Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Site-Specific C-H Chalcogenation of Quinoxalin-2(1*H*)-ones Enabled by Selectfluor Reagent

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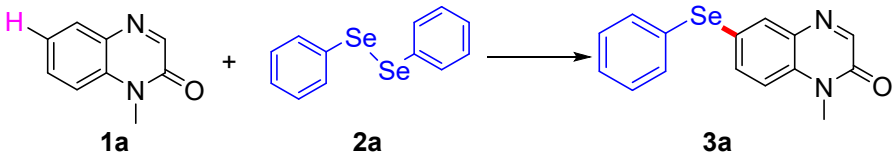
Contents

1 General information

All commercial reagents and solvents were used without purification. TLC analyses were carried out on pre-coated silica gel plates with F_{254} indicator by UV light (254 nm and 365 nm). Purification of reaction products was carried out by flash chromatography using 300-400 mesh silica. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. High resolution mass spectra (HR MS) were obtained on Thermo Scientific LTQ Orbitrap XL instrument using the ESI technique. IR spectra were recorded on Shimadazu IR-408 Fourier transform infrared spectrophotometer using a thin film supported on KBr pellets. Melting points were measured on an XT4A microscopic apparatus uncorrected.

2 Screening the reaction conditions



1a **2a** **3a**

Table S1 Screening the molar ratio of **1a** and **2a**[a]

Entry	the molar ratio of **1a** and **2a**	Yields (%)[b]
1	1:0.5	43
2	1:1	75
3	1:1.5	75
4	1:2	75

[a] Reaction conditions: 4-methylquinoline **1a** (0.2 mmol, 28.6 mg), diphenyl diselenide **2a**, Selectfluor agent (0.5 mmol, 177.0 mg) in CH_3CN (2.0 mL) at 80 °C for 3.0 h.

[b] Isolated yield.

3 Copies of spectra of products

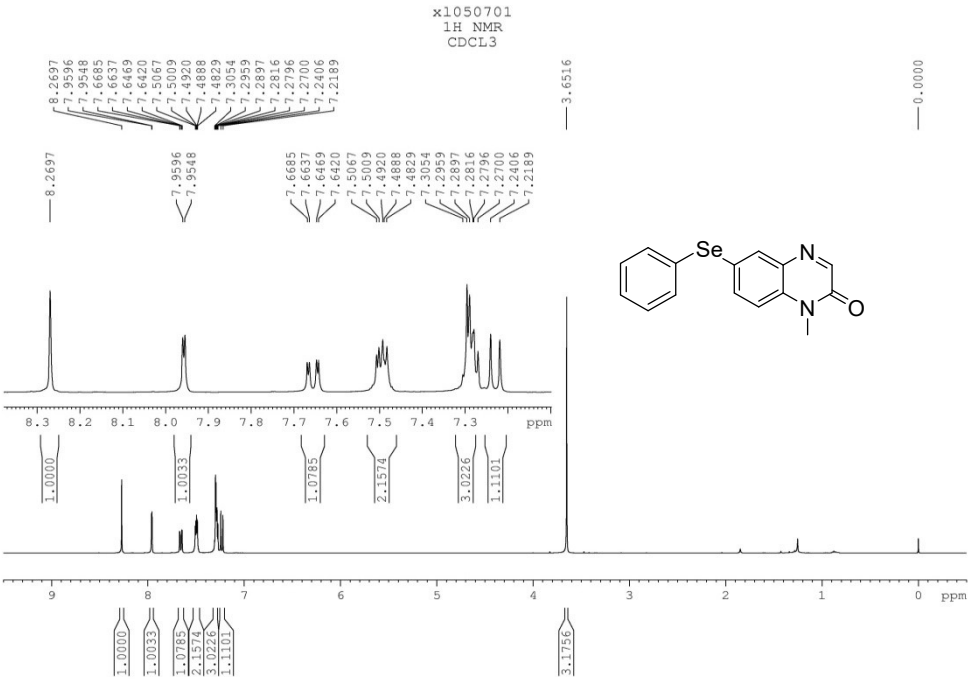


Fig. S1 ^{1}H NMR spectrum of compound **3a**

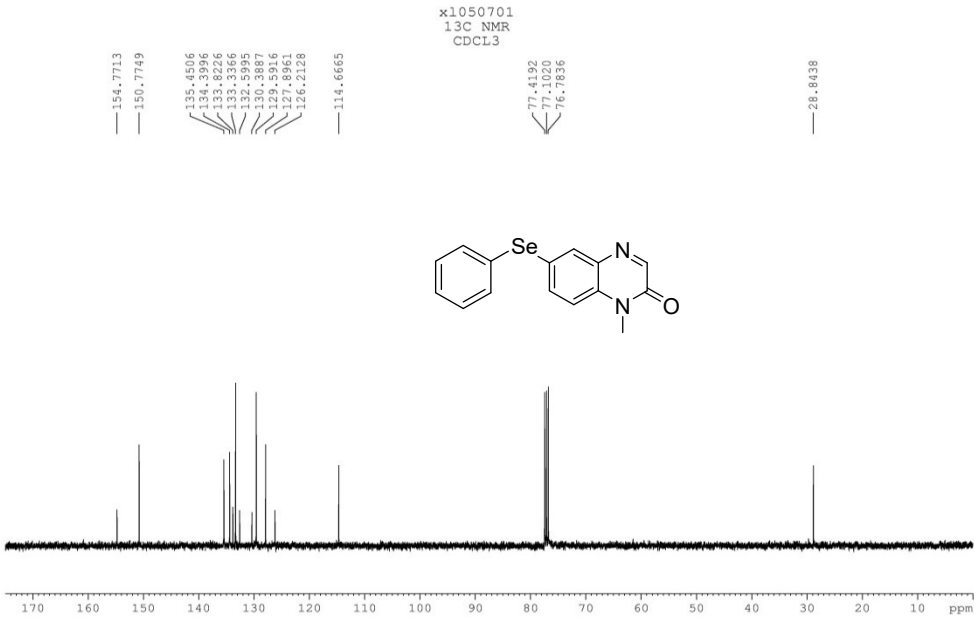


Fig. S2 ^{13}C NMR spectrum of compound **3a**

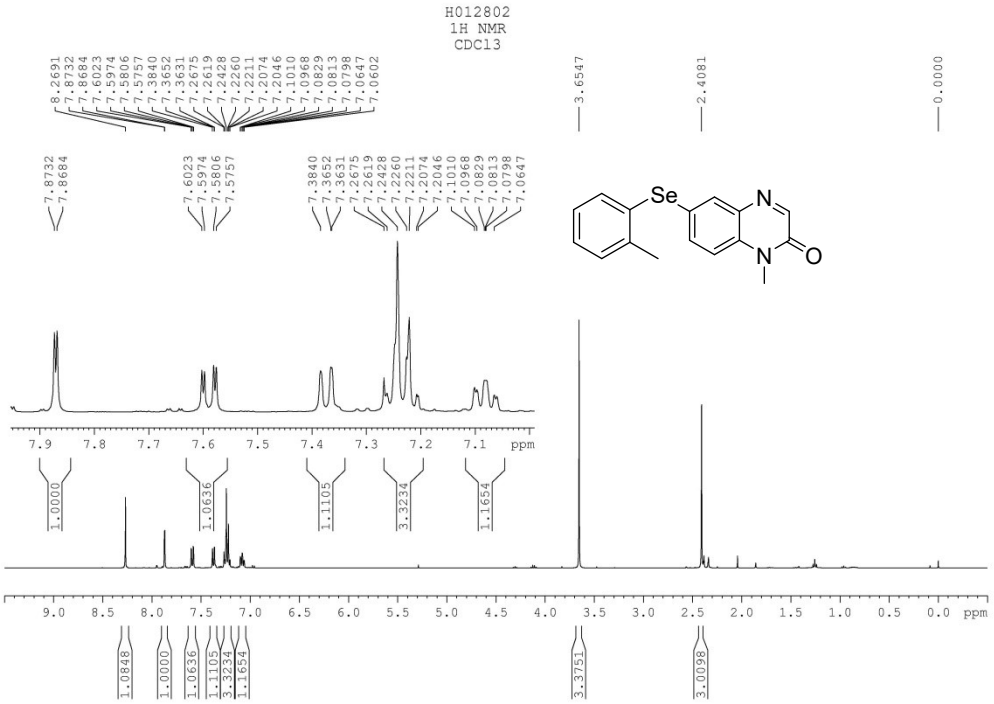


Fig. S3 ^{1}H NMR spectrum of compound **3b**

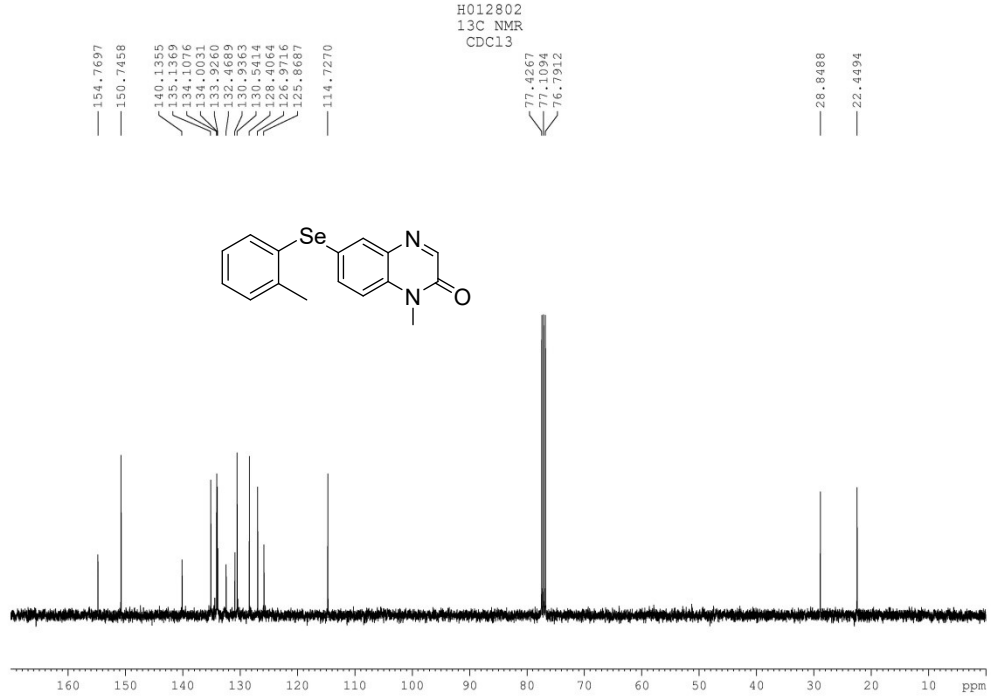


Fig. S4 ^{13}C NMR spectrum of compound **3b**

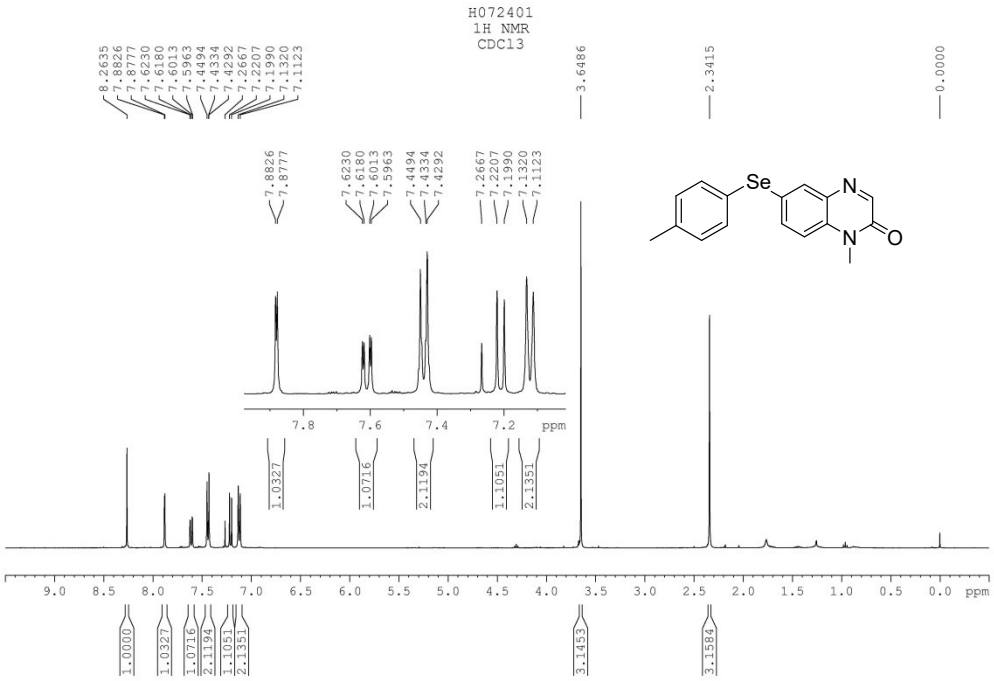


Fig. S5 ^{1}H NMR spectrum of compound **3c**

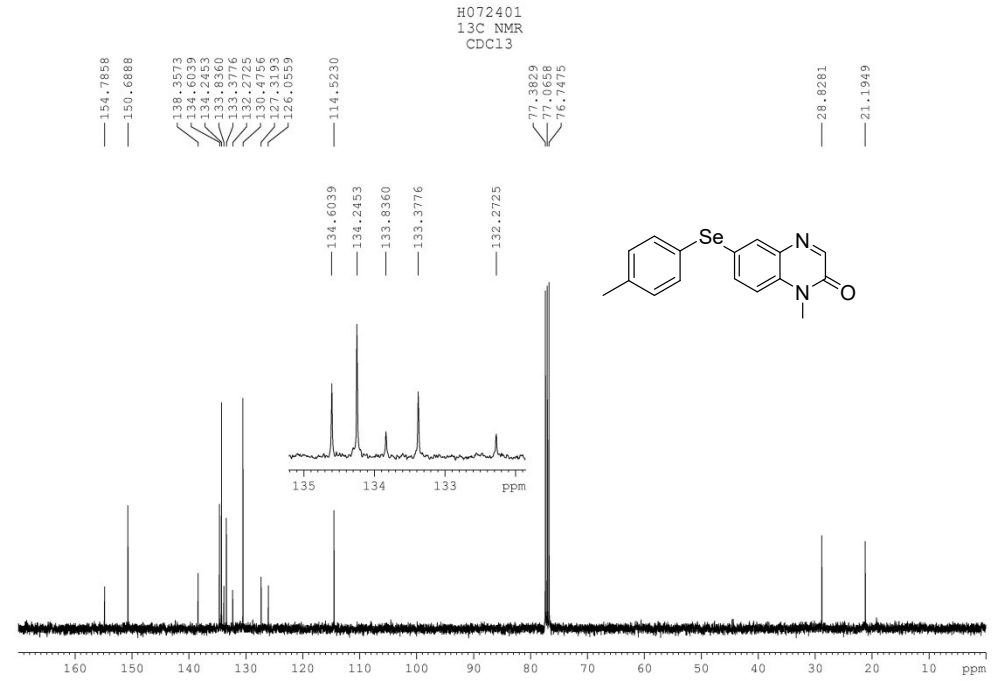


Fig. S6 ^{13}C NMR spectrum of compound **3c**

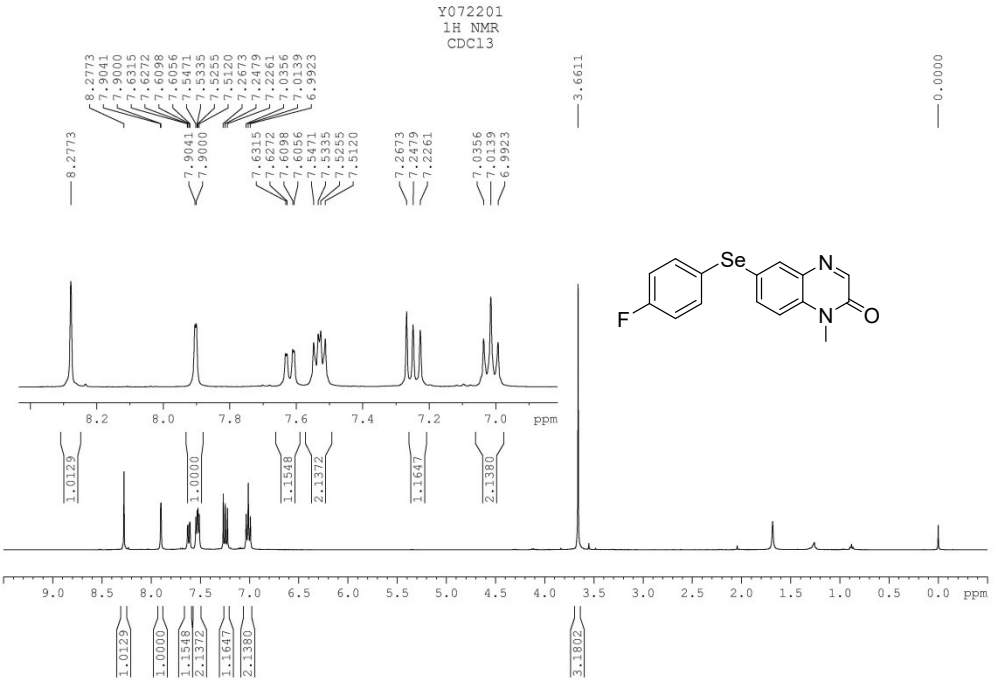


Fig. S7 ^{1}H NMR spectrum of compound **3d**

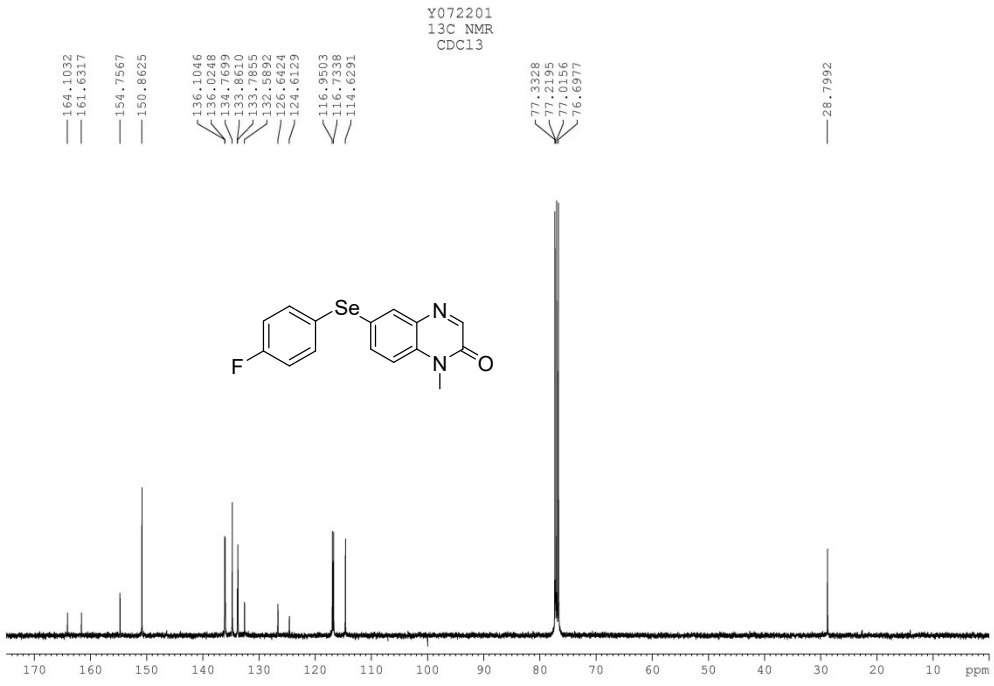


Fig. S8 ^{13}C NMR spectrum of compound **3d**

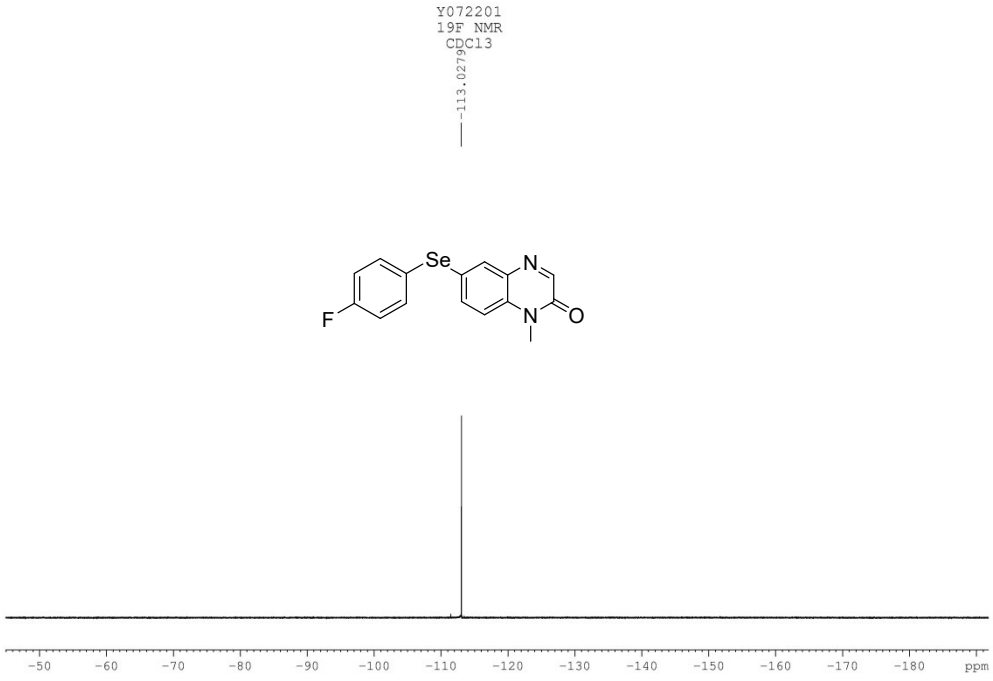


Fig. S9 ^{19}F NMR spectrum of compound **3d**

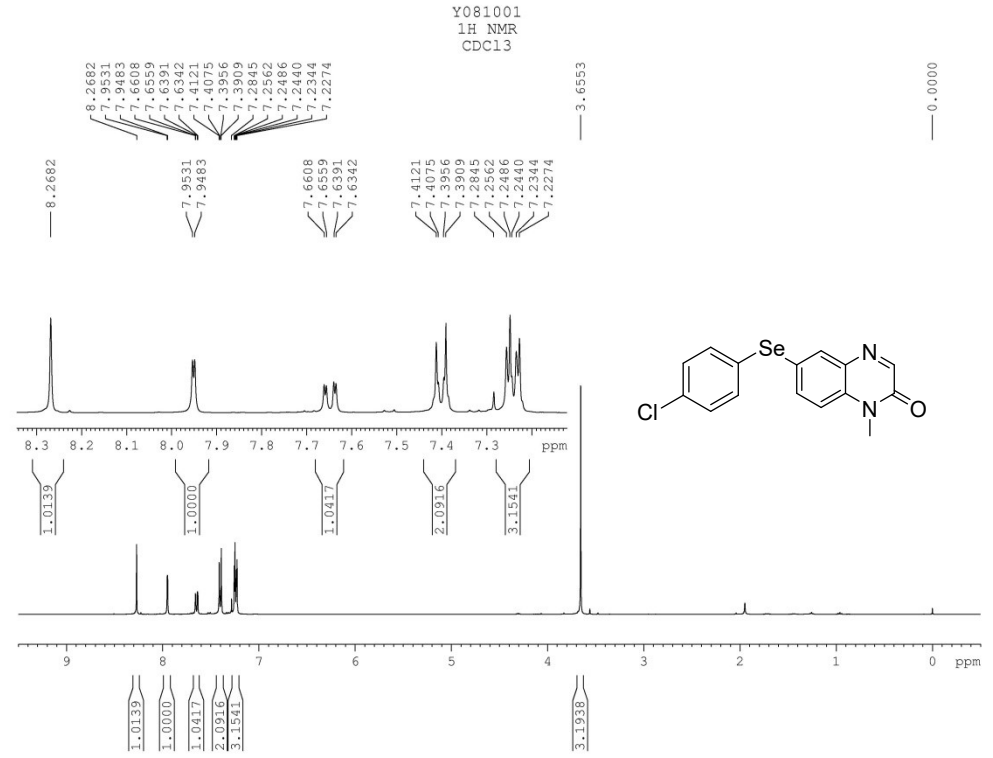


Fig. S10 ^{1}H NMR spectrum of compound **3e**

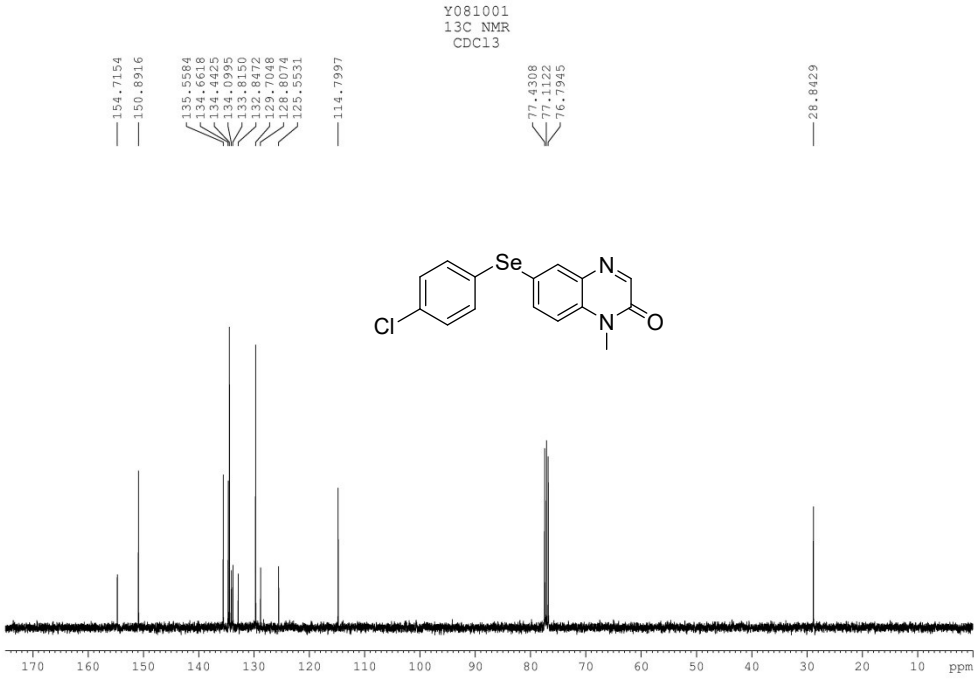


Fig. S11 ^{13}C NMR spectrum of compound **3e**

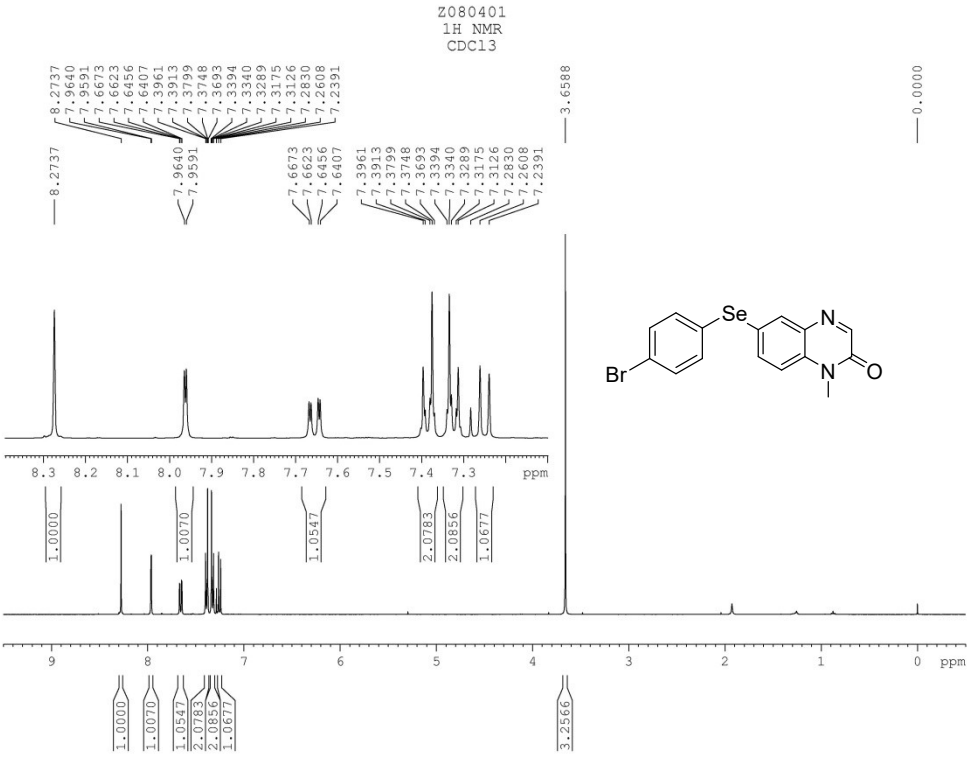


Fig. S12 ^{1}H NMR spectrum of compound **3f**

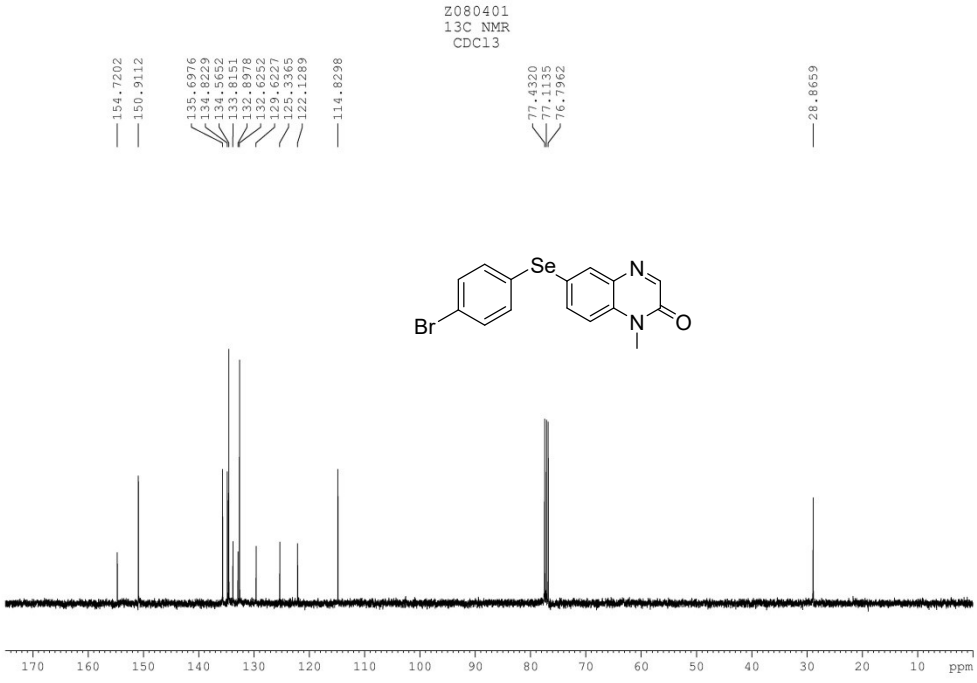


Fig. S13 ^{13}C NMR spectrum of compound **3f**

Fig. S14 ^{1}H NMR spectrum of compound **3g**

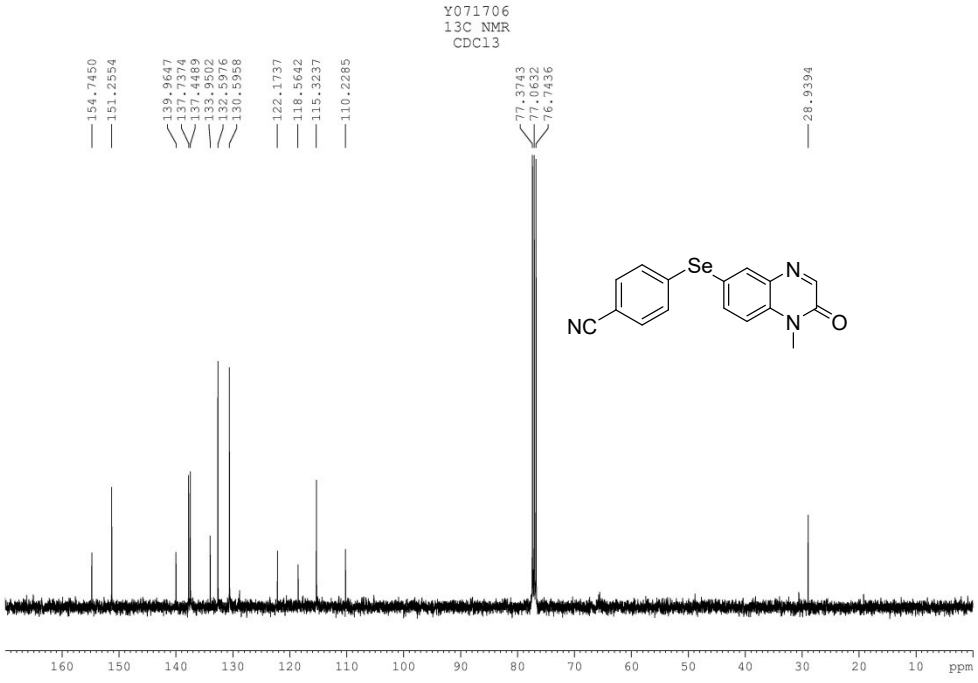


Fig. S15 ^{13}C NMR spectrum of compound **3g**

Fig. S16 ^{1}H NMR spectrum of compound **3h**

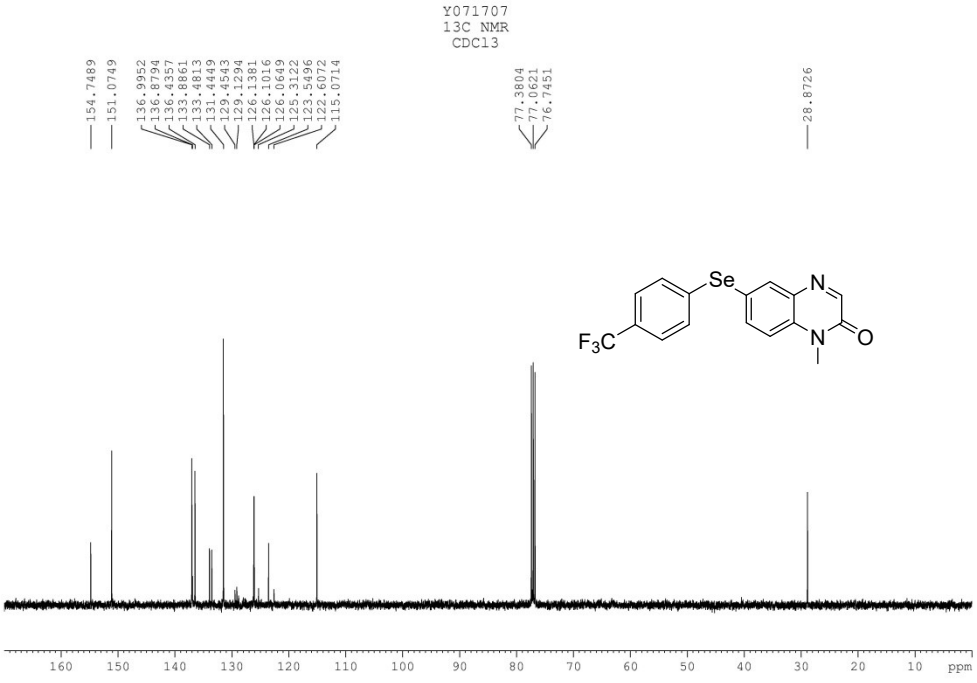


Fig. S17 ^{13}C NMR spectrum of compound **3h**

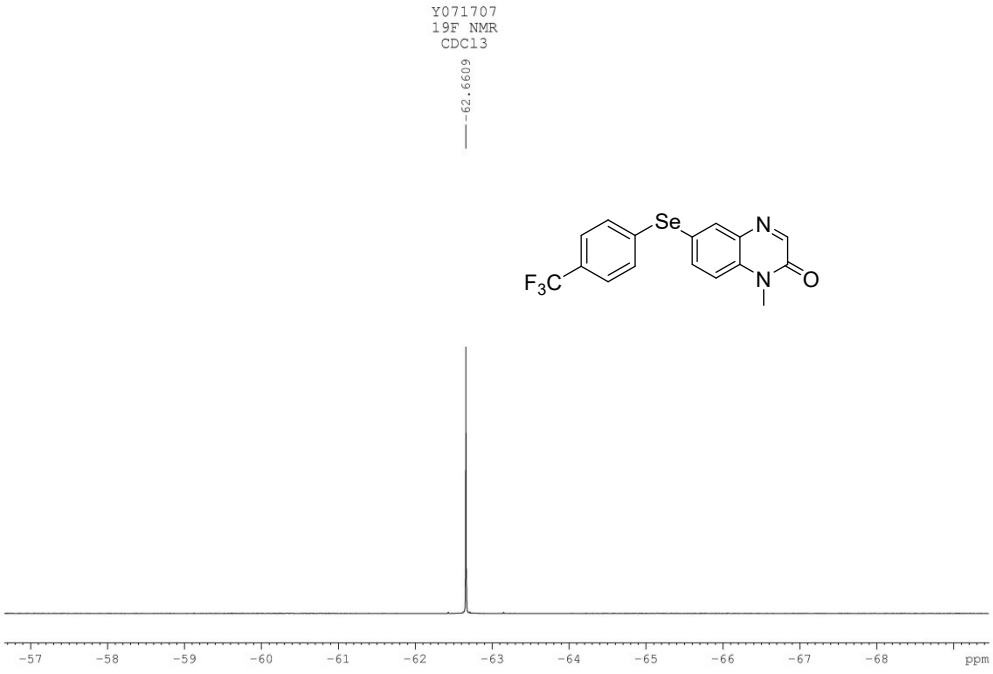


Fig. S18 ^{19}F NMR spectrum of compound **3h**

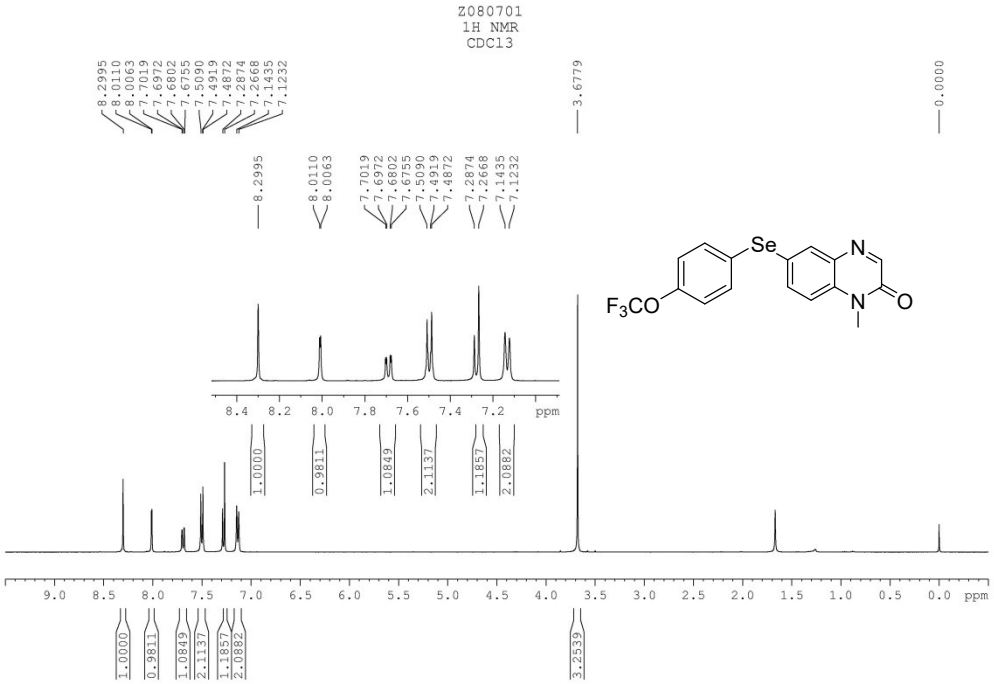


Fig. S19 ^{1}H NMR spectrum of compound **3i**

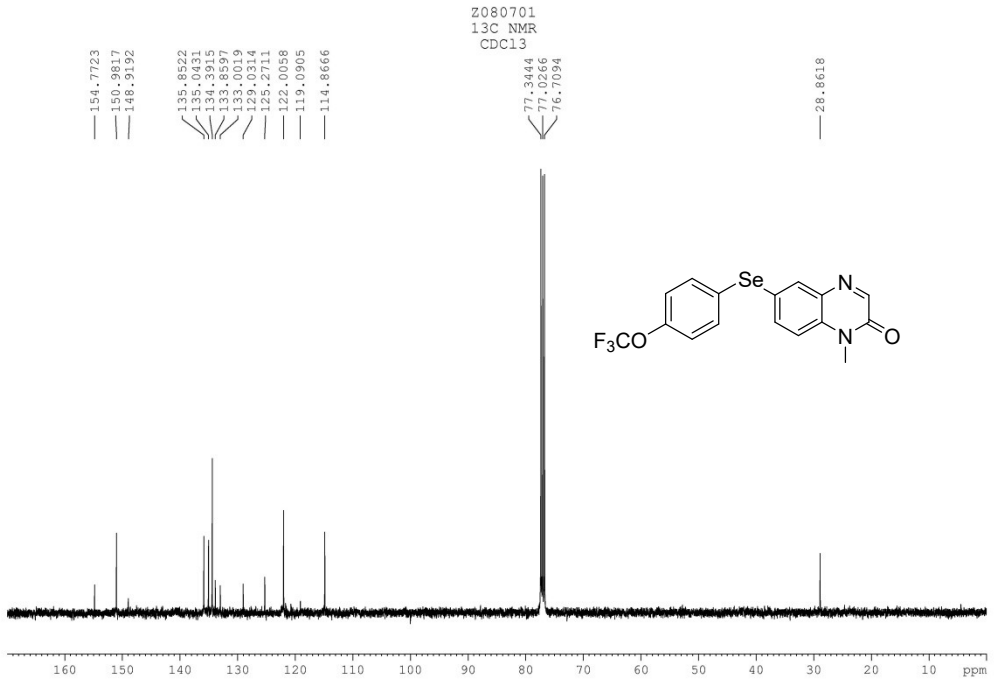


Fig. S20 ^{13}C NMR spectrum of compound **3i**

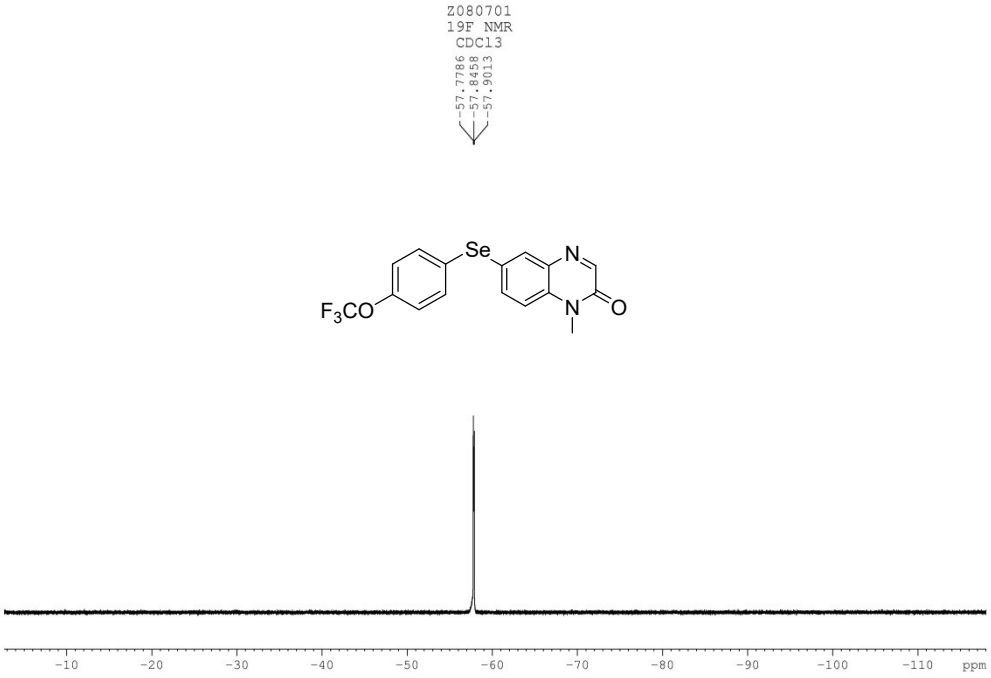


Fig. S21 ^{19}F NMR spectrum of compound **3i**

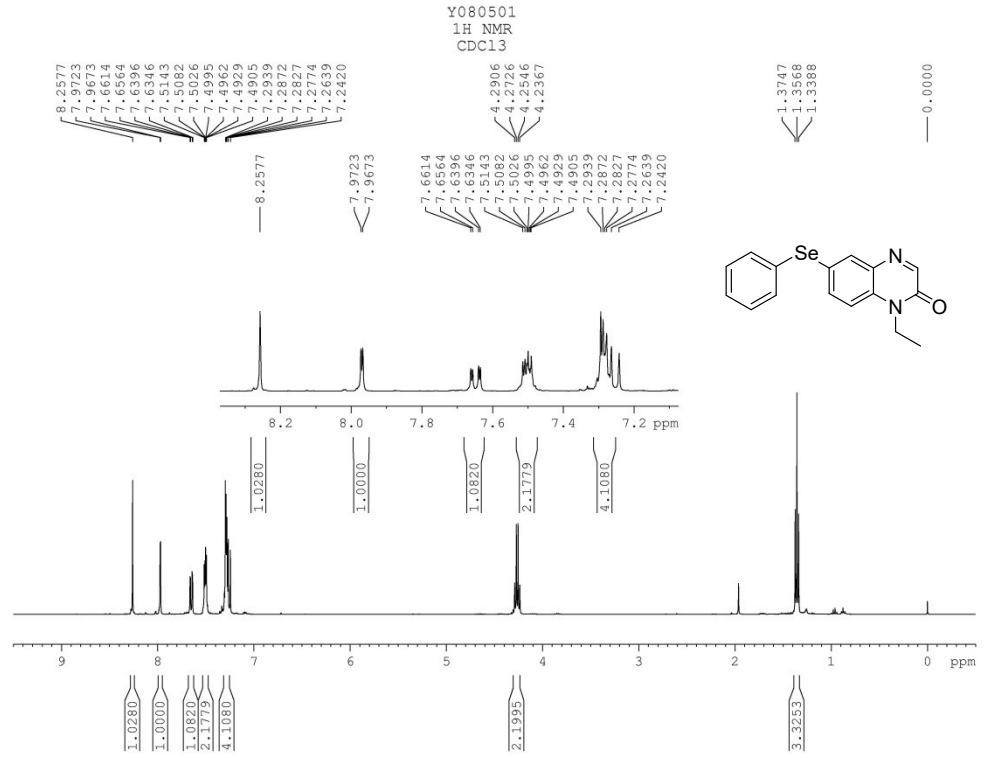


Fig. S22 ^{1}H NMR spectrum of compound **3k**

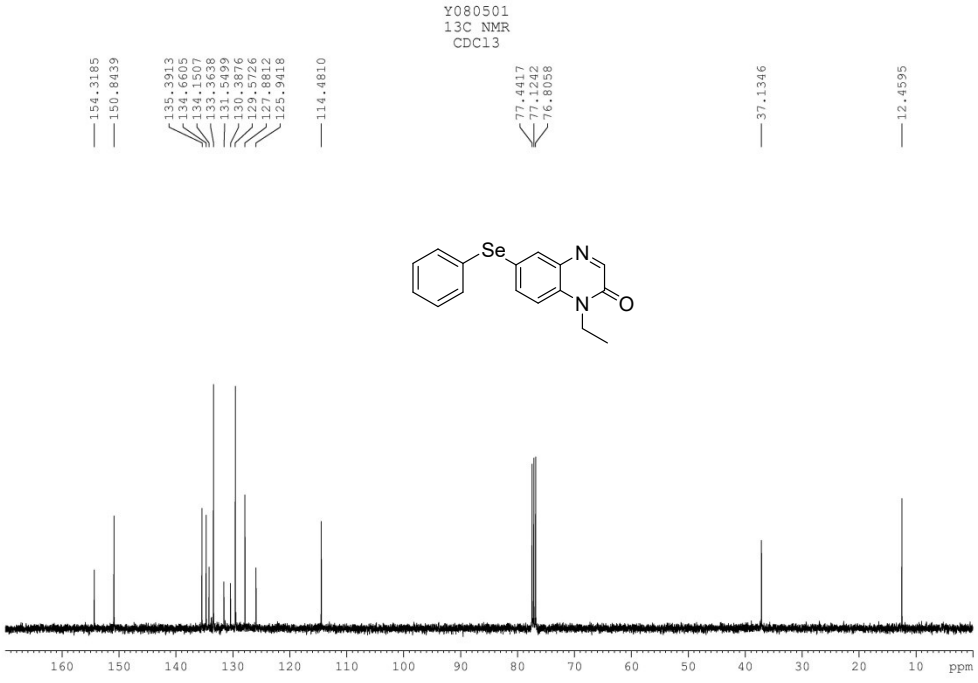


Fig. S23 ^{13}C NMR spectrum of compound **3k**

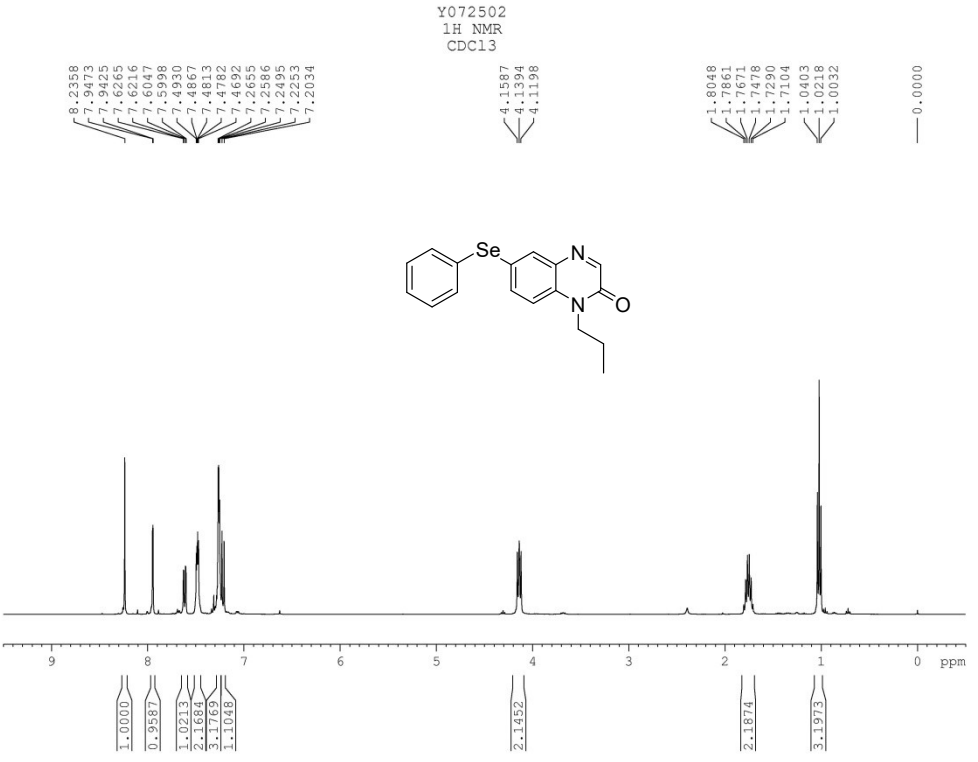


Fig. S24 ^{1}H NMR spectrum of compound **3l**

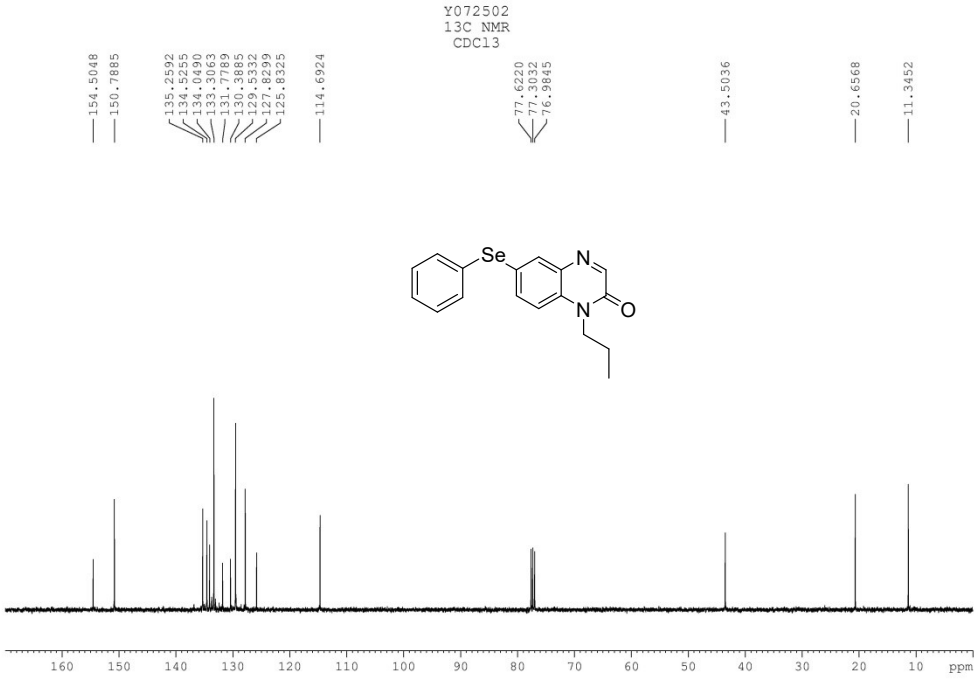


Fig. S25 ^{13}C NMR spectrum of compound **3l**

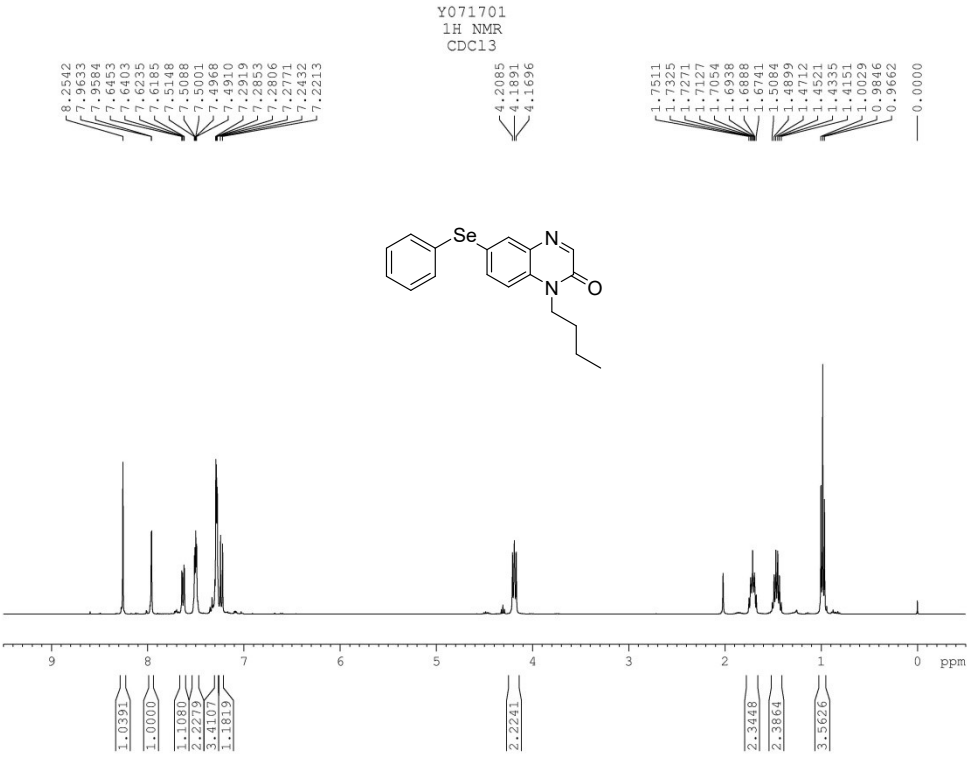


Fig. S26 ^{1}H NMR spectrum of compound **3m**

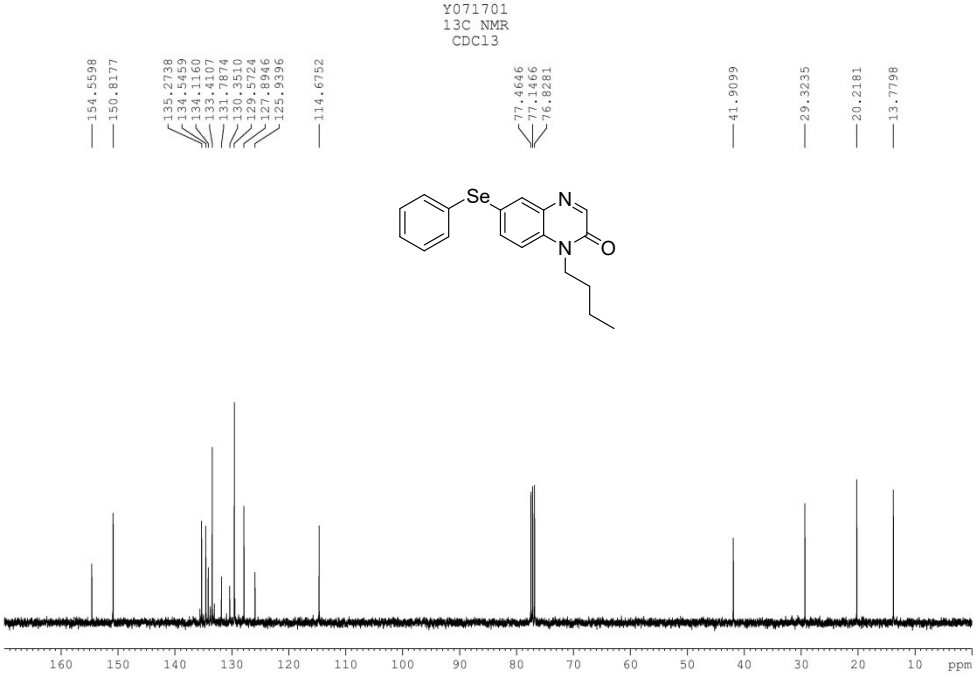


Fig. S27 ^{13}C NMR spectrum of compound **3m**

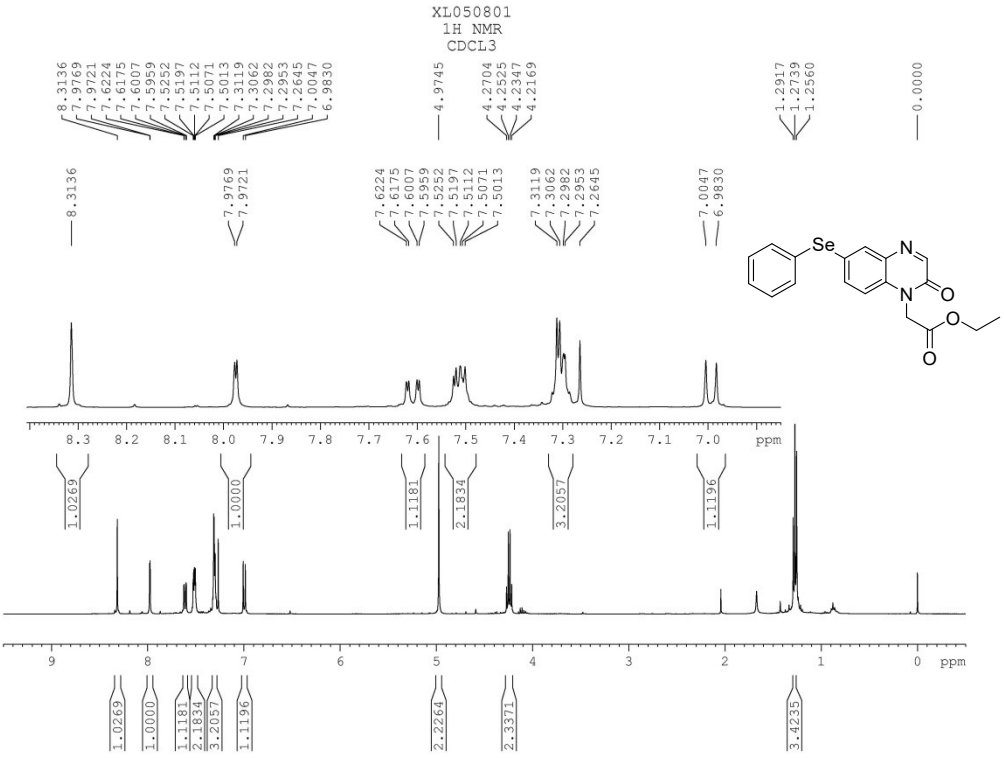


Fig. S28 ^{1}H NMR spectrum of compound **3n**

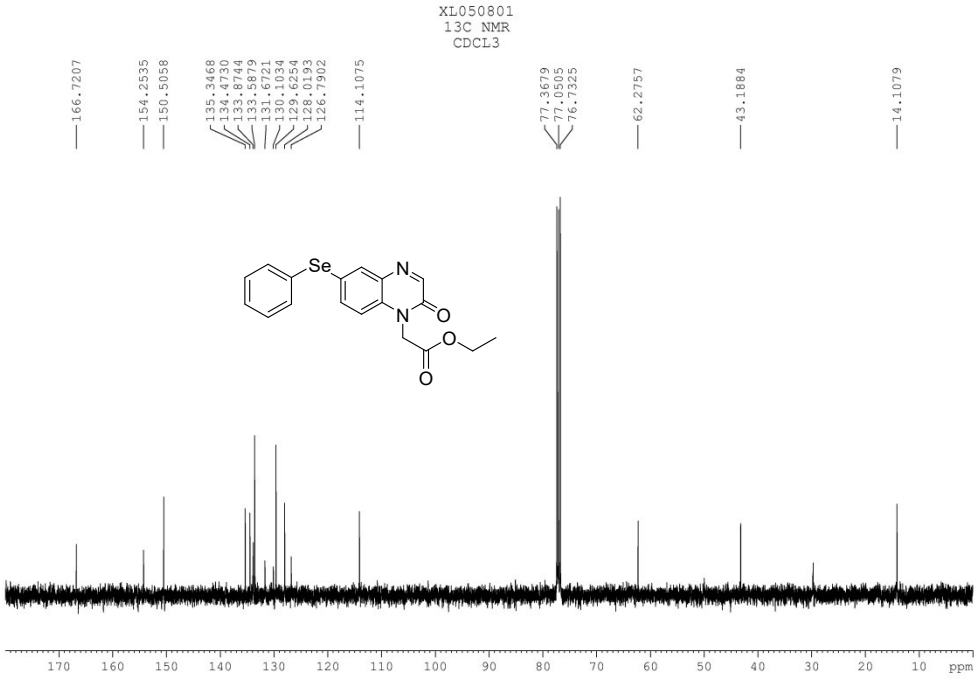


Fig. S29 ^{13}C NMR spectrum of compound **3n**

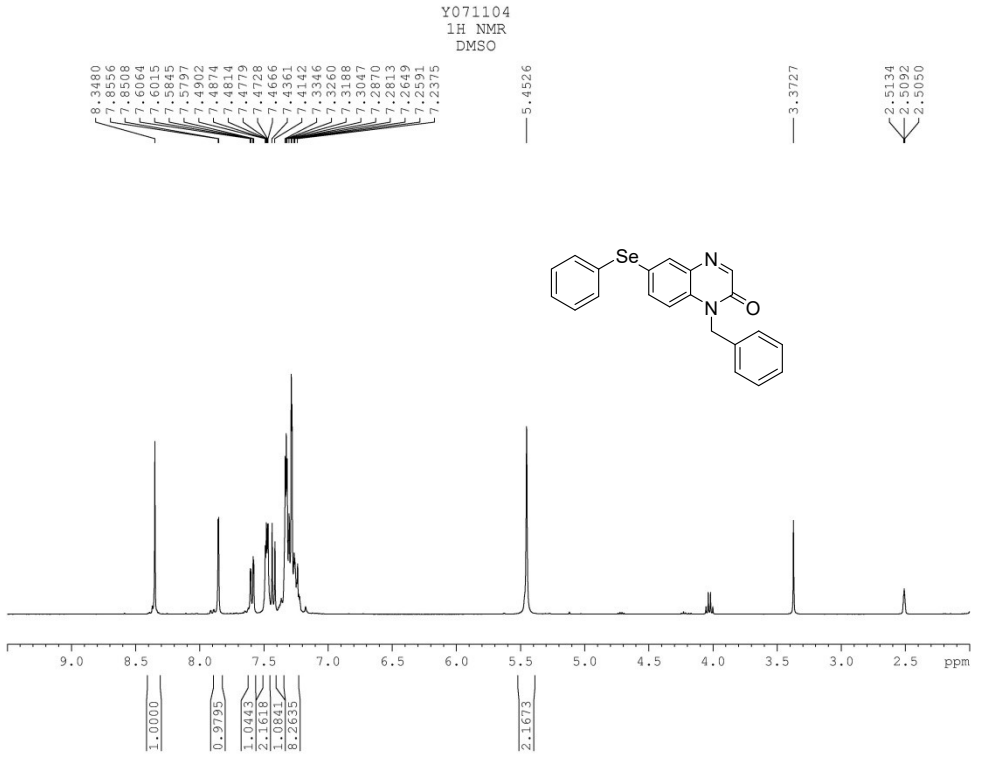


Fig. S30 ^{1}H NMR spectrum of compound **3o**

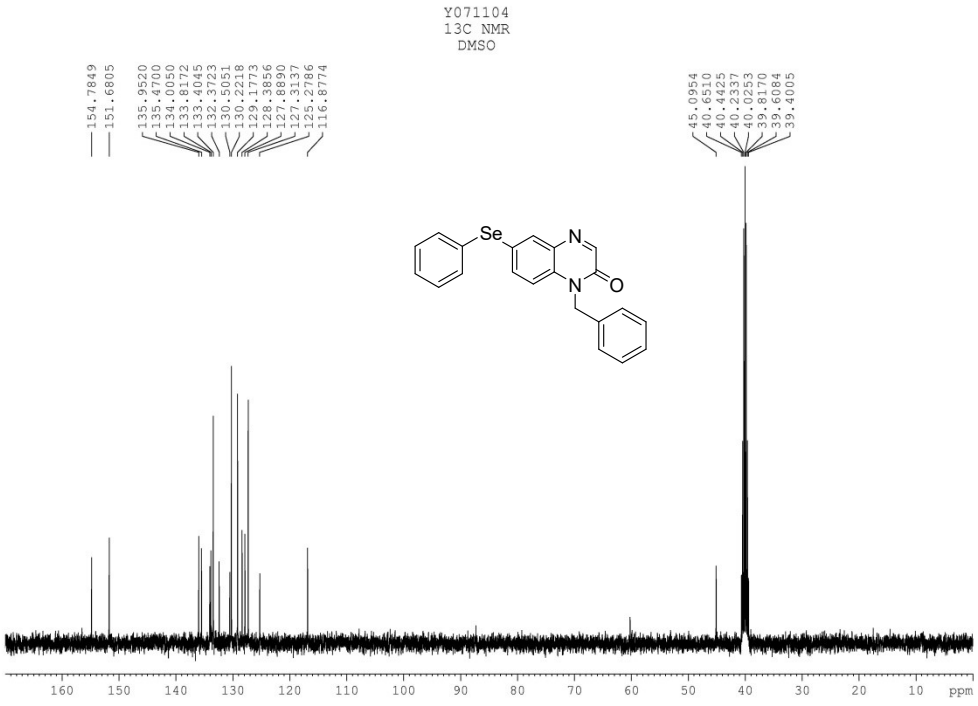


Fig. S31 ^{13}C NMR spectrum of compound **3o**

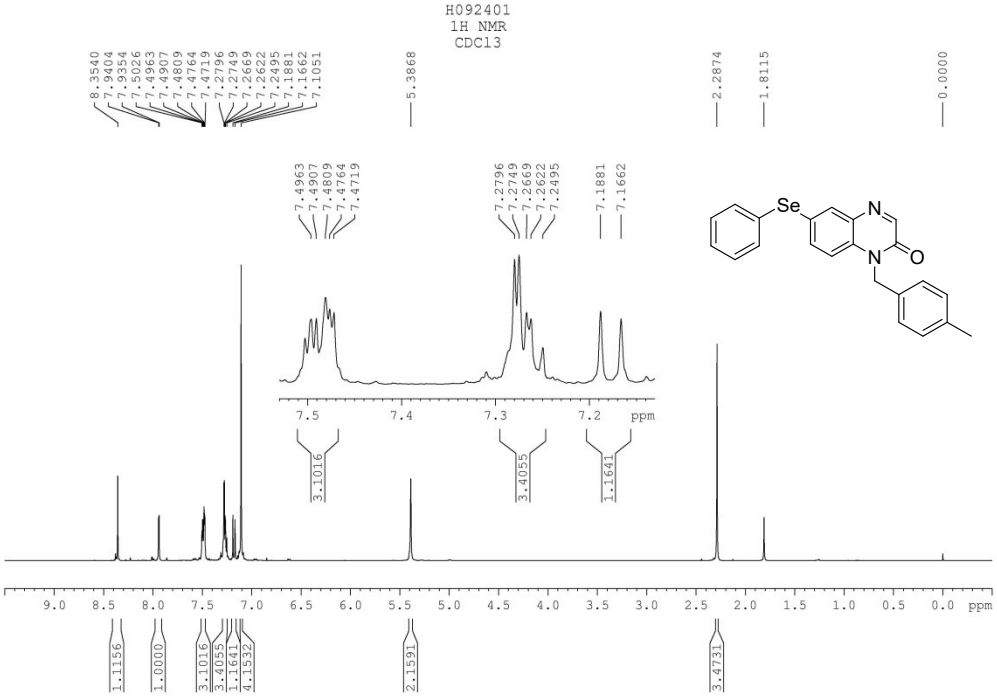


Fig. S32 ^{1}H NMR spectrum of compound **3p**

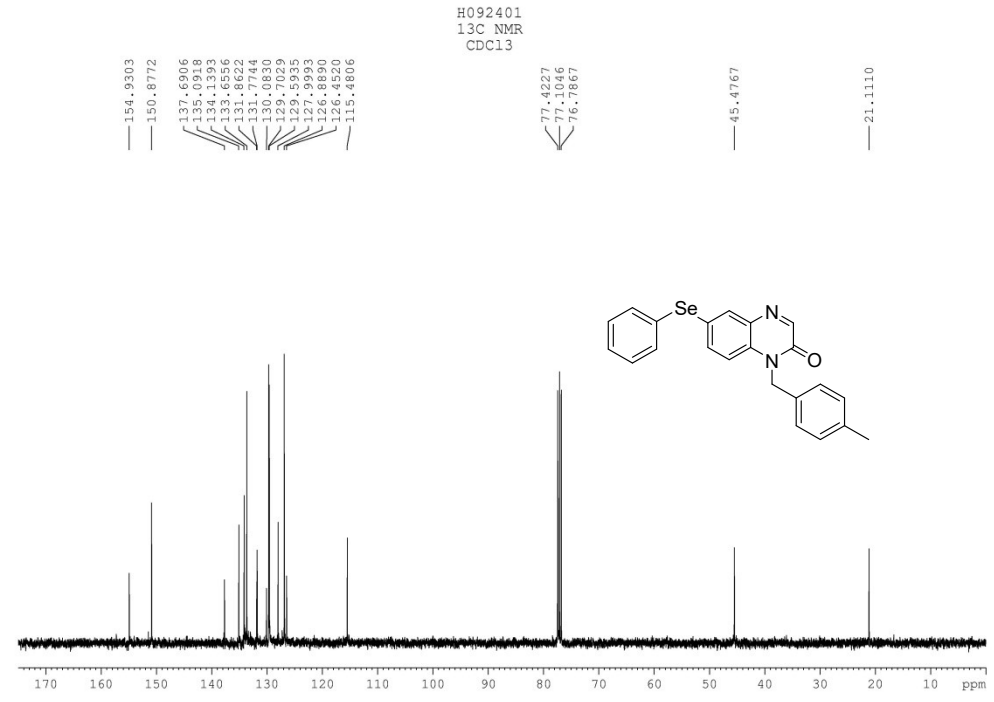


Fig. S33 ^{13}C NMR spectrum of compound **3p**

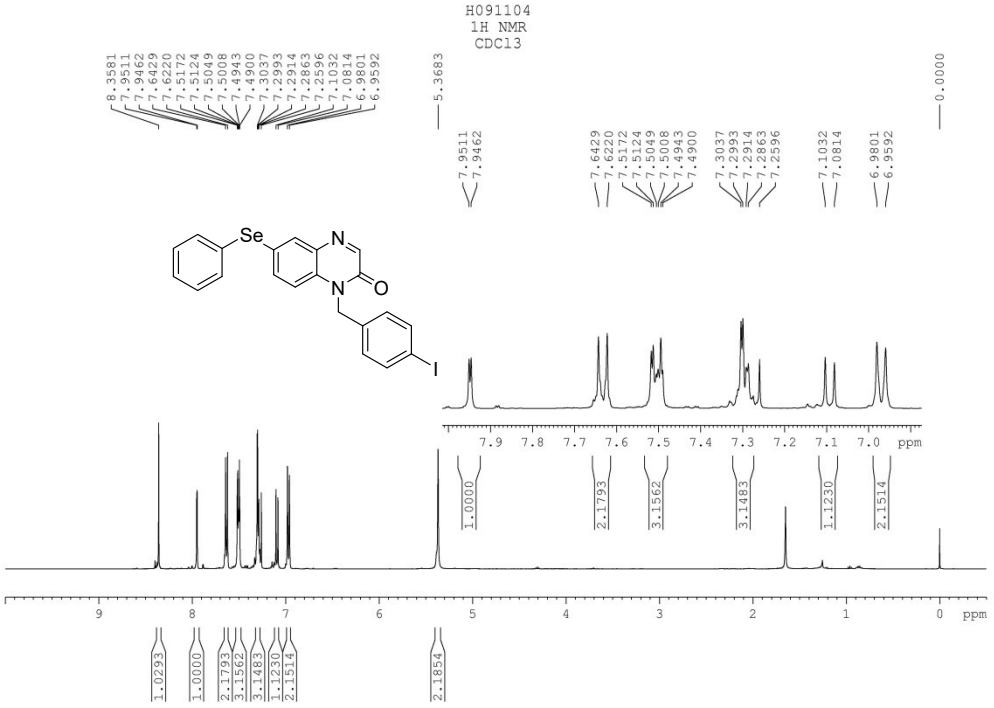


Fig. S34 ^{1}H NMR spectrum of compound **3q**

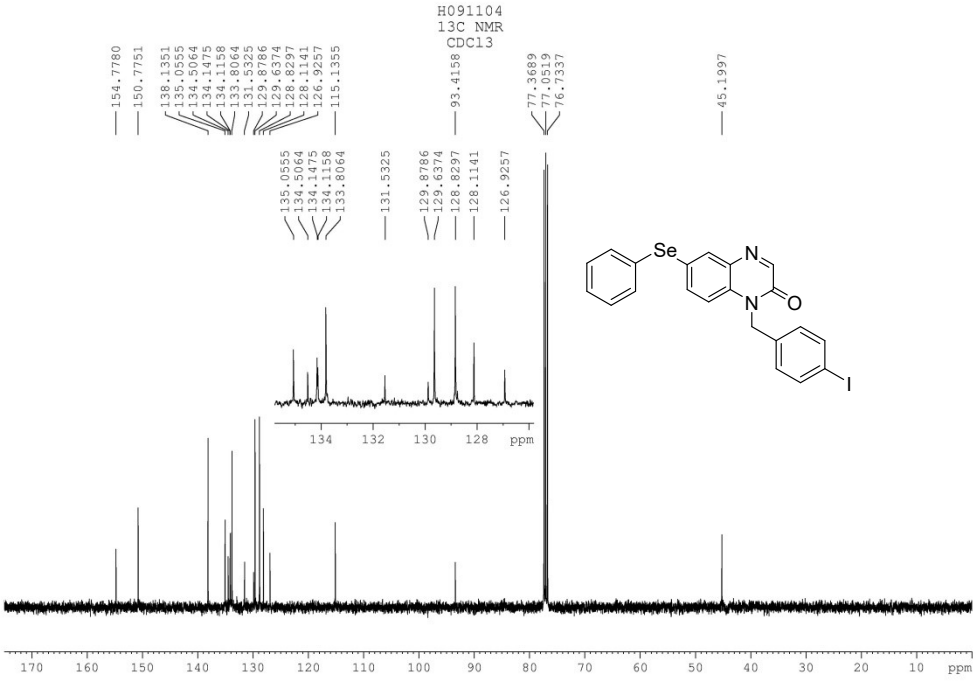


Fig. S35 ^{13}C NMR spectrum of compound **3q**

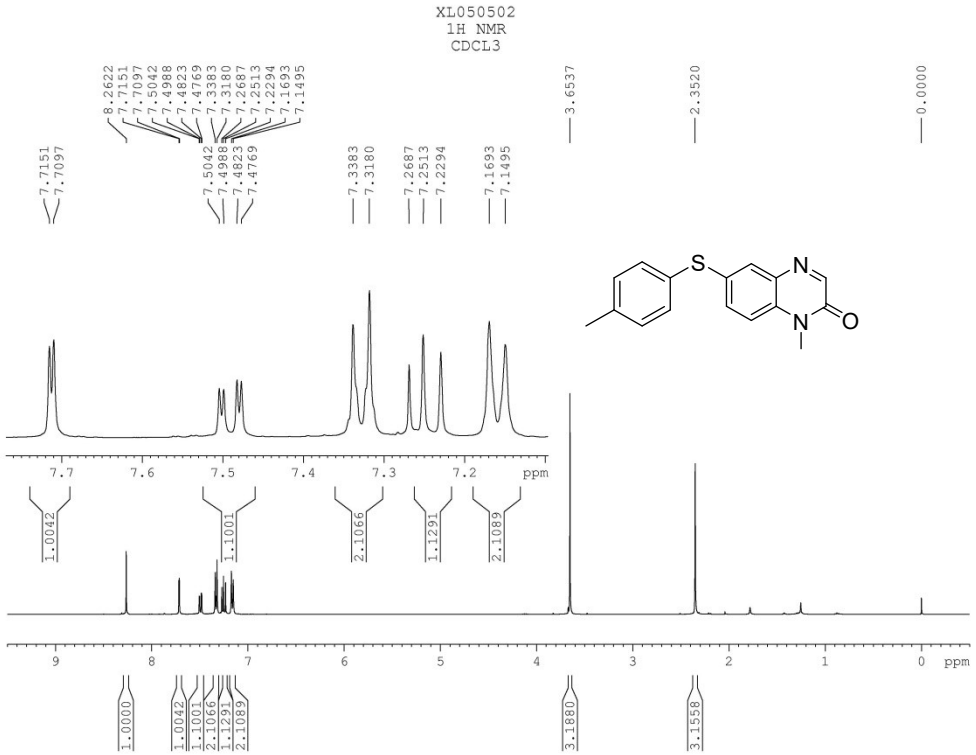


Fig. S36 ^{1}H NMR spectrum of compound **5a**

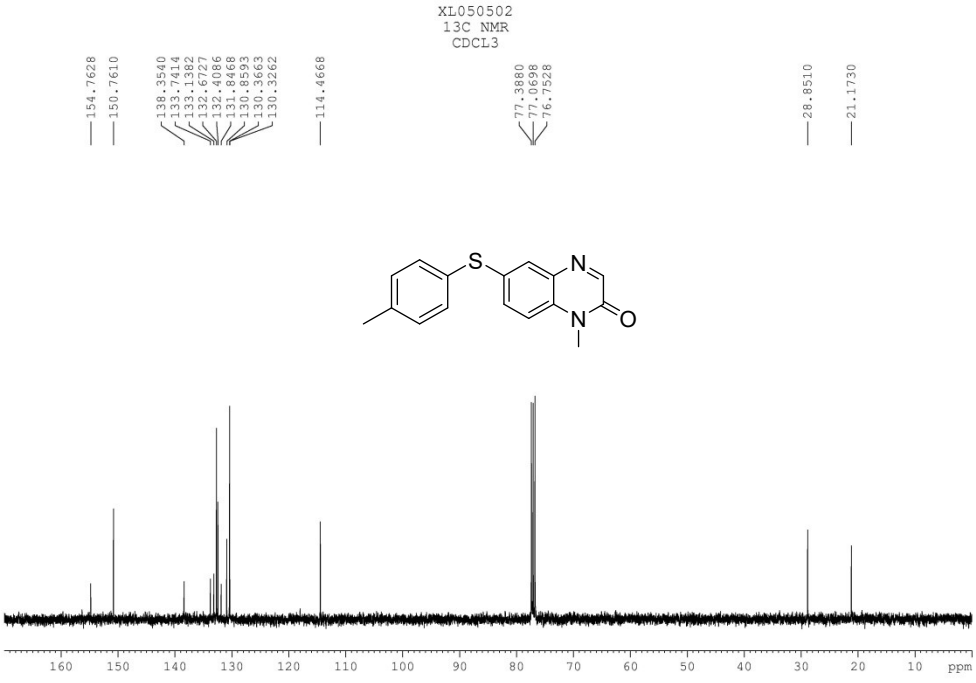


Fig. S37 ^{13}C NMR spectrum of compound **5a**

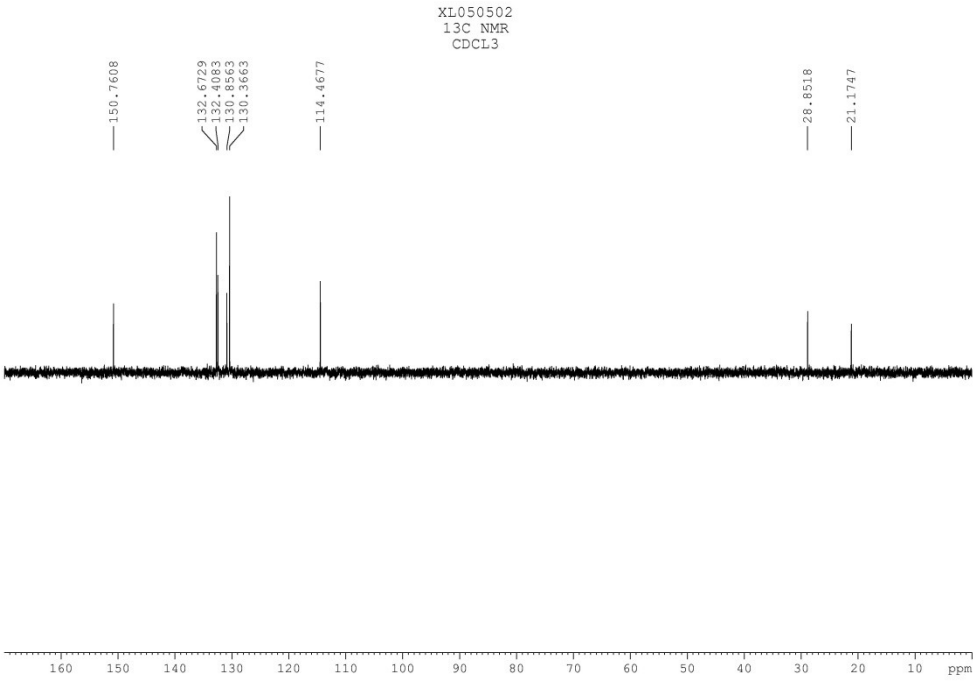


Fig. S38 DEPT135 spectrum of compound **5a**

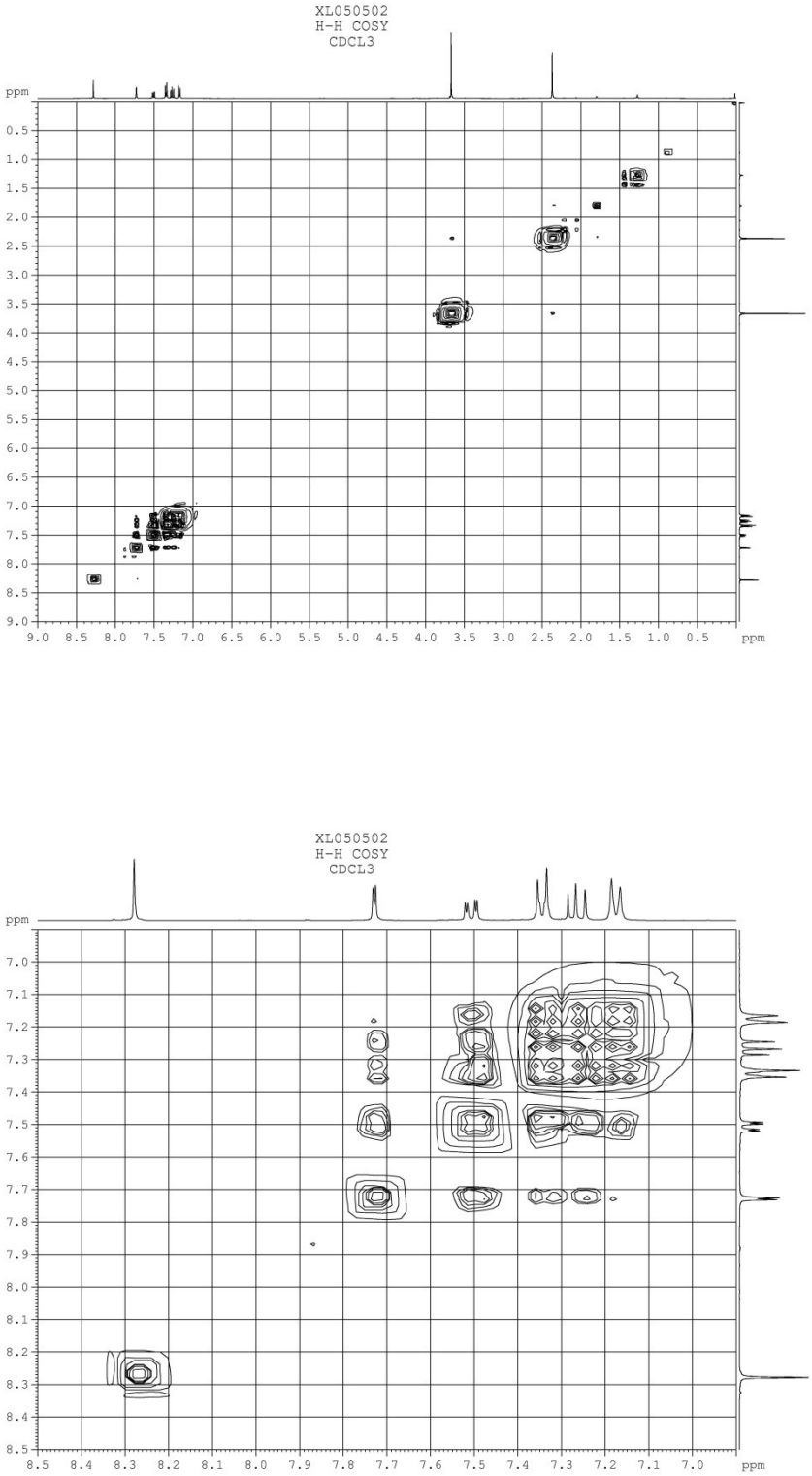


Fig. S39 H-H COSY spectrum of compound **5a**

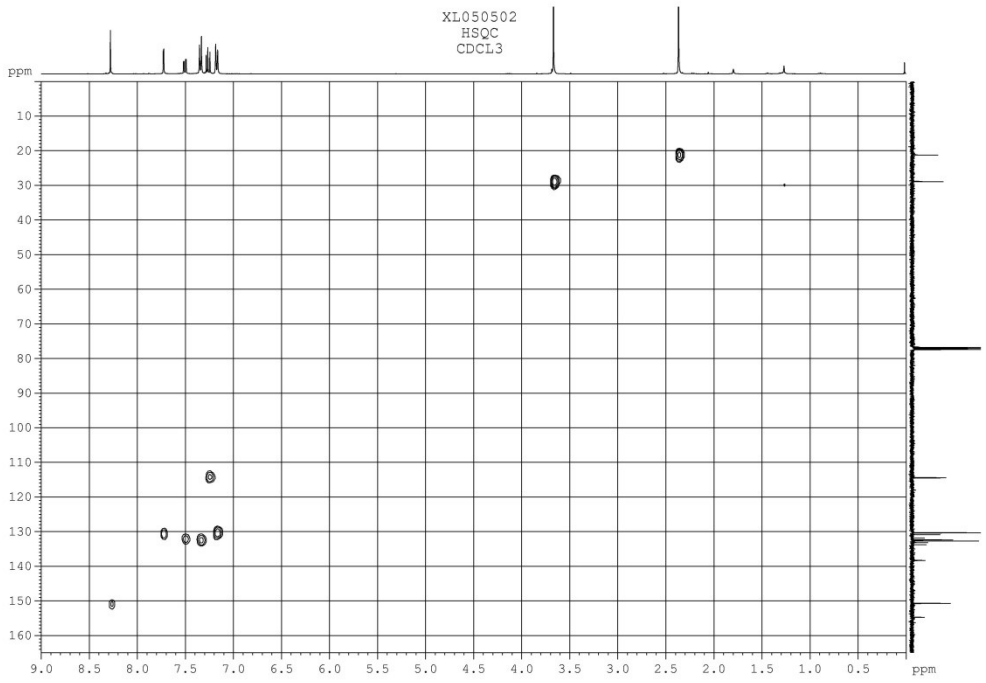


Fig. S40 HSQC spectrum of compound **5a**

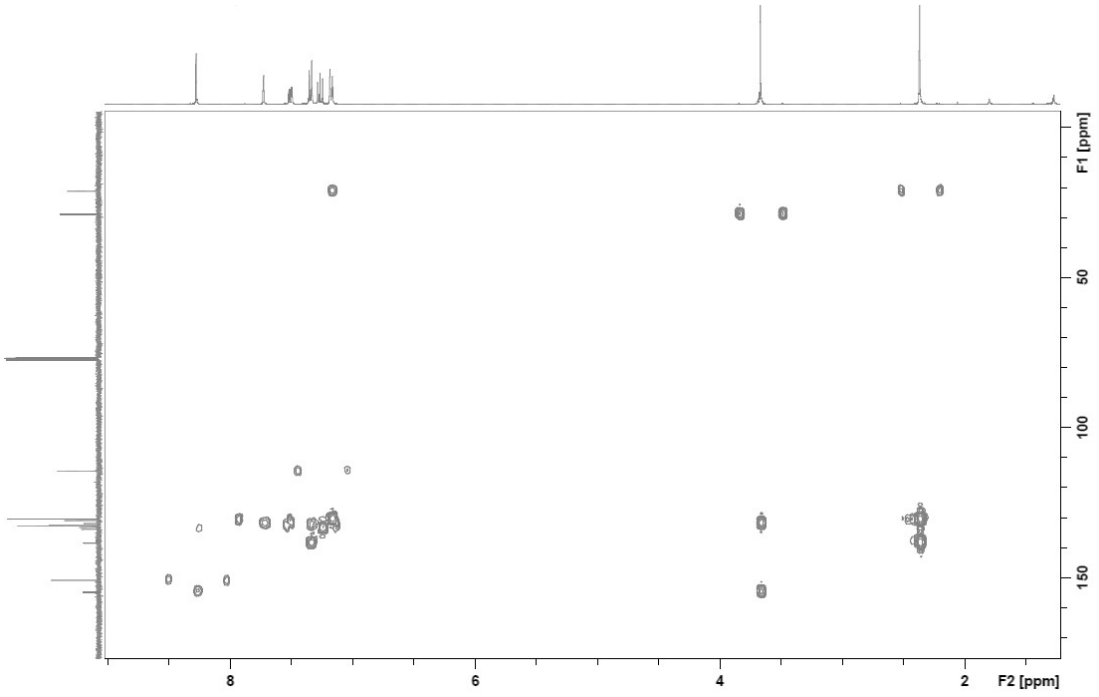


Fig. S41 HMBC spectrum of compound **5ª**

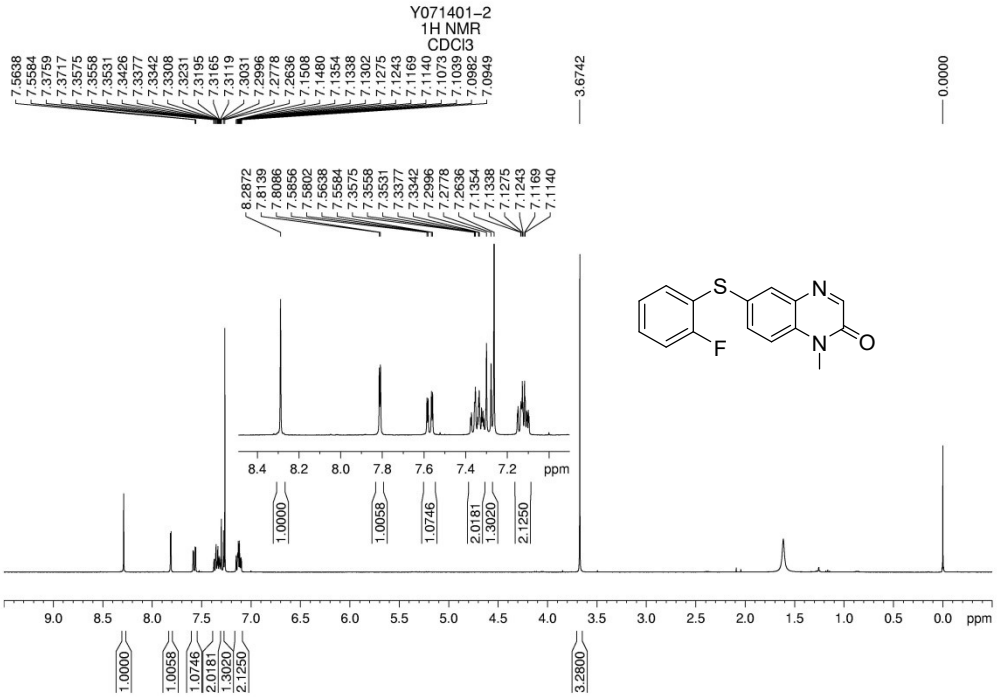


Fig. S42 ^{1}H NMR spectrum of compound **5b**

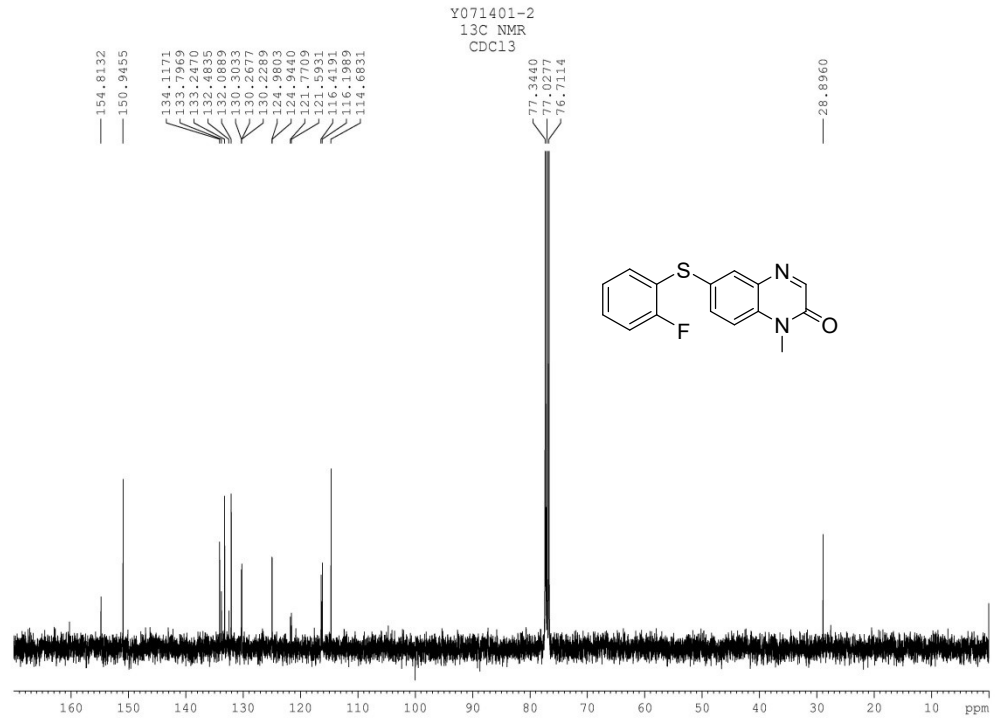


Fig. S43 ^{13}C NMR spectrum of compound **5b**

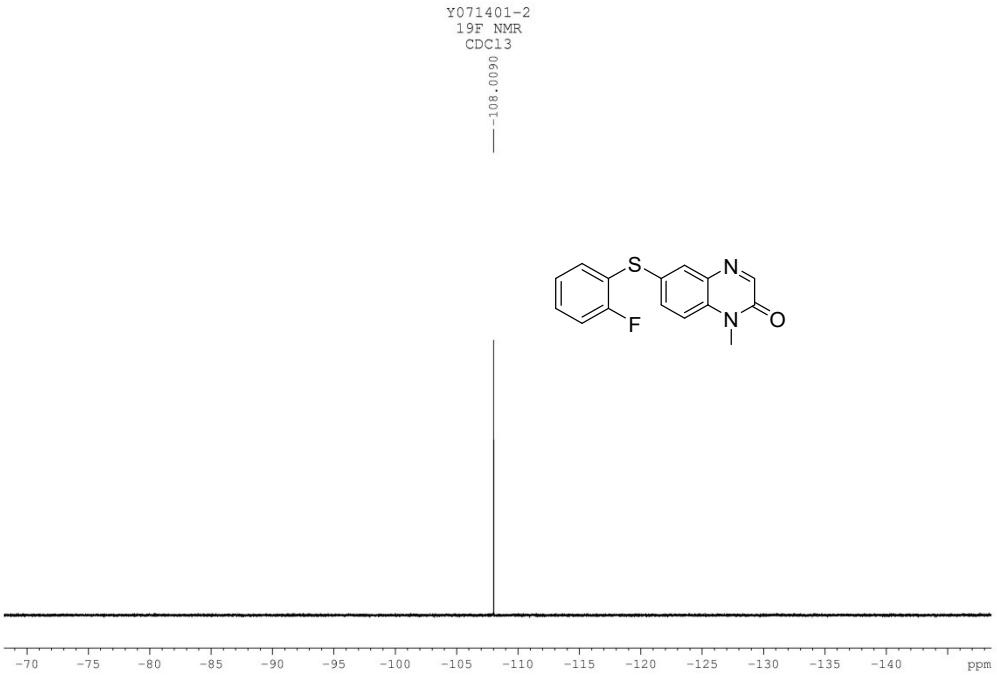


Fig. S44 ^{19}F NMR spectrum of compound **5b**

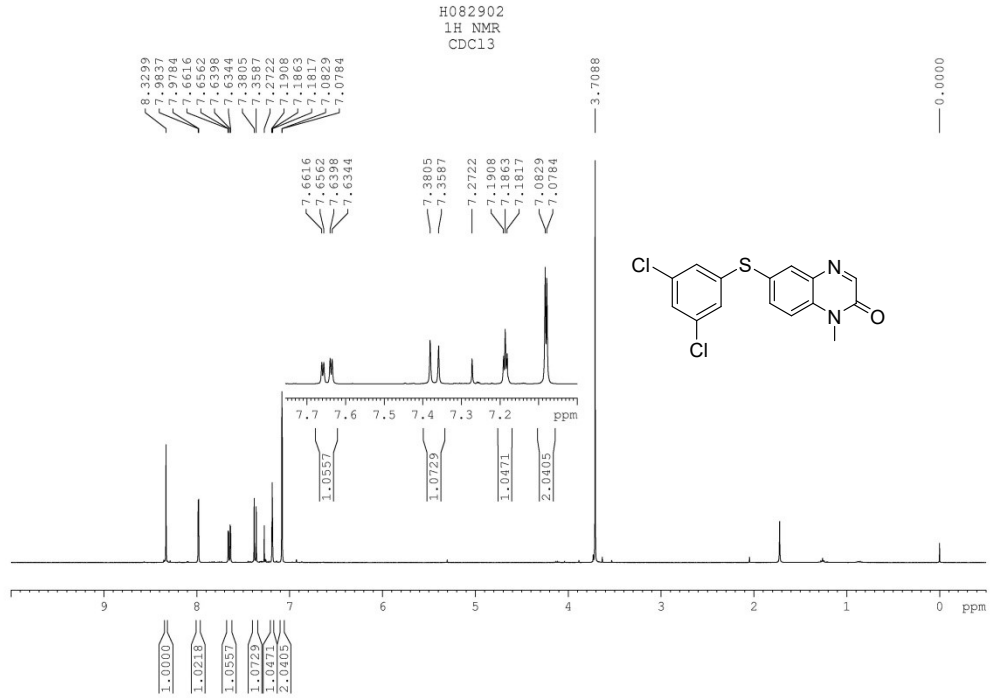


Fig. S45 ^{1}H NMR spectrum of compound **5c**

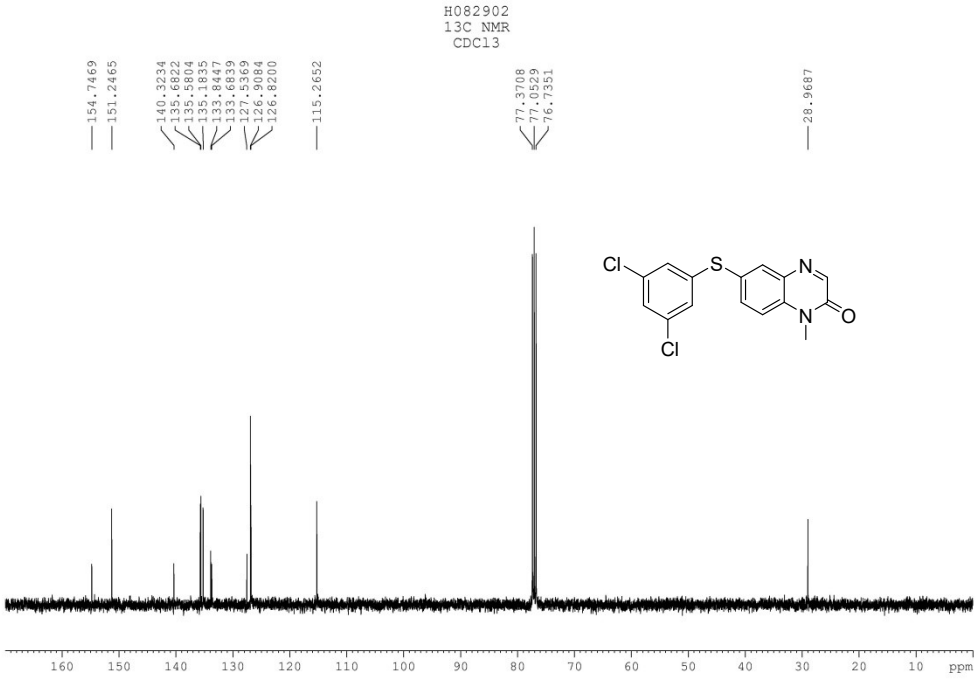


Fig. S46 ^{13}C NMR spectrum of compound **5c**

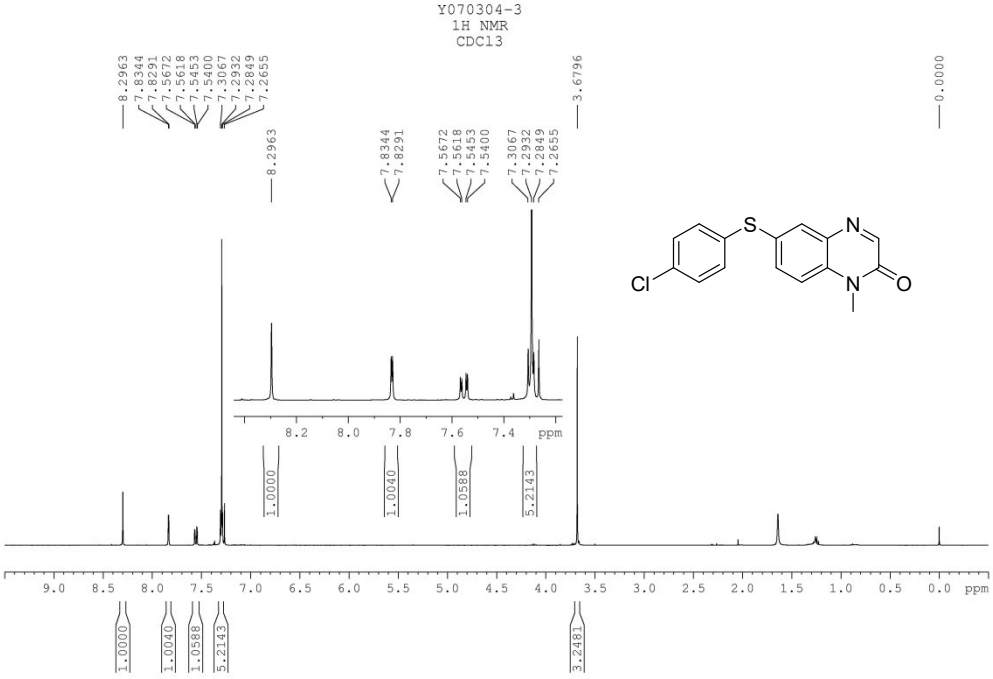


Fig. S47 ^{1}H NMR spectrum of compound **5d**

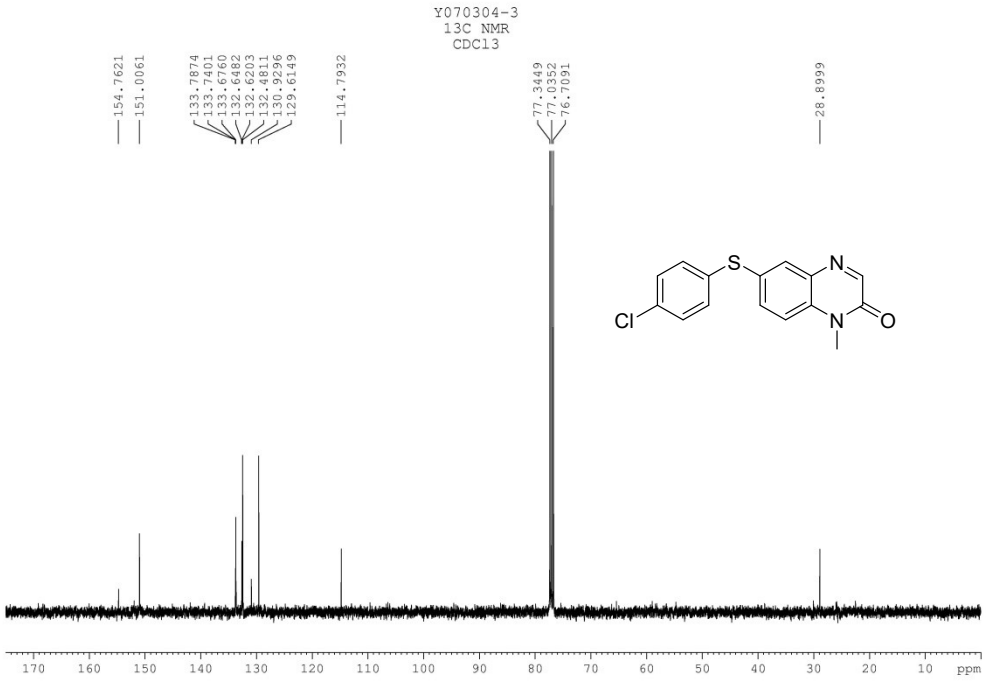


Fig. S48 ^{13}C NMR spectrum of compound **5d**

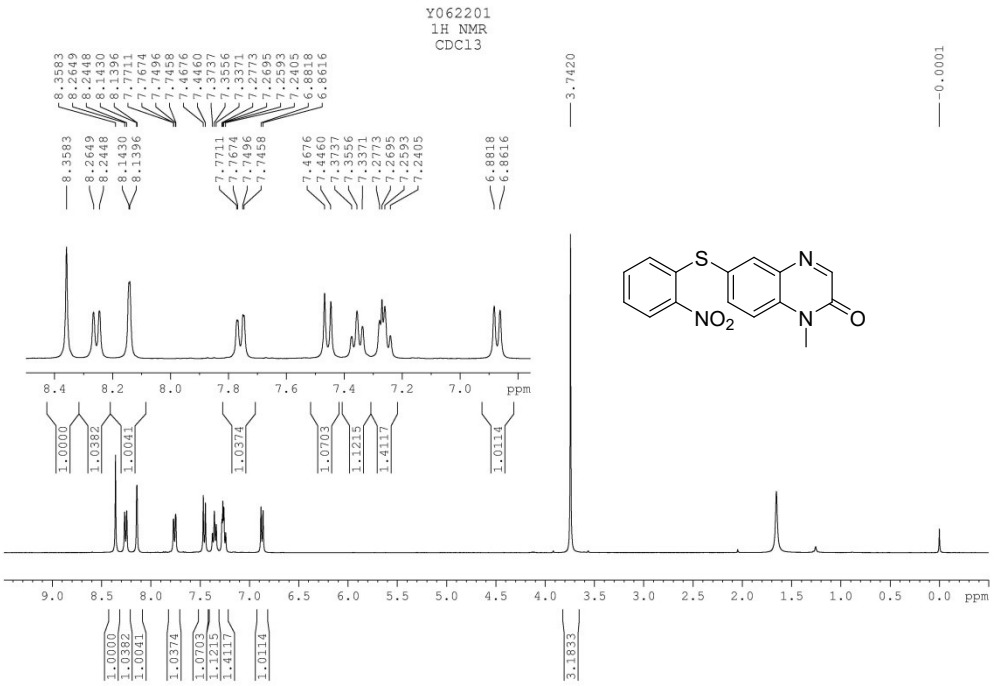


Fig. S49 ^{1}H NMR spectrum of compound **5e**

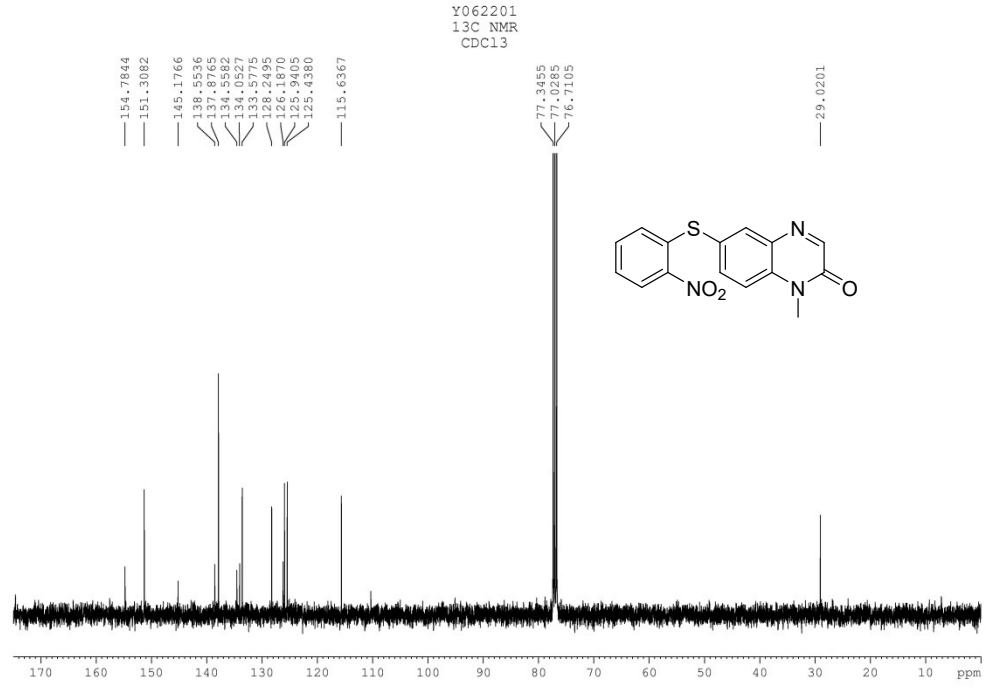


Fig. S50 ^{13}C NMR spectrum of compound **5e**

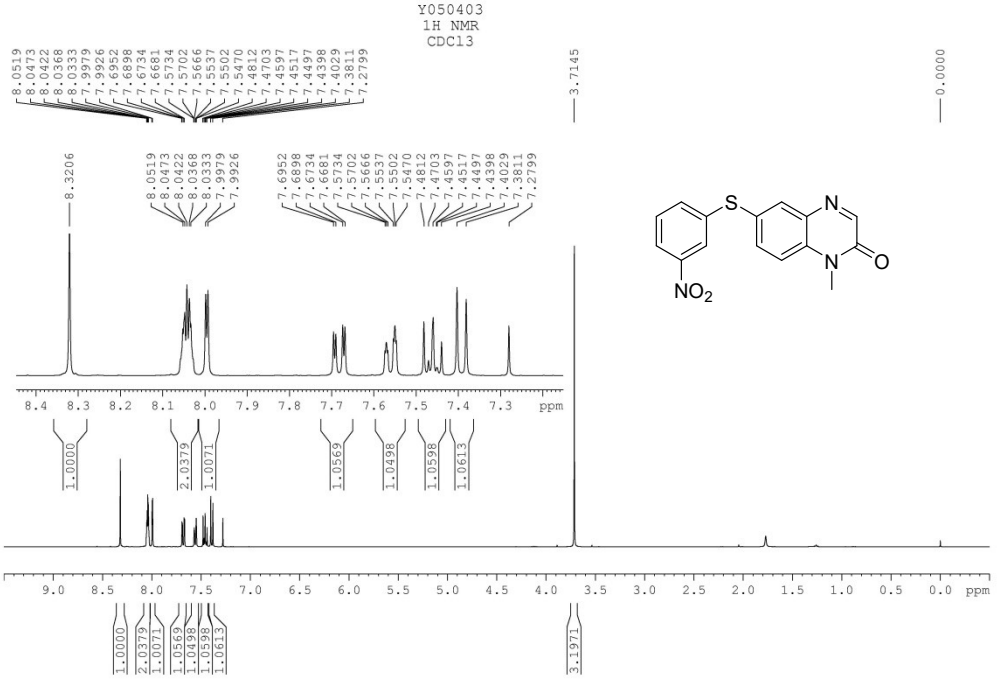


Fig. S51 ^{1}H NMR spectrum of compound **5f**

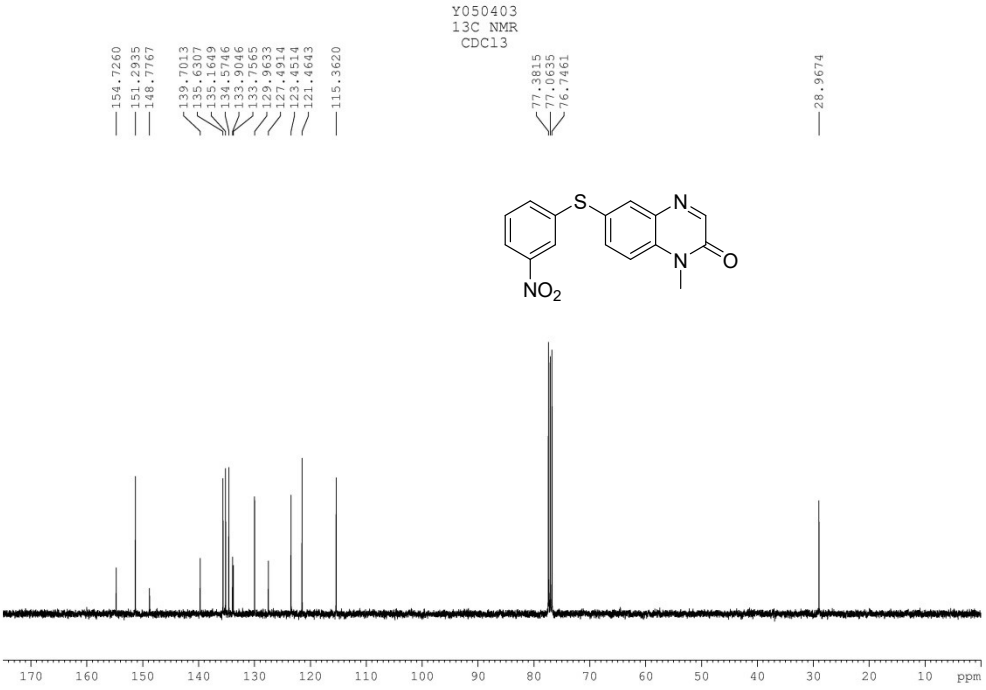


Fig. S52 ^{13}C NMR spectrum of compound **5f**

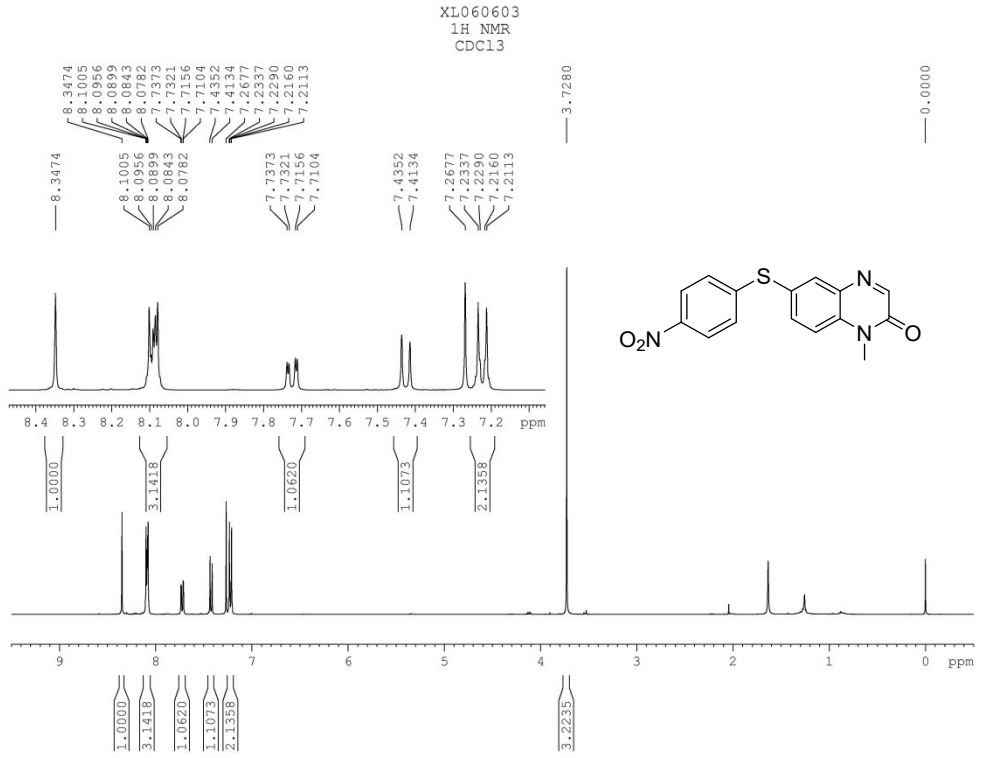


Fig. S53 ^{1}H NMR spectrum of compound **5g**

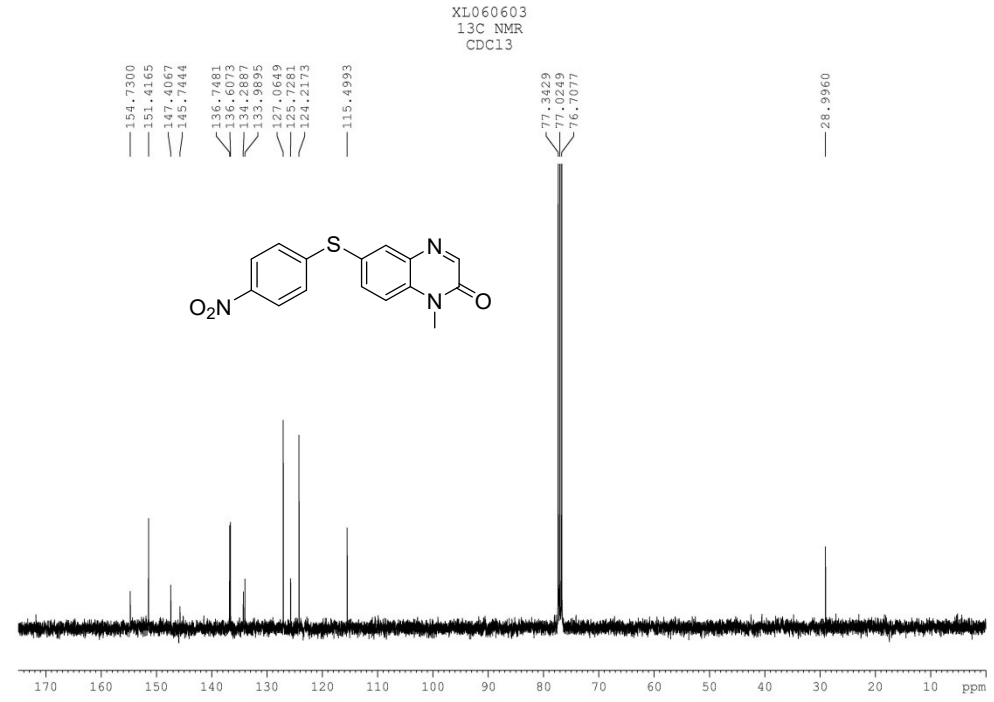


Fig. S54 ^{13}C NMR spectrum of compound **5g**

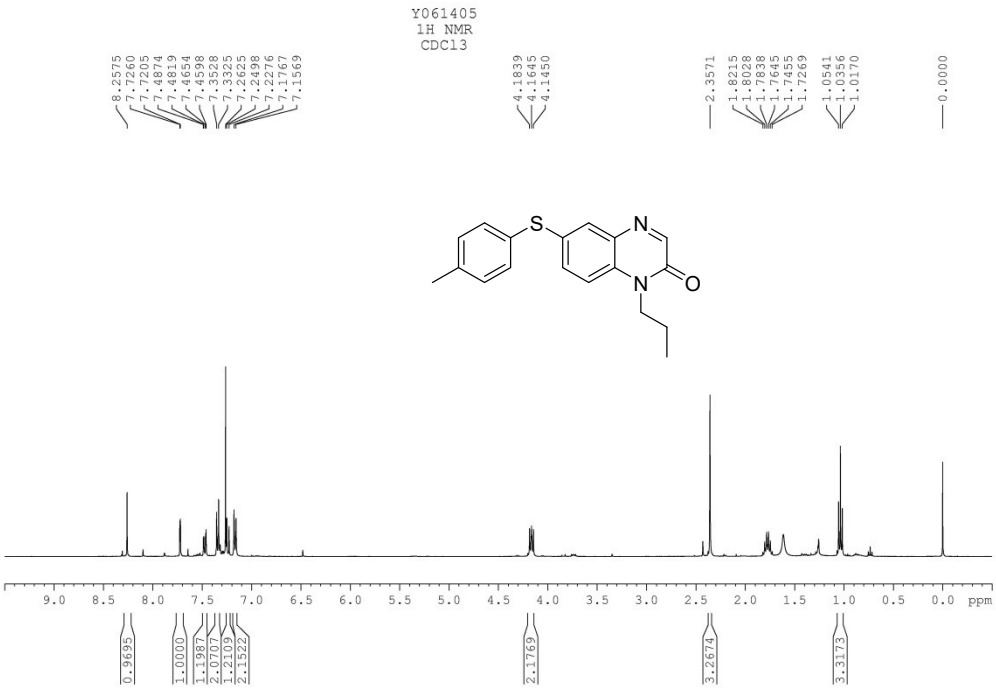


Fig. S55 ^{1}H NMR spectrum of compound **5h**

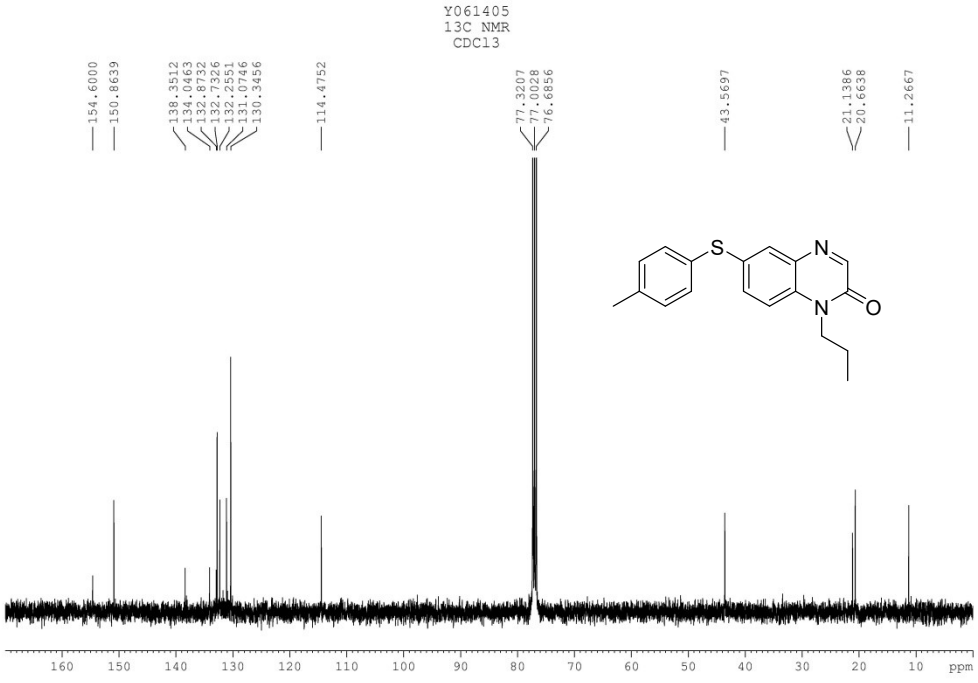


Fig. S6 ^{13}C NMR spectrum of compound **5h**

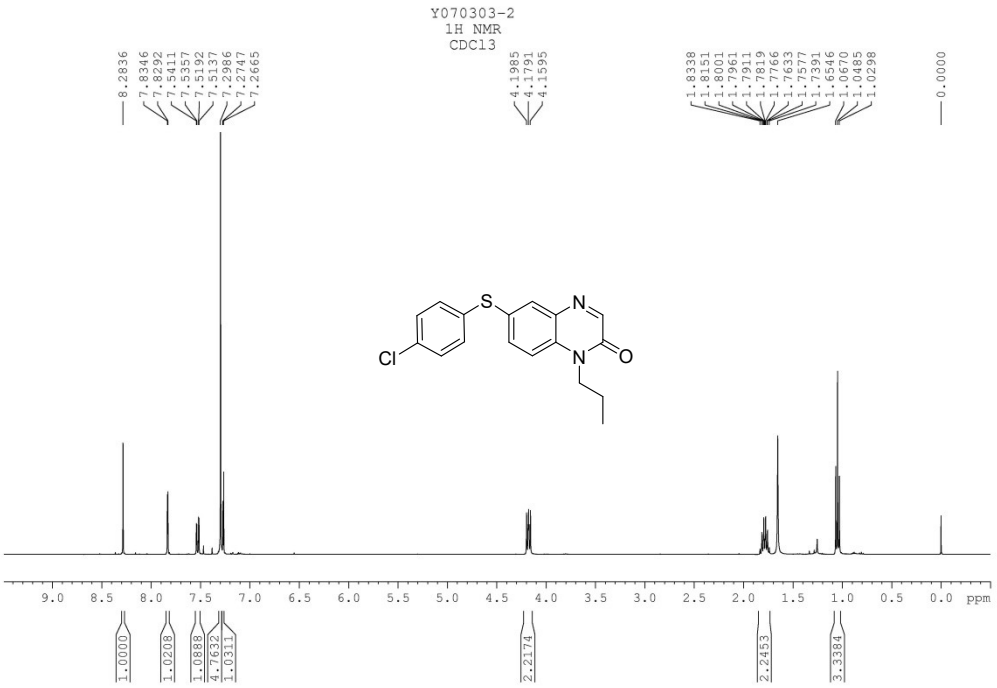


Fig. S57 ^{1}H NMR spectrum of compound **5i**

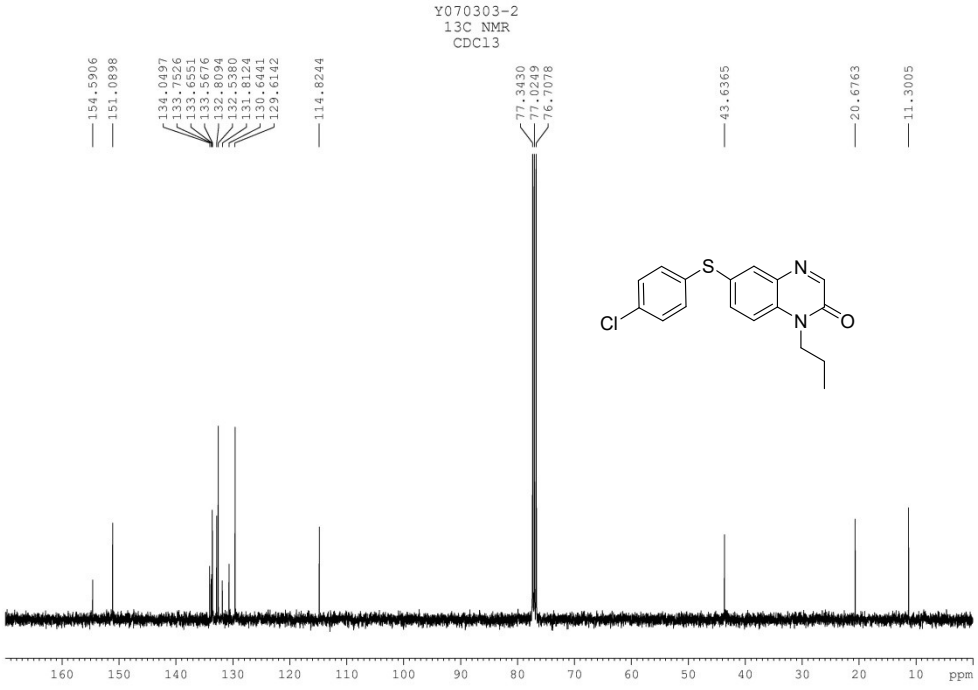


Fig. S58 ^{13}C NMR spectrum of compound **5i**

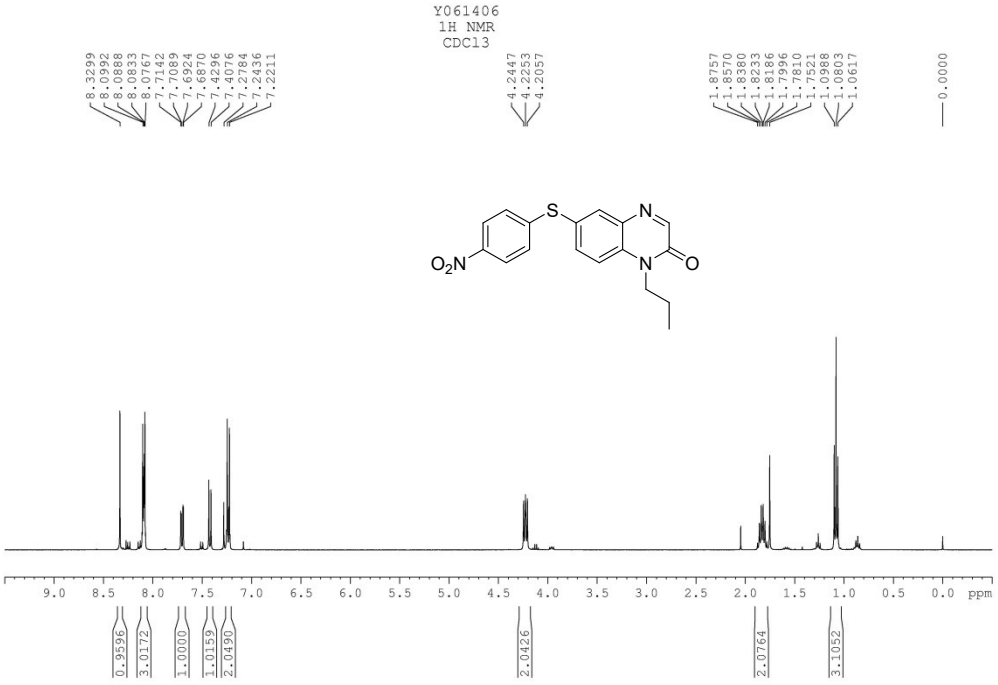


Fig. S59 ^{1}H NMR spectrum of compound **5j**

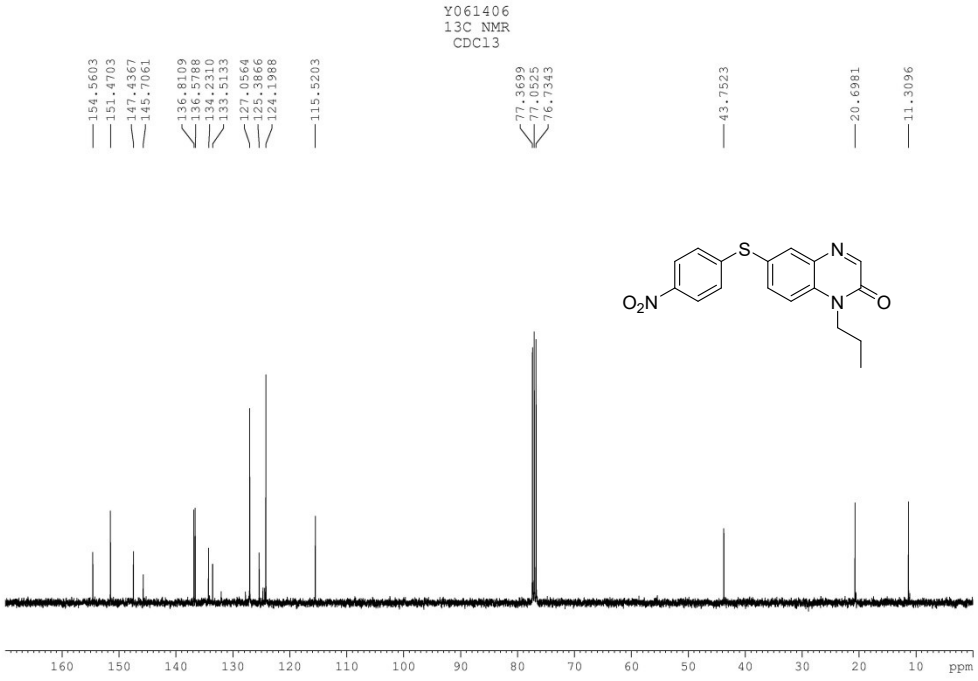


Fig. S60 ^{13}C NMR spectrum of compound **5j**

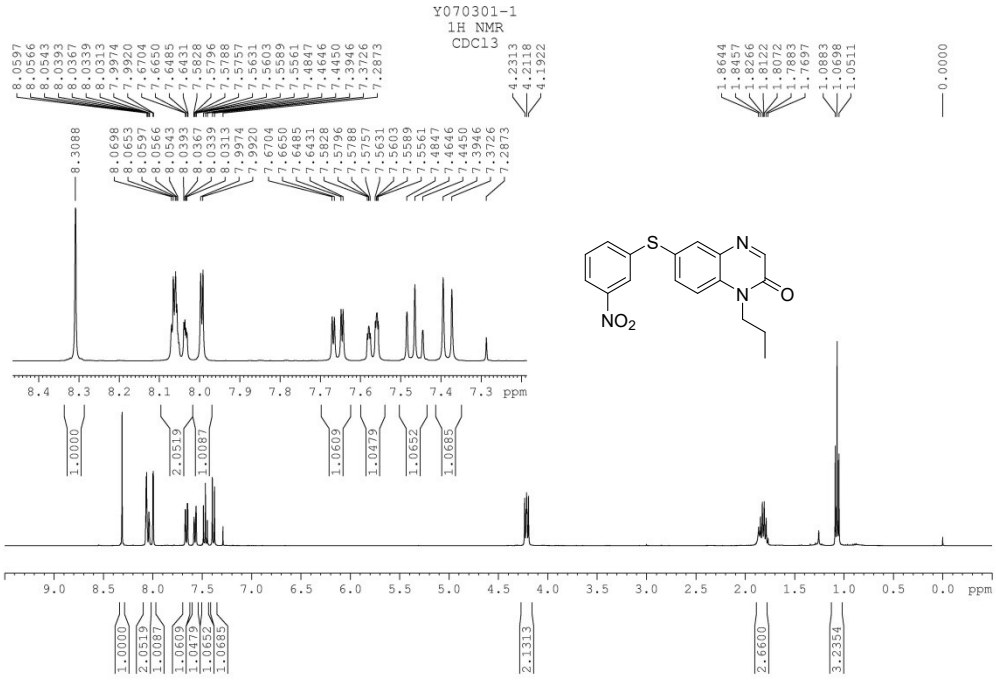


Fig. S61 ^{1}H NMR spectrum of compound **5k**

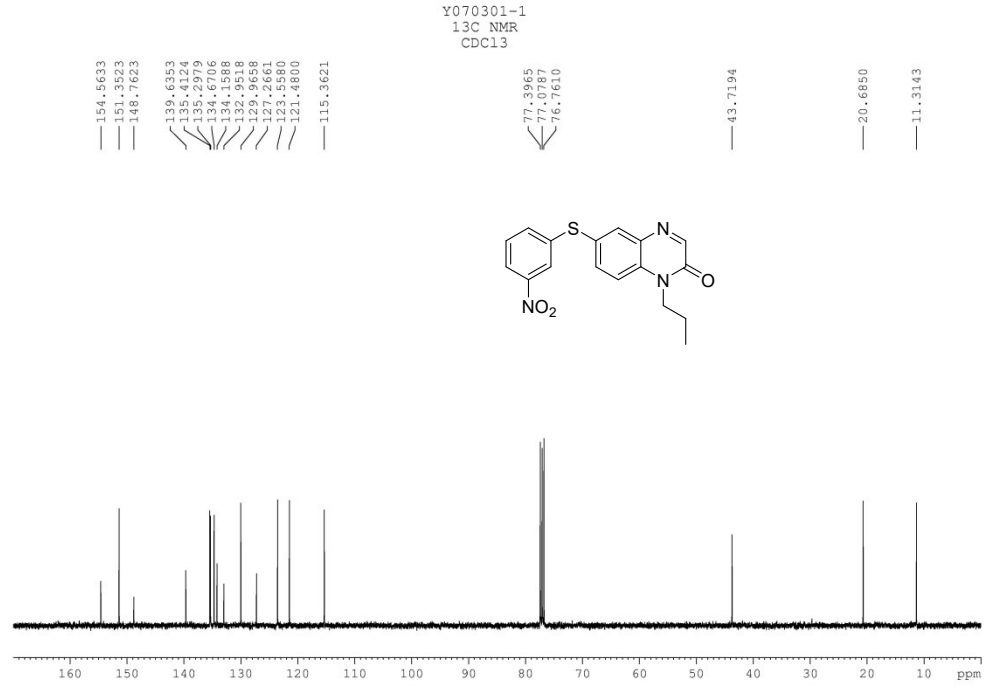


Fig. S62 ^{13}C NMR spectrum of compound **5k**

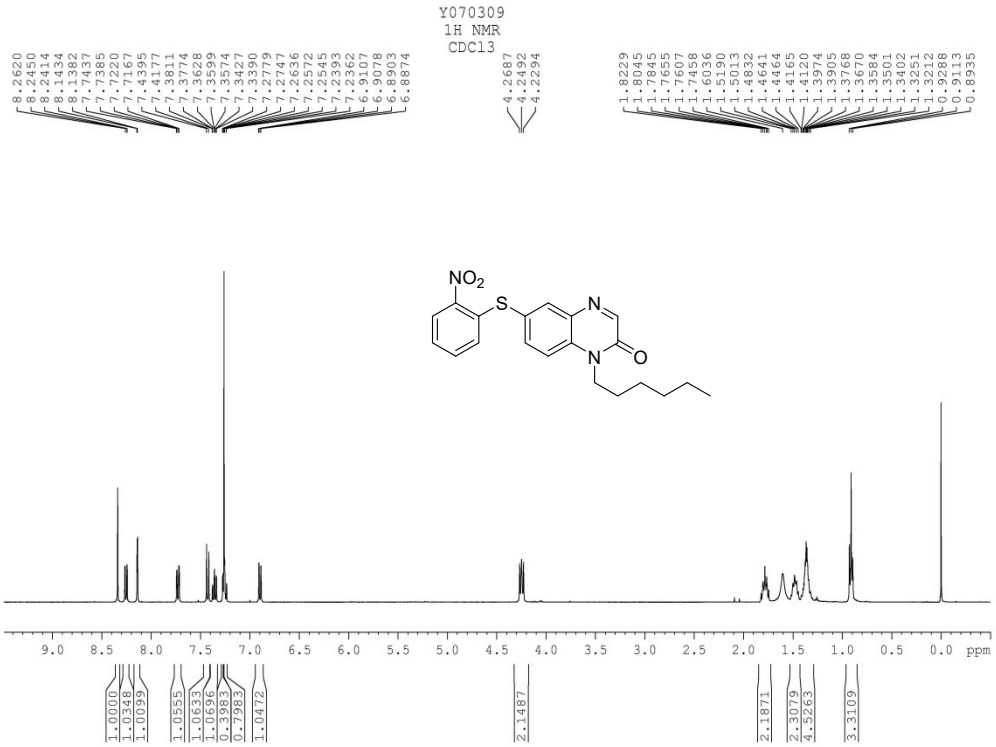


Fig. S63 ^{1}H NMR spectrum of compound **5l**

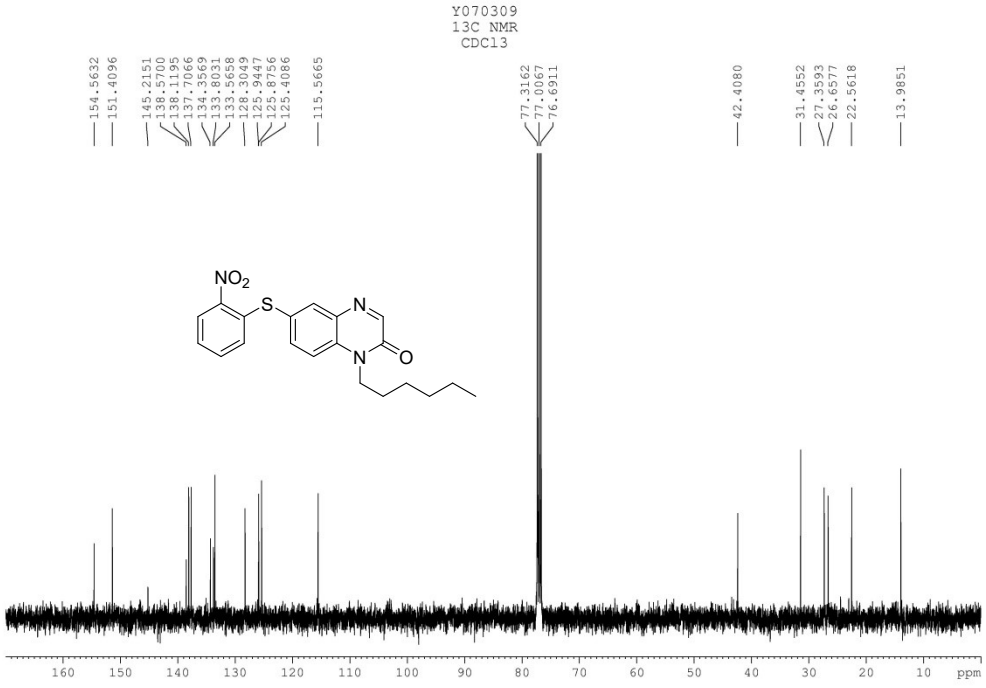


Fig. S64 ^{13}C NMR spectrum of compound **5l**

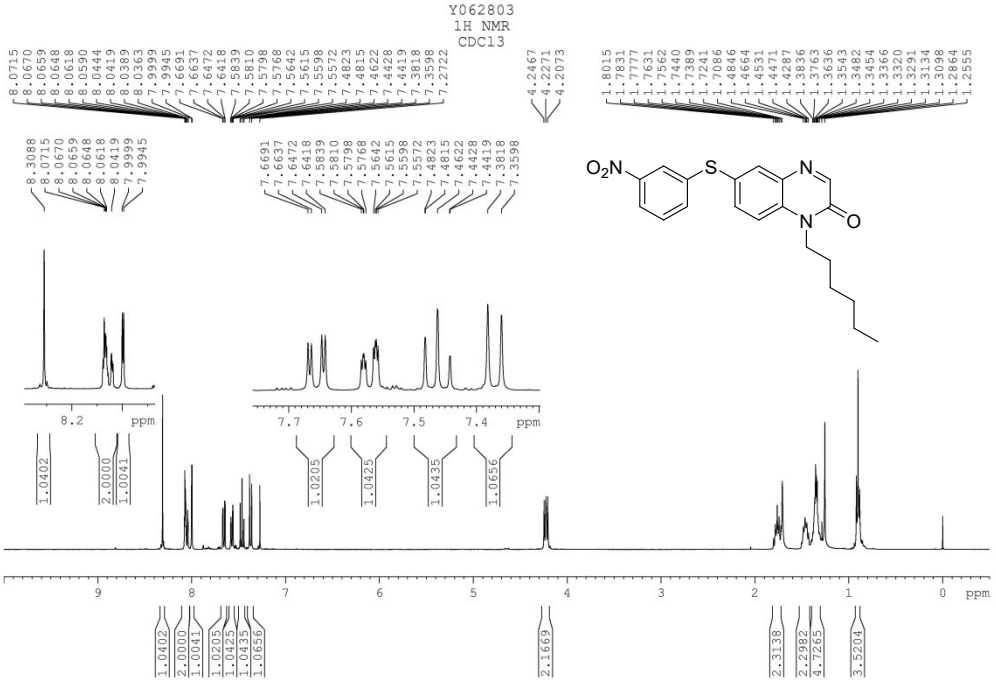


Fig. S65 ^{1}H NMR spectrum of compound **5m**

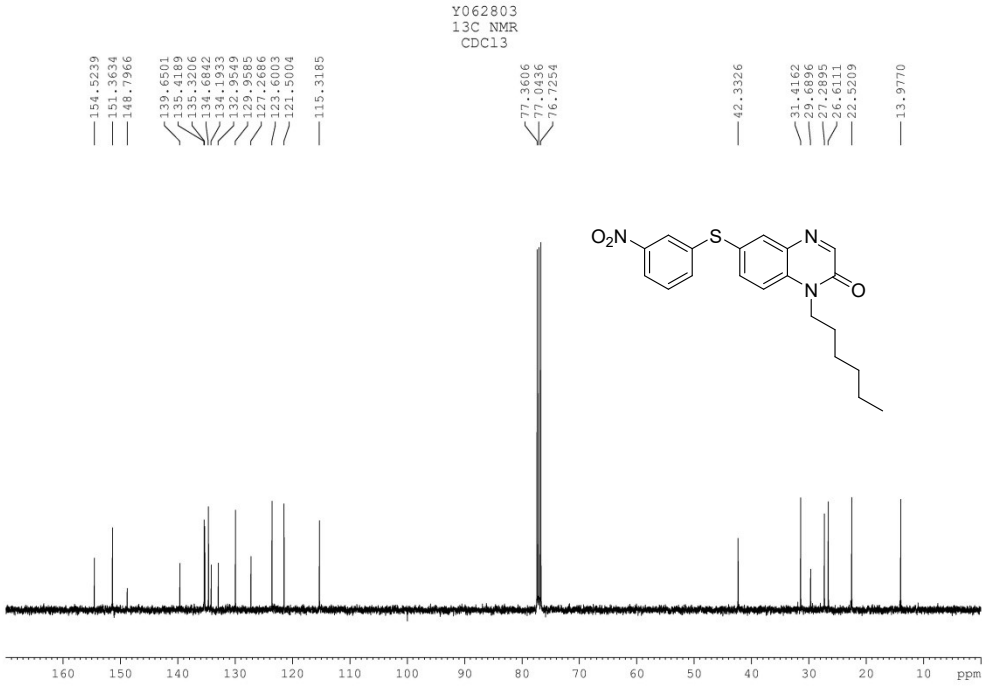


Fig. S66 ^{13}C NMR spectrum of compound **5m**

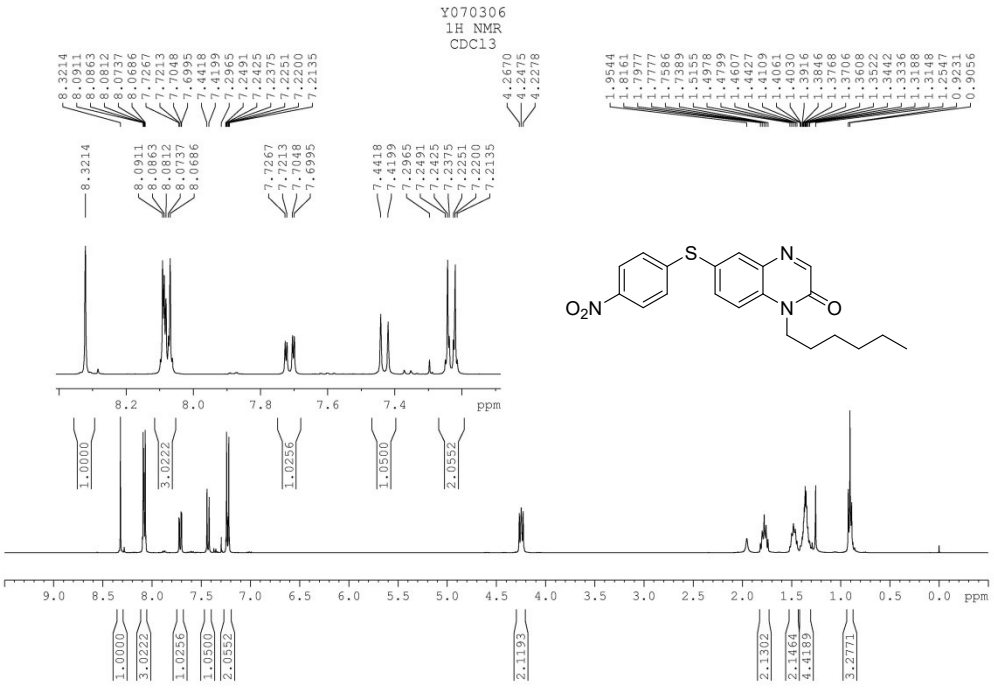


Fig. S67 ^{1}H NMR spectrum of compound **5n**

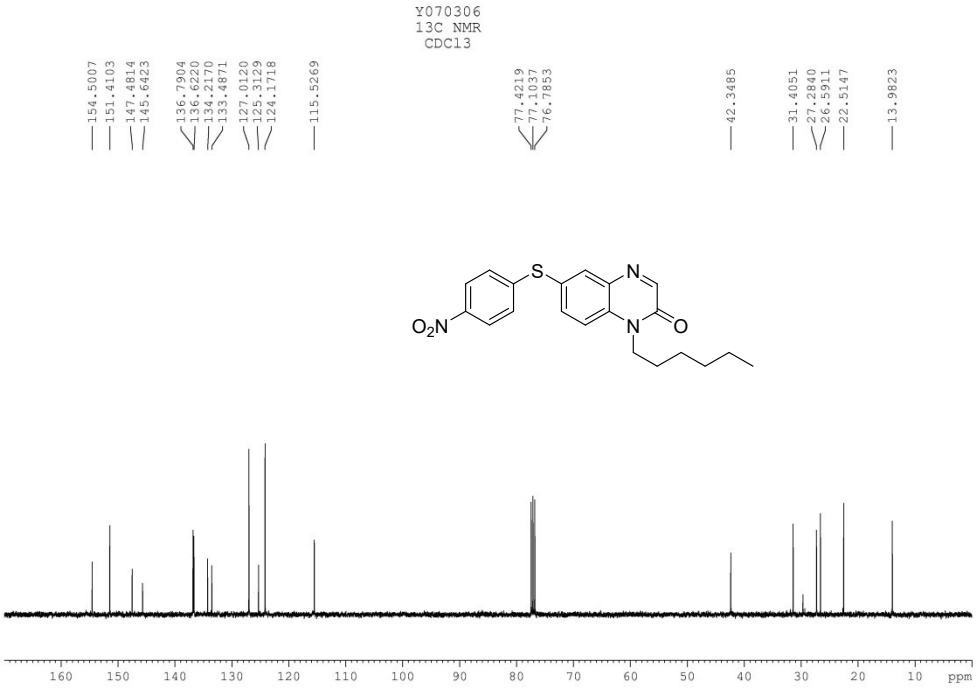


Fig. S68 ^{13}C NMR spectrum of compound **5n**

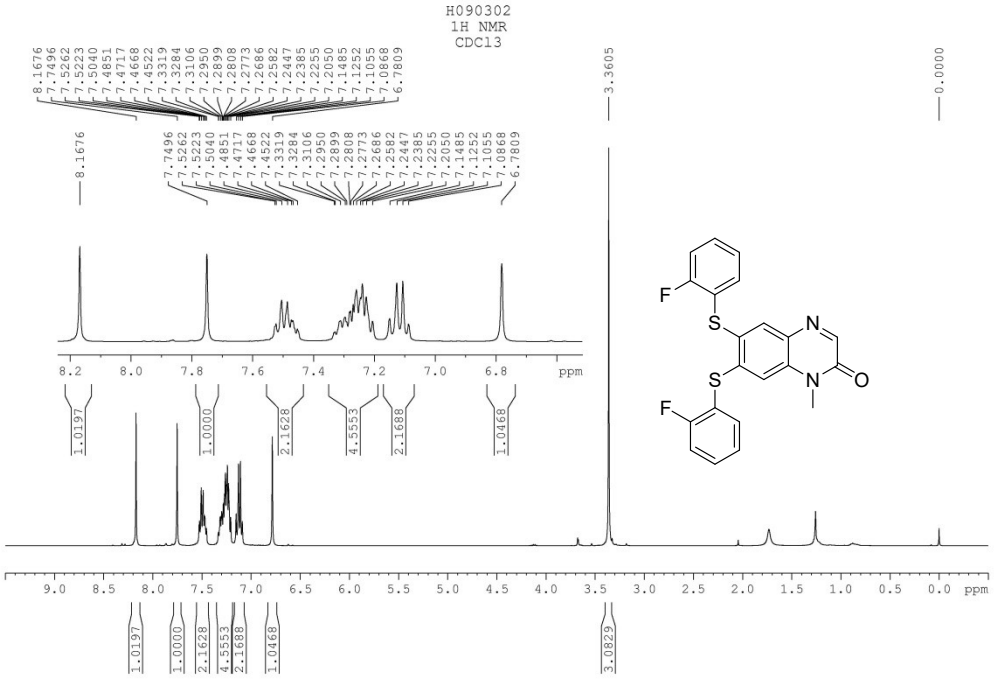


Fig. S69 ^{1}H NMR spectrum of compound **6a**

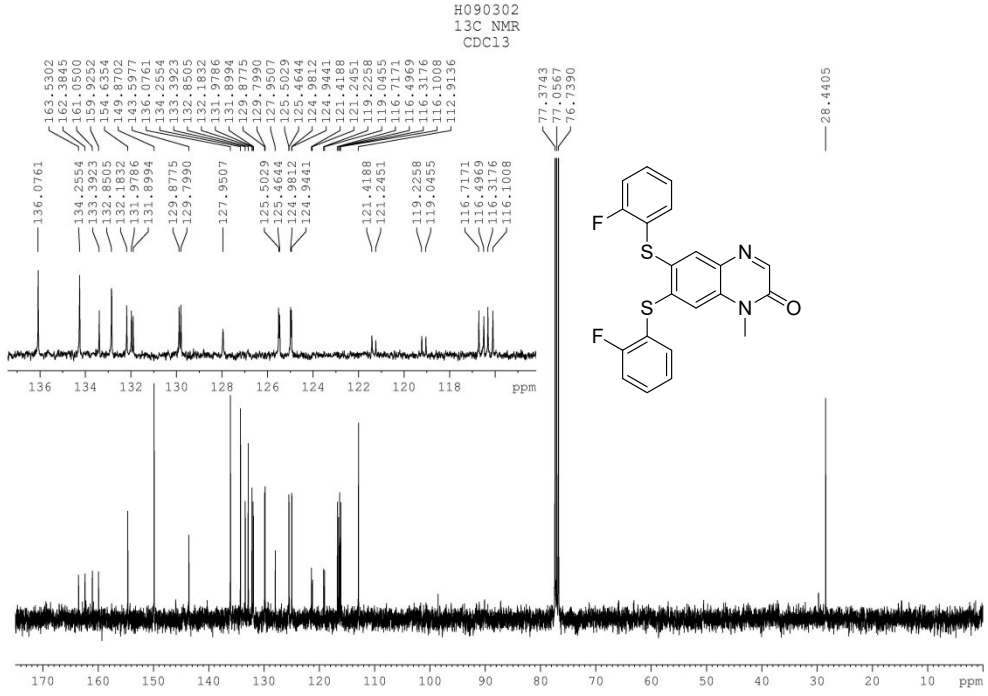


Fig. S70 ^{13}C NMR spectrum of compound **6a**

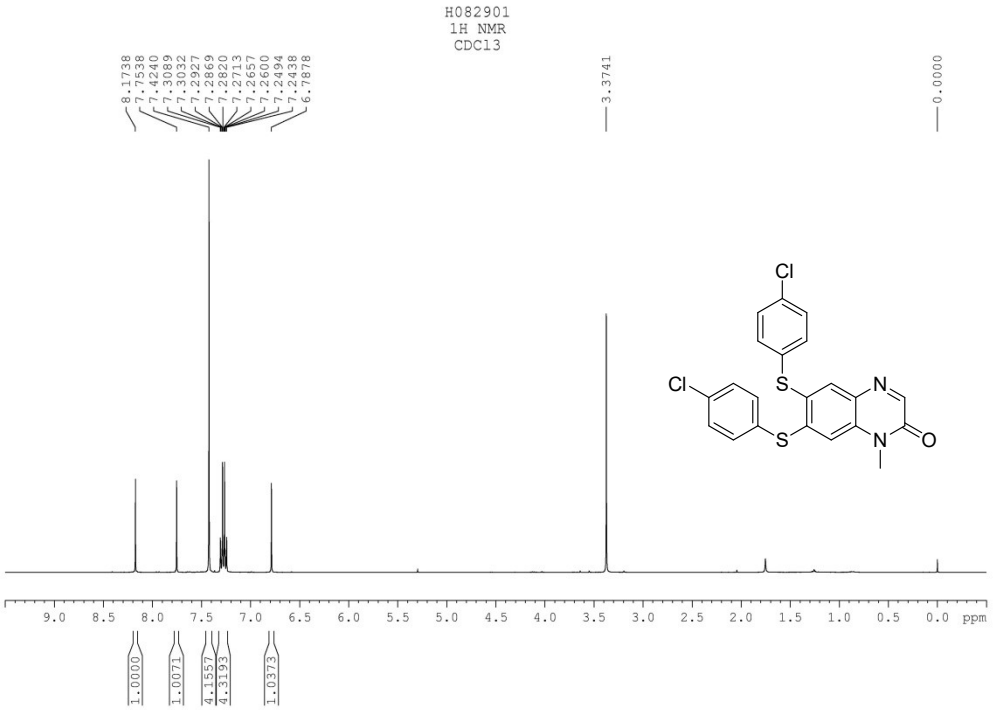


Fig. S71 ^{1}H NMR spectrum of compound **6b**

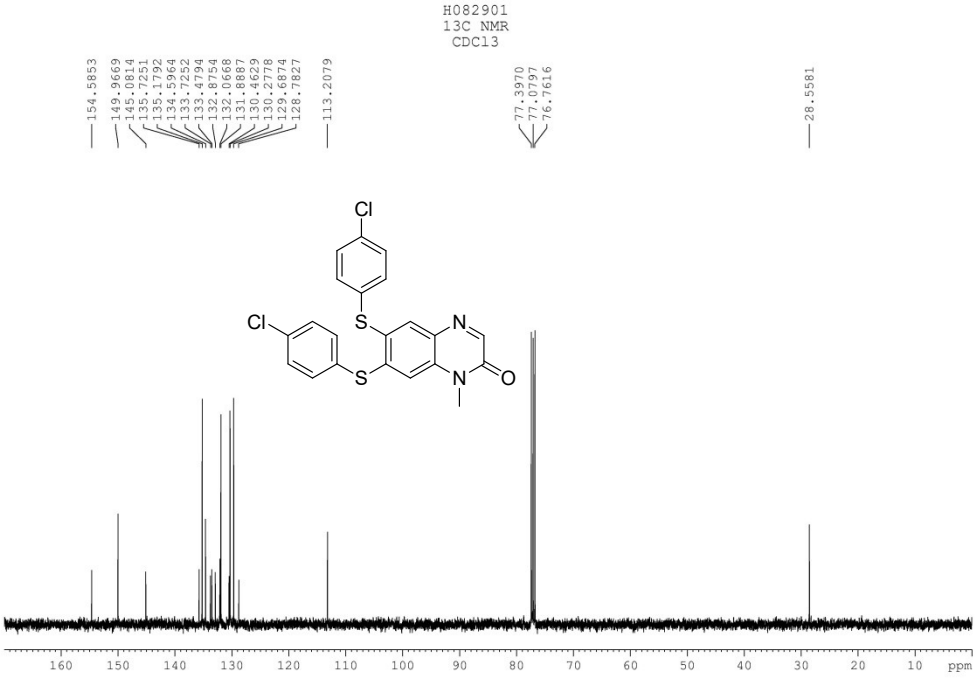


Fig. S72 ^{13}C NMR spectrum of compound **6b**

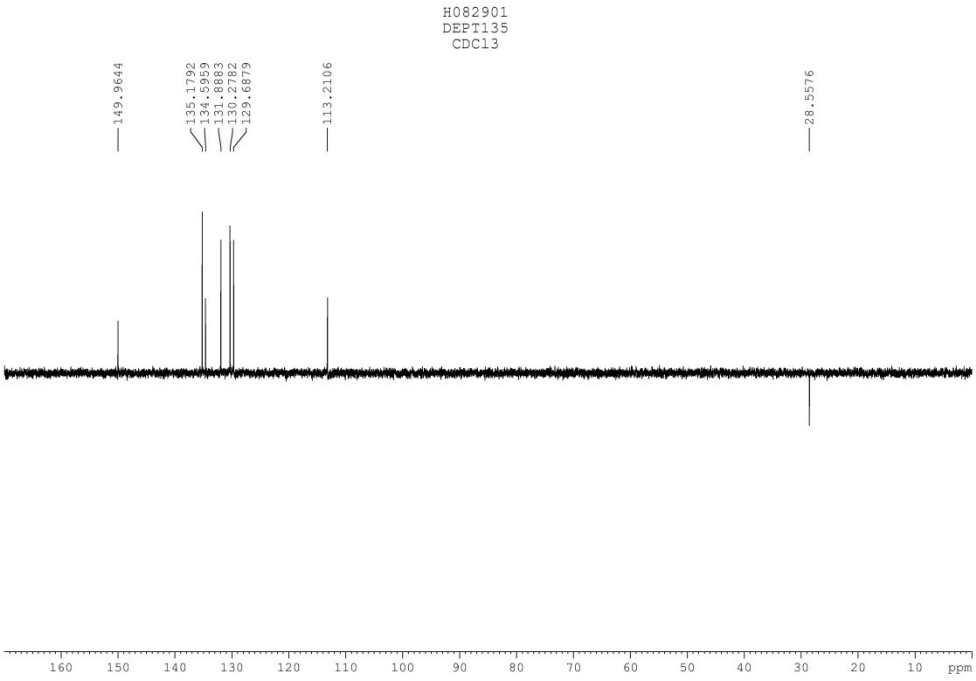


Fig. S73 DEPT135 spectrum of compound **6b**

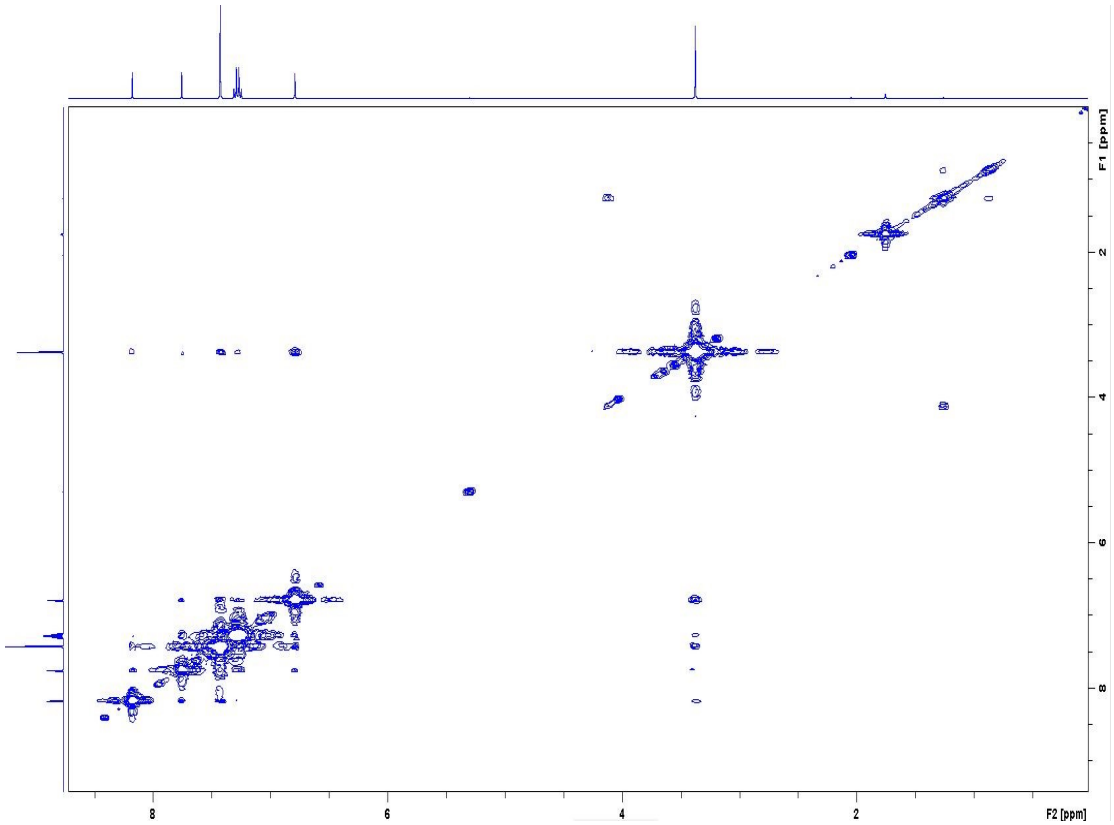


Fig. S74 H-H COSY spectrum of compound **6b**

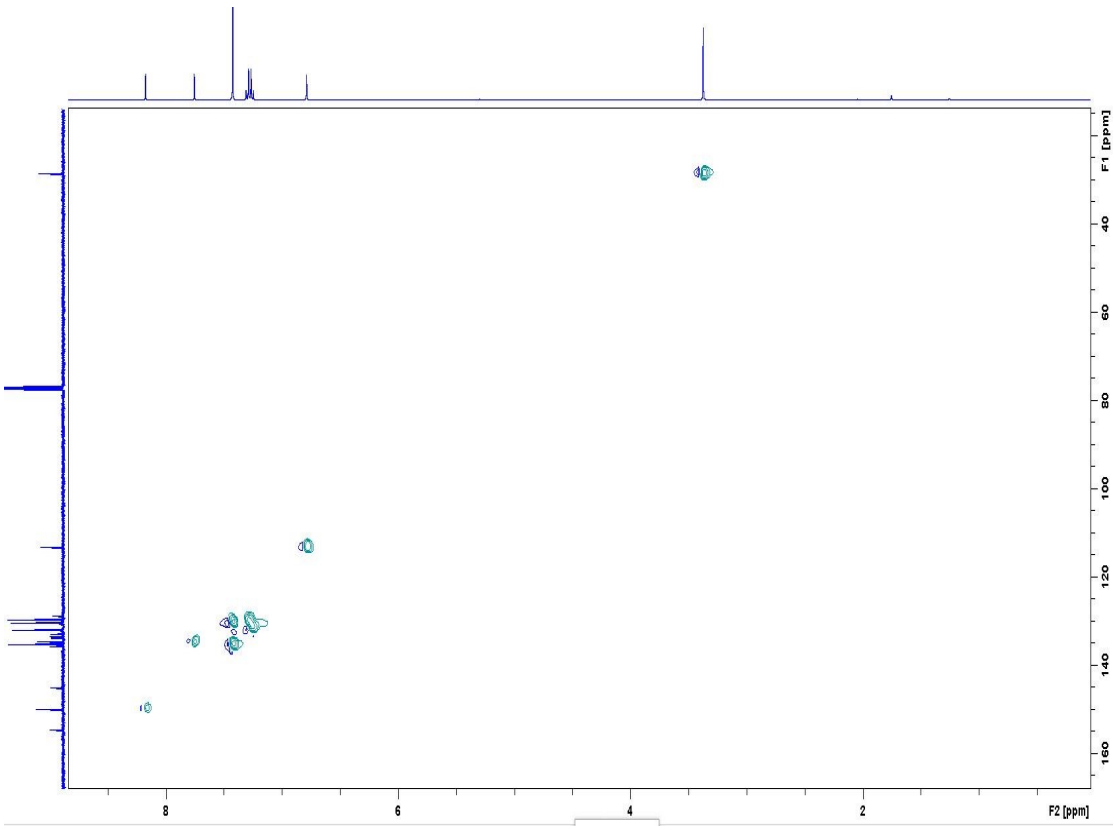


Fig. S75 HSQC spectrum of compound **6b**

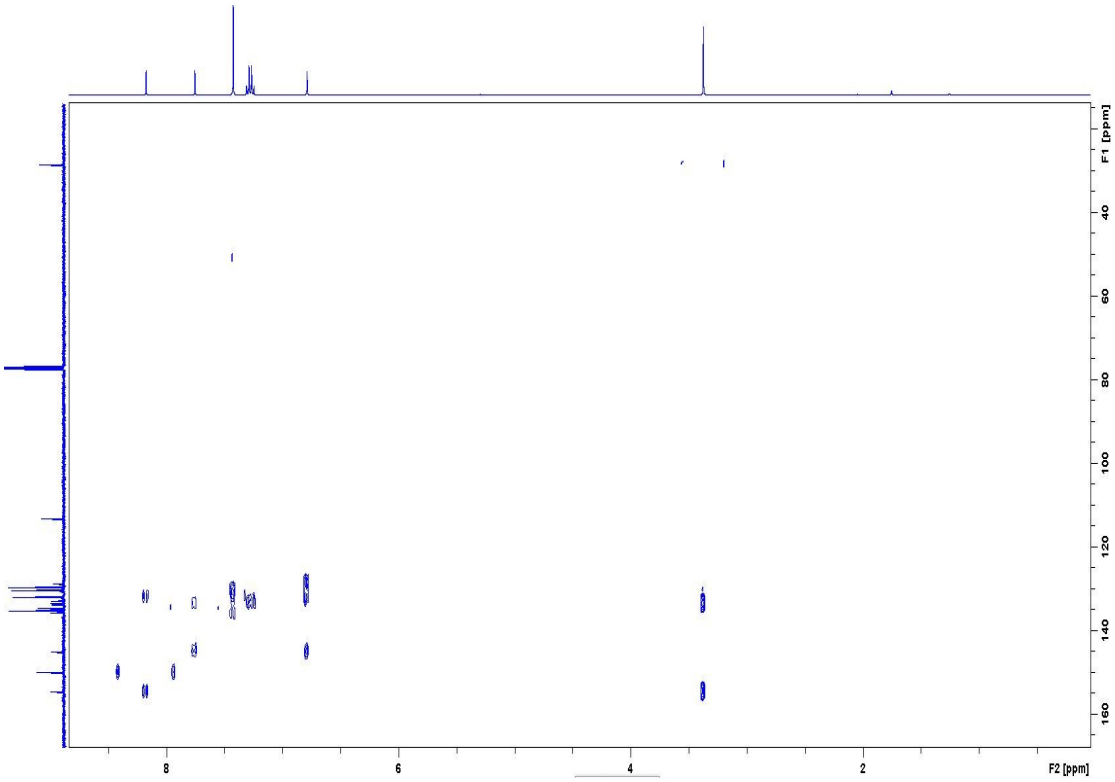


Fig. S76 HMBC spectrum of compound **6b**

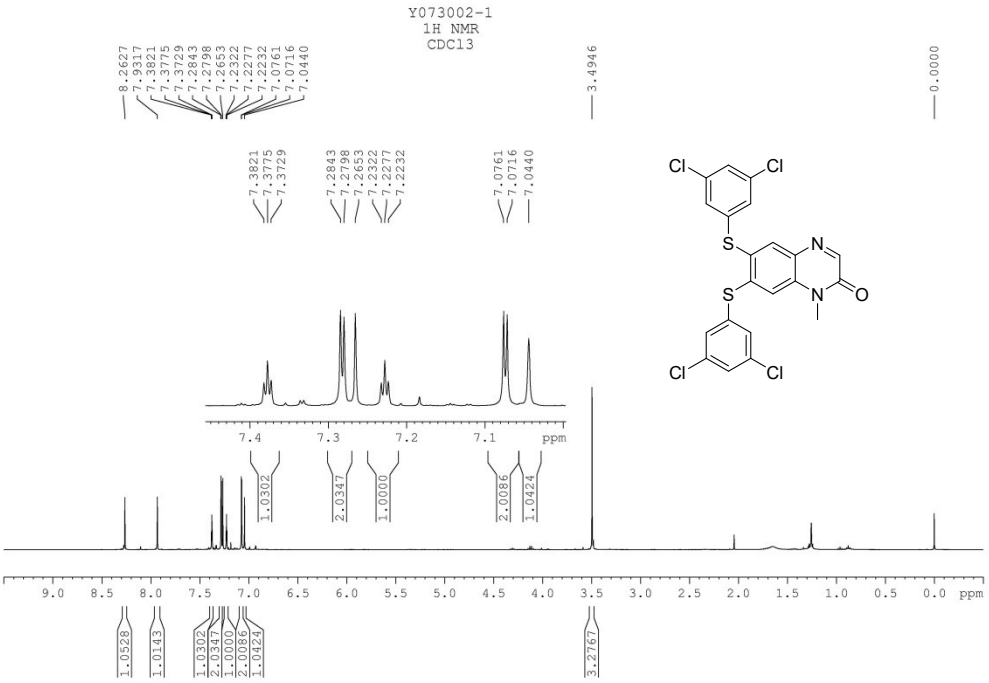


Fig. S77 ^{1}H NMR spectrum of compound **6c**

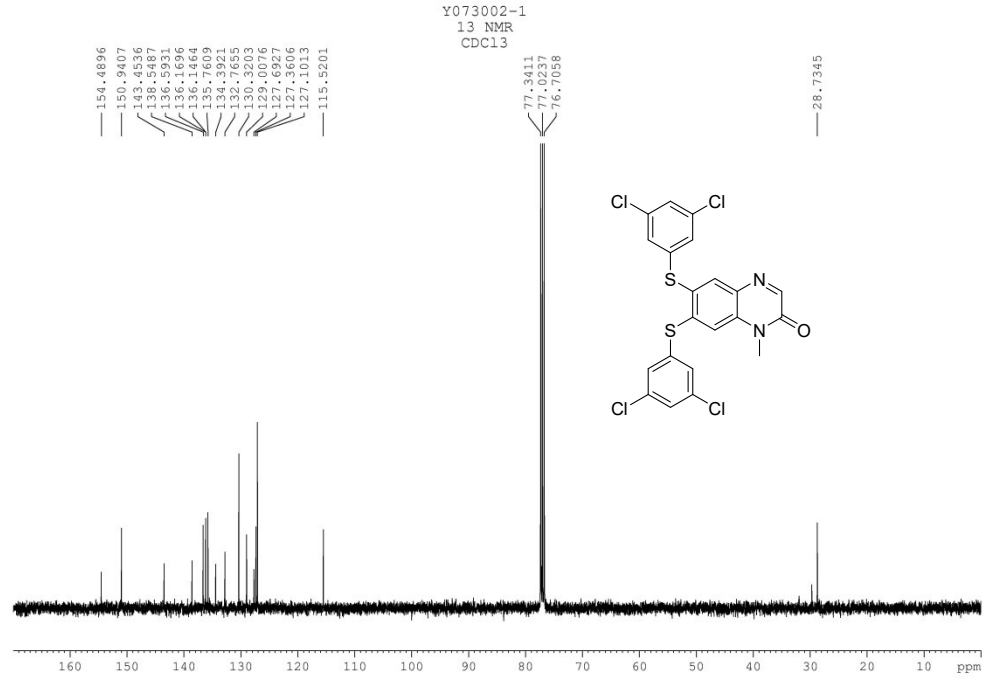


Fig. S78 ^{13}C NMR spectrum of compound **6c**

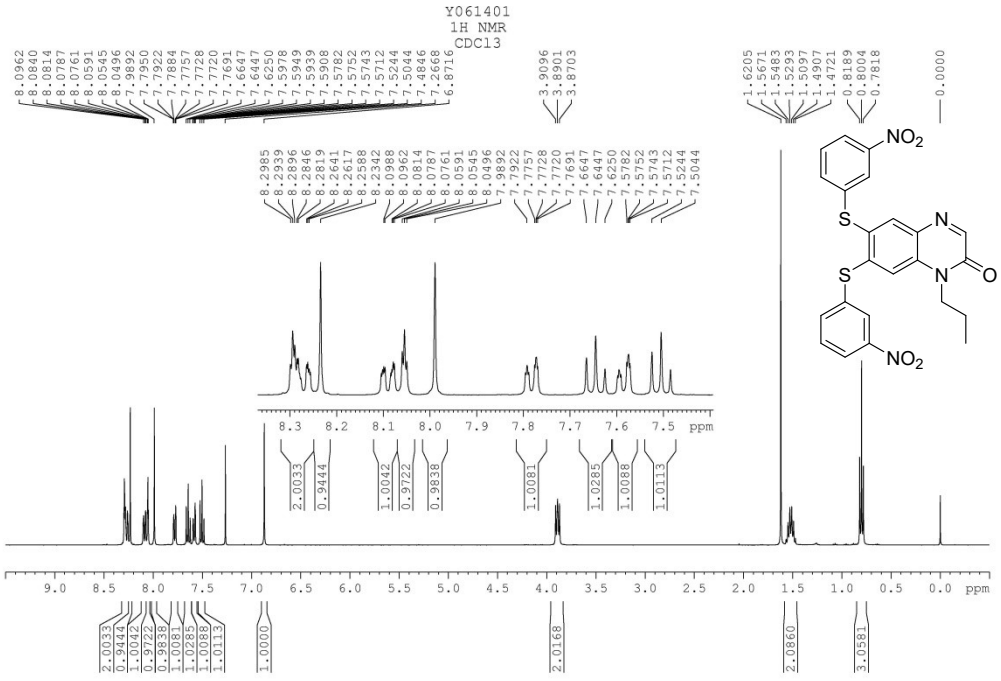


Fig. S79 ^{1}H NMR spectrum of compound **6d**

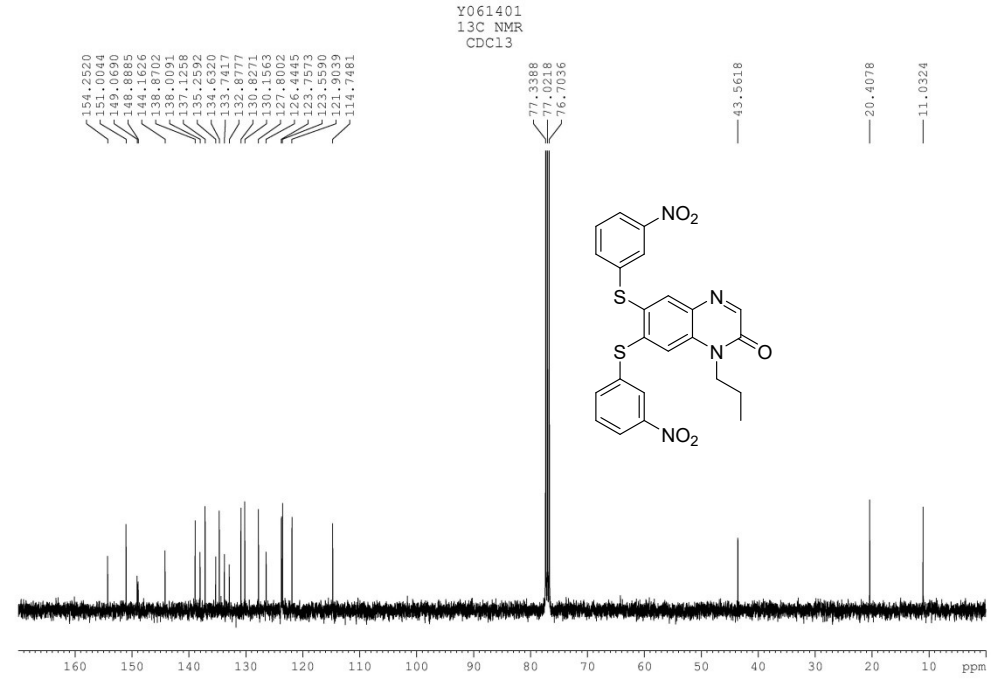


Fig. S80 ^{13}C NMR spectrum of compound **6d**

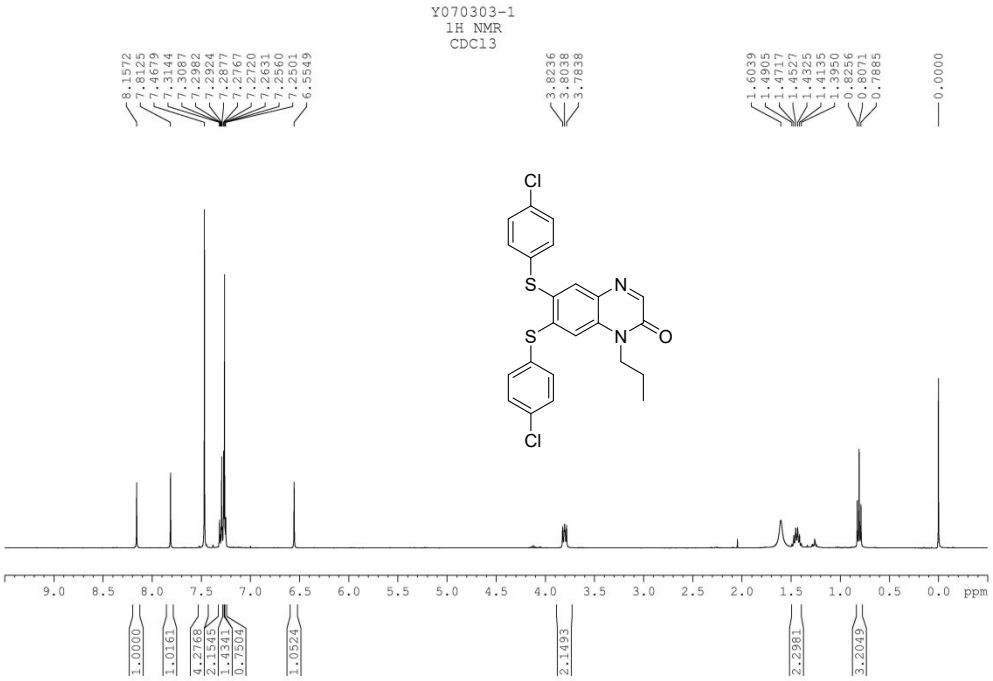


Fig. S81 ^{1}H NMR spectrum of compound **6e**

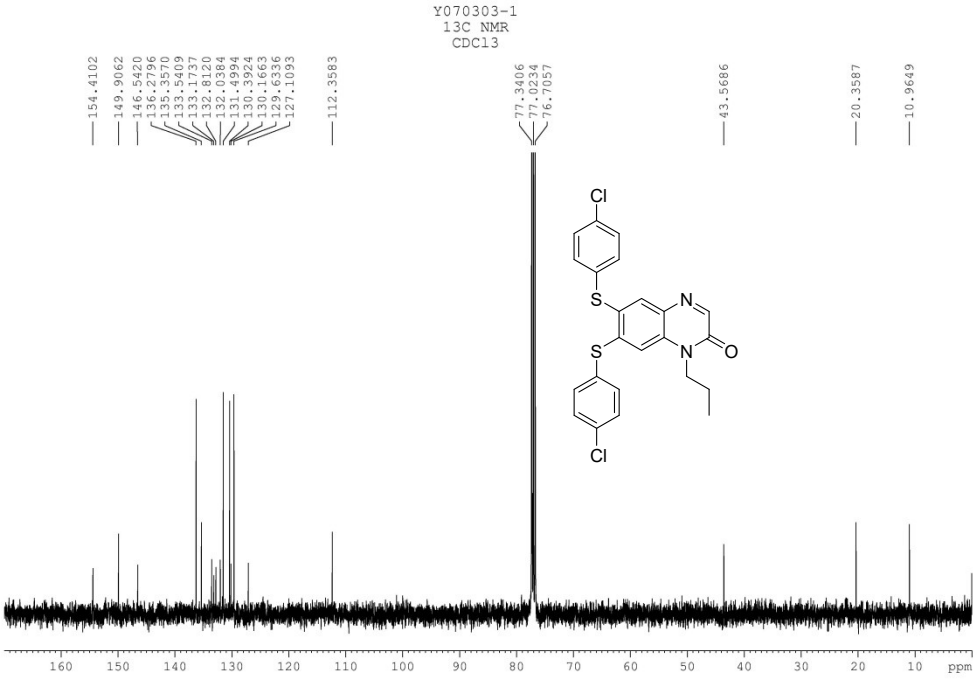


Fig. S82 ^{13}C NMR spectrum of compound **6e**

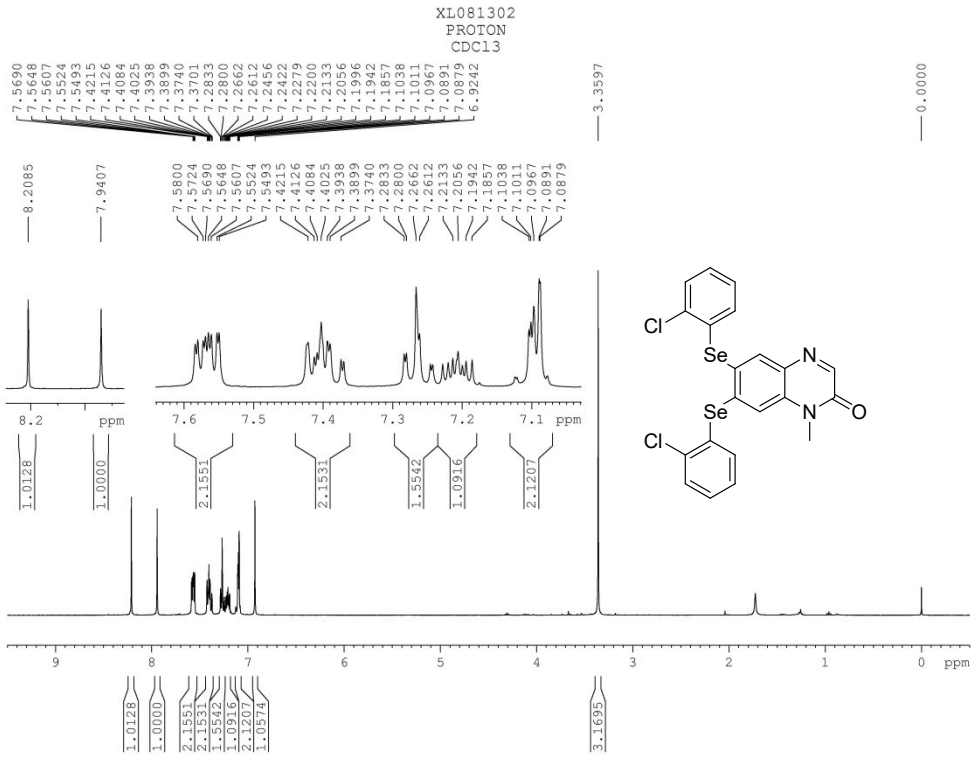


Fig. S83 ^{1}H NMR spectrum of compound **6f**

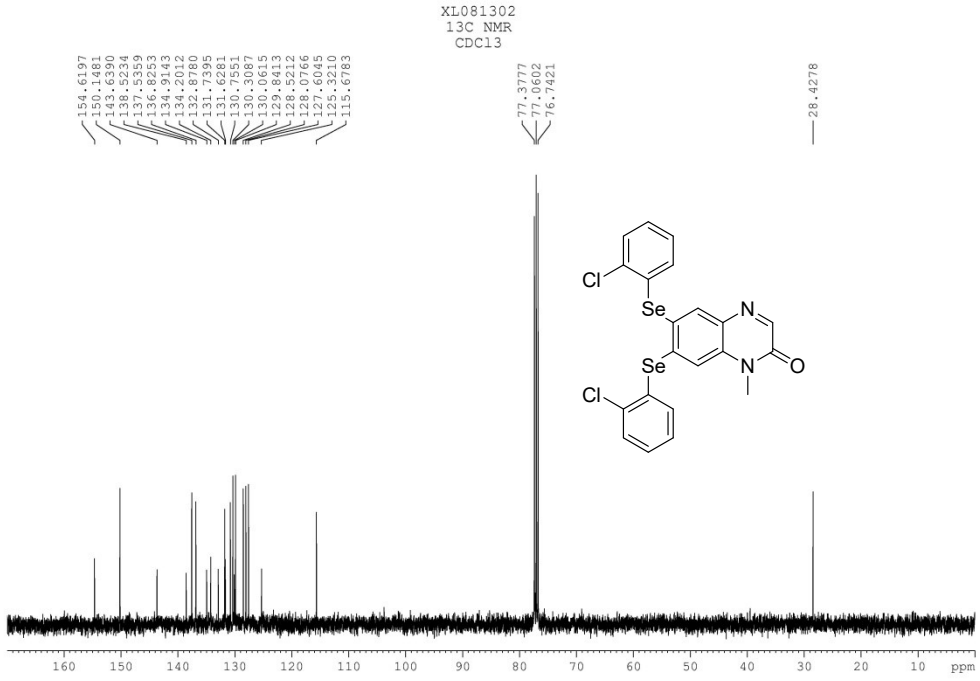


Fig. S84 ^{13}C NMR spectrum of compound **6f**

4 Crystal structure and crystal data for compound 3b

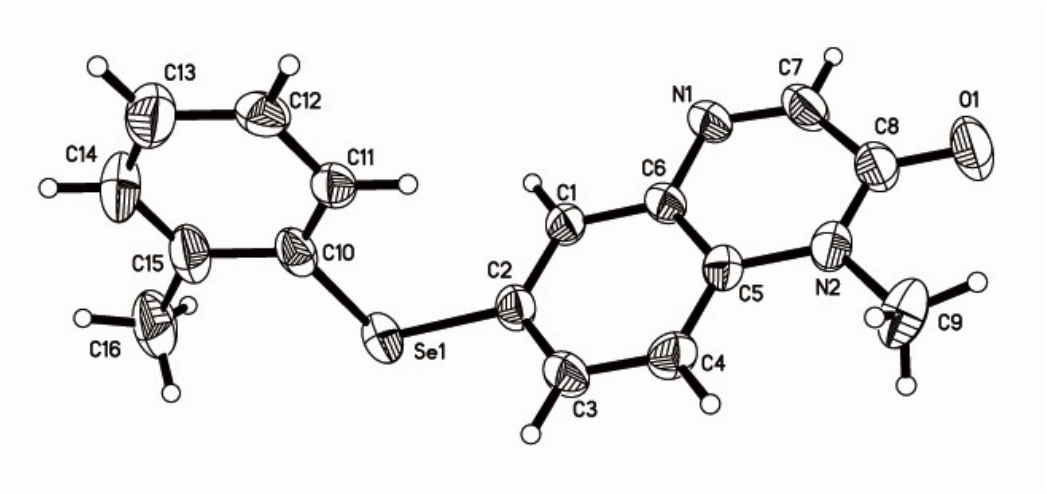


Fig. S85 Crystal structure of compound **3b**

Table S2 Crystal data and structure refinement for **3b**

Identification code	3b
Empirical formula	$C_{16}H_{14}N_2OSe$
Formula weight	329.25
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.7522(6)
b/Å	22.4728(12)
c/Å	8.7952(5)
α/°	90
β/°	111.858(8)
γ/°	90
Volume/Å^3	1422.11(17)
Z	4
ρ_{calc}g/cm^3	1.538
μ/mm^{-1}	3.543
F(000)	664.0
Crystal size/mm^3	0.246 × 0.149 × 0.082
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.534 to 134.138
Index ranges	-9 ≤ h ≤ 9, -26 ≤ k ≤ 17, -10 ≤ l ≤ 10
Reflections collected	5344
Independent reflections	2534 [R_{int} = 0.0389, R_{sigma} = 0.0533]
Data/restraints/parameters	2534/0/183
Goodness-of-fit on F^2	1.266
Final R indexes [I>=2σ (I)]	R_1 = 0.0825, wR_2 = 0.1935
Final R indexes [all data]	R_1 = 0.0967, wR_2 = 0.2008
Largest diff. peak/hole / e Å^{-3}	0.75/-0.43

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3b**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
Se1	-1986.0(13)	3679.7(4)	806.3(11)	74.1(4)
O1	5314(10)	5608(3)	8169(8)	101(2)
N1	3462(9)	4243(3)	6283(8)	65.2(17)
N2	3189(9)	5467(3)	5573(8)	59.7(15)
C1	1027(10)	4054(3)	3704(8)	56.6(17)
C2	-297(11)	4239(3)	2248(8)	57.3(17)
C3	-429(11)	4836(4)	1860(9)	66(2)
C4	722(12)	5250(3)	2941(9)	69(2)
C5	2032(11)	5064(3)	4435(8)	55.6(17)
C6	2189(10)	4458(3)	4794(8)	56.5(17)
C7	4423(11)	4630(4)	7322(10)	75(2)
C8	4366(11)	5273(4)	7080(10)	70(2)
C9	3140(16)	6105(4)	5237(14)	92(3)
C10	-522(12)	3373(3)	-340(8)	63(2)
C11	1251(11)	3564(3)	-55(9)	60.4(18)
C12	2311(10)	3333(4)	-928(10)	67(2)
C13	1513(17)	2883(5)	-2071(12)	97(3)
C14	-270(17)	2700(5)	-2341(12)	95(3)
C15	-1326(14)	2931(4)	-1515(10)	79(3)
C16	-3313(16)	2726(5)	-1857(13)	107(4)

Table S4 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se1	66.7(6)	79.5(6)	61.0(5)	-15.1(4)	6.3(4)	-10.8(5)
O1	86(5)	108(5)	89(4)	-41(4)	12(4)	-28(4)
N1	58(4)	68(4)	54(3)	3(3)	3(3)	6(3)
N2	62(4)	54(3)	67(4)	-14(3)	30(3)	-8(3)
C1	63(4)	44(4)	53(4)	-1(3)	11(3)	4(3)
C2	65(4)	55(4)	47(4)	-3(3)	15(3)	-2(3)
C3	71(5)	66(5)	44(4)	6(3)	3(3)	6(4)
C4	90(6)	45(4)	63(4)	12(3)	19(4)	12(4)
C5	60(4)	55(4)	50(4)	-8(3)	18(3)	0(3)
C6	58(4)	56(4)	44(3)	3(3)	5(3)	6(3)
C7	60(5)	86(6)	57(4)	0(4)	-2(4)	-2(4)
C8	58(5)	82(6)	66(5)	-18(4)	18(4)	-7(4)
C9	129(9)	55(5)	108(7)	-17(5)	63(7)	-16(5)
C10	76(5)	51(4)	42(3)	6(3)	0(3)	-5(4)
C11	66(5)	51(4)	53(4)	3(3)	9(3)	6(3)
C12	43(4)	83(6)	71(5)	3(4)	18(4)	3(4)
C13	119(9)	97(8)	72(6)	-15(5)	34(6)	7(7)
C14	119(9)	93(7)	77(6)	-41(5)	38(6)	-26(6)
C15	100(7)	64(5)	56(4)	-11(4)	10(4)	-16(5)
C16	119(9)	90(7)	90(7)	-32(6)	15(6)	-41(7)

Table S5 Bond Lengths for **3b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Se1	C2	1.915(7)	C3	C4	1.391(11)
Se1	C10	1.906(9)	C4	C5	1.392(10)
O1	C8	1.225(10)	C5	C6	1.394(10)
N1	C6	1.400(9)	C7	C8	1.458(12)
N1	C7	1.281(10)	C10	C11	1.372(11)
N2	C5	1.399(9)	C10	C15	1.401(10)
N2	C8	1.371(10)	C11	C12	1.416(11)
N2	C9	1.463(10)	C12	C13	1.398(13)
C1	C2	1.373(10)	C13	C14	1.376(15)
C1	C6	1.382(10)	C14	C15	1.382(14)
C2	C3	1.378(10)	C15	C16	1.526(14)

Table S6 Bond Angles for **3b**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C10	Se1	C2	101.1(3)	C5	C6	N1	121.4(7)
C7	N1	C6	116.9(7)	N1	C7	C8	126.3(7)
C5	N2	C9	121.9(7)	O1	C8	N2	123.4(9)
C8	N2	C5	120.3(7)	O1	C8	C7	121.2(9)
C8	N2	C9	117.7(7)	N2	C8	C7	115.4(7)
C2	C1	C6	121.1(7)	C11	C10	Se1	122.9(6)
C1	C2	Se1	120.6(5)	C11	C10	C15	119.8(9)
C1	C2	C3	119.0(7)	C15	C10	Se1	117.3(7)
C3	C2	Se1	120.4(6)	C10	C11	C12	122.0(7)
C2	C3	C4	120.8(7)	C13	C12	C11	117.7(8)
C3	C4	C5	120.1(7)	C14	C13	C12	119.2(10)
C4	C5	N2	122.0(7)	C13	C14	C15	123.4(9)
C4	C5	C6	118.6(7)	C10	C15	C16	119.9(9)
C6	C5	N2	119.5(7)	C14	C15	C10	117.8(9)
C1	C6	N1	118.2(7)	C14	C15	C16	122.3(8)
C1	C6	C5	120.3(6)				

Table S7 Torsion Angles for **3b**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Se1	C2	C3	C4	176.3(7)	C6	C1	C2	Se1	-176.5(6)
Se1	C10	C11	C12	-179.5(6)	C6	C1	C2	C3	1.6(13)
Se1	C10	C15	C14	-179.2(7)	C7	N1	C6	C1	-174.8(8)
Se1	C10	C15	C16	1.4(11)	C7	N1	C6	C5	2.6(12)
N1	C7	C8	O1	178.3(9)	C8	N2	C5	C4	175.2(8)
N1	C7	C8	N2	-1.4(14)	C8	N2	C5	C6	-5.1(11)
N2	C5	C6	N1	1.0(12)	C9	N2	C5	C4	-2.2(12)
N2	C5	C6	C1	178.4(7)	C9	N2	C5	C6	177.5(8)
C1	C2	C3	C4	-1.8(13)	C9	N2	C8	O1	3.0(13)
C2	C1	C6	N1	177.7(7)	C9	N2	C8	C7	-177.3(8)
C2	C1	C6	C5	0.2(13)	C10	C11	C12	C13	-2.0(12)
C2	C3	C4	C5	0.2(14)	C11	C10	C15	C14	0.7(13)
C3	C4	C5	N2	-178.6(8)	C11	C10	C15	C16	-178.7(8)
C3	C4	C5	C6	1.6(13)	C11	C12	C13	C14	2.3(15)
C4	C5	C6	N1	-179.2(8)	C12	C13	C14	C15	-1.1(18)
C4	C5	C6	C1	-1.8(12)	C13	C14	C15	C10	-0.4(17)
C5	N2	C8	O1	-174.6(8)	C13	C14	C15	C16	179.0(11)
C5	N2	C8	C7	5.2(11)	C15	C10	C11	C12	0.6(11)
C6	N1	C7	C8	-2.4(14)					

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3b**.

Atom	*x*	*y*	*z*	U(eq)
H1	1144	3651	3960	68
H3	-1298	4963	863	79
H4	617	5651	2666	82
H7	5234	4488	8327	90
H9A	1946	6262	5124	137
H9B	3349	6171	4241	137
H9C	4091	6302	6126	137
H11	1773	3855	736	73
H12	3497	3476	-748	80
H13	2179	2710	-2643	116
H14	-791	2405	-3119	115
H16A	-3382	2555	-883	160
H16B	-3667	2435	-2716	160
H16C	-4138	3061	-2189	160

5. ^{1}H NMR spectra of Selectfluor, PhSeSePh, PhSeSePh + Selectfluor, etc

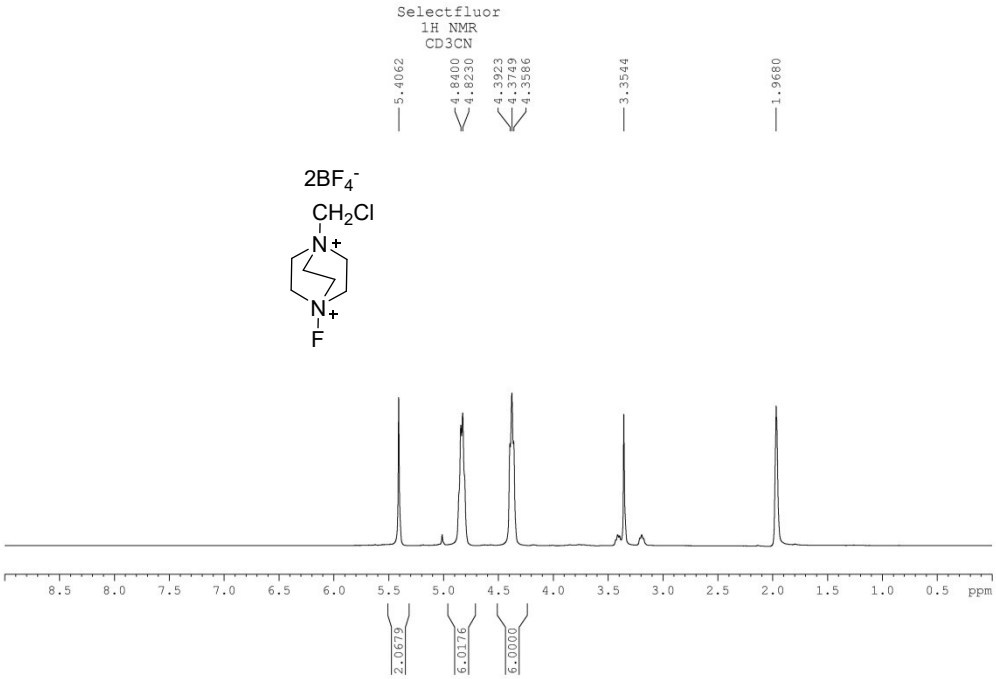


Fig. S86 ^{1}H NMR spectrum of Selectfluor

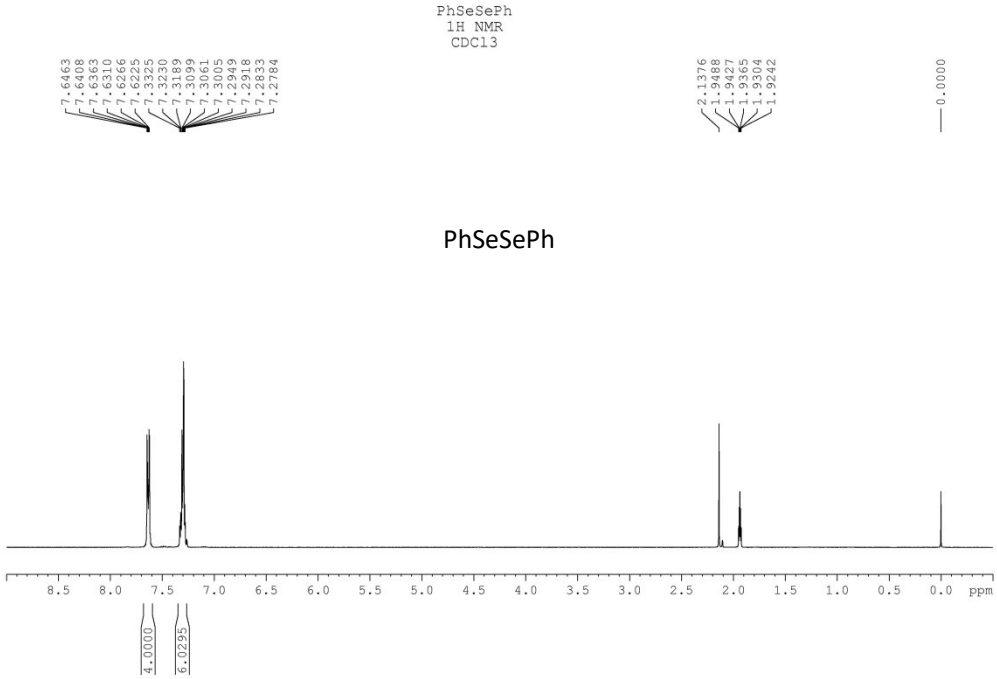


Fig. S87 ^{1}H NMR spectrum of PhSeSePh

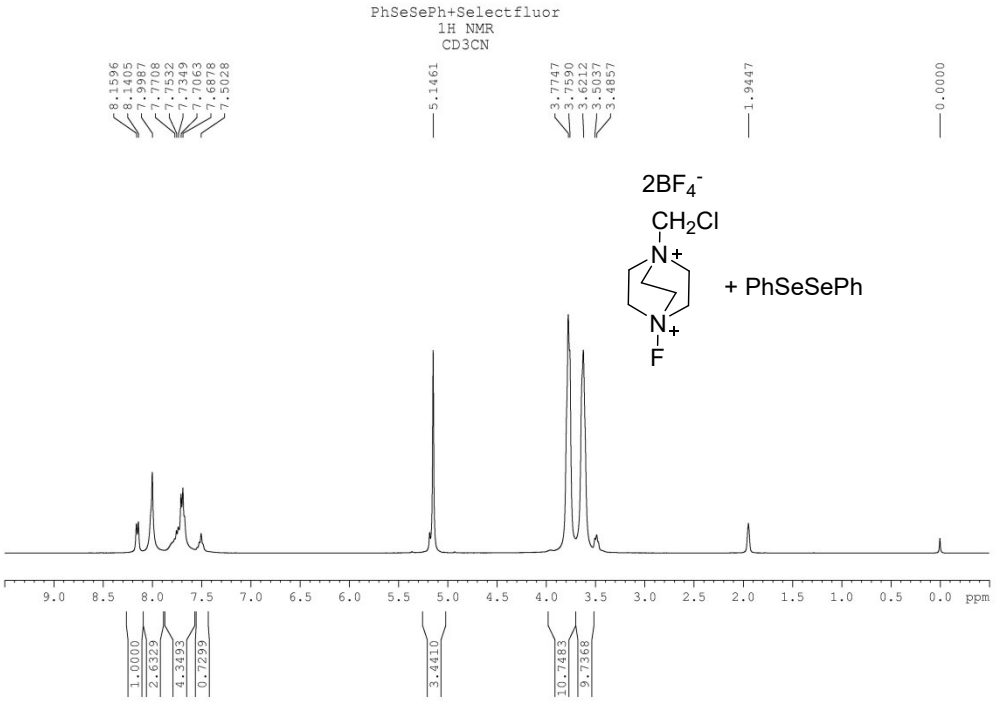


Fig. S88 ^{1}H NMR spectrum of Selectfluor + PhSeSePh

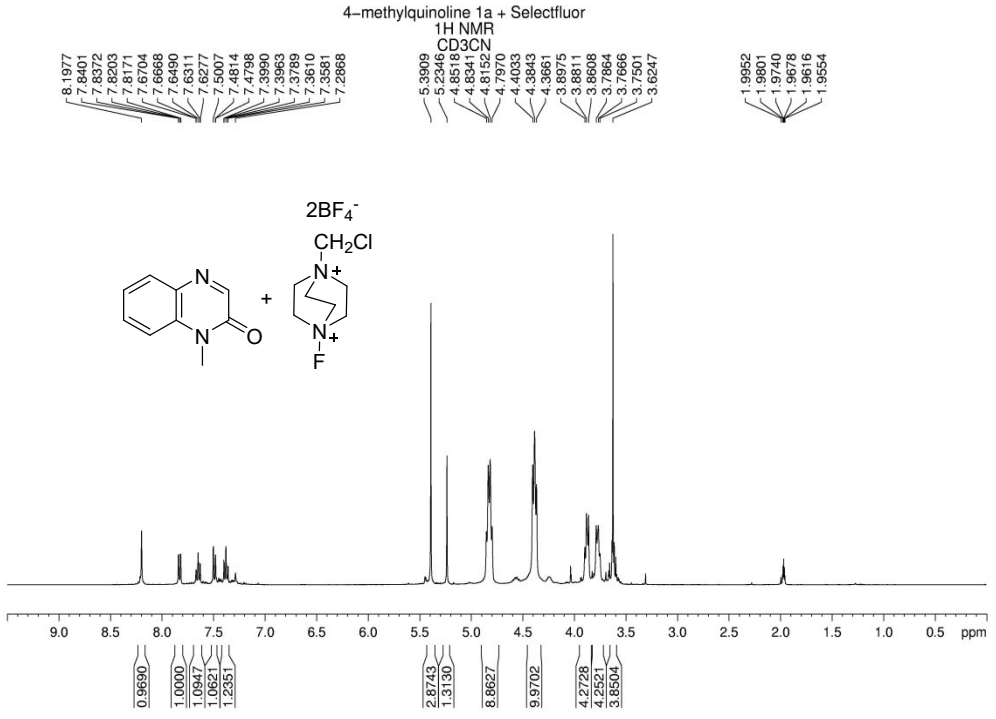


Fig. S89 ^{1}H NMR spectrum of 4-methylquinoline **1a** + Selectfluor