Supporting Information

Concise Synthesis of 2,3-Disubstituted Quinoline Derivatives via Ruthenium-Catalyzed Three-Component Deaminative Coupling Reaction of Anilines, Aldehydes and Amines

Aldiyar Shakenov, Krishna Prasad Gnyawali and Chae S. Yi*

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233 United States
*E-mail: chae.yi@marquette.edu

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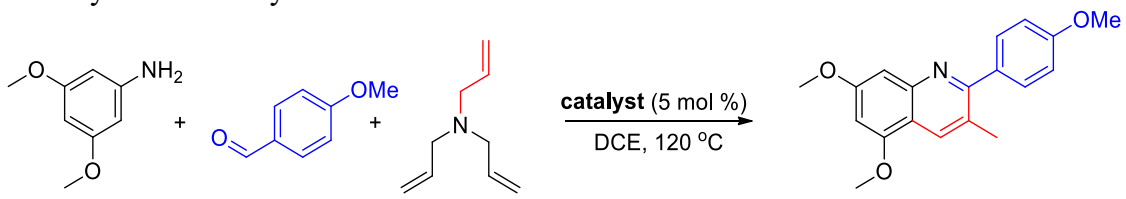
1. General Information. All operations were carried out in a nitrogen-filled glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Solvents were freshly distilled over appropriate drying reagents. Benzene, toluene, and hexanes were distilled from purple solutions of sodium and benzophenone, and dichloromethane was dried over calcium hydride prior to use. All organic substrates were received from commercial sources and were used without further purification. Column chromatography was performed on Silicycle ultrapure silica gel P60 (40-63 μm particle size), and thin layer chromatography was performed on EMD Millipore glass back TLC plates pre-coated with silica gel 60 GF_{254}. The ^{1}H, ^{2}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Varian 300 or 400 MHz FT-NMR spectrometer, and the data are reported in parts per million (ppm) relative to TMS, with the residual solvent peak as an internal reference. Multiplicities are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constant(s) in Hz. Mass spectra were recorded from Shimadzu GCMS-QP2010 SE spectrometer with an SH-Rxi-5sil MS, fused silica (crossbond 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane) column (30 m, 0.25 mm, 0.25 μm). High resolution mass spectra (HRMS) were obtained at the Analytical Instrumentation Center, School of Pharmacy, University of Wisconsin-Madison, Madison, WI.

2. Experimental Procedures: General Procedure for the Coupling Reaction of an Aniline with an Aldehyde and an Amine. In a glove box, complex **1** (11 mg, 5 mol %), an aniline (0.3 mmol), an aldehyde (0.3 mmol) and an amine (0.3 mmol) were dissolved in 1,2-dichloroethane (1.5 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box and was stirred in an oil bath set at 120 °C for 20 h. The reaction tube was taken out of the oil bath and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC-MS. The analytically pure product was isolated by column chromatography on silica gel (40-63 μm particle size, hexanes/EtOAc = 100:1 to 95:5). The product was characterized by NMR and GC-MS spectroscopic methods.

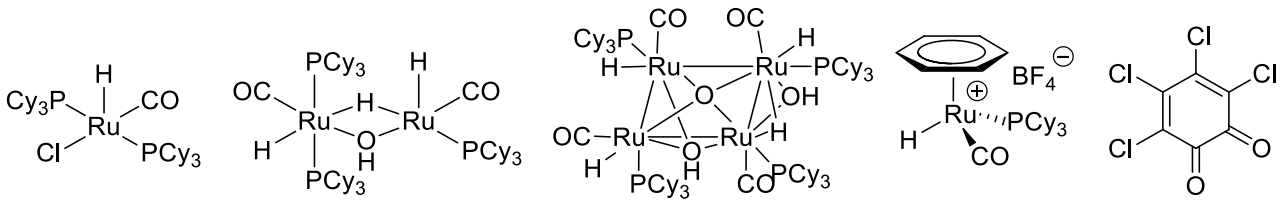
Catalyst Screening and Optimization Study. In a glove box, catalyst (5 mol %), 3,5-dimethoxyaniline (1.5 mmol) and triallylamine (1.5 mmol) were dissolved in 1,2-dichloroethane (1.5 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box and was stirred in an oil bath at 120 °C for 24 h. The product yield was determined by GC-MS by using hexamethylbenzene as an internal standard. The results are summarized in Table S1.

Table S1. Catalyst Screening and Optimization for the Reaction of 3,5-Dimethoxyaniline, 4-Methoxybenzaldehyde and Triallylamine.



entry	catalyst	additive (mol %)	yield (%)[a,b]
1	**1**	-	78
2	**1**	**L1** (10)[c]	20
3	**1**	$HBF_4 \cdot OEt_2$ (10)	<5
4	**1**	AgOAc (30)	<5
5	$[(PCy_3)(CO)RuH]_4(\mu\text{-}O)(\mu\text{-}OH)_2$	-	30
6	$[(PCy_3)(CO)RuH]_4(\mu\text{-}O)(\mu\text{-}OH)_2$	**L1** (10)[c]	29
7	$[(C_6H_6)(CO)(PCy_3)RuH]^+BF_4^-$	-	30
8	$[(p\text{-cymene})RuCl_2]_2$	-	40
9	$RuCl_3 \cdot nH_2O$	-	51
10	$(PPh_3)_3RuCl_2$	-	44
11	$Ru_3(CO)_{12}$	-	27
12	$(PPh_3)_3(CO)RuH_2$	-	0
13	$[(PCy_3)_2(CO)(CH_3CN)_2RuH]^+BF_4^-$	-	33
14	$[(COD)RuCl_2]_x$	-	0
15	$AlCl_3$	-	0
16	PCy_3	-	<5

[a]Reaction conditions: catalyst (5 mol %), 3,5-dimethoxyaniline (0.3 mmol), 4-methoxybenzaldehyde (0.3 mmol), triallylamine (0.3 mmol), 1,2-dichloroethane (1.5 mL), 20 h, 120 °C. [b] GC yields using hexamethylbenzene as an internal standard. [c] **L1** = 3,4,5,6-tetrachloro-1,2-benzoquinone.



1 **2** **3** **4** **L1**

Table S2. Solvent Screening Study for the Reaction of 3,5-Dimethoxyaniline, 4-Methoxybenzaldehyde and Triallylamine.

entry	solvent	yield (%)[a,b]
1	1,2-dichloroethane	78
2	1,2-dichloroethane: toluene (1:1)	41
3	1,2-dichloroethane: 1,4-dioxane (1:1)	63
4	1,4-dioxane	45
5	dichloromethane	61
6	toluene	56
7	tetrahydrofuran	60
8	benzene	44
9	chlorobenzene	48

[a] Reaction conditions: **1** (5 mol %), 3,5-dimethoxyaniline (0.30 mmol), 4-methoxybenzaldehyde (0.30 mmol), triallylamine (0.3 mmol), solvent (1.5 mL), 20 h, 120 °C. [b] GC yields using hexamethylbenzene as an internal standard

Table S3. Catalyst Loading Study for the Reaction of 3,5-Dimethoxyaniline, 4-Methoxybenzaldehyde and Triallylamine

entry	catalyst loading (mol %)	yield (%)[a,b]
1	1	27
2	3	70
3	5	76
4	10	61
6	20	60

[a] Reaction conditions: 3,5-dimethoxyaniline (0.30 mmol), 4-methoxybenzaldehyde (0.30 mmol), 1,2-dichloroethane (1.5 mL), 20 h, 120 °C. [b] GC yields using hexamethylbenzene as an internal standard

Table S4. Optimal Temperature Survey for the Reaction of 3,5-Dimethoxyaniline, 4-Methoxybenzaldehyde and Triallylamine

entry	Temperature (°C)	yield (%)[a,b]
1	140	67
2	120	75
3	100	47
4	80	5
5	60	6

[a] Reaction conditions: **1** (5 mol %), 3,5-dimethoxyaniline (0.30 mmol), 4-methoxybenzaldehyde (0.30 mmol), triallylamine (0.3 mmol), solvent (1.5 mL), 20 h, 120 °C. [b] GC yields using hexamethylbenzene as an internal standard

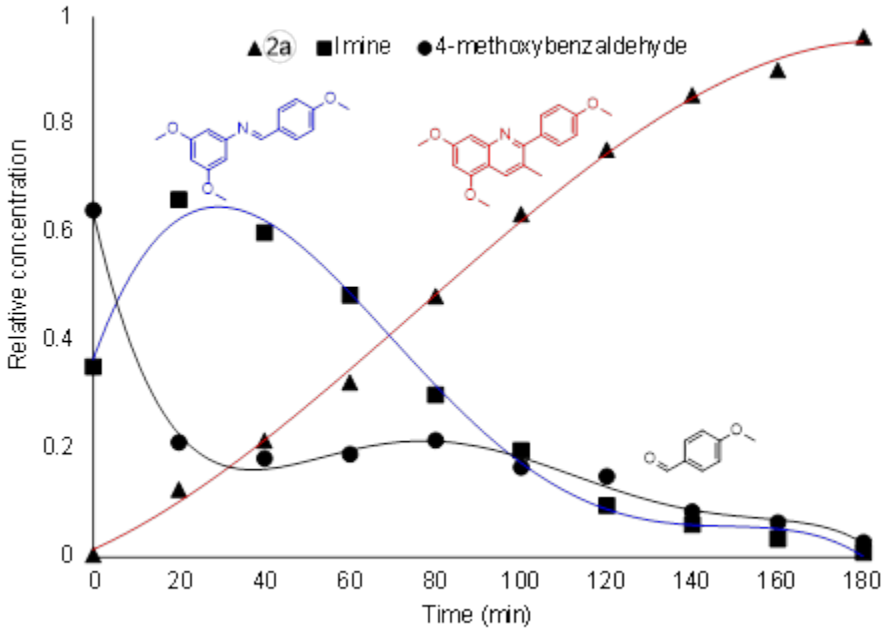
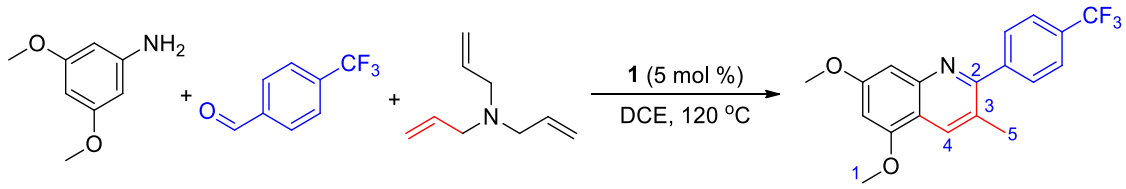


Figure S1. The Reaction Profile from the Reaction of 3,5-Dimethoxyaniline and *p*-OMe-C_6H_4CHO with Triallylamine. *p*-OMe-C_6H_4CHO (●), **2a** (▲), 3,5-Dimethoxy-*N*-(4-methoxybenzylidene)aniline (**4a**) (■).

3. Reaction Profile Experiment. In a glove box, complex **1** (72 mg, 0.1 mmol), 3,5-dimethoxyaniline (15 mg, 0.1 mmol), 4-methoxybenzaldehyde (14 mg, 0.1 mmol) and triallylamine (14 mg, 0.1 mmol) were dissolved in CD_2Cl_2 (0.5 mL) in a J-Young NMR tube equipped with a Teflon screw cap stopcock. The tube was brought out of the glove box and was emersed in an oil bath set at 120 °C. The tube was taken out of the oil bath at 20 min intervals, was immediately cooled in an ice-water bath and was analyzed by ^{1}H NMR. The product

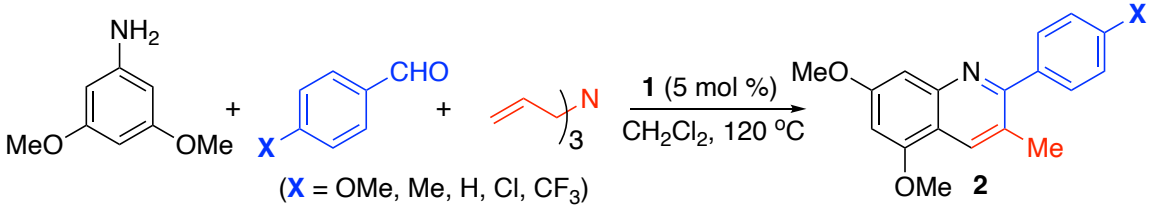
concentration was measured by monitoring the appearance of the product signals on ^{1}H NMR, which was normalized against the internal standard peak (hexamethylbenzene).

4. Carbon Kinetic Isotope Effect Study. In a glove box, complex **1** (36 mg, 5 mol %), 3,5-dimethoxyaniline (153 mg, 1.0 mmol), 4-(trifluoromethyl)benzaldehyde (174 mg, 1.0 mmol) and triallylamine (137 mg, 1.0 mmol) were dissolved in 1,2-dichloroethane (1.5 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The resulting mixture was stirred in an oil bath at 120 °C for 20 h. The procedure was repeated two more times, and the product conversion was determined by GC (91%, 88% and 87% conversion). For low conversion samples, complex **1** (36 mg, 5 mol %), 3,5-dimethoxyaniline (153 mg, 1.0 mmol), 4-(trifluoromethyl)benzaldehyde (174 mg, 1.0 mmol) and triallylamine (137 mg, 1.0 mmol) were dissolved in 1,2-dichloroethane (1.5 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar, and the resulting mixture was stirred for in an oil bath at 120 °C for 4 h. The procedure was repeated two more times, and the product conversion was determined by GC (14%, 18% and 15% conversion). The ^{13}C{^{1}H} NMR analysis of the isolated product **2e** was performed by following Singleton's NMR method.[S1] The NMR sample was prepared identically by dissolving **2e** (200 mg) in $CDCl_3$ (0.5 mL) in a 5 mm high precision NMR tube. The ^{13}C{^{1}H} NMR spectra were recorded with H-decoupling and 45-degree pulses. A 60 s delay between pulses was imposed to minimize T_1 variations (d1 = 120 s, at = 5.0 s, np = 245098, nt = 512, dm = 'nny'). The data obtained were summarized in Table S2.



carbon no.	high conv. R_0	low conv. R_1	R_0/R_1	calculated KIE
1 (ref)	1.000	1.000	1.000	1.000
2	1.080	1.088	0.992	0.993
3	1.267	1.256	1.009	1.009
4	1.057	1.061	0.996	0.996
5	1.189	1.142	1.041	**1.041**

Table S5. ^{13}C Integration of the Product **2e** at High Conversion (R_0, 88% Conversion), at Low Conversion (R_1, 16% Conversion), and the Calculated R_0/R_1.



5. Hammett Study. In a glove box, complex **1** (5 mol %), 3,5-dimethoxyaniline (0.5 mmol) and triallylamine (0.5 mmol) were dissolved in CD_2Cl_2 (0.5 mL) in a 25 mL reaction tube. The solution was divided into five equal portions, transferred into five separate J-Young NMR tubes, and *p*-X-C_6H_5CHO (X = OMe, Me, H, Cl, CF_3) (0.1 mmol) was added to each reaction tube. The tubes were brought out of the glove box and were immersed in an oil bath at 120 °C. The tubes were taken out of the bath at 20 min intervals, immediately cooled in ice-water bath and were analyzed by ^1H NMR. The rate of reaction was measured by monitoring product peaks and normalized using hexamethylbenzene as an internal standard. The k_{obs} of each reaction was determined from first-order plot of -*ln*[(3,5-dimethoxyaniline)$_t$/(3,5-dimethoxyaniline)$_0$] vs time. The Hammett plot of log(k_X/k_H) vs σ_p is shown in Figure S2.

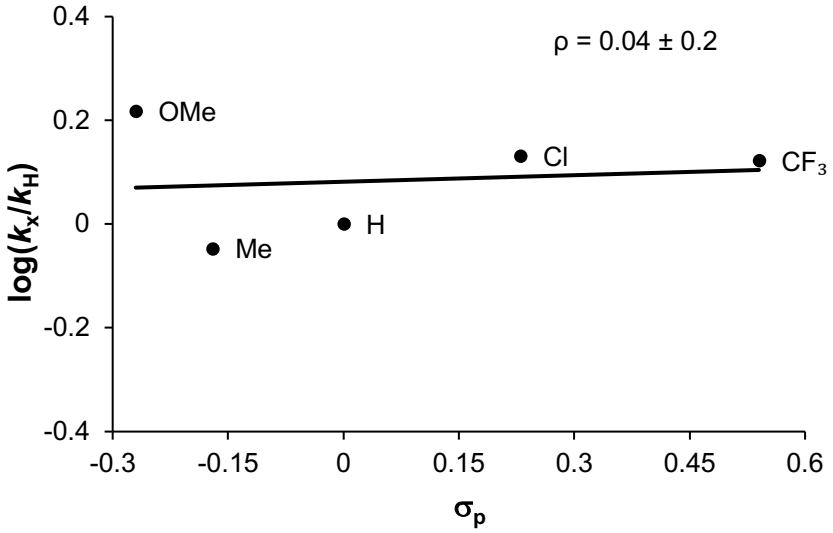


Figure S2. Hammett Plot from the Reaction of 3,5-Dimethoxyaniline with *p*-X-C_6H_4CHO (X = OMe, Me, H, Cl, CF_3) and Triallylamine.

6. Generation and Detection of Catalytically Relevant Species. The imine substrate ((3-(dimethylamino)-1-phenylpropylidene)-3,5-dimethoxyaniline) (**6a**) was synthesized from the reaction of 3-(dimethylamino)-1-phenylpropan-1-one (178 mg, 1.0 mmol) with 3,5-dimethoxyaniline (154 mg, 1.0 mmol) in CH_2Cl_2 (2 mL), which was stirred at room temperature for 24 h. In a glove box, complex **1** (11 mg, 5 mol %) and product **6a** (0.3 mmol) were dissolved in 1,2-dichloroethane (1.5 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box and was immersed in an oil bath set at 120 °C. The tube was taken out of the oil bath after 20 h. The product yield was determined by GC-MS by using hexamethylbenzene as an internal standard. The resulting quinoline **2k** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5).

Spectroscopic Detection of Catalytically Relevant Species. In glovebox, the complex **1** (73 mg, 0.10 mmol) was dissolved in CD_2Cl_2 (0.2 mL) in an J-Young NMR tube equipped with resealable stopcock. The imine substrate 2-(((3,5-dimethoxyphenyl)imino)methyl)phenol (**4b**) (52 mg, 0.2 mmol) was added to the mixture. The reaction was monitored by ^1H NMR after heating for 120 s at 120 °C. After recording the $^{31}P\{^1H\}$ NMR, a small sample was taken from the reaction tube and was analyzed with LC-MS. The LC-MS spectra are shown in Figure S3.

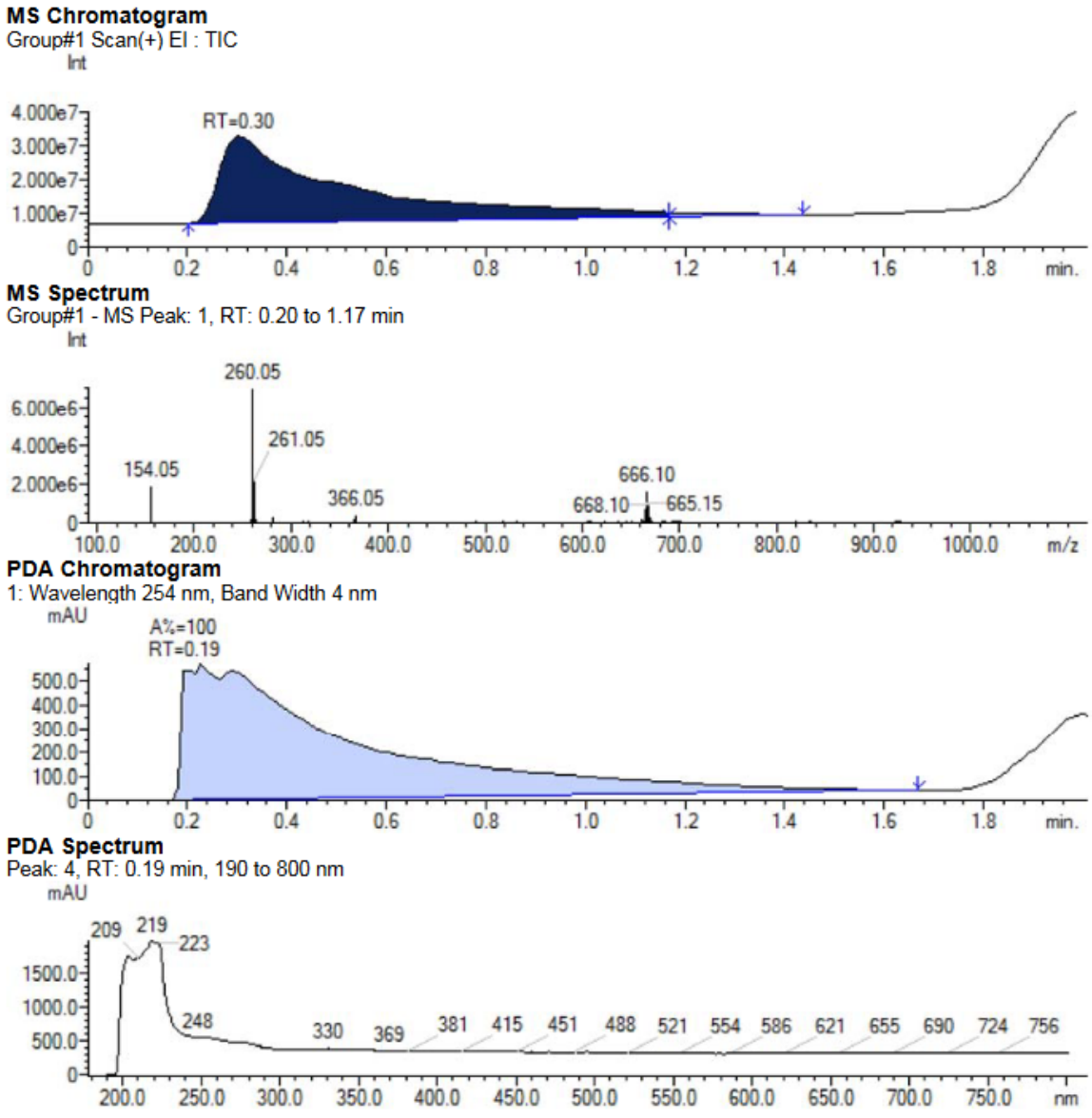


Figure S3. LC-MS spectra from the Reaction Mixture of **1** and 2-(((3,5-Dimethoxyphenyl)imino)methyl)phenol (**4a**).

7. X-Ray Crystallographic Analysis of 2n and 2r. For **2n**: Single crystals of **2n** were grown in CH_2Cl_2/hexanes at room temperature. A suitable crystal was selected and mounted on an Oxford SuperNova diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, and Atlas CCD area detector. The crystal was kept at 99.95(10) K during data collection. Using Olex2[S2], the structure was solved with the olex2.solve[S3] structure solution program using Charge Flipping and refined with the SHELXL[S4] refinement package using Least Squares minimization.

For **2r**: Single crystals of **2r** were grown in CH_2Cl_2/hexanes at room temperature. A suitable crystal was selected and mounted on an Oxford SuperNova diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, and Atlas CCD area detector. The crystal was kept at 99.95(10) K during data collection. Using Olex2[S2], the structure was solved with the olex2.solve[S3] structure solution program using Charge Flipping and refined with the SHELXL[S4] refinement package using Least Squares minimization.

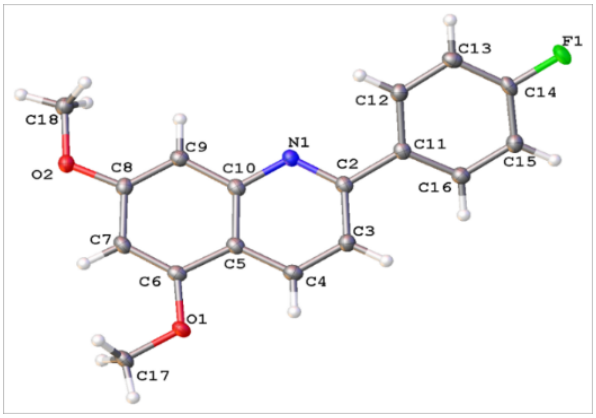


Figure S4. Molecular Structure of **2n**.

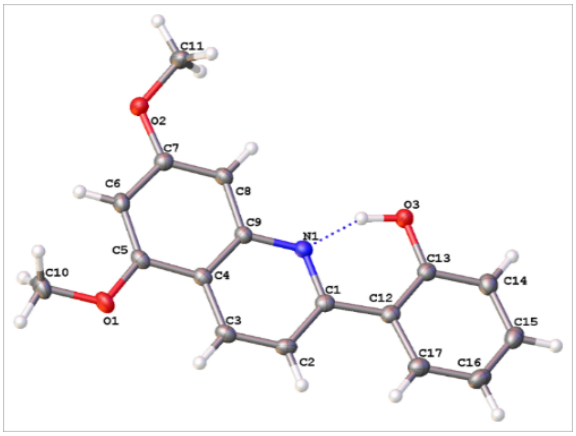


Figure S5. Molecular Structure of **2r**.

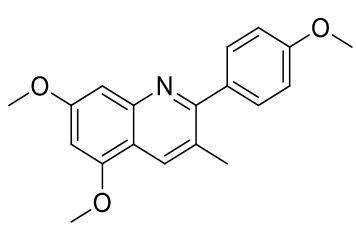
Table S6. Crystal Data and Structure Refinement for **2n**.

Empirical formula	$C_{17}H_{14}FNO_2$
Formula weight	283.29
Temperature/K	99.95(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	26.2945(5)
b/Å	3.86139(6)
c/Å	25.3106(4)
α/°	90
β/°	94.4637(17)
γ/°	90
Volume/Å^3	2562.08(8)
Z	8
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	0.879
F(000)	1184.0
Crystal size/mm^3	0.44 × 0.199 × 0.026
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.006 to 140.822
Index ranges	$-32 \leq h \leq 31$, $-4 \leq k \leq 4$, $-30 \leq l \leq 30$
Reflections collected	12360
Independent reflections	2437 [R_{int} = 0.0235, R_{sigma} = 0.0149]
Data/restraints/parameters	2437/0/192
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0870
Final R indexes [all data]	R_1 = 0.0367, wR_2 = 0.0912
Largest diff. peak/hole / e Å^{-3}	0.20/-0.24

Table S7. Crystal Data and Structure Refinement for **2r**.

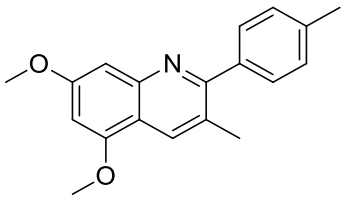
Empirical formula	$C_{17}H_{15}NO_3$
Formula weight	281.30
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.9864(5)
b/Å	4.87230(14)
c/Å	18.6483(6)
α/°	90
β/°	102.739(3)
γ/°	90
Volume/Å^3	1328.16(7)
Z	4
ρ_{calc}g/cm^3	1.407
μ/mm^{-1}	0.097
F(000)	592.0
Crystal size/mm^3	0.762 × 0.198 × 0.153
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.684 to 59.412
Index ranges	$-20 \leq h \leq 20$, $-6 \leq k \leq 5$, $-25 \leq l \leq 25$
Reflections collected	15671
Independent reflections	3460 [R_{int} = 0.0278, R_{sigma} = 0.0275]
Data/restraints/parameters	3460/0/196
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0464, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1256
Largest diff. peak/hole / e Å^{-3}	0.34/-0.28

8. Characterization Data of the Products.



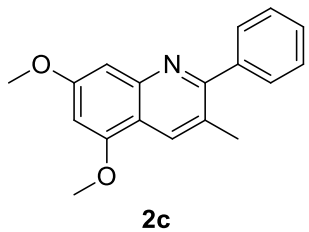
2a

5,7-Dimethoxy-2-(4-methoxyphenyl)-3-methylquinoline (2a). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-methoxybenzaldehyde (41 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2a** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 70 mg (75%). Data for **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.07-6.96 (m, 3H), 6.48 (d, J = 1.9 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.86 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7, 160.5, 159.6, 155.5, 148.7, 133.6, 131.8, 130.4, 126.0, 115.8, 113.7, 99.6, 97.9, 55.8, 55.7, 55.5, 20.7 ppm; GC-MS for $C_{19}H_{19}NO_3$, m/z = 309 (M^+); HRMS (ESI-TOF) Calcd for $C_{19}H_{20}NO_3$ ([M + H]$^+$) 310.1438, Found 310.1437.



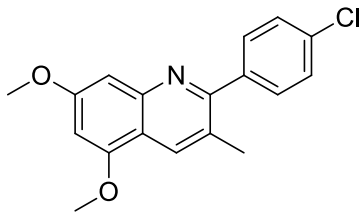
2b

5,7-Dimethoxy-3-methyl-2-(*p*-tolyl)quinoline (2b). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-methylbenzaldehyde (36 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2b** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 64 mg (73%). Data for **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 2.2 Hz, 1H), 6.54-6.44 (m, 1H), 3.94 (d, J = 19.9 Hz, 6H), 2.42 (s, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.9, 160.6, 155.5, 148.6, 138.2, 137.8, 131.7, 129.0, 128.8, 126, 115.9, 99.7, 97.9, 55.8, 55.6, 21.4, 20.6 ppm; GC-MS for $C_{19}H_{19}NO_2$, m/z = 293 (M^+); HRMS (ESI-TOF) Calcd for $C_{19}H_{20}NO_2$ ([M + H]$^+$) 294.1489, Found 294.1488.



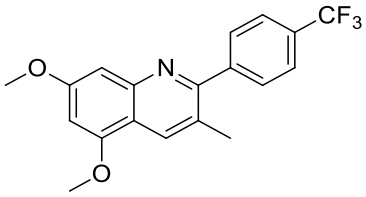
2c

5,7-Dimethoxy-3-methyl-2-phenylquinoline (2c). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), benzaldehyde (32 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2c** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 65 mg (78%). Data for **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.57 (d, J = 7.9 Hz, 2H), 7.44 (dt, J = 23.4, 7.2 Hz, 3H), 7.11-6.99 (m, 1H), 6.50 (d, J = 1.6 Hz, 1H), 3.95 (d, J = 26.6 Hz, 6H), 2.42 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.0, 160.7, 155.5, 148.7, 141.2, 131.8, 128.9, 128.4, 128.1, 126.1, 116, 99.8, 98.1, 55.9, 55.7, 20.5 ppm; GC-MS for $C_{18}H_{17}NO_2$, m/z = 279 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{18}NO_2$ ([M + H]$^+$) 280.1326, Found 280.1332.



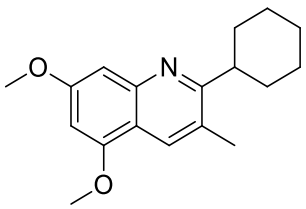
2d

2-(4-Chlorophenyl)-5,7-dimethoxy-3-methylquinoline (2d). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-chlorobenzaldehyde (42 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2d** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 64 mg (68%). Data for **2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.03 (s, 1H), 6.50 (d, J = 1.8 Hz, 1H), 3.94 (d, J = 24.8 Hz, 6H), 2.40 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.9, 159.6, 155.5, 148.7, 139.5, 134.3, 132.1, 130.4, 128.6, 125.7, 116.2, 99.6, 98.3, 55.9, 55.7, 20.4 ppm; GC-MS for $C_{18}H_{16}ClNO_2$, *m/z* = 313 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{17}ClNO_2$ ([M + H]$^+$) 314.0942, Found 314.0943.



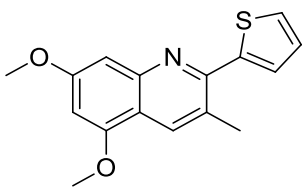
2e

5,7-Dimethoxy-3-methyl-2-(4-(trifluoromethyl)phenyl)quinoline (2e). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (52 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 70 mg (67%). Data for **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.80-7.60 (m, 4H), 7.02 (s, 1H), 6.50 (s, 1H), 3.93 (d, J = 24.8 Hz, 6H), 2.39 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.0, 159.3, 155.5, 148.7, 144.7, 132.2, 129.4, 125.7, 125.6, 125.3 (dd, J_{CF} = 7.5, 3.8 Hz), 123.0, 116.3, 99.5, 98.4, 55.9, 55.7, 20.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68 ppm; GC-MS for $C_{19}H_{16}F_3NO_2$, *m/z* = 347 (M^+); HRMS (ESI-TOF) Calcd for $C_{19}H_{17}F_3NO_2$ ([M + H]$^+$) 348.1206, Found 348.1204.



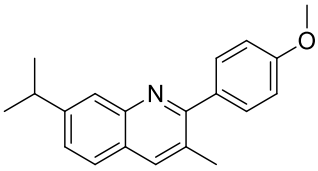
2f

2-Cyclohexyl-5,7-dimethoxy-3-methylquinoline (2f). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), cyclohexanescarbaldehyde (34 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2f** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 38 mg (45%). Data for **2f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 6.97 (s, 1H), 6.43 (d, J = 2.0 Hz, 1H), 3.96-3.91 (m, 6H), 2.97 (m, 1H), 2.46 (s, 3H), 1.93-1.76 (m, 7H), 1.49-1.37 (m, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.4, 160.2, 155.5, 148.9, 130.7, 125.8, 115.1, 99.5, 97.3, 55.8, 55.7, 42.8, 31.9, 27.0, 26.2, 19.2 ppm; GC-MS for $C_{18}H_{23}NO_2$, *m/z* = 285 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{24}NO_2$ ([M + H]$^+$) 286.1802, Found 286.1803.



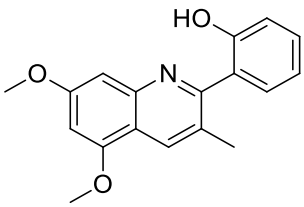
2g

5,7-Dimethoxy-3-methyl-2-(thiophen-2-yl)quinoline (2g). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), thiophene-2-carbaldehyde (34 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2g** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 44 mg (51%). Data for **2g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.58 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.46 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.15 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.45 (d, *J* = 2.2 Hz, 1H), 3.94 (d, *J* = 3.5 Hz, 6H), 2.67 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.9, 155.4, 152.9, 148.6, 145.5, 132.7, 128, 127.7, 127.7, 125, 115.6, 99.3, 98.1, 55.8, 55.7, 21.8 ppm; GC-MS for $C_{16}H_{15}NO_2S$, *m/z* = 285 (M^+); HRMS (ESI-TOF) Calcd for $C_{16}H_{16}NO_2S$ ($[M + H]^+$) 286.0896, Found 286.0895.



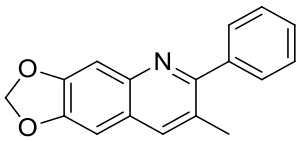
2h

7-Isopropyl-2-(4-methoxyphenyl)-3-methylquinoline (2h). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3-isopropylaniline (41 mg, 0.3 mmol), 4-methoxybenzaldehyde (41 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2h** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 27 mg (30%). Data for **2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (d, *J* = 9.0 Hz, 2H), 7.7 (d, *J* = 8.5 Hz, 1H), 7.6 (d, *J* = 8.3 Hz, 2H), 7.4 (m, 1H), 7.0 (d, *J* = 8.3 Hz, 2H), 3.9 (s, 3H), 3.2-3.1 (m, 1H), 2.5 (s, 3H), 1.4 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 159.7, 149.8, 147.0, 136.6, 133.7, 130.4, 128.5, 126.6, 126.5, 126.0, 125.4, 113.8, 55.5, 34.4, 23.9, 20.8 ppm; GC-MS for $C_{21}H_{25}NO_2$, *m/z* = 291 (M^+); HRMS (ESI-TOF) Calcd for $C_{21}H_{26}NO_2$ ($[M + H]^+$) 292.1696, Found 292.1695.



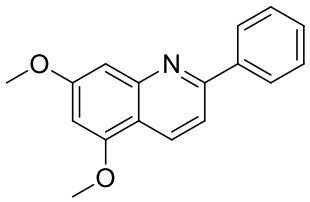
2i

2-(5,7-Dimethoxy-3-methylquinolin-2-yl)phenol (2i). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 2-hydroxybenzaldehyde (37 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2i** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 39 mg (44%). Data for **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.72-7.63 (m, 1H), 7.36-7.27 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.99-6.86 (m, 2H), 6.51-6.45 (m, 1H), 3.95 (d, *J* = 17.2 Hz, 6H), 2.67 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.5, 158.5, 158.2, 155.5, 146.1, 134.9, 130.9, 130.0, 126.3, 121.9, 118.4, 118.1, 115.5, 98.5, 97.9, 55.9, 55.8, 22.2 ppm; GC-MS for $C_{18}H_{17}NO_3$, *m/z* = 295 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{18}NO_3$ ($[M + H]^+$) 296.1281, Found 296.1281.



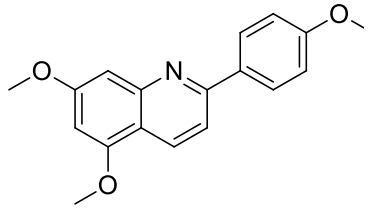
2j

7-Methyl-6-phenyl-[1,3]dioxolo[4,5]quinoline (2j). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), benzo[1,3]dioxol-5-amine (41 mg, 0.3 mmol), benzaldehyde (32 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2j** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 30 mg (38%). Data for **2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.60-7.37 (m, 6H), 7.02 (s, 1H), 6.09 (s, 2H), 2.41 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.1, 150.2, 147.9, 144.7, 141.0, 136.1, 129.0, 128.4, 128.1, 127.4, 124.6, 105.9, 101.9, 101.7, 20.4 ppm; GC-MS for $C_{17}H_{13}NO_2$, *m/z* = 263 (M^+); HRMS (ESI-TOF) Calcd for $C_{17}H_{14}NO_2$ ($[M + H]^+$) 264.1019, Found 264.1019.



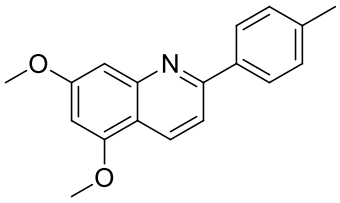
2k

5,7-Dimethoxy-2-phenylquinoline (2k). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), benzaldehyde (36 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2k** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 31 mg (40%). Data for **2k**:^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dt, *J* = 8.6, 1.1 Hz, 1H), 8.13 (dt, *J* = 8.2, 1.2 Hz, 2H), 7.68 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.55-7.48 (m, 2H), 7.48-7.42 (m, 1H), 7.37-7.30 (m, 1H), 7.12 (dd, *J* = 2.2, 1.2 Hz, 1H), 6.50 (t, *J* = 1.7 Hz, 1H), 3.96 (d, *J* = 1.3 Hz, 6H) ppm; $^{13}C\{^{1}H\}$ NMR 101 MHz, $CDCl_3$) δ 161.6, 158.1, 156.0, 131.7, 129.3, 128.9, 127.6, 116.1, 115.7, 100.0, 98.1, 92.1, 90.4, 55.9, 55.8 ppm; GC-MS for $C_{17}H_{15}NO_2$, *m/z* = 265 (M^+); ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[S5]



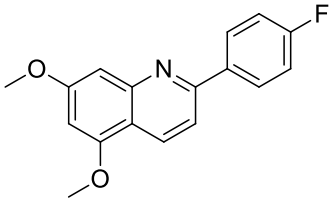
2l

5,7-Dimethoxy-2-(4-methoxyphenyl)quinoline (2l). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-methoxybenzaldehyde (41 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2l** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 51 mg (57%). Data for **2l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.7 Hz, 1H), 8.15-8.05 (m, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.10 (s, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 2.2 Hz, 1H), 3.97 (d, *J* = 4.6 Hz, 6H), 3.88 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6, 160.9, 157.6, 156.1, 150.3, 132.2, 131.7, 129.0, 115.6, 115.4, 114.3, 99.9, 97.8, 55.9, 55.8, 55.5 ppm; GC-MS for $C_{18}H_{17}NO_3$, *m/z* = 295 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{18}NO_3$ ($[M + H]^+$) 296.1281, Found 296.1266.



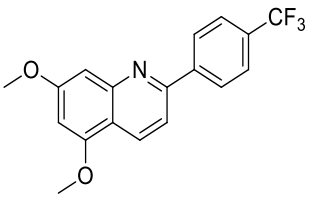
2m

5,7-Dimethoxy-2-(*p*-tolyl)quinoline (2m). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-methylbenzaldehyde (36 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2m** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 35 mg (42%). Data for **2m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 8.7, 2.4 Hz, 1H), 8.08-8.00 (m, 2H), 7.66 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.35-7.28 (m, 2H), 7.10 (s, 1H), 6.48 (s, 1H), 3.96 (s, 6H), 2.43 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.4, 158.1, 156.0, 150.5, 139.3, 137.1, 131.4, 129.6, 127.5, 115.8, 115.5, 100.1, 97.8, 55.8, 55.7, 21.4 ppm; GC-MS for $C_{18}H_{17}NO_2$, *m/z* = 279 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{18}NO_2$ ([M + H]$^+$) 280.1332, Found 280.1335.



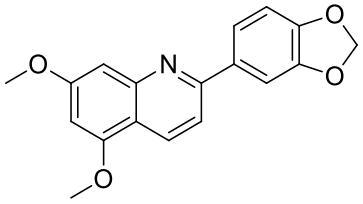
2n

2-(4-Fluorophenyl)-5,7-dimethoxyquinoline (2n). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-flourobenzaldehyde (37 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2n** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 44 mg (52%). Data for **2n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.6, 0.8 Hz, 1H), 8.19-8.05 (m, 2H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.24-7.14 (m, 2H), 7.10 (d, *J* = 2.1 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 1H), 3.97 (d, *J* = 6.2 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.1, 162.6, 161.8, 157.0, 156.1, 150.4, 131.9, 129.6, 129.5, 115.9, 115.7 (d, J_{CF} = 1.7 Hz), 99.9, 98.2, 55.9, 55.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.79 ppm; GC-MS for $C_{17}H_{14}FNO_2$, *m/z* = 283 (M^+); HRMS (ESI-TO2oalcd for $C_{17}H_{15}FNO_2$ ([M + H]$^+$) 284.1081, Found 284.1089.



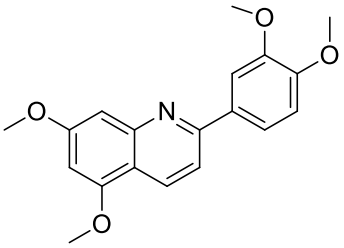
2o

5,7-Dimethoxy-2-(4-(trifluoromethyl)phenyl)quinoline (2o). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-(triflouromethyl)benzaldehyde (52 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2o** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 53 mg (53%). Data for **2o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.6 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.09 (s, 1H), 6.53 (s, 1H), 3.98 (d, *J* = 7.3 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.9, 156.4, 156.0, 150.5, 143.1, 132.0, 127.9, 126.8, 125.8 (dd, J_{CF} = 7.6, 4.0 Hz), 123.0, 116.1, 115.9, 100.0, 98.6, 55.9, 55.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.79 ppm; GC-MS for $C_{18}H_{14}F_3NO_2$, *m/z* = 333 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{15}F_3NO_2$ ([M + H]$^+$) 334.1049, Found 334.1055.



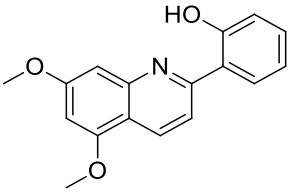
2p

2-(Benzo[1,3]dioxol-5-yl)-5,7-dimethoxyquinoline (2p). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), benzo[1,3]dioxole-5-carbaldehyde (45 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2p** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 41 mg (44%). Data for **2p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 1.7 Hz, 1H), 7.64 (dd, J = 8.1, 1.8 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.12 (s, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.49 (d, J = 2.2 Hz, 1H), 6.04 (s, 2H), 3.97 (d, J = 4.7 Hz, 6H) ppm; ^{13}C{^{1}H}(101 MHz, $CDCl_3$) δ 161.7, 157.4, 156.1, 148.9, 148.4, 131.8, 122.0, 115.7, 115.5, 108.6, 108.1, 101.5, 99.8, 98.1, 55.9, 55.8 ppm; GC-MS for $C_{18}H_{15}NO_4$, *m/z* = 309 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{16}NO_4$ ($[M + H]^+$) 310.1074, Found 310.1081.



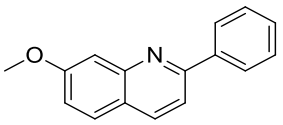
2q

2-(3,4-Dimethoxyphenyl)-5,7-dimethoxyquinoline (2q). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 3,4-dimethoxybenzaldehyde (50 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2q** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 43 mg (44%). Data for **2q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.68-7.62 (m, 2H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 2.2 Hz, 1H), 4.05 (s, 3H), 3.99-3.94 (m, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.8, 157.4, 156.1, 150.5, 149.4, 131.9, 120.5, 115.6, 115.4, 111.1, 110.6, 99.7, 98.0, 56.2, 56.1, 55.9, 55.8 ppm; GC-MS for $C_{19}H_{19}NO_4$, *m/z* = 325 (M^+); HRMS (ESI-TOF) Calcd for $C_{19}H_{20}NO_4$ ($[M + H]^+$) 326.1387, Found 326.1391.



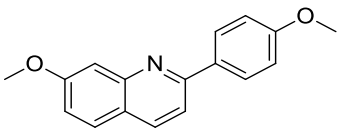
2r

2-(5,7-Dimethoxyquinolin-2-yl)phenol (2r). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), salicylaldehyde (37 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2r** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 45 mg (53%). Data for **2r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.9 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.35 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.98-6.87 (m, 2H), 6.49 (d, *J* = 2.1 Hz, 1H), 3.96 (d, *J* = 7.9 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.3, 160.9, 158.2, 156.1, 146.6, 132.5, 131.9, 127.0, 118.9, 118.7, 118.7, 114.9, 113.9, 98.3, 97.9, 55.8, 55.8 ppm; GC-MS for $C_{17}H_{15}NO_3$, *m/z* = 281 (M^+); HRMS (ESI-TOF) Calcd for $C_{17}H_{16}NO_3$ ($[M + H]^+$) 282.1125, Found 282.1129.



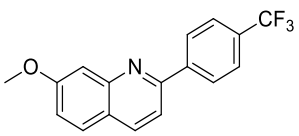
2s

7-Methoxy-2-phenylquinoline (2s). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3-methoxyaniline (37 mg, 0.3 mmol), benzaldehyde (32 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2s** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 26 mg (37%). Data for **2s**:^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 3H), 7.73 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.62-7.58 (m, 1H), 7.51 (dt, *J* = 13.0, 6.9 Hz, 3H), 7.20 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.99 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.3, 157.6, 137.0, 137.0, 129.5, 129.0, 128.6, 127.8, 122.6, 119.9, 117.1, 107.4, 106.4, 55.8 ppm; GC-MS for $C_{16}H_{13}NO$, *m/z* = 235 (M^+); HRMS (ESI-TOF) Calcd for $C_{16}H_{14}NO$ ([M + H]$^+$) 236.10699, Found 236.1075.



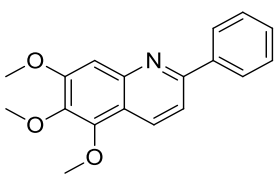
2t

7-Methoxy-2-(4-methoxyphenyl)quinoline (2t). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3-methoxyaniline (37 mg, 0.3 mmol), 4-methoxybenzaldehyde (41 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2t** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 25 mg (31%). Data for **2t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 12.4, 8.7 Hz, 3H), 7.68 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.48 (s, 1H), 7.15 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 3.98 (s, 3H), 3.88 (s, 3H) ppm;$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.1, 160.9, 158.7, 157.2, 149.8, 136.7, 129.1, 128.6, 122.2, 119.3, 116.6, 114.3, 107.3, 55.7, 55.5 ppm; GC-MS for $C_{17}H_{13}NO_3$, *m/z* = 279 (M^+); ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature values.[S6]



2u

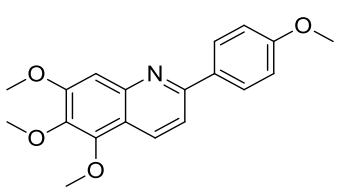
7-Methoxy-2-(4-(trifluoromethyl)phenyl)quinoline (2u). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3-methoxyaniline (37 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (52 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2u** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 37 mg (41%). Data for **2u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.79 (s, 1H), 7.77-7.74 (m, 2H), 7.72 (d, *J* = 3.2 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.22 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.99 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.4, 156.0, 150.0, 143.1, 139.3, 137.0, 128.7, 128.0, 125.8 (dd, J_{CF} = 7.9, 4.0 Hz), 122.9, 120.4, 116.9, 107.6, 106.2, 55.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.69 ppm; GC-MS for $C_{17}H_{12}F_3NO$, *m/z* = 303 (M^+); HRMS (ESI-TOF) Calcd for $C_{17}H_{13}F_3NO$ ([M + H]$^+$) 304.0944, Found 304.0945.



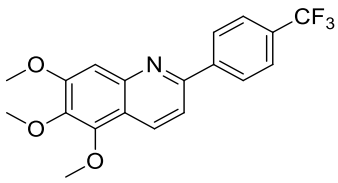
2v

5,6,7-Trimethoxy-2-phenylquinoline (2v). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,4,5-trimethoxyaniline (55 mg, 0.3 mmol), benzaldehyde (46 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2v** was isolated using column chromatography on silica gel (hexanes/EtOAc

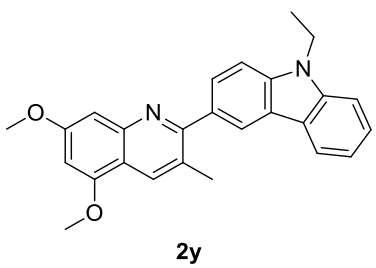
= 100:1 to 95:5). Yield: 35 mg (39%). Data for **2v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 7.0 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.48 (dt, *J* = 23.2, 8.2 Hz, 4H), 4.09 (s, 3H), 4.04 (s, 3H), 4.00 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.9, 156.4, 147.1, 145.8, 142.7, 140.9, 131.6, 129.4, 129.0, 127.6, 118.3, 116.9, 104.3, 61.8, 61.4, 56.3 ppm; GC-MS for $C_{18}H_{17}NO_3$, *m/z* = 295 (M^+); HRMS (ESI-TOF) Calcd for $C_{18}H_{18}NO_3$ ($[M + H]^+$) 296.1281, Found 296.1294.


2w

5,6,7-Trimethoxy-2-(4-methoxyphenyl)quinoline (2w). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,4,5-trimethoxyaniline (55 mg, 0.3 mmol),4-methoxybenzaldehyde (41 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2w** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 49 mg (50%). Data for **2w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.6 Hz, 1H), 8.10 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.6 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 7.04 (d, J = 8.6 Hz, 2H), 4.08 (s, 3H), 4.03 (s, 3H), 3.99 (s, 3H), 3.88 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.1, 154.0, 147.1, 144.9, 140.7, 130.5, 129.1, 128.1, 118.0, 116.4, 114.4, 114.2, 103.9, 61.8, 61.4, 61.2, 56.4 ppm; GC-MS for $C_{19}H_{19}NO_4$, *m/z* = 325 (M^+); HRMS (ESI-TOF) Calcd for $C_{19}H_{20}NO_4$ ($[M + H]^+$) 326.1386, Found 326.1402.

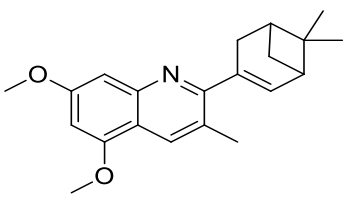

2x

5,6,7-Trimethoxy-2-(4-(trifluoromethyl)phenyl)quinoline (2x). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,4,5-trimethoxyaniline (55 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (52 mg, 0.3 mmol) and triethylamine (30 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2x** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 47 mg (43%). Data for **2x**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 8.0 Hz, 2H), 7.80 – 7.69 (m, 3H), 7.33 (s, 1H), 4.09 (s, 3H), 4.04 (s, 3H), 4.01 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.5, 155.3, 147.0, 146.2, 143.2, 141.2, 131.6, 131.1, 130.8, 127.8, 125.8 (dd, J_{CF} = 7.5, 4.0 Hz), 118.7, 116.7, 104.5, 61.8, 61.4, 56.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.62 ppm; GC-MS for $C_{19}H_{16}F_3NO_3$, *m/z* = 363 (M^+); HRMS (ESI-TOF) Calcd for $C_{19}H_{17}F_3NO_3$ ($[M + H]^+$) 364.1155, Found 364.1156.


2y

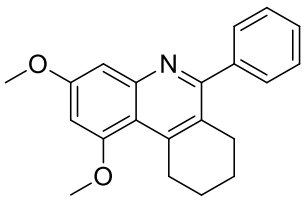
3-(5,7-Dimethoxy-3-methylquinolin-2-yl)-9-ethyl-9*H*-carbazole (2y). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 9-ethyl-9H-carbazole-3-carbaldehyde (67 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2y** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 53 mg (44%). Data for **2y**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.3 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.49 (dd, *J* = 15.0, 7.9 Hz, 3H), 7.26-7.23 (m, 1H), 7.16-7.10 (m, 1H), 6.52 (d, *J* = 1.9 Hz, 1H), 4.43 (q, *J* = 7.3 Hz, 2H), 4.01

(s, 3H), 3.94 (s, 3H), 2.53 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.8, 160.7, 155.6, 148.8, 140.5, 139.9, 132.0, 131.8, 127.0, 126.4, 125.8, 123.3, 123.0, 121.3, 120.8, 119.1, 115.8, 108.7, 108.3, 99.8, 97.9, 55.9, 55.7, 37.8, 21.0, 14.0 ppm; GC-MS for $C_{22}H_{26}N_2O_2$, *m/z* = 396 (M^+); HRMS (ESI-TOF) Calcd for $C_{22}H_{27}N_2O_2$ ($[M + H]^+$) 397.1911, Found 397.1908.



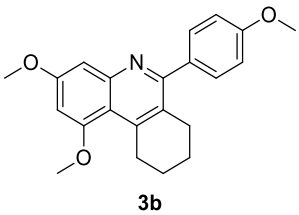
2z

2-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-3-yl)-5,7-dimethoxy-3-methylquinoline (2z). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), myrtenal (50 mg, 0.3 mmol) and triallylamine (41 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **2z** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 37 mg (38%). Data for **2z**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.00 (d, J = 2.1 Hz, 1H), 6.43 (d, J = 2.2 Hz, 1H), 5.95 (m, 1H), 3.92 (d, J = 8.1 Hz, 6H), 2.69 (m, 1H), 2.58 (m, 1H), 2.51 (m, 2H), 2.42 (d, J = 0.8 Hz, 3H), 2.21 (m, 1H), 1.53 (d, J = 8.7 Hz, 1H), 1.37 (s, 3H), 1.09 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) 161.2, 160.3, 155.4, 149.1, 148.7, 131.3, 125.7, 124.9, 115.5, 99.9, 97.6, 55.8, 55.7, 46.2, 40.7, 38.3, 32.3, 32.1, 26.5, 21.8, 20.4 ppm; GC-MS for $C_{21}H_{25}NO_2$, *m/z* = 323 (M^+); HRMS (ESI-TOF) Calcd for $C_{21}H_{26}NO_2$ ($[M + H]^+$) 324.1958, Found 324.1955.



3a

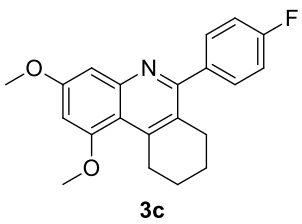
1,3-Dimethoxy-6-phenyl-7,8,9,10-tetrahydrophenanthridine (3a). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), benzaldehyde (36 mg, 0.3 mmol) and 4-(cyclohex-1-en-1-yl)morpholine (50 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3a** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 32 mg (33%). Data for **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.37 (m, 5H), 7.09 (s, 1H), 6.50 (s, 1H), 3.89 (s, 6H), 3.49 (t, J = 6.1 Hz, 2H), 2.65 (t, J = 5.9 Hz, 2H), 1.82 (p, J = 5.9 Hz, 2H), 1.73-1.65 (m, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0, 159.6, 158.6, 149.0, 145.2, 141.4, 128.6, 128.3, 127.9, 126.1, 115.6, 101.1, 98.9, 55.6, 55.6, 30.2, 29.2, 23.2, 22.3 ppm; GC-MS for $C_{21}H_{21}NO_2$, *m/z* = 319 (M^+); HRMS (ESI-TOF) Calcd for $C_{21}H_{22}NO_2$ ($[M + H]^+$) 320.1645, Found 320.1660.



3b

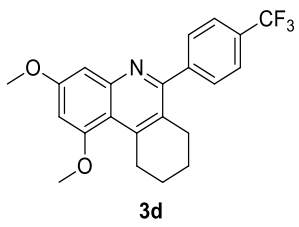
1,3-Dimethoxy-6-(4-methoxyphenyl)-7,8,9,10-tetrahydrophenanthridine (3b). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), benzaldehyde (36 mg, 0.3 mmol) and 4-(cyclohex-1-en-1-yl)morpholine (50 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3b** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 58 mg (55%). Data for **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.07 (s, 1H), 6.98 (d, J = 8.1 Hz, 2H), 6.49 (d, J = 1.7 Hz, 1H), 3.92-3.83 (m, 8H), 3.49 (t, J = 6.3 Hz, 2H), 2.68 (t, J = 6.1 Hz, 2H), 1.82 (m, 3H), 1.69 (m, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.7, 159.5, 159.4, 158.5,

149.2, 144.9, 130.0, 128.9, 126.3, 115.4, 113.7, 101.1, 98.7, 55.5, 55.5, 55.4, 30.1, 29.4, 23.2, 22.4 ppm; GC-MS for $C_{22}H_{23}NO_3$, *m/z* = 349 (M^+); HRMS (ESI-TOF) Calcd for $C_{22}H_{24}NO_3$ ($[M + H]^+$) 350.1750, Found 350.1766.



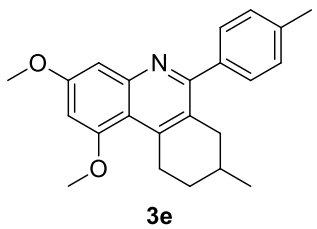
3c

6-(4-Fluorophenyl)-1,3-dimethoxy-7,8,9,10-tetrahydrophenanthridine (3c). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-fluorobenzaldehyde (37 mg, 0.3 mmol) and 4-(cyclohex-1-en-1-yl)morpholine (50 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3c** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 64 mg (63%). Data for **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.13 (t, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.89 (s, 6H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.63 (t, *J* = 6.3 Hz, 2H), 1.82 (m, 2H), 1.69 (m, 2H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.9, 161.4, 159.7, 158.6, 149.1, 145.3, 137.5, 130.6 (d, J_{CF} = 8.3 Hz), 126.1, 115.6, 115.2 (d, J_{CF} = 22.3 Hz), 101.0, 99.0, 55.6, 55.6, 30.2, 29.3, 23.1, 22.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.68 ppm; GC-MS for $C_{21}H_{20}FNO_2$, *m/z* = 337 (M^+); HRMS (ESI-TOF) Calcd for $C_{21}H_{21}FNO_2$ ($[M + H]^+$) 338.1551, Found 338.1547.



3d

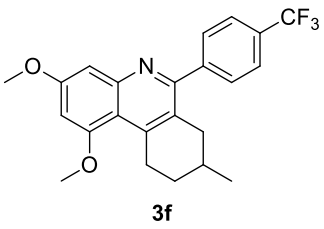
1,3-Dimethoxy-6-(4-(trifluoromethyl)phenyl)-7,8,9,10-tetrahydrophenanthridine (3d). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (52 mg, 0.3 mmol) and 4-(cyclohex-1-en-1-yl)morpholine (50 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3d** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 60 mg (52%). Data for **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 2.2 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 3.90 (d, *J* = 6.6 Hz, 6H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 6.1 Hz, 2H), 1.83 (dt, *J* = 12.3, 6.2 Hz, 2H), 1.71 (dt, *J* = 11.5, 6.0 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.9, 159.6, 158.7, 149.3, 145.6, 145.3, 130.3, 129.9, 129.2, 125.8, 125.4 (dd, J_{CF} = 7.4, 3.6 Hz), 115.9, 101.1, 99.3, 55.7, 55.6, 30.2, 29.2, 23.2, 22.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.64 ppm; GC-MS for $C_{22}H_{20}F_3NO_2$, *m/z* = 387 (M^+); HRMS (ESI-TOF) Calcd for $C_{22}H_{21}F_3NO_2$ ($[M + H]^+$) 388.1519, Found 388.1516.



3e

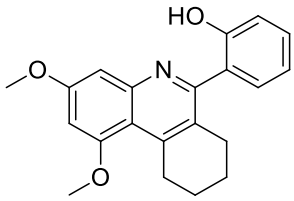
1,3-Dimethoxy-8-methyl-6-(*p*-tolyl)-7,8,9,10-tetrahydrophenanthridine (3e). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-methylbenzaldehyde (36 mg, 0.3 mmol) and 4-(4-methylcyclohex-1-en-1-yl)morpholine (54 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3e** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 50 mg (48%). Data for **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 7.05 (s, 1H), 6.48 (d, *J* = 2.3 Hz, 1H), 3.89 (s, 6H), 3.70 (d, *J* = 19.5 Hz, 1H), 3.34 (dt, *J* = 18.8, 8.3 Hz, 1H), 2.68 (dd, *J* = 16.5, 5.4 Hz, 1H), 2.41 (s, 3H), 2.31 (dd, *J* = 16.2, 11.1 Hz, 1H), 1.98-1.85

(m, 1H), 1.68 (s, 1H), 1.42-1.30 (m, 1H), 0.98 (d, J = 4.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.1, 159.6, 158.6, 149.3, 144.5, 138.7, 137.6, 129.0, 128.6, 126.0, 115.4, 101.2, 98.8, 55.6, 55.6, 37.6, 31.4, 30.2, 28.3, 21.9, 21.5 ppm; GC-MS for $C_{23}H_{25}NO_2$, m/z = 347 (M^+); HRMS (ESI-TOF) Calcd for $C_{23}H_{26}NO_2$ ([M + H]$^+$) 348.1958, Found 348.1959.



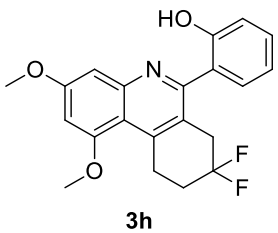
3f

1,3-Dimethoxy-8-methyl-6-(4-(trifluoromethyl)phenyl)-7,8,9,10-tetrahydrophenanthridine (3f). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (52 mg, 0.3 mmol) and 4-(4-methylcyclohex-1-en-1-yl)morpholine (54 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3f** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 54 mg (45%). Data for **3f**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.03 (s, 1H), 6.52 (d, J = 2.3 Hz, 1H), 3.91 (d, J = 7.6 Hz, 6H), 3.79-3.68 (m, 1H), 3.42-3.31 (m, 1H), 2.61 (dd, J = 17.0, 4.2 Hz, 1H), 2.29 (dd, J = 16.7, 10.1 Hz, 1H), 2.01-1.92 (m, 1H), 1.79-1.67 (m, 1H), 1.38 (m, 1H), 1.00 (d, J = 6.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.0, 159.5, 158.7, 149.3, 145.2, 130.3, 130.0, 129.2, 125.5, 125.4 (dd, J_{CF} = 7.8, 3.8 Hz), 123.0, 115.8, 101.1, 99.3, 55.7, 55.7, 37.5, 31.3, 30.2, 28.3, 21.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43 ppm; GC-MS for $C_{23}H_{22}F_3NO_2$, m/z = 401 (M^+); HRMS (ESI-TOF) Calcd for $C_{23}H_{23}F_3NO_2$ ([M + H]$^+$) 402.1675, Found 402.1671.



3g

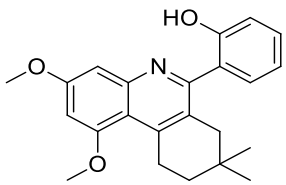
2-(1,3-Dimethoxy-7,8,9,10-tetrahydrophenanthridin-6-yl)phenol (3g). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), salicylaldehyde (37 mg, 0.3 mmol) and 4-(cyclohex-1-en-1-yl)morpholine (50 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3g** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 49 mg (49%). Data for **3g**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 1H), 7.30-7.24 (m, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.94-6.86 (m, 2H), 6.47 (d, J = 2.4 Hz, 1H), 3.90 (d, J = 9.8 Hz, 6H), 3.54-3.43 (m, 2H), 2.92 (t, J = 6.1 Hz, 2H), 1.86 (p, J = 6.5 Hz, 2H), 1.65 (p, J = 5.9 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.1, 158.6, 158.0, 157.2, 147.5, 147.1, 130.5, 130.3, 127.3, 123.2, 118.6, 118.1, 115.2, 99.6, 99.2, 55.7, 55.7, 30.1, 29.9, 23.1, 22.4 ppm; GC-MS for $C_{21}H_{21}NO_3$, m/z = 335 (M^+); HRMS (ESI-TOF) Calcd for $C_{21}H_{22}NO_3$ ([M + H]$^+$) 336.1594, Found 336.1597.



3h

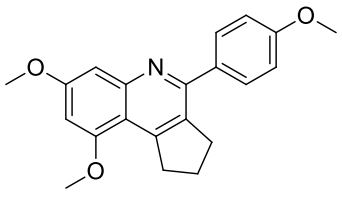
2-(8,8-Difluoro-1,3-dimethoxy-7,8,9,10-tetrahydrophenanthridin-6-yl)phenol (3h). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), salicylaldehyde (37 mg, 0.3 mmol) and 4-(4,4-difluorocyclohex-1-en-1-yl)morpholine (61 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3h** was isolated using column chromatography on silica gel

(hexanes/EtOAc = 100:1 to 95:5). Yield: 67 mg (60%). Data for **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.99-6.90 (m, 3H), 6.52 (s, 1H), 3.92 (s, 6H), 3.72 (t, J = 6.6 Hz, 2H), 3.35 (t, J = 14.6 Hz, 2H), 2.30-2.17 (m, 2H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.8, 158.2, 157.9, 155.9, 147.4, 144.5, 141.6, 131.0, 129.9, 122.4, 119.6, 118.7, 114.2, 99.6, 99.2, 55.8, 55.8, 36.6 (t, J_{CF} = 27.3 Hz), 30.3 (t, J_{CF} = 23.8 Hz) , 27.9 (t, J_{CF} = 5.0 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.24 ppm; GC-MS for $C_{21}H_{19}F_2NO_3$, m/z = 371 (M^+); HRMS (ESI-TOF) Calcd for $C_{21}H_{20}F_2NO_3$ ([M + H]$^+$) 372.1406, Found 372.1407.



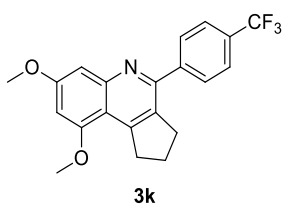
3i

2-(8,8-Dimethyl-1,3-dimethoxy-7,8,9,10-tetrahydrophenanthridin-6-yl)phenol (3i). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), salicylaldehyde (37 mg, 0.3 mmol) and 4-(4,4-dimethylcyclohex-1-en-1-yl)morpholine (58 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3i** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 59 mg (54%). Data for **3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 6.93 (t, J = 7.4 Hz, 1H), 6.52 (s, 1H), 3.92 (s, 6H), 3.56 (t, J = 6.4 Hz, 2H), 2.73 (s, 2H), 1.65 (t, J = 6.4 Hz, 2H), 0.90 (s, 6H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 158.7, 157.9, 157.3, 147.4, 146.6, 130.6, 130.4, 126.1, 122.5, 118.6, 118.0, 115.0, 99.4, 99.1, 55.8, 55.8, 42.9, 35.5, 28.6, 28.1, 27.6 ppm; GC-MS for $C_{23}H_{25}NO_3$, m/z = 363 (M^+); HRMS (ESI-TOF) Calcd for $C_{23}H_{26}NO_3$ ([M + H]$^+$) 364.1907, Found 364.1905.



3j

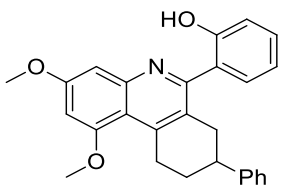
7,9-Dimethoxy-4-(4-methoxyphenyl)-2,3-dihydro-1*H*-cyclopentaquinoline (3j). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-methoxybenzaldehyde (41 mg, 0.3 mmol) and 4-(cyclopent-1-en-1-yl)morpholine (46 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3j** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 51 mg (52%). Data for **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.10 (s, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.45 (d, J = 1.7 Hz, 1H), 3.92 (d, J = 5.4 Hz, 6H), 3.87 (s, 3H), 3.54 (t, J = 7.5 Hz, 2H), 3.10 (t, J = 7.5 Hz, 2H), 2.12 (p, J = 7.6 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 160.0, 157.4, 155.7, 151.3, 150.1, 133.2, 132.8, 130.2, 114.1, 113.8, 100.3, 98.0, 55.7, 55.6, 55.5, 35.4, 32.7, 25.4 ppm; GC-MS for $C_{21}H_{21}NO_3$, m/z = 335 (M^+); HRMS (ESI-TOF) Calcd for $C_{21}H_{22}NO_3$ ([M + H]$^+$) 336.1594, Found 336.1593.



3k

7,9-Dimethoxy-4-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-cyclopentaquino line (3k). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (52 mg, 0.3 mmol) and 4-(cyclopent-1-en-1-yl)morpholine (46 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3k** was isolated using column chromatography on silica gel

(hexanes/EtOAc = 100:1 to 95:5). Yield: 53 mg (48%). Data for **3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.9 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.12 (s, 1H), 6.49 (s, 1H), 3.92 (d, J = 7.5 Hz, 6H), 3.56 (t, J = 7.4 Hz, 2H), 3.06 (t, J = 7.4 Hz, 2H), 2.13 (p, J = 7.2 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.9, 160.6, 157.3, 154.5, 151.9, 150.2, 132.8, 129.1, 125.3 (dd, J_{CF} = 7.5, 3.6 Hz), 114.6, 100.2, 98.6, 92.1, 90.4, 55.6, 55.6, 35.4, 32.3, 25.3 ppm; GC-MS for $C_{21}H_{18}F_3NO_2$, *m/z* = 373 (M^+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.67 ppm; HRMS (ESI-TOF) Calcd for $C_{21}H_{19}F_3NO_2$ ($[M + H]^+$) 374.1383, Found 374.1376.

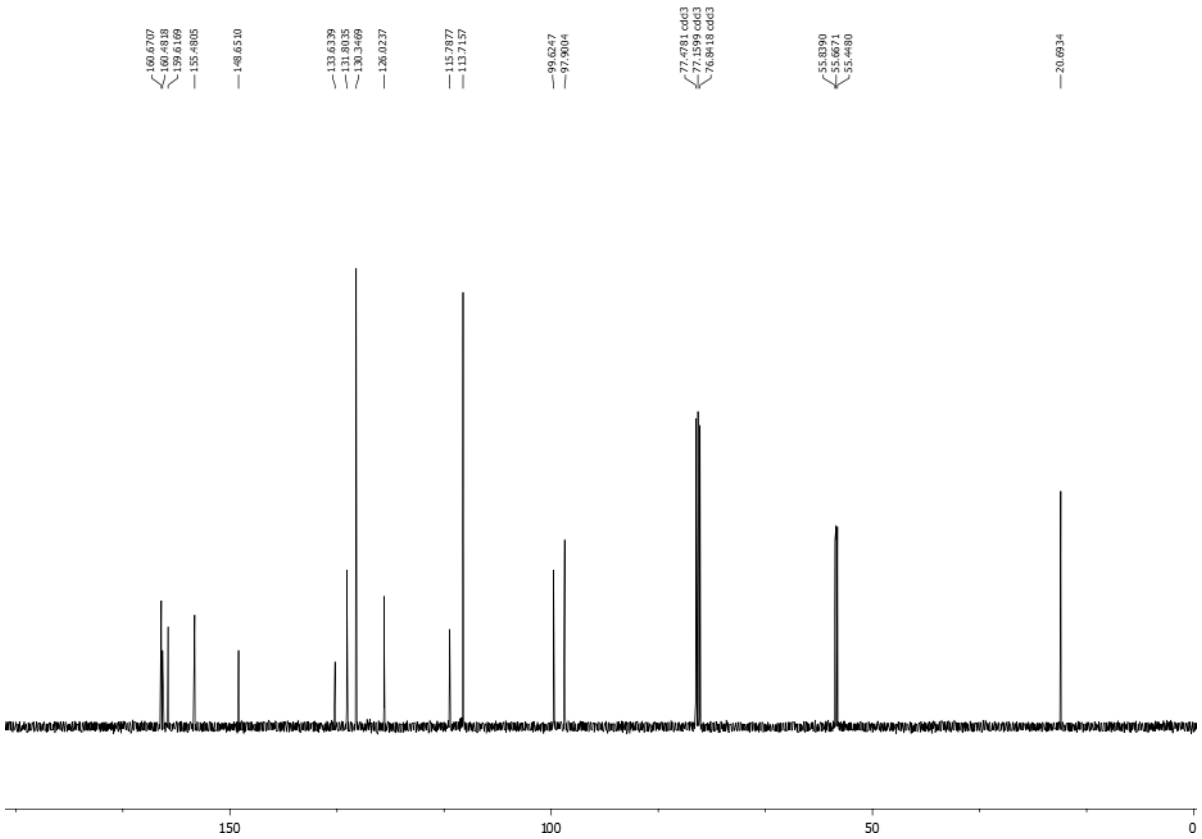


3l

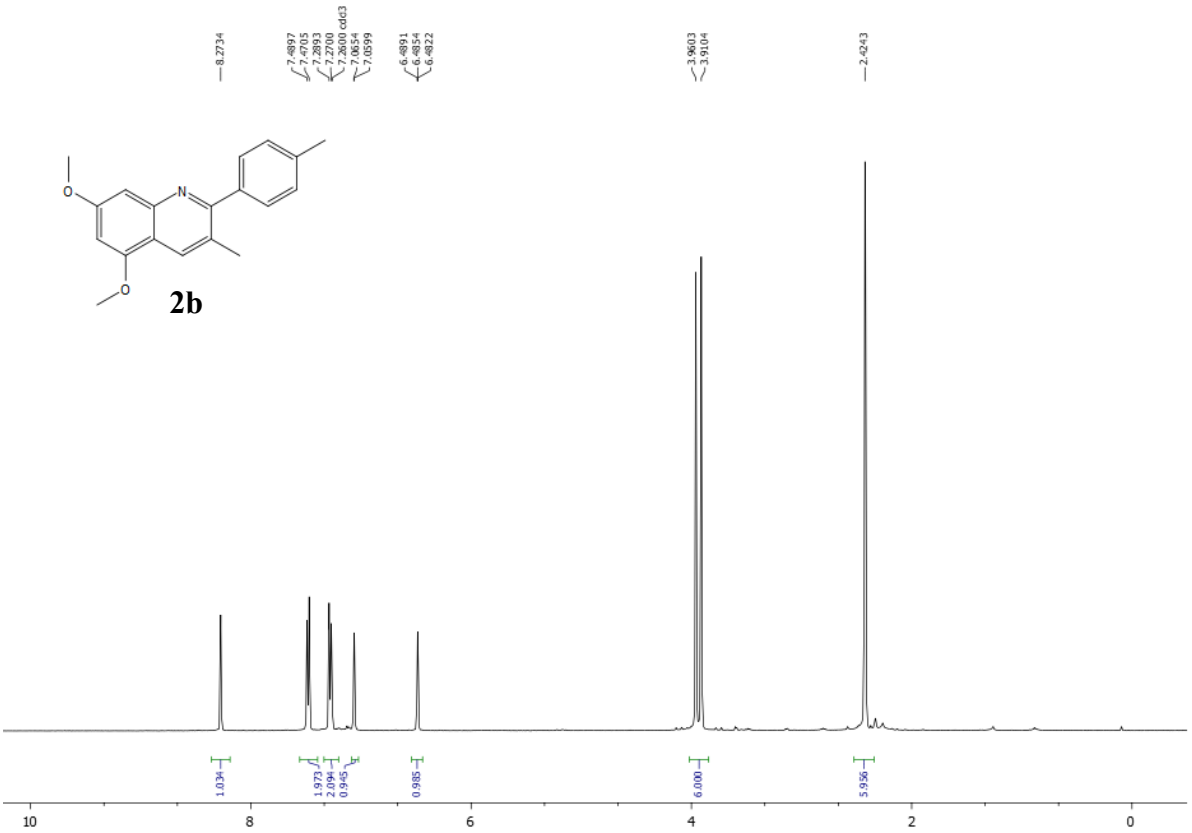
2-(1,3-Dimethoxy-8-phenyl-7,8,9,10-tetrahydrophenanthridin-6-yl)phenol (3l). A 1,2-dicholoroethane (1.5 mL) solution of complex **1** (11 mg, 5 mol %), 3,5-dimethoxyaniline (46 mg, 0.3 mmol), salicylaldehyde (37 mg, 0.3 mmol) and 4-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)morpholine (73 mg, 0.3 mmol) was stirred at 125 °C for 20 h. The product **3l** was isolated using column chromatography on silica gel (hexanes/EtOAc = 100:1 to 95:5). Yield: 54.3 mg (44%). Data for **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27-7.20 (m, 4H), 7.08-6.99 (m, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 2.3 Hz, 1H), 3.98-3.89 (m, 6H), 3.59-3.48 (m, 1H), 3.13 (q, *J* = 8.2, 4.9 Hz, 2H), 2.78-2.70 (m, 1H), 2.26 (d, *J* = 11.7 Hz, 1H), 2.02 (m, 1H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 158.7, 157.7, 157.1, 147.5, 146.8, 146.0, 130.7, 130.2, 128.7, 127.0, 126.9, 126.5, 122.5, 118.9, 118.1, 115.1, 99.5, 99.2, 55.8, 39.8, 37.9, 31.1, 30.1 ppm; GC-MS for $C_{27}H_{25}NO_3$, *m/z* = 411 (M^+); HRMS (ESI-TOF) Calcd for $C_{27}H_{26}NO_3$ ($[M + H]^+$) 412.1907, Found 412.1908.

9. ^{1}H NMR of 2a (400 MHz, $CDCl_3$)

^{13}C{^{1}H} NMR of 2a (101 MHz, $CDCl_3$)

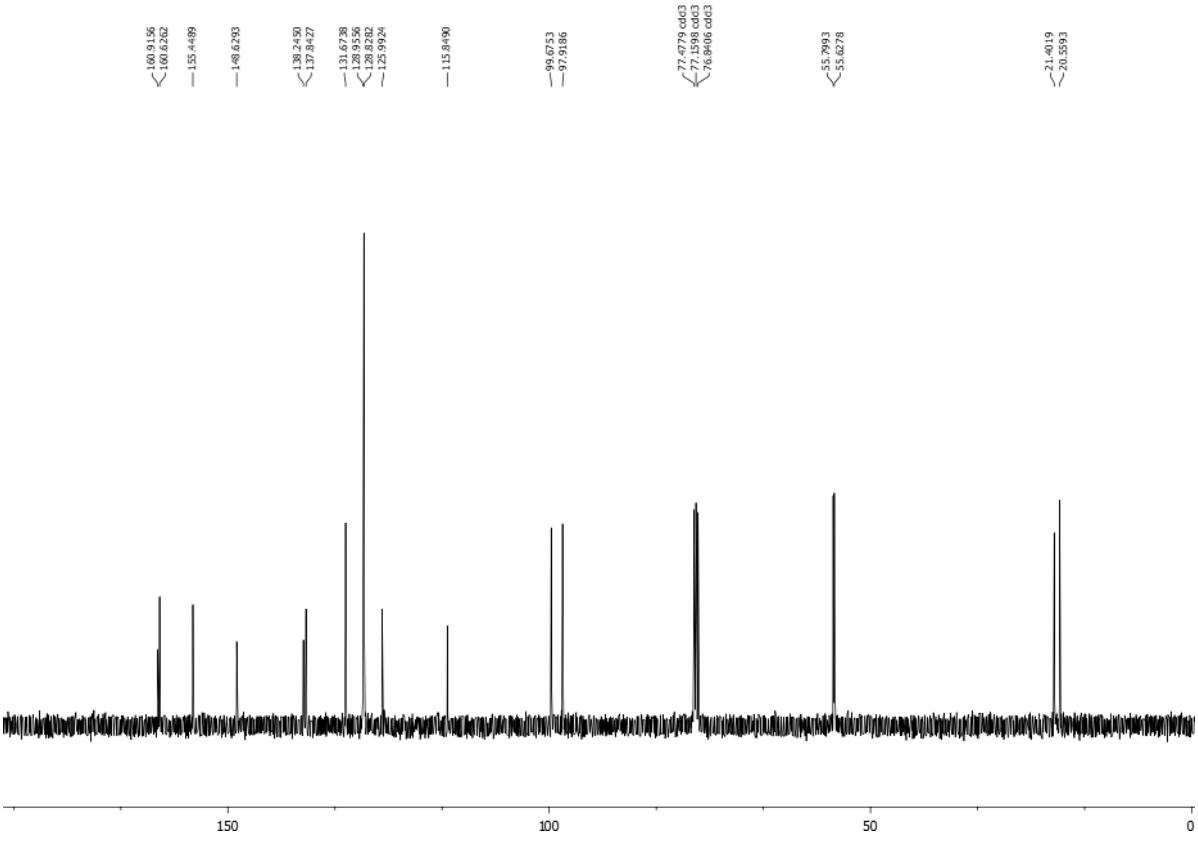


^{1}H NMR of 2b (400 MHz, $CDCl_3$)

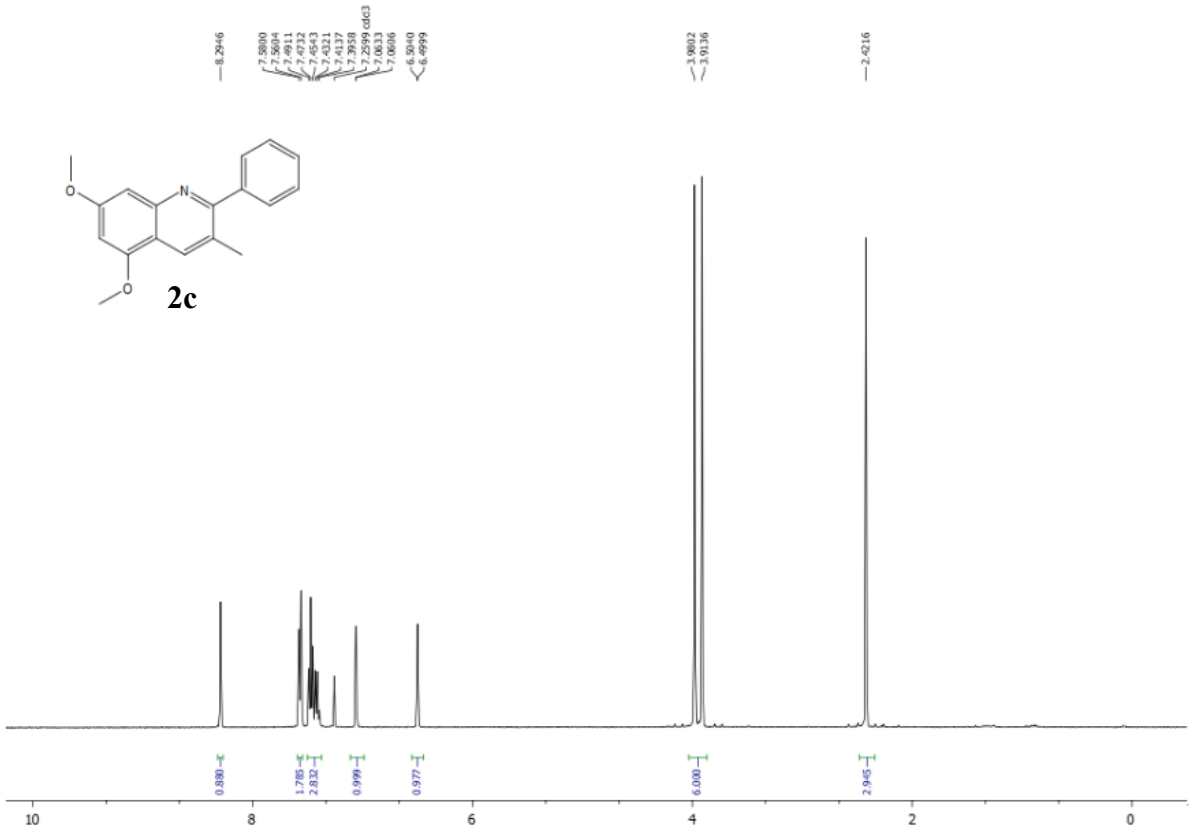


2b

^{13}C{^{1}H} NMR of 2b (101 MHz, $CDCl_3$)

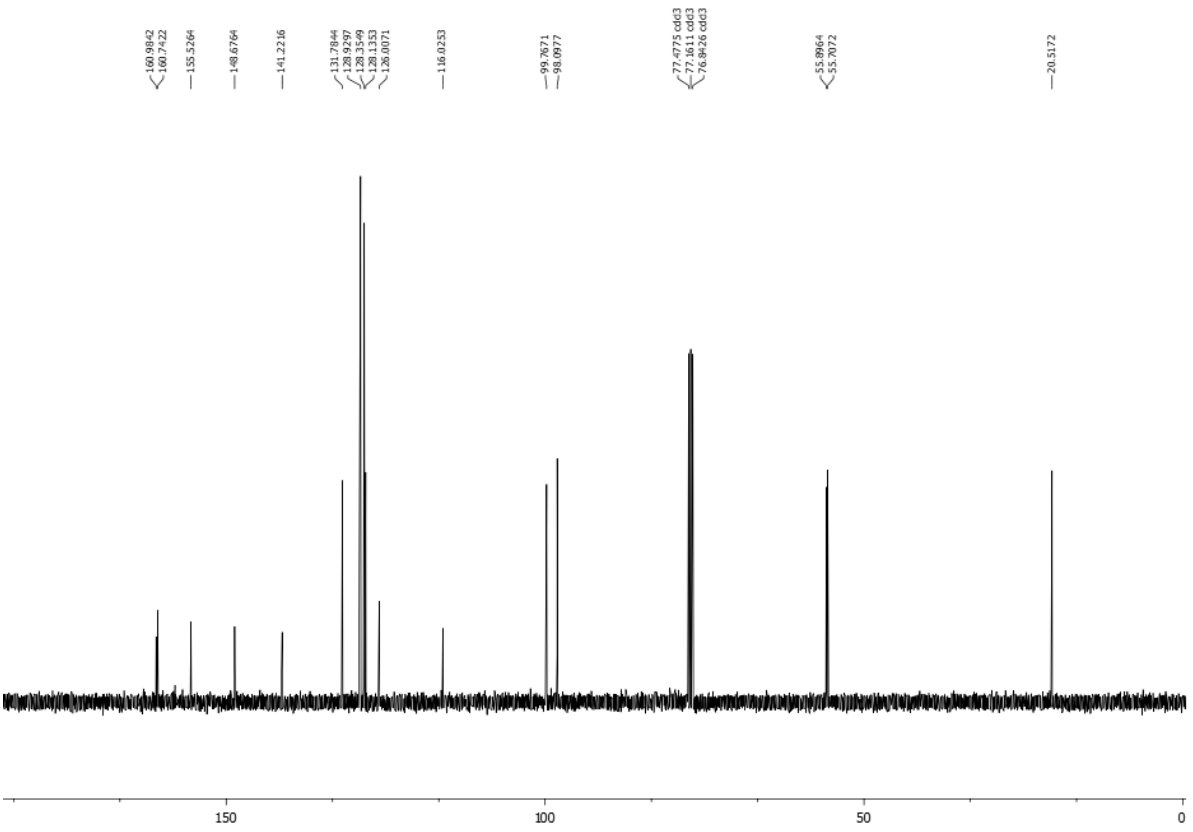


^{1}H NMR of 2c (400 MHz, $CDCl_3$)

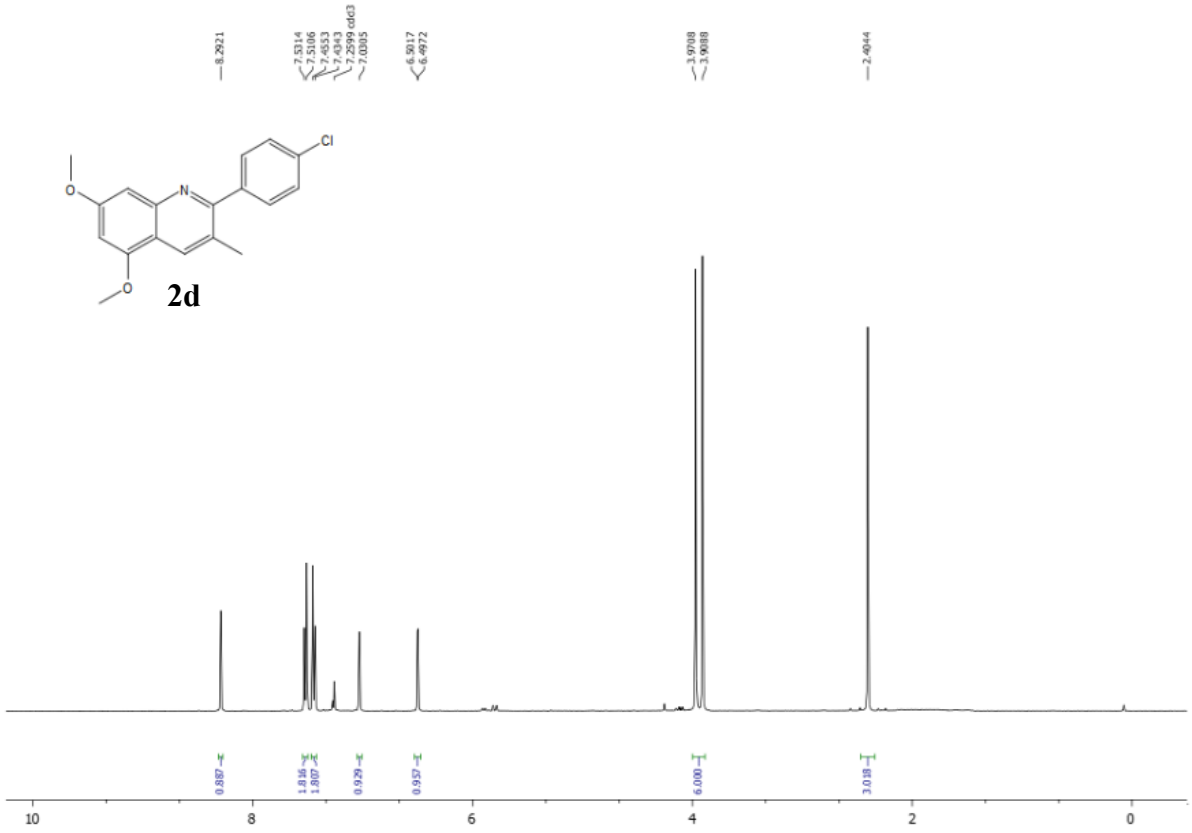


2c

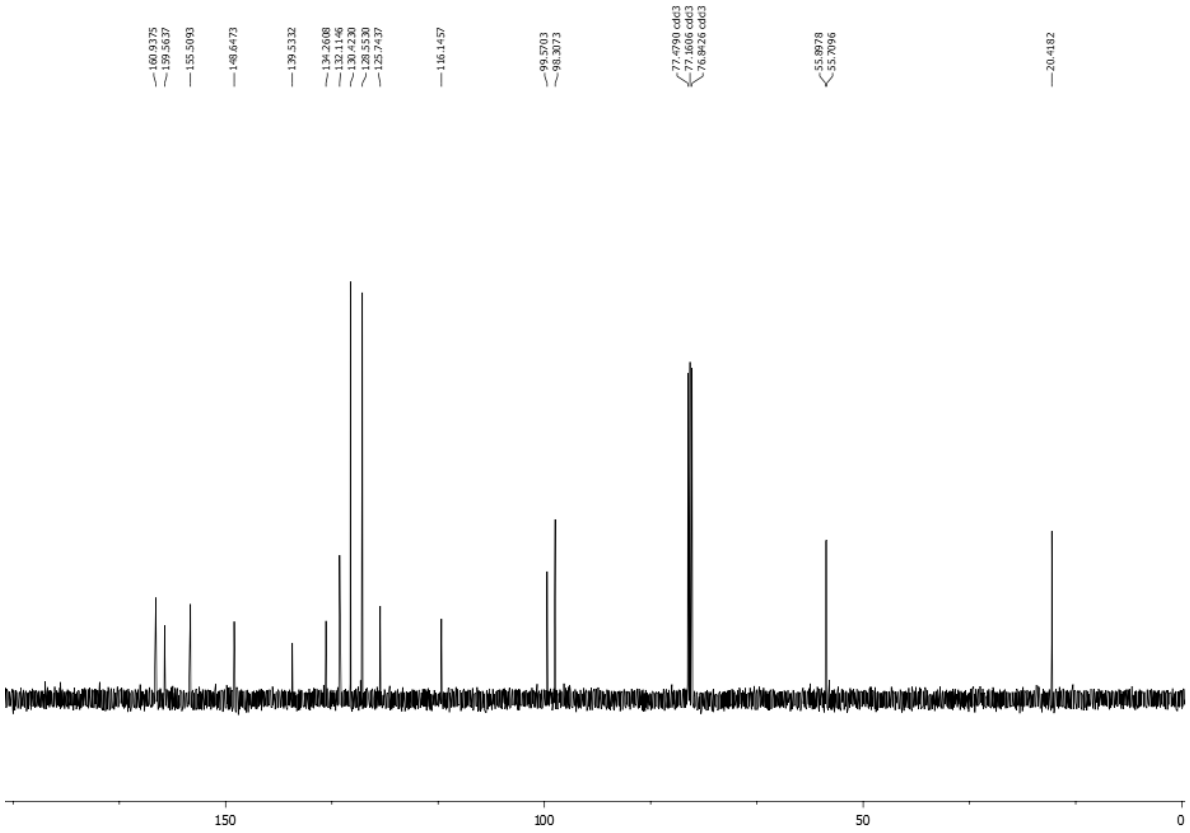
^{13}C{^{1}H} NMR of 2c (101 MHz, $CDCl_3$)



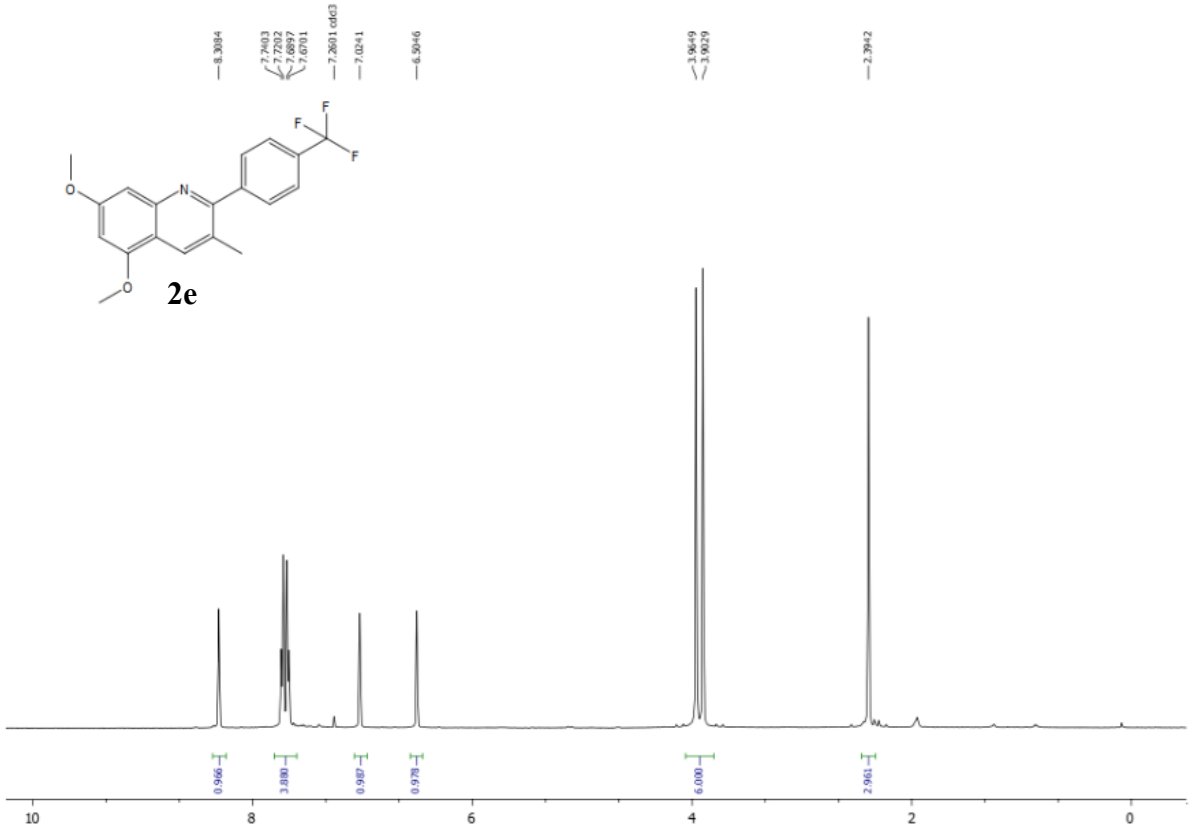
^{1}H NMR of 2d (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 2d (101 MHz, $CDCl_3$)

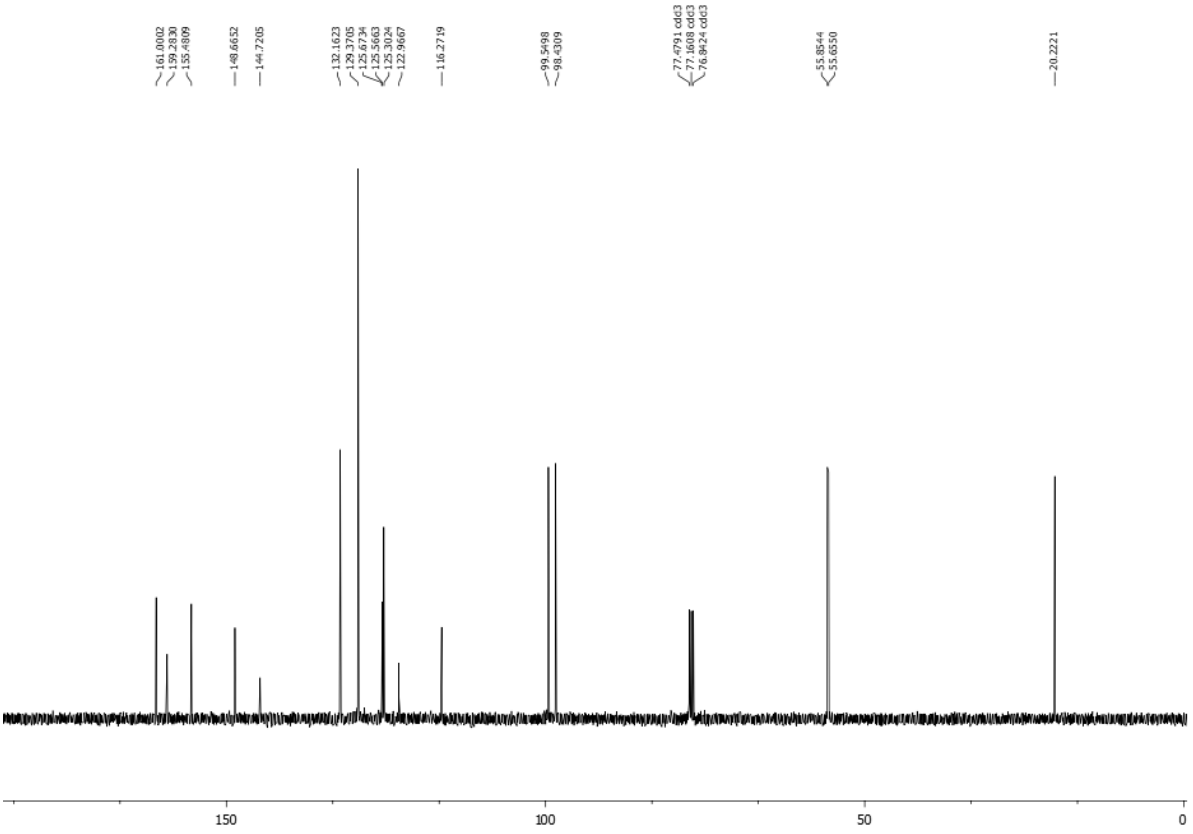


^{1}H NMR of 2e (400 MHz, $CDCl_3$)

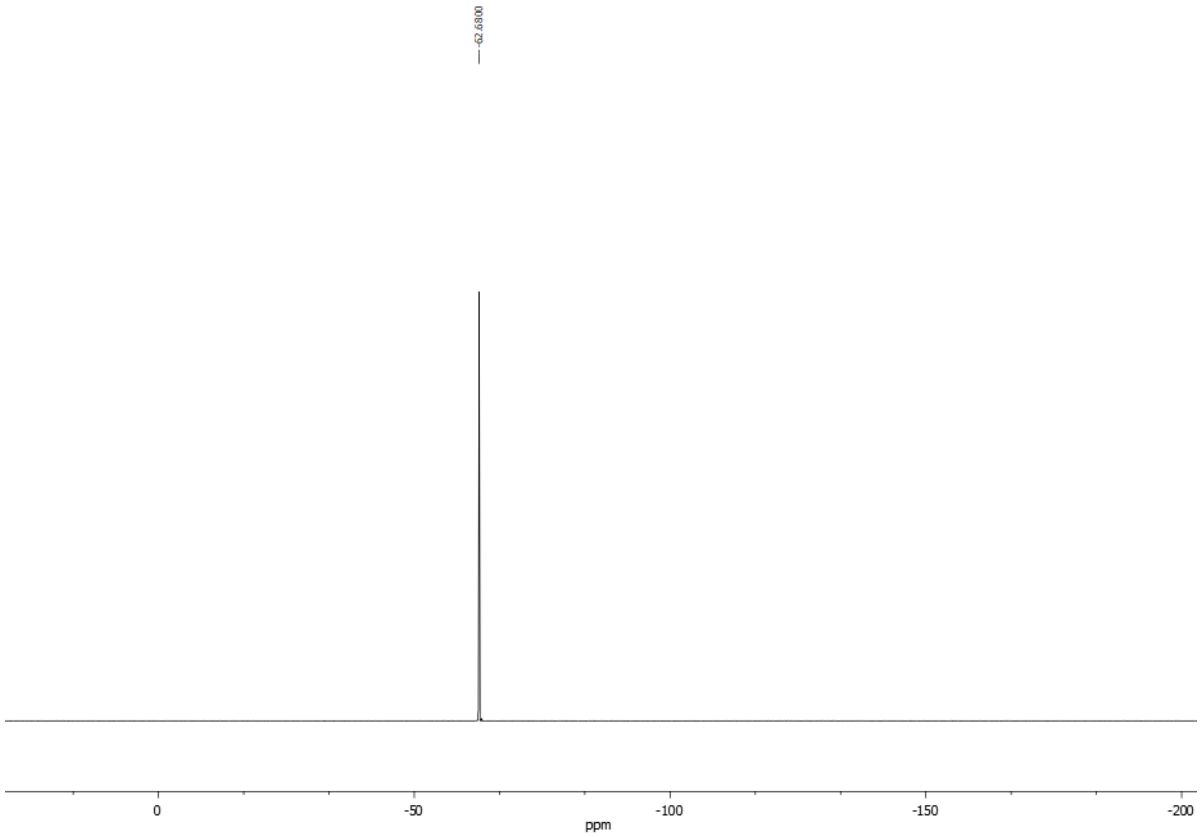


2e

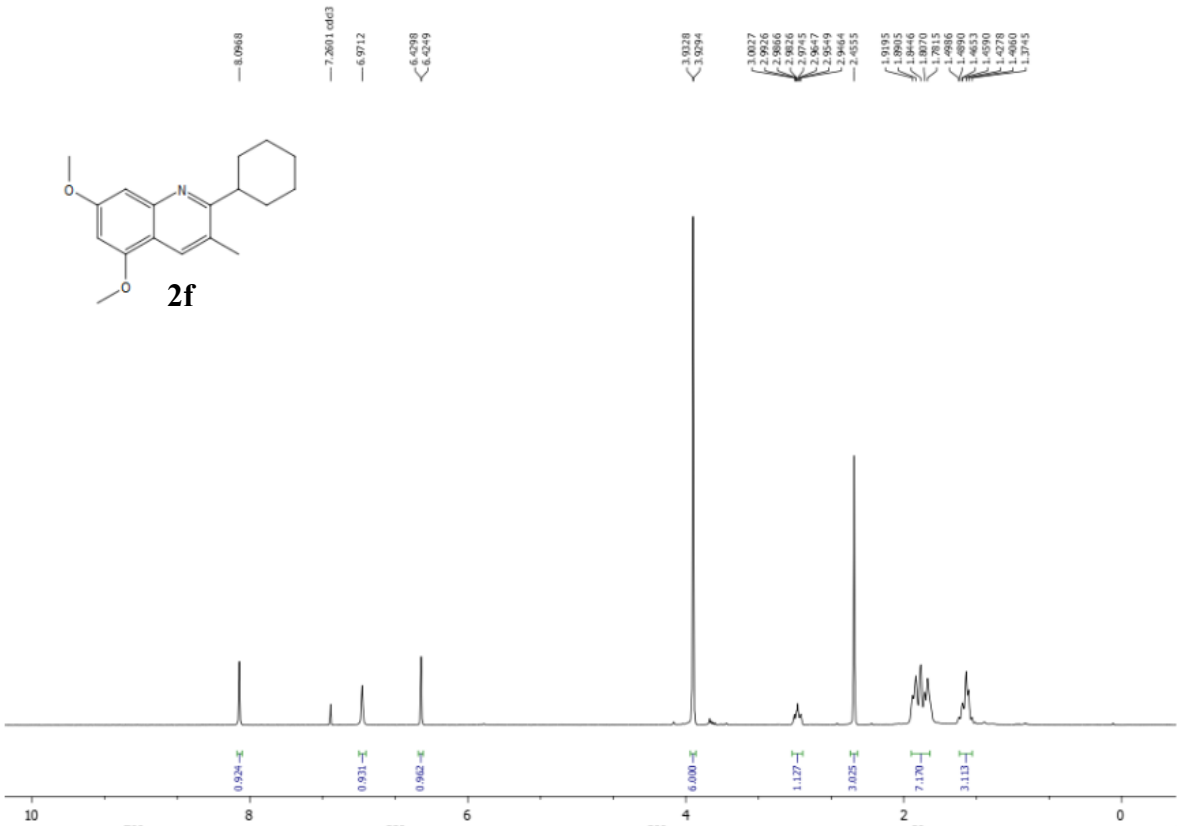
^{13}C{^{1}H} NMR of 2e (101 MHz, $CDCl_3$)



^{19}F NMR of 2e (376 MHz, $CDCl_3$)

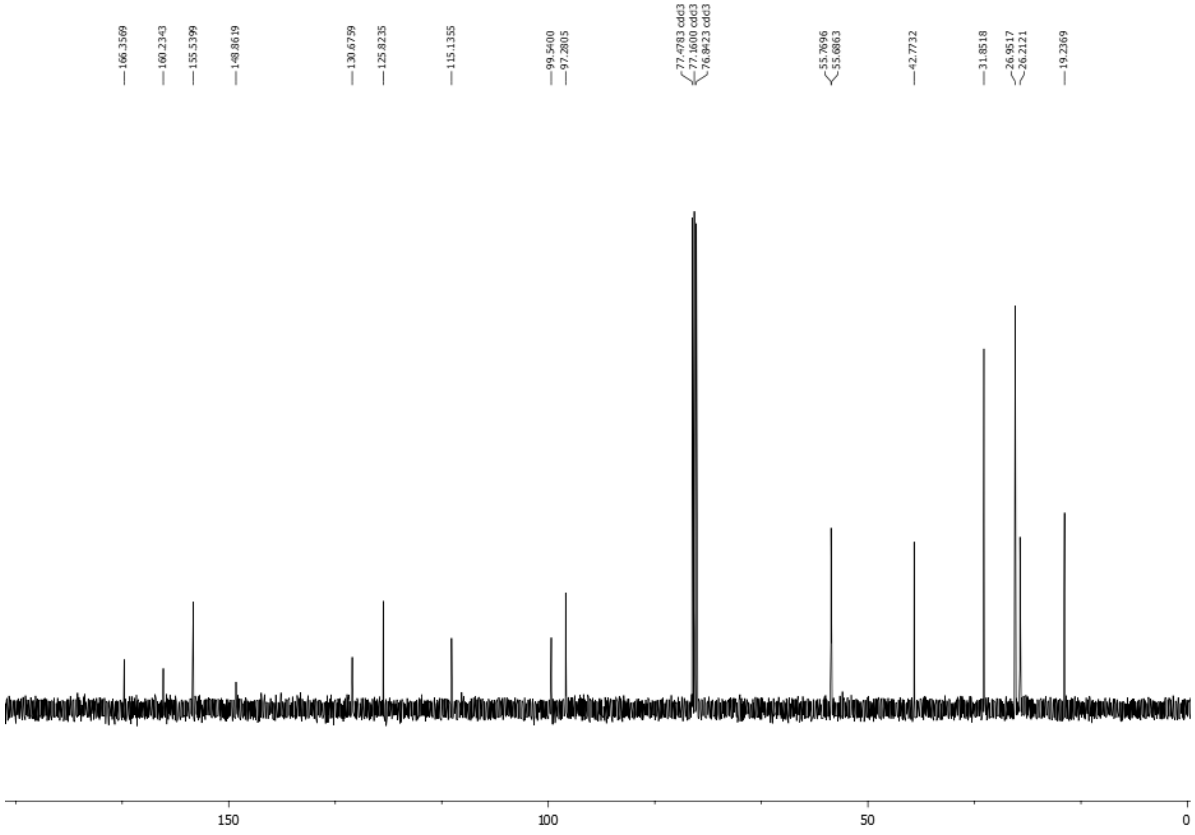


^{1}H NMR of 2f (400 MHz, $CDCl_3$)

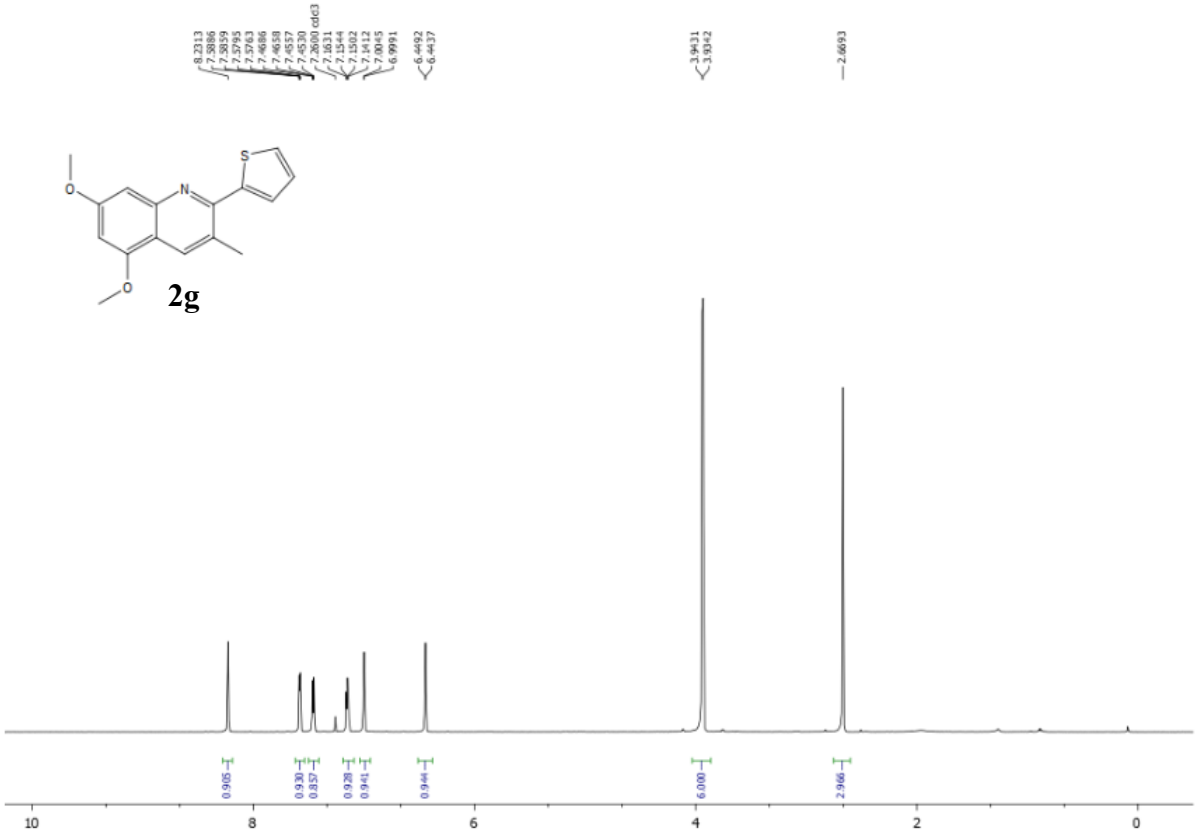


2f

^{13}C{^{1}H} NMR of 2f (101 MHz, $CDCl_3$)

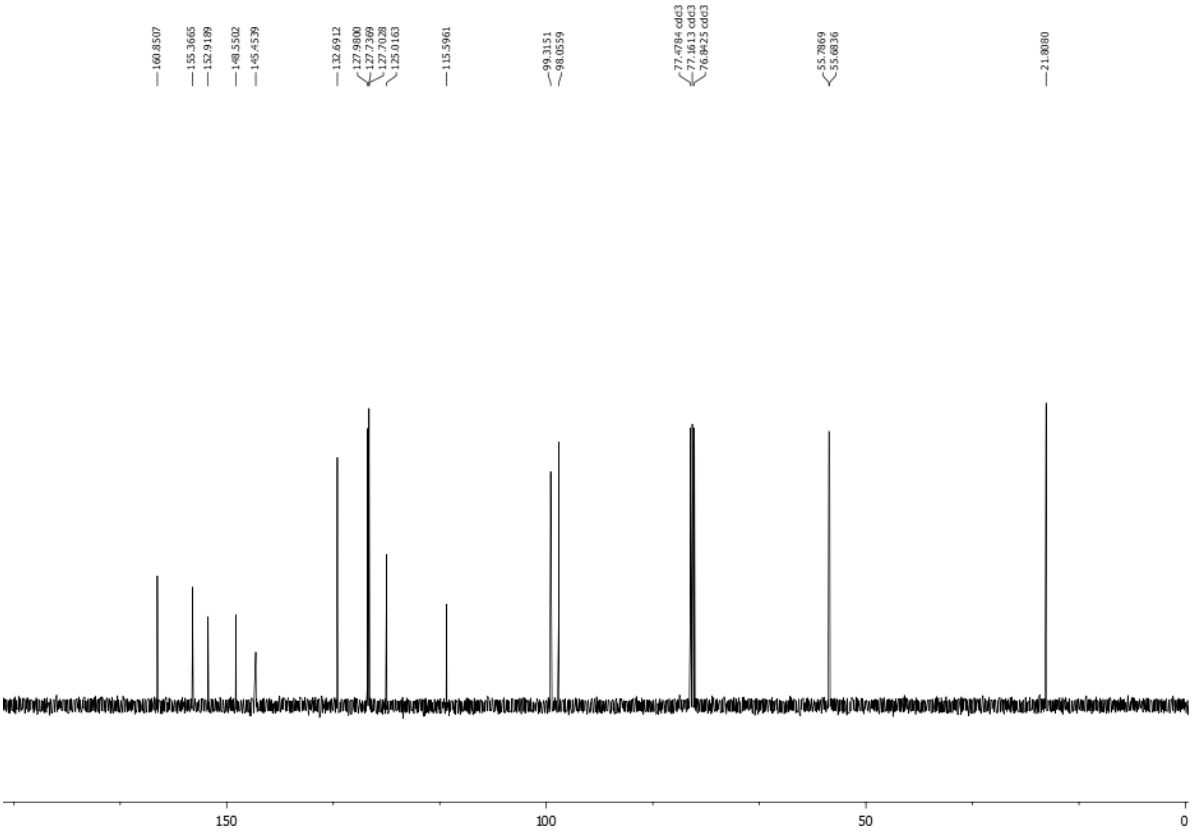


^{1}H NMR of 2g (400 MHz, $CDCl_3$)

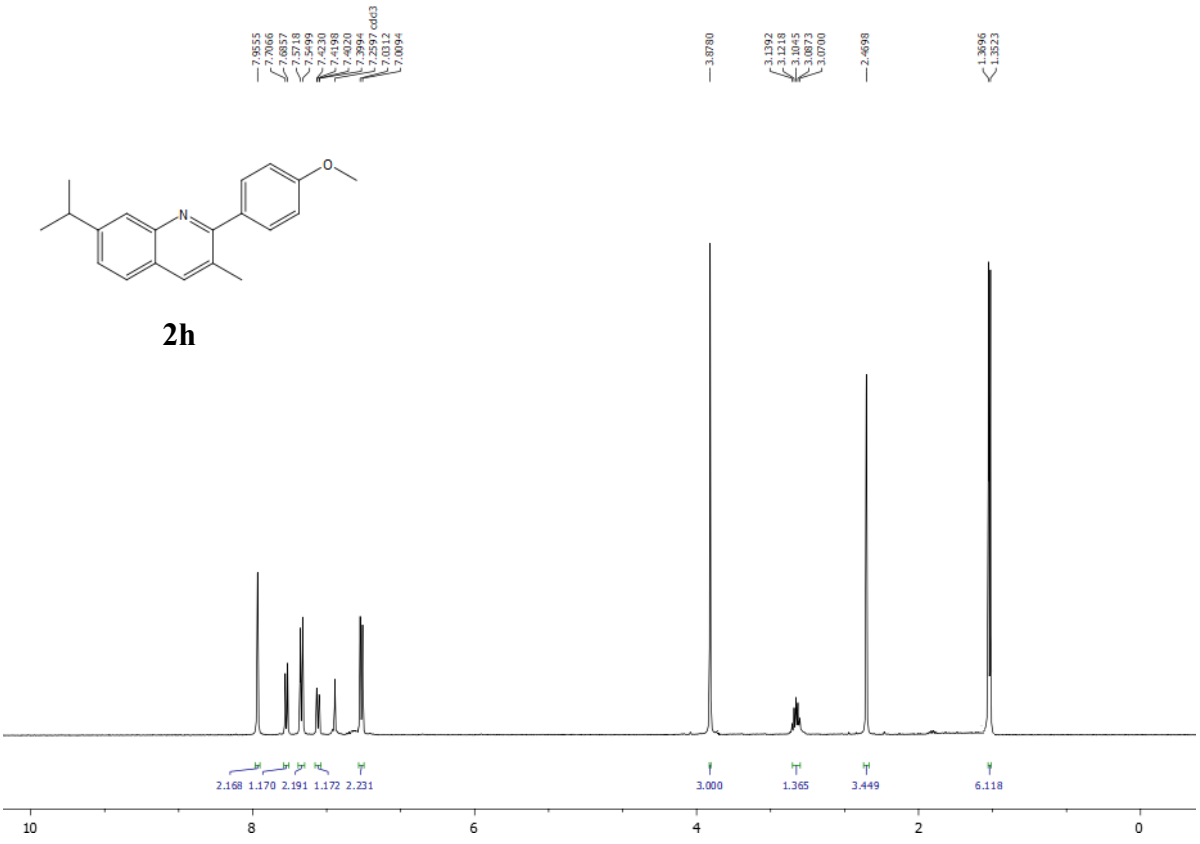


2g

^{13}C{^{1}H} NMR of 2g (101 MHz, $CDCl_3$)

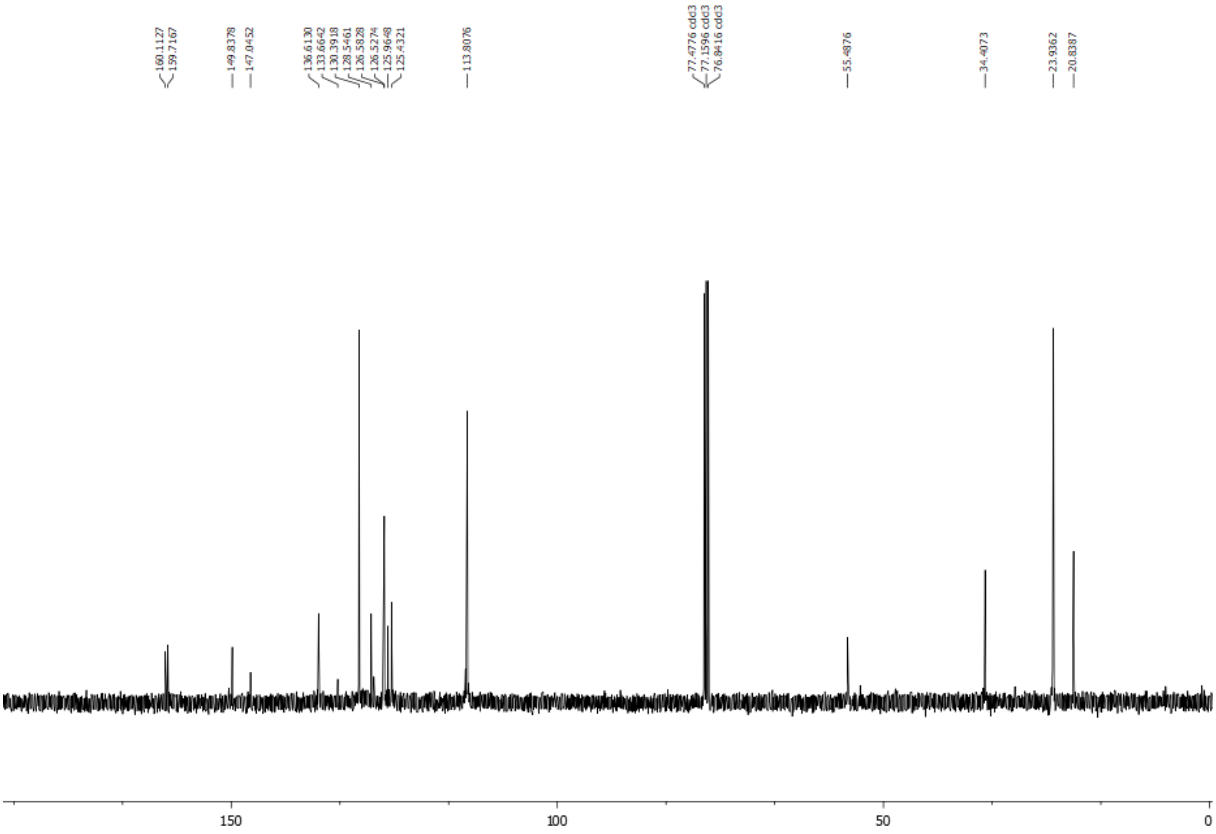


^{1}H NMR of 2h (400 MHz, $CDCl_3$)

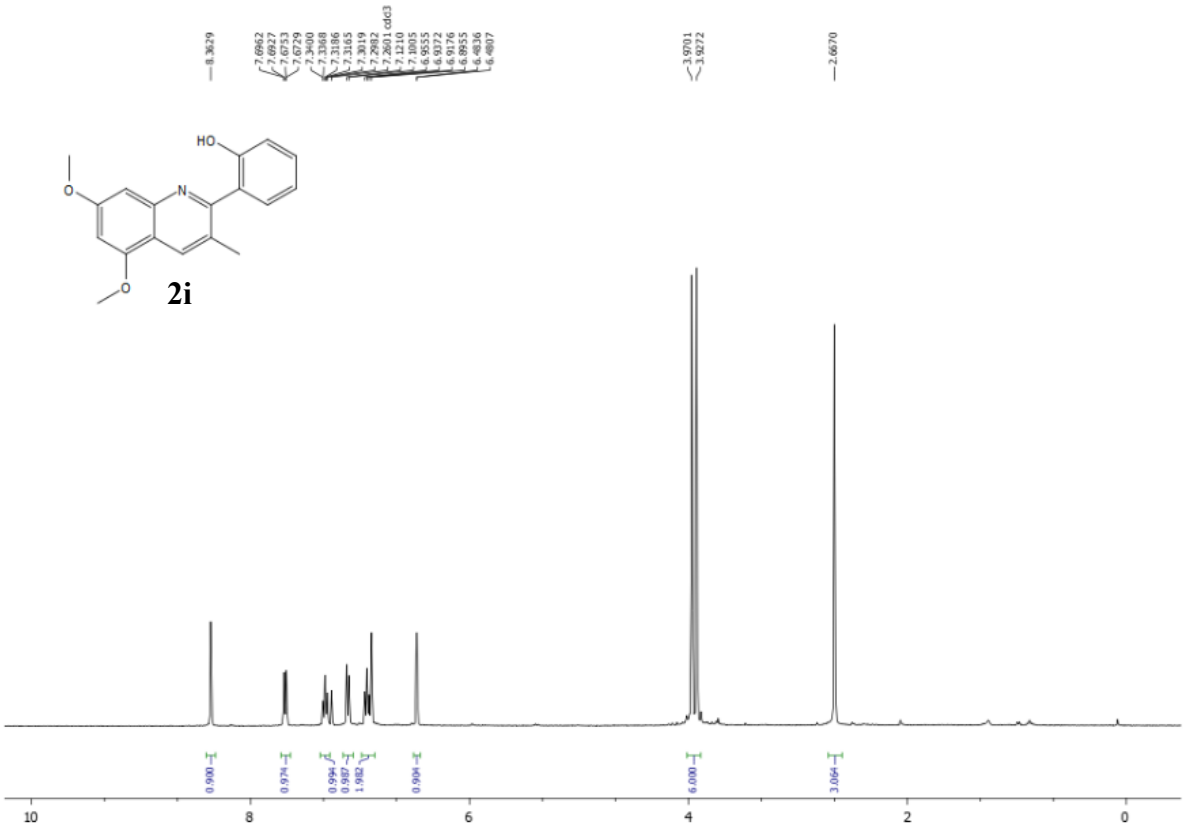


2h

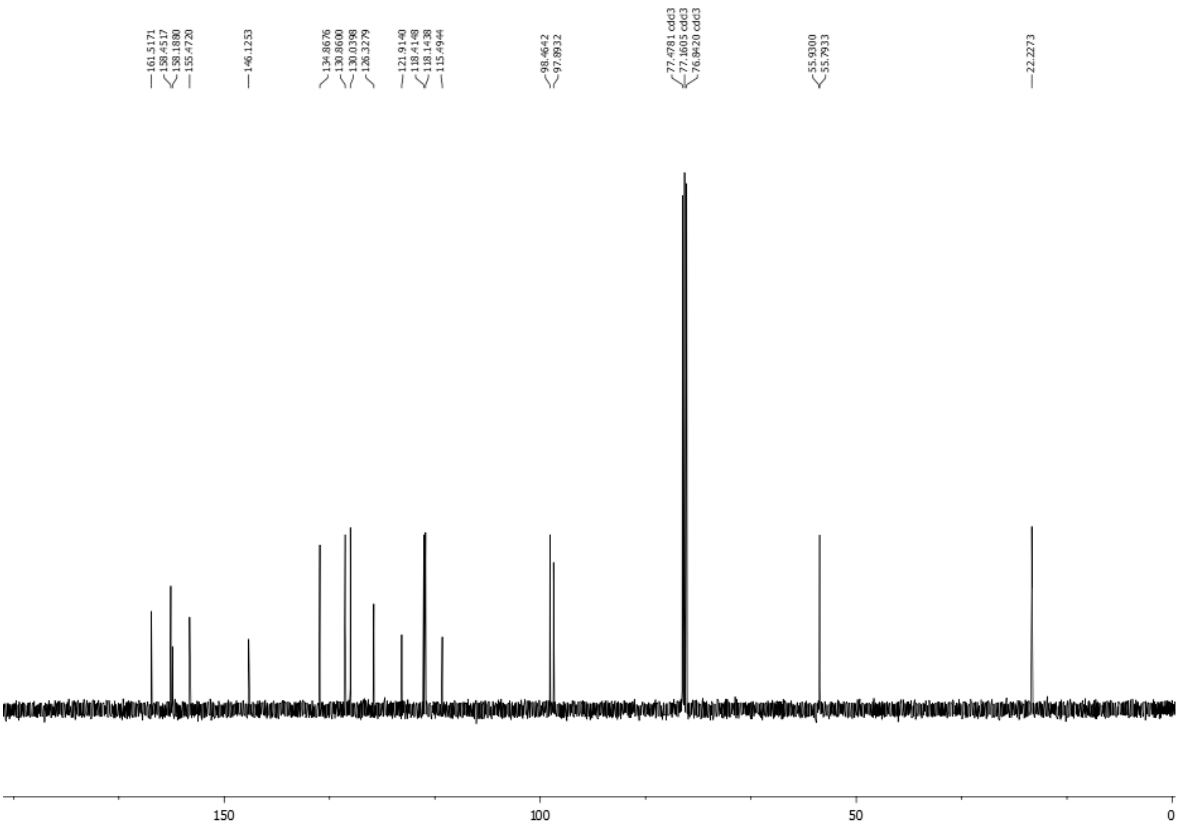
^{13}C{^{1}H} NMR of 2h (101 MHz, $CDCl_3$)



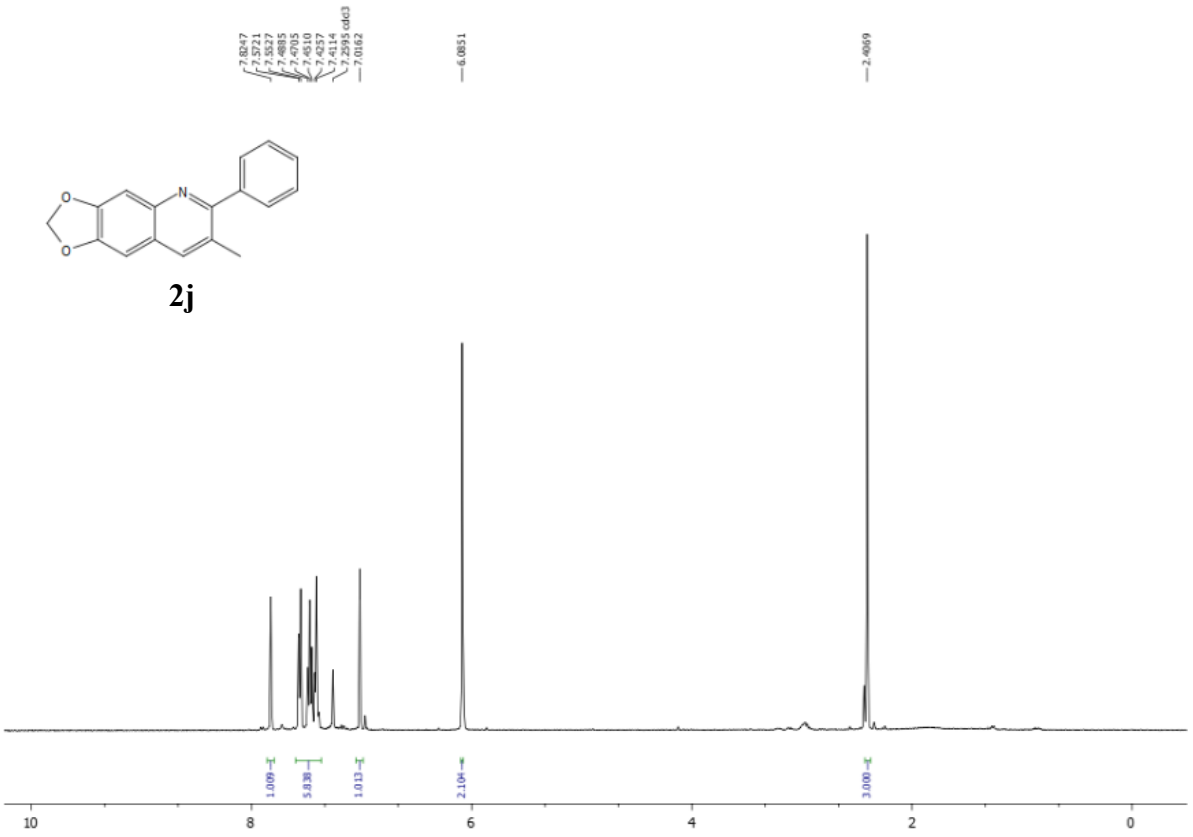
^{1}H NMR of 2i (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 2i (101 MHz, $CDCl_3$)

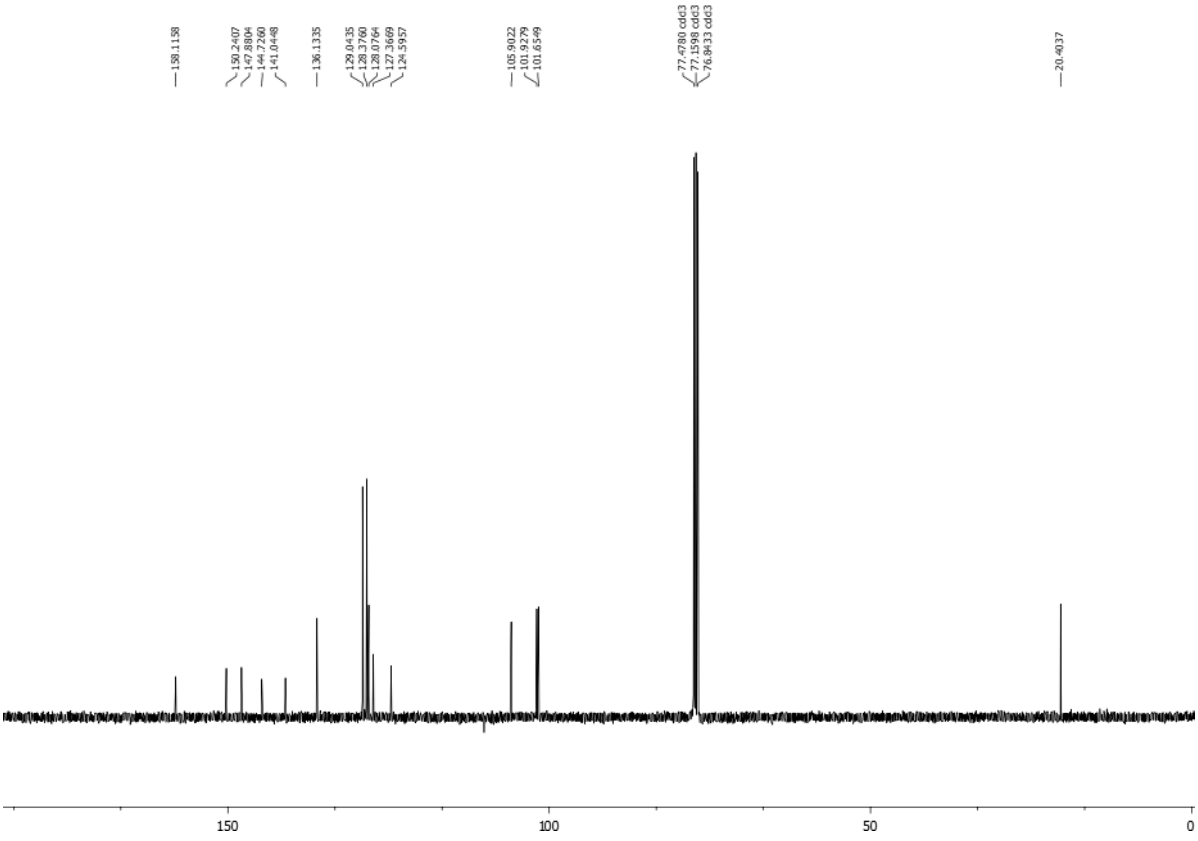


^{1}H NMR of 2j (400 MHz, $CDCl_3$)

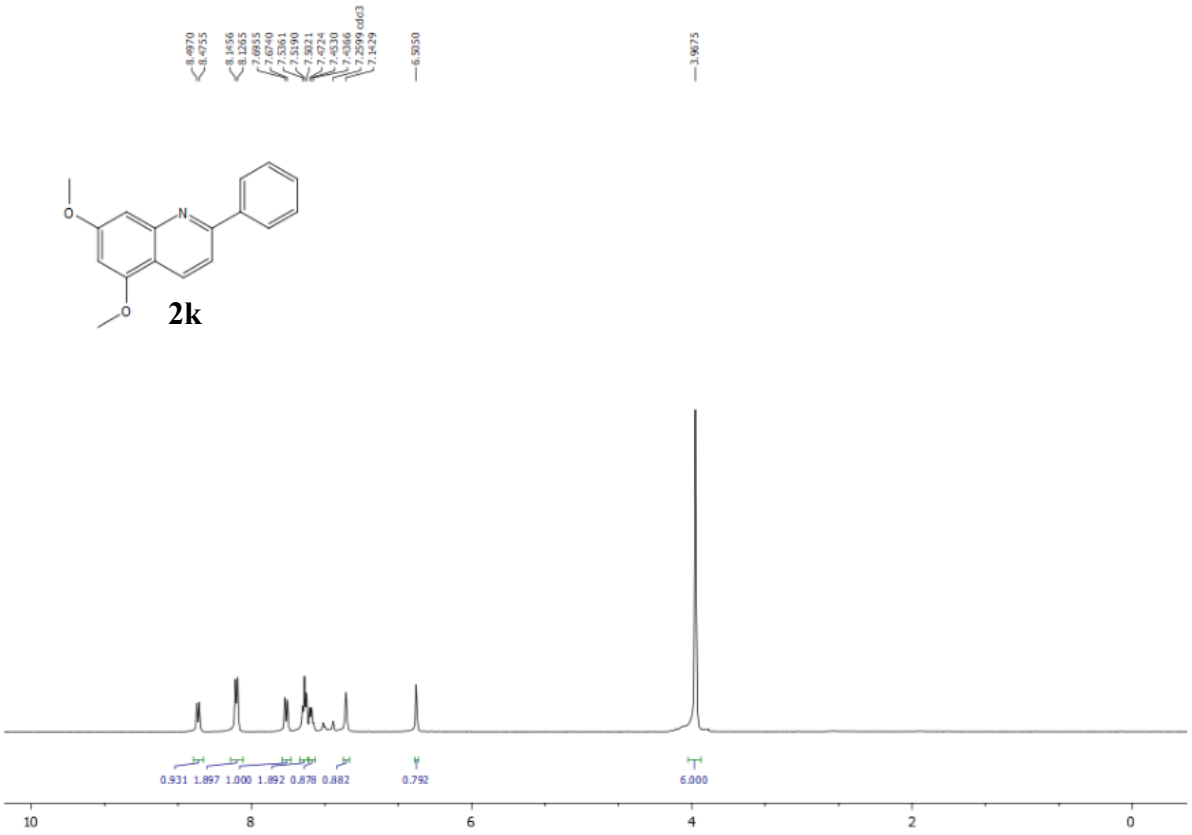


2j

^{13}C{^{1}H} NMR of 2j (101 MHz, $CDCl_3$)

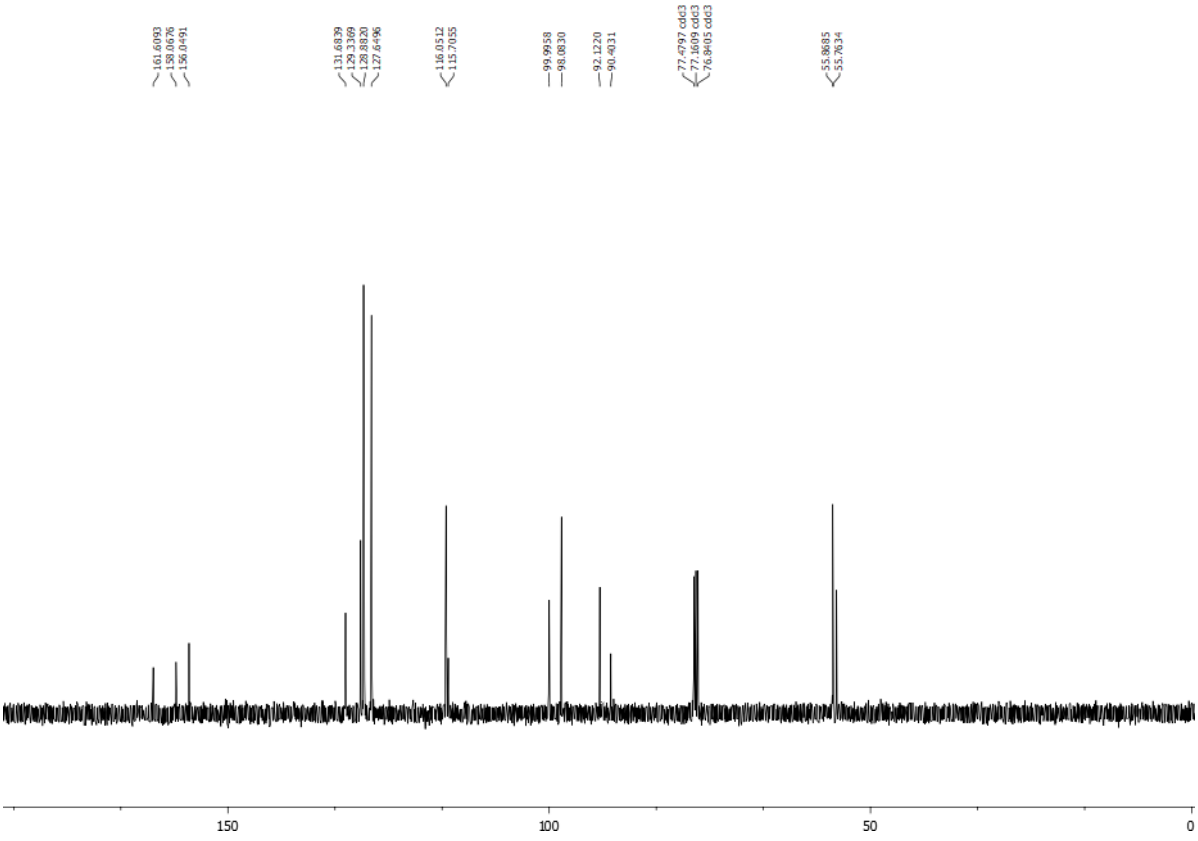


^{1}H NMR of 2k (400 MHz, $CDCl_3$)

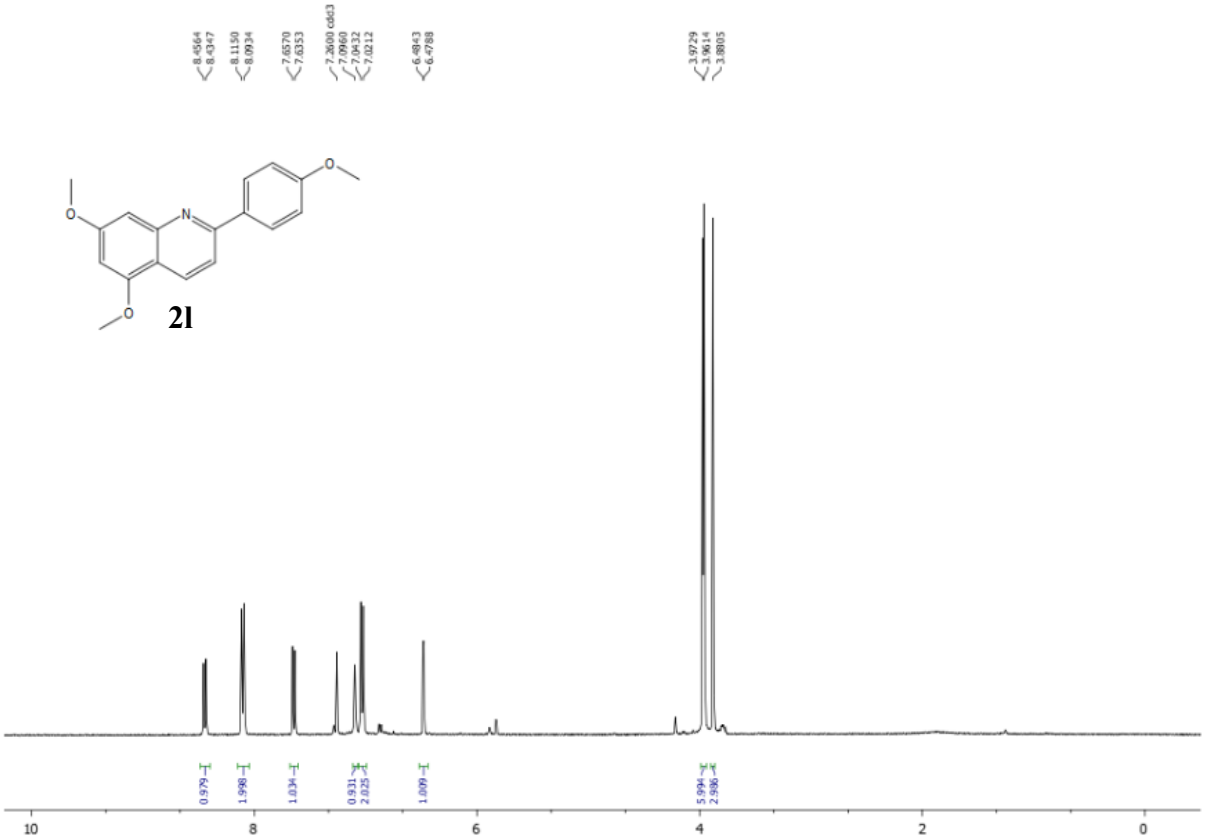


2k

^{13}C{^{1}H} NMR 2k (101 MHz, $CDCl_3$)

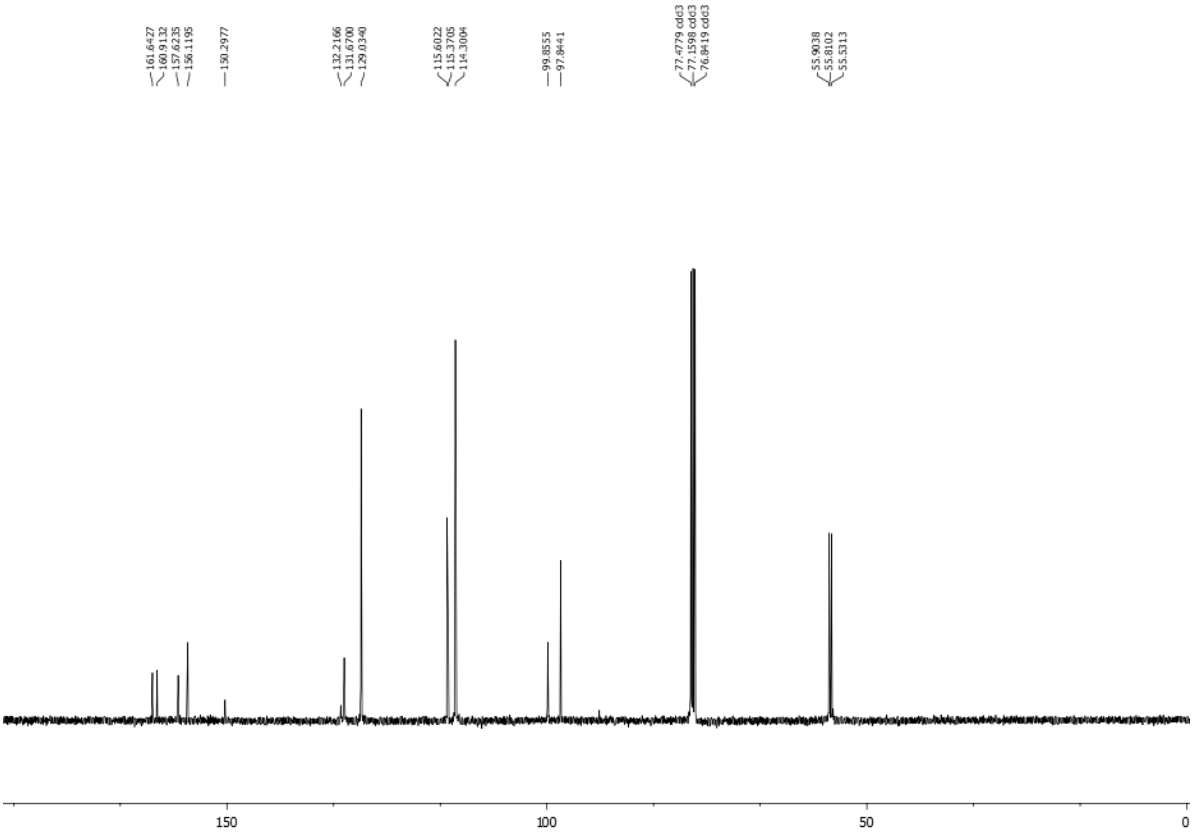


^{1}H NMR of 2l (400 MHz, $CDCl_3$)

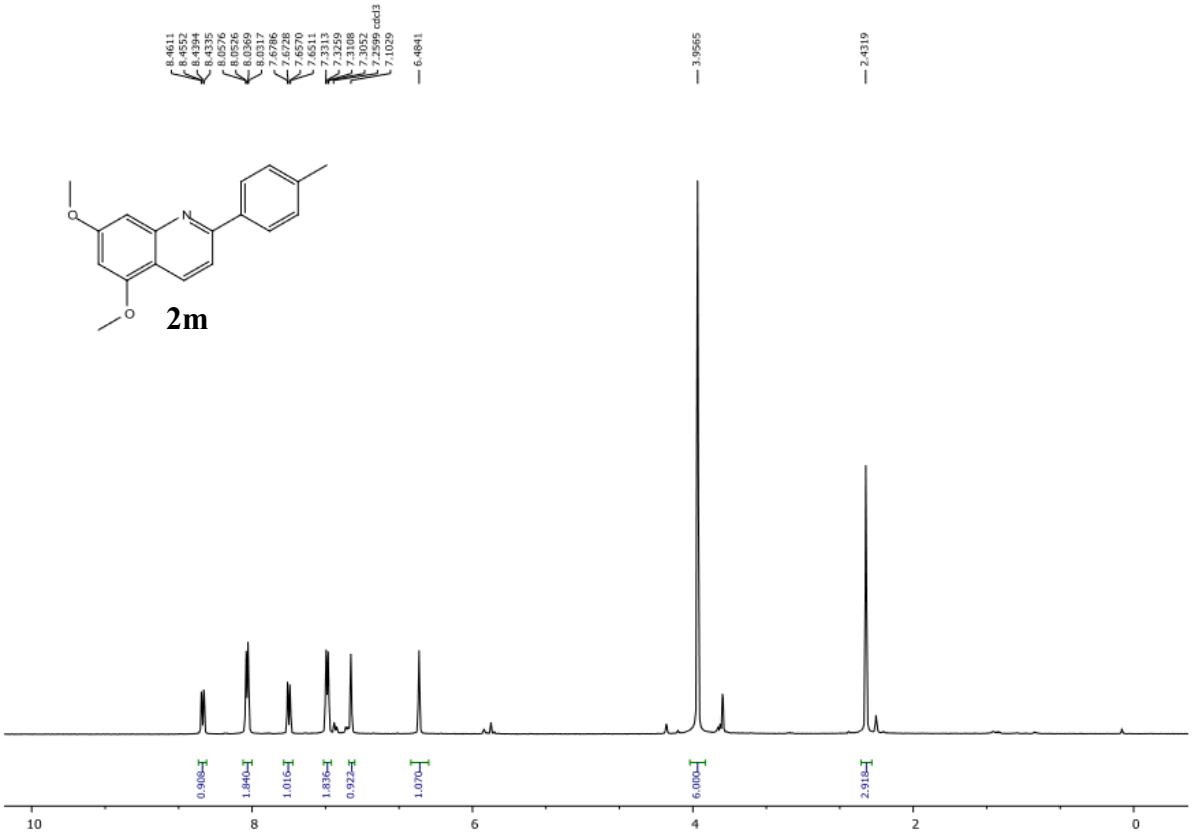


2l

^{13}C{^{1}H} NMR of 2l (101 MHz, $CDCl_3$)

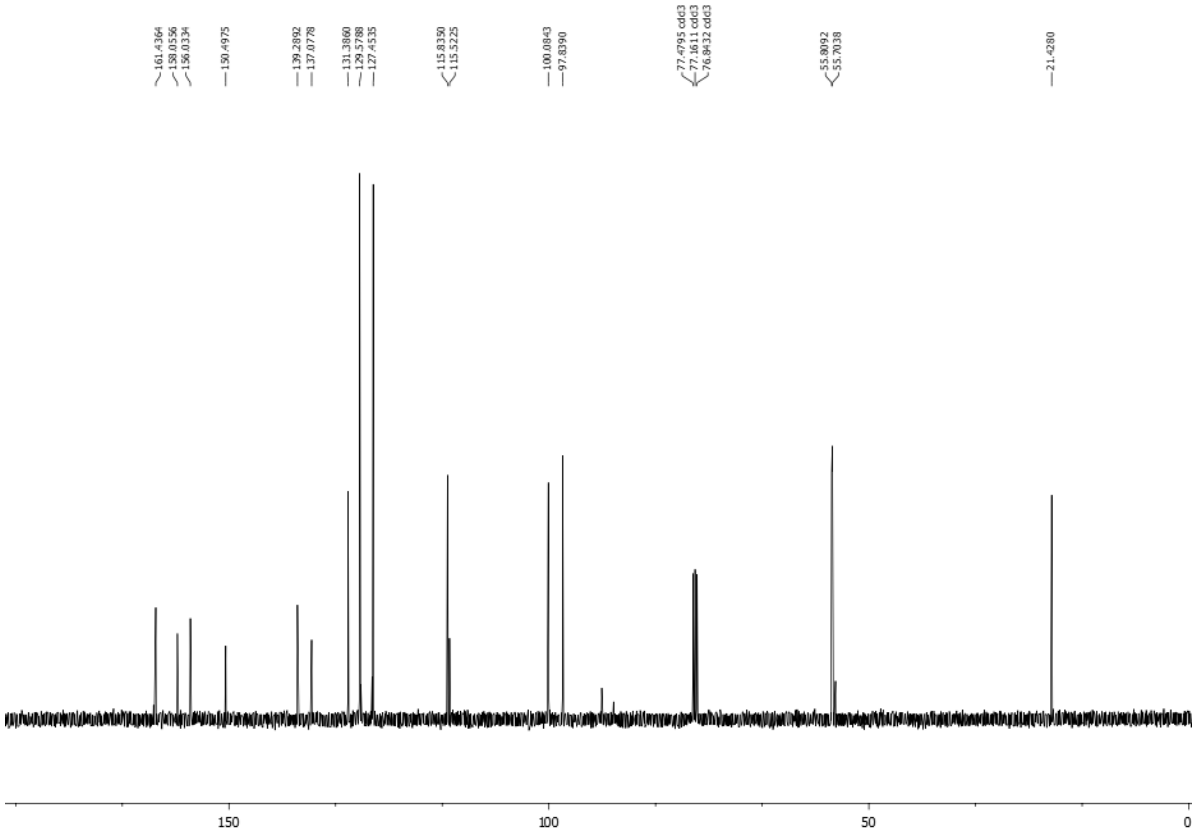


^{1}H NMR of 2m (400 MHz, $CDCl_3$)

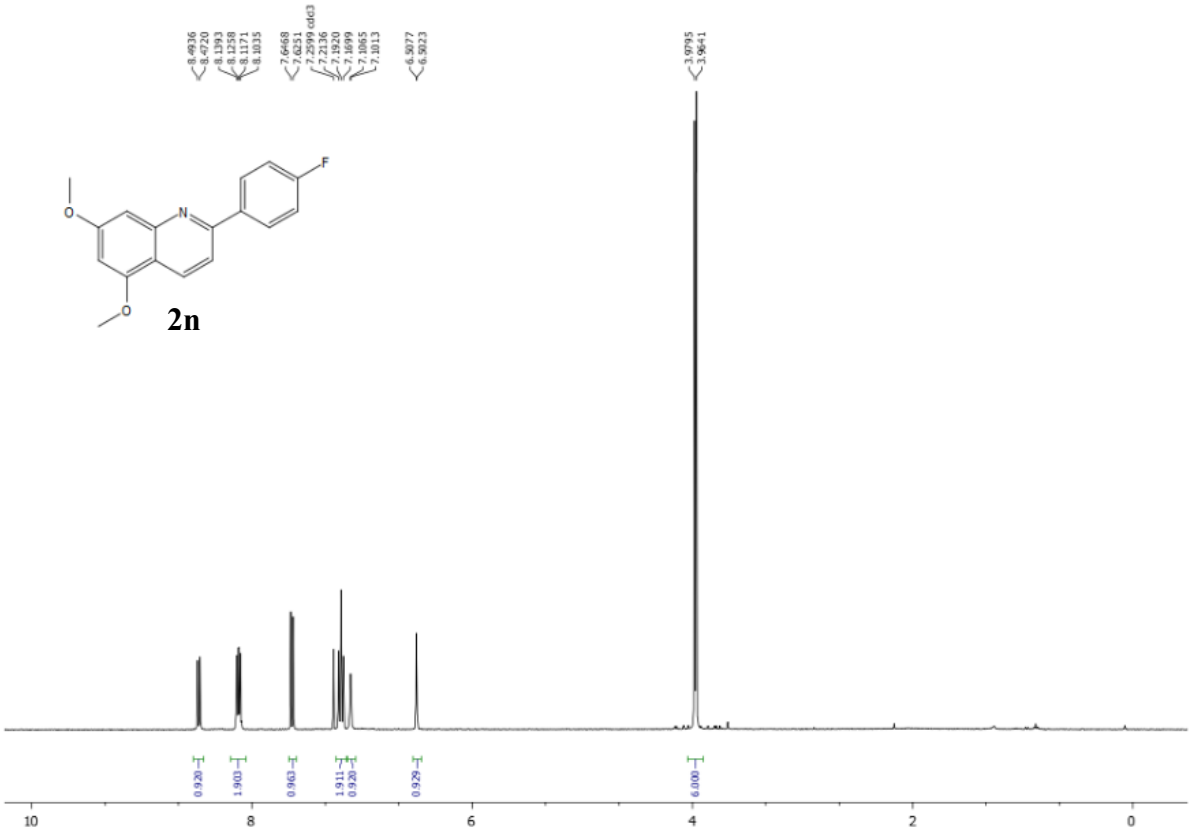


2m

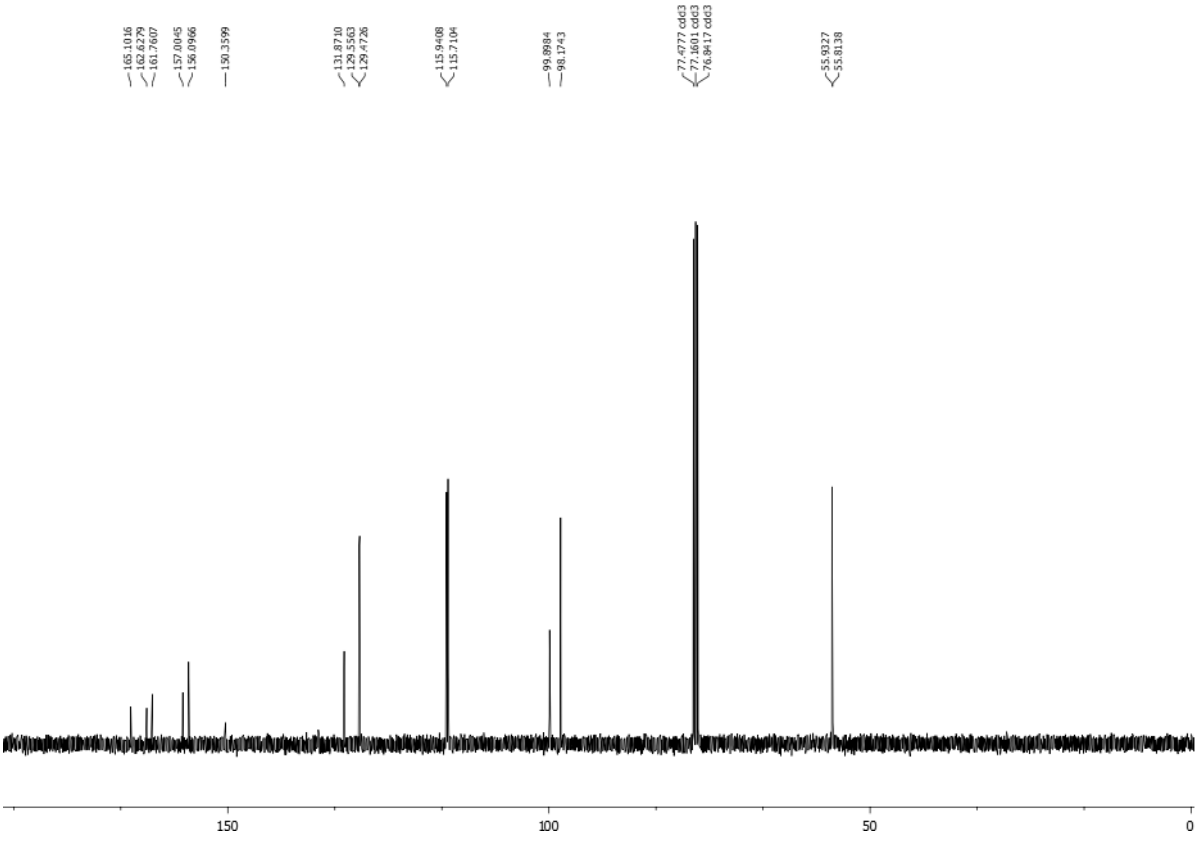
^{13}C{^{1}H} NMR of 2m (101 MHz, $CDCl_3$)



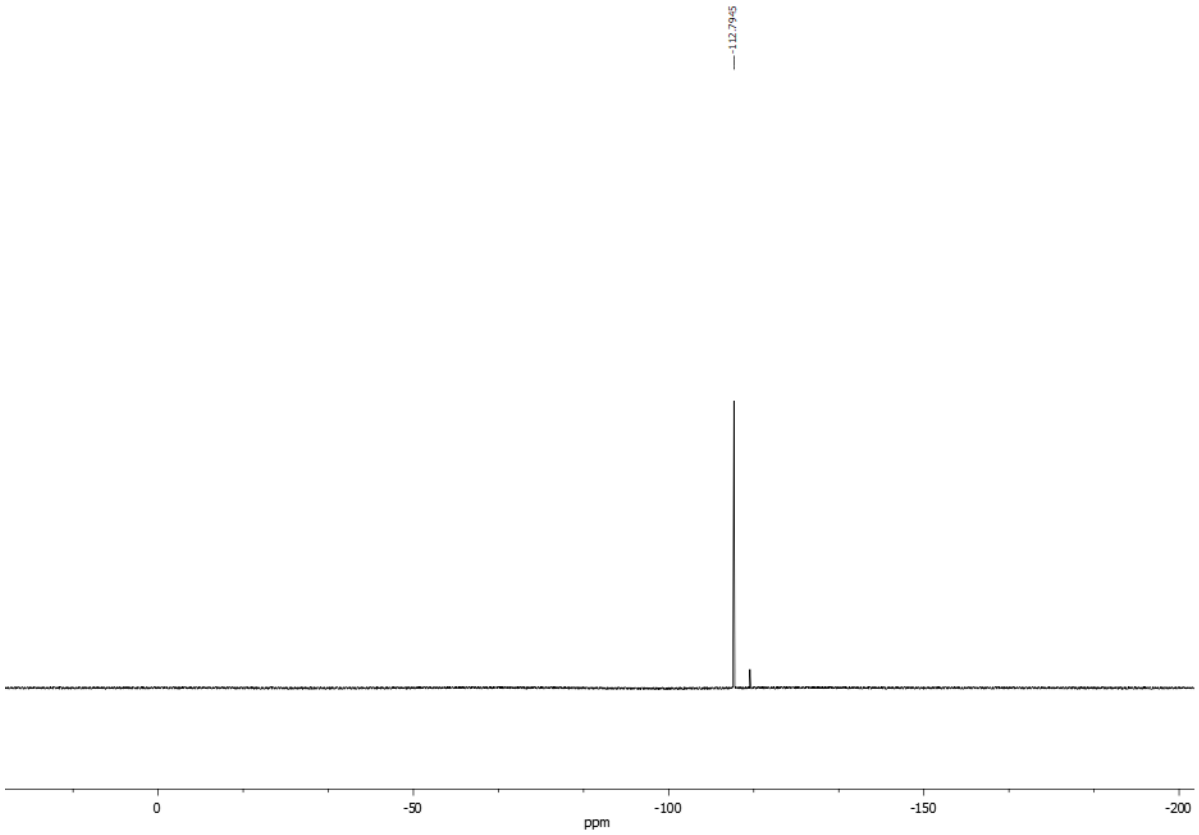
^{1}H NMR of 2n (400 MHz, $CDCl_3$)



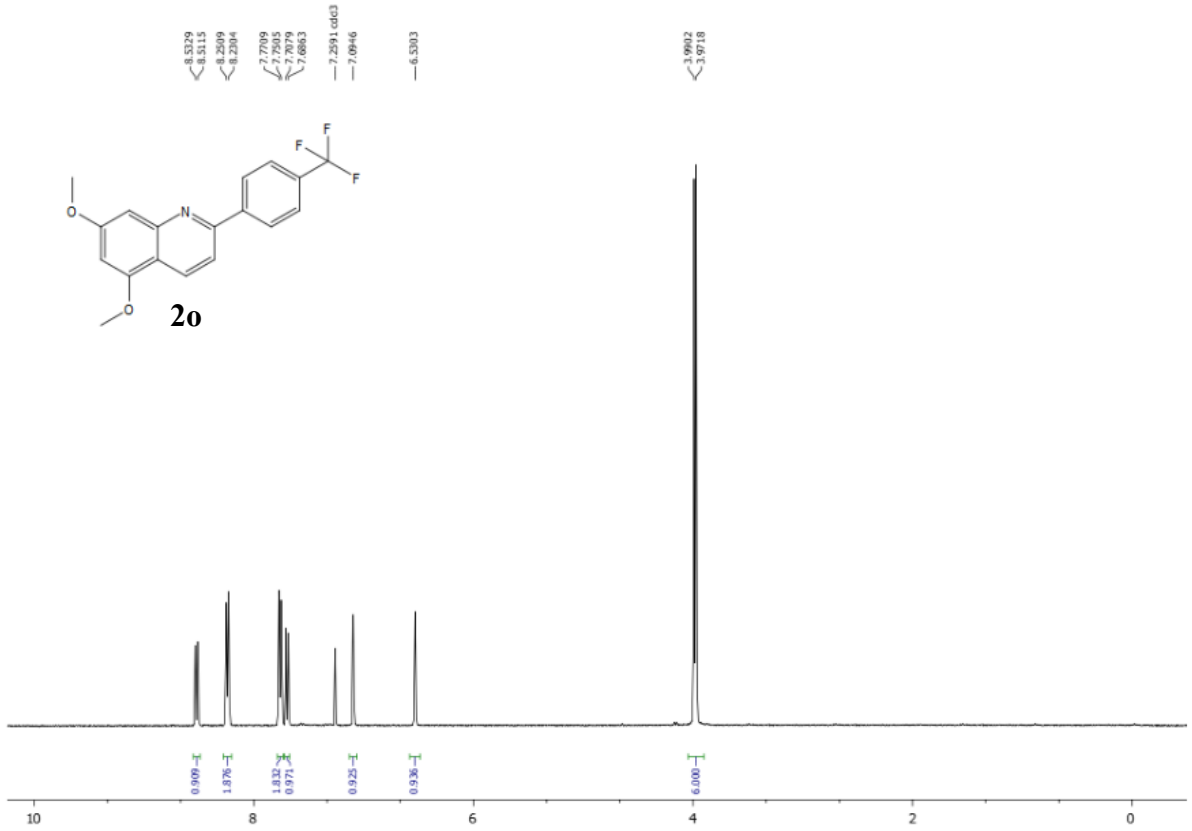
^{13}C{^{1}H} NMR of 2n (101 MHz, $CDCl_3$)



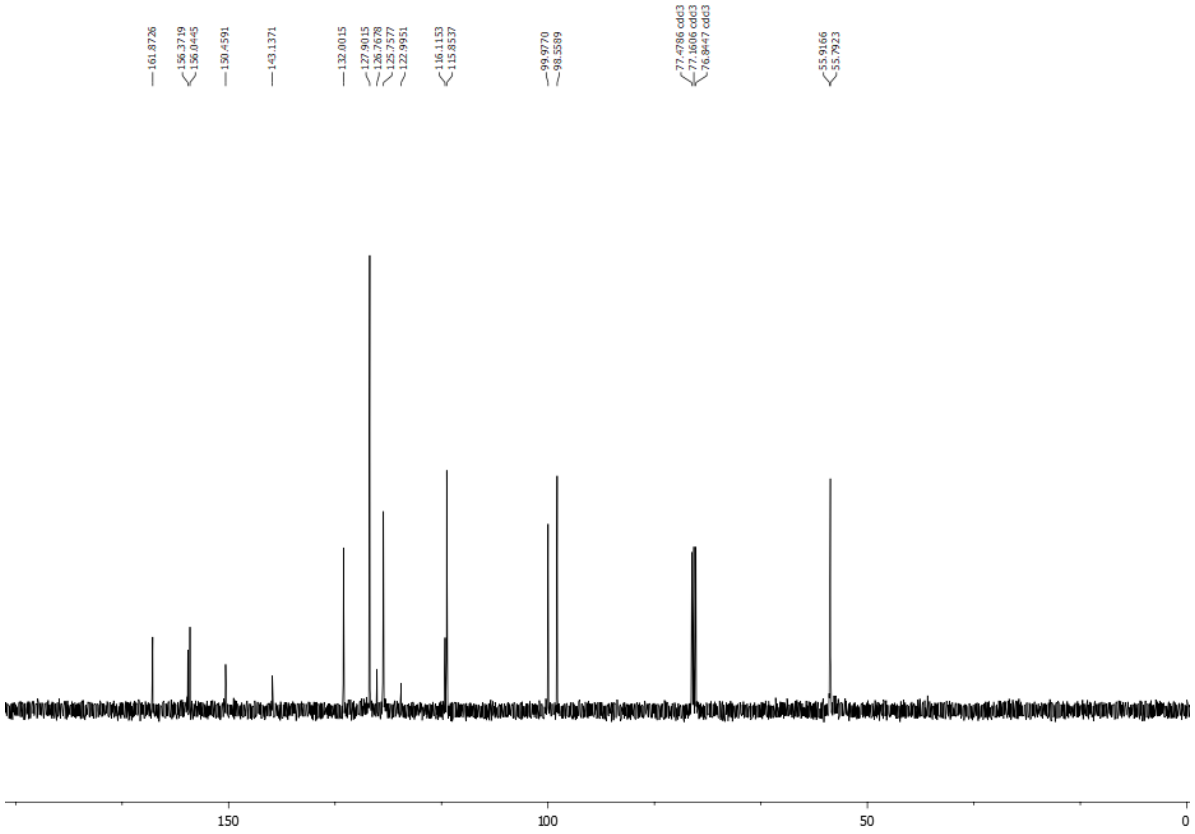
^{19}F NMR of 2n (376 MHz, $CDCl_3$)



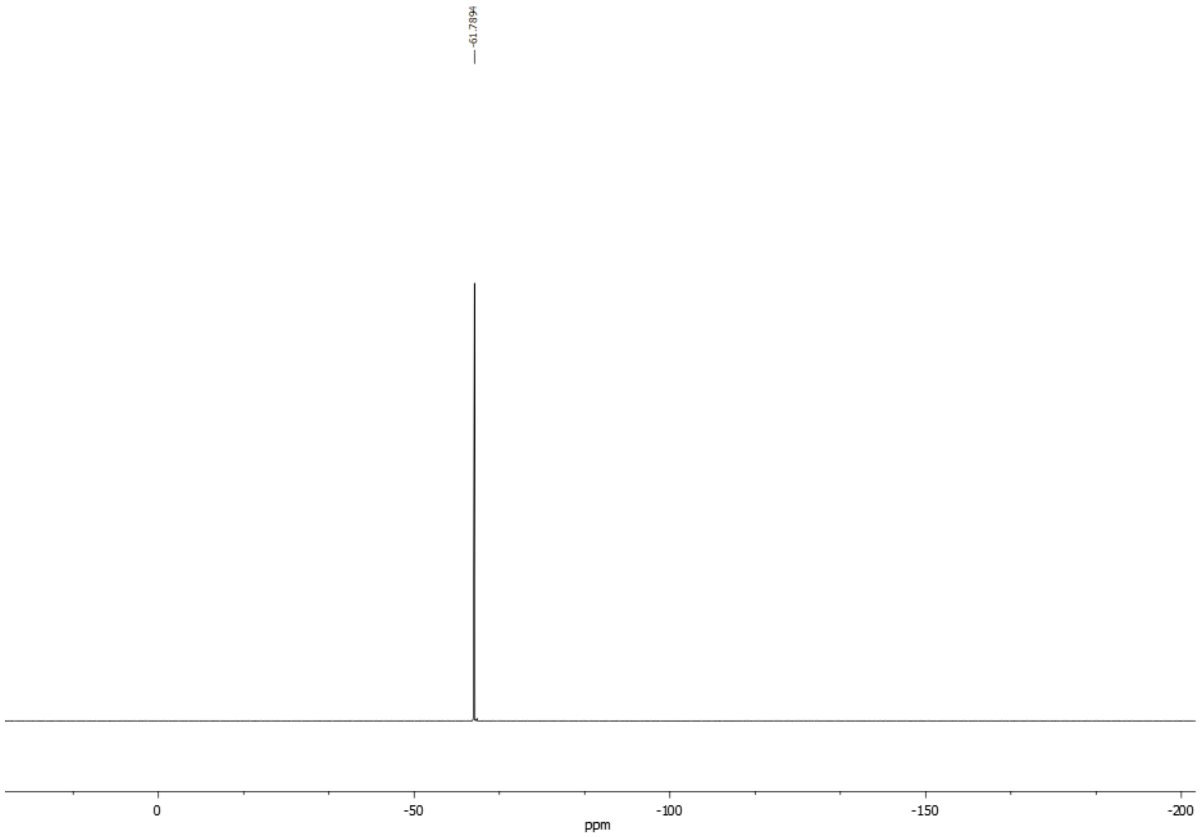
^{1}H NMR of 2o (400 MHz, $CDCl_3$)



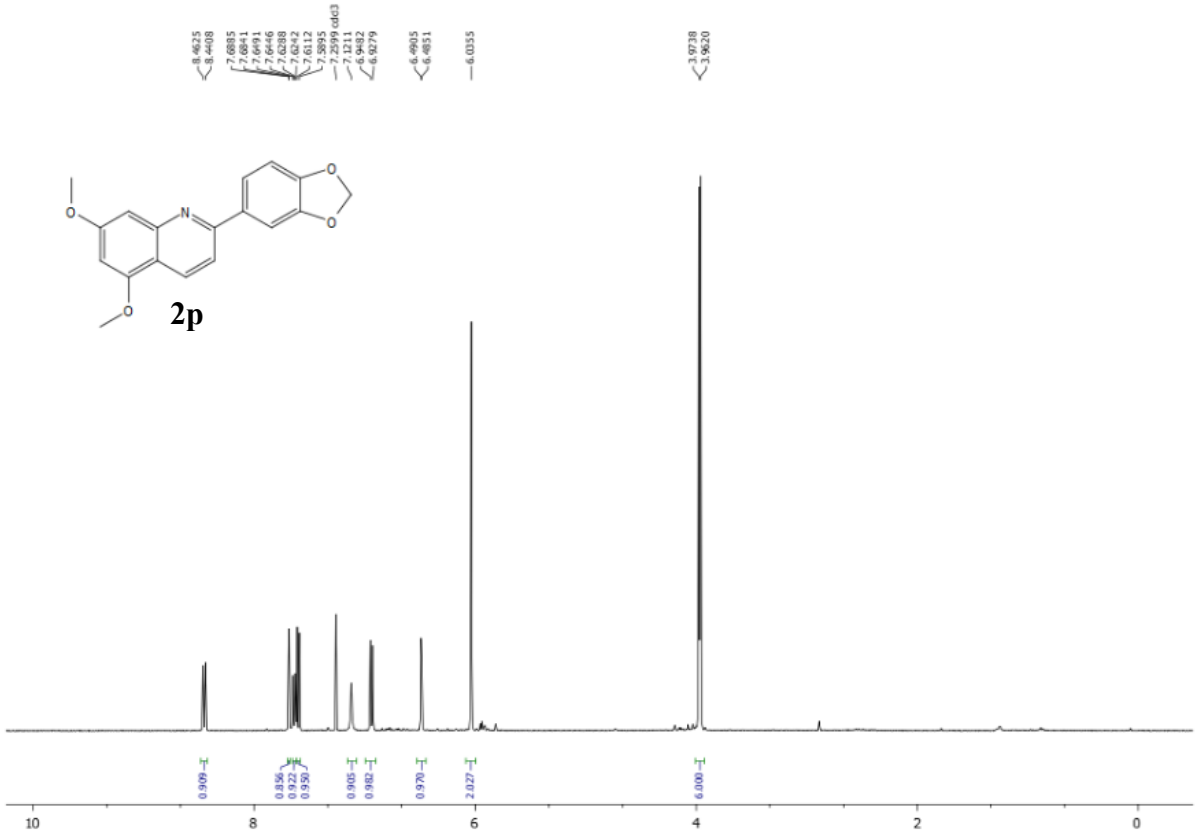
^{13}C{^{1}H} NMR of 2o (101 MHz, $CDCl_3$)



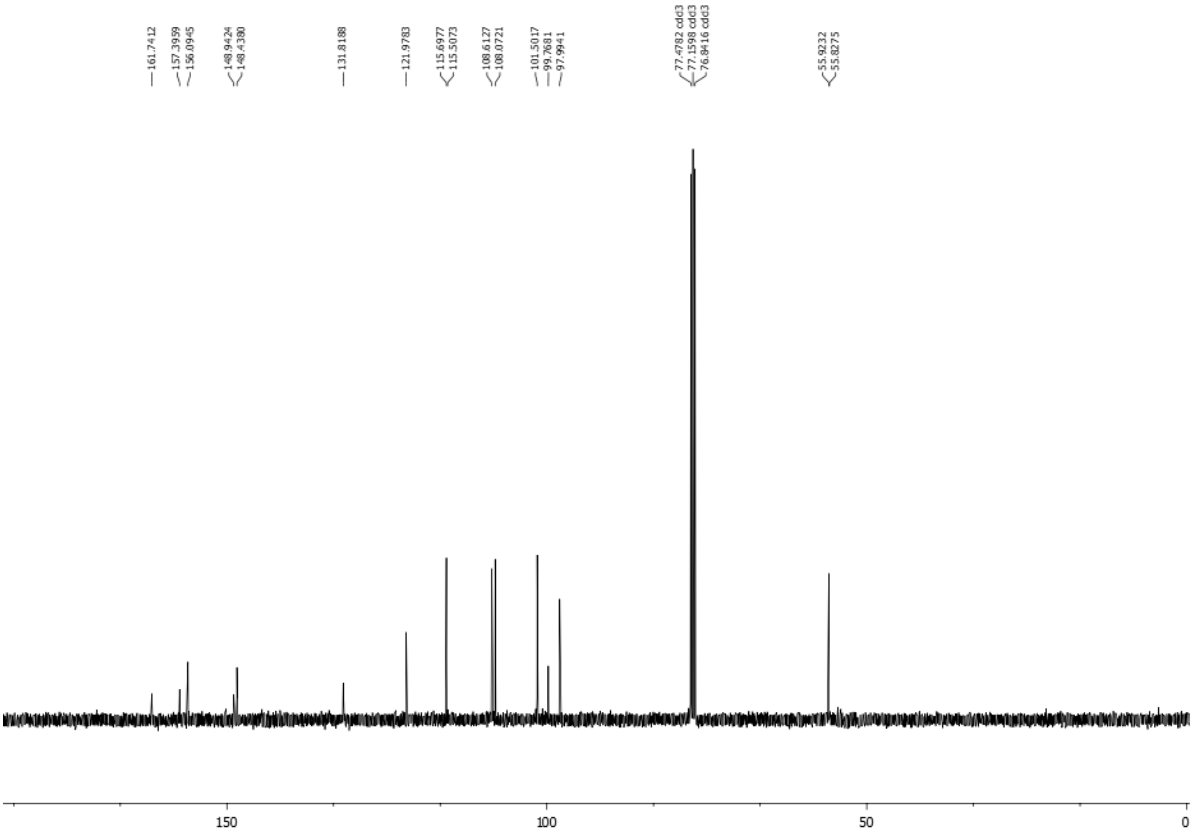
^{19}F NMR of 2o (376 MHz, $CDCl_3$)



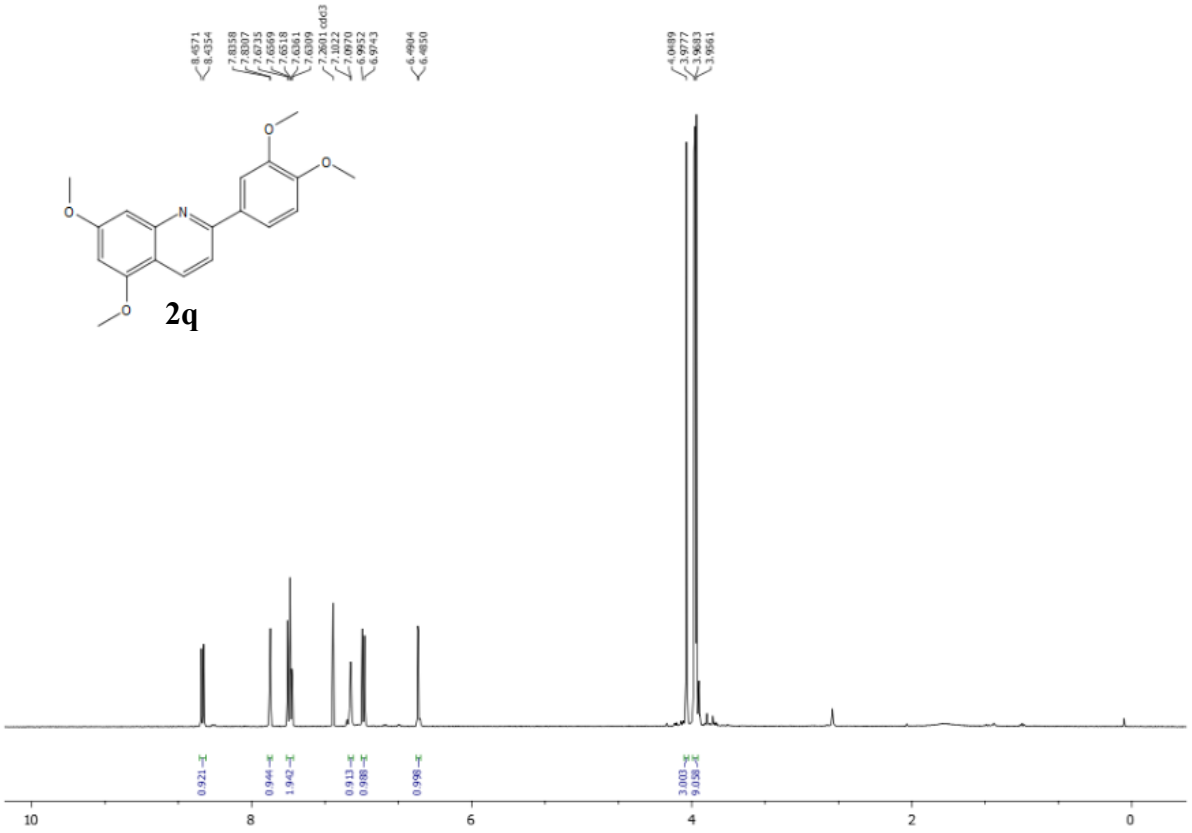
^{1}H NMR of 2p (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 2p (101 MHz, $CDCl_3$)

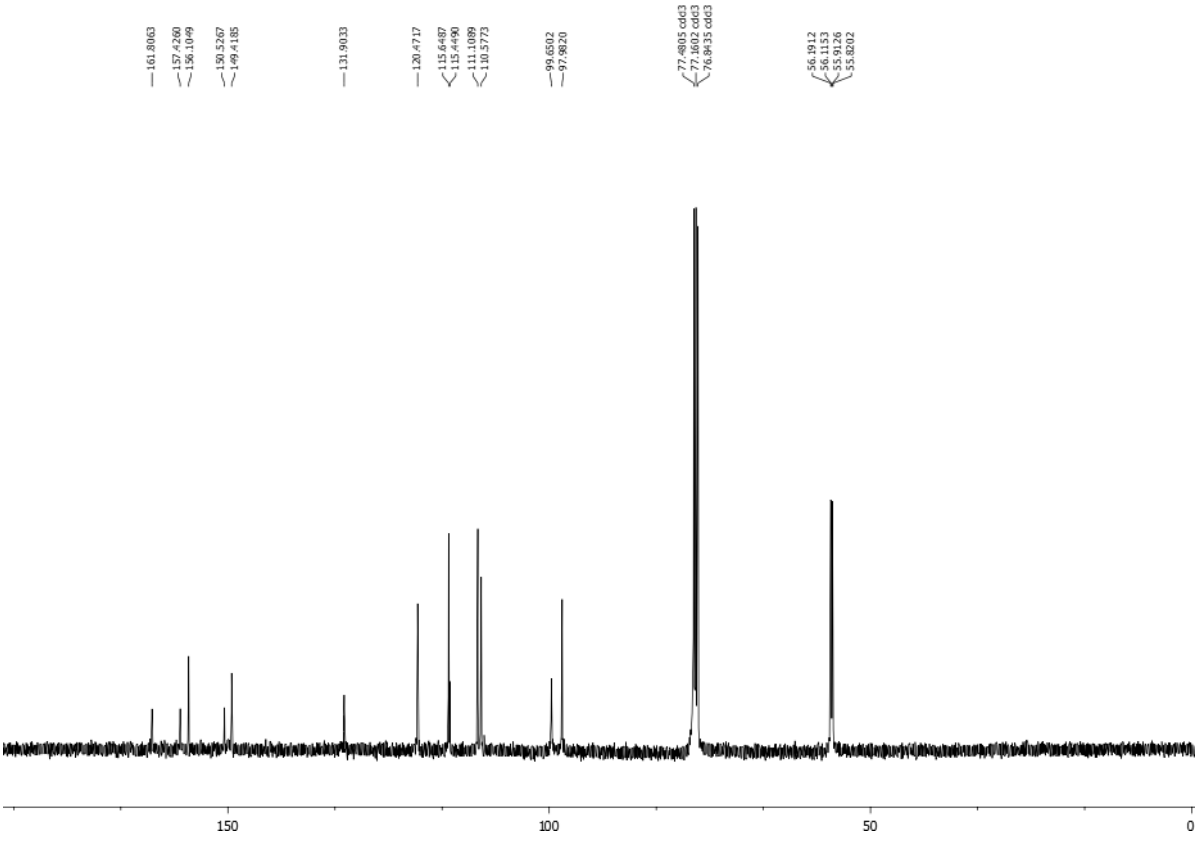


^{1}H NMR of 2q (400 MHz, $CDCl_3$)

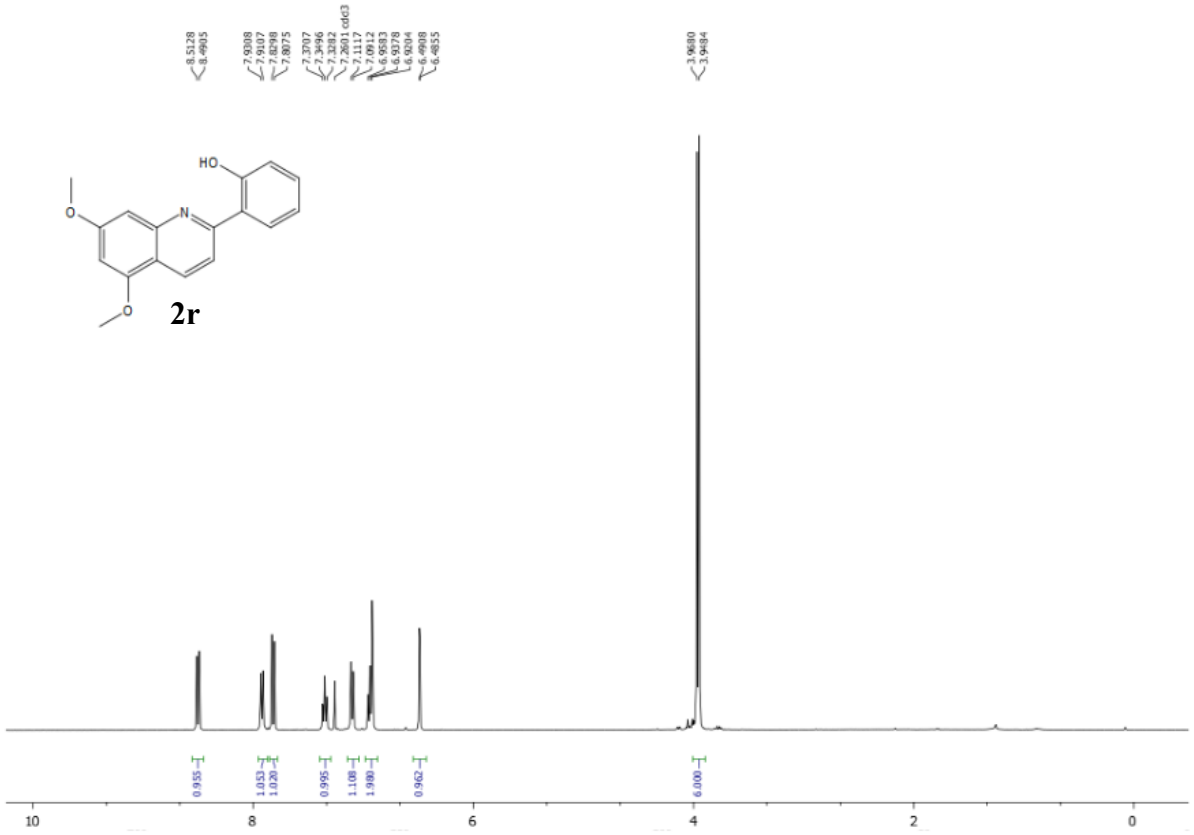


2q

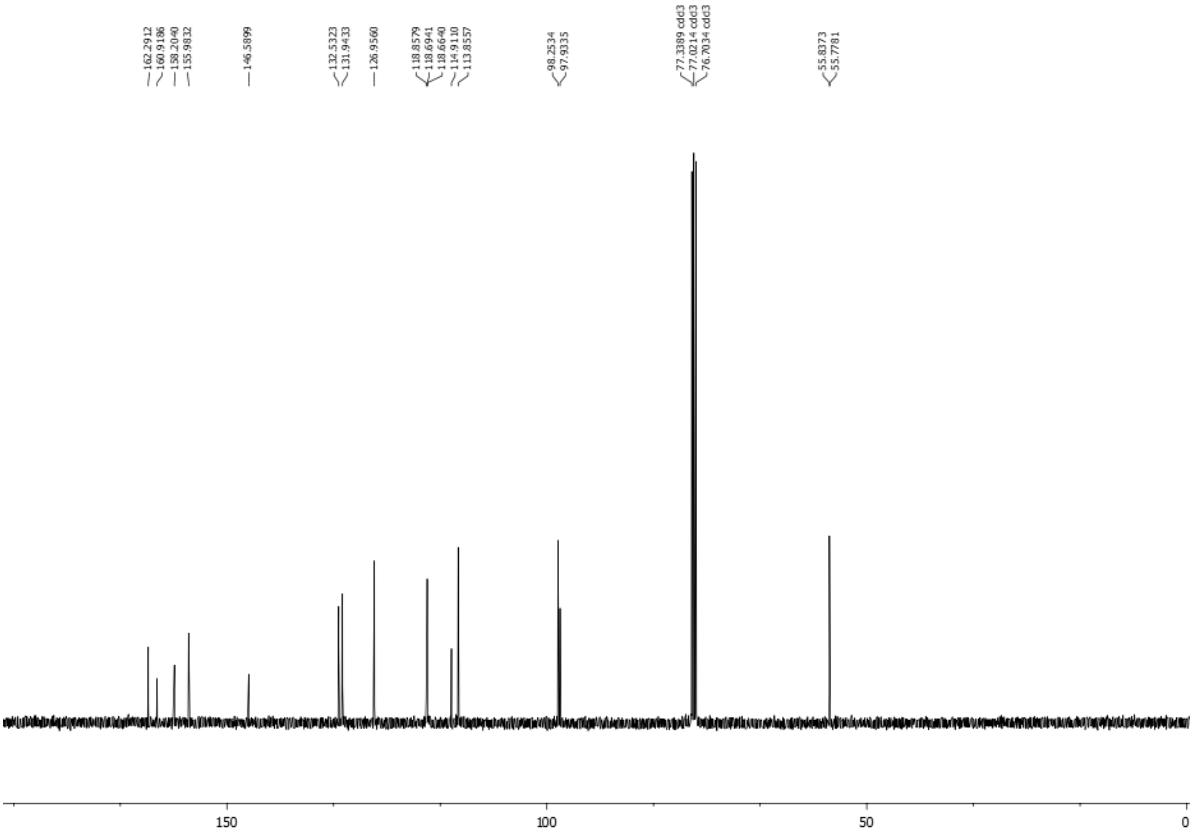
^{13}C{^{1}H} NMR of 2q (101 MHz, $CDCl_3$)



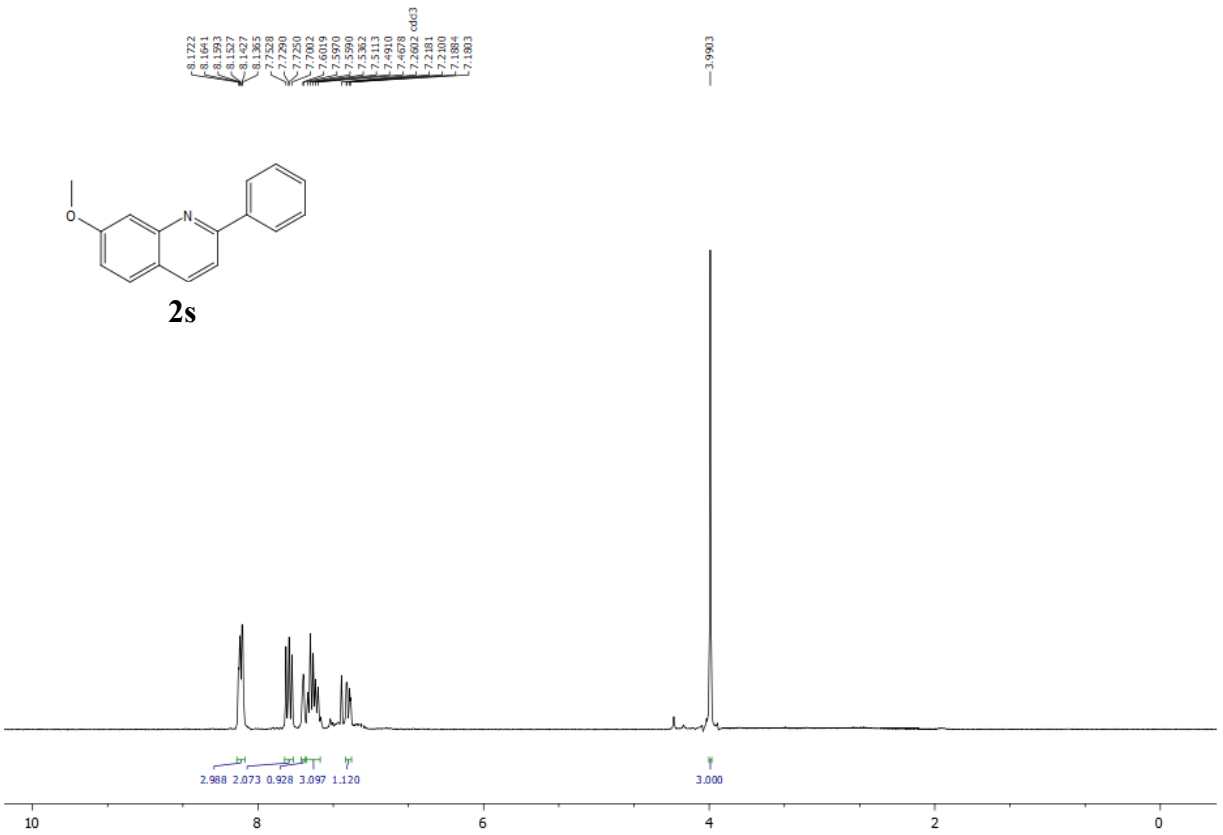
^{1}H NMR of 2r (400 MHz, $CDCl_3$)



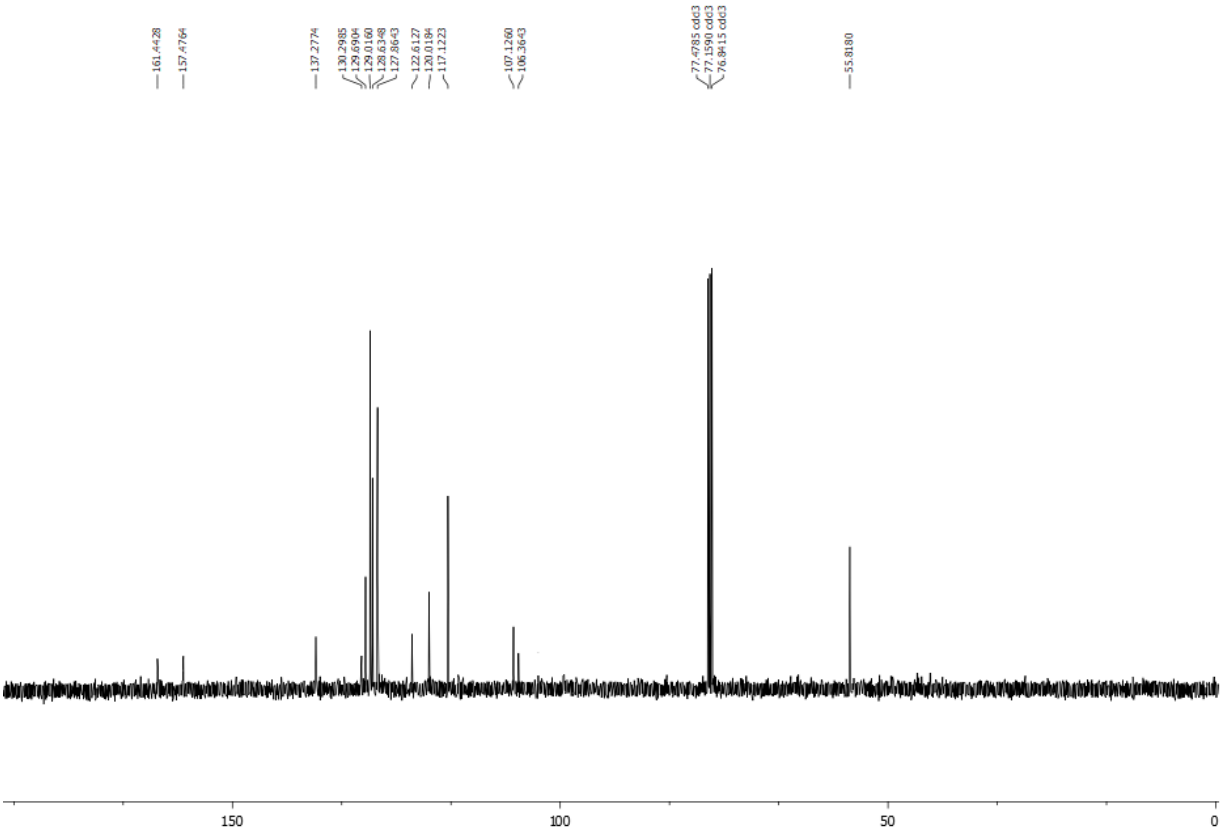
^{13}C{^{1}H} NMR of 2r (101 MHz, $CDCl_3$)



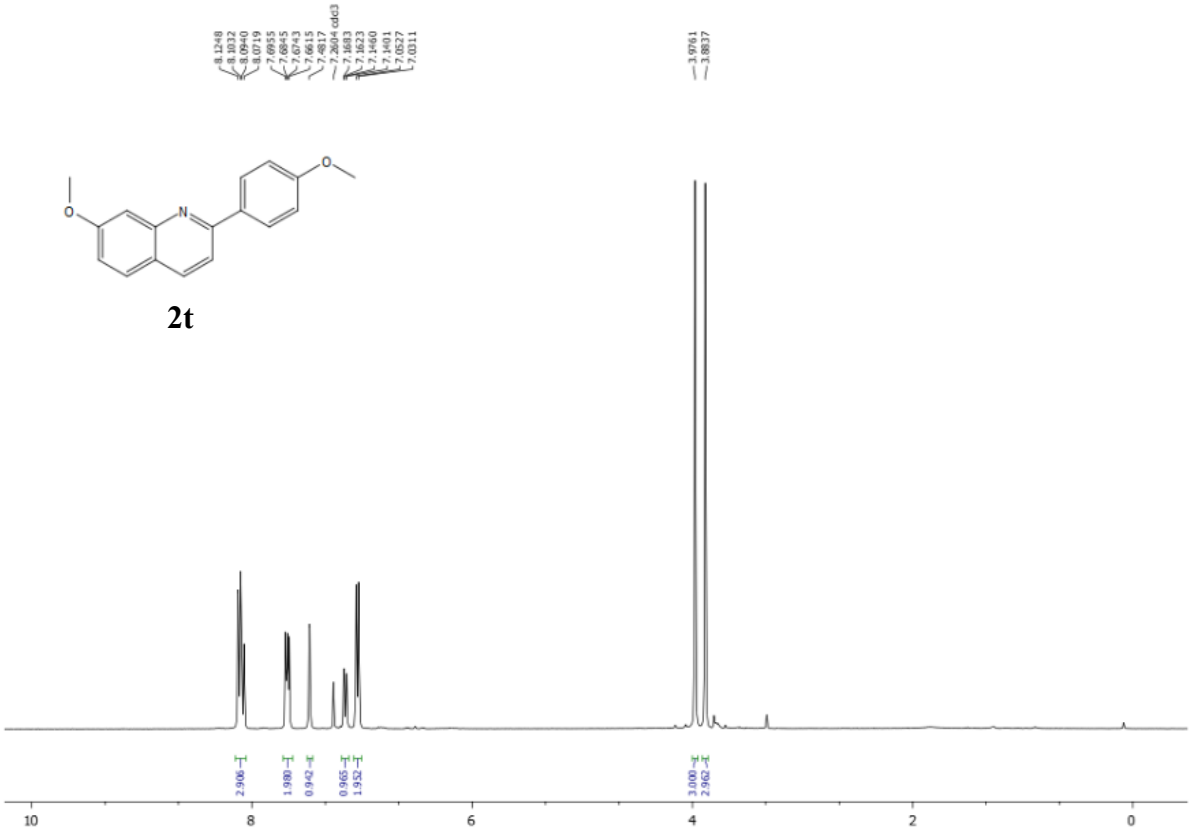
^{1}H NMR of 2s (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 2s (101 MHz, $CDCl_3$)

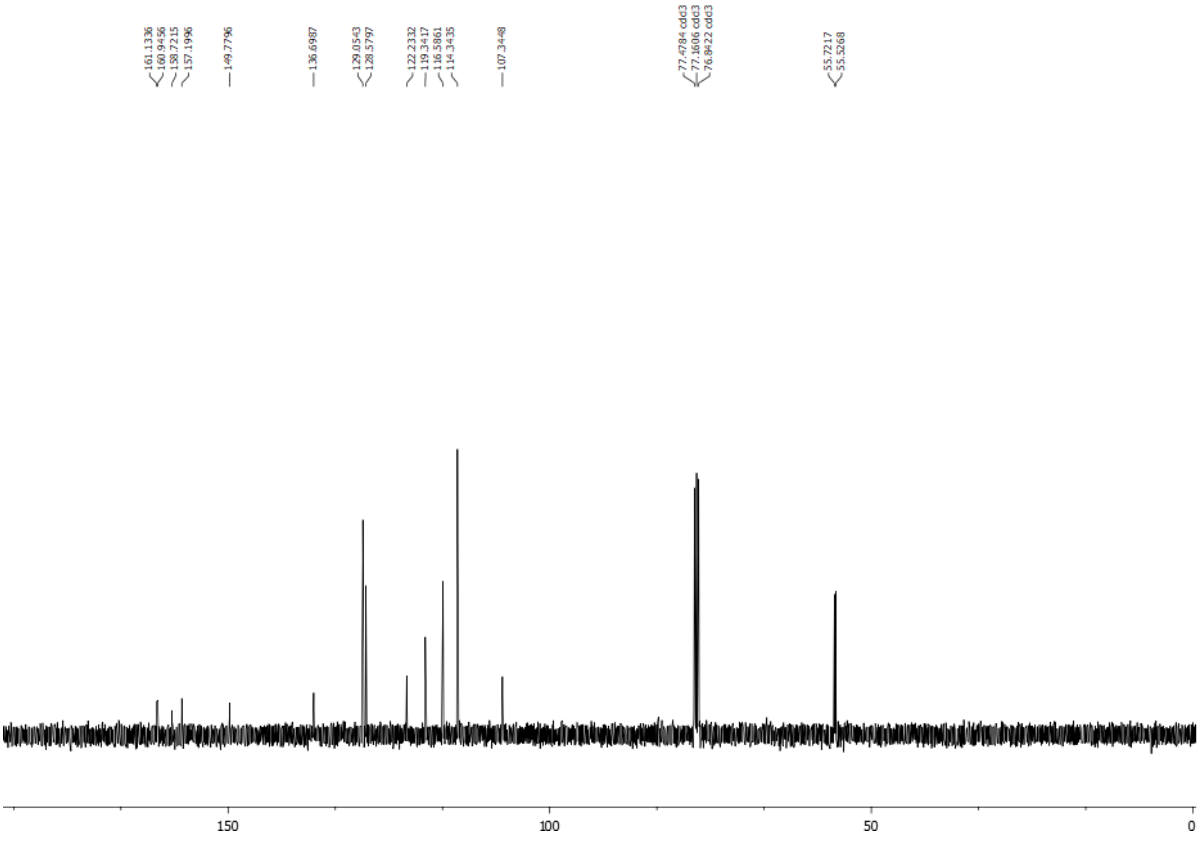


^{1}H NMR of 2t (400 MHz, $CDCl_3$)

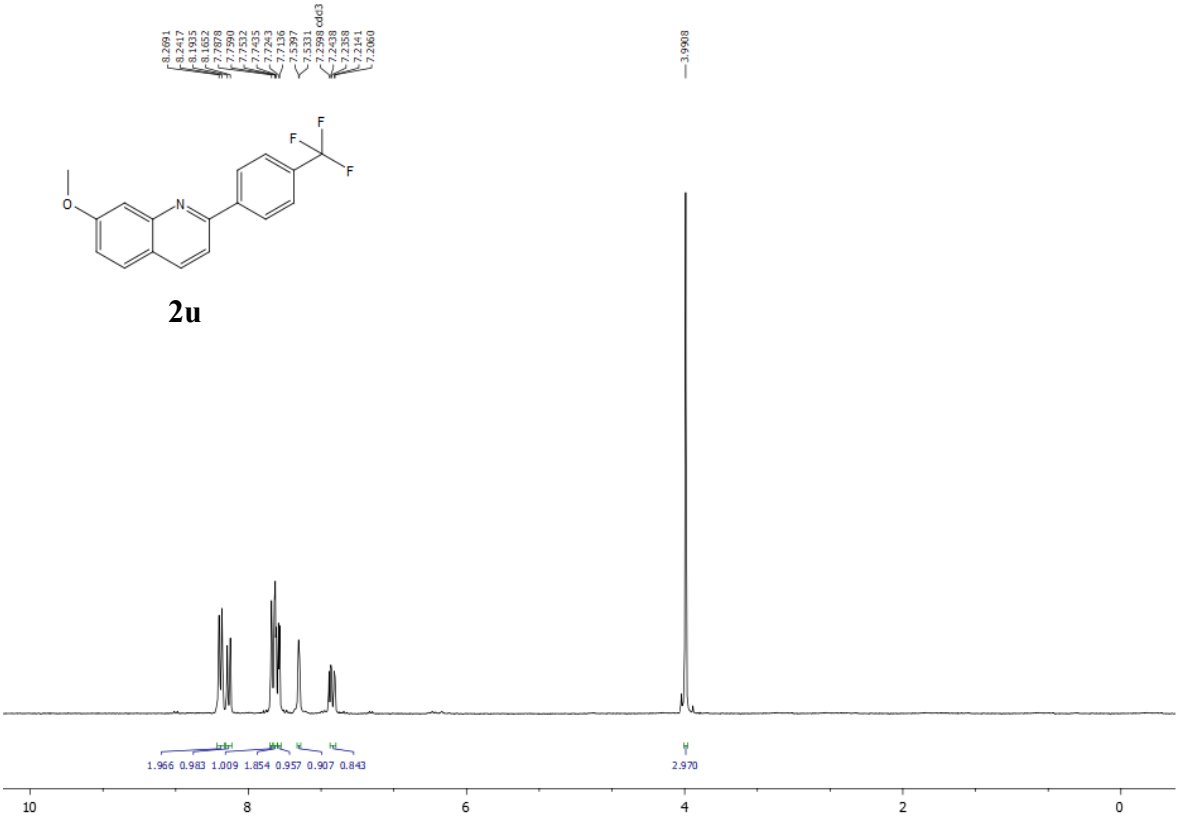


2t

^{13}C{^{1}H} NMR of 2t (101 MHz, $CDCl_3$)

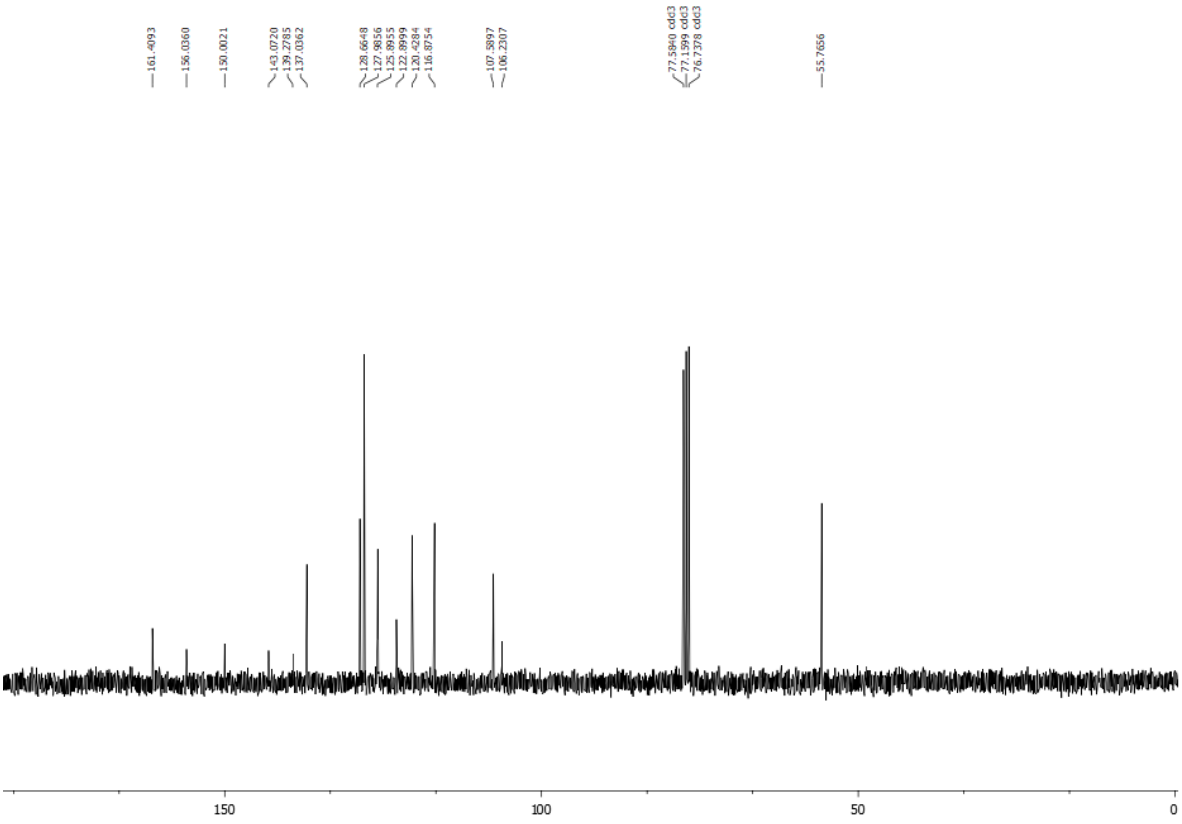


^{1}H NMR of 2u (400 MHz, $CDCl_3$)

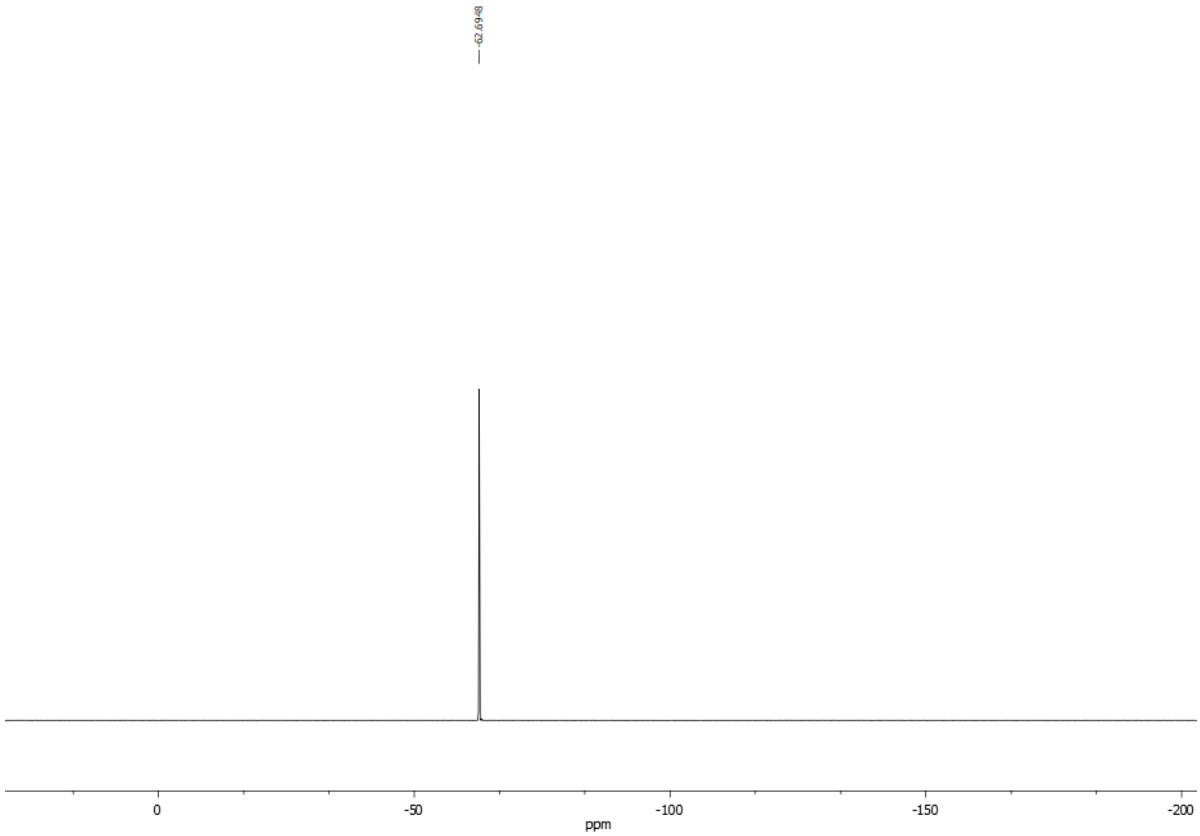


2u

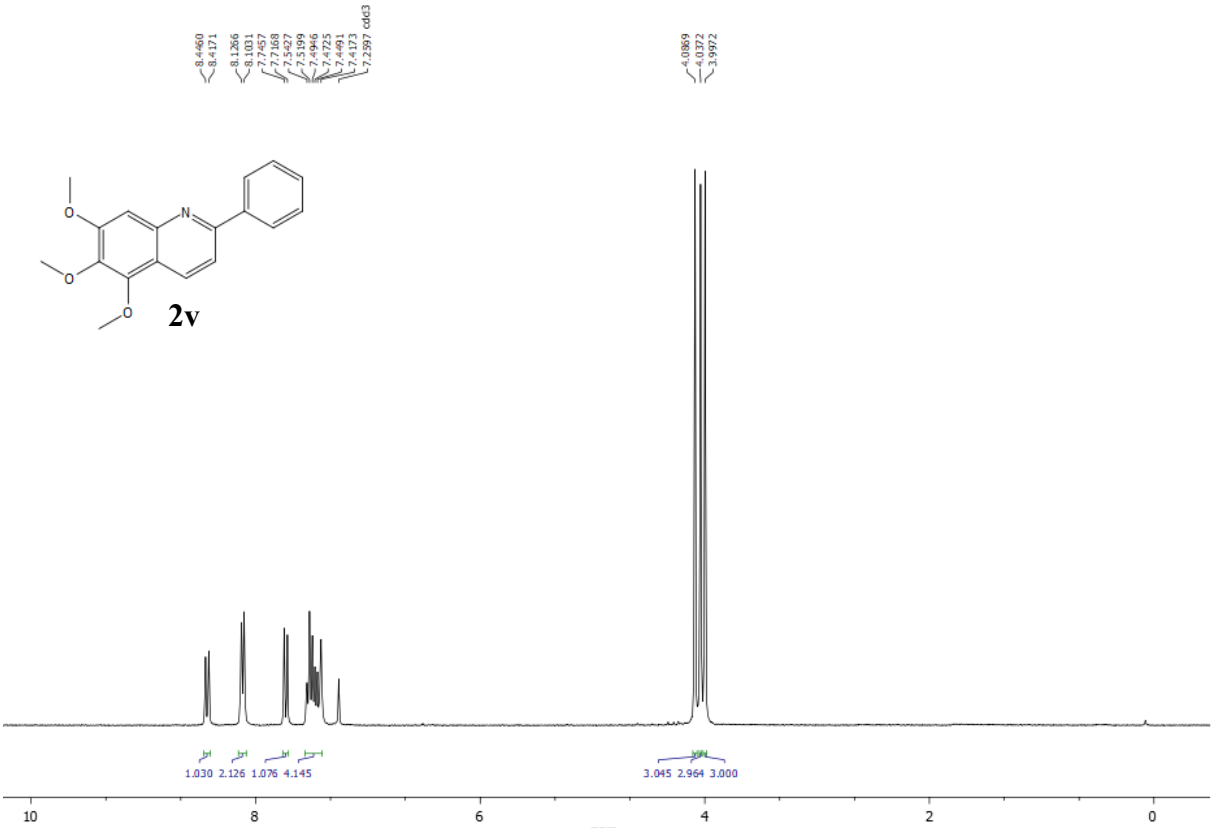
^{13}C{^{1}H} NMR of 2u (101 MHz, $CDCl_3$)



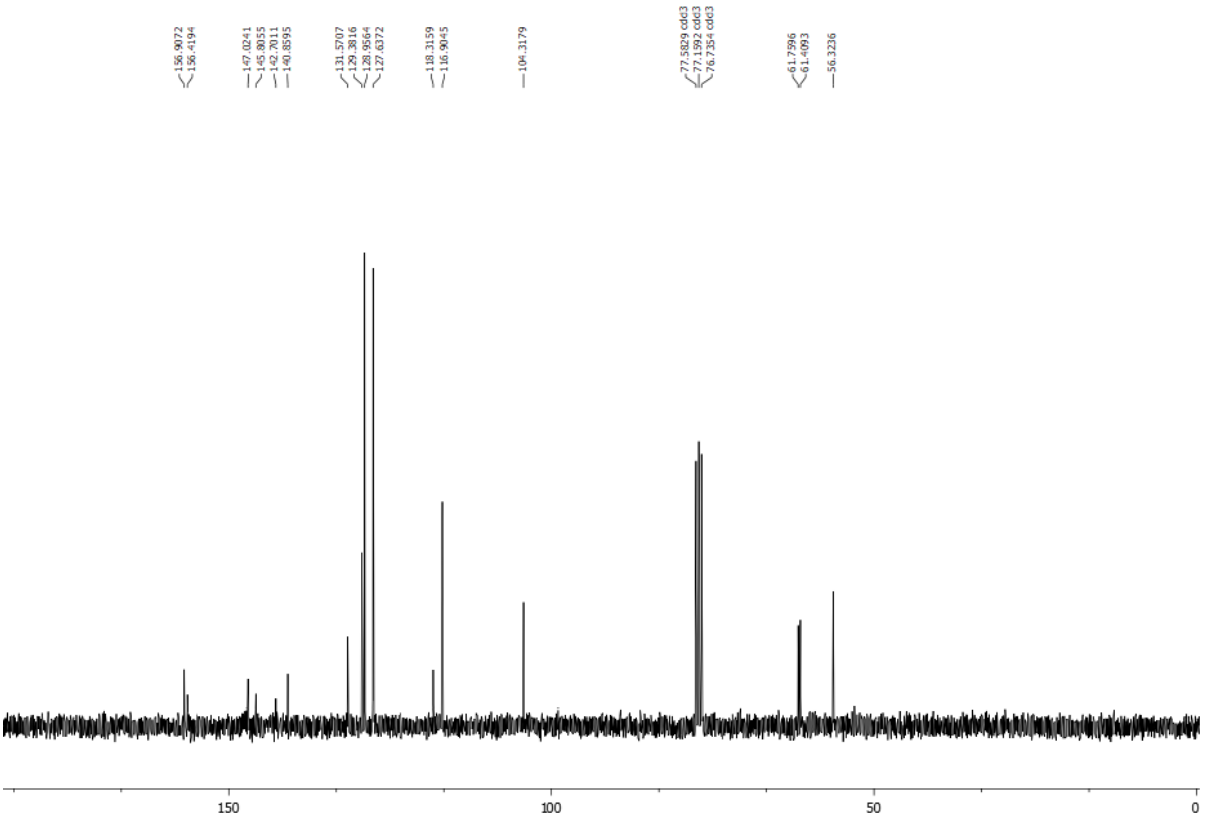
^{19}F NMR of 2u (376 MHz, $CDCl_3$)



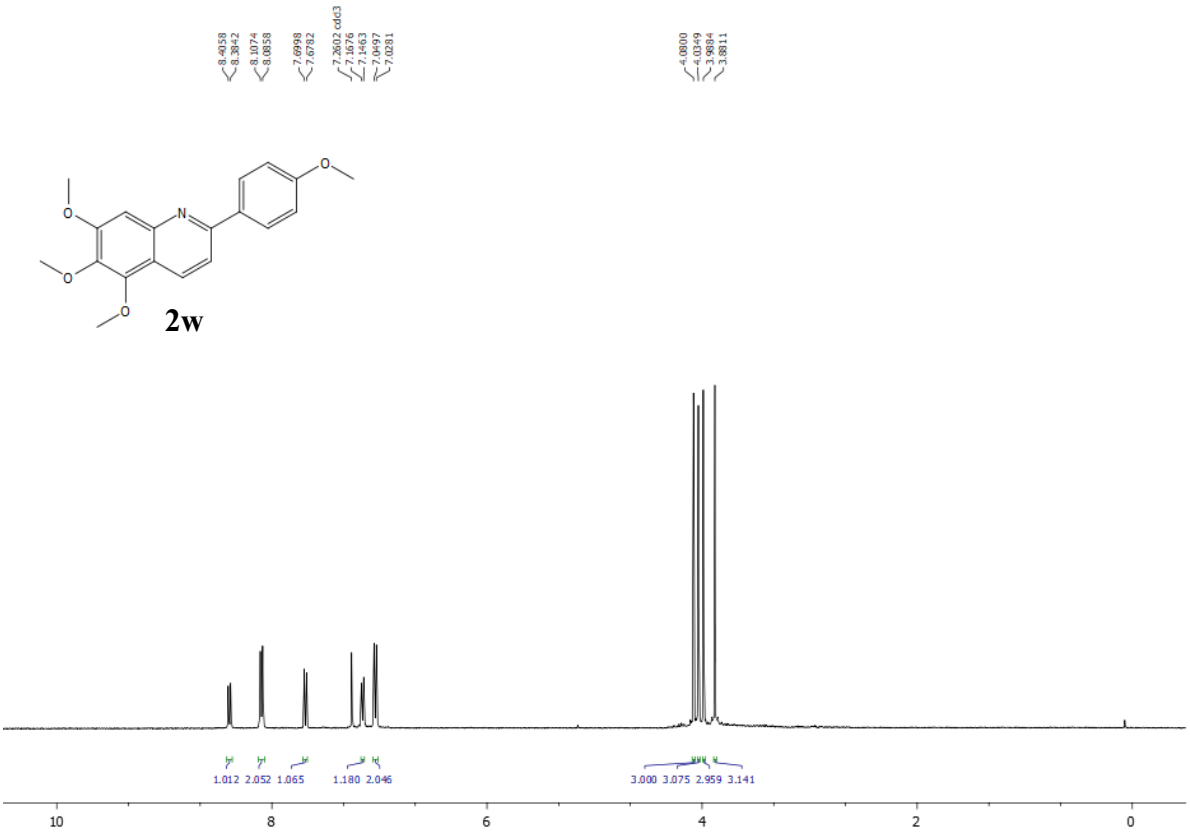
^{1}H NMR of 2v (400 MHz, $CDCl_3$)



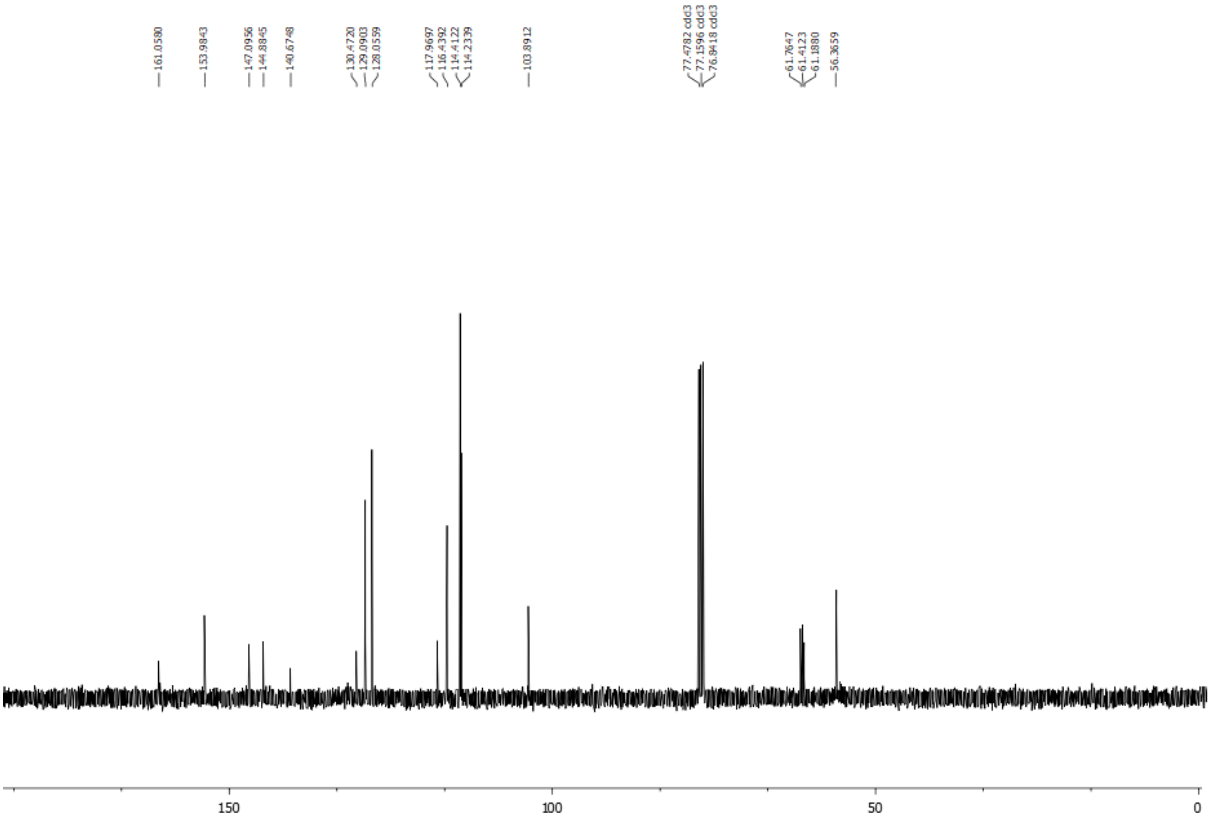
^{13}C{^{1}H} NMR of 2v (101 MHz, $CDCl_3$)



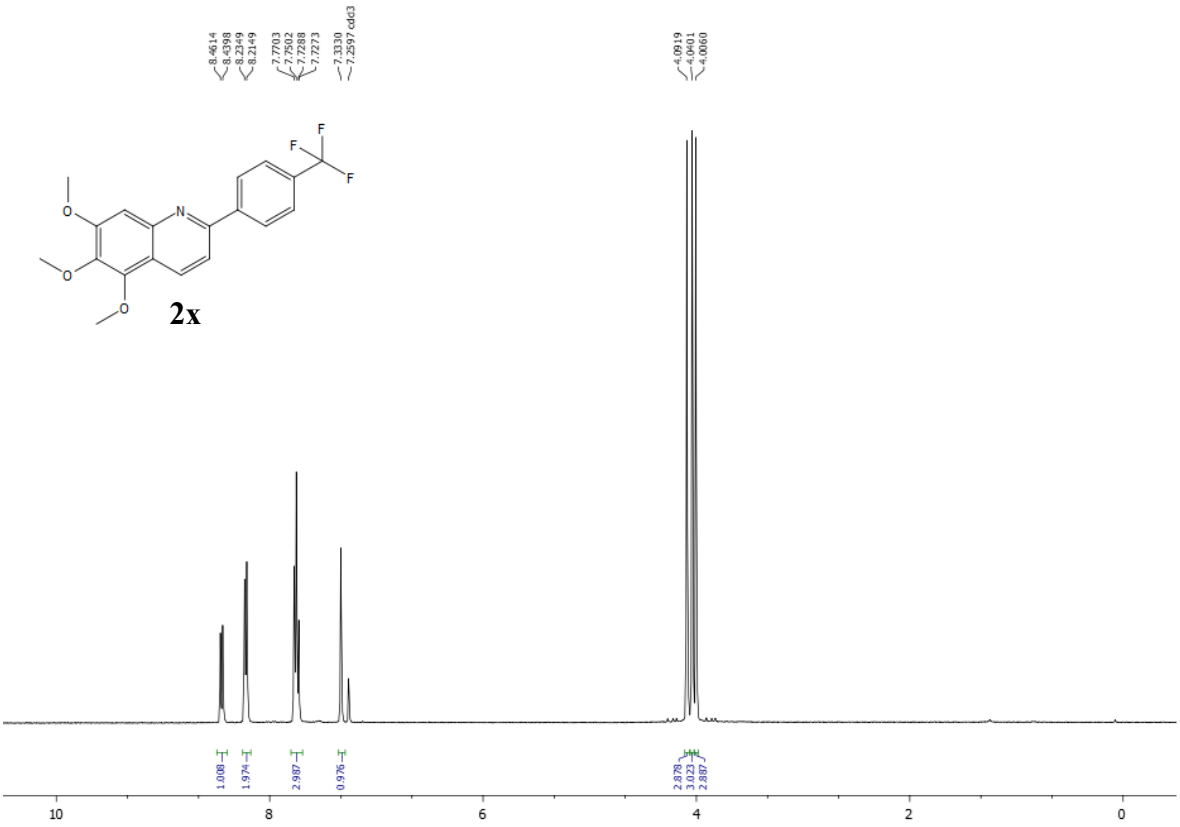
^{1}H NMR of 2w (400 MHz, $CDCl_3$)



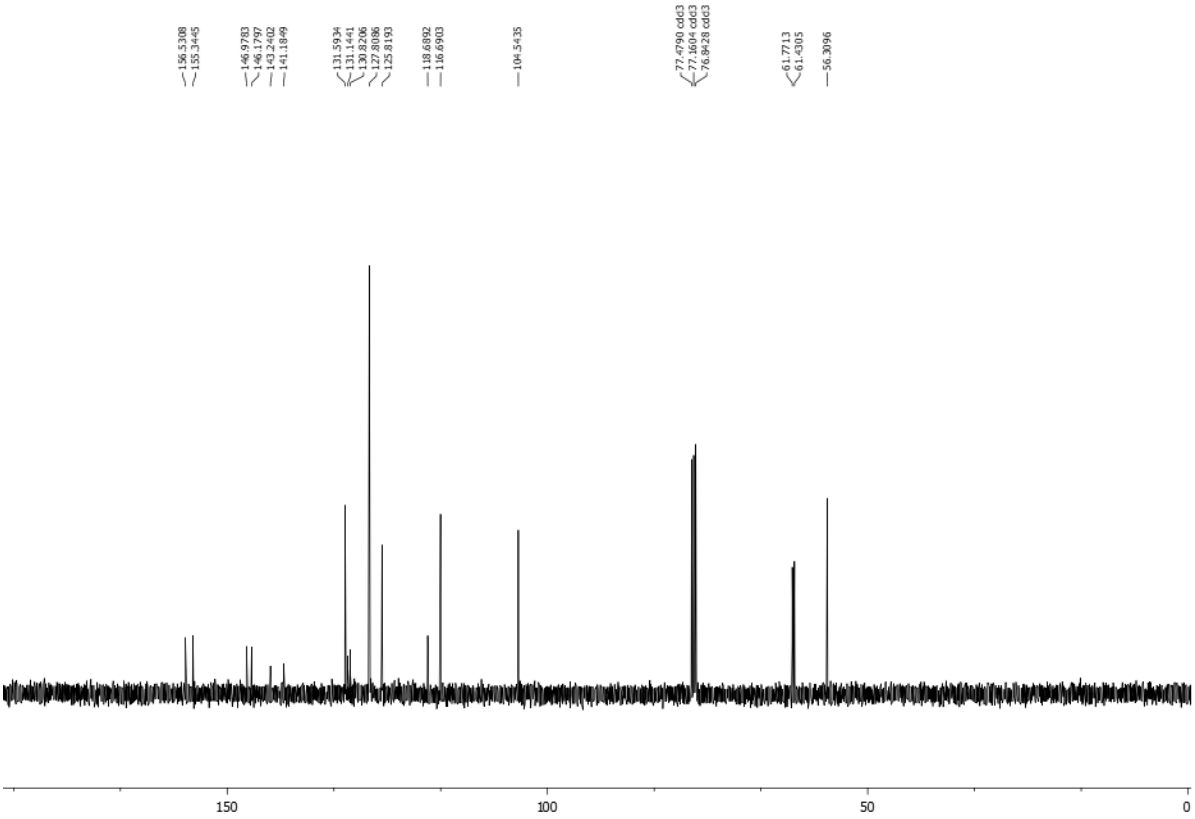
^{13}C{^{1}H} NMR of 2w (101 MHz, $CDCl_3$)



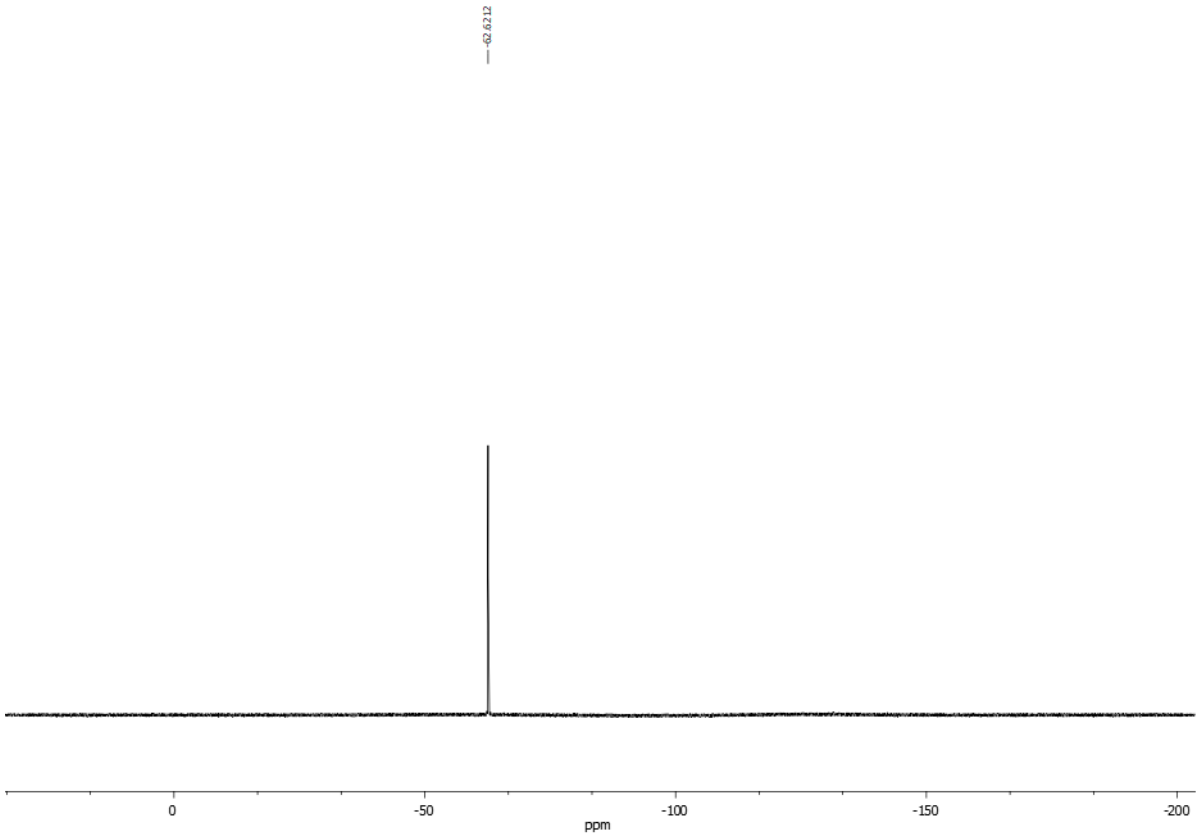
^{1}H NMR of 2x (400 MHz, $CDCl_3$)



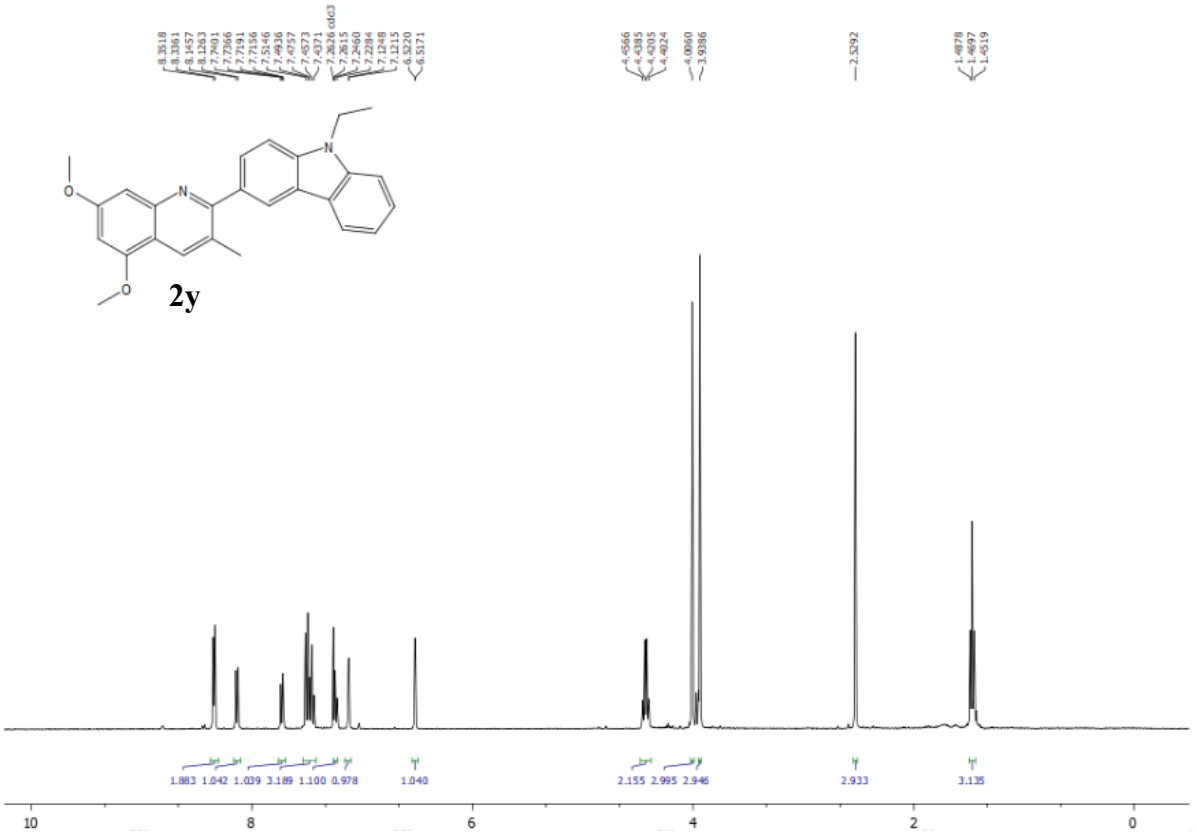
^{13}C{^{1}H} NMR of 2x (101 MHz, $CDCl_3$)



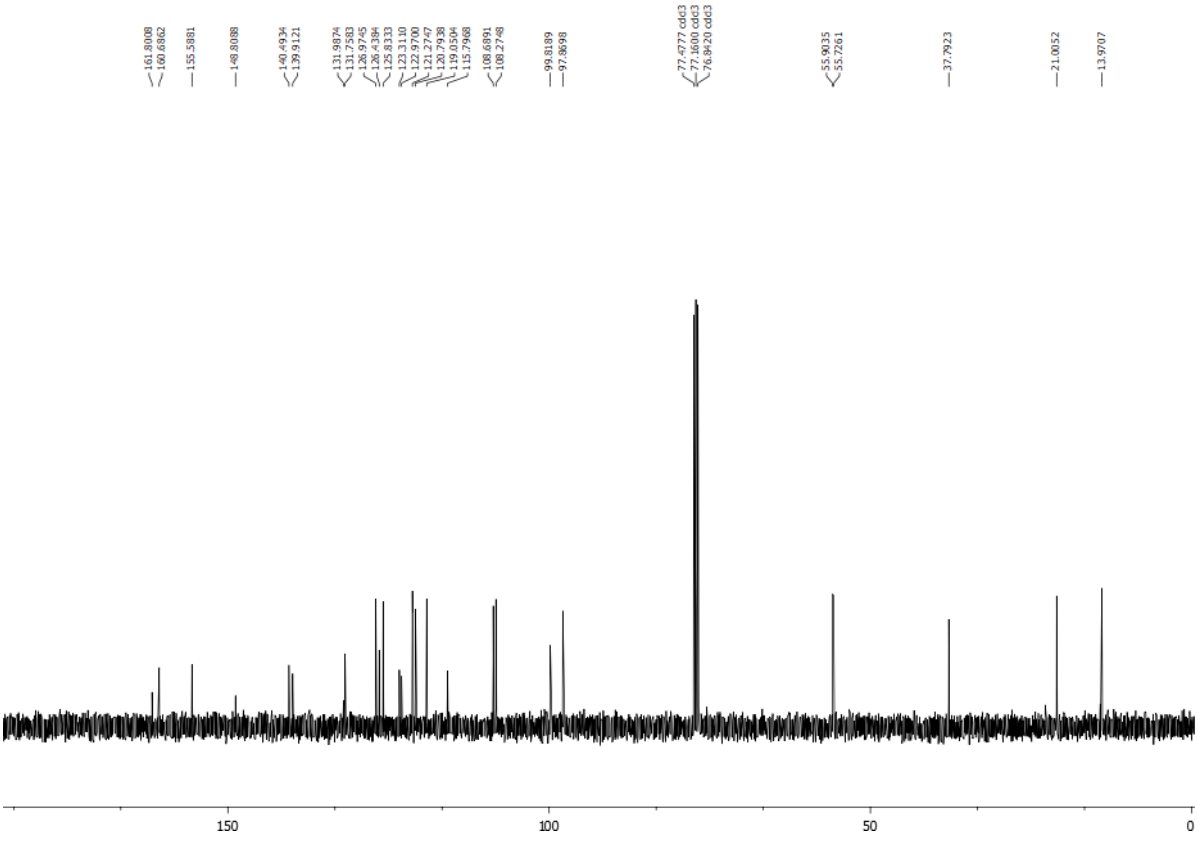
^{19}F NMR of 2x (376 MHz, $CDCl_3$)



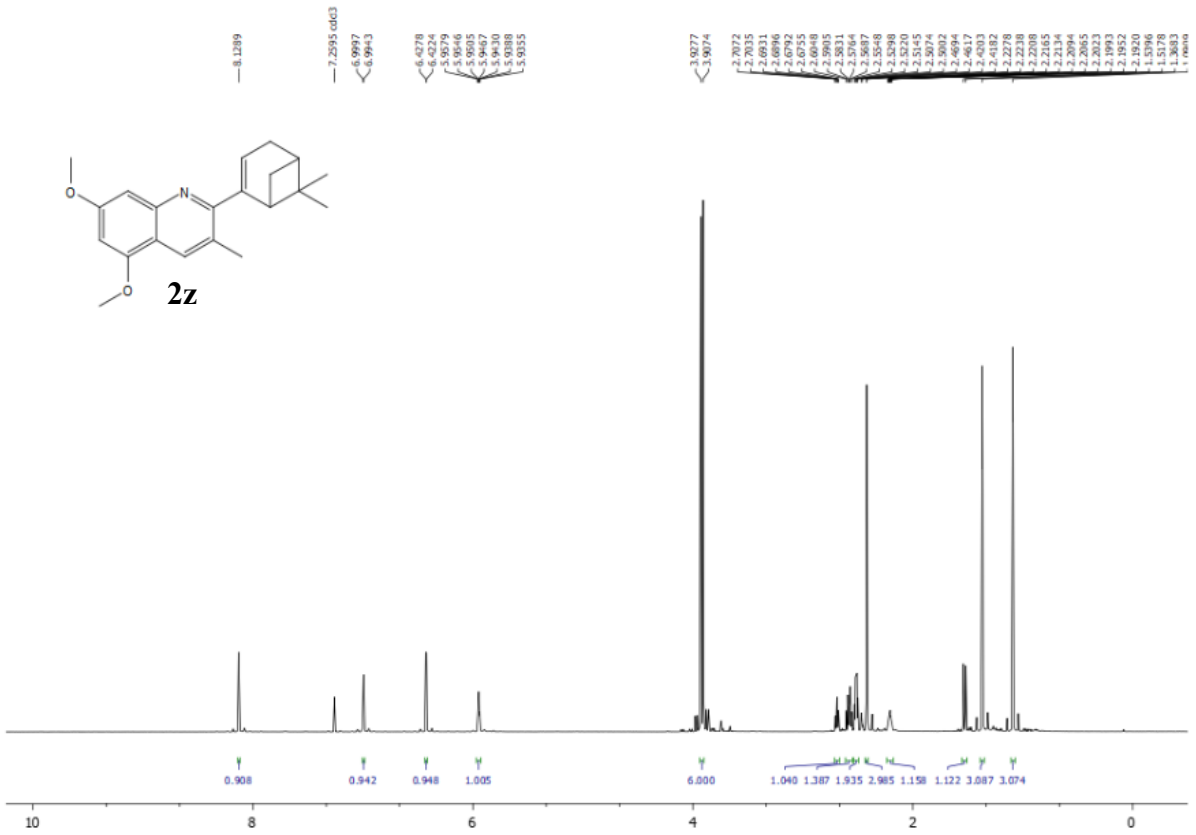
^{1}H NMR of 2y (400 MHz, $CDCl_3$)



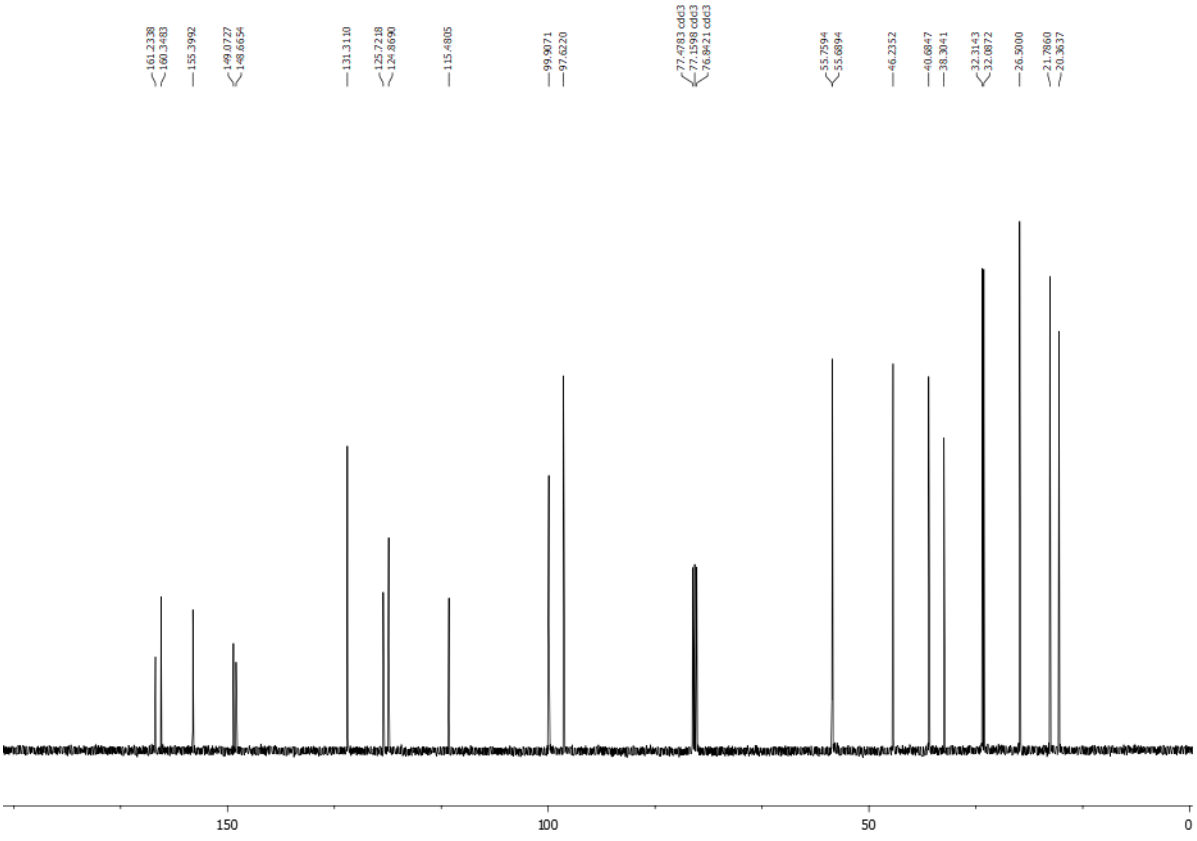
^{13}C{^{1}H} NMR of 2y (101 MHz, CDCl3)



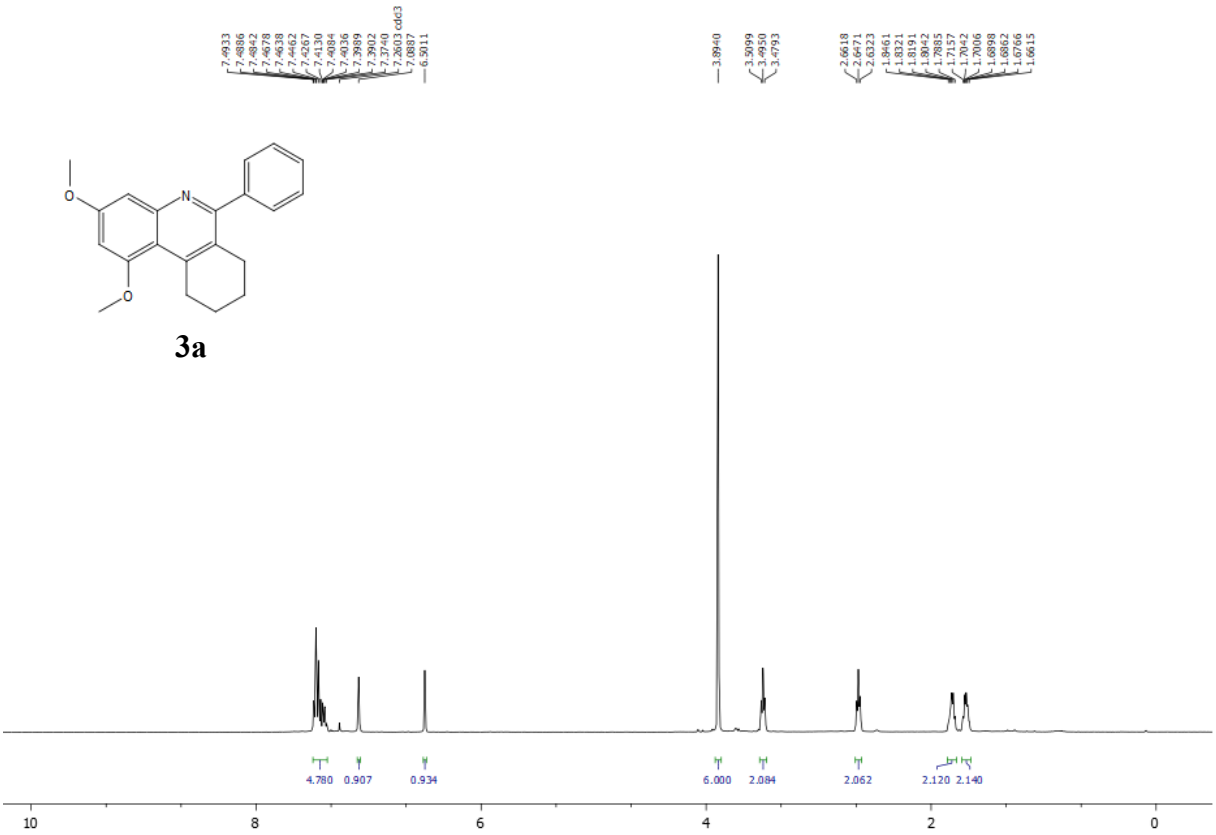
^{1}H NMR of 2z (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 2z (101 MHz, $CDCl_3$)

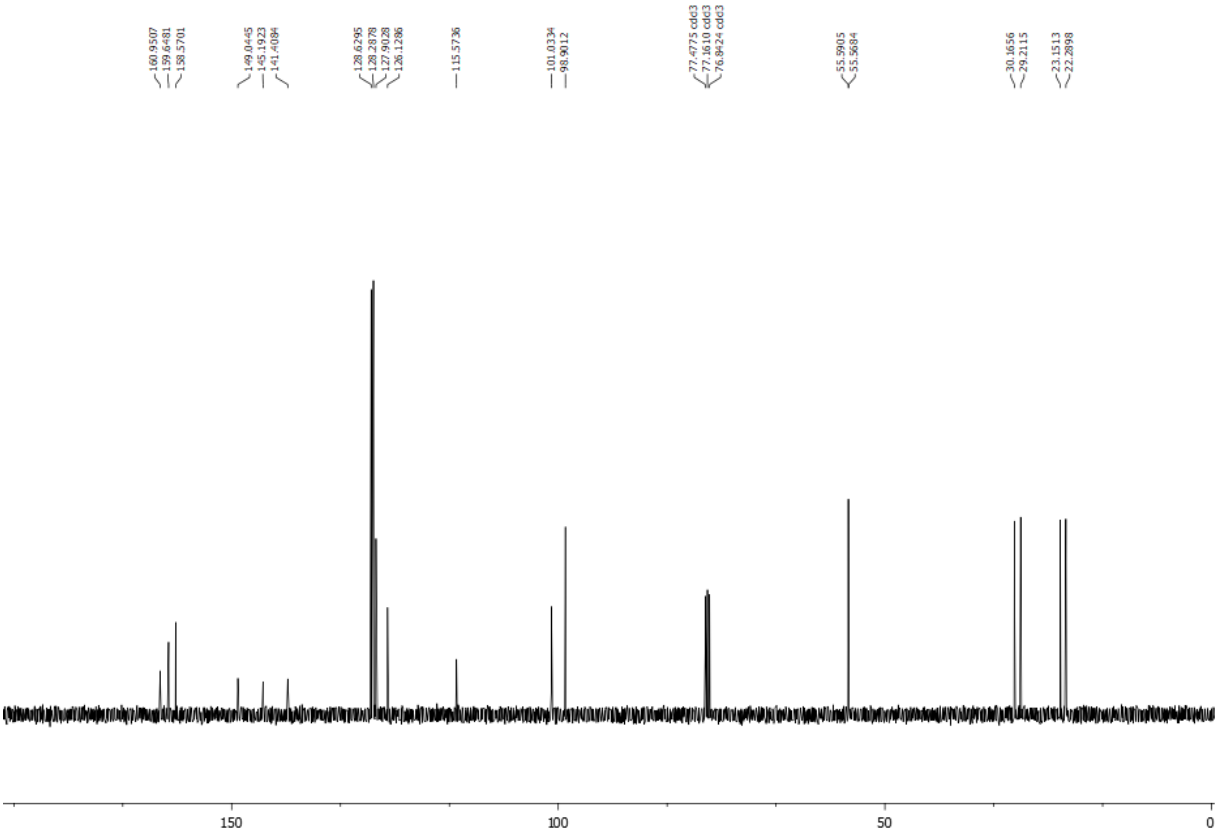


^{1}H NMR of 3a (400 MHz, $CDCl_3$)

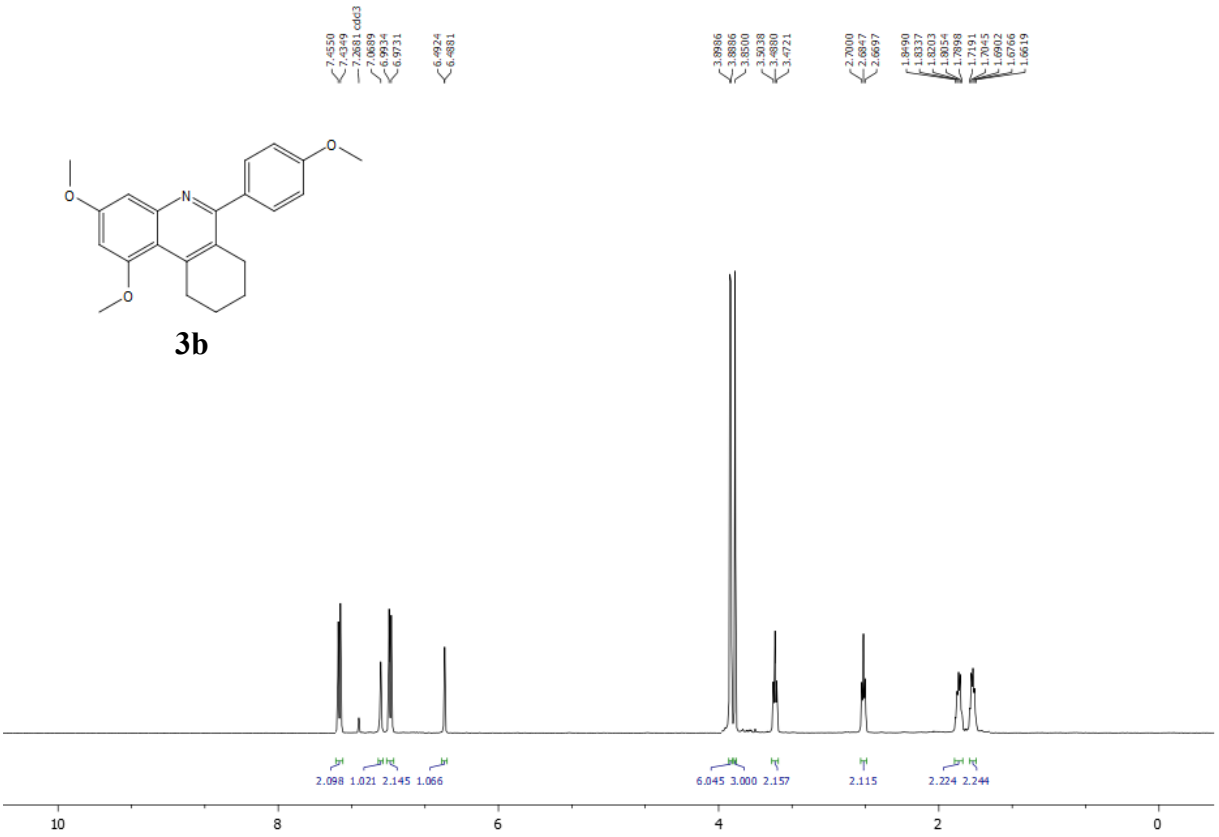


3a

^{13}C{^{1}H} NMR of 3a (101 MHz, $CDCl_3$)

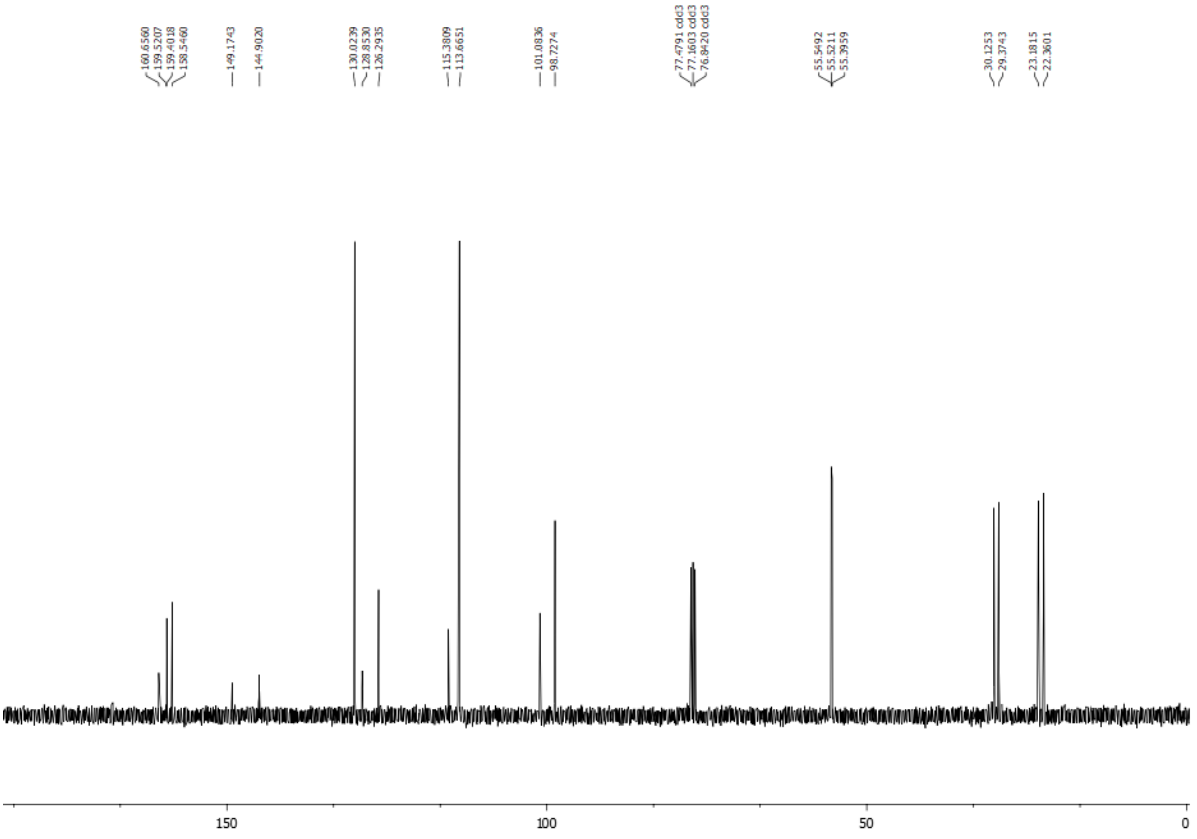


^{1}H NMR of 3b (400 MHz, $CDCl_3$)

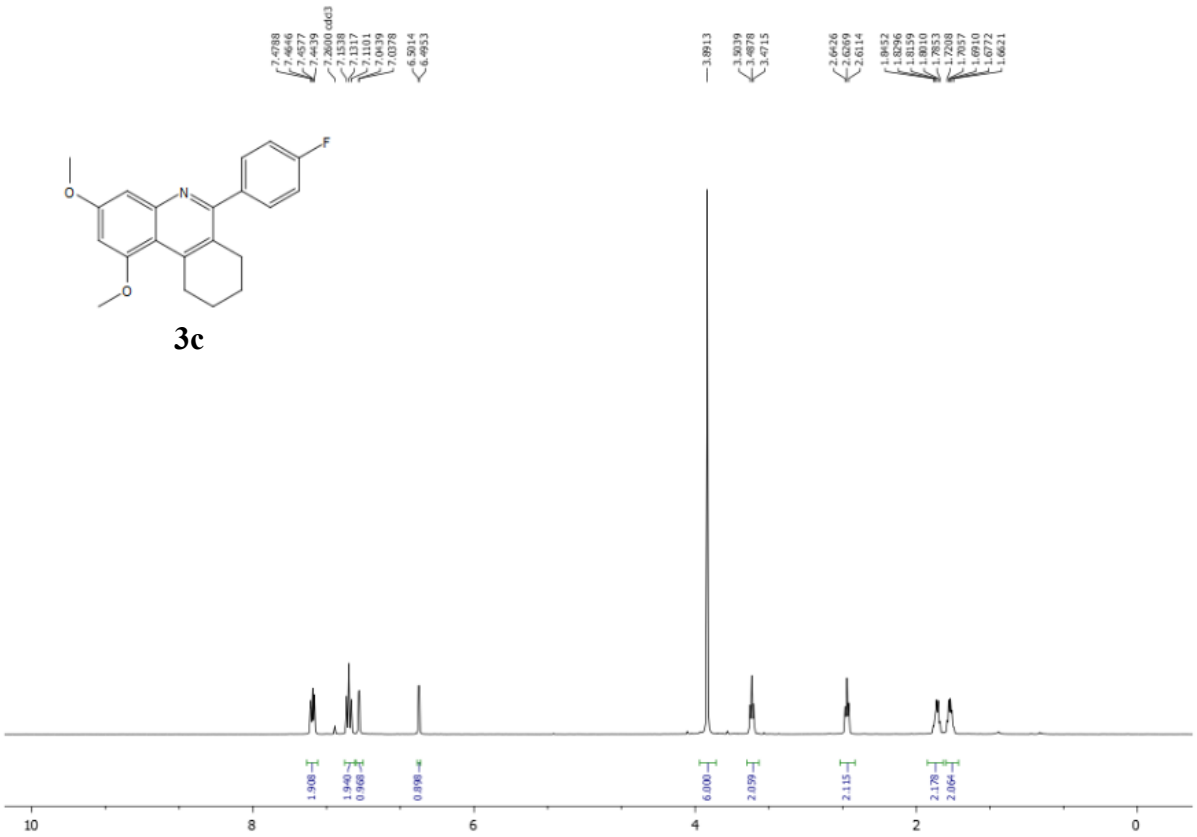


3b

^{13}C{^{1}H} NMR of 3b (101 MHz, $CDCl_3$)

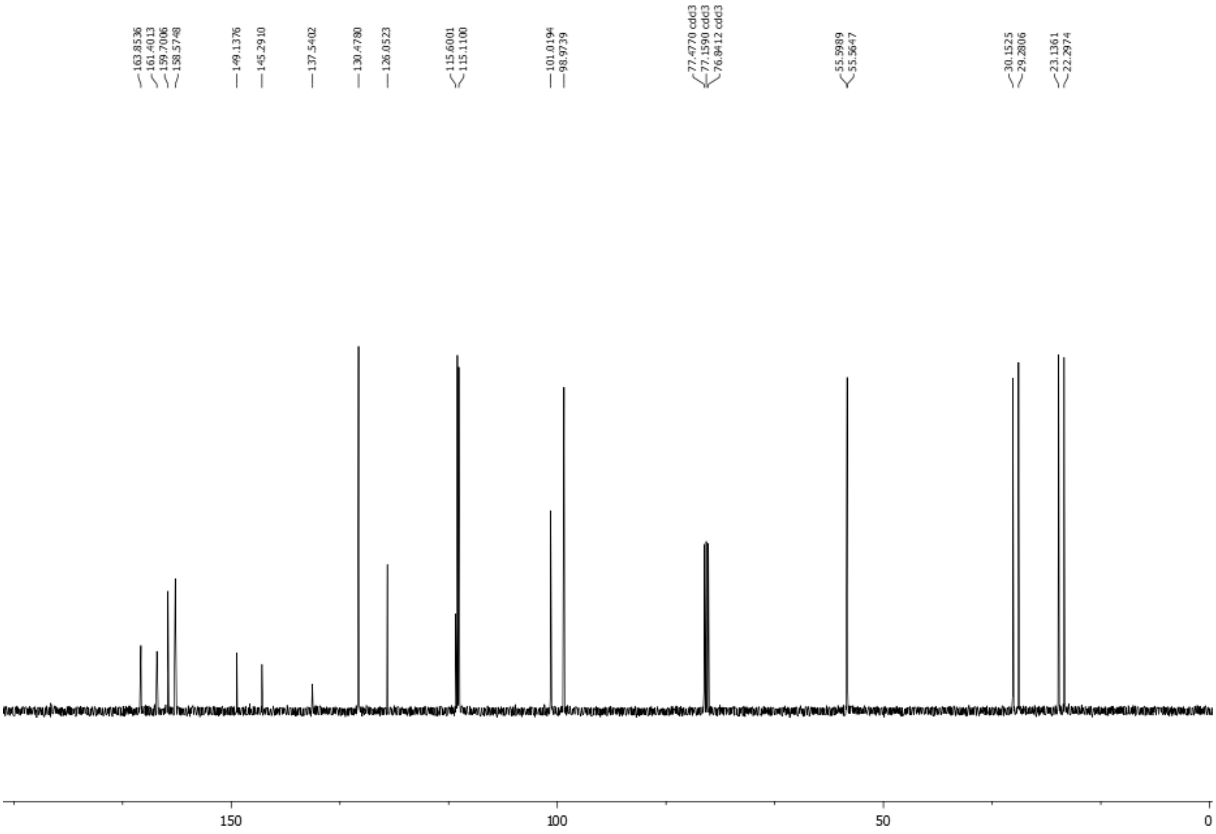


^{1}H NMR of 3c (400 MHz, $CDCl_3$)

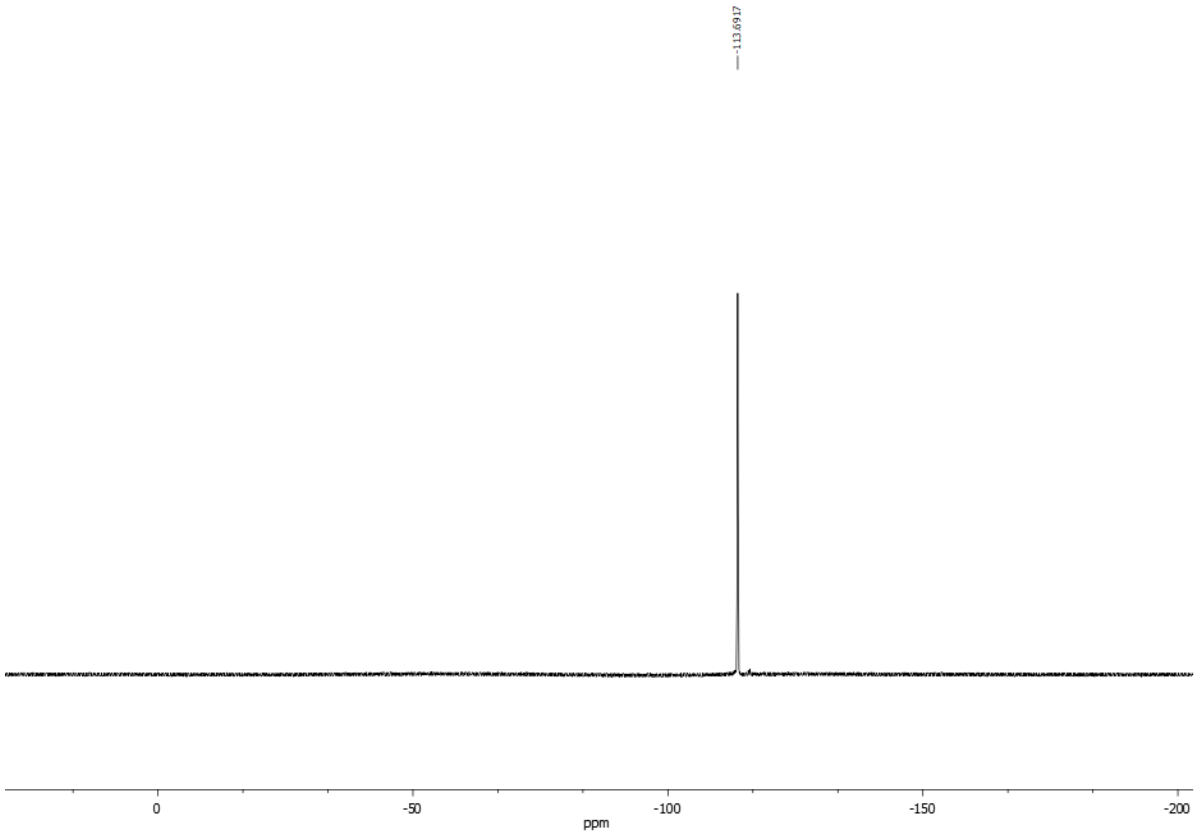


3c

^{13}C{^{1}H} NMR of 3c (101 MHz, $CDCl_3$)



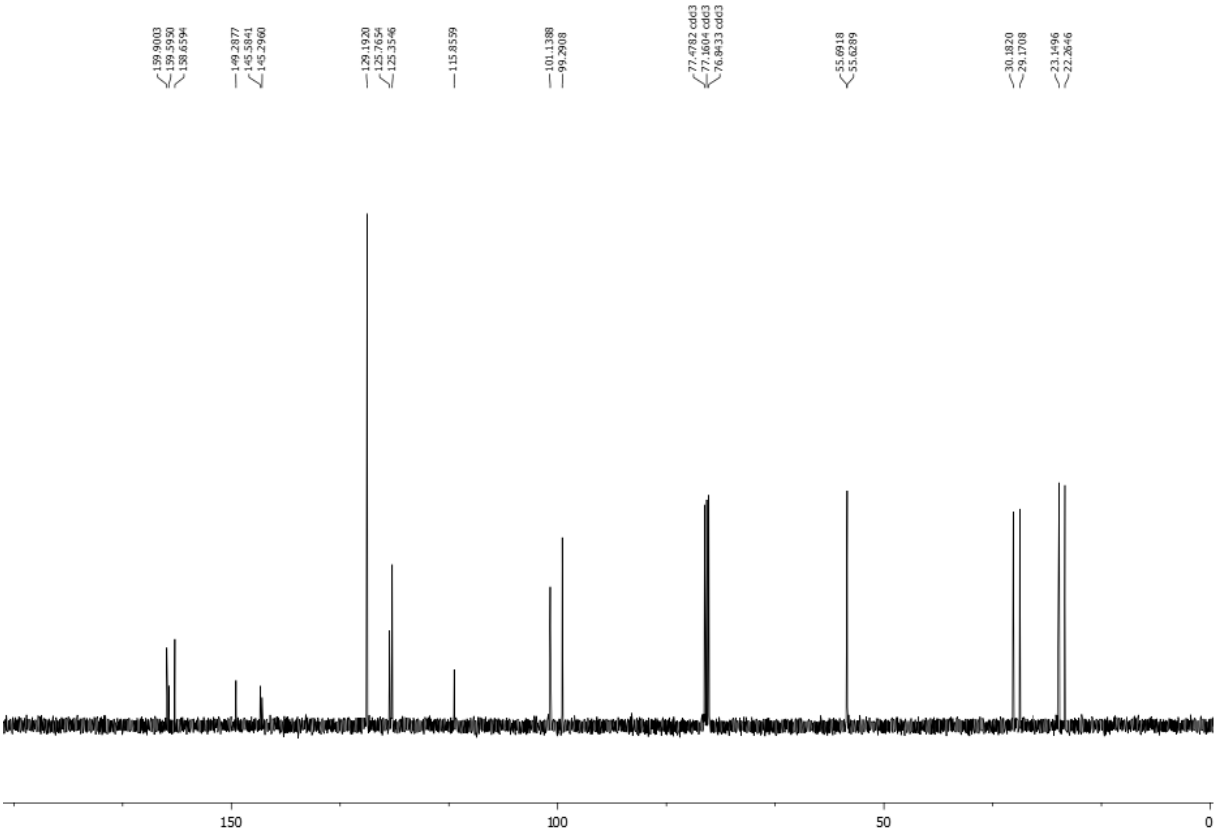
^{19}F NMR of 3c (376 MHz, $CDCl_3$)



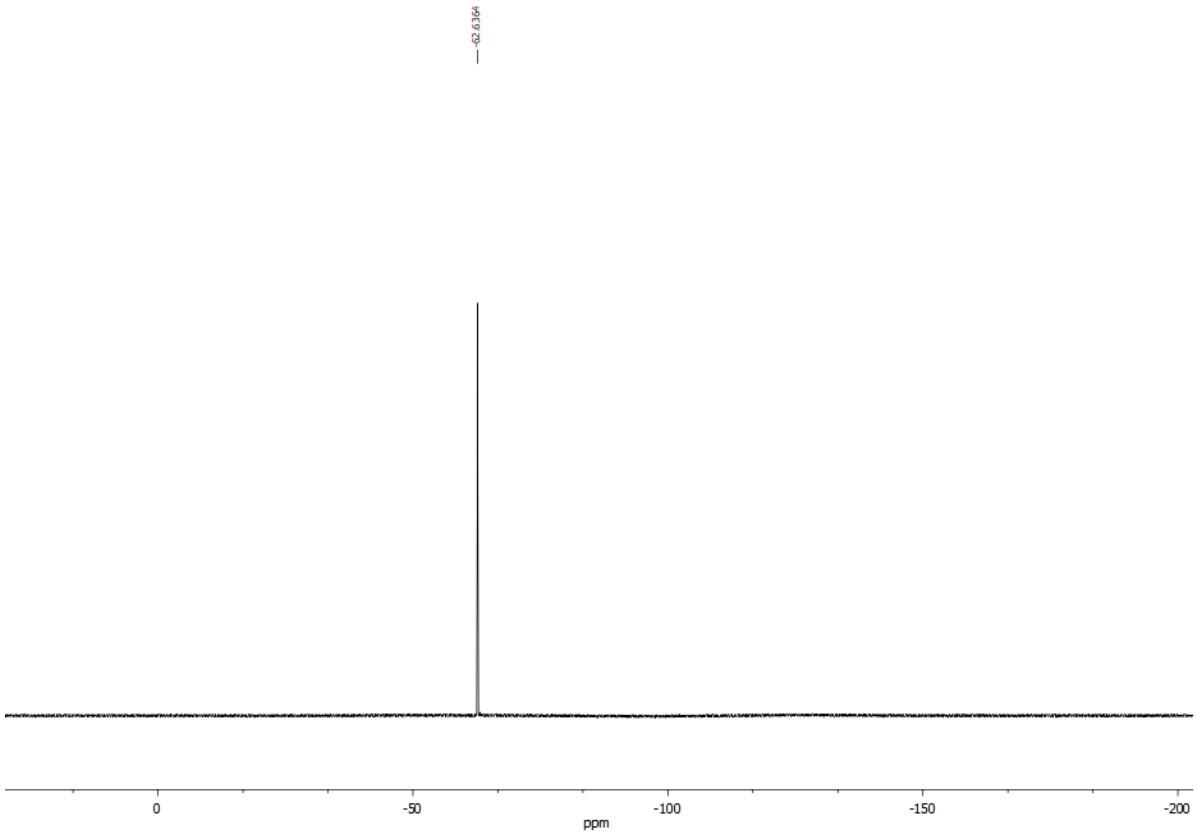
^{1}H NMR of 3d (400 MHz, $CDCl_3$)

3d

^{13}C{^{1}H} NMR of 3d (101 MHz, $CDCl_3$)



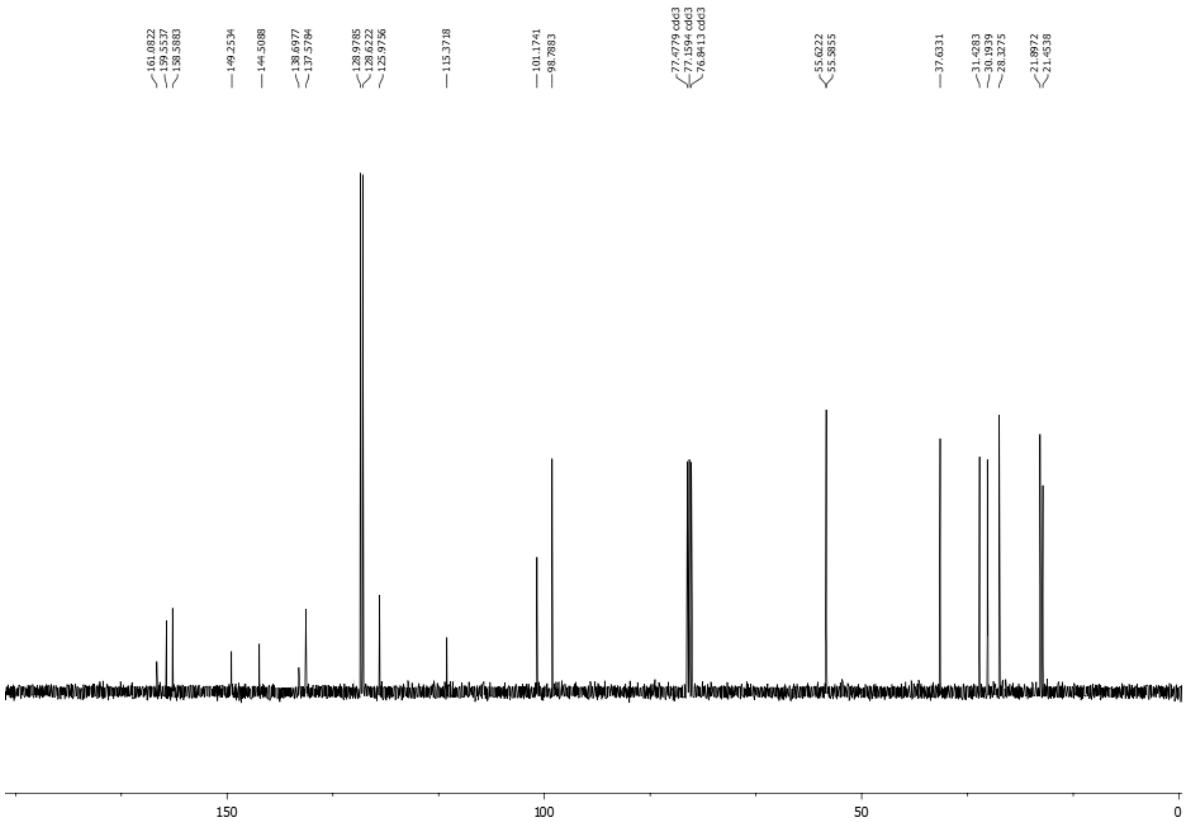
^{19}F NMR of 3d (376 MHz, $CDCl_3$)



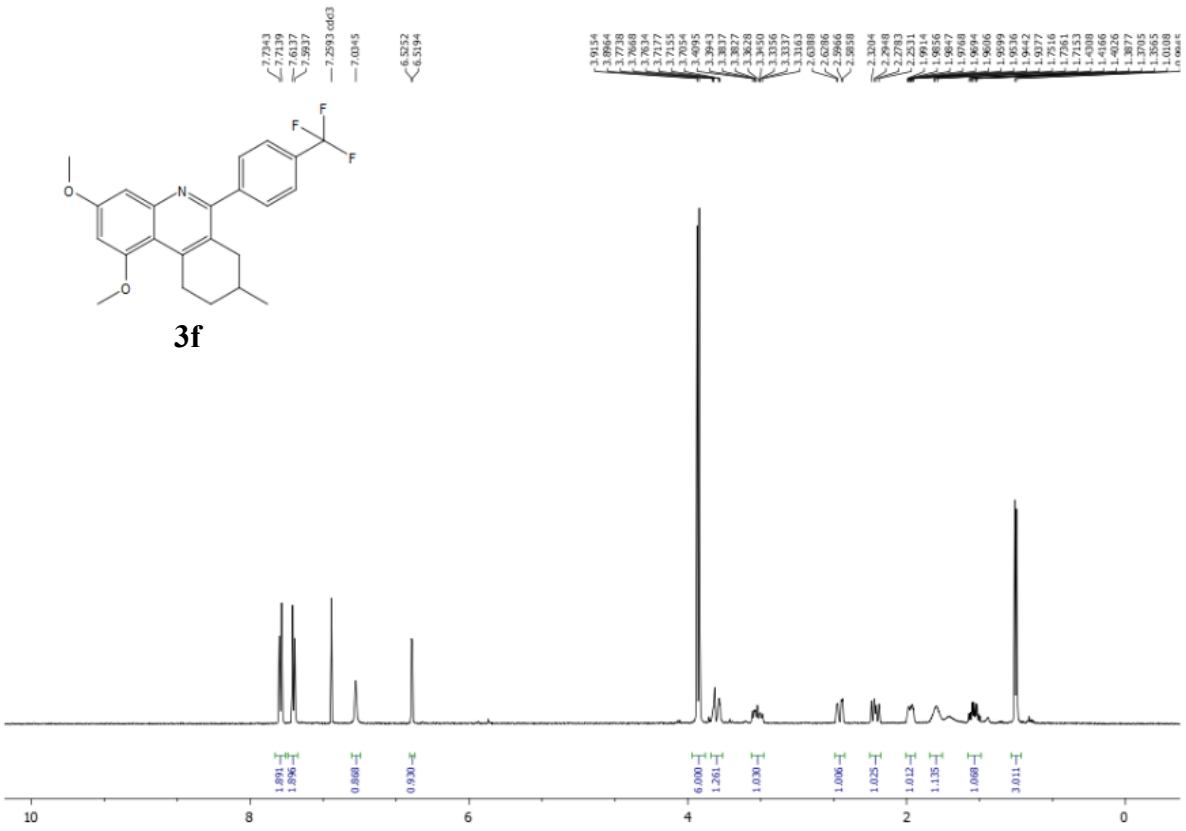
^{1}H NMR of 3e (400 MHz, $CDCl_3$)

3e

^{13}C{^{1}H} NMR of 3e (101 MHz, $CDCl_3$)

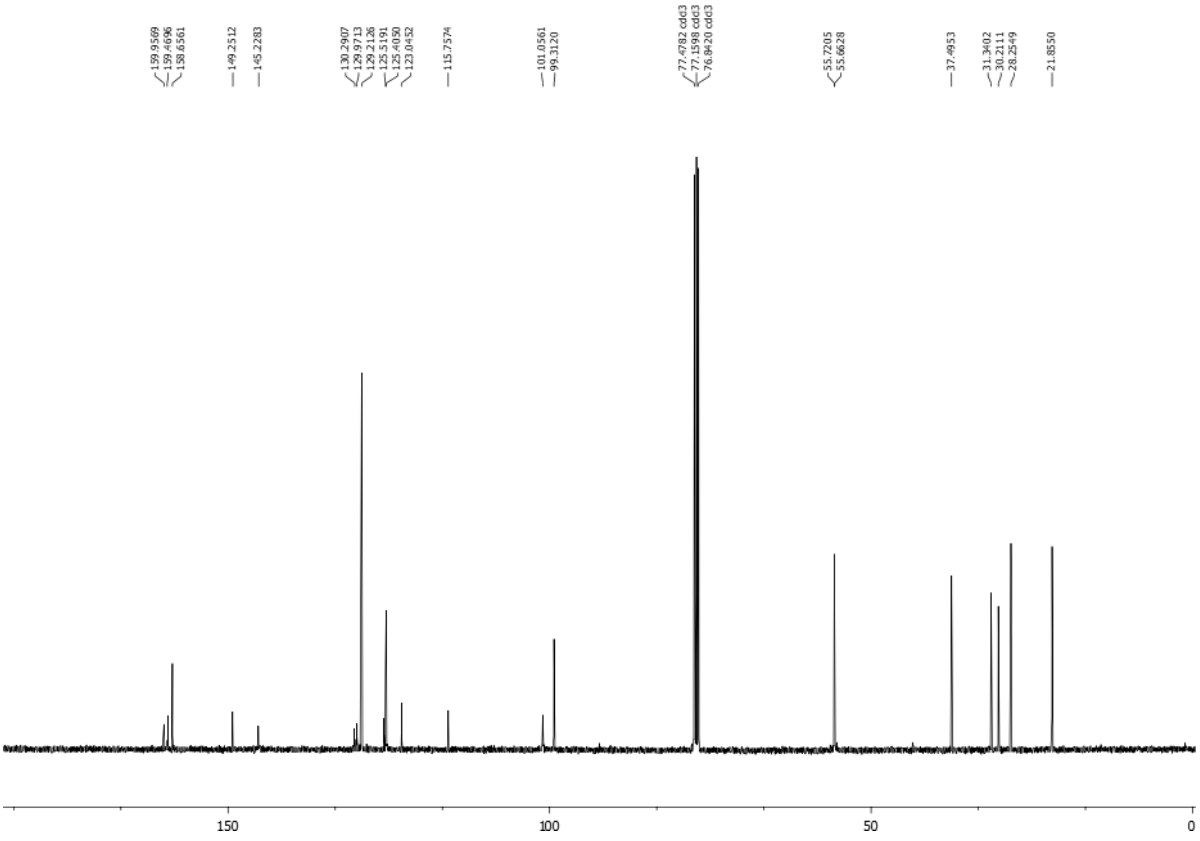


^{1}H NMR of 3f (400 MHz, $CDCl_3$)

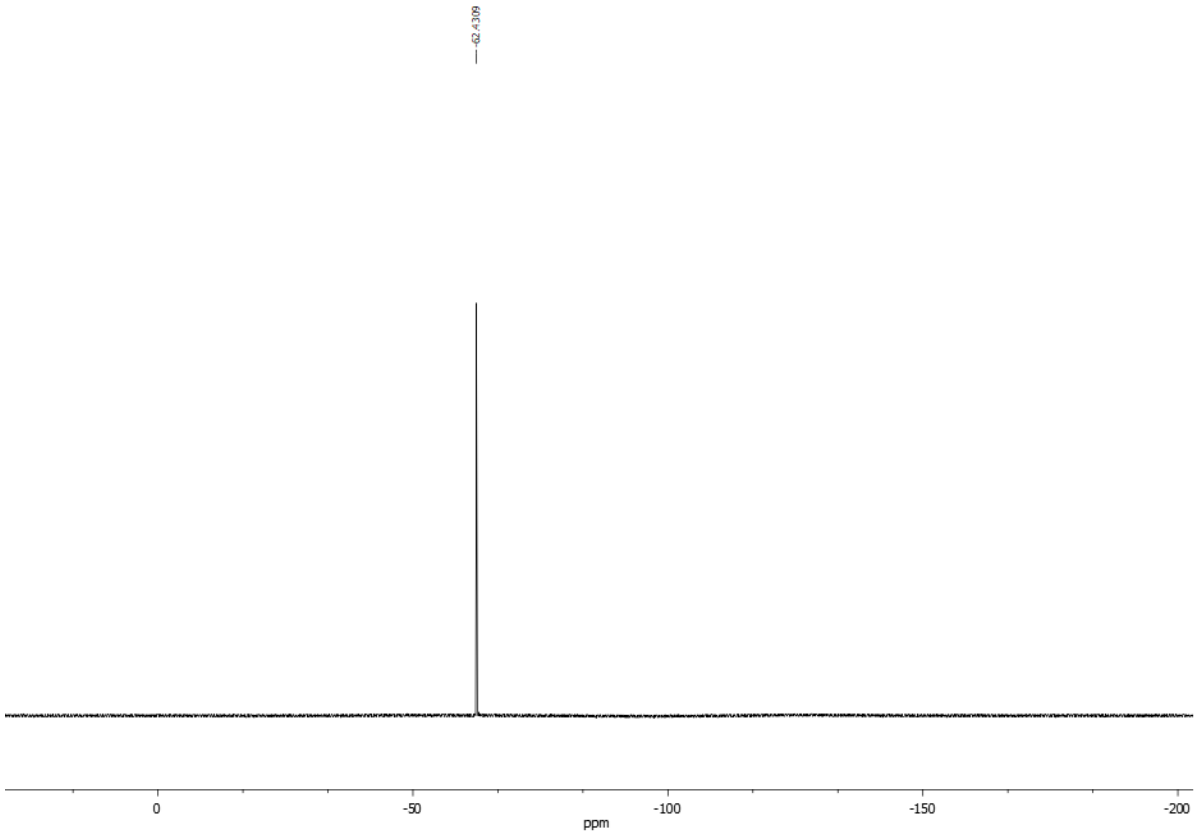


3f

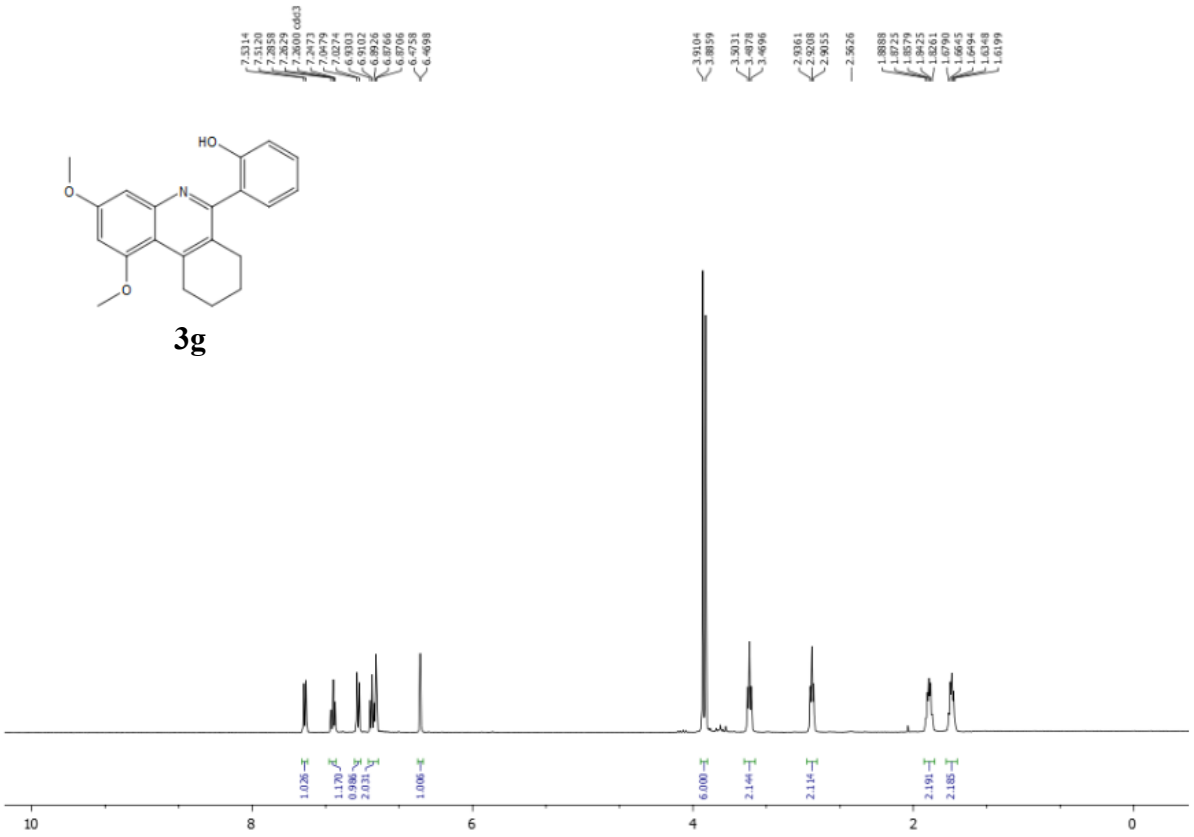
^{13}C{^{1}H} NMR of 3f (101 MHz, $CDCl_3$)



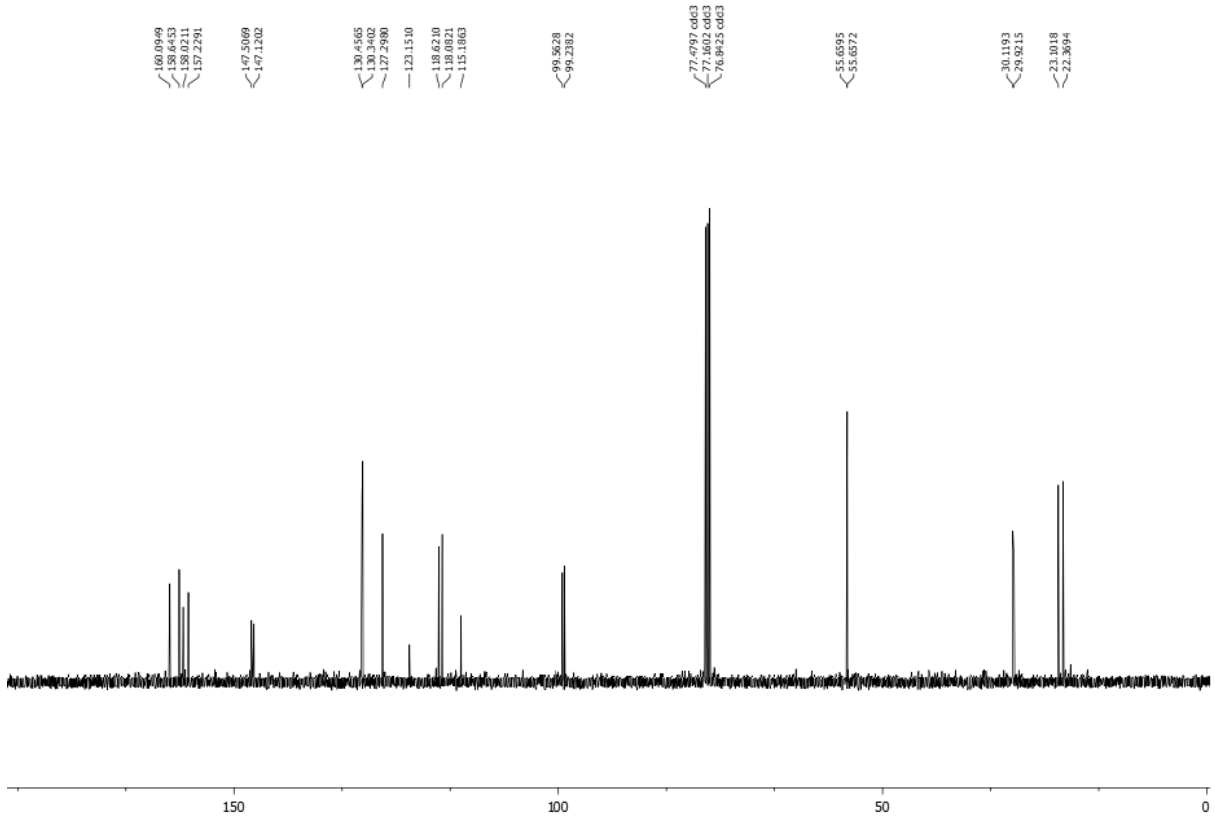
^{19}F NMR of 3f (376 MHz, $CDCl_3$)



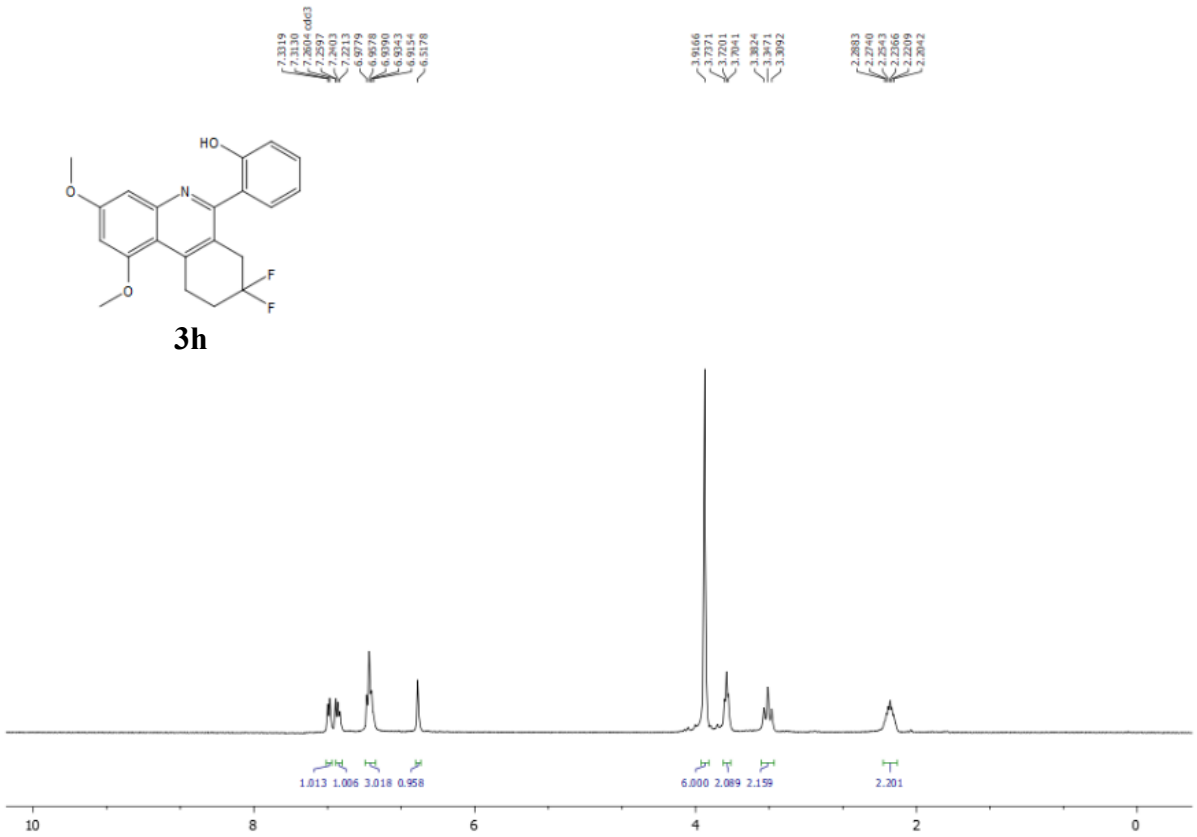
^{1}H NMR of 3g (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 3g (101 MHz, $CDCl_3$)

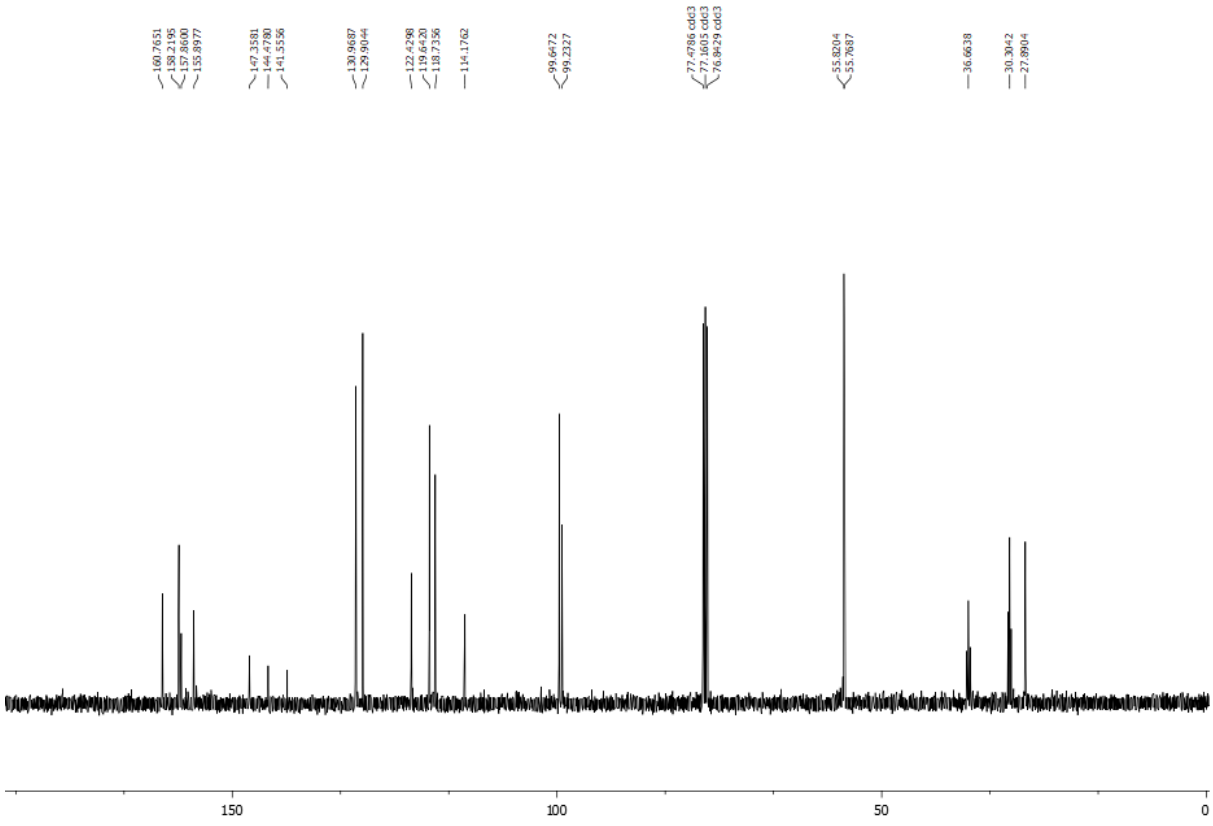


^{1}H NMR of 3h (400 MHz, $CDCl_3$)

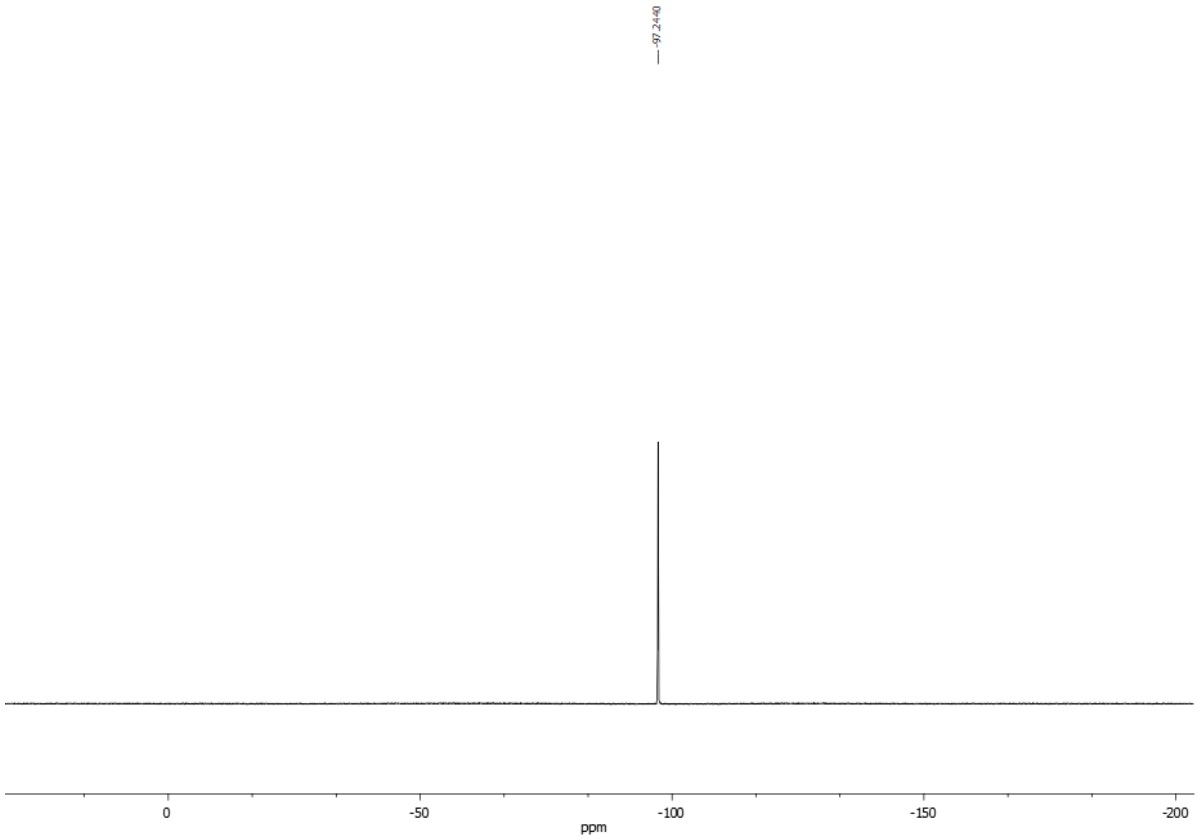


3h

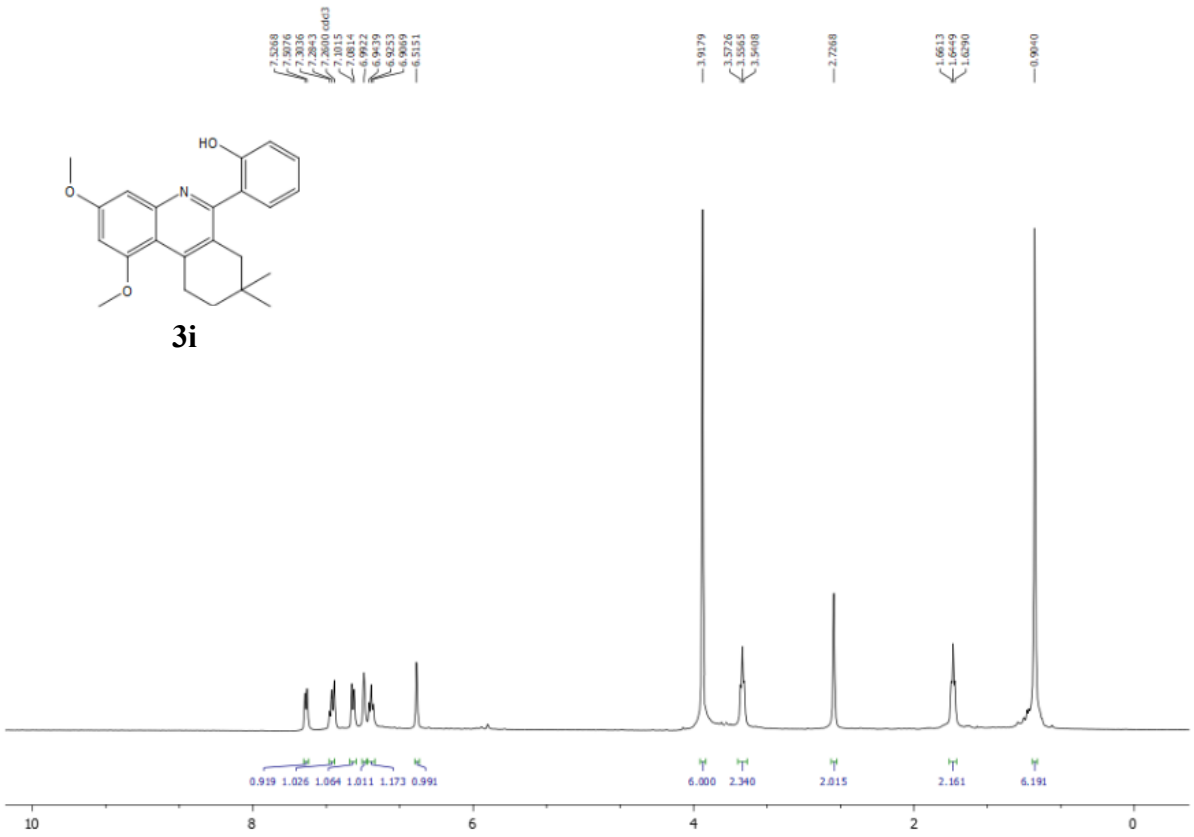
^{13}C{^{1}H} NMR of 3h (101 MHz, $CDCl_3$)



^{19}F NMR of 3h (376 MHz, $CDCl_3$)

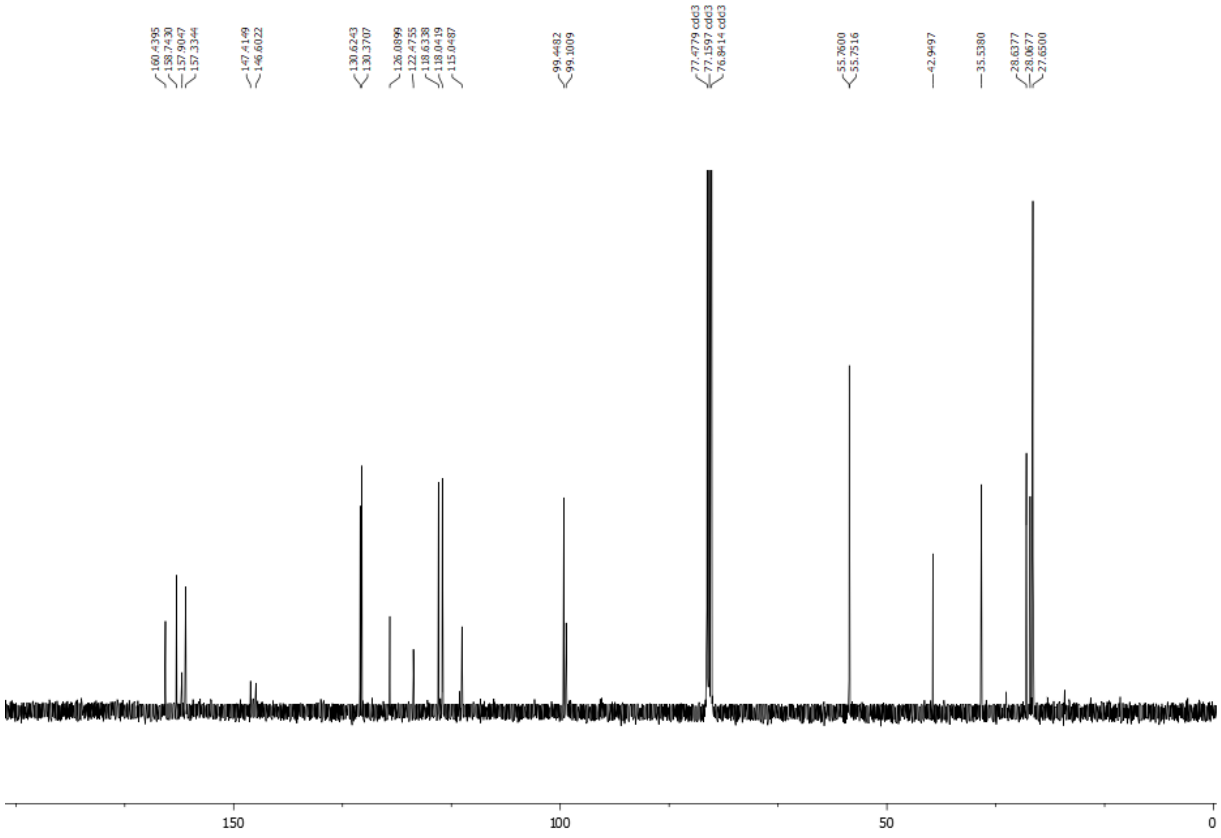


^{1}H NMR of 3i (400 MHz, $CDCl_3$)

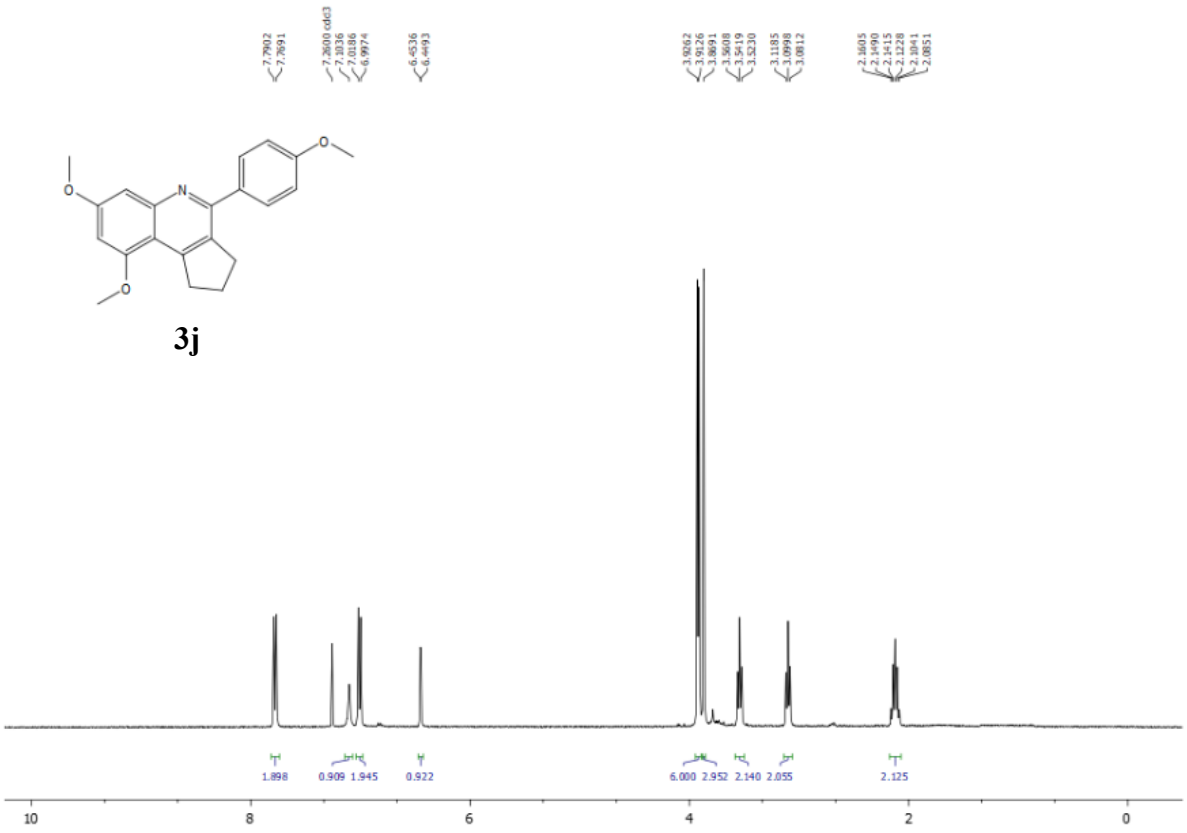


3i

^{13}C{^{1}H} NMR of 3i (101 MHz, $CDCl_3$)

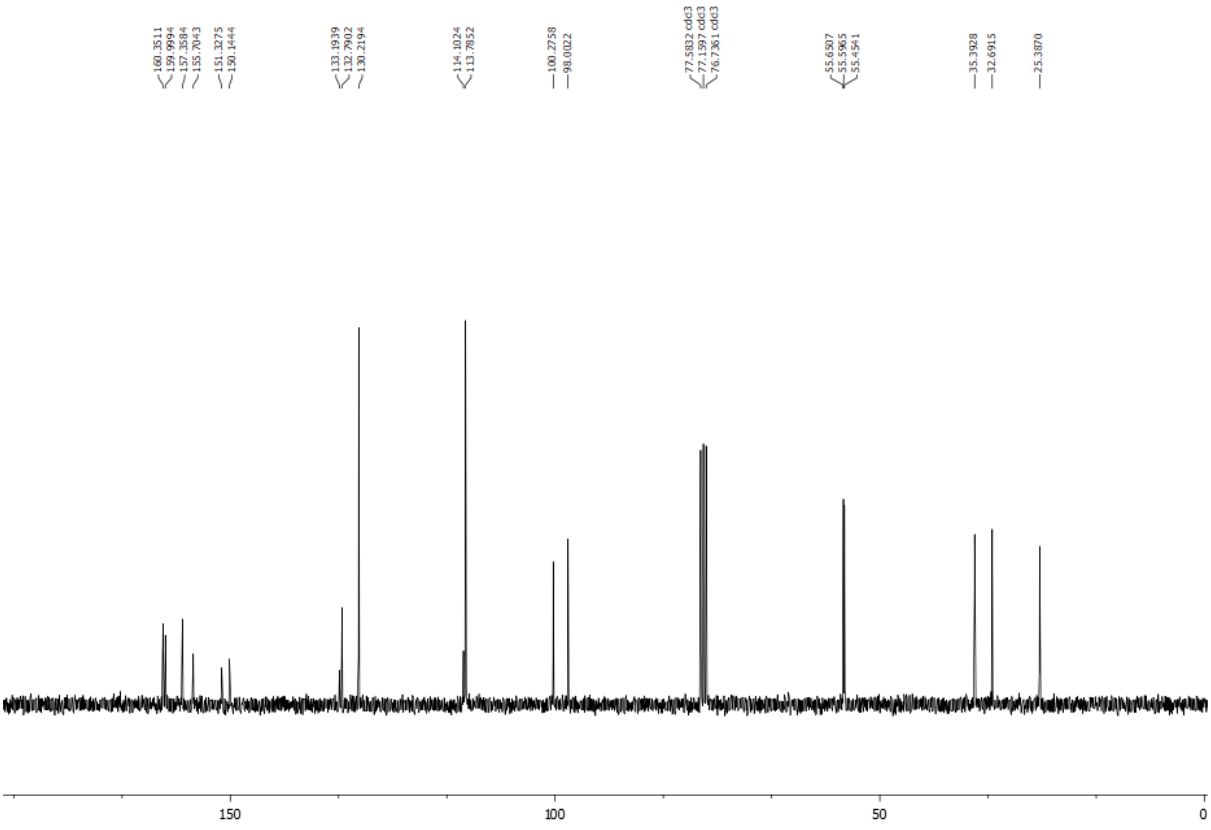


^{1}H NMR of 3j (400 MHz, $CDCl_3$)

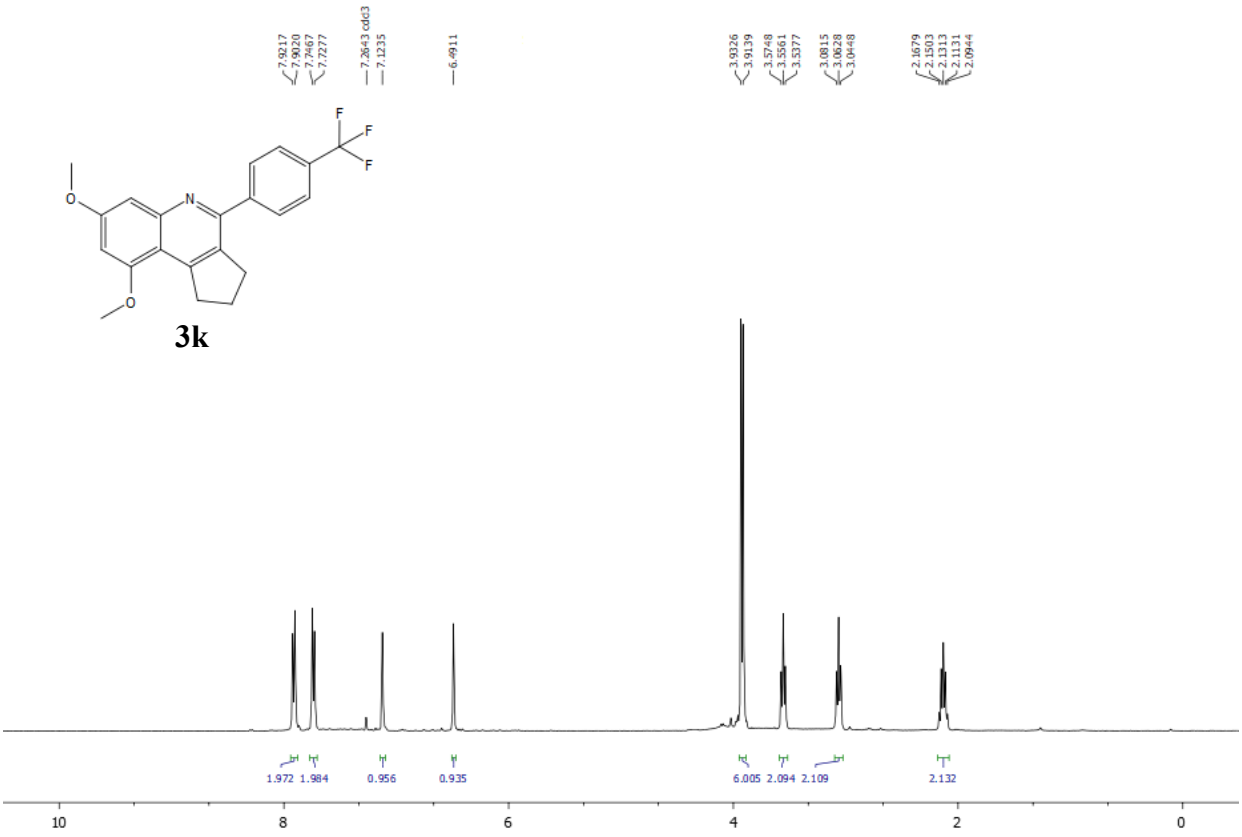


3j

^{13}C{^{1}H} NMR of 3j (101 MHz, $CDCl_3$)

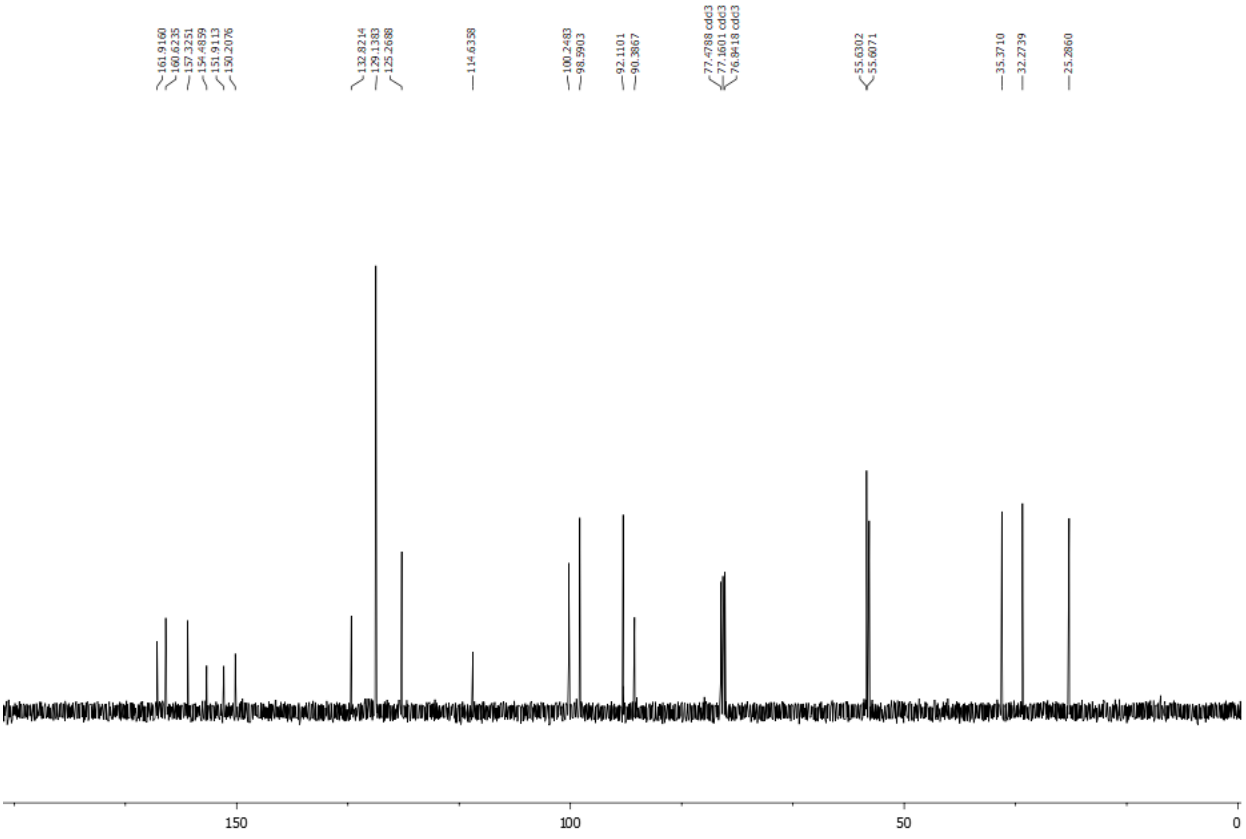


^{1}H NMR of 3k (400 MHz, $CDCl_3$)

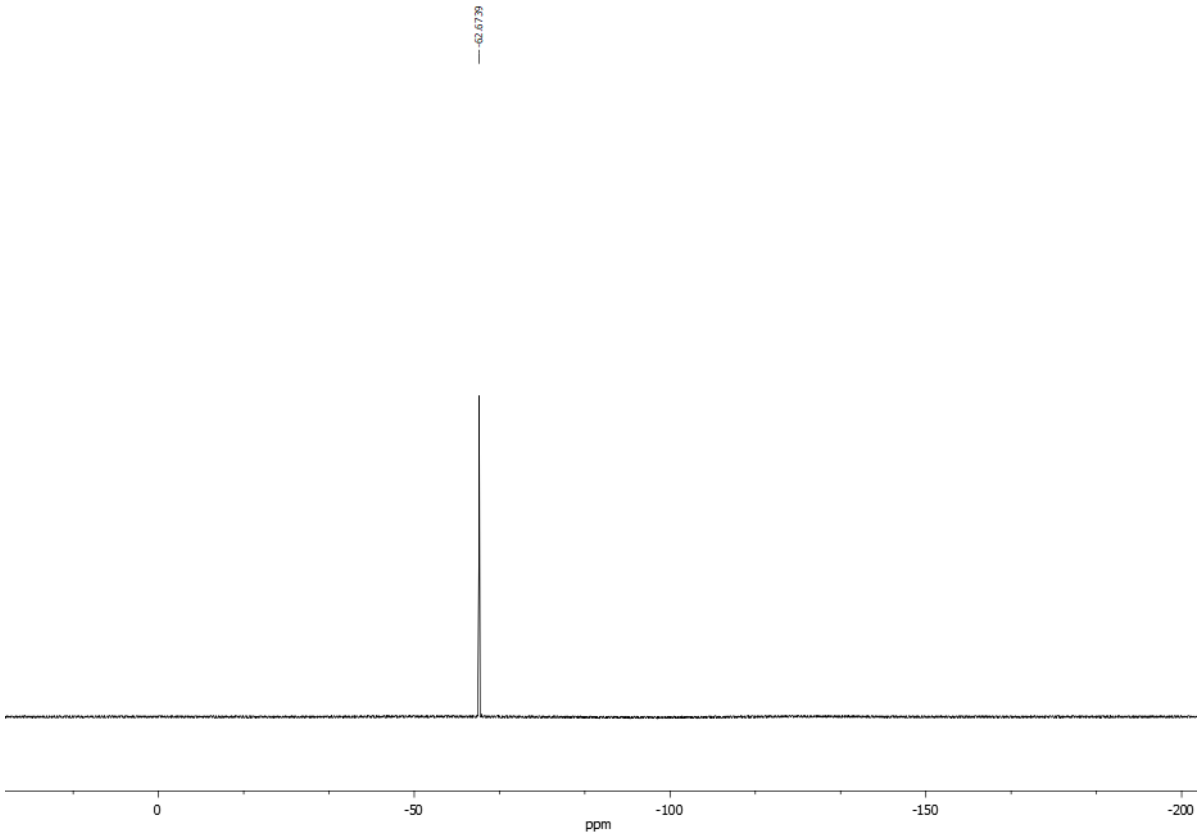


3k

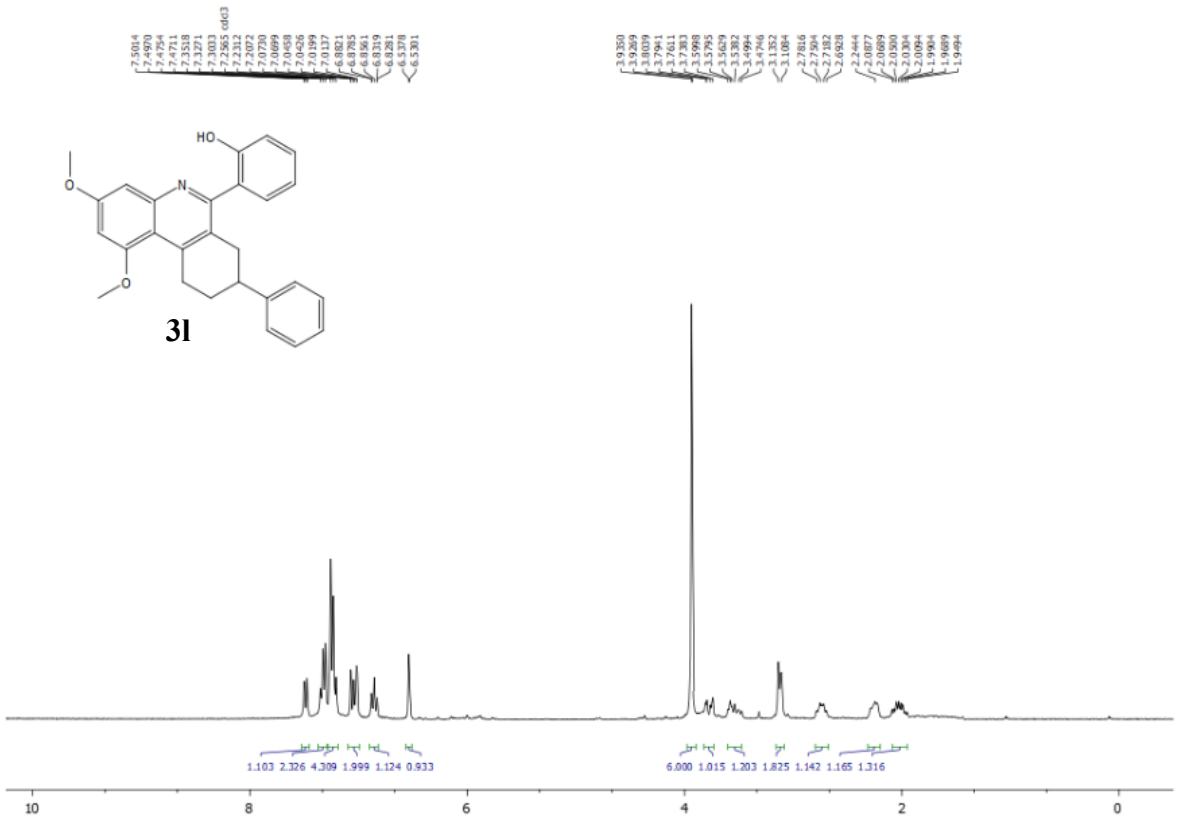
^{13}C{^{1}H} NMR of 3k (101 MHz, $CDCl_3$)



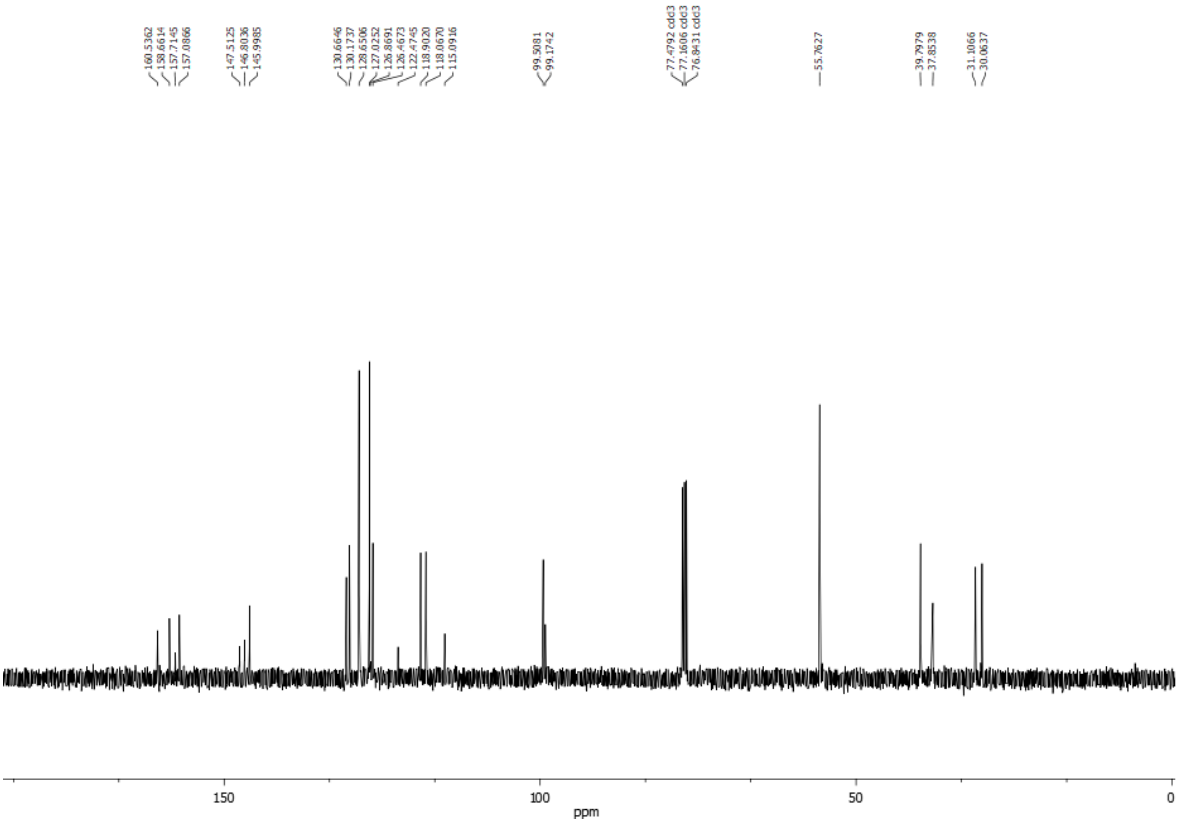
^{19}F NMR of 3k (376 MHz, $CDCl_3$)



^{1}H NMR of 3l (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 3l (101 MHz, $CDCl_3$)



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