Supplementary Information

Ligand-Free Iron Carbonyl Catalyzed Transfer Hydrogenation Strategy: Synthesis of N-Heterocycles

Junhwa Hong,[a] Seok Beom Lee,[a] Seung Hyun Choi,[a] Jinwoo Lee,[a] Honghui Lee,[a] Joonseok Jang,[a] and Suckchang Hong*[a,b]

[a] Research Institute of Pharmaceutical Sciences, College of Pharmacy, Seoul National University, Seoul, Republic of Korea

[b] Natural Products Research Institute, College of Pharmacy, Seoul National University, Seoul, Republic of Korea

* Corresponding authors. E-mails: schong17@snu.ac.kr

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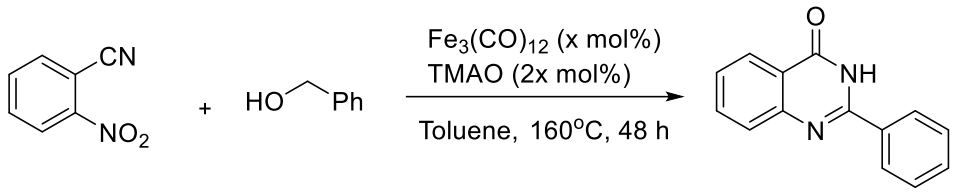
1. General information

All commercially available reagents and solvents (purchased from Sigma-Aldrich, TCI, Alfa-Aesar, Acros, Combi-block) were used without further purification unless otherwise noted. All reactions were carried out in oven-dried round bottom flask & seal tube. Reactions were monitored by thin layer chromatography on silica gel 60 F254 plate (Merck, Darmstadt, Germany) using UV illumination at 254 nm (VL-4.LC, Vilber Lourmat, Eberhardzell, Germany). Column chromatography was performed on silica gel (230~400 mesh; Zeochem, Lake Zurich, Switzerland), using mixture of hexane and EtOAc as eluents. Melting points were measured on a Büchi B-540 melting point apparatus and were not corrected. Nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were measured on JEOL JNM-ECZ400s [400 MHz (^{1}H), 100 MHz (^{13}C)] spectrometer. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm. Coupling constants (*J*) are expressed in hertz (Hz). All high-resolution mass spectra (HR-MS) were acquired using fast atom bombardments (FAB) ionization method on a double-focusing magnetic sector mass spectrometer, JMS-700 MStation mass spectrometer (JEOL, Tokyo, Japan). Melting points were measured on a Büchi B-540 melting point apparatus.

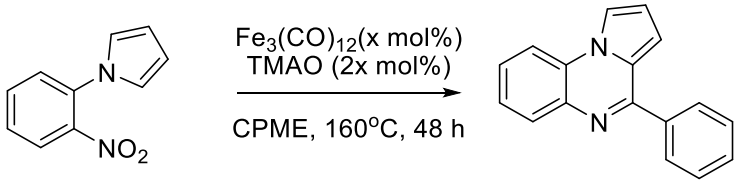
2. Supplementary tables

Table S1. Optimization for quinazolinones using 2-nitrobenzonitrile



Entry	Time (hr)	Catalyst (mol%)	Base/Additive	Yield (%)[a]
1	48	3	-	43
2	48	3	K-OtBu	38
3	48	3	KOH	10
4	48	3	NH_4OH	-
5	48	3	Water	Trace
6	48	6	-	66

Table S2. Optimization for pyrrolo[1,2-α]quinoxalines

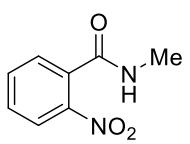


Entry	Catalyst (mol %)	Atmosphere	Time (hr)	Yield (%)[a]
1	$Fe_3(CO)_{12}$ (2)	O_2	24	trace[b]
2	$Fe_3(CO)_{12}$ (2)	Ar	24	27
3	$Fe_3(CO)_{12}$ (2)	Ar	48	30
4	$Fe_3(CO)_{12}$ (3)	Ar	48	85
5	$Fe_3(CO)_{12}$ (4)	Ar	48	90
6[c]	$Fe_3(CO)_{12}$ (4)	Ar	48	85

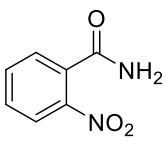
[a] Yields refer to isolated products. [b] Dihydro-quinoxaline was observed as a major product. [c] Toluene was used instead of CPME.

3. Synthetic procedures for substrates

List of substrates



1a



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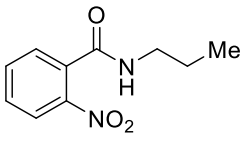

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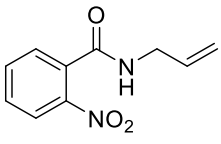

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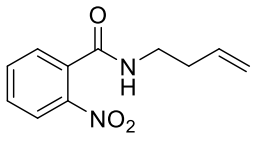

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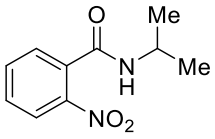

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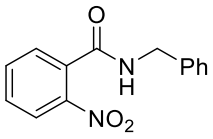

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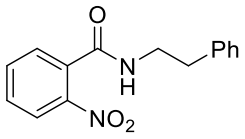

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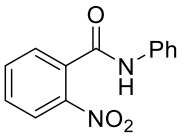

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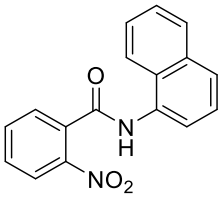

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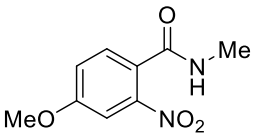

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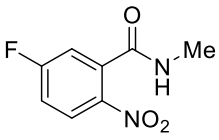

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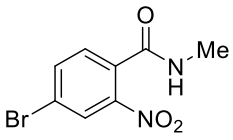

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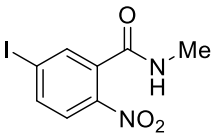

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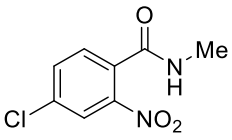

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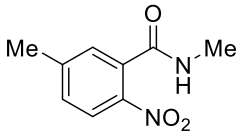

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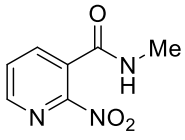
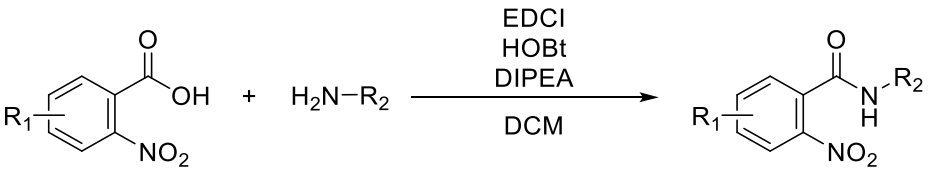


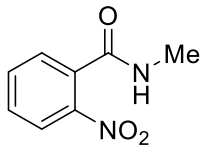
1q

Synthesis of substrates: 1a, 1c-1q[1]



Synthesis of amide moiety

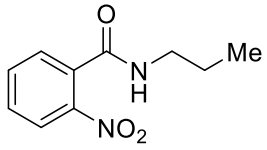
To a dried 100 mL round-bottom flask were added 2-nitrobenzoic acid (1.0 equiv.), EDCI (1.2 equiv.), HOBt (1.2 equiv.), dry DCM (0.2 M) under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min. Subsequently, the corresponding alkyl amine (1.2 equiv.) and DIPEA (3 equiv.) were added to the mixture. The reaction mixture was stirred overnight at room temperature. Upon completion, the reaction was quenched with H_2O (50 mL), and extracted with DCM (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the desired amide product.



1a

N-methyl-2-nitrobenzamide (1a)

: Following the above procedure, 2-nitrobenzoic acid (334.2 mg, 2.0 mmol), methylamine hydrochloride (162.1 mg, 2.4 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1a** was obtained as white solid (328.6 mg, 91% yield); mp = 107-109 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.54 (td, *J* = 7.8, 1.4 Hz, 1H), 7.45 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.23 (s, 1H), 2.94 (d, *J* = 5.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.3, 146.5, 133.8, 133.0, 130.5, 128.8, 124.6, 27.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_8H_9N_2O_3$ 181.0613; Found 181.0615.

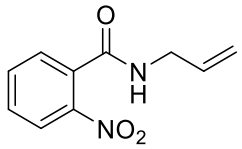


1c

2-nitro-N-propylbenzamide (1c)

: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), propylamine (212.8 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography

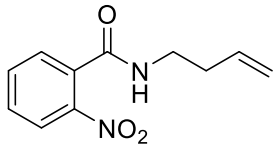
(hexane : EtOAc = 1 : 1), **1a** was obtained as white solid (506.0 mg, 81% yield); mp = 70-72 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.62 (td, *J* = 7.4, 1.1 Hz, 1H), 7.53 (td, *J* = 7.8, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.11 (s, 1H), 3.38-3.33 (m, 2H), 1.62 (td, *J* = 14.6, 7.3 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.6, 146.5, 133.7, 133.3, 130.4, 128.8, 124.6, 42.1, 22.6, 11.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{10}H_{13}N_2O_3$ 209.0926; Found 209.0932.



1d

N-allyl-2-nitrobenzamide (1d)

: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), allylamine hydrochloride (336.8 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1d** was obtained as white solid (578.0 mg, 93% yield); mp = 68-70 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.64 (td, *J* = 7.4, 1.4 Hz, 1H), 7.55 (td, *J* = 7.8, 1.7 Hz, 1H), 7.49 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.17 (s, 1H), 5.95-5.86 (m, 1H), 5.27 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.17 (dq, *J* = 10.1, 1.4 Hz, 1H), 4.03 (tt, *J* = 5.8, 1.5 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.5, 146.5, 133.8, 133.5, 133.0, 130.6, 128.8, 124.6, 117.3, 42.7; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_3$ 207.0770; Found 207.0766.

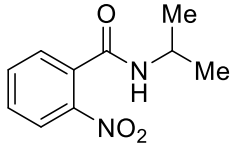


1e

N-(but-3-en-1-yl)-2-nitrobenzamide (1e)

: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), 3-buten-1-amine (256.0 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1e** was obtained as white solid (575.2 mg, 87% yield); mp = 70-72 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.65 (td, *J* = 7.5,

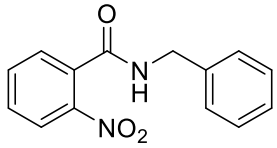
1.2 Hz, 1H), 7.56 (td, *J* = 7.8, 1.4 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.89-5.76 (m, 2H), 5.19-5.10 (m, 2H), 3.53 (q, *J* = 6.4 Hz, 2H), 2.43-2.37 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.6, 146.6, 135.1, 133.8, 133.2, 130.5, 128.8, 124.7, 117.8, 39.2, 33.5; HRMS (FAB) m/z: [M] Calcd for $C_{11}H_{13}N_2O_3$ 221.0926; Found 221.0930.



1f

N-isopropyl-2-nitrobenzamide (1f)

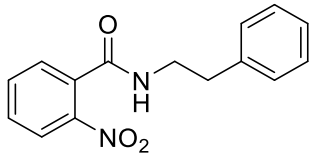
: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), isopropylamine (212.8 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1f** was obtained as white solid (513.2 mg, 82% yield); mp = 139-141 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 5.66 (s, 1H), 4.28 (td, *J* = 13.5, 6.9 Hz, 1H), 1.27 (d, *J* = 6.2 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.8, 146.5, 133.8, 133.5, 130.4, 128.9, 124.6, 42.5, 22.6; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{10}H_{13}N_2O_3$ 209.0926; Found 209.0930.



1g

N-benzyl-2-nitrobenzamide (1g)

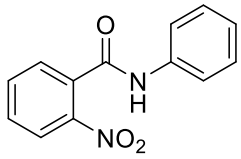
: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), benzylamine (385.7 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1g** was obtained as white solid (670.6 mg, 87% yield); mp = 120-122 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H), 7.59-7.51 (m, 2H), 7.41-7.28 (m, 5H), 6.12 (s, 1H), 4.64 (d, *J* = 5.5 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.4, 146.6, 137.5, 133.8, 133.0, 130.7, 129.0, 128.8, 128.2, 128.0, 124.8, 44.5; HRMS (FAB) m/z: [M] Calcd for $C_{14}H_{13}N_2O_3$ 257.0926; Found 257.0935.



1h

2-nitro-N-phenethylbenzamide (1h)

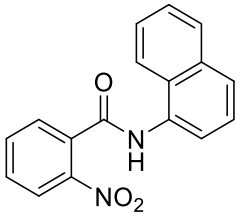
: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), phenethylamine (436.3 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1.5 : 1), **1h** was obtained as white solid (563.8 mg, 70% yield); mp = 117-119 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.63 (td, *J* = 7.4, 1.2 Hz, 1H), 7.55 (td, *J* = 7.9, 1.5 Hz, 1H), 7.40 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.34-7.21 (m, 5H), 5.85 (s, 1H), 3.74 (q, *J* = 6.6 Hz, 2H), 2.97 (t, *J* = 6.9 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.6, 146.6, 138.8, 133.8, 133.2, 130.6, 129.0, 128.9, 128.7, 126.8, 124.7, 41.3, 35.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}N_2O_3$ 271.1083; Found 271.1087.



1i

2-nitro-N-phenylbenzamide (1i)

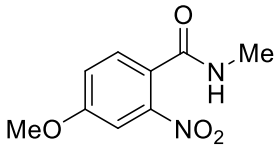
: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), aniline (335.3 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1.5 : 1), **1i** was obtained as white solid (595.2 mg, 82% yield); mp = 154-156 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.45-7.67 (5H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.5, 146.5, 137.4, 134.1, 133.0, 130.9, 129.3, 128.8, 125.4, 124.9, 120.6; HRMS (FAB) m/z: [M] Calcd for $C_{13}H_{11}N_2O_3$ 243.0770; Found 243.0764.



1j

N-(naphthalen-1-yl)-2-nitrobenzamide (1j)

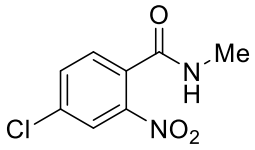
: Following the above procedure, 2-nitrobenzoic acid (501.4 mg, 3.0 mmol), 1-naphthylamine (515.5 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1.5 : 1), **1j** was obtained as brown solid (240.3 mg, 27% yield); mp = 202-204 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H), 8.20 (d, J = 8.3 Hz, 1H), 8.14 (t, J = 4.8 Hz, 1H), 8.00-7.90 (m, 3H), 7.86 (d, J = 8.3 Hz, 1H), 7.82-7.75 (m, 2H), 7.60-7.56 (m, 3H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 165.2, 146.6, 134.2, 133.8, 132.9, 130.9, 129.5, 128.3, 128.1, 126.2, 126.1, 126.1, 125.6, 124.3, 122.9, 122.6; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_3$ 293.0926; Found 293.0917.



1k

4-methoxy-N-methyl-2-nitrobenzamide (1k)

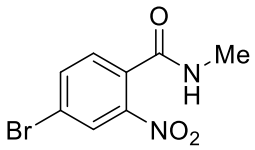
: Following the above procedure, 4-methoxy-2-nitrobenzoic acid (197.2 mg, 1.0 mmol), methylamine hydrochloride (81.0 mg, 1.2 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1k** was obtained as white solid (190.8 mg, 91% yield); mp = 162-164 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 2.3 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.13 (dd, J = 8.5, 2.5 Hz, 1H), 5.86 (s, 1H), 3.89 (s, 3H), 2.99 (d, J = 5.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.1, 160.9, 148.1, 129.9, 125.2, 119.3, 109.7, 56.2, 27.2; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_9H_{11}N_2O_4$ 211.0719; Found 211.0713.



1l

4-chloro-N-methyl-2-nitrobenzamide (1l)

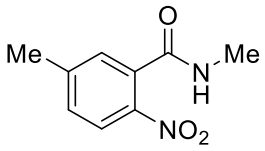
: Following the above procedure, 4-chloro-2-nitrobenzoic acid (604.7 mg, 3.0 mmol), methylamine hydrochloride (243.1 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1l** was obtained as white solid (547.2 mg, 85% yield); mp = 150-152 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.8 Hz, 1H), 7.62 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 5.99 (s, 1H), 3.00 (d, *J* = 4.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.2, 147.2, 136.6, 133.8, 131.3, 130.0, 124.9, 27.2; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_8H_8ClN_2O_3$ 215.0223; Found 215.0221.



1m

4-bromo-N-methyl-2-nitrobenzamide (1m)

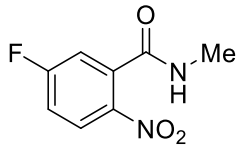
: Following the above procedure, 4-bromo-2-nitrobenzoic acid (738.1 mg, 3.0 mmol), methylamine hydrochloride (243.1 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1m** was obtained as white solid (646.6 mg, 85% yield); mp = 180-182 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.66 (d, *J* = 4.1 Hz, 1H), 8.26 (d, *J* = 1.8 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 2.75 (d, *J* = 4.6 Hz, 3H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 164.8, 148.0, 136.1, 131.1, 130.7, 126.8, 122.8, 26.1; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_8H_8BrN_2O_3$ 258.9718; Found 258.9724.



1n

N,5-dimethyl-2-nitrobenzamide (1n)

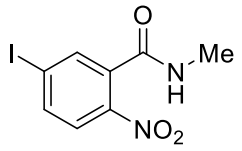
: Following the above procedure, 5-methyl-2-nitrobenzoic acid (543.4 mg, 3.0 mmol), methylamine hydrochloride (243.1 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1n** was obtained as white solid (461.8 mg, 79% yield); mp = 129-131 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.7 Hz, 1H), 7.31 (dd, J = 8.3, 1.4 Hz, 1H), 7.25 (d, J = 1.4 Hz, 1H), 6.05 (s, 1H), 2.96 (d, J = 5.1 Hz, 3H), 2.43 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.6, 145.5, 144.1, 133.2, 130.8, 129.4, 124.7, 27.0, 21.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_9H_{11}N_2O_3$ 195.0770; Found 195.0778.



1o

5-fluoro-N-methyl-2-nitrobenzamide (1o)

: Following the above procedure, 5-fluoro-2-nitrobenzoic acid (555.3 mg, 3.0 mmol), methylamine hydrochloride (243.1 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), **1o** was obtained as white solid (495.5 mg, 83% yield); mp = 124-126 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (q, J = 4.6 Hz, 1H), 7.24-7.14 (m, 2H), 6.13 (s, 1H), 2.97 (d, J = 5.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.3 (d, J_{CF} = 257.8 Hz), 166.0, 163.7 (d, J_{CF} = 257.8 Hz), 142.4, 136.0 (d, J_{CF} = 7.6 Hz), 135.9 (d, J_{CF} = 7.6 Hz), 127.7, 127.6, 117.5 (d, J_{CF} = 22.9 Hz), 117.3 (d, J_{CF} = 22.9 Hz), 116.4 (d, J_{CF} = 24.8 Hz), 116.2 (d, J_{CF} = 24.8 Hz), 27.1; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -101.41; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_8H_8FN_2O_3$ 199.0519; Found 199.0516.

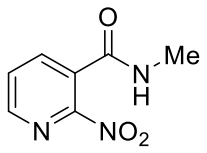


1p

5-iodo-N-methyl-2-nitrobenzamide (1p)

: Following the above procedure, 5-iodo-2-nitrobenzoic acid (439.5 mg, 1.5 mmol), methylamine hydrochloride (121.5 mg, 1.8 mmol) were used as a starting material. After purification by

column chromatography (hexane : EtOAc = 1 : 1), **1p** was obtained as white solid (404.0 mg, 88% yield); mp = 195-197 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 5.86 (s, 1H), 3.02 (d, *J* = 5.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.6, 146.0, 139.7, 137.9, 134.3, 126.0, 101.2, 27.2; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_8H_8IN_2O_3$ 306.9580; Found 306.9563.



1q

N-methyl-2-nitronicotinamide (1q)

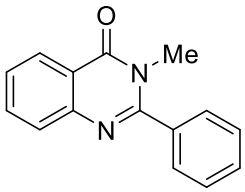
: Following the above procedure, 2-nitronicotinic acid (504.3 mg, 3.0 mmol), methylamine hydrochloride (243.1 mg, 3.6 mmol) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 2), **1q** was obtained as white solid (385.8 mg, 71% yield); mp = 163-165 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.62 (q, *J* = 2.1 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.67 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.01 (s, 1H), 3.03 (d, *J* = 5.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.8, 149.8, 139.3, 128.2, 127.1, 27.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_7H_8N_3O_3$ 182.0566; Found 182.0571.

Starting materials **8a**, **8b**, **8e** were synthesized through known procedures and characterization data were consistent with the literature.[2]

4. Synthesis of quinazolinones

4-1. General procedure A using N-substituted 2-nitrobenzamide

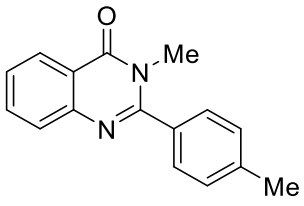
To an oven-dried borosilicate glass tube were added substrate **1** (0.30 mmol, 1.0 equiv.), alcohol **2** (0.60 mmol, 2.0 equiv.), $Fe_3(CO)_{12}$ (4.5 mg, 3 mol%), and trimethylamine N-oxide (1.4 mg, 6 mol%) under an argon atmosphere. The tube was sealed with a rubber septum and flushed with argon balloon. Toluene (0.3 mL) was then added via syringe. The reaction vessel was recharged with Ar, then tightly sealed with a screw cap, and the mixture was stirred at 160 ℃ in an oil bath for 48 h. After completion, the reaction mixture was cooled to room temperature. The crude residue was directly purified by flash column chromatography on silica gel to afford the desired product.



3aa

3-methyl-2-phenylquinazolin-4(3H)-one (3aa)

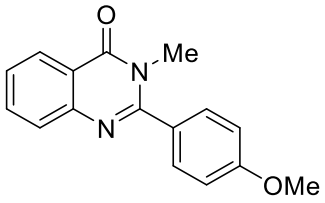
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), benzyl alcohol **2a** (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3aa** was obtained as white solid (64.5 mg, 91% yield); mp = 101-103 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34-8.32 (m, 1H), 7.75 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.58-7.48 (m, 6H), 3.50 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.8, 156.3, 147.4, 135.5, 134.5, 130.2, 129.0, 128.1, 127.6, 127.1, 126.8, 120.7, 34.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O$ 237.1028; Found 237.1026.



3ab

3-methyl-2-(p-tolyl)quinazolin-4(3H)-one (3ab)

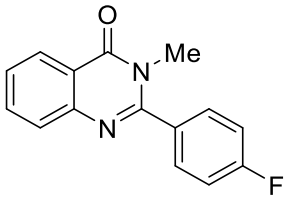
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-methylbenzyl alcohol **2b** (73.3 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ab** was obtained as white solid (56.5 mg, 75% yield); mp = 128-130 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33-8.30 (m, 1H), 7.76-7.70 (m, 2H), 7.50-7.44 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 2H), 3.50 (s, 3H), 2.43 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.9, 156.4, 147.5, 140.4, 134.3, 132.7, 129.6, 128.1, 127.6, 126.9, 126.8, 120.6, 34.4, 21.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O$ 251.1184; Found 251.1190.



3ac

2-(4-methoxyphenyl)-3-methylquinazolin-4(3H)-one (3ac)

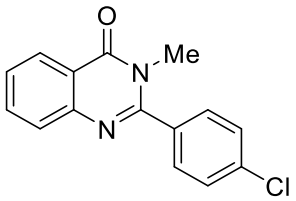
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-methoxybenzyl alcohol **2c** (74.7 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ac** was obtained as white solid (53.5 mg, 67% yield); mp = 140-142 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32-8.30 (m, 1H), 7.76-7.71 (m, 2H), 7.53 (dt, *J* = 9.3, 2.3 Hz, 2H), 7.49-7.45 (m, 1H), 7.02 (dt, *J* = 9.2, 2.4 Hz, 2H), 3.87 (s, 3H), 3.52 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.1, 161.1, 156.1, 147.5, 134.4, 129.9, 127.9, 127.5, 126.9, 126.8, 120.5, 114.3, 55.6, 34.6; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1134; Found 267.1131.



3ad

2-(4-fluorophenyl)-3-methylquinazolin-4(3H)-one (3ad)

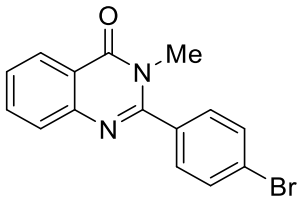
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-fluorobenzyl alcohol **2d** (65.5 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ad** was obtained as white solid (57.6 mg, 76% yield); mp = 163-165 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 8.5, 1.1 Hz, 1H), 7.78-7.74 (m, 1H), 7.71 (dd, J = 8.2, 0.9 Hz, 1H), 7.61-7.56 (m, 2H), 7.52-7.48 (m, 1H), 3.50 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.0 (d, J_{CF} = 249.4 Hz), 162.8, 162.5 (d, J_{CF} = 249.4 Hz), 155.3, 147.3, 134.5, 131.7 (d, J_{CF} = 2.8 Hz), 131.7 (d, J_{CF} = 2.8 Hz), 130.4 (d, J_{CF} = 8.6 Hz), 130.4 (d, J_{CF} = 8.6 Hz), 127.6 (d, J_{CF} = 33.6 Hz), 127.3 (d, J_{CF} = 33.6 Hz), 126.8, 120.6, 116.3 (d, J_{CF} = 22.1 Hz), 116.1 (d, J_{CF} = 22.1 Hz), 34.4; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -113.71; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}FN_2O$ 255.0934; Found 255.0941.



3ae

2-(4-chlorophenyl)-3-methylquinazolin-4(3H)-one (3ae)

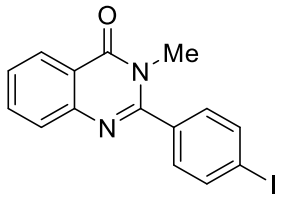
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-chlorobenzyl alcohol **2e** (85.5 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ae** was obtained as white solid (73.6 mg, 91% yield); mp = 169-171 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 7.6, 1.1 Hz, 1H), 7.78-7.71 (m, 2H), 7.55-7.49 (m, 5H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.7, 155.2, 147.2, 136.6, 134.6, 133.8, 129.7, 129.3, 128.7, 128.3, 127.5, 127.4, 126.9, 120.6, 34.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}ClN_2O$ 271.0638; Found: 271.0640.



3af

2-(4-bromophenyl)-3-methylquinazolin-4(3H)-one (3af)

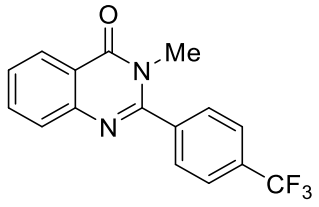
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-bromobenzyl alcohol **2f** (112.2 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3af** was obtained as white solid (76.0 mg, 80% yield); mp = 165-167 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.79-7.71 (m, 2H), 7.68 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.53-7.49 (m, 1H), 7.47 (dt, *J* = 8.6, 2.1 Hz, 2H), 3.50 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.7, 155.2, 147.3, 134.6, 134.4, 132.3, 129.9, 127.7, 127.4, 126.9, 124.7, 120.7, 34.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}BrN_2O$ 315.0133; Found 315.0140.



3ag

2-(4-iodophenyl)-3-methylquinazolin-4(3H)-one (3ag)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-iodobenzyl alcohol **2g** (140.4 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ag** was obtained as white solid (77.0 mg, 71% yield); mp = 167-169 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.78-7.72 (m, 2H), 7.53-7.49 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.6, 155.4, 147.1, 138.2, 134.7, 134.6, 129.9, 127.5, 127.4, 126.9, 120.6, 96.7, 34.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}IN_2O$ 362.9994; Found 362.9997.

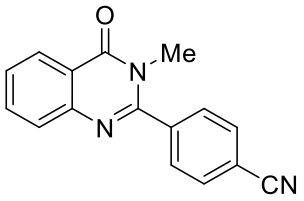


3ah

3-methyl-2-(4-(trifluoromethyl)phenyl)quinazolin-4(3H)-one (3ah)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-(trifluoromethyl)benzyl alcohol **2h** (82.2 μL, 0.6 mmol) were used as starting material. After purification by column

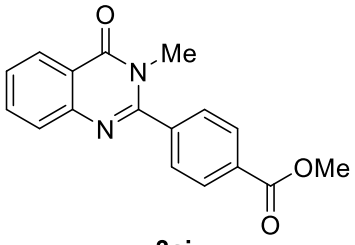
chromatography (hexane : EtOAc = 4 : 1), **3ah** was obtained as white solid (65.3 mg, 72% yield); mp = 132-134 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.82-7.71 (m, 6H), 7.53 (td, *J* = 7.4, 1.5 Hz, 1H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.6, 154.8, 147.3, 138.9, 134.7, 132.8 (q, J_{CF} = 32.6 Hz), 132.5 (q, J_{CF} = 32.6 Hz), 132.2 (q, J_{CF} = 32.6 Hz), 131.8 (q, J_{CF} = 32.6 Hz), 128.8, 127.7, 127.6, 126.9, 126.2 (q, J_{CF} = 2.8 Hz), 126.2 (q, J_{CF} = 2.8 Hz), 126.1 (q, J_{CF} = 2.8 Hz), 126.1 (q, J_{CF} = 2.8 Hz), 125.2 (d, J_{CF} = 271.4 Hz), 122.4 (d, J_{CF} = 271.4 Hz), 120.8, 34.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -62.86; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}F_3N_2O$ 305.0902; Found 305.0908.



3ai

4-(3-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)benzonitrile (3ai)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-cyanobenzyl alcohol **2i** (79.9 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ai** was obtained as white solid (52.0 mg, 66% yield); mp = 231-233 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.85-7.83 (m, 2H), 7.78 (td, *J* = 7.6, 1.4 Hz, 1H), 7.73-7.70 (m, 3H), 7.56-7.52 (m, 1H), 3.48 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.4, 154.2, 147.1, 139.5, 134.7, 132.8, 129.2, 127.8, 127.7, 126.9, 120.8, 118.0, 114.2, 34.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}N_3O$ 262.0980; Found 262.0986.

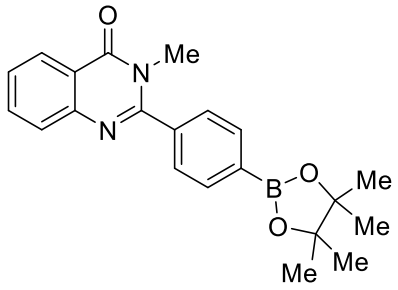


3aj

methyl 4-(3-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)benzoate (3aj)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), methyl-4-(hydroxymethyl)benzoate **2j** (122.5 μL, 0.6 mmol) were used as starting material. After

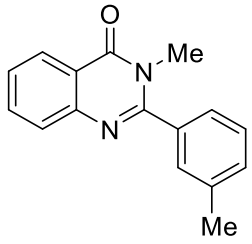
purification by column chromatography (hexane : EtOAc = 4 : 1), **3aj** was obtained as white solid (29.4 mg, 33% yield); mp = 200-202 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 8.7, 0.9 Hz, 1H), 8.21 (dt, *J* = 8.3, 1.8 Hz, 2H), 7.80-7.73 (m, 2H), 7.67 (dt, *J* = 8.3, 1.8 Hz, 2H), 7.55-7.51 (m, 1H), 3.97 (s, 3H), 3.48 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.3, 162.6, 155.3, 147.1, 139.3, 134.7, 131.8, 130.3, 128.4, 127.6, 127.5, 126.9, 120.7, 52.6, 34.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_3$ 295.1083; Found 295.1080.



3ak

3-methyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)quinazolin-4(3H)-one (3ak)

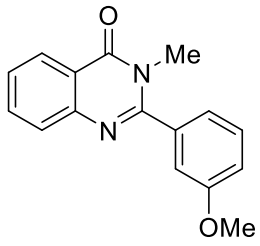
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-(hydroxymethyl)phenylboronic acid pinacol ester **2k** (140.5 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 5 : 1), **3ak** was obtained as white solid (30.4 mg, 28% yield); mp = 107-109 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 2.1 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.53-7.49 (m, 1H), 3.47 (s, 3H), 1.37 (s, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.8, 156.2, 147.4, 137.8, 135.3, 134.5, 127.7, 127.4, 127.2, 126.9, 120.7, 84.3, 34.3, 25.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}BN_2O_3$ 363.1880; Found 363.1883.



3al

3-methyl-2-(m-tolyl)quinazolin-4(3H)-one (3al)

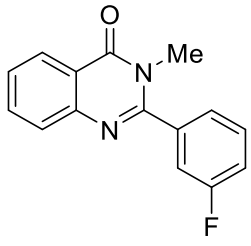
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 3-methylbenzyl alcohol **2l** (72.2 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3al** was obtained as white solid (60.1 mg, 80% yield); mp = 119-120 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.77-7.72 (m, 2H), 7.51-7.47 (m, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34-7.31 (m, 2H), 3.49 (s, 3H), 2.43 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.8, 156.4, 147.4, 139.0, 135.4, 134.4, 130.9, 128.8, 128.6, 127.6, 127.0, 126.8, 125.0, 120.6, 34.3, 21.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O$ 251.1184; Found 251.1185.



3am

2-(3-methoxyphenyl)-3-methylquinazolin-4(3H)-one (3am)

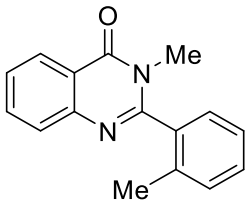
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 3-methylbenzyl alcohol **2m** (74.6 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3am** was obtained as white solid (56.2 mg, 70% yield); mp = 108-110 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.8 Hz, 1H), 7.76-7.74 (m, 2H), 7.53-7.48 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.12-7.09 (m, 2H), 7.05 (dd, *J* = 7.8, 2.3 Hz, 1H), 3.86 (s, 3H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.7, 160.0, 156.1, 147.3, 136.6, 134.4, 130.2, 127.6, 127.2, 126.8, 120.7, 120.3, 116.0, 113.6, 55.6, 34.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1134; Found 267.1131.



3an

2-(3-fluorophenyl)-3-methylquinazolin-4(3H)-one (3an)

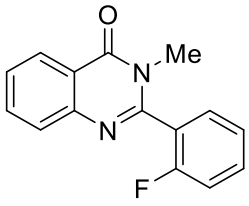
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 3-fluorobenzyl alcohol **2n** (65.0 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3an** was obtained as white solid (67.0 mg, 89% yield); mp = 159-161 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34-8.31 (m, 1H), 7.78-7.71 (m, 2H), 7.54-7.48 (m, 2H), 7.35 (dt, J = 7.8, 1.3 Hz, 1H), 7.32-7.29 (m, 1H), 7.23 (tq, J = 8.5, 1.1 Hz, 1H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.0 (d, J_{CF} = 247.5 Hz), 162.6, 161.6 (d, J_{CF} = 247.5 Hz), 154.8, 147.2, 137.4 (d, J_{CF} = 7.7 Hz), 137.3 (d, J_{CF} = 7.7 Hz), 134.6, 130.9 (d, J_{CF} = 8.6 Hz), 130.8 (d, J_{CF} = 8.6 Hz), 127.7, 127.4, 126.9, 124.0, 123.9, 120.7, 117.4 (d, J_{CF} = 21.1 Hz), 117.2 (d, J_{CF} = 21.1 Hz), 115.8 (d, J_{CF} = 23.1 Hz), 115.5 (d, J_{CF} = 23.1 Hz), 34.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -110.83; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}FN_2O$ 255.0934; Found 255.0930.



3ao

3-methyl-2-(o-tolyl)quinazolin-4(3H)-one (3ao)

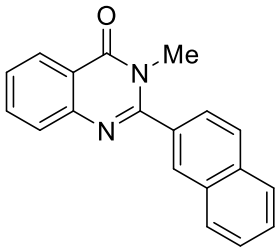
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 2-methylbenzyl alcohol **2o** (70.5 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ao** was obtained as white solid (57.8 mg, 77% yield); mp = 85-87 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.36-8.34 (m, 1H), 7.79-7.73 (m, 2H), 7.54-7.50 (m, 1H), 7.43-7.39 (m, 1H), 7.36-7.33 (m, 3H), 3.35 (s, 3H), 2.25 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.6, 156.1, 147.5, 135.4, 135.2, 134.4, 130.9, 130.0, 127.6, 127.2, 126.8, 126.6, 120.8, 32.8, 19.2; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O$ 251.1184; Found 251.1185.



3ap

2-(2-fluorophenyl)-3-methylquinazolin-4(3H)-one (3ap)

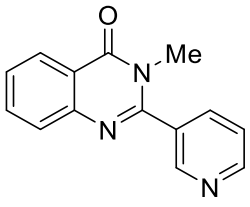
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 2-fluorobenzyl alcohol **2c** (64.5 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ac** was obtained as white solid (63.8 mg, 84% yield); mp = 130-132 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.36-8.33 (m, 1H), 7.79-7.72 (m, 2H), 7.58-7.50 (m, 3H), 7.34 (td, J = 7.5, 1.1 Hz, 1H), 7.24-7.20 (m, 1H), 3.48 (d, J = 1.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3, 160.6 (d, J_{CF} = 248.4 Hz), 158.1 (d, J_{CF} = 248.4 Hz), 152.0, 147.4, 134.4, 132.4 (d, J_{CF} = 7.7 Hz), 132.3 (d, J_{CF} = 7.7 Hz), 130.3, 130.3, 127.6 (d, J_{CF} = 23.0 Hz), 127.4 (d, J_{CF} = 23.0 Hz), 126.8, 125.2, 125.2, 123.8, 123.6, 120.9, 116.3 (d, J_{CF} = 20.1 Hz), 116.1 (d, J_{CF} = 20.1 Hz), 32.9 (d, J_{CF} = 2.9 Hz), 32.9 (d, J_{CF} = 2.9 Hz); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -113.71; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}FN_2O$ 255.0934; Found 355.0941.



3aq

3-methyl-2-(naphthalen-2-yl)quinazolin-4(3H)-one (3aq)

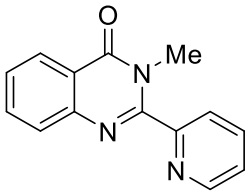
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 2-naphthalenemethanol **2q** (94.9 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 5 : 1), **3aq** was obtained as white solid (51.5 mg, 60% yield); mp = 155-157 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.38-8.35 (m, 1H), 8.11 (s, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.93 (dd, J = 9.2, 6.0 Hz, 2H), 7.78 (dd, J = 4.8, 1.1 Hz, 2H), 7.64-7.56 (m, 3H), 7.55-7.50 (m, 1H), 3.55 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.9, 156.3, 147.6, 134.5, 133.8, 133.1, 132.8, 128.9, 128.7, 128.3, 128.0, 127.7, 127.6, 127.2, 126.9, 124.9, 120.7, 34.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O$ 287.1184; Found 287.1177.



3ar

3-methyl-2-(pyridin-3-yl)quinazolin-4(3H)-one (3ar)

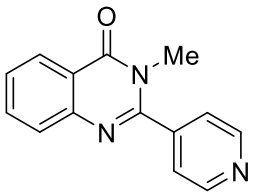
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 3-pyridinemethanol **2r** (58.3 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 5 : 1), **3ar** was obtained as white solid (36.6 mg, 51% yield); mp = 178-180 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.78 (d, *J* = 4.1 Hz, 1H), 8.33 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.95 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.80-7.72 (m, 2H), 7.55-7.48 (m, 2H), 3.52 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.5, 153.4, 151.0, 148.9, 147.2, 136.0, 134.7, 131.7, 127.7, 127.7, 126.9, 123.7, 120.7, 34.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N_3O$ 238.0980; Found 238.0979.



3as

3-methyl-2-(pyridin-2-yl)quinazolin-4(3H)-one (3as)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 2-pyridinemethanol **2s** (57.9 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 5 : 1), **3as** was obtained as white solid (49.1 mg, 69% yield); mp = 160-162 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.2 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.92 (td, *J* = 7.7, 1.5 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 3.7 Hz, 2H), 7.55-7.51 (m, 1H), 7.46 (dd, *J* = 6.7, 5.3 Hz, 1H), 3.62 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.7, 154.1, 153.7, 149.1, 147.1, 137.6, 134.4, 127.6, 127.5, 127.0, 124.9, 124.6, 121.1, 33.7; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N_3O$ 238.0980; Found 238.0977.

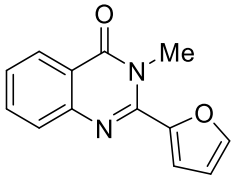


3at

3-methyl-2-(pyridin-4-yl)quinazolin-4(3H)-one (3at)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 4-pyridinemethanol **2t** (65.5 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane :

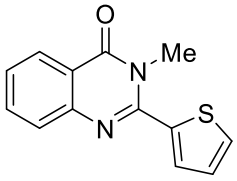
EtOAc = 5 : 1), **3at** was obtained as white solid (64.1 mg, 90% yield); mp = 181-183 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.6, 1.4 Hz, 2H), 8.33 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.78 (td, *J* = 7.6, 1.4 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.56-7.52 (m, 1H), 7.50 (q, *J* = 2.0 Hz, 2H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.4, 153.7, 150.7, 147.2, 142.9, 134.7, 127.8, 127.8, 127.0, 122.5, 120.9, 34.1; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N_3O$ 238.0980; Found 238.0979.



3au

2-(furan-2-yl)-3-methylquinazolin-4(3H)-one (3au)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), furfuryl alcohol **2u** (52.1 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3au** was obtained as white solid (21.5 mg, 32% yield); mp = 121-123 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 3.7 Hz, 2H), 7.65 (d, *J* = 1.4 Hz, 1H), 7.50-7.44 (m, 1H), 7.16 (d, *J* = 3.7 Hz, 1H), 6.61 (q, *J* = 1.7 Hz, 1H), 3.77 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.6, 147.7, 147.4, 146.6, 144.9, 134.5, 127.6, 127.2, 126.9, 120.6, 115.8, 112.0, 33.2; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}N_2O_2$ 227.0821; Found 227.0823.

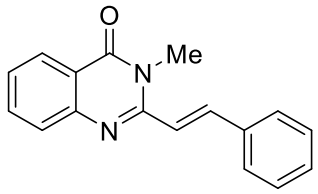


3av

3-methyl-2-(thiophen-2-yl)quinazolin-4(3H)-one (3av)

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 2-thiophenemethanol **2v** (56.8 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 3 : 1), **3av** was obtained as white solid (36.2 mg, 50% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.30-8.28 (m, 1H), 7.76-7.70 (m, 2H), 7.55 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.52-7.45 (m, 2H), 7.16 (dd, *J* = 5.3, 3.9 Hz, 1H), 3.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.9, 150.2,

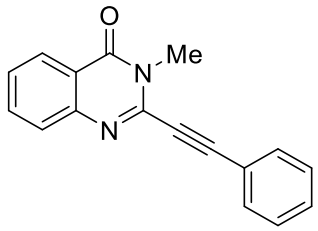
147.4, 137.2, 134.4, 129.9, 129.5, 127.6, 127.1, 126.9, 120.3, 34.2; HRMS (FAB) m/z: [M] Calcd for $C_{13}H_{11}N_2OS$ 243.0592; Found 243.0596.



3aw

(E)-3-methyl-2-styrylquinazolin-4(3H)-one (3aw)

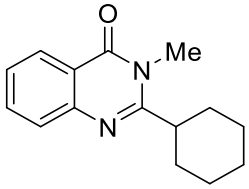
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), cinnamyl alcohol **2w** (73.6 μL, 0.57 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3aw** was obtained as white solid (61.7 mg, 78% yield); mp = 156-158 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.28 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.99 (d, *J* = 15.6 Hz, 1H), 7.76-7.71 (m, 2H), 7.63 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.46-7.37 (m, 4H), 7.12 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.5, 152.5, 147.6, 141.3, 135.5, 134.3, 130.0, 129.1, 128.0, 127.4, 127.0, 126.6, 120.6, 119.1, 30.9; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1184; Found 263.1180.



3ax

3-methyl-2-(phenylethynyl)quinazolin-4(3H)-one (3ax)

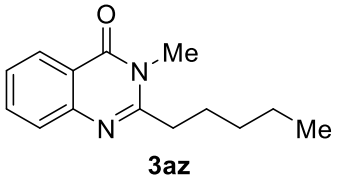
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 3-phenyl-2-propyn-1-ol **2x** (74.8 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ax** was obtained as white solid (17.1 mg, 22% yield); mp = 162-164 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.31-8.29 (m, 1H), 7.78-7.73 (m, 2H), 7.67-7.65 (m, 2H), 7.52-7.40 (m, 4H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.7, 147.7, 140.7, 134.5, 132.6, 130.6, 128.8, 127.8, 127.6, 126.9, 121.5, 120.4, 94.5, 82.5, 33.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O$ 261.1028; Found 261.1031.



3ay

2-cyclohexyl-3-methylquinazolin-4(3H)-one (3ay)

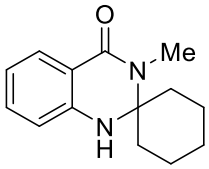
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), cyclohexanemethanol **2y** (73.8 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ay** was obtained as white solid (8.0 mg, 11% yield); mp = 123-125 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.72-7.67 (m, 1H), 7.64-7.62 (m, 1H), 7.43-7.39 (m, 1H), 3.66 (s, 3H), 2.82 (tt, *J* = 11.4, 3.1 Hz, 1H), 1.97-1.91 (m, 4H), 1.79-1.71 (m, 3H), 1.47-1.30 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.0, 160.4, 147.6, 134.1, 127.2, 126.8, 126.3, 120.4, 42.5, 31.2, 30.2, 26.3, 26.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}N_2O$ 243.1497; Found 243.1493.



3az

3-methyl-2-pentylquinazolin-4(3H)-one (3az)

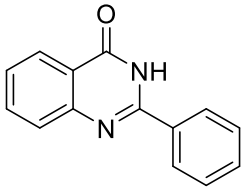
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), 1-hexanol **2z** (75.3 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3az** was obtained as white solid (8.9 mg, 13% yield); mp = 108-110 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.73-7.69 (m, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.45-7.40 (m, 1H), 3.63 (s, 3H), 2.82 (t, *J* = 8.0 Hz, 2H), 1.87-1.80 (m, 2H), 1.50-1.37 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.7, 157.5, 147.4, 134.2, 126.9, 126.9, 126.5, 120.3, 35.9, 31.7, 30.7, 26.8, 22.6, 14.1; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}N_2O$ 231.1497; Found 231.1494.



3aaa

3'-methyl-1'H-spiro[cyclohexane-1,2'-quinazolin]-4'(3'H)-one (3aaa)

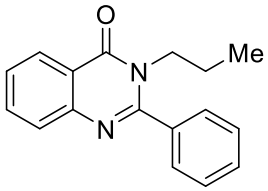
: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), cyclohexanol **2aa** (93.7 μL, 0.9 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3aaa** was obtained as white solid (28.7 mg, 42% yield); mp = 209-211 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.27 (ddd, *J* = 8.7, 6.7, 1.4 Hz, 1H), 6.84-6.80 (m, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 4.56 (s, 1H), 3.07 (s, 3H), 2.03 (dd, *J* = 12.4, 1.8 Hz, 2H), 1.78-1.70 (m, 6H), 1.49-1.38 (m, 2H), 1.19 (qt, *J* = 13.3, 3.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.9, 144.1, 133.2, 128.8, 119.1, 117.0, 114.9, 33.0, 26.6, 24.7, 22.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}N_2O$ 231.1497; Found 231.1501.



3ba

2-phenylquinazolin-4(3H)-one (3ba)

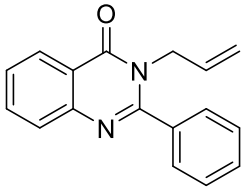
: Following the general procedure A, 2-nitrobenzamide (49.8 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ba** was obtained as white solid (45.0 mg, 68% yield); mp = 91-93 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.54 (s, 1H), 8.19 (dd, *J* = 8.0, 1.2 Hz, 2H), 8.16 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.85-7.81 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.61-7.50 (m, 4H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 162.4, 152.5, 148.7, 134.5, 132.8, 131.4, 128.6, 127.8, 127.4, 126.5, 125.9, 121.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_2O$ 223.0871; Found 223.0879.



3ca

2-phenyl-3-propylquinazolin-4(3H)-one (3ca)

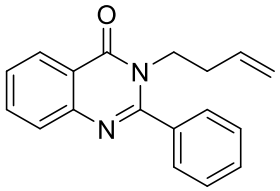
: Following the general procedure A, **1c** (62.5 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ca** was obtained as white solid (58.9 mg, 74% yield); mp = 101-103 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 9.1, 0.9 Hz, 1H), 7.75 (dd, *J* = 4.8, 1.1 Hz, 2H), 7.52-7.48 (m, 6H), 3.96-3.92 (m, 2H), 1.68-1.59 (m, 2H), 0.76 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.2, 156.5, 147.2, 135.6, 134.5, 130.0, 128.9, 127.9, 127.5, 127.1, 126.9, 121.0, 47.6, 22.2, 11.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O$ 265.1341; Found 265.1340.



3da

3-allyl-2-phenylquinazolin-4(3H)-one (3da)

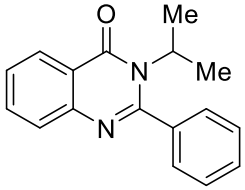
: Following the general procedure A, **1d** (61.9 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3da** was obtained as white solid (47.1 mg, 60% yield); mp = 104-106 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 4.1 Hz, 2H), 7.56-7.47 (m, 6H), 5.92-5.82 (m, 1H), 5.19-5.16 (m, 1H), 4.94 (dd, *J* = 17.0, 0.9 Hz, 1H), 4.61-4.60 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.0, 156.5, 147.1, 135.1, 134.7, 132.3, 130.2, 128.8, 128.1, 127.5, 127.3, 127.1, 120.9, 117.7, 48.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1184; Found 263.1182.



3ea

3-(but-3-en-1-yl)-2-phenylquinazolin-4(3H)-one (3ea)

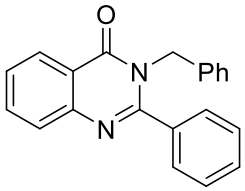
: Following the general procedure A, **1e** (66.1 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ea** was obtained as white solid (64.8 mg, 78% yield); mp = 102-104 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.8 Hz, 1H), 7.76-7.75 (m, 2H), 7.55-7.49 (m, 6H), 5.62-5.52 (m, 1H), 4.95-4.87 (m, 2H), 4.09-4.05 (m, 2H), 2.36 (q, *J* = 7.3 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.2, 156.3, 147.1, 135.5, 134.5, 134.0, 130.1, 128.9, 128.1, 127.5, 127.2, 126.9, 121.0, 117.7, 45.3, 33.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O$ 277.1341; Found 277.1349.



3fa

3-isopropyl-2-phenylquinazolin-4(3H)-one (3fa)

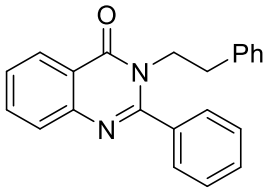
: Following the general procedure A, **1f** (62.5 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3fa** was obtained as white solid (18.0 mg, 23% yield); mp = 131-133 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.31-8.29 (m, 1H), 7.76-7.69 (m, 2H), 7.52 (s, 5H), 7.50-7.46 (m, 1H), 4.39-4.29 (m, 1H), 1.59 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.5, 156.9, 146.8, 143.2, 135.7, 135.3, 130.4, 129.5, 129.1, 128.1, 122.3, 91.5, 34.6; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O$ 265.1341; Found 265.1343.



3ga

3-benzyl-2-phenylquinazolin-4(3H)-one (3ga)

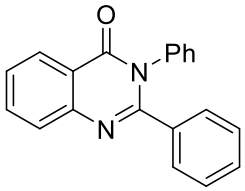
: Following the general procedure A, **1g** (76.9 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ga** was obtained as white solid (37.6 mg, 40% yield); mp = 91-93 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39-8.37 (m, 1H), 7.81-7.75 (m, 2H), 7.55-7.51 (m, 1H), 7.49-7.45 (m, 1H), 7.42-7.38 (m, 2H), 7.34 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.21 (t, *J* = 3.2 Hz, 3H), 6.93 (q, *J* = 3.2 Hz, 2H), 5.28 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.6, 156.5, 147.4, 136.7, 135.4, 134.7, 130.0, 128.7, 128.7, 128.4, 128.1, 127.7, 127.6, 127.3, 127.3, 127.1, 121.0, 48.9; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_2O$ 313.1341; Found 313.1346.



3ha

3-phenethyl-2-phenylquinazolin-4(3H)-one (3ha)

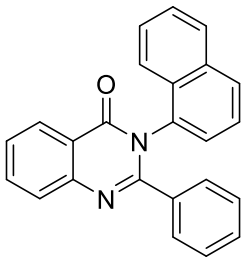
: Following the general procedure A, **1h** (81.1 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ha** was obtained as white solid (59.9 mg, 61% yield); mp = 176-178 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.80-7.74 (m, 2H), 7.56-7.48 (m, 4H), 7.39 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.20-7.18 (m, 3H), 6.89-6.87 (m, 2H), 4.22-4.18 (m, 2H), 2.92 (t, *J* = 7.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3, 156.3, 147.3, 137.9, 135.5, 134.6, 130.0, 128.9, 128.7, 127.9, 127.7, 127.2, 126.9, 126.8, 121.1, 47.7, 34.8; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O$ 327.1497; Found 327.1488.



3ia

2,3-diphenylquinazolin-4(3H)-one (3ia)

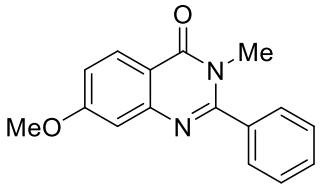
: Following the general procedure A, **1i** (72.7 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ia** was obtained as white solid (30.5 mg, 34% yield); mp = 153-155 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 7.85-7.79 (m, 2H), 7.56-7.52 (m, 1H), 7.33 (qd, *J* = 4.1, 1.8 Hz, 3H), 7.30-7.19 (m, 5H), 7.17-7.15 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.4, 155.3, 147.7, 137.8, 135.6, 134.9, 129.4, 129.3, 129.1, 128.6, 128.1, 127.9, 127.4, 127.4, 121.1; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O$ 299.1184; Found 299.1191.



3ja

3-(naphthalen-1-yl)-2-phenylquinazolin-4(3H)-one (3ja)

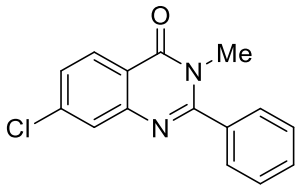
: Following the general procedure A, **1j** (81.1 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ja** was obtained as white solid (13.6 mg, 13% yield); mp = 212-215 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.41-8.39 (m, 1H), 7.92-7.84 (m, 3H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.68-7.66 (m, 1H), 7.60-7.56 (m, 1H), 7.55-7.48 (m, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.25-7.23 (m, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.4, 156.3, 147.9, 135.4, 135.0, 134.7, 134.1, 130.6, 129.6, 129.5, 128.7, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 126.6, 125.2, 122.5, 121.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{24}H_{17}N_2O$ 349.1341; Found 349.1346.



3ka

7-methoxy-3-methyl-2-phenylquinazolin-4(3H)-one (3ka)

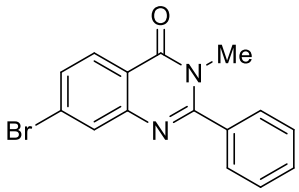
: Following the general procedure A, **1k** (63.1 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ka** was obtained as white solid (68.9 mg, 86% yield); mp = 91-93 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 1H), 7.57-7.51 (m, 5H), 7.12 (d, *J* = 2.3 Hz, 1H), 7.07 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.90 (s, 3H), 3.47 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.7, 162.4, 157.0, 149.7, 135.7, 130.2, 129.0, 128.4, 128.0, 117.4, 114.3, 108.0, 55.8, 34.2; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1134; Found 267.1131.



3la

7-chloro-3-methyl-2-phenylquinazolin-4(3H)-one (3la)

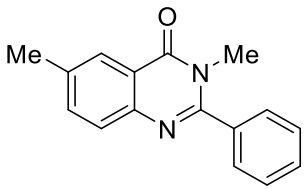
: Following the general procedure A, **1l** (64.8 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3la** was obtained as white solid (59.2 mg, 73% yield); mp = 91-93 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.57-7.52 (m, 5H), 7.44 (dd, *J* = 8.5, 2.1 Hz, 1H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3, 157.5, 148.4, 140.6, 135.2, 130.5, 129.1, 128.3, 128.1, 127.8, 127.2, 119.1, 34.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}ClN_2O$ 271.0638; Found 271.0645.



3ma

7-bromo-3-methyl-2-phenylquinazolin-4(3H)-one (3ma)

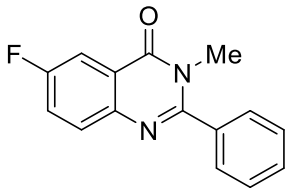
: Following the general procedure A, **1m** (77.7 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ma** was obtained as white solid (70.1 mg, 74% yield); mp = 149-151 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.58-7.53 (m, 5H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.4, 157.5, 148.3, 135.1, 130.5, 130.5, 130.3, 129.2, 129.1, 128.3, 128.1, 119.5, 34.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}BrN_2O$ 315.0133; Found 315.0142.



3na

3,6-dimethyl-2-phenylquinazolin-4(3H)-one (3na)

: Following the general procedure A, **1n** (58.3 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3na** was obtained as white solid (65.9 mg, 88% yield); mp = 135-137 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.4 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.58-7.49 (m, 6H), 3.49 (s, 3H), 2.50 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.8, 155.5, 145.3, 137.4, 136.0, 135.5, 130.1, 129.0, 128.2, 127.4, 126.2, 120.4, 34.4, 21.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}N_2O$ 251.1184; Found 251.1188.

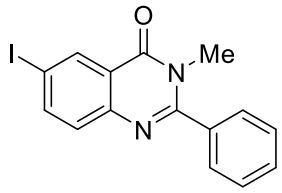


3oa

6-fluoro-3-methyl-2-phenylquinazolin-4(3H)-one (3oa)

: Following the general procedure A, **1o** (59.4 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3oa** was obtained as white solid (65.7 mg, 86% yield); mp = 143-145 ℃; ^{1}H-NMR (400

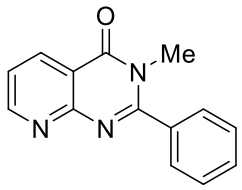
MHz, $CDCl_3$) δ 7.95 (dd, J = 8.7, 2.7 Hz, 1H), 7.76 (q, J = 4.6 Hz, 1H), 7.58-7.52 (m, 5H), 7.50-7.45 (m, 1H), 3.50 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_{CF} = 247.5 Hz), 162.2 (d, J_{CF} = 3.8 Hz), 162.1 (d, J_{CF} = 3.8 Hz), 159.9 (d, J_{CF} = 247.5 Hz), 155.6, 144.0, 135.2, 130.4, 130.1 (d, J_{CF} = 7.6 Hz), 130.0 (d, J_{CF} = 7.6 Hz), 129.1, 128.2, 123.3 (d, J_{CF} = 24.0 Hz), 123.0 (d, J_{CF} = 24.0 Hz), 121.9 (d, J_{CF} = 8.6 Hz), 121.8 (d, J_{CF} = 8.6 Hz), 111.8 (d, J_{CF} = 24.0 Hz), 111.5 (d, J_{CF} = 24.0 Hz), 34.5; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -112.14; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}FN_2O$ 255.0934; Found 255.0928.



3pa

6-iodo-3-methyl-2-phenylquinazolin-4(3H)-one (3pa)

: Following the general procedure A, **1p** (91.8 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3pa** was obtained as white solid (79.1 mg, 73% yield); mp = 139-141 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 2.3 Hz, 1H), 8.01 (dd, J = 8.7, 1.8 Hz, 1H), 7.57-7.51 (m, 5H), 7.47 (d, J = 8.7 Hz, 1H), 3.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.5, 156.9, 146.8, 143.2, 135.7, 135.3, 130.4, 129.5, 129.1, 128.1, 122.3, 91.5, 34.6; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}IN_2O$ 362.9994; Found 362.9986.



3qa

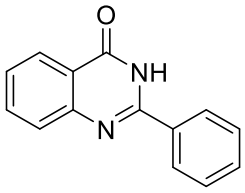
3-methyl-2-phenylpyrido[2,3-d]pyrimidin-4(3H)-one (3qa)

: Following the general procedure A, **1q** (54.3 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3qa** was obtained as white solid (36.5 mg, 51% yield); mp = 207-209 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 4.6 Hz, 1H), 8.63 (dd, J = 7.9, 2.2 Hz, 1H), 7.65-7.63 (m, 2H), 7.53-

7.48 (m, 3H), 7.43 (q, J = 4.1 Hz, 1H), 3.54 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.3, 159.6, 157.5, 156.4, 136.4, 134.9, 130.6, 128.8, 128.5, 122.5, 115.7, 34.8; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N_3O$ 238.0980; Found 238.0985.

4-2. General procedure B using 2-nitrobenzonitriles

To an oven-dried borosilicate glass tube were added substrate **4** (0.30 mmol, 1.0 equiv.), alcohol **2** (0.60 mmol, 2.0 equiv.), $Fe_3(CO)_{12}$ (10.8 mg, 6 mol%), and trimethylamine N-oxide (2.7 mg, 12 mol%) under an argon atmosphere. The tube was sealed with a rubber septum and flushed with argon balloon. Toluene (1.0 mL) was then added via syringe. The reaction vessel was recharged with Ar, then tightly sealed with a screw cap, and the mixture was stirred at 160 ℃ in an oil bath for 48 h. After completion, the reaction mixture was cooled to room temperature. The crude residue was directly purified by filtration or flash column chromatography on silica gel to afford the desired product.

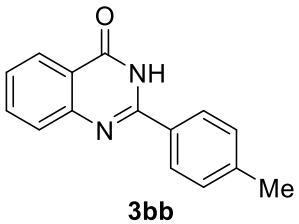


3ba

2-phenylquinazolin-4(3H)-one (3ba)

: Following the general procedure B, 2-nitrobenzonitrile (44.4 mg, 0.3 mmol), benzyl alcohol (62.1 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ba** was obtained as white solid (43.7 mg, 66% yield).

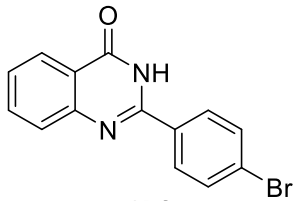
All characterization data of the obtained product **3ba** are identical to those of the compound prepared according to general procedure A.



3bb

2-(p-tolyl)quinazolin-4(3H)-one (3bb)

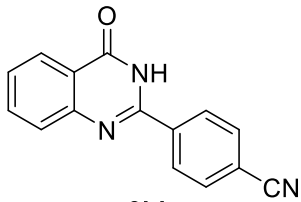
: Following the general procedure B, 2-nitrobenzonitrile (44.4 mg, 0.3 mmol), 4-methylbenzyl alcohol **2b** (73.3 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3bb** was obtained as white solid (38.0 mg, 54% yield); mp = 241-243 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 1H), 8.34-8.32 (m, 1H), 8.15 (d, *J* = 8.3 Hz, 2H), 7.84-7.77 (m, 2H), 7.52-7.48 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.9, 151.9, 149.7, 142.4, 135.0, 130.1, 129.9, 128.0, 127.5, 126.7, 126.5, 120.9, 21.7; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O$ 237.1028; Found 237.1026.



3bf

2-(4-bromophenyl)quinazolin-4(3H)-one (3bf)

: Following the general procedure B, 2-nitrobenzonitrile (44.4 mg, 0.3 mmol), 4-bromobenzyl alcohol **2f** (112.2 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3bf** was obtained as white solid (34.3 mg, 38% yield); mp = 310-312 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.14 (t, *J* = 9.6 Hz, 3H), 7.86-7.82 (m, 1H), 7.75 (t, *J* = 8.4 Hz, 3H), 7.53 (t, *J* = 6.9 Hz, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 162.3, 151.6, 148.5, 134.7, 132.0, 131.6, 129.8, 127.5, 126.8, 125.9, 125.2, 121.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}BrN_2O$ 300.9976; Found 300.9988.

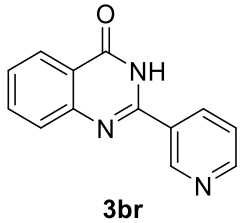


3bi

4-(4-oxo-3,4-dihydroquinazolin-2-yl)benzonitrile (3bi)

: Following the general procedure B, 2-nitrobenzonitrile (44.4 mg, 0.3 mmol), 4-cyanobenzyl alcohol **2i** (79.9 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3bi** was obtained as white solid (29.0 mg, 39% yield);

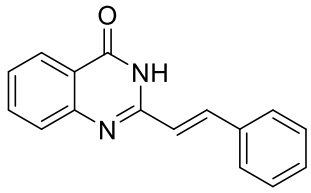
mp = 206-208 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.73 (s, 1H), 8.35 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 6.4 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3, 151.2, 148.4, 137.1, 134.7, 132.5, 128.6, 127.7, 127.2, 125.9, 121.2, 118.4, 113.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}N_3O$ 248.0824; Found 248.0839.



3br

2-(pyridin-3-yl)quinazolin-4(3H)-one (3br)

: Following the general procedure B, 2-nitrobenzonitrile (44.4 mg, 0.3 mmol), 3-pyridinemethanol **2r** (58.3 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3br** was obtained as white solid (31.6 mg, 47% yield); mp = 275-277 °C; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.73 (s, 1H), 9.30 (d, *J* = 2.3 Hz, 1H), 8.76-8.75 (m, 1H), 8.50 (td, *J* = 5.0, 3.1 Hz, 1H), 8.17 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.88-7.76 (m, 2H), 7.60-7.53 (m, 2H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 162.2, 151.8, 150.9, 148.8, 148.5, 135.4, 134.7, 128.8, 127.5, 126.9, 125.9, 123.5, 121.1; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}N_3O$ 224.0824; Found 224.0826.

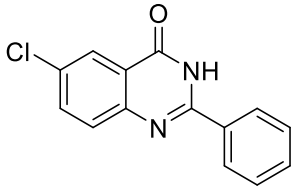


3bw

(E)-2-styrylquinazolin-4(3H)-one (3bw)

: Following the general procedure B, 2-nitrobenzonitrile (44.4 mg, 0.3 mmol), cinnamyl alcohol **2w** (73.6 μL, 0.57 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3bw** was obtained as white solid (28.5 mg, 38% yield); mp = 250-252 °C; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.23 (s, 1H), 8.11 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.95 (d, *J* = 16.0 Hz, 1H), 7.82-7.78 (m, 1H), 7.67 (q, *J* = 3.8 Hz, 3H), 7.50-7.39 (m, 4H),

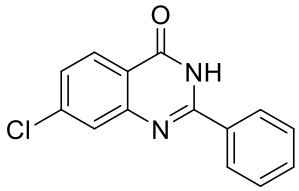
7.01 (d, J = 16.0 Hz, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 162.0, 151.7, 149.0, 138.1, 135.0, 134.4, 129.7, 129.1, 127.6, 127.0, 126.1, 125.9, 121.3, 121.1; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O$ 249.1028; Found 249.1029.



3ra

6-chloro-2-phenylquinazolin-4(3H)-one (3ra)

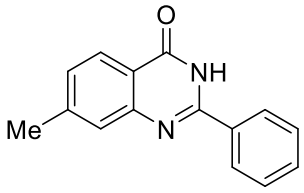
: Following the general procedure B, 5-chloro-2-nitrobenzonitrile (54.8 mg, 0.3 mmol), benzyl alcohol (62.4 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ra** was obtained as white solid (36.7 mg, 48% yield); mp = 246-248 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.72 (s, 1H), 8.17 (d, J = 6.9 Hz, 2H), 8.09 (d, J = 2.3 Hz, 1H), 7.86 (dd, J = 8.8, 2.7 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.62-7.53 (m, 3H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 161.5, 153.0, 147.5, 134.7, 132.6, 131.6, 130.7, 129.7, 128.6, 127.9, 124.9, 122.2; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}ClN_2O$ 257.0482; Found 257.0476.



3sa

7-chloro-2-phenylquinazolin-4(3H)-one (3sa)

: Following the general procedure B, 4-chloro-2-nitrobenzonitrile (54.8 mg, 0.3 mmol), benzyl alcohol (62.4 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3sa** was obtained as white solid (35.1 mg, 46% yield); mp = 274-276 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 1H), 8.15 (dd, J = 12.8, 7.9 Hz, 3H), 7.78 (d, J = 1.8 Hz, 1H), 7.63-7.53 (m, 4H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 161.7, 153.8, 149.8, 139.2, 132.4, 131.7, 128.6, 127.9, 126.8, 126.5, 119.8; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}ClN_2O$ 257.0482; Found 257.0479.

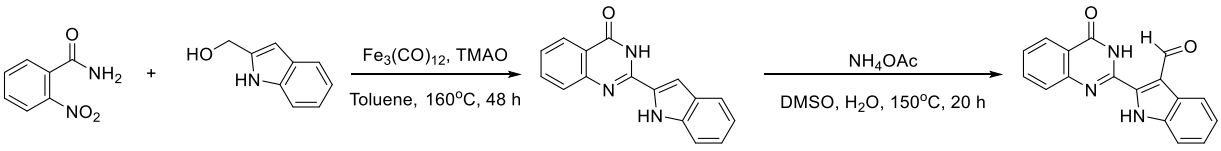


3ta

7-methyl-2-phenylquinazolin-4(3H)-one (3ta)

: Following the general procedure B, 2-nitro-p-tolunitrile (48.6 mg, 0.3 mmol), benzyl alcohol (62.4 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3ta** was obtained as white solid (21.7 mg, 31% yield); mp = 299-301 °C; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 8.18-8.16 (m, 2H), 8.04 (d, J = 7.6 Hz, 1H), 7.60-7.52 (m, 4H), 7.34 (d, J = 8.4 Hz, 1H), 2.47 (s, 3H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 162.2, 152.4, 148.8, 145.1, 132.8, 131.3, 128.6, 128.0, 127.7, 127.1, 125.7, 118.6, 21.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O$ 237.1028; Found 237.1033.

4-3. Procedure for the synthesis of Bouchardatine[3, 4]



1b **2ab** **3bab** **9** (Bouchardatine)

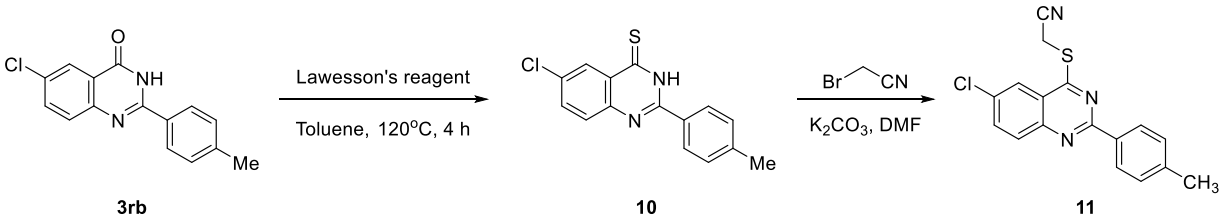
*Synthesis of **3bab***

: Following the general procedure A, **1b** (49.8 mg, 0.3 mmol), 1H-indole-2-methanol (147.2 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3bab** was obtained as yellow solid (40.8 mg, 52% yield); mp = 323-325 °C; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.60 (s, 1H), 11.79 (s, 1H), 8.16 (dd, J = 7.7, 1.5 Hz, 1H), 7.85 (td, J = 7.7, 1.5 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.7 Hz, 2H), 7.55-7.48 (m, 2H), 7.23 (t, J = 7.7 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H); ^{13}C-NMR (100 M+Hz, DMSO-d_6) δ 161.9, 148.7, 146.6, 137.7, 134.7, 130.1, 127.5, 126.9, 126.3, 126.1, 124.1, 121.5, 121.1, 120.0, 112.4, 105.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}N_3O$ 262.0980; Found 262.0982.

*Synthesis of **9** (bouchardatine)*

To a 25 mL two neck round-bottom flask containing compound **1b** (0.219 mmol, 57.2 mg) was added NH_4OAc (0.876 mmol, 67.5 mg) and a mixture of DMSO/H_2O (1.50 mL/0.088 mL) under an argon atmosphere. The mixture was refluxed at 150 ℃ for 20 h. After completion, the mixture was cooled to room temperature and quenched with H_2O (25 mL), followed by extraction with ethyl acetate (2 x 50 mL). The combined organic layers were washed with brine (25 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (hexane : EtOAc = 3 : 1) to afford the desired product **10** as yellow solid (31.7 mg, 50% yield); mp = 300-302 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 13.63 (s, 1H), 13.15 (s, 1H), 10.49 (s, 1H), 8.28-8.20 (m, 2H), 7.93-7.89 (m, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 187.5, 161.2, 148.4, 145.3, 135.8, 135.8, 134.9, 127.6, 127.5, 127.4, 126.1, 125.4, 123.3, 121.8, 120.2, 115.1, 113.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}N_3O_2$ 290.0930; Found 290.0932.

4-4. Procedure for the synthesis of compound 11[5]



*Synthesis of **3rb***

: Following the general procedure A, **1r** (60.2mg, 0.3 mmol), **2b** (73.3 mg, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3rb** was obtained as white solid (42.3 mg, 57% yield); mp = 283-285 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 4.6 Hz, 1H), 8.63 (dd, J = 7.9, 2.2 Hz, 1H), 7.65-7.63 (m, 2H), 7.53-7.48 (m, 3H), 7.43 (q, J = 4.1 Hz, 1H), 3.54 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.3, 159.6, 157.5, 156.4, 136.4, 134.9, 130.6, 128.8, 128.5, 122.5, 115.7, 34.8; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}ClN_2O$ 271.0638; Found 271.0630.

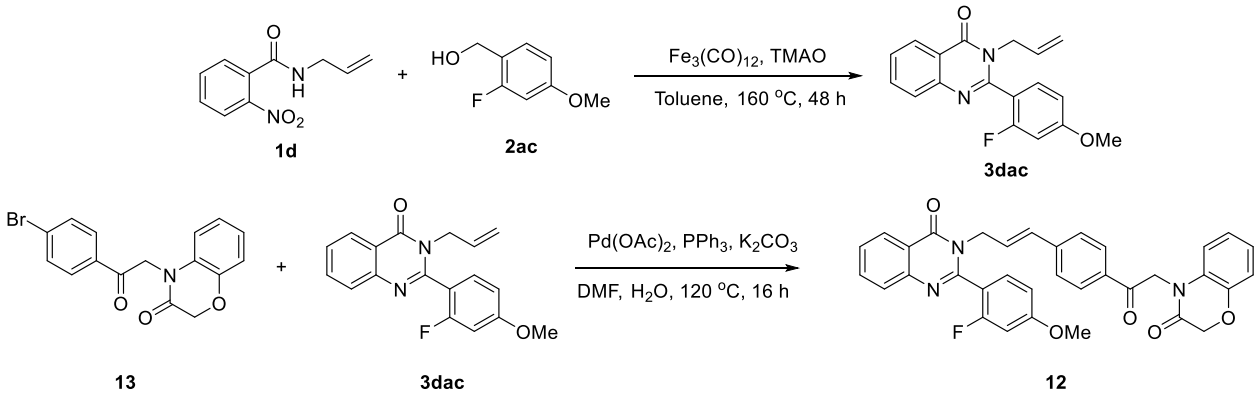
*Synthesis of **10***

To a solution of **3rb** (0.722 mmol, 195.5 mg) in toluene (0.06 M) was added Lawesson's reagent (0.794 mmol, 321.3 mg) under an argon atmosphere. The mixture was stirred at 120 ℃ for 4 h. After completion, the mixture was cooled to room temperature and filtered with dichloromethane to give desired product **10** as yellow solid (147.0 mg, 71% yield); mp = 196-198 ℃; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 13.96 (s, 1H), 8.49 (d, J = 2.3 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.87 (dd, J = 8.8, 2.7 Hz, 1H), 7.82-7.69 (m, 1H), 7.33 (d, J = 7.7 Hz, 2H), 2.36 (s, 3H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 152.0, 141.9, 135.4, 132.2, 129.1, 129.0, 128.5, 128.5, 127.9, 21.1; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}ClN_2S$ 287.0410; Found 287.0400.

*Synthesis of **11***

To a 25 mL oven-dried round-bottom flask containing a solution of **10** (0.400 mmol, 114.6 mg) in pyridine (0.2 M) was added bromoacetonitrile (30.6 μL, 0.440 mmol) under an argon atmosphere. The mixture was stirred at reflux with 70℃ for 12 h. After completion of the reaction, the mixture was cooled to room temperature and quenched with water. The aqueous layer was extracted with ethyl acetate (2 x 50 mL), The combined organic layers were washed with brine (25 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane : EtOAc = 5 : 1) to give the desired product **11** as white solid (91.2 mg, 70% yield); mp = 200-202 ℃; ^{1}H-NMR ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 1.5 Hz, 1H), 7.80 (dd, J = 8.8, 1.9 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 4.24 (s, 2H), 2.45 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.8, 159.5, 147.9, 141.8, 135.4, 134.3, 132.9, 131.0, 129.7, 128.8, 122.4, 116.1, 21.7, 15.4; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}ClN_3S$ 326.0519; Found 326.0523.

4-5. Procedure for the synthesis of compound 12[6]



*Synthesis of **3dac***

: Following the general procedure A, **1d** (61.9mg, 0.3 mmol), **2ac** (78.9 μL, 0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3dac** was obtained as white solid (44.7 mg, 48% yield); mp = 131-133 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.79-7.74 (m, 2H), 7.54-7.50 (m, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.73 (dd, *J* = 11.4, 2.3 Hz, 1H), 5.77 (dq, *J* = 22.5, 5.3 Hz, 1H), 5.08 (dd, *J* = 10.1, 0.9 Hz, 1H), 4.87 (dd, *J* = 17.4, 0.9 Hz, 2H), 4.34 (s, 1H), 3.86 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J_{CF} = 10.6 Hz), 162.6 (d, J_{CF} = 10.6 Hz), 161.9, 161.3 (d, J_{CF} = 247.5 Hz), 158.9 (d, J_{CF} = 247.5 Hz), 151.7, 147.2, 134.6, 131.8, 131.0, 131.0, 127.6 (d, J_{CF} = 11.5 Hz), 127.5 (d, J_{CF} = 11.5 Hz), 127.1, 121.1, 117.9, 115.7 (d, J_{CF} = 16.3 Hz), 115.6 (d, J_{CF} = 16.3 Hz), 110.7 (d, J_{CF} = 1.9 Hz), 110.6 (d, J_{CF} = 1.9 Hz), 102.2 (d, J_{CF} = 25.0 Hz), 102.0 (d, J_{CF} = 25.0 Hz), 56.0, 47.8; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -111.16; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}FN_2O_2$ 311.1196; Found 311.1200.

Substrate **13** was synthesized through known procedures and characterization data were consistent with the literature.[6]

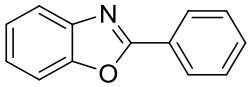
*Synthesis of **12***

To a 100 mL two-neck round bottom flask, **3dac** (0.322 mmol, 100.0 mg), **13** (0.293 mmol, 101.4 mg), potassium carbonate (0.352 mmol, 48.6 mg), triphenylphosphine (0.0293 mmol, 7.68 mg), palladium(II) acetate (0.0293 mmol, 6.58 mg) was added in DMF (42 mL)/H_2O (2l mL) under an argon atmosphere. The mixture was refluxed at 120 ℃ for 16 h. After completion, the mixture

was cooled to room temperature and quenched with H_2O (25 mL), followed by extraction with ethyl acetate (2 x 50 mL). The combined organic layers were washed with brine (25 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane : EtOAc = 2.5 : 1) to give the desired product **12** as white solid (105.6 mg, 57% yield); mp = 212-214 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.82-7.75 (m, 2H), 7.57-7.53 (m, 1H), 7.38 (t, *J* = 8.5 Hz, 3H), 7.03-6.96 (m, 2H), 6.92 (td, *J* = 7.6, 1.8 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.76 (dd, *J* = 11.5, 2.3 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.32-6.18 (m, 2H), 5.29 (d, *J* = 8.0 Hz, 2H), 5.02 (s, 1H), 4.71 (s, 2H), 4.61 (s, 1H), 3.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.3, 165.3, 162.8 (d, J_{CF} = 10.5 Hz), 162.7 (d, J_{CF} = 10.5 Hz), 162.0, 151.4, 147.3, 145.3, 141.9, 134.7, 133.8, 132.3, 131.0, 129.0, 128.6, 127.7 (d, J_{CF} = 11.4 Hz), 127.6 (d, J_{CF} = 11.4 Hz), 127.1 (d, J_{CF} = 26.7 Hz), 127.0, 126.8 (d, J_{CF} = 26.7 Hz), 124.2, 123.0, 121.1, 117.3, 114.8, 110.8, 102.3 (d, J_{CF} = 23.8 Hz), 102.1 (d, J_{CF} = 23.8 Hz), 67.7, 56.0, 48.0, 47.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -110.86; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{34}H_{27}FN_3O_5$ 576.1935; Found 576.1927.

5. Synthesis of benzoxazoles[7]

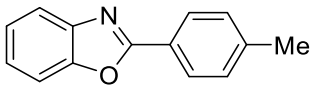
To an oven-dried borosilicate glass tube were added 2-nitrophenol substrate **6** (0.30 mmol, 1.0 equiv.), alcohol **2** (0.45 mmol, 1.5 equiv.), $Fe_3(CO)_{12}$ (4.5 mg, 3 mol%), and trimethylamine N-oxide (1.4 mg, 6 mol%) under an argon atmosphere. The tube was sealed with a rubber septum and flushed with argon balloon. *o*-Xylene (1.0 mL) was then added via syringe. The reaction vessel was recharged with Ar, then tightly sealed with a screw cap, and the mixture was stirred at 160 ℃ in an oil bath for 24 h. After completion, the reaction mixture was cooled to room temperature. The crude residue was directly purified by flash column chromatography on silica gel to afford the desired product.



6aa

2-phenylbenzo[d]oxazole (6aa)

: Following the above procedure, 2-nitrophenol (41.7 mg, 0.30 mmol), benzyl alcohol (46.6 μL, 0.45 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), **6aa** was obtained as white solid (44.2 mg, 76% yield). mp = 103-105 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.28-8.26 (m, 2H), 7.81-7.76 (m, 1H), 7.61-7.50 (m, 4H), 7.36 (dt, *J* = 9.8, 3.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.2, 150.9, 142.2, 131.7, 129.1, 127.7, 127.3, 125.2, 124.7, 120.1, 110.7; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{13}H_{10}NO$ 196.0762; Found 196.0752.

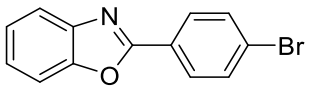


6ab

2-(p-tolyl)benzo[d]oxazole (6ab)

: Following the above procedure, 2-nitrophenol (41.7 mg, 0.30 mmol), 4-methylbenzyl alcohol **2b** (55.0 mg, 0.45 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), **6ab** was obtained as white solid (53.1 mg, 85% yield); mp = 115-117 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 2H), 7.79-7.74 (m, 1H), 7.60-7.55 (m, 1H), 7.37-7.32 (m, 4H), 2.45 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.5, 150.8,

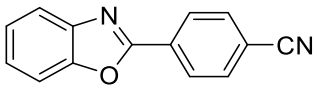
142.3, 142.2, 129.8, 127.7, 125.0, 124.6, 124.6, 120.0, 110.6, 21.8; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}NO$ 210.0919; Found 210.0916.



6af

2-(4-bromophenyl)benzo[d]oxazole (6af)

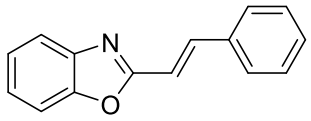
: Following the above procedure, 2-nitrophenol (41.7 mg, 0.30 mmol), 4-bromobenzyl alcohol **2f** (84.2 mg, 0.45 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), **6af** was obtained as white solid (69.4 mg, 84% yield); mp = 156-158 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (dt, *J* = 9.0, 2.1 Hz, 2H), 7.80-7.75 (m, 1H), 7.67 (dt, *J* = 9.0, 2.1 Hz, 2H), 7.60-7.56 (m, 1H), 7.39-7.35 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.3, 150.9, 142.2, 132.4, 129.2, 126.4, 126.3, 125.6, 124.9, 120.3, 110.8; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{13}H_9BrNO$ 273.9868; Found 278.9864.



6ai

4-(benzo[d]oxazol-2-yl)benzonitrile (6ai)

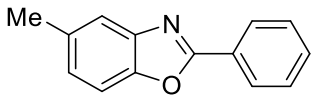
: Following the above procedure, 2-nitrophenol (41.7 mg, 0.30 mmol), 4-cyanobenzyl alcohol **2i** (59.9 mg, 0.45 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), **6ai** was obtained as white solid (46.1 mg, 68% yield); mp = 203-205 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.36-8.34 (m, 2H), 7.82-7.80 (m, 3H), 7.62-7.60 (m, 1H), 7.44-7.37 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.0, 151.0, 142.0, 132.8, 131.2, 128.1, 126.3, 125.3, 120.7, 118.3, 114.9, 111.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_9N_2O$ 221.0715; Found 221.0711.



6aw

(E)-2-styrylbenzo[d]oxazole (6aw)

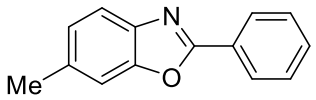
: Following the above procedure, 2-nitrophenol (41.7 mg, 0.30 mmol), cinnamyl alcohol **2w** (58.1 μL, 0.45 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), **6aw** was obtained as white solid (34.1 mg, 51% yield); mp = 83-85 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 16.5 Hz, 1H), 7.73 (q, *J* = 3.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.56-7.52 (m, 1H), 7.45-7.39 (m, 3H), 7.37-7.31 (m, 2H), 7.10 (dd, *J* = 27.2, 10.7 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.0, 150.6, 142.1, 139.8, 135.3, 130.0, 129.1, 127.8, 125.4, 124.7, 120.0, 114.0, 110.5; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}N_2O$ 222.0919; Found 222.0915.



6ba

5-methyl-2-phenylbenzo[d]oxazole (6ba)

: Following the above procedure, 5-methyl-2-nitrophenol (45.9 mg, 0.30 mmol), benzyl alcohol (46.6 μL, 0.45 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), **6ba** was obtained as white solid (37.5 mg, 60% yield); mp = 101-103 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.54-7.51 (m, 3H), 7.39 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 2.51 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.7, 151.2, 140.0, 135.7, 131.4, 129.0, 127.6, 127.5, 126.0, 119.5, 110.9, 21.9; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}NO$ 210.0919; Found 210.0921.



6ca

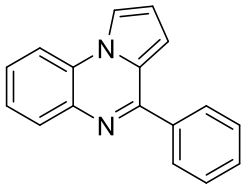
6-methyl-2-phenylbenzo[d]oxazole (6ca)

: Following the above procedure, 4-methyl-2-nitrophenol (45.9 mg, 0.30 mmol), benzyl alcohol (46.6 μL, 0.45 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), **6ca** was obtained as white solid (41.1 mg, 66% yield); mp = 93-95 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.26-8.23 (m, 2H), 7.56 (s, 1H), 7.52 (td, *J* = 5.3, 3.5 Hz, 3H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 2.49 (s, 3H); ^{13}C-NMR

(100 MHz, $CDCl_3$) δ 163.3, 149.2, 142.5, 134.5, 131.5, 129.0, 127.7, 127.5, 126.4, 120.1, 110.1, 21.7; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}NO$ 210.0919; Found 210.0913.

6. Synthesis of pyrrolo[1,2-α]quinoxalines[8]

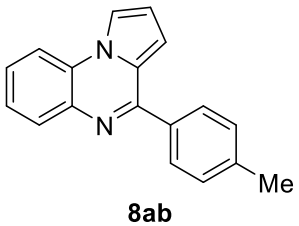
To an oven-dried borosilicate glass tube were added substrate **8** (0.30 mmol, 1.0 equiv.), alcohol **2** (0.60 mmol, 2.0 equiv.), $Fe_3(CO)_{12}$ (6.0 mg, 4 mol%), and trimethylamine N-oxide (1.8 mg, 8 mol%) under an argon atmosphere. The tube was sealed with a rubber septum and flushed with argon balloon. CPME (1.0 mL) was then added via syringe. The reaction vessel was recharged with Ar, then tightly sealed with a screw cap, and the mixture was stirred at 160 ℃ in an oil bath for 48 h. After completion, the reaction mixture was cooled to room temperature. The crude residue was directly purified by flash column chromatography on silica gel to afford the desired product.



8aa

4-phenylpyrrolo[1,2-a]quinoxaline (8aa)

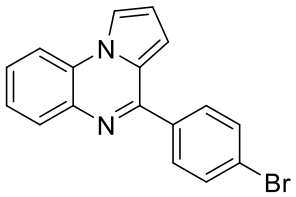
: Following the above procedure, **7a** (56.5 mg, 0.30 mmol), benzyl alcohol (64.9 μL, 0.60 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), **8aa** was obtained as pale-yellow solid (66.0 mg, 90% yield). m.p = 85-86 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 8.01 (dt, *J* = 5.4, 2.1 Hz, 3H), 7.89 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.58-7.51 (m, 4H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 1H), 6.91 (dd, *J* = 3.7, 2.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.4, 138.2, 136.0, 130.2, 130.1, 128.8, 128.7, 127.7, 127.2, 125.5, 125.4, 115.0, 114.3, 113.8, 109.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2$ 245.1079; Found 245.1083.



8ab

4-(p-tolyl)pyrrolo[1,2-a]quinoxaline (8ab)

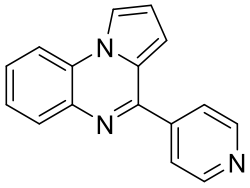
: Following the above procedure, **7a** (56.5 mg, 0.30 mmol), 4-methylbenzyl alcohol **2b** (73.3 mg, 0.60 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), **8ab** was obtained as pale-yellow solid (61.4 mg, 79% yield). m.p = 80-82 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.89-7.87 (m, 1H), 7.54-7.44 (m, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 3.7 Hz, 1H), 6.92 (t, *J* = 3.2 Hz, 1H), 2.46 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.3, 140.5, 129.8, 129.5, 128.8, 127.6, 127.2, 125.6, 125.4, 115.2, 114.4, 113.8, 21.6; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2$ 259.1235; Found 259.1228.



8af

4-(4-bromophenyl)pyrrolo[1,2-a]quinoxaline (8af)

: Following the above procedure, **7a** (56.5 mg, 0.30 mmol), 4-bromobenzyl alcohol **2f** (112.2 mg, 0.60 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), **8af** was obtained as white solid (89.1 mg, 92% yield); m.p = 160-162 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2H), 7.92-7.88 (m, 3H), 7.68 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.56-7.45 (m, 2H), 6.97-6.90 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.3, 137.5, 136.3, 131.9, 130.4, 130.4, 127.9, 127.3, 125.6, 125.2, 124.3, 115.0, 114.3, 113.8, 108.6; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}BrN_2$ 323.0184; Found 323.0186.

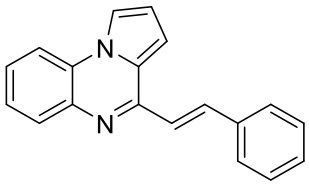


8at

4-(pyridin-4-yl)pyrrolo[1,2-a]quinoxaline (8at)

: Following the above procedure, **7a** (56.5 mg, 0.30 mmol), 4-pyridinemethanol **2t** (65.5 mg, 0.60 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), **8at** was obtained as yellow solid (66.3 mg, 71% yield). m.p = 150-

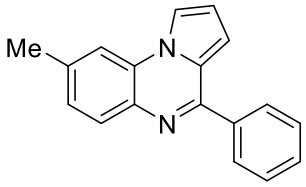
152 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.5 Hz, 2H), 8.06-8.04 (m, 2H), 7.92-7.89 (m, 3H), 7.57 (td, *J* = 7.8, 1.4 Hz, 1H), 7.51-7.47 (m, 1H), 7.00 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.94 (dd, *J* = 3.7, 2.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.9, 150.4, 145.8, 136.0, 130.6, 128.4, 127.4, 125.7, 124.8, 123.0, 115.2, 114.5, 113.8, 108.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}N_3$ 246.1031; Found 246.1036.



8aw

(E)-4-styrylpyrrolo[1,2-a]quinoxaline (8aw)

: Following the above procedure, **7a** (56.5 mg, 0.30 mmol), cinnamyl alcohol **2w** (77.4 μL, 0.60 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), **8aw** was obtained as yellow solid (83.3 mg, 80% yield). m.p = 128-130 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 15.6 Hz, 1H), 8.01-7.96 (m, 2H), 7.87-7.84 (m, 1H), 7.72-7.70 (m, 2H), 7.53 (d, *J* = 16.0 Hz, 1H), 7.49-7.41 (m, 4H), 7.38-7.34 (m, 1H), 7.12 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.92 (q, *J* = 2.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.0, 136.6, 136.5, 136.4, 130.0, 129.2, 128.9, 127.8, 127.4, 127.2, 126.2, 125.5, 123.4, 114.6, 113.9, 113.8, 106.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2$ 271.1235; Found 271.1233.

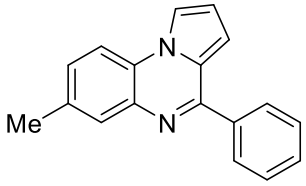


8ba

8-methyl-4-phenylpyrrolo[1,2-a]quinoxaline (8ba)

: Following the above procedure, **7b** (60.7 mg, 0.30 mmol), benzyl alcohol (62.2 μL, 0.60 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), **8ba** was obtained as pale-yellow solid (70.7 mg, 91% yield). m.p = 76-78 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05-7.99 (m, 4H), 7.69 (s, 1H), 7.57-7.52 (m, 3H), 7.29 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.02 (d, *J* = 3.7 Hz, 1H), 6.91 (q, *J* = 2.3 Hz, 1H), 2.57 (s, 3H); ^{13}C-NMR (100 MHz,

$CDCl_3$) δ 153.3, 138.4, 130.1, 129.6, 128.9, 128.7, 126.9, 125.4, 115.0, 114.4, 113.9, 109.4, 22.0; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2$ 259.1235; Found 259.1241.



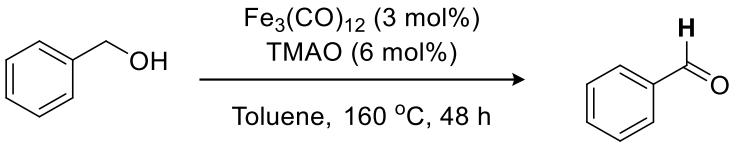
8ca

8-methyl-4-phenylpyrrolo[1,2-a]quinoxaline (8ca)

: Following the above procedure, **7c** (60.7 mg, 0.30 mmol), benzyl alcohol (62.2 μL, 0.60 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), **8ca** was obtained as pale-yellow solid (58.0 mg, 75% yield). m.p = 96-98 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01-7.96 (m, 3H), 7.85 (d, *J* = 0.9 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.56-7.49 (m, 3H), 7.34 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.97 (q, *J* = 1.8 Hz, 1H), 6.87 (q, *J* = 2.3 Hz, 1H), 2.51 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.5, 138.7, 136.4, 135.2, 130.2, 129.8, 128.8, 128.7, 125.5, 125.2, 114.5, 113.8, 113.5, 108.6, 21.3; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2$ 259.1235; Found 259.1241.

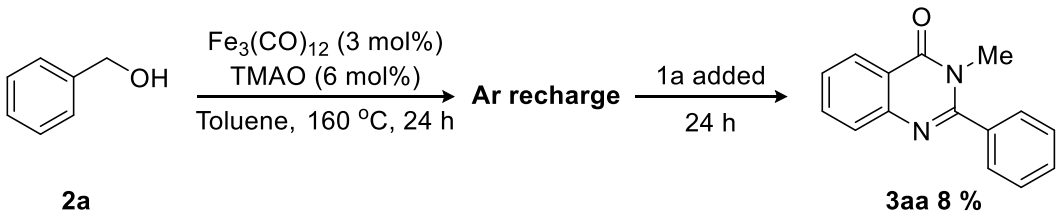
7. Mechanistic Study

7-1. Control study



2a **2a', quant**

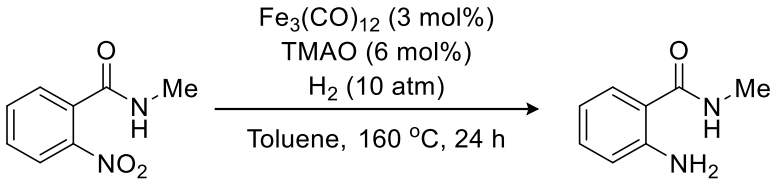
To an oven-dried borosilicate glass tube were added benzyl alcohol **2** (0.30 mmol, 1.0 equiv.), $Fe_3(CO)_{12}$ (4.5 mg, 3 mol%), and trimethylamine N-oxide (1.4 mg, 6 mol%) under an argon atmosphere. The tube was sealed with a rubber septum and flushed with argon balloon. Toluene (0.3 mL) was then added via syringe. The reaction vessel was recharged with Ar, then tightly sealed with a screw cap, and the mixture was stirred at 160 ℃ in an oil bath for 48 h. After completion, the reaction mixture was cooled to room temperature, quenched with H_2O (50 mL), and extracted with DCM (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The reaction yield was determined by ^1H NMR analysis of the crude residue, which confirmed the formation of benzaldehyde **2a'** with quant yield.



2a **3aa 8 %**

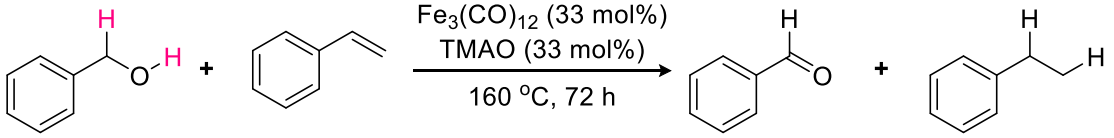
To an oven-dried borosilicate glass tube were added benzyl alcohol **2** (0.30 mmol, 1.0 equiv.), $Fe_3(CO)_{12}$ (4.5 mg, 3 mol%), and trimethylamine N-oxide (1.4 mg, 6 mol%) under an argon atmosphere. The tube was sealed with a rubber septum and flushed with argon balloon. Toluene (0.3 mL) was then added via syringe. The reaction vessel was recharged with Ar, then tightly sealed with a screw cap, and the mixture was stirred at 160 ℃ in an oil bath for 24 h. After stirred for 24 h, the screw cap was removed and the mixture was purged with argon for 30 min. Subsequently, **1a** was added, the vessel was resealed with a screw cap, and the mixture was stirred for an additional 24 h. After completion, the reaction mixture was cooled to room

temperature. The crude residue was directly purified by flash column chromatography on silica gel to afford the desired product **3aa** with 8 % yield. The result suggests that the gas generated during alcohol oxidation plays a critical role in the reduction of nitro groups.



1a **1a' 50 %**

To a high-pressure reactor were added **1a** (0.30 mmol, 1.0 equiv.), $Fe_3(CO)_{12}$ (4.5 mg, 3 mol%.), trimethylamine N-oxide (1.4 mg, 6 mol%.), and toluene (1.0 mL). The vessel was sealed and charged with hydrogen gas (10 atm), then stirred at 160 ℃ in an oil bath for 24 h. After completion, the reaction mixture was cooled to room temperature. The crude residue was directly purified by flash column chromatography on silica gel to afford the desired product N-methyl-2-aminobenzamide **1a'** with 50 % yield. The result suggests that the nitro group reduction can proceed via $Fe_3(CO)_{12}$ and molecular hydrogen.



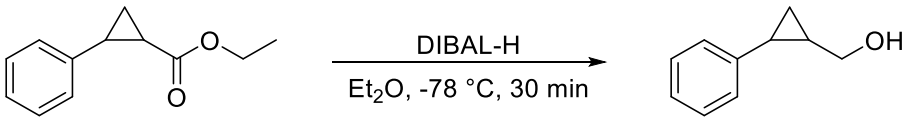
2a, 50 eq **Styrene, 1 eq** **2a', quant** **Ethylbenzene, 14 %**

To a Schlenk flask (Flask 1) were added benzyl alcohol **2a** (0.60 mmol, 2.0 equiv.), $Fe_3(CO)_{12}$ (4.5 mg, 3 mol%.), and trimethylamine N-oxide (1.4 mg, 6 mol%.) under an argon atmosphere. The flask was sealed with a rubber septum and flushed with argon balloon. Toluene (0.3 mL) was then added via syringe. In a separate Schlenk flask (Flask 2), styrene and THF were added to Pd/C (10 wt%). The two flasks were connected via a gas-transfer bridge under an inert atmosphere. The mixture in Flask 1 was heated at 160 ℃ in an oil bath for 48 h under reflux. After completion, the reaction mixture at the flask 2 was filtered through a pad of Celite, and the solvent was removed under reduced pressure. The crude residue was determined by ^{1}H NMR analysis, and ethylbenzene was detected in 14 % yield.[9]

Figure **S1**. Molecular hydrogen generation through oxidation of benzyl alcohol and reduction of styrene

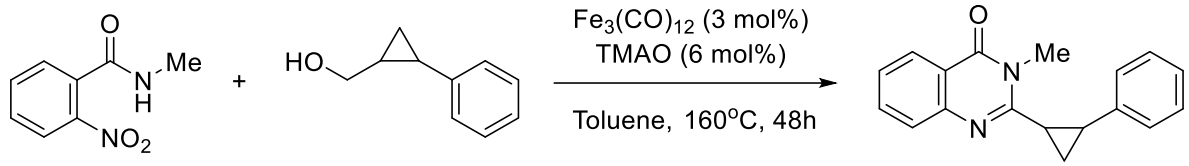
7-2. Radical clock experiment

Synthesis of (2-phenylcyclopropyl)methanol[10]



2ad

To a 50 mL round-neck bottom flask were added ethyl 2-phenylcyclopropanecarboxylate and anhydrous diethyl ether under an argon atmosphere. The reaction mixture was cooled to -78℃, and diisobutylaluminum hydride (DIBAL-H) was added dropwise over 30 min. The mixture was stirred at -78℃ for 1 h. After completion, the reaction was quenched with saturated aqueous NH_4Cl, and the resulting mixture was filtered through a pad of Celite. The filtrate was washed with H_2O (50 mL) and extracted with DCM (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford the crude product.



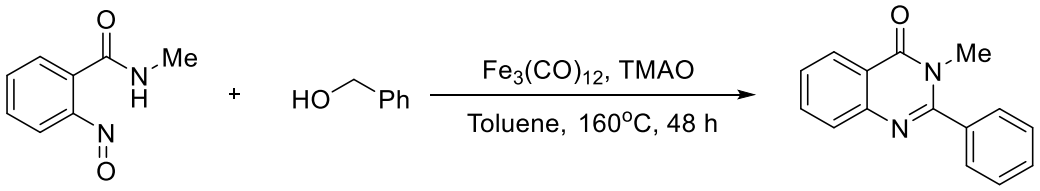
1a **2ad** **3aad**

: Following the general procedure A, **1a** (54.0 mg, 0.3 mmol), (2-phenylcyclopropyl)methanol **2ad** (0.6 mmol) were used as starting material. After purification by column chromatography (hexane : EtOAc = 4 : 1), **3aad** was obtained as white solid (20.7 mg, 25% yield); mp = 113-115 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.72-7.68 (m, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.44-7.40 (m, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.27-7.24 (m, 1H), 7.23-7.19 (m, 2H), 3.69 (s, 3H), 2.63-2.58 (m, 1H), 2.30-2.25 (m, 1H), 2.14-2.09 (m, 1H), 1.60-1.56 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.6, 156.5, 147.5, 140.5, 134.2, 129.0, 128.8, 128.4, 127.0, 126.9, 126.8, 126.3, 126.1, 120.4, 30.7, 27.5, 26.2, 16.9; HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O$ 277.1341; Found 277.1345. The ring-opened compound was not observed.

7-3. Stepwise confirmation experiment

Confirmation of nitroso

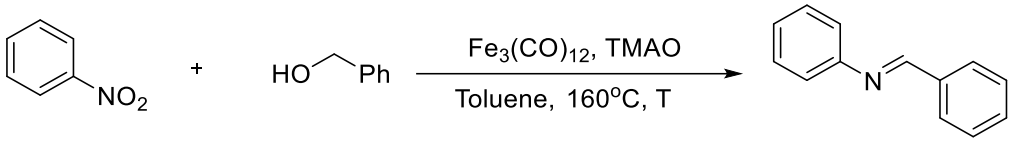
To confirm the plausibility of nitroso intermediate, we synthesized it independently and subjected it to the standard reaction conditions. The same quinazolinone product was obtained in comparable yield, supporting the involvement of nitroso as a true intermediate.

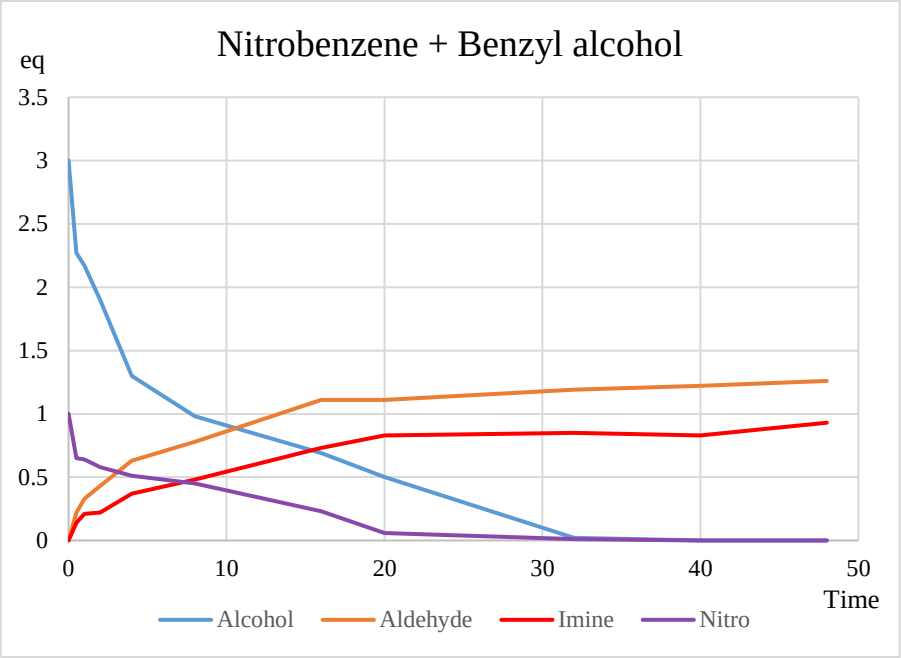


2a, 1 eq **3aa**

Following the general procedure A, N-methyl-2-nitrosobenzene (49.3 mg, 0.3 mmol), benzyl alcohol (31.1 μL, 0.3 mmol) were used as starting material. As a result, **3aa** was obtained with 90% yield.

7-4. Substrate distribution during Reaction progress





8. DFT calculations

8-1. Computational details

All density functional theory (DFT) calculations were performed by Gaussian 16 software package.[11] Geometry optimizations and frequency analyses were performed at the level of the B3LYP functional[12] and a def2-SVP basis set[13] in gas phase. Single point energies were further refined at the M06-2X functional and a def2-TZVP basis set[14] level using SMD solvation model (solvent = toluene).[15] Throughout the paper, the energies presented are the M062X-calculated Gibbs free energies in the Toluene solvent with B3LYP-calculated thermodynamic corrections.

8-2. Gibbs energy profiles

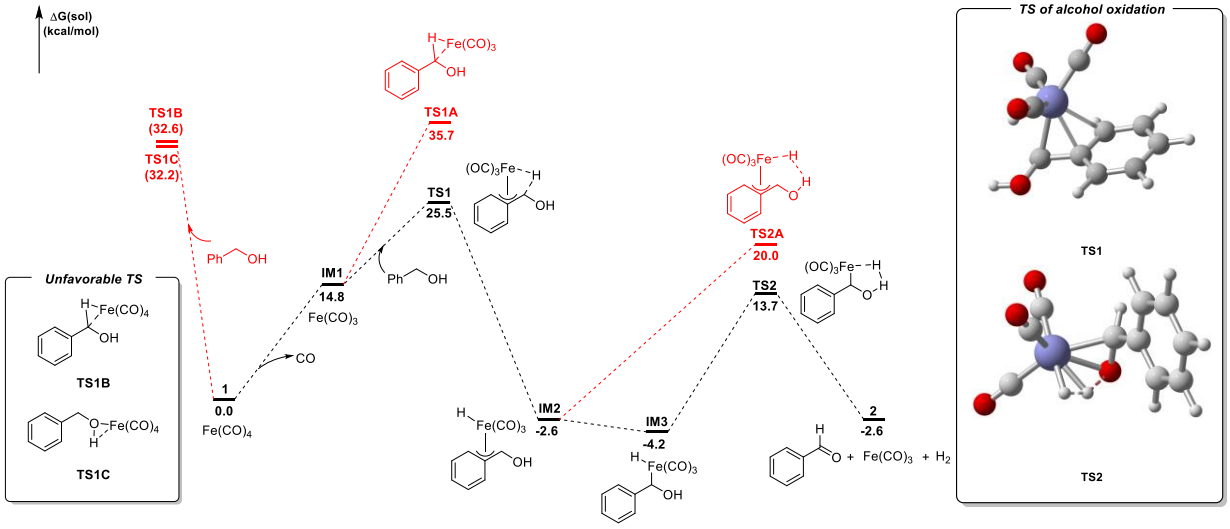


Figure **S2**. Oxidation of benzyl alcohol with iron tricarbonyl

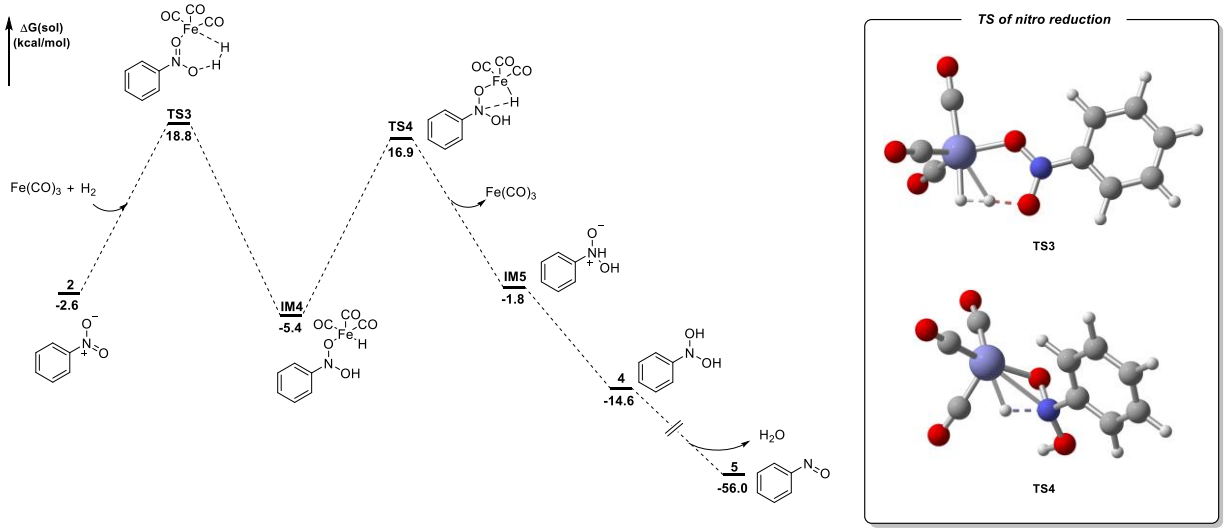


Figure **S3**. Reduction of nitrobenzene with iron tricarbonyl.

8-3. Energy correlation

	E(SCF) /TZ	Thermal corr	G(sol)
$Fe(CO)_4$	-1716.951707	-0.030083	-1716.98179
CO	-113.3177971	-0.024359	-113.3421561
$Fe(CO)_3$	-1603.584883	-0.031099	-1603.615982
Benzyl alcohol	-346.7660108	0.084564	-346.6814468
Benzaldehyde	-345.5648911	0.061893	-345.5029981
Nitrobenzene	-436.7513468	0.053008	-436.6983388
H_2	-1.168010205	-0.008282	-1.176292205
TS1	-1950.346441	0.083452	-1950.262989
TS1A	-1950.327437	0.080768	-1950.246669
TS1B	-2063.693342	0.081349	-2063.611993
IM2	-1950.376062	0.08459	-1950.291472
IM3	-1950.377267	0.08325	-1950.294017
TS2	-1950.345251	0.079798	-1950.265453
TS2A	-1950.331166	0.079783	-1950.251383
TS3	-2041.523333	0.06687	-2041.456463
IM4	-2041.564848	0.069834	-2041.495014
TS4	-2041.529194	0.069783	-2041.459411
IM5	-437.9468277	0.073558	-437.8732697
NO_2H_2	-437.9255906	0.072791	-437.8527996
H_2O	-76.4303994	-0.006306	-76.4367054
Nitrosobenzene	-361.5311066	0.048965	-361.4821416

8-4. Cartesian coordinates of computed structures

TS1

C	1.951086	-1.682147	0.876547
C	0.985491	-0.723405	1.283865
C	1.055581	0.605302	0.779775
C	2.107227	0.937988	-0.131539
C	3.046038	-0.005504	-0.491539
C	2.961944	-1.330737	0.003002
H	1.900974	-2.693571	1.287121
H	0.341420	-0.957452	2.131246
H	2.156598	1.957243	-0.517127

H	3.856909	0.267953	-1.171416
H	3.710052	-2.069349	-0.296073
C	-0.005020	1.552290	1.120155
C	-0.386569	1.494457	2.149389
C	-1.495729	1.282675	0.375697
O	0.222105	2.830821	0.669121
H	-0.505121	3.404782	0.946861
Fe	-0.832746	0.002821	-0.068488
C	-0.915161	-1.538117	-1.001663
C	-2.105825	-0.551690	1.049186
C	-0.812384	0.930742	-1.603147
C	-3.012845	-0.834324	1.704371
C	-0.972215	-2.517690	-1.598184
C	-0.929671	1.530141	-2.579417

TS1A

C	-3.389963	-1.209725	-0.779830
C	-2.086661	-0.739567	-0.946760
C	-1.659217	0.428225	-0.292013
C	-2.565332	1.108888	0.542816
C	-3.867262	0.633411	0.712644
C	-4.284012	-0.525429	0.050334
H	-3.710002	-2.114346	-1.302849
H	-1.391300	-1.273623	-1.599060
H	-2.246516	2.002100	1.088105
H	-4.556070	1.166069	1.373136
H	-5.303468	-0.896382	0.182473
C	-0.263094	0.937373	-0.465117
H	0.266456	0.416145	-1.370389
H	0.525455	0.599642	0.999418
O	-0.169949	2.298835	-0.562777
H	-1.056906	2.690428	-0.589146
Fe	1.361714	-0.082867	-0.057411

C	2.824086	-1.073036	-0.416424
C	2.421598	1.325259	0.261531
C	0.632669	-1.499495	0.745691
O	3.110913	2.185553	0.590174
O	3.761520	-1.703987	-0.628814
O	0.233879	-2.374267	1.380639

TS1B

C	3.800858	1.290868	0.835562
C	2.626825	1.274060	0.077693
C	2.291042	0.152577	-0.697627
C	3.158732	-0.949790	-0.697881
C	4.337537	-0.932692	0.053847
C	4.661568	0.188067	0.824674
H	4.048147	2.171563	1.434874
H	1.958080	2.138492	0.079408
H	2.906139	-1.835076	-1.289769
H	5.001005	-1.801837	0.044492
H	5.580389	0.201138	1.416969
C	1.037836	0.161799	-1.557937
H	0.772603	-0.879050	-1.831005
H	1.285831	0.666840	-2.515422
O	-0.038931	0.879775	-1.015218
H	-0.229924	0.792471	0.455111
Fe	-1.498325	0.000198	0.088376
C	-2.395971	-0.794185	-1.329169
C	-0.398531	-1.329868	0.671108
C	-2.611387	-0.410716	1.437451
C	-2.166437	1.704388	0.081078
O	-3.317369	-0.666500	2.301500
O	0.249094	-2.174027	1.089024
O	-2.896373	-1.266822	-2.238817
O	-2.548702	2.779233	0.077856

IM2

C	-1.785621	-1.755573	-1.007690
C	-0.817534	-0.763528	-1.314136
C	-0.993555	0.573589	-0.853663
C	-2.169063	0.869275	-0.088095
C	-3.102199	-0.109054	0.179680
C	-2.907743	-1.439512	-0.267348
H	-1.646275	-2.767804	-1.395718
H	-0.072176	-0.990667	-2.076644
H	-2.312367	1.893270	0.259993
H	-4.003659	0.144013	0.744254
H	-3.655438	-2.204502	-0.044006
C	0.090087	1.531547	-1.007332
H	0.582225	1.544958	-1.990833
H	2.081258	0.720165	0.728932
C	-0.185633	2.799816	-0.518804
H	0.627959	3.320142	-0.545429
Fe	0.880269	0.007466	0.197541
C	1.111573	-1.591457	0.999981
C	2.167613	-0.222870	-1.026835
C	0.318924	0.848142	1.689466
O	3.078044	-0.287645	-1.724938
O	1.255663	-2.613553	1.500323
O	0.106499	1.414253	2.663322

IM3

C	3.914418	0.983216	0.325823
C	2.607683	1.244607	-0.089186
C	1.747139	0.199824	-0.475115
C	2.243812	-1.116426	-0.436625
C	3.557058	-1.376351	-0.040446
C	4.398334	-0.328742	0.347751
H	4.562086	1.811439	0.625367
H	2.243344	2.275492	-0.117426

H	1.603161	-1.965249	-0.698211
H	3.921620	-2.406784	-0.025505
H	5.423650	-0.534238	0.665194
C	0.363621	0.538283	-0.887833
H	0.284871	1.551962	-1.297133
H	-0.457887	-1.261092	0.548403
O	-0.304538	-0.356782	-1.776352
H	0.154514	-1.212883	-1.799588
Fe	-1.303036	-0.126950	-0.027531
C	-2.340421	1.282096	-0.582479
C	-2.614574	-1.360419	0.148047
C	-1.087067	0.382163	1.642784
O	-3.387345	-2.195116	0.285177
O	-3.009642	2.170005	-0.853607
O	-0.873029	0.675962	2.732079

TS2

C	3.687348	1.154940	0.088296
C	2.394322	1.099719	-0.430849
C	1.729602	-0.132791	-0.574665
C	2.402042	-1.309904	-0.200386
C	3.697057	-1.251653	0.320639
C	4.344031	-0.021305	0.470515
H	4.187577	2.120975	0.196790
H	1.885127	2.022734	-0.723754
H	1.912817	-2.277433	-0.335920
H	4.207823	-2.176252	0.602940
H	5.357715	0.021925	0.876939
C	0.358371	-0.164110	-1.141525
H	0.195327	0.533367	-1.978633
H	-0.483893	-1.282339	0.943892
O	-0.299079	-1.332897	-1.282698
H	-0.379338	-1.620543	-0.018948
Fe	-1.307467	-0.192261	0.057171

C	-2.194512	0.988814	-0.999125
C	-2.841289	-0.989148	0.643028
C	-0.874131	1.002488	1.306442
O	-3.781999	-1.482424	1.066877
O	-2.746606	1.748149	-1.651535
O	-0.560571	1.741428	2.124360

TS2A

C	2.947843	-0.000748	0.868367
C	2.055047	1.031818	0.848714
C	1.052114	1.137449	-0.196140
C	1.013467	0.104684	-1.223289
C	2.015205	-0.932139	-1.175542
C	2.930655	-1.002000	-0.160892
H	3.700231	-0.056746	1.659076
H	2.092827	1.812539	1.613588
H	0.630739	0.365299	-2.212790
H	2.035851	-1.663597	-1.988325
H	3.673861	-1.802910	-0.143221
C	0.368309	2.394450	-0.338810
H	0.680819	3.211320	0.339476
H	-1.529555	0.674838	-1.347203
O	-0.516263	2.670866	-1.194407
H	-1.072317	1.530429	-1.351464
Fe	-0.796754	-0.124065	-0.101754
C	-0.148373	-1.179830	1.199559
C	-2.056815	0.608231	0.963393
C	-1.484429	-1.520074	-0.976267
O	-2.930627	1.000611	1.597759
O	0.224162	-1.868138	2.035764
O	-1.984144	-2.390406	-1.536379

TS3

C	3.357578	-1.213477	-0.000119

C	2.371350	-0.210553	-0.000138
C	2.721762	1.152535	-0.000050
C	4.069931	1.500526	0.000062
C	5.063362	0.512453	0.000085
C	4.699929	-0.839290	-0.000007
H	3.058672	-2.260921	-0.000186
H	1.942103	1.913610	-0.000067
H	4.348559	2.557104	0.000133
H	6.118234	0.796496	0.000174
H	5.470529	-1.614050	0.000013
N	1.014554	-0.586296	-0.000239
O	0.671579	-1.830622	-0.000317
O	0.099116	0.300029	-0.000195
Fe	-1.752335	-0.114059	-0.000065
H	-1.601519	-1.731263	-0.000287
H	-0.650594	-1.728989	-0.000284
C	-2.090037	1.664835	0.000060
C	-2.785766	-0.444482	1.424341
C	-2.786495	-0.444292	-1.423987
O	-2.306520	2.788229	0.000120
O	-3.479988	-0.686912	-2.306880
O	-3.478791	-0.687213	2.307570

IM4

C	3.382132	0.849995	-0.294624
C	2.089789	0.366471	-0.021733
C	1.916996	-0.990385	0.292891
C	3.020889	-1.844723	0.337257
C	4.305977	-1.367957	0.064614
C	4.475293	-0.015827	-0.250383
H	3.517323	1.904565	-0.529366
H	0.921001	-1.380423	0.500012
H	2.867944	-2.898129	0.587130
H	5.165127	-2.042345	0.095272

H	5.473447	0.376962	-0.462449
N	0.972544	1.249211	-0.145697
O	1.351870	2.556901	0.213768
O	-0.122954	0.911288	0.585030
Fe	-1.465629	-0.168330	-0.018127
H	-0.664345	-0.515124	-1.251115
H	0.870419	3.110380	-0.421490
C	-2.514871	0.302714	1.479798
C	-2.228365	-1.776964	-0.344142
C	-2.339222	0.666177	-1.288095
O	-3.207329	0.593332	2.333761
O	-2.836985	1.248972	-2.138963
O	-2.622611	-2.818093	-0.603637

TS4

C	-3.220312	0.883690	0.070565
C	-1.941842	0.334456	-0.068098
C	-1.762720	-1.052416	-0.137010
C	-2.874413	-1.893026	-0.078993
C	-4.159591	-1.356161	0.053065
C	-4.325115	0.028947	0.127854
H	-3.346385	1.963028	0.128010
H	-0.761679	-1.480988	-0.248110
H	-2.732634	-2.974830	-0.137755
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O	-1.144107	2.519689	-0.163133
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Fe	1.396397	-0.128402	-0.065697
H	0.236705	0.786187	0.903143
H	-0.295652	2.994693	-0.125722
C	2.508930	-0.504446	-1.434780
C	2.005997	-1.469107	0.958699

C	1.985116	1.110865	1.013082
O	3.309118	-0.607287	-2.249829
O	2.509766	1.930327	1.642148
O	2.302061	-2.350244	1.632145

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^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR spectra of all compounds

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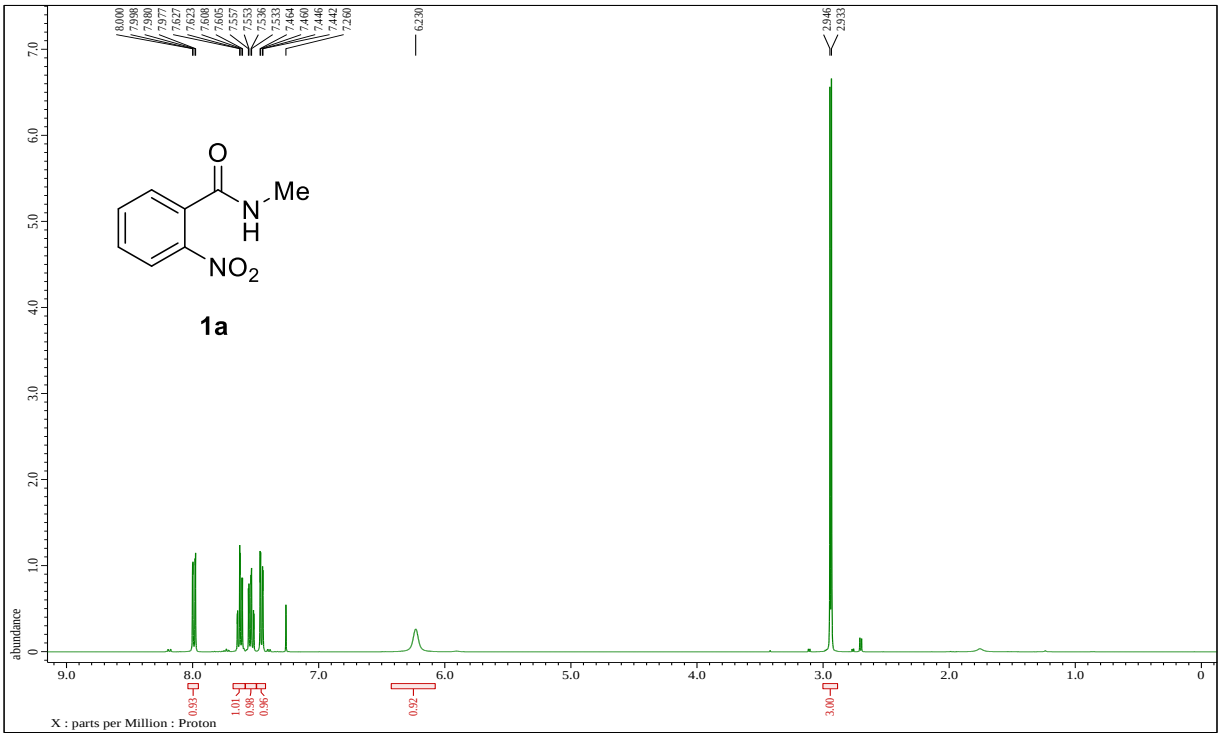

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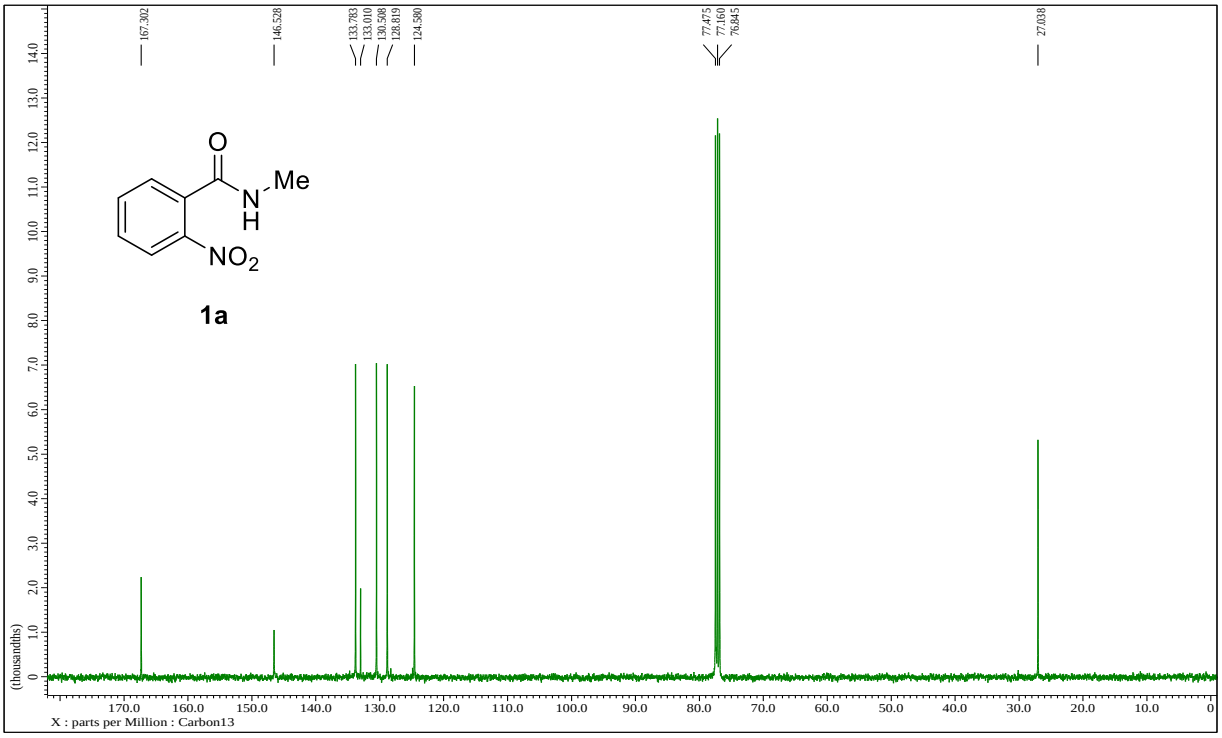

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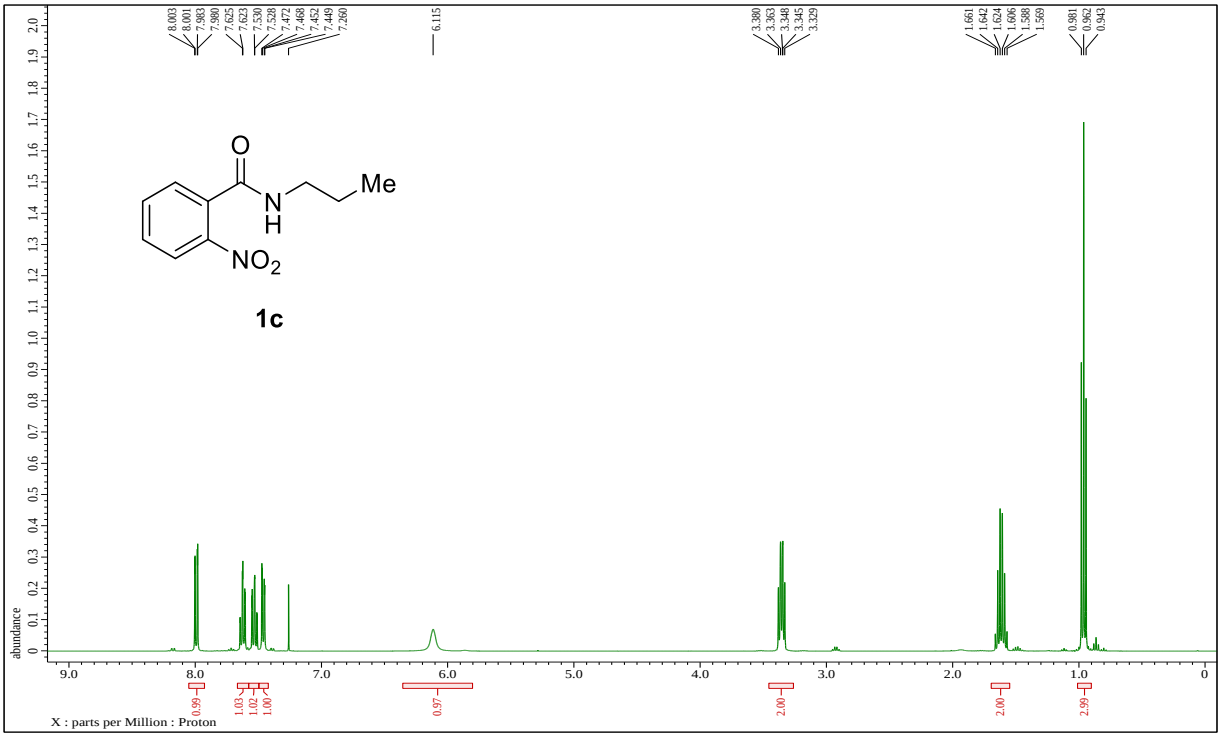

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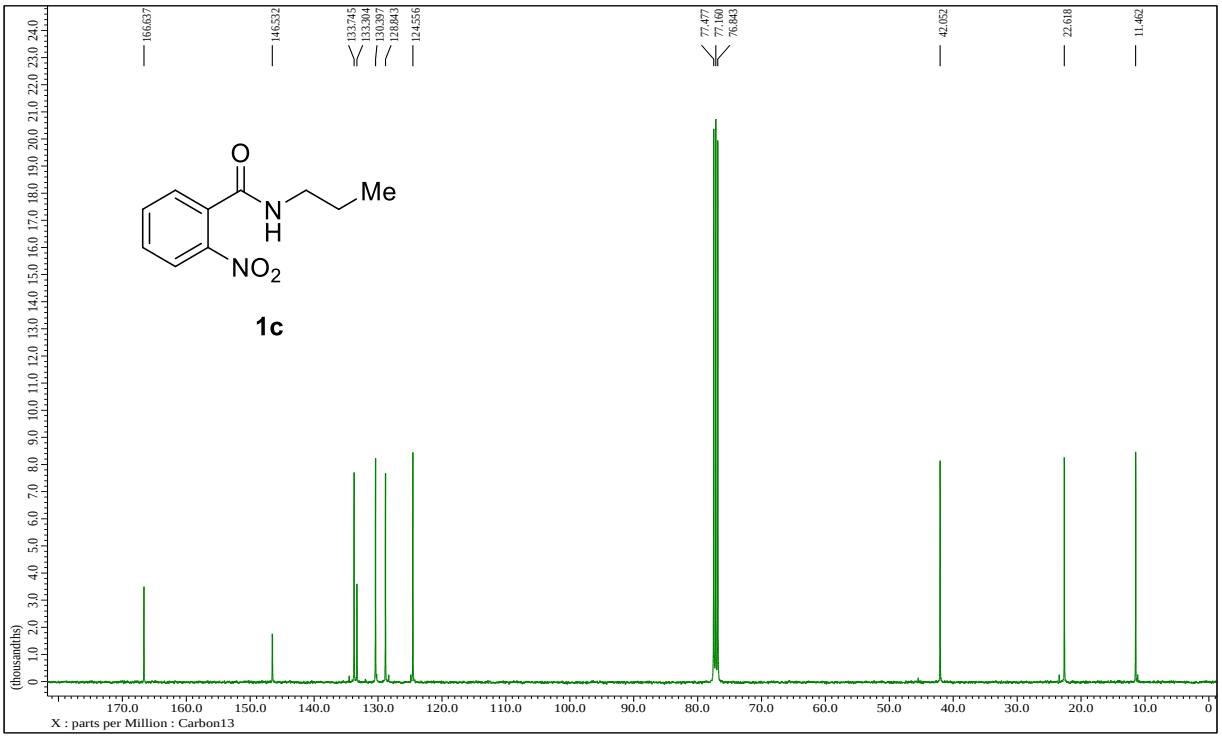

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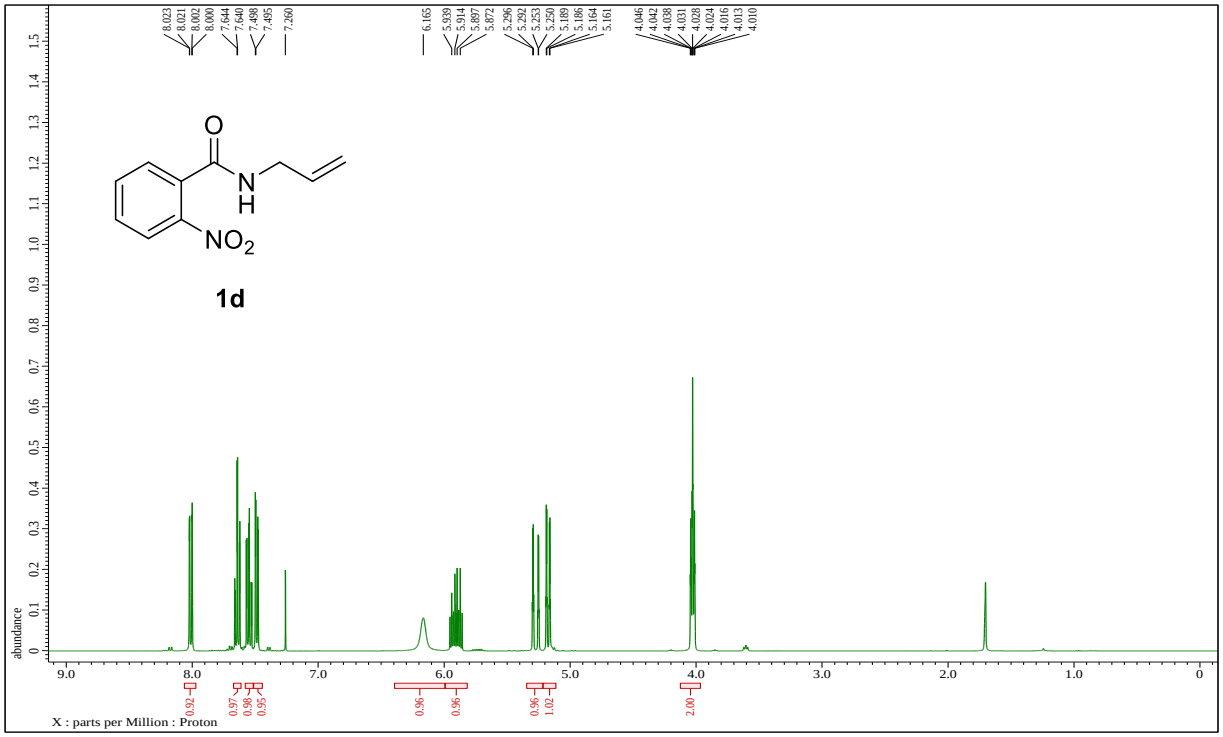

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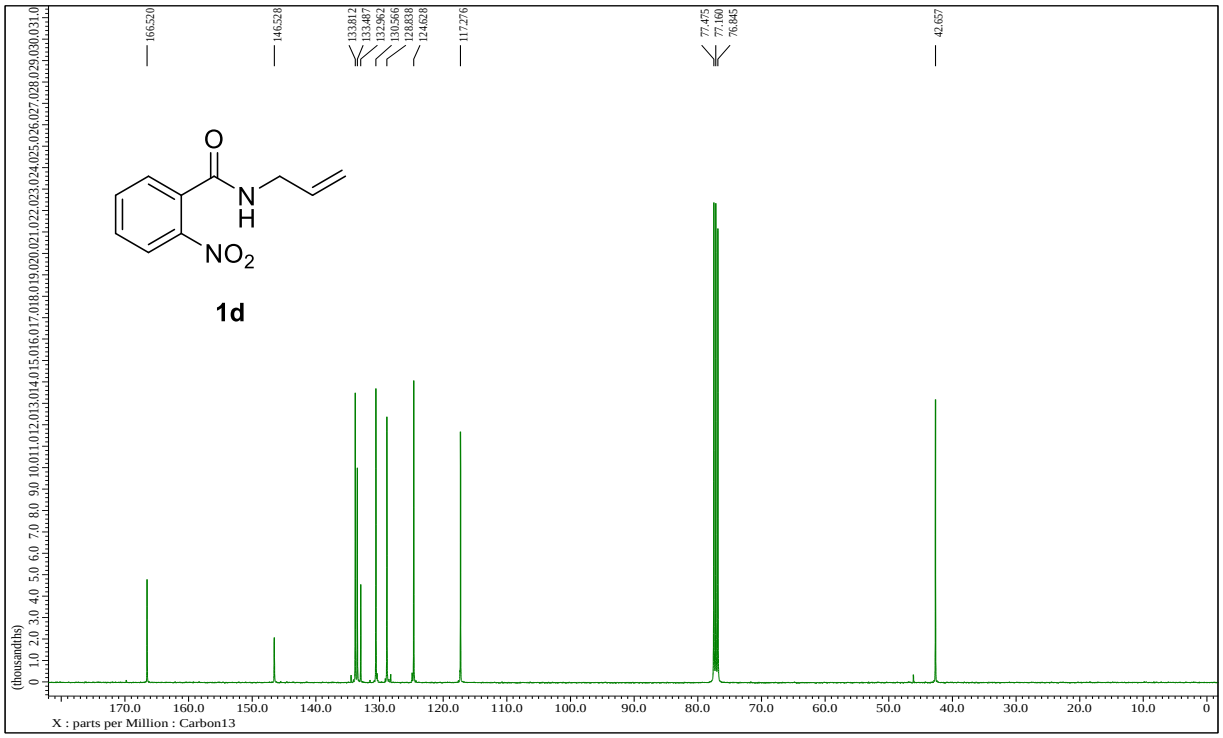

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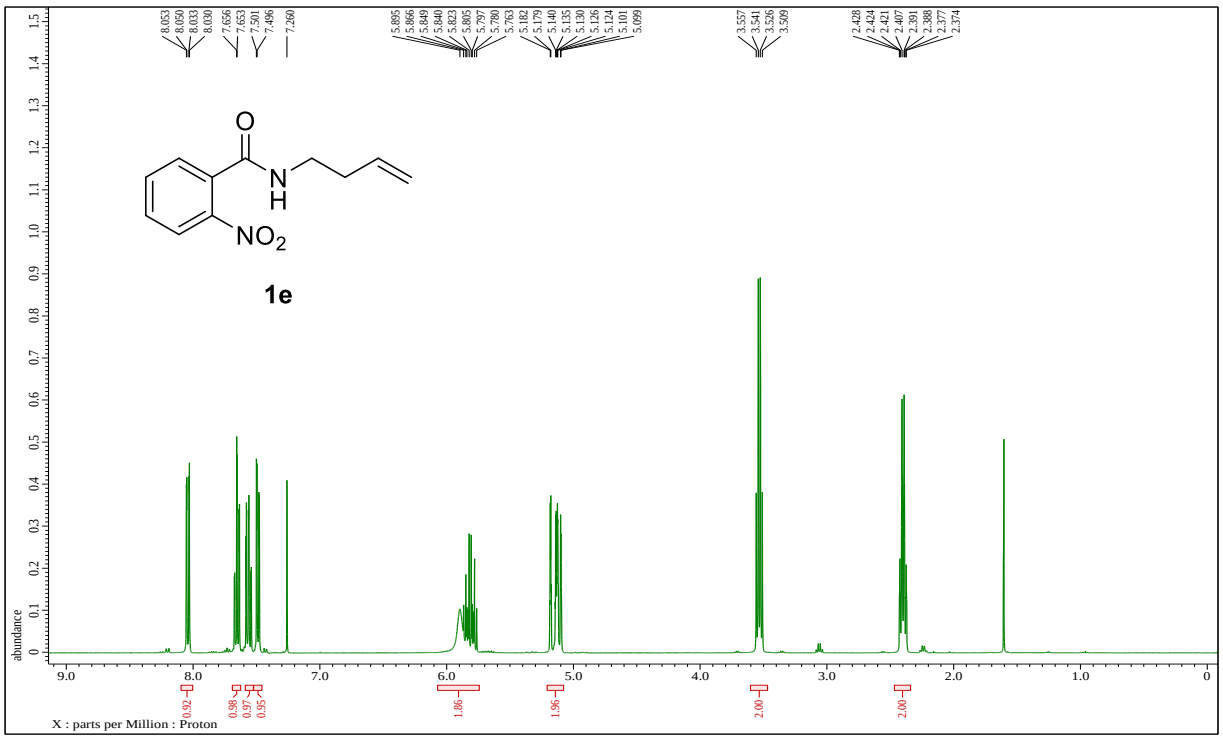

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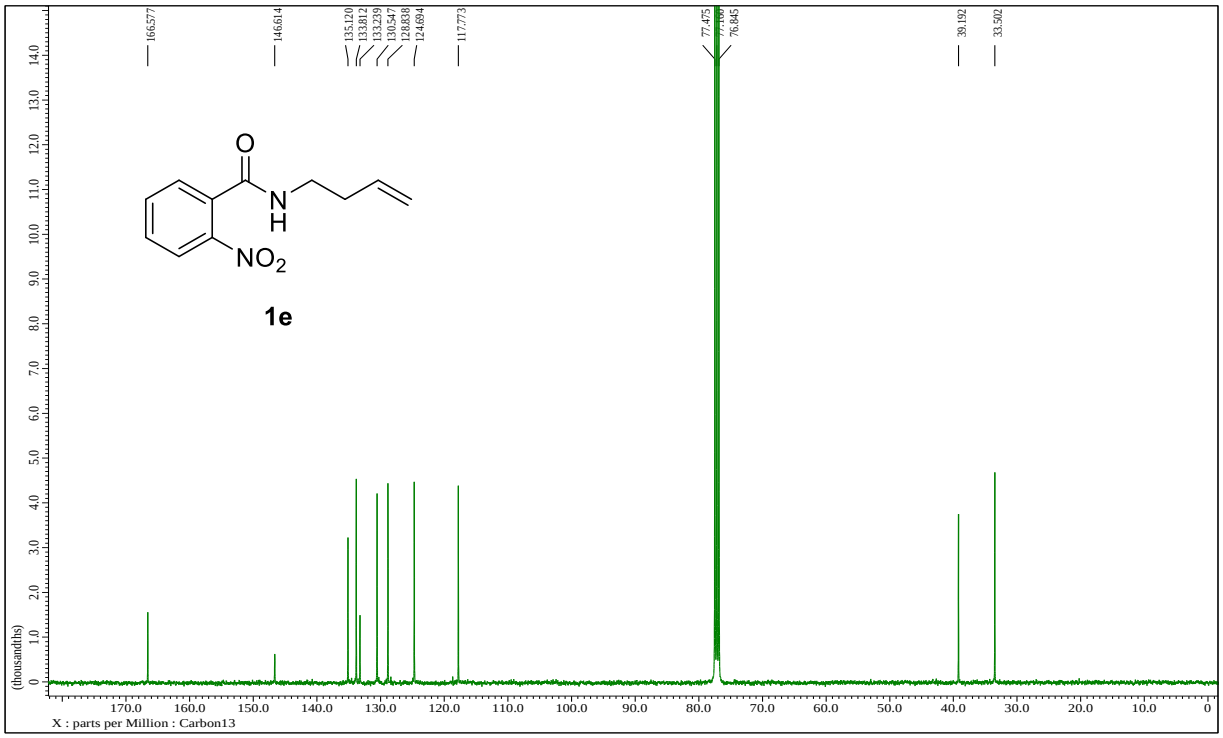

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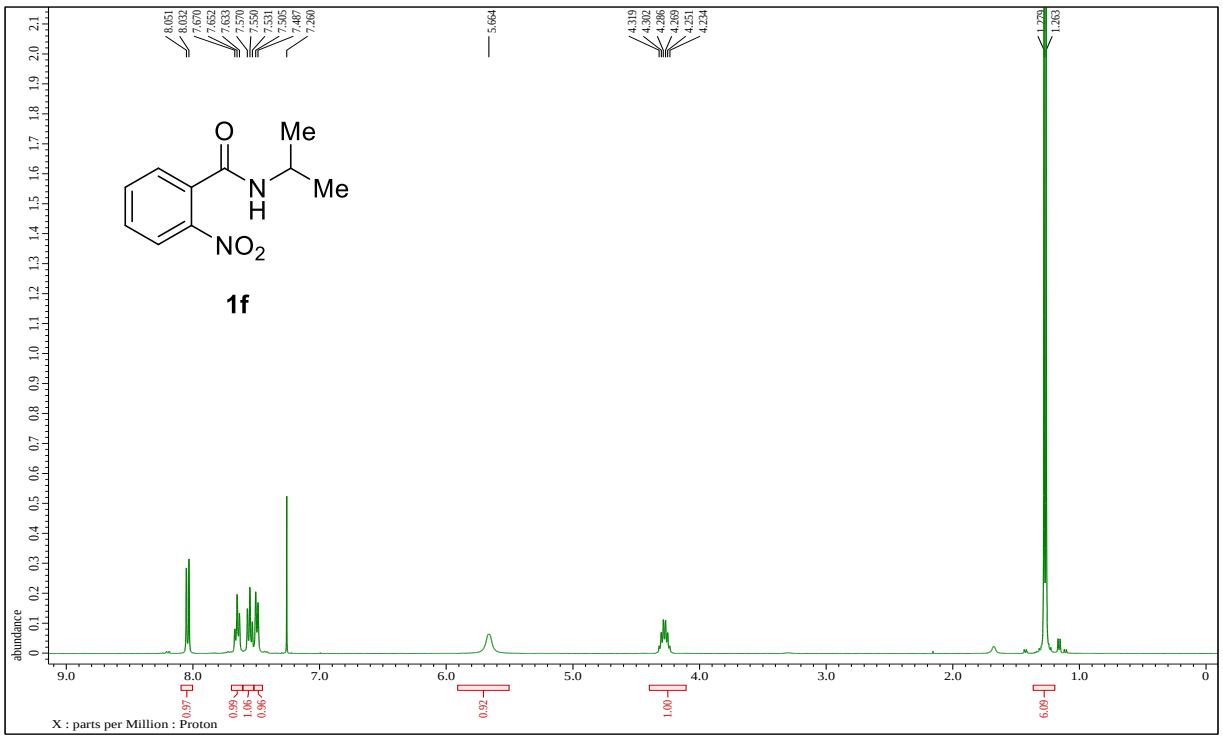

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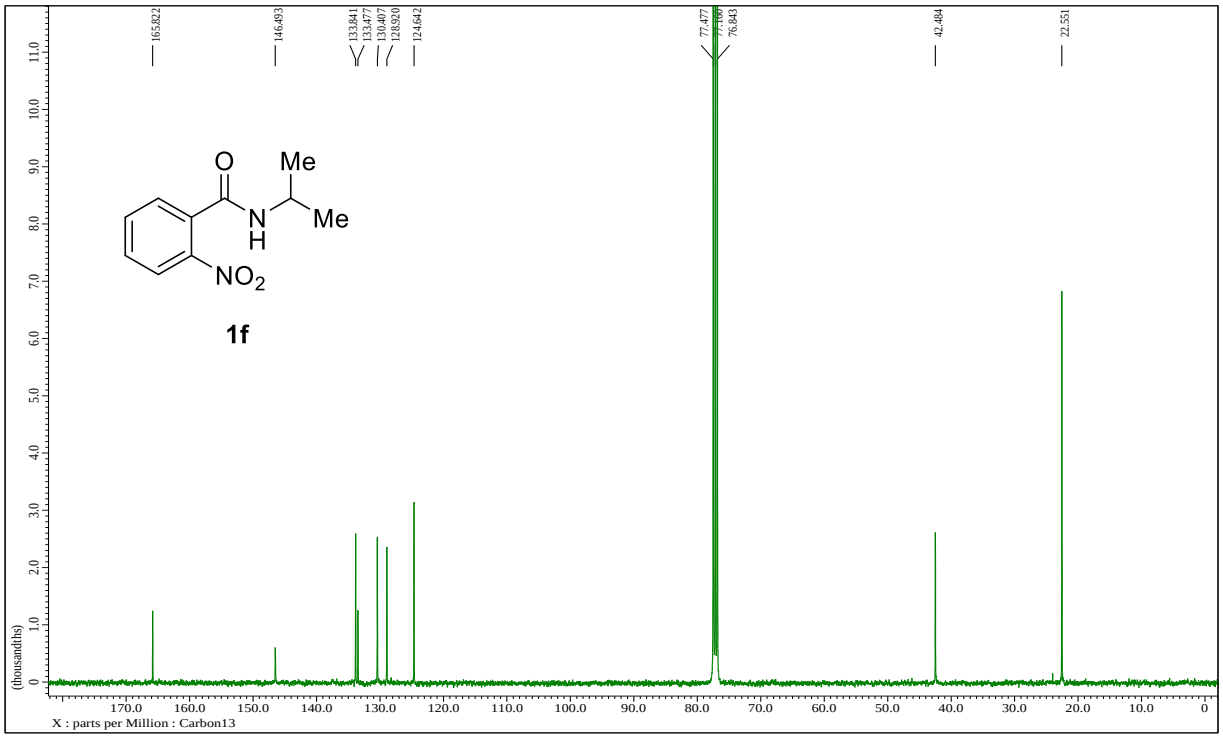

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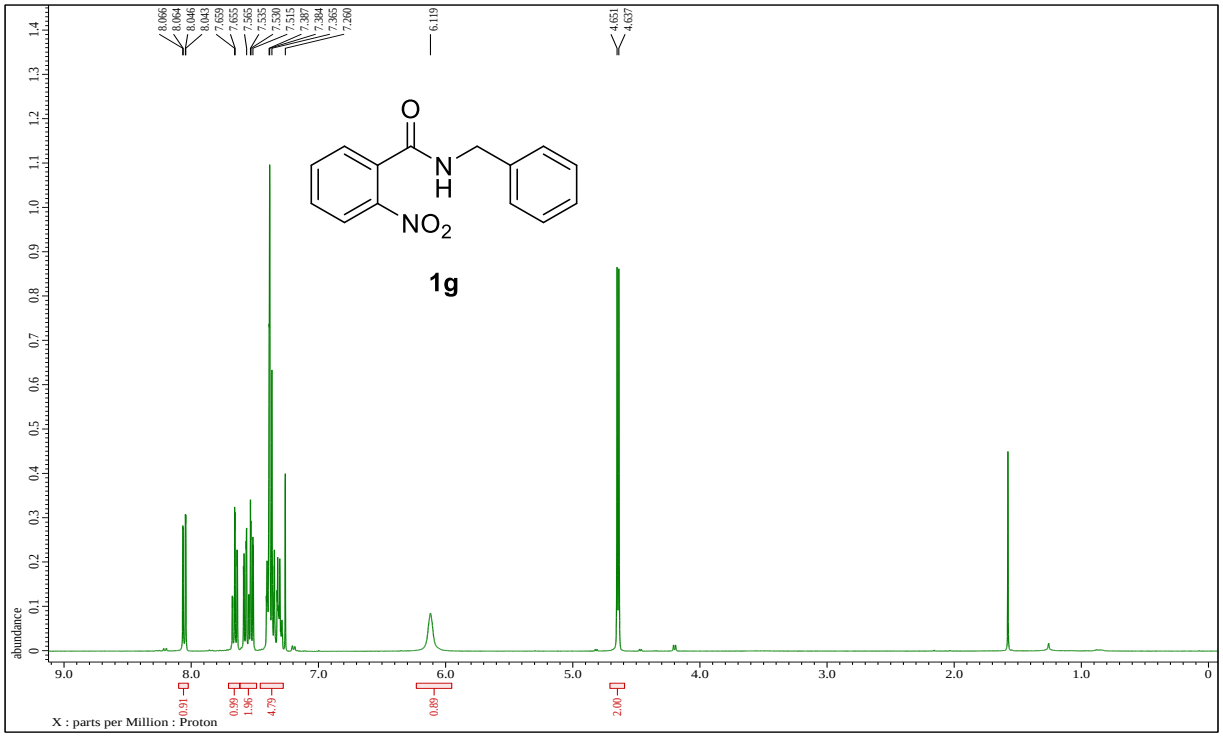

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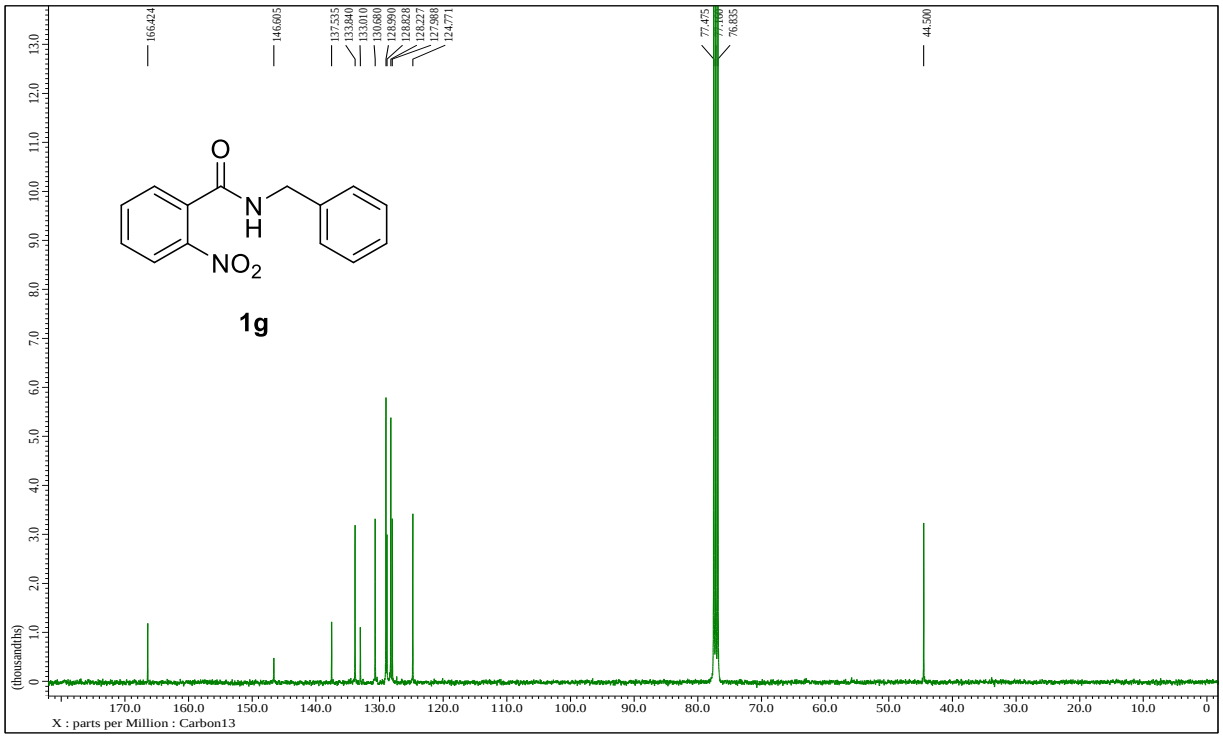

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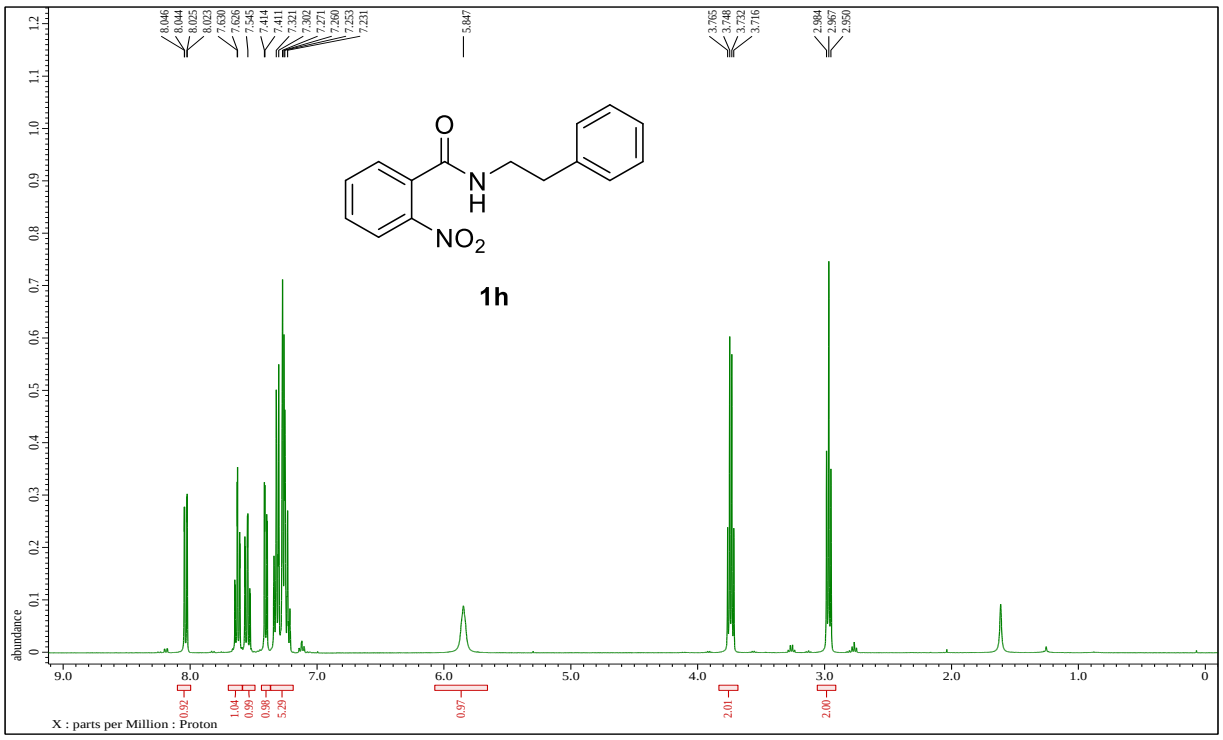

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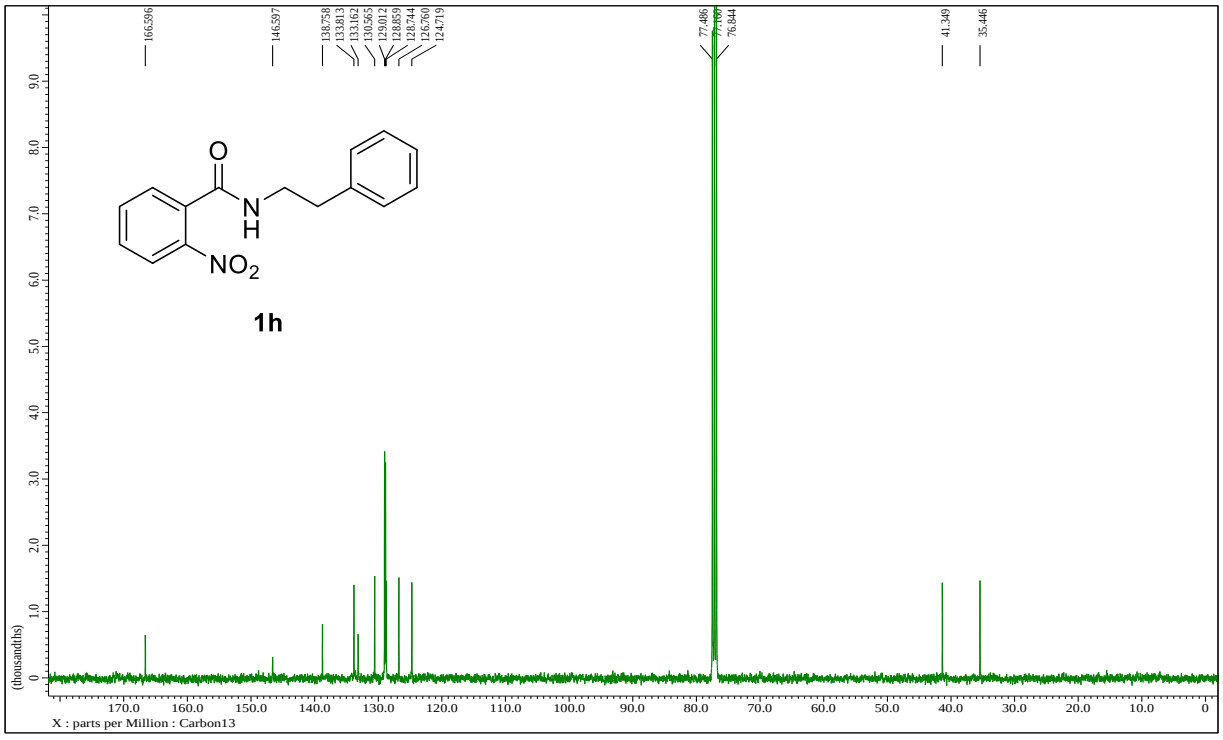

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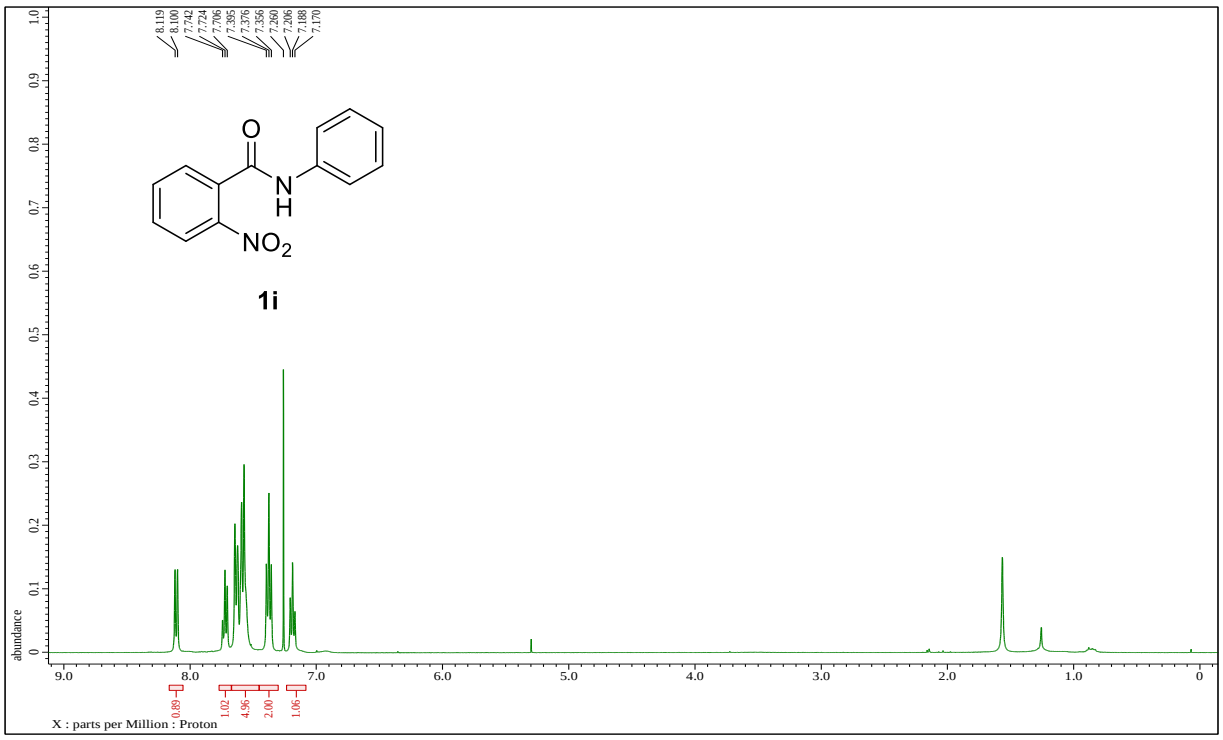

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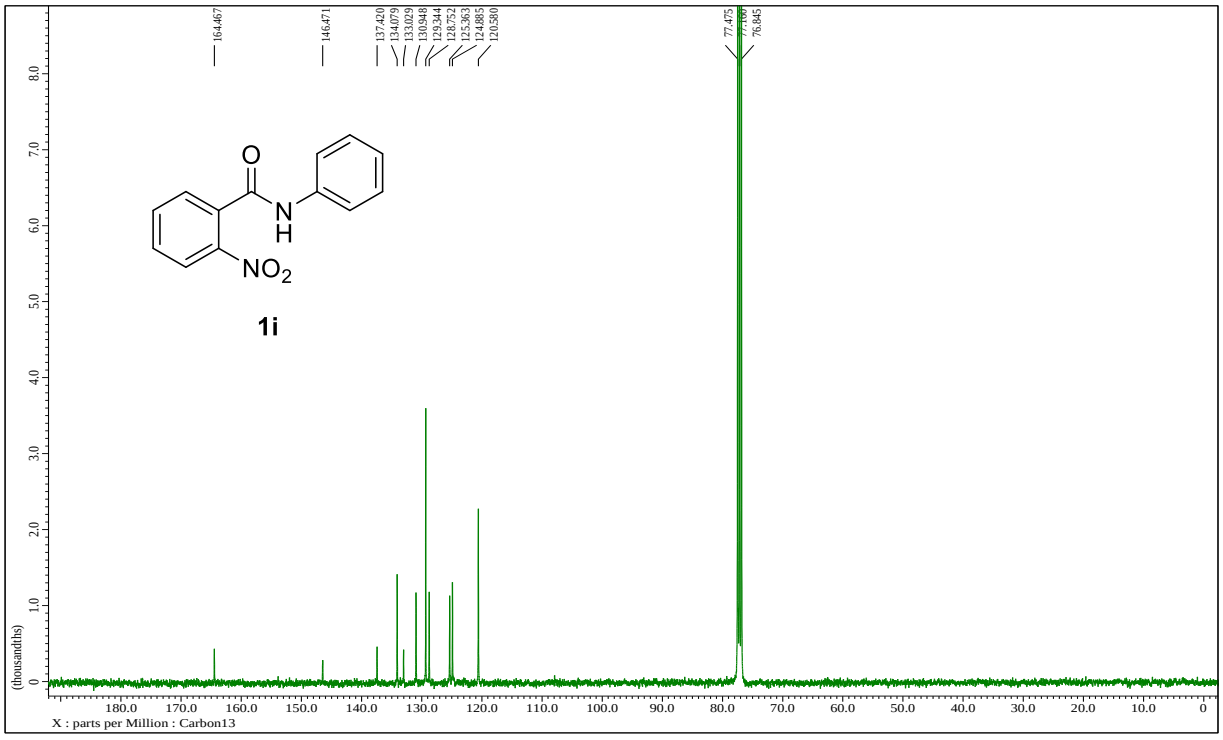

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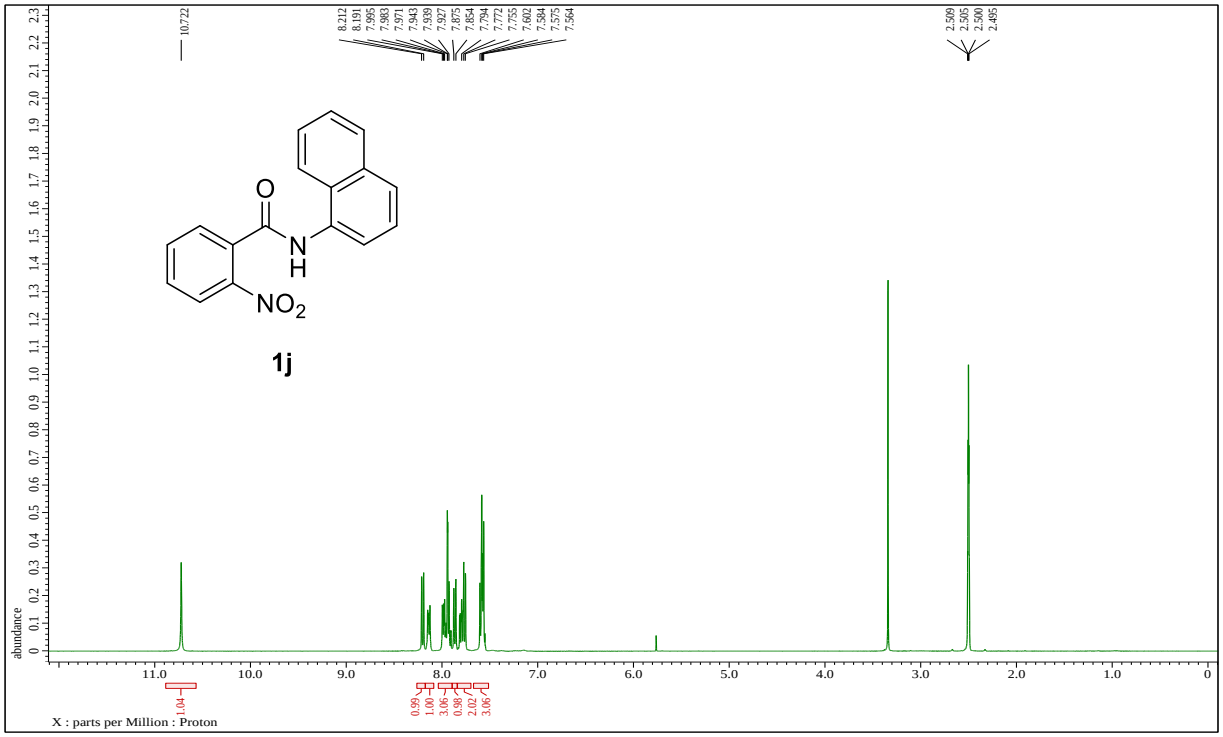

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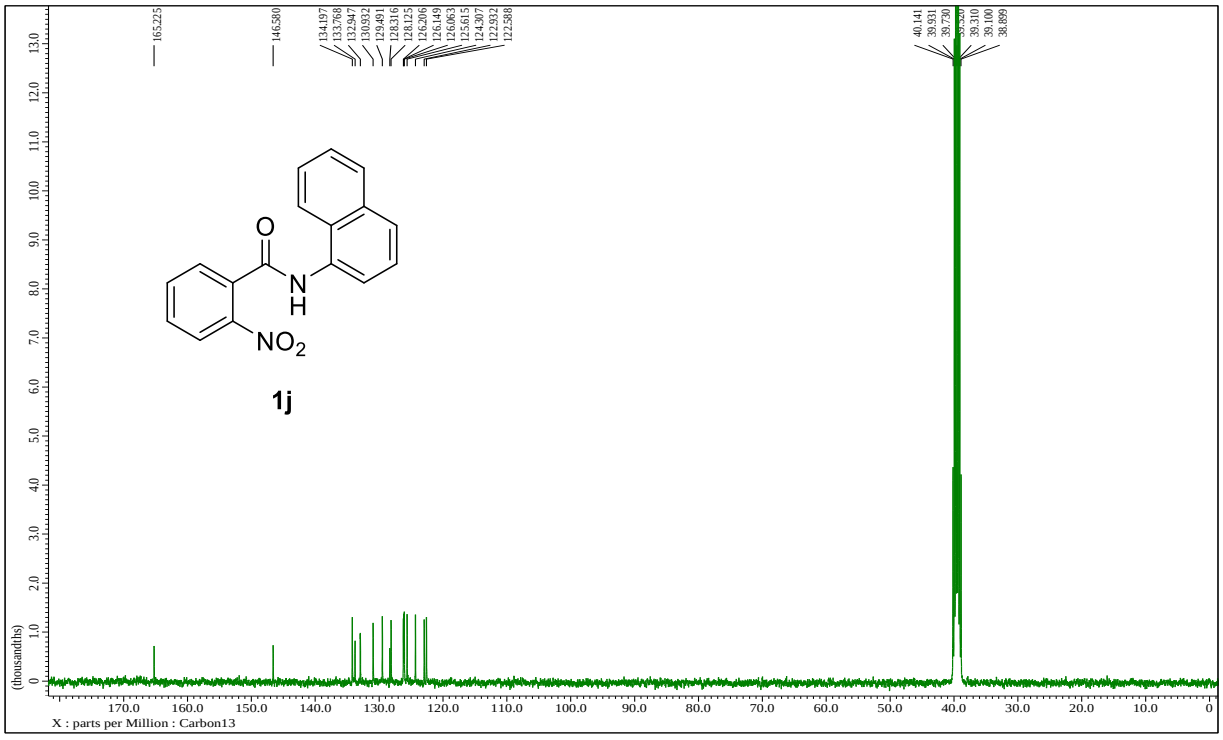

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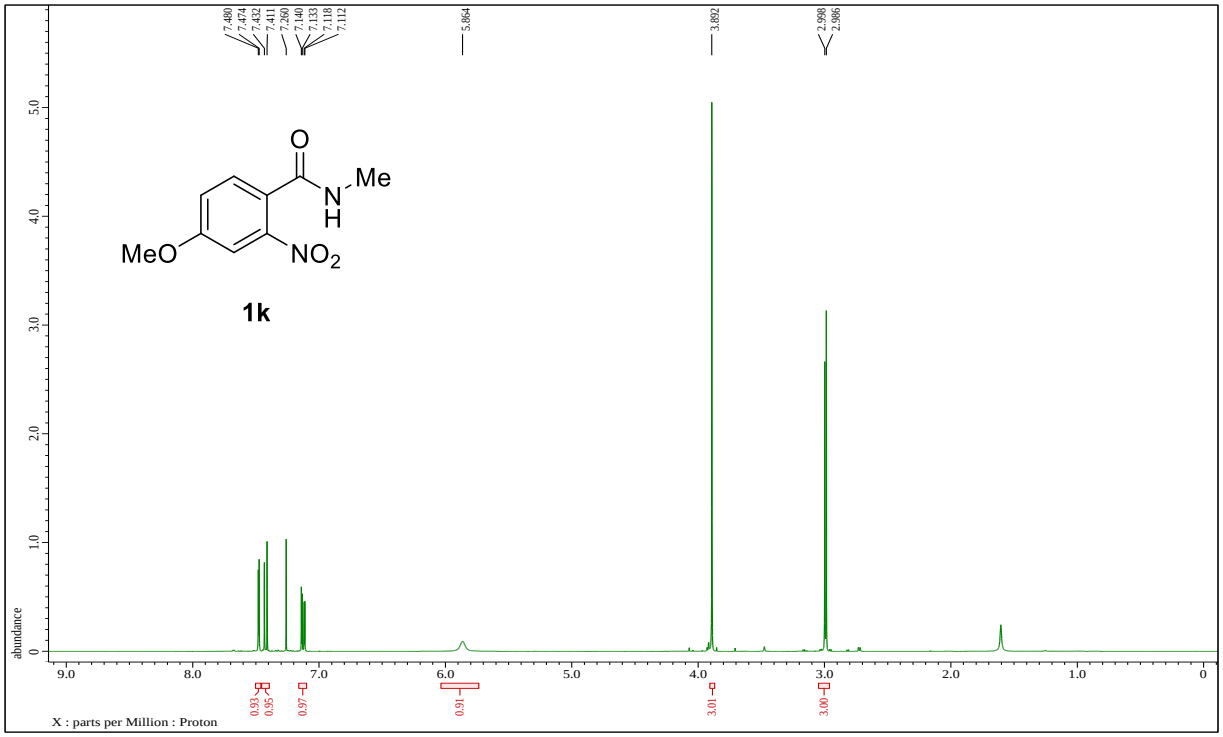

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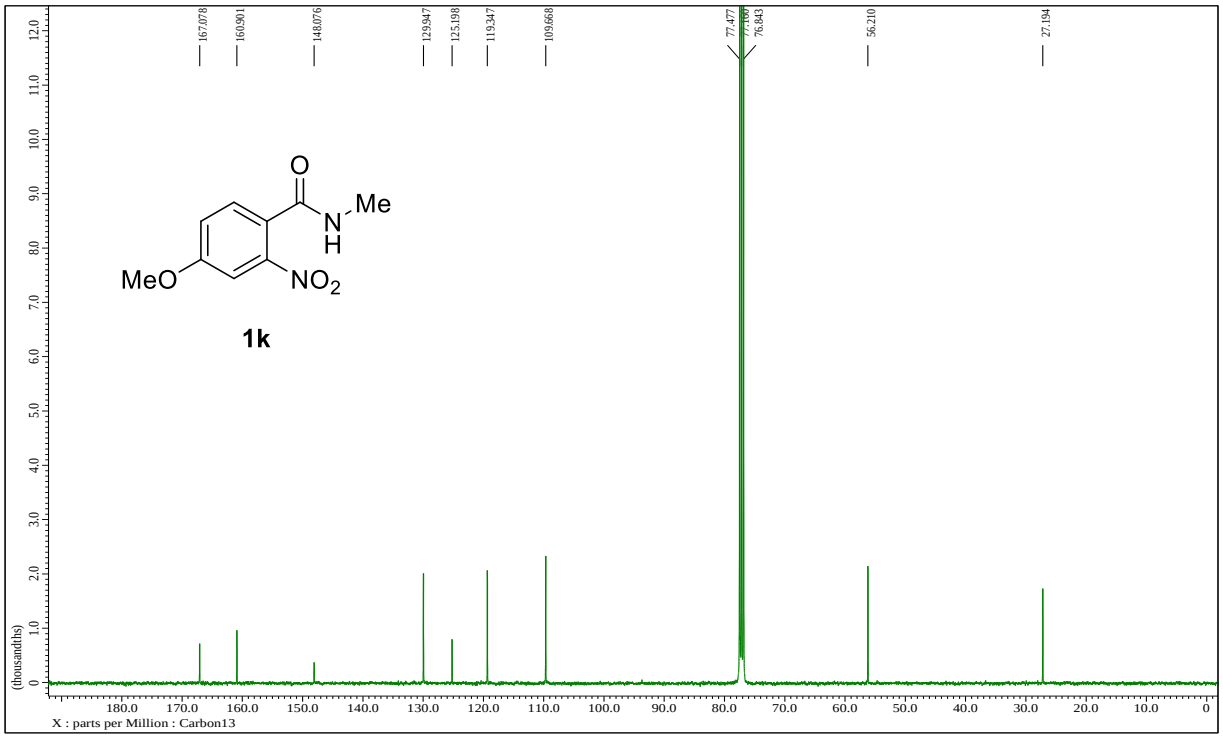

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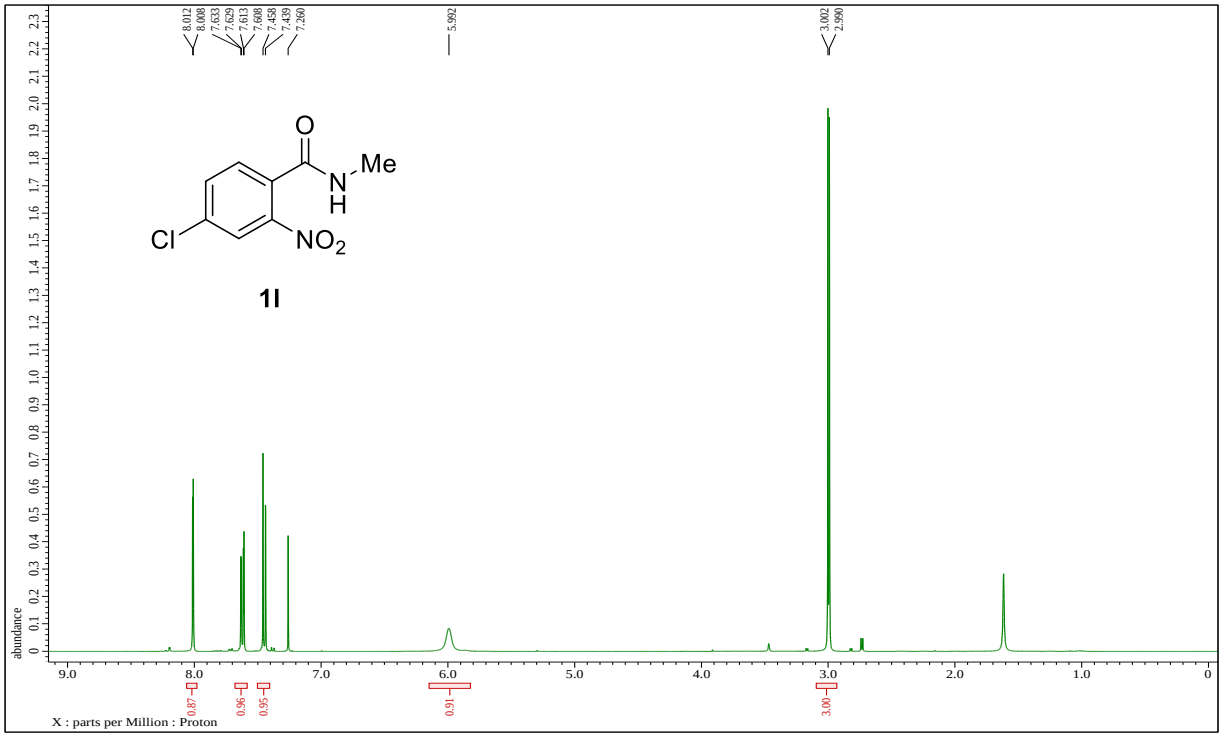

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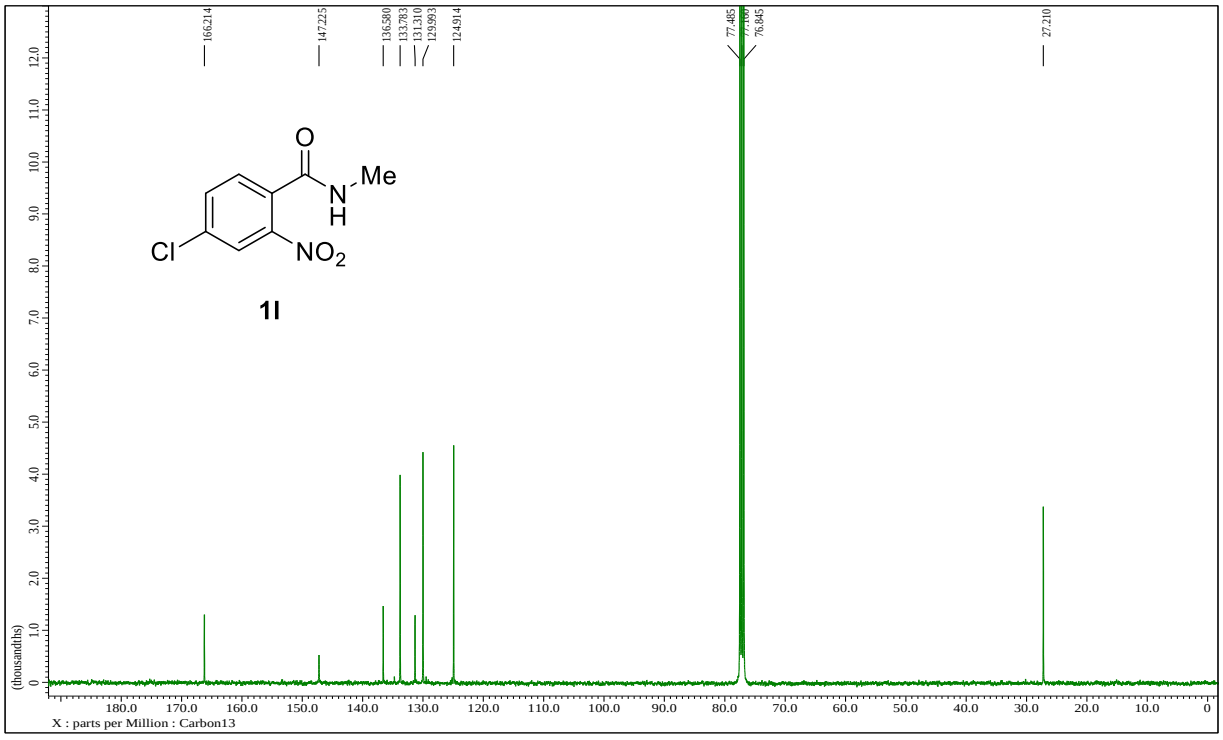

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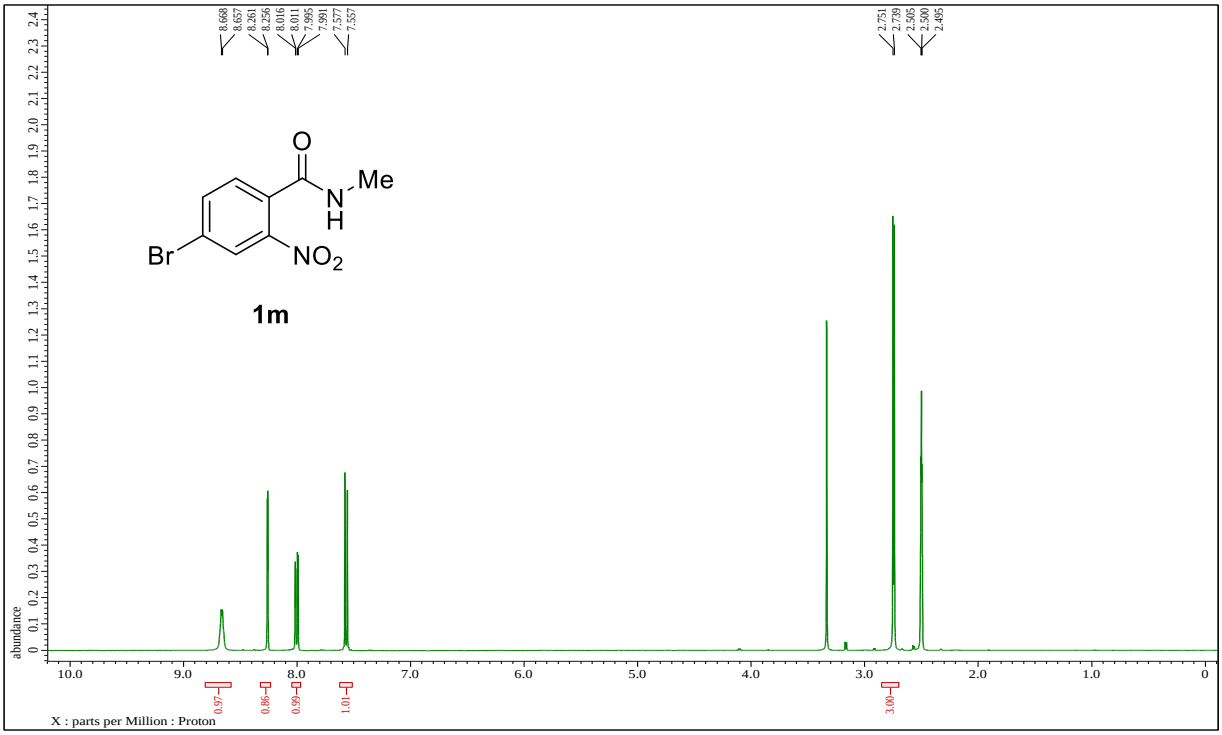

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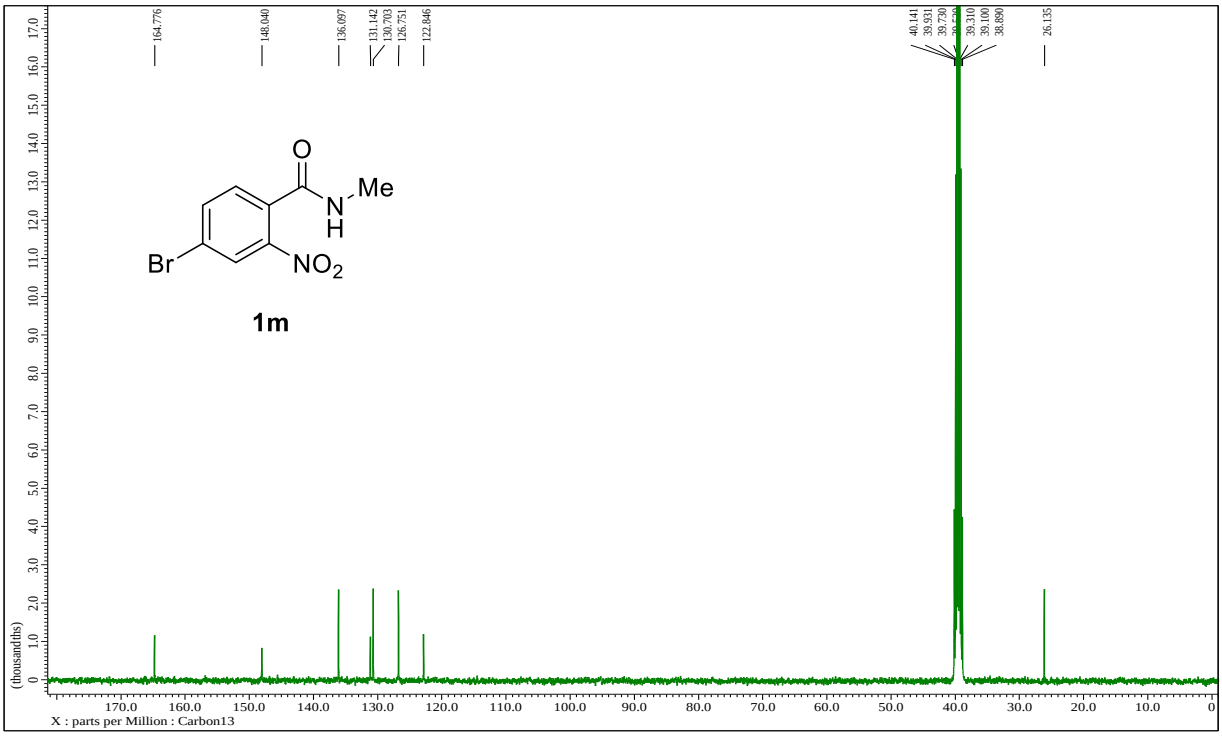

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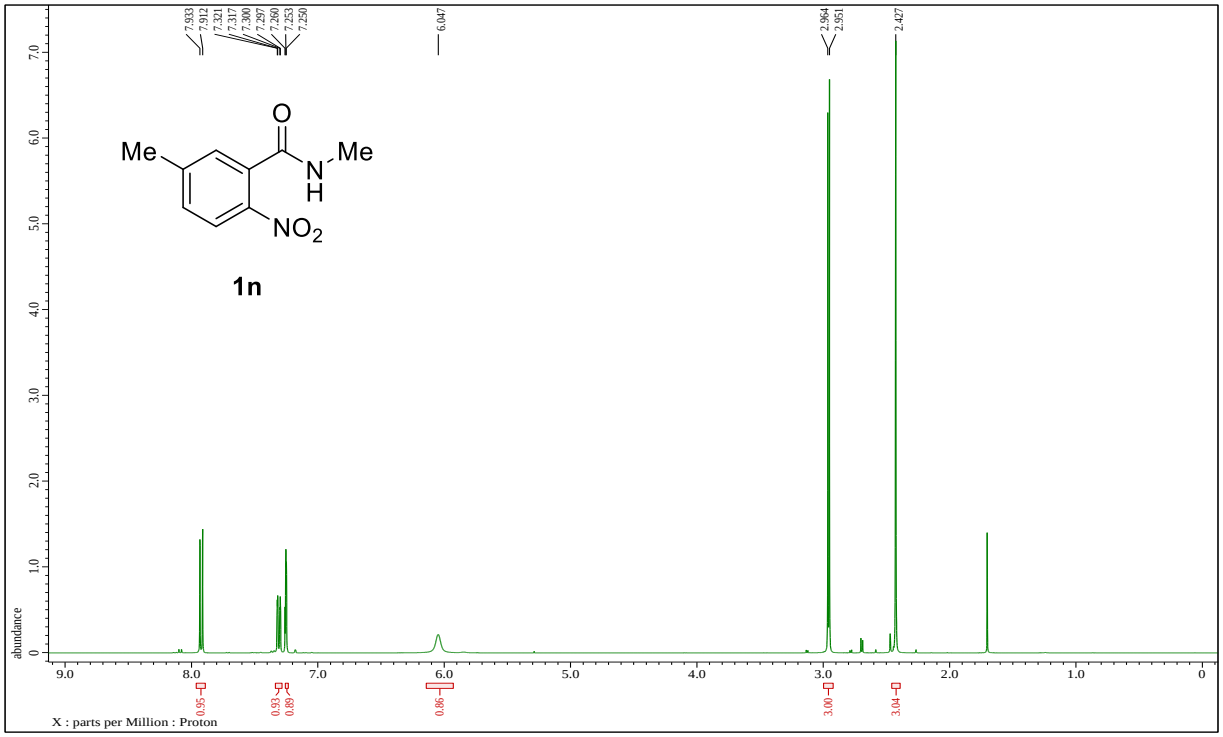

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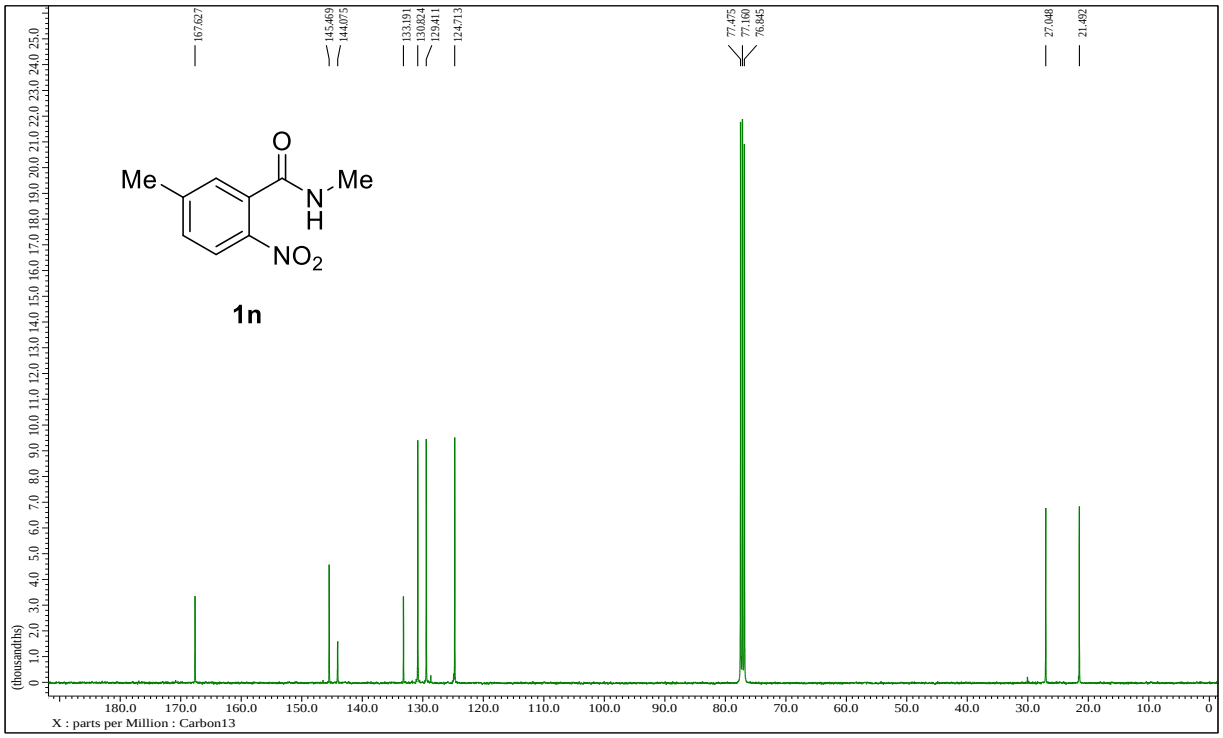
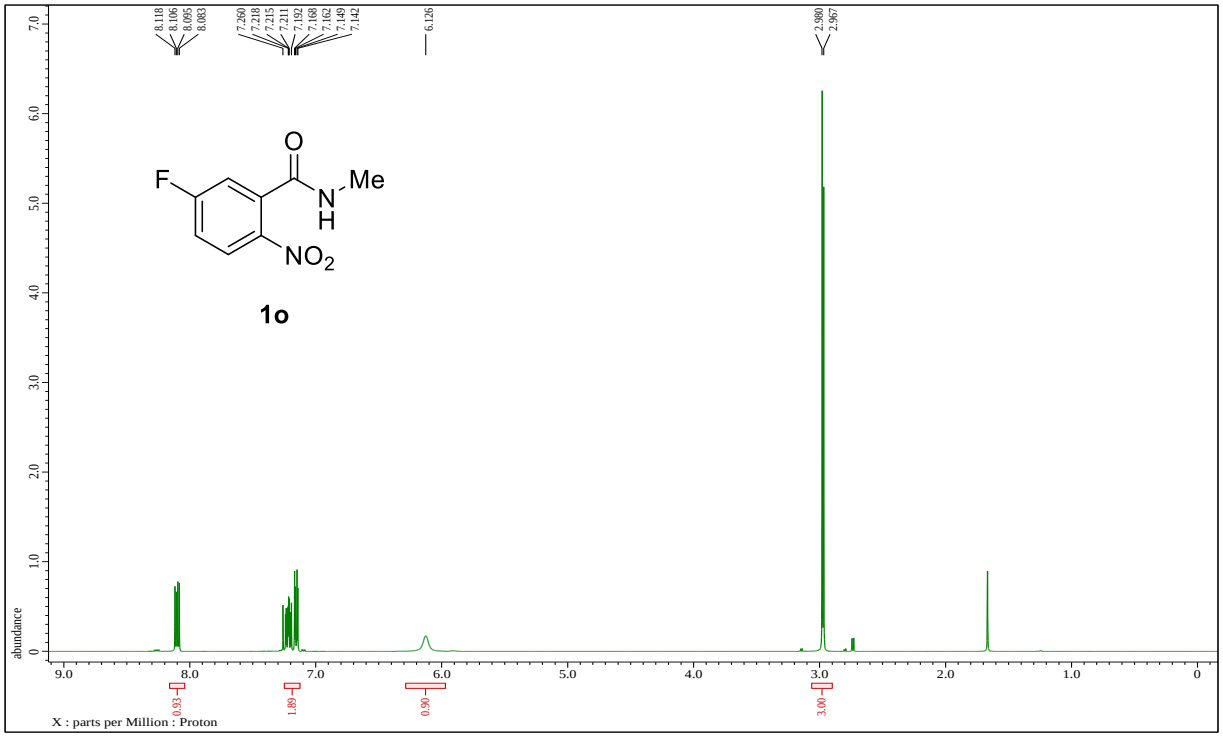
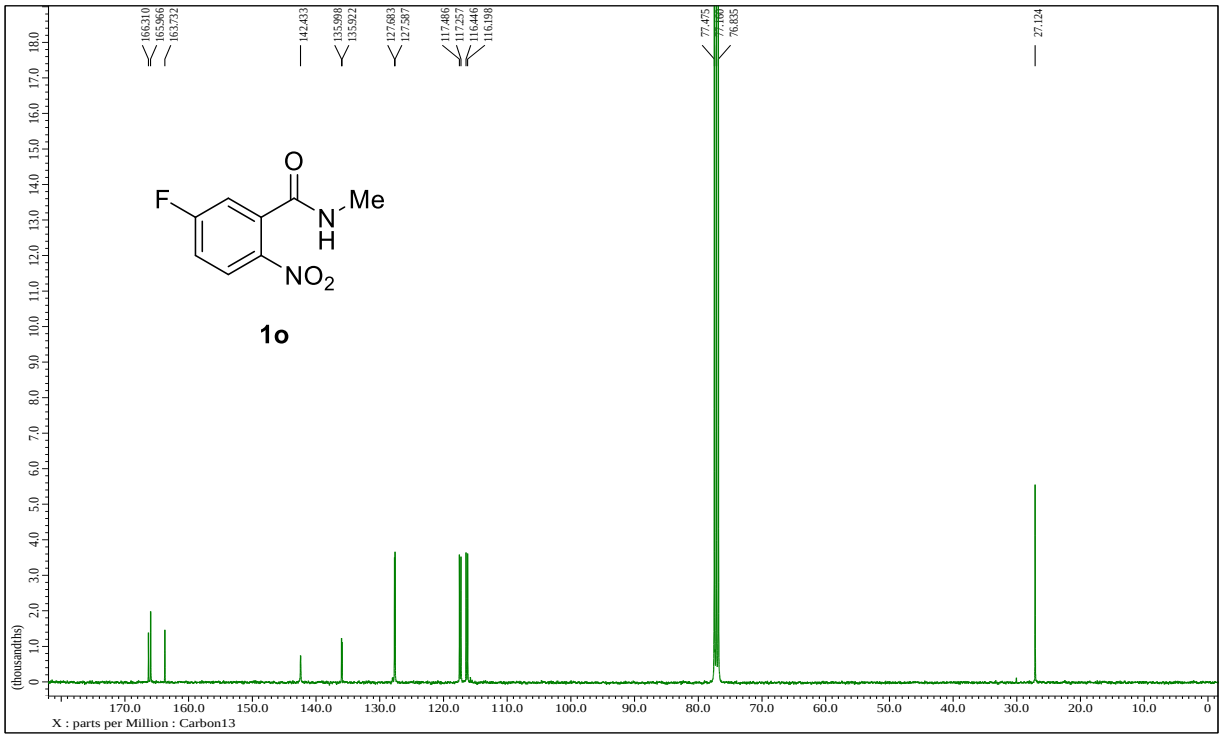


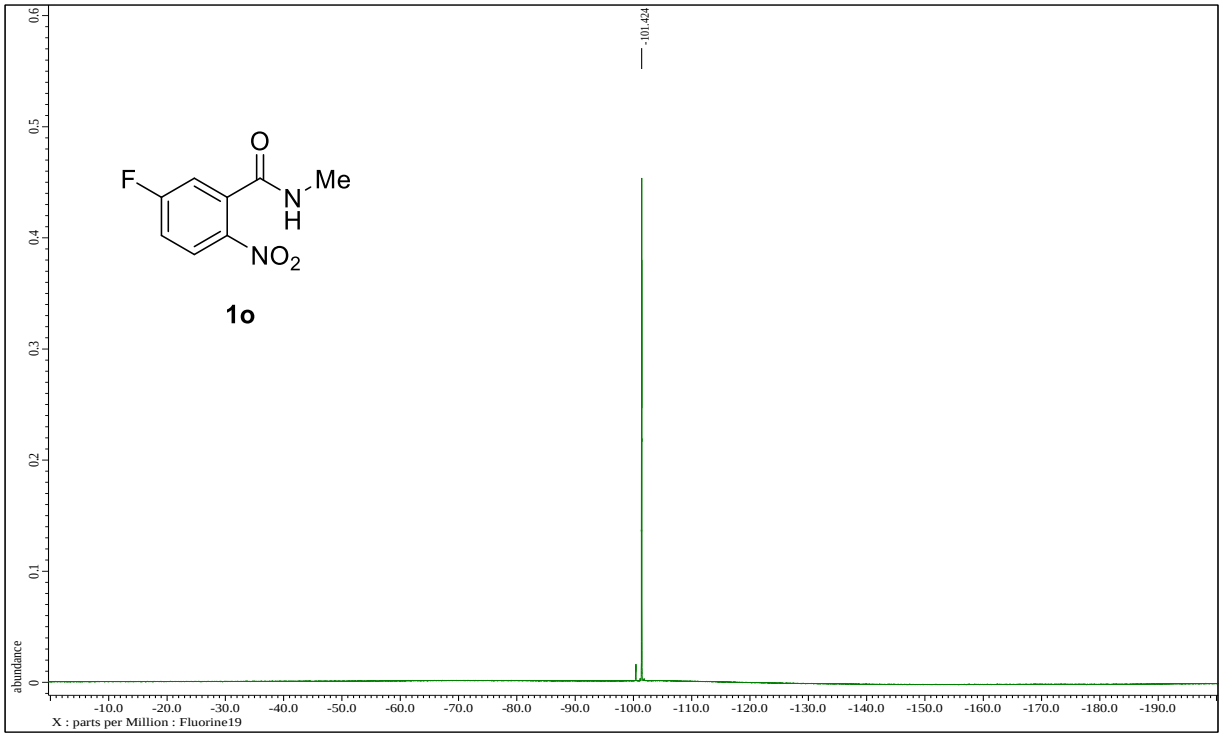
1o ^{1}H-NMR (400 MHz, $CDCl_3$)



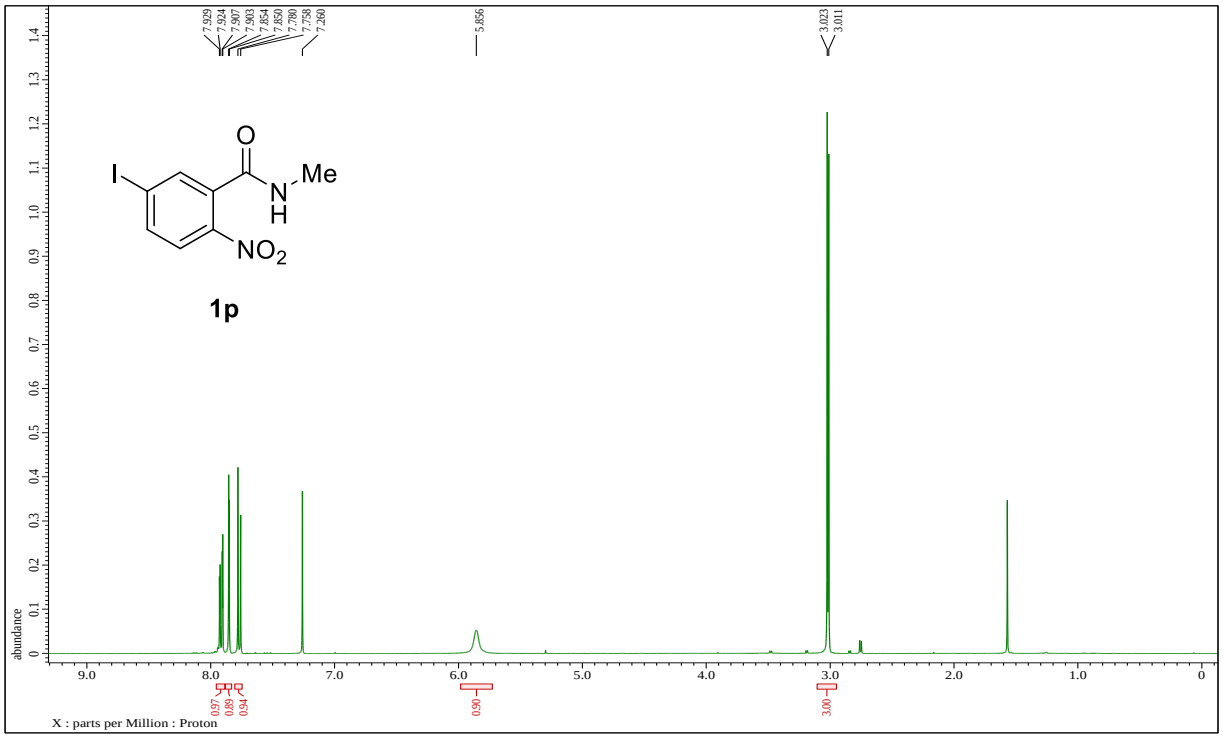
1o ^{13}C-NMR (100 MHz, $CDCl_3$)



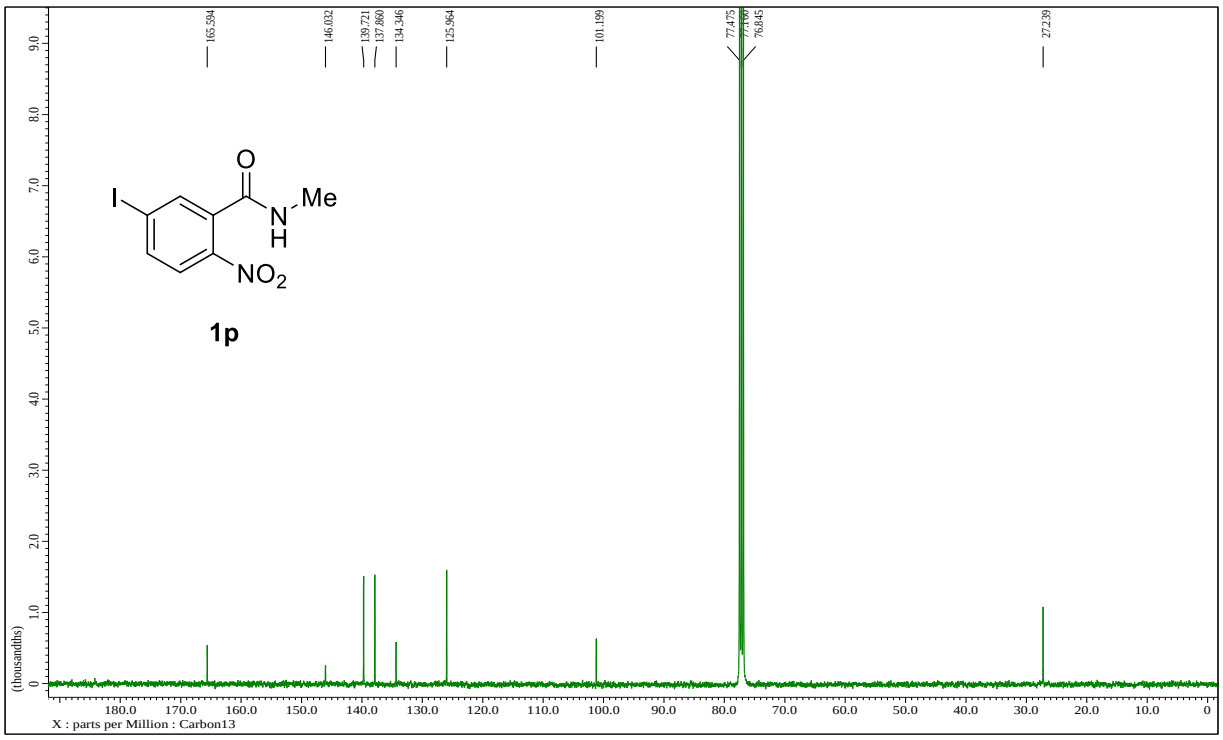
1o ^{19}F-NMR (376 MHz, $CDCl_3$)



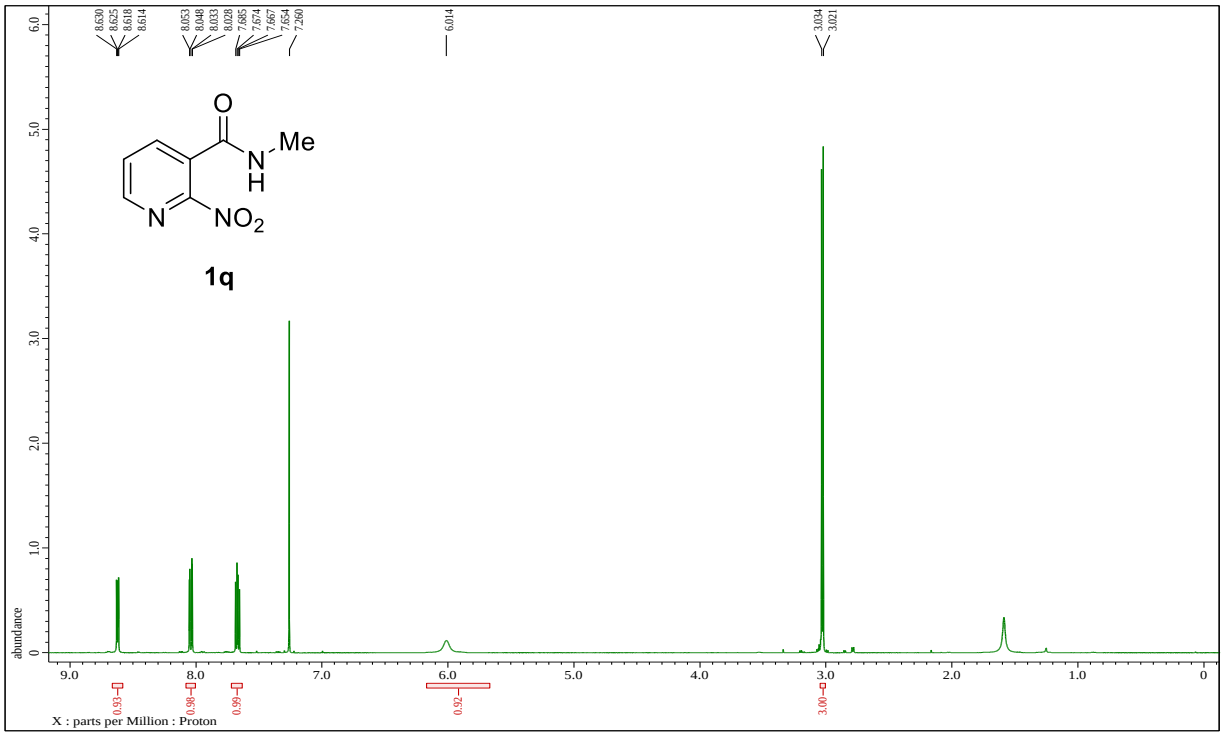
1p ^{1}H-NMR (400 MHz, $CDCl_3$)



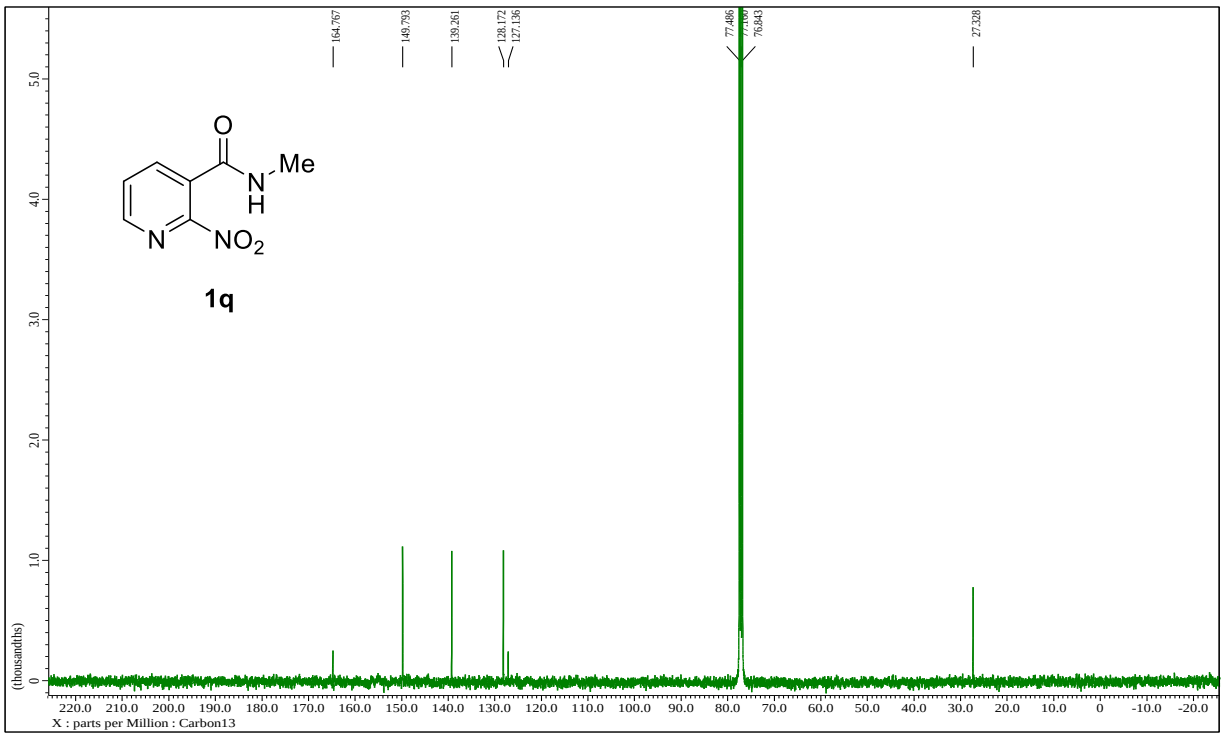
1p ^{13}C-NMR (100 MHz, $CDCl_3$)



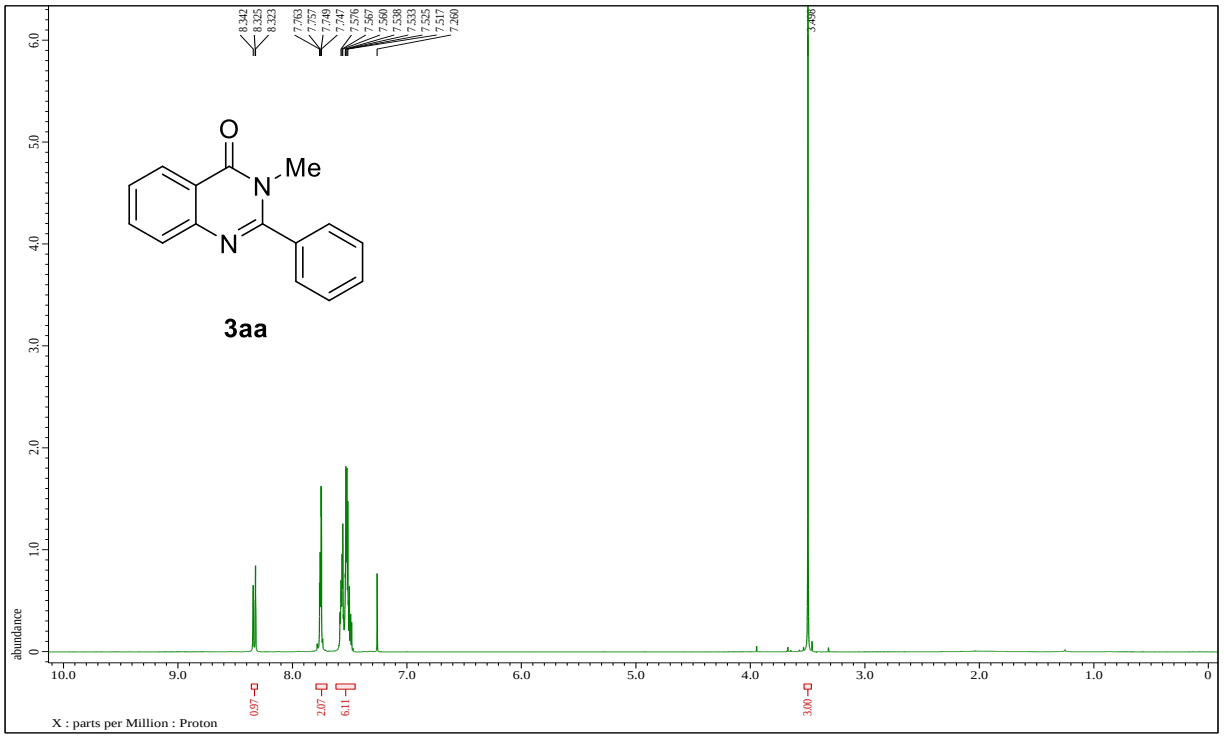
1q ^{1}H-NMR (400 MHz, $CDCl_3$)



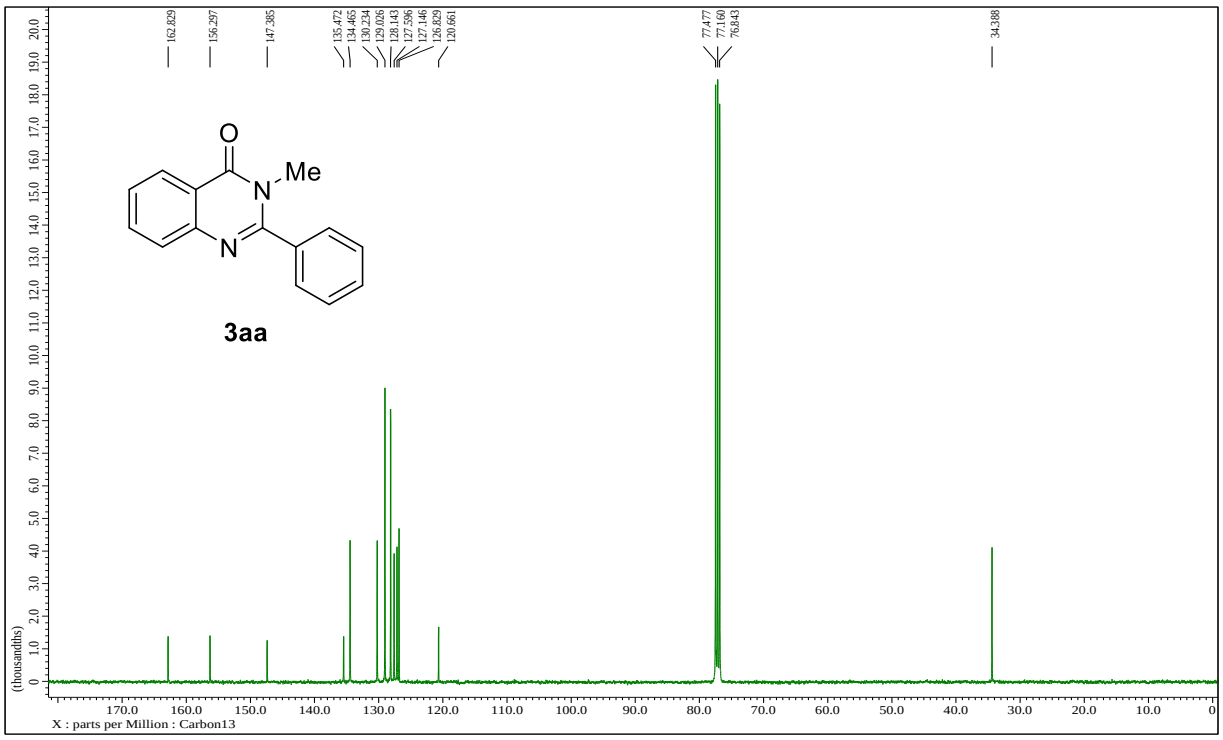
1q ^{13}C-NMR (100 MHz, $CDCl_3$)



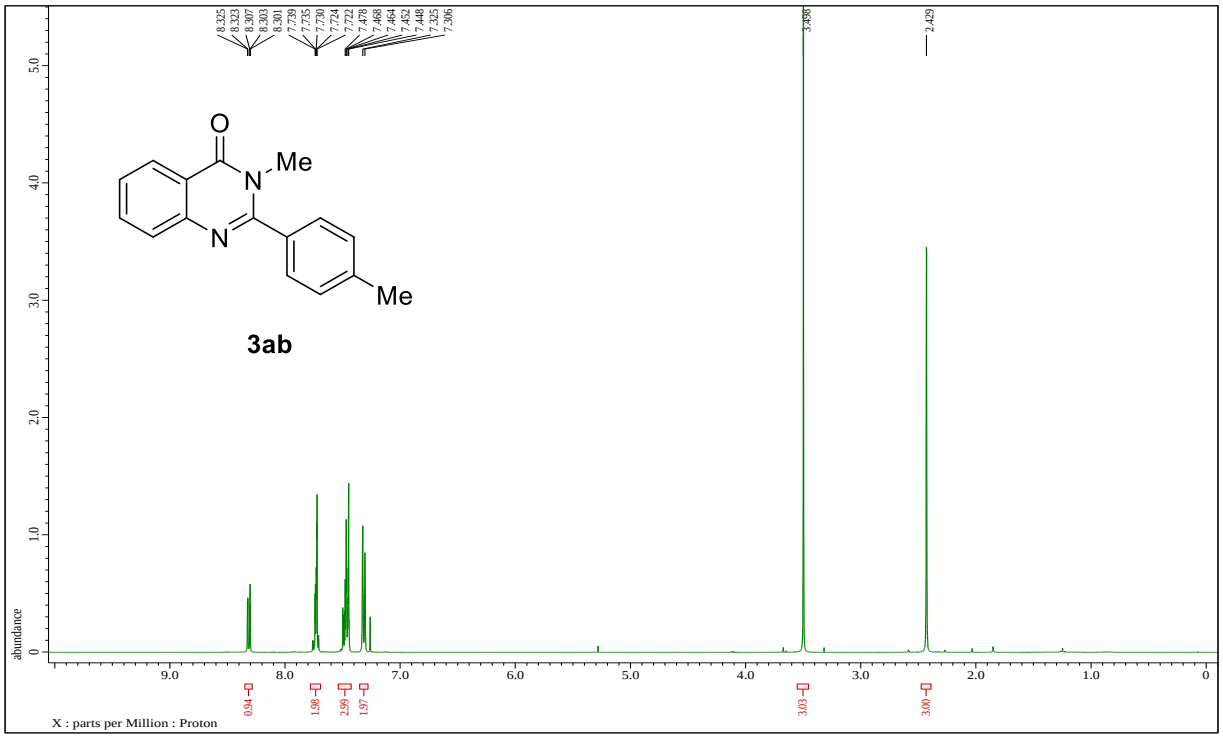
3aa ^{1}H-NMR (400 MHz, $CDCl_3$)



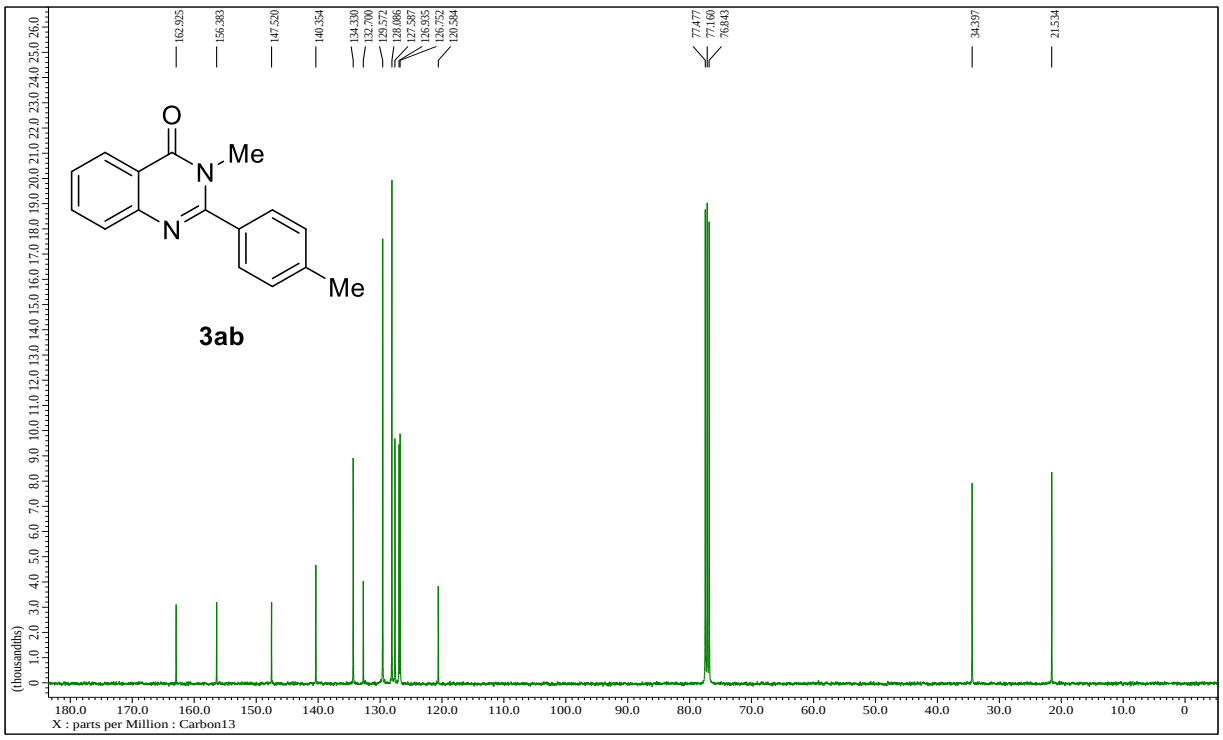
3aa ^{13}C-NMR (100 MHz, $CDCl_3$)



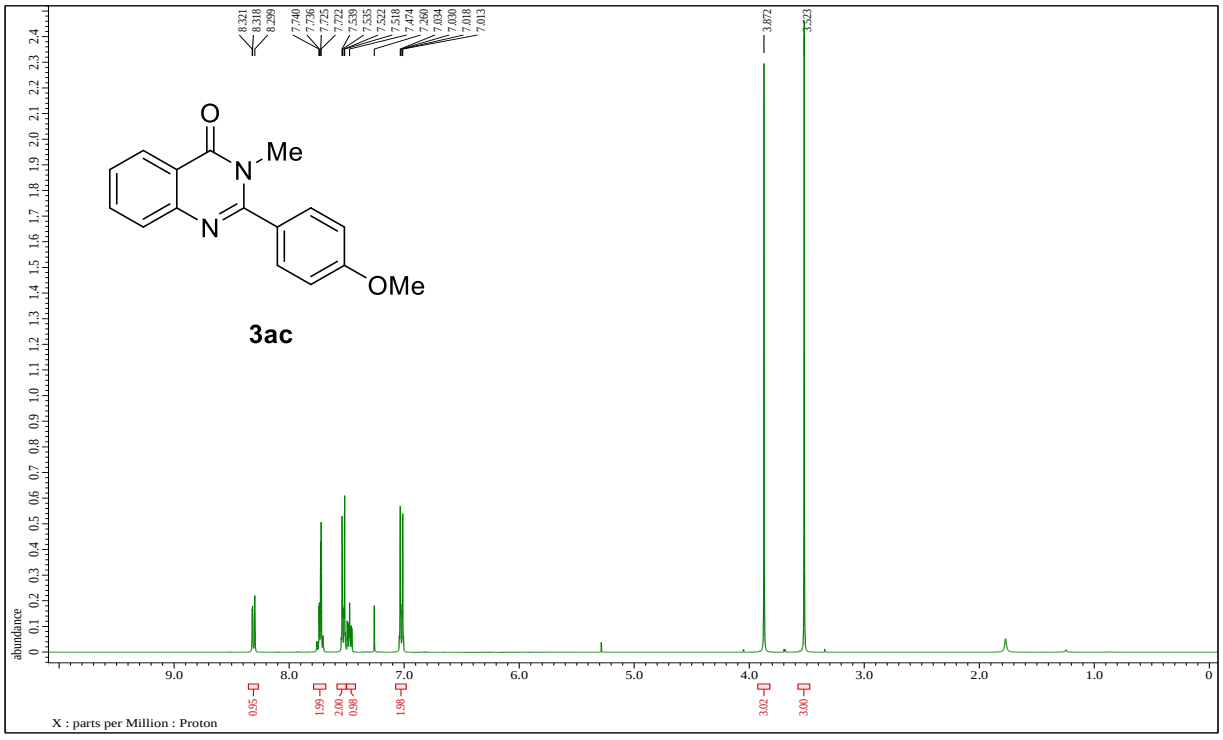
3ab ^{1}H-NMR (400 MHz, $CDCl_3$)



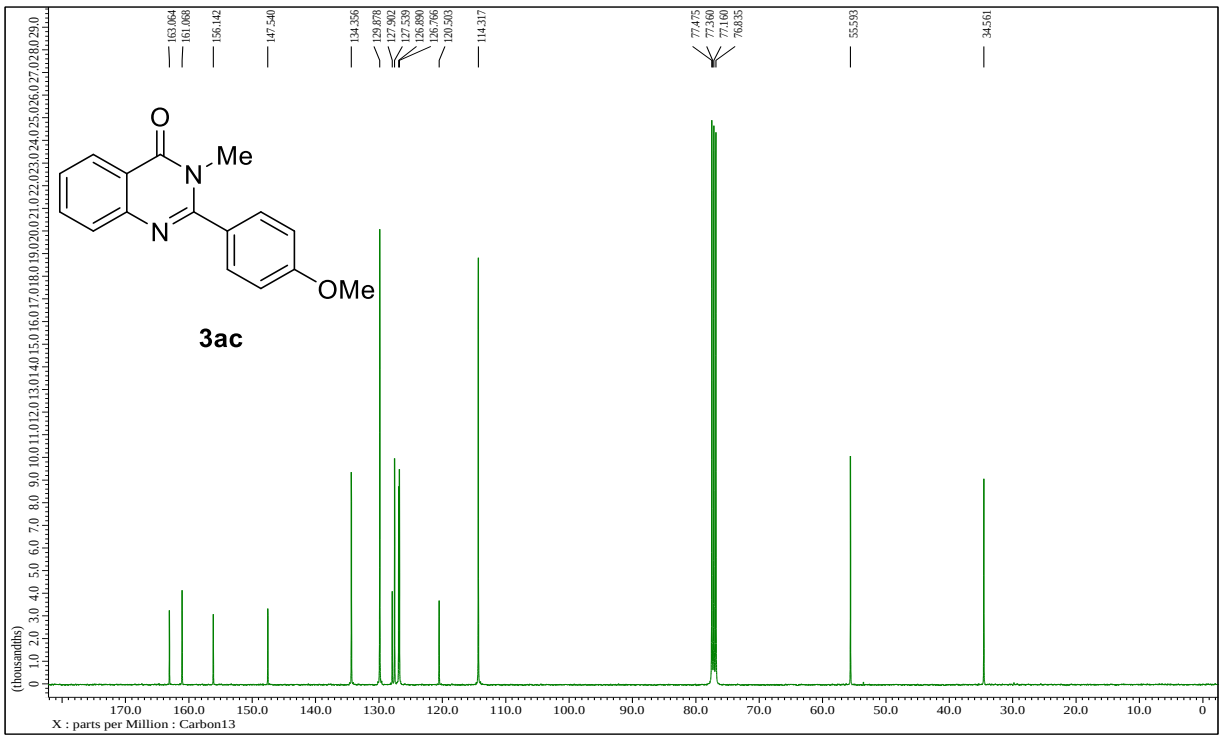
3ab ^{13}C-NMR (100 MHz, $CDCl_3$)



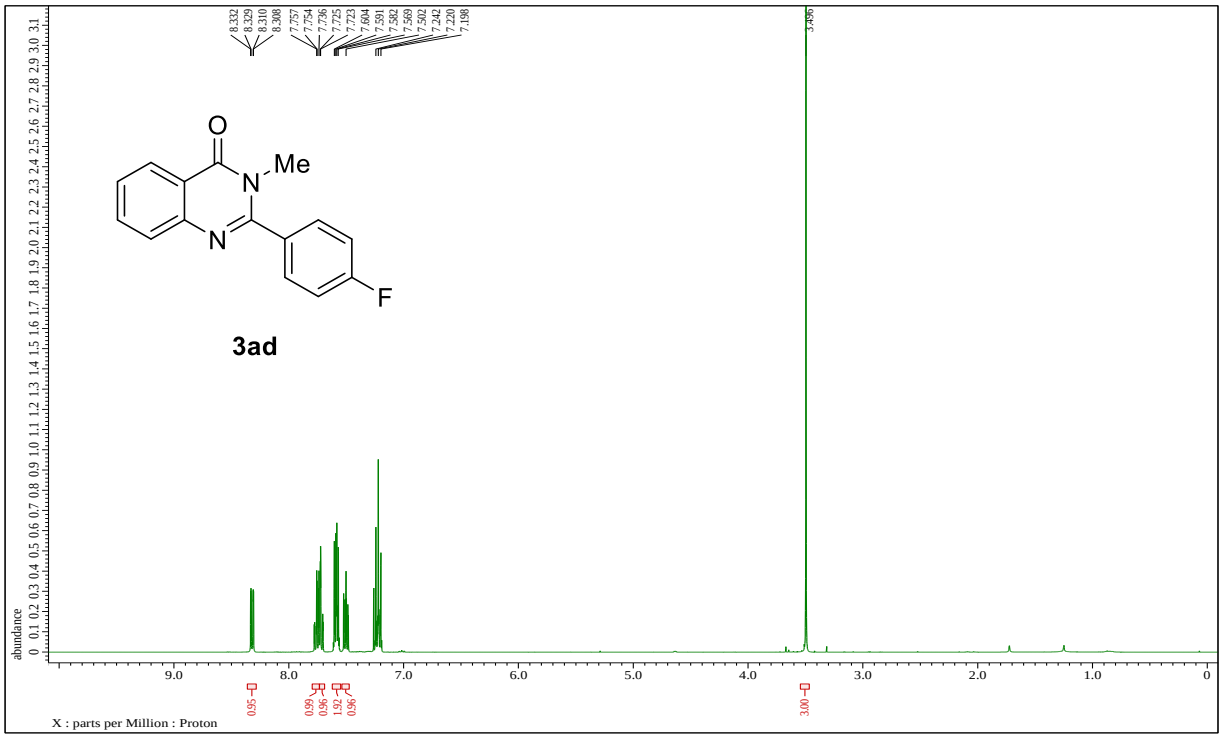
3ac ^{1}H-NMR (400 MHz, $CDCl_3$)



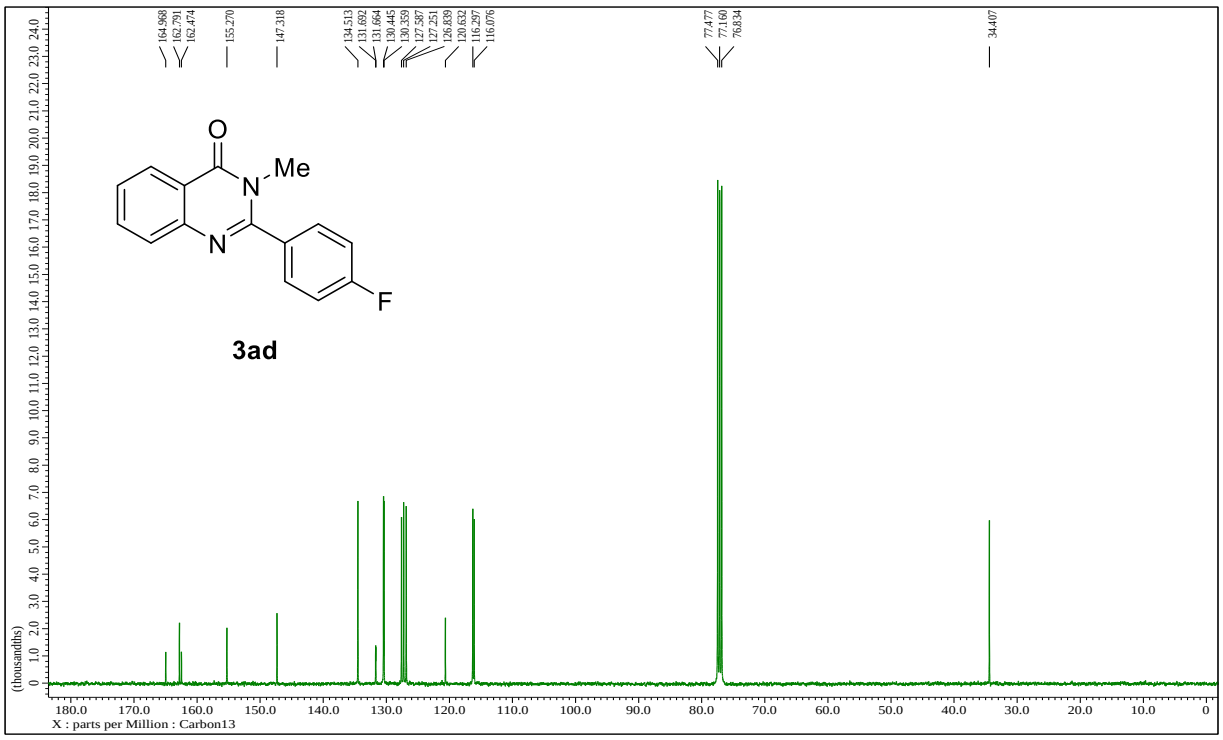
3ac ^{13}C-NMR (100 MHz, $CDCl_3$)



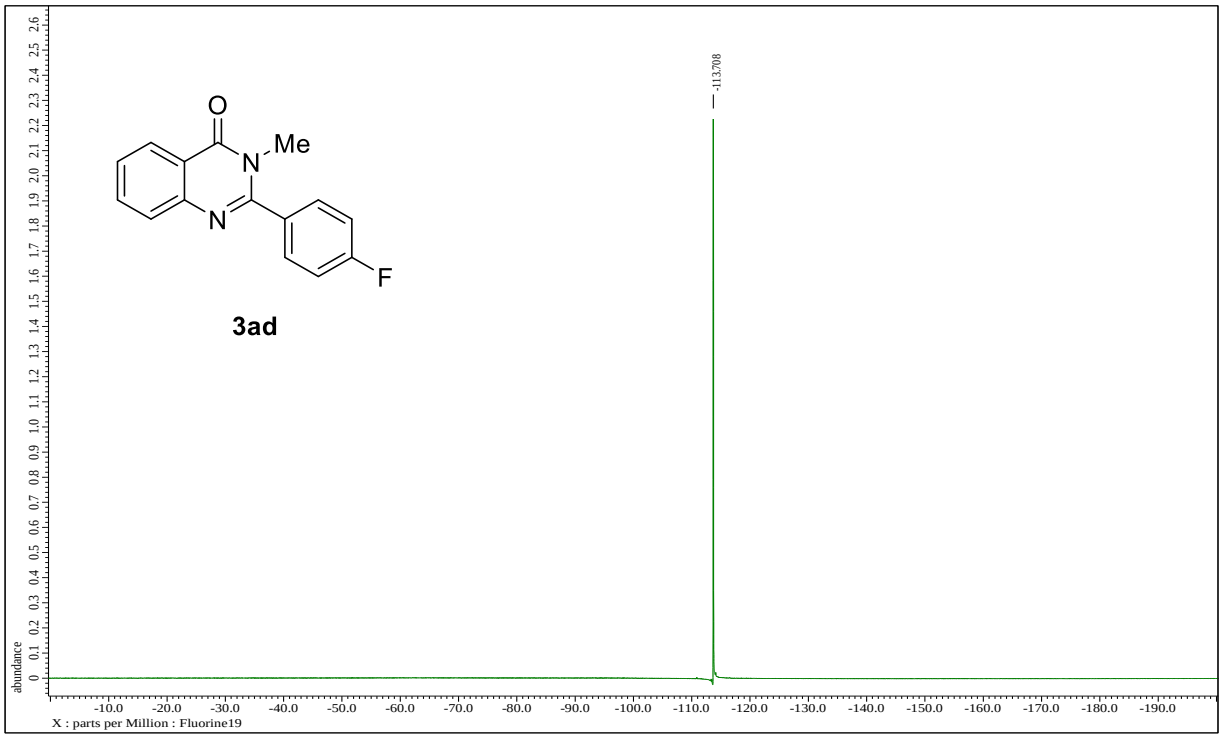
3ad ^{1}H-NMR (400 MHz, $CDCl_3$)



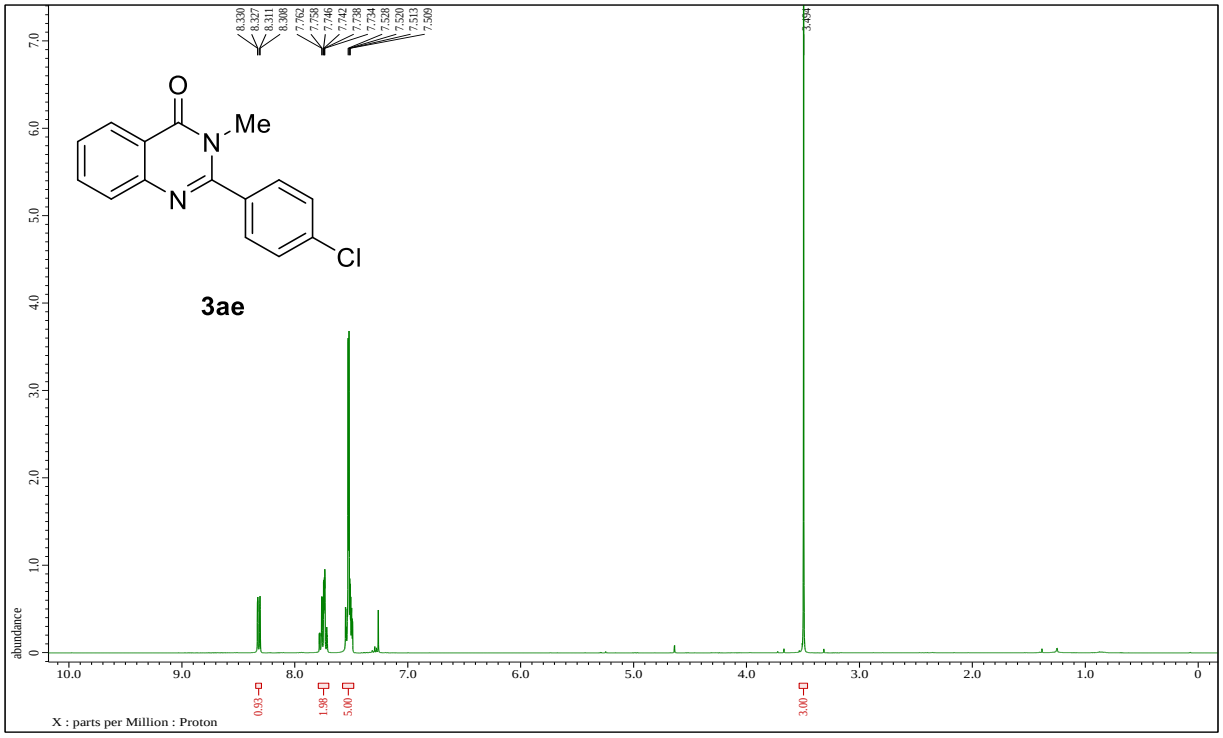
3ad ^{13}C-NMR (100 MHz, $CDCl_3$)



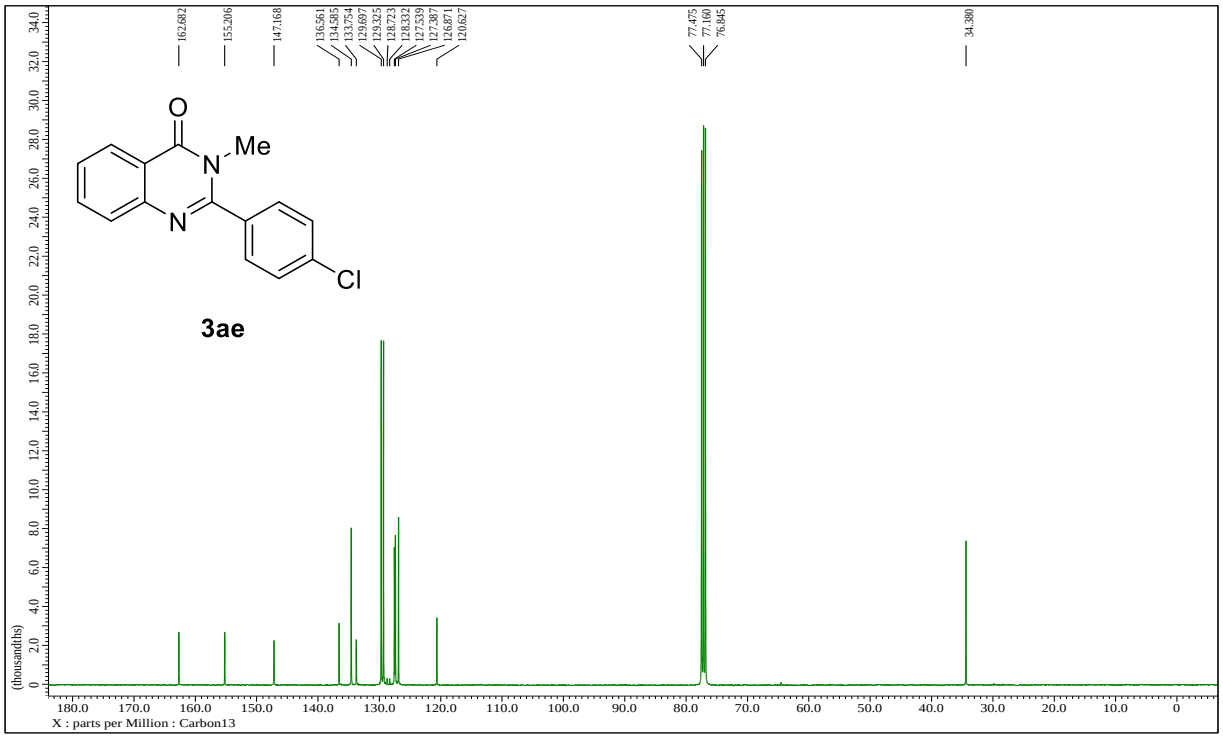
3ad ^{19}F-NMR (376 MHz, $CDCl_3$)



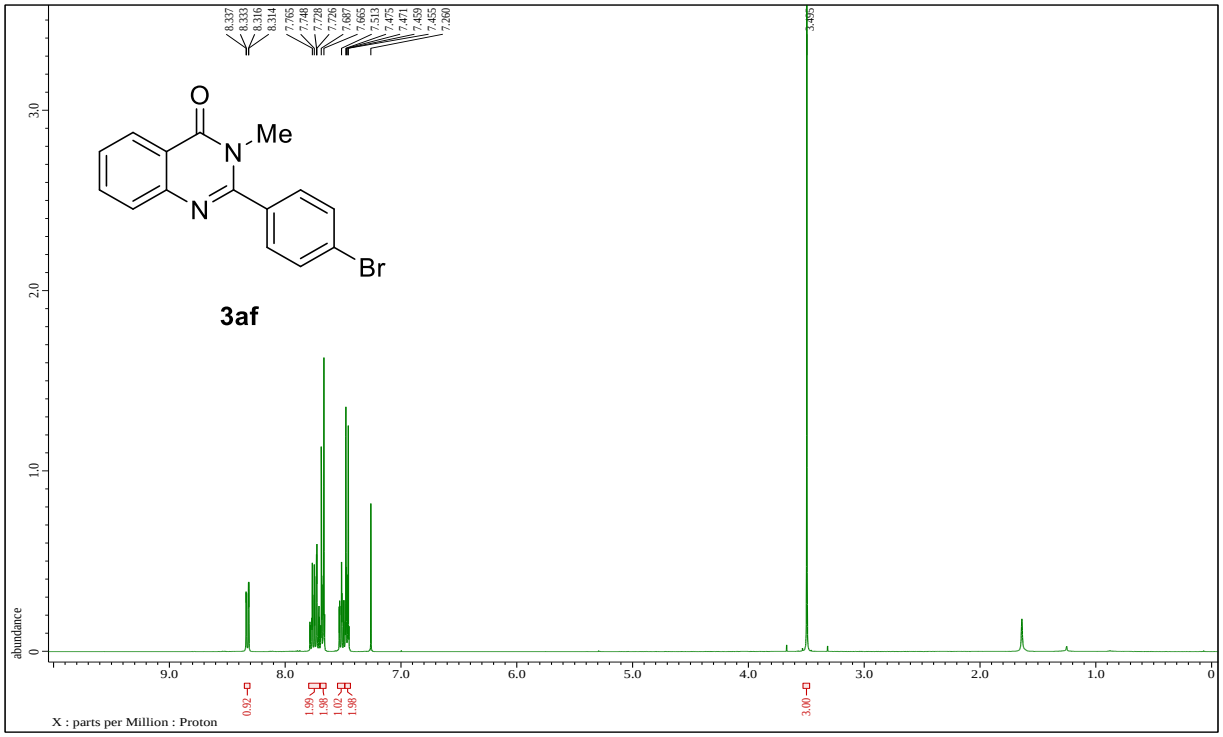
3ae ^{1}H-NMR (400 MHz, $CDCl_3$)



3ae ^{13}C-NMR (100 MHz, $CDCl_3$)



3af ^{1}H-NMR (400 MHz, $CDCl_3$)



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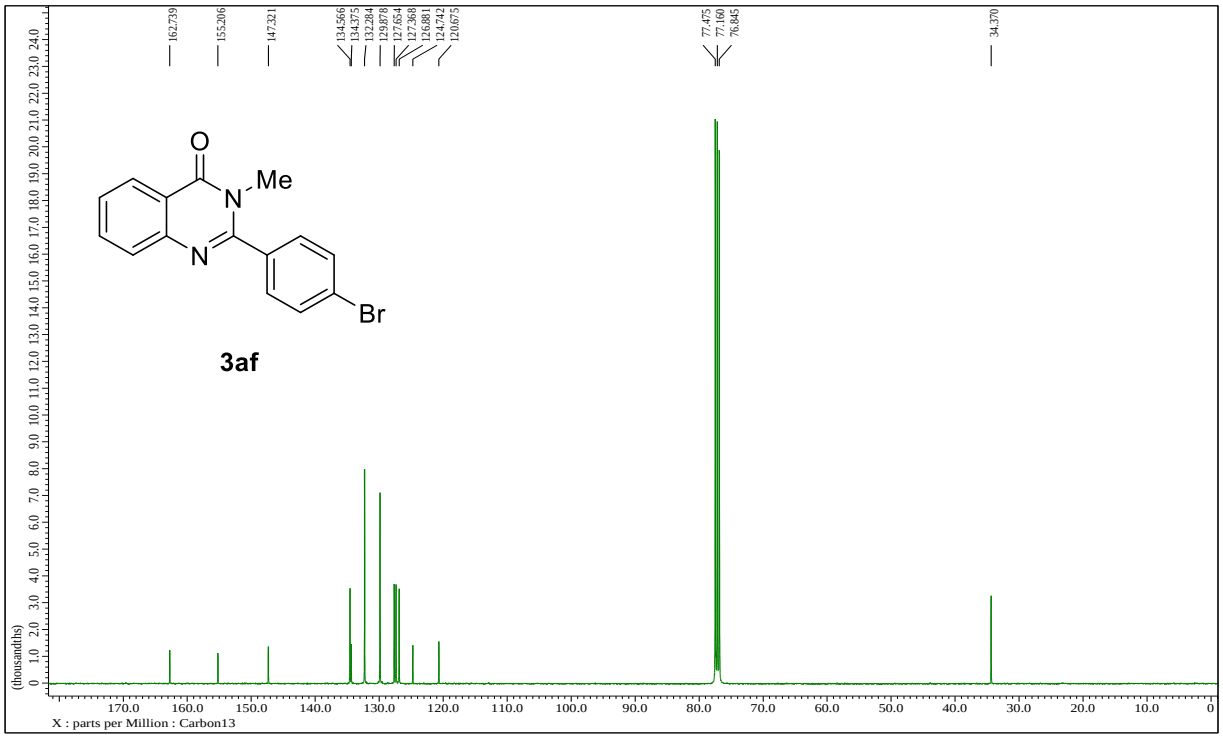
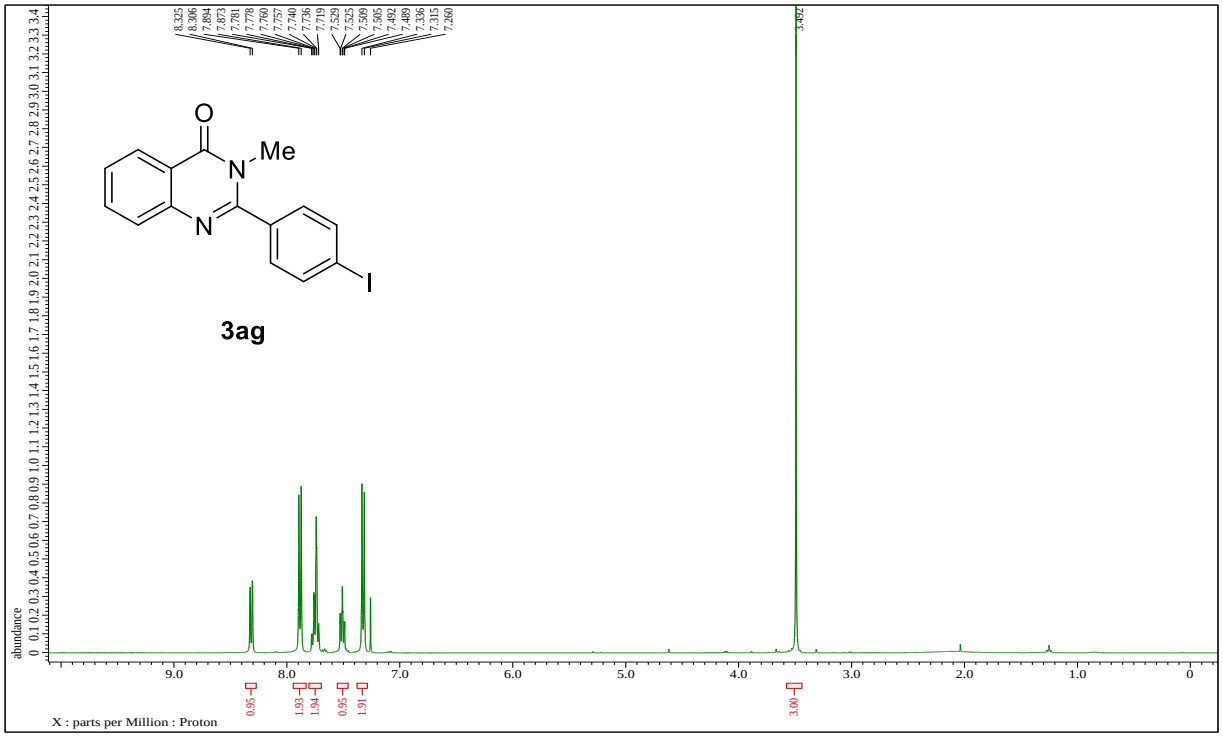


3ag ^{1}H-NMR (400 MHz, $CDCl_3$)



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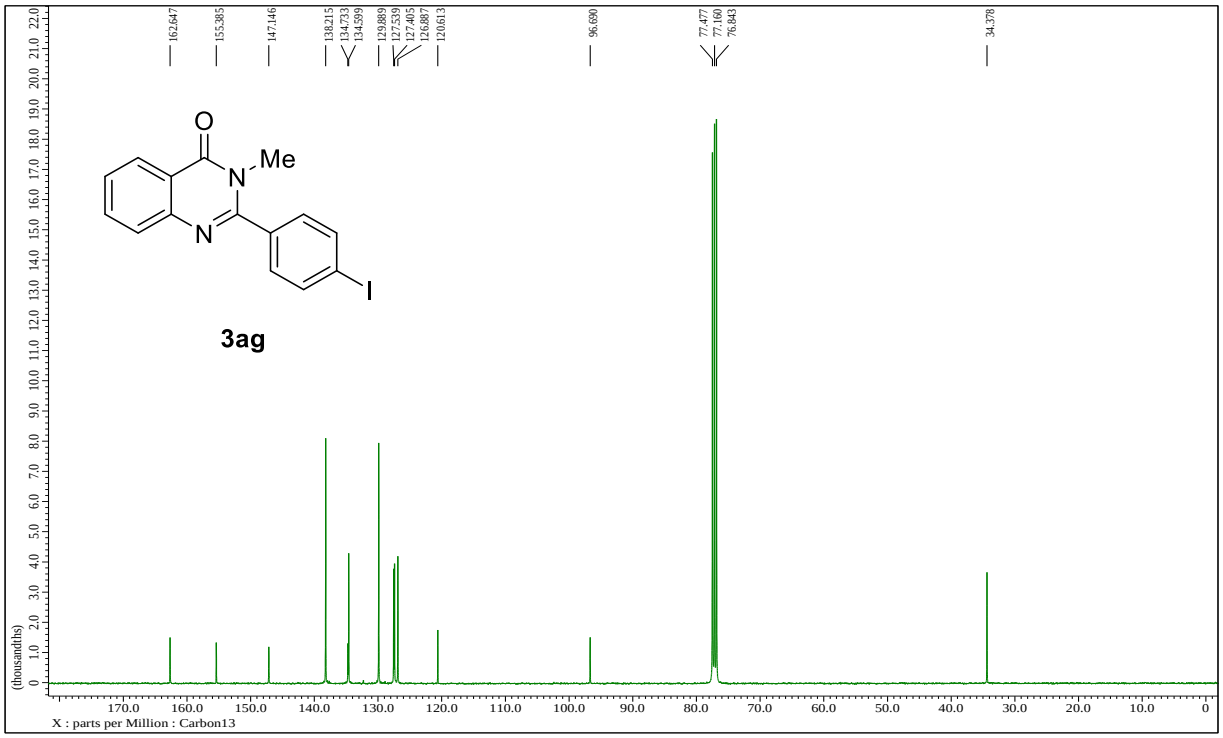
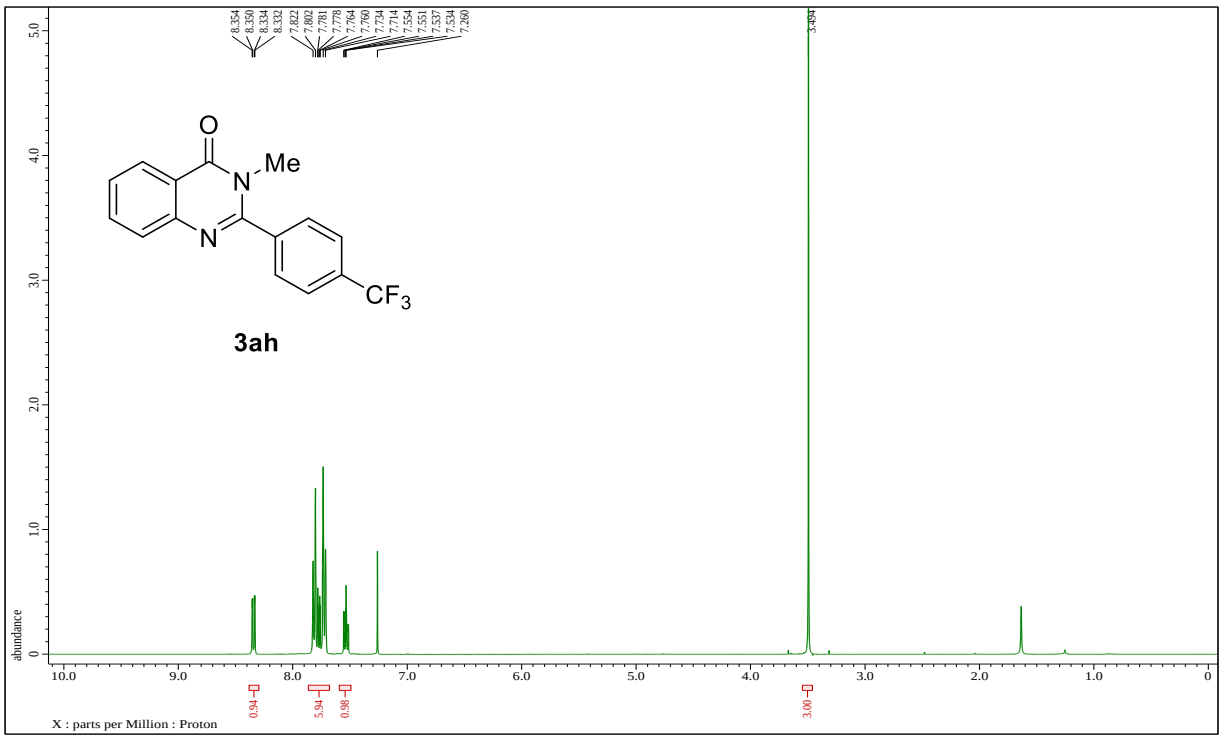
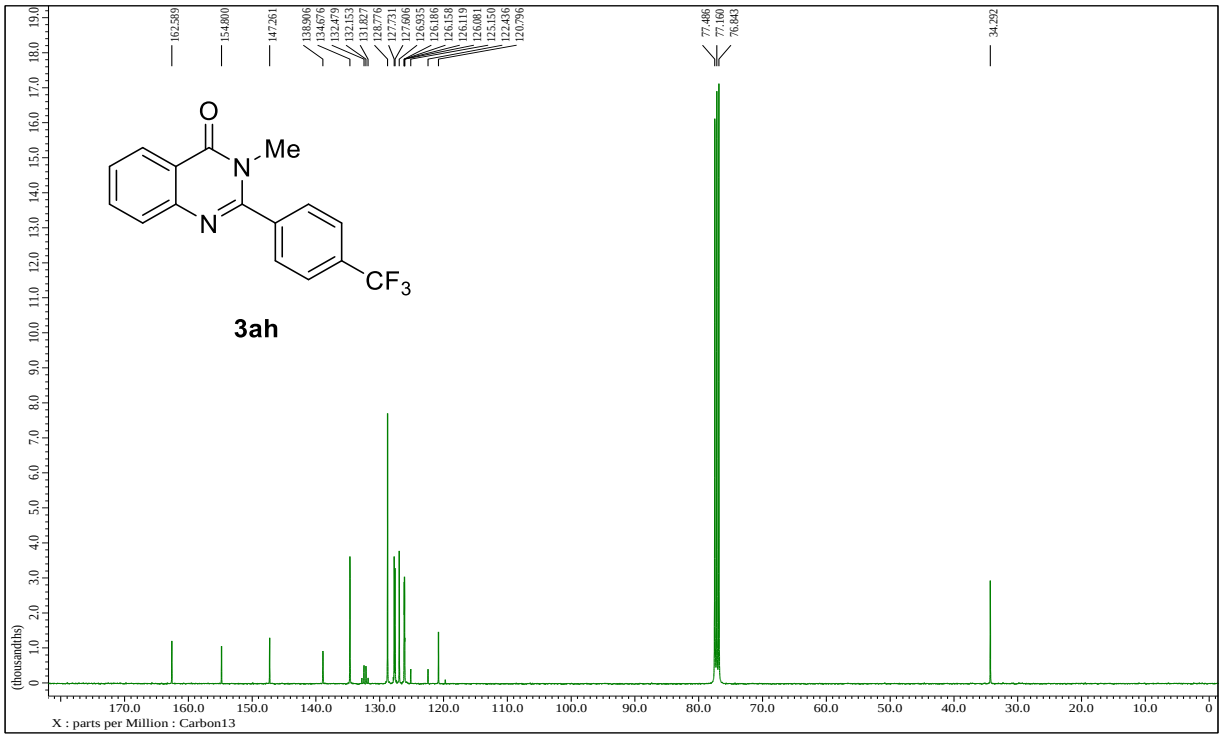


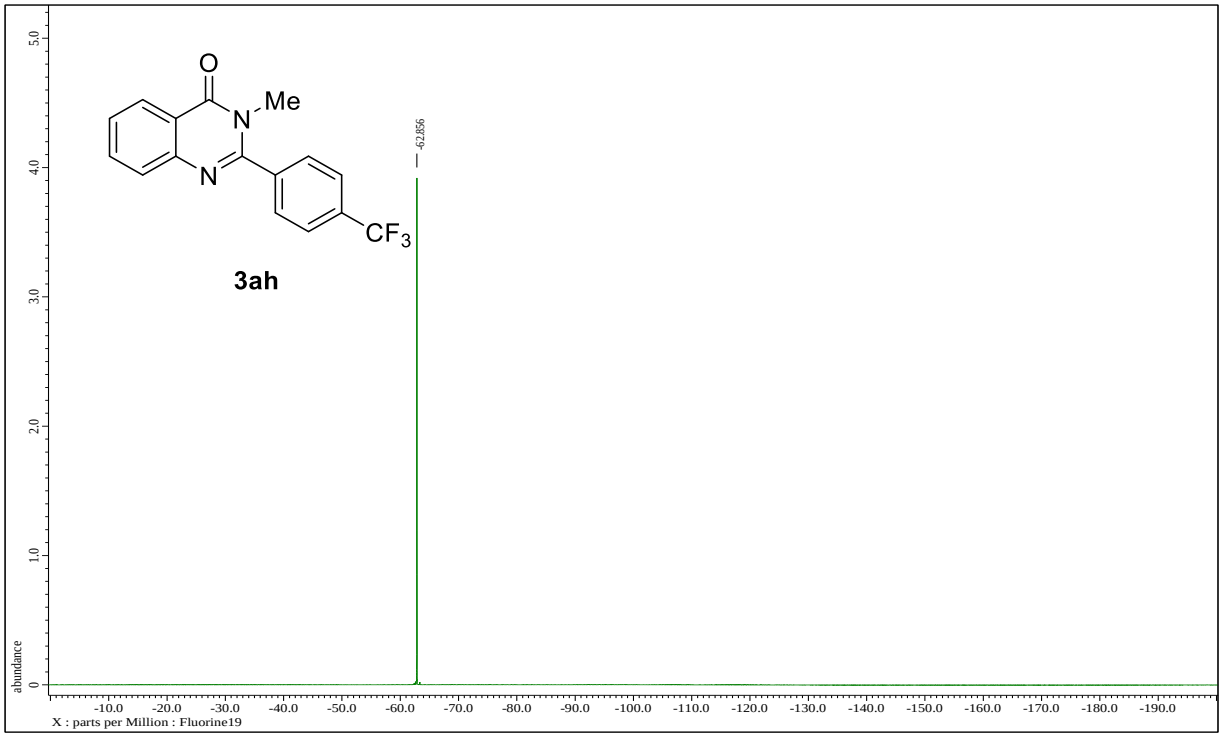
3ah ^{1}H-NMR (400 MHz, $CDCl_3$)



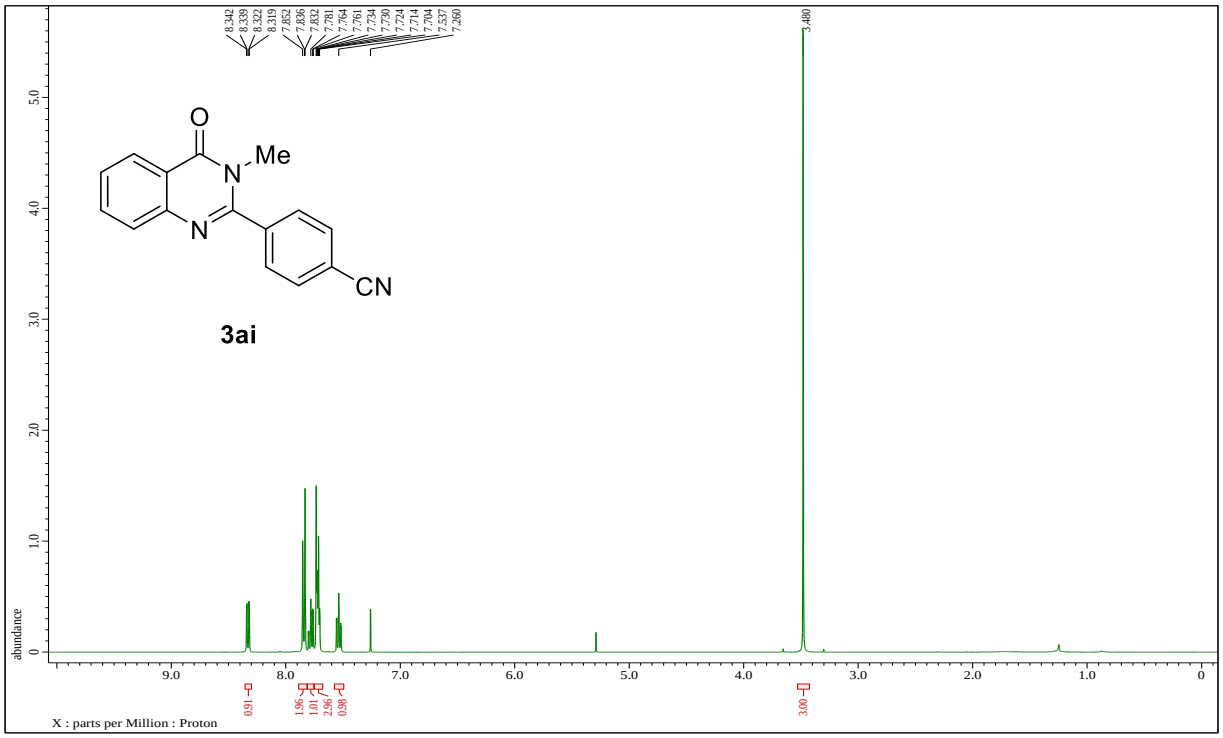
3ah ^{13}C-NMR (100 MHz, $CDCl_3$)



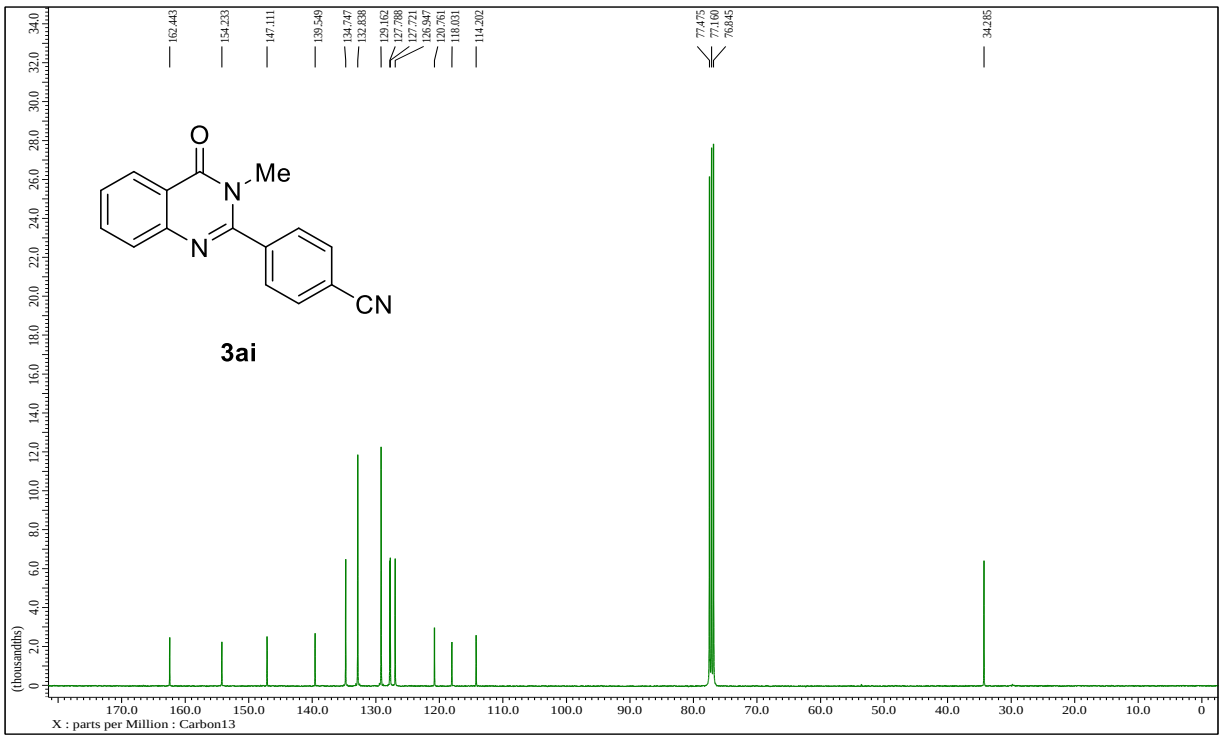
3ah ^{19}F-NMR (376 MHz, $CDCl_3$)



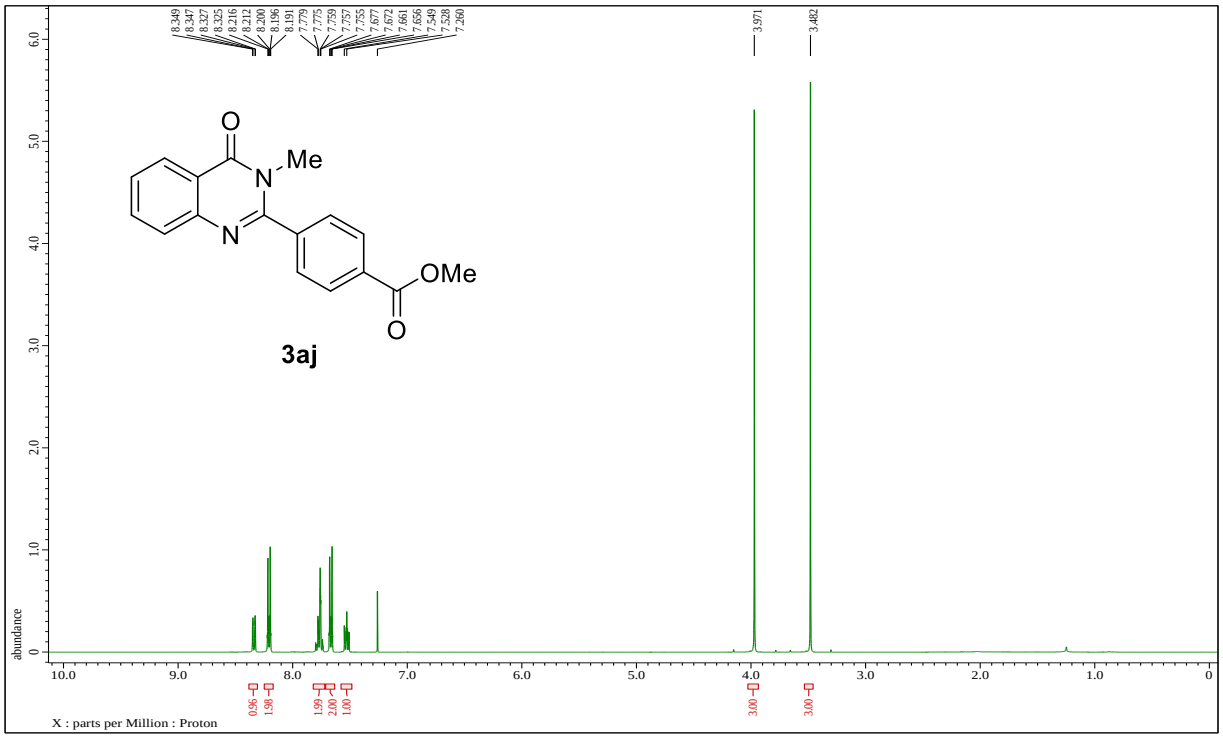
3ai ^{1}H-NMR (400 MHz, $CDCl_3$)



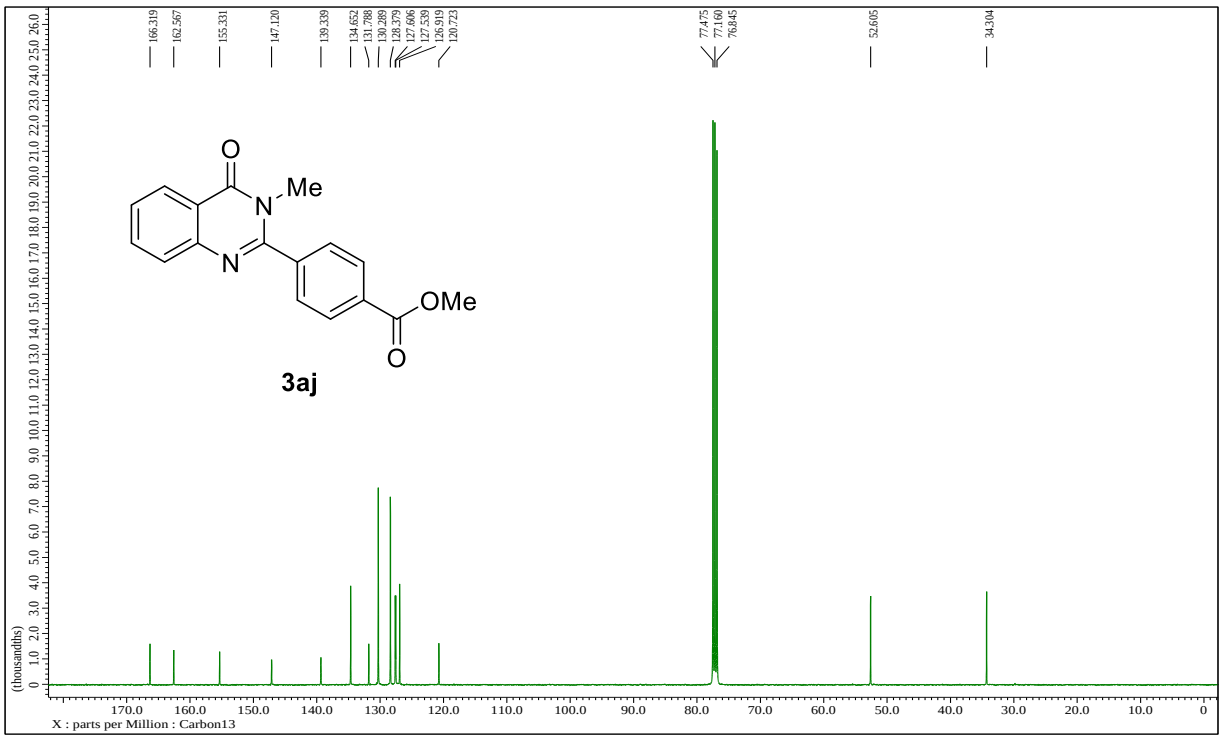
3ai ^{13}C-NMR (100 MHz, $CDCl_3$)



3aj ^{1}H-NMR (400 MHz, $CDCl_3$)



3aj ^{13}C-NMR (100 MHz, $CDCl_3$)



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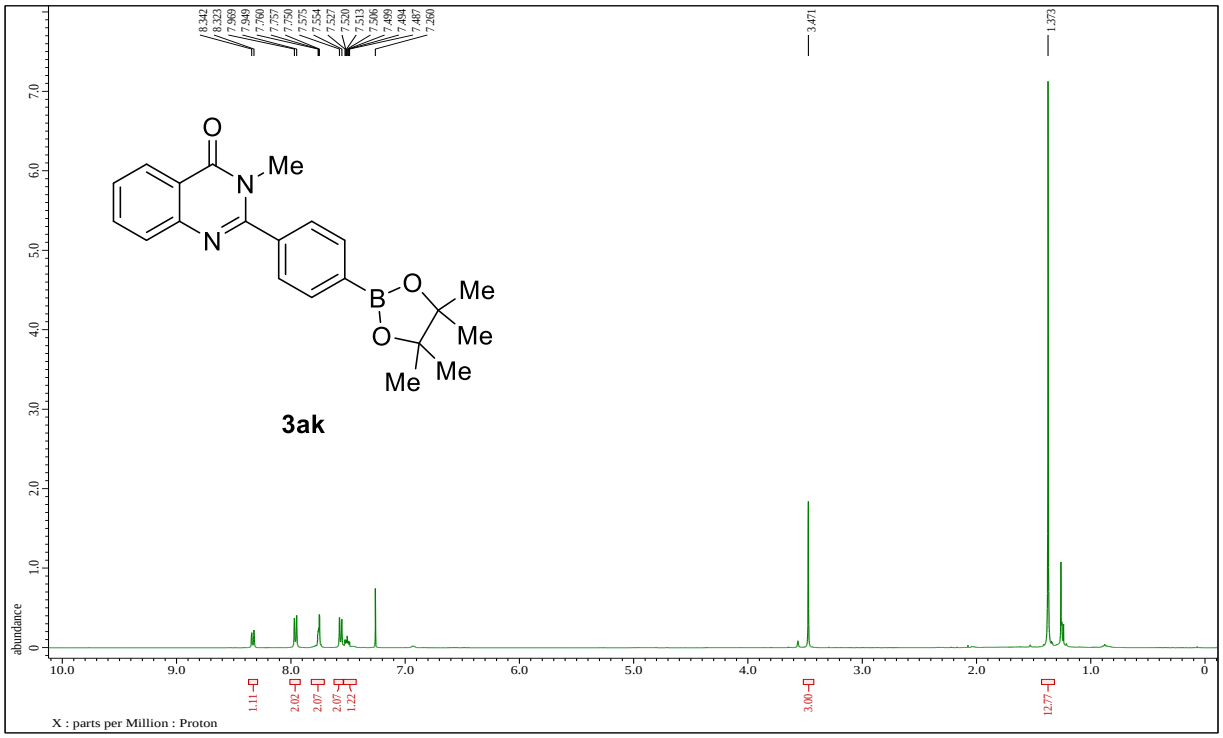

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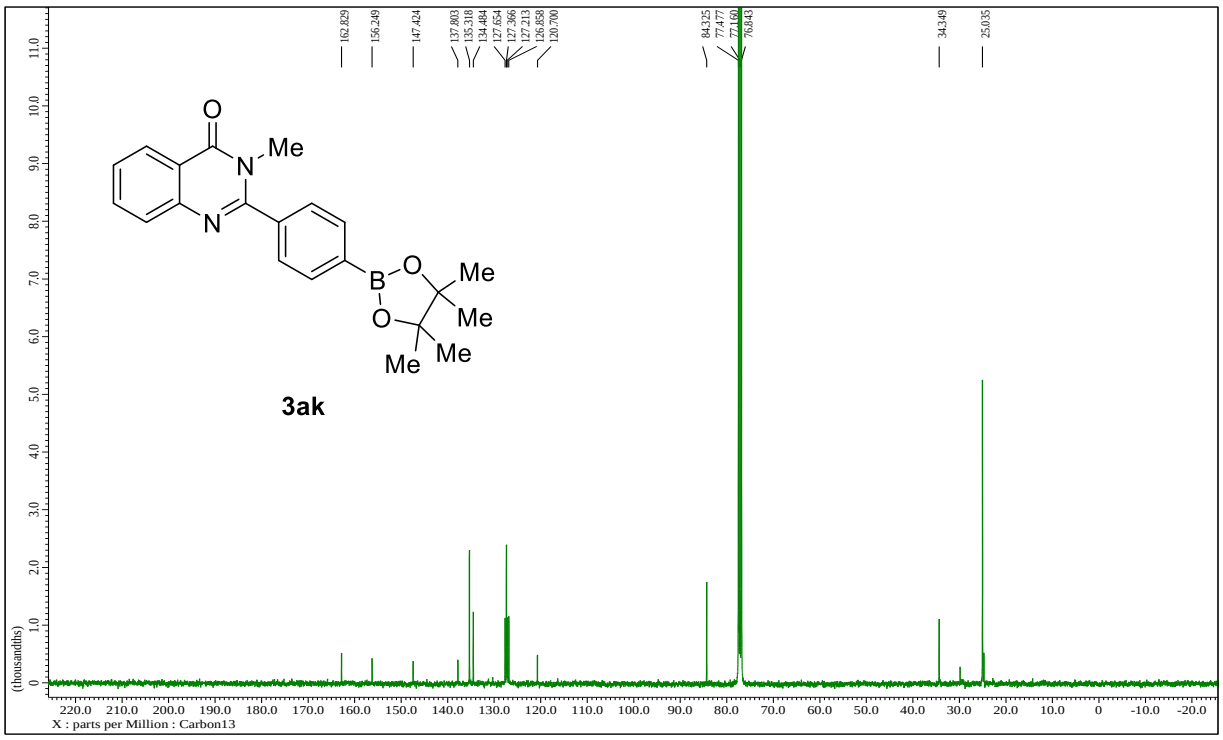

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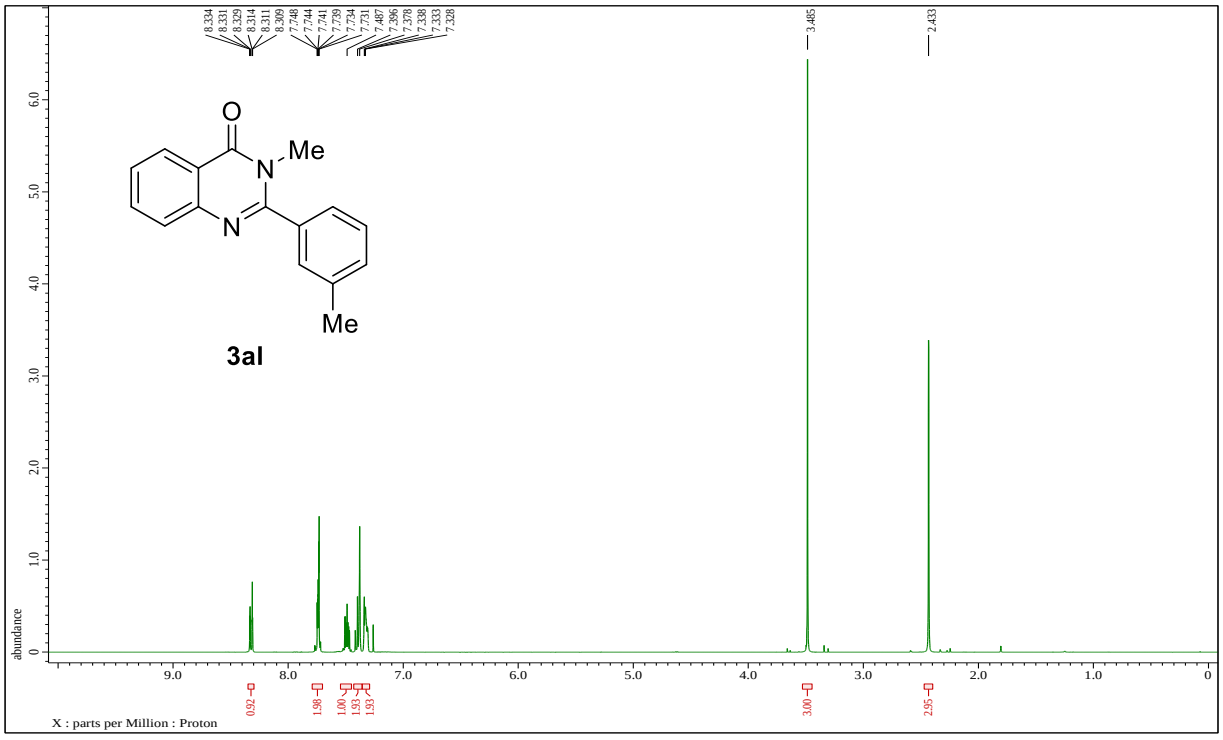
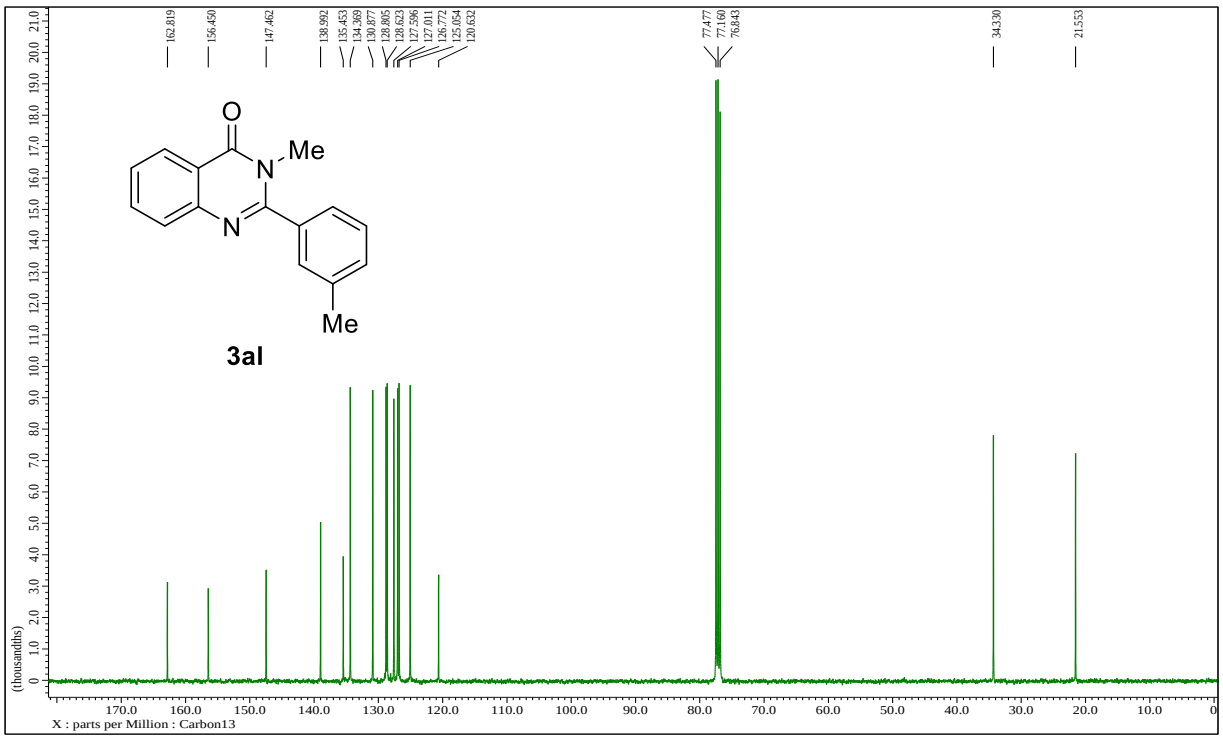
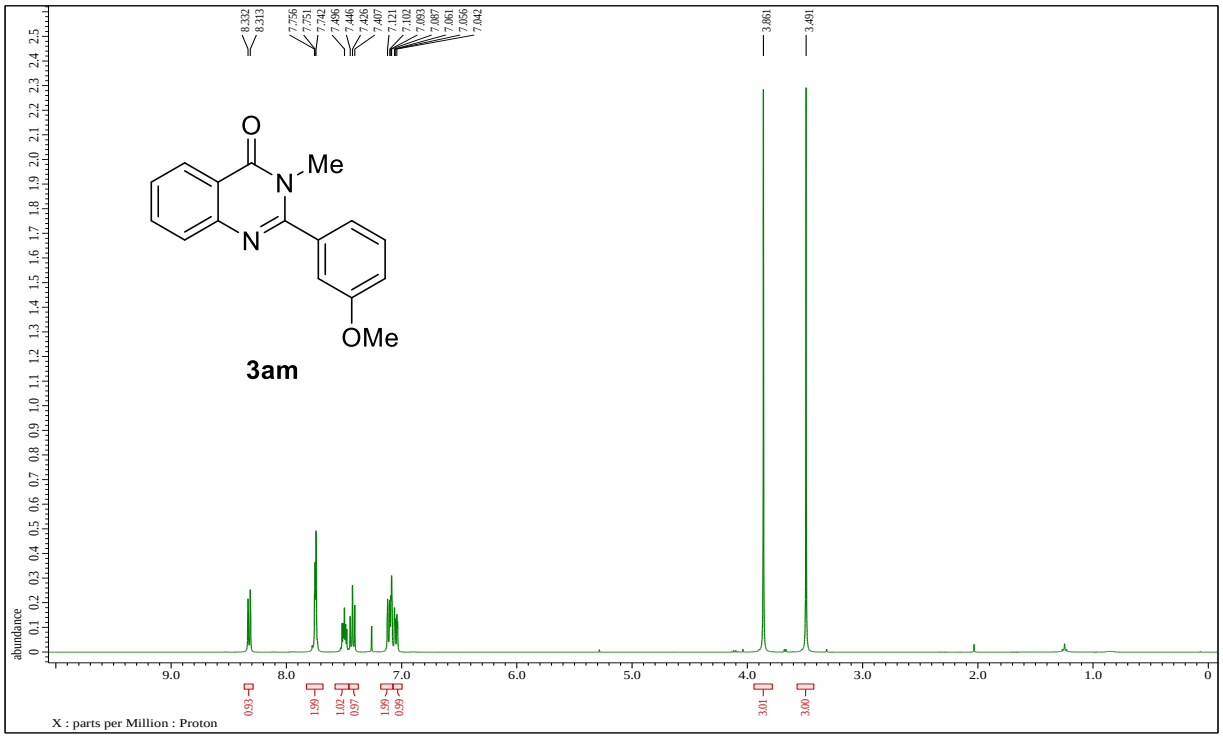


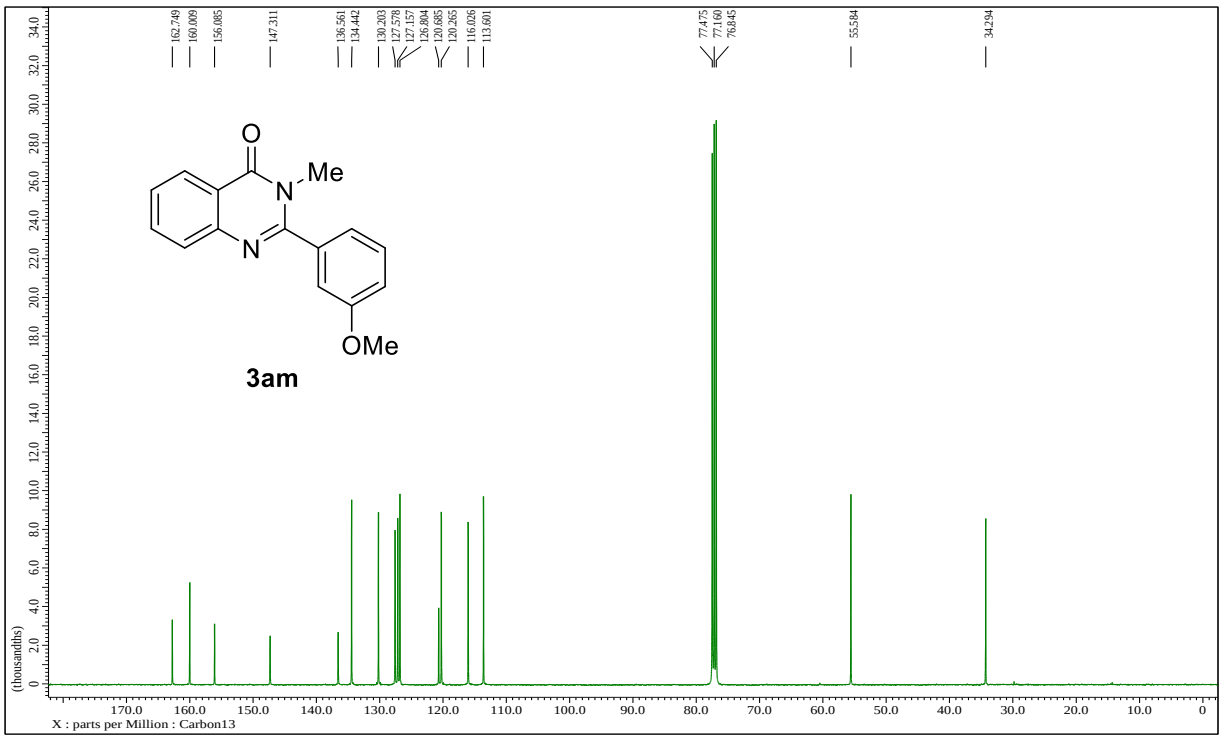
3al ^{13}C-NMR (100 MHz, $CDCl_3$)



3am ^{1}H-NMR (400 MHz, $CDCl_3$)



3am ^{13}C-NMR (100 MHz, $CDCl_3$)



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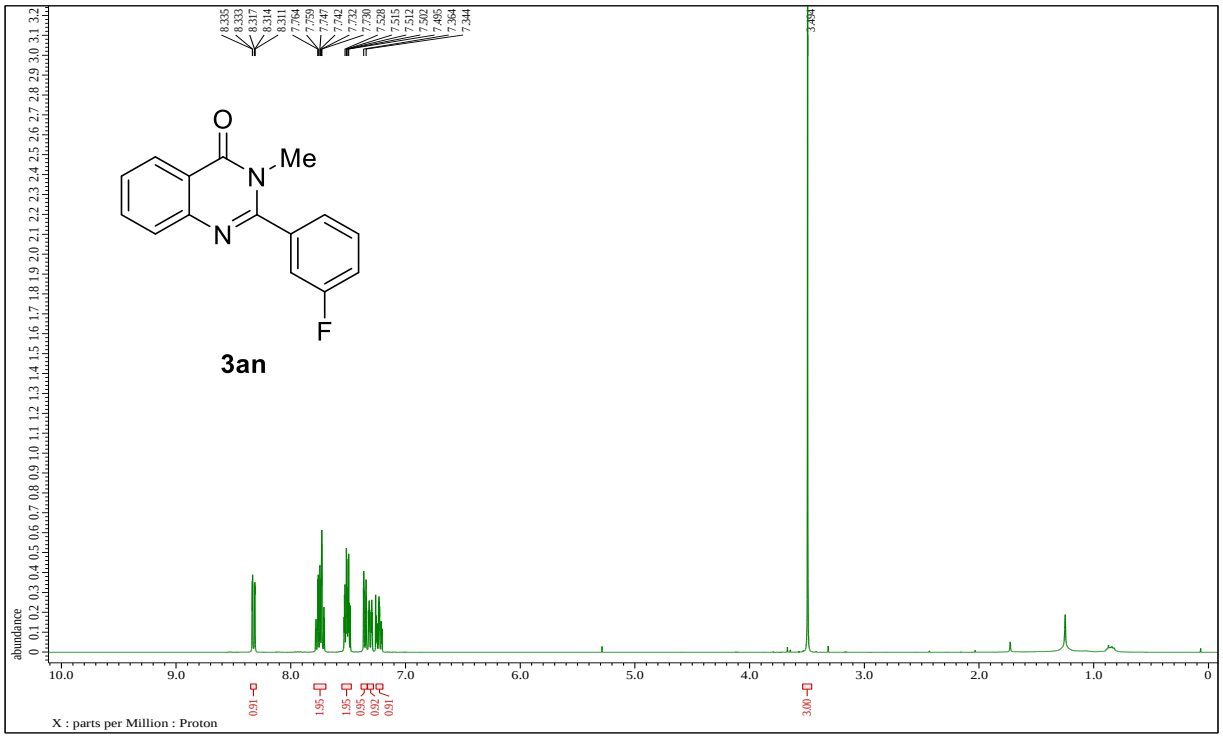
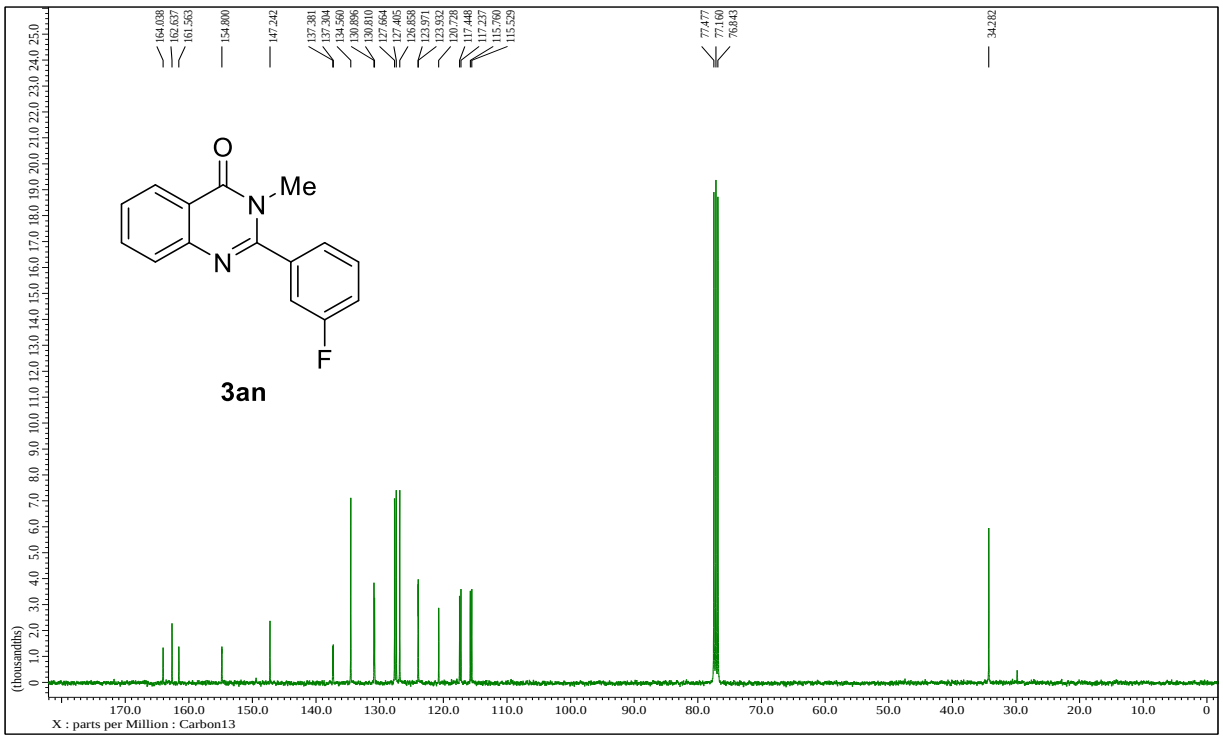
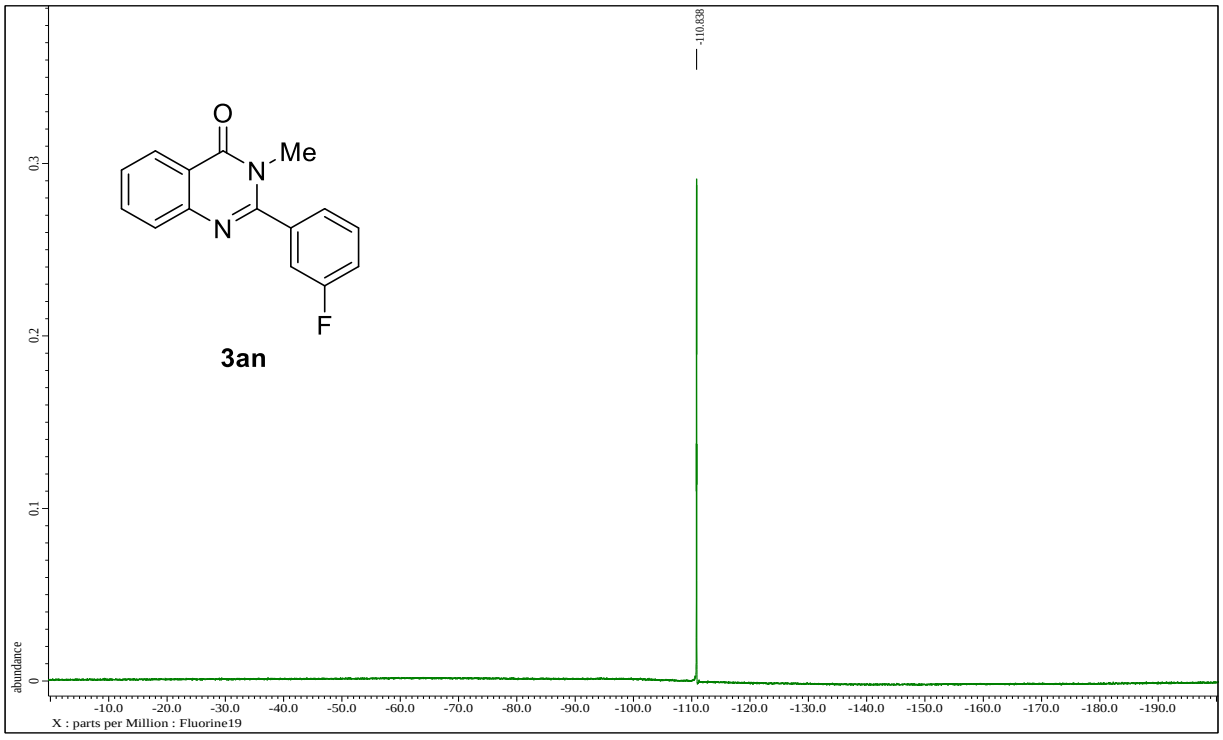


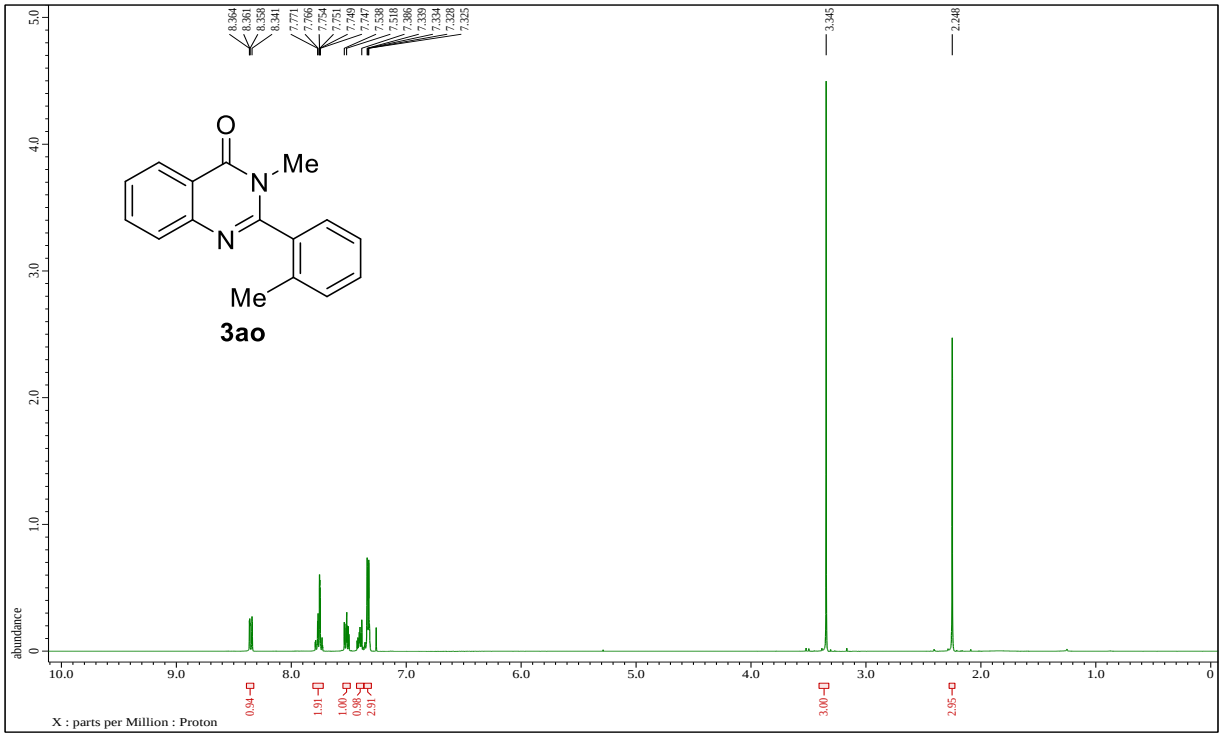
3an ^{13}C-NMR (100 MHz, $CDCl_3$)



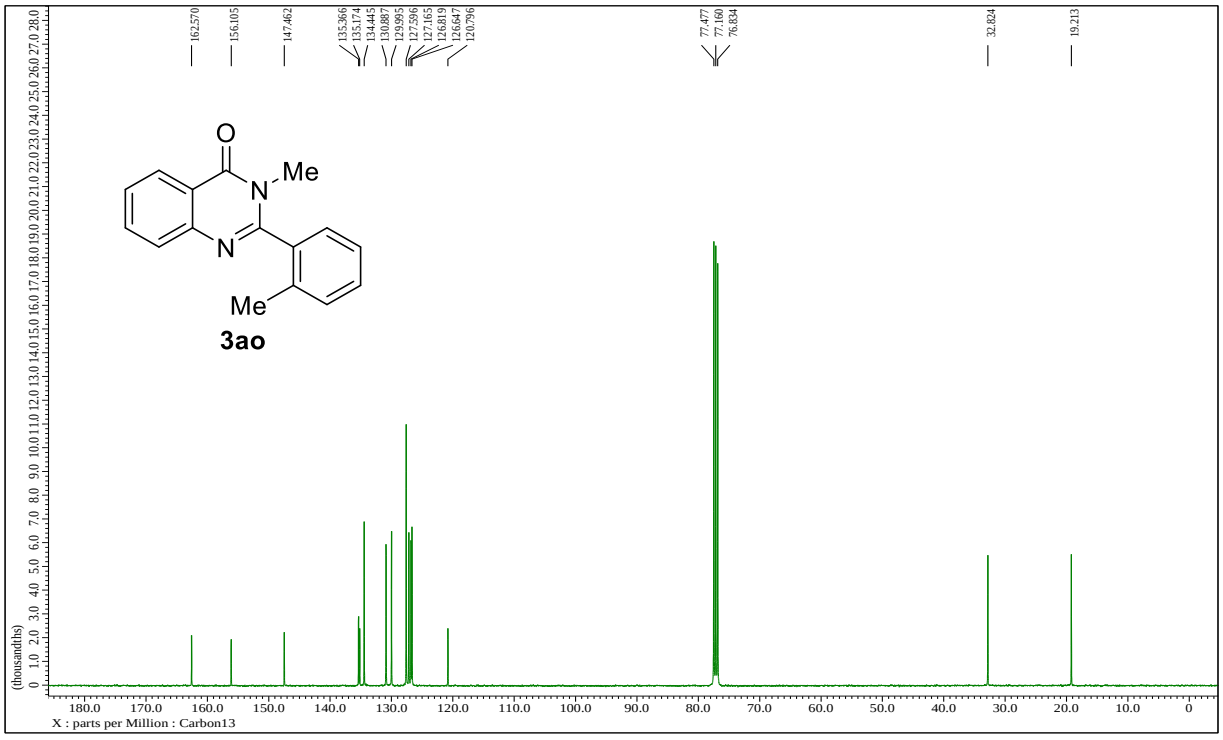
3an ^{19}F-NMR (376 MHz, $CDCl_3$)



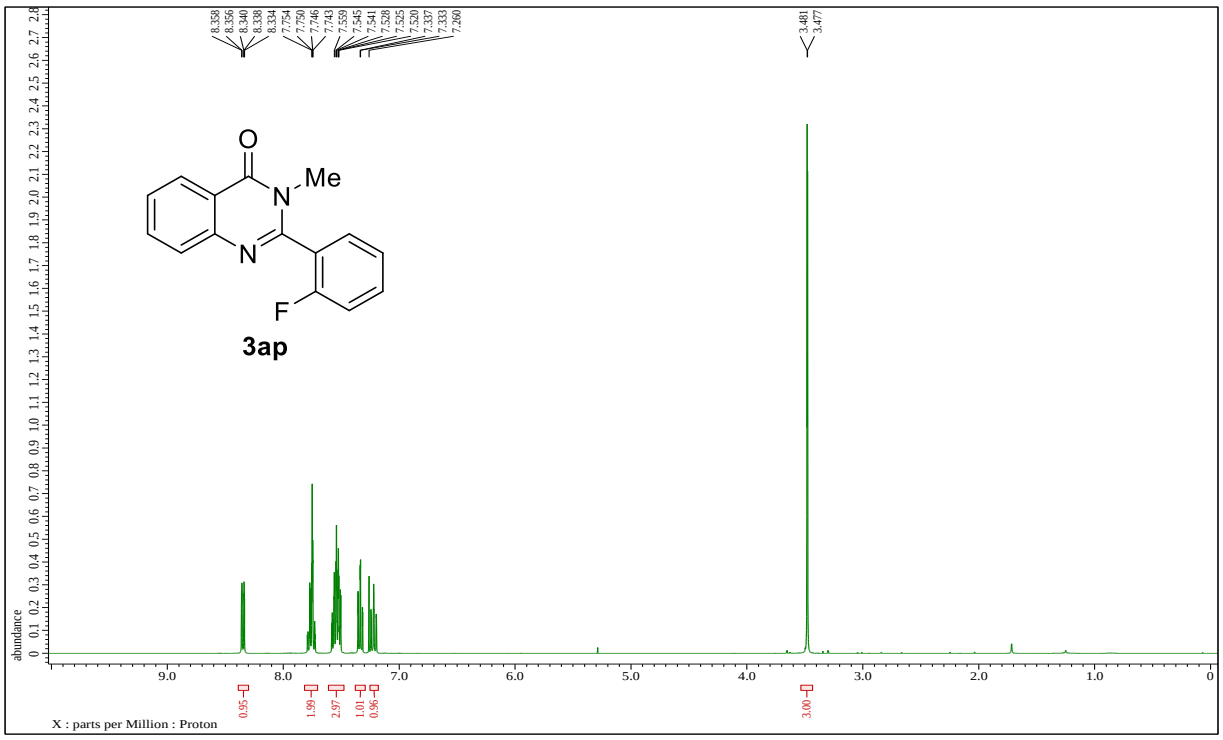
3ao ^{1}H-NMR (400 MHz, $CDCl_3$)



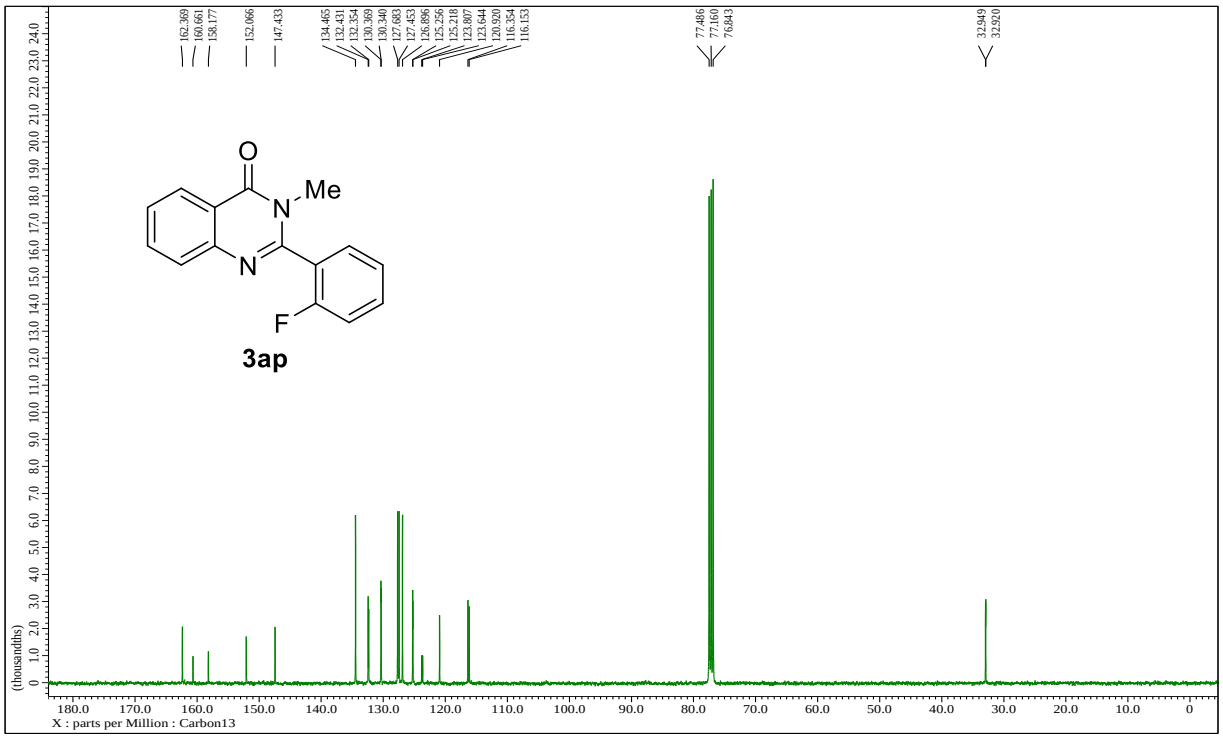
3ao ^{13}C-NMR (100 MHz, $CDCl_3$)



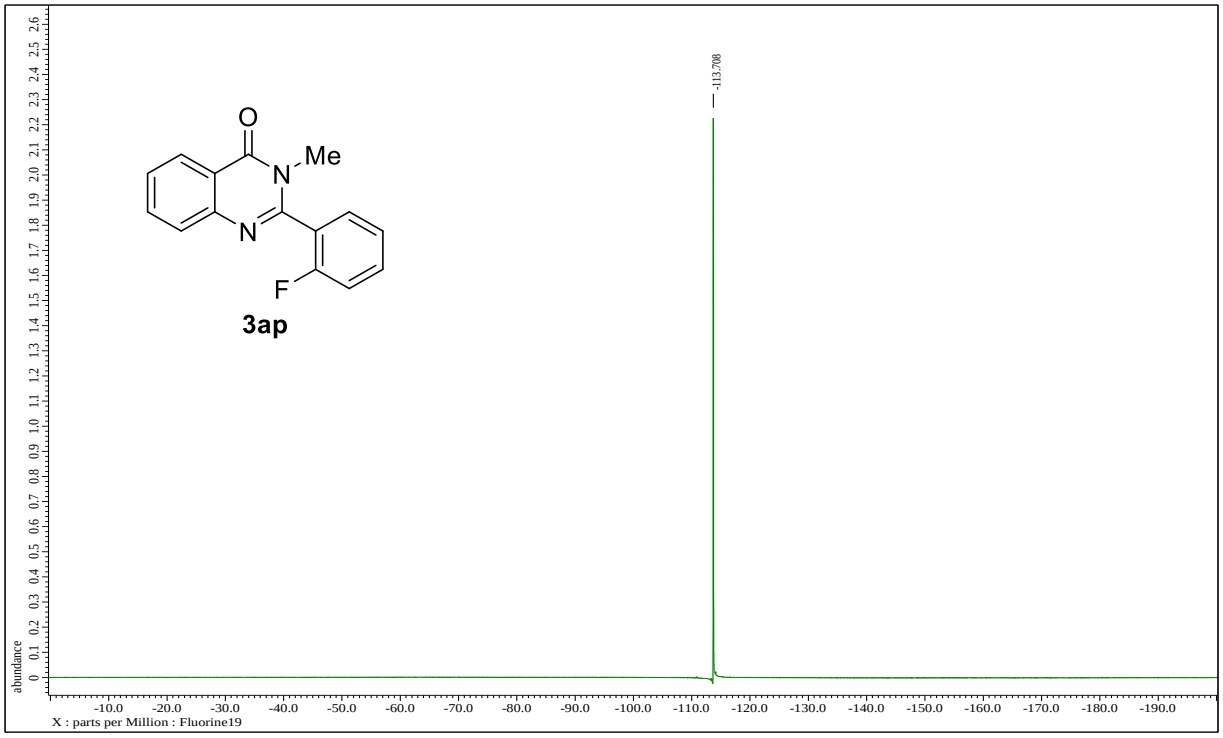
3ap ^{1}H-NMR (400 MHz, $CDCl_3$)



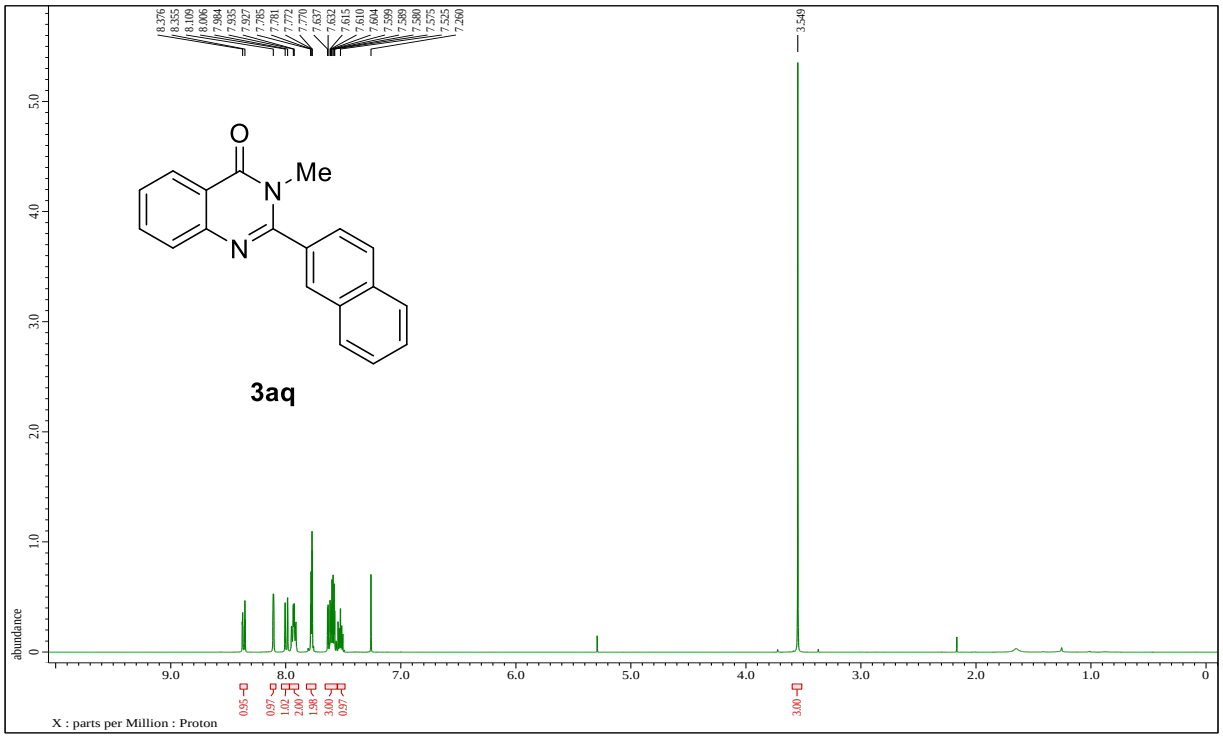
3ap ^{13}C-NMR (100 MHz, $CDCl_3$)



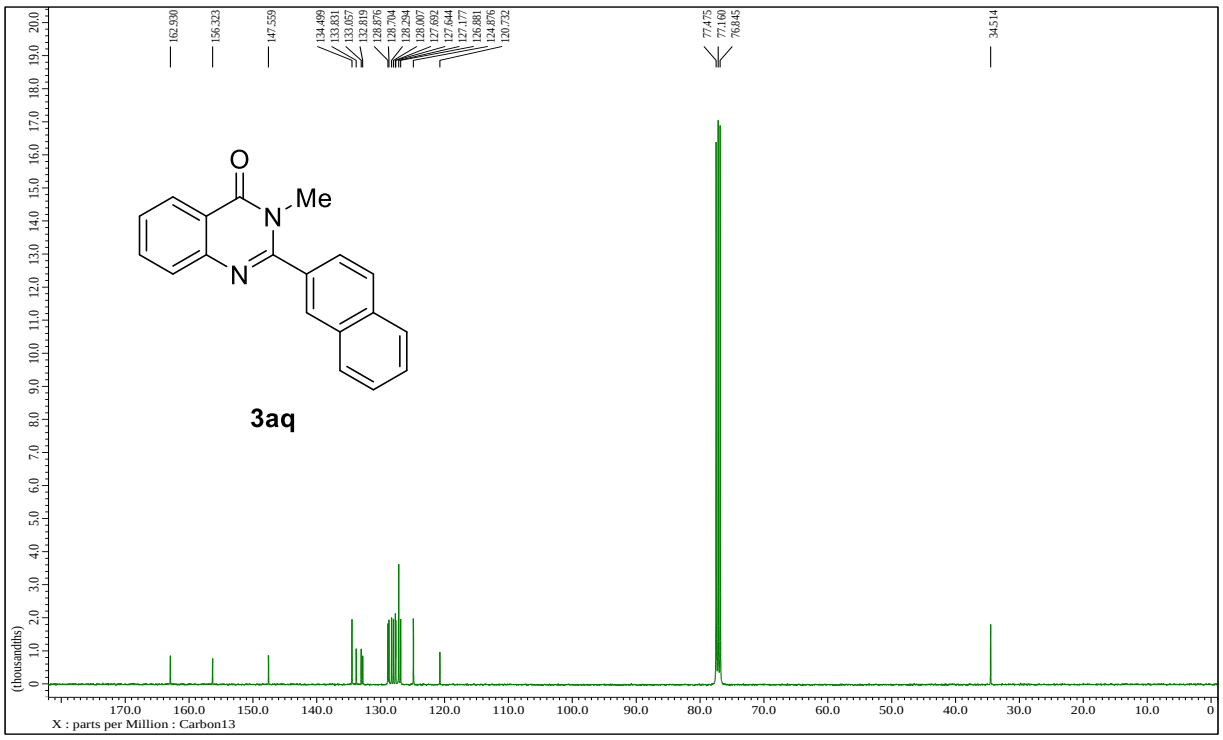
3ap ^{19}F-NMR (376 MHz, $CDCl_3$)



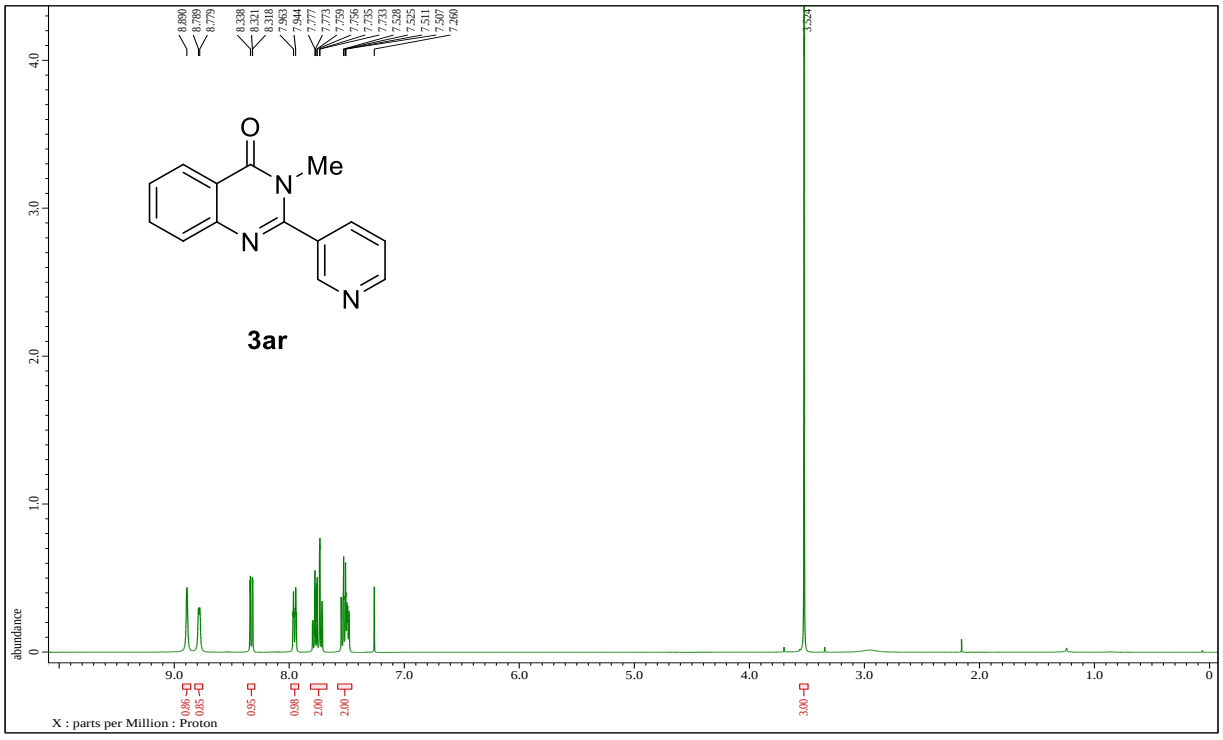
3aq ^{1}H-NMR (400 MHz, $CDCl_3$)



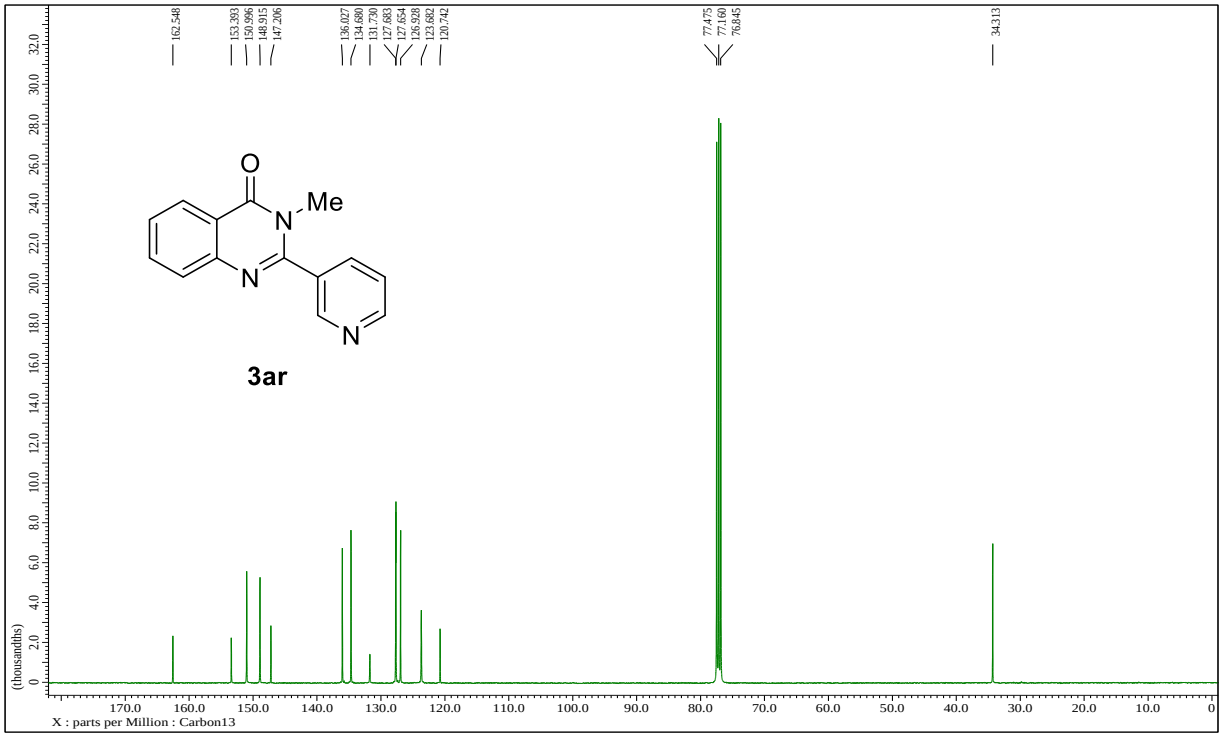
3aq ^{13}C-NMR (100 MHz, $CDCl_3$)



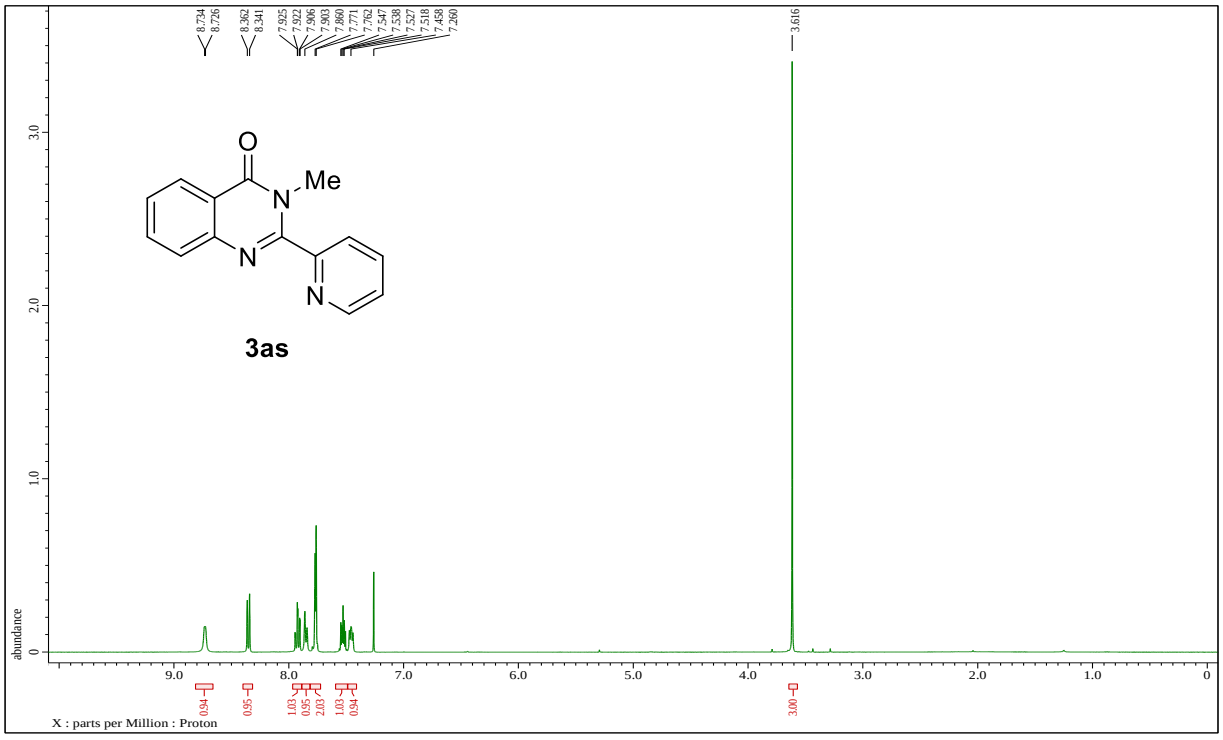
3ar ^{1}H-NMR (400 MHz, $CDCl_3$)



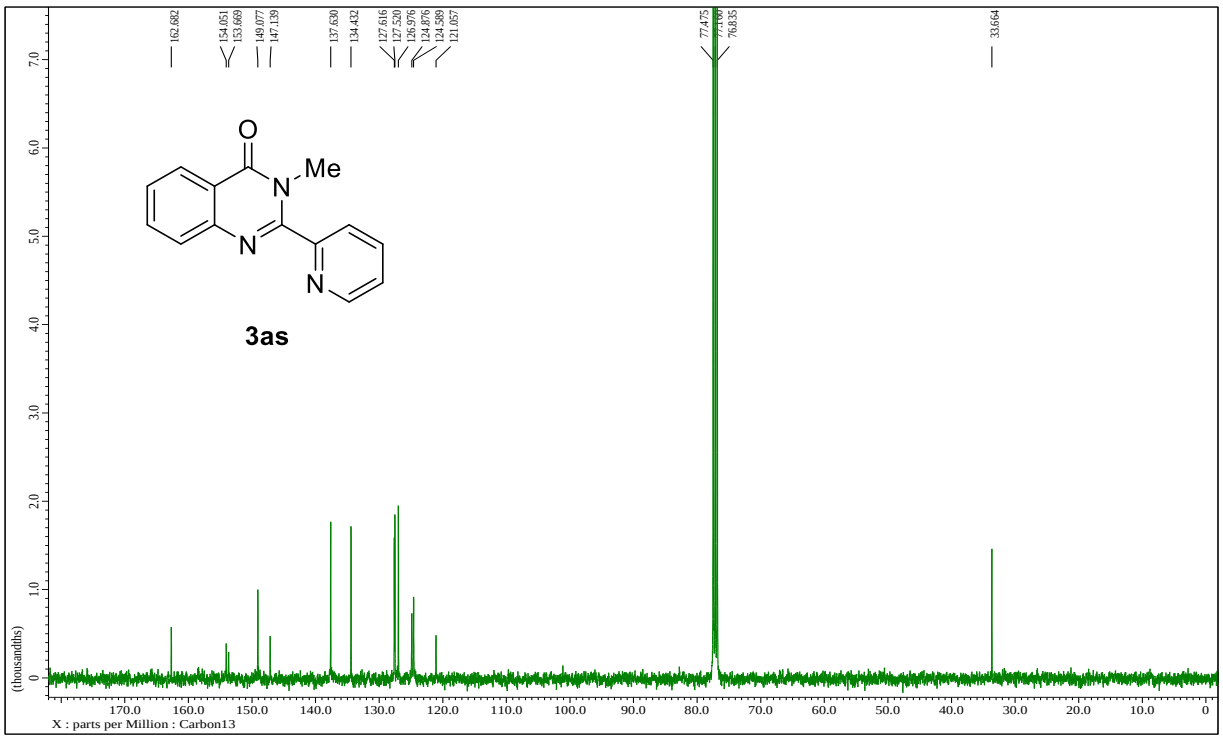
3ar ^{13}C-NMR (100 MHz, $CDCl_3$)



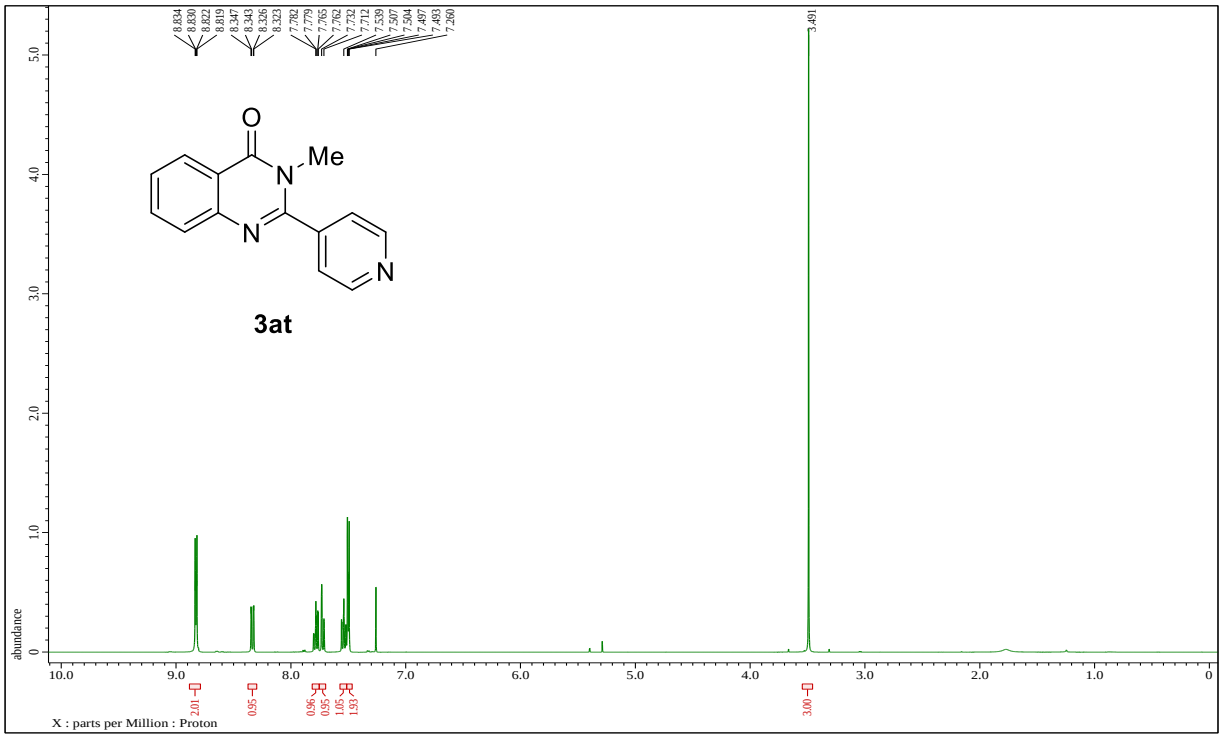
3as ^{1}H-NMR (400 MHz, $CDCl_3$)



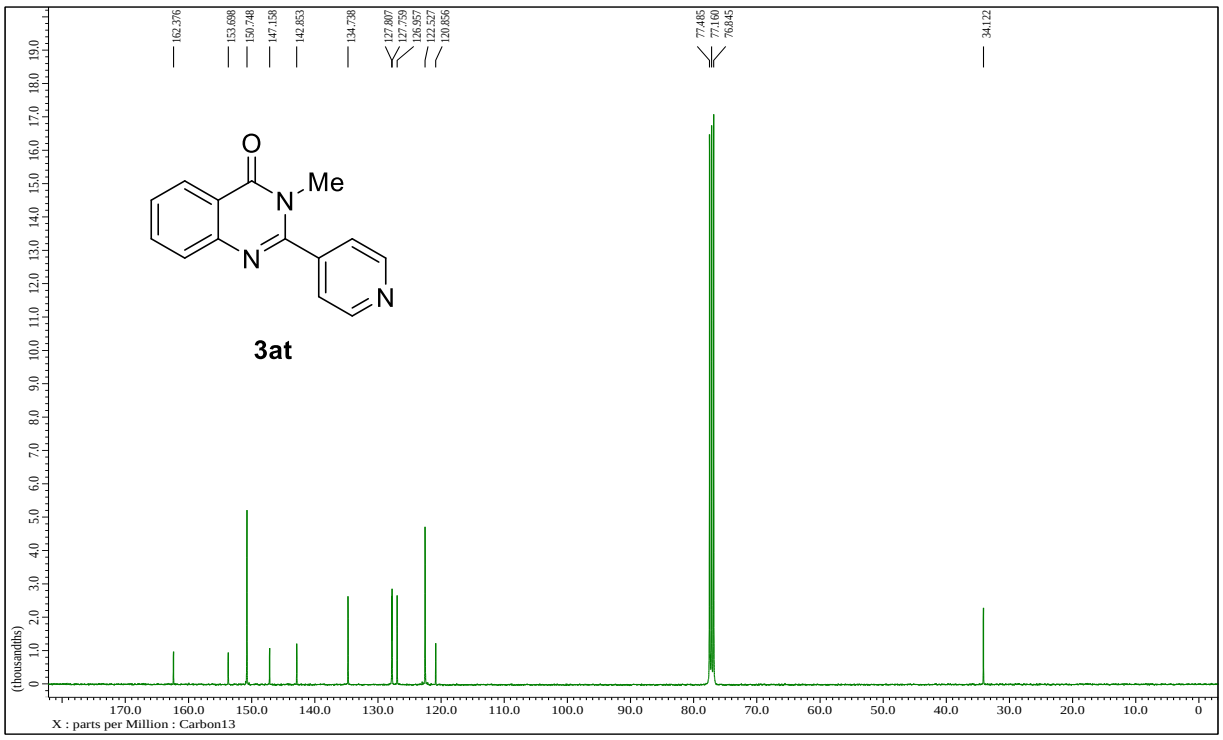
3as ^{13}C-NMR (100 MHz, $CDCl_3$)



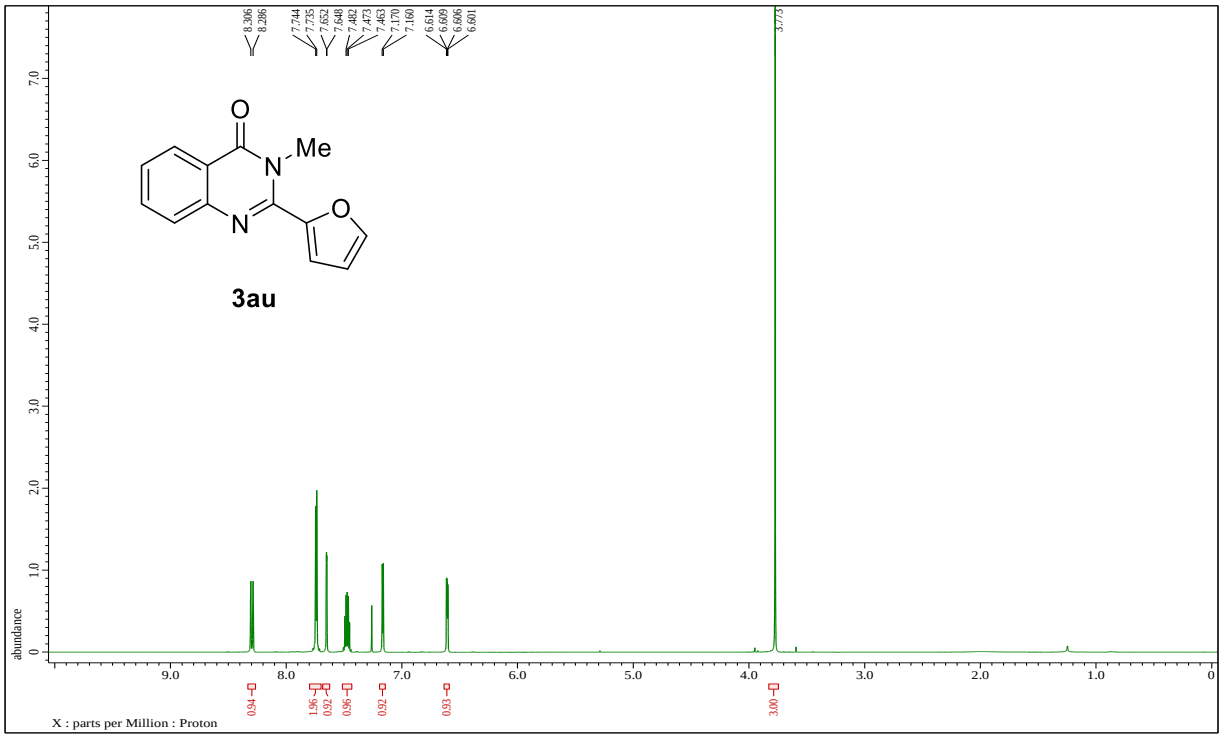
3at ^{1}H-NMR (400 MHz, $CDCl_3$)



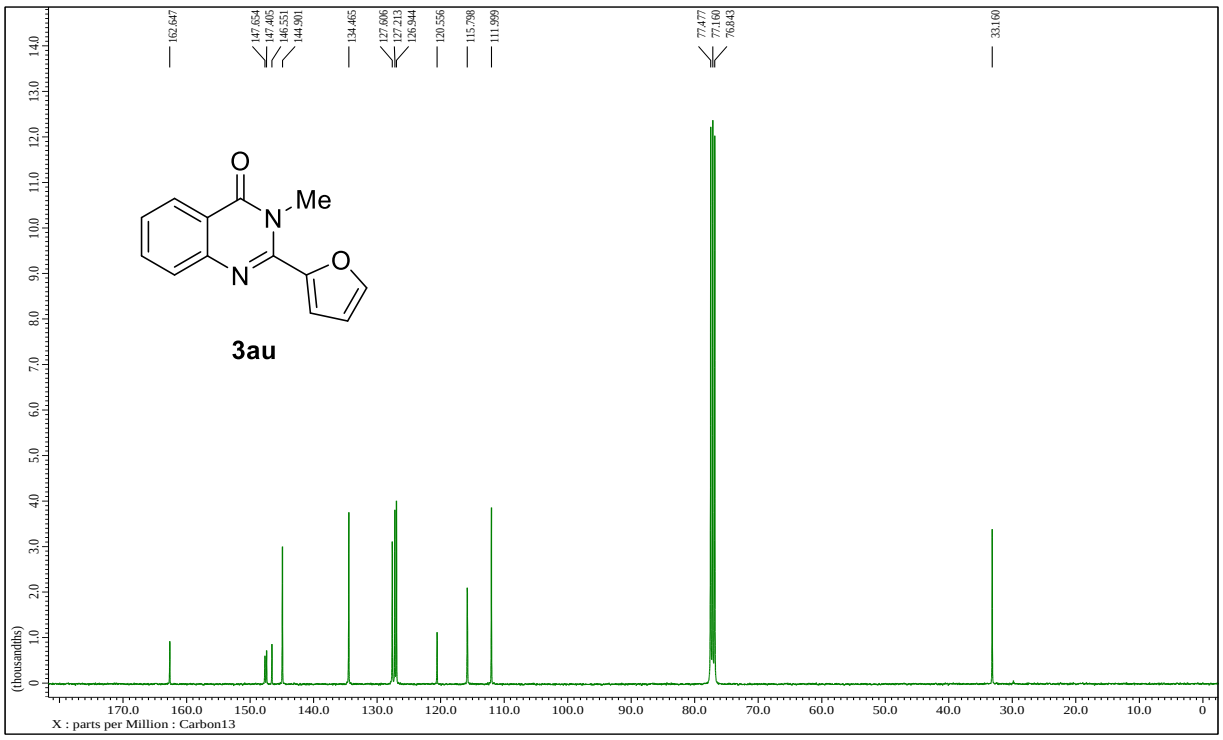
3at ^{13}C-NMR (100 MHz, $CDCl_3$)



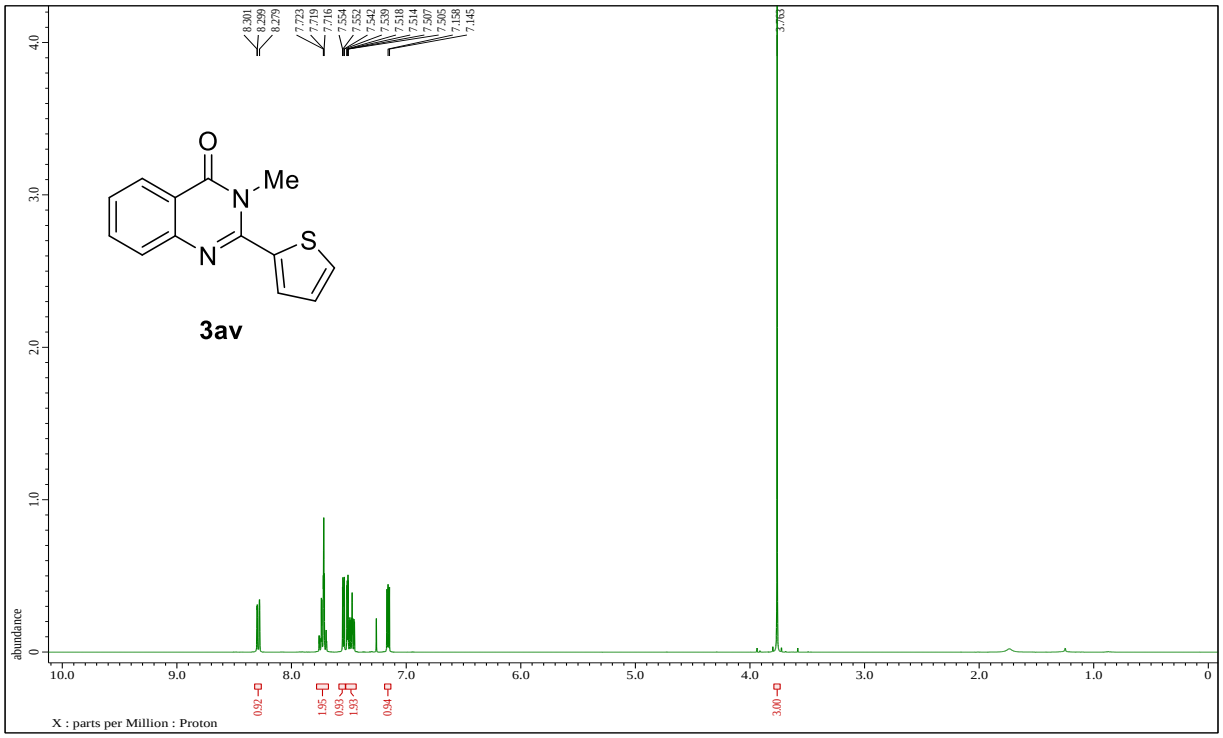
3au ^{1}H-NMR (400 MHz, $CDCl_3$)



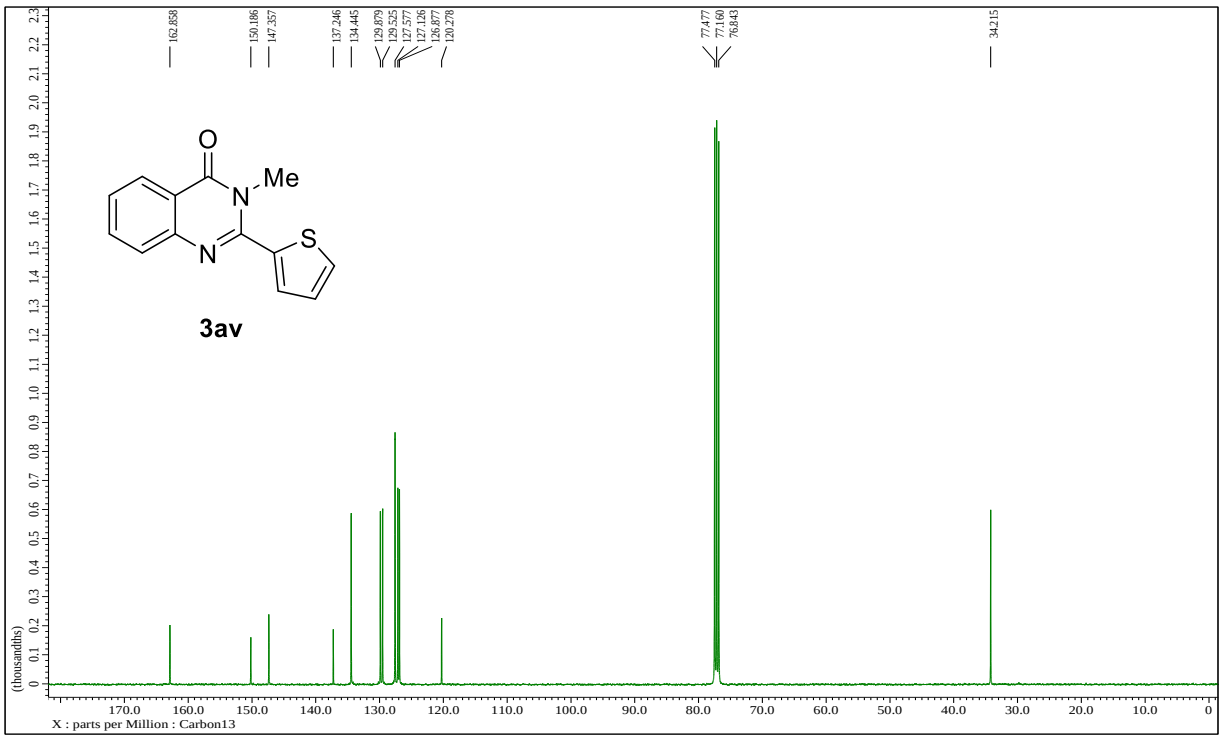
3au ^{13}C-NMR (100 MHz, $CDCl_3$)



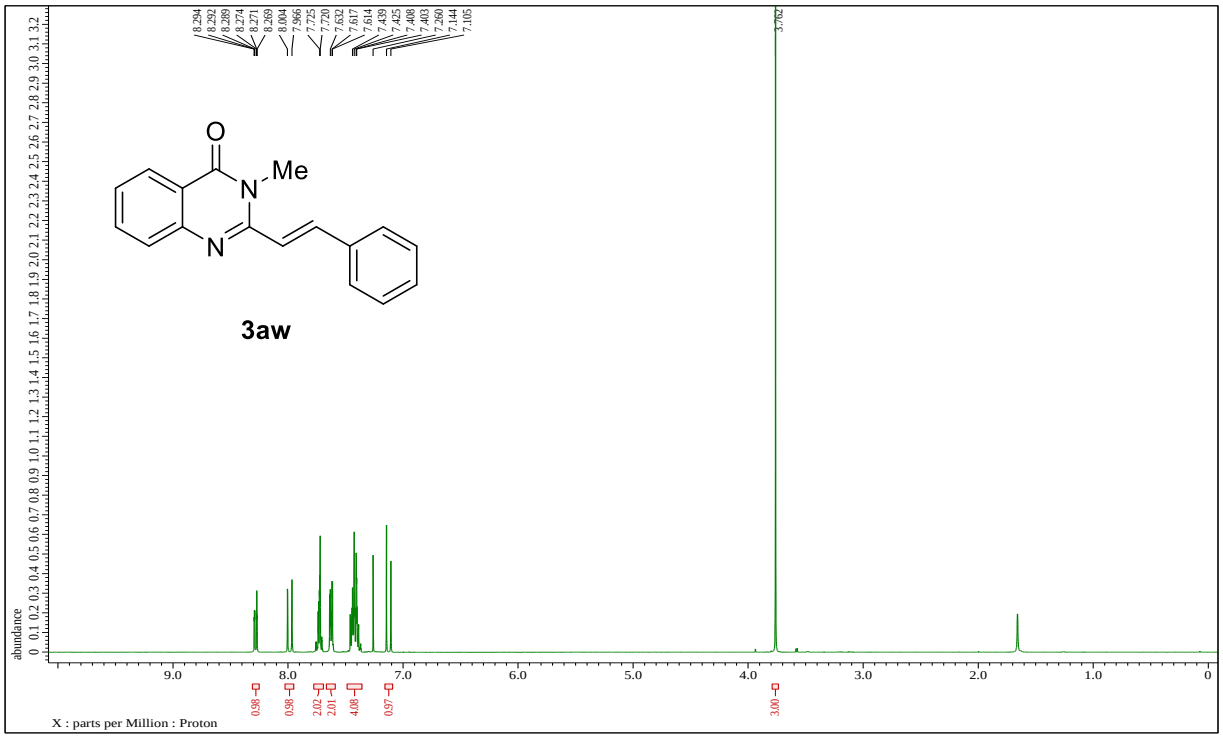
3av ^{1}H-NMR (400 MHz, $CDCl_3$)



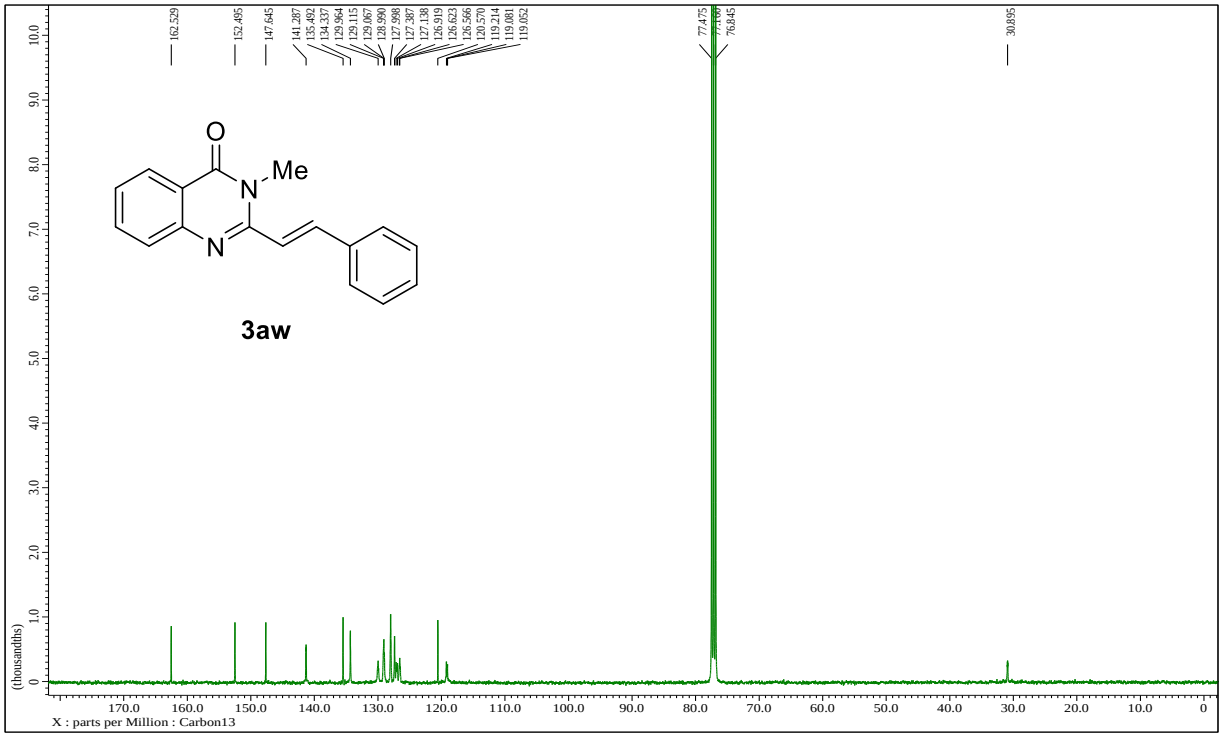
3av ^{13}C-NMR (100 MHz, $CDCl_3$)



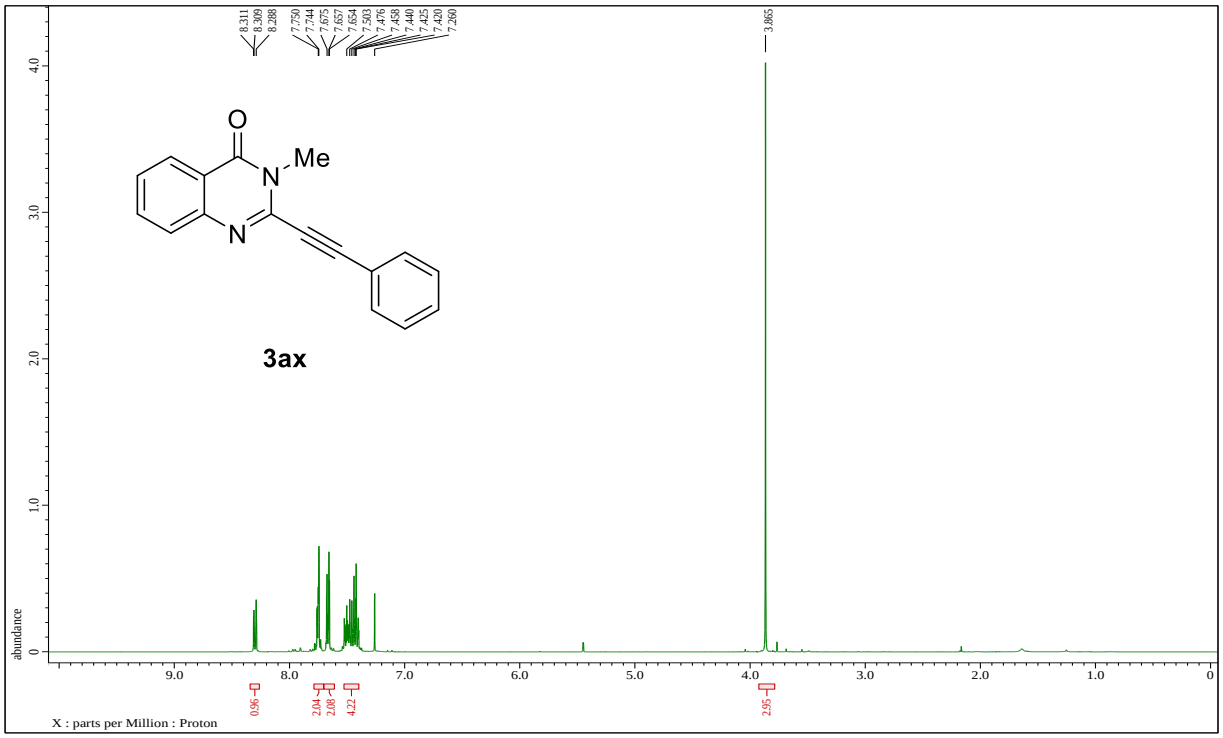
3aw ^{1}H-NMR (400 MHz, $CDCl_3$)



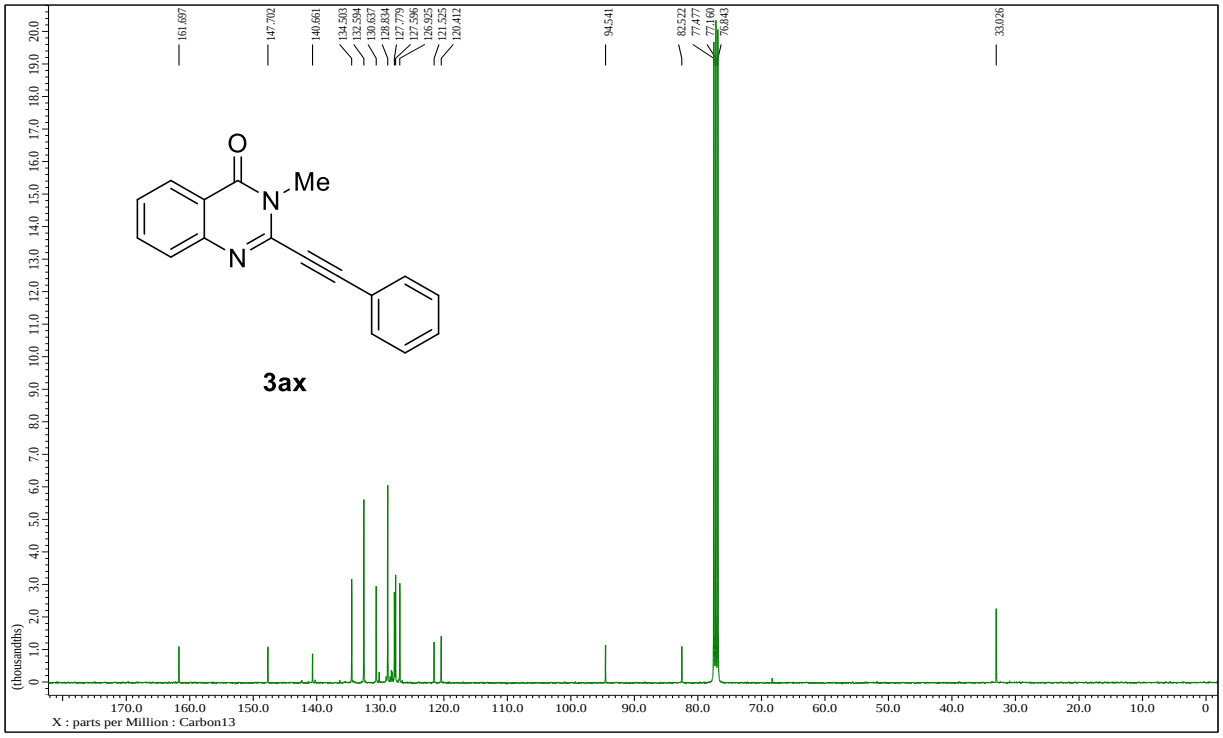
3aw ^{13}C-NMR (100 MHz, $CDCl_3$)



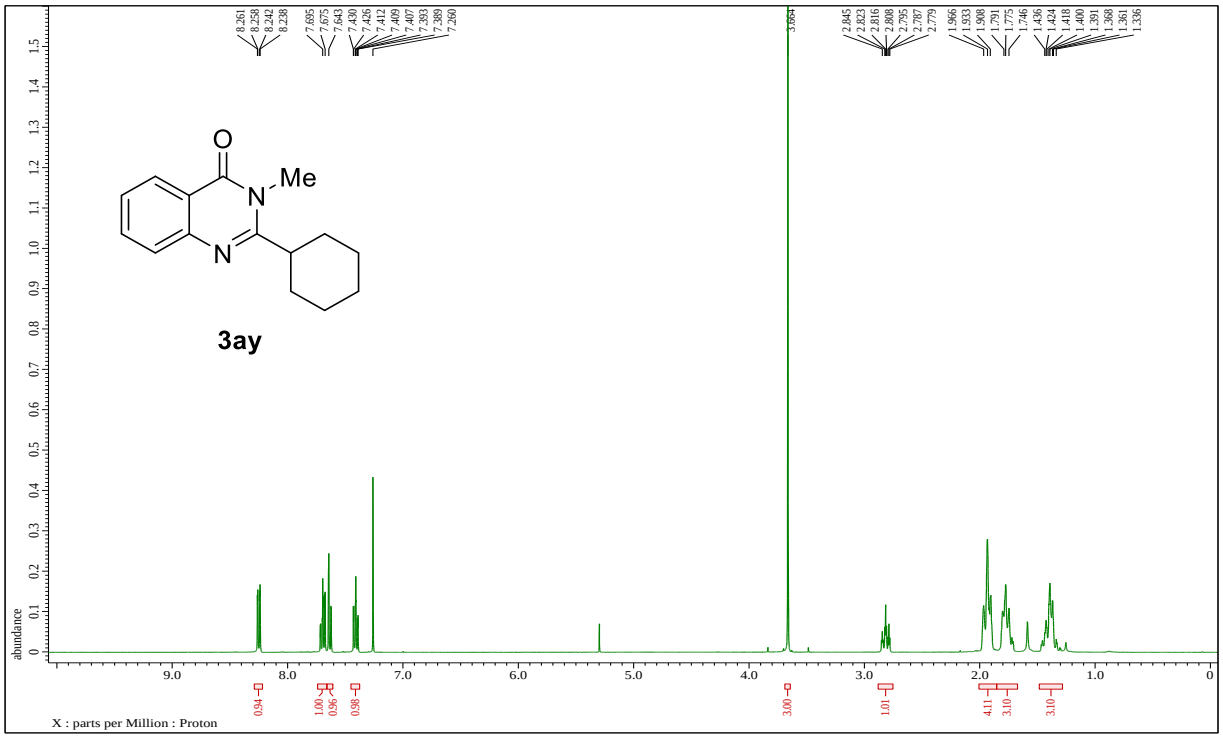
3ax ^{1}H-NMR (400 MHz, $CDCl_3$)



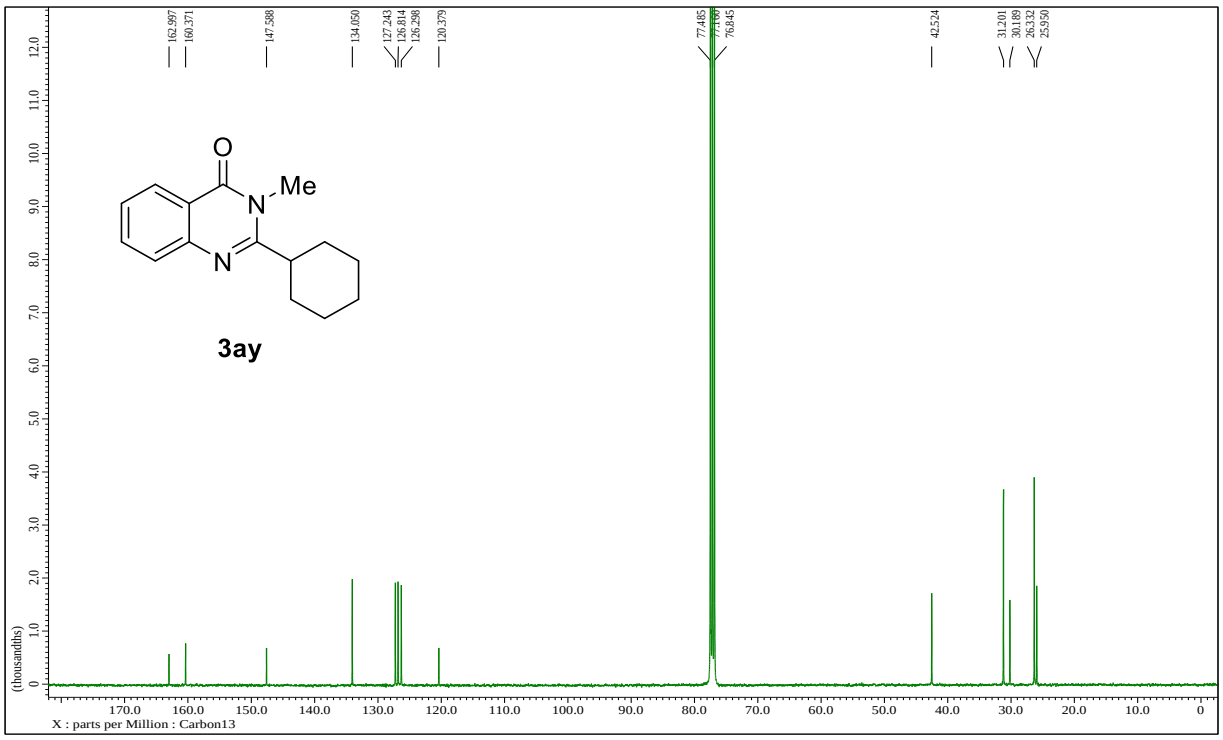
3ax ^{13}C-NMR (100 MHz, $CDCl_3$)



3ay ^{1}H-NMR (400 MHz, $CDCl_3$)



3ay ^{13}C-NMR (100 MHz, $CDCl_3$)



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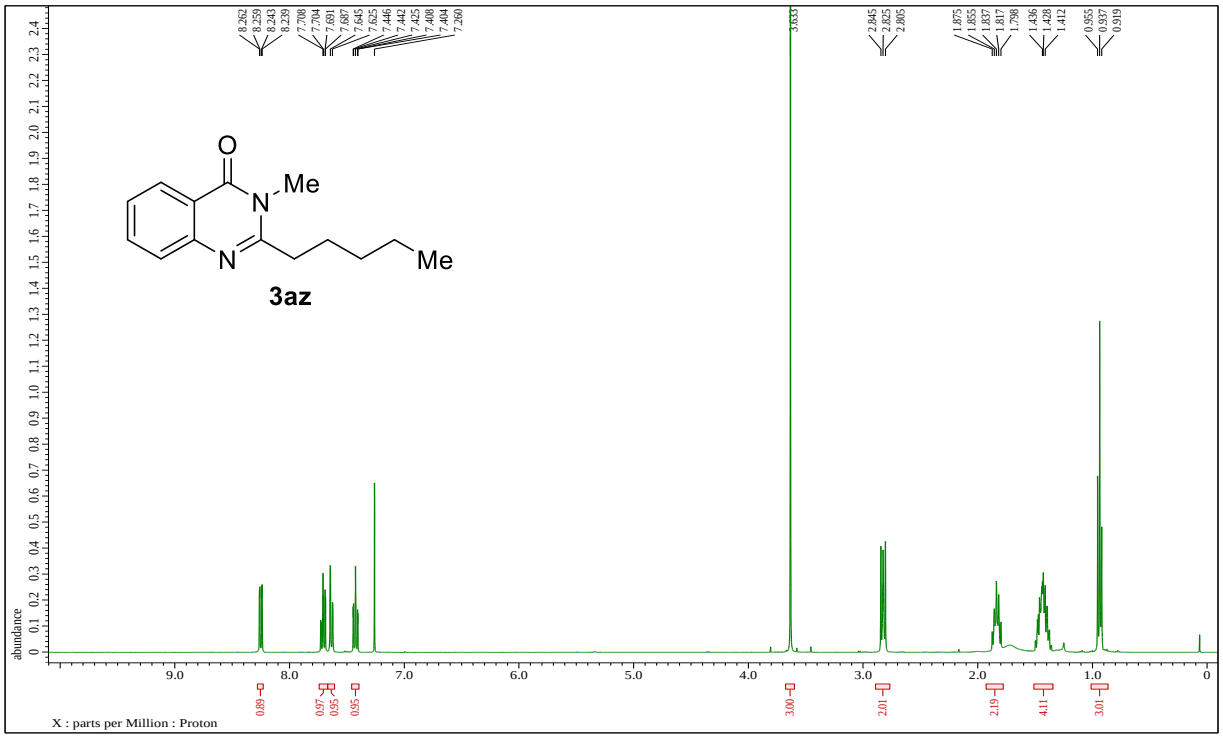

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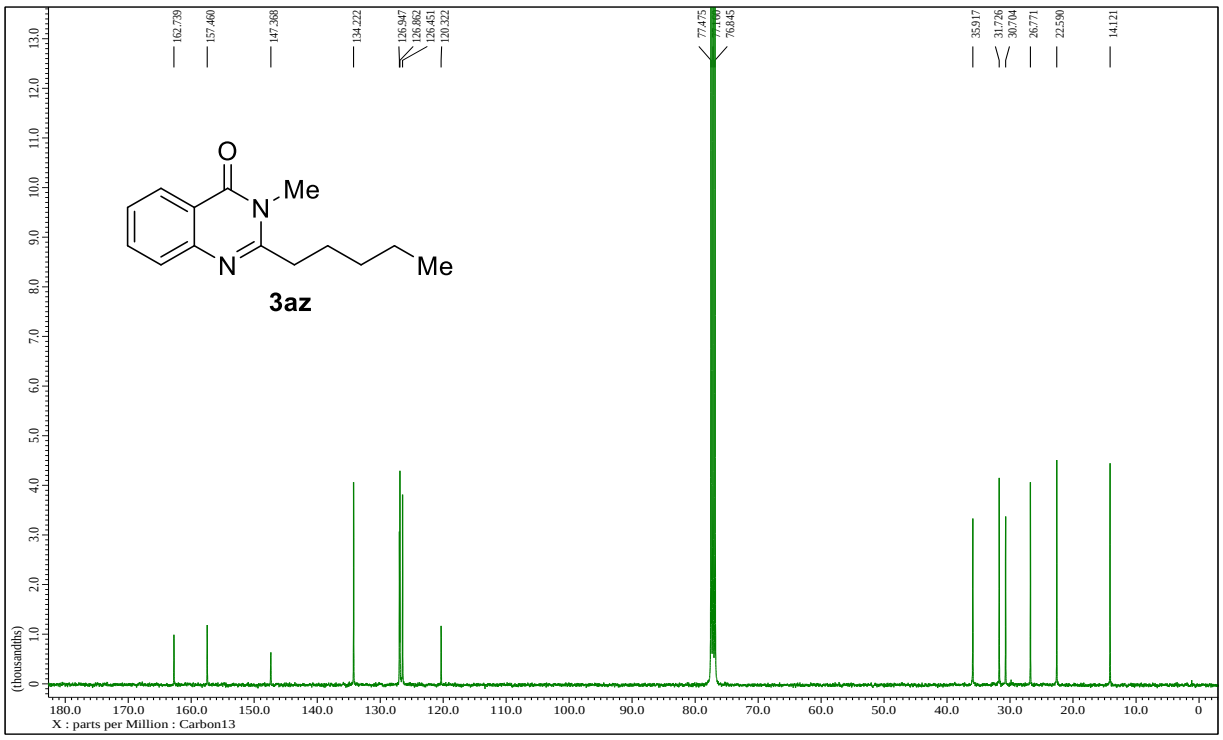
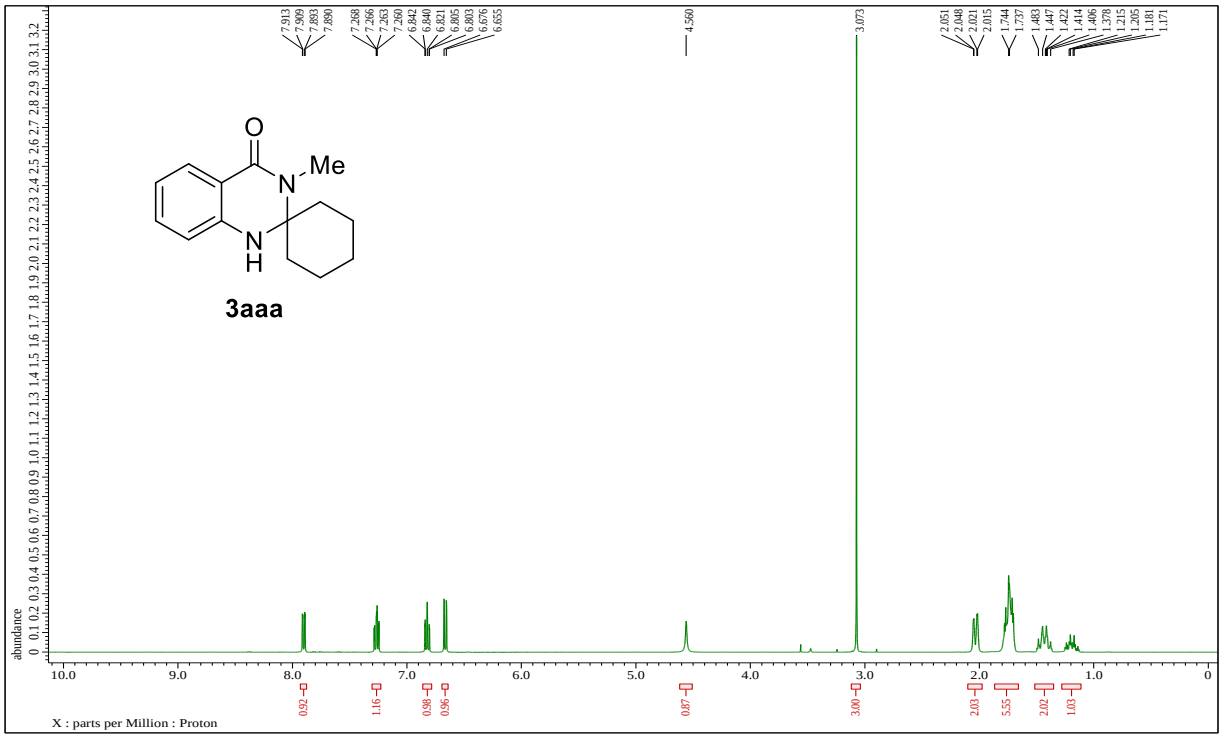
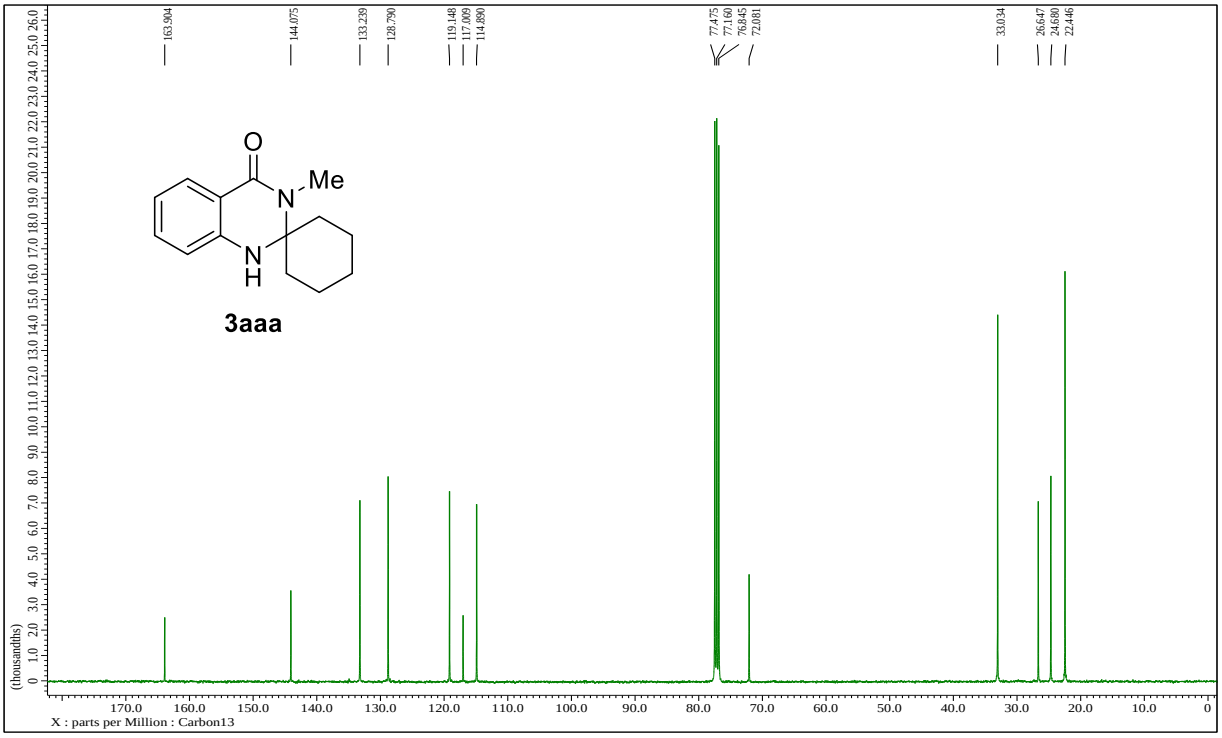


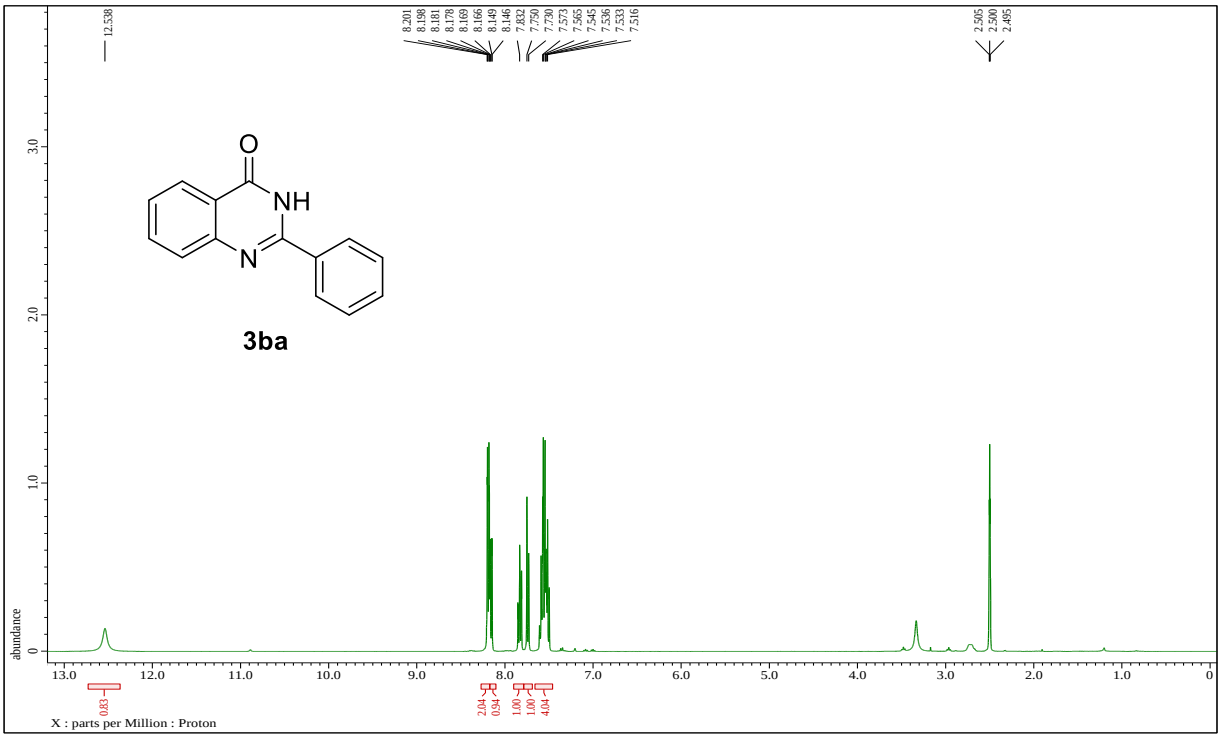
3aaa ^{1}H-NMR (400 MHz, $CDCl_3$)



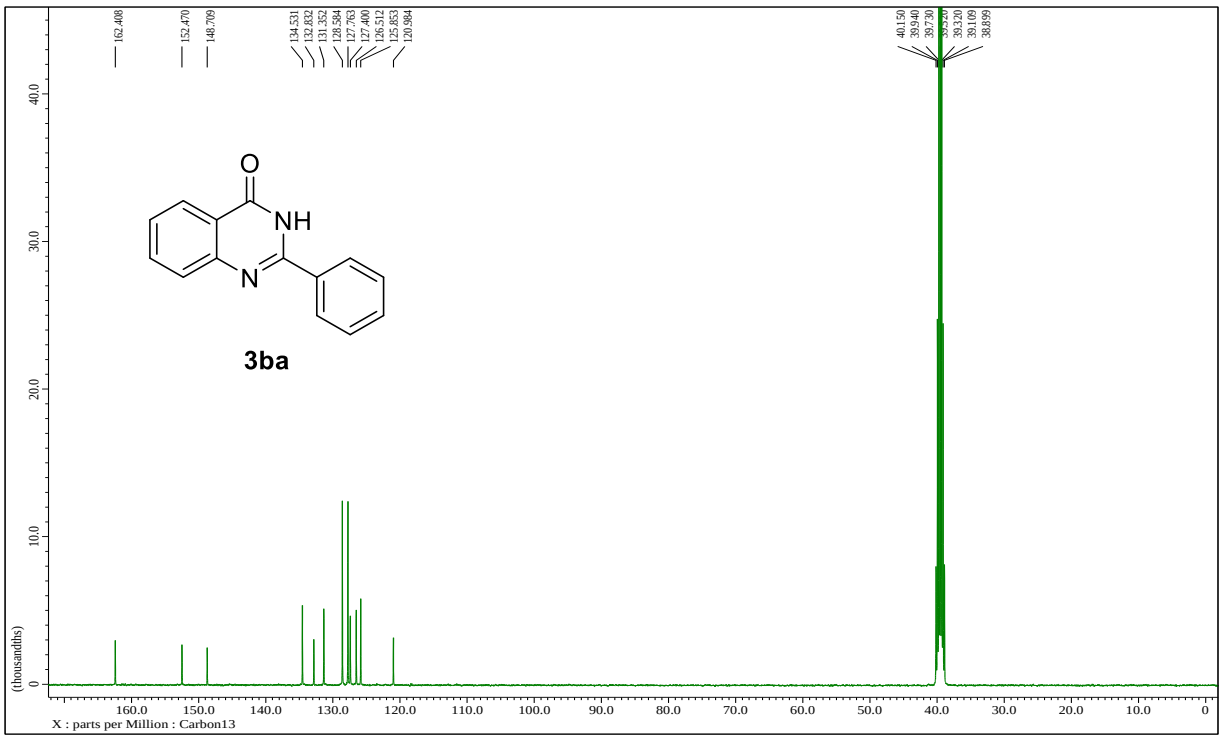
3aaa ^{13}C-NMR (100 MHz, $CDCl_3$)



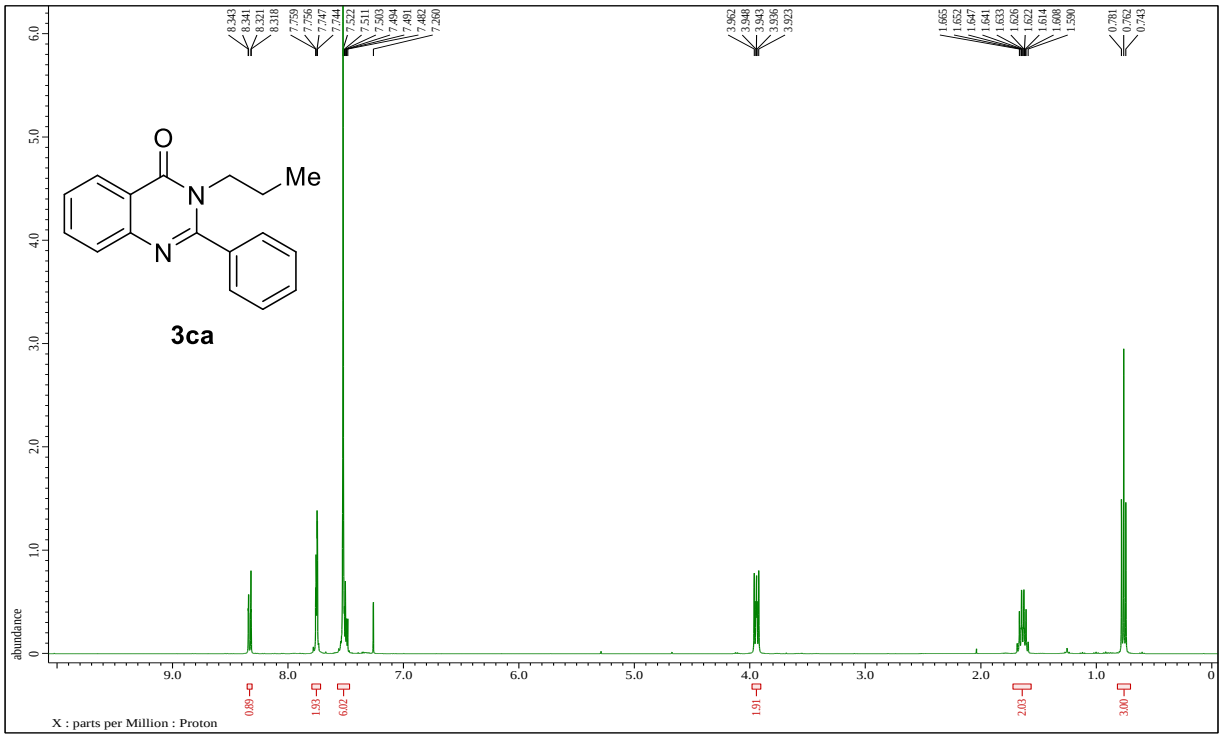
3ba ^{1}H-NMR (400 MHz, $CDCl_3$)



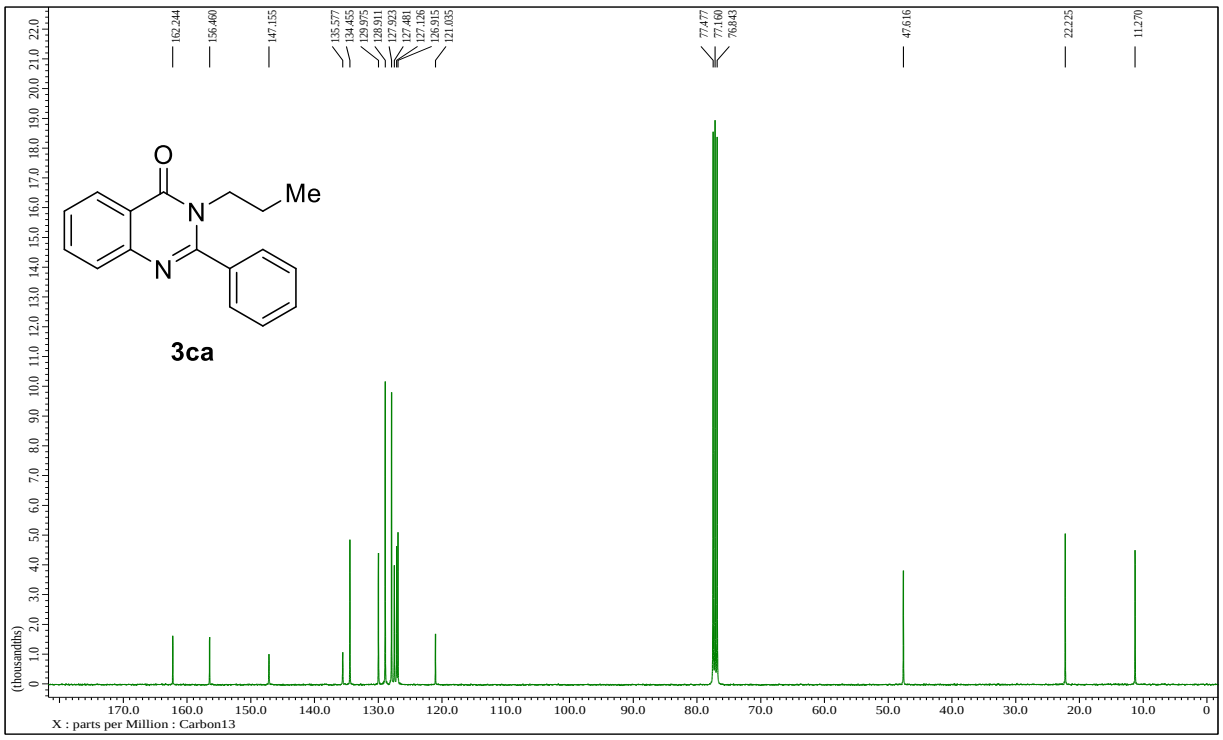
3ba ^{13}C-NMR (100 MHz, $CDCl_3$)



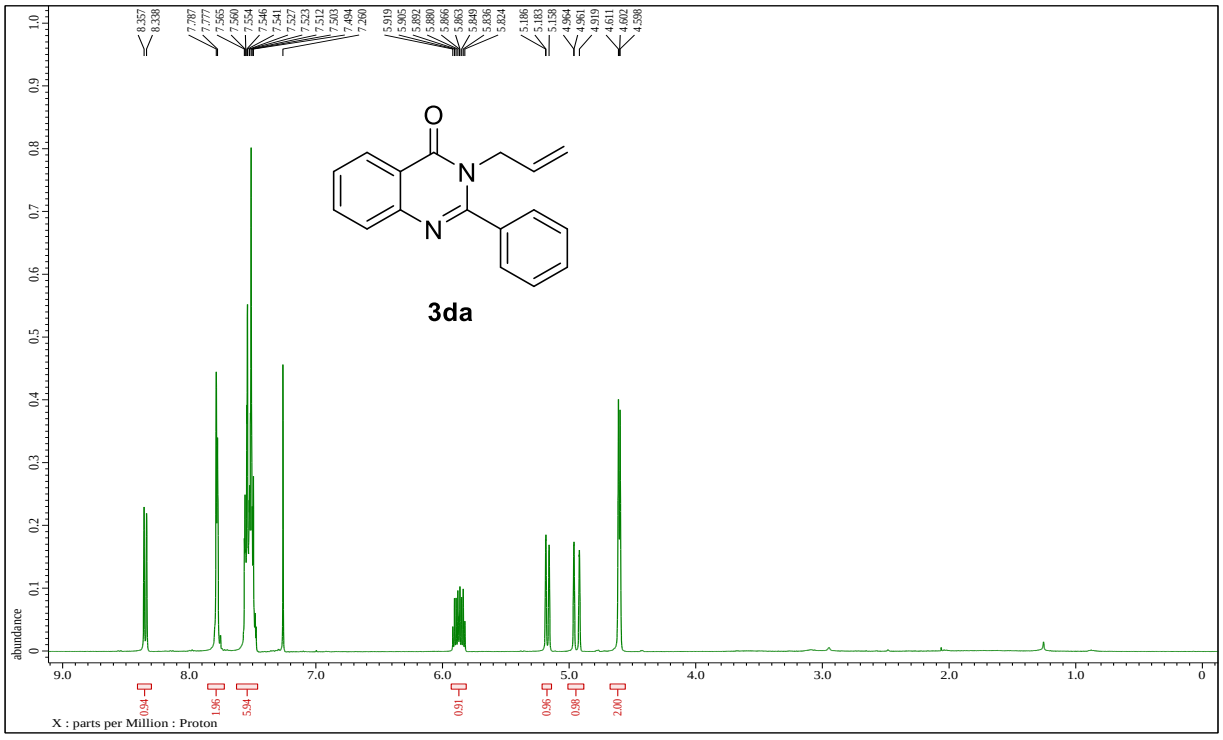
3ca ^{1}H-NMR (400 MHz, $CDCl_3$)



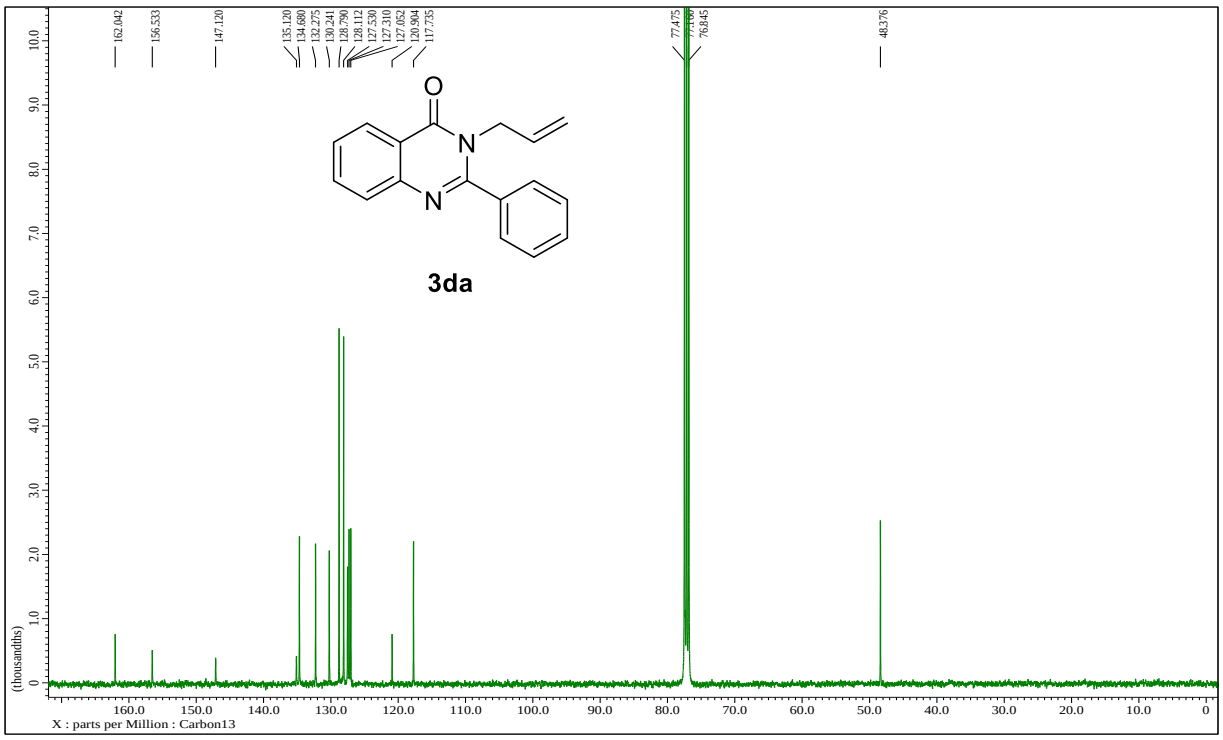
3ca ^{13}C-NMR (100 MHz, $CDCl_3$)



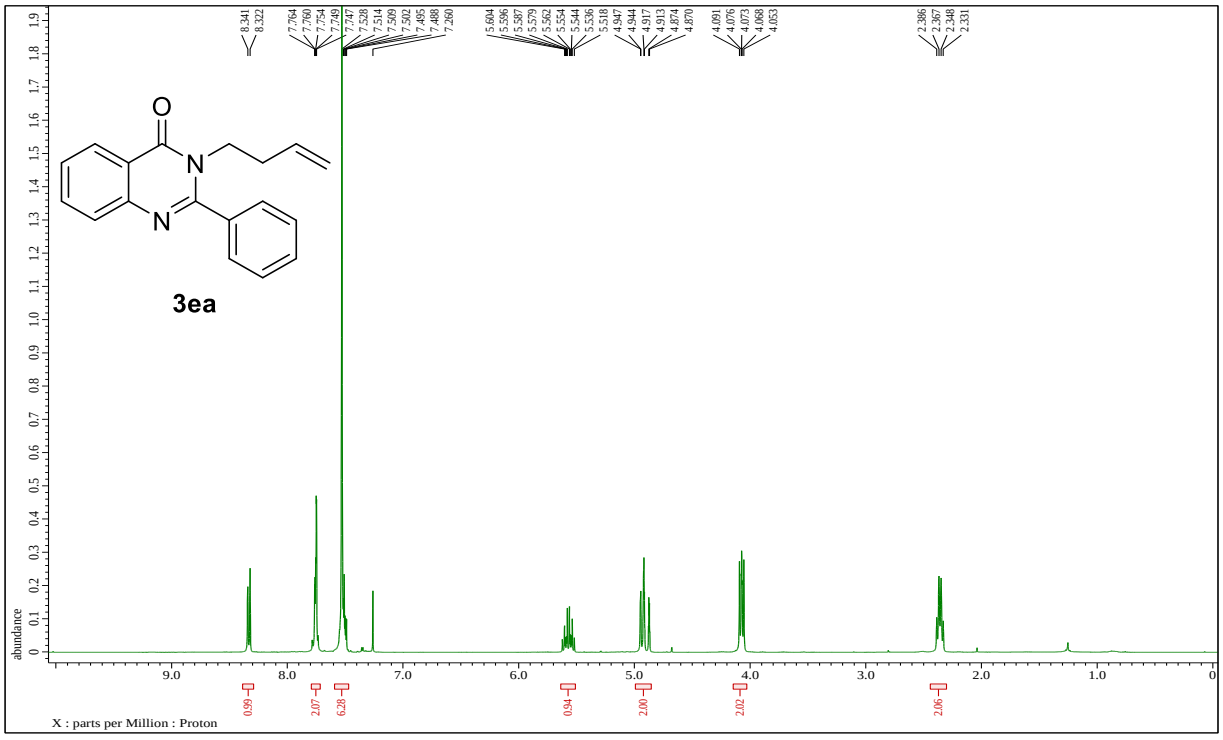
3da ^{1}H-NMR (400 MHz, $CDCl_3$)



3da ^{13}C-NMR (100 MHz, $CDCl_3$)



3ea ^{1}H-NMR (400 MHz, $CDCl_3$)



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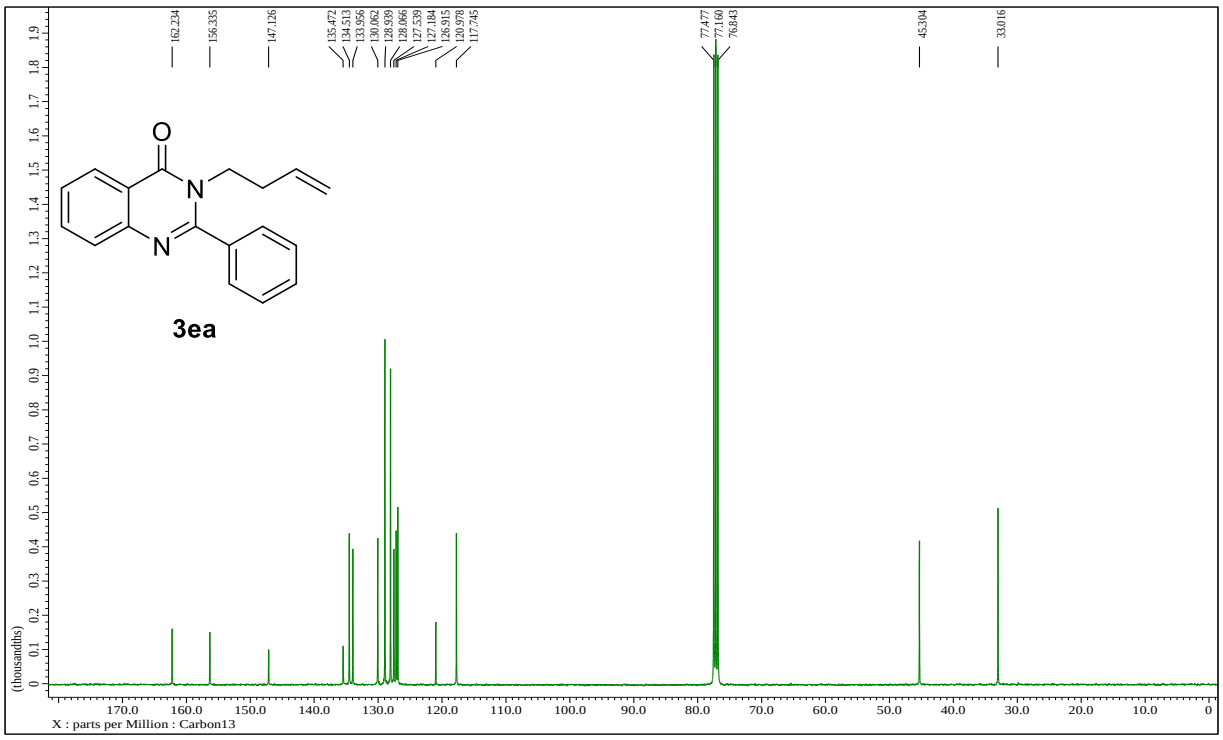
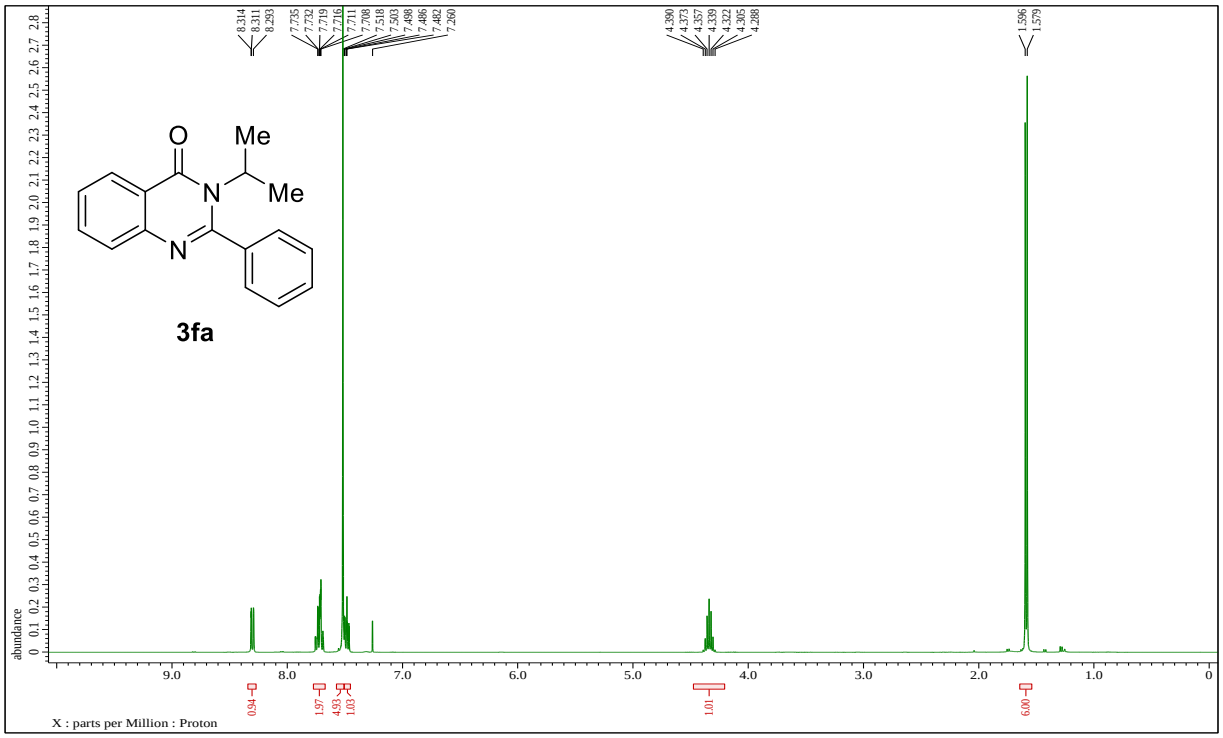
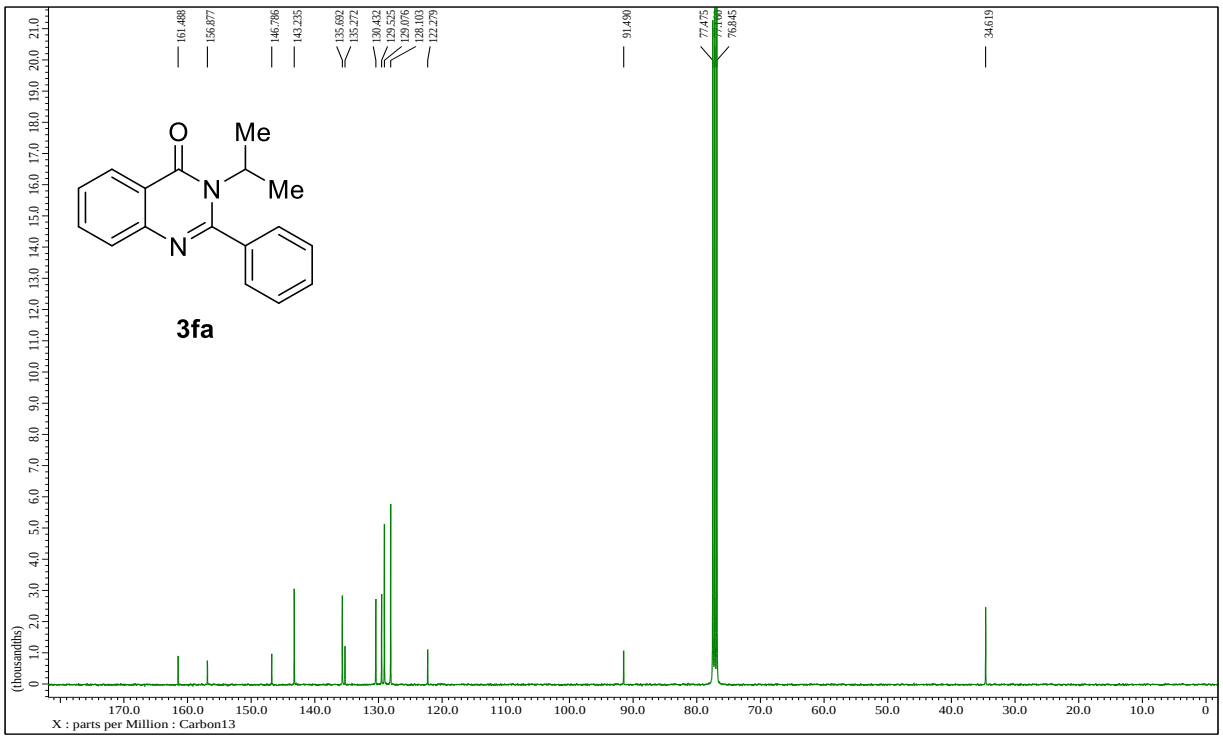


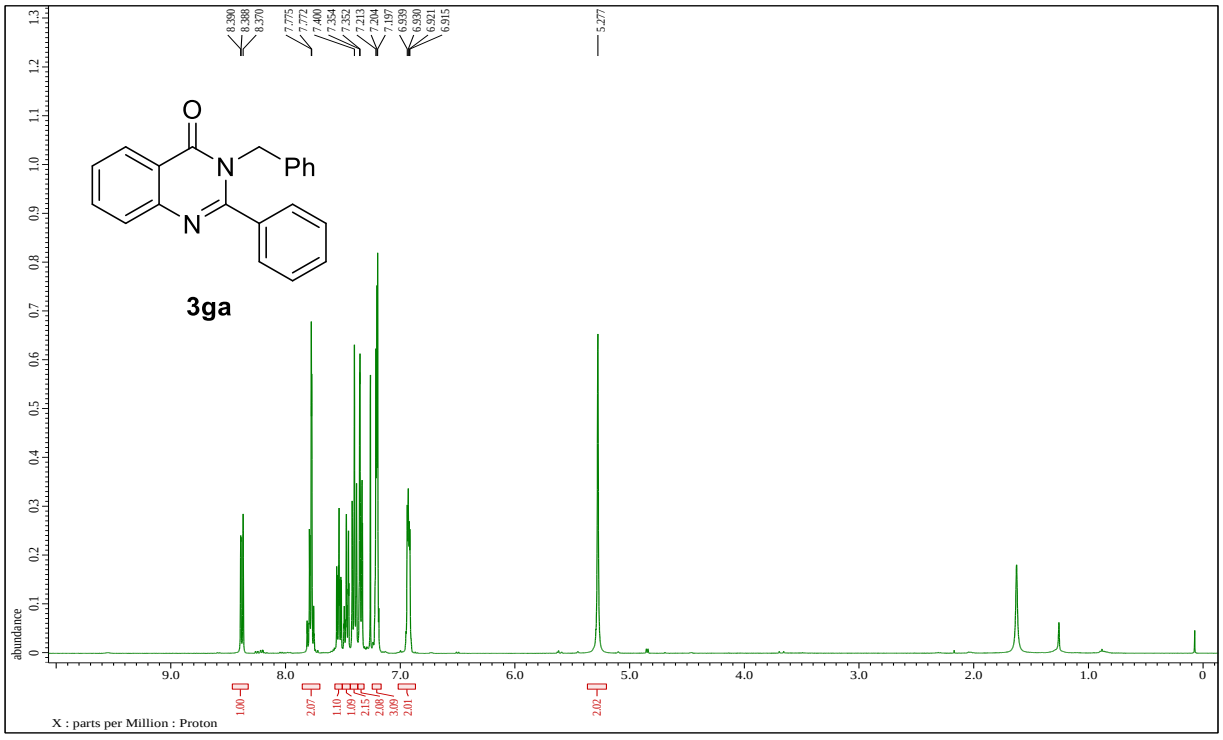
3fa ^{1}H-NMR (400 MHz, $CDCl_3$)



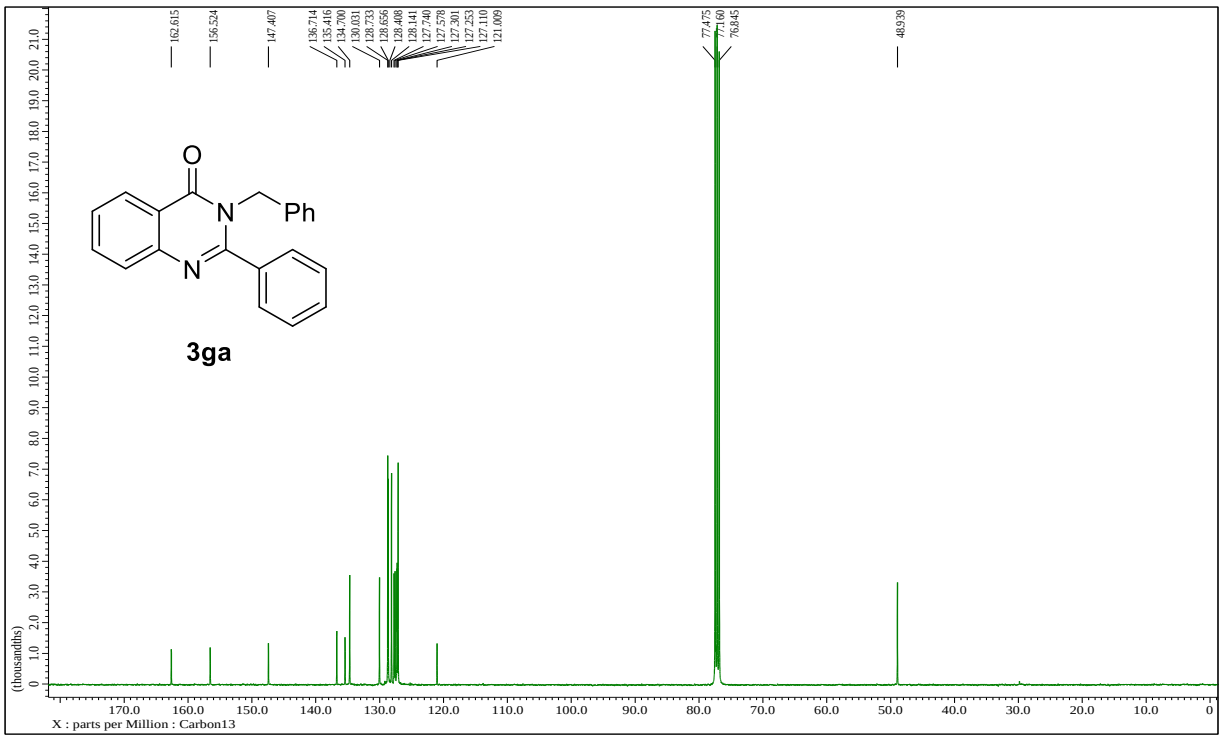
3fa ^{13}C-NMR (100 MHz, $CDCl_3$)



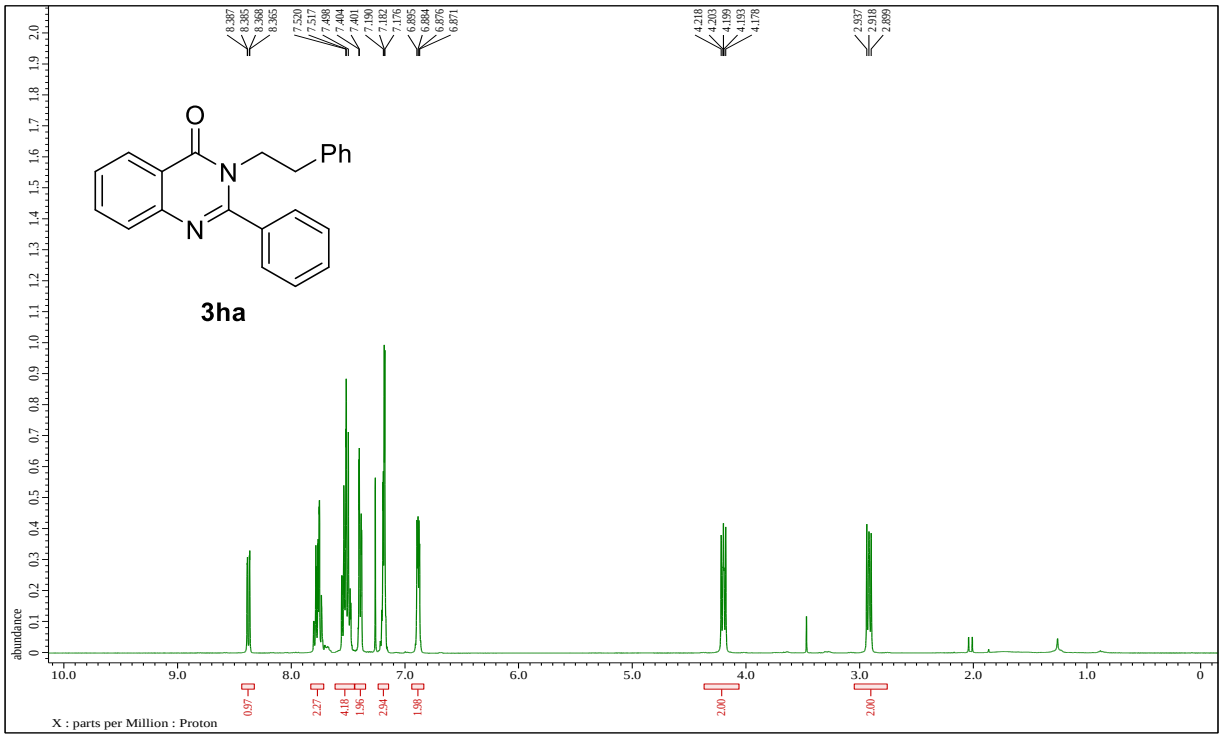
3ga ^{1}H-NMR (400 MHz, $CDCl_3$)



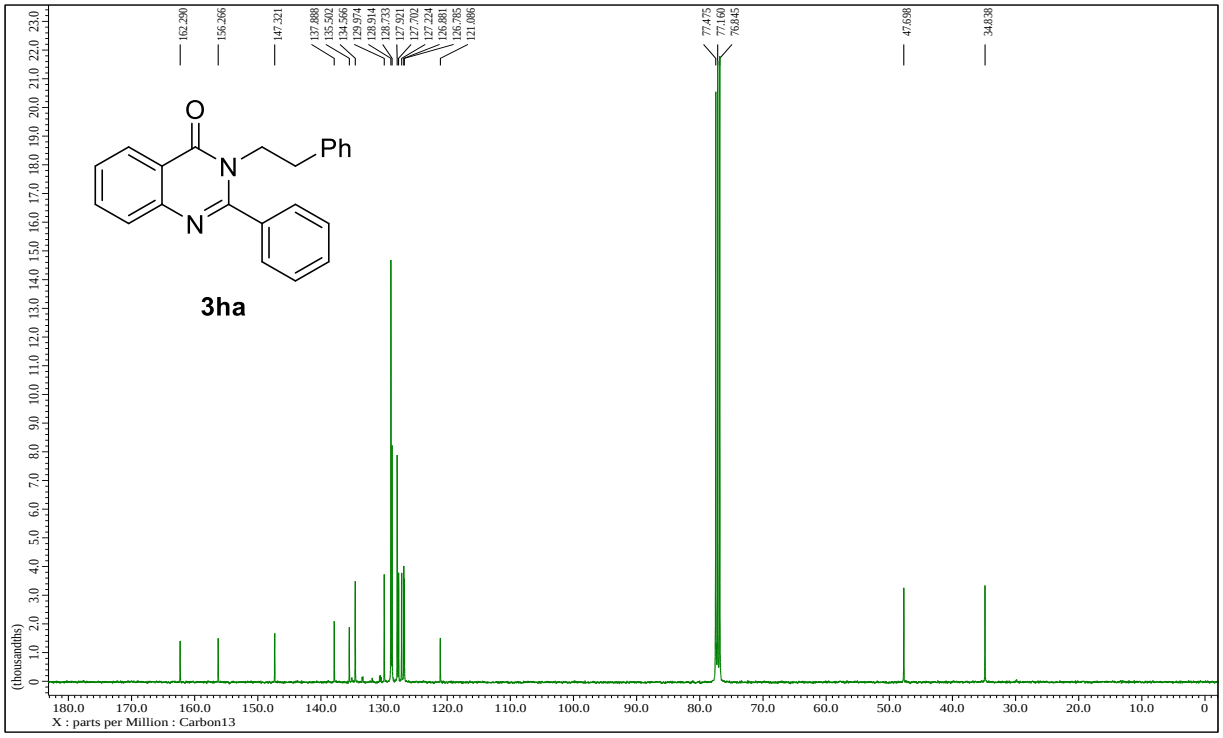
3ga ^{13}C-NMR (100 MHz, $CDCl_3$)



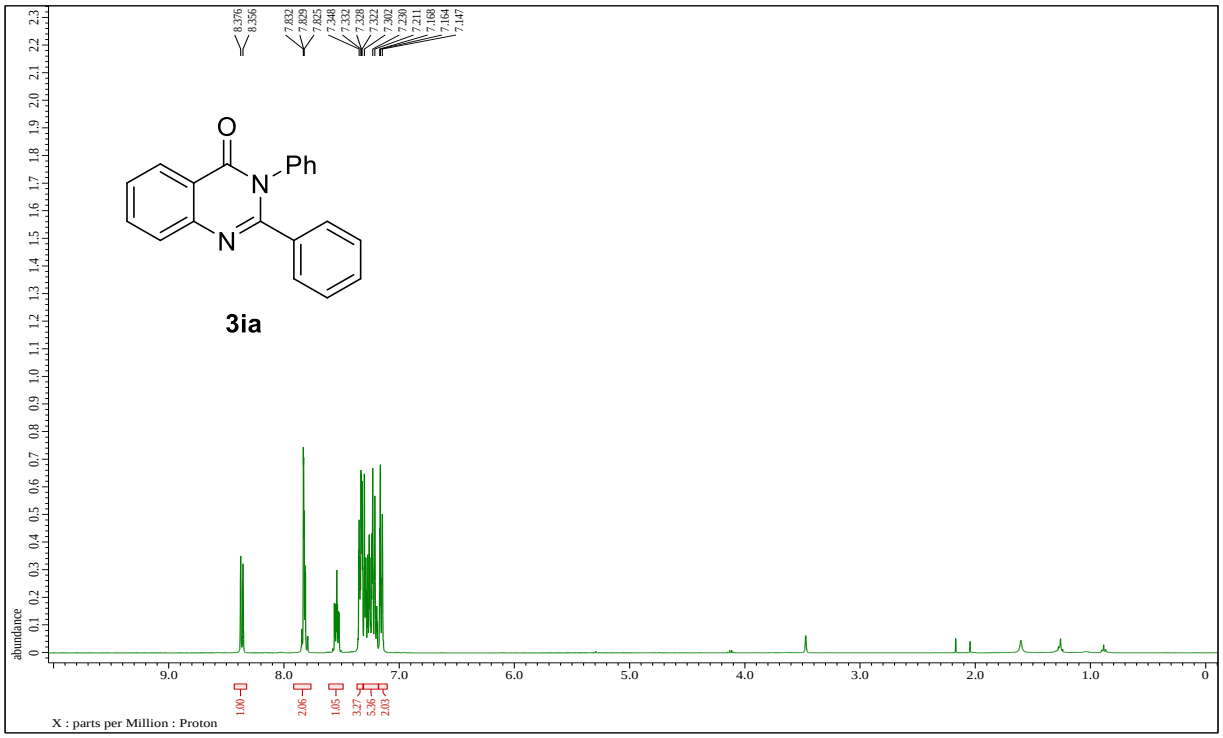
3ha ^{1}H-NMR (400 MHz, $CDCl_3$)



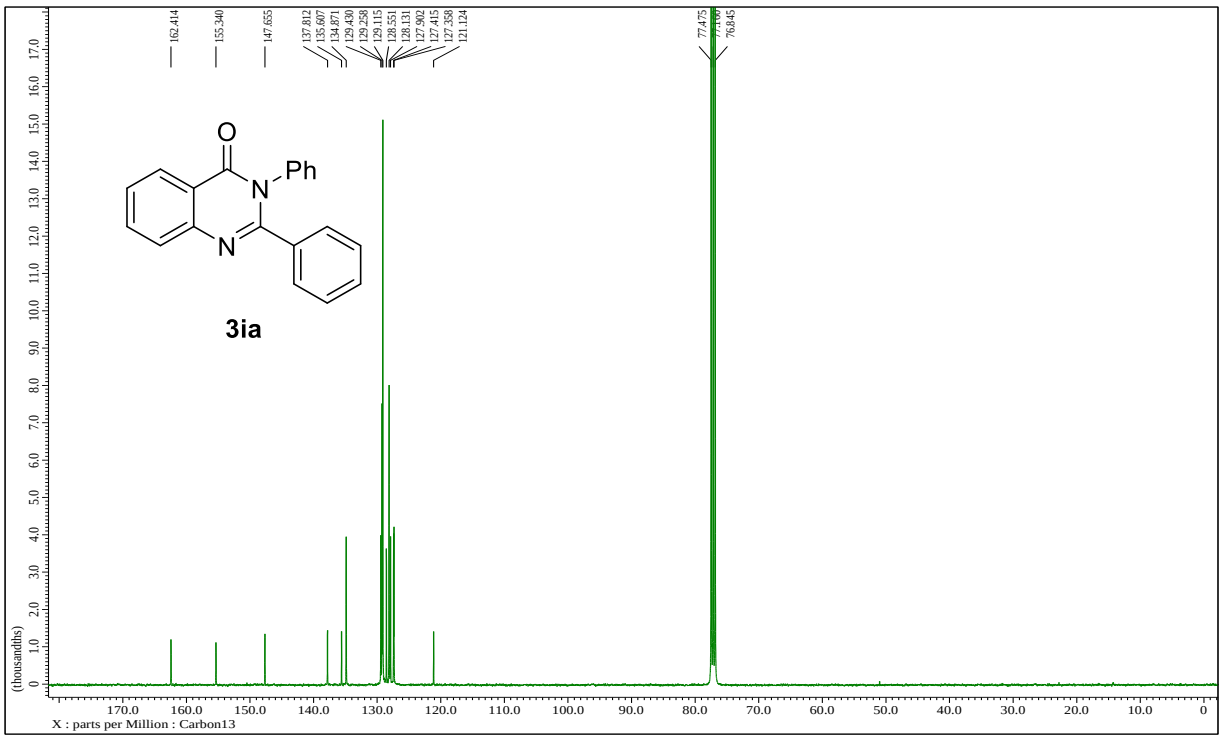
3ha ^{13}C-NMR (100 MHz, $CDCl_3$)



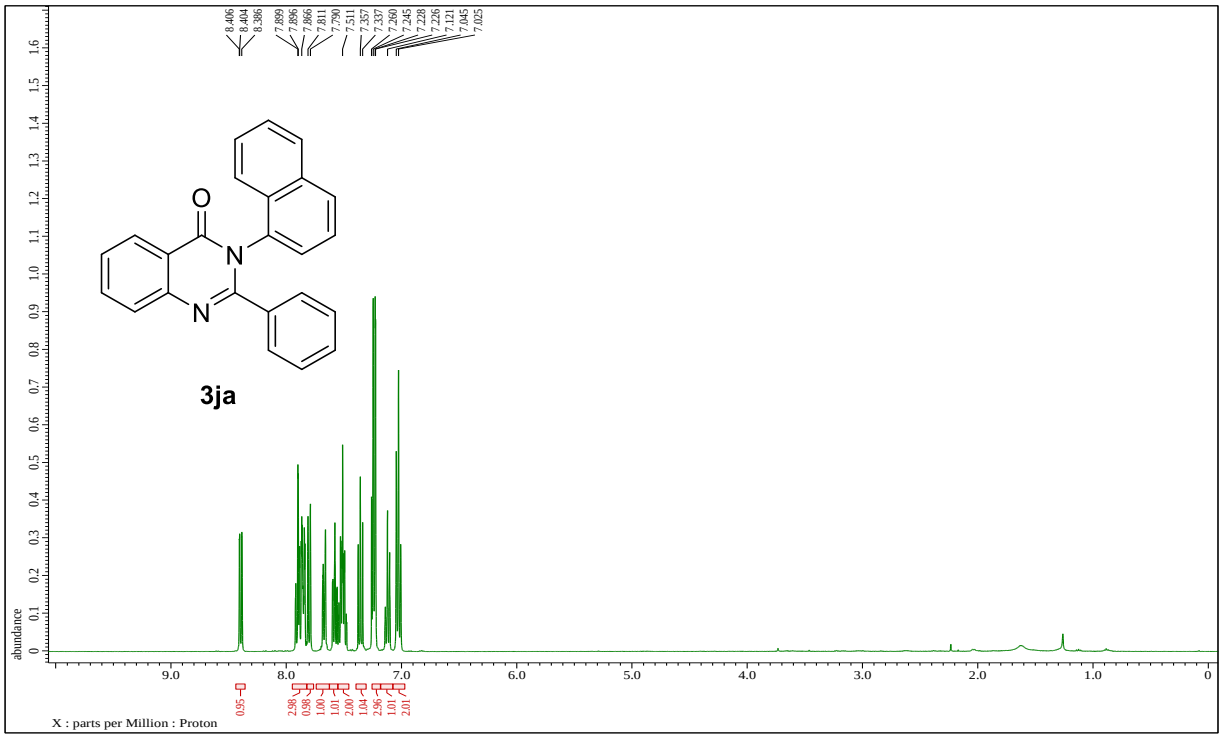
3ia ^{1}H-NMR (400 MHz, $CDCl_3$)



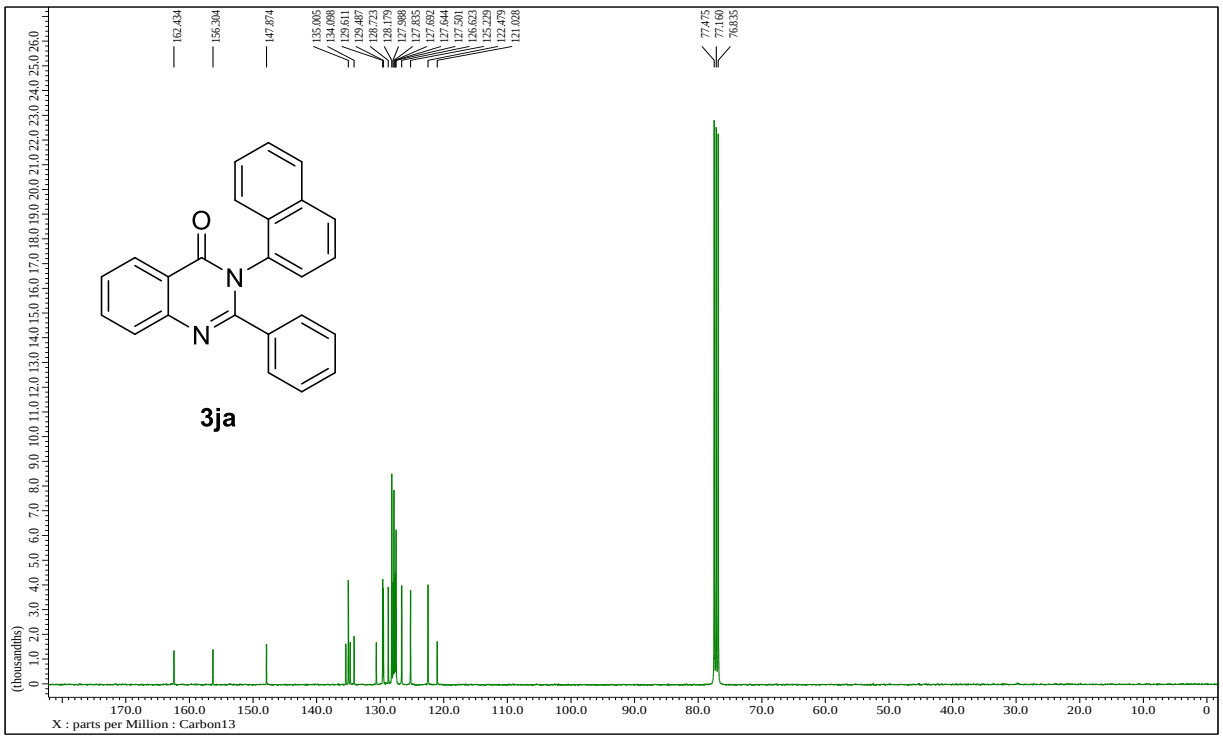
3ia ^{13}C-NMR (100 MHz, $CDCl_3$)



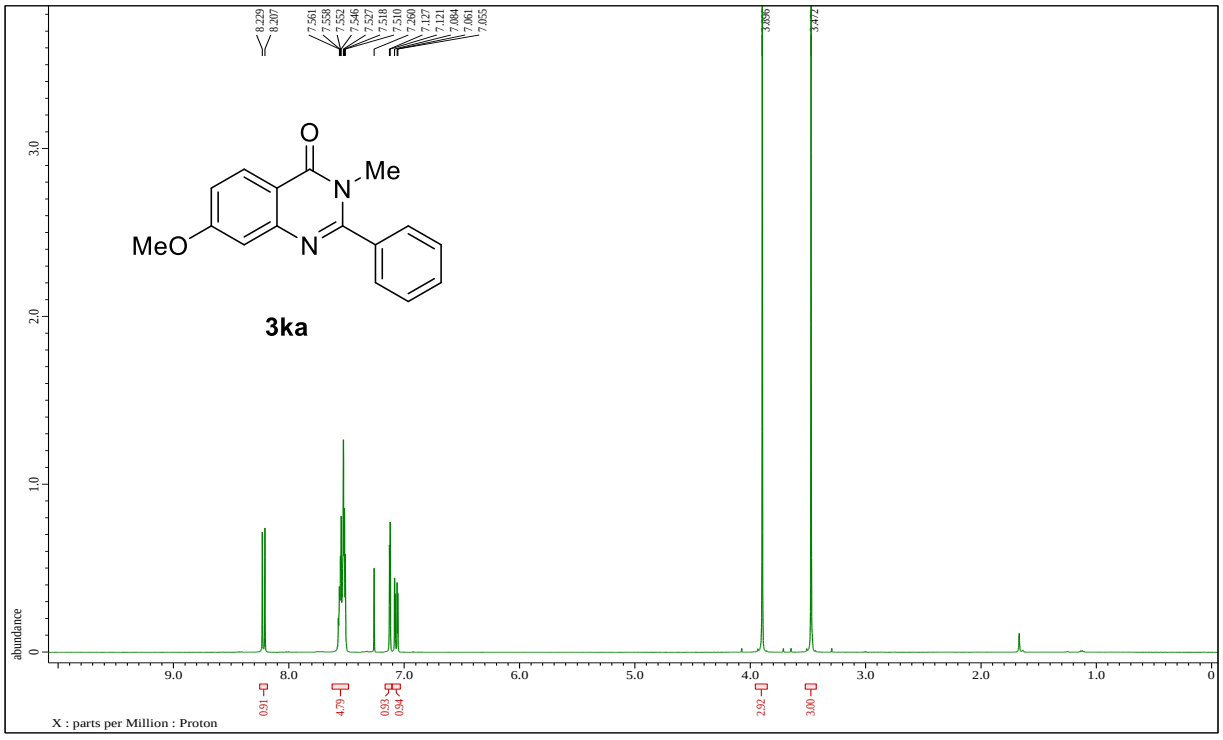
3ja ^{1}H-NMR (400 MHz, $CDCl_3$)



3ja ^{13}C-NMR (100 MHz, $CDCl_3$)



3ka ^{1}H-NMR (400 MHz, $CDCl_3$)



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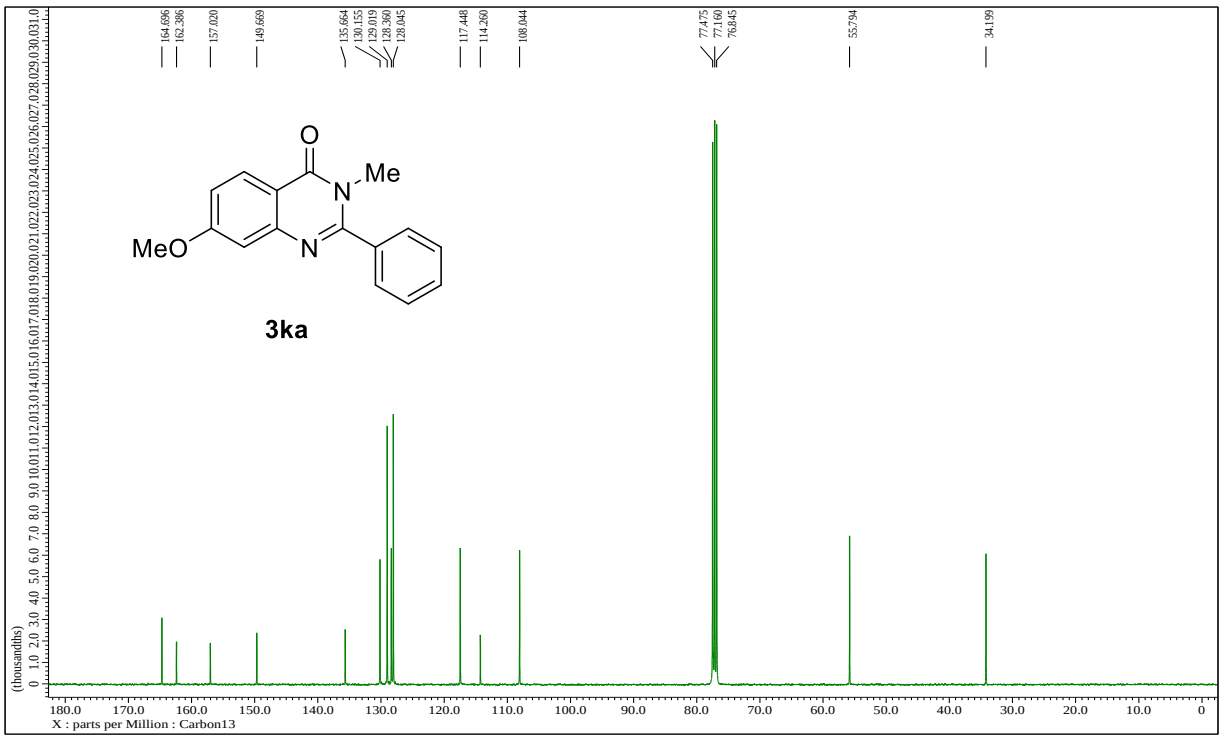
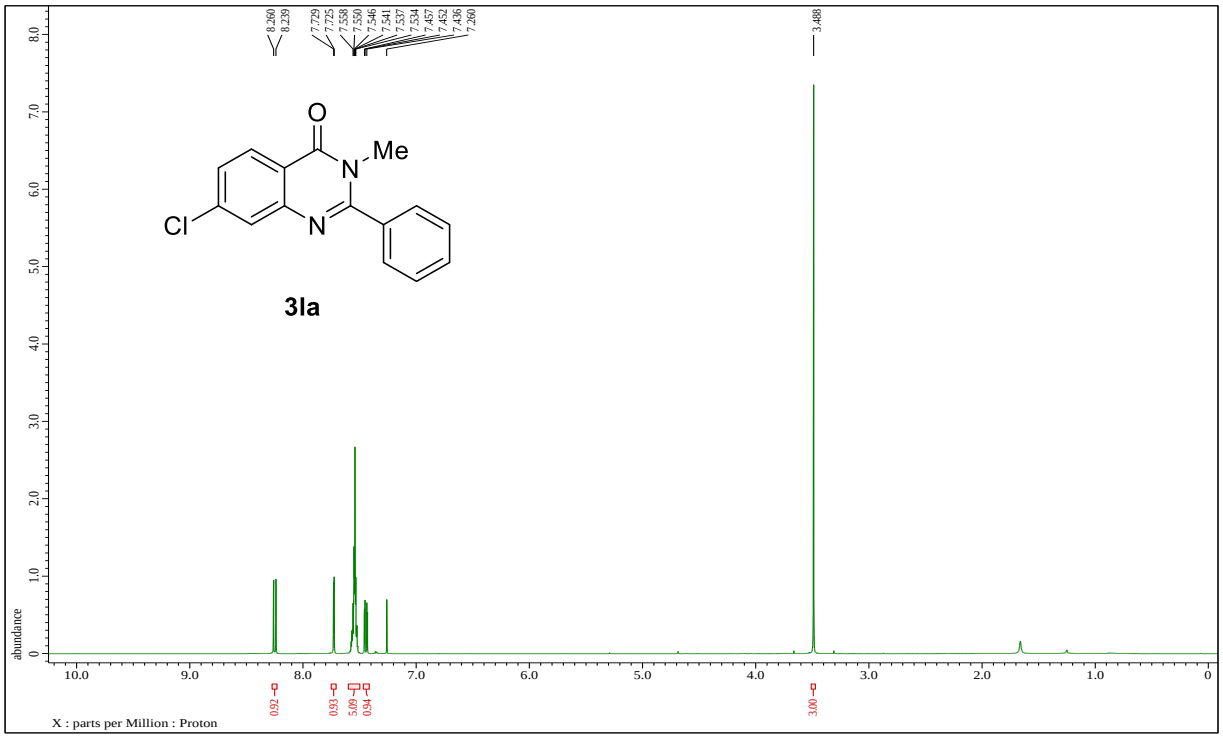


3la ^{1}H-NMR (400 MHz, $CDCl_3$)



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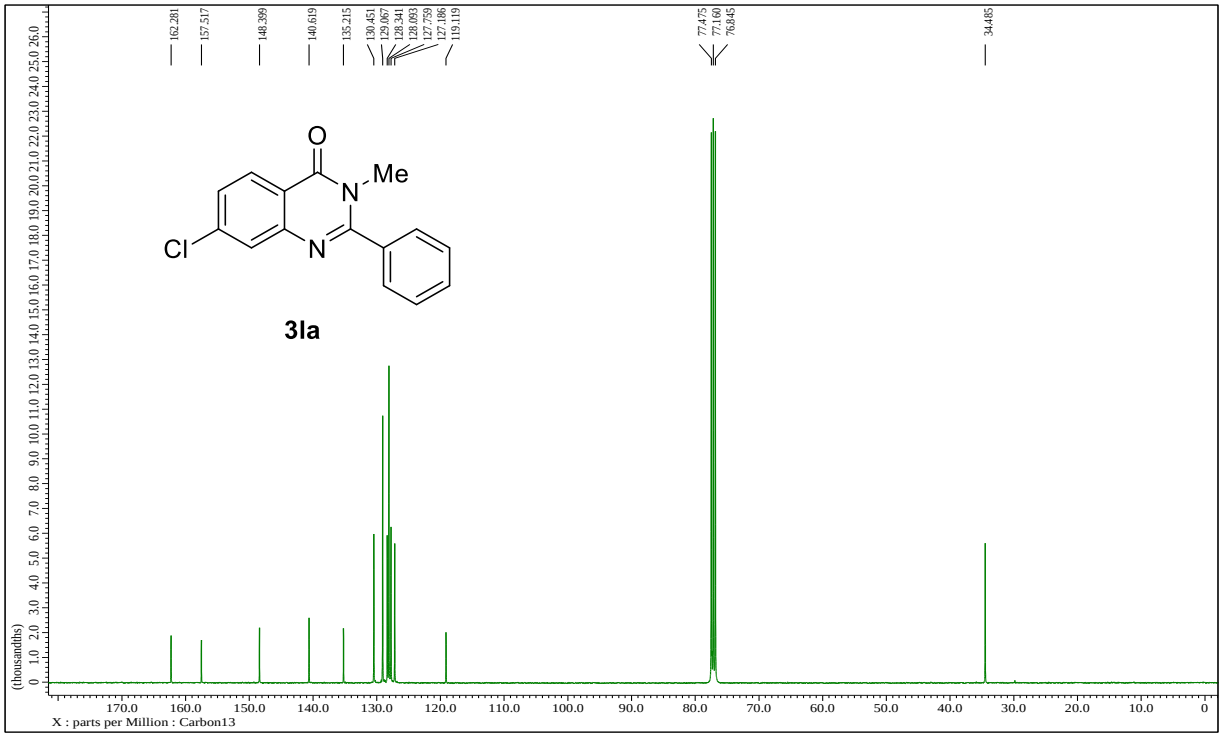
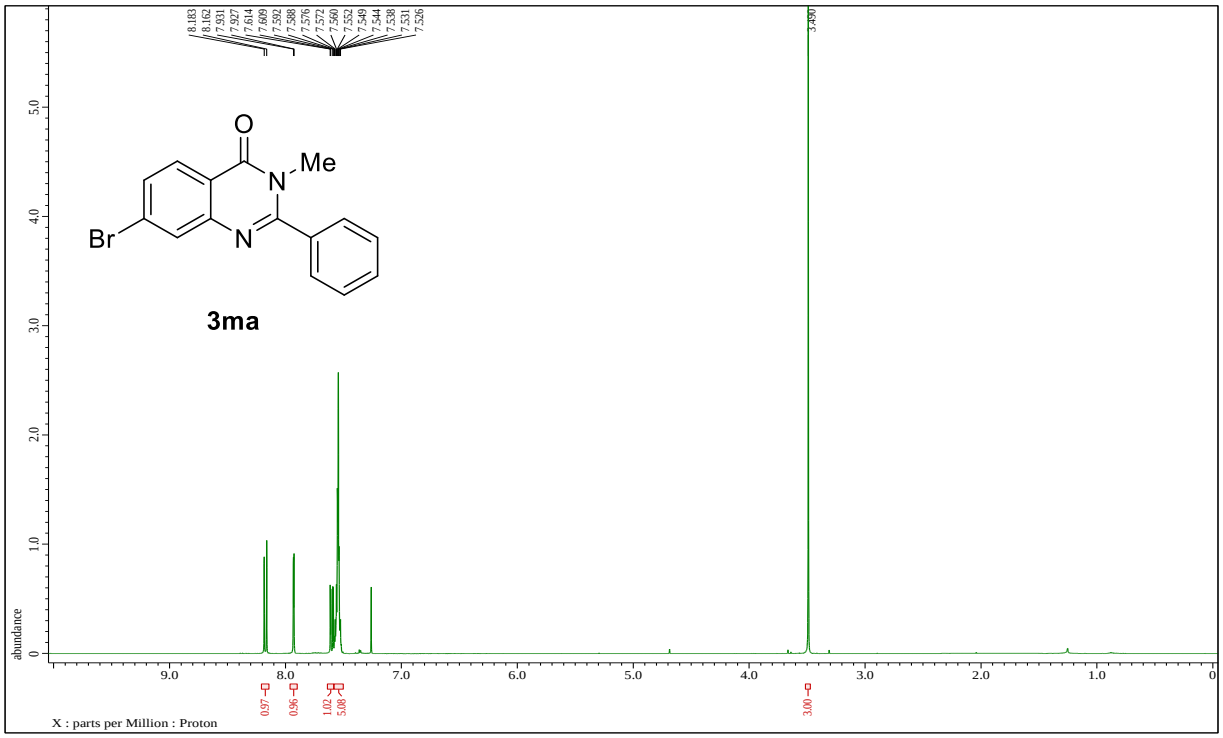
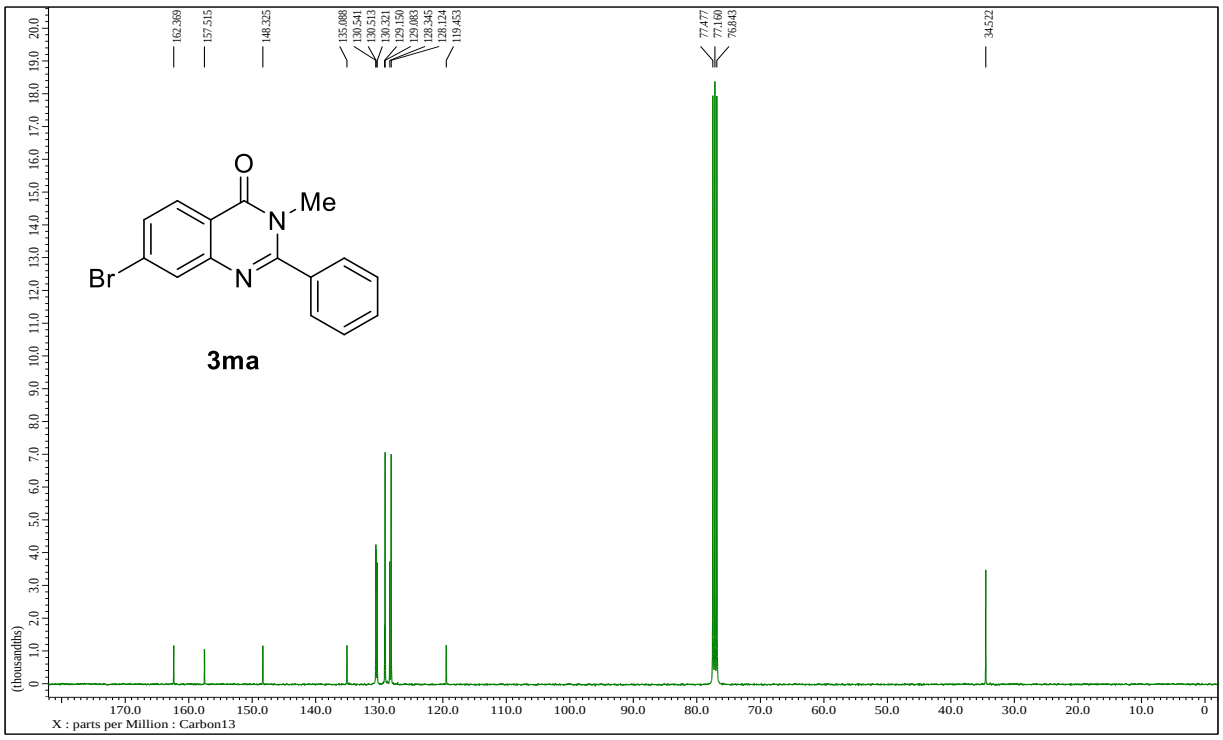


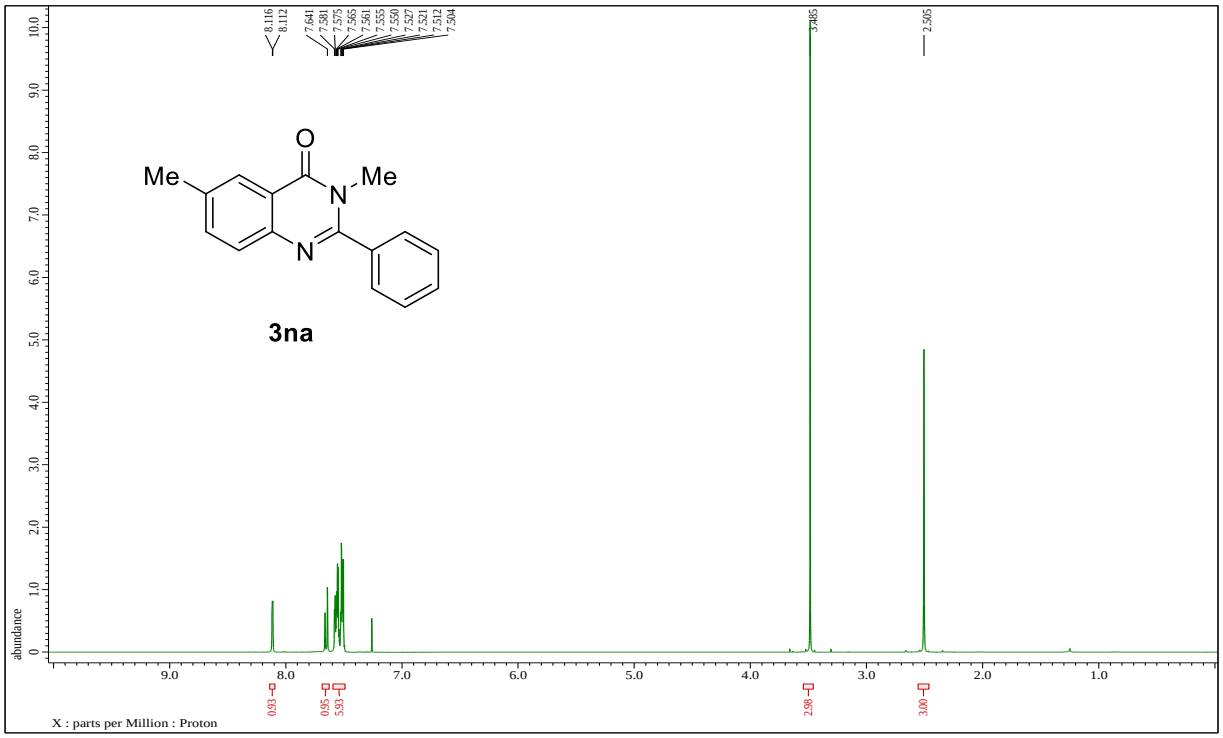
3ma ^{1}H-NMR (400 MHz, $CDCl_3$)



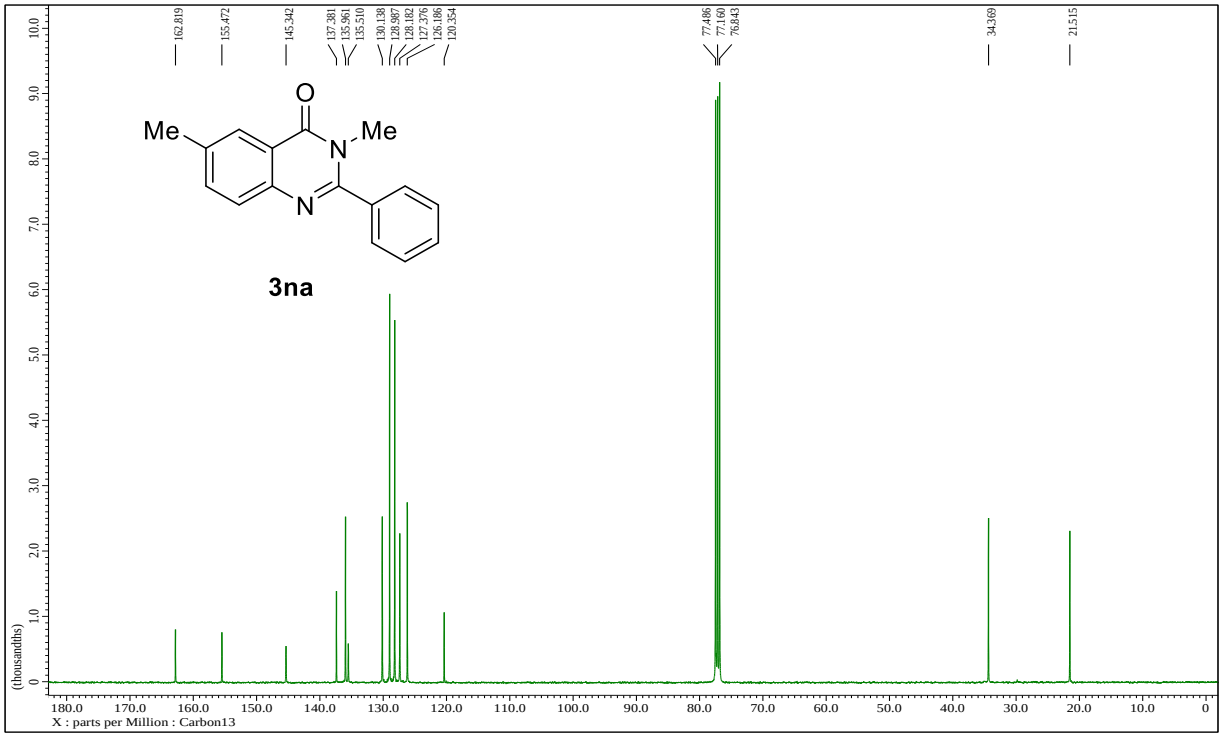
3ma ^{13}C-NMR (100 MHz, $CDCl_3$)



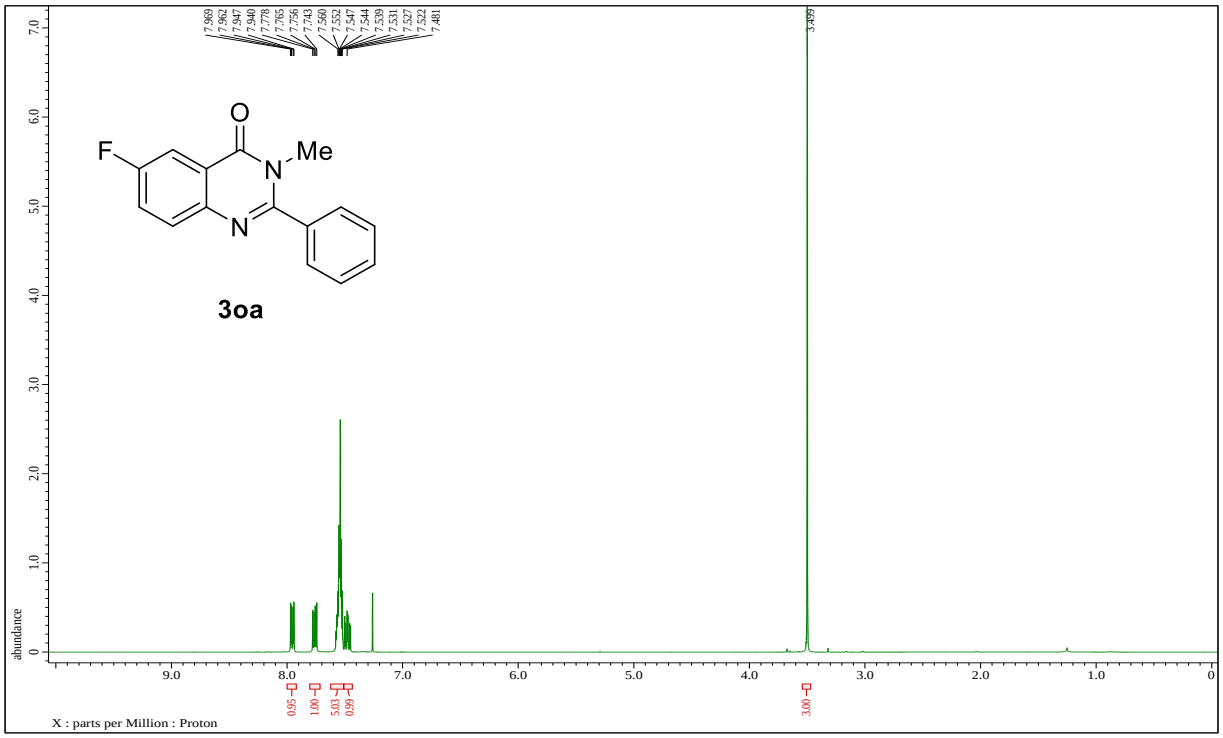
3na ^{1}H-NMR (400 MHz, $CDCl_3$)



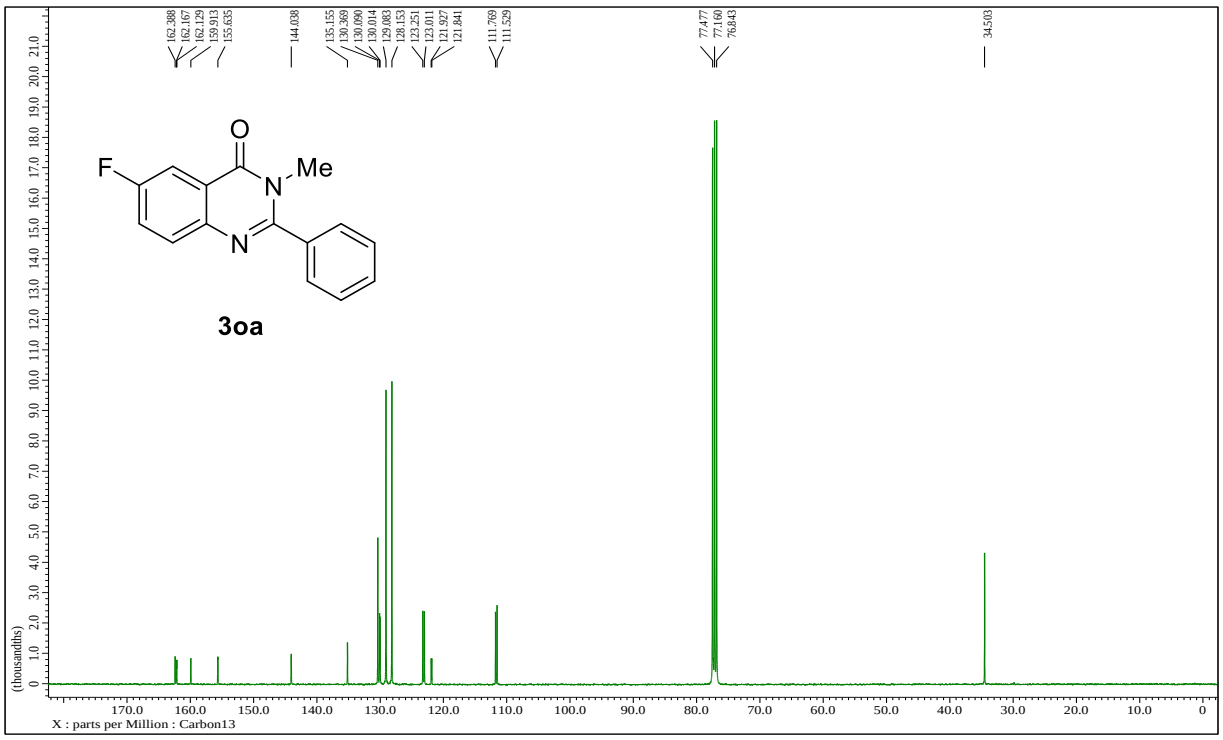
3na ^{13}C-NMR (100 MHz, $CDCl_3$)



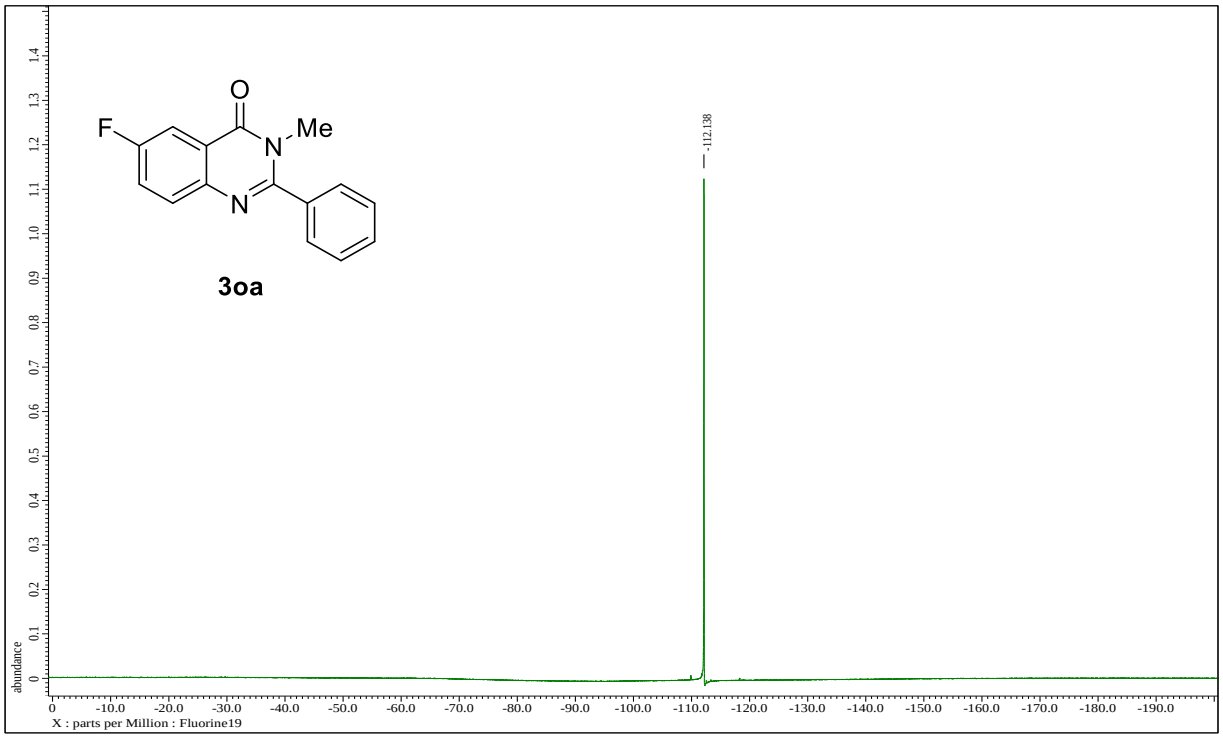
3oa ^{1}H-NMR (400 MHz, $CDCl_3$)



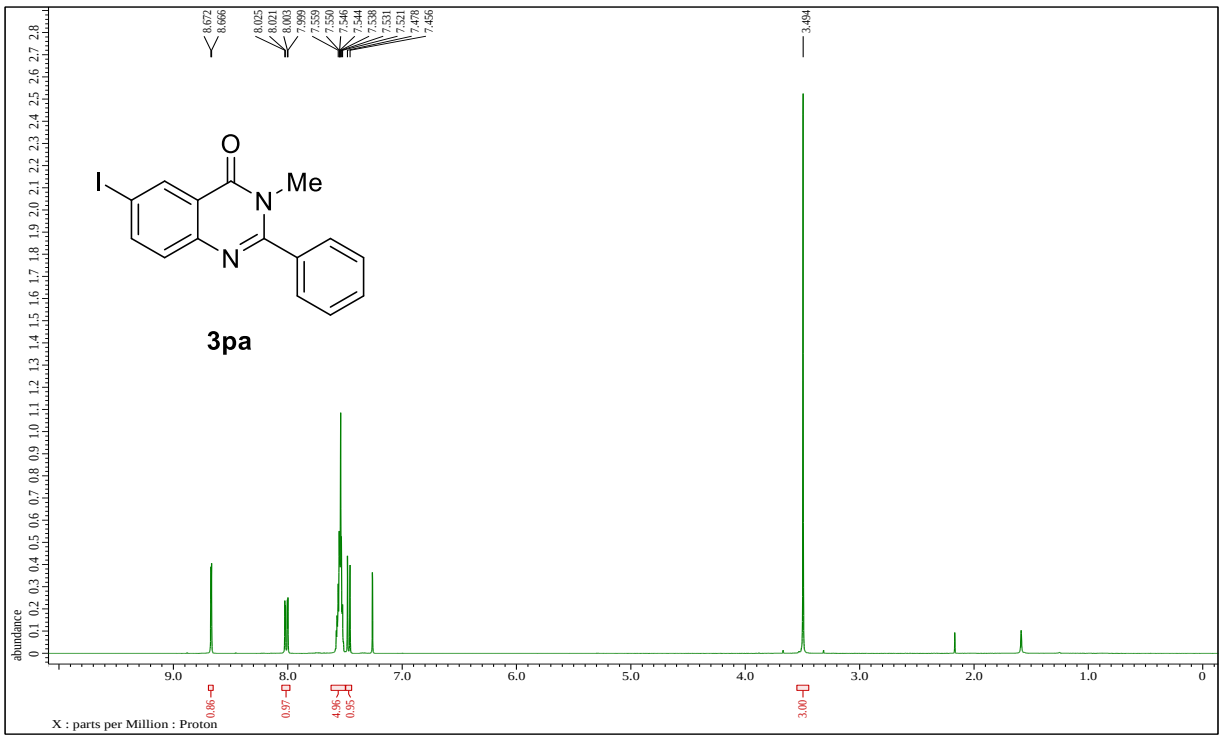
3oa ^{13}C-NMR (100 MHz, $CDCl_3$)



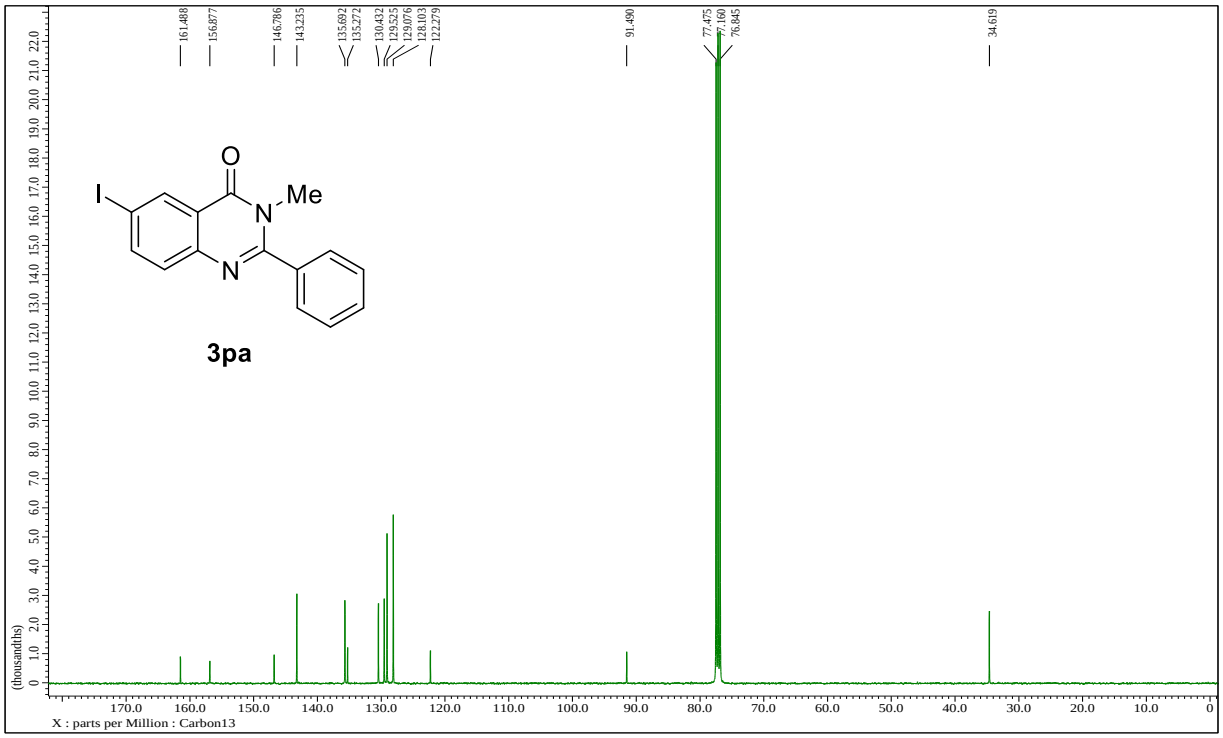
3oa ^{19}F-NMR (376 MHz, $CDCl_3$)



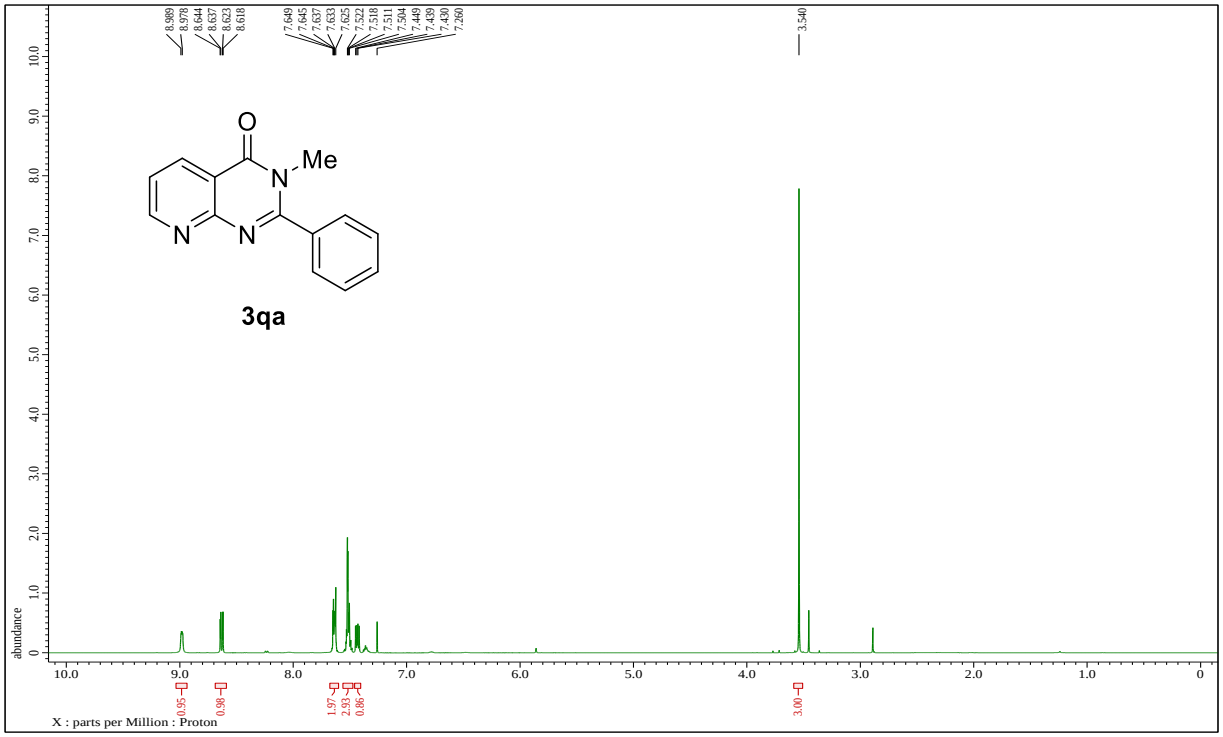
3pa ^{1}H-NMR (400 MHz, $CDCl_3$)



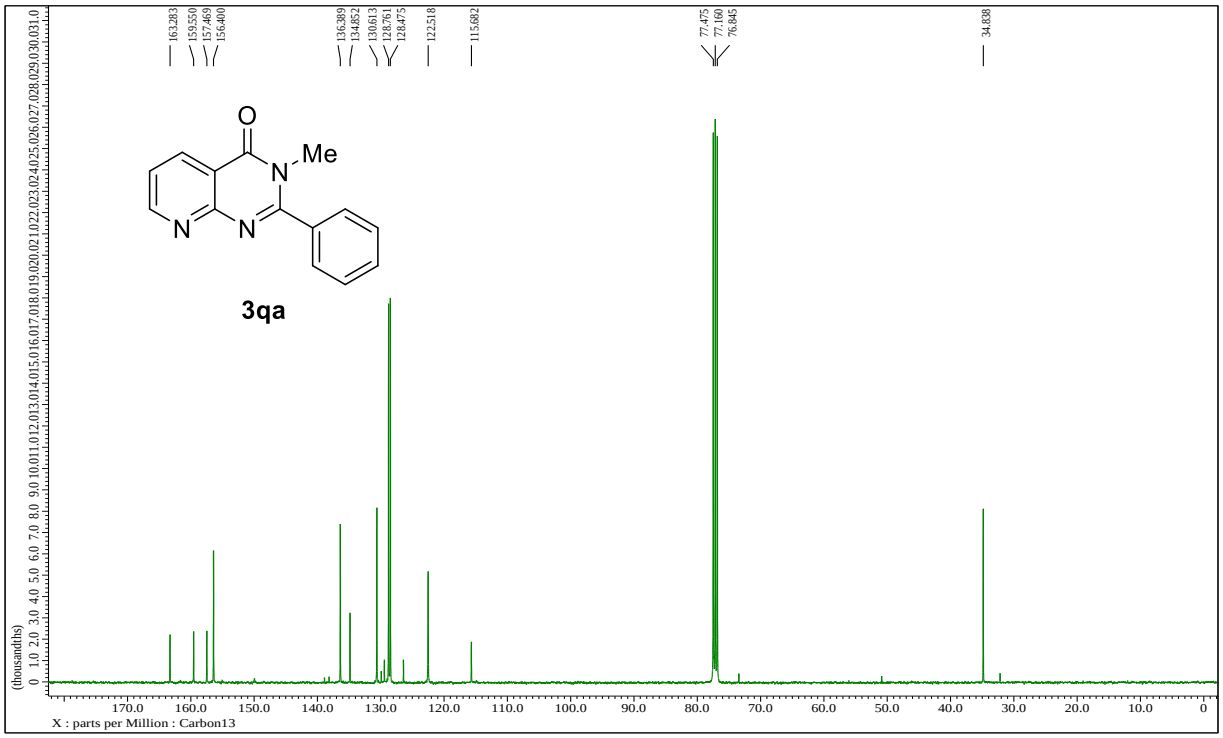
3pa ^{13}C-NMR (100 MHz, $CDCl_3$)



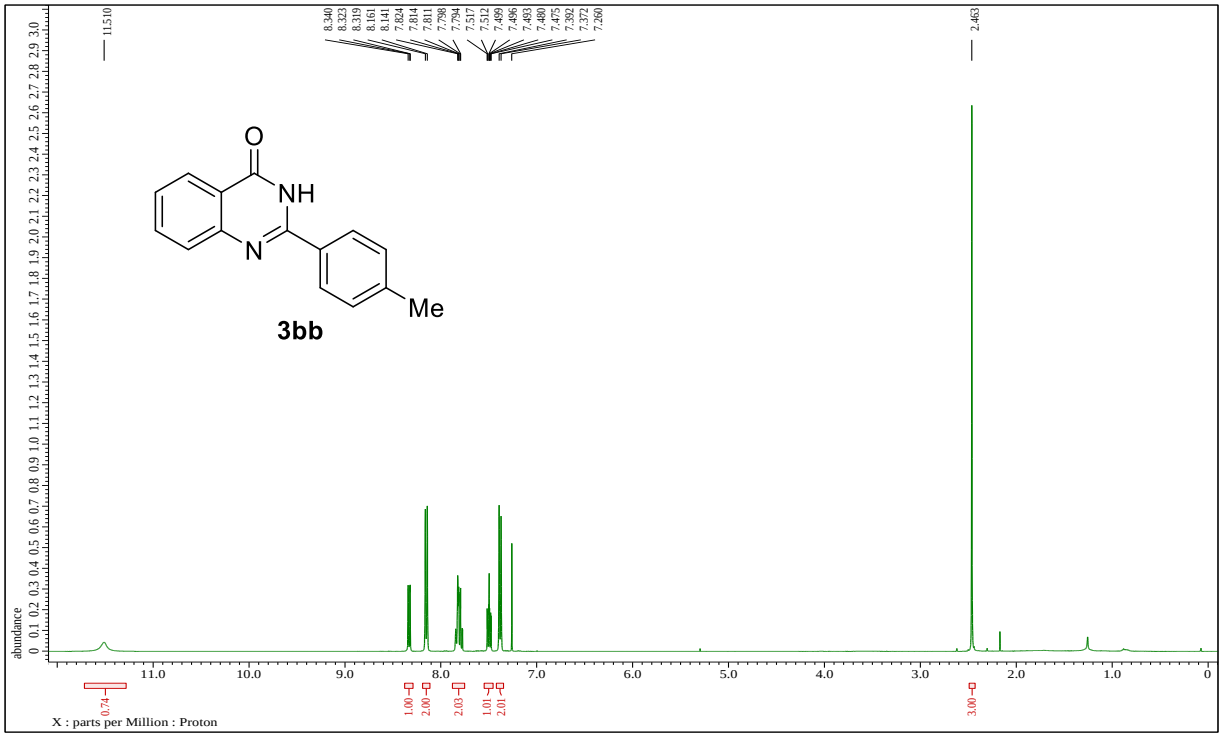
3qa ^{1}H-NMR (400 MHz, $CDCl_3$)



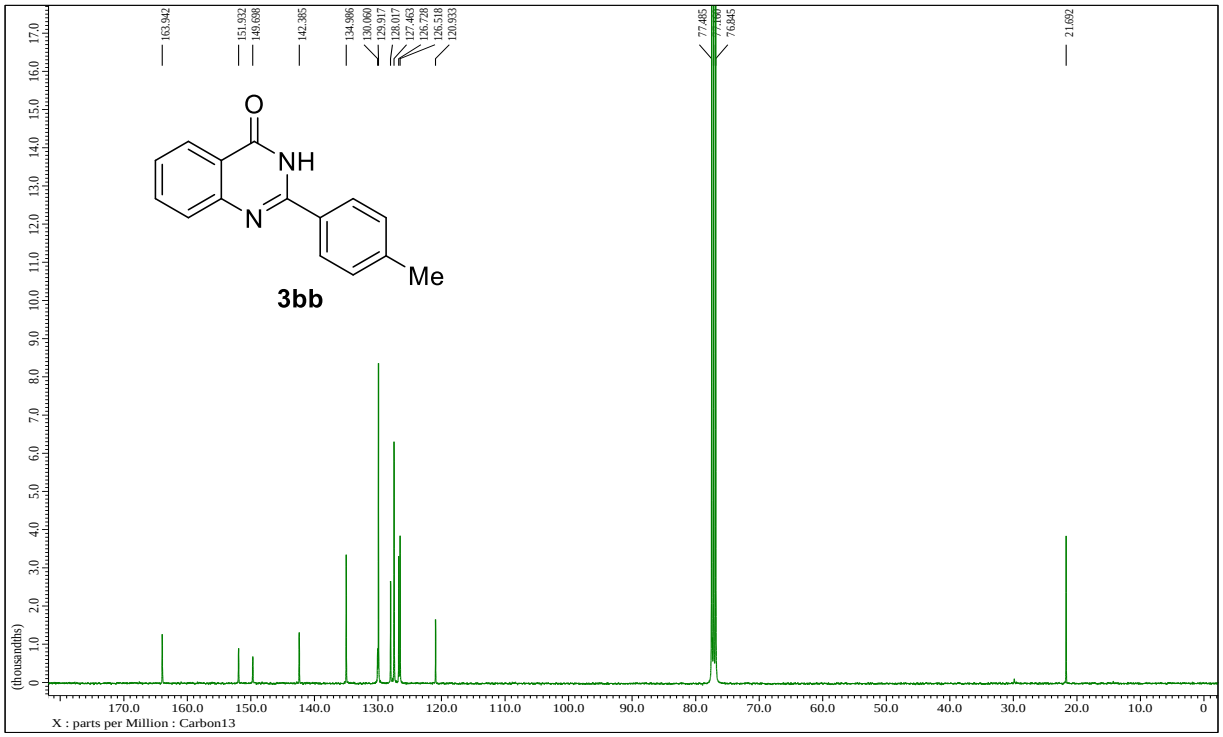
3qa ^{13}C-NMR (100 MHz, $CDCl_3$)



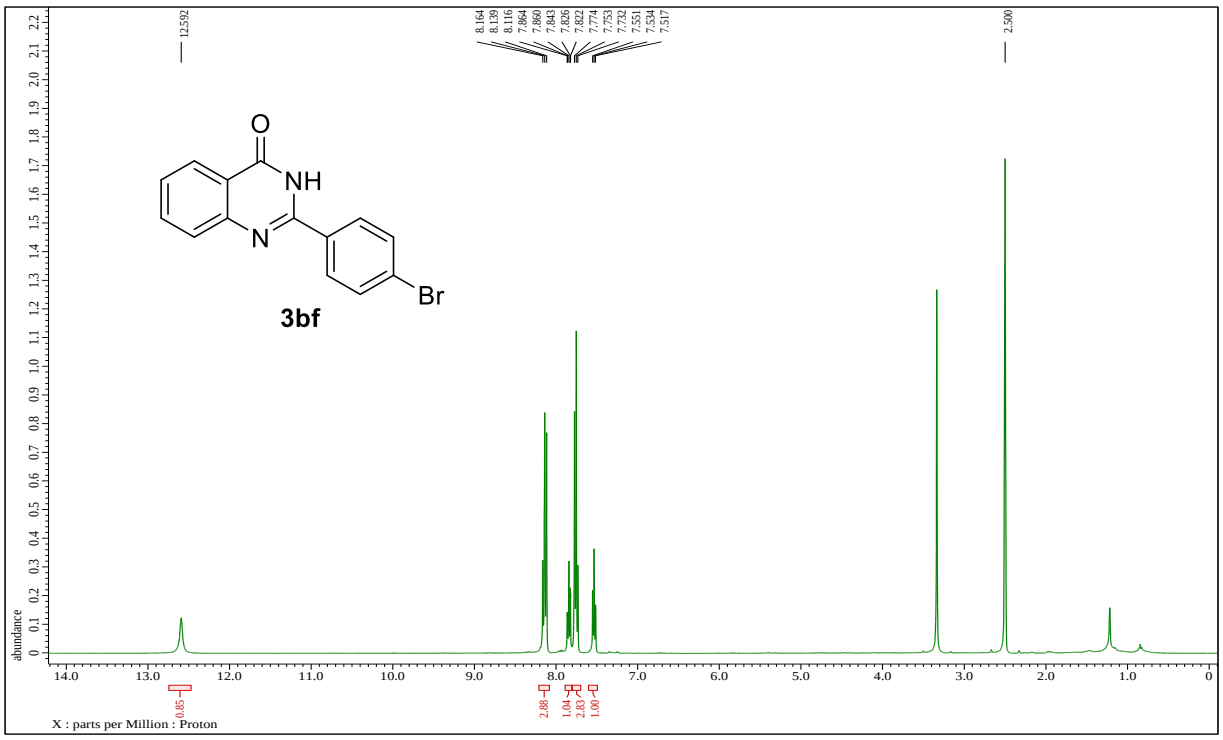
3bb ^{1}H-NMR (400 MHz, $CDCl_3$)



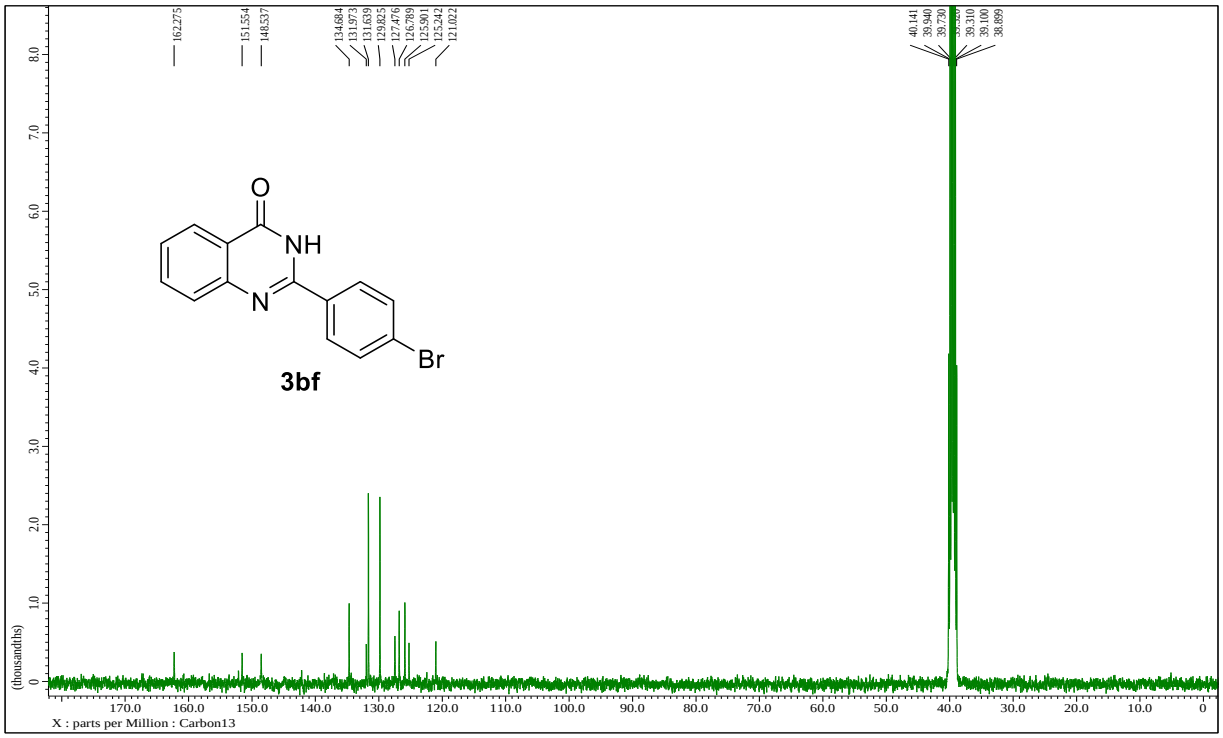
3bb ^{13}C-NMR (100 MHz, $CDCl_3$)



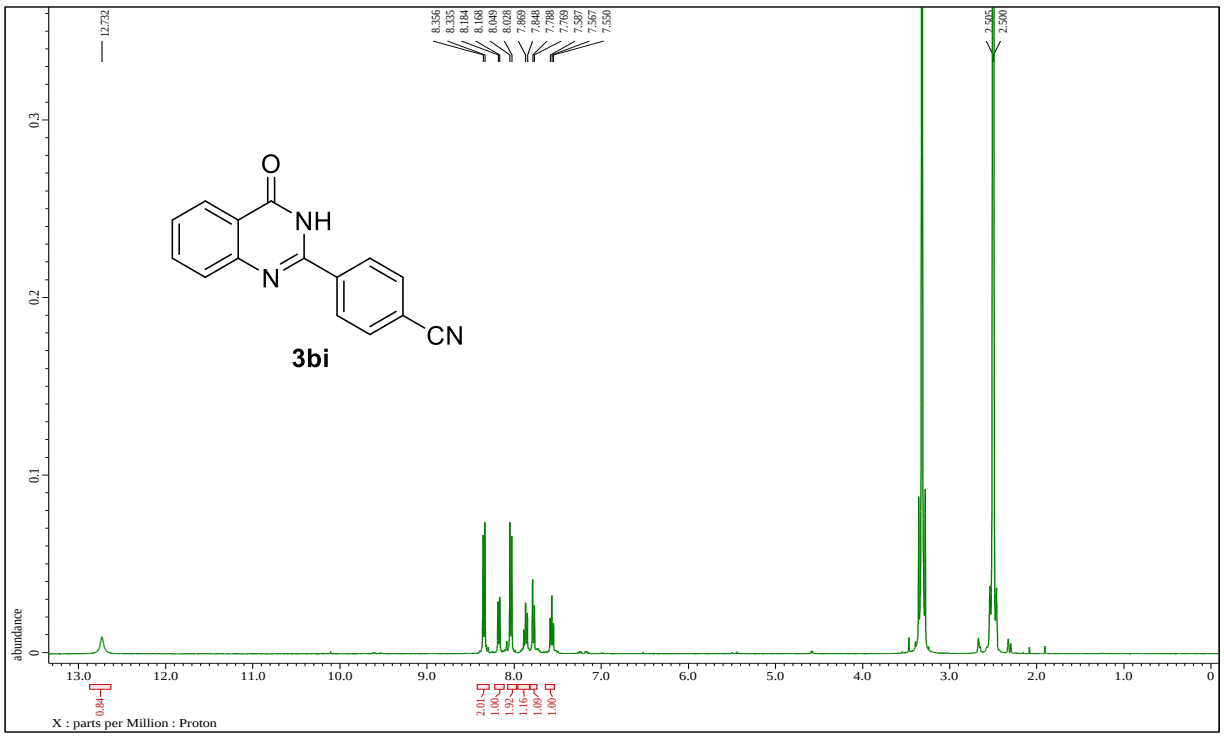
3bf ^{1}H-NMR (400 MHz, DMSO-d_6)



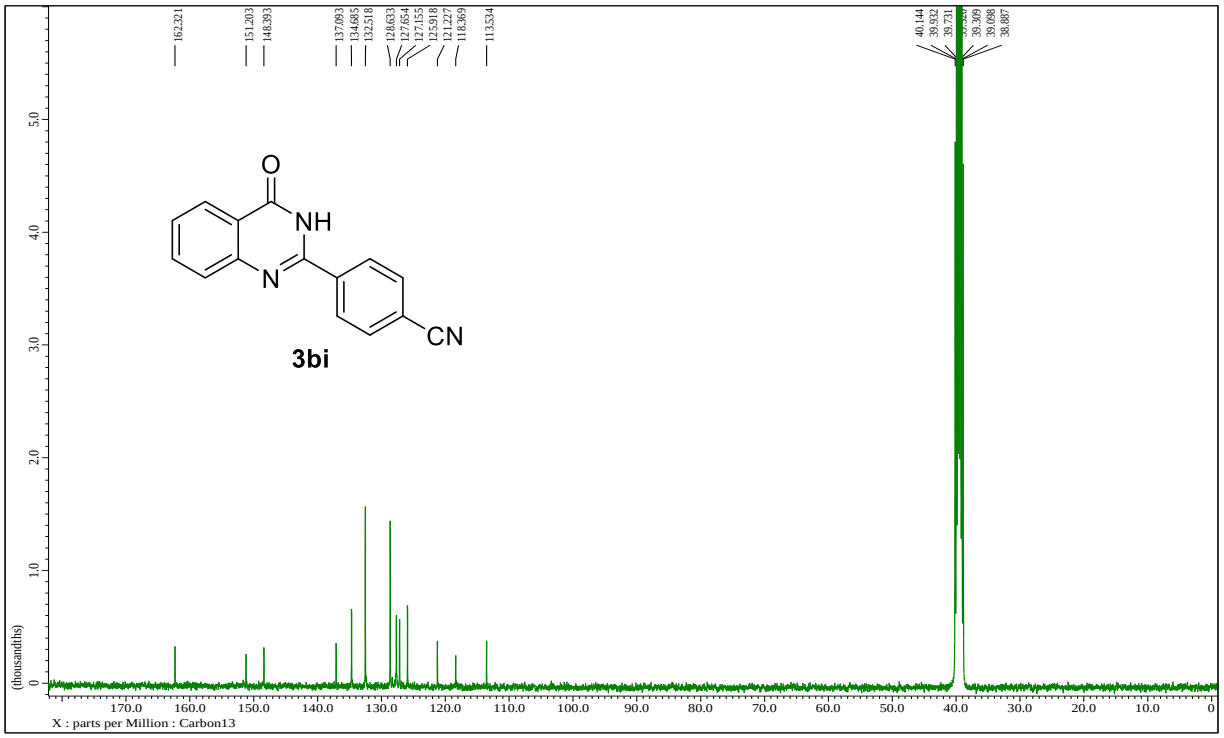
3bf ^{13}C-NMR (100 MHz, DMSO-d_6)



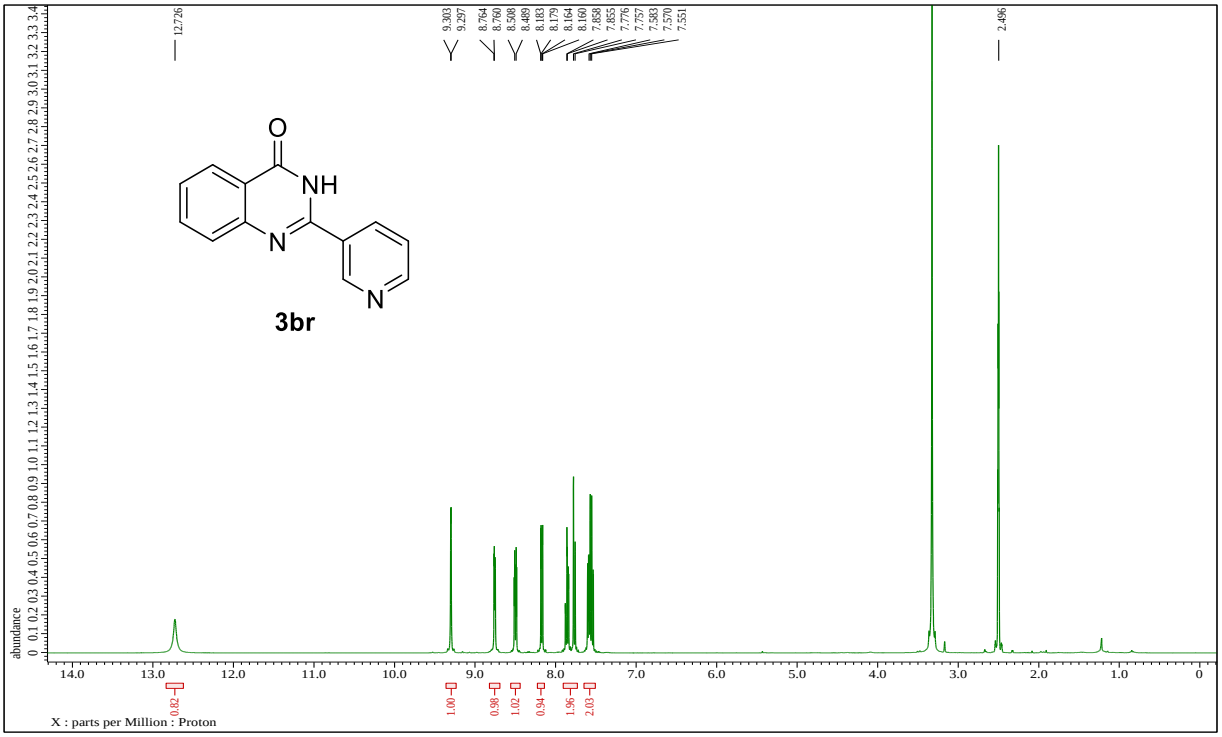
3bi ^{1}H-NMR (400 MHz, DMSO-d_6)



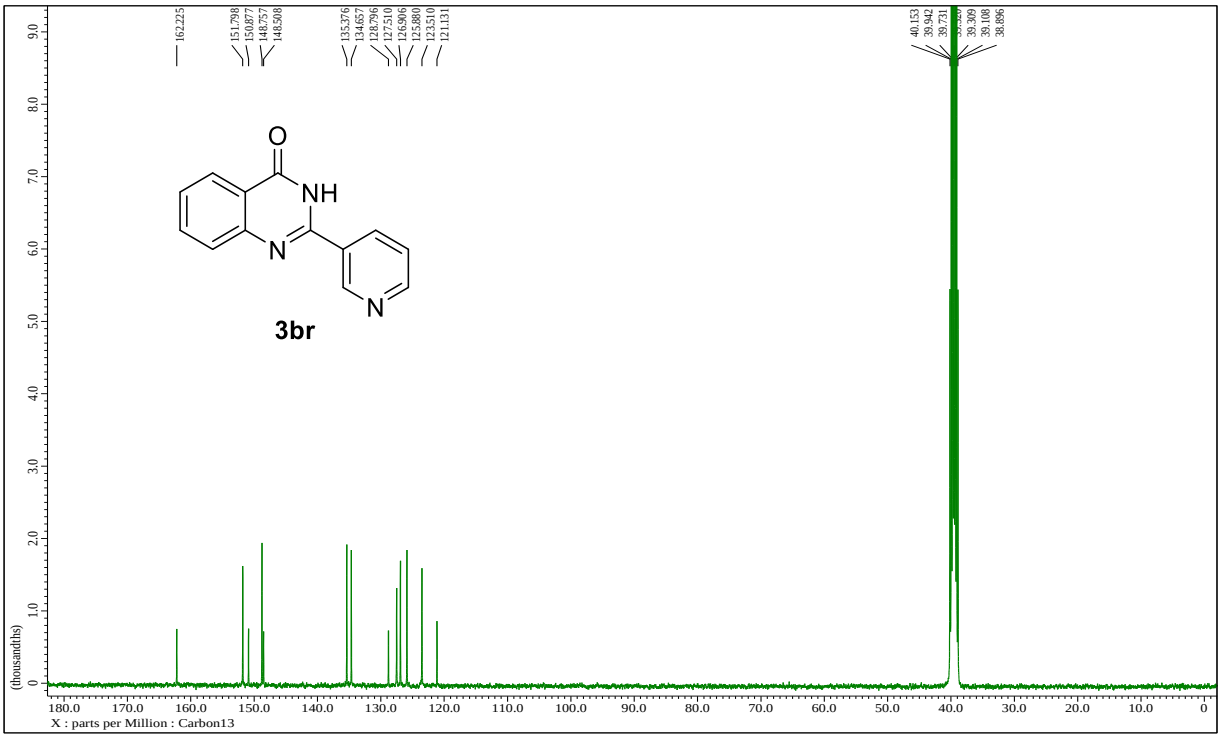
3bi ^{13}C-NMR (100 MHz, DMSO-d_6)



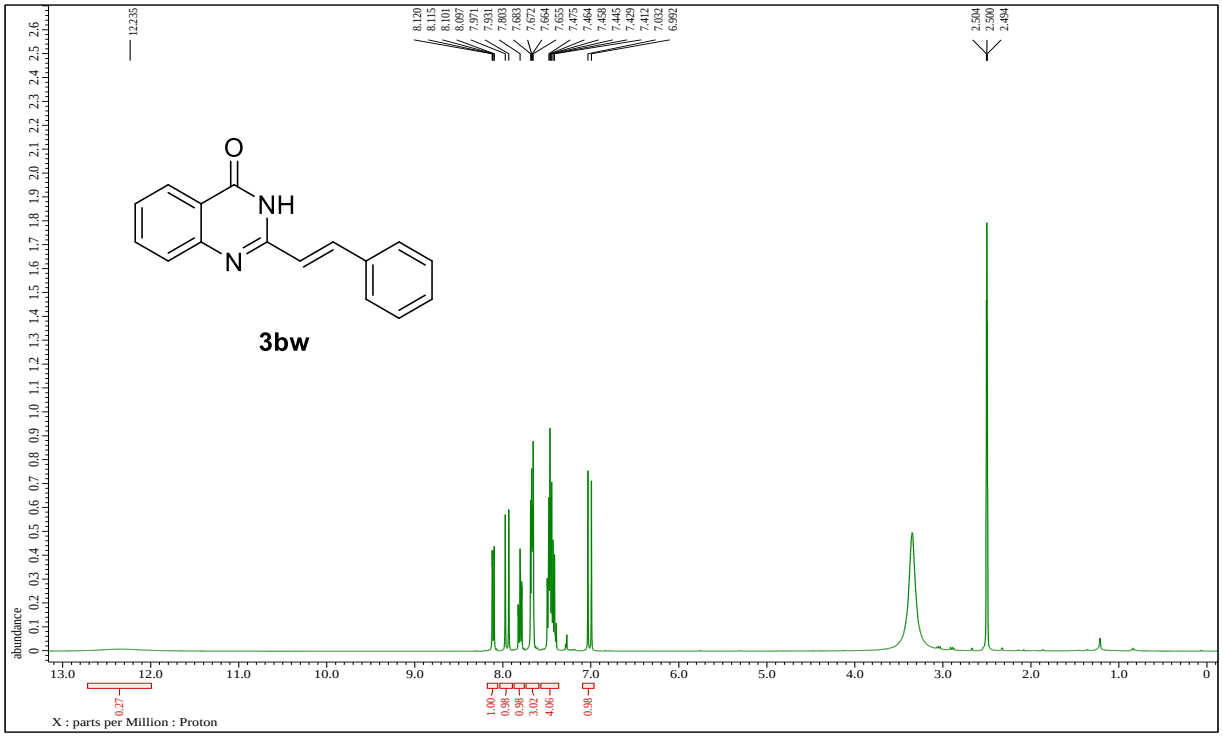
3br ^{1}H-NMR (400 MHz, DMSO-d_6)



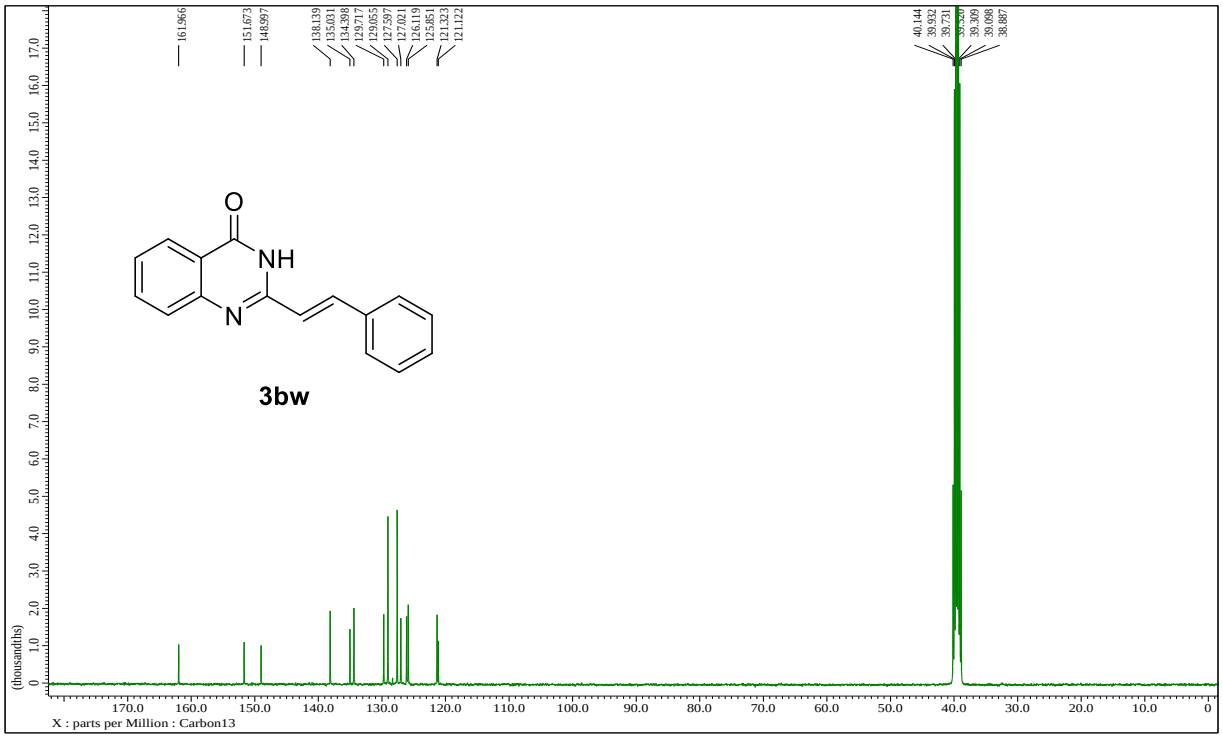
3br ^{13}C-NMR (100 MHz, DMSO-d_6)



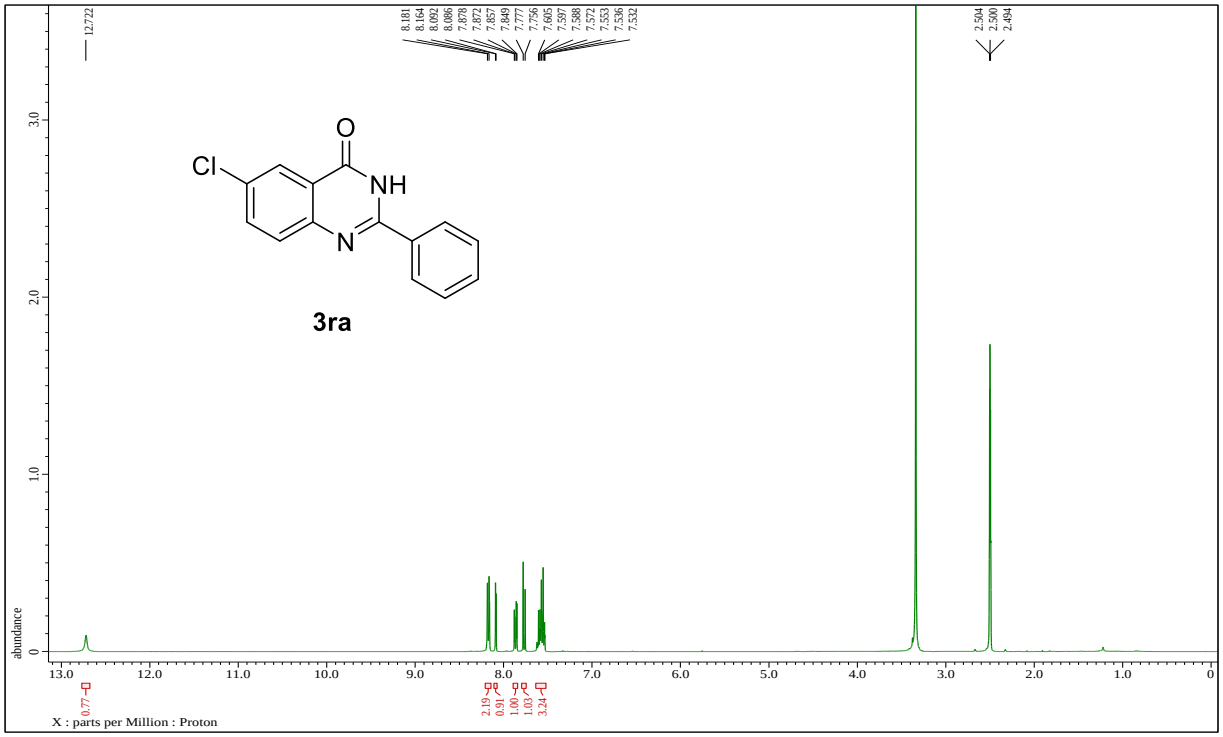
3bw ^{1}H-NMR (400 MHz, DMSO-d_6)



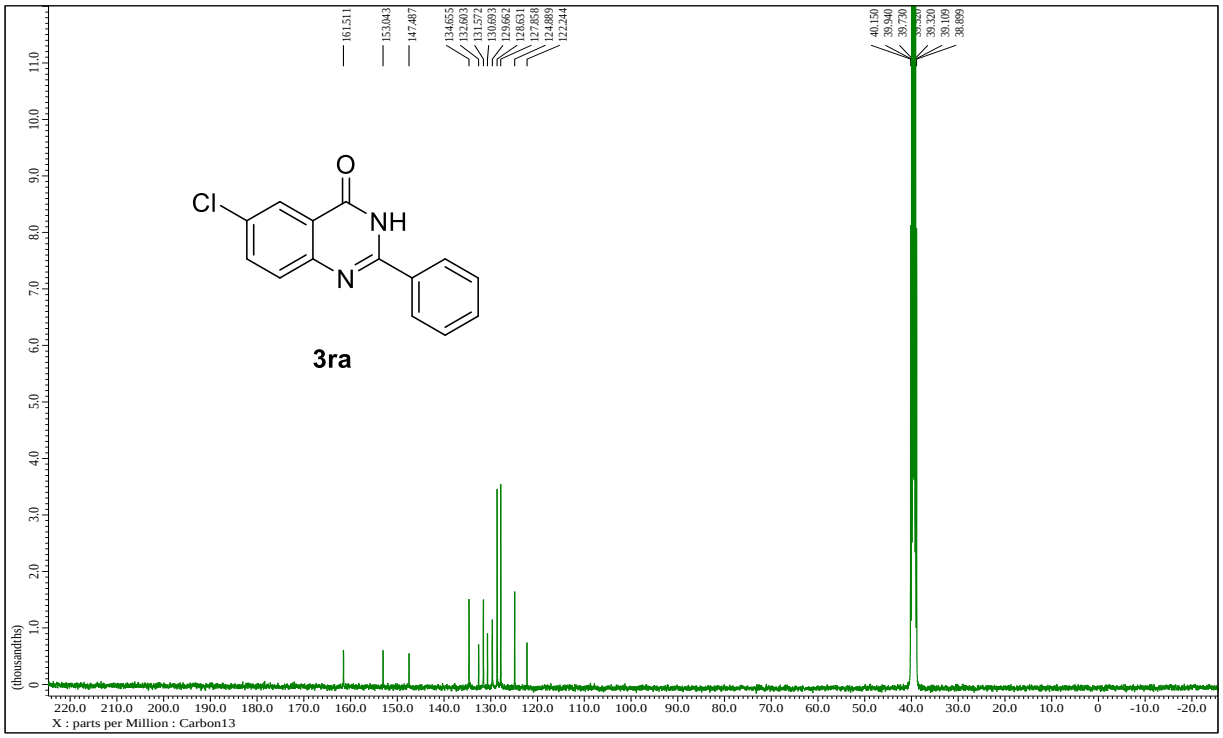
3bw ^{13}C-NMR (100 MHz, DMSO-d_6)



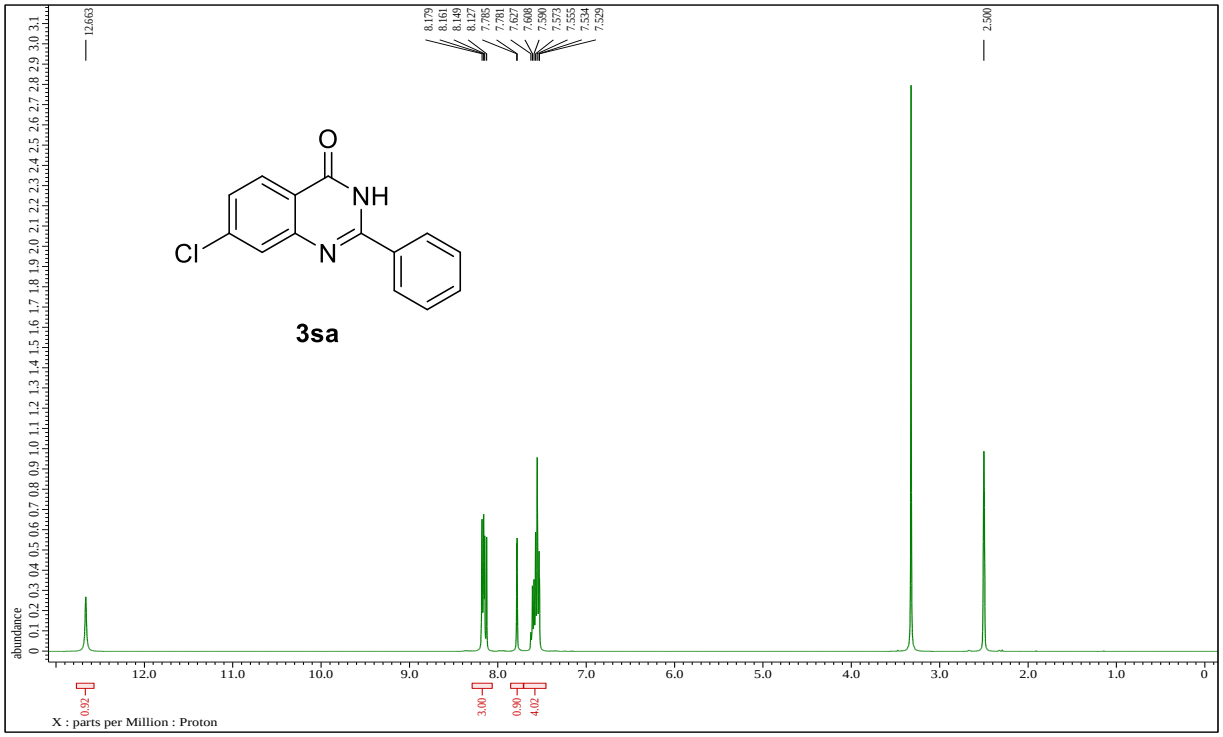
3ra ^{1}H-NMR (400 MHz, DMSO-d_6)



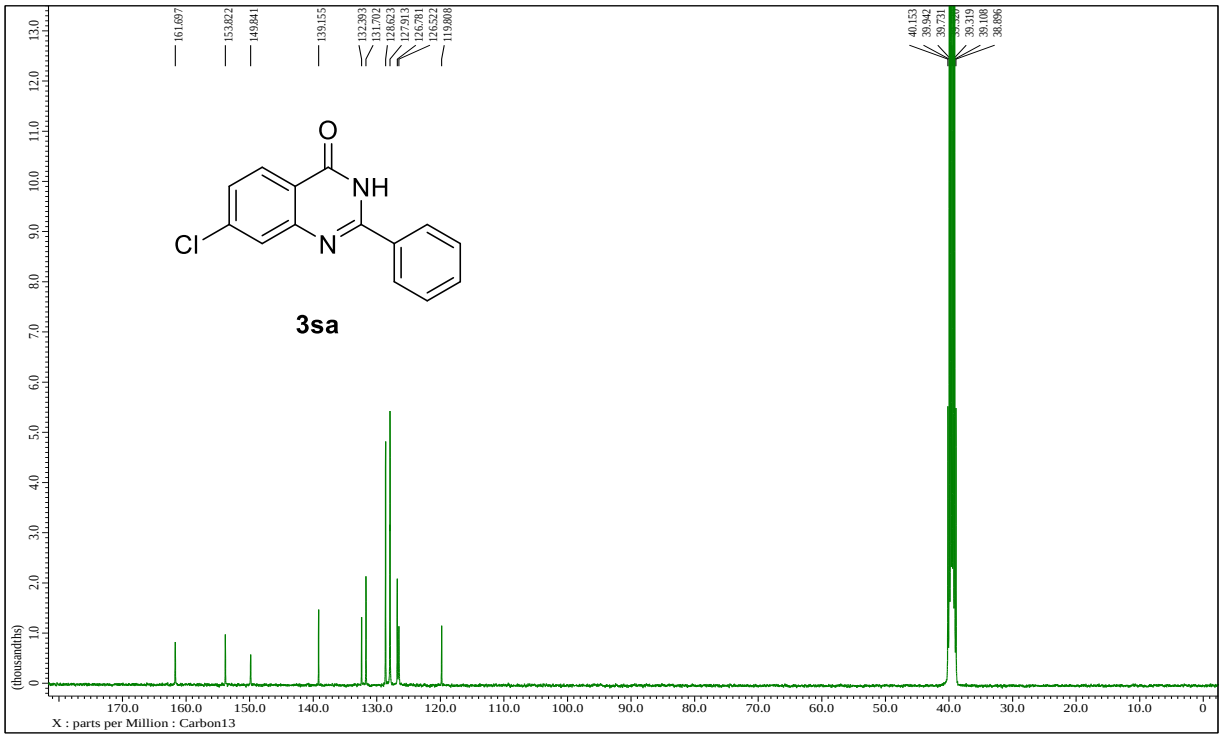
3ra ^{13}C-NMR (100 MHz, DMSO-d_6)



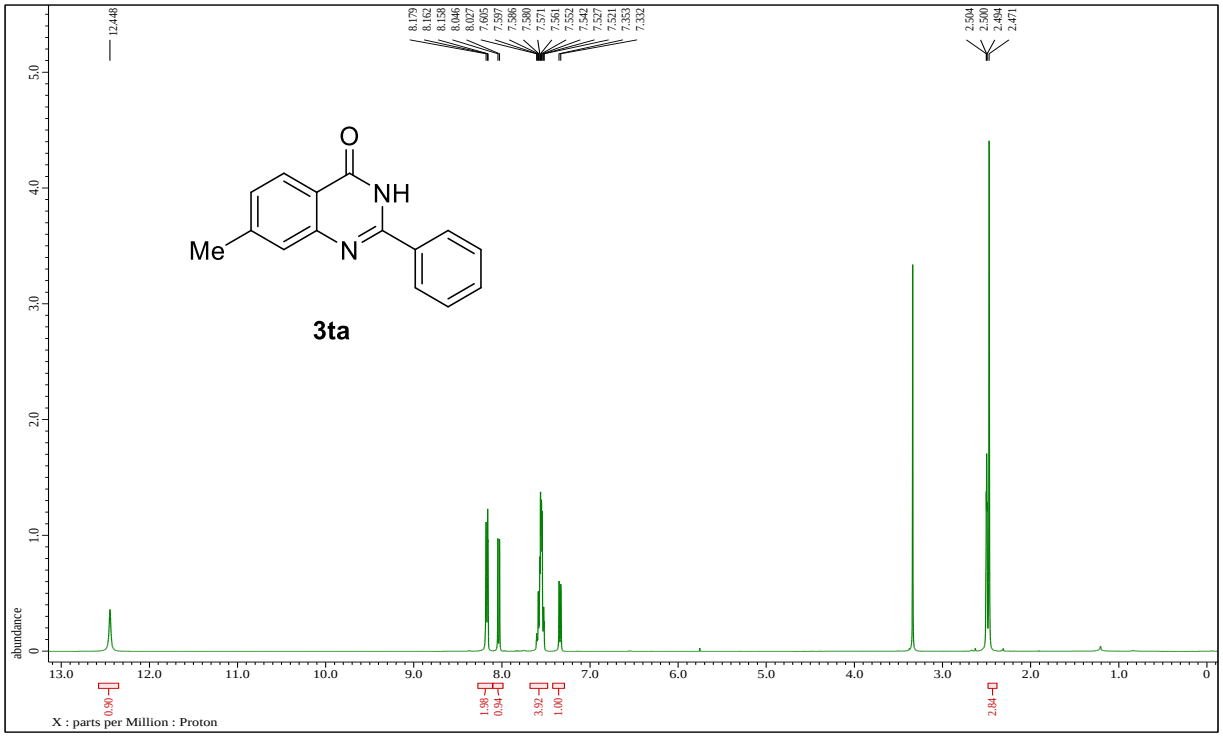
3sa ^{1}H-NMR (400 MHz, DMSO-d_6)



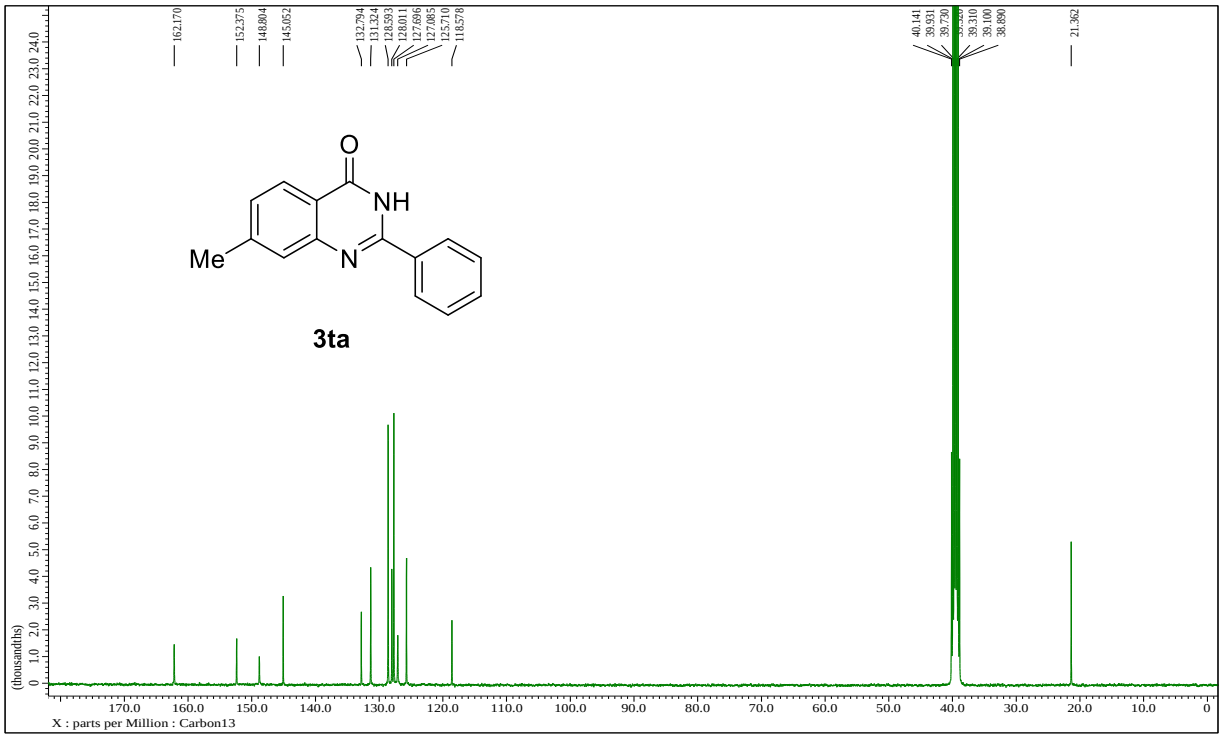
3sa ^{13}C-NMR (100 MHz, DMSO-d_6)



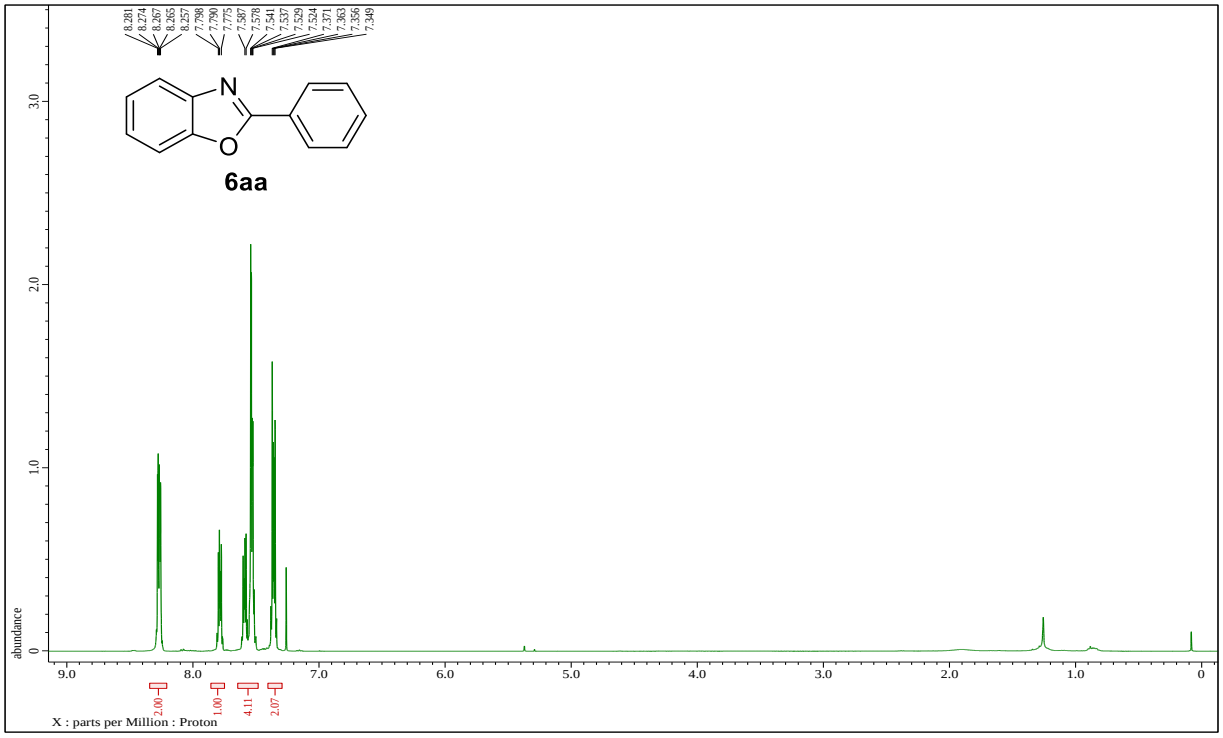
3ta ^{1}H-NMR (400 MHz, DMSO-d_6)



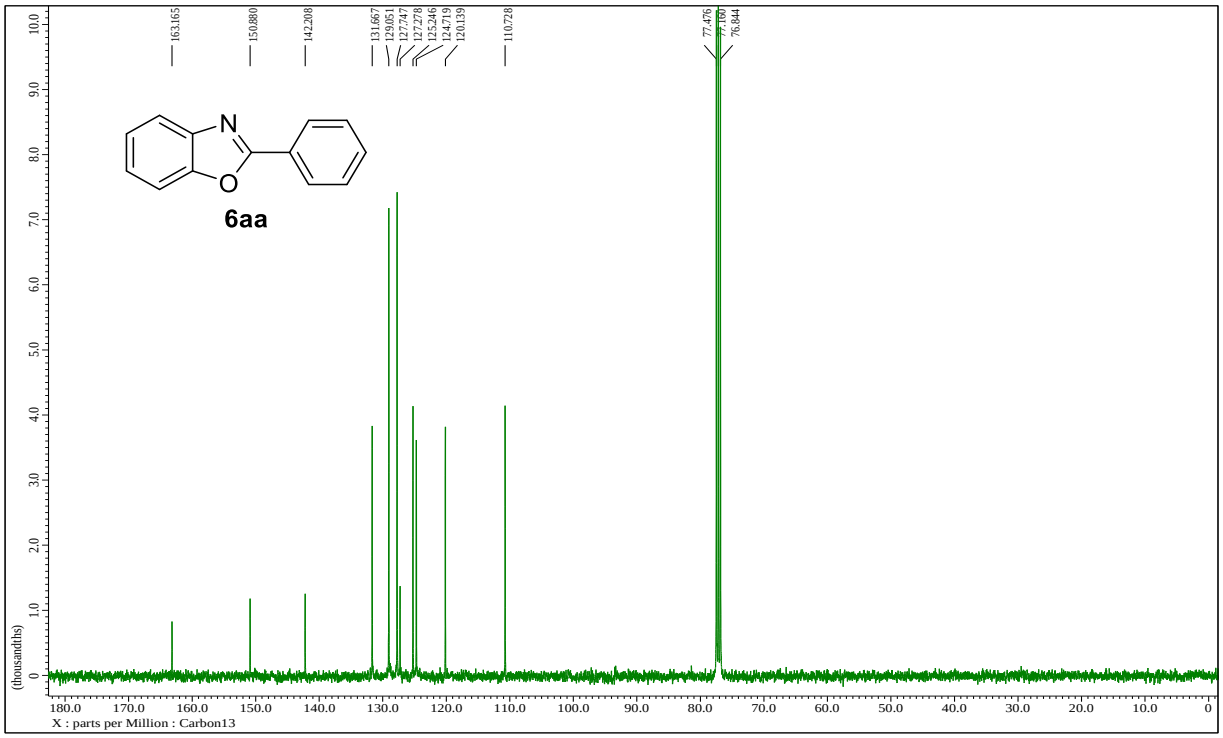
3ta ^{13}C-NMR (100 MHz, DMSO-d_6)



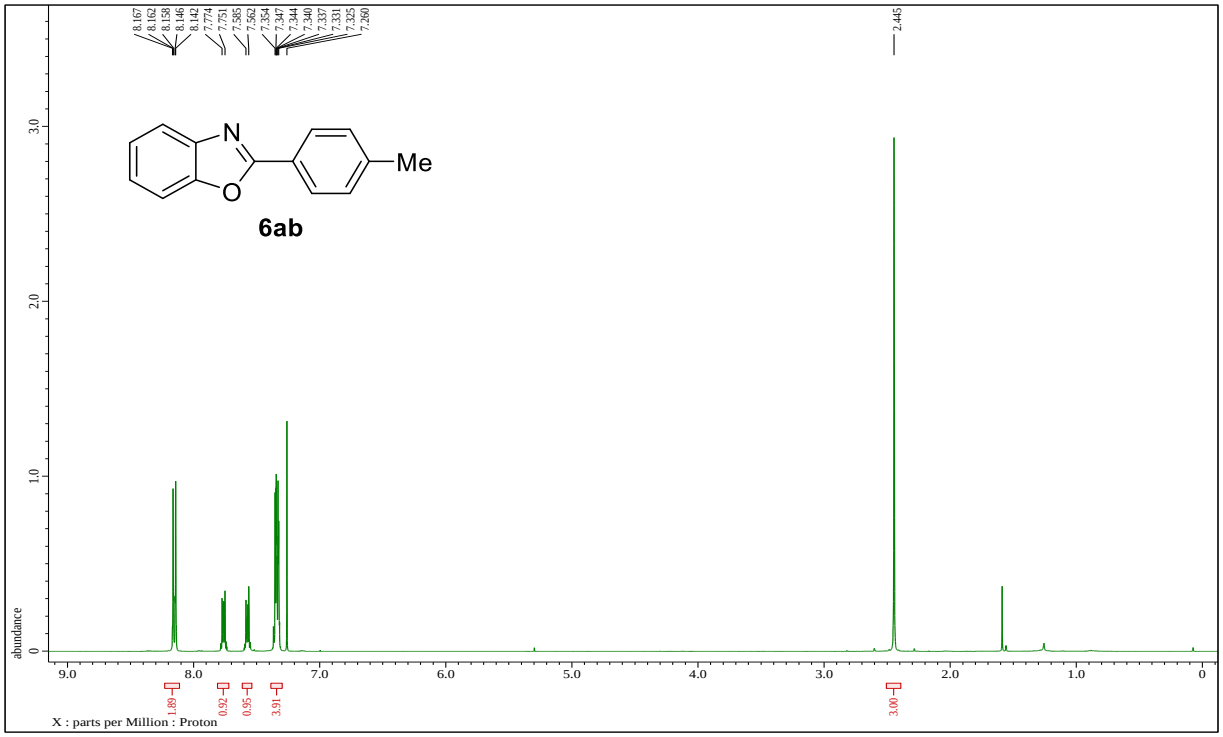
6aa ^{1}H-NMR (400 MHz, $CDCl_3$)



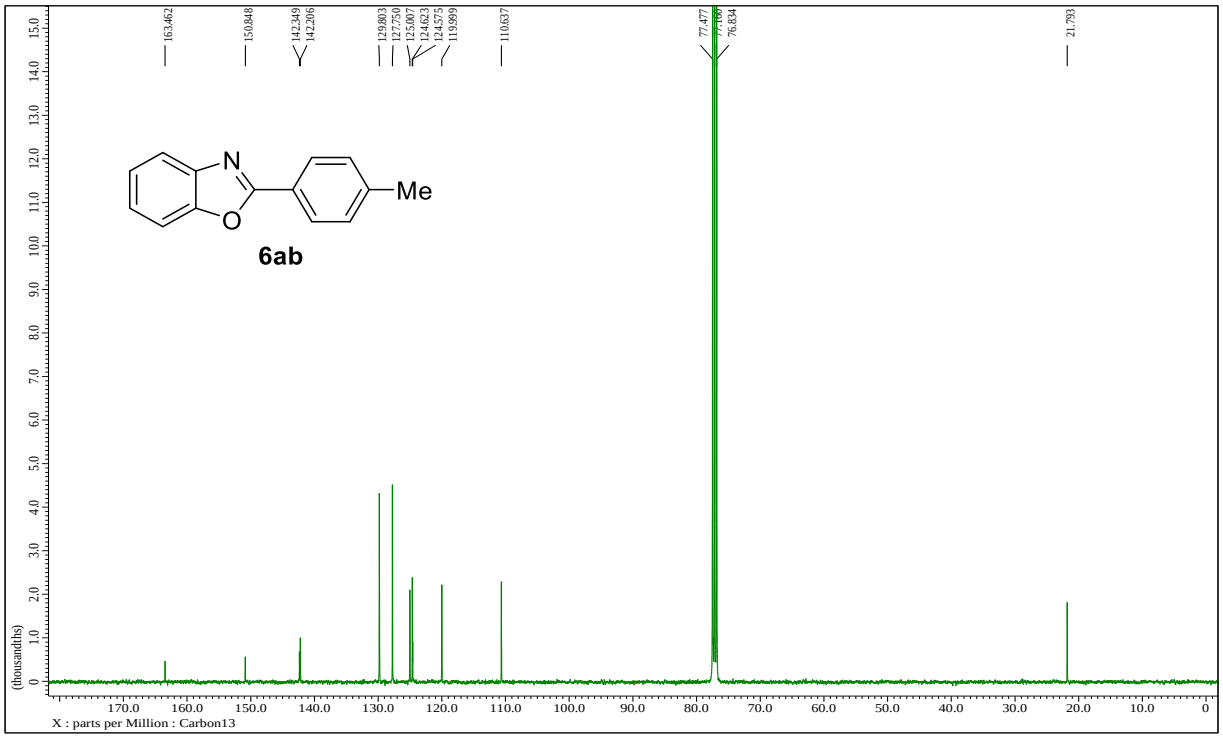
6aa ^{13}C-NMR (100 MHz, $CDCl_3$)



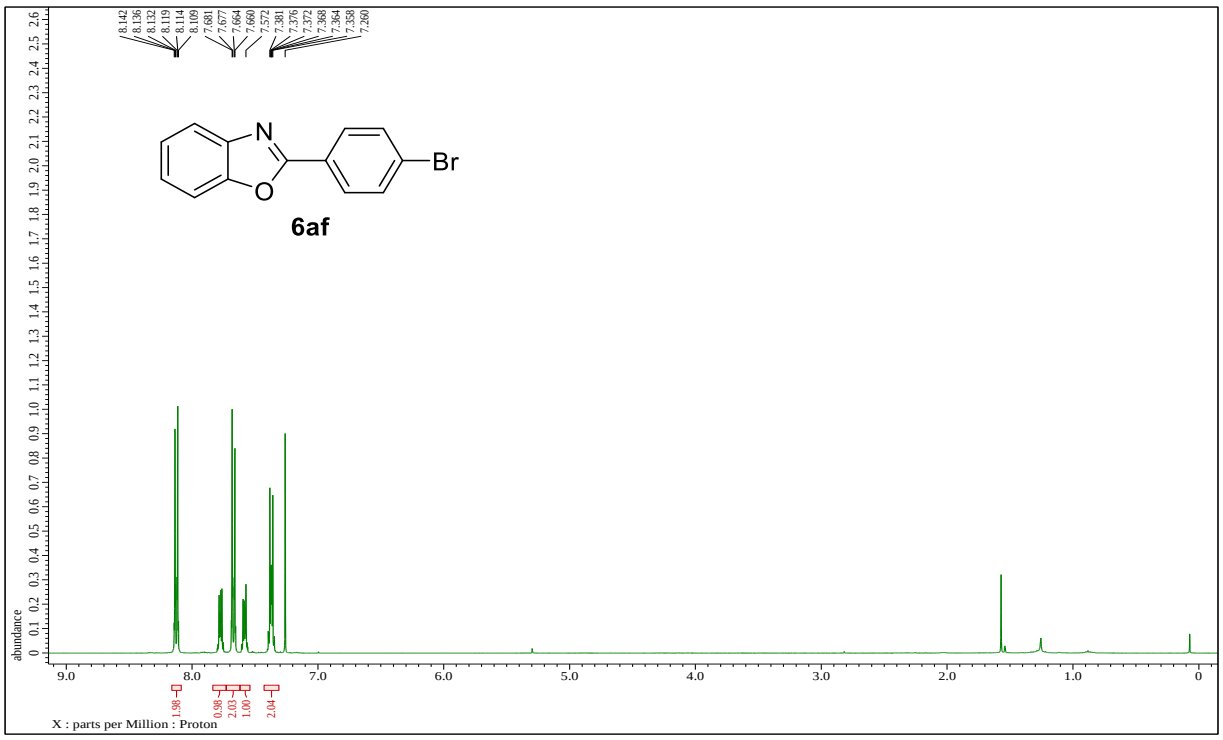
6ab ^{1}H-NMR (400 MHz, $CDCl_3$)



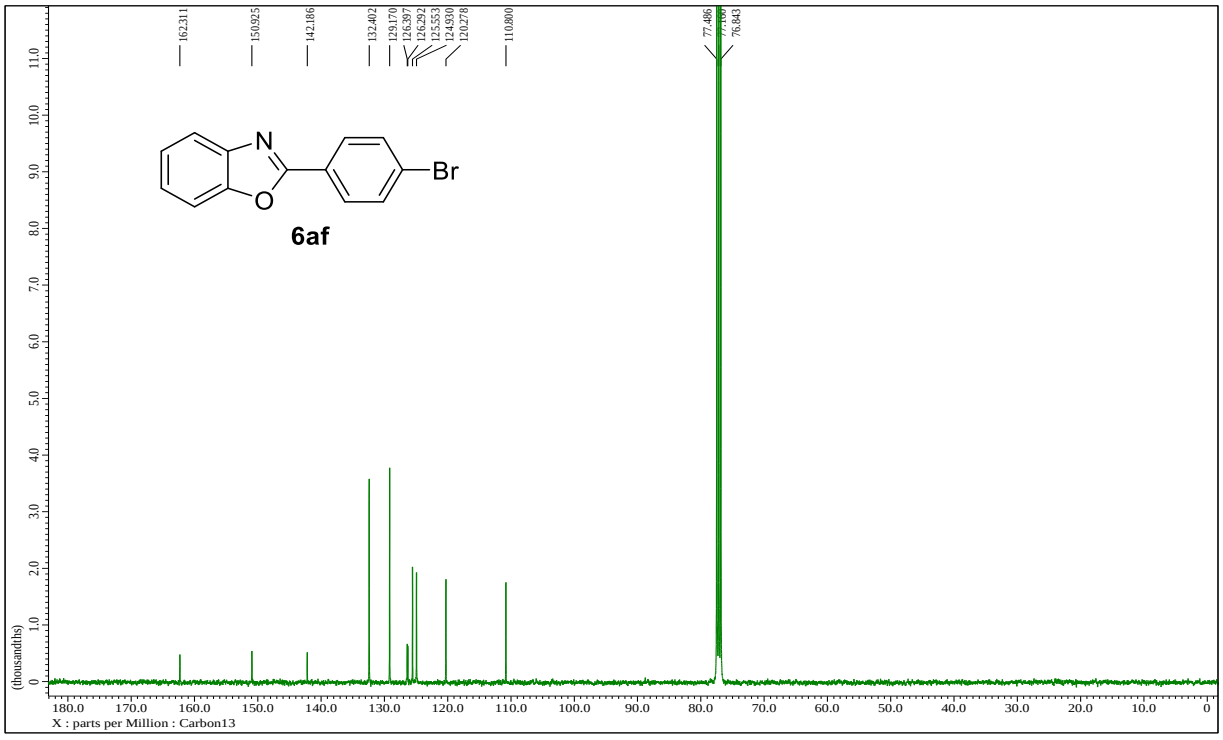
6ab ^{13}C-NMR (100 MHz, $CDCl_3$)



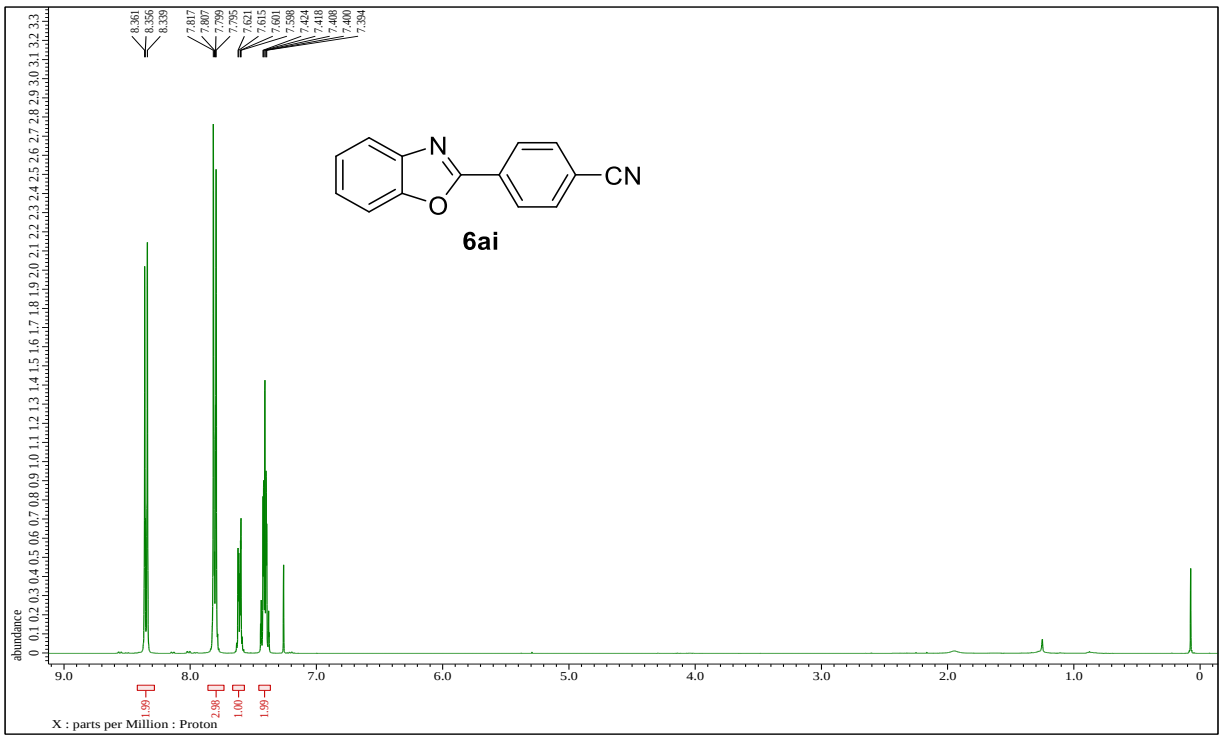
6af ^{1}H-NMR (400 MHz, $CDCl_3$)



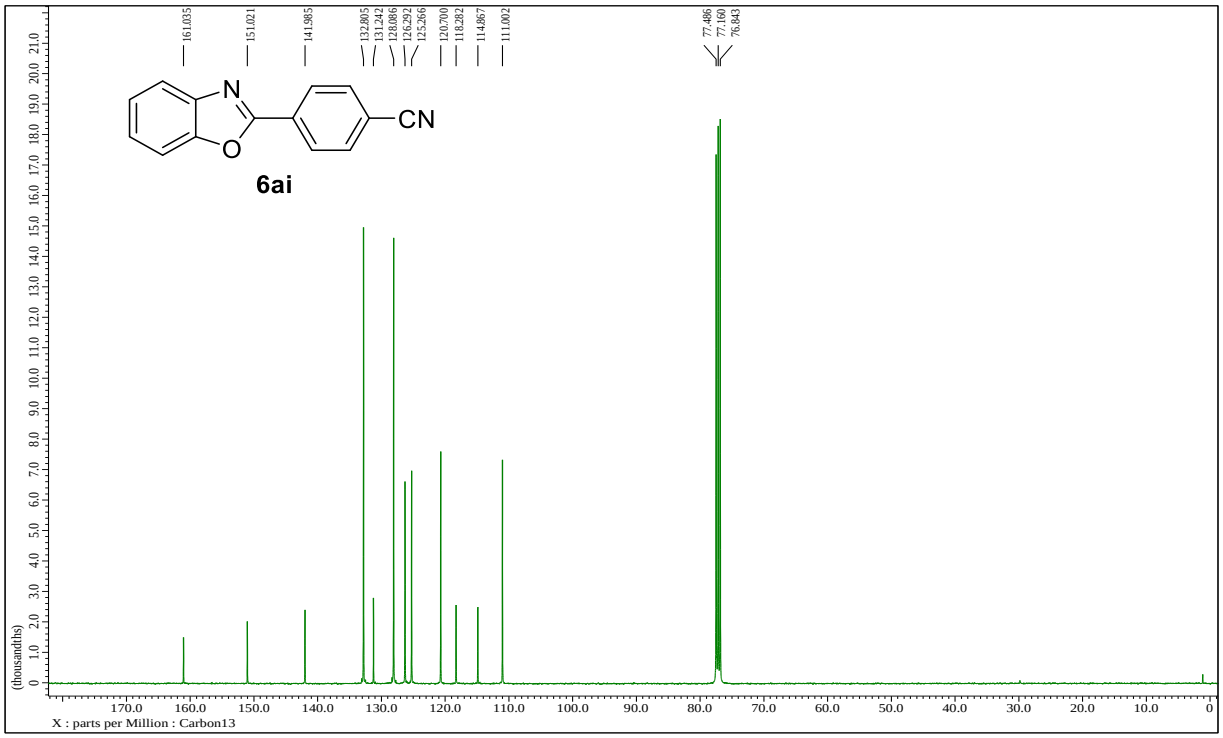
6af ^{13}C-NMR (100 MHz, $CDCl_3$)



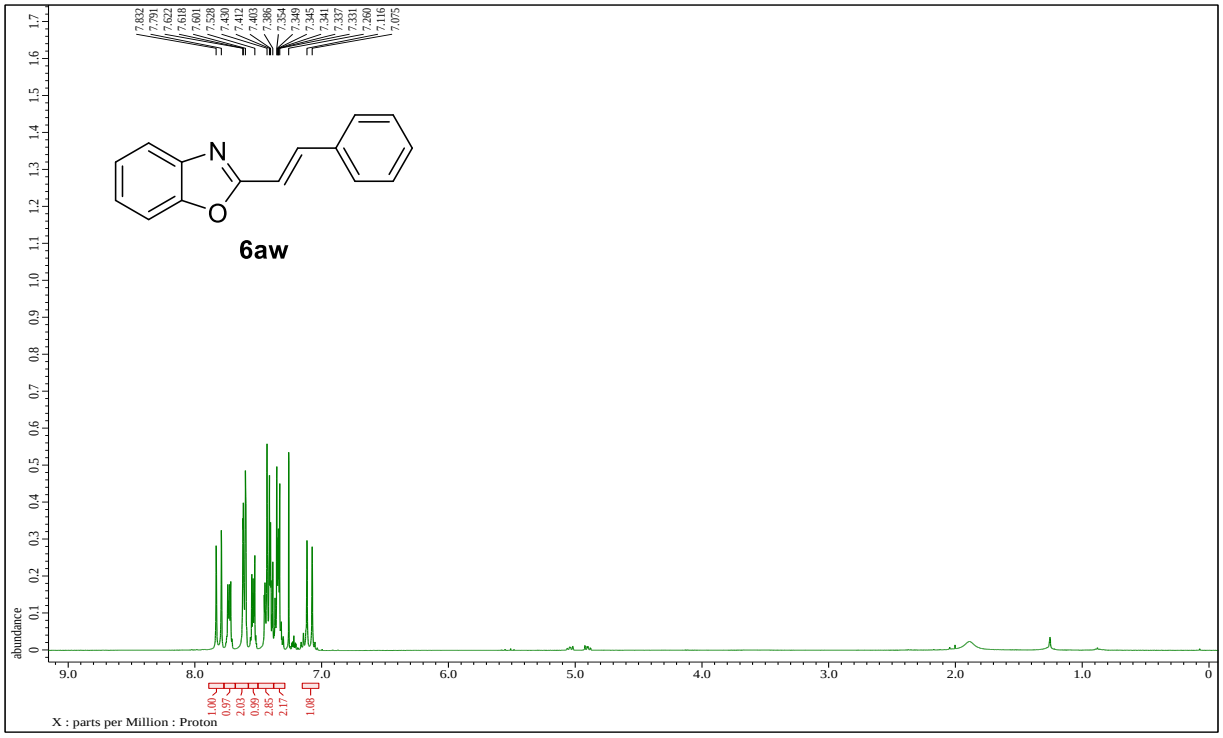
6ai ^{1}H-NMR (400 MHz, $CDCl_3$)



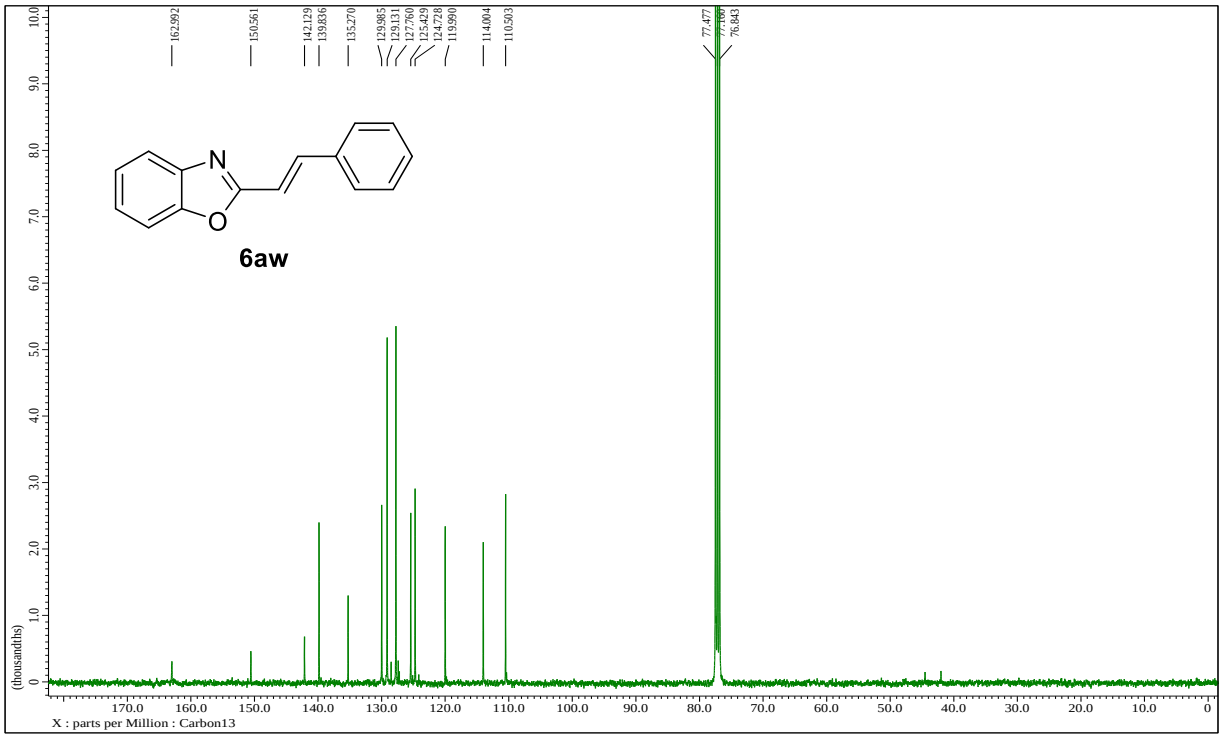
6ai ^{13}C-NMR (100 MHz, $CDCl_3$)



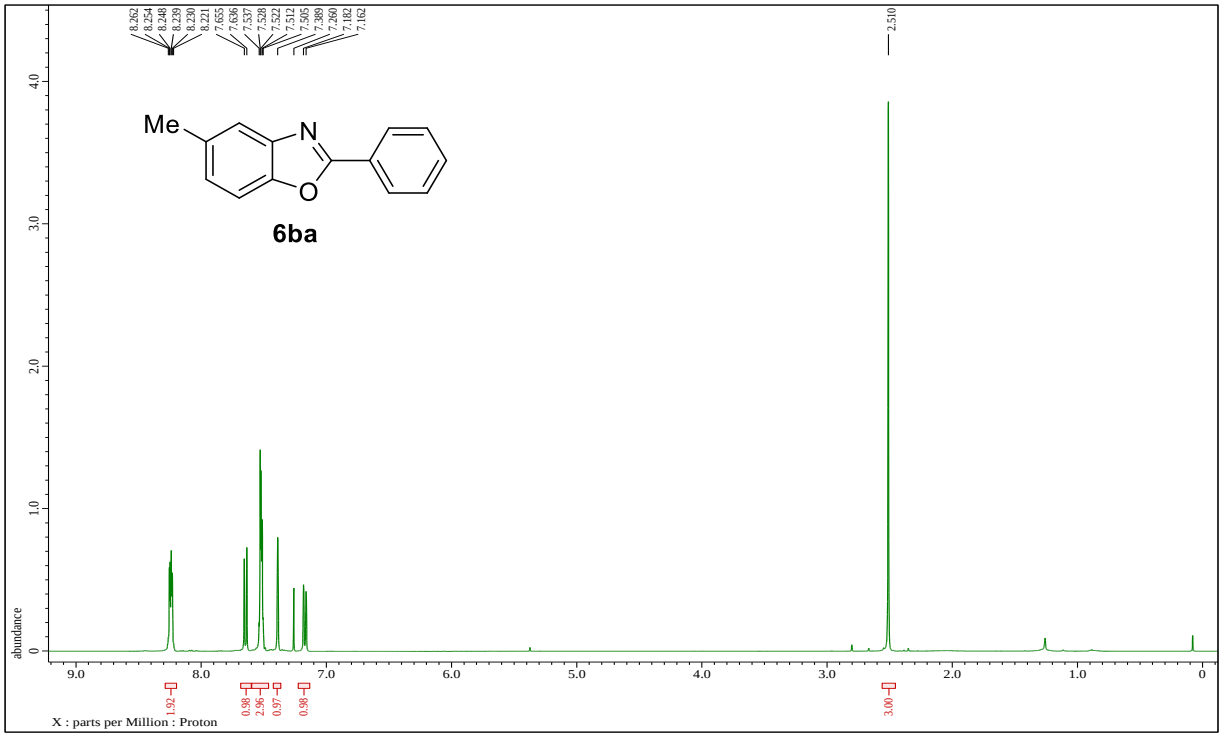
6aw ^{1}H-NMR (400 MHz, $CDCl_3$)



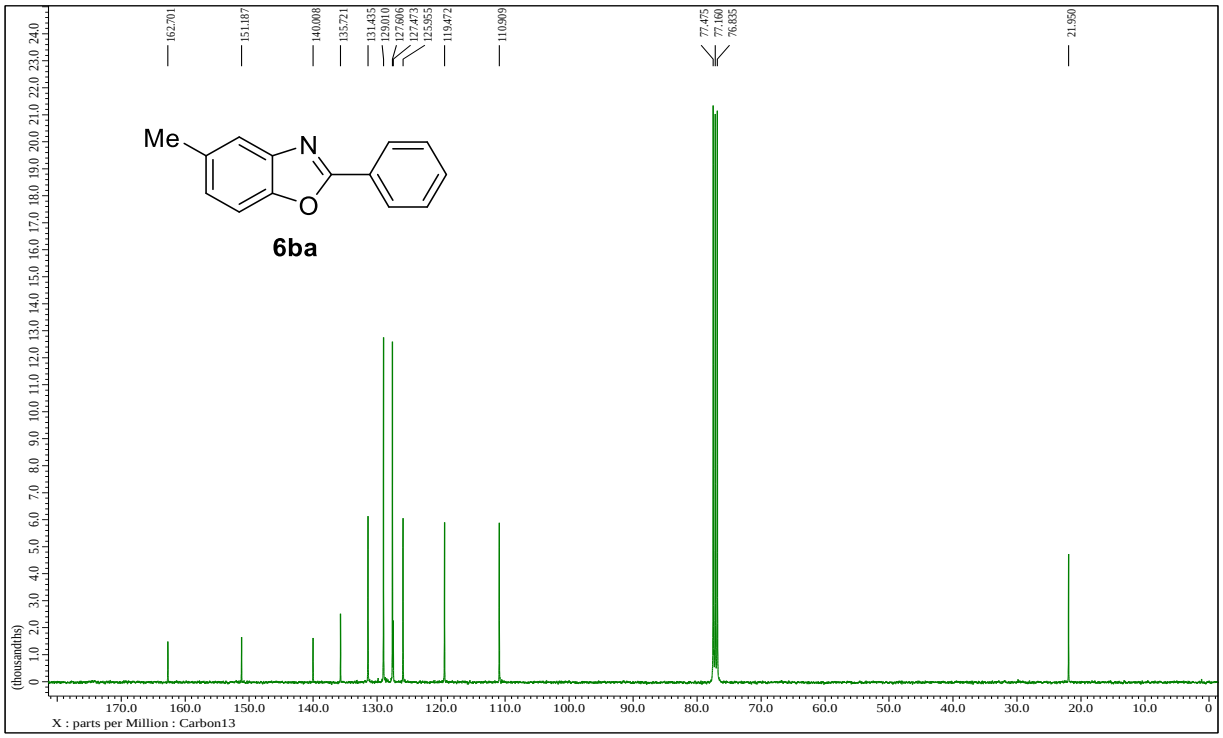
6aw ^{13}C-NMR (100 MHz, $CDCl_3$)



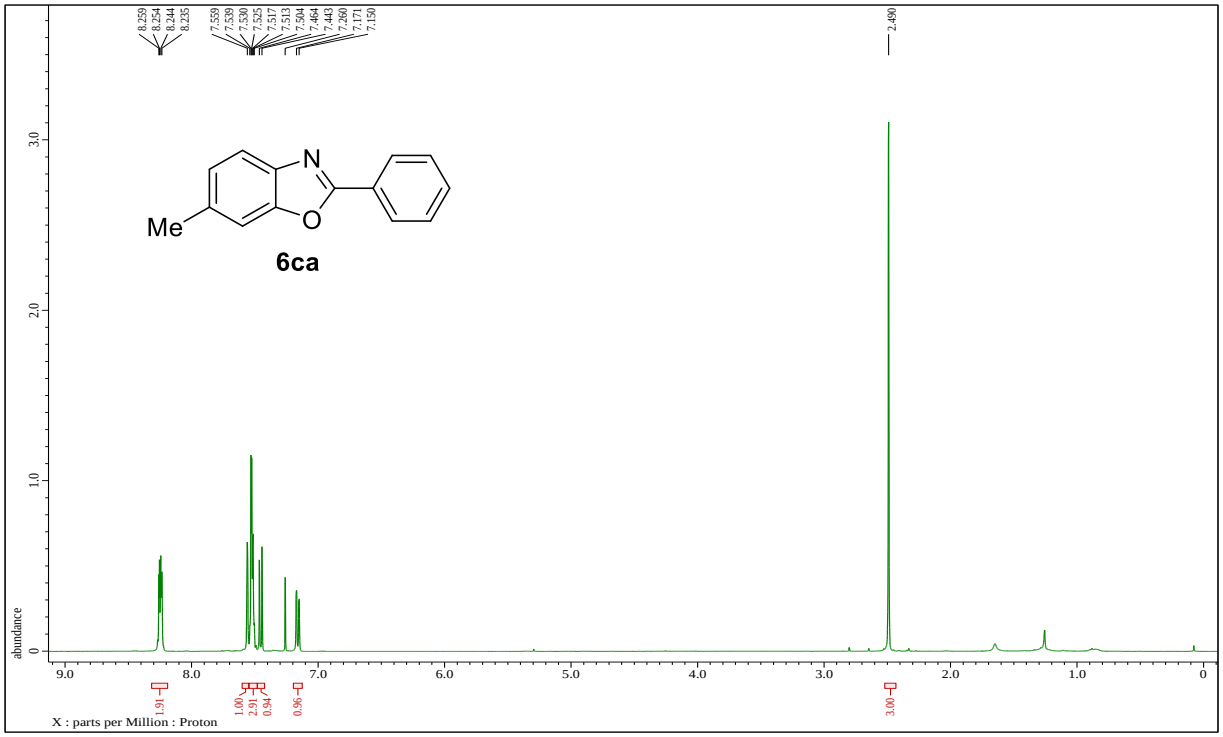
6ba ^{1}H-NMR (400 MHz, $CDCl_3$)



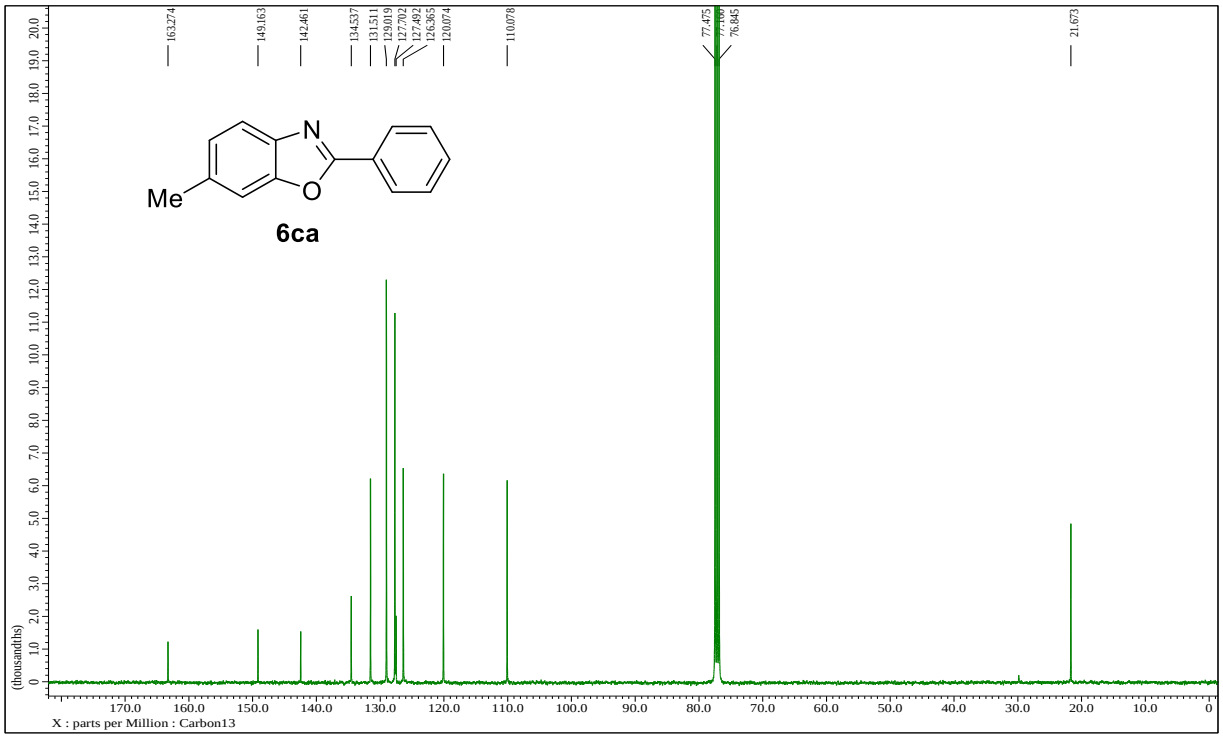
6ba ^{13}C-NMR (100 MHz, $CDCl_3$)



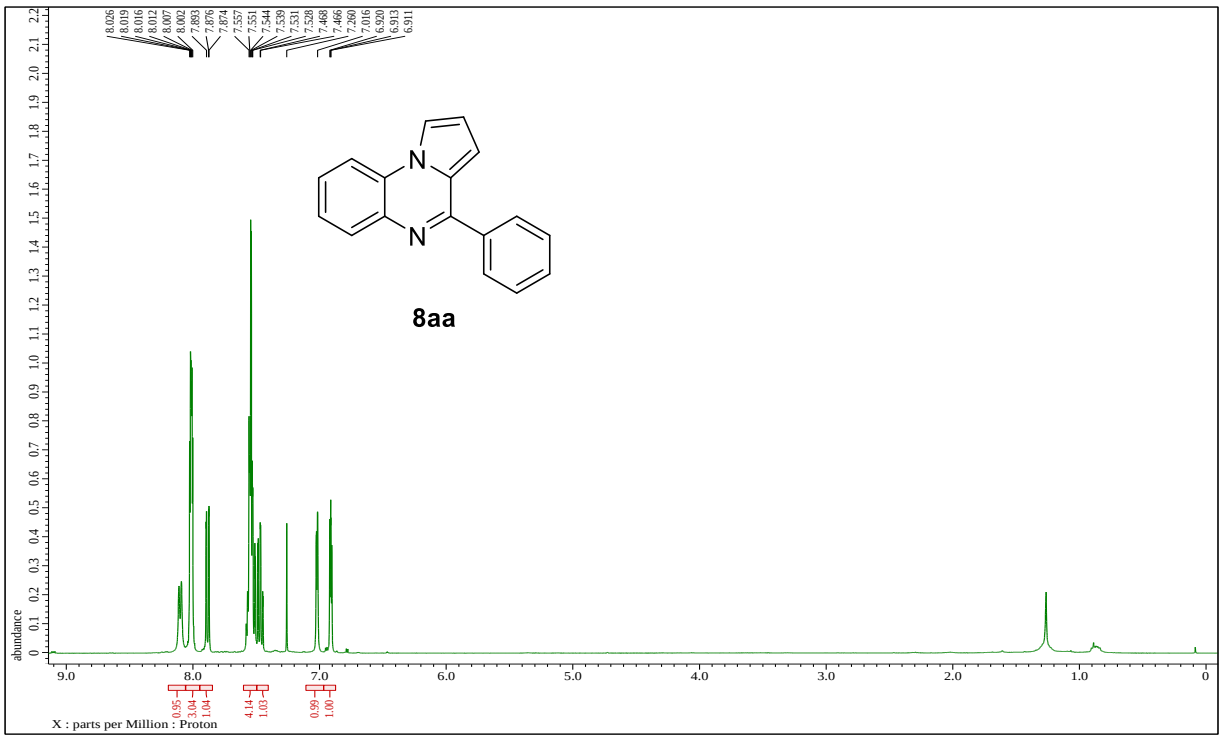
6ca ^{1}H-NMR (400 MHz, $CDCl_3$)



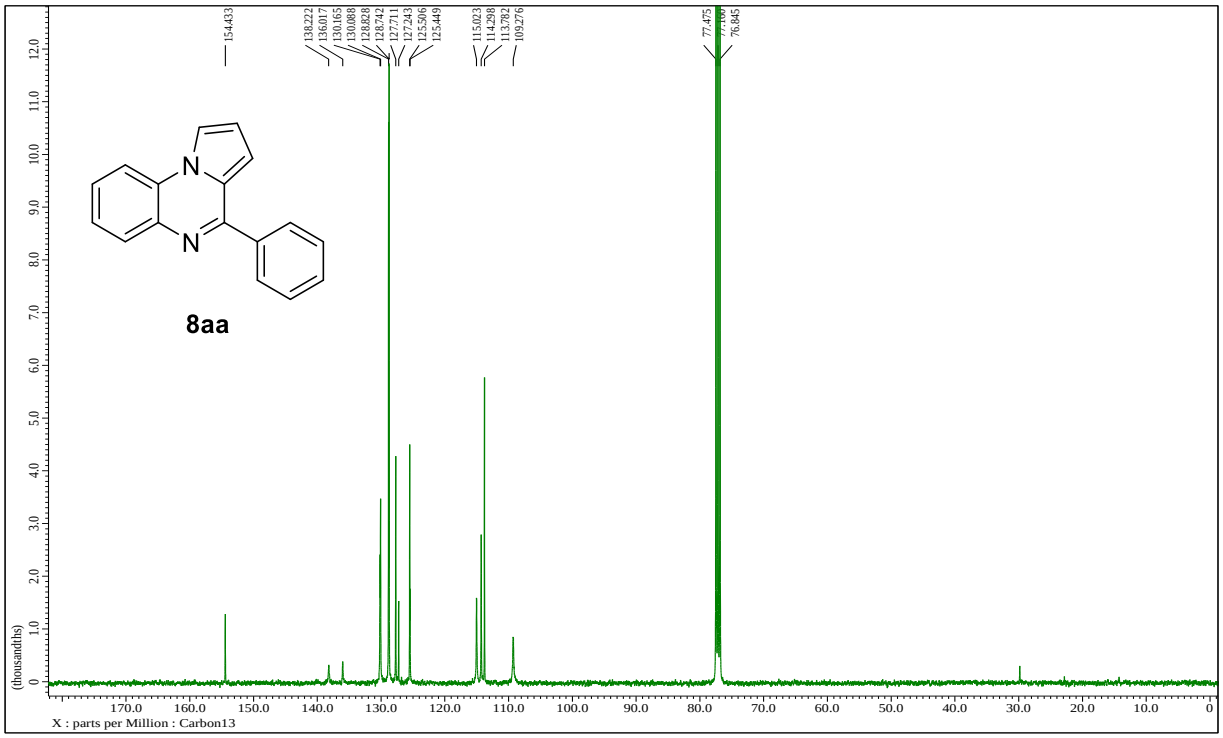
6ca ^{13}C-NMR (100 MHz, $CDCl_3$)



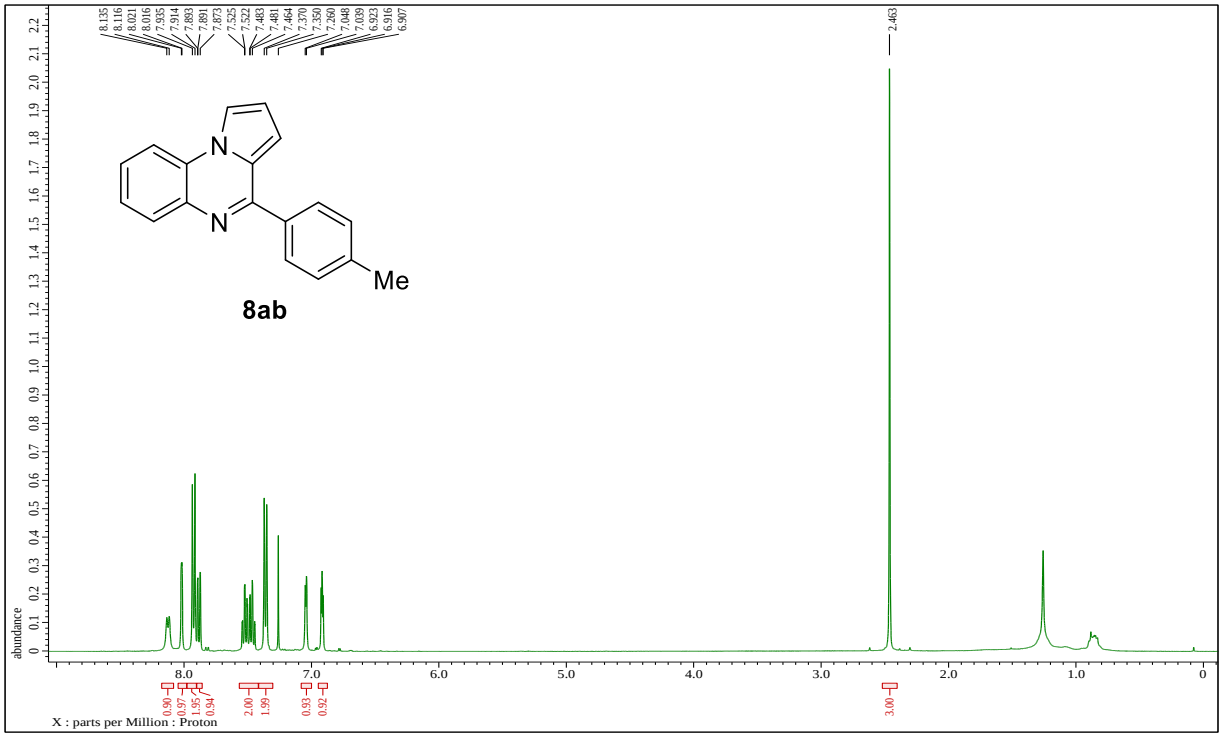
8aa ^{1}H-NMR (400 MHz, $CDCl_3$)



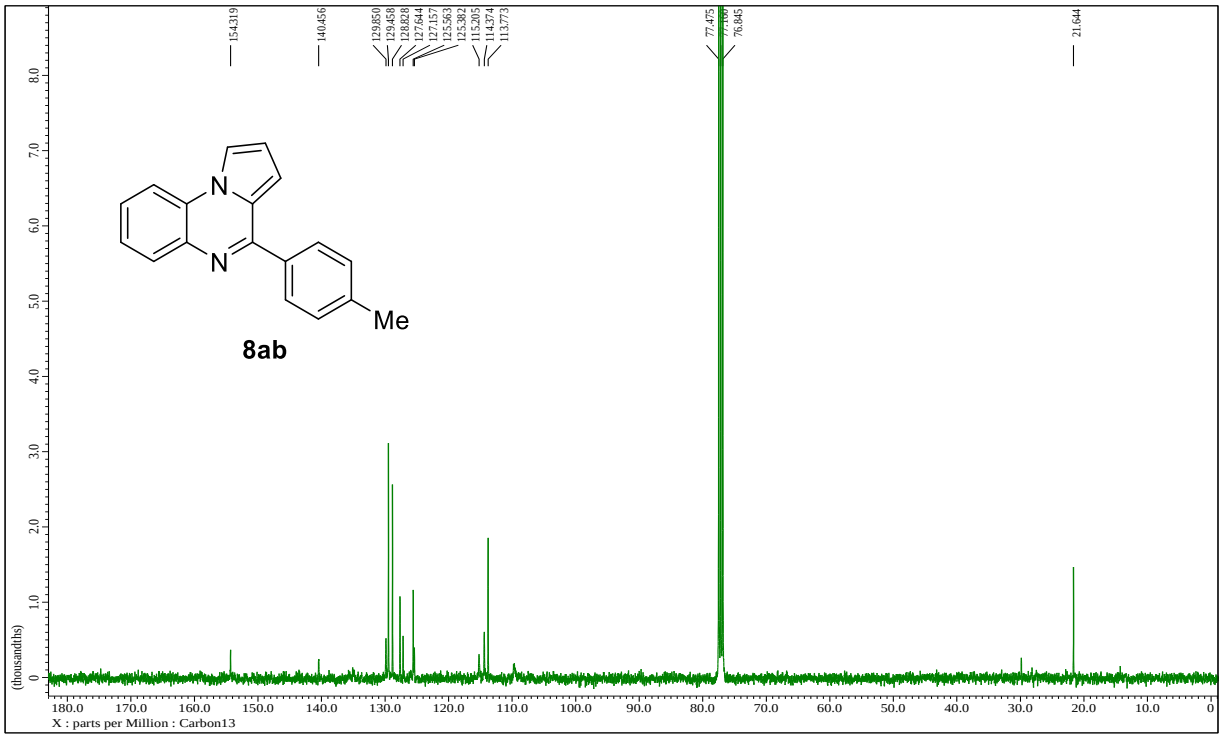
8aa ^{13}C-NMR (100 MHz, $CDCl_3$)



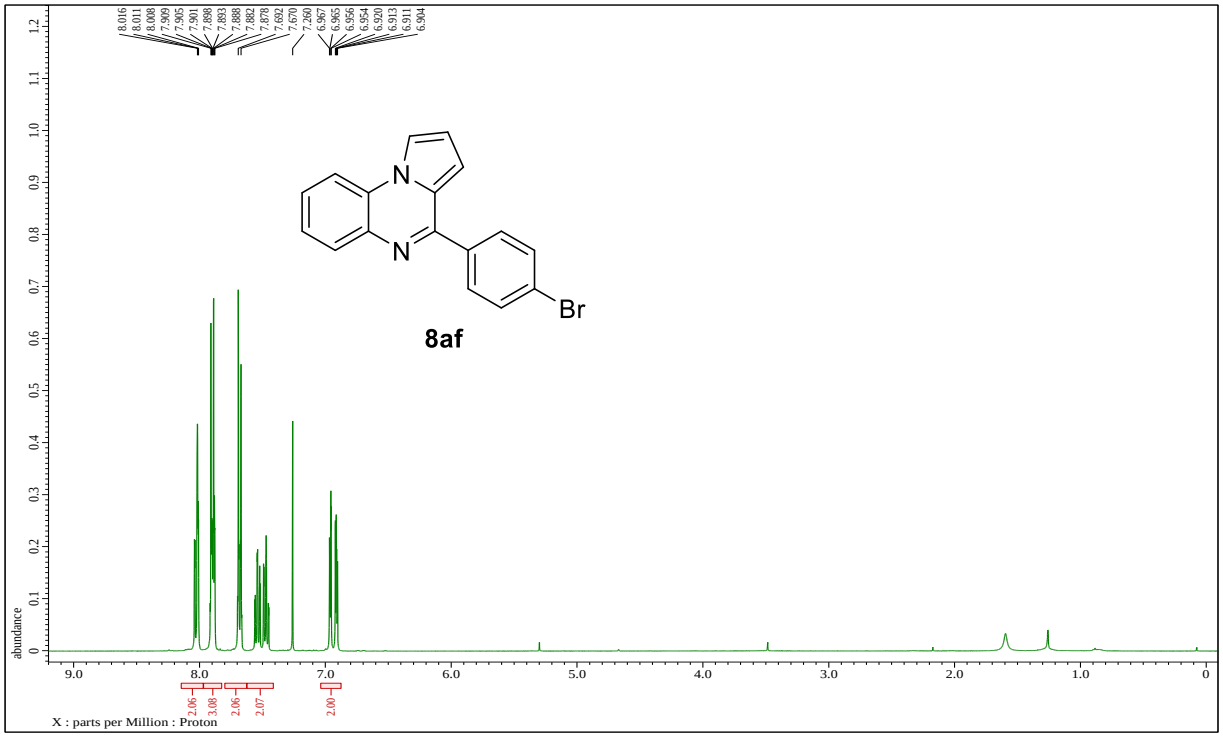
8ab ^{1}H-NMR (400 MHz, $CDCl_3$)



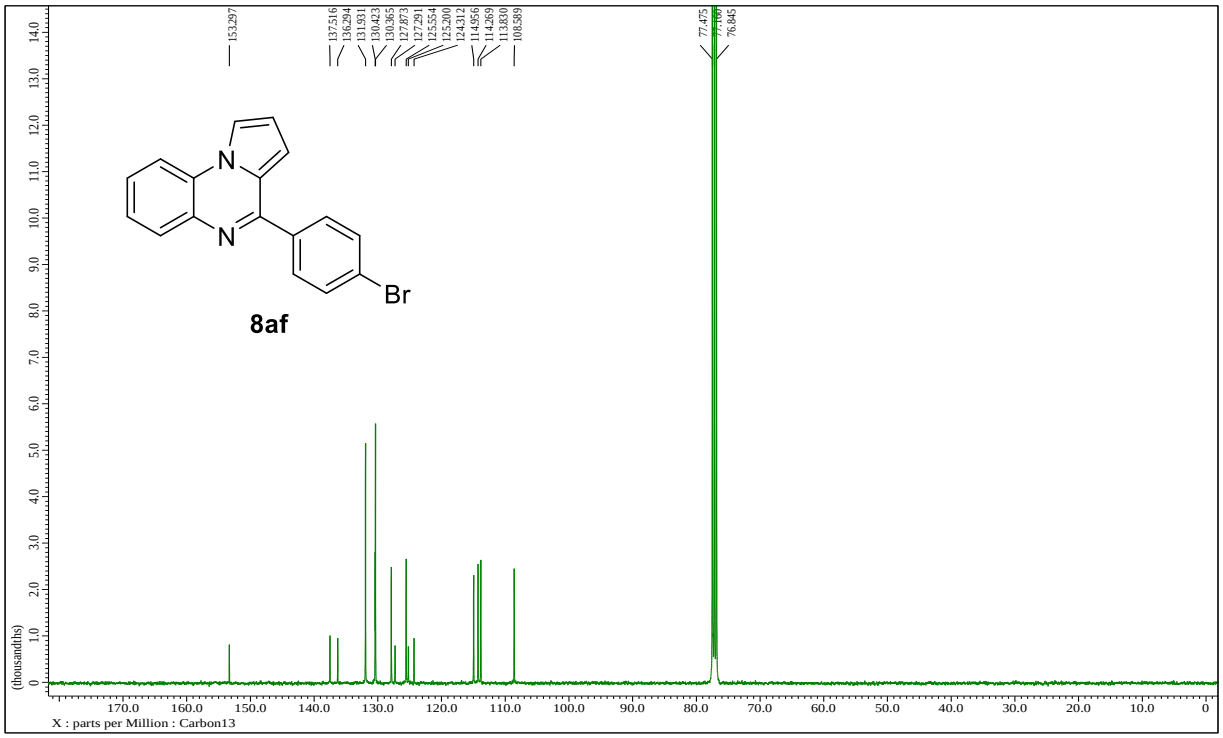
8ab ^{13}C-NMR (100 MHz, $CDCl_3$)



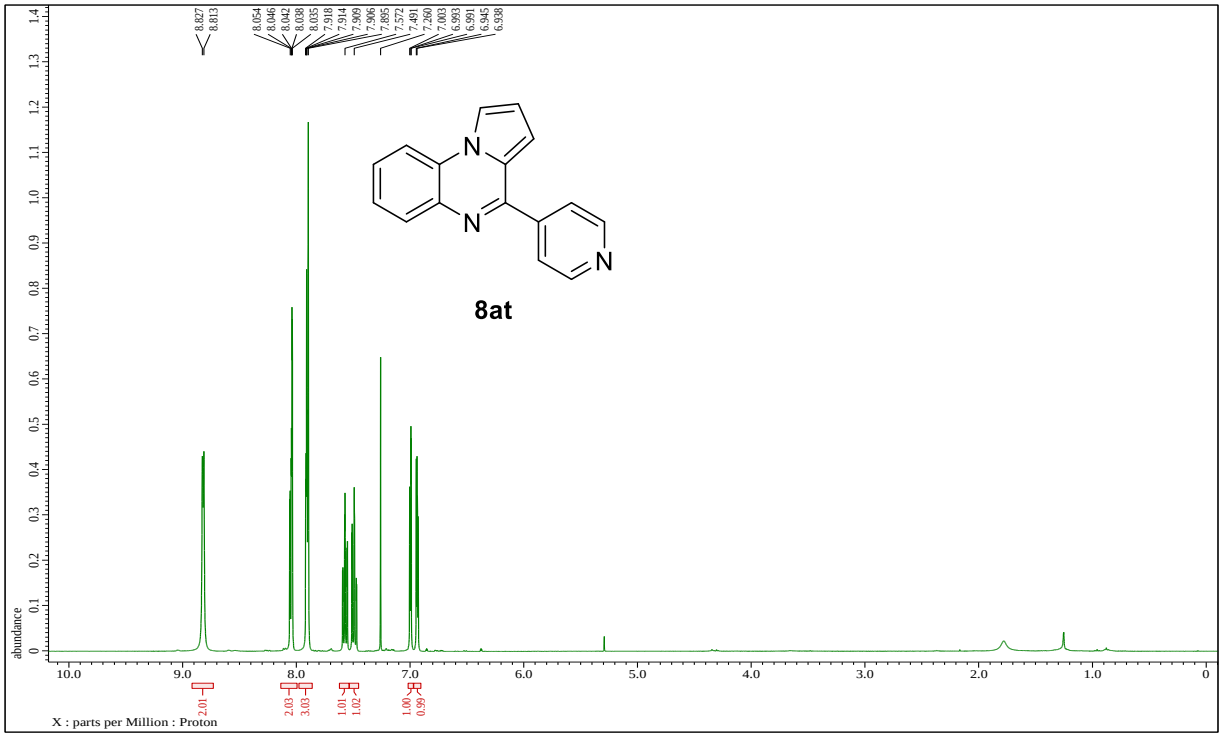
8af ^{1}H-NMR (400 MHz, $CDCl_3$)



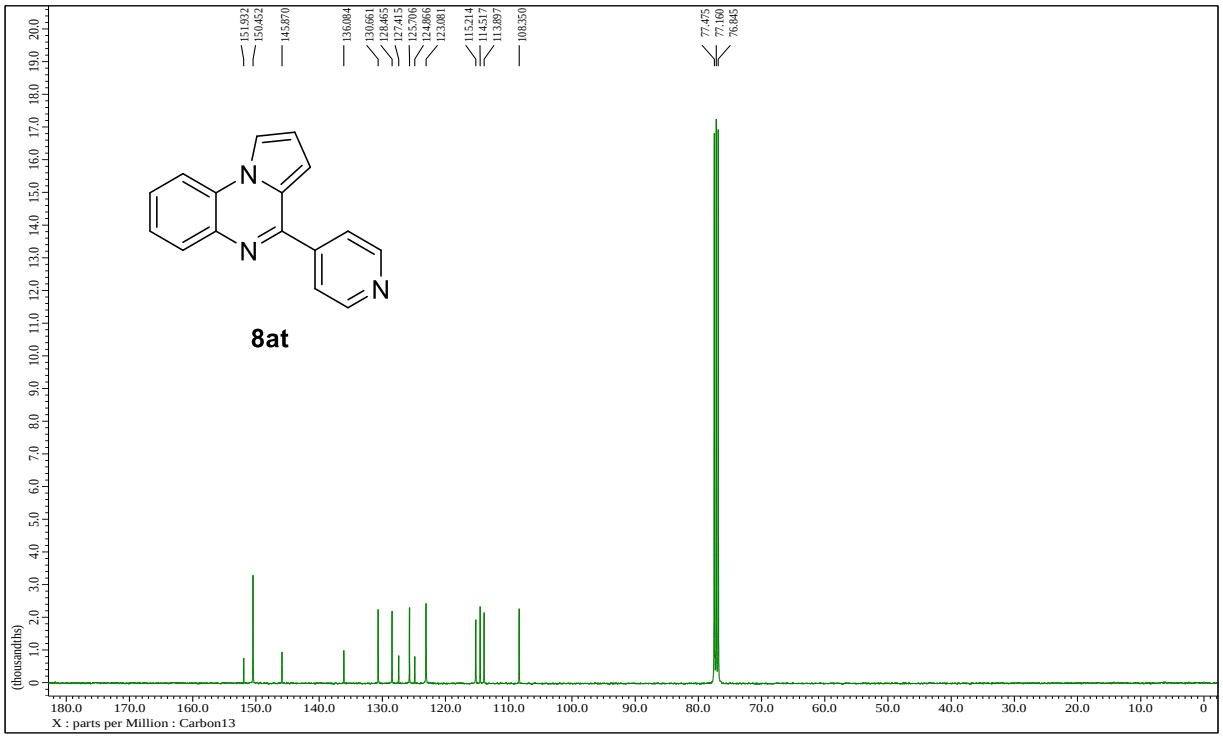
8af ^{13}C-NMR (100 MHz, $CDCl_3$)



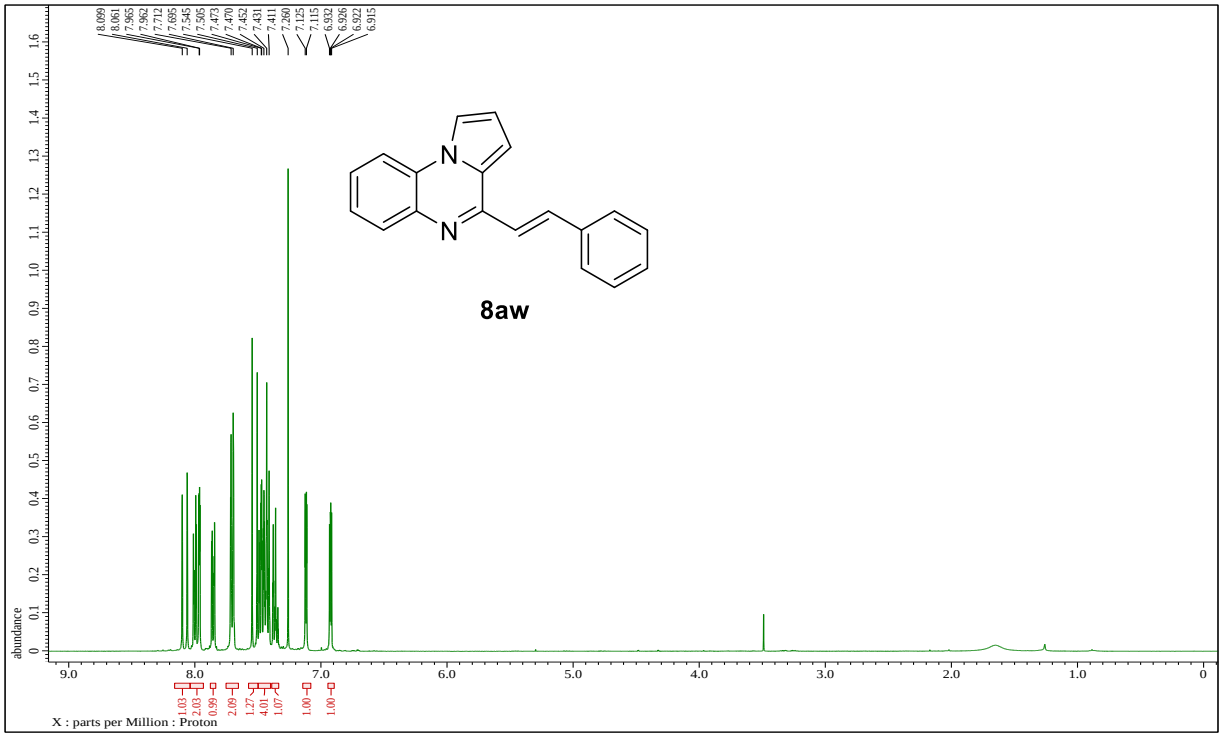
8at ^{1}H-NMR (400 MHz, $CDCl_3$)



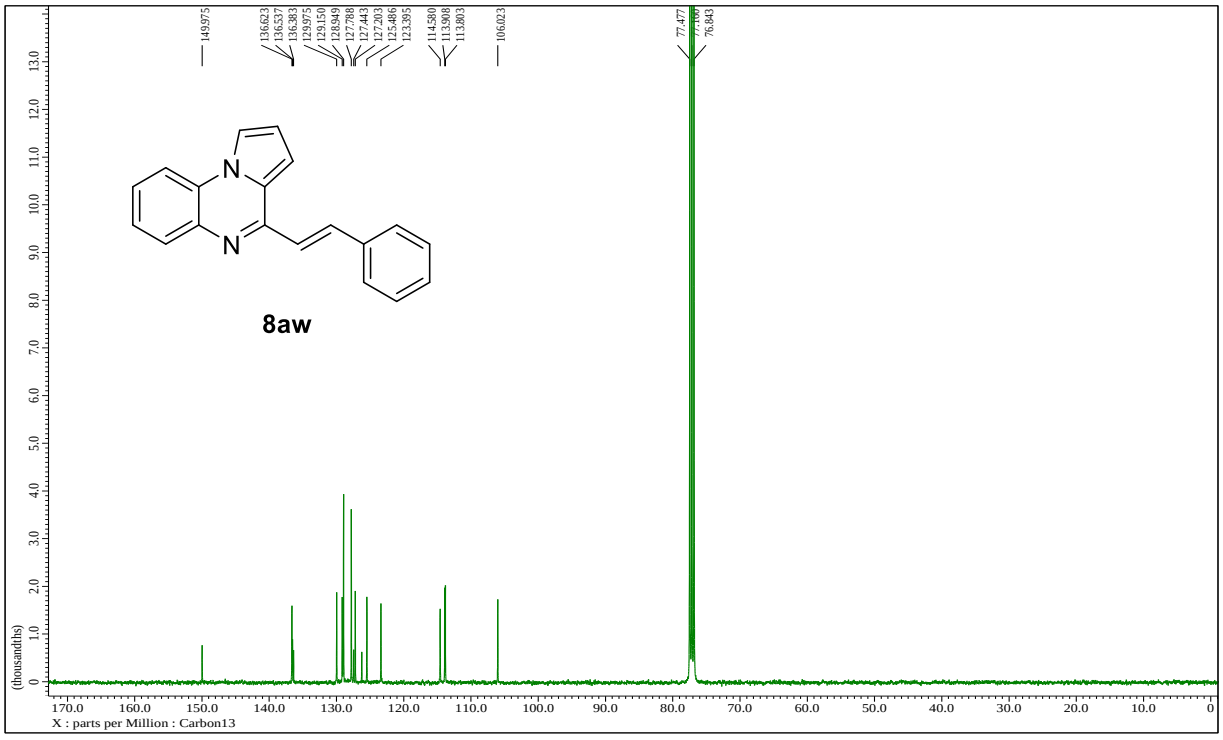
8at ^{13}C-NMR (100 MHz, $CDCl_3$)



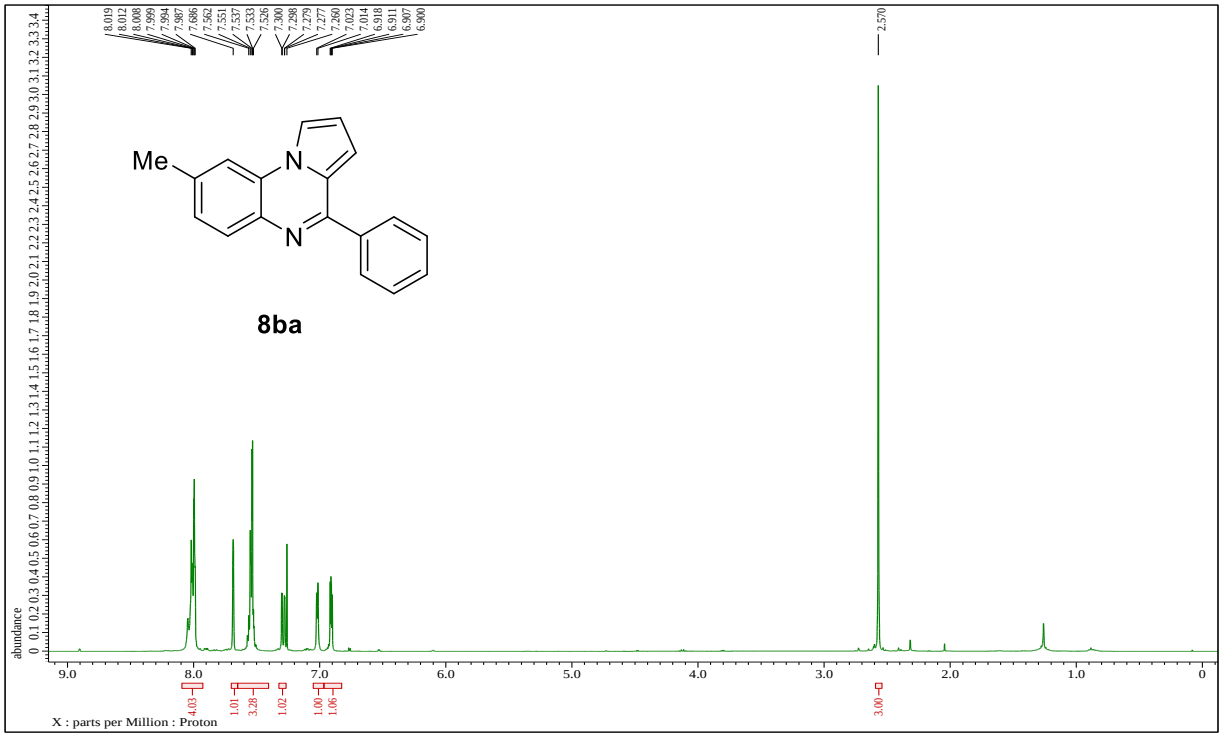
8aw ^{1}H-NMR (400 MHz, $CDCl_3$)



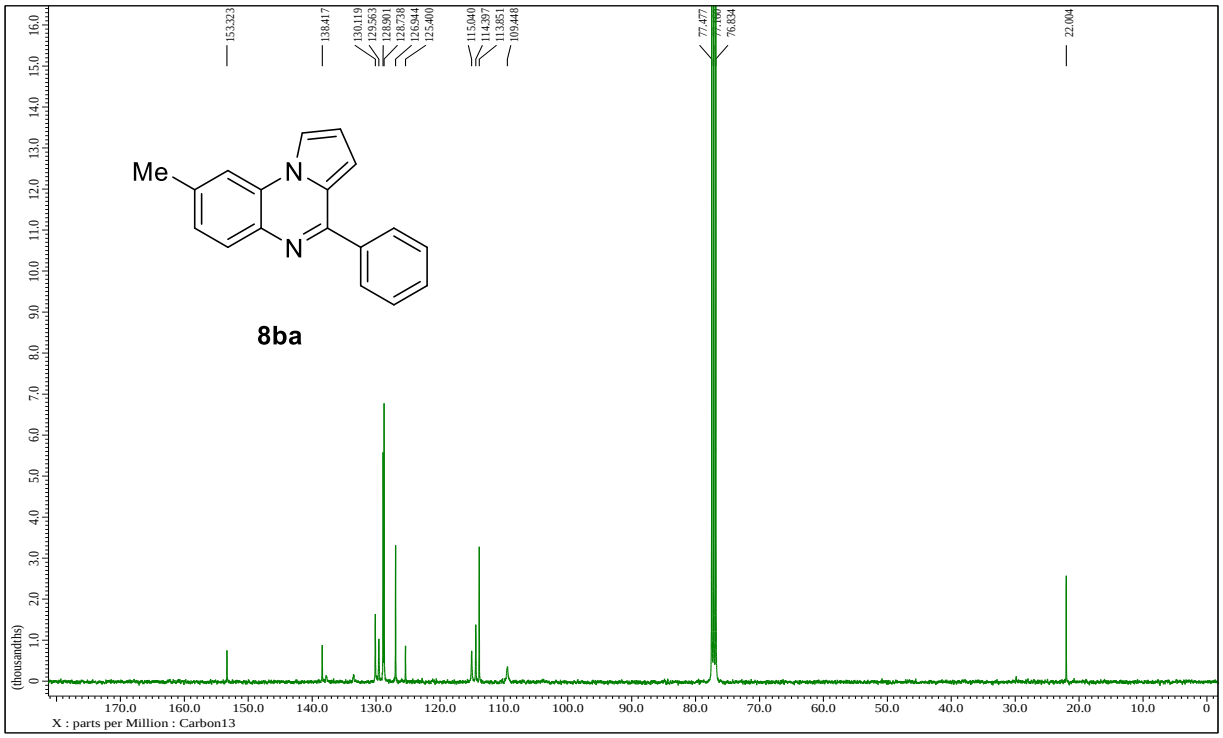
8aw ^{13}C-NMR (100 MHz, $CDCl_3$)



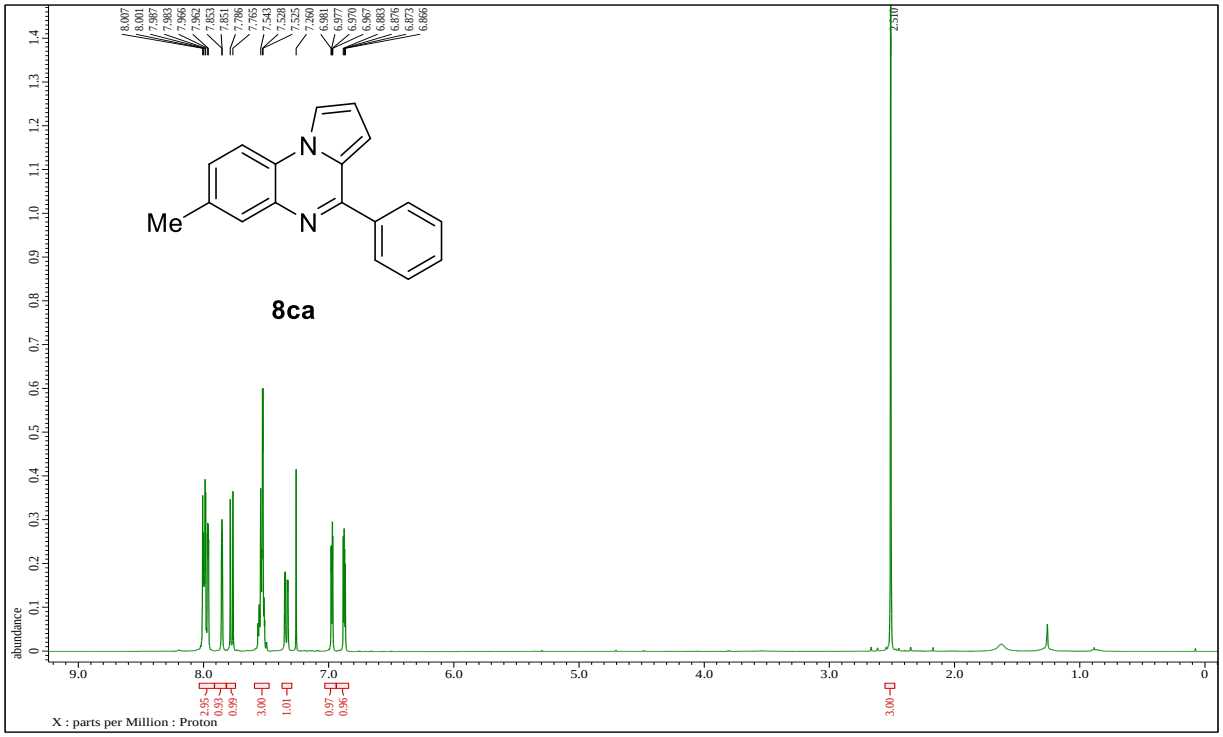
8ba ^{1}H-NMR (400 MHz, $CDCl_3$)



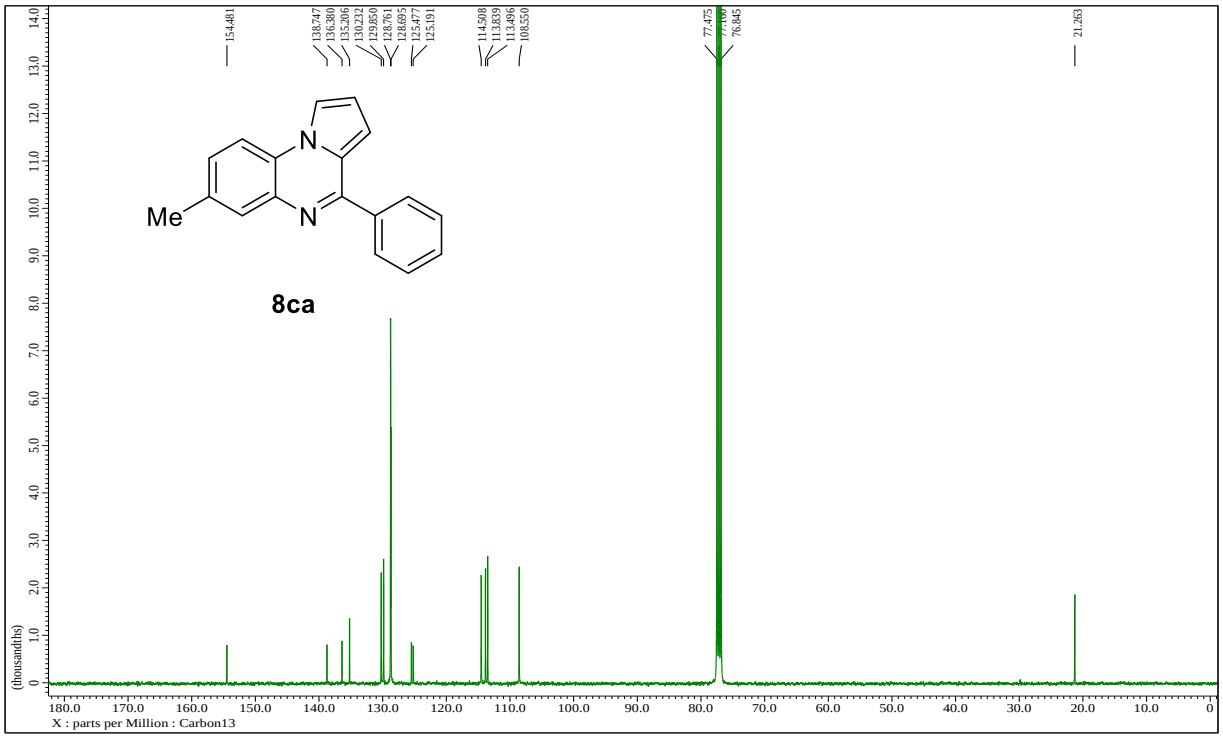
8ba ^{13}C-NMR (100 MHz, $CDCl_3$)



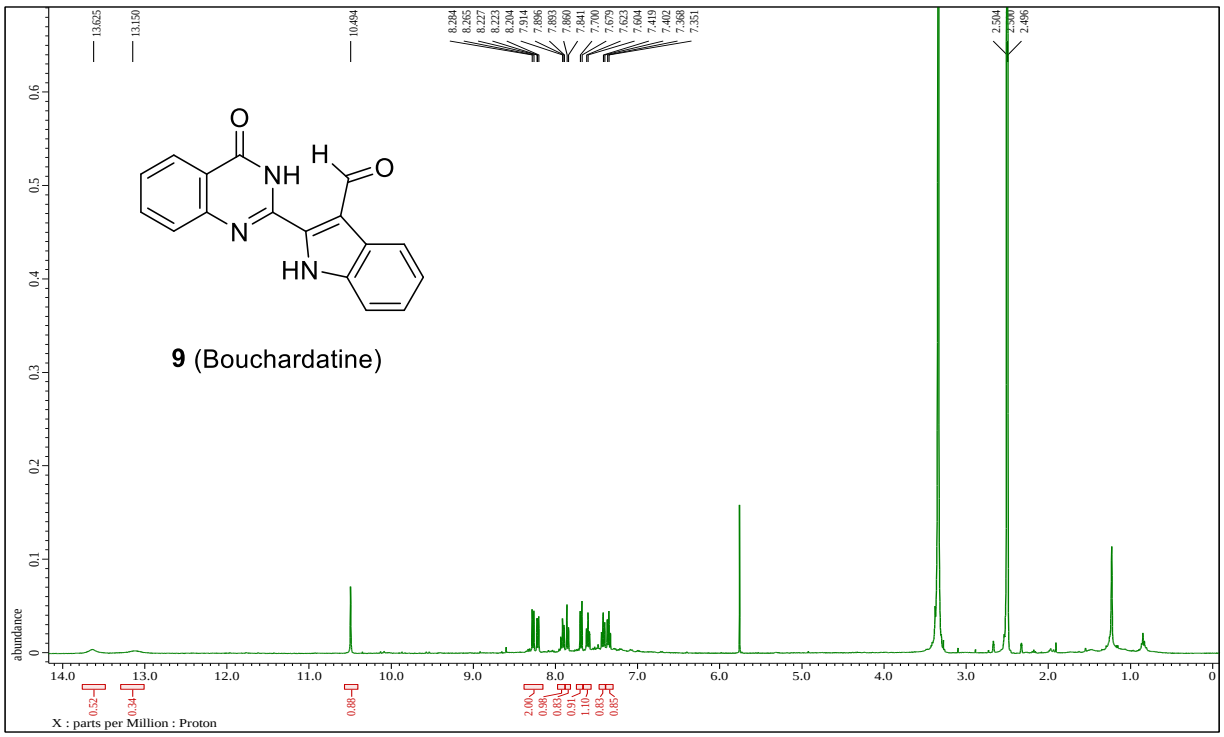
8ca ^{1}H-NMR (400 MHz, $CDCl_3$)



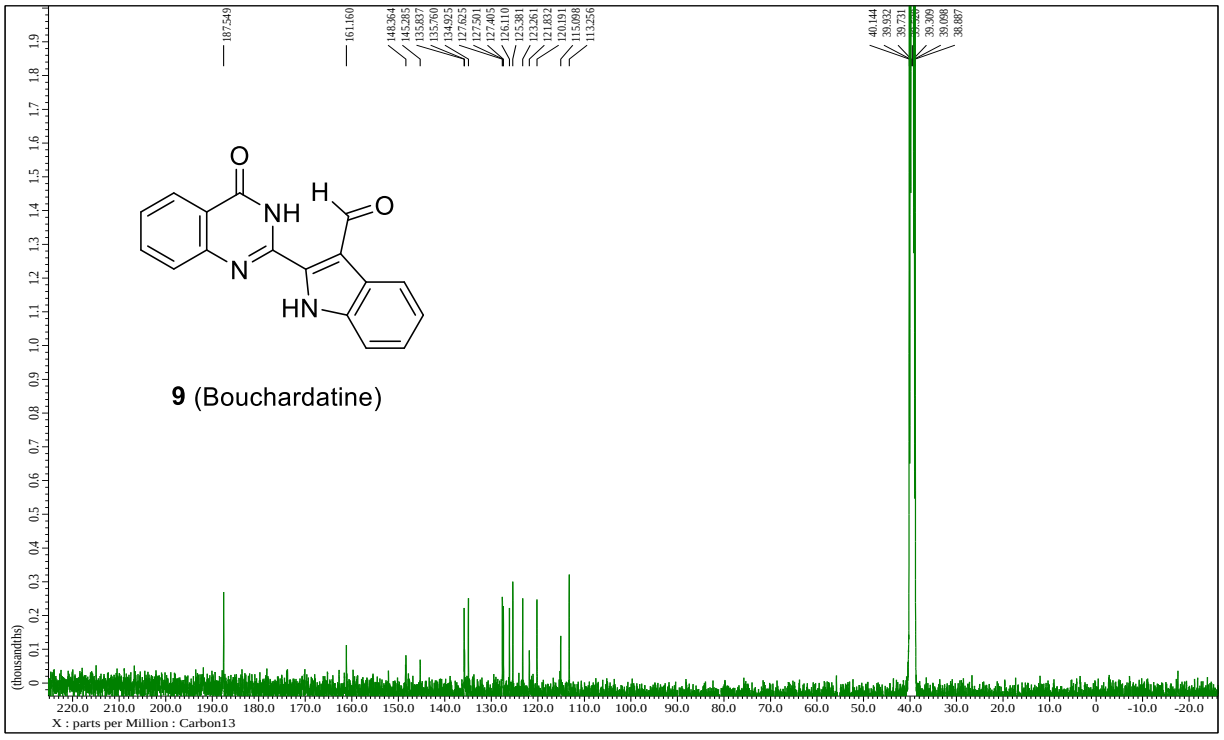
8ca ^{13}C-NMR (100 MHz, $CDCl_3$)



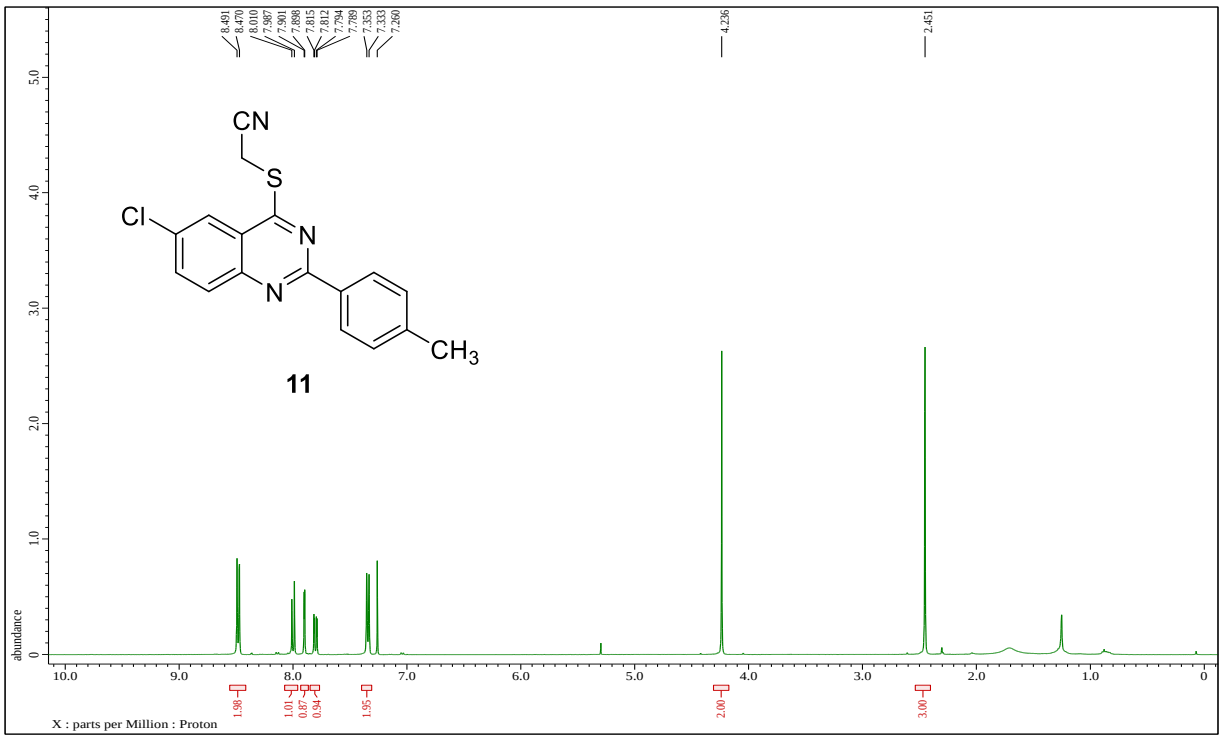
9 ^{1}H-NMR (400 MHz, DMSO-d_6)



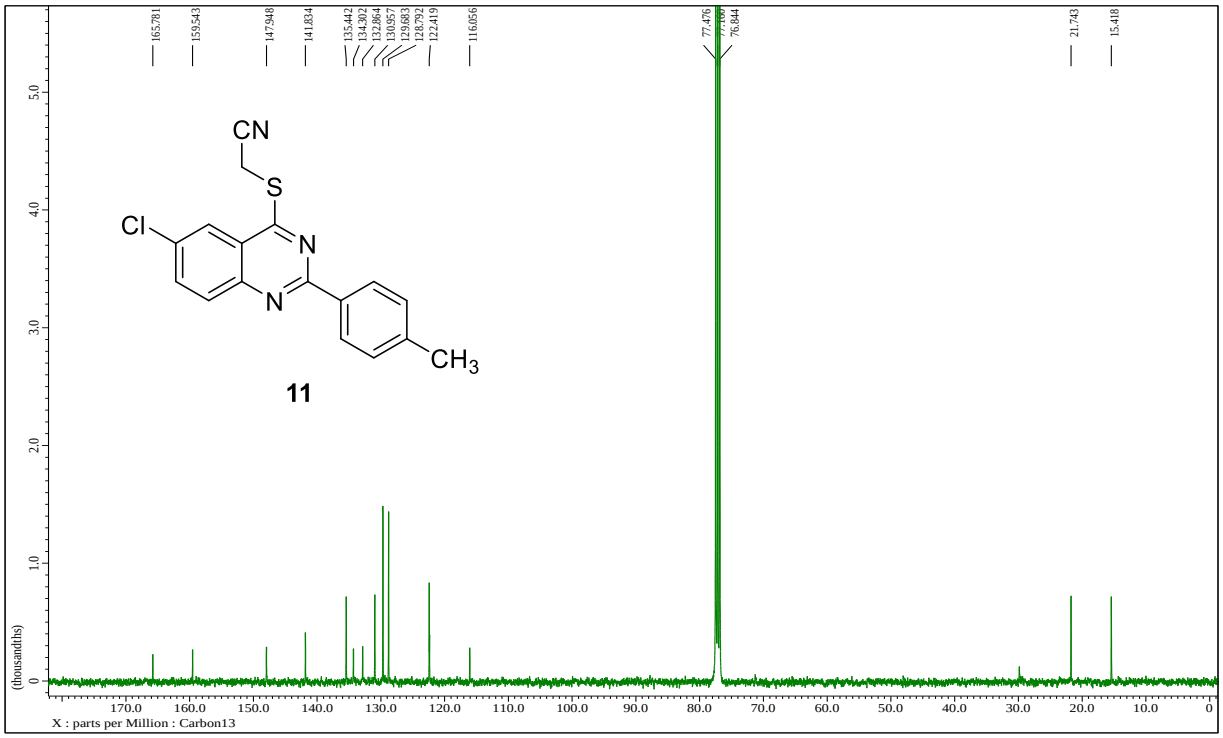
9 ^{13}C-NMR (100 MHz, DMSO-d_6)



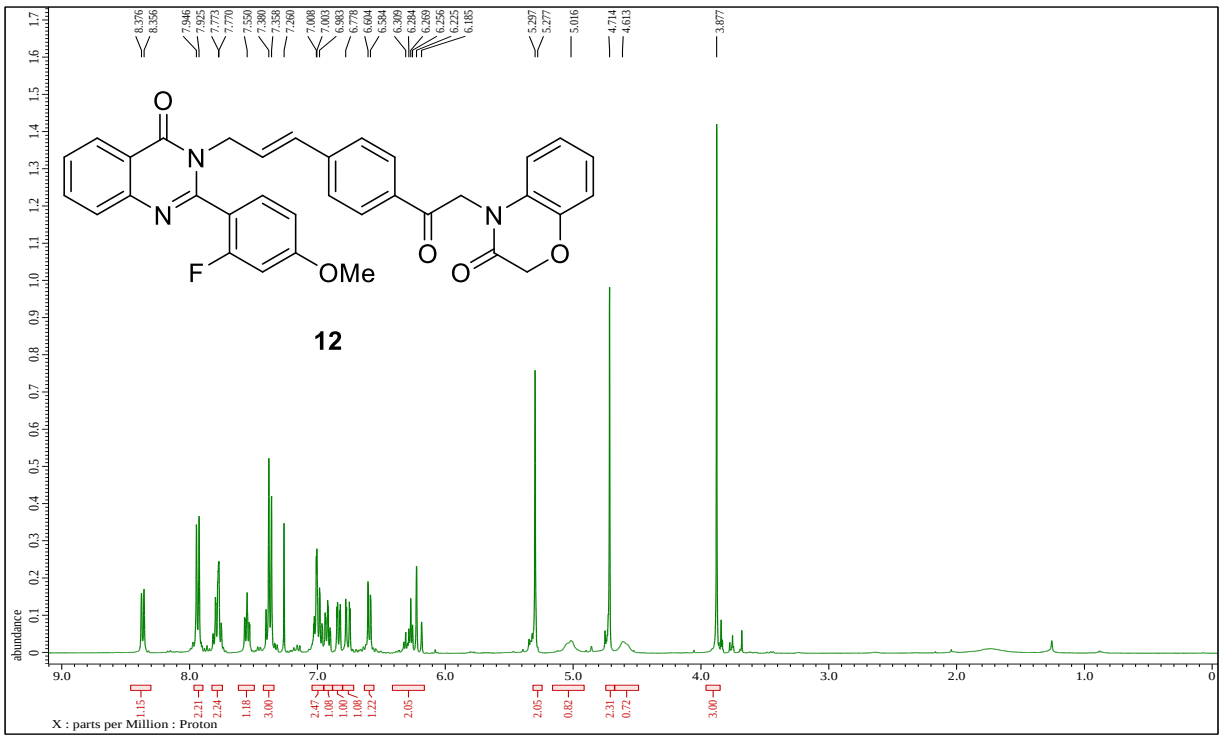
11 ^{1}H-NMR (400 MHz, $CDCl_3$)



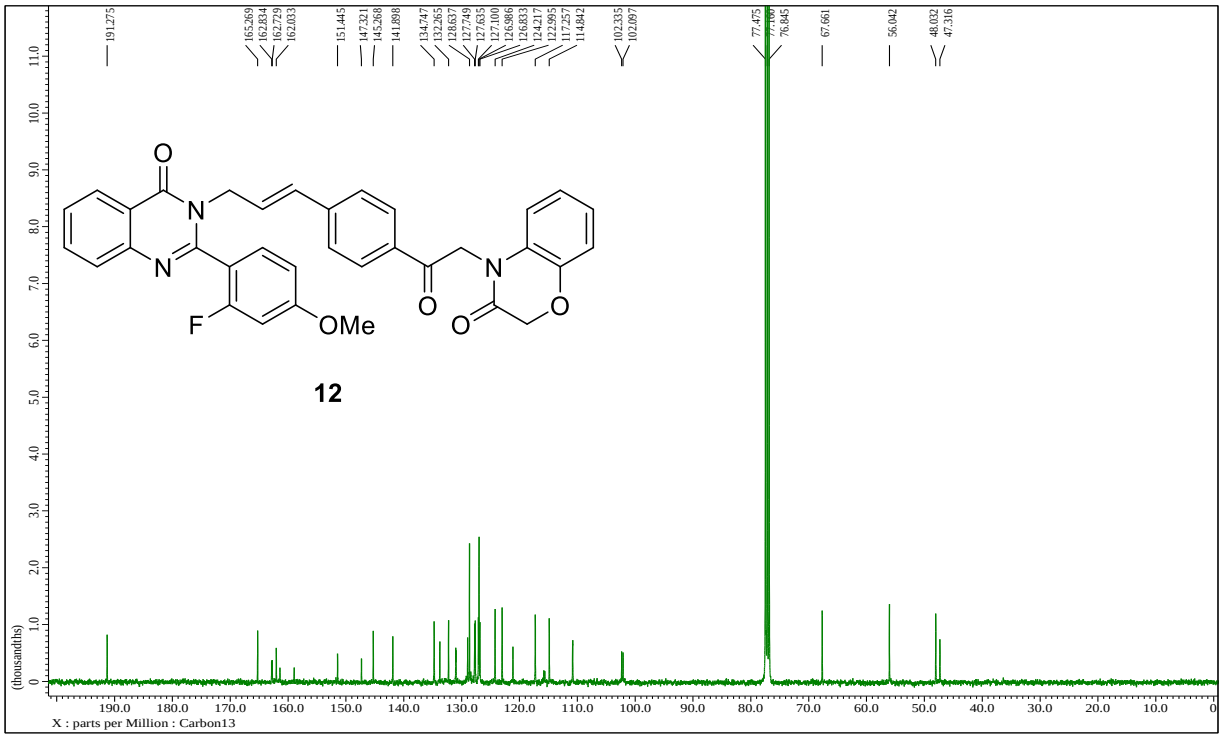
11 ^{13}C-NMR (100 MHz, $CDCl_3$)



12 ^{1}H-NMR (400 MHz, $CDCl_3$)



12 ^{13}C-NMR (100 MHz, $CDCl_3$)



12 ^{19}F-NMR (376 MHz, $CDCl_3$)