Supporting Information

Palladium(II) N,N,O-Pincer Type Complexes Mediated Dehydrogenative Coupling of Alcohols to Quinazolines

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1. X-ray Crystallography

A single crystal with high quality and exhibiting good morphology was chosen for X-ray diffraction intensity measurements. The X-ray diffraction intensity data was collected at room temperature (293 K) on a Bruker D8 Quest Eco diffractometer using MoKα radiation (0.71073 A˚). During the data collection, the crystal to detector distance was set to 4.5 cm. The data collection was monitored by APEX-III program suit.[1] further, the integration, Lorentz and polarization corrections and merging of data were carried out using SAINT.The absorption correction was performed by SADABS[1] and the data was averaged using SORTAV software.[2] The hydrogen atoms of all C−H, N−H and O−H hydrogen bonds were located from the difference Fourier map and were refined isotropically. Idealized methyl group H-atom position was calculated geometrically [C−H = 0.96 A]˚ and refined using riding model with Uiso(H) = 1.5 Ueq(C). The structure was solved by direct methods using SHELXS-2014 [3] and refined by SHELXL-2014 [4] programs incorporated to WINGX package.[5]The ORTEP of the molecule with displacement ellipsoids drawn at 50% probability level are shown in (Fig. 1). The molecular and packing diagrams were generated using the software MERCURY.[6]The CCDC numbers for the complexes **1** and **2** are 1940737 and 1939404 respectively.

2. NMR spectra for complexes

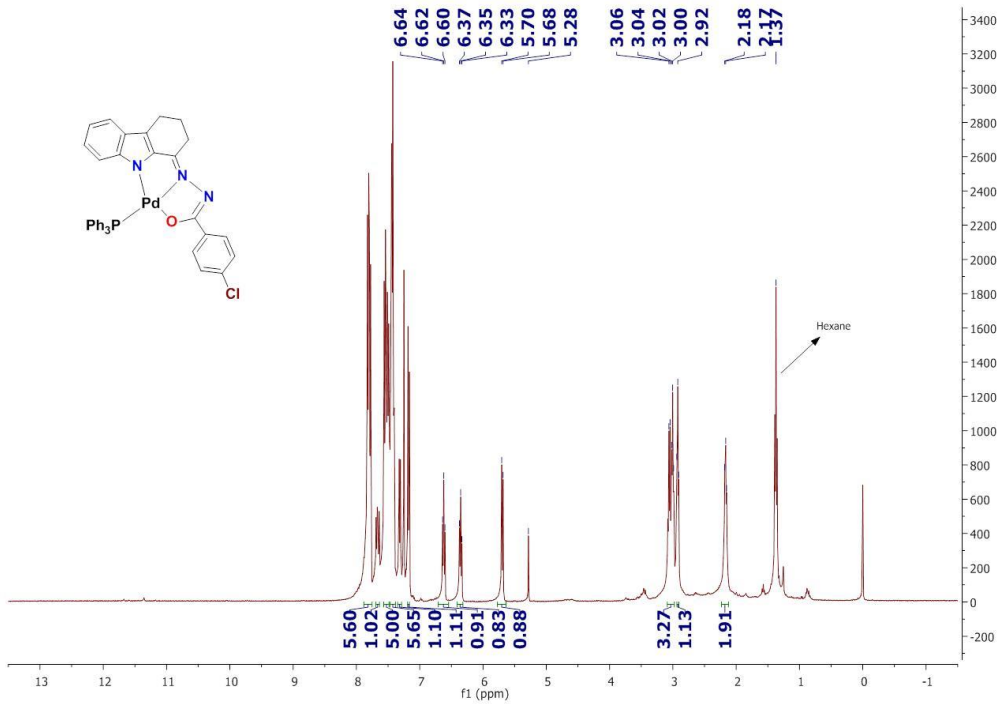


Figure S1.[1]H NMR spectrum of complex **1** in $CDCl_3$ (400 MHz, 300 K).

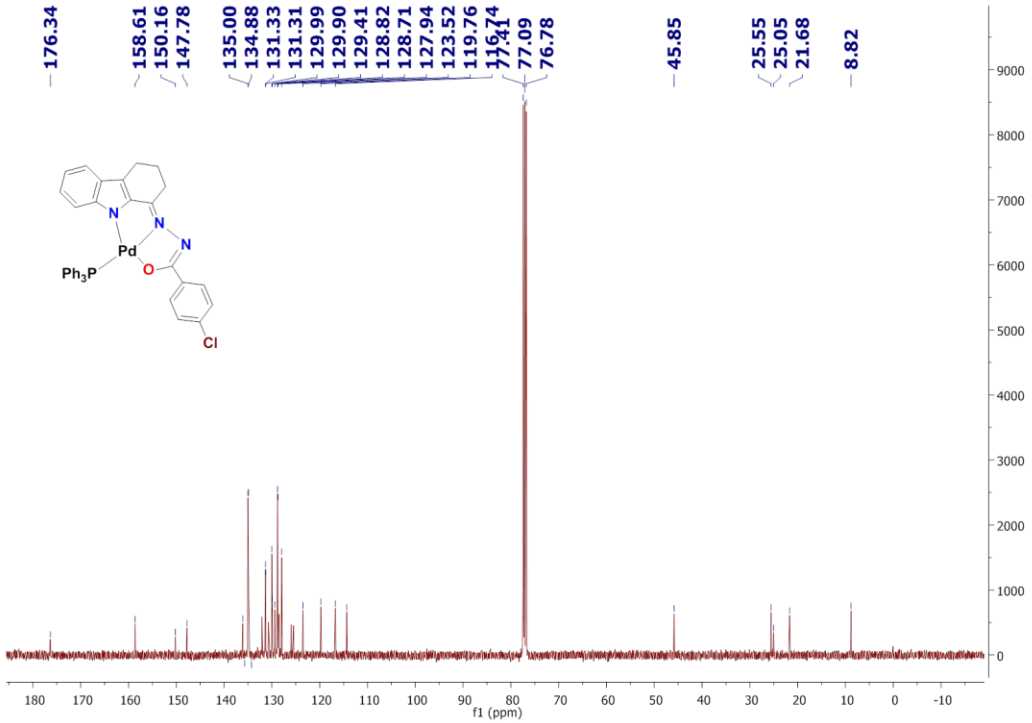


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** in $CDCl_3$ (100 MHz, 300 K).

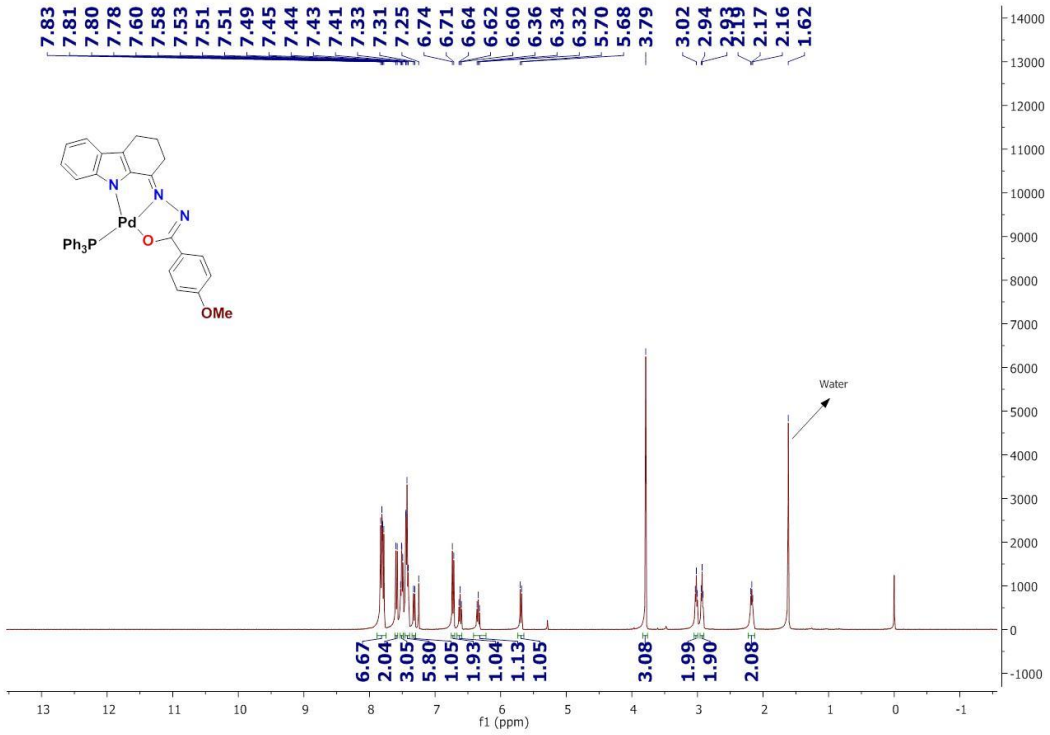


Figure S3. ^{1}H NMR spectrum of complex **2** in $CDCl_3$ (400 MHz, 300 K).

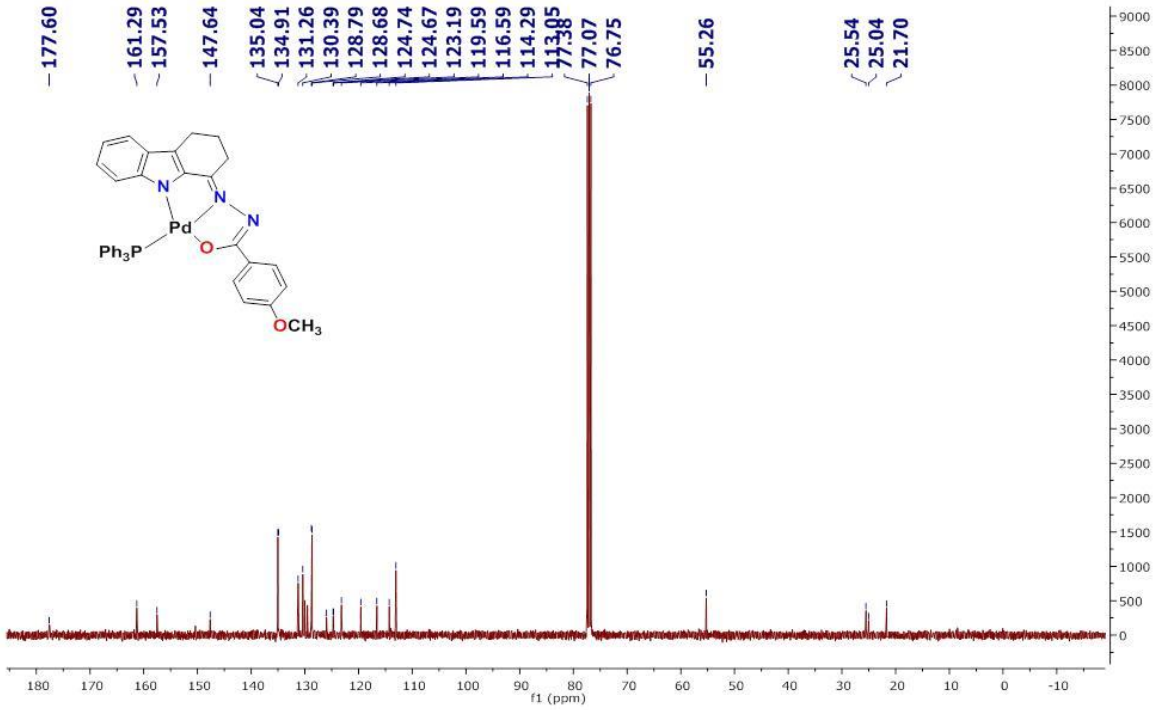


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** in $CDCl_3$ (100 MHz, 300 K).

3. Mass spectraof complexes

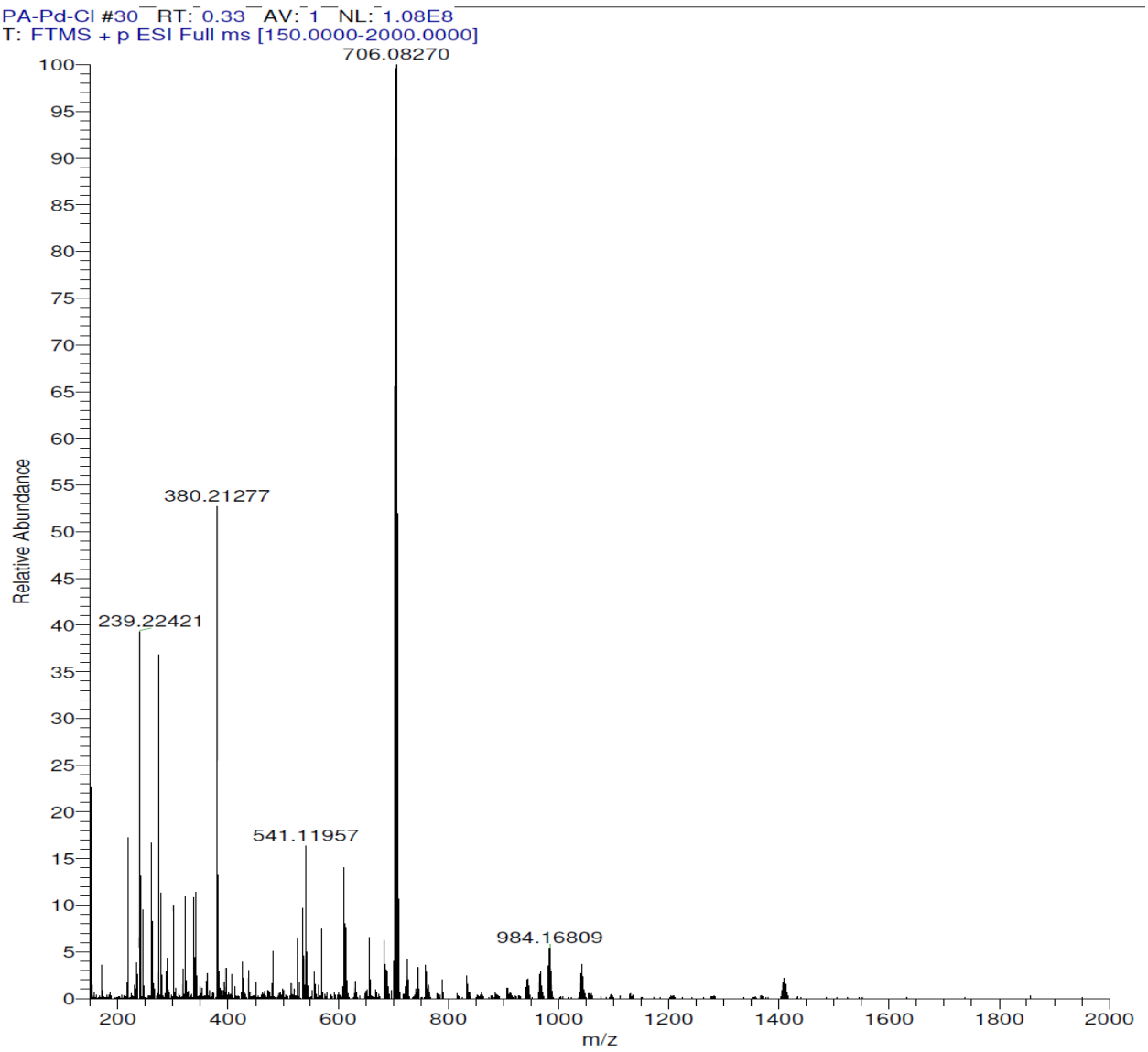


Figure S5. HRMS spectrum of complex **1**

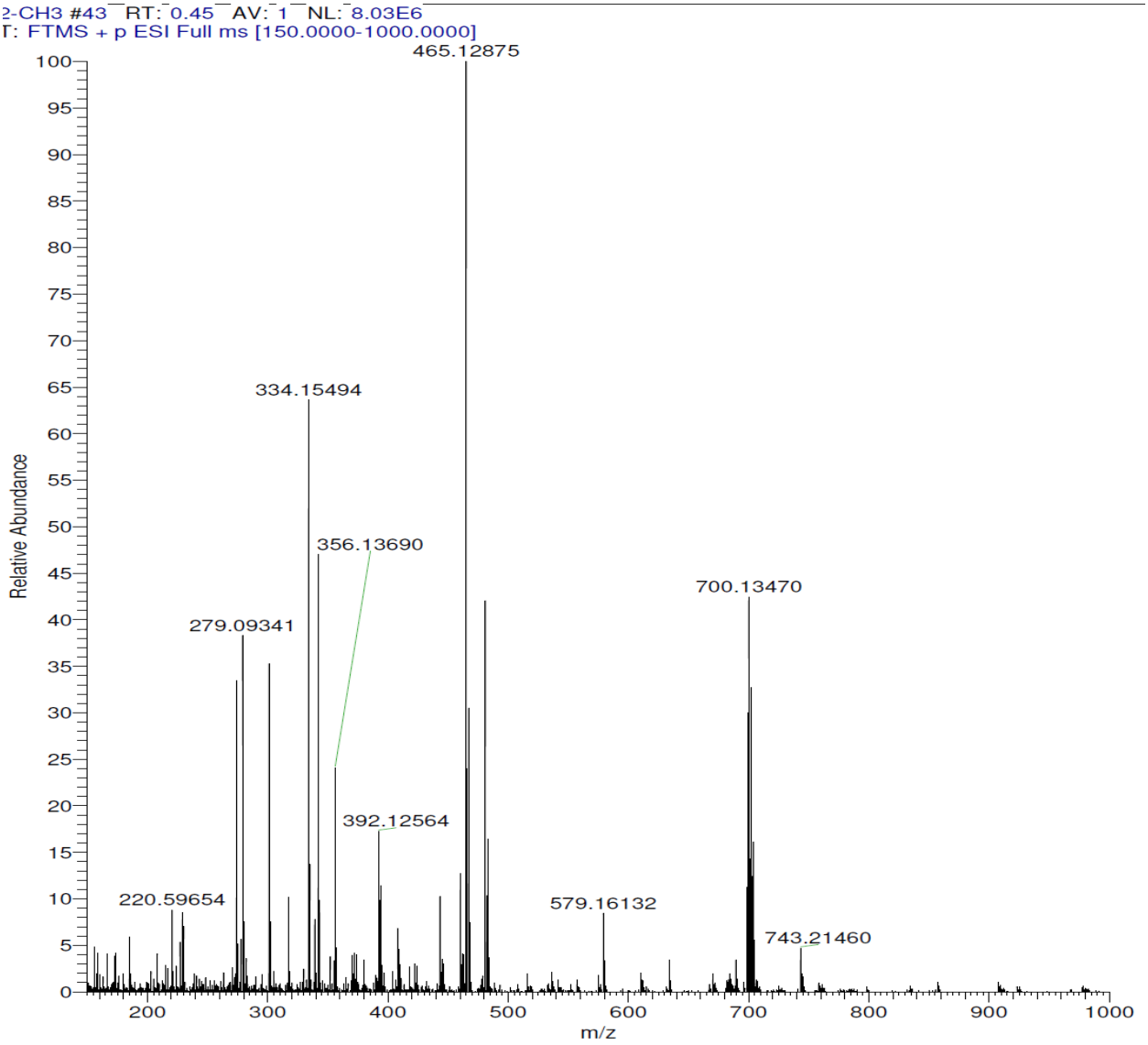


Figure S6. HRMS spectrum of complex **2**

4. Crystal data, and refinement parameters

Identification code	Complex **1**	Complex **2**
Empirical formula	$C_{38}H_{31}Cl_3N_3OPPd$	$C_{38}H_{32}N_3O_2PPd$
Formula weight	789.38	700.04
Temperature/K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	P21/c
a/Å	11.6578(4)	11.3299(3)
b/Å	12.3412(5)	7.9601(2)
c/Å	13.2461(5)	35.2801(8)
α/°	112.1310(10)	90
β/°	97.3090(10)	98.1770(10)
γ/°	99.9970(10)	90
Volume/$Å^3$	1699.33(11)	3149.46(14)
Z	2	4
$\rho_{calc}g/cm^3$	1.543	1.476
μ/mm^{-1}	0.865	0.68
F(000)	800.0	1432.0
Crystal size/mm^3	0.293 × 0.287 × 0.22	0.431 × 0.387 × 0.242
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.752 to 56.526	5.62 to 56.56
Index ranges	$-15 \le h \le 11$, $-16 \le k \le 16$, $-17 \le l \le 12$	$-15 \le h \le 14$, $-10 \le k \le 7$, $-45 \le l \le 46$
Reflections collected	8358	27474
Independent reflections	8358 [Rint = 0.0095, Rsigma = 0.0438]	7687 [Rint = 0.0194, Rsigma = 0.0189]
Data/restraints/ parameters	8358/0/540	7687/0/523
Goodness-of-fit on F^2	0.983	1.230
Final R indexes [I>=2σ (I)]	R1 = 0.0295, wR2 = 0.0754	R1 = 0.0357, wR2 = 0.0727
Final R indexes [all data]	R1 = 0.0349, wR2 = 0.0779	R1 = 0.0394, wR2 = 0.0740
Largest diff. peak/hole / e $Å^{-3}$	0.63/-0.48	0.34/-0.74

Table S2Selected bond distances and bond angles

	Complex 1	**Complex 2**
Bond distances (Å)		
Pd(1)-P	2.2924(4)	2.2824(6)
Pd (1)-O(1)	2.032(2)	2.017(1)
Pd (1)-N(1)	2.048(2)	2.038(2)
Pd (1)-N(2)	1.991(1)	1.986(2)
Bond angles (°)		
O(1)- Pd(1)-P	97.07(4)	94.33(5)
O(1)- Pd(1)-N(1)	159.26(7)	159.71(7)
N(1)- Pd(1)-P	103.67(5)	105.92(5)
N(2)- Pd(1)-P	174.60(5)	171.63(5)
N(2)- Pd(1)-O(1)	77.67(6)	77.86(7)
N(2)- Pd(1)-N(1)	81.61(7)	81.98(7)

5.NMR spectra of quinazoline products

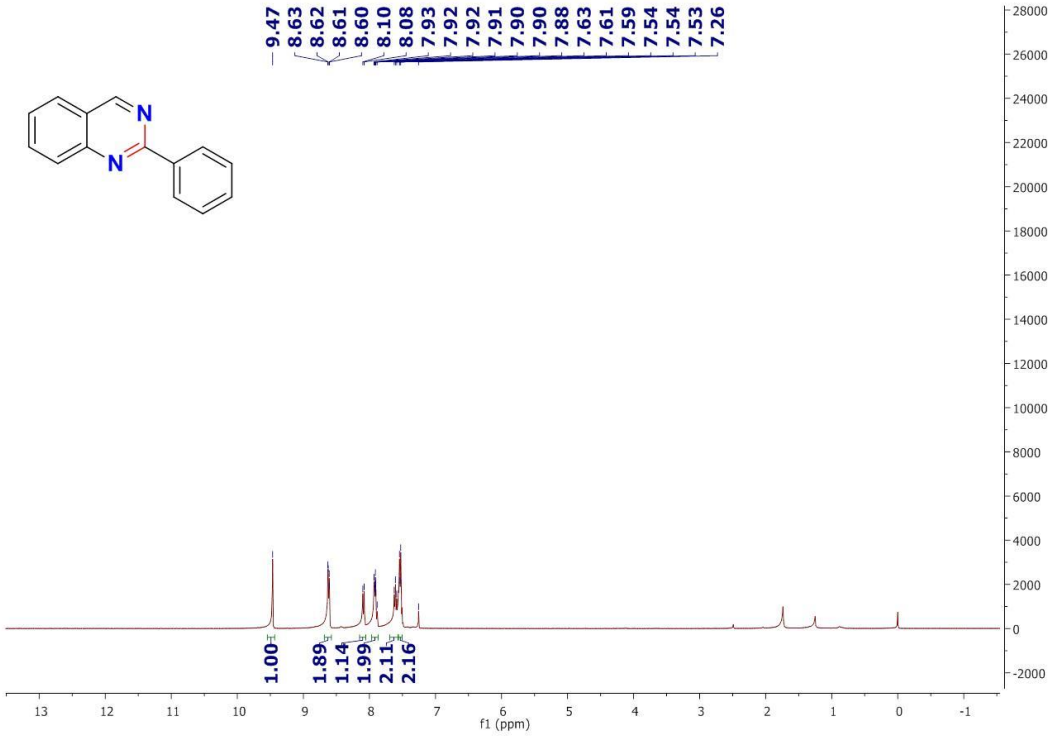


Figure S7.[1]H NMR spectrum of **3a** in $CDCl_3$(400 MHz, 300 K).

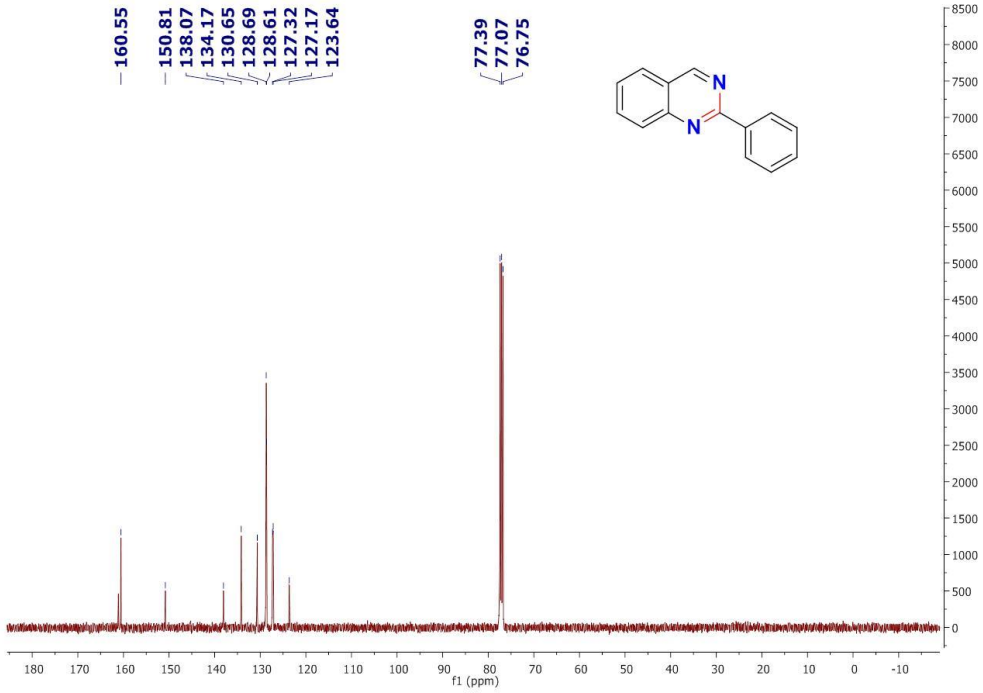


Figure S8.[13]C{[1]H} NMR spectrum of **3a** in $CDCl_3$(100 MHz, 300 K).

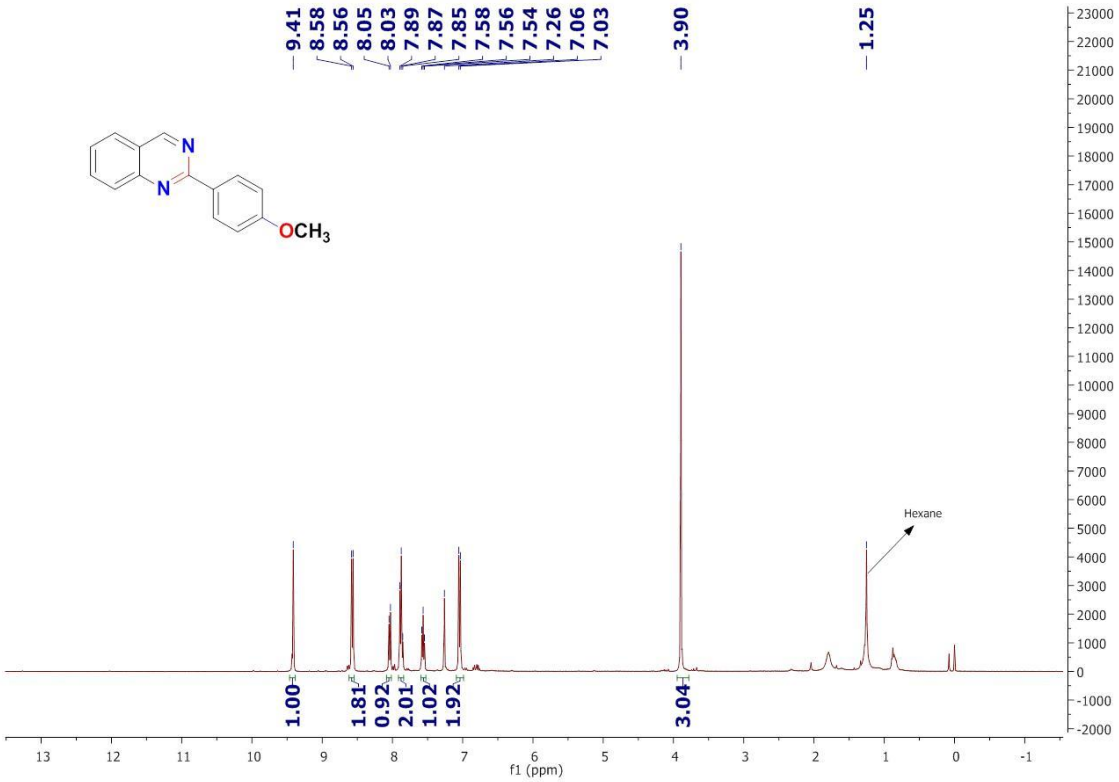


Figure S9.^{1}H NMR spectrum of **3b** in $CDCl_3$(400 MHz, 300 K).

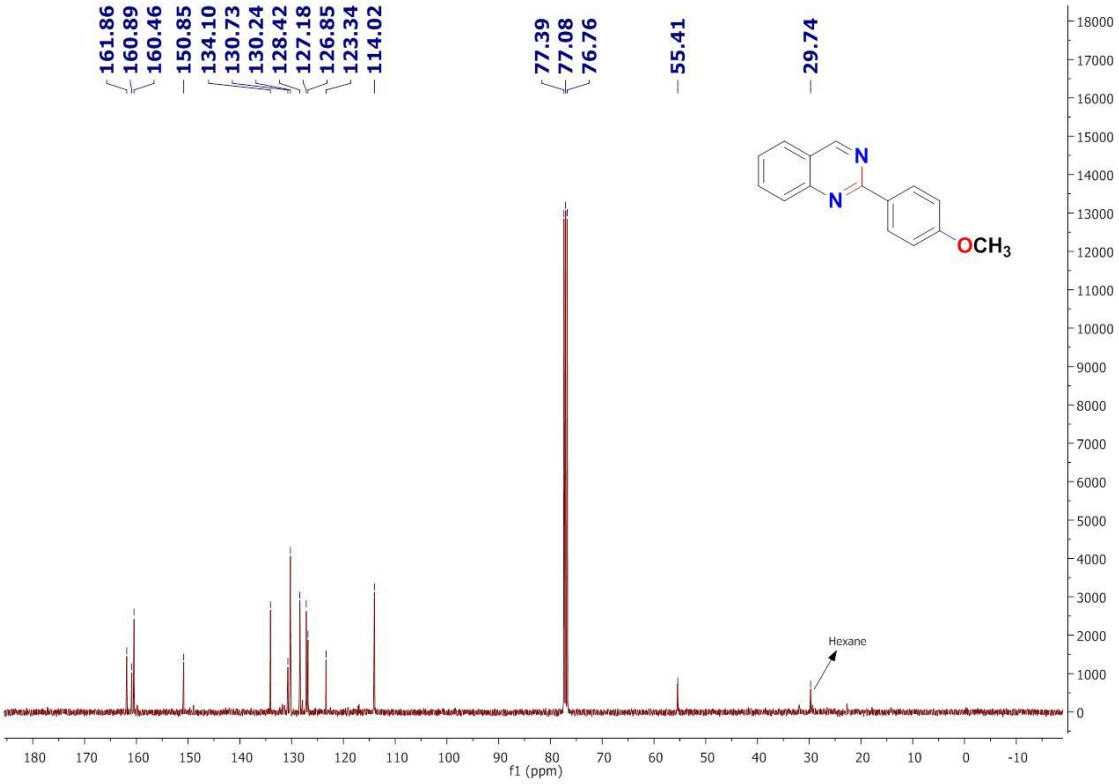


Figure S10.$^{13}C\{^{1}H\}$ NMR spectrum of**3b**in $CDCl_3$(100 MHz, 300 K).

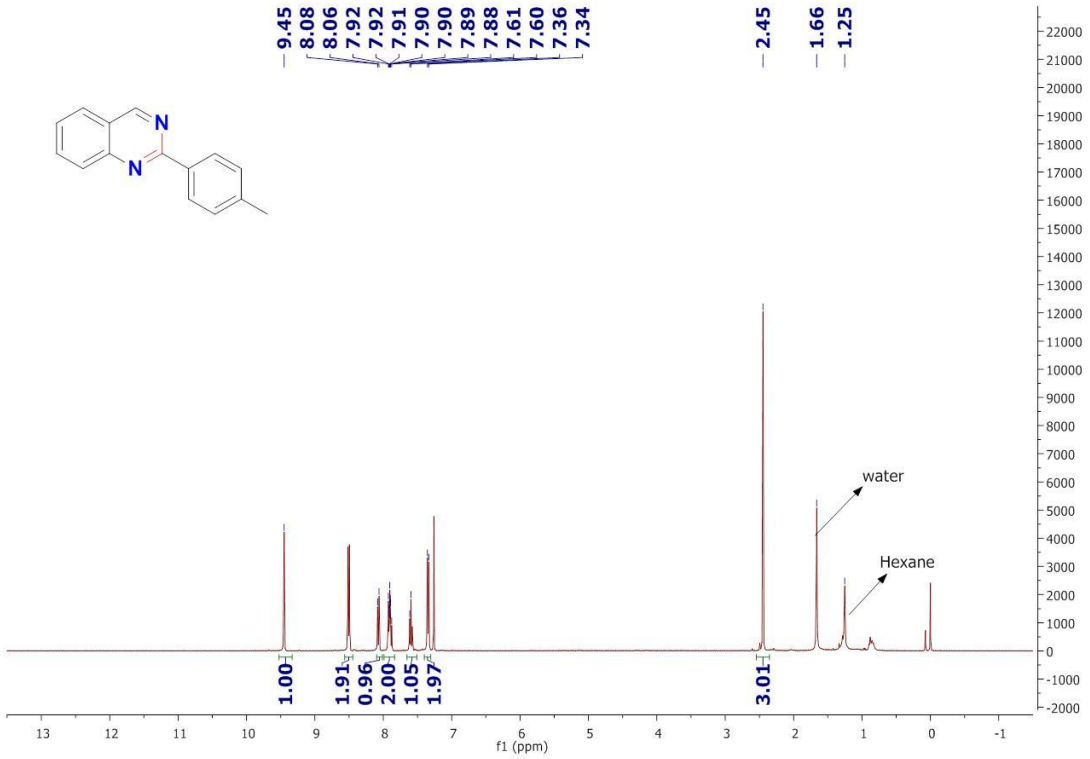


Figure S11. ^{1}H NMR spectrum of **3c** in $CDCl_3$(400 MHz, 300 K).

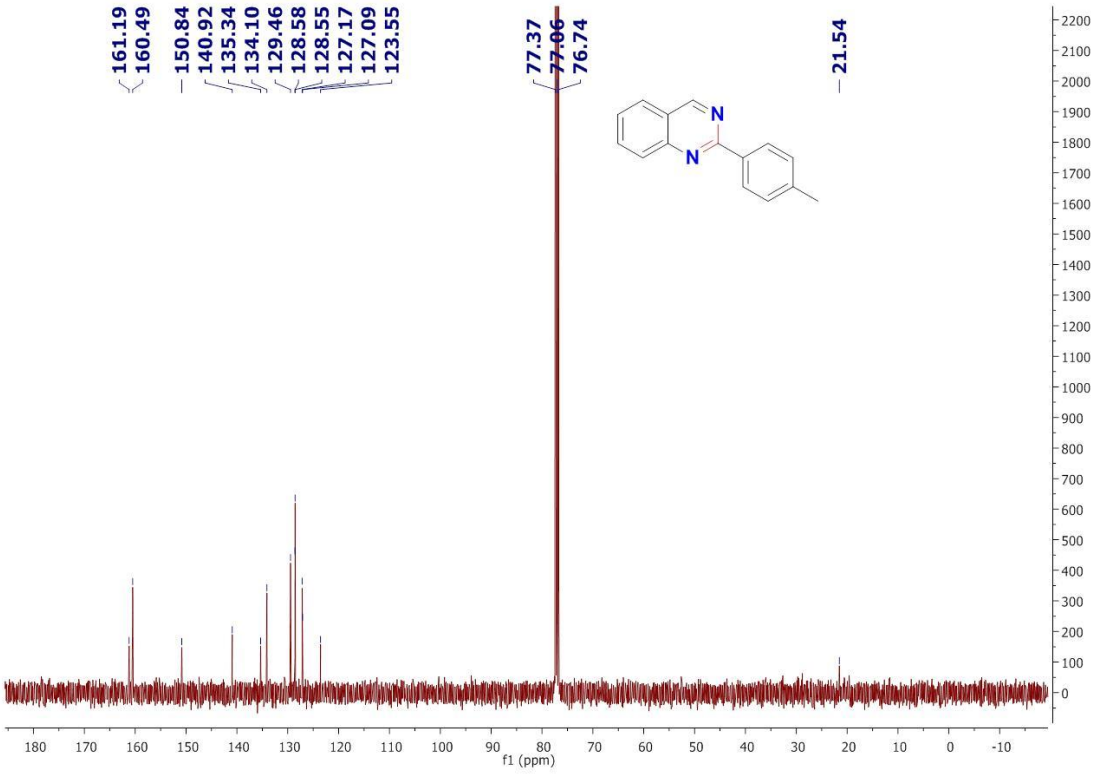


Figure S12.$^{13}C\{^{1}H\}$ NMR spectrum of**3c** in $CDCl_3$(100 MHz, 300 K)

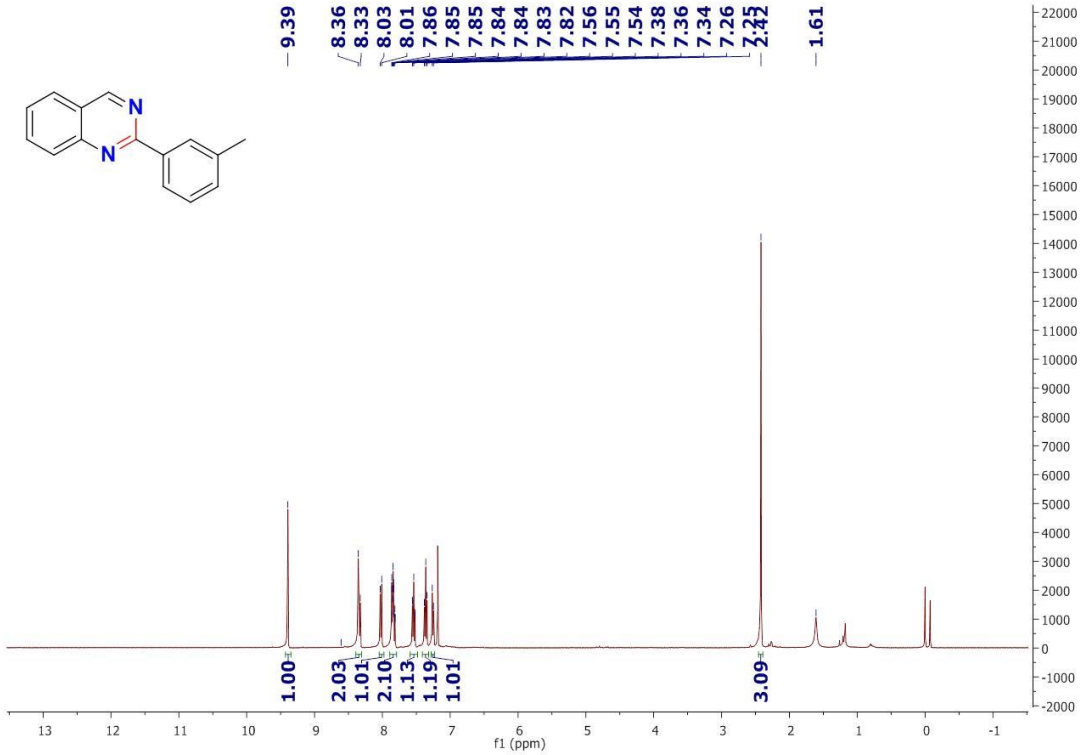


Figure S13. ^{1}H NMR spectrum of **3d** in $CDCl_3$(400 MHz, 300 K)

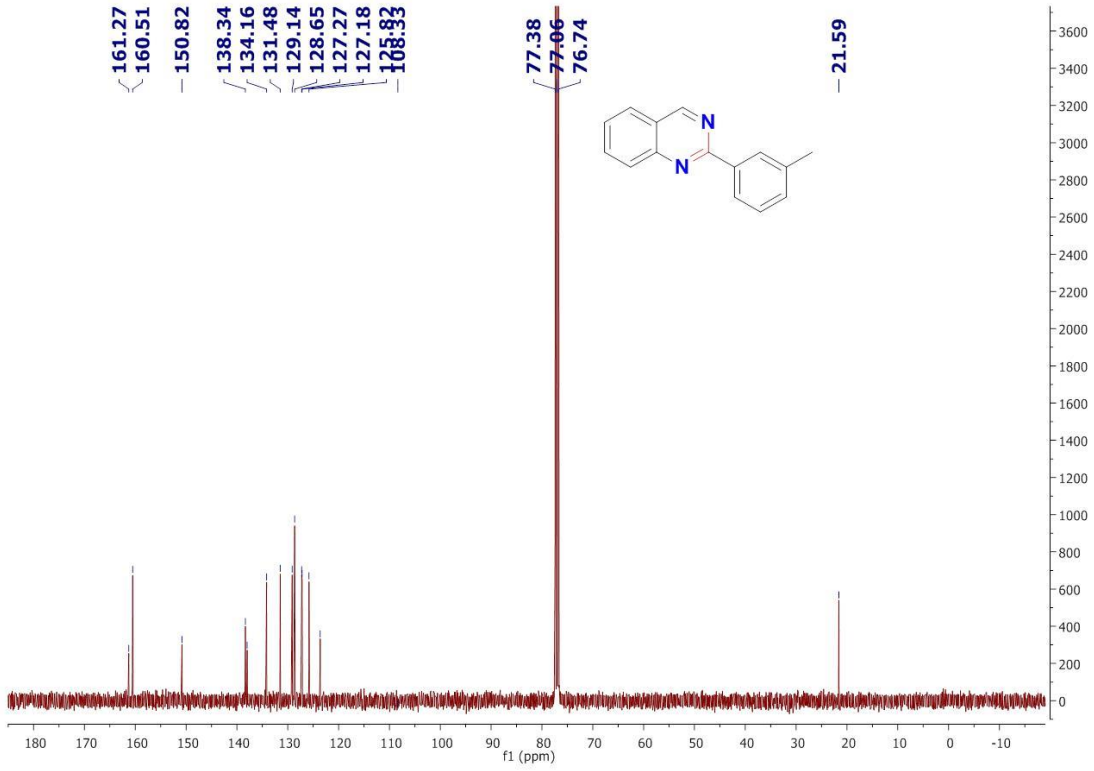


Figure S14.$^{13}C\{^{1}H\}$ NMR spectrum of**3d** in $CDCl_3$(100 MHz, 300 K).

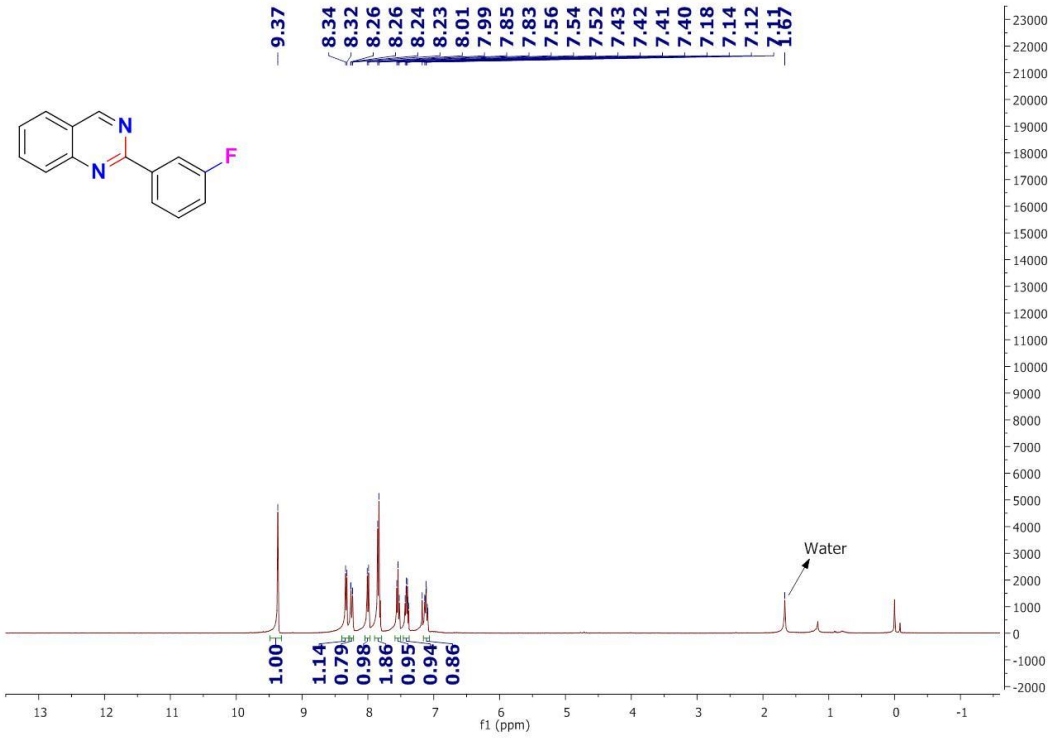


Figure S15. ^{1}H NMR spectrum of **3e** in $CDCl_3$(400 MHz, 300 K).

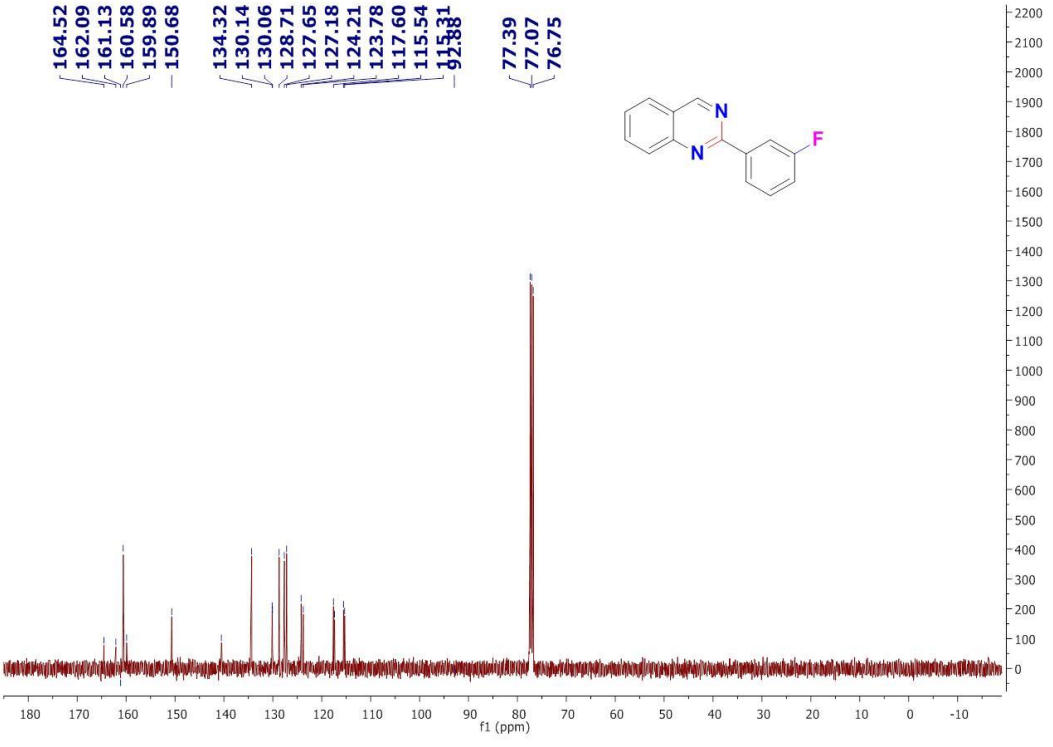


Figure S16.$^{13}C\{^{1}H\}$ NMR spectrum of**3e**in $CDCl_3$(100 MHz, 300 K).

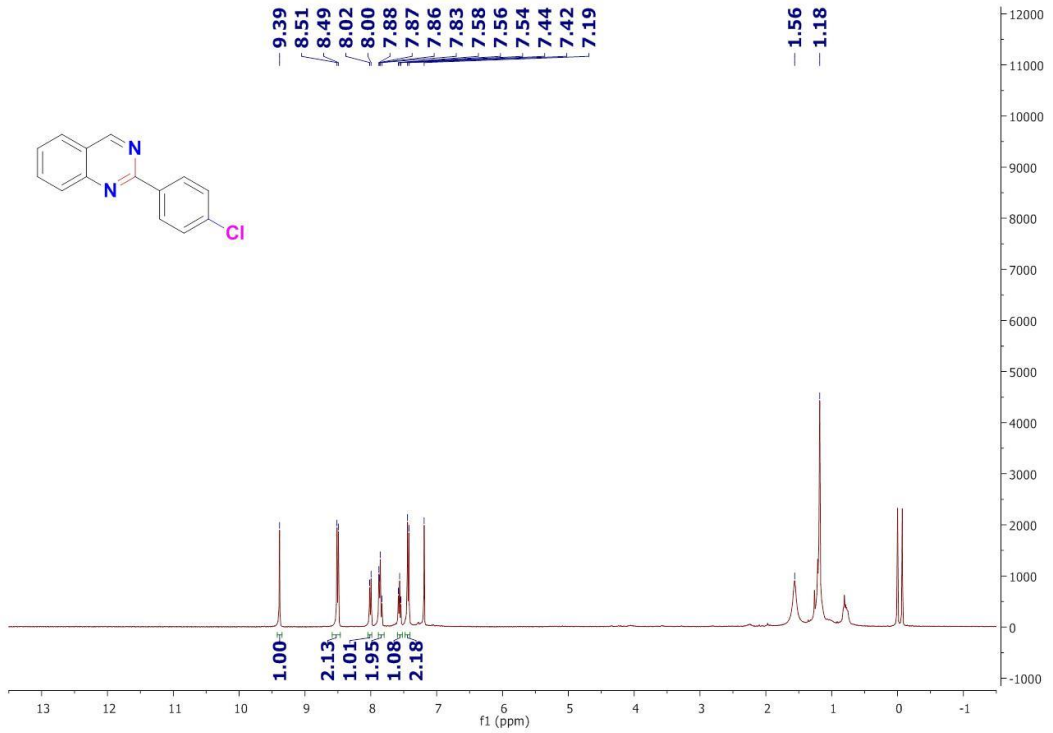


Figure S17. ^{1}H NMR spectrum of **3f** in $CDCl_3$(400 MHz, 300 K).

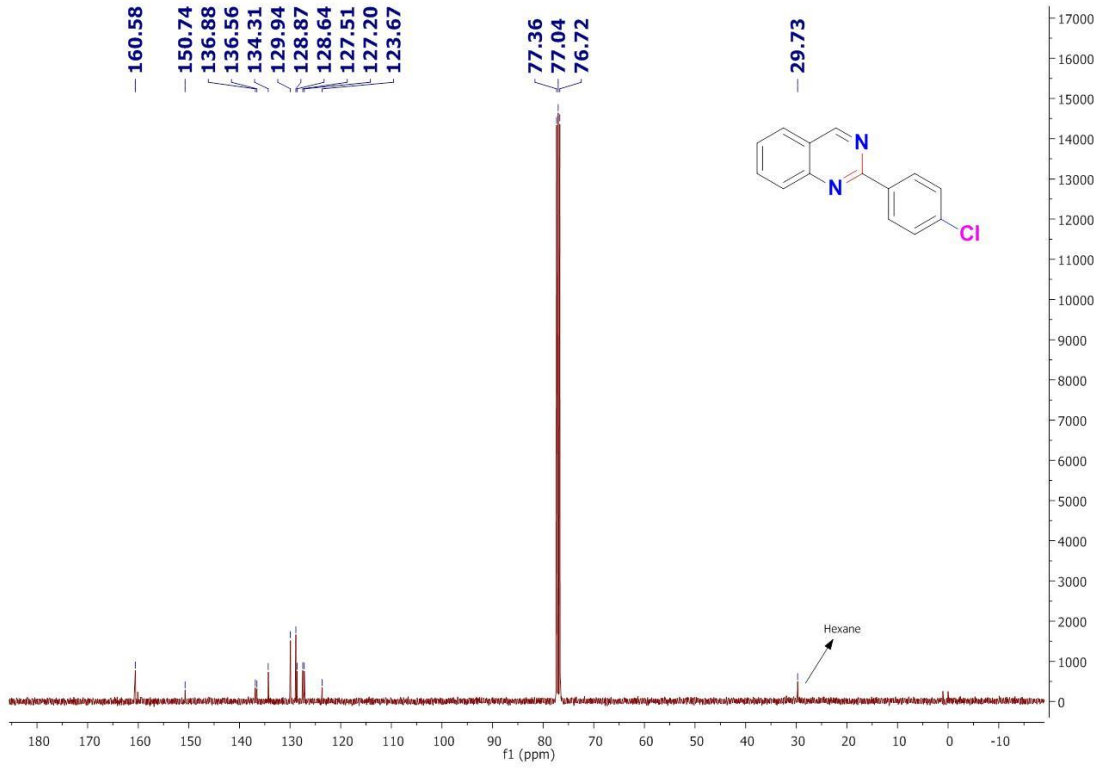


Figure S18.^{13}C{^{1}H} NMR spectrum of**3f**in $CDCl_3$(100 MHz, 300 K).

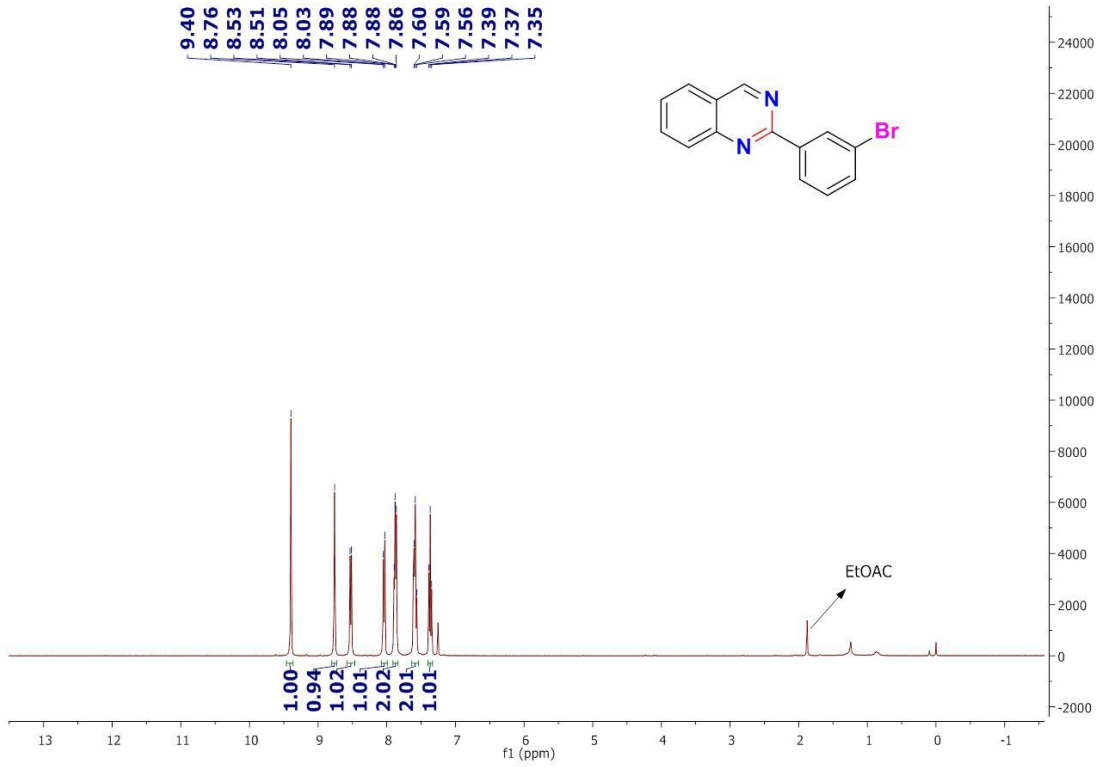


Figure S19. ^{1}H NMR spectrum of **3g** in $CDCl_3$(400 MHz, 300 K).

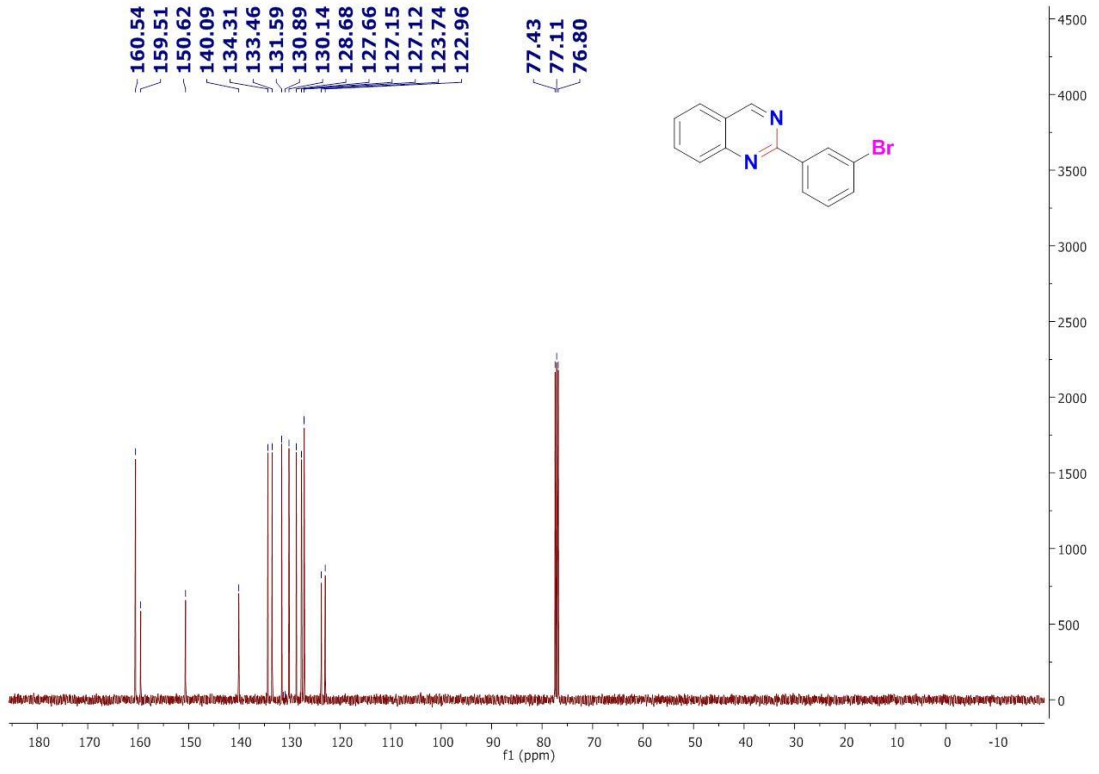


Figure S20.^{13}C{^{1}H} NMR spectrum of**3g**in $CDCl_3$(100 MHz, 300 K).

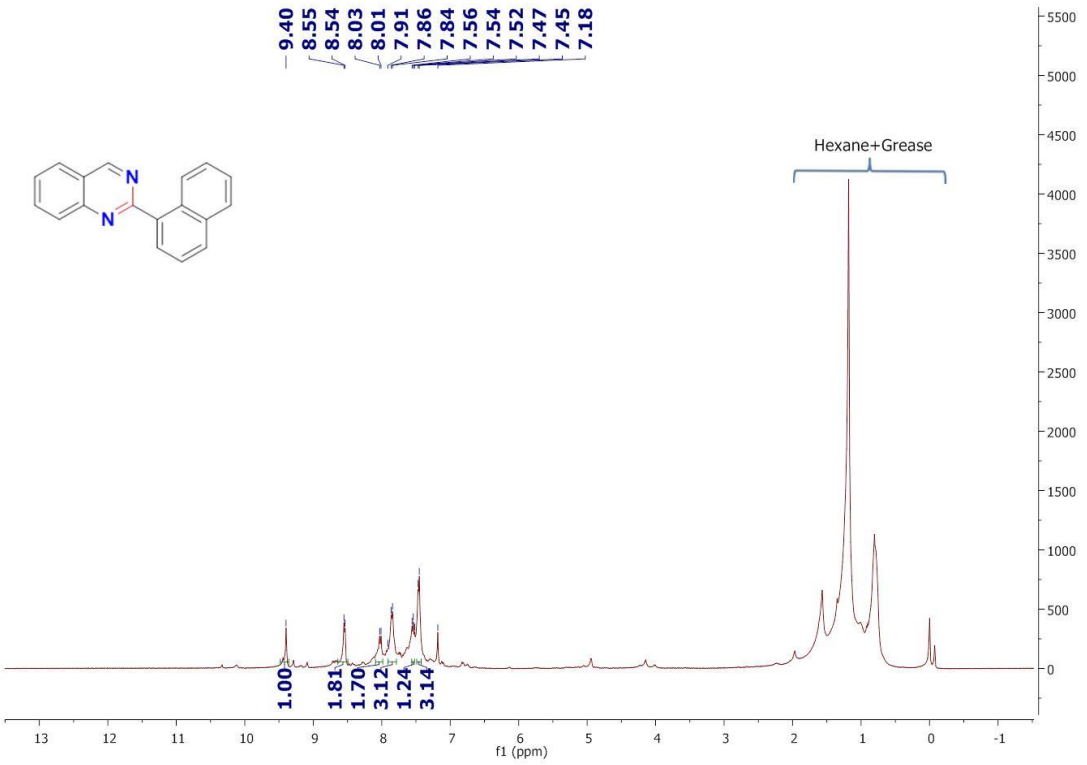


Figure S21. ^{1}H NMR spectrum of **3h** in $CDCl_3$(400 MHz, 300 K).

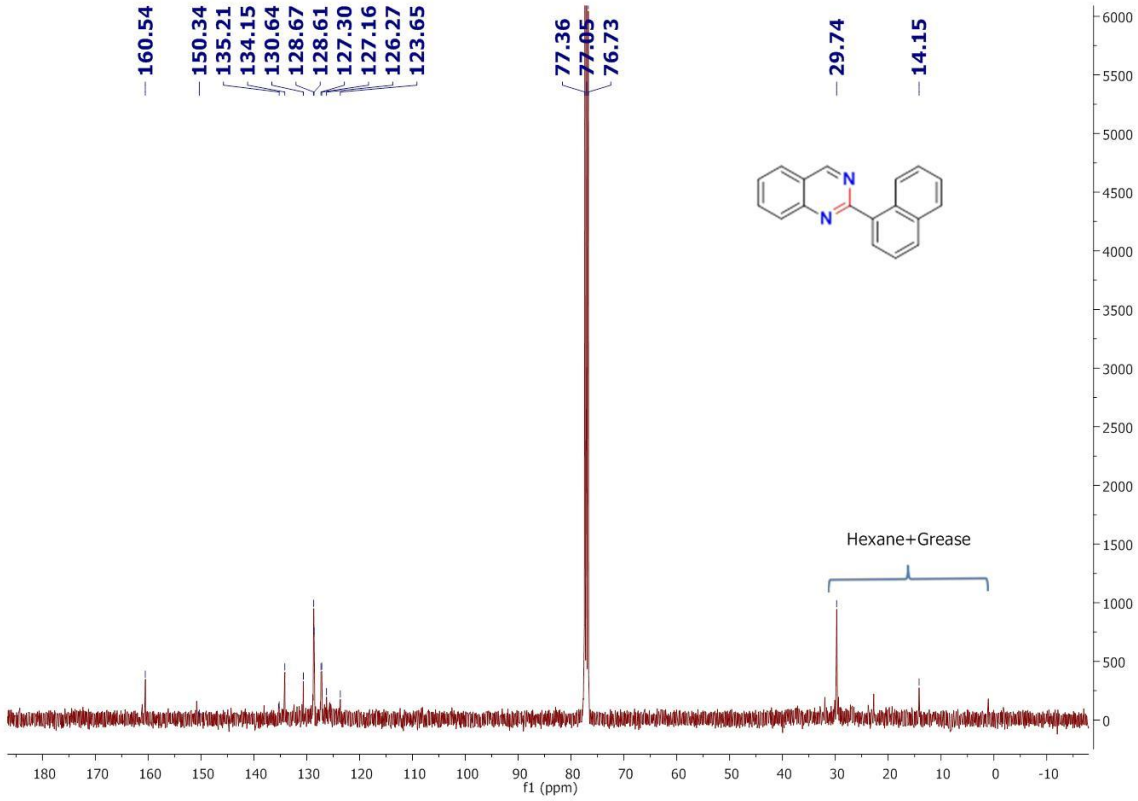
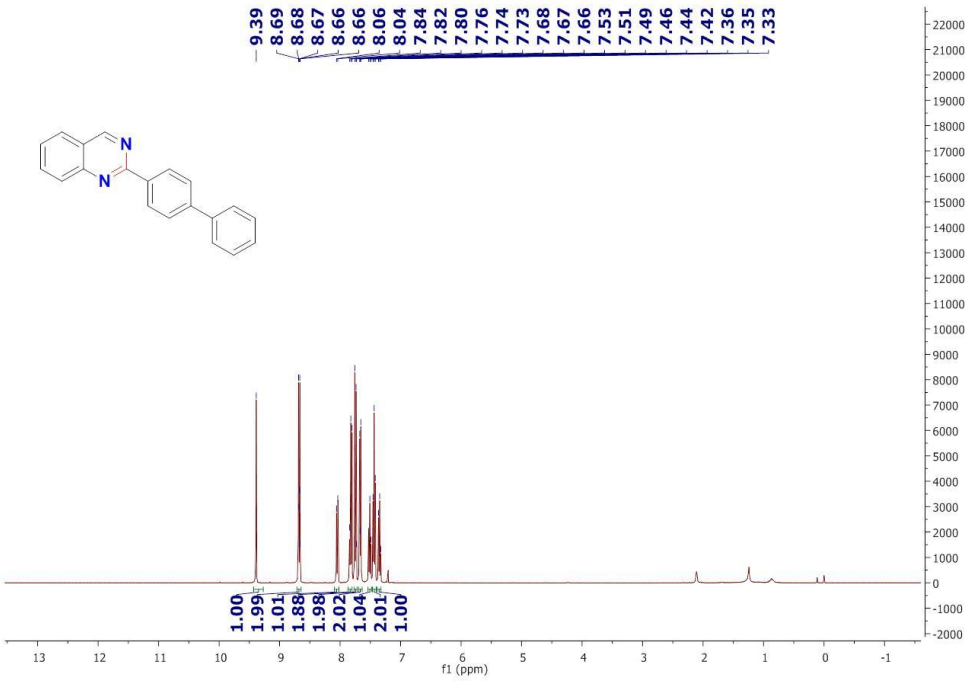


Figure S22.$^{13}C\{^{1}H\}$ NMR spectrum of**3h**in $CDCl_3$(100 MHz, 300 K)



FigureS23. ^{1}H NMR spectrum of **3i** in $CDCl_3$(400 MHz, 300 K)

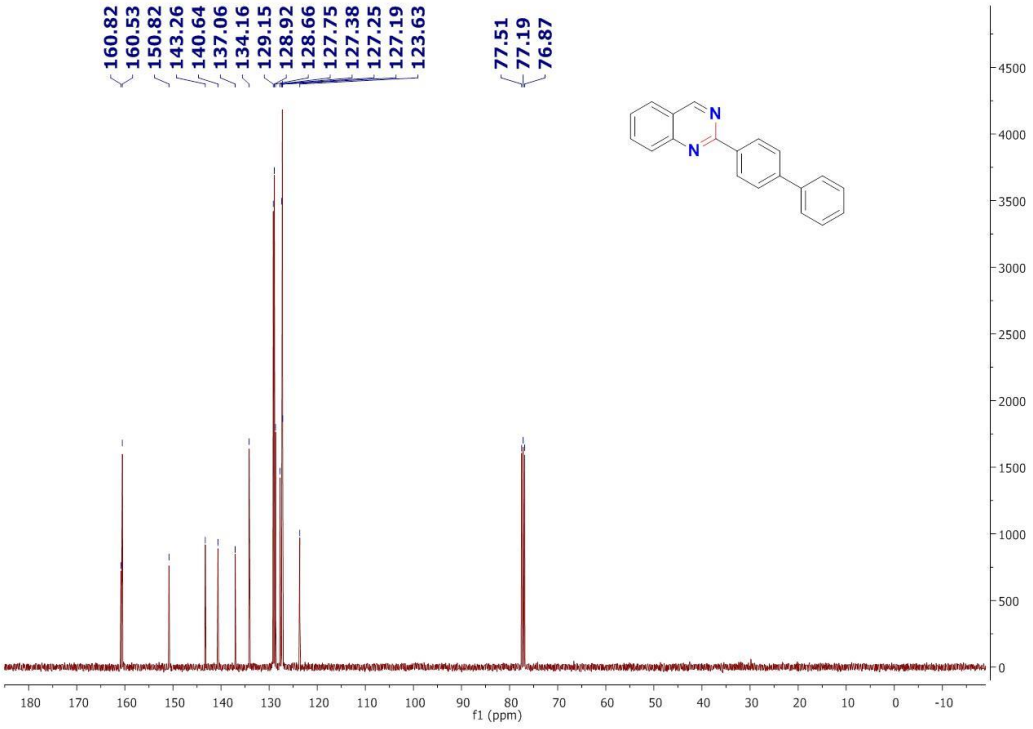


Figure S24.^{13}C{^{1}H} NMR spectrum of**3i**in $CDCl_3$(100 MHz, 300 K).

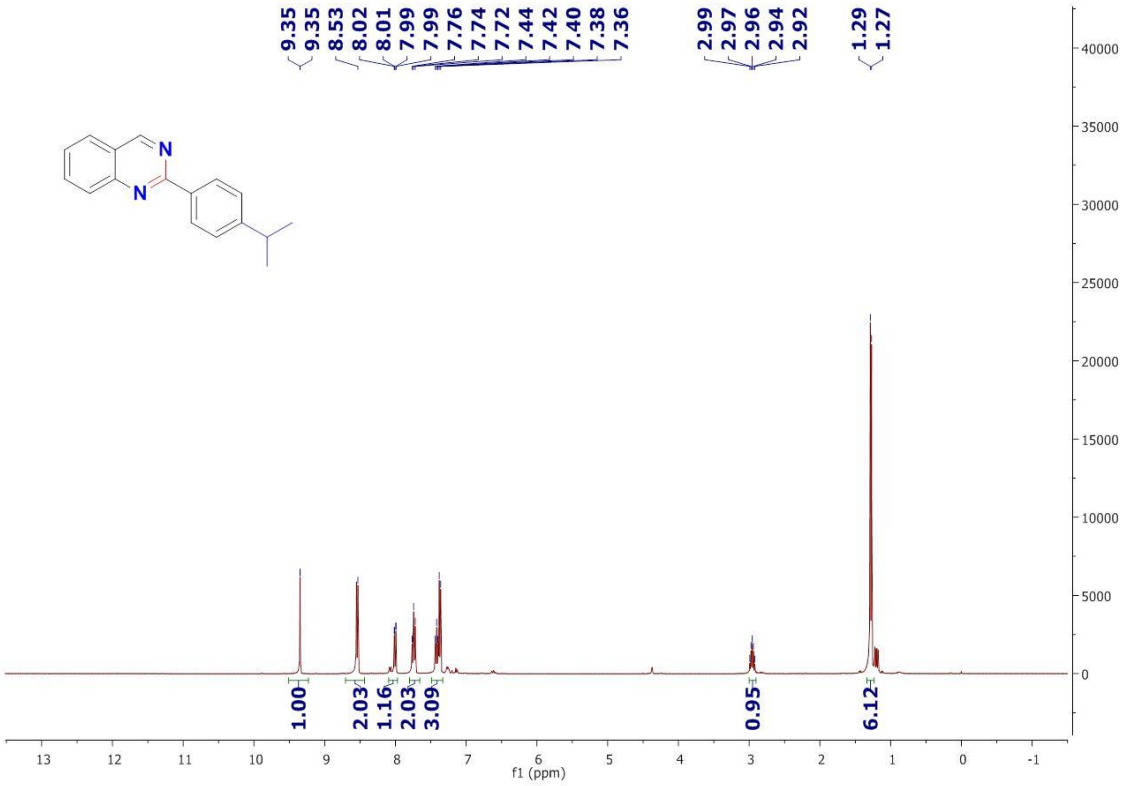


Figure S25. ^{1}H NMR spectrum of **3j** in $CDCl_3$(400 MHz, 300 K).

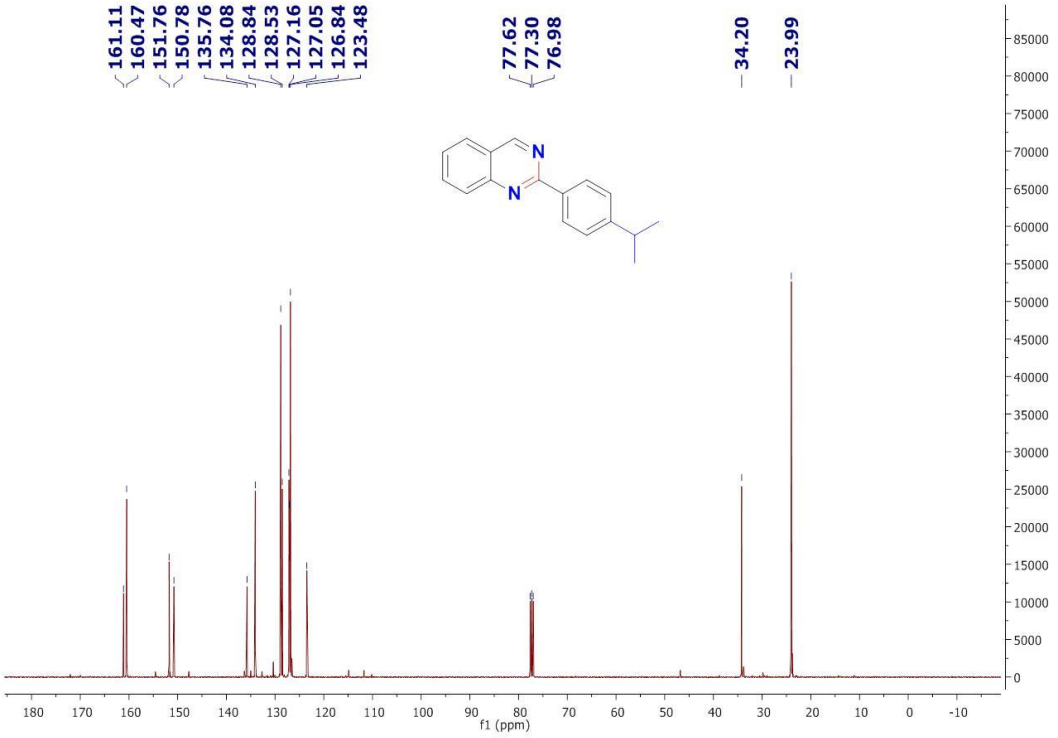


Figure S26.$^{13}C\{^{1}H\}$ NMR spectrum of**3j**in $CDCl_3$(100 MHz, 300 K).

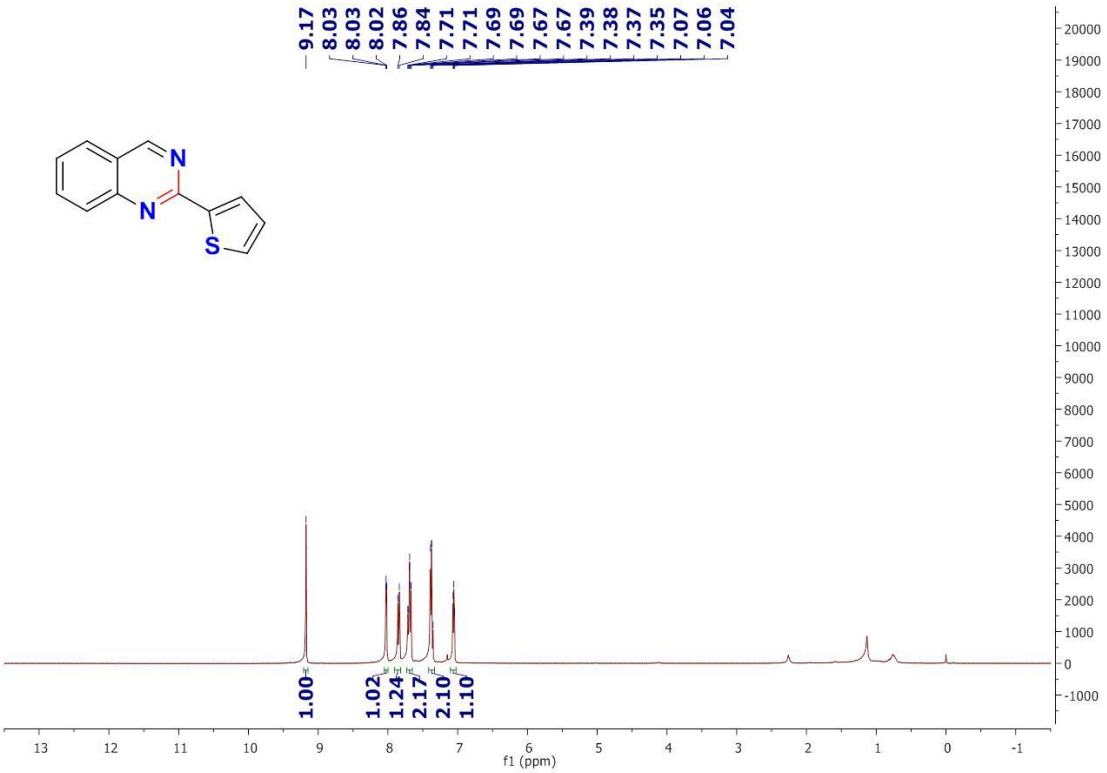


Figure S27. ^{1}H NMR spectrum of **3k** in $CDCl_3$(400 MHz, 300 K).

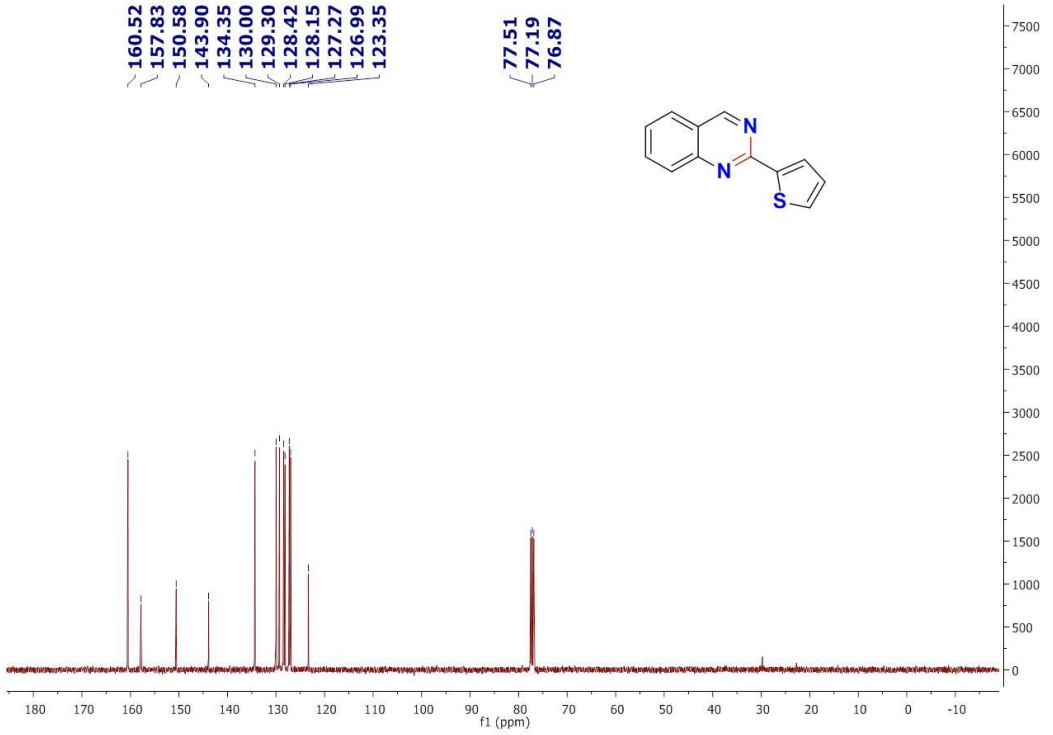


Figure S28.$^{13}C\{^{1}H\}$ NMR spectrum of**3k**in $CDCl_3$(100 MHz, 300 K).

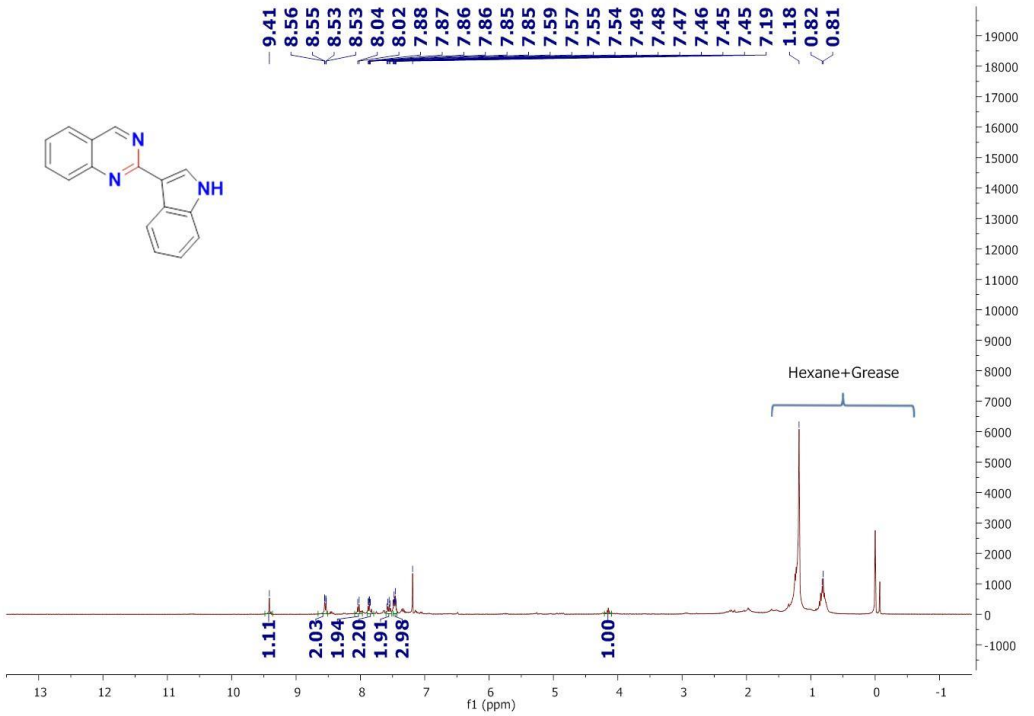


Figure S29. ^{1}H NMR spectrum of **3l** in $CDCl_3$(400 MHz, 300 K).

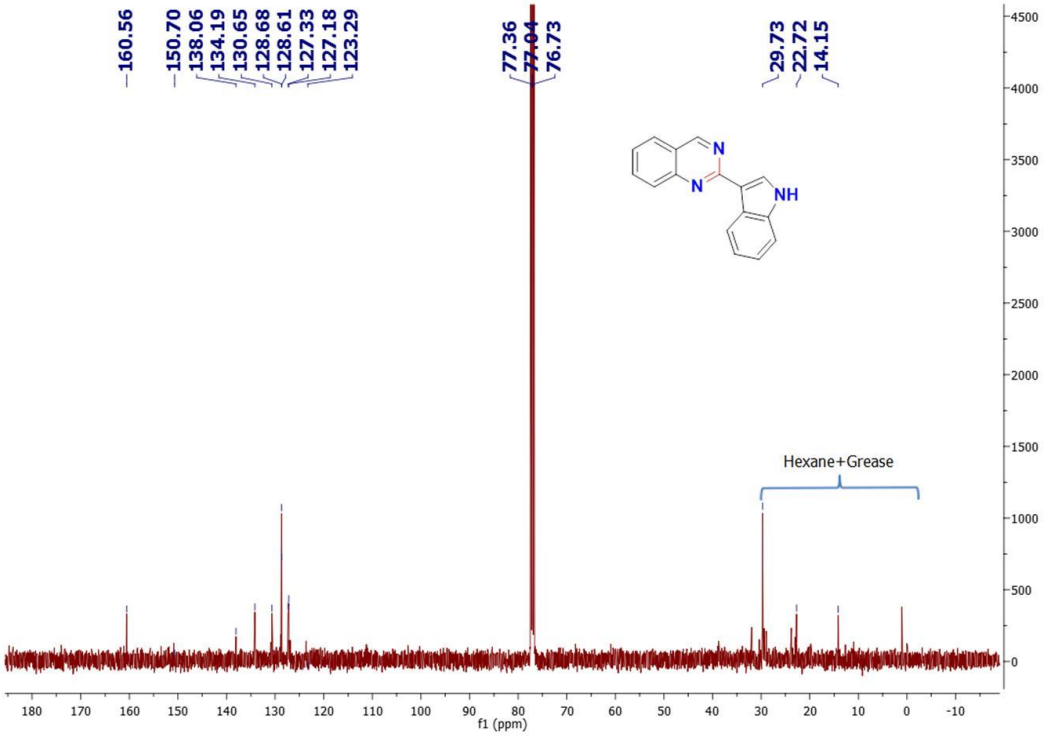


Figure S30.^{13}C{^{1}H} NMR spectrum of**3l**in $CDCl_3$(100 MHz, 300 K).

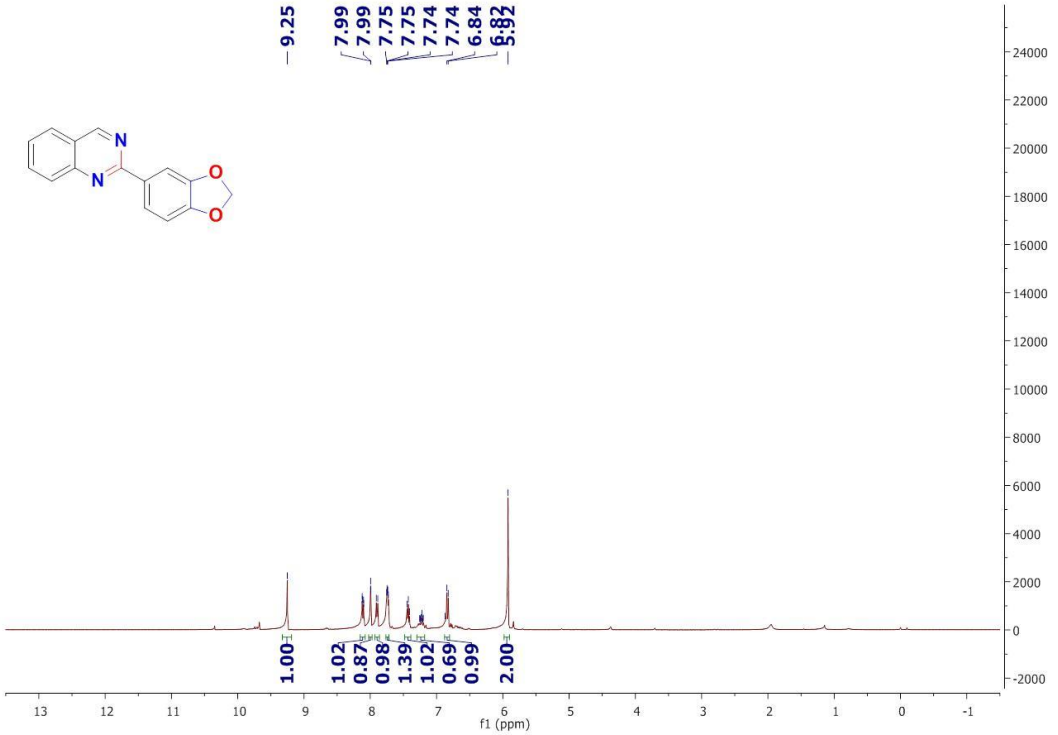


Figure S31. ^{1}H NMR spectrum of **3m** in $CDCl_3$(400 MHz, 300 K).

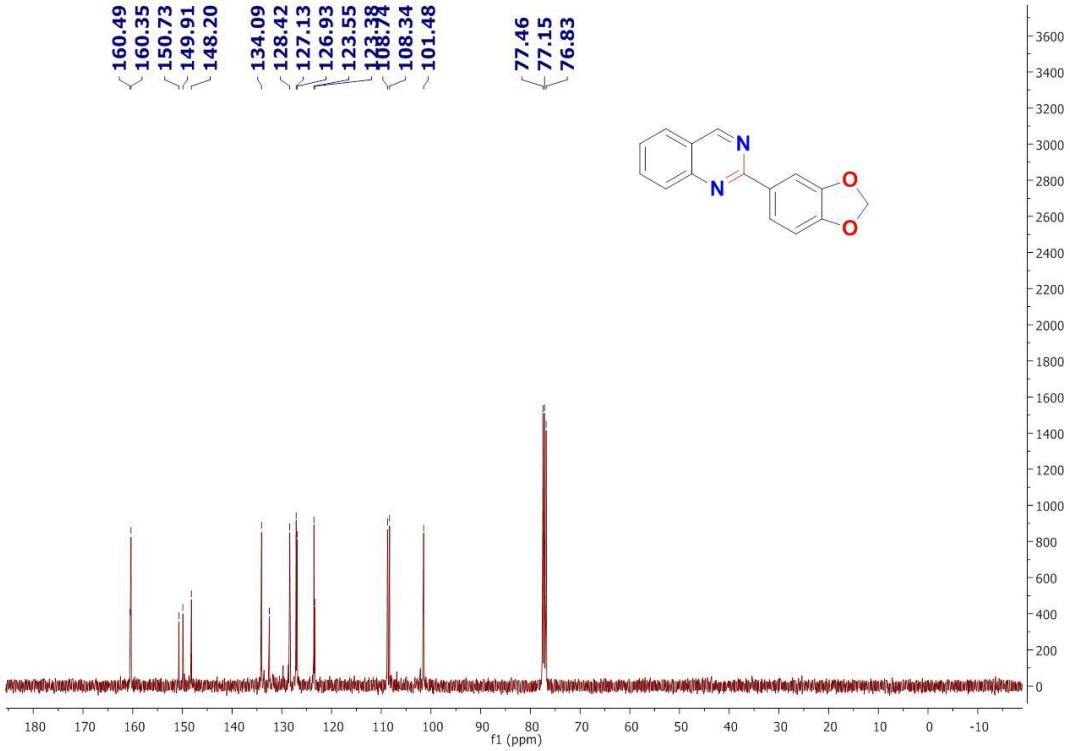


Figure S32.^{13}C{^{1}H} NMR spectrum of**3m**in $CDCl_3$(100 MHz, 300 K).

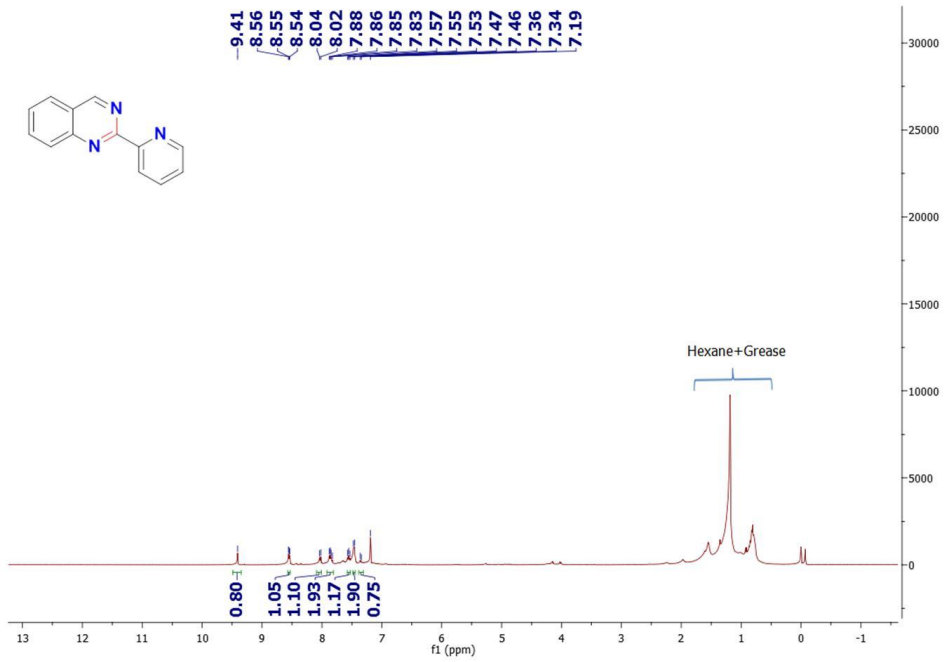


Figure S33. ^{1}H NMR spectrum of **3n** in $CDCl_3$(400 MHz, 300 K).

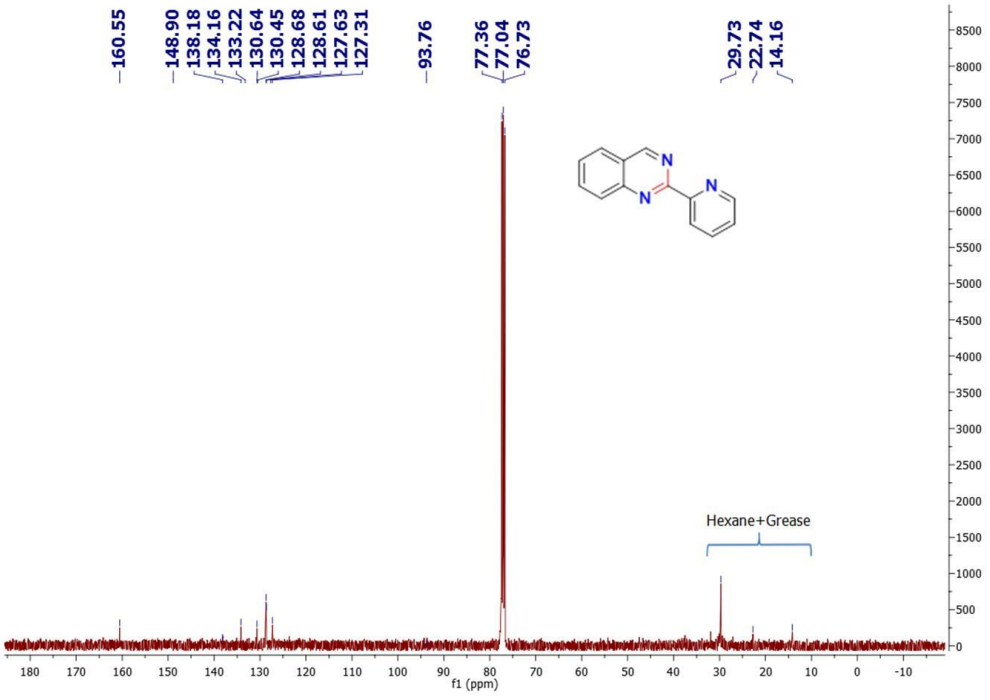


Figure S34.^{13}C{^{1}H} NMR spectrum of**3n**in $CDCl_3$(100 MHz, 300 K).

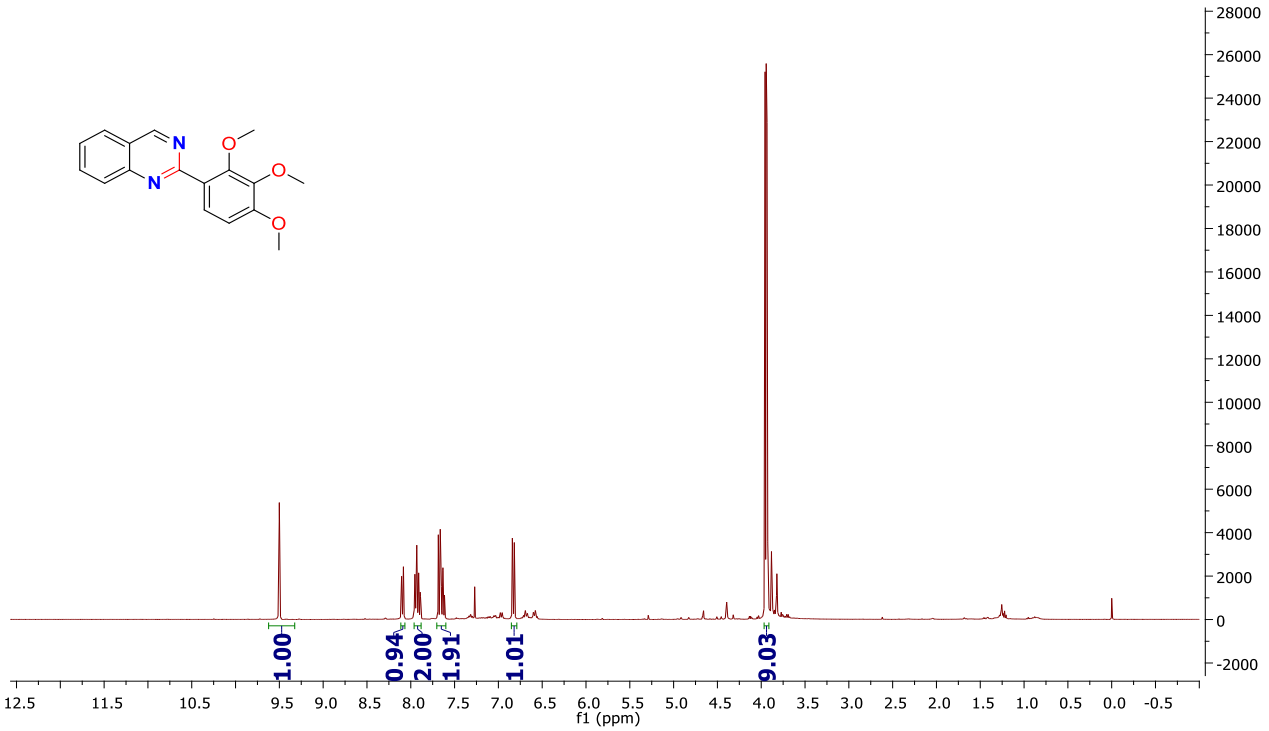


Figure S35. ^{1}H NMR spectrum of **3o** in $CDCl_3$(400 MHz, 300 K)

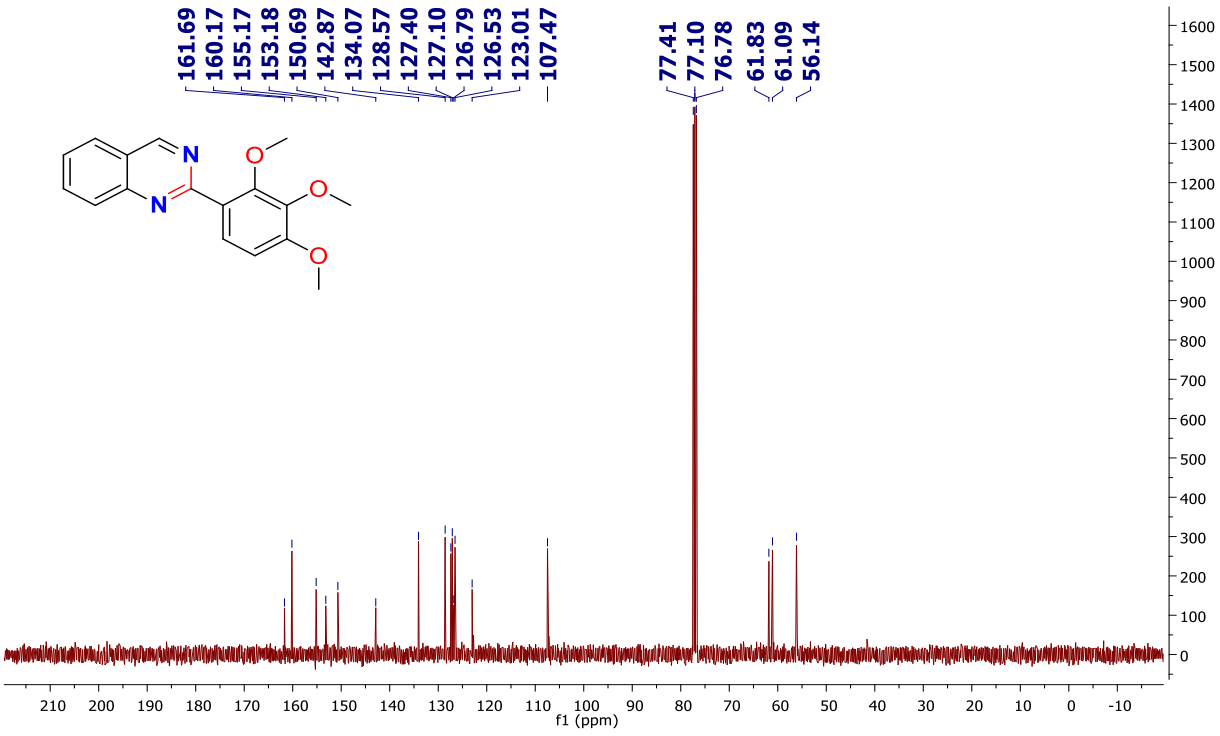


Figure S36.$^{13}C\{^{1}H\}$ NMR spectrum of**3o**in $CDCl_3$(100 MHz, 300 K).

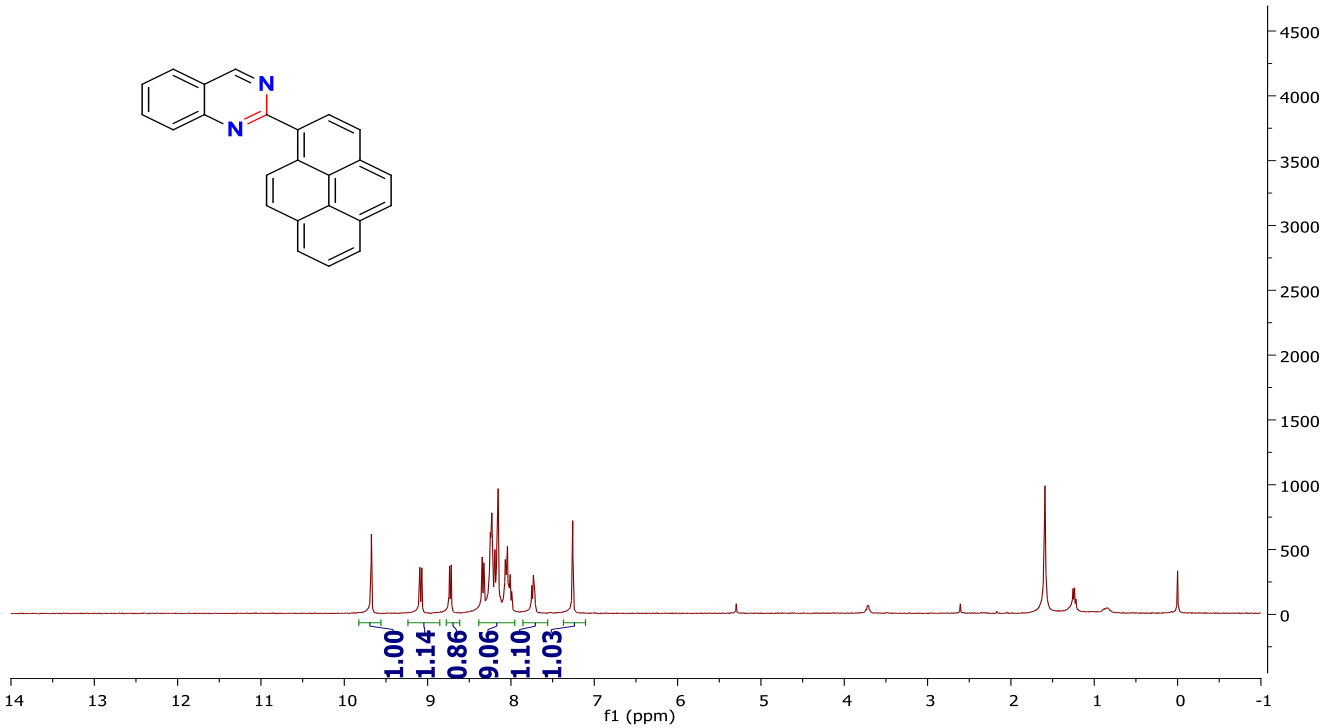


Figure S37. ^{1}H NMR spectrum of **3p** in $CDCl_3$(400 MHz, 300 K).

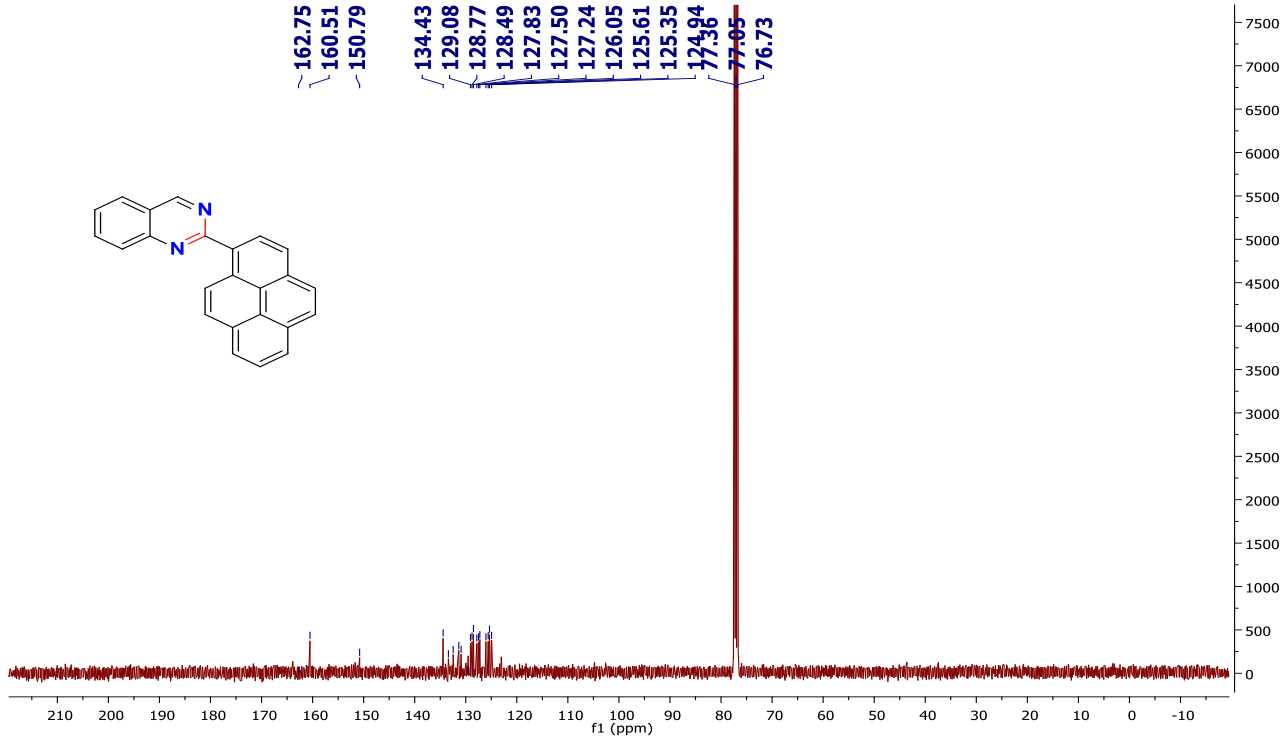


Figure S38.^{13}C{^{1}H} NMR spectrum of**3p** in $CDCl_3$(100 MHz, 300 K).

6. Intermediate for aldehydes, quinazoline characterization data and NMR spectra

Benzaldehyde(1a')

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.90 – 7.83 (m, 1H), 7.61 (s, 1H), 7.52 (d, *J* = 6.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.65, 136.35, 134.56, 133.67, 129.80, 129.03.

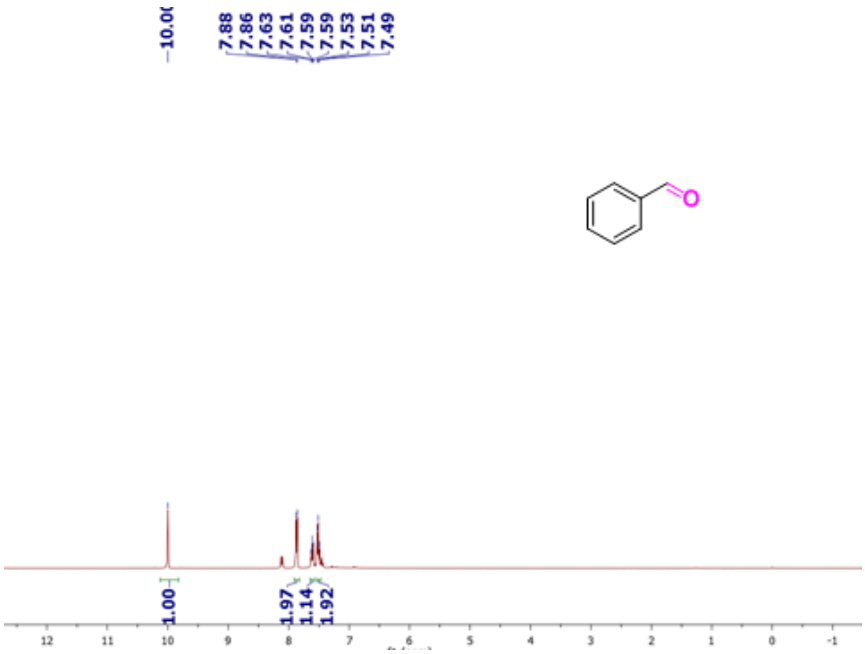


Figure S39.^{1}H NMR spectrum of **1a'** in $CDCl_3$(400 MHz, 300 K).

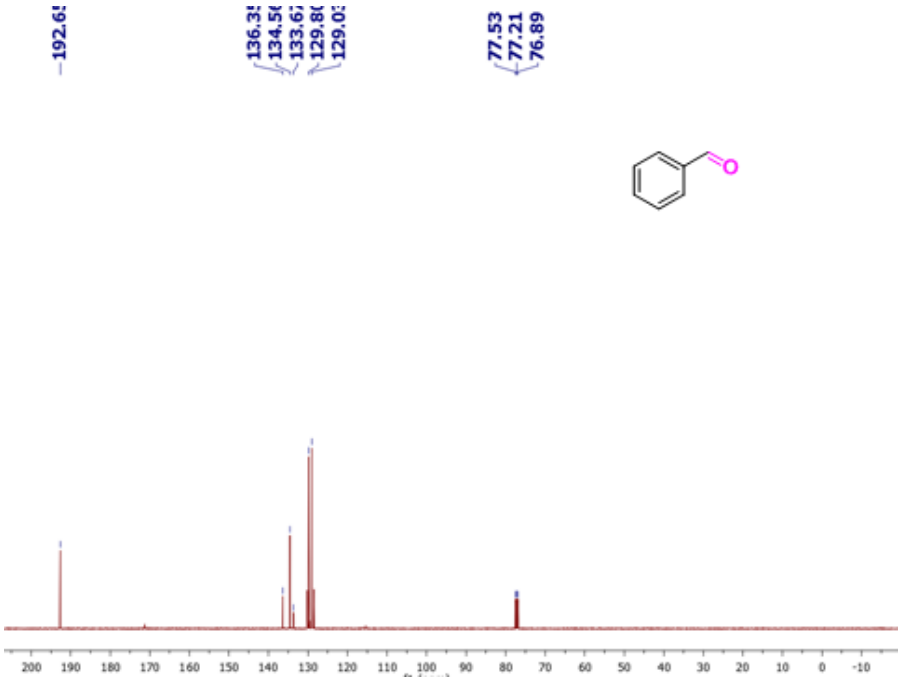


Figure S40.^{13}C{^{1}H} NMR spectrum of**1a'**in $CDCl_3$(100 MHz, 300 K).

Cyclic aminalIntermediate

2-phenyl-1,2,3,4-tetrahydroquinazoline (2a')

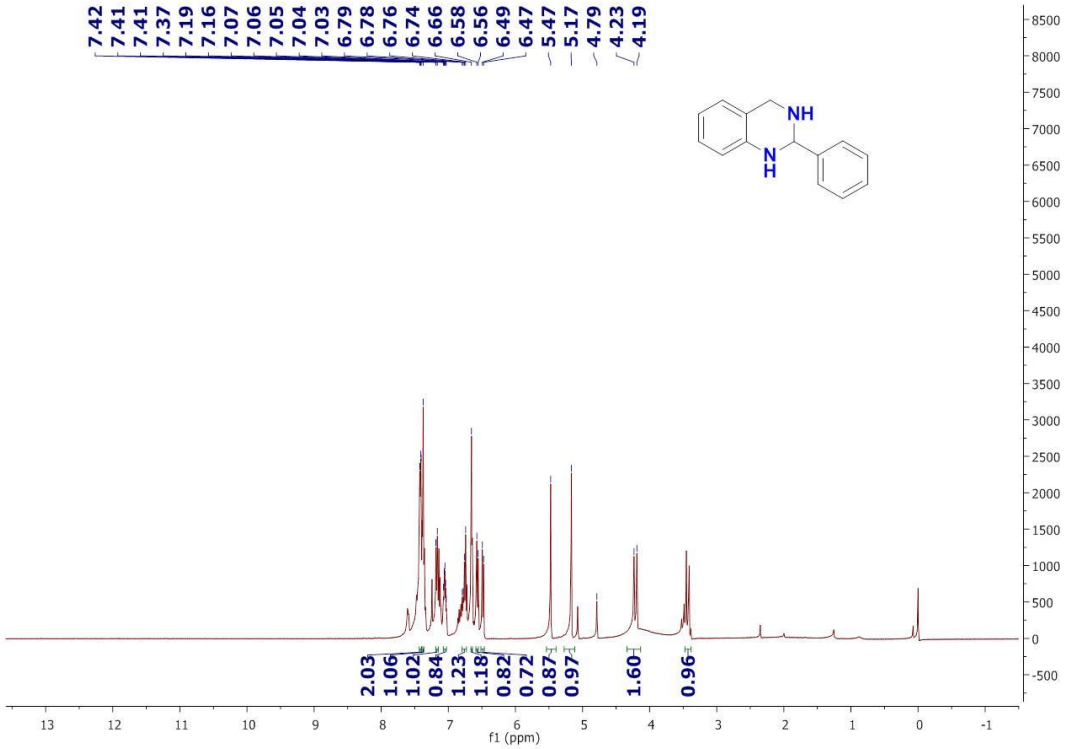


Figure S41.[1]H NMR spectrum of**2a'**in $CDCl_3$(400 MHz, 300 K).

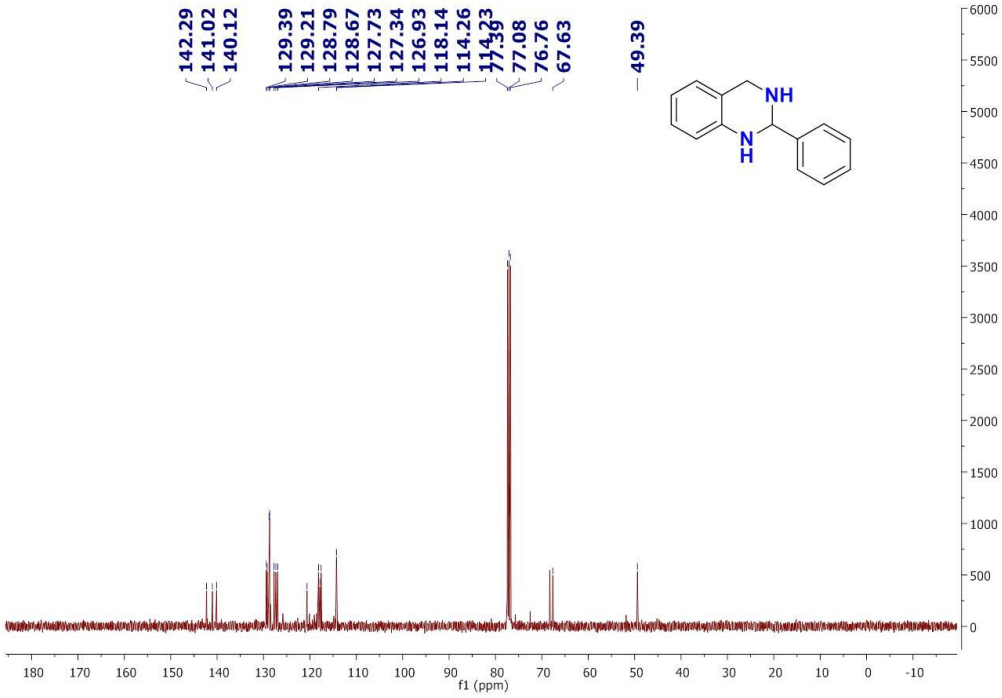


Figure S42. [13]C NMR spectrum of**2a'** in $CDCl_3$(100 MHz, 300 K).

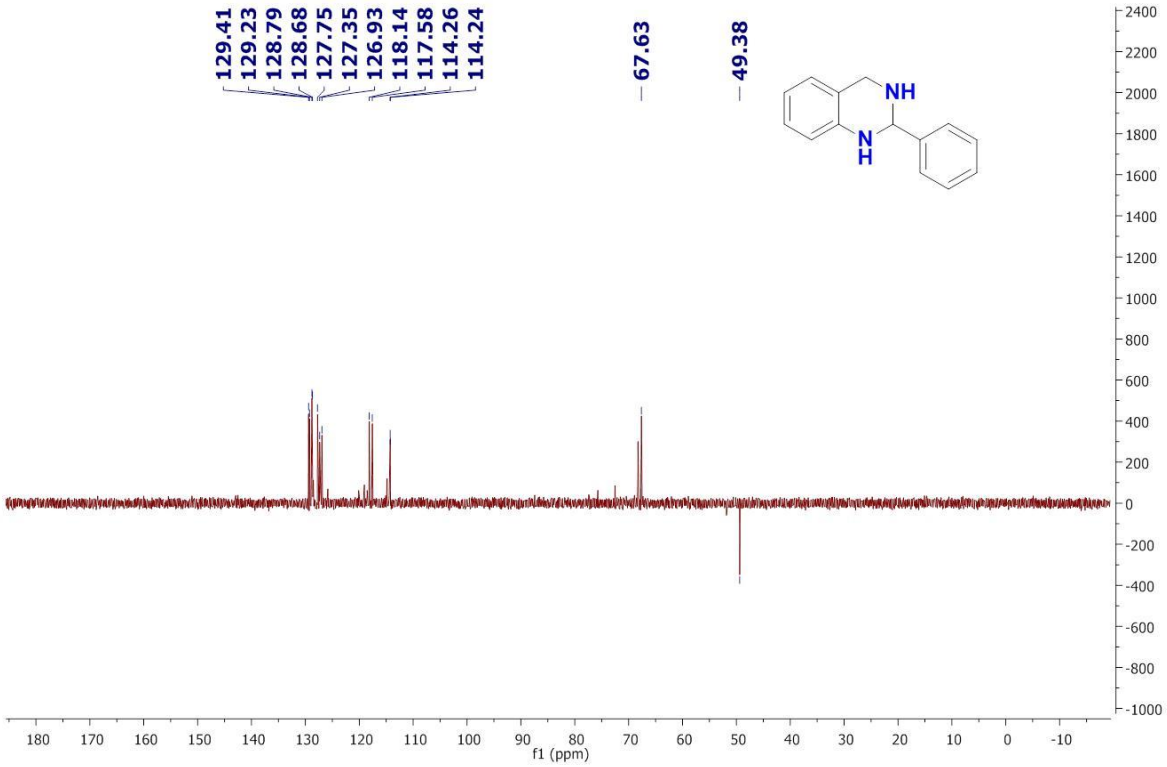


Figure S43. DEPT ^{13}C NMR spectrum of **2a'** in $CDCl_3$(100 MHz, 300 K).

7. Mass spectra of quinazoline intermediates

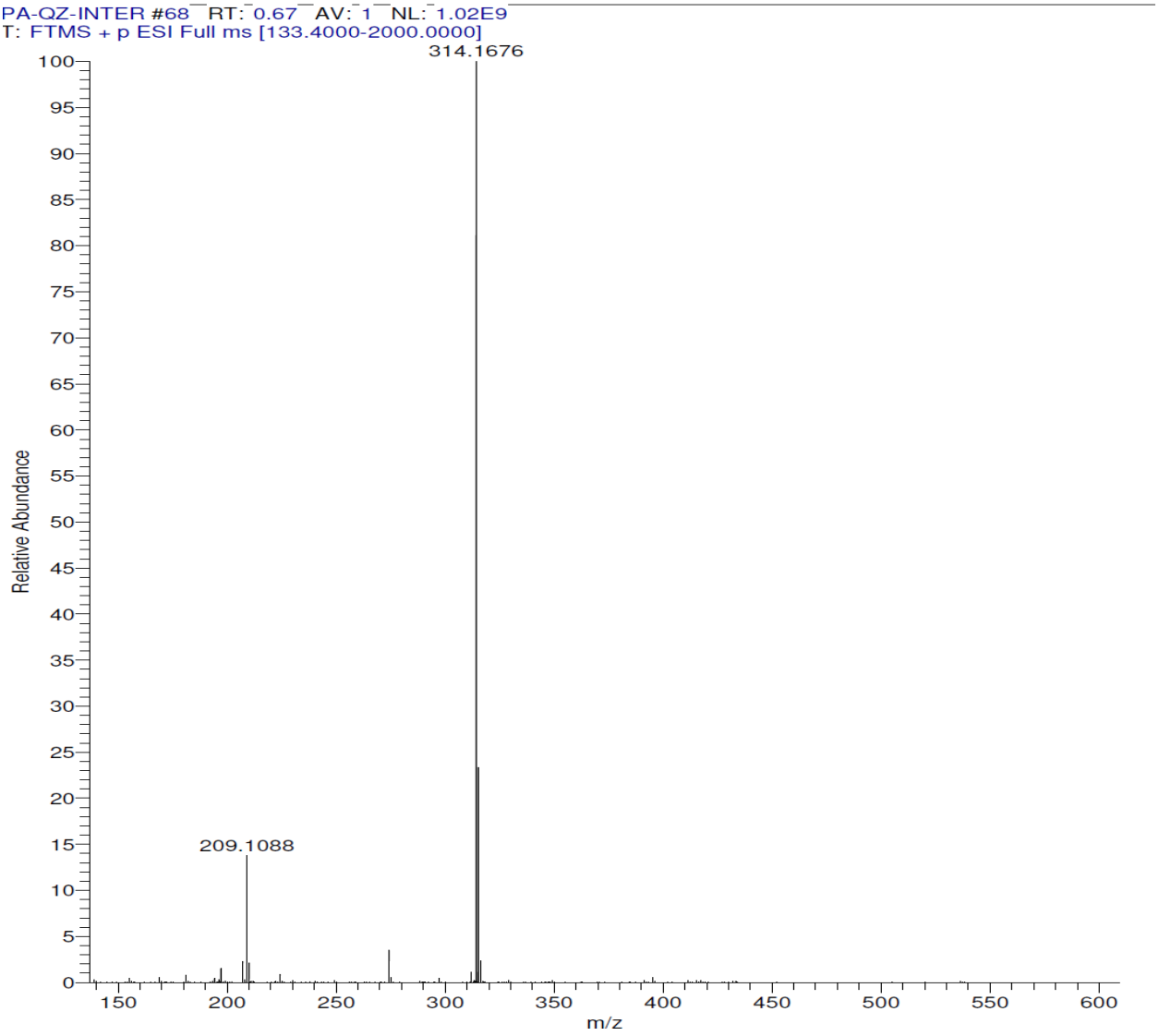


Figure S44.HRMS spectrum of **2a'** in methanol.

8. References

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