.0 Hz, 1H), 7.30–7.27 (m, 2H), 6.79 (d, *J* = 3.8 Hz, 1H), 3.29 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.2, 136.2, 136.1, 133.7, 133.4, 129.1, 128.3, 127.2, 126.8, 126.1, 126.1, 124.7, 123.7, 115.1, 107.7, 95.1, 77.5, 34.7, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_2$ $[M+H]^+$: 336.0786; found: 336.0782.

2-(5-(4-bromo-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1d)



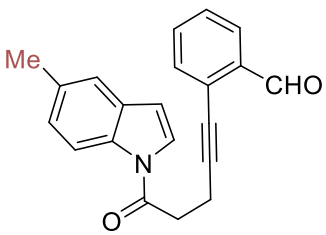
The title compound was prepared following general procedure A in 78% yield (593 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 158–160 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.53–7.47 (m, 3H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.39 (td, *J* = 7.4, 1.1 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 3.8 Hz, 1H), 3.27 (t, *J* = 7.3 Hz, 2H), 3.02 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.2, 136.0, 135.9, 133.6, 133.3, 130.9, 128.3, 127.2, 126.8, 126.7, 126.3, 124.7, 115.6, 114.6, 109.3, 95.1, 77.5, 34.7, 14.9; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_2$ $[M+H]^+$: 380.0281; found: 380.0281.

1-(5-(2-formylphenyl)pent-4-ynoyl)-1*H*-indole-4-carbonitrile (1e)



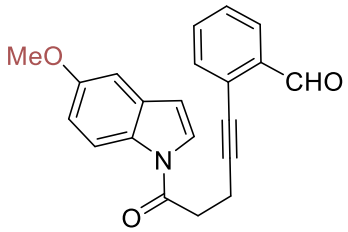
The title compound was prepared following general procedure A in 73% yield (476 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 15:1) to afford the product as a colorless solid, mp 161–163 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.68 (d, *J* = 3.8 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.53–7.47 (m, 2H), 7.44–7.38 (m, 2H), 6.89 (d, *J* = 3.8 Hz, 1H), 3.34 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.7, 169.3, 136.0, 135.3, 133.7, 133.3, 132.0, 128.4, 128.2, 127.2, 126.7, 126.7, 125.2, 121.1, 117.5, 107.5, 103.8, 94.8, 77.6, 34.7, 14.9; **HRMS (ESI)** calcd for $C_{21}H_{15}N_2O_2$ $[M+H]^+$: 327.1128; found: 327.1125.

2-(5-(5-methyl-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1f)



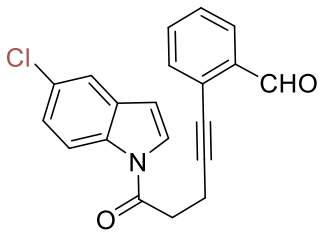
The title compound was prepared following general procedure A in 71% yield (448 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 151–153 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 8.33 (d, *J* = 7.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.54–7.48 (m, 2H), 7.44 (d, *J* = 3.0 Hz, 1H), 7.42–7.37 (m, 1H), 7.36 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 3.7 Hz, 1H), 3.27 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.9, 169.0, 136.1, 133.8, 133.7, 133.5, 133.4, 130.6, 128.3, 127.2, 127.1, 126.6, 124.3, 120.9, 116.2, 109.5, 95.5, 77.4, 34.7, 21.4, 15.1; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1335.

2-(5-(5-methoxy-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1g)



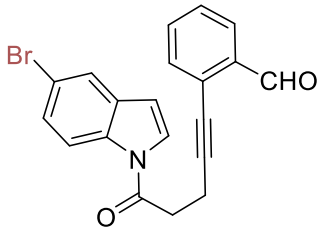
The title compound was prepared following general procedure A in 74% yield (490 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 22:1) to afford the product as a colorless solid, mp 143–145 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 8.36 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.57–7.43 (m, 3H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.03 (s, 1H), 6.97 (dd, *J* = 9.0, 1.6 Hz, 1H), 6.60 (d, *J* = 3.5 Hz, 1H), 3.85 (s, 3H), 3.27 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.9, 168.8, 156.6, 136.1, 133.7, 133.4, 131.4, 130.3, 128.3, 127.2, 127.0, 124.9, 117.3, 113.6, 109.5, 103.7, 95.5, 77.5, 55.7, 34.5, 15.1; **HRMS (ESI)**calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1283.

2-(5-(5-chloro-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1h)



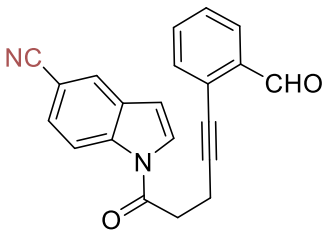
The title compound was prepared following general procedure A in 78% yield (524 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 157–159 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.40 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.56–7.47 (m, 4H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.31 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 3.28 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.0, 136.1, 133.9, 133.7, 133.4, 131.5, 129.4, 128.3, 127.2, 126.9, 125.4, 125.4, 120.5, 117.6, 108.9, 95.1, 77.5, 34.6, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_2$ $[M+H]^+$: 336.0786; found: 336.0788.

2-(5-(5-bromo-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1i)



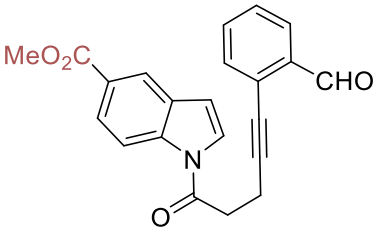
The title compound was prepared following general procedure A in 62% yield (471 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 144–146 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.37 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.54–7.48 (m, 3H), 7.47 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 3.8 Hz, 1H), 3.29 (t, *J* = 7.3 Hz, 2H), 3.04 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.0, 136.1, 134.3, 133.7, 133.4, 132.0, 128.3, 128.1, 127.2, 126.8, 125.3, 123.6, 117.9, 117.1, 108.8, 95.1, 77.5, 34.6, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_2$ $[M+H]^+$: 380.0281; found: 380.0282.

1-(5-(2-formylphenyl)pent-4-ynoyl)-1*H*-indole-5-carbonitrile (1j)



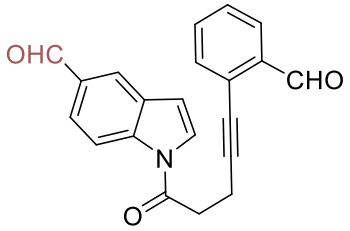
The title compound was prepared following general procedure A in 71% yield (463 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 15:1) to afford the product as a colorless solid, mp 162–164 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.48 (s, 1H), 8.57 (d, *J* = 8.6 Hz, 1H), 7.89 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 3.7 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.53–7.47 (m, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 3.7 Hz, 1H), 3.33 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.7, 169.3, 137.3, 136.0, 133.7, 133.3, 130.3, 128.4, 128.4, 127.3, 126.7, 126.3, 125.6, 119.4, 117.4, 109.1, 107.3, 94.8, 77.6, 34.8, 14.9; **HRMS (ESI)** calcd for $C_{21}H_{15}N_2O_2$ $[M+H]^+$: 327.1128; found: 327.1129.

Methyl 1-(5-(2-formylphenyl)pent-4-ynoyl)-1*H*-indole-5-carboxylate (1k)



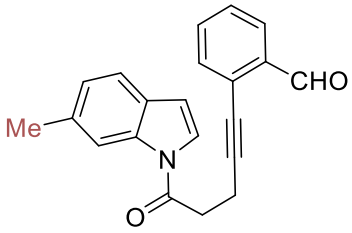
The title compound was prepared following general procedure A in 70% yield (503 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 15:1) to afford the product as a colorless solid, mp 187–189 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.51 (d, *J* = 8.7 Hz, 1H), 8.30 (s, 1H), 8.06 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.54–7.48 (m, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 3.7 Hz, 1H), 3.94 (s, 3H), 3.31 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.3, 167.2, 138.2, 136.1, 133.7, 133.4, 130.1, 128.3, 127.2, 126.8, 126.6, 125.4, 125.8, 123.2, 116.2, 110.0, 95.1, 77.5, 52.1, 34.8, 15.0; **HRMS (ESI)** calcd for $C_{22}H_{18}NO_4$ $[M+H]^+$: 360.1230; found: 360.1235.

1-(5-(2-formylphenyl)pent-4-ynoyl)-1*H*-indole-5-carbaldehyde (1l)



The title compound was prepared following general procedure A in 83% yield (547 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 14:1) to afford the product as a colorless solid, mp 153–155 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 10.05 (s, 1H), 8.59 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 1.1 Hz, 1H), 7.88 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 3.8 Hz, 1H), 7.53–7.46 (m, 2H), 7.40–7.37 (m, 1H), 6.78 (d, *J* = 3.5 Hz, 1H), 3.32 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.9, 191.7, 169.3, 139.0, 136.0, 133.7, 133.3, 132.5, 130.5, 128.3, 127.2, 126.7, 126.5, 125.9, 123.7, 116.9, 110.0, 95.0, 77.5, 34.8, 14.9; **HRMS (ESI)** calcd for $C_{21}H_{16}NO_3$ $[M+H]^+$: 330.1125; found: 330.1129.

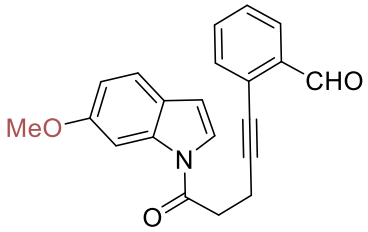
2-(5-(6-methyl-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1m)



The title compound was prepared following general procedure A in 78% yield (492 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 134–136 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.52 (s, 1H), 8.33 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.53–7.48 (m, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.41–7.36 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 3.7 Hz, 1H), 3.26 (t, *J* = 7.3 Hz, 2H), 3.02 (t, *J* = 7.3 Hz, 2H), 2.49 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.1, 136.0, 135.9, 135.4, 133.6, 133.3, 128.2,

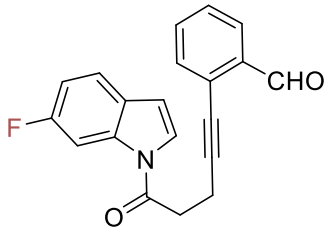
128.0, 127.1, 127.0, 125.2, 123.5, 120.4, 116.8, 109.6, 95.4, 77.3, 34.7, 21.9, 15.0; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1336.

2-(5-(6-methoxy-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1n)



The title compound was prepared following general procedure A in 81% yield (537 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 22:1) to afford the product as a colorless solid, mp 130–132 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 8.09 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.53–7.48 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.40–7.37 (m, 1H), 7.34 (d, *J* = 3.7 Hz, 1H), 6.92 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.59 (d, *J* = 3.7 Hz, 1H), 3.88 (s, 3H), 3.25 (t, *J* = 7.3 Hz, 2H), 3.01 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.3, 158.4, 136.6, 136.0, 133.6, 133.3, 128.2, 127.1, 127.0, 123.8, 122.8, 121.2, 113.2, 109.5, 100.6, 95.4, 77.3, 55.6, 34.6, 14.9; **HRMS (ESI)**calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1284.

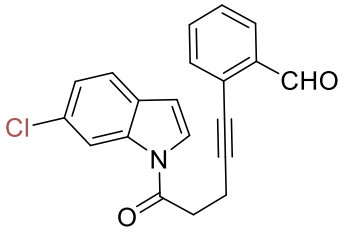
2-(5-(6-fluoro-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1o)



The title compound was prepared following general procedure A in 87% yield (556 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 15:1) to afford the product as a colorless solid, mp 156–158 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 8.22 (d, *J* = 6.0 Hz, 1H), 7.86 (dd, *J* = 4.8, 4.0 Hz, 1H), 7.53–7.42 (m, 4H), 7.40–7.35 (m, 1H), 7.03 (tt, *J* = 8.9, 2.4 Hz, 1H), 6.62 (t, *J* = 3 Hz, 1H), 3.26 (td, *J* = 7.4, 2.3 Hz, 2H), 3.01 (td, *J* = 7.4, 2.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.7, 169.1, 161.3 (d, *J* = 241.1 Hz), 136.0, 135.6 (d, *J* = 13.0 Hz), 133.6, 133.3, 128.3, 127.1, 126.9, 126.4, 124.4 (d, *J* = 3.9 Hz), 121.4 (d, *J* = 9.8 Hz),

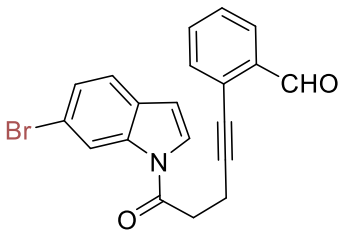
112.0 (d, *J* = 24.3 Hz), 109.3, 104.0 (d, *J* = 28.7 Hz), 95.2, 77.4, 34.5, 14.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –116.06 – –116.18 (m); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_2$ $[M+H]^+$: 320.1081; found: 320.1085.

2-(5-(6-chloro-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1p)



The title compound was prepared following general procedure A in 77% yield (517 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 128–130 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.53 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.53–7.48 (m, 2H), 7.46 (dd, *J* = 6.0, 2.1 Hz, 2H), 7.40 (td, *J* = 6.8, 1.0 Hz, 1H), 7.28–7.23 (m, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 3.27 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.1, 136.0, 135.8, 133.7, 133.4, 131.2, 128.7, 128.3, 127.2, 126.9, 124.7, 124.4, 121.5, 116.9, 109.3, 95.1, 77.5, 34.6, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{14}ClNNaO_2$ $[M+Na]^+$: 358.0605; found: 358.0602.

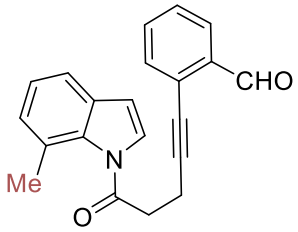
2-(5-(6-bromo-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1q)



The title compound was prepared following general procedure A in 73% yield (555 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 143–145 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.70 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.54–7.48 (m, 2H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.44–7.38 (m, 3H), 6.64 (d, *J* = 3.7 Hz, 1H), 3.28 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.1,

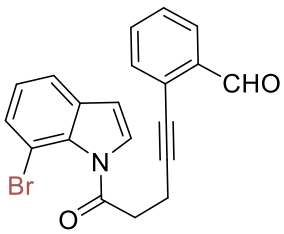
136.2, 136.1, 133.7, 133.4, 129.1, 128.3, 127.2, 127.2, 126.9, 124.6, 121.9, 119.7, 119.0, 109.4, 95.1, 77.5, 34.6, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_2$ $[M+H]^+$: 380.0281; found: 380.0282.

2-(5-(7-methyl-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1r)



The title compound was prepared following general procedure A in 67% yield (423 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 95–97 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 7.89 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.54–7.47 (m, 2H), 7.45 (d, *J* = 3.8 Hz, 1H), 7.41–7.39 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 3.8 Hz, 1H), 3.30 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.57 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 168.5, 136.0, 135.1, 133.7, 133.4, 131.9, 128.3, 128.3, 127.1, 126.9, 126.6, 125.5, 124.2, 118.5, 109.5, 95.3, 77.4, 35.4, 22.6, 15.7; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1336.

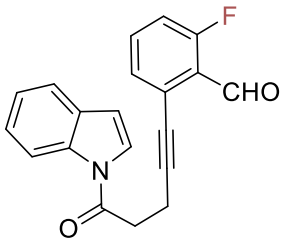
2-(5-(7-bromo-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1s)



The title compound was prepared following general procedure A in 73% yield (555 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 15:1) to afford the product as a colorless solid, mp 80–82 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.48 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.51–7.45 (m, 3H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 3H), 6.63 (d, *J* = 3.7 Hz, 1H), 3.28 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H); **^{13}C**

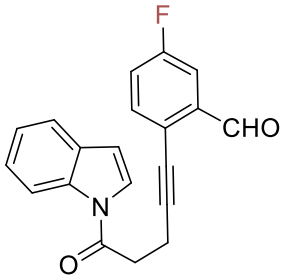
NMR (150 MHz, $CDCl_3$) δ 191.7, 168.1, 135.9, 134.4, 134.3, 133.6, 133.3, 130.3, 128.2, 127.0, 126.8, 126.7, 124.9, 120.2, 108.9, 108.5, 95.0, 77.5, 36.0, 15.7; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_2$ $[M+H]^+$: 380.0281; found: 380.0284.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-6-fluorobenzaldehyde (1t)



The title compound was prepared following general procedure A in 85% yield (543 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 131–133 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 3.7 Hz, 1H), 7.45 (td, *J* = 8.1, 5.5 Hz, 1H), 7.37 (td, *J* = 7.2, 1.1 Hz, 1H), 7.32–7.27 (m, 2H), 7.08 (t, *J* = 6.5 Hz, 1H), 6.67 (d, *J* = 3.4 Hz, 1H), 3.30 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 188.3, 169.1, 162.4 (d, *J* = 262.3 Hz), 135.5, 134.6 (d, *J* = 10.6 Hz), 130.3, 129.6 (d, *J* = 3.5 Hz), 127.2 (d, *J* = 3.3 Hz), 125.2, 124.4 (d, *J* = 8.1 Hz), 124.2, 123.8, 120.8, 116.5, 116.3, 109.5, 96.2, 77.4 (d, *J* = 4.0 Hz), 34.5, 15.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –116.40 (dd, *J* = 10.5, 5.5 Hz); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_2$ $[M+H]^+$: 320.1081; found: 320.1084.

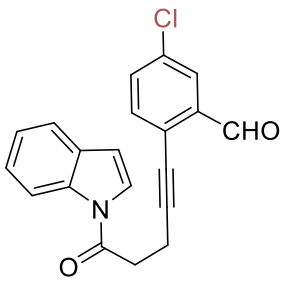
2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-4-fluorobenzaldehyde (1u)



The title compound was prepared following general procedure A in 90 % yield (575 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 150–152 ℃; **^{1}H NMR**

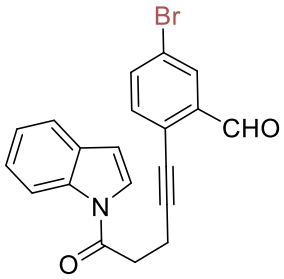
(600 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.47 (d, *J* = 7.9 Hz, 1H), 7.91 (dd, *J* = 8.7, 5.9 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 3.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.17 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.09 (td, *J* = 8.3, 2.3 Hz, 1H), 6.68 (d, *J* = 3.7 Hz, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.2, 168.9, 165.6 (d, *J* = 256.7 Hz), 135.6, 132.8 (d, *J* = 2.8 Hz), 130.3, 129.9 (d, *J* = 10.2 Hz), 129.4 (d, *J* = 11.2 Hz), 125.3, 124.1, 123.9, 120.9, 119.9 (d, *J* = 23.3 Hz), 116.5, 116.2 (d, *J* = 22.1 Hz), 109.7, 96.7, 76.3 (d, *J* = 2.8 Hz), 34.5, 15.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –103.43 – –103.52 (m); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_2$ $[M+H]^+$: 320.1081; found: 320.1088.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-4-chlorobenzaldehyde (1v)



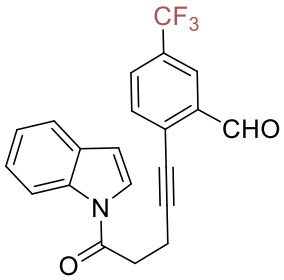
The title compound was prepared following general procedure A in 87 % yield (584 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 141–143 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.43 (s, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 1.5 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 7.2, 2.7 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 3.7 Hz, 1H), 3.28 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.5, 168.9, 140.1, 135.5, 134.4, 133.1, 130.3, 128.8, 128.4, 128.3, 125.3, 124.1, 123.9, 120.9, 116.5, 109.7, 96.8, 76.2, 34.5, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_2$ $[M+H]^+$: 336.0786; found: 336.0791.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-5-bromobenzaldehyde (1w)



The title compound was prepared following general procedure A in 75 % yield (570 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 137–139 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.42 (s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 7.61 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 3.5 Hz, 1H), 7.41–7.32 (m, 2H), 7.29 (td, *J* = 7.8, 0.8 Hz, 1H), 6.67 (d, *J* = 3.7 Hz, 1H), 3.27 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.4, 169.0, 137.2, 136.5, 135.5, 134.7, 130.3, 130.1, 125.6, 125.3, 124.1, 123.9, 122.7, 120.9, 116.5, 109.7, 96.7, 76.5, 34.5, 15.0; **HRMS (ESI)**calcd for $C_{20}H_{15}BrNO_2$ $[M+H]^+$: 380.0281; found: 380.0282.

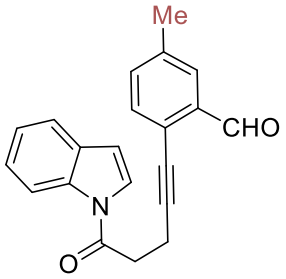
2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-5-(trifluoromethyl)benzaldehyde (1x)



The title compound was prepared following general procedure A in 82 % yield (606 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 123–125 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.12 (s, 1H), 7.72 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 3.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 3.7 Hz, 1H), 3.26 (t, *J* = 7.1 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.3,

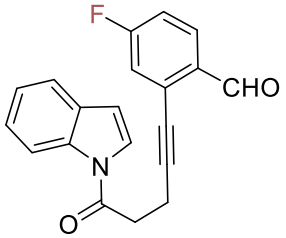
168.8, 136.2, 135.5, 133.9, 130.2, 130.3 (q, J = 13.0 Hz), 130.1 (q, J = 1.5Hz), 129.7 (q, J = 3.3 Hz), 125.3, 124.1 (q, J = 2.0 Hz), 124.0, 123.8, 120.9, 116.4, 109.6, 98.4, 76.3, 34.3, 15.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –63.04 (s); **HRMS (ESI)** calcd for $C_{21}H_{14}F_3NNaO_2$ $[M+Na]^+$: 392.0869; found: 392.0865.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-5-methylbenzaldehyde (1y)



The title compound was prepared following general procedure A in 83 % yield (524 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 117–119 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 8.48 (d, J = 8.1 Hz, 1H), 7.69 (s, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.49 (d, J = 3.6 Hz, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 6.67 (d, J = 3.7 Hz, 1H), 3.29 (t, J = 7.3 Hz, 2H), 3.03 (t, J = 7.1 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 192.1, 169.2, 138.6, 135.9, 135.6, 134.6, 133.3, 130.3, 127.4, 125.3, 124.2, 123.9, 120.9, 116.6, 109.6, 94.4, 77.4, 34.8, 21.2, 15.1; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1338.

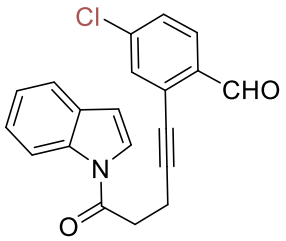
2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-5-fluorobenzaldehyde (1z)



The title compound was prepared following general procedure A in 83 % yield (530 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 145–147 ℃; **^{1}H NMR**

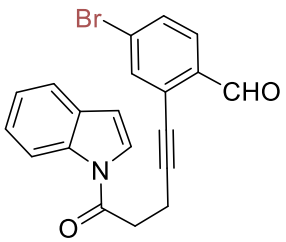
(600 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.47 (d, *J* = 7.9 Hz, 1H), 7.91 (dd, *J* = 8.7, 5.9 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 3.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.17 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.09 (td, *J* = 8.3, 2.3 Hz, 1H), 6.68 (d, *J* = 3.7 Hz, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 169.0, 162.1 (d, *J* = 252.5 Hz), 138.0 (d, *J* = 6.4 Hz), 135.5, 135.3 (d, *J* = 7.6 Hz), 130.3, 125.3, 124.1, 123.9, 123.0 (d, *J* = 2.5 Hz), 121.1 (d, *J* = 22.6 Hz), 120.9, 116.5, 113.4 (d, *J* = 22.8 Hz), 109.6, 95.1, 76.3, 34.6, 14.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –109.49 – –109.58 (m); **HRMS (ESI)**calcd for $C_{20}H_{15}FNO_2$ $[M+H]^+$: 320.1081; found: 320.1085.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-4-chlorobenzaldehyde (1aa)



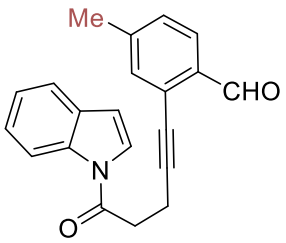
The title compound was prepared following general procedure A in 87 % yield (584 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 144–146 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.43 (s, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.47 (d, *J* = 3.5 Hz, 1H), 7.39–7.35 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 3.7 Hz, 1H), 3.28 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.5, 168.9, 140.1, 135.5, 134.4, 133.1, 130.3, 128.8, 128.4, 128.3, 125.3, 124.1, 123.9, 120.9, 116.5, 109.7, 96.8, 76.2, 34.5, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_2$ $[M+H]^+$: 336.0786; found: 336.0789.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-4-bromobenzaldehyde (1ab)



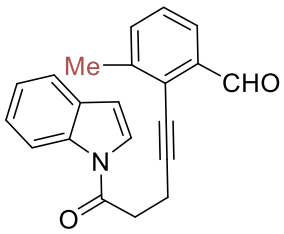
The title compound was prepared following general procedure A in 78 % yield (593 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 140–142 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.43 (s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.48 (d, *J* = 3.6 Hz, 1H), 7.39 (td, *J* = 8.0, 1.1 Hz, 1H), 7.29 (td, *J* = 7.0, 0.8 Hz, 1H), 6.68 (d, *J* = 3.7 Hz, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.7, 168.9, 136.0, 135.6, 134.8, 131.7, 130.3, 128.7, 128.4, 128.4, 125.3, 124.1, 123.9, 120.9, 116.5, 109.7, 96.9, 76.1, 34.5, 15.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_2$ $[M+H]^+$: 380.0281; found: 380.0290.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-4-methylbenzaldehyde (1ac)



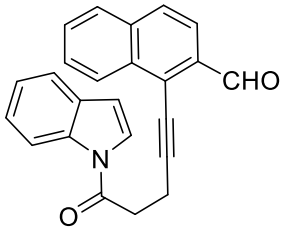
The title compound was prepared following general procedure A in 88 % yield (555 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 151–153 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.45 (s, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.37 (td, *J* = 7.3, 1.0 Hz 1H), 7.31–7.27 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 3.8 Hz, 1H), 3.27 (t, *J* = 6 Hz, 2H), 3.02 (t, *J* = 6 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.4, 169.1, 144.7, 135.5, 133.8, 133.8, 130.3, 129.3, 127.2, 126.9, 125.3, 124.2, 123.8, 120.9, 116.5, 109.6, 94.8, 77.5, 34.7, 21.5, 15.0; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1337.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-3-methylbenzaldehyde (1ad)



The title compound was prepared following general procedure A in 75 % yield (473 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 104–106 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.54 (s, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 3.1 Hz, 1H), 7.42–7.33 (m, 2H), 7.32–7.22 (m, 2H), 6.65 (d, *J* = 3.3 Hz, 1H), 3.26 (t, *J* = 7.1 Hz, 2H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.4, 169.0, 141.6, 136.2, 135.5, 134.7, 130.2, 127.6, 126.7, 125.2, 124.4, 124.1, 123.8, 120.8, 116.5, 109.5, 99.9, 75.9, 34.8, 20.3, 15.1; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1331.

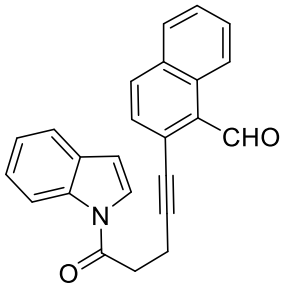
1-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-2-naphthaldehyde (1ae)



The title compound was prepared following general procedure A in 67 % yield (471 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a pale-yellow solid, mp 146–148 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.75 (s, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.64 (td, *J* = 8.0, 1.1 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.56–7.54 (m, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.40 (td, *J* = 7.0, 1.0 Hz, 1H), 7.30 (td, *J* = 7.0, 1.0 Hz, 1H), 6.68 (d, *J* = 3.8 Hz, 1H), 3.37 (t, *J* = 7.2 Hz, 2H), 3.20 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 192.3, 169.1, 135.7, 135.6, 134.4, 133.3, 130.3, 129.2, 128.5, 128.3, 127.7, 127.5, 127.2,

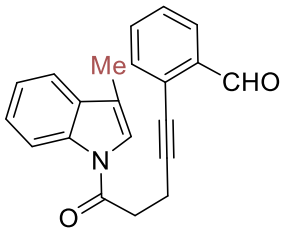
125.3, 124.1, 123.9, 121.8, 120.9, 116.6, 109.7, 101.5, 75.3, 34.7, 15.4; **HRMS (ESI)** calcd for $C_{24}H_{18}NO_2$ $[M+H]^+$: 352.1332; found: 352.1337.

2-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-1-naphthaldehyde (1af)



The title compound was prepared following general procedure A in 64 % yield (450 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a pale-yellow solid, mp 128–130 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.99 (s, 1H), 9.27 (d, *J* = 8.7 Hz, 1H), 8.50 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.56–7.50 (m, 2H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 3.7 Hz, 1H), 3.29 (t, *J* = 7.4 Hz, 2H), 3.07 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.4, 169.0, 135.6, 134.3, 132.9, 131.6, 130.4, 130.3, 130.1, 129.5, 129.5, 128.1, 127.2, 125.4, 125.3, 124.2, 123.8, 120.9, 116.5, 109.6, 97.9, 78.6, 34.6, 15.2; **HRMS (ESI)** calcd for $C_{24}H_{18}NO_2$ $[M+H]^+$: 352.1332; found: 352.1336.

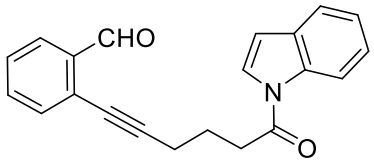
2-(5-(3-methyl-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1ag)



The title compound was prepared following general procedure A in 70 % yield (442 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a pale-yellow solid, mp 111–113 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.52 (s, 1H), 8.45 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.53–7.48

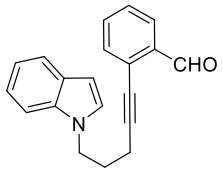
(m, 3H), 7.41–7.36 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.24 (s, 1H), 3.24 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.29 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 168.7, 136.0, 135.8, 133.6, 133.3, 131.3, 129.8, 128.2, 127.0, 127.0, 126.2, 125.3, 123.5, 121.1, 118.8, 116.5, 95.6, 34.6, 15.0, 9.6; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1335.

2-(6-(1*H*-indol-1-yl)-6-oxohex-1-yn-1-yl)benzaldehyde (1ah)



The title compound was prepared following general procedure A in 70 % yield (442 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a pale-yellow solid, mp 73–75 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 8.47 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.52–7.48 (m, 3H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.27 (t, *J* =7.5 Hz, 1H), 6.65 (d, *J* = 3.7 Hz, 1H), 3.14 (t, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 6.8 Hz, 2H), 2.20 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.6, 170.5, 135.9, 135.5, 133.6, 133.3, 130.2, 128.0, 127.3, 126.9, 125.0, 124.4, 123.6, 120.8, 116.5, 109.2, 96.3, 77.5, 34.2, 23.2, 18.9; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_2$ $[M+H]^+$: 316.1332; found: 316.1336.

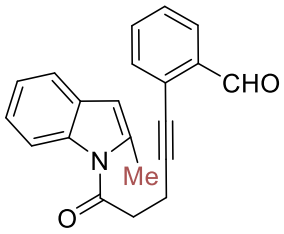
2-(5-(1*H*-indol-1-yl)pent-1-yn-1-yl)benzaldehyde (1ai)



The title compound was prepared following general procedure A in 72 % yield (413.8 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a white solid, mp 71–73 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.55 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.59–

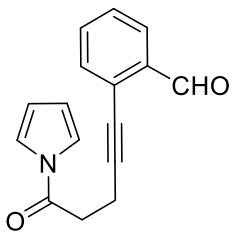
7.51 (m, 2H), 7.46–7.38 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 3.1 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 4.36 (t, *J* = 6.6 Hz, 2H), 2.47 (t, *J* = 6.8 Hz, 2H), 2.21–2.16 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.7, 136.0, 135.9, 133.7, 133.4, 128.7, 128.2, 127.9, 127.4, 127.1, 121.5, 121.0, 119.4, 109.2, 101.4, 96.1, 77.5, 44.9, 28.8, 17.0; **HRMS (ESI)** calcd for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1383; found: 288.1383.

2-(5-(2-methyl-1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)benzaldehyde (1aj)



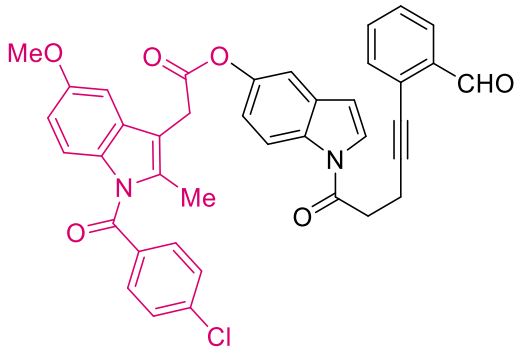
The title compound was prepared following general procedure A in 64 % yield (403.7 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a pale-yellow solid, mp 120–122 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.54 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 2H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 5.6 Hz, 1H), 7.27 (m, 2H), 6.41 (s, 1H), 3.35 (t, *J* = 6.9 Hz, 2H), 3.05 (t, *J* = 6.9 Hz, 2H), 2.68 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 171.1, 137.3, 136.2, 136.0, 133.6, 133.3, 129.8, 128.2, 127.1, , 127.0, 123.7, 123.3, 120.0, 115.2, 110.1, 95.6, 77.2, 37.7, 17.8, 15.5; **HRMS (ESI)** calcd for $C_{21}H_{17}NO_2$ $[M+H]^+$: 316.1332; found: 316.1347.

2-(5-oxo-5-(1*H*-pyrrol-1-yl)pent-1-yn-1-yl)benzaldehyde (1ak)



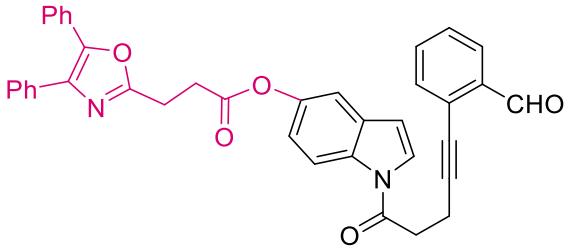
The title compound was prepared following general procedure A in 75 % yield (377 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 15:1) to afford the product as a pale-yellow solid, mp 101–103 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.46 (s, 1H), 7.86 (dd, *J* = 7.7 Hz, 0.7 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.39 (td, *J* = 7.3 Hz, 0.6 Hz, 1H), 7.33 (s, 2H), 6.30 (t, *J* = 2.4 Hz, 2H), 3.19 (t, *J* = 7.3 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.7, 168.3, 136.0, 133.6, 133.3, 128.2, 127.0, 126.8, 118.9, 113.4, 95.1, 77.3, 33.5, 14.9; **HRMS (ESI)** calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$: 250.1019; found: 250.1015.

1-(5-(2-formylphenyl)pent-4-ynoyl)-1*H*-indol-5-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (1al)



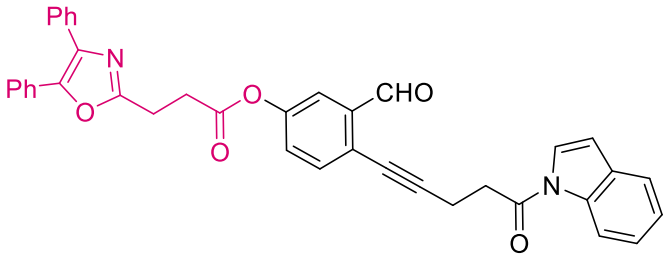
The title compound was prepared following general procedure B in 73% overall yield for 3 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 7:1) to afford the product as a pale-yellow solid, mp 128–130 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.46 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.53–7.45 (m, 5H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.61 (d, *J* = 3.7 Hz, 1H), 3.93 (s, 2H), 3.84 (s, 3H), 3.27 (t, *J* = 7.3 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.47 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 169.6, 169.0, 168.3, 156.1, 147.0, 139.3, 136.2, 136.0, 133.8, 133.7, 133.3, 133.3, 131.2, 131.0, 130.9, 130.5, 129.1, 128.3, 127.1, 126.9, 125.4, 118.7, 117.2, 115.0, 113.3, 112.0, 111.8, 109.4, 101.2, 95.2, 77.4, 55.7, 34.5, 30.5, 15.0, 13.4; **HRMS (ESI)** calcd for $C_{39}H_{29}ClN_2NaO_6$ $[M+Na]^+$: 679.1606; found: 679.1598.

1-(5-(2-formylphenyl)pent-4-ynoyl)-1*H*-indol-5-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (1am)



The title compound was prepared following general procedure B in 66% overall yield for 3 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 6:1) to afford the product as a pale-yellow solid, mp 139–141 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.52 (s, 1H), 8.47 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.70–7.65 (m, 2H), 7.62–7.57 (m, 2H), 7.53–7.47 (m, 3H), 7.42–7.31 (m, 8H), 7.10 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.59 (d, *J* = 3.7 Hz, 1H), 3.33 (t, *J* = 7.3 Hz, 2H), 3.27 (t, *J* = 7.3 Hz, 2H), 3.19 (t, *J* = 7.3 Hz, 2H), 3.02 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 171.0, 168.9, 161.4, 147.0, 145.5, 136.0, 135.1, 133.7, 133.3, 133.3, 132.4, 131.0, 128.9, 128.6, 128.5, 128.5, 128.3, 128.1, 127.9, 127.1, 126.9, 126.5, 125.3, 118.9, 117.2, 113.4, 109.4, 95.2, 77.4, 34.5, 31.3, 23.6, 15.0; **HRMS (ESI)** calcd for $C_{38}H_{29}N_2O_5$ $[M+H]^+$: 593.2071; found: 593.2078.

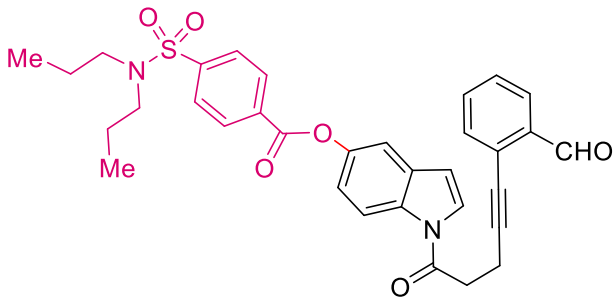
4-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-3-formylphenyl 3-(4,5-diphenyl-oxazol-2-yl)propanoate (1an)



The title compound was prepared following general procedure C in 75% overall yield for 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 7:1) to afford the product as a colorless solid, mp 163–165 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.46 (s, 1H), 8.48 (d, *J* = 7.9 Hz, 1H), 7.69–7.62 (m,

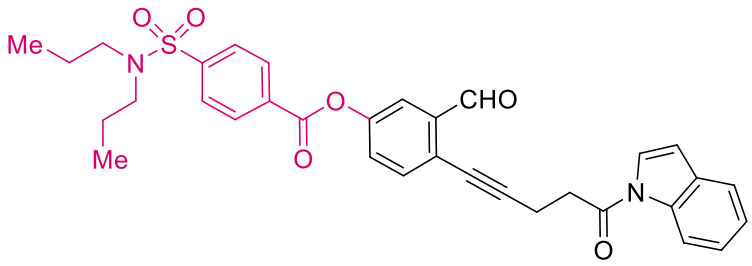
3H), 7.58 (t, *J* = 6.7 Hz, 3H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 3.4 Hz, 1H), 7.41–7.31 (m, 7H), 7.31–7.27 (m, 2H), 6.67 (d, *J* = 3.7 Hz, 1H), 3.33–3.24 (m, 4H), 3.17 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.7, 170.1, 169.0, 161.1, 150.3, 145.6, 137.3, 135.5, 135.1, 134.5, 132.3, 130.3, 128.8, 128.6, 128.5, 128.5, 128.1, 127.8, 127.2, 126.5, 125.3, 124.5, 124.1, 123.8, 120.9, 120.0, 116.5, 109.6, 95.5, 76.6, 34.6, 31.1, 23.3, 15.0; **HRMS (ESI)** calcd for $C_{38}H_{29}N_2O_5$ $[M+H]^+$: 593.2071; found: 593.2075.

1-(5-(2-formylphenyl)pent-4-ynoyl)-1*H*-indol-5-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1ao)



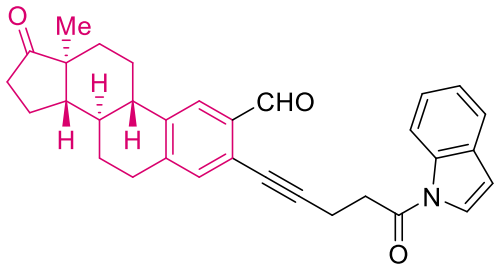
The title compound was prepared following general procedure B in 70% overall yield for 3 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 5:1) to afford the product as a pale-yellow solid, mp 125–127 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 3.7 Hz, 1H), 7.51–7.46 (m, 2H), 7.42 (d, *J* = 2.2 Hz, 1H), 7.39–7.34 (m, 1H), 7.18 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 3.27 (t, *J* = 7.2 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 4H), 3.01 (t, *J* = 7.2 Hz, 2H), 1.59–1.51 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.7, 169.0, 164.1, 146.8, 144.7, 135.9, 133.6, 133.4, 133.3, 132.7, 131.0, 130.6, 128.2, 127.0, 126.8, 125.6, 118.6, 117.3, 113.3, 109.2, 95.2, 77.3, 49.8, 34.4, 21.8, 14.9, 11.1; **HRMS (ESI)** calcd for $C_{33}H_{33}N_2O_6S$ $[M+H]^+$: 585.2054; found: 585.2046.

4-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-3-formylphenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1ap)



The title compound was prepared following general procedure C in 72% overall yield for 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 7:1) to afford the product as a pale-yellow solid, mp 156–158 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.58 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* = 2.8 Hz, 1H), 7.48 (d, *J* = 3.6 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 3.7 Hz, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 4H), 3.04 (t, *J* = 7.2 Hz, 2H), 1.61–1.51 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.7, 169.0, 163.3, 150.2, 145.2, 137.4, 135.5, 134.7, 132.0, 130.8, 130.3, 127.2, 127.1, 125.3, 124.8, 124.1, 123.8, 120.9, 119.9, 116.5, 109.6, 95.9, 76.5, 49.8, 34.6, 21.8, 15.0, 11.1; **HRMS (ESI)** calcd for $C_{33}H_{33}N_2O_6S$ $[M+H]^+$: 585.2054; found: 585.2043.

(8*R*,9*S*,13*S*,14*S*)-3-(5-(1*H*-indol-1-yl)-5-oxopent-1-yn-1-yl)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-2-carbaldehyde (1aq)



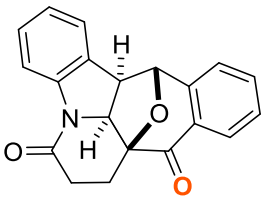
The title compound was prepared following general procedure D in 45% yield (619 mg). It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1 to 5:1) to give the product as a pale-yellow solid, mp 193–195 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.40 (s, 1H), 8.44 (d, *J* = 6.9 Hz, 1H), 7.76 (s, 1H), 7.54 (d, *J* =

7.5 Hz, 1H), 7.44 (s, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28–7.22 (m, 1H), 7.19 (s, 1H), 6.62 (d, *J* = 2.5 Hz, 1H), 3.20 (t, *J* = 6.9 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.92–2.79 (m, 2H), 2.54–2.36 (m, 2H), 2.23–2.05 (m, 2H), 2.05–1.88 (m, 3H), 1.65–1.32 (m, 6H), 0.86 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 220.1, 191.5, 169.1, 143.4, 140.5, 135.4, 133.6, 133.5, 130.2, 125.1, 124.2, 124.1, 124.0, 123.7, 120.8, 116.4, 109.4, 94.2, 50.2, 47.6, 43.9, 37.5, 35.6, 34.6, 31.2, 29.2, 25.8, 25.2, 21.3, 14.9, 13.6; **HRMS (ESI)** calcd for $C_{32}H_{32}NO_3$ $[M+H]^+$: 478.2377; found: 478.2376.

4. General procedure for PtI$_4$-catalyzed oxidative and dearomative [3 + 2] cycloaddition

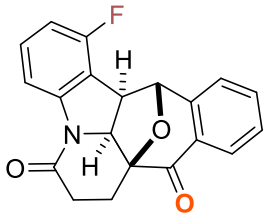
To a dried round-bottom flask equipped with a stirring bar were charged with **1** (0.2 mmol), 4Å MS (200 mg), phenylmethylsulfoxide (PMSO) (56 mg, 0.4 mmol) and PtI$_4$ (1.4 mg, 2 μmol), anhydrous toluene (2 mL) was added under an argon atmosphere. The reaction was stirred at 80 ºC for 12 h. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature, filtered through a pad of Celite and rinsed with EtOAc. 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 **3**.

(4^1*S,8b*R**,9*R**,14a*S**)-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6] cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3a)**



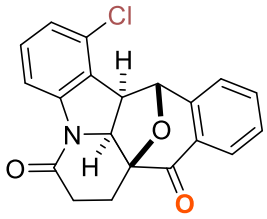
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give the product **3a** in 99% yield (62.8 mg) as a colorless solid, mp 246–248 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H), 7.50 (td, *J* = 7.6, 0.9 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.14 (td, *J* = 7.5, 0.7 Hz, 1H), 5.26 (s, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.08 (ddd, *J* = 14.2, 5.1, 2.9 Hz, 1H), 2.68–2.58 (m, 2H), 1.83 (td, *J* = 13.8, 5.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.3, 170.3, 146.1, 143.7, 134.9, 129.7, 129.1, 128.8, 127.9, 127.7, 124.3, 124.2, 123.5, 116.0, 91.4, 85.6, 67.7, 55.1, 33.6, 27.1; **HRMS (ESI)** calcd for $C_{20}H_{16}NO_3$ $[M+H]^+$: 318.1125; found: 318.1122.

(4^1*S,8b*R**,9*R**,14a*S**)-8-fluoro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3b)**



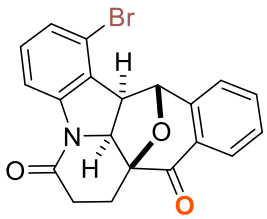
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 5:1) to give **3b** in 75% yield (50.3 mg) as a pale-yellow solid, mp 186–188 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.65 (td, *J* = 7.5, 1.1 Hz, 1H), 7.49 (td, *J* = 7.7, 0.8 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.28 (td, *J* = 8.2, 5.9 Hz, 1H), 6.83 (t, *J* = 8.6 Hz, 1H), 5.34 (s, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.04 (d, *J* = 8.0 Hz, 1H), 3.08 (ddd, *J* = 14.2, 5.4, 2.6 Hz, 1H), 2.67–2.55 (m, 2H), 1.80 (td, *J* = 14.2, 4.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.9, 170.3, 158.9 (d, *J* = 246.1 Hz), 145.9 (d, *J* = 7.8 Hz), 145.7, 135.1, 131.3 (d, *J* = 8.0 Hz), 128.9, 127.7, 127.6, 123.9, 116.0 (d, *J* = 20.7 Hz), 111.9 (d, *J* = 3.3 Hz), 110.8 (d, *J* = 19.3 Hz), 91.2, 83.9, 68.3, 51.9, 33.5, 26.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –119.65 (dd, *J* = 8.7, 5.9 Hz); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_3$ $[M+H]^+$: 336.1030; found: 336.1024.

(4^1*S,8b*R**,9*R**,14a*S**)-8-chloro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3c)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 5:1) to give **3c** in 89% yield (62.6 mg) as a pale-yellow solid, mp 225–227 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.65 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48 (td, *J* = 7.6, 1.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 5.41 (s, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.09 (ddd, *J* = 14.2, 5.4, 2.6 Hz, 1H), 2.67–2.54 (m, 2H), 1.81 (td, *J* = 14.2, 5.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.9, 170.4, 145.8, 144.8, 135.0, 130.7, 130.2, 128.8, 127.8, 127.7, 127.6, 123.9, 123.7, 114.3, 91.3, 83.4, 67.6, 54.5, 33.5, 27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_3$ $[M+H]^+$: 352.0735; found: 352.0730.

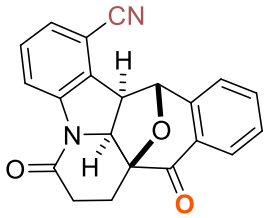
(4^1*S,8b*R**,9*R**,14a*S**)-8-bromo-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3d)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3d** in 92% yield (72.9 mg) as a colorless solid, mp 237–239 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 5.44 (s, 1H), 4.61 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.09 (ddd, *J* = 14.2, 5.2, 2.3 Hz, 1H), 2.68–2.54 (m, 2H), 1.81 (td, *J* = 14.2, 4.9 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.9, 170.4, 145.8, 144.6, 135.0, 130.9, 129.8, 128.8, 127.7, 127.6, 126.8,

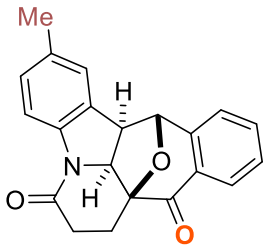
123.8, 119.1, 114.9, 91.3, 83.4, 67.3, 56.1, 33.5, 27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_3$ $[M+H]^+$: 396.0230; found: 396.0230.

(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-8-carbonitrile (3e)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3e** in 70% yield (47.9 mg) as a pale-yellow solid, mp 258–260 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.30 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 5.47 (s, 1H), 4.72 (d, *J* = 8.0 Hz, 1H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.13 (dd, *J* = 14.1, 2.5 Hz, 1H), 2.71–2.58 (m, 2H), 1.83 (td, *J* = 14.2, 4.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.5, 170.6, 145.2, 144.6, 135.5, 134.0, 130.2, 129.1, 127.6, 127.5, 126.6, 124.1, 120.1, 116.9, 108.7, 91.4, 84.3, 68.0, 54.7, 33.5, 26.9; **HRMS (ESI)** calcd for $C_{21}H_{15}N_2O_3$ $[M+H]^+$: 343.1077; found: 343.1079.

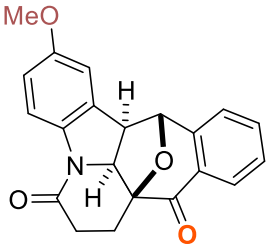
(4^1*S,8b*R**,9*R**,14a*S**)-7-methyl-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3f)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3f** in 90% yield (59.6 mg) as a colorless solid, mp 201–203 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.17 (s, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 5.23 (s,

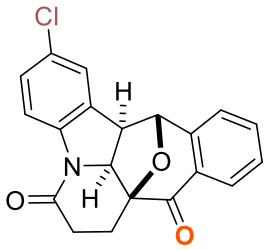
1H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.89 (d, *J* = 8.0 Hz, 1H), 3.05 (ddd, *J* = 7.3, 4.9, 2.9 Hz, 1H), 2.64–2.53 (m, 2H), 2.36 (s, 3H), 1.79 (td, *J* = 13.6, 5.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.3, 170.0, 146.1, 141.5, 134.9, 133.9, 129.8, 129.5, 128.7, 127.9, 127.7, 124.8, 123.5, 115.6, 91.4, 85.5, 67.8, 55.1, 33.5, 27.1, 21.0; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1273.

(4^1*S,8b*R**,9*R**,14a*S**)-7-methoxy-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3g)**



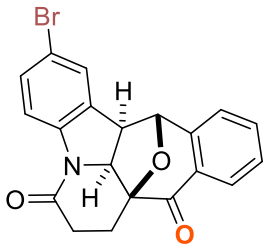
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3g** in 93% yield (64.6 mg) as a colorless solid, mp 225–227 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.63 (td, *J* = 7.5, 1.1 Hz, 1H), 7.47 (td, *J* = 7.5, 0.6 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.24 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.89 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.04 (ddd, *J* = 14.2, 4.9, 3.0 Hz, 1H), 2.63–2.52 (m, 2H), 1.85–1.75 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.2, 169.6, 156.8, 146.0, 137.5, 134.9, 131.1, 128.8, 127.9, 127.7, 123.5, 116.5, 113.3, 110.7, 91.5, 85.4, 68.0, 55.8, 55.2, 33.4, 27.1; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_4$ $[M+H]^+$: 348.1230; found: 348.1227.

(4^1*S,8b*R**,9*R**,14a*S**)-7-chloro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3h)**



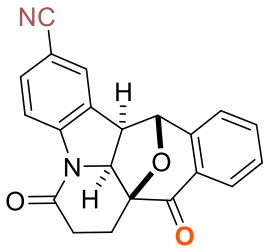
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3h** in 95% yield (66.8 mg) as a pale-yellow solid, mp 161–163 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.65 (td, *J* = 7.5, 0.9 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.33 (s, 1H), 7.24 (dd, *J* = 8.6, 1.5 Hz, 1H), 5.23 (s, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 3.90 (d, *J* = 8.0 Hz, 1H), 3.06 (ddd, *J* = 14.2, 5.1, 2.6 Hz, 1H), 2.64–2.53 (m, 2H), 1.83–1.74 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.9, 170.2, 145.6, 142.3, 135.0, 131.5, 129.0, 128.9, 127.7, 127.7, 124.5, 123.5, 116.8, 91.3, 85.4, 68.0, 54.8, 33.4, 27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_3$ $[M+H]^+$: 352.0735; found: 352.0728.

(4^1*S,8b*R**,9*R**,14a*S**)-7-bromo-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3i)**



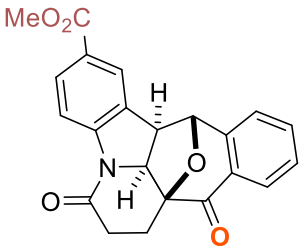
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3i** in 90% yield (71.3 mg) as a colorless solid, mp 187–189 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.65 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.48 (d, *J* = 0.9 Hz, 1H), 7.41–7.36 (m, 2H), 5.23 (s, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.06 (ddd, *J* = 14.2, 5.3, 2.6 Hz, 1H), 2.65–2.53 (m, 2H), 1.79 (td, *J* = 14.1, 5.1 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.9, 170.2, 145.6, 142.8, 135.0, 131.9, 131.9, 128.9, 127.7, 127.4, 123.5, 117.2, 116.4, 91.3, 85.4, 68.0, 54.7, 33.4,27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_3$ $[M+H]^+$: 396.0230; found: 396.0233.

(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxy-benzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-7-carbonitrile (3j)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3j** in 82% yield (56.1 mg) as a colorless solid, mp 246–248 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.69 (td, *J* = 7.5, 0.9 Hz, 1H), 7.66 (s, 1H), 7.61 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 5.26 (s, 1H), 4.69 (d, *J* = 8.0 Hz, 1H), 3.98 (d, *J* = 8.0 Hz, 1H), 3.10 (ddd, *J* = 14.2, 5.3, 2.6 Hz, 1H), 2.71–2.57 (m, 2H), 1.81 (td, *J* = 14.2, 4.9 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 194.5, 170.8, 147.1, 145.3, 135.2, 134.1, 130.9, 129.2, 128.1, 127.8, 127.6, 123.6, 118.8, 116.2, 107.1, 91.2, 85.5, 68.1, 54.5, 33.5, 26.8; **HRMS (ESI)** calcd for $C_{21}H_{15}N_2O_3$ $[M+H]^+$: 343.1077; found: 343.1077.

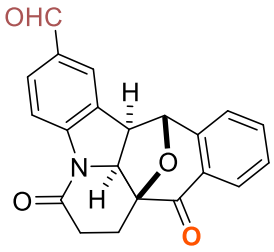
Methyl(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-7-carboxylate (3k)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3k** in 84% yield (63.1 mg) as a colorless solid, mp 212–214 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 5.27 (s, 1H), 4.68 (d, *J* = 8.0 Hz, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.09 (ddd, *J* = 14.2, 4.9, 2.4 Hz, 1H), 2.70–2.58 (m, 2H), 1.81 (td, *J* = 14.1, 5.0 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 194.9, 170.7, 166.5, 147.4, 145.7, 135.1, 131.5, 130.1, 129.0, 127.7, 126.0, 125.9,

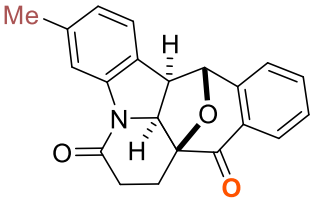
123.7, 115.2, 91.2, 85.6, 68.2, 54.6, 52.1, 33.6, 26.9; **HRMS (ESI)** calcd for $C_{22}H_{18}NO_5$ $[M+H]^+$: 376.1179; found: 376.1175.

(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-7-carbaldehyde (3l)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3l** in 94% yield (64.9 mg) as a pale-yellow solid, mp 234–236 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.92 (s, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.95 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 5.27 (s, 1H), 4.70 (d, *J* = 8.0 Hz, 1H), 4.00 (d, *J* = 8.0 Hz, 1H), 3.09 (ddd, *J* = 14.2, 5.1, 2.6 Hz, 1H), 2.70–2.58 (m, 2H), 1.80 (td, *J* = 14.0, 5.2 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.7, 190.7, 171.0, 148.6, 145.5, 135.2, 134.2, 132.9, 131.2, 129.0, 127.7, 127.6, 124.1, 123.6, 115.6, 91.2, 85.6, 68.4, 54.3, 33.6, 26.9; **HRMS (ESI)** calcd for $C_{21}H_{16}NO_4$ $[M+H]^+$: 346.1074; found: 346.1071.

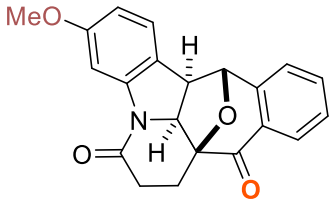
(4^1*S,8b*R**,9*R**,14a*S**)-6-methyl-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3m)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3m** in 90% yield (59.6 mg) as a pale-yellow solid, mp 183–185 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.6 Hz, 1H), 7.93 (s, 1H), 7.63 (td, *J* = 7.5, 1.1 Hz, 1H), 7.47 (td, *J* = 7.6, 0.8 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.20 (s, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.89 (d, *J* = 8.0 Hz, 1H), 3.04 (ddd, *J* =

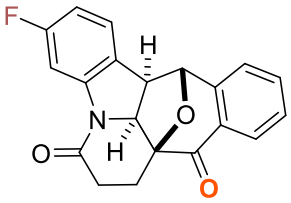
14.1, 5.2, 2.7 Hz, 1H), 2.65–2.53 (m, 2H), 2.36 (s, 3H), 1.79 (dt, *J* = 13.9, 5.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.3, 170.3, 146.1, 143.8, 139.3, 134.9, 128.7, 127.8, 127.6, 126.8, 124.9, 123.9, 123.5, 116.5, 91.3, 85.6, 68.0, 54.7, 33.6, 27.0, 21.6; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1273.

(4^1*S,8b*R**,9*R**,14a*S**)-6-methoxy-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3n)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3n** in 88% yield (61.1 mg) as a colorless solid, mp 173–175 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 6.65 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.18 (s, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.04 (ddd, *J* = 14.1, 4.9, 2.8 Hz, 1H), 2.64–2.52 (m, 2H), 1.78 (td, *J* = 13.8, 5.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.2, 170.4, 160.6, 146.1, 144.9, 134.9, 128.7, 127.8, 127.6, 124.5, 123.5, 121.5, 110.6, 101.5, 91.2, 85.7, 68.5, 55.6, 54.4, 33.6, 27.0; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_4$ $[M+H]^+$: 348.1230; found: 348.1223.

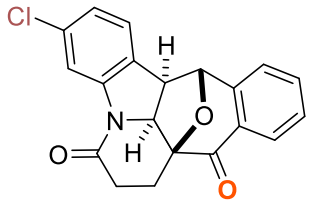
(4^1*S,8b*R**,9*R**,14a*S**)-6-fluoro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3o)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to afford give **3o** in 92% yield (61.7 mg) as a colorless solid, mp 230–232 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.81 (dd, *J* = 9.9, 2.3 Hz, 1H), 7.65 (td, *J* = 7.5, 0.9 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.30–7.25 (m, 1H), 6.80

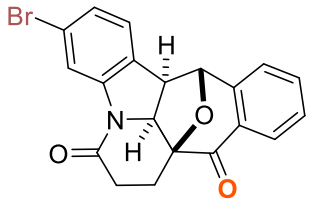
(td, *J* = 8.5, 2.4 Hz, 1H), 5.21 (s, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.07 (ddd, *J* = 14.2, 5.2, 2.6 Hz, 1H), 2.67–2.54 (m, 2H), 1.80 (td, *J* = 14.0, 5.1 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.0, 170.4, 163.2 (d, *J* = 245.0 Hz), 145.8, 144.9 (d, *J* = 12.8 Hz), 135.0, 128.9, 127.8, 127.7, 125.2 (d, *J* = 2.6 Hz), 124.9 (d, *J* = 10.1 Hz), 123.5, 110.7 (d, *J* = 23.3 Hz), 104.1 (d, *J* = 28.7 Hz), 91.3, 85.6, 68.7, 54.4, 33.5, 27.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –111.74 (td, *J* = 9.3, 5.5 Hz); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_3$ $[M+H]^+$: 336.1030; found: 336.1023.

(4^1*S,8b*R**,9*R**,14a*S**)-6-chloro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3p)**



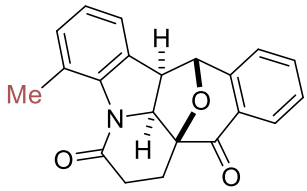
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to afford give **3p** in 90% yield (63.3 mg) as a colorless solid, mp 169–171 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 1.8 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.66 (td, *J* = 7.5, 1.1 Hz, 1H), 7.50 (td, *J* = 7.7, 0.7 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.10 (dd, *J* = 8.0, 1.9 Hz, 1H), 5.21 (s, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 8.0 Hz, 1H), 3.08 (ddd, *J* = 14.2, 5.4, 2.6 Hz, 1H), 2.68–2.55 (m, 2H), 1.81 (td, *J* = 14.2, 4.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.0, 170.4, 145.8, 144.7, 135.0, 134.9, 129.0, 128.2, 127.8, 127.8, 124.9, 124.2, 123.5, 116.3, 91.4, 85.6, 68.4, 54.6, 33.5, 27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_3$ $[M+H]^+$: 352.0735; found: 352.0732.

(4^1*S,8b*R**,9*R**,14a*S**)-6-bromo-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3q)**



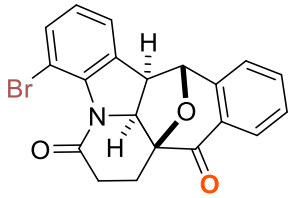
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to afford give **3q** in 85% yield (67.4 mg) as a colorless solid, mp 149–151 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 1.4 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.27–7.24 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 5.21 (s, 1H), 4.64 (d, *J* = 8.0 Hz, 1H), 3.90 (d, *J* = 8.0 Hz, 1H), 3.08 (ddd, *J* = 14.2, 5.4, 2.5 Hz, 1H), 2.68–2.55 (m, 2H), 1.81 (td, *J* = 14.2, 4.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.0, 170.4, 145.8, 144.8, 135.0, 129.0, 128.8, 127.8, 127.8, 127.1, 125.4, 123.5, 122.8, 119.1, 91.4, 85.5, 68.2, 54.7, 33.5, 27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_3$ $[M+H]^+$: 396.0230; found: 396.0226.

(4^1*S,8b*R**,9*R**,14a*S**)-5-methyl-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3r)**



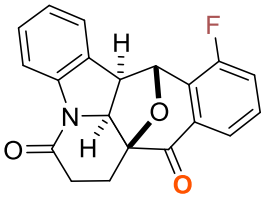
Column chromatography (eluent: petroleum ether/EtOAc = 10:1 to 4:1) to give **3r** in 86% yield (57.0 mg) as a pale-yellow solid, mp 190–192 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.64 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48 (td, *J* = 7.6, 0.8 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.13–7.08 (m, 2H), 5.27 (s, 1H), 4.78 (d, *J* = 7.9 Hz, 1H), 3.76 (d, *J* = 7.9 Hz, 1H), 3.14 (ddd, *J* = 14.4, 7.4, 3.0 Hz, 1H), 2.71 (td, *J* = 13.3, 7.4 Hz, 1H), 2.60 (ddd, *J* = 13.7, 5.8, 3.0 Hz, 1H), 2.43 (s, 3H), 2.02 (ddd, *J* = 14.3, 13.2, 5.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.4, 169.5, 146.6, 142.8, 134.9, 131.9, 131.5, 128.7, 128.5, 128.0, 127.8, 125.5, 123.3, 121.3, 91.1, 84.4, 69.8, 56.7, 32.8, 26.5, 22.1; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1273.

(4^1*S,8b*R**,9*R**,14a*S**)-5-bromo-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3s)**



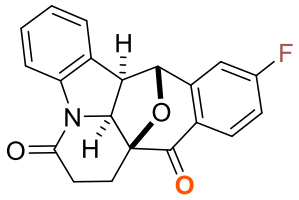
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3s** in 84% yield (66.6 mg) as a pale-yellow solid, mp 218–220 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.1 Hz, 1H), 7.53–7.47 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 5.27 (s, 1H), 4.90 (d, *J* = 7.7 Hz, 1H), 3.79 (d, *J* = 7.7 Hz, 1H), 3.18 (ddd, *J* = 14.6, 8.2, 3.4 Hz, 1H), 2.72 (ddd, *J* = 13.8, 11.7, 8.3 Hz, 1H), 2.62 (ddd, *J* = 13.9, 6.6, 3.5 Hz, 1H), 2.11 (ddd, *J* = 14.6, 11.7, 6.6 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 194.8, 168.7, 146.3, 143.5, 135.0, 134.4, 134.0, 128.9, 128.0, 127.9, 126.6, 123.2, 122.9, 112.1, 90.5, 83.9, 70.7, 57.4, 31.8, 26.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_3$ $[M+H]^+$: 396.0230; found: 396.0219.

(4^{1}*S,8b*R**,9*R**,14a*S**)-10-fluoro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^{1}*H*)-dione (3t)**



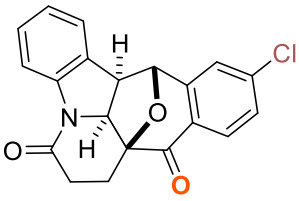
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3t** in 91% yield (61 mg) as a colorless solid, mp 228–230 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.45 (td, *J* = 7.9, 5.3 Hz, 1H), 7.41–7.35 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.60 (s, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 3.98 (d, *J* = 8.0 Hz, 1H), 3.04 (ddd, *J* = 14.2, 4.9, 2.5 Hz, 1H), 2.66–2.54 (m, 2H), 1.81 (td, *J* = 14.1, 4.9 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 194.2, 170.2, 157.4, 155.7, 143.7, 132.9 (d, *J* = 17.2 Hz), 129.8 (d, *J* = 7.4 Hz), 129.7 (d, *J* = 3.4 Hz), 129.2, 129.2, 124.4 (d, *J* = 22.9 Hz), 123.3 (d, *J* = 3.4 Hz), 121.5 (d, *J* = 20.6 Hz), 115.9, 91.3, 79.1 (d, *J* = 2.7 Hz), 67.5, 54.6, 33.5, 27.1; **^{19}F NMR (565 MHz, CDCl$_3$)** δ –121.55 (dd, *J* = 8.5, 5.2 Hz); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_3$ $[M+H]^+$: 336.1030; found: 336.1024.

(4^1*S,8b*R**,9*R**,14a*S**)-11-fluoro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3u)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3u** in 81% yield (54.3 mg) as a colorless solid, mp 212–214 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (dd, *J* = 5.5 Hz, 3.1, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.19–7.11 (m, 2H), 7.09 (dd, *J* = 8.0, 2.3 Hz, 1H), 5.22 (s, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.07 (ddd, *J* = 14.2, 5.3, 2.6 Hz, 1H), 2.68–2.54 (m, 2H), 1.82 (td, *J* = 14.1, 5.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 193.8, 170.2, 167.2, 165.5, 149.1 (d, *J* = 8.5 Hz), 143.7, 131.2 (d, *J* = 9.9 Hz), 129.3, 129.3, 124.5 (d, *J* = 3.0 Hz), 124.3 (d, *J* = 5.2 Hz), 116.3 (d, *J* = 22.3 Hz), 116.1, 110.8 (d, *J* = 22.6 Hz), 91.4, 85.3, 67.7, 55.0, 33.6, 26.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –99.87 (dt, *J* = 13.9, 7.1 Hz); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_3$ $[M+H]^+$: 336.1030; found: 336.1024.

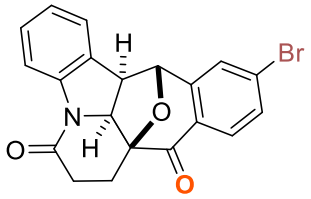
(4^1*S,8b*R**,9*R**,14a*S**)-11-chloro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3v)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3v** in 95% yield (66.8 mg) as a colorless solid, mp 212–214 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.43 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.40 (d, *J* = 1.5 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.19 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.93 (d, *J* = 8.0 Hz, 1H), 3.03 (ddd, *J* = 14.2, 5.2, 2.5 Hz, 1H), 2.65–2.51 (m, 2H), 1.79 (td, *J* = 14.2, 4.9 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.2, 170.1, 147.4, 143.6, 141.3, 129.4, 129.3, 129.2, 126.2,

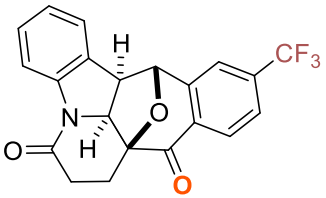
124.2, 123.8, 115.9, 91.4, 85.0, 67.5, 54.9, 33.5, 26.9; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_3$ $[M+H]^+$: 352.0735; found: 352.0729.

(4^1*S,8b*R**,9*R**,14a*S**)-11-bromo-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3w)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3w** in 97% yield (76.9 mg) as a colorless solid, mp 223–225 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.61 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.18 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.94 (d, *J* = 8.0 Hz, 1H), 3.03 (ddd, *J* = 14.2, 5.3, 2.5 Hz, 1H), 2.66–2.51 (m, 2H), 1.79 (td, *J* = 9.2, 4.9 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.4, 170.1, 147.4, 143.6, 132.2, 130.2, 129.3, 129.2, 129.2, 126.8, 126.6, 124.2, 115.9, 91.5, 84.9, 67.5, 54.9, 33.5, 26.9; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_3$ $[M+H]^+$: 396.0230; found: 396.0224.

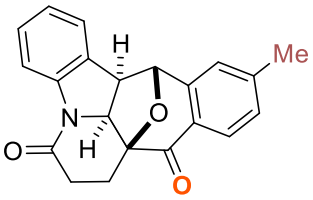
(4^1*S,8b*R**,9*R**,14a*S**)-11-(trifluoromethyl)-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3x)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3x** in 80% yield (61.7 mg) as a colorless solid, mp 225–227 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.32 (s, 1H), 4.64 (d, *J* = 8.0 Hz, 1H), 3.98 (d, *J* = 8.0 Hz, 1H), 3.06 (ddd, *J* = 14.2, 5.2, 2.4 Hz, 1H), 2.69–2.56 (m, 2H), 1.85 (td, *J* = 14.2, 4.9 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ

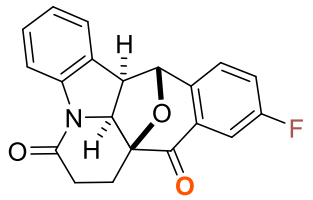
194.4, 170.0, 146.6, 143.6, 135.9 (d, *J* = 32.8 Hz), 130.5, 129.3, 129.1, 128.5, 125.7, 124.4 (d, *J* = 3.5 Hz), 124.1, 120.8, 116.0, 91.7, 85.2, 67.5, 54.9, 33.5, 27.0; **^{19}F NMR (565 MHz, CDCl$_3$)** δ –63.19 (s); **HRMS (ESI)** calcd for $C_{21}H_{15}F_3NO_3$ $[M+H]^+$: 386.0999; found: 386.0996.

(4^1*S,8b*R**,9*R**,14a*S**)-11-methyl-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3y)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3y** in 83% yield (55.0 mg) as a pale-yellow solid, mp 218–220 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 8.8 Hz, 1H), 7.18 (s, 1H), 7.12 (td, *J* = 7.4, 0.6 Hz, 1H), 5.18 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 8.0 Hz, 1H), 3.06 (ddd, *J* = 14.2, 5.1, 2.9 Hz, 1H), 2.66–2.55 (m, 2H), 2.47 (s, 3H), 1.79 (td, *J* = 13.7, 5.7 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 194.9, 170.4, 146.4, 146.2, 143.7, 129.8, 129.6, 129.0, 127.8, 125.4, 124.2, 124.1, 124.0, 115.9, 91.3, 85.7, 67.8, 55.1, 33.6, 27.0, 22.1; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1273.

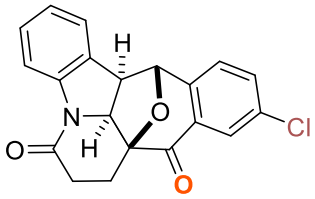
(4^1*S,8b*R**,9*R**,14a*S**)-12-fluoro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3z)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3z** in 98% yield (65.7 mg) as a pale-yellow solid, mp 210–212 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.8 Hz, 1H), 7.37–7.31 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.24 (s, 1H), 4.59

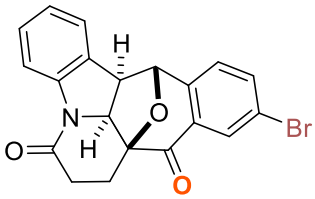
(d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.03 (ddd, *J* = 14.2, 5.0, 2.6 Hz, 1H), 2.64–2.53 (m, 2H), 1.80 (td, *J* = 13.6, 4.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.3, 170.1, 163.3, 161.6, 143.6, 142.2 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 6.9 Hz), 129.4, 129.1, 125.7 (d, *J* = 7.5 Hz), 124.2 (d, *J* = 4.0 Hz), 121.9 (d, *J* = 22.5 Hz), 115.9, 114.0 (d, *J* = 22.5 Hz), 91.1, 85.0, 67.5, 55.0, 33.5, 27.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –110.70 (td, *J* = 8.2, 5.0 Hz); **HRMS (ESI)** calcd for $C_{20}H_{15}FNO_3$ $[M+H]^+$: 336.1030; found: 336.1023.

(4^1*S,8b*R**,9*R**,14a*S**)-12-chloro-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3aa)**



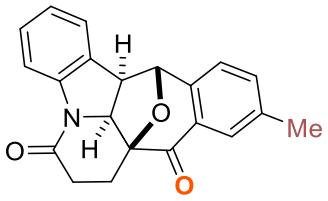
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3aa** in 98% yield (69.0 mg) as a colorless solid, mp 226–228 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 7.59 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.38–7.32 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.22 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.02 (ddd, *J* = 14.1, 5.1, 2.5 Hz, 1H), 2.65–2.53 (m, 2H), 1.79 (td, *J* = 14.2, 5.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.1, 170.1, 144.3, 143.6, 135.0, 134.6, 129.3, 129.2, 129.2, 127.5, 125.2, 124.2, 115.9, 91.3, 85.0, 67.5, 55.0, 33.5, 27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}ClNO_3$ $[M+H]^+$: 352.0735; found: 352.0729.

(4^1*S,8b*R**,9*R**,14a*S**)-12-bromo-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3ab)**



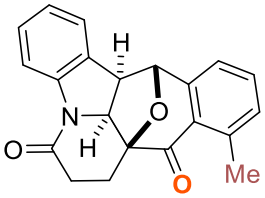
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3ab** in 97% yield (76.9 mg) as a pale-yellow solid, mp 222–224 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.74 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.31–7.25 (m, 2H), 7.12 (td, *J* = 7.4, 0.6 Hz, 1H), 5.21 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.02 (ddd, *J* = 14.2, 5.3, 2.6 Hz, 1H), 2.65–2.52 (m, 2H), 1.79 (dt, *J* = 14.1, 5.2 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.0, 170.1, 144.7, 143.6, 137.5, 130.5, 129.4, 129.3, 129.2, 125.4, 124.2, 122.8, 115.9, 91.3, 85.1, 67.5, 54.9, 33.5, 27.0; **HRMS (ESI)** calcd for $C_{20}H_{15}BrNO_3$ $[M+H]^+$: 396.0230; found: 396.0223.

(4^1*S,8b*R**,9*R**,14a*S**)-12-methyl-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3ac)**



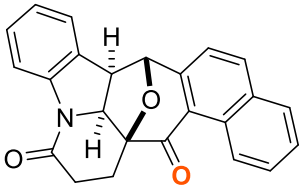
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3ac** in 92% yield (61.0 mg) as a colorless solid, mp 205–207 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.44 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.32–7.25 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.21 (s, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.90 (d, *J* = 8.0 Hz, 1H), 3.05 (ddd, *J* = 14.1, 4.9, 2.9 Hz, 1H), 2.65–2.55 (m, 2H), 2.42 (s, 3H), 1.83–1.75 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.5, 170.3, 143.7, 143.4, 138.8, 135.7, 129.8, 129.0, 127.8, 127.7, 124.2, 124.1, 123.4, 115.9, 91.3, 85.5, 67.7, 55.2, 33.6, 27.1, 21.1; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1274.

(4^1*S,8b*R**,9*R**,14a*S**)-13-methyl-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3ad)**



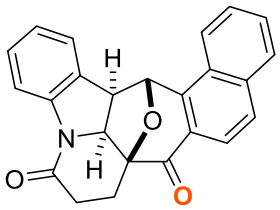
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3ad** in 91% yield (60.3 mg) as a colorless solid, mp 215–217 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.19 (s, 1H), 4.59 (d, *J* = 7.9 Hz, 1H), 3.92 (d, *J* = 7.9 Hz, 1H), 3.07–2.98 (m, 1H), 2.69 (s, 3H), 2.65–2.57 (m, 2H), 1.87–1.76 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 197.1, 170.2, 146.6, 143.7, 142.9, 134.0, 132.2, 129.9, 128.9, 125.7, 124.2, 124.1, 121.6, 115.9, 91.6, 86.1, 68.1, 54.8, 33.8, 27.6, 22.2; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1273.

(4^1*S,8b*R**,9*R**,16a*S**)-1,2,8b,9-tetrahydro-3*H*-9,16a-epoxybenzo[*b*]naphtha [2',1':5,6]cyclohepta[1,2,3-*hi*]indolizine-3,16(4^1*H*)-dione (3ae)**



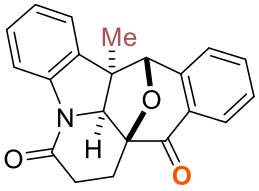
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3ae** in 90% yield (66.1 mg) as a yellow solid, mp 229–231 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.34 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.32 (s, 1H), 4.57 (d, *J* = 7.9 Hz, 1H), 3.94 (d, *J* = 7.9 Hz, 1H), 3.17–3.10 (m, 1H), 2.73–2.61 (m, 2H), 1.87 (ddd, *J* = 13.9, 12.1, 7.1 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 196.9, 170.3, 147.9, 144.0, 136.7, 133.4, 131.0, 130.0, 129.6, 129.1, 128.8, 126.9, 126.3, 124.2, 124.1, 122.1, 121.2, 116.0, 91.8, 86.1, 67.9, 54.8, 33.9, 28.0; **HRMS (ESI)** calcd for $C_{24}H_{18}NO_3$ $[M+H]^+$: 368.1281; found: 368.1272.

(4^1*S,8b*R**,9*R**,16a*S**)-1,2,8b,9-tetrahydro-3*H*-9,16a-epoxybenzo[*b*]naphtha [1',2':5,6]cyclohepta[1,2,3-*hi*]indolizine-3,16(4^1*H*)-dione (3af)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to give **3af** in 62% yield (45.6 mg) as a yellow solid, mp 211–213 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 1.3 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.97 (dd, *J* = 6.6, 2.4 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.78–7.71 (m, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.04 (s, 1H), 4.65 (d, *J* = 7.9 Hz, 1H), 3.97 (d, *J* = 7.9 Hz, 1H), 3.15 (ddd, *J* = 14.2, 5.1, 2.8 Hz, 1H), 2.70–2.60 (m, 2H), 1.87 (td, *J* = 13.9, 5.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.9, 170.4, 145.0, 143.9, 136.2, 129.7, 129.5, 129.4, 129.2, 128.9, 127.9, 127.1, 125.3, 124.3, 124.1, 123.2, 122.2, 116.1, 91.1, 82.0, 68.1, 54.8, 33.6, 27.1; **HRMS (ESI)** calcd for $C_{24}H_{18}NO_3$ $[M+H]^+$: 368.1281; found: 368.1273.

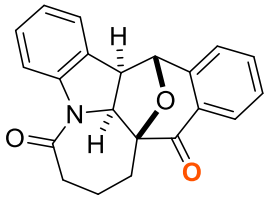
(4^1*S,8b*R**,9*R**,14a*S**)-8b-methyl-1,2,8b,9-tetrahydro-3*H*-9,14a-epoxybenzo[*b*] benzo[5,6]cyclohepta[1,2,3-*hi*]indolizine-3,14(4^1*H*)-dione (3ag)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 5:1) to give **3ag** in 54% yield (35.8 mg) as a colorless solid, mp 194–196 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.65 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51 (td, *J* = 7.6, 0.9 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.33–7.28 (m, 2H), 7.15 (td, *J* = 7.2, 0.8 Hz, 1H), 5.13 (s, 1H), 4.08 (s, 1H), 3.00 (ddd, *J* = 14.1, 5.0, 2.8 Hz, 1H), 2.65–2.55 (m, 2H), 1.78–1.70 (m, 1H), 1.00 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.8, 170.7, 143.6, 143.1, 135.9, 134.4, 128.9, 128.9, 128.7, 127.3, 125.6, 124.3, 122.5, 115.6, 91.7,

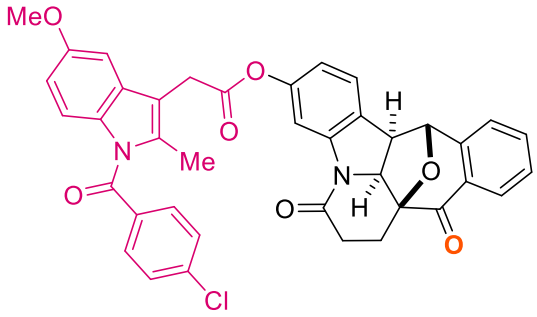
88.4, 74.5, 57.8, 33.7, 27.7, 24.0; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1278.

(4^1*S,8b*R**,9*R**,14a*S**)-2,3,8b,9-tetrahydro-15-oxa-4a-aza-9,14a-methanobenzo[*b*]indeno[1,2,3-*ef*]heptalene-4,14(1H,4a^1*H*)-dione (3ah)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3ah** in 61% yield (40.4 mg) as a pale-yellow solid, mp 214–216 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.28 (s, 1H), 4.83 (d, *J* = 8.4 Hz, 1H), 4.18 (d, *J* = 8.4 Hz, 1H), 2.77 (td, *J* = 12.6, 9.2 Hz, 1H), 2.68–2.57 (m, 2H), 2.43 (dd, *J* = 14.3, 5.0 Hz, 1H), 2.12 (ddd, *J* = 20.4, 13.5, 7.1 Hz, 1H), 1.72 (td, *J* = 13.9, 6.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 196.3, 170.9, 145.5, 143.7, 134.7, 129.8, 129.1, 128.8, 128.4, 127.4, 124.2, 124.1, 123.9, 116.4, 89.5, 83.3, 67.1, 54.8, 35.1, 29.0, 18.5; **HRMS (ESI)** calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1281; found: 332.1278.

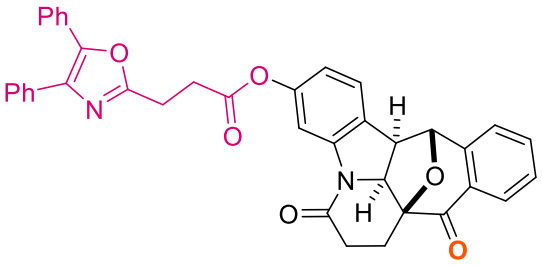
(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-7-yl2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3al)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3al** in 99% yield (133.3 mg) as a pale-yellow solid, mp 170–172 ℃; **^{1}H NMR (600 MHz,**

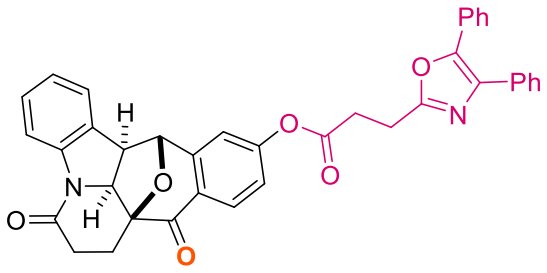
$CDCl_3$) δ 8.04 (t, *J* = 8.8 Hz, 2H), 7.69–7.65 (m, 2H), 7.61 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48–7.44 (m, 3H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 1.9 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.98 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.22 (s, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 2H), 3.87 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.05 (ddd, *J* = 14.1, 5.1, 2.7 Hz, 1H), 2.63–2.52 (m, 2H), 2.45 (s, 3H), 1.83–1.74 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.9, 170.1, 169.4, 168.2, 156.0, 146.9, 145.7, 141.4, 139.3, 136.2, 134.9, 133.7, 131.1, 130.8, 130.8, 130.4, 129.2, 129.1, 128.8, 127.7, 127.6, 123.5, 123.4, 121.6, 117.7, 116.2, 114.9, 111.8, 111.6, 101.3, 91.3, 85.2, 68.1, 55.7, 54.8, 33.3, 30.4, 27.0, 13.4; **HRMS (ESI)** calcd for $C_{39}H_{30}ClN_2O_7$ $[M+H]^+$: 673.1736; found: 673.1723.

(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxy-benzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-7-yl3-(4,5-diphenyloxazol-2-yl)propanoate (3am)**



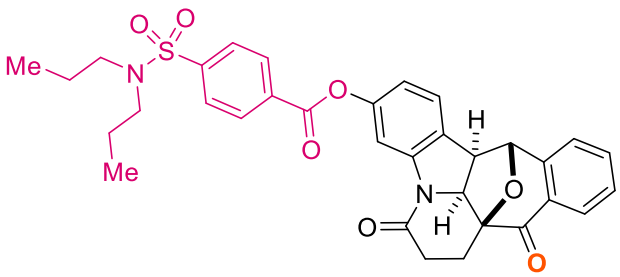
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3am** in 90% yield (109.6 mg) as a light-greenish solid, mp 150–152 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.7 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.62–7.57 (m, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39–7.34 (m, 4H), 7.34–7.30 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.19 (s, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 8.0 Hz, 1H), 3.32 (t, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 7.4 Hz, 2H), 3.07 (ddd, *J* = 14.1, 5.1, 2.6 Hz, 1H), 2.66–2.56 (m, 2H), 1.81 (td, *J* = 13.9, 5.3 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 195.0, 170.9, 170.1, 161.4, 147.0, 145.7, 145.6, 141.5, 135.1, 134.9, 132.4, 130.8, 128.9, 128.8, 128.7, 128.6, 128.1, 127.8, 127.8, 127.7, 126.5, 123.6, 121.8, 117.9, 116.4, 91.4, 85.3, 68.1, 54.9, 33.4, 31.2, 27.0, 23.5; **HRMS (ESI)** calcd for $C_{38}H_{28}N_2NaO_6$ $[M+Na]^+$: 631.1840; found: 631.1854.

(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-11-yl3-(4,5-diphenyloxazol-2-yl)propanoate (3an)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3an** in 80% yield (97.4 mg) as a colorless solid, mp 196–198 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.70–7.65 (m, 2H), 7.62–7.57 (m, 2H), 7.40–7.35 (m, 4H), 7.35–7.28 (m, 3H), 7.22 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.21–7.18 (m, 2H), 7.10 (td, *J* = 7.5, 0.8 Hz, 1H), 5.09 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 8.0 Hz, 1H), 3.33 (td, *J* = 10.7, 4.0 Hz, 2H), 3.21 (td, *J* = 10.6, 4.1 Hz, 2H), 3.05 (ddd, *J* = 14.1, 5.2, 2.6 Hz, 1H), 2.66–2.55 (m, 2H), 1.81 (td, *J* = 14.1, 5.1 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 194.1, 170.2, 170.0, 161.1, 155.4, 147.8, 145.7, 143.6, 135.1, 132.3, 129.8, 129.4, 129.1, 128.8, 128.7, 128.6, 128.6, 128.2, 127.7, 126.5, 125.5, 124.4, 124.2, 122.0, 116.8, 115.9, 91.4, 85.3, 67.6, 54.8, 33.6, 31.2, 26.9, 23.4; **HRMS (ESI)** calcd for $C_{38}H_{29}N_2O_6$ $[M+H]^+$: 609.2020; found: 609.2013.

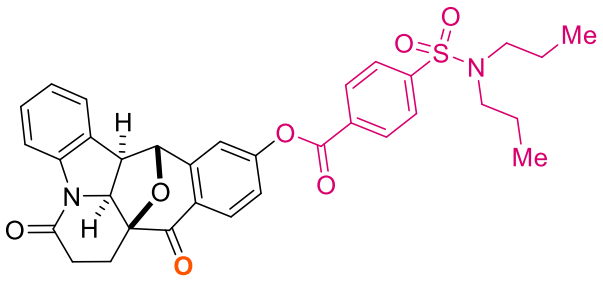
(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxybenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-7-yl4-(*N*,*N*-dipropylsulfamoyl) benzoate (3ao)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3ao** in 89% yield (106.9 mg) as a colorless solid, mp 169–171 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)**

δ 8.30 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.47 (td, *J* = 7.6, 0.8 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 1.9 Hz, 1H), 7.12 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.28 (s, 1H), 4.67 (d, *J* = 8.0 Hz, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.14–3.10 (m, 4H), 3.10–3.04 (m, 1H), 2.66–2.53 (m, 2H), 1.87–1.75 (m, 1H), 1.61–1.49 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 194.9, 170.1, 164.0, 146.9, 145.7, 145.0, 141.7, 135.0, 132.5, 131.0, 130.7, 128.9, 127.7, 127.7, 127.1, 123.5, 121.8, 117.9, 116.4, 91.3, 85.3, 68.1, 54.9, 49.8, 33.4, 27.0, 21.8, 11.1; **HRMS (ESI)** calcd for $C_{33}H_{33}N_2O_7S$ $[M+H]^+$: 601.2003; found: 601.2004.

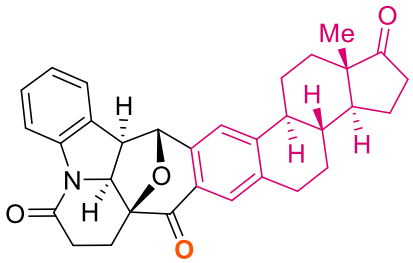
(4^1*S,8b*R**,9*R**,14a*S**)-3,14-dioxo-2,3,4^1,8b,9,14-hexahydro-1*H*-9,14a-epoxy-benzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-11-yl-4-(*N*,*N*-dipropylsulfamoyl) benzoate (3ap)**



Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3ap** in 90% yield (108.1 mg) as a colorless solid, mp 271–274 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.33 (d, *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 9.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.37–7.33 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.26 (s, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.03 (d, *J* = 8.0 Hz, 1H), 3.19–3.12 (m, 4H), 3.08 (ddd, *J* = 14.1, 5.0, 2.7 Hz, 1H), 2.69–2.57 (m, 2H), 1.84 (td, *J* = 13.8, 5.4 Hz, 1H), 1.61–1.52 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 194.1, 170.2, 163.1, 155.3, 148.0, 145.6, 143.7, 131.9, 130.9, 130.0, 129.4, 129.2, 127.3, 125.9, 124.3, 124.3, 122.1, 116.9, 116.0, 91.5, 85.4, 67.7, 55.0, 49.9, 33.6, 27.0, 21.9, 11.1; **HRMS (ESI)** calcd for $C_{33}H_{33}N_2O_7S$ $[M+H]^+$: 601.2003; found: 601.1997.

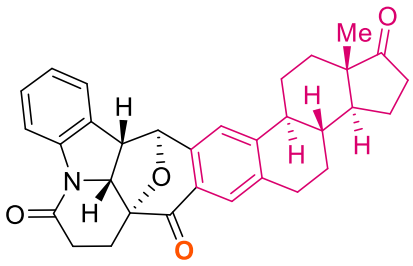
Column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to give **3aq** and **3aq'** in respective yields of 47% (46.4 mg) and 45% (44.4 mg).

(3a*S*,3b*R*,7a*S*,7a1*S*,15b*R*,16*R*,17b*S*,19a*S*)-19a-methyl-3,3a,3b,4,5,7a1,8,9,15b,16,17b,18,19,19a-tetradecahydro-1*H*,10*H*-7a,16-epoxybenzo[b]cyclopenta[7',8']phenanthro[3',2':5,6]cyclohepta[1,2,3-hi]indolizine-1,7,10(2H)-trione (3aq)



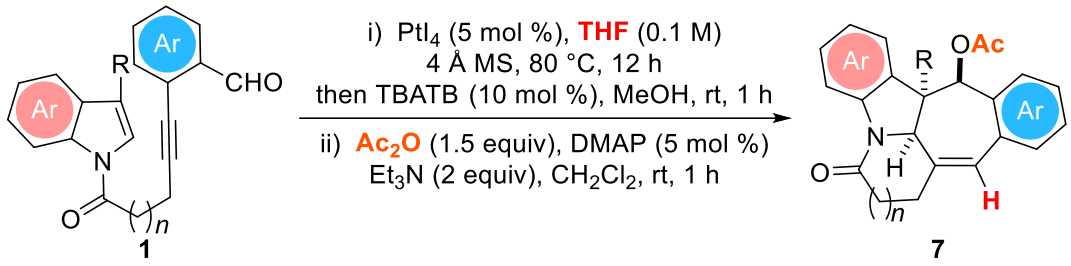
3aq: Colorless solid, mp 218–220 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.32–7.28 (m, 2H), 7.12 (td, *J* = 7.4, 0.6 Hz, 1H), 5.19 (s, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.89 (d, *J* = 8.0 Hz, 1H), 3.05 (ddd, *J* = 14.1, 4.9, 2.9 Hz, 1H), 3.02–2.95 (m, 2H), 2.65–2.56 (m, 2H), 2.57–2.49 (m, 2H), 2.38 (td, *J* = 11.3, 4.0 Hz, 1H), 2.21–2.12 (m, 1H), 2.12–2.01 (m, 3H), 1.78 (td, *J* = 13.7, 5.8 Hz, 1H), 1.70–1.60 (m, 3H), 1.58–1.44 (m, 3H), 0.93 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 220.2, 195.3, 170.4, 148.0, 143.7, 143.5, 137.6, 129.8, 129.0, 127.9, 125.4, 124.3, 124.2, 120.4, 116.0, 91.3, 85.8, 67.9, 55.2, 50.5, 47.8, 45.0, 37.6, 35.7, 33.7, 31.5, 29.1, 27.1, 26.1, 25.6, 21.5, 13.8; **HRMS (ESI)** calcd for $C_{32}H_{32}NO_4$ $[M+H]^+$: 494.2326; found: 494.2321.

(3a*S*,3b*R*,7a*R*,7a^{1}*R*,15bS,16*S*,17b*S*,19a*S*)-19a-methyl-3,3a,3b,4,5,7a1,8,9,15b,16,17b,18,19,19a-tetradecahydro-1*H*,10*H*-7a,16-epoxybenzo[b]cyclopenta[7',8']phenanthro[3',2':5,6]cyclohepta[1,2,3-hi]indolizine-1,7,10(2H)-trione (3aq')



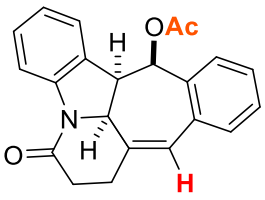
3aq': Colorless solid, mp 225–227 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.29–7.25 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.18 (s, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 8.0 Hz, 1H), 3.09–2.98 (m, 2H), 2.98–2.89 (m, 1H), 2.65–2.57 (m, 2H), 2.57–2.47 (m, 2H), 2.37 (td, *J* = 11.5, 3.6 Hz, 1H), 2.22–2.13 (m, 1H), 2.13–2.01 (m, 3H), 1.78 (td, *J* = 13.6, 5.9 Hz, 1H), 1.71–1.60 (m, 3H), 1.59–1.45 (m, 3H), 0.94 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 220.2, 195.3, 170.4, 148.0, 143.7, 143.6, 137.6, 129.8, 129.0, 127.9, 125.5, 124.3, 124.1, 120.3, 115.9, 91.2, 85.8, 67.8, 55.2, 50.5, 47.7, 44.9, 37.6, 35.7, 33.7, 31.4, 29.0, 27.1, 26.0, 25.6, 21.6, 13.8; **HRMS (ESI)** calcd for $C_{32}H_{32}NO_4$ $[M+H]^+$: 494.2326; found: 494.2325.

5. General procedure for PtI_4-catalyzed cascade hydrogenative and dearomative [3 + 2] cycloaddition/deacetalization/acetylation



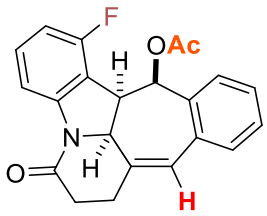
To a dried 10 mL round-bottom flask equipped with a magnetic stir bar were added **1** (0.2 mmol, 1.0 equiv.), 4Å MS (200 mg) and PtI_4 (7.0 mg, 0.01 mmol). Then mixture was then dissolved in anhydrous THF (2 mL) under argon atmosphere and stirred at 80 ^oC for 12 h. Upon completion, the reaction mixture was cooled to room temperature, then tetrabutylammonium tribromide (TBATB) (9.6 mg, 0.02mmol) 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 × 3). The combined organic phases are washed with brine, and dried over $MgSO_4$, and concentrated under reduced pressure to afford the crude alcohol product. The crude alcohol was dissolved in anhydrous CH_2Cl_2 (4 mL), then 4-dimethylaminopyridine (DMAP) (0.01 mmol, 5 mol %), trimethylamine (Et_3N) (0.4 mmol, 2 equiv), acetic anhydride (0.3 mmol, 1.5 equiv) were added sequentially. The resulting reaction mixture was stirred at room temperature for 1 h (monitored by TLC), 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 **7**.

(4^1*S,8b*R**,9*R**)-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta [1,2,3-*hi*]indolizin-9-yl acetate (7a)**



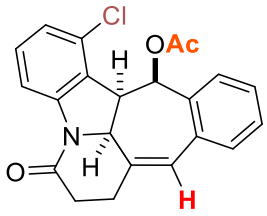
Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 3:1) to give **7a** in 78% yield (53.9 mg) as a pale-yellow solid, mp 117–119 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.28–7.23 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.53 (s, 1H), 5.92 (s, 1H), 4.96 (d, *J* = 8.6 Hz, 1H), 3.75 (d, *J* = 8.6 Hz, 1H), 2.89–2.80 (m, 2H), 2.74–2.58 (m, 2H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.3, 141.4, 136.0, 134.1, 134.0, 131.6, 131.6, 130.5, 129.0, 128.6, 127.4, 125.3, 124.7, 124.1, 117.5, 79.1, 62.7, 49.7, 33.8, 32.8, 20.4; **HRMS (ESI)** calcd for $C_{22}H_{20}NO_3$ $[M+H]^+$: 346.1438; found: 346.1438.

(4^1*S,8b*R**,9*R**)-8-fluoro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7b)**



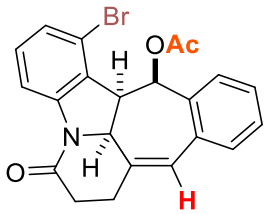
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 4:1) to give **7b** in 71% yield (51.6 mg) as a pale-yellow solid, mp 163–165 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29–7.22 (m, 3H), 6.83 (t, *J* = 8.6 Hz, 1H), 6.53 (s, 1H), 6.04 (s, 1H), 4.93 (d, *J* = 8.5 Hz, 1H), 3.92 (d, *J* = 8.6 Hz, 1H), 2.88–2.77 (m, 2H), 2.74–2.56 (m, 2H), 1.65 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.3, 158.6 (d, *J* = 246.4 Hz), 143.5 (d, *J* = 7.4 Hz), 135.7, 133.9, 133.3, 131.6, 130.7, 130.5 (d, *J* = 8.0 Hz), 129.0, 127.6, 125.7, 117.7 (d, *J* = 20.1 Hz), 113.4 (d, *J* = 3.3 Hz), 111.3 (d, *J* = 19.7 Hz), 76.8, 63.2, 46.5, 33.7, 32.6, 20.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –119.47 (dd, *J* = 8.8, 5.9 Hz); **HRMS (ESI)** calcd for $C_{22}H_{19}FNO_3$ $[M+H]^+$: 364.1343; found: 364.1340.

(4^1*S,8b*R**,9*R**)-8-chloro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate(7c)**



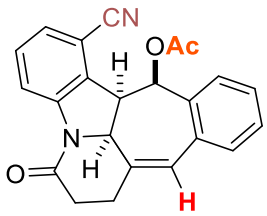
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7c** in 63% yield (47.9 mg) as a pale-yellow solid, mp 176–178 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.26–7.24 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.54 (s, 1H), 6.16 (s, 1H), 4.92 (d, *J* = 8.4 Hz, 1H), 3.83 (d, *J* = 8.4 Hz, 1H), 2.90–2.79 (m, 2H), 2.73–2.57 (m, 2H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.7, 142.8, 135.9, 133.9, 133.2, 131.6, 130.5, 130.1, 130.1, 129.3, 129.0, 127.6, 125.7, 124.8, 116.0, 75.9, 62.9, 48.7, 33.8, 32.7, 20.4; **HRMS (ESI)** calcd for $C_{22}H_{19}ClNO_3$ $[M+H]^+$: 380.1048; found: 380.1046.

(4^1*S,8b*R**,9*R**)-8-bromo-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7d)**



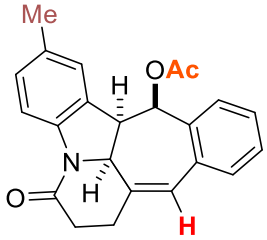
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7d** in 67% yield (56.9 mg) as a pale-yellow solid, mp 185–187 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31–7.23 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.54 (s, 1H), 6.19 (s, 1H), 4.93 (d, *J* = 8.3 Hz, 1H), 3.76 (d, *J* = 8.3 Hz, 1H), 2.90–2.78 (m, 2H), 2.74–2.57 (m, 2H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.58, 168.31, 142.75, 135.88, 133.84, 133.19, 131.57, 131.21, 130.43, 130.27, 129.02, 127.82, 127.68, 125.75, 119.00, 116.62, 76.00, 62.69, 50.20, 33.79, 32.69, 20.42; **HRMS (ESI)** calcd for $C_{22}H_{19}BrNO_3$ $[M+H]^+$: 424.0543; found: 424.0542.

(4^1*S,8b*R**,9*R**)-8-cyano-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7e)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7e** in 50% yield (37 mg) as a pale-yellow solid, mp 197–199 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.39–8.34 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.43–7.38 (m, 2H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.29–7.26 (m, 2H), 6.58 (s, 1H), 6.15 (s, 1H), 5.00 (d, *J* = 8.5 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 2.92–2.81 (m, 2H), 2.77–2.58 (m, 2H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.4, 168.6, 142.5, 135.6, 135.4, 133.7, 132.5, 131.6, 130.7, 129.6, 129.3, 128.0, 127.7, 126.2, 121.7, 116.5, 108.7, 77.2, 63.0, 49.2, 33.7, 32.6, 20.3; **HRMS (ESI)** calcd for $C_{23}H_{18}N_2NaO_3$ $[M+Na]^+$: 393.1210; found: 393.1210.

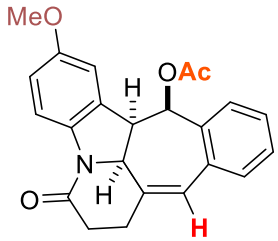
(4^1*S,8b*R**,9*R**)-7-methyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate(7f)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 2:1) to give **7f** in 80% yield (57.5 mg) as a light-greenish solid, mp 78–80 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.40 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.26–7.22 (m, 2H), 7.19 (s, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.50 (s, 1H), 5.88 (s, 1H), 4.91 (d, *J* = 8.5 Hz, 1H), 3.67 (d, *J* = 8.6 Hz, 1H), 2.86–2.78 (m, 2H), 2.72–2.55 (m, 2H), 2.36 (s, 3H), 1.65 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.8, 167.9, 139.1, 136.1, 134.3, 134.1, 131.7, 131.5, 130.5, 129.1, 128.9, 127.4, 125.2, 124.6, 117.2, 79.2,

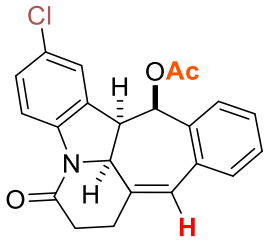
62.8, 49.6, 33.7, 32.8, 21.1, 20.4; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1597.

(4^1*S,8b*R**,9*R**)-7-methoxy-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate(7g)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7g** in 71% yield (53.3 mg) as a green solid, mp 131–132 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.25–7.21 (m, 2H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.50 (s, 1H), 5.90 (s, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.67 (d, *J* = 8.5 Hz, 1H), 2.85–2.77 (m, 2H), 2.71–2.54 (m, 2H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 167.6, 158.0, 136.0, 135.1, 134.1, 134.1, 133.2, 131.6, 130.5, 129.0, 127.4, 125.2, 118.2, 113.5, 109.9, 78.9, 62.9, 55.6, 49.8, 33.6, 32.9, 20.4; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$: 376.1543; found: 376.1546.

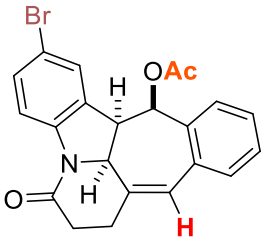
(4^1*S,8b*R**,9*R**)-7-chloro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7h)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 4:1) to give **7h** in 74% yield (56.2 mg) as a pale-yellow solid, mp 187–189 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.42–7.32 (m, 3H), 7.26–7.23 (m, 3H) 6.51 (s, 1H), 5.85 (s, 1H), 4.94 (d, *J* = 8.5 Hz, 1H), 3.69 (d, *J* = 8.6 Hz, 1H), 2.84–2.80 (m, 2H), 2.71–2.56 (m, 2H), 1.65 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.2, 140.1, 135.7, 133.9,

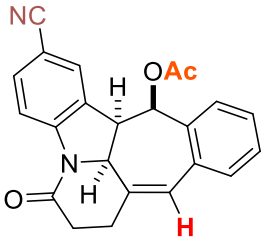
133.5, 133.5, 131.6, 130.5, 129.4, 129.1, 128.6, 127.5, 125.5, 124.3, 118.4, 78.9, 62.9, 49.4, 33.6, 32.6, 20.3; **HRMS (ESI)** calcd for $C_{22}H_{19}ClNO_3$ $[M+H]^+$: 380.1048; found: 380.1053.

(4^1*S,8b*R**,9*R**)-7-bromo-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7i)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7i** in 60% yield (50.9 mg) as a pale-green solid, mp 169–171 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.42–7.38 (m, 2H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.28–7.23 (m, 2H), 6.52 (s, 1H), 5.84 (s, 1H), 4.95 (d, *J* = 8.4 Hz, 1H), 3.71 (d, *J* = 8.7 Hz, 1H), 2.88–2.79 (m, 2H), 2.74–2.56 (m, 2H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.3, 140.6, 135.7, 134.0, 133.5, 131.6, 131.5, 130.6, 129.1, 127.6, 127.2, 125.6, 118.9, 117.0, 79.0, 62.9, 49.4, 33.7, 32.7, 20.4; **HRMS (ESI)** calcd for $C_{22}H_{19}BrNO_3$ $[M+H]^+$: 424.0543; found: 424.0543.

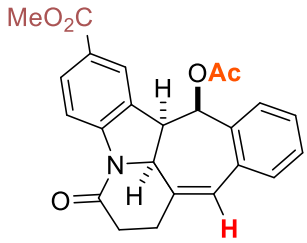
(4^1*S,8b*R**,9*R**)-7-cyano-3-oxo-1,2,3,41,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7j)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7j** in 55% yield (40.7 mg) as a pale-yellow solid, mp 170–172 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 8.3 Hz, 1H), 7.68 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.29–7.26 (m, 2H), 6.56 (s, 1H), 5.87 (s, 1H), 5.02 (d, *J* = 8.6 Hz, 1H), 3.81 (d, *J* = 8.6 Hz, 1H), 2.95–2.80 (m, 2H), 2.75–2.73 (m, 1H), 2.68–

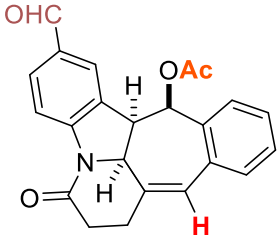
2.62 (m, 1H), 1.66 (s, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.5, 169.0, 145.1, 135.4, 133.8, 133.6, 132.9, 132.8, 131.7, 130.7, 129.3, 127.9, 127.8, 126.0, 118.8, 117.7, 107.6, 78.9, 63.0, 49.3, 33.7, 32.4, 20.3; **HRMS (ESI)** calcd for $C_{23}H_{19}N_2O_3$ $[M+H]^+$: 371.1390; found: 371.1389.

Methyl(4^1*S,8b*R**,9*R**)-9-acetoxy-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo-[5,6] cyclohepta[1,2,3-*hi*]indolizine-7-carboxylate (7k)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 4:1) to give **7k** in 66% yield (53.3 mg) as a colorless solid, mp 186–188 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.26–7.23 (m, 2H), 6.53 (s, 1H), 5.89 (s, 1H), 5.00 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H), 3.78 (d, *J* = 8.7 Hz, 1H), 2.87–2.82 (m, 2H), 2.73–2.70 (m, 1H), 2.66–2.60 (m, 1H), 1.63 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.5, 168.8, 166.4, 145.3, 135.8, 133.9, 133.7, 132.0, 131.6, 131.0, 130.6, 129.1, 127.6, 126.3, 125.7, 125.6, 116.7, 79.1, 63.1, 52.0, 49.3, 33.8, 32.5, 20.3; **HRMS (ESI)** calcd for $C_{24}H_{22}NO_5$ $[M+H]^+$: 404.1492; found: 404.1491.

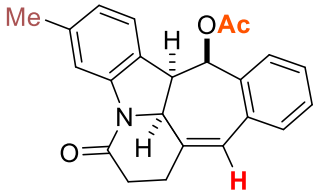
(4^1*S,8b*R**,9*R**)-7-formyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclo-hepta[1,2,3-*hi*]indolizin-9-yl acetate(7l)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 2:1) to give **7l** in 50% yield (37.3 mg) as a pale-yellow solid, mp 112–114 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.93 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.94 (s, 1H), 7.81 (dd, *J* = 8.2, 1.1 Hz, 1H),

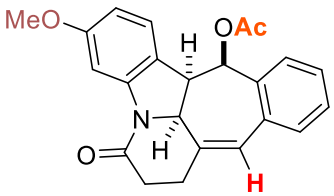
7.40 (d, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H),7.27–7.24 (m, 2H), 6.54 (s, 1H), 5.90 (s, 1H), 5.03 (d, *J* = 8.7 Hz, 1H), 3.82 (d, *J* = 8.7 Hz, 1H), 2.89–2.83 (m, 2H), 2.75–2.72 (m, 1H), 2.68–2.61 (m, 1H), 1.63 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.7, 169.5, 169.0, 146.5, 135.7, 133.9, 133.1, 133.1, 132.9, 132.7, 131.6, 130.6, 129.2, 127.7, 125.8, 124.6, 117.1, 79.1, 63.2, 49.2, 33.8, 32.4, 20.3; **HRMS (ESI)** calcd for $C_{23}H_{20}NO_4$ $[M+H]^+$: 374.1387; found: 374.1391.

(4^1*S,8b*R**,9*R**)-6-methyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7m)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7m** in 64% yield (46 mg) as a pale-yellow solid, mp 190–192 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.99 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.30–7.21 (m, 3H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 5.90 (s, 1H), 4.93 (d, *J* = 8.5 Hz, 1H), 3.69 (d, *J* = 8.6 Hz, 1H), 2.85–2.82 (m, 2H), 2.71–2.68 (m, 1H), 2.64–2.58 (m, 1H), 2.38 (s, 3H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.8, 168.2, 141.6, 138.6, 136.1, 134.2, 134.2, 131.6, 130.5, 129.0, 128.8, 127.4, 125.5, 125.3, 123.7, 118.2, 79.1, 63.1, 49.4, 33.8, 32.8, 21.7, 20.5; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1597.

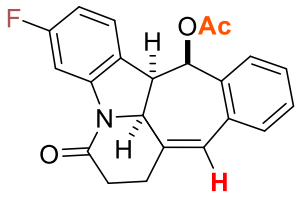
(4^1*S,8b*R**,9*R**)-6-methoxy-3-oxo-1,2,3,41,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7n)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7n** in 68% yield (51.1 mg) as a pale-yellow solid, mp 176–178 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)**

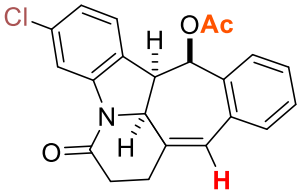
δ 7.81 (d, *J* = 2.3 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29–7.19 (m, 3H), 6.69 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.50 (s, 1H), 5.87 (s, 1H), 4.94 (d, *J* = 8.5 Hz, 1H), 3.82 (s, 3H), 3.67 (d, *J* = 8.6 Hz, 1H), 2.83–2.79 (m, 2H), 2.70–2.67 (m, 1H), 2.64–2.58 (m, 1H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.3, 160.0, 142.6, 136.0, 134.1, 134.0, 131.5, 130.5, 128.9, 127.4, 125.3, 124.3, 123.4, 111.0, 103.2, 79.1, 63.4, 55.5, 49.1, 33.8, 32.7, 20.4; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$: 376.1543; found: 376.1548.

(4^1*S,8b*R**,9*R**)-6-fluoro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7o)**



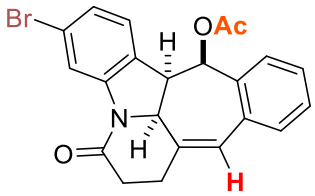
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7o** in 63% yield (45.8 mg) as a pale-yellow solid, mp 165–167 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (dd, *J* = 10.0, 2.4 Hz, 1H), 7.39–7.31 (m, 3H), 7.26–7.24 (m, 2H), 6.84 (td, *J* = 8.6, 2.5 Hz, 1H), 6.52 (s, 1H), 5.88 (s, 1H), 4.99 (d, *J* = 8.6 Hz, 1H), 3.72 (d, *J* = 8.6 Hz, 1H), 2.86–2.81 (m, 2H), 2.73–2.70 (m, 1H), 2.65–2.59 (m, 1H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.4, 162.8 (d, *J* = 244.2 Hz), 142.7 (d, *J* = 12.5 Hz), 135.8, 134.1, 133.6, 131.7, 130.6, 129.1, 127.6, 127.0 (d, *J* = 2.5 Hz), 125.6, 124.8 (d, *J* = 10.0 Hz), 111.4 (d, *J* = 23.1 Hz), 105.6 (d, *J* = 28.4 Hz), 79.0, 63.5, 49.2, 33.7, 32.6, 20.4; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –112.13 (td, *J* = 9.4, 5.4 Hz); **HRMS (ESI)** calcd for $C_{22}H_{19}FNO_3$ $[M+H]^+$: 364.1343; found: 364.1347.

(4^1*S,8b*R**,9*R**)-6-chloro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7p)**



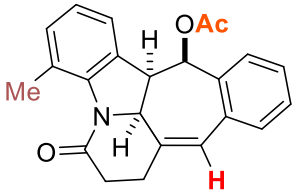
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7p** in 64% yield (48.6 mg) as a pale-yellow solid, mp 164–166 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 1.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.27–7.23 (m, 2H), 7.11 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.52 (s, 1H), 5.87 (s, 1H), 4.97 (d, *J* = 8.7 Hz, 1H), 3.72 (d, *J* = 8.7 Hz, 1H), 2.87–2.83 (m, 2H), 2.75–2.71 (m, 1H), 2.67–2.61 (m, 1H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.4, 142.5, 135.7, 134.2, 134.0, 133.5, 131.6, 130.6, 130.1, 129.1, 127.5, 125.6, 124.8, 124.7, 117.7, 78.8, 63.2, 49.3, 33.7, 32.6, 20.4; **HRMS (ESI)** calcd for $C_{22}H_{19}ClNO_3$ $[M+H]^+$: 380.1048; found: 380.1052.

(4^1*S,8b*R**,9*R**)-6-bromo-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7q)**



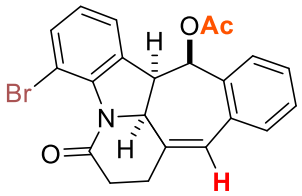
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7q** in 57% yield (48.4 mg) as a pale-yellow solid, mp 154–156 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.33 (d, *J* = 1.3 Hz, 1H), 7.40–7.36 (m, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28–7.21 (m, 4H), 6.52 (s, 1H), 5.87 (s, 1H), 4.96 (d, *J* = 8.7 Hz, 1H), 3.70 (d, *J* = 8.7 Hz, 1H), 2.84–2.80 (m, 2H), 2.72–2.69 (m, 1H), 2.64–2.58 (m, 1H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.4, 142.7, 135.7, 134.0, 133.5, 131.6, 130.7, 130.6, 129.1, 127.6, 127.5, 125.6, 125.2, 122.2, 120.5, 78.8, 63.1, 49.4, 33.7, 32.6, 20.4; **HRMS (ESI)** calcd for $C_{22}H_{19}BrNO_3$ $[M+H]^+$: 424.0543; found: 424.0546.

(4^1*S,8b*R**,9*R**)-7-methyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7r)**



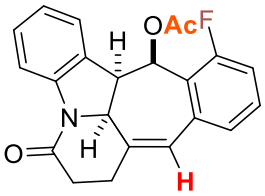
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 4:1) to give **7r** in 70% yield (50.3 mg) as a colorless solid, mp 163–165 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.33 (td, *J* = 7.6, 1.1 Hz, 1H), 7.26–7.24 (m, 3H), 7.15–7.14 (m, 2H), 6.50 (s, 1H), 5.97 (s, 1H), 5.00 (d, *J* = 8.3 Hz, 1H), 3.59 (d, *J* = 8.3 Hz, 1H), 2.96 (dd, *J* = 17.5, 5.6 Hz, 1H), 2.93–2.88 (m, 1H), 2.63 (dd, *J* = 12.4, 5.9 Hz, 1H), 2.50–2.44 (m, 1H), 2.33 (s, 3H), 1.72 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.1, 170.0, 140.7, 136.8, 135.2, 134.6, 134.1, 131.5, 130.9, 130.5, 129.7, 128.8, 127.3, 125.9, 124.7, 121.5, 79.2, 64.7, 51.2, 34.4, 32.9, 20.8, 20.5; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1597.

(4^1*S,8b*R**,9*R**)-7-bromo-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7s)**



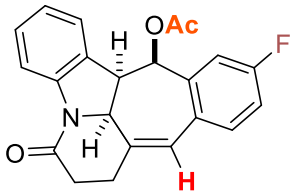
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 4:1) to give **7s** in 55% yield (46.7 mg) as a pale-yellow solid, mp 201–203 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28–7.22 (m, 3H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.50 (s, 1H), 5.95 (s, 1H), 5.06 (d, *J* = 8.3 Hz, 1H), 3.64 (d, *J* = 8.3 Hz, 1H), 3.00 (dd, *J* = 17.9, 5.9 Hz, 1H), 2.96–2.90 (m, 1H), 2.62 (dd, *J* = 12.5, 6.0 Hz, 1H), 2.47–2.41 (m, 1H), 1.73 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.1, 169.5, 141.5, 137.5, 136.4, 134.7, 134.0, 133.2, 131.5, 130.5, 129.0, 127.4, 127.0, 124.9, 123.2, 113.8, 78.9, 65.0, 51.7, 34.5, 32.6, 20.8; **HRMS (ESI)** calcd for $C_{22}H_{19}BrNO_3$ $[M+H]^+$: 424.0543; found: 424.0543.

(4^1*S,8b*R**,9*R**)-10-fluoro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cycloheptа[1,2,3-*hi*]indolizin-9-yl acetate (7t)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 2:1) to give **7t** in 37% yield (26.9 mg) as a pale-yellow solid, mp 90–92 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 6.1 Hz, 1H), 7.33–7.27 (m, 2H), 7.16 (td, *J* = 7.5, 0.9 Hz, 1H), 7.03–6.98 (m, 2H), 6.53 (s, 1H), 6.44 (s, 1H), 4.97 (d, *J* = 8.6 Hz, 1H), 3.72 (d, *J* = 8.7 Hz, 1H), 2.90–2.80 (m, 2H), 2.74–2.57 (m, 2H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.4, 168.3, 159.8 (d, *J* = 248.4 Hz), 141.3, 136.3, 135.4, 131.4, 130.0 (d, *J* = 9.5 Hz), 128.7, 127.1 (d, *J* = 3.2 Hz), 124.9, 124.7 (d, *J* = 2.8 Hz), 124.4, 123.6 (d, *J* = 13.2 Hz), 117.5, 114.5 (d, *J* = 23.9 Hz), 69.0 (d, *J* = 7.2 Hz), 62.6, 49.8, 33.7, 32.8, 20.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –117.52 (dd, *J* = 9.4, 5.6 Hz); **HRMS (ESI)** calcd for $C_{22}H_{19}FNO_3$ $[M+H]^+$: 364.1343; found: 364.1346.

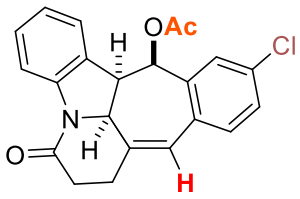
(4^1*S,8b*R**,9*R**)-11-fluoro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[b]benzo[5,6]cycloheptа[1,2,3-*hi*]indolizin-9-yl acetate (7u)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 2:1) to give **7u** in 66% yield (48 mg) as a pale-yellow solid, mp 85–87 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (t, *J* = 7.0 Hz, 1H), 7.38 (d, *J* = 6.4 Hz, 1H), 7.31–7.13 (m, 4H), 7.03–7.01 (m, 1H), 6.48 (s, 1H), 5.81 (s, 1H), 4.95 (d, *J* = 7.3 Hz, 1H), 3.72 (t, *J* = 6.9 Hz, 1H), 2.87–2.77 (m, 2H), 2.72–2.55 (m, 2H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.2, 161.3 (d, *J* = 249.4 Hz), 141.4, 138.0 (d, *J* = 6.9 Hz), 133.5, 133.3 (d, *J* = 7.8 Hz), 131.3, 130.3 (d, *J* = 3.4 Hz), 128.7, 124.8, 124.2, 124.1, 117.6 (d, *J* = 11.0 Hz), 117.6, 115.7 (d, *J* = 20.9 Hz), 78.4, 62.6, 49.4, 33.7, 32.7, 20.3; **^{19}F NMR (565 MHz,**

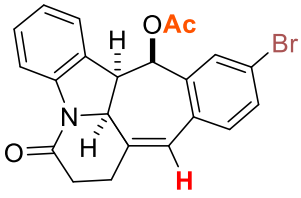
$CDCl_3$) δ –113.72– –113.76 (m); **HRMS (ESI)** calcd for $C_{22}H_{19}FNO_3$ $[M+H]^+$: 364.1343; found: 364.1348.

(4^1*S,8b*R**,9*R**)-11-chloro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cycl-ohepta[1,2,3-*hi*]indolizin-9-yl acetate (7v)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 2:1) to give **7v** in 72% yield (54.7 mg) as a pale-yellow solid, mp 92–94 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32–7.27 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.47 (s, 1H), 5.82 (s, 1H), 4.94 (d, *J* = 8.5 Hz, 1H), 3.71 (d, *J* = 8.6 Hz, 1H), 2.85–2.80 (m, 2H), 2.70–2.67 (m, 1H), 2.63–2.57 (m, 1H), 1.65 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.1, 141.4, 137.5, 134.7, 132.9, 132.8, 132.6, 131.2, 130.4, 128.9, 128.7, 124.8, 124.2, 124.1, 117.5, 78.3, 62.6, 49.4, 33.6, 32.7, 20.3; **HRMS (ESI)** calcd for $C_{22}H_{19}ClNO_3$ $[M+H]^+$: 380.1048; found: 380.1052.

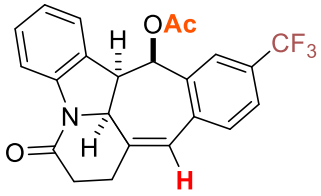
(4^1*S,8b*R**,9*R**)-11-bromo-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cycl-ohepta[1,2,3-*hi*]indolizin-9-yl acetate (7w)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 2:1) to give **7w** in 76% yield (64.5 mg) as a pale-yellow solid, mp 190–192 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.44 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.45 (s, 1H), 5.81 (s, 1H), 4.93 (d, *J* = 8.6 Hz, 1H), 3.71 (d, *J* = 8.7 Hz, 1H), 2.86–2.78 (m, 2H), 2.70–2.67 (m, 1H), 2.64–2.57 (m, 1H), 1.65 (s, 3H); **^{13}C NMR**

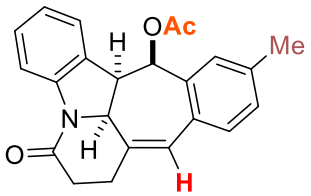
(150 MHz, $CDCl_3$) δ 169.6, 168.1, 141.4, 137.7, 134.9, 133.3, 133.1, 133.0, 131.9, 131.2, 128.7, 124.8, 124.3, 124.1, 121.0, 117.5, 78.2, 62.6, 49.5, 33.6, 32.7, 20.3; **HRMS (ESI)** calcd for $C_{22}H_{19}BrNO_3$ $[M+H]^+$: 424.0543; found: 424.0544.

(4^1*S,8b*R**,9*R**)-3-oxo-11-(trifluoromethyl)-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7x)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7x** in 61% yield (50.4 mg) as a yellow solid, mp 167–169 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.58 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.31 (td, *J* = 7.6, 0.9 Hz, 1H), 7.16 (td, *J* = 7.5, 0.8 Hz, 1H), 6.56 (s, 1H), 5.94 (s, 1H), 4.98 (d, *J* = 8.6 Hz, 1H), 3.76 (d, *J* = 8.7 Hz, 1H), 2.92–2.82 (m, 2H), 2.76–2.72 (m, 1H), 2.66–2.60 (m, 1H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.1, 141.4, 137.7, 137.0, 136.6, 131.9, 131.0, 129.2 (q, *J* = 32.6 Hz), 128.8, 127.4 (q, *J* = 3.8 Hz), 125.8 (q, *J* = 3.5 Hz), 124.8, 124.6, 124.1 (q, *J* = 3.9 Hz), 122.8, 117.5, 78.4, 62.6, 49.6, 33.5, 32.8, 20.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ –62.43 (s); **HRMS (ESI)** calcd for $C_{23}H_{19}F_3NO_3$ $[M+H]^+$: 414.1312; found: 414.1318.

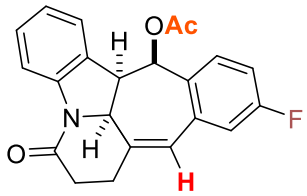
(4^1*S,8b*R**,9*R**)-11-methyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7y)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7y** in 57% yield (41 mg) as a pale-green solid, mp 83–85 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.30 (td, *J* = 8.0, 1.1 Hz, 1H), 7.22 (s, 1H), 7.17–7.11 (m, 3H), 6.49 (s, 1H), 5.88 (d, *J* = 0.9 Hz, 1H), 4.94 (d, *J* = 8.4 Hz, 1H), 3.71

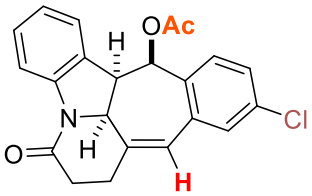
(d, *J* = 8.6 Hz, 1H), 2.87–2.78 (m, 2H), 2.72–2.57 (m, 2H), 2.36 (s, 3H), 1.65 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 169.8, 168.3, 141.5, 137.5, 135.9, 132.9, 131.8, 131.7, 131.4, 131.3, 129.6, 128.6, 125.3, 124.7, 124.1, 117.6, 79.2, 62.8, 49.7, 33.9, 32.8, 21.0, 20.5; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1599.

(4^1*S,8b*R**,9*R**)-12-fluoro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7z)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 2:1) to give **7z** in 66% yield (48 mg) as a colorless solid, mp 139–141 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.38–7.36 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.96–6.89 (m, 2H), 6.44 (s, 1H), 5.89 (s, 1H), 4.96 (d, *J* = 8.6 Hz, 1H), 3.72 (d, *J* = 8.7 Hz, 1H), 2.89–2.79 (m, 2H), 2.71–2.68 (m, 1H), 2.64–2.58 (m, 1H), 1.65 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 169.7, 168.1, 162.7 (d, *J* = 247.9 Hz), 141.4, 136.4 (d, *J* = 8.0 Hz), 135.6, 132.5 (d, *J* = 8.5 Hz), 132.1 (d, *J* = 3.2 Hz), 131.4, 128.6, 124.7, 124.2, 124.0, 118.0 (d, *J* = 22.0 Hz), 117.5, 113.9 (d, *J* = 21.1 Hz), 78.2, 62.6, 49.7, 33.6, 32.7, 20.3; **^{19}F NMR (565 MHz, CDCl$_3$)** δ –113.00 – –113.11(m);**HRMS (ESI)** calcd for $C_{22}H_{19}FNO_3$ $[M+H]^+$: 364.1343; found: 364.1349.

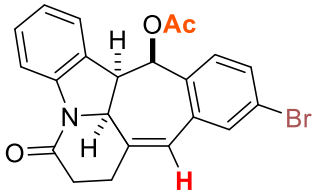
(4^1*S,8b*R**,9*R**)-12-chloro-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7aa)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7aa** in 72% yield (54.7 mg) as a colorless solid, mp 83–85 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J*

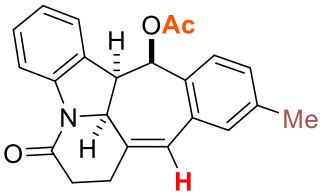
= 7.7 Hz, 1H), 7.24–7.17 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.43 (s, 1H), 5.86 (s, 1H), 4.95 (d, *J* = 8.6 Hz, 1H), 3.71 (d, *J* = 8.7 Hz, 1H), 2.88–2.80 (m, 2H), 2.71–2.68 (m, 2H), 2.64–2.57 (m, 1H), 1.64 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 168.1, 141.4, 135.9, 135.8, 134.7, 134.4, 132.0, 131.2, 131.2, 128.7, 127.2, 124.7, 124.0, 124.0, 117.5, 78.3, 62.5, 49.6, 33.6, 32.7, 20.3; **HRMS (ESI)** calcd for $C_{22}H_{19}ClNO_3$ $[M+H]^+$: 380.1048; found: 380.1053.

(4^1*S,8b*R**,9*R**)-12-bromo-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cycloheptа[1,2,3-*hi*]indolizin-9-yl acetate (7ab)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7ab** in 80% yield (67.9 mg, 0.2 mmol scale) as a light-green solid, mp 130–132 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.40–7.33 (m, 3H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.13 (td, *J* = 7.4, 0.9 Hz, 1H), 6.42 (s, 1H), 5.84 (s, 1H), 4.94 (d, *J* = 8.6 Hz, 1H), 3.70 (d, *J* = 8.7 Hz, 1H), 2.87–2.78 (m, 2H), 2.72–2.68 (m, 1H), 2.64–2.58 (m, 1H), 1.64 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.8, 168.3, 141.4, 136.2, 135.9, 135.0, 134.3, 132.3, 131.4, 130.3, 128.8, 124.9, 124.1, 124.0, 123.0, 117.6, 78.4, 77.3, 62.7, 49.6, 33.7, 32.8, 20.4; **HRMS (ESI)** calcd for $C_{22}H_{19}BrNO_3$ $[M+H]^+$: 424.0543; found: 424.0547.

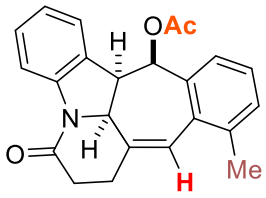
(4^1*S,8b*R**,9*R**)-12-methyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cycloheptа[1,2,3-*hi*]indolizin-9-yl acetate (7ac)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7ac** in 55% yield (39.5 mg) as a colorless solid, mp 84–86 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)**

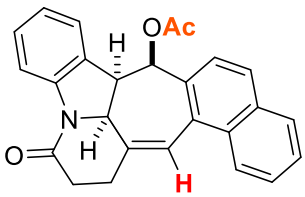
δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.30–7.28 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.07 (s, 1H), 7.06 (d, *J* = 6.9 Hz, 1H), 6.48 (s, 1H), 5.90 (s, 1H), 4.95 (d, *J* = 8.6 Hz, 1H), 3.72 (d, *J* = 8.6 Hz, 1H), 2.88–2.78 (m, 2H), 2.71–2.68 (m, 1H), 2.65–2.58 (m, 1H), 2.35 (s, 3H), 1.64 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.8, 168.3, 141.5, 138.9, 134.0, 133.9, 133.3, 132.4, 131.7, 130.6, 128.6, 128.1, 125.5, 124.7, 124.2, 117.5, 78.9, 62.8, 49.8, 33.8, 32.9, 21.0, 20.5; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1599.

(4^1*S,8b*R**,9*R**)-13-methyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7ad)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7ad** in 61% yield (43.9 mg) as a pale-yellow solid, mp 169–171 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32–7.23 (m, 2H), 7.22–7.09 (m, 3H), 6.61 (s, 1H), 5.90 (s, 1H), 4.98 (d, *J* = 8.9 Hz, 1H), 3.76 (d, *J* = 9.0 Hz, 1H), 2.95–2.72 (m, 3H), 2.67–2.55 (m, 1H), 2.40 (s, 3H), 1.67 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.7, 168.7, 141.3, 137.7, 136.5, 134.4, 132.3, 131.6, 131.1, 128.4, 128.3, 127.3, 124.5, 124.0, 121.8, 117.4, 79.1, 62.5, 50.6, 33.6, 32.8, 20.5, 20.4; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1597.

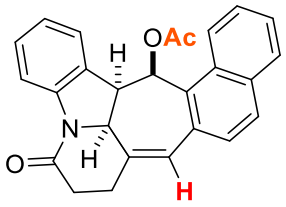
(4^1*S,8b*R**,9*R**)-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]naphtho[2',1':5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7ae)**



Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7ae** in 38% yield (30.1 mg) as a yellow solid, mp 114–116 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)**

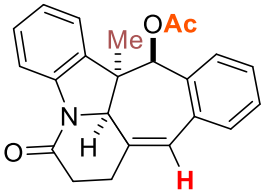
δ 8.21 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.61–7.49 (m, 3H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24 (s, 1H), 7.16 (td, *J* = 7.4, 0.7 Hz, 1H), 6.01 (d, *J* = 0.6 Hz, 1H), 5.07 (d, *J* = 9.2 Hz, 1H), 3.90 (d, *J* = 9.3 Hz, 1H), 3.05–3.00 (m, 1H), 2.95–2.91 (m, 1H), 2.87–2.82 (m, 1H), 2.72–2.66 (m, 1H), 1.71 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 170.0, 169.1, 141.5, 136.6, 134.6, 133.6, 132.2, 131.6, 129.7, 128.7, 128.6, 128.2, 128.1, 126.7, 126.3, 124.6, 124.0, 123.7, 120.4, 117.4, 79.2, 62.3, 51.8, 33.6, 32.8, 20.5; **HRMS (ESI)** calcd for $C_{26}H_{22}NO_3$ $[M+H]^+$: 396.1594; found: 396.1596.

(4^1*S,8b*R**,9*R**)-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]naphtho[1',2':5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7af)**



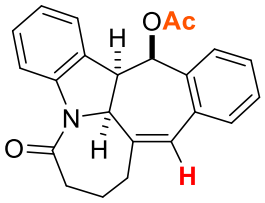
Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 3:1) to give **7af** in 35% yield (27.7 mg) as a yellow solid, mp 184–186 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.54 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.56–7.46 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.11 (s, 1H), 6.66 (s, 1H), 5.01 (d, *J* = 8.7 Hz, 1H), 3.76 (d, *J* = 8.9 Hz, 1H), 2.99–2.61 (m, 4H), 1.69 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.9, 168.4, 141.4, 135.2, 132.8, 132.4, 132.1, 131.7, 131.0, 129.3, 129.1, 128.7, 128.6, 127.3, 126.0, 126.0, 124.8, 124.2, 122.9, 117.5, 71.8, 62.5, 50.3, 33.7, 32.5, 20.3; **HRMS (ESI)** calcd for $C_{26}H_{22}NO_3$ $[M+H]^+$: 396.1594; found: 396.1595.

(4^1*R,8b*R**,9*S**)-8b-methyl-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-9-yl acetate (7ag)**



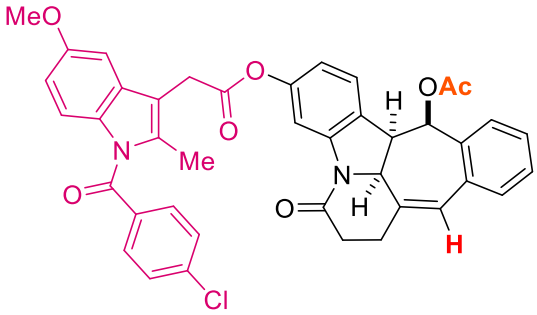
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 4:1) to give **7ag** in 47% yield (33.8 mg) as a pale-yellow solid, mp 181–183 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.39–7.36 (m, 1H), 7.36–7.33 (m, 1H), 7.33–7.28 (m, 2H), 7.28–7.23 (m, 3H), 7.17 (td, *J* = 7.5, 0.9 Hz, 1H), 6.53 (s, 1H), 5.74 (s, 1H), 4.56 (s, 1H), 2.90–2.79 (m, 2H), 2.72–2.58 (m, 2H), 1.59 (s, 3H), 1.16 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.5, 167.9, 141.6, 136.6, 134.3, 133.8, 133.2, 131.8, 131.7, 128.9, 128.4, 127.5, 125.4, 124.9, 122.1, 117.3, 83.0, 69.7, 50.0, 34.1, 33.6, 23.0, 20.3; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1591.

(4a^1*S,8b*R**,9*R**)-4-oxo-1,3,4,4a^1,8b,9-hexahydro-2*H*-4a-azabenzo[*b*]indeno [1,2,3-*ef*]heptalen-9-yl acetate (7ah)**



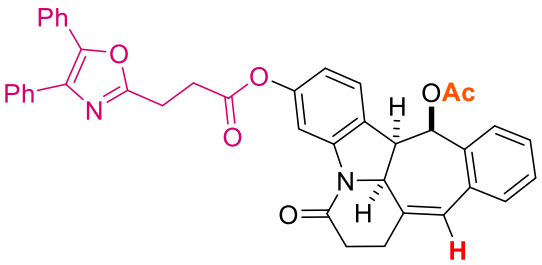
Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 2:1) to give **7ah** in 54% yield (38.8 mg) as a colorless solid, mp 241–243 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.34–7.30 (m, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.09–7.03 (m, 2H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.97–6.93 (m, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 1.3 Hz, 1H), 6.40 (s, 1H), 5.22 (d, *J* = 11.7 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 2.89–2.80 (m, 1H), 2.76–2.65 (m, 2H), 2.57 (td, *J* = 12.6, 4.1 Hz, 1H), 2.34 (s, 3H), 2.18–2.09 (m, 1H), 1.86 (td, *J* = 15.1, 2.5 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.9, 169.8, 143.2, 140.4, 134.7, 132.0, 129.3, 129.2, 128.6, 127.7, 127.3, 126.7, 125.5, 124.6, 123.5, 116.9, 71.9, 63.1, 53.9, 42.8, 38.9, 25.7, 21.3; **HRMS (ESI)** calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594; found: 360.1600.

(4a^1*S,8b*R**,9*R**)-9-acetoxy-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6] cyclohepta[1,2,3-*hi*]indolizin-7-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl -1*H*-indol-3-yl)acetate (7al)**



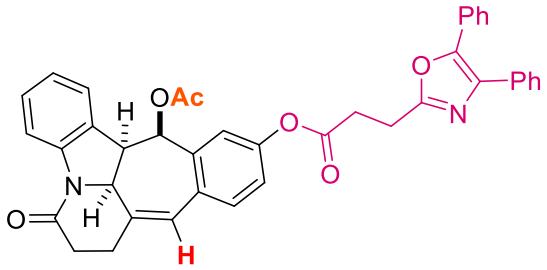
Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 3:1) to give **7al** in 75% yield (105.2 mg) as a light-green solid, mp 153–155 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.7 Hz, 1H), 7.71–7.66 (m, 2H), 7.50–7.45 (m, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.25–7.22 (m, 2H), 7.17 (d, *J* = 2.2 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.99 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.51 (s, 1H), 5.86 (s, 1H), 4.96 (d, J = 8.5 Hz, 1H), 3.91 (s, 2H), 3.85 (s, 3H), 3.70 (d, *J* = 8.6 Hz, 1H), 2.88–2.78 (m, 2H), 2.73–2.54 (m, 2H), 2.47 (s, 3H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.6, 169.4, 168.2, 168.1, 156.1, 147.3, 139.3, 139.2, 136.2, 135.7, 134.0, 133.8, 133.7, 133.0, 131.6, 131.1, 130.8, 130.5, 130.4, 129.1, 127.5, 125.5, 121.3, 118.0, 117.5, 115.0, 111.9, 111.8, 101.1, 78.8, 63.0, 55.7, 50.0, 33.6, 32.7, 30.4, 20.4, 13.4; **HRMS (ESI)** calcd for $C_{41}H_{34}ClN_2O_7$ $[M+H]^+$: 701.2049; found: 701.2038.

(4^1*S,8b*R**,9*R**)-9-acetoxy-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyc-lohepta[1,2,3-*hi*]indolizin-7-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (7am)**



Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 3:1) to give **7am** in 46% yield (58.6 mg) as a colorless solid, mp 124–126 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.40–7.29 (m, 8H), 7.27–7.22 (m, 2H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.51 (s, 1H), 5.84 (s, 1H), 4.96 (d, *J* = 8.5 Hz, 1H), 3.67 (d, *J* = 8.6 Hz, 1H), 3.31 (t, *J* = 7.3 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.88–2.79 (m, 2H), 2.74–2.66 (m, 1H), 2.65–2.57 (m, 1H), 1.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.8, 169.6, 168.1, 161.4, 147.2, 145.5, 139.3, 135.8, 135.1, 134.0, 133.7, 133.0, 132.4, 131.6, 130.6, 129.1, 128.9, 128.6, 128.5, 128.5, 128.0, 127.8, 127.5, 126.5, 125.5, 121.5, 118.1, 117.6, 78.9, 63.0, 49.6, 33.7, 32.8, 31.2, 23.5, 20.4; **HRMS (ESI)** calcd for $C_{40}H_{33}N_2O_6$ $[M+H]^+$: 637.2333; found: 637.2327.

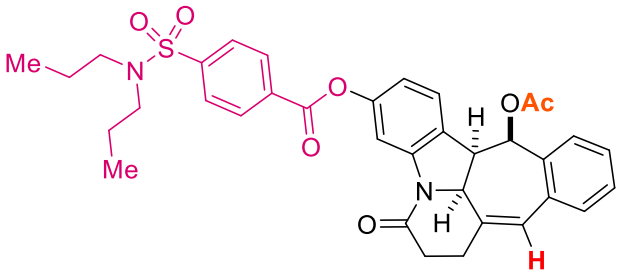
(4^1*S,8b*R**,9*R**)-9-acetoxy-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-11-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (7an)**



Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 2:1) to give **7an** in 65% yield (82.8 mg) as a pale-yellow solid, mp 103–105 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.70–7.65 (m, 2H), 7.62–7.58 (m, 2H), 7.40–7.35 (m, 4H), 7.35–7.28 (m, 5H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.14 (td, *J* = 7.5, 0.7 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.49 (s, 1H), 5.83 (s, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 3.74 (d, *J* = 8.7 Hz, 1H), 3.30 (t, *J* = 7.2 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.87–2.77 (m, 2H), 2.72–2.56 (m, 2H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.5, 169.5, 168.2, 161.2, 149.3, 145.5, 141.4, 137.3, 135.1, 134.0, 132.6, 132.3, 132.0, 131.4, 128.8, 128.6, 128.5, 128.5, 128.0, 127.8, 126.5, 124.7, 124.4, 124.1, 123.6,

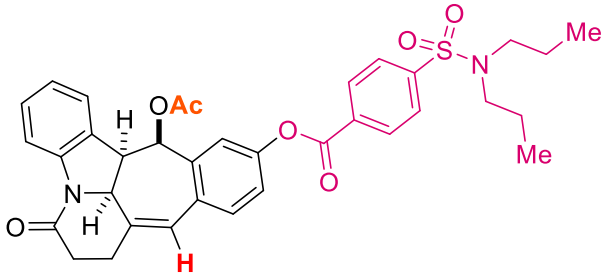
121.9, 117.5, 78.4, 62.6, 49.3, 33.7, 32.7, 31.1, 23.3, 20.3; **HRMS (ESI)** calcd for $C_{40}H_{33}N_2O_6$ $[M+H]^+$: 637.2333; found: 637.2343.

(4^1*S,8b*R**,9*R**)-9-acetoxy-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-7-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (7ao)**



Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 3:1) to give **7ao** in 46% yield (57.8 mg) as a pale-yellow solid, mp 114–116 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.32 (d, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.38–7.34 (m, 2H), 7.33–7.31 (m, 1H), 7.27–7.22 (m, 2H), 7.15 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.53 (s, 1H), 5.92 (s, 1H), 5.02 (d, *J* = 8.5 Hz, 1H), 3.77 (d, *J* = 8.6 Hz, 1H), 3.14 (t, *J* = 7.6 Hz, 4H), 2.89–2.82 (m, 2H), 2.75–2.69 (m, 1H), 2.67–2.58 (m, 1H), 1.69 (s, 3H), 1.61–1.52 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.3, 163.9, 147.2, 144.9, 139.5, 135.7, 134.1, 133.7, 133.2, 132.7, 131.7, 130.7, 130.5, 129.1, 127.6, 127.1, 125.6, 121.5, 118.2, 117.6, 78.8, 63.1, 49.8, 49.7, 33.7, 32.8, 21.9, 20.4, 11.1; **HRMS (ESI)** calcd for $C_{35}H_{37}N_2O_7S$ $[M+H]^+$: 629.2316; found: 629.2317.

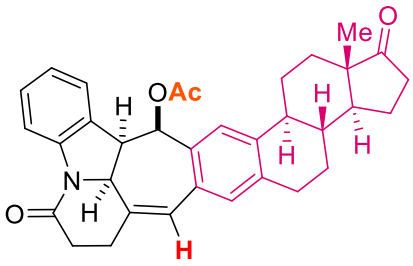
(4^1*S,8b*R**,9*R**)-9-acetoxy-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-11-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (7ap)**



Column chromatography (eluent: petroleum ether/EtOAc = 5:1 to 2:1) to give **7ap** in 70% yield (88.0 mg) as a light-green solid, mp 106–108 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.29 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H),

7.36 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.53 (s, 1H), 5.85 (s, 1H), 4.97 (d, *J* = 8.5 Hz, 1H), 3.79 (d, *J* = 8.6 Hz, 1H), 3.13 (t, *J* = 7.6 Hz, 4H), 2.91–2.80 (m, 2H), 2.74–2.57 (m, 2H), 1.66 (s, 3H), 1.61–1.50 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.2, 163.6, 149.2, 145.0, 141.4, 137.4, 134.4, 132.8, 132.4, 132.3, 131.3, 130.7, 128.6, 127.1, 124.7, 124.3, 124.0, 123.6, 121.9, 117.5, 78.5, 62.6, 49.8, 49.3, 33.7, 32.7, 21.8, 20.3, 11.1; **HRMS (ESI)** calcd for $C_{35}H_{37}N_2O_7S$ $[M+H]^+$: 629.2316; found: 629.2135.

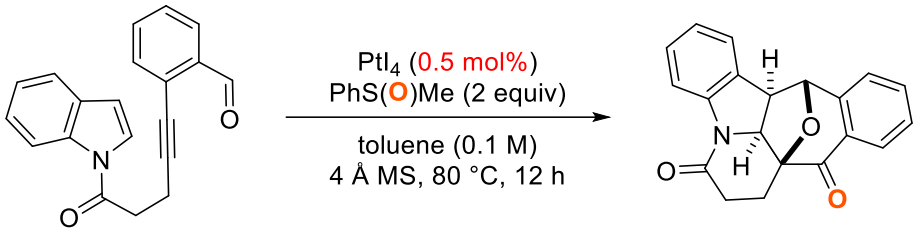
(3a*R*,3b*S*,7a^1*S,15b*R**,16*R**,17b*R*,19a*R*)-19a-methyl-1,10-dioxo-2,3,3a,3b,4,5,7a^1,8,9,10,15b,16,17b,18,19,19a-hexadecahydro-1*H*-benzo[*b*]cyclopenta[7',8']phenanthro[3',2':5,6]cyclohepta[1,2,3-*hi*]indolizin-16-yl acetate (7aq)**



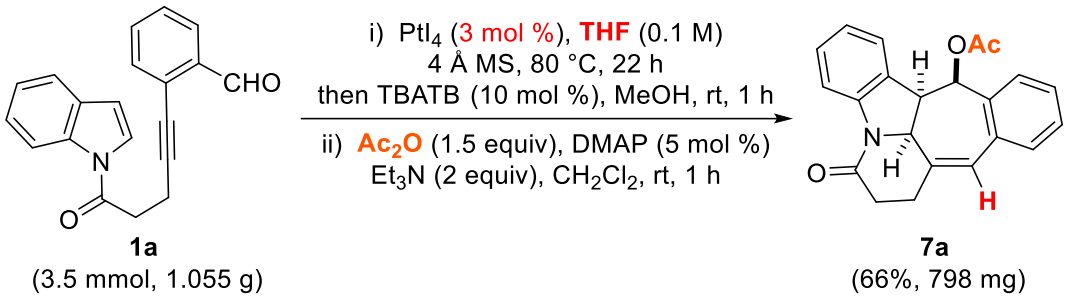
Column chromatography (eluent: petroleum ether/EtOAc = 6:1 to 3:1) to give **7aq** as a mixture of inseparable diastereoisomers in a ratio of 1:1 in 50% yield (52.2 mg); pale-yellow solid, mp 221–223 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.33–7.29 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.99 (s, 1H), 6.46 (s, 1H), 5.89 (d, *J* = 9.4 Hz, 1H), 4.93 (d, *J* = 8.5 Hz, 1H), 3.73 (d, *J* = 8.6 Hz, 1H), 2.97–2.88 (m, 2H), 2.87–2.78 (m, 2H), 2.73–2.56 (m, 2H), 2.55–2.46 (m, 2H), 2.36–2.11 (m, 2H), 2.10–1.96 (m, 3H), 1.70–1.40 (m, 9H), 0.92 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 220.6, 220.5, 169.8, 169.7, 168.3, 168.2, 141.5, 141.5, 139.3, 139.1, 137.3, 137.3, 133.6, 133.5, 133.4, 133.3, 132.3, 132.2, 131.7, 134.6, 128.6, 127.9, 127.7, 125.1, 15.0, 124.7, 124.1, 117.5, 79.2, 79.2, 62.8, 62.8, 50.4, 50.3, 49.8, 47.9, 44.2, 44.2, 38.1, 37.9, 35.8, 35.7, 33.9, 32.8, 32.8, 31.5, 31.4, 29.0, 28.9, 26.3, 26.2, 25.8, 25.5, 21.5, 20.5, 20.4, 13.8, 13.8; **HRMS (ESI)** calcd for $C_{34}H_{36}NO_4$ $[M+H]^+$: 522.2639; found: 522.2646.

6. Gram-Scale experiments and selected transformations

*6.1. Gram-Scale Synthesis of **3a** and **7a***



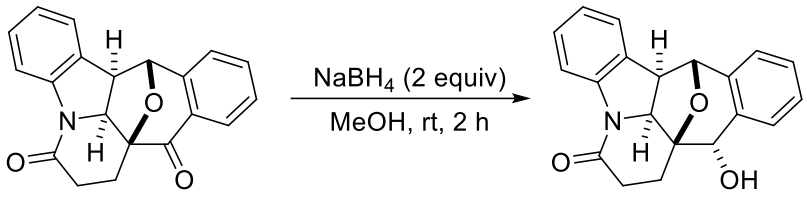
To a dried round-bottom flask equipped with a stirring bar were charged with **1a** (1.055 g, 3.5 mmol), 4Å MS (3.5 g), phenylmethylsulfoxide (PMSO) (981 mg, 7 mmol) and PtI_4 (12.3 mg, 17.5 μmol), anhydrous toluene (35 mL) was added under an argon atmosphere. The reaction was stirred at 80 ºC for 12 h. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature, filtered through a pad of Celite and rinsed with EtOAc. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to afford the product **3a** (1.077 g, 97% yield).



To a dried 100 mL round-bottom flask equipped with a magnetic stir bar were added **1a** (1.055 g, 3.5 mmol), 4Å MS (3.5 g), and PtI_4 (73.8 mg, 105 μmol). The reaction mixture was then dissolved in anhydrous THF (35 mL) under argon atmosphere and stirred at 80 ºC for 22 h. Upon completion, the reaction mixture was cooled to room temperature, tetrabutylammonium tribromide (TBATB, 168.8 mg, 0.35 mmol) and MeOH (35 mL) were then 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 $NaHCO_3$ (30 mL) and extracted with EtOAc (30 mL × 3). The combined organic phases are washed with brine, and dried over $MgSO_4$, and concentrated under reduced pressure to afford the crude alcohol product. The crude alcohol was dissolved in anhydrous CH_2Cl_2 (30 mL), then 4-dimethylaminopyridine (DMAP) (0.175 mmol, 5 mol %), trimethylamine (Et_3N) (7 mmol, 2 equiv), acetic anhydride (5.25 mmol, 1.5 equiv) were added sequentially. The resulting reaction mixture was stirred at room temperature for 1 h (monitored by TLC), the solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 25:1 to 3:1) to afford the product **7a** (798 mg, 66% yield).

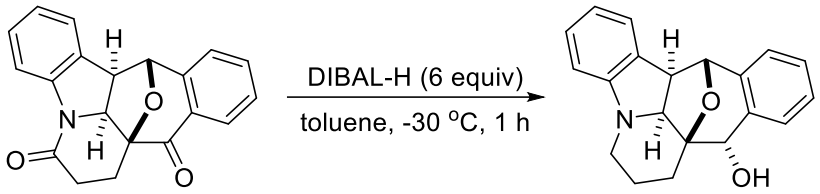
6.2. *Synthetic applications*



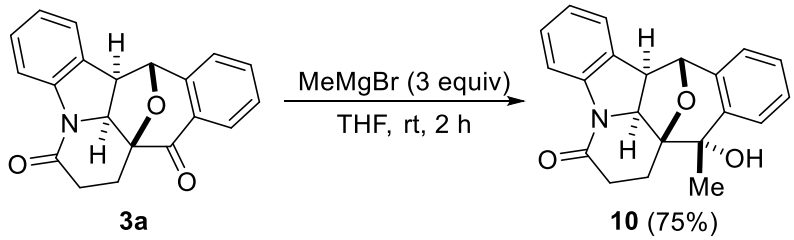
3a **8** (99%)

To a solution of **3a** (63.5 mg, 0.2 mmol) in MeOH (4 mL) at 0 ℃ was added $NaBH_4$ (15.1 mg, 0.4 mmol), the resulting mixture was stirred at room temperature for 2 h until full consumption of the starting material (as indicated by TLC). Upon completion, the reaction mixture was quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (5 mL × 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 = 10:1 to 2:1) to afford the product **8** in 99% yield (63.2 mg) as a colorless solid, 260–262 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.28–7.24 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.09 (td, *J* = 7.4, 0.8 Hz, 1H), 5.22 (d, *J* = 6.5 Hz, 1H), 5.16 (d, *J* = 8.4 Hz, 1H), 5.03 (s, 1H), 3.86 (d, *J* = 8.4 Hz, 1H), 2.77–2.69 (m, 2H), 2.56–2.47 (m, 2H), 2.15 (td, *J* = 14.7, 3.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.0, 143.5, 140.3, 134.4, 130.8, 128.7,

128.4, 128.2, 126.9, 124.3, 124.0, 122.6, 115.7, 87.1, 85.7, 75.3, 65.0, 56.4, 33.9, 33.1; **HRMS (ESI)** calcd for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1281; found: 320.1282.

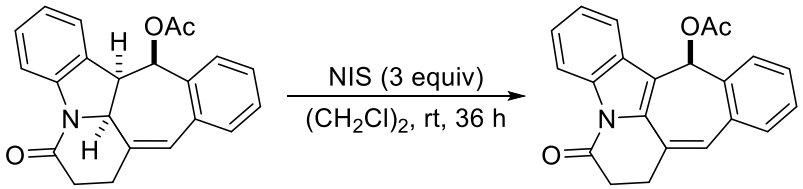


To a solution of **3a** (63.5 mg, 0.2 mmol) in toluene (4 mL) at -30 °C was added DIBAL-H (1.0 M in hexane, 1.2 mL) dropwise and the reaction mixture was stirred -30 ℃ for 2 h. The reaction mixture was quenched carefully with hydrochloric acid (1 N, 5 mL) and ethyl acetate and vigorously stirred for 1 h, extracted with EtOAc (8 mL × 2) and the combined organic layers were washed with brine, dried over MgSO4. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 9:1 to 2:1) to furnish the desired product **9** in 45% yield (27.2 mg) as a colorless solid, 167–169 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.28–7.23 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 4.85 (s, 1H), 4.74 (s, 1H), 4.63 (d, *J* = 8.3 Hz, 1H), 3.86 (d, *J* = 8.3 Hz, 1H), 3.69 (d, *J* = 14.0 Hz, 1H), 3.03–2.96 (m, 1H), 2.26 (td, *J* = 13.9, 4.8 Hz, 1H), 2.08 (d, *J* = 14.5 Hz, 1H), 1.82–1.73 (m, 1H), 1.51–1.45 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 151.9, 140.6, 134.8, 130.9, 128.5, 128.1, 127.8, 127.3, 123.9, 123.0, 117.2, 106.8, 83.8, 83.0, 74.1, 62.4, 57.7, 437, 30.7, 18.3; **HRMS (ESI)** calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489; found: 306.1492.



To a solution of **3a** (63.5 mg, 0.2 mmol) in THF (2 mL) at 0 °C was added MeMgBr (1.0 M in THF, 0.6 mL) and the resulting mixture was stirred at room temperature for

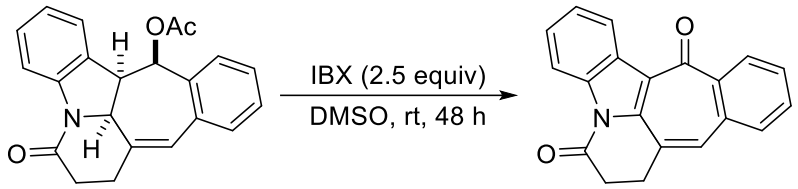
2 h. The reaction mixture was quenched by with saturated NH_4Cl (2 mL), extracted with EtOAc (6 mL × 2). The combined organic layers were washed are washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 9:1 to 3:1) to provide the product **10** in 75% yield (74.7 mg) as a colorless solid, 230–232 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.30–7.22 (m, 3H), 7.07 (t, *J* = 6.2 Hz, 2H), 5.16 (d, *J* = 8.6 Hz, 1H), 5.07 (s, 1H), 3.77 (d, *J* = 8.5 Hz, 1H), 2.82 (dt, *J* = 14.6, 3.4 Hz, 1H), 2.69 (td, *J* = 15.0, 4.1 Hz, 1H), 2.56 (s, 1H), 2.50 (dt, *J* = 14.9, 2.8 Hz, 1H), 1.75 (td, *J* = 14.8, 3.0 Hz, 1H), 1.72 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 172.0, 143.6, 139.7, 139.1, 130.3, 128.6, 128.4, 128.0, 126.2, 124.1, 123.9, 121.8, 115.4, 89.6, 85.7, 75.2, 66.6, 57.7, 34.3, 31.2, 28.1; **HRMS (ESI)** calcd for $C_{21}H_{20}NO_3$ $[M+H]^+$: 334.1438; found: 334.1440.



7a **11** (48%)

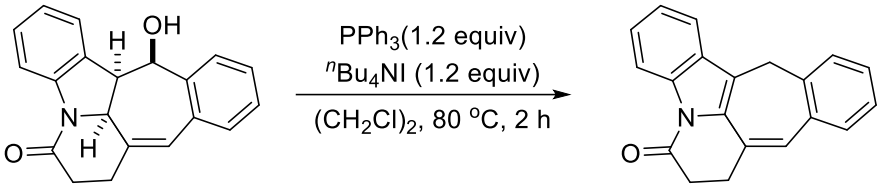
To a solution of **7a** (69.1 mg, 0.2 mmol) in $(CH_2Cl)_2$ (2 mL) at room temperature was added *N*-iodosuccinimide (NIS, 135 mg, 0.6 mmol) under an argon atmosphere. The resulting mixture was stirred at room temperature for 36 h until full consumption of the starting material (as indicated by TLC). The reaction mixture was evaporated, and directly subjected to silica gel column chromatography (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to afford the desired product **11** (32.8 mg, 48% yield) as a pale-yellow solid, mp 103–105 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.56 (s, 1H), 7.43–7.33 (m, 5H), 7.33 (s, 1H), 6.94 (s, 1H), 3.37–2.82 (m, 4H), 2.53 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.0, 169.0, 136.1, 135.9, 135.0, 132.8, 132.2, 132.1, 130.2, 129.6, 129.0, 128.5, 126.2, 126.1, 124.6, 118.3, 116.6,

113.0, 50.6, 34.0, 30.9, 28.0; **HRMS (ESI)** calcd for $C_{22}H_{17}NNaO_3$ $[M+Na]^+$: 366.1101; found: 366.1100.



7a **12** (81%)

To a solution of **7a** (69.1 mg, 0.2 mmol) in DMSO (2 mL) at room temperature was added 2-iodoxybenzoic acid (IBX, 140 mg, 0.5 mmol), the resulting mixture was stirred at room temperature for 48 h. The reaction mixture was quenched with brine and extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were 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 = 10:1 to 4:1) to afford the desired product **12** (48.5 mg, 81% yield) as a yellow solid, mp 191–193 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.89 (d, *J* = 7.5 Hz, 1H), 8.79 (d, *J* = 7.5 Hz, 1H), 8.63 (d, *J* = 7.7 Hz, 1H), 7.72 (s, 3H), 7.60–7.48 (m, 2H), 7.36 (s, 1H), 3.29 (t, *J* = 6.9 Hz, 2H), 3.09 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 178.0, 165.3, 135.7, 132.5, 130.2, 129.9, 129.5, 128.7, 127.9, 125.5, 125.3, 123.2, 123.0, 122.7, 120.8, 118.9, 116.2, 111.1, 28.0, 24.9; **HRMS (ESI)** calcd for $C_{20}H_{14}NO_2$ [M+H]+: 300.1019; found: 300.1030.



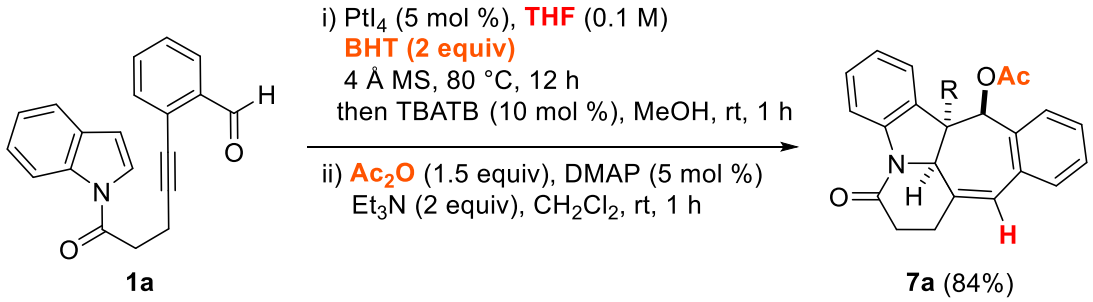
6a **13** (72%)

Following slightly modified literature procedure, to an oven-dried round-bottom flask equipped with a stirring bar were added **6a** (69.1 mg, 0.2 mmol), triphenylphosphine (62.9 mg, 0.24 mmol), tetrabutylammonium iodide (69.1 mg, 0.2 mmol) and anhydrous $(CH_2Cl)_2$ (1 mL) under an argon atmosphere.[S4] The mixture was allowed to stir at 60 °C for 2 h. After the mixture was cooled to room temperature and directly subjected to silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1 to 15:1) to

afford the pure product **13** in 72% yield (41.1 mg) as a colorless solid, mp 159–161 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48–8.42 (m, 1H), 7.75–7.67 (m, 1H), 7.37–7.31 (m, 5H), 7.28–7.24 (m, 1H), 6.95 (s, 1H), 3.88 (s, 2H), 3.04–2.97 (m, 2H), 2.97–2.90 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.4, 135.7, 135.6, 135.1, 132.5, 129.8, 129.2, 129.0, 128.8, 128.7, 127.4, 126.3, 125.5, 124.1, 118.4, 116.9, 116.6, 34.5, 30.9, 30.3; **HRMS (ESI)**calcd for $C_{20}H_{16}NO$ $[M+H]^+$: 286.1226; found: 286.1228.

7. Control experiments with 1a and 4a

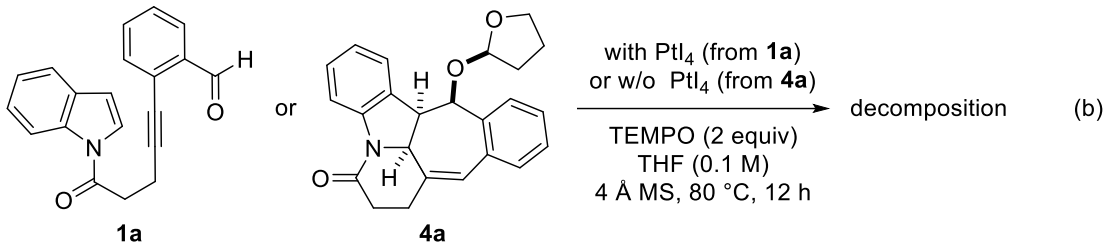
7.1. Control experiment with 1a to probe the reaction proceeded involving a H• atom or hydride shift pathway



To a dried 10 mL round-bottom flask equipped with a magnetic stir bar were added **1a** (0.2 mmol, 1.0 equiv.), 4Å MS (200 mg), radical scavenger (**BHT**, 0.4 mmol, 2.0 equiv) and PtI_4 (7.0 mg, 0.01 mmol) under argon atmosphere. Then THF (2 mL) was added and the reaction mixture stirred at 80 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature, TBATB (9.6 mg, 0.02mmol) and MeOH (2 mL) were then 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 × 3). The combined organic phases are washed with brine, and dried over $MgSO_4$, and concentrated under reduced pressure to afford the crude alcohol product. The crude alcohol was dissolved in anhydrous CH_2Cl_2 (4 mL), then 4-dimethylaminopyridine (DMAP) (0.01 mmol, 5 mol %), trimethylamine (Et_3N) (0.4 mmol, 2 equiv), acetic anhydride (0.3 mmol, 1.5 equiv) were added sequentially. The resulting reaction

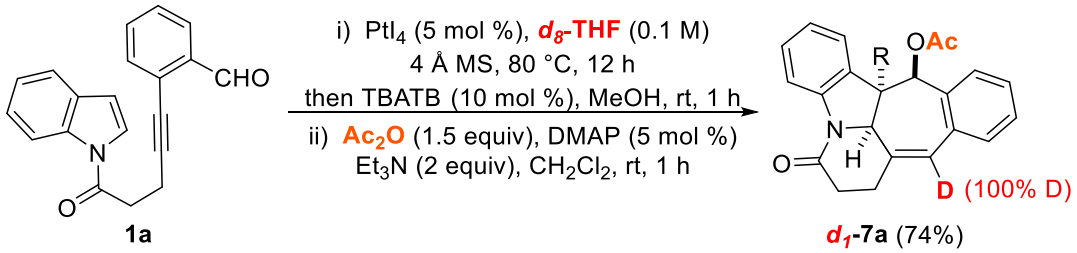
mixture was stirred at room temperature for 1 h (monitored by TLC), the solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 25:1 to 3:1) to provide 7a in 84% yield (51.3 mg).

*7.2. Control experiment with **1a** and **4a** in the presence of TEMPO*



In a dried 10 mL round-bottom flask was charged with **1a** or **4a** (0.1 mmol), 4Å MS (100 mg), PtI_4 (5 mol%， in the case of **4a**, without PtI_4) and TEMPO (0.2 mmol, 2.0 equiv). Then anhydrous THF (1 mL) was added under argon atmosphere and the reaction was stirred at 80 °C for 12 h. *Decomposition products were observed based on TLC analysis as well as crude ^1H NMR analysis for both conditions. These results hinted at (1) the instability of the intermediacy of the THF-incorporated addition adduct and (2) a pathway involving H• atom transfer from THF was less likely to be operative.*

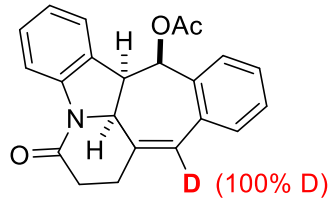
7.3 Deuterium labeling experiment



To a dried 10 mL round-bottom flask equipped with a magnetic stir bar were added **1a** (0.2 mmol, 1.0 equiv.), 4Å MS (200 mg) and PtI_4 (7.0 mg, 0.01 mmol) under argon atmosphere. Then d_8-THF (2 mL) was added and the reaction mixture stirred at 80 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature, tetrabutylammonium tribromide (TBATB) (9.6 mg, 0.02mmol) and MeOH (2 mL) were then added. The resulting reaction mixture was stirred at room temperature for 1

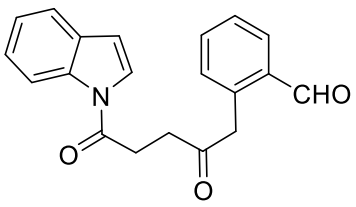
h (monitored by TLC), filtered through a pad of Celite and rinsed with EtOAc. The filtrate was washed with saturated $NaHCO_3$ (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phases are washed with brine, and dried over $MgSO_4$, and concentrated under reduced pressure to afford the crude alcohol product. The crude alcohol was dissolved in anhydrous CH_2Cl_2 (4 mL), then 4-dimethylaminopyridine (DMAP) (0.01 mmol, 5 mol %), trimethylamine (Et_3N) (0.4 mmol, 2 equiv), acetic anhydride (0.3 mmol, 1.5 equiv) were added sequentially. The resulting reaction mixture was stirred at room temperature for 1 h (monitored by TLC), the solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 25:1 to 3:1) to afford the desired product ***d*$_1$-7** in 74% yield (51.3 mg).

((4^1*S,8b*R**,9*R**)-3-oxo-1,2,3,4^1,8b,9-hexahydrobenzo[*b*]benzo[5,6]cyclohepta [1,2,3-*hi*]indolizin-9-yl acetate (*d*$_1$-7a)**



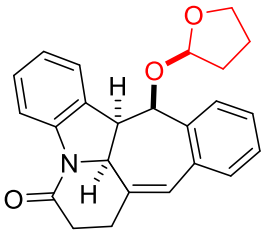
Pale-yellow solid, mp 94–96 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 6.2 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.25–7.23 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.92 (s, 1H), 4.93 (d, *J* = 8.6 Hz, 1H), 3.72 (d, *J* = 8.6 Hz, 1H), 2.85–2.80 (m, 2H), 2.74–2.58 (m, 2H), 1.66 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.7, 168.3, 141.4, 136.0, 134.1, 134.0, 131.6, 131.6, 130.5, 129.0, 128.6, 127.4, 125.3, 124.7, 124.1, 117.5, 79.1, 62.7, 49.7, 33.8, 32.8, 20.4; **HRMS (ESI)** calcd for $C_{22}H_{19}DNO_3$ $[M+H]^+$: 347.1500; found: 347.1497.

2-(5-(1*H*-inden-1-yl)-2,5-dioxopentyl)benzaldehyde (2a)



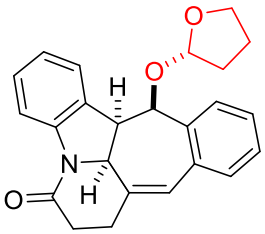
Yellow solid; mp 97–99 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.01 (s, 1H), 8.43 (d, *J* = 8.2 Hz, 1H), 7.83–7.79 (m, 1H), 7.59–7.53 (m, 2H), 7.52–7.47 (m, 2H), 7.36–7.31 (m, 1H), 7.30–7.24 (m, 2H), 6.62 (d, *J* = 3.7 Hz, 1H), 4.25 (s, 2H), 3.25 (t, *J* = 6.3 Hz, 2H), 3.17 (t, *J* = 6.3 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.4, 193.5, 170.4, 135.6, 135.5, 135.3, 134.1, 133.8, 132.8, 130.3, 127.7, 125.0, 124.5, 123.6, 120.8, 116.5, 109.2, 47.7, 36.5, 29.7; **HRMS (ESI)**calcd for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1281; found: 320.1284.

(4^1*S,8b*R**,9*R**)-9-(((*R**)-tetrahydrofuran-2-yl)oxy)-1,4^1,8b,9-tetrahydrobenzo [*b*]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-3(2*H*)-one (4a)**



Colorless solid, mp 154–156 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.36–7.18 (m, 5H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.46 (s, 1H), 4.87 (d, *J* = 8.4 Hz, 1H), 4.74 (s, 1H), 4.63 (s, 1H), 3.60 (d, *J* = 8.5 Hz, 1H), 3.34–3.32 (m, 1H), 2.85–2.72 (m, 2H), 2.68–2.41 (m, 3H), 1.46 (s, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.3, 142.2, 137.7, 134.6, 134.5, 133.8, 131.8, 130.2, 128.5, 127.9, 126.9, 124.9, 124.2, 123.9, 117.4, 99.3, 79.8, 66.1, 62.9, 50.4, 33.9, 33.0, 32.3, 22.4; **HRMS (ESI)** calcd for $C_{24}H_{24}NO_3$ $[M+H]^+$: 374.1751; found: 374.1757.

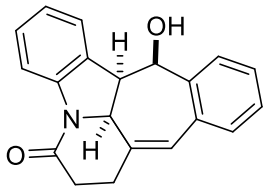
(4^1*S,8b*R**,9*R**)-9-(((*S**)-tetrahydrofuran-2-yl)oxy)-1,4^1,8b,9-tetrahydrobenzo [b]benzo[5,6]cyclohepta[1,2,3-*hi*]indolizin-3(*2H*)-one (5a)**



Colorless solid, mp 168–170 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.35–7.19 (m, 5H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.49 (s, 1H),

4.87 (d, *J* = 8.4 Hz, 1H), 4.60 (s, 1H), 4.47 (s, 1H), 3.58 (d, *J* = 8.4 Hz, 1H), 3.45 (q, *J* = 7.8 Hz, 1H), 3.17 (q, 8.1 Hz, 1H), 2.85–2.75 (m, 2H), 2.69–2.51 (m, 2H), 1.66–1.55 (m, 1H), 1.55–1.46 (m, 1H), 1.46–1.37 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 168.5, 142.1, 140.2, 134.1, 133.9, 133.5, 131.2, 128.8, 128.2, 127.9, 127.1, 125.1, 124.4, 123.6, 117.6, 104.9, 84.4, 66.4, 62.9, 51.0, 33.8, 32.8, 32.2, 22.8; **HRMS (ESI)** calcd for $C_{24}H_{24}NO_3$ $[M+H]^+$: 374.1751; found: 374.1756.

(4^1*S,8b*R**,9*R**)-9-hydroxy-1,4^1,8b,9-tetrahydrobenzo[*b*]benzo[5,6]cyclohepta [1,2,3-*hi*]indolizin-3(2*H*)-one (6a)**



Yellow solid, mp 150–152 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 7.6 Hz, 1H), 7.38–7.15 (m, 7H), 6.54 (s, 1H), 4.94 (d, *J* = 8.4 Hz, 1H), 4.83 (s, 1H), 3.74 (d, *J* = 8.7 Hz, 1H), 2.82–2.61 (m, 4H), 2.12 (s, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 168.7, 141.9, 139.8, 134.8, 133.5, 132.4, 131.7, 129.1, 128.6, 128.5, 127.6, 125.3, 124.5, 123.8, 117.3, 79.8, 62.3, 51.9, 33.5, 32.5; **HRMS (ESI)**calcd for $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1332; found: 304.1337.

8. ^{1}H, ^{13}C and ^{19}F NMR Spectra

Figure S1 ^{1}H NMR (600 MHz, $CDCl_3$) of **1a**

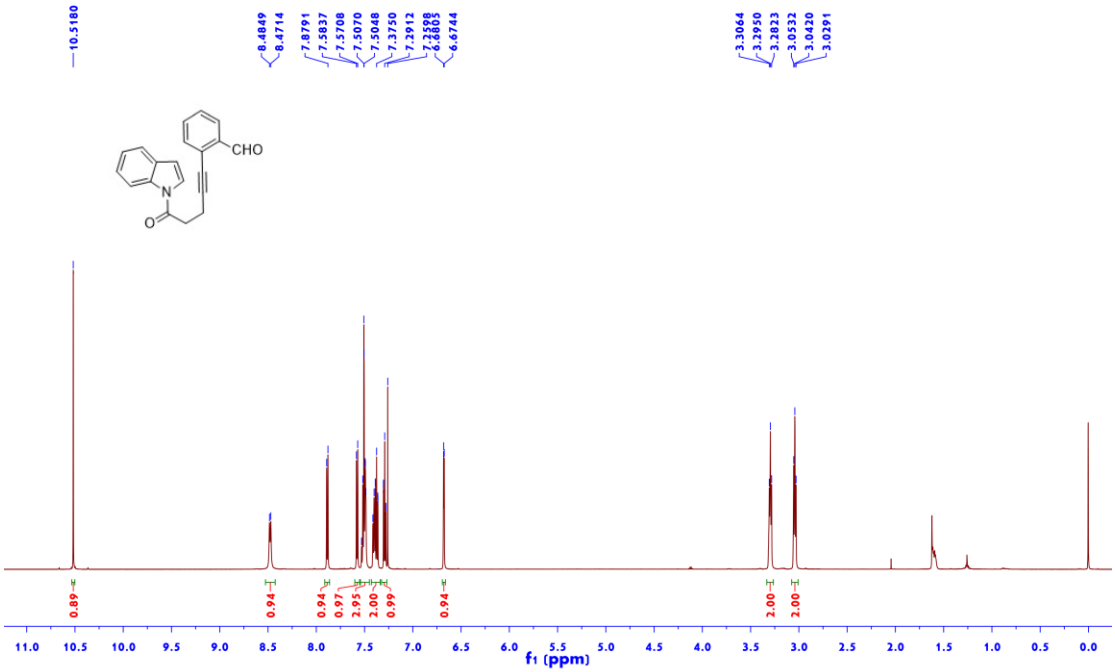


Figure S2 ^{13}C NMR (150 MHz, $CDCl_3$) of **1a**

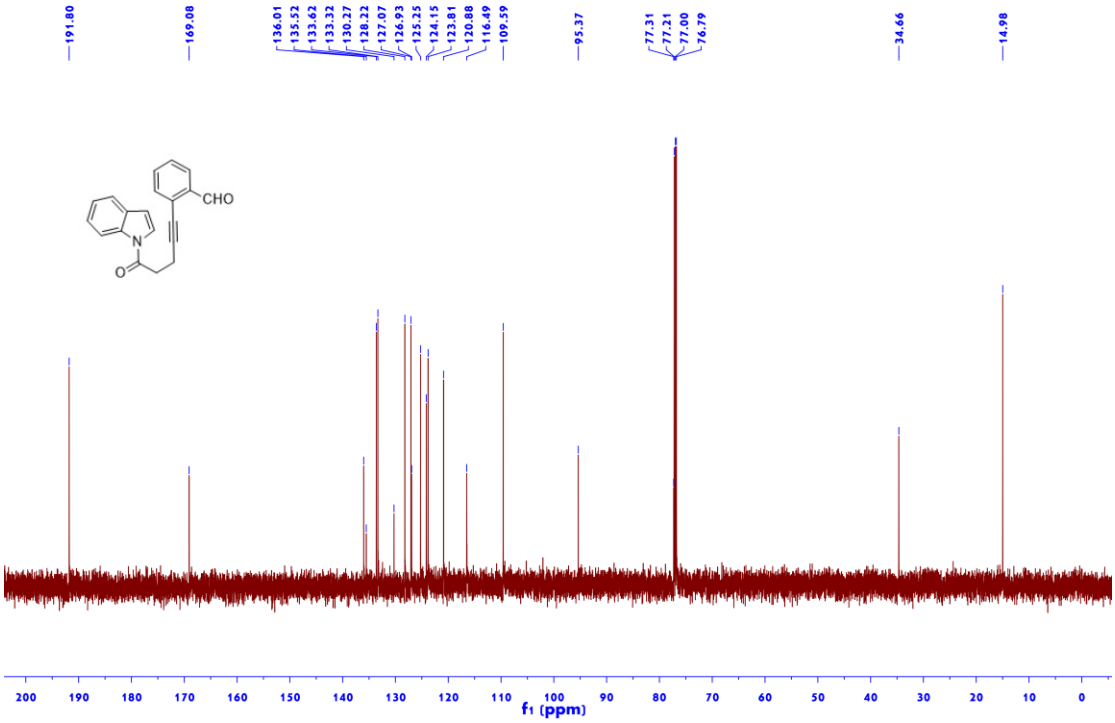


Figure S3 ^{1}H NMR (600 MHz, $CDCl_3$) of **1b**

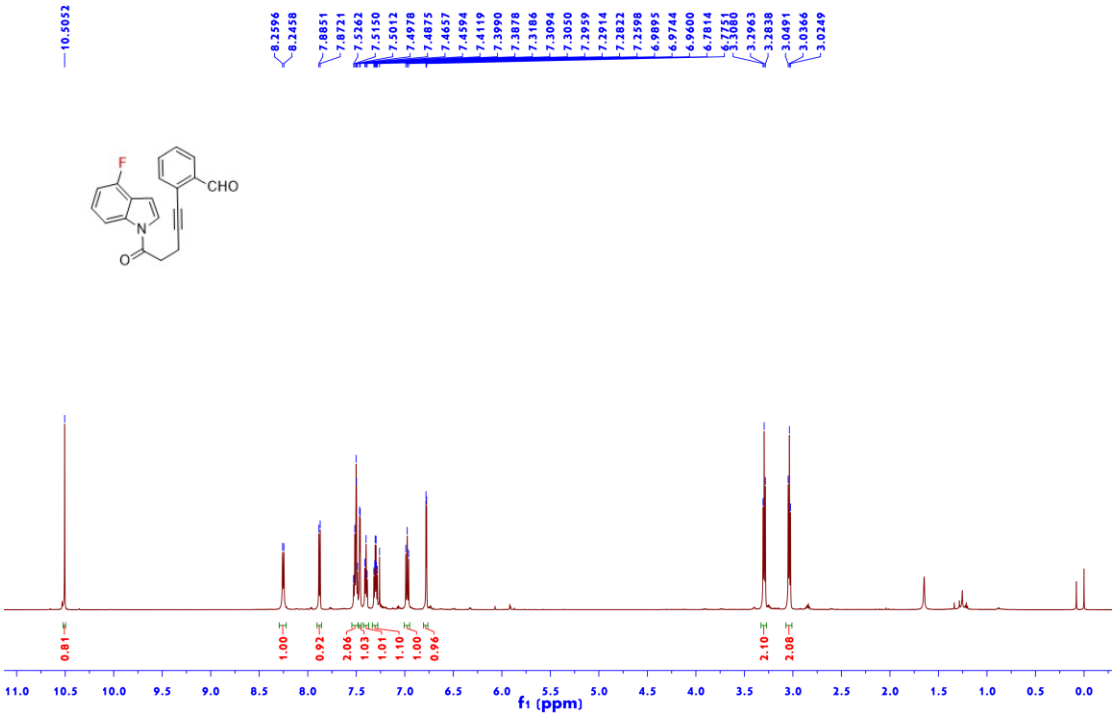


Figure S4 ^{13}C NMR (150 MHz, $CDCl_3$) of **1b**

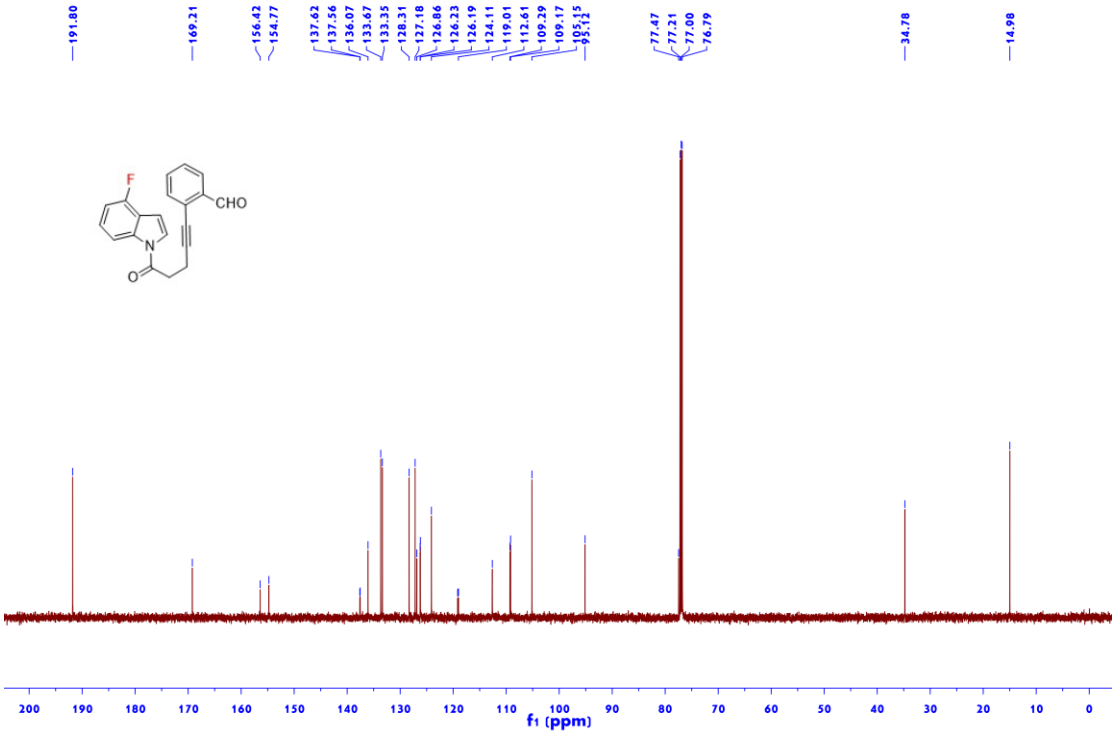


Figure S5 ^{19}F NMR (565 MHz, $CDCl_3$) of **1b**

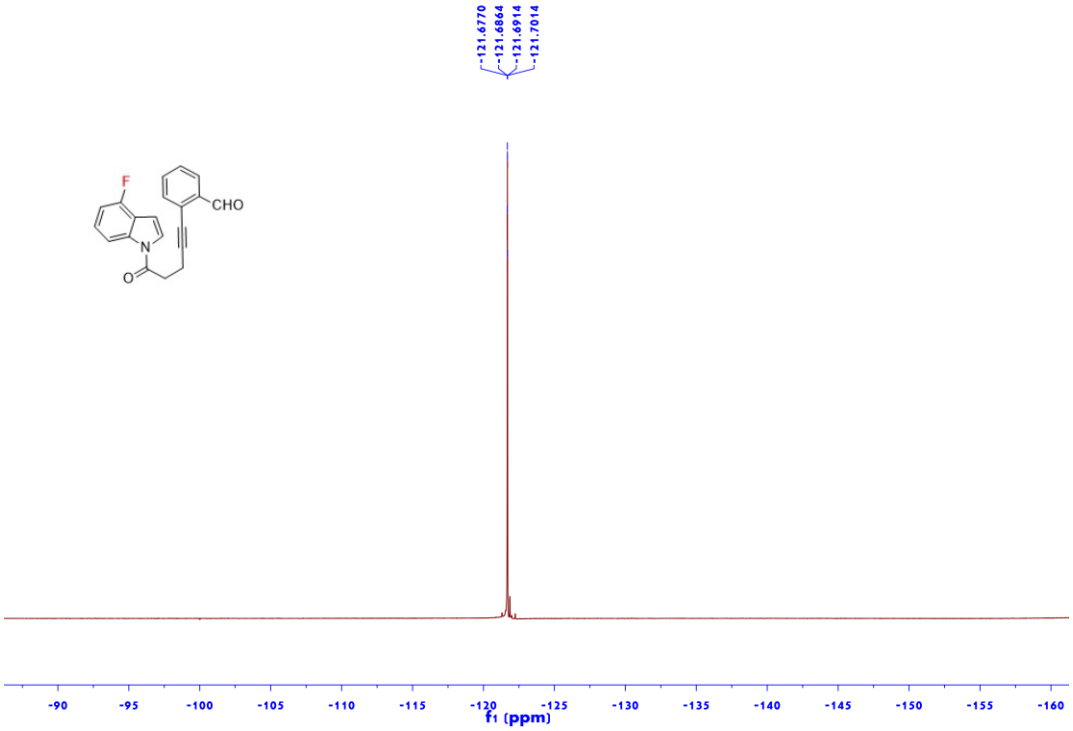


Figure S6 ^{1}H NMR (600 MHz, $CDCl_3$) of **1c**

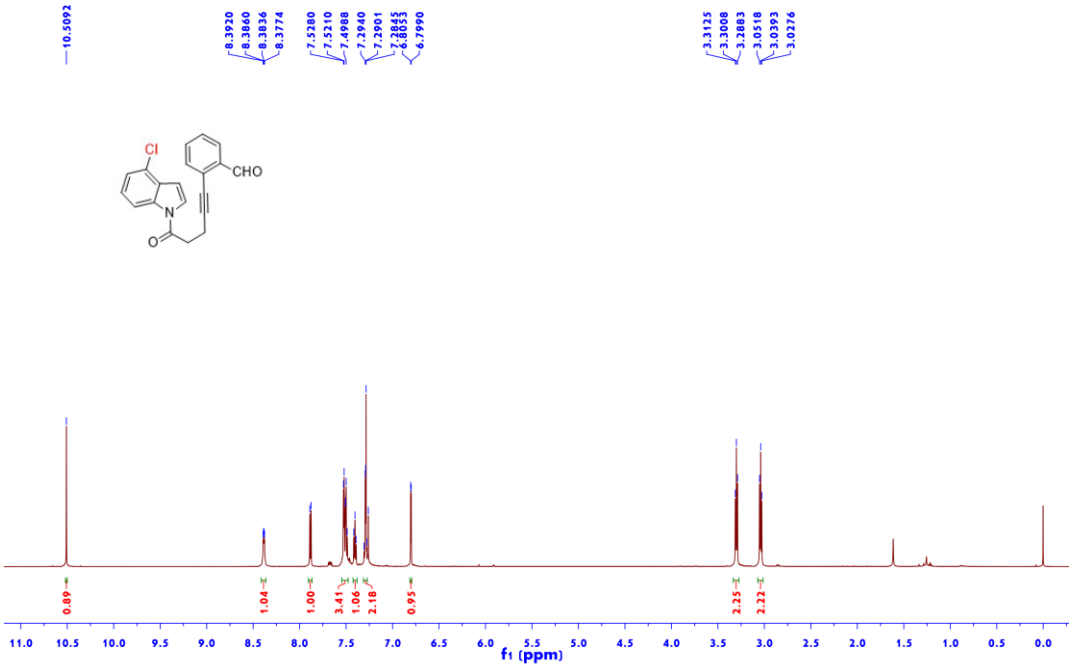


Figure S7 ^{13}C NMR (150 MHz, $CDCl_3$) of **1c**

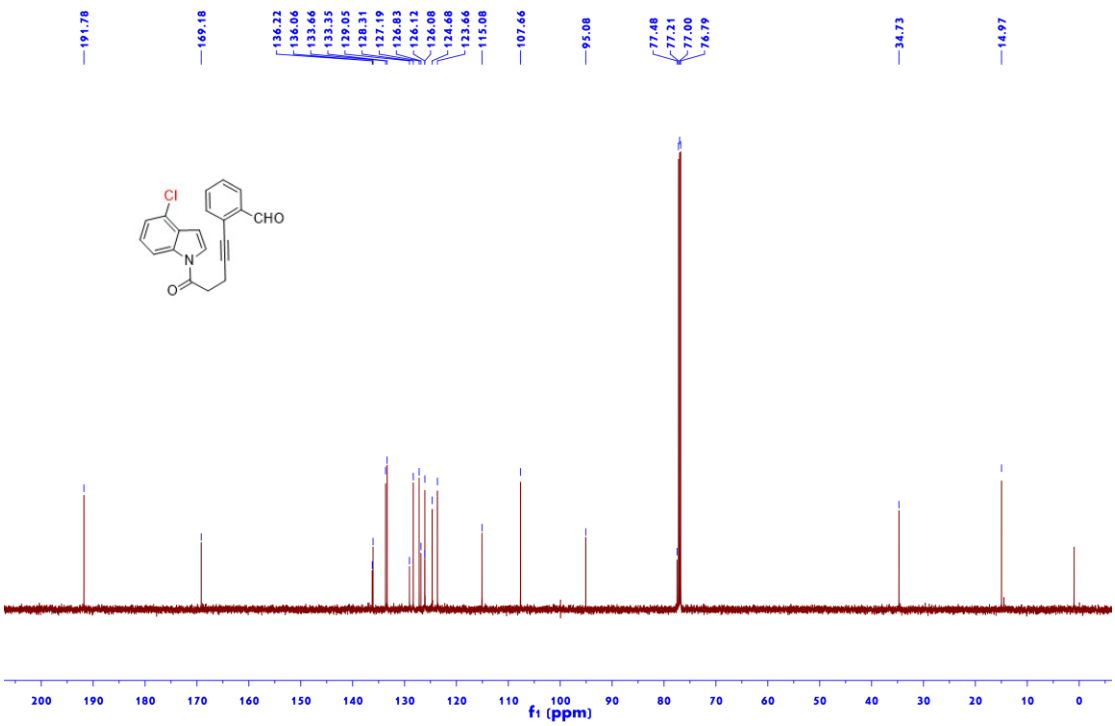


Figure S8 ^{1}H NMR (600 MHz, $CDCl_3$) of **1d**

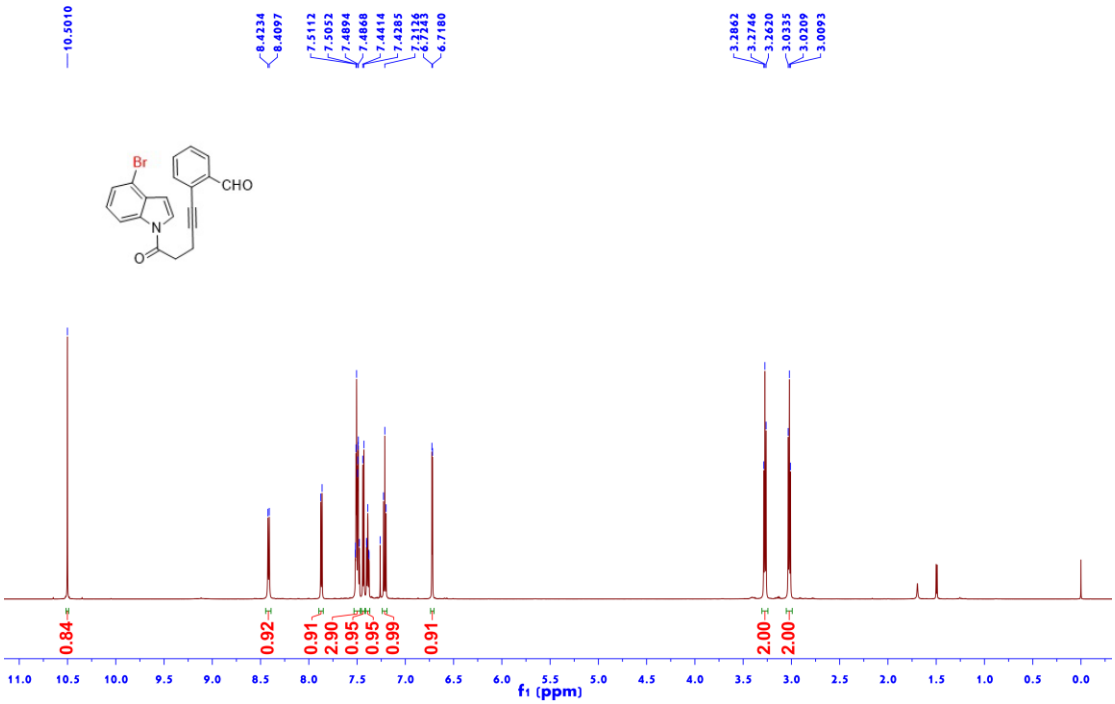


Figure S9 ^{13}C NMR (150 MHz, $CDCl_3$) of **1d**

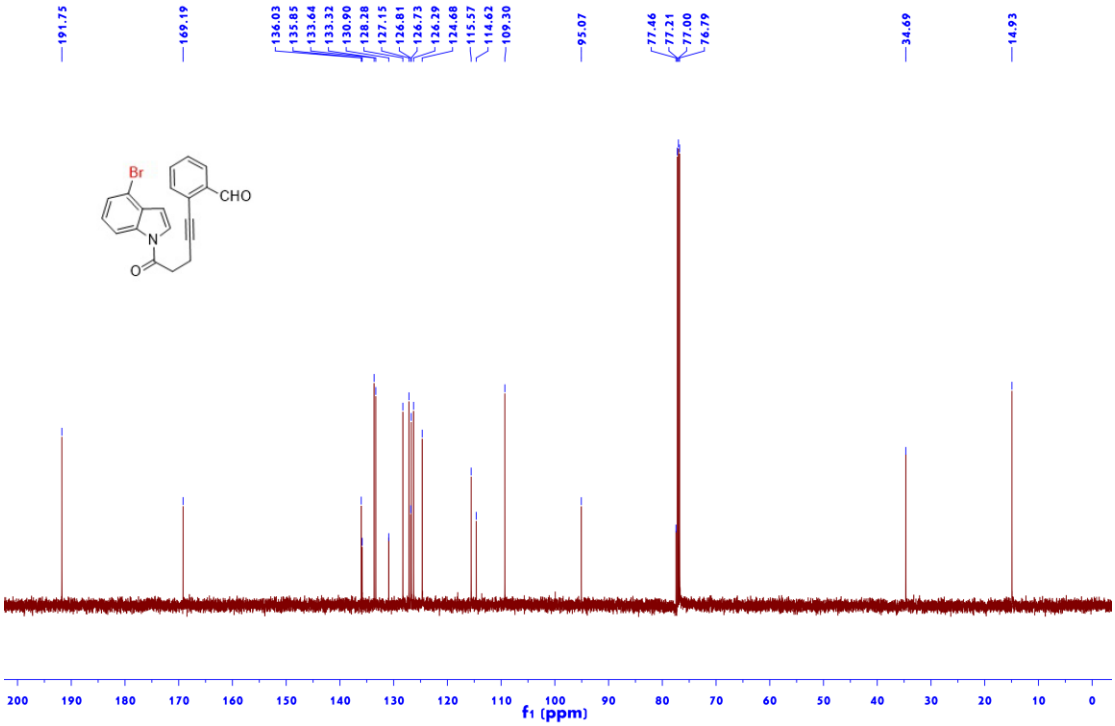


Figure S10 ^{1}H NMR (600 MHz, $CDCl_3$) of **1e**

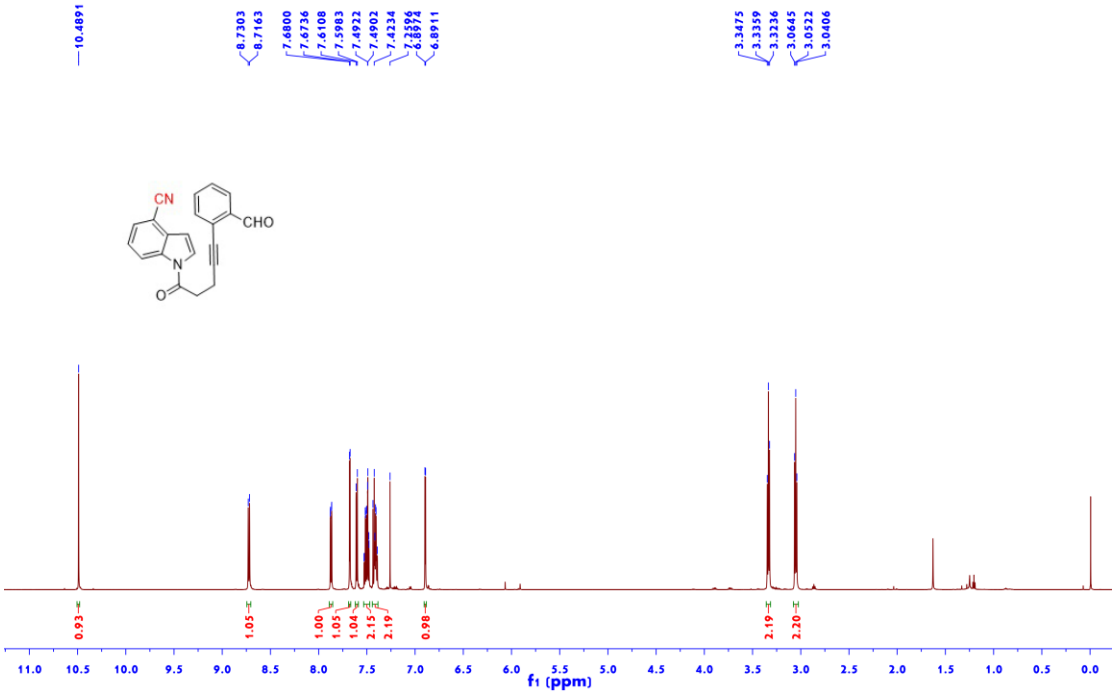


Figure S11 ^{13}C NMR (150 MHz, $CDCl_3$) of **1e**

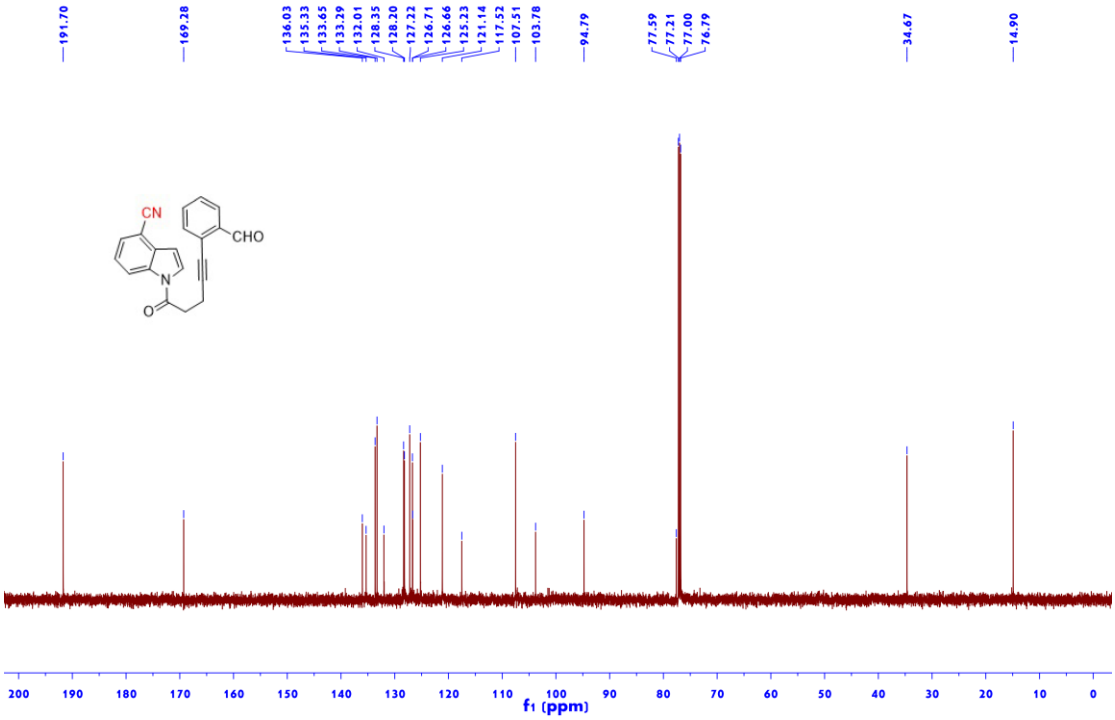


Figure S12 ^{1}H NMR (600 MHz, $CDCl_3$) of **1f**

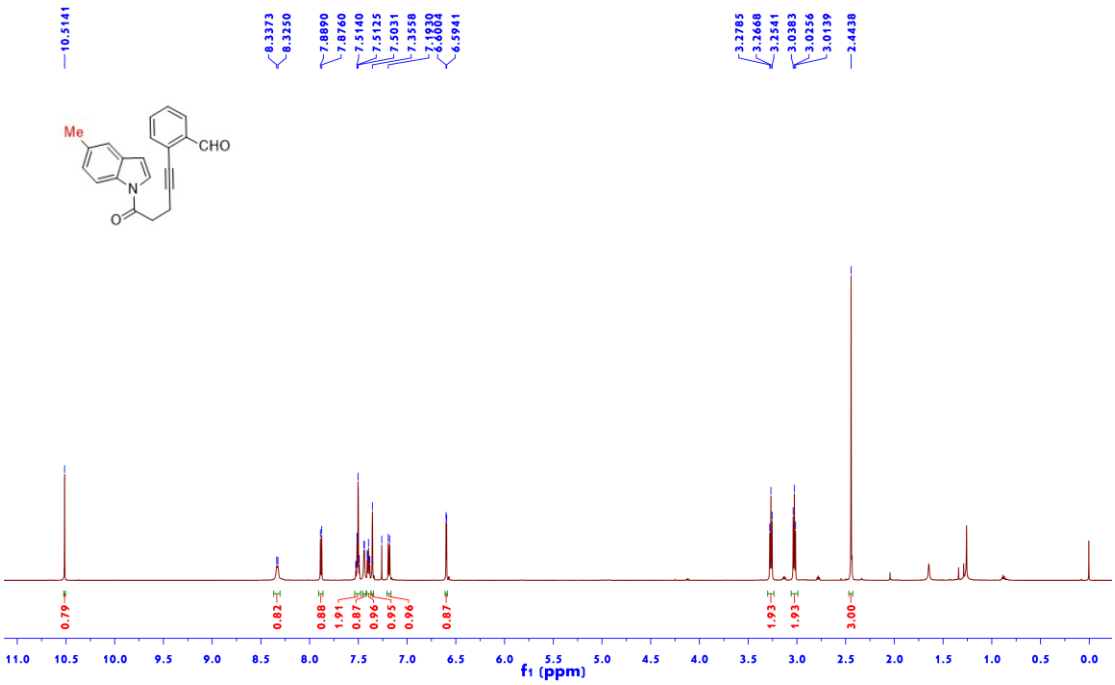


Figure S13 ^{13}C NMR (150 MHz, $CDCl_3$) of **1f**

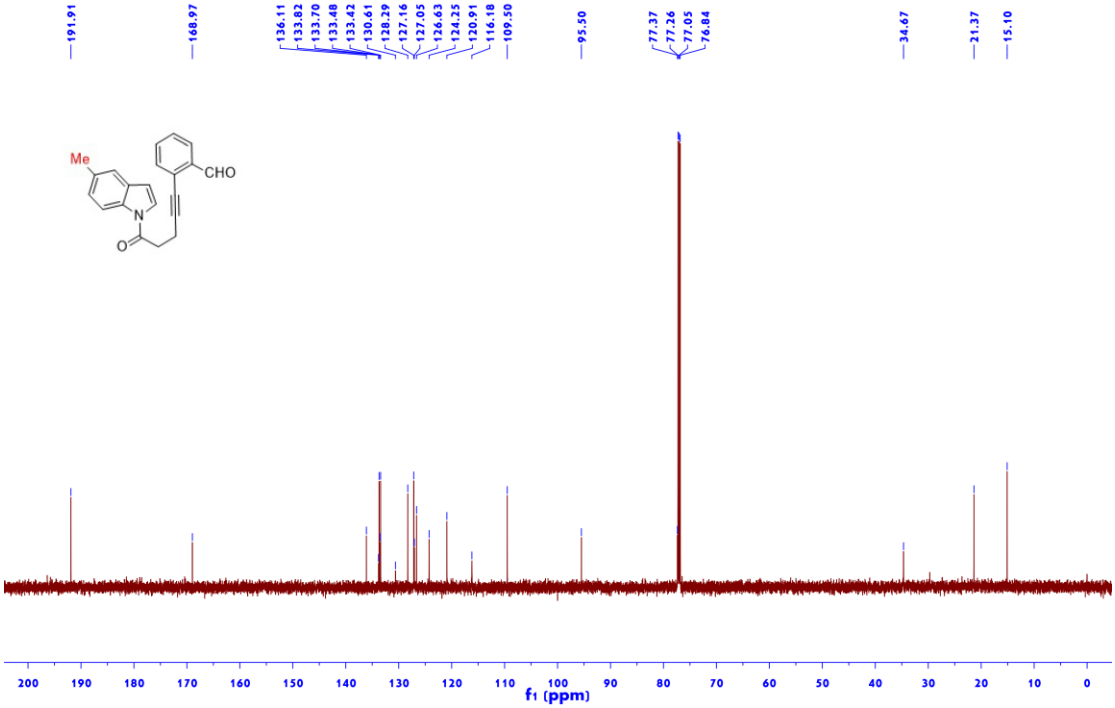


Figure S14 ^{1}H NMR (600 MHz, $CDCl_3$) of **1g**

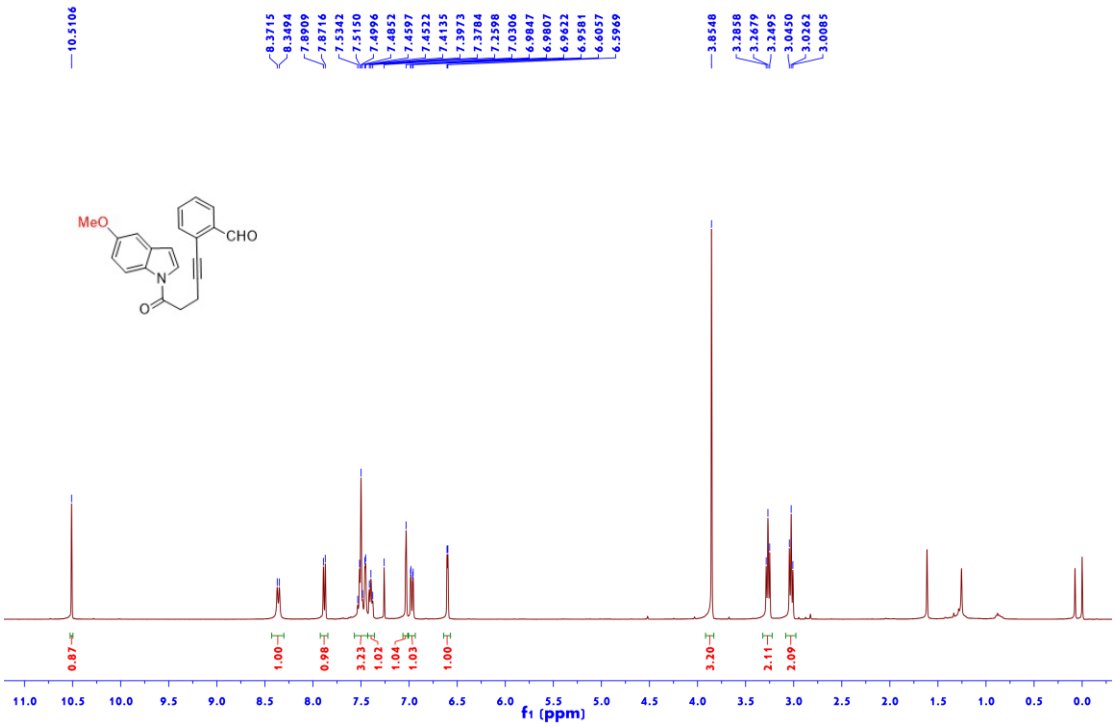


Figure S15 ^{13}C NMR (150 MHz, $CDCl_3$) of **1g**

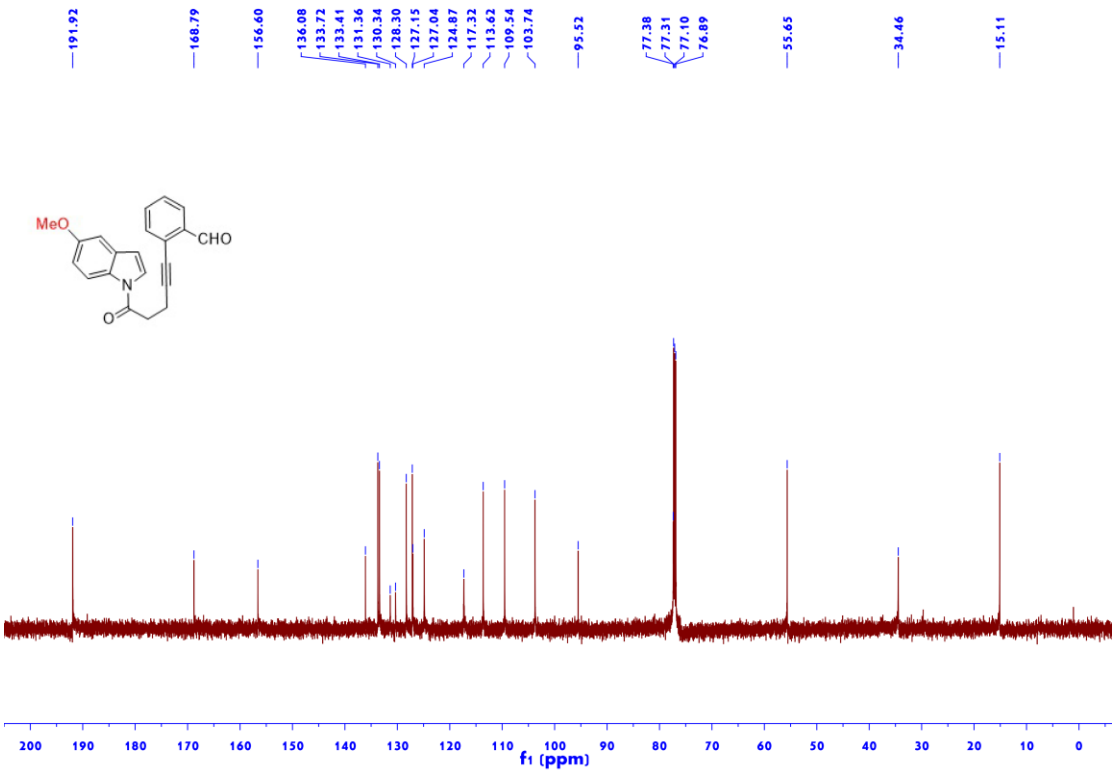


Figure S16 ^{1}H NMR (600 MHz, $CDCl_3$) of **1h**

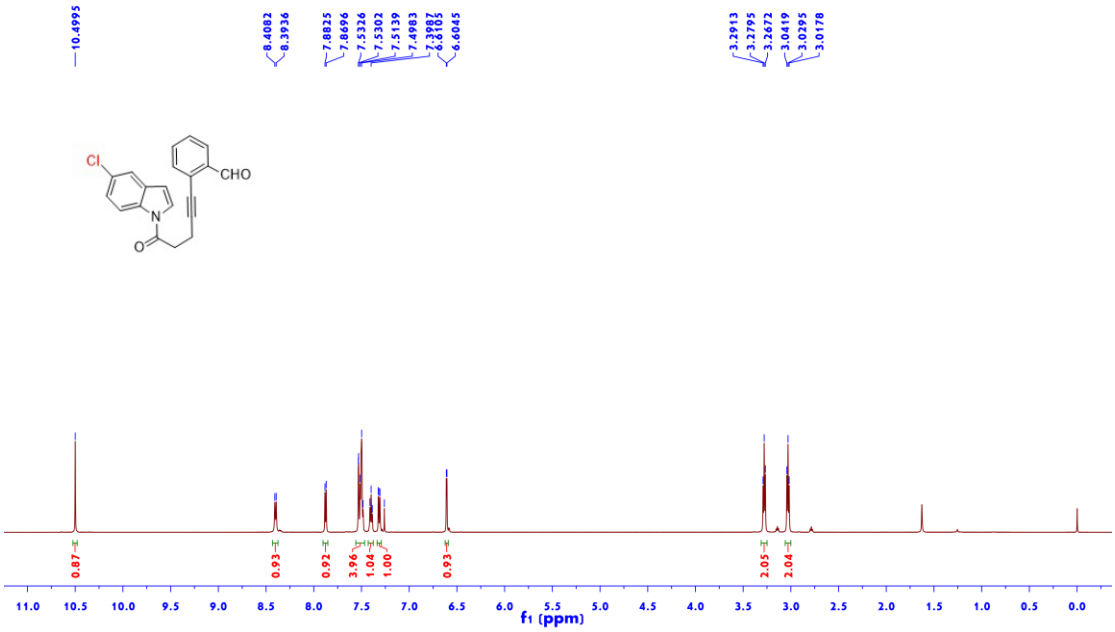


Figure S17 ^{13}C NMR (150 MHz, $CDCl_3$) of **1h**

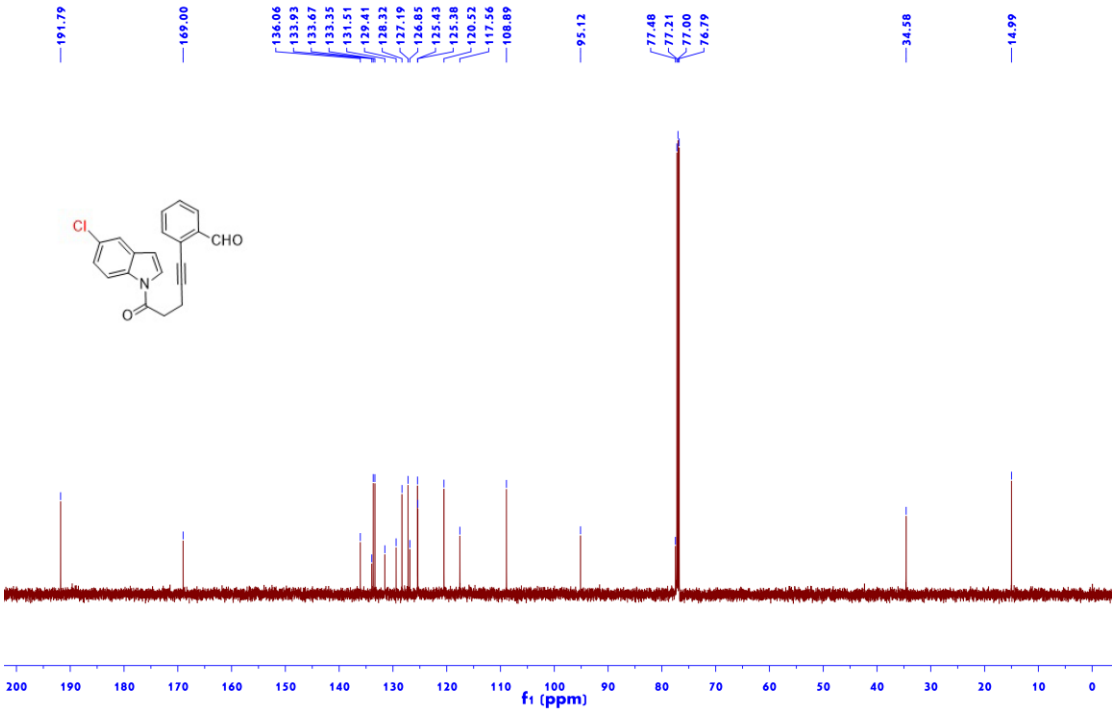


Figure S18 ^{1}H NMR (600 MHz, $CDCl_3$) of **1i**

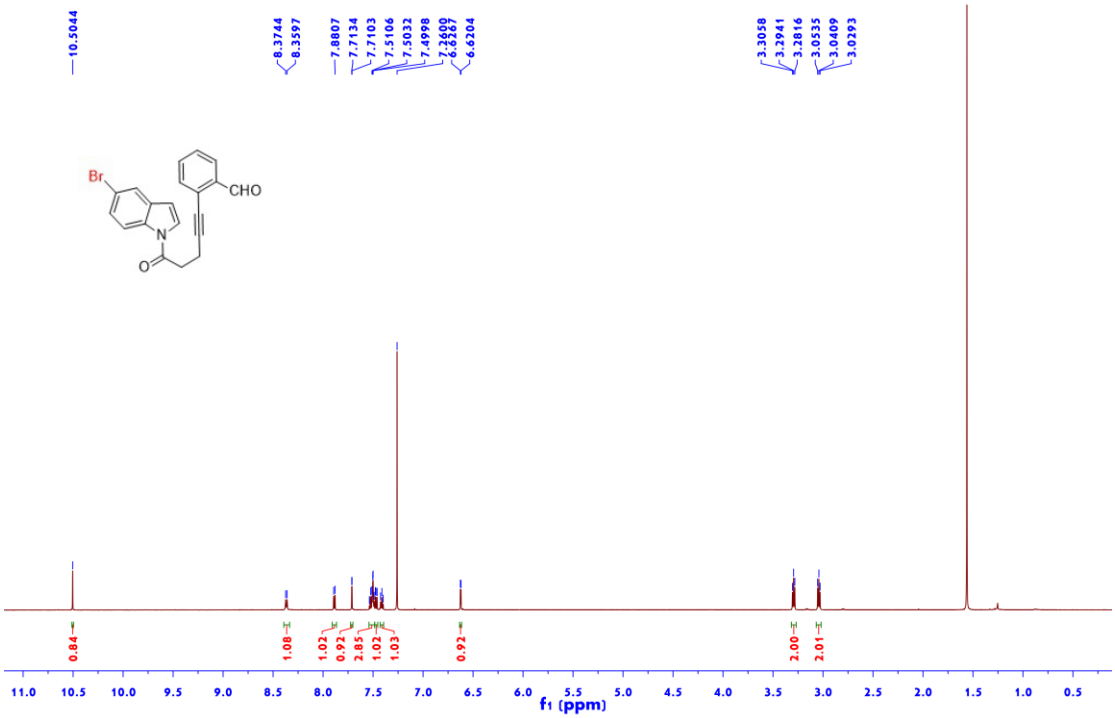


Figure S19 ^{13}C NMR (150 MHz, $CDCl_3$) of **1i**

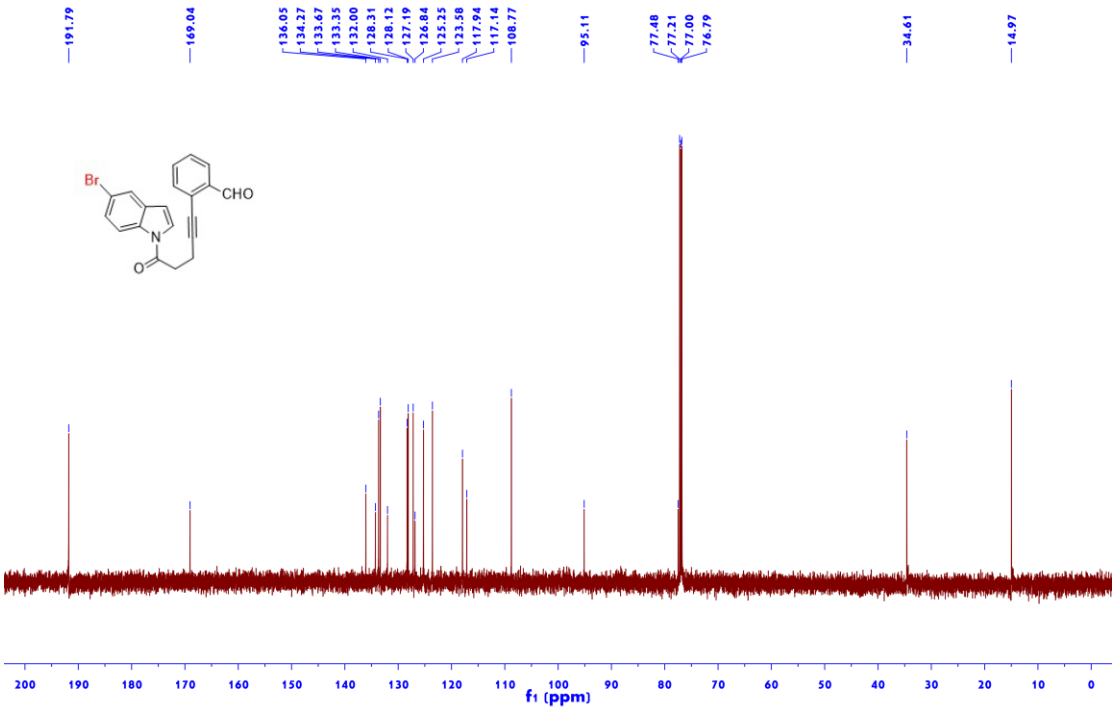


Figure S20 ^{1}H NMR (600 MHz, $CDCl_3$) of **1j**

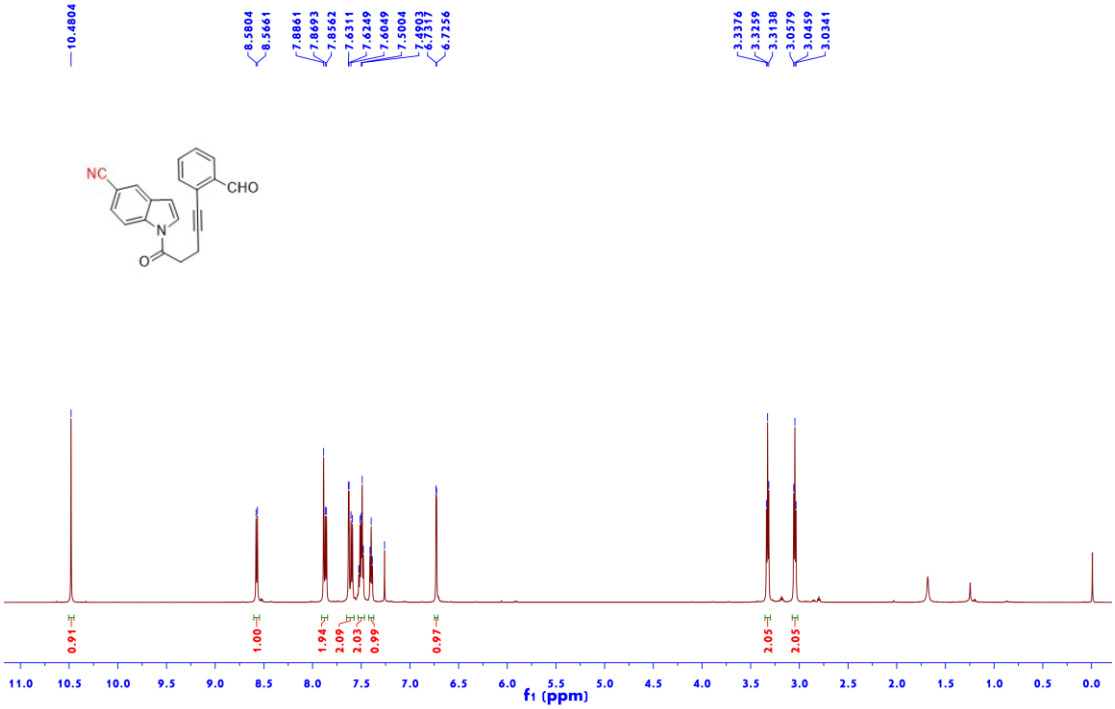


Figure S21 ^{13}C NMR (150 MHz, $CDCl_3$) of **1j**

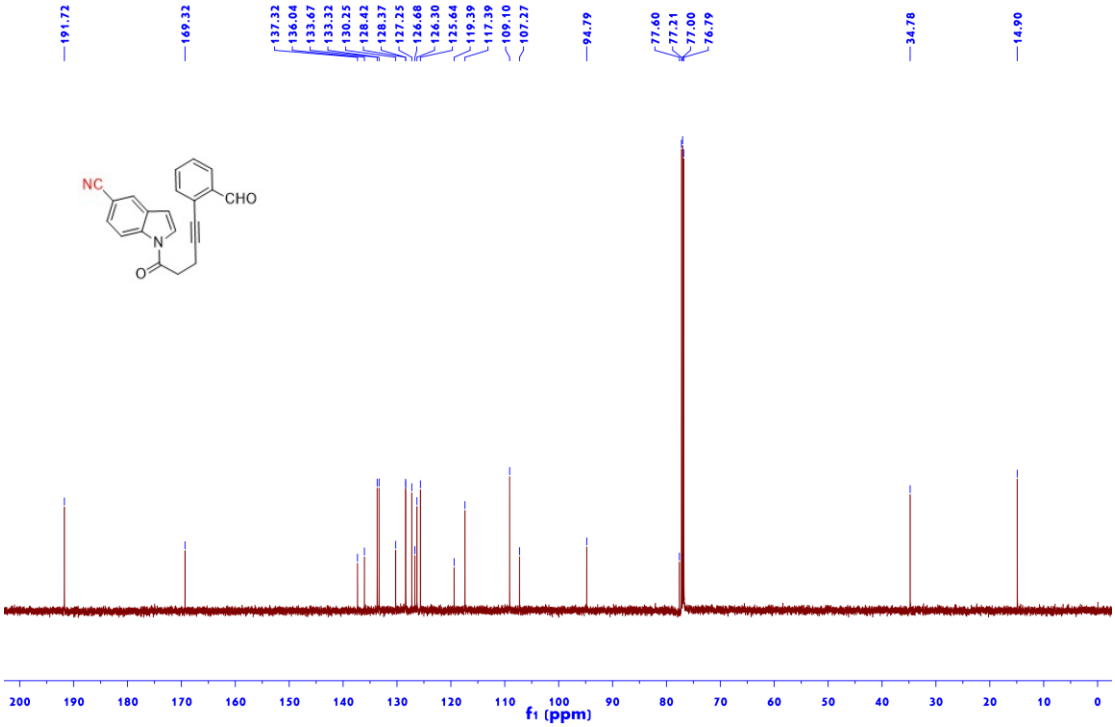


Figure S22 ^{1}H NMR (600 MHz, $CDCl_3$) of **1k**

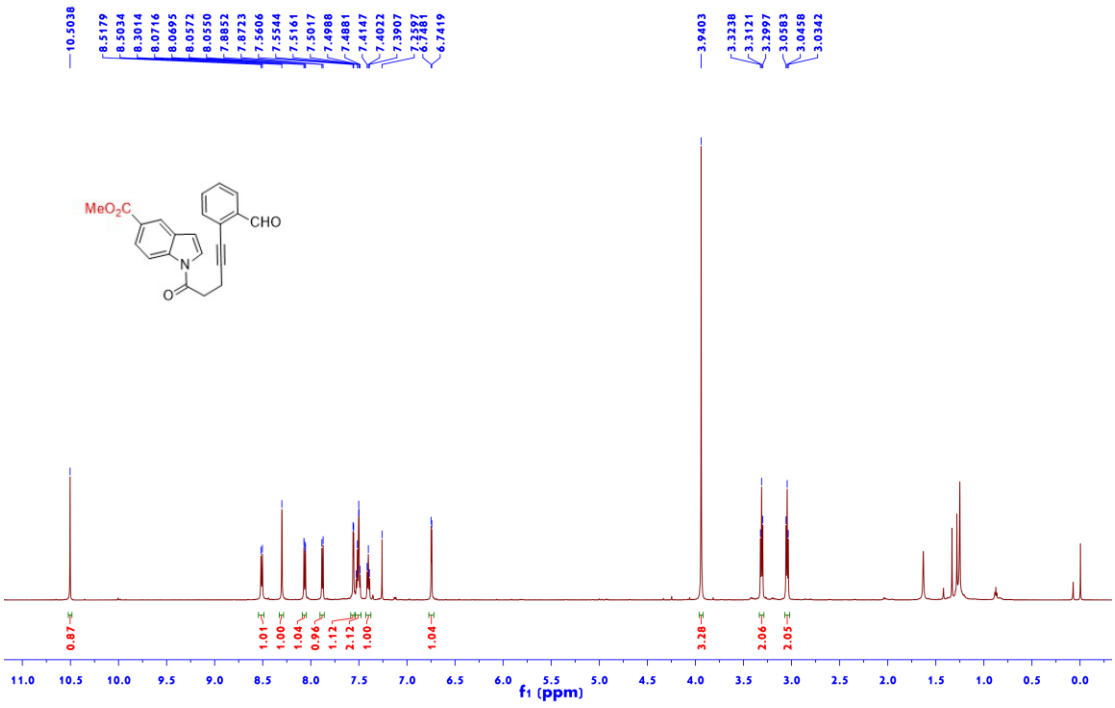


Figure S23 ^{13}C NMR (150 MHz, $CDCl_3$) of **1k**

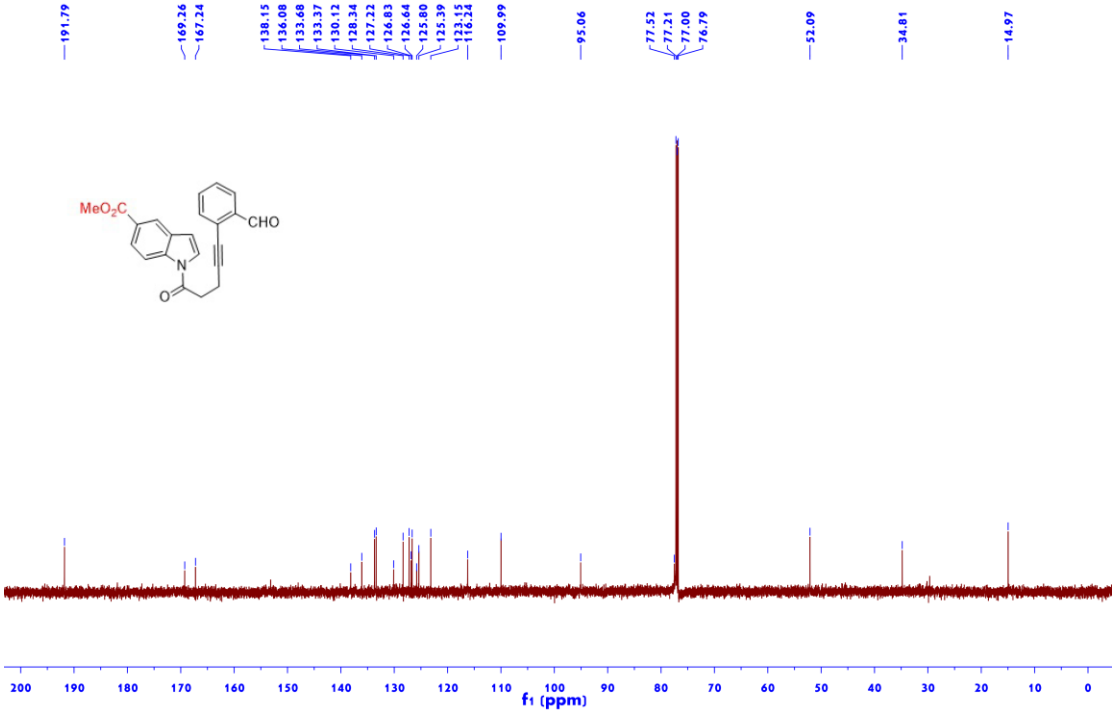


Figure S24 ^{1}H NMR (600 MHz, $CDCl_3$) of **1l**

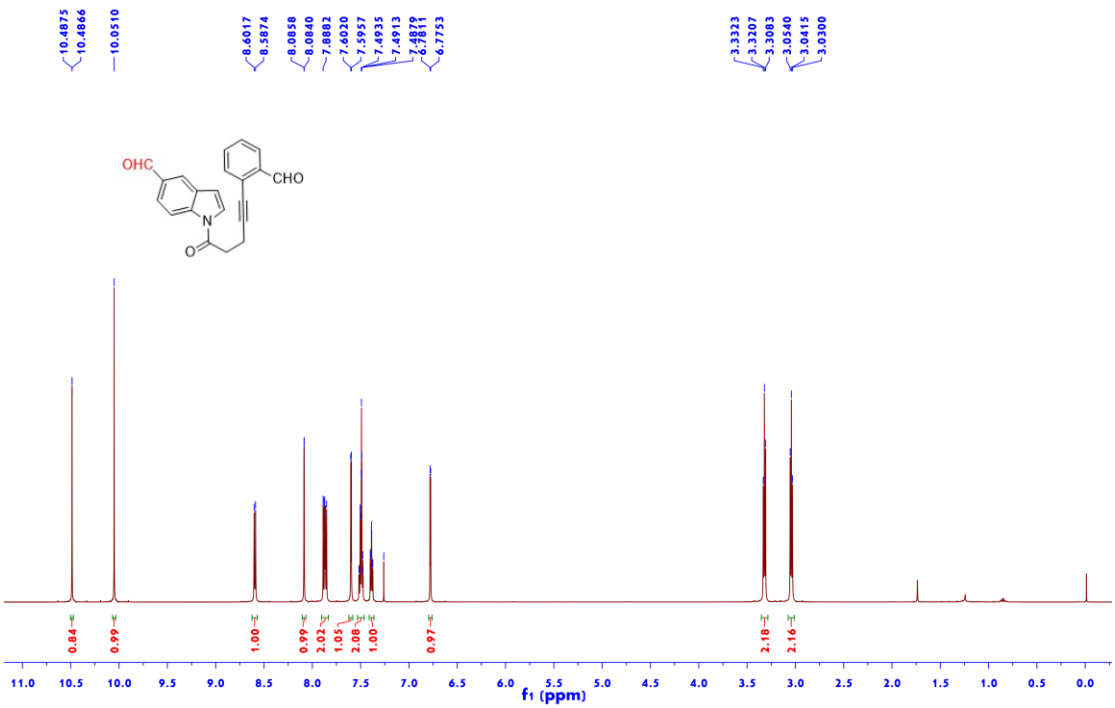


Figure S25 ^{13}C NMR (150 MHz, $CDCl_3$) of **1l**

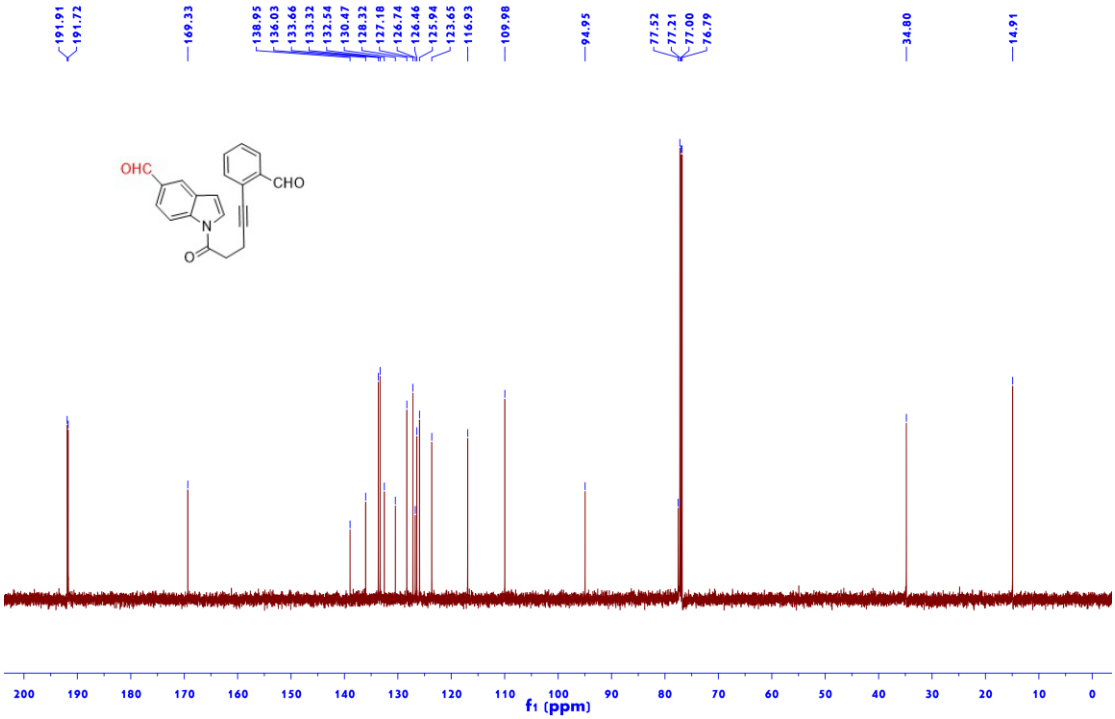


Figure S26 ^{1}H NMR (600 MHz, $CDCl_3$) of **1m**

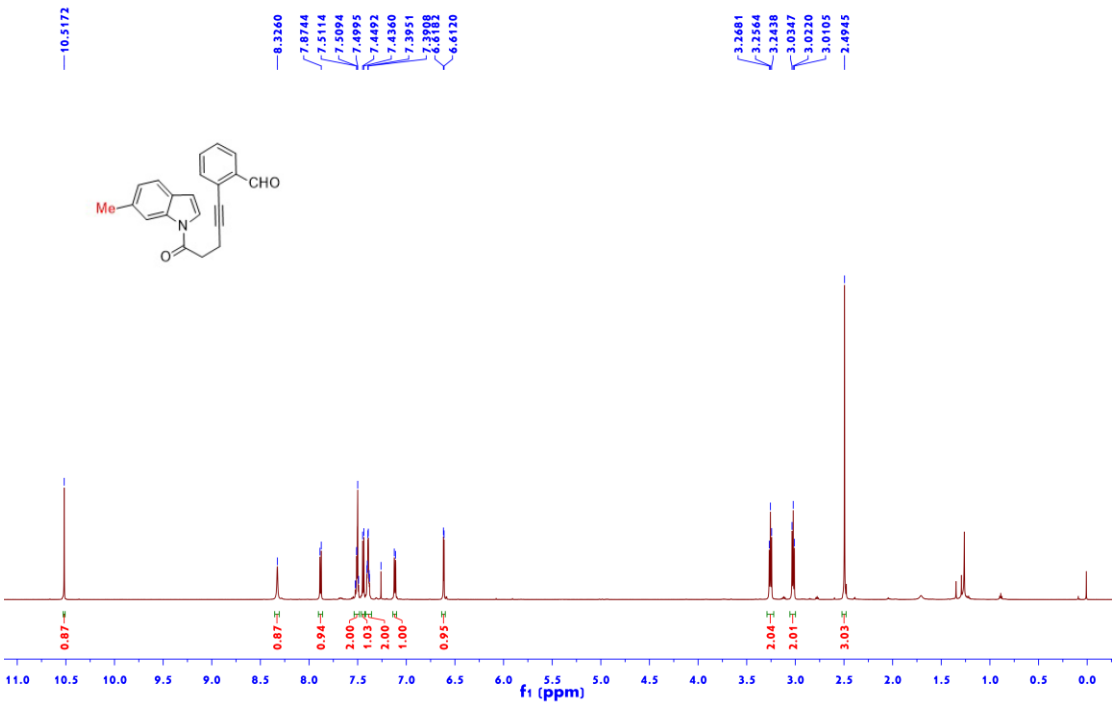


Figure S27 ^{13}C NMR (150 MHz, $CDCl_3$) of **1m**

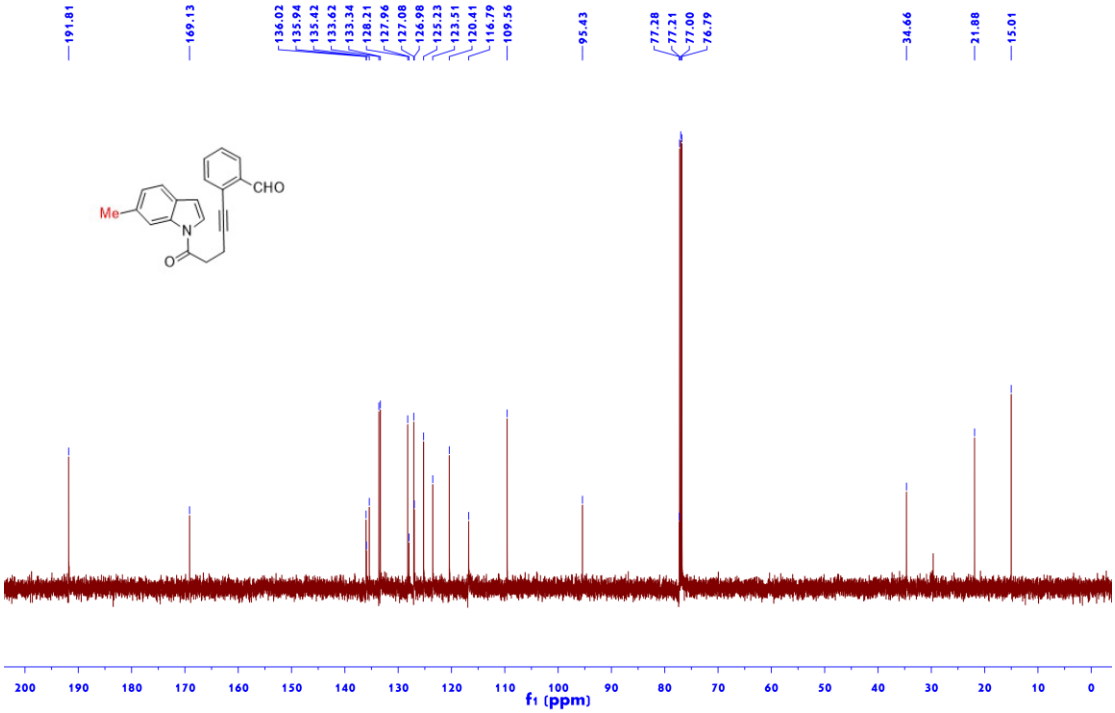


Figure S28 ^{1}H NMR (600 MHz, $CDCl_3$) of **1n**

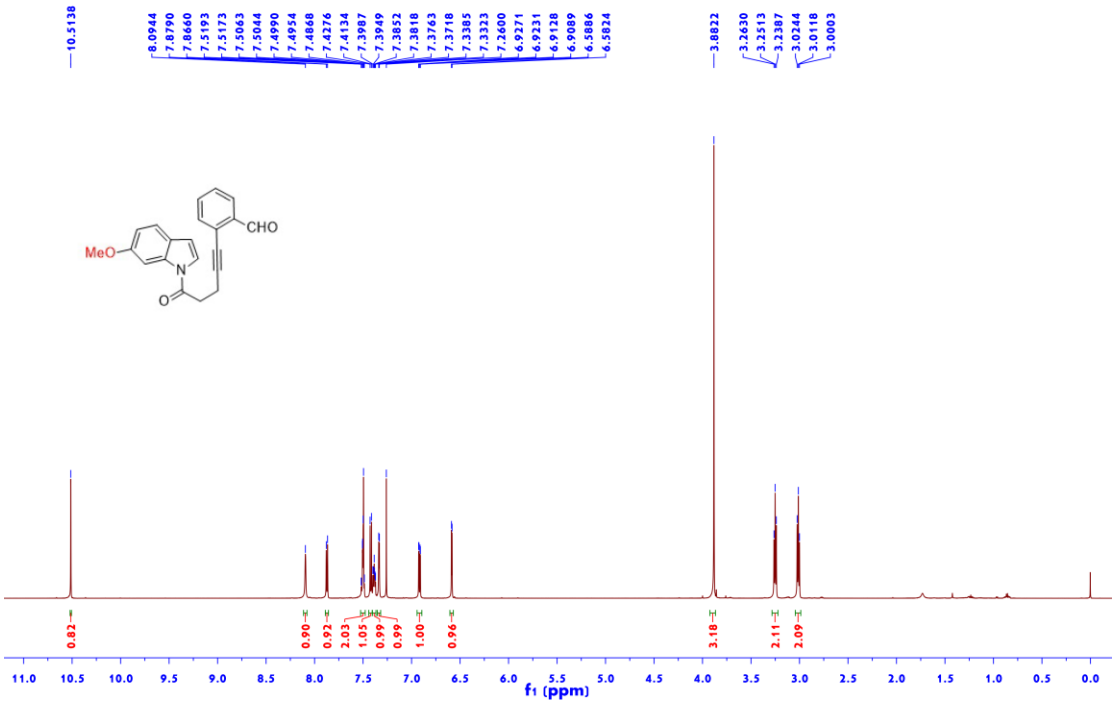


Figure S29 ^{13}C NMR (150 MHz, $CDCl_3$) of **1n**

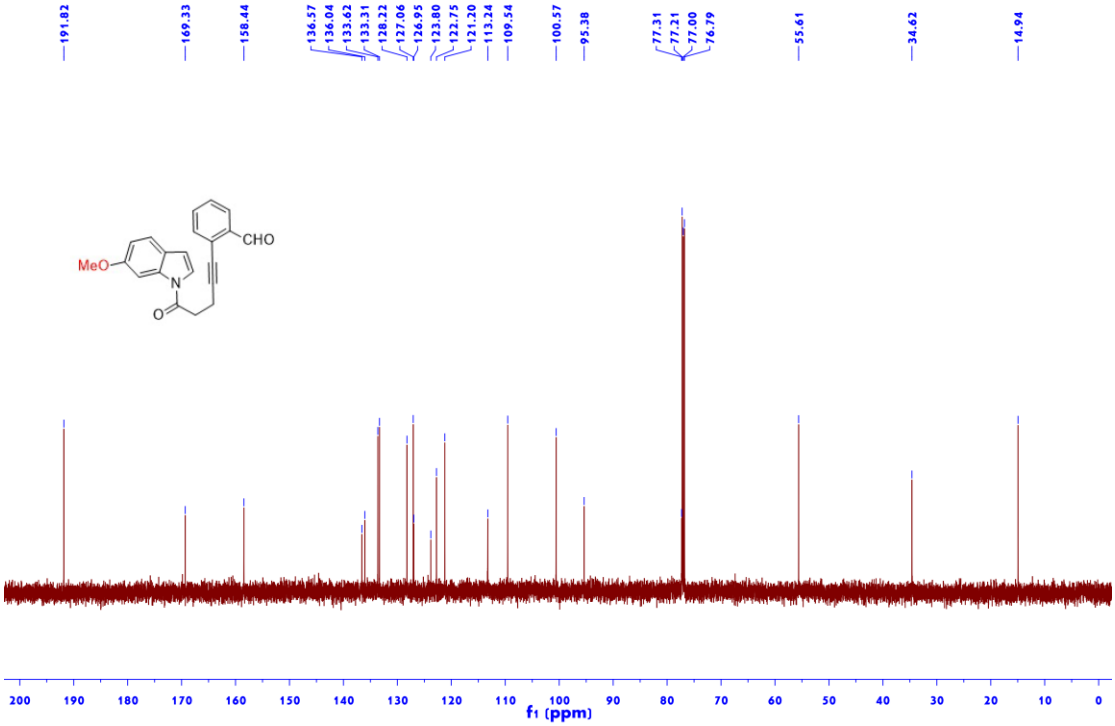


Figure S30 ^{1}H NMR (600 MHz, $CDCl_3$) of **1o**

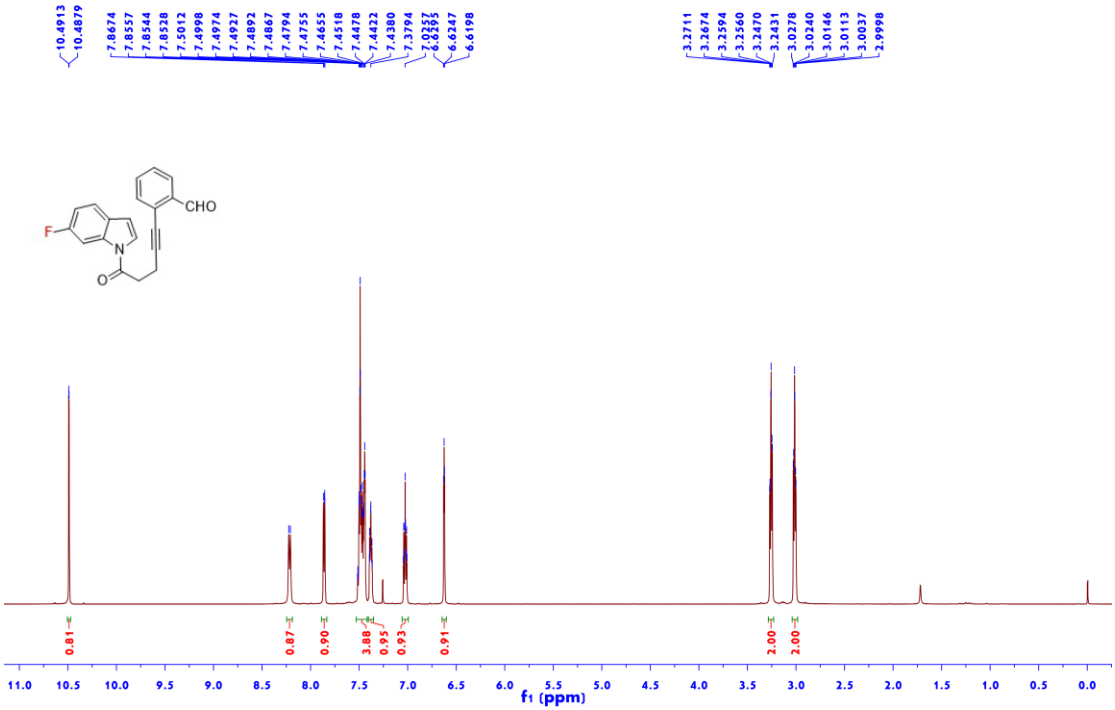


Figure S31 ^{13}C NMR (150 MHz, $CDCl_3$) of **1o**

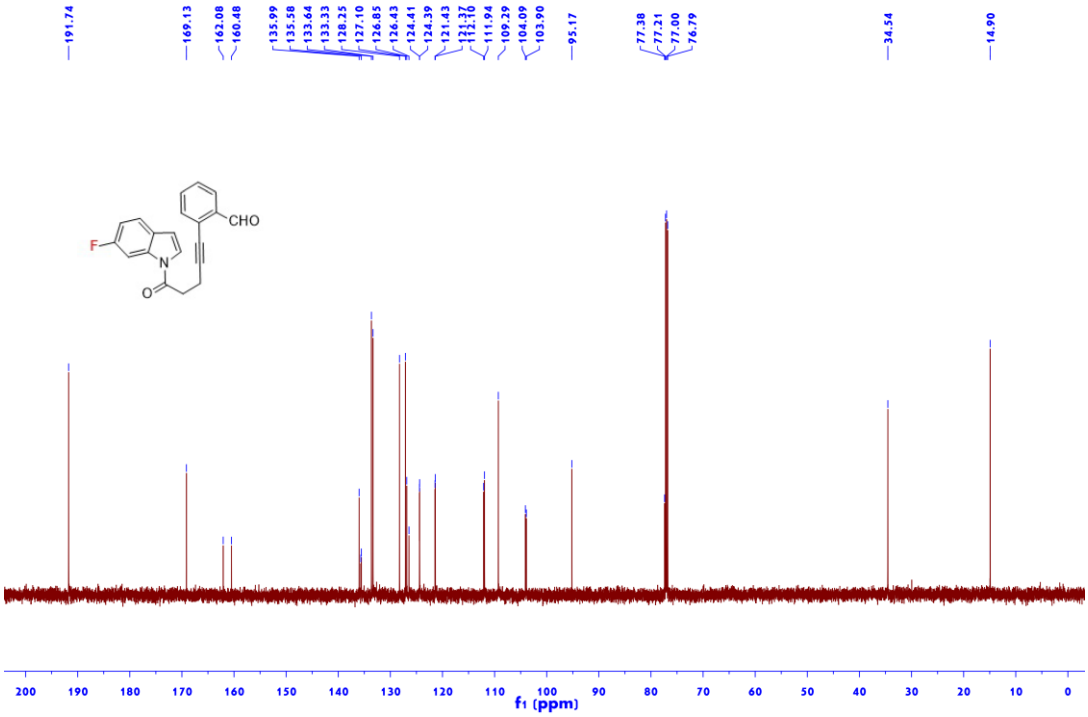


Figure S32 ^{19}F NMR (565 MHz, $CDCl_3$) of **1o**

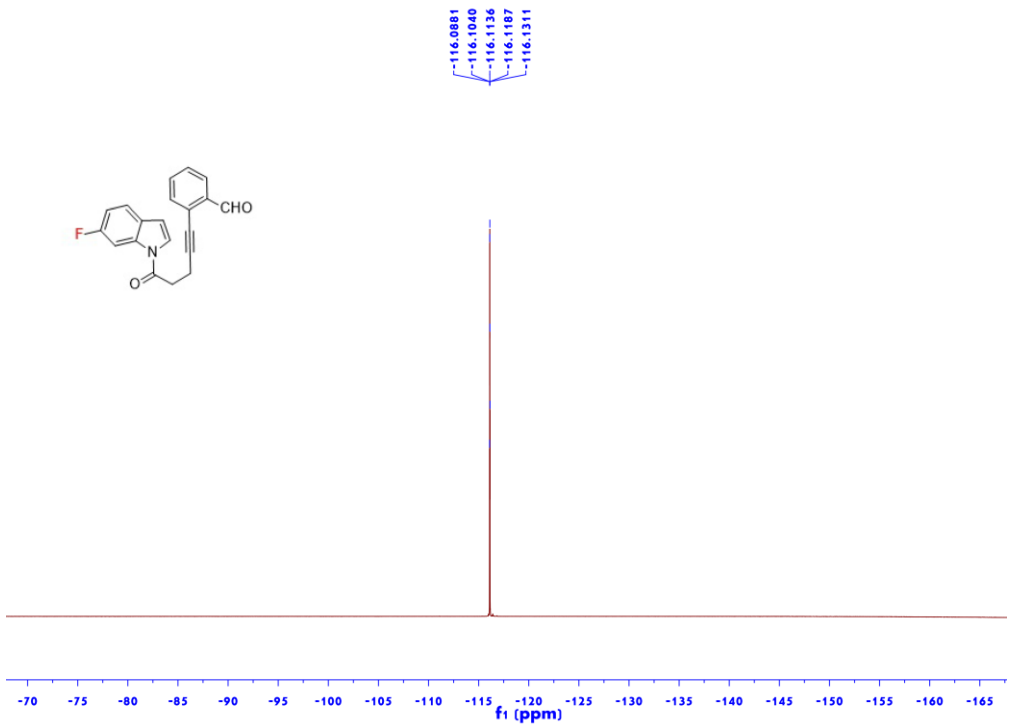


Figure S33 ^{1}H NMR (600 MHz, $CDCl_3$) of **1p**

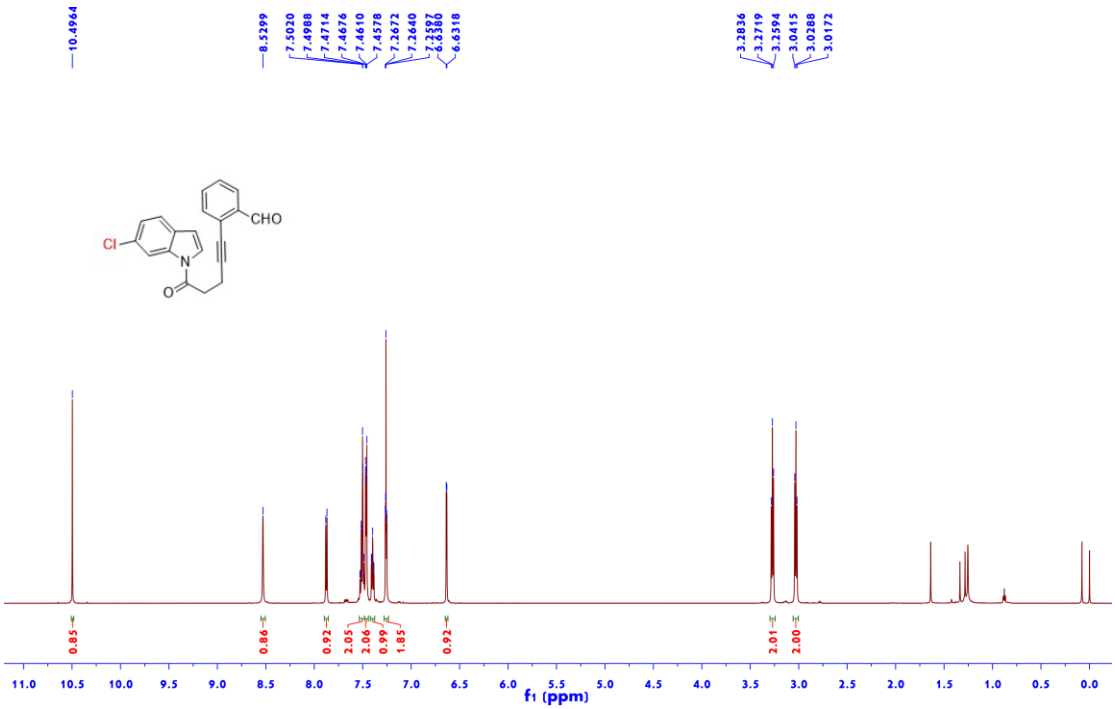


Figure S34 ^{13}C NMR (150 MHz, $CDCl_3$) of **1p**

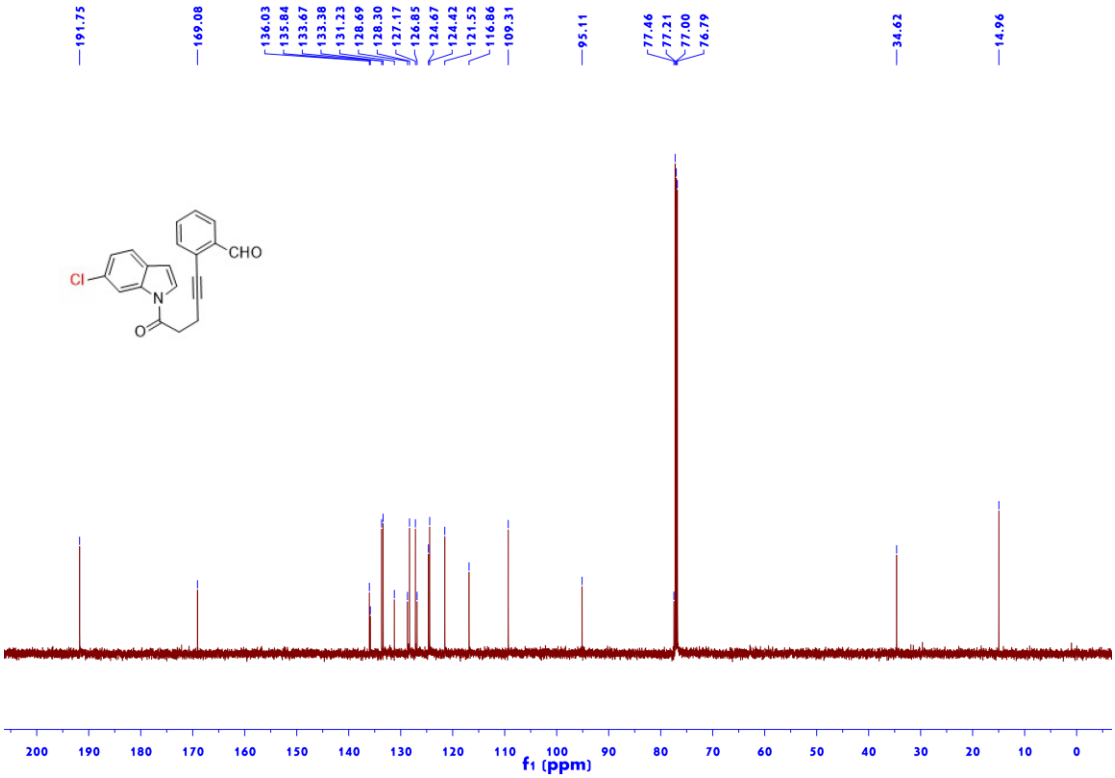


Figure S35 ^{1}H NMR (600 MHz, $CDCl_3$) of **1q**

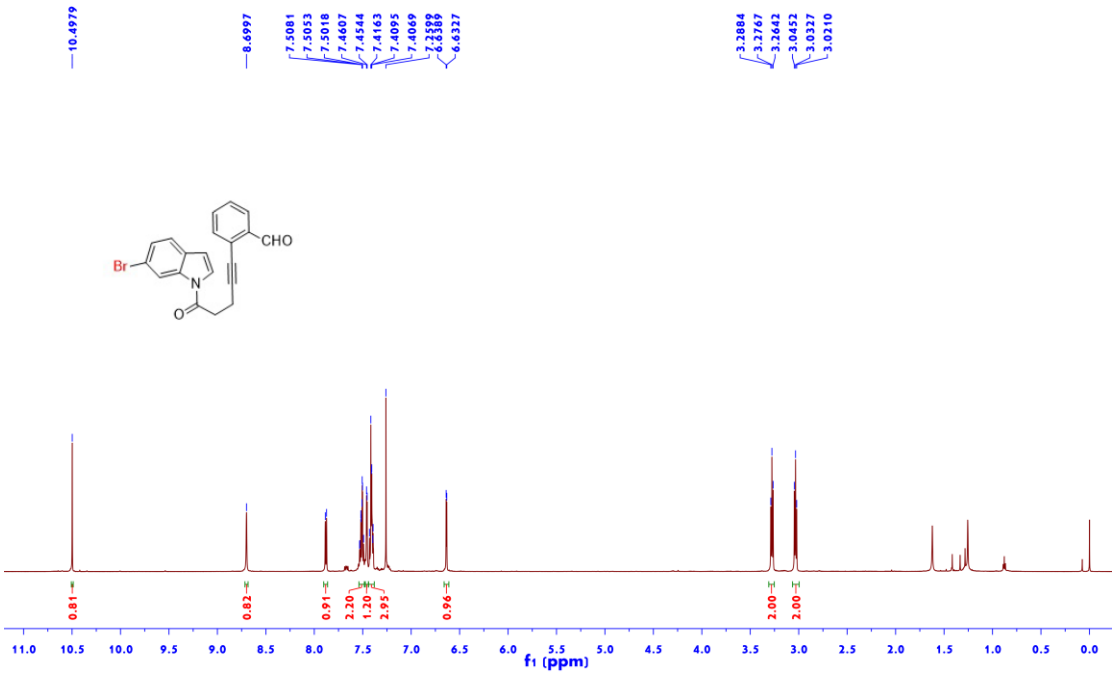


Figure S36 ^{13}C NMR (150 MHz, $CDCl_3$) of **1q**

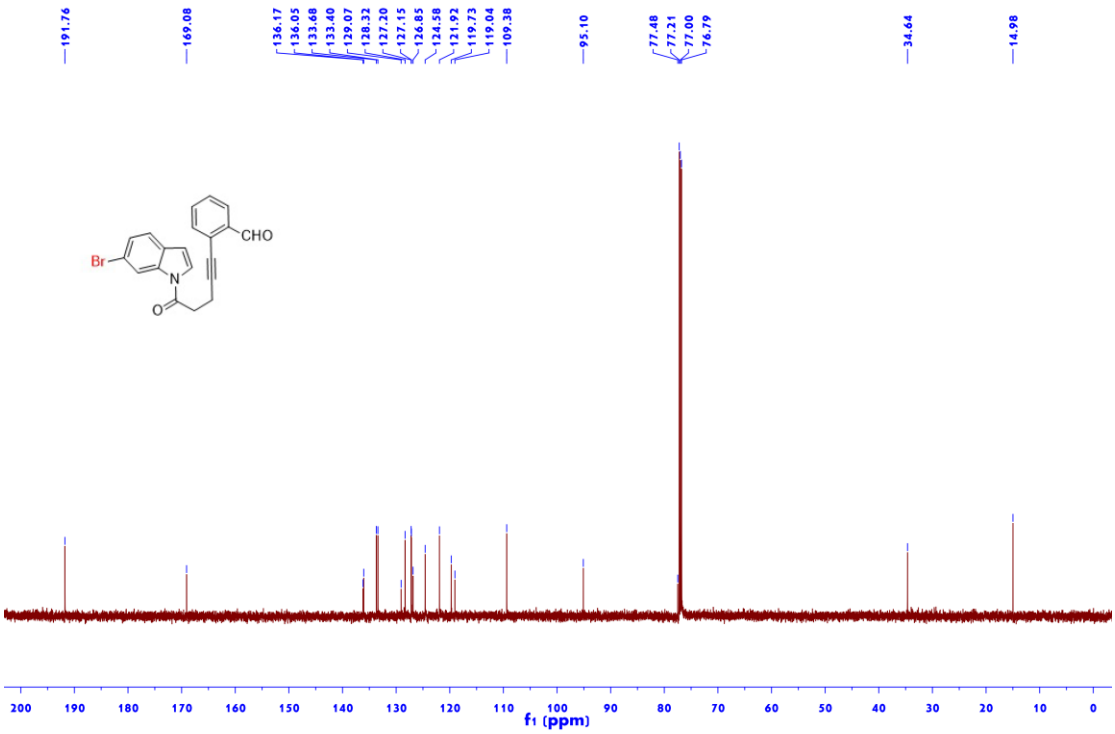


Figure S37 ^{1}H NMR (600 MHz, $CDCl_3$) of **1r**

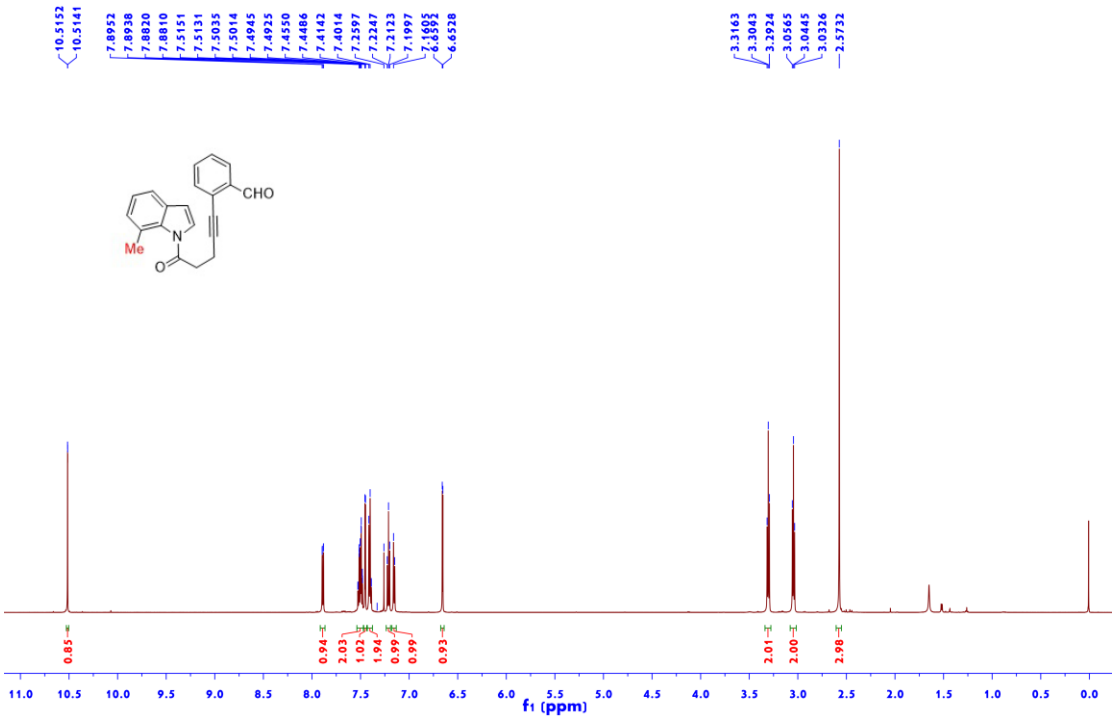


Figure S38 ^{13}C NMR (150 MHz, $CDCl_3$) of **1r**

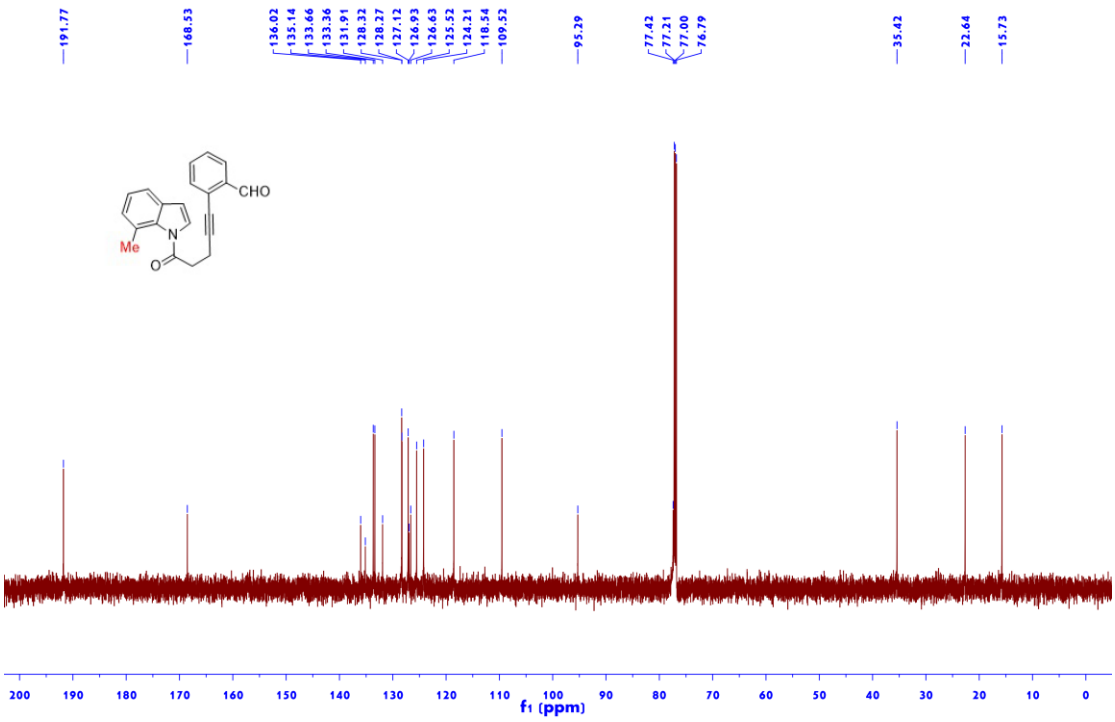


Figure S39 ^{1}H NMR (600 MHz, $CDCl_3$) of **1s**

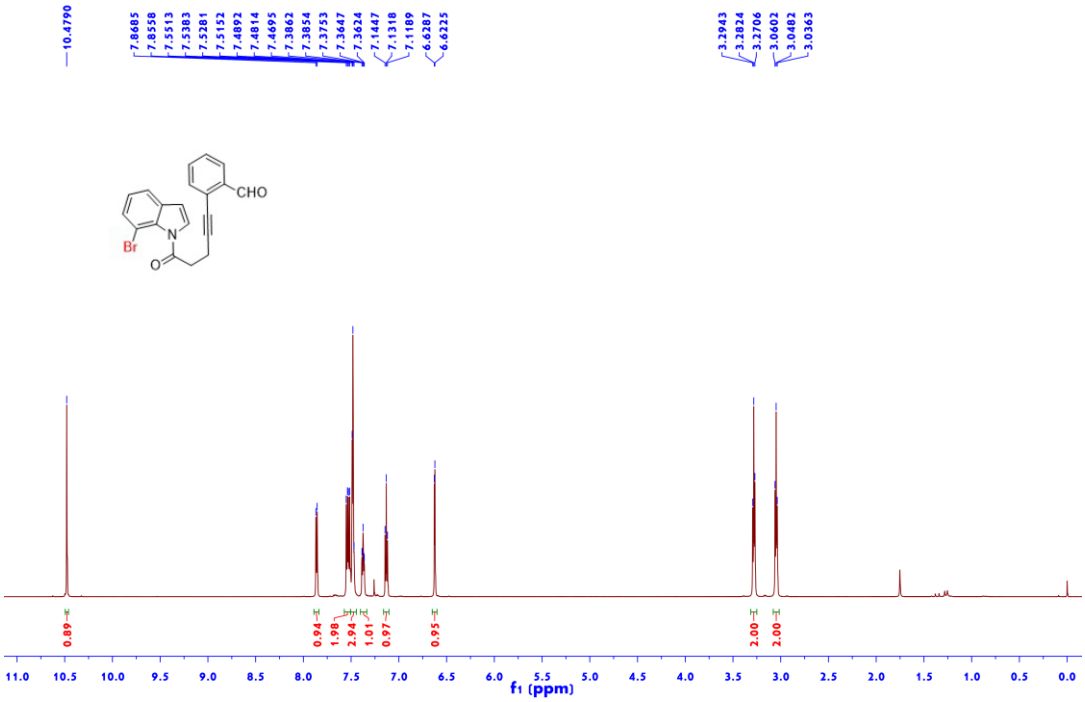


Figure S40 ^{13}C NMR (150 MHz, $CDCl_3$) of **1s**

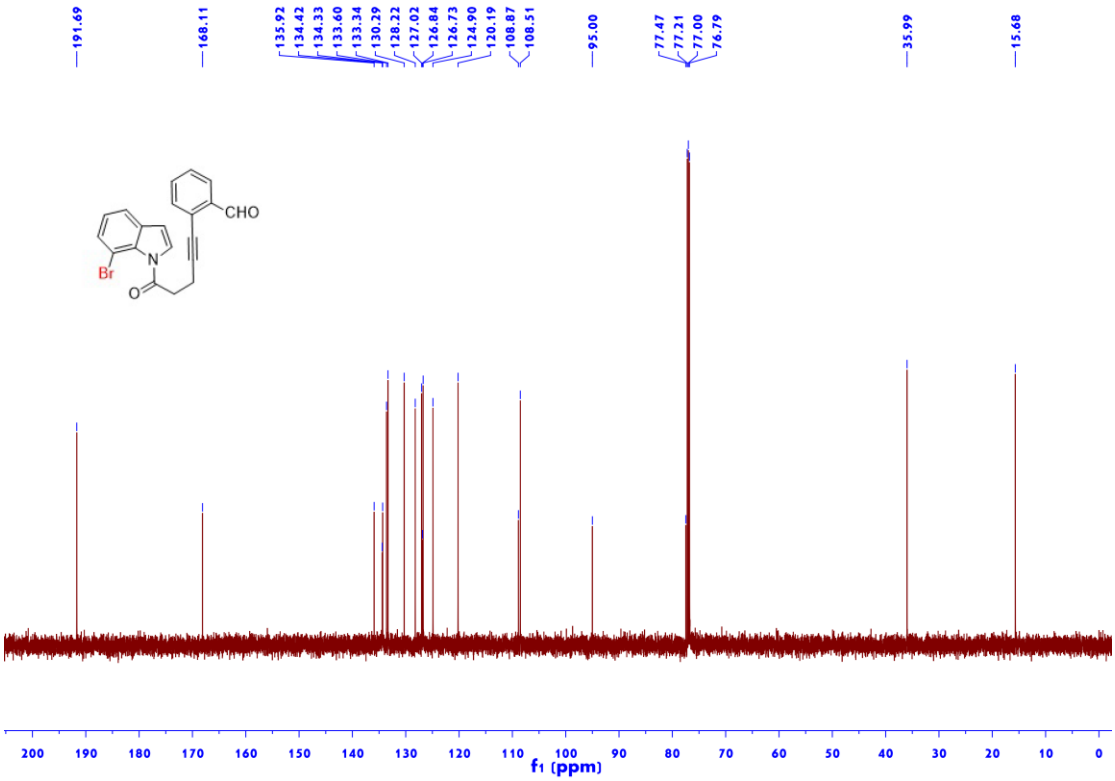


Figure S41 ^{1}H NMR (600 MHz, $CDCl_3$) of **1t**

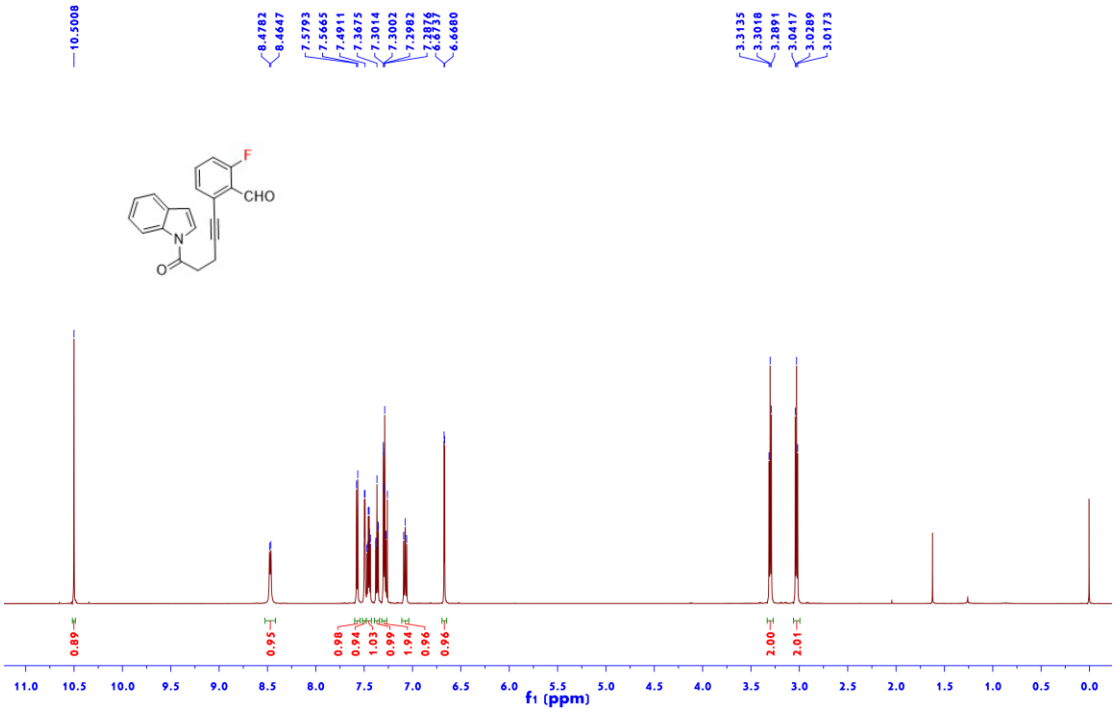


Figure S42 ^{13}C NMR (150 MHz, $CDCl_3$) of **1t**

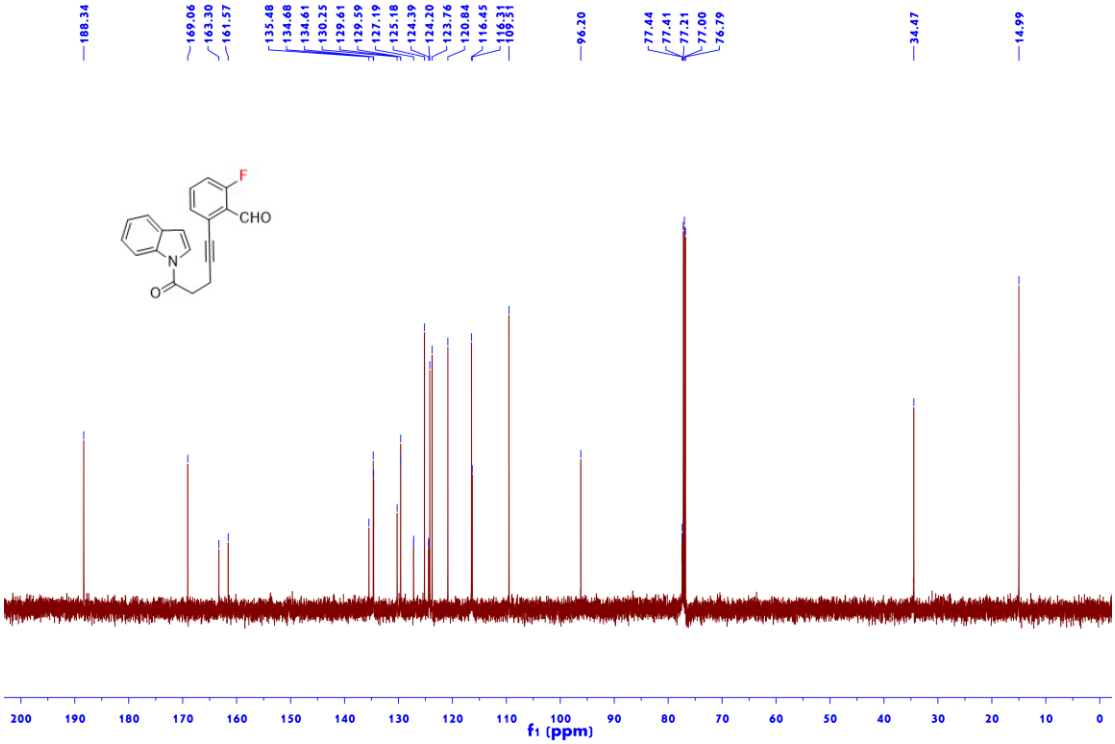


Figure S43 ^{19}F NMR (565 MHz, $CDCl_3$) of **1t**

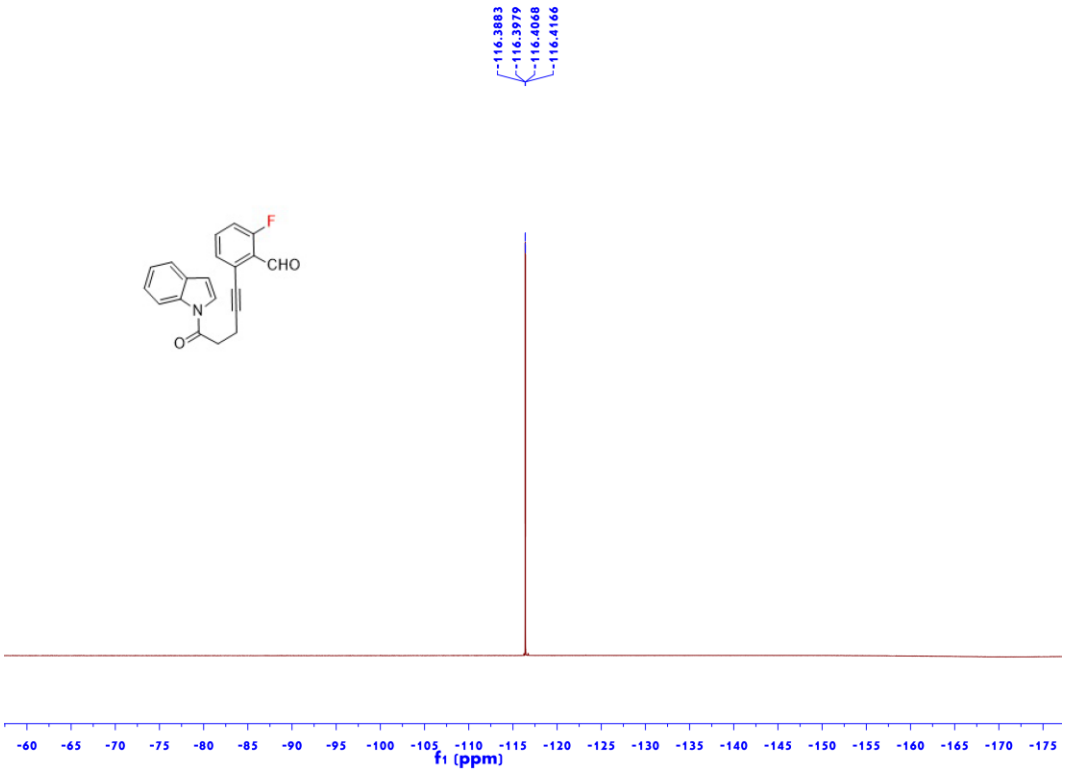


Figure S44 ^{1}H NMR (600 MHz, $CDCl_3$) of **1u**

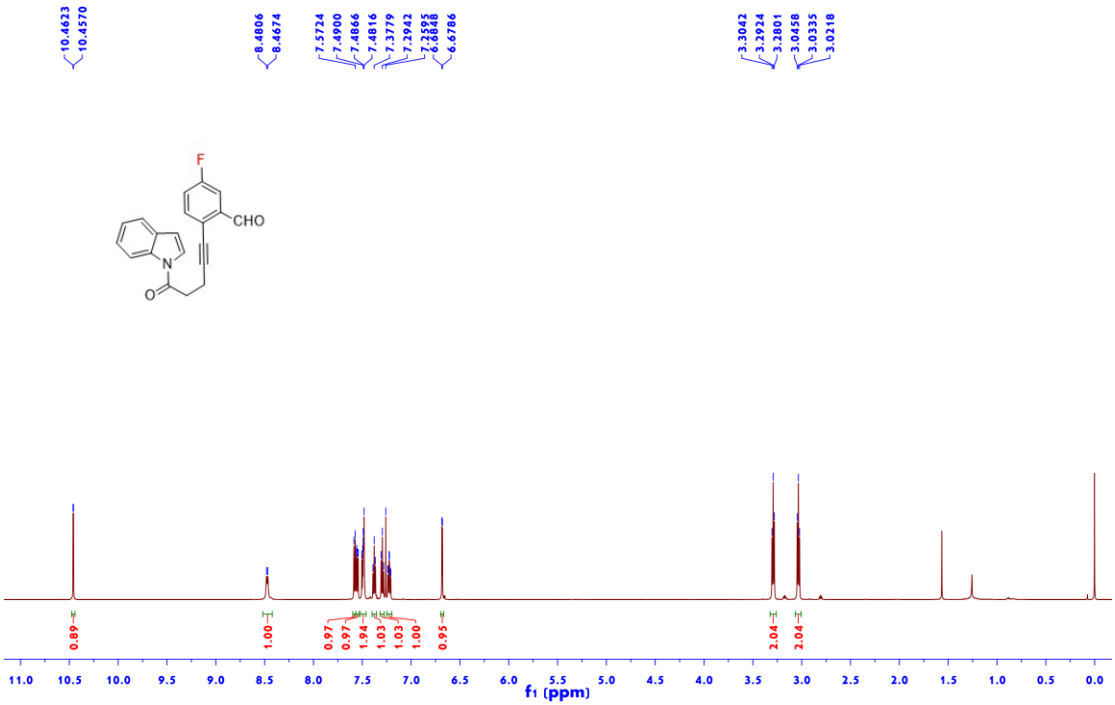


Figure S45 ^{13}C NMR (150 MHz, $CDCl_3$) of **1u**

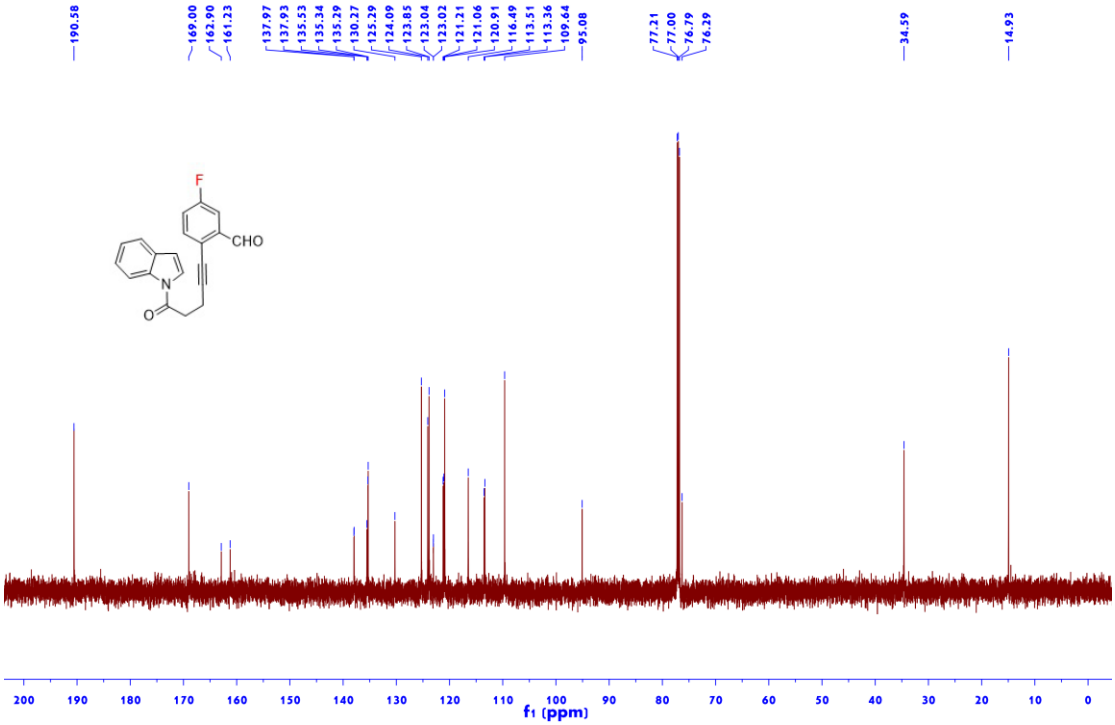


Figure S46 ^{19}F NMR (565 MHz, $CDCl_3$) of **1u**

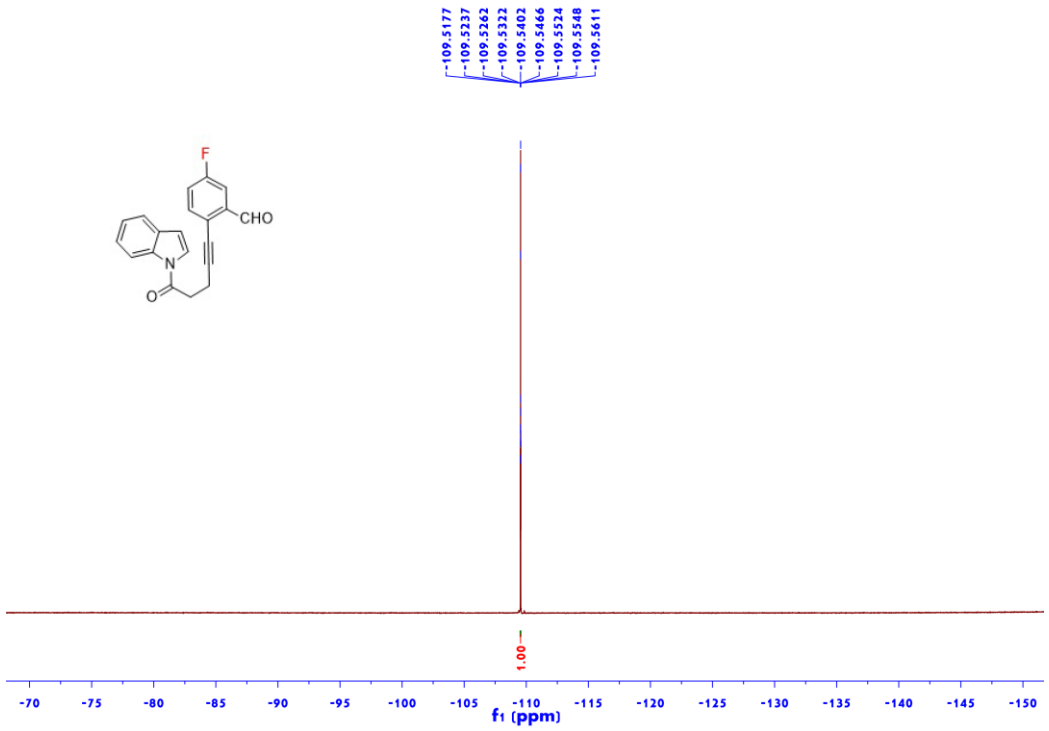


Figure S47 ^{1}H NMR (600 MHz, $CDCl_3$) of **1v**

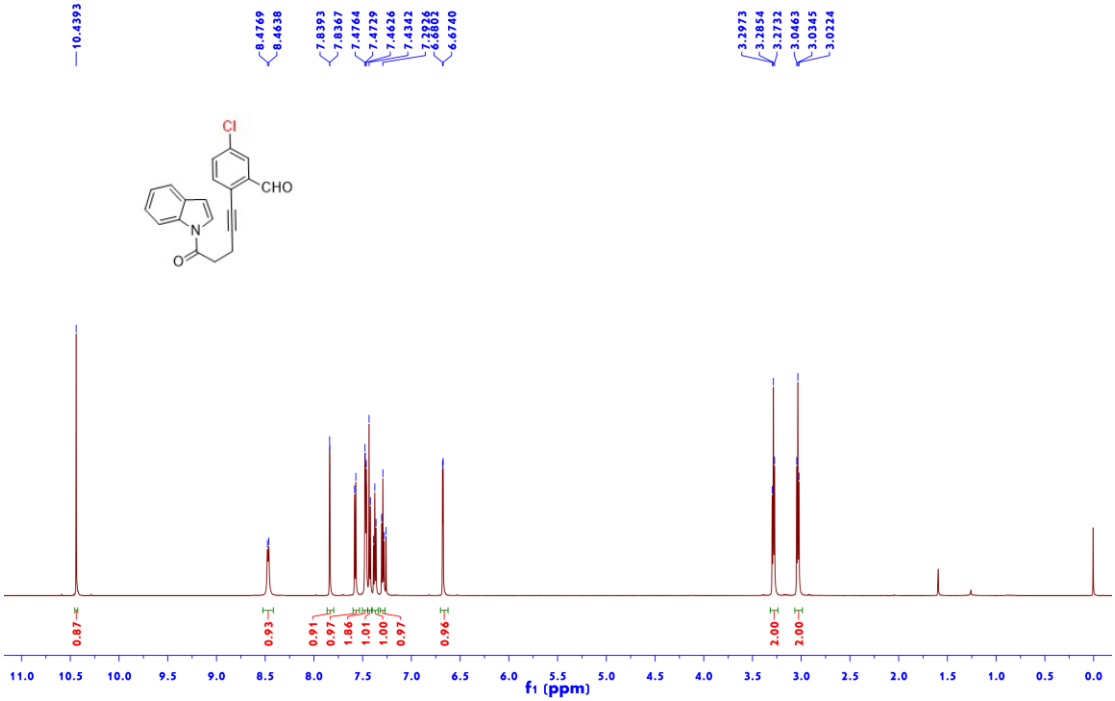


Figure S48 ^{13}C NMR (150 MHz, $CDCl_3$) of **1v**

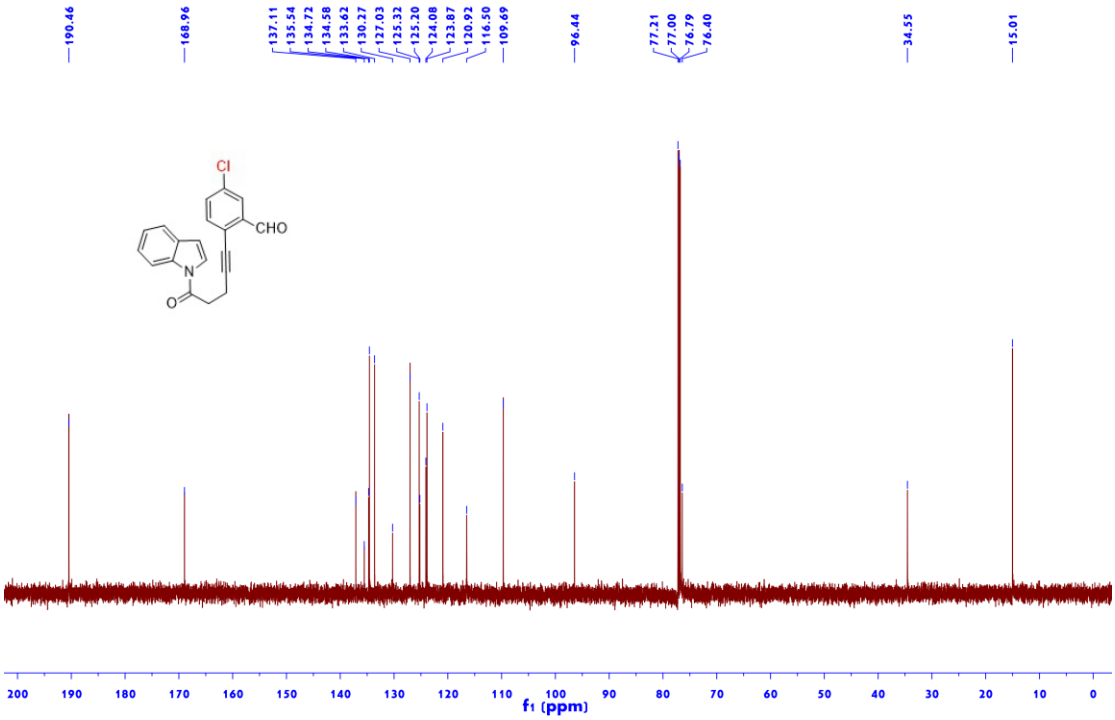


Figure S49 ^{1}H NMR (600 MHz, $CDCl_3$) of **1w**

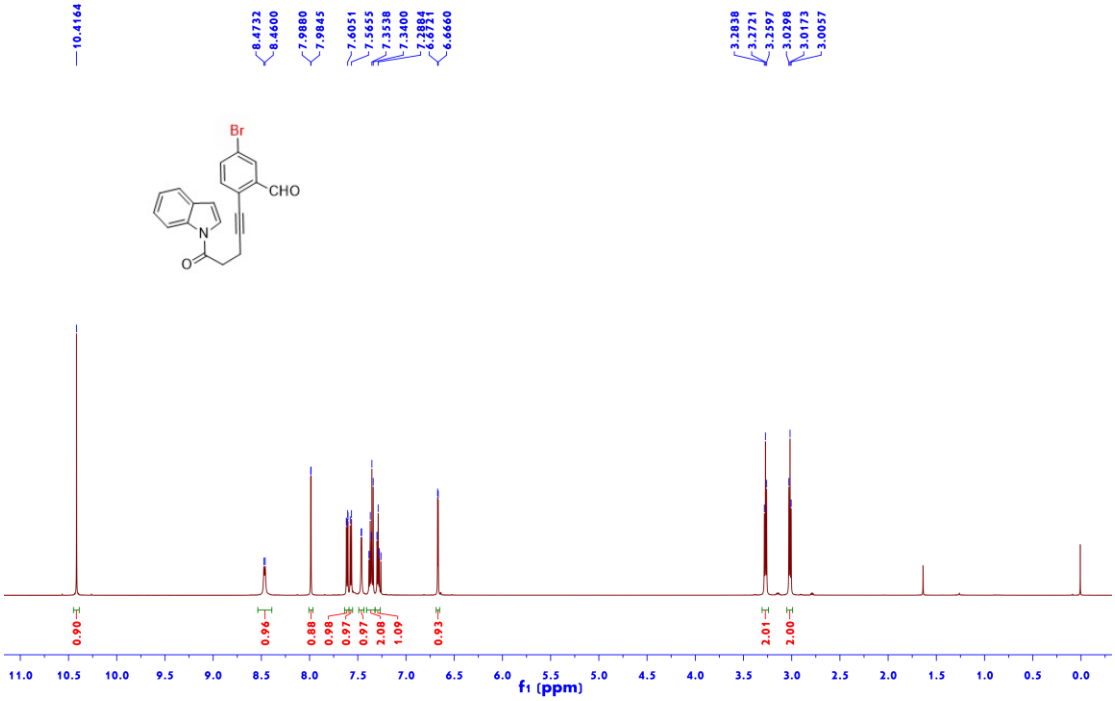


Figure S50 ^{13}C NMR (150 MHz, $CDCl_3$) of **1w**

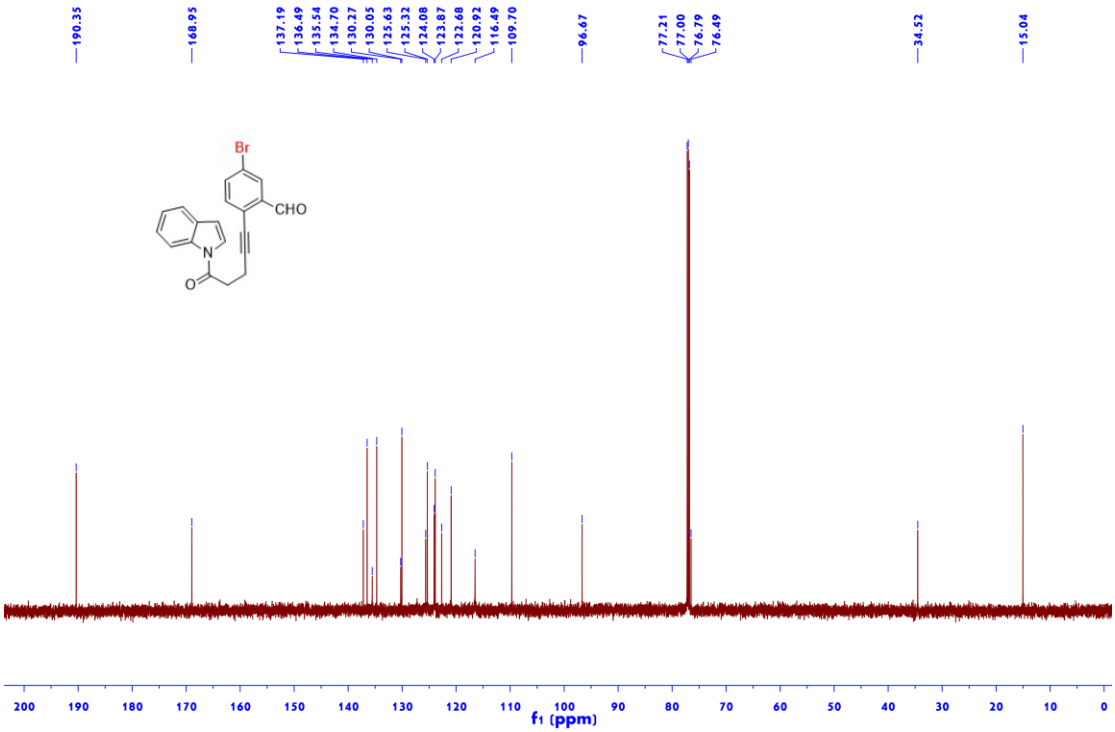


Figure S51 ^{1}H NMR (600 MHz, $CDCl_3$) of **1x**

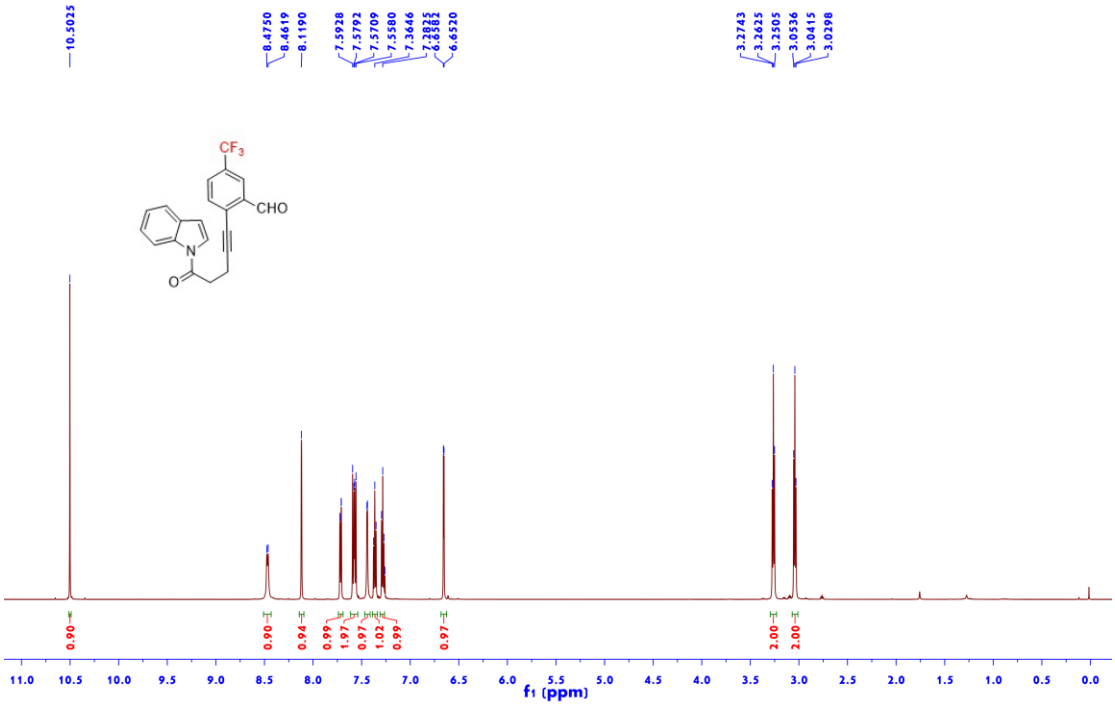


Figure S52 ^{13}C NMR (150 MHz, $CDCl_3$) of **1x**

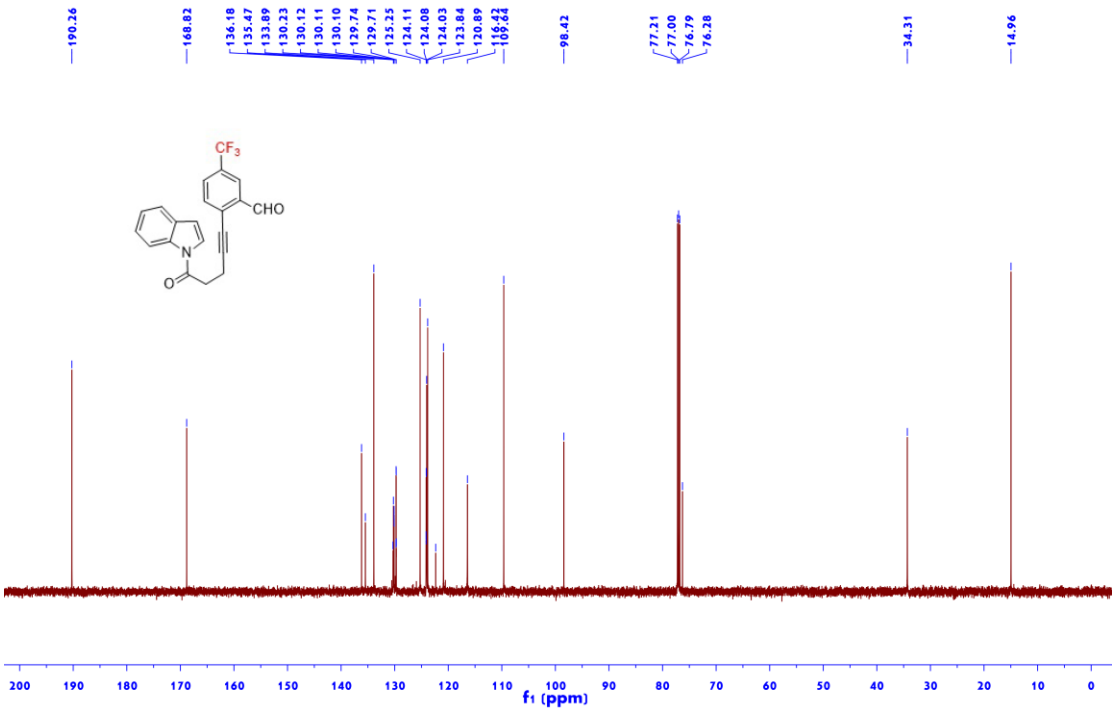


Figure S53 ^{19}F NMR (565 MHz, $CDCl_3$) of **1x**

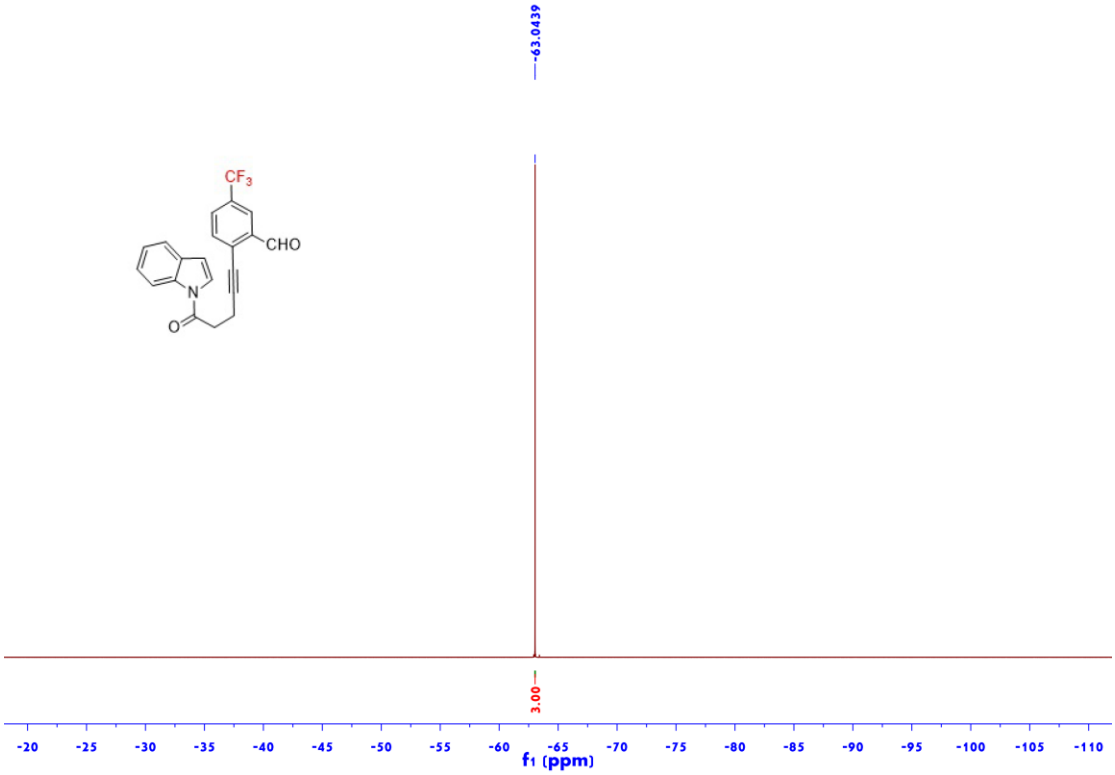


Figure S54 ^{1}H NMR (600 MHz, $CDCl_3$) of **1y**

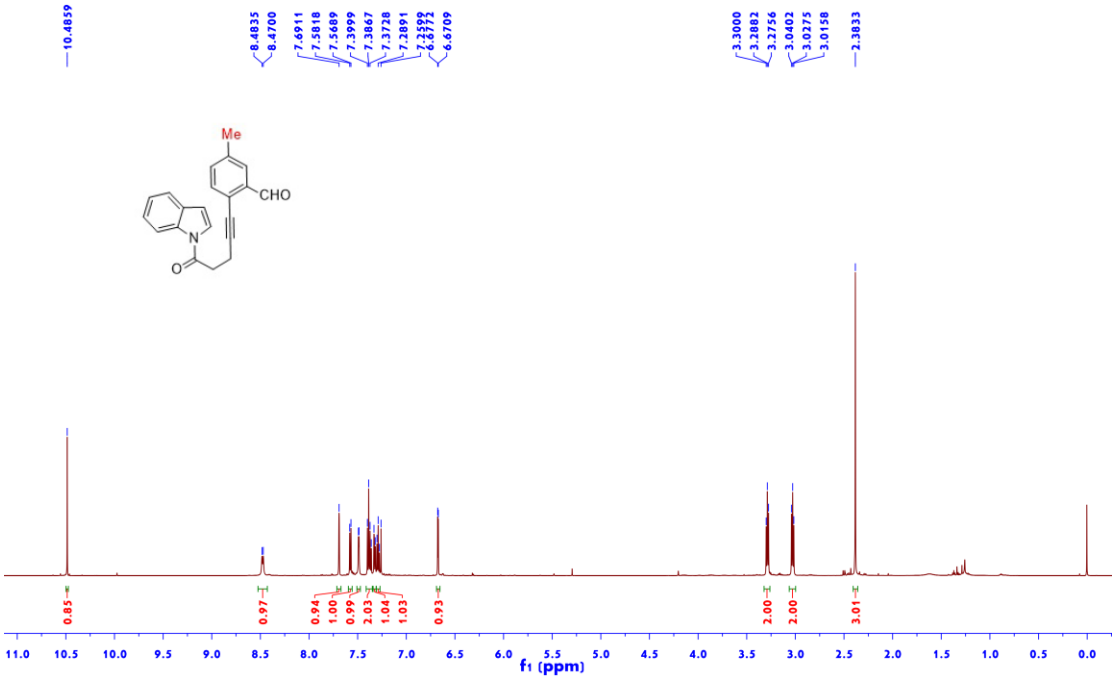


Figure S55 ^{13}C NMR (150 MHz, $CDCl_3$) of **1y**

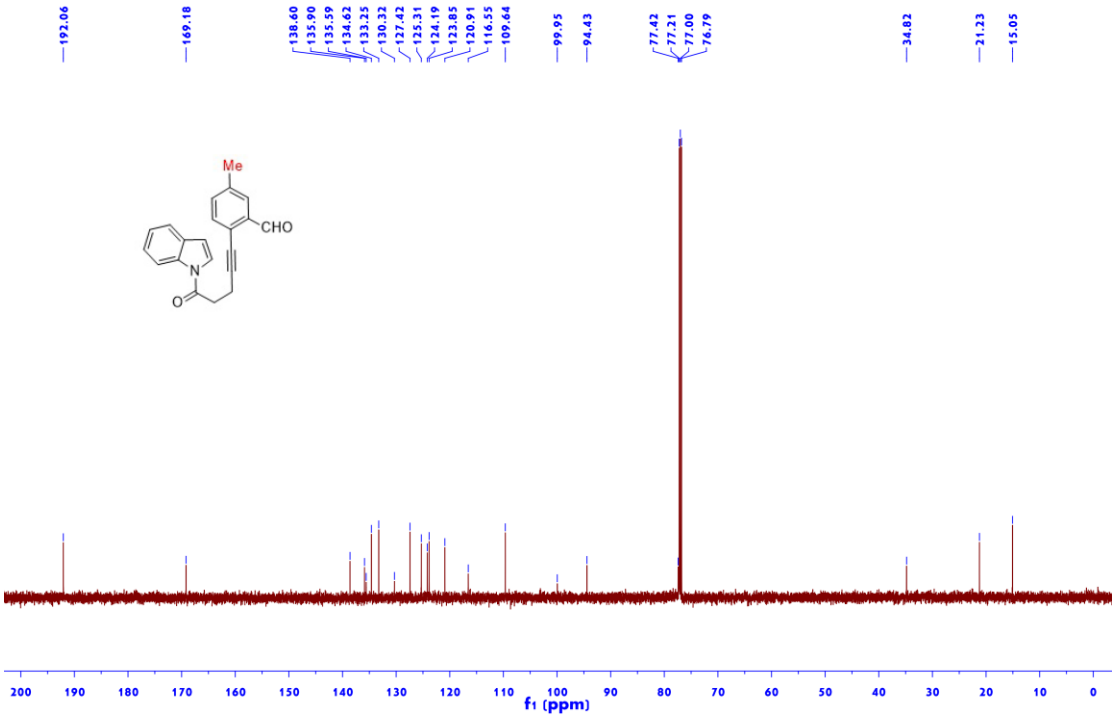


Figure S56 ^{1}H NMR (600 MHz, $CDCl_3$) of **1z**

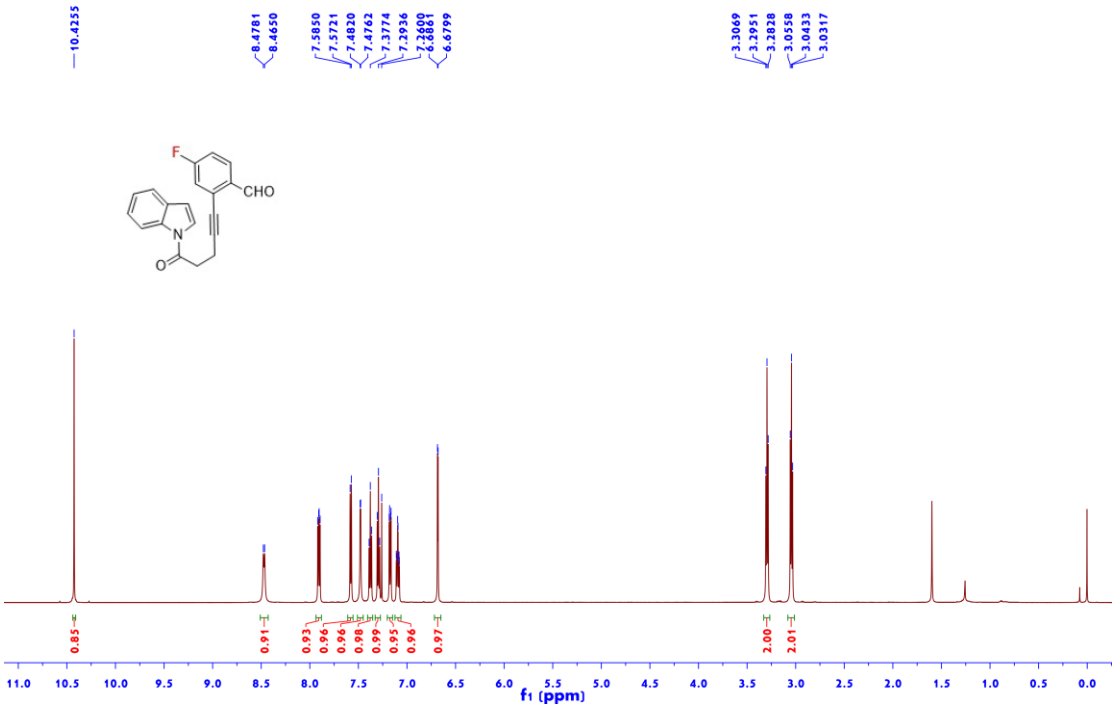


Figure S57 ^{13}C NMR (150 MHz, $CDCl_3$) of **1z**

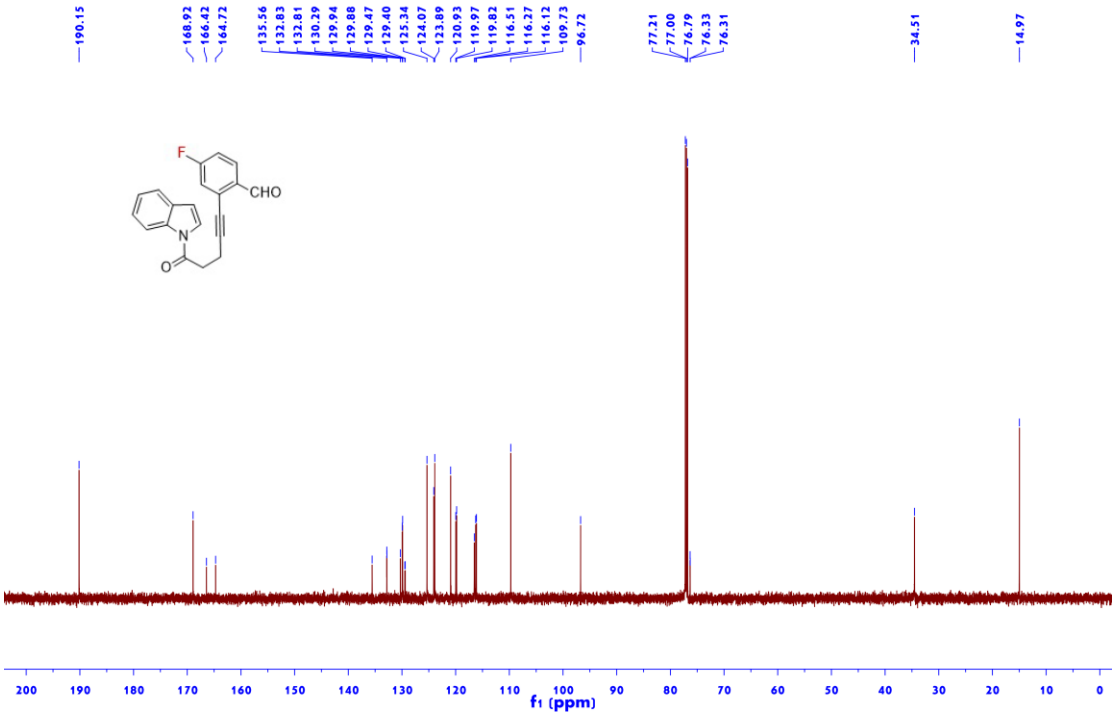


Figure S58 ^{19}F NMR (565 MHz, $CDCl_3$) of **1z**

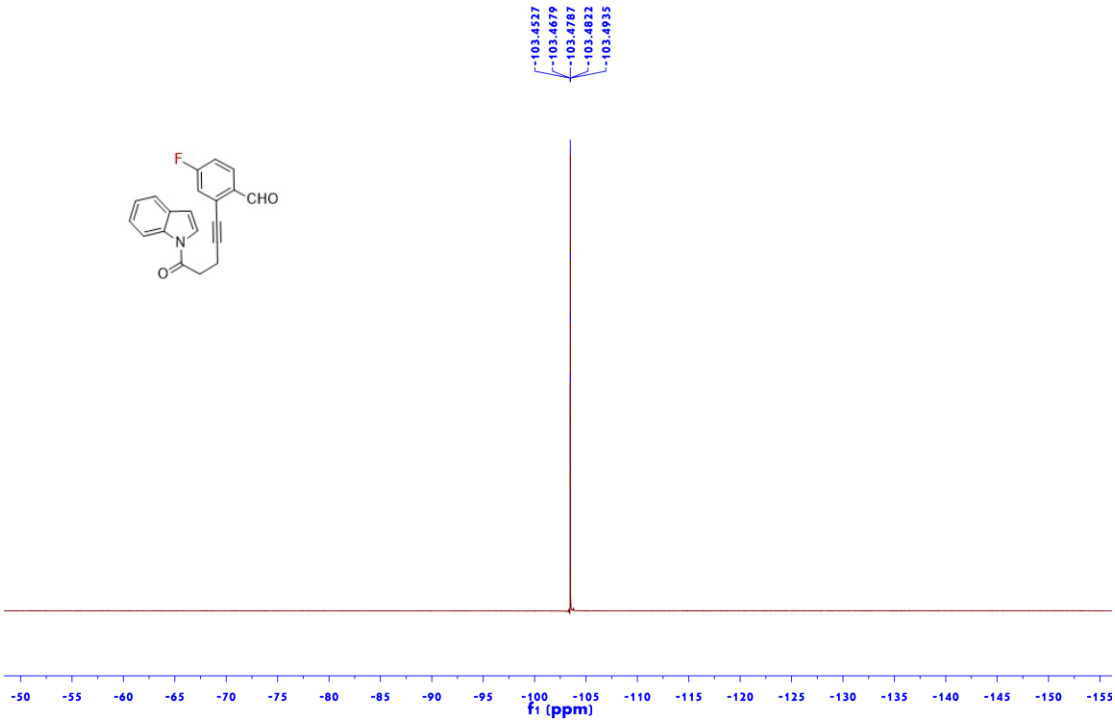


Figure S59 ^{1}H NMR (600 MHz, $CDCl_3$) of **1aa**

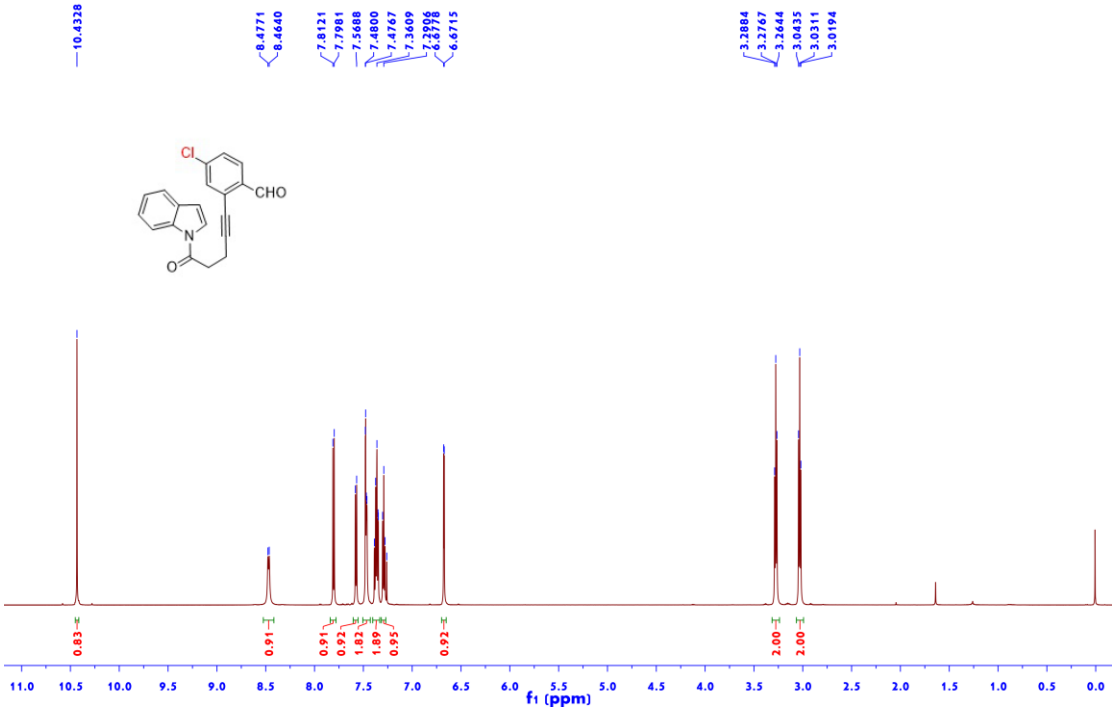


Figure S60 ^{13}C NMR (150 MHz, $CDCl_3$) of **1aa**

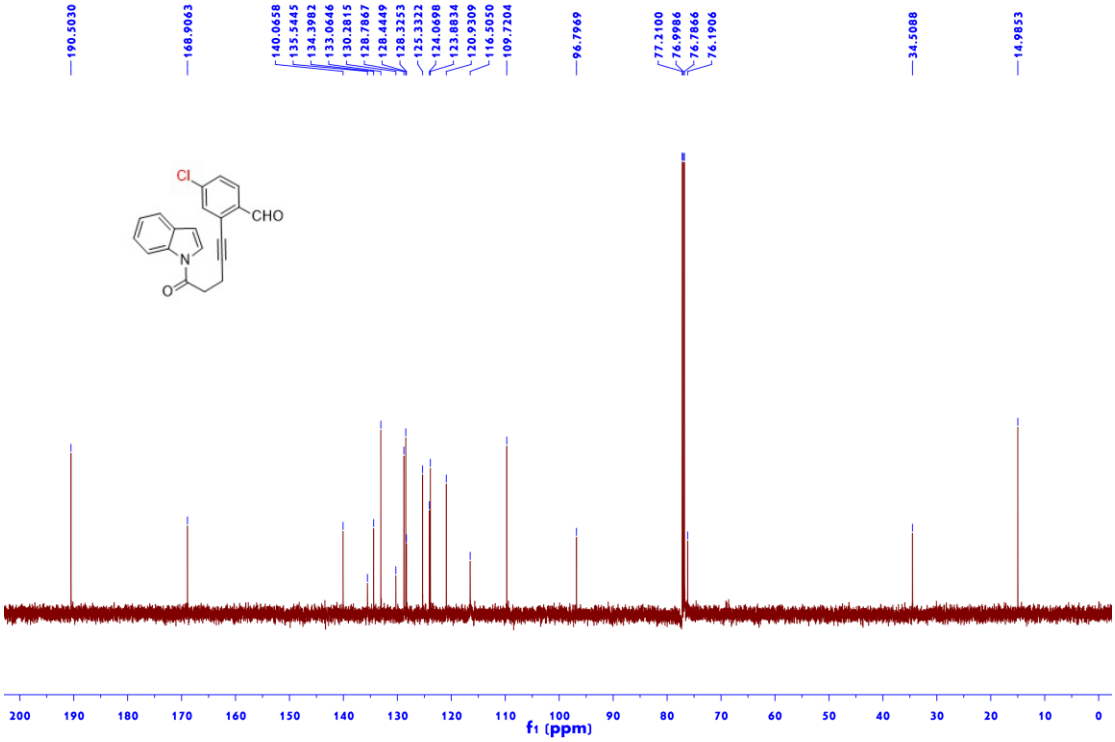


Figure S61 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ab**

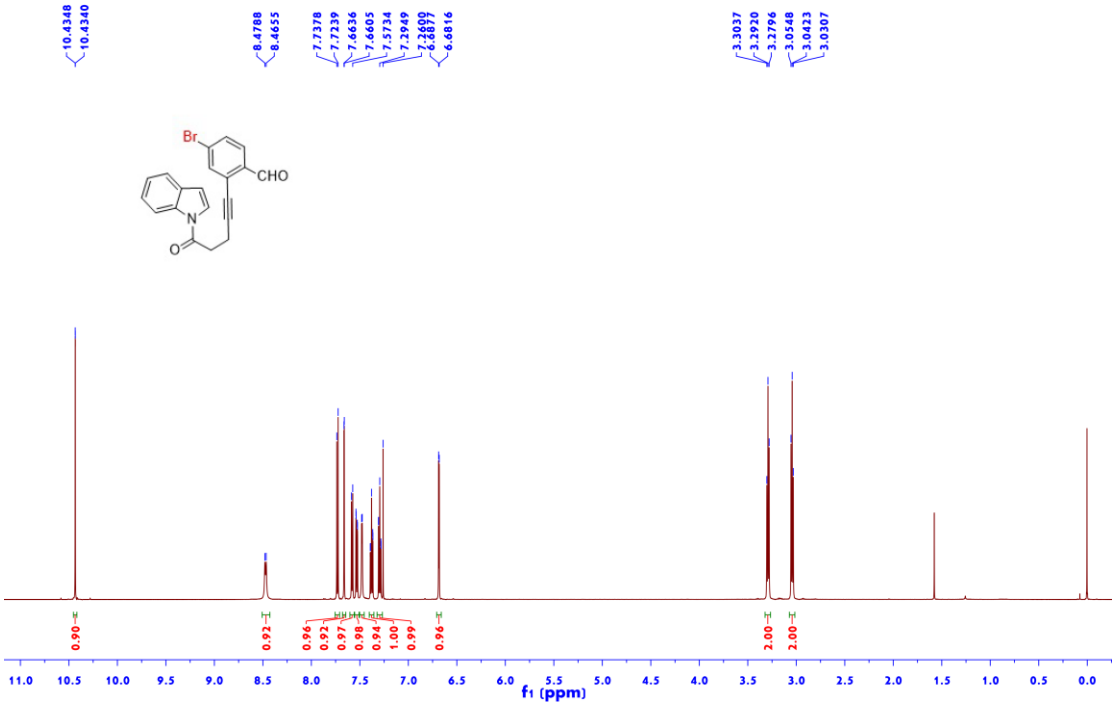


Figure S62 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ab**

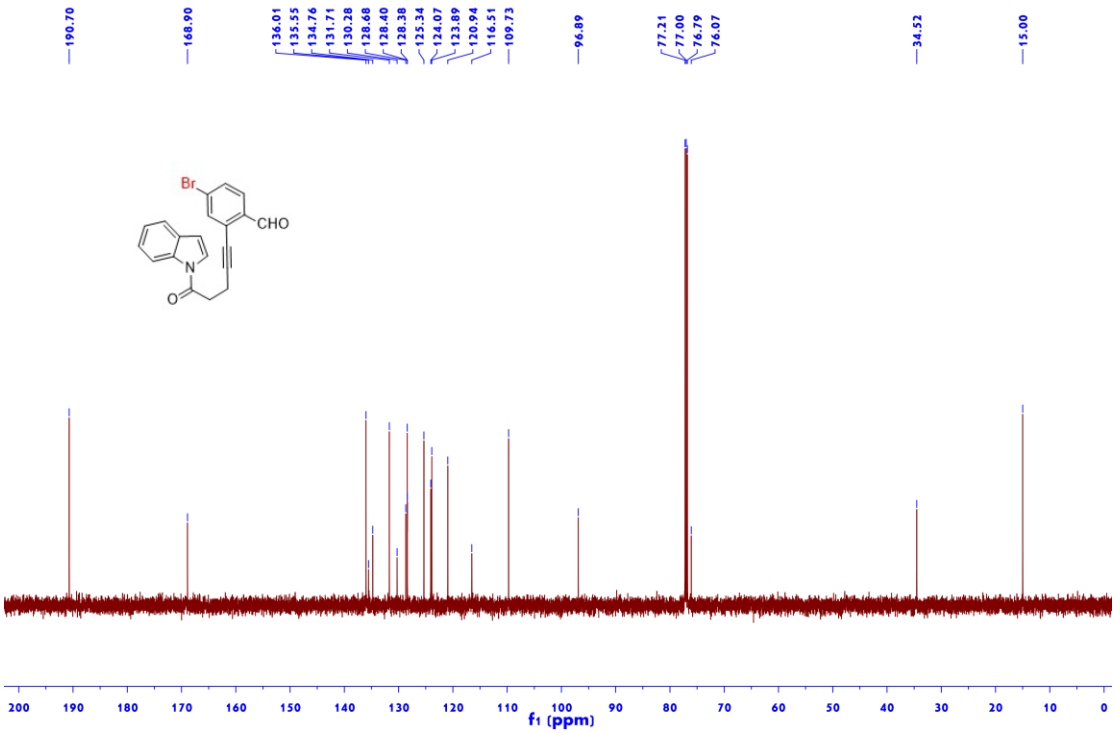


Figure S63 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ac**

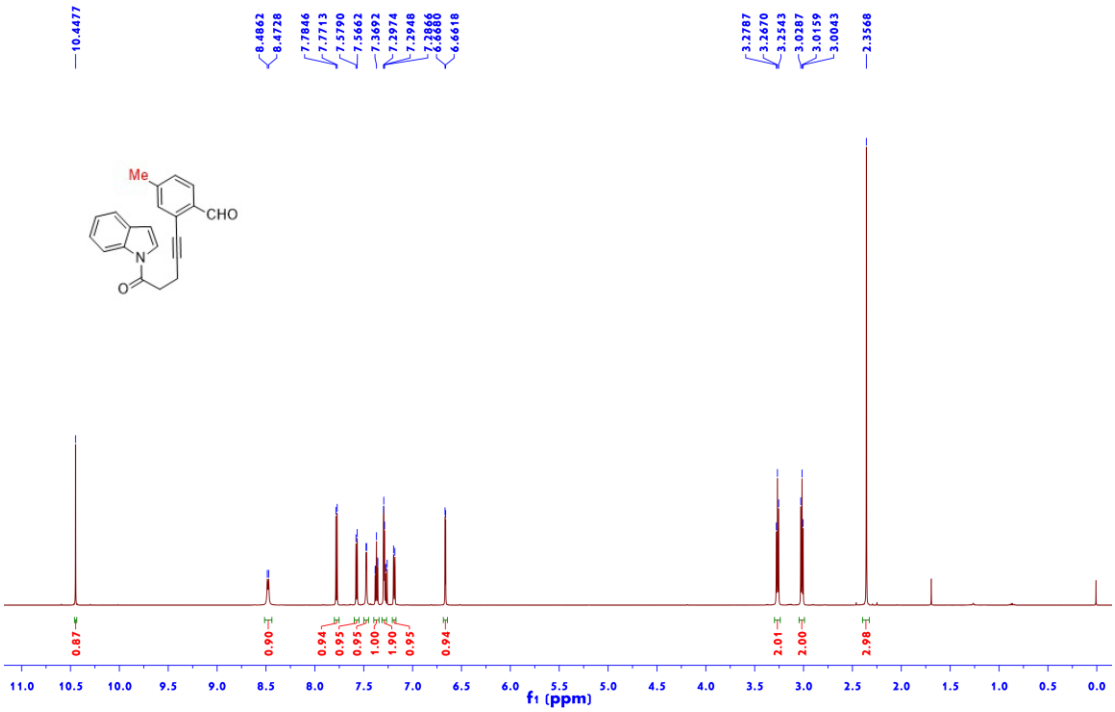


Figure S64 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ac**

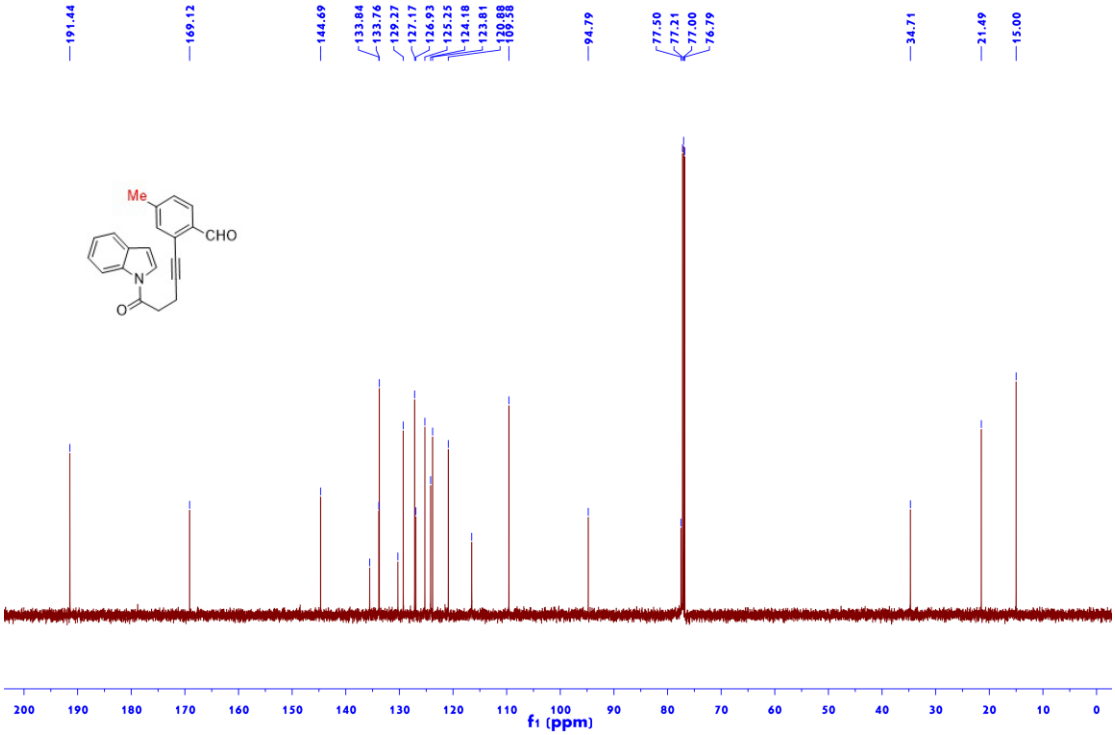


Figure S65 ^{1}H NMR (400 MHz, $CDCl_3$) of **1ad**

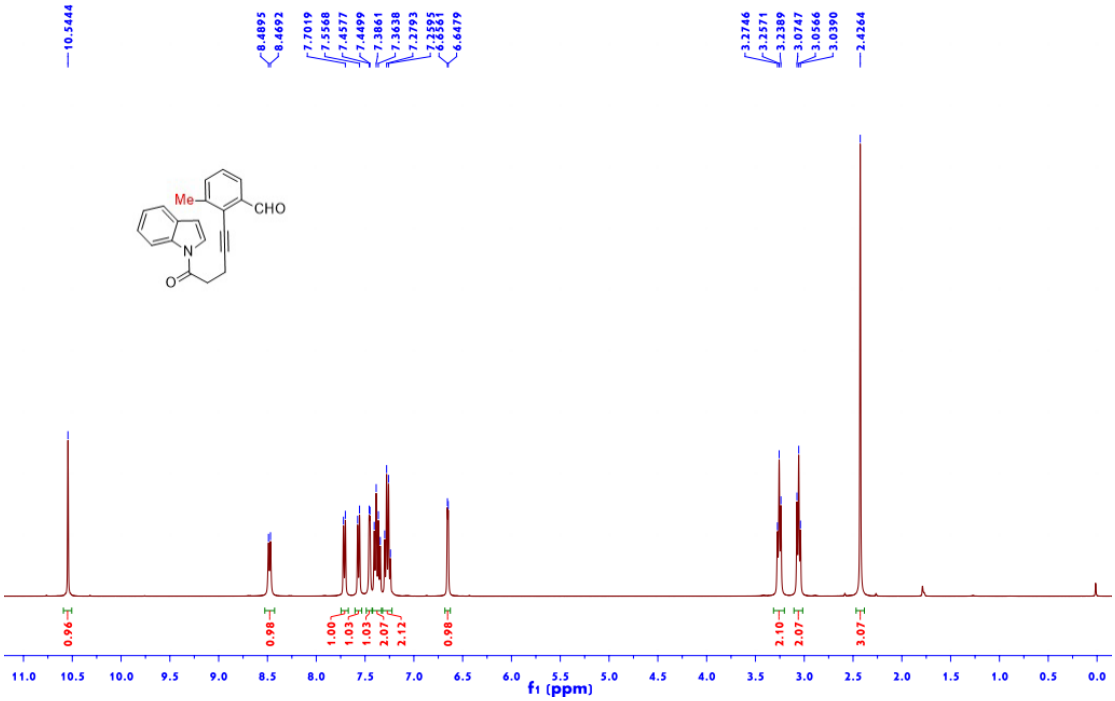


Figure S66 ^{13}C NMR (100 MHz, $CDCl_3$) of **1ad**

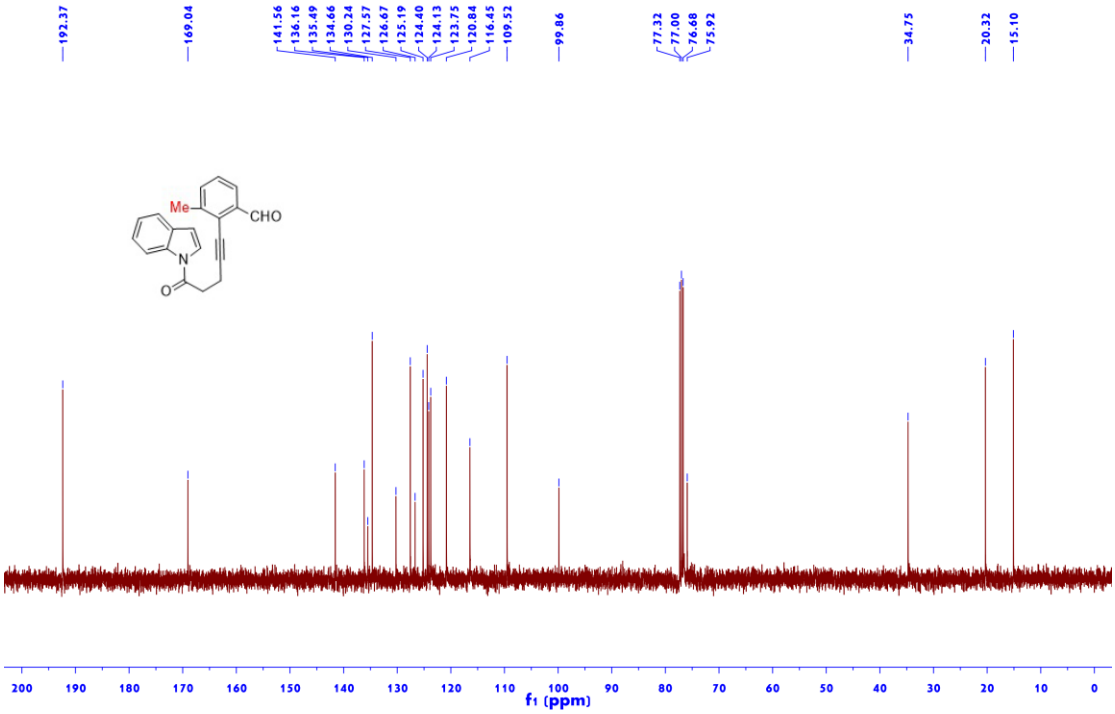


Figure S67 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ae**

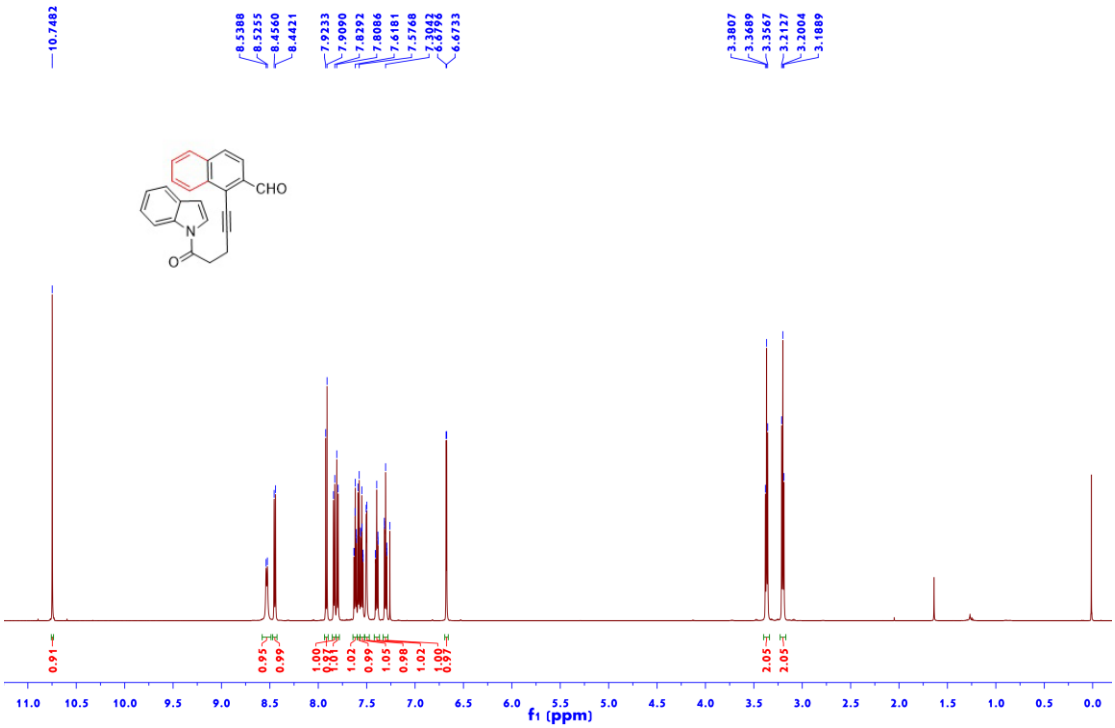


Figure S68 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ae**

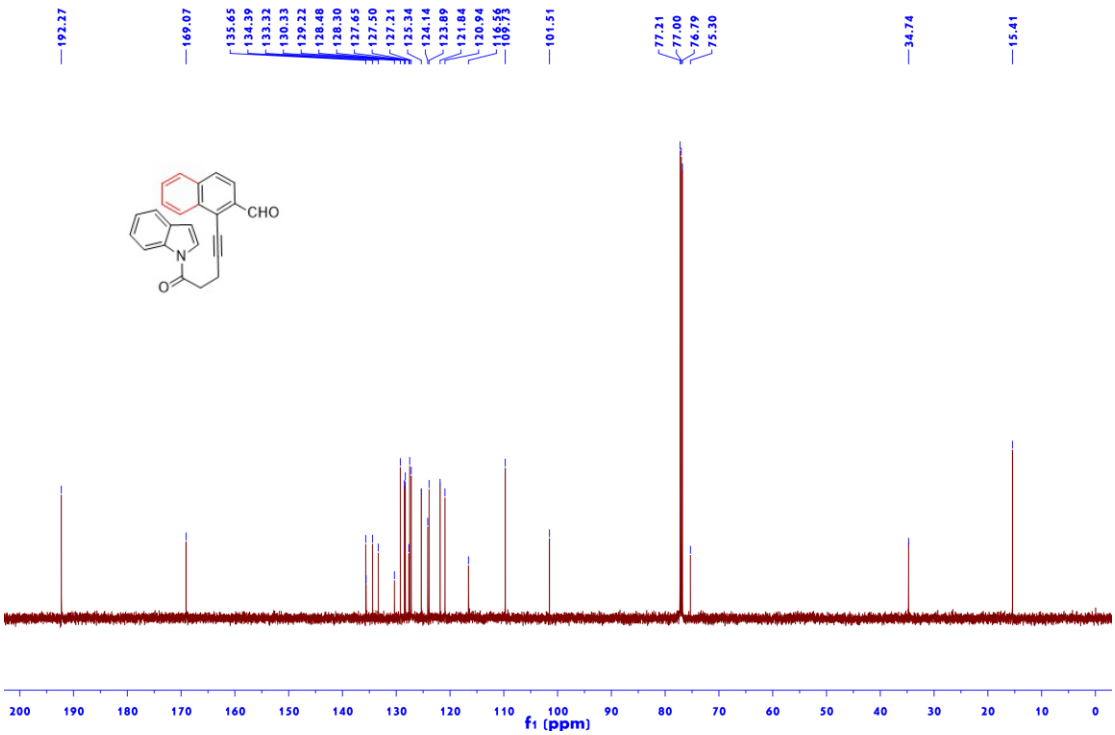


Figure S69 ^{1}H NMR (600 MHz, $CDCl_3$) of **1af**

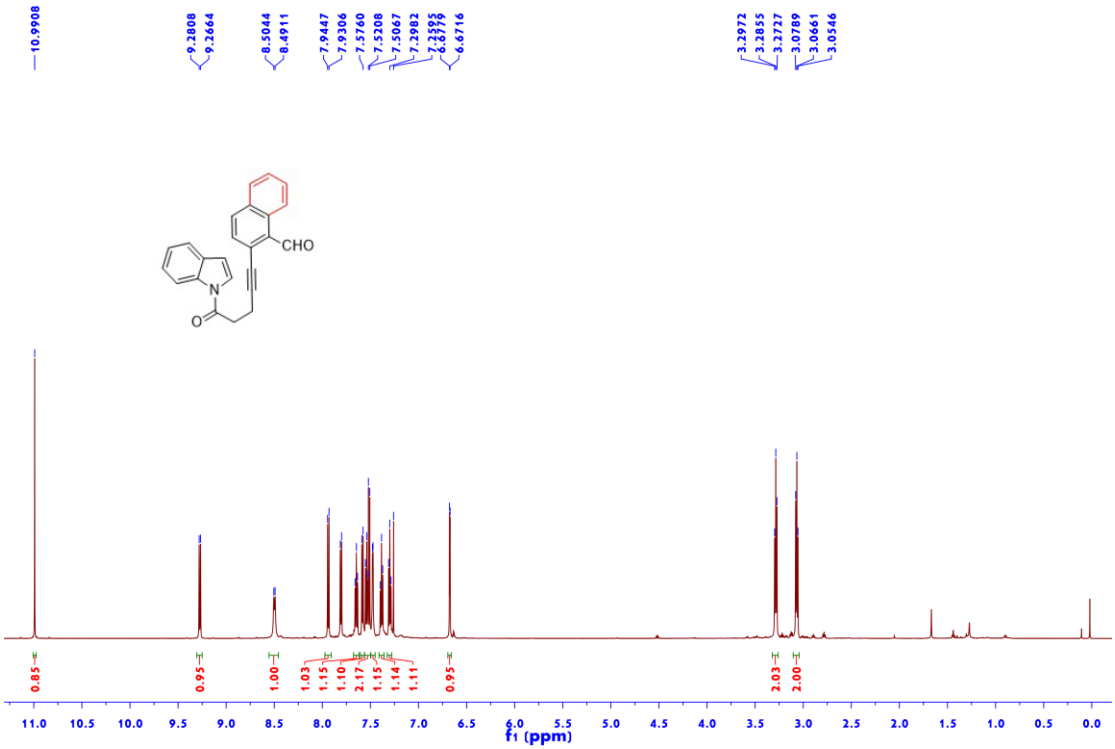


Figure S70 ^{13}C NMR (150 MHz, $CDCl_3$) of **1af**

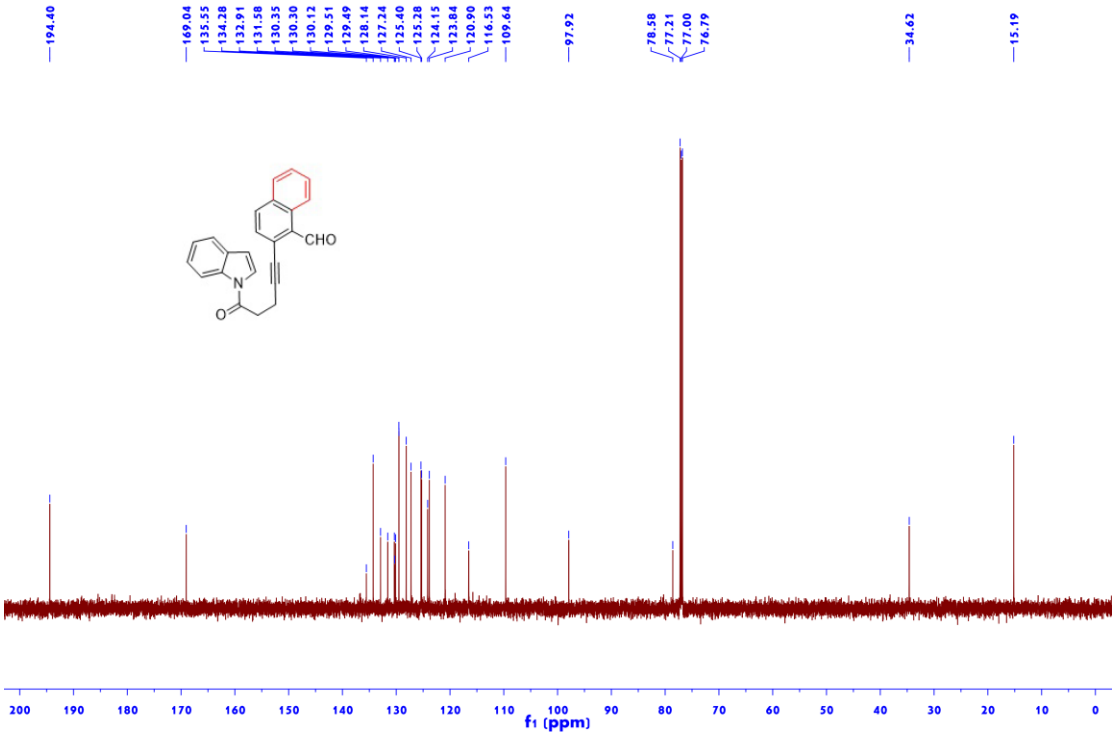


Figure 71 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ag**

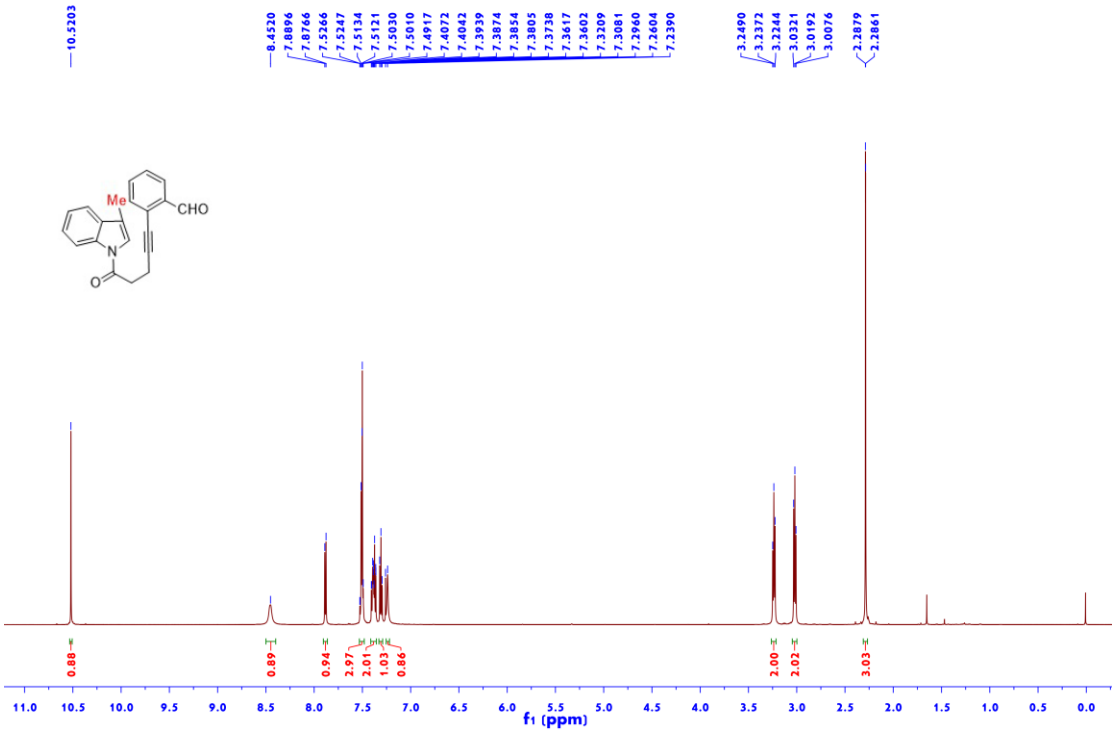


Figure 72 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ag**

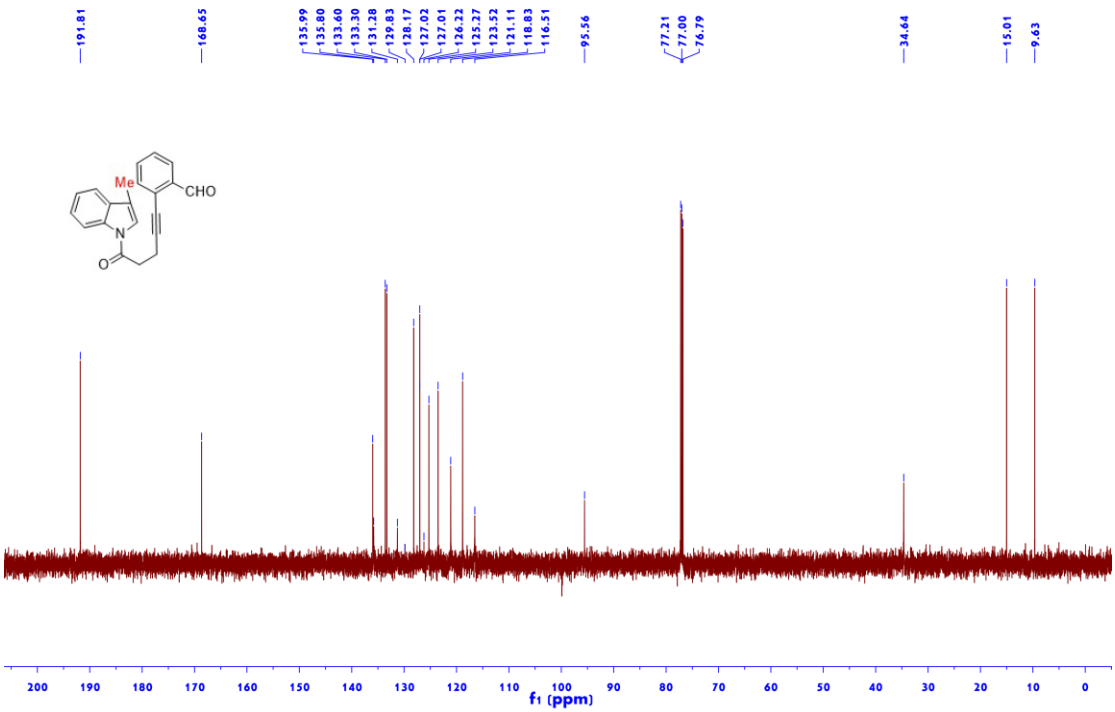


Figure S73 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ah**

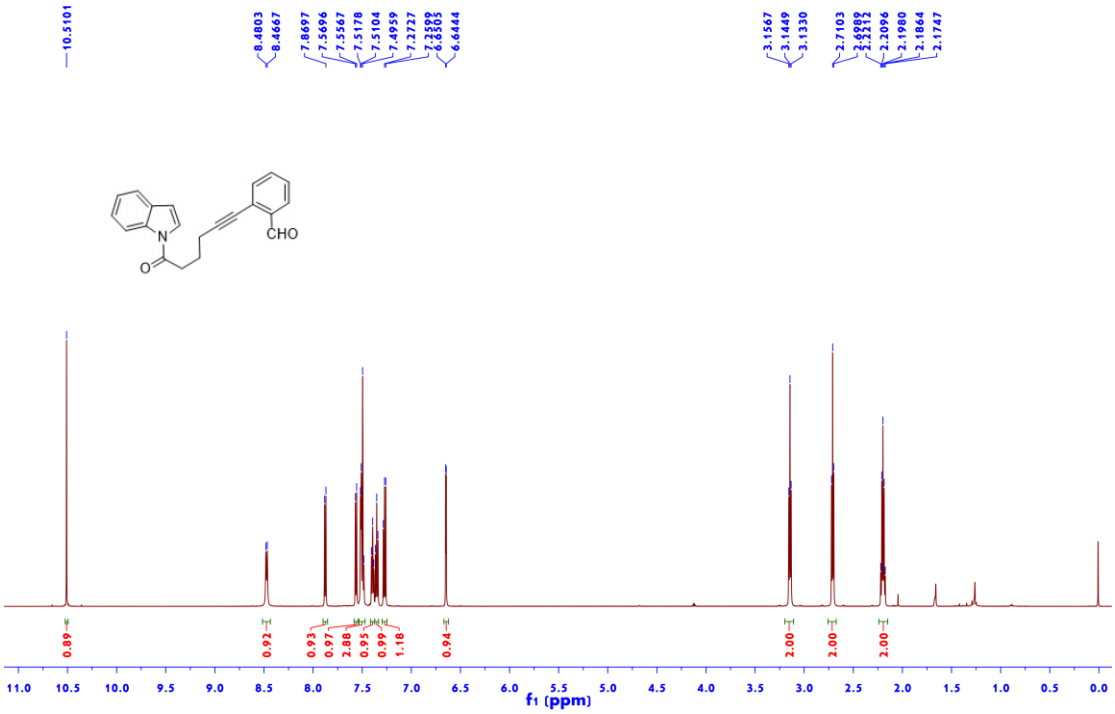


Figure S74 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ah**

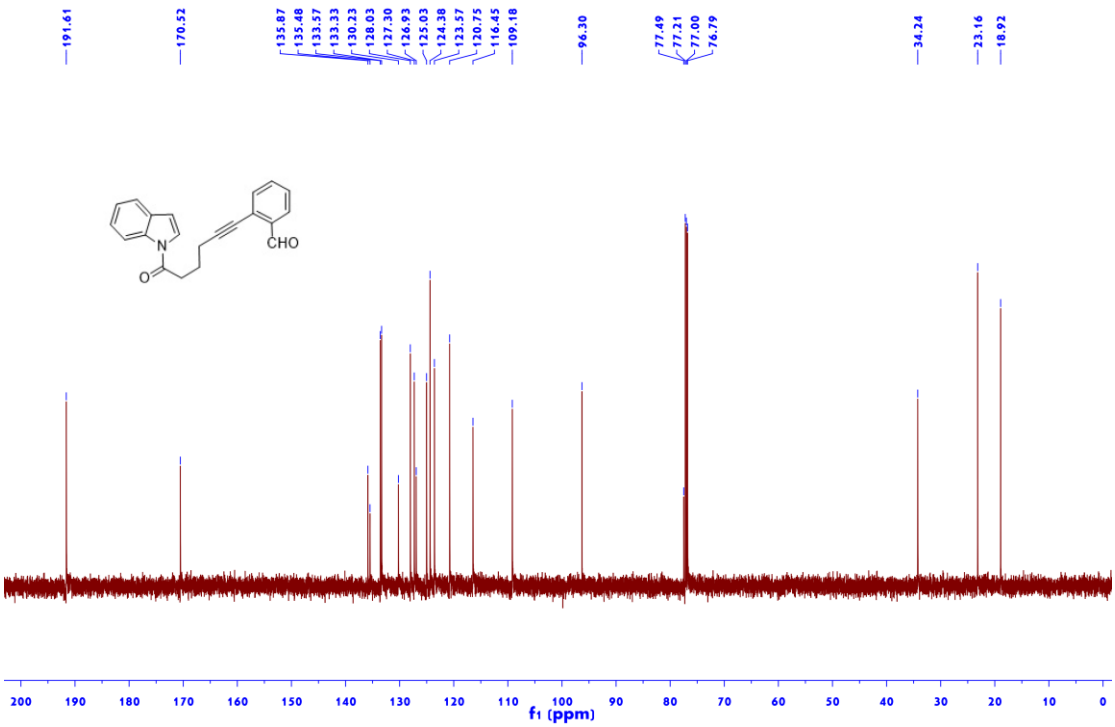


Figure S75 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ai**

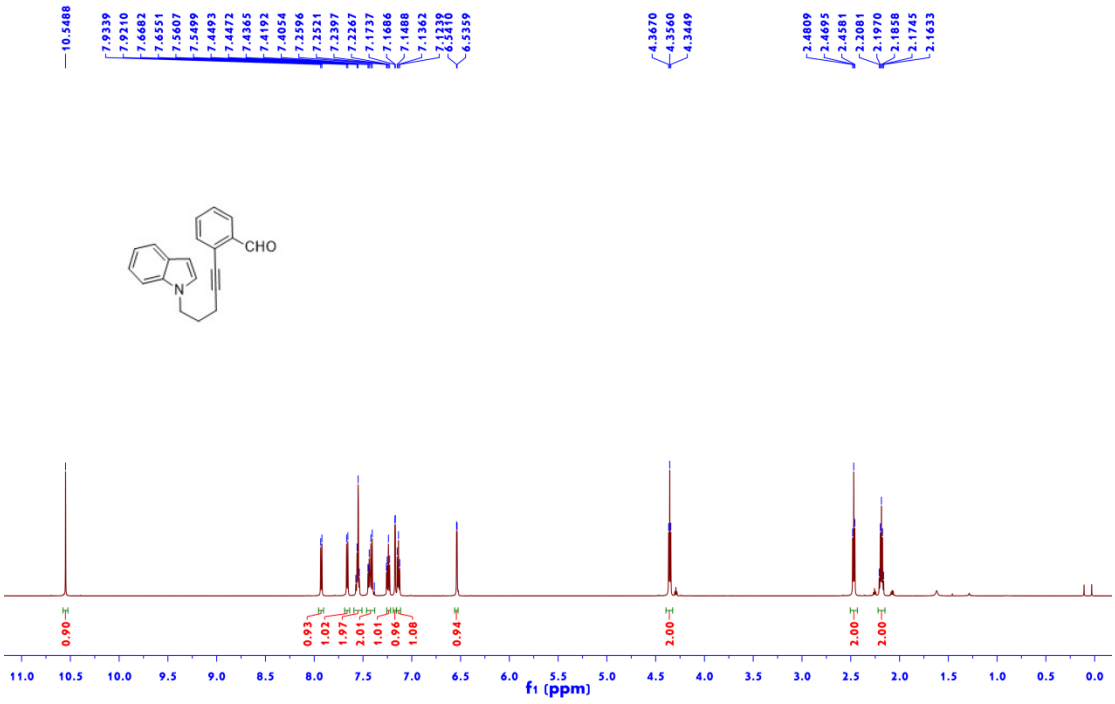


Figure S76 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ai**

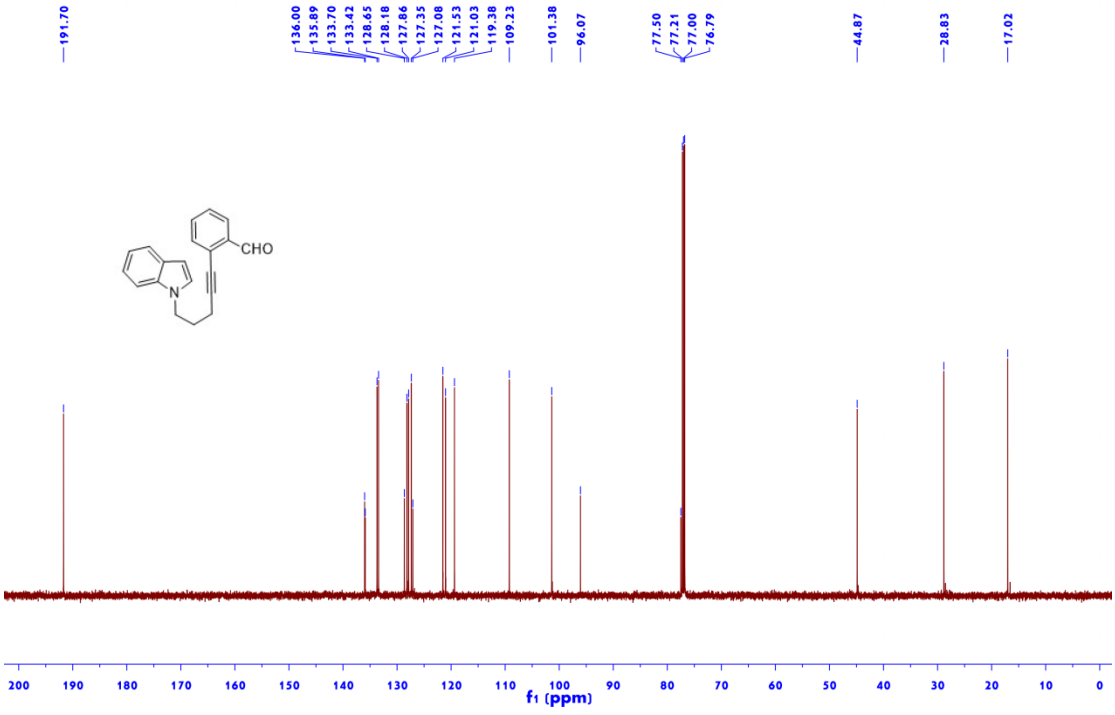


Figure S77 ^{1}H NMR (600 MHz, $CDCl_3$) of **1aj**

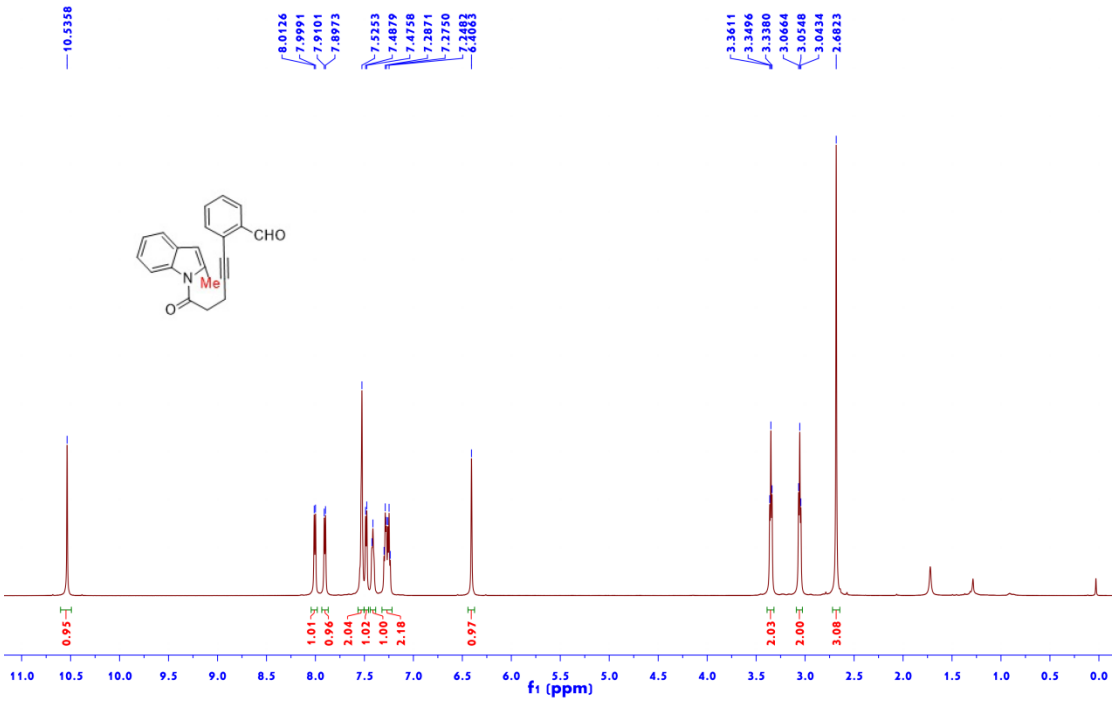


Figure S78 ^{13}C NMR (150 MHz, $CDCl_3$) of **1aj**

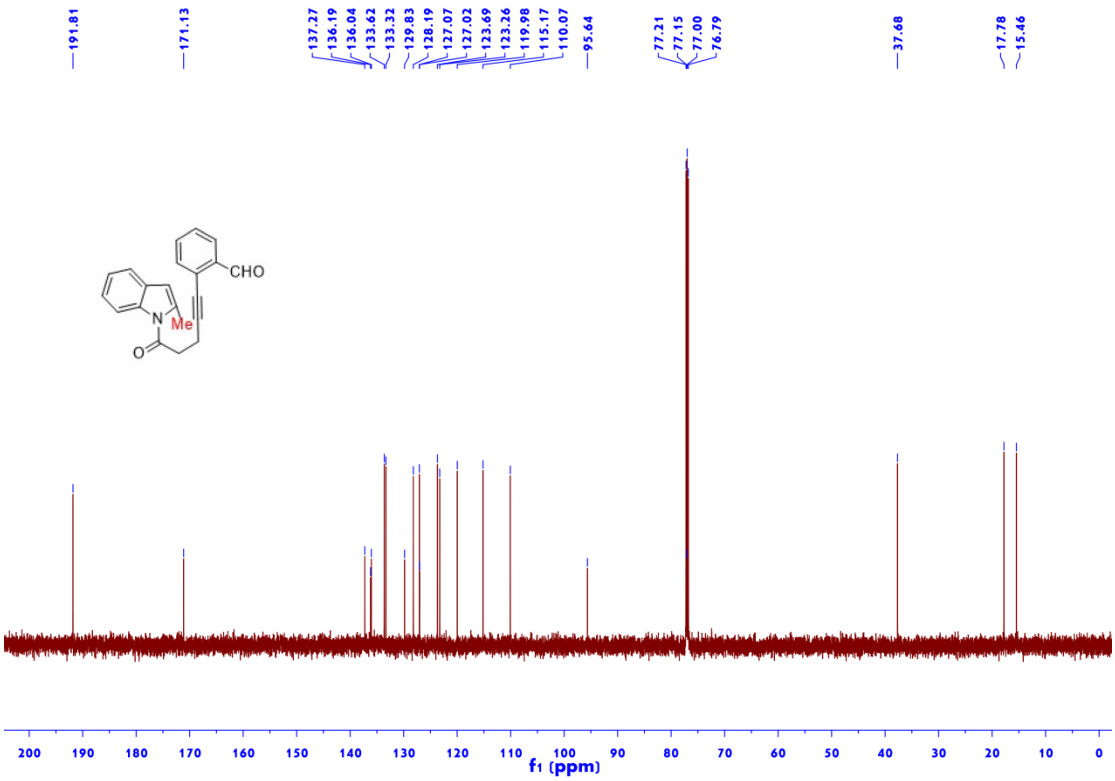


Figure S79 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ak**

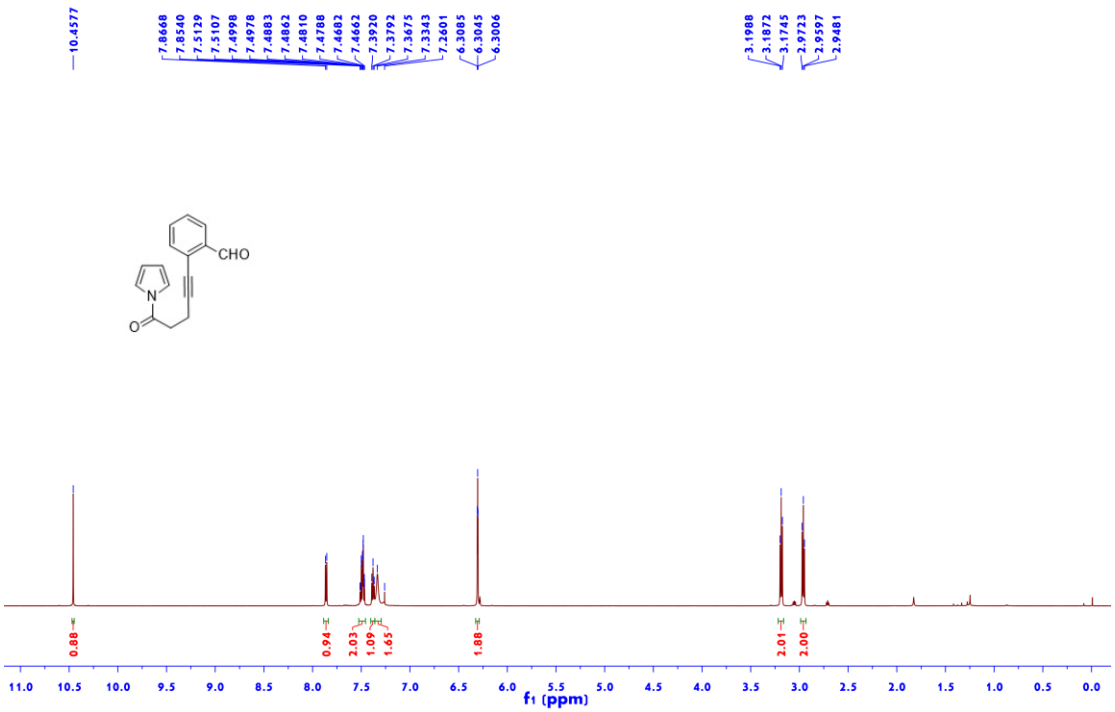


Figure S80 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ak**

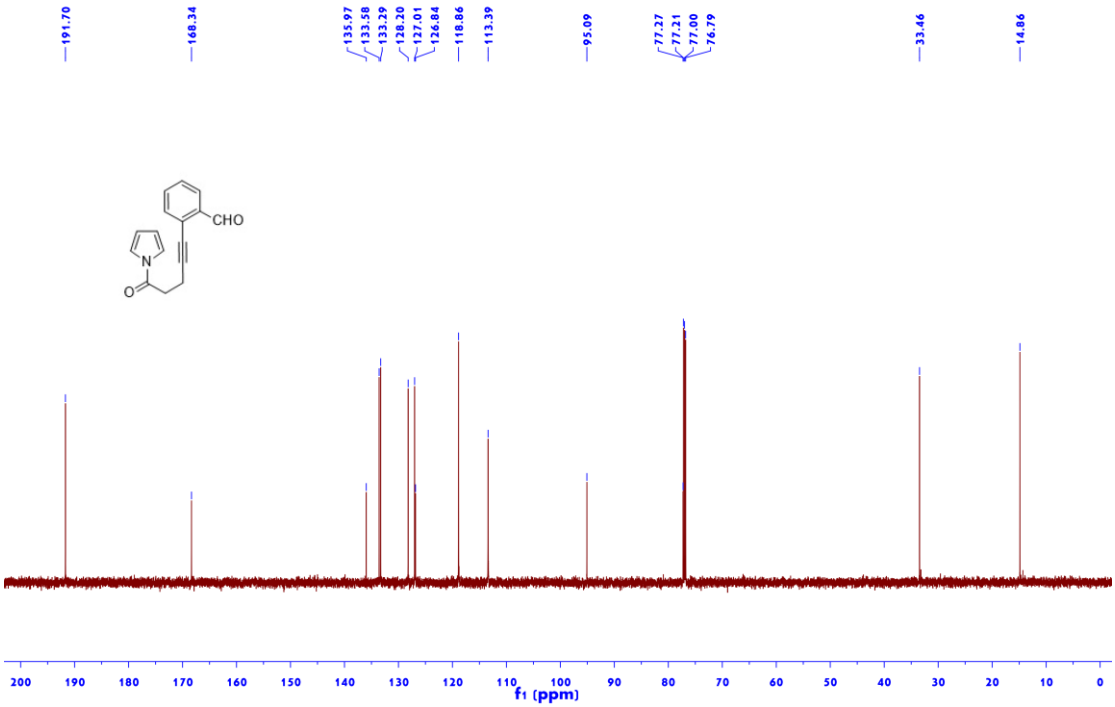


Figure S81 ^{1}H NMR (600 MHz, $CDCl_3$) of **1al**

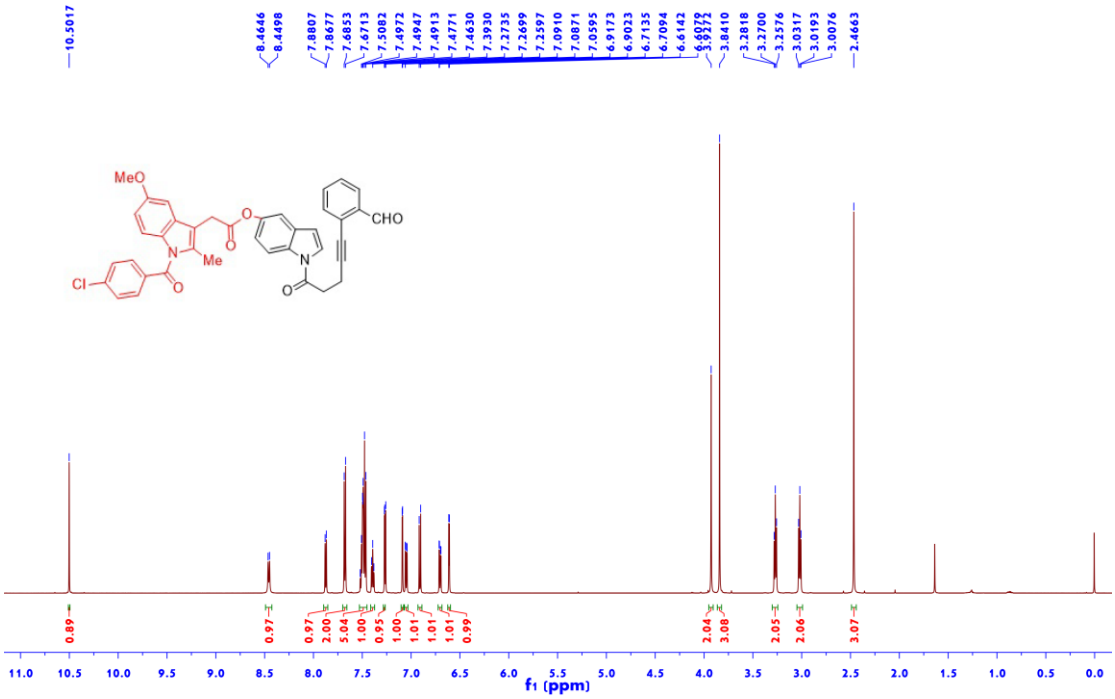


Figure S82 ^{13}C NMR (150 MHz, $CDCl_3$) of **1al**

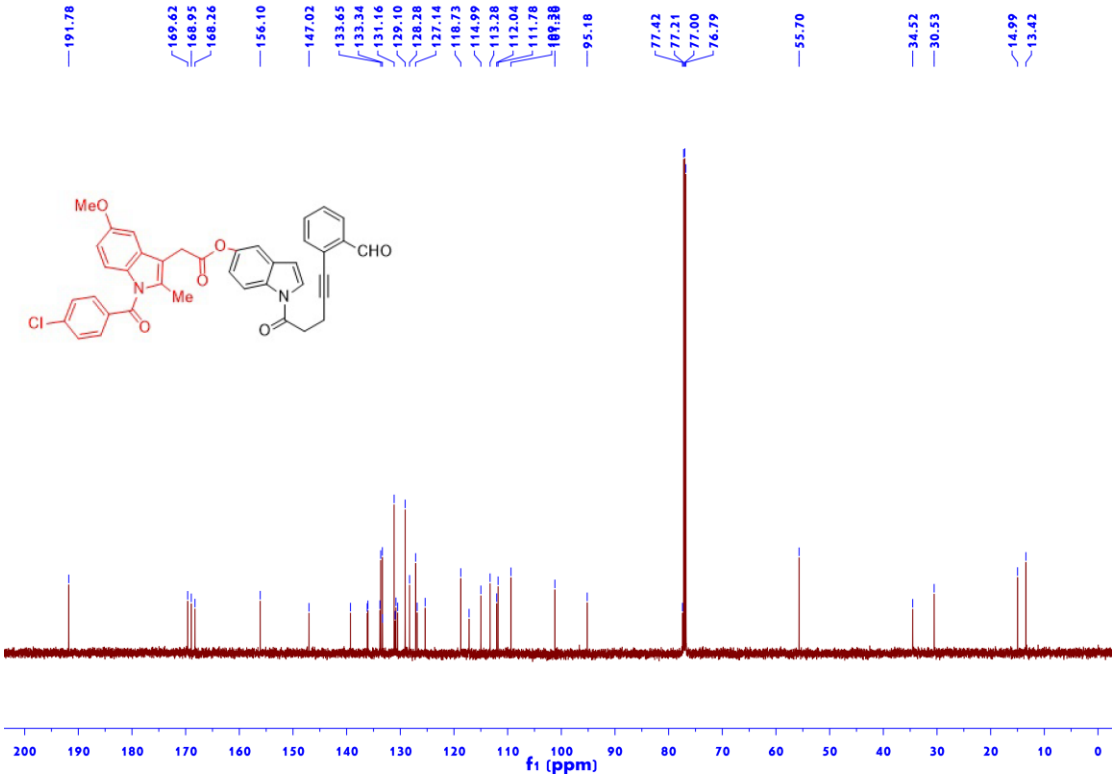


Figure S83 ^{1}H NMR (600 MHz, $CDCl_3$) of **1am**

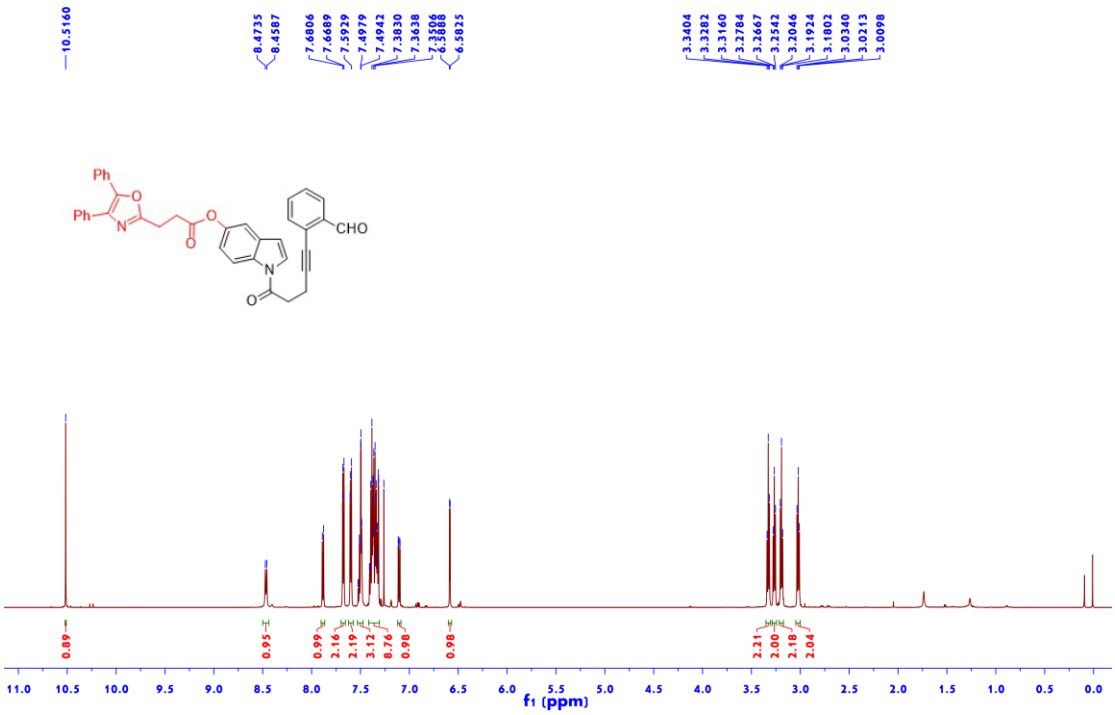


Figure S83 ^{13}C NMR (150 MHz, $CDCl_3$) of **1am**

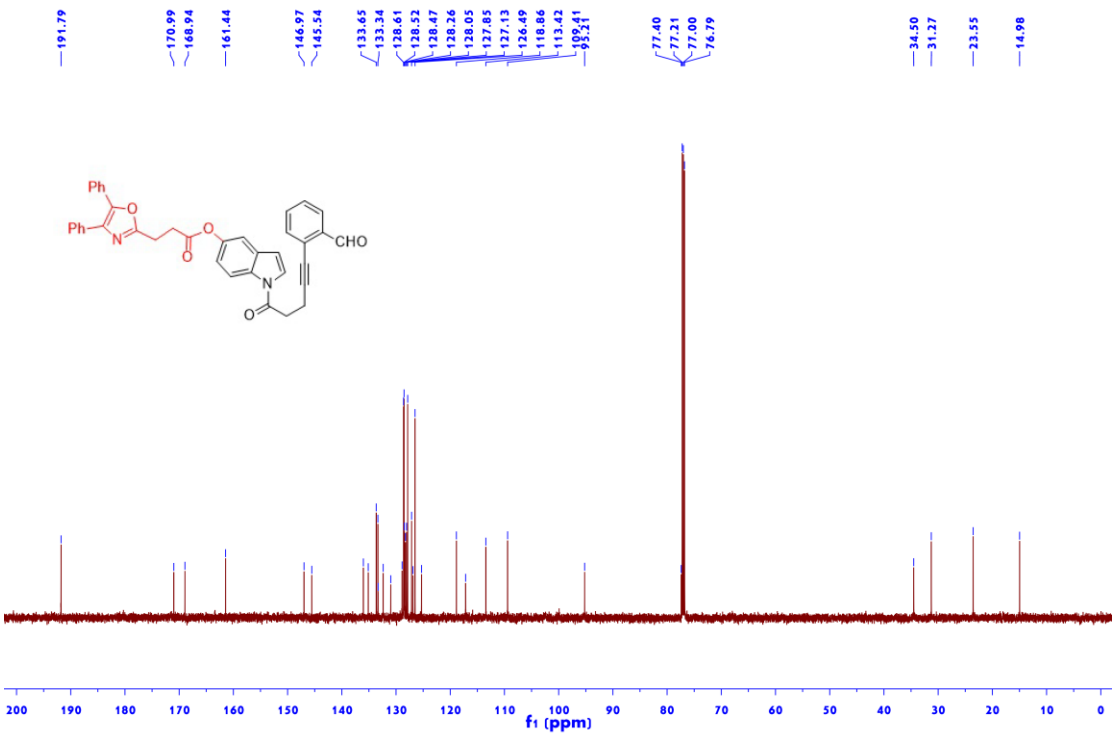


Figure S85 ^{1}H NMR (600 MHz, $CDCl_3$) of **1an**

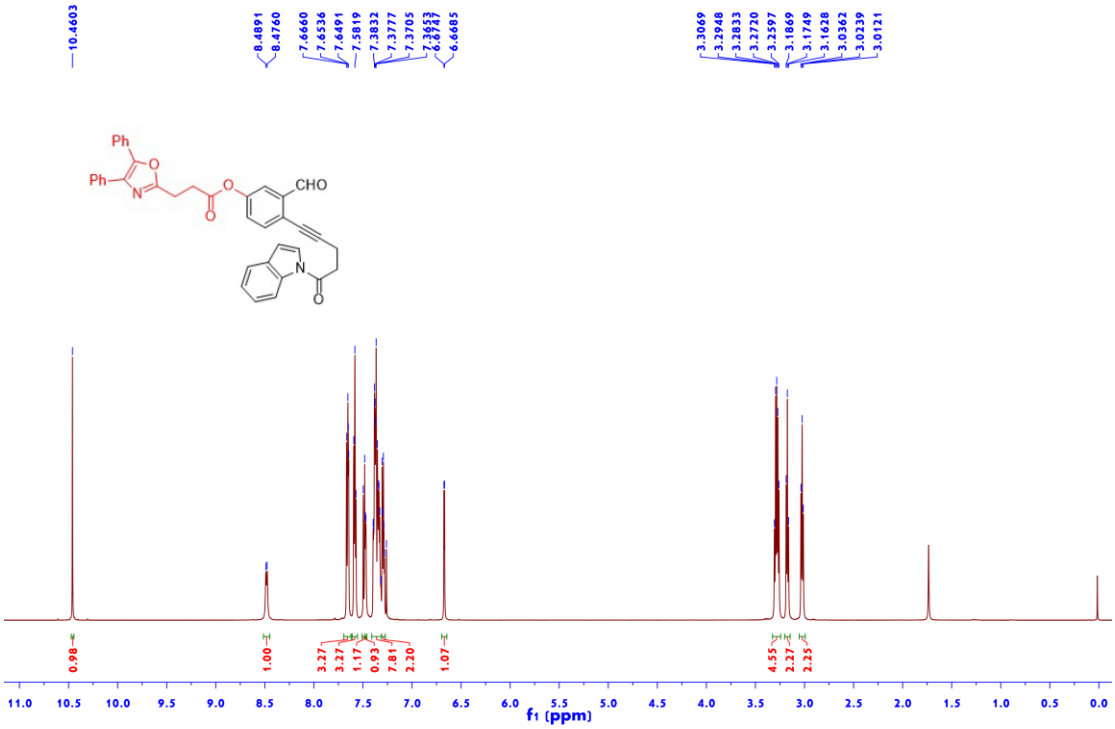


Figure S86 ^{13}C NMR (150 MHz, $CDCl_3$) of **1an**

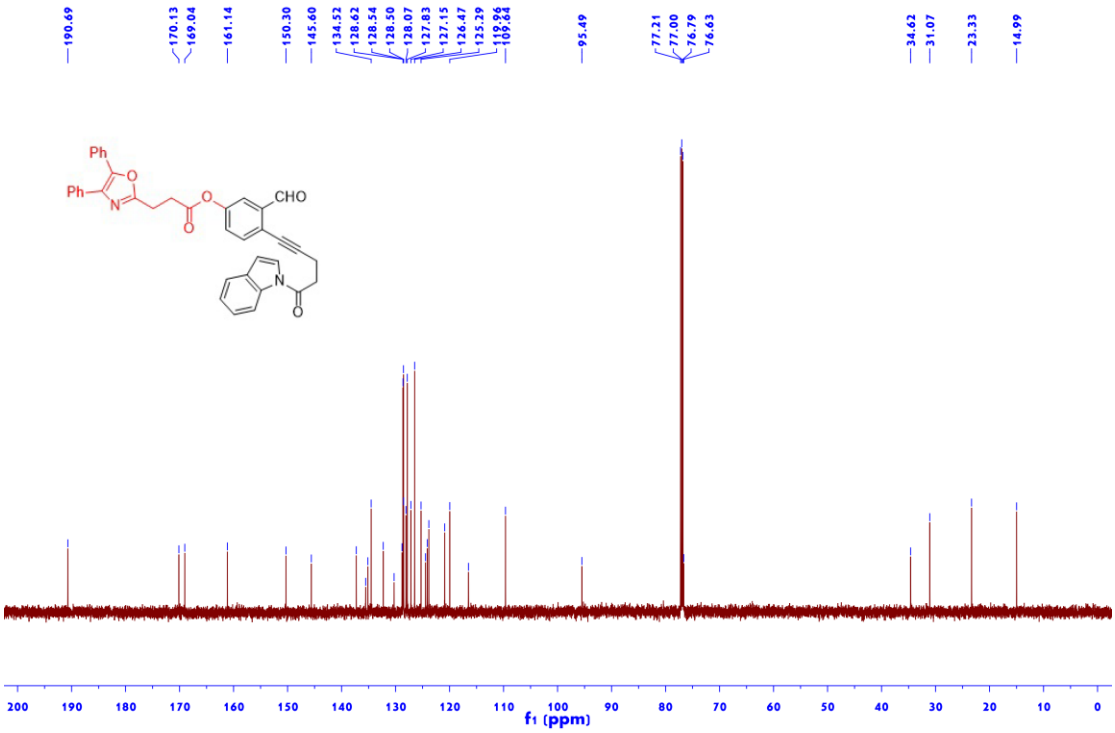


Figure S87 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ao**

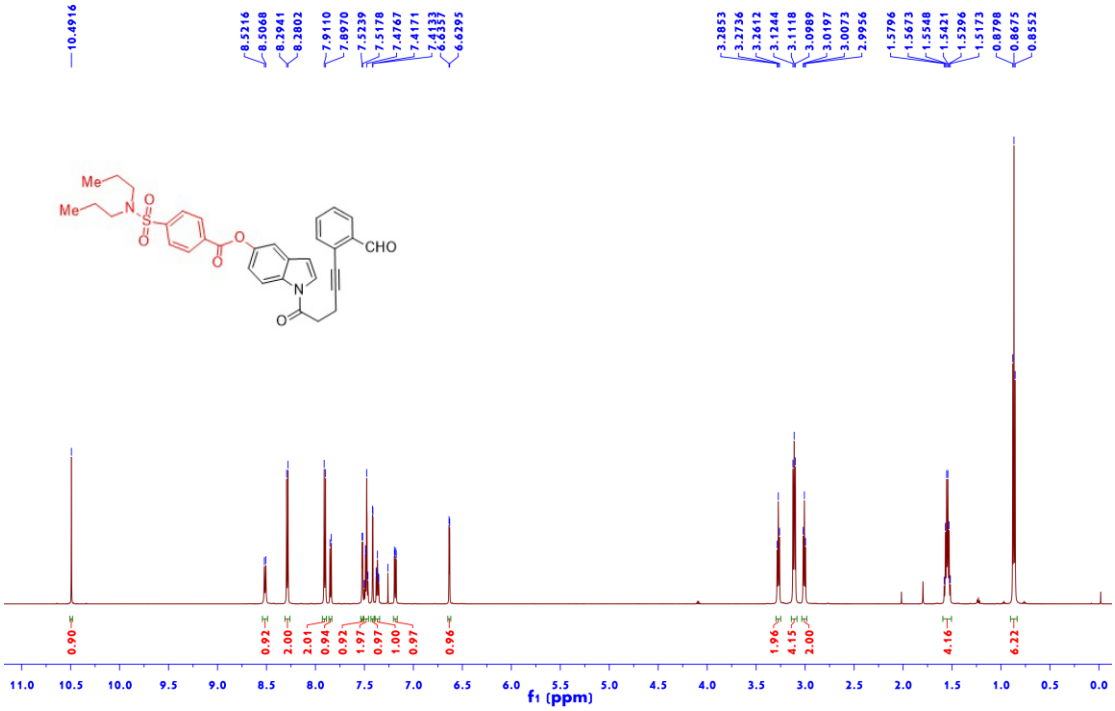


Figure S88 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ao**

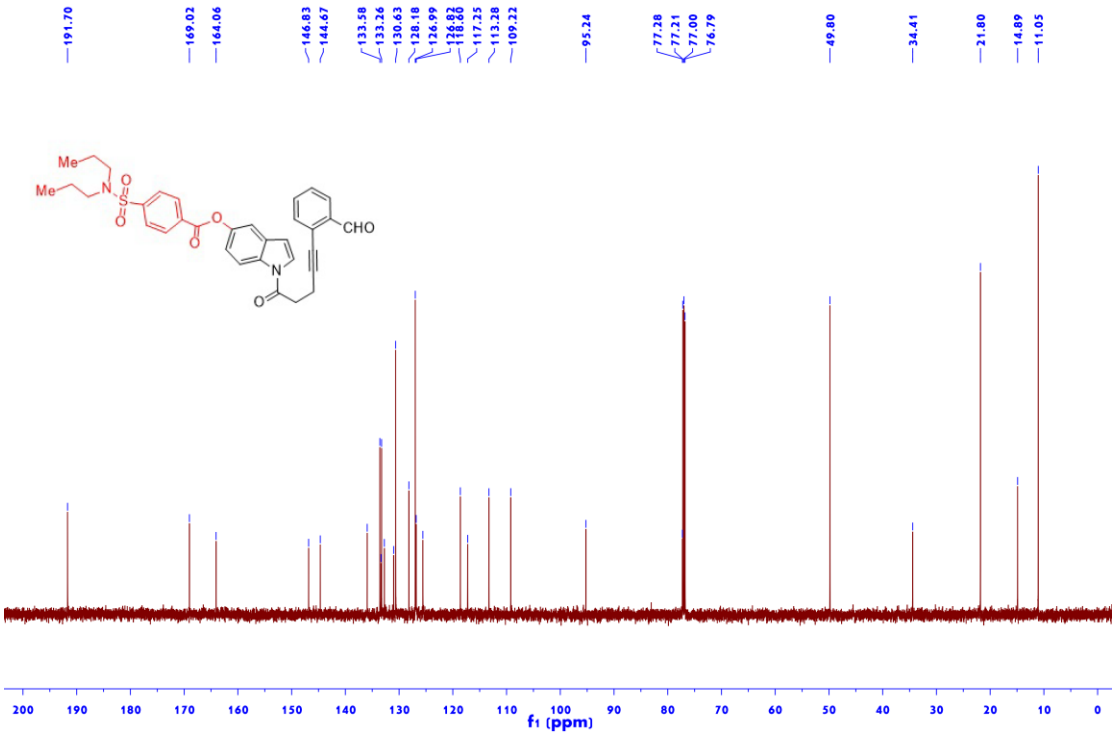


Figure S89 ^{1}H NMR (600 MHz, $CDCl_3$) of **1ap**

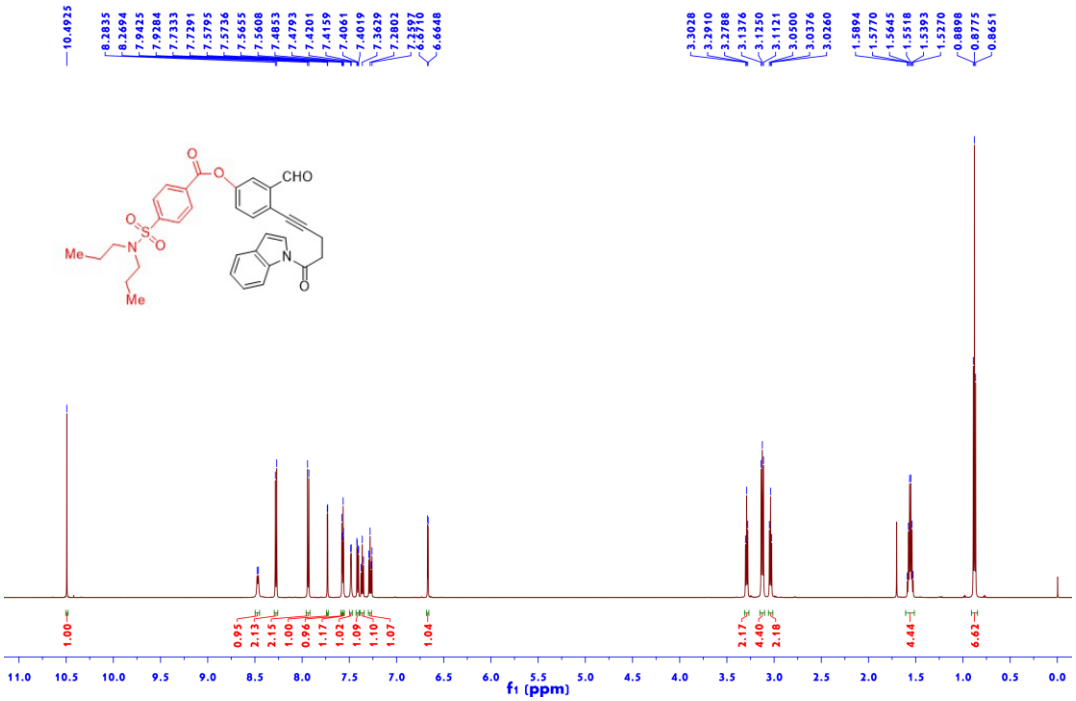


Figure S90 ^{13}C NMR (150 MHz, $CDCl_3$) of **1ap**

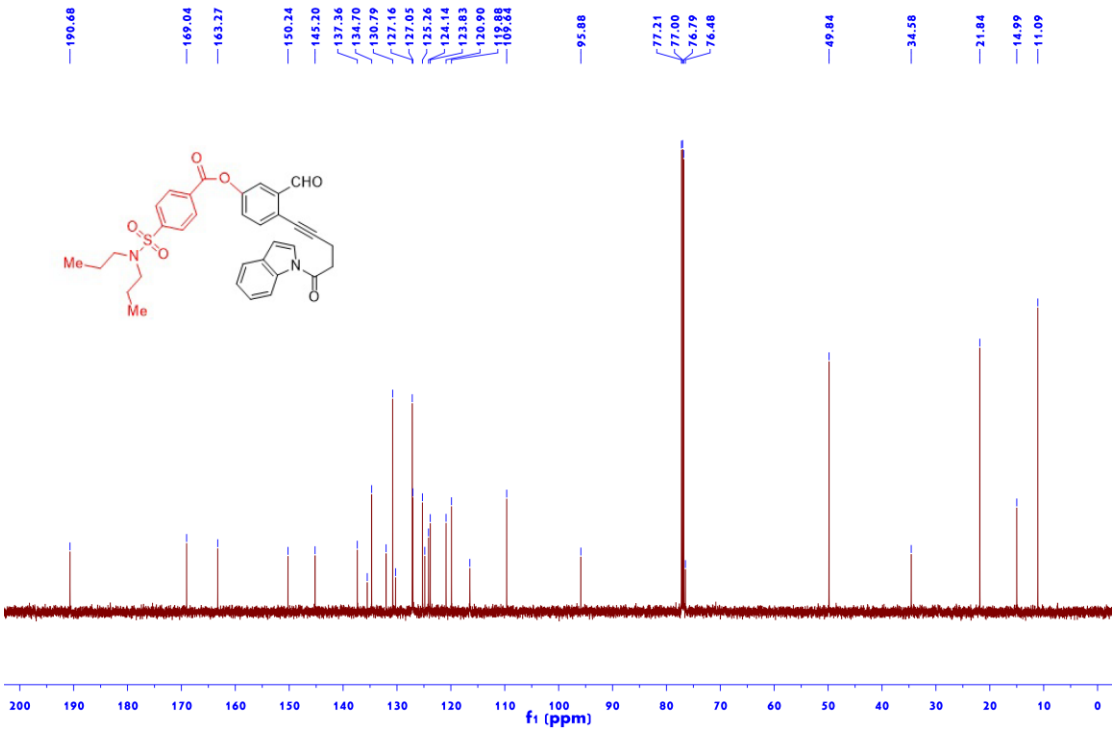


Figure S91 ^{1}H NMR (600 MHz, $CDCl_3$) of **1aq**

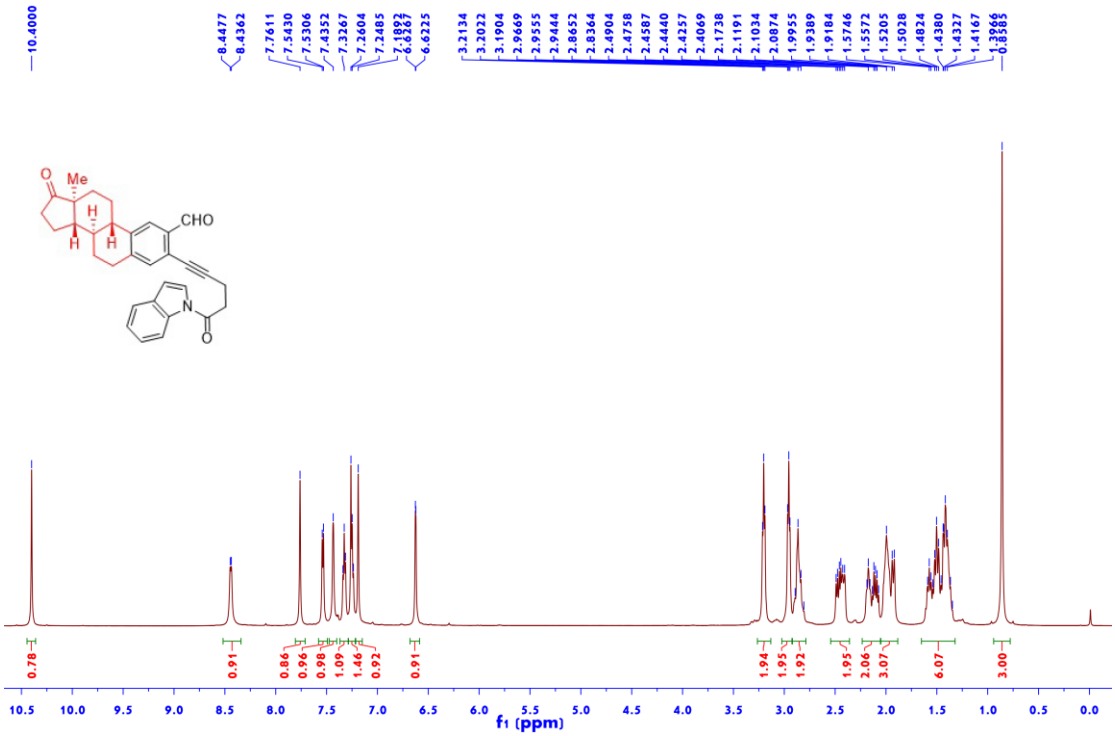


Figure S92 ^{13}C NMR (150 MHz, $CDCl_3$) of **1aq**

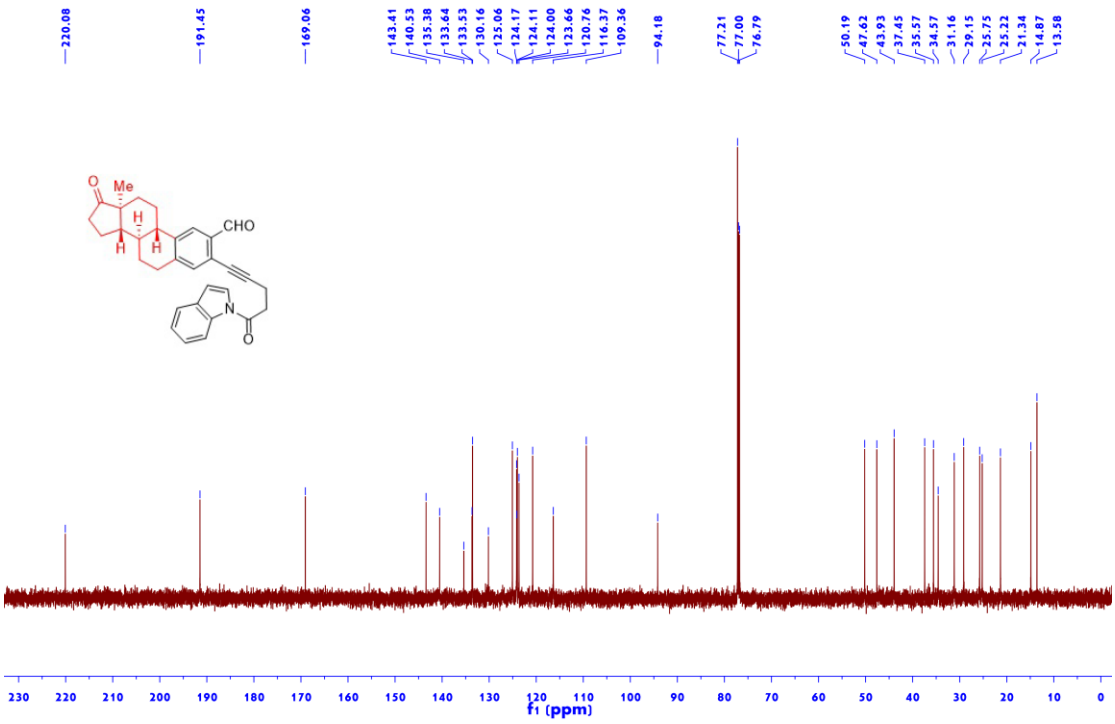


Figure S93 ^{1}H NMR (600 MHz, $CDCl_3$) of **2a**

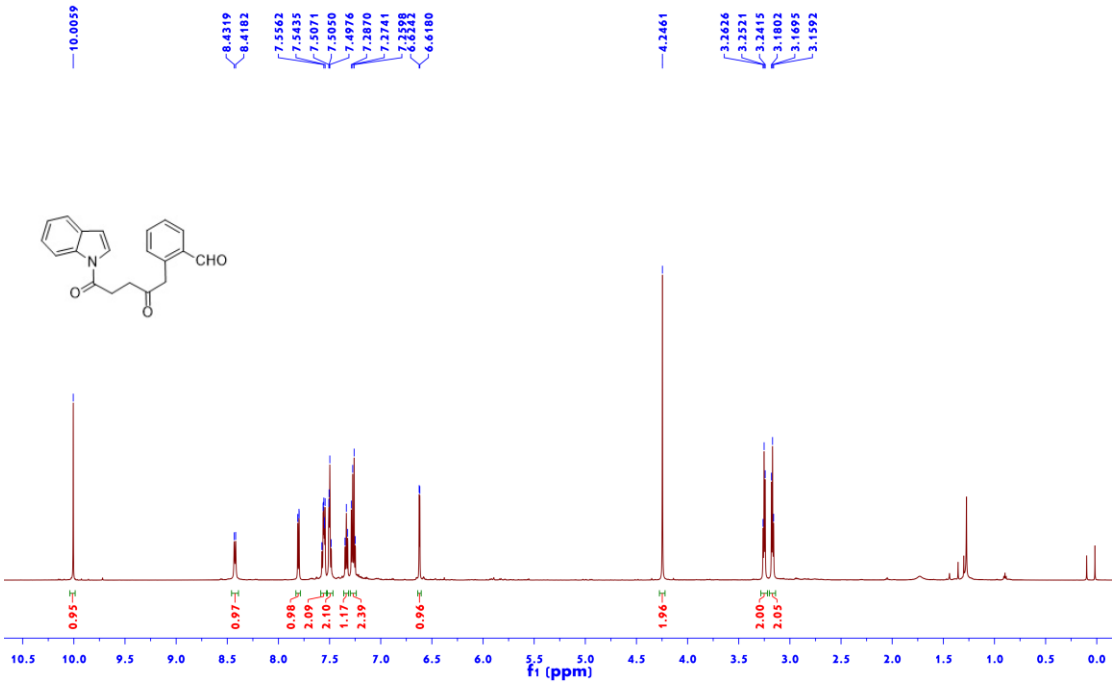


Figure S94 ^{13}C NMR (150 MHz, $CDCl_3$) of **2a**

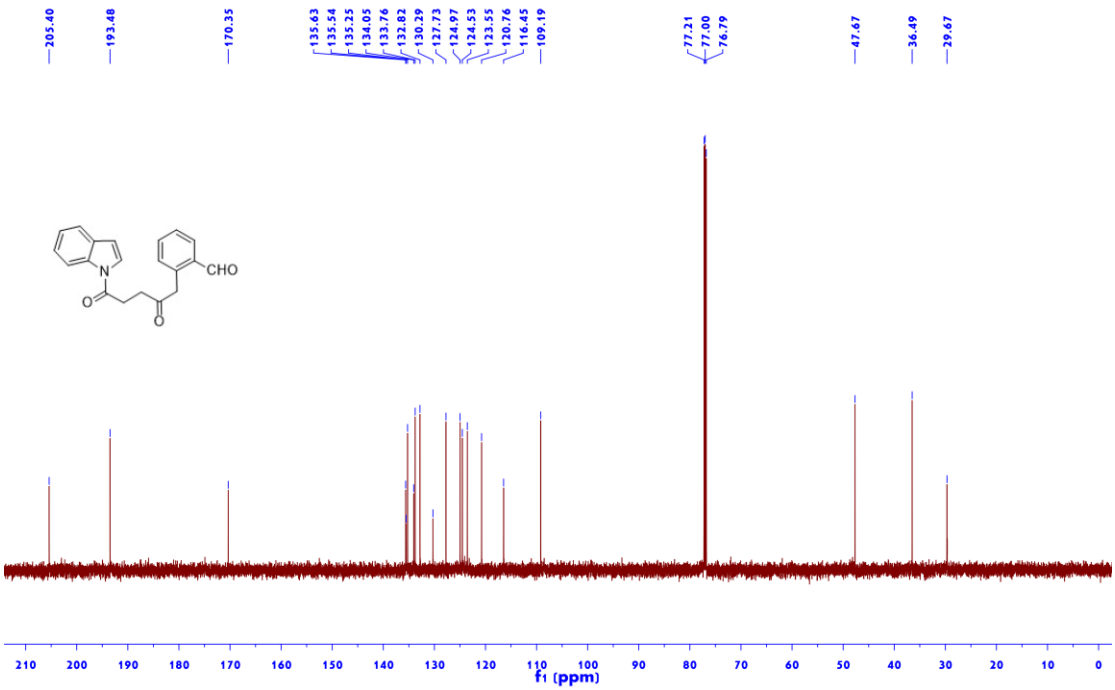


Figure S95 ^{1}H NMR (600 MHz, $CDCl_3$) of **3a**

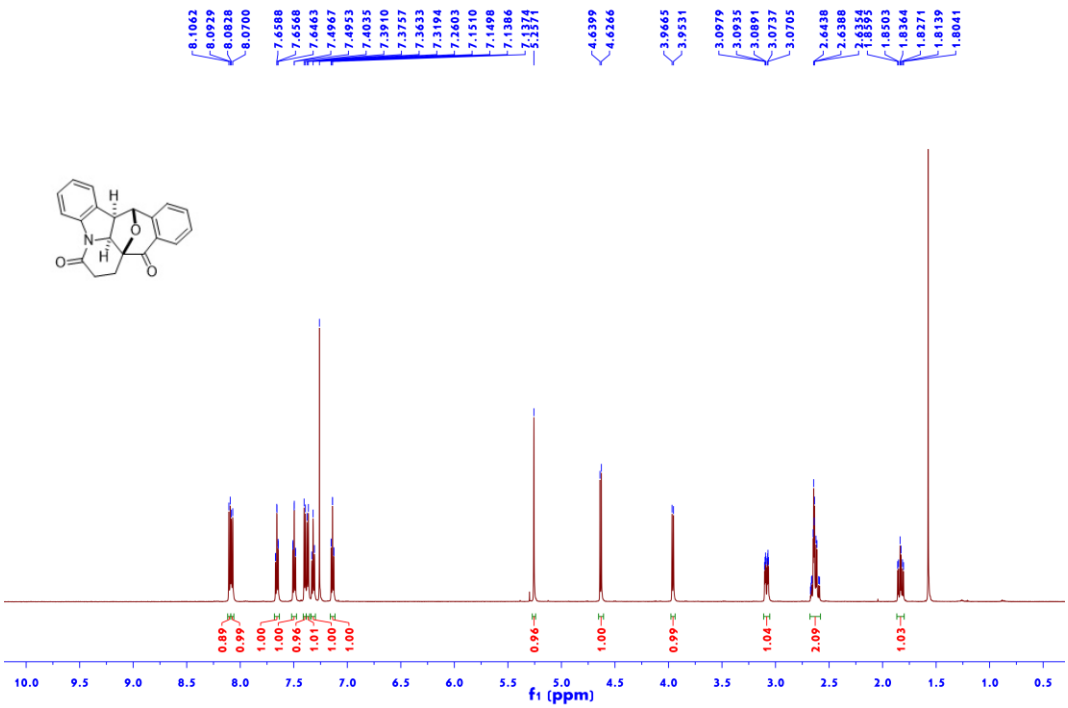


Figure S96 ^{13}C NMR (150 MHz, $CDCl_3$) of **3a**

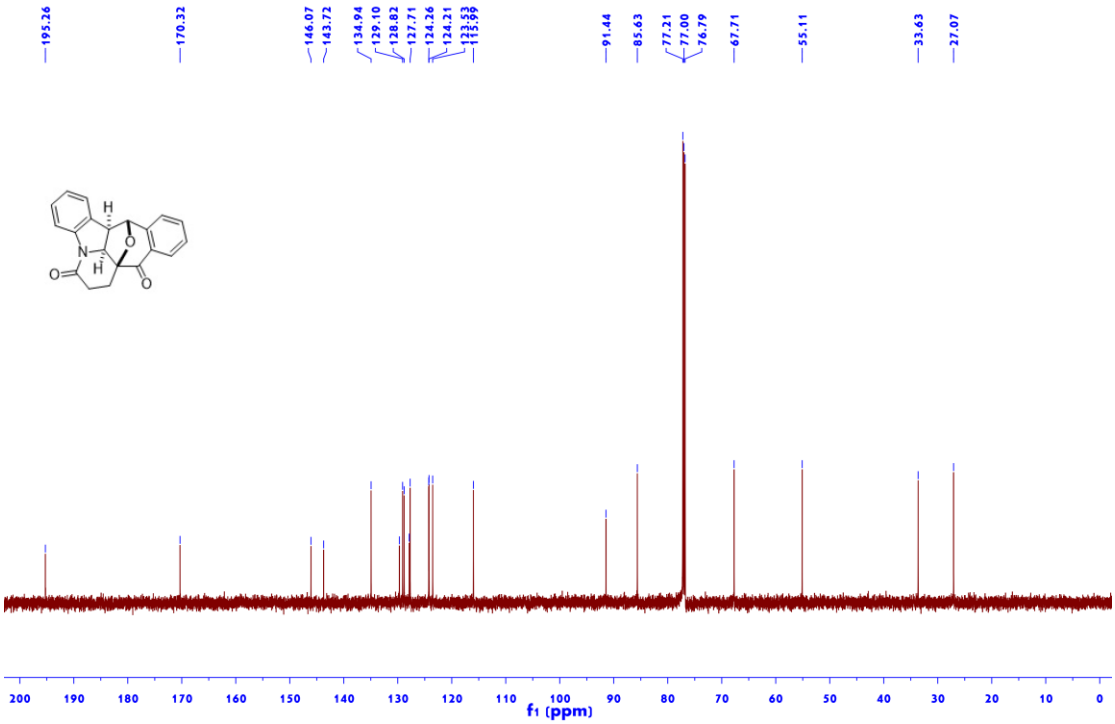


Figure S97 ^{1}H NMR (600 MHz, $CDCl_3$) of **3b**

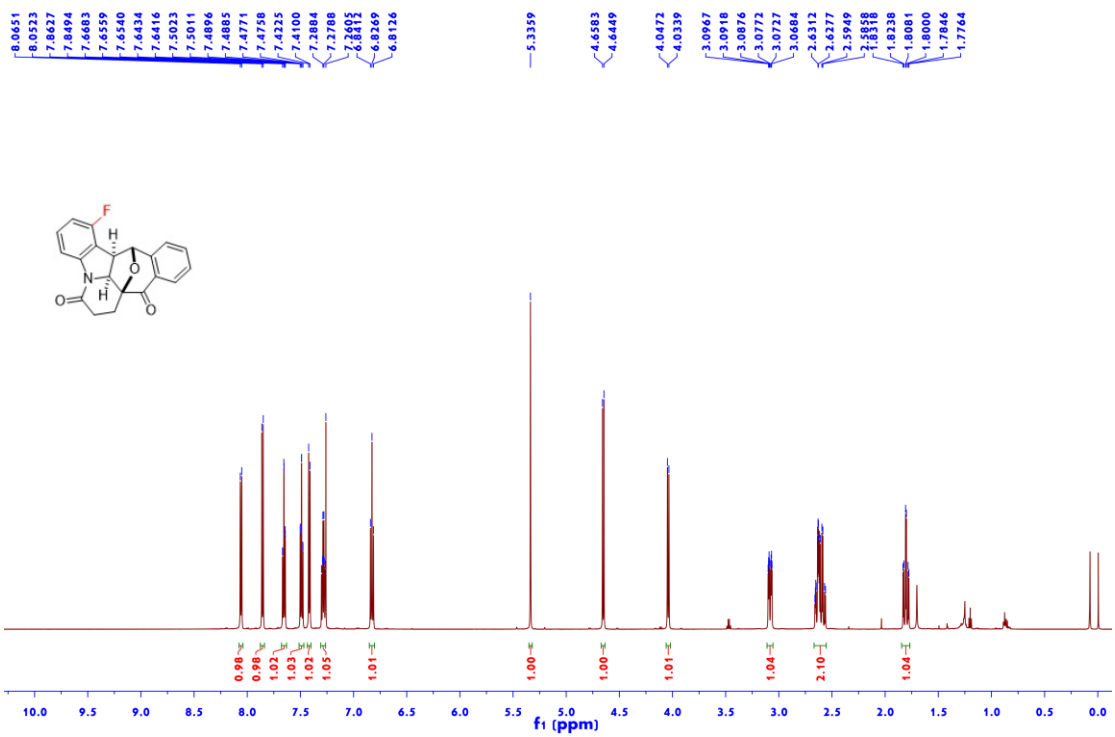


Figure S98 ^{13}C NMR (150 MHz, $CDCl_3$) of **3b**

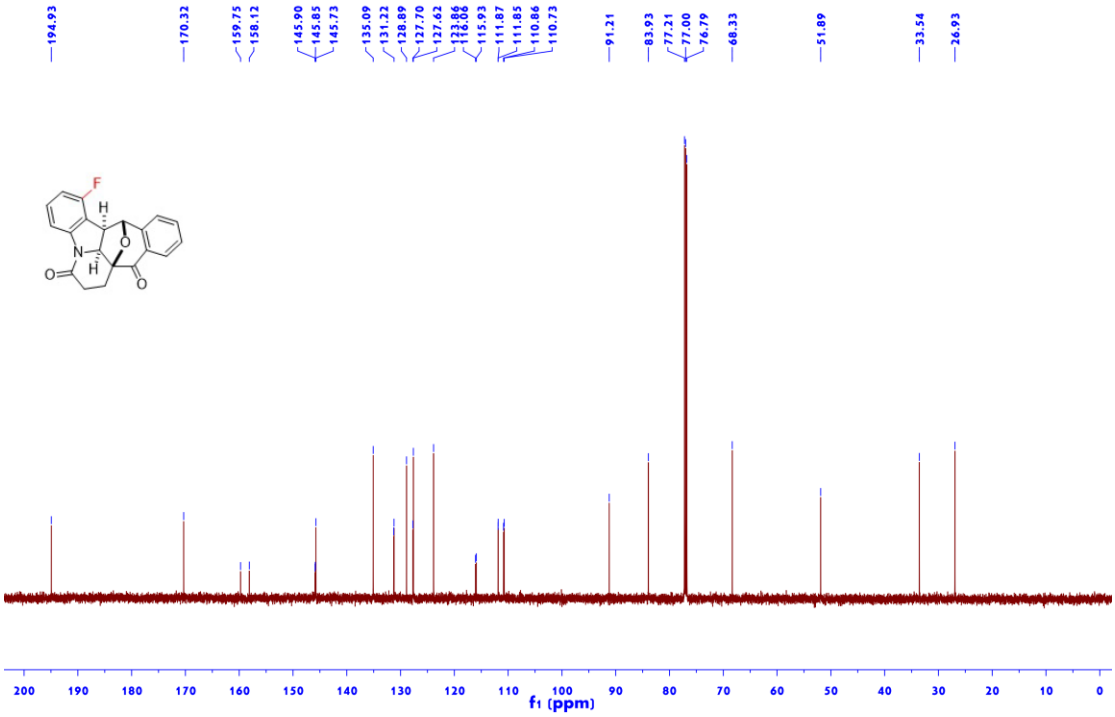


Figure S99 ^{19}F NMR (565 MHz, $CDCl_3$) of **3b**

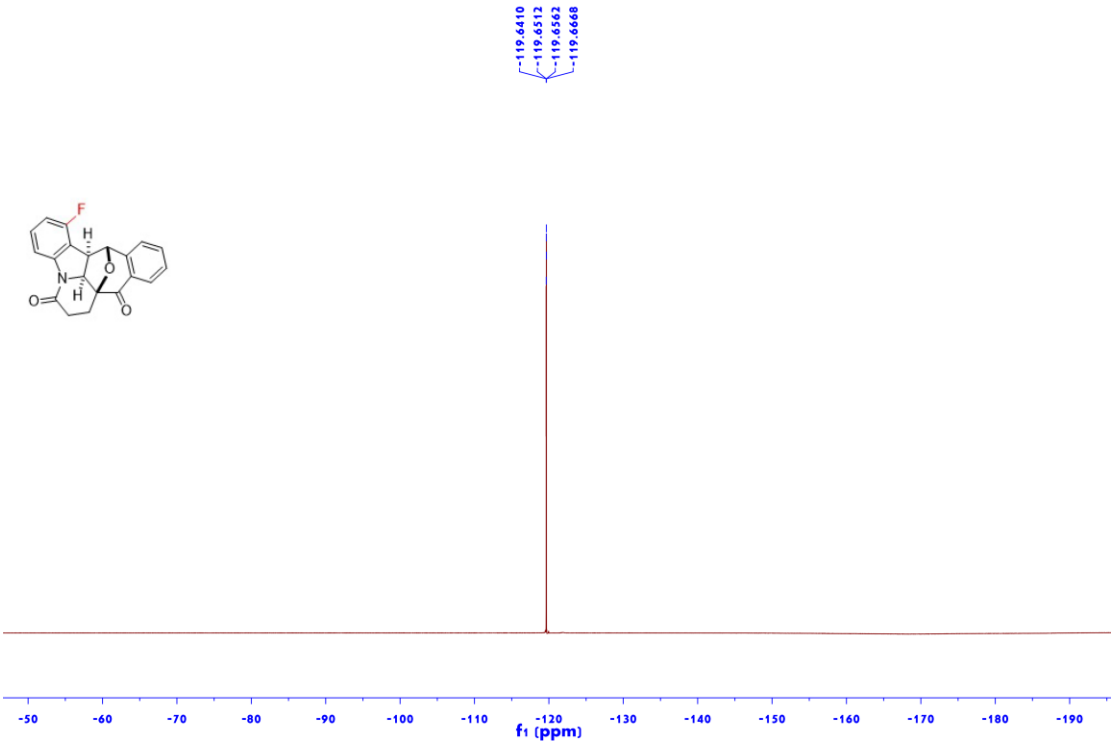


Figure S100 ^{1}H NMR (600 MHz, $CDCl_3$) of **3c**

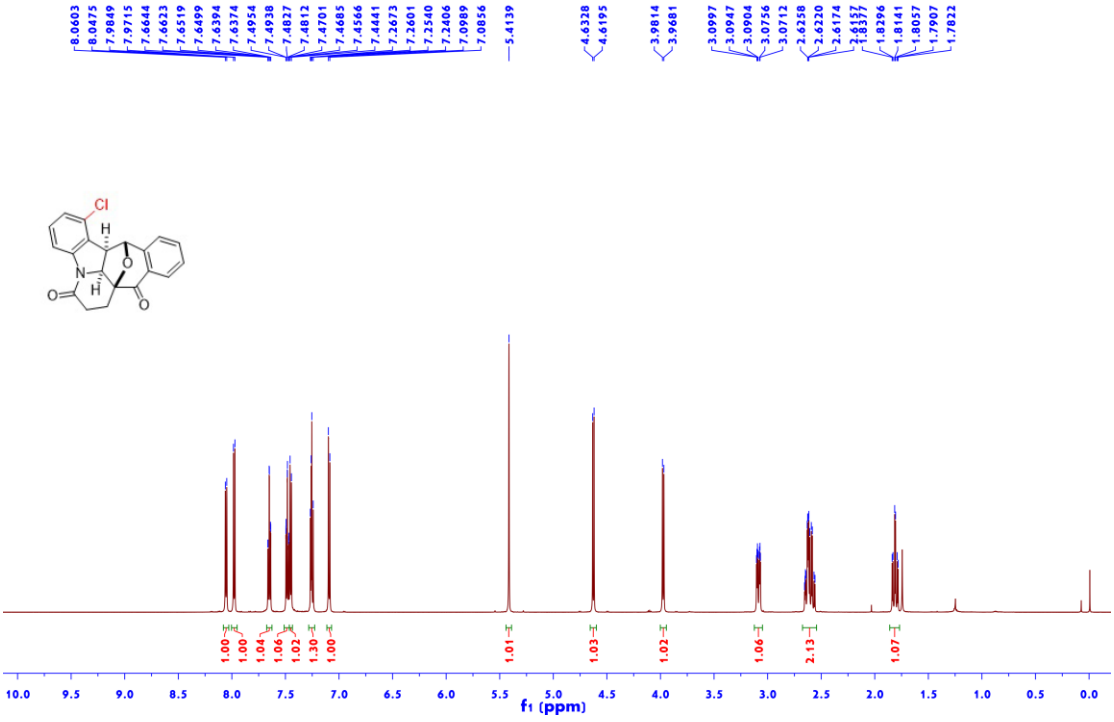


Figure S101 ^{13}C NMR (150 MHz, $CDCl_3$) of **3c**

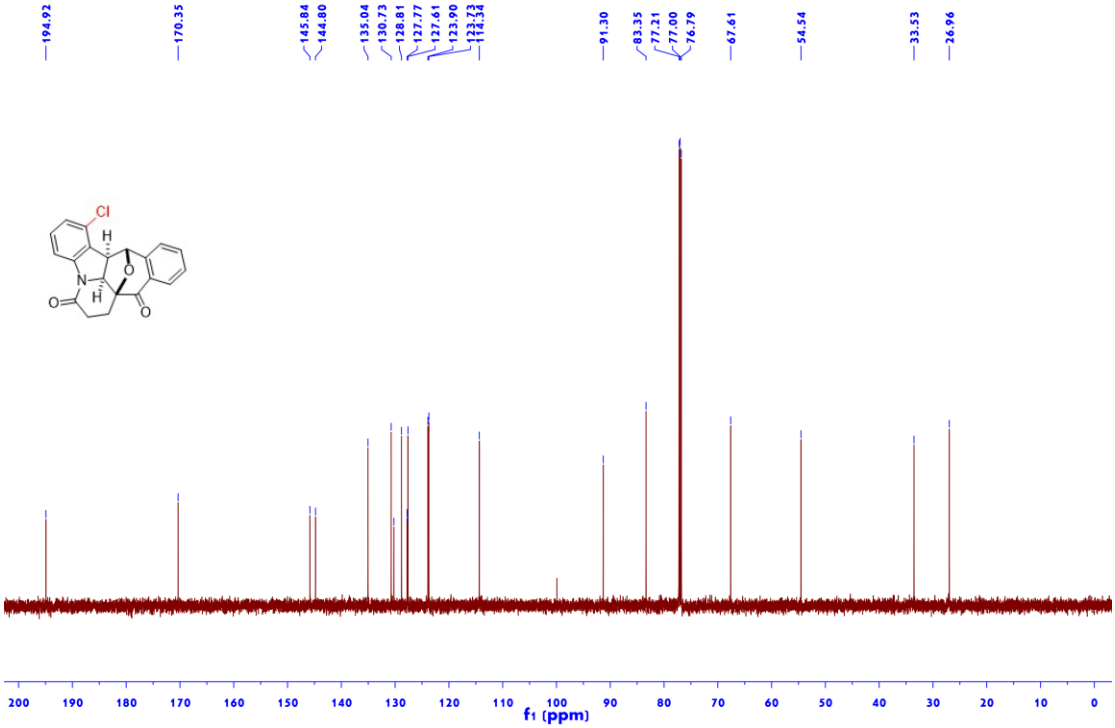


Figure S102 ^{1}H NMR (600 MHz, $CDCl_3$) of **3d**

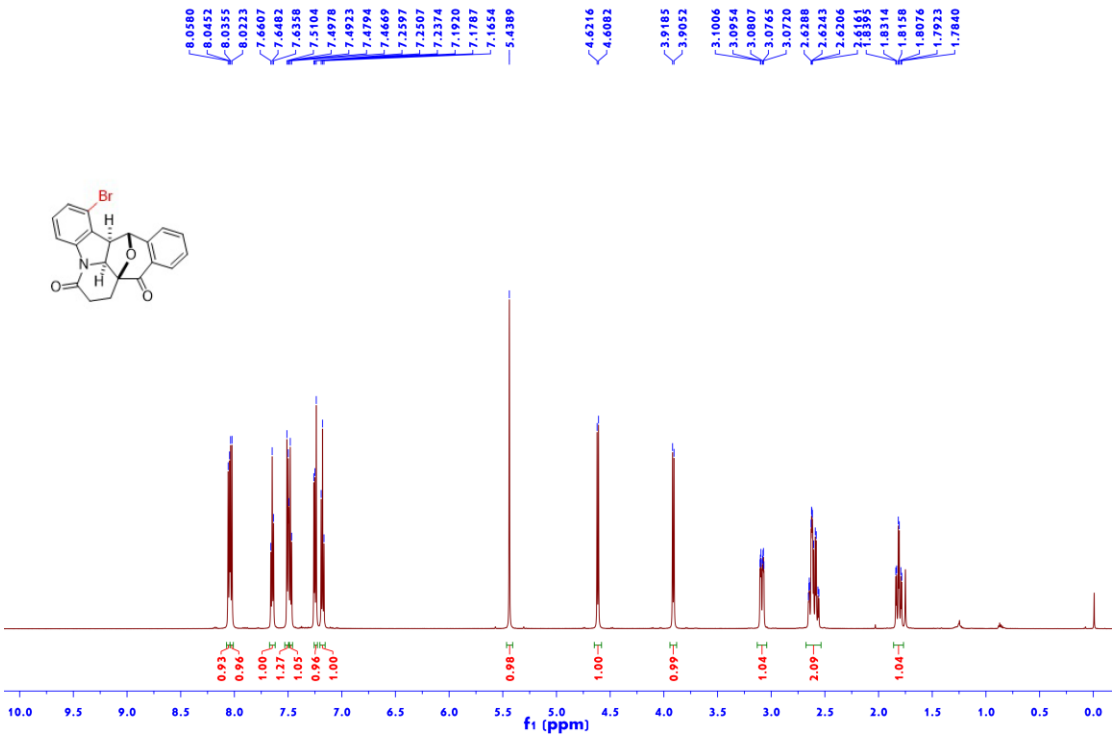


Figure S103 ^{13}C NMR (150 MHz, $CDCl_3$) of **3d**

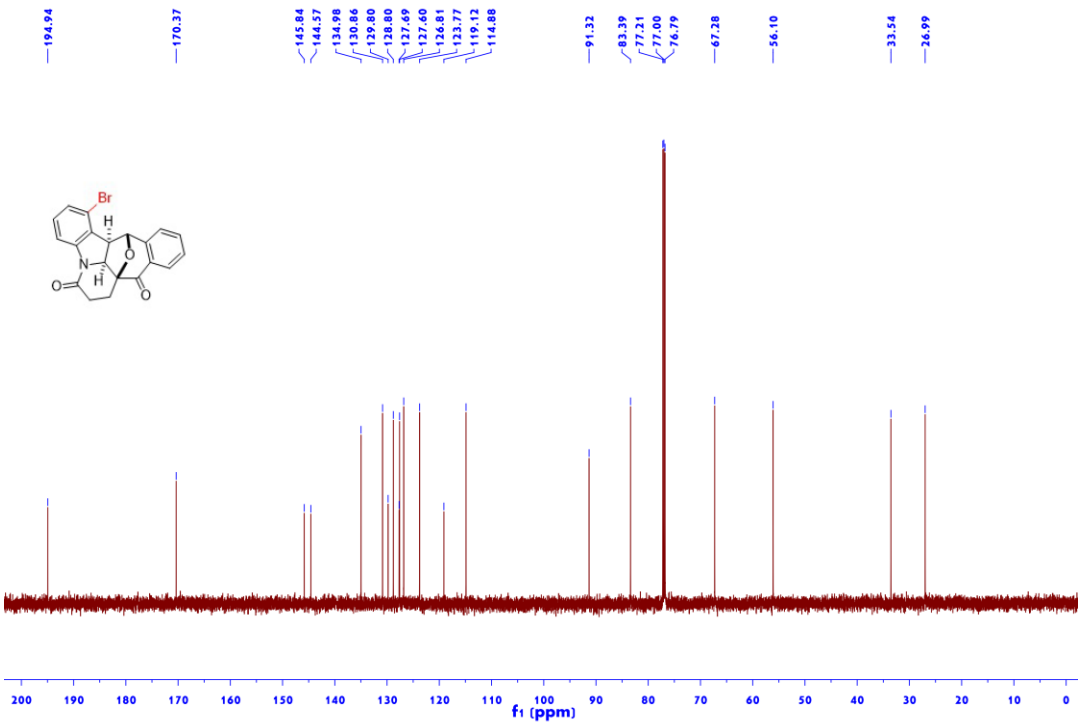


Figure S104 ^{1}H NMR (600 MHz, $CDCl_3$) of **3e**

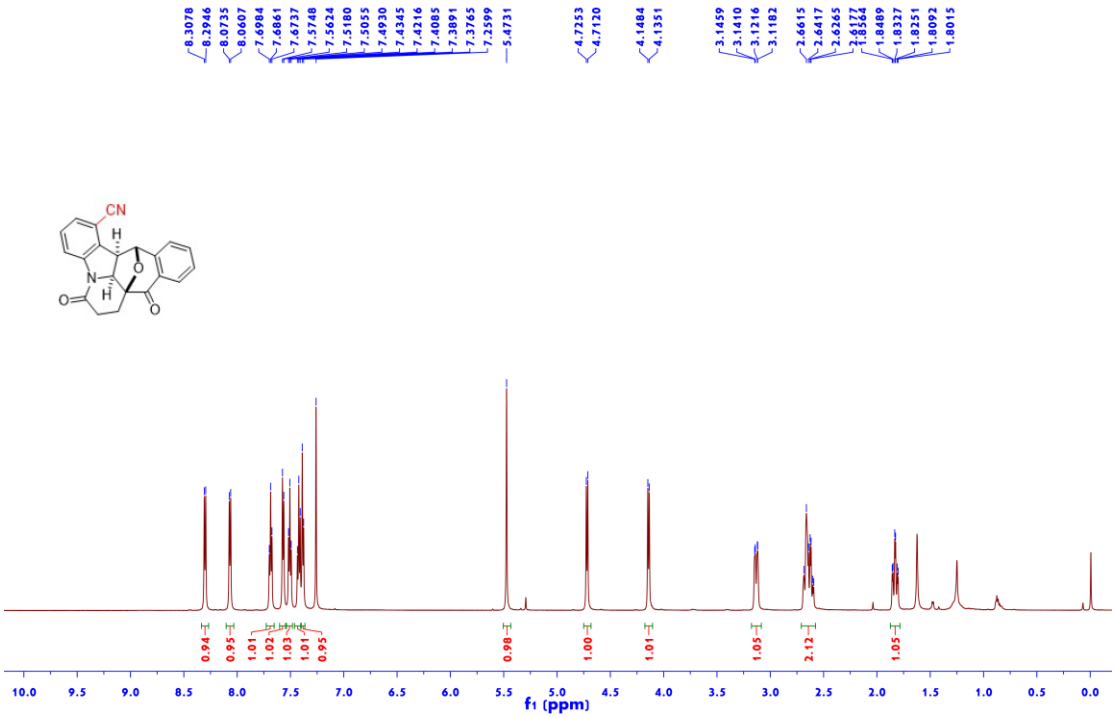


Figure S105 ^{13}C NMR (150 MHz, $CDCl_3$) of **3e**

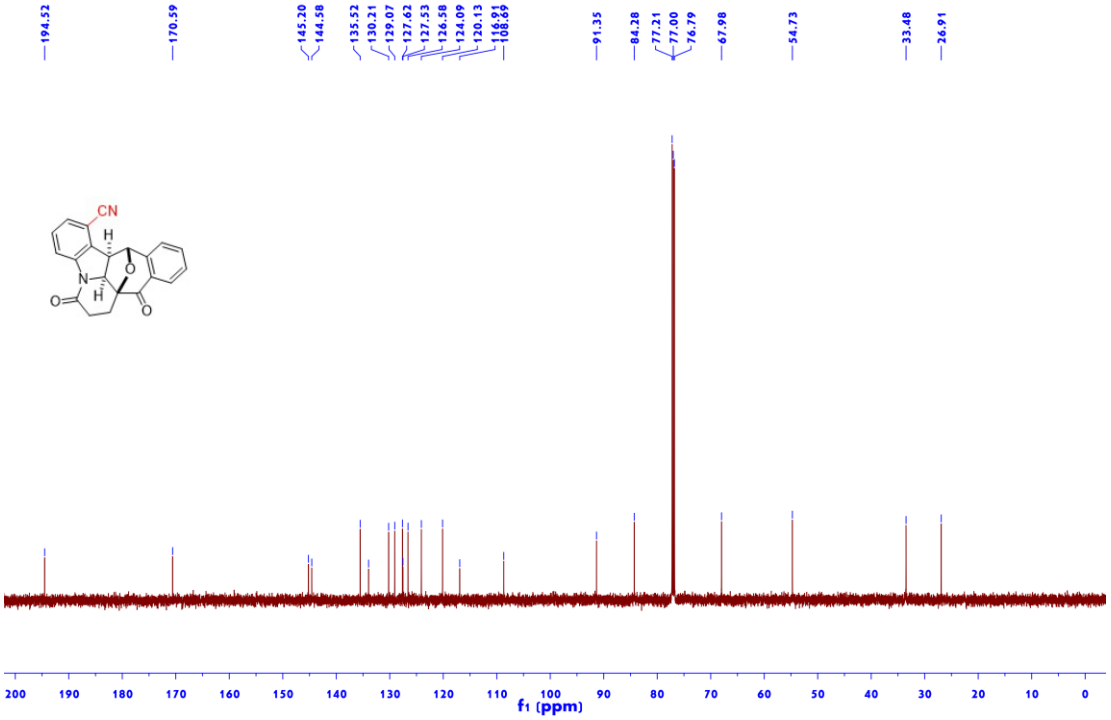


Figure S106 ^{1}H NMR (600 MHz, $CDCl_3$) of **3f**

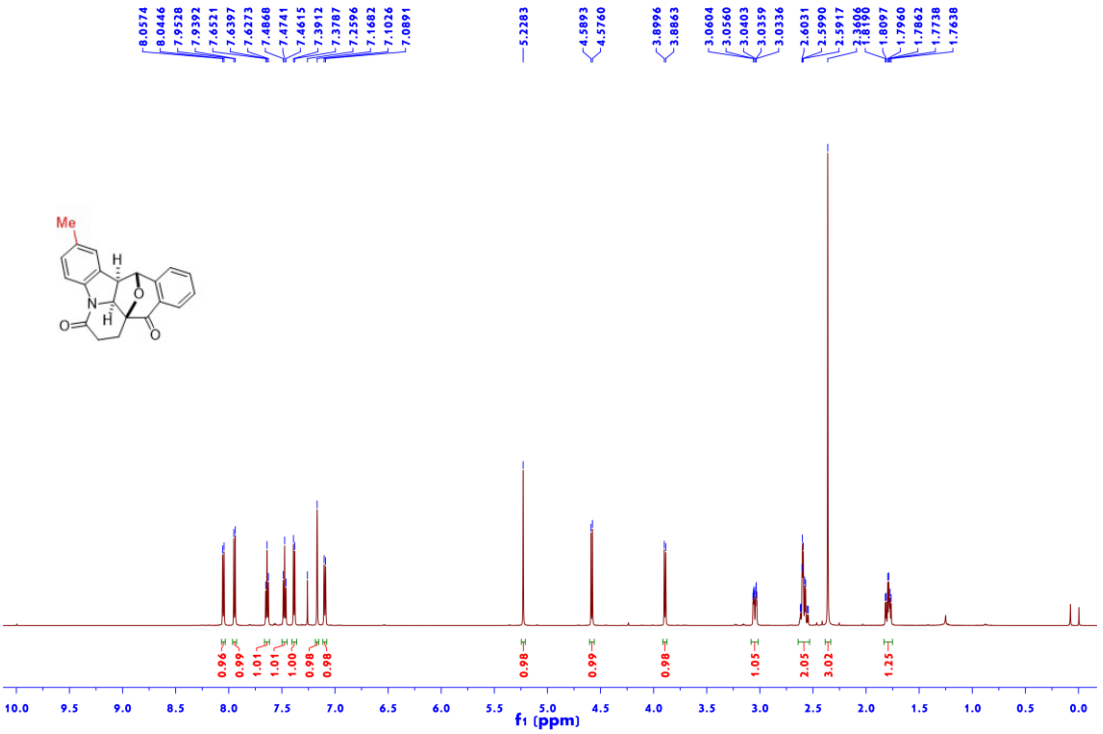


Figure S107 ^{13}C NMR (150 MHz, $CDCl_3$) of **3f**

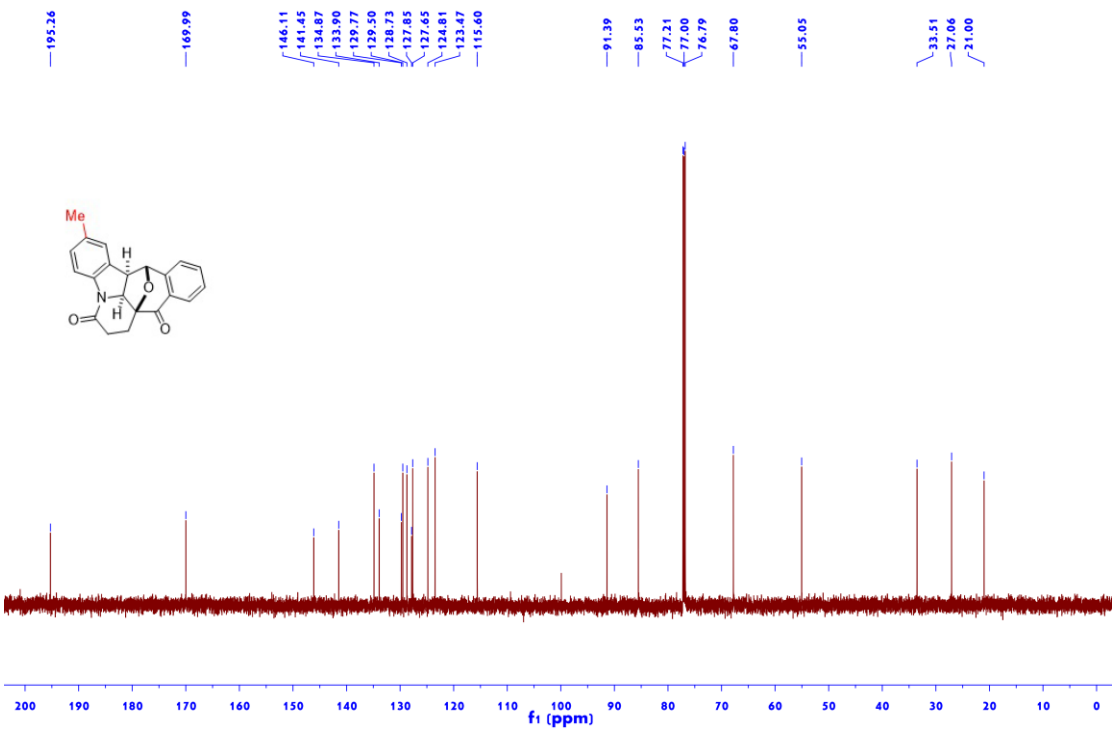


Figure S108 ^{1}H NMR (600 MHz, $CDCl_3$) of **3g**

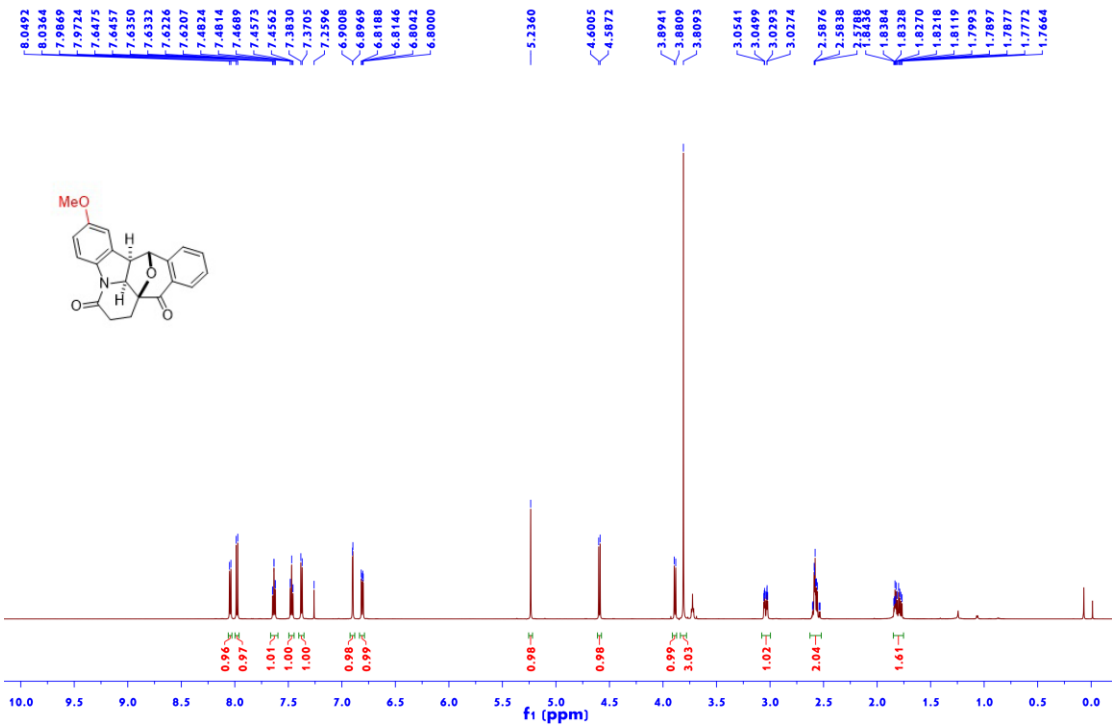


Figure S109 ^{13}C NMR (150 MHz, $CDCl_3$) of **3g**

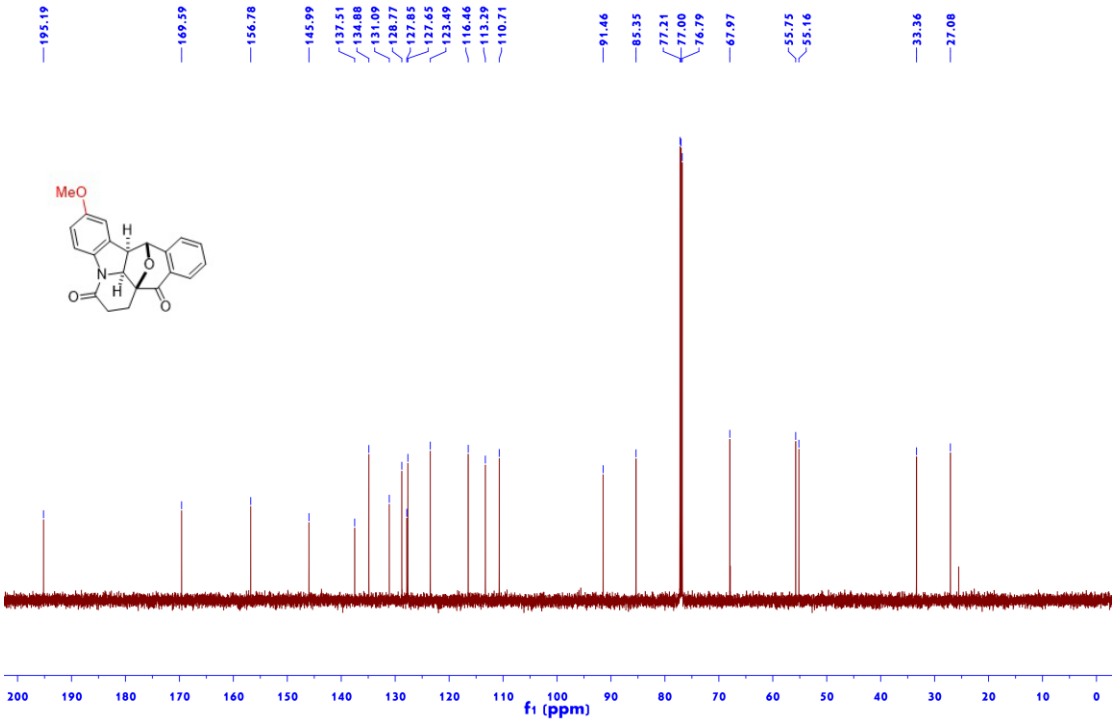


Figure S110 ^{1}H NMR (600 MHz, $CDCl_3$) of **3h**

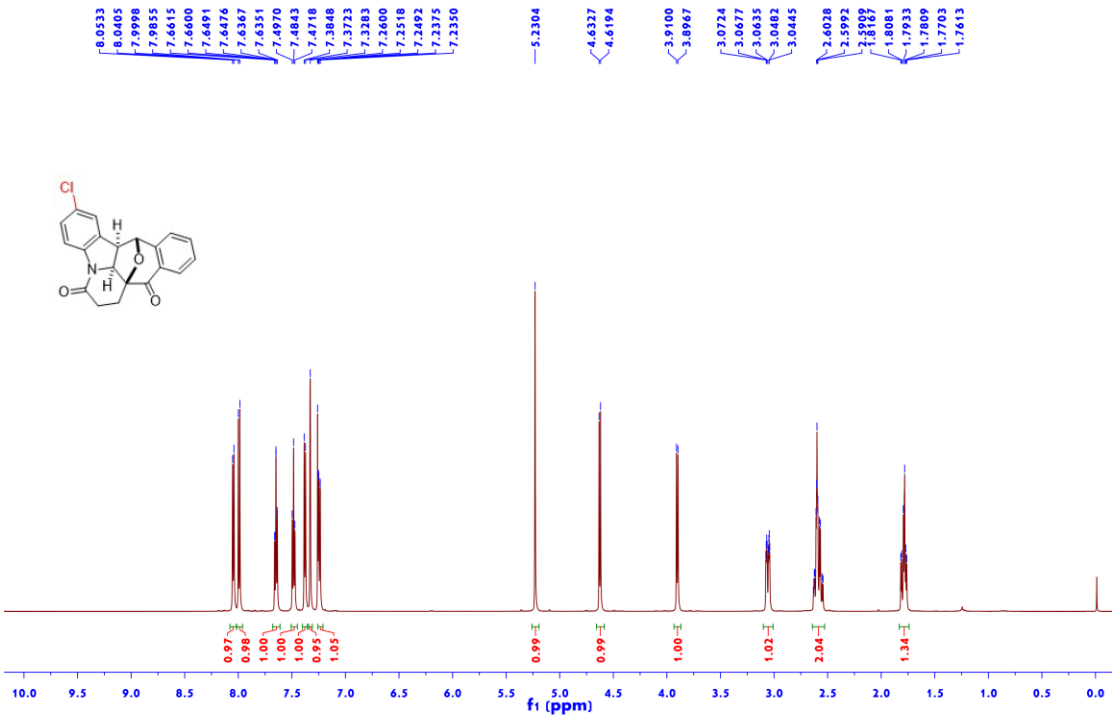


Figure S111 ^{13}C NMR (150 MHz, $CDCl_3$) of **3h**

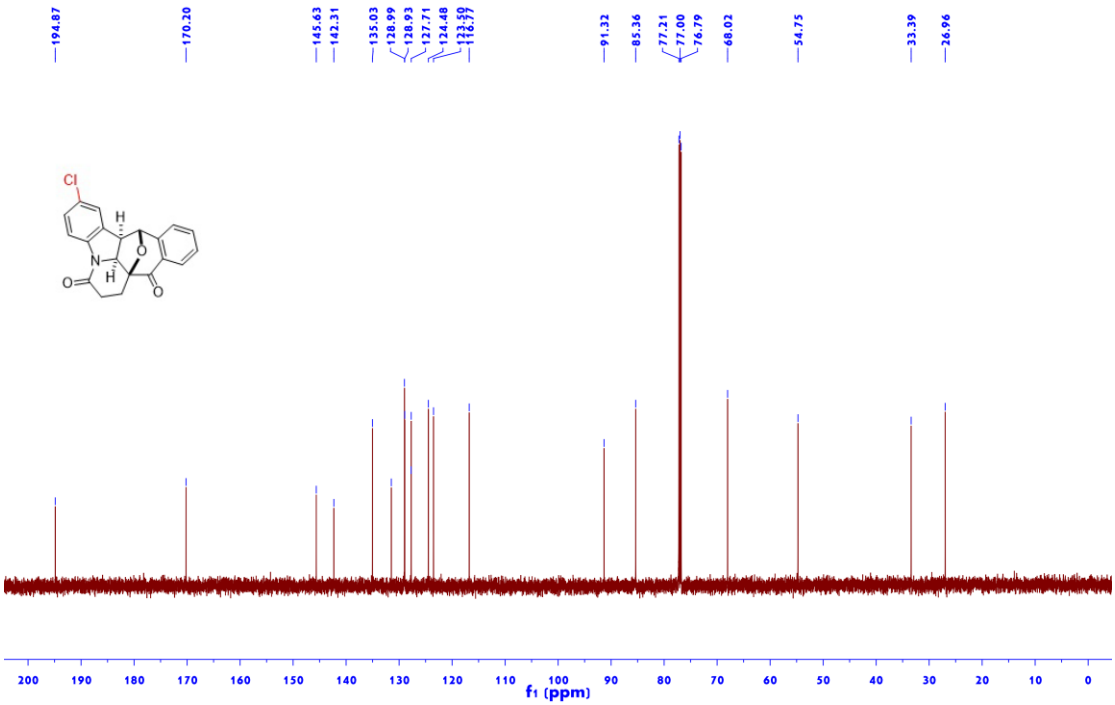


Figure S112 ^{1}H NMR (600 MHz, $CDCl_3$) of **3i**

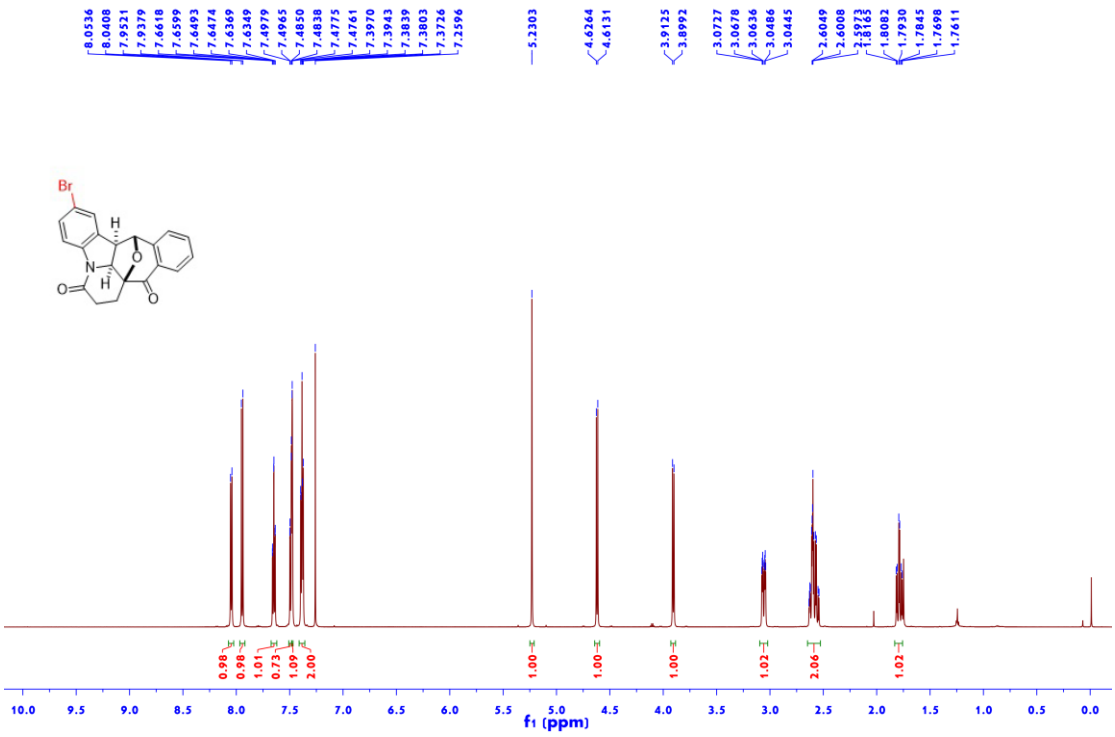


Figure S113 ^{13}C NMR (150 MHz, $CDCl_3$) of **3i**

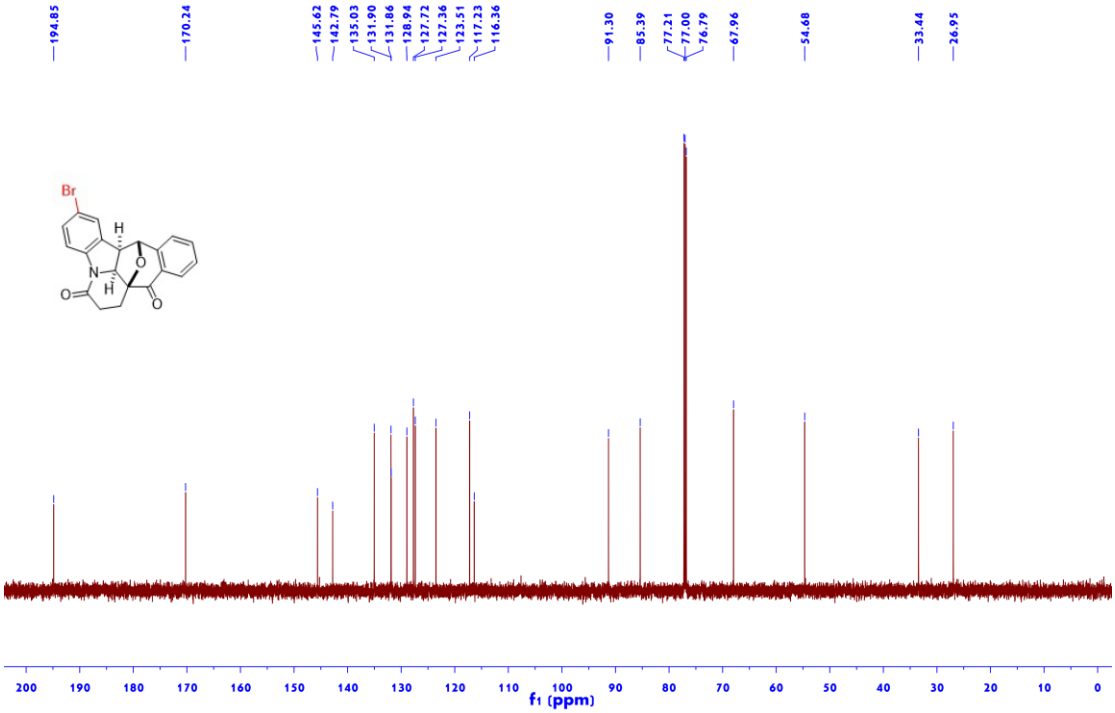


Figure S114 ^{1}H NMR (600 MHz, $CDCl_3$) of **3j**

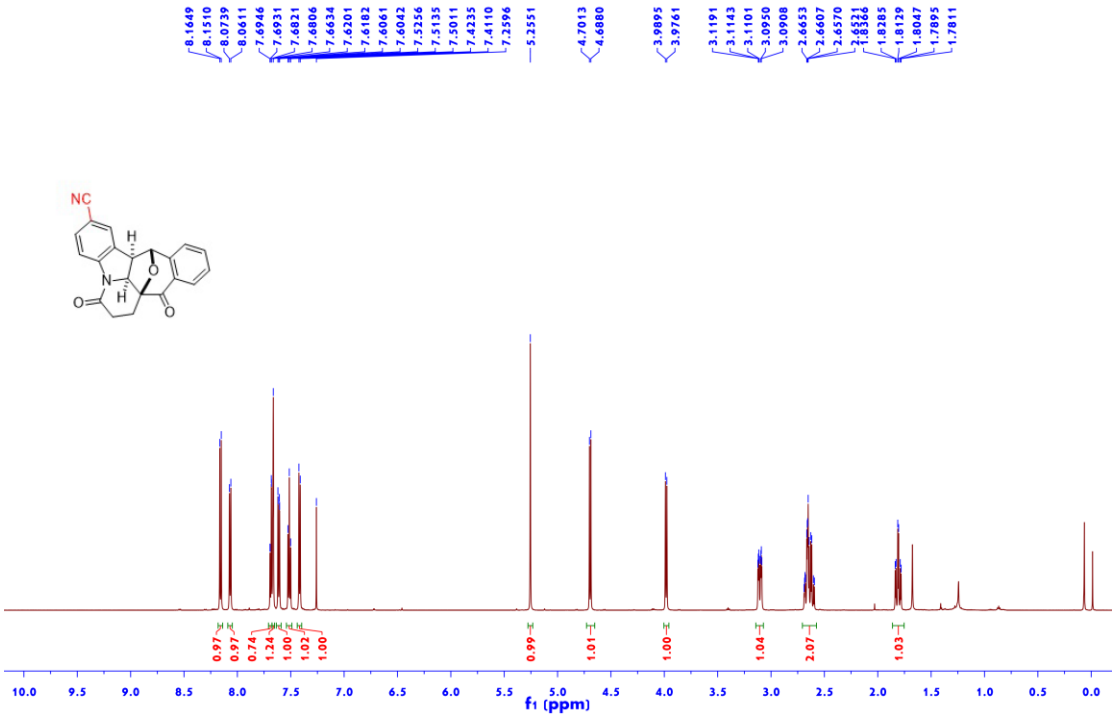


Figure S115 ^{13}C NMR (150 MHz, $CDCl_3$) of **3j**

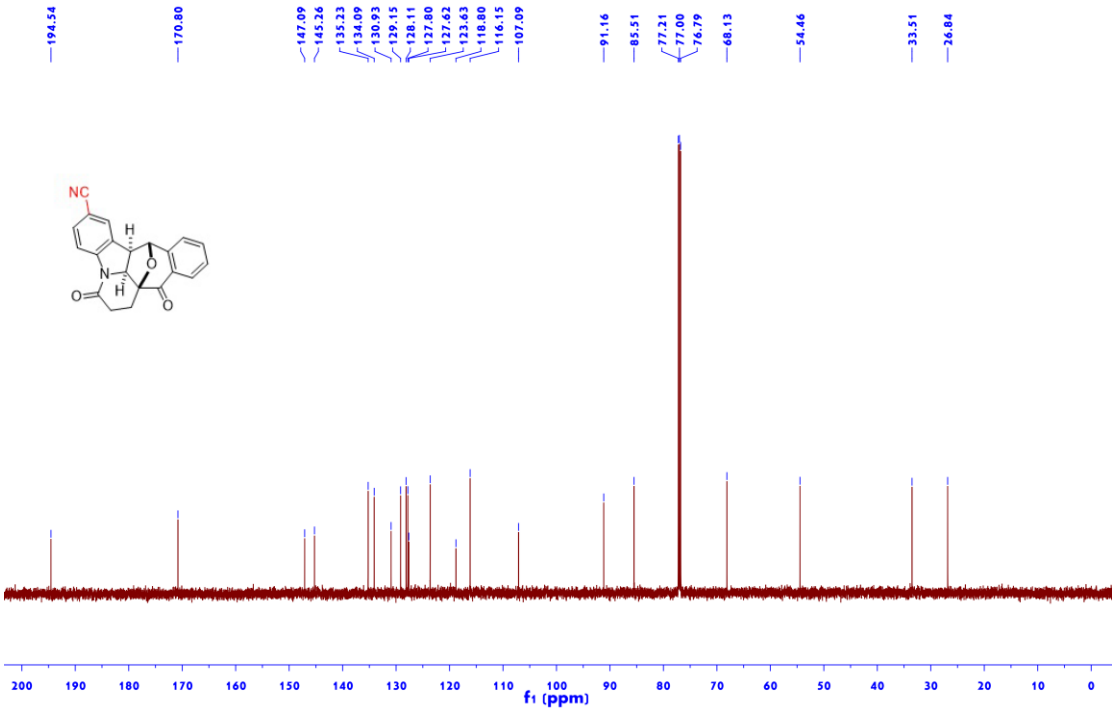


Figure S116 ^{1}H NMR (600 MHz, $CDCl_3$) of **3k**

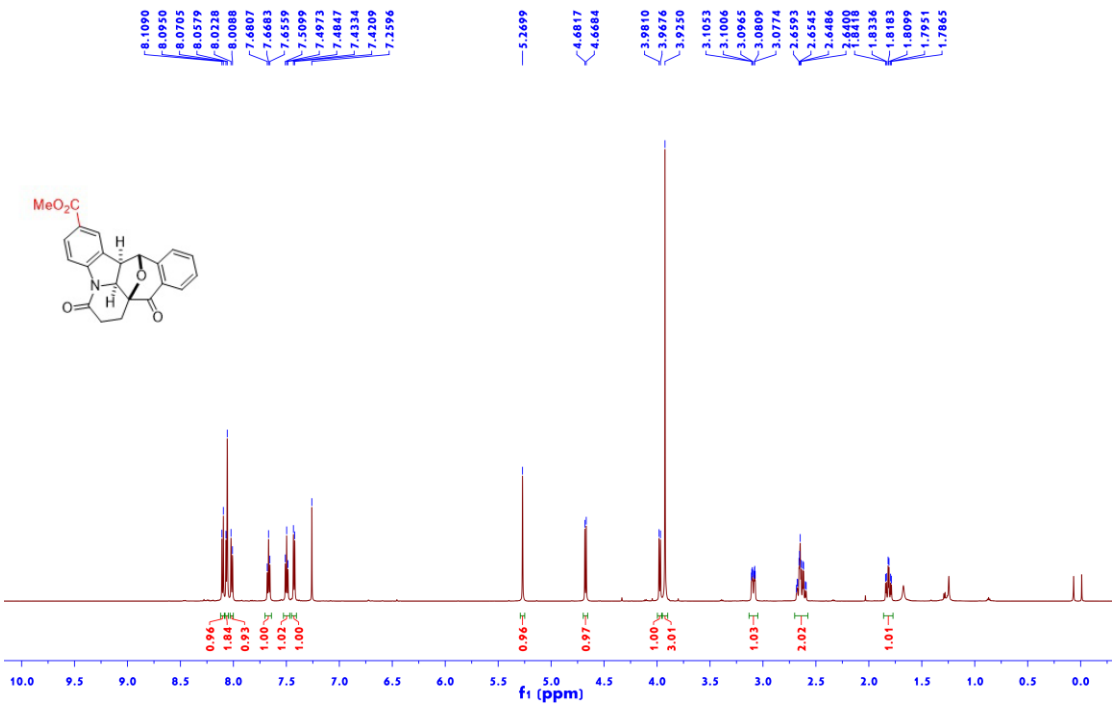


Figure S117 ^{13}C NMR (150 MHz, $CDCl_3$) of **3k**

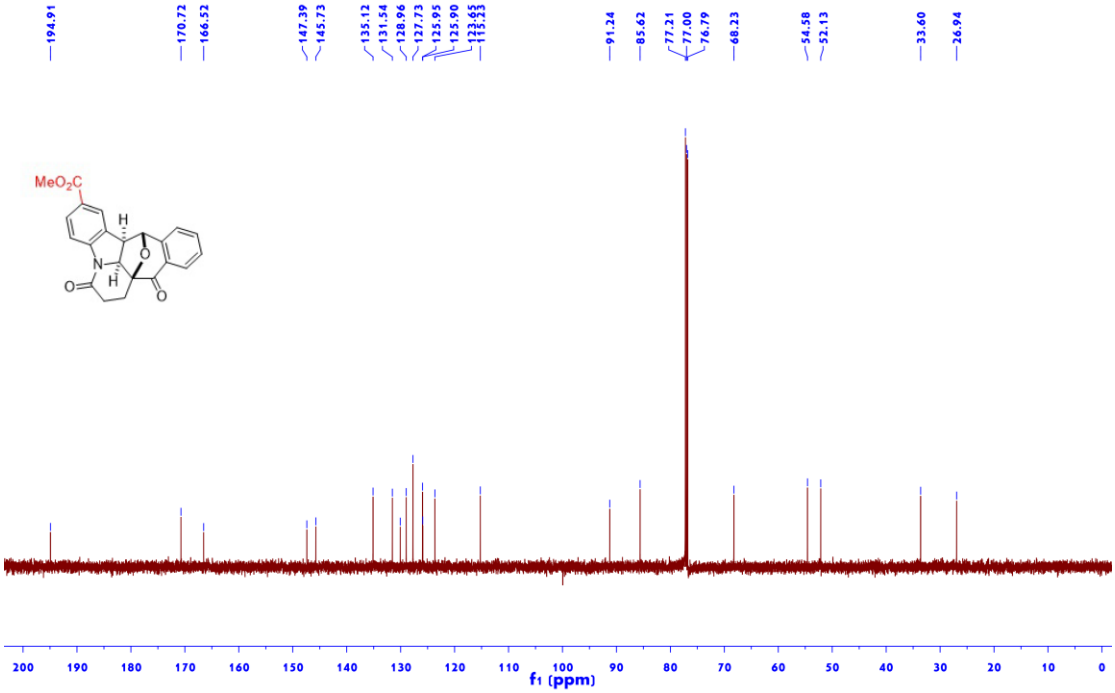


Figure S118 ^{1}H NMR (600 MHz, $CDCl_3$) of **3l**

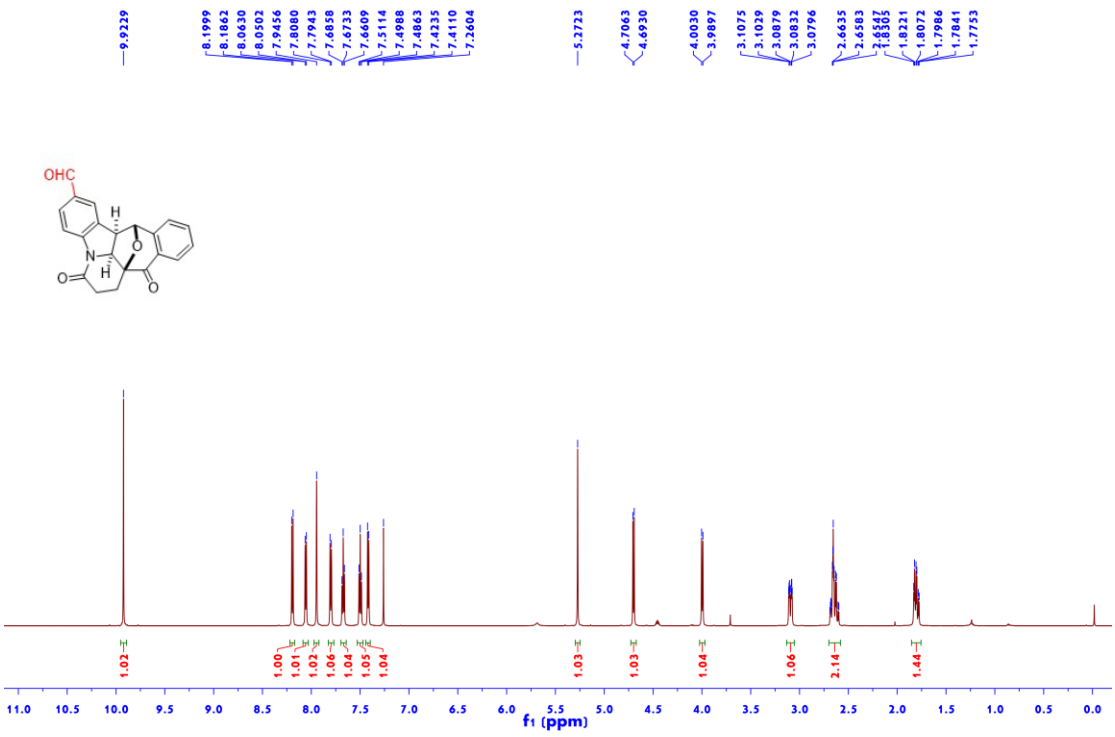


Figure S119 ^{13}C NMR (150 MHz, $CDCl_3$) of **3l**

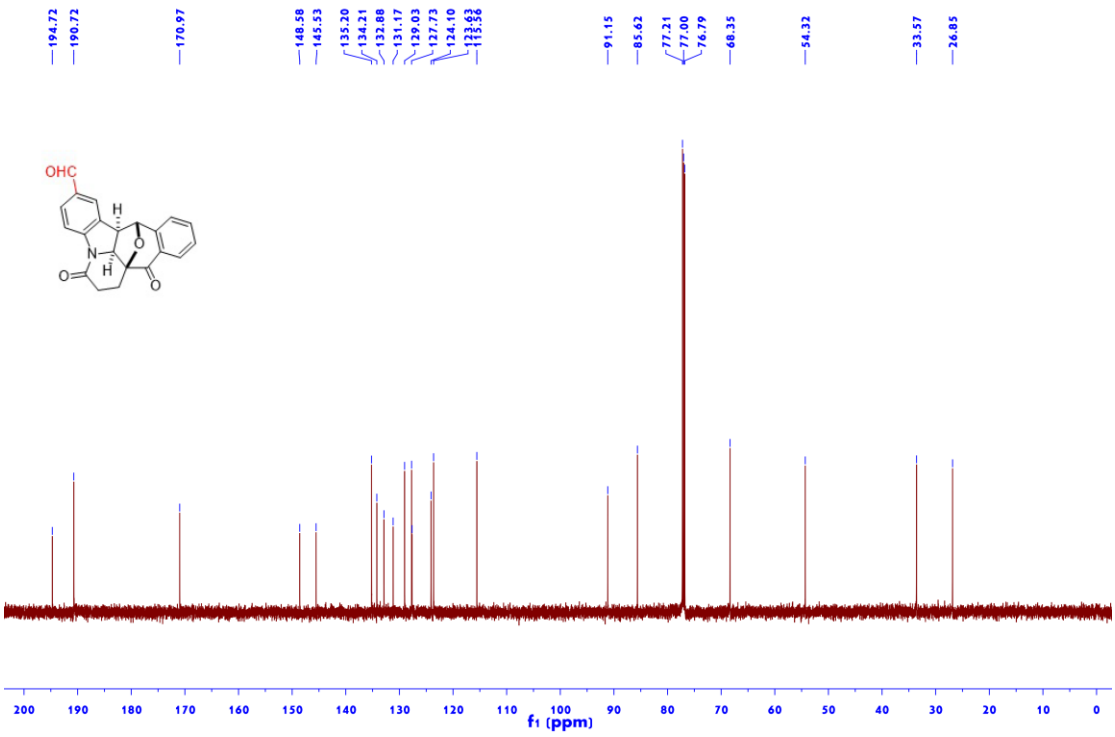


Figure S120 ^{1}H NMR (600 MHz, $CDCl_3$) of **3m**

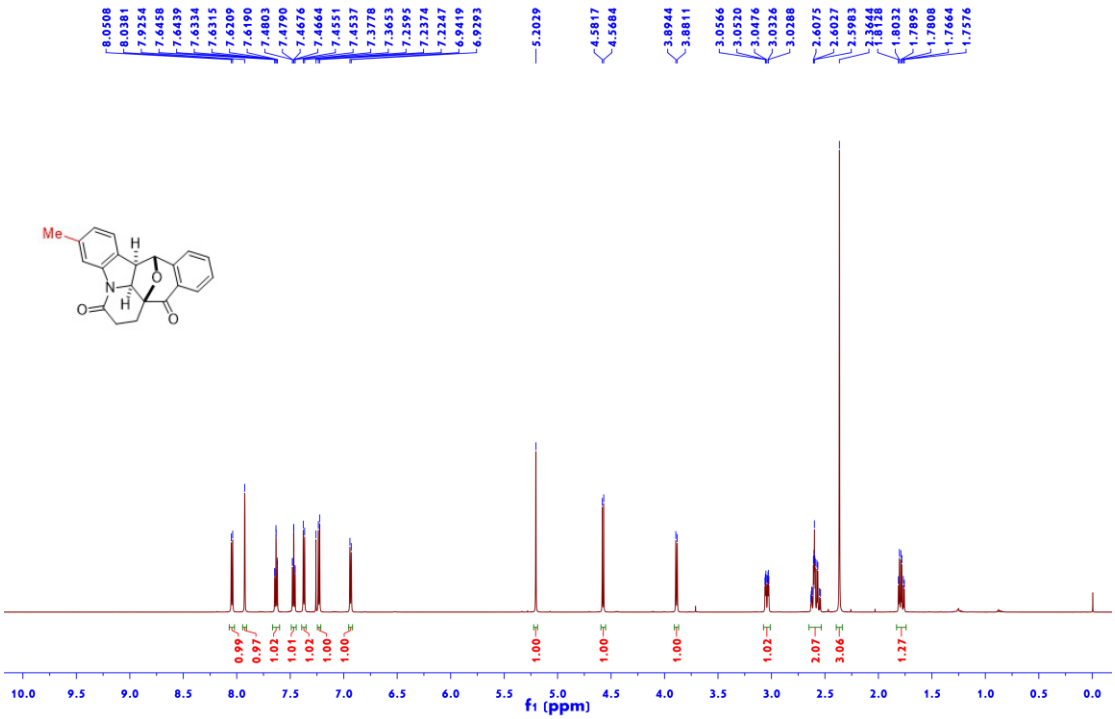


Figure S121 ^{13}C NMR (150 MHz, $CDCl_3$) of **3m**

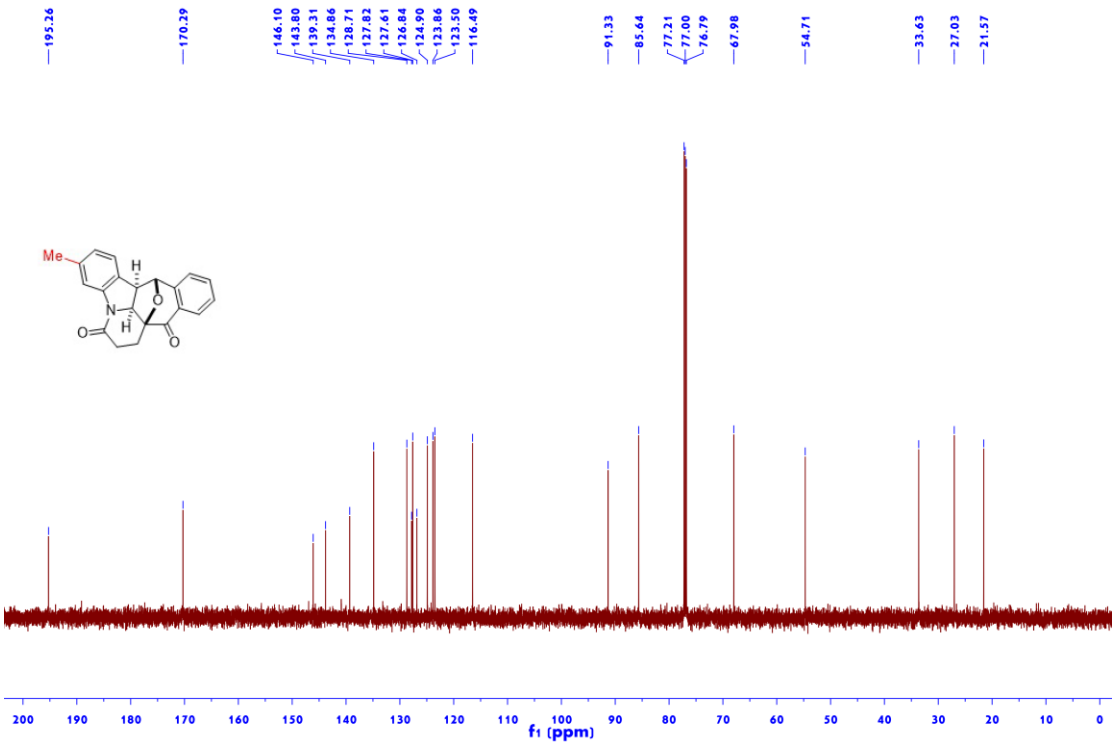


Figure S122 ^{1}H NMR (600 MHz, $CDCl_3$) of **3n**

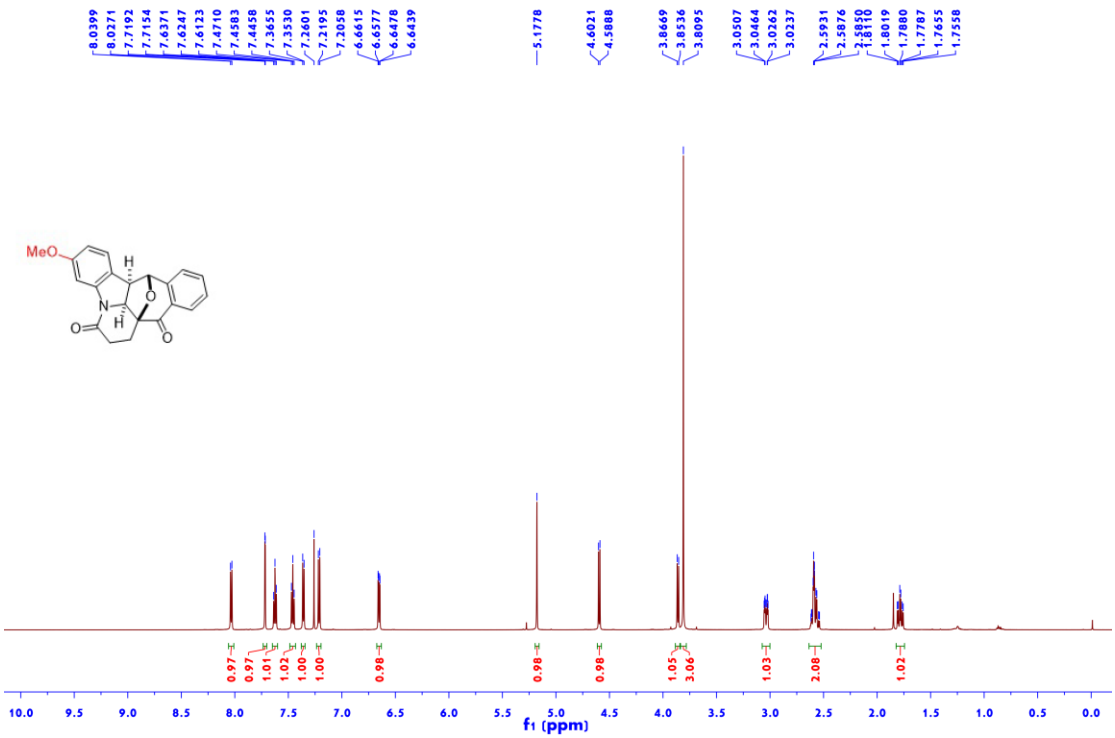


Figure S123 ^{13}C NMR (150 MHz, $CDCl_3$) of **3n**

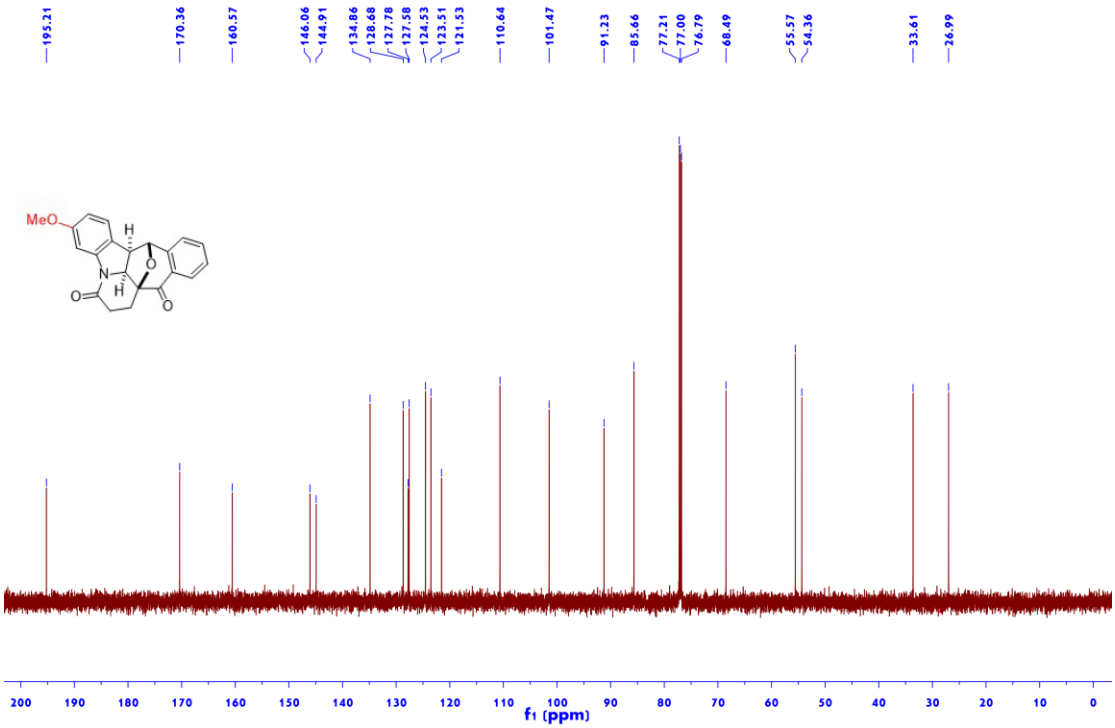


Figure S124 ^{1}H NMR (600 MHz, $CDCl_3$) of **3o**

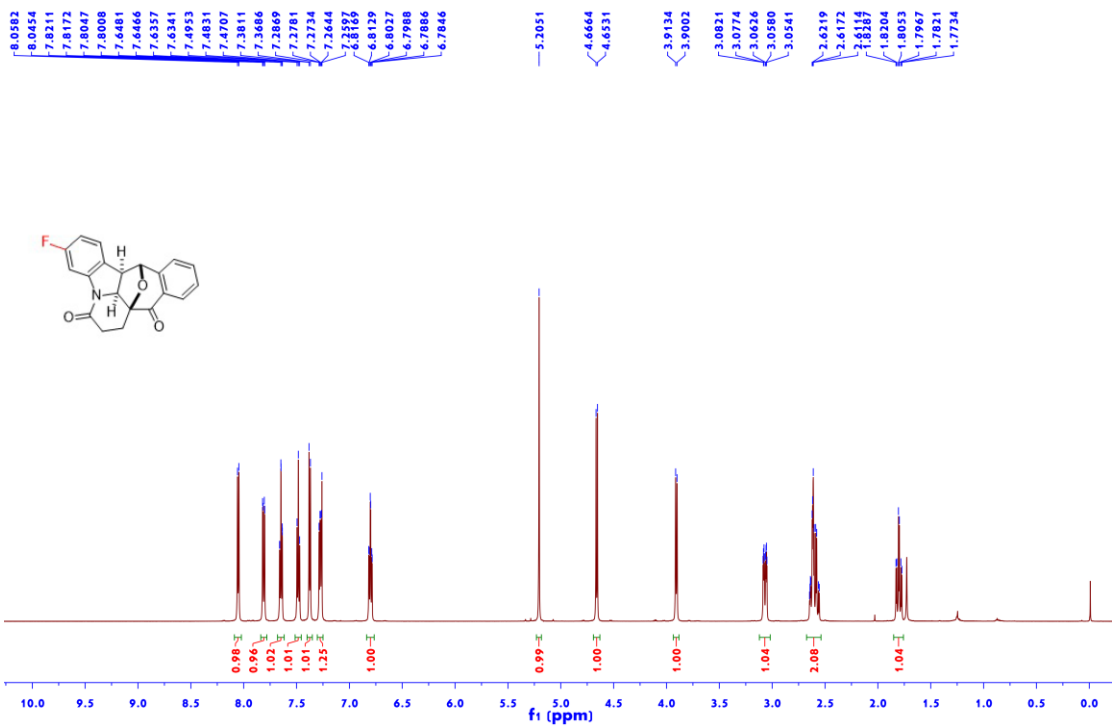


Figure S125 ^{13}C NMR (150 MHz, $CDCl_3$) of **3o**

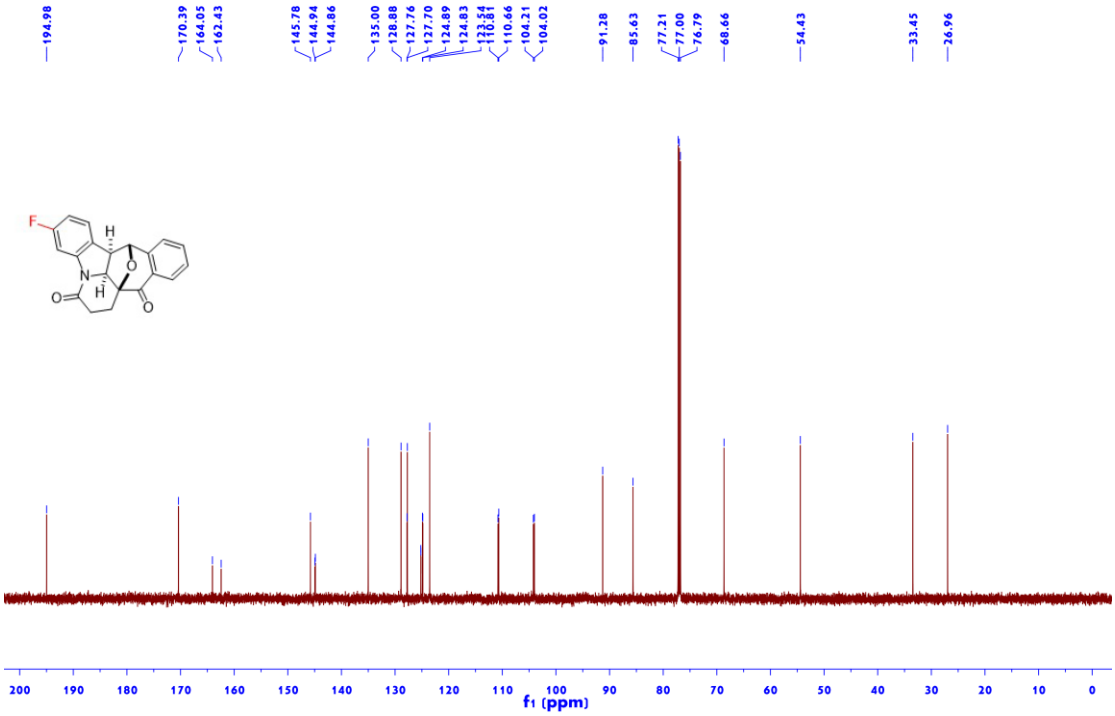


Figure S126 ^{19}F NMR (565 MHz, $CDCl_3$) of **3o**

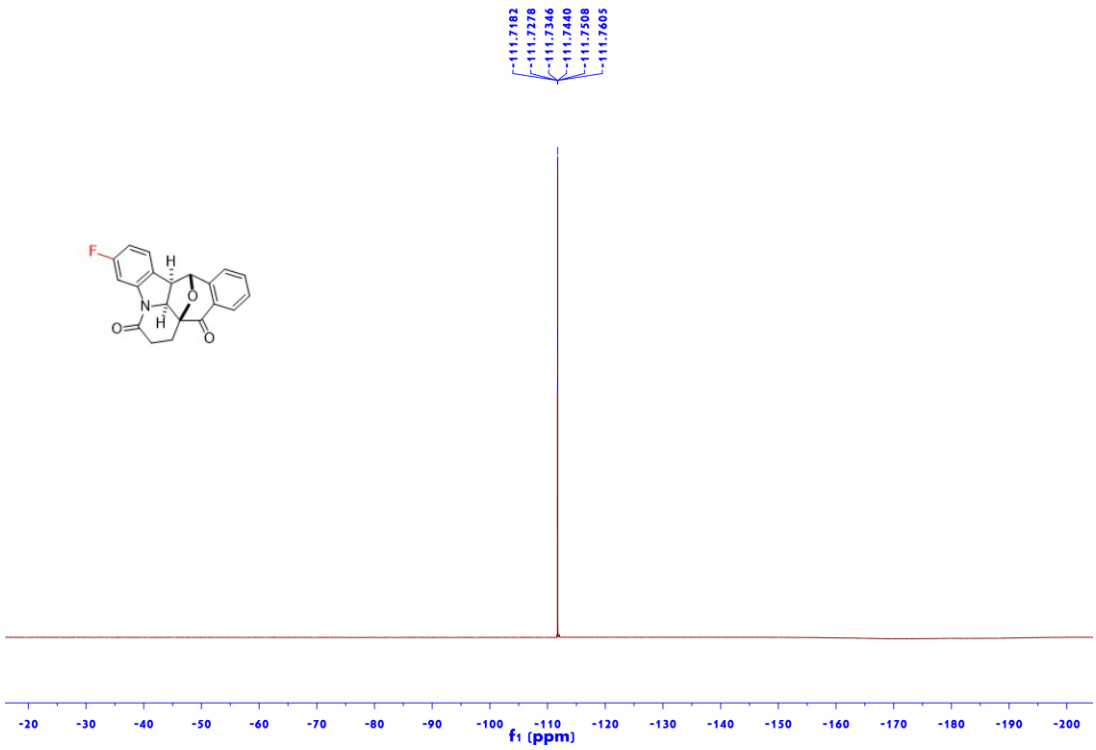


Figure S127 ^{1}H NMR (600 MHz, $CDCl_3$) of **3p**

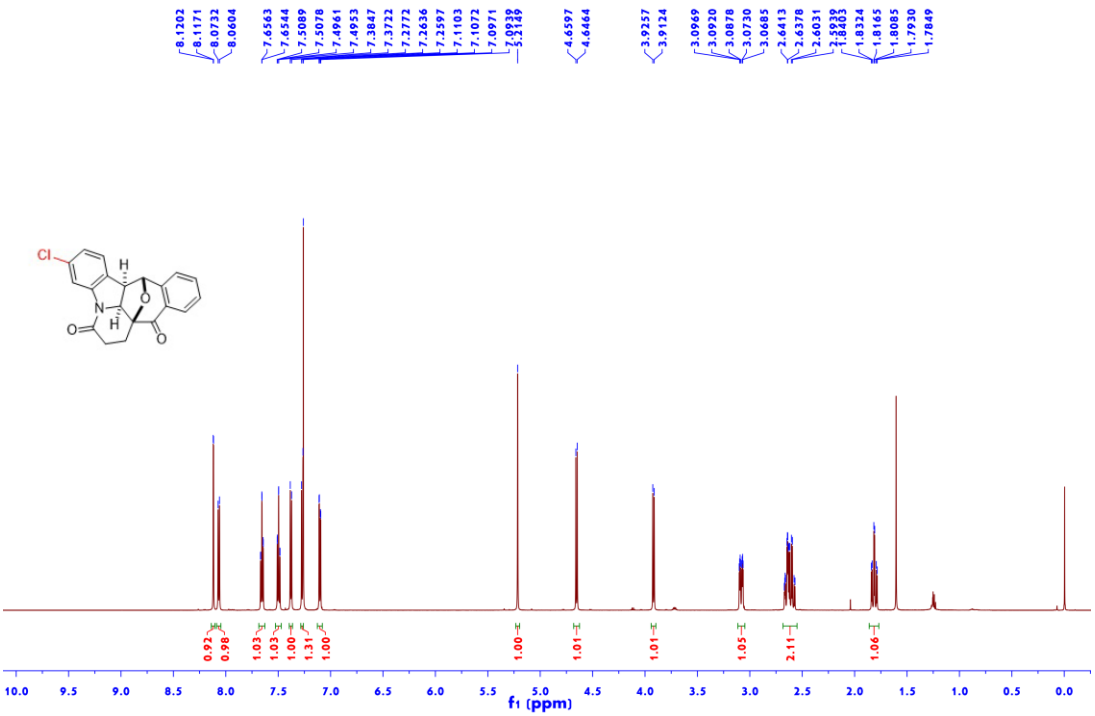


Figure S128 ^{13}C NMR (150 MHz, $CDCl_3$) of **3p**

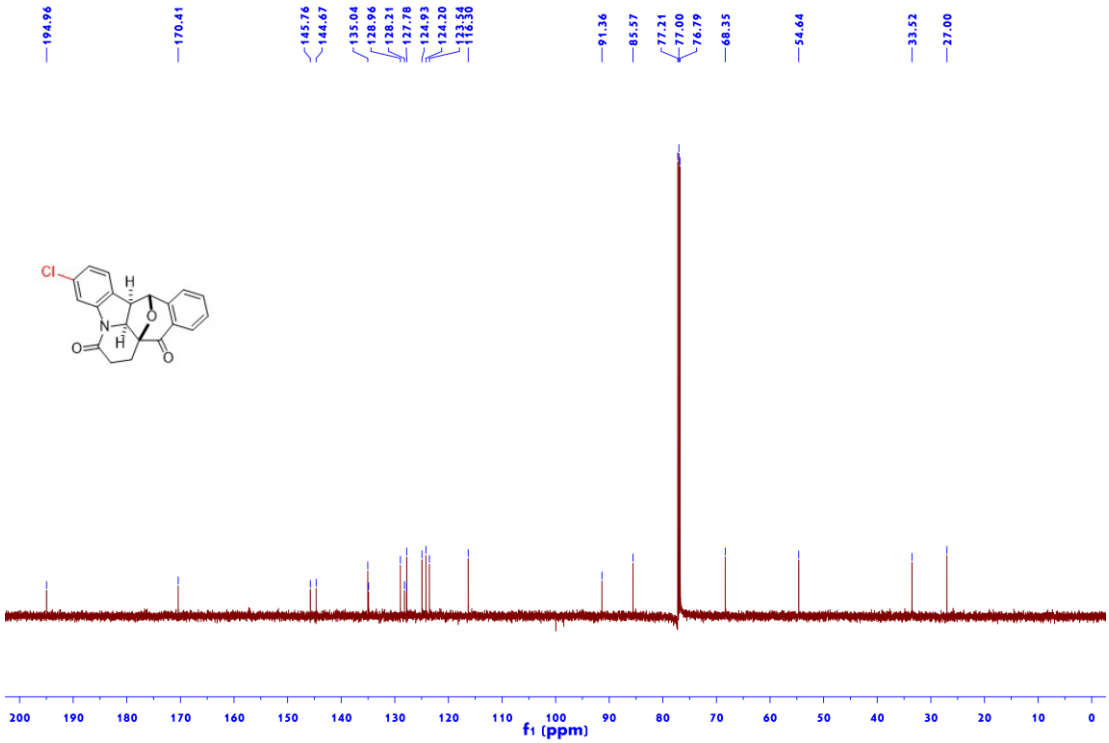


Figure S129 ^{1}H NMR (600 MHz, $CDCl_3$) of **3q**

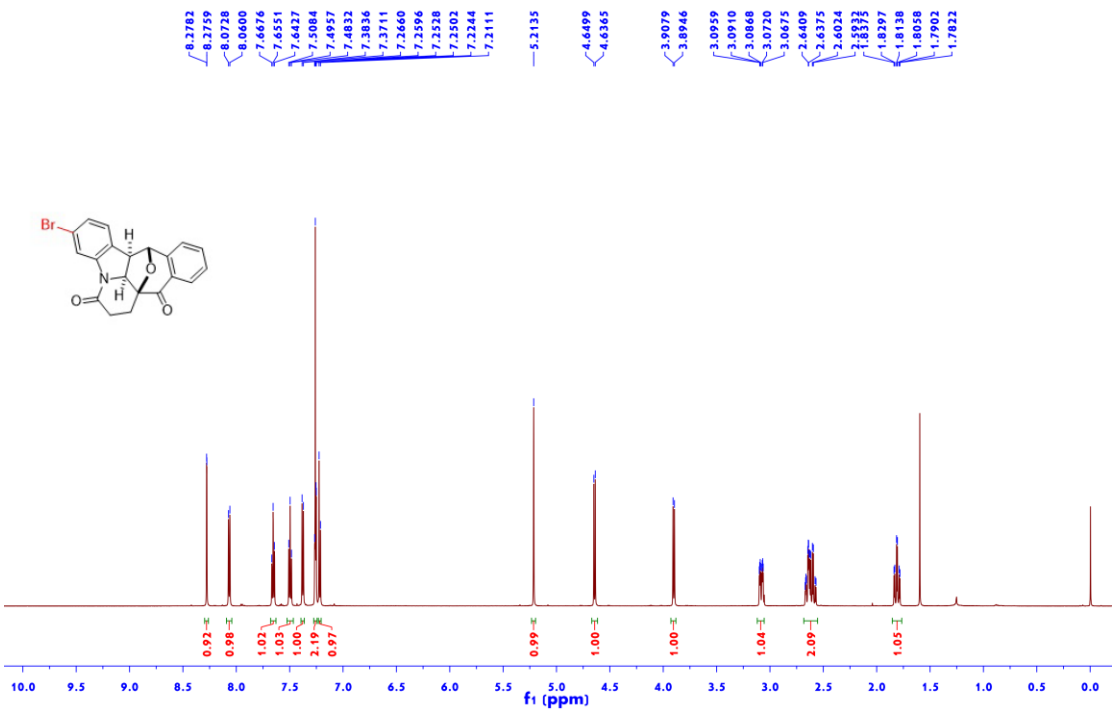


Figure S130 ^{13}C NMR (150 MHz, $CDCl_3$) of **3q**

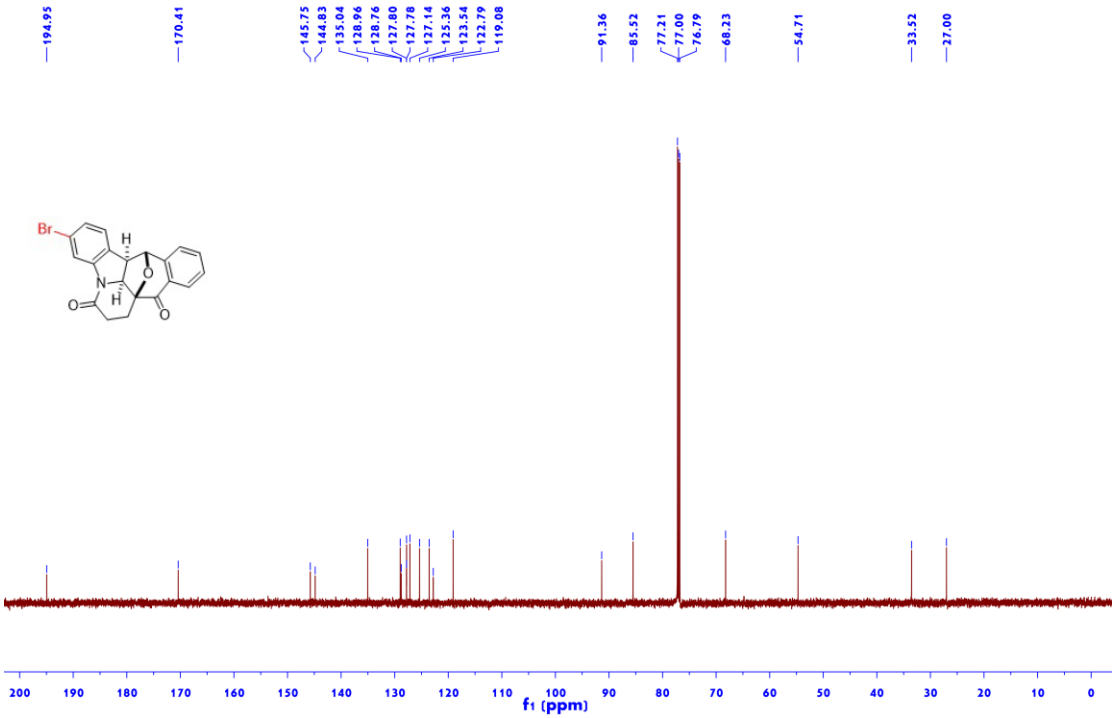


Figure S131 ^{1}H NMR (600 MHz, $CDCl_3$) of **3r**

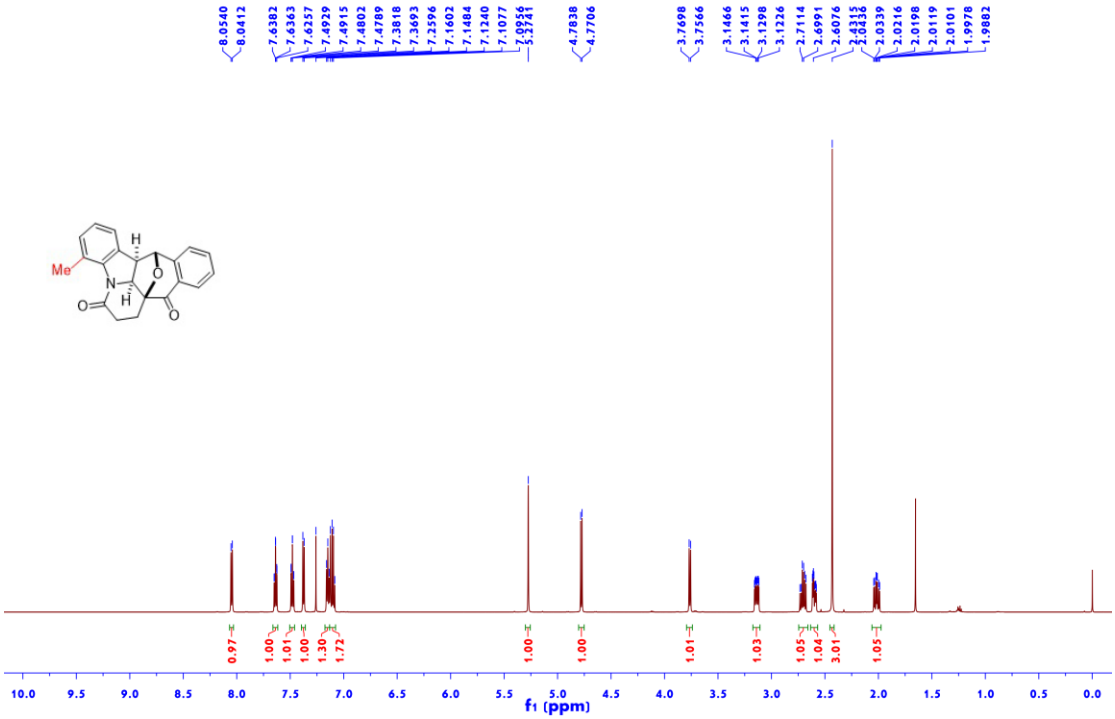


Figure S132 ^{13}C NMR (150 MHz, $CDCl_3$) of **3r**

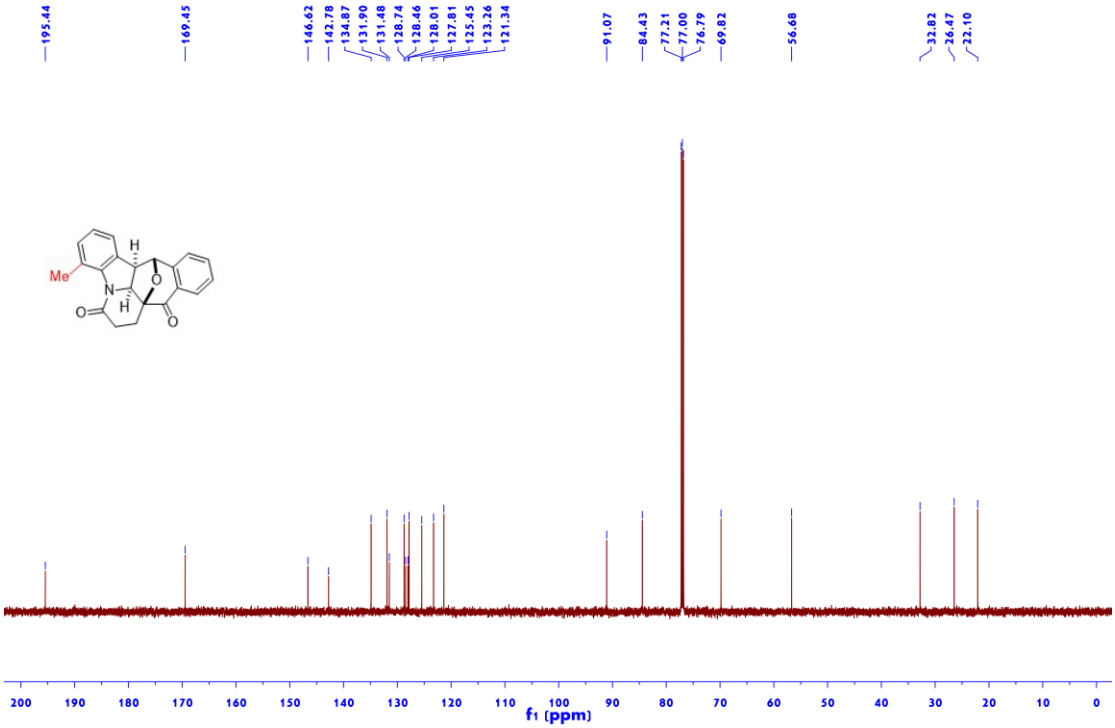


Figure S133 ^{1}H NMR (600 MHz, $CDCl_3$) of **3s**

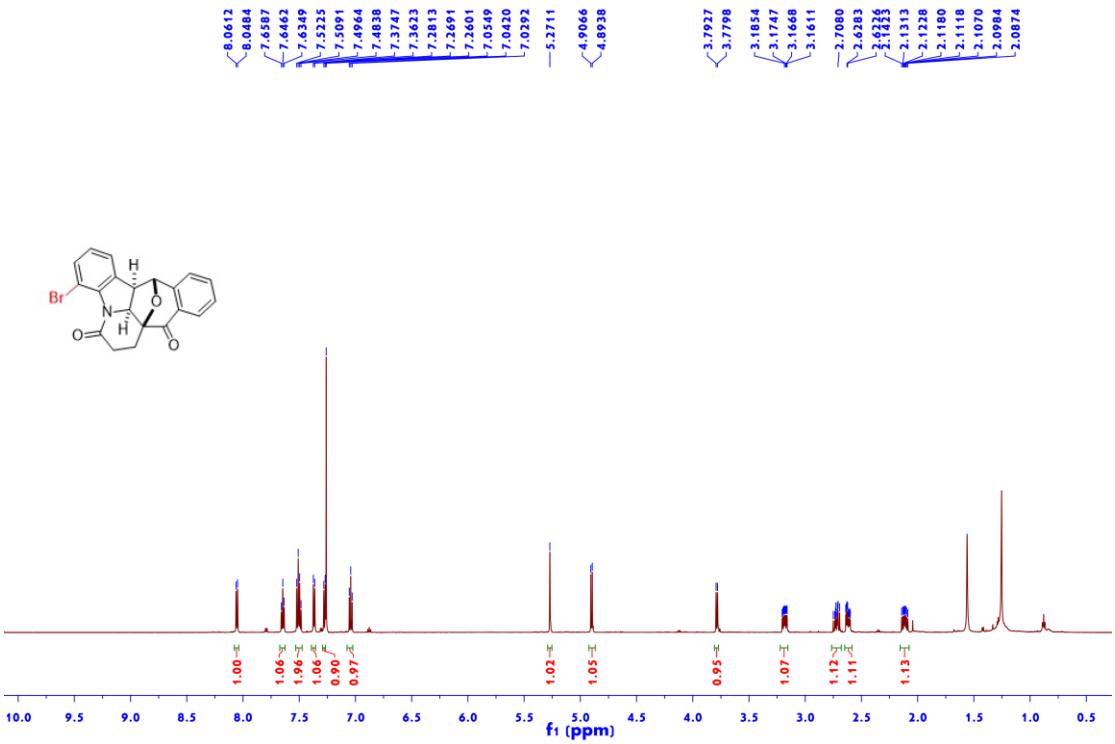


Figure S134 ^{13}C NMR (150 MHz, $CDCl_3$) of **3s**

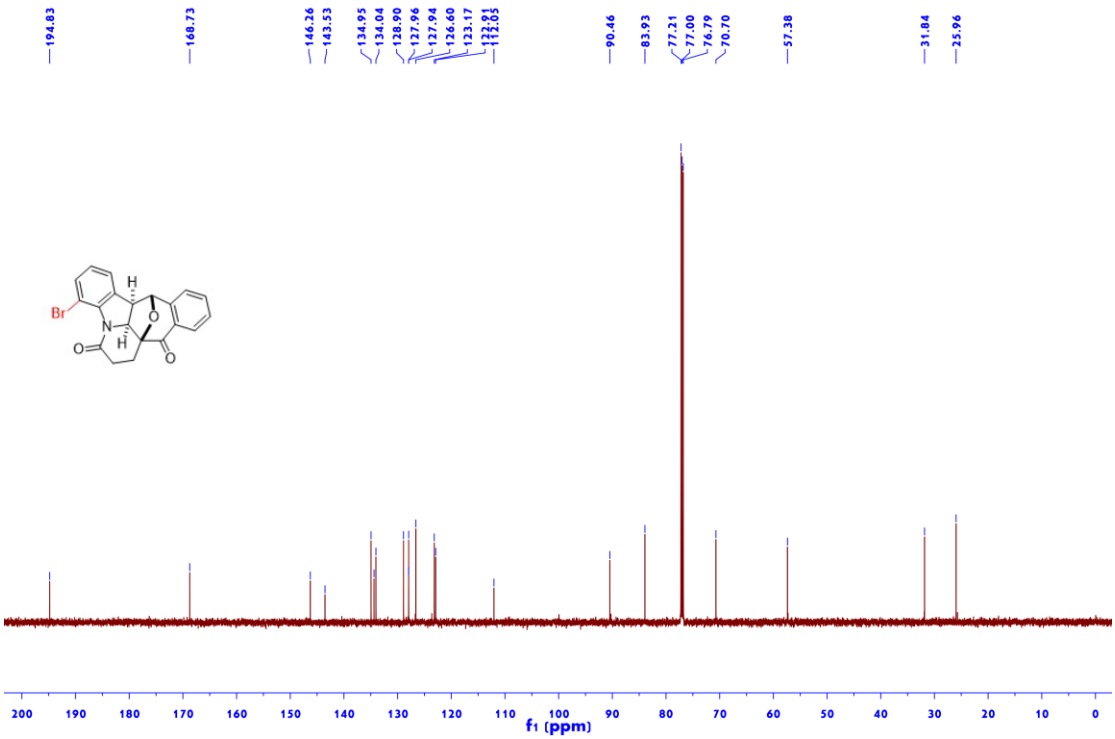


Figure S135 ^{1}H NMR (600 MHz, $CDCl_3$) of **3t**

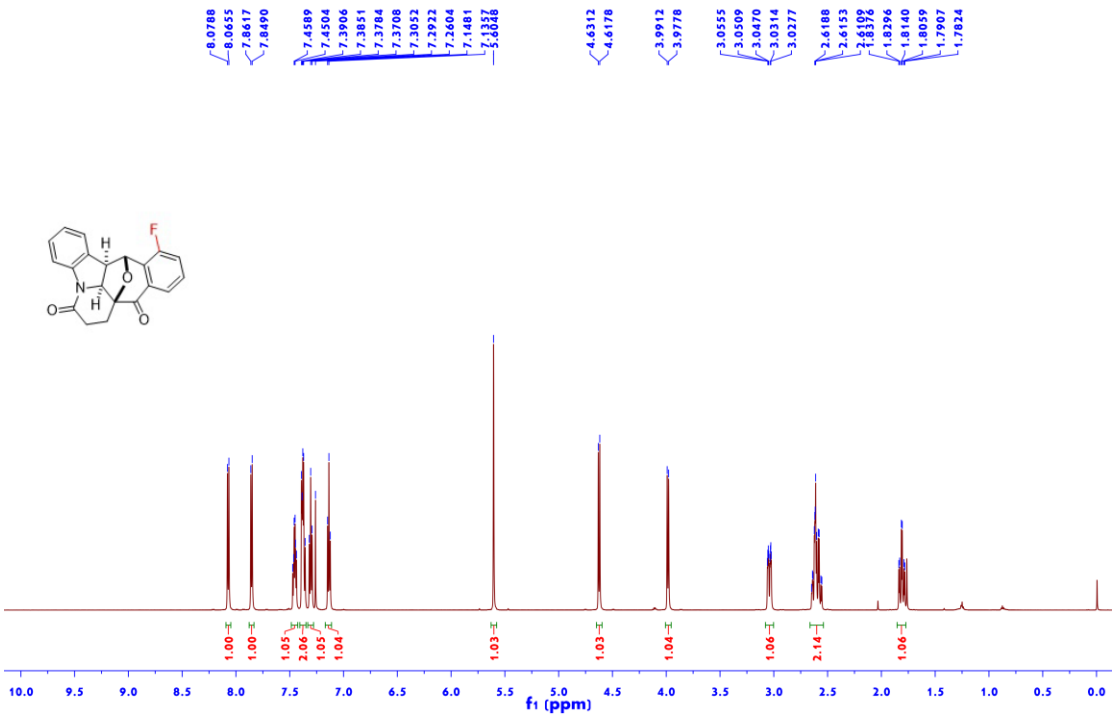


Figure S136 ^{13}C NMR (150 MHz, $CDCl_3$) of **3t**

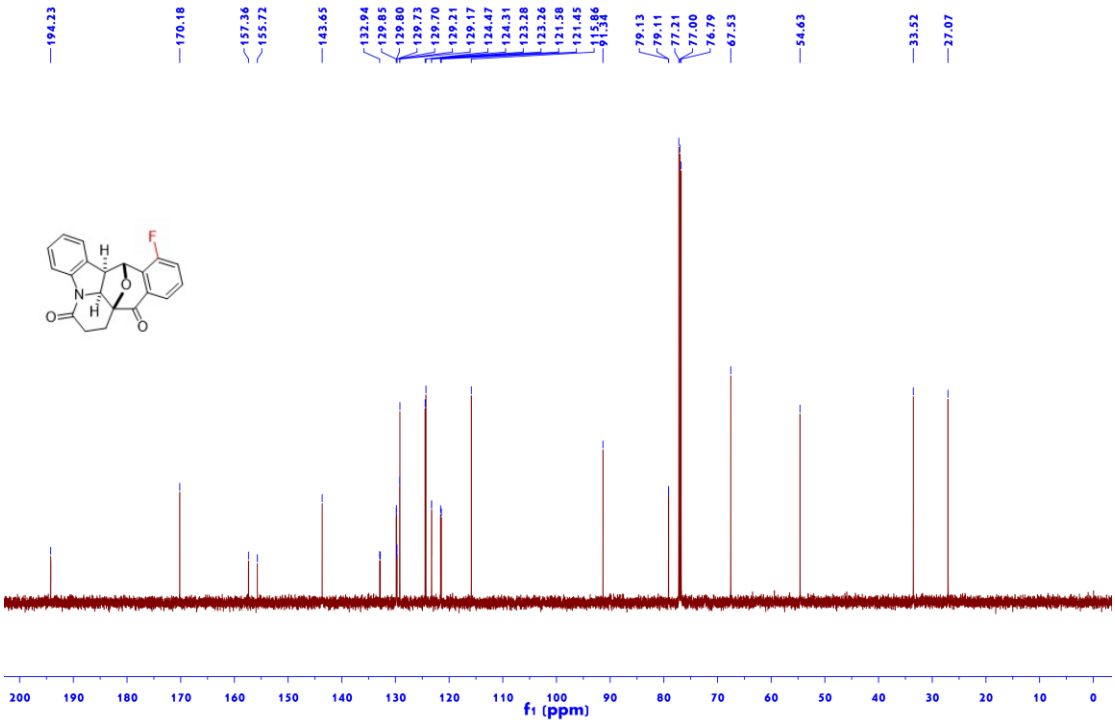


Figure S137 ^{19}F NMR (565 MHz, $CDCl_3$) of **3t**

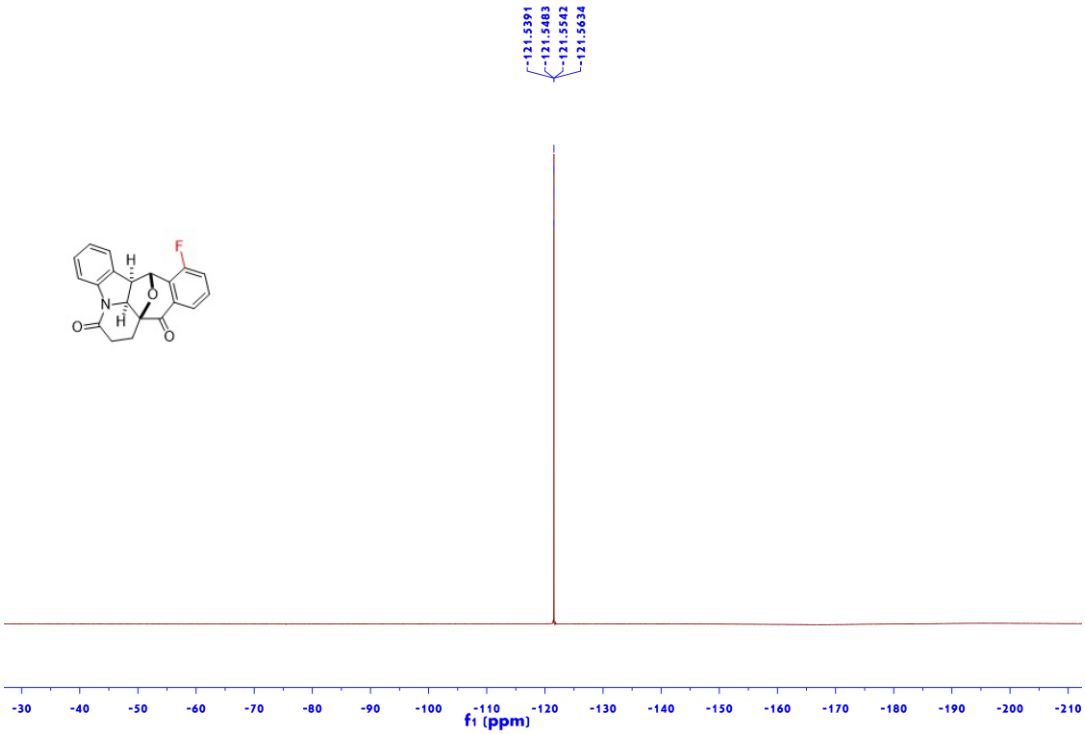


Figure S138 ^{1}H NMR (600 MHz, $CDCl_3$) of **3u**

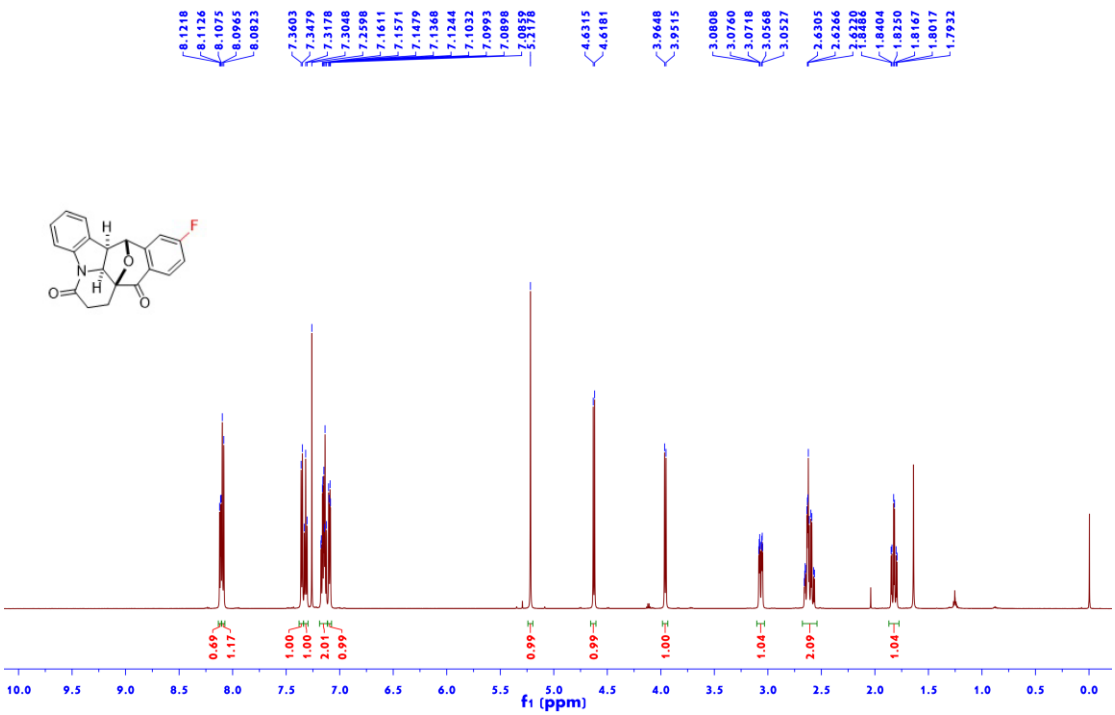


Figure S139 ^{13}C NMR (150 MHz, $CDCl_3$) of **3u**

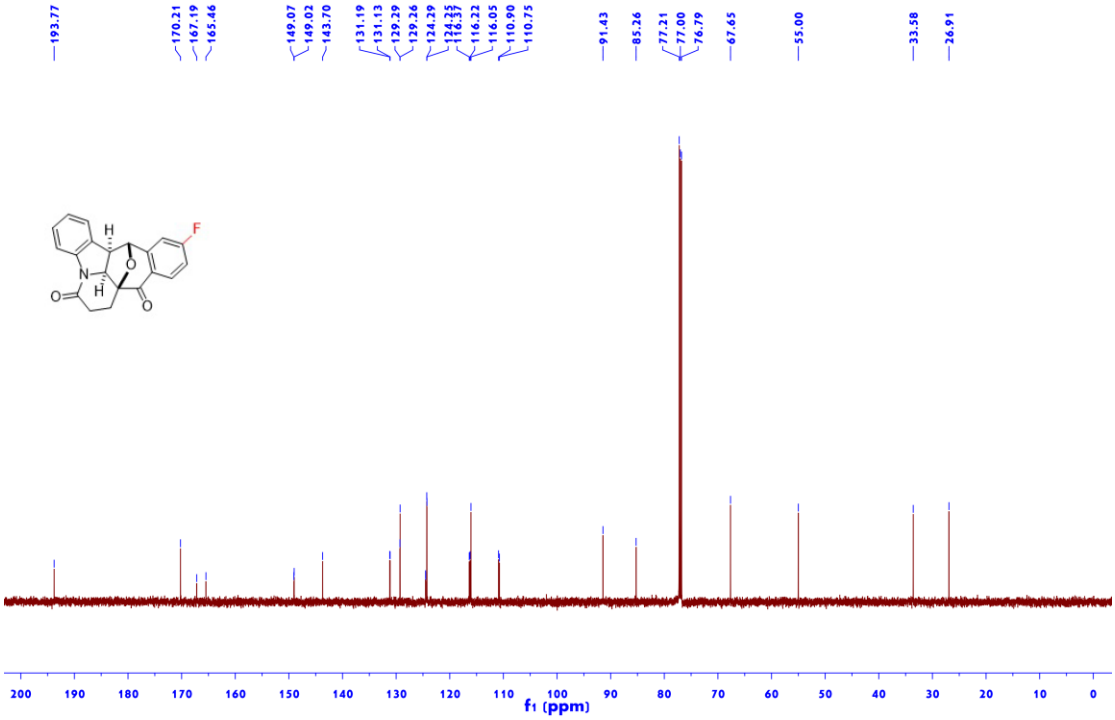


Figure S140 ^{19}F NMR (565 MHz, $CDCl_3$) of **3u**

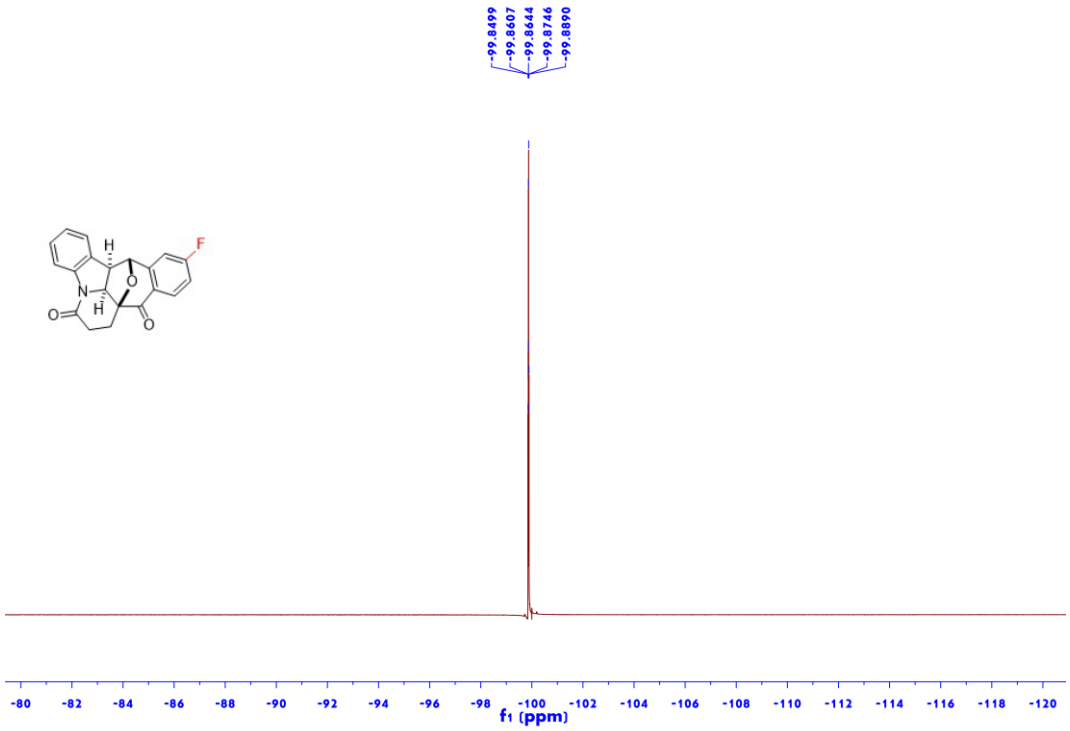


Figure S141 ^{1}H NMR (600 MHz, $CDCl_3$) of **3v**

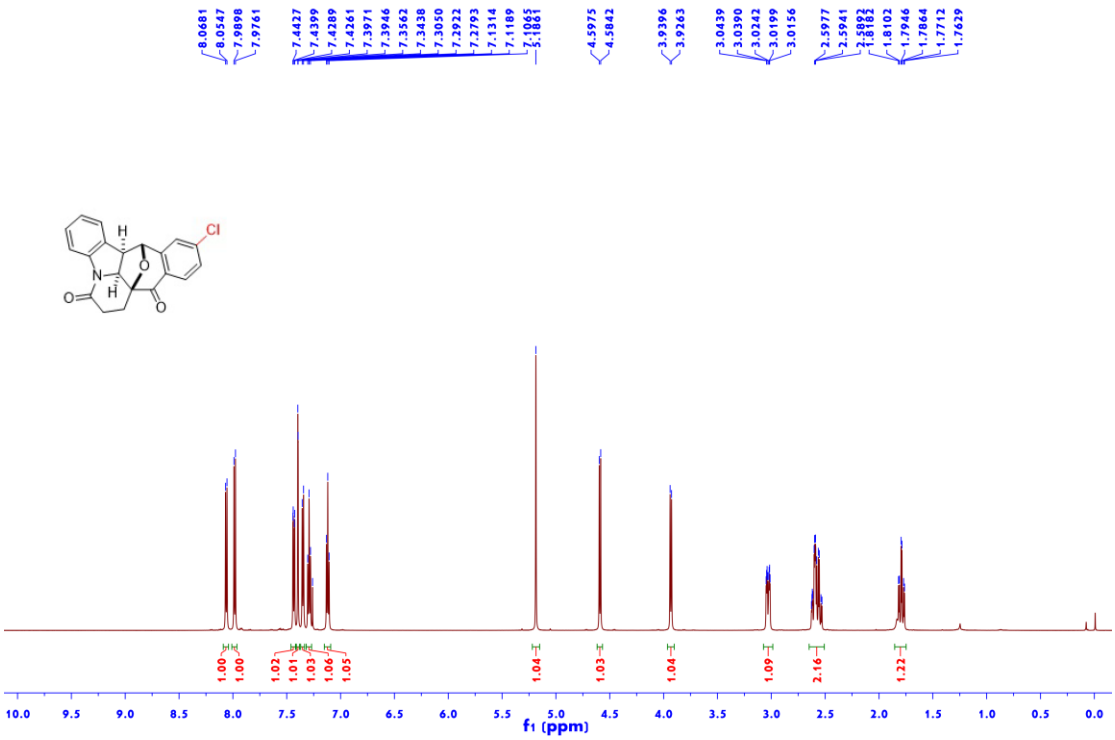


Figure S142 ^{13}C NMR (150 MHz, $CDCl_3$) of **3v**

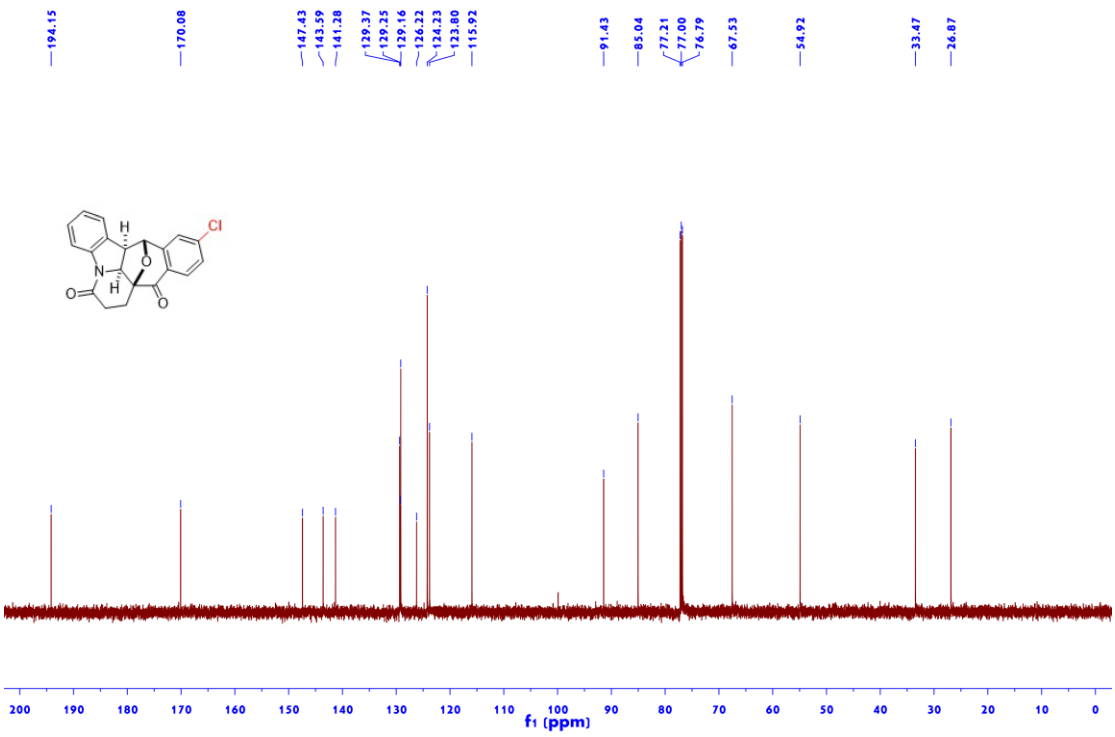


Figure S143 ^{1}H NMR (600 MHz, $CDCl_3$) of **3w**

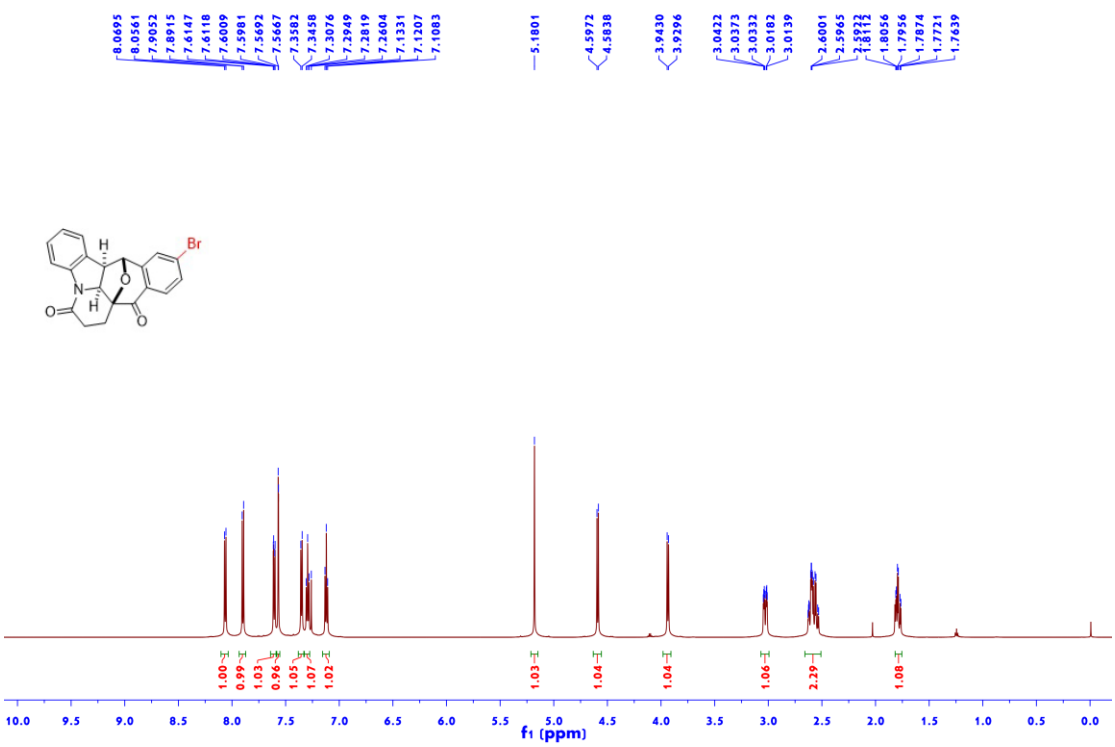


Figure S144 ^{13}C NMR (150 MHz, $CDCl_3$) of **3w**

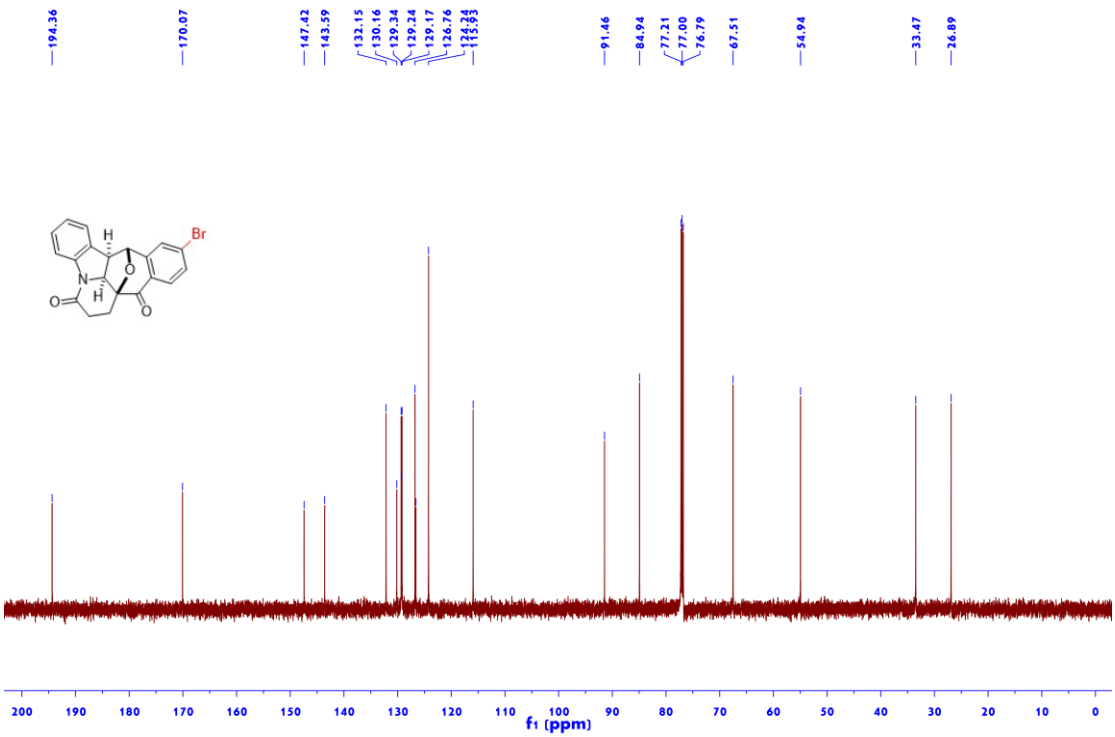


Figure S145 ^{1}H NMR (600 MHz, $CDCl_3$) of **3x**

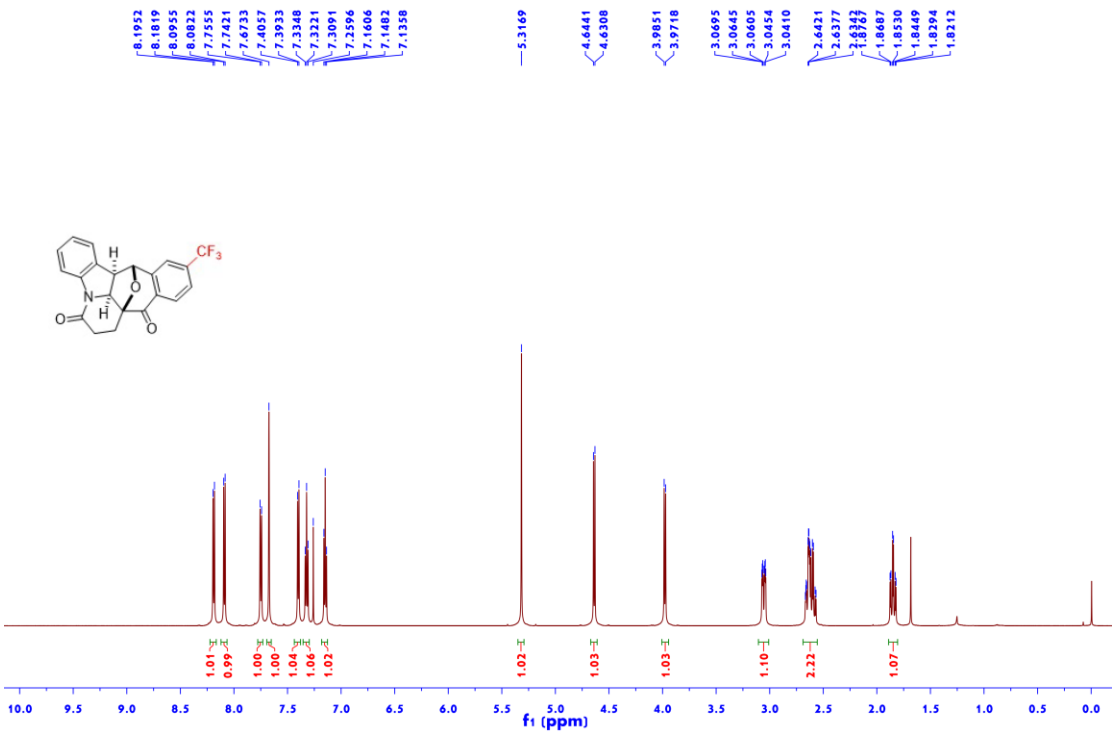


Figure S146 ^{13}C NMR (150 MHz, $CDCl_3$) of **3x**

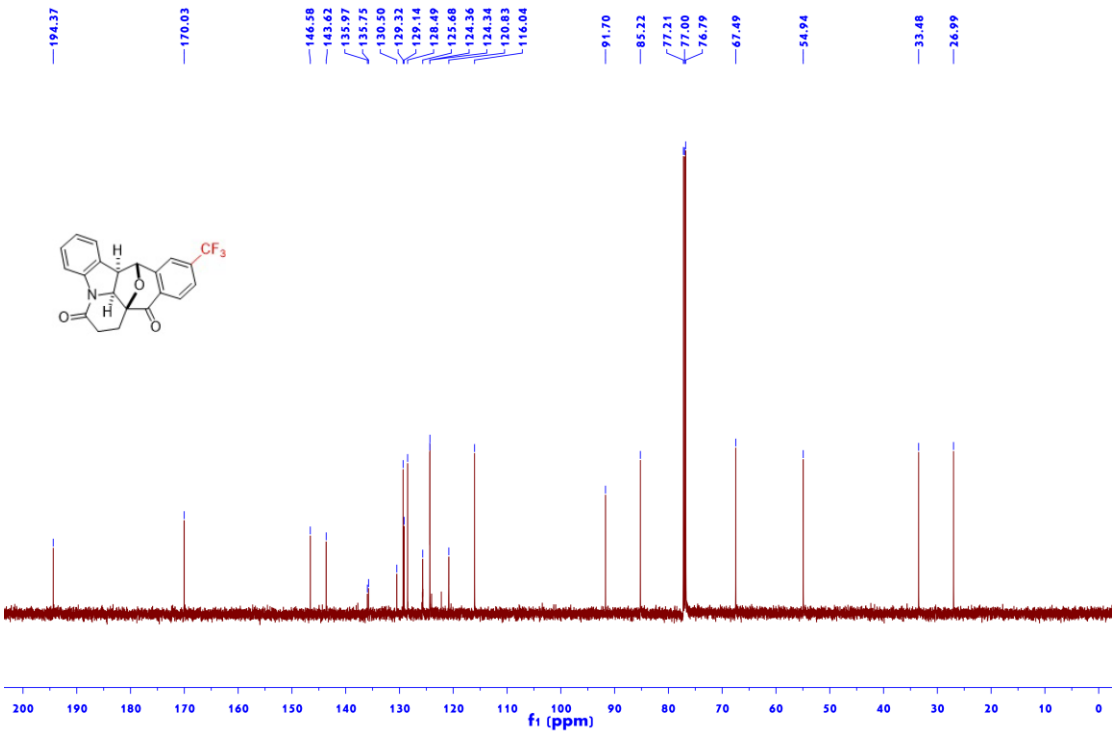


Figure S147 ^{19}F NMR (565 MHz, $CDCl_3$) of **3x**

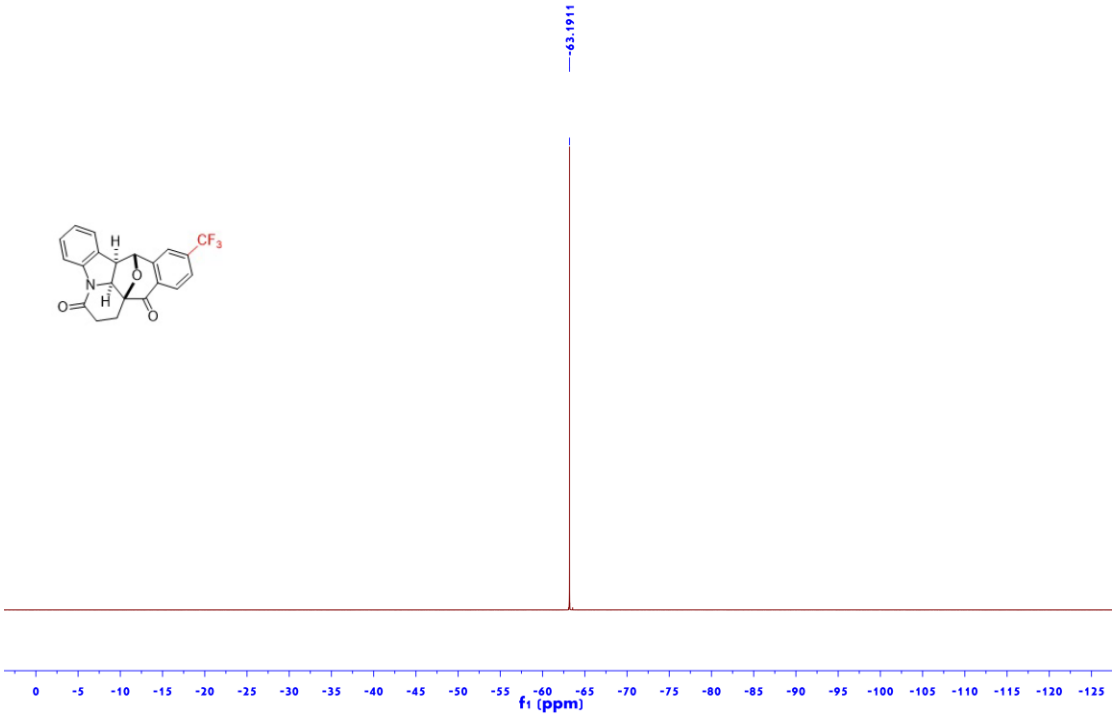


Figure S148 ^{1}H NMR (600 MHz, $CDCl_3$) of **3y**

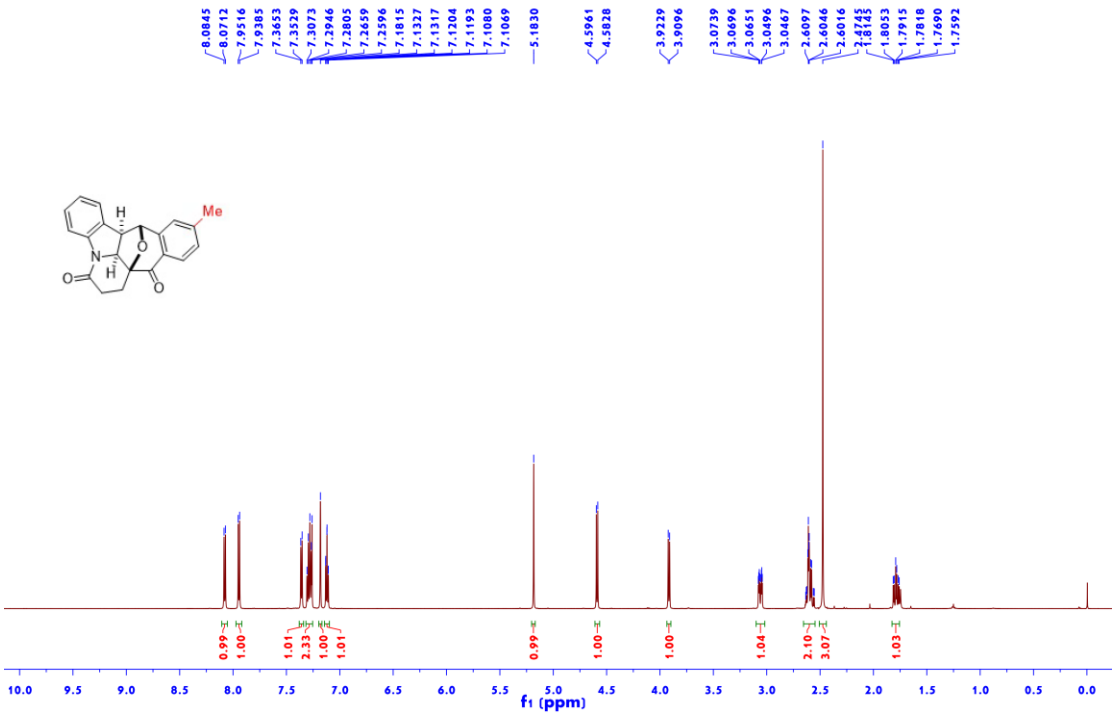


Figure S149 ^{13}C NMR (150 MHz, $CDCl_3$) of **3y**

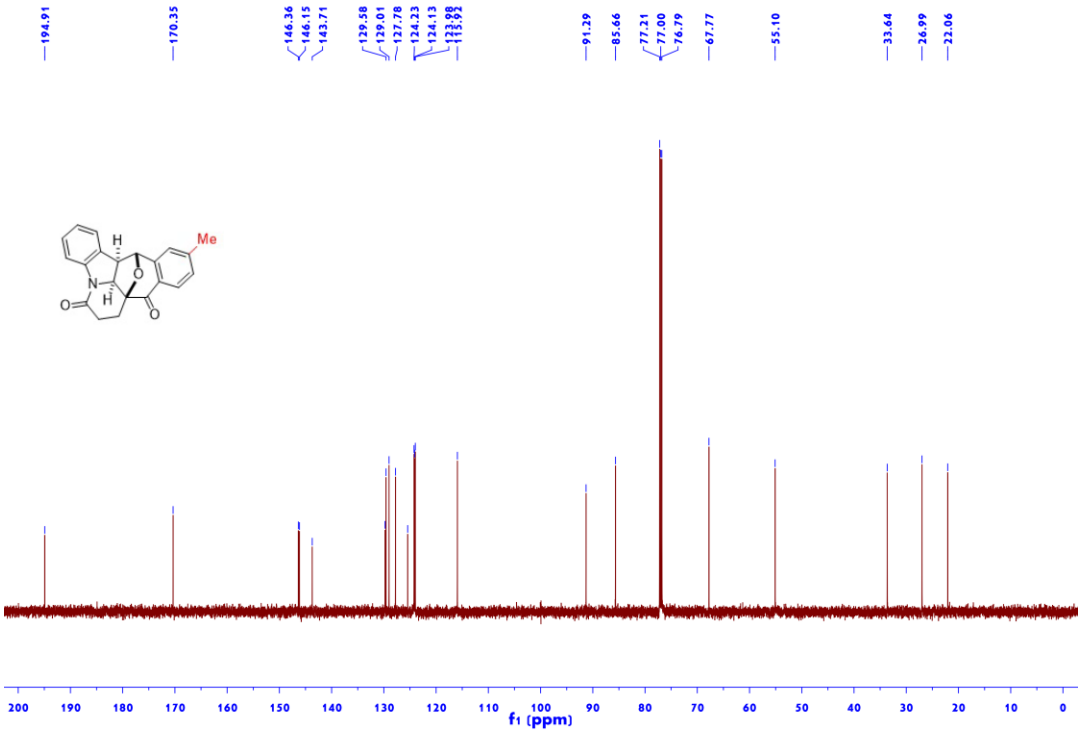


Figure S150 ^{1}H NMR (600 MHz, $CDCl_3$) of **3z**

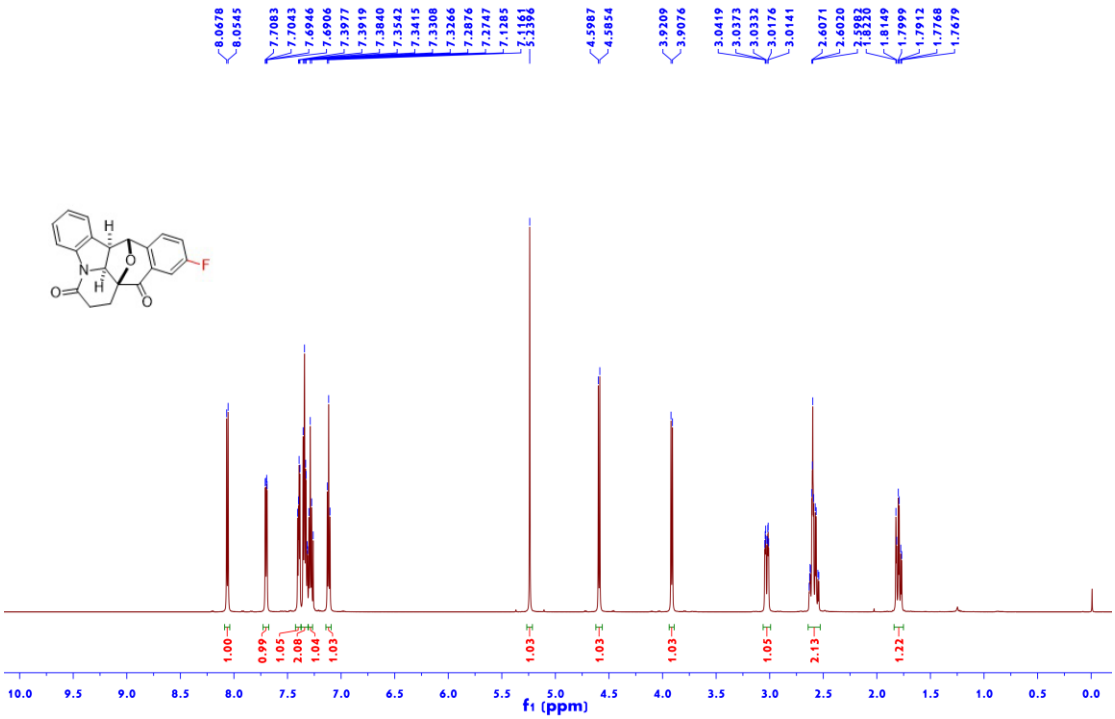


Figure S151 ^{13}C NMR (150 MHz, $CDCl_3$) of **3z**

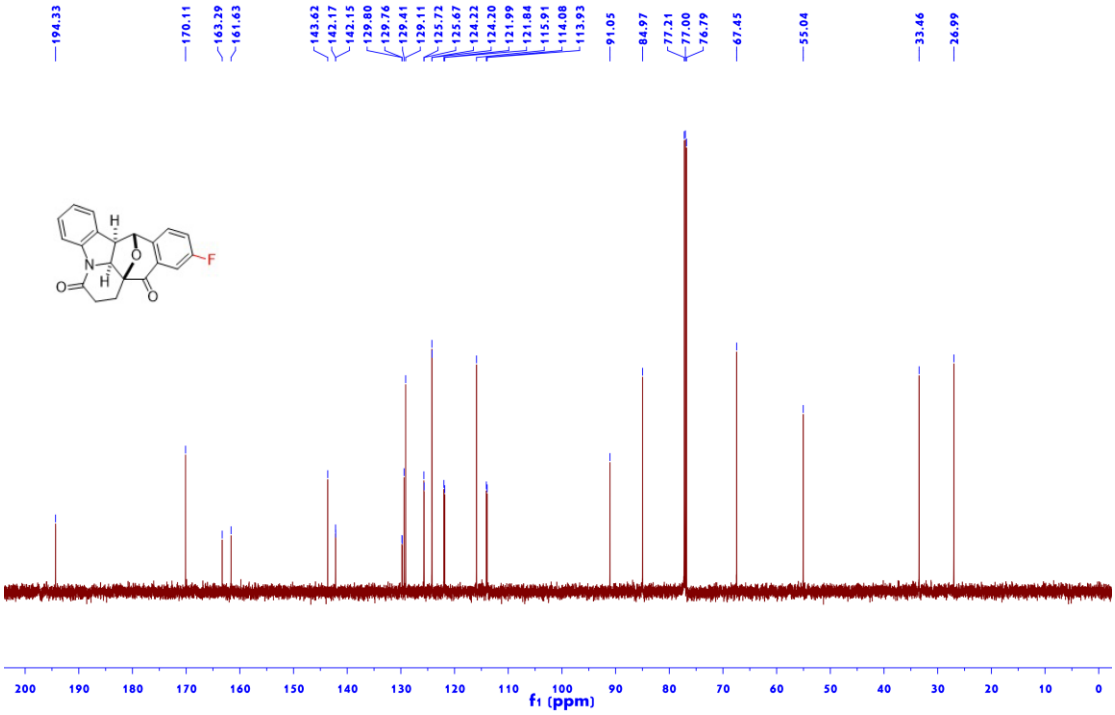


Figure S152 ^{19}F NMR (565 MHz, $CDCl_3$) of **3z**

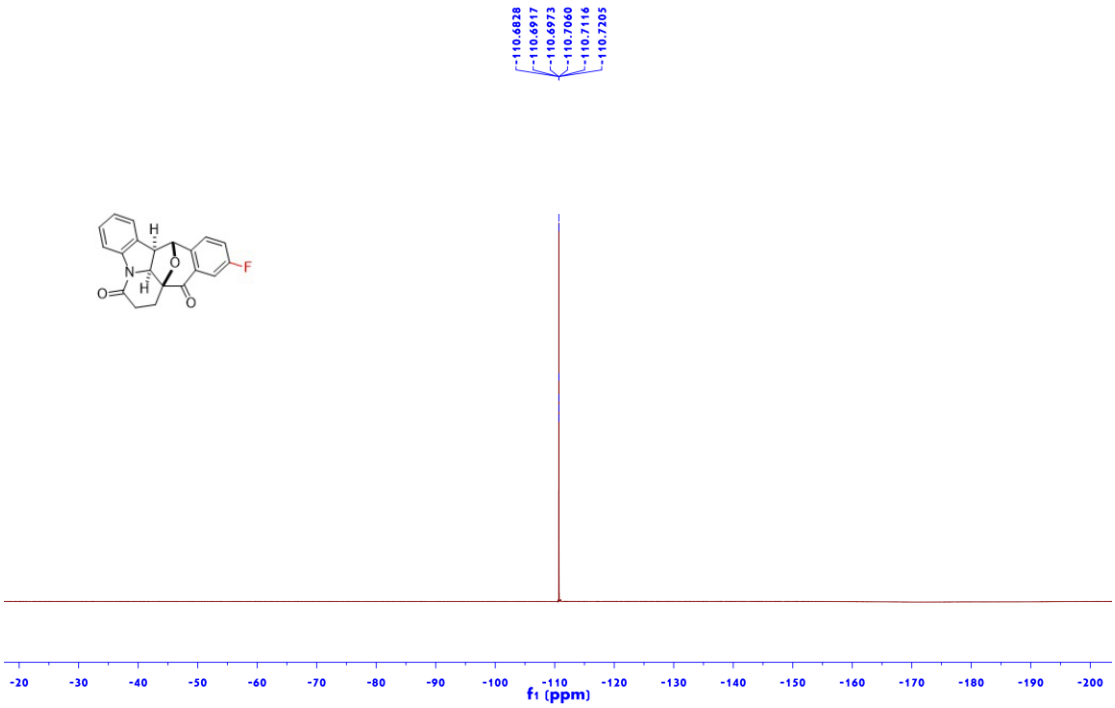


Figure S153 ^{1}H NMR (600 MHz, $CDCl_3$) of **3aa**

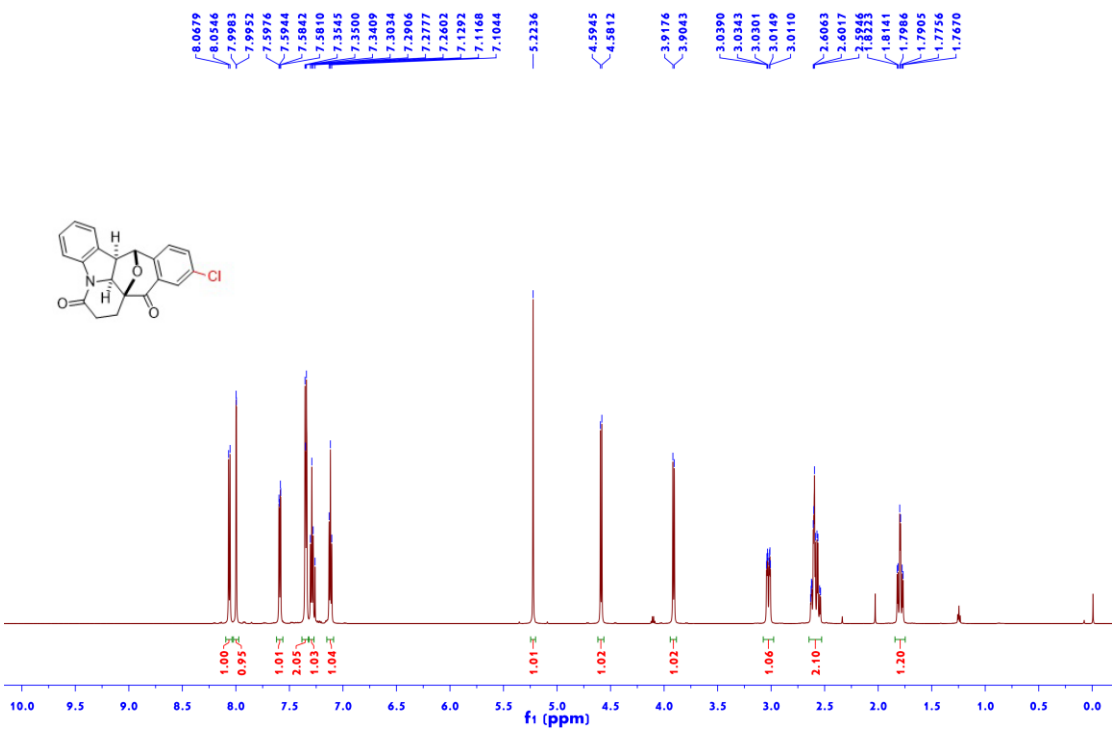


Figure S154 ^{13}C NMR (150 MHz, $CDCl_3$) of **3aa**

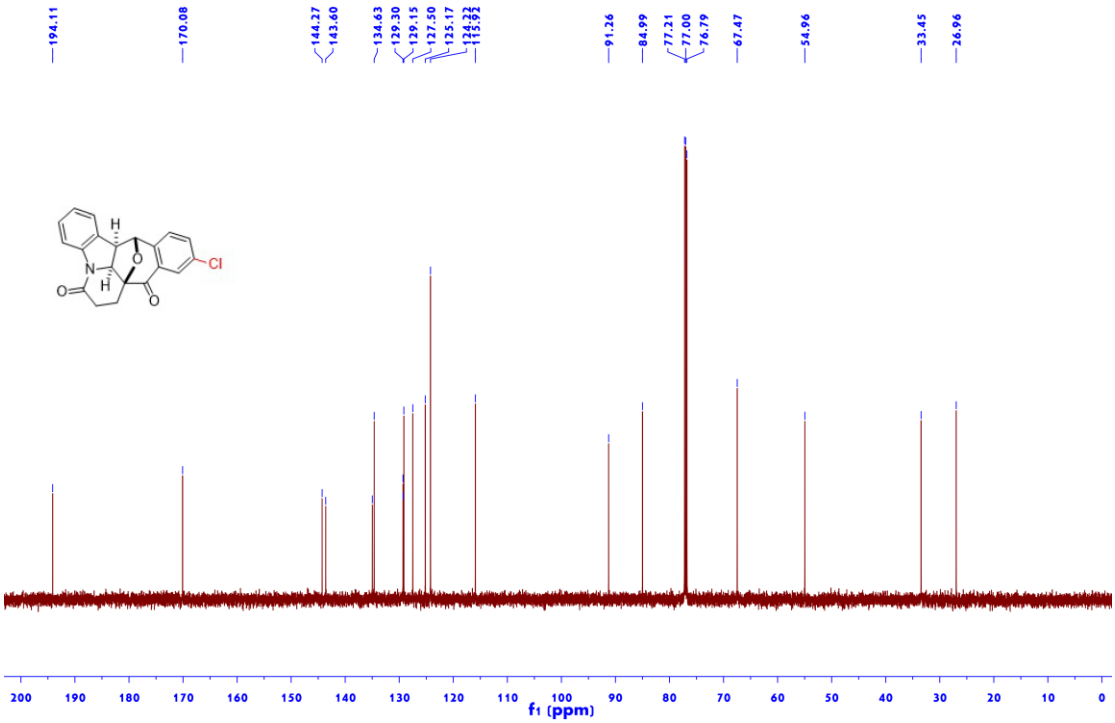


Figure S155 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ab**

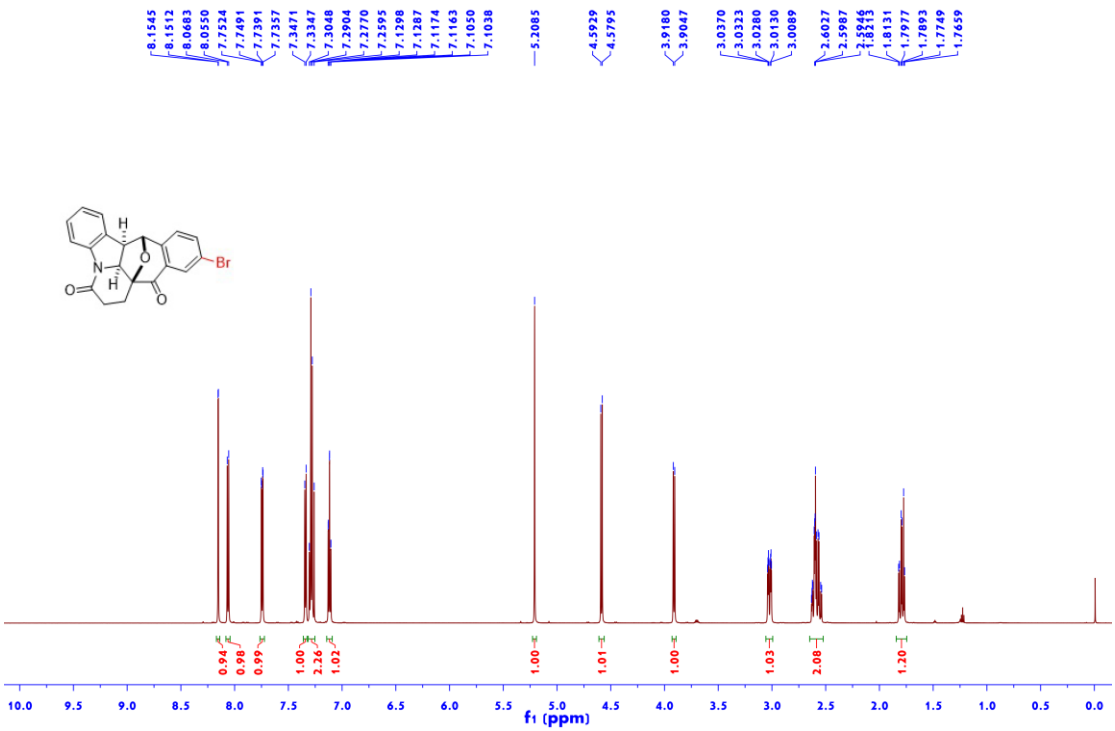


Figure S156 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ab**

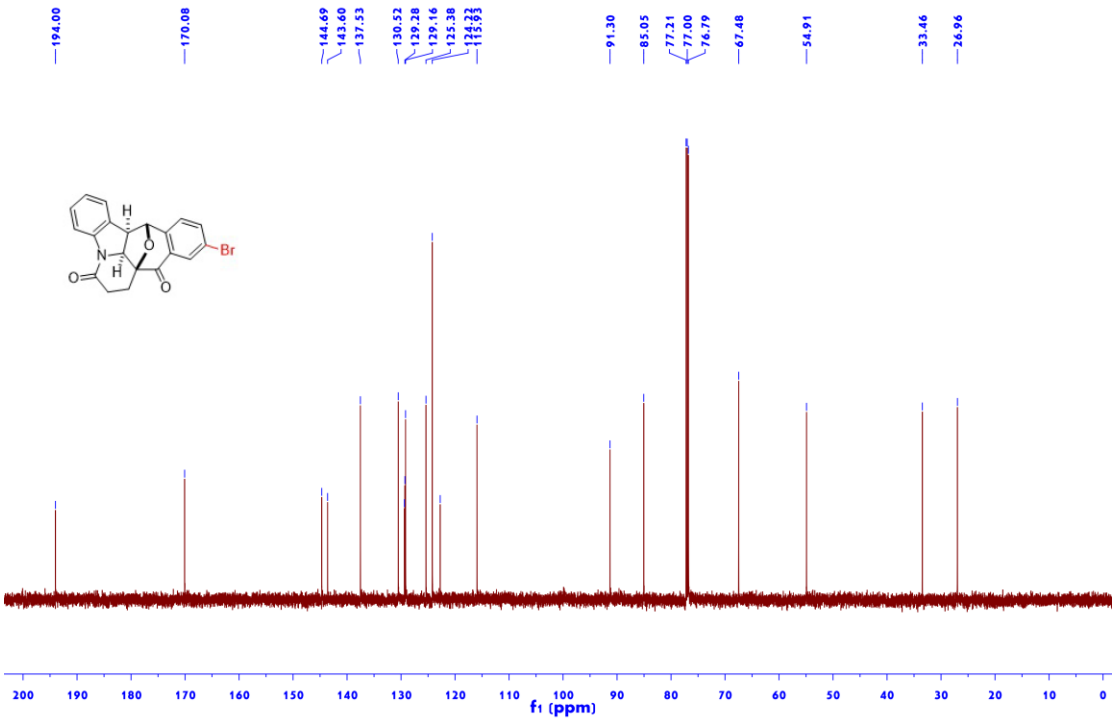


Figure S157 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ac**

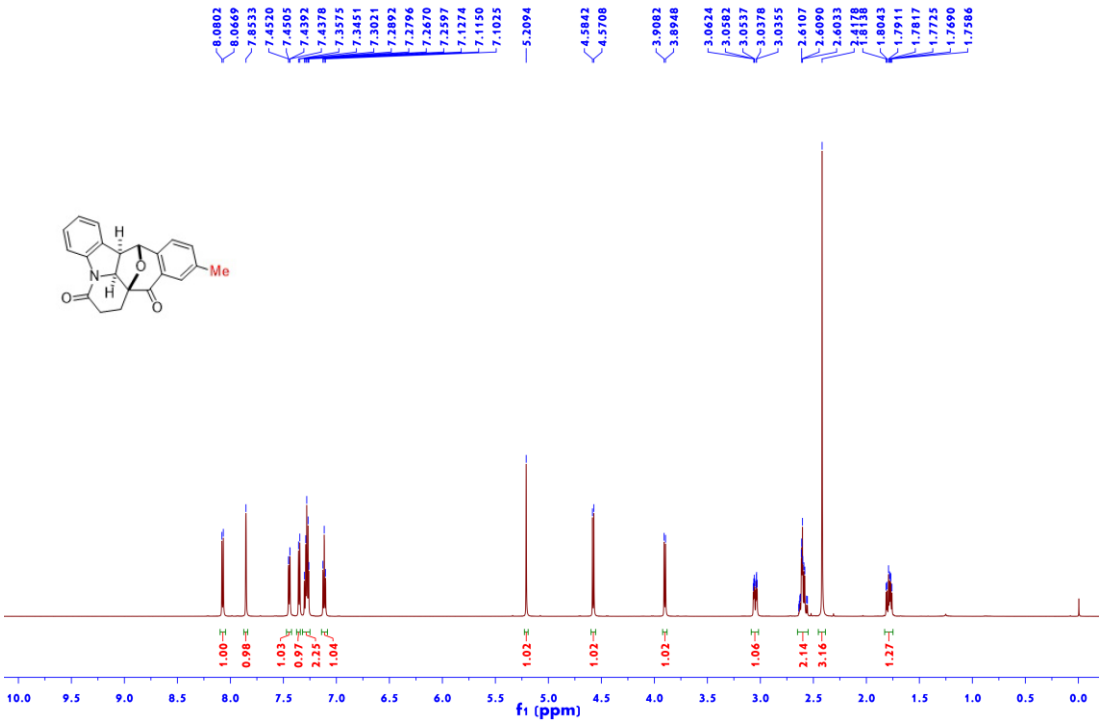


Figure S158 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ac**

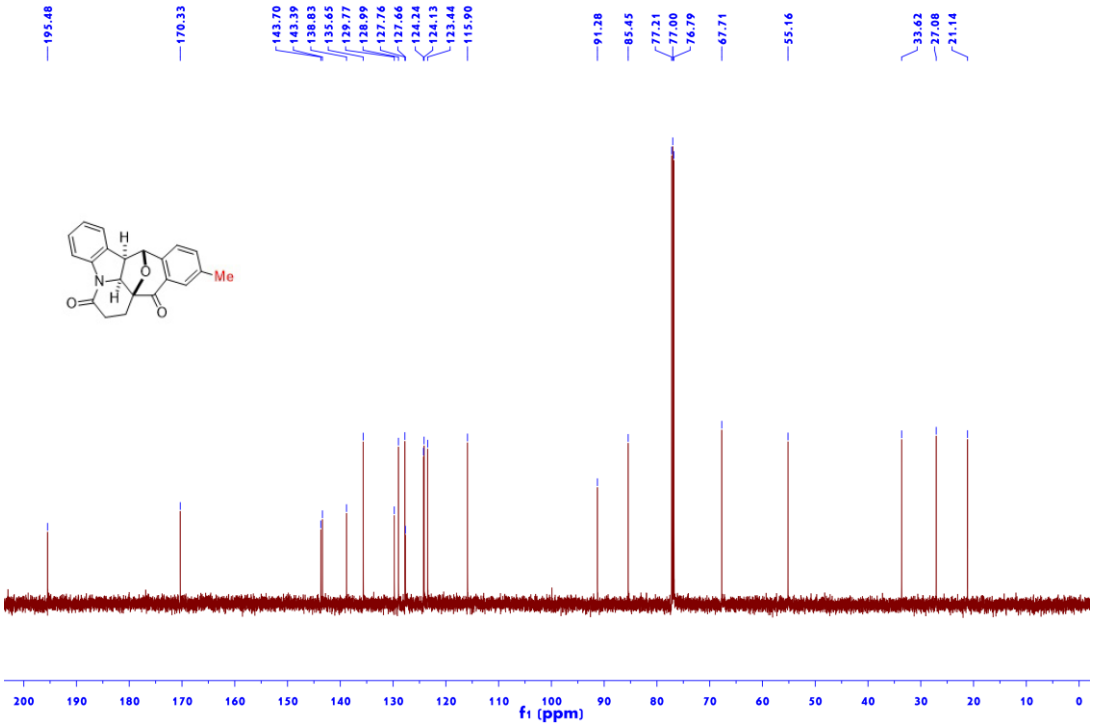


Figure S159 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ad**

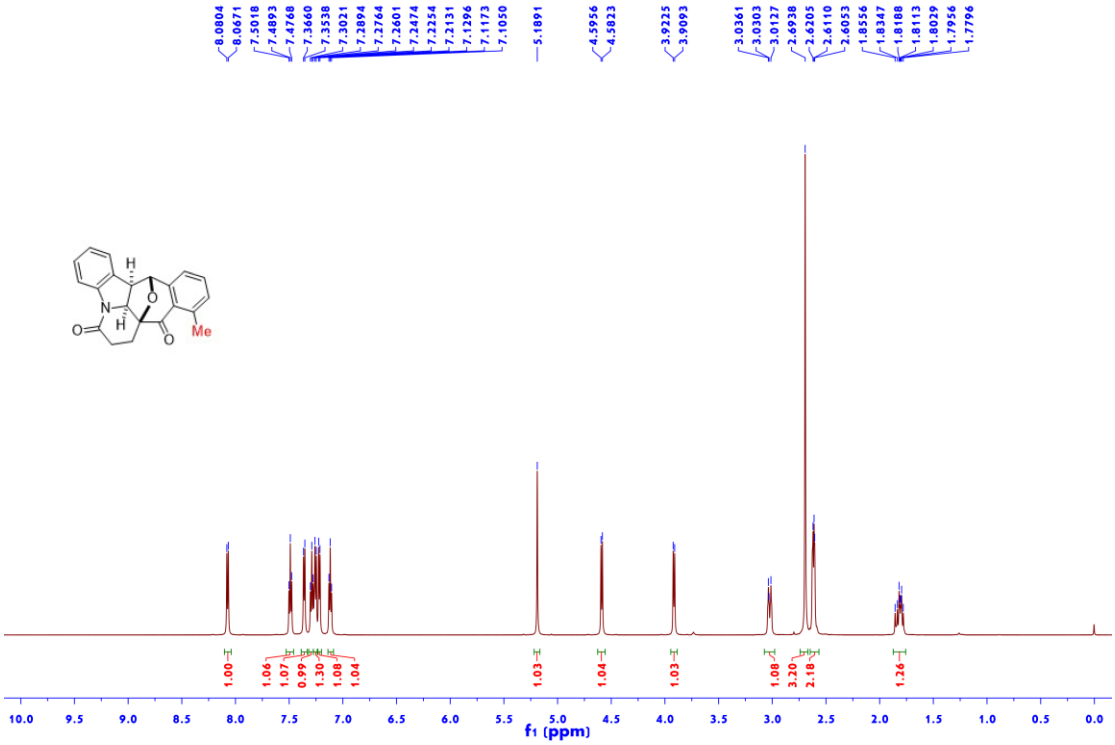


Figure S160 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ad**

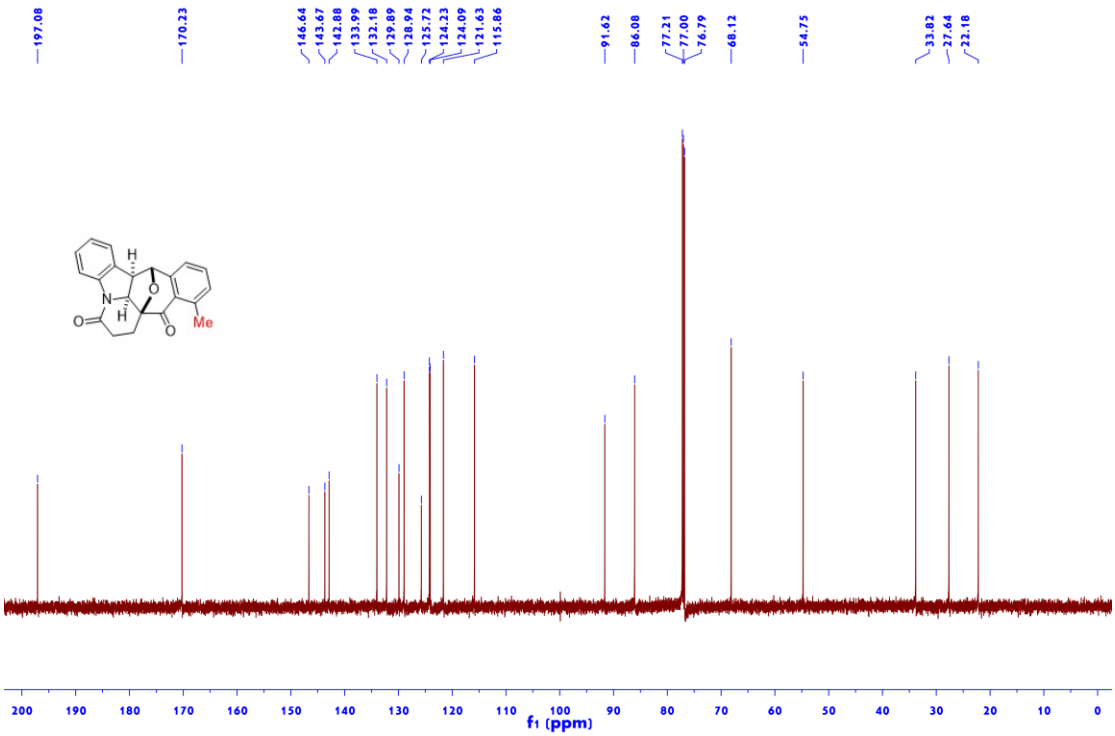


Figure S161 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ae**

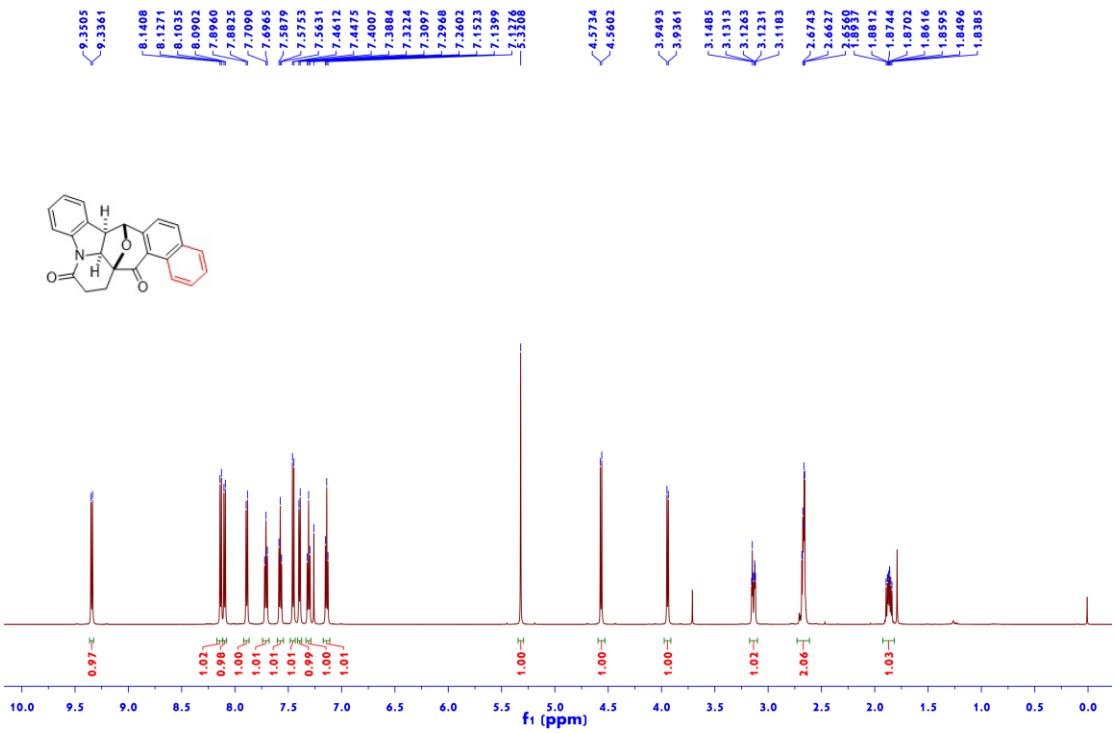


Figure S162 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ae**

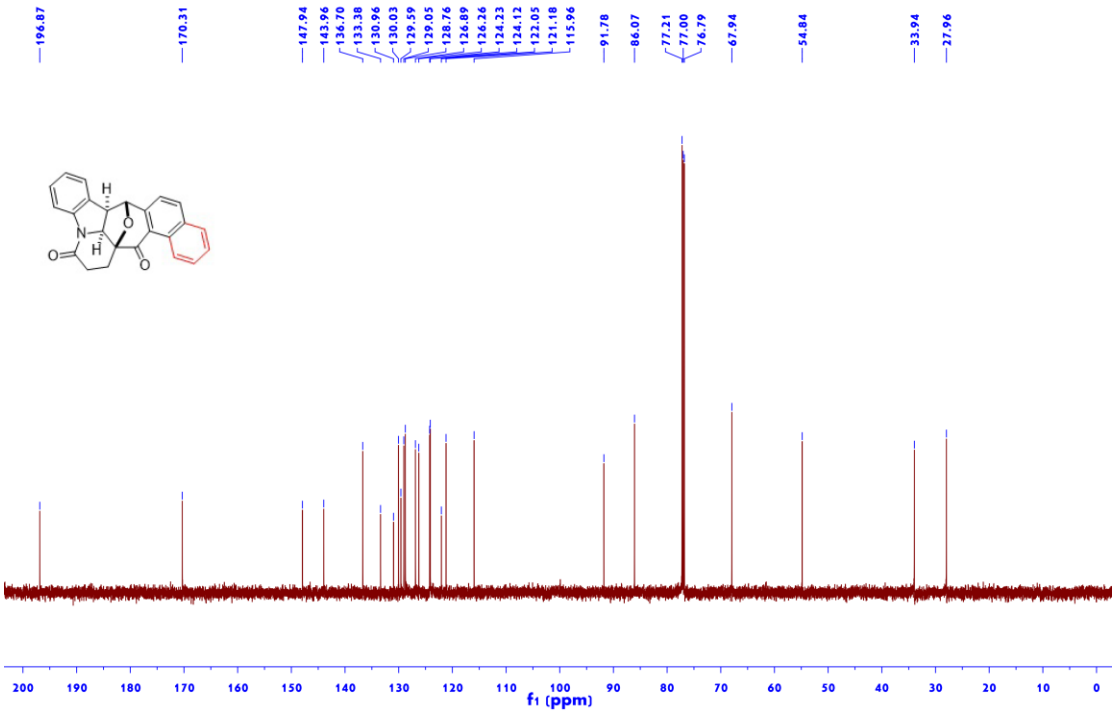


Figure S163 ^{1}H NMR (600 MHz, $CDCl_3$) of **3af**

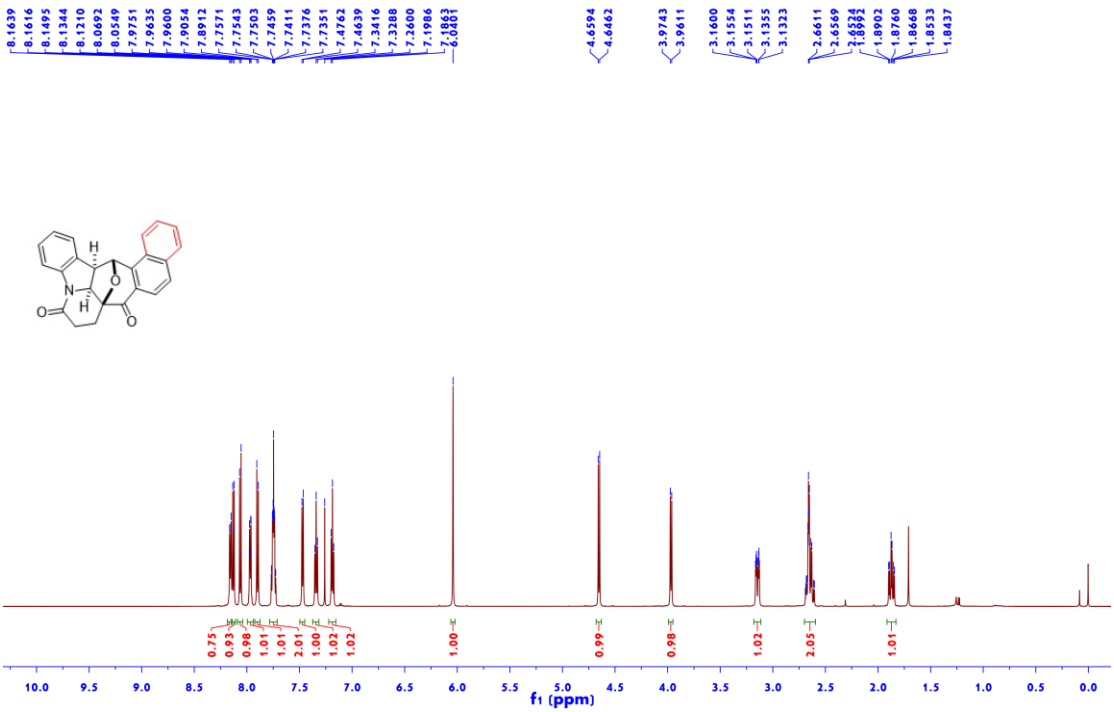


Figure S164 ^{13}C NMR (150 MHz, $CDCl_3$) of **3af**

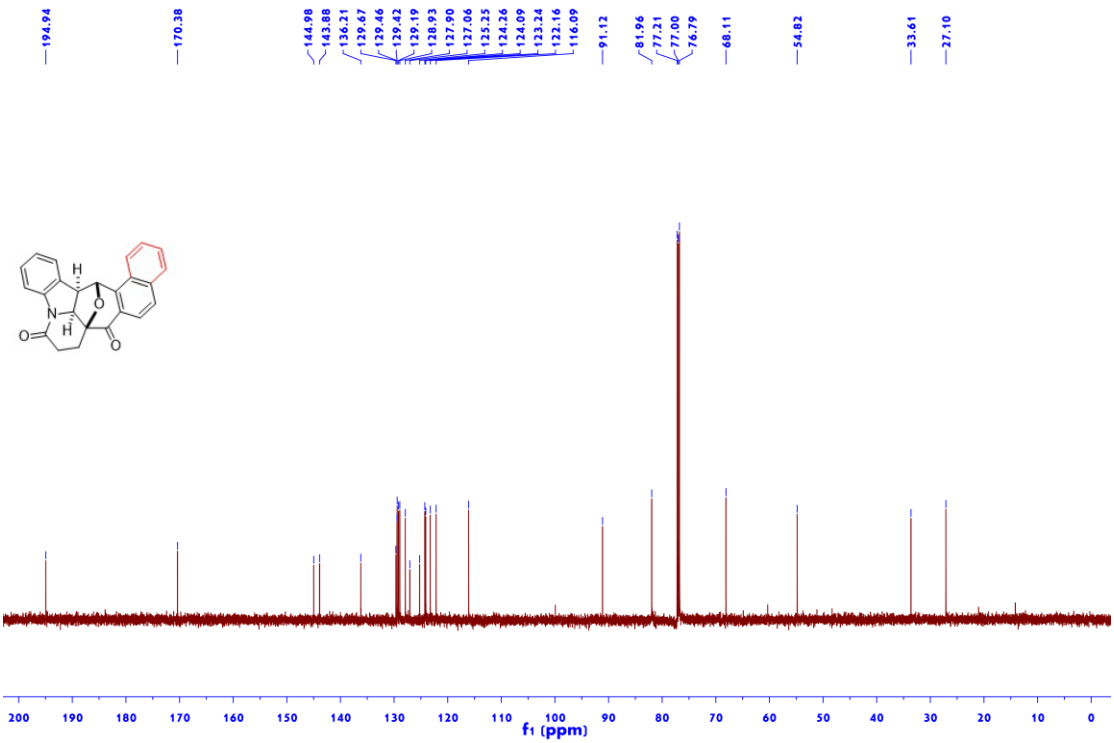


Figure S165 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ag**

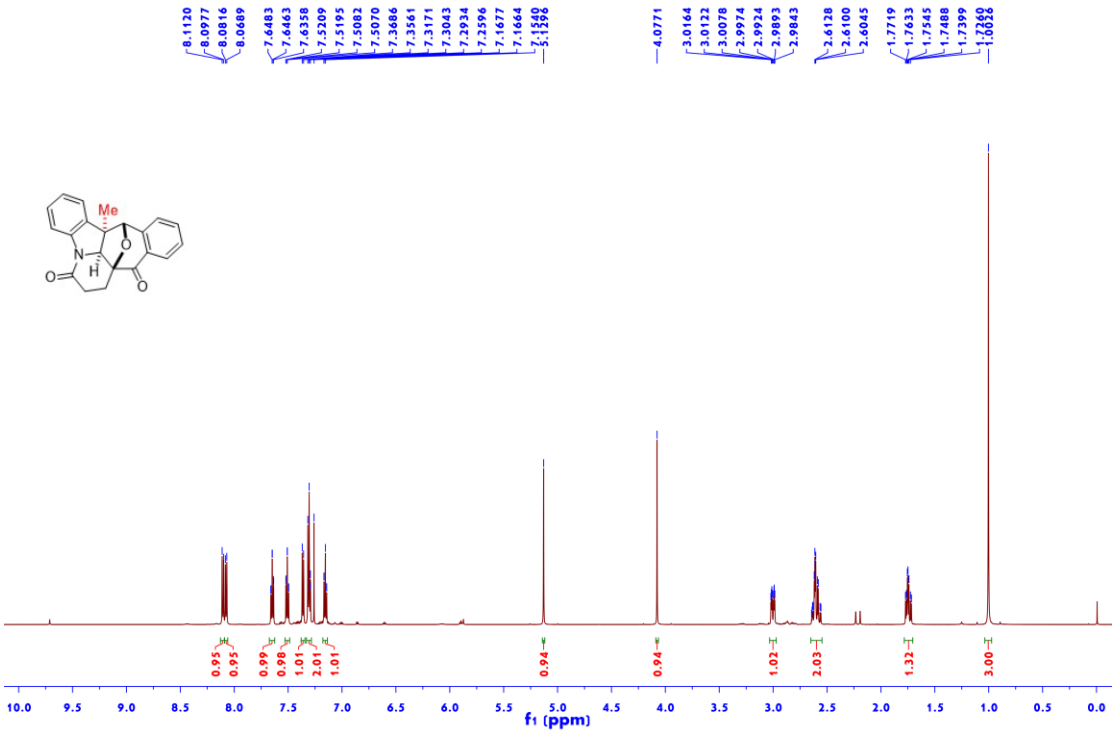


Figure S166 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ag**

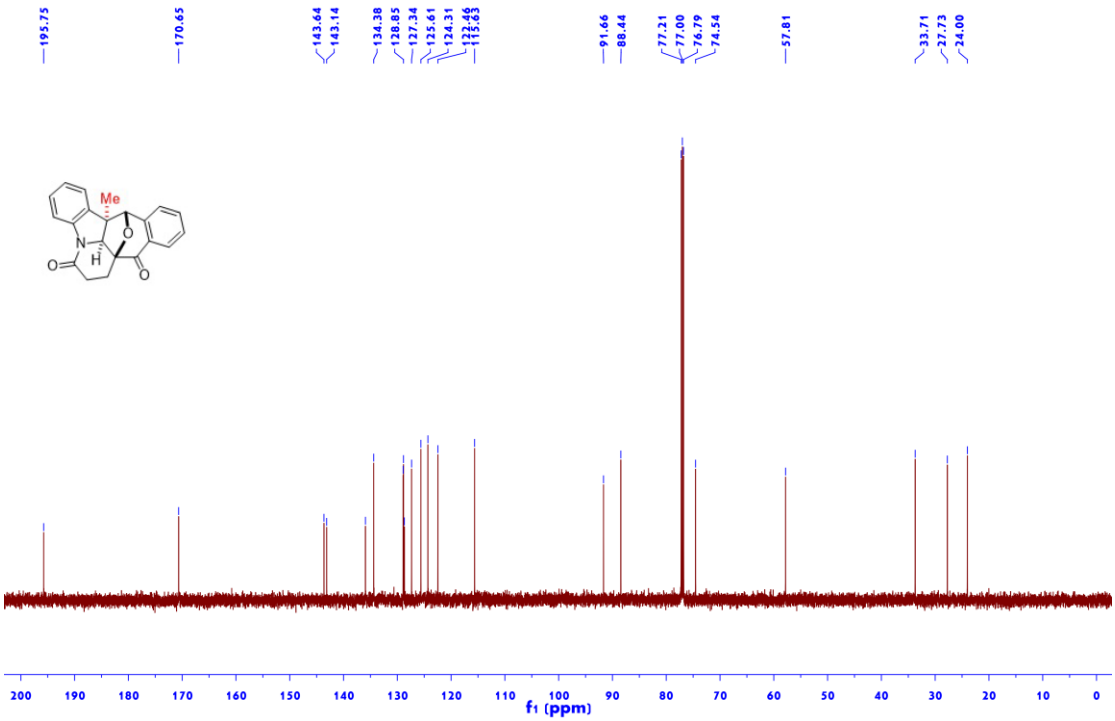


Figure S167 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ah**

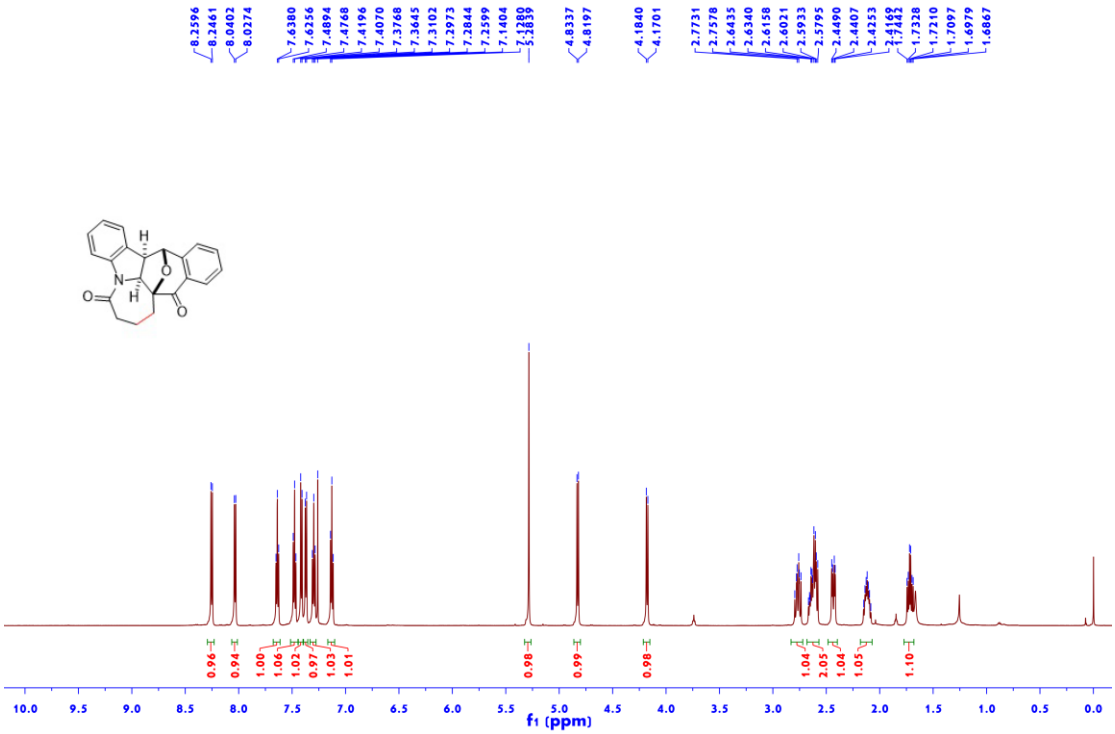


Figure S168 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ah**

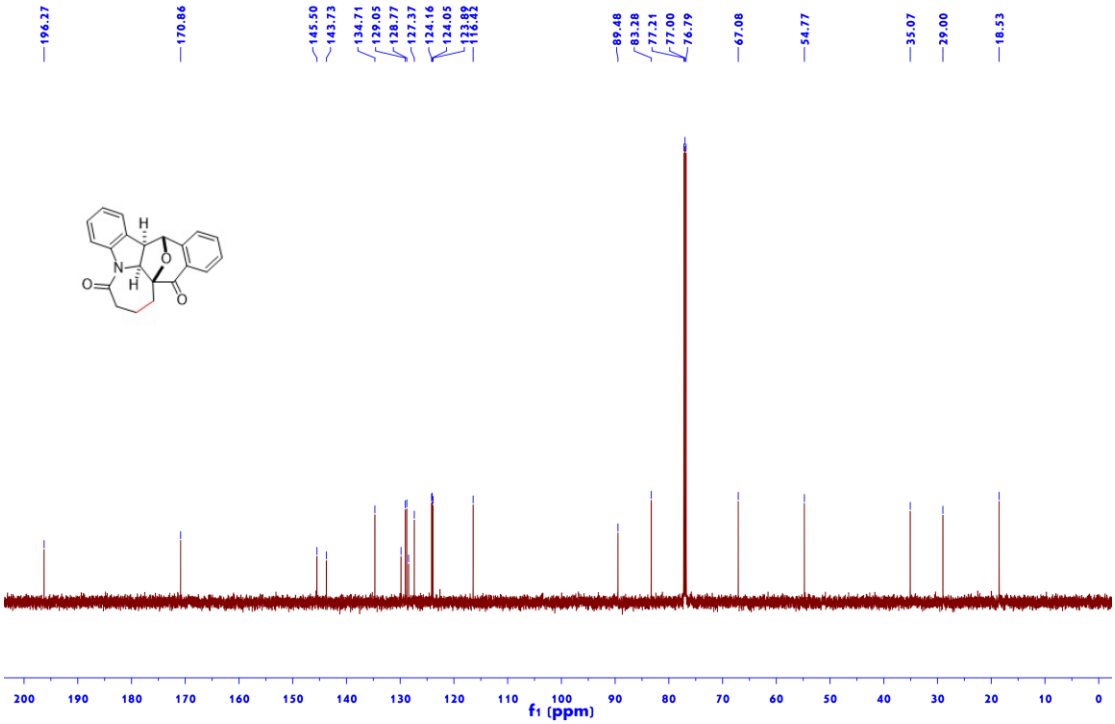


Figure S169 ^{1}H NMR (600 MHz, $CDCl_3$) of **3al**

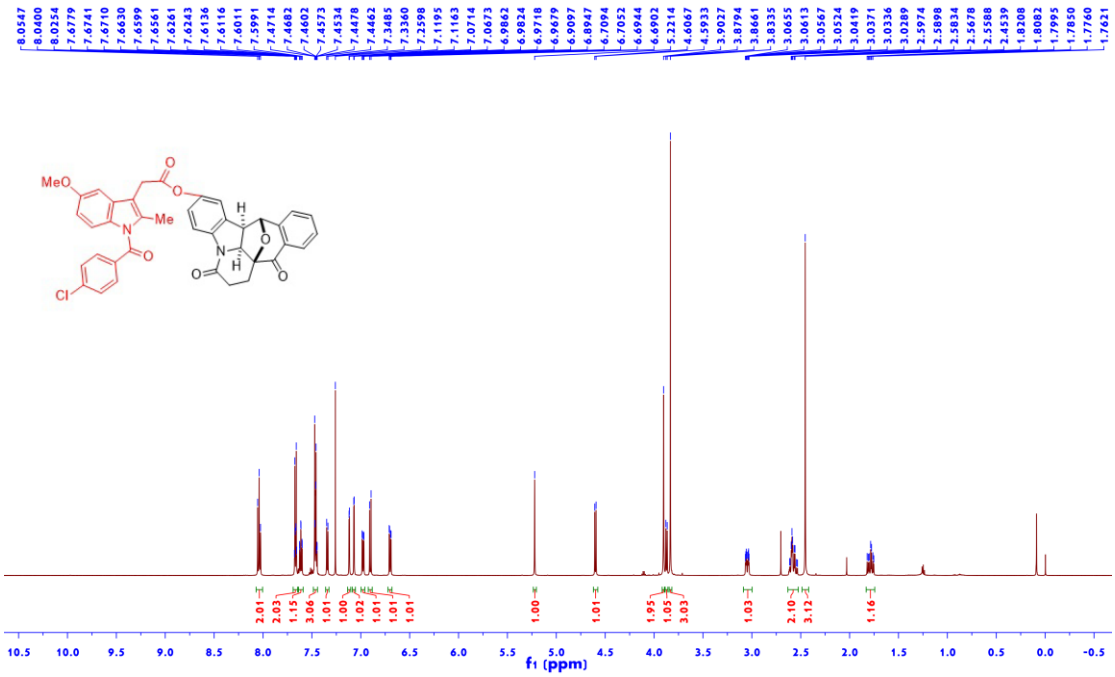


Figure S170 ^{13}C NMR (150 MHz, $CDCl_3$) of **3al**

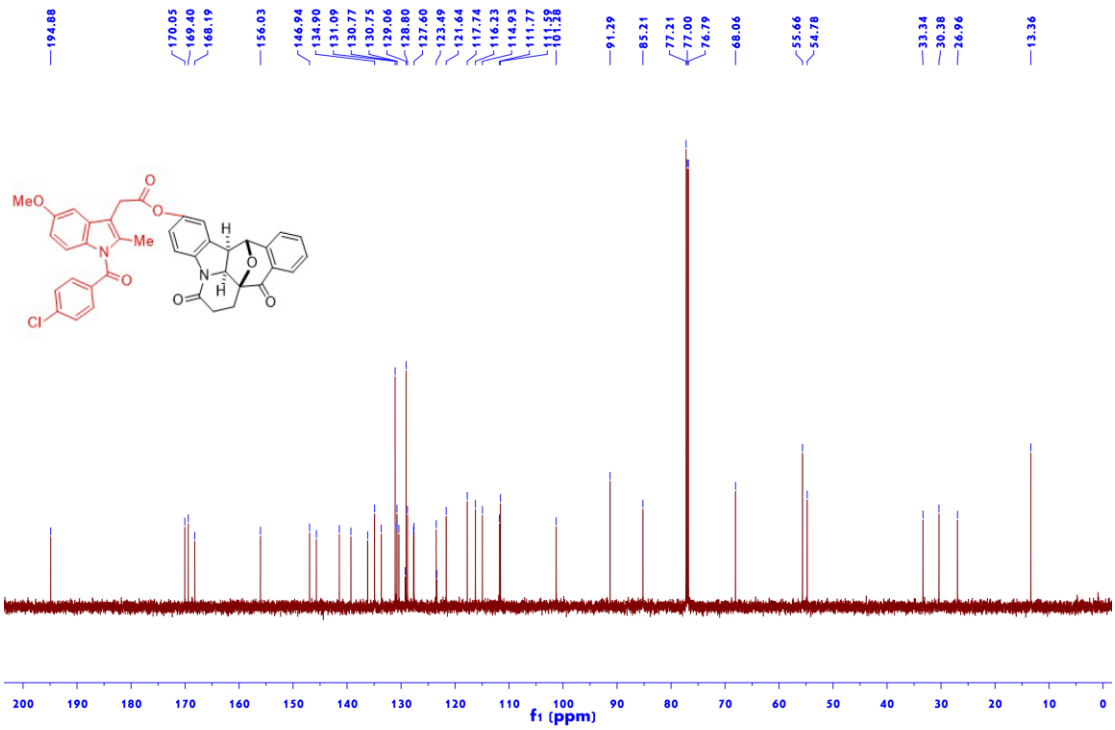


Figure S171 ^{1}H NMR (600 MHz, $CDCl_3$) of **3am**

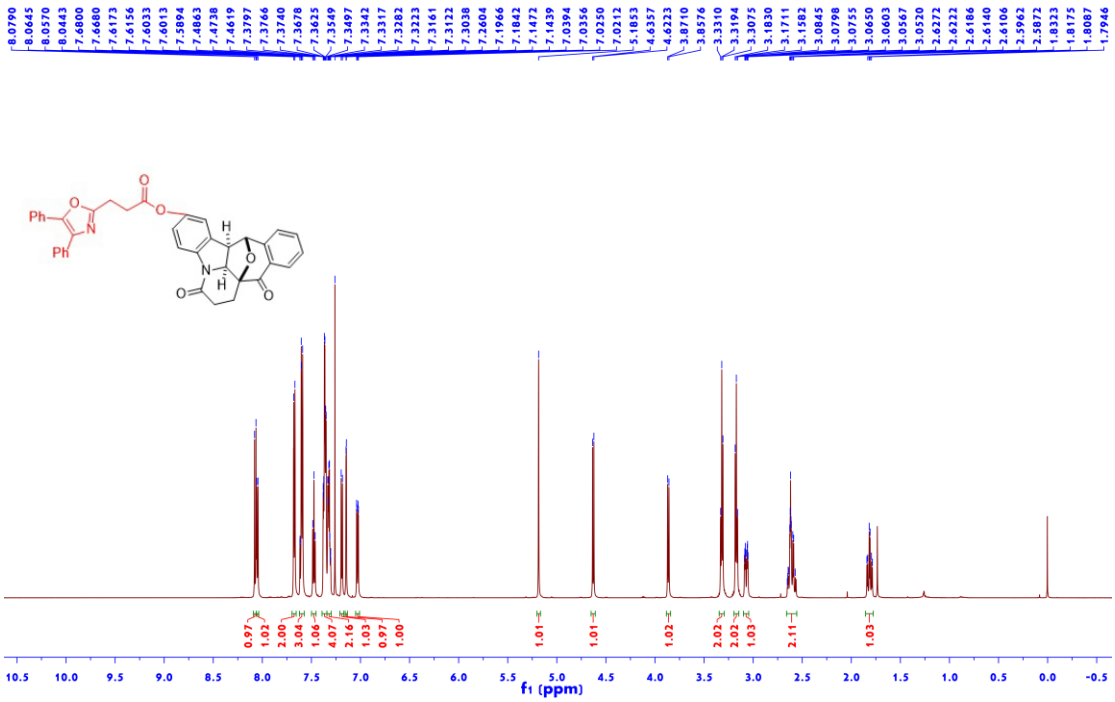


Figure S172 ^{13}C NMR (150 MHz, $CDCl_3$) of **3am**

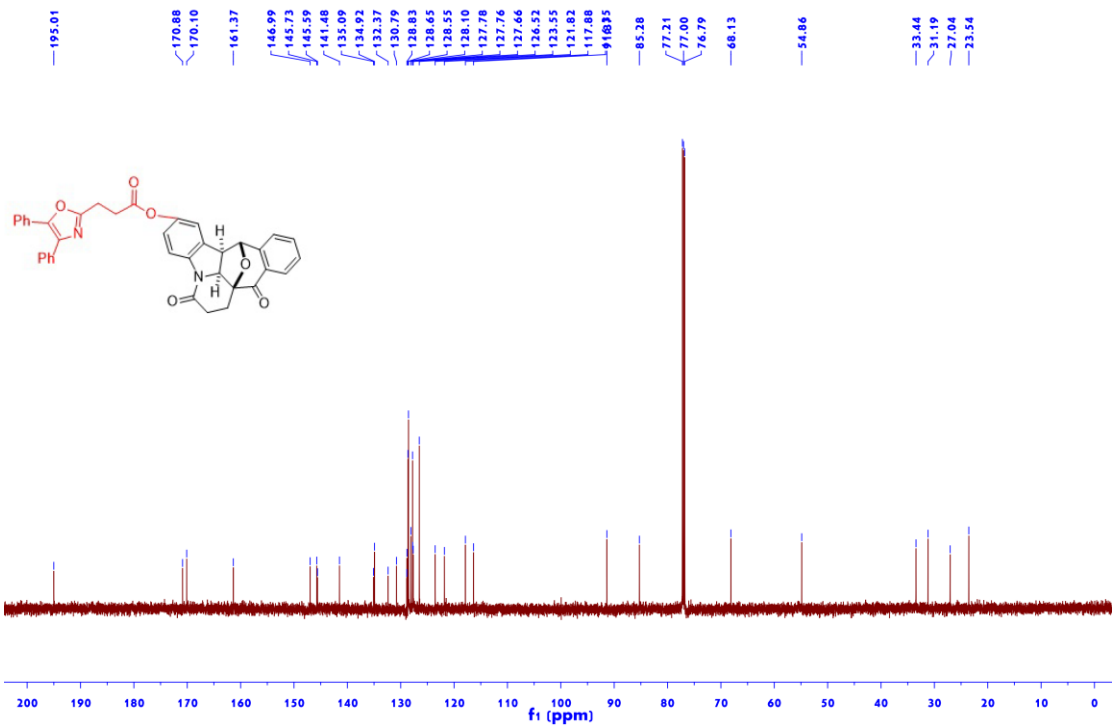


Figure S173 ^{1}H NMR (600 MHz, $CDCl_3$) of **3an**

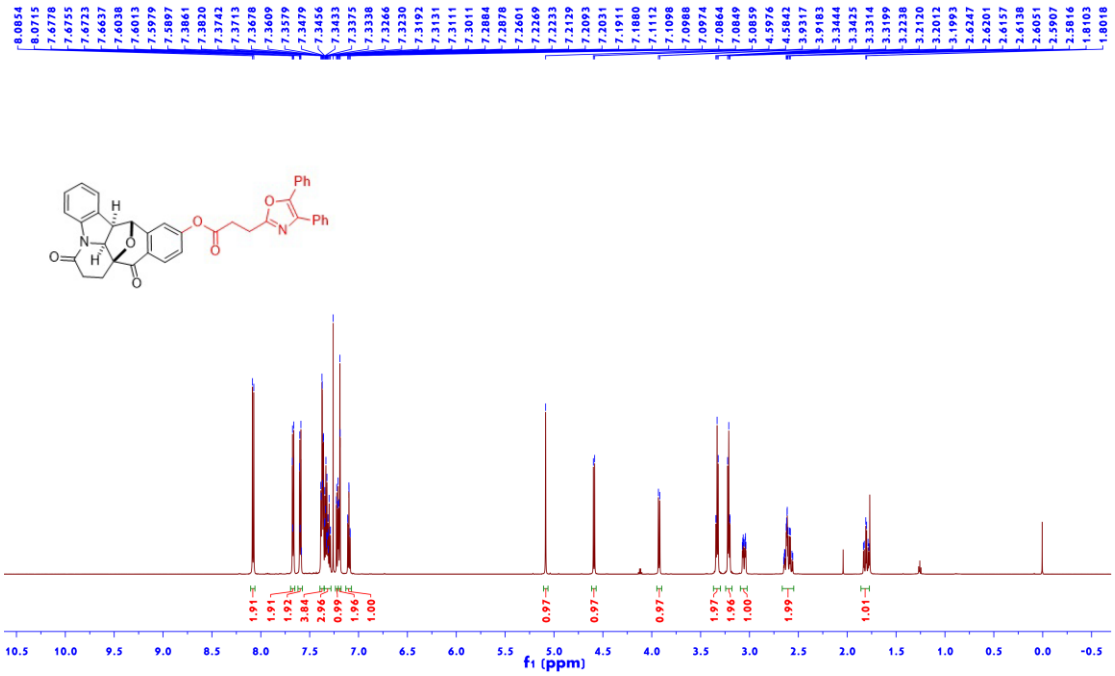


Figure S174 ^{13}C NMR (150 MHz, $CDCl_3$) of **3an**

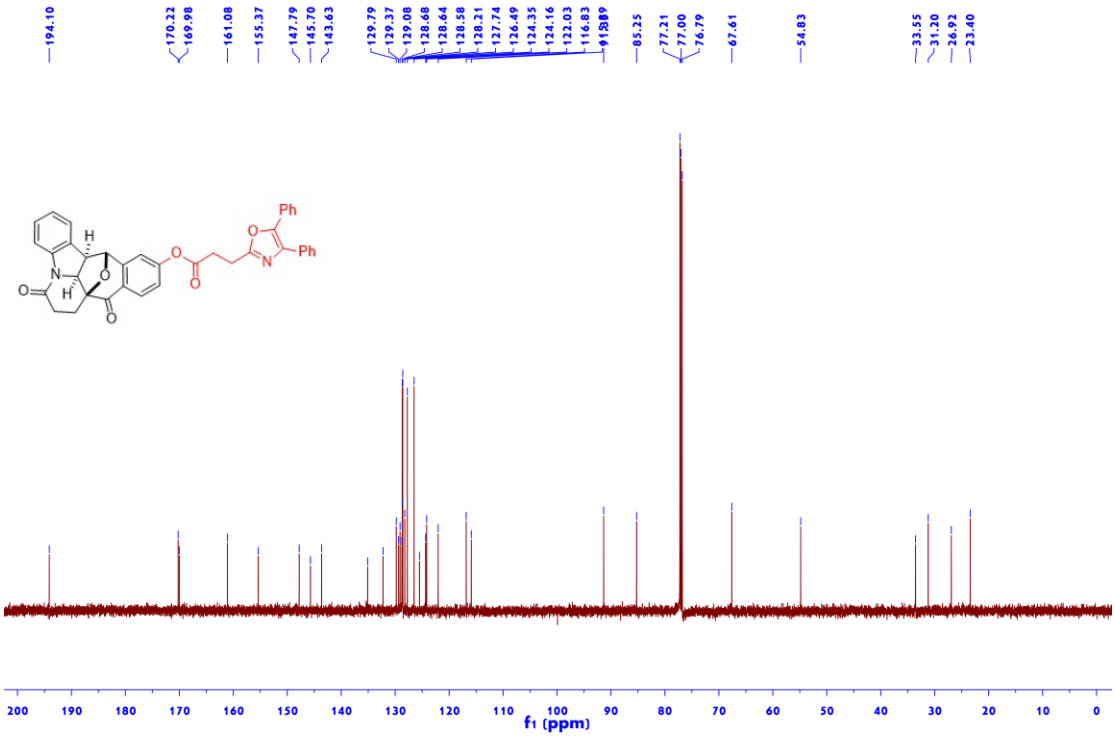


Figure S175 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ao**

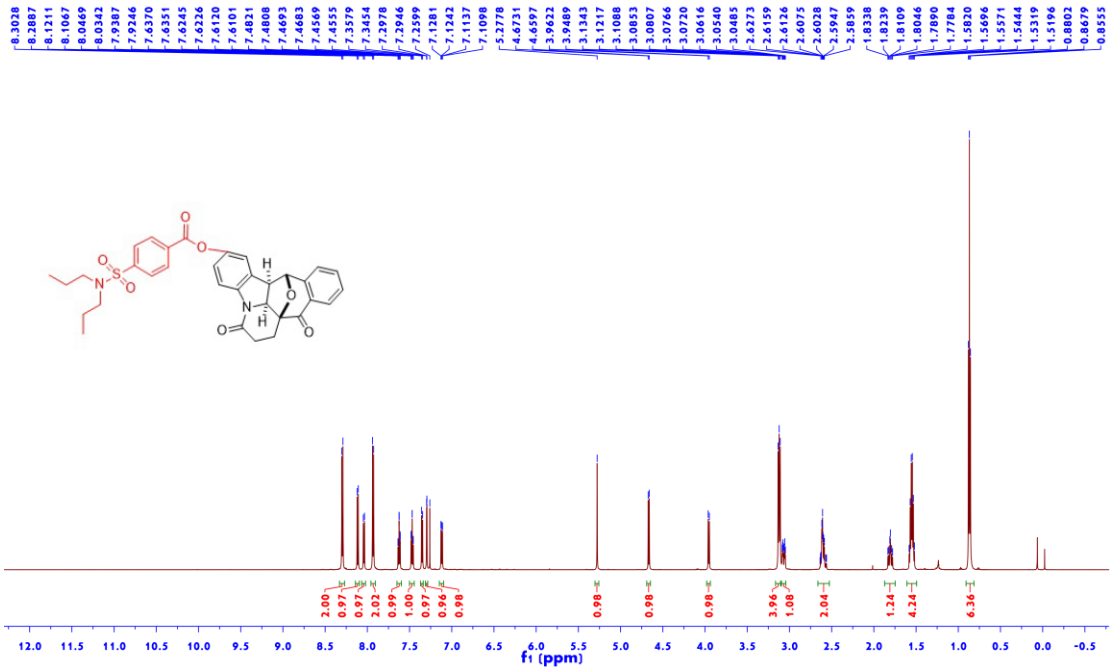


Figure S176 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ao**

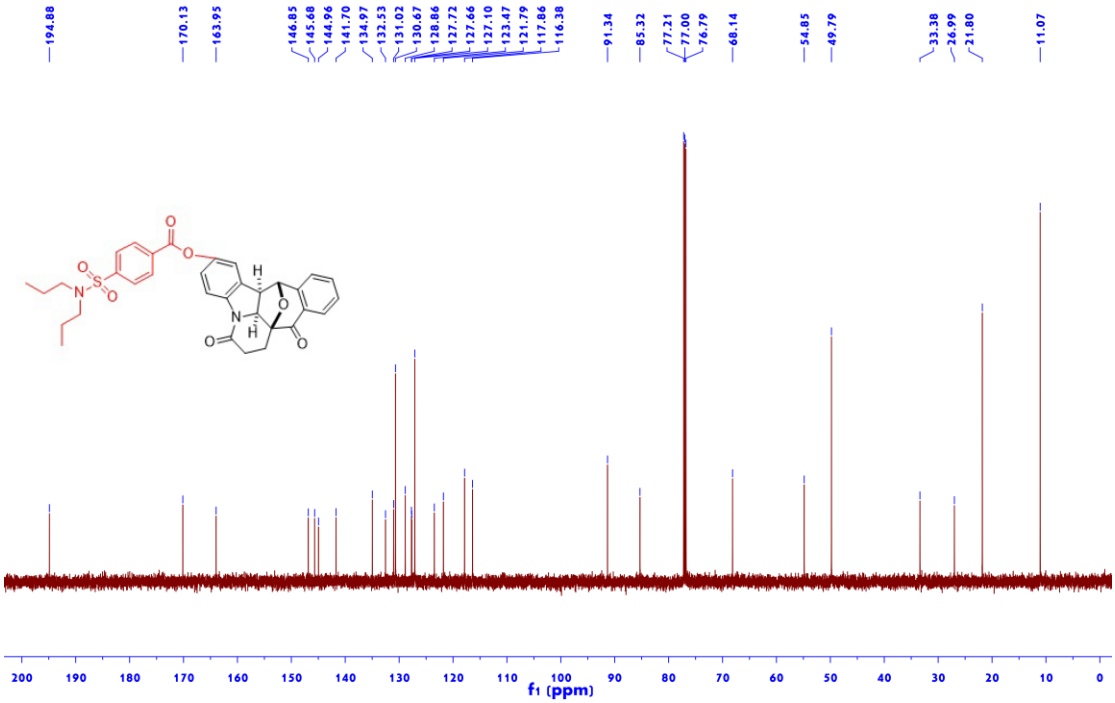


Figure S177 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ap**

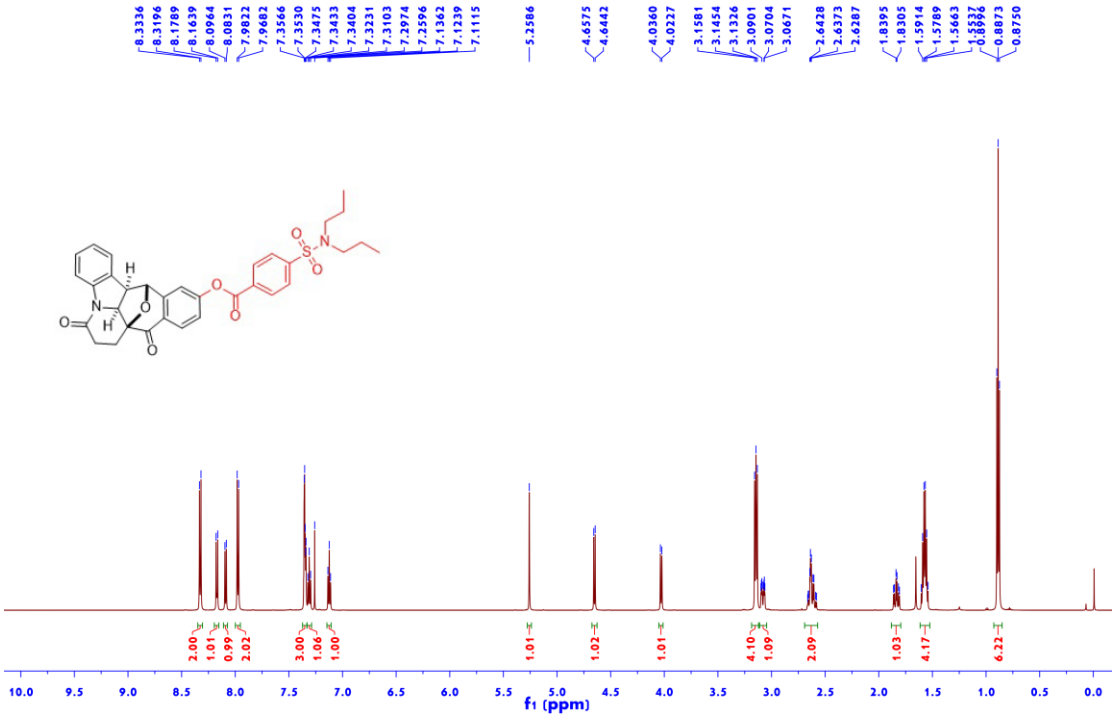


Figure S178 ^{13}C NMR (150 MHz, $CDCl_3$) of **3ap**

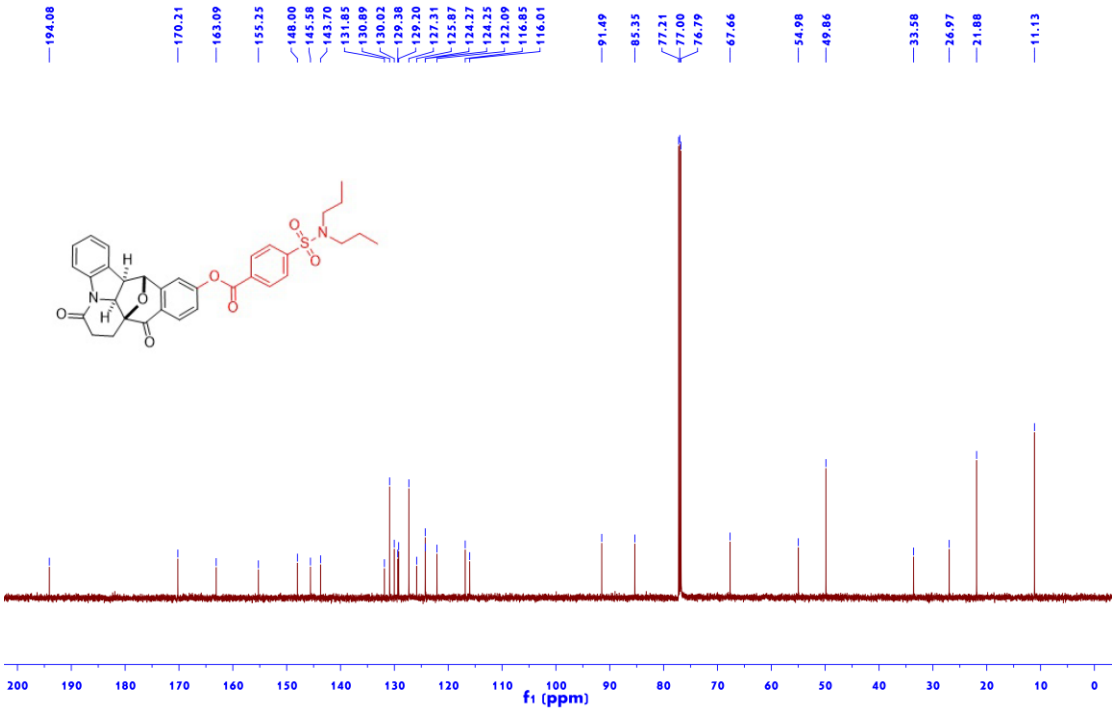


Figure S179 ^{1}H NMR (600 MHz, $CDCl_3$) of **3aq**

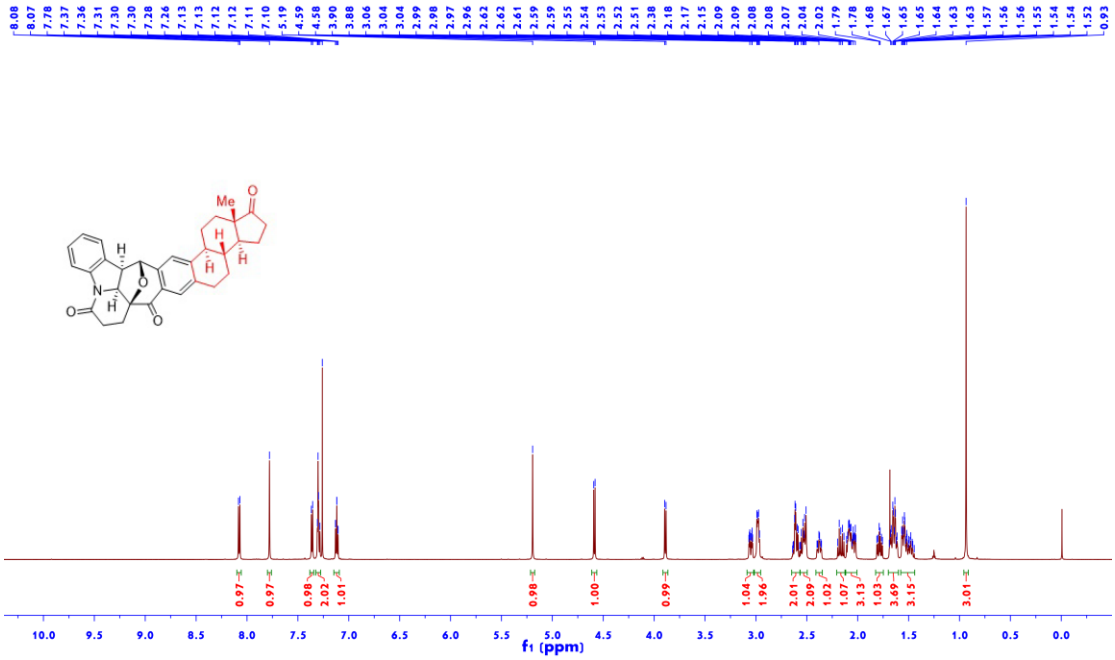


Figure S180 ^{13}C NMR (150 MHz, $CDCl_3$) of **3aq**

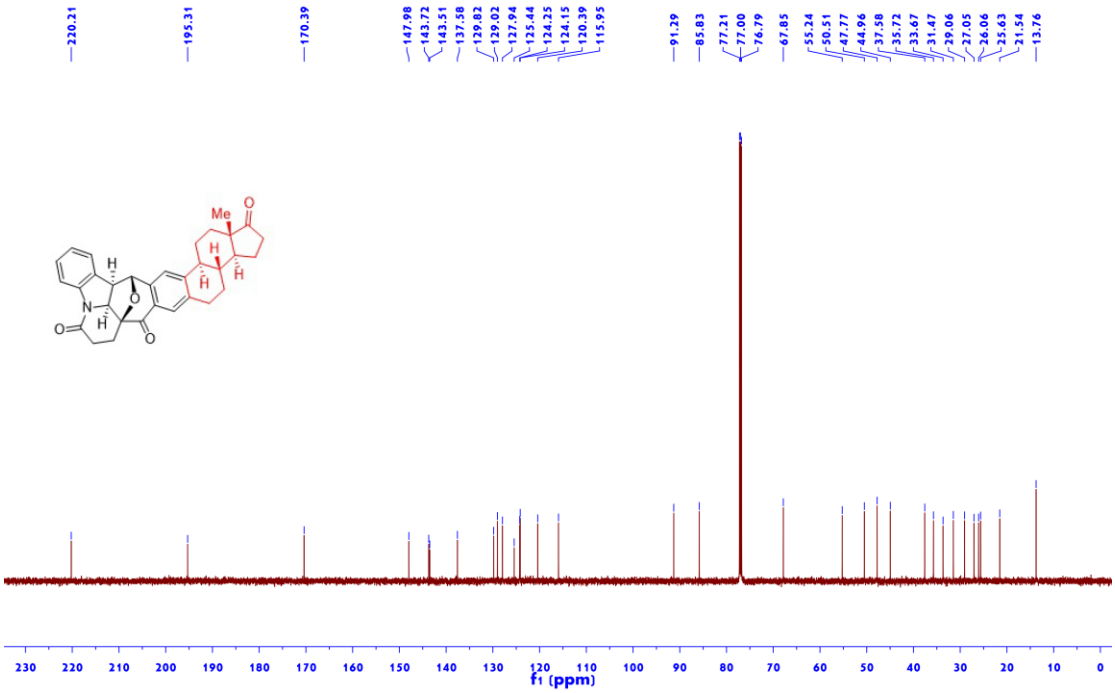


Figure S181 ^{1}H NMR (600 MHz, $CDCl_3$) of **3aq'**

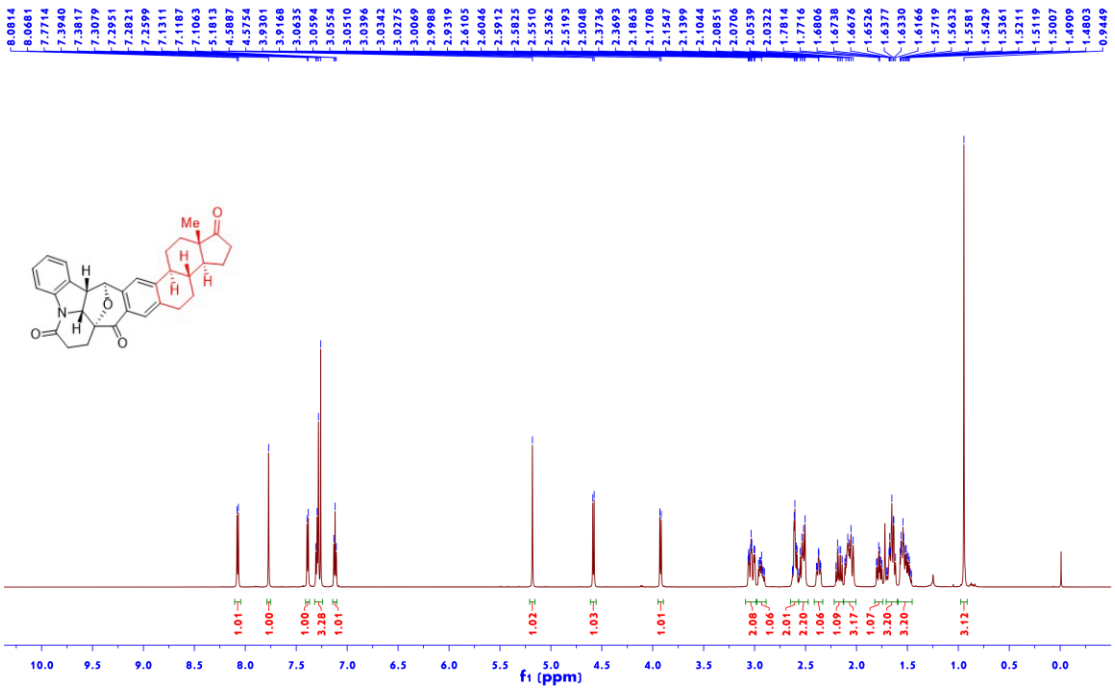


Figure S182 ^{13}C NMR (150 MHz, $CDCl_3$) of **3aq'**

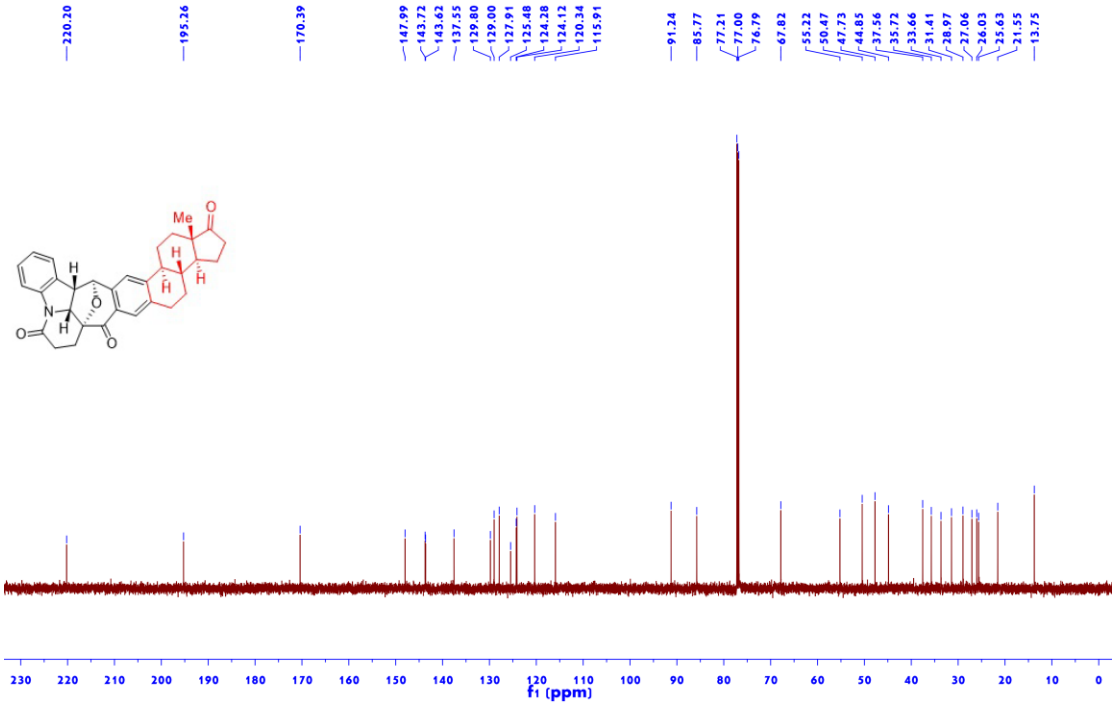


Figure S183 ^{1}H NMR (400 MHz, $CDCl_3$) of **4a**

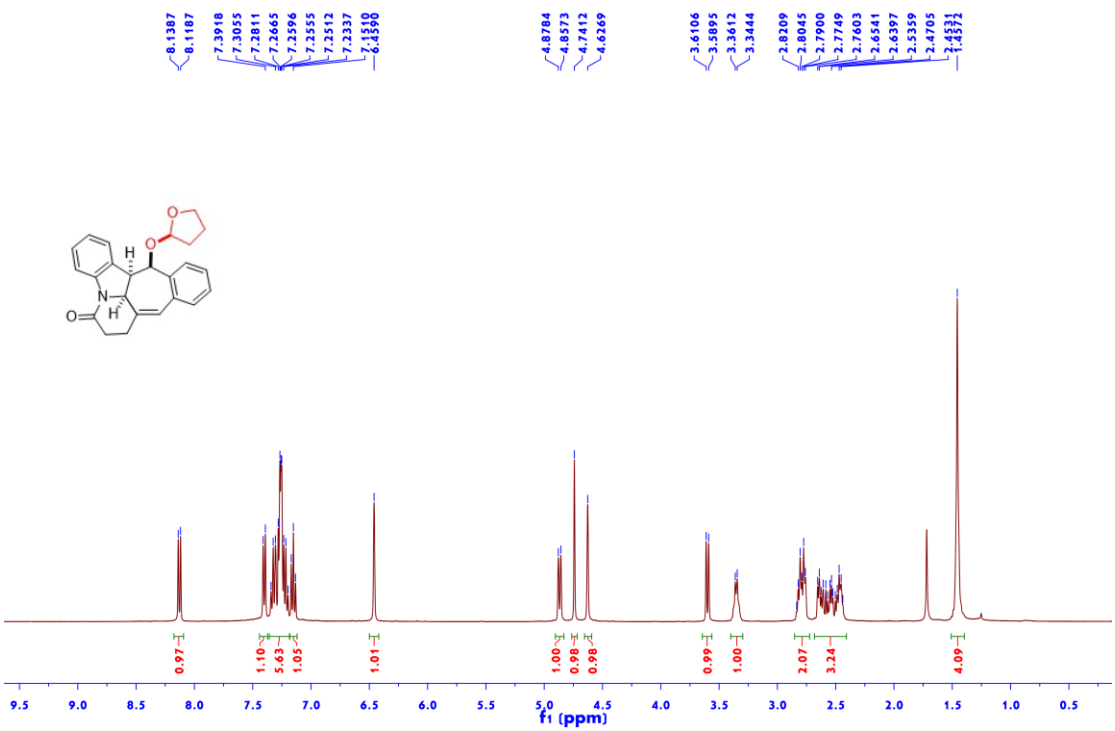


Figure S184 ^{13}C NMR (100 MHz, $CDCl_3$) of **4a**

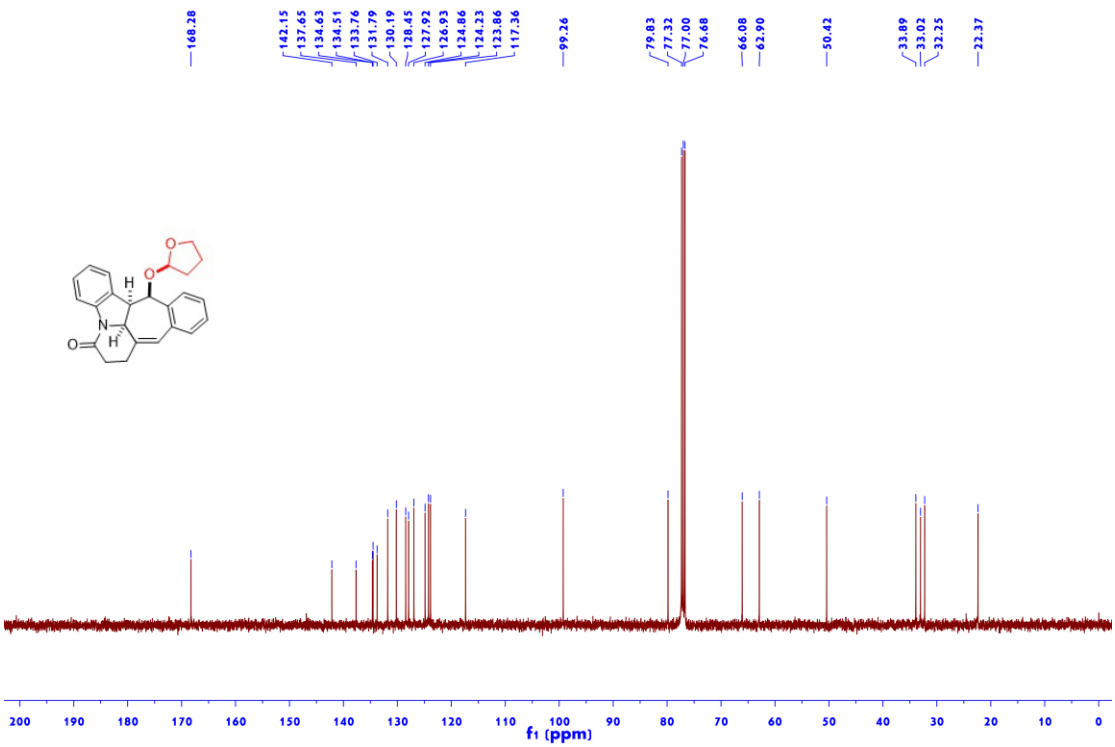


Figure S185 ^{1}H NMR (600 MHz, $CDCl_3$) of **5a**

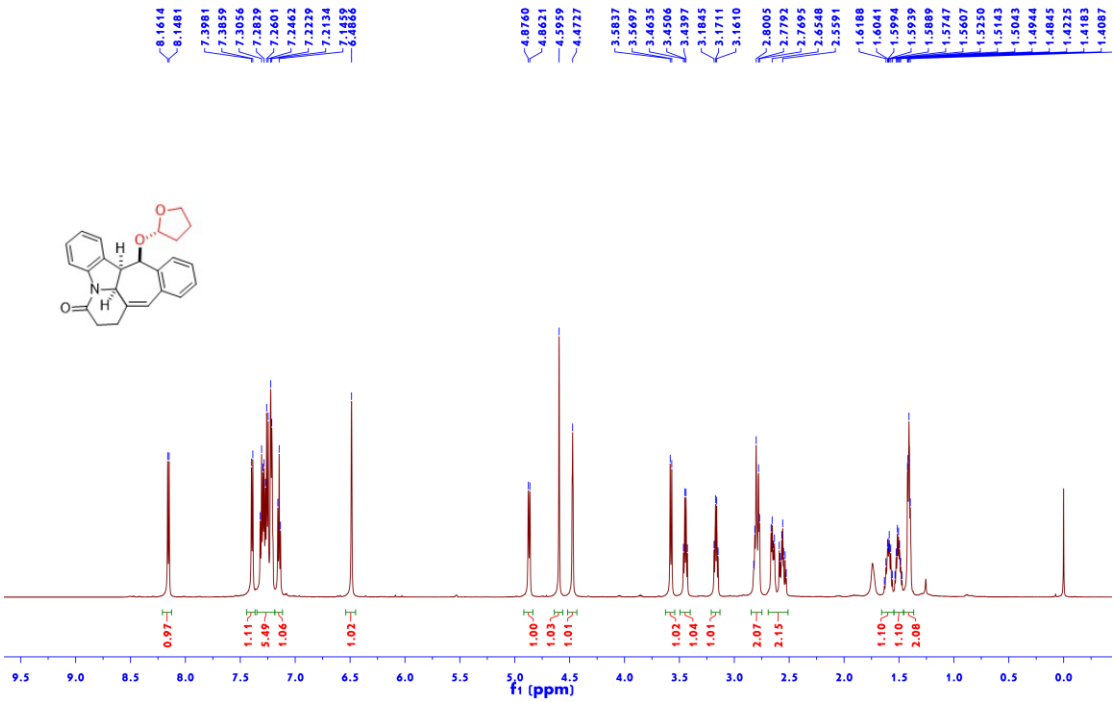


Figure S186 ^{13}C NMR (150 MHz, $CDCl_3$) of **5a**

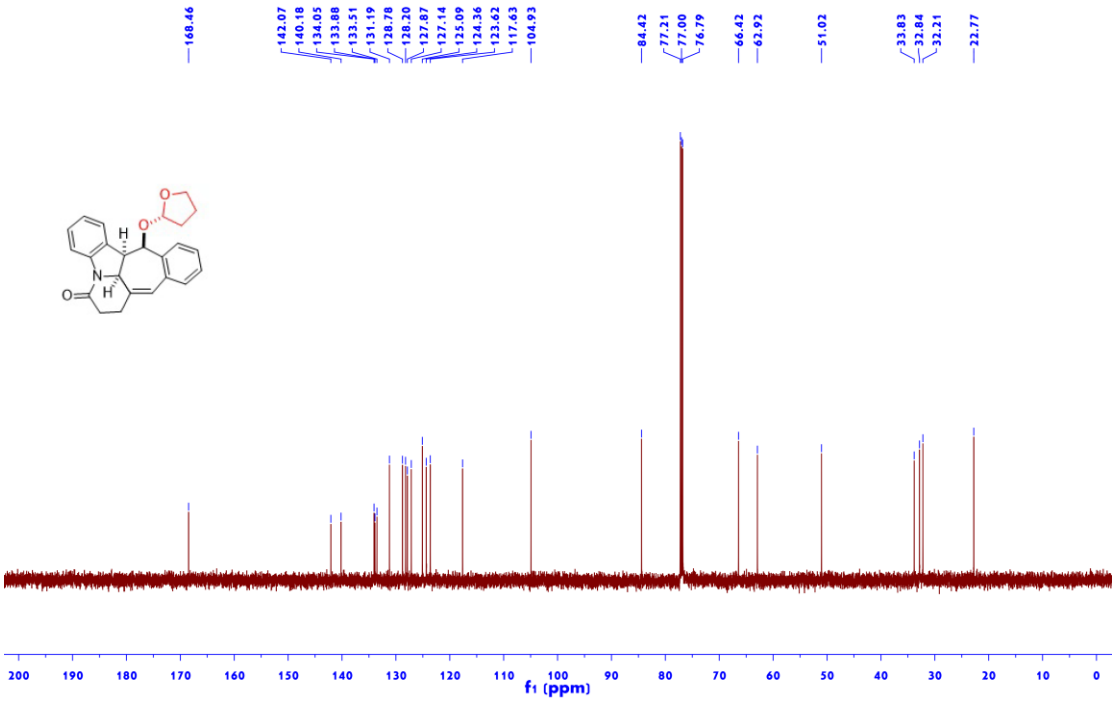


Figure S187 ^{1}H NMR (600 MHz, $CDCl_3$) of **6a**

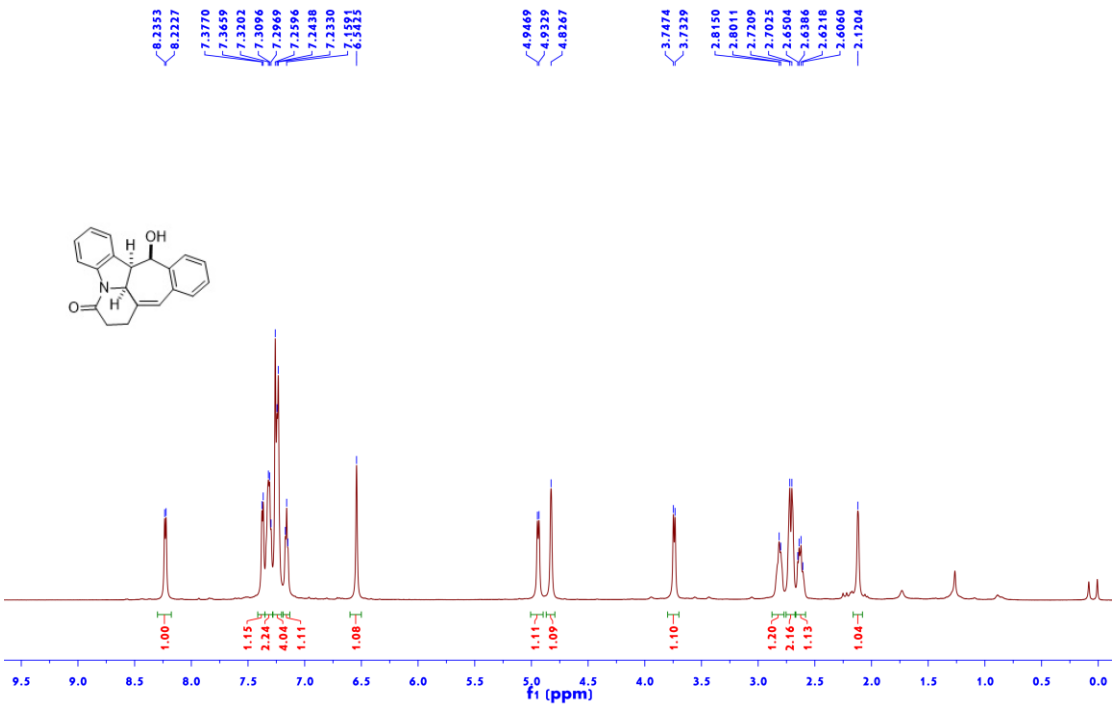


Figure S188 ^{13}C NMR (150 MHz, $CDCl_3$) of **6a**

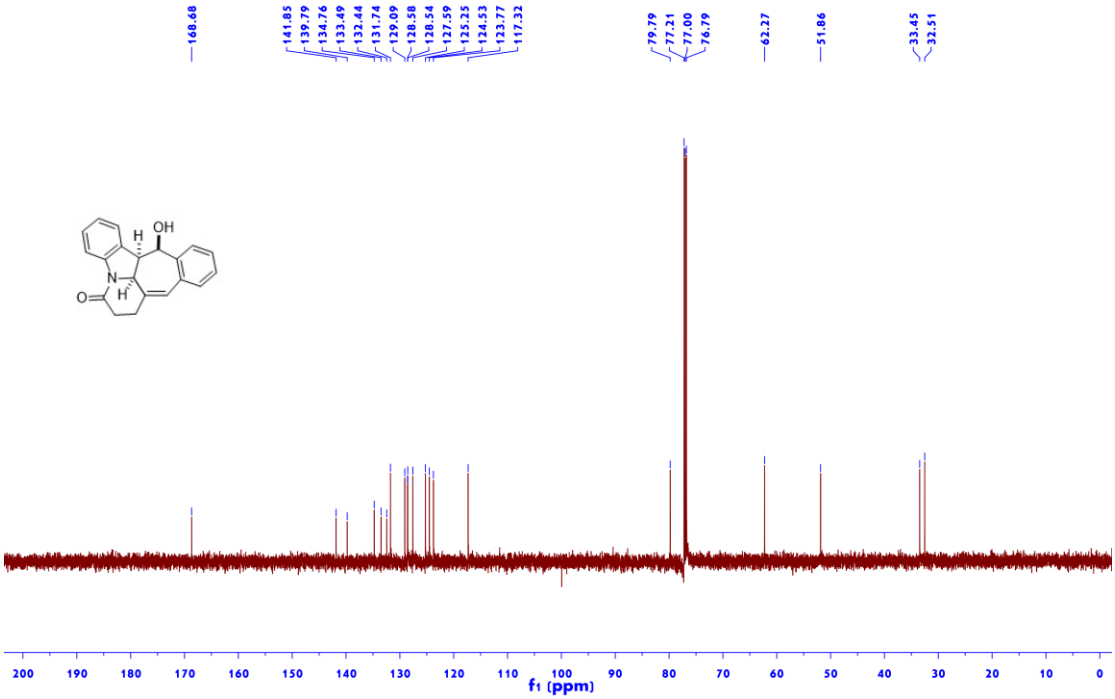


Figure S189 ^{1}H NMR (600 MHz, $CDCl_3$) of **7a**

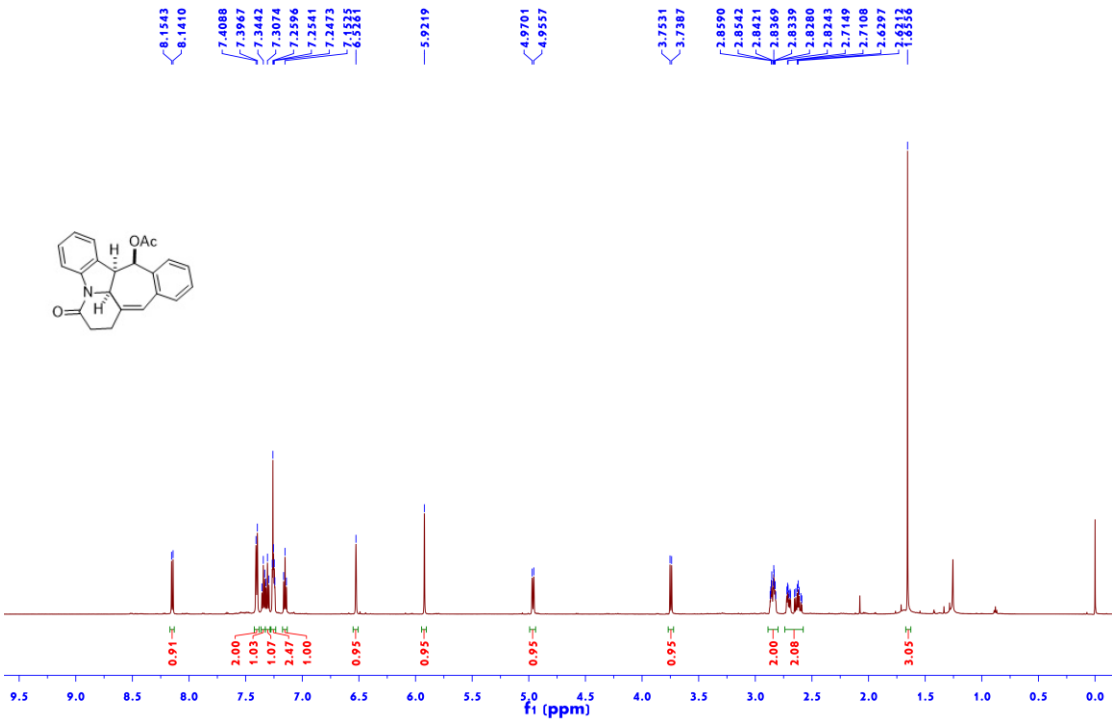


Figure S190 ^{13}C NMR (150 MHz, $CDCl_3$) of **7a**

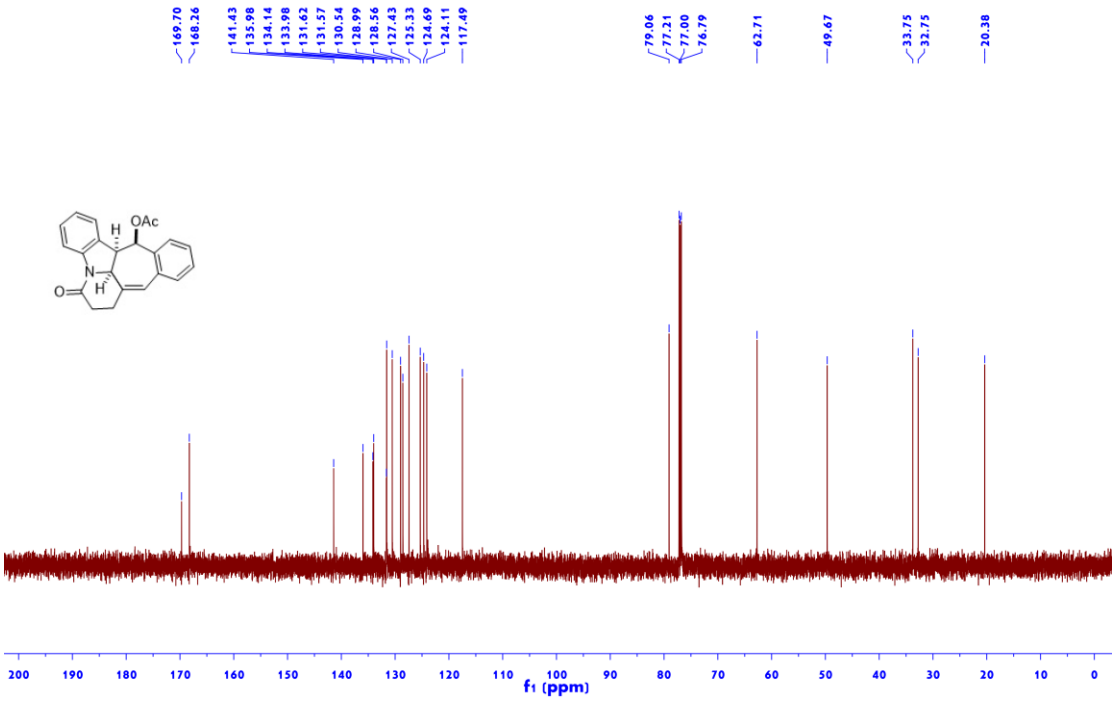


Figure S191 ^{1}H NMR (600 MHz, $CDCl_3$) of ***d*$_1$-7a**

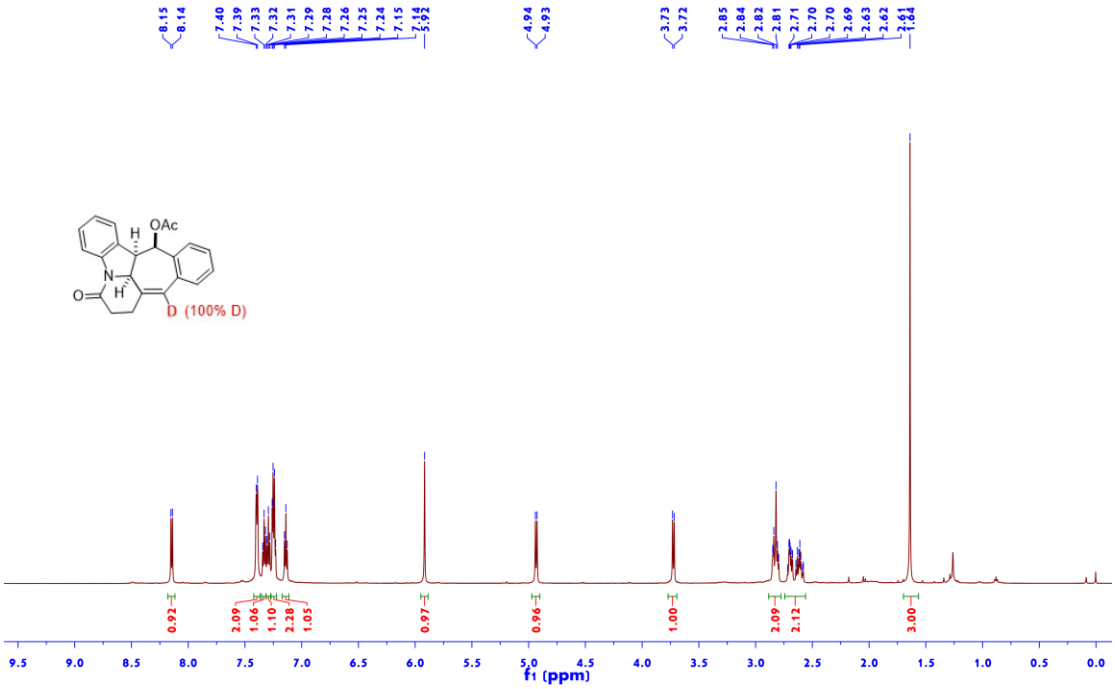


Figure S192 ^{13}C NMR (150 MHz, $CDCl_3$) of ***d*$_1$-7a**

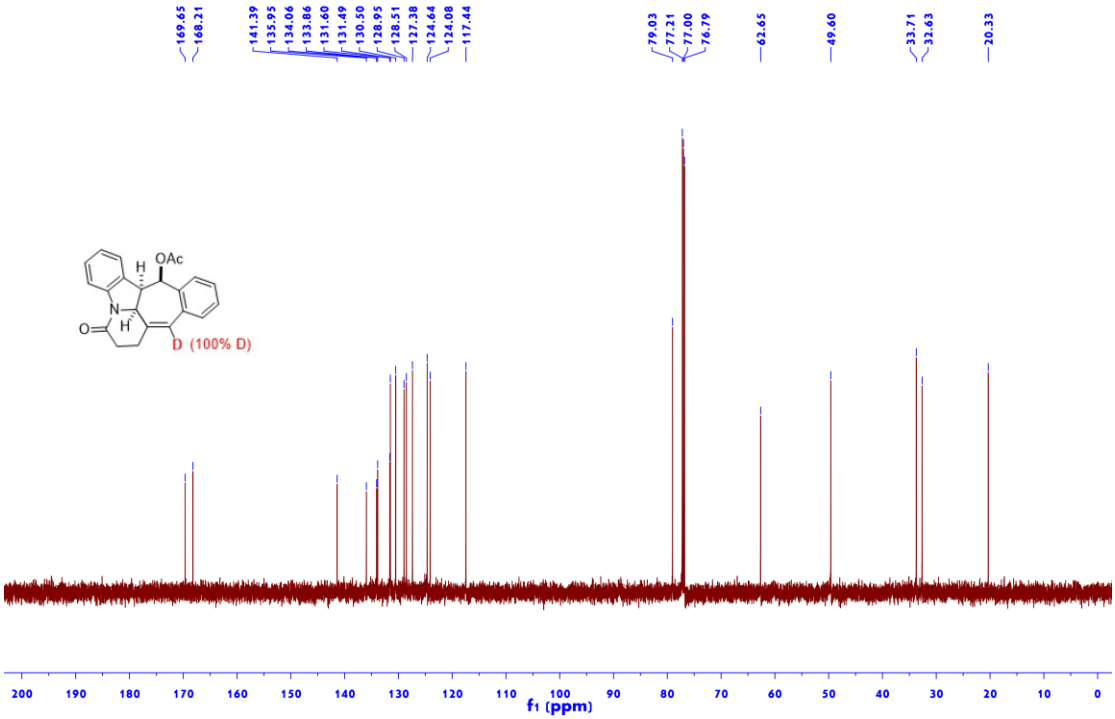


Figure S193 ^{1}H NMR (600 MHz, $CDCl_3$) of **7b**

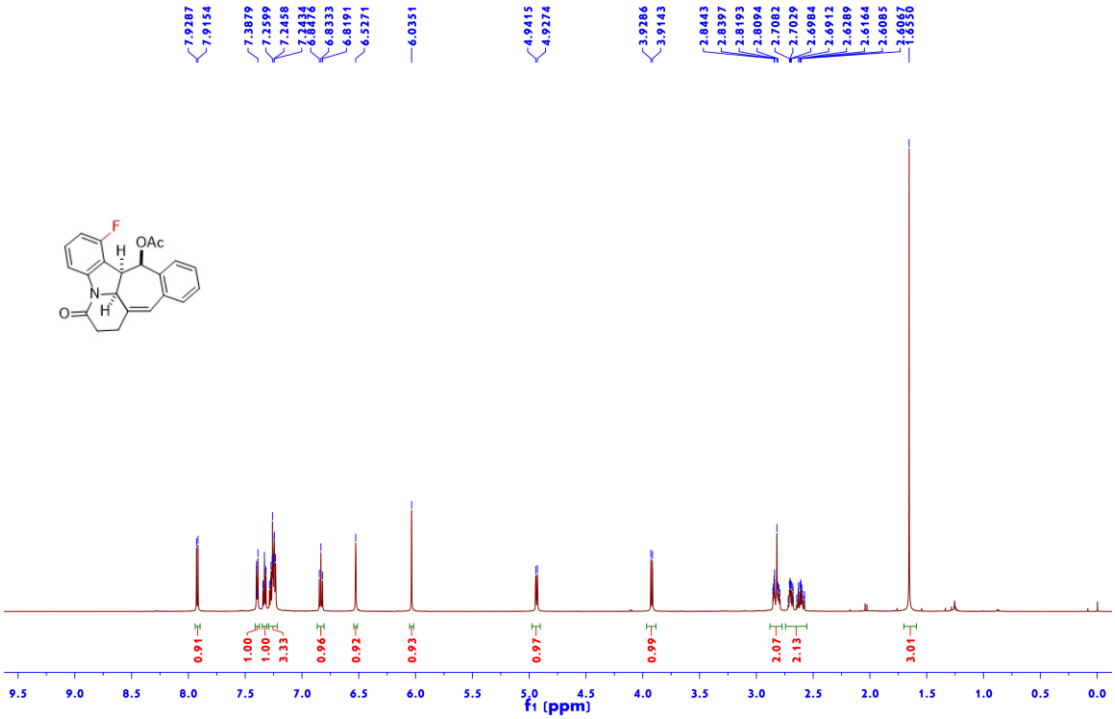


Figure S194 ^{13}C NMR (150 MHz, $CDCl_3$) of **7b**

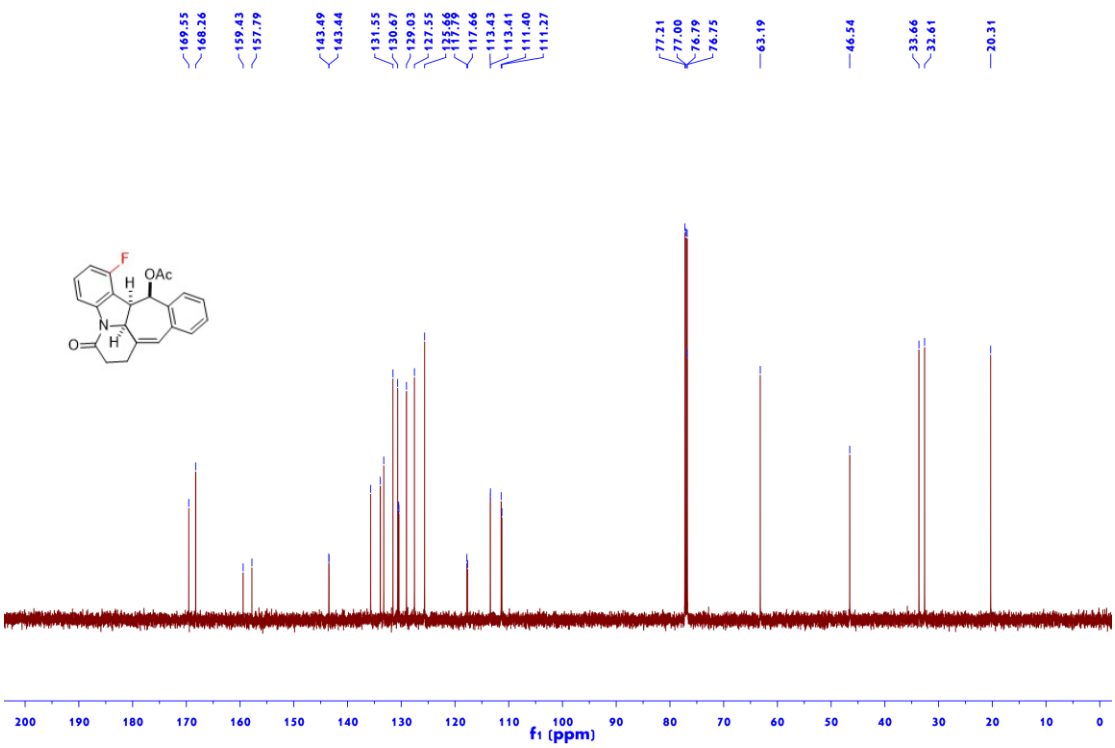


Figure S195 ^{19}F NMR (565 MHz, $CDCl_3$) of **7b**

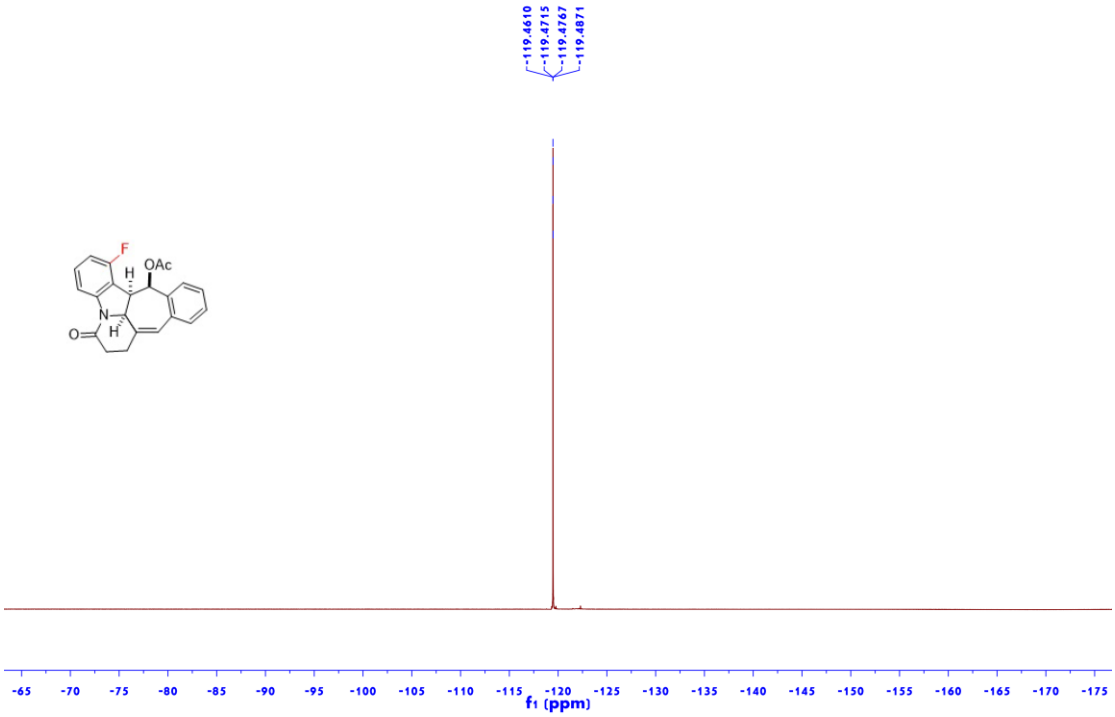


Figure S196 ^{1}H NMR (600 MHz, $CDCl_3$) of **7c**

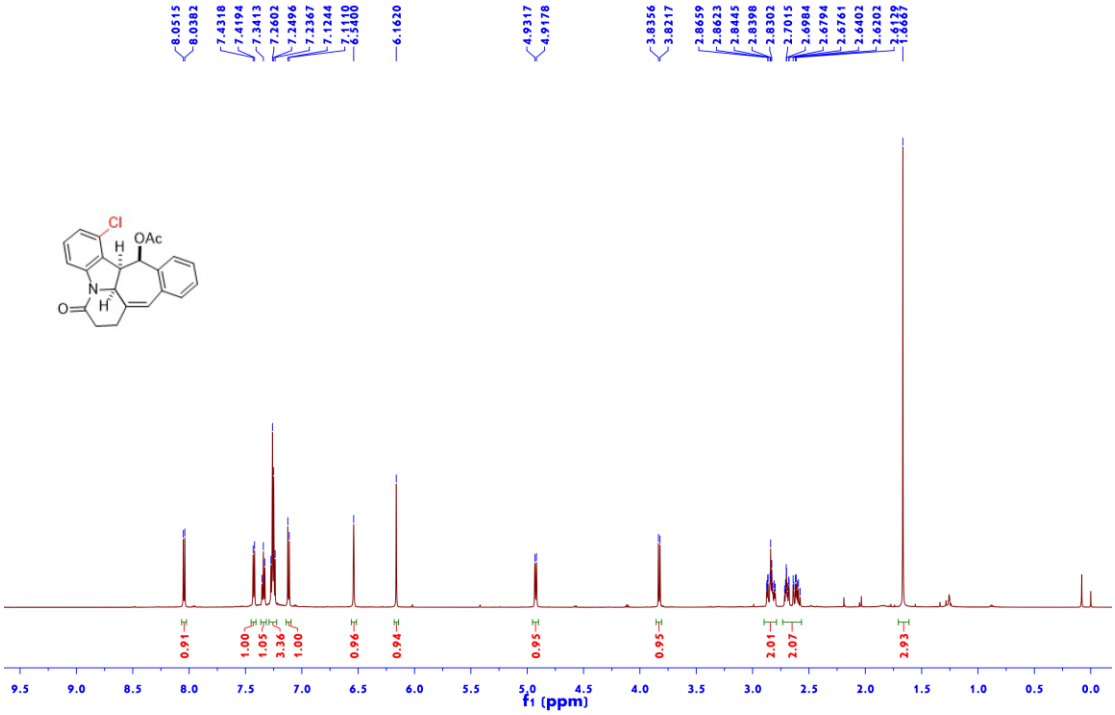


Figure S197 ^{13}C NMR (150 MHz, $CDCl_3$) of **7c**

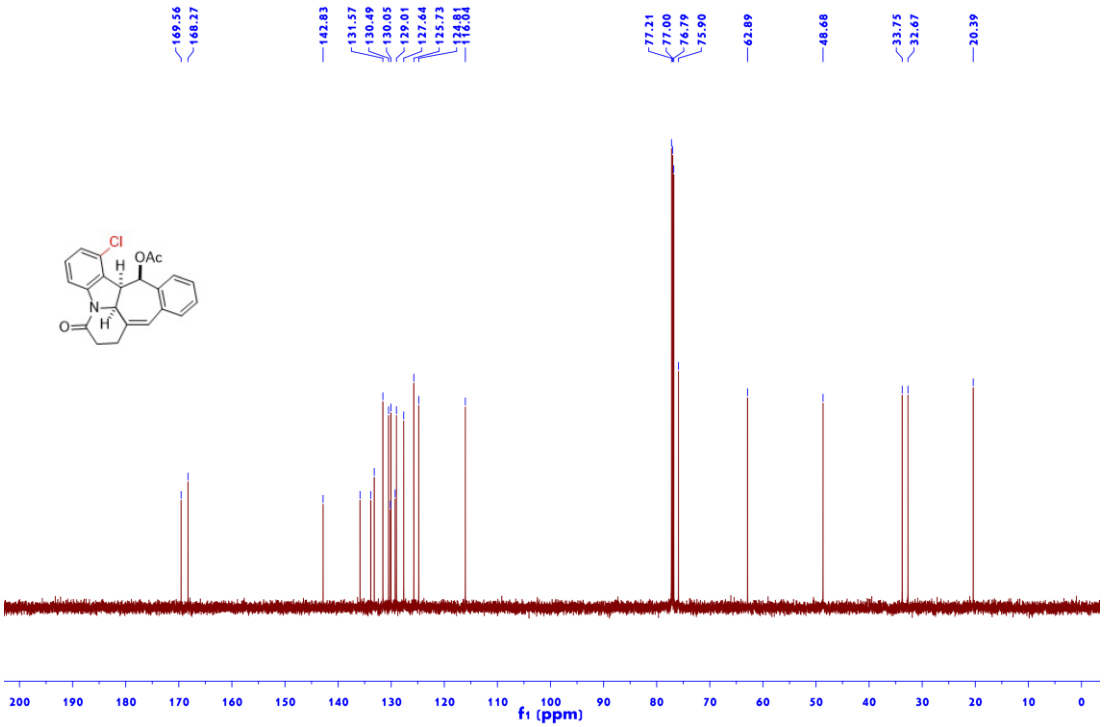


Figure S198 ^{1}H NMR (600 MHz, $CDCl_3$) of **7d**

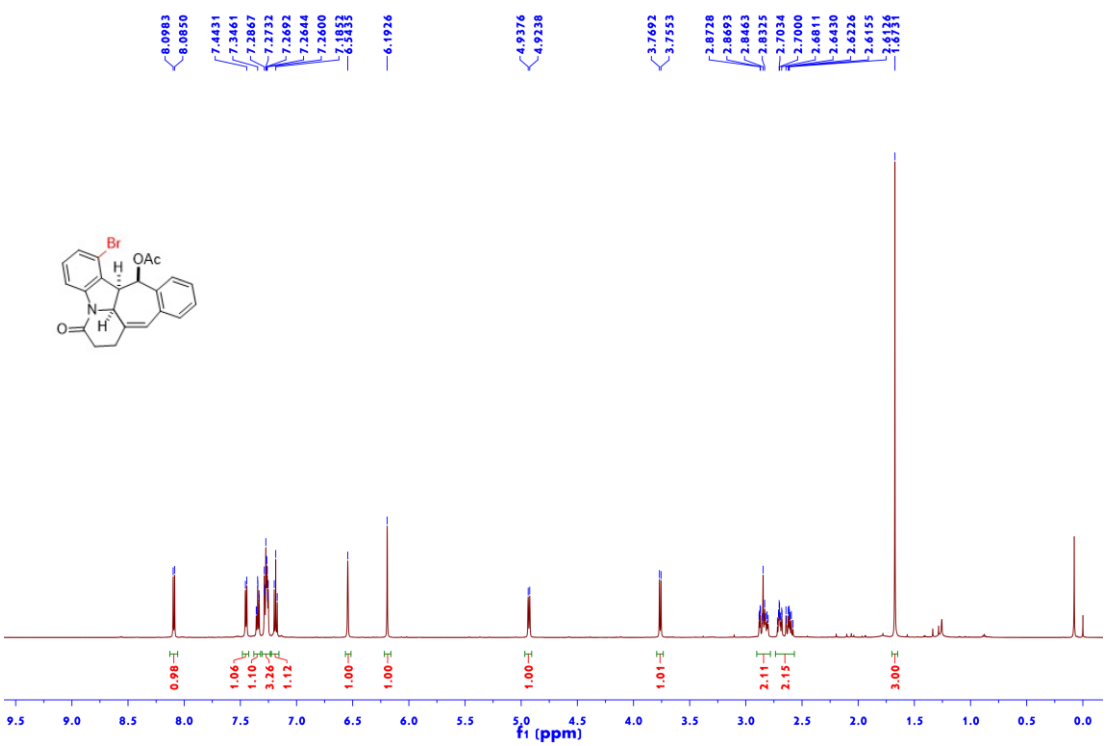


Figure S199 ^{13}C NMR (150 MHz, $CDCl_3$) of **7d**

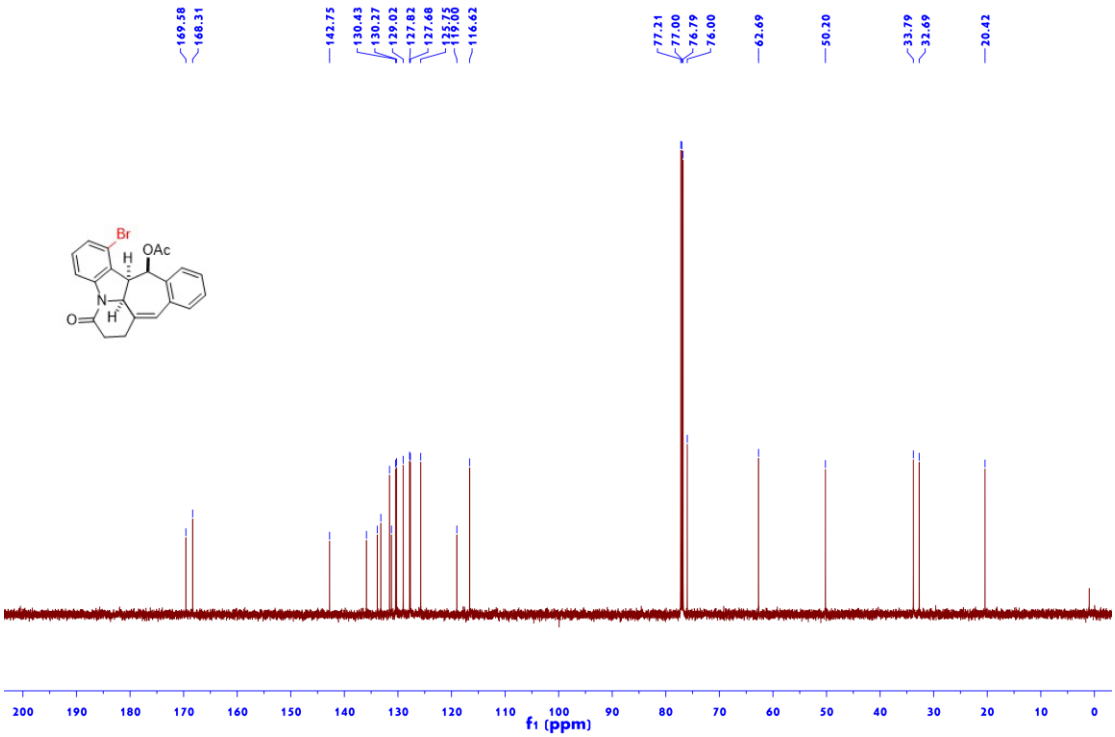


Figure S200 ^{1}H NMR (600 MHz, $CDCl_3$) of **7e**

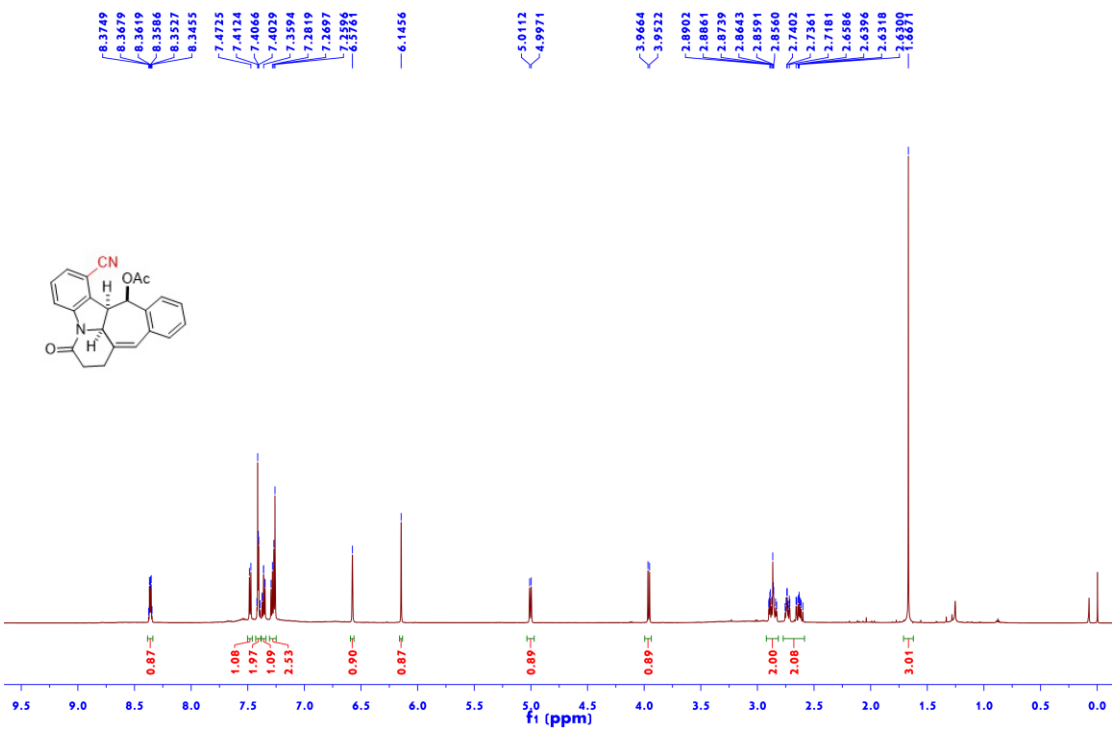


Figure S201 ^{13}C NMR (150 MHz, $CDCl_3$) of **7e**

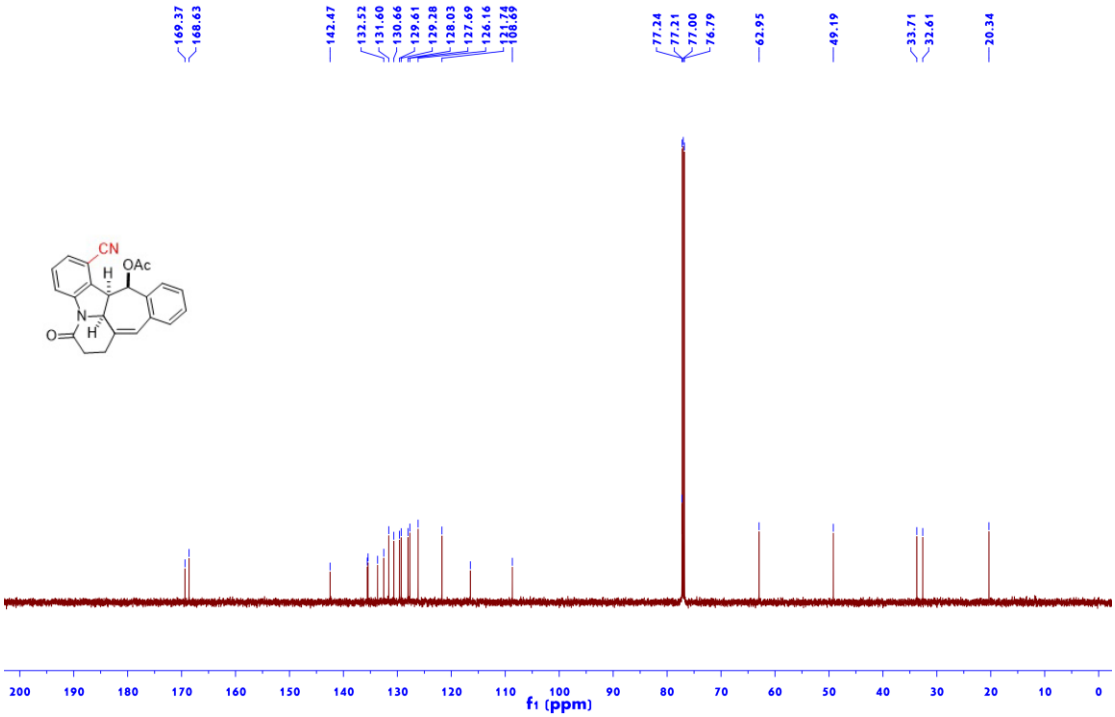


Figure S202 ^{1}H NMR (600 MHz, $CDCl_3$) of **7f**

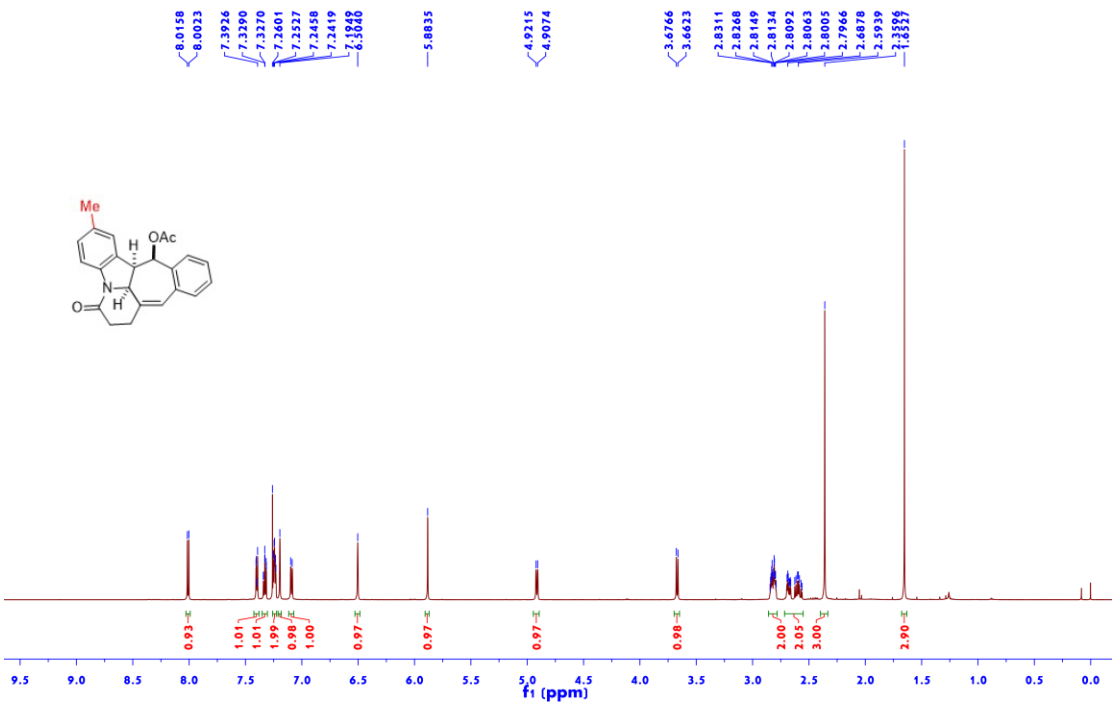


Figure S203 ^{13}C NMR (150 MHz, $CDCl_3$) of **7f**

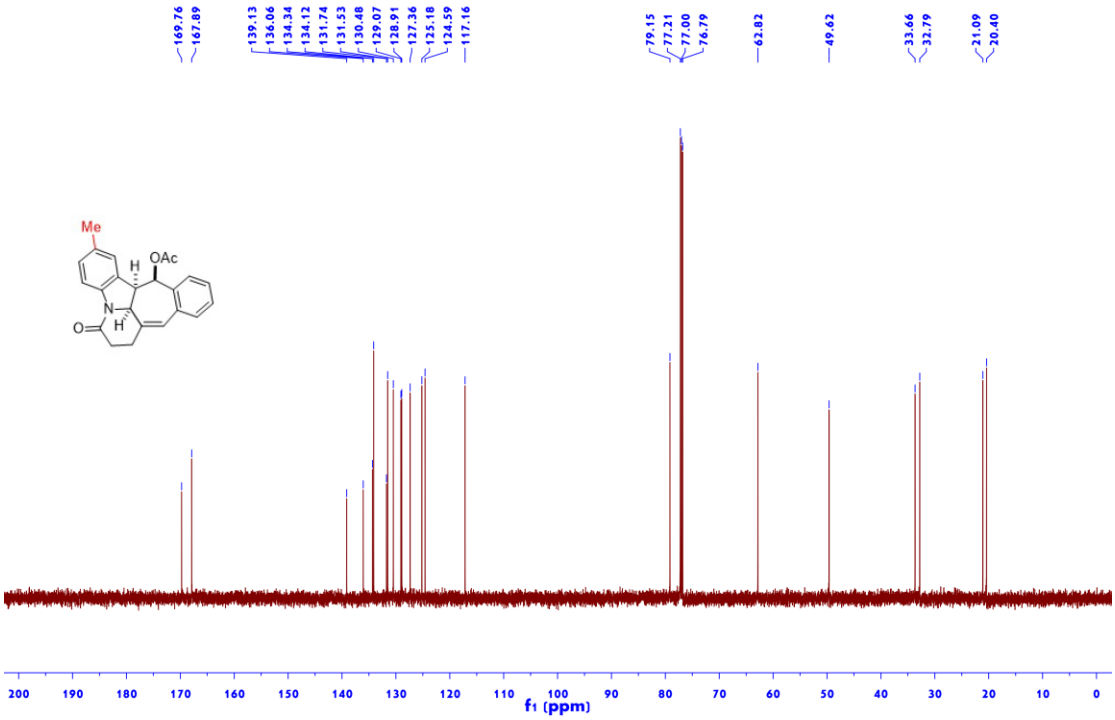


Figure S204 ^{1}H NMR (600 MHz, $CDCl_3$) of **7g**

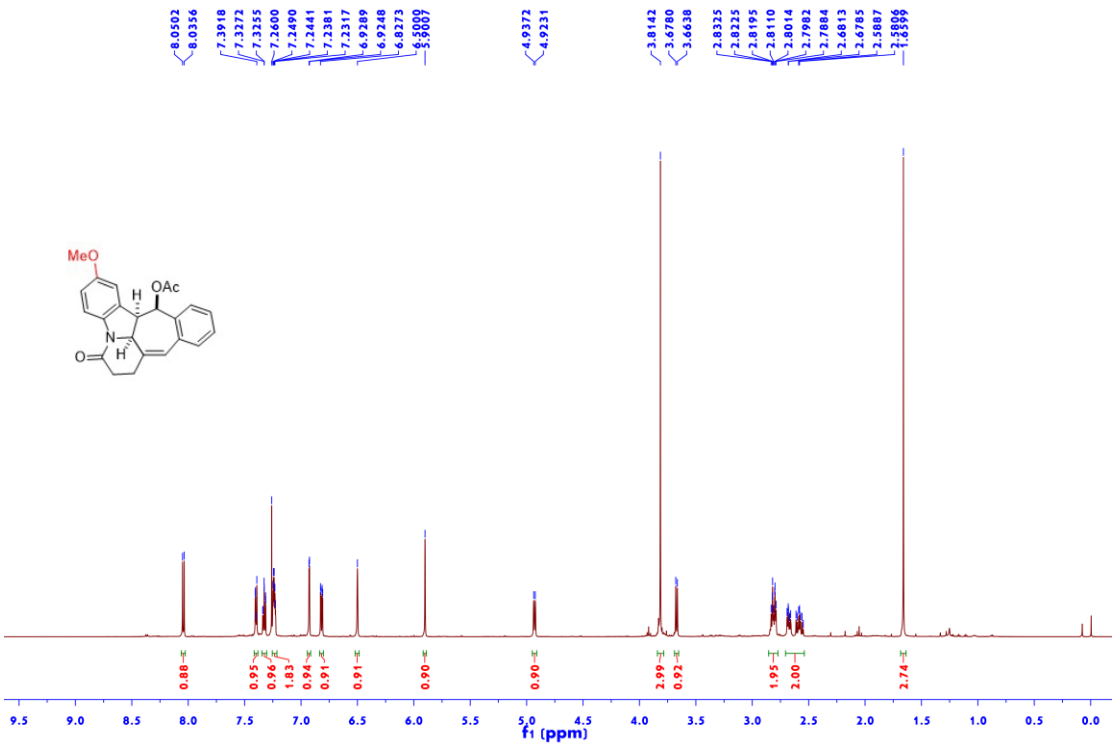


Figure S205 ^{13}C NMR (150 MHz, $CDCl_3$) of **7g**

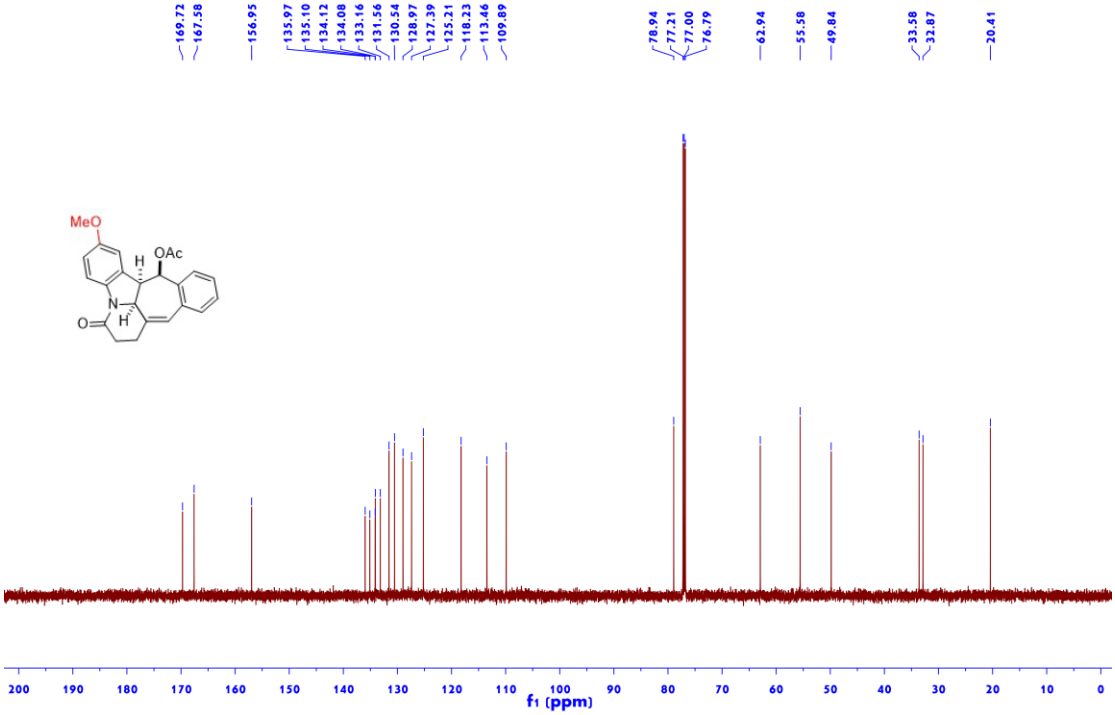


Figure S206 ^{1}H NMR (600 MHz, $CDCl_3$) of **7h**

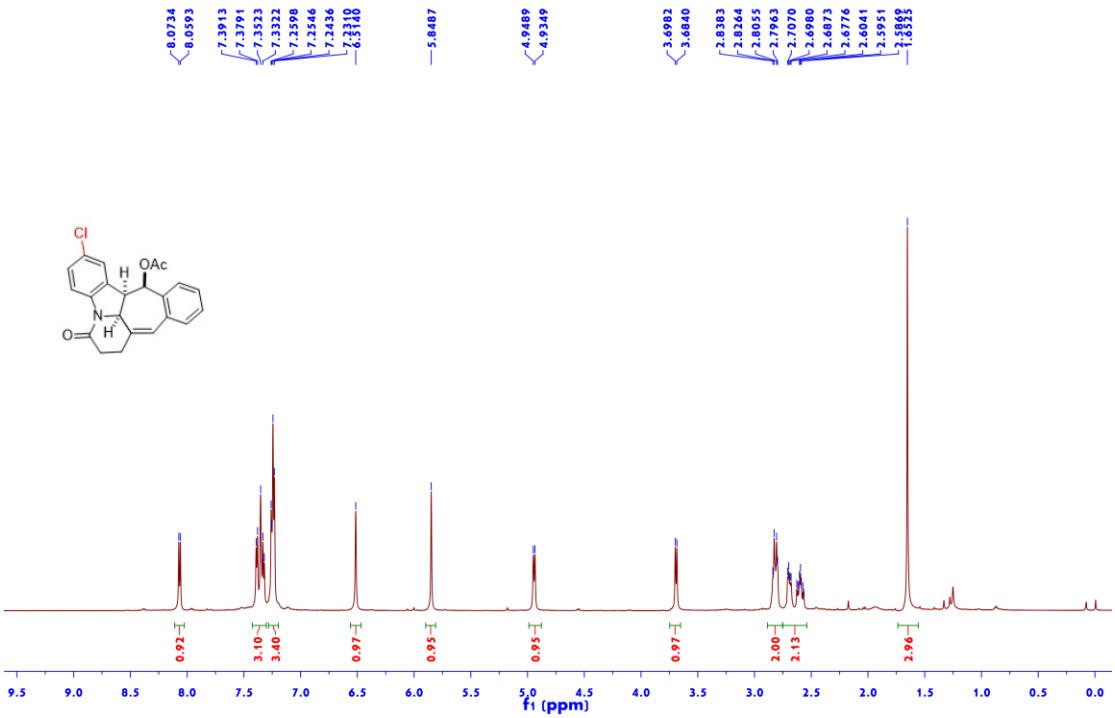


Figure S207 ^{13}C NMR (150 MHz, $CDCl_3$) of **7h**

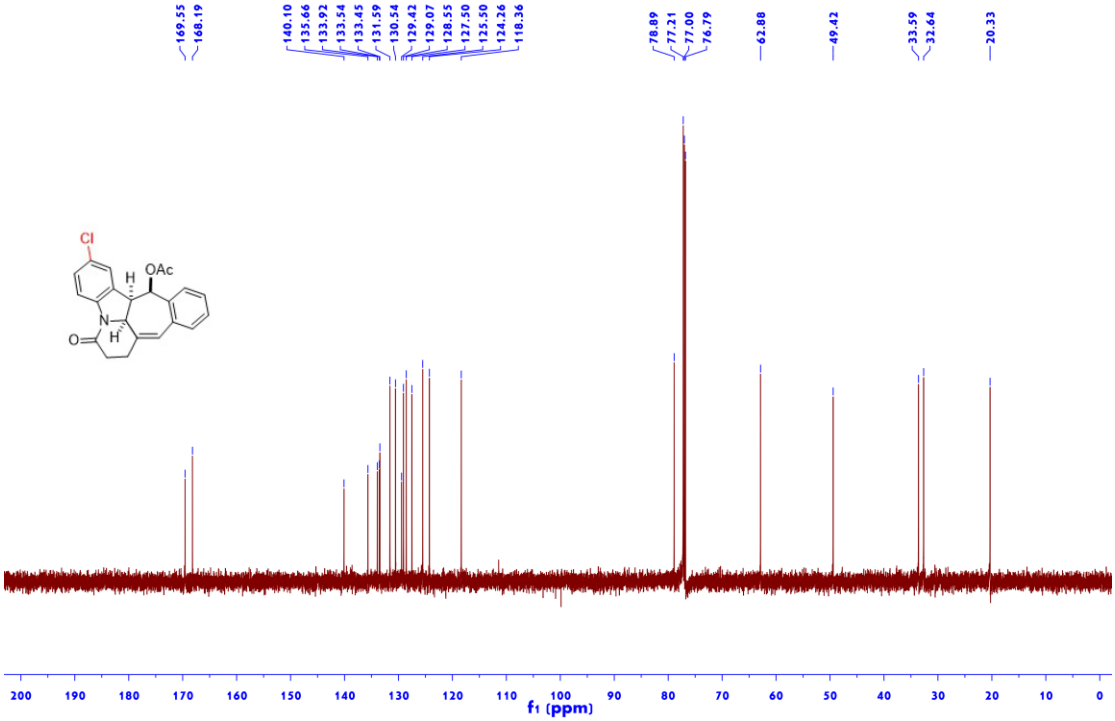


Figure S208 ^{1}H NMR (600 MHz, $CDCl_3$) of **7i**

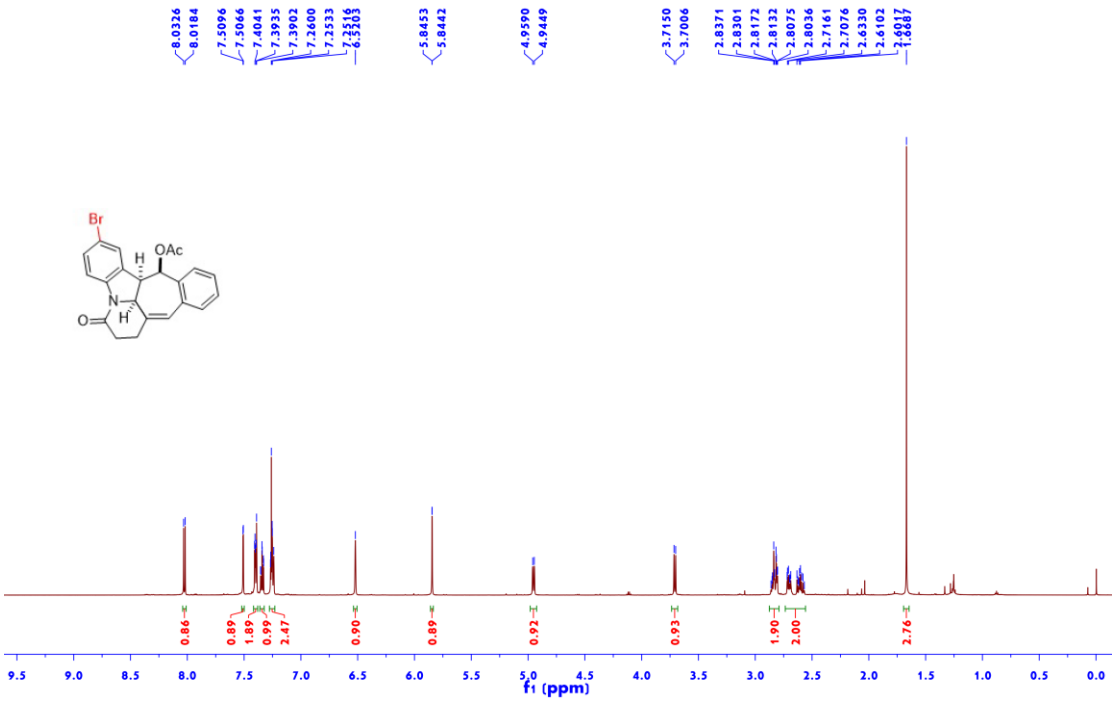


Figure S209 ^{13}C NMR (150 MHz, $CDCl_3$) of **7i**

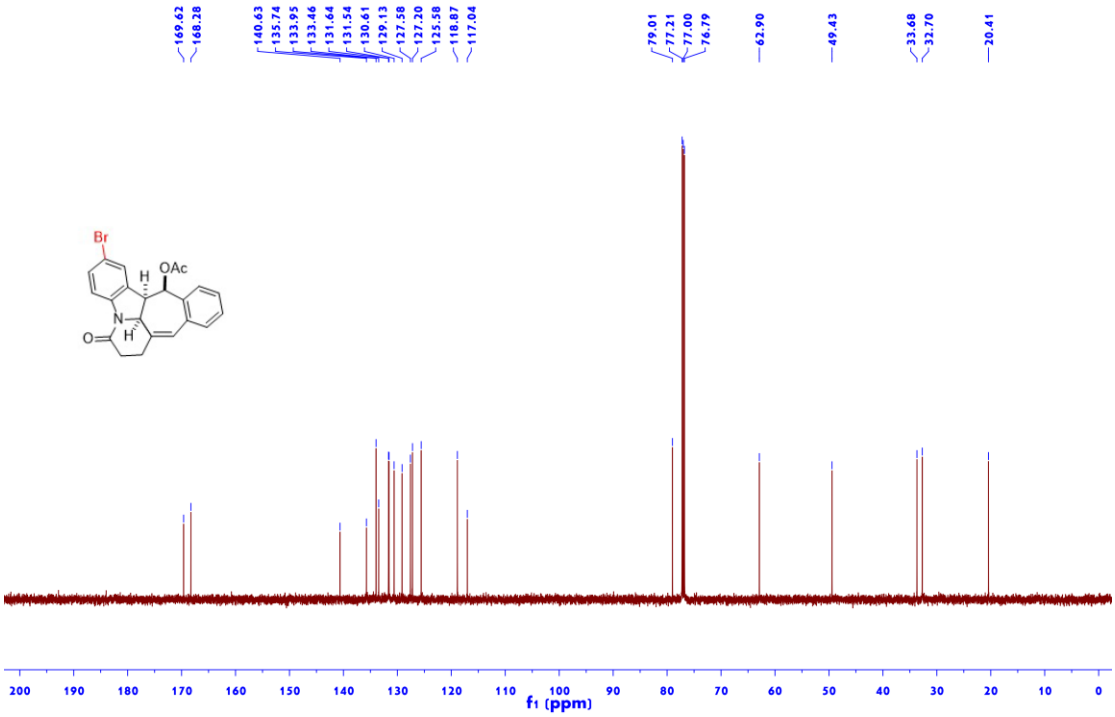


Figure S210 ^{1}H NMR (600 MHz, $CDCl_3$) of **7j**

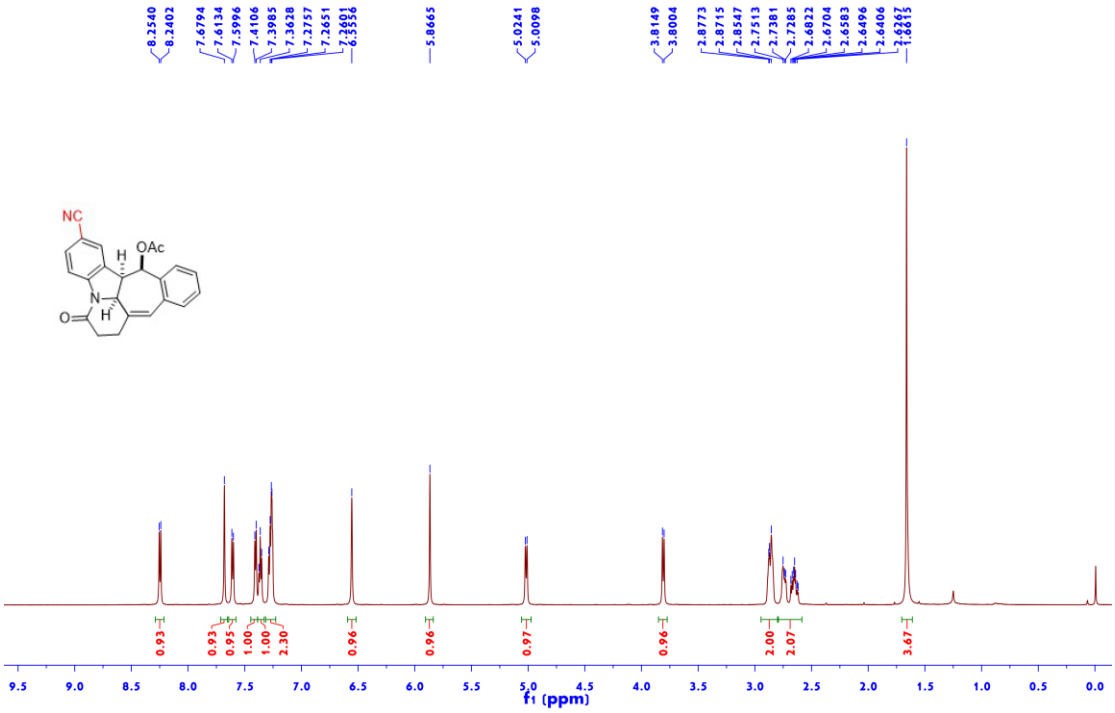


Figure S211 ^{13}C NMR (150 MHz, $CDCl_3$) of **7j**

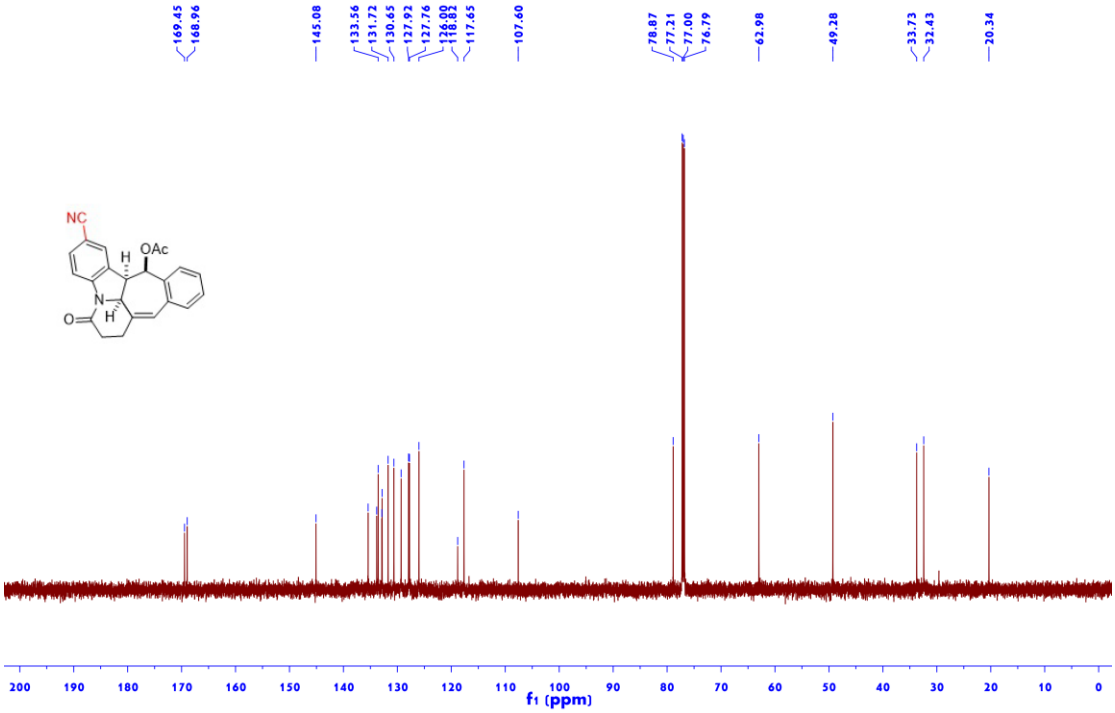


Figure S212 ^{1}H NMR (600 MHz, $CDCl_3$) of **7k**

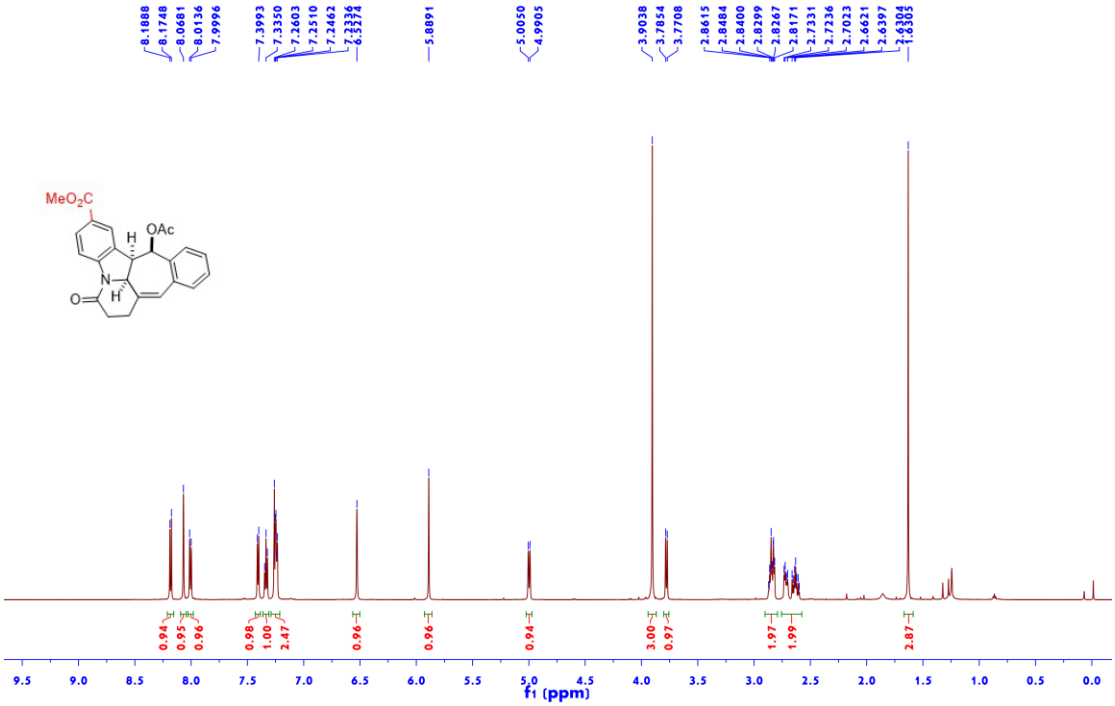


Figure S213 ^{13}C NMR (150 MHz, $CDCl_3$) of **7k**

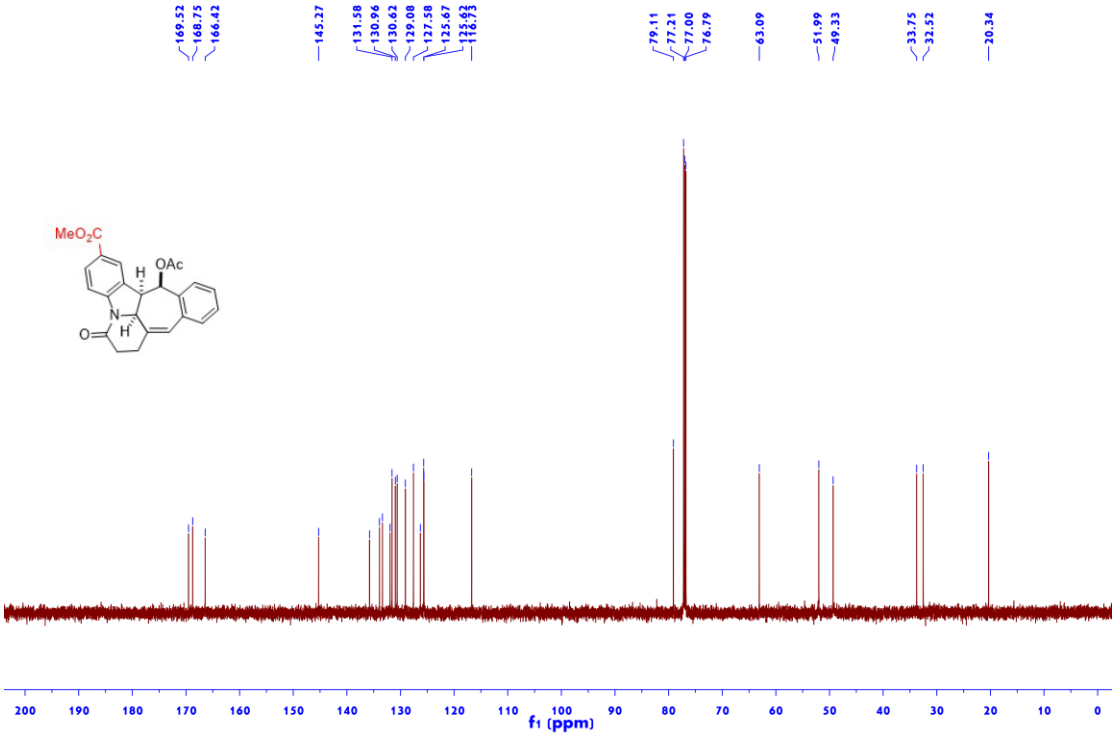


Figure S214 ^{1}H NMR (600 MHz, $CDCl_3$) of **7l**

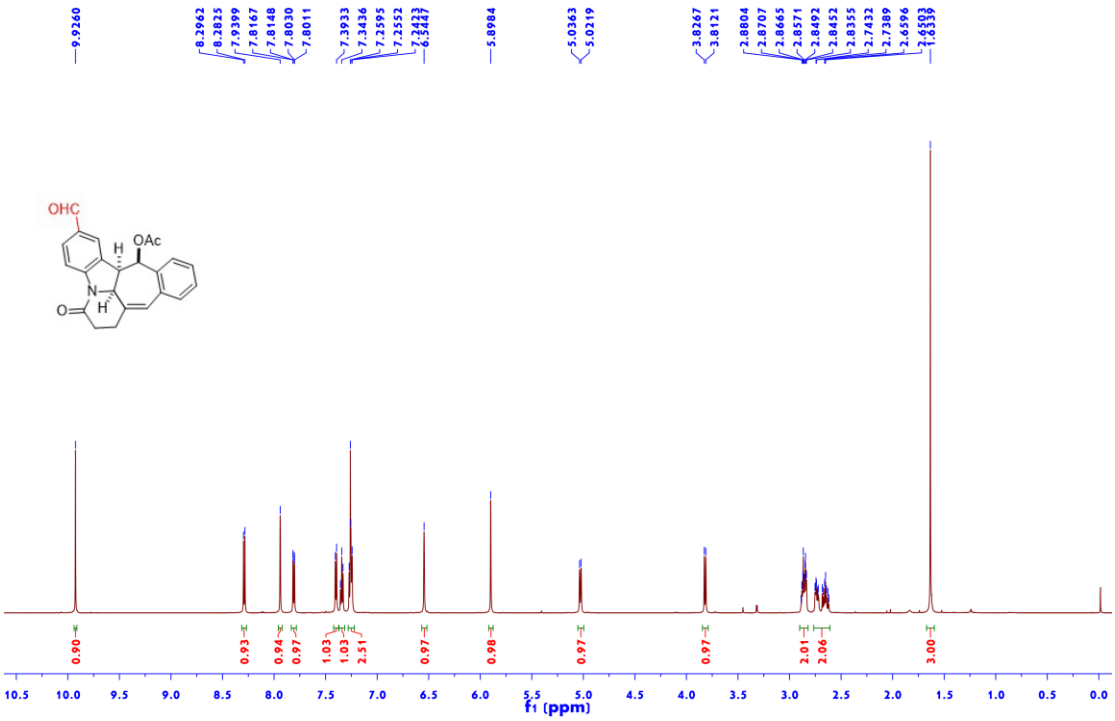


Figure S215 ^{13}C NMR (150 MHz, $CDCl_3$) of **7l**

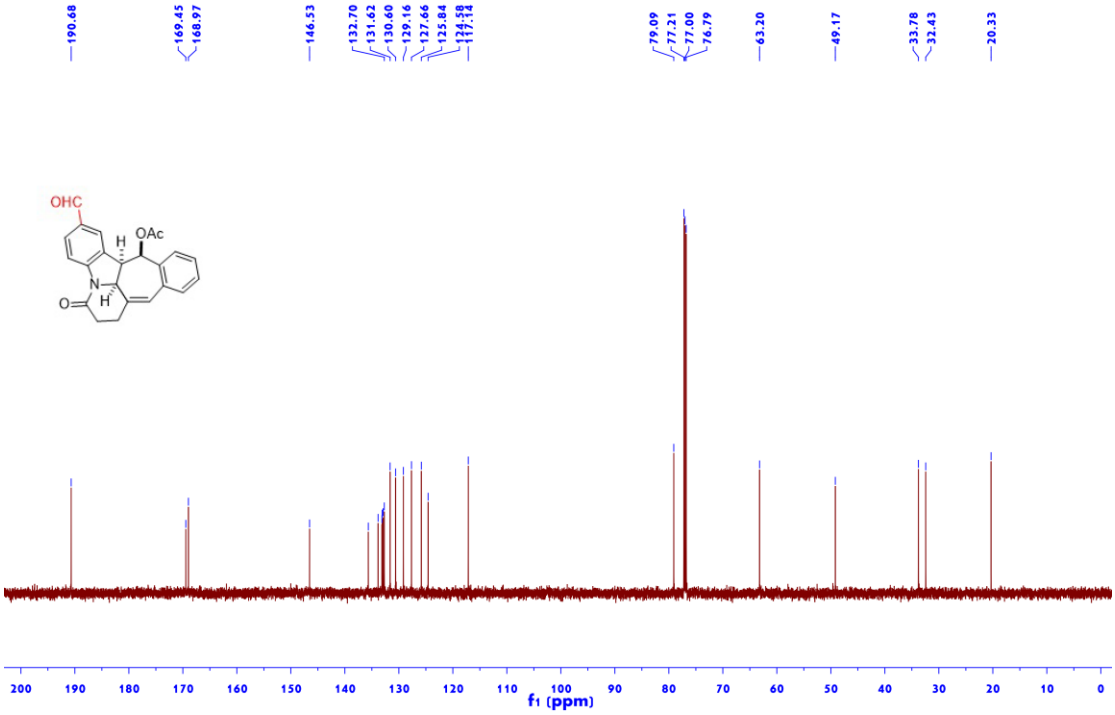


Figure S216 ^{1}H NMR (600 MHz, $CDCl_3$) of **7m**

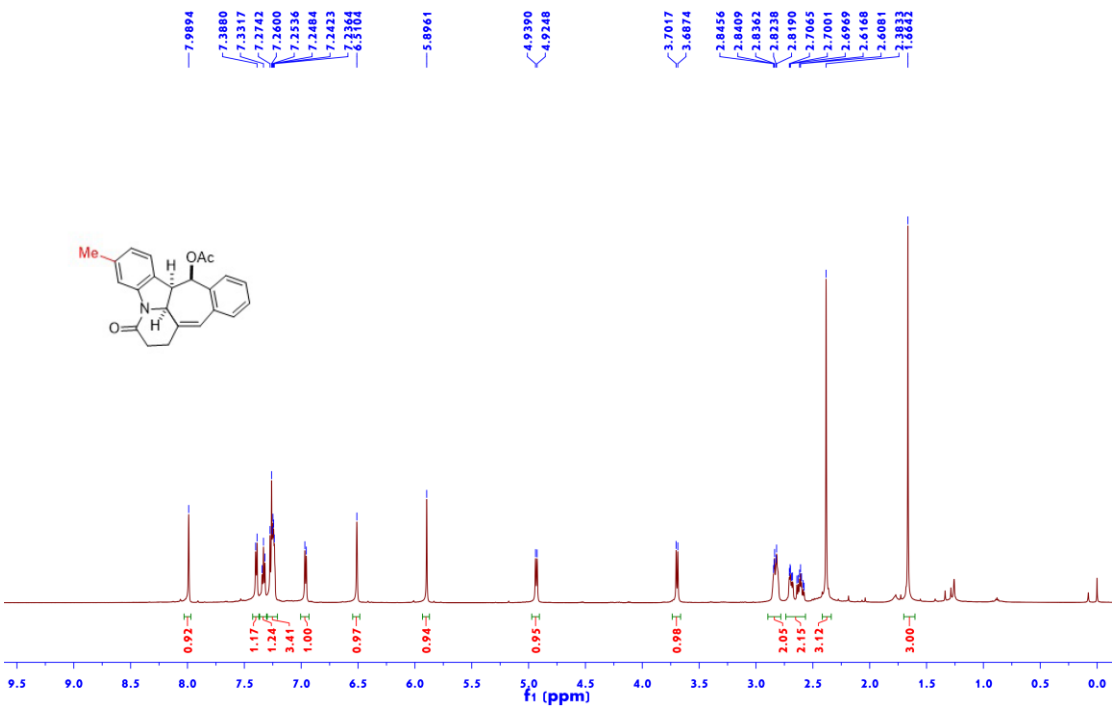


Figure S217 ^{13}C NMR (150 MHz, $CDCl_3$) of **7m**

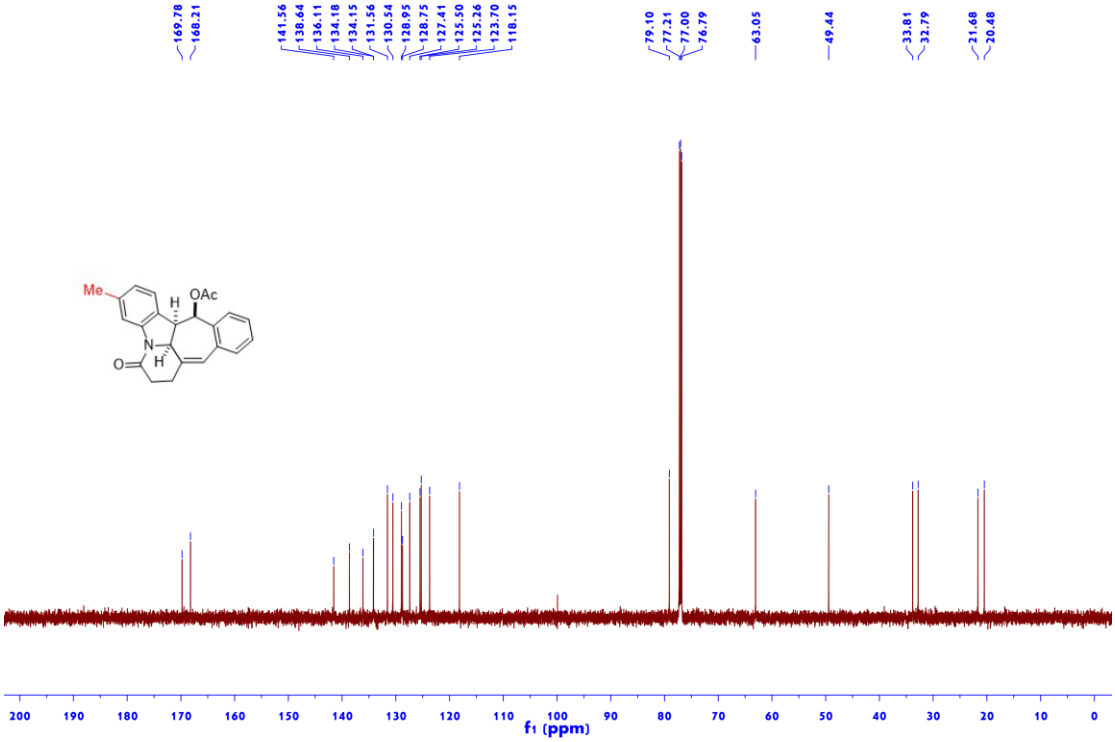


Figure S218 ^{1}H NMR (600 MHz, $CDCl_3$) of **7n**

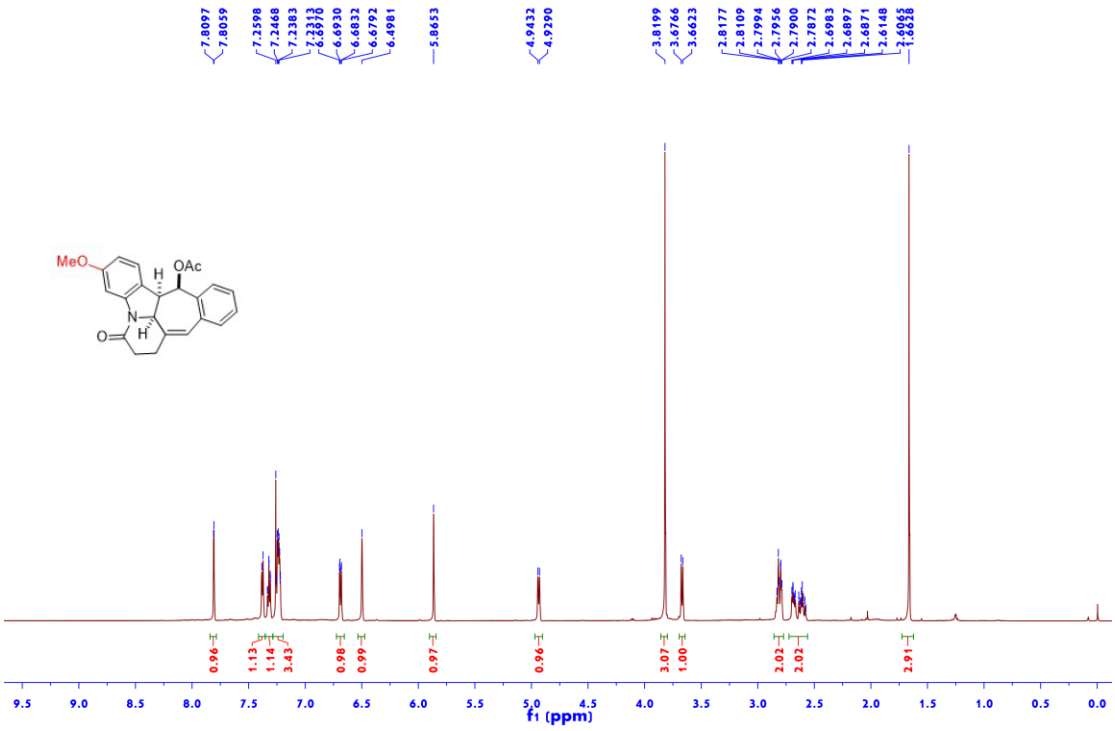


Figure S219 ^{13}C NMR (150 MHz, $CDCl_3$) of **7n**

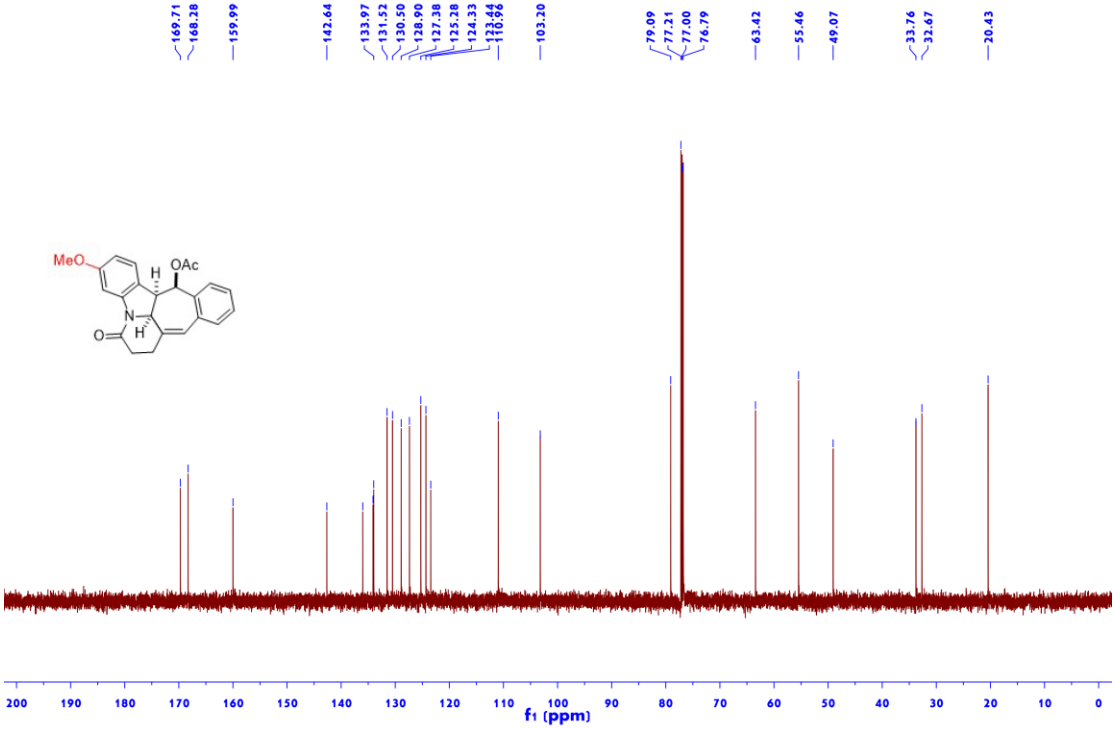


Figure S220 ^{1}H NMR (600 MHz, $CDCl_3$) of **7o**

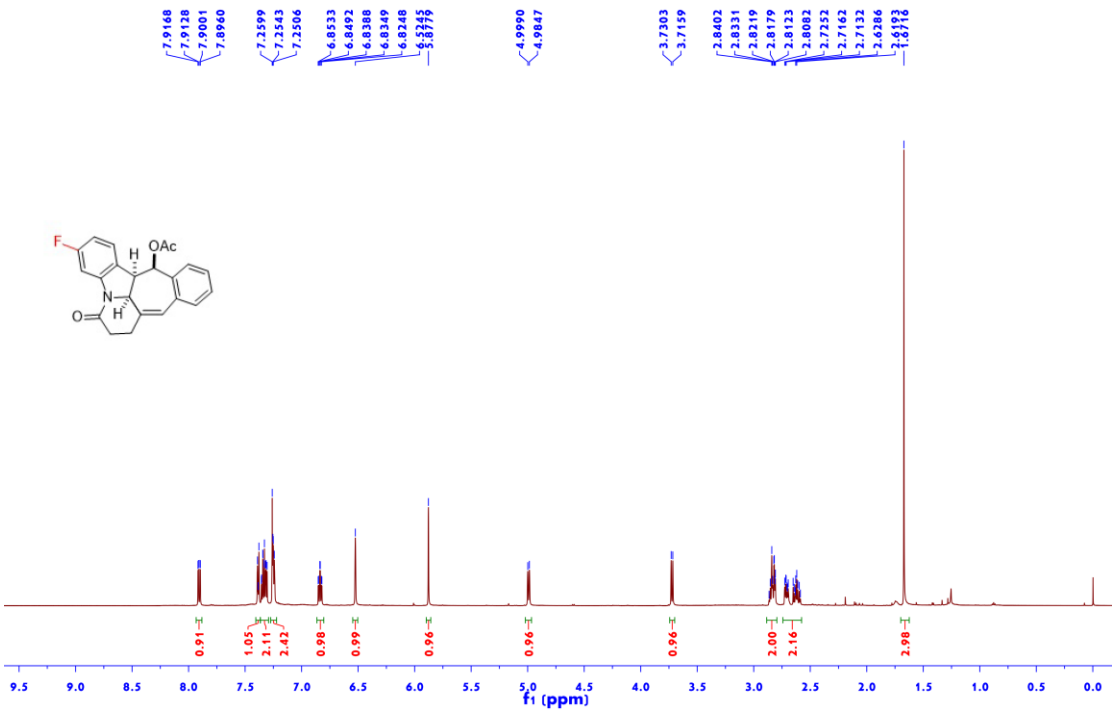


Figure S221 ^{13}C NMR (150 MHz, $CDCl_3$) of **7o**

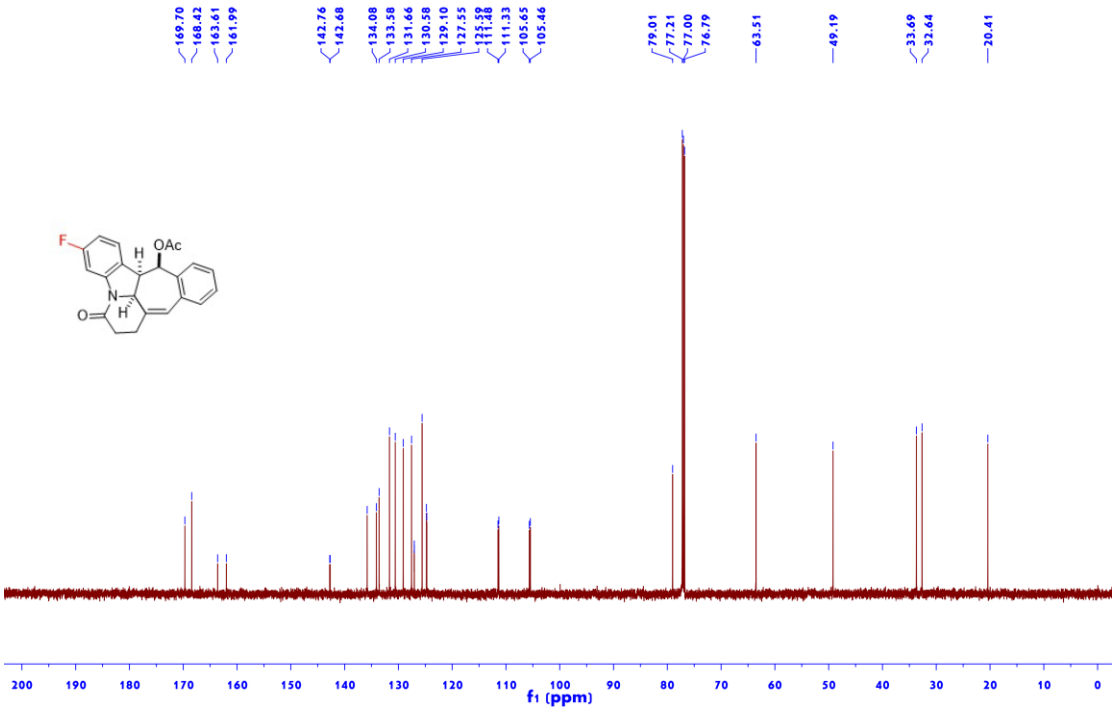


Figure S222 ^{19}F NMR (565 MHz, $CDCl_3$) of **7o**

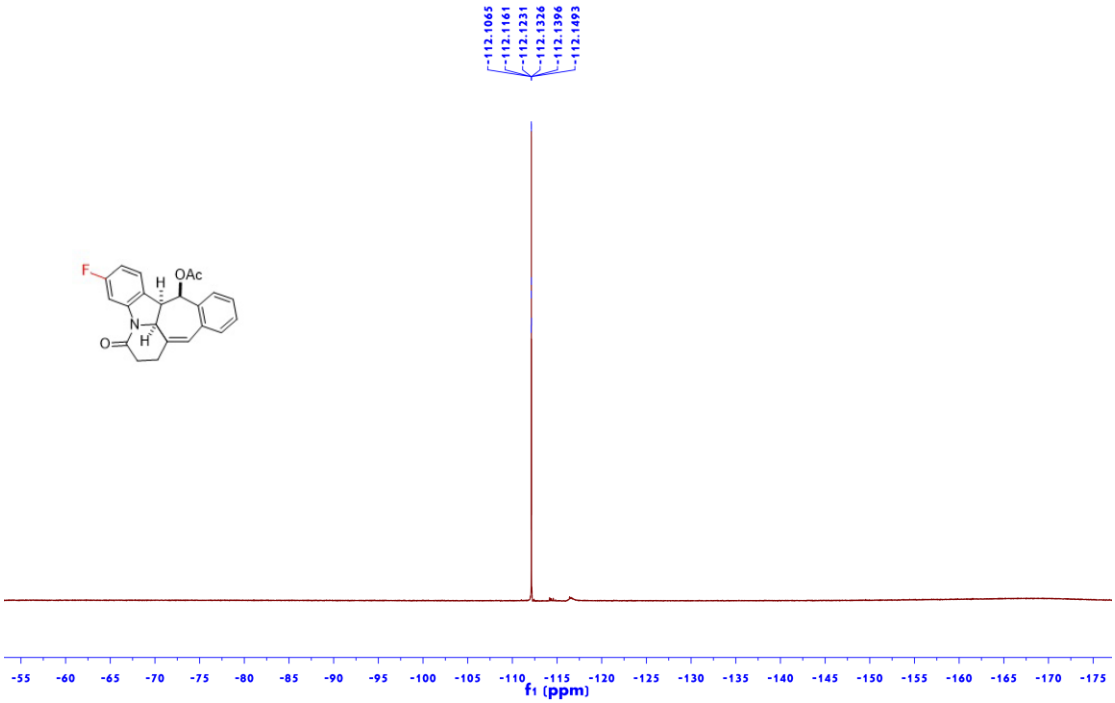


Figure S223 ^{1}H NMR (600 MHz, $CDCl_3$) of **7p**

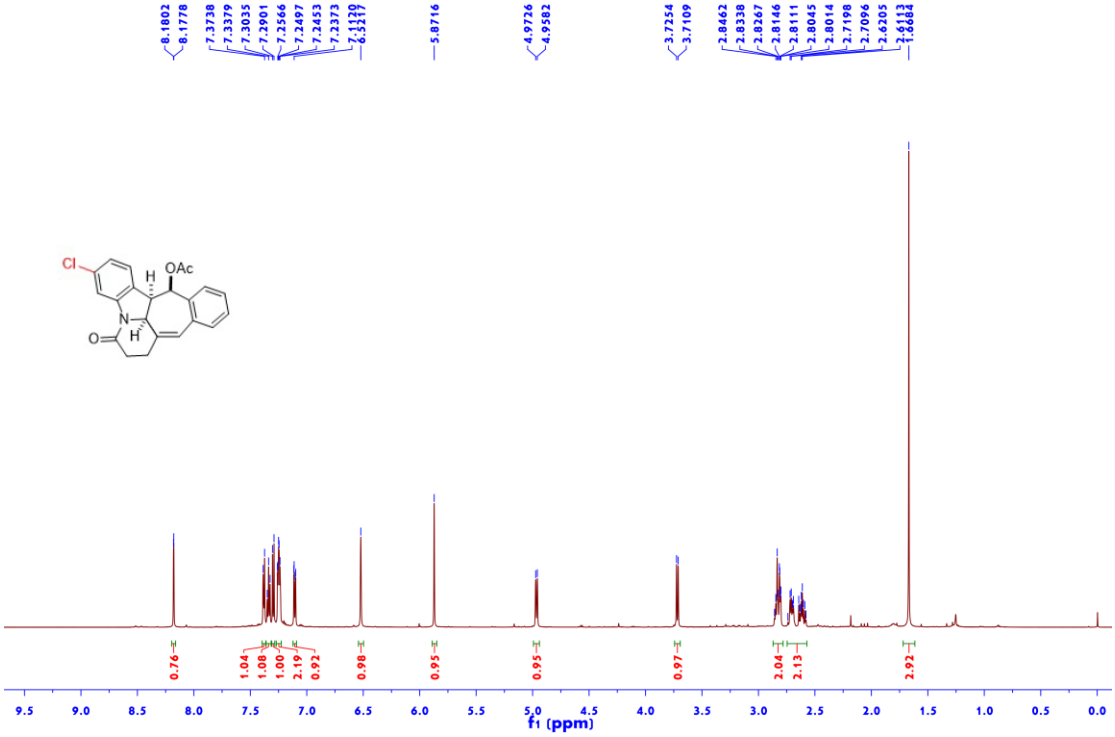


Figure S224 ^{13}C NMR (150 MHz, $CDCl_3$) of **7p**

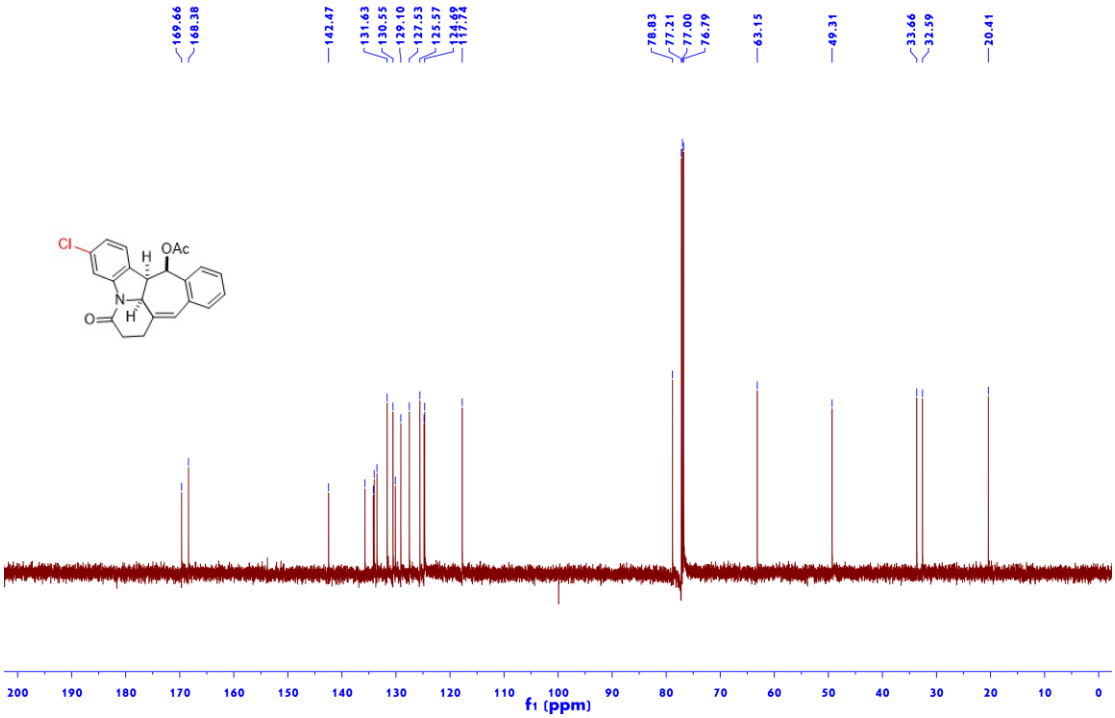


Figure S225 ^{1}H NMR (600 MHz, $CDCl_3$) of **7q**

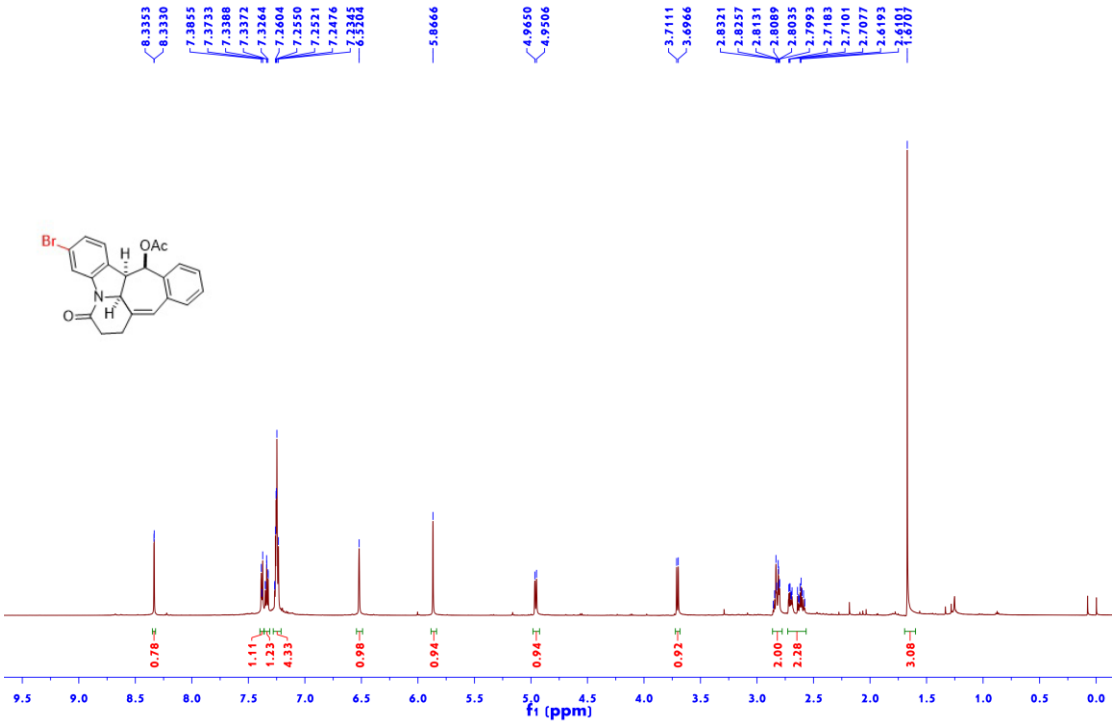


Figure S226 ^{13}C NMR (150 MHz, $CDCl_3$) of **7q**

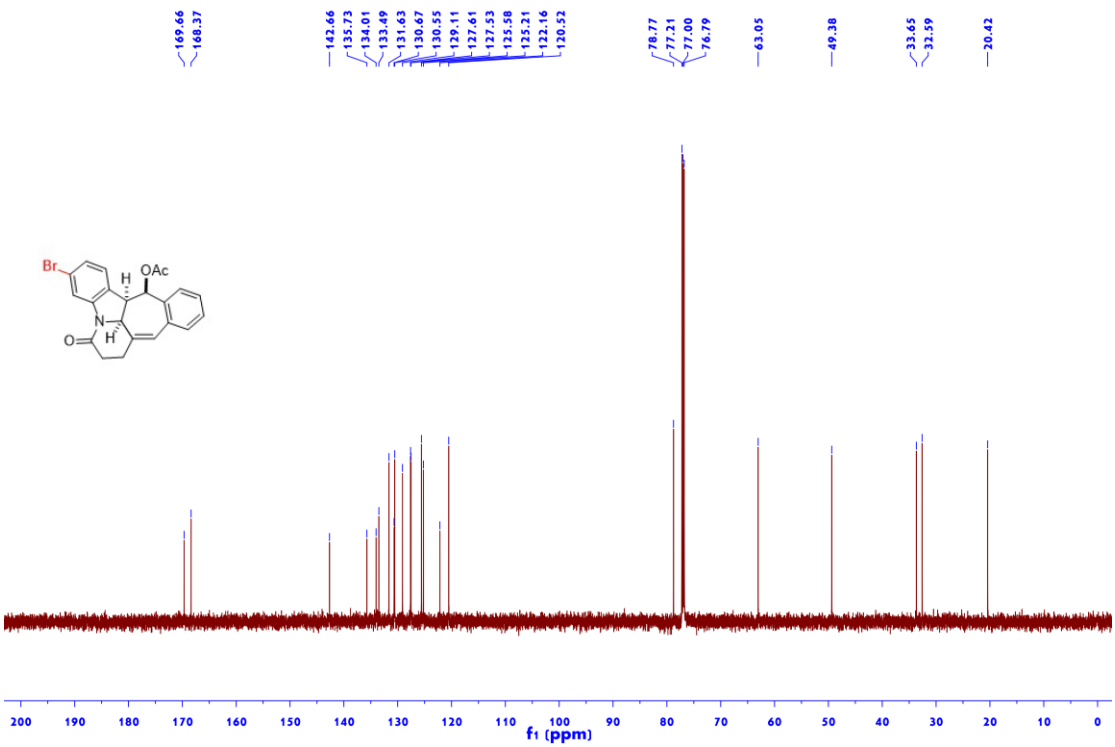


Figure S227 ^{1}H NMR (600 MHz, $CDCl_3$) of **7r**

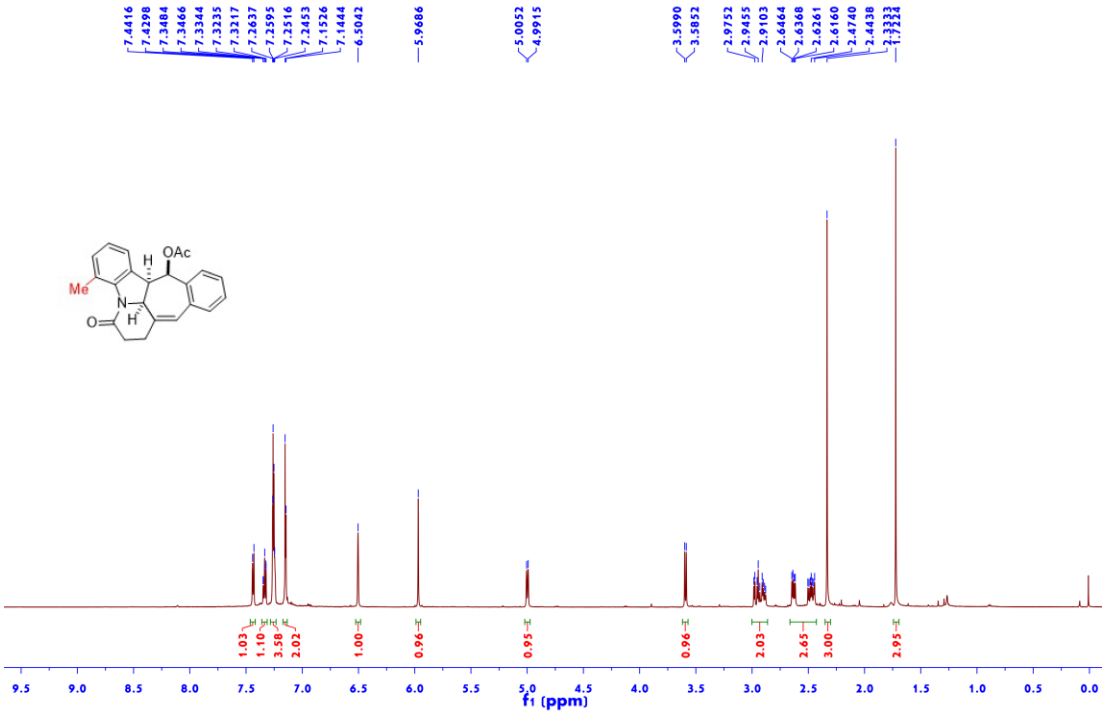


Figure S228 ^{13}C NMR (150 MHz, $CDCl_3$) of **7r**

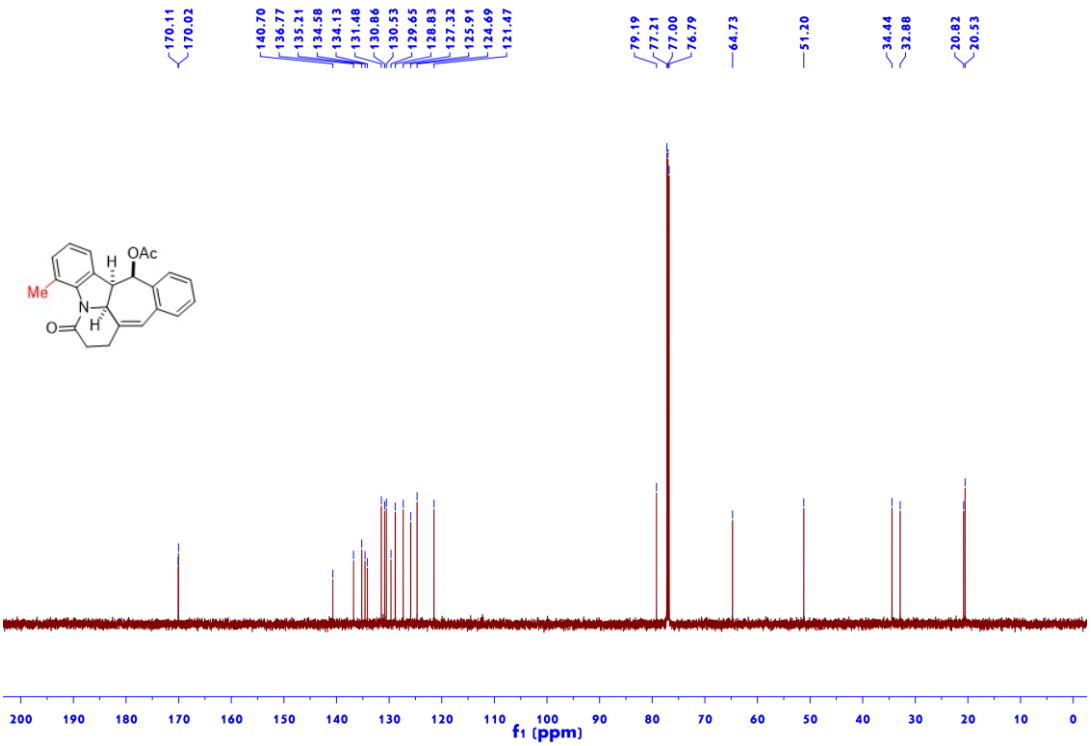


Figure S229 ^{1}H NMR (600 MHz, $CDCl_3$) of **7s**

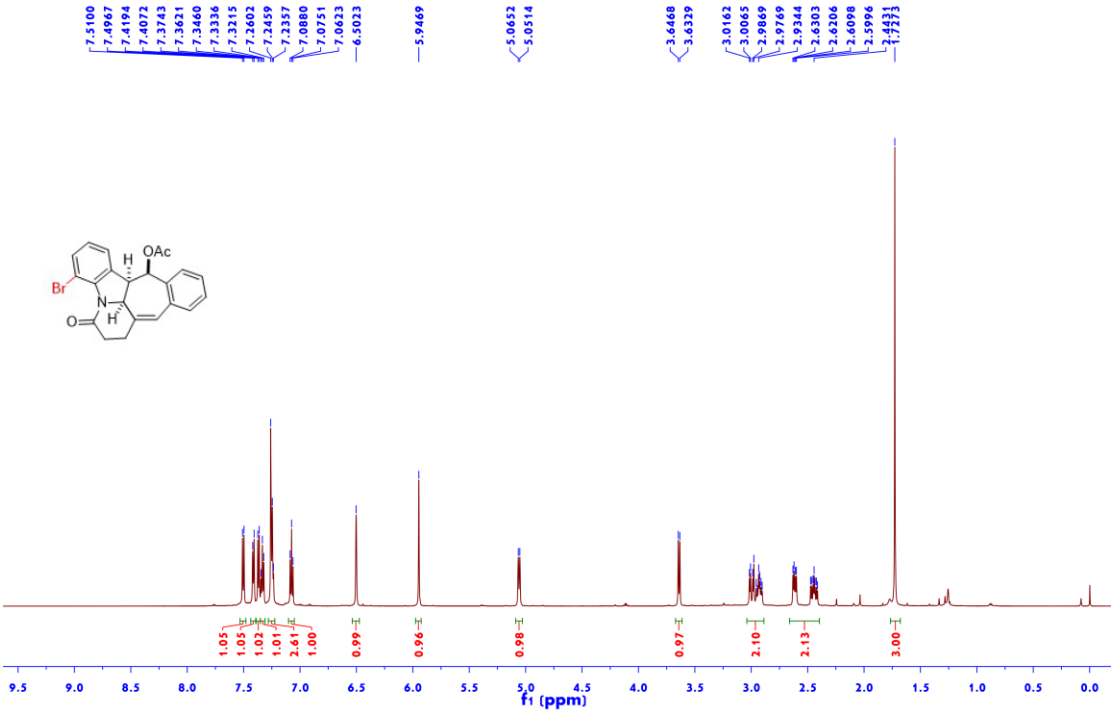


Figure S230 ^{13}C NMR (150 MHz, $CDCl_3$) of **7s**

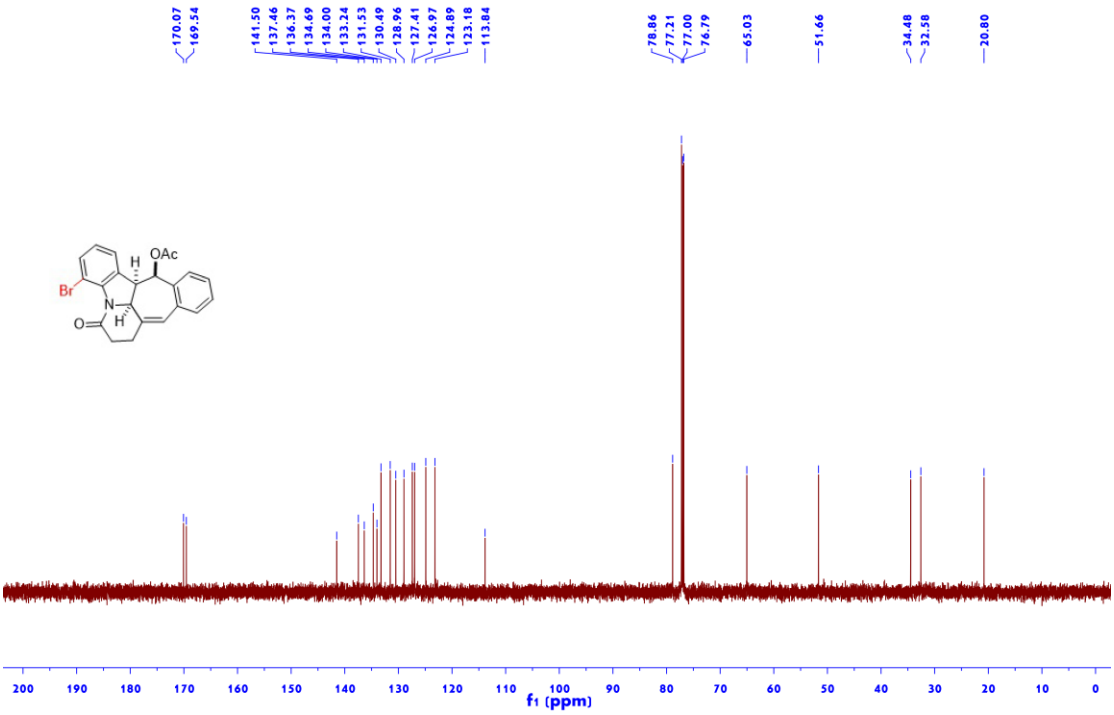


Figure S231 ^{1}H NMR (600 MHz, $CDCl_3$) of **7t**

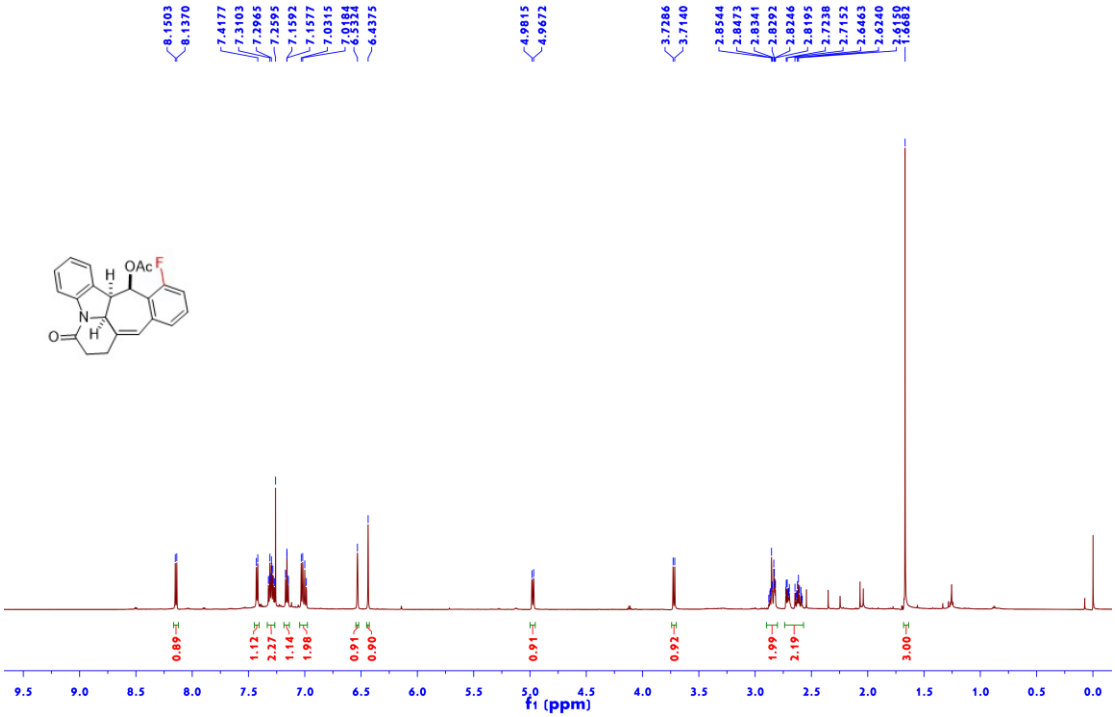


Figure S232 ^{13}C NMR (150 MHz, $CDCl_3$) of **7t**

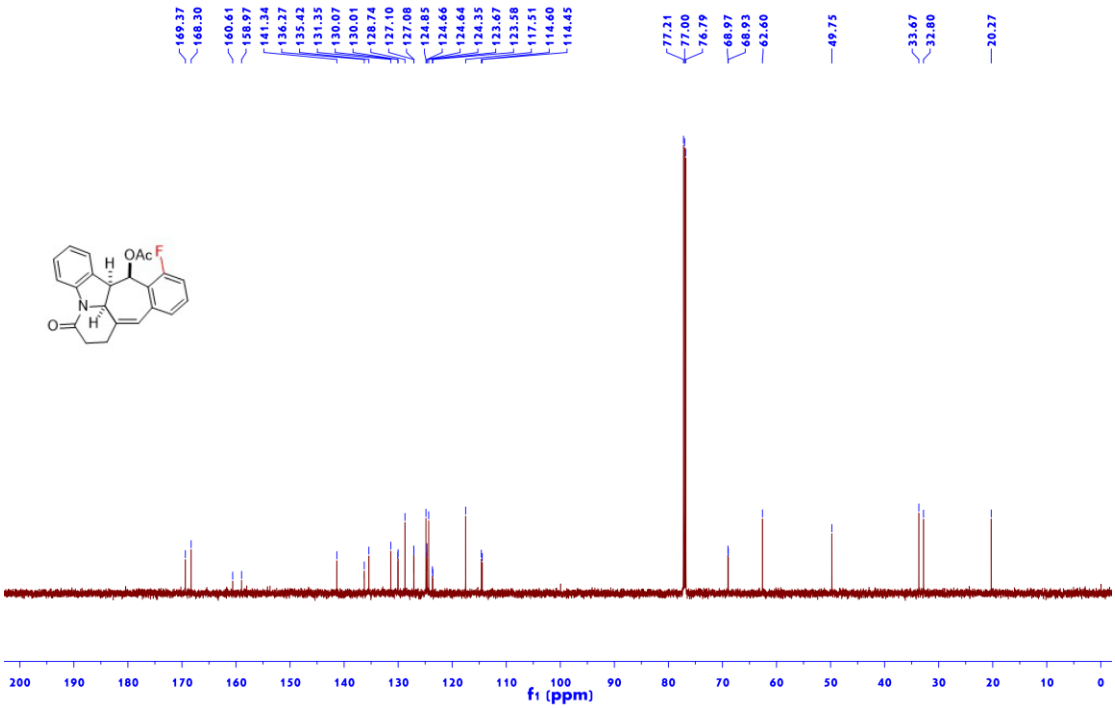


Figure S233 ^{19}F NMR (565 MHz, $CDCl_3$) of **7t**

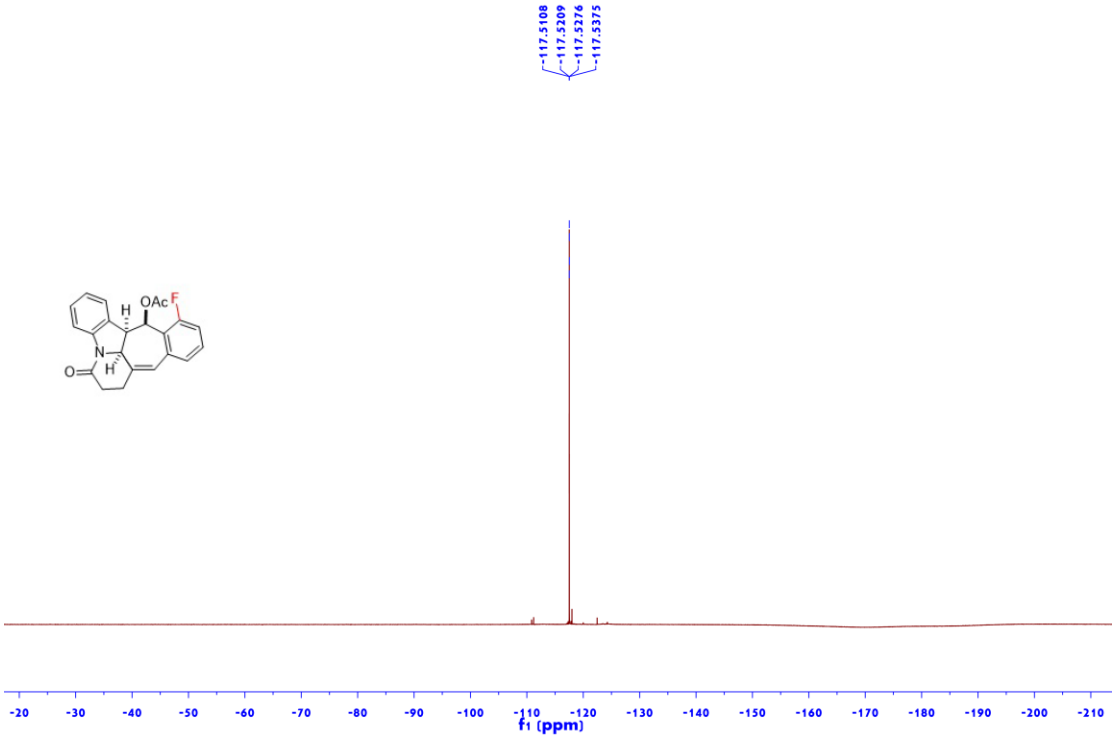


Figure S234 ^{1}H NMR (600 MHz, $CDCl_3$) of **7u**

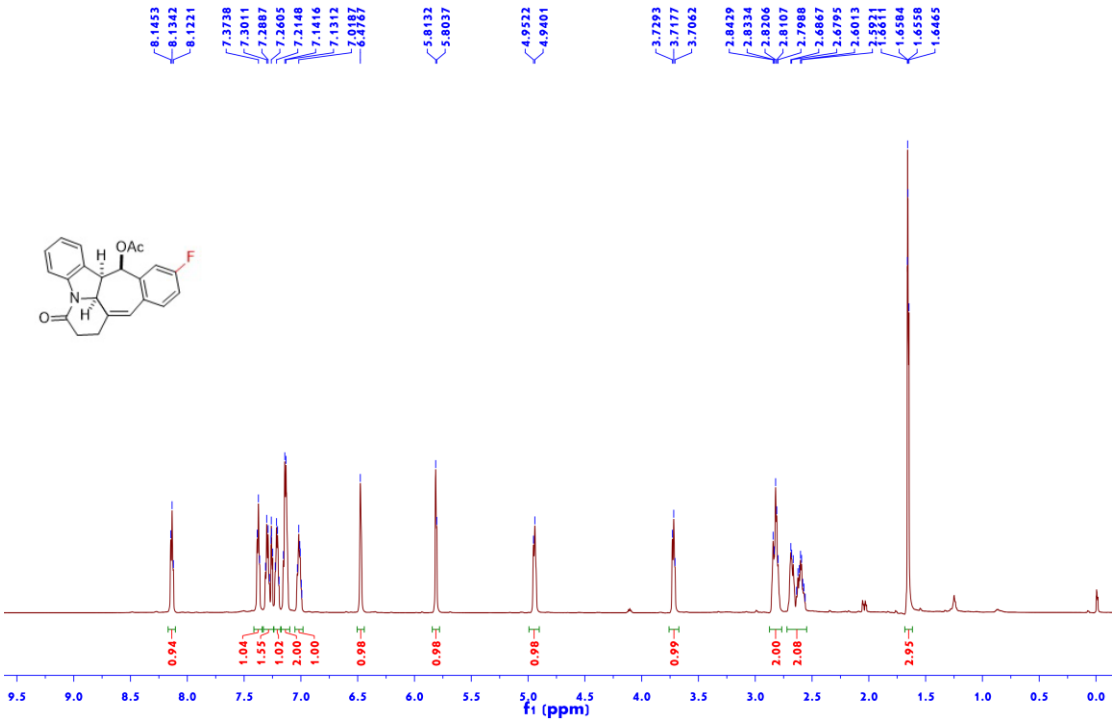


Figure S235 ^{13}C NMR (150 MHz, $CDCl_3$) of **7u**

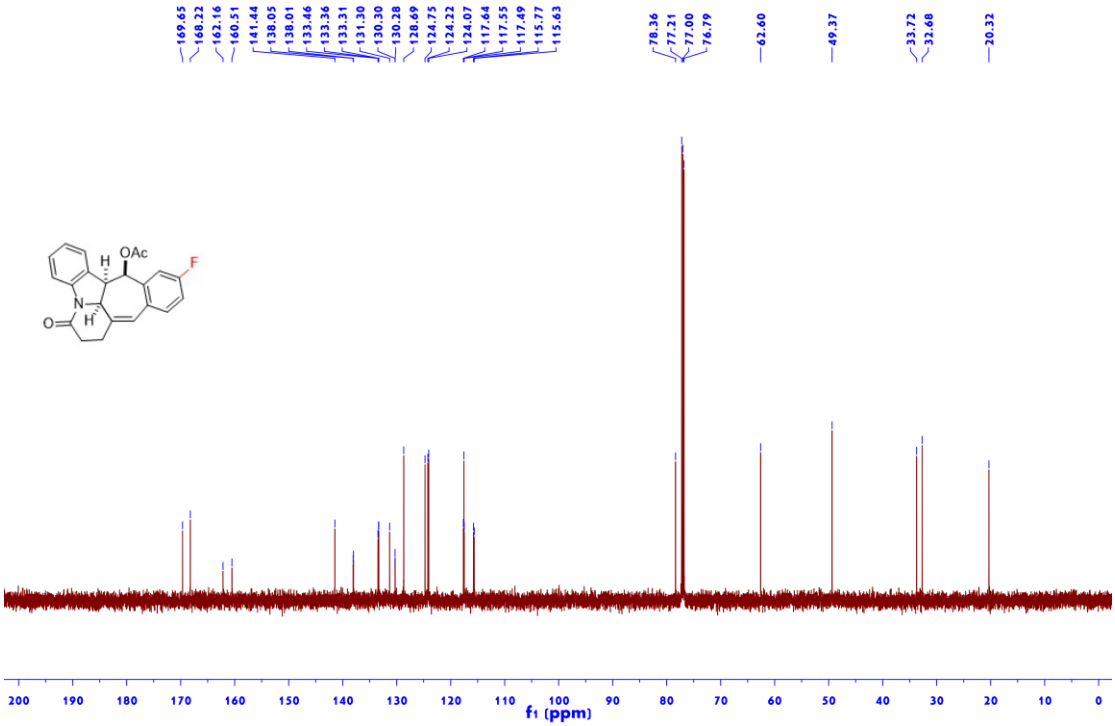


Figure S236 ^{19}F NMR (565 MHz, $CDCl_3$) of **7u**

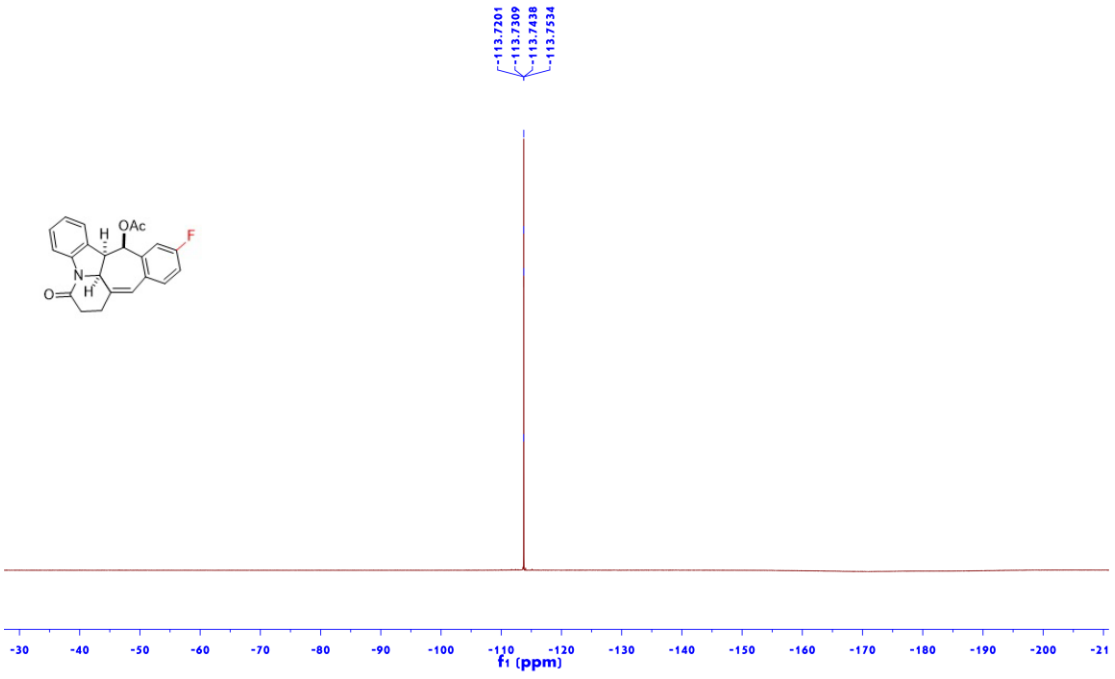


Figure S237 ^{1}H NMR (600 MHz, $CDCl_3$) of **7v**

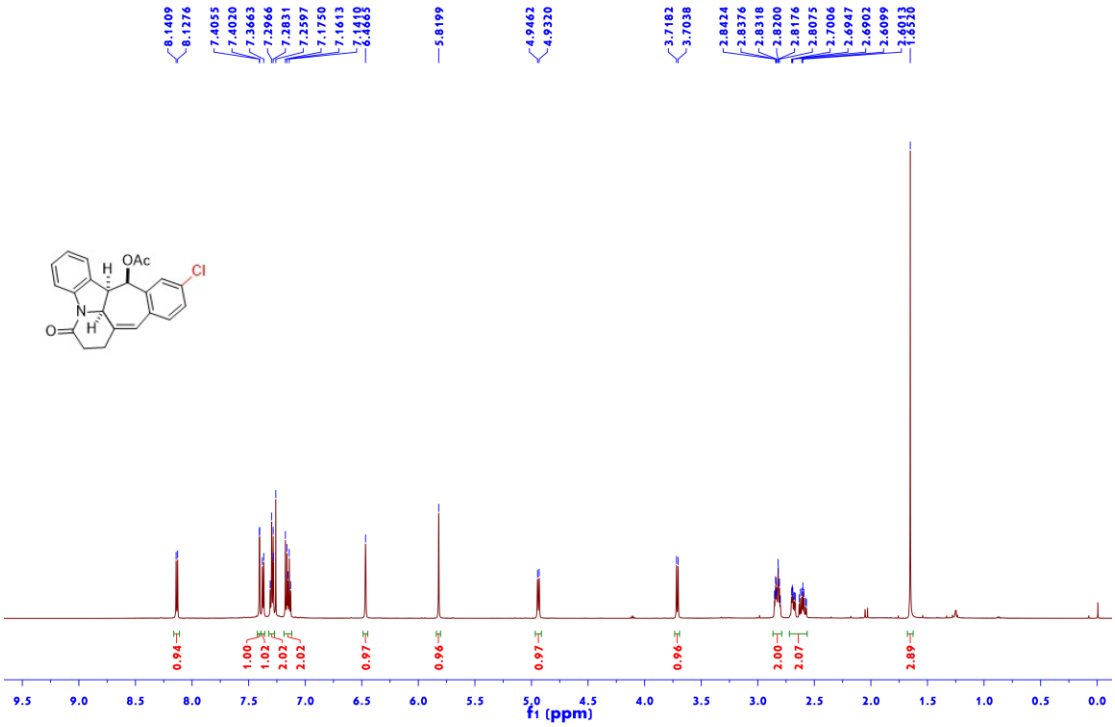


Figure S238 ^{13}C NMR (150 MHz, $CDCl_3$) of **7v**

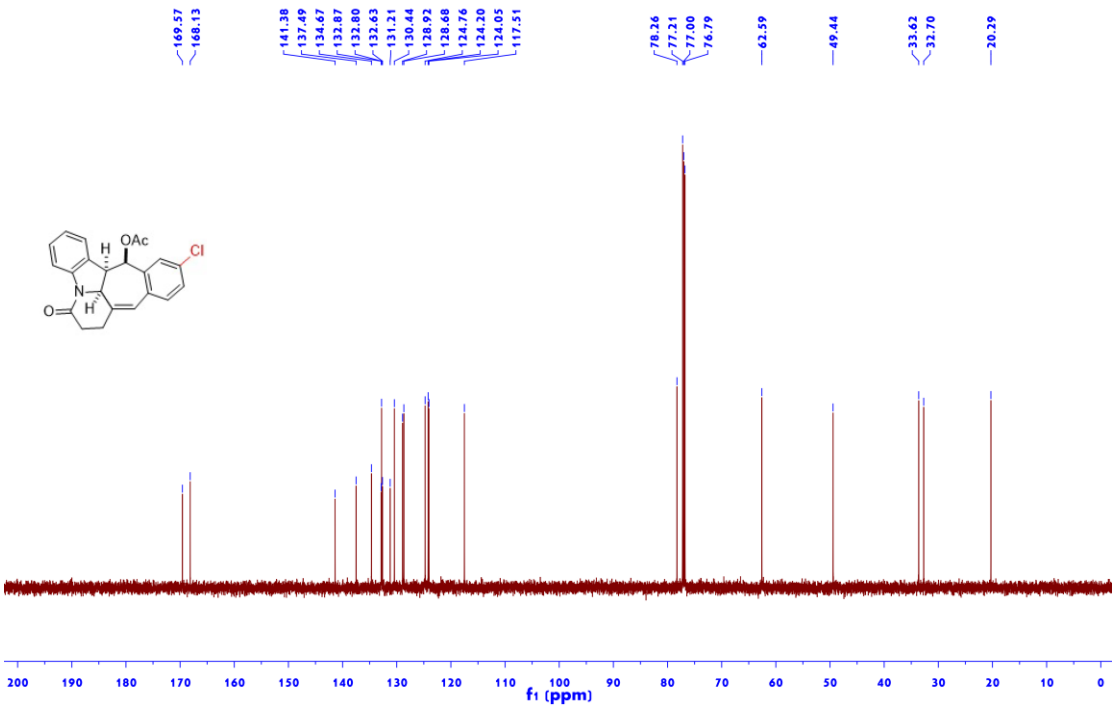


Figure S239 ^{1}H NMR (600 MHz, $CDCl_3$) of **7w**

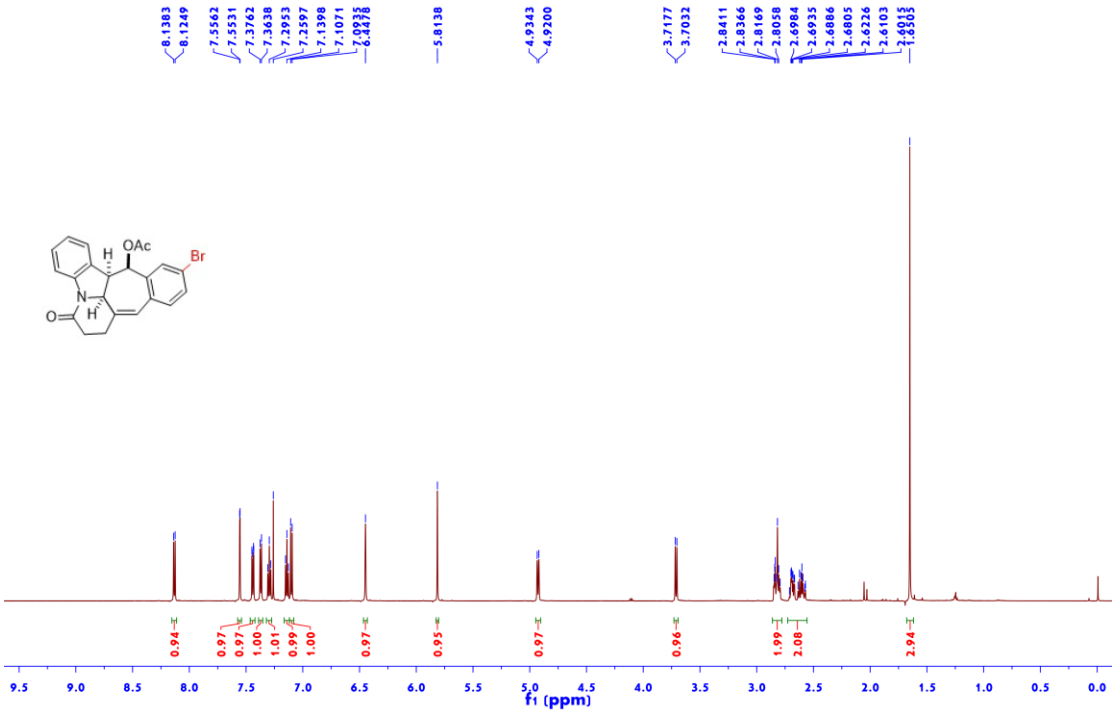


Figure S240 ^{13}C NMR (150 MHz, $CDCl_3$) of **7w**

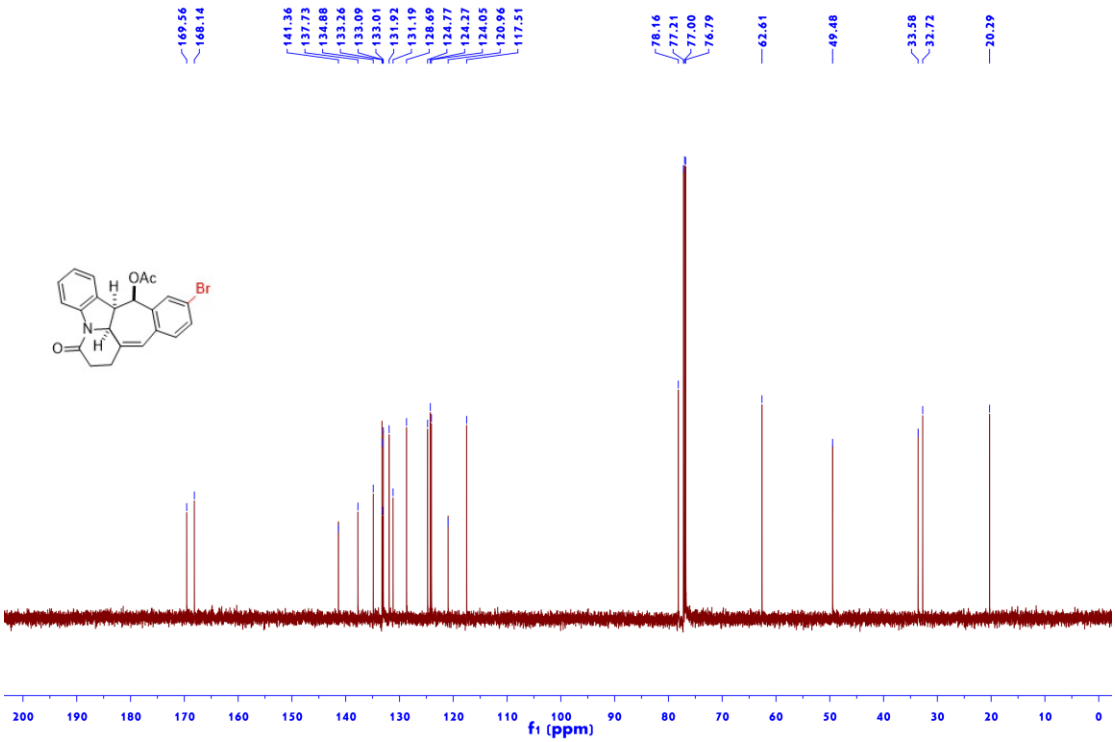


Figure S241 ^{1}H NMR (600 MHz, $CDCl_3$) of **7x**

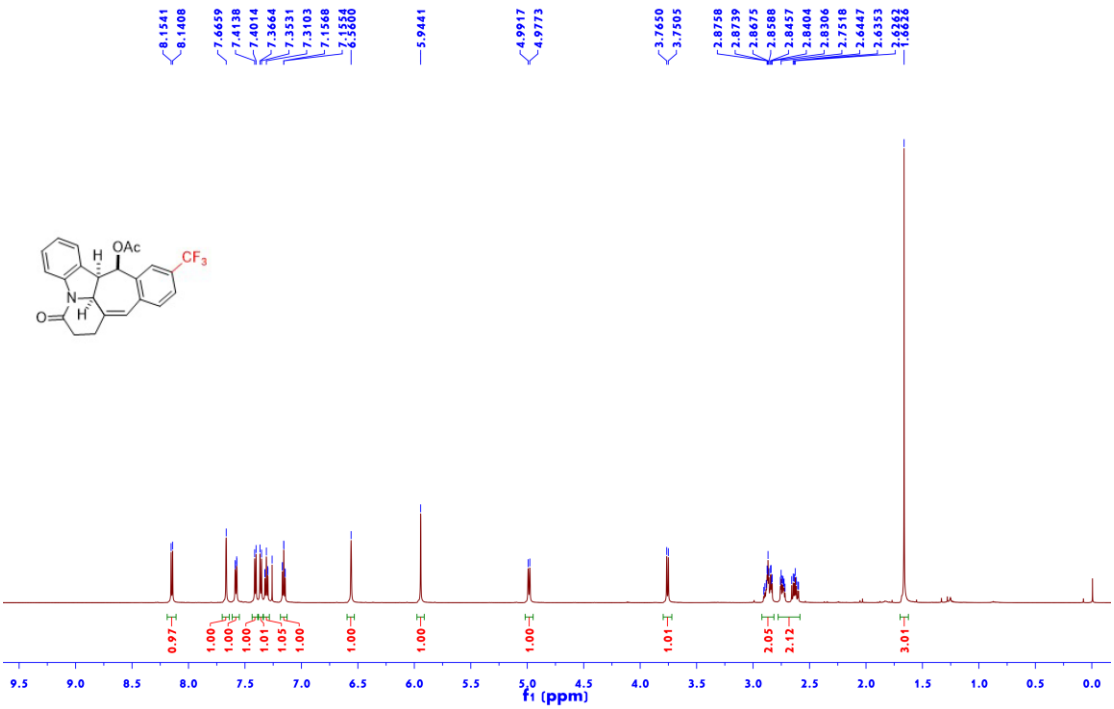


Figure S242 ^{13}C NMR (150 MHz, $CDCl_3$) of **7x**

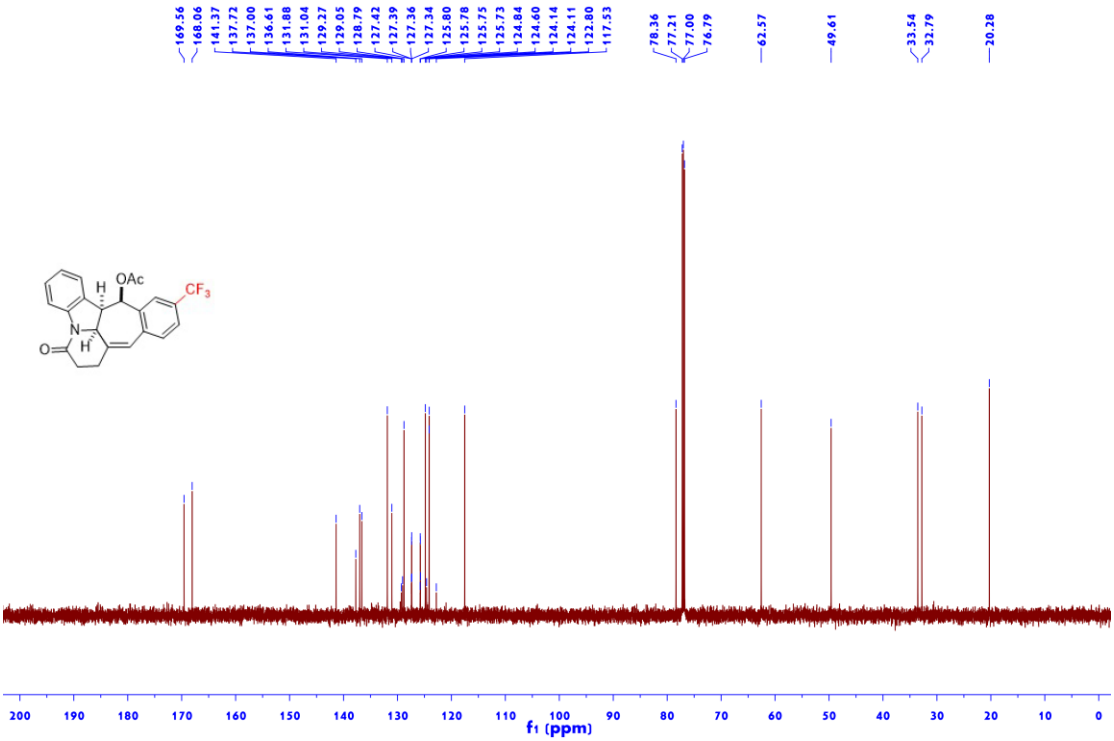


Figure S243 ^{19}F NMR (565 MHz, $CDCl_3$) of **7x**

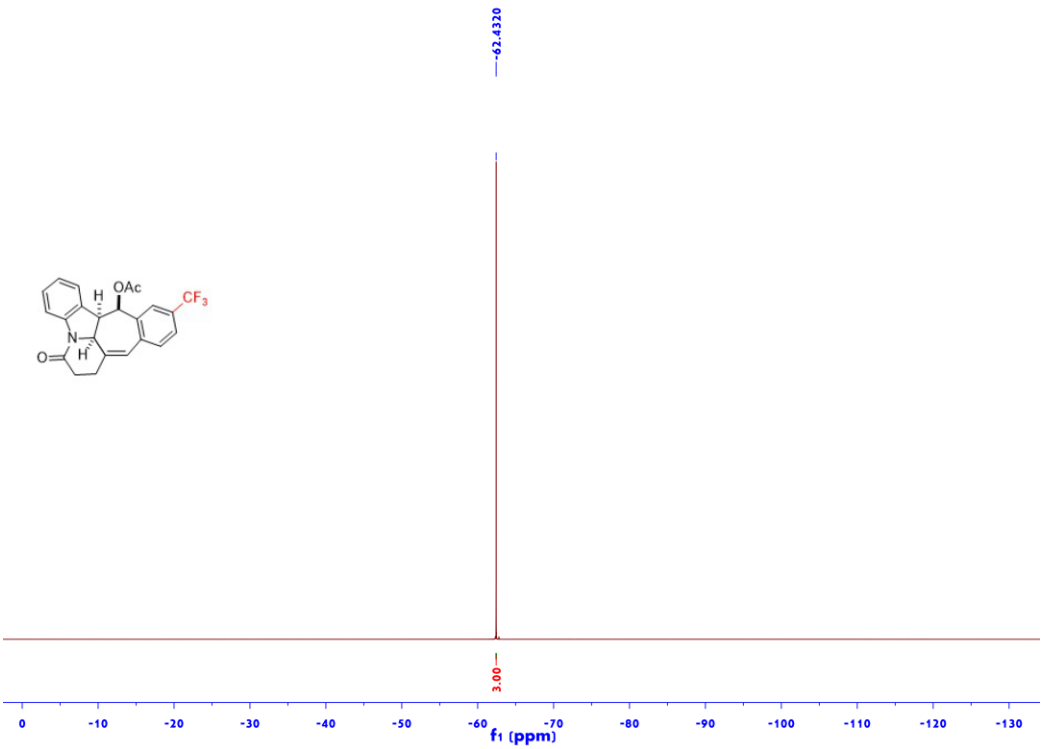


Figure S244 ^{1}H NMR (600 MHz, $CDCl_3$) of **7y**

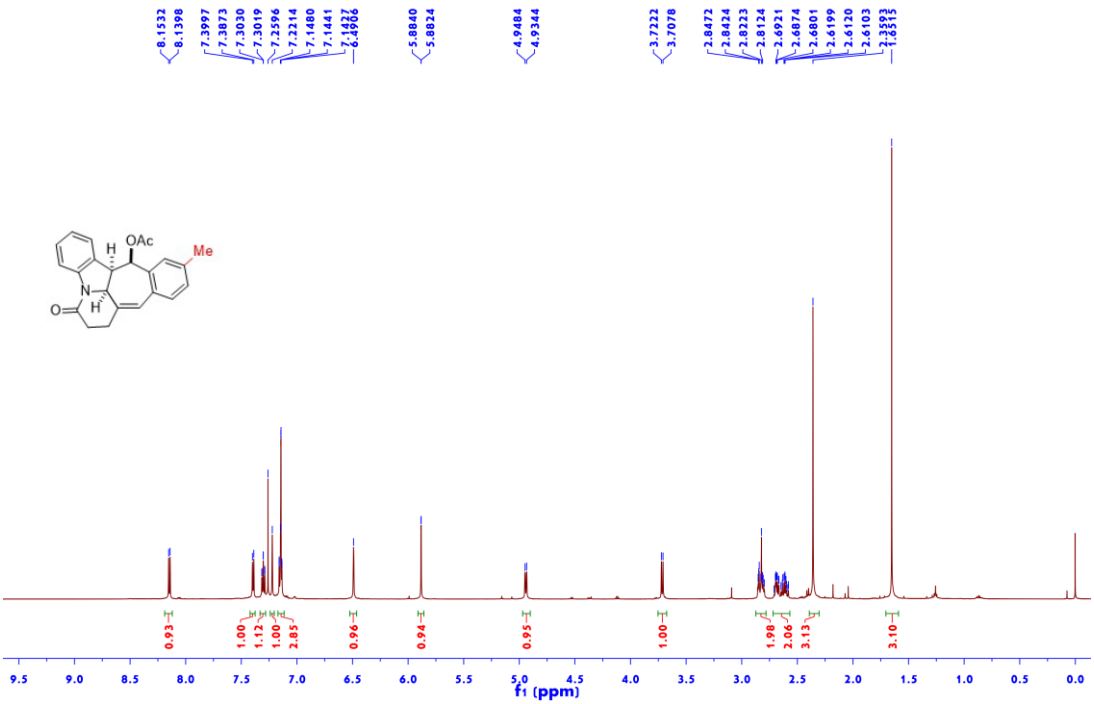


Figure S245 ^{13}C NMR (150 MHz, $CDCl_3$) of **7y**

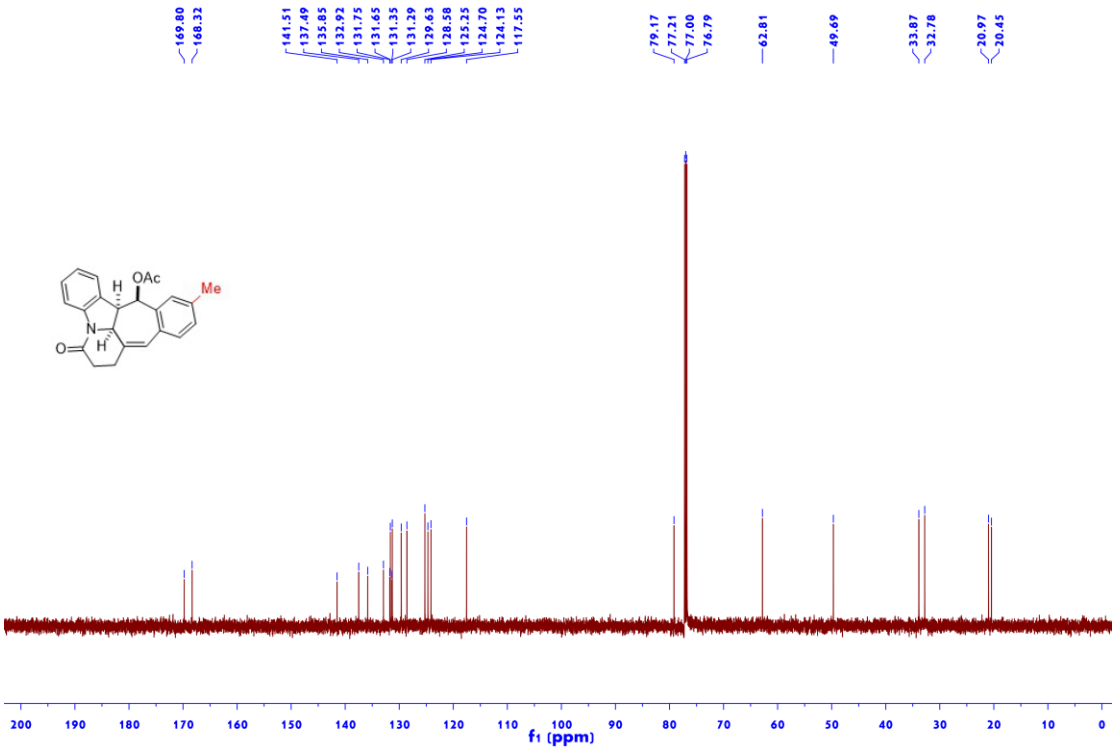


Figure S246 ^{1}H NMR (600 MHz, $CDCl_3$) of **7z**

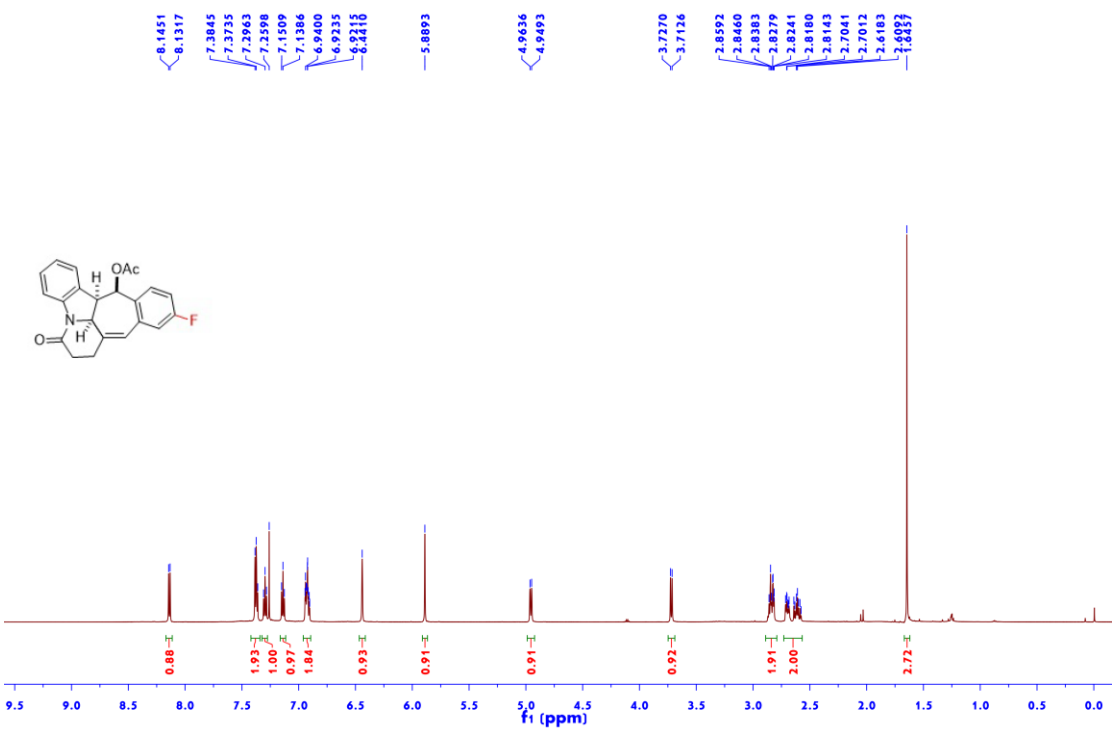


Figure S247 ^{13}C NMR (150 MHz, $CDCl_3$) of **7z**

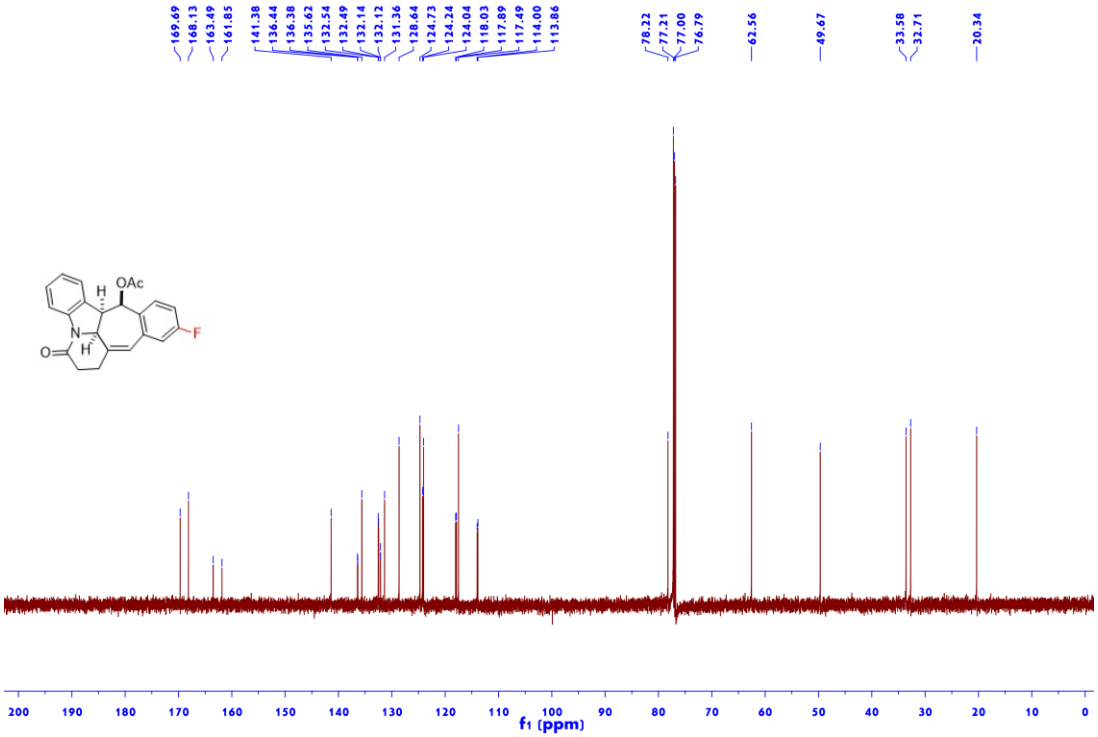


Figure S248 ^{19}F NMR (565 MHz, $CDCl_3$) of **7z**

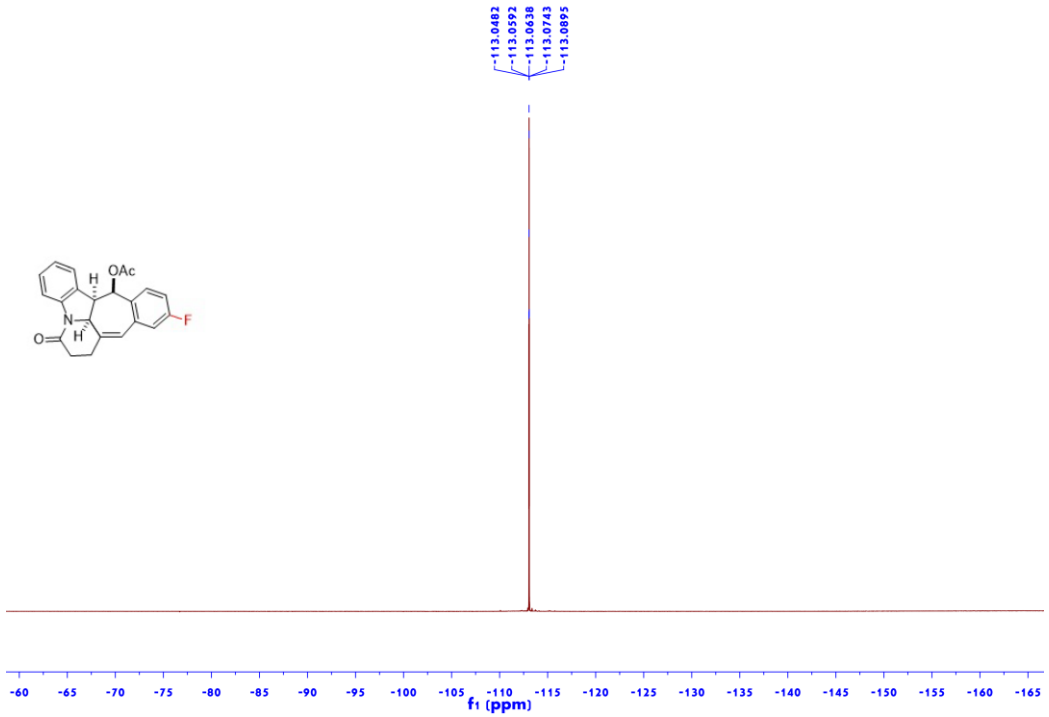


Figure S249 ^{1}H NMR (600 MHz, $CDCl_3$) of **7aa**

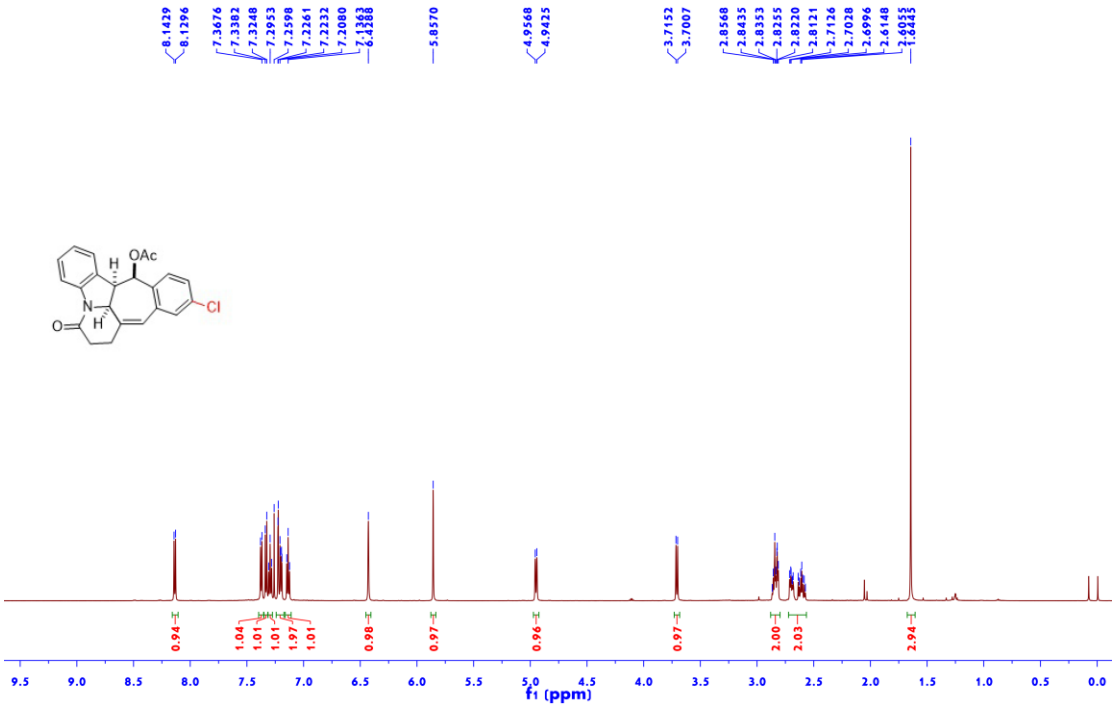


Figure S250 ^{13}C NMR (150 MHz, $CDCl_3$) of **7aa**

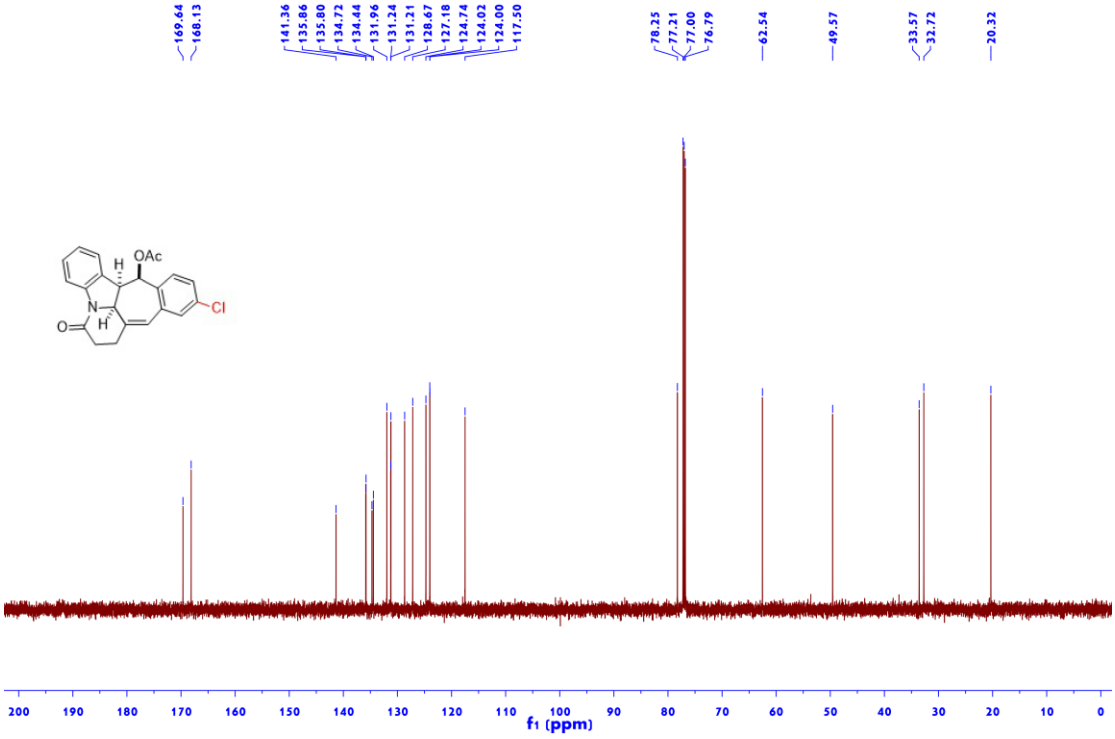


Figure S251 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ab**

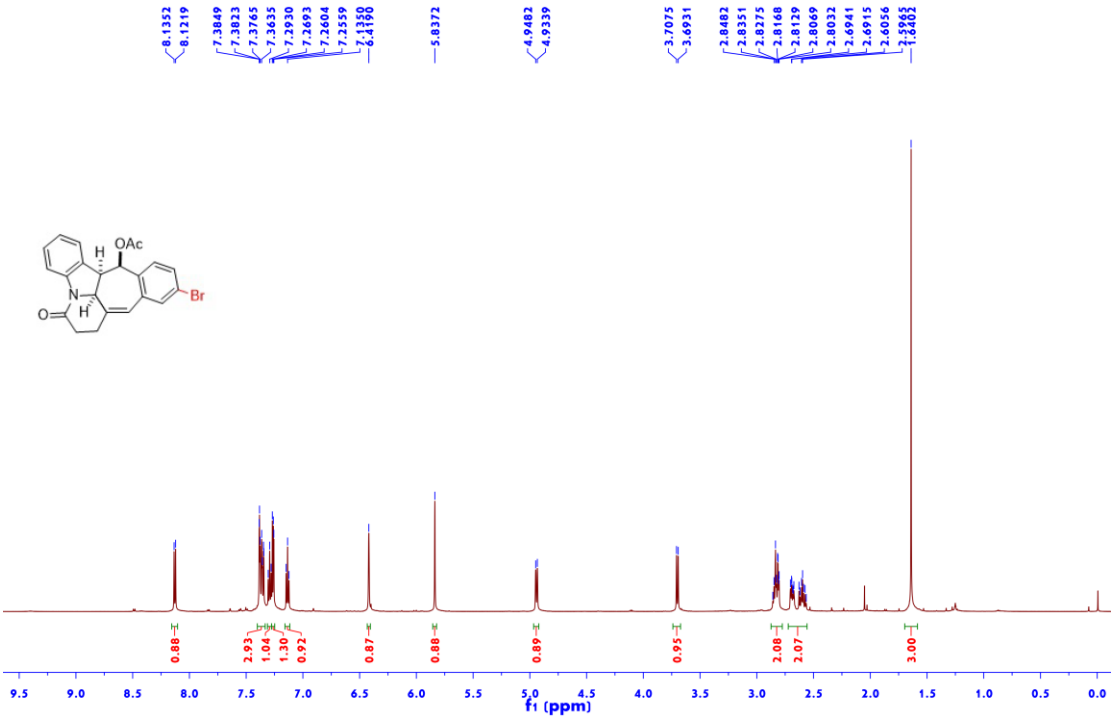


Figure S252 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ab**

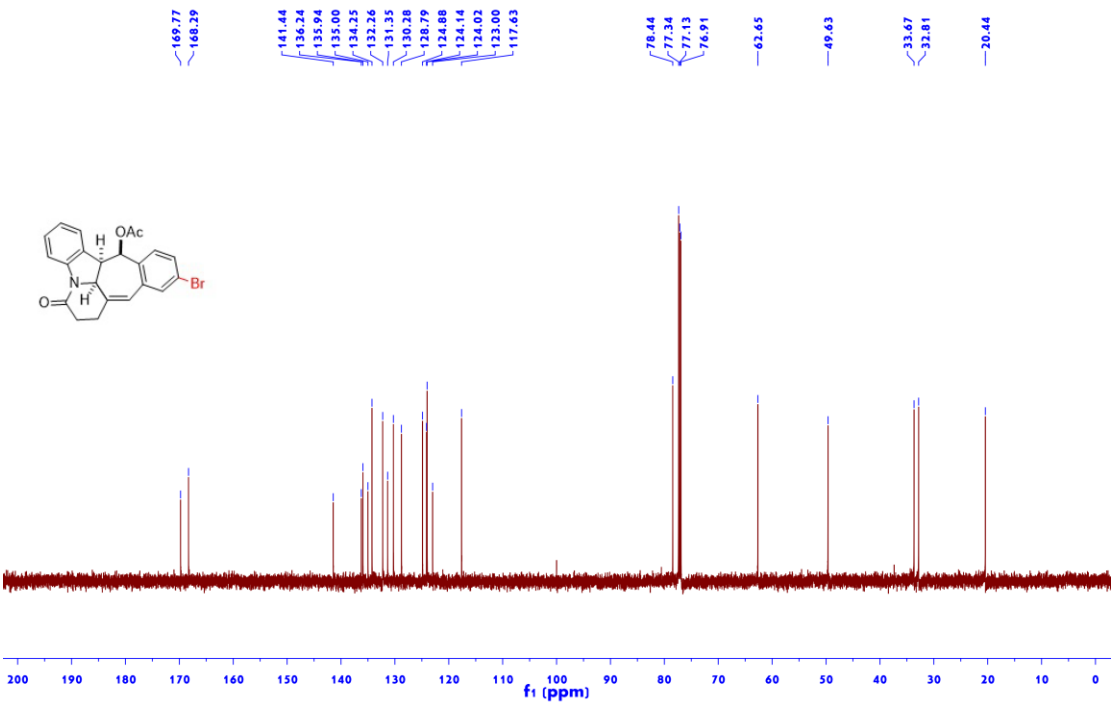


Figure S253 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ac**

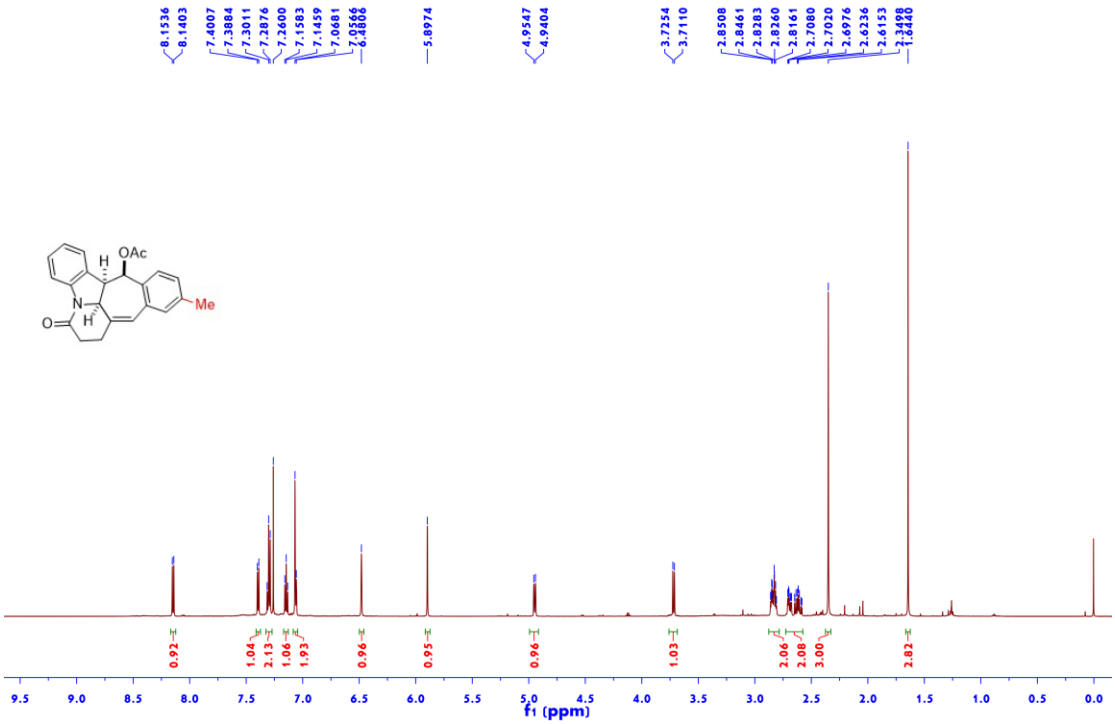


Figure S254 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ac**

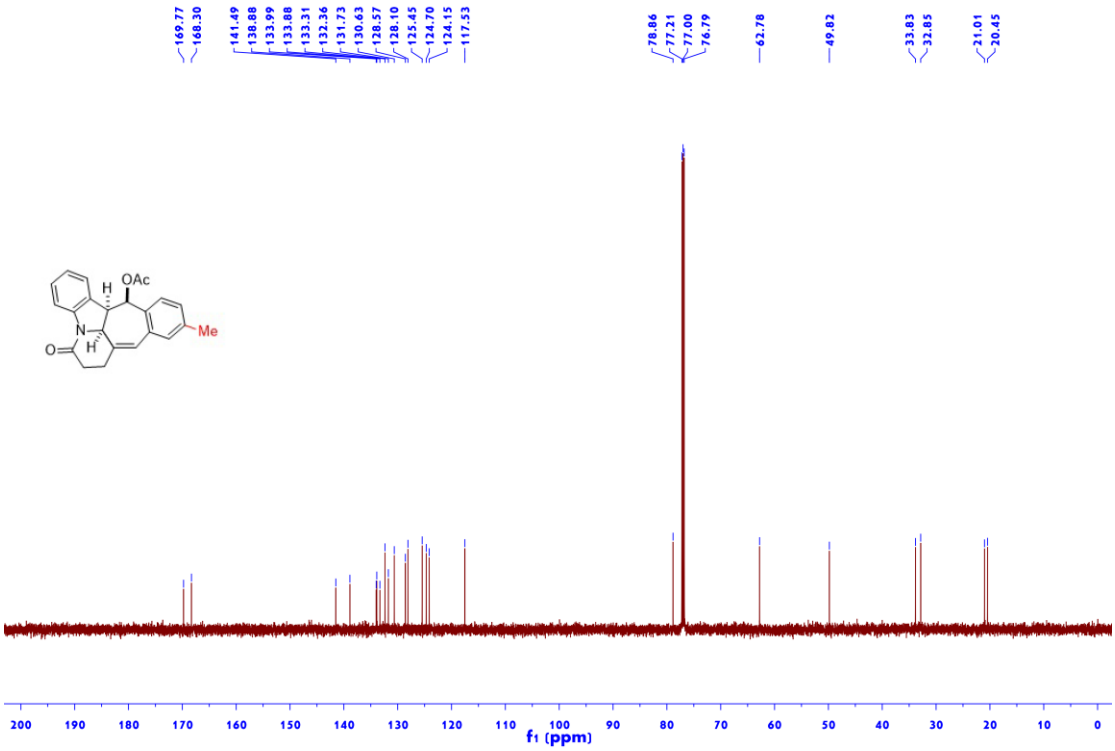


Figure S255 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ad**

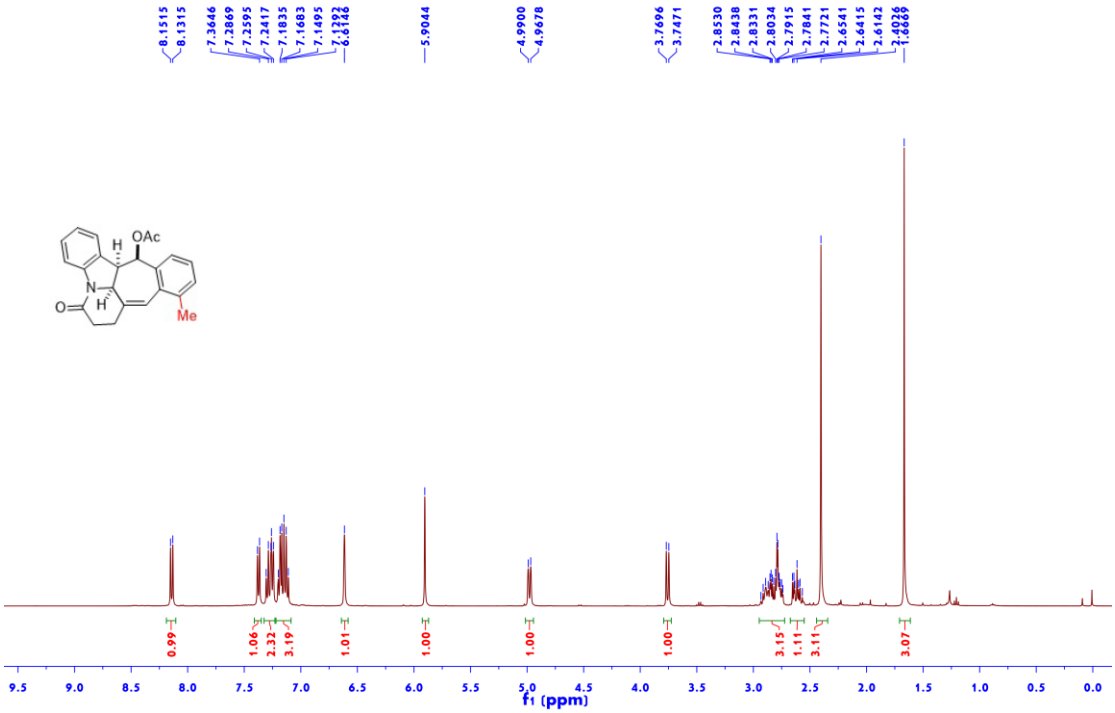


Figure S256 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ad**

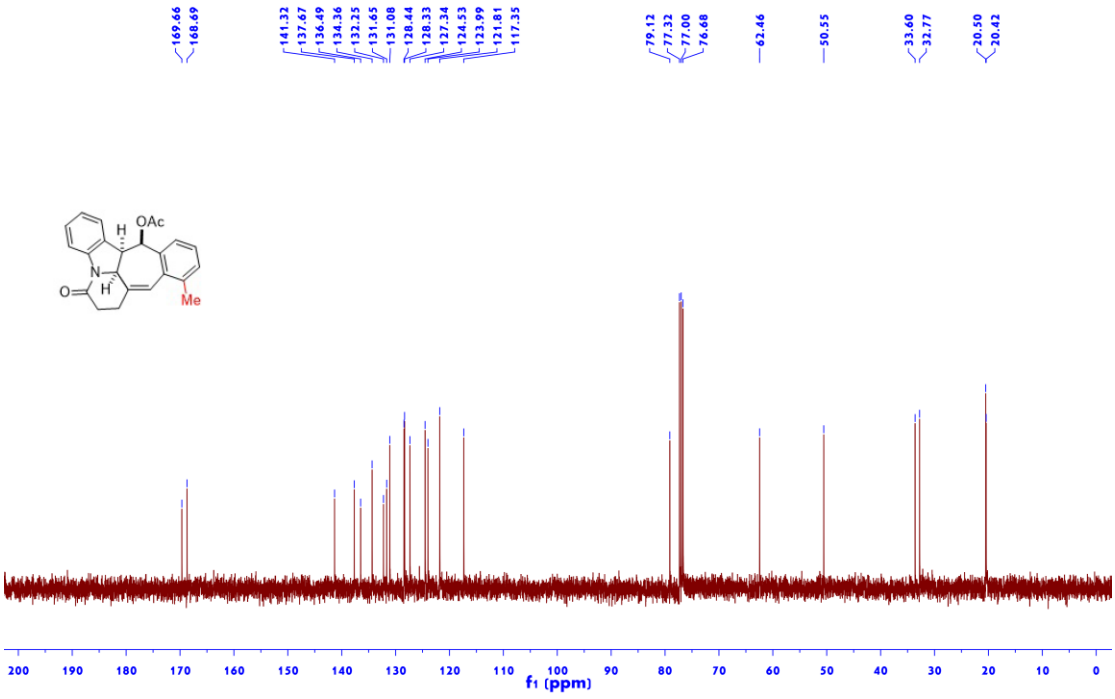


Figure S257 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ae**

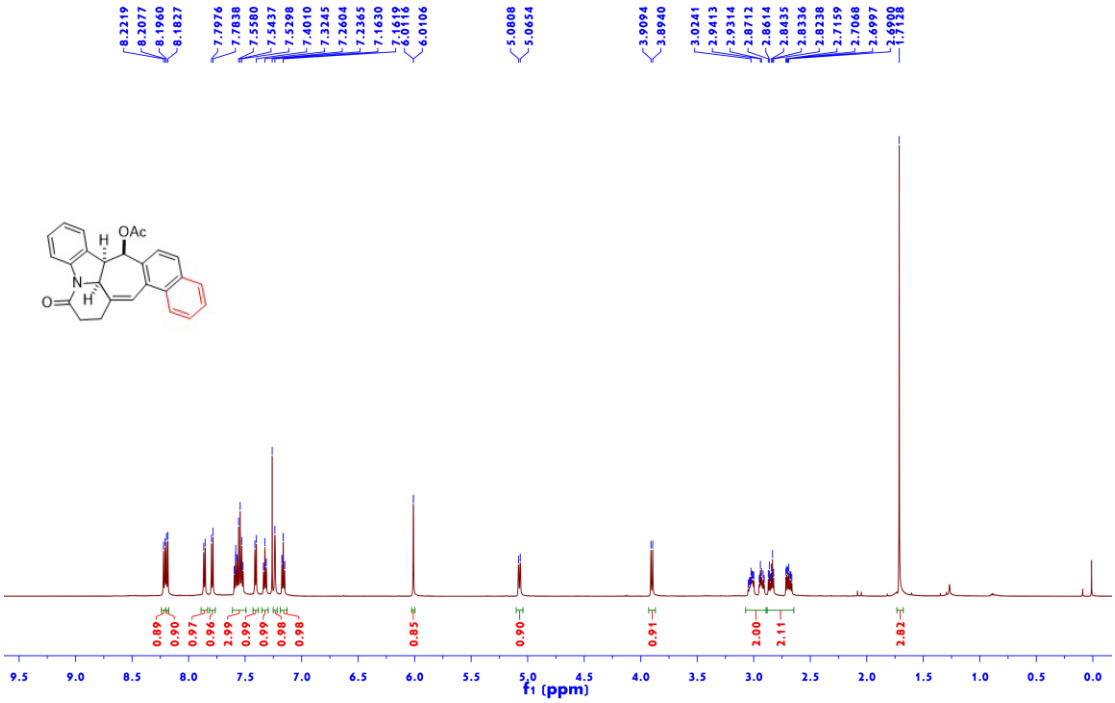


Figure S258 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ae**

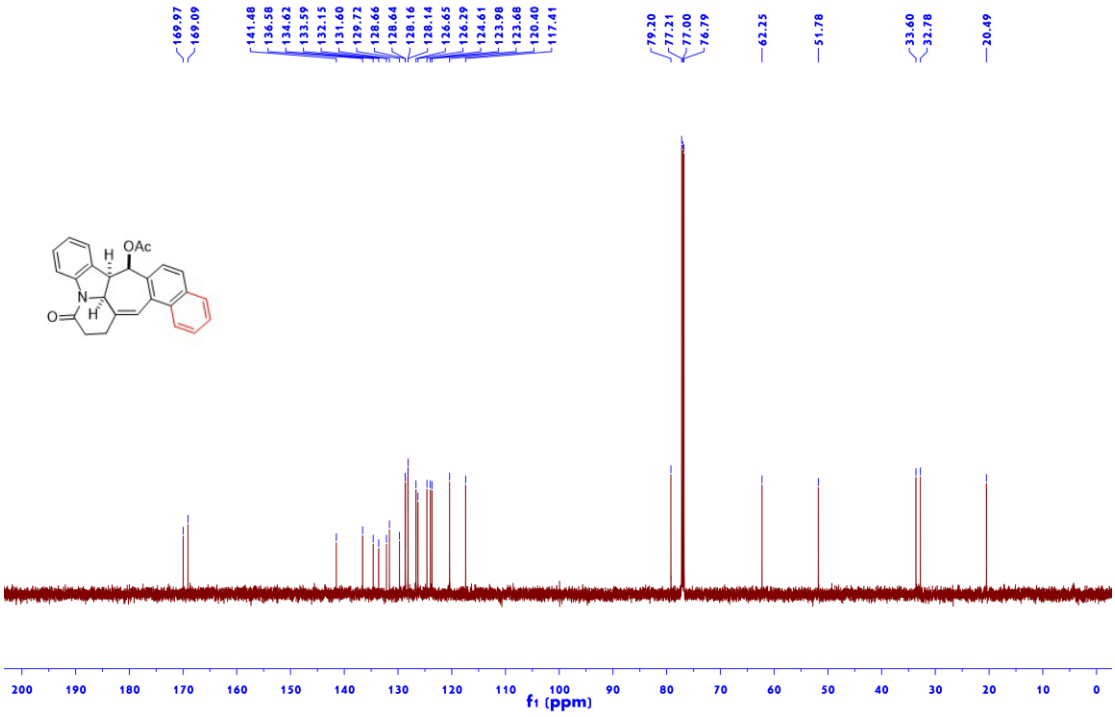


Figure S259 ^{1}H NMR (600 MHz, $CDCl_3$) of **7af**

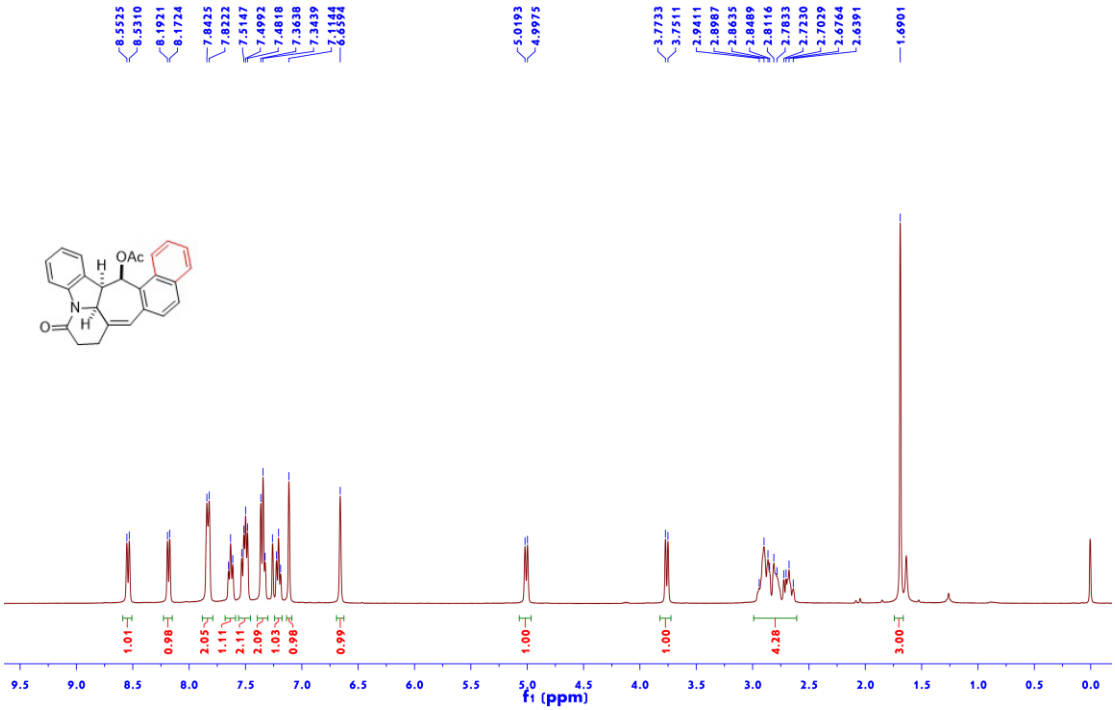


Figure S260 ^{13}C NMR (150 MHz, $CDCl_3$) of **7af**

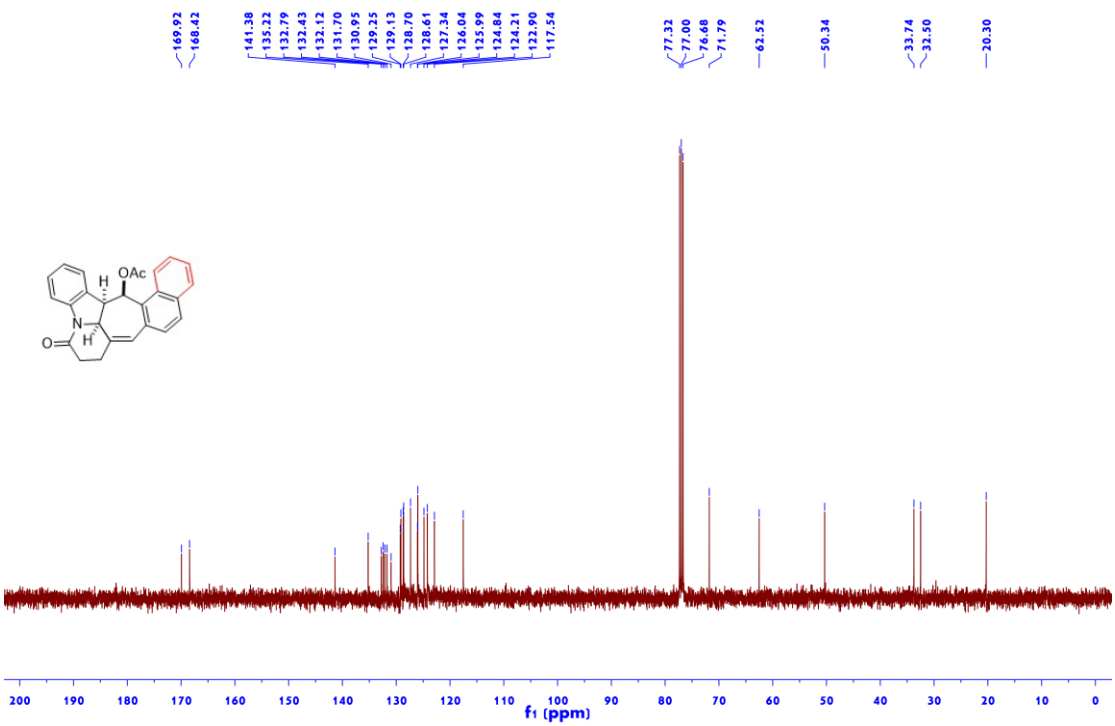


Figure S261 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ag**

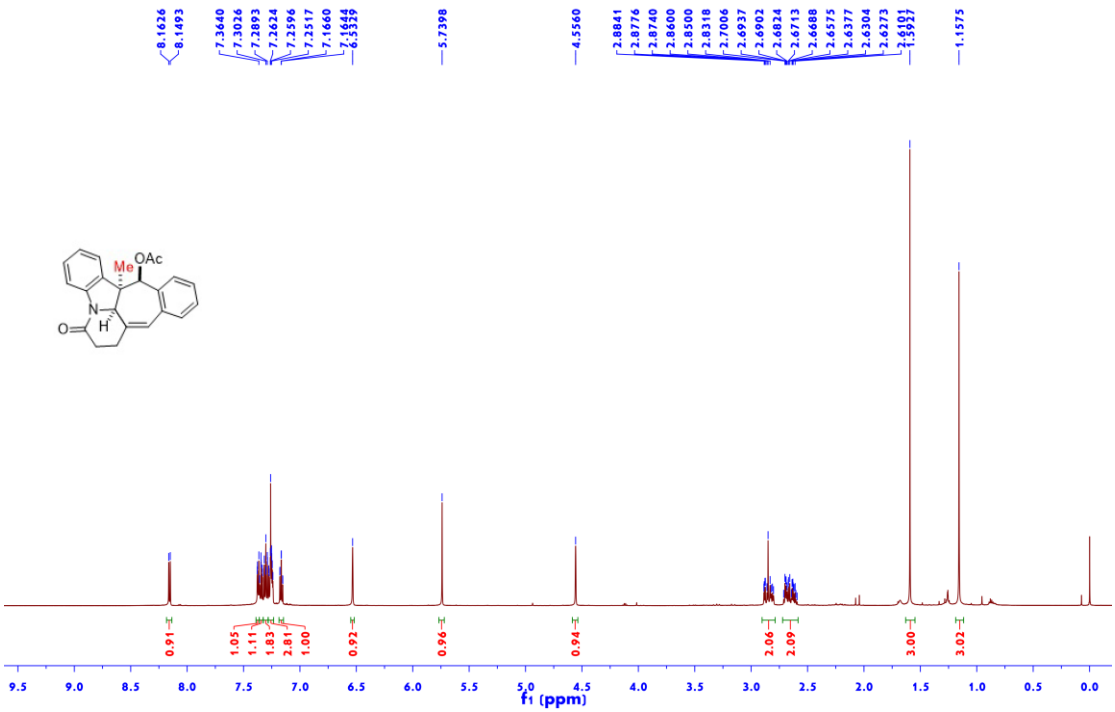


Figure S262 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ag**

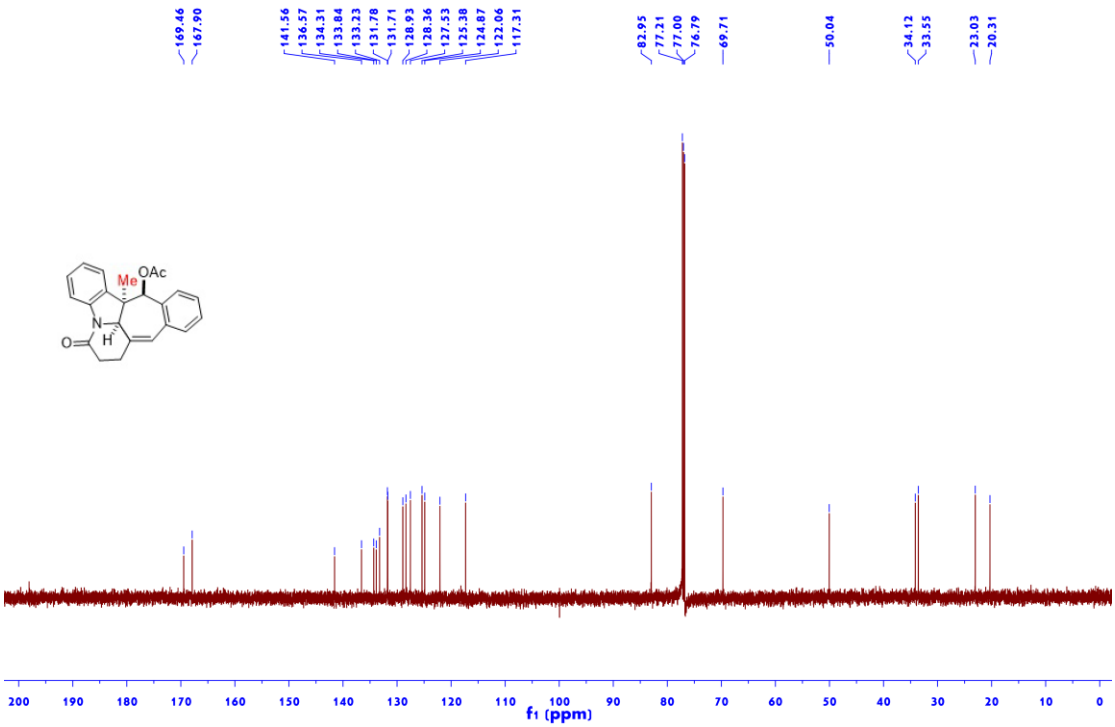


Figure S263 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ah**

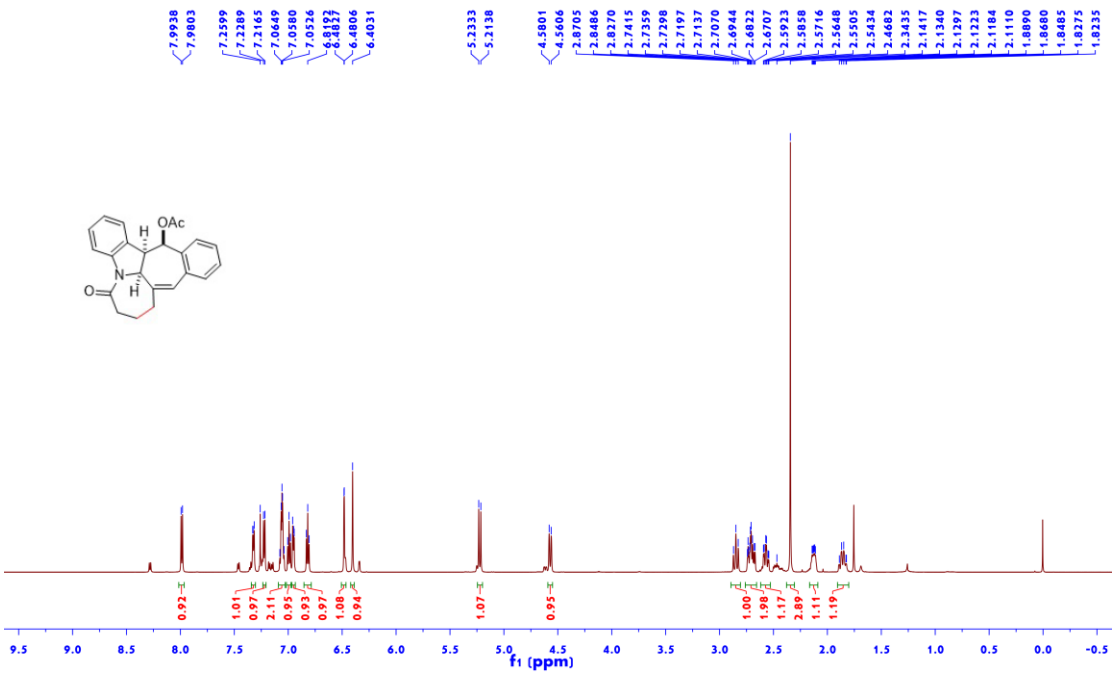


Figure S264 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ah**

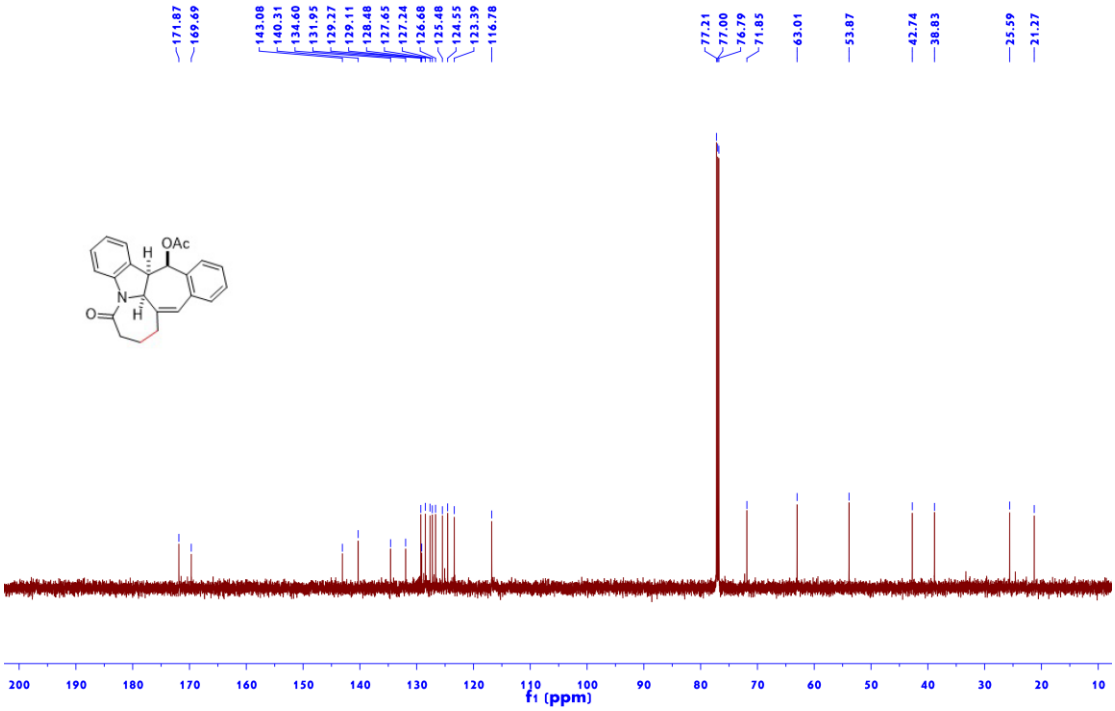


Figure S265 ^{1}H NMR (600 MHz, $CDCl_3$) of **7al**

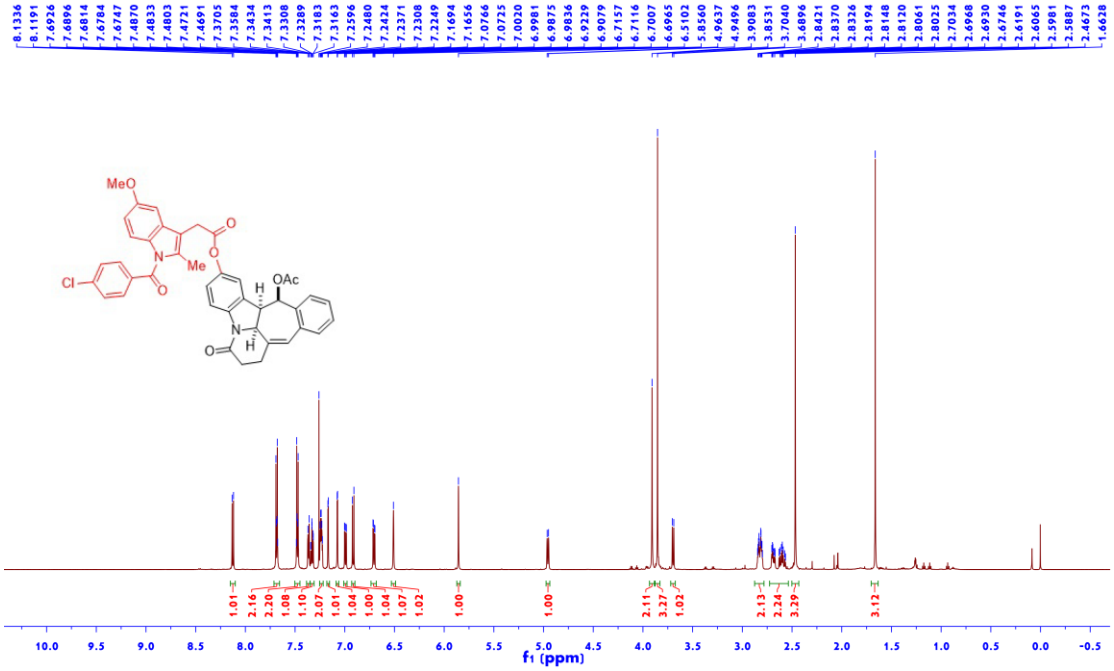


Figure S266 ^{13}C NMR (150 MHz, $CDCl_3$) of **7al**

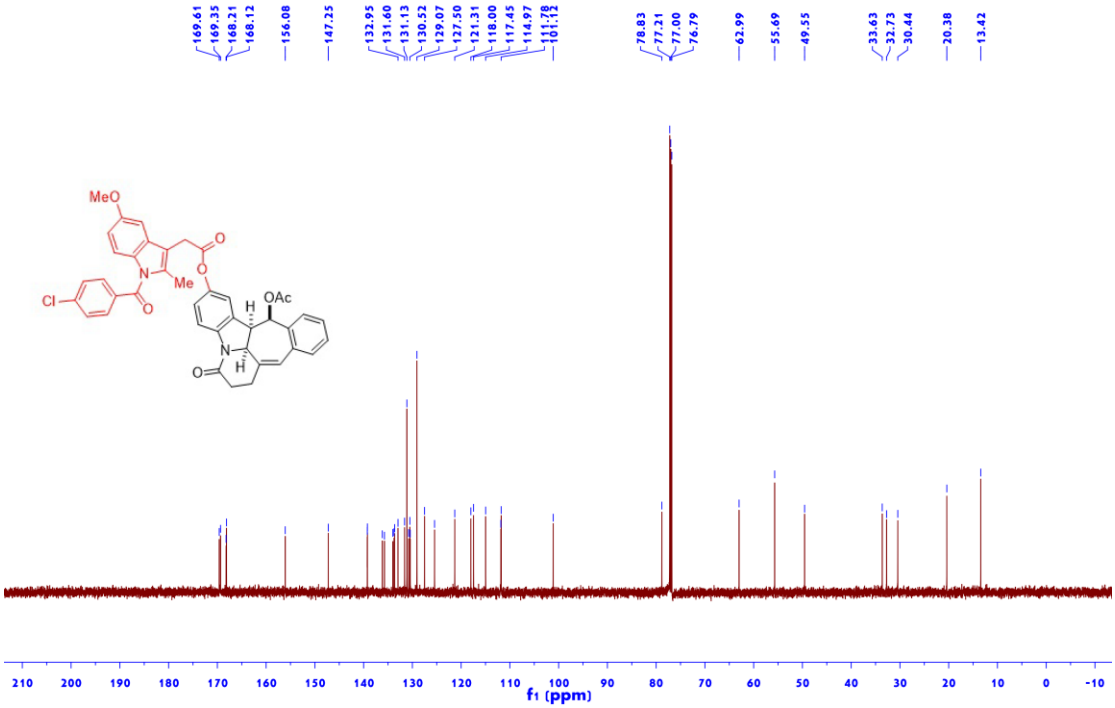


Figure S267 ^{1}H NMR (600 MHz, $CDCl_3$) of **7am**

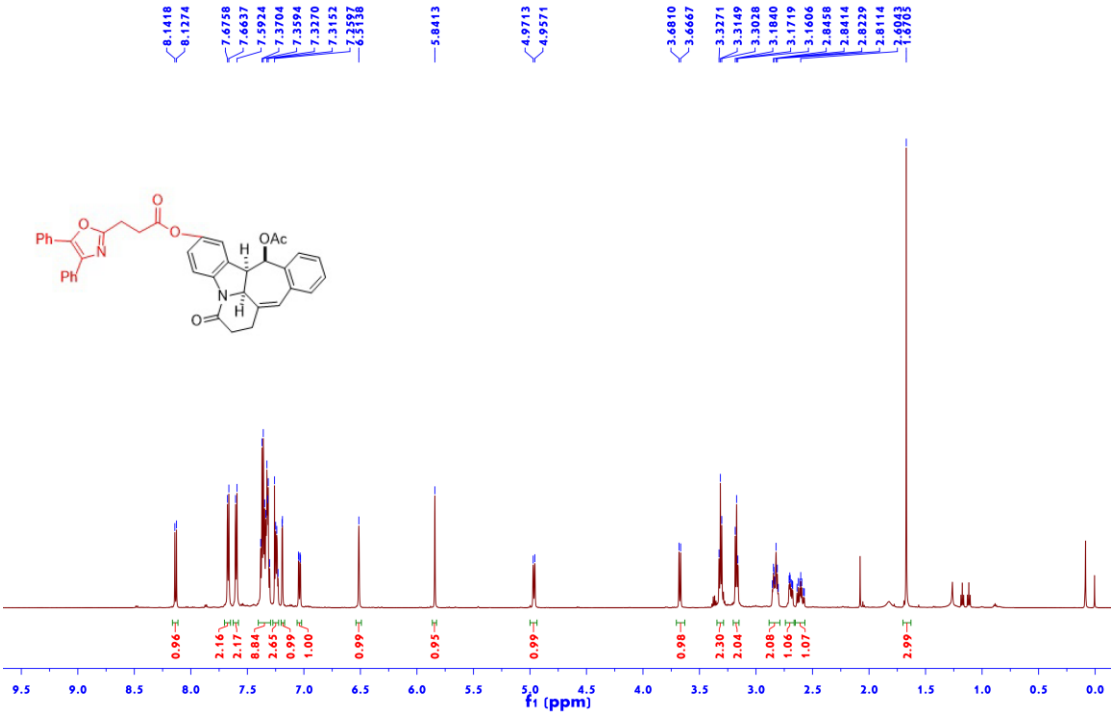


Figure S268 ^{13}C NMR (150 MHz, $CDCl_3$) of **7am**

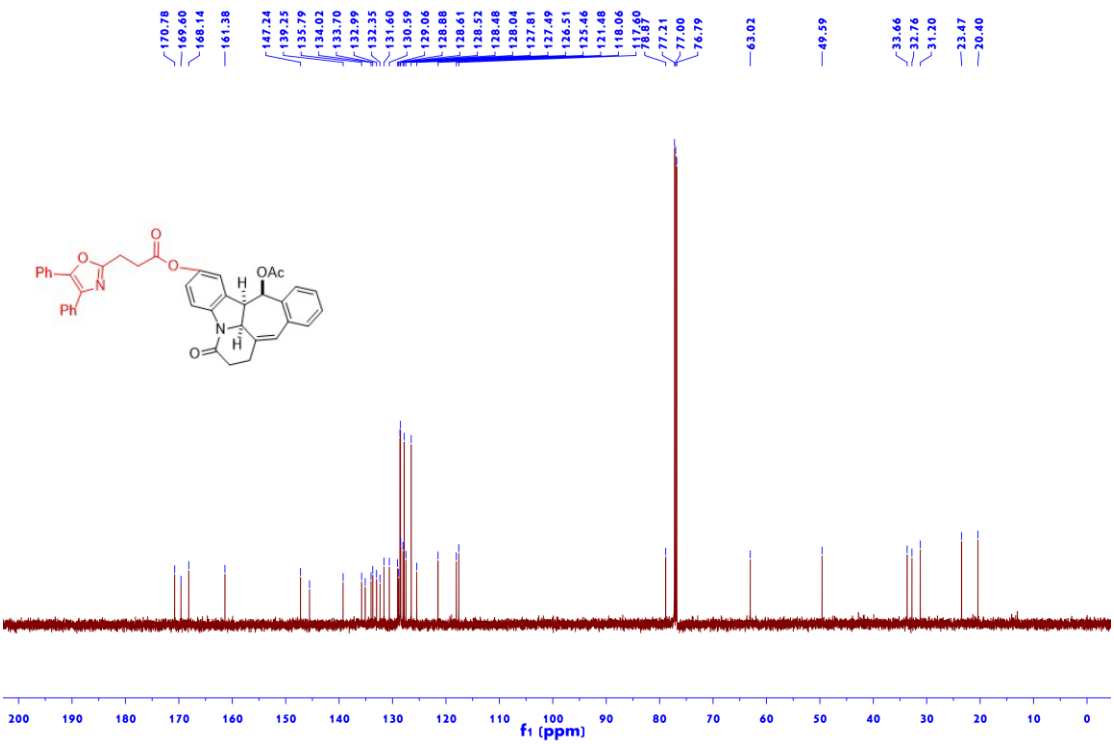


Figure S269 ^{1}H NMR (600 MHz, $CDCl_3$) of **7an**

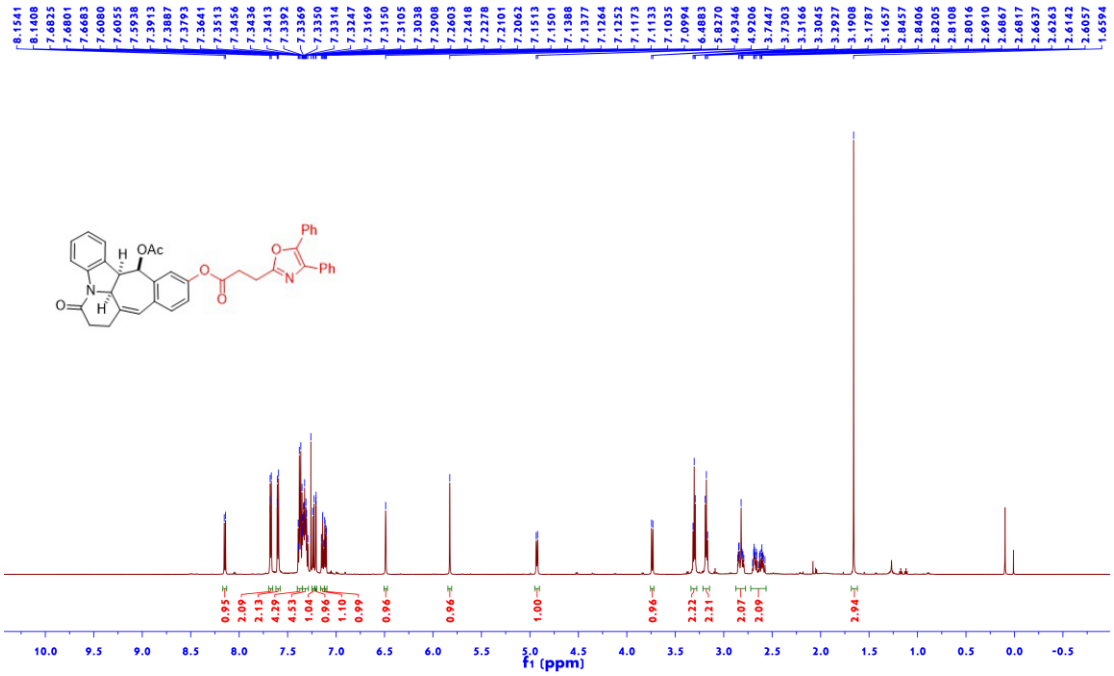


Figure S270 ^{13}C NMR (150 MHz, $CDCl_3$) of **7an**

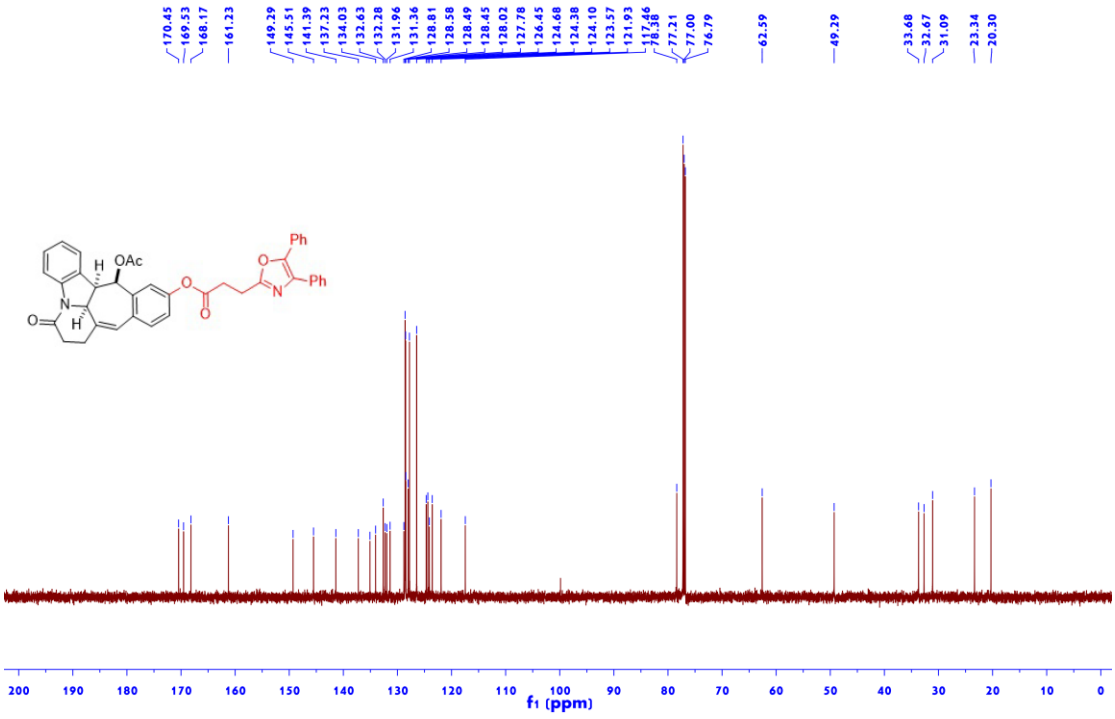


Figure S271 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ao**

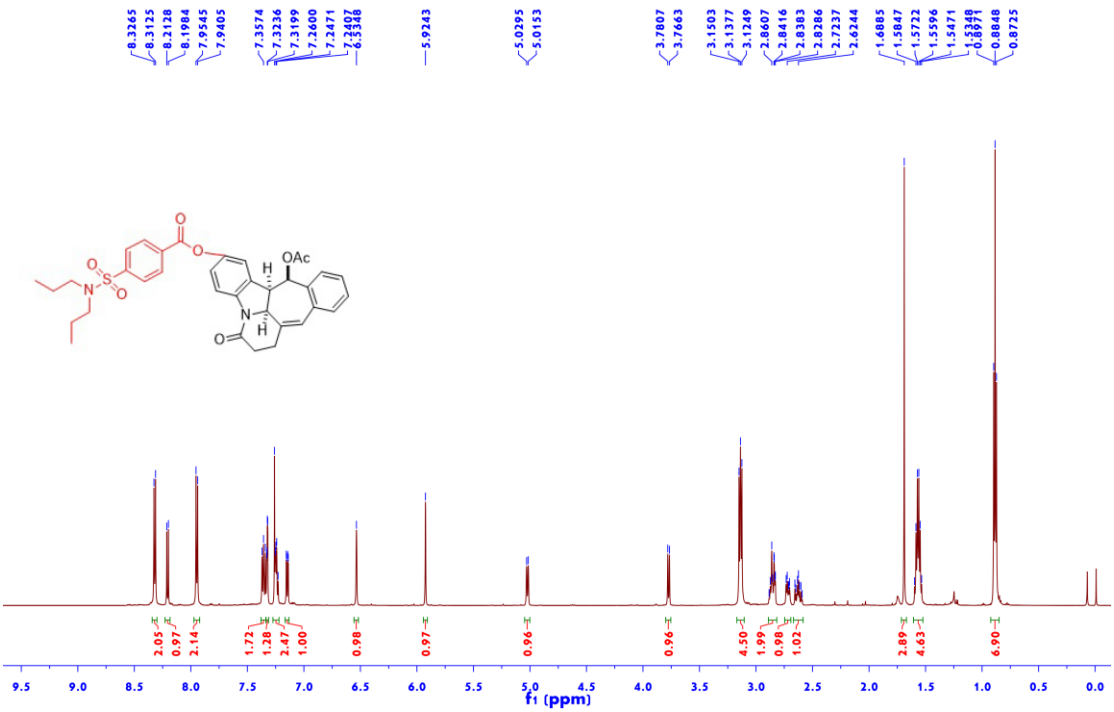


Figure S272 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ao**

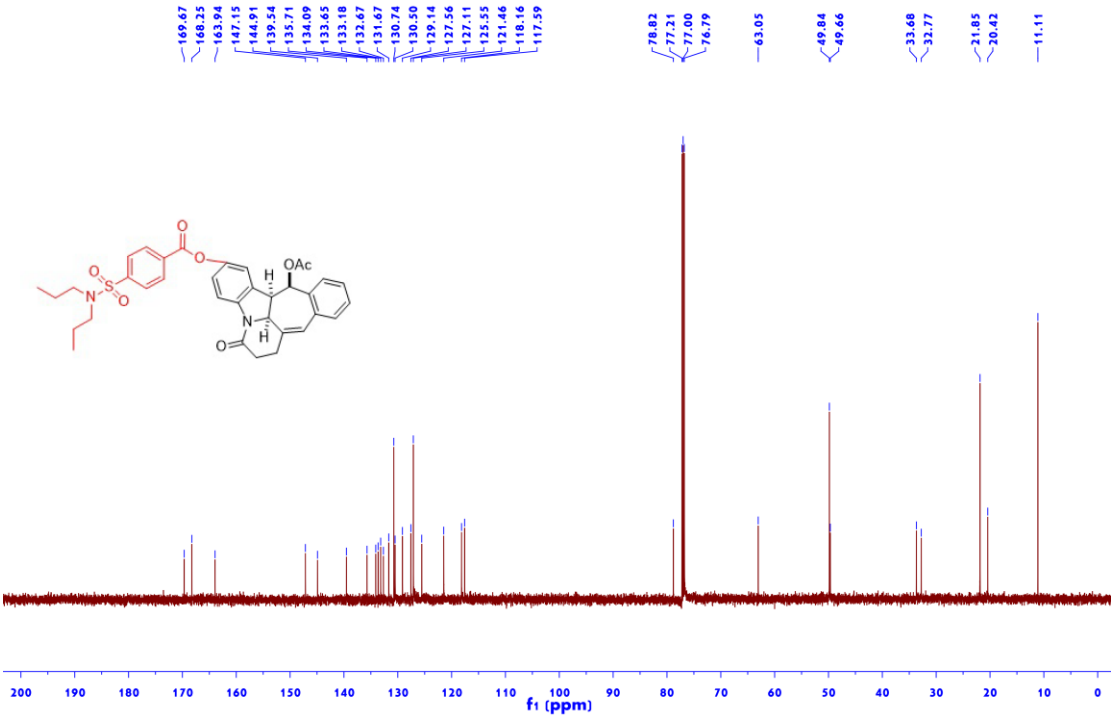


Figure S273 ^{1}H NMR (600 MHz, $CDCl_3$) of **7ap**

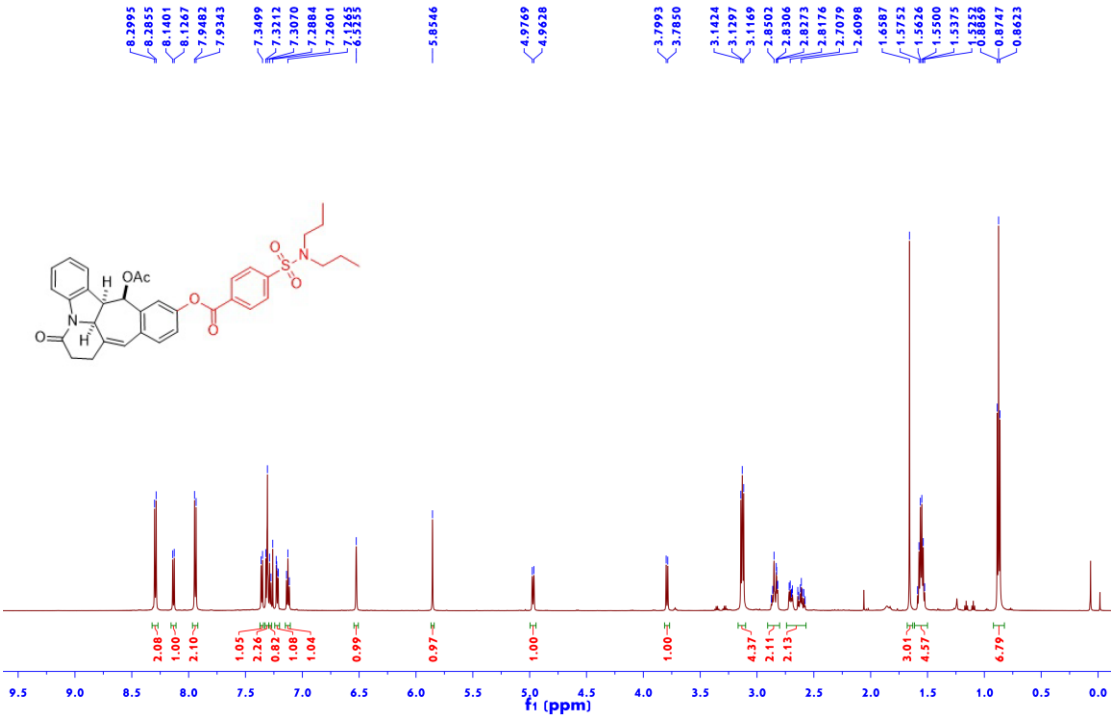


Figure S274 ^{13}C NMR (150 MHz, $CDCl_3$) of **7ap**

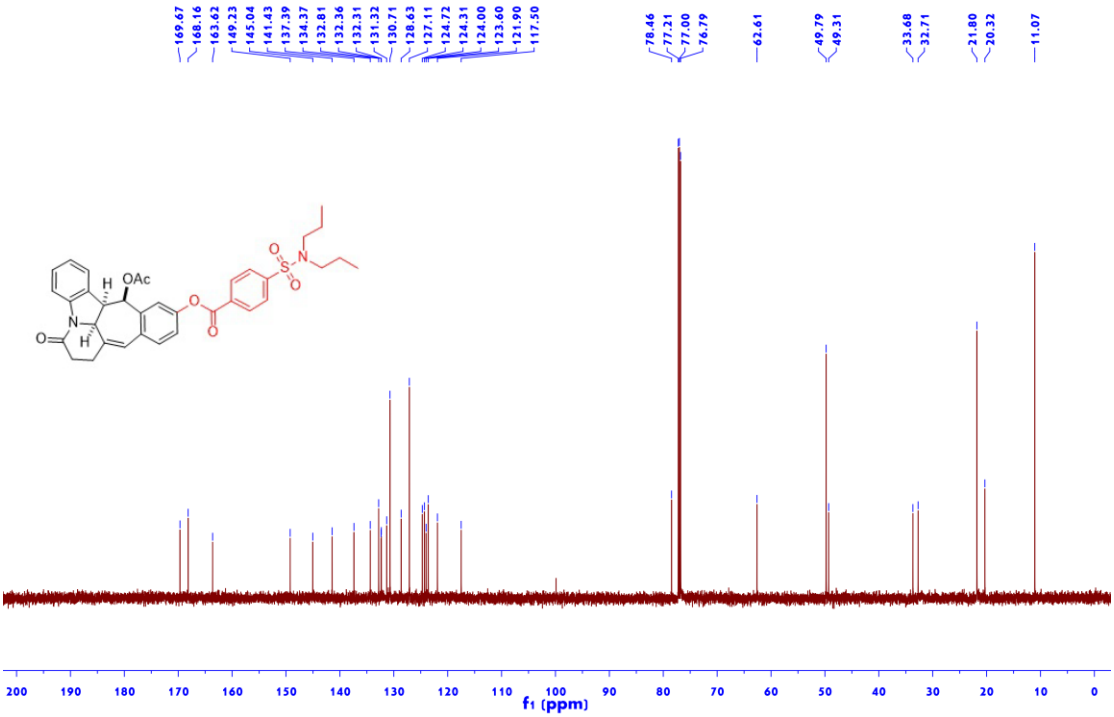


Figure S275 ^{1}H NMR (600 MHz, $CDCl_3$) of **7aq**

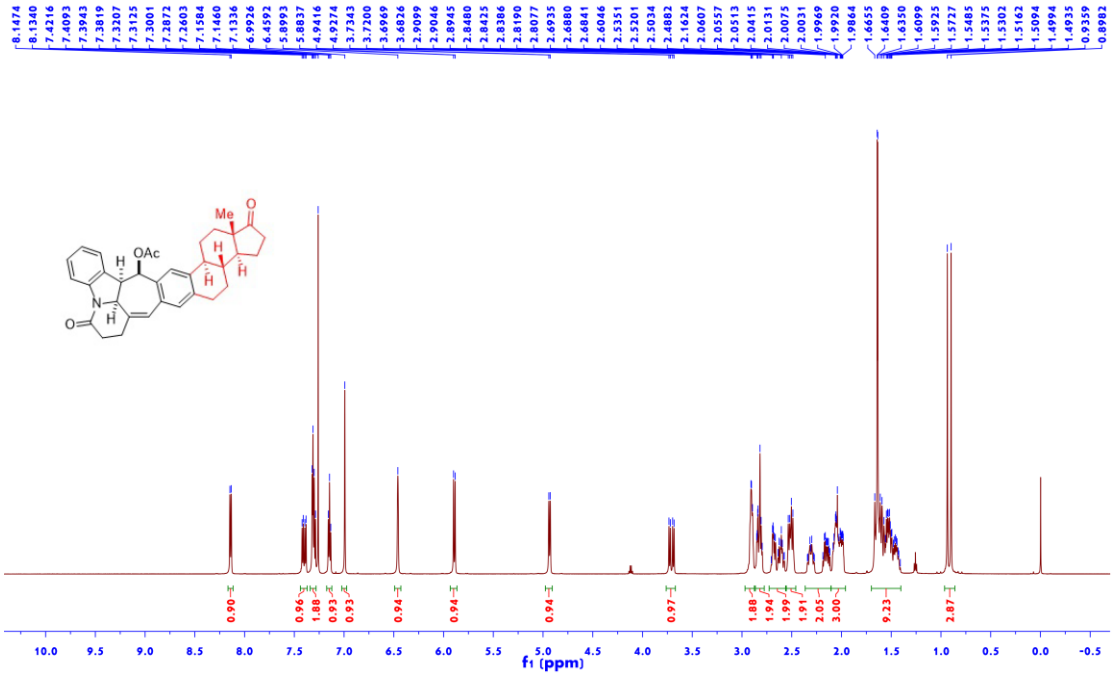


Figure S276 ^{13}C NMR (150 MHz, $CDCl_3$) of **7aq**

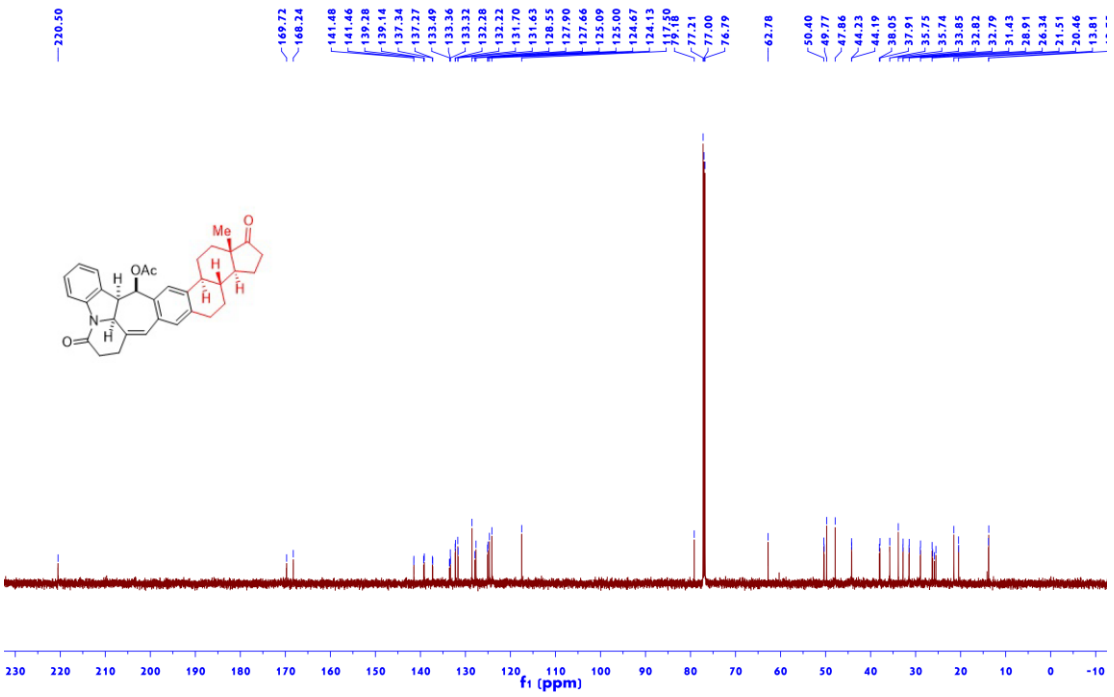


Figure S277 ^{1}H NMR (600 MHz, $CDCl_3$) of **8**

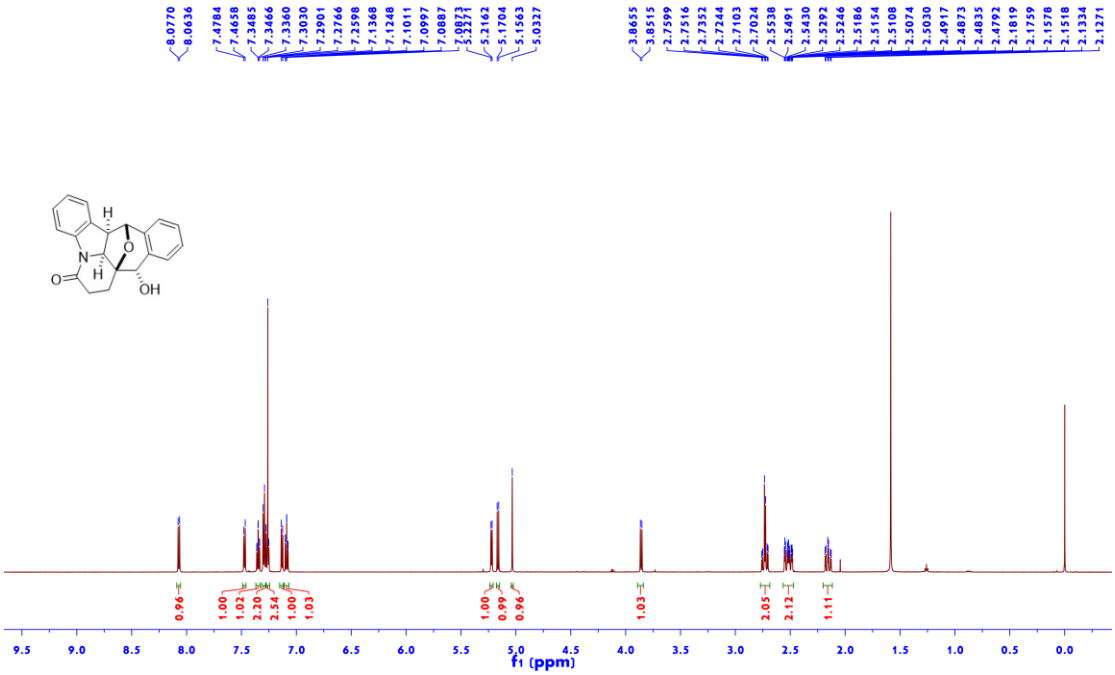


Figure S278 ^{13}C NMR (150 MHz, $CDCl_3$) of **8**

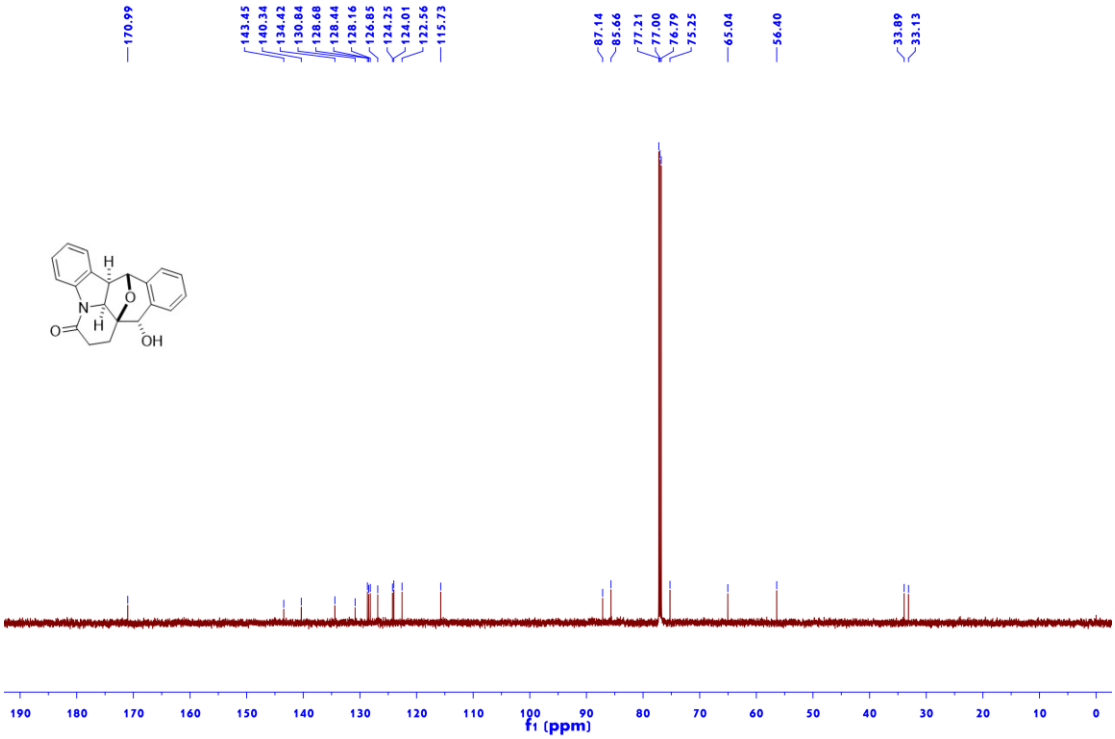


Figure S279 ^{1}H NMR (600 MHz, $CDCl_3$) of **9**

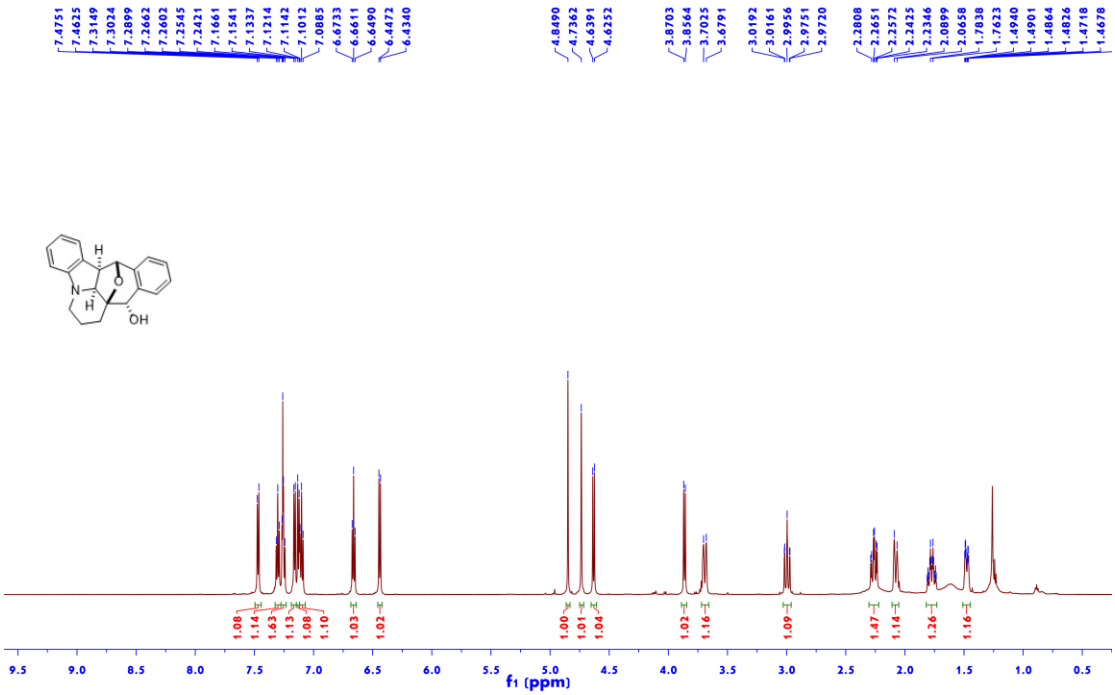


Figure S280 ^{13}C NMR (150 MHz, $CDCl_3$) of **9**

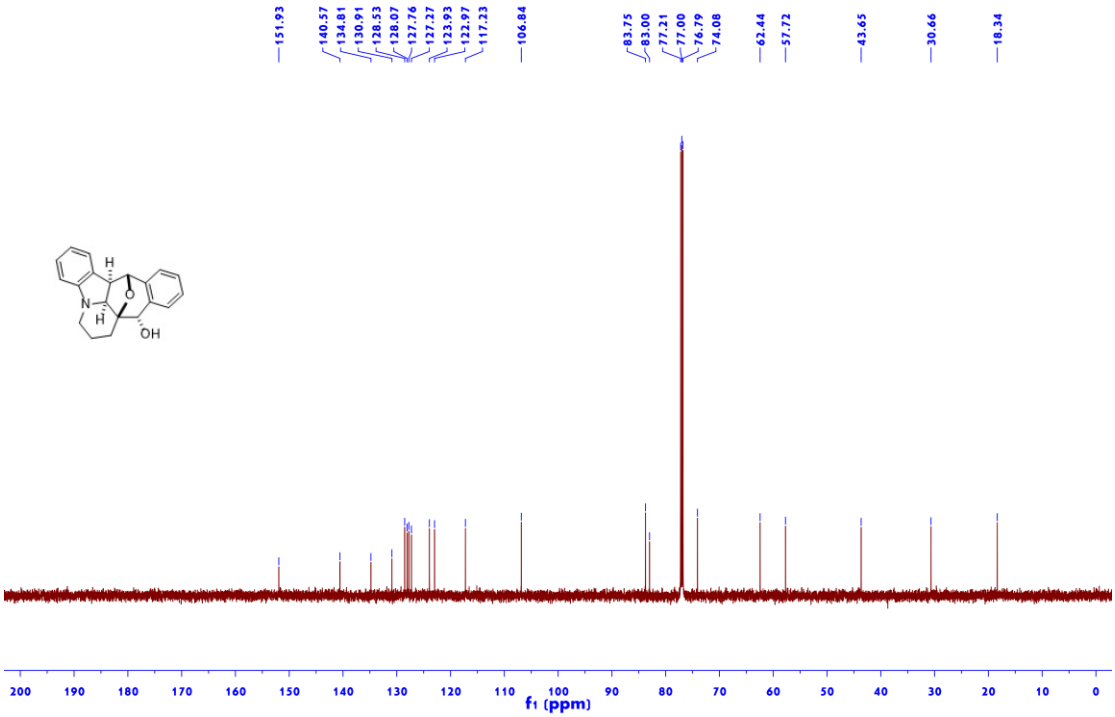


Figure S281 ^{1}H NMR (600 MHz, $CDCl_3$) of **10**

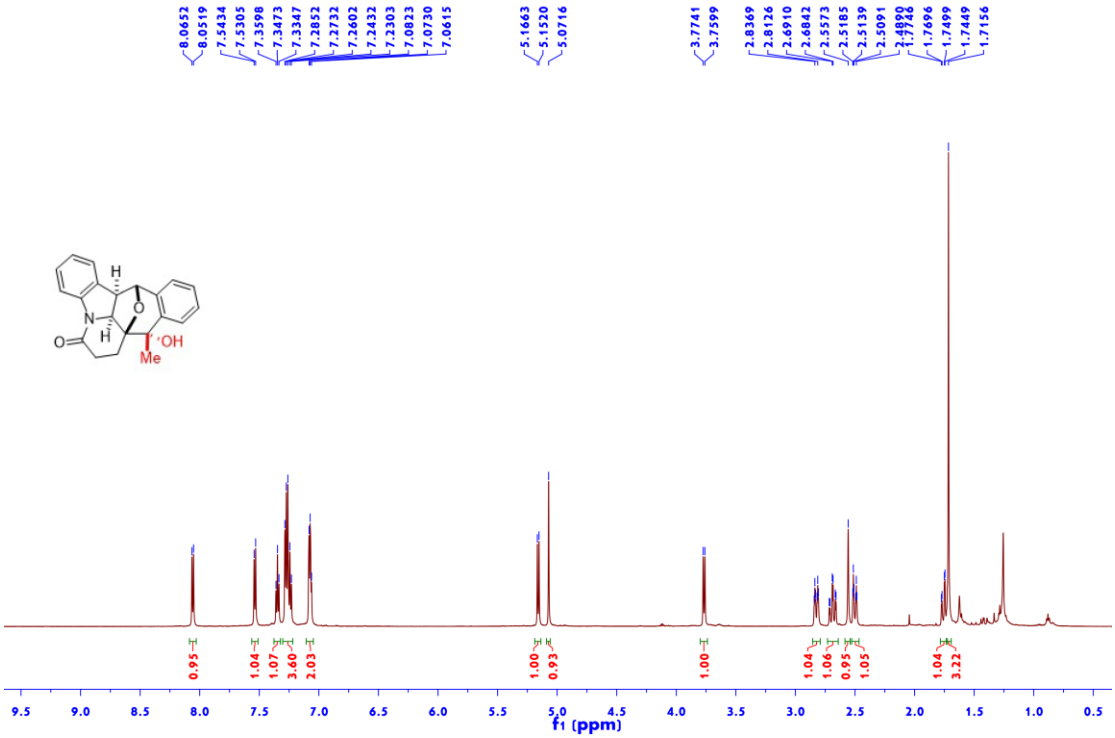


Figure S282 ^{13}C NMR (150 MHz, $CDCl_3$) of **10**

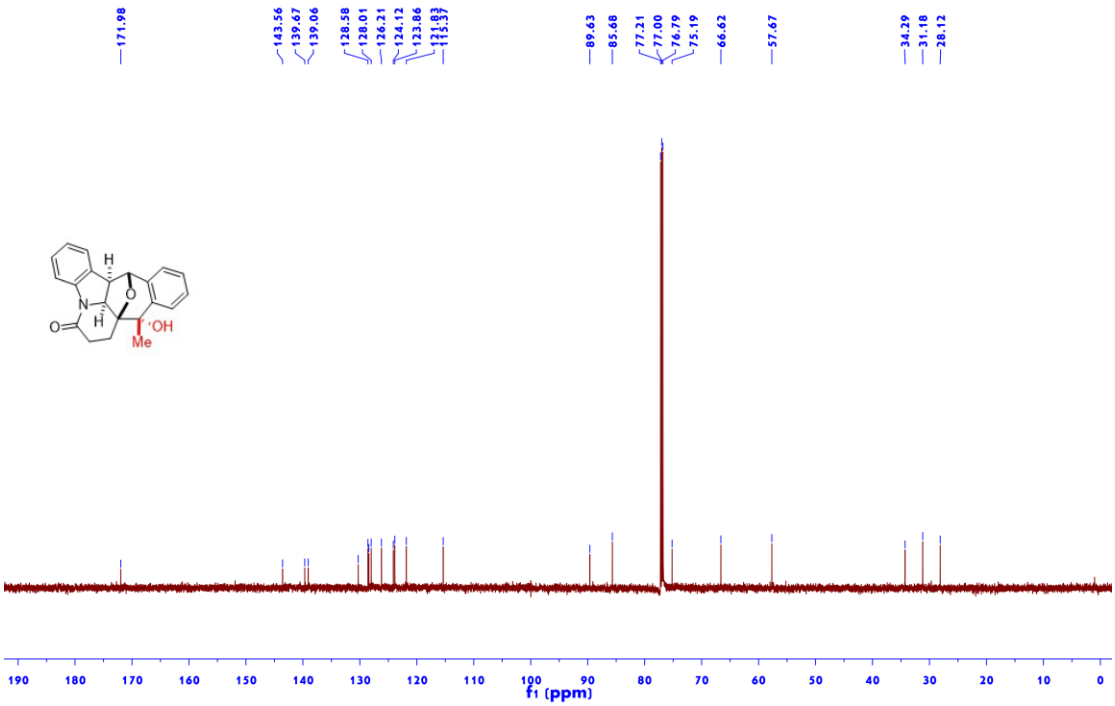


Figure S283 ^{1}H NMR (400 MHz, $CDCl_3$) of **11**

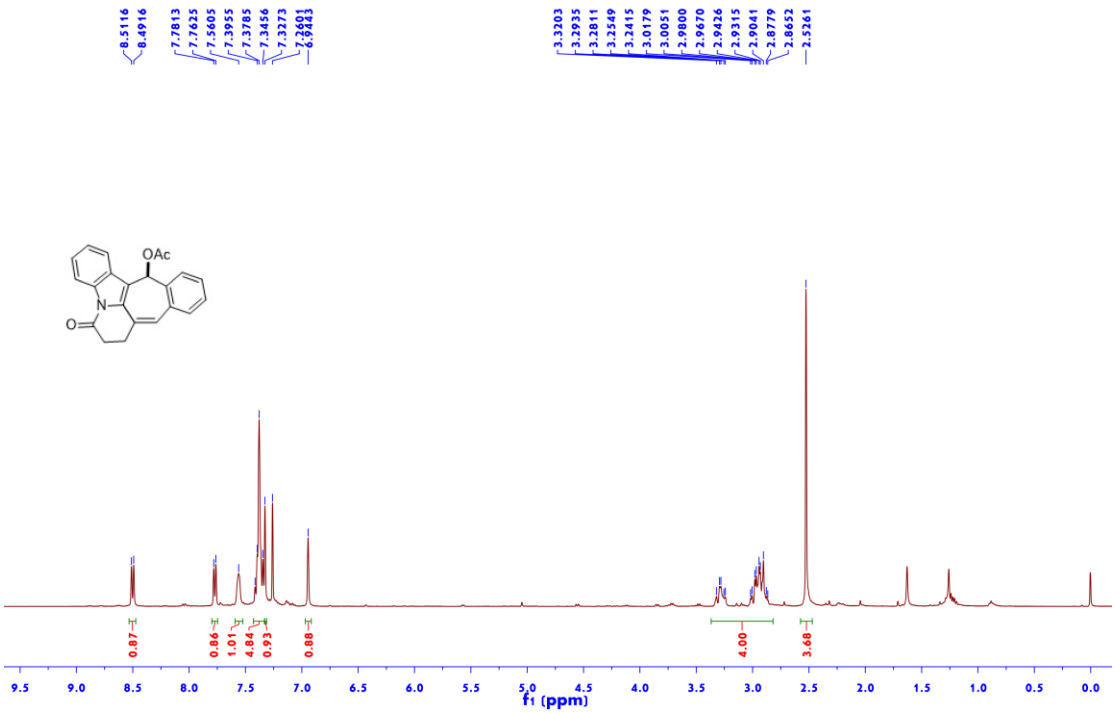


Figure S284 ^{13}C NMR (100 MHz, $CDCl_3$) of **11**

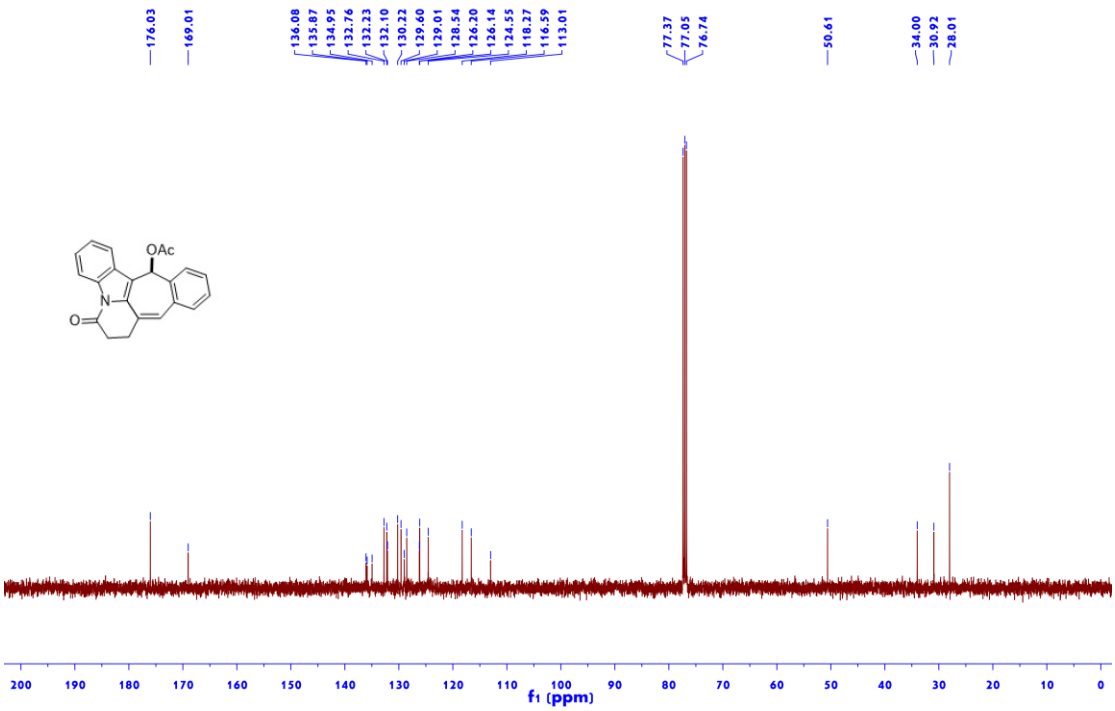


Figure S285 ^{1}H NMR (400 MHz, $CDCl_3$) of **12**

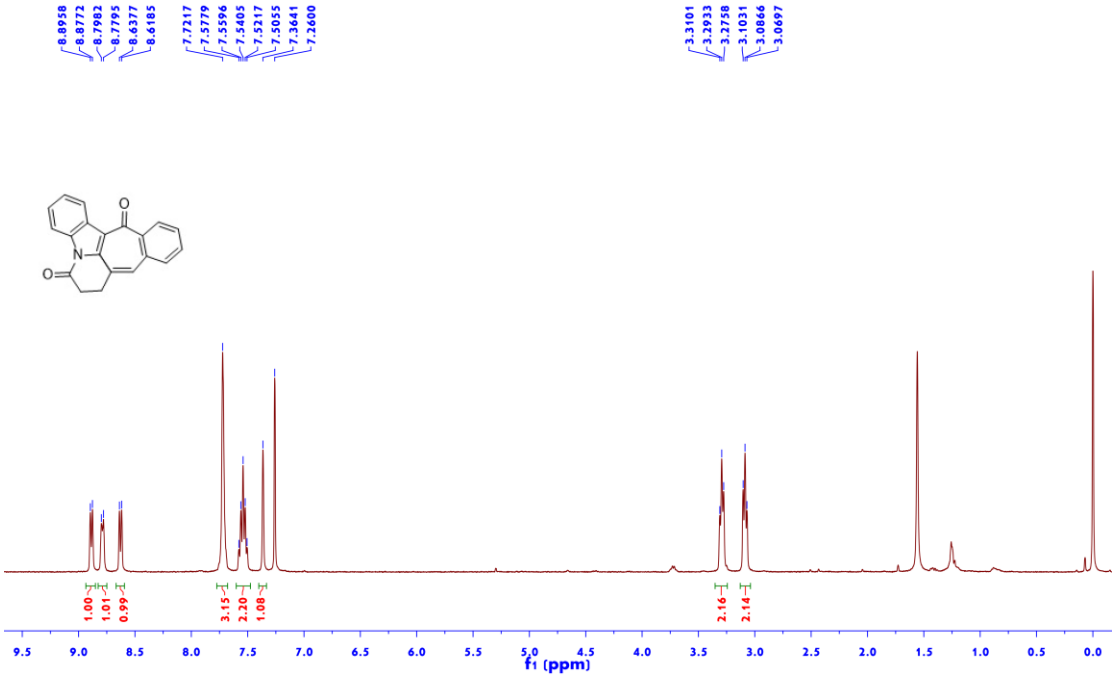


Figure S286 ^{13}C NMR (150 MHz, DMSO-d_6) of **12**

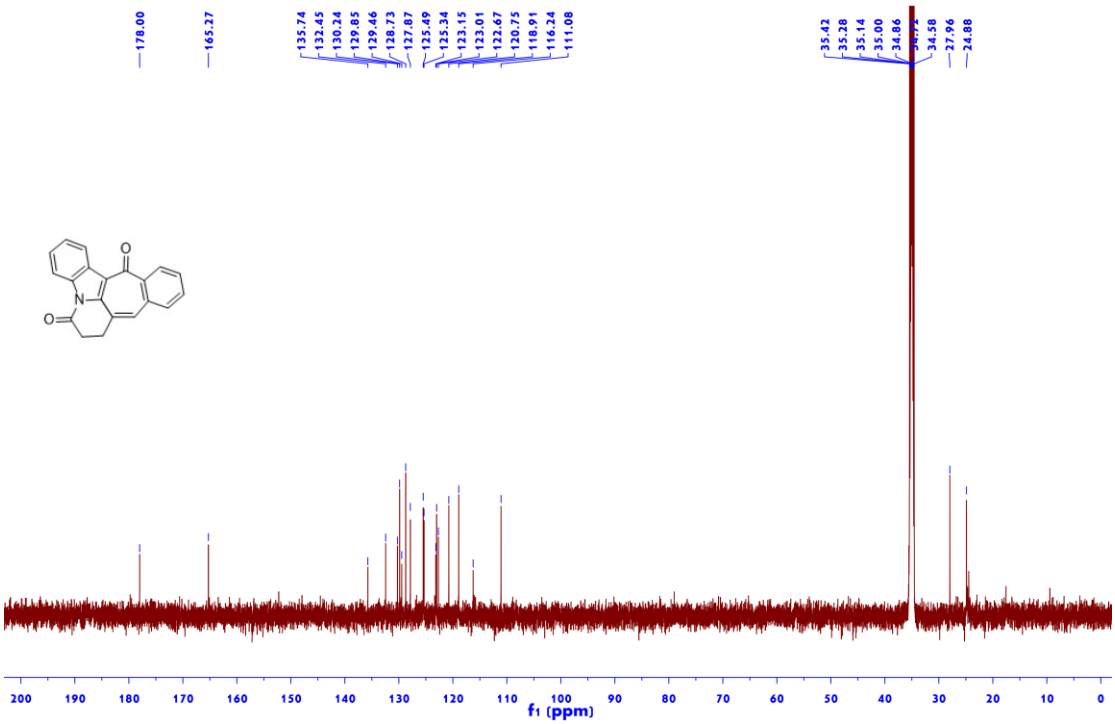


Figure S287 ^{1}H NMR (400 MHz, $CDCl_3$) of **13**

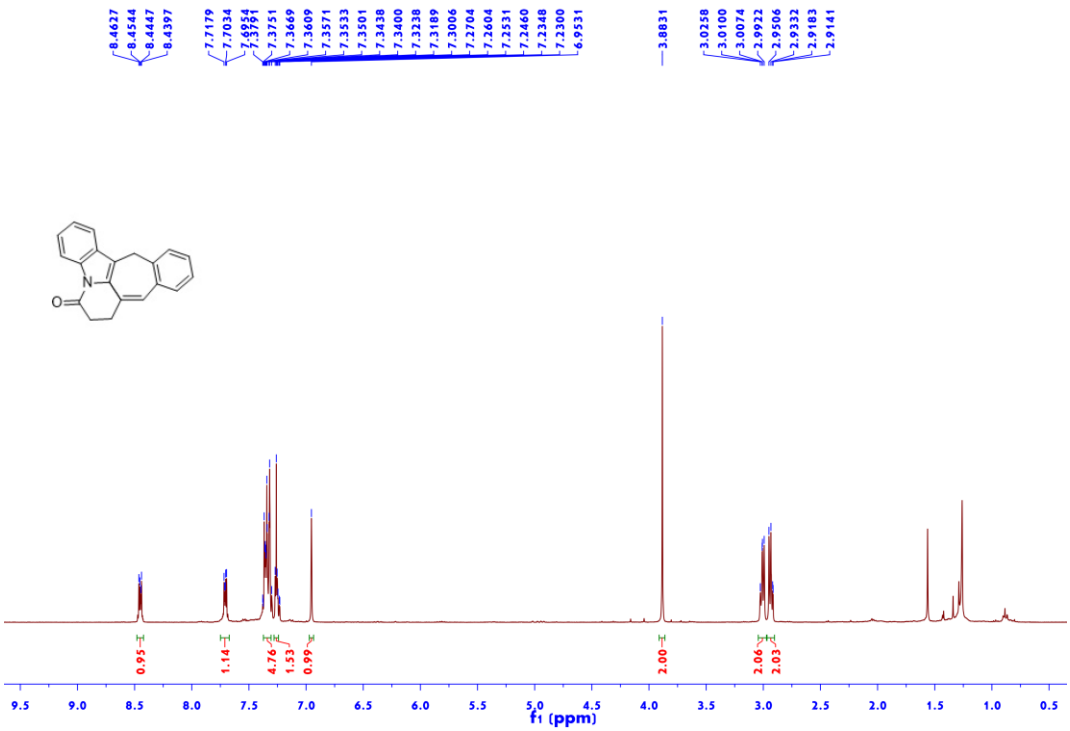
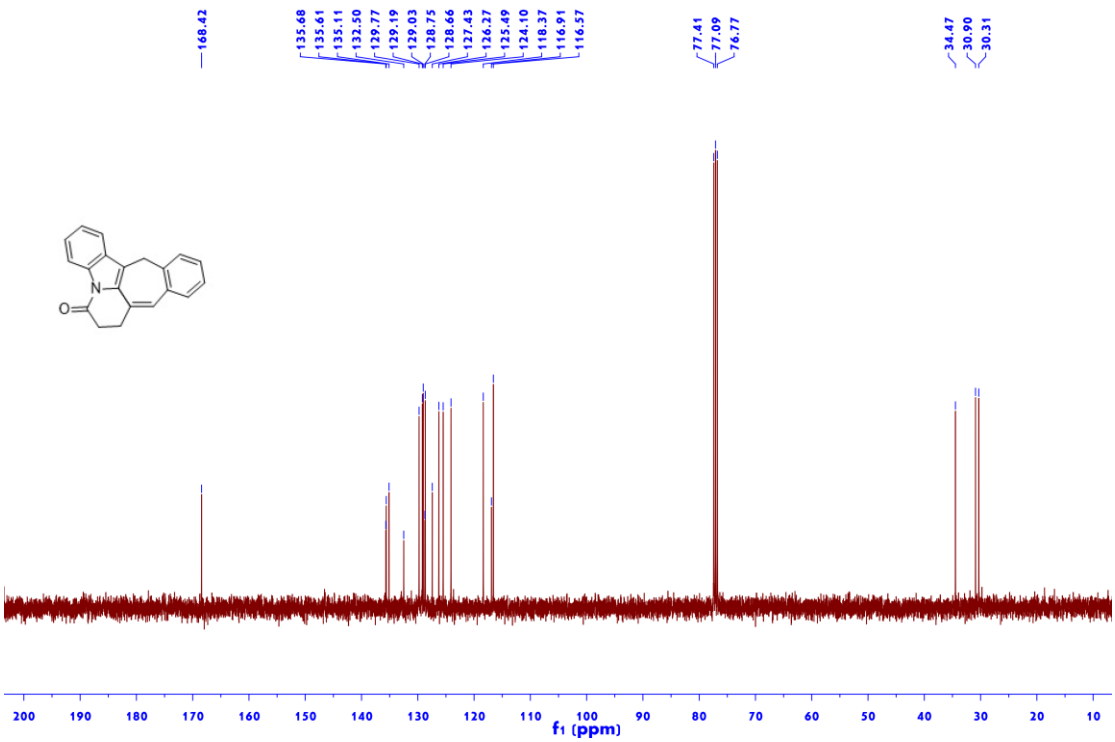


Figure S288 ^{13}C NMR (100 MHz, $CDCl_3$) of **13**



9. X-ray crystal structures of 3a, 3aq', 4a, 5a, 7ah, 10, and 12

Crystal preparation: Compounds **3a, 4a, 5a, 7ah and 10** (40 mg) was dissolved in hexane/EA = 9:1 (10 mL) in 25 mL round bottom flask and Compounds **3aq' and 12** (30 mg) were dissolved in hexane/EA/MeOH = 8:1:1 (10 mL) in 25 mL round bottom flask and the resultant solution were allowed to slowly evaporate at ambient temperature to get pure crystals suitable for X-ray diffraction analysis. The intensity data were collected at 100 K or 150 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. More information on crystal structures can also be obtained from the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers 2189547 (**3a**), 2189548 (**3aq'**), 2156622 (**4a**), 2156624 (**5a**), 2156625 (**7ah**), 2189549 (**10**) and 2157370 (**12**), respectively.

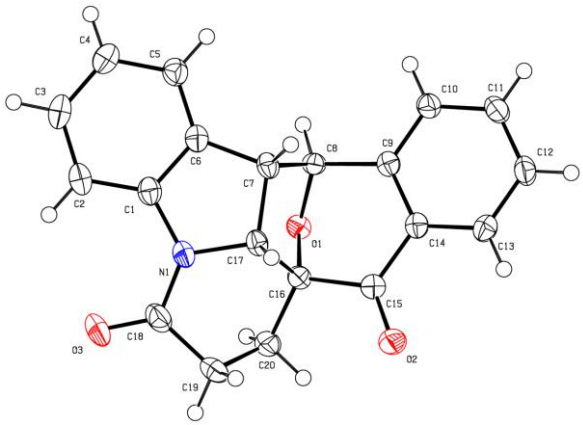


Figure S289. ORTEP Drawing of **3a** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2189547).

Table S2 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{20}H_{15}NO_3$
Formula weight	317.33
Temperature/K	149.98(10)
Crystal system	monoclinic
Space group	$P2_1/c$

a/Å	10.8645(7)
b/Å	15.3909(10)
c/Å	8.9312(5)
α/°	90
β/°	104.325(7)
γ/°	90
Volume/Å3	1446.99(16)
Z	4
ρcalcg/cm3	1.457
μ/mm-1	0.099
F(000)	664.0
Crystal size/mm3	0.14 ×0.13 ×0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.688 to 50
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 18, -9 ≤ l ≤ 10
Reflections collected	6326
Independent reflections	2558 [R_{int} = 0.0276, R_{sigma} = 0.0371]
Data/restraints/parameters	2558/0/217
Goodness-of-fit on F2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.0930
Final R indexes [all data]	R_1 = 0.0542, wR_2 = 0.1020
Largest diff. peak/hole / e Å^{-3}	0.16/-0.24

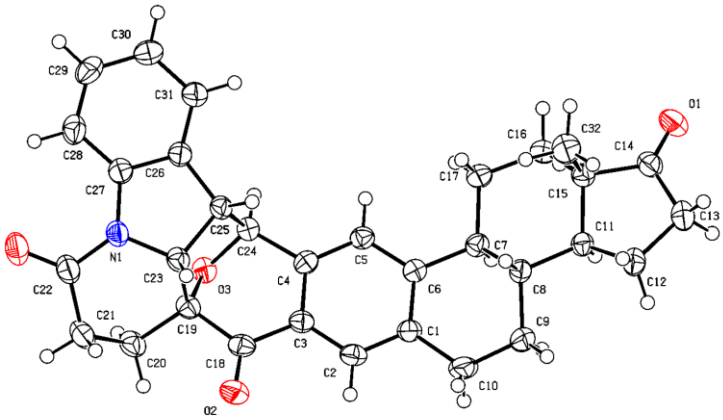


Figure S290. ORTEP Drawing of **3aq'** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2189548).

Table S3 Crystal data and structure refinement for 3aq'.

Identification code	**3aq'**
Empirical formula	$C_{32}H_{31}NO_4$
Formula weight	493.58

Temperature/K	170.02(18)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.7872(2)
b/Å	22.5373(5)
c/Å	14.1266(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2479.25(10)
Z	4
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	0.692
F(000)	1048.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/ °	7.386 to 147.954
Index ranges	$-9 \le h \le 6$, $-19 \le k \le 28$, $-17 \le l \le 17$
Reflections collected	9526
Independent reflections	4916 [R_{int} = 0.0289, R_{sigma} = 0.0348]
Data/restraints/parameters	4916/0/335
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1199
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.1222
Largest diff. peak/hole / e Å^{-3}	0.27/-0.39
Flack parameter	0.02(14)

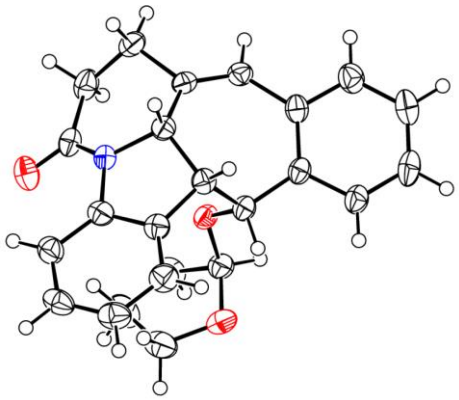


Figure S291. ORTEP Drawing of **4a** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2156622).

Table S4 Crystal data and structure refinement for 4a.

Identification code	**4a**
Empirical formula	C24H23NO3
Formula weight	373.43
Temperature/K	150.1(3)
Crystal system	monoclinic
Space group	P21/n
a/Å	12.7477(8)
b/Å	21.8900(14)
c/Å	14.6259(13)
α/°	90
β/°	94.106(7)
γ/°	90
Volume/Å3	4070.9(5)
Z	8
ρcalcg/cm3	1.219
μ/mm-1	0.080
F(000)	1584.0
Crystal size/mm3	0.14 × 0.13 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.398 to 49.998
Index ranges	-12 ≤ h ≤ 15, -25 ≤ k ≤ 26, -17 ≤ l ≤ 17
Reflections collected	18529
Independent reflections	7162 [Rint = 0.0531, Rsigma = 0.0699]
Data/restraints/parameters	7162/15/505
Goodness-of-fit on F2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0624, wR2 = 0.1424
Final R indexes [all data]	R1 = 0.0951, wR2 = 0.1660
Largest diff. peak/hole / e Å^{-3}	0.47/-0.65

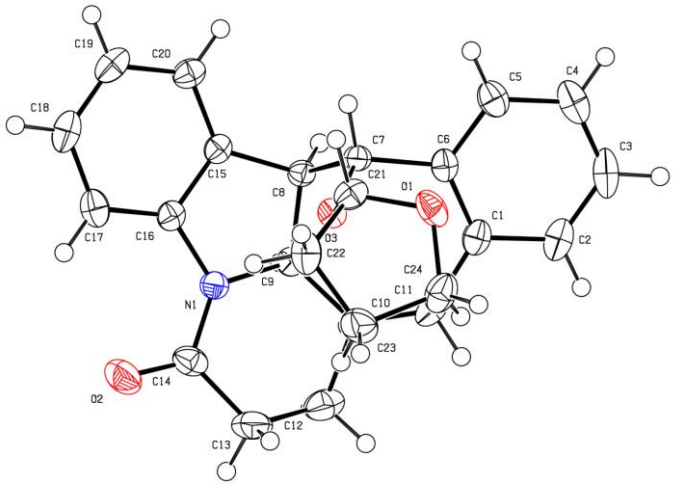


Figure S292. ORTEP Drawing of **5a** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2156624).

Table S5 Crystal data and structure refinement for 5a.

Identification code	**5a**
Empirical formula	$C_{24}H_{23}NO_3$
Formula weight	373.43
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.8590(8)
b/Å	15.1688(8)
c/Å	22.7080(16)
α/°	90
β/°	90
γ/°	90
Volume/Å3	3740.4(4)
Z	8
ρcalcg/cm3	1.326
μ/mm-1	0.087
F(000)	1584.0
Crystal size/mm3	0.13 × 0.1 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.95 to 49.994
Index ranges	-10 ≤ h ≤ 12, -17 ≤ k ≤ 18, -27 ≤ l ≤ 20
Reflections collected	9596
Independent reflections	3286 [R_{int} = 0.0291, R_{sigma} = 0.0329]
Data/restraints/parameters	3286/0/253

Goodness-of-fit on F2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.0979
Final R indexes [all data]	R_1 = 0.0545, wR_2 = 0.1051
Largest diff. peak/hole / e Å^{-3}	0.39/-0.17

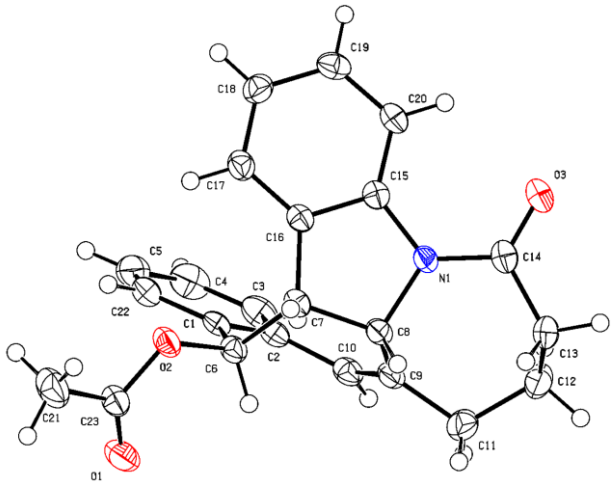


Figure S293. ORTEP Drawing of **7ah** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2156625).

Table S6 Crystal data and structure refinement for 7ah.

Identification code	**7ah**
Empirical formula	$C_{23}H_{21}NO_3$
Formula weight	359.41
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.0345(10)
b/Å	11.2376(11)
c/Å	12.1940(9)
α/°	90
β/°	99.022(7)
γ/°	90
Volume/Å3	1764.0(3)
Z	4
ρcalcg/cm3	1.353
μ/mm-1	0.090

F(000)	760.0
Crystal size/mm3	0.13 ×0.12 ×0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.812 to 49.998
Index ranges	-15 ≤ h ≤ 11, -11 ≤ k ≤ 13, -13 ≤ l ≤ 14
Reflections collected	7427
Independent reflections	3121 [R_{int} = 0.0385, R_{sigma} = 0.0586]
Data/restraints/parameters	3121/0/245
Goodness-of-fit on F2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.0967
Final R indexes [all data]	R_1 = 0.0714, wR_2 = 0.1126
Largest diff. peak/hole / e Å^{-3}	0.17/-0.19

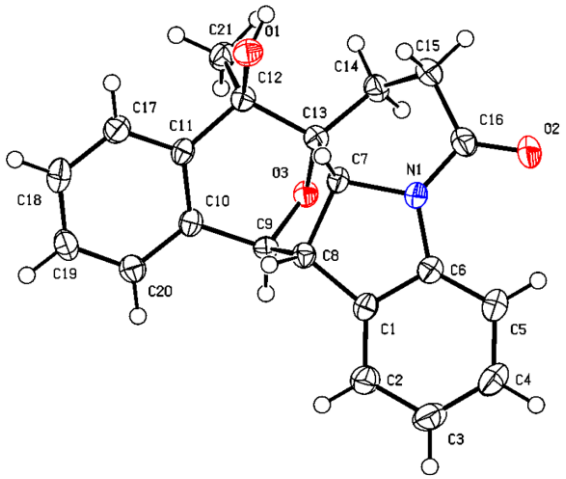


Figure S294. ORTEP Drawing of **10** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2189549).

Table S7 Crystal data and structure refinement for 10.

Identification code	**10**
Empirical formula	$C_{42}H_{38}N_2O_6$
Formula weight	666.74
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.9118(8)
b/Å	11.4750(3)
c/Å	13.8228(5)
α/°	90

β/°	108.290(4)
γ/°	90
Volume/Å^3	3300.0(2)
Z	4
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	0.724
F(000)	1408.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.5 to 143.03
Index ranges	-19 ≤ h ≤ 26, -13 ≤ k ≤ 14, -15 ≤ l ≤ 16
Reflections collected	17657
Independent reflections	6181 [R_{int} = 0.0442, R_{sigma} = 0.0393]
Data/restraints/parameters	6181/0/456
Goodness-of-fit on F^2	1.183
Final R indexes [I>=2σ (I)]	R_1 = 0.0855, wR_2 = 0.2178
Final R indexes [all data]	R_1 = 0.0896, wR_2 = 0.2192
Largest diff. peak/hole / e Å^{-3}	0.35/-0.32

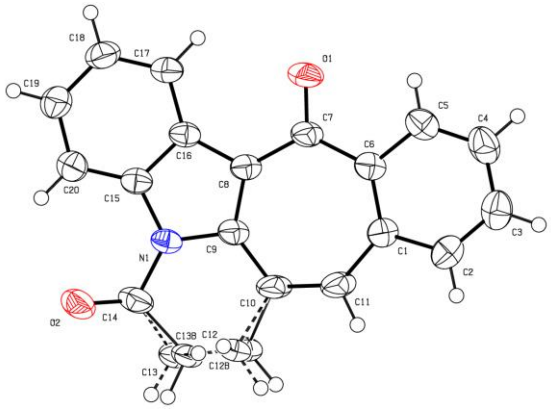


Figure S295. ORTEP Drawing of **12** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2157370).

Table S8 Crystal data and structure refinement for 12.

Identification code	**12**
Empirical formula	$C_{20}H_{13}NO_2$
Formula weight	299.31
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.30360(10)
b/Å	15.7882(3)
c/Å	20.5752(4)
α/°	90
β/°	90
γ/°	90
Volume/Å3	2697.39(8)
Z	8
ρcalcg/cm3	1.474
μ/mm-1	0.767
F(000)	1248.0
Crystal size/mm3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/ °	8.596 to 147.46
Index ranges	$-10 \leq h \leq 8$, $-19 \leq k \leq 18$, $-22 \leq l \leq 25$
Reflections collected	6939
Independent reflections	2673 [R_{int} = 0.1133, R_{sigma} = 0.0726]
Data/restraints/parameters	2673/0/228
Goodness-of-fit on F2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0706, wR_2 = 0.1935
Final R indexes [all data]	R_1 = 0.0757, wR_2 = 0.2020
Largest diff. peak/hole / e Å^{-3}	0.29/-0.36

10. References

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