Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Transition-Metal-Free Intramolecular Double Hydrofunctionalization of Alkyne to Access 6/7/5-Fused Heterocyclic Skeletons

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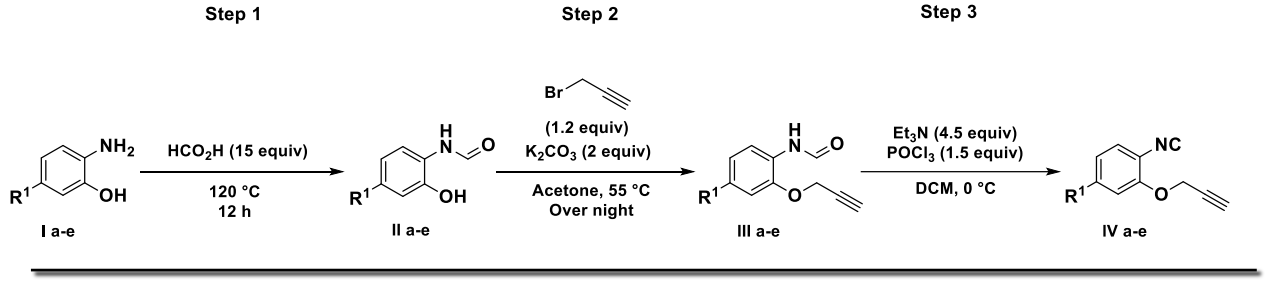
1. General Consideration

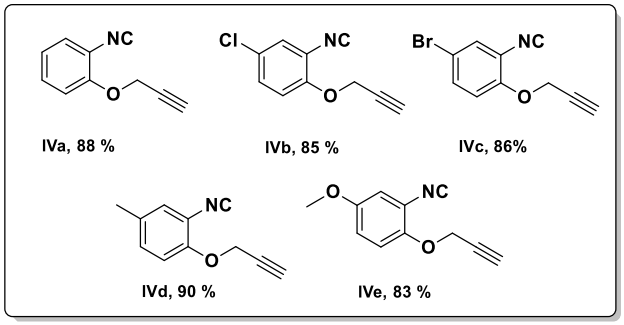
All reagents and starting materials were purchased at reagent grade and used without further purification. Silica gel column chromatography was carried out using silica Gel 60 (230–400 mesh). Melting points (m. p.) were determined in capillary tubes with an Electrothermal 9100 digital melting point apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was performed using a pre-coated TLC plate (silica gel 60 F_{254}) and visualized under ultraviolet (UV) light. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 250, 300, and 400 MHz spectrometer. Chemical shifts and coupling constants are reported as δ/ppm and Hz, respectively. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet). High-resolution mass spectra (HRMS-ESI) were run on a Waters LCT Premier XE™ TOF (Time of Flight) mass spectrometer. Single-crystal X-ray data was measured on a Bruker APEX-II Quazar area detector.

2. Experimental Procedures

2.1. General procedure for the synthesis of aryloisonitriles IVa-h.

2.1.1. General procedure for the synthesis of *O*- propargyloxy aryloisonitriles IVa -f.



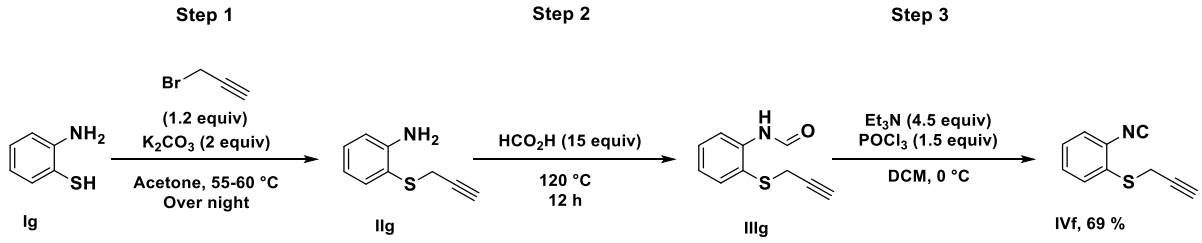


Step 1: Formamide derivatives were synthesized in the same as previously reported procedures. A solution of aminophenol (1 equiv) in HCO_2H (10-20 equiv) was heated under reflux at 120 °C for 12 h. After the completion of the reaction, the reaction mixture was added 5% HCl and was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel to give formamide or was used for the next step without further purification.[1]

Step 2: To a solution of phenols *N*-(2-hydroxyphenyl)formamide (10 mmol, 1.0 equiv) and potassium carbonate (20 mmol, 2.0 equiv) in acetone (30 mL) was added propargyl bromide (24 mmol, 1.2 equiv). The resulting mixture was then stirred at 55-60 °C for 12 hours. After filtration through celite and washing with ethyl acetate, the solvent was removed under reduced pressure and the residue was extracted with EtOAc (3 × 100 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was used for the next step without further purification.

Step 3: A solution of *N*-(2-(proparyloxy)phenyl)formamide (8.5 mmol, 1.0 equiv) and Et_3N (38.25 mmol, 4.5 equiv) in DCM (50 mL) was cooled at 0 °C, then $POCl_3$ (12.75 mmol, 1.5 equiv) was added dropwise. After the reaction was completed, a saturated Na_2CO_3 aqueous solution was added at 0 °C and the mixture was extracted with DCM (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. the residue was purified by flash column chromatography (SiO_2, *n*-hexane/EtOAc (2:1)). [2]

2.1.2. General procedure for the synthesis of *S*- propargyl aryloisonitriles IVf.



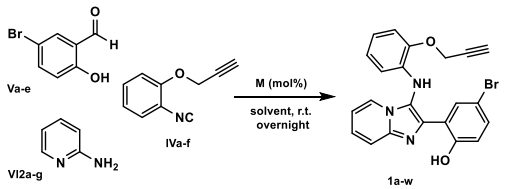
Step1: To a solution of phenols thioaniline (10 mmol, 1.0 equiv) and potassium carbonate (20 mmol, 2.0 equiv) in acetone (30 mL) was added propargyl bromide (24 mmol, 1.2 equiv). The resulting mixture was then stirred at 55-60 °C for 12 hours. After filtration through celite and washing with ethyl acetate, the solvent was removed under reduced pressure and the residue was extracted with EtOAc (3 × 100 mL) and

the combined organic phases were dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was used for the next step without further purification.

Step 2: A solution of *S*- propargylaniline (1.0 equiv) in HCO_2H (10-20 equiv) was heated under reflux at 120 °C for 12 h. After the completion of the reaction, HCl 5% was added to the reaction mixture and extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel to give formamide, or was used for the next step without further purification.

Step 3: A solution of *S*-(2-(proparyl)phenyl)formamide (8.5 mmol, 1.0 equiv) and Et_3N (38.25 mmol, 4.5 equiv) in DCM (50 mL) was cooled at 0 °C, then $POCl_3$ (12.75 mmol, 1.5 equiv) was added dropwise. After the completion of the reaction, a saturated Na_2CO_3 aqueous solution was added at 0 °C and the mixture was extracted with DCM (3 ×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. the residue was purified by flash column chromatography (SiO_2, *n*-hexane/EtOAc (2:1)).

Table S1. Optimization of the Reaction Conditions[a]

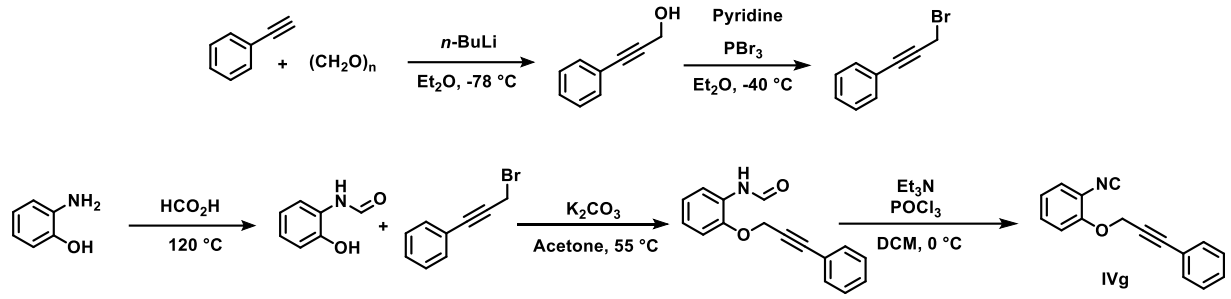


entry	catalyst (mol%)	solvent	yield [b] %
1	_	CH_3CN	Trace
2	_	MeOH	Trace
3	$InCl_3$ (5)	MeOH	13
4	$InCl_3$ (5)	CH_3CN	26
5	$BiCl_3$(5)	MeOH	47
6	$BiCl_3$ (5)	CH_3CN	51
7	TFA (5)	CH_3CN	37
8	PTSA (5)	CH_3CN	37
9	$Sc(OTf)_3$ (5)	MeOH	58
10	$Sc(OTf)_3$ (5)	CH_3CN	70
11	**$Sc(OTf)_3$ (10)**	**CH_3CN**	**75**
12	$Sc(OTf)_3$ (15)	CH_3CN	75

13	$Sc(OTf)_3$ (15)	CH_2Cl_2	53
14	$Sc(OTf)_3$ (15)	EtOH	48

[a]Reaction conditions: **1a** (1 equiv), **2a** (1 equiv), **3a** (1 equiv), $Sc(OTf)_3$ (10 mol%), and solvent, room temperature, overnight. [b] Isolated yields.

2.1.3 General procedure for the synthesis of 1-isocyano-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (IVg)



Step 1: The 1-isocyano-2-((3-phenylprop-2-yn-1-yl)oxy)benzene was synthesized in the same as previously reported procedures.[3] To a solution of phenylacetylene (2.7 ml, 25 mmol, 1.00 equiv) in Et_2O (50 mL) at –78 °C was added *n*-BuLi in hexane (2.5 M, 11 mL, 27 mmol, 1.10 equiv) dropwise. The clear, slightly yellowish solution was stirred at –78 °C for 30 min, then solid paraformaldehyde (1.50 g, 50 mmol, 2.03 equiv) was added. The reactionmixture was slowly warmed to rt over 2.5 h, then further stirred at rt for 12 h. The reaction was quenched with saturated aqueous NH_4Cl (50 mL), then the phases were separated. After extraction with Et_2O (3 x 50 mL), the combined organic phases were washed with saturated aqueous NaCl (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by chromatography on silica gel (*n*-hexane : EtOAc 2:1) provided 3-phenyl-2-propyn-1-ol as a clear, yellowish oil.

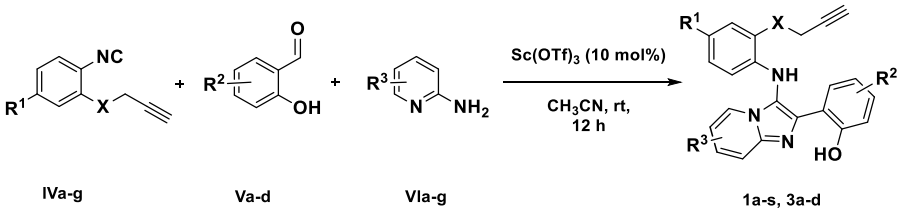
Step 2: To a solution of 3-phenyl-2-propyn-1-ol (3.25 mL, 10 mmol) and pyridine (0.5 mmol, 0.05 equiv) in Et_2O (3 mL) at -40 °C was added dropwise phosphorus tribromide (4.5 mmol, 0.5 equiv). The mixture was stirred at -40 °C for 1 hour, then was allowed to warm slowly to room temperature for 24 hours. Brine (15 mL) was poured in the reaction mixture at 0 °C, the mixture was extracted 3 times with Et_2O (10 mL). The combined organic phases were then washed 2 times with water (10 mL), 2 times with $NaHCO_3$ sat. (10 mL) and finally 2 times with brine (10 mL). The resulting organic phase was dried over Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography in pure *n*-hexane.

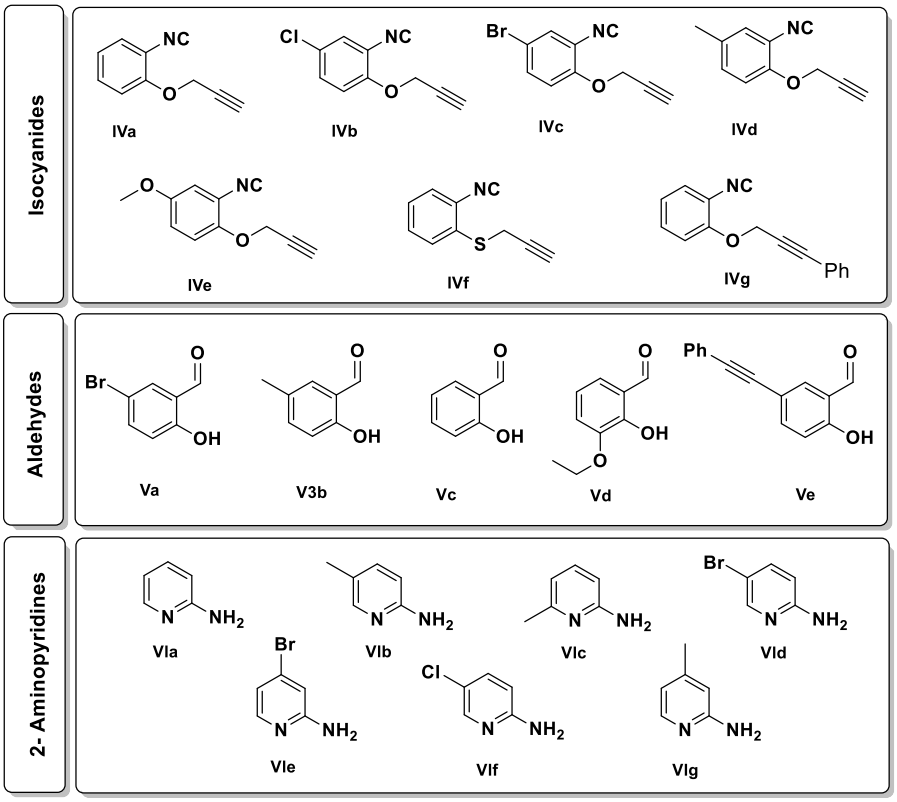
Step 3: To a solution of phenols *N*-(2-hydroxyphenyl)formamide (10 mmol, 1.0 equiv) and potassium carbonate (20 mmol, 2.0 equiv) in acetone (30 mL) was added (3-bromoprop-

1-yn-1-yl)benzene (24 mmol, 1.2 equiv). The resulting mixture was stirred at 55-60 °C for 12 hours. After filtration through celite and washing with ethyl acetate, the solvent was removed under reduced pressure and the residue was extracted with EtOAc (3 × 100 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was used for the next step without further purification.

Step 4: A solution of N-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)formamide (8.5 mmol, 1.0 equiv) and Et_3N (38.25 mmol, 4.5 equiv) in DCM (50 mL) was cooled at 0 °C, then $POCl_3$ (12.75 mmol, 1.5 equiv) was added dropwise. After the reaction was completed, a saturated Na_2CO_3 aqueous solution was added at 0 °C and the mixture was extracted with DCM (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. the residue was purified by flash column chromatography (SiO_2, *n*-hexane/EtOAc (2:1)).

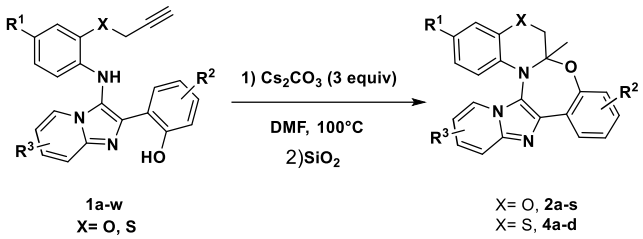
General procedure for the synthesis of GBB products 1a-s, 3a-d.





To a solution of 2-aminopyridines **VIa-g** (1.0 mmol, 1.0 equiv), aldehydes **Va-e** (1.0 mmol, 1.0 equiv) and scandium triflate (10 mol%, 0.1 equiv) in acetonitrile (1.0 M), isocyanides **IVa-f** (1.0 mmol, 1.0 equiv) was added and stirred for 12 h at room temperature. After completion of the reaction, the solid was filtered and washed with acetonitrile. The mixture was filtrated through celite and washed with dichloromethane to afford pure imidazopyridine (1a-s, 3a-d).

2.2. General procedure for the synthesis of *N*-fused (benzooxazine, benzothiazine, quinoxaline)- 1,3-benzoxazepines.

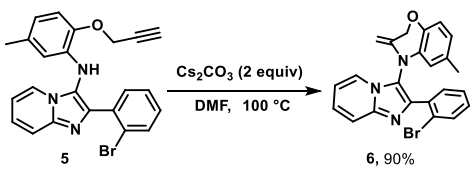


To a Schlenk tube were added imidazopyridines (0.2 mmol, 1.0 equiv), cesium carbonate (3.0 equiv), and DMF (1 mL). The reaction was stirred at 100 °C in an oil bath for 12 h. The reaction process was monitored by thin-layer chromatography. The solvent of the reaction was removed under reduced pressure and then completion of the reaction was done on a preparative silica plate using *n*-hexane/EtOAc as an eluent to afford the products.

2.4 General procedure for the synthesis of GBB product 5.

To a solution of 2-aminopyridines (1.0 mmol, 1.0 equiv), 2-bromobenzealdehydes (1.0 mmol, 1.0 equiv), and scandium triflate (10 mol%, 0.1 equiv) in acetonitrile (1.0 M), isocyanides **IVd** (1.0 mmol, 1.0 equiv) was added and stirred for 12 h at room temperature. After completion of the reaction, the solid was filtered and washed with acetonitrile. The mixture was filtrated through celite and washed with dichloromethane to afford pure **5**.

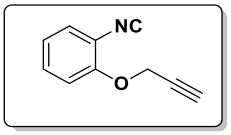
2.5 General procedure for the synthesis of 6.



To a Schlenk tube were added imidazopyridines **5** (0.2 mmol, 1.0 equiv), cesium carbonate (2.0 equiv), and DMF (1 mL). The reaction was stirred at 100 °C in an oil bath for 12 h. The reaction process was monitored by thin-layer chromatography. After the completion of the reaction, the mixture of the reaction was concentrated in vacuo and the residue was purified by flash column chromatography (SiO_2, *n*-hexane/EtOAc (4:1)).

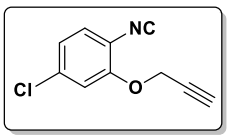
3. Compound Characterization Data

1-isocyano-2-(prop-2-yn-1-yloxy)benzene. (Ⅳa)



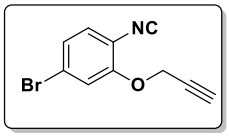
Light green solid; **mp =** 93-94 °C; (968 mg, **Yield**= 88 %); R_f = 0.6 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) =7.39 (t, 1H, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 4.84 (d, *J* = 2.4 Hz, 2H), 2.59 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 167.8, 152.8, 130.2, 127.9, 121.5, 116.7, 113.5, 77.4, 76.6, 56.5. **HRMS-ESI (+)** (m/z): calc. for $C_{10}H_7NO$ $[M+H]^+$ 158.0603, found 158.0593.

4-Chloro-1-isocyano-2-(prop-2-yn-1-yloxy)benzene. (Ⅳb)



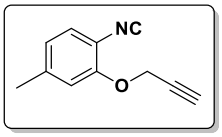
Pink solid; **mp =** 96-97 °C; (1.14 g, **Yield**= 85 %); R_f = 0.6 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.35 (s, 1H), 7.34 (dd, *J* = 8.7, 2.6 Hz, 1 H), 7.08 (d, *J* = 8.7 Hz, 1H), 4.82 (d, *J* = 2.4 Hz, 2H), 2.59 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 169.5, 151.5, 130.3, 130.2, 127.6, 126.2, 114.5, 77.1, 76.9, 56.8. **HRMS-ESI (+)** (m/z): calc. for $C_{10}H_6{}^{35}ClNO$ $[M+H]^+$ 192.0216, found 192.0208.

1-Isocyano-2-(prop-2-yn-1-yloxy)benzene. (Ⅳc)



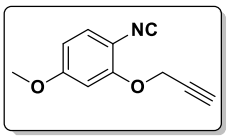
Light yellow solid; **mp =** 95-97 °C; (1.42 g, **Yield**= 86 %); R_f = 0.6 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.53 (s, 1H), 7.50 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 4.84 (d, *J* = 2.4 Hz, 2H), 2.60 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 169.7, 152.1, 133.1 (2C), 130.5, 115.0, 113.0, 77.2, 76.9, 56.8.

1-Isocyano-4-methyl-2-(prop-2-yn-1-yloxy)benzene. (Ⅳd)



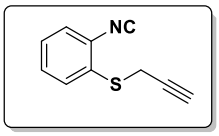
Cream solid; **mp =** 94-95 °C; (1.08 g, **Yield**= 90 %); R_f = 0.6 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.17 (s, 1H), 7.15 (d, *J* = 9.1 Hz, 1 H), 7.01 (d, *J* = 9.1 Hz, 1H), 4.79 (d, *J* = 2.4 Hz, 2H), 2.55 (t, *J* = 2.4 Hz, 1H), 2.29 (s, 3H); **^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 167.3, 150.7, 131.4, 130.7, 128.2, 128.1, 113.6, 77.6, 76.4, 56.6, 20.2. **HRMS-ESI (+)** (m/z): calc. for $C_{11}H_9NO$ $[M+H]^+$ 172.0760, found 172.0755.

1-isocyano-4-methoxy-2-(prop-2-yn-1-yloxy)benzene. (Ⅳe)



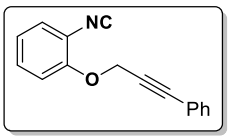
Colorless solid; **mp =** 93-95 °C; (1.09 g, **Yield**= 83 %); R_f = 0.6 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.06 (d, *J* = 9.5 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.88 (*br* s, 1H), 4.75 (d, *J* = 2.4 Hz, 2H), 3.77 (s, 3H), 2.54 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 167.9, 153.7, 146.7, 117.1, 115.5, 115.4, 112.6, 77.4, 75.9, 57.1, 55.4. **HRMS-ESI (+)** (m/z): calc. for $C_{11}H_9NO_2$ $[M+H]^+$ 188.0711, found 188.0707.

(2-isocyanophenyl)(prop-2-yn-1-yl)sulfane. (Ⅳf)



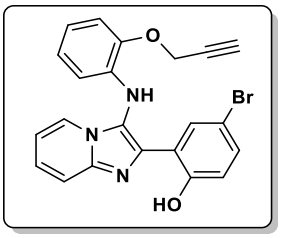
Yellow solid, **mp** = 94-96 °C; (837 mg, **Yield**= 69 %); R_f = 0.6 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 7.66 (td, *J* = 8.0, 1.2 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.6 Hz), 7.58 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 4.09 (d, *J* = 2.6 Hz, 2H), 3.29 (t, *J* = 2.6 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 168.7, 133.6, 133.3, 130.7, 128.4, 127.8, 127.2, 79.8, 74.8, 19.8. **HRMS-ESI (+)** (m/z): calc. for $C_{10}H_7NS$ $[M+H]^+$ 174.0377, found 174.3963.

1-isocyano-2-((3-phenylprop-2-yn-1-yl)oxy)benzene. (Ⅳg)



Light yellow solid; **mp =** 97-99 °C; (1.3 g, **Yield**= 7%); R_f = 0.6 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) =7.49-7.40 (m, 2H), 7.41 – 7.26 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.99 (td, *J* = 7.7, 1.2 Hz, 1H), 5.05 (s, 2H).**^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 167.7, 152.7, 131.3, 129.7, 128.4, 127.8, 127.39 121.5, 120.9, 116.5, 113.4, 87.8, 82.3, 57.1. **HRMS-ESI (+)** (m/z): calc. for $C_{16}H_{12}NO$ $[M+H]^+$ 234.0913, found 234.0915.

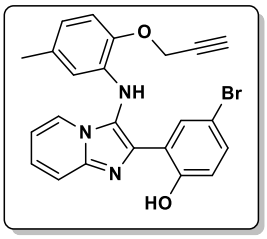
4-Bromo-2-(3-((2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-a]pyridin-2-yl)phenol. (1a)



Light green solid; **mp =** 200-202 °C; (313 mg, **Yield**= 72%); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ (ppm) = 13.21 (*br* s, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 8.00 (s, 1H), 7.80 (*br* s, 1H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.45 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.06 (dd, *J* = 7.3, 7.2 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.80- 6.58 (m, 2H), 5.93 (d, *J* = 7.9 Hz, 1H), 4.97 (*br* s, 2H), 3.65 (*br* s, 1H). **^{13}C {^{1}H} NMR (75 MHz, DMSO-*d*$_6$)** δ (ppm) =156.2, 145.5, 142.4, 139.8, 134.4, 131.6, 128.8, 126.7, 123.1, 122.3, 119.1, 119.0 (2C), 118.4, 116.3, 113.9, 113.4, 111.9, 109.9, 79.5, 78.4, 56.6. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{16}{}^{79}BrN_3O_2$ $[M+H]^+$ 464.0504, found 464.0496.

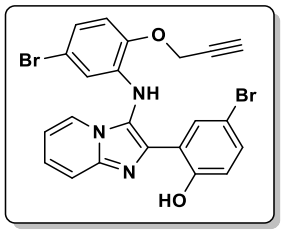
4-Bromo-2-(3-((5-methyl-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl

phenol. (1b)



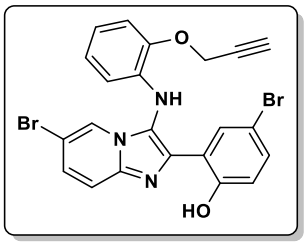
Yellow solid; **mp =** 177-179 °C; (336 mg, **Yield**= 75%); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 13.26 (br s, 1H), 7.99 (d, *J* = 2.5 Hz, 1H), 7.94 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.62 (dt, *J* = 9.0, 1.1 Hz, 1H), 7.34 (ddd, *J* = 9.1, 6.8, 1.3 Hz, 1H), 7.26 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.89 (td, *J* = 6.9, 1.2 Hz), 6.66 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.07 (br s, 1H), 5.97 (d, *J* = 2.1 Hz, 1H), 4.92 (d, *J* = 2.4 Hz, 2H), 2.65 (t, *J* = 2.4 Hz, 1H), 2.07 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm) = 157.7, 143.1, 140.3, 138.3, 133.9, 132.5, 129.5, 126.6, 125.8, 122.5, 119.9, 119.0, 117.4, 116.7, 116.2, 112.9, 112.9, 112.8, 78.7, 75.9, 75.8, 56.9, 20.9. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O_2$ $[M+H]^+$ 448.0661, found 448.0652.

4-Bromo-2-(3-((5-bromo-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl)Phenol. (1c)



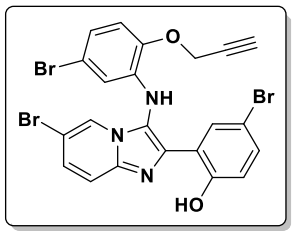
Yellow solid; **mp =** 190-191 °C; (359 mg, **Yield**= 70 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, CDCl$_3$)** δ (ppm) = 13.09 (br s, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 2.5 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.29 (dd, *J* = 7.3, 7.2 Hz, 1H), 7.19 (d, *J* = 1.6 Hz, 1H), 7.17-7.14 (m, 1H), 6.90 (d, *J* = 1.8 Hz, 2H), 6.90- 6.80 (m, 2H), 6.16 (*br* s, 1H), 6.08 (*br* s, 1H), 4.85 (d, *J* = 3.2 Hz, 2H), 2.58 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (76 MHz, CDCl$_3$)** δ (ppm) = 156.9, 144.5, 140.5, 135.4, 132.3, 128.8, 126.4, 122.7, 122.3, 119.4, 117.6, 117.0, 115.3, 115.1 (2C), 114.2, 113.6 (2C), 110.7, 77.9, 76.6, 57.2. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 511.9609, found 511.9603.

4-Bromo-2-(6-bromo-3-((2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl) Phenol. (1d)



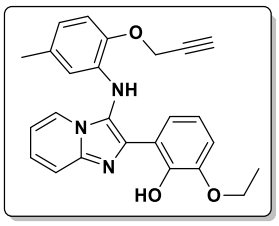
Brown solid; **mp =** 183-185 °C; (328 mg, **Yield**= 64 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 12.93 (s, 1H), 8.24 (d, *J* = 1.1 Hz, 1H), 7.96 (d, *J* = 2.5 Hz, 1H), 7.82 (*br* s, 1H), 7.77 (d, *J* = 10.3 Hz, 1H), 7.58 (dd, *J* = 9.5, 1.9 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.19 (d, *J* = 9.5 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.79 (td, *J* = 7.7, 1.6 Hz, 1H), 6.69 (dd, *J* = 8.0, 7.9 Hz, 1H), 6.06 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.01 (d, *J* = 2.4 Hz, 2H), 3.65 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.5, 145.9, 138.7, 136.1, 134.4, 132.3, 129.9, 129.4, 123.3, 122.6, 120.0, 119.8, 119.5, 118.4, 118.1, 114.1, 112.5, 110.5, 108.0, 79.9, 78.9, 56.9. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 511.9609, found 511.9603.

4-Bromo-2-(6-bromo-3-((5-bromo-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*] pyridin-2-yl)phenol. (1e)



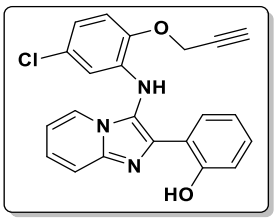
Brown solid; **mp =** 182-184 °C; (391 mg, **Yield**= 66 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 12.89 (*br* s, 1H), 8.35 (d, *J* = 1.8 Hz, 1H), 8.03 (*br* s, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.78 (d, *J* = 9.4 Hz, 1H), 7.60 (dd, *J* = 9.4, 1.9 Hz, 1H), 7.33 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.22 (d, *J* = 2.4 Hz, 1H), 5.00 (d, *J* = 2.4 Hz, 2H), 3.69 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.5, 145.3, 139.07, 136.4, 136.0, 132.5, 130.2, 129.2, 123.4, 122.0, 119.6, 119.0, 118.2, 118.1, 115.8, 114.7, 114.2, 110.5, 108.1, 79.4, 79.3, 57.1. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{14}{}^{79}Br_3N_3O_2$ $[M+H]^+$ 589.8710, found 589.8700.

2-Ethoxy-6-(3-((5-methyl-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl Phenol. (1f)



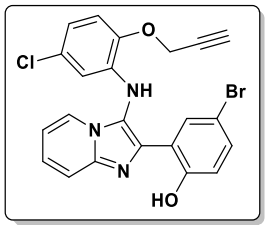
Light brown solid; **mp =** 237-238 °C; (285 mg, **Yield**= 69 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 13.23 (*br* s, 1H), 7.92 (d, *J* = 6.8 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.3, 8.2 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.88 (t, *J* = 6.8 Hz, 1H), 6.86 (d, *J* = 8 Hz, 1H), 6.73 (dd, *J* = 7.6, 7.7 Hz, 1H), 6.63 (dd, *J*= 8.4, 1.2 Hz, 1H), 6.13 (*br* s, 1H), 6.00 (d, *J* = 2.1 Hz, 1H), 4.88 (d, *J* = 2.4 Hz, 2H), 4.17 (q, *J* = 6.9 Hz, 2H), 2.61 (t, *J* = 2.4 Hz, 1H), 2.06 (s, 3H), 1.52 (t, *J* = 6.9 Hz, 3H). **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm) = 147.9, 143.1, 140.2, 133.9, 132.5, 125.9, 122.6, 119.8, 118.9, 118.5, 117.0, 116.9, 116.8, 116.4, 116.3, 113.4, 113.0, 112.8, 78.7, 75.9, 75.8, 64.5, 56.9, 20.8, 15.0. **HRMS-ESI (+)** (m/z): calc. for $C_{25}H_{23}N_3O_3$ $[M+H]^+$ 414.1812, found 414.1810.

2-(3-((5-Chloro-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl)phenol. (1g)



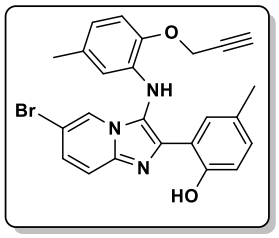
yellow solid; **mp =** 157-159 °C; (261 mg, **Yield**= 67 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 13.04 (*br* s, 1H), 7.90 (d, *J* = 6.8 Hz, 1H), 7.81 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.66 (d, *J* = 9.1 Hz, 1H), 7.35 (ddd, *J* = 9.1, 6.9, 1.6 Hz, 1H), 7.20 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.06 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.92 (td, *J* = 8.6, 1.2 Hz, 1H), 6.8 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.77 (td, *J* = 8.2, 1.7 Hz, 1H), 6.23 (*br* s, 1H), 6.15 (d, *J* = 2.4 Hz, 1H), 4.91 (d, *J* = 2.4 Hz, 2H), 2.65 (t, *J* = 2.4 Hz, 1H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm) = 157.7, 143.7, 140.4, 135.4, 129.8, 128.0, 126.4, 126.2, 122.3, 119.2, 119.0, 117.5 (2C) , 116.8, 115.8, 115.6, 113.6, 113.3, 112.1, 78.0, 76.5, 57.0. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{16}{}^{35}ClN_3O_2$ $[M+H]^+$ 390.1006, found 390.1002.

4-Bromo-2-(3-((5-chloro-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl Phenol. (1h)



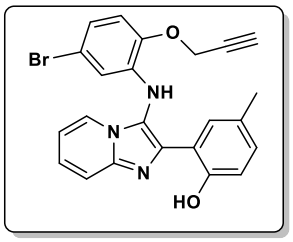
Colorless solid; **mp =** 207-209 °C; (244 mg, **Yield**= 52 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 13.13 (*br* s, 1H), 7.91 (d, *J* = 6.8 Hz, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.36 (ddd, *J* = 9.0, 6.8, 1.3 Hz, 1H), 7.24 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 1H), 6.95-6.91 (m, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.22 (*br* s, 1H), 6.10 (d, *J* = 2.5 Hz, 1H), 4.94 (d, *J* = 2.5 Hz, 2H), 2.68 (t, *J* = 2.4 Hz, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 156.7, 144.0, 140.3, 135.2, 132.3, 128.8, 127.8, 126.6, 122.4, 119.6, 119.3, 117.5, 116.8, 116.4, 113.8 (2C), 113.6, 112.4, 110.8, 78.0, 76.7, 57.2. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br^{35}ClN_3O_2$ $[M+H]^+$ 468.0111, found 468.0103.

2-(6-Bromo-3-((5-methyl-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl) -4-methylphenol. (1i)



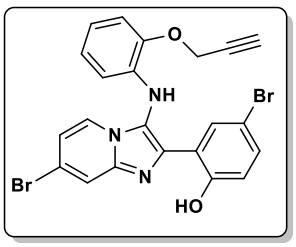
Yellow solid; **mp =** 143-145 °C; (286 mg, **Yield**= 62 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (250 MHz, DMSO)** δ (ppm)= 12.51 (*br* s, 1H), 8.18 (*br* s, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.61 (*br* s, 2H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 5.83 (*br* s, 1H), 4.92 (*br* s, 2H), 3.59 (*br* s, 1H), 2.05 (s, 3H), 1.93 (s, 3H). **^{13}C {^{1}H} NMR (63 MHz, DMSO-*d_6*)** δ (ppm) = 155.1, 143.8, 138.7, 137.7, 134.8, 131.6, 130.6, 129.4, 127.5, 127.4, 123.0, 119.9, 119.5, 117.9, 117.0, 116.0, 114.2, 113.0, 107.6, 80.0, 78.6, 56.9, 20.9, 20.8. **HRMS-ESI (+)** (m/z): calc. for $C_{24}H_{20}{}^{79}BrN_3O_2$ $[M+H]^+$ 462.0812, found 462.0810.

2-(3-((5-Bromo-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-a]pyridin-2-yl)-4-methyl phenol. (1j)



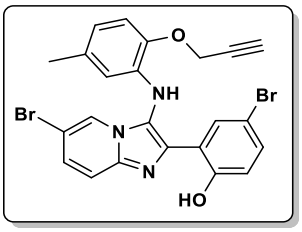
Yellow solid; **mp =** 173-175 °C; (269 mg, **Yield**= 60 %); R_f = 0.4 (1:5 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d_6*)** δ (ppm) 12.78 (*br* s, 1H), 8.10 (dt, *J* = 6.8, 1.2 Hz, 1H), 8.05 (*br* s, 1H), 7.78 (ddd, *J* = 9.0, 7.2, 1.1 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.48 (ddd, *J* = 9.0, 6.8, 1.3 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.10 (td, *J* = 6.8, 1.2 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.01 (d, *J* = 2.4 Hz, 1H), 5.04 (d, *J* = 2.4 Hz, 2H), 3.73 (t, *J* = 2.4 Hz, 1H), 2.12 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d_6*)** δ (ppm) 160.0, 149.8, 145.2, 142.0, 141.8, 135.3, 132.2, 132.0, 131.8, 128.2, 126.2, 122.5, 122.0, 121.5, 120.9, 120.5, 119.0, 118.9, 118.7, 84.3, 84.0, 61.7, 25.7. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O_2$ $[M+H]^+$ 448.0656, found 448.0654.

4-Bromo-2-(3-((5-bromo-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl) Phenol. (1k)



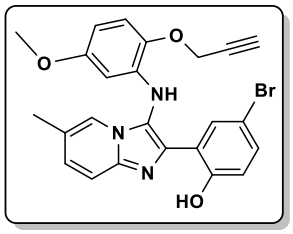
Light yellow solid; **mp =** 190-192 °C; (359 mg, **Yield**= 70 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ (ppm) = 12.85 (*br* s, 1H), 8.10 (*br* s, 1H), 8.02- 7.90 (m, 2H), 7.79 (*br* s, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.22- 7.11 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.76 (dd, *J* = 7.8, 7.3 Hz, 1H), 6.66 (t, *J* = 7.7 Hz, 1H), 6.00 (d, *J* = 7.7 Hz, 1H), 4.97 (s, 2H), 3.64 (t, *J* = 2.5 Hz, 1H). **^{13}C {^{1}H} NMR (75 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.0, 145.5, 140.0, 135.5, 134.2, 131.9, 129.0, 124.1, 122.3, 119.7, 119.6, 119.4, 119.0, 118.5, 118.2, 116.8, 113.8, 112.1, 110.1, 79.5, 78.4, 56.7. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 511.9605, found 511.9603.

4-Bromo-2-(6-bromo-3-((5-methyl-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*] pyridine-2-yl)phenol. (1l)



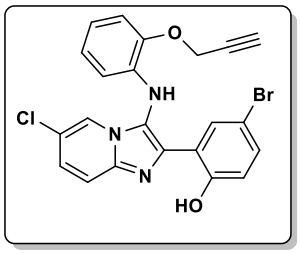
Yellow solid; **mp =** 166-168 °C; (385 mg, **Yield**= 73 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 12.95 (*br* s, 1H), 8.23 (d, *J* = 1.9 Hz, 1H), 7.97 (d, *J* = 2.5 Hz, 1H), 7.78 (d, *J* = 10.3 Hz, 1H), 7.73 (*br* s, 1H), 7.59 (dd, *J* = 9.5, 1.9 Hz, 1H), 7.32 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.59 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.90 (d, *J* = 2.0 Hz, 1H), 4.94 (d, *J* = 2.4 Hz, 2H), 3.62 (t, *J* = 2.4 Hz, 1H), 1.98 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.5, 144.0, 138.8, 136.1, 134.4, 132.3, 131.7, 130.0, 129.4, 123.3, 120.3, 120.0, 119.6, 118.5, 118.1, 114.4, 113.1, 110.5, 108.0, 80.0, 78.8, 57.1, 20.9. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{17}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 525.9761, found 525.9766.

4-Bromo-2-(3-((5-methoxy-2-(prop-2-yn-1-yloxy)phenyl)amino)-6-methylimidazo[1,2-*a*] pyridin-2-yl)phenol. (1m)



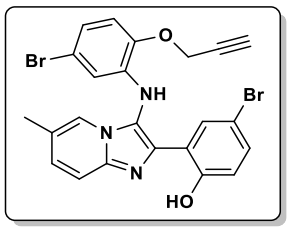
Light green solid; **mp =** 172-174 °C; (282 mg, **Yield**= 59 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 13.27 (*br* s, 1H), 7.98 (d, *J* = 2.5 Hz, 1H), 7.90 – 7.88 (m, 2H), 7.71 (dd, *J* = 9.2, 1.0 Hz, 1H), 7.36 (dd, *J* = 9.2, 1.7 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.34 (dd, *J* = 8.8, 2.9 Hz, 1H), 5.46 (d, *J* = 2.9 Hz, 1H), 4.93 (d, *J* = 2.4 Hz, 2H), 3.67 (t, *J* = 2.4 Hz, 1H), 3.49 (s, 3H), 2.33 (d, *J* = 1.2 Hz, 3H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.6, 155.4, 140.2, 139.3, 136.5, 135.5, 132.0, 130.3, 129.1, 123.6, 120.8, 119.5, 118.9, 118.8, 116.3, 115.9, 110.4, 102.2, 99.5, 80.3, 78.9, 57.8, 55.4, 18.2. **HRMS-ESI (+)** (m/z): calc. for $C_{24}H_{20}{}^{79}BrN_3O_3$ $[M+H]^+$ 478.0761, found 478.0765.

4-Bromo-2-(6-chloro-3-((2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl) phenol. (1n)



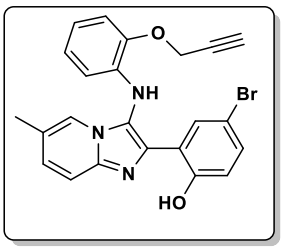
Yellow solid; **mp =** 223-224 °C; (295 mg, **Yield**= 63 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 12.92 (s, 1H), 8.21 (dd, *J* = 2.1, 0.9 Hz, 1H), 7.98 (d, *J* = 2.6 Hz, 1H), 7.84 (dd, *J* = 5.6 Hz, *J* = 1 Hz, 1H), 7.83 (*br* s, 1H), 7.53 (dd, *J* = 9.5, 2.0 Hz, 1H), 7.33 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.20 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.81 (td, *J* = 7.7, 1.6 Hz, 1H), 6.71 (td, *J* = 7.6, 1.3 Hz, 1H), 6.07 (dd, *J* = 7.8, 1.6 Hz, 1H), 5.01 (d, *J* = 2.4 Hz, 2H), 3.67 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.5, 146.0, 138.8, 136.4, 134.5, 132.4, 129.5, 127.9, 122.7, 121.3, 121.1, 120.3, 119.9, 119.6, 118.5, 117.9, 114.2, 112.6, 110.6, 79.9, 79.0, 57.0. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br^{35}ClN_3O_2$ $[M+H]^+$ 467.4111, found 468.0107.

4-Bromo-2-(3-((5-bromo-2-(prop-2-yn-1-yloxy)phenyl)amino)-6-methylimidazo[1,2-*a*] pyridin-2-yl)phenol. (1o)



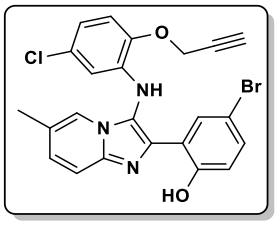
Brown solid; **mp =** 240-242 °C; (358 mg, **Yield**= 68 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 13.25 (s, 1H), 8.06 (s, 1H), 7.92 (*br* s, 1H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.30 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.04 (d, *J* = 2.3 Hz, 1H), 5.01 (d, *J* = 2.4 Hz, 2H), 3.71 (t, *J* = 2.4 1H), 2.33 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.6, 145.1, 139.4, 136.9, 135.4, 132.1, 130.5, 128.9, 123.8, 121.7, 120.7, 119.6, 118.6, 118.0, 116.3, 115.8, 114.2, 114.0, 110.4, 79.4, 79.4, 57.0, 18.1. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{117}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 525.9761, found 525.9767.

4-Bromo-2-(6-methyl-3-((2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl) phenol. (1p)



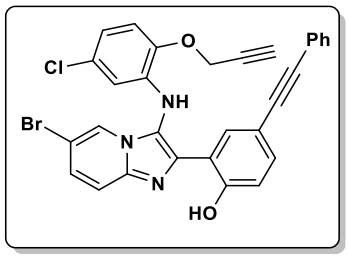
Yellow solid; **mp =** 158-159 °C; (327 mg, **Yield**= 73 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 13.30 (*br* s, 1H), 7.87 (*br* s, 1H), 7.70 (*br* s, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.18 – 7.11 (m, 2H), 6.89 – 6.84 (m, 2H), 6.77 (dd, *J* = 8.8, 7.2 Hz, 1H), 6.15 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.11 (*br* s, 1H), 4.96 (d, *J* = 2.4 Hz, 2H), 2.67 (t, *J* = 2.4 Hz, 1H), 2.31 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 156.8, 145.4, 139.7, 135.6, 134.1, 131.8, 129.2, 128.8, 123.0, 122.7, 120.1, 119.9, 119.1, 118.0, 117.1, 116.1, 112.7, 112.5, 110.6, 78.6, 76.2, 57.0, 18.4. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O_2$ $[M+H]^+$ 448.0656, found 448.0657.

4-Bromo-2-(3-((5-chloro-2-(prop-2-yn-1-yloxy)phenyl)amino)-6-methylimidazo[1,2-*a*] pyridine2-yl)phenol. (1q)



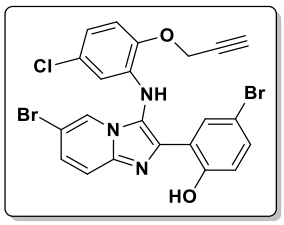
Yellow solid; **mp =** 134-135 °C; (319 mg, **Yield**= 66 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 13.26 (s, 1H), 8.09 (*br* s, 1H), 7.94-7.91 (m, 1H), 7.91 (d, *J* = 2.5 Hz, 1H), 7.71 (dd, *J* = 9.2, 0.9 Hz, 1H), 7.37 (dd, *J* = 9.2, 1.7 Hz, 1H), 7.32 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.94 (d, *J* = 2.5 Hz, 1H), 5.03 (d, *J* = 2.4 Hz, 2H), 3.73 (t, *J* = 2.4 Hz, 1H), 2.34 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.6, 144.7, 139.5, 136.7, 135.4, 133.5, 132.1, 130.5, 129.0, 126.5, 123.8, 120.7, 119.6, 118.7, 118.1, 116.4, 115.4, 111.4, 110.4, 79.6, 79.4, 57.2,18.1. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{17}{}^{79}Br^{35}ClN_3O_2$ $[M+H]^+$ 482.0267, found 482.0260.

2-(6-Bromo-3-((5-chloro-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl) -4-(phenylethynyl)phenol. (1r)



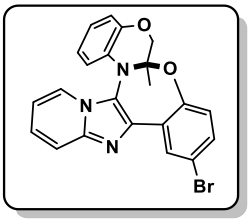
Light Brown solid; **mp =** 199-201 °C; (341 mg, **Yield**= 60 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, CDCl$_3$)** δ (ppm) =12.95 (*br* s, 1H), 7.98 (*br* s, 1H), 7.82 (d, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 9.3 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.32-7.28 (m, 1H), 7.25 (d, 2.1 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 2H), 7.19 (*br* s, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.76 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 4.81 (d, *J* = 2.3 Hz), 2.48 (t, *J* = 2.2 Hz). **^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$)** δ (ppm) = 156.5, 144.1, 142.1, 135.1, 133.5, 131.4 (2c), 130.2, 130.0, 128.3 (2C), 128.1, 127.9, 123.7, 122.5, 120.0, 118.1, 117.4, 115.4, 114.2, 113.7, 112.4, 108.7, 89.7, 87.5, 77.9, 76.7, 57.4. **HRMS-ESI (+)** (m/z): calc. for $C_{30}H_{19}{}^{79}Br^{35}ClN_3O_2$ $[M+H]^+$ 568.0423, found 568.0424.

4-Bromo-2-(6-bromo-3-((5-chloro-2-(prop-2-yn-1-yloxy)phenyl)amino)imidazo[1,2-*a*] pyridin-2-yl)phenol. (1s)



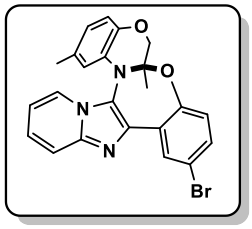
Brown solid; **mp =** 140-151 °C; (334 mg, **Yield**= 61 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 13.90 (*br* s, 1H), 8.03 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 2.6 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.48 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.29 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.10 (dd, *J* =7.5, 2.5 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.89 (d, *J* = 2.8 Hz,1H), 5.01 (d, *J* = 2.4 Hz, 2H), 3.71 (t, *J* = 2.4 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 148.2, 144.8, 140.6, 136.6, 135.5, 132.2, 129.3, 127.3, 126.5, 123.5, 119.8, 118.7, 118.5, 117.0, 115.5, 114.1, 112.2, 111.5, 108.4, 79.6, 79.4, 57.2. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{14}{}^{79}Br_2{}^{35}ClN_3O_2$ $[M+H]^+$ 545.9216, found 545.9214.

16-Bromo-12a-methyl-12,12a-dihydrobenzo[f]benzo[5,6][1,4]oxazino[3,4-b]pyrido[2',1':2,3]imidazo[4,5-d][1,3]oxazepine. (2a)



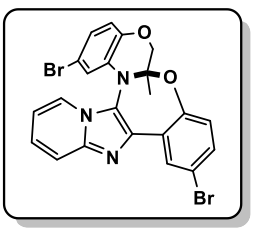
Colorless solid; **mp =** 192-194 °C; (72 mg, **Yield**= 83 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ (ppm) = 8.45 (*br* s, 1H), 8.03 (d, *J* = 6.8 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.46 - 7.35 (m, 2H), 7.06 (dd, *J* = 6.8, 6.7 Hz, 1H), 6.95 (t, *J* = 9.2, 8.7 Hz, 2H), 6.84 (t, *J* = 7.7 Hz, 1H), 6.71 (t, *J* = 7.7 Hz, 1H), 5.92 (d, *J* = 8.0 Hz, 1H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.53 (d, *J* = 11.3 Hz, 1H), 1.19 (s, 3H). **^{13}C {^{1}H} NMR (75 MHz, DMSO-*d*$_6$)** δ (ppm) = 151.3, 143.6, 142.7, 141.5, 133.7, 131.7, 130.0, 129.3, 126.0, 123.9, 123.5, 123.1, 122.1, 121.1, 117.5, 116.6, 115.2, 114.2, 113.1, 80.9, 71.3, 18.9. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{16}{}^{79}BrN_3O_2$ $[M+H]^+$ 434.0505, found 434.0500.

16-Bromo-8,12*a*-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4- *b*]pyrido [2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2b)



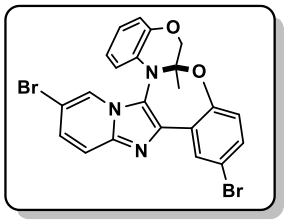
Colorless solid; **mp =** 173-175 °C; (75 mg, **Yield**= 84 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm)= 8.64 (d, *J* = 2.6 Hz, 1H), 7.86 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.37-7.33 (m, 1H), 7.32 (dd, *J* = 8.8, 2.4 Hz, 1H), 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.94-6.91 (m, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.69 (dd, *J* = 8.1, 1.1 Hz, 1H, 1H), 5.83 (d, *J* = 1.2 Hz, 1H), 4.67 (d, *J* = 11.1 Hz, 1H), 4.47 (d, *J* = 11.1 Hz, 1H), 2.06 (s, 3H), 1.29 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm)= 151.5, 143.2, 141.6, 135.1, 132.1, 131.6, 130.1, 129.6, 125.5, 123.7 (2C), 122.9, 122.8, 121.4, 118.0, 116.9, 116.0, 115.3, 112.8, 81.0, 72.4, 20.8, 19.7. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O_2$ $[M+H]^+$ 448.0656, found 448.0655.

8,16-Dibromo-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-d][1,3]oxazepine. (2c)



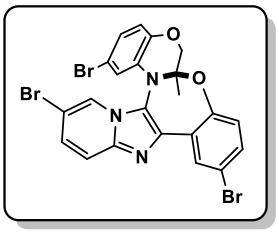
Colorless solid; **mp =** 206-207 °C; (77 mg, **Yield**= 75 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (250 MHz, DMSO-*d*$_6$)** δ (ppm) = δ 8.44 (d, *J* = 2.6 Hz, 1H), 8.09 (d, *J* = 6.8 Hz, 1H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.14-6.89 (m, 4H), 5.95 (d, *J* = 2.4 Hz, 1H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 1.18 (s, 3H). **^{13}C {^{1}H} NMR (63 MHz, DMSO-*d*$_6$)** δ (ppm) = 151.5, 143.4, 134.4, 132.4, 132.0, 129.8, 126.8, 125.1, 124.4, 123.9, 123.3, 120.7, 119.0, 118.2, 117.8, 114.8, 113.9, 113.1, 81.0, 71.6, 19.0. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 511.9605, found 511.9604.

3,16-dibromo-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-b]pyrido pyrido[2',1':2,3]imidazo[4,5-d][1,3]oxazepine. (2d)



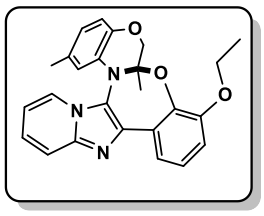
Colorless solid; **mp =** 236-238 °C; (73 mg, **Yield**= 71 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane)**^{1}H NMR (250 MHz, $CDCl_3$)** δ (ppm)= 8.58 (*br* s, 1H), 7.97 (*br* s, 1H), 7.60 (d, *J* = 9.6 Hz, 1H), 7.39- 7.30 (m, 2H), 7.05 – 6.85 (m, 3H), 6.75 (dd, *J* = 7.6, 7.3 Hz, 1H), 6.02 (d, *J* = 8.0 Hz, 1H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.48 (d, *J* = 11.1 Hz, 1H), 1.28 (s, 3H). **^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$)** δ (ppm)= 151.5, 143.8, 141.5, 132.4, 130.1, 129.7, 128.8, 123.7, 122.7(2c), 122.5, 122.1, 121.4, 118.6(2C), 117.2, 115.4, 107.7, 102.2, 80.7, 72.3, 19.6. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 511.9605, found 511.9604.

3,8,16-Tribromo-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2e)



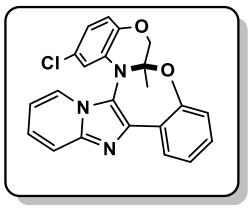
Colorless solid; **mp =** 256-257 °C; (77 mg, **Yield**= 65 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (250 MHz, $CDCl_3$)** δ (ppm)= 8.57 (*br* s, 1H), 7.94 (*br* s, 1H), 7.61 (d, *J* = 9.25 Hz, 1H), 7.45 – 7.23 (m, 2H), 7.09 – 6.79 (m, 3H), 6.09 (*br* s, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 1.26 (s, 3H). **^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$)** δ (ppm)= 151.3, 143.1, 141.8, 136.3, 132.6, 131.0, 130.3, 129.3, 125.6, 123.7, 122.3, 120.6, 118.8(2C), 118.7, 118.2, 115.6, 113.9, 108.1, 80.6, 72.4, 19.5. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{14}{}^{79}Br_3N_3O_2$ $[M+H]^+$ 589.8710, found 589.8706.

14-Ethoxy-8,12*a*-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*]pyrido [2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2f)



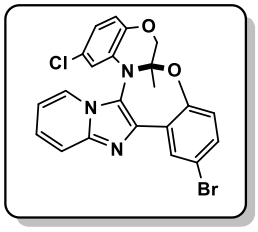
Colorless solid; **mp =** 154-156 °C; (30 mg, **Yield**= 36 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.81 (d, *J* = 6.8 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.33 (dd, *J* = 7.4, 7.2 Hz, 1H), 7.10 (dd, *J* = 8.0, 7.8 Hz, 1H), 6.94-6.87 (m, 3H), 6.65 (d, *J* = 8.3 Hz, 1H), 5.79 (*br* s, 1H), 4.65 (d, *J* = 11.0 Hz, 1H), 4.51 (d, *J* = 11.0 Hz, 1H), 4.14-4.01 (m, 2H), 2.04 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.38 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 151.3, 143.1, 142.9, 142.0, 136.5, 131.5, 130.0, 125.1, 123.6, 122.9, 122.8, 122.2, 121.0, 120.0, 117.9, 116.9, 115.7, 115.0, 112.5, 84.1, 72.2, 65.4, 20.9, 20.8, 15.0. **HRMS-ESI (+)** (m/z): calc. for $C_{25}H_{23}N_3O_3$ $[M+H]^+$ 414.1812, found 414.1814.

8-Chloro-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*]pyrido[2', 1' :2, 3]imidazo[4,5-*d*][1,3]oxazepine. (2g)



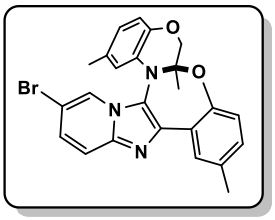
Colorless solid; **mp =** 203-204 °C; (22 mg, **Yield**= 28 %); R_f = 0.4 (1:6 ethyl acetate/*n*- Hexane); **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm)= 8.43 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.28 (dd, *J* =8.4, 7.9 Hz, 1H), 7.23-7.16 (m, 1H), 7.10 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.99 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.87 (dd, *J* = 7.0, 6.7 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.92 (d, *J* = 2.4 Hz, 1H), 4.63 (d, *J* = 11.1 Hz, 1H), 4.39 (d, *J* = 11.1 Hz, 1H), 1.21 (s, 3H). **^{13}C {^{1}H} NMR (76 MHz, $CDCl_3$)** δ (ppm)= 152.2, 143.2, 142.6, 131.2, 129.8, 128.0, 126.7, 125.8, 122.8, 122.4, 122.1, 121.9, 120.4, 120.2, 118.1, 118.0, 115.6, 113.2, 80.4, 72.6, 19.6. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{16}{}^{35}ClN_3O_2$ $[M+H]^+$ 390.1006, found 390.1005.

16-Bromo-8-chloro-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido [2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2h)



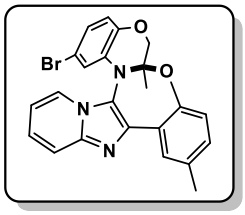
Colorless solid; **mp =** 147-148 °C; (72 mg, **Yield**= 77 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (250 MHz, $CDCl_3$)** δ (ppm) = 8.62 (*br* s, 1H), 7.79 (d, *J* = 6.7 Hz, 1H), 7.71 (d, *J* = 9 Hz, 1H), 7.36- 7.30 (m, 2H), 6.99-6.76 (m, 3H), 5.97 (*br* s, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 1.26 (s, 3H). **^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$)** δ (ppm)= 151.3, 143.4, 142.5, 135.3, 132.2, 131.0, 130.2, 126.7, 125.7, 123.6, 122.4, 122.3, 118.2, 118.0(2C), 115.6(2C), 113.1, 80.6, 72.4, 19.5. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br{}^{35}ClN_3O_2$ $[M+H]^+$ 468.0111, found 468.0105.

3-Bromo-8,12*a*,16-trimethyl-12,12*a*-dihydrobenzo[f]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2i)



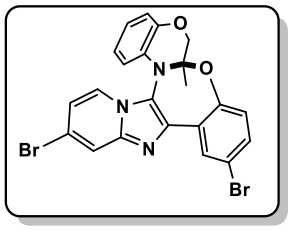
light Yellow solid; **mp =** 154-156 °C; (62 mg, **Yield**= 67 %); R_f = 0.4 (1:6 ethyl acetate/*n*- Hexane); **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm)= 8.17 (*br* s, 1H), 7.91 (*br* s, 1H), 7.58 (d, *J* = 9.5 Hz, 1H), 7.30 (dd, *J* = 9.5, 1.9 Hz, 1H), 6.99 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.60 (dd, *J* = 8.1, 2.4 Hz, 1H), 5.72 (*br* s, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 1H), 2.29 (s, 3H), 1.99 (s, 3H), 1.18 (s, 3H). **^{13}C {^{1}H} NMR (76 MHz, $CDCl_3$)** δ (ppm)= 150.4, 141.7, 141.4, 137.2, 132.0, 131.6, 130.8, 129.7, 128.9, 127.8, 123.0, 122.6, 121.9, 121.2, 119.7, 118.4, 117.0, 115.9, 107.6, 80.5, 72.5, 20.9, 20.5, 19.6. **HRMS-ESI (+)** (m/z): calc. for $C_{24}H_{20}{}^{79}BrN_3O_2$ $[M+H]^+$ 462.0812, found 462.0812.

8-Bromo-12*a*,16-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido[2', 1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2j)



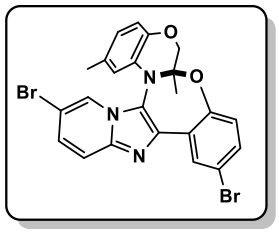
Colorless solid; **mp =** 180-182 °C; (66 mg, **Yield**= 74 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm)= 8.33 (d, *J* = 1.3 Hz, 1H), 7.83 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.80 (d, *J* = 9.4 Hz, 1H), 7.39-7.34 (m, 1H), 7.10 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.00 – 6.98 (m, 1H), 6.98 – 6.93 (m, 3H), 6.95 (dd, *J* = 6.8, 1.2 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.13 (d, *J* = 2.2 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H), 4.48 (d, *J* = 11.1 Hz, 1H), 2.41 (s, 3H), 1.29 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm)= 150.0, 143.2, 136.3, 132.3, 131.6, 130.8, 128.0, 125.8, 125.1, 122.4, 121.7, 120.2, 119.9, 118.5, 118.3 (2C), 117.9, 113.8, 113.2, 80.2, 72.6, 20.5, 19.5. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O_2$ $[M+H]^+$ 448.0656, found 448.0652.

2,16-Dibromo-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4*b*]pyrido[2', 1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2k)



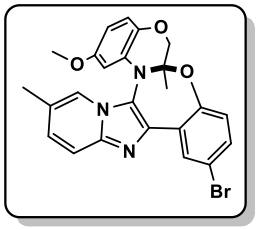
Colorless solid; **mp =** 239-240 °C; (77 mg, **Yield**= 75 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm)= 8.65 (d, *J* = 2.6 Hz, 1H), 8.07 (*br* s, 1H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.39 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.96-6.90 (m,1H), 6.80-6.74 (m, 1H), 6.04 (dd, *J* = 8.1, 1.4 Hz, 1H), 4.72 (d, *J* = 11.2 Hz, 1H), 4.51 (d, *J* = 11.2 Hz, 1H), 1.33 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm)= 151.7, 143.9, 141.6, 133.7, 130.6, 129.2, 124.0, 123.4 (2C), 123.3, 122.3, 121.5, 119.0 (2C), 117.6, 115.9, 115.3, 80.9, 72.3, 19.7. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 511.9605, found 511.9608.

3,16-Dibromo-8,12*a*-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b* pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine]. (2l)



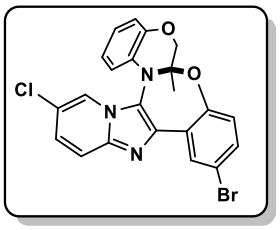
Colorless solid; **mp** = 180-185 °C; (75 mg, **Yield**= 71 %); R_f = 0.4 (1:6 ethyl acetate/*n*- Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.60 (d, *J* = 2.6 Hz, 1H), 8.01 (*br* s, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.40 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.35 (dd, *J* =8.7, 2.6 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 5.82 (*br* s, 1H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.47 (d, *J* = 11.1 Hz, 1H), 2.10 (s, 3H), 1.29 (s, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 151.6, 141.6, 136.0, 132.4, 131.7, 130.1 (2C), 129.3, 129.0, 123.7, 123.2, 122.6, 122.3, 121.4, 118.6, 117.1, 115.9, 115.3, 107.7, 80.9, 72.3, 20.9, 19.7. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{17}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 525.9761, found 525.9763.

16-Bromo-8-methoxy-3,12*a*-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4] oxazino[3,4-*b*]pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2m)



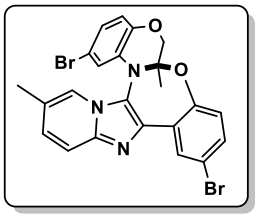
Colorless solid; **mp =** 215-217 °C; (71 mg, **Yield**= 74 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.62 (d, *J* = 2.6 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.33 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.20 (dd, *J* = 9.5, 1.6 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.46 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.67 (d, *J* = 2.8 Hz, 1H), 4.67 (d, *J* = 11.1 Hz, 1H), 4.46 (d, *J* = 11.1 Hz, 1H), 3.58 (s, 3H), 2.38 (s, 3H), 1.29 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm)= 154.7, 151.4, 142.3, 137.9, 134.8, 132.0, 130.8, 130.1 (2C), 129.0, 123.7, 123.0, 122.8, 120.8, 120.3, 117.3 (2C), 115.4, 106.2, 102.9, 81.0, 72.5, 55.6, 19.8, 18.4. **HRMS-ESI (+)** (m/z): calc. for $C_{24}H_{20}{}^{79}BrN_3O_3$ $[M+H]^+$ 478.0761, found 478.0763.

16-Bromo-3-chloro-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2n)



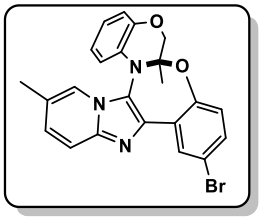
Colorless solid; **mp =** 215-216 °C; (63 mg, **Yield**= 67 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm)= 8.64 (d, *J* = 2.5 Hz, 1H), 7.94 (d, *J* = 1.4 Hz, 1H), 7.77 (d, *J* = 9.6 Hz, 1H), 7.39-7.34 (m, 2H), 7.05 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.95 (td, *J* = 7.7, 1.4 Hz, 1H)., 6.79 (td, *J* = 7.7, 1.6 Hz, 1H), 6.05 (dd, *J* = 8.1, 1.5 Hz, 1H), 4.72 (d, *J* = 11.2 Hz, 1H), 4.52 (d, *J* = 11.2 Hz, 1H), 1.33 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm)= 151.7, 147.2, 143.9, 140.6, 134.2, 133.3, 130.4, 129.4, 128.8, 123.9, 123.2, 122.8, 122.3, 121.6, 120.8, 117.7, 117.5, 115.7, 115.4, 80.9, 72.3, 19.7. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br^{35}ClN_3O_2$ $[M+H]^+$ 468.0111, found 468.0107.

8,16-Dibromo-3,12*a*-dimethyl-12,12*a*-dihydrobenzo[f]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2o)



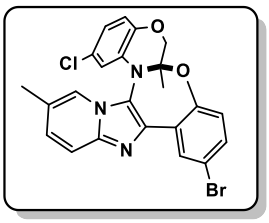
Colorless solid; **mp =** 228-230 °C; (80 mg, **Yield**= 76 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (250 MHz, $CDCl_3$)** δ (ppm) = 8.41 (*br* s, 1H), 7.92 (*br* s, 1H), 7.63 (d, *J* = 9.4 Hz, 1H), 7.40 (d, *J* = 9.1 Hz, 1H), 7.29 (d, *J* = 9.7 Hz, 1H), 7.09-6.80 (m, 3H), 5.94 (*br* s, 1H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 2.28 (s, *J* = 12.4 Hz, 3H), 1.16 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 151.2, 143.1, 142.6, 135.3, 132.1, 131.5, 130.2, 129.0, 128.8, 125.2, 123.6, 123.2, 122.8, 120.2, 119.9, 118.5, 117.6, 115.5, 113.89, 80.6, 72.5, 19.6, 18.5. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{17}{}^{79}Br_2N_3O_2$ $[M+H]^+$ 525.9761, found 525.9760.

16-Bromo-3,12*a*-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]oxazino[3,4-*b*] pyrido[2',1'2,3]imidazo[4,5-*d*][1,3]oxazepine. (2p)



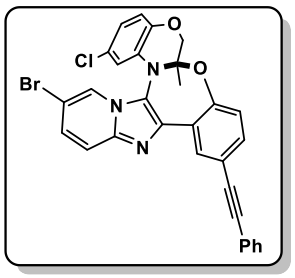
Colorless solid; **MP=** 252-253 °C; (75 mg, **Yield**= 84 %); R_f = 0.3 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 8.62 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J*= 9.2 Hz, 1H), 7.64 (*br* s, 1H), 7.32 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.20 (d, *J* = 9.2 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.91 (td, *J* = 7.7, 1.5 Hz, 1H), 6.75 (td, *J* = 7.7, 1.5 Hz, 1H), 6.06 (dd, *J* = 8.1, 1.4 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H), 4.51 (d, *J* = 11.0 Hz, 1H), 2.38 (s, 3H), 1.31 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm)= 151.4, 143.8, 142.4, 134.9, 131.9, 130.2, 130.0, 128.7, 123.6, 123.1, 122.8, 122.4, 122.0, 121.1, 120.3, 117.4, 117.1, 115.8, 115.3, 80.7, 72.4, 19.7, 18.3. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O_2$ $[M+H]^+$ 448.0656, found 448.0655.

16-Bromo-8-chloro-3,12*a*-dimethyl-12,12*a*- dihydrobenzo[*f*]benzo[5,6][1,4] oxazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2q)



Colorless solid; **mp =** 238-240 °C; (79 mg, **Yield**= 82 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 8.63 (d, *J* = 2.5 Hz, 1H), 7.67 (d, *J* = 9.3 Hz, 1H), 7.61 (*br* s, 1H), 7.34 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.23 (d, *J* = 9.2 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.86 (dd, *J* = 8.4, 2..0 Hz, 1H), 6.01 (d, *J* = 2.1 Hz, 1H), 4.70 (d, *J* = 11.2 Hz, 1H), 4.49 (d, *J* = 11.2 Hz, 1H), 2.40 (s, 3H), 1.29 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm) = 151.1, 142.6, 135.2, 132.1, 131.1, 130.1, 129.0, 126.7, 123.6, 123.2, 122.8, 122.2, 120.2, 119.9, 118.0, 117.5, 115.7, 115.5, 80.5, 72.5, 19.9, 18.4. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{17}{}^{79}Br{}^{35}ClN_3O_2$ $[M+H]^+$ 482.0267, found 482.0268.

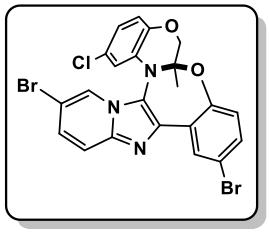
3-Bromo-8-chloro-12*a*-methyl-16-(phenylethynyl)-12,12*a*-dihydrobenzo[*f*] benzo oxazino[3,4-*b*]pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2r)



Colorless solid; **mp =** 200-201 °C; (79 mg, **Yield**= 69 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm)= 8.71 (d, *J* = 2.2 Hz, 1H), 8.02 (*br* s, 1H), 7.79 (d, *J* = 9.6 Hz, 1H), 7.58- 7.55 (m, 2H), 7.52-7.44 (m, 2H), 7.40 – 7.33 (m, 3H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.91 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.02 (d, *J* = 2.3 Hz, 1H), 4.74 (d, *J* = 11.2 Hz, 1H), 4.51 (d, *J* = 11.3 Hz, 1H), 1.33 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm)= 166.0, 152.2, 142.6, 141.0, 135.0, 133.5, 131.7 (2C), 131.6 (2C), 130.4, 128.4 (2C), 128.2, 127.0, 123.3, 123.0, 122.4, 120.4, 118.5, 118.3, 118.2, 115.3, 109.4, 89.5, 88.4, 81.0, 72.4, 19.7. **HRMS-ESI (+)** (m/z): calc. for $C_{30}H_{19}{}^{79}Br{}^{35}ClN_3O_2$ $[M+H]^+$ 568.0423, found 568.0424.

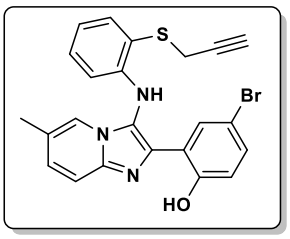
3,16-Dibromo-8-chloro-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]

oxazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (2s)



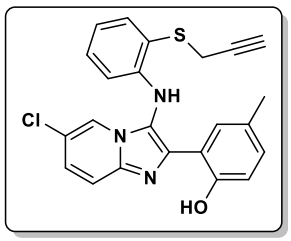
Colorless solid; **mp =** 223-225 °C; (72 mg, **Yield**= 66 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.60 (d, *J* = 2.6 Hz, 1H), 7.97-7.96 (m, 1H), 7.64 (d, *J* = 9.5 Hz, 1H), 7.42 (dd, *J* = 9.5, 1.8 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.88 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.99 (d, *J* = 2.3 Hz, 1H), 4.70 (d, *J* = 11.2 Hz, 1H), 4.49 (d, *J* = 11.2 Hz, 1H), 1.29 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 151.3, 142.6, 141.8, 136.3, 132.6, 130.7, 130.3, 129.3, 126.8, 123.7, 122.6, 122.3, 122.2, 120.6, 118.9, 118.3, 115.6, 115.4, 108.2, 80.6, 72.4, 19.5. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{14}{}^{79}Br_2{}^{35}ClN_3O_2$ $[M+H]^+$ 545.9216, found 545.9214.

4-Bromo-2-(6-methyl-3-((2-(prop-2-yn-1-ylthio)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl)phenol. (3a)



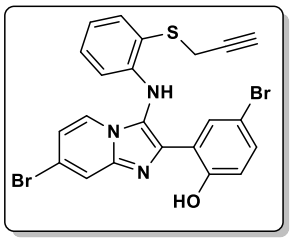
Light yellow solid; **mp =** 210-211 °C; (316 mg, **Yield**= 68 %); R_f = 0.35 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ (ppm) = δ 13.17 (*br* s, 1H), 8.06 (d, *J* = 2.2 Hz, 1H), 7.92 (*br* s, 1H), 7.87 (*br* s, 1H), 7.67 (d, *J* = 11.4 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 9.2 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.03 (dd, *J* = 7.8, 7.3 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.82 – 6.73 (m, 1H), 5.96 (d, *J* = 8.4 Hz,1H), 3.82 (d, *J* = 2.4 Hz, 2H), 3.22 (d, *J* = 2.5 Hz, 1H), 2.28 (s, 3H). **^{13}C {^{1}H} NMR (75 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.1, 145.7, 139.1, 136.3, 135.2, 131.6, 130.6, 129.8, 128.7, 123.1, 120.4, 119.5, 119.0, 118.4, 118.2, 117.6, 115.8, 111.7, 109.9, 80.3, 74.6, 22.6, 17.7. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3OS$ $[M+H]^+$ 464.0433, found 464.0427.

2-(6-Chloro-3-((2-(prop-2-yn-1-ylthio)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl)-4-methyl phenol. (3b)



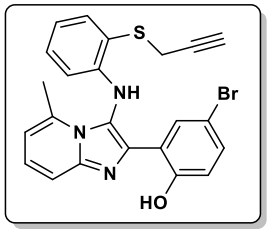
Yellow solid; **mp =** 187-189 °C; (273 mg, **Yield**= 65 %); R_f = 0.35 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 12.42 (s, 1H), 8.30 (dd, *J* = 2.1, 0.9 Hz, 1H), 8.06 (*br* s, 1H), 7.84 (dd, *J* = 9.5, 0.9 Hz, 1H), 7.60 (dd, *J* = 7.6, *J* =1.6, 1H), 7.58 (*br* s, 1H), 7.52 (dd, *J* = 9.5, 2.1 Hz, 1H), 7.09-7.04 (m, 1H), 6.99 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.82 (td, *J* = 7.5, 1.2 Hz,1H), 6.05 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.85 (d, *J* = 2.6 Hz, 2H), 3.23 (t, *J* = 2.6 Hz, 1H), 2.08 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 155.1, 146.1, 139.0, 138.1, 136.7, 131.0, 130.7, 127.6, 127.5, 125.4, 121.4, 120.9, 120.0, 119.3, 118.1, 117.8, 117.1, 116.2, 112.4, 80.9, 75.0, 22.6, 20.8. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{35}ClN_3OS$ $[M+H]^+$ 420.0934, found 420.0937.

4-bromo-2-(7-bromo-3-((2-(prop-2-yn-1-ylthio)phenyl)amino)imidazo[1,2-*a*]pyridin-2-yl) phenol. (3c)



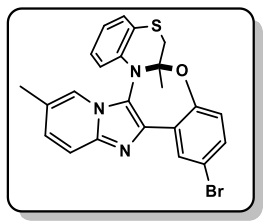
Light brown solid; **mp =** 188-189 °C; (339 mg, **Yield**= 64 %); R_f = 0.35 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ(ppm) = 12.79 (*br* s, 1H), 8.19 (dd, *J* = 2.0, 0.8 Hz, 1H), 8.15 (*br* s, 1H), 8.04 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.95 (d, *J* = 2.5 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.34 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.26 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.10-7.04 (m, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.83 (td, *J* = 7.5, 1.3 Hz, 1H), 6.05 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.83 (d, *J* = 2.6 Hz, 2H), 3.27 (t, *J* = 2.6 Hz, 1H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.4, 145.8, 140.7, 136.7, 136.1, 132.5, 131.1, 129.5, 124.7, 120.4, 120.2, 119.6, 119.5, 119.1, 118.7, 118.2, 117.5, 112.4, 110.5, 80.9, 75.1, 23.1. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}{}^{79}Br_2N_3OS$ $[M+H]^+$ 527.9377, found 527.9374.

4-Bromo-2-(5-methyl-3-((2-(prop-2-yn-1-ylthio)phenyl)amino)imidazo[1,2-*a*] pyridin-2-yl)phenol. (3d)



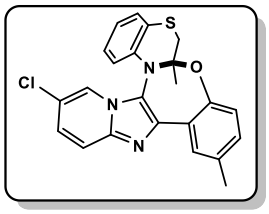
Yellow solid; **MP=** 224-226 °C; (265 mg, **Yield**= 57 %); R_f = 0.35 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) = 13.24 (*br* s, 1H), 8.12 (*br* s, 1H), 8.01 (d, *J* = 2.5 Hz, 1H), 7.65 (d, *J* = 9.9 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.38 (dd, *J* = 9.0, 6.9 Hz, 1H), 7.31 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.13-7.08 (m, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.84-6.76 (m, 2H), 6.01 (d, *J* = 6.9 Hz, 1H), 3.79 (d, *J* = 2.6 Hz, 1H), 3.77 (d, *J* = 2.6 Hz, 1H), 3.22 (t, *J* = 2.6 Hz, 1H), 2.68 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) = 156.8, 148.2, 142.1, 136.9, 136.8, 132.3, 131.3, 129.1, 127.6, 119.9, 119.6 (2C), 119.5, 118.6, 116.9, 115.3, 115.1, 112.9, 110.4, 80.5, 75.1, 23.0, 18.6. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3OS$ $[M+H]^+$ 464.0428, found 464.0428.

16-Bromo-3,12*a*-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]thiazino[3,4-*b*] pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (4a)



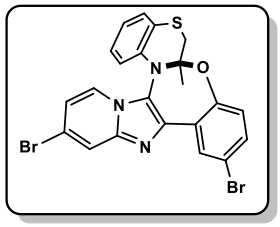
Cream solid; **mp =** 226-227 °C; (67 mg, **Yield**= 72 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 8.71 (d, *J* = 2.5 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.52 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.36 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.11 (dd, *J* = 9.2, 1.8 Hz, 1H), 7.05 (ddd, *J* = 7.6, 7.4, 1.8 Hz, 1H), 7.00 (ddd, *J* = 7.4, 7.1, 1.8 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.73 (br s, 1H), 6.26 (dd, *J* = 7.7, 1.6 Hz, 1H), 3.48 (d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 13.6, 1H), 2.18 (s, 3H), 1.62 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)** δ (ppm) = 151.0, 141.6, 139.9, 132.4, 131.6, 129.6, 129.5, 129.2, 128.7, 127.8, 123.7, 122.6, 122.2, 122.0, 121.4, 121.0, 119.9, 116.7, 116.2, 93.4, 43.9, 22.8, 18.4. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3OS$ $[M+H]^+$ 464.0428, found 464.0426.

3-Chloro-12*a*,16-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]thiazino[3,4-*b*]pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (4b)



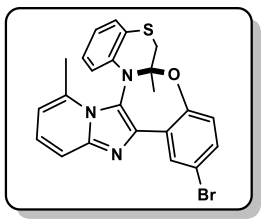
Colorless solid; **mp =** (177-178) °C; (61 mg, **Yield**= 73 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.38 (d, *J* = 2.8 Hz,1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.54 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.22 (dd, *J* = 9.5, 2.0 Hz, 1H), 7.12 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.06 (ddd, *J* = 7.6, 7.0, 1.9 Hz, 1H), 7.02 (td, *J* = 7.4, 1.6 Hz, 1H), 6.98 (dd, *J* = 2.0, 0.9 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.25 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.47 (d, *J* = 13.6 Hz, 1H), 3.35 (d, *J* = 13.6 Hz, 1H), 2.46 (s, 3H), 1.62 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 150.1, 140.3, 139.5, 133.1, 131.4, 130.6, 129.8, 129.7, 128.0, 127.5, 124.9, 123.0, 122.0, 121.6, 121.2, 120.9, 120.2, 119.6, 117.3, 93.4, 43.9, 22.7, 20.7. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{35}ClN_3OS$ $[M+H]^+$ 420.0934, found 420.0665.

2,16-Dibromo-12*a*-methyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]thiazino[3,4-*b*]pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (4c)



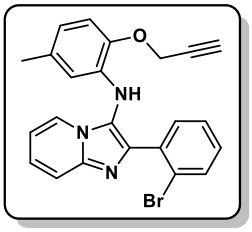
Colorless solid; **mp =** 185-187 °C; (73 mg, **Yield**= 69 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.67 (d, *J* = 2.5 Hz, 1H), 7.86 (*br* s, 1H), 7.54 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.07 (ddd, *J* = 7.5, 7.1, 1.6 Hz, 1H), 7.02 (ddd, *J* = 7.5, 7.3, 1.6 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.79 (d, *J* = 7.3 Hz, 1H), 6.74 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.28 (dd, *J* = 7.8, 1.5 Hz, 1H), 3.47 (d, *J* = 13.7 Hz, 1H), 3.34 (d, *J* = 13.7 Hz, 1H), 1.62 (s, 3H). **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)** δ (ppm) = 151.2, 142.6, 139.7, 133.4, 131.8, 129.8, 129.7, 128.0, 127.7, 125.2, 123.7, 122.9, 121.9, 119.9, 119.8, 119.4, 119.0, 116.3, 116.0, 93.8, 44.1, 22.5. **HRMS-ESI (+)** (m/z): calc. for $C_{22}H_{15}Br_2N_3OS$ $[M+H]^+$ 527.9377, found 527.9377.

16-Bromo-4,12*a*-dimethyl-12,12*a*-dihydrobenzo[*f*]benzo[5,6][1,4]thiazino[3,4-*b*]pyrido[2',1':2,3]imidazo[4,5-*d*][1,3]oxazepine. (4d)



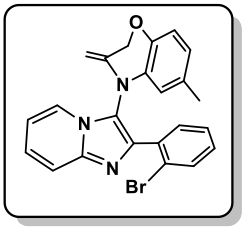
Cream solid; **mp =** 213-214 °C; (62 mg, **Yield**= 67 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (500 MHz, $CDCl_3$)** δ (ppm) = 8.46 (d, *J* = 2.6 Hz), 7.57 (d, *J* = 9.0 Hz), 7.35-7.29 (m, 2H), 7.16 (dd, *J* = 9.0, 6.7 Hz), 6.91 (d, *J* = 8.5 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.47 (d, *J* = 6.9 Hz), 5.92 (d, *J* = 8.0 Hz), 3.49 (*br* s, 2H), 2.39 (s, 3H), 1.75 (s, 3H). **^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)** δ (ppm) = 151.5, 145.5, 143.8, 138.0, 135.9, 131.9, 131.8, 130.5, 128.6, 128.5, 127.3, 127.2, 125.8, 124.8, 124.0, 121.9, 118.6, 116.0, 113.8, 93.4, 40.6, 26.2, 18.0. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3OS$ $[M+H]^+$ 464.0428, found 464.0424.

2-(2-Bromophenyl)-N-(5-methyl-2-(prop-2-yn-1-yloxy)phenyl)imidazo[1,2-a]pyridin-3-amine. (5)



Green solid; **mp =** 196-198 °C; (346 mg, **Yield**= 80 %); R_f = 0.35 (1:2 ethyl acetate/*n*-Hexane); **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.85 (d, *J* = 6.9 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.32 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.19 (td, *J* = 7.7, 1.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.80 (dd, *J* = 6.9, 6.8 Hz, 1H), 6.53 (d, *J* = 8.1, 2.1 Hz, 1H), 6.23 (*br* s, 1H), 5.89 (d, *J* = 2.1 Hz,1H), 4.74 (d, *J* = 2.4 Hz, 2H), 2.50 (t, *J* = 2.4 Hz, 1H), 2.06 (s, 3H). **^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 143.1, 142.3, 139.2, 134.9, 134.5, 132.9, 132.5, 132.4, 132.2, 129.6, 127.2, 124.8, 123.4, 123.2, 119.4, 119.2, 118.0, 113.0, 112.2, 78.7, 75.7, 57.2, 20.9. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O$ $[M+H]^+$ 432.0713, found 432.0722.

4-(2-(2-Bromophenyl)imidazo[1,2-*a*]pyridin-3-yl)-6-methyl-3-methylene-3,4-dihydro-2H-benzo[*b*][1,4]oxazine. (6)

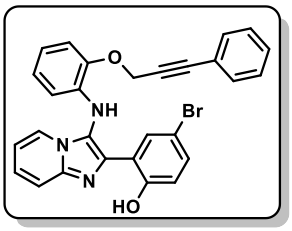


Colorless solid; **mp =** 221-223 °C; (78 mg, **Yield**= 90 %); R_f = 0.5 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.79 (d, *J* = 9.1 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.37-7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 7.20-7.13 (m, 1H), 6.85 (td, *J* = 6.9, 1.7 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.60 – 6.54 (m, 1H), 6.24 – 6.21 (m, 1H), 4.65 (d, *J* = 12.4 Hz, 1H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.03 (*br* s, 1H), 3.79 (d, *J* = 1.6 Hz, 1H), 2.08 (s, 3H). **^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 143.3, 143.1, 141.9, 139.5, 133.8, 132.3, 131.4, 130.1, 129.9, 127.1, 125.6, 123.3, 122.8, 118.7, 118.3, 117.3, 115.0, 114.5, 112.9, 112.6, 87.5, 67.8, 20.8. **HRMS-ESI (+)** (m/z): calc. for $C_{23}H_{18}{}^{79}BrN_3O$ $[M+H]^+$ 432.0713, found 432.0716.

The mixture of intermediate and product of 2a (crude)

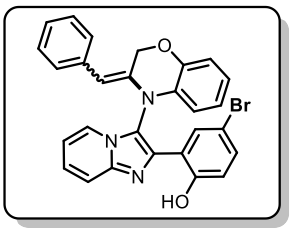
Colorless solid; **^{1}H NMR (300 MHz, $CDCl_3$)** (mixture of intermediate and product (10:1)) δ (ppm) = 13.03 (s, 1H, intermediate), 7.85 (d, *J* = 7.2 Hz, 1H, product) 7.78 – 7.63 (m, 2H, mixture of intermediate and product), 7.61 (d, *J* =2.1 Hz, 1H, mixture of intermediate and product), 7.46-7.34 (m, 1H, mixture of intermediate and product), 7.33 – 7.21 (m, 1H, mixture of intermediate and product), 7.07 (dd, *J* = 8.0, 2.0 Hz, 1H, intermediate), 7.02-6.81 (m, 3H, mixture of intermediate and product), 6.74 (t, *J* = 8.1 Hz, 1H, mixture of intermediate and product), 6.18 (d, *J* = 8.1 Hz, 1H, intermediate), 6.04 (d, *J* = 8.0 Hz, 1H, product), 4.85 (*br* s, 2H, intermediate), 4.70 (d, *J* = 11.1 Hz, 1H, product), 4.49 (d, *J* = 11.1 Hz, 1H, product), 4.12 (s, 1H, intermediate), 3.74 (s, 1H, intermediate), 1.29 (s, 3H, product). **^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** (mixture of intermediate and product) δ (ppm) = 156.5, 145.8, 140.9, 138.1, 137.8, 132.2, 128.9, 128.5, 126.2, 122.6, 122.0, 121.6, 118.8, 117.1, 116.8, 116.6, 114.3, 113.5, 113.2, 110.5, 87.4, 67.5.

4-bromo-2-(3-((2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)amino)imidazo[1,2-a]pyridin-2-yl)phenol. (7a)



Yellow solid; **mp =** 153-155 °C; (254 mg, **Yield**= 50 %); R_f = 0.4 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 13.22 (br s, 1H), 7.91 (s, 1H), 7.88 (d, *J* = 6.8 Hz, 1H), 7.62 – 7.44 (m, 3H), 7.42 – 7.23 (m, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.87 (dd, *J* = 8.7, 8.3 Hz, 2H), 6.74 (dd, *J* = 7.2, 7.1 Hz, 2H), 6.17 (s, 1H), 6.12 (d, *J* = 6.8 Hz, 1H), 5.17 (s, 2H).**^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 156.3, 145.3, 139.8, 136.3, 133.6, 131.5, 131.4, 128.5, 128.3, 127.8, 125.4, 122.1, 121.7, 119.6, 118.6, 117.4, 117.1, 116.2, 112.6, 112.5, 112.0, 110.2, 87.2, 83.5, 57.5. **HRMS-ESI (+)** (m/z): calc. for $C_{28}H_{21}{}^{79}BrN_3O_2$ $[M+H]^+$ 510.0801, found 510.0803.

2-(3-(3-benzylidene-2,3-dihydro-4H-benzo[b][1,4]oxazin-4-yl)imidazo[1,2-a]pyridin-2-yl)-4-bromophenol. (8a)



Colorless solid; **mp =** 189-191 °C; (55 mg, **Yield**= 54 %); R_f = 0.5 (1:6 ethyl acetate/*n*-Hexane);**^{1}H NMR (300 MHz, $CDCl_3$)** (Mixture of two diastereomers, 70:30) δ (ppm) = 12.66 (br s, 1H), 7.73 (d, *J* = 6.8 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 6.8 Hz, 1H), 7.41 (dd, *J* = 9.3, 6.9 Hz, 1H), 7.38 – 7.16 (m, 4H), 7.15-7.05 (m, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.96-6.81 (m, 4H), 6.75 (dd, *J* = 7.6, 7.2 Hz, 2H), 6.59 (dd, *J* = 7.5, 7.3 Hz, 2H), 6.36 (d, *J* = 7.5 Hz, 1H), 6.15 (d, *J* = 8.1 Hz, 1H), 6.09 (d, *J* = 8.1 Hz, 1H), 5.68 (s, 1H), 5.50 (s, 1H), 5.28 (d, *J* = 7.8 Hz, 1H), 5.01 (d, *J* = 7.8 Hz, 1H), 4.87 (dd, *J* = 8.1, 7.9 Hz 2H). **^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)** δ (ppm) = 156.6, 146.2, 141.0, 138.1, 134.9, 133.3, 132.1, 129.0, 128.7, 128.6, 127.8, 126.9, 125.9, 122.5, 121.9, 121.5, 118.8, 117.0, 116.8, 116.5, 114.5, 113.5, 113.2, 110.4, 105.3, 62.9. **HRMS-ESI (+)** (m/z): calc. for $C_{28}H_{21}{}^{79}BrN_3O_2$ $[M+H]^+$ 510.0801, found 510.0812.

4. References

1. T. Okitsu, K. Nagase, N. Nishio, A. Wada, *Org. lett*, **2012** *14*, 708-711.
2. S. Su, J. Li, M. Sun, H. Zhao, Y. Chen, J. Li, *Chem. Comm,* **2018***, 54*, 9611-9614.
3. T. Tian, X. Wang, L. Lv, Z. Li, *Eur. J. Org. Chem*., **2020**. 2020, 4425-4428.

5. X-Ray Crystallographic Analysis

The structure of product **5** (CCDC 2291860) was recrystallized from the ethyl acetate/*n*-Hexane.

Chemie : Saeed Balalaie
Probe : 5
Dateinamen : sba189.*
Operateur : F. Rominger
Gerät : Bruker APEX-II Quazar area detector

Table 2: Crystal data and structure refinement for 5.

Identification code	5
Empirical formula	$C_{23}H_{18}BrN_3O$
Formula weight	432.31
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Z	4
Unit cell dimensions	a = 9.9612(7) Å α = 90 deg.
	b = 15.0034(9) Å β = 99.6334(18) deg.
	c = 13.3232(9) Å γ = 90 deg.
Volume	1963.1(2) $Å^3$
Density (calculated)	1.46 g/cm^3
Absorption coefficient	2.11 mm^{-1}
Crystal shape	prism
Crystal size	0.141 x 0.127 x 0.091 mm^3
Crystal colour	colourless
Theta range for data collection	2.1 to 26.0 deg.
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-16 \le l \le 16$
Reflections collected	19708
Independent reflections	3870 (R(int) = 0.0555)
Observed reflections	2502 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.85 and 0.77
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3870 / 0 / 254
Goodness-of-fit on F^2	1.03
Final R indices (I>2sigma(I))	R1 = 0.042, wR2 = 0.089
Largest diff. peak and hole	0.31 and -0.43 $eÅ^{-3}$

Tabel 3: Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for sba189. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	**x**	**y**	**z**	**U_{eq}**
Br1	0.4512(1)	0.5002(1)	0.1818(1)	0.0609(2)
N1	0.4394(2)	0.3170(2)	0.3148(2)	0.0300(6)
C2	0.5689(3)	0.3507(2)	0.3440(2)	0.0250(7)
C3	0.6648(3)	0.2873(2)	0.3387(2)	0.0244(6)
N4	0.8072(2)	0.2902(2)	0.3578(2)	0.0260(6)
C5	0.8246(4)	0.2153(2)	0.5192(3)	0.0512(10)
H5A	0.7308	0.2000	0.5047	0.061
H5B	0.8782	0.1975	0.5817	0.061
C6	0.8806(3)	0.2615(2)	0.4522(2)	0.0330(7)
C7	1.0225(3)	0.2959(3)	0.4717(3)	0.0492(10)
H7A	1.0208	0.3603	0.4874	0.059
H7B	1.0736	0.2653	0.5320	0.059
O8	1.0918(2)	0.2832(1)	0.3878(2)	0.0401(6)
C11	1.0211(3)	0.3168(2)	0.2981(2)	0.0288(7)
C12	0.8790(3)	0.3199(2)	0.2811(2)	0.0240(6)
C13	0.8112(3)	0.3502(2)	0.1880(2)	0.0310(7)
H13	0.7145	0.3526	0.1757	0.037
C14	0.8832(3)	0.3775(2)	0.1119(2)	0.0379(8)
C15	1.0230(4)	0.3742(2)	0.1313(3)	0.0431(9)
H15	1.0729	0.3925	0.0800	0.052

C16	1.0919(3)	0.3448(2)	0.2232(3)	0.0386(8)
H16	1.1886	0.3438	0.2353	0.046
C18	0.8052(4)	0.4121(3)	0.0122(3)	0.0628(12)
H18A	0.8693	0.4274	-0.0335	0.094
H18B	0.7537	0.4654	0.0251	0.094
H18C	0.7422	0.3661	-0.0195	0.094
C21	0.5443(3)	0.5167(2)	0.3167(2)	0.0330(8)
C22	0.5936(3)	0.4443(2)	0.3768(2)	0.0260(7)
C23	0.6686(3)	0.4628(2)	0.4723(3)	0.0351(8)
H23	0.7060	0.4149	0.5146	0.042
C24	0.6899(3)	0.5492(2)	0.5069(3)	0.0431(9)
H24	0.7419	0.5601	0.5722	0.052
C25	0.6366(3)	0.6193(2)	0.4475(3)	0.0412(8)
H25	0.6493	0.6786	0.4723	0.049
C26	0.5641(3)	0.6037(2)	0.3514(3)	0.0390(8)
H26	0.5282	0.6521	0.3093	0.047
N31	0.5949(2)	0.2107(2)	0.3026(2)	0.0260(6)
C32	0.4573(3)	0.2324(2)	0.2907(2)	0.0286(7)
C33	0.3616(3)	0.1652(2)	0.2565(2)	0.0390(8)
H33	0.2668	0.1768	0.2500	0.047
C34	0.4063(4)	0.0842(2)	0.2329(3)	0.0437(9)
H34	0.3421	0.0387	0.2100	0.052
C35	0.5470(4)	0.0660(2)	0.2419(3)	0.0431(9)
H35	0.5762	0.0094	0.2221	0.052
C36	0.6401(3)	0.1283(2)	0.2782(2)	0.0364(8)
H36	0.7347	0.1154	0.2867	0.044

Table 4: Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for 5.

Atom	**x**	**y**	**z**	**U_{eq}**
H5A	0.7308	0.2000	0.5047	0.061
H5B	0.8782	0.1975	0.5817	0.061
H7A	1.0208	0.3603	0.4874	0.059
H7B	1.0736	0.2653	0.5320	0.059
H13	0.7145	0.3526	0.1757	0.037
H15	1.0729	0.3925	0.0800	0.052
H16	1.1886	0.3438	0.2353	0.046
H18A	0.8693	0.4274	-0.0335	0.094
H18B	0.7537	0.4654	0.0251	0.094
H18C	0.7422	0.3661	-0.0195	0.094
H23	0.7060	0.4149	0.5146	0.042
H24	0.7419	0.5601	0.5722	0.052
H25	0.6493	0.6786	0.4723	0.049
H26	0.5282	0.6521	0.3093	0.047
H33	0.2668	0.1768	0.2500	0.047
H34	0.3421	0.0387	0.2100	0.052
H35	0.5762	0.0094	0.2221	0.052
H36	0.7347	0.1154	0.2867	0.044

Tabel 5: Anisotropic displacement parameters ($Å^2$) for 5. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ (h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12})$

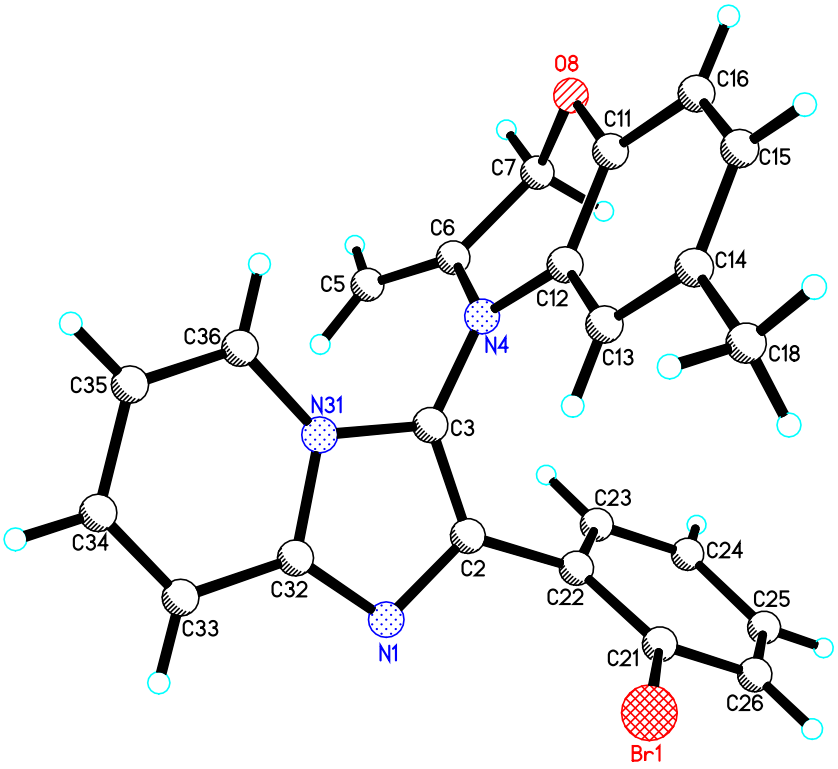
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	0.0716(3)	0.0528(3)	0.0487(2)	0.0104(2)	-0.0183(2)	0.0021(2)

N1	0.0224(13)	0.0278(14)	0.0392(15)	-0.0020(12)	0.0033(11)	-0.0030(11)
C2	0.0228(16)	0.0238(16)	0.0287(16)	-0.0007(13)	0.0049(12)	-0.0015(12)
C3	0.0228(15)	0.0232(16)	0.0272(16)	0.0016(13)	0.0044(12)	-0.0025(12)
N4	0.0211(13)	0.0262(13)	0.0310(14)	0.0054(11)	0.0050(11)	0.0008(10)
C5	0.053(2)	0.061(2)	0.037(2)	0.0161(19)	-0.0012(17)	0.0008(19)
C6	0.0332(18)	0.0343(18)	0.0297(17)	0.0055(15)	-0.0004(14)	0.0070(14)
C7	0.040(2)	0.061(3)	0.042(2)	0.0073(18)	-0.0055(17)	0.0013(18)
O8	0.0226(11)	0.0446(14)	0.0514(15)	0.0054(12)	0.0008(10)	0.0068(10)
C11	0.0243(16)	0.0196(15)	0.0416(19)	-0.0027(14)	0.0031(14)	0.0008(12)
C12	0.0247(15)	0.0174(14)	0.0300(16)	-0.0021(13)	0.0046(13)	-0.0004(12)
C13	0.0281(17)	0.0326(18)	0.0317(17)	-0.0026(14)	0.0031(14)	-0.0038(13)
C14	0.047(2)	0.0364(19)	0.0314(18)	-0.0039(15)	0.0103(16)	-0.0066(16)
C15	0.049(2)	0.038(2)	0.049(2)	-0.0023(18)	0.0312(18)	-0.0035(17)
C16	0.0279(18)	0.0289(18)	0.063(2)	-0.0058(17)	0.0209(17)	-0.0011(14)
C18	0.076(3)	0.075(3)	0.037(2)	0.013(2)	0.010(2)	-0.012(2)
C21	0.0281(16)	0.0320(19)	0.0380(18)	0.0011(15)	0.0033(13)	0.0000(14)
C22	0.0206(15)	0.0202(16)	0.0375(18)	-0.0023(14)	0.0057(13)	-0.0018(12)
C23	0.0350(18)	0.0263(16)	0.044(2)	0.0008(16)	0.0053(15)	-0.0047(14)
C24	0.048(2)	0.035(2)	0.045(2)	-0.0047(17)	0.0023(17)	-0.0082(17)
C25	0.047(2)	0.0234(17)	0.056(2)	-0.0070(17)	0.0175(18)	-0.0066(15)
C26	0.037(2)	0.0235(18)	0.058(2)	0.0090(16)	0.0134(17)	0.0008(14)
N31	0.0254(13)	0.0232(13)	0.0292(14)	0.0007(11)	0.0044(11)	0.0000(11)
C32	0.0269(16)	0.0286(17)	0.0300(17)	0.0007(14)	0.0042(13)	-0.0012(13)
C33	0.0360(19)	0.0312(19)	0.046(2)	0.0008(16)	-0.0031(16)	-0.0084(15)
C34	0.054(2)	0.0292(19)	0.043(2)	-0.0009(16)	-0.0068(17)	-0.0123(16)
C35	0.061(2)	0.0207(17)	0.047(2)	-0.0058(16)	0.0065(18)	-0.0013(16)
C36	0.045(2)	0.0239(17)	0.041(2)	0.0007(15)	0.0074(16)	0.0056(15)

Table 6: Bond lengths (Å) and angles (deg) for 5.

Br1-C21	1.897(3)	C21-C22	1.389(4)
N1-C32	1.329(4)	C22-C23	1.391(4)
N1-C2	1.380(3)	C23-C24	1.381(4)
C2-C3	1.358(4)	C23-H23	0.9500
C2-C22	1.478(4)	C24-C25	1.369(5)
C3-N31	1.387(3)	C24-H24	0.9500
C3-N4	1.399(3)	C25-C26	1.381(5)
N4-C6	1.411(4)	C25-H25	0.9500
N4-C12	1.413(4)	C26-H26	0.9500
C5-C6	1.325(4)	N31-C36	1.374(4)
C5-H5A	0.9500	N31-C32	1.392(4)
C5-H5B	0.9500	C32-C33	1.410(4)
C6-C7	1.486(4)	C33-C34	1.349(4)
C7-O8	1.421(4)	C33-H33	0.9500
C7-H7A	0.9900	C34-C35	1.413(5)
C7-H7B	0.9900	C34-H34	0.9500
O8-C11	1.377(4)	C35-C36	1.348(4)
C11-C16	1.380(4)	C35-H35	0.9500
C11-C12	1.397(4)	C36-H36	0.9500
C12-C13	1.387(4)	C32-N1-C2	105.2(2)
C13-C14	1.396(4)	C3-C2-N1	111.1(2)
C13-H13	0.9500	C3-C2-C22	126.7(2)
C14-C15	1.374(5)	N1-C2-C22	122.2(2)
C14-C18	1.514(5)	C2-C3-N31	106.4(2)
C15-C16	1.372(5)	C2-C3-N4	132.0(3)
C15-H15	0.9500	N31-C3-N4	121.6(2)
C16-H16	0.9500	C3-N4-C6	120.7(2)
C18-H18A	0.9800	C3-N4-C12	119.9(2)
C18-H18B	0.9800	C6-N4-C12	119.4(2)
C18-H18C	0.9800	C6-C5-H5A	120.0
C21-C26	1.387(4)	C6-C5-H5B	120.0

H5A-C5-H5B	120.0
C5-C6-N4	123.1(3)
C5-C6-C7	124.0(3)
N4-C6-C7	112.7(3)
O8-C7-C6	112.9(3)
O8-C7-H7A	109.0
C6-C7-H7A	109.0
O8-C7-H7B	109.0
C6-C7-H7B	109.0
H7A-C7-H7B	107.8
C11-O8-C7	112.8(2)
O8-C11-C16	119.3(3)
O8-C11-C12	120.7(3)
C16-C11-C12	120.0(3)
C13-C12-C11	119.0(3)
C13-C12-N4	121.4(3)
C11-C12-N4	119.6(3)
C12-C13-C14	120.9(3)
C12-C13-H13	119.6
C14-C13-H13	119.6
C15-C14-C13	118.7(3)
C15-C14-C18	122.1(3)
C13-C14-C18	119.1(3)
C16-C15-C14	121.2(3)
C16-C15-H15	119.4
C14-C15-H15	119.4
C15-C16-C11	120.2(3)
C15-C16-H16	119.9
C11-C16-H16	119.9
C14-C18-H18A	109.5
C14-C18-H18B	109.5
H18A-C18-H18B	109.5
C14-C18-H18C	109.5
H18A-C18-H18C	109.5
H18B-C18-H18C	109.5
C26-C21-C22	121.8(3)
C26-C21-Br1	117.3(2)
C22-C21-Br1	120.9(2)
C21-C22-C23	117.1(3)
C21-C22-C2	123.2(3)
C23-C22-C2	119.8(3)
C24-C23-C22	121.4(3)
C24-C23-H23	119.3
C22-C23-H23	119.3
C25-C24-C23	120.4(3)
C25-C24-H24	119.8
C23-C24-H24	119.8
C24-C25-C26	119.8(3)
C24-C25-H25	120.1
C26-C25-H25	120.1
C25-C26-C21	119.4(3)
C25-C26-H26	120.3
C21-C26-H26	120.3
C36-N31-C3	131.5(3)
C36-N31-C32	122.6(2)
C3-N31-C32	105.9(2)
N1-C32-N31	111.4(2)
N1-C32-C33	130.6(3)
N31-C32-C33	118.0(3)
C34-C33-C32	119.2(3)
C34-C33-H33	120.4
C32-C33-H33	120.4
C33-C34-C35	121.0(3)
C33-C34-H34	119.5
C35-C34-H34	119.5
C36-C35-C34	120.7(3)
C36-C35-H35	119.7
C34-C35-H35	119.7
C35-C36-N31	118.4(3)
C35-C36-H36	120.8
N31-C36-H36	120.8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C16
C11
C15
C7
C6
C5
C14
C12
N4
C13
C18
C36
C35
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C23
C24
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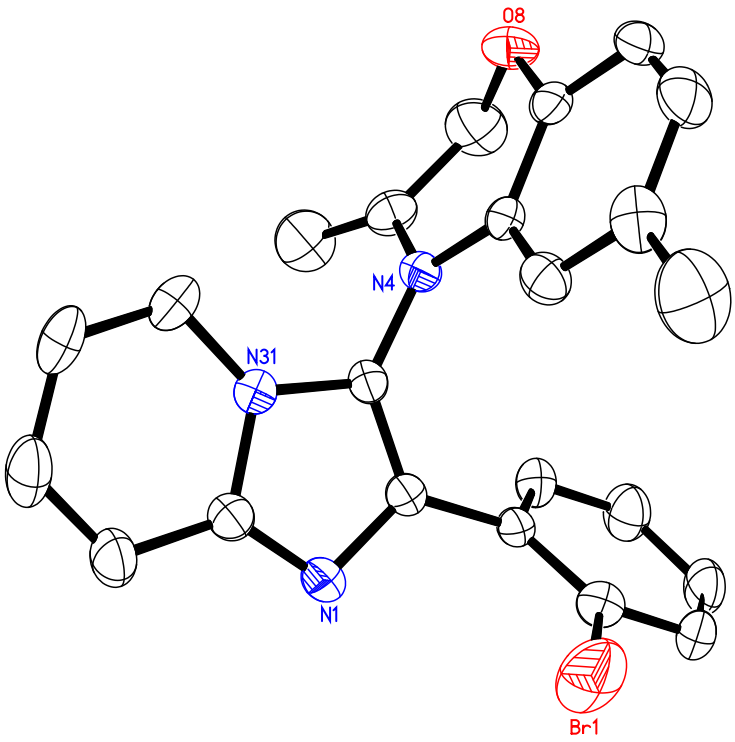
C2
C22
C25
C32
C33
N1
C21
C26
Br1


O8
N4
N31
N1
Br1

Suggestion for a short experimental part:

sba189: colourless crystal (prism), dimensions 0.141 x 0.127 x 0.091 mm^3, crystal system monoclinic, space group $P2_1/n$, Z=4, a=9.9612(7) Å, b=15.0034(9) Å, c=13.3232(9) Å, alpha=90 deg, beta=99.6334(18) deg, gamma=90 deg, V=1963.1(2) $Å^3$, rho=1.463 g/cm^3, T=200(2) K, $Theta_{max}$= 26.020 deg, radiation MoKα, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 5.01and a completeness of 99.9% to a resolution of 0.81 Å, 19708 reflections measured, 3870 unique (R(int)=0.0555), 2502 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=2.11mm^{-1}, T_{min}=0.77, T_{max}=0.85, structure solved with SHELXT-2018/2 (Sheldrick 2015)[2] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2018/3 (Sheldrick, 2018) software[3], 254 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values R1(F)=0.042, wR(F^2)=0.089 for observed reflections, residual electron density -0.43 to 0.31 $eÅ^{-3}$. CCDC ..... contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Lit. 1: (SADABS-2016/2 - Bruker AXS area detector scaling and absorption correction)
Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10.

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

Lit. 3: (program SHELXL-2018/3 (Sheldrick, 2018) for structure refinement)
Sheldrick G. M., Acta Cryst. (2015). C71, 3-8

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

The structure of product **2b** (CCDC 2291859) was recrystallized from the ethyl acetate/*n*-Hexane.

Chemie : Saeed Balalaie
Probe : S5i
Dateinamen : sba197.*
Operateur : F. Rominger
Gerät : Bruker APEX-II Quazar area detector

Table 1: Crystal data and structure refinement for 2b.

Identification code	2b
Empirical formula	$C_{23}H_{18}BrN_3O_2$
Formula weight	448.31
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Z	4
Unit cell dimensions	a = 7.8608(5) Å α =90 deg.

	b = 18.2829(12) Å β = 96.3335(12) deg.
	c = 13.4885(9) Å γ = 90 deg.
Volume	1926.7(2) Å^3
Density (calculated)	1.55 g/cm^3
Absorption coefficient	2.16 mm^{-1}
Crystal shape	brick
Crystal size	0.116 x 0.098 x 0.091 mm^3
Crystal colour	colourless
Theta range for data collection	1.9 to 29.3 deg.
Index ranges	-10≤h≤10, -24≤k≤24, -18≤l≤17
Reflections collected	21995
Independent reflections	4871 (R(int) = 0.0417)
Observed reflections	3754 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.85 and 0.77
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4871 / 0 / 264
Goodness-of-fit on F^2	1.03
Final R indices (I>2sigma(I))	R1 = 0.034, wR2 = 0.068
Largest diff. peak and hole	0.34 and -0.44 eÅ^{-3}

Tabel 2: Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for sba197. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	**x**	**y**	**z**	**U_{eq}**
Br1	0.1120(1)	0.0088(1)	0.6485(1)	0.0347(1)
N1	0.6439(2)	0.1951(1)	0.6632(1)	0.0221(3)
C2	0.5142(2)	0.2355(1)	0.6124(1)	0.0189(4)
C3	0.5651(2)	0.3059(1)	0.5987(1)	0.0188(4)
N4	0.4801(2)	0.3636(1)	0.5467(1)	0.0192(3)
C5	0.3808(2)	0.3424(1)	0.4540(1)	0.0219(4)
O6	0.2219(2)	0.3068(1)	0.4723(1)	0.0253(3)
C7	0.3232(3)	0.4120(1)	0.3978(1)	0.0260(4)
H7A	0.4254	0.4376	0.3783	0.031
H7B	0.2506	0.3984	0.3359	0.031
O8	0.2300(2)	0.4610(1)	0.4539(1)	0.0301(3)
C9	0.4838(3)	0.2961(1)	0.3887(2)	0.0292(5)
H9A	0.5950	0.3192	0.3840	0.044
H9B	0.4215	0.2918	0.3219	0.044
H9C	0.5013	0.2472	0.4181	0.044
N11	0.7329(2)	0.3105(1)	0.6413(1)	0.0181(3)
C12	0.7736(2)	0.2415(1)	0.6812(1)	0.0199(4)
C13	0.9388(2)	0.2323(1)	0.7331(1)	0.0248(4)
H13	0.9715	0.1866	0.7629	0.030
C14	1.0500(3)	0.2891(1)	0.7400(2)	0.0268(4)
H14	1.1611	0.2828	0.7744	0.032
C15	1.0032(2)	0.3582(1)	0.6967(2)	0.0259(4)
H15	1.0833	0.3974	0.7021	0.031
C16	0.8452(2)	0.3684(1)	0.6477(1)	0.0226(4)
H16	0.8127	0.4144	0.6186	0.027

C21	0.2865(2)	0.4670(1)	0.5538(1)	0.0231(4)
C22	0.4039(2)	0.4183(1)	0.6025(1)	0.0191(4)
C23	0.4415(2)	0.4243(1)	0.7056(1)	0.0224(4)
H23	0.5192	0.3905	0.7396	0.027
C24	0.3683(3)	0.4782(1)	0.7602(2)	0.0254(4)
C25	0.2580(3)	0.5279(1)	0.7087(2)	0.0300(5)
H25	0.2108	0.5665	0.7440	0.036
C26	0.2157(3)	0.5220(1)	0.6069(2)	0.0282(4)
H26	0.1379	0.5558	0.5731	0.034
C28	0.3998(3)	0.4790(1)	0.8727(2)	0.0373(5)
H28A	0.3778	0.5282	0.8973	0.056
H28B	0.5189	0.4654	0.8937	0.056
H28C	0.3231	0.4439	0.9001	0.056
C31	0.2162(2)	0.2386(1)	0.5159(1)	0.0216(4)
C32	0.3455(2)	0.2041(1)	0.5798(1)	0.0201(4)
C33	0.3101(2)	0.1346(1)	0.6171(1)	0.0226(4)
H33	0.3961	0.1095	0.6591	0.027
C34	0.1530(3)	0.1023(1)	0.5938(1)	0.0252(4)
C35	0.0242(3)	0.1369(1)	0.5330(2)	0.0286(5)
H35	-0.0847	0.1145	0.5182	0.034
C36	0.0573(3)	0.2047(1)	0.4943(1)	0.0270(4)
H36	-0.0300	0.2288	0.4521	0.032

Tabel 3: Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for 2b.

Atom	**x**	**y**	**z**	**U_{eq}**
H7A	0.4254	0.4376	0.3783	0.031
H7B	0.2506	0.3984	0.3359	0.031
H9A	0.5950	0.3192	0.3840	0.044
H9B	0.4215	0.2918	0.3219	0.044
H9C	0.5013	0.2472	0.4181	0.044
H13	0.9715	0.1866	0.7629	0.030
H14	1.1611	0.2828	0.7744	0.032
H15	1.0833	0.3974	0.7021	0.031
H16	0.8127	0.4144	0.6186	0.027
H23	0.5192	0.3905	0.7396	0.027
H25	0.2108	0.5665	0.7440	0.036
H26	0.1379	0.5558	0.5731	0.034
H28A	0.3778	0.5282	0.8973	0.056
H28B	0.5189	0.4654	0.8937	0.056
H28C	0.3231	0.4439	0.9001	0.056
H33	0.3961	0.1095	0.6591	0.027
H35	-0.0847	0.1145	0.5182	0.034
H36	-0.0300	0.2288	0.4521	0.032

Tabel 4: Anisotropic displacement parameters ($Å^2$) for 2b. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ (h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12})$

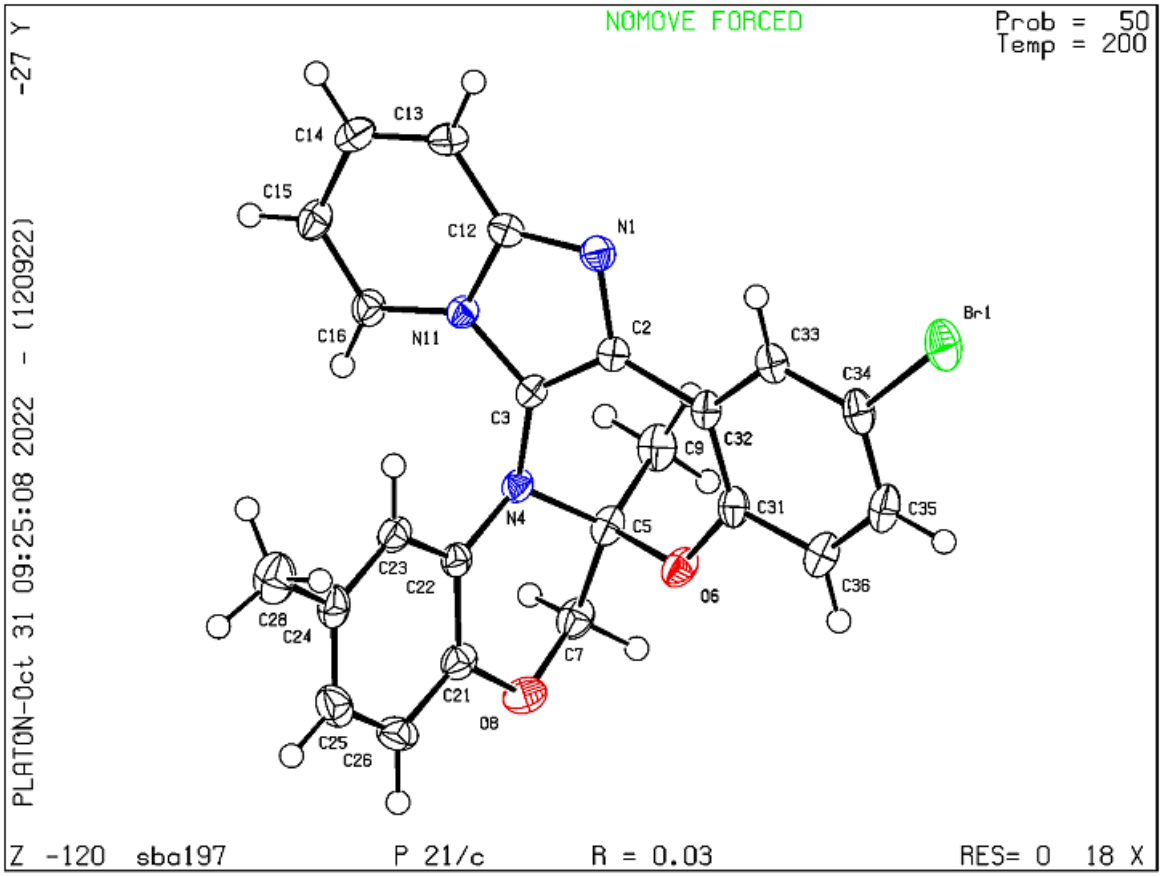
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.0385(1)	0.0250(1)	0.0417(1)	-0.0006(1)	0.0100(1)	-0.0139(1)
N1	0.0219(9)	0.0198(8)	0.0247(8)	0.0021(6)	0.0030(7)	-0.0011(6)
C2	0.0195(9)	0.0201(9)	0.0174(9)	-0.0002(7)	0.0032(7)	-0.0015(7)
C3	0.0169(9)	0.0215(9)	0.0176(9)	-0.0002(7)	-0.0001(7)	-0.0011(7)
N4	0.0195(8)	0.0194(7)	0.0176(8)	0.0016(6)	-0.0026(6)	-0.0014(6)
C5	0.0220(10)	0.0257(9)	0.0176(9)	0.0030(7)	0.0002(8)	-0.0062(8)
O6	0.0209(7)	0.0279(7)	0.0262(7)	0.0064(6)	-0.0021(6)	-0.0062(6)
C7	0.0274(11)	0.0292(10)	0.0203(10)	0.0056(8)	-0.0028(8)	-0.0046(8)
O8	0.0293(8)	0.0328(8)	0.0263(7)	0.0056(6)	-0.0052(6)	0.0049(6)
C9	0.0343(12)	0.0322(11)	0.0215(10)	-0.0011(8)	0.0053(9)	-0.0057(9)
N11	0.0176(8)	0.0188(7)	0.0178(8)	0.0011(6)	0.0014(6)	-0.0007(6)
C12	0.0215(9)	0.0196(9)	0.0192(9)	0.0023(7)	0.0045(7)	0.0013(7)
C13	0.0233(10)	0.0247(10)	0.0259(10)	0.0040(8)	-0.0001(8)	0.0049(8)
C14	0.0193(10)	0.0346(11)	0.0254(10)	0.0001(8)	-0.0021(8)	0.0027(8)
C15	0.0213(10)	0.0281(10)	0.0280(11)	0.0004(8)	0.0008(8)	-0.0063(8)
C16	0.0227(10)	0.0204(9)	0.0243(10)	0.0023(7)	0.0010(8)	-0.0036(8)
C21	0.0196(10)	0.0237(9)	0.0256(10)	0.0047(8)	0.0011(8)	-0.0037(8)
C22	0.0173(9)	0.0173(8)	0.0225(10)	0.0017(7)	0.0021(7)	-0.0041(7)
C23	0.0185(9)	0.0235(9)	0.0245(10)	0.0012(7)	-0.0003(8)	-0.0033(7)
C24	0.0222(10)	0.0271(10)	0.0275(10)	-0.0049(8)	0.0055(8)	-0.0083(8)
C25	0.0270(11)	0.0231(10)	0.0417(13)	-0.0058(9)	0.0120(10)	-0.0034(8)
C26	0.0232(10)	0.0198(9)	0.0418(12)	0.0062(8)	0.0047(9)	0.0019(8)
C28	0.0379(13)	0.0456(13)	0.0293(12)	-0.0096(10)	0.0076(10)	-0.0058(11)
C31	0.0256(10)	0.0227(9)	0.0166(9)	-0.0019(7)	0.0036(8)	-0.0061(8)
C32	0.0212(10)	0.0209(9)	0.0186(9)	-0.0027(7)	0.0036(8)	-0.0053(7)
C33	0.0262(10)	0.0202(9)	0.0222(10)	-0.0026(7)	0.0064(8)	-0.0040(8)
C34	0.0314(11)	0.0215(9)	0.0241(10)	-0.0040(8)	0.0097(9)	-0.0089(8)
C35	0.0260(11)	0.0341(11)	0.0261(10)	-0.0075(9)	0.0047(9)	-0.0125(9)
C36	0.0238(10)	0.0349(11)	0.0219(10)	-0.0017(8)	0.0009(8)	-0.0084(9)

Tabel 5: Bond lengths (Å) and angles (deg) for 2b.

Br1-C34	1.9030(19)	C7-H7B	0.9900
N1-C12	1.329(2)	O8-C21	1.376(2)
N1-C2	1.379(2)	C9-H9A	0.9800
C2-C3	1.366(2)	C9-H9B	0.9800
C2-C32	1.467(3)	C9-H9C	0.9800
C3-N11	1.382(2)	N11-C16	1.375(2)
C3-N4	1.395(2)	N11-C12	1.395(2)
N4-C22	1.423(2)	C12-C13	1.416(3)
N4-C5	1.452(2)	C13-C14	1.355(3)
C5-O6	1.453(2)	C13-H13	0.9500
C5-C9	1.518(3)	C14-C15	1.423(3)
C5-C7	1.525(3)	C14-H14	0.9500
O6-C31	1.382(2)	C15-C16	1.354(3)
C7-O8	1.427(2)	C15-H15	0.9500
C7-H7A	0.9900	C16-H16	0.9500

C21-C26	1.387(3)	C16-N11-C12	123.64(15)
C21-C22	1.394(3)	C3-N11-C12	105.81(14)
C22-C23	1.394(3)	N1-C12-N11	111.62(16)
C23-C24	1.393(3)	N1-C12-C13	131.13(17)
C23-H23	0.9500	N11-C12-C13	117.25(16)
C24-C25	1.387(3)	C14-C13-C12	119.45(18)
C24-C28	1.511(3)	C14-C13-H13	120.3
C25-C26	1.381(3)	C12-C13-H13	120.3
C25-H25	0.9500	C13-C14-C15	121.17(18)
C26-H26	0.9500	C13-C14-H14	119.4
C28-H28A	0.9800	C15-C14-H14	119.4
C28-H28B	0.9800	C16-C15-C14	120.28(18)
C28-H28C	0.9800	C16-C15-H15	119.9
C31-C36	1.396(3)	C14-C15-H15	119.9
C31-C32	1.407(3)	C15-C16-N11	118.19(17)
C32-C33	1.407(2)	C15-C16-H16	120.9
C33-C34	1.374(3)	N11-C16-H16	120.9
C33-H33	0.9500	O8-C21-C26	117.34(17)
C34-C35	1.384(3)	O8-C21-C22	122.44(17)
C35-C36	1.380(3)	C26-C21-C22	120.16(18)
C35-H35	0.9500	C21-C22-C23	118.48(17)
C36-H36	0.9500	C21-C22-N4	119.73(16)
C12-N1-C2	105.02(15)	C23-C22-N4	121.79(16)
C3-C2-N1	111.12(16)	C24-C23-C22	121.90(18)
C3-C2-C32	126.59(17)	C24-C23-H23	119.1
N1-C2-C32	122.29(16)	C22-C23-H23	119.1
C2-C3-N11	106.40(16)	C25-C24-C23	118.07(18)
C2-C3-N4	130.45(17)	C25-C24-C28	121.39(18)
N11-C3-N4	122.97(16)	C23-C24-C28	120.41(19)
C3-N4-C22	118.19(15)	C26-C25-C24	121.02(19)
C3-N4-C5	114.39(14)	C26-C25-H25	119.5
C22-N4-C5	115.16(14)	C24-C25-H25	119.5
N4-C5-O6	111.31(14)	C25-C26-C21	120.27(19)
N4-C5-C9	112.23(16)	C25-C26-H26	119.9
O6-C5-C9	111.87(15)	C21-C26-H26	119.9
N4-C5-C7	107.88(15)	C24-C28-H28A	109.5
O6-C5-C7	104.12(15)	C24-C28-H28B	109.5
C9-C5-C7	109.01(16)	H28A-C28-H28B	109.5
C31-O6-C5	123.00(15)	C24-C28-H28C	109.5
O8-C7-C5	113.78(15)	H28A-C28-H28C	109.5
O8-C7-H7A	108.8	H28B-C28-H28C	109.5
C5-C7-H7A	108.8	O6-C31-C36	112.47(17)
O8-C7-H7B	108.8	O6-C31-C32	127.60(16)
C5-C7-H7B	108.8	C36-C31-C32	119.86(17)
H7A-C7-H7B	107.7	C31-C32-C33	117.80(17)
C21-O8-C7	116.10(15)	C31-C32-C2	125.20(16)
C5-C9-H9A	109.5	C33-C32-C2	116.99(17)
C5-C9-H9B	109.5	C34-C33-C32	120.98(18)
H9A-C9-H9B	109.5	C34-C33-H33	119.5
C5-C9-H9C	109.5	C32-C33-H33	119.5
H9A-C9-H9C	109.5	C33-C34-C35	121.27(18)
H9B-C9-H9C	109.5	C33-C34-Br1	118.91(15)
C16-N11-C3	130.55(15)	C35-C34-Br1	119.81(14)

C36-C35-C34	118.63(18)
C36-C35-H35	120.7
C34-C35-H35	120.7
C35-C36-C31	121.42(19)
C35-C36-H36	119.3
C31-C36-H36	119.3



Datablock sba197 - ellipsoid plot

sba197: colourless crystal (brick), dimensions 0.116 x 0.098 x 0.091 mm^3, crystal system monoclinic, space group $P2_1/c$, Z=4, a=7.8608(5) Å, b=18.2829(12) Å, c=13.4885(9) Å, alpha=90 deg, beta=96.3335(12) deg, gamma=90 deg, V=1926.7(2) $Å^3$, rho=1.546 g/cm^3, T=200(2) K, $Theta_{max}$= 29.272 deg, radiation $MoK\alpha$, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.13 and a completeness of 92.6% to a resolution of 0.73 Å, 21995 reflections measured, 4871 unique (R(int)=0.0417), 3754 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=2.16mm^{-1}, T_{min}=0.77, T_{max}=0.85, structure solved with SHELXT-2018/2 (Sheldrick 2015)[2] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2018/3 (Sheldrick, 2018) software[3], 264 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values R1(F)=0.034, $wR(F^2)$=0.068 for observed reflections, residual electron density -0.44 to 0.34 $eÅ^{-3}$. CCDC ..... contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

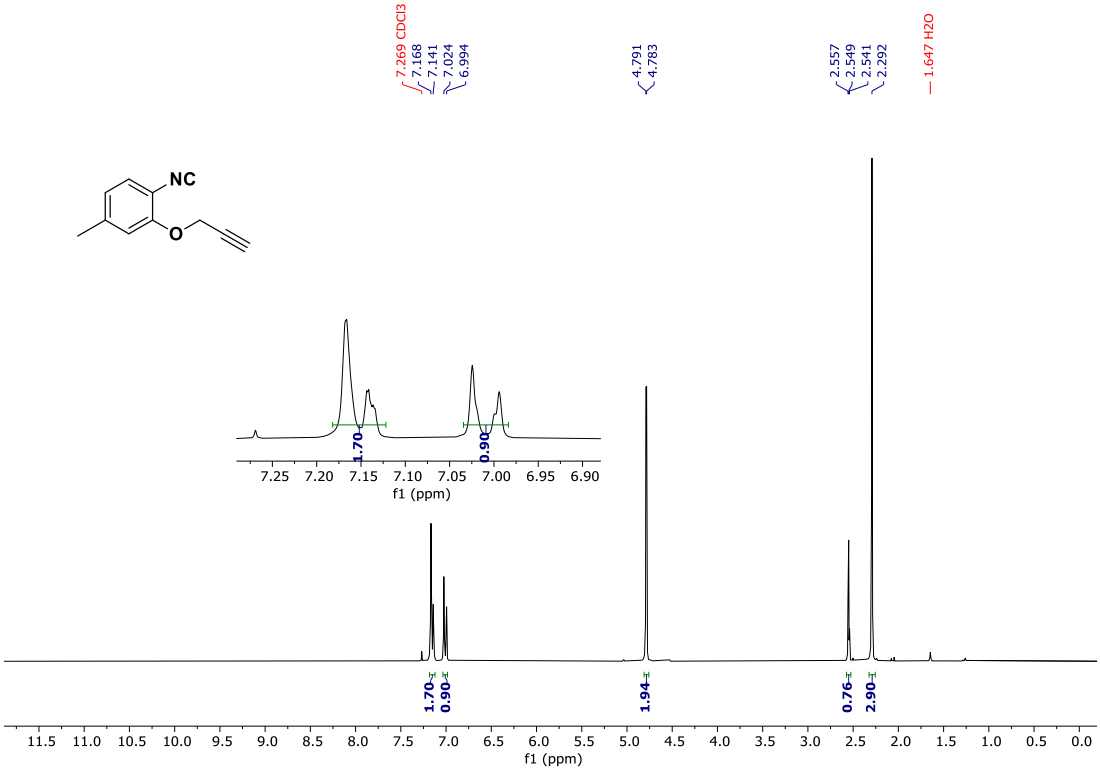
Lit. 1: (SADABS-2016/2 - Bruker AXS area detector scaling and absorption correction)
Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10.

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

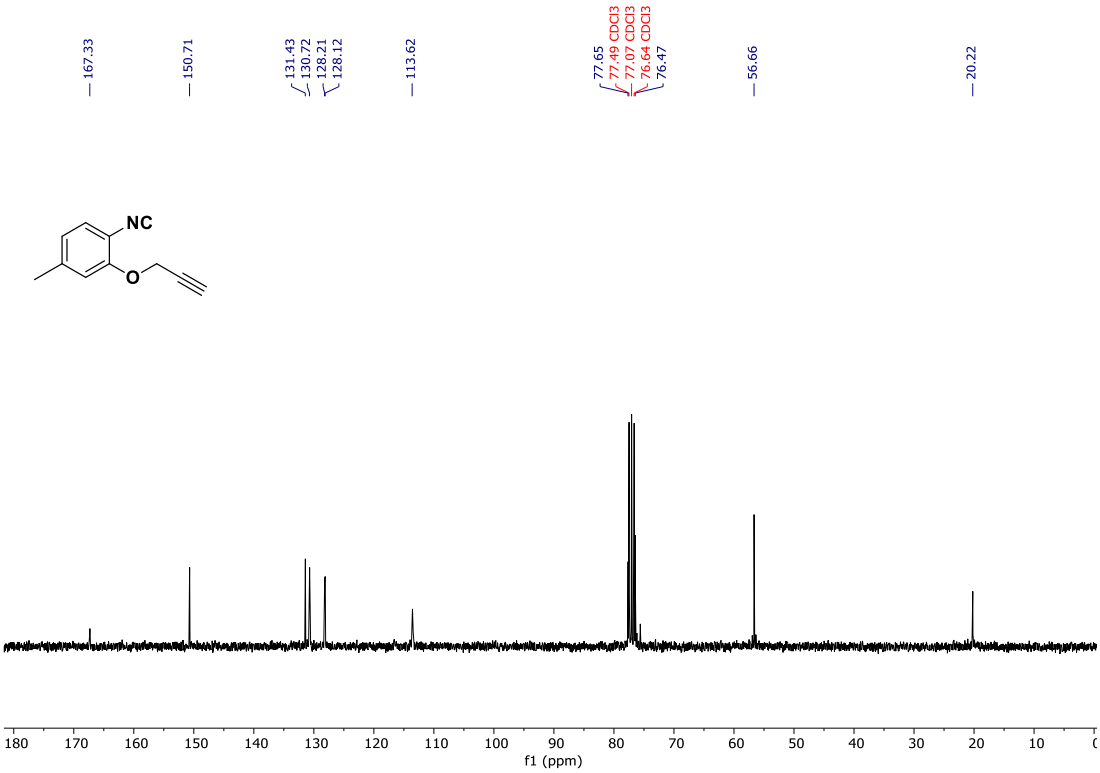
Lit. 3: (program SHELXL-2018/3 (Sheldrick, 2018) for structure refinement)
Sheldrick G. M., Acta Cryst. (2015). C71, 3-8.

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

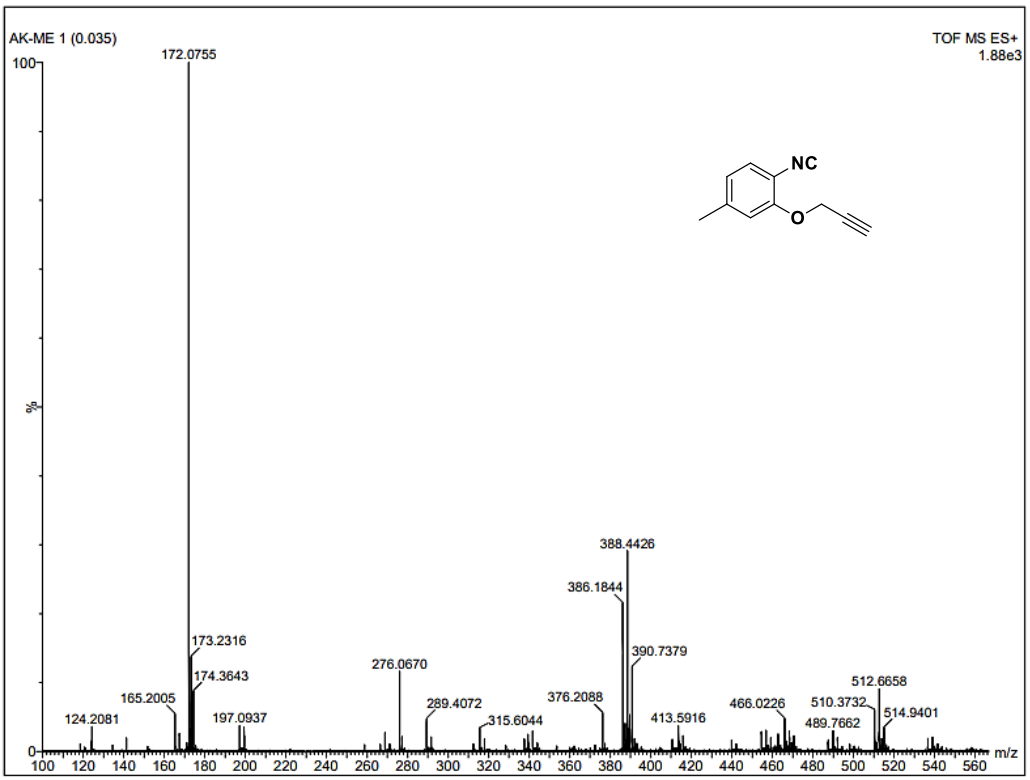
6. ^{1}H-NMR and ^{13}C-NMR of Unknown Compounds



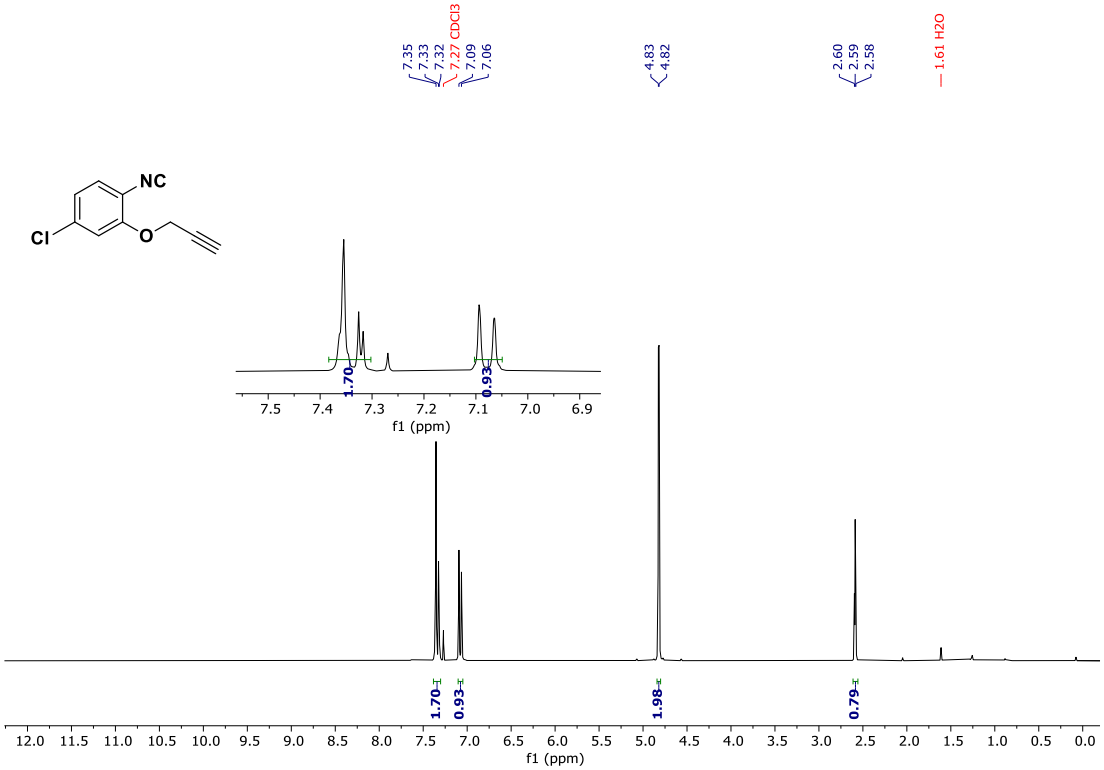
^{1}H NMR (300 MHz, $CDCl_3$) of **IVa**



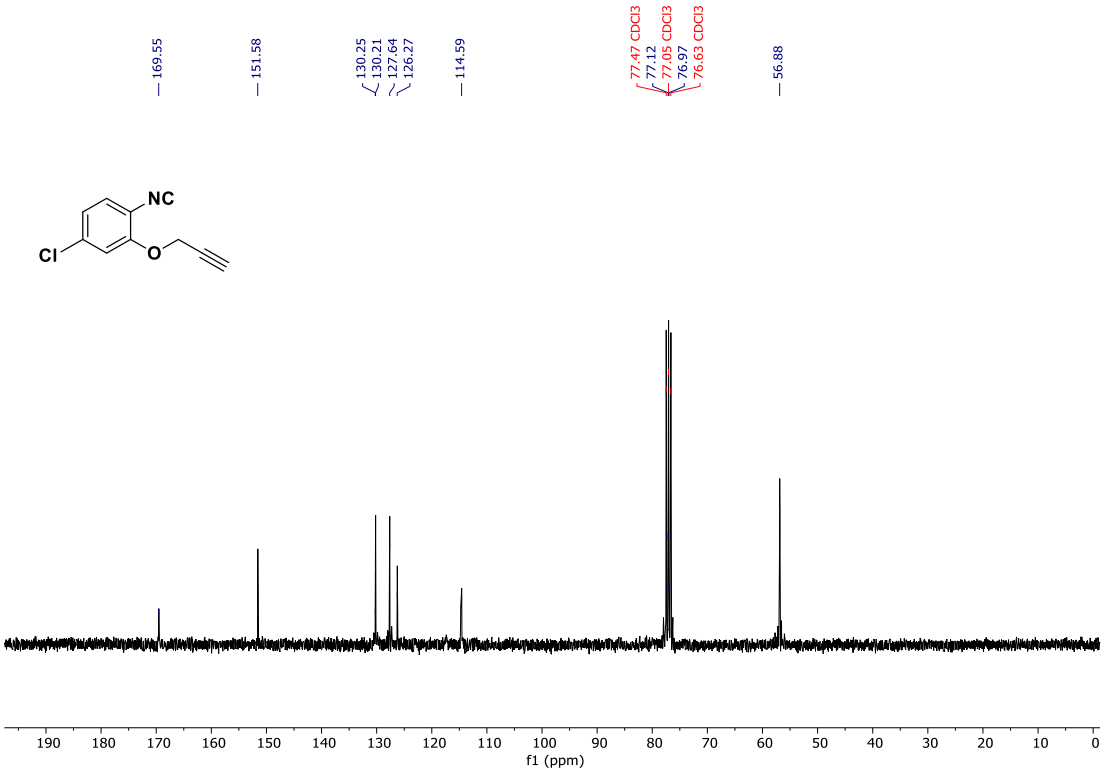
^{13}C NMR (75 MHz, $CDCl_3$) of **IVa**



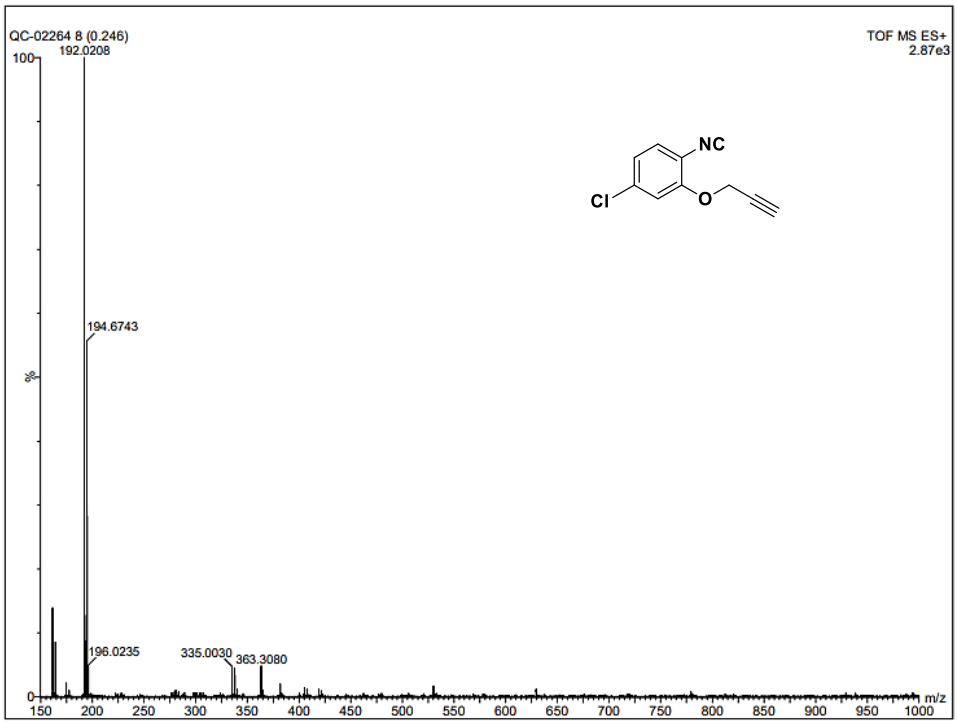
HRMS-ESI (+) of **IVa**



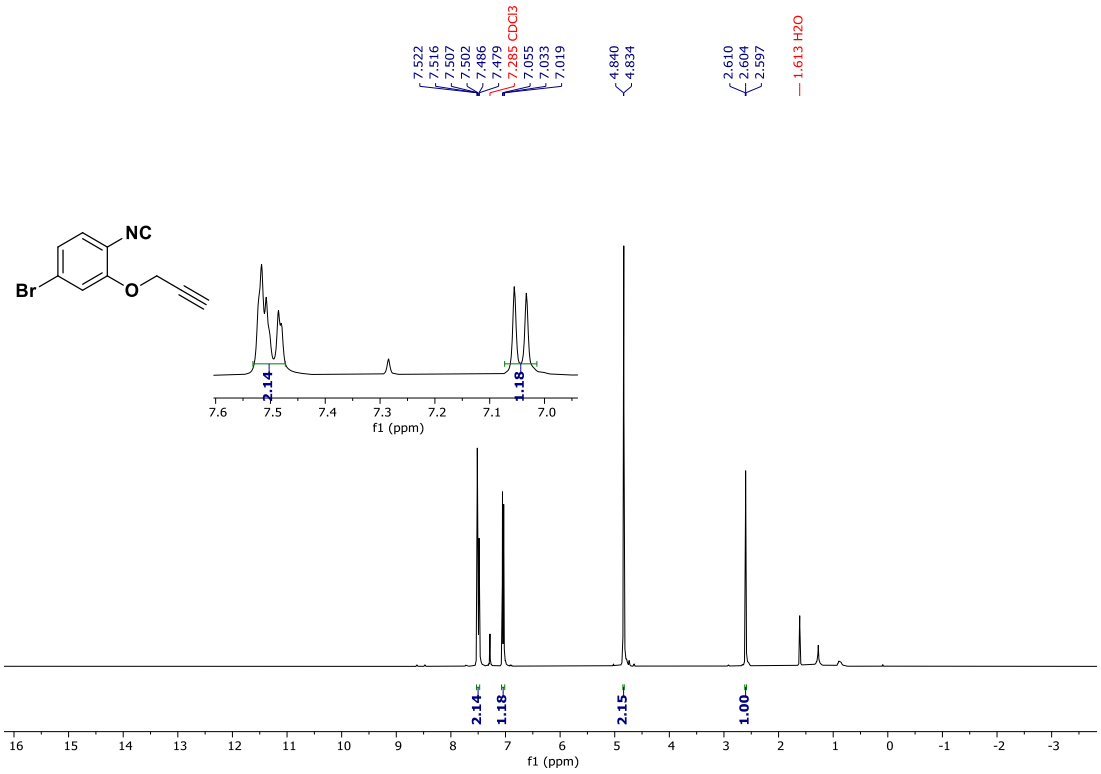
^{1}H NMR (300 MHz, $CDCl_3$) of **IVb**



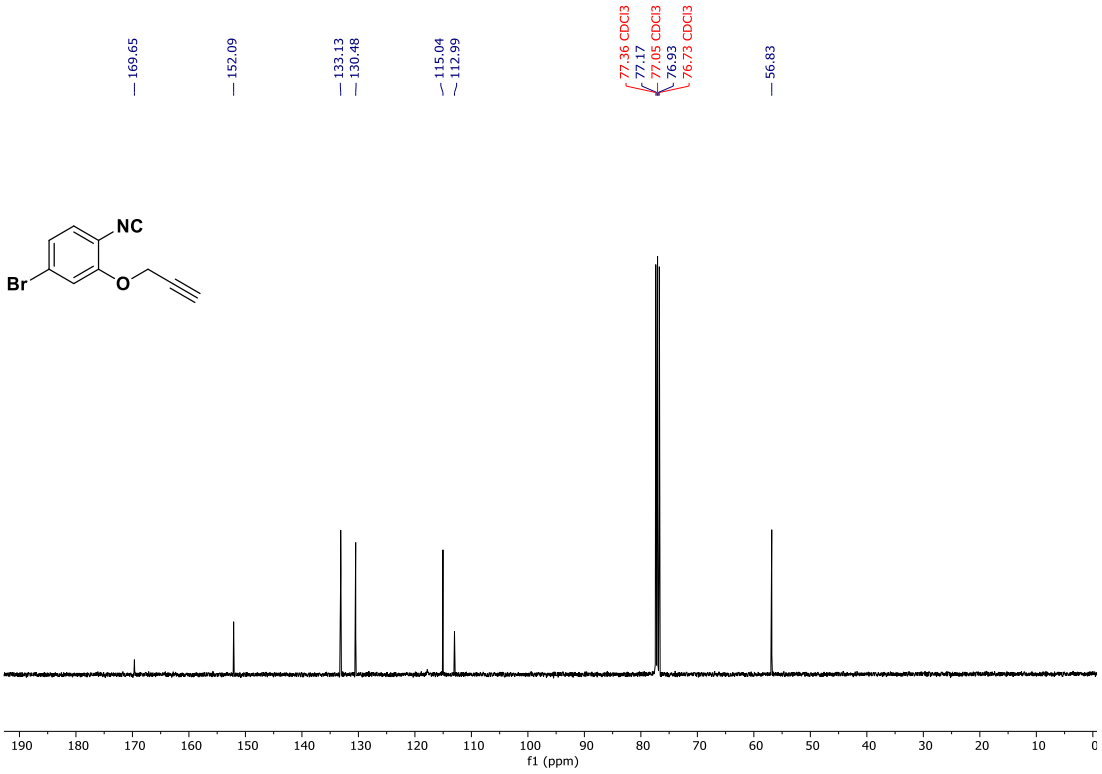
^{13}C NMR (75 MHz, $CDCl_3$) of **IVb**



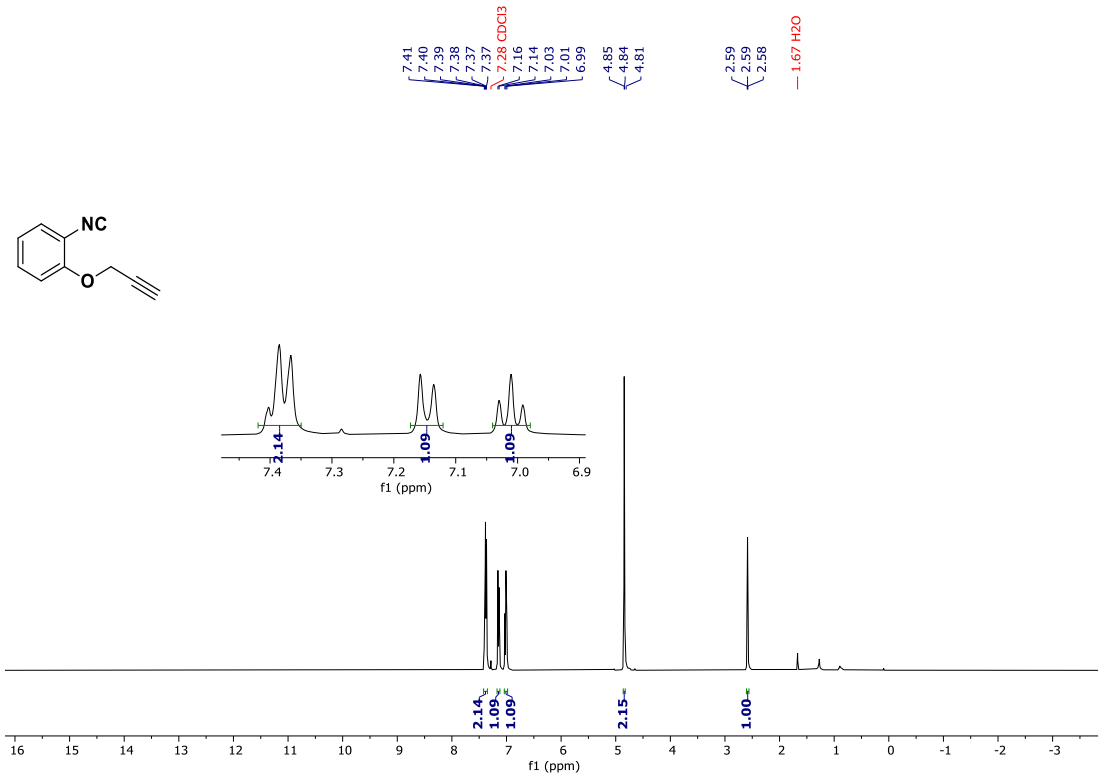
HRMS-ESI (+) of **IVb**



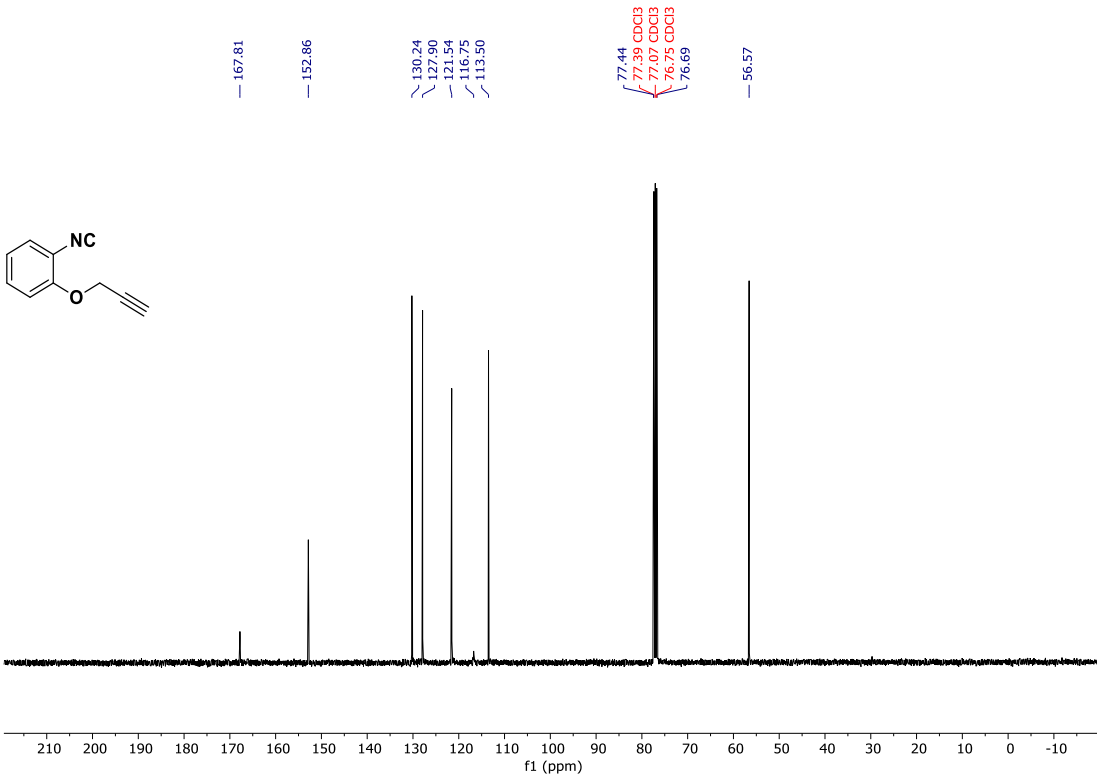
^{1}H NMR (400 MHz, $CDCl_3$) of **IVc**



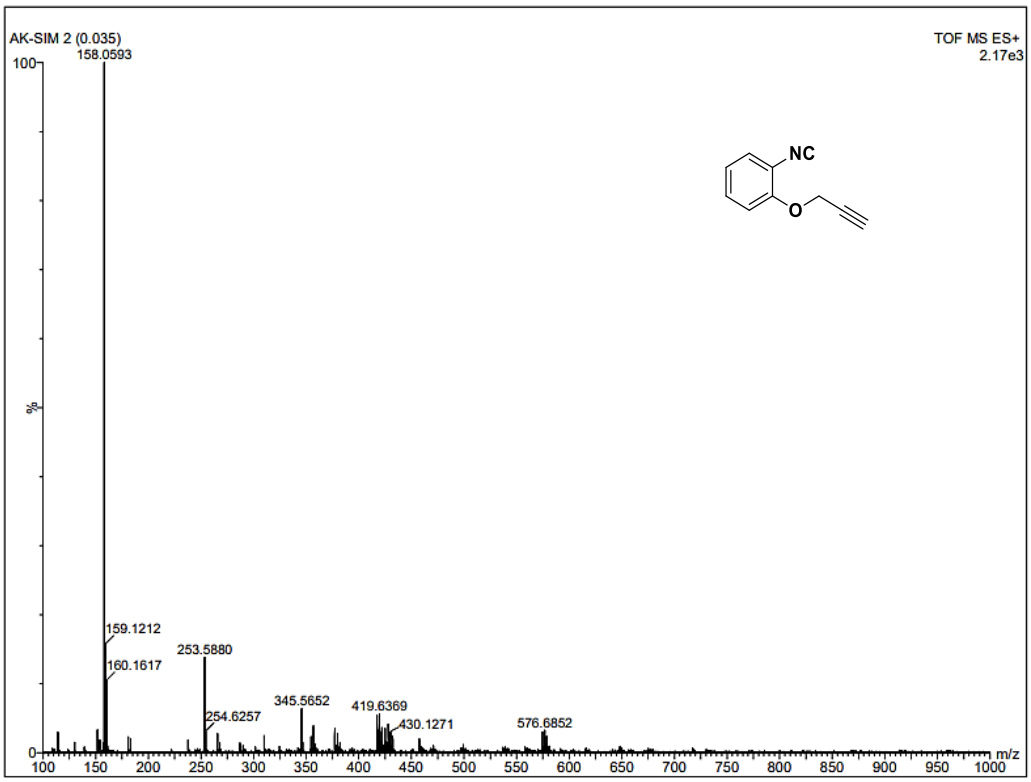
^{13}C NMR (101 MHz, $CDCl_3$) of **IVc**



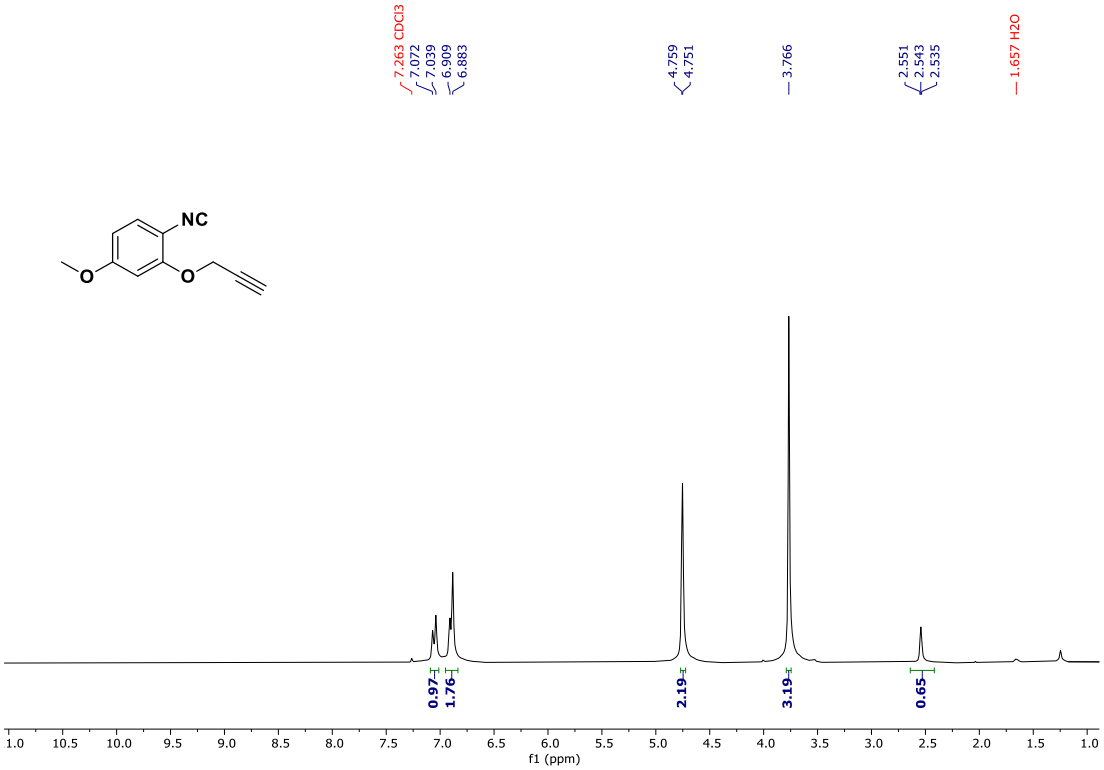
^{1}H NMR (400 MHz, $CDCl_3$) of **IVd**



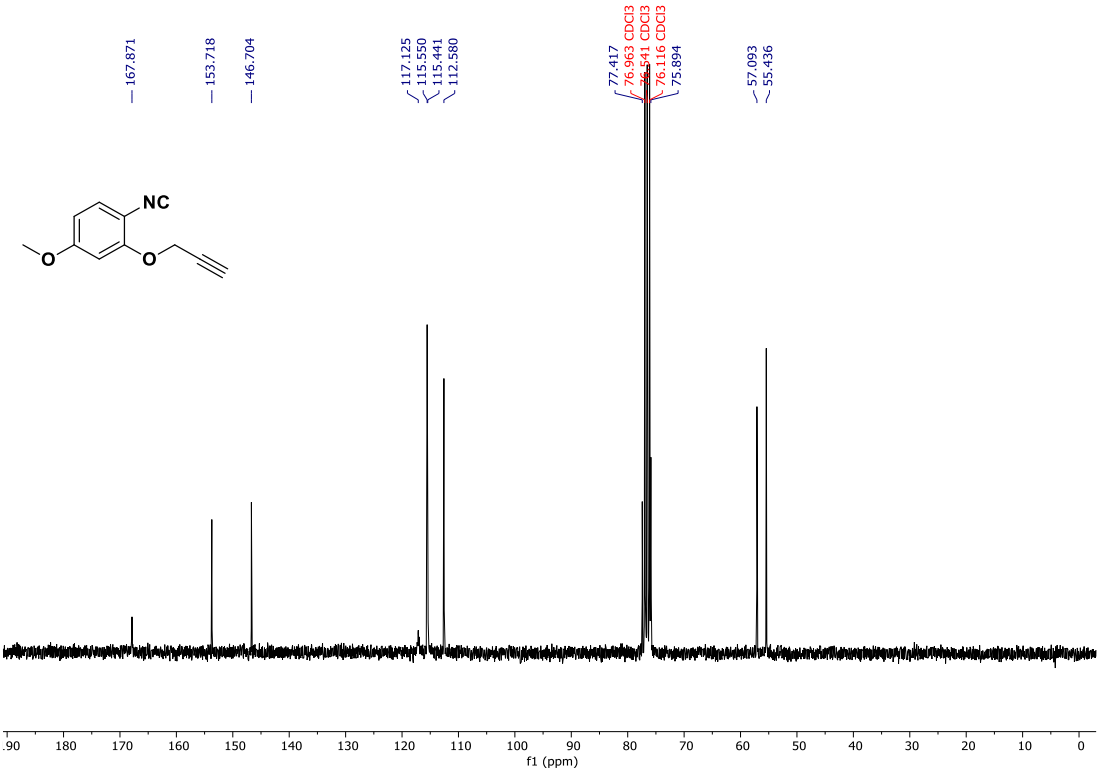
^{13}C NMR (101 MHz, $CDCl_3$) of **IVd**



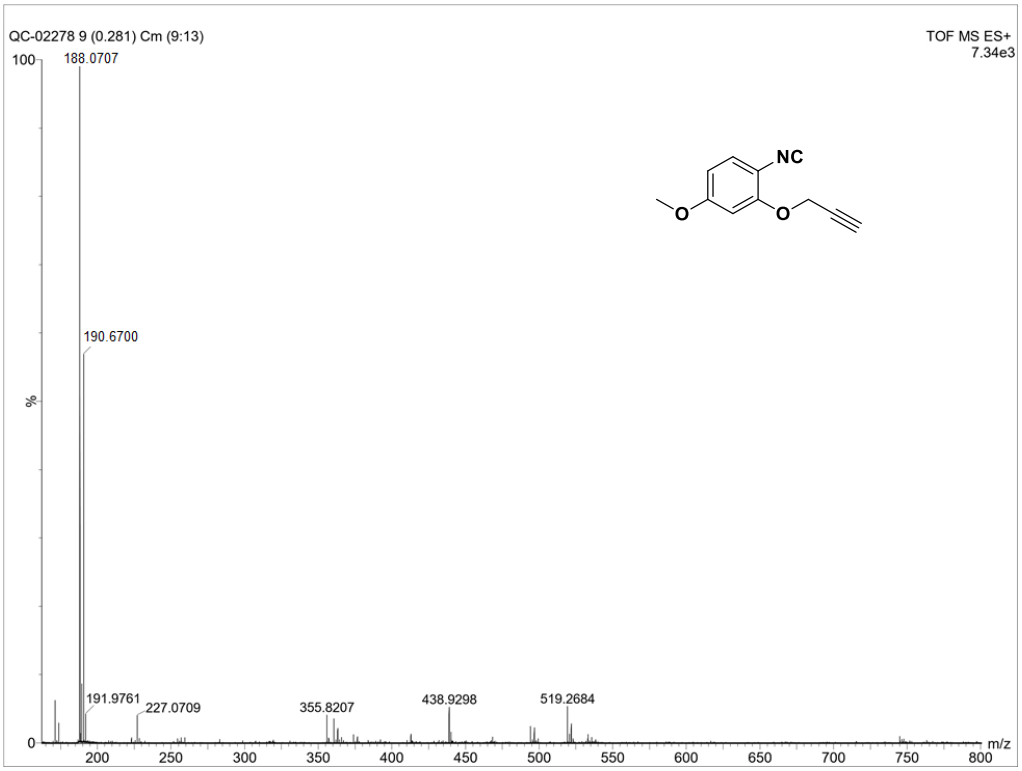
HRMS-ESI (+) of **IVd**



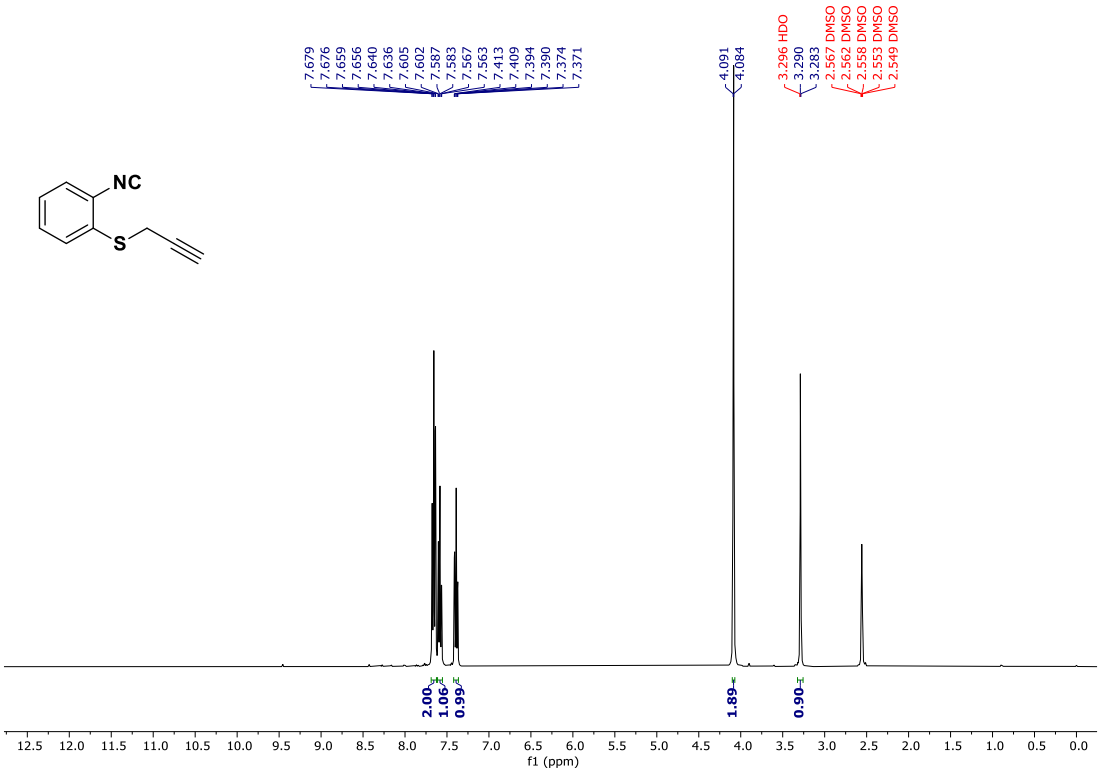
^{1}H NMR (300 MHz, $CDCl_3$) of **IVe**



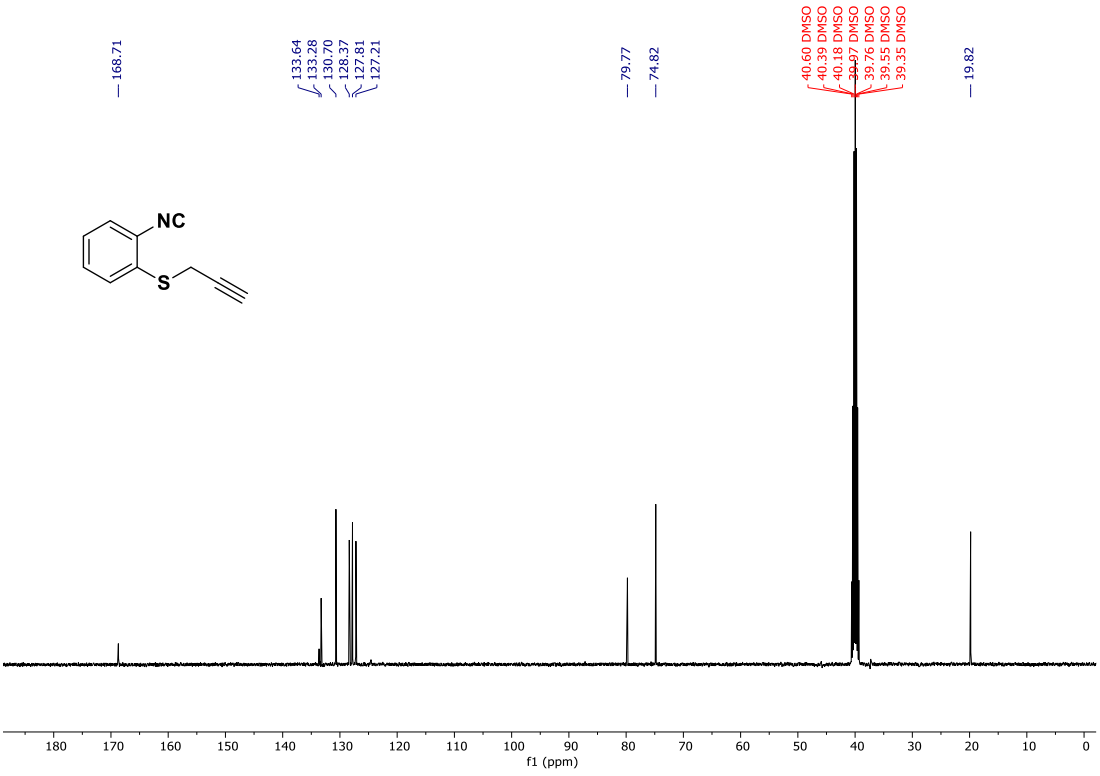
^{13}C NMR (75 MHz, $CDCl_3$) of **IVe**



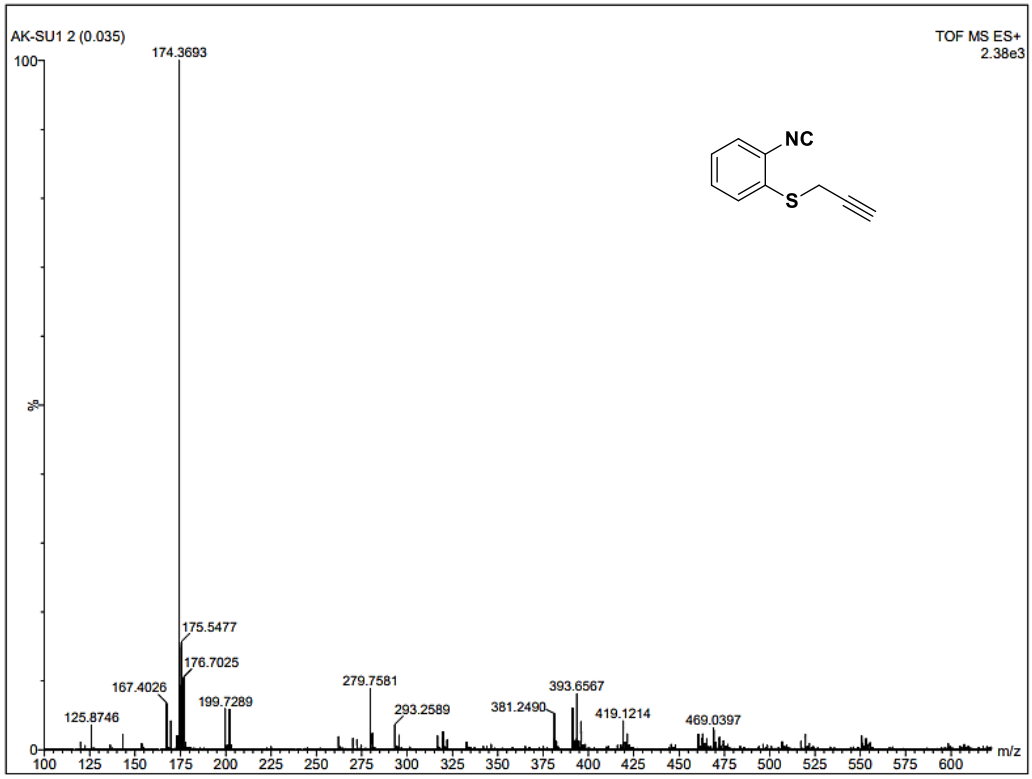
HRMS-ESI (+) of **IVe**



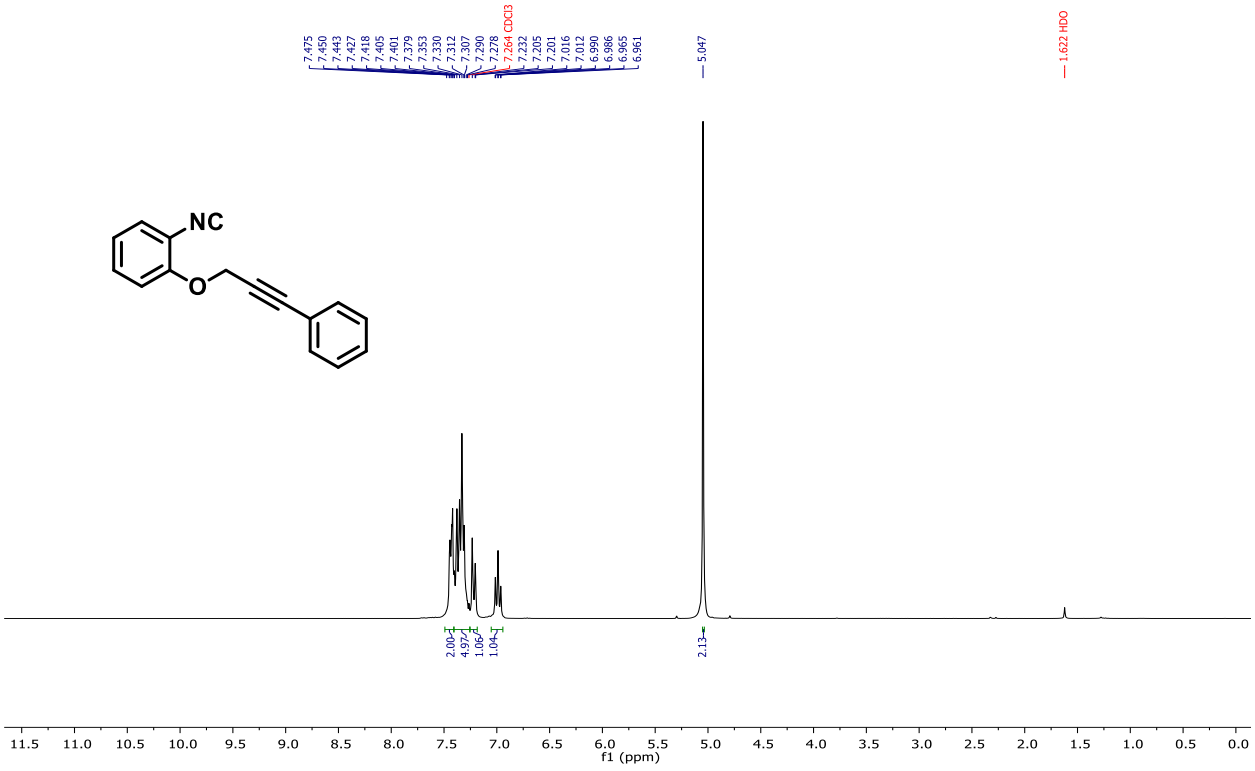
^{1}H NMR (400 MHz, DMSO-d_6) of **IVf**



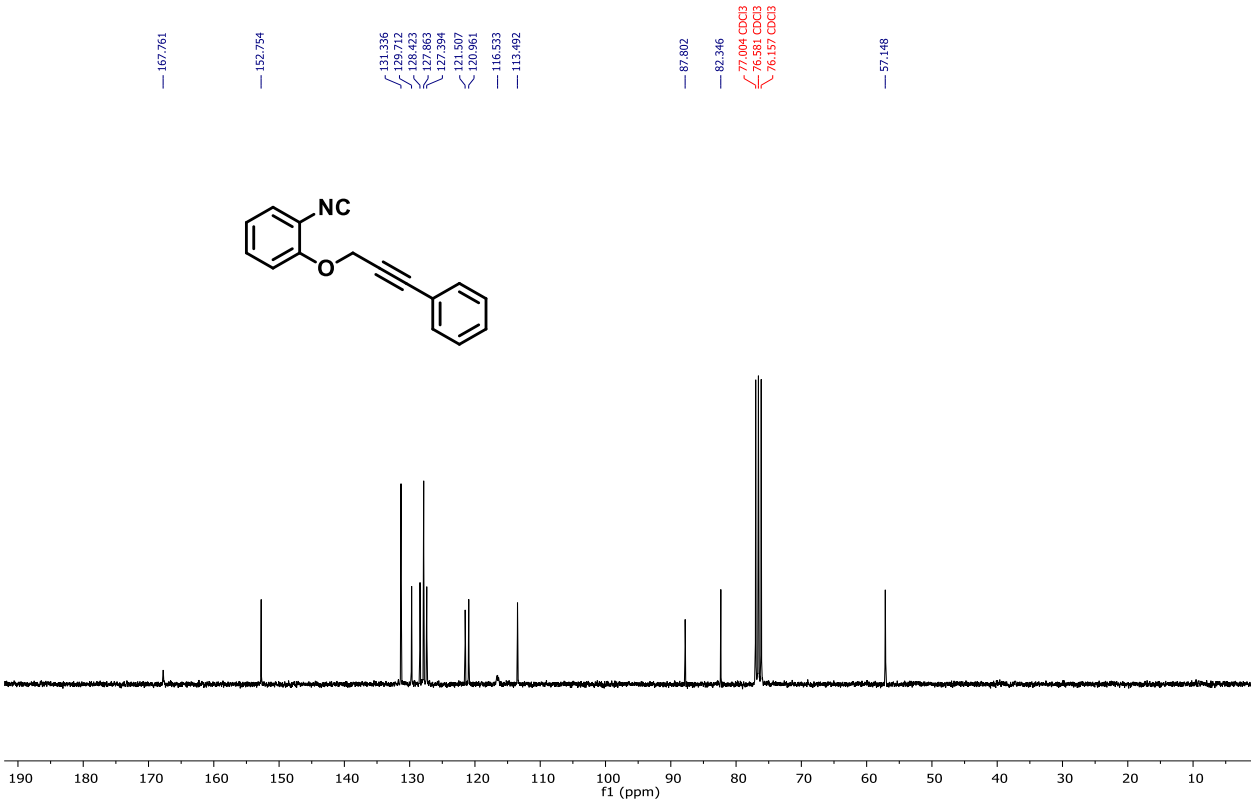
^{13}C NMR (101 MHz, DMSO-d_6) of **IVf**



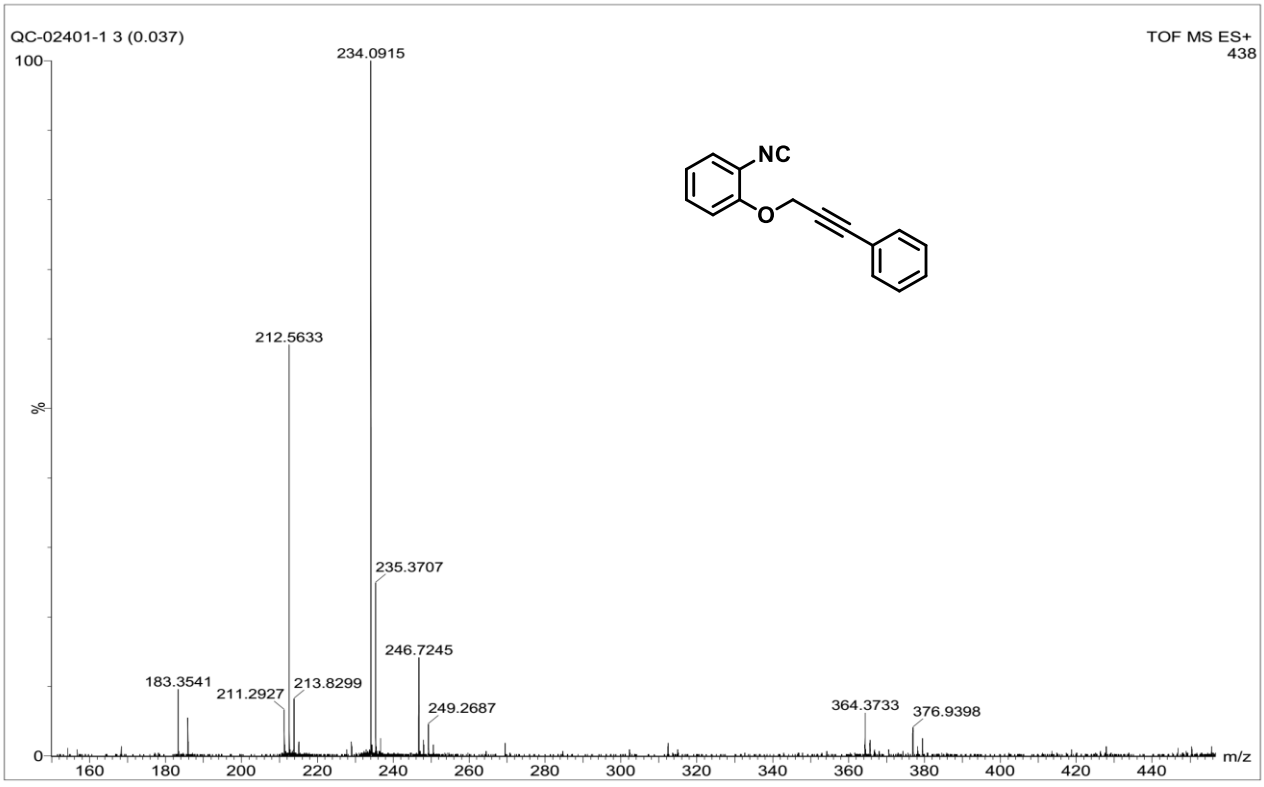
HRMS-ESI (+) of **1f**



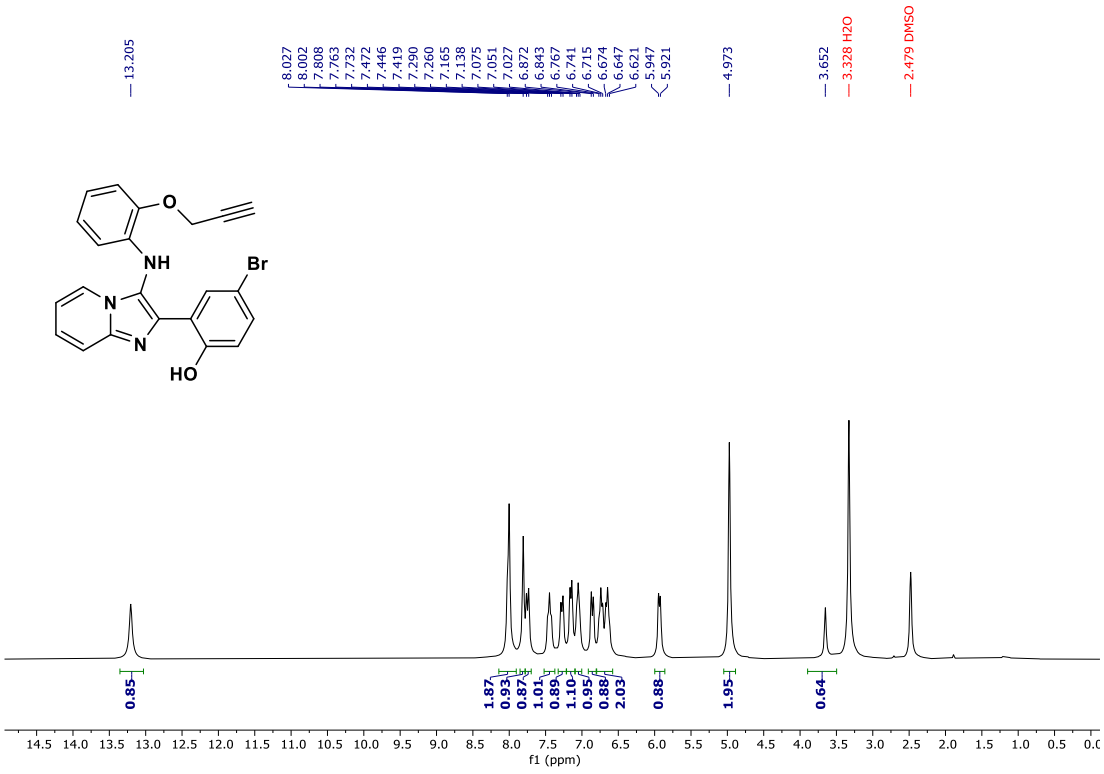
^{1}H NMR (300 MHz, $CDCl_3$) of **IVg**



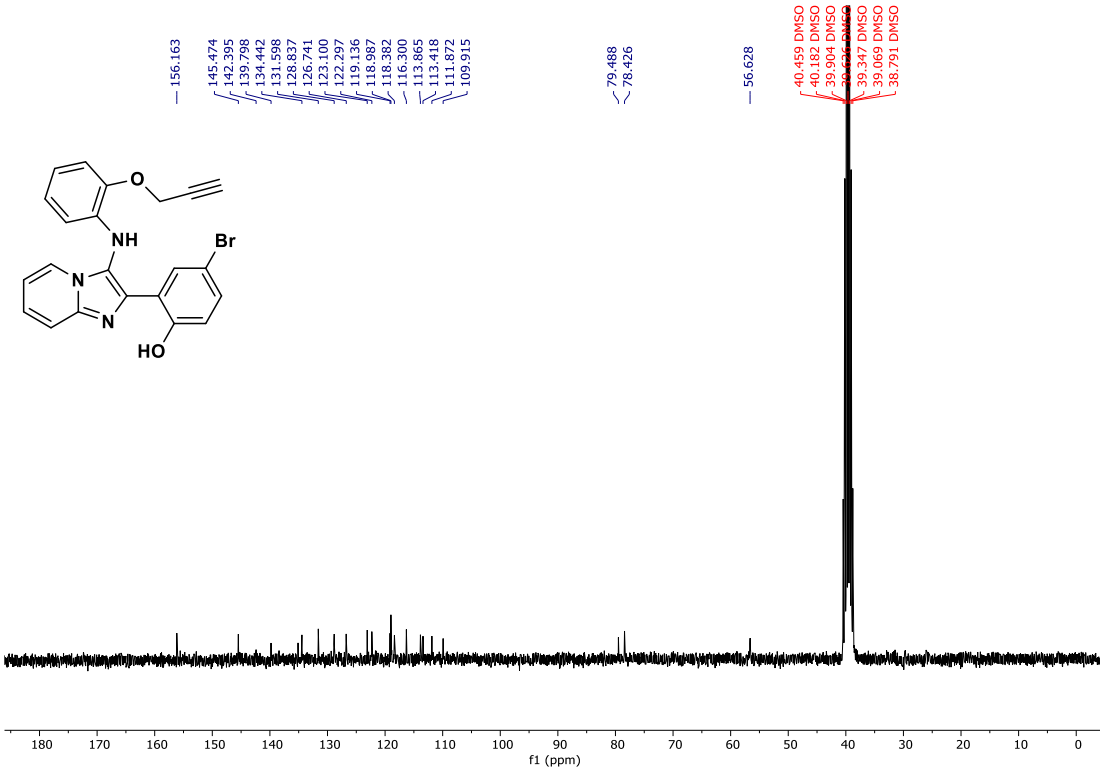
^{13}C NMR (75 MHz, DMSO-d_6) of **IVg**



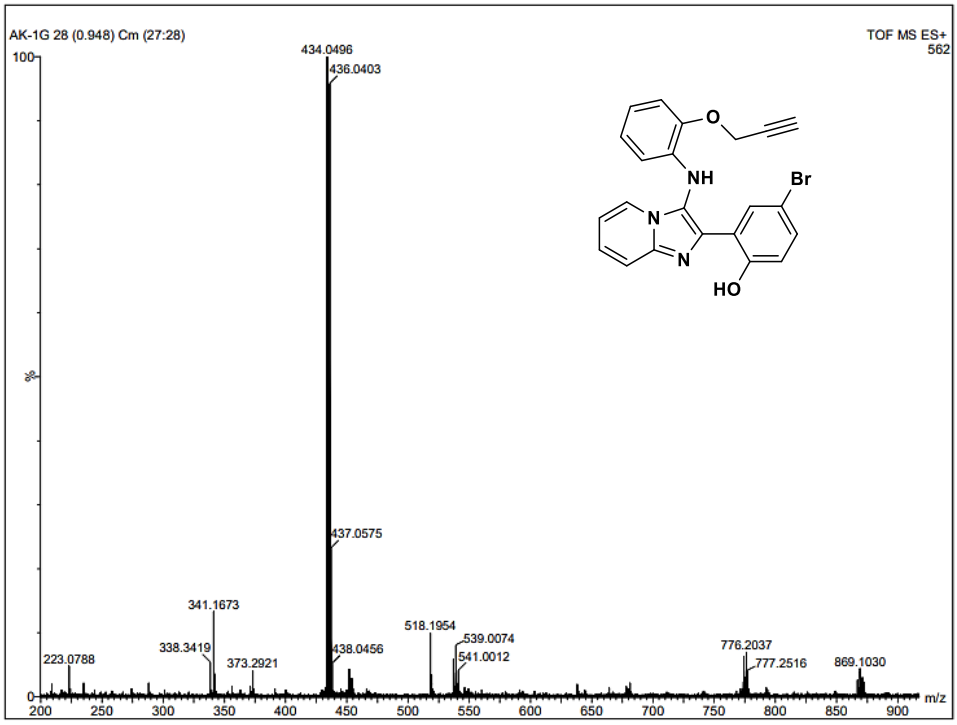
HRMS-ESI (+) of **IVg**



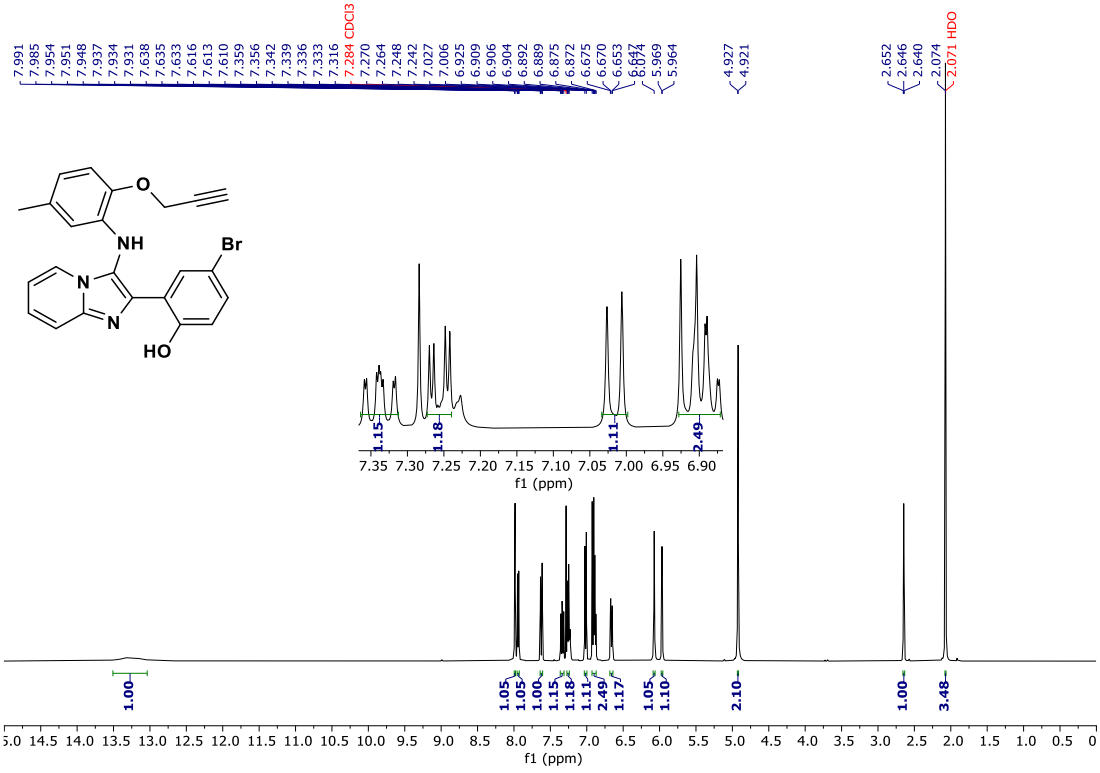
^{1}H NMR (300 MHz, DMSO-d_6) of **1a**



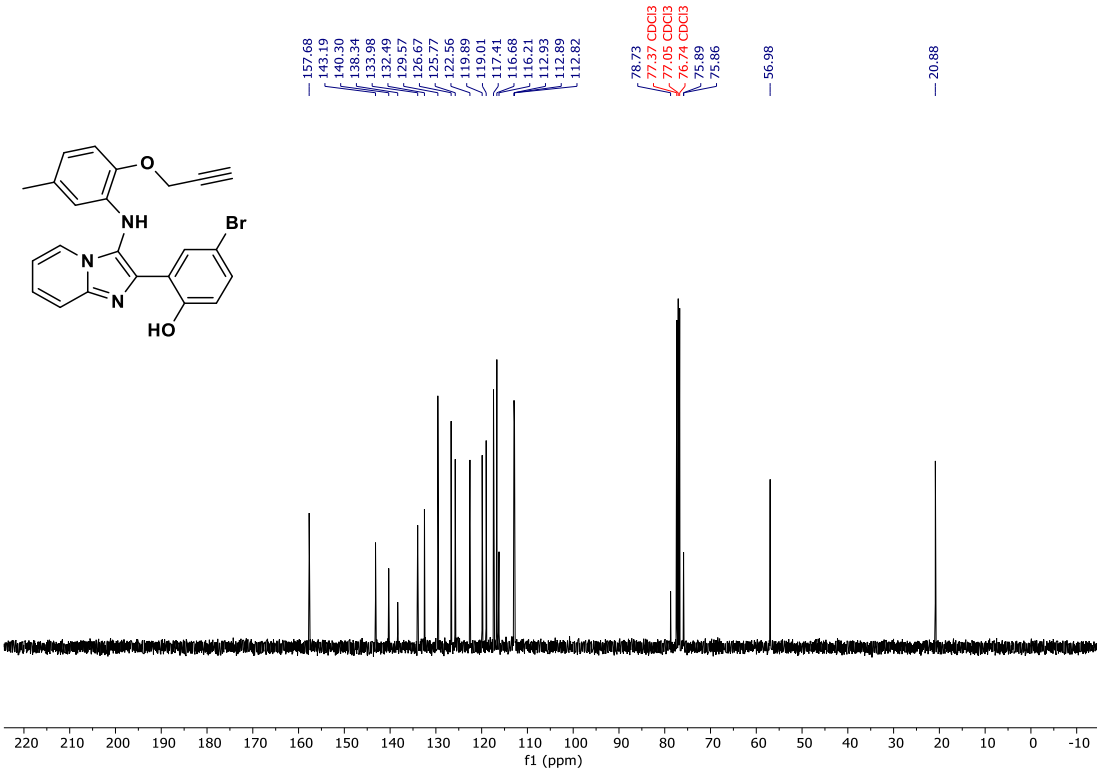
^{13}C NMR (75 MHz, DMSO-d_6) of **1a**



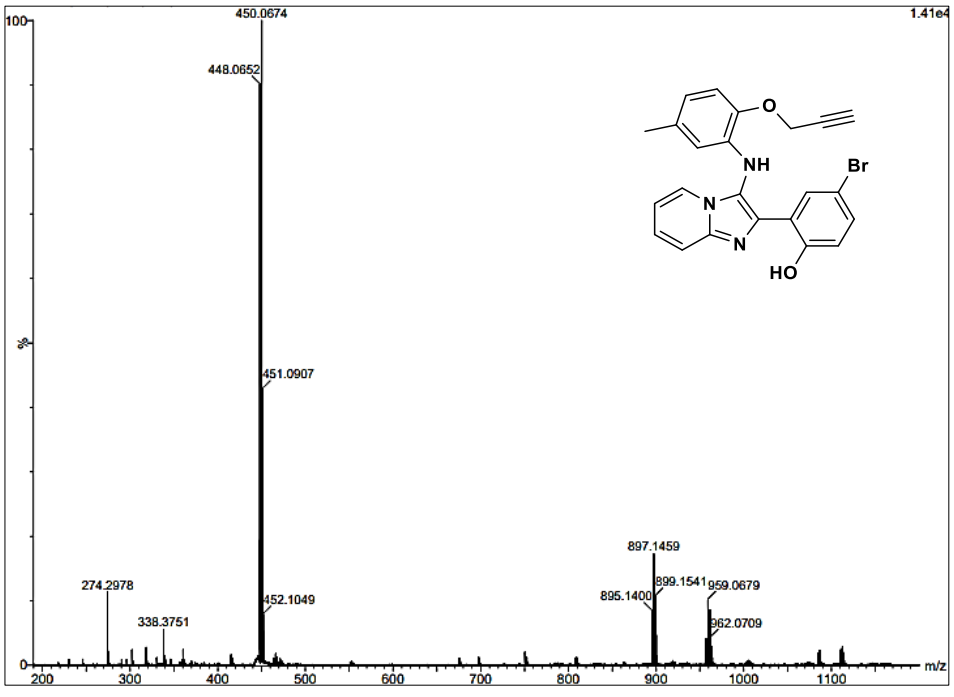
HRMS-ESI (+) of **1a**



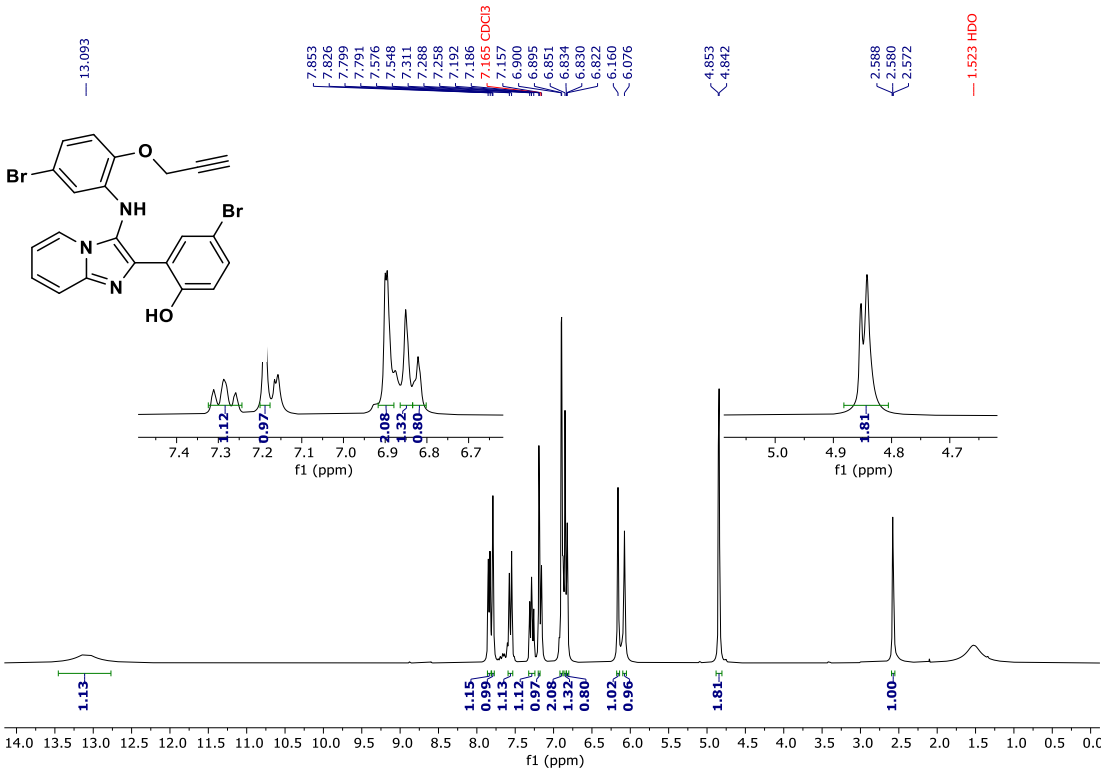
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



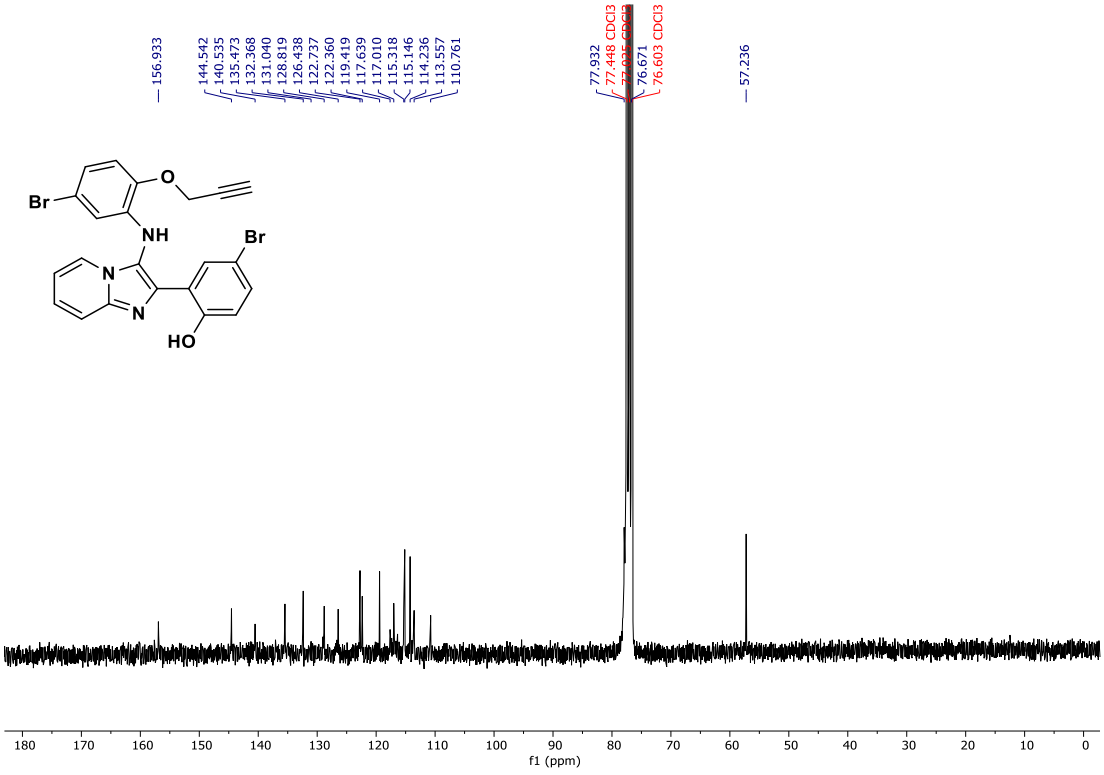
^{13}C NMR (101 MHz, $CDCl_3$) of **1b**



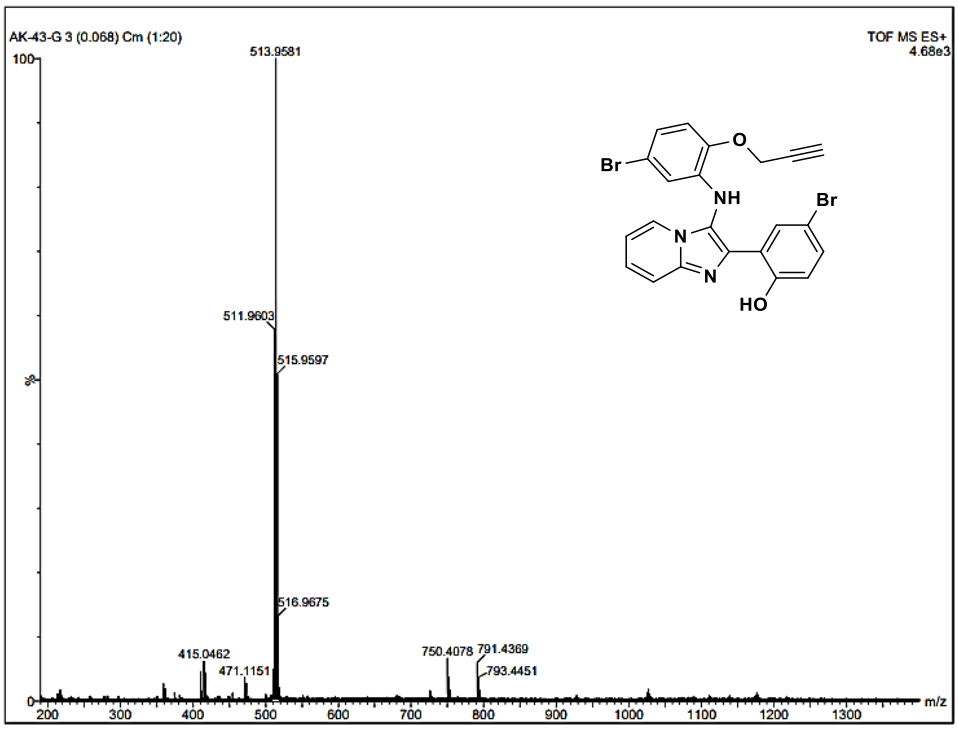
HRMS-ESI (+) of **1b**



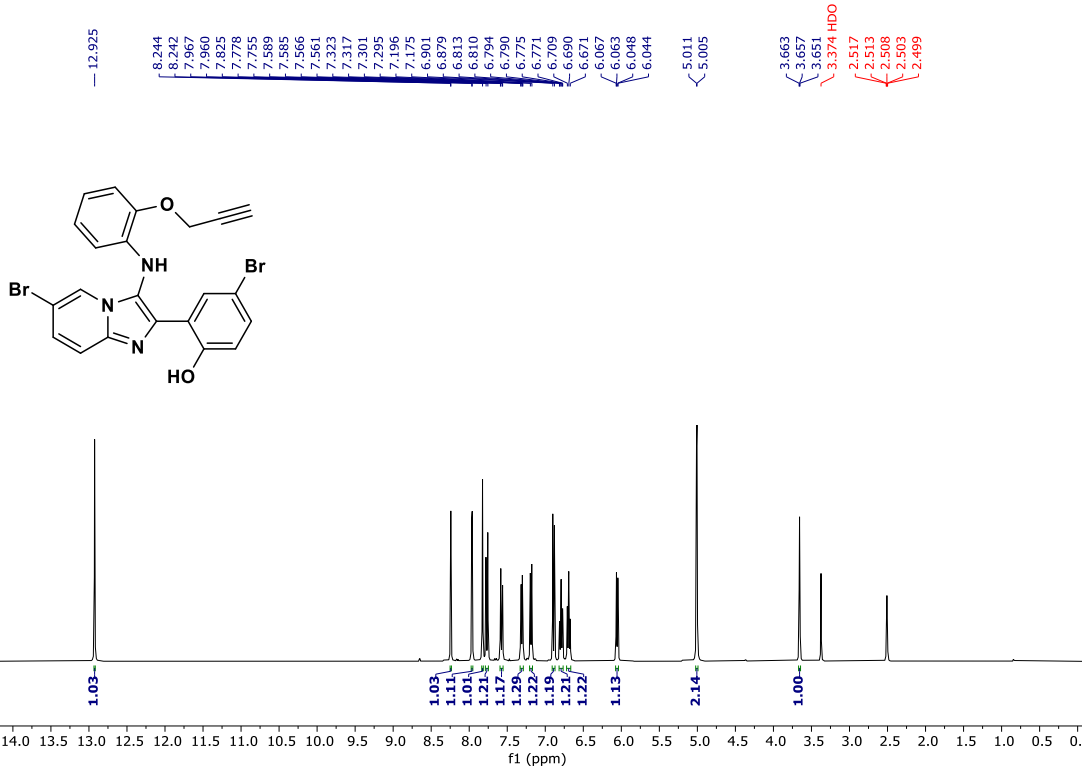
^{1}H NMR (300 MHz, $CDCl_3$) of **1c**



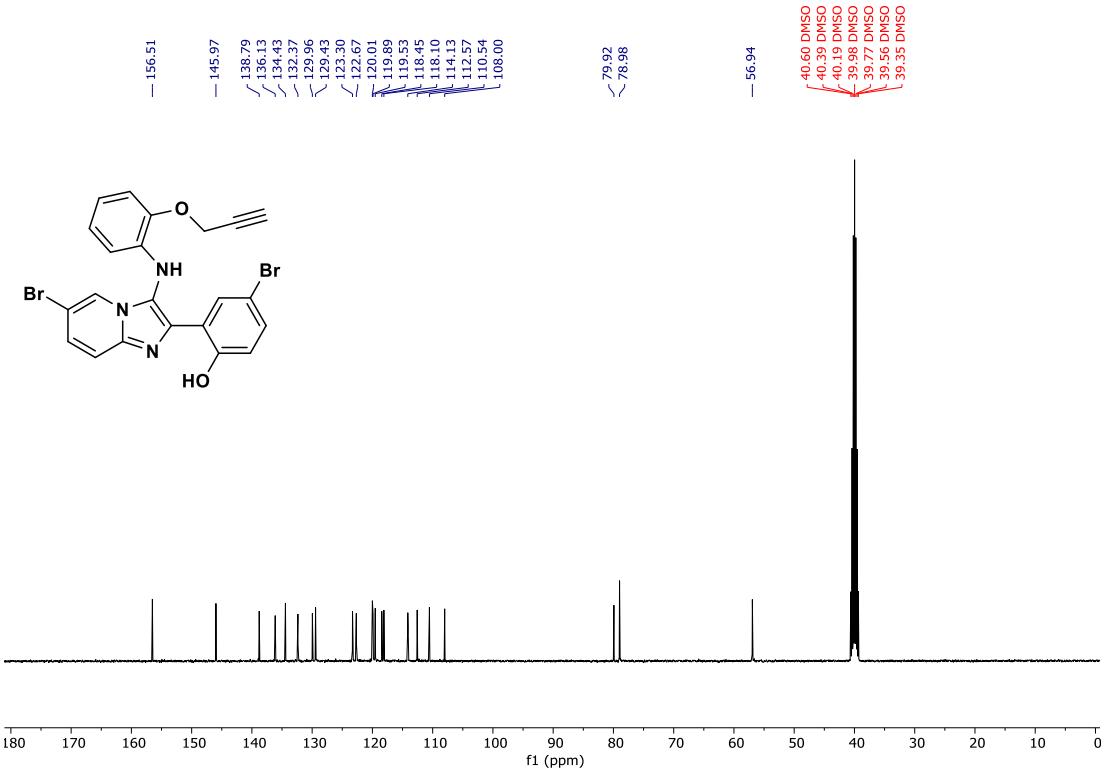
^{13}C NMR (75 MHz, $CDCl_3$) of **1c**



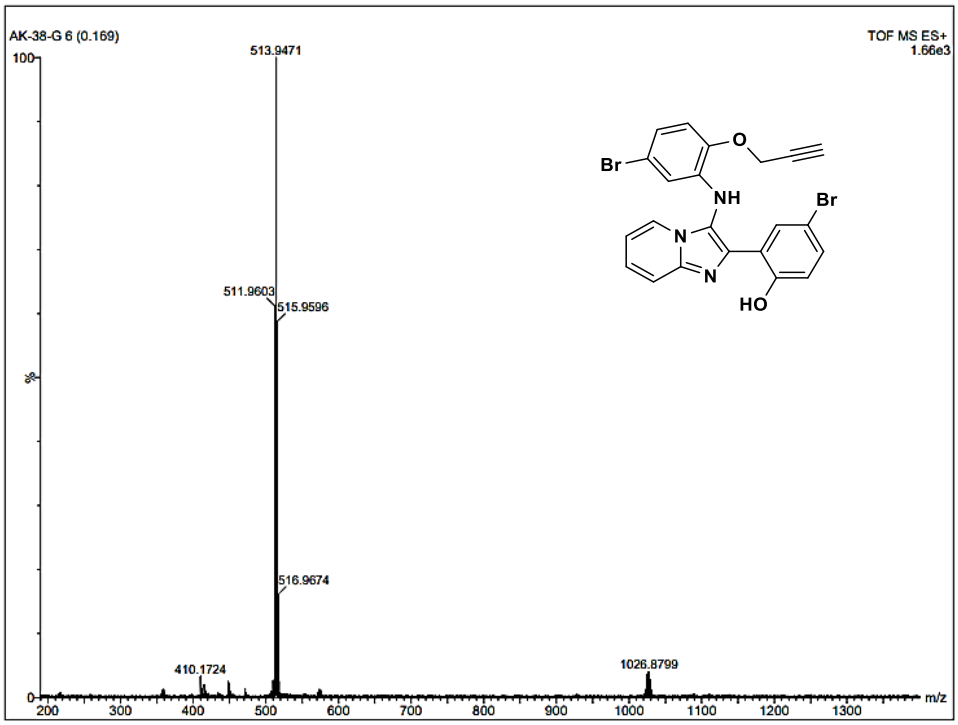
HRMS-ESI (+) of **1c**



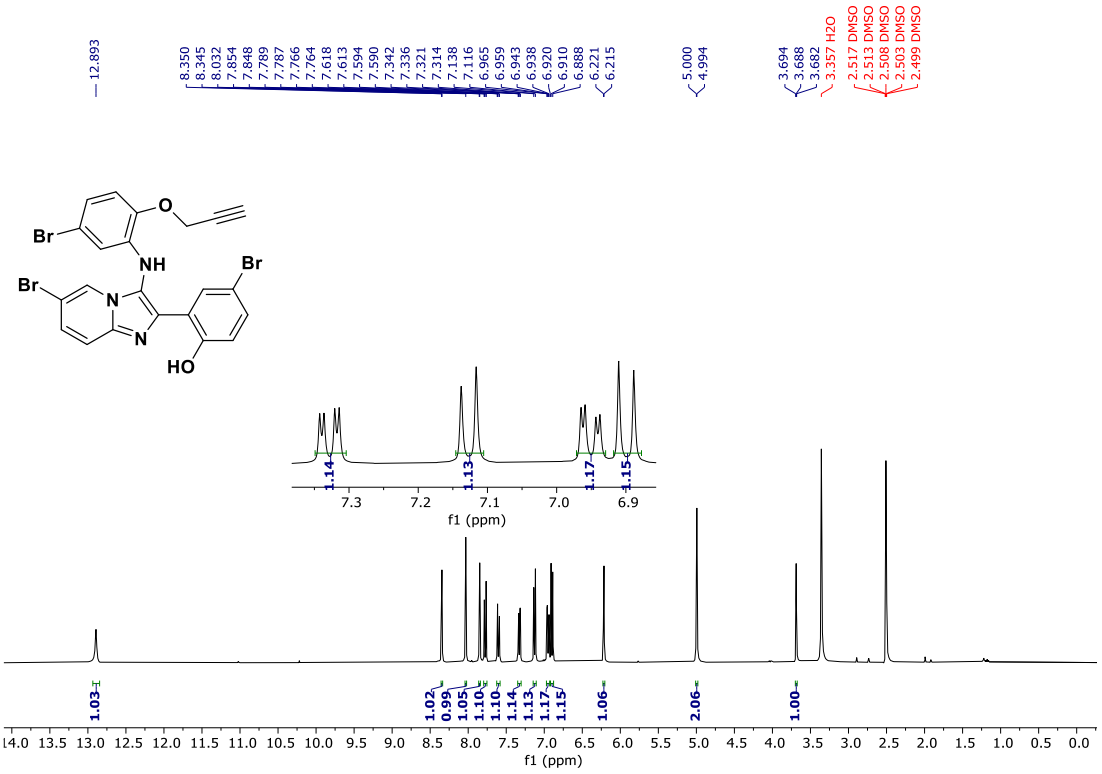
^{1}H NMR (400 MHz, DMSO-d_6) of **1d**



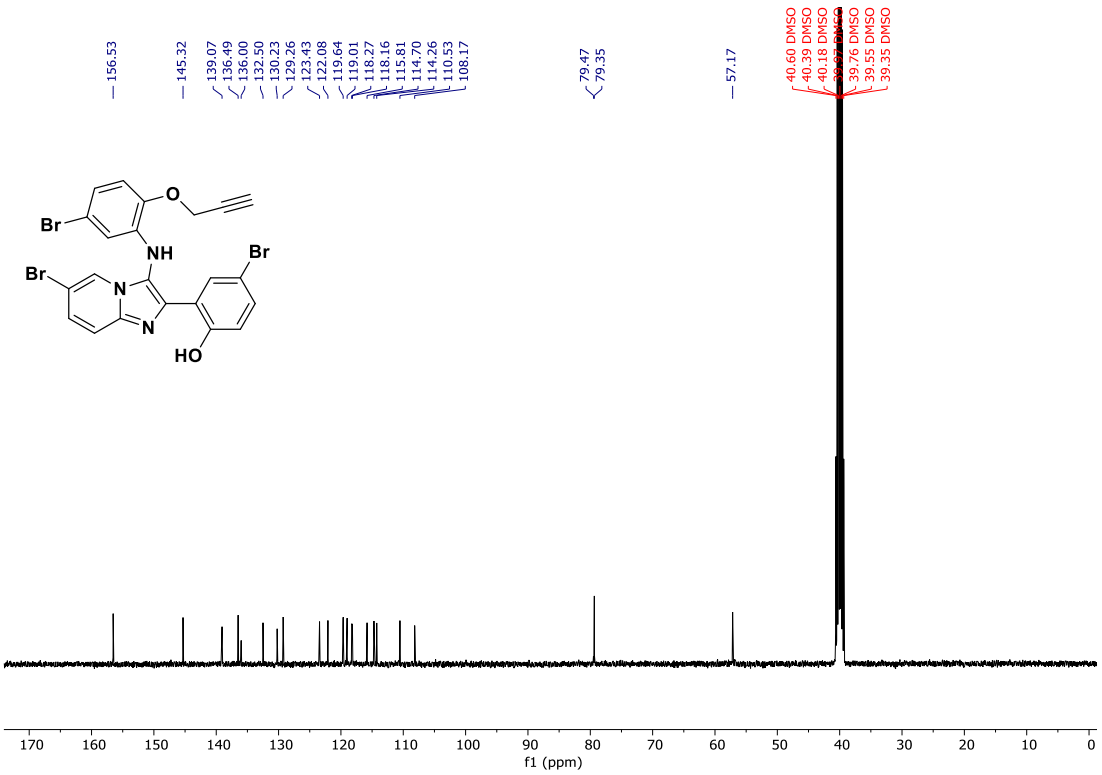
^{13}C NMR (101 MHz, DMSO-d_6) of **1d**



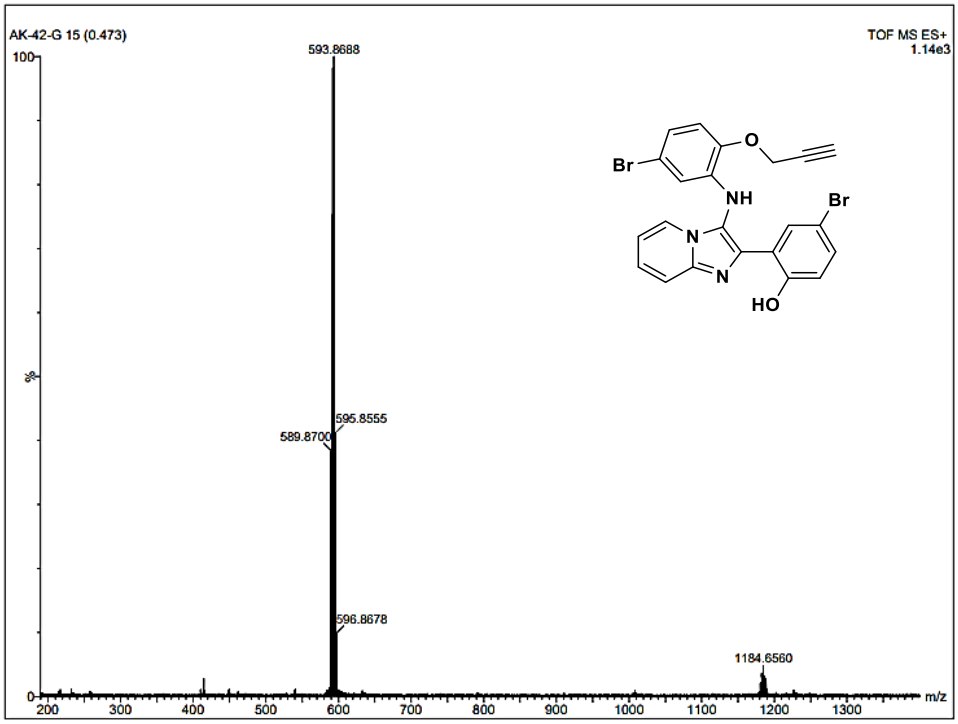
HRMS-ESI (+) of **1d**



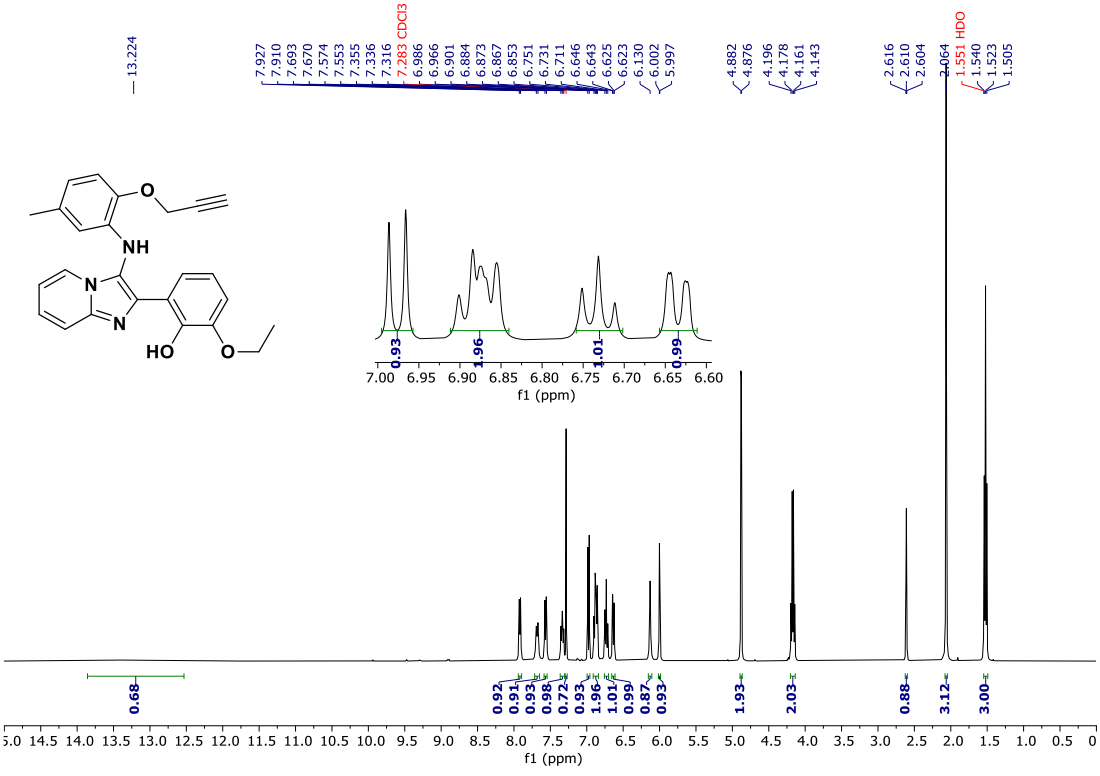
^{1}H NMR (400 MHz, DMSO-d_6) of **1e**



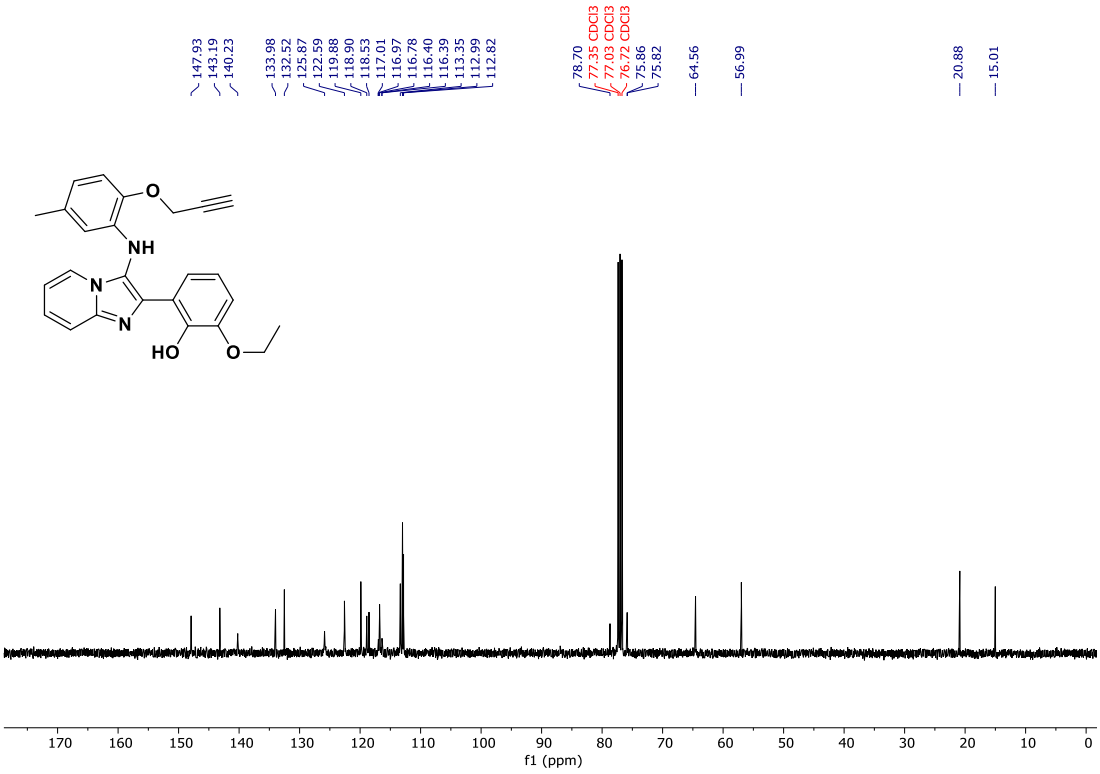
^{13}C NMR (101 MHz, DMSO-d_6) of **1e**



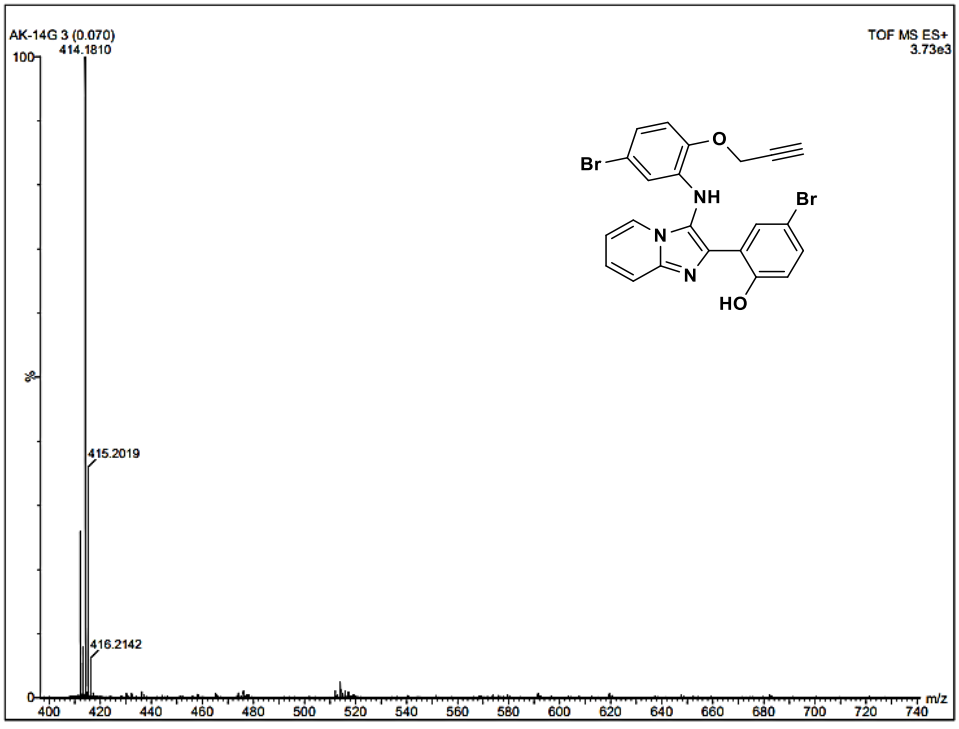
HRMS-ESI (+) of **1e**



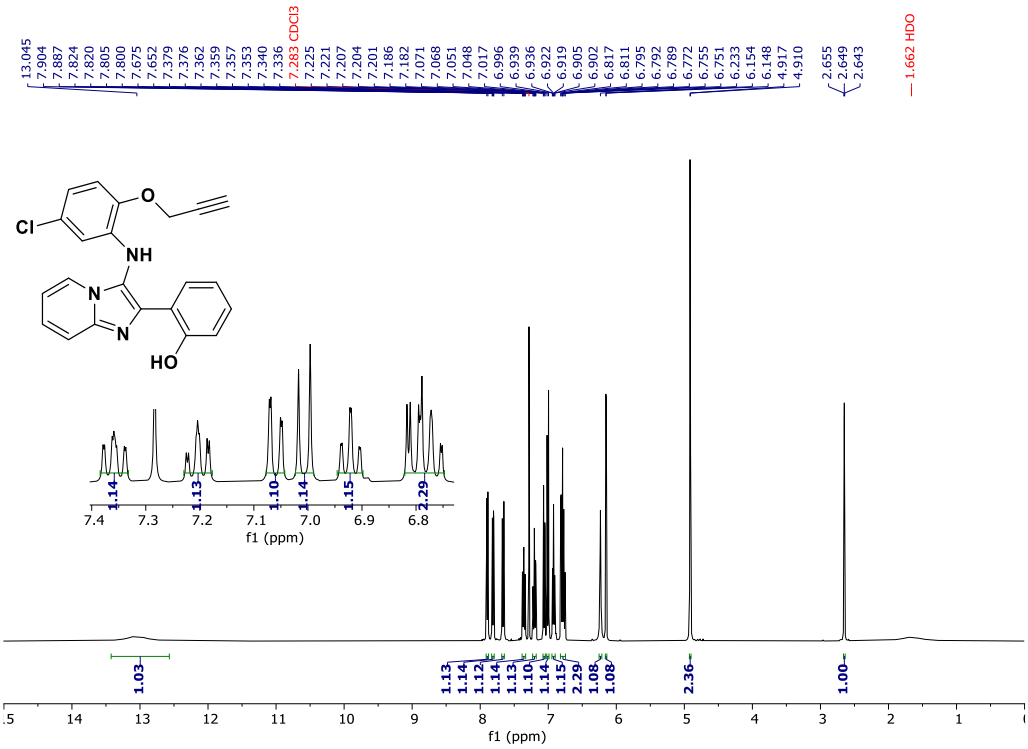
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



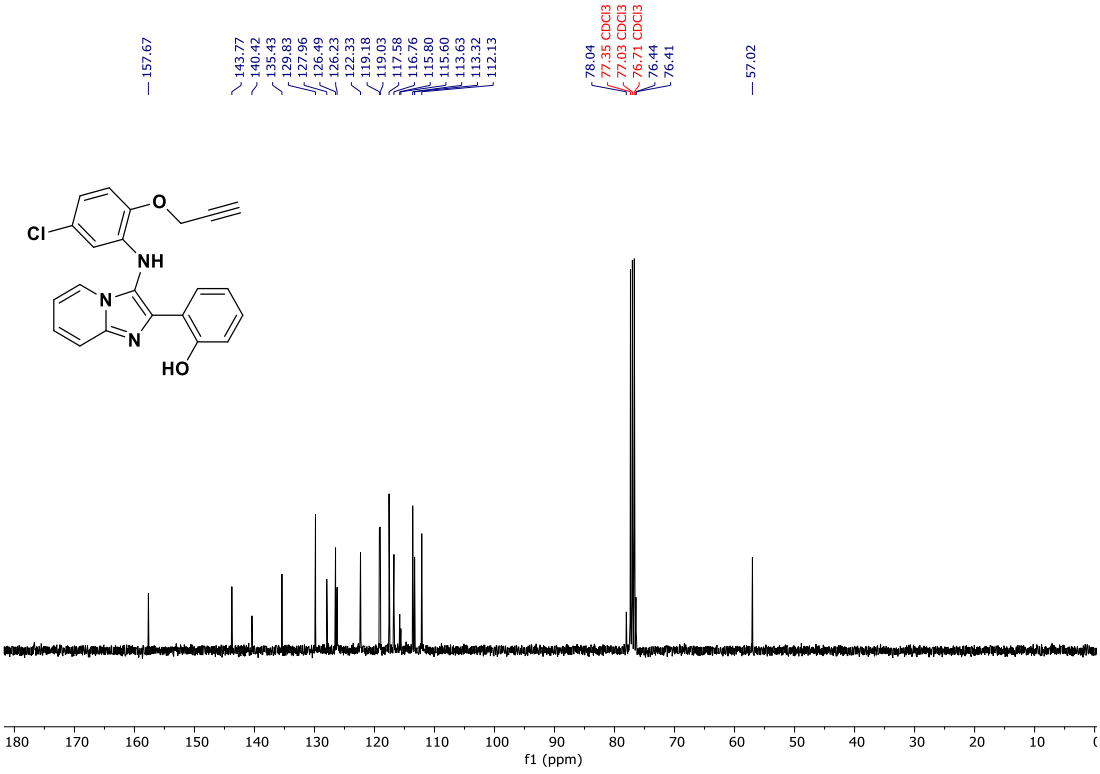
^{13}C NMR (101 MHz, $CDCl_3$) of **1f**



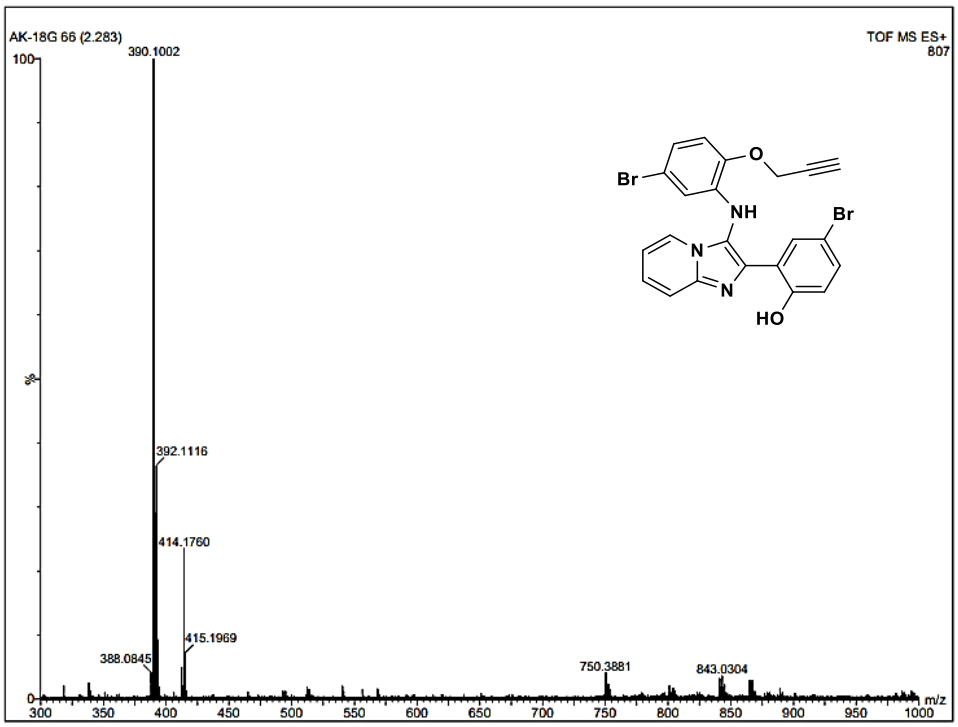
HRMS-ESI (+) of **1f**



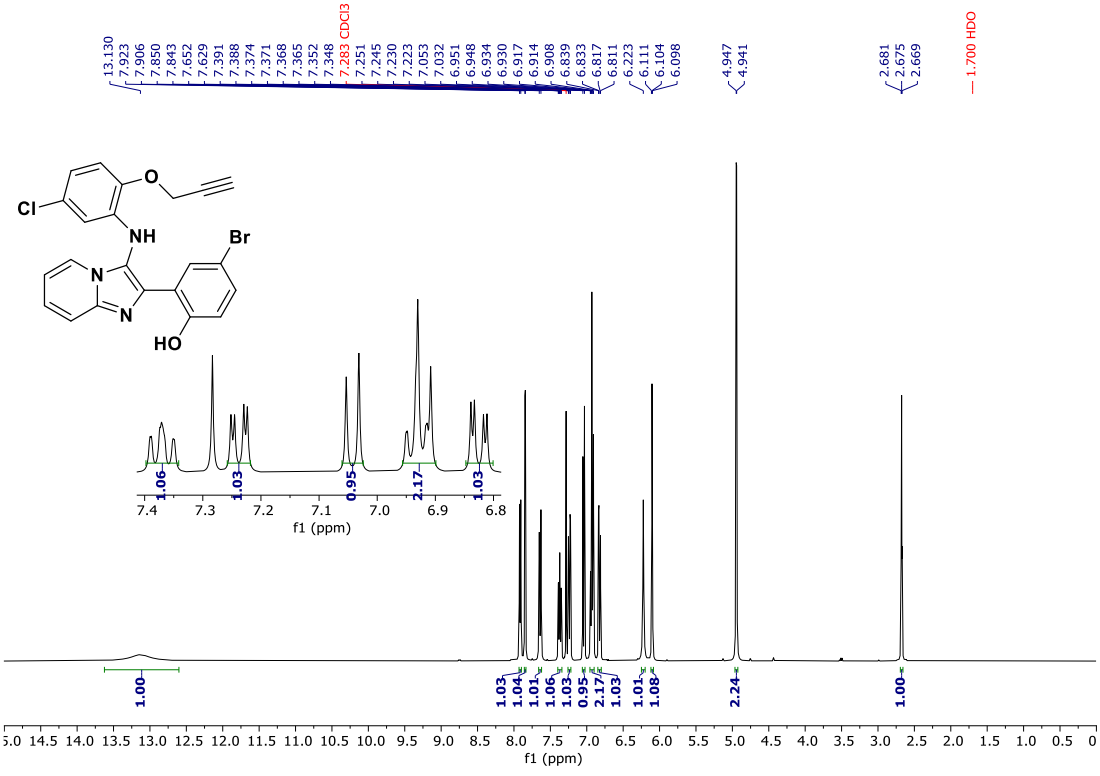
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



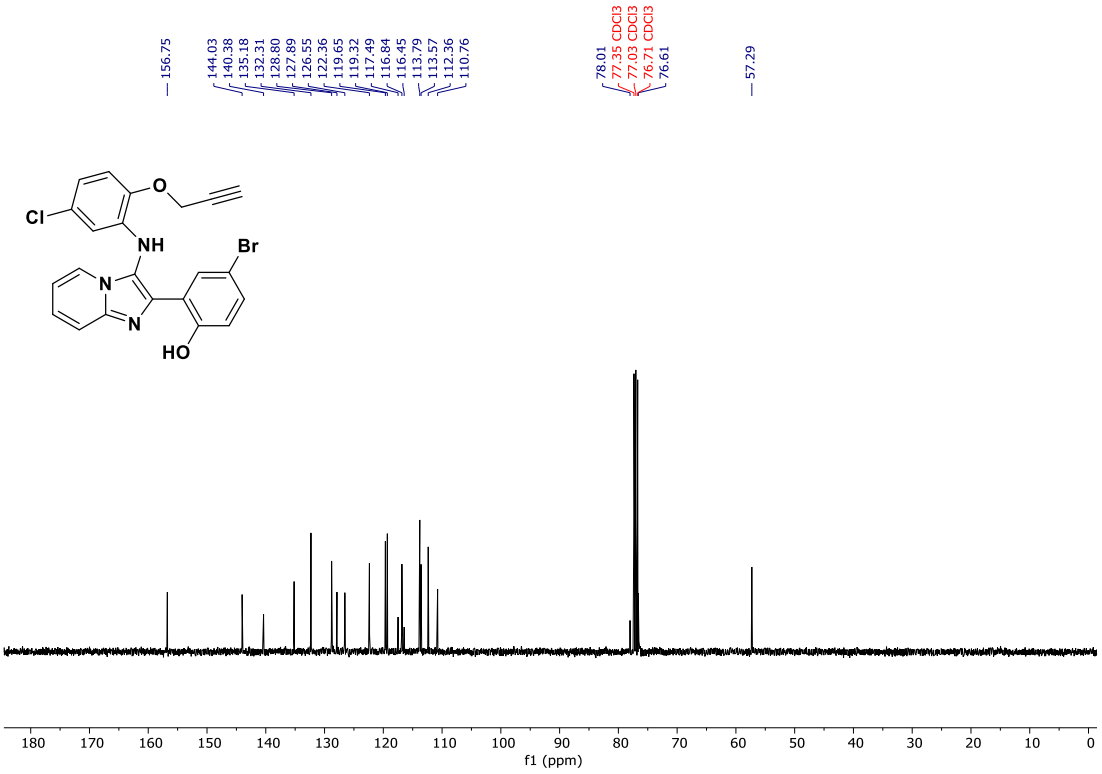
^{13}C NMR (101 MHz, $CDCl_3$) of **1g**



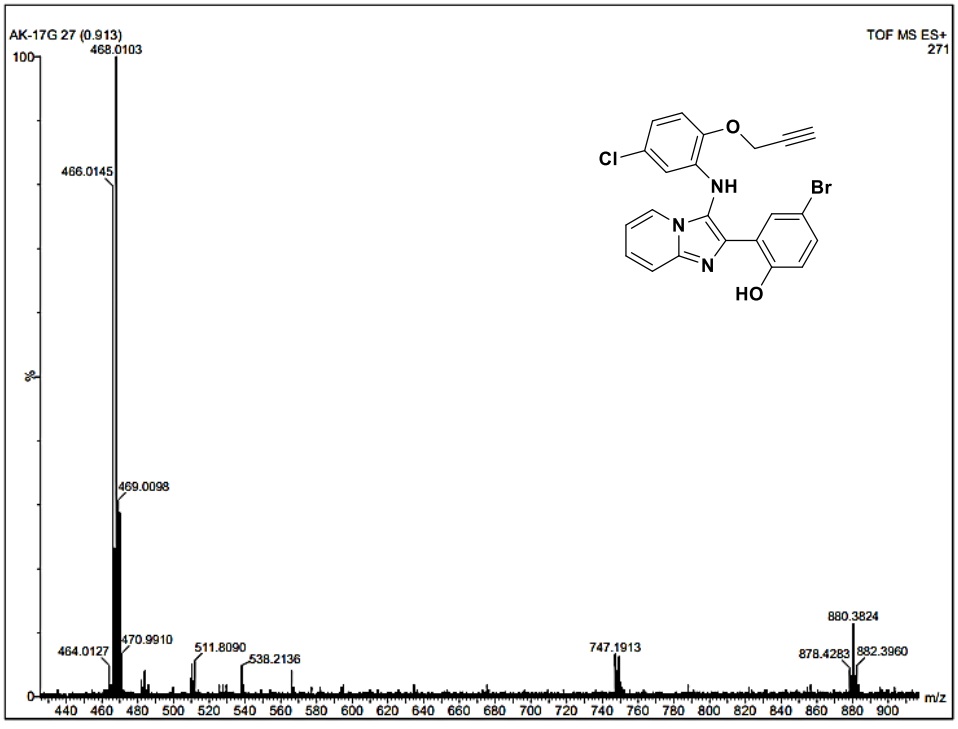
HRMS-ESI (+) of **1g**



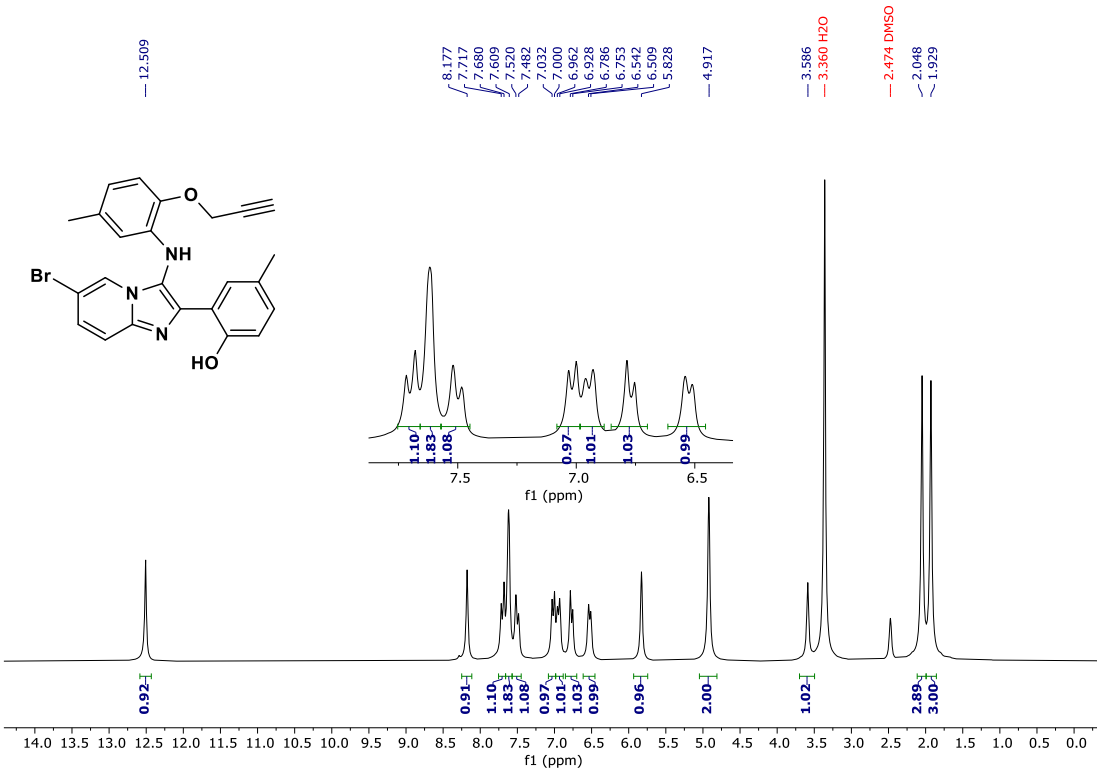
^{1}H NMR (400 MHz, $CDCl_3$) of **1h**



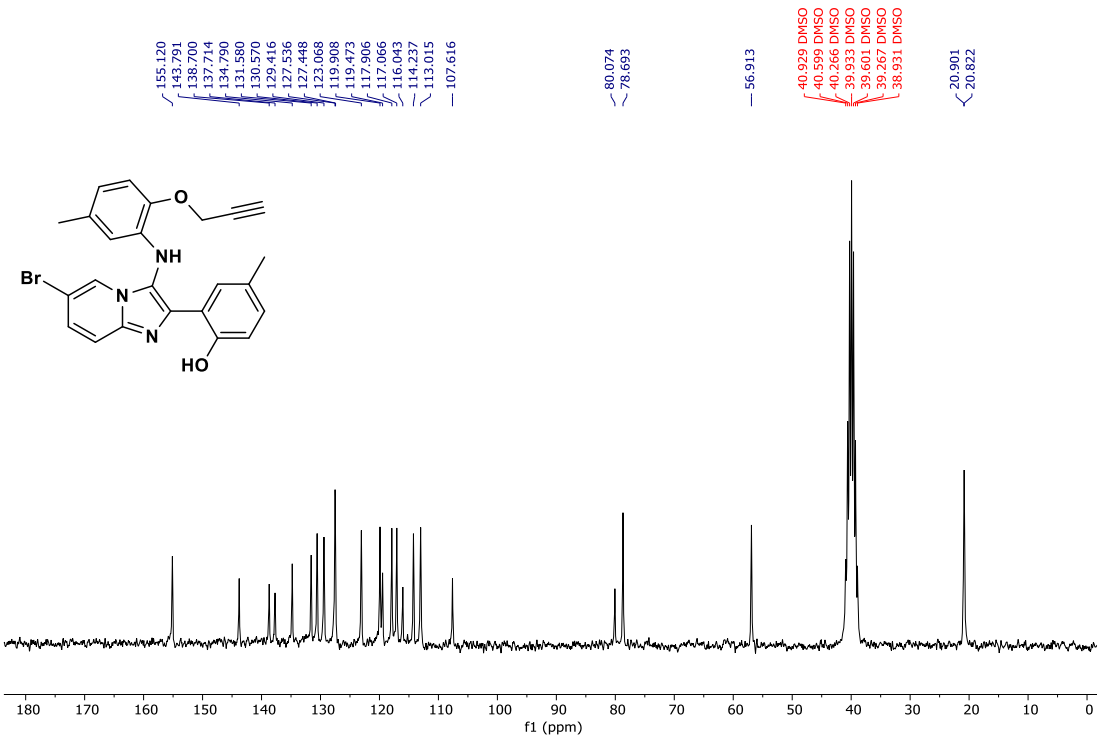
^{13}C NMR (101 MHz, $CDCl_3$) of **1h**



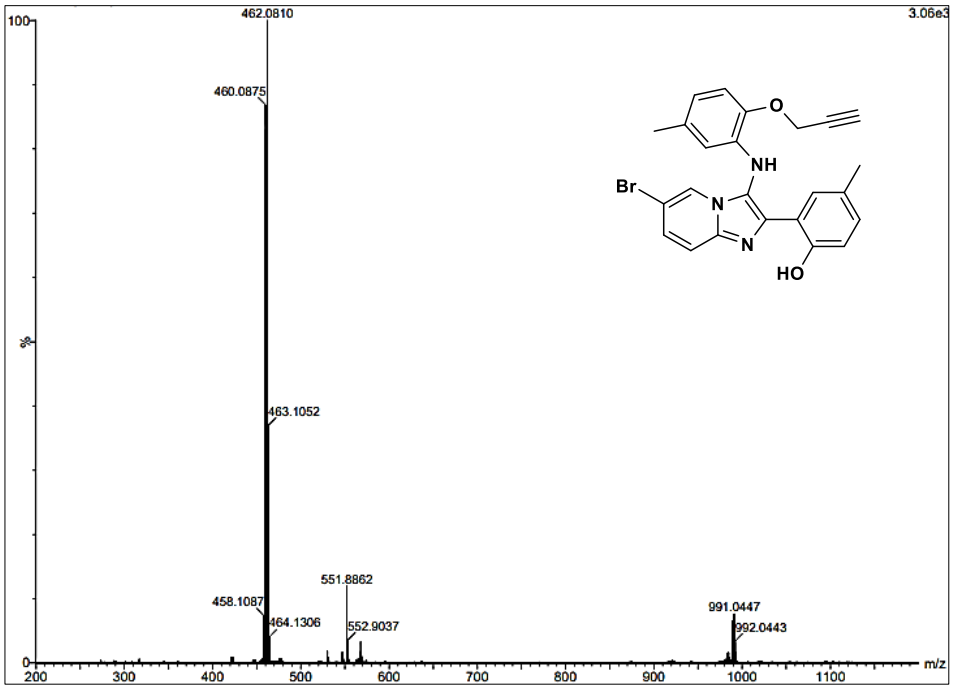
HRMS-ESI (+) of **1h**



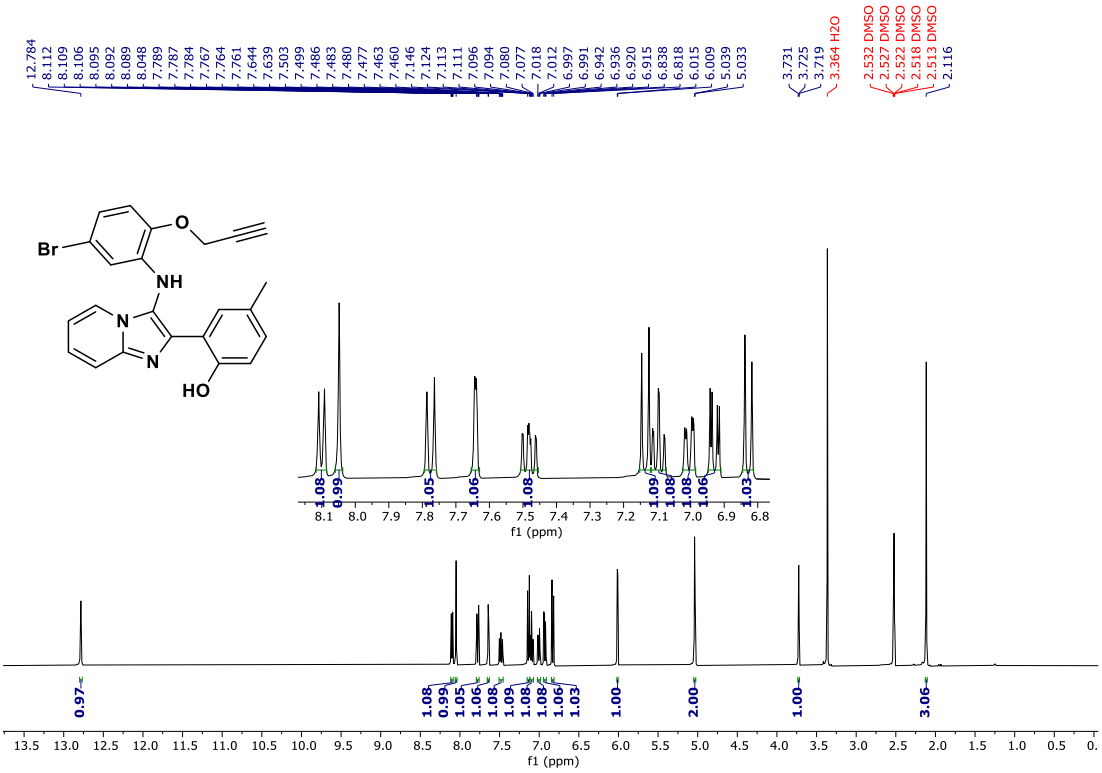
^{1}H NMR (250 MHz, $CDCl_3$) of **1i**



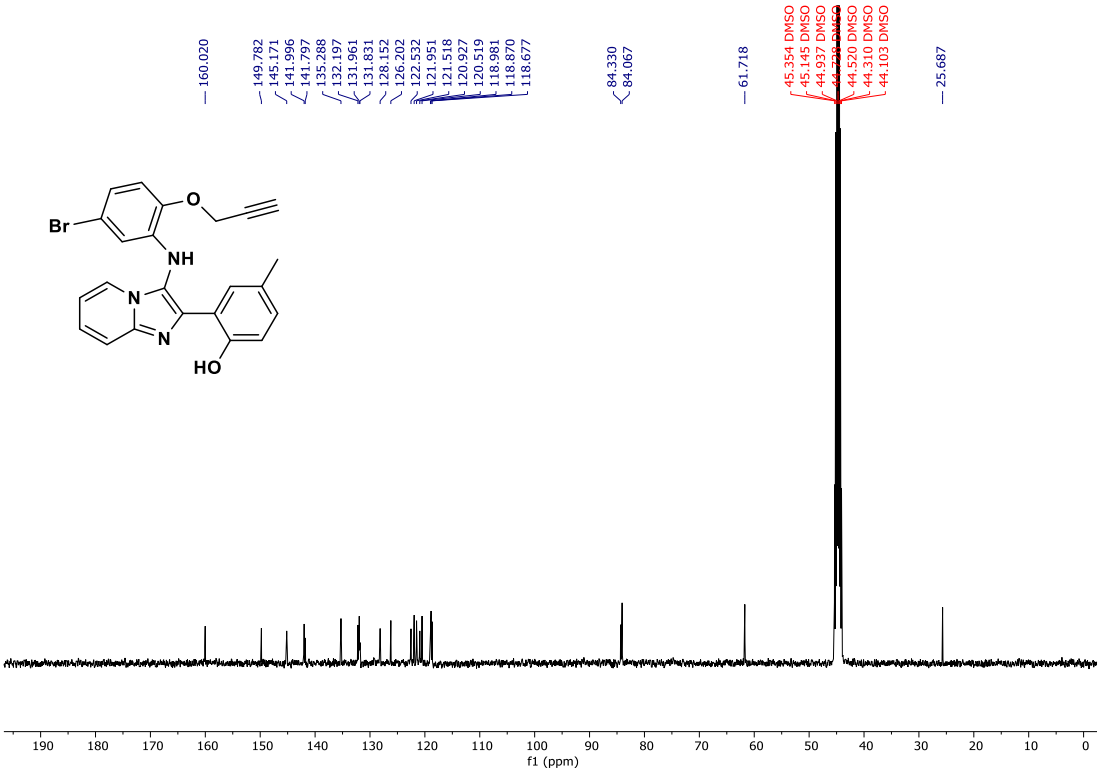
^{13}C NMR (63 MHz, $CDCl_3$) of **1i**



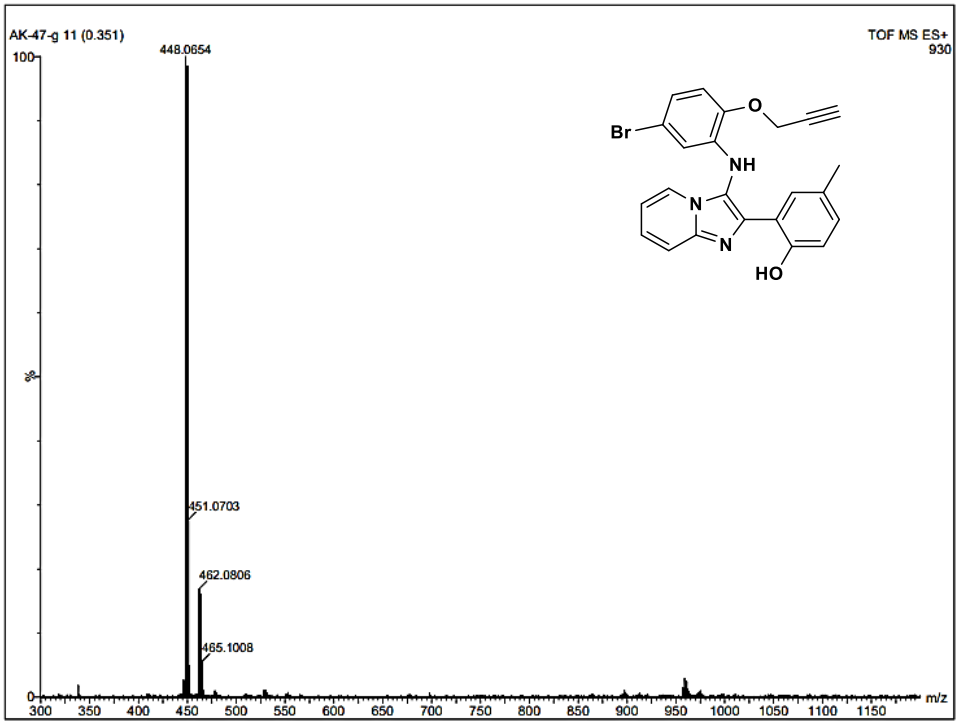
HRMS-ESI (+) of **1i**



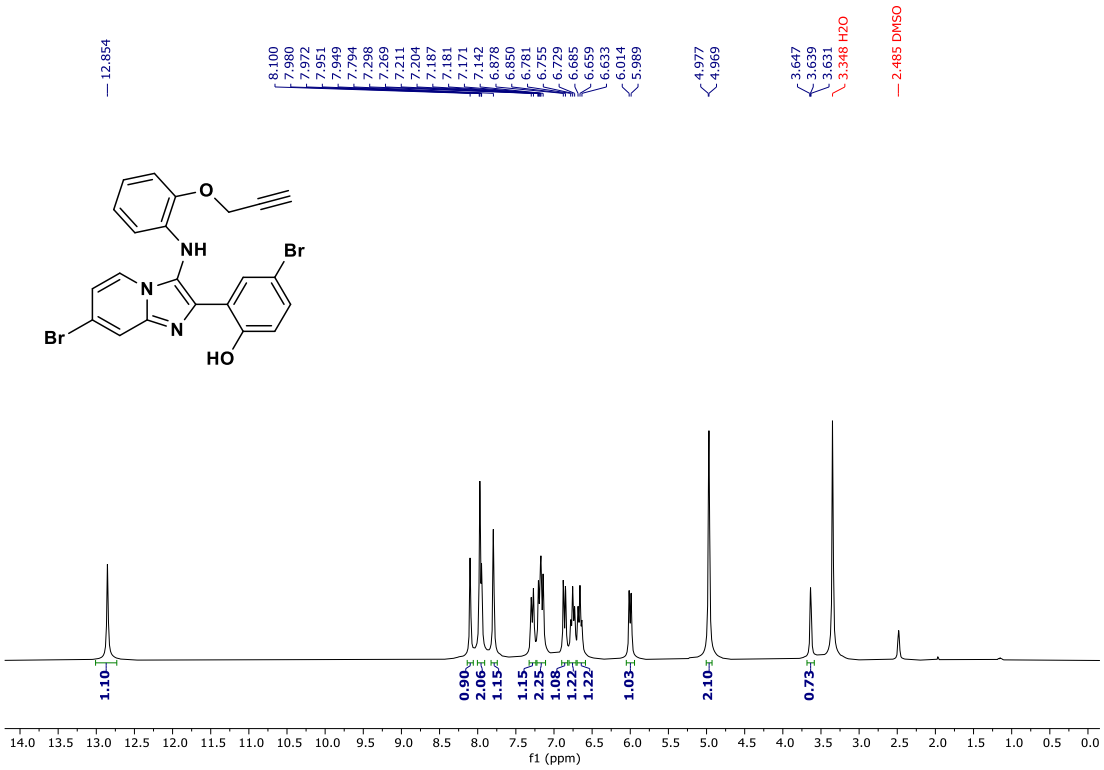
^{1}H NMR (400 MHz, DMSO-d_6) of **1j**



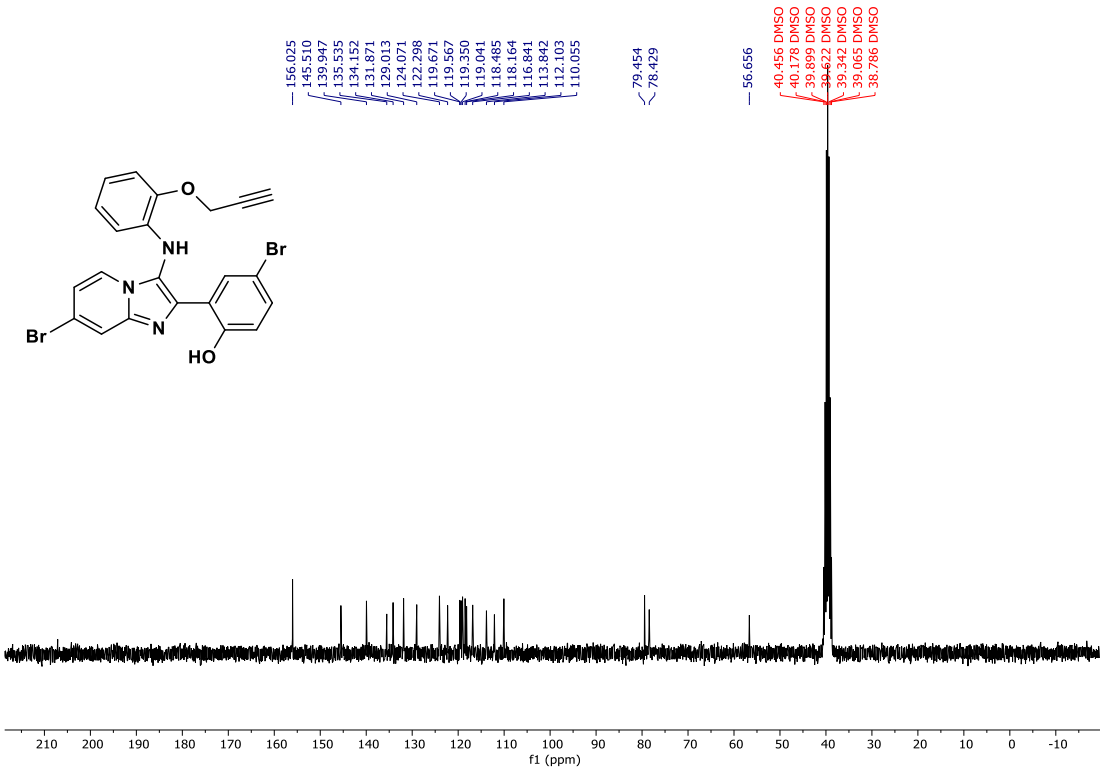
^{13}C NMR (101 MHz, DMSO-d_6) of **1j**



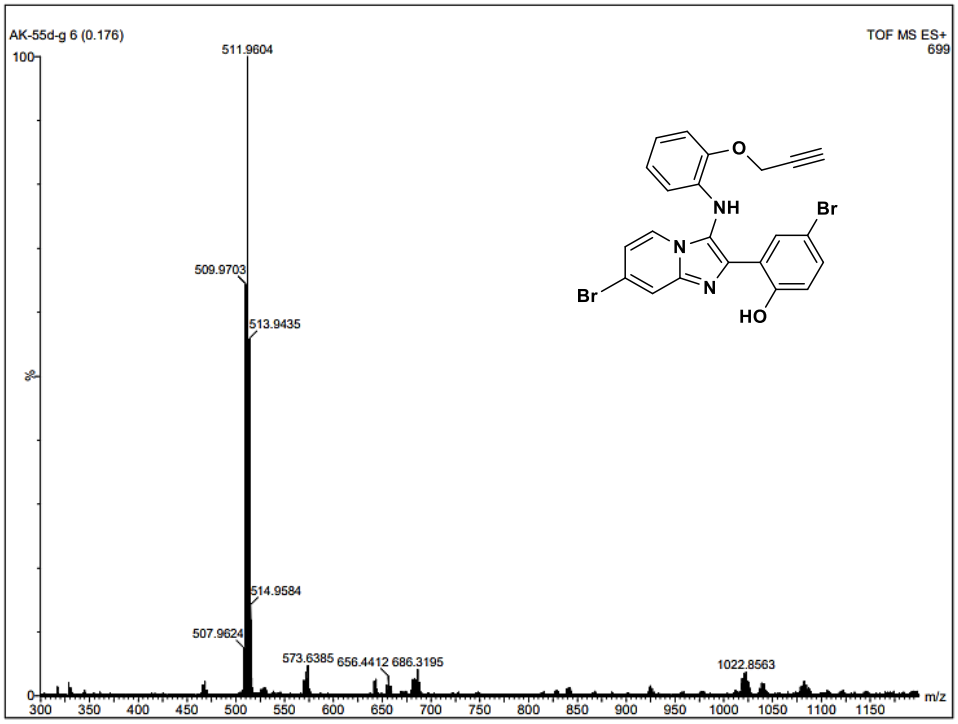
HRMS-ESI (+) of **1j**



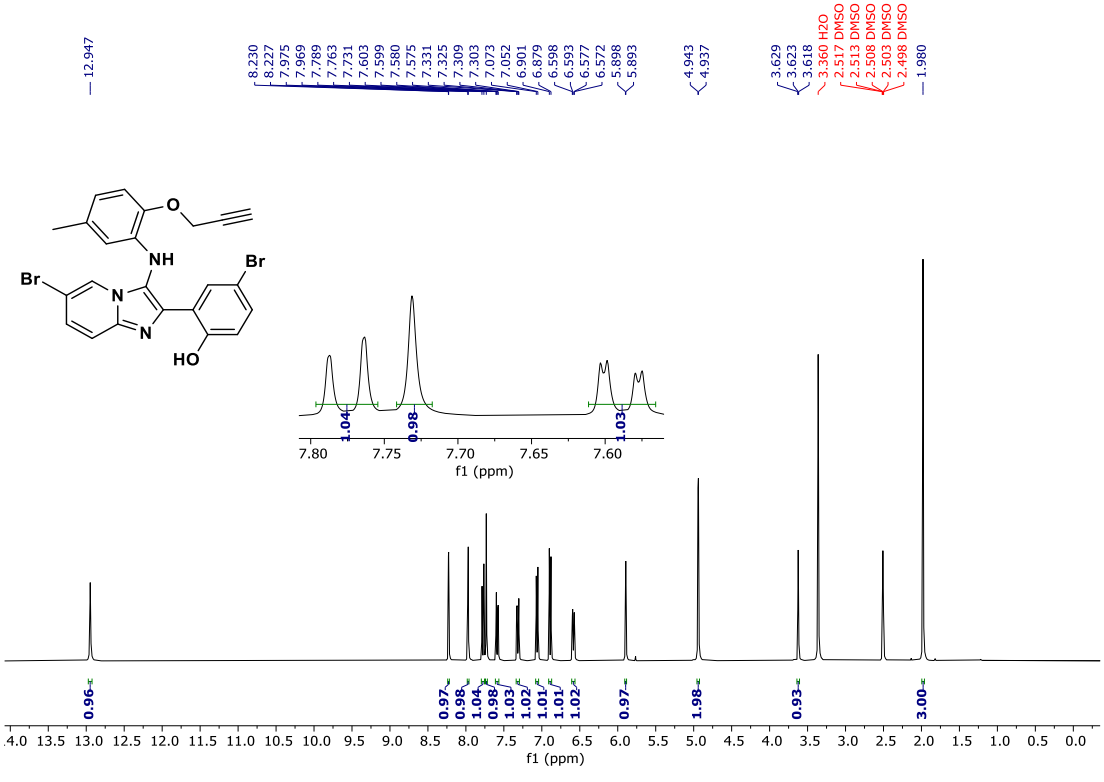
^{1}H NMR (300 MHz, DMSO-d_6) of **1k**



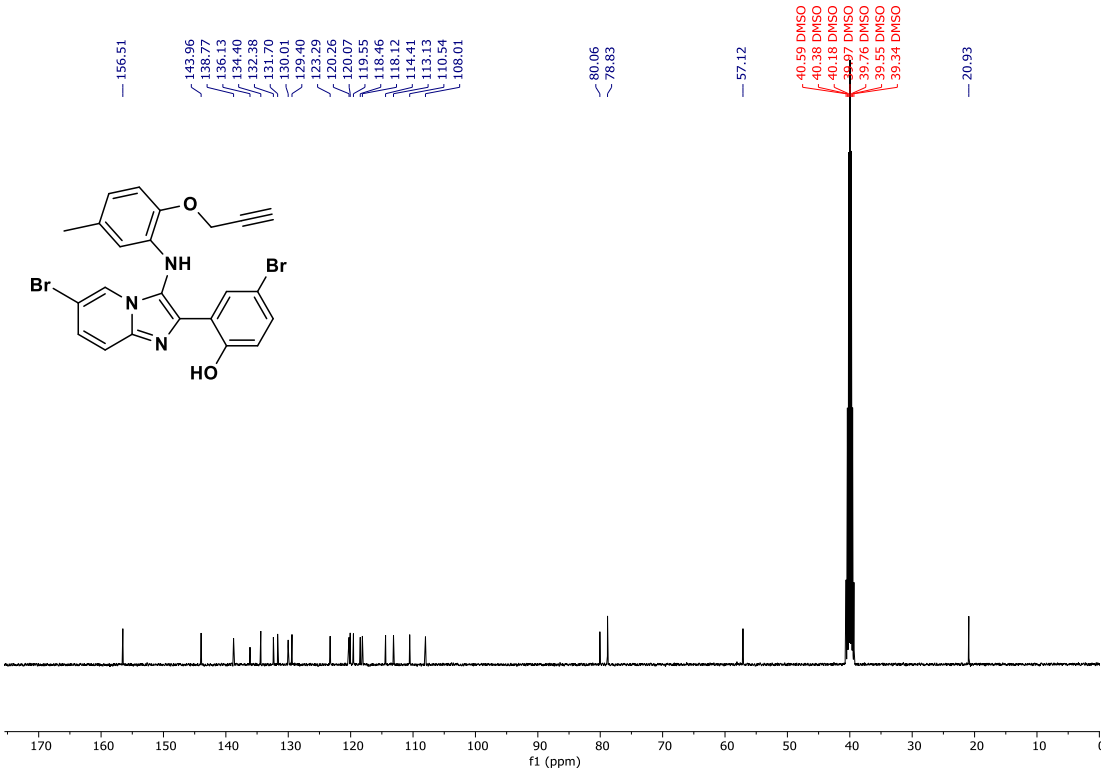
^{13}C NMR (75 MHz, DMSO-d_6) of **1k**



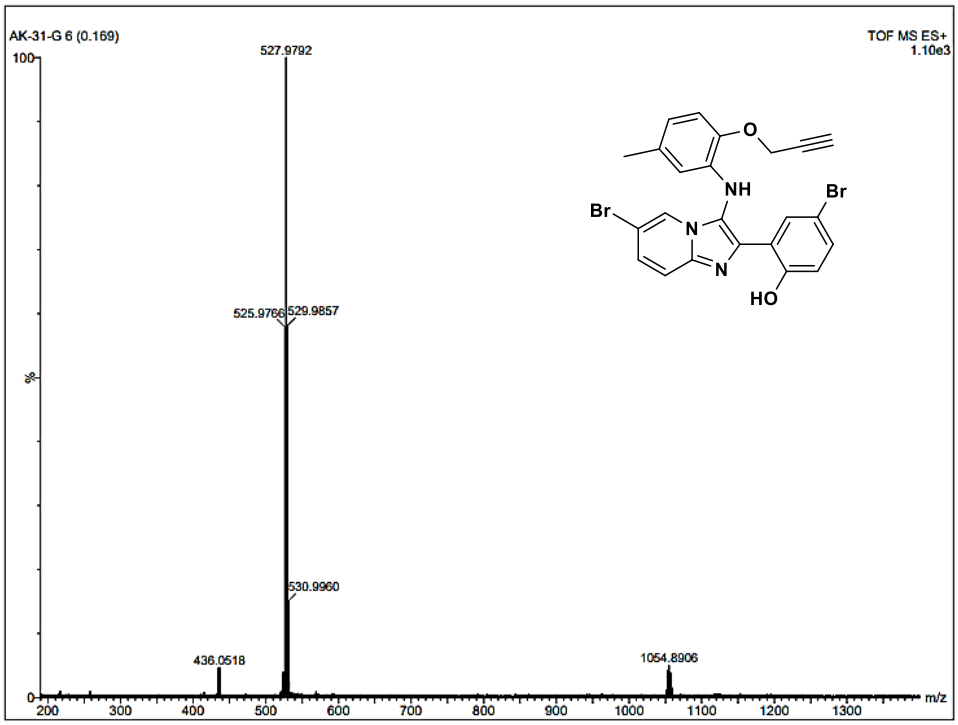
HRMS-ESI (+) of **1k**



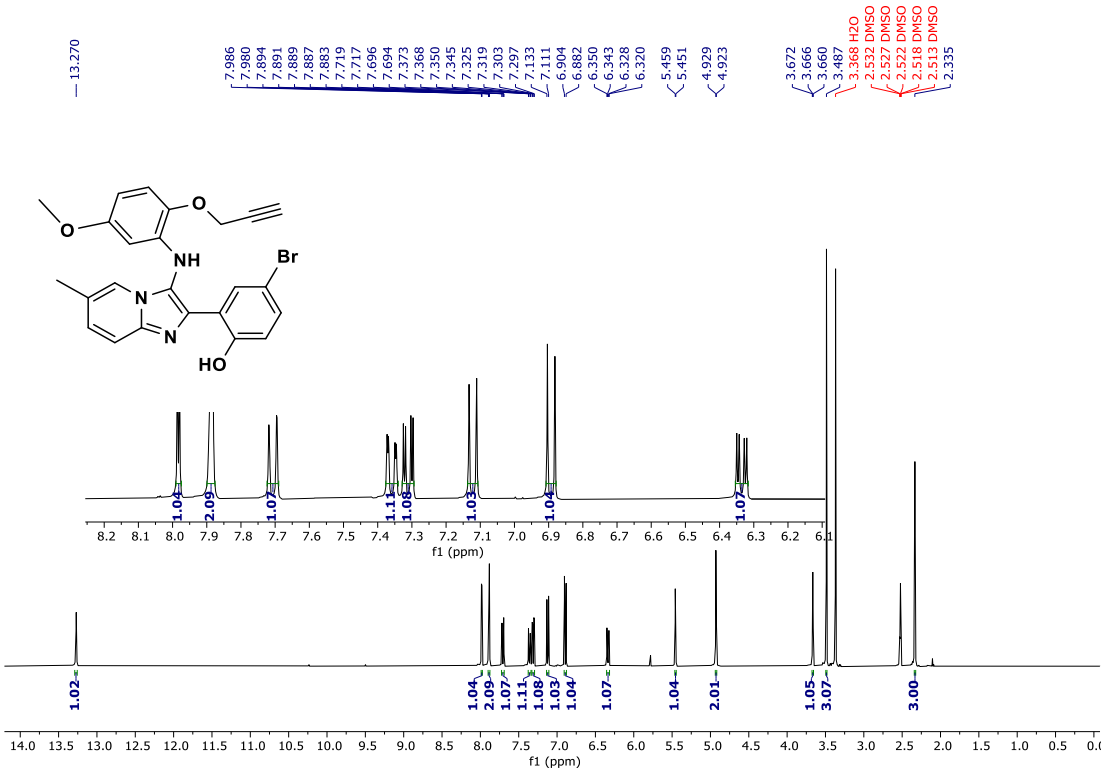
^{1}H NMR (400 MHz, DMSO-d_6) of**1l**



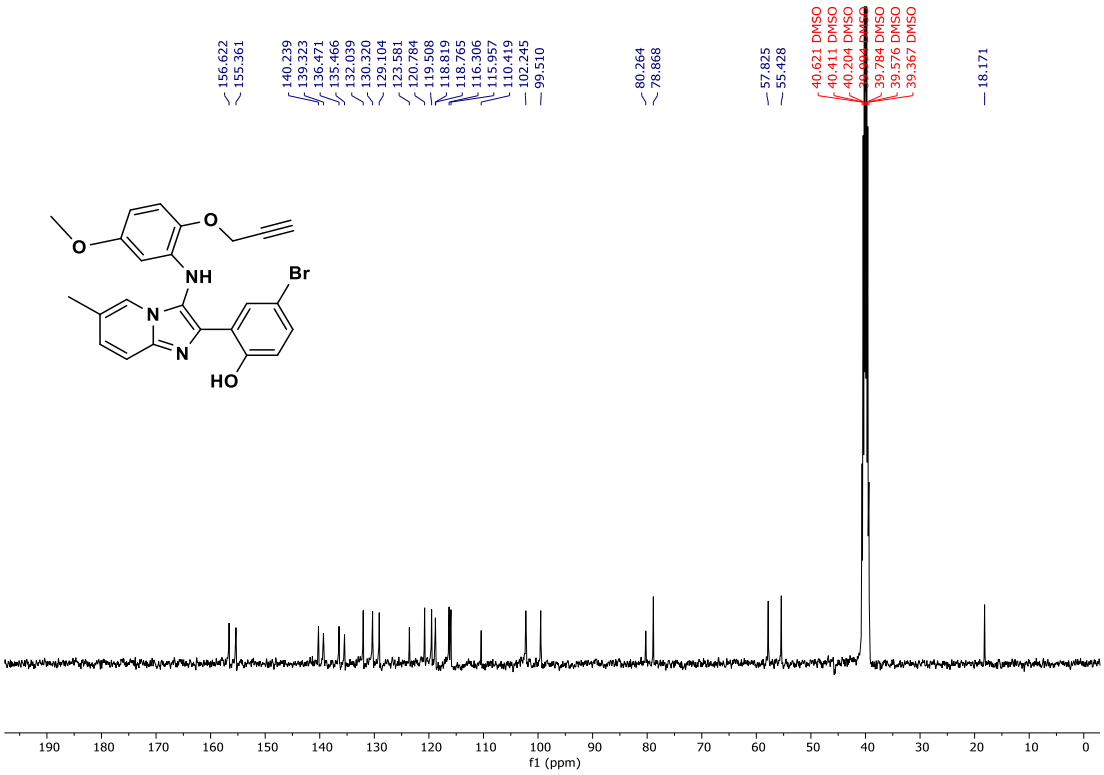
^{13}C NMR (101 MHz, DMSO-d_6) of **S1l**



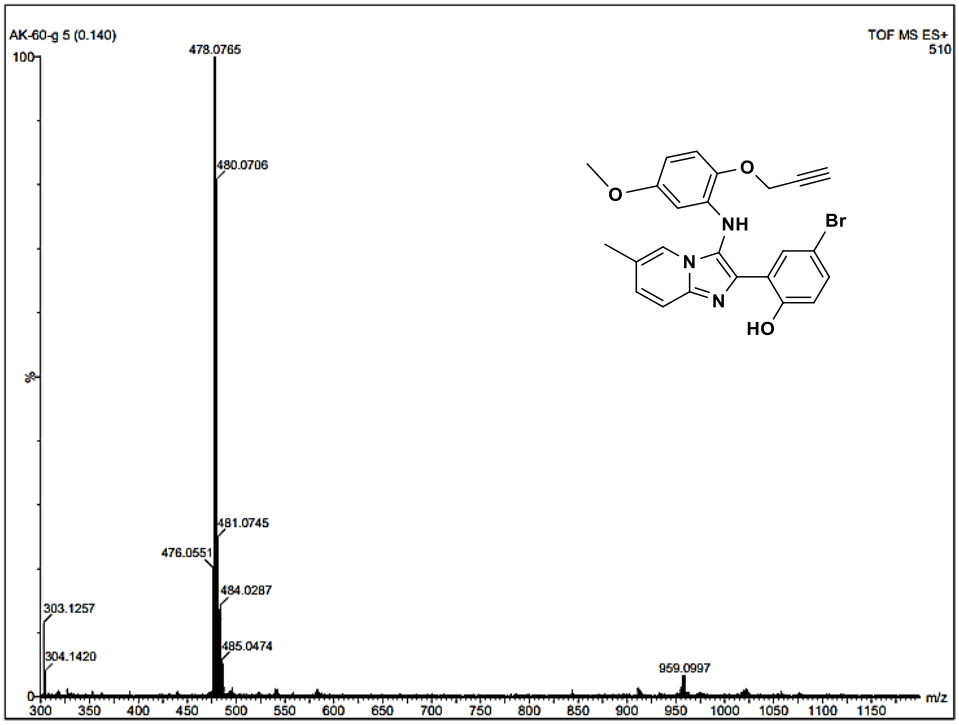
HRMS-ESI (+) of **1l**



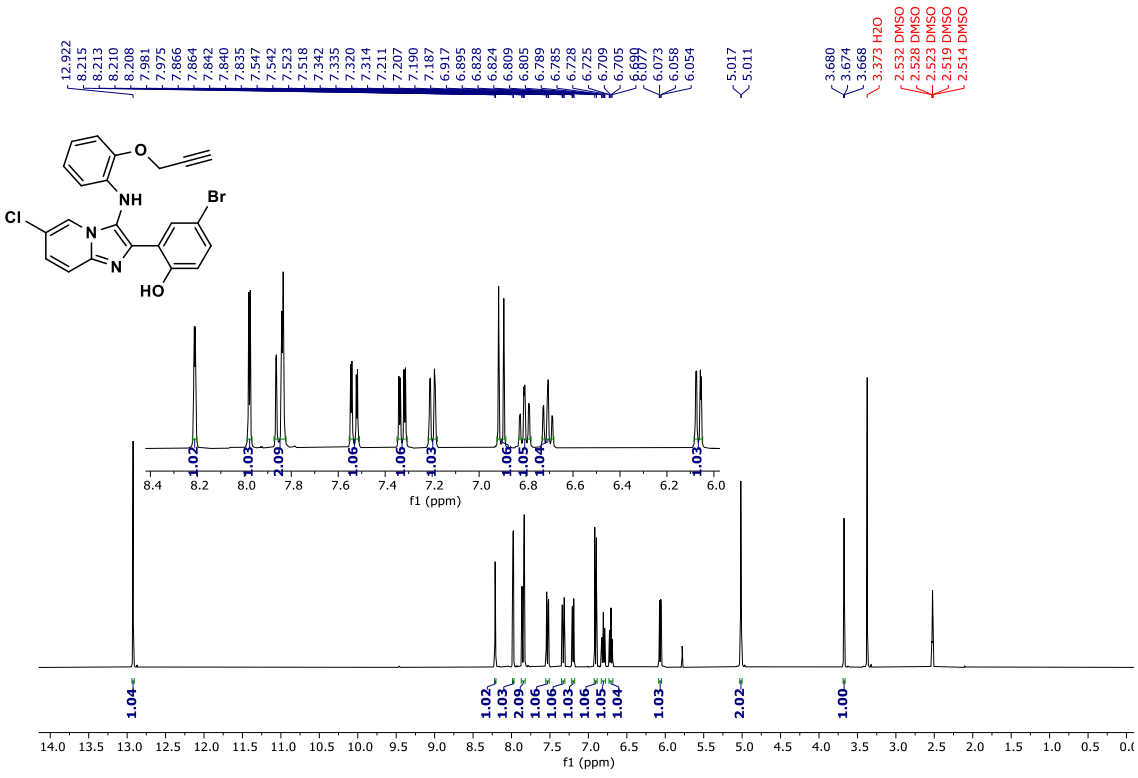
^{1}H NMR (400 MHz, DMSO-d_6) of **1m**



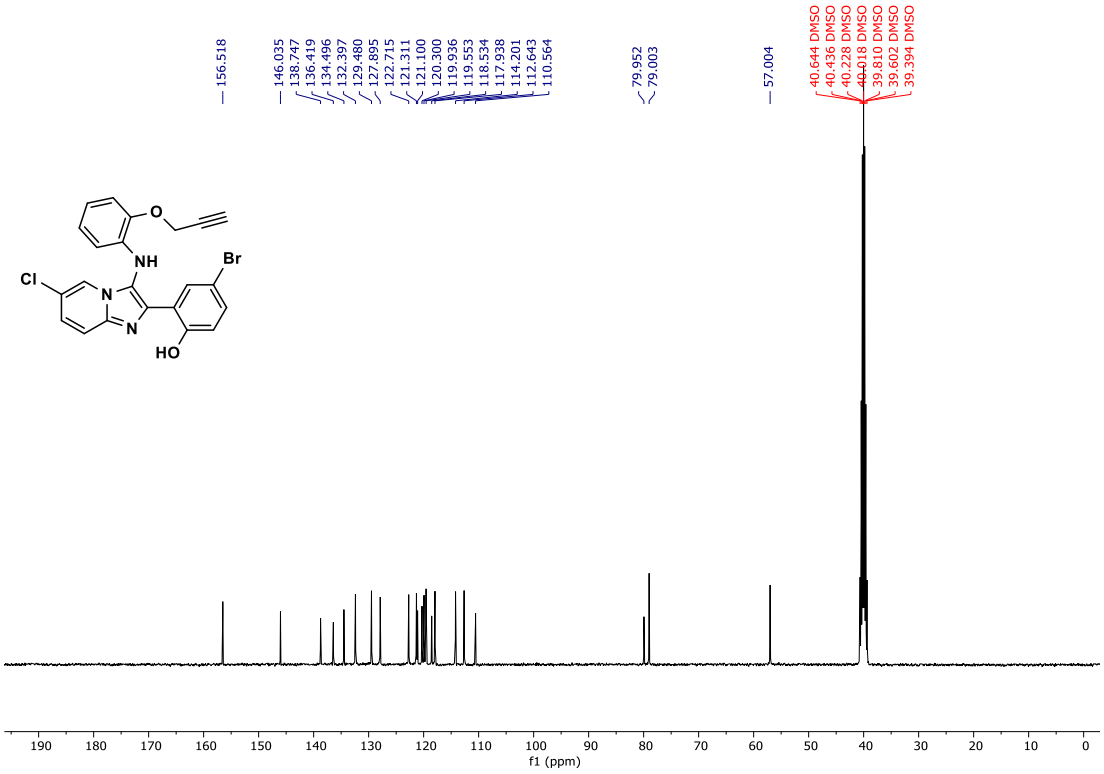
^{13}C NMR (101 MHz, DMSO-d_6) of **1m**



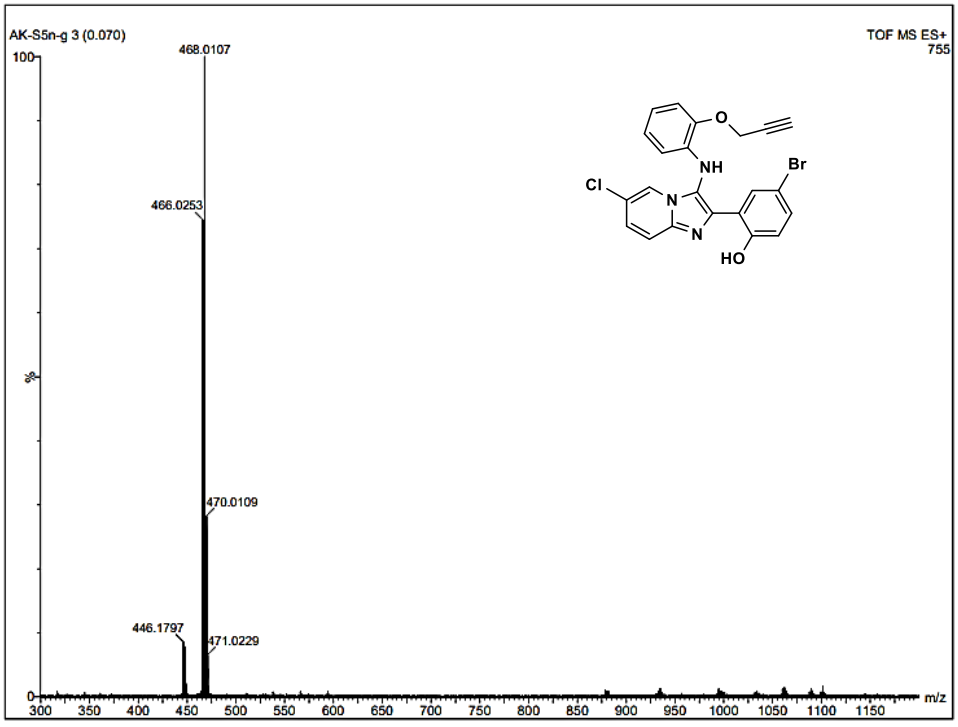
HRMS-ESI (+) of **1m**



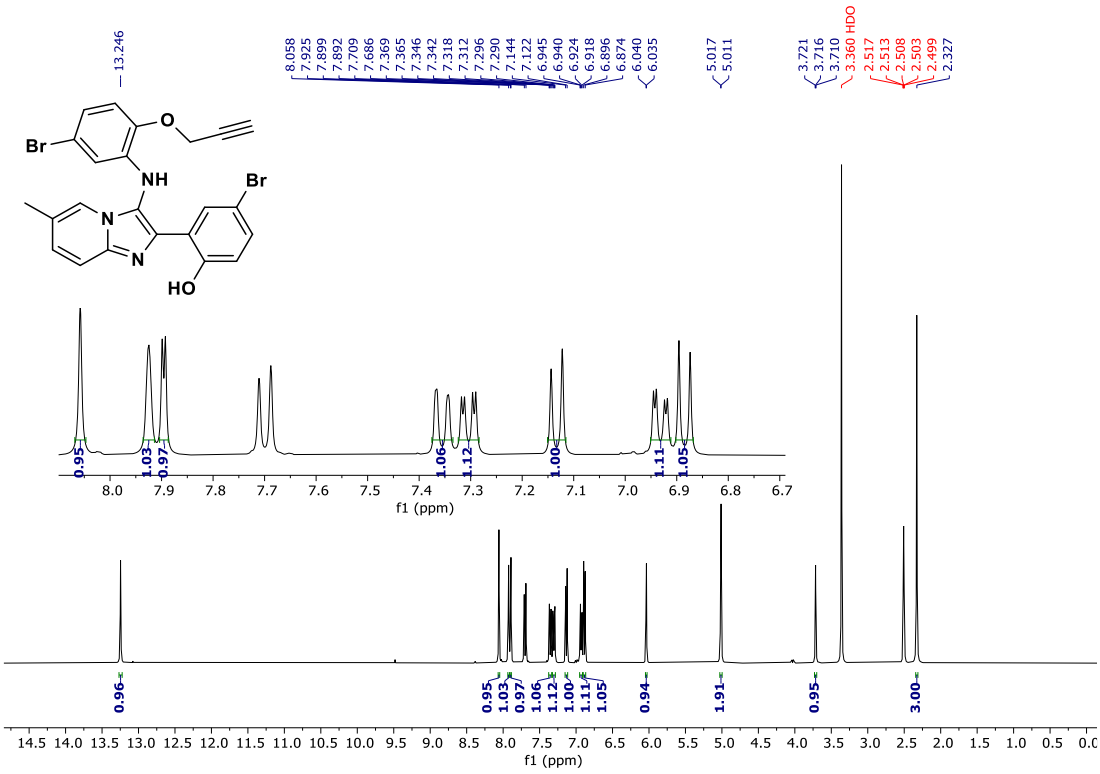
^{1}H NMR (400 MHz, DMSO-d_6) of **1n**



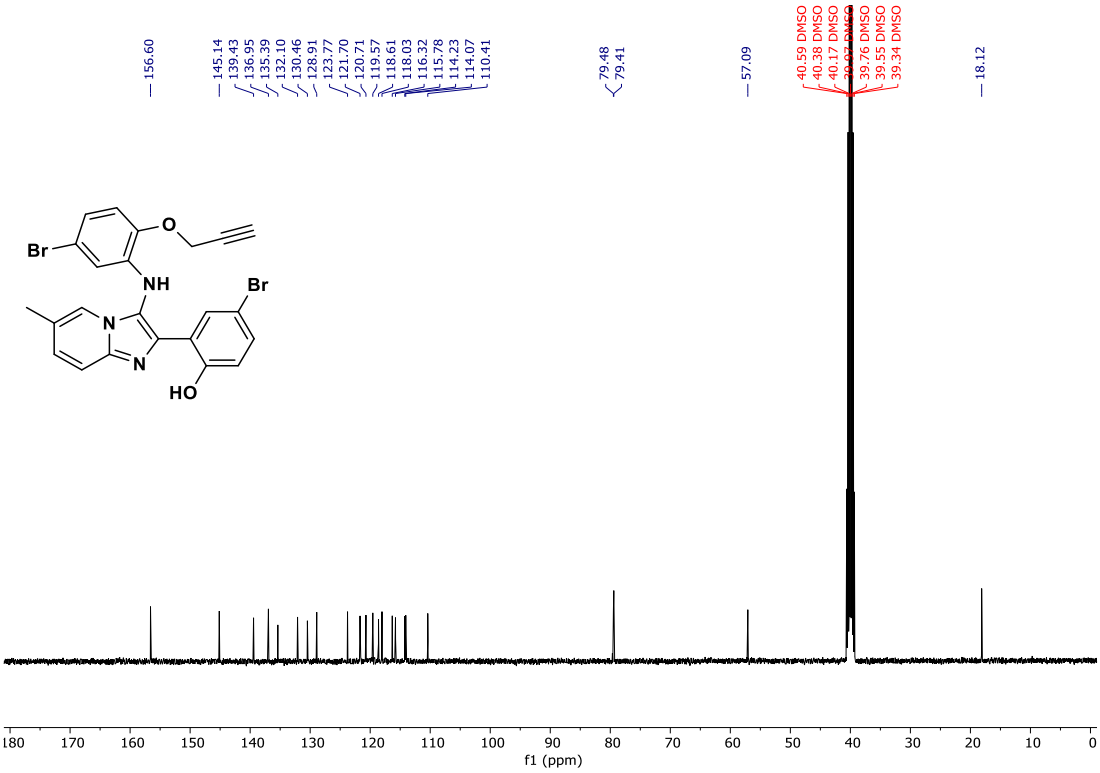
^{13}C NMR (101 MHz, DMSO-d_6) of **1n**



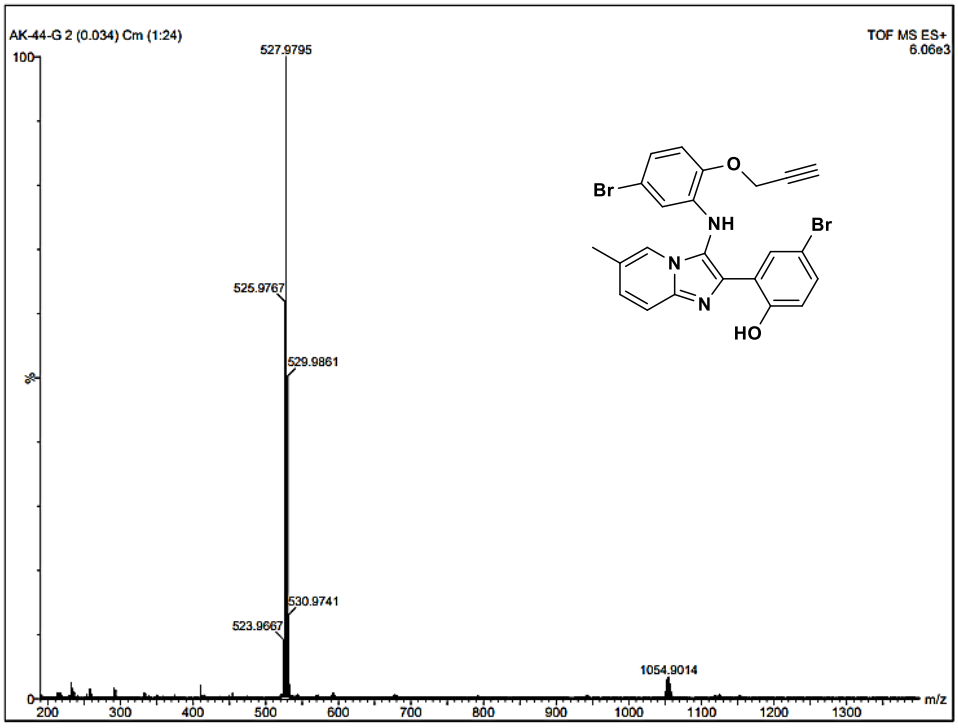
HRMS-ESI (+) of **1n**



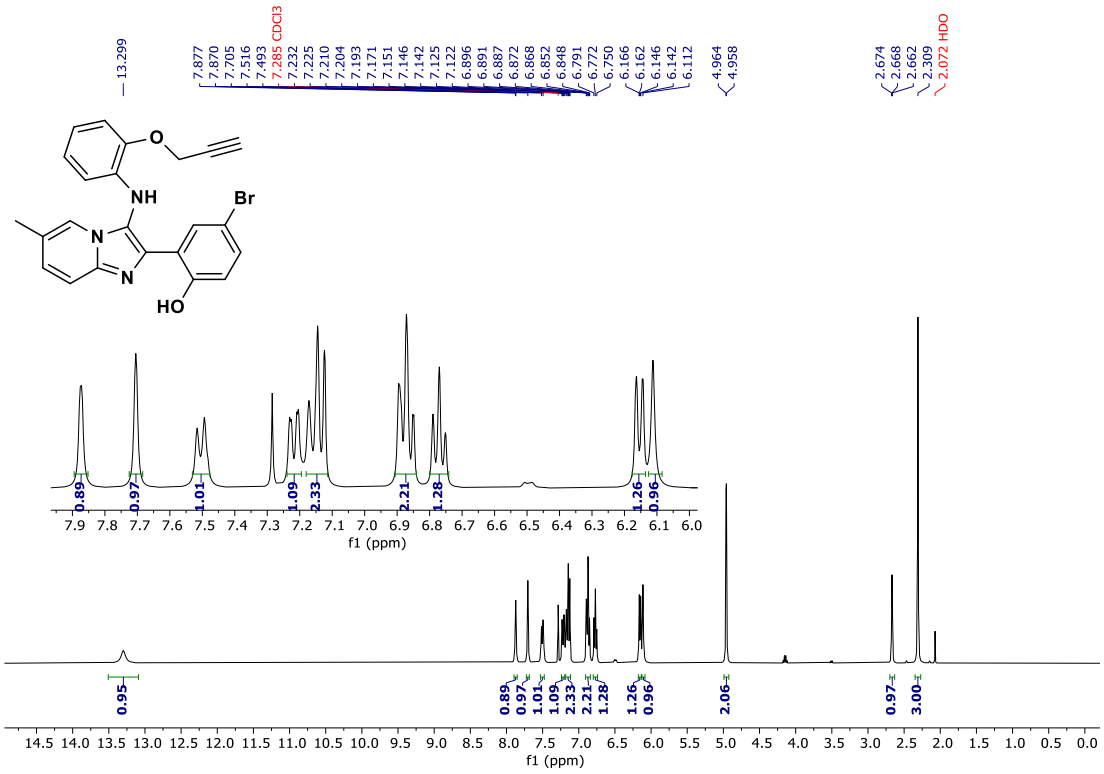
^{1}H NMR (400 MHz, DMSO-d_6) of **1o**



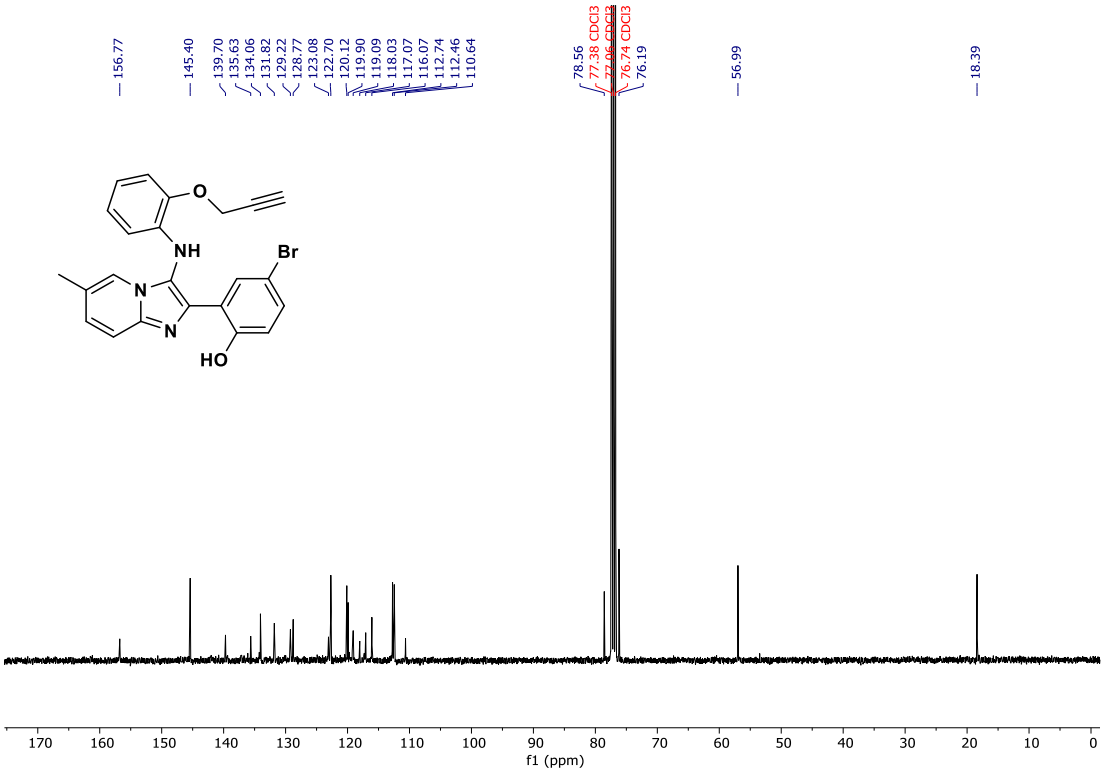
^{13}C NMR (101 MHz, DMSO-d_6) of **1o**



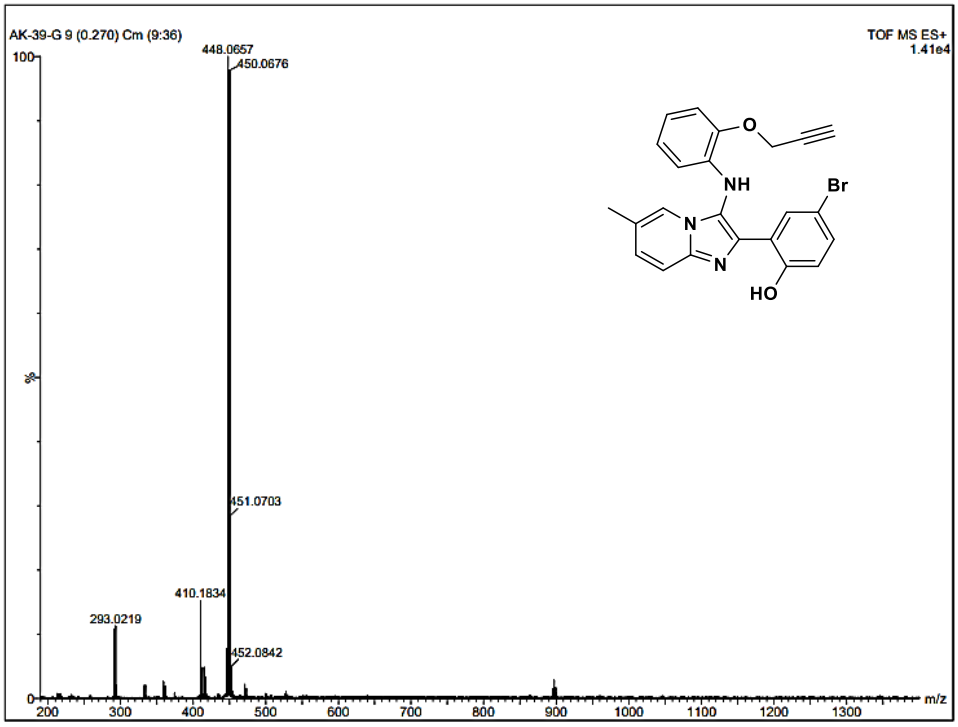
HRMS-ESI (+) of **1o**



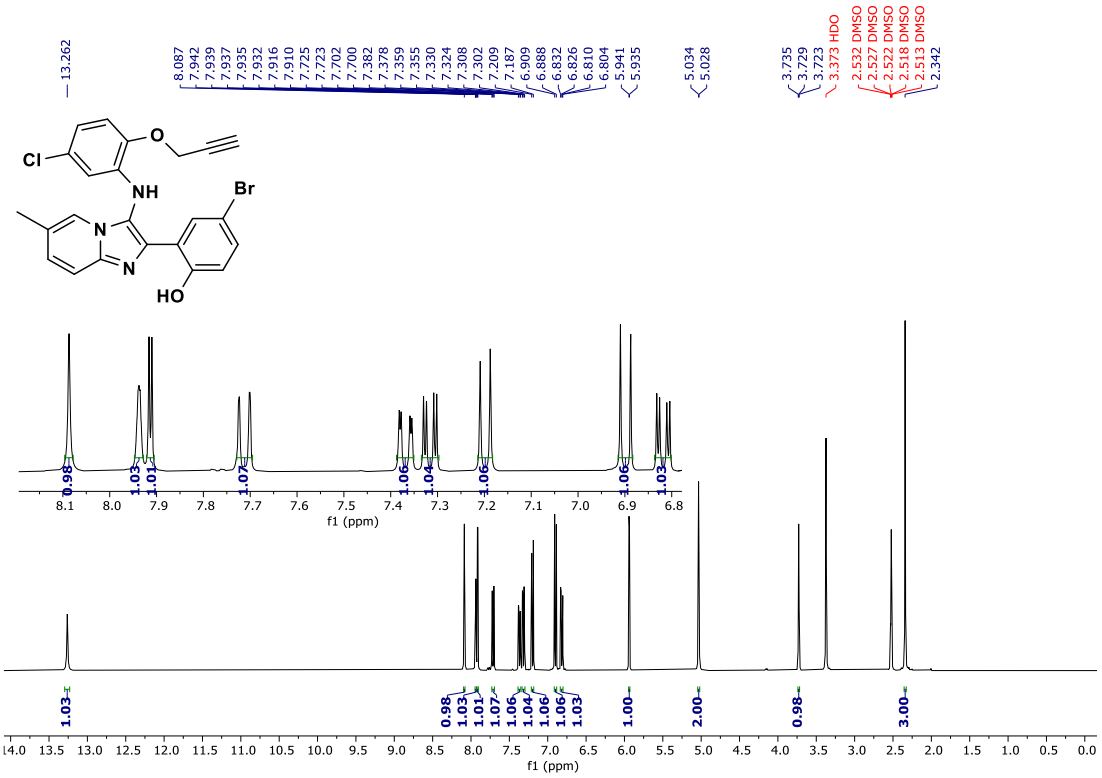
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



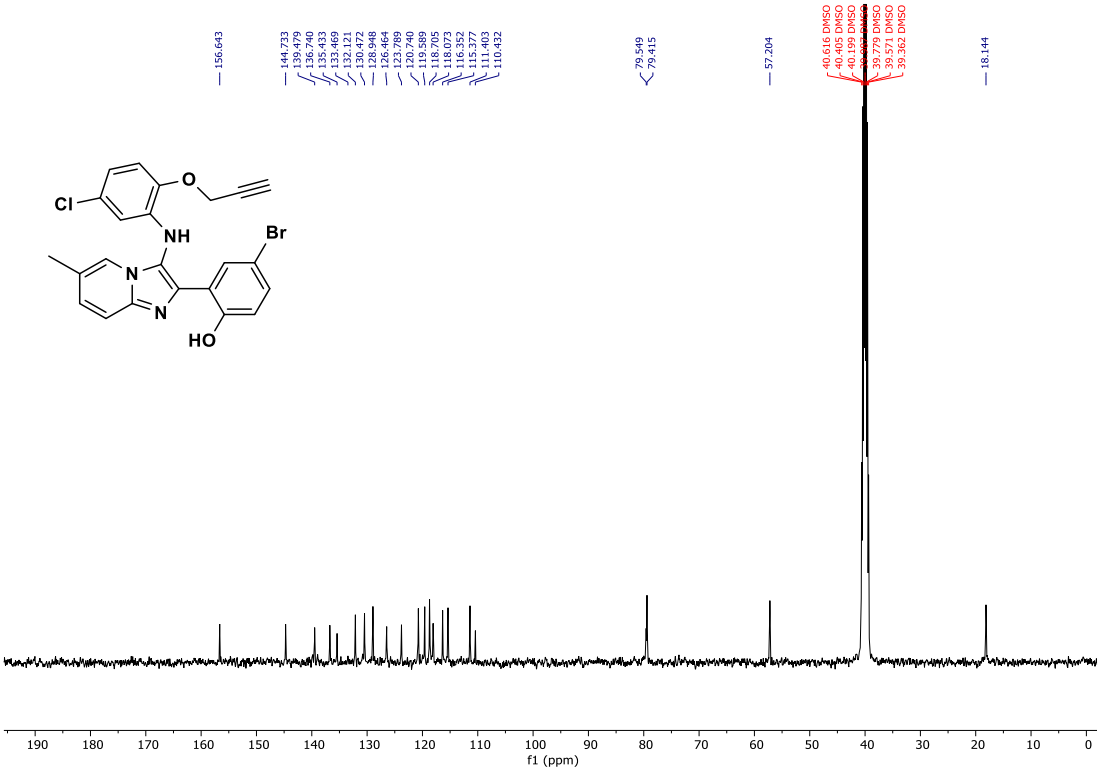
^{13}C NMR (101 MHz, $CDCl_3$) of **1p**



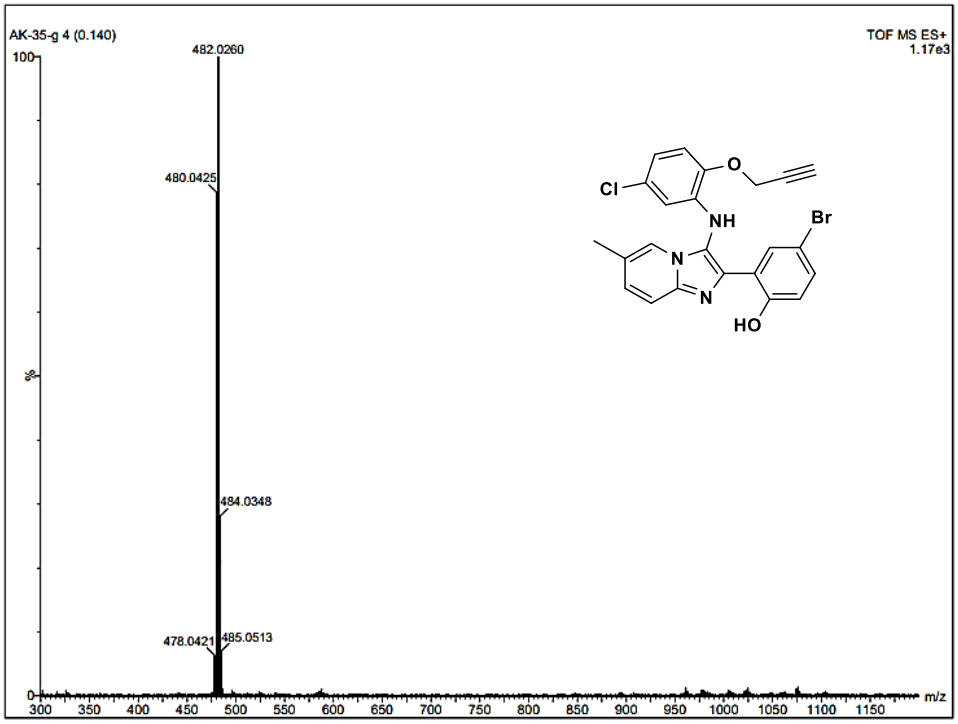
HRMS-ESI (+) of **1p**



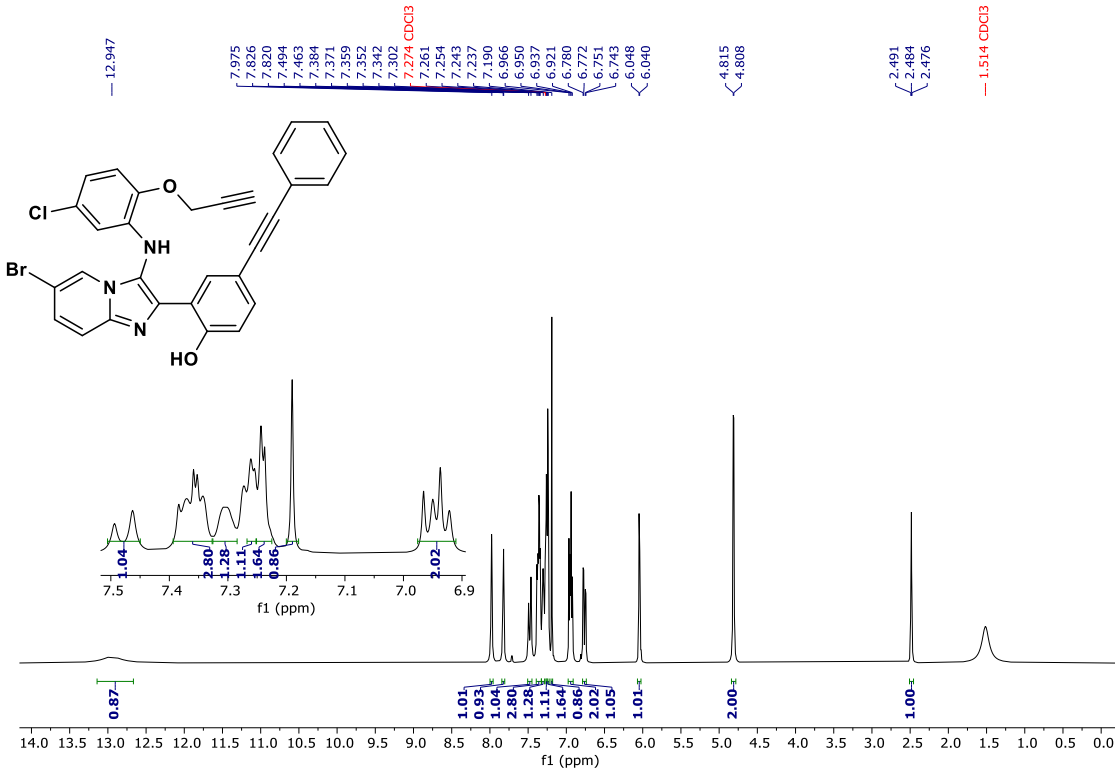
^{1}H NMR (400 MHz, DMSO-d_6) of **1q**



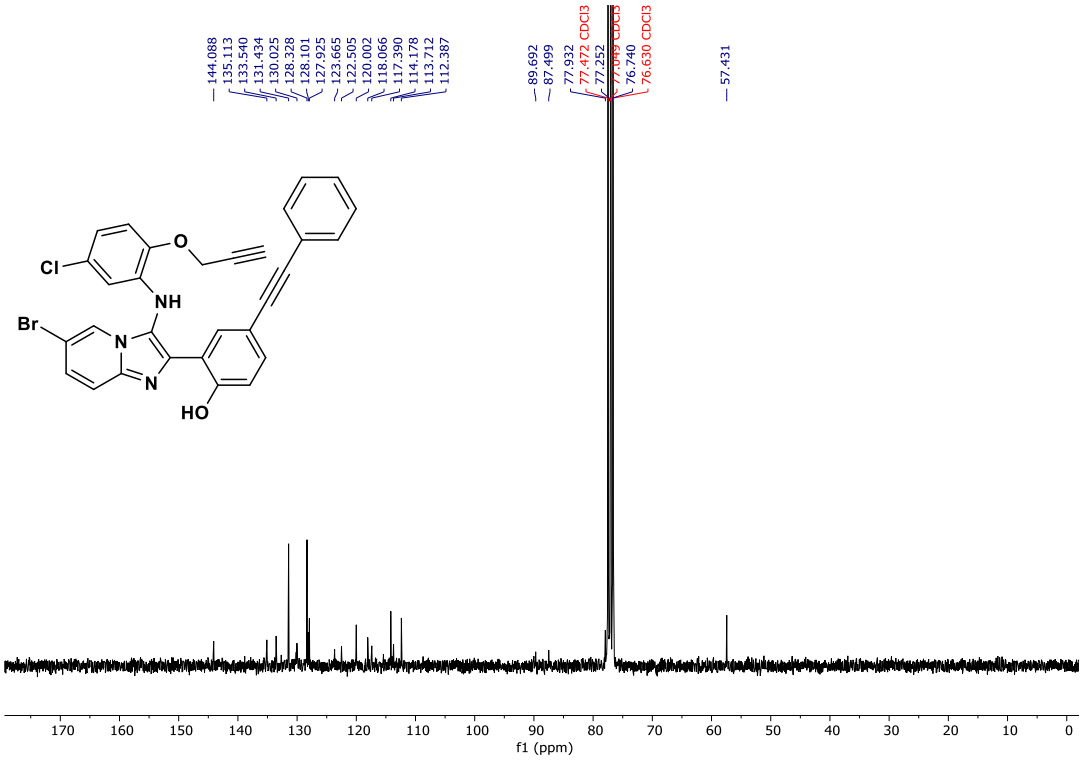
^{13}C NMR (101 MHz, DMSO-d_6) of **1q**



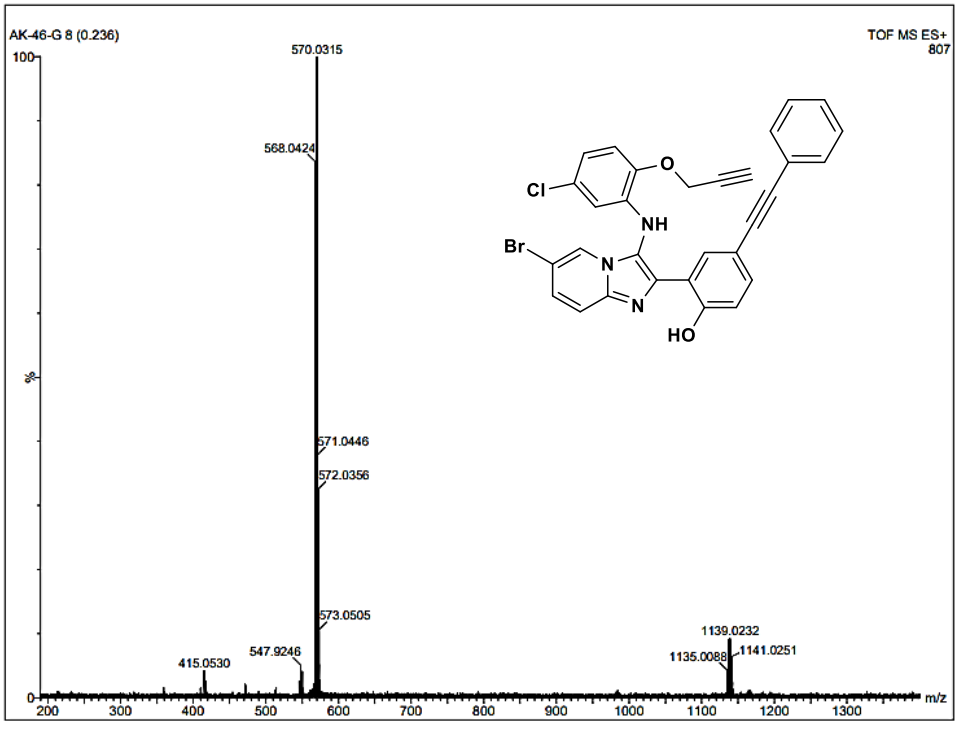
HRMS-ESI (+) of **1q**



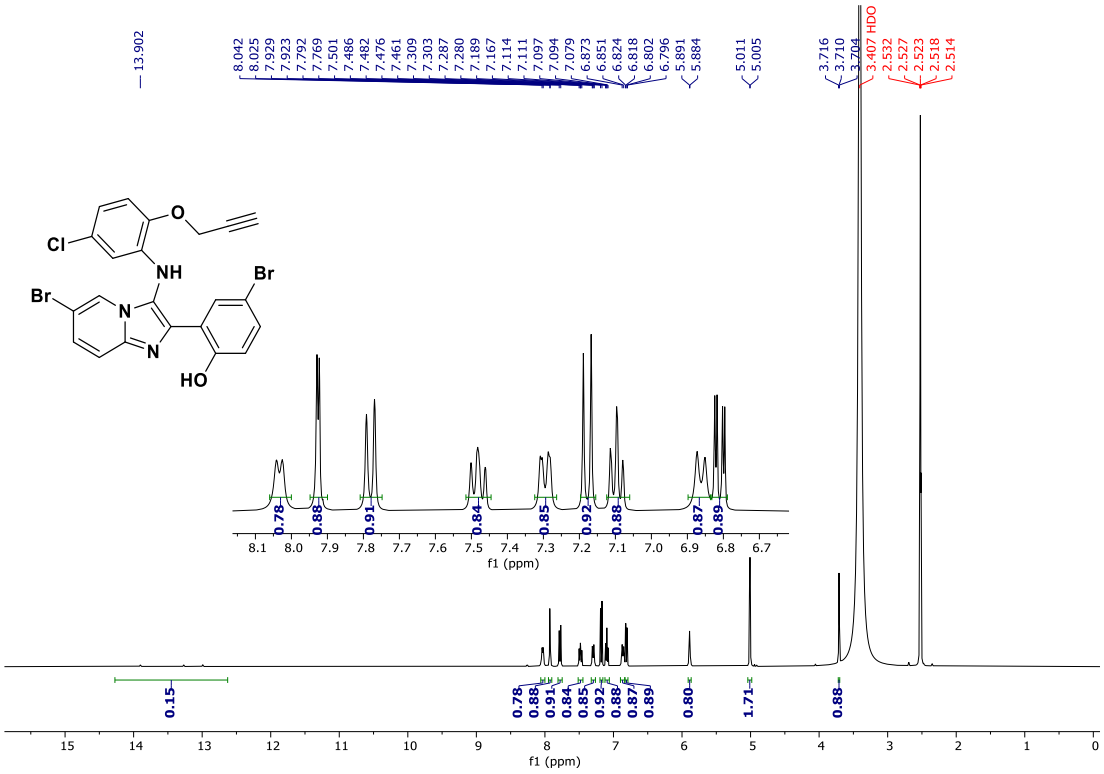
^{1}H NMR (300 MHz, $CDCl_3$) of **1r**



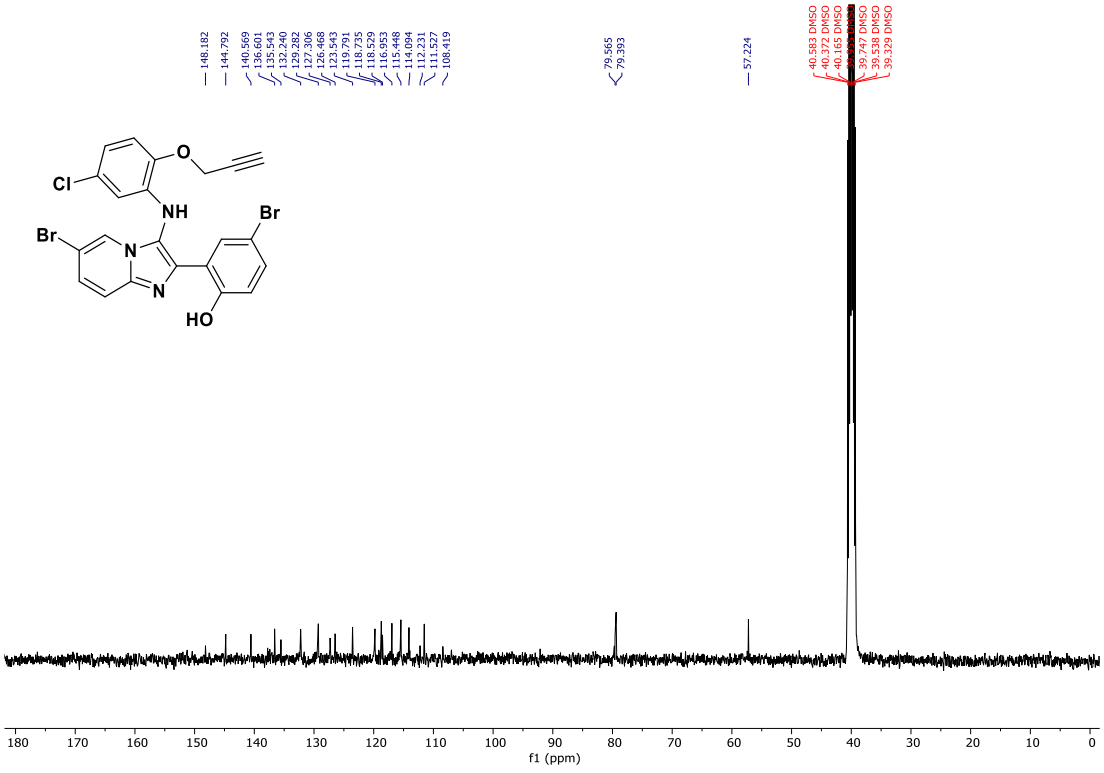
^{13}C NMR (75 MHz, $CDCl_3$) of **1r**



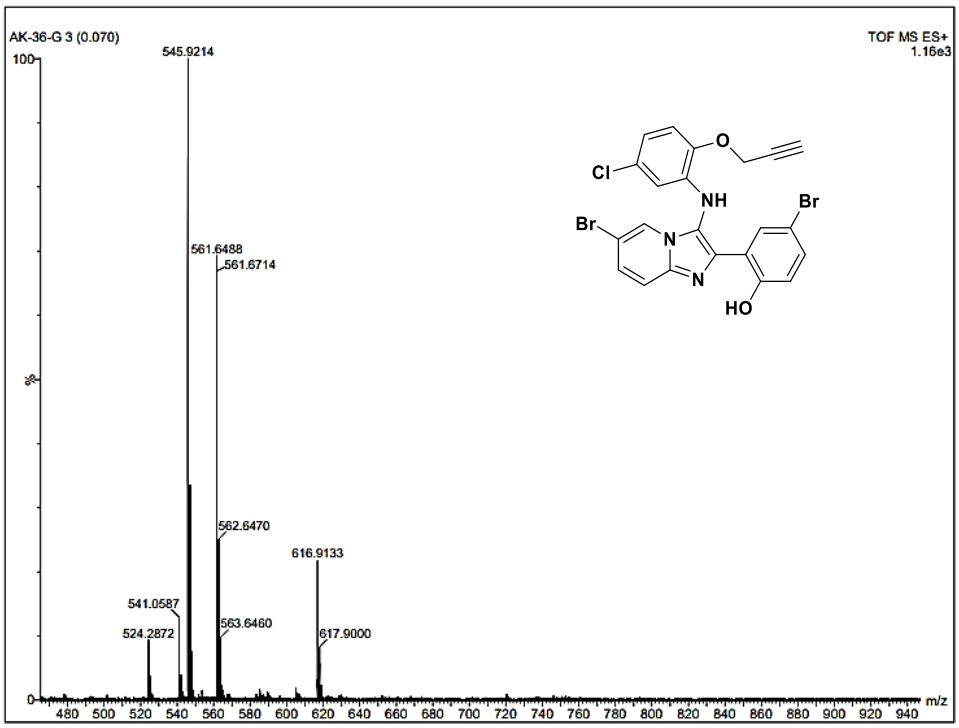
HRMS-ESI (+) of **1r**



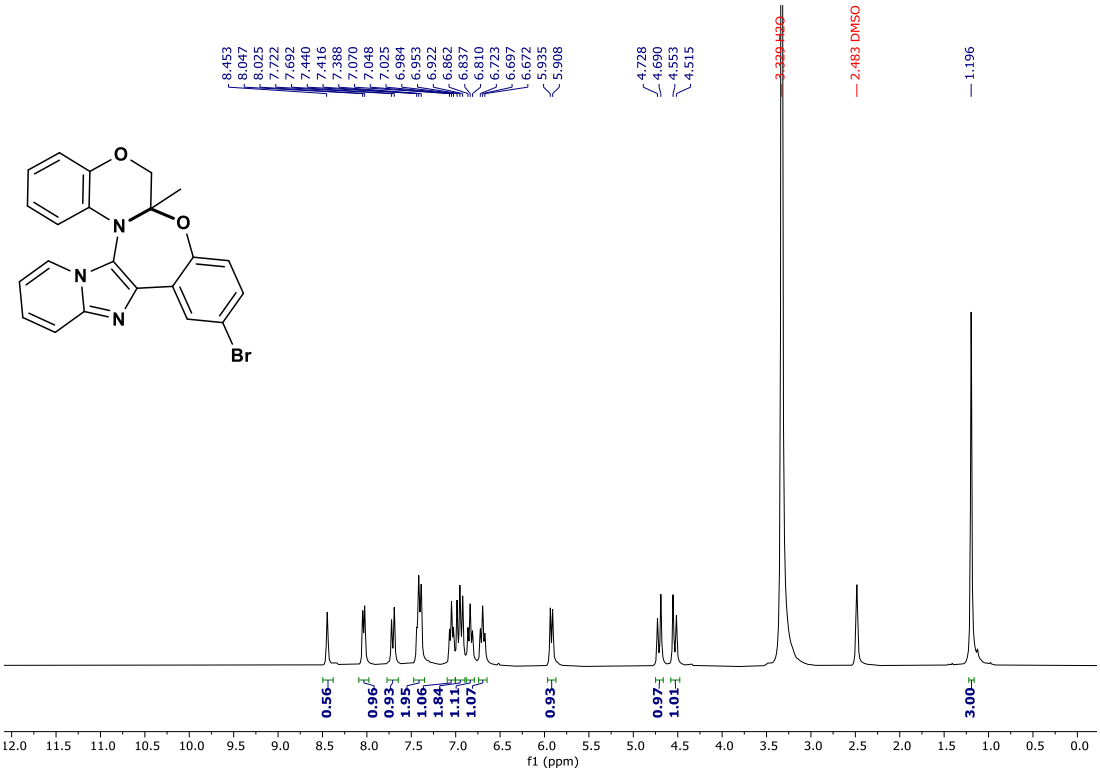
^{1}H NMR (400 MHz, DMSO-d_6) of **1s**



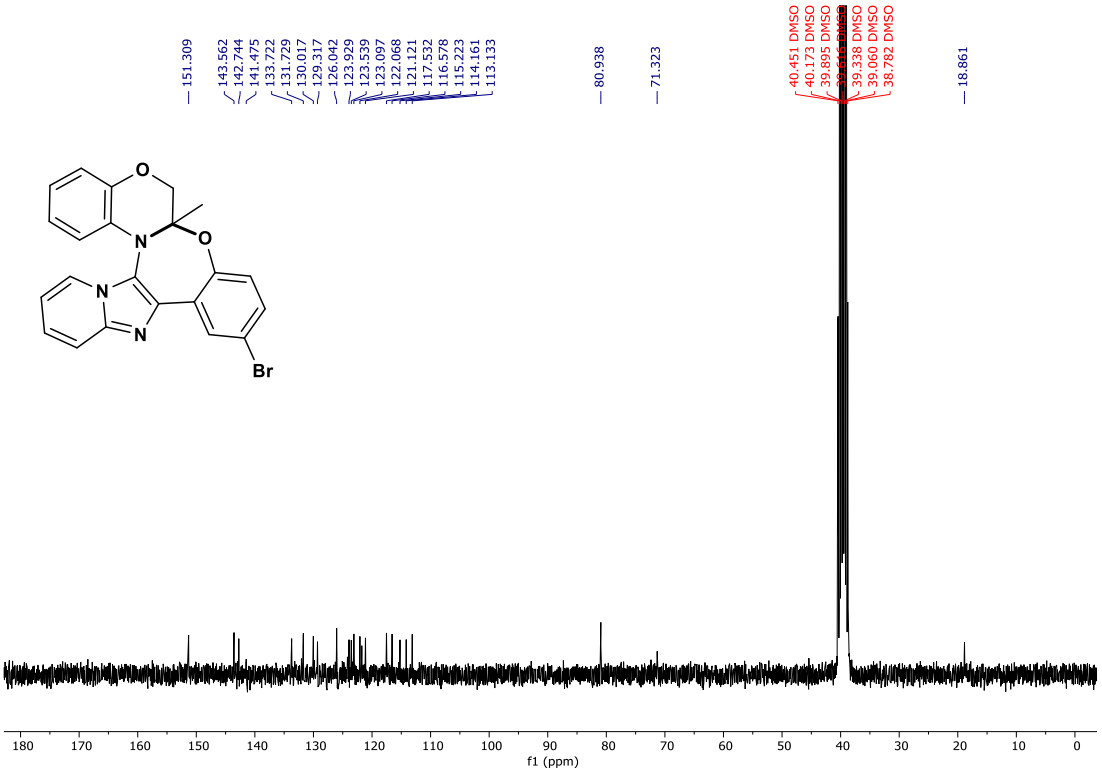
^{13}C NMR (101 MHz, DMSO-d_6) of **1s**



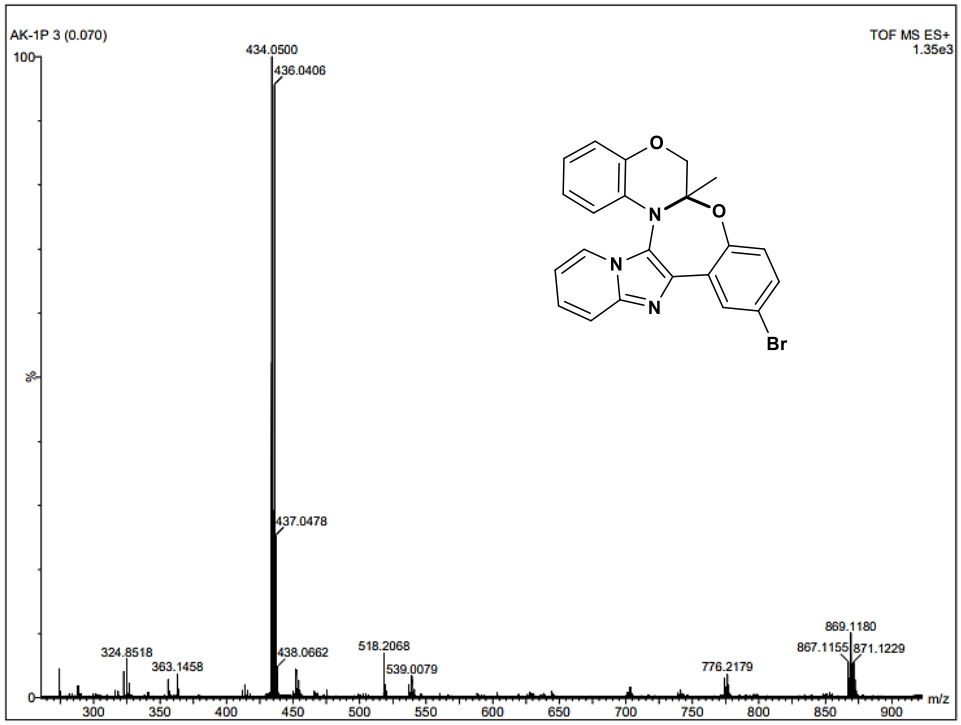
HRMS-ESI (+) of **1s**



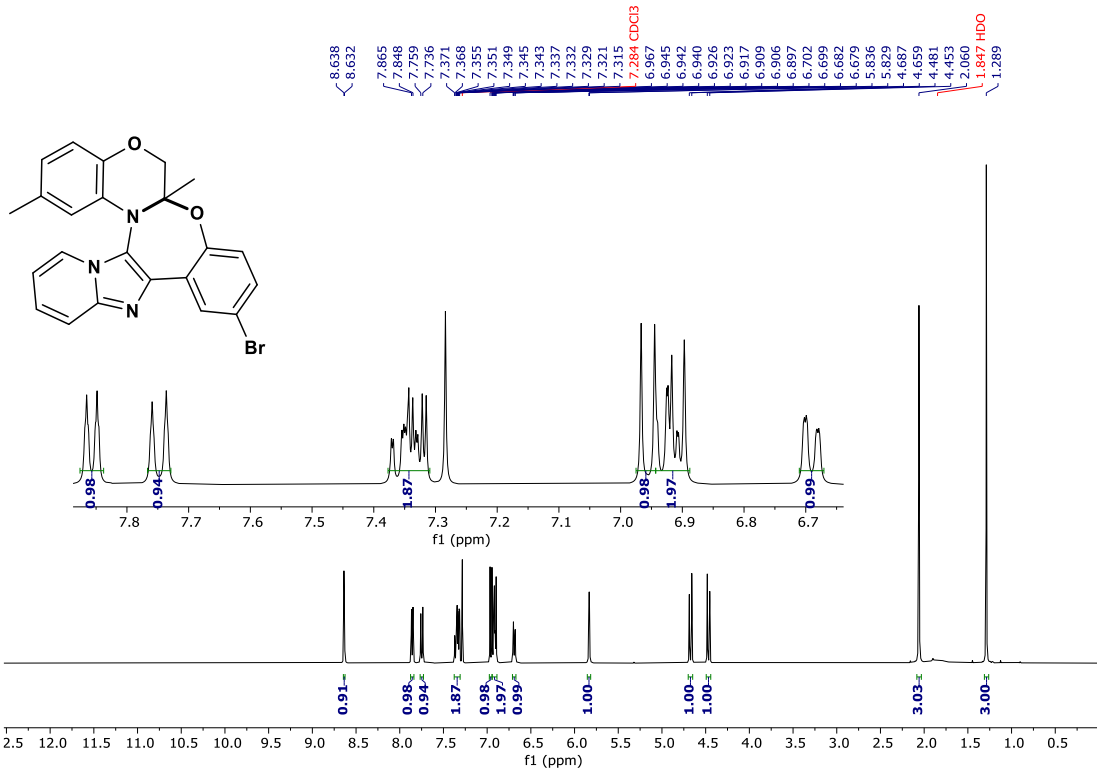
^{1}H NMR (300 MHz, DMSO-d_6) of **2a**



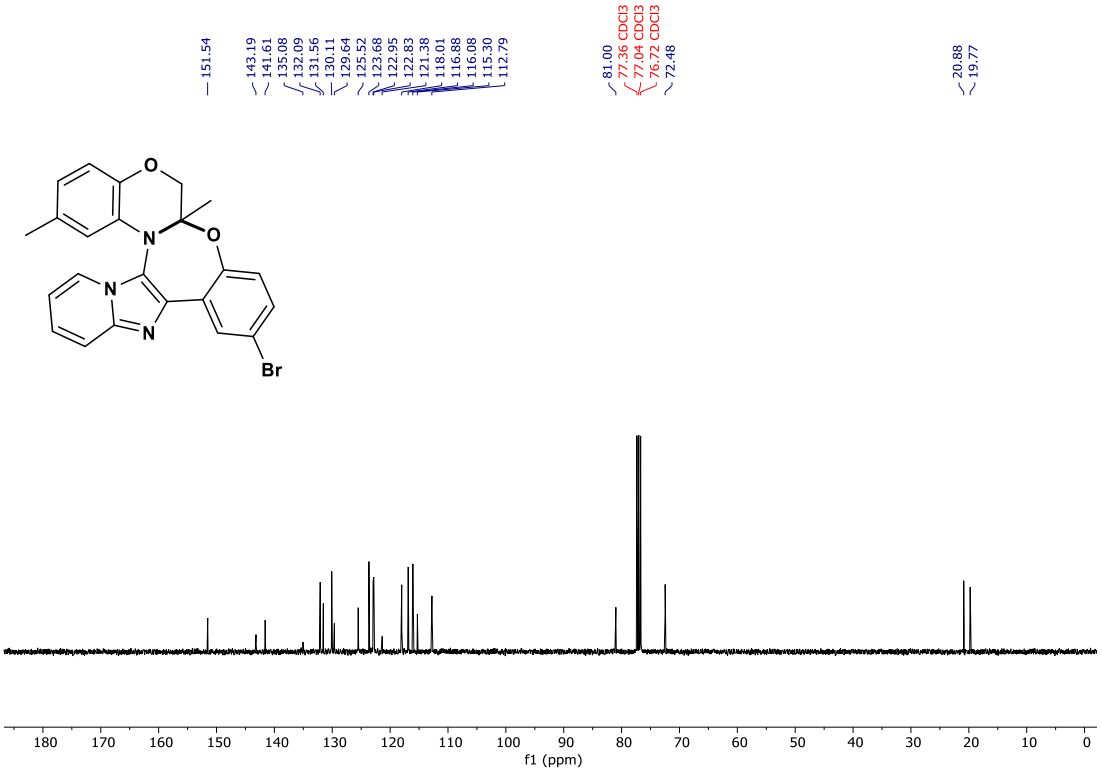
^{13}C NMR (101 MHz, DMSO-d_6) of **2a**



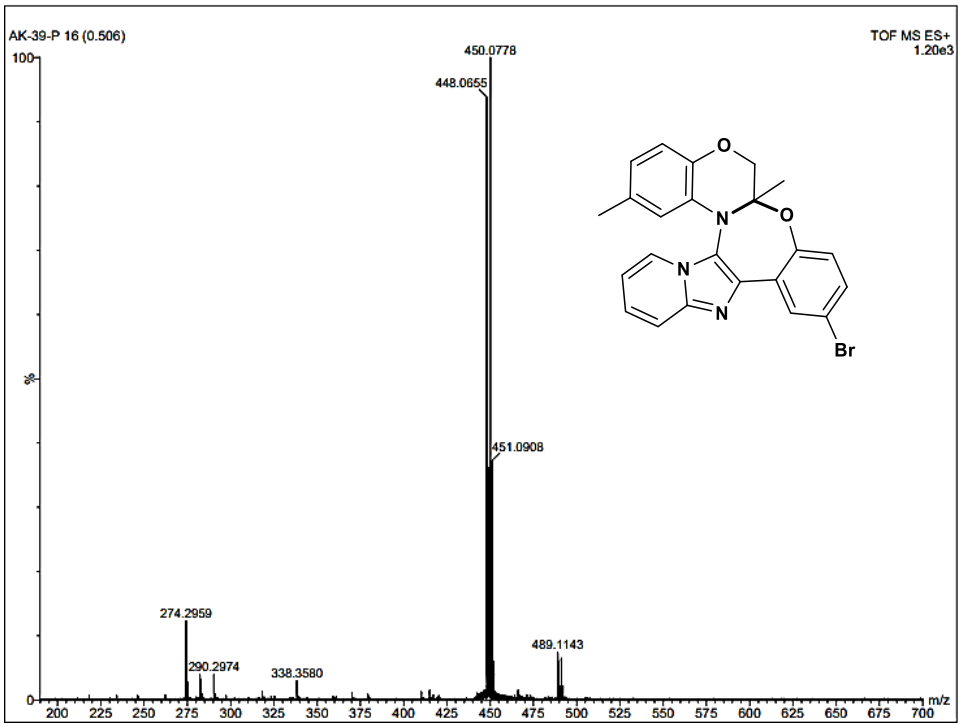
HRMS-ESI (+) of **2a**



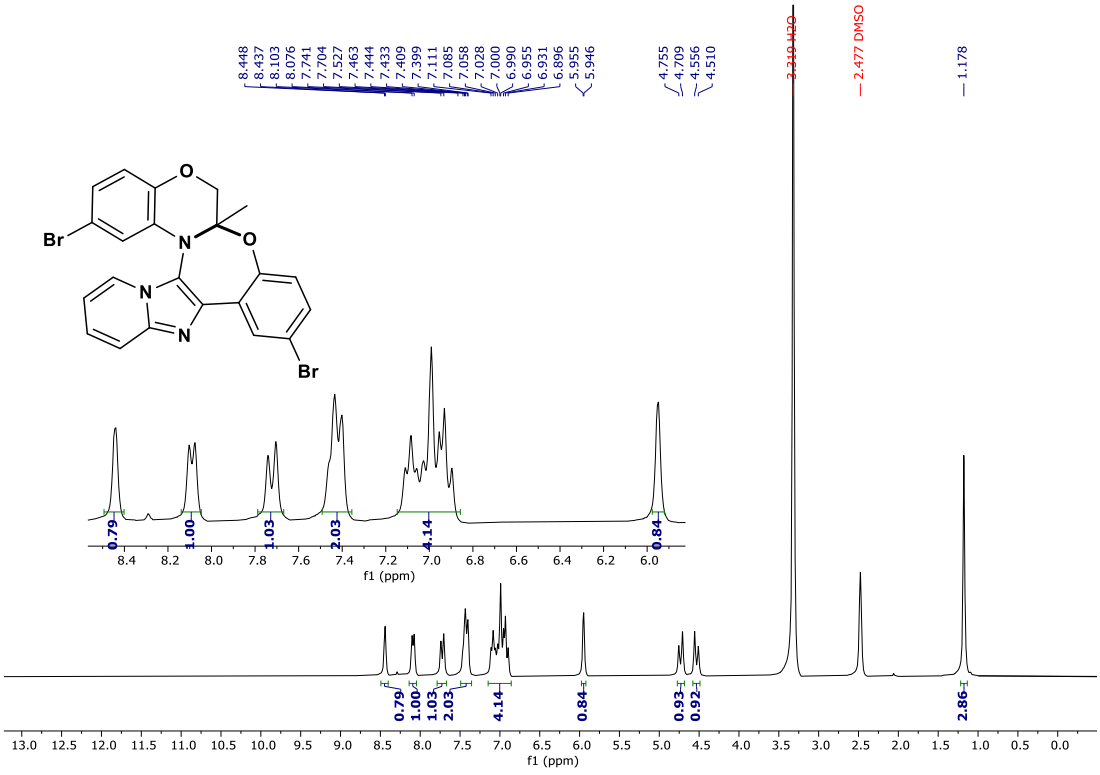
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



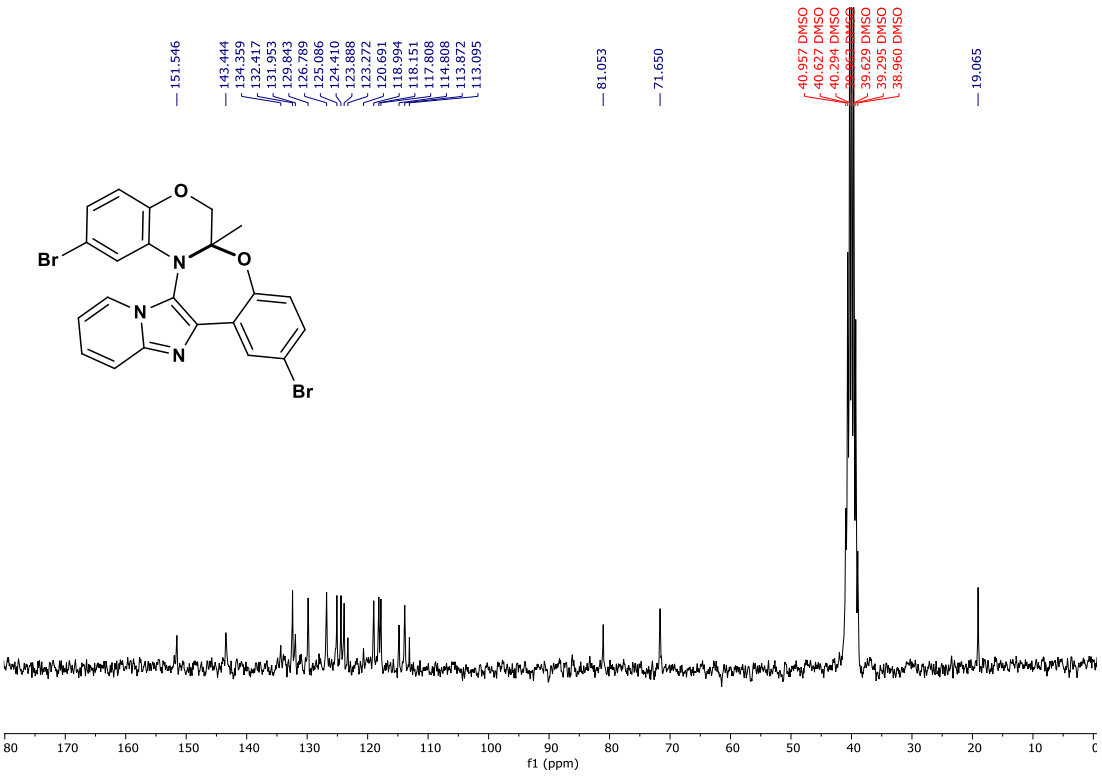
^{13}C NMR (101 MHz, $CDCl_3$) of **2b**



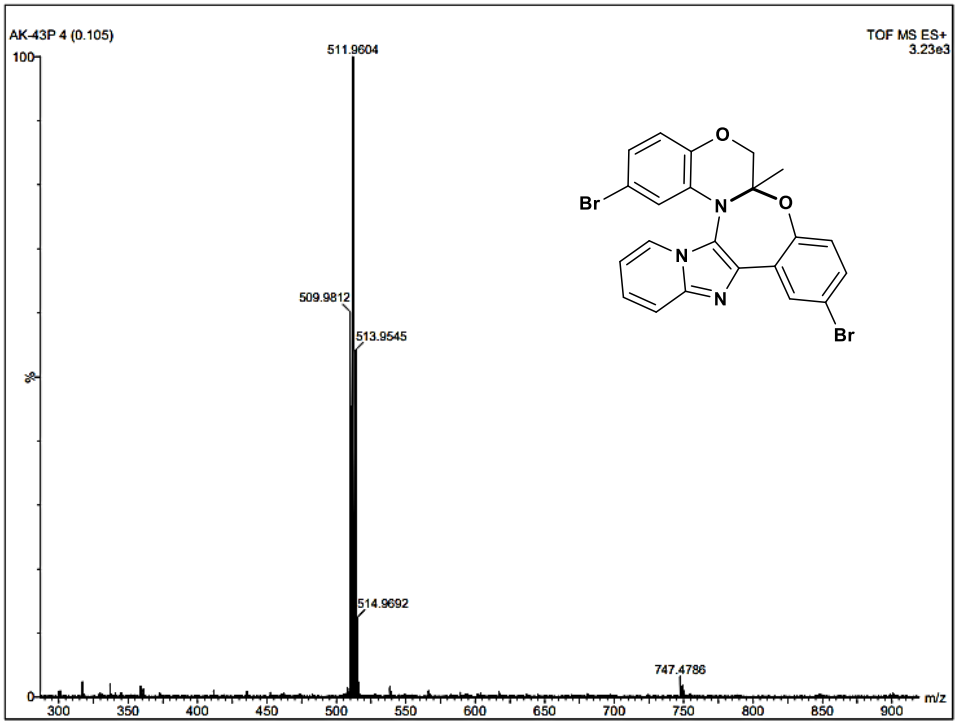
HRMS-ESI (+) of **2b**



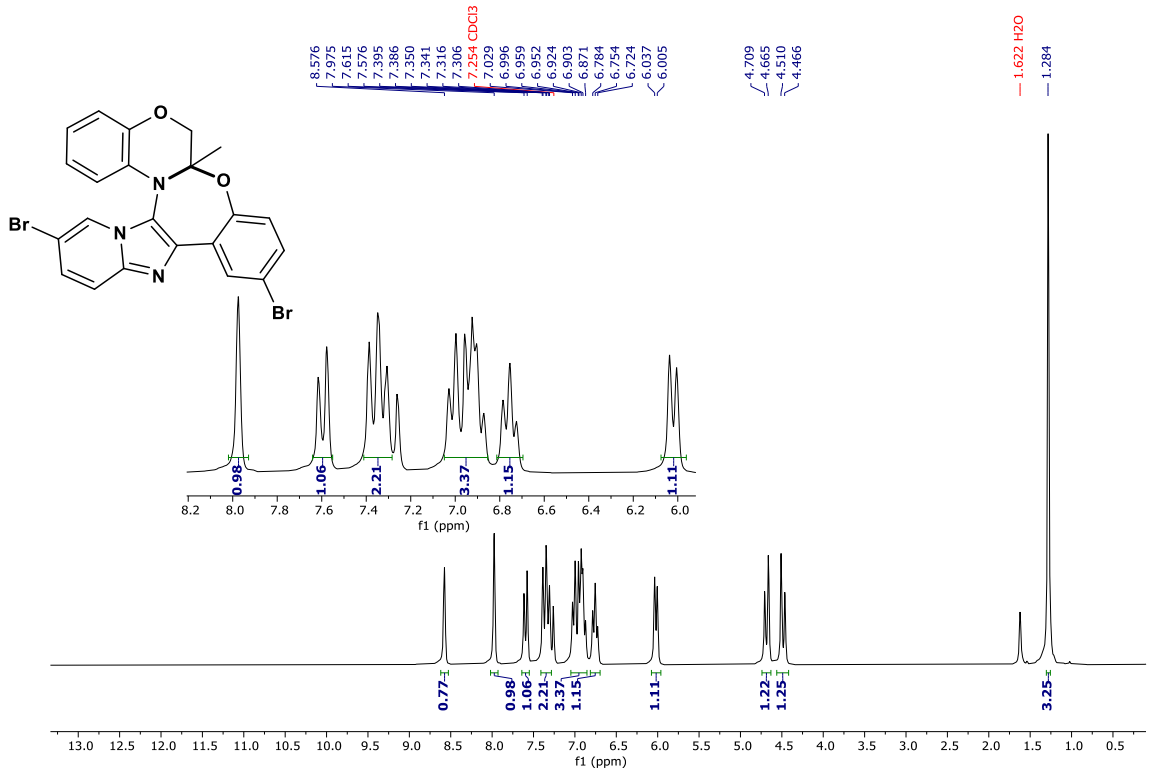
^{1}H NMR (250 MHz, $CDCl_3$) of **2c**



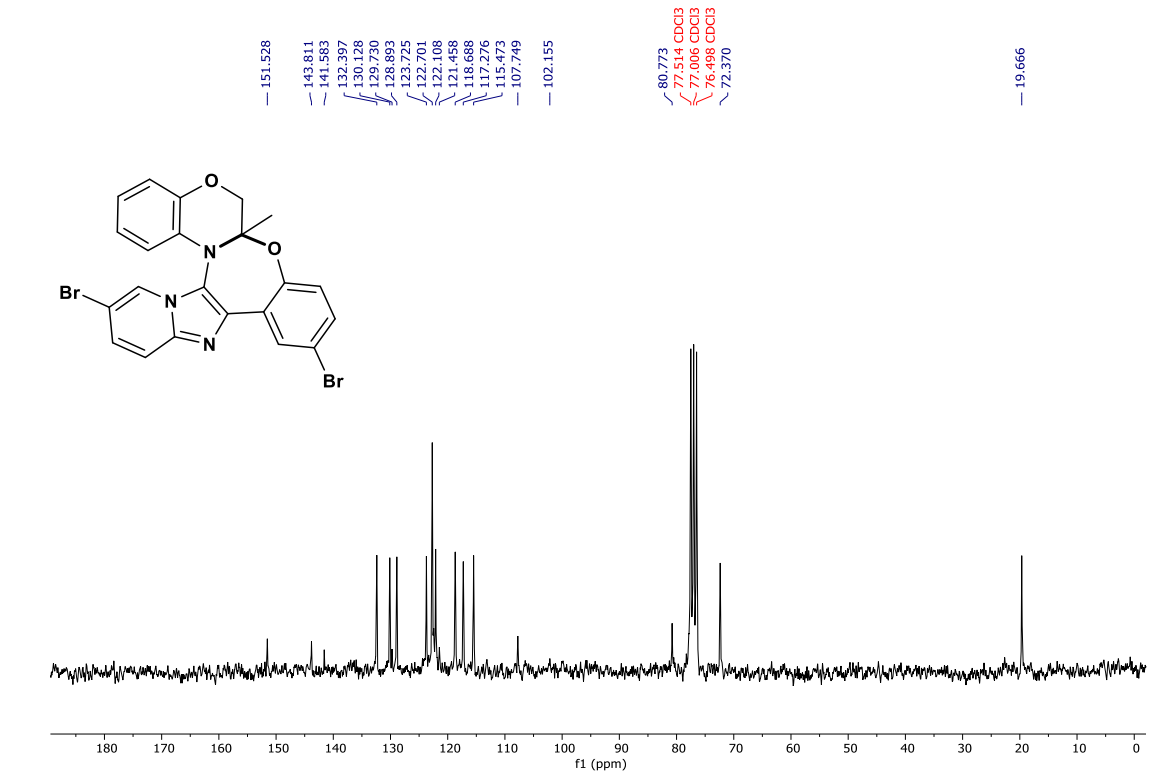
^{13}C NMR (63 MHz, $CDCl_3$) of **2c**



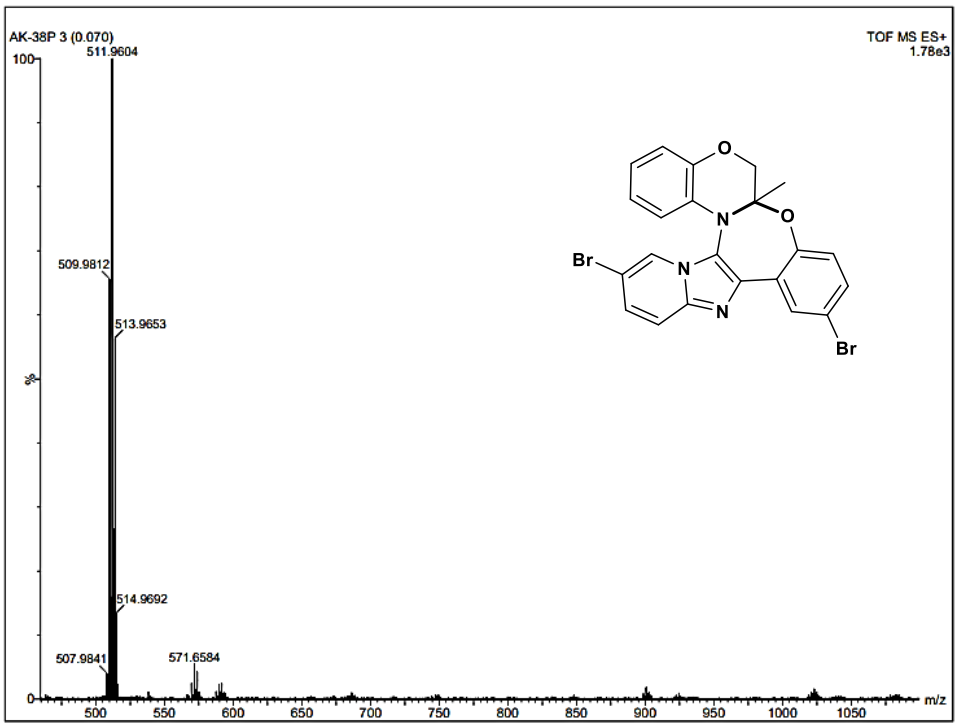
HRMS-ESI (+) of **2c**



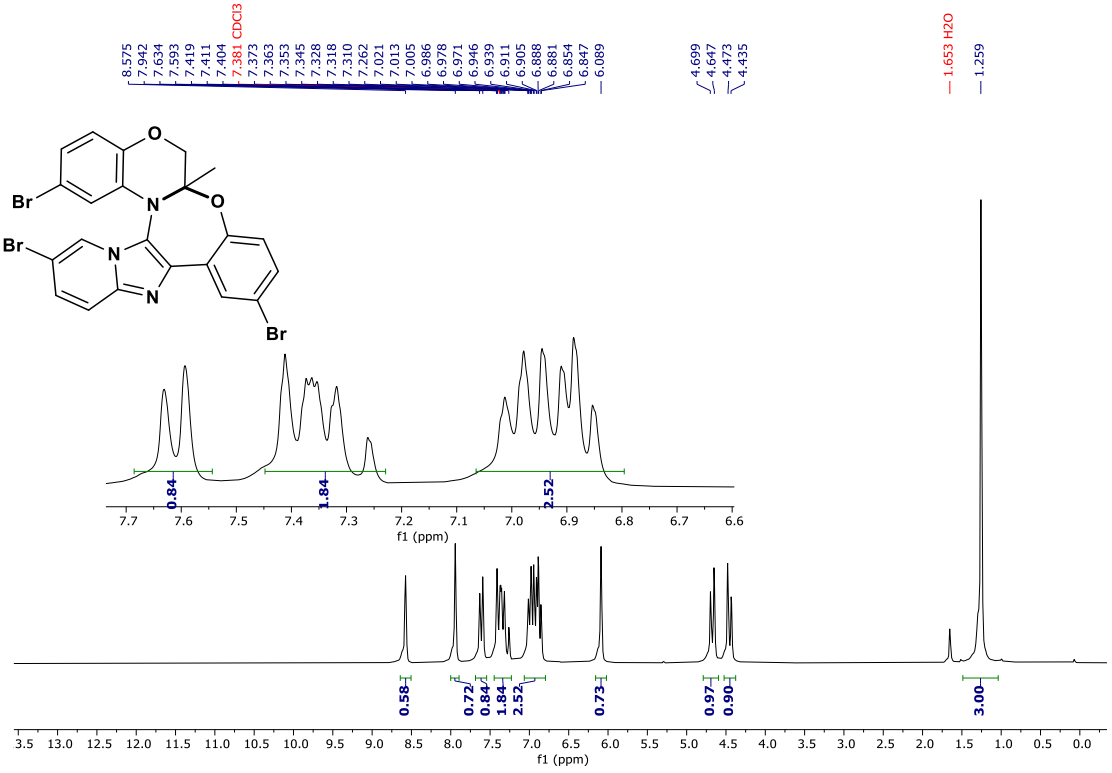
^{1}H NMR (400 MHz, $CDCl_3$) of **2d**



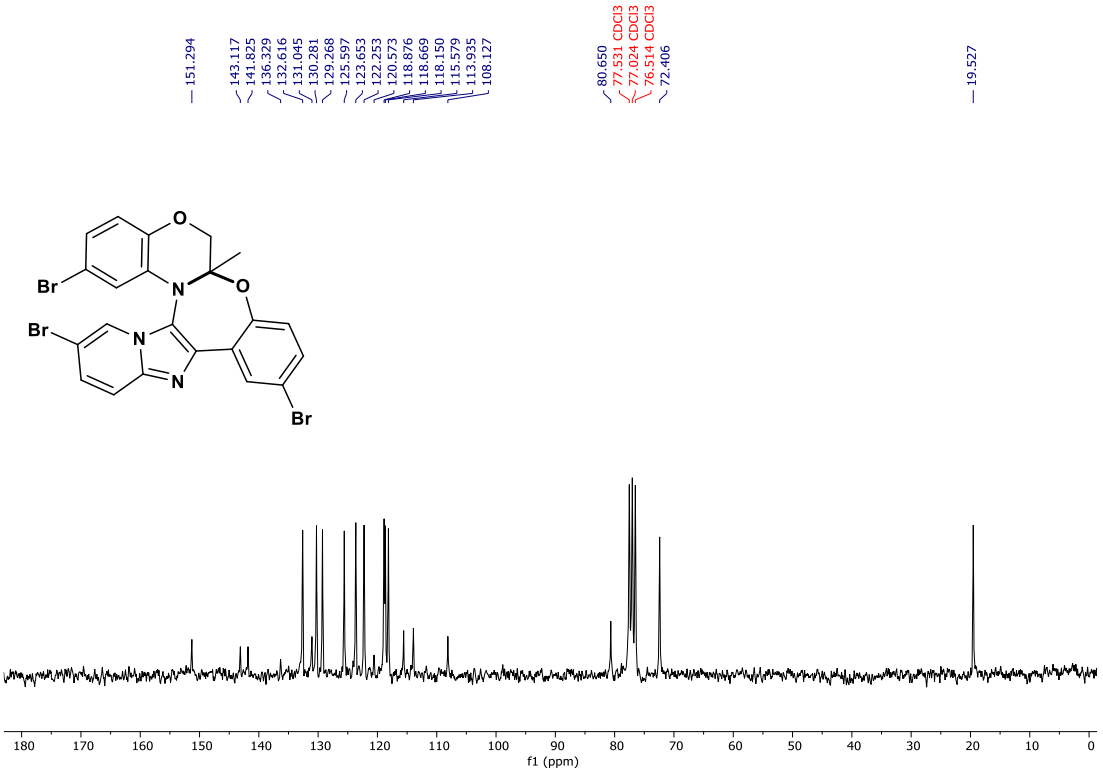
^{13}C NMR (101 MHz, $CDCl_3$) of **2d**



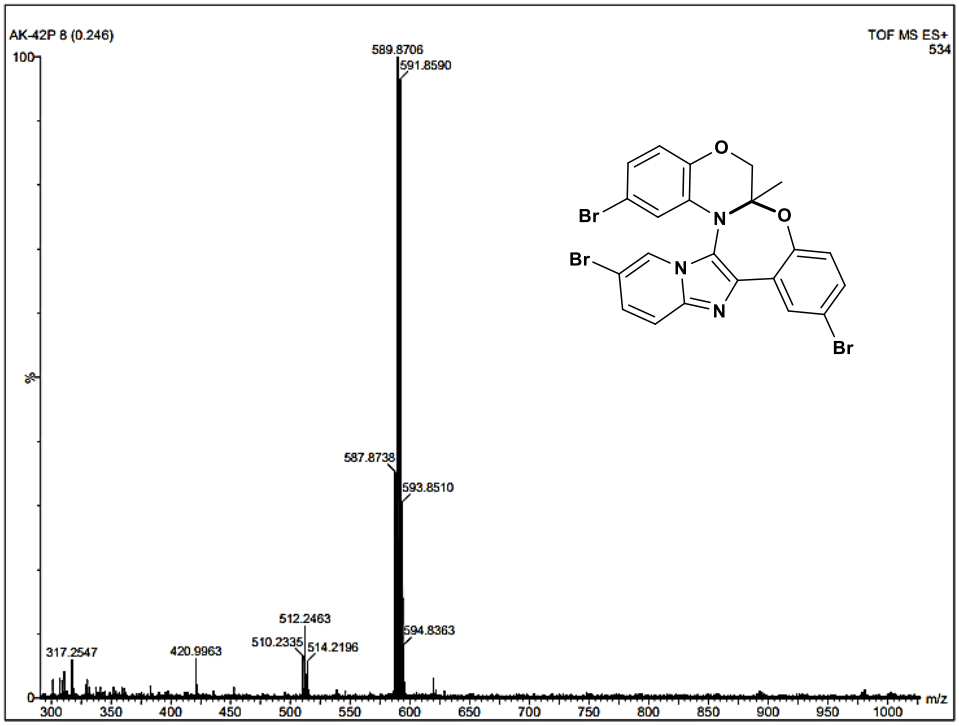
HRMS-ESI (+) of **2d**



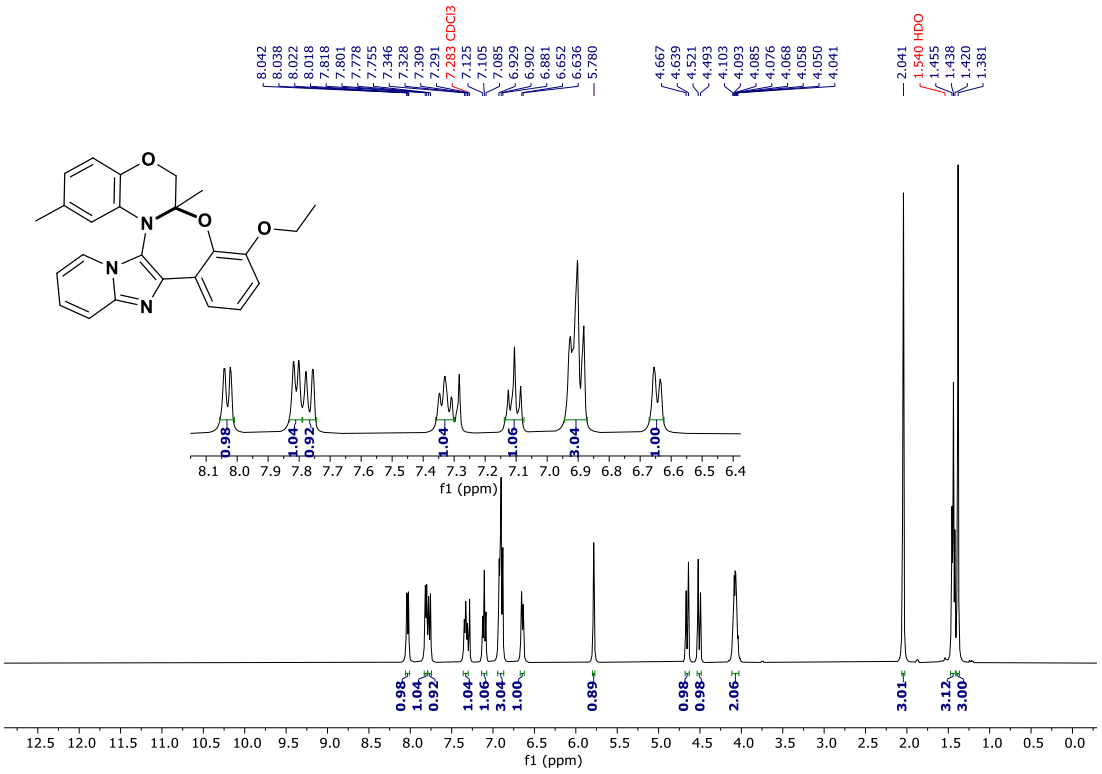
^{1}H NMR (250 MHz, $CDCl_3$) of **2e**



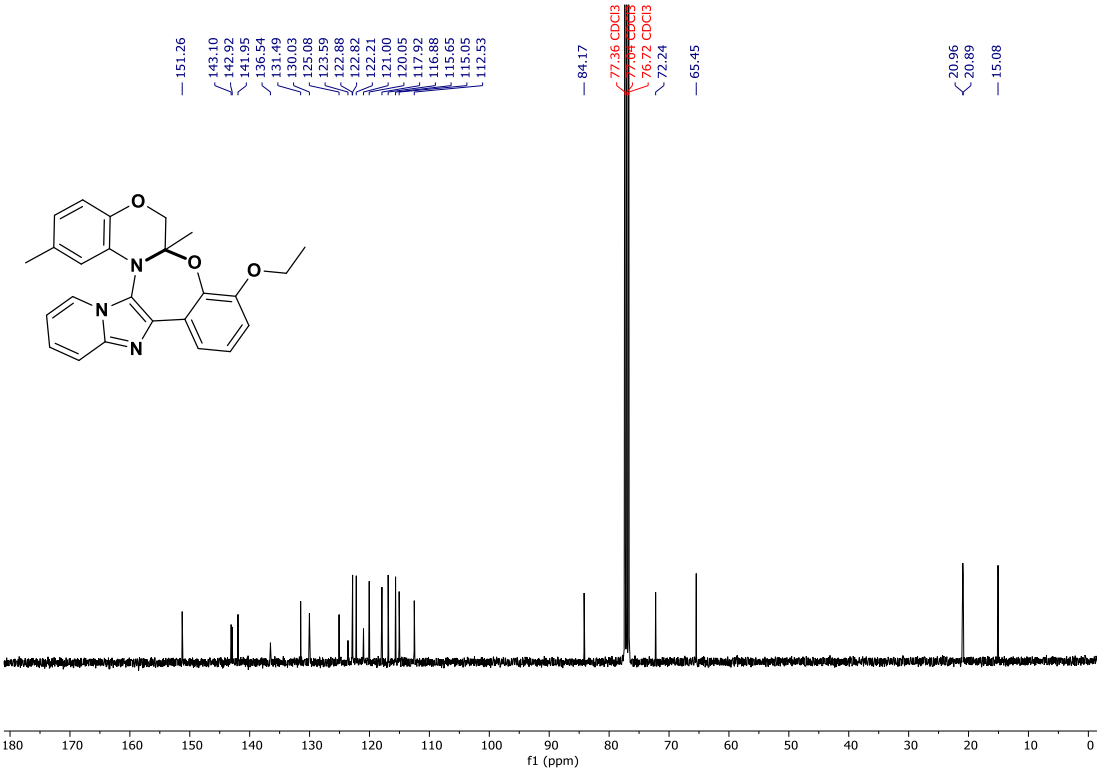
^{13}C NMR (63 MHz, $CDCl_3$) of **2e**



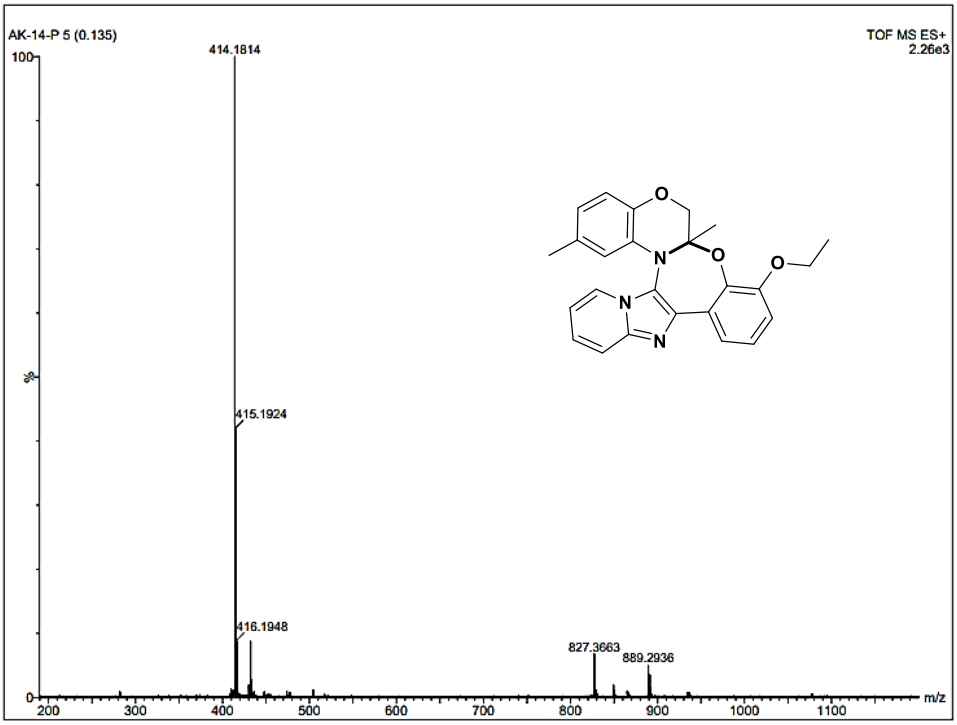
HRMS-ESI (+) of **2e**



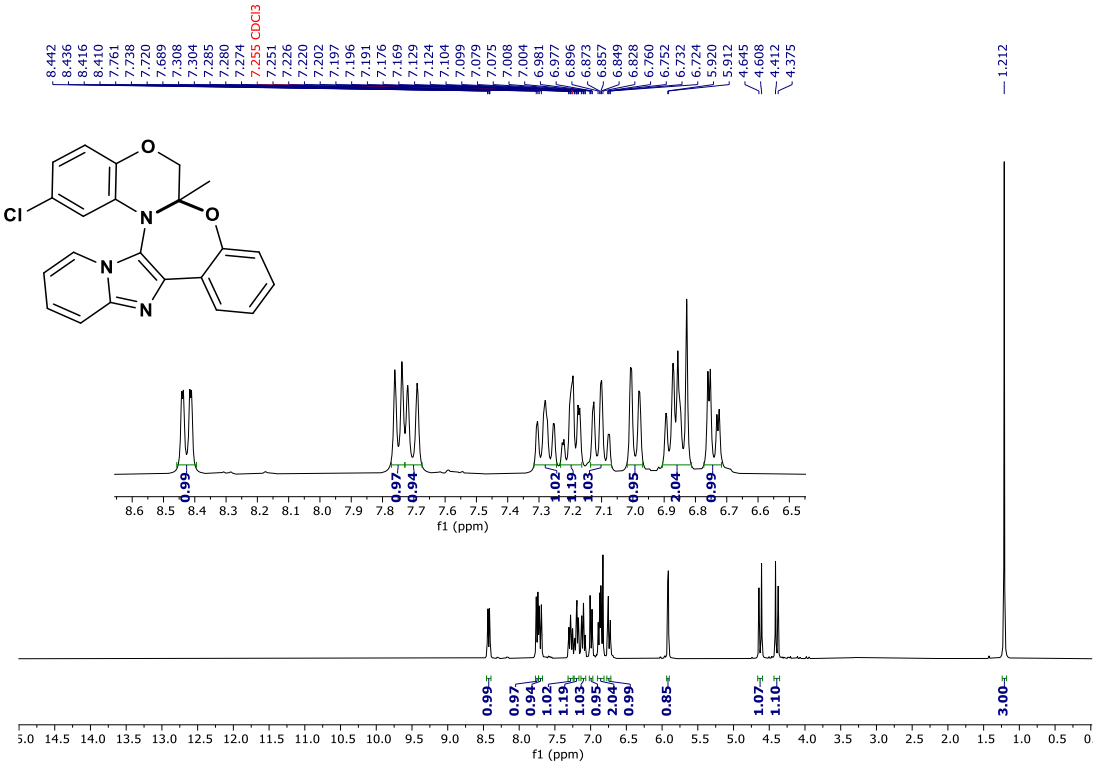
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



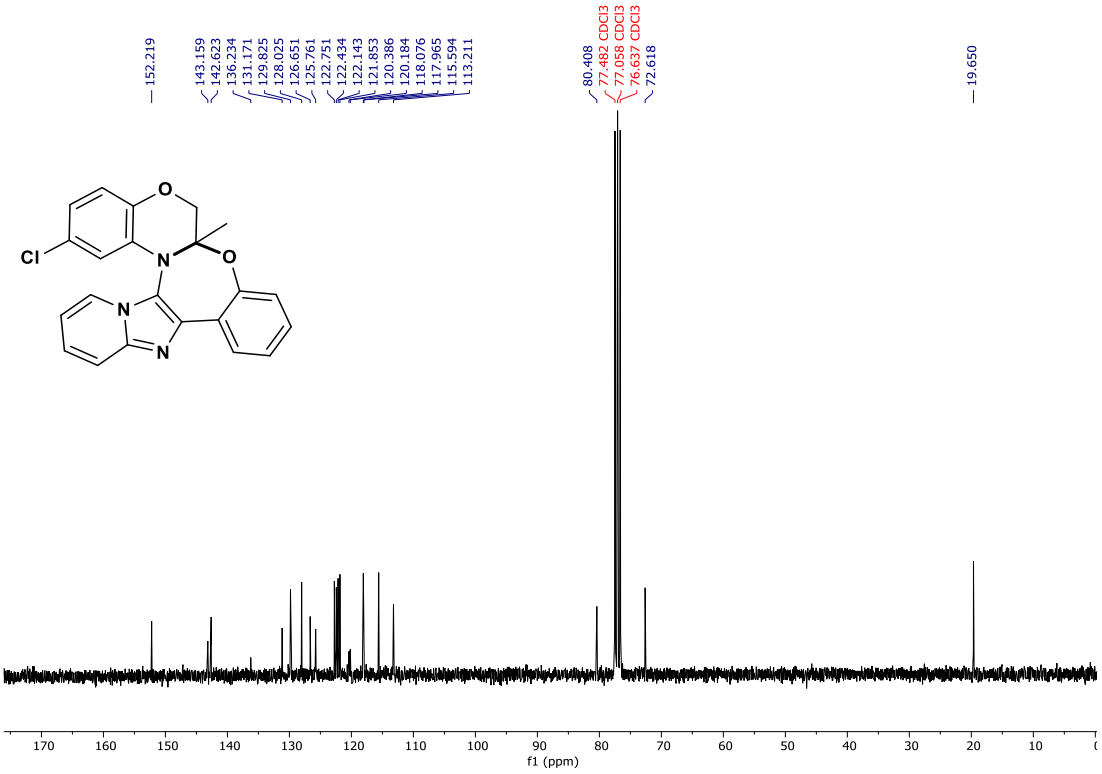
^{13}C NMR (101 MHz, $CDCl_3$) of **2f**



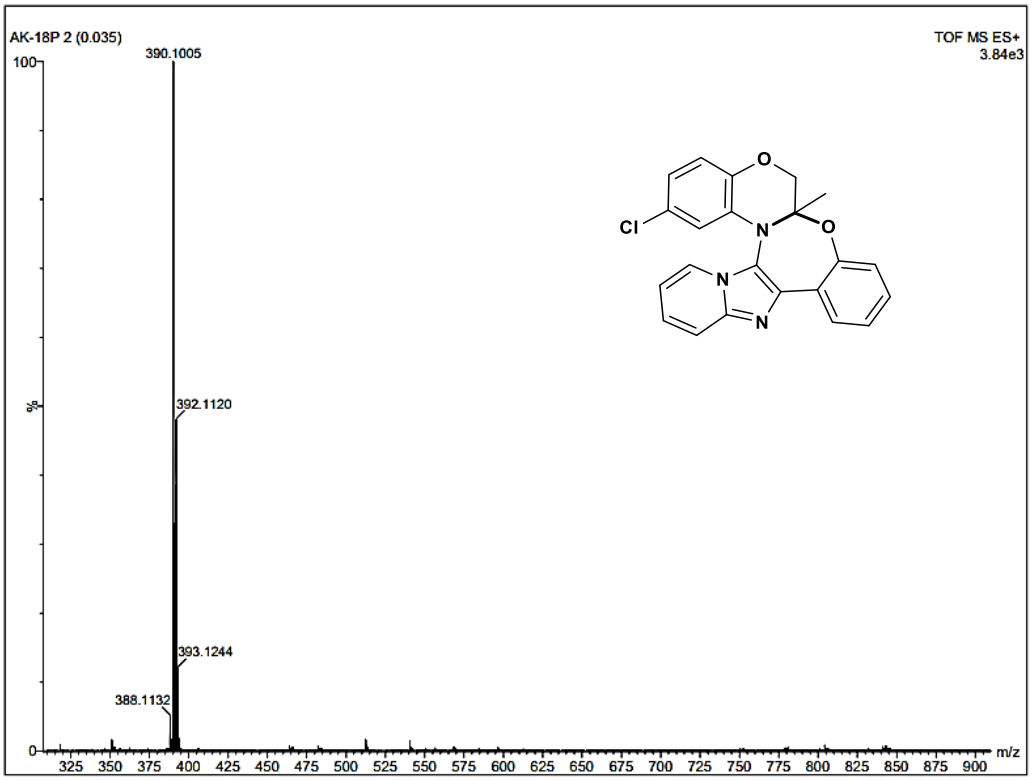
HRMS-ESI (+) of **2f**



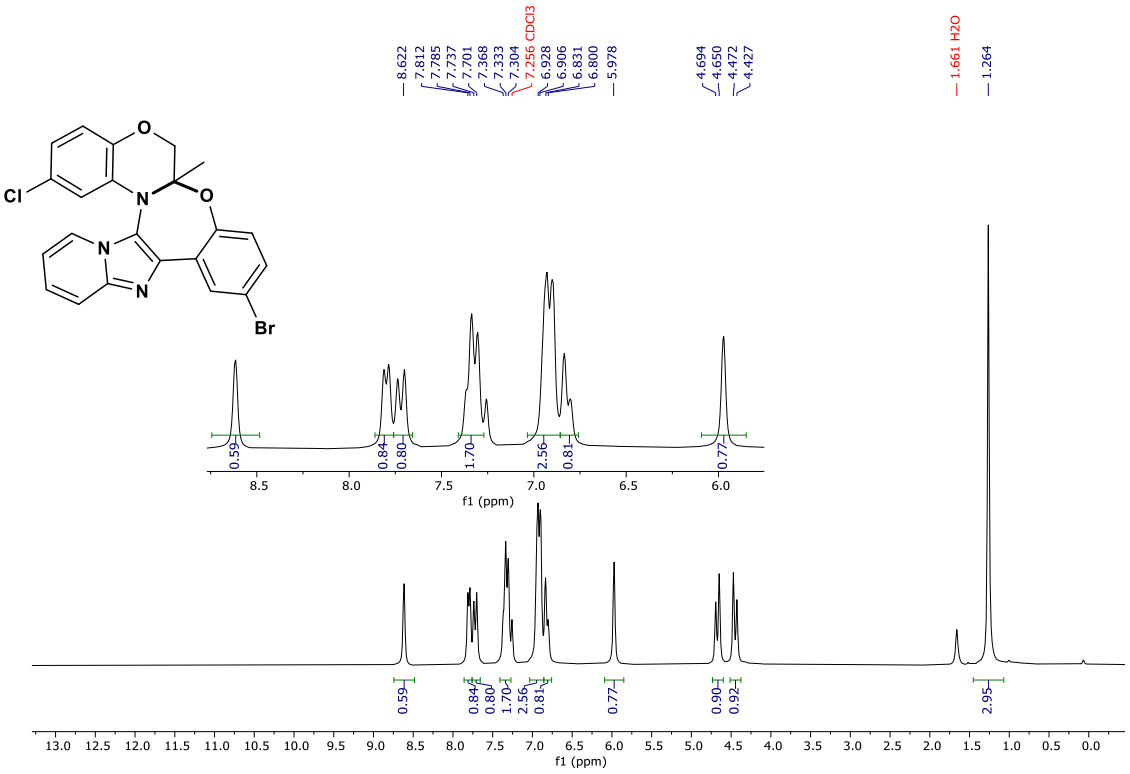
^{1}H NMR (300 MHz, $CDCl_3$) of **2g**



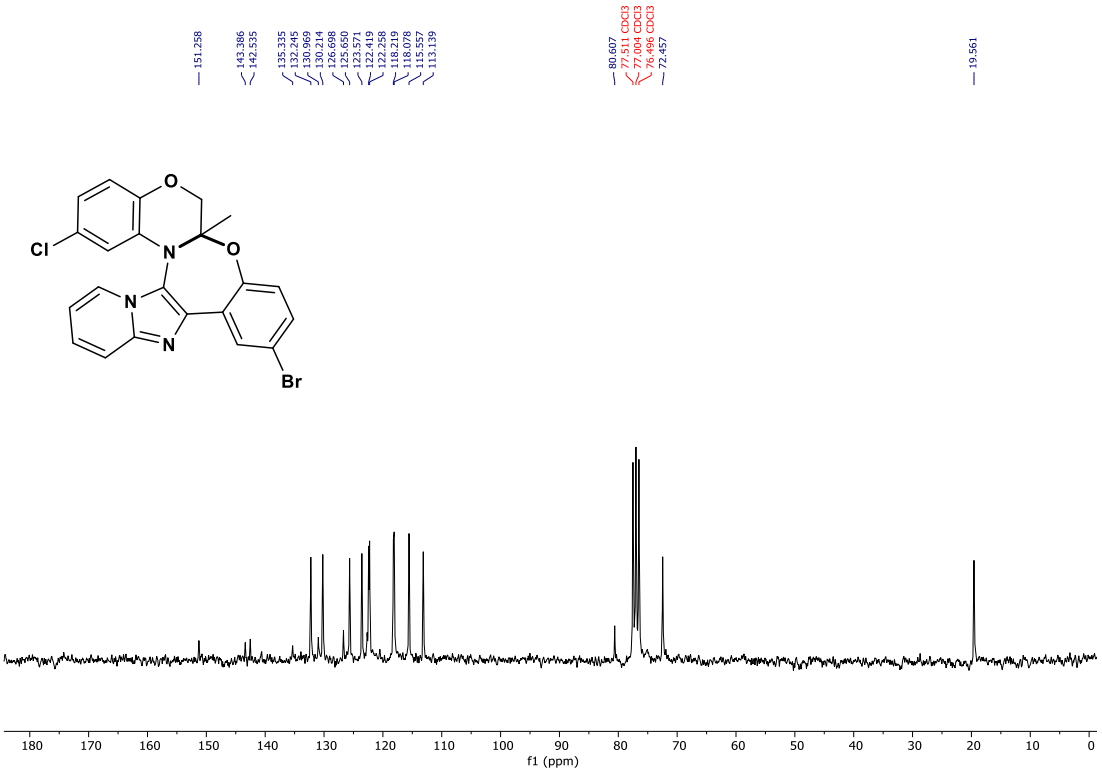
^{13}C NMR (76 MHz, $CDCl_3$) of **2g**



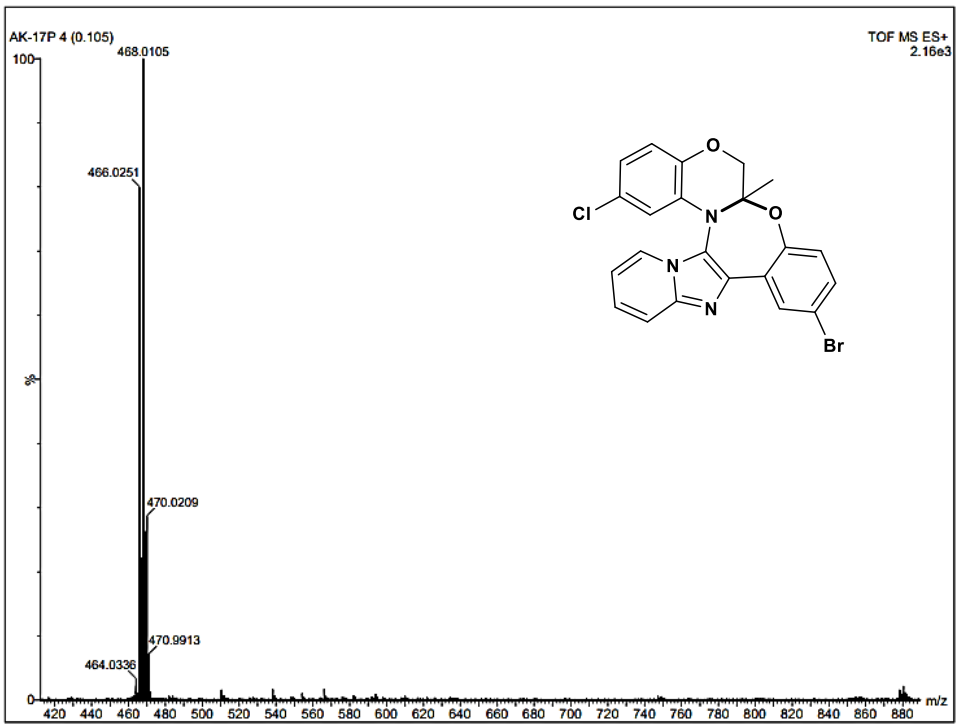
HRMS-ESI (+) of **2g**



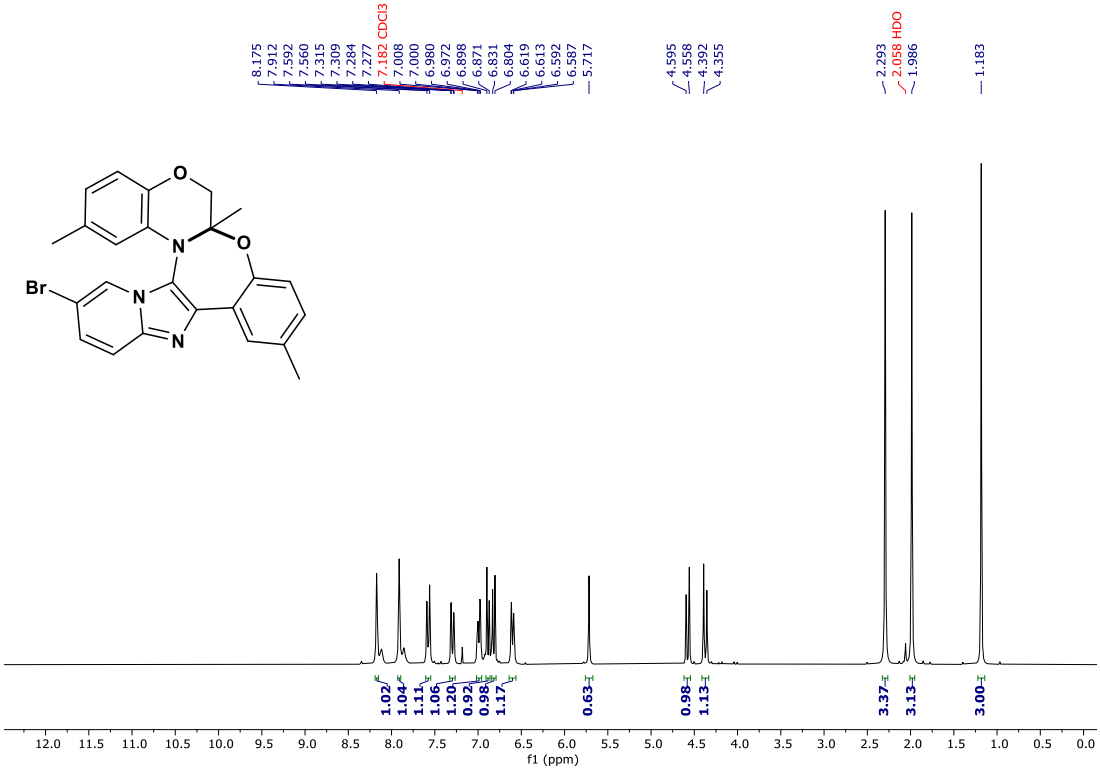
^{1}H NMR (250 MHz, $CDCl_3$) of **2h**



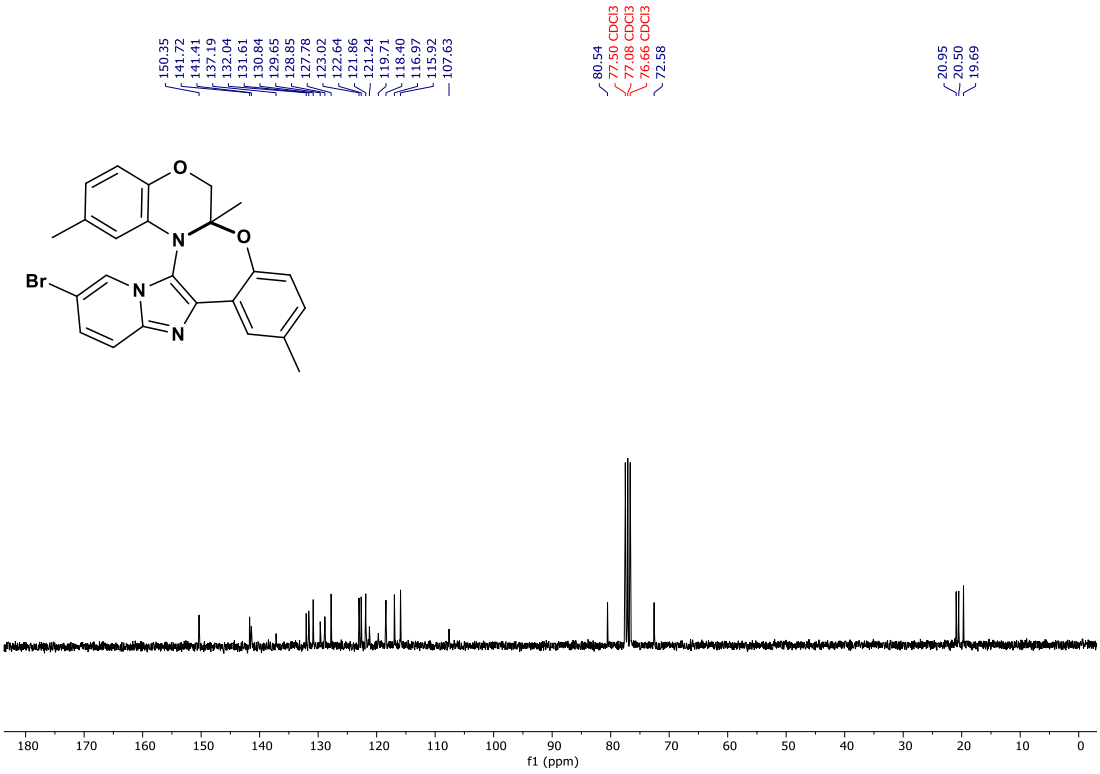
^{13}C NMR (63 MHz, $CDCl_3$) of **2h**



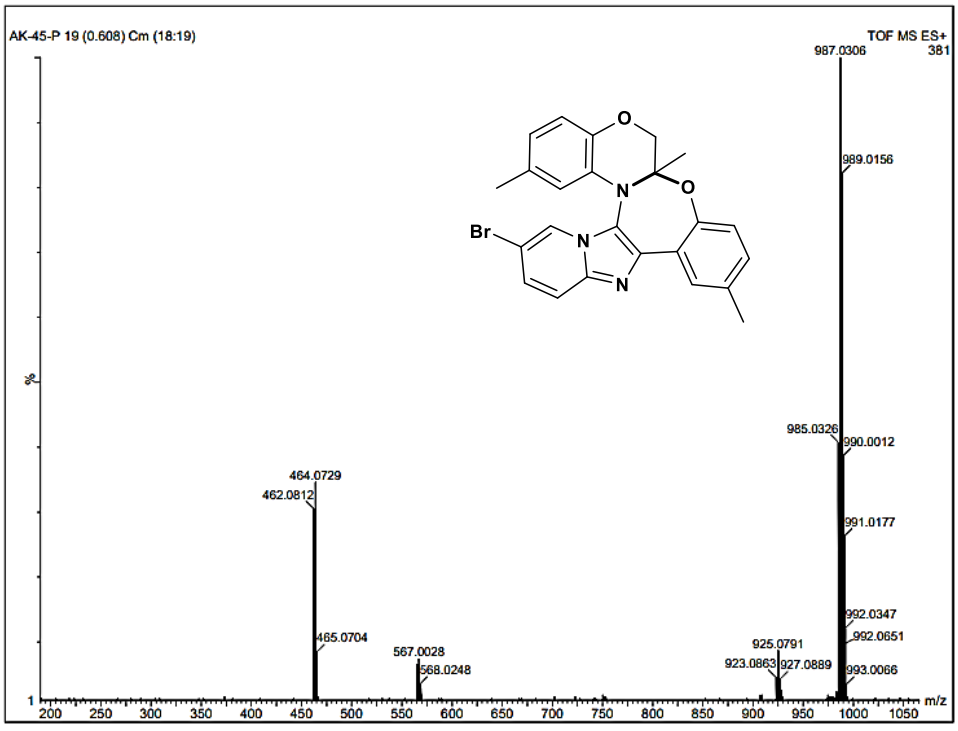
HRMS-ESI (+) of **2h**



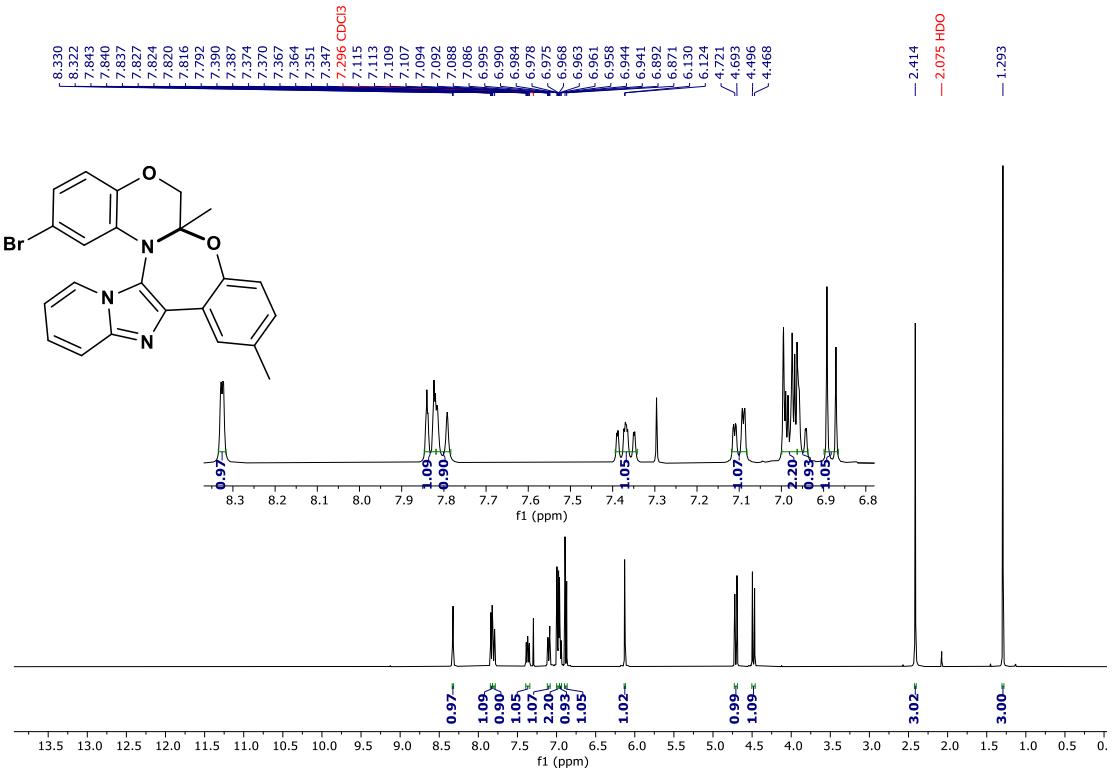
^{1}H NMR (301 MHz, $CDCl_3$) of **2i**



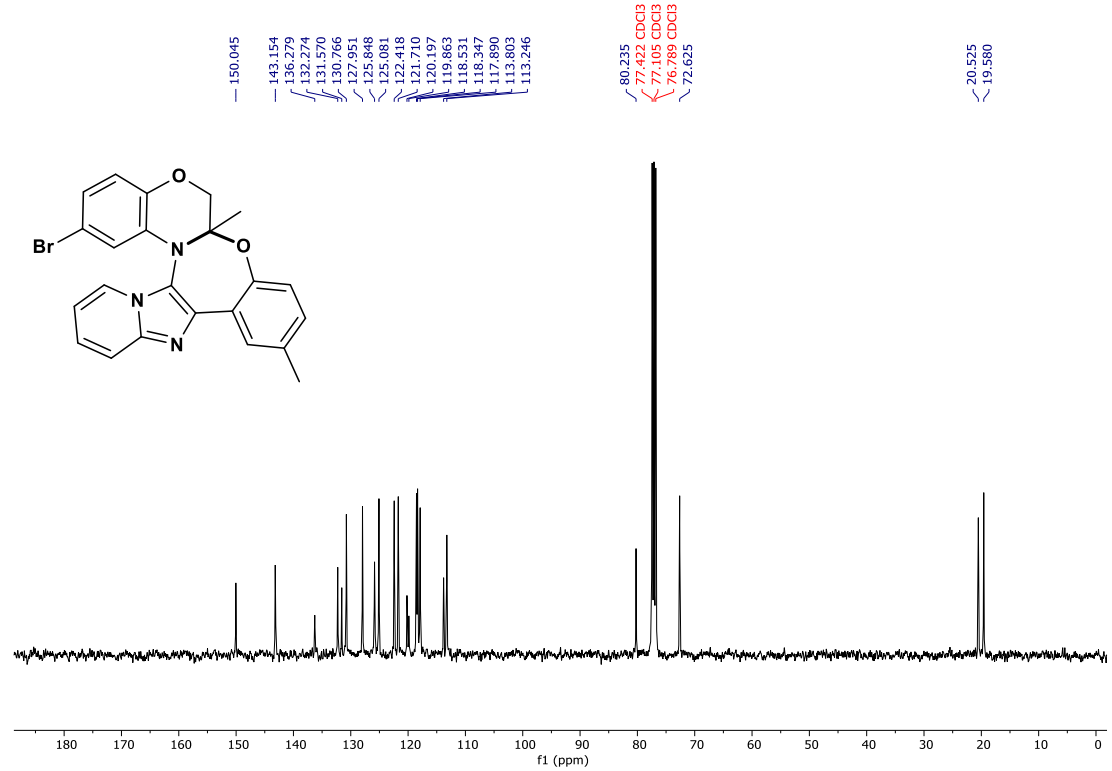
^{13}C NMR (76 MHz, $CDCl_3$) of **2i**



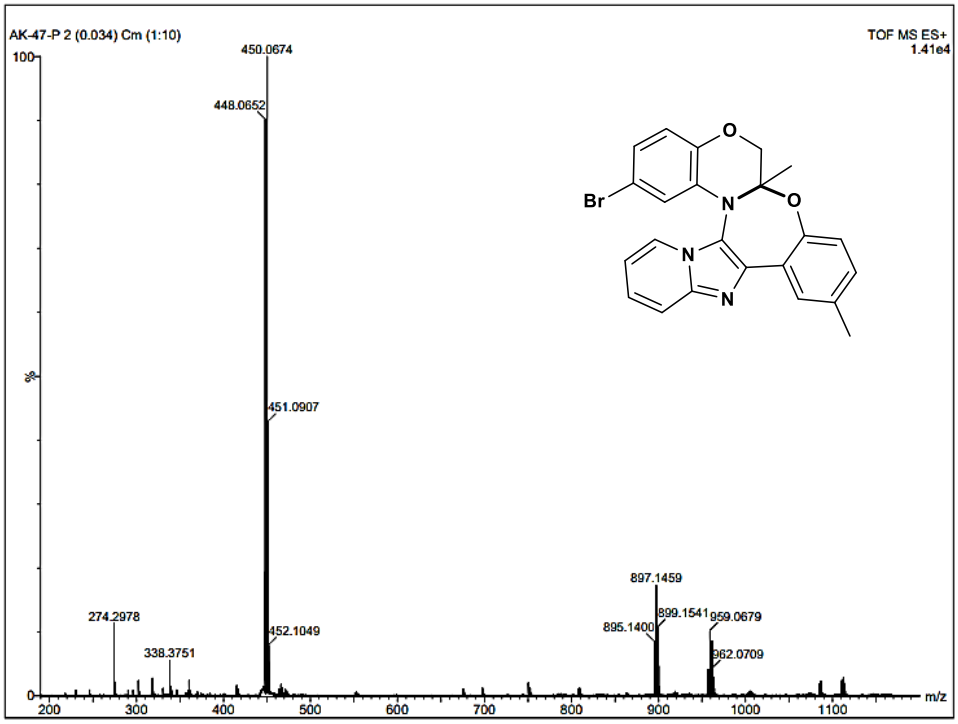
HRMS-ESI (+) of **2i**



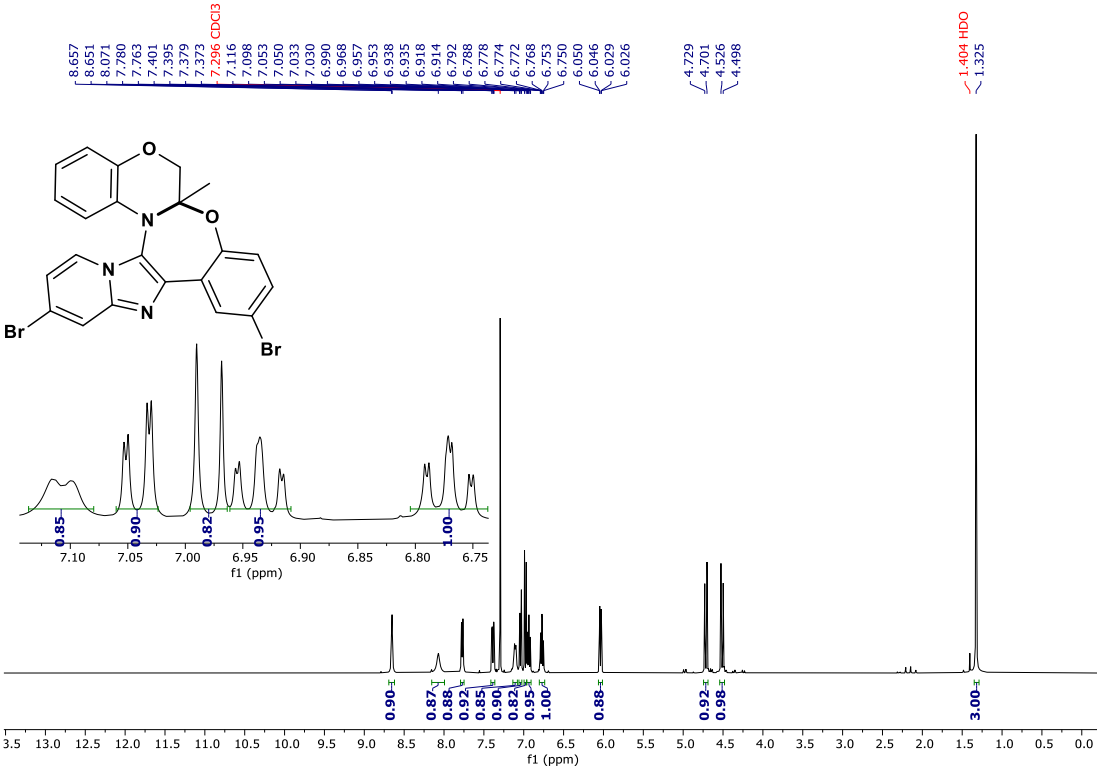
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



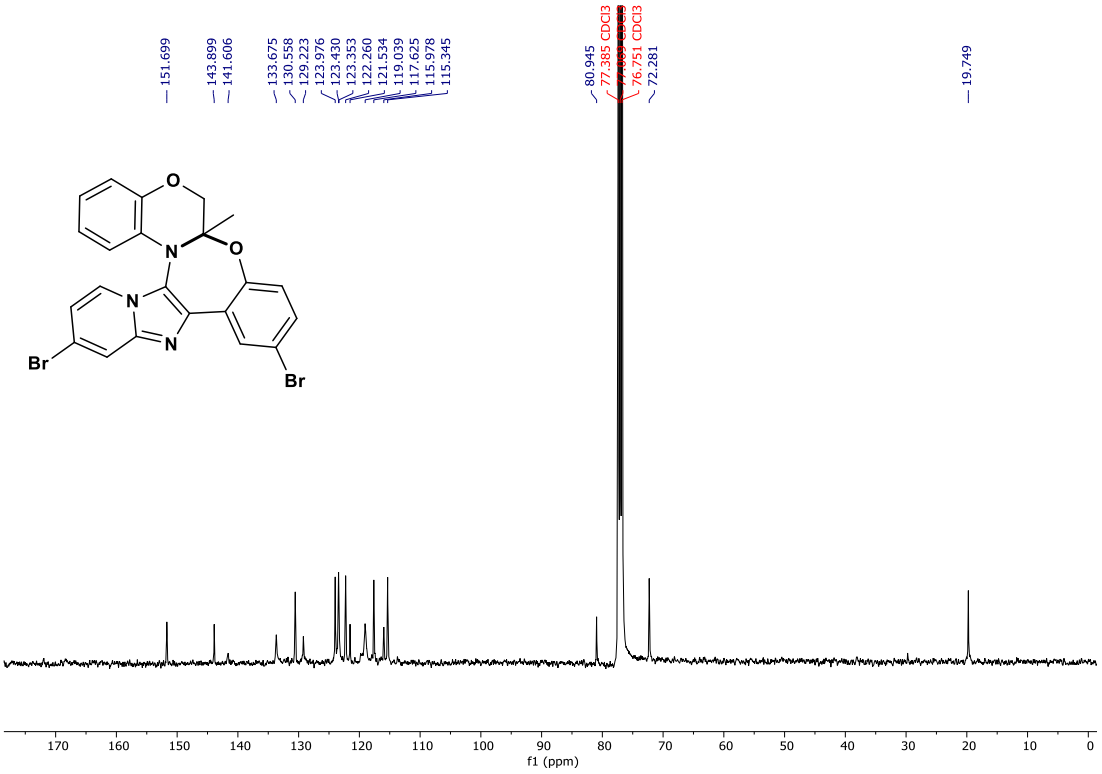
^{13}C NMR (101 MHz, $CDCl_3$) of **2j**



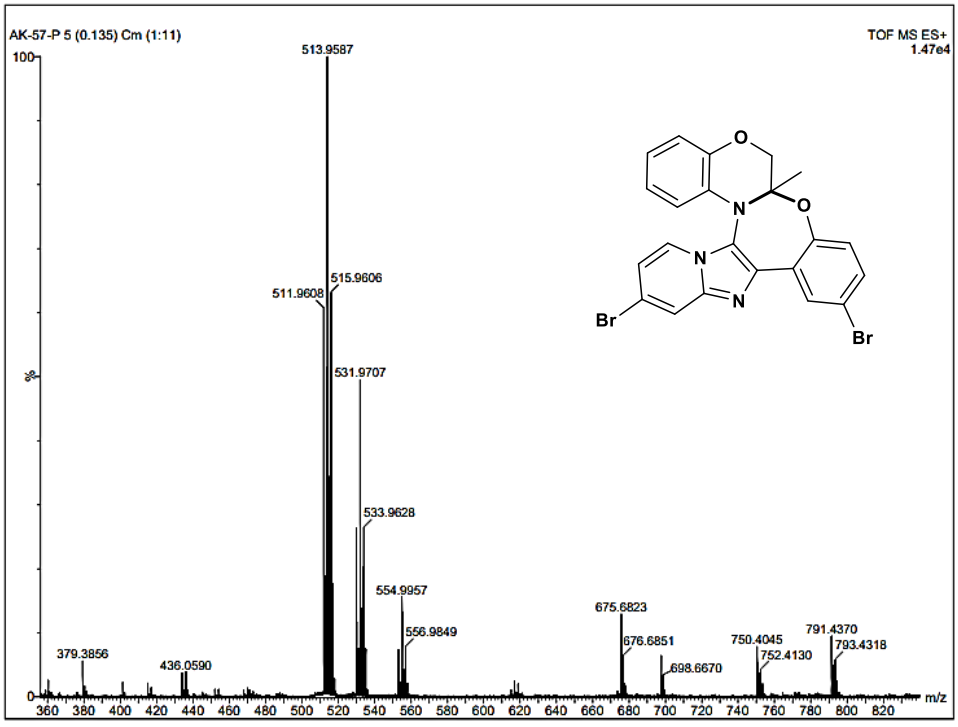
HRMS-ESI (+) of **2j**



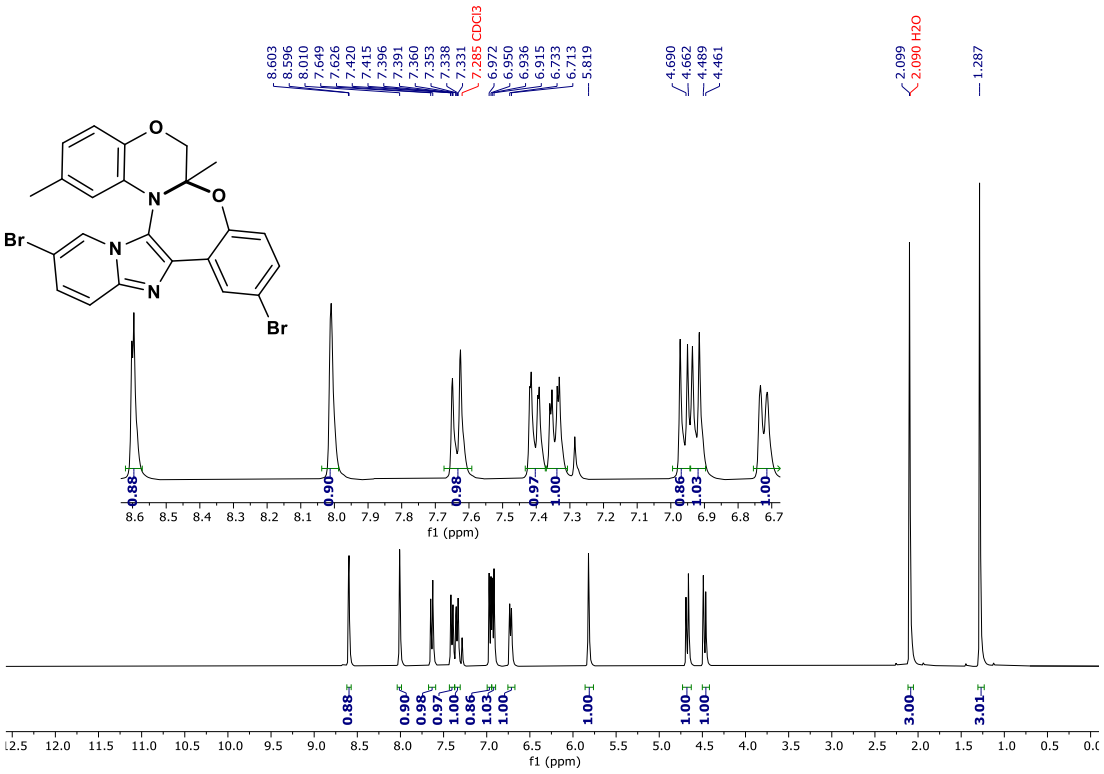
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



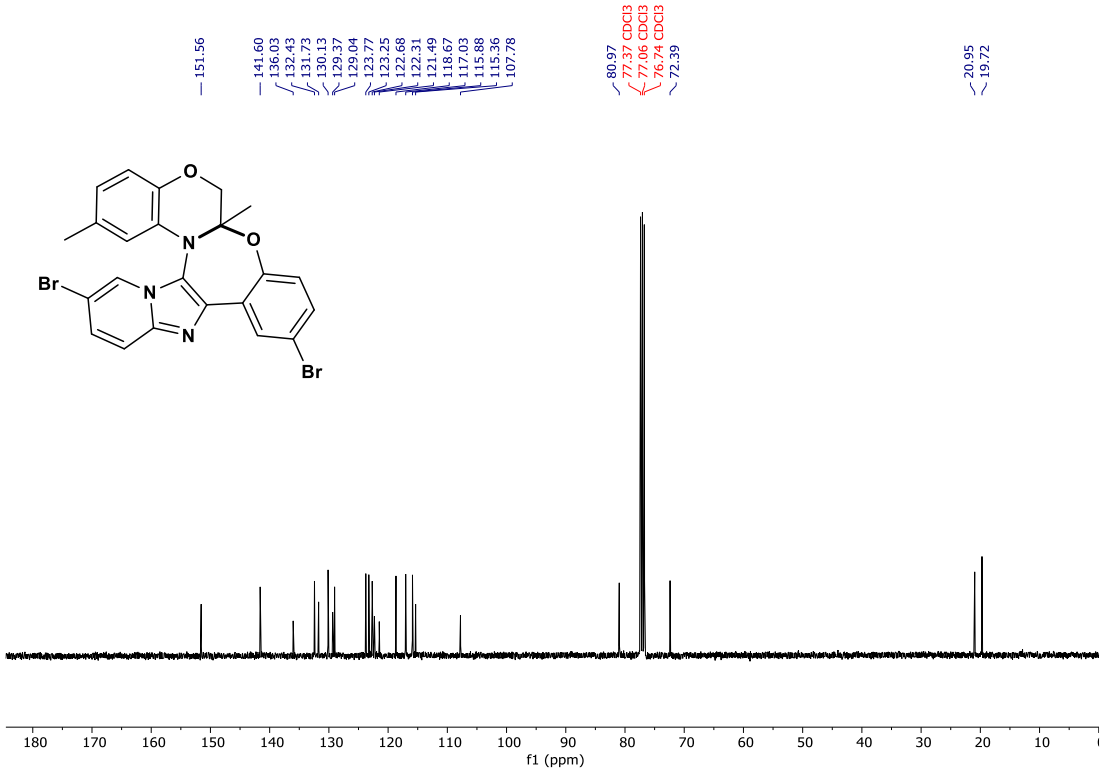
^{13}C NMR (101 MHz, $CDCl_3$) of **2k**



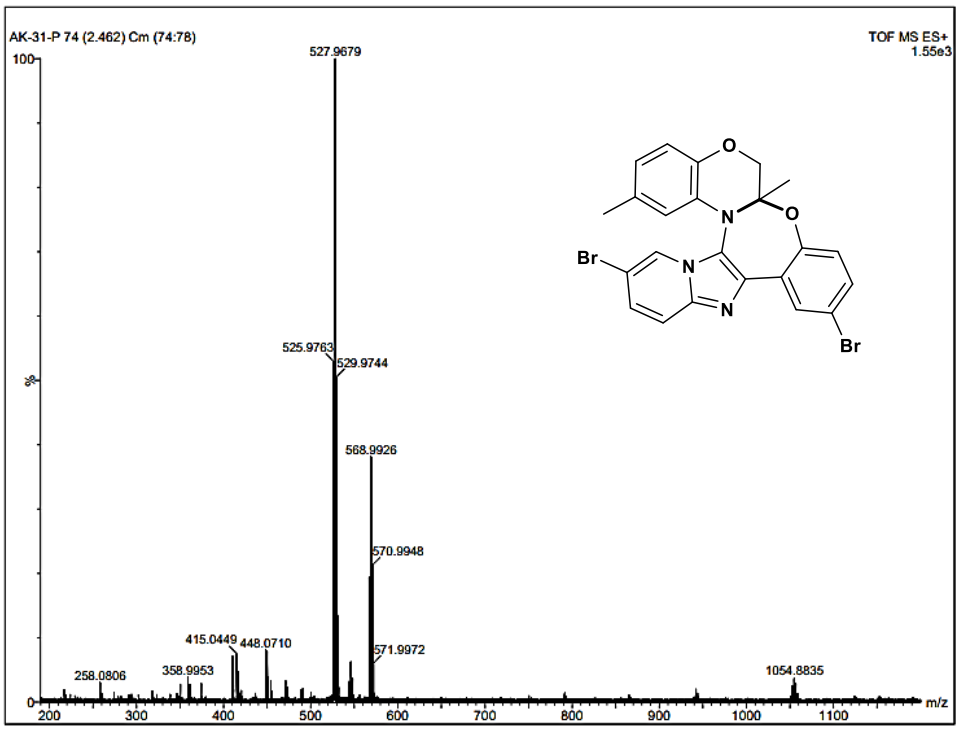
HRMS-ESI (+) of **2k**



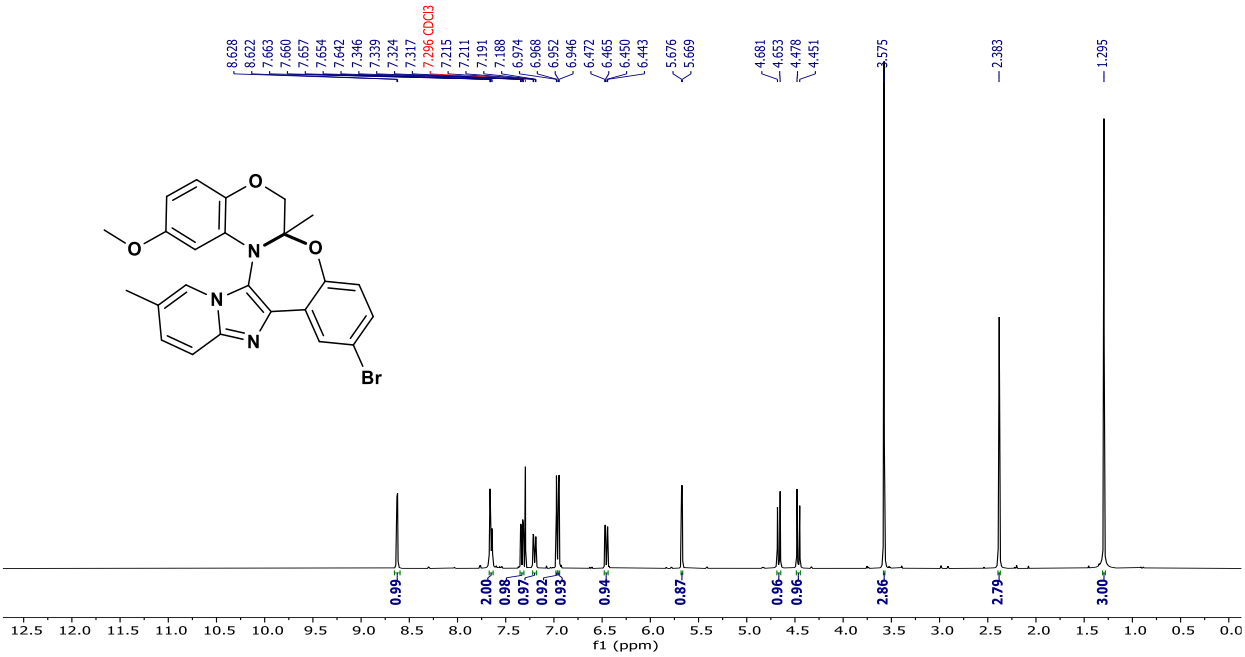
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



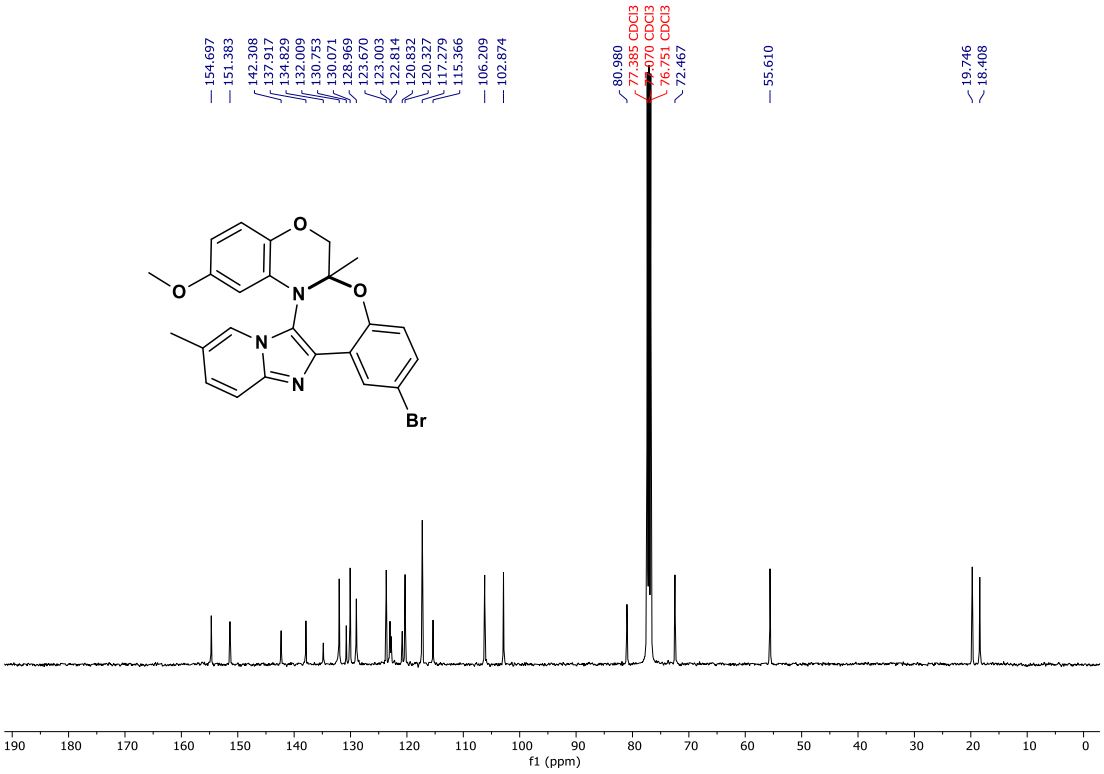
^{13}C NMR (101 MHz, $CDCl_3$) of **2l**



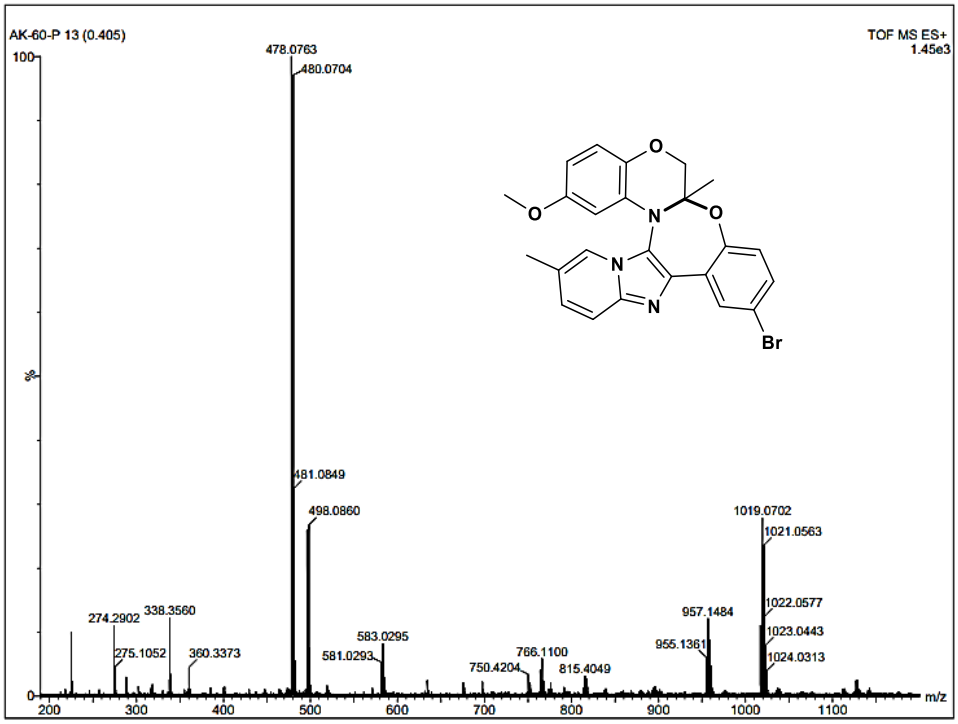
HRMS-ESI (+) of **2l**



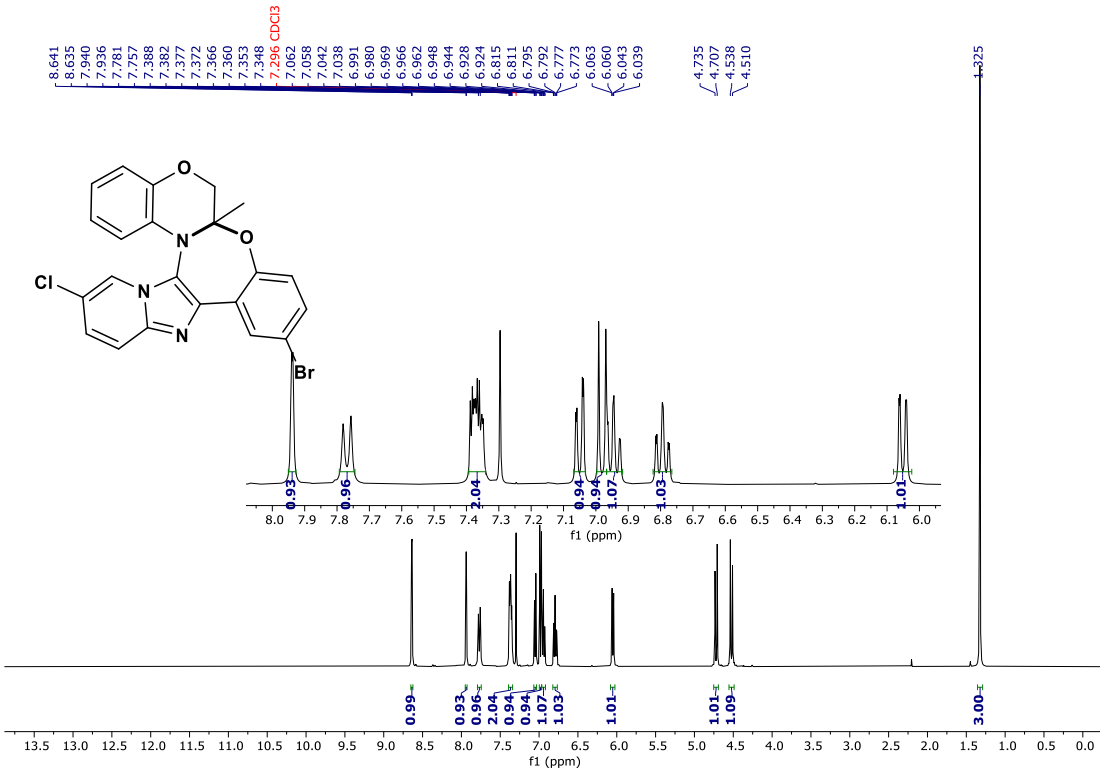
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



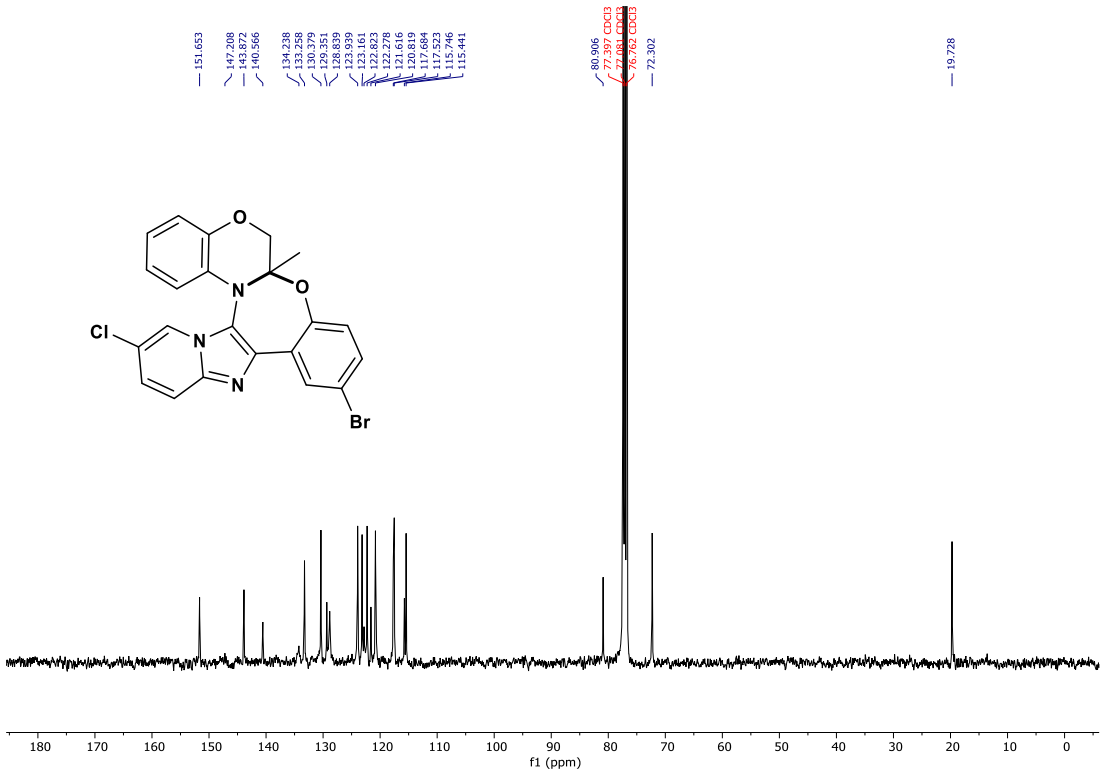
^{13}C NMR (101 MHz, $CDCl_3$) of **2m**



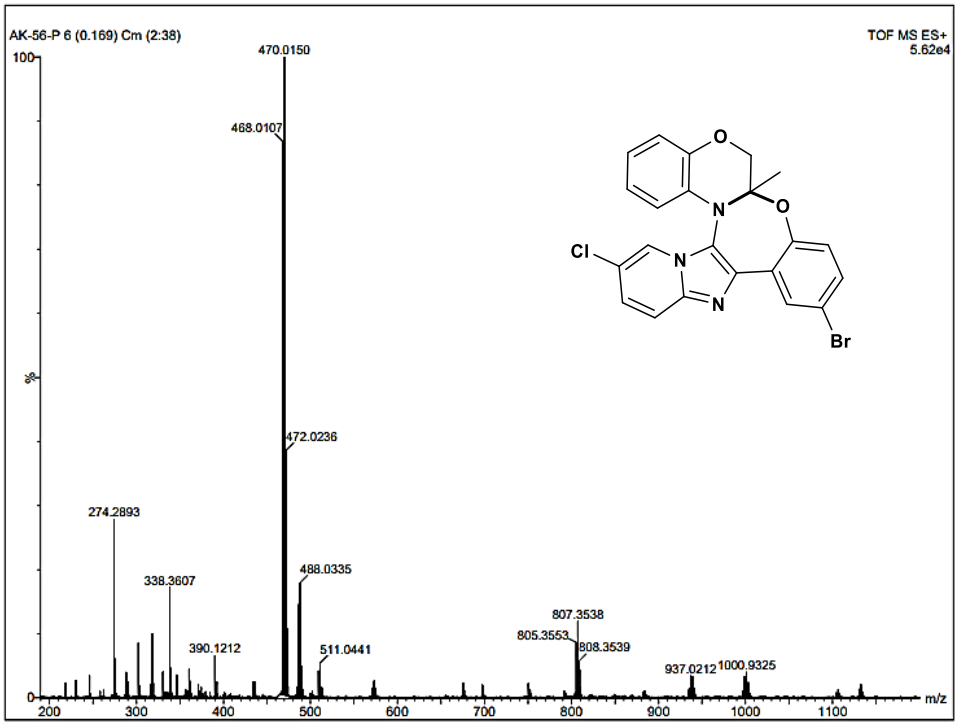
HRMS-ESI (+) of **2m**



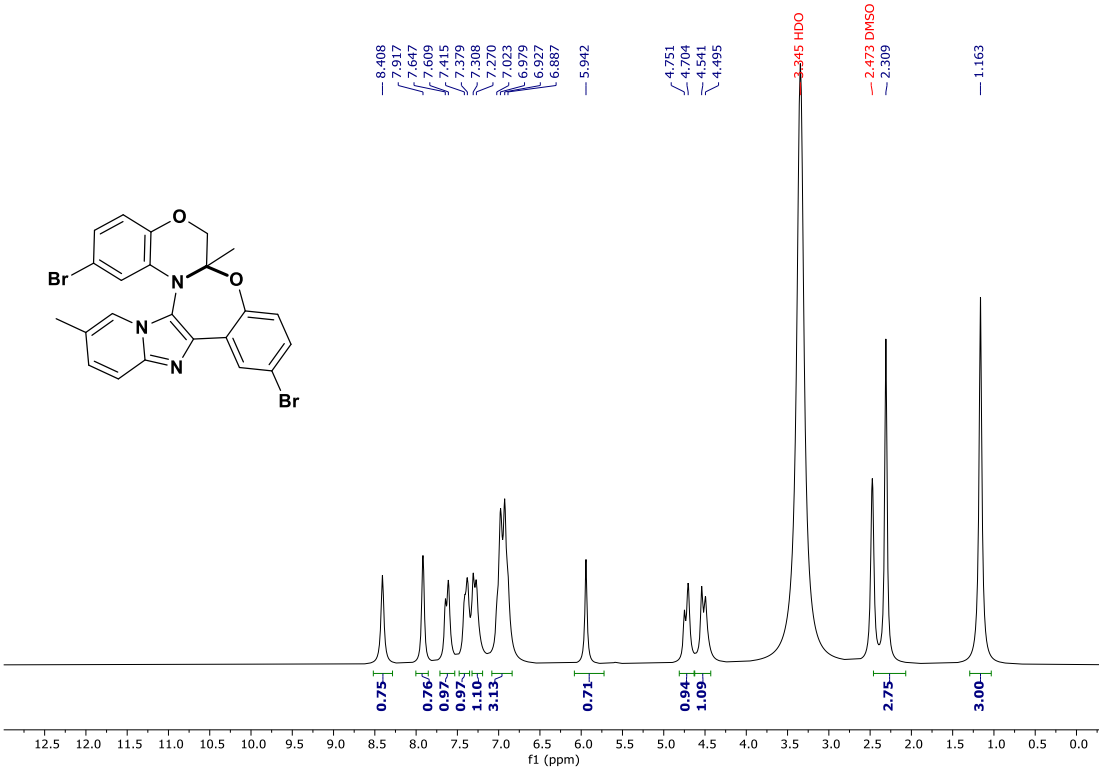
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



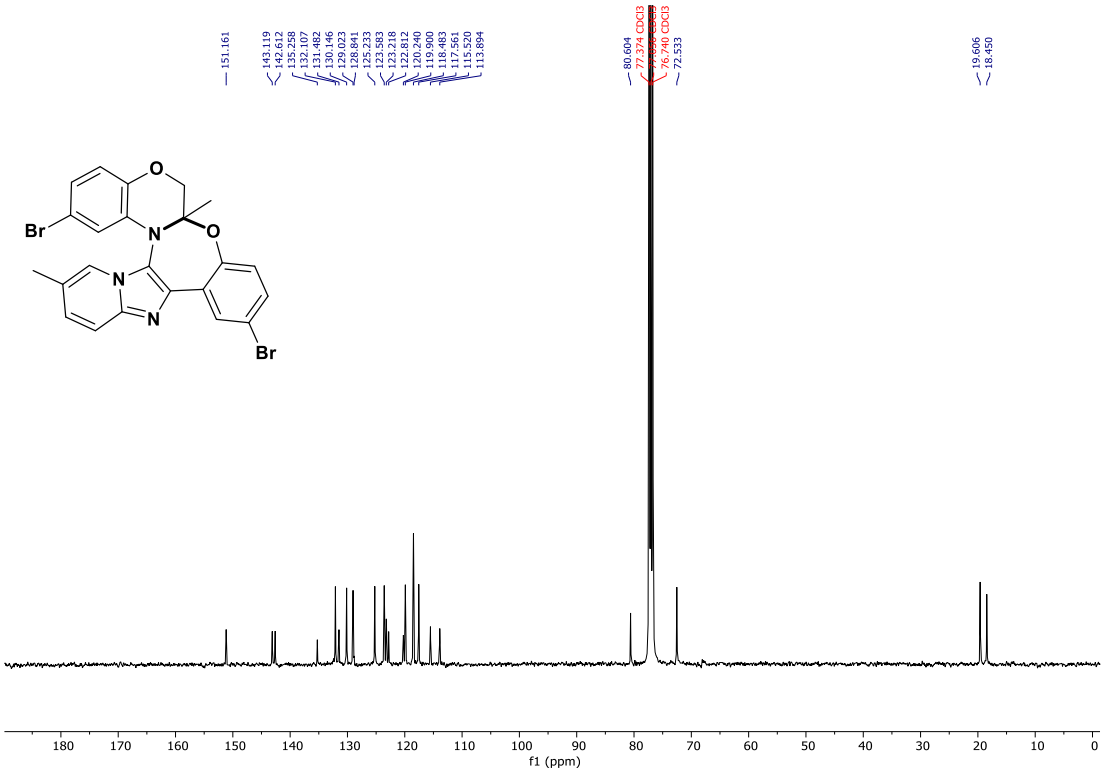
^{13}C NMR (101 MHz, $CDCl_3$) of **2n**



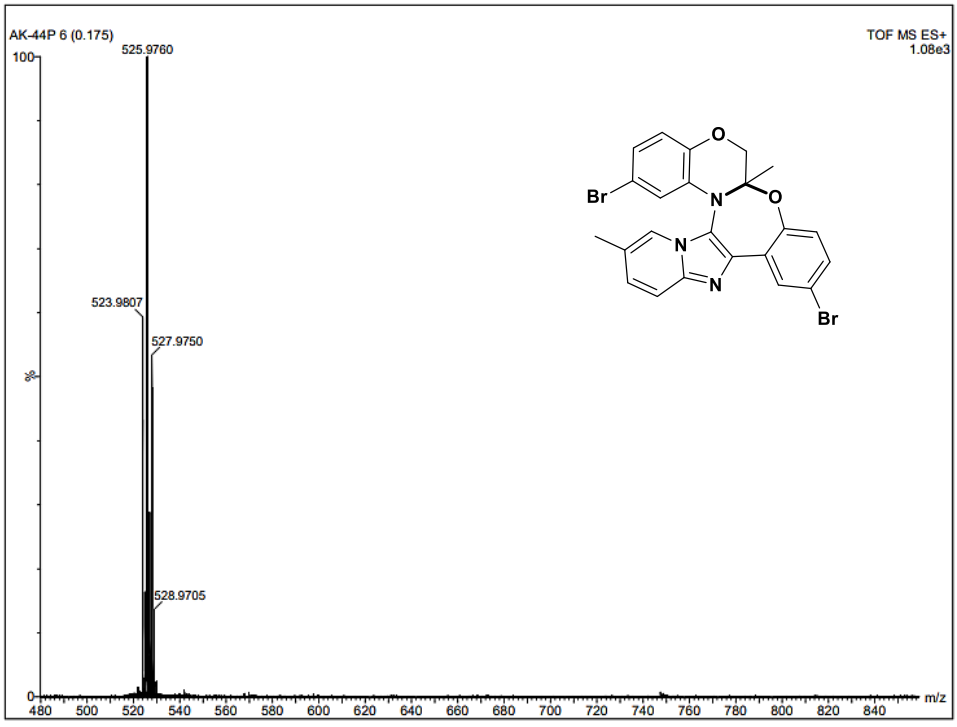
HRMS-ESI (+) of **2n**



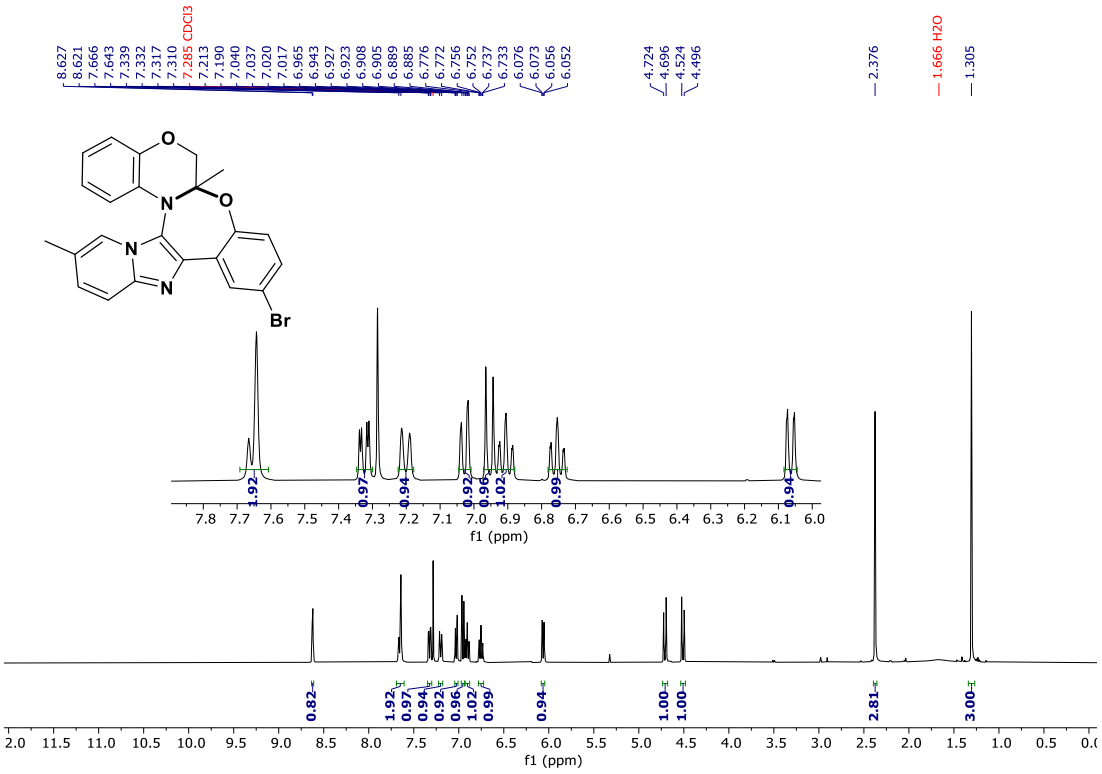
H NMR (400 MHz, $CDCl_3$) of **2o**



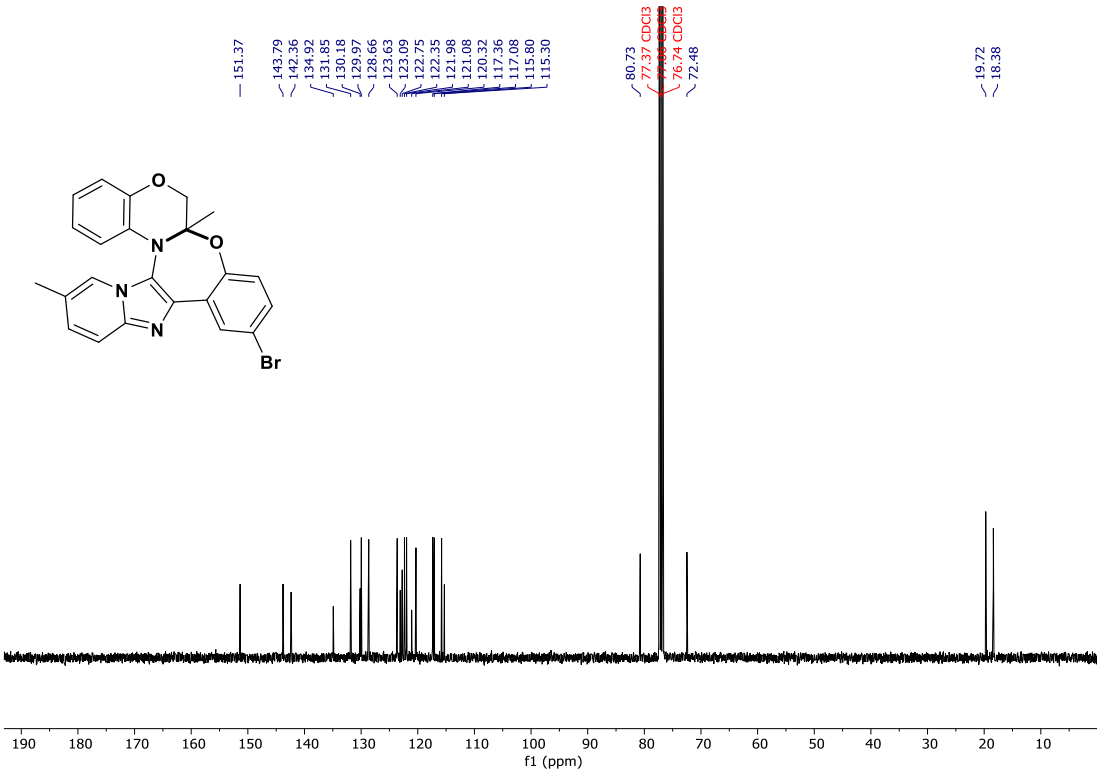
^{13}C NMR (101 MHz, $CDCl_3$) of **2o**



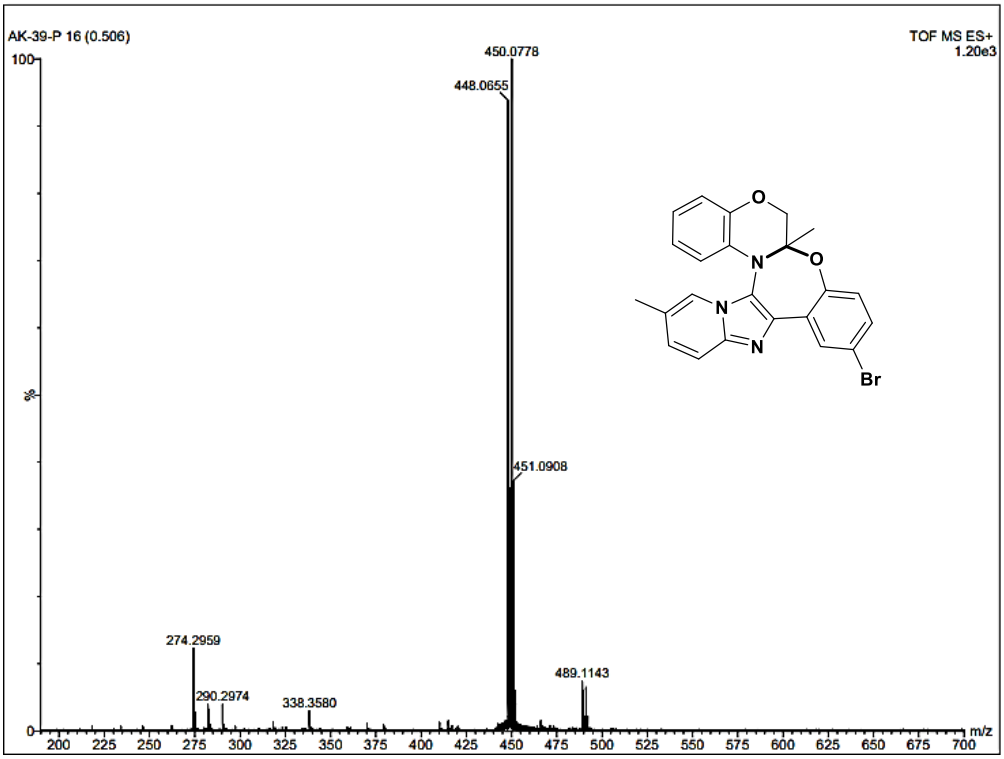
HRMS-ESI (+) of **2o**



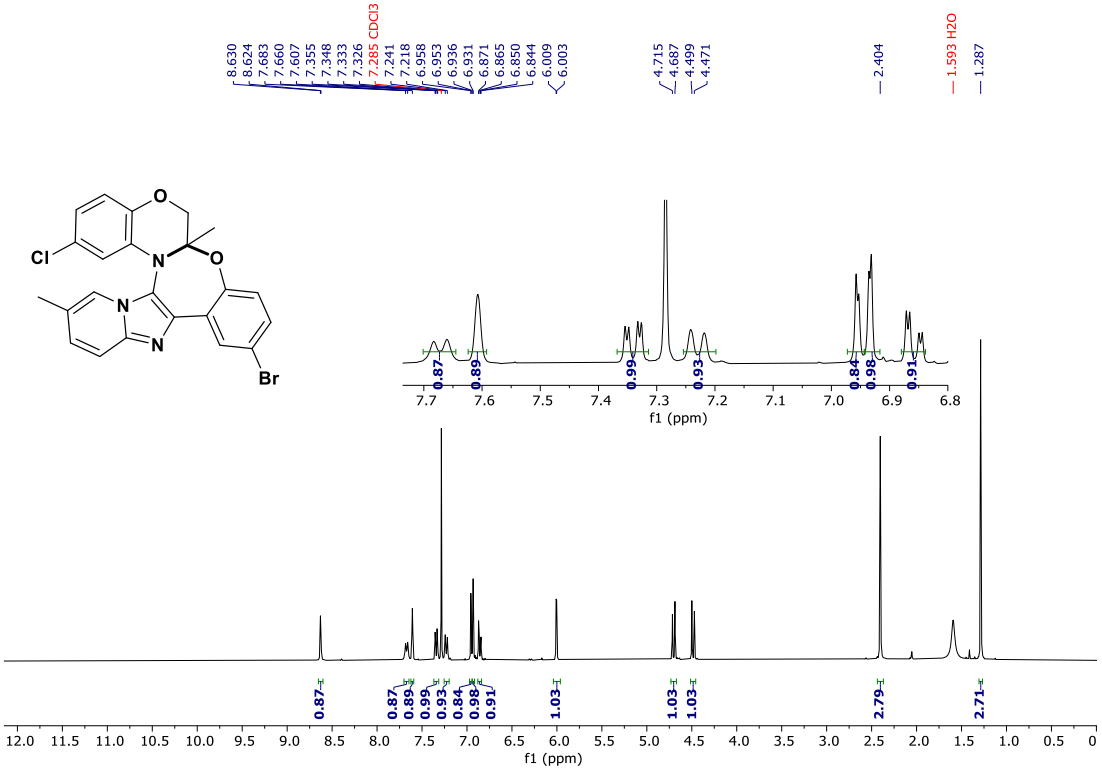
H NMR (400 MHz, $CDCl_3$) of **2p**



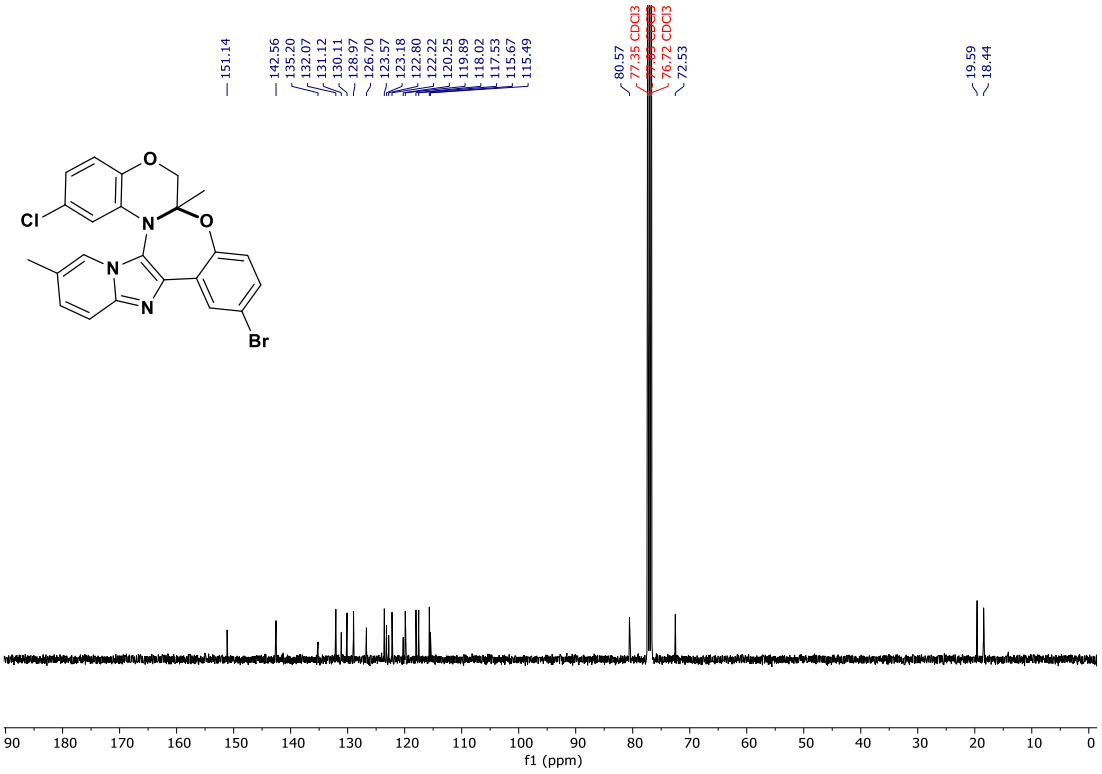
^{13}C NMR (101 MHz, $CDCl_3$) of **2p**



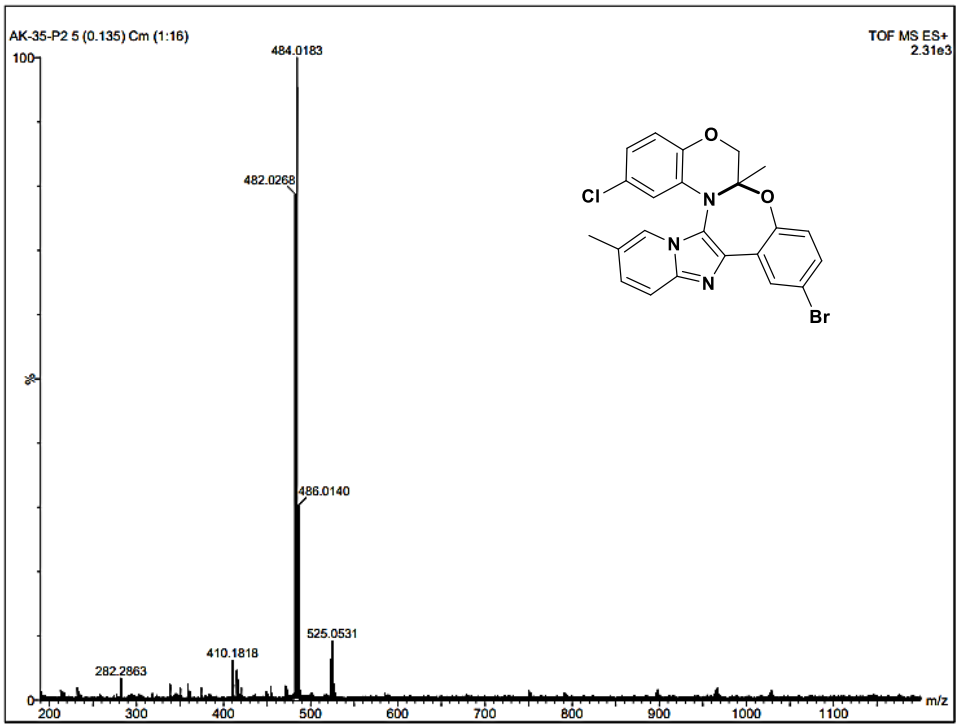
HRMS-ESI (+) of **2p**



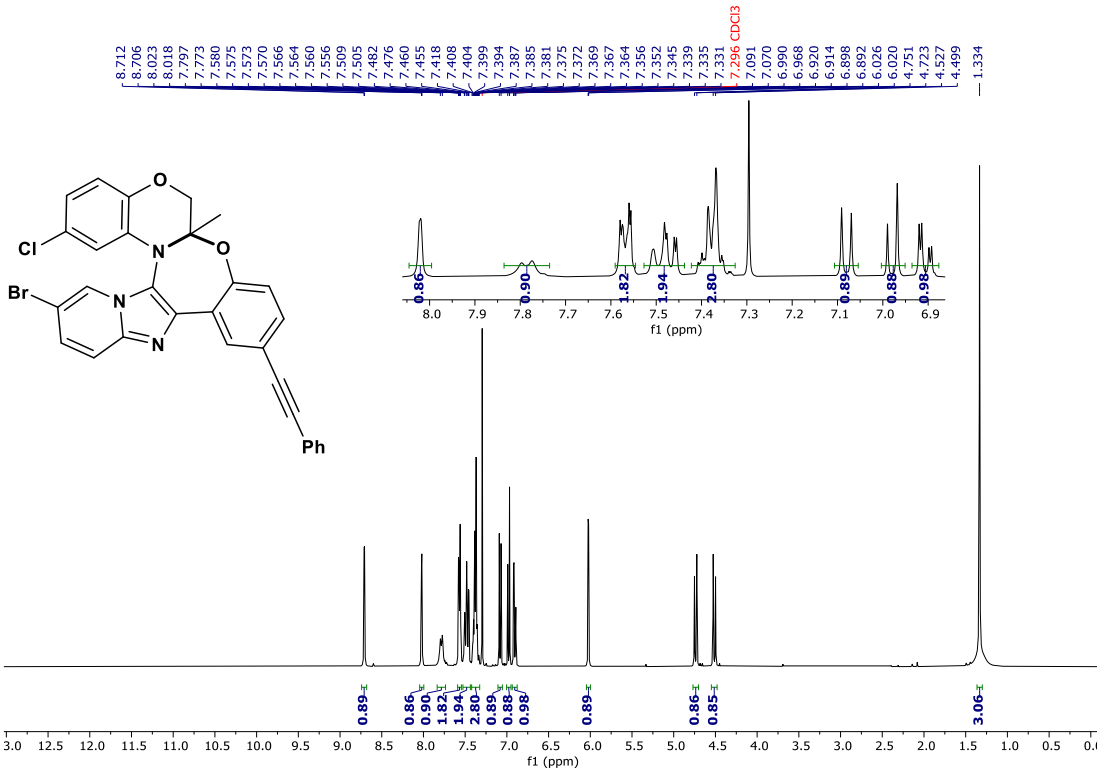
H NMR (400 MHz, $CDCl_3$) of **2q**



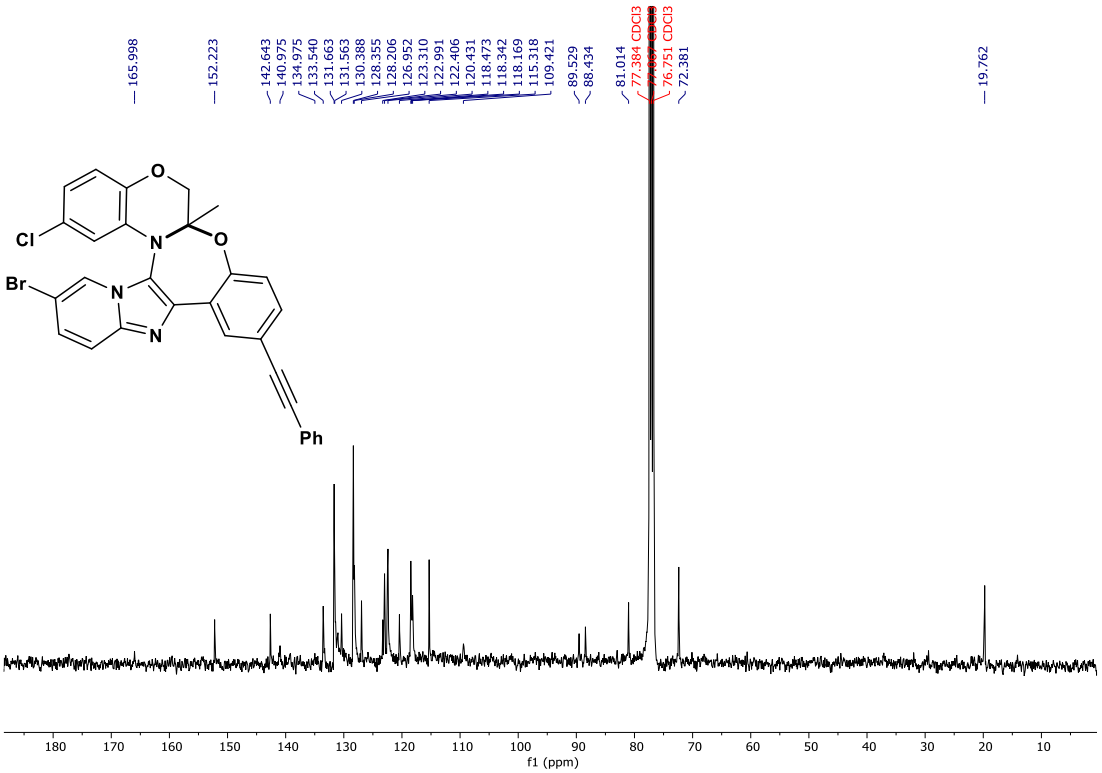
^{13}C NMR (101 MHz, $CDCl_3$) of **2q**



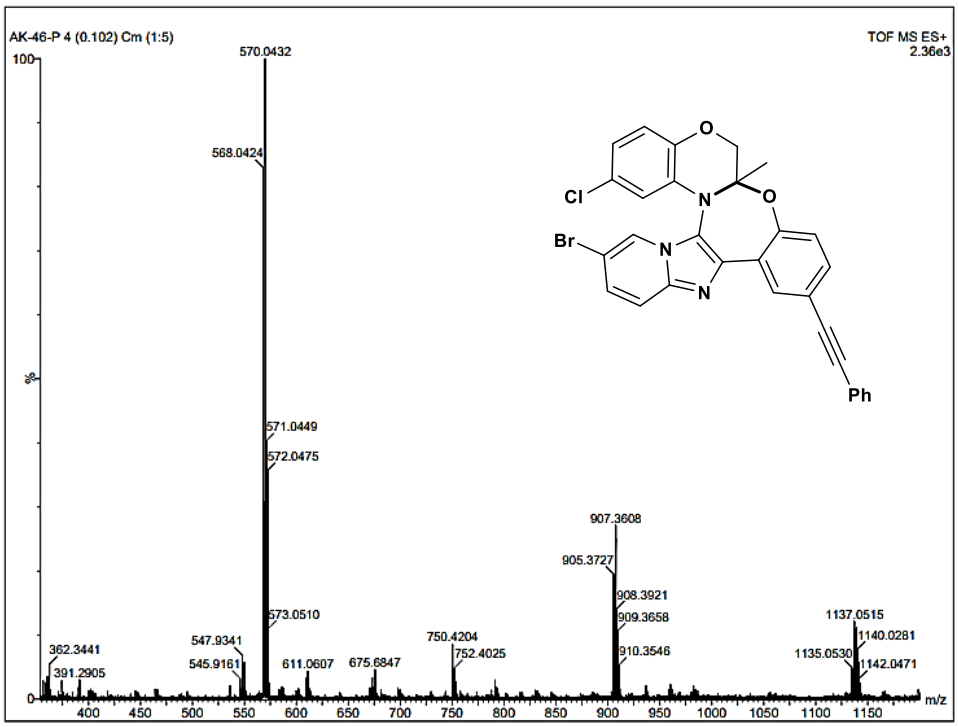
HRMS-ESI (+) of **2q**



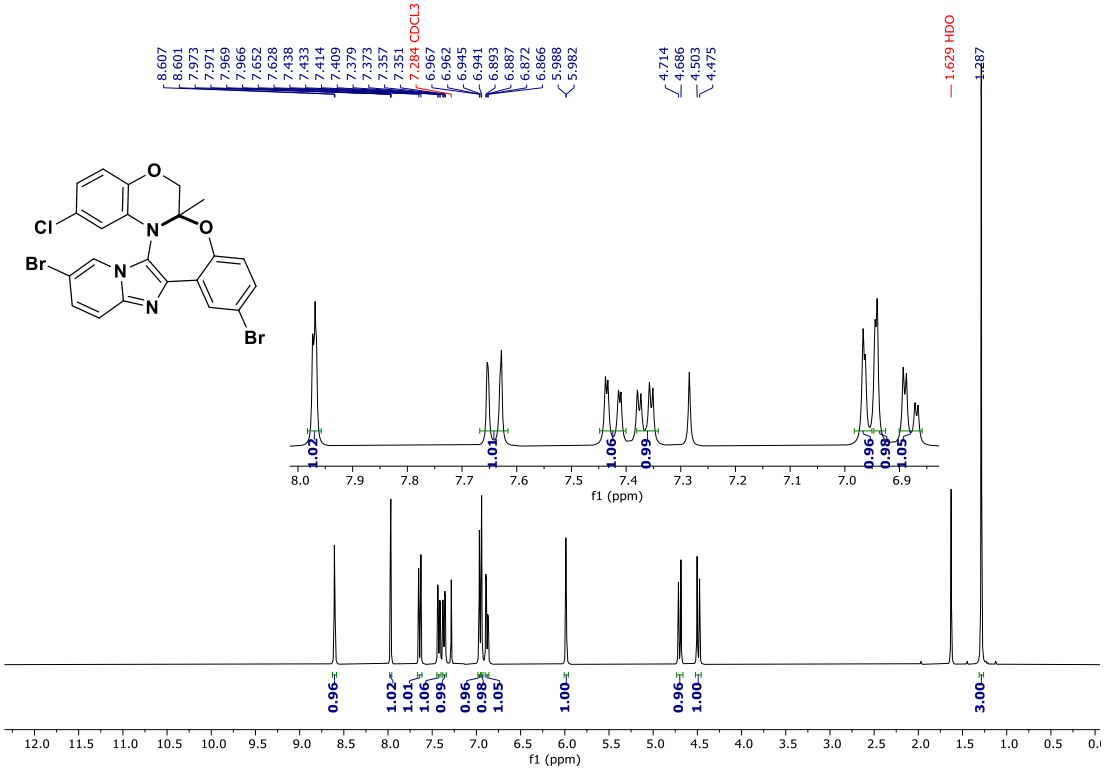
^{1}H NMR (400 MHz, $CDCl_3$) of **2r**



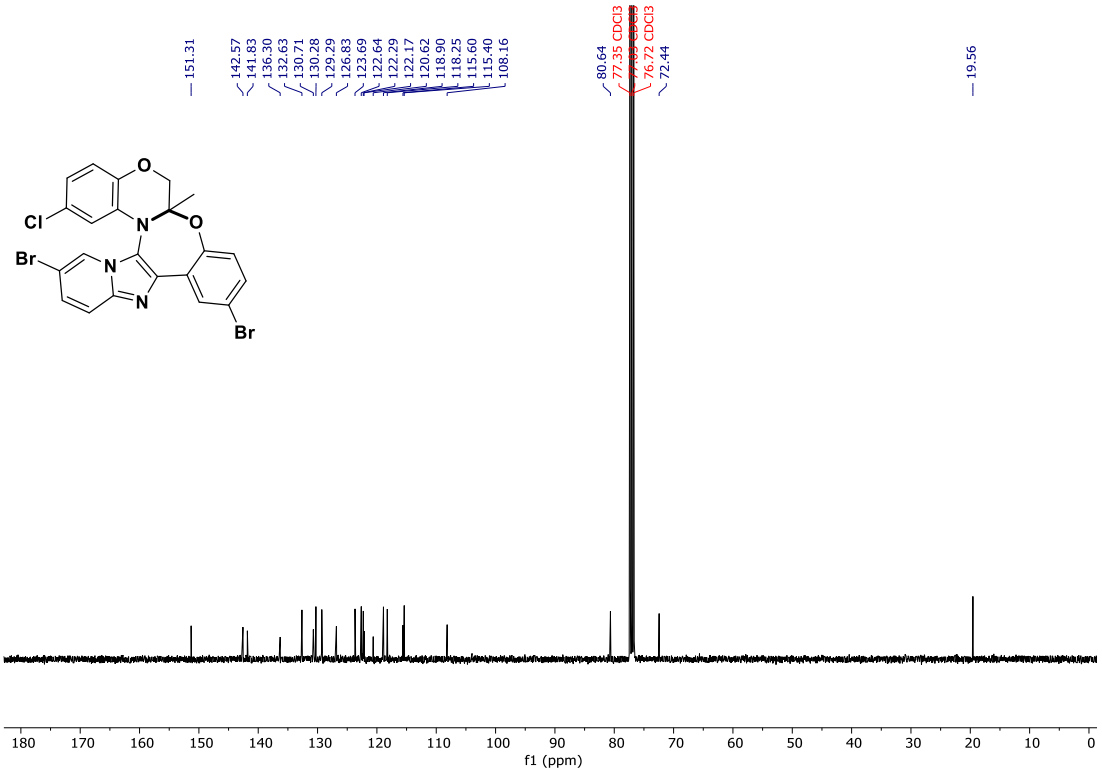
^{13}C NMR (101 MHz, $CDCl_3$) of **2r**



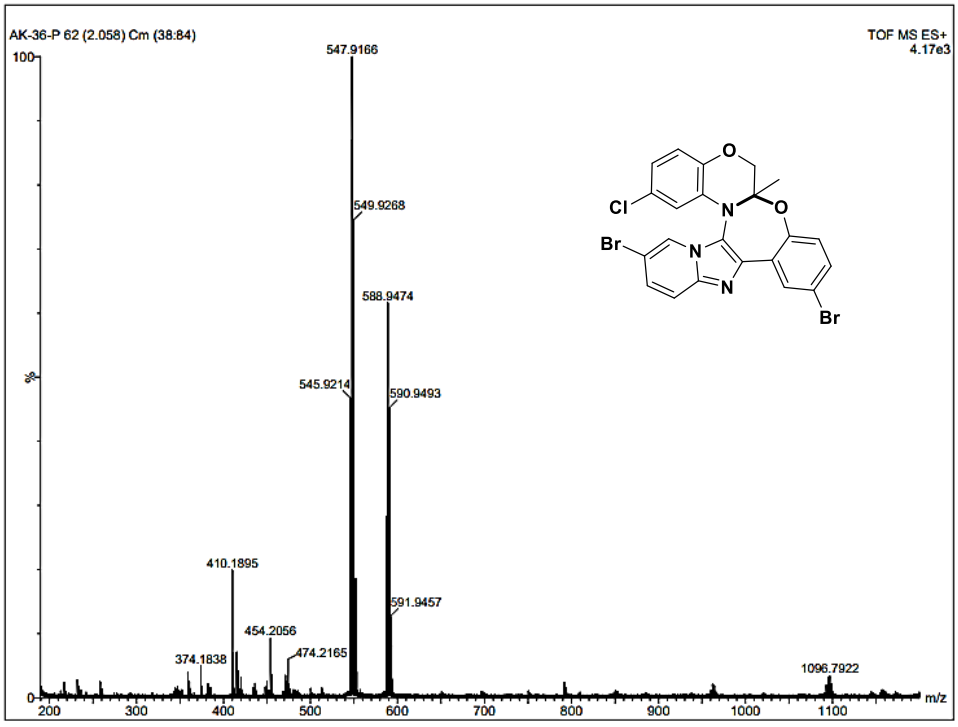
HRMS-ESI (+) of **2r**



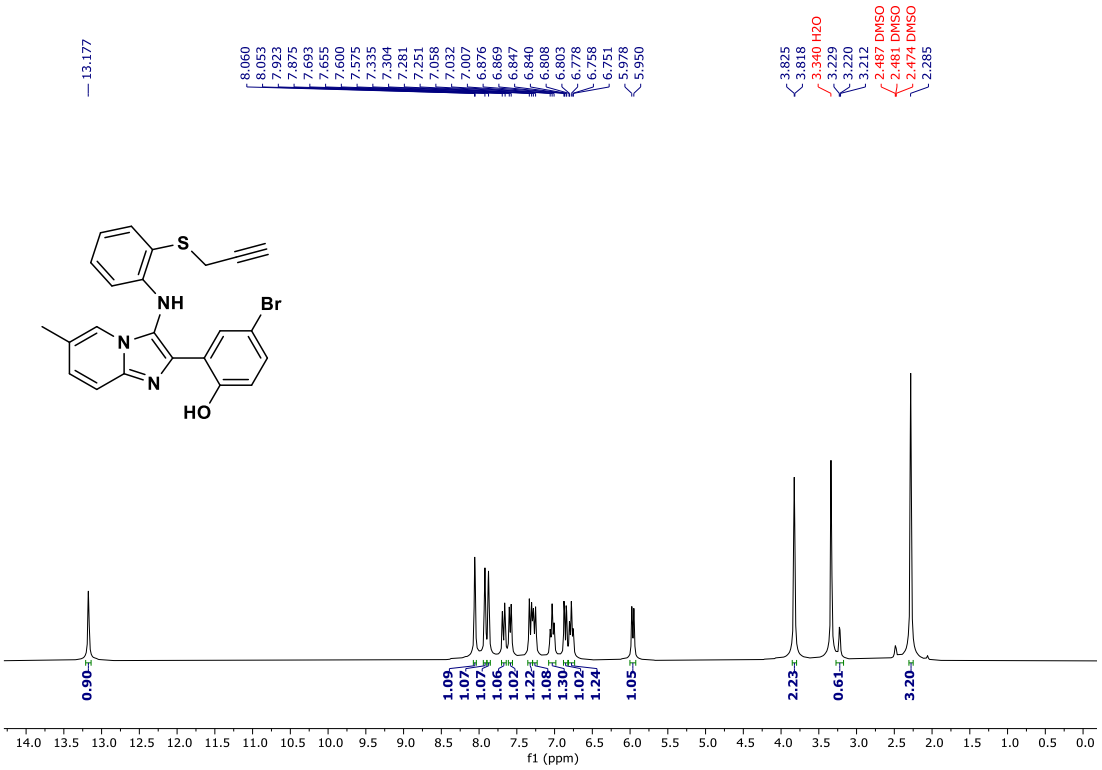
^{1}H NMR (400 MHz, $CDCl_3$) of **2s**



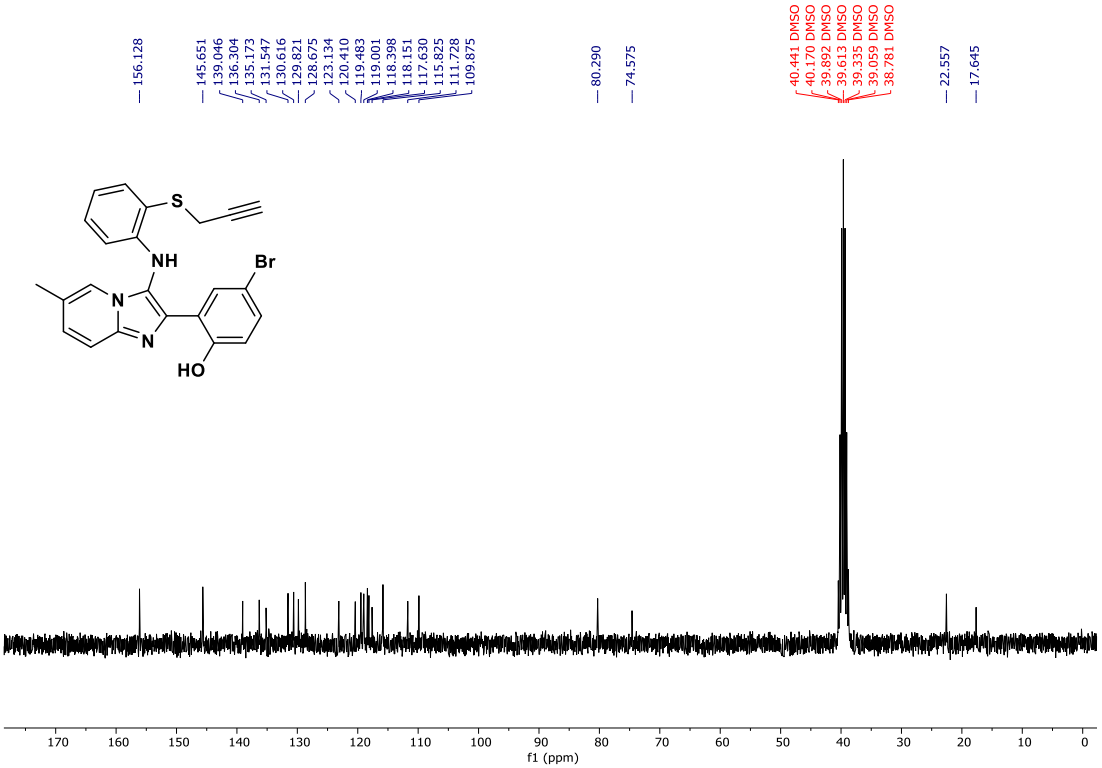
^{13}C NMR (101 MHz, $CDCl_3$) of **2s**



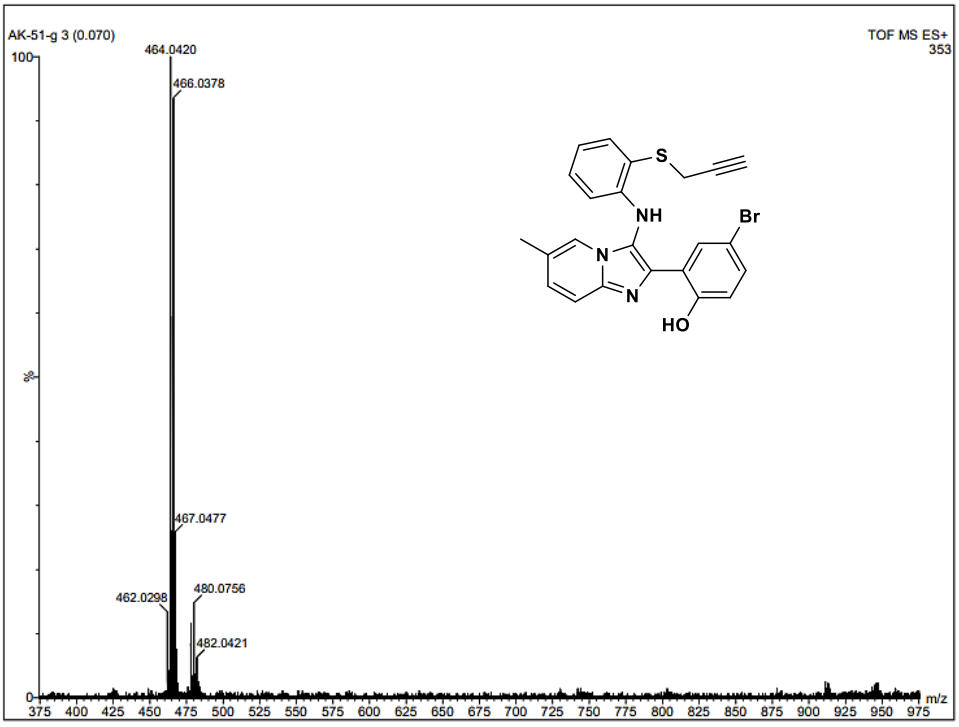
HRMS-ESI (+) of **2s**



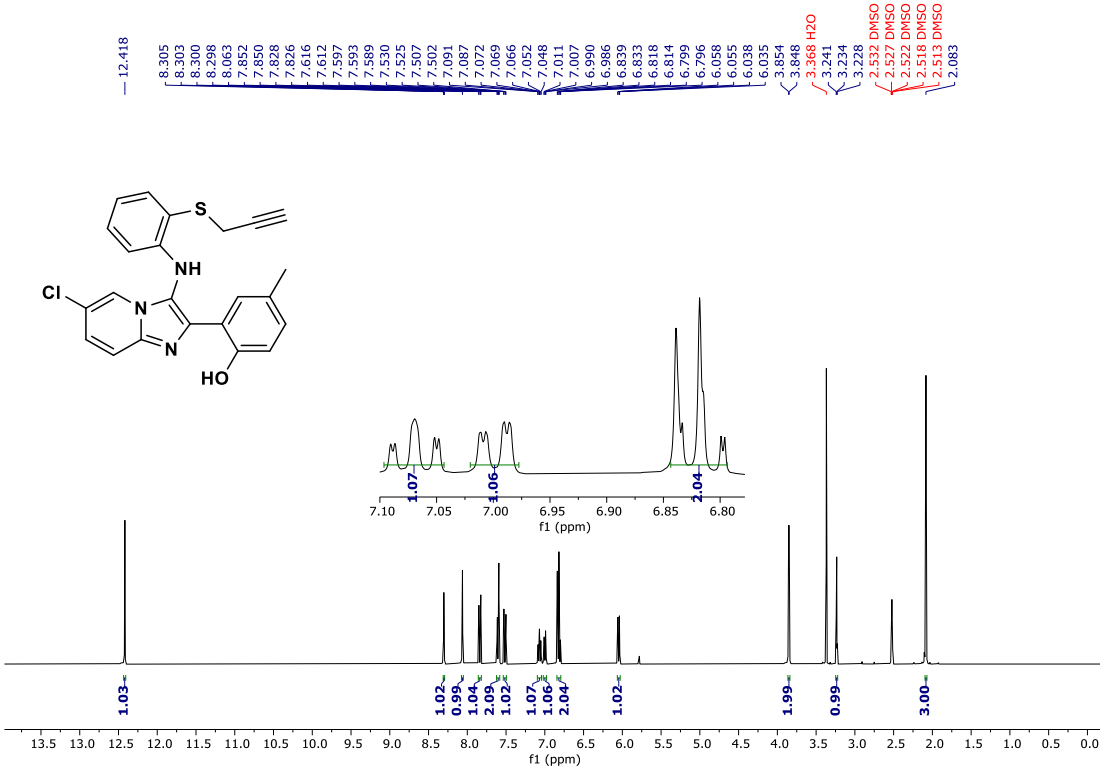
^{1}H NMR (300 MHz, DMSO-d_6) of **3a**



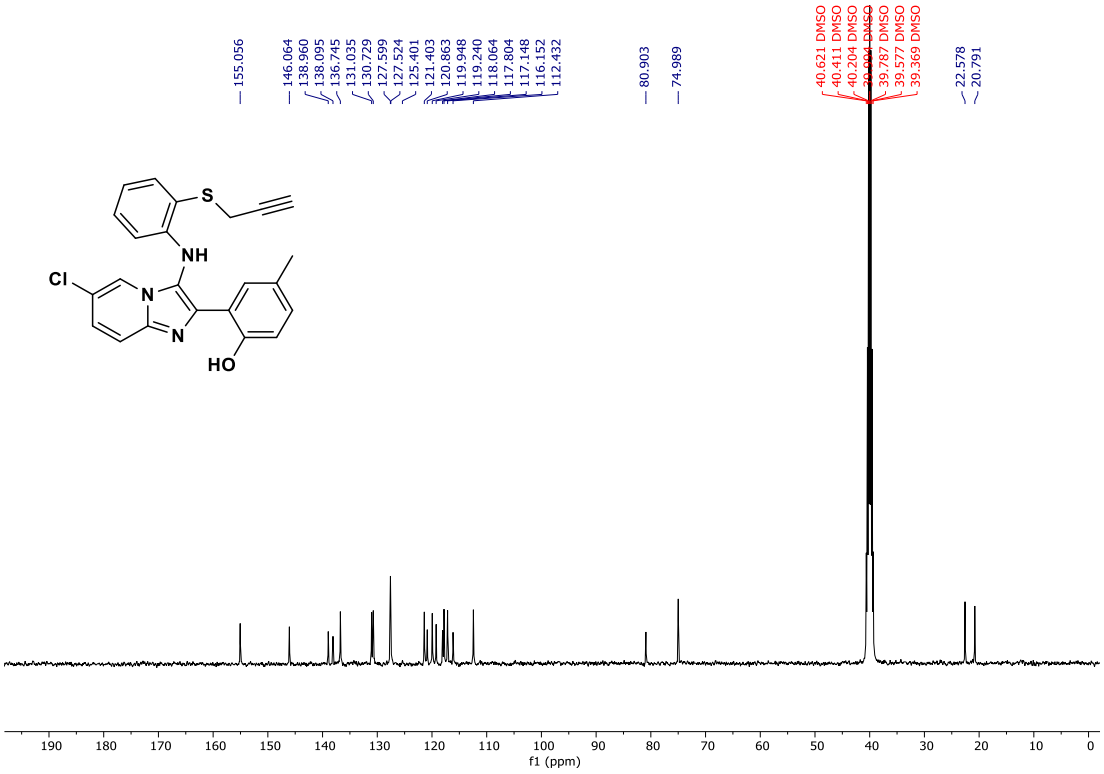
^{13}C NMR (75 MHz, DMSO-d_6) of **3a**



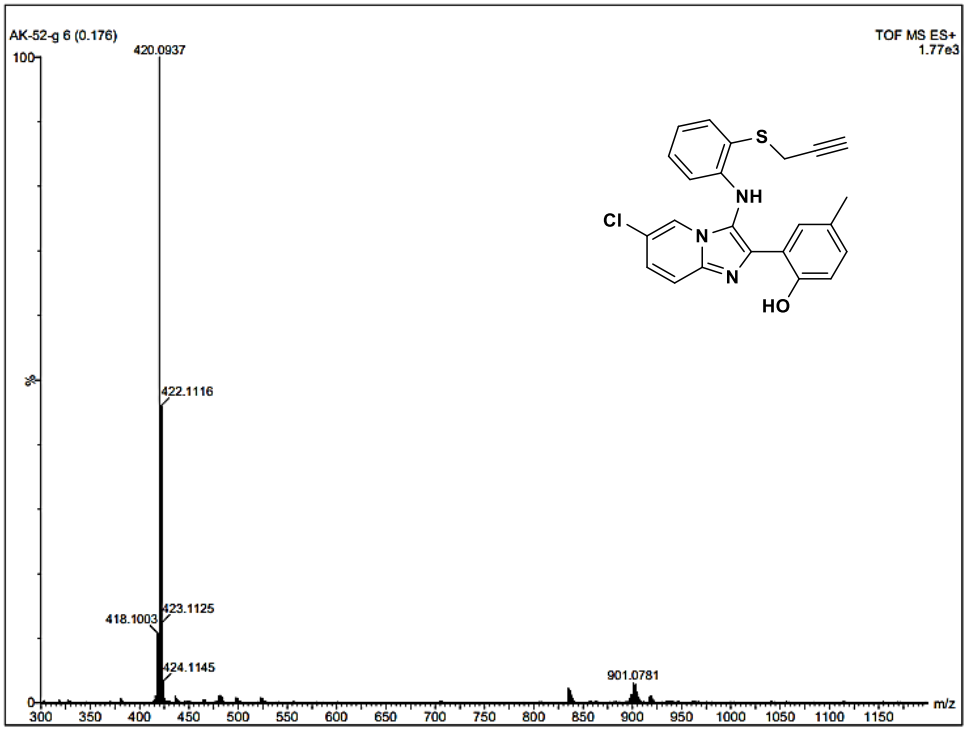
HRMS-ESI (+) of **3a**



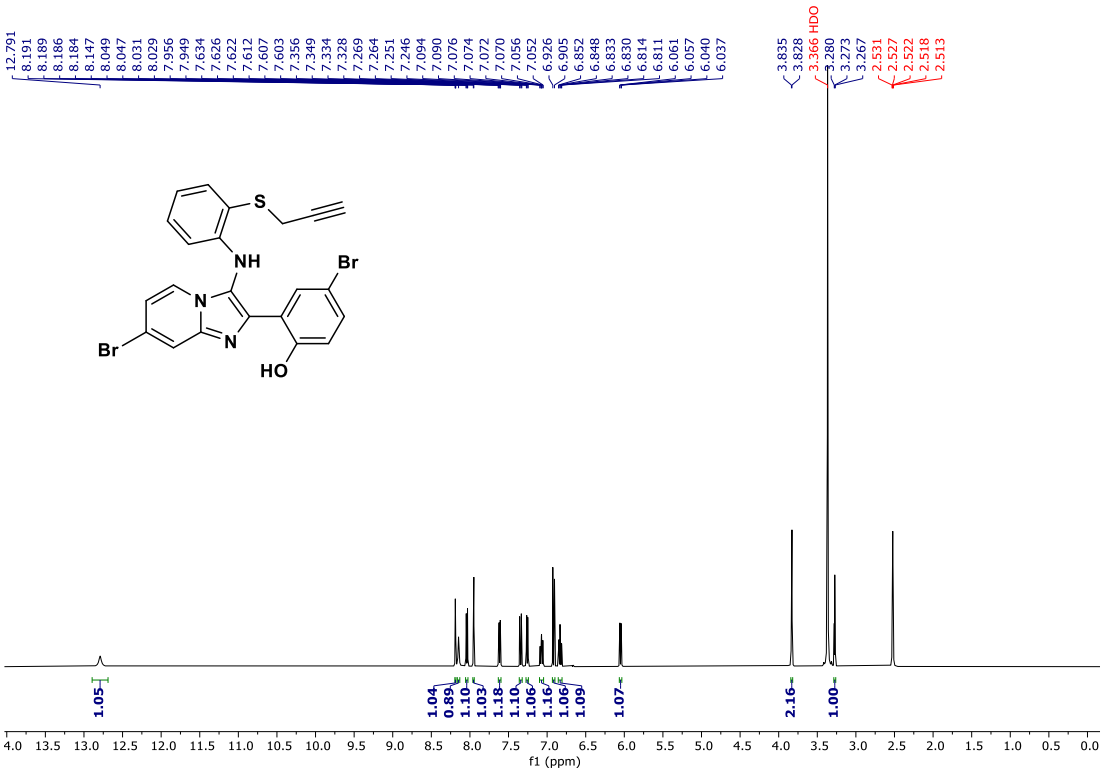
^{1}H NMR (400 MHz, DMSO-d_6) of **3b**



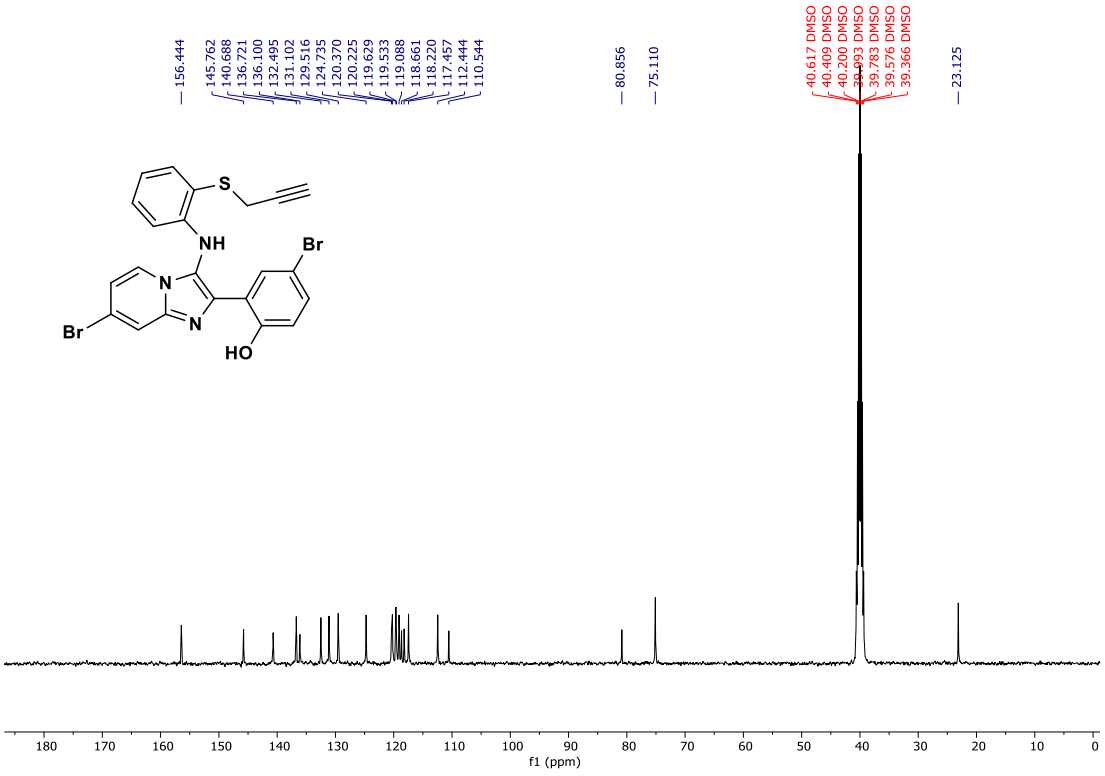
^{13}C NMR (101 MHz, DMSO-d_6) of **3b**



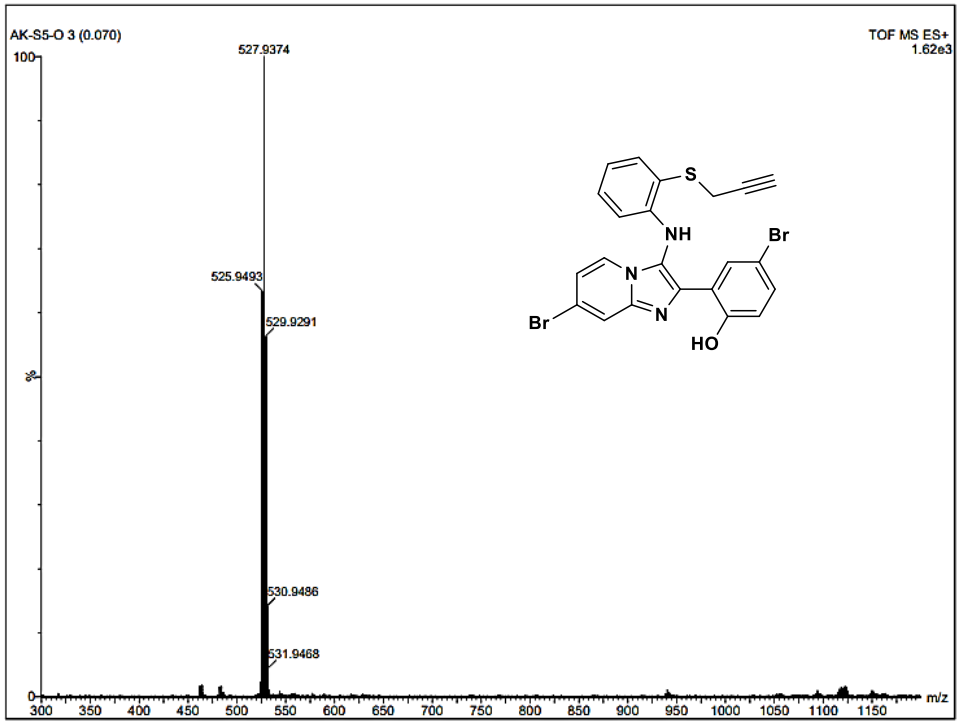
HRMS-ESI (+) of **3b**



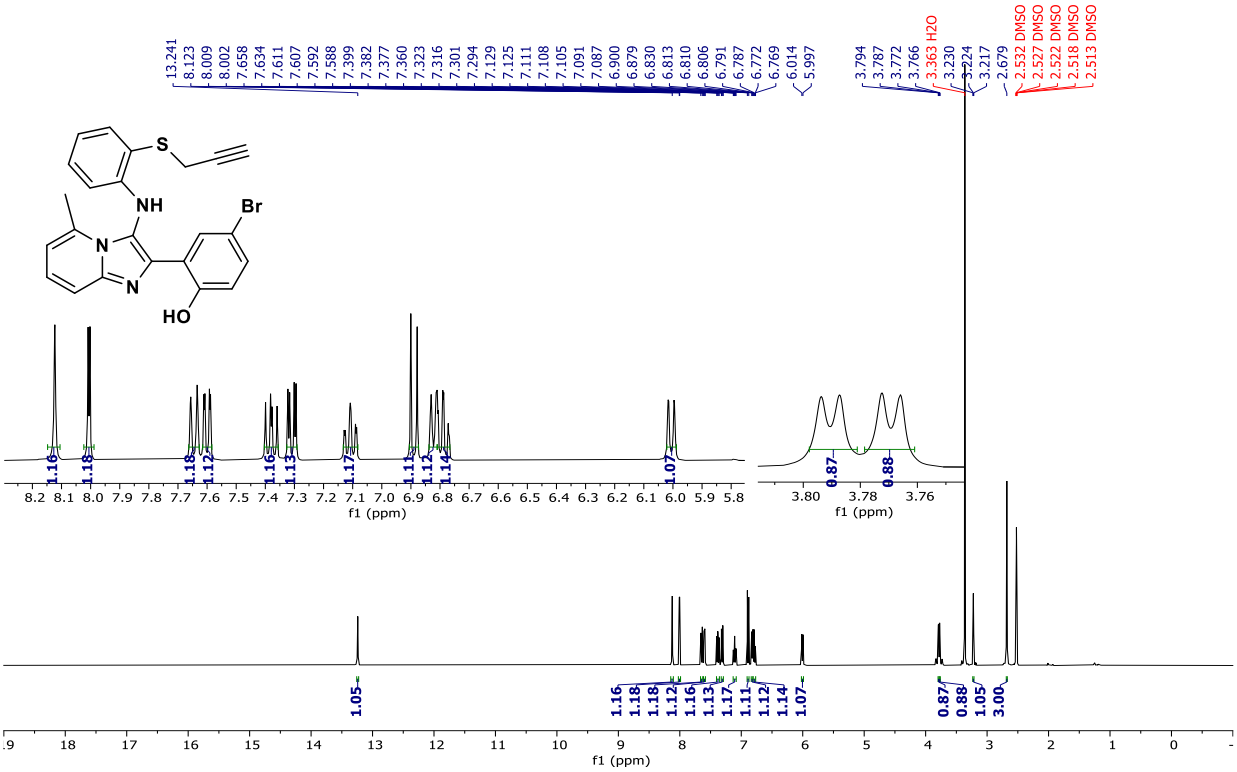
^{1}H NMR (400 MHz, DMSO-d_6) of **3c**



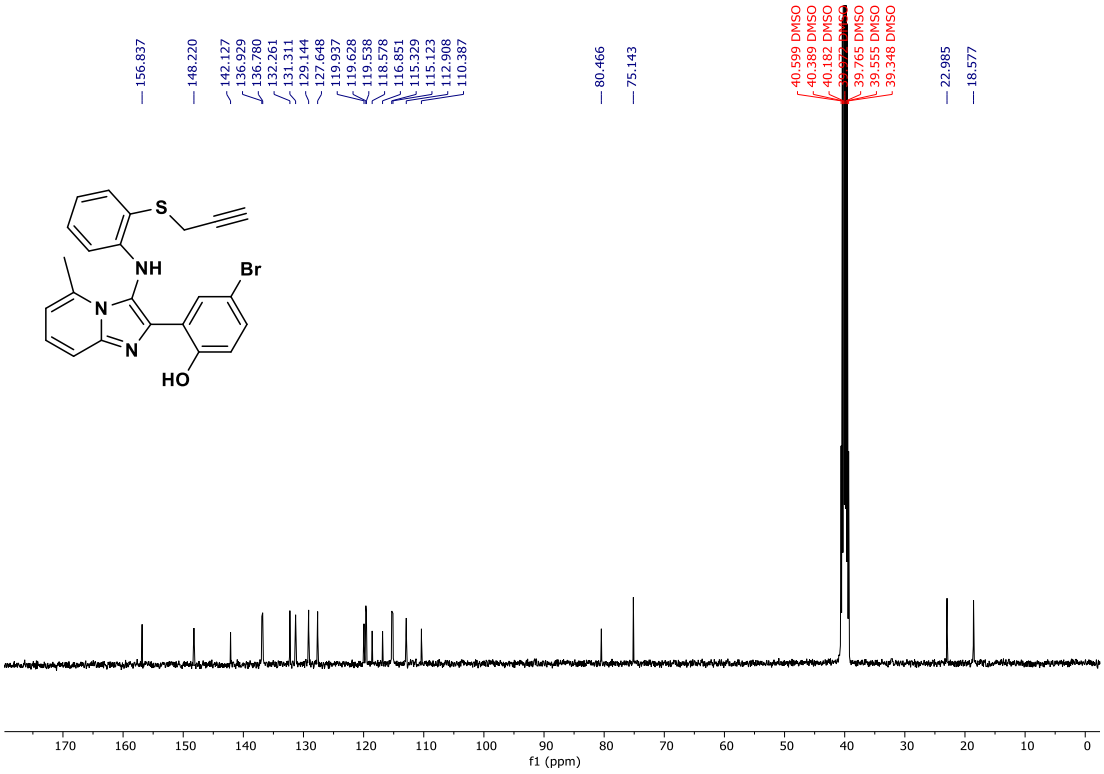
^{13}C NMR (101 MHz, DMSO-d_6) of **3c**



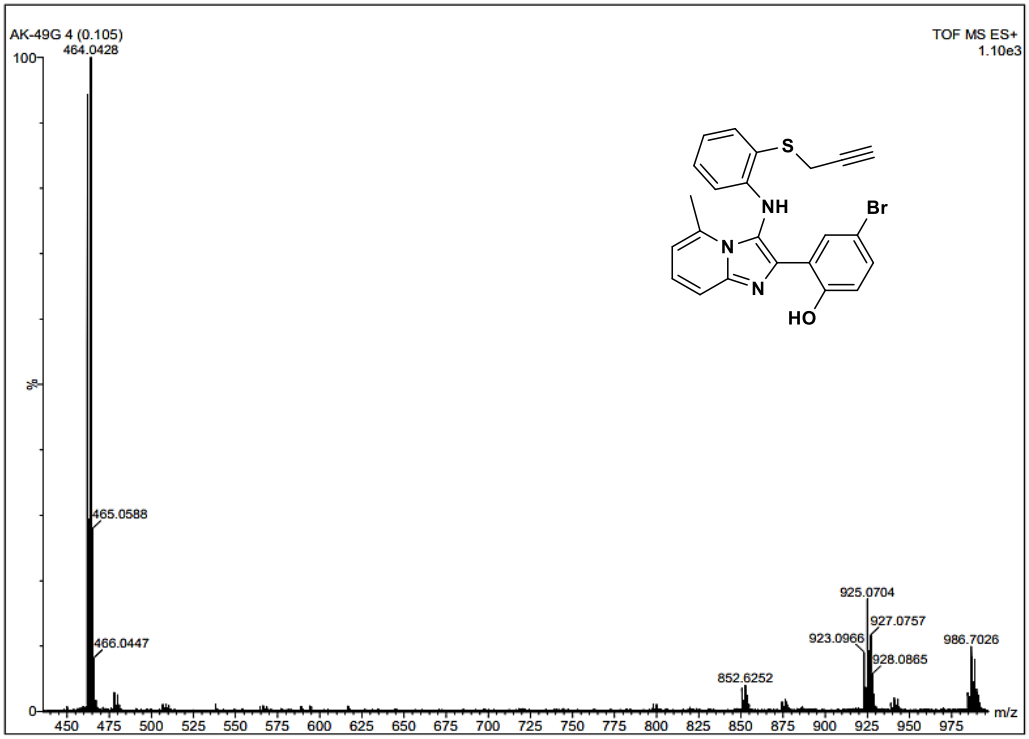
HRMS-ESI (+) of **3c**



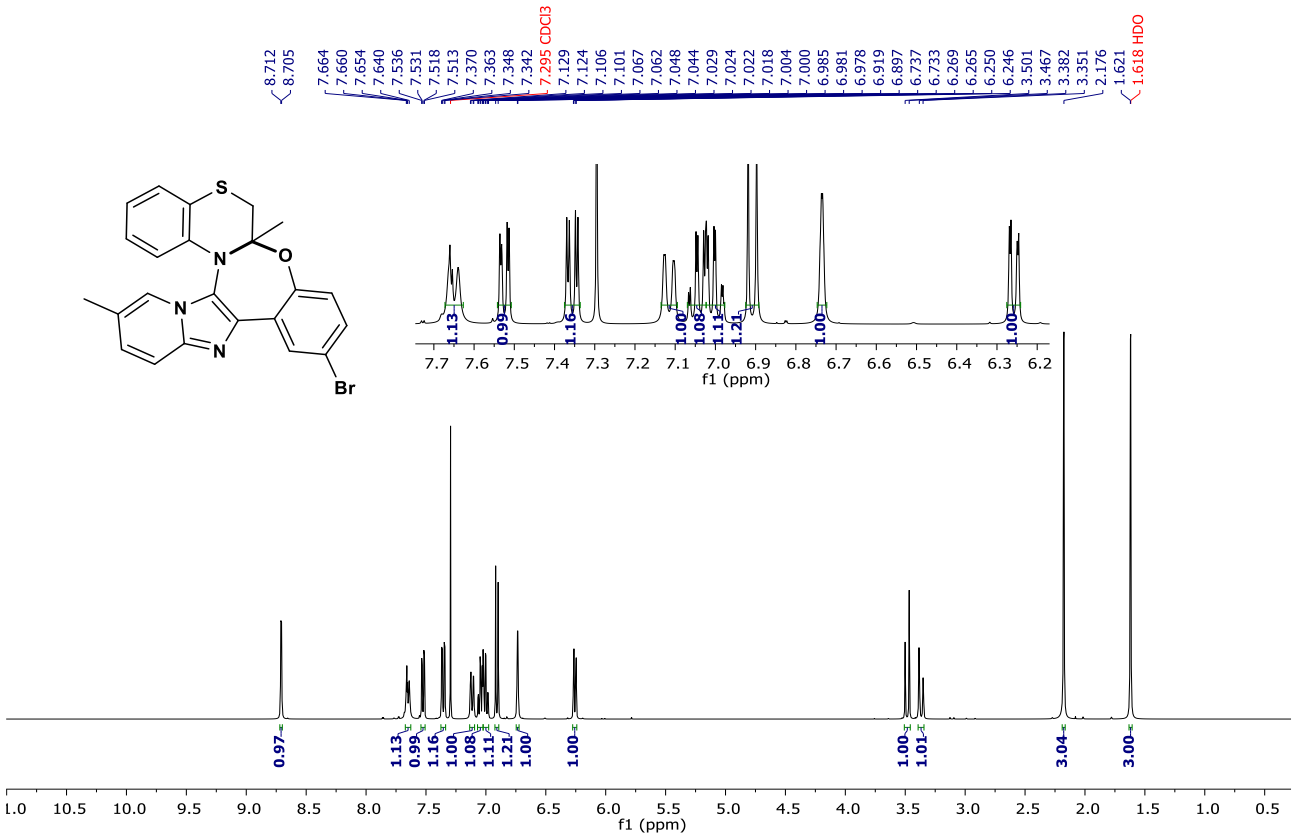
^{1}H NMR (400 MHz, DMSO-d_6) of **3d**



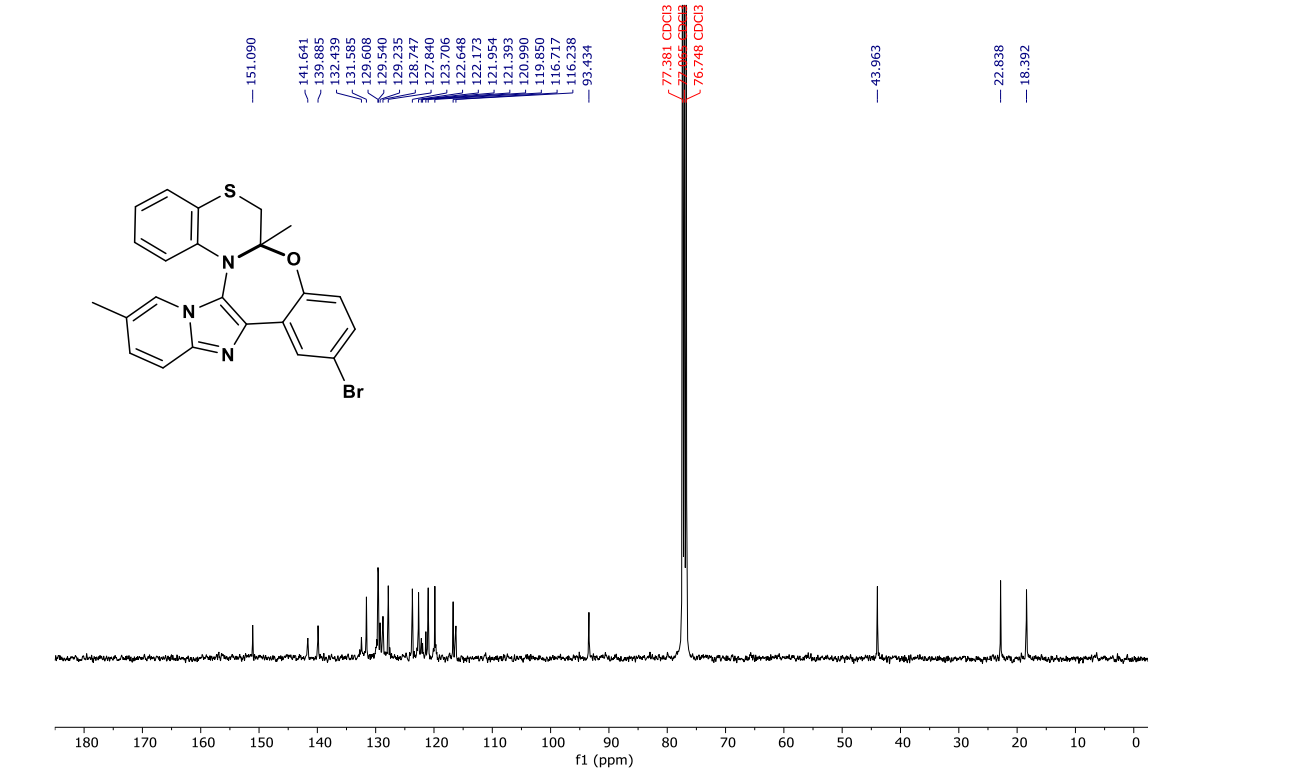
^{13}C NMR (101 MHz, DMSO-d_6) of **3d**



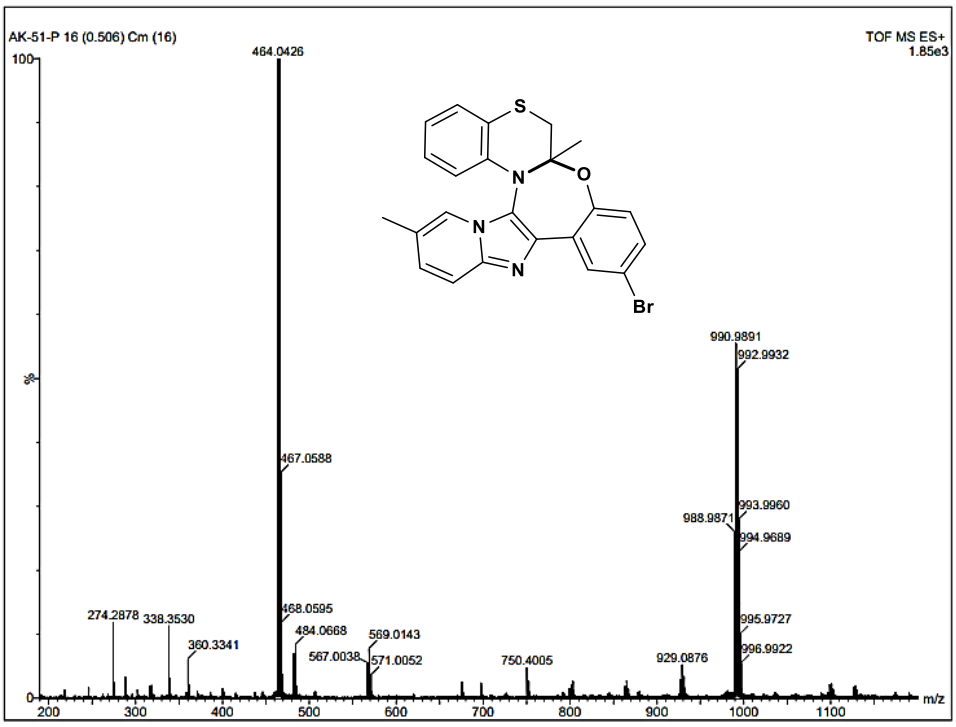
HRMS-ESI (+) of **3d**



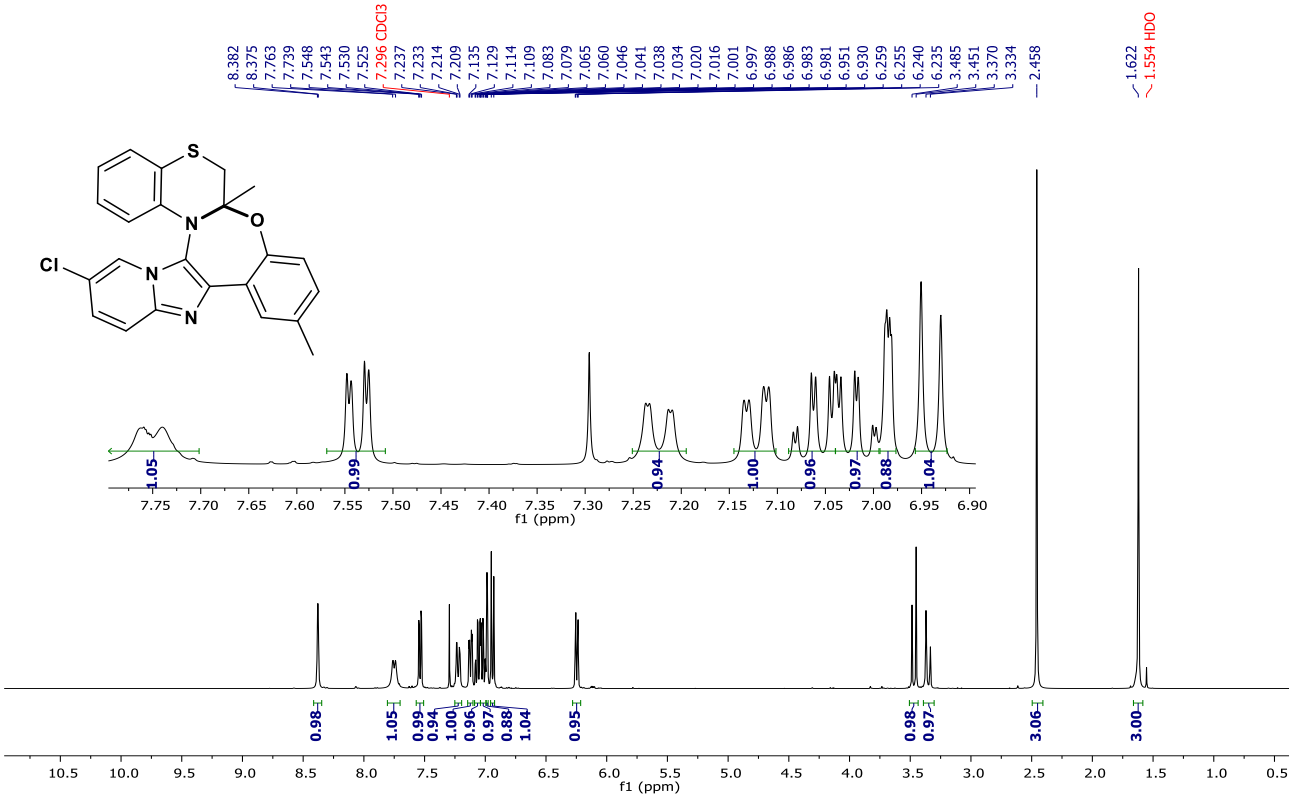
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



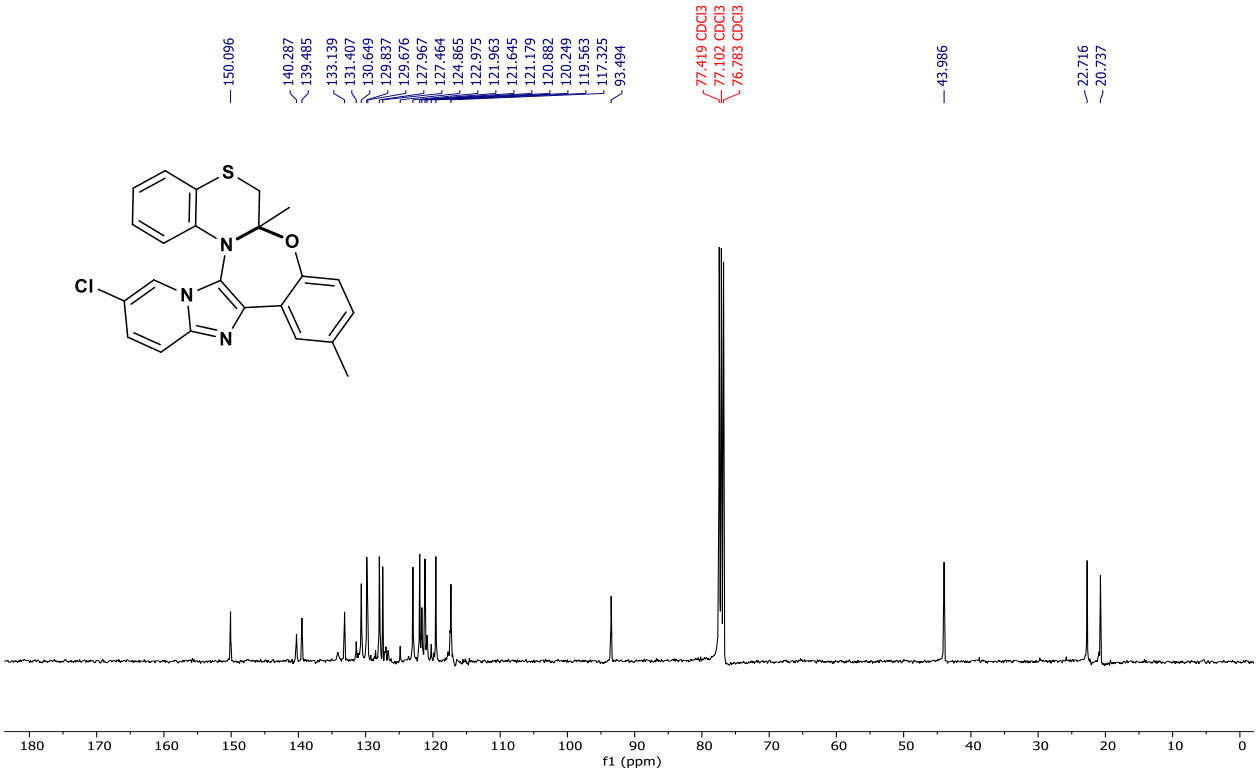
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



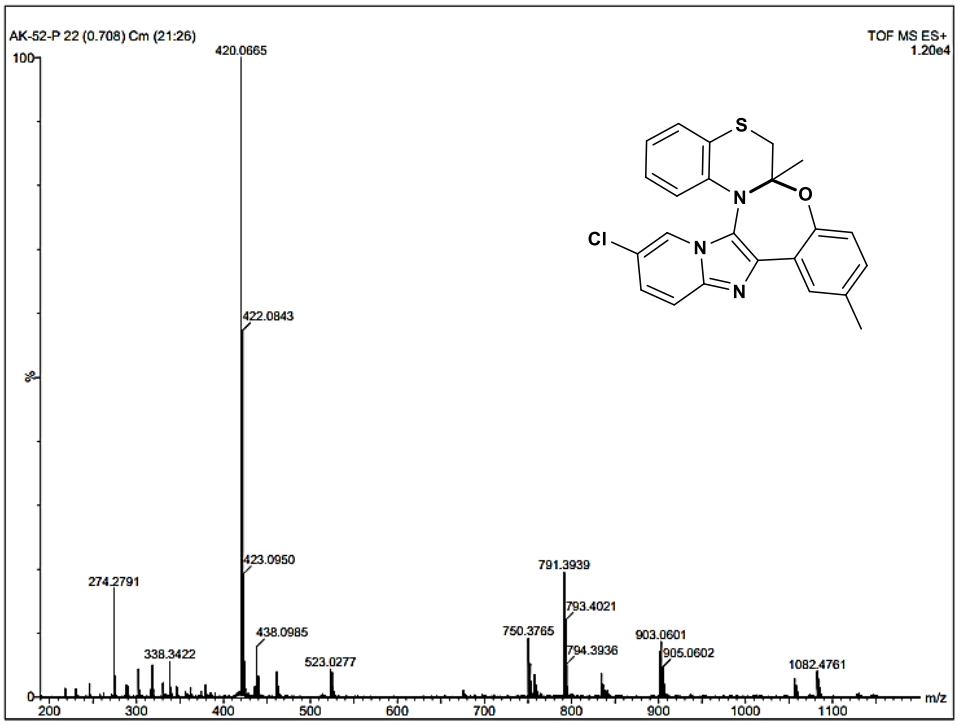
HRMS-ESI (+) of **4a**



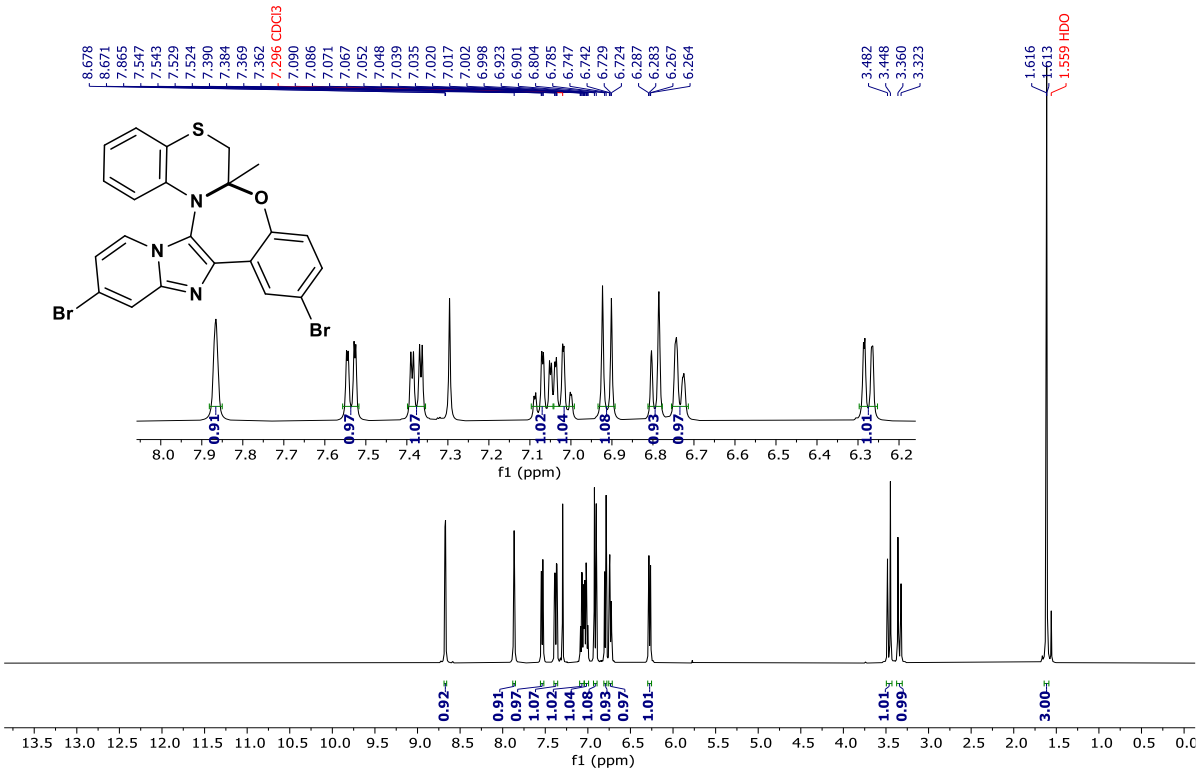
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



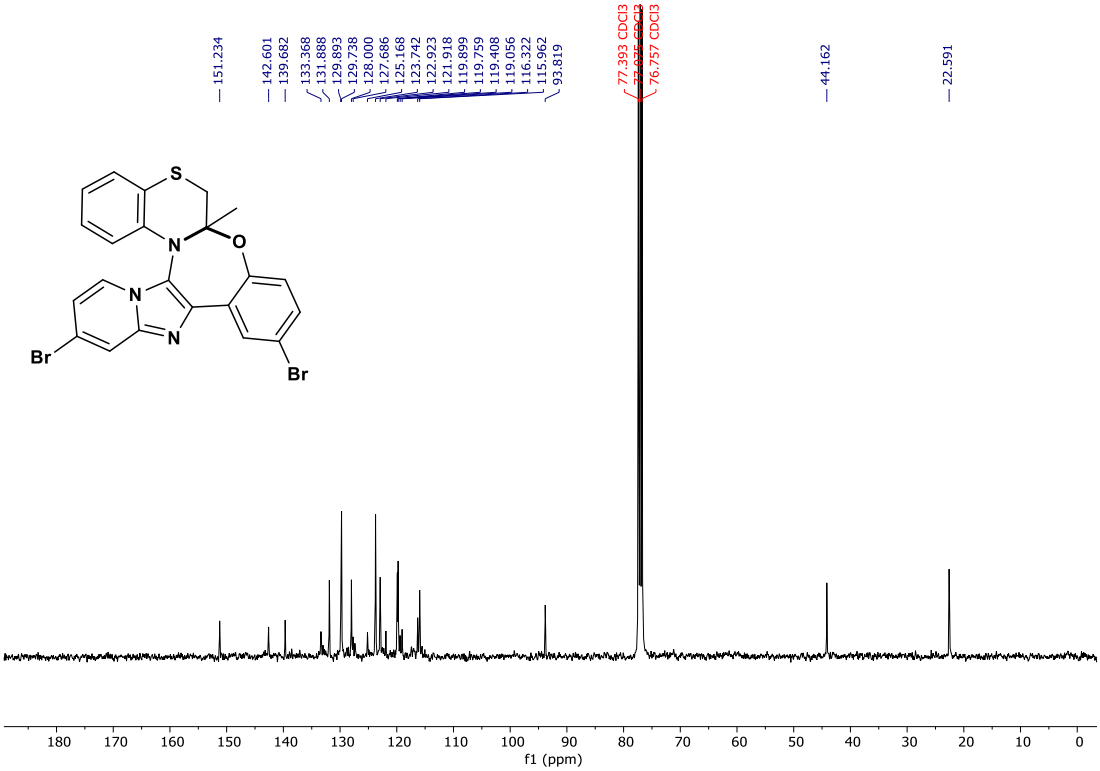
^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



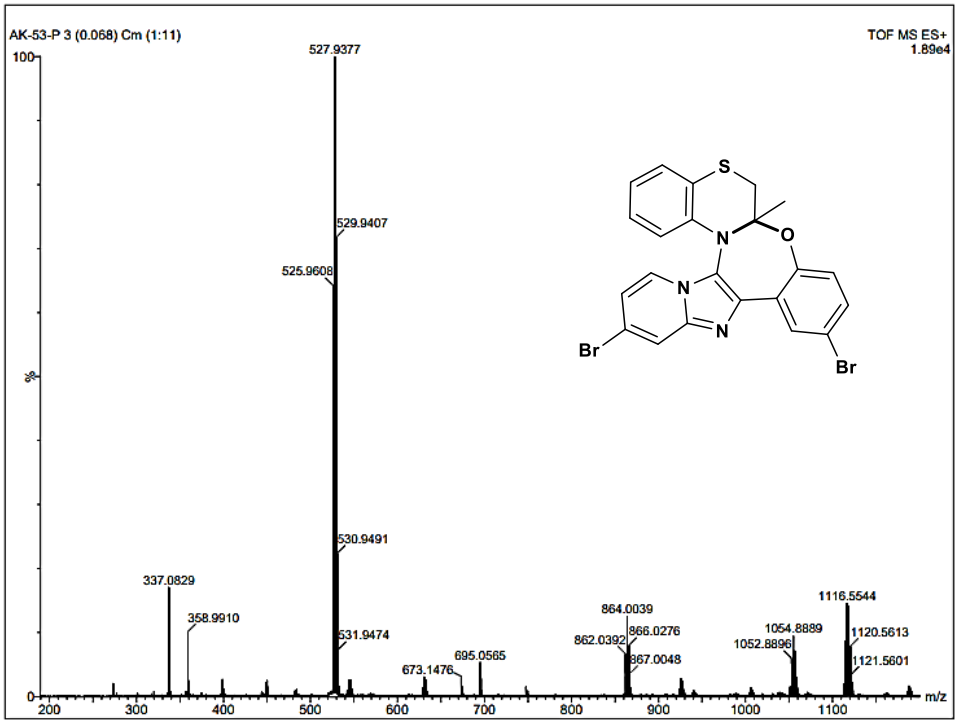
HRMS-ESI (+) of **4b**



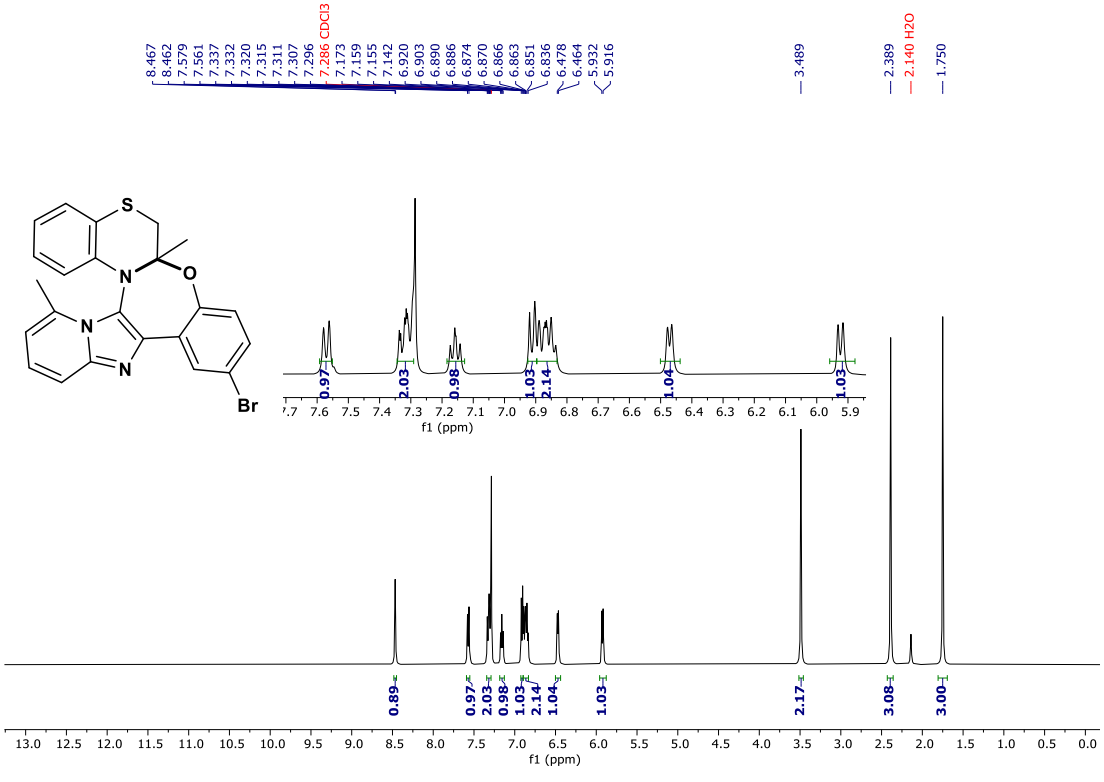
H NMR (400 MHz, $CDCl_3$) of **4c**



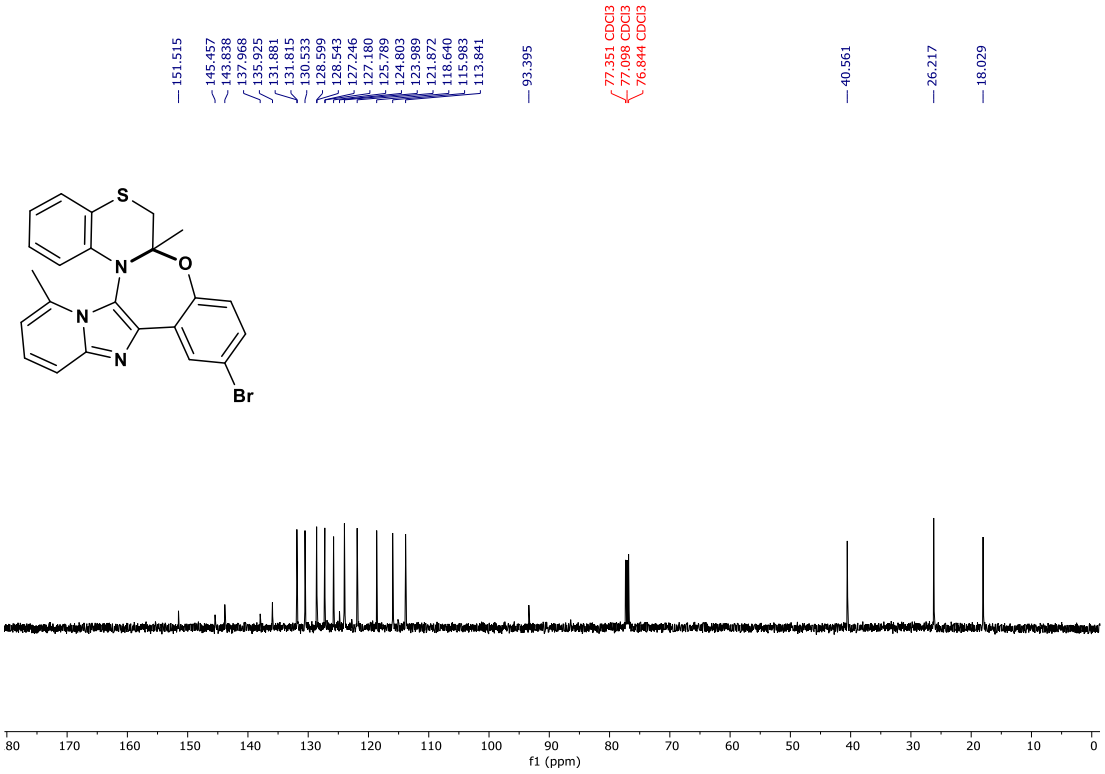
^{13}C NMR (101 MHz, $CDCl_3$) of **4c**



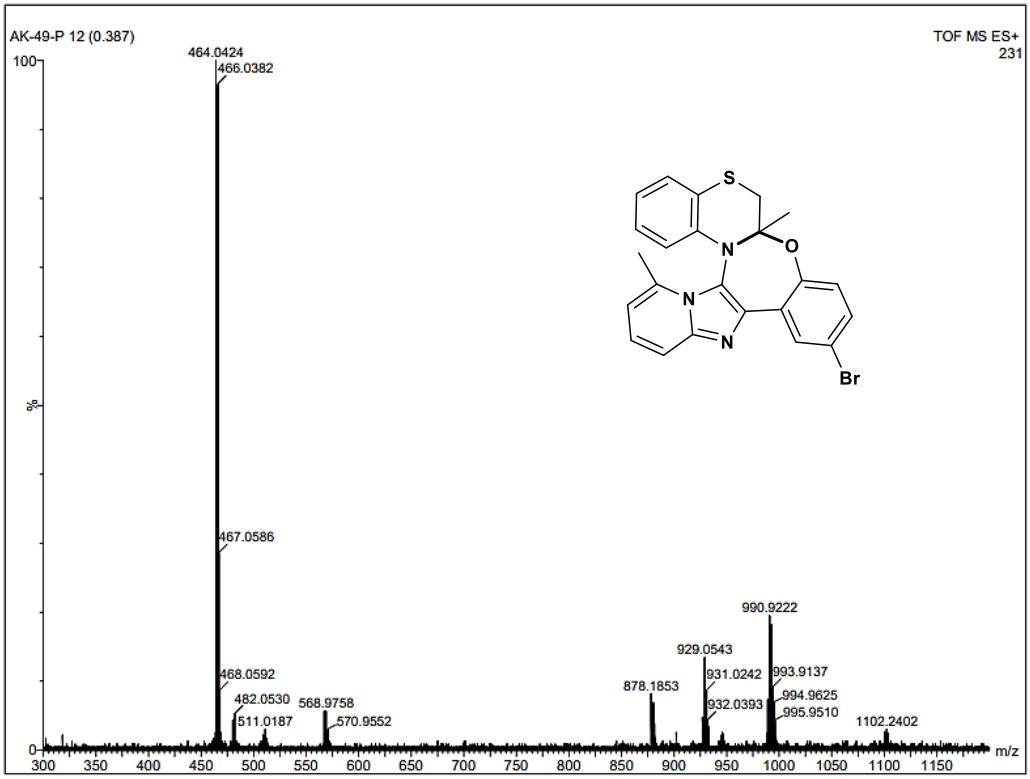
HRMS-ESI (+) of **4c**



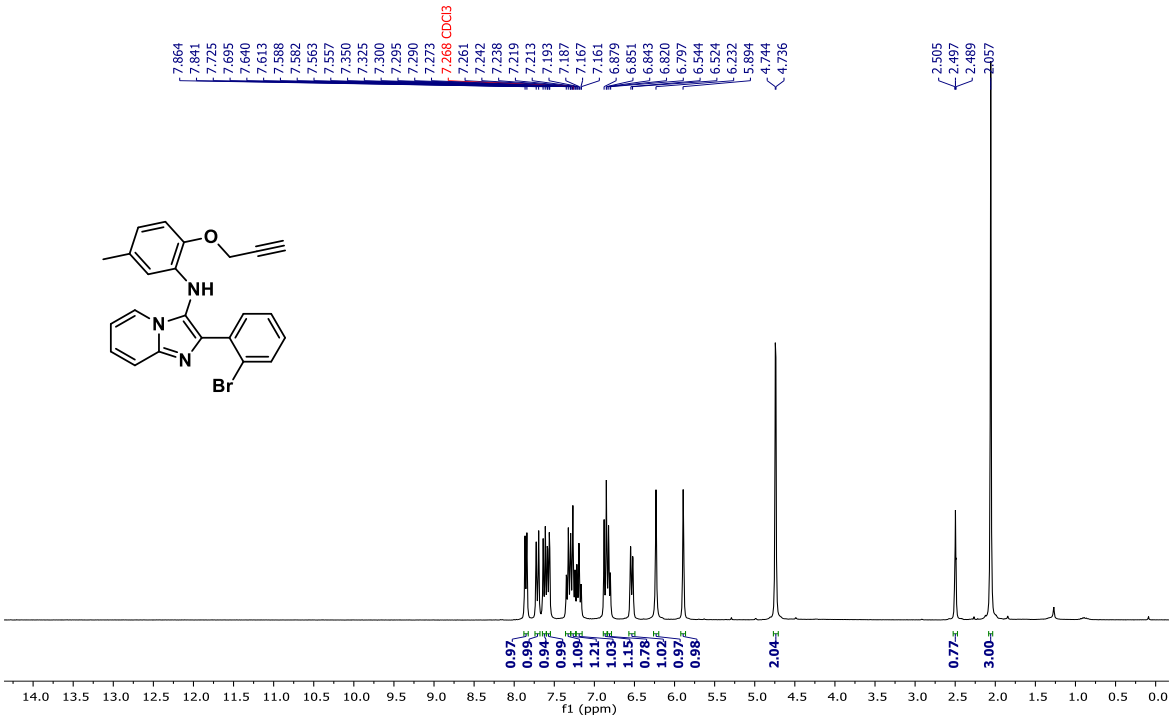
^{1}H NMR (500 MHz, $CDCl_3$) of **4d**



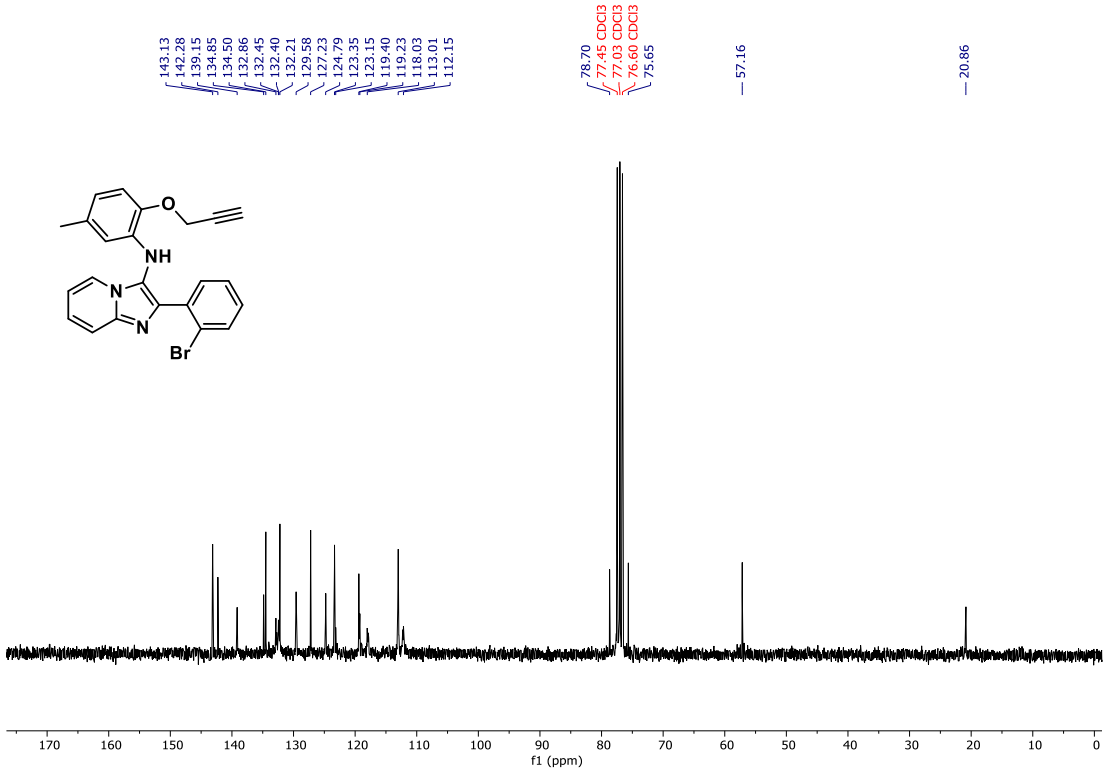
^{13}C NMR (126 MHz, $CDCl_3$) of **4d**



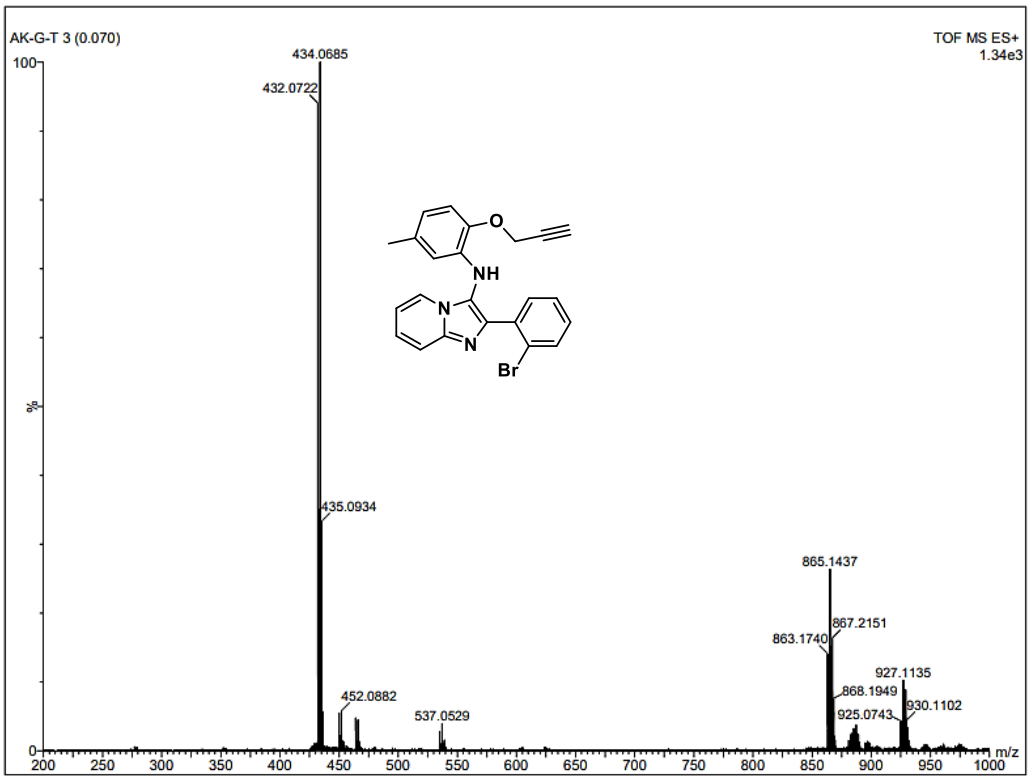
HRMS-ESI (+) of **4d**



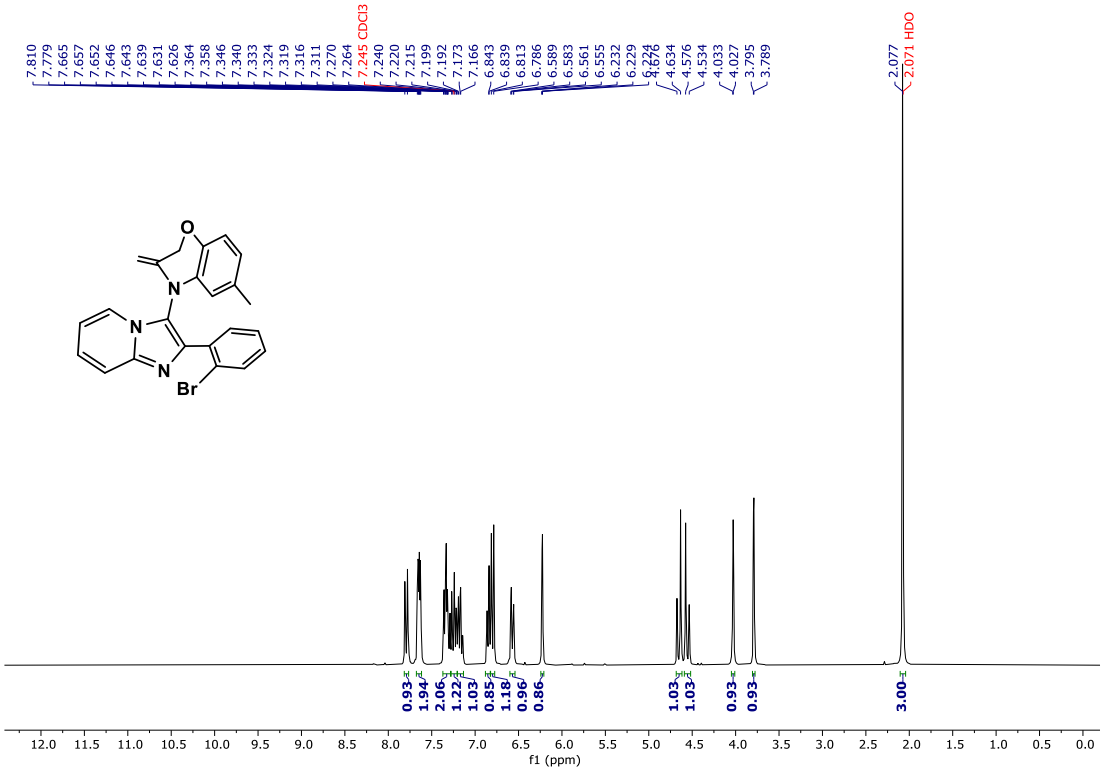
^{1}H NMR (300 MHz, $CDCl_3$) of **5**



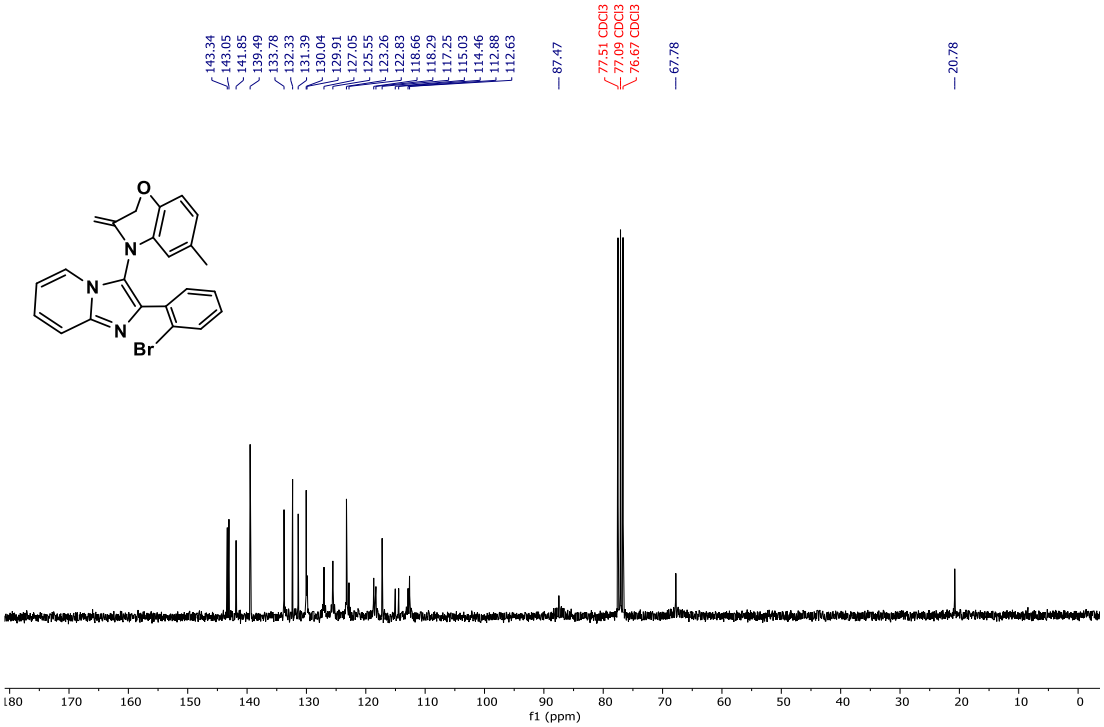
^{13}C NMR (75 MHz, $CDCl_3$) of **5**


AK-G-T 3 (0.070)
TOF MS ES+
1.34e3
100
%
0
434.0685
432.0722
435.0934
452.0882
537.0529
865.1437
867.2151
863.1740
927.1135
868.1949
930.1102
925.0743
NH
N
N
O
Br
200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
m/z

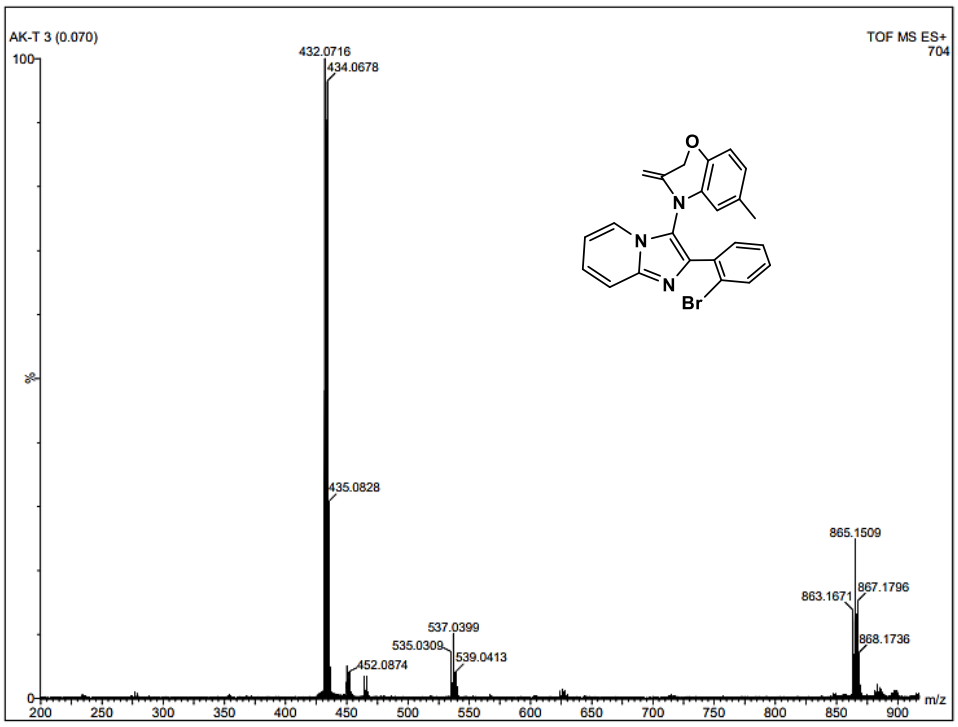
HRMS-ESI (+) of **5**


7.810 7.779 7.665 7.657 7.652 7.646 7.643 7.639 7.631 7.626 7.364 7.358 7.346 7.340 7.333 7.324 7.319 7.316 7.311 7.270 7.264 7.245 CDCl3 7.240 7.220 7.215 7.199 7.192 7.173 7.166 6.843 6.839 6.813 6.786 6.589 6.583 6.561 6.555 6.232 6.229 4.634 4.576 4.534 4.033 4.027 3.795 3.789
2.077 2.071 HDO
O
N
N
N
Br
0.93 1.94 2.06 1.22 1.03 0.85 1.18 0.96 0.86 1.03 1.03 0.93 0.93 3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

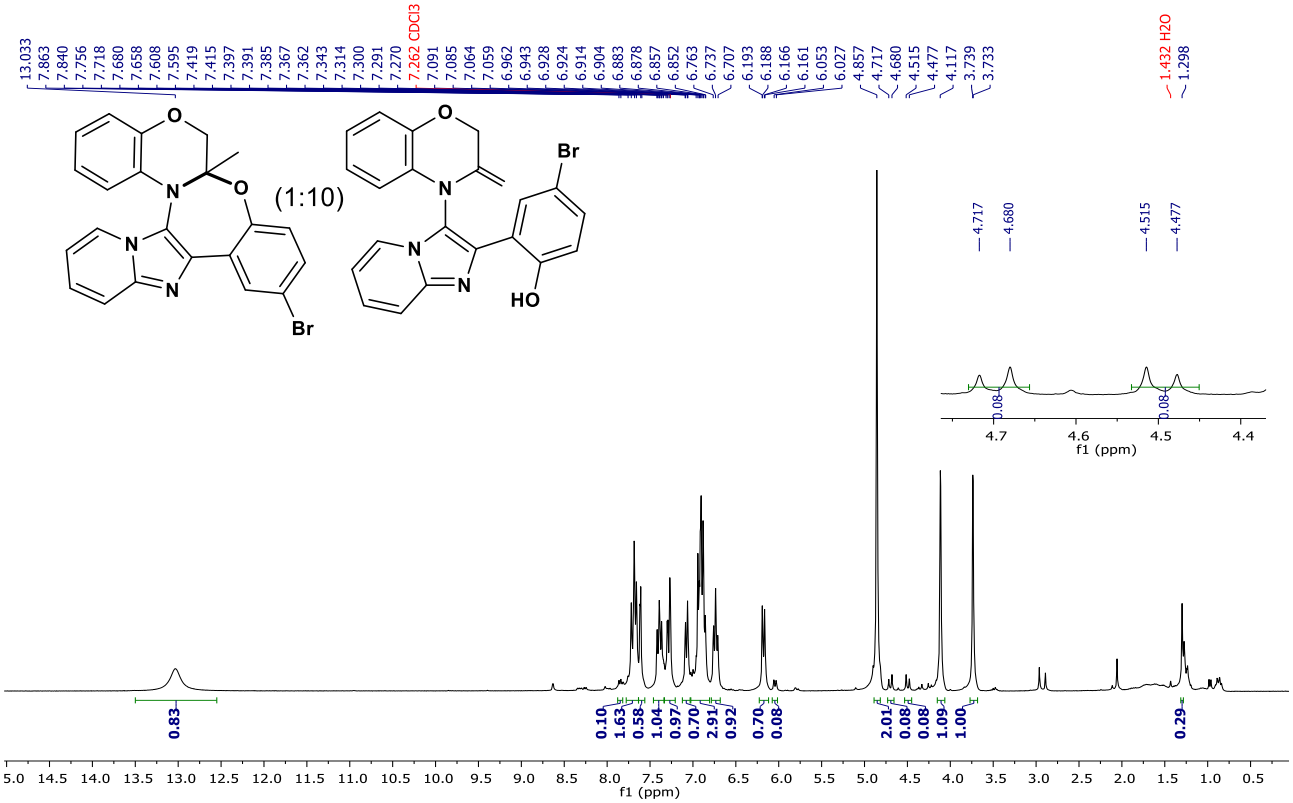
^{1}H NMR (300 MHz, $CDCl_3$) of **6**



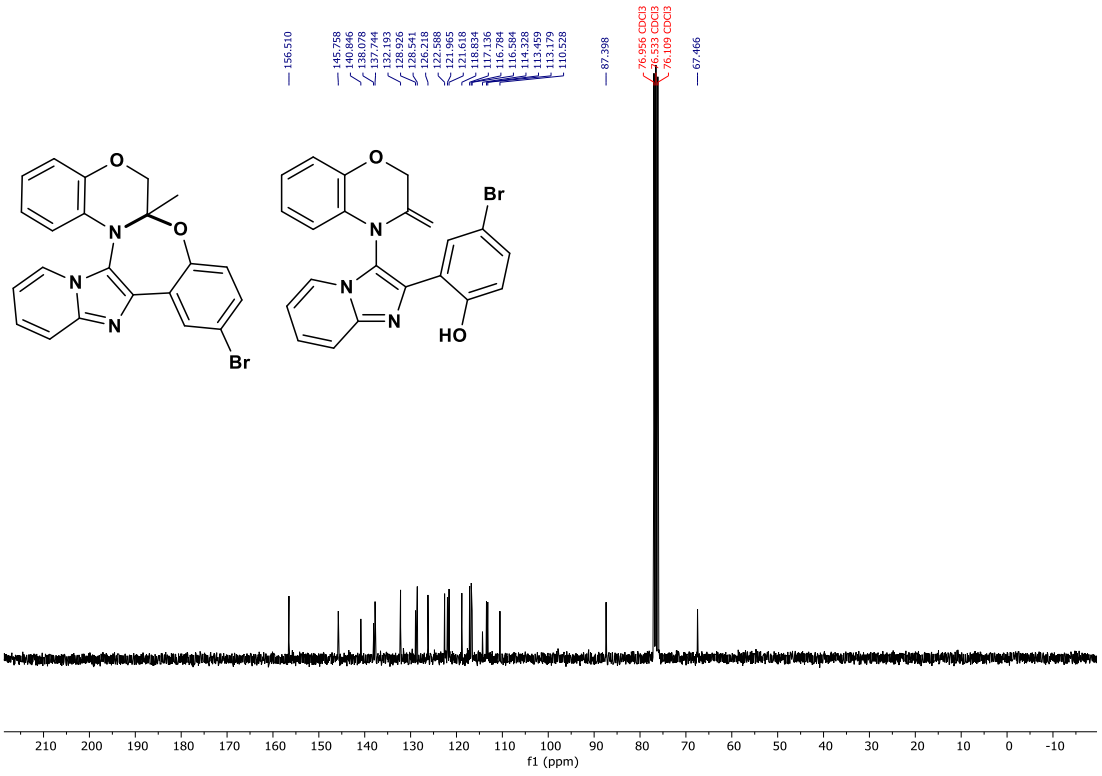
^{13}C NMR (75 MHz, $CDCl_3$) of **6**



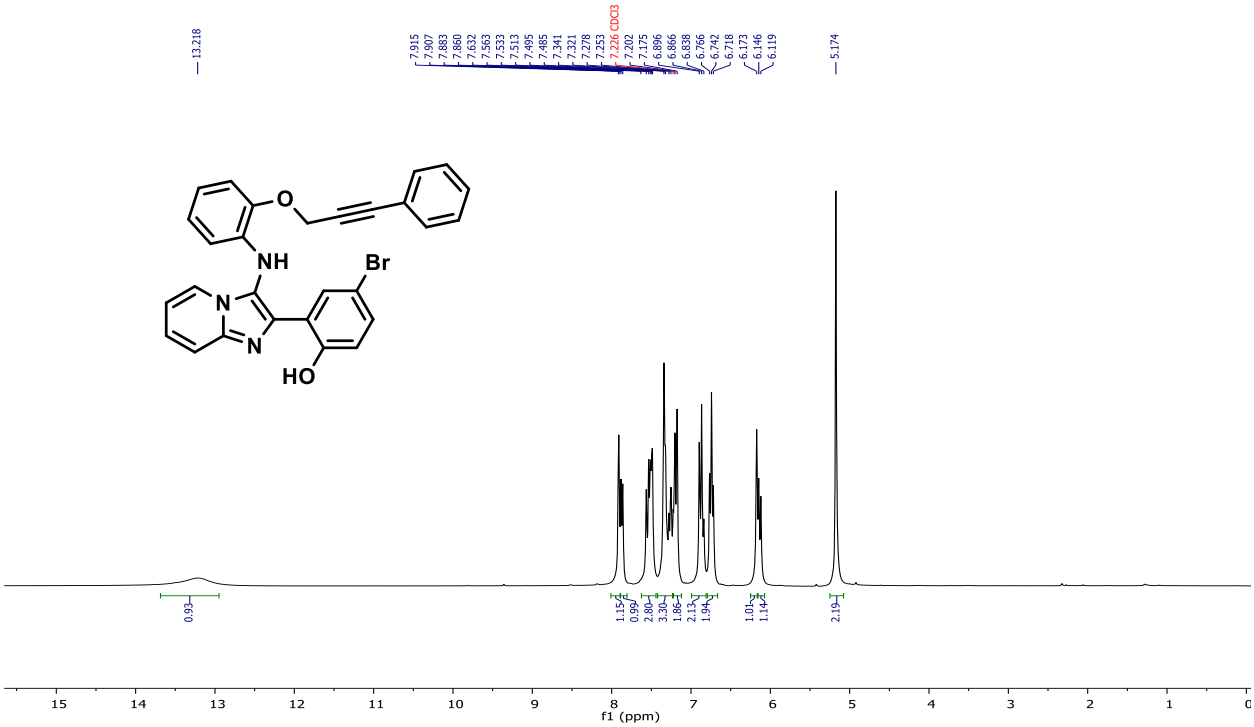
HRMS-ESI (+) of **6**



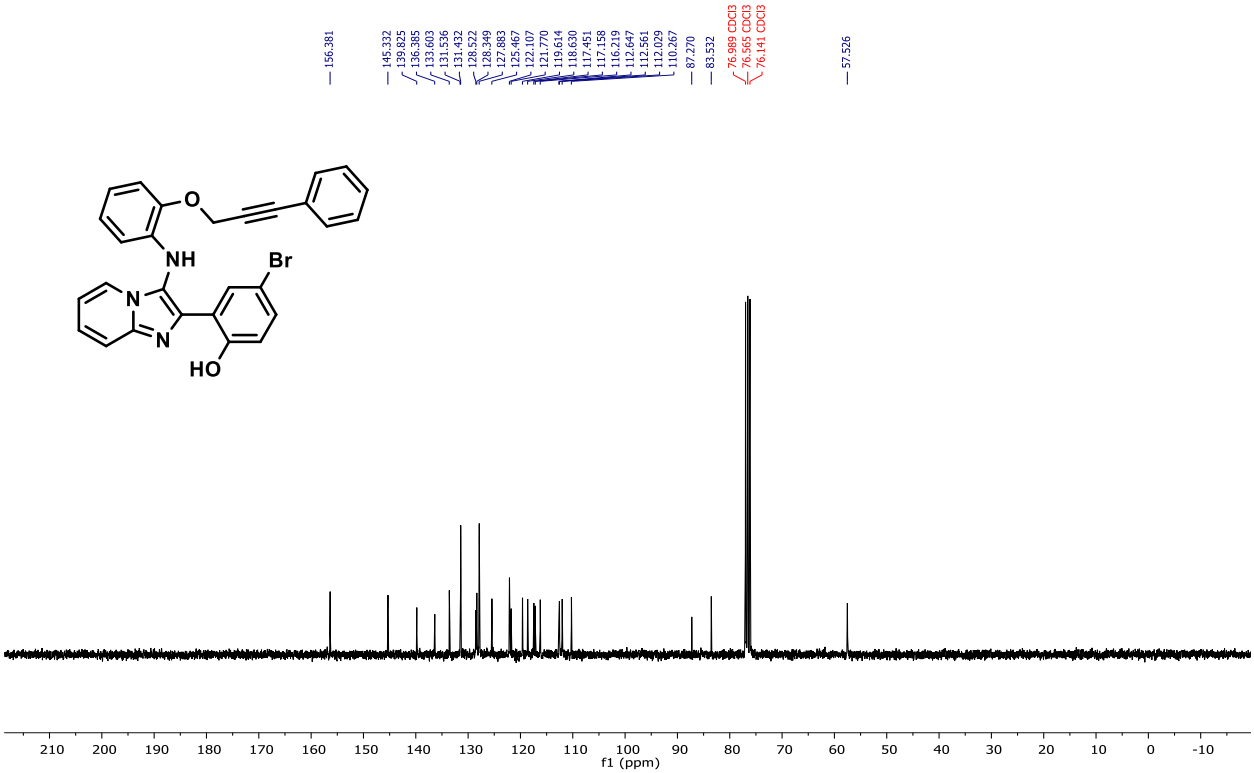
^{1}H NMR (300 MHz, $CDCl_3$) of mixture of intermediate and product **2a**



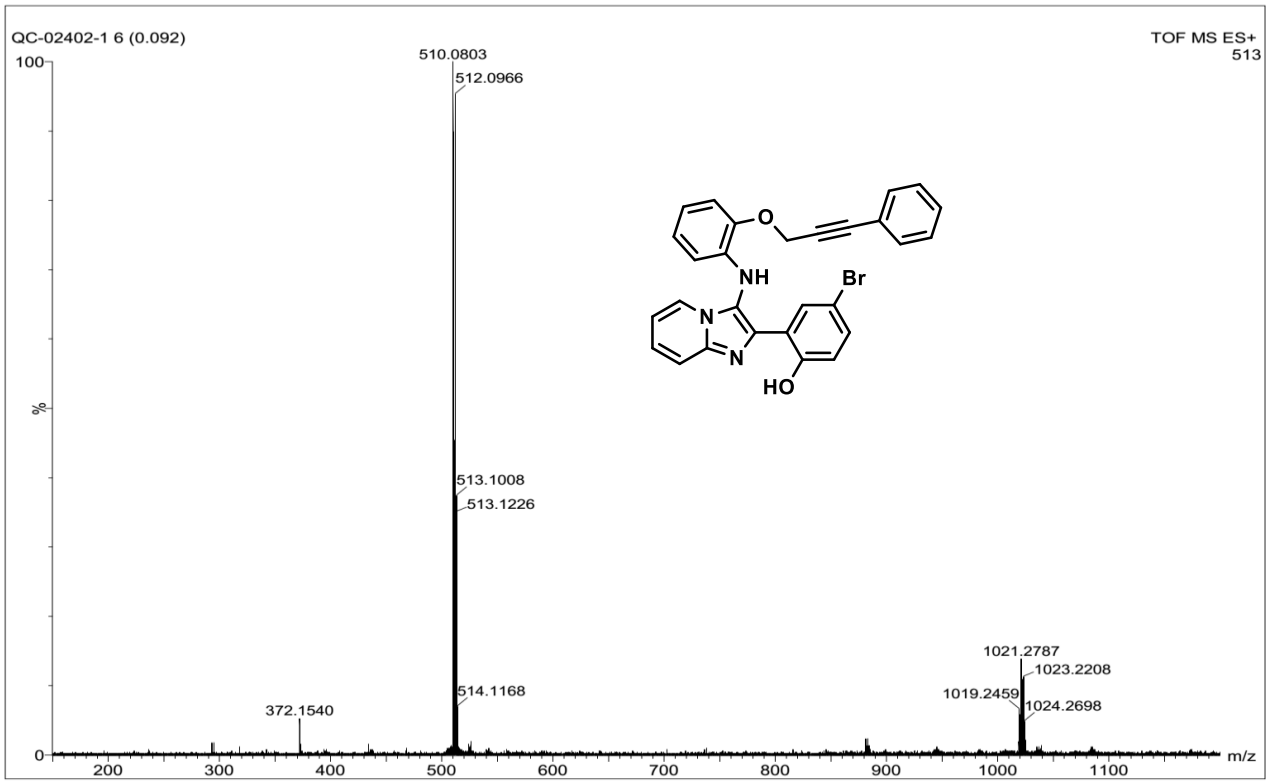
^{13}C NMR (75 MHz, $CDCl_3$) of mixture of intermediate and product of **2a**



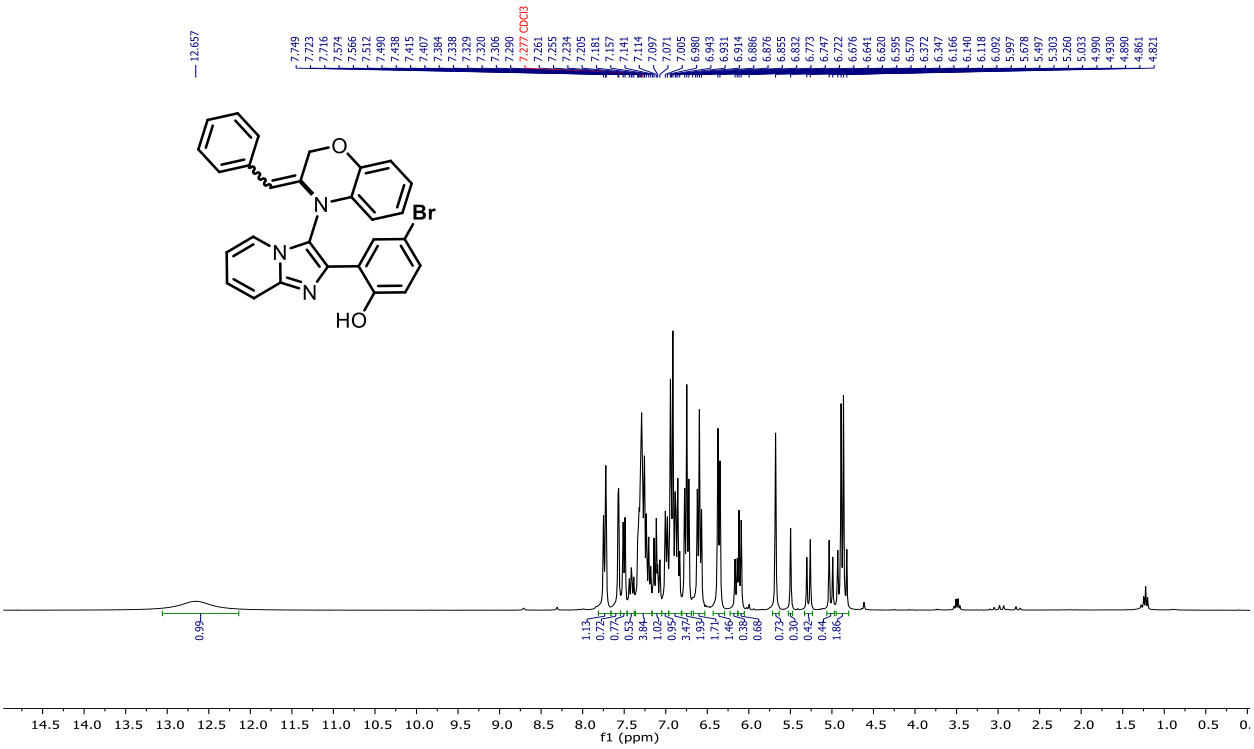
^{1}H NMR (300 MHz, $CDCl_3$) of **7a**



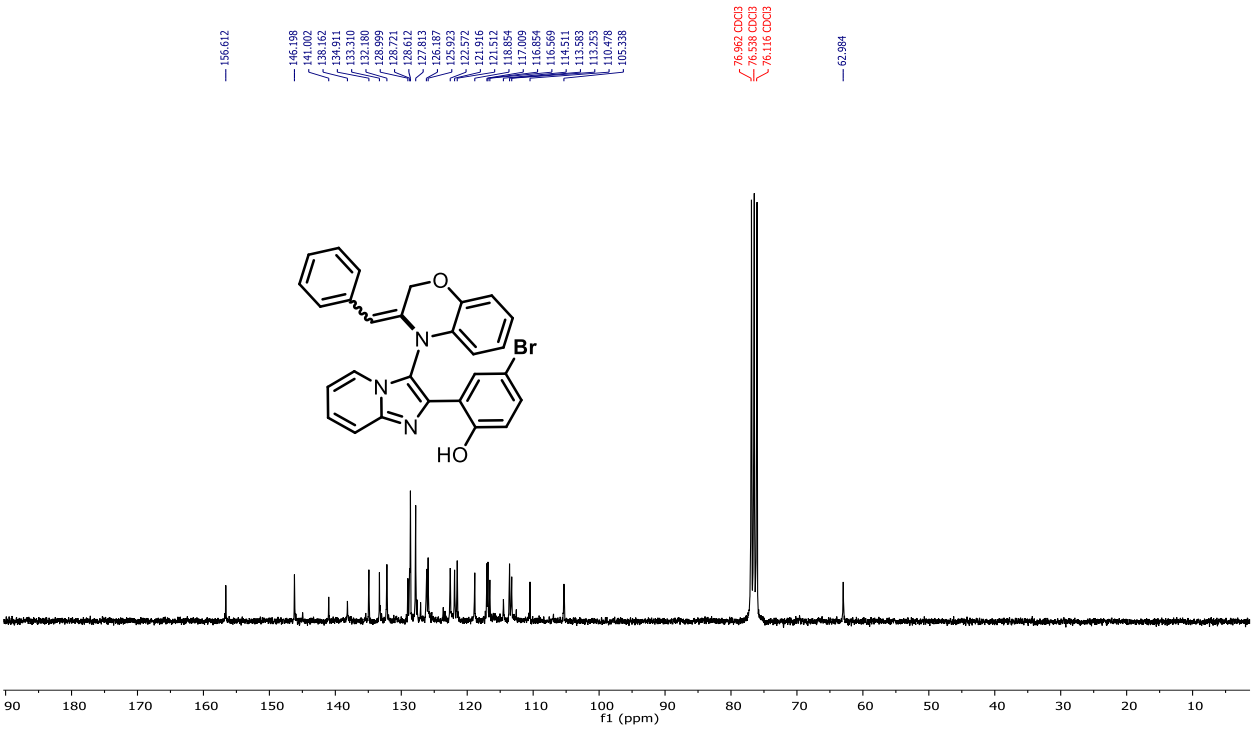
^{13}C NMR (75 MHz, $CDCl_3$) of **7a**



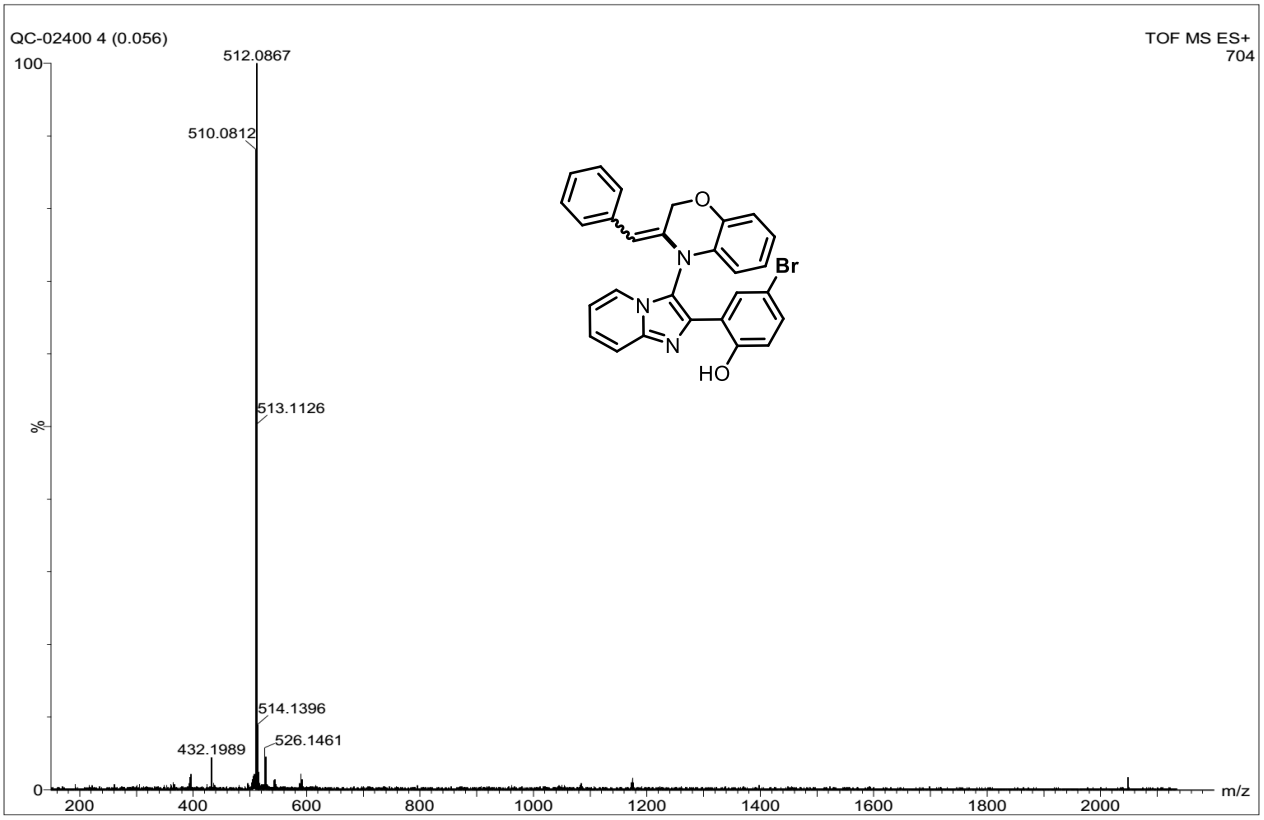
HRMS-ESI (+) of **7a**



^{1}H NMR (300 MHz, $CDCl_3$) of **8a**



^{13}C NMR (75 MHz, $CDCl_3$) of **8a**



HRMS-ESI (+) of **8a**