Supporting Information

Iodine-catalyzed oxidative functionalization of purines with (thio)ethers or methylarenes for the synthesis of purin-8-one analogues

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Ⅰ. General Information

All reactions were carried out in flame-dried sealed tubes with magnetic stirring under an air atmosphere unless otherwise noted. All alkyl ethers, thioethers and methylarenes were purchased from commercial supplies and used without further purification unless otherwise stated. C_6 and N_7 substituted purines were synthesized from 6-chloropurine and 2,6-dichloropurine according to Huang′s method[1] and Kelley′s method[2]. Purification of reaction products was carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd. silica gel (300−400 mesh). Melting points were determined with a Büchi Melting Point B-545 instrument. Unless otherwise, the ^{1}H NMR spectra were obtained at 400 MHz or 500 MHz in $CDCl_3$ or DMSO-d_6, the ^{13}C NMR spectra were recorded at 101 MHz or 126 MHz in $CDCl_3$ or DMSO-d_6, with TMS or a residual nondeuterated solvent peak as the internal standard using a Bruker DRX-400 or Bruker Ascend^{TM} 500 spectrometer. All coupling constants (J values) were reported in Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), doublet of quartets (dq), triplet (t), triplet of doublets (td), doublet of triplets (dt) and quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Gas chromatograph mass spectra analyses were performed on a SHIMADZU model GCMS-QP5000 spectrometer. High-resolution mass spectra (HRMS) were collected on an IF-TOF spectrometer.

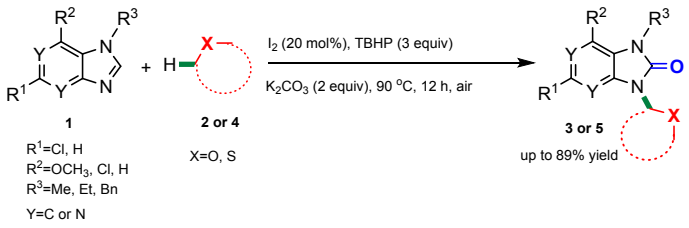
Ⅱ. General procedure for the synthesis of starting purine derivatives 1

In a 100 mL single neck flask, the corresponding 6-chloropurine (10 mmol, 1.0 equiv) and sodium methoxide (12 mmol, 1.2 equiv) were dissolved in methanol (20 mL). The mixture was stirred at 65 °C (oil bath) for 18 h. The reaction mixture was cooled to room temperature, and then concentrated under reduced pressure. The solid was dissolved in water (20 mL) and the pH adjusted to neutral with HCl. A large amount of white solids precipitated. The solid was filtred and dries then dissolved in CH_3CN (25 mL), then K_2CO_3 (12 mmol, 1.2 equiv), and bromoethane (12 mmol, 1.2 equiv) or benzyl chloride (12 mmol, 1.2 equiv) were added. The resulting solution was stirred at 75 °C (oil bath) for 18 h. The reaction mixture was cooled to room temperature, and concentrated under reduced pressure. The solid was dissolved in ethyl acetate (30 mL), and then filtered. The solvent

was removed under reduced pressure and the residue purified by flash column chromatography (petroleum ether : ethyl acetate = 4 : 1) , 6-chloropurine and 2,6-dichloropurine have the same operation, then obtained the starting purine derivatives **1**.

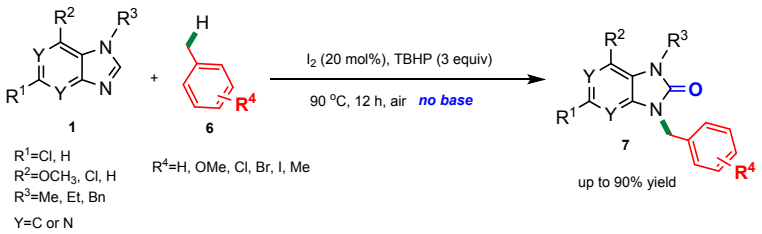
Ⅲ. General Procedure for the Direct Alkylation and Benzylation of Purines

General Procedure for the Direct Alkylation of Purines:



Purine derivatives (**1**) (0.1 mmol), I_2 (20 mmol%, 0.02 mmol), K_2CO_3 (2 equiv, 0.2 mmol), alkyl ethers or thioethers (**2** or **4**) (4 mmol) and TBHP (3 equiv, 0.3 mmol, aq.70% in water) were successively added into a sealed tube. The reaction mixture was stirred at 90 °C (oil bath) under air for 12 h. The mistrate was then concentrated under reduced pressure and purified by flash column chromatography on silica gel or preparative TLC on GF254 (petroleum ether : ethyl acetate = 8 : 1) to afford the corresponding product **3** or **5**.

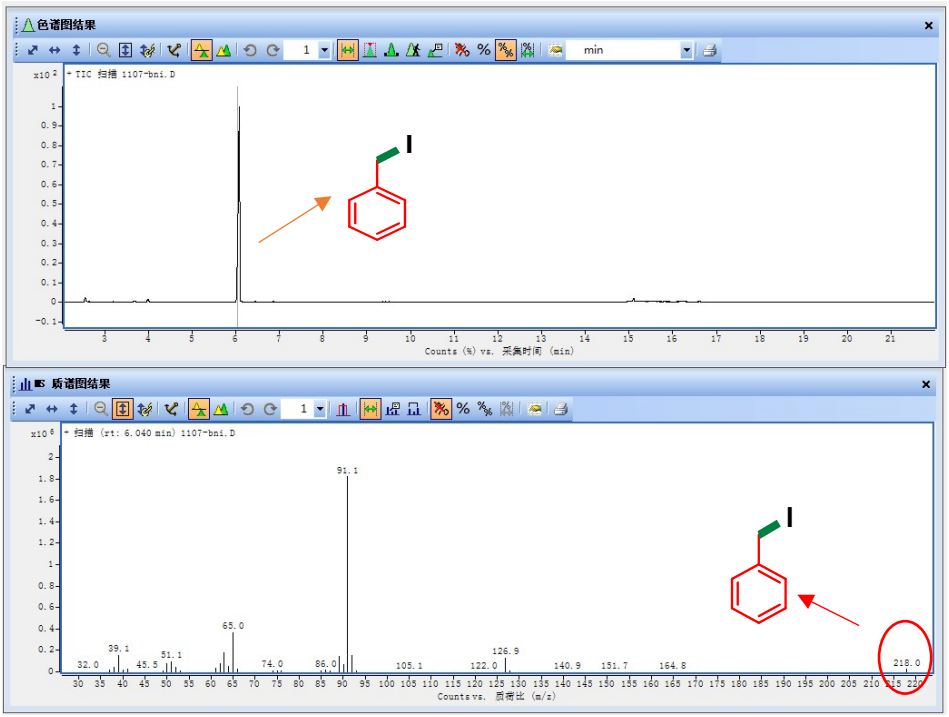
General Procedure for the Direct Benzylation of Purines:



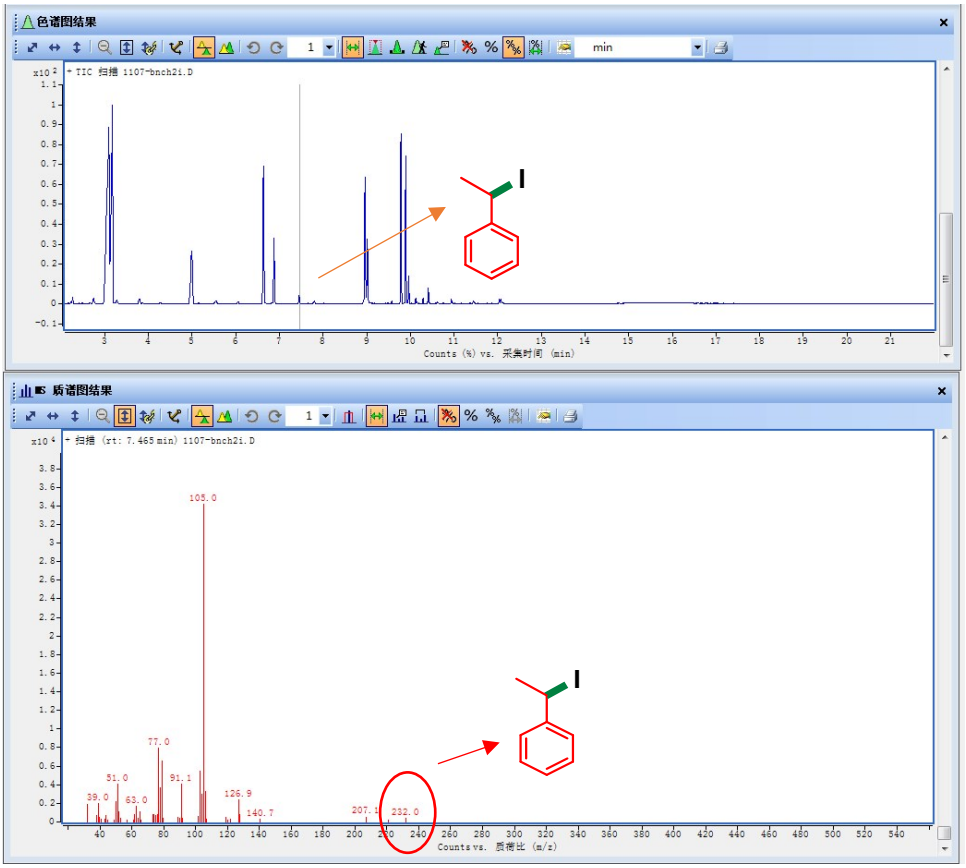
Purine derivatives (**1**) (0.1 mmol), I_2 (20 mmol%, 0.02 mmol), methylarenes (**6**) (4 mmol) and TBHP (3 equiv, 0.3 mmol, aq.70% in water) were successively added into a sealed tube. The reaction mixture was stirred at 90 °C (oil bath) under air for 12 h. The mistrate was then concentrated under reduced pressure and purified by flash column chromatography on silica gel or preparative TLC on GF254 (petroleum ether : ethyl acetate = 8 : 1) to afford the corresponding product **7**.

Ⅳ. GCMS of BnI， $BnCH_2I$, BnC_2H_4I (Scheme 2)

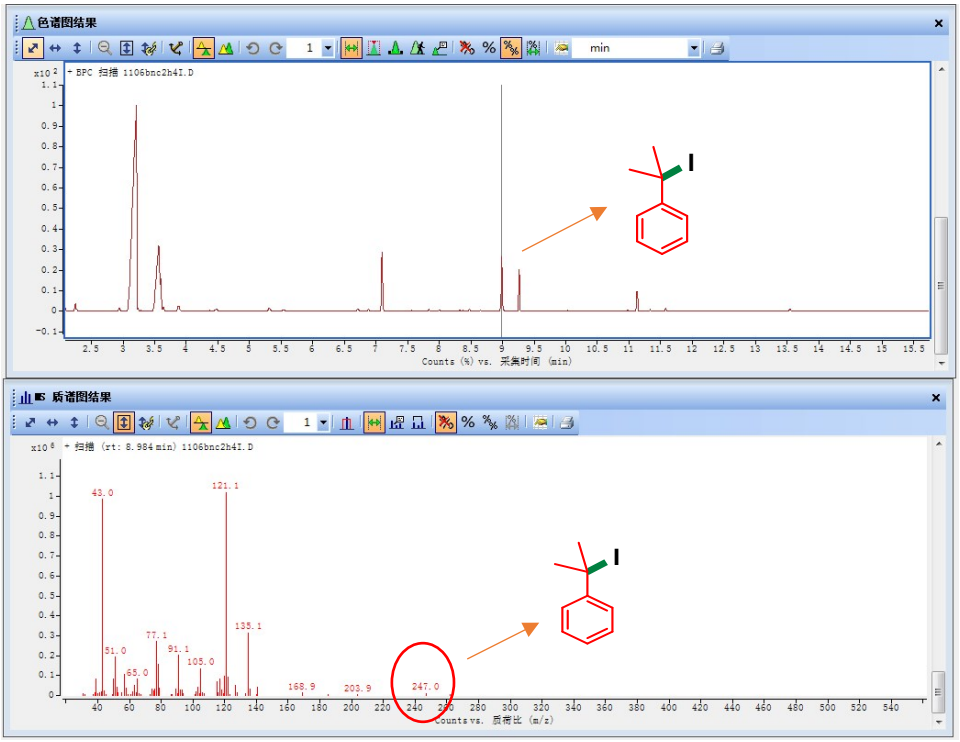
Scheme 2(d)



Scheme 2(e)



Scheme 2(f)



Ⅴ. X-ray Crystallographic analysis for product 7g

Crystal data have been deposited to CCDC, number 2041079.

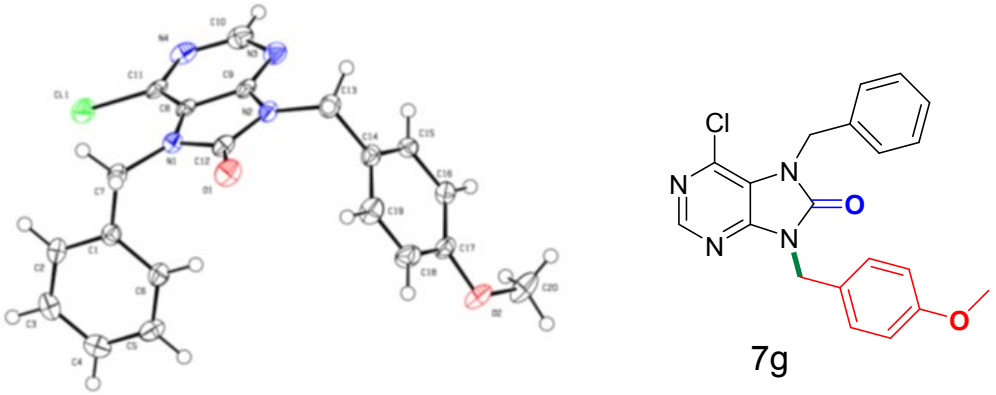


Figure S1. The single crystal structure of 7g (the ellipsoid contour probability level is 50%)

Table S1. Crystal data and structure refinement for 7g

Identification code	7g
Empirical formula	$C_{20}H_{17}ClN_4O_2$
Formula weight	380.83
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.3648(11)
b/Å	14.4679(12)
c/Å	8.6646(7)
α/°	90
β/°	101.100(8)
γ/°	90
Volume/Å^3	1767.1(2)
Z	4
ρ_{calc}g/cm^3	1.431
μ/mm^{-1}	0.240
F(000)	792.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.034 to 49.992
Index ranges	-17 ≤ h ≤ 16, -17 ≤ k ≤ 17, -8 ≤ l ≤ 10
Reflections collected	7572
Independent reflections	3103 [R_{int} = 0.0285, R_{sigma} = 0.0394]

Data/restraints/parameters	3103/0/245
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.0903
Largest diff. peak/hole / e Å^{-3}	0.27/-0.27

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7g. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	5093.2(3)	7393.7(3)	9474.2(6)	33.09(15)
O1	2307.7(8)	4697.1(9)	9926.9(14)	32.0(3)
O2	164.7(8)	4028.7(10)	2244.8(14)	33.9(3)
N1	3503.6(9)	5740.1(10)	9673.9(15)	20.2(3)
N2	3403.5(9)	4417.4(10)	8318.8(15)	20.3(3)
N3	4721.8(10)	4645.0(11)	7018.5(15)	25.6(3)
N4	5533.2(10)	6093.6(11)	7644.6(16)	27.3(4)
C1	2658.7(11)	7231.2(12)	9828.1(18)	21.5(4)
C2	2859.6(13)	8146.4(13)	10239(2)	30.1(4)
C3	2294.8(13)	8857.6(13)	9516(2)	32.4(4)
C4	1522.1(13)	8659.9(13)	8345(2)	30.1(4)
C5	1316.5(12)	7754.4(14)	7919(2)	30.4(4)
C6	1877.6(11)	7041.4(13)	8654.9(19)	25.9(4)
C7	3242.5(12)	6461.4(13)	10701.4(19)	24.7(4)
C8	4215.9(11)	5740.1(12)	8810.4(17)	18.0(4)
C9	4148.9(11)	4905.4(12)	7967.1(17)	19.7(4)
C10	5397.6(12)	5274.7(14)	6934(2)	29.1(4)
C11	4932.1(11)	6322.9(12)	8584.5(18)	21.4(4)
C12	2986.4(12)	4924.9(12)	9374.8(18)	23.0(4)
C13	3028.7(12)	3525.7(12)	7661(2)	26.4(4)
C14	2277.7(12)	3638.5(11)	6187.5(19)	22.3(4)
C15	2503.6(12)	3581.6(12)	4716(2)	24.1(4)
C16	1823.8(12)	3699.4(12)	3351(2)	23.9(4)
C17	895.4(12)	3879.6(12)	3483(2)	24.6(4)
C18	657.4(12)	3934.1(14)	4961(2)	31.1(4)
C19	1341.6(13)	3813.7(14)	6291(2)	30.9(4)
C20	332.7(14)	3832.2(16)	707(2)	40.5(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 7g. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	4.8(2)	24.5(3)	46.7(3)	-2.5(2)	-1.2(2)	-7.08(19)
O1	28.2(7)	38.3(8)	30.4(6)	3.1(6)	7.6(6)	-8.0(6)
O2	22.6(6)	47.0(9)	28.0(6)	2.1(6)	-5.4(5)	-3.5(6)
N1	19.8(7)	22.4(8)	17.8(7)	-0.3(6)	2.1(6)	-1.3(6)
N2	21.3(7)	18.9(8)	18.8(7)	1.4(6)	-0.9(6)	-2.5(6)
N3	24.9(7)	32.5(9)	18.4(7)	1.1(7)	1.6(6)	1.5(7)
N4	20.9(7)	36.2(10)	23.5(7)	6.6(7)	1.3(6)	-0.9(7)
C1	1.4(8)	27.7(10)	16.5(8)	-3.4(7)	6.1(7)	-1.3(7)
C2	31.5(9)	31.6(11)	24.6(9)	-9.6(9)	-1.0(8)	-1.9(9)
C3	39.9(11)	24.1(10)	33.9(10)	-7.3(9)	9.3(9)	-1.1(9)
C4	30.7(10)	29.4(11)	31.7(9)	4.7(9)	10.2(8)	5.5(8)
C5	21.0(9)	35.3(11)	32.0(9)	2.0(9)	-2.0(8)	-0.7(8)
C6	23.1(9)	25.5(10)	27.9(9)	-3.1(8)	2.3(7)	-4.7(8)
C7	25.8(9)	29.8(10)	17.1(8)	-4.2(8)	0.5(7)	-0.6(8)
C8	16.9(8)	21.4(9)	12.8(7)	5.0(7)	-4.3(6)	0.7(7)
C9	19.9(8)	22.8(9)	13.5(7)	4.2(7)	-4.4(7)	0.7(7)
C10	24.8(9)	41.1(12)	21.5(8)	2.4(9)	4.6(7)	2.3(9)
C11	17.9(8)	21.9(10)	20.0(8)	6.1(7)	-7.0(7)	-1.2(7)
C12	20.8(9)	27.1(10)	19.0(8)	4.4(8)	-1.1(7)	-2.4(8)
C13	29.4(9)	19.1(9)	27.2(9)	2.3(8)	-3.4(8)	-3.0(8)
C14	24.8(9)	15.8(9)	24.5(9)	0.7(7)	0.0(7)	-3.9(7)
C15	19.5(8)	20.3(9)	30.8(9)	-3.5(8)	0.5(7)	0.8(7)
C16	24.7(9)	24.2(10)	22.3(8)	-3.2(8)	3.5(7)	-2.8(8)
C17	20.7(9)	22.5(10)	27.4(9)	0.0(8)	-3.6(7)	-4.5(7)
C18	17.5(9)	41.1(12)	34.9(10)	-2.8(9)	5.7(8)	-2.7(8)
C19	28.9(10)	39.5(12)	24.9(9)	-1.1(9)	6.4(8)	-6.2(9)
C20	33.2(10)	59.8(15)	24.5(9)	4.0(10)	-4.7(8)	-12.3(10)

Table 4 Bond Lengths for 7g

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C11	1.7260(18)	C1	C6	1.389(2)
O1	C12	1.211(2)	C1	C7	1.507(2)
O2	C17	1.366(2)	C2	C3	1.383(3)
O2	C20	1.428(2)	C3	C4	1.382(3)
N1	C7	1.467(2)	C4	C5	1.378(3)
N1	C8	1.379(2)	C5	C6	1.387(3)

N1	C12	1.391(2)	C8	C9	1.405(2)
N2	C9	1.365(2)	C8	C11	1.373(2)
N2	C12	1.395(2)	C13	C14	1.513(2)
N2	C13	1.470(2)	C14	C15	1.377(2)
N3	C9	1.325(2)	C14	C19	1.388(2)
N3	C10	1.344(2)	C15	C16	1.392(2)
N4	C10	1.332(2)	C16	C17	1.385(2)
N4	C11	1.338(2)	C17	C18	1.390(2)
C1	C2	1.387(3)	C18	C19	1.374(3)

Table 5 Bond Angles for 7g.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	O2	C20	117.33(14)	N2	C9	C8	107.85(14)
C8	N1	C7	129.24(14)	N3	C9	N2	126.80(16)
C8	N1	C12	108.92(13)	N3	C9	C8	125.35(15)
C12	N1	C7	121.76(14)	N4	C10	N3	128.37(16)
C9	N2	C12	109.18(14)	N4	C11	Cl1	116.59(12)
C9	N2	C13	127.72(14)	N4	C11	C8	121.58(16)
C12	N2	C13	123.02(14)	C8	C11	Cl1	121.82(13)
C9	N3	C10	112.49(15)	O1	C12	N1	126.76(16)
C10	N4	C11	116.60(15)	O1	C12	N2	126.56(16)
C2	C1	C6	118.39(16)	N1	C12	N2	106.68(14)
C2	C1	C7	120.56(15)	N2	C13	C14	112.40(14)
C6	C1	C7	120.96(16)	C15	C14	C13	121.18(15)
C3	C2	C1	121.27(16)	C15	C14	C19	118.32(15)
C4	C3	C2	119.78(18)	C19	C14	C13	120.49(16)
C5	C4	C3	119.62(17)	C14	C15	C16	121.84(16)
C4	C5	C6	120.55(17)	C17	C16	C15	118.83(16)
C5	C6	C1	120.39(17)	O2	C17	C16	124.86(15)
N1	C7	C1	113.80(13)	O2	C17	C18	115.25(15)
N1	C8	C9	107.37(14)	C16	C17	C18	119.88(15)
C11	C8	N1	137.05(16)	C19	C18	C17	120.15(16)
C11	C8	C9	115.58(15)	C18	C19	C14	120.97(16)

Table 6 Torsion Angles for 7g.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C17	C18	C19	-178.73(17)	C9	C8	C11	N4	-1.3(2)
N1	C8	C9	N2	0.28(17)	C10	N3	C9	N2	-179.08(15)
N1	C8	C9	N3	-178.97(14)	C10	N3	C9	C8	0.0(2)

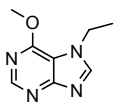
N1	C8	C11	Cl1	-2.1(3)	C10	N4	C11	Cl1	-178.75(12)
N1	C8	C11	N4	178.81(16)	C10	N4	C11	C8	0.4(2)
N2	C13	C14	C15	95.83(19)	C11	N4	C10	N3	1.0(3)
N2	C13	C14	C19	-83.4(2)	C11	C8	C9	N2	-179.63(13)
C1	C2	C3	C4	-0.9(3)	C11	C8	C9	N3	1.1(2)
C2	C1	C6	C5	0.0(2)	C12	N1	C7	C1	-97.01(18)
C2	C1	C7	N1	-135.81(16)	C12	N1	C8	C9	-0.57(17)
C2	C3	C4	C5	0.6(3)	C12	N1	C8	C11	179.31(18)
C3	C4	C5	C6	0.1(3)	C12	N2	C9	N3	179.35(14)
C4	C5	C6	C1	-0.4(3)	C12	N2	C9	C8	0.11(17)
C6	C1	C2	C3	0.6(3)	C12	N2	C13	C14	87.22(19)
C6	C1	C7	N1	47.7(2)	C13	N2	C9	N3	-4.1(3)
C7	N1	C8	C9	-177.48(14)	C13	N2	C9	C8	176.62(14)
C7	N1	C8	C11	2.4(3)	C13	N2	C12	O1	3.1(3)
C7	N1	C12	O1	-2.4(2)	C13	N2	C12	N1	-177.17(13)
C7	N1	C12	N2	177.82(13)	C13	C14	C15	C16	-178.88(16)
C7	C1	C2	C3	-175.91(16)	C13	C14	C19	C18	178.79(17)
C7	C1	C6	C5	176.53(15)	C14	C15	C16	C17	0.1(3)
C8	N1	C7	C1	79.6(2)	C15	C14	C19	C18	-0.5(3)
C8	N1	C12	O1	-179.60(15)	C15	C16	C17	O2	178.53(16)
C8	N1	C12	N2	0.63(17)	C15	C16	C17	C18	-0.4(3)
C9	N2	C12	O1	179.78(16)	C16	C17	C18	C19	0.3(3)
C9	N2	C12	N1	-0.46(17)	C17	C18	C19	C14	0.1(3)
C9	N2	C13	C14	-88.85(19)	C19	C14	C15	C16	0.4(3)
C9	N3	C10	N4	-1.2(2)	C20	O2	C17	C16	11.1(3)
C9	C8	C11	Cl1	177.77(11)	C20	O2	C17	C18	-169.95(17)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7g.

Atom	*x*	*y*	*z*	U(eq)
H2	3383.95	8284.61	11015.23	36
H3	2434.78	9466.81	9816.2	39
H4	1142.99	9135.27	7847.8	36
H5	796.95	7620.24	7130.19	36
H6	1729.92	6432.55	8361.32	31
H7A	3817.27	6722.05	11320.17	30
H7B	2887.1	6180.81	11424.36	30
H10	5826.07	5118.71	6297.31	35
H13A	2759.08	3194.74	8443.86	32

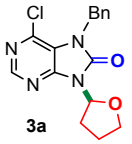
H13B	3546.02	3157.46	7417.47	32
H15	3127.85	3461.01	4632.48	29
H16	1989.99	3657.97	2367.67	29
H18	33.6	4052.4	5050.55	37
H19	1175.14	3850.04	7274.59	37
H20A	-246.26	3906.97	-47.73	61
H20B	554.07	3207.86	671.99	61
H20C	803.31	4249.57	462.52	61

Ⅵ. Analytical Data for the Products



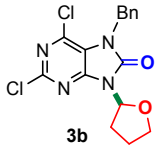
1f **7-ethyl-6-methoxy-7*H*-purine (1f):** White solid; mp 50-52 °C; 0.5g (10mmol), 29% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.02 (s, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 4.14

(s, 3H), 1.50 (t, *J* = Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 157.1, 152.0, 144.9, 112.8, 54.1, 42.8, 16.8; HRMS (ESI): $[M+H]^+$ calculated for $C_8H_{11}N_4O$: 179.0933, found: 179.0941; IR(KBr): 3421.6, 3135.2, 1616.6, 1561.1, 1485.2, 1404.4, 1348.9, 1273.0, 1131.9, 879.4, 799.5, 618.4.



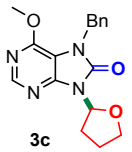
3a

7-benzyl-6-chloro-9-(tetrahydrofuran-2-yl)-7*H*-purin-8(9*H*)-one (3a): White solid; mp 56-58 °C; 29.4 mg, 89% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.44-7.23 (m, 5H), 6.36 (dd, *J* = 7.7, 4.8 Hz, 1H), 5.34 (s, 2H), 4.33 (q, *J* = 7.7 Hz, 1H), 4.15-3.90 (m, 1H), 2.88-2.61 (m, 1H), 2.56-2.27 (m, 2H), 2.09 (dd, *J* = 11.7, 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 150.5, 149.9, 136.2, 128.9, 128.0, 127.3, 119.4, 83.6, 70.3, 45.2, 29.2, 25.9; HRMS (ESI): $[M+Na]^+$ calculated for $C_{16}H_{15}ClN_4NaO_2$: 353.0776, found: 353.0779; IR(KBr): 3062.6, 3029.9, 2954.5, 2883.1, 1732.5, 1603.0, 1574.8, 1472.0, 1432.1, 1167.4, 1139.2, 1061.5, 750.7, 698.9, 618.8.



3b

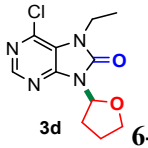
7-benzyl-2,6-dichloro-9-(tetrahydrofuran-2-yl)-7*H*-purin-8(9*H*)-one (3b): Yellow solid; mp 41-43 °C; 29.8 mg, 82% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.26 (m, 5H), 6.30 (dd, J = 7.6, 4.7 Hz, 1H), 5.29 (s, 2H), 4.34-4.27 (m, 1H), 4.04-3.97 (m, 1H), 2.72-2.61 (m, 1H), 2.51-2.35 (m, 2H), 2.11-2.01 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 151.3, 151.0, 136.4, 135.9, 128.9, 128.2, 127.3, 118.4, 83.9, 70.4, 45.3, 29.5, 25.8; HRMS (ESI): $[M+Na]^+$ calculated for $C_{16}H_{14}Cl_2N_4NaO_2$: 387.0386, found: 387.0390; IR(KBr): 3062.6, 3032.7, 2965.3, 2885.6, 1738.8, 1606.6, 1569.2, 1468.9, 1394.7, 1285.0, 1140.4, 1055.7, 744.0, 701.6, 577.0.



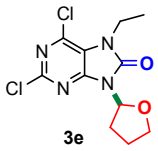
3c

7-benzyl-6-methoxy-9-(tetrahydrofuran-2-yl)-7*H*-purin-8(9*H*)-one (3c): White solid; mp 56-58 °C; 25.8 mg, 79% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 6.7 Hz, 1H), 6.29 (dd, *J* = 7.7, 5.0 Hz, 1H), 5.14 (s, 2H), 4.44-4.20 (m, 1H), 4.05 (s, 3H), 3.98 (td, *J* = 7.7, 4.7 Hz, 1H), 2.90-2.65 (m, 1H), 2.61-2.41 (m, 1H), 2.36-2.25 (m, 1H), 2.03 (dt, *J* = 11.8, 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 152.3, 150.1, 148.7, 137.1, 128.6, 128.1, 127.8, 107.7, 83.2, 69.9, 53.8, 46.1, 29.1, 26.0;

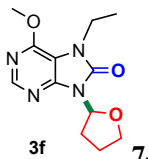
HRMS (ESI): $[M+Na]^+$ calculated for $C_{17}H_{18}N_4NaO_3$: 349.1271, found: 349.1275; IR(KBr): 3037.6, 2955.4, 2925.4, 2848.2, 1726.3, 1621.6, 1586.7, 1467.0, 1437.1, 1342.3, 1157.9, 1068.1, 1020.8, 749.0, 704.1, 619.4.



3d **6-chloro-7-ethyl-9-(tetrahydrofuran-2-yl)-7*H*-purin-8(9*H*)-one (3d):** White solid; mp 35-36 °C; 22.3 mg, 83% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 6.31 (dd, *J* = 7.7, 4.9 Hz, 1H), 4.31 (q, *J* = 7.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.01 (td, *J* = 7.7, 4.9 Hz, 1H), 2.80-2.64 (m, 1H), 2.48 (dt, *J* = 13.4, 6.4 Hz, 1H), 2.37 (td, *J* = 13.4, 6.8 Hz, 1H), 2.13-2.00 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 150.2, 149.8, 135.8, 119.3, 83.4, 70.2, 37.1, 29.2, 25.9, 15.5; HRMS (ESI): $[M+Na]^+$ calculated for $C_{11}H_{13}ClN_4NaO_2$: 291.0619, found 291.0622; IR(KBr): 3065.1, 2980.3, 2885.6, 1730.3, 1606.6, 1574.2, 1477.0, 1354.8, 1207.7, 1165.3, 1063.1, 624.3.

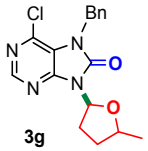


3e **2,6-dichloro-7-ethyl-9-(tetrahydrofuran-2-yl)-7*H*-purin-8(9*H*)-one (3e):** Yellow solid; mp 32-34 °C; 24.2 mg, 80% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.19 (dd, *J* = 7.6, 4.7 Hz, 1H), 4.23 (q, *J* = 7.5 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.96-3.89 (m, 1H), 2.64-2.53 (m, 1H), 2.46-2.37 (m, 1H), 2.35-2.25 (m, 1H), 2.03-1.95 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 151.2, 150.7, 136.0, 118.3, 83.7, 70.4, 37.3, 29.4, 25.8, 15.4; HRMS (ESI): $[M+Na]^+$ calculated for $C_{11}H_{12}Cl_2N_4NaO_2$: 325.0230, found: 325.0229; IR(KBr): 2978.5, 1742.8, 1608.4, 1571.0, 1485.8, 1401.8, 1312.6, 1288.5, 1097.6, 931.9, 618.8.

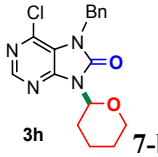


3f **7-ethyl-6-methoxy-9-(tetrahydrofuran-2-yl)-7*H*-purin-8(9*H*)-one (3f):** White solid; mp 48-50 °C; 20.1 mg, 76% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 6.20 (dd, *J* = 7.6, 5.1 Hz, 1H), 4.22 (q, *J* = 7.5 Hz, 1H), 4.01 (s, 3H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.91-3.87 (m, 1H), 2.73-2.62 (m, 1H), 2.45-2.34 (m, 1H), 2.30-2.18 (m, 1H), 2.01-1.90 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 151.8, 149.8, 148.6, 107.6, 83.0, 69.8, 53.9,

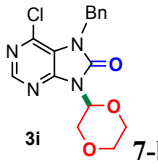
37.7, 29.0, 25.9, 15.2; HRMS (ESI): $[M+Na]^+$ calculated for $C_{12}H_{16}N_4NaO_3$: 287.1115, found: 287.1117; IR(KBr): 3414.4, 3033.4, 2971.5, 2883.4, 1722.6, 1627.6, 1476.5, 1428.4, 1404.6, 1350.9, 1270.3, 1236.1, 1194.6, 1068.5, 663.3.



3g **7-benzyl-6-chloro-9-(5-methyltetrahydrofuran-2-yl)-7*H*-purin-8(9*H*)-one (3g):** White solid; mp 72-74 °C; 22.4 mg, 65% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, J = 5.4 Hz, 1H), 7.26-7.18 (m, 5H), 6.32 (t, J = 6.5 Hz, 0.6H), 6.20 (dd, J = 8.1, 3.4 Hz, 0.4H), 5.25 (s, 2H), 4.64-4.58 (m, 0.6H), 4.13-4.07 (m, 0.4H), 2.84-2.75 (m, 0.6H), 2.70-2.63 (m, 0.4H), 2.43-2.21 (m, 2H), 1.61-1.54 (m, 1H), 1.30 (d, J = 6.0 Hz, 1.2H), 1.21 (d, J = 6.1 Hz, 1.8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 152.2, 150.5, 150.5, 150.0, 149.8, 136.3, 136.2, 136.2, 128.8, 128.0, 127.4, 119.4, 83.4, 82.9, 77.9, 77.8, 45.2, 33.8, 32.3, 29.7, 29.6, 20.7, 20.3; HRMS(ESI): $[M+Na]^+$ calculated for $C_{17}H_{17}ClN_4NaO_2$: 367.0932, found: 367.0936; IR(KBr): 3060.1, 3035.1, 2970.3, 2927.9, 2870.6, 1736.3, 1609.1, 1574.2, 1477.0, 1429.6, 1382.2, 1172.8, 1135.4, 1085.6, 749.0, 701.6, 604.4.

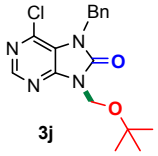


3h **7-benzyl-6-chloro-9-(tetrahydro-2H-pyran-2-yl)-7*H*-purin-8(9*H*)-one (3h):** Yellow solid; mp 51-53 °C; 26.5 mg, 77% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.25-7.18 (m, 5H), 5.54 (d, J = 11.2 Hz, 1H), 5.26 (s, 2H), 4.10- 4.04 (m, 1H), 3.67-3.60 (m, 1H), 2.94-2.83 (m, 1H), 2.03-1.96 (m, 1H), 1.74-1.58 (m, 3H), 1.53-1.47 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 150.7, 149.9, 136.4, 136.1, 128.8, 128.0, 127.3, 119.3, 81.6, 69.2, 45.4, 28.0, 24.8, 23.3; HRMS(ESI): $[M+Na]^+$ calculated for $C_{17}H_{17}ClN_4NaO_2$: 367.0932, found: 367.0936; IR(KBr): 3057.6, 3027.7, 2937.9, 2853.1, 1741.2, 1606.6, 1574.7, 1479.5, 1427.1, 1145.4, 1080.6, 1040.7, 721.6, 699.1, 629.3.

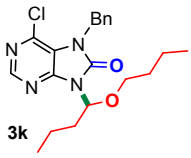


3i **7-benzyl-6-chloro-9-(1,4-dioxan-2-yl)-7*H*-purin-8(9*H*)-one (3i):** White solid; mp 109-111 °C; 29.5 mg, 81% yield; ^{1}H NMR (400 MHz, Chloroform-*d* $_3$) δ 8.41 (s, 1H), 7.26-7.19 (m, 5H), 5.75 (dd, *J* = 10.1, 2.8 Hz, 1H), 5.26 (s, 2H), 4.73-4.67 (m, 1H), 3.96-3.92 (m, 2H), 3.81-

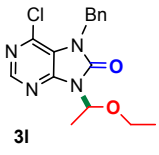
3.71 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 150.7, 149.7, 136.8, 135.9, 128.9, 128.2, 127.4, 119.4, 78.0, 67.7, 66.2, 65.7, 45.5; HRMS(ESI): $[M+Na]^+$ calculated for $C_{16}H_{15}ClN_4NaO_3$: 369.0725, found: 369.0729; IR(KBr): 2962.8, 2922.9, 2855.6, 1736.2, 1654.0, 1606.6, 1579.2, 1477.0, 1118.0, 1030.7, 1003.3, 724.1, 699.1, 629.3.



3j **7-benzyl-9-(tert-butoxymethyl)-6-chloro-7*H*-purin-8(9*H*)-one (3j):** Yellow solid; mp 36-38 °C; 31.3 mg, 86% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.24-7.20 (m, 5H), 5.35 (s, 2H), 5.26 (s, 2H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 151.0, 150.2, 136.3, 136.2, 128.8, 128.0, 127.3, 119.5, 75.4, 64.4, 45.3, 27.9; HRMS(ESI): $[M+Na]^+$ calculated for $C_{17}H_{19}ClN_4NaO_2$: 369.1089, found: 369.1096; IR(KBr): 3062.6, 3032.6, 2975.3, 2935.4, 1743.7, 1606.6, 1579.2, 1491.9, 1402.2, 1369.8, 1185.3, 1140.4, 1073.1, 744.0, 699.1, 621.8.

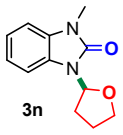


3k **7-benzyl-9-(1-butoxybutyl)-6-chloro-7*H*-purin-8(9*H*)-one (3k):** White solid; mp 64-65 °C; 28.7 mg, 74% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.35-7.29 (m, 5H), 5.67 (t, J = 7.0 Hz, 1H), 5.37 (s, 2H), 3.55-3.48 (m, 1H), 3.45-3.39 (m, 1H), 2.49-2.39 (m, 1H), 2.25-2.17 (m, 1H), 1.56-1.51 (m, 2H), 1.39-1.26 (m, 4H), 0.97 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 150.8, 150.0, 136.5, 136.4, 128.9, 128.0, 127.1, 119.1, 84.9, 69.3, 45.3, 34.6, 31.2, 19.2, 18.7, 13.7, 13.5; HRMS(ESI): $[M+Na]^+$ calculated for $C_{20}H_{25}ClN_4NaO_2$: 411.1558, found: 411.1559; IR(KBr): 3067.5, 3035.1, 2962.8, 2930.4, 2873.1, 1736.2, 1604.1, 1571.7, 1469.5, 1429.6, 1377.2, 1175.3, 1127.9, 1075.6, 734.0, 699.1, 537.1.

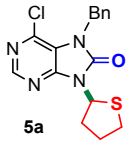


3l **7-benzyl-6-chloro-9-(1-ethoxyethyl)-7*H*-purin-8(9*H*)-one (3l):** Yellow solid; mp 101-103 °C; 25.9 mg, 78% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.76- 6.92 (m, 5H), 5.86 (q, *J* = 6.2 Hz, 1H), 5.36 (d, *J* = 2.7 Hz, 2H), 3.65-3.53 (m, 1H), 3.51-3.37 (m, 1H), 1.91 (d, *J* = 6.3 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 150.8, 149.9, 136.5, 136.3, 128.9, 128.1, 127.2, 119.2, 81.0, 64.7, 45.3, 19.4, 14.8; HRMS(ESI): $[M+Na]^+$

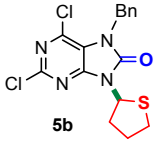
calculated for $C_{16}H_{17}ClN_4NaO_2$: 355.0932, found: 355.0935; IR(KBr): 2982.8, 2925.4, 2853.1, 1738.7, 1604.1, 1574.2, 1477.0, 1382.2, 1187.8, 1122.9, 746.5, 699.1, 609.4.



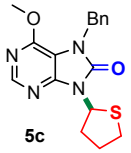
3n **methyl-3-(tetrahydrofuran-2-yl)-1*H*-benzo[d]imidazol-2(3*H*)-one(3n):** White solid; mp 153-155 °C; 18.5 mg, 85% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.98 (dt, *J* = 23.0, 8.0 Hz, 3H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.02 (t, *J* = 6.4 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 1H), 3.87-3.81 (m, 1H), 3.25 (s, 3H), 2.48-2.40 (m, 1H), 2.17 (dq, *J* = 11.6, 5.5 Hz, 2H), 1.97 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 130.3, 127.6, 121.5, 121.2, 109.3, 107.5, 84.2, 68.6, 28.7, 26.8, 25.6; HRMS(ESI): $[M+H]^+$ calculated for $C_{12}H_{14}N_2O_2$: 219.1128, found: 219.1129; IR(KBr): 3490.8, 3411.3, 3062.5, 2954.2, 2882.3, 1713.2, 1618.8, 1495.8, 1391.7, 1318.5, 1201.8, 1178.7, 1060.5, 927.3, 752.2, 619.7, 561.4.



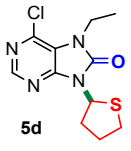
5a **7-benzyl-6-chloro-9-(tetrahydrothiophen-2-yl)-7*H*-purin-8(9*H*)-one (5a):** White solid; mp 55-57 °C; 26.0 mg, 75% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.35-7.28 (m, 5H), 6.35 (dd, *J* = 8.0, 6.0 Hz, 1H), 5.33 (s, 2H), 3.49 (td, *J* = 9.6, 5.5 Hz, 1H), 3.00 (m, 1H), 2.84-2.57 (m, 2H), 2.51-2.36 (m, 1H), 2.21-1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 150.4, 149.5, 136.2, 136.2, 128.9, 128.0, 127.3, 119.4, 60.6, 45.3, 34.6, 34.2, 31.8; HRMS(ESI): $[M+Na]^+$ calculated for $C_{16}H_{15}ClN_4NaOS$: 369.0547, found: 369.0550; IR(KBr): 3065.1, 2930.4, 2853.1, 1733.7, 1601.6, 1576.7, 1479.5, 1434.6, 1167.8, 1137.9, 1075.6, 744.0, 699.1, 539.6.



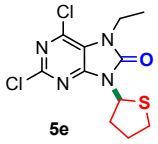
5b **7-benzyl-2,6-dichloro-9-(tetrahydrothiophen-2-yl)-7*H*-purin-8(9*H*)-one (5b):** Yellow solid; mp 39-41 °C; 26.6 mg, 70% yield; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36-7.27 (m, 5H), 6.30 (t, J = 6.8 Hz, 1H), 5.30 (s, 2H), 3.52-3.44 (m, 1H), 3.03-2.97 (m, 1H), 2.66-2.57 (m, 2H), 2.49-2.40 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 150.9, 136.4, 135.8, 129.0, 128.2, 127.3, 118.4, 60.9, 45.4, 34.8, 34.4, 31.9; HRMS(ESI): $[M+Na]^+$ calculated for $C_{16}H_{14}Cl_2N_4NaOS$: 403.0158, found: 403.0155; IR(KBr): 2925.4, 2855.6, 1746.2, 1606.6, 1571.7, 1484.4, 1399.7, 1227.7, 1140.4, 1073.1, 749.0, 701.6, 621.8.



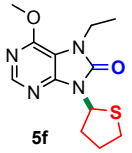
5c **7-benzyl-6-methoxy-9-(tetrahydrothiophen-2-yl)-7*H*-purin-8(9*H*)-one (5c):** White solid; mp 116-118 °C; 22.6 mg, 66% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.28-7.26 (m, 1H), 6.35-6.19 (m, 1H), 5.14 (s, 2H), 4.05 (s, 3H), 3.48 (td, *J* = 9.1, 8.6, 5.0 Hz, 1H), 2.97 (dt, *J* = 10.2, 4.4 Hz, 1H), 2.75-2.66 (m, 1H), 2.62 (dt, *J* = 10.7, 5.1 Hz, 1H), 2.39 (dq, *J* = 12.2, 6.3, 5.5 Hz, 1H), 2.08-2.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 152.0, 150.0, 148.3, 137.1, 128.7, 128.1, 127.9, 107.8, 60.2, 53.9, 46.3, 34.5, 34.3, 31.8; HRMS(ESI): $[M+Na]^+$ calculated for $C_{17}H_{18}N_4NaO_2S$: 365.1043, found: 365.1051; IR(KBr): 3032.6, 2935.4, 2855.6, 1718.8, 1621.6, 1472.0, 1434.6, 1399.7, 1339.8, 1272.5, 1157.9, 1093.0, 741.5, 699.1, 601.9.



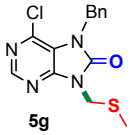
5d **6-chloro-7-ethyl-9-(tetrahydrothiophen-2-yl)-7*H*-purin-8(9*H*)-one (5d):** White solid; mp 33-35 °C; 19.0 mg, 67% yield; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (s, 1H), 6.32 (t, J = 7.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.52-3.45 (m, 1H), 3.02-2.97 (m, 1H), 2.70-2.59 (m, 2H), 2.45-2.38 (m, 1H), 2.11-2.04 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 150.1, 149.4, 135.8, 119.4, 60.4, 37.3, 34.6, 34.2, 31.8, 15.5; HRMS(ESI): $[M+Na]^+$ calculated for $C_{11}H_{13}ClN_4NaOS$: 307.0391, found: 307.0393; IR(KBr): 3060.1, 2977.8, 2940.4, 2860.6, 1728.8, 1606.6, 1574.2, 1477.0, 1354.8, 1197.7, 1167.8, 1095.5, 542.1.



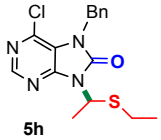
5e **2,6-dichloro-7-ethyl-9-(tetrahydrothiophen-2-yl)-7*H*-purin-8(9*H*)-one (5e):** Yellow solid; mp 30-32 °C; 21.9mg, 69% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.26 (dd, *J* = 8.1, 5.5 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.47 (td, *J* = 10.1, 9.5, 5.4 Hz, 1H), 3.00 (dd, *J* = 16.5, 4.0 Hz, 1H), 2.72-2.52 (m, 2H), 2.50-2.34 (m, 1H), 2.18-2.01 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.4, 150.8, 150.5, 135.9, 118.4, 60.6, 37.4, 34.7, 34.4, 31.9, 15.5; HRMS(ESI): $[M+Na]^+$ calculated for $C_{11}H_{12}Cl_2N_4NaOS$: 341.0001, found: 341.0003; IR(KBr): 2976.8, 2935.9, 2858.6, 1737.0, 1606.9, 1568.4, 1485.5, 1398.4, 1228.1, 1177.6, 1074.8, 867.2, 769.0, 711.6, 618.0, 574.2.



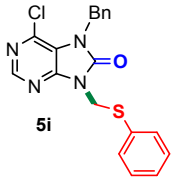
5f **7-ethyl-6-methoxy-9-(tetrahydrothiophen-2-yl)-7*H*-purin-8(9*H*)-one (5f):** White solid; mp 106-108 °C; 17.9 mg, 64% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 6.31 (t, 1H), 4.09 (s, 3H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.56-3.42 (m, 1H), 2.98 (dd, *J* = 16.2, 4.1 Hz, 1H), 2.77-2.56 (m, 2H), 2.45-2.34 (m, 1H), 2.05 (dd, *J* = 12.3, 6.3 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 151.6, 149.8, 148.3, 107.7, 60.1, 54.0, 37.9, 34.5, 34.3, 31.8, 15.3; HRMS(ESI): $[M+Na]^+$ calculated for $C_{12}H_{16}N_4NaO_2S$: 303.0886, found: 303.0890; IR(KBr): 2942.7, 1719.8, 1622.0, 1472.9, 1429.2, 1355.5, 1272.8, 1113.1, 1092.2, 997.8, 779.7.



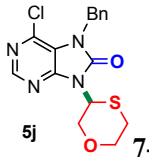
5g **7-benzyl-6-chloro-9-((methylthio)methyl)-7*H*-purin-8(9*H*)-one (5g):** Yellow solid; mp 69-71 °C; 21.8 mg, 68% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 7.34-7.30 (m, 5H), 5.35 (s, 2H), 5.07 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 150.8, 149.8, 136.3, 136.1, 128.9, 128.1, 127.3, 119.5, 45.5, 44.2, 16.1; HRMS(ESI): $[M+Na]^+$ calculated for $C_{14}H_{13}ClN_4NaOS$: 343.0391, found: 343.0393; IR(KBr): 3065.1, 3032.6, 2925.4, 2848.2, 1733.7, 1611.6, 1581.7, 1484.4, 1427.1, 1392.2, 1170.3, 1135.4, 1068.1, 736.5, 701.6, 604.4.



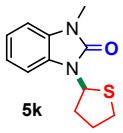
5h **7-benzyl-6-chloro-9-(1-(ethylthio)ethyl)-7*H*-purin-8(9*H*)-one (5h):** White solid; mp 80-82 °C; 21.9 mg, 63% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 7.34-7.29 (m, 5H), 5.84 (q, J = 7.2 Hz, 1H), 5.35 (d, *J* = 3.4 Hz, 2H), 2.65-2.60 (m, 1H), 2.53-2.48 (m, 1H), 1.98 (d, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 150.6, 149.6, 136.4, 136.3, 128.9, 128.1, 127.3, 119.3, 53.8, 45.4, 26.0, 19.8, 14.6; HRMS(ESI): $[M+Na]^+$ calculated for $C_{16}H_{17}ClN_4NaOS$: 371.0704, found: 371.0710; IR(KBr): 3062.6, 2967.8, 2927.9, 2850.6, 1731.3, 1604.1, 1569.2, 1474.5, 1429.6, 1352.3, 1170.3, 1120.5, 1075.6, 744.0, 701.6, 534.6.



7-benzyl-6-chloro-9-((phenylthio)methyl)-7*H*-purin-8(9*H*)-one (5i): White solid; mp 83-85 °C; 26.4 mg, 69% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.45-7.43 (d, 2H), 7.33-7.28 (t, 3H), 7.26-7.20 (t, 5H), 5.34 (s, 2H), 5.28 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 150.7, 149.5, 136.2, 136.1, 133.2, 132.0, 129.1, 128.9, 128.5, 128.1, 127.3, 119.3, 45.4, 45.2; HRMS(ESI): $[M+Na]^+$ calculated for $C_{19}H_{15}ClN_4NaOS$: 405.0547, found: 405.0551; IR(KBr): 3065.1, 2925.4, 2853.1, 1738.7, 1606.6, 1581.7, 1491.9, 1444.6, 1167.8, 1135.4, 746.5, 696.6, 599.4.

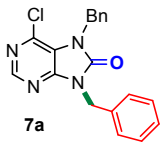


7-benzyl-6-chloro-9-(1,4-oxathian-3-yl)-7*H*-purin-8(9*H*)-one (5j): White solid; mp 143-145 °C; 26.1 mg, 72% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 7.35-7.29 (s, 5H), 5.68 (d, J = 7.6 Hz, 1H), 5.34 (s, 2H), 4.67-4.61 (t, 1H), 4.19-4.09 (t, 2H), 3.99-3.93 (t, 1H), 3.16-3.01 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 150.6, 149.6, 136.6, 136.0, 128.9, 128.2, 127.4, 119.4, 70.1, 67.9, 49.7, 45.6, 28.4; HRMS(ESI): $[M+Na]^+$ calculated for $C_{16}H_{15}ClN_4NaO_2S$: 385.0496, found: 385.0500; IR(KBr): 3065.1, 3030.1, 2925.4, 2853.1, 1733.7, 1601.6, 1579.2, 1472.0, 1432.1, 1167.8, 1142.9, 1105.5, 746.5, 704.1, 629.3.

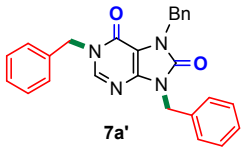


1-methyl-3-(tetrahydrothiophen-2-yl)-1*H*-benzo[d]imidazol-2(3*H*)-one(5k):

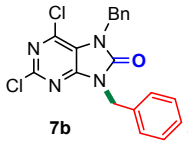
White solid; mp 138-140 °C; 18.7 mg, 80% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.4 Hz, 1H), 7.00 (m, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 7.1 Hz, 1H), 6.26 (t, *J* = 7.7 Hz, 1H), 3.29 (s, 3H), 3.21 (td, *J* = 10.4, 5.2 Hz, 1H), 2.98-2.92 (m, 1H), 2.38-2.24 (m, 3H), 2.04-1.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 130.3, 127.0, 121.4, 121.0, 110.3, 107.6, 60.8, 34.3, 33.9, 30.9, 27.1; HRMS (ESI): $[M+H]^+$ calculated for $C_{12}H_{15}N_2OS$: 235.0900, found: 235.0904; IR(KBr): 2936.8, 2864.3, 1705.4, 1616.5, 1497.7, 1391.9, 1249.2, 1055.1, 907.2, 745.6, 689.5, 560.9, 438.9.



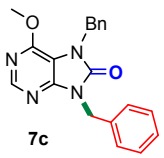
7a **7,9-dibenzyl-6-chloro-7,9-dihydro-8*H*-purin-8-one (7a)[3]:** Colorless oil; 24.5 mg, 70% yield; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.49 (s, 1H), 7.54 (d, J = 7.0 Hz, 2H), 7.34 (dt, J = 13.8, 6.4 Hz, 8H), 5.35 (s, 2H), 5.19 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 150.8, 150.2, 136.4, 136.0, 135.4, 128.9, 128.9, 128.7, 128.3, 128.1, 127.4, 119.3, 45.4, 44.5; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{16}N_4OCl$: 351.1013, found: 351.1021; IR(KBr): 3063.1, 3032.6, 2927.4, 2851.4, 1732.4, 1604.1, 1577.9, 1496.1, 1435.7, 1398.9, 1349.5, 1260.5, 1169.9, 1013.9, 747.2, 699.0, 537.3.



7a' **1,7,9-tribenzyl-7,9-dihydro-1*H*-purine-6,8-dione(7a'):** White solid; mp 62-64 °C; 9.3 mg, 22% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63-7.51 (m, 5H), 7.44-7.27 (m, 11H), 5.49 (s, 2H), 5.32 (s, 2H), 5.27 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 151.5, 148.7, 141.1, 137.4, 136.5, 135.3, 129.2, 128.8, 128.7, 128.6, 128.5, 128.3, 127.9, 127.6, 107.2, 50.3, 46.7, 44.6; HRMS (ESI): $[M+H]^+$ calculated for $C_{26}H_{23}N_4O_2$: 423.1816, found: 423.1815; IR(KBr): 3031.2, 2952.5, 1703.3, 1657.2, 1540.1, 1453.4, 1386.3, 1253.9, 1119.9, 1070.5, 943.1, 821.0, 723.9, 695.8, 518.2, 499.9.

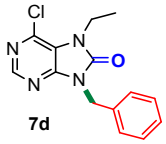


7b **7,9-dibenzyl-2,6-dichloro-7,9-dihydro-8*H*-purin-8-one (7b):** Yellow solid; mp 114-116 °C; 28.4 mg, 74% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.7 Hz, 1H), 7.34 (m, 9H), 5.32 (s, 2H), 5.16 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 151.7, 151.2, 136.2, 136.0, 134.9, 128.9, 128.9, 128.9, 128.5, 128.2, 127.3, 118.3, 45.5, 44.7; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{15}N_4OCl_2$: 385.0623, found: 385.0629; IR(KBr): 3063.7, 3029.0, 2925.3, 2853.1, 1955.8, 1732.2, 1609.9, 1576.9, 1450.1, 1397.0, 1281.7, 1141.5, 1013.9, 906.1, 876.5, 753.4, 695.7, 574.2, 450.3.



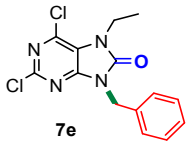
7c **7,9-dibenzyl-6-methoxy-7,9-dihydro-8*H*-purin-8-one (7c)[3]:** White solid; mp 80-82 °C; 24.6 mg, 71% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.51 (d, *J* = 7.3

Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 2H), 7.37-7.25 (m, 6H), 5.20 (s, 2H), 5.16 (s, 2H), 4.08 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 152.4, 150.4, 149.1, 137.2, 136.2, 128.7, 128.7, 128.5, 128.1, 128.0, 127.9, 107.6, 53.9, 46.4, 44.1; HRMS (ESI): $[M+H]^+$ calculated for $C_{20}H_{19}N_4O_2$: 347.1508, found: 347.1514; IR(KBr): 3444.5, 1717.8, 1626.6, 1496.0, 1339.4, 1107.4, 1029.1, 697.9, 613.5.



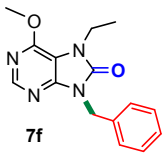
7d

9-benzyl-6-chloro-7-ethyl-7,9-dihydro-8*H*-purin-8-one (7d): Light yellow oil; 17.9 mg, 62% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.26 (dt, *J* = 13.8, 7.4 Hz, 3H), 5.09 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 150.4, 150.1, 135.5, 135.5, 128.7, 128.7, 128.2, 119.2, 44.2, 37.3, 15.6; HRMS (ESI): $[M+H]^+$ calculated for $C_{14}H_{14}N_4OCl$: 289.0856, found: 289.0865; IR(KBr): 3063.2, 3033.4, 2977.7, 2934.7, 1731.9, 1604.5, 1577.9, 1497.0, 1351.0, 1259.4, 1169.5, 1095.5, 933.6, 820.0, 748.7, 641.3, 538.6.



7e

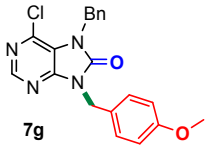
9-benzyl-2,6-dichloro-7-ethyl-7,9-dihydro-8*H*-purin-8-one (7e): Yellow solid; mp 88-90 °C; 21.3 mg, 66% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.26 (dt, *J* = 14.3, 6.9 Hz, 3H), 5.06 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 151.6, 150.8, 135.6, 134.9, 128.8, 128.8, 128.3, 118.3, 44.5, 37.4, 15.6; HRMS (ESI): $[M+H]^+$ calculated for $C_{14}H_{13}N_4OCl_2$: 323.0466, found: 323.0475; IR(KBr): 3448.3, 3065.8, 2929.6, 2853.6, 1957.4, 1871.6, 1731.6, 1609.6, 1575.4, 1454.7, 1348.1, 1230.3, 1084.9, 930.7, 862.5, 710.3, 676.6, 574.8, 448.7.



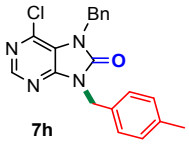
7f

9-benzyl-7-ethyl-6-methoxy-7,9-dihydro-8*H*-purin-8-one (7f)[3]: White solid; mp 95-97 °C; 17. 1 mg, 60% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.28 (dt, *J* = 15.1, 7.0 Hz, 3H), 5.11 (s, 2H), 4.07 (s, 3H), 4.07-4.01 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 152.3, 150.1, 149.0, 136.3, 128.6, 128.4, 127.9, 107.4, 54.0, 44.0, 37.9, 15.4; HRMS (ESI): $[M+H]^+$ calculated for $C_{15}H_{17}N_4O_2$: 285.1352,

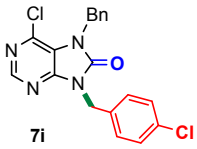
found: 285.1361; IR(KBr): 3293.2, 3063.7, 3033.4, 2977.9, 2948.7, 1964.4, 1905.4, 1716.5, 1617.8, 1584.6, 1502.7, 1472.4, 1347.3, 1292.2, 1116.0, 1023.5, 955.6, 888.4, 788.6, 660.9, 568.0, 487.5.



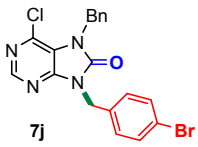
7g **7-benzyl-6-chloro-9-(4-methoxybenzyl)-7,9-dihydro-8*H*-purin-8-one (7g):** White solid; mp 124-126 °C; 29.7 mg, 78% yield; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.48 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.37-7.25 (m, 5H), 6.87 (d, J = 8.4 Hz, 2H), 5.34 (s, 2H), 5.12 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 153.1, 150.8, 150.2, 136.3, 135.9, 130.3, 128.9, 128.0, 127.6, 127.4, 119.3, 114.2, 55.3, 45.4, 44.0; HRMS (ESI): $[M+H]^+$ calculated for $C_{20}H_{18}N_4O_2Cl$: 381.1118, found: 381.1123; IR(KBr): 3065.1, 3035.6, 2982.3, 2940.8, 2845.7, 2360.1, 2342.1, 1864.4, 1741.1, 1605.3, 1574.0, 1513.3, 1494.6, 1428.0, 1303.5, 1258.5, 1166.3, 1058.6, 935.3, 832.9, 744.6, 688.8.



7h **7-benzyl-6-chloro-9-(4-methylbenzyl)-7,9-dihydro-8*H*-purin-8-one (7h):** White solid; mp 92-94 °C; 28.0 mg, 77% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.39-7.27 (m, 5H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.35 (s, 2H), 5.16 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 150.8, 150.3, 138.1, 136.4, 135.9, 132.5, 129.5, 128.9, 128.7, 128.0, 127.4, 119.3, 45.4, 44.2, 21.2; HRMS (ESI): $[M+H]^+$ calculated for $C_{20}H_{18}N_4OCl$: 365.1169, found: 365.1178; IR(KBr): 3034.9, 2953.9, 2924.8, 1945.5, 1871.1, 1741.8, 1605.2, 1571.2, 1454.6, 1361.8, 1252.3, 1137.0, 939.0, 843.9, 739.9, 694.8, 544.9, 471.8.

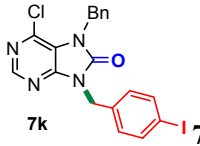


7i **7-benzyl-6-chloro-9-(4-chlorobenzyl)-7,9-dihydro-8*H*-purin-8-one (7i):** White solid; mp 101-103 °C; 31.1 mg, 81% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.38-7.16 (m, 7H), 5.34 (s, 2H), 5.13 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 150.8, 150.1, 136.2, 136.1, 134.3, 133.8, 130.2, 129.0, 128.9, 128.1, 127.4, 119.3, 45.4, 43.7; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{15}N_4OCl_2$: 385.0623, found: 385.0632; IR(KBr): 3455.8, 2058.2, 3033.1, 2967.4, 2923.4, 2849.7, 2360.0, 1862.4, 1732.5, 1606.1, 1583.8, 1498.9, 1397.1, 1274.0, 1172.0, 1013.8, 920.0, 838.2, 752.8, 697.2, 571.5.



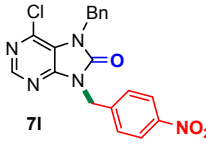
7j **7-benzyl-9-(4-bromobenzyl)-6-chloro-7,9-dihydro-8*H*-purin-8-one (7j):**

White solid; mp 140-142 °C; 35.5 mg, 83% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.35-7.28 (m, 5H), 5.34 (s, 2H), 5.12 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 150.8, 150.0, 136.2, 136.2, 134.3, 132.0, 130.5, 128.9, 128.1, 127.4, 122.5, 119.3, 45.4, 43.8; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{15}N_4OClBr$: 429.0118, found: 429.0126; IR(KBr): 3087.8, 3030.4, 2865.2, 2849.5, 1865.6, 1730.5, 1605.8, 1583.2, 1498.1, 1354.5, 1273.8, 1171.4, 1012.4, 900.4, 736.2, 697.5, 536.9, 476.2.



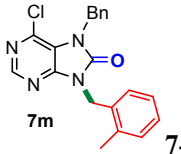
7k **7-benzyl-6-chloro-9-(4-iodobenzyl)-7,9-dihydro-8*H*-purin-8-one (7k):**

White solid; mp 163-165 °C; 39.0 mg, 82% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.42-7.08 (m, 7H), 5.35 (s, 2H), 5.11 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 150.8, 150.0, 138.0, 136.2, 136.2, 134.9, 130.7, 128.9, 128.1, 127.4, 119.3, 94.2, 45.5, 43.9; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{15}N_4OClI$: 476.9979, found: 476.9980; IR(KBr): 3031.2, 2964.7, 2849.5, 1909.5, 1867.8, 1722.8, 1605.9, 1581.9, 1495.0, 1354.8, 1225.0, 1170.9, 1014.8, 919.5, 836.7, 752.7, 697.5, 570.7, 472.0.



7l **7-benzyl-6-chloro-9-(4-nitrobenzyl)-7,9-dihydro-8*H*-purin-8-one (7l):**

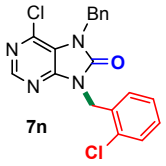
White solid; mp 138-140 °C; 28.4 mg, 72% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.37-7.29 (m, 4H), 7.26 (s, 1H), 5.35 (s, 2H), 5.25 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 150.9, 149.9, 147.9, 142.1, 136.5, 136.0, 129.6, 129.0, 128.2, 127.4, 124.1, 119.4, 45.6, 44.0; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{15}N_5O_3Cl$: 396.0858, found: 396.0860; IR(KBr): 3054.2, 3028.5, 2865.1, 2846.0, 1859.3, 1736.1, 1601.3, 1579.2, 1495.5, 1358.5, 1278.6, 1172.6, 1010.5, 901.9, 733.2, 694.8.



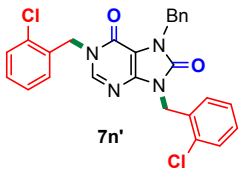
7m **7-benzyl-6-chloro-9-(2-methylbenzyl)-7,9-dihydro-8*H*-purin-8-one (7m):**

White solid; mp 80-82 °C; 26.9 mg, 74% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H),

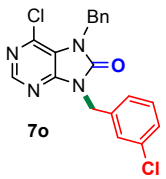
7.37 (d, J = 6.4 Hz, 4H), 7.32 (dd, J = 9.6, 4.5 Hz, 2H), 7.22 (d, J = 3.9 Hz, 2H), 7.17 (dd, J = 7.6, 4.1 Hz, 1H), 5.38 (s, 2H), 5.22 (s, 2H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 150.8, 150.5, 136.4, 136.3, 136.0, 133.3, 130.7, 128.9, 128.4, 128.2, 128.1, 127.4, 126.3, 119.3, 45.4, 42.0, 19.6; HRMS (ESI): $[M+H]^+$ calculated for $C_{20}H_{18}N_4OCl$: 365.1169, found: 365.1178; IR(KBr): 3438.3, 3066.1, 3025.3, 2924.6, 2853.5, 1947.3, 1911.6, 1723.5, 1613.9, 1492.0, 1352.9, 1299.6, 1162.0, 1068.8, 958.9, 897.0, 775.1, 661.5, 540.0.



7-benzyl-6-chloro-9-(2-chlorobenzyl)-7,9-dihydro-8*H*-purin-8-one (7n): White solid; mp 100-102 °C; 30.7 mg, 80% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 7.46-7.27 (m, 5H), 7.21 (m, 4H), 5.39 (s, 2H), 5.34 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 150.9, 150.3, 136.3, 136.2, 133.1, 132.4, 129.9, 129.3, 128.9, 128.8, 128.1, 127.4, 127.0, 119.4, 45.5, 42.2; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{15}N_4OCl_2$: 385.0623, found: 385.0627; IR(KBr): 3451.7, 3066.5, 3033.7, 1881.4, 1731.9, 1606.6, 1581.6, 1498.5, 1433.6, 1356.5, 1267.0, 1171.7, 1139.6, 1013.7, 918.2, 753.3, 693.1, 538.3.

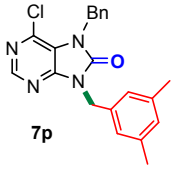


7-benzyl-1,9-bis(2-chlorobenzyl)-7,9-dihydro-1*H*-purine-6,8-dione (7n'): White solid; mp 65-67 °C; 7.4 mg, 15% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.37 (s, 7H), 7.19 (dd, J = 5.6, 3.4 Hz, 4H), 7.08-6.99 (m, 2H), 5.48 (d, J = 5.6 Hz, 4H), 5.40 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 151.2, 149.0, 141.6, 135.1, 134.3, 133.6, 133.0, 132.8, 129.8, 129.7, 129.2, 128.8, 128.7, 128.3, 127.1, 127.0, 126.9, 126.6, 107.0, 50.5, 44.6, 42.5; HRMS (ESI): $[M+Na]^+$ calculated for $C_{26}H_{20}Cl_2N_4NaO_2$: 513.0856, found: 513.0862; IR(KBr): 3432.9, 3063.5, 2965.4, 1672.7, 1562.4, 1457.3, 1346.2, 1276.5, 1092.4, 1018.2, 756.0, 659.3.

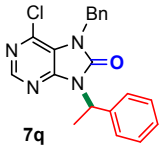


7-benzyl-6-chloro-9-(3-chlorobenzyl)-7,9-dihydro-8*H*-purin-8-one (7o): Yellow solid; mp 62-64 °C; 29.6 mg, 77% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.49 (s, 1H), 7.42-7.21 (m, 8H), 5.35 (s, 2H), 5.14 (s, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0,

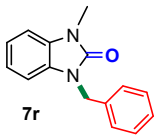
150.9, 150.1, 137.2, 136.2, 136.2, 134.7, 130.2, 128.9, 128.7, 128.6, 128.1, 127.4, 126.8, 119.3, 45.5, 43.8; HRMS (ESI): $[M+H]^+$ calculated for $C_{19}H_{15}N_4OCl_2$: 385.0623, found: 385.0631; IR(KBr): 3450.0, 3062.8, 3032.4, 2930.5, 2850.3, 1954.6, 1873.3, 1735.1, 1602.9, 1578.3, 1493.9, 1455.0, 1345.8, 1253.1, 1170.3, 1134.7, 1078.0, 1029.3, 899.0, 825.4, 749.7, 698.0, 565.3, 460.2.



7p **7-benzyl-6-chloro-9-(3,5-dimethylbenzyl)-7,9-dihydro-8*H*-purin-8-one (7p):** White solid; mp 93-95 °C; 27.2 mg, 72% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.46-7.26 (m, 5H), 7.12 (s, 2H), 6.96 (s, 1H), 5.37 (s, 2H), 5.13 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 150.8, 150.3, 138.5, 136.4, 136.0, 135.2, 130.0, 128.9, 128.1, 127.4, 126.2, 119.3, 45.4, 44.4, 21.3; HRMS (ESI): $[M+H]^+$ calculated for $C_{21}H_{20}N_4OCl$: 379.1326, found: 379.1331; IR(KBr): 3455.8, 3067.3, 2917.4, 2857.0, 2735.9, 2360.0, 1941.1, 1899.2, 1732.3, 1606.7, 1577.5, 1454.5, 1349.5, 1257.8, 1135.0, 901.2, 704.9, 692.4, 540.3.

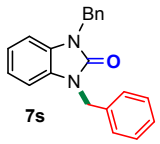


7q **7-benzyl-6-chloro-9-(1-phenylethyl)-7,9-dihydro-8*H*-purin-8-one (7q):** Yellow solid; mp 62-64 °C; 24.8 mg, 68% yield; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (s, 1H), 7.61 (d, J = 7.5 Hz, 2H), 7.48-7.18 (m, 8H), 5.92 (d, J = 7.3 Hz, 1H), 5.35 (s, 2H), 2.11 (d, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 150.5, 150.3, 139.7, 136.5, 136.0, 128.9, 128.7, 128.2, 128.0, 127.5, 127.3, 119.1, 52.9, 45.3, 17.7; HRMS (ESI): $[M+H]^+$ calculated for $C_{20}H_{18}N_4OCl$: 365.1169, found: 365.1178; IR(KBr): 3063.8, 3032.0, 2981.6, 2935.3, 1954.2, 1876.5, 1728.5, 1602.8, 1572.6, 1478.8, 1396.7, 1332.4, 1173.1, 1139.0, 1028.2, 938.0, 845.0, 748.7, 697.6, 570.9.

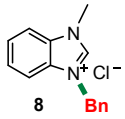


7r **1-benzyl-3-methyl-1,3-dihydro-2*H*-benzo[d]imidazol-2-one (7r)[3]:** White solid; mp 85-87 °C; 21.4 mg, 90% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.15-7.10 (m, 1H), 6.93 (dt, *J* = 22.8, 7.7 Hz, 2H), 6.79 (d, *J* = 7.7 Hz, 2H), 4.94 (s, 2H), 3.27 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 136.6, 130.0, 129.0, 128.6, 127.6, 127.6, 121.2, 121.1, 108.0, 107.4, 44.6, 27.0; HRMS (ESI): $[M+H]^+$ calculated for $C_{15}H_{15}N_2O$:

239.1184, found: 239.1191; IR(KBr): 3402.0, 3026.9, 2921.9, 1911.2, 1856.6, 1711.8, 1617.6, 1499.7, 1398.7, 1246.8, 1121.5, 1097.3, 925.2, 836.7, 731.7, 635.4, 557.7, 455.5.



7s **1,3-dibenzyl-1,3-dihydro-2*H*-benzo[d]imidazol-2-one (7s)[3]:** White solid; mp 106-108 °C; 27.6 mg, 88% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.4 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 4H), 7.33-7.26 (m, 2H), 7.03 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.98-6.93 (m, 2H), 5.17 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 136.6, 129.4, 128.9, 127.8, 127.7, 121.5, 108.5, 45.0; HRMS (ESI): $[M+H]^+$ calculated for $C_{21}H_{19}N_2O$: 315.1497, found: 315.1506; IR(KBr): 3366.6, 3063.7, 3025.2, 2925.4, 1946.8, 1875.2, 1697.3, 1608.4, 1586.7, 1491.8, 1407.3, 1355.9, 1201.9, 1164.0, 1079.2, 915.3, 849.3, 751.0, 697.2.

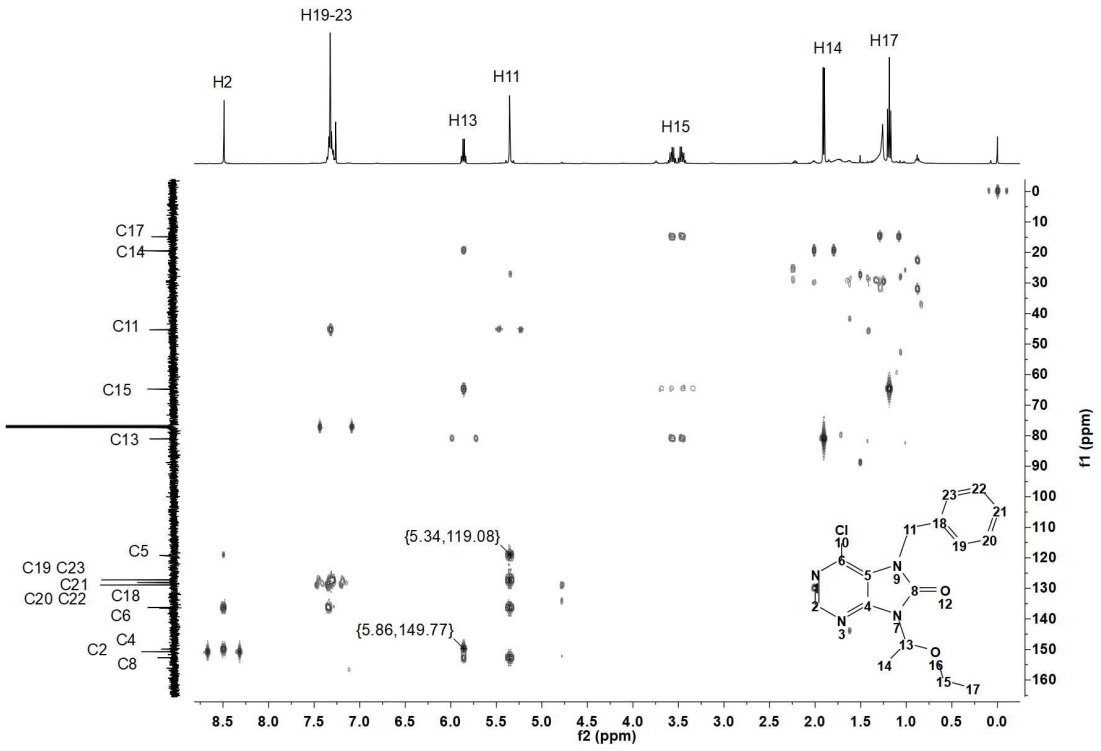


8 **3-benzyl-1-methyl-1*H*-benzo[d]imidazol-3-ium chloride (8):** White solid; mp 95-97 °C; 1.55 g (5 mmol), 60% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1H), 8.01 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 16.0, 6.4 Hz, 4H), 7.35 (q, *J* = 12.3, 9.4 Hz, 3H), 5.85 (s, 2H), 4.13 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 143.6, 134.6, 132.4, 131.0, 131.0, 129.4, 129.1, 128.8, 127.0, 127.0, 114.2, 50.2, 33.9; HRMS (ESI) calculated for $[C_{15}H_{15}N_2]^+$: 223.1230, found: 223.1236; IR(KBr): 3358.8, 3063.5, 2965.4, 1672.7, 1562.4, 1457.3, 1346.2, 1206.9, 1092.4, 1018.2, 851.4, 756.0, 659.3.

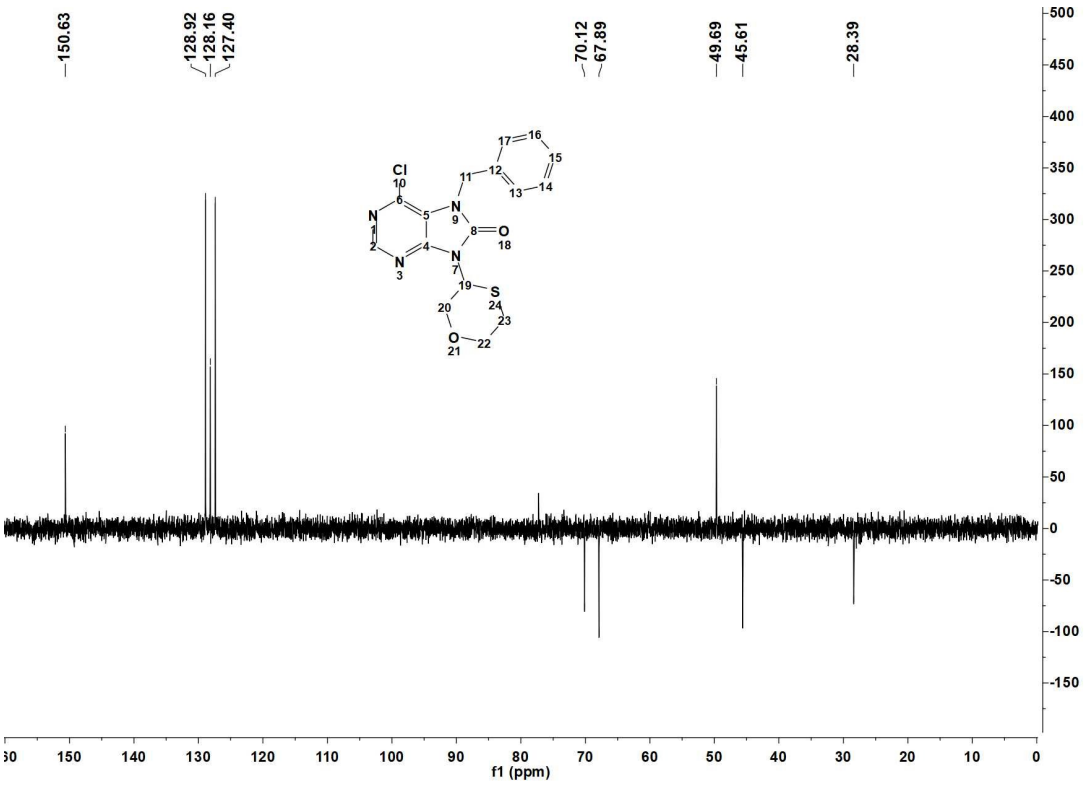
Ⅶ. Reference

1. L.-K. Huang, Y.-C. Cherng, Y.-R. Cheng, J.-P. Jang, Y.-L. Chao and Y.-J. Cherng, *Tetrahedron*, 2007, **63**, 5323-5327.
2. J. L. Kelley, R. G. Davis, T. E. W. McLean, T. R. C. Glen, F. E. Soroko and B. R. Cooper, *J. Med. Chem.*, 1995, **38**, 3884-3888.
3. J.-P. Li, Y. Huang, M.-S. Xie, G.-R. Qu, H.-Y. Niu, H.-X. Wang, B.-W. Qin and H.-M. Guo, *J. Org. Chem.*, 2013, **78**, 12629-12636.

Ⅷ. HMBC spectrum for 3l

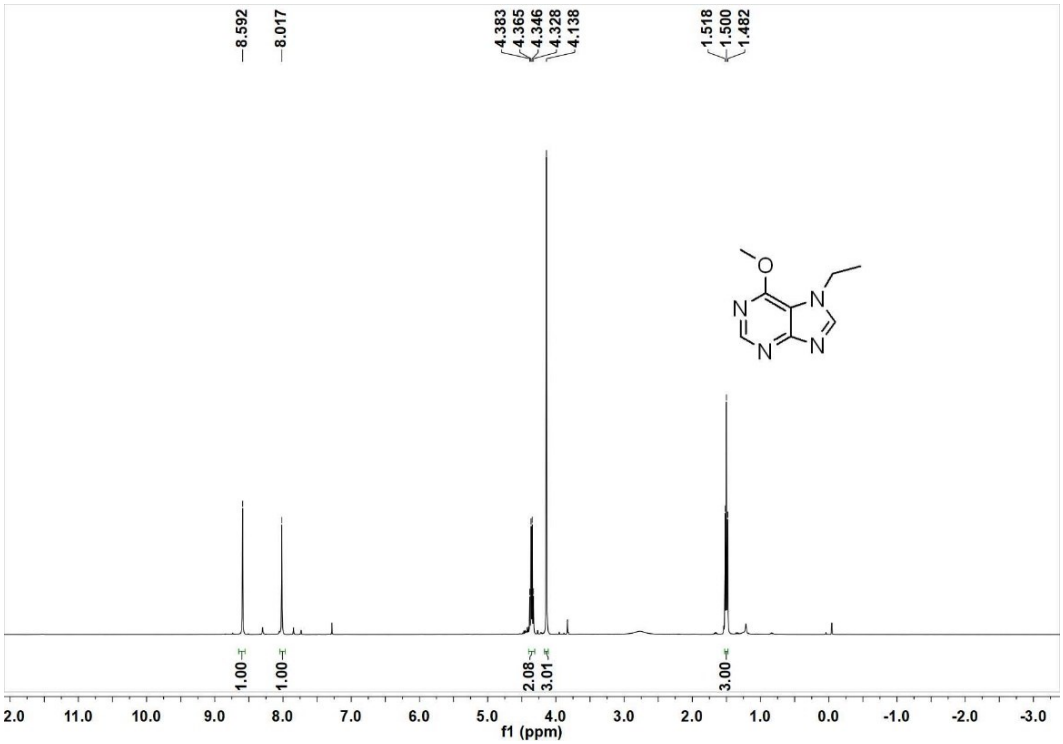


Ⅸ. DEPT spectrum (100 MHz, $CDCl_3$) of 5j

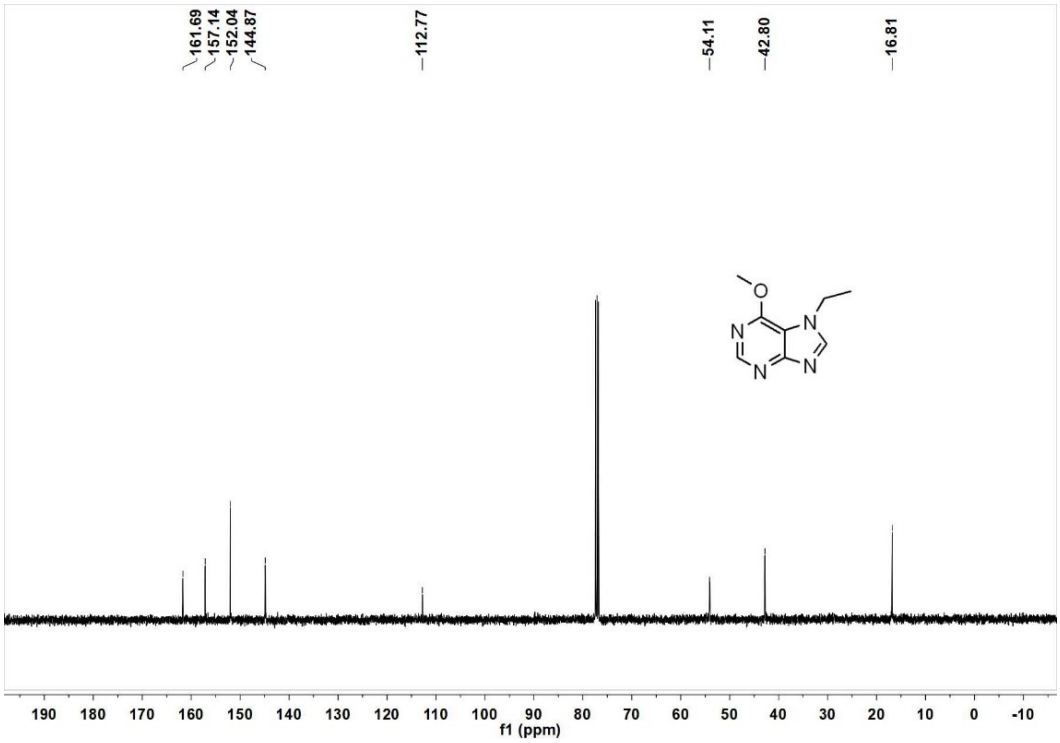


Ⅹ. ^{1}H NMR and ^{13}C NMR spectrum for all isolated products.

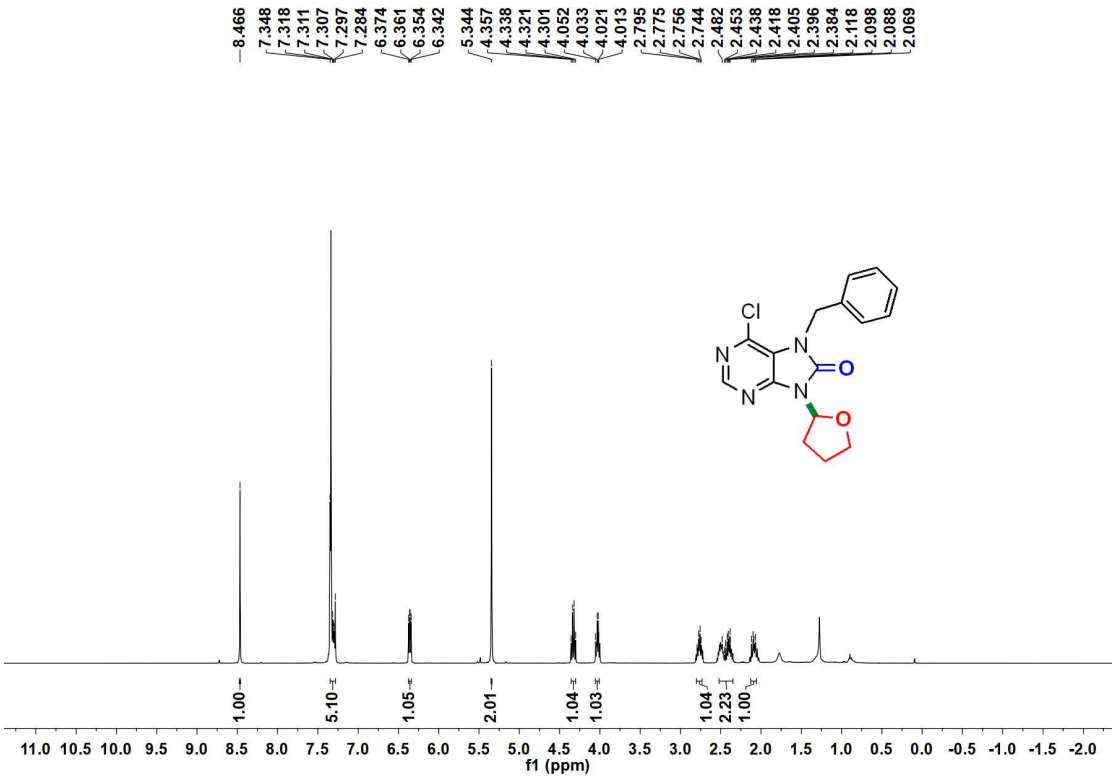
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1f**



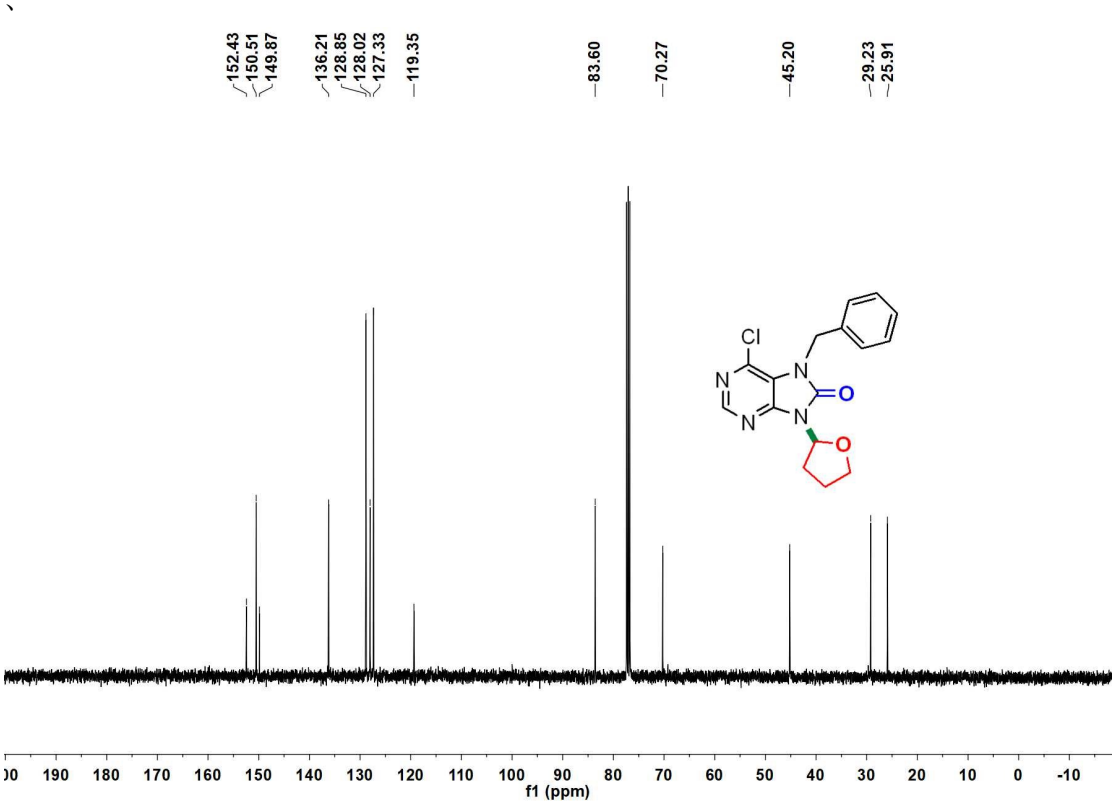
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1f**



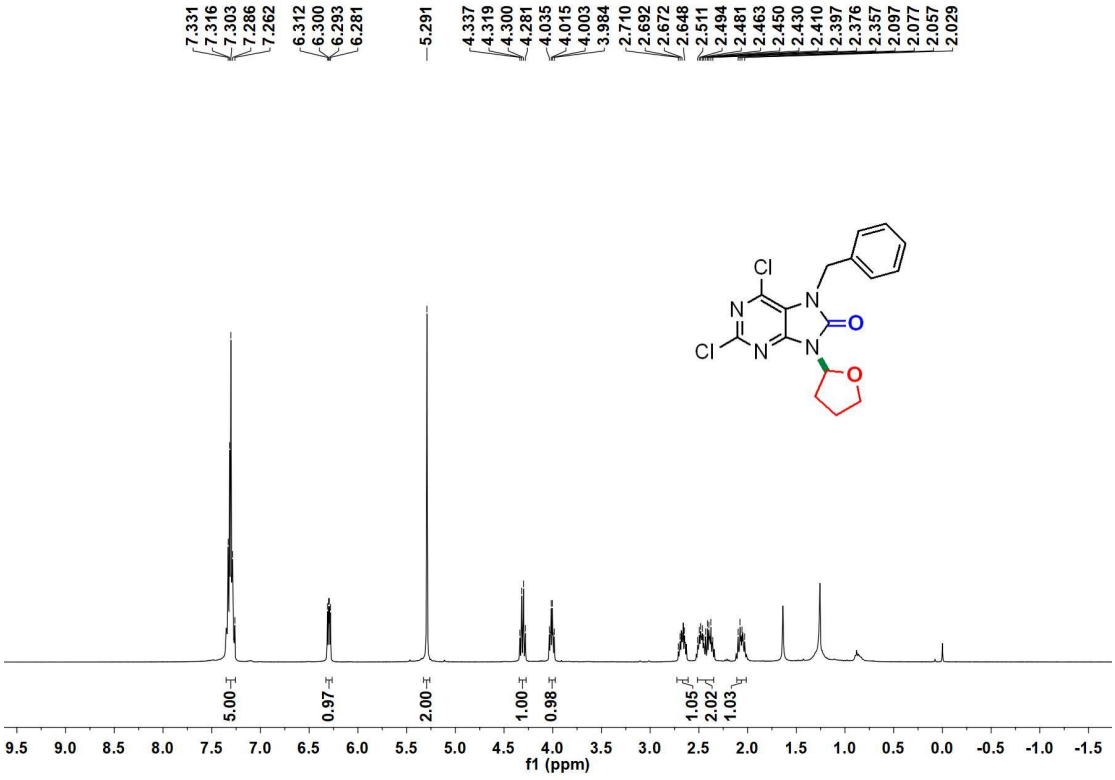
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



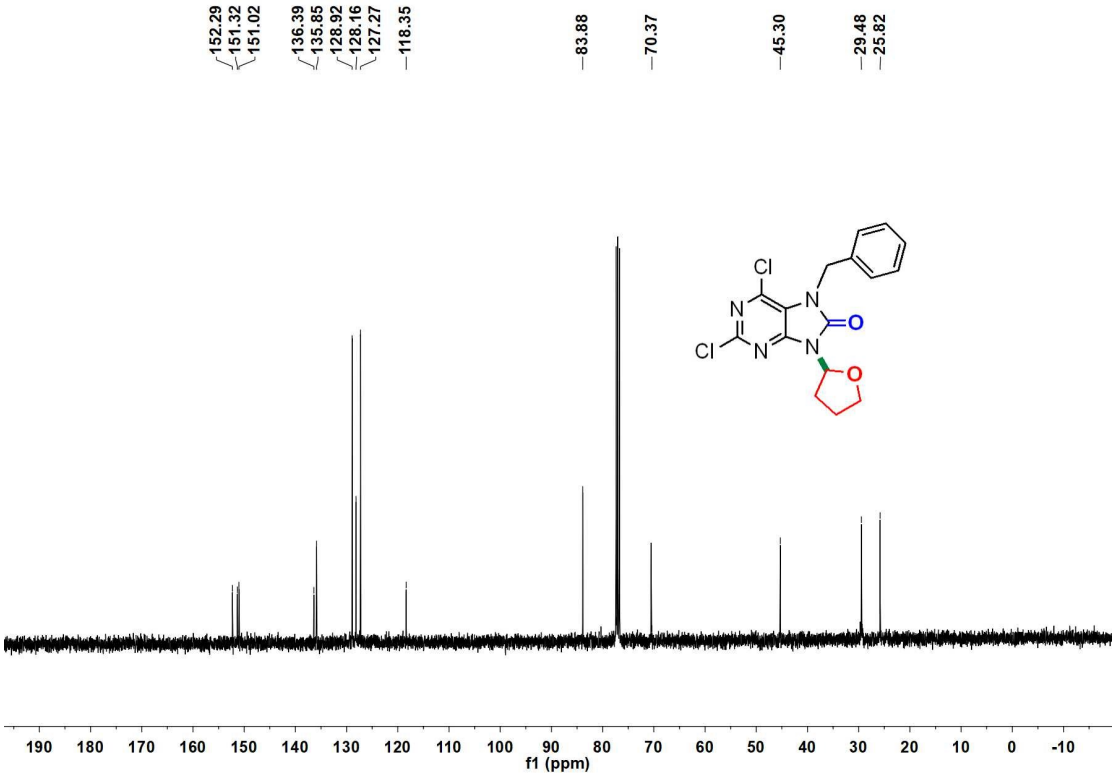
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3a**



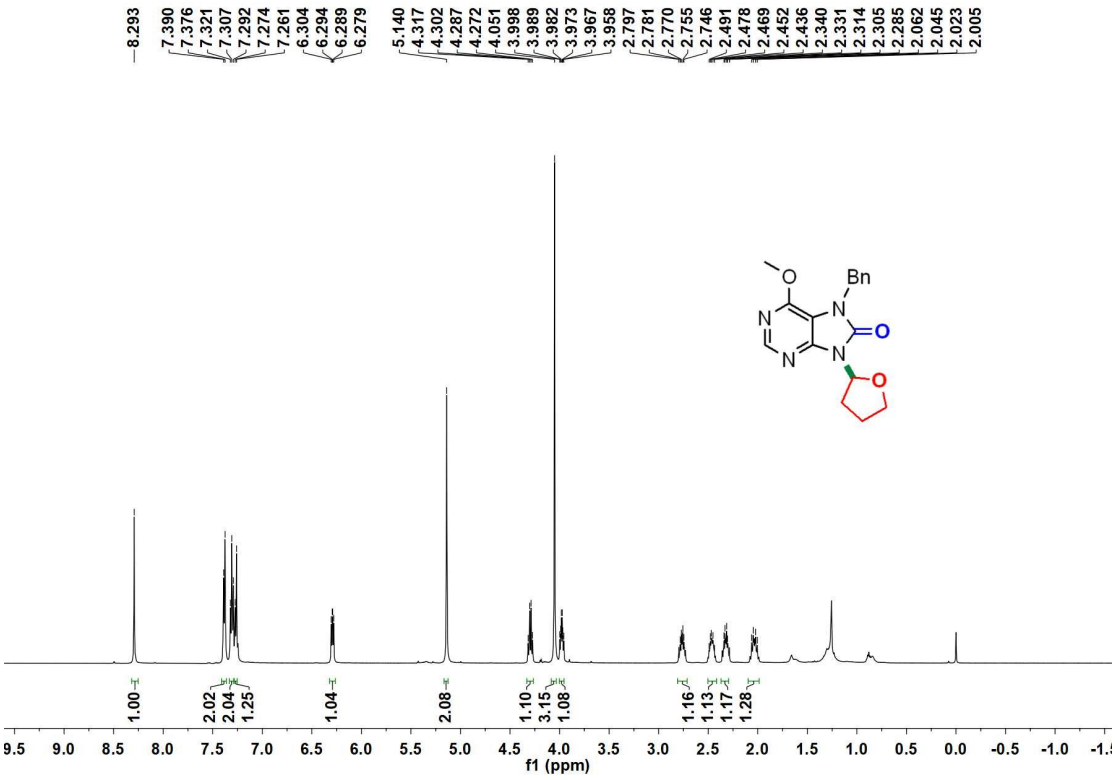
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**



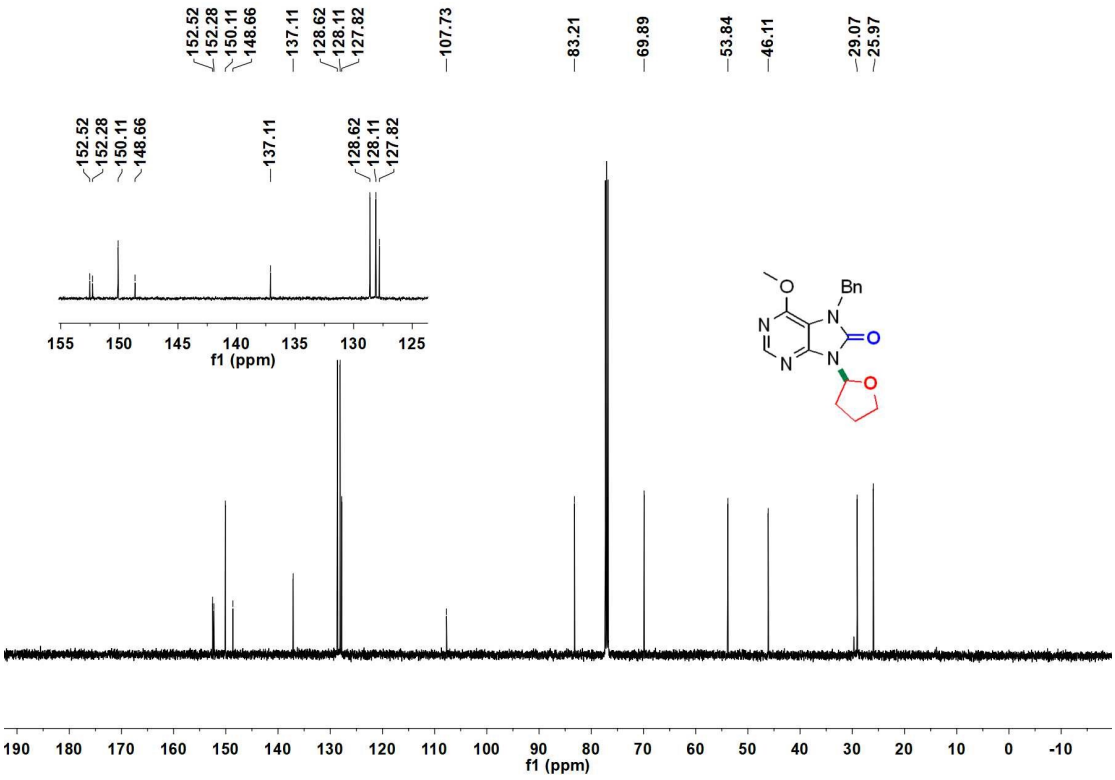
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3b**



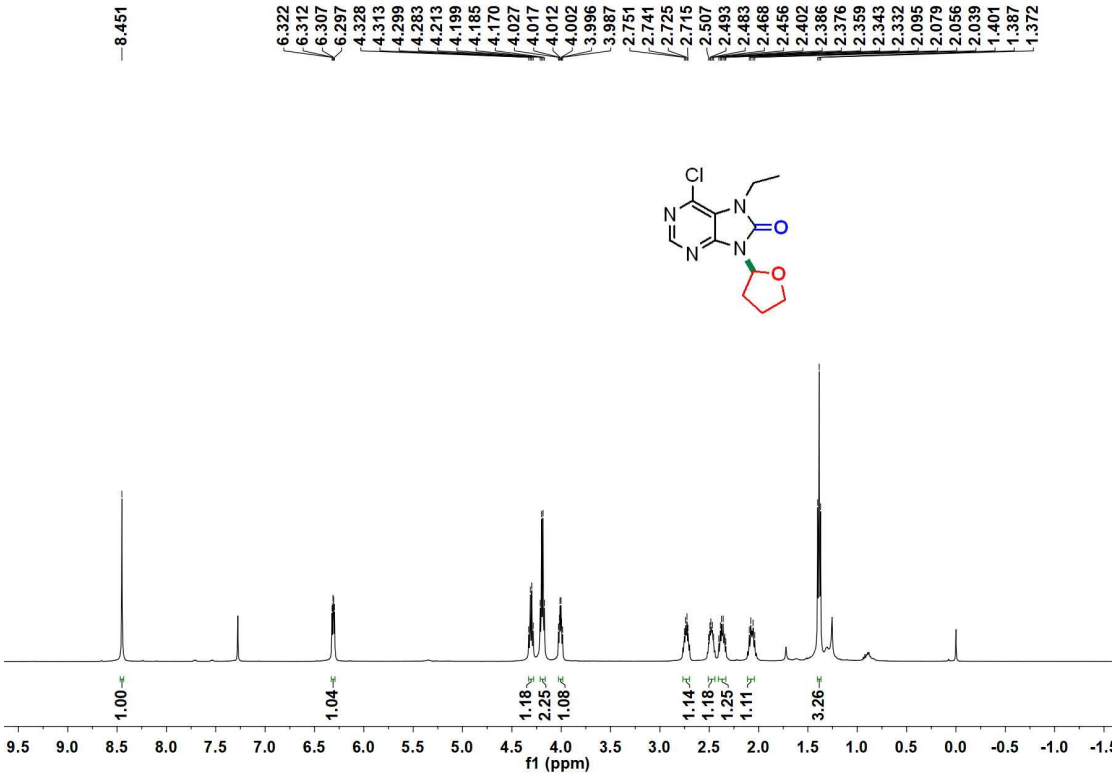
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3c**



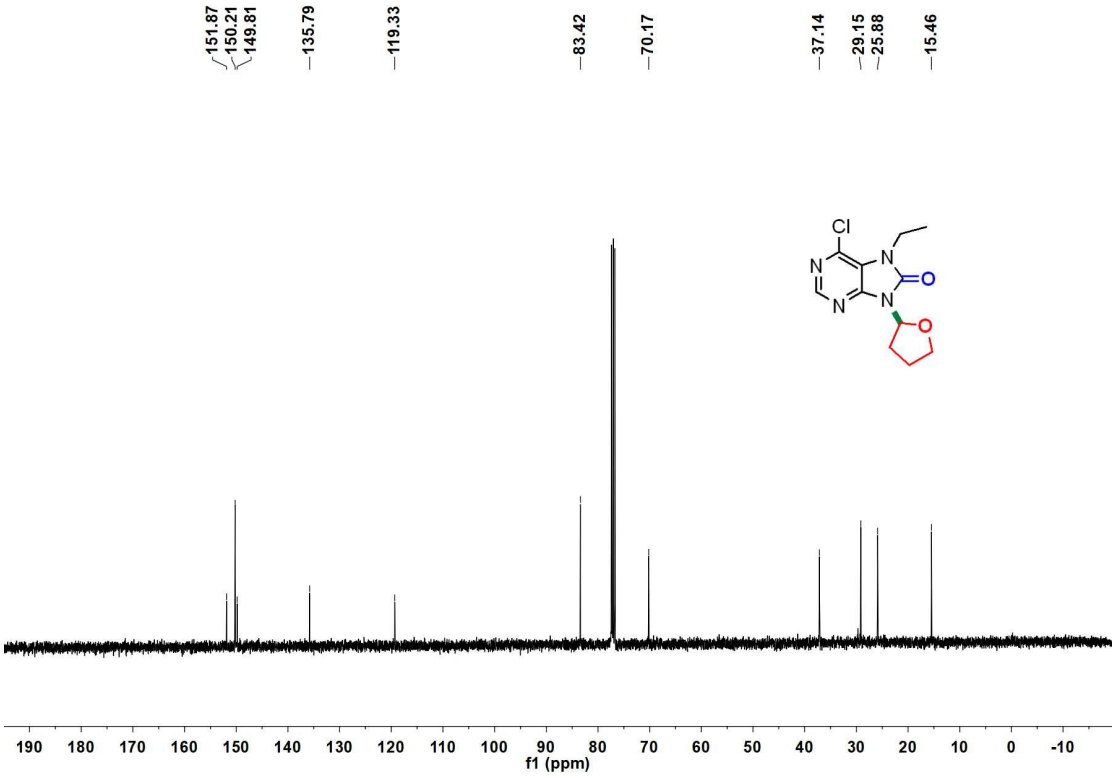
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3c**



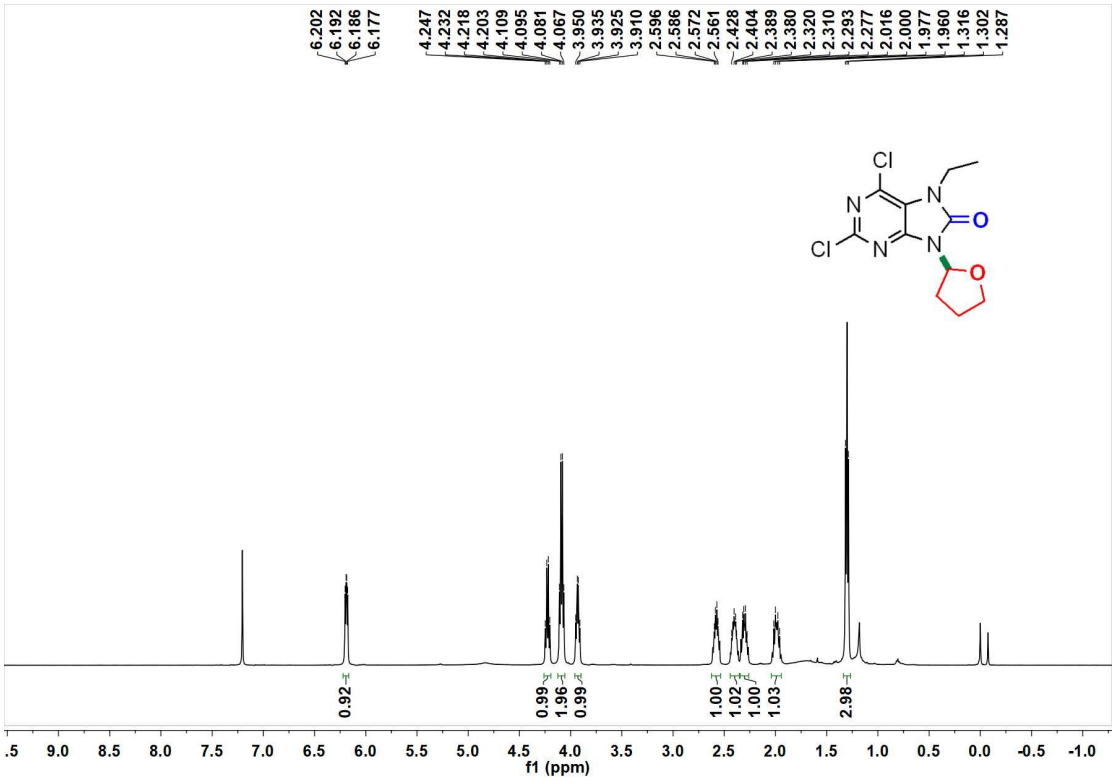
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3d**



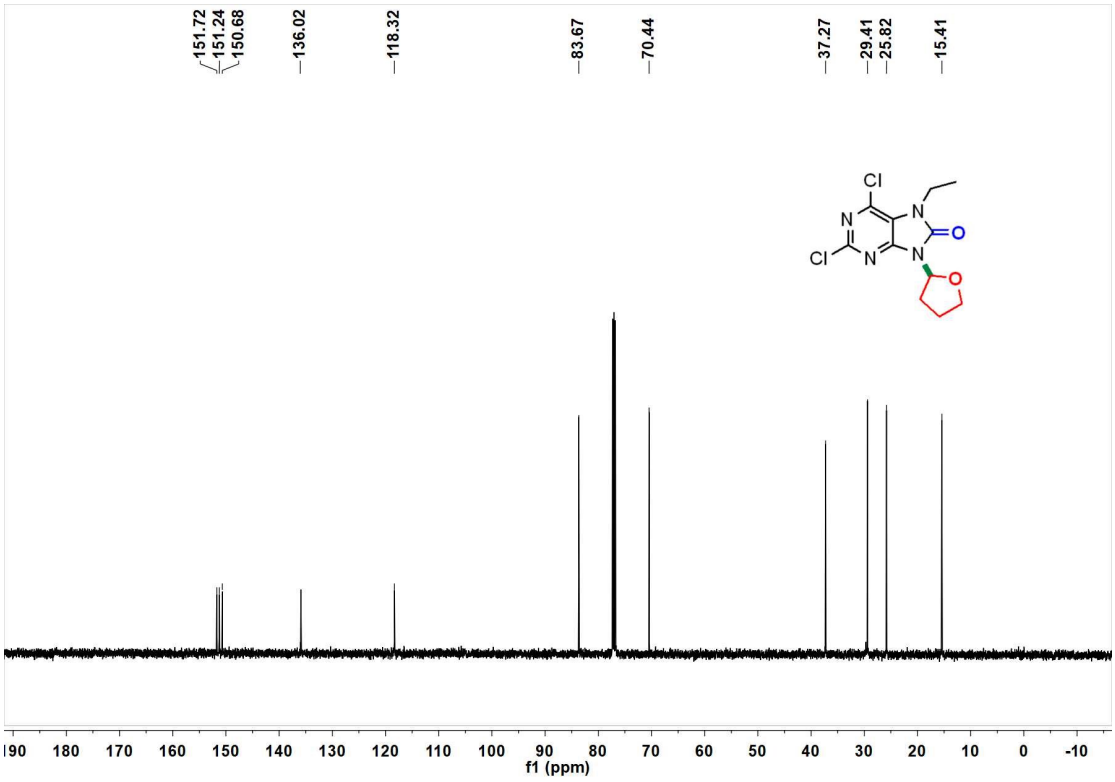
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3d**



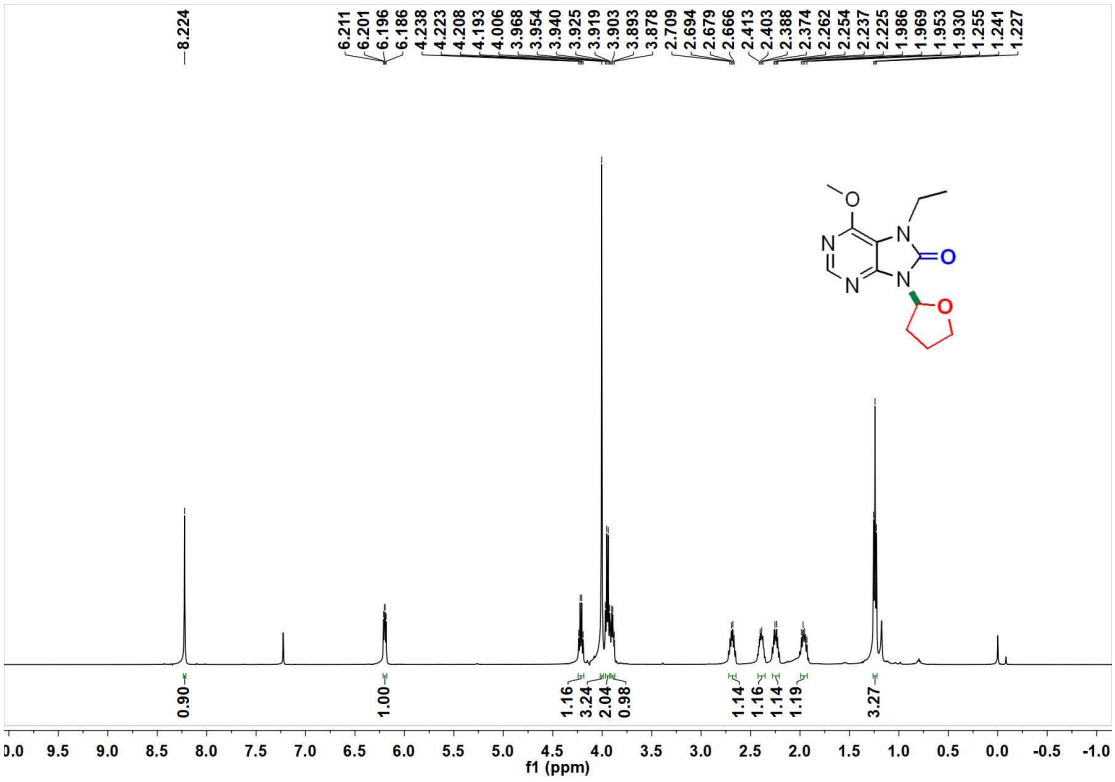
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3e**



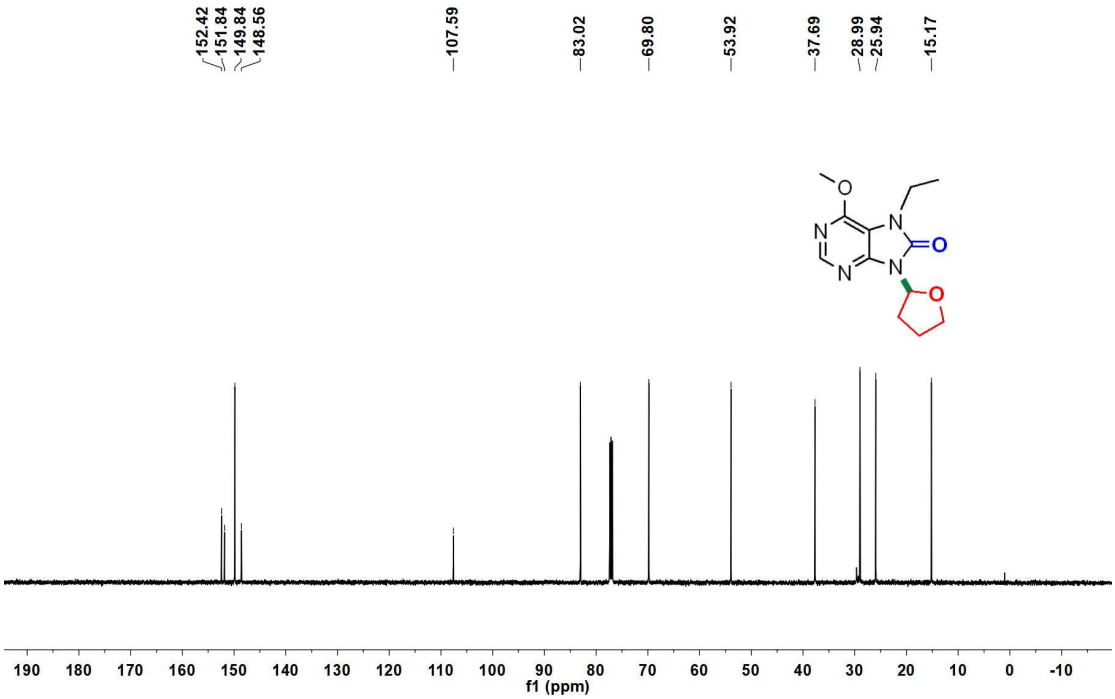
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3e**



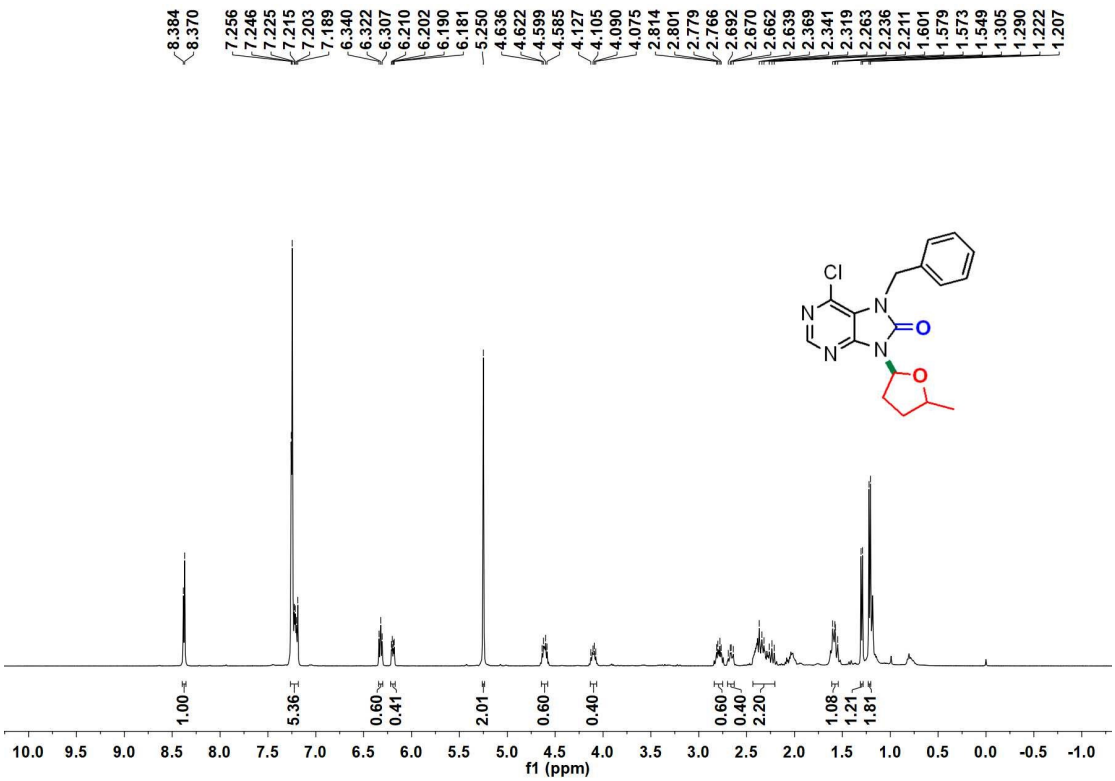
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3f**



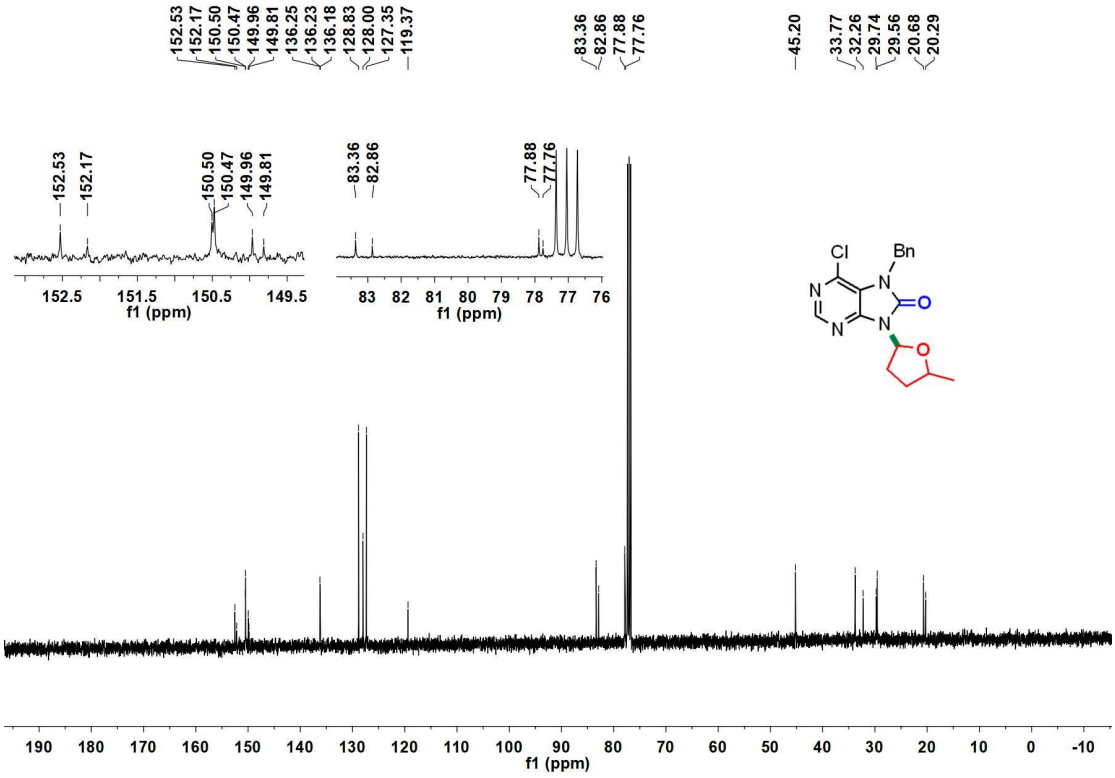
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3f**



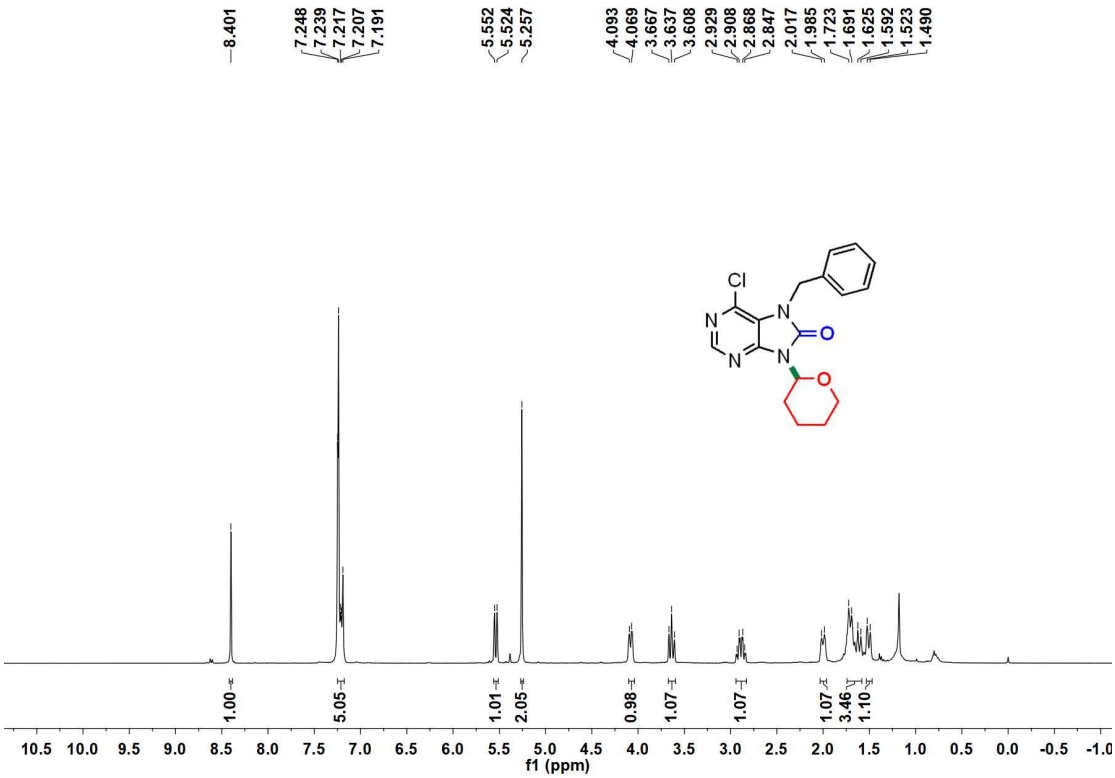
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g**



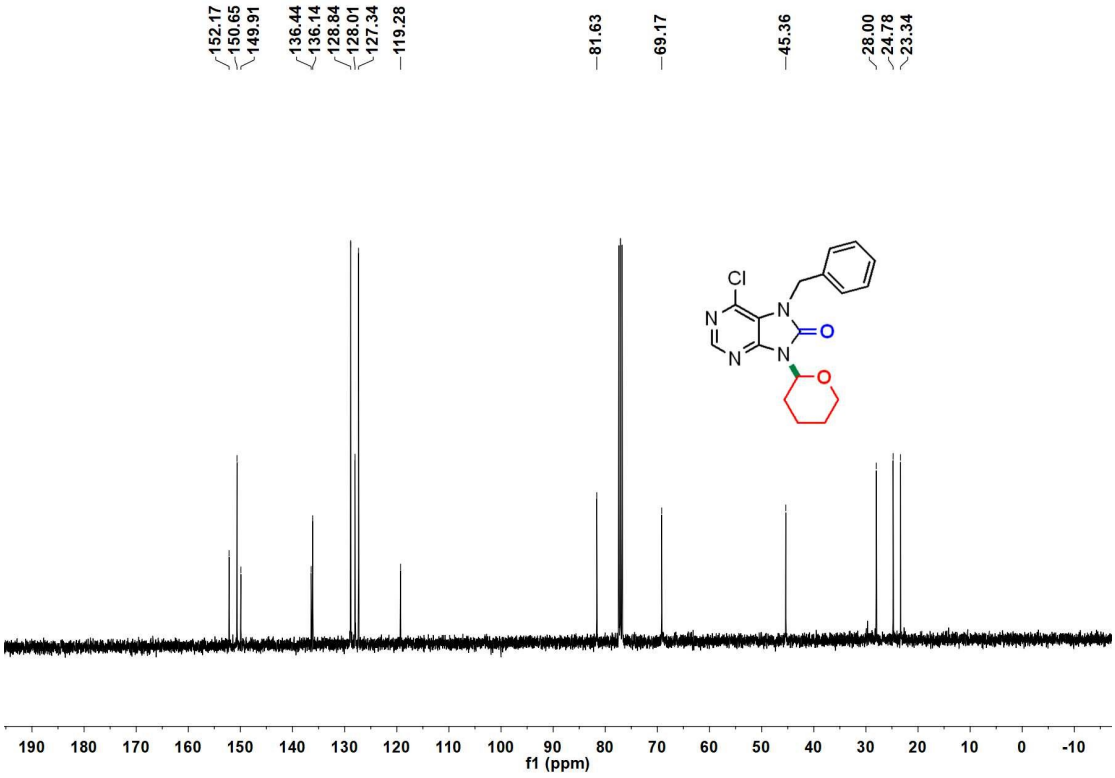
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3g**



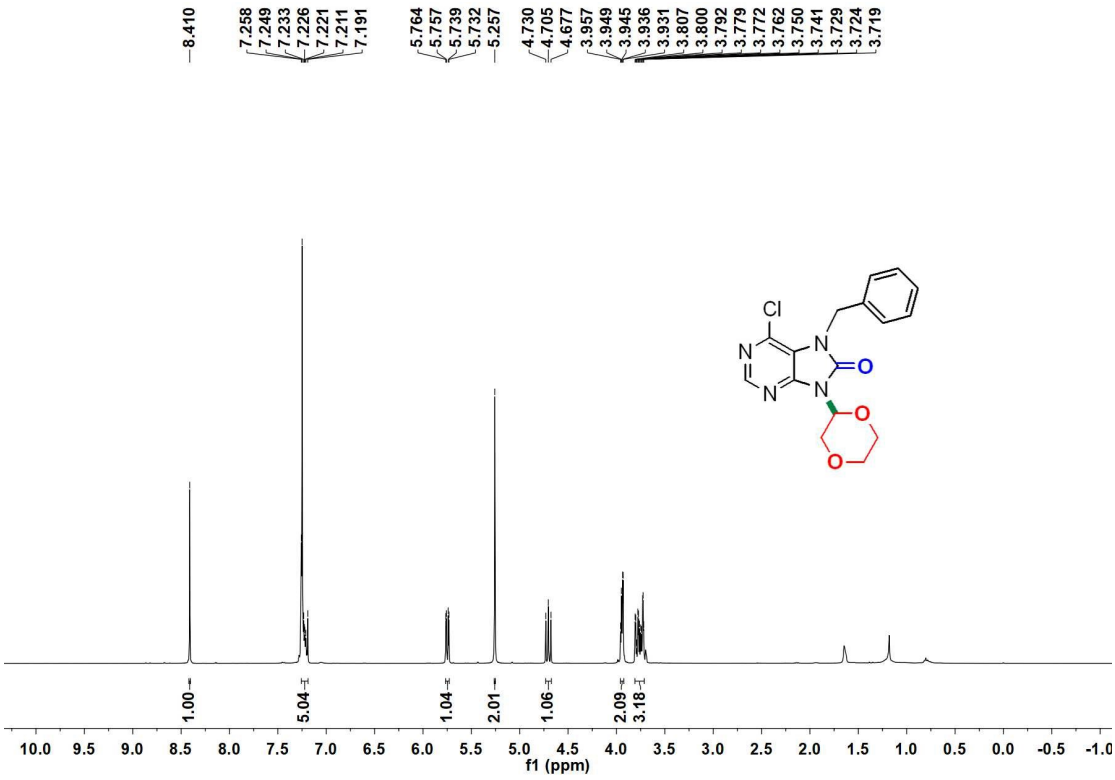
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3h**



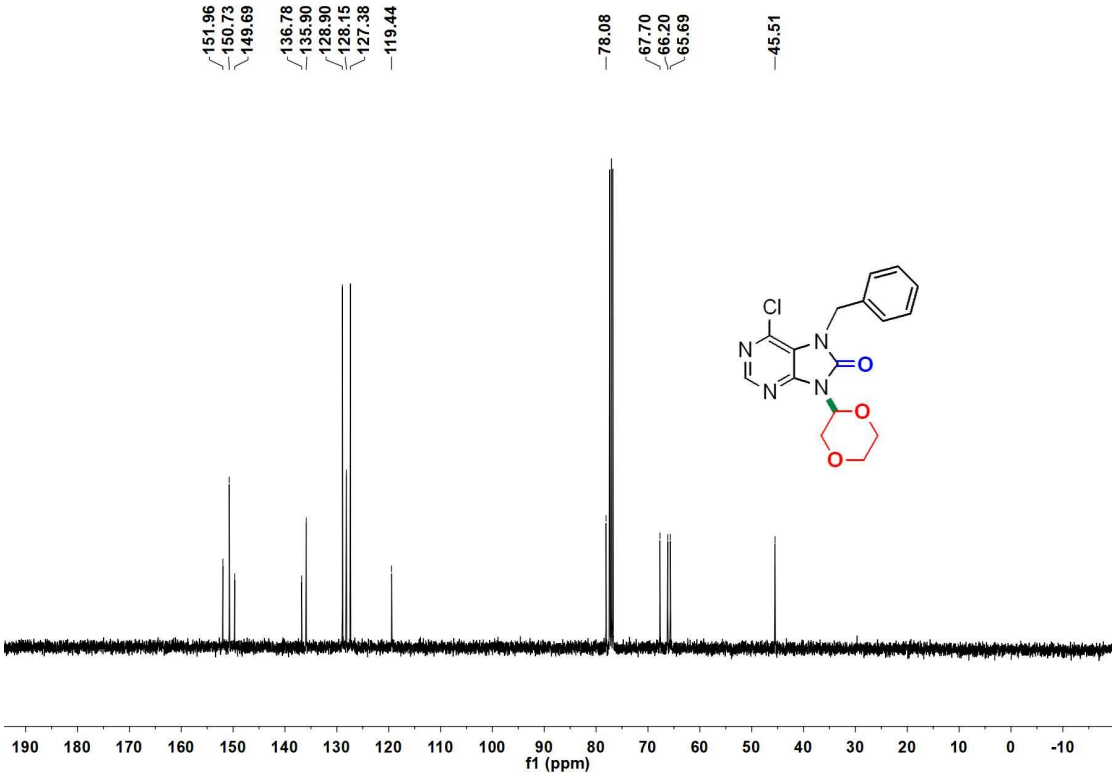
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3h**



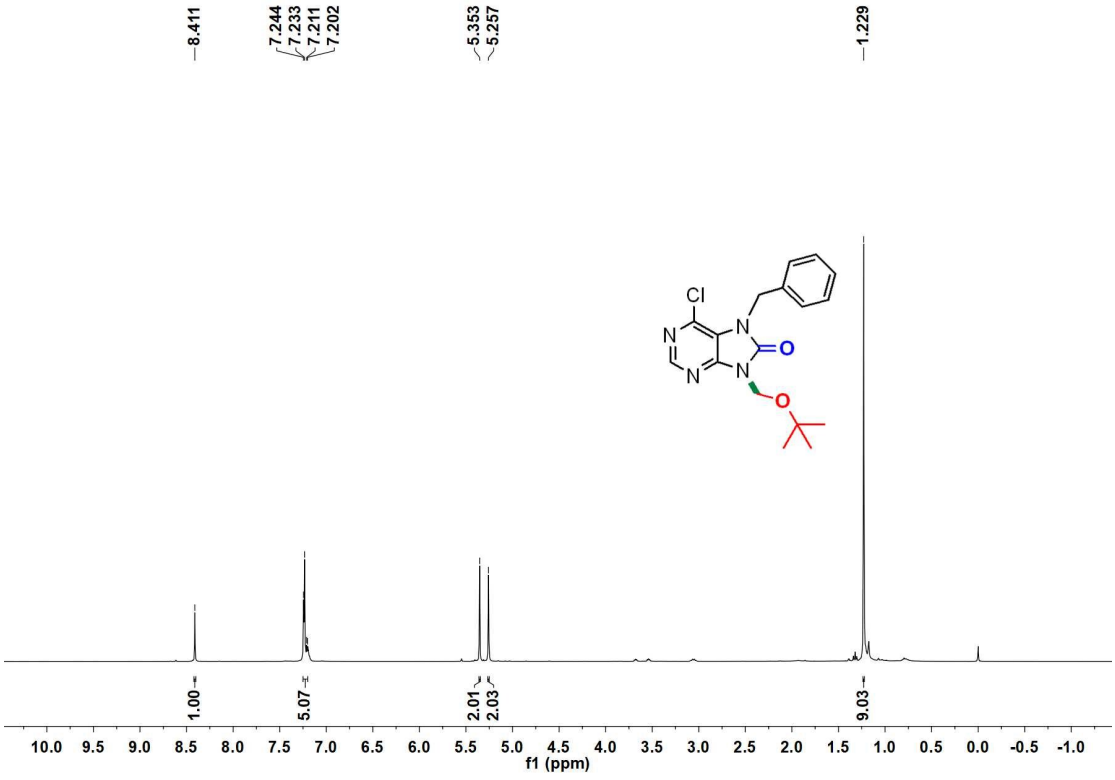
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3i**



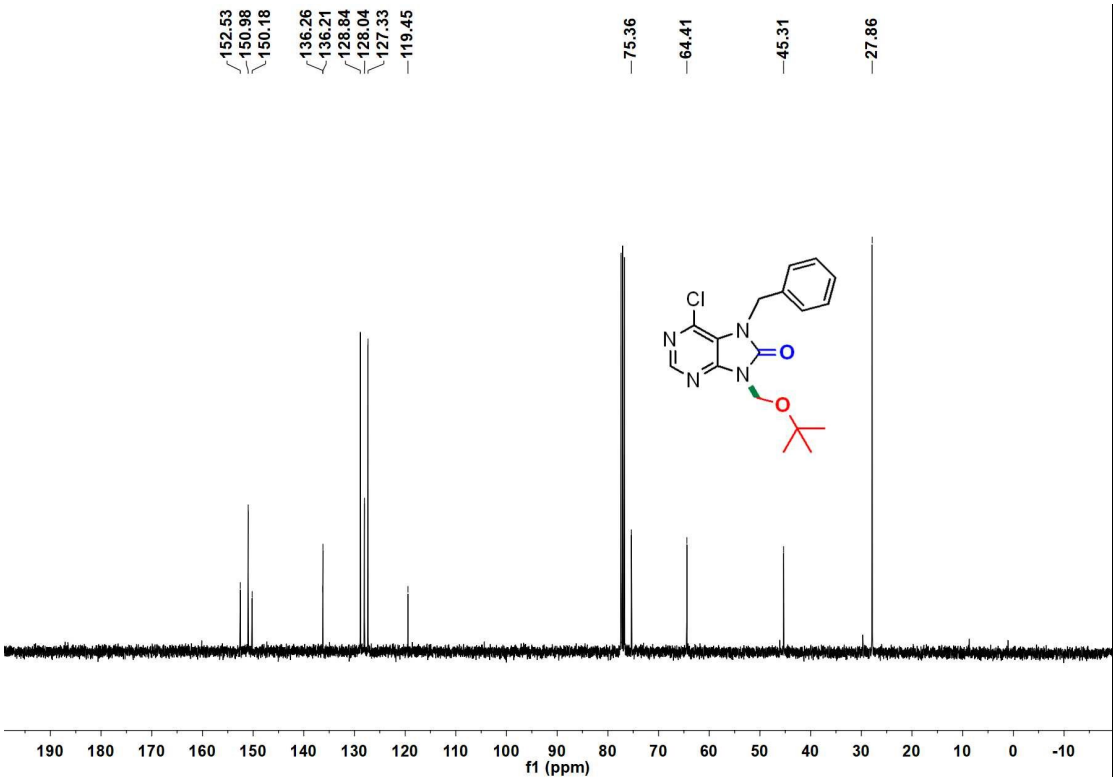
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3i**



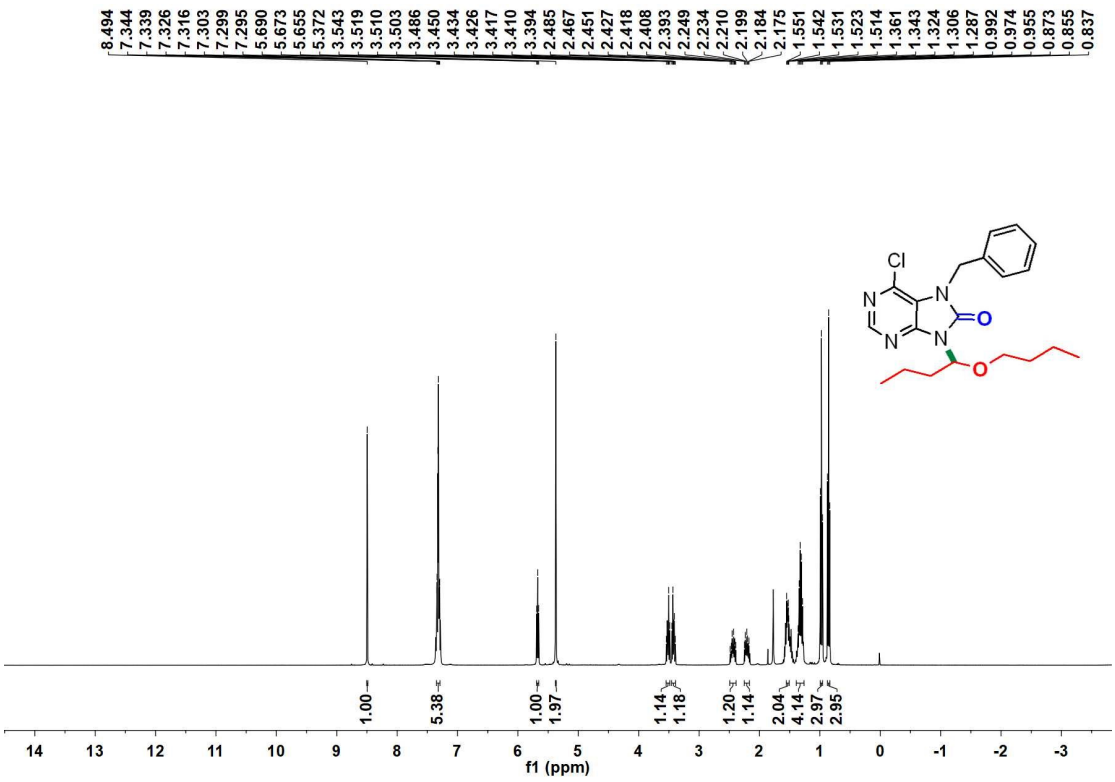
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3j**



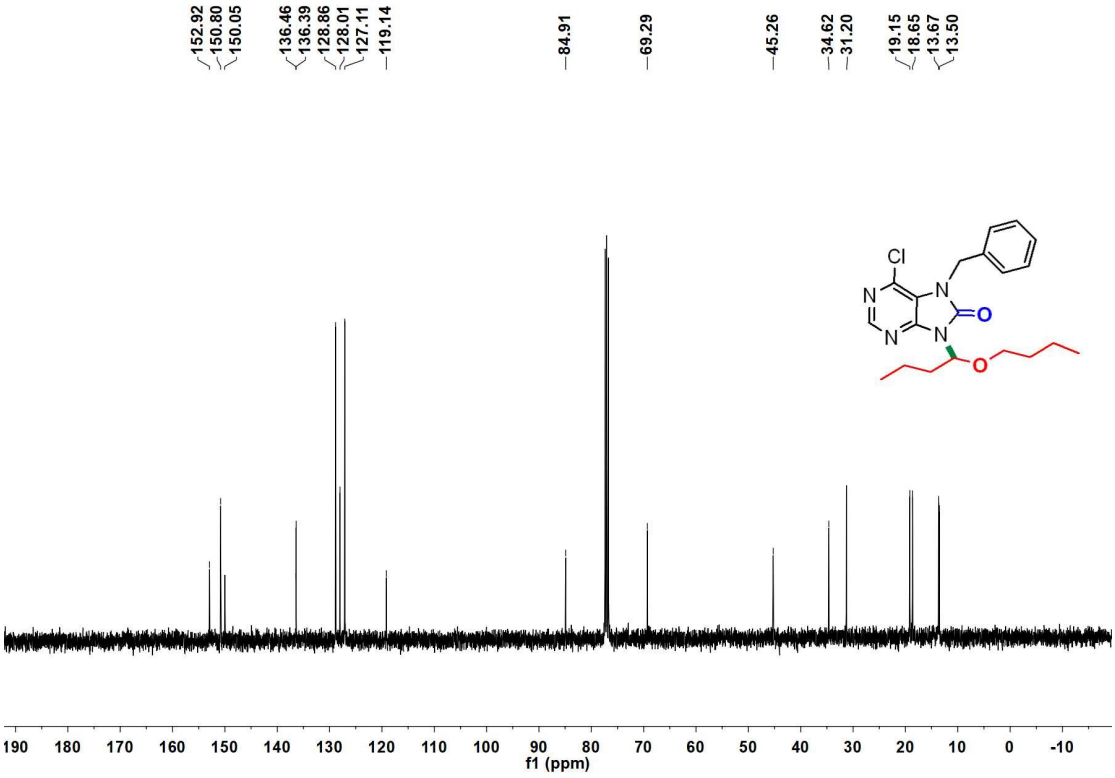
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3j**



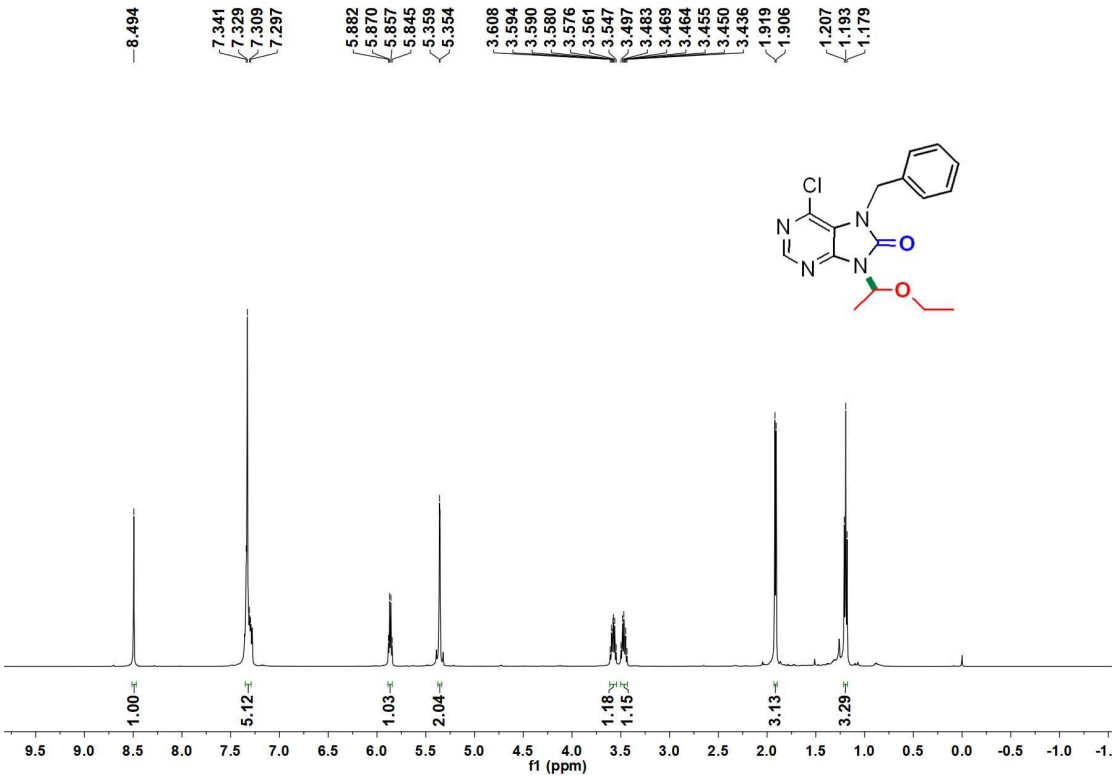
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3k**



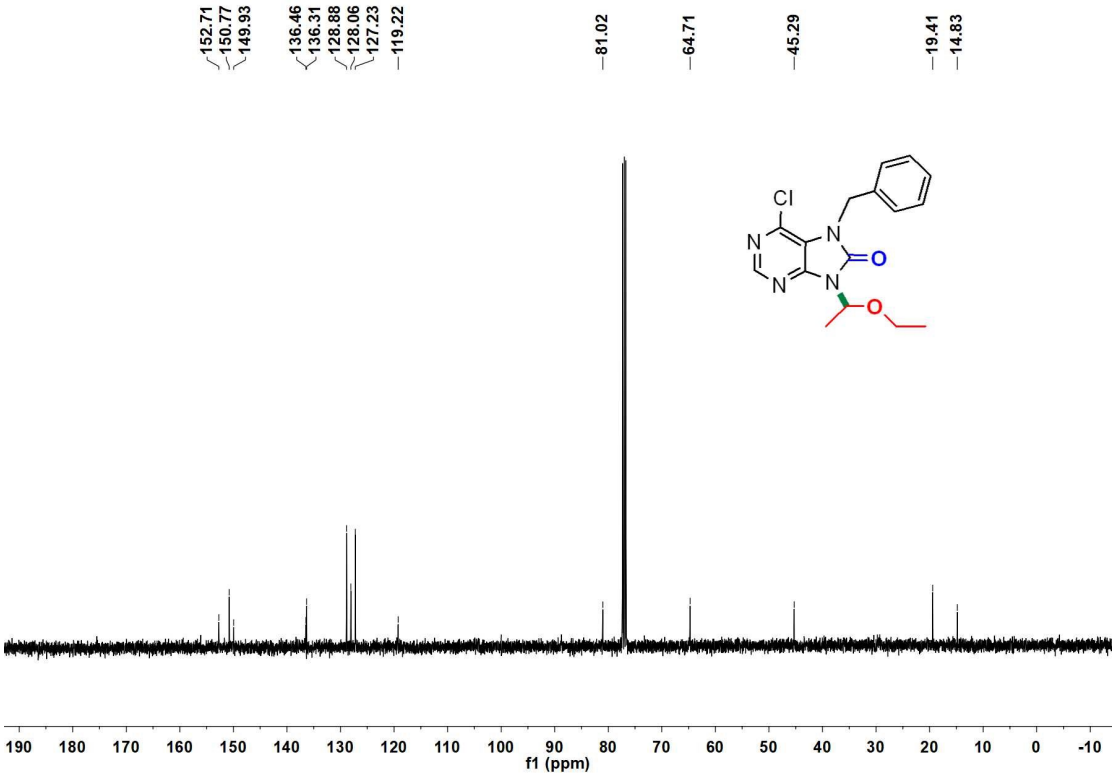
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3k**



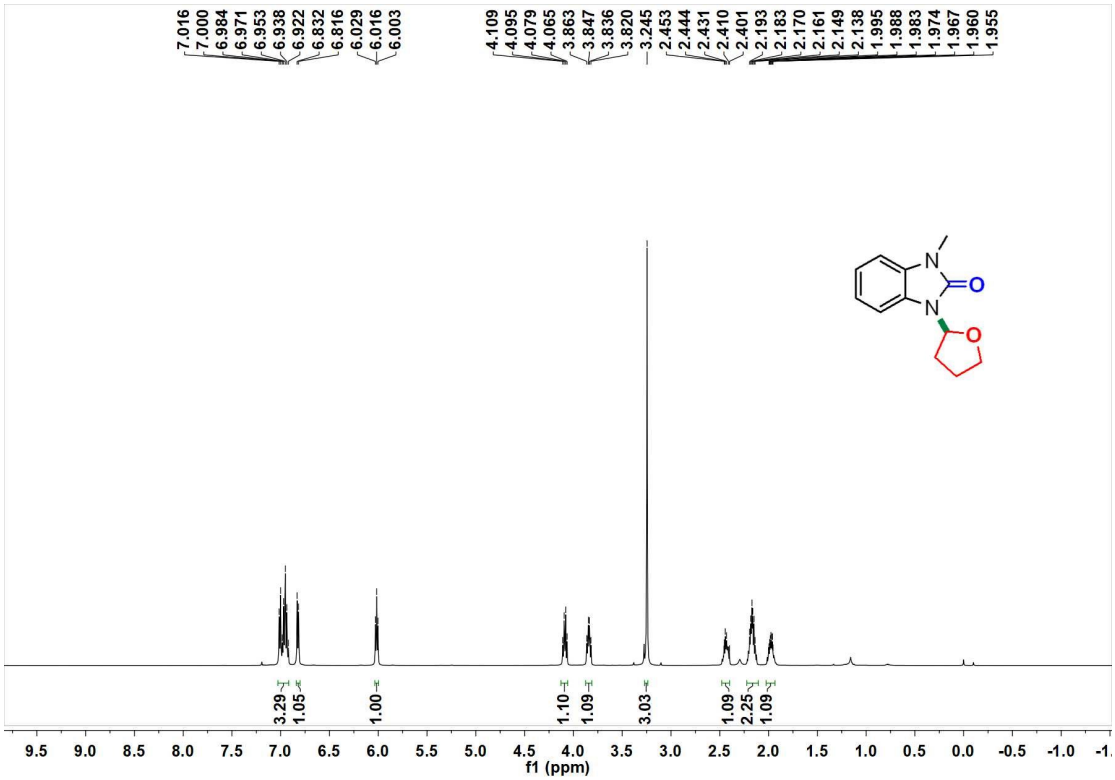
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3l**



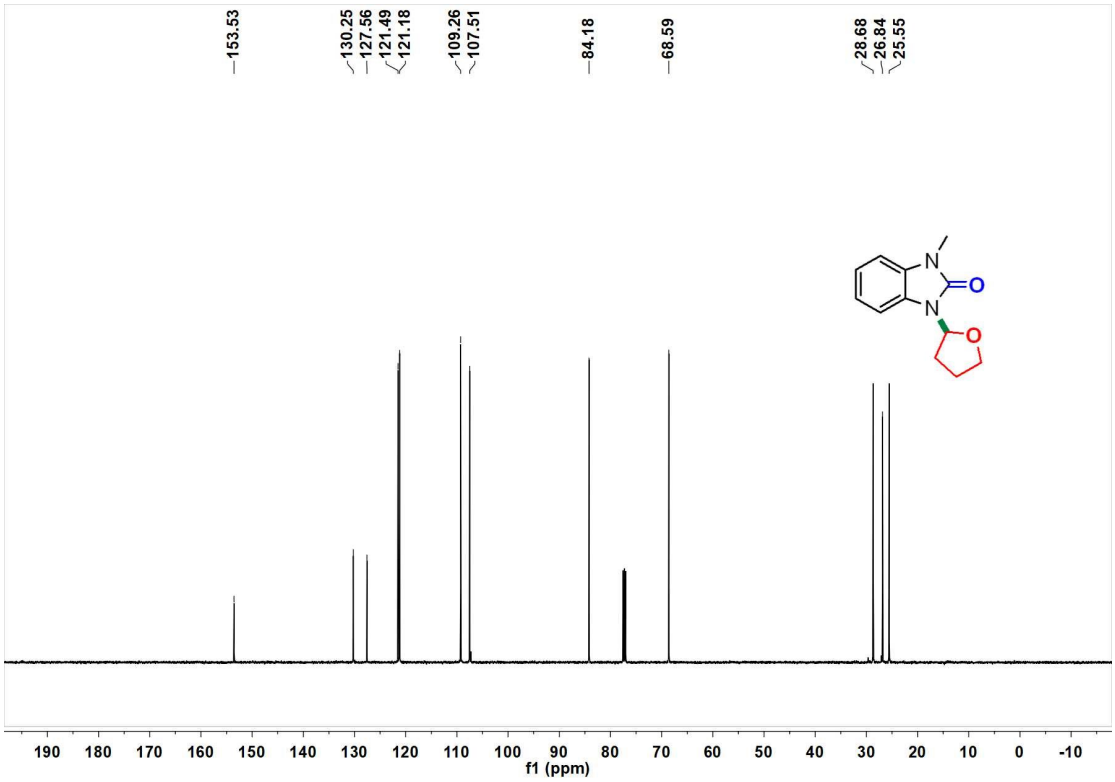
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3l**



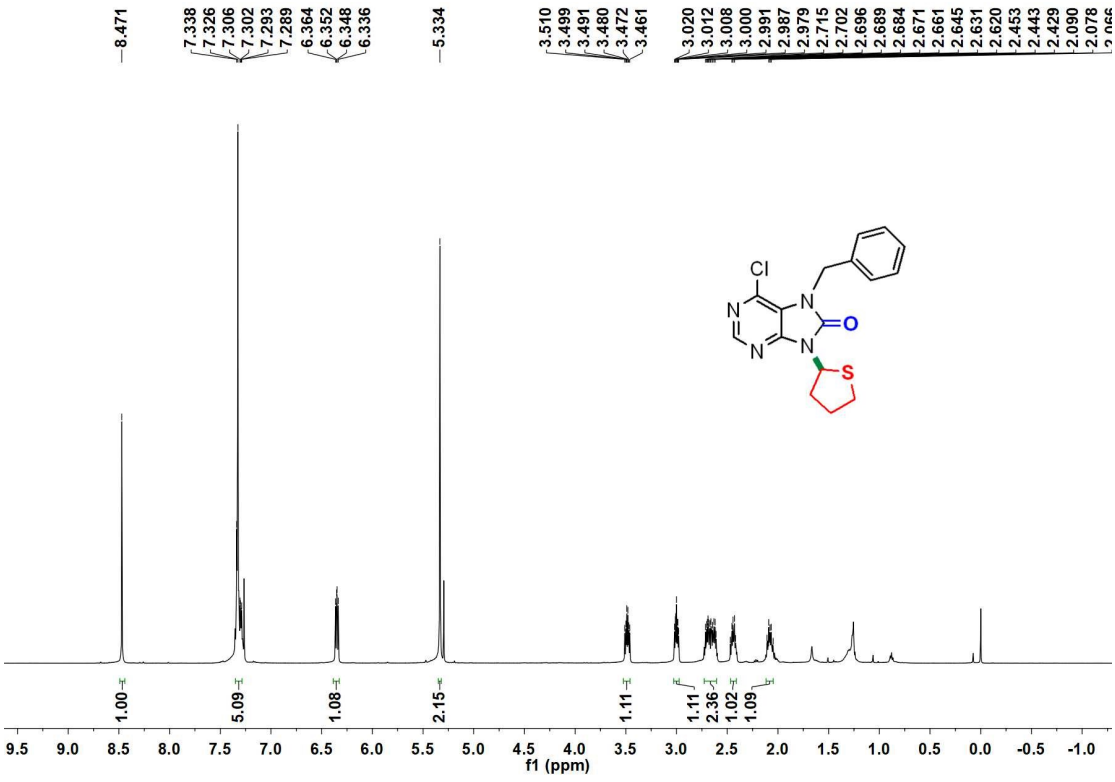
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3n**



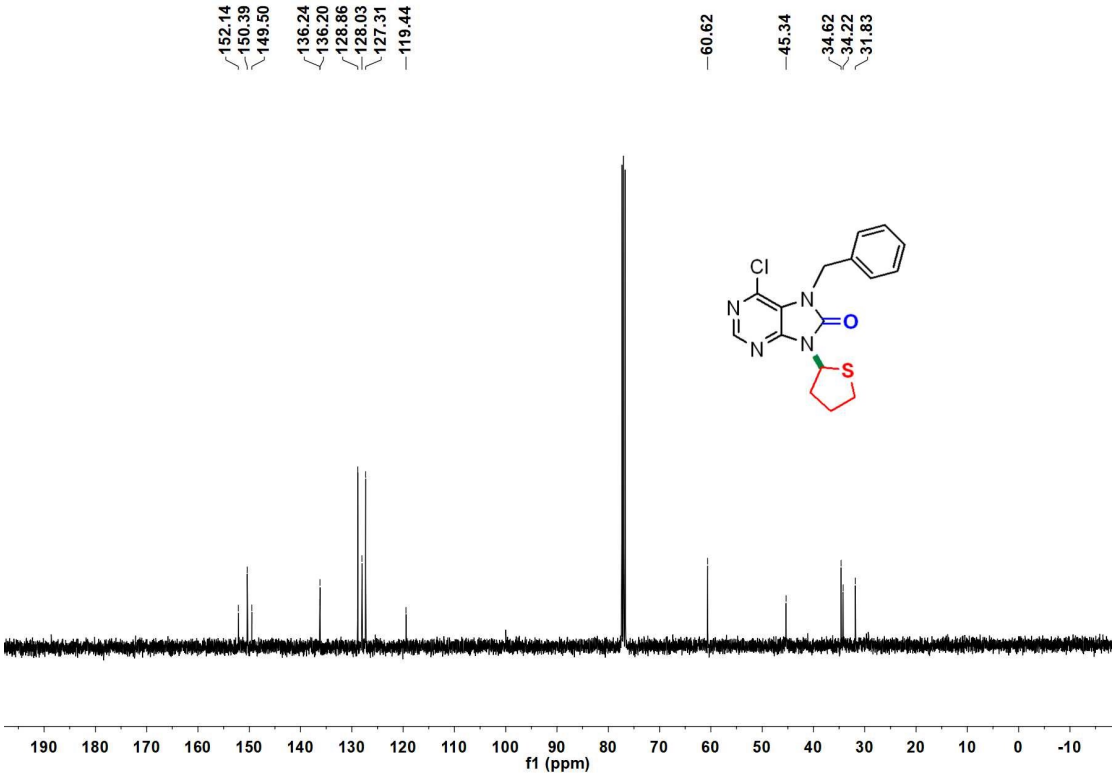
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3n**



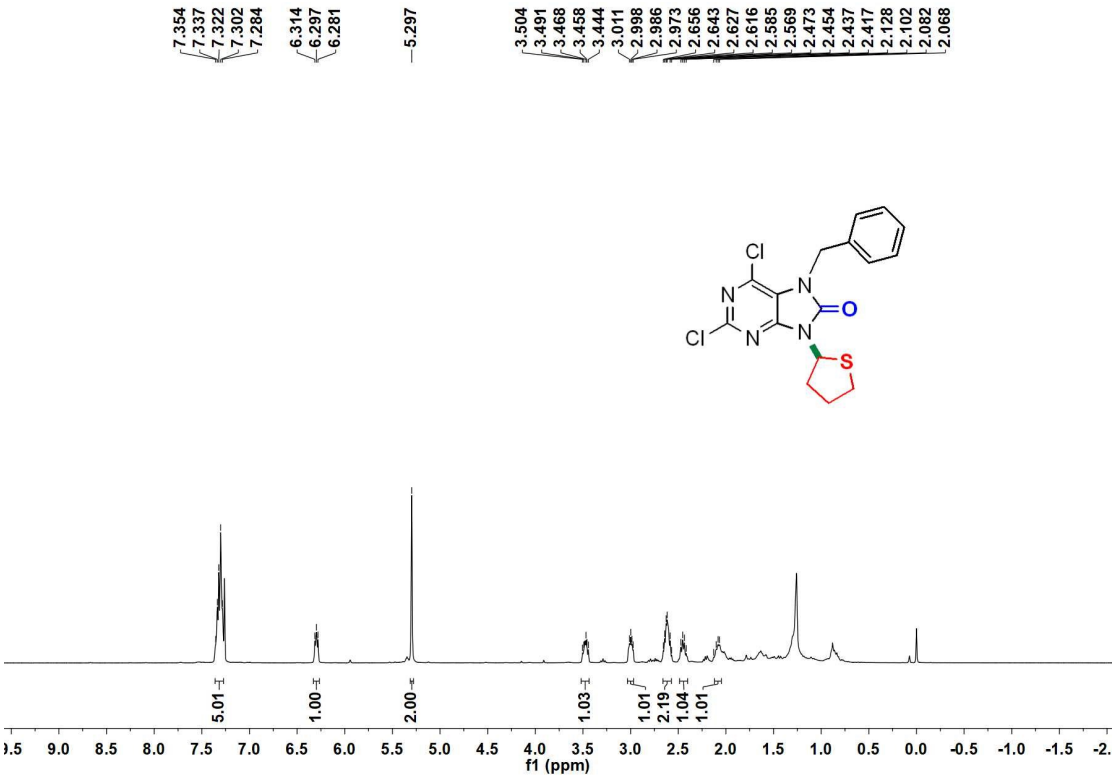
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5a**



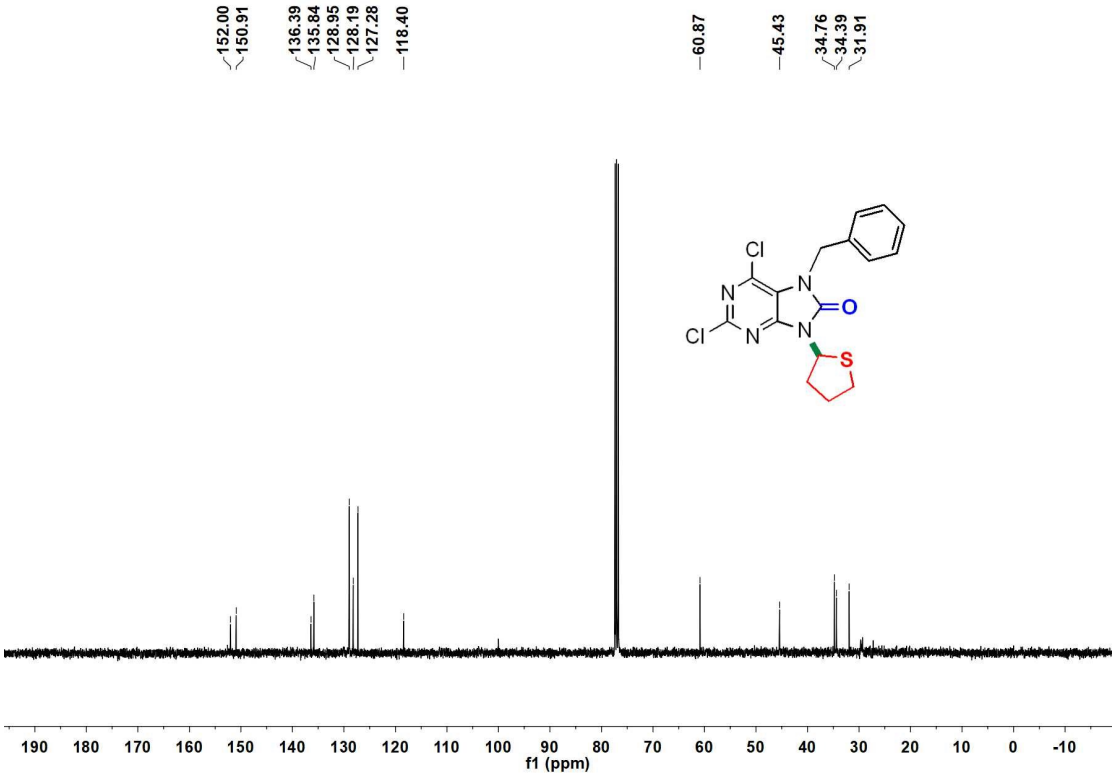
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5a**



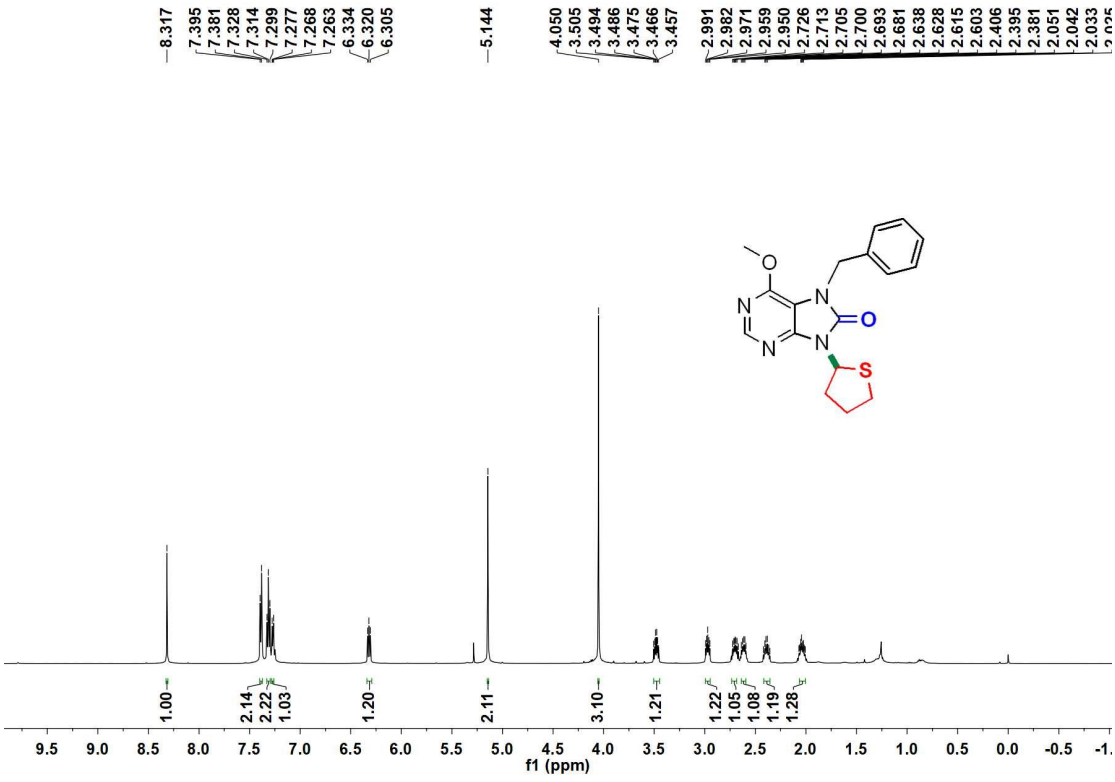
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**



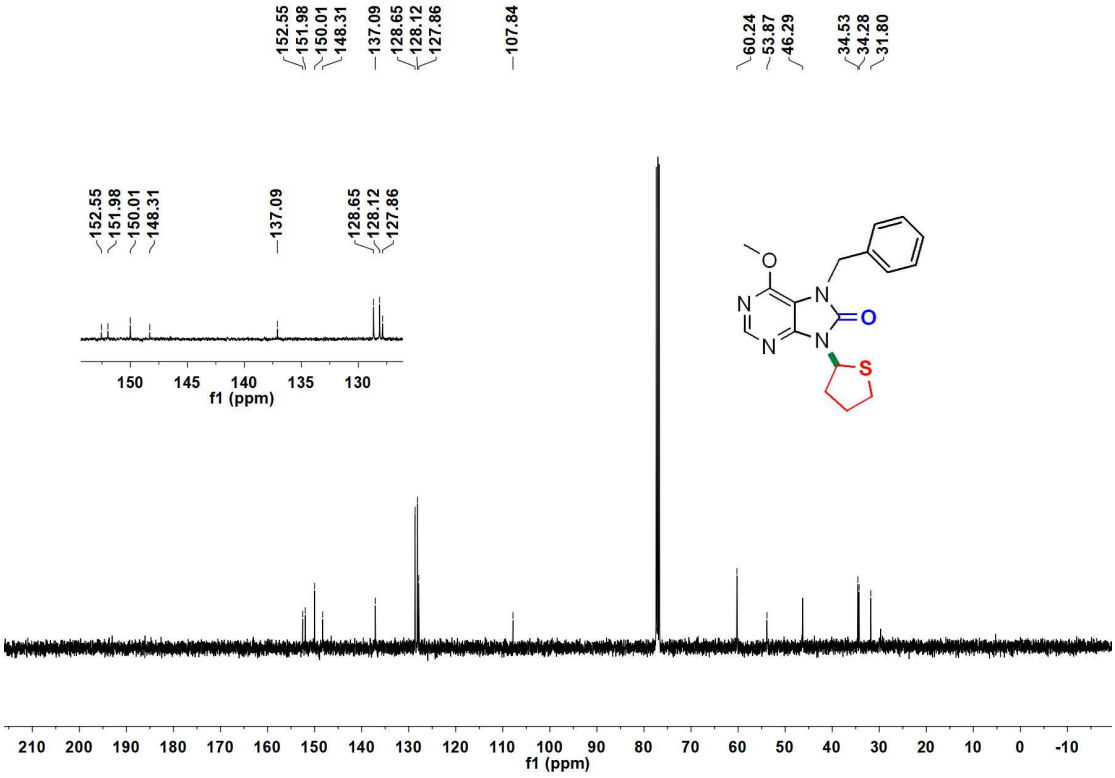
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5b**



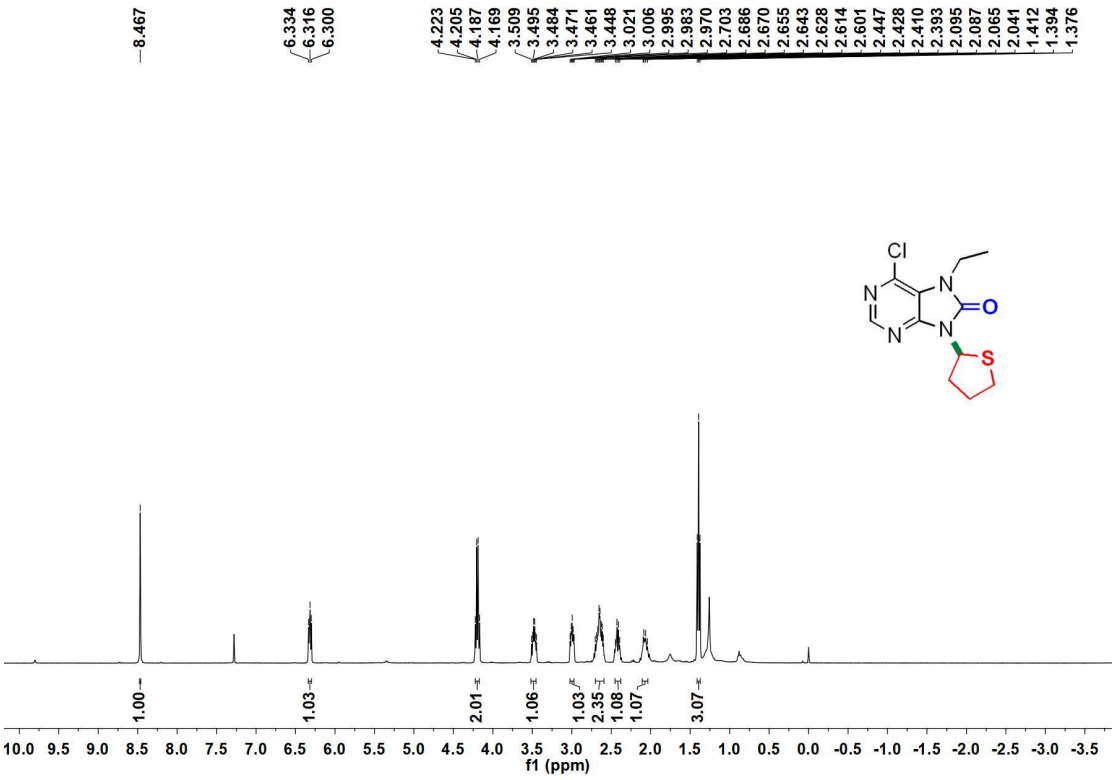
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5c**



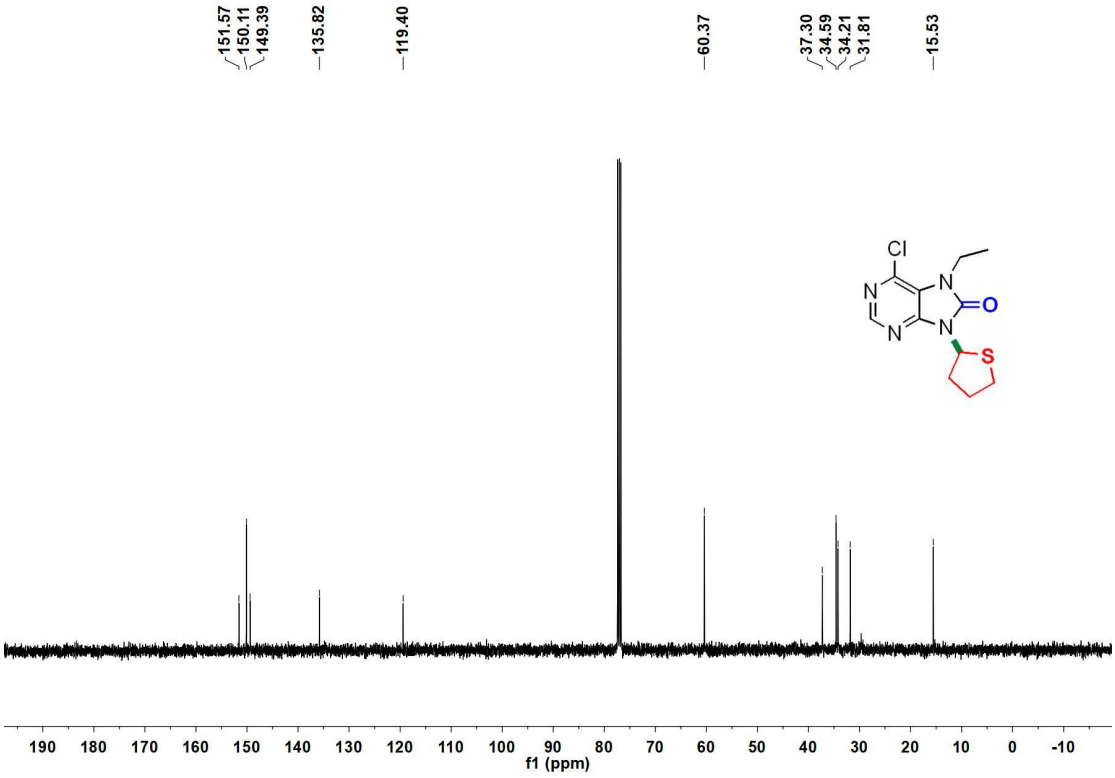
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5c**



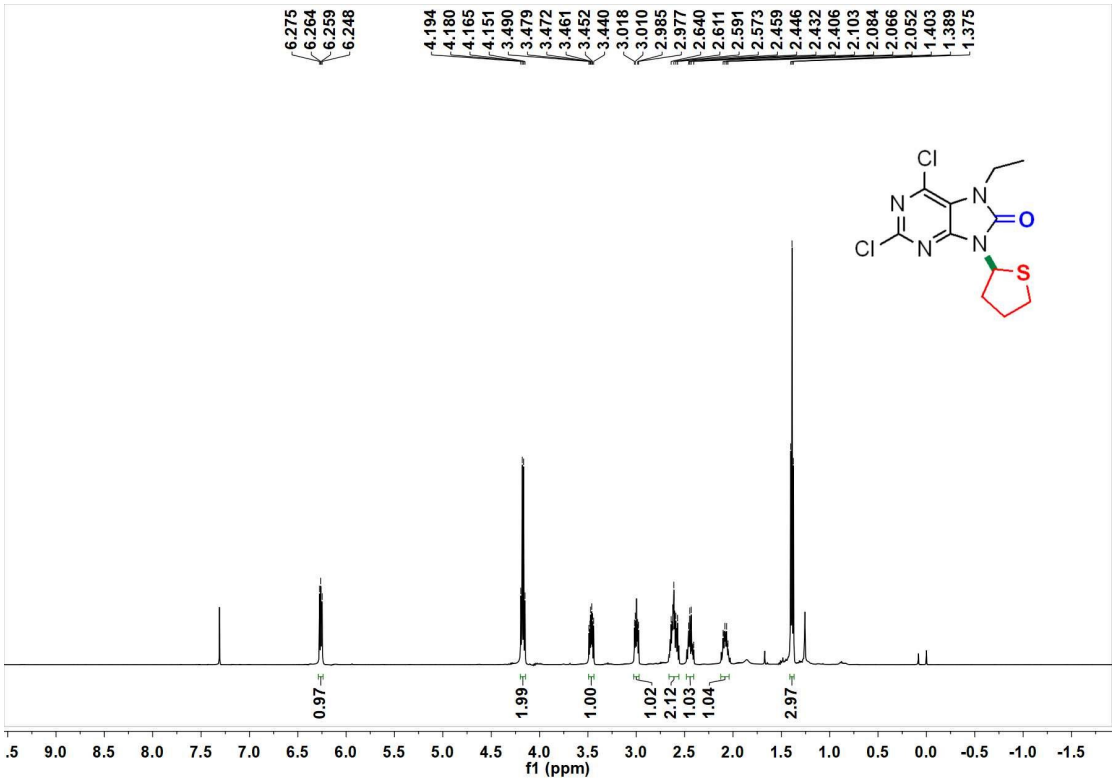
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5d**



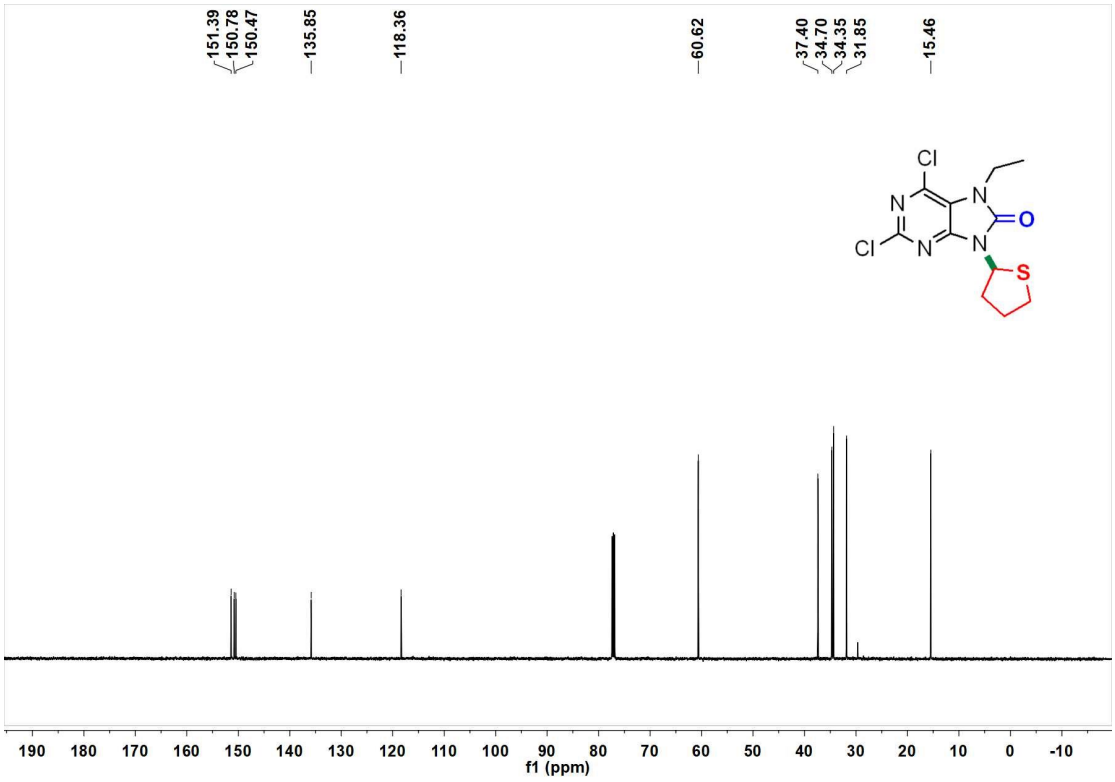
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5d**



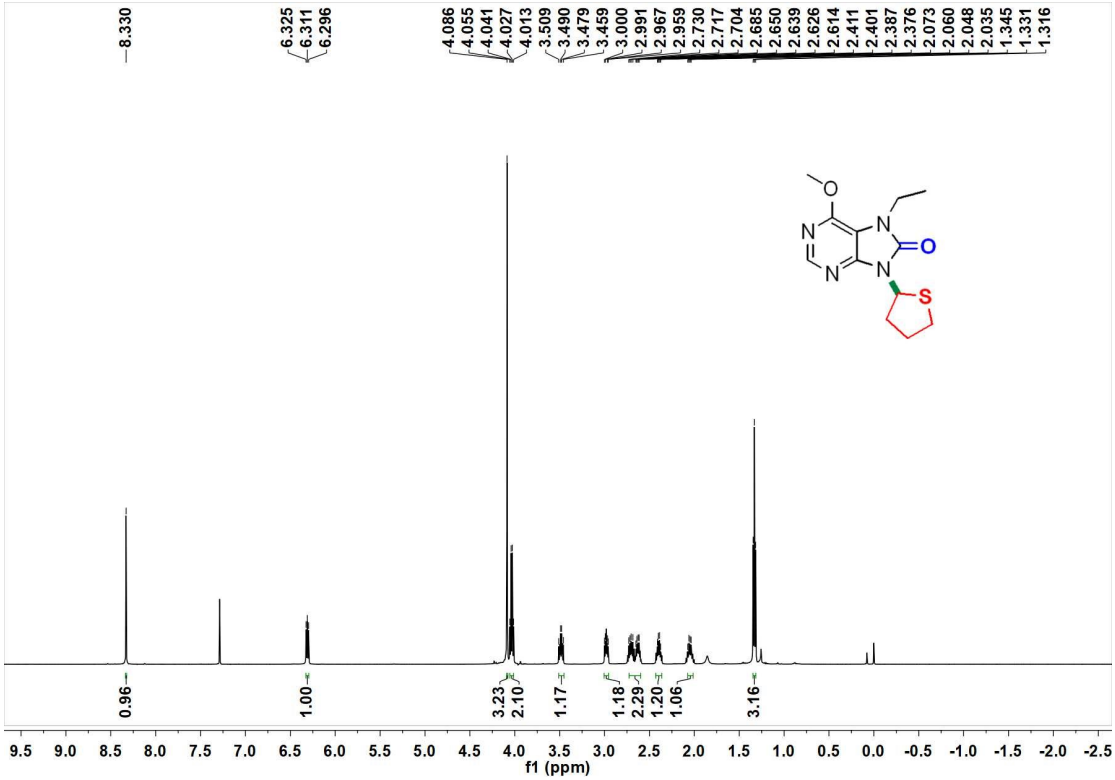
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5e**



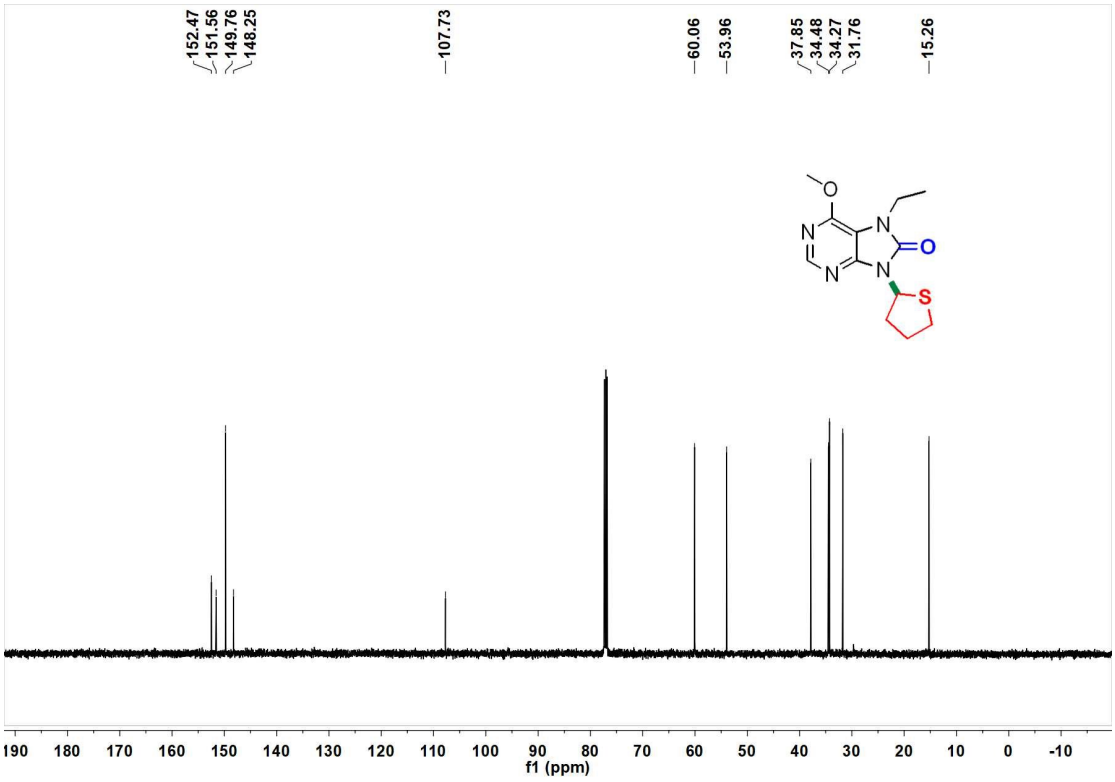
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **5e**



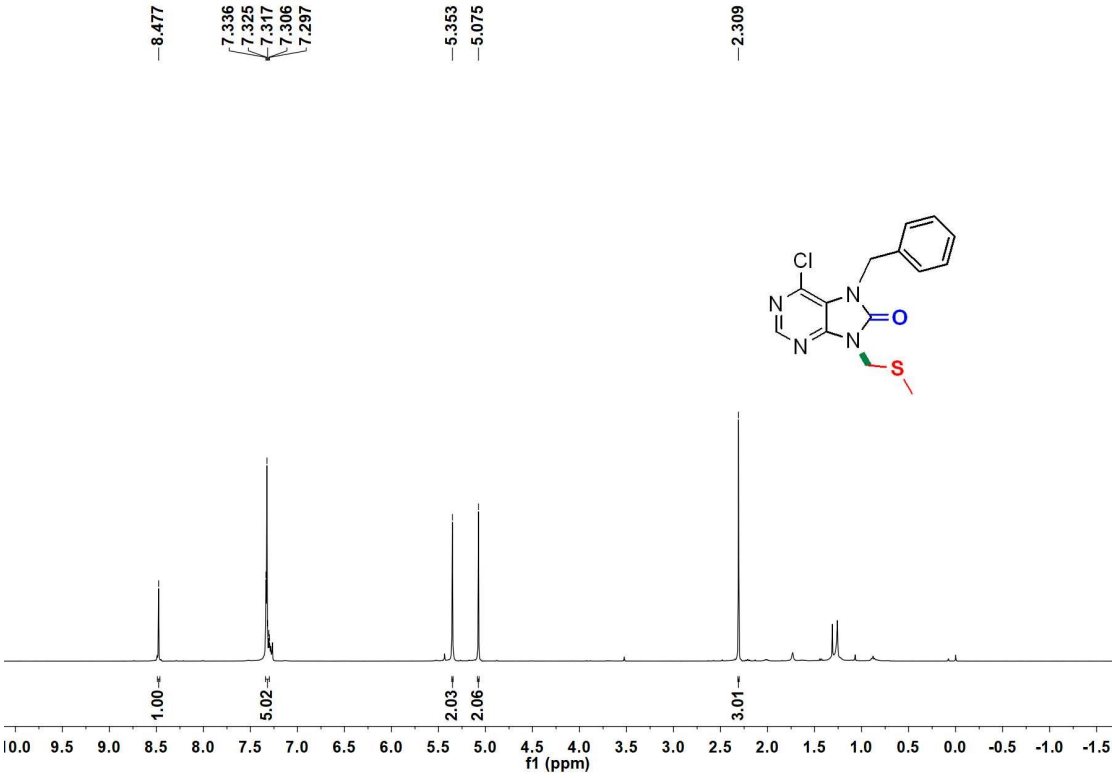
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5f**



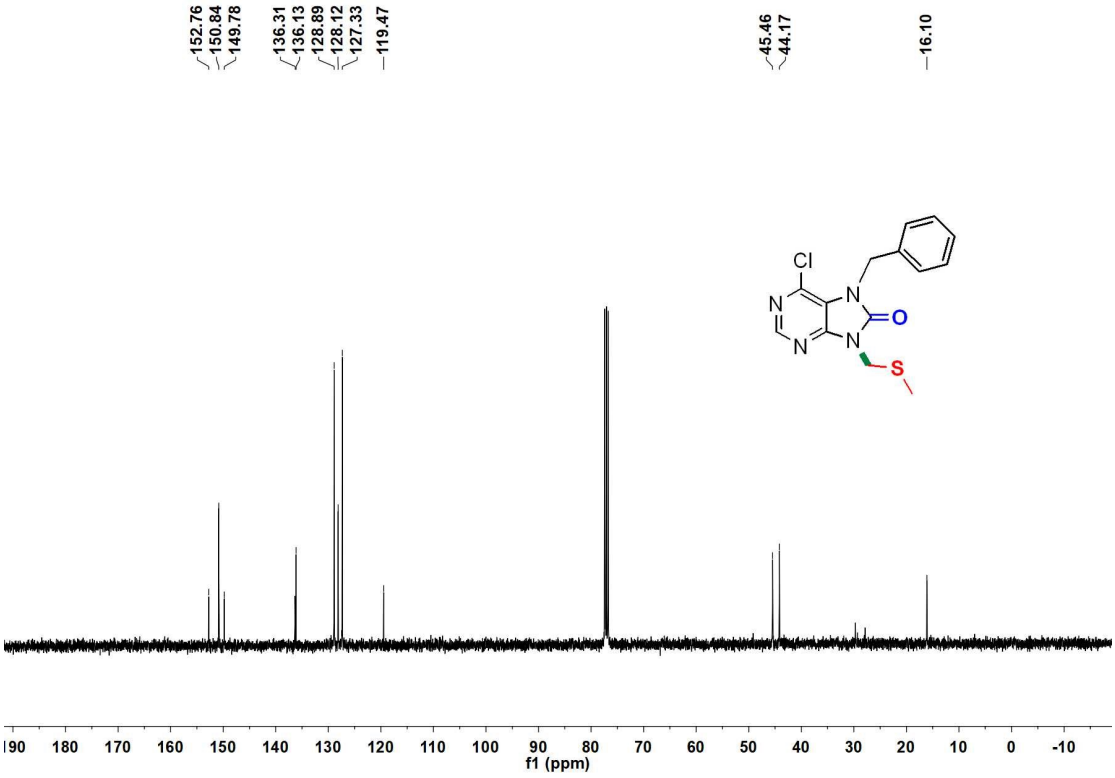
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **5f**



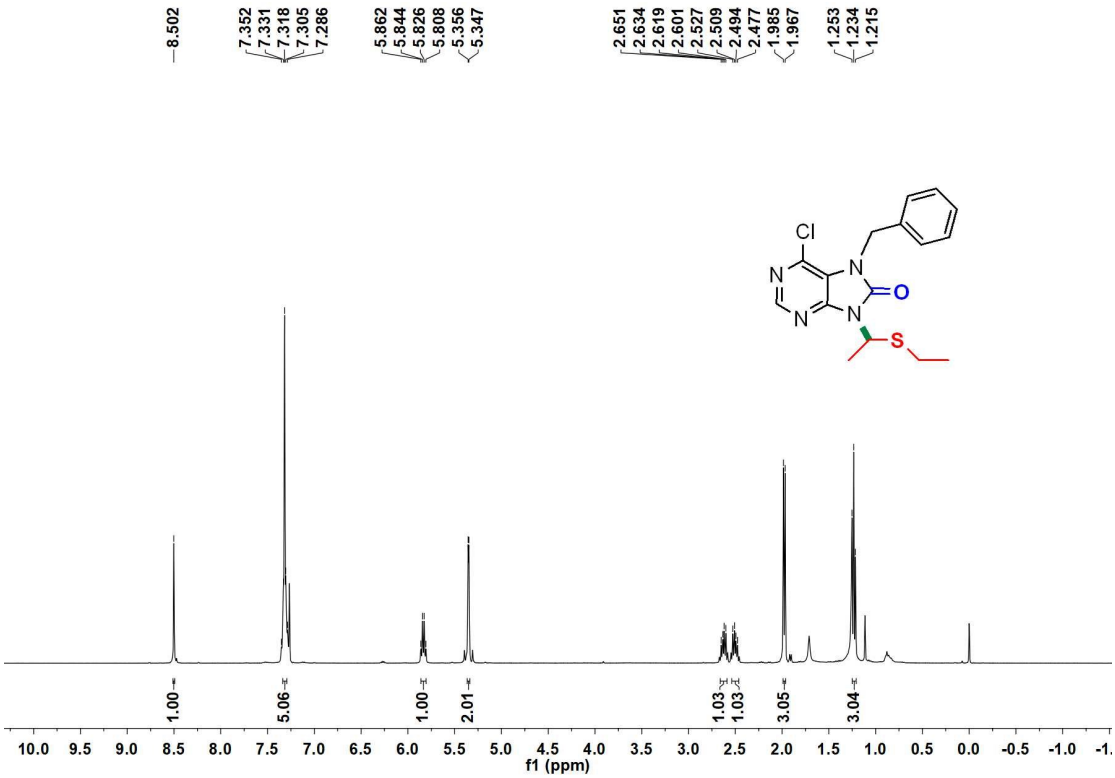
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5g**



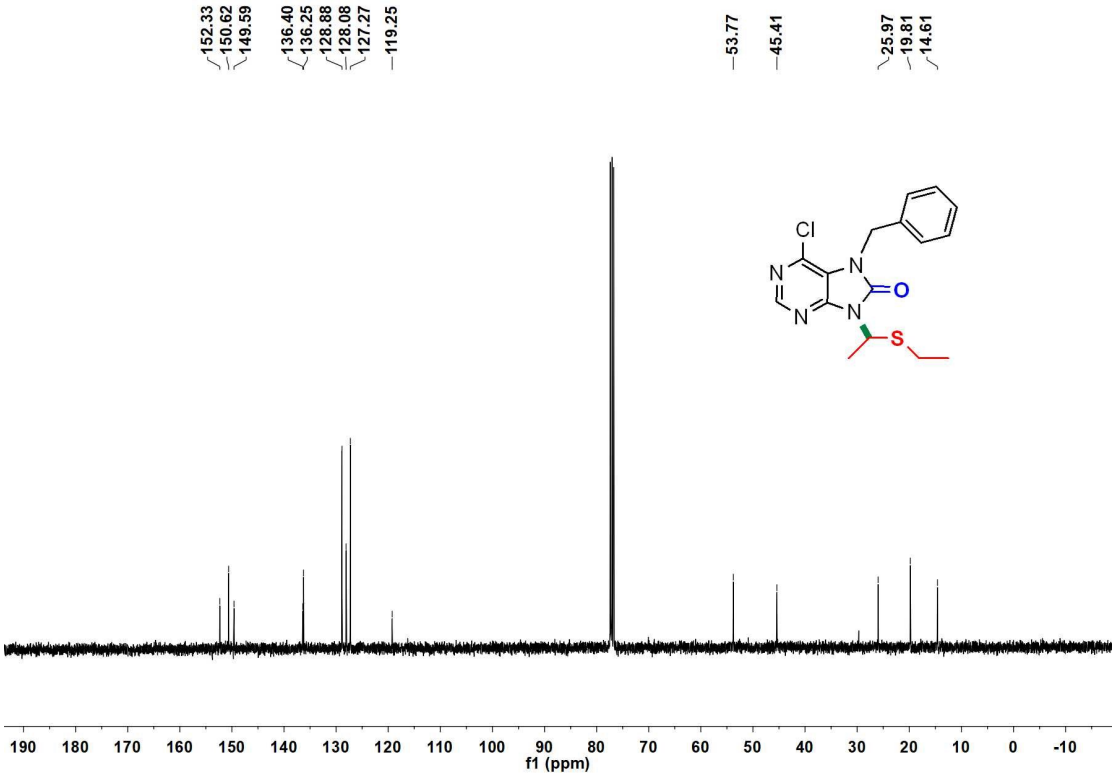
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5g**



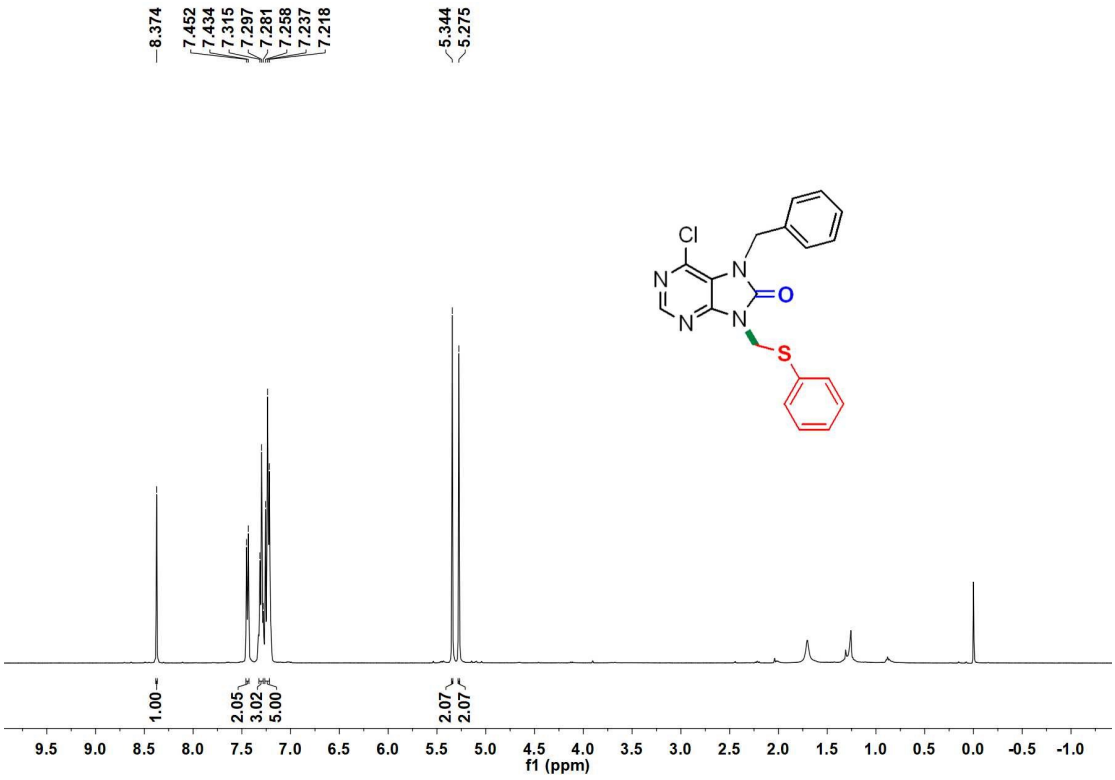
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5h**



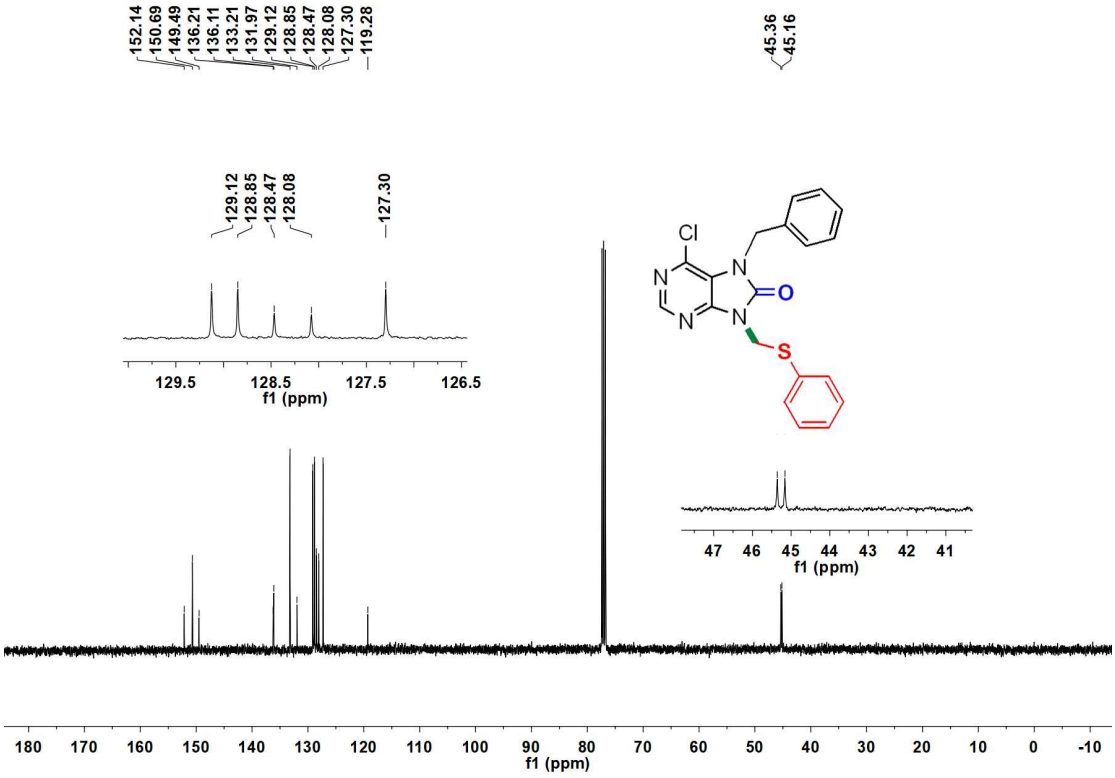
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5h**



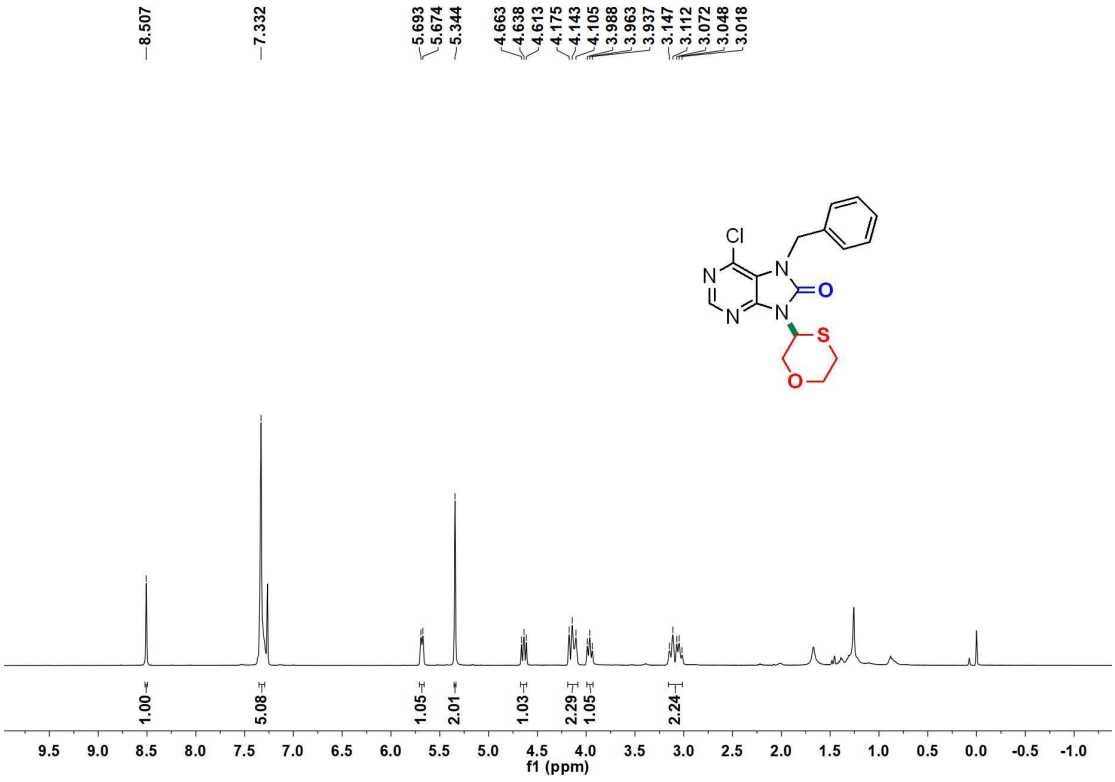
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5i**



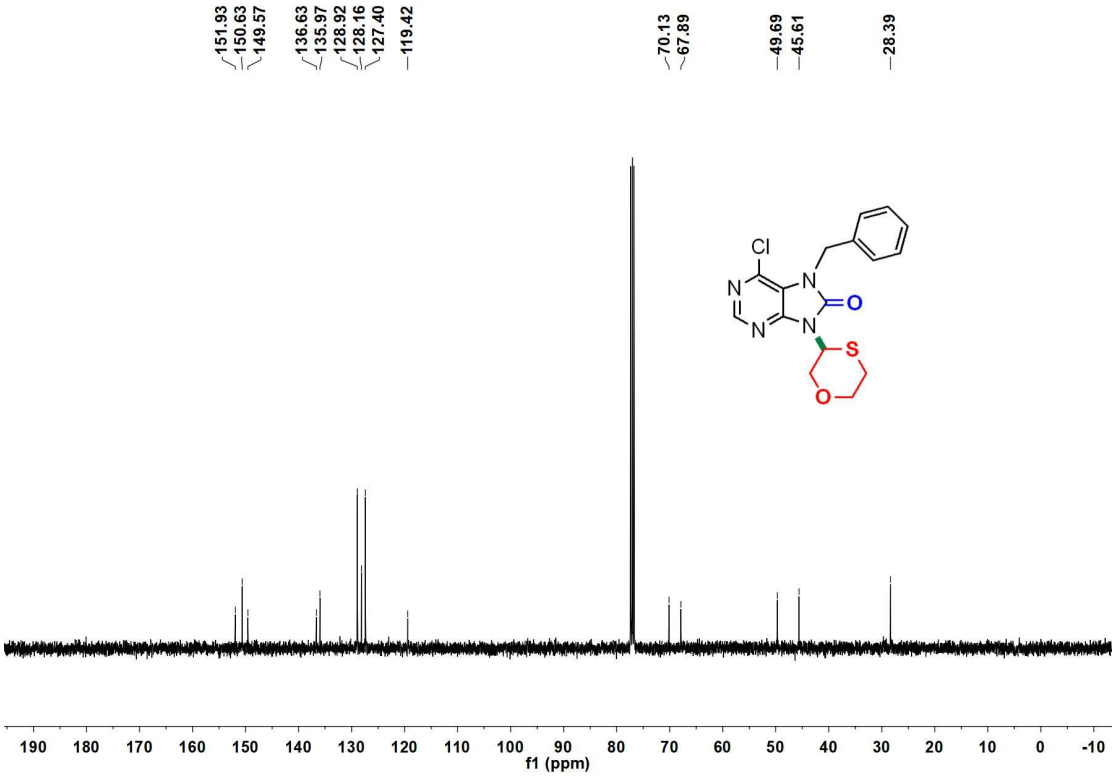
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5i**



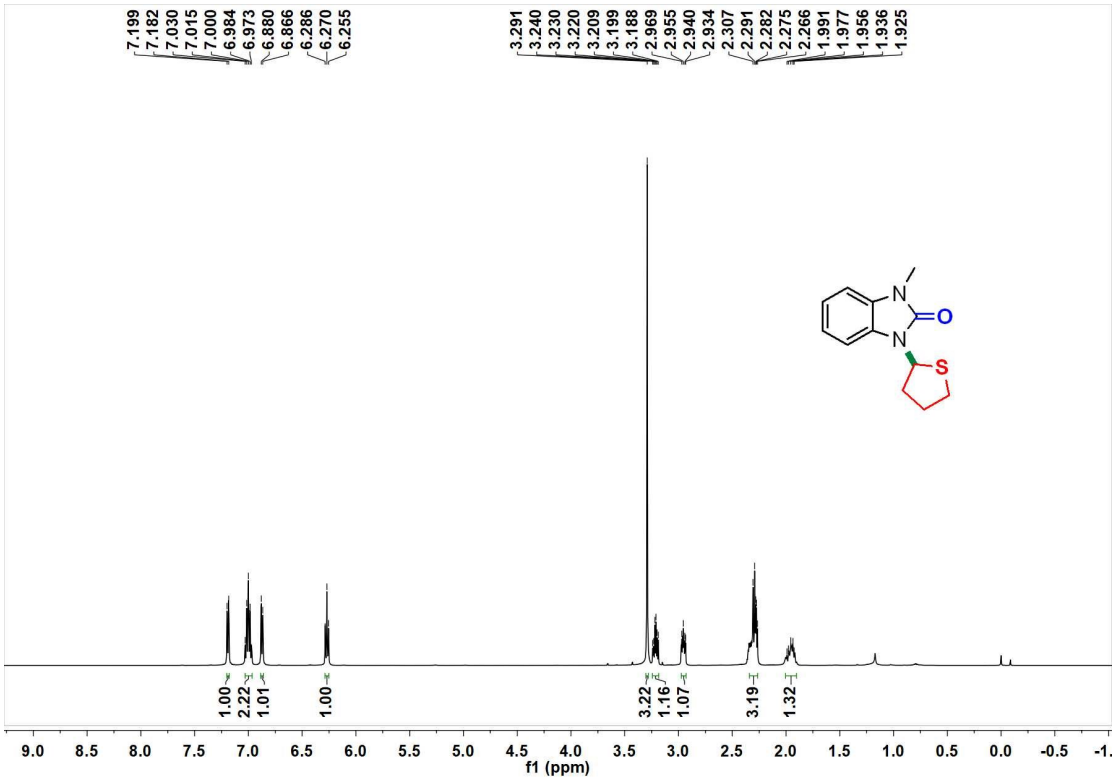
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5j**



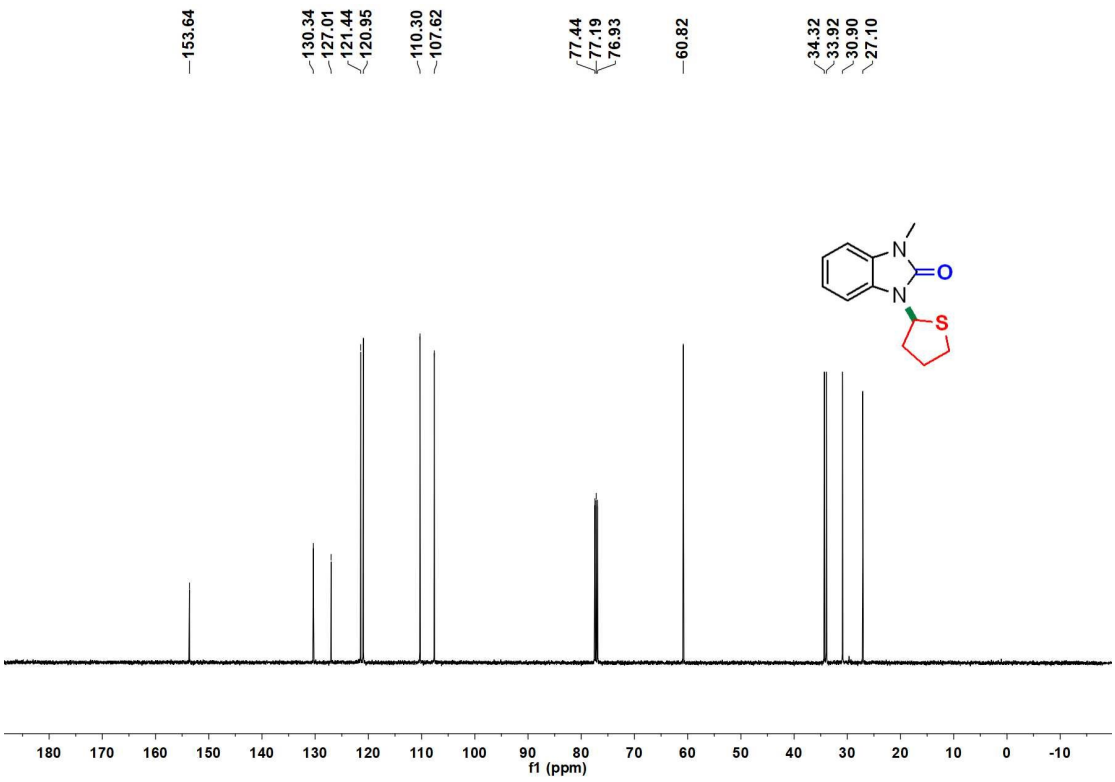
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5j**



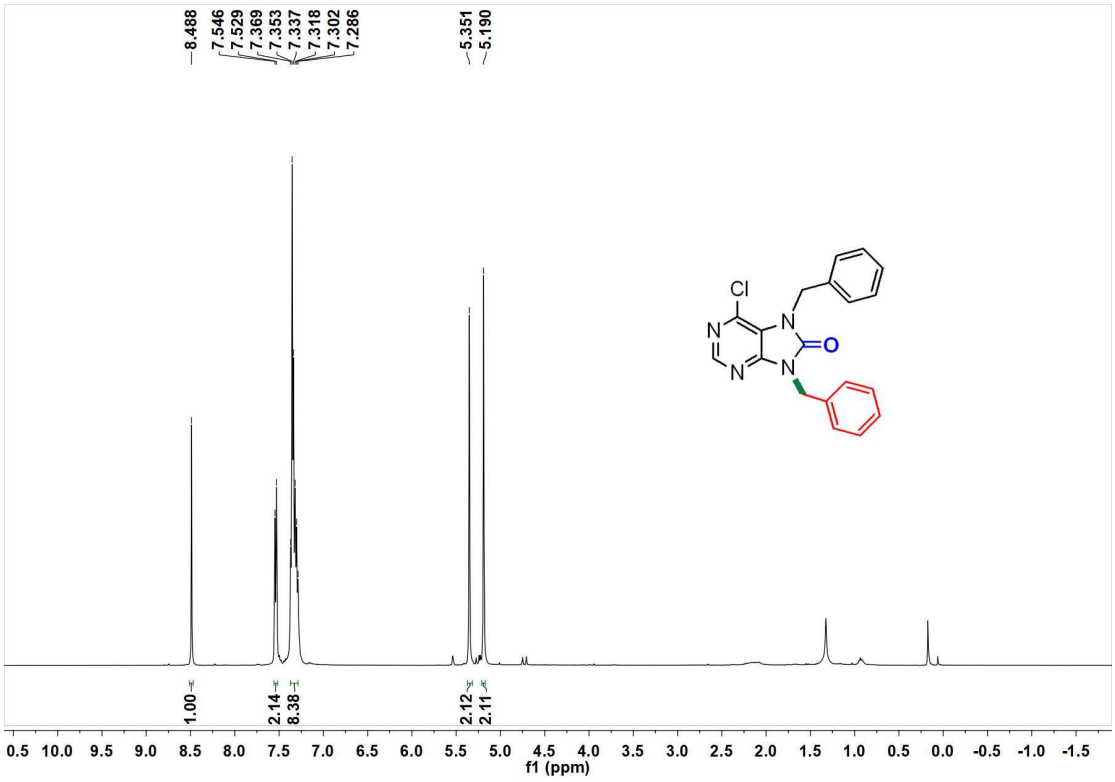
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5k**



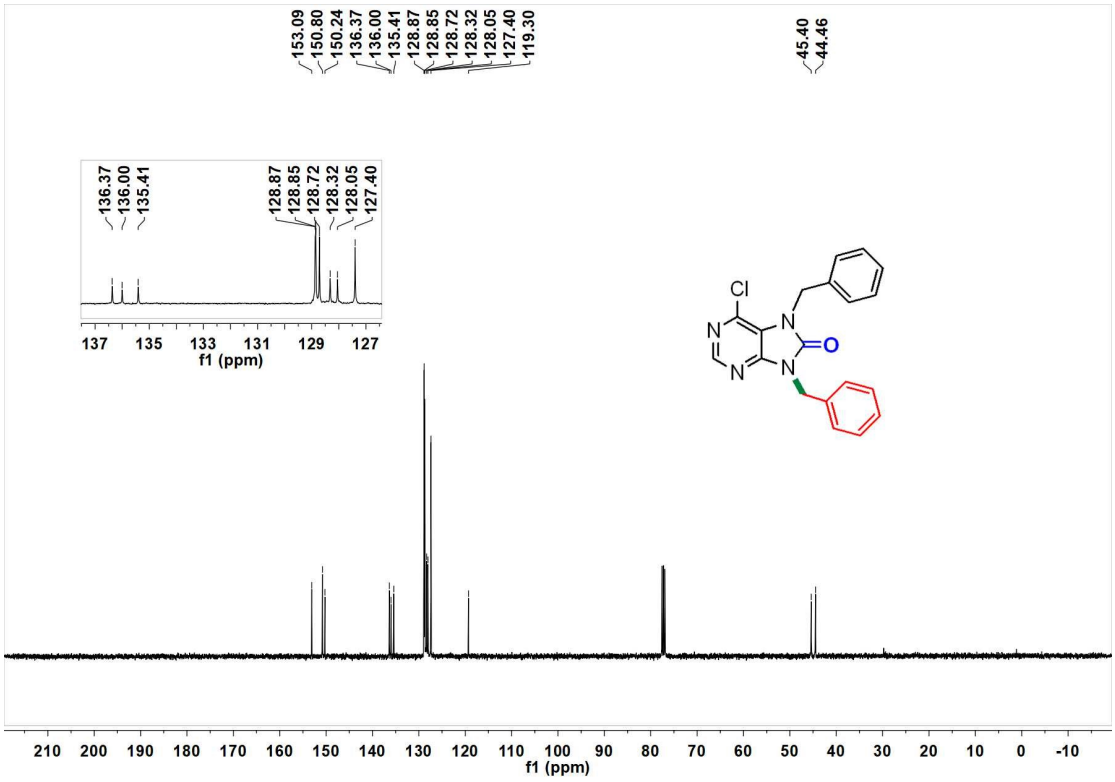
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **5k**



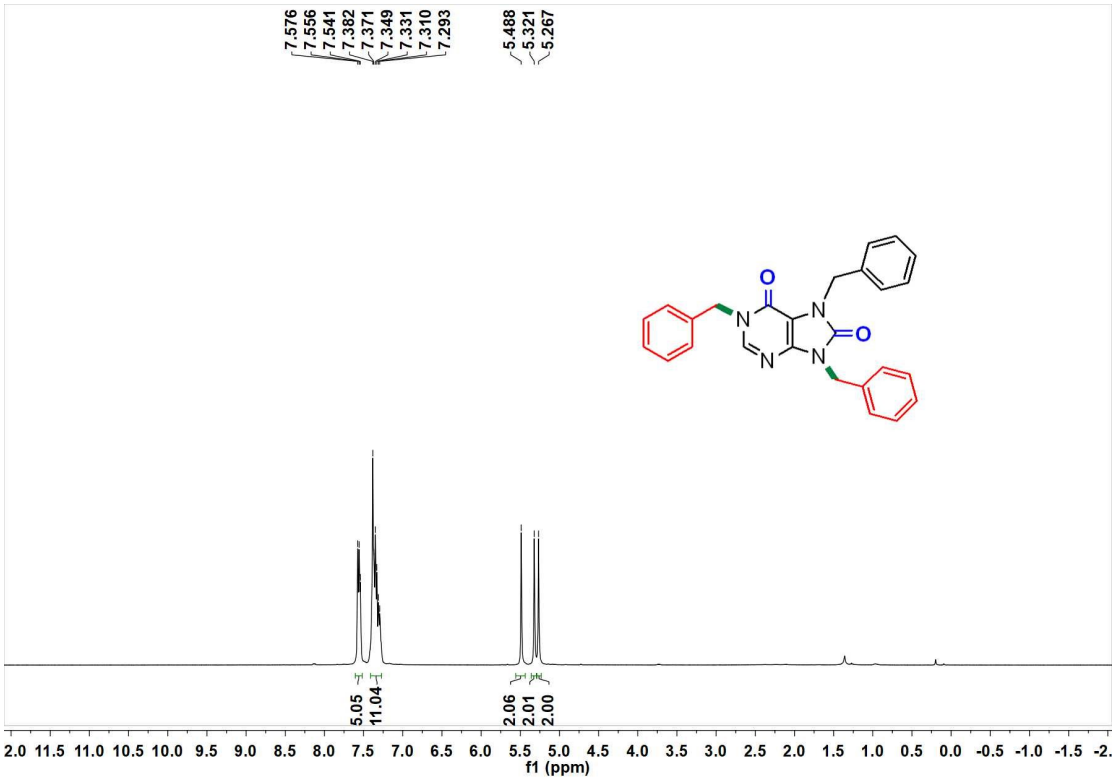
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a**



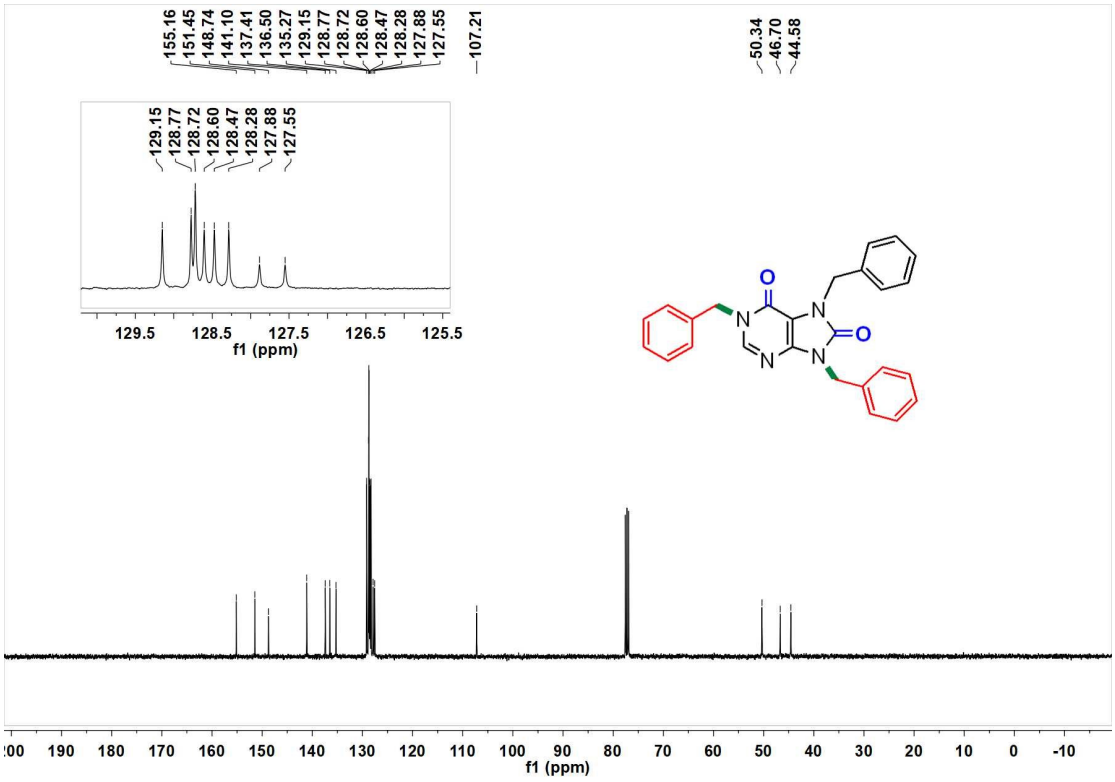
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7a**



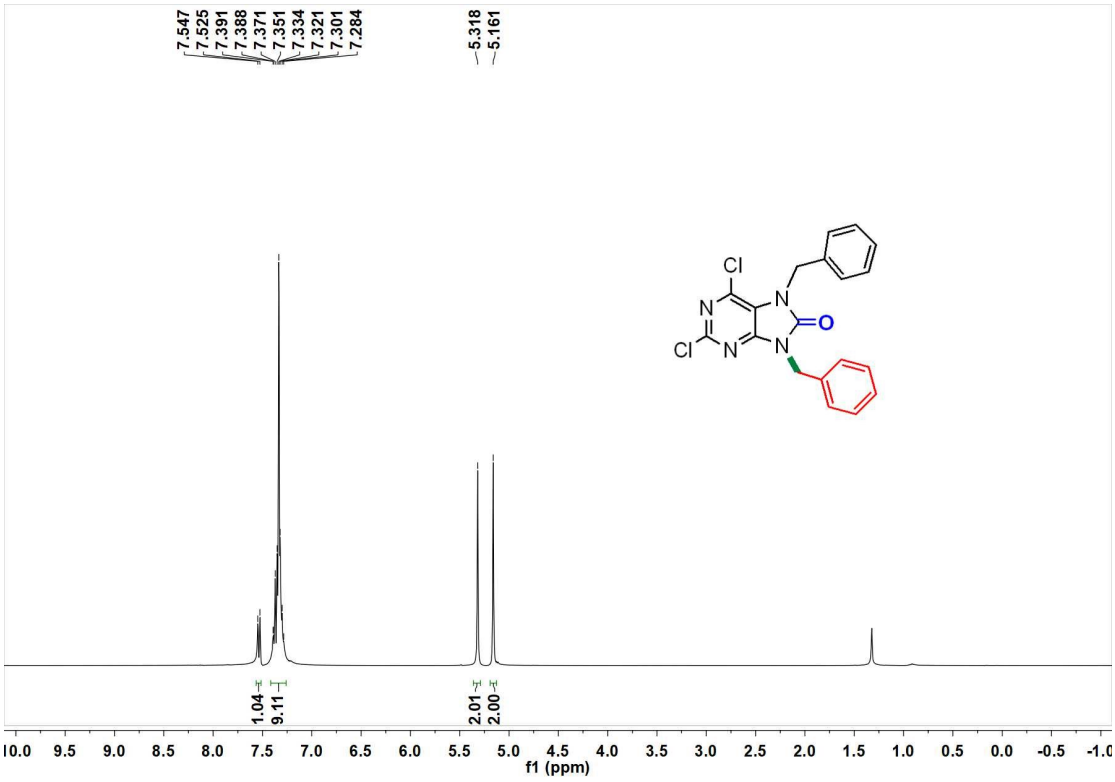
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a'**



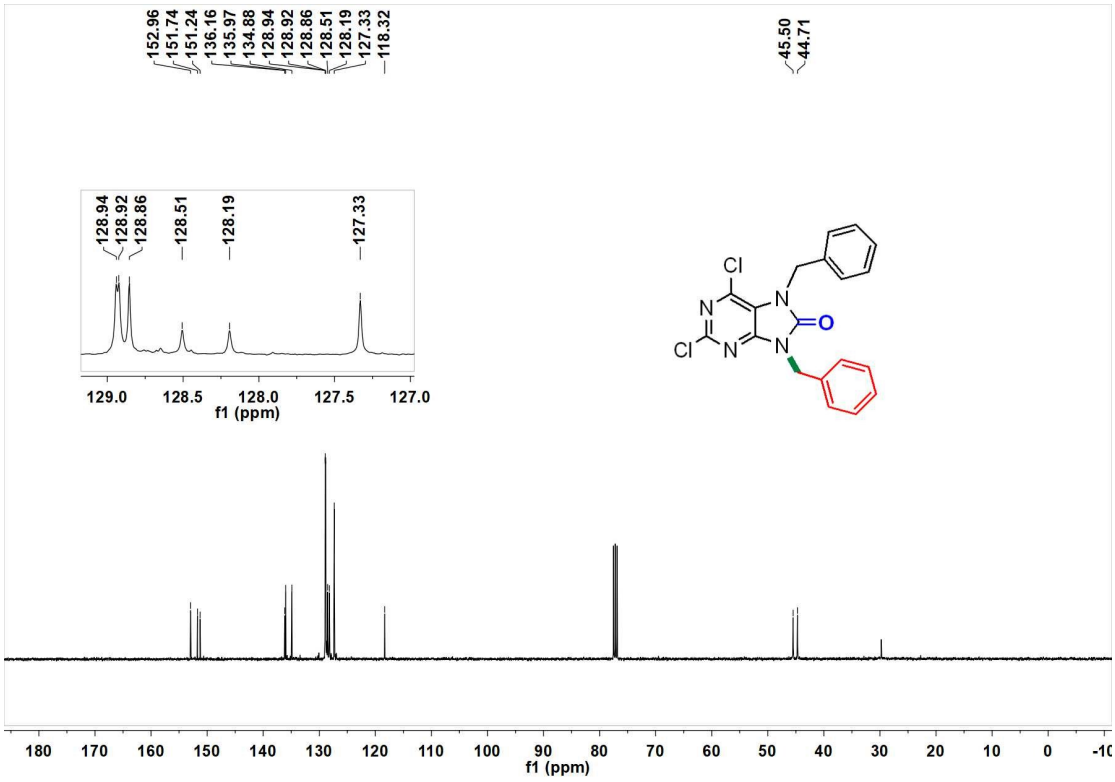
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7a'**



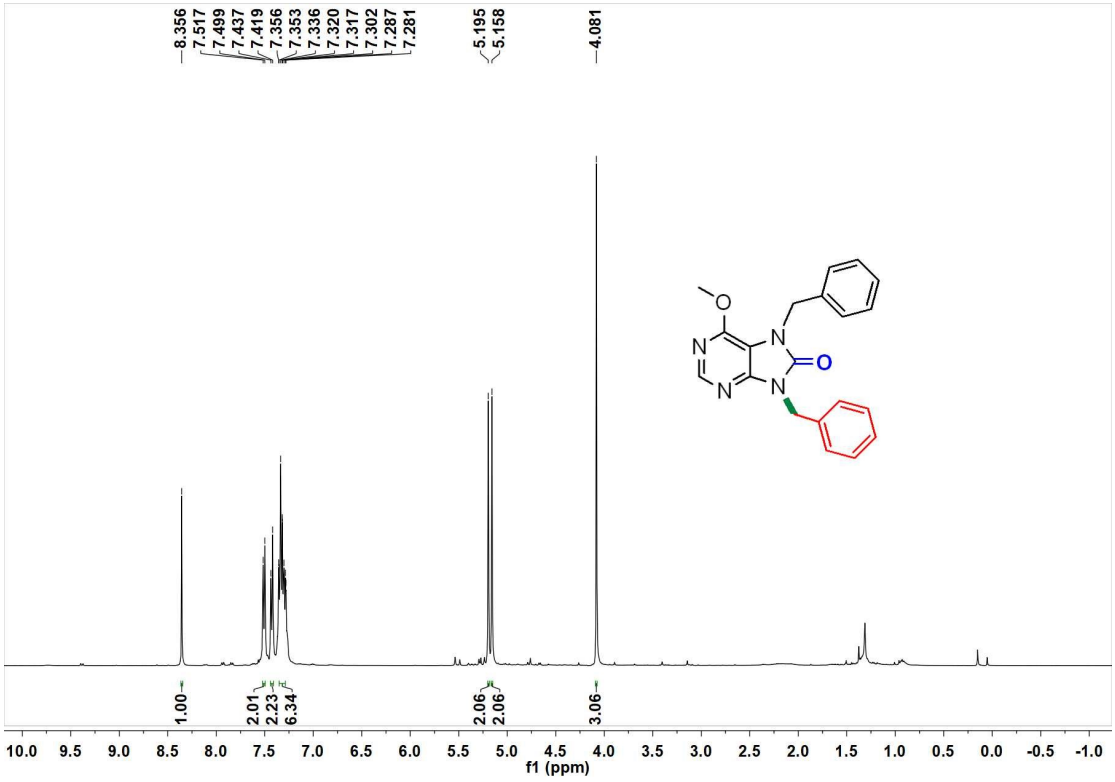
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7b**



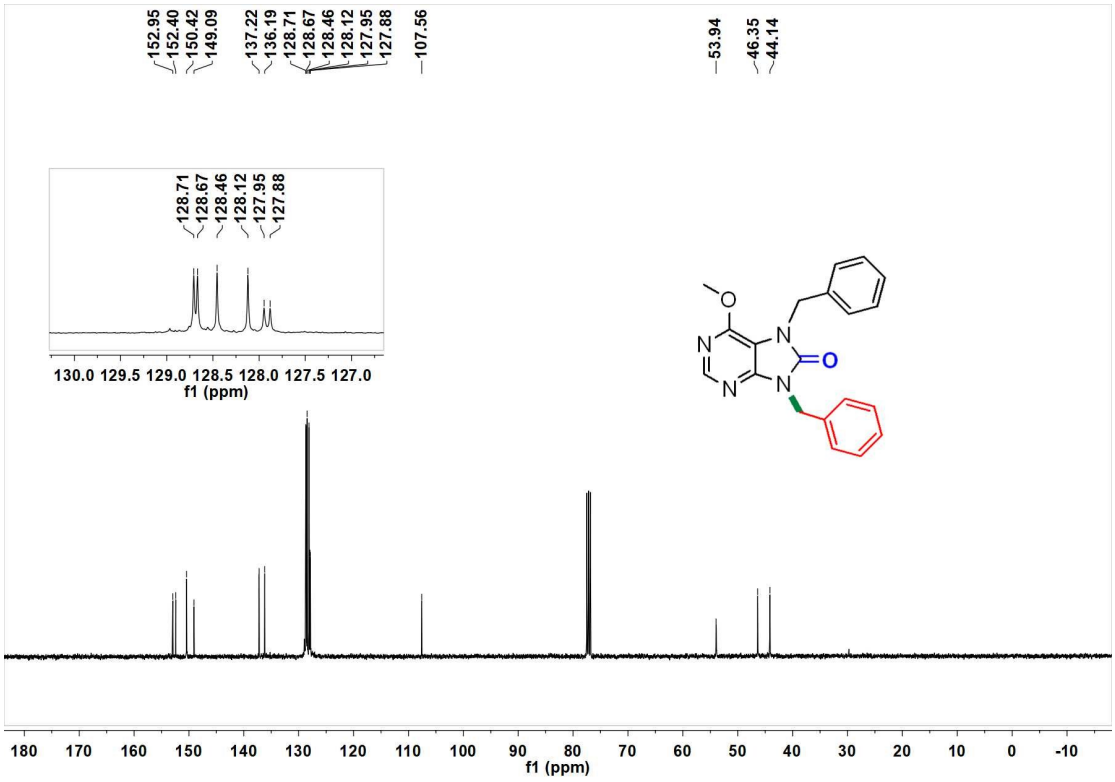
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7b**



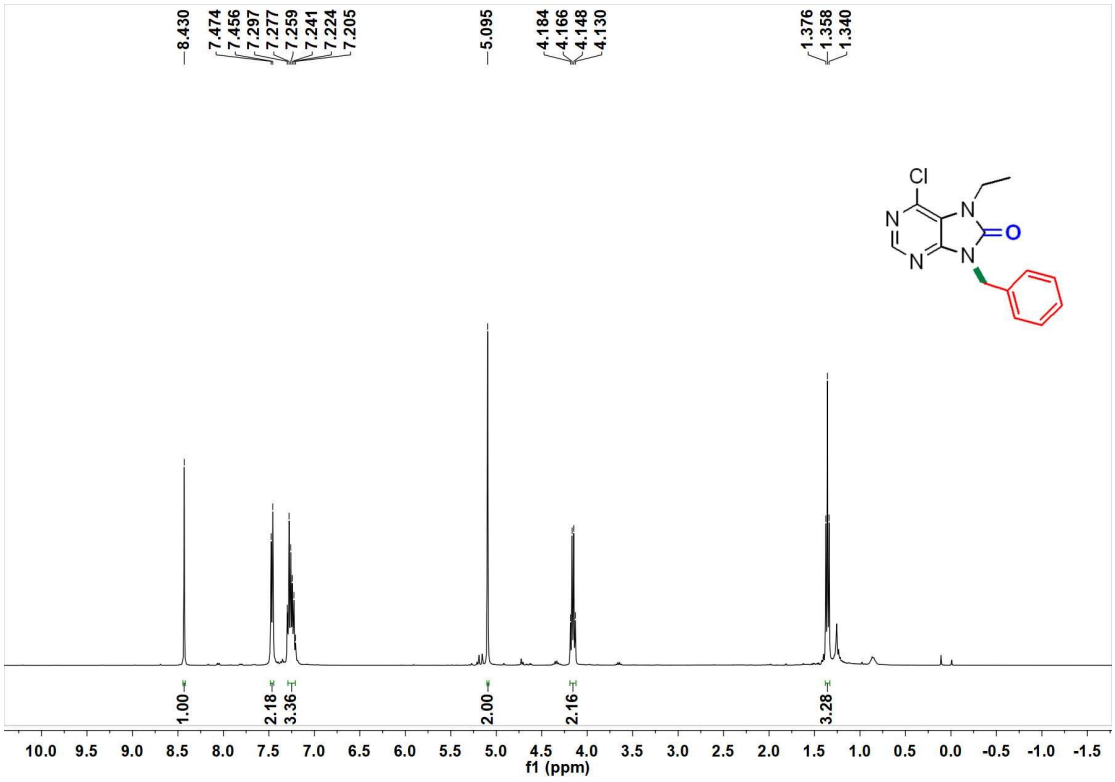
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7c**



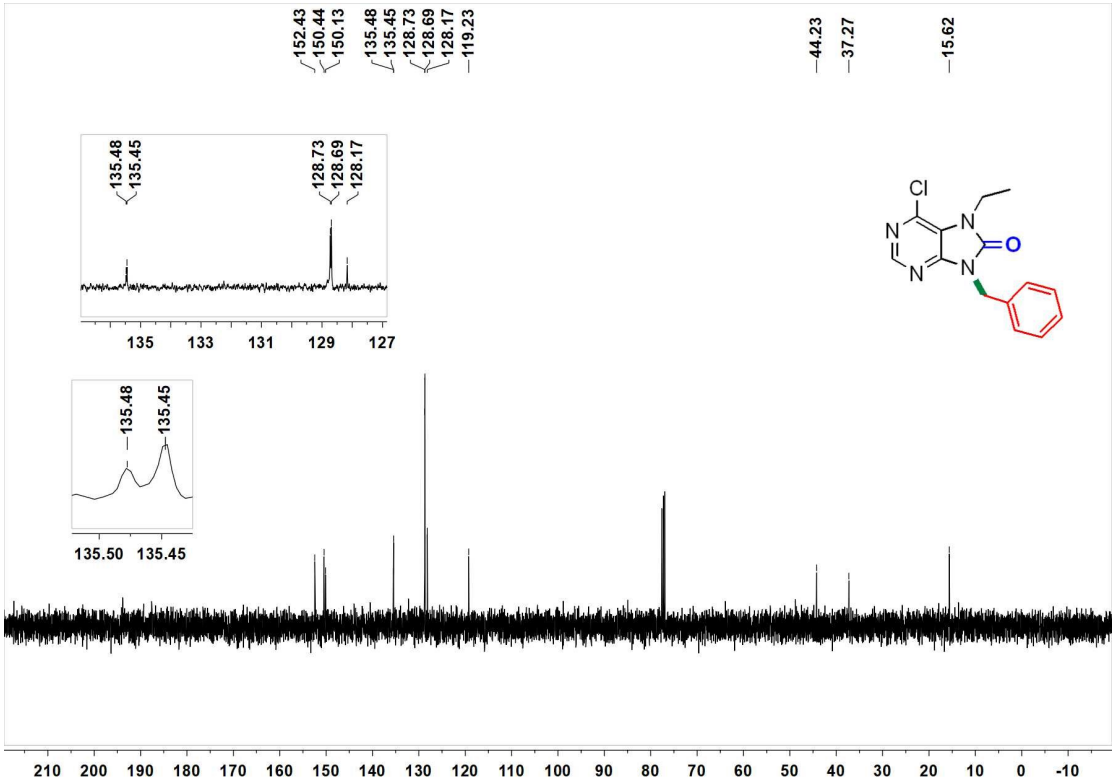
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7c**



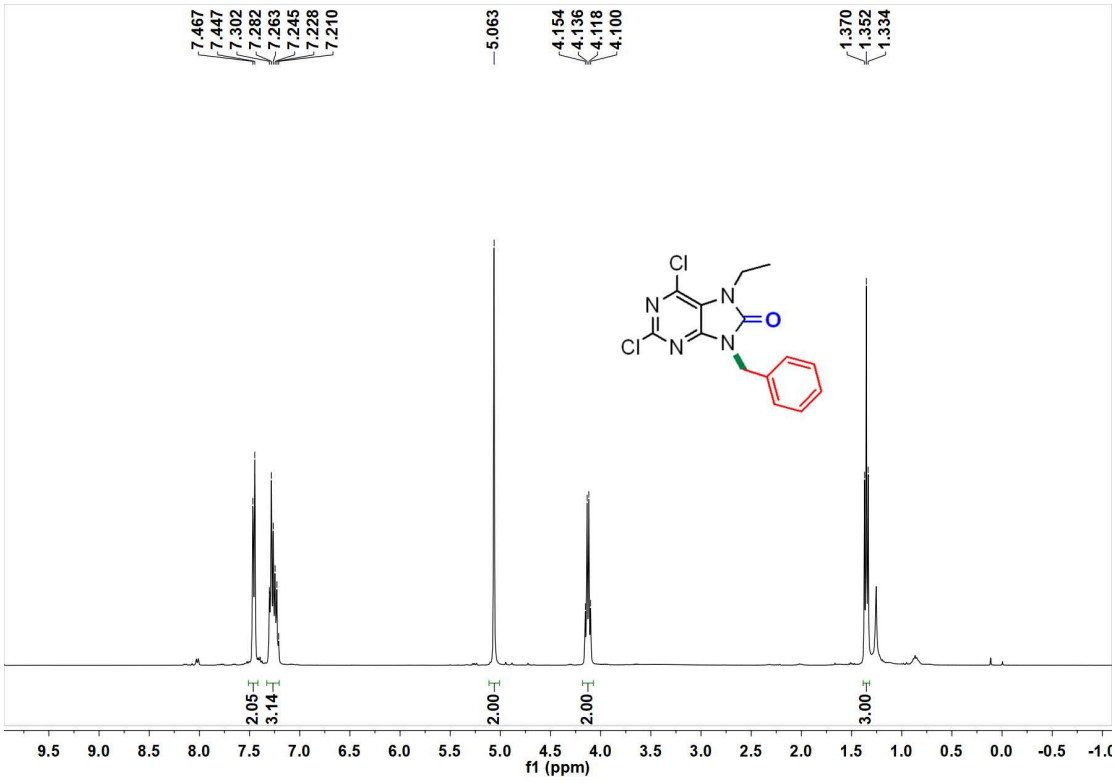
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7d**



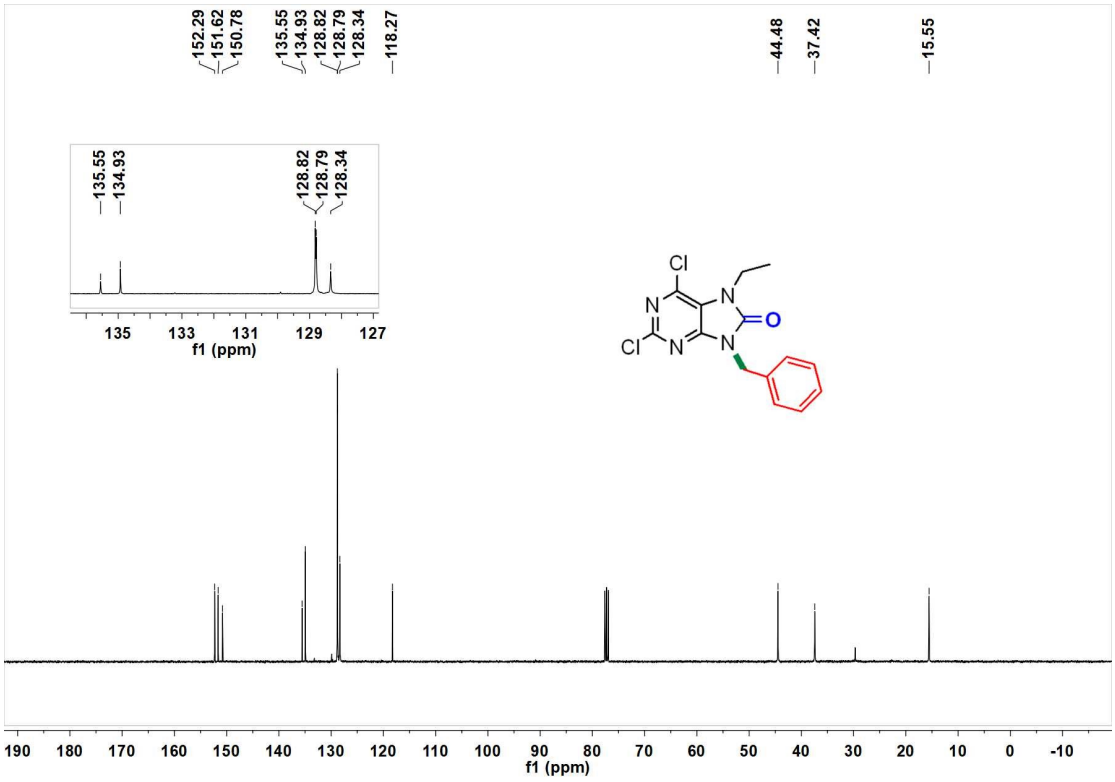
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7d**



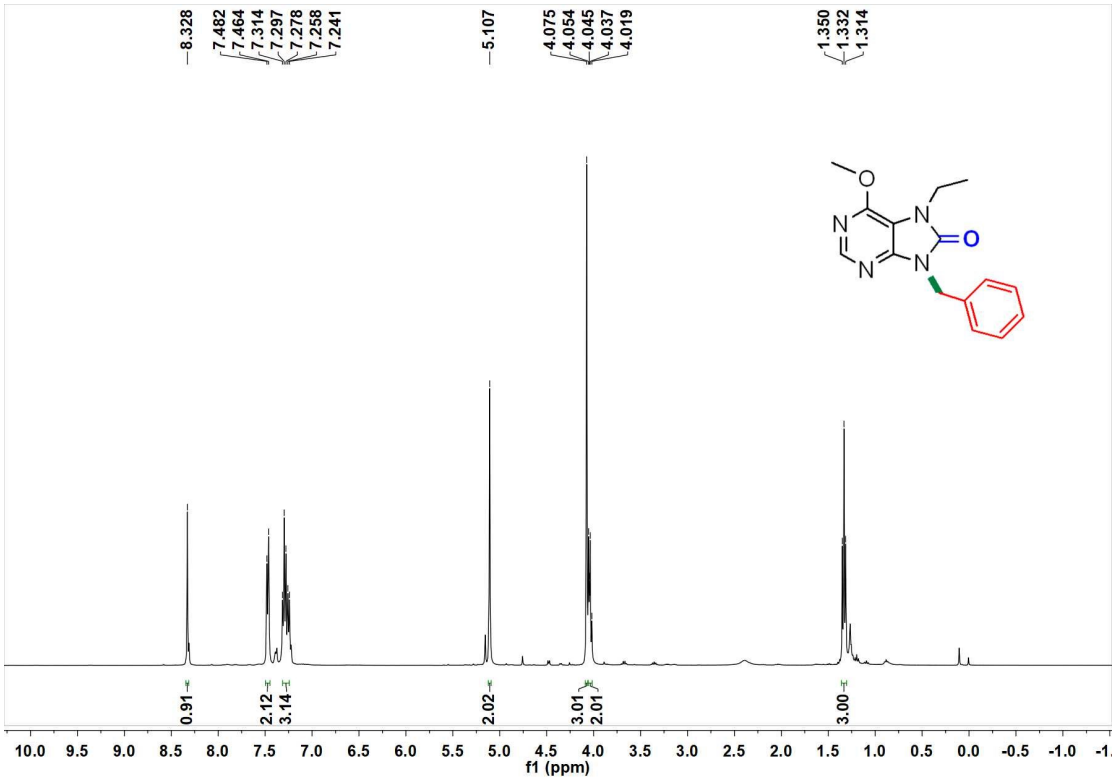
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7e**



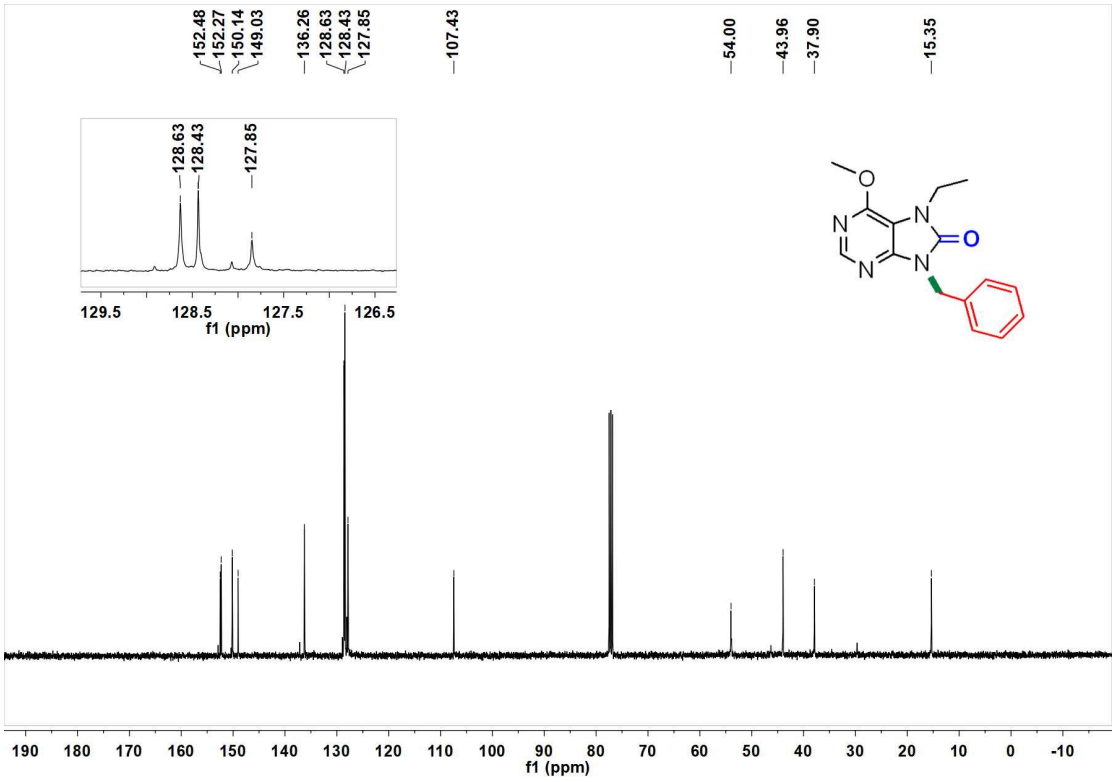
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7e**



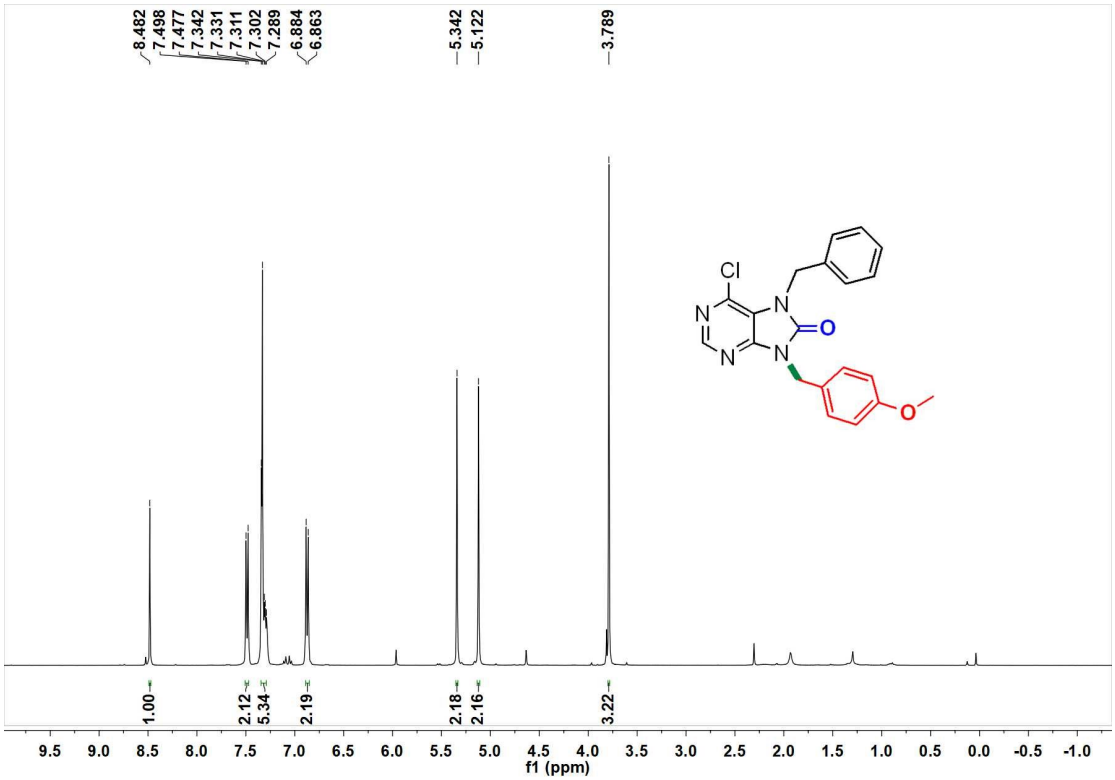
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7f**



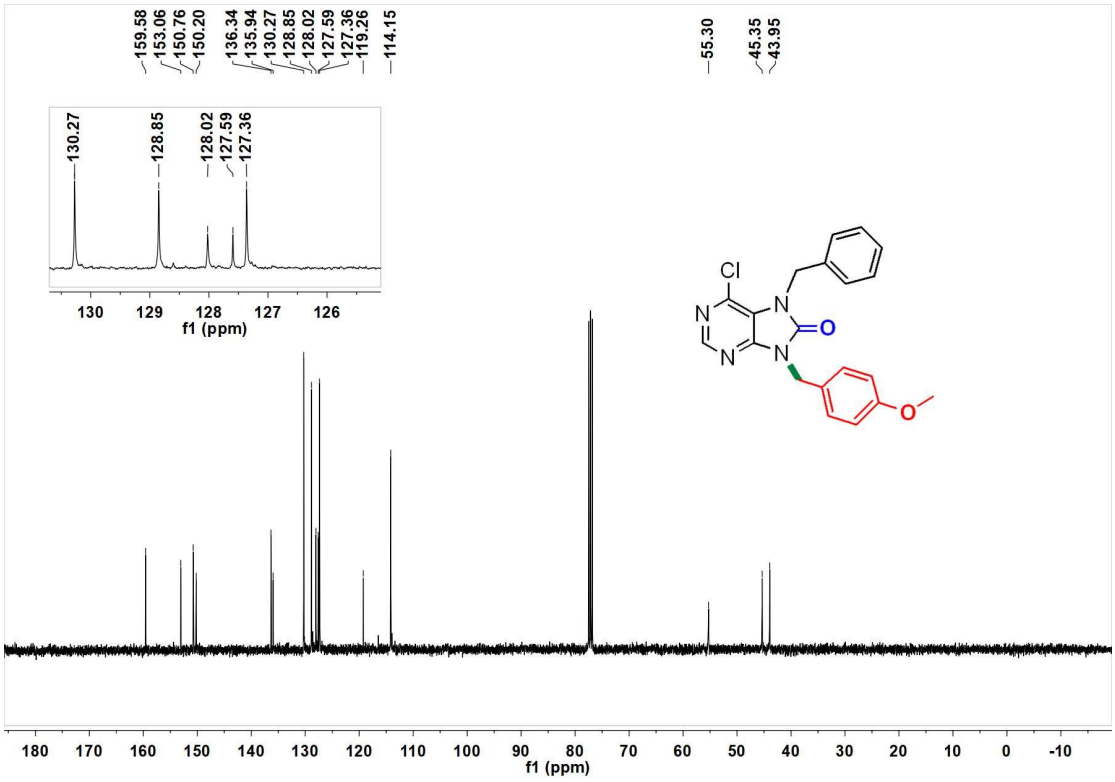
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7f**



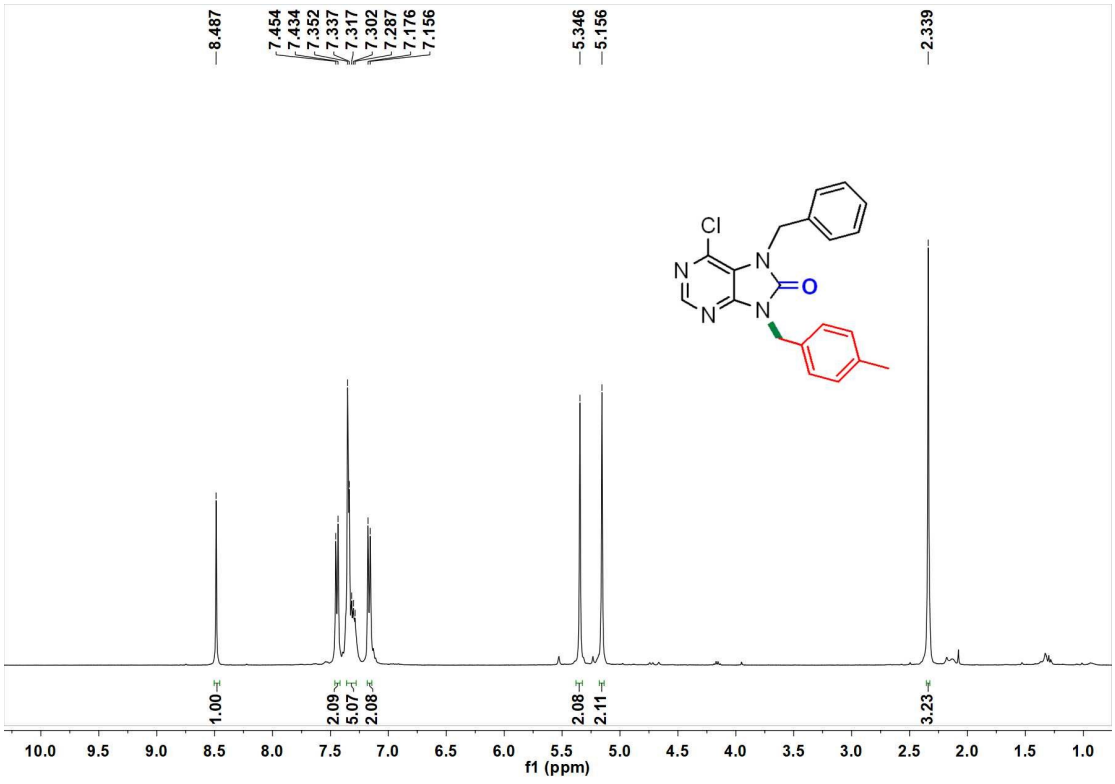
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7g**



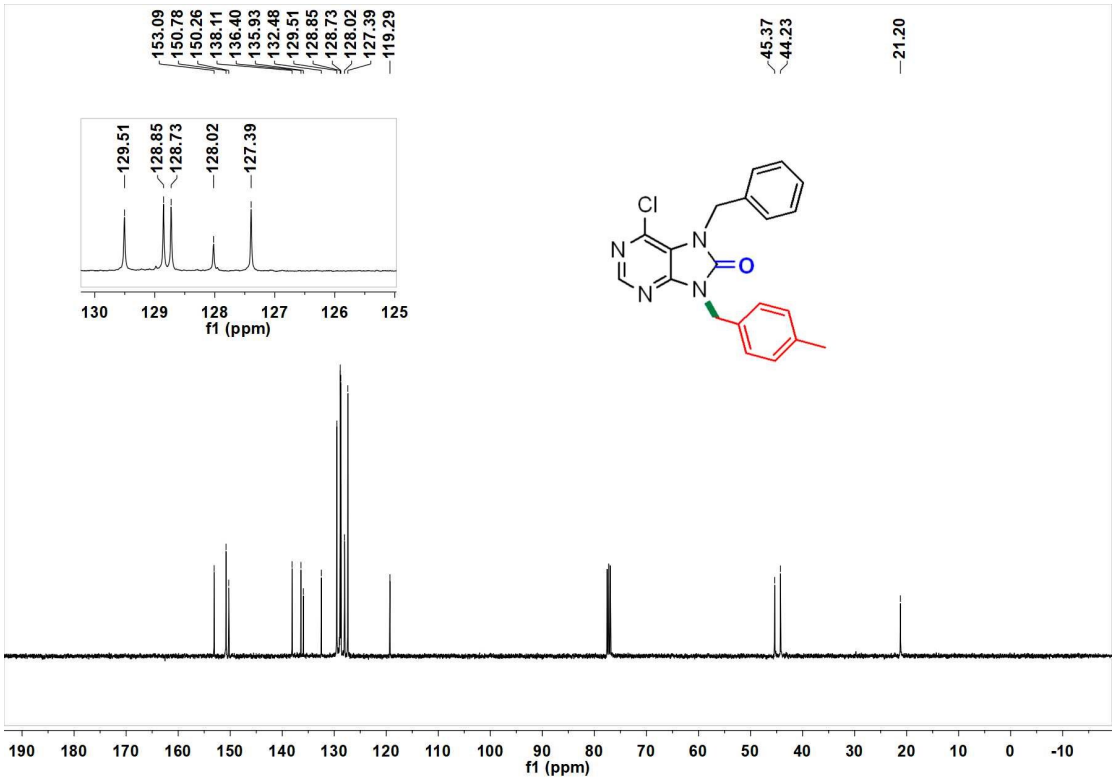
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7g**



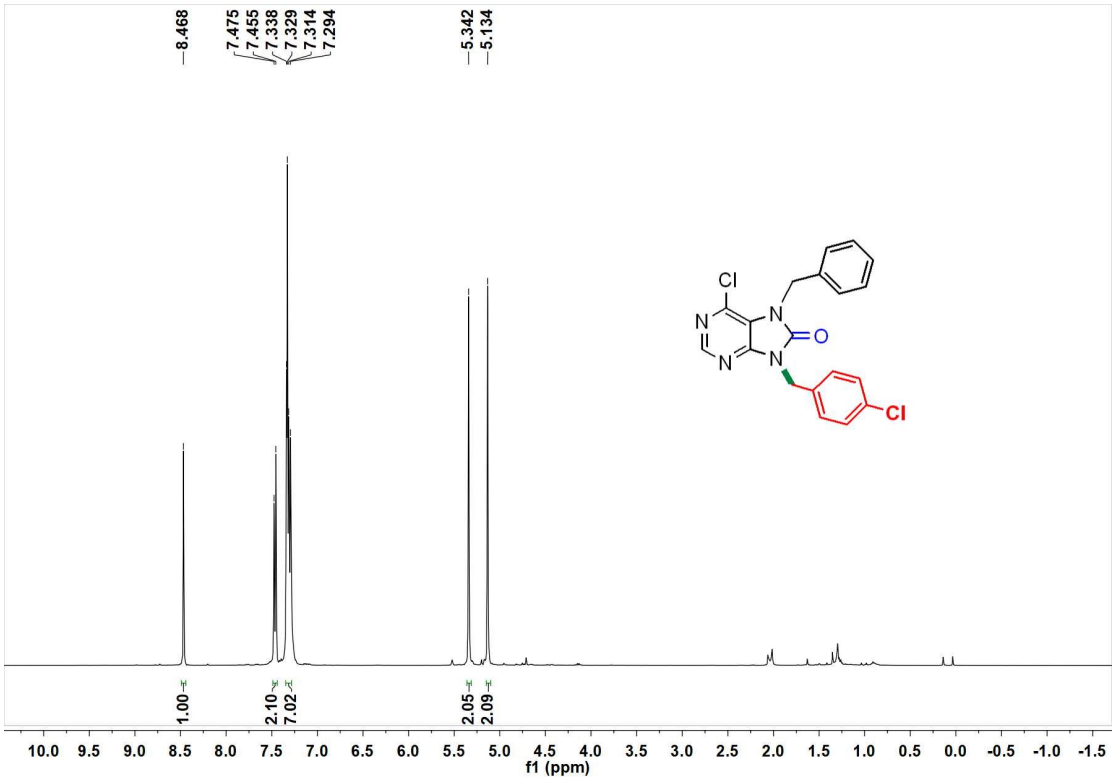
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7h**



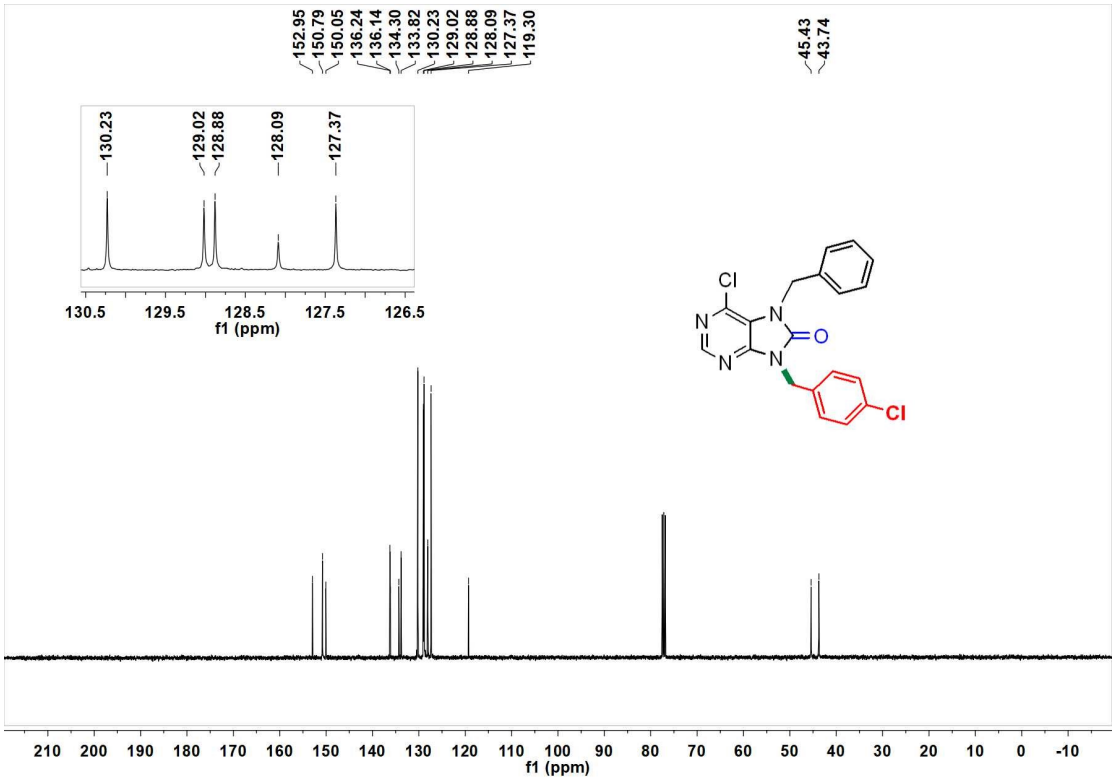
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7h**



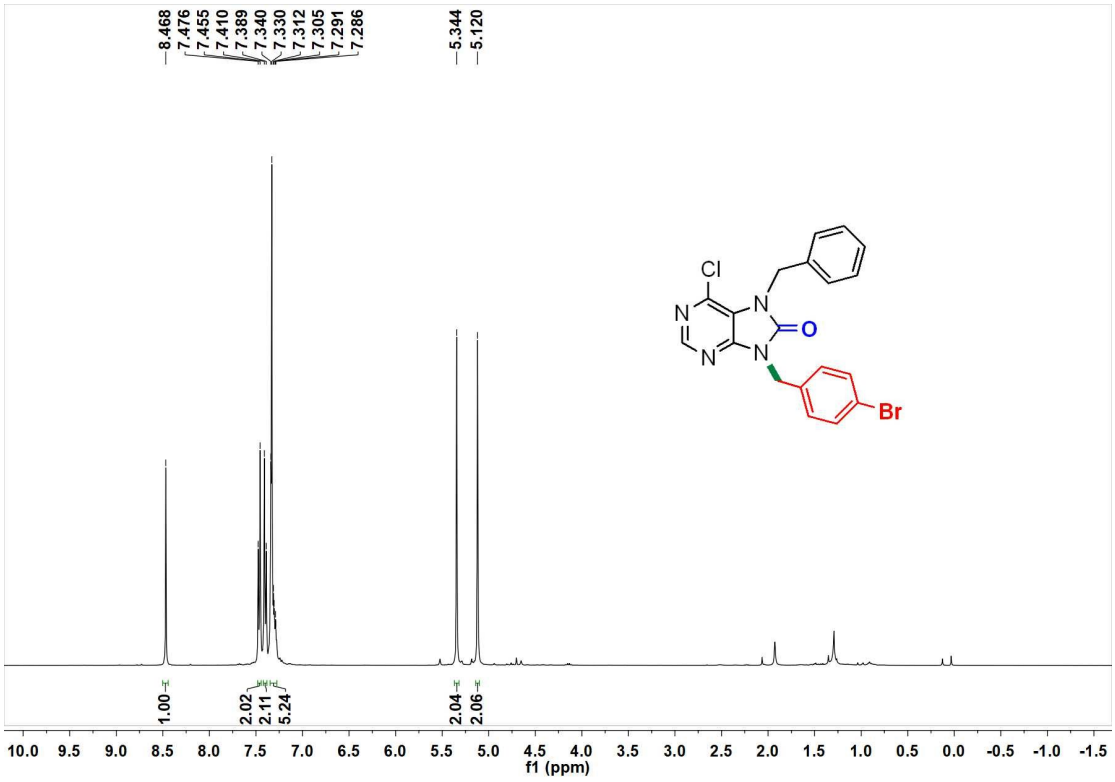
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7i**



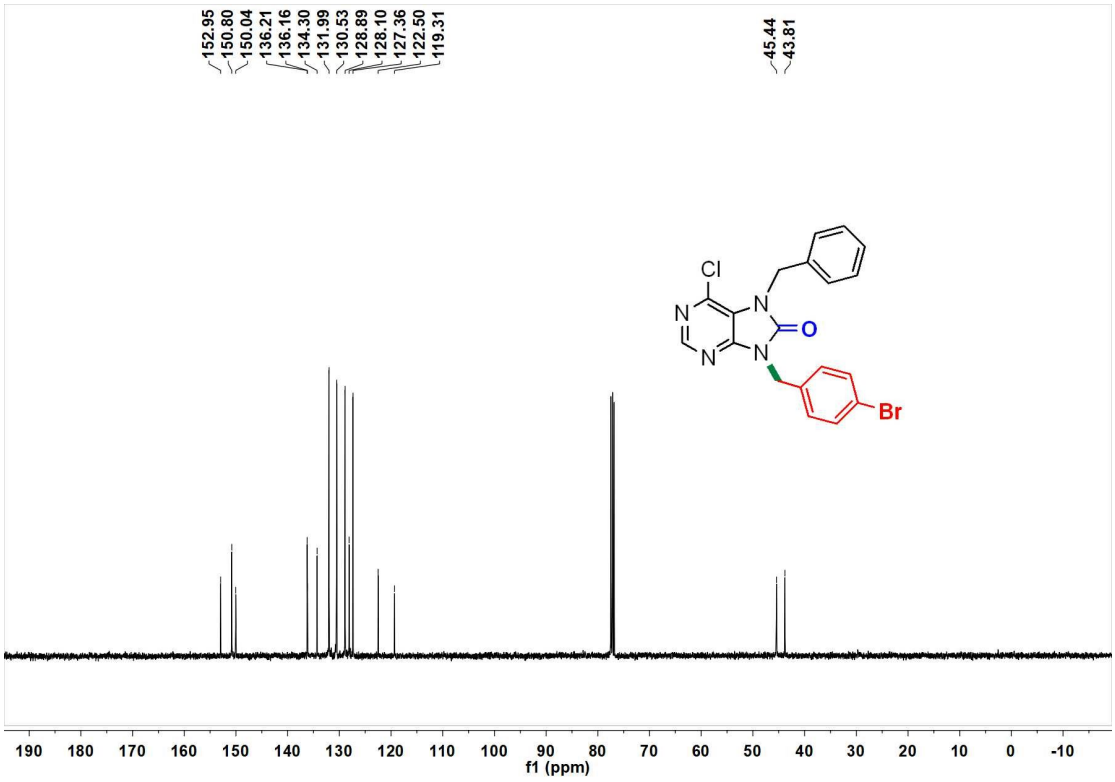
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7i**



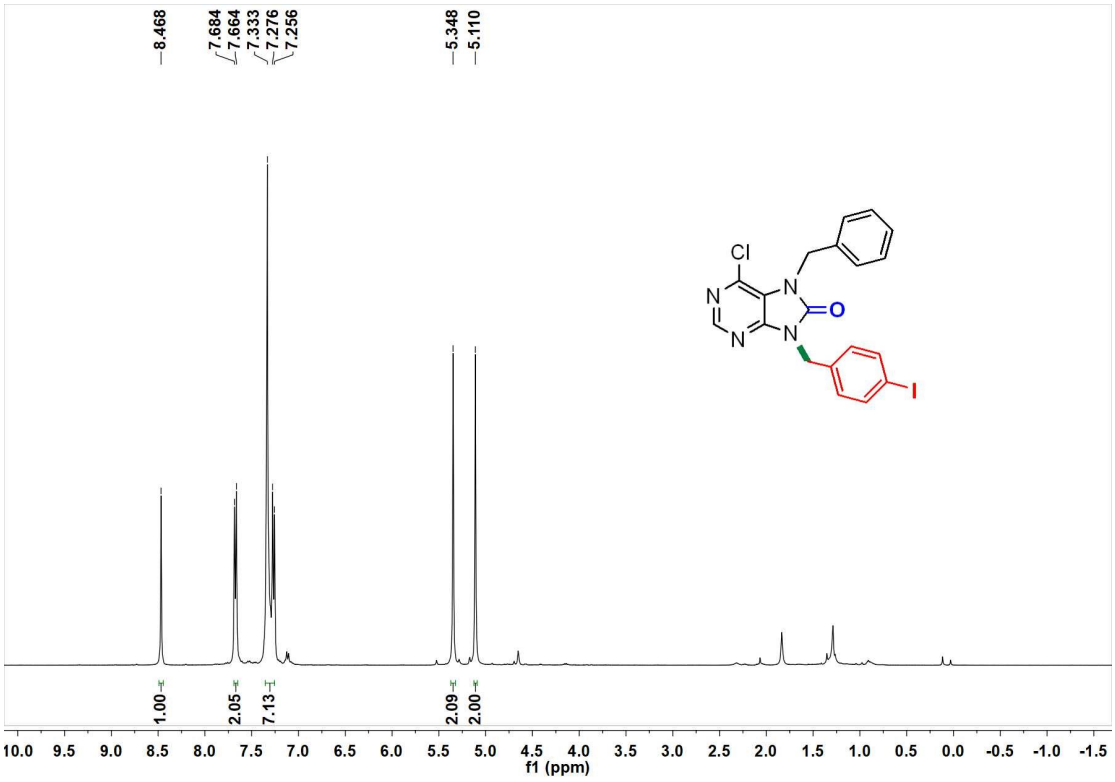
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7j**



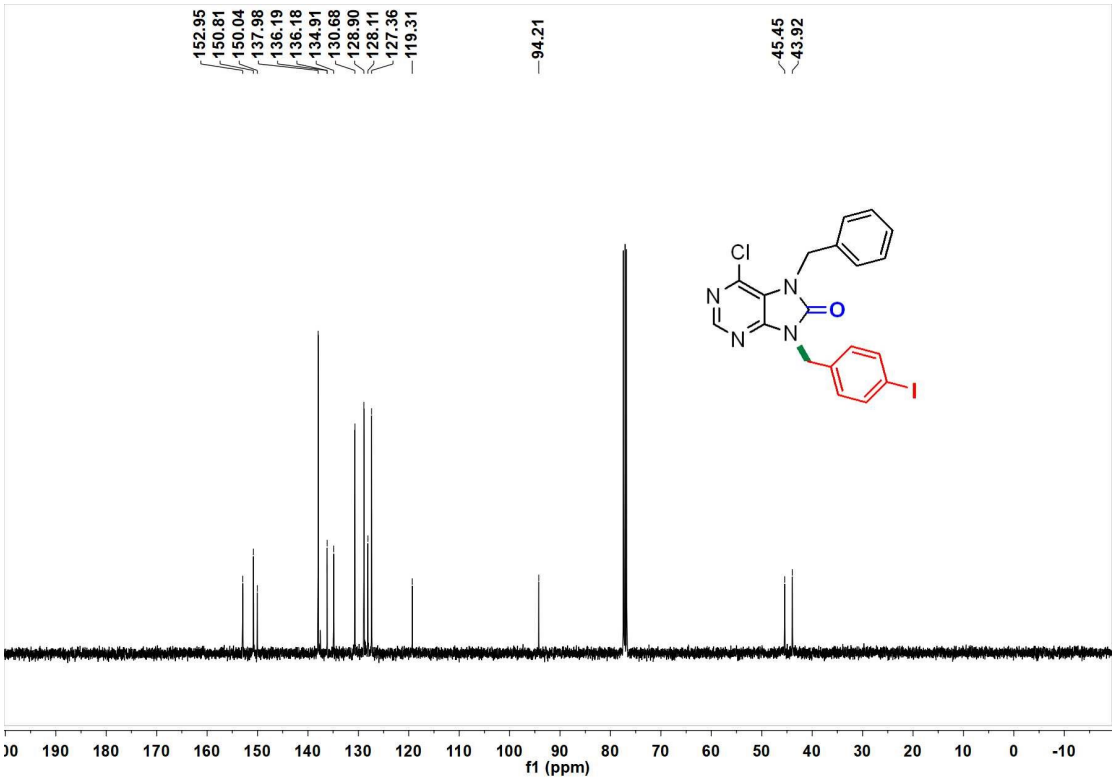
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7j**



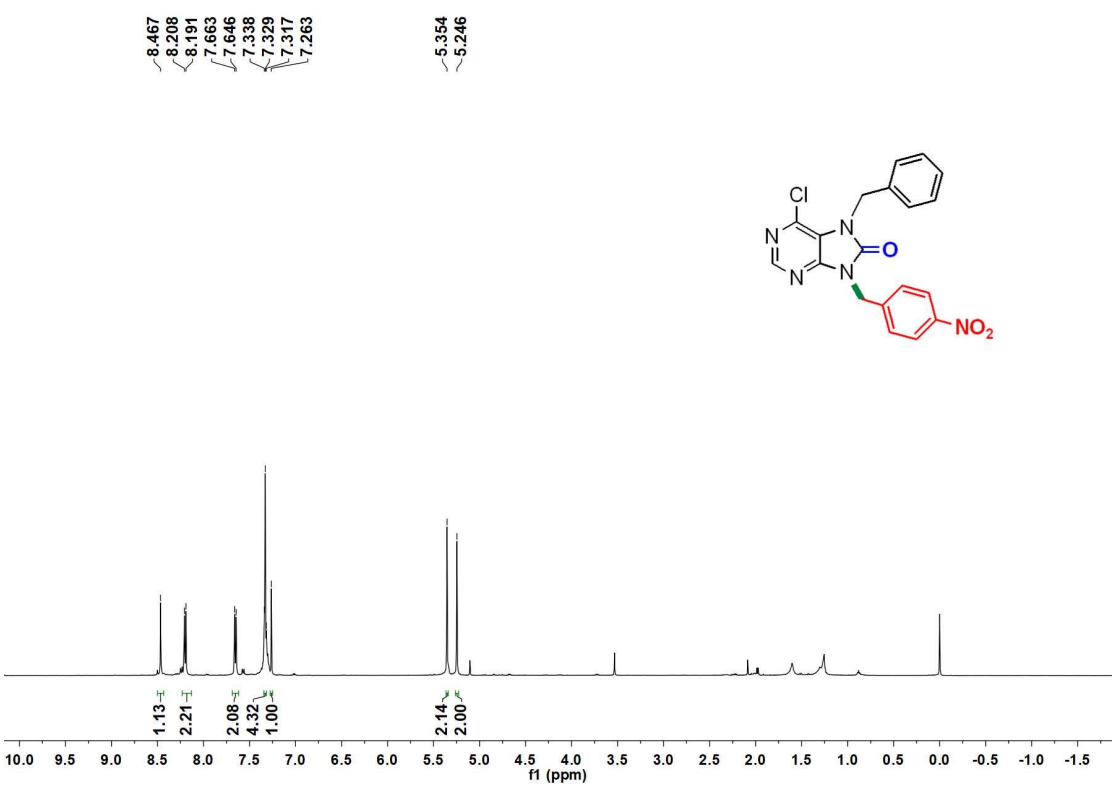
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7k**



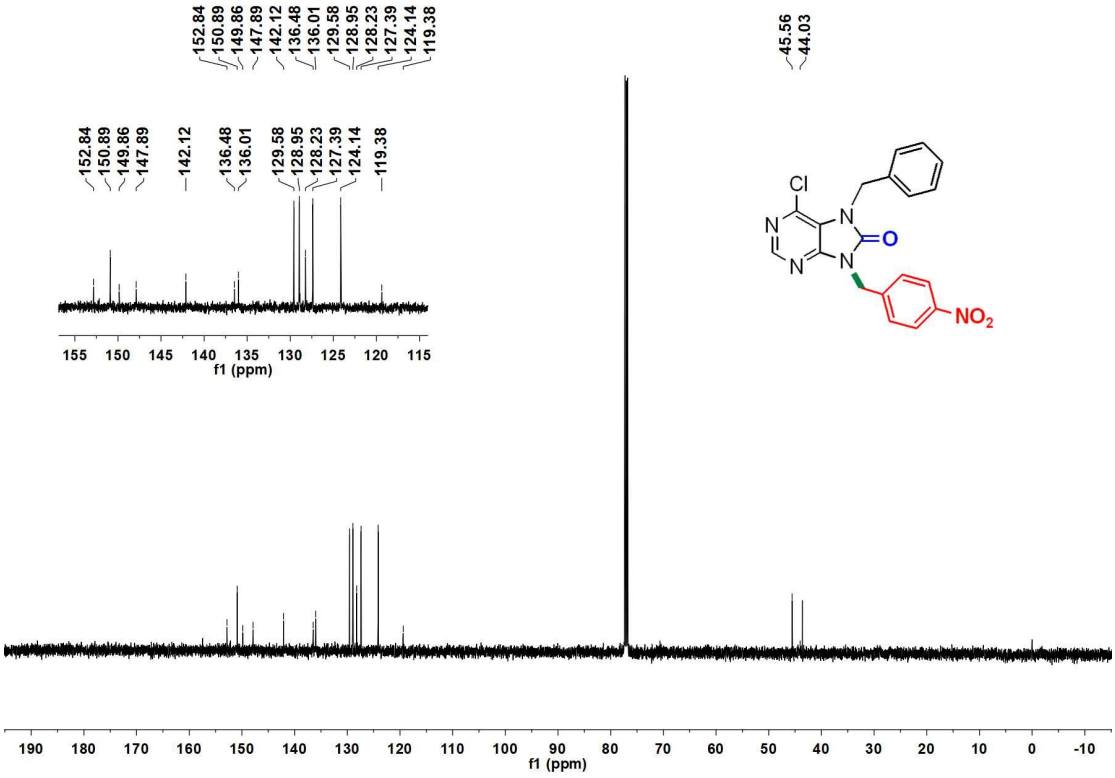
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7k**



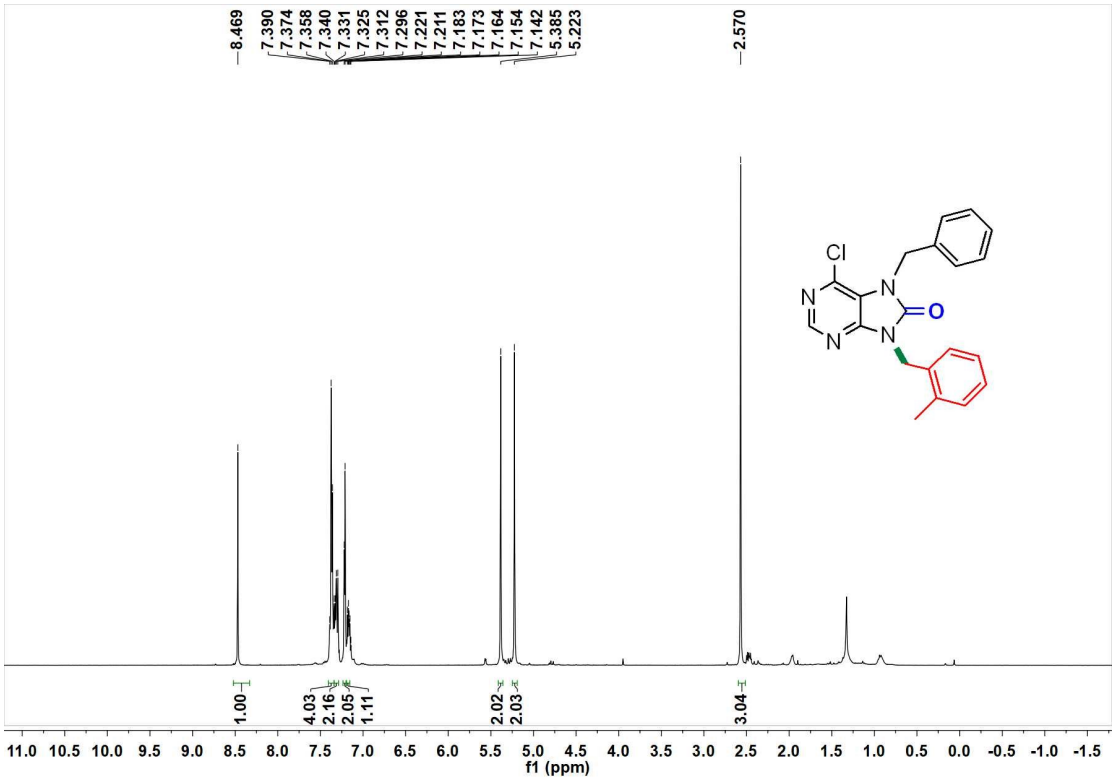
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7l**



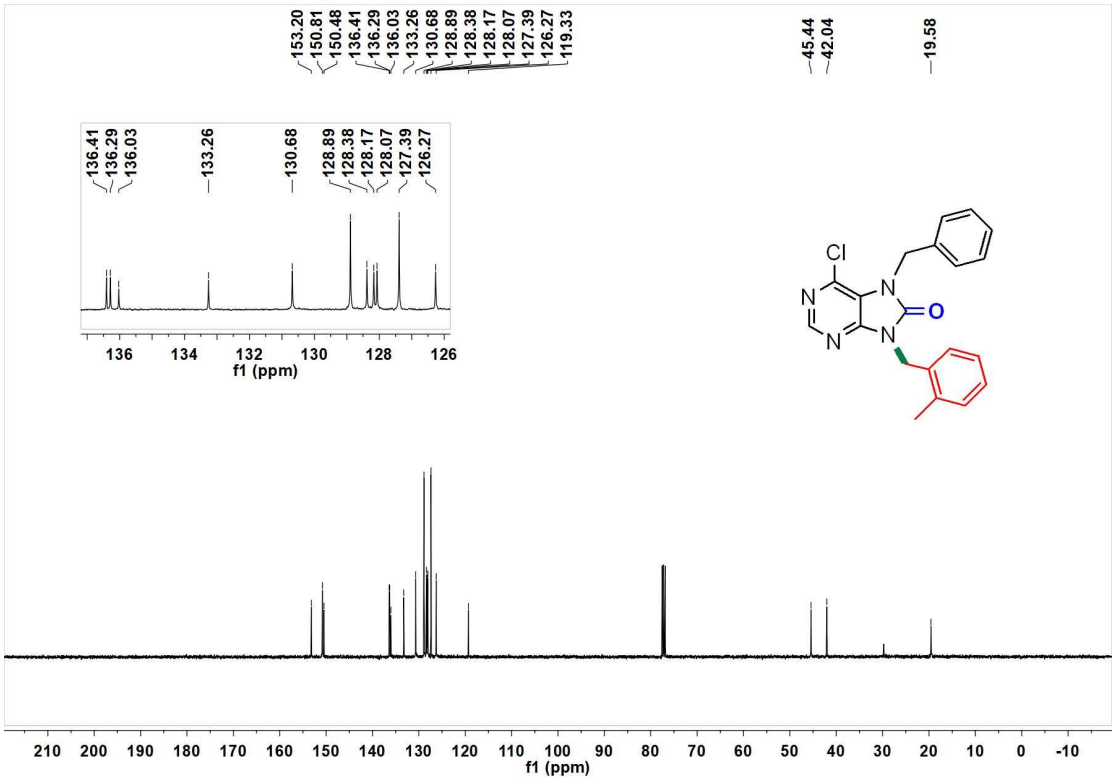
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **7l**



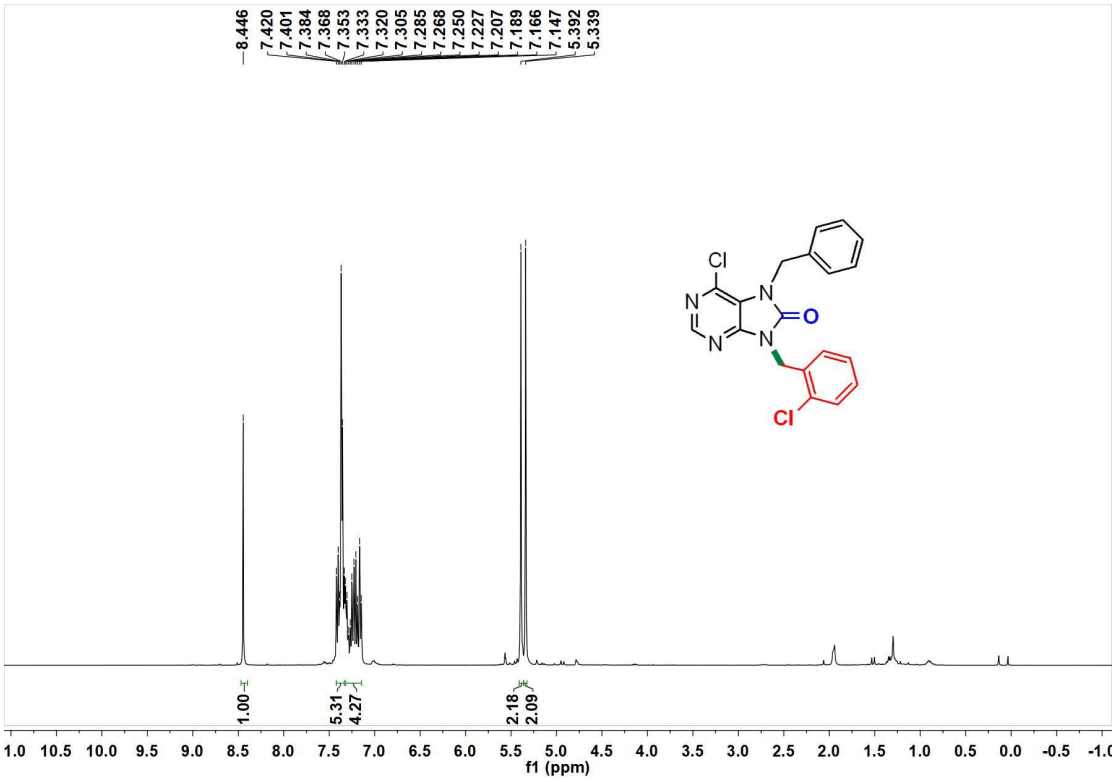
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7m**



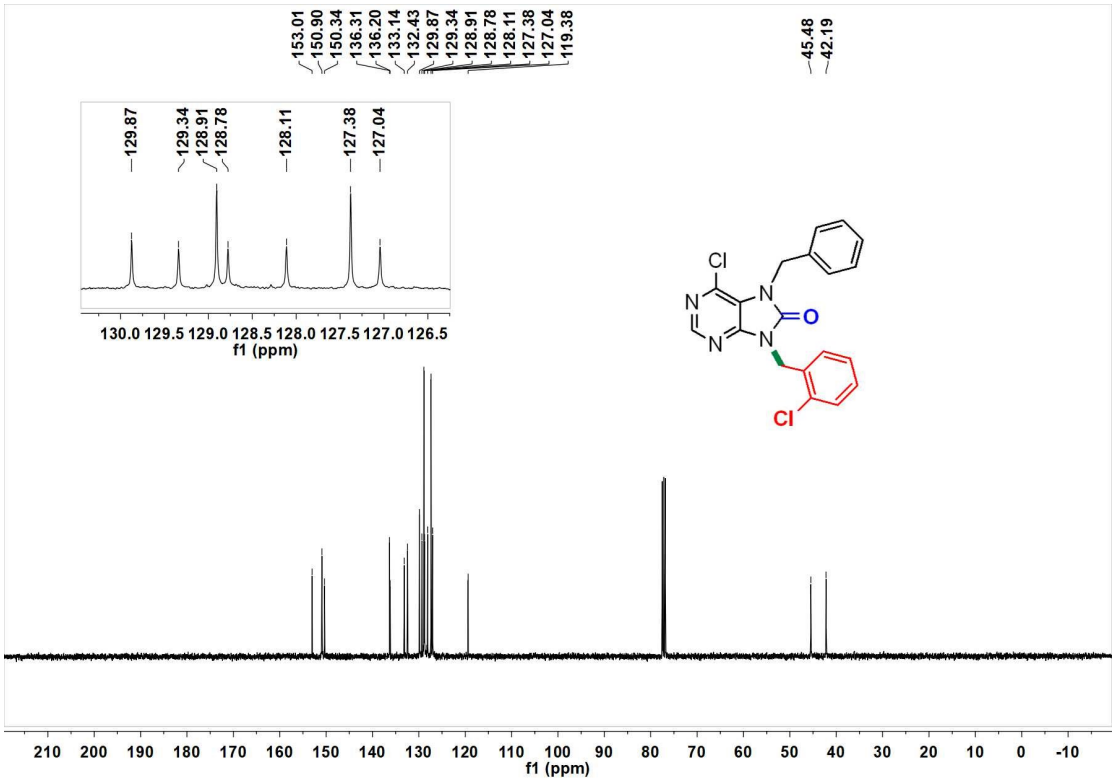
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7m**



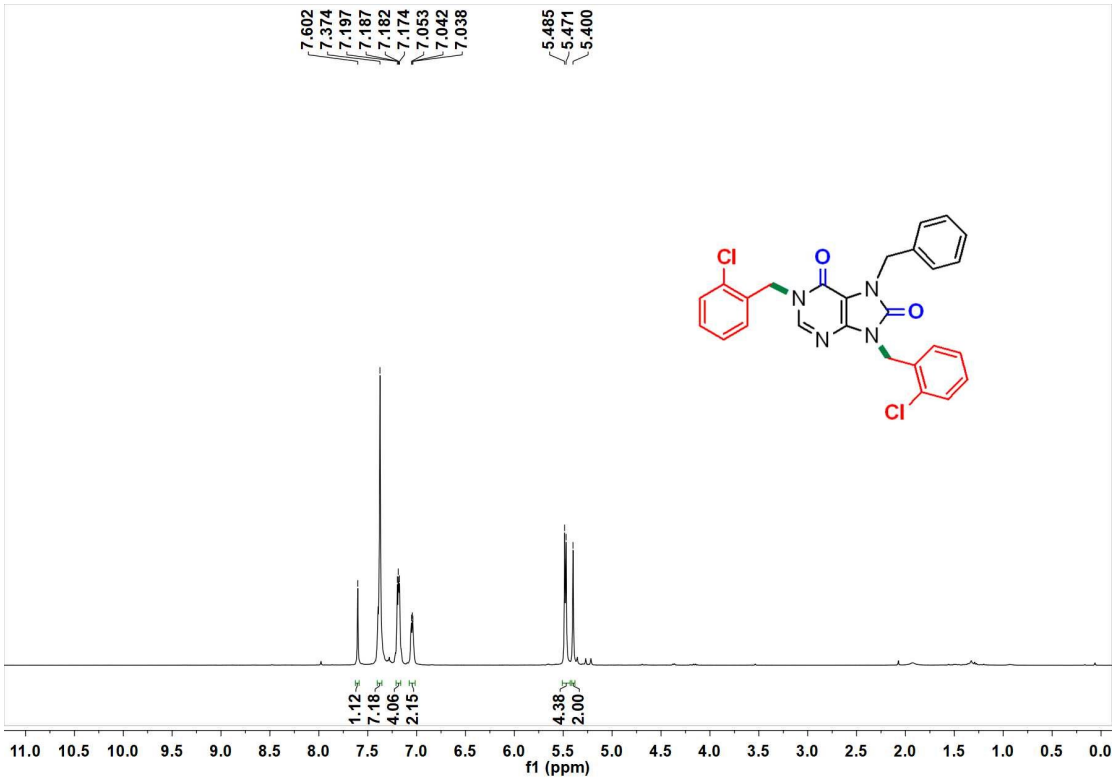
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7n**



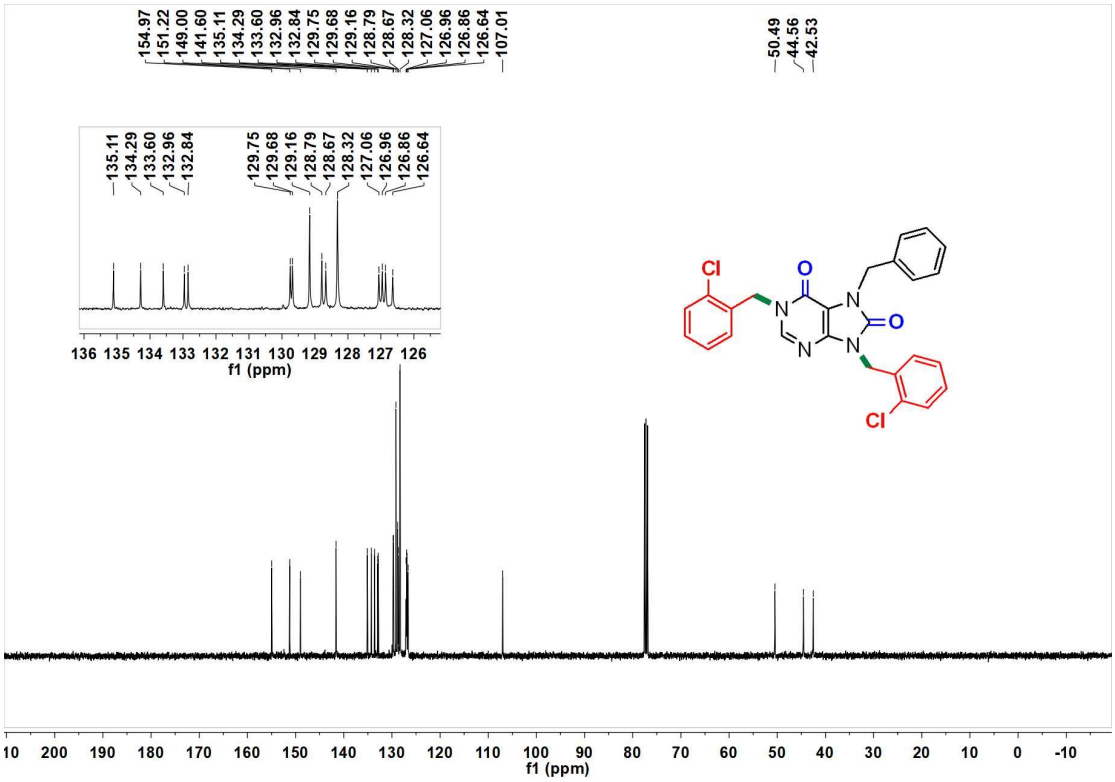
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7n**



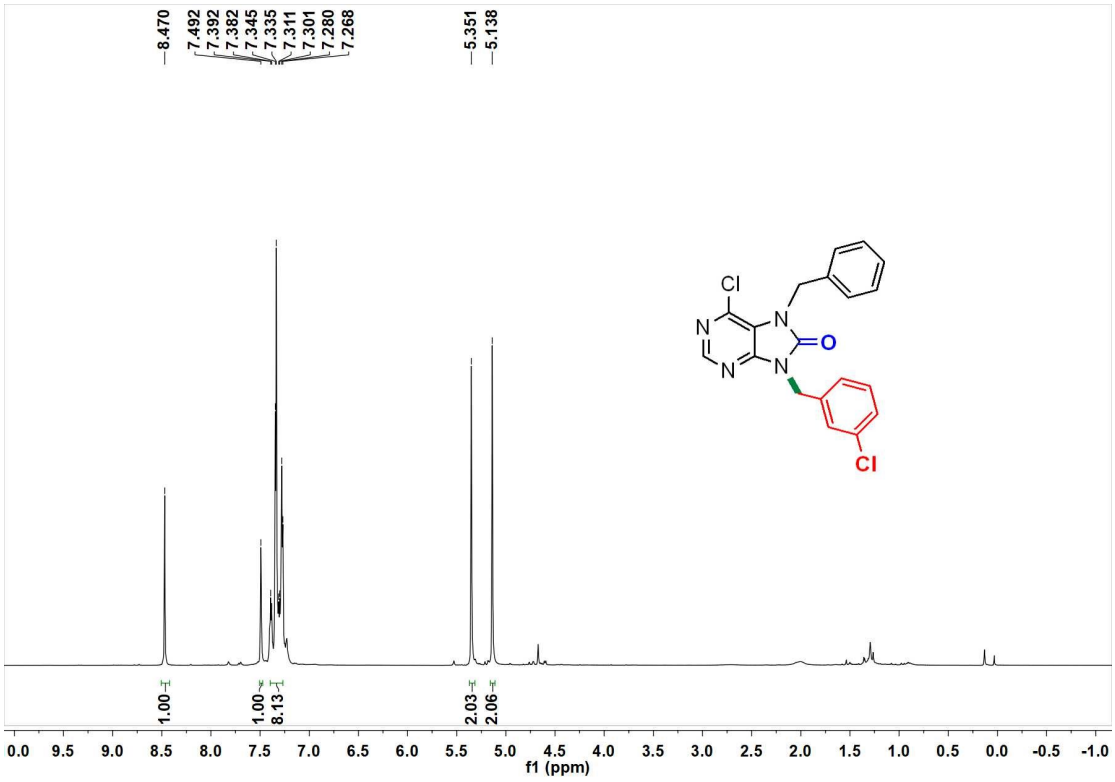
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7n'**



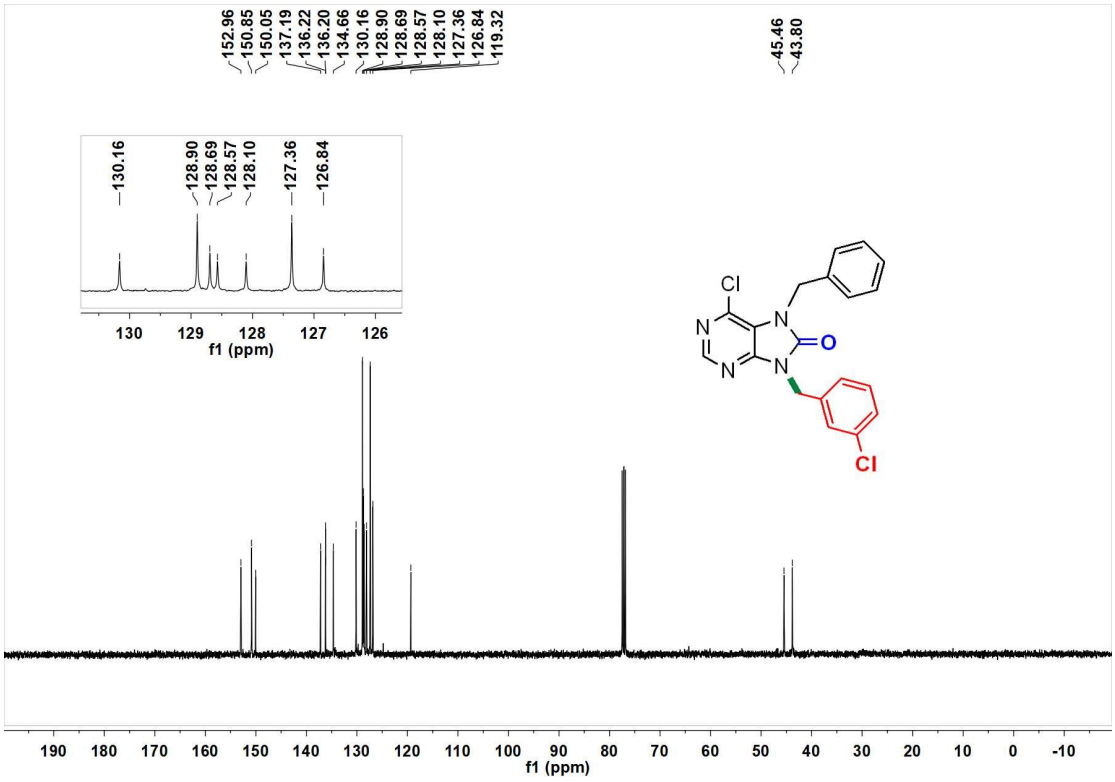
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **7n'**



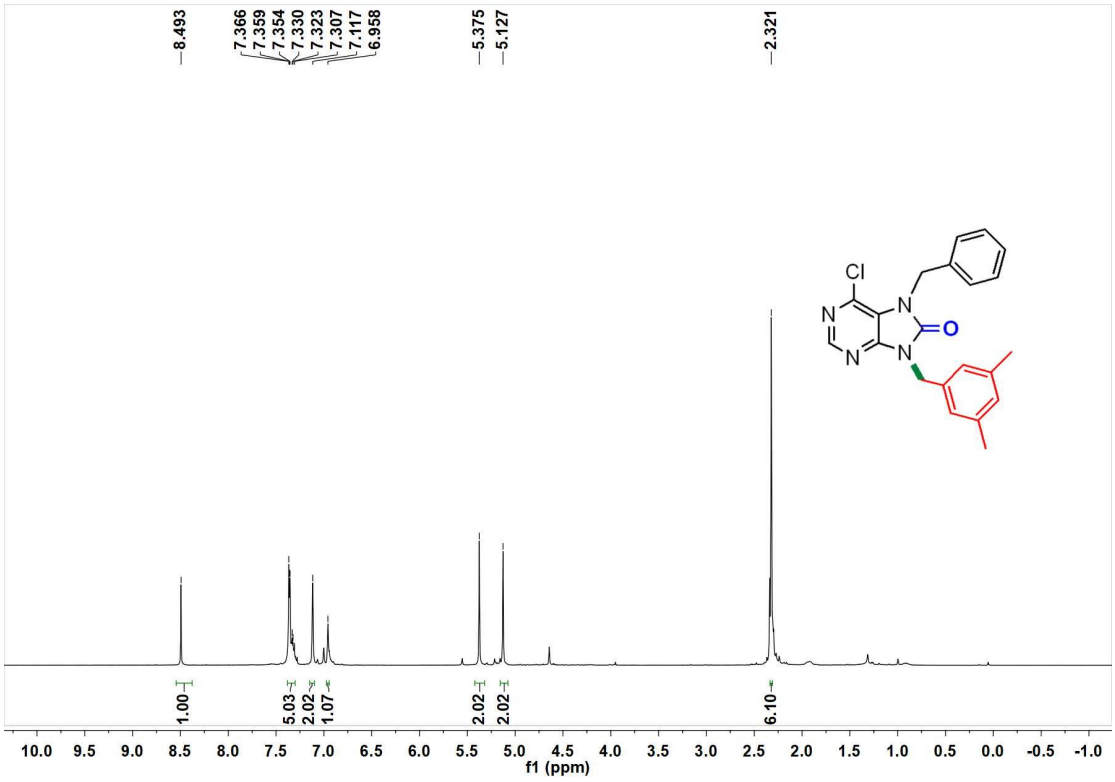
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7o**



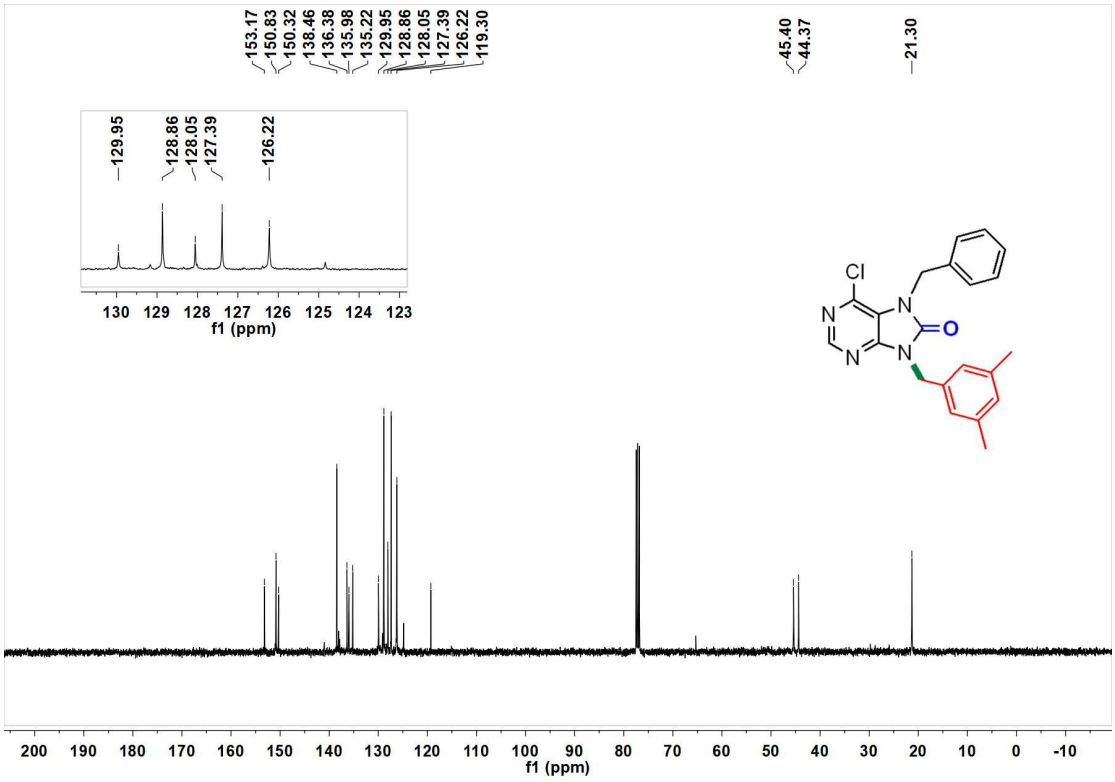
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7o**



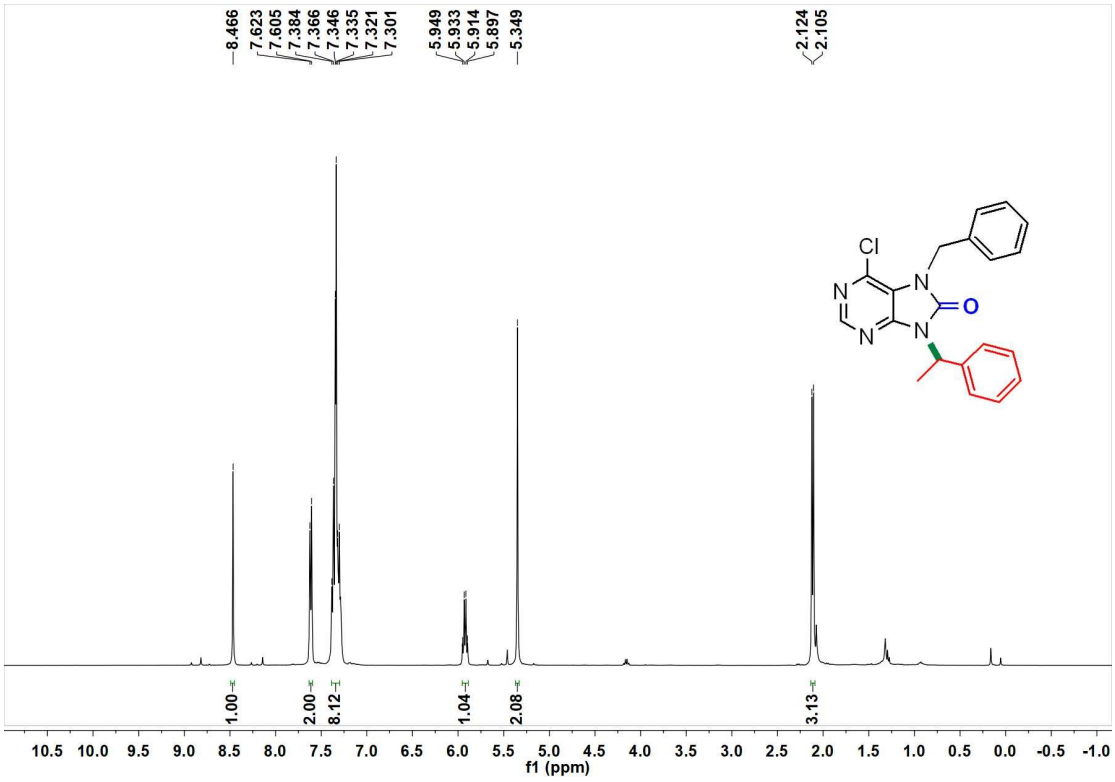
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7p**



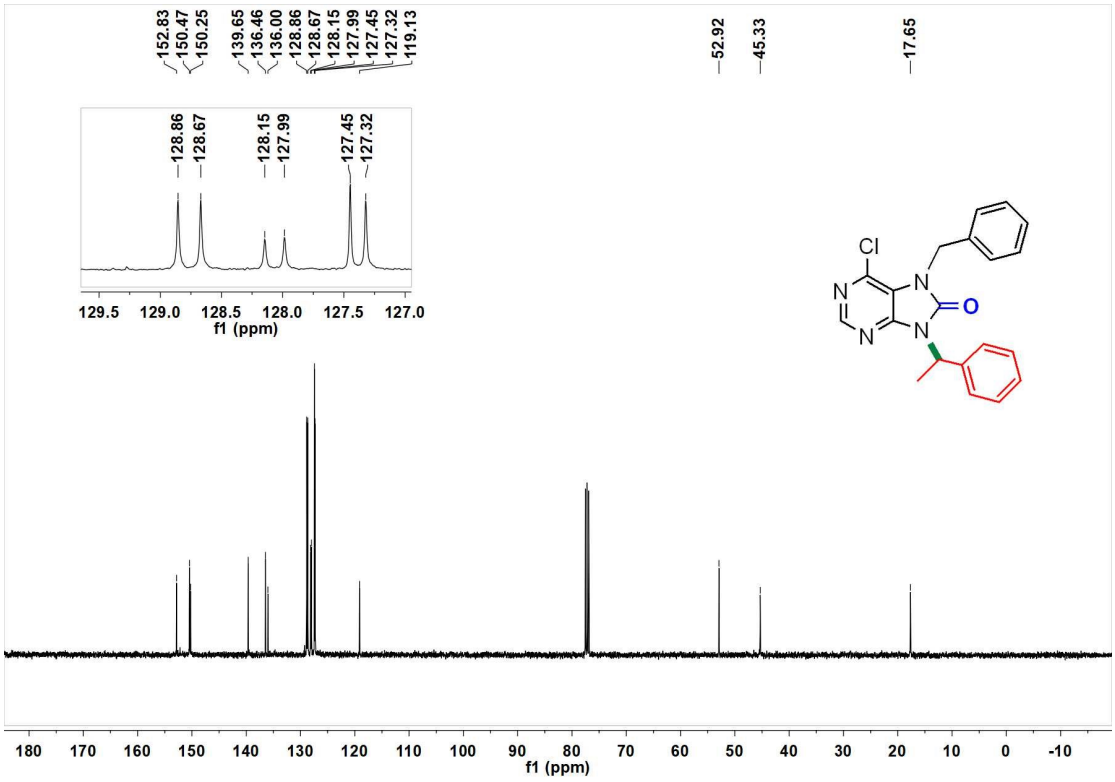
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7p**



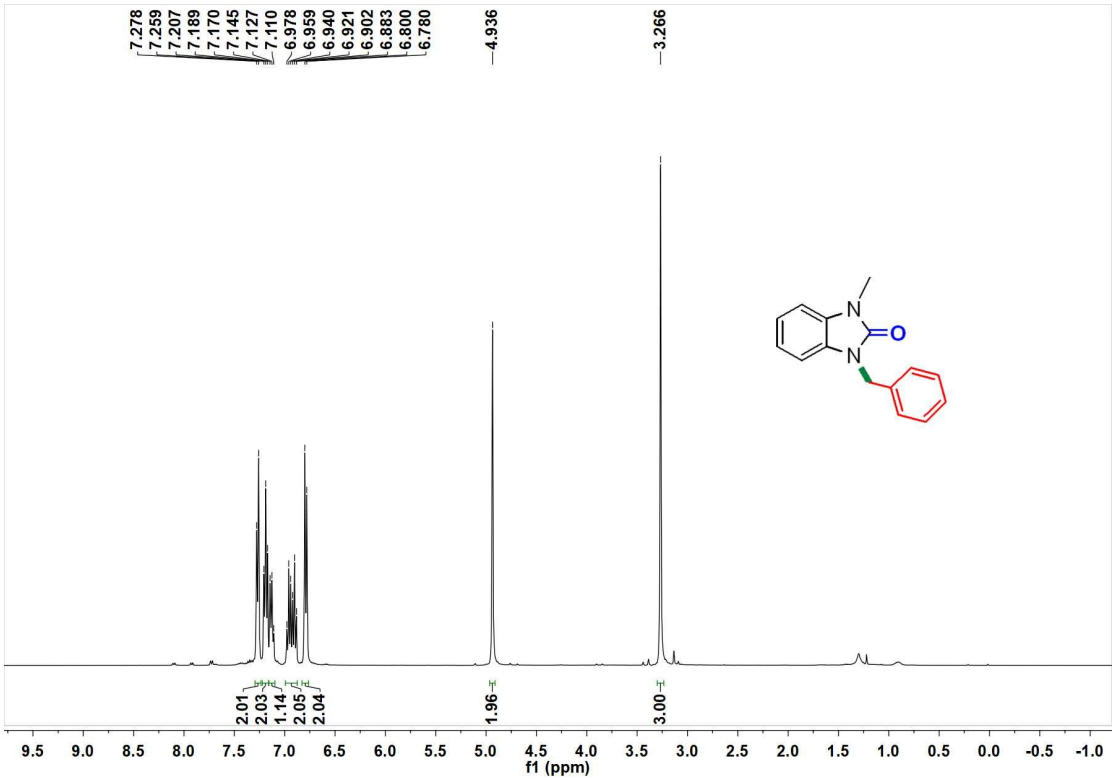
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7q**



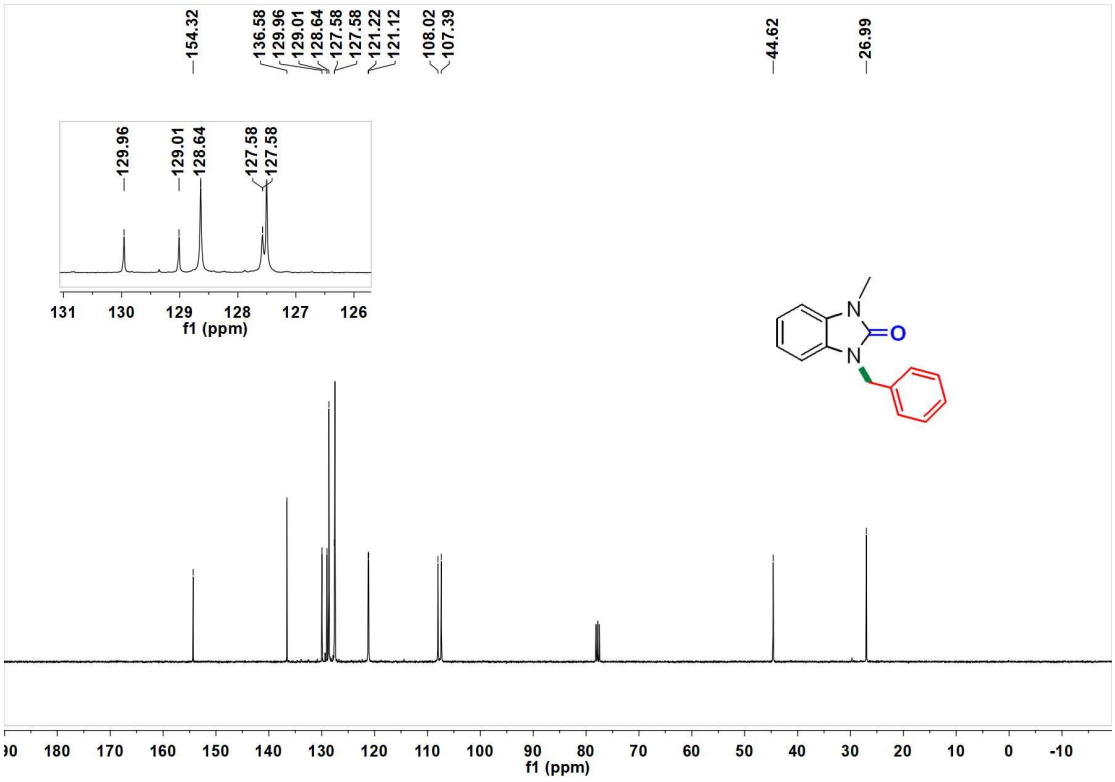
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7q**



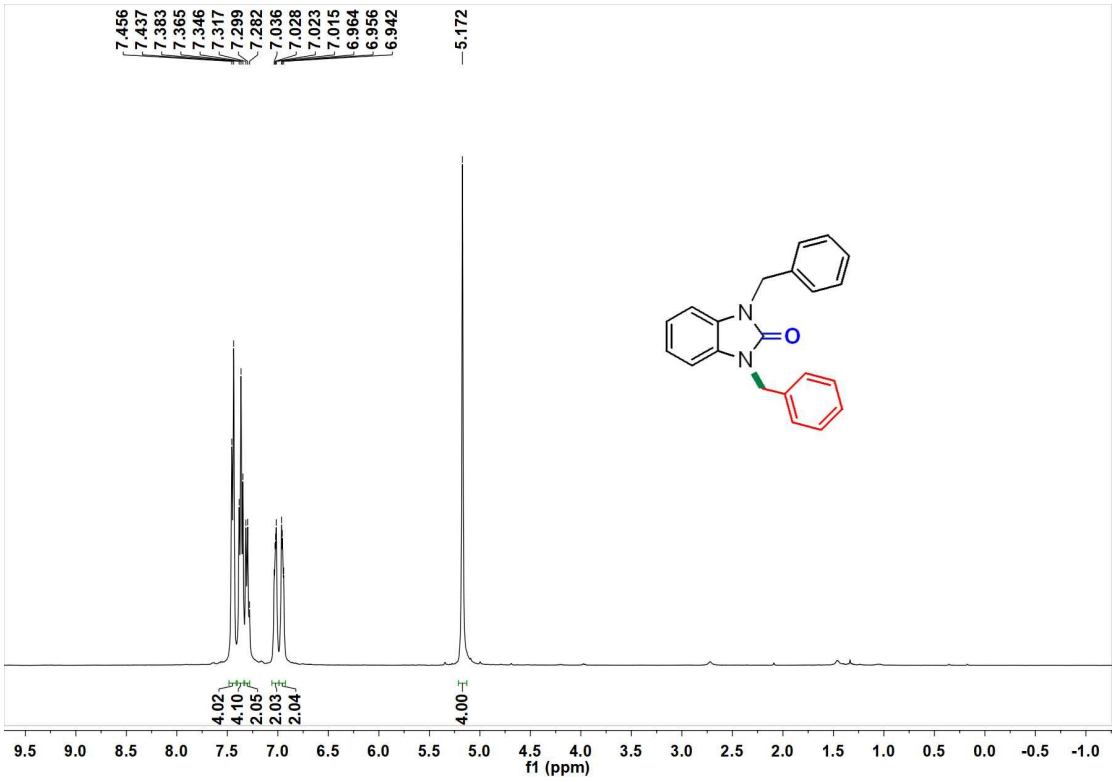
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7r**



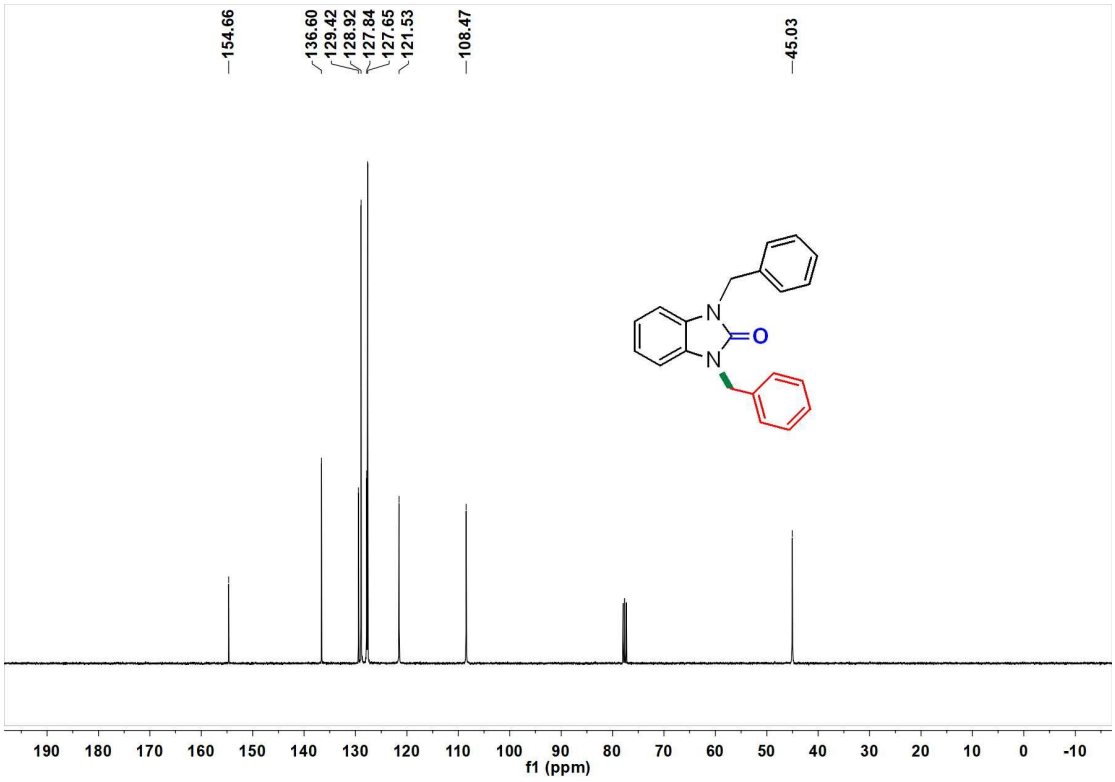
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7r**



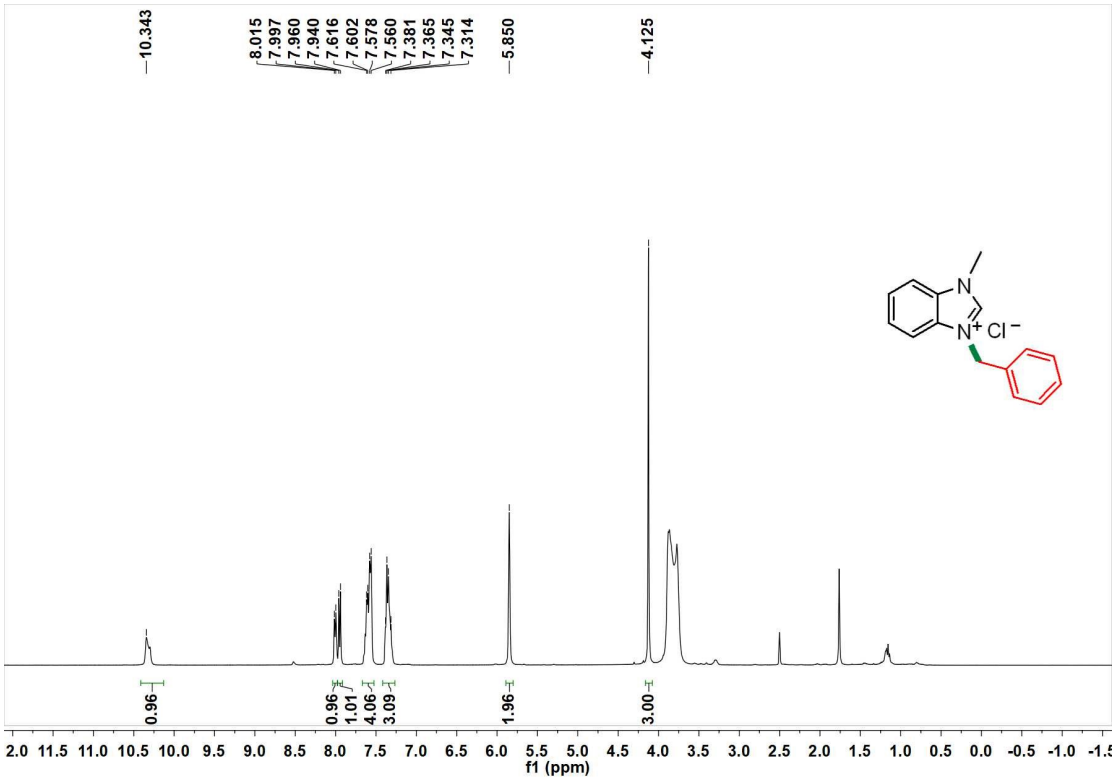
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7s**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7s**



^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8**



^{13}C NMR spectrum (101 MHz, DMSO-d_6) of **8**