# Supporting Information

## Rh(III)-Catalyzed Vinylic C–H Activation/Annulation of 4-Amino-2-quinolones with Alkynes: Thermodynamically Controlled Site-Selectivity via Reversible Alkyne Insertion

Naohiro Hirako, Takeshi Yasui,* and Yoshihiko Yamamoto*

*Department of Basic Medicinal Sciences, Graduate School of Pharmaceutical Sciences, Nagoya University, Furo-cho Chikusa, Nagoya 464-8603, Japan*

t-yasui@ps.nagoya-u.ac.jp, yamamoto-yoshi@ps.nagoya-u.ac.jp

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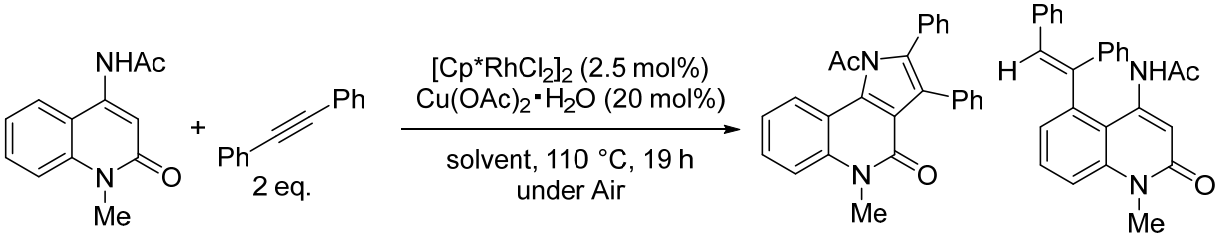
# 1. Optimization of Reaction Conditions

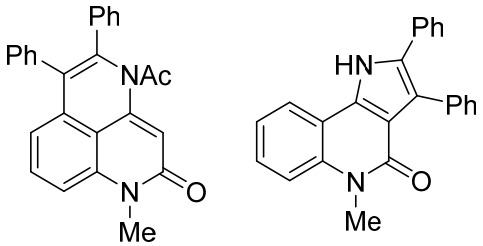
**Table S1.** Optimization of reaction conditions[a]




**1b** **2a** **3ba** **4ba**

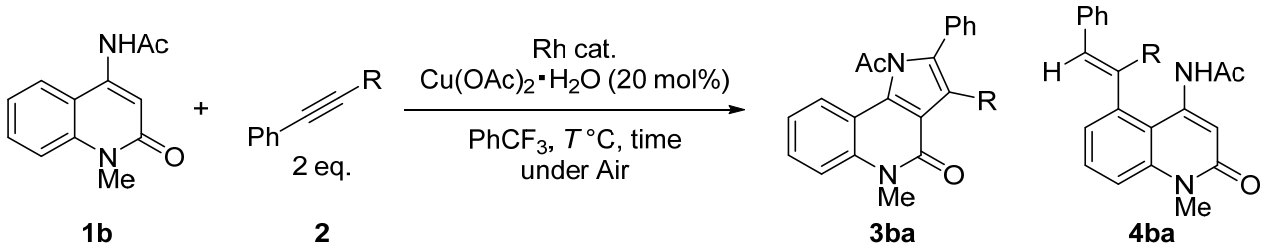
| entry | additive | solvent | **3ba** (%) | **4ba** (%) | **1b** (%) | memo |
|---|---|---|---|---|---|---|
| 1[b] | $AgSbF_6$ (10 mol%) | DCE | 43 | n.d. | n.d. | **5ba** was obtained in 48% yield. |
| 2[b] | - | DCE | 63 | n.d. | n.d. | |
| 3 | - | DCE | 10 | 7 | 59 | AgOAc(2 eq.) was used instead of $Cu(OAc)_2 \cdot H_2O$ |
| 4 | - | DCE | 62 | n.d. | n.d. | A trace amount of **5ba** was obtained. |
| 5 | - | DCE | n.d. | n.d. | 91 | Run at 100 ºC |
| 6 | - | *t*-AmOH | 20 | n.d. | 67 | |
| 7 | - | DMF | n.d. | n.d. | 27 | **3ba'** was obtained in 54% yield. |
| 8 | - | DMA | n.d. | n.d. | 21 | **3ba'** was obtained in 54% yield. |
| 9 | - | MeCN | n.d. | n.d. | - | complex mixture |
| 10 | - | toluene | n.d. | n.d. | 87 | |
| 11 | - | $PhCF_3$ | 68 | n.d. | n.d. | |
| 12 | AgOAc (10 mol%) | $PhCF_3$ | 25 | 35 | n.d. | |
| 13 | NaOAc (2 eq.) | $PhCF_3$ | 18 | n.d. | 40 | |

[a]Reaction conditions: **1b** (0.2 mmol), **2a** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (20 mol%), $[Cp^*RhCl_2]_2$ (2.5 mol%), solvent (2 mL). Isolated yields are reported. [b]$Cu(OAc)_2 \cdot H_2O$ (2 eq.) were used under an Ar atmosphere. n.d. = not detected.




**5ba** **3ba'**

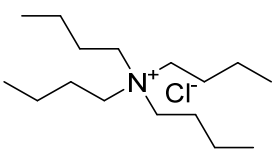
**Table S2.** Effect of rhodium catalysts and temperature[a]



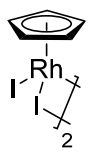

**1b** **2** **3ba** **4ba**

| entry | R | Rh cat. (mol%) | additive (eq.) | *T* | time | **3ba** (%)[b] | **4ba** (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | Ph | $[Cp^*RhCl_2]_2$ (2.5) | - | 110 | 19 h | (68) | n.d. |
| 2 | Me | $[Cp^*RhCl_2]_2$ (2.5) | - | 110 | 12 h | 87(85) | n.d. |
| 3 | Ph | $Cp^*Rh(OAc)_2 \cdot H_2O$ (5) | - | 110 | 19 h | 61(65) | 6(5) |
| 4 | Me | $Cp^*Rh(OAc)_2 \cdot H_2O$ (5) | - | 110 | 12 h | 75(75) | 8(8) |
| 5[c] | Ph | $[Cp^*RhCl_2]_2$ (2.5) | - | 100 | 19 h | n.d. | n.d. |
| 6[c] | Ph | $Cp^*Rh(OAc)_2 \cdot H_2O$ (5) | - | 100 | 19 h | 23 | 10 |
| 7[c] | Ph | $Cp^*Rh(OAc)_2 \cdot H_2O$ (5) | - | 70 | 6 days | 29(27) | 23(24) |
| 8[c] | Me | $Cp^*Rh(OAc)_2 \cdot H_2O$ (5) | - | 40 | 7 days | 13 | 8 |
| 9 | Me | $[Cp^*RhCl_2]_2$ (2.5) | AcOH (1) | 110 | 19 h | n.d. | n.d. |
| 10 | Me | $[Cp^*RhCl_2]_2$ (2.5) | HFIP (1) | 110 | 19 h | 24 | n.d. |
| 11 | Me | $Cp^*Rh(OAc)_2 \cdot H_2O$ (5) | TBACl (0.2) | 70 | 24 h | n.d. | n.d. |
| 12 | Ph | $[CpRhI_2]_2$ (5) | - | 110 | 19 h | n.d. | n.d. |
| 13 | Ph | $[Cp^ERhCl_2]_2$ (5) | - | 110 | 19 h | 14 | n.d. |

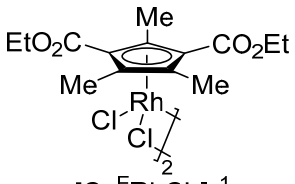
[a]Reaction conditions: **1b** (0.2 mmol), **2** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (20 mol%), Rh cat. (2.5 or 5 mol%), $PhCF_3$ (2 mL). [b]Yields were determined by $^1H$ NMR analysis. Isolated yields are shown in parentheses. [c]DCE was used as a solvent. n.d. = not detected.




TBACl




$[CpRhI_2]_2$




$[Cp^ERhCl_2]_2$[1]

## 2. General Information

**General Considerations:** All air- and moisture-sensitive reactions were performed under an argon (Ar) atmosphere. Analytical thin layer chromatography was performed using 0.25 mm silica gel plate (Merck TLC Silica gel 60 $F_{254}$). Column chromatography was performed on silica gel (Cica silica gel 60N) with solvents specified below. Melting points were recorded on SRS OptiMelt MPA100. NMR spectra were recorded on JEOL ESC-400 spectrometer ($^1$H/400 MHz,$^{13}$C/100 MHz and $^{19}$F/376 MHz,) for samples in $CDCl_3$ and DMSO-$d_6$, $CD_3OD$ solutions at 25 ˚C. $^1$H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at ($CDCl_3$ and $CD_3OD$ δ 0.00 ppm for tetramethylsilane, DMSO-$d_6$ δ 2.49 ppm for the DMSO). $^{13}$C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the solvent peak ($CDCl_3$, δ 77.00 ppm, DMSO, δ 39.52 ppm). $^{19}$F NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ −63.7 ppm for $\alpha,\alpha,\alpha$-trifluorotoluene as an external standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. Infrared spectra were recorded on JASCO FT/IR-230 spectrometer. High-resolution mass spectra were recorded on JEOL JMS-T100LP mass spectrometer.

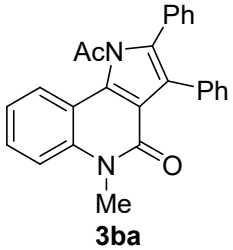
**Reagents and Solvents:** Alkynes **2b-f**[2], **2h-j**[3], **2k**[4], **2l**[4], **2m**[5], **2n**[4], **2o**[3], **2p**[4], **2r**[6], **2s**[7], **2t**[8], Cp*Rh(OAc)$_2$·$H_2O$[9] and [Cp*$RhCl_2$]$_2$[10] were prepared according to the literature. Unless otherwise noted below, commercial reagents and solvents were purchased from Aldrich, Kanto Chemical, TCI, and Wako and used as received.

## 3. Representative Procedure for the Rhodium-Catalyzed C–H Functionalization of 1

A Schlenk tube was charged with [Cp*$RhCl_2$]$_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), Cu(OAc)$_2$·$H_2O$ (7.9 mg, 0.040 mmol, 20 mol%), **1b** (43.2 mg, 0.20 mmol), **2a** (71.4 mg, 0.40 mmol) and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at 110 °C for 19 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with $CHCl_3$ to remove the metal salts. After concentration in vacuo, the residue was purified by silica gel column chromatography (Hexane/EtOAc = 3:1) to give **3ba**.

## 4. Characterization of 3,4-Fused 2-Quinolone Derivatives 3

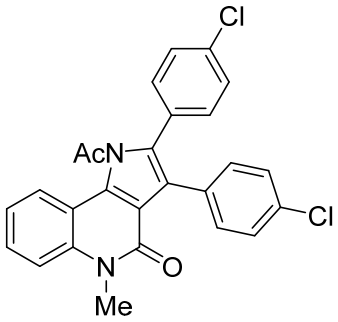
**1-Acetyl-5-methyl-2,3-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3ba)**



**3ba**

**Analytical data for 3ba:** 68% yield; white solid. Colorless crystals (mp 230.5–230.9 °C) for X-ray crystallographic analysis were obtained by recrystallization from DCM and hexane; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, $J$ = 8.5, 1.4 Hz, 1H), 7.55-7.43 (m, 2H), 7.36-7.20 (m, 11H), 3.76 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.4, 159.2, 138.3, 134.2, 132.8, 132.7, 131.0 (2C), 130.7 (2C), 128.59, 128.55 (2C), 128.3, 127.3 (2C), 126.8, 124.0, 122.3, 121.7, 115.5, 115.3, 113.5, 29.6, 29.3, One C$sp^2$ signal is missing due to overlapping; IR (neat) 3002, 1749, 1654 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{26}H_{21}N_2O_2$ 393.1603, found 393.1624.

**1-Acetyl-2,3-bis(4-chlorophenyl)-5-methyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bb)**

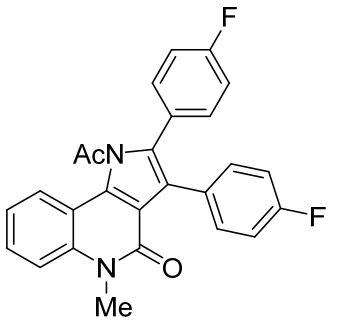


**3bb**

**3bb** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1 to 3:1).

**Analytical data for 3bb:** 60% yield; yellow amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.56-7.43 (m, 2H), 7.34-7.30 (m, 2H), 7.25-7.16 (m, 7H), 3.76 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.9, 159.1, 138.4, 135.1, 133.1, 133.04, 133.00, 132.8, 132.3 (2C), 132.0 (2C), 131.0, 129.0 (2C), 128.6, 127.8 (2C), 123.1, 122.3, 121.9, 115.6, 115.0, 113.3, 29.7, 29.4; IR (KBr) 3061, 1751, 1655 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{18}Cl_2N_2NaO_2$ 483.0643, found 483.0657.

**1-Acetyl-2,3-bis(4-fluorophenyl)-5-methyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bc)**

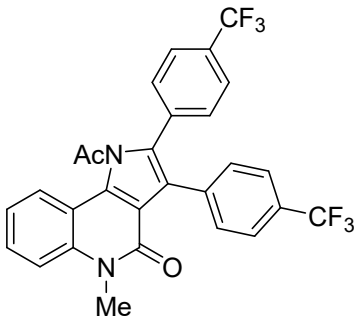


**3bc**

**3bc** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3bc:** 63% yield; yellow amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.55-7.47 (m, 2H), 7.26-7.21 (m, 5H), 7.08-7.00 (m, 2H), 7.00-6.93 (m, 2H), 3.76 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.0, 162.8 (d, $^{1}J_{CF}$ = 250.2 Hz), 162.0 (d, $^{1}J_{CF}$ = 246.3 Hz), 159.2, 138.3, 133.2, 132.8, 132.7 (d, $^{3}J_{CF}$ = 8.6 Hz, 2C), 132.6 (d, $^{3}J_{CF}$ = 8.6 Hz, 2C), 128.5 (d, $^{4}J_{CF}$ = 3.8 Hz), 126.4 (d, $^{4}J_{CF}$ = 3.8 Hz), 123.2, 122.3, 121.9, 115.9 (d, $^{2}J_{CF}$ = 22.0 Hz, 2C), 115.6, 115.1, 114.5 (d, $^{2}J_{CF}$ = 21.1 Hz, 2C), 113.4, 29.6, 29.4, One C*sp*$^2$ signal is missing due to overlapping; $^{19}$F NMR (376 MHz, $CDCl_3$): δ –112.4, –116.5; IR (KBr) 3005, 1760, 1656 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{18}F_2N_2NaO_2$ 451.1234, found 451.1216.

**1-Acetyl-5-methyl-2,3-bis(4-(trifluoromethyl)phenyl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bf)**

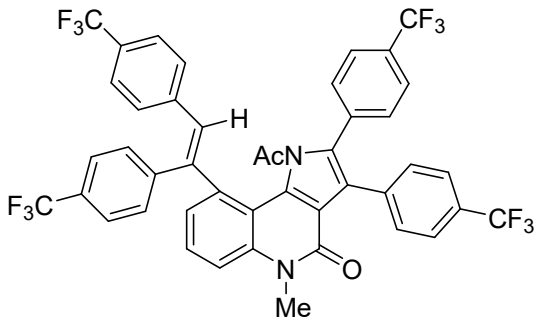


**3bf**

**3bf** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3bf:** 32% yield; yellow amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.57-7.49 (m, 4H), 7.42-7.36 (m, 4H), 7.31-7.27 (m, 1H), 3.77 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.6, 159.0, 138.5, 136.2, 133.7, 133.5, 132.8, 131.3, 131.1, 130.9 (q, $^{2}J_{CF}$ = 32.6 Hz, 2C), 129.2 (q, $^{2}J_{CF}$ = 32.6 Hz, 2C), 129.0, 125.7 (q, $^{3}J_{CF}$ = 3.8 Hz, 2C), 124.5 (q, $^{3}J_{CF}$ = 3.8 Hz, 2C), 124.2 (q, $^{1}J_{CF}$ = 272.2 Hz), 123.7 (q, $^{1}J_{CF}$ = 271.3 Hz), 123.5, 122.3, 122.1, 115.7, 114.9, 113.1, 29.7, 29.4; $^{19}$F NMR (376 MHz, $CDCl_3$): δ –63.4, –63.7; IR (neat) 1654, 1612 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{28}H_{19}F_6N_2O_2$ 529.1351, found 529.1368.

**(*E*)-1-Acetyl-9-(1,2-bis(4-(trifluoromethyl)phenyl)vinyl)-5-methyl-2,3-bis(4-(trifluoromethyl)phenyl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bf')**

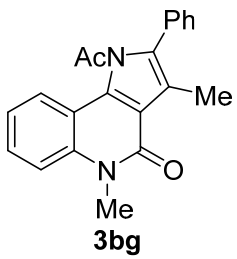


**3bf'**

**3bf'** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 1:1).

**Analytical data for 3bf':** 21% yield; white solid. Colorless crystals (mp 171.2–172.0 °C) for X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$ and hexane; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63-7.48 (m, 5H), 7.48-7.39 (m, 6H), 7.25-7.15 (m, 6H), 7.11 (s, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 3.79 (s, 3H), 2.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.4, 158.6, 142.1, 141.4, 140.1, 140.0, 139.6, 136.2, 135.6, 135.5, 133.9, 132.9, 131.6, 130.9, 130.8 (q, $^2J_{CF}$ = 32.6 Hz, 2C), 130.6, 130.3 (q, $^2J_{CF}$ = 32.6 Hz, 2C), 129.8 (q, $^2J_{CF}$ = 32.6 Hz, 2C), 129.4, 129.2 (q, $^2J_{CF}$ = 32.6 Hz, 2C), 128.7, 126.4, 125.6 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 125.0, 124.9 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 124.4 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 124.3, 124.1 (q, $^1J_{CF}$ = 272.2 Hz), 123.9 (q, $^1J_{CF}$ = 272.2 Hz), 123.8 (q, $^1J_{CF}$ = 272.2 Hz), 123.6 (q, $^1J_{CF}$ = 277.0 Hz), 118.8, 115.6, 112.8, 29.9, 28.4, One C*sp*$^2$ signal is missing due to overlapping; $^{19}$F NMR (376 MHz, $CDCl_3$): δ –63.5 (3F), –63.6 (6F), –63.8 (3F); IR (neat) 1654 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{44}H_{26}F_{12}N_2NaO_2$ 865.1700, found 865.1687.

**1-Acetyl-3,5-dimethyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bg)**

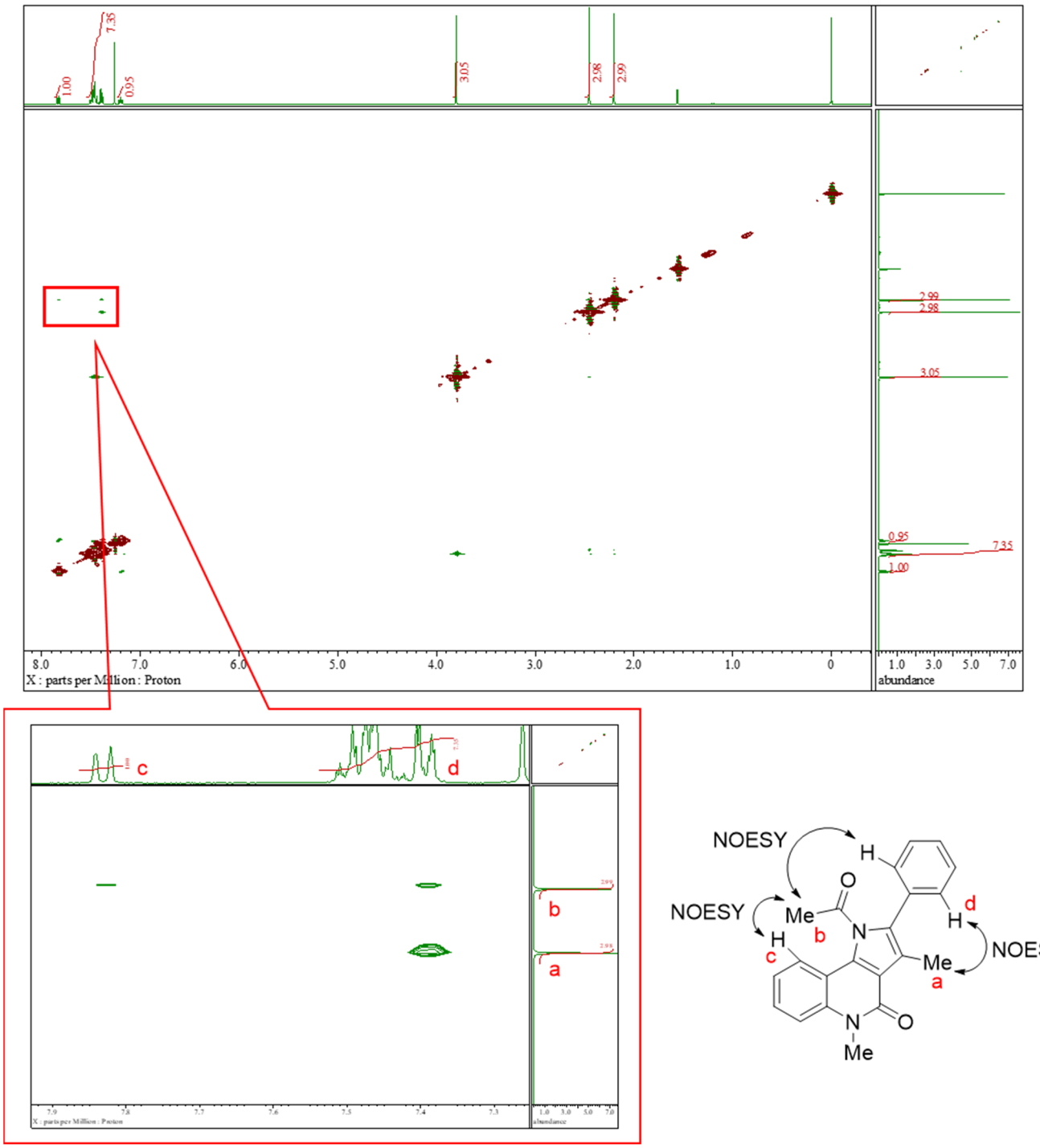


**3bg**

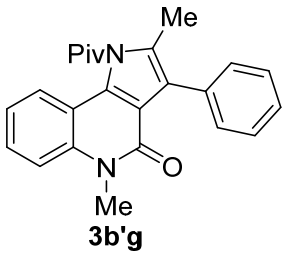
**3bg** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3bg:** 85% yield; yellow amorphous solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.53-7.36 (m, 7H), 7.20 (ddd, *J* = 8.7, 5.3, 2.5 Hz, 1H), 3.80 (s, 3H), 2.45 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.1, 160.4, 138.3, 133.7, 132.9, 131.3, 130.3 (2C), 128.8 (2C), 128.6, 128.1, 122.6, 121.6, 119.5, 116.6, 115.4, 114.0, 29.3, 29.2, 10.7; IR (neat) 1734, 1648 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{19}N_2O_2$ 331.1447, found 331.1429.

The stereochemistry of **3bg** was assigned by NOESY experiments. The arrows shown below indicate the observed cross peaks.



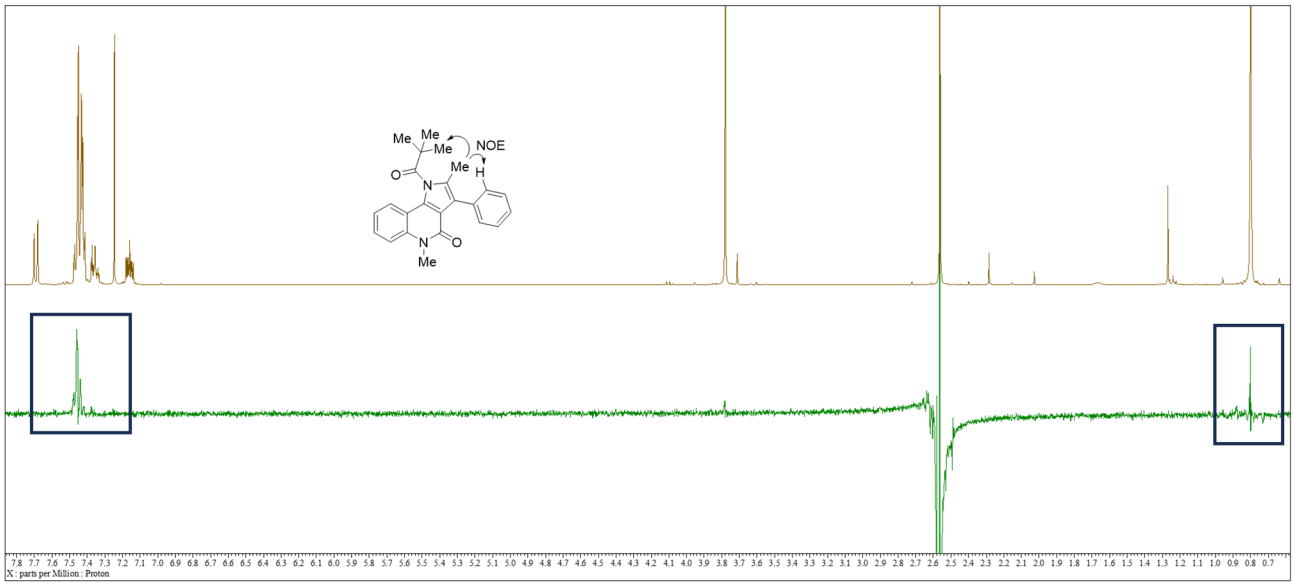
**2,5-Dimethyl-3-phenyl-1-pivaloyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3b'g)**



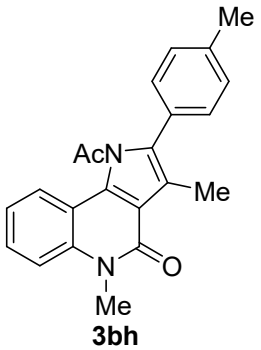
**3b'g**

**3b'g** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3b'g:** 95% yield; white amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, $J$ = 8.2 Hz, 1H), 7.51-7.43 (m, 6H), 7.41-7.35 (m, 1H), 7.18 (ddd, $J$ = 8.0, 5.0, 3.0 Hz, 1H), 3.80 (s, 3H), 2.58 (s, 3H), 0.82 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.4, 160.6, 138.0, 133.5, 132.0, 131.0, 130.7, 128.6, 128.2, 127.9, 121.6, 121.3, 118.0, 115.4, 115.0, 114.2, 45.9, 29.0, 27.4, 10.9; IR (KBr) 1736, 1649 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{24}N_2NaO_2$ 395.1736, found 395.1739. The stereochemistry of **3b'g** was assigned by NOE experiments. The arrows shown below indicate the observed cross peaks.




**1-Acetyl-3,5-dimethyl-2-(*p*-tolyl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bh)**

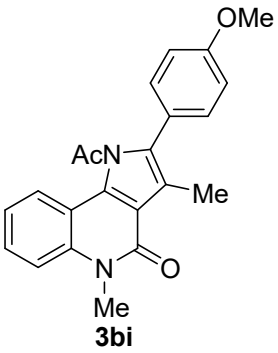


**3bh**

**3bh** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3bh:** 79% yield; white solid (mp 206.7–208.8 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J$ = 7.8 Hz, 1H), 7.50-7.42 (m, 2H), 7.32-7.27 (m, 4H), 7.19 (ddd, $J$ = 8.1, 5.6, 2.8 Hz, 1H), 3.80 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.2, 160.4, 138.6, 138.3, 133.8, 132.8, 130.2 (2C), 129.5 (2C), 128.3, 128.0, 122.6, 121.6, 119.2, 116.7, 115.3, 114.0, 29.4, 29.2, 21.4, 10.7; IR (KBr) 1743, 1647 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{20}N_2NaO_2$ 367.1422, found 367.1411.

**1-Acetyl-2-(4-methoxyphenyl)-3,5-dimethyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bi)**

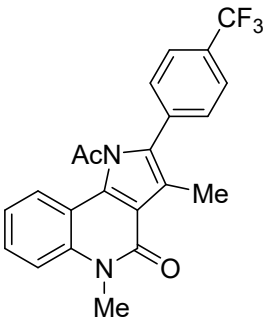


**3bi**

**3bi** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 2:1).

**Analytical data for 3bi:** 71% yield; white solid (mp 170.3–173.2 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.48-7.44 (m, 2H), 7.34-7.29 (m, 2H), 7.19 (ddd, *J* = 8.4, 5.4, 2.8 Hz, 1H), 7.04-6.99 (m, 2H), 3.88 (s, 3H), 3.80 (s, 3H), 2.43 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.2, 160.4, 159.8, 138.2, 133.6, 132.6, 131.6 (2C), 127.9, 123.3, 122.5, 121.6, 119.0, 116.6, 115.3, 114.2 (2C), 114.0, 55.3, 29.3, 29.2, 10.7; IR (neat) 3003, 1739, 1648, 1250 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_3$ 361.1552, found 361.1543.

**1-Acetyl-3,5-dimethyl-2-(4-(trifluoromethyl)phenyl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bj)**

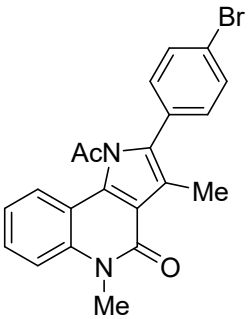


**3bj**

**3bj** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1). The obtained solid was reprecipitated from $CHCl_3$ and $Et_2O$ for melting point determination.

**Analytical data for 3bj:** 85% yield; white solid (mp 190.5–191.0 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.58-7.44 (m, 4H), 7.22 (ddd, *J* = 8.2, 6.6, 1.6 Hz, 1H), 3.80 (s, 3H), 2.47 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.6, 160.2, 138.5, 134.9, 133.5, 132.1, 130.7, 130.5 (q, $^{2}J_{CF}$ = 32.6 Hz, 2C), 128.5, 125.7 (q, $^{3}J_{CF}$ = 2.9 Hz, 2C), 123.9 (q, $^{1}J_{CF}$ = 272.2 Hz), 122.6, 121.8, 120.6, 116.6, 115.5, 113.7, 29.5, 29.2, 10.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –63.6; IR (neat) 1739, 1653, 1325 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{18}F_3N_2O_2$ 399.1320, found 399.1309.

**1-Acetyl-2-(4-bromophenyl)-3,5-dimethyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bk)**

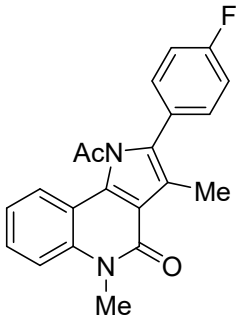


**3bk**

**3bk** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3bk:** 83% yield; yellow amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.65-7.60 (m, 2H), 7.51-7.43 (m, 2H), 7.28-7.25 (m, 2H), 7.21 (ddd, *J* = 8.2, 6.4, 1.8 Hz, 1H), 3.80 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.7, 160.3, 138.4, 133.2, 132.4, 132.0 (2C), 131.9 (2C), 130.1, 128.3, 123.0, 122.6, 121.7, 119.9, 116.6, 115.4, 113.8, 29.4, 29.2, 10.7; IR (KBr) 1744, 1646 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{17}BrN_2NaO_2$ 431.0371, found 431.0398.

**1-Acetyl-2-(4-fluorophenyl)-3,5-dimethyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bl)**

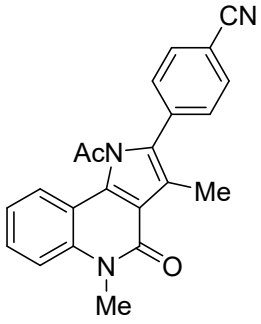


**3bl**

**3bl** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3bl:** 80% yield; yellow amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.50-7.45 (m, 2H), 7.41-7.35 (m, 2H), 7.24-7.16 (m, 3H), 3.80 (s, 3H), 2.43 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.8, 162.8 (d, $^{1}J_{CF}$ = 250.2 Hz), 160.3, 138.3, 133.0, 132.6, 132.3 (d, $^{3}J_{CF}$ = 8.6 Hz, 2C), 128.2, 127.2 (d, $^{4}J_{CF}$ = 2.9 Hz), 122.6, 121.7, 119.7, 116.6, 115.9 (d, $^{2}J_{CF}$ = 21.1 Hz, 2C), 115.4, 113.9, 29.3, 29.2, 10.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –112.9; IR (KBr) 2928, 1748, 1647 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{17}FN_2NaO_2$ 371.1172, found 371.1142.

**4-(1-Acetyl-3,5-dimethyl-4-oxo-4,5-dihydro-1*H*-pyrrolo[3,2-*c*]quinolin-2-yl)benzonitrile (3bm)**

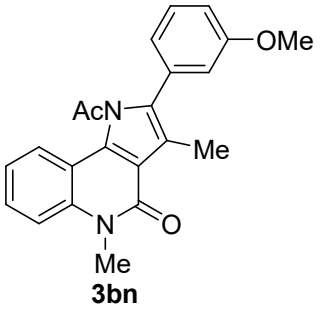


**3bm**

**3bm** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 2:1).

**Analytical data for 3bm:** 67% yield; white amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 3H), 7.58-7.46 (m, 4H), 7.26-7.21 (m, 1H), 3.80 (s, 3H), 2.48 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 160.2, 138.6, 135.8, 133.9, 132.4 (2C), 131.7, 130.9 (2C), 128.7, 122.7, 121.9, 121.2, 118.4, 116.7, 115.6, 113.6, 112.2, 29.5, 29.3, 10.8; IR (KBr) 3066, 2226, 1739, 1651 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{17}N_3NaO_2$ 378.1219, found 378.1228.

**1-Acetyl-2-(3-methoxyphenyl)-3,5-dimethyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bn)**

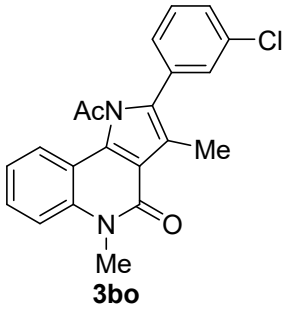


**3bn**

**3bn** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1 to 3:1).

**Analytical data for 3bn:** 78% yield; yellow solid (mp 139.7–142.1 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.49-7.44 (m, 2H), 7.40 (m, 1H), 7.19 (ddd, *J* = 8.2, 6.0, 2.3 Hz, 1H), 7.00-6.92 (m, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 2.47 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.1, 160.3, 159.7, 138.3, 133.4, 132.8, 132.6, 129.9, 128.0, 122.6, 122.5, 121.6, 119.4, 116.5, 115.8, 115.3, 114.1, 113.9, 55.3, 29.3, 29.2, 10.7; IR (KBr) 3058, 1746, 1640 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{20}N_2NaO_3$ 383.1372, found 383.1348.

**1-Acetyl-2-(3-chlorophenyl)-3,5-dimethyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bo)**

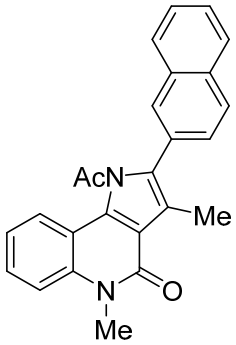


**3bo**

**3bo** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3bo:** 80% yield; yellow solid (mp 191.5–192.8 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.52-7.44 (m, 3H), 7.44-7.39 (m, 4H), 7.23-7.18 (m, 1H), 3.80 (s, 3H), 2.45 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.5, 160.3, 138.4, 134.7, 133.3, 133.0, 132.1, 130.3, 130.0, 128.8, 128.6, 128.3, 122.7, 121.7, 120.2, 116.6, 115.4, 113.8, 29.4, 29.2, 10.7; IR (KBr) 3049, 1749, 1642 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{17}ClN_2NaO_2$ 387.0876, found 387.0857.

**1-Acetyl-3,5-dimethyl-2-(naphthalen-2-yl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bp)**

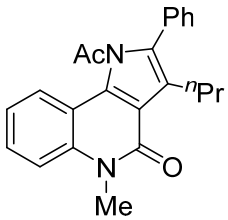


**3bp**

**3bp** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3bp:** 75% yield; white solid (mp 213.0–213.9 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 1H), 7.94-7.89 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.61-7.54 (m, 2H), 7.53-7.45 (m, 3H), 7.21 (ddd, *J* = 8.8, 4.9, 2.8 Hz, 1H), 3.82 (s, 3H), 2.50 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.1, 160.4, 138.4, 133.7, 133.12, 133.10, 132.9, 129.7, 128.7, 128.6, 128.2, 128.1, 127.8, 127.5, 126.9, 126.8, 122.7, 121.7, 120.0, 116.7, 115.4, 114.0, 29.4, 29.2, 10.8; IR (KBr) 2928, 1743, 1645cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{20}N_2NaO_2$ 403.1423, found 403.1397.

**1-Acetyl-5-methyl-2-phenyl-3-propyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bq)**

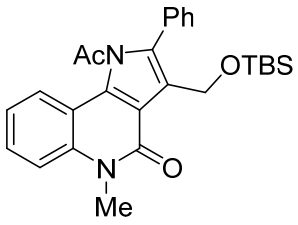


**3bq**

**3bq** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3bq:** 81% yield; yellow amorphous solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.50-7.44 (m, 5H), 7.40-7.36 (m, 2H), 7.19 (ddd, *J* = 8.1, 5.6, 2.8 Hz, 1H), 3.80 (s, 3H), 2.78-2.74 (m, 2H), 2.20 (s, 3H), 1.69-1.64 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.0, 159.9, 138.3, 133.8, 133.2, 131.5, 130.5 (2C), 128.7 (2C), 128.4, 128.0, 124.4, 122.6, 121.5, 116.2, 115.3, 113.8, 29.30, 29.26, 26.8, 24.7, 14.2; IR (neat) 2959, 1741, 1649, 1251 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2$ 359.1760, found 359.1730.

**1-Acetyl-3-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-methyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3br)**

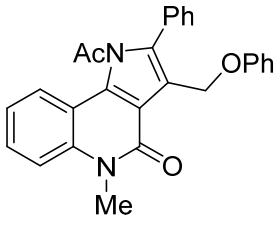


**3br**

**3br** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 10:1).

**Analytical data for 3br:** 80% yield; colorless gum; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.62-7.53 (m, 2H), 7.51-7.41 (m, 5H), 7.18 (ddd, *J* = 8.2, 6.2, 2.1 Hz, 1H), 4.96 (s, 2H), 3.79 (s, 3H), 2.24 (s, 3H), 0.90 (s, 9H), 0.10 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.4, 159.5, 138.3, 136.4, 132.7, 130.7, 130.4 (2C), 128.9, 128.5 (2C), 128.1, 122.2, 122.0, 121.6, 115.4, 115.3, 113.7, 55.5, 29.5, 29.4, 26.1 (3C), 18.6 , –5.2 (2C); IR (neat) 2928, 1748, 1652, 1254 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{33}N_2O_3Si$ 461.2260, found 461.2283.

**1-Acetyl-5-methyl-3-(phenoxymethyl)-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bs)**

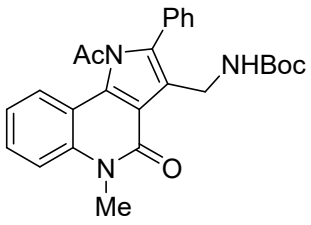


**3bs**

**3bs** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3bs:** 76% yield; yellow solid (mp 209.5–211.3 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.54-7.48 (m, 4H), 7.47-7.42 (m, 3H), 7.29-7.18 (m, 3H), 7.03-6.98 (m, 2H), 6.93 (ddd, *J* = 7.1, 7.1, 0.9 Hz, 1H), 5.31 (s, 2H), 3.80 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.2, 159.6, 158.8, 138.4, 137.3, 133.0, 130.2 (2C), 130.0, 129.3 (2C), 129.2, 128.9 (2C), 128.4, 122.3, 121.8, 120.7, 117.8, 115.6, 115.5, 115.1 (2C), 113.6, 60.7, 29.5, 29.3; IR (neat) 1749, 1653 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{23}N_2O_3$ 423.1709, found 423.1712.

***tert*-Butyl((1-acetyl-5-methyl-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrolo[3,2-*c*]quinolin-3-yl)methyl)carbamate (3bt)**

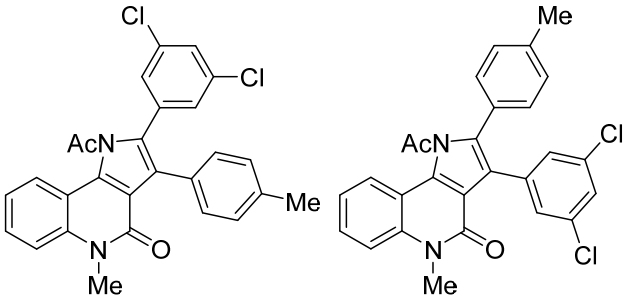


**3bt**

**3bt** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3bt:** 66% yield; white solid (mp 178.5–180.5 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.60-7.41 (m, 7H), 7.23 (ddd, *J* = 8.4, 5.8, 2.8 Hz, 1H), 6.60 (br s, 1H), 4.39 (d, *J* = 6.0 Hz, 2H), 3.84 (s, 3H), 2.20 (s, 3H), 1.43 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.2, 160.2, 155.7, 138.2, 134.2, 133.4, 130.5 (2C), 130.0, 129.2, 129.0 (2C), 128.5, 122.5, 122.0, 120.1, 116.1, 115.6, 113.7, 78.6, 35.3, 29.6, 29.4, 28.5 (3C); IR (neat) 3392, 2978, 1748, 1707, 1636 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{26}H_{28}N_3O_4$ 446.2080, found 446.2108.

**1-Acetyl-2-(3,5-dichlorophenyl)-5-methyl-3-(*p*-tolyl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one with 1-acetyl-3-(3,5-dichlorophenyl)-5-methyl-2-(*p*-tolyl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3bu)**

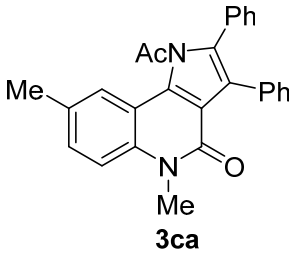



**3bu**

**3bu** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1). Regioisomers (1:1) could be separated by column chromatography.

**Analytical data for 3bu: regioisomer-1** 20 % yield; yellow amorphous solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.58-7.42 (m, 2H), 7.25-7.20 (m, 2H), 7.20-7.10 (m, 6H), 3.76 (s, 3H),2.38 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.2, 159.0, 139.3, 138.3, 136.2, 134.9, 133.6, 132.6, 130.5 (C2), 129.6 (C4), 128.5, 127.0, 126.7, 122.3, 121.8, 120.9, 115.6, 114.9, 113.3, 29.6, 29.5, 21.4 One C*sp*$^2$ signals are missing due to overlapping; IR (KBr) 1408, 1360 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{20}Cl_2N_2NaO_2$ 497.0800, found 497.0812. **regioisomer-2** 20% yield; yellow amorphous solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.57-7.45 (m, 2H), 7.33-7.25 (m, 2H), 7.20-7.05 (m, 6H), 3.74 (s, 3H),2.39 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.5, 159.1, 138.6, 137.0, 135.1, 133.7, 133.5, 131.2, 130.6 (2C), 129.3 (2C), 128.9 (2C), 128.8, 128.5 (2C), 126.2, 125.6, 122.6, 122.0, 115.7, 115.5, 113.4, 29.8, 29.5, 21.4; IR (KBr) 1645, 1402, 1360; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{20}Cl_2N_2NaO_2$ 497.0800, found 497.0783.

**1-Acetyl-5,8-dimethyl-2,3-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3ca)**

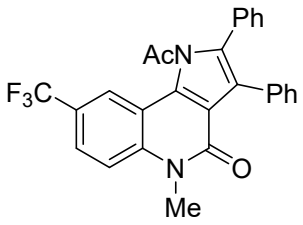



**3ca**

**3ca** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3ca:** 69% yield; yellow solid (mp 177.5–179.4 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.40-7.17 (m, 12H), 3.73 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.4, 159.1, 136.4, 134.1, 132.9, 132.6, 131.1, 131.0 (2C), 130.8 (2C), 129.5, 128.54, 128.52 (2C), 127.3 (2C), 126.8, 124.1, 122.3, 115.4, 113.5, 29.6, 29.3, 21.1, Two C*sp*$^2$ signals are missing due to overlapping; IR (KBr) 2919, 1753, 1646 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{22}N_2NaO_2$ 429.1579, found 429.1573.

**1-Acetyl-5-methyl-2,3-diphenyl-8-(trifluoromethyl)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3da)**

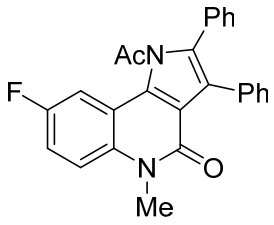


**3da**

**3da** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 4:1).

**Analytical data for 3da:** 74% yield; yellow solid (mp 210.3–211.4 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 0.9 Hz, 1H), 7.72 (dd, *J* = 8.9, 1.6 Hz, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.37-7.30 (m, 3H), 7.28-7.23 (m, 7H), 3.77 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.9, 159.1, 140.2, 135.1, 132.4, 131.9, 130.9 (2C), 130.6 (2C), 128.9, 128.7 (2C), 127.4 (2C), 127.0, 124.6, 124.4, 124.1 (q, $^{1}J_{CF}$ = 272.2 Hz), 123.7 (q, $^{2}J_{CF}$ = 32.6 Hz), 120.0, 119.9 (q, $^{3}J_{CF}$ = 3.8 Hz), 116.1, 115.7, 113.5, 29.6, 29.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –62.7; IR (KBr) 3059, 1750, 1659 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{19}F_3N_2NaO_2$ 483.1296, found 483.1289.

**1-Acetyl-8-fluoro-5-methyl-2,3-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3ea)**

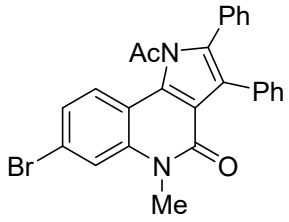


**3ea**

**3ea** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3ea:** 57% yield; white amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 10.3, 6.0 Hz, 1H), 7.41 (dd, *J* = 9.2, 5.0 Hz, 1H), 7.36-7.30 (m, 3H), 7.25-7.19 (m, 8H), 3.74 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.1, 158.8, 157.4 (d, $^{1}J_{CF}$ = 240.6 Hz), 134.9, 134.7, 132.6, 131.8, 130.9 (2C), 130.6, 130.5 (2C), 128.8, 128.7 (2C), 127.4 (2C), 126.9, 124.3, 116.8 (d, $^{3}J_{CF}$ = 8.6 Hz), 116.1, 115.7 (d, $^{2}J_{CF}$ = 23.0 Hz), 114.4 (d, $^{3}J_{CF}$ = 8.6 Hz), 108.4 (d, $^{2}J_{CF}$ = 25.9 Hz), 29.63, 29.56; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –121.1; IR (KBr) 3060, 1734, 1647 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{19}FN_2NaO_2$ 433.1328, found 433.1312.

**1-Acetyl-7-bromo-5-methyl-2,3-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3fa)**

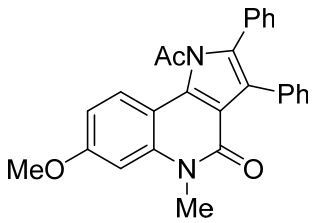


**3fa**

**3fa** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3fa:** 73% yield; yellow solid (mp 191.3–192.5 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.3 Hz, 1H), 7.57 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.37-7.31 (m, 3H), 7.28-7.23 (m, 8H), 3.82 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.9, 158.8, 137.1, 134.9, 132.5, 131.3, 130.9 (2C), 130.7, 130.6 (2C), 128.8, 128.7, 128.6 (2C), 127.4 (2C), 126.9, 124.9, 124.2, 117.0, 116.0, 115.2, 114.7, 29.50, 29.46; IR (KBr) 3056, 1751, 1653 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{19}BrN_2NaO_2$ 493.0528, found 493.0540.

**1-Acetyl-7-methoxy-5-methyl-2,3-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3ga)**

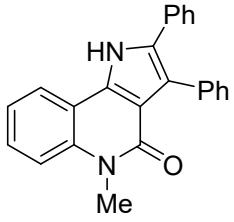


**3ga**

**3ga** was prepared following the representative procedure and purified by flash column chromatography on silica gel (Hexane/EtOAc = 3:1).

**Analytical data for 3ga:** 72% yield; white solid (mp 183.8–184.9 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.7 Hz, 1H), 7.36-7.19 (m, 10H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.93 (s, 3H), 3.71 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.5, 159.7, 159.4, 140.1, 133.33, 133.28, 133.0, 131.0 (2C), 130.6 (2C), 128.5 (2C), 128.4, 127.3 (2C), 126.7, 124.0, 123.8, 113.6, 108.4, 107.5, 100.4, 55.5, 29.5, 29.4, One C*sp*$^2$ signal is missing due to overlapping; IR (KBr) 3006, 1735, 1641 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{22}N_2NaO_3$ 445.1528, found 445.1509.

**5-Methyl-2,3-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]quinolin-4-one (3ba')**



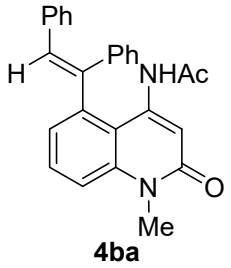
**3ba'**

A Schlenk tube was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), $Cu(OAc)_2 \cdot H_2O$ (8.0 mg, 0.040 mmol, 20 mol%), **1b** (43.2 mg, 0.20 mmol), **2a** (71.3 mg, 0.40 mmol), and DMF (2.0 mL). The reaction mixture was stirred at 110 °C for 19 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with $CHCl_3$ to remove the metal salts. After concentration in vacuo, the residue was purified by silica gel column chromatography (Hexane/EtOAc = 3:1) to give **3ba'** (38.1 mg, 54%) as a yellow solid (mp 217.2–218.1 °C).

**Analytical data for 3ba':** $^1$H NMR (400 MHz, $CDCl_3$) δ 9.18 (br s, 1H), 7.84-7.77 (m, 1H), 7.51-7.40 (m, 4H), 7.31-7.20 (m, 9H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.9, 137.6, 134.0, 133.9, 132.5, 131.9, 131.0 (2C), 128.4 (2C), 127.9 (2C), 127.6 (2C), 127.3, 126.6, 121.7, 121.2, 120.6, 115.2, 113.62, 113.58, 29.0, One C*sp*$^2$ signal is missing due to overlapping; IR (neat) 3178, 1615, 1575 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{18}N_2NaO$ 373.1317, found 373.1303.

## 5. Isolation and Characterization of C5-Functionalized 2-Quinolone Derivatives 4 and 5

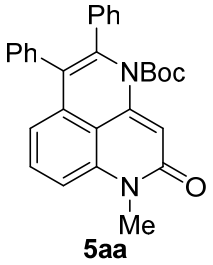
### (*E*)-*N*-(5-(1,2-Diphenylvinyl)-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)acetamide (4ba)



**4ba**

This product was observed when Cp*Rh(OAc)$_2$·H$_2$O (3.7 mg, 0.010 mmol, 5 mol%) was used instead of [Cp*RhCl$_2$]$_2$ in the representative procedure (Table 1, entry 5). Purified by silica gel column chromatography (Hexane/EtOAc = 3:1 to 1:1) afforded **4ba** (3.9 mg, 5%) as a yellow solid along with **3ba** (51.0 mg, 65%). Colorless crystals (mp 123.0–123.6 °C) for X-ray crystallographic analysis were obtained by recrystallization from toluene. **Analytical data for 4ba:** $^1$H NMR (400 MHz, CDCl$_3$) δ 9.32 (br s, 1H), 7.72 (br s, 1H), 7.54 (dd, *J* = 8.5, 7.6 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.30-7.22 (m, 8H), 7.19-7.15 (m, 2H), 7.01 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.87 (s, 1H), 3.74 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.1, 162.4, 142.3, 142.1, 141.5, 140.1, 138.1, 135.4, 132.2, 129.6, 129.3 (2C), 129.2 (2C), 128.8 (2C), 128.6 (2C), 128.3, 126.4, 114.8, 113.3, 109.9, 30.0, 25.5, One C*sp*$^2$ signal is missing due to overlapping; IR (KBr) 3378, 1712, 1650 cm$^{-1}$; HRMS (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{26}H_{22}N_2NaO_2$ 417.1579, found 417.1568.

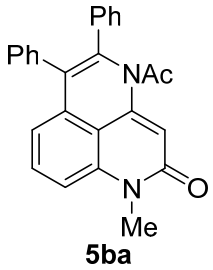
### *tert*-Butyl 1-methyl-2-oxo-5,6-diphenyl-1,2-dihydro-4*H*-benzo[*de*][1,6]naphthyridine-4-carboxylate (5aa)



**5aa**

A Schlenk tube was charged with [Cp*RhCl$_2$]$_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), Cu(OAc)$_2$·H$_2$O (7.9 mg, 0.40 mmol, 20 mol%), **1a** (55.1 mg, 0.20 mmol), **2a** (71.2 mg, 0.40 mmol), and DCE (2.0 mL). The reaction mixture was stirred at 110 °C for 24 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with CHCl$_3$ to remove the metal salts. After concentration in vacuo, the residue was purified by silica gel column chromatography (Hexane/EtOAc = 1:1) to give **5aa** (72.8 mg, 78%) as a yellow solid (mp 242.2–242.7 °C). **Analytical data for 5aa:** $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.25-7.13 (m, 8H), 7.06 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.0 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 3.60 (s, 3H), 1.08 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.2, 150.5, 144.9, 140.7, 136.8, 135.6, 135.1, 133.6, 131.7, 131.2 (2C), 130.2 (2C), 128.3 (2C), 127.7 (2C), 127.1, 120.0, 116.0, 113.5, 110.8, 93.4, 85.5, 29.2, 28.2, 26.8 (3C); IR (KBr) 2981, 1758, 1634 cm$^{-1}$; HRMS (ESI) *m/z*: [M+Na]$^+$ calcd for $C_{29}H_{26}N_2NaO_3$ 473.1841, found 473.1841.

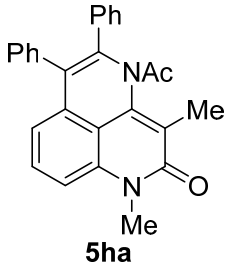
**4-Acetyl-1-methyl-5,6-diphenyl-1*H*-benzo[*de*][1,6]naphthyridin-2(4*H*)-one (5ba)**



**5ba**

A Schlenk tube was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), $AgSbF_6$ (7.1 mg, 0.020 mmol, 10 mol%), $Cu(OAc)_2 \cdot H_2O$ (79.8 mg, 0.40 mmol), **1b** (43.2 mg, 0.20 mmol), **2a** (71.3 mg, 0.40 mmol), and DCE (2.0 mL). The reaction mixture was stirred at 110 °C for 19 h under Ar atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through pad of Celite® with $CHCl_3$ to remove the metal salts. After concentration in vacuo, the residue was purified by silica gel column chromatography (Hexane/EtOAc = 4:1 to 2:1) to give **5ba** (37.2 mg, 47%) as a yellow solid (along with **3ba** (34.0 mg, 43%). The obtained solid was reprecipitated from $CHCl_3$ and hexane for melting point determination (mp 171.2–172.0 °C). **Analytical data for 5ba:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 8.2 Hz, 1H), 7.34-7.22 (m, 4H), 7.20-7.05 (m, 7H), 6.72 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1 H), 3.64 (s, 3H), 1.95 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.6, 161.6, 140.8, 139.2, 138.5, 136.2, 134.5, 132.8, 130.9, 129.5 (2C), 129.2 (2C), 128.5 (2C), 128.0 (2C), 127.7, 127.3, 126.2, 122.1, 118.1, 114.3, 30.0, 23.3, One C$sp^2$ signal is missing due to overlapping; IR (neat) 3001, 1625, 1592 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{26}H_{21}N_2O_2$ 393.1603, found 393.1615.

**4-Acetyl-1,3-dimethyl-5,6-diphenyl-1*H*-benzo[*de*][1,6]naphthyridin-2(4*H*)-one (5ha)**

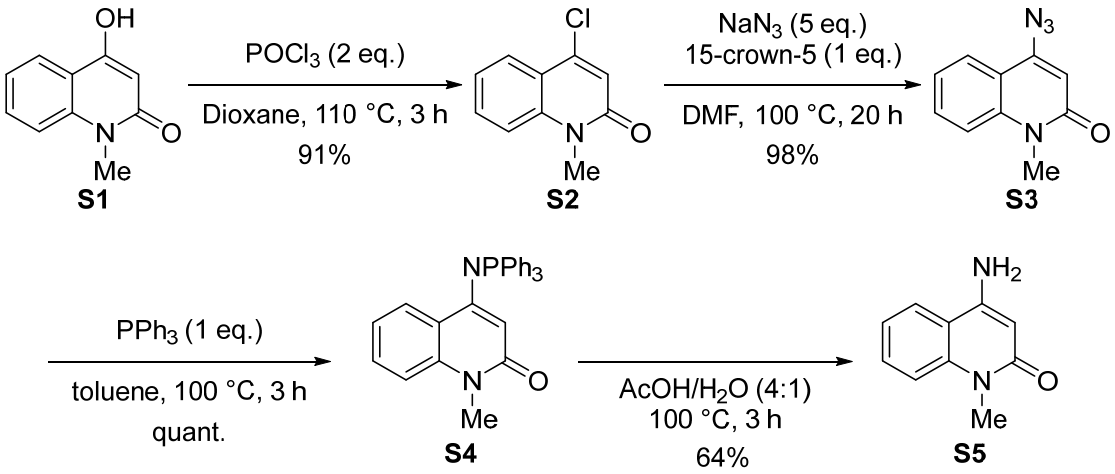


**5ha**

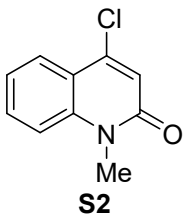
A Schlenk tube was charged with $Cp^*Rh(OAc)_2 \cdot H_2O$ (3.7 mg, 0.010 mmol, 5 mol%), $Cu(OAc)_2 \cdot H_2O$ (7.9 mg, 0.040 mmol), **1h** (46.1 mg, 0.20 mmol), **2a** (71.1 mg, 0.40 mmol), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at 110 °C for 43 h under Ar atmosphere using oil bath. Then, the mixture was cooled to room temperature and filtered through pad of Celite® with $CHCl_3$ to remove the metal salts. After concentration in vacuo, the residue was purified by silica gel column chromatography (Hexane/EtOAc = 2:1 to 1:1 to EtOAc only) to give **5ha** (29.4 mg, 36%) as a white solid along with **4ha** (6.5 mg, 8%). Colorless crystals (mp 213.1–213.5 °C) for X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$ and hexane. **Analytical data for 5ha:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42-7.33 (m, 4H), 7.25-7.20 (m, 3H), 7.20-7.14 (m, 5H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.76 (s, 3H), 2.31 (s, 3H), 1.87 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.2, 162.9, 139.8, 138.0, 137.0, 136.2, 136.0, 131.2, 130.4 (2C), 130.2, 129.5, 129.2 (2C), 128.7 (2C), 128.1 (2C), 127.9, 127.6, 124.9, 119.6, 116.7, 112.7, 30.0, 25.5, 15.6; IR (neat) 2922, 1695, 1641 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{22}N_2NaO_2$ 429.1579, found 429.1589.

# 6. Synthesis and Characterization of 2-Quinolone substrates 1

**Synthesis and Characterization of 1a and 1b**

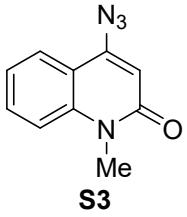



**4-Chloro-1-methylquinolin-2(1*H*)-one (S2)**[11]



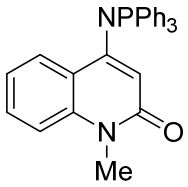

To a dioxane suspension (20 mL) of **S1** (3.50 g, 20.0 mmol) was added $POCl_3$ (6.13 g, 40.0 mmol) at room temperature in a 200 mL flask. The reaction mixture was stirred at 110 °C for 2 h. After cooling to room temperature, the mixture was poured into 40 mL of iced water. The resulting solution was neutralized with 0.5 M NaOH aq. The solution was extracted with diethyl ether (3 x 40 mL). The combined organic layer was washed with water (2 x 60 mL) and brine (40 mL), dried over $MgSO_4$, and concentrated in vacuo. Reprecipitation of the product from ethanol to give **S2** (3.53 g, 91%) as a white amorphous solid. **Analytical data for S2:** $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.65 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.33 (ddd, *J* = 7.6, 7.6, 0.9 Hz, 1H), 6.91 (s, 1H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.9, 144.2, 139.7, 131.8, 126.2, 122.6, 121.0, 119.2, 114.3, 29.5; IR (neat) 3085, 1644 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9ClNO$ 194.0373, found 194.0390.

**4-Azido-1-methylquinolin-2(1*H*)-one (S3)**




To a DMF suspension (50 mL) of **S2** (3.87 g, 20.0 mmol) and $NaN_3$ (6.61 g, 101.6 mmol) was added 15-crown-5 (4.0 mL, 20.0 mmol) at room temperature in a 200 mL flask. The reaction mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the mixture was poured into water (100 mL). The precipitated solid was filtered, washed with water (50 ml) and hexane (20 ml). The product **S3** (3.92 g, 98%) was obtained as a yellow solid (mp 246.5–248.3 °C). **Analytical data for S3:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.63 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.25-7.23 (m, 1H), 6.48 (s, 1H), 3.71 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.8, 148.4, 140.0, 131.9, 123.9, 122.0, 115.8, 114.2, 106.6, 29.3; IR (neat) 2128, 1639 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9N_4O$ 201.0776, found 201.0775.

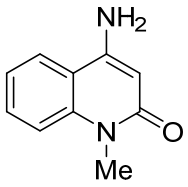
**1-Methyl-4-((triphenyl-l$^5$-phosphaneylidene)amino)quinolin-2(1*H*)-one (S4)**



**S4**

A suspension of **S3** (2.00 g, 10.0 mmol) and $PPh_3$ (2.62 g, 10.0 mmol) in toluene (20 mL) was stirred at 100 °C for 3 h. After cooling to room temperature, the mixture was concentrated in vacuo. The residue was triturated with diethyl ether (50 mL) and filtered to give **S4** (4.34 g, quant.) as a white solid (mp 244.5–246.3 °C). **Analytical data for S4:** $^1$H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.83-7.78 (m, 6H), 7.59-7.54 (m, 3H), 7.52-7.47 (m, 7H), 7.28-7.23 (m, 2H), 5.58 (d, *J* = 0.9 Hz, 1H), 3.60 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.9, 157.0, 140.3, 132.6 (d, *J* = 9.6 Hz, C6), 132.2 (d, *J* = 1.9 Hz, C3), 129.9, 129.0 (d, *J* = 100.6 Hz, C3), 128.9 (d, *J* = 12.5 Hz, C6), 126.2, 123.4 (d, *J* = 24.9 Hz), 120.6, 113.6, 103.2 (d, *J* = 11.5 Hz), 28.6; $^{31}$P NMR (162 MHz, $CHCl_3$) δ 10.02; IR (neat) 1614, 1278 cm$^{-1}$; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{28}H_{23}N_2NaOP$ 457.1446, found 457.1428.

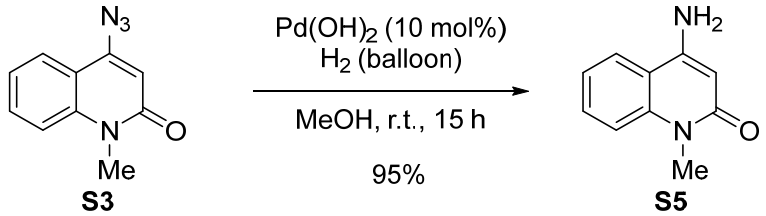
**4-Amino-1-methylquinolin-2(1*H*)-one (S5)**



**S5**

A solution of **S4** (1.30 g, 3.00 mmol) in AcOH (22.5 mL) and $H_2O$ (7.5 mL) was stirred at 100 °C for 3 h. After cooling to room temperature, the mixture was neutralized with 0.5 M NaOH aq. The mixture was extracted with DCM (3 x 20 mL). The combined organic layer was washed with water (2 x 20 mL) and brine (20 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/MeOH = 9:1) to furnish **S5** (334.5 mg, 64%) as a white solid (mp 216.5–217.2 °C). **Analytical data for S5:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (td, *J* = 7.9, 1.1 Hz, 1H),7.55 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.23 (m, 1H), 5.93 (s, 1H), 4.48 (br s, 2H), 3.67 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 162.1, 152.0, 140.1, 130.7, 123.0, 120.5, 114.72, 114.67, 93.3, 28.1; IR (neat) 3196, 2873, 1625 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{10}H_{11}N_2O$ 175.0871, found 175.0855.

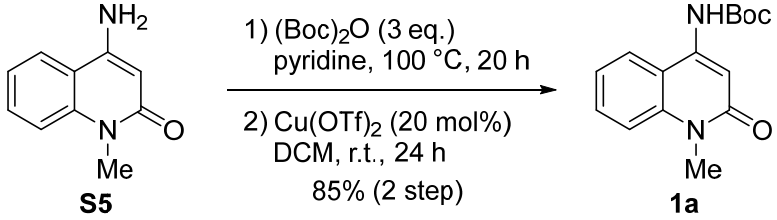
During our study, we found that **S5** can also be prepared from **S3** as shown below.

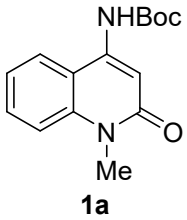


**S3** **S5**

To a MeOH suspension (100 ml) of **S3** (3.92 g, 19.6 mmol) was added $Pd(OH)_2$ (280.8 mg, 2 mmol) under Ar atmosphere. Subject the vessel twice to evacuation followed by purging with a hydrogen balloon. After the reaction mixture was stirred at room temperature for 15 h, filtered through a pad of Celite® with MeOH to remove the metal salts, and concentrated in vacuo to afford **S5** (3.24 mg, 95%) as a yellow solid.

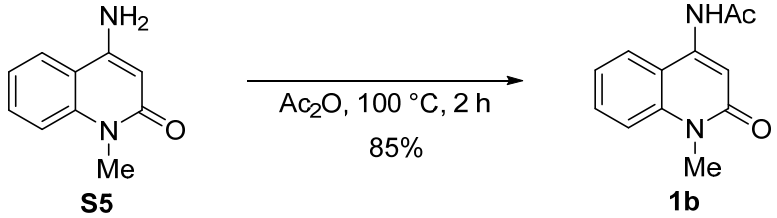
***tert*-Butyl (1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)carbamate (1a)**

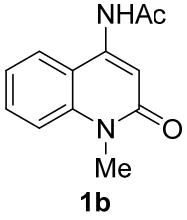



To a pyridine solution (1.5 mL) of **S5** (541.5 mg, 3.11 mmol) was added $Boc_2O$ (2.1 mL, 9.00 mmol) in a 100 mL flask. The reaction mixture was stirred at 80 ℃ for 20 h. After cooling to room temperature, the resulting mixture was concentrated in vacuo. The residue was dissolved in DCM (6 ml), to which $Cu(OTf)_2$ (228.0 mg, 0.630 mmol) was added, and the mixture was stirred at room temperature for 24 h. The reaction mixture was quenched with water (20 mL) and the whole mixture was extracted with DCM (3 x 20 mL). The combined organic layer was washed with water (2 x 20 mL), brine (20 mL), and dried over $MgSO_4$, and concentrated. The residue was purified by a silica gel column chromatography to furnish **1a** (724.2 mg, 85%) as a yellow amorphous solid. **Analytical data for 1a:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65-7.51 (m, 2H), 7.45-7.36 (m, 2H), 7.30-7.22 (m, 1H), 6.93 (br s, 1H), 3.69 (s, 3H), 1.56 (s, 9H); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 162.9, 151.9, 142.1, 140.1, 131.0, 121.8, 121.0, 115.1, 106.7, 82.1, 29.3, 28.7, 28.3 (3C); IR (neat) 3234, 2980, 1736, 1637, 1618, 1583, 1537, 1152 cm$^{-1}$; HRMS (DART) *m/z* $[M+H]^+$ calcd for $C_{15}H_{19}N_2O_4$ 275.1396, found 275.1403.

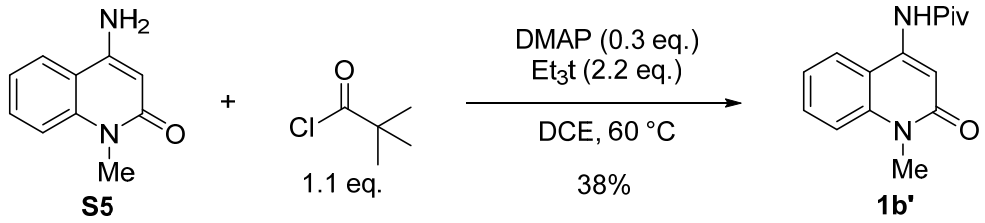
***N*-(1-Methyl-2-oxo-1,2-dihydroquinolin-4-yl)acetamide (1b)**

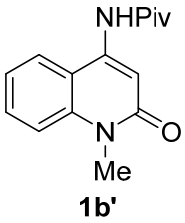



An $Ac_2O$ solution (5 mL) of **S5** (334.5 g, 1.92 mmol) was stirred at 100 ℃ for 2 h. After cooling to room temperature, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/MeOH = 19:1) to furnish **1b** (348.8 mg, 84%) as a white solid (mp 213.8–216.4 ℃). **Analytical data for 1b:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66-7.46 (m, 4H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.32-7.27 (m, 1H), 3.71 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.7, 161.8, 146.7, 140.5, 131.9, 123.4, 123.0, 122.6, 118.4, 115.1, 29.7, 26.3; IR (neat) 3309, 1708, 1638, 1579 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{13}N_2O_2$ 217.0977, found 217.0985.

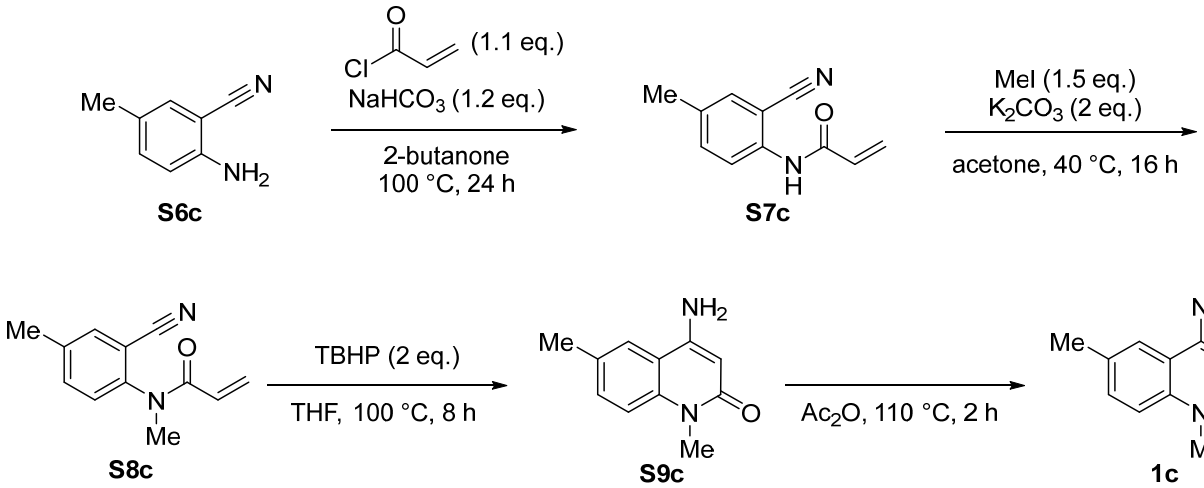
***N*-(1-Methyl-2-oxo-1,2-dihydroquinolin-4-yl)pivalamide (1b')**



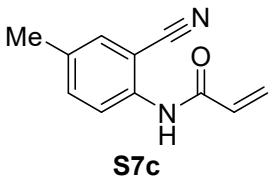




To a suspension of **S5** (88.8 mg, 0.51 mmol), $Et_3N$ (153 µL, 1.10 mmol) and DMAP (18.4 mg, 0.15 mmol) in DCE (3 mL) was added pivaloyl chloride (67 µL, 0.55 mmol) at room temperature under Ar atmosphere. The reaction mixture was stirred at 60 °C for 96 h. After cooling to room temperature, the mixture was diluted with water and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with water (2 x 40 mL) and brine (20 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc only) to furnish **1b'** (50.4 mg, 38%) as a white solid (mp 208.8–210.5 °C). **Analytical data for 1b':** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (br s, 1H), 7.64-7.59 (m, 2H), 7.48-7.41 (m, 2H), 7.31-7.26 (m, 1H), 3.71 (s, 3H), 1.41 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.7, 162.7, 140.9, 140.2, 131.0, 121.8, 120.2, 115.6, 115.2, 109.9, 40.5, 29.3, 27.6 (3C); IR (neat) 3308, 1638, 1618, 1584 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{19}N_2O_2$ 259.1447, found 259.1417.

**Synthesis and Characterization of 1c-g**



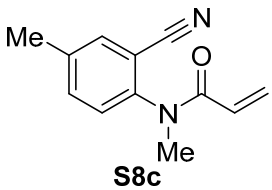
***N*-(2-Cyano-4-methylphenyl)acrylamide (S7c)**



**S7c**

To a suspension of **S6c**[12] (1.18 g, 8.9 mmol) and $NaHCO_3$ (901.5 mg, 10.7 mmol) in 2-butanone (30 mL) was added acryloyl chloride (792 μL, 9.8 mmol) at room temperature under Ar atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was diluted with water and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with water (2 x 40 mL) and brine (40 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 8:1) to furnish **S7c** (1.30 g, 78%) as a white solid. The obtained solid was reprecipitated from $CHCl_3$ and hexane for melting point determination (mp 189.1–189.5 °C). **Analytical data for S7c:** $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1H), 7.63 (br s, 1H), 7.46-7.36 (m, 2H), 6.49 (dd, *J* = 16.9, 0.9 Hz, 1H), 6.31 (ddd, *J* = 17.2, 10.3, 0.9 Hz, 1H), 5.87 (dd, *J* = 10.0, 0.9 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.5, 137.9, 135.1, 134.4, 132.2, 130.5, 129.2, 121.3, 116.5, 101.9, 20.5; IR (KBr) 3675, 2230, 1662 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{11}N_2O$ 187.0871, found 187.0856.

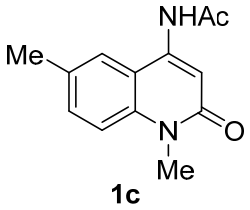
***N*-(2-Cyano-4-methylphenyl)-*N*-methylacrylamide (S8c)**



**S8c**

To a suspension of **S7c** (1.30 g, 7.0 mmol) and $K_2CO_3$ (2.13 g, 15.4 mmol) in acetone (35 mL) was added MeI (654 μL, 10.5 mmol) at room temperature under Ar atmosphere. The reaction mixture was stirred at 40 °C for 16 h. After cooling to room temperature, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 4:1) to give **S8c** (1.32 g, 94%) as a white amorphous solid. **Analytical data for S8c:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.47 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 6.42 (d, *J* = 16.9 Hz, 1H), 5.90 (dd, *J* = 16.7, 10.3 Hz, 1H), 5.57 (d, *J* = 10.1 Hz, 1H), 3.37 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.4, 143.4, 139.1, 135.0, 134.2, 129.2, 128.8, 127.4, 115.8, 112.2, 36.9, 20.8; IR (KBr) 3036, 2231, 1666 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{13}N_2O$ 201.1028, found 201.1053.

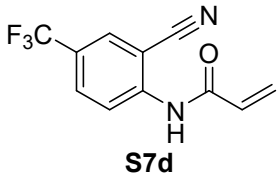
***N*-(1,6-Dimethyl-2-oxo-1,2-dihydroquinolin-4-yl)acetamide (1c)**



**1c**

**S8c** (801 mg, 4.0 mmol), TBHP (70% aqueous solution, 769 μL, 8.0 mmol), and THF (25 mL) were added in a sealed tube with a Teflon-lined cap. The mixture was stirred at 100 ℃ for 8 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc only) to give **S9c**, which still contained a small amount of inseparable impurities. This mixture was used for the next reaction without further purification. An $Ac_2O$ solution (2 mL) of **S9c** was stirred at 100 ℃ for 2 h. After cooling to room temperature, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/MeOH = 19:1). A white solid (mp 189.9–190.1 ℃) was obtained by reprecipitation from $CHCl_3$ and $Et_2O$ to furnish **1c** (237 mg, 18%). **Analytical data for 1c:** $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.79 (br s, 1H), 7.92 (s, 1H), 7.50-7.41 (m, 2H), 7.24 (s, 1H) 3.55 (s, 3H), 2.41 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 170.0, 162.1, 161.5, 142.6, 141.6, 124.9, 109.1, 108.9, 106.0, 99.1, 55.6, 29.0, 24.3; IR (KBr) 3258, 2945, 1645 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{15}N_2O_2$ 231.1134, found 231.1123.

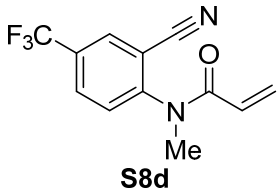
***N*-(2-Cyano-4-(trifluoromethyl)phenyl)acrylamide (S7d)**



**S7d**

This compound was prepared from **S6d**[13] in 71% yield in a similar manner to the synthesis of **S7c** from **S6c**. **Analytical data for S7d:** white solid (mp 148.9–150.7 ℃); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, $J$ = 8.2 Hz, 1H), 7.91 (br s, 1H), 7.88-7.82 (m, 2H), 6.55 (dd, $J$ = 16.9, 0.9 Hz, 1H), 6.36 (dd, $J$ = 16.9, 11.0 Hz, 1H), 5.96 (dd, $J$ = 10.1, 0.9 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.6, 143.2, 131.2 (q, $^3J_{CF}$ = 3.8 Hz), 130.5, 130.0, 129.5 (q, $^3J_{CF}$ = 3.8 Hz), 126.4 (q, $^2J_{CF}$ = 34.5 Hz), 122.8 (q, $^1J_{CF}$ = 272.2 Hz), 121.1, 115.1, 101.7; $^{19}$F NMR (376 MHz, $CDCl_3$): δ –63.6; IR (KBr) 3340, 2236, 1689 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{11}H_8F_3N_2O$ 241.0559, found 241.0586.

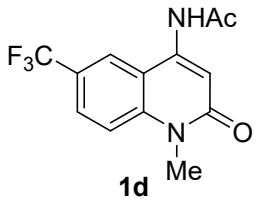
***N*-(2-Cyano-4-(trifluoromethyl)phenyl)-*N*-methylacrylamide (S8d)**



**S8d**

This compound was prepared from **S7d** in 82% yield in a similar manner to the synthesis of **S8c** from **S7c**. **Analytical data for S8d:** white amorphous solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, $J$ = 1.8 Hz, 1H), 7.93 (dd, $J$ = 8.5, 2.0 Hz, 1H), 7.49 (d, $J$ = 8.2 Hz, 1H), 6.75 (s, 1H), 6.49 (dd, $J$ = 16.5, 1.4 Hz, 1H), 5.94 (br s, 1H), 5.70 (d, $J$ = 10.1 Hz, 1H), 3.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.1, 149.2, 131.1 (q, $^3J_{CF}$ = 2.8 Hz), 130.942 (q, $^3J_{CF}$ = 2.8 Hz), 130.942 (q, $^2J_{CF}$ = 35.5Hz), 130.2, 130.1, 126.9, 122.5 (q, $^1J_{CF}$ =273.2 Hz), 114.6, 113.3, 37.2; $^{19}$F NMR (376 MHz, $CDCl_3$): δ –63.9; IR (KBr) 3079, 2233, 1668 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{11}F_3N_2O$ 255.0745, found 255.0771.

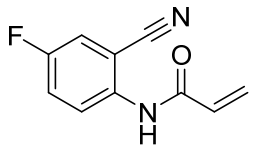
***N*-(1-Methyl-2-oxo-6-(trifluoromethyl)-1,2-dihydroquinolin-4-yl)acetamide (1d)**



**1d**

This compound was prepared from **S8d** in 23% yield in a similar manner to the synthesis of **1c** from **S8c**. **Analytical data for 1d:** yellow solid (mp 196.4–198.4 °C); $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 10.06 (s, 1H), 8.52 (s, 1H), 7.96 (d, $J$ = 9.2 Hz, 1H), 7.73 (d, $J$ = 8.7 Hz, 1H), 7.39 (s, 1H), 3.62 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 170.3, 161.6, 142.1 (q, $^{3}J_{CF}$ = 3.8 Hz), 127.20, 127.17, 124.4 (q, $^{1}J_{CF}$ = 271.5 Hz), 121.9 (q, $^{2}J_{CF}$ = 32.6 Hz), 120.9, 116.2, 115.1, 109.6, 29.2, 24.4; $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ –62.6; IR (KBr) 3275, 2959, 1684 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{12}F_3N_2O_2$ 285.0851, found 285.0865.

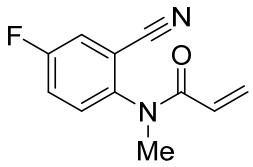
***N*-(2-Cyano-4-fluorophenyl)acrylamide (S7e)**



**S7e**

This compound was prepared from 2-amino-5-fluorobenzonitrile **S6e**[12, 14] in 75% yield in a similar manner to the synthesis of **S7c** from **S6c**. **Analytical data for S7e:** white solid (mp 161.0–162.3 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, $J$ = 9.4, 4.8 Hz, 1H), 7.69 (br s, 1H), 7.39-7.28 (m, 2H), 6.51 (dd, $J$ = 16.5, 0.9 Hz, 1H), 6.32 (dd, $J$ = 16.9, 10.1 Hz, 1H), 5.90 (dd, $J$ = 10.1, 0.9 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.5, 158.0 (d, $^{1}J_{CF}$ = 248.2 Hz), 136.9 (d, $^{4}J_{CF}$ = 2.9 Hz), 130.2, 129.7, 123.6 (q, $^{3}J_{CF}$ = 7.7 Hz), 121.8 (d, $^{2}J_{CF}$ = 22.0 Hz), 118.5 (d, $^{2}J_{CF}$ = 25.9 Hz), 115.2 (d, $^{4}J_{CF}$ = 2.9 Hz), 103.2 (d, $^{3}J_{CF}$ = 8.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$): δ –116.4; IR (KBr) 3271, 2231, 1666 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{10}H_8FN_2O$ 191.0621, found 191.0629.

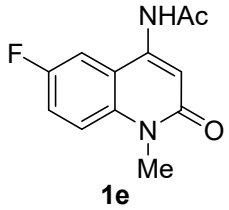
***N*-(2-Cyano-4-fluorophenyl)-*N*-methylacrylamide (S8e)**



**S8e**

This compound was prepared from **S7e** in 88% yield in a similar manner to the synthesis of **S8c** from **S7c**. **Analytical data for S8e:** brown solid (mp 91.2–93.5 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, $J$ = 7.3, 2.3 Hz, 1H), 7.43-7.36 (m, 1H), 7.36-7.30 (m, 1H), 6.45 (d, $J$ = 16.9 Hz, 1H), 5.87 (dd, $J$ = 16.5, 10.5 Hz, 1H), 5.62 (d, $J$ = 10.5 Hz, 1H), 3.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.3, 161.0 (d, $^{1}J_{CF}$ = 253.0 Hz), 142.4, 131.5 (d, $^{3}J_{CF}$ = 8.6 Hz), 129.5, 127.0, 121.8 (d, $^{2}J_{CF}$ = 22.0 Hz), 120.7 (d, $^{2}J_{CF}$ = 25.9 Hz), 114.5, 114.1 (d, $^{3}J_{CF}$ = 9.6 Hz), 37.0; $^{19}$F NMR (376 MHz, $CDCl_3$): δ –110.6; IR (KBr) 3073, 2235, 1664 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{10}FN_2O$ 205.0777, found 205.0804.

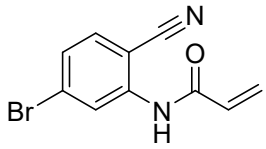
***N*-(6-Fluoro-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)acetamide (1e)**



**1e**

This compound was prepared from **S8e** in 16% yield in a similar manner to the synthesis of **1c** from **S8c**. **Analytical data for 1e:** white solid (mp 225.1–227.5 °C); $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 9.92 (br s, 1H), 8.04 (dd, $J$ = 10.3, 2.5 Hz, 1H), 7.58-7.48 (m, 2H), 7.31 (s, 1H), 3.56 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 170.2, 161.3, 157.0 (d, $^{1}J_{CF}$ = 238.7 Hz), 141.8 (d, $^{4}J_{CF}$ = 2.9 Hz), 136.5, 118.5 (d, $^{2}J_{CF}$ = 24.0 Hz), 117.1 (d, $^{3}J_{CF}$ = 7.7 Hz), 116.2 (d, $^{3}J_{CF}$ = 8.6 Hz), 109.5, 109.0 (d, $^{2}J_{CF}$ = 24.9 Hz), 29.1, 24.3; $^{19}$F NMR (376 MHz, DMSO-$d_6$): δ –122.6; IR (KBr) 3323, 3061, 1642 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{12}FN_2O_2$ 235.0883, found 235.0861.

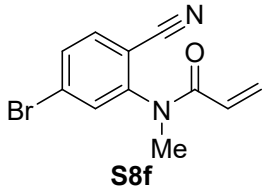
***N*-(5-Bromo-2-cyanophenyl)acrylamide (S7f)**



**S7f**

This compound was prepared from **S6f**[15] in 90% yield in a similar manner to the synthesis of **S7c** from **S6c**. **Analytical data for S7f:** white amorphous solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, $J$ = 9.6 Hz, 1H), 7.75-7.69 (m, 2H), 7.65 (br s, 1H), 6.51 (dd, $J$ = 16.9, 0.9 Hz, 1H), 6.31 (dd, $J$ = 16.9, 10.1 Hz, 1H), 5.91 (d, $J$ = 10.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.5, 139.5, 137.4, 134.4, 130.2, 129.9, 122.6, 116.4, 115.0, 103.4; IR (KBr) 3342, 2229, 1683 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{10}H_8BrN_2O$ 250.9820, found 250.9829.

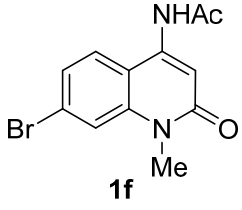
***N*-(5-Bromo-2-cyanophenyl)-*N*-methylacrylamide (S8f)**



**S8f**

This compound was prepared from **S7f** in 83% yield in a similar manner to the synthesis of **S8c** from **S7c**. **Analytical data for S8f:** white solid (mp 98.7–99.7 °C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, $J$ = 2.3 Hz, 1H), 7.79 (dd, $J$ = 8.2, 2.3 Hz, 1H), 7.20 (d, $J$ = 8.7 Hz, 1H), 6.45 (dd, $J$ = 16.9, 1.4 Hz, 1H), 5.89 (br s, 1H), 5.63 (d, $J$ = 8.7 Hz, 1H), 3.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.1, 145.0, 137.4, 136.4, 130.8, 129.6, 127.0, 121.9, 114.4, 114.2, 36.9; IR (KBr) 2236, 1664 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{10}BrN_2O$ 264.9977, found 264.9962.

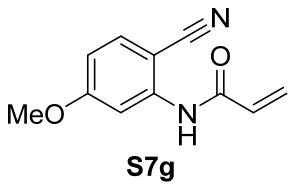
***N*-(7-Bromo-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)acetamide (1f)**



**1f**

This compound was prepared from **S8f** in 7% yield in a similar manner to the synthesis of **1c** from **S8c**. **Analytical data for 1f:** white amorphous solid; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 9.82 (s, 1H), 8.31 (d, $J$ = 1.8 Hz, 1H), 7.75 (dd, $J$ = 9.2, 2.3 Hz, 1H), 7.45 (d, $J$ = 8.7 Hz, 1H), 7.27 (s, 1H), 3.51 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 170.2, 161.3, 141.5, 138.9, 133.5, 125.3, 117.4, 116.8, 113.9, 109.4, 29.0, 24.4; IR (KBr) 3060, 1635, 1612 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{12}BrN_2O_2$ 295.0082, found 295.0105.

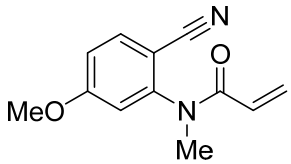
***N*-(2-Cyano-5-methoxyphenyl)acrylamide (S7g)**



**S7g**

This compound was prepared from **S6g**[12, 14] in 75% yield in a similar manner to the synthesis of **S7c** from **S6c**. **Analytical data for S7g:** white solid (mp 141.5–143.7 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.3 Hz, 1H), 7.69 (br s, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.50 (dd, *J* = 16.9, 0.9 Hz, 1H), 6.31 (dd, *J* = 16.9, 10.1 Hz, 1H), 5.89 (dd, *J* = 10.1, 0.9 Hz, 1H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.7, 142.3, 133.3, 130.5, 129.5, 116.8, 111.6, 105.5, 93.1, 55.7; IR (KBr) 3240, 2222, 1672 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{11}N_2O_2$ 203.0821, found 203.0848.

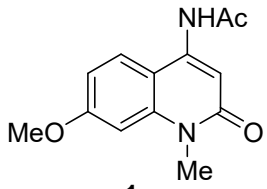
***N*-(2-Cyano-5-methoxyphenyl)-*N*-methylacrylamide (S8g)**



**S8g**

This compound was prepared from **S7g** in 95% yield in a similar manner to the synthesis of **S8c** from **S7c**. **Analytical data for S8g:** white solid (mp 81.5–82.7 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 1H), 6.97 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.80 (d, *J* = 2.3 Hz, 1H), 6.45 (dd, *J* = 16.7, 1.6 Hz, 1H), 5.94 (dd, *J* = 16.3, 10.3 Hz, 1H), 5.61 (d, *J* = 10.1 Hz, 1H), 3.88 (s, 3H), 3.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.1, 163.7, 147.6, 135.1, 128.8, 127.3, 116.0, 115.2, 114.2, 103.8, 55.9, 36.7; IR (KBr) 2228, 1664 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{13}N_2O_2$ 217.0977, found 217.0961.

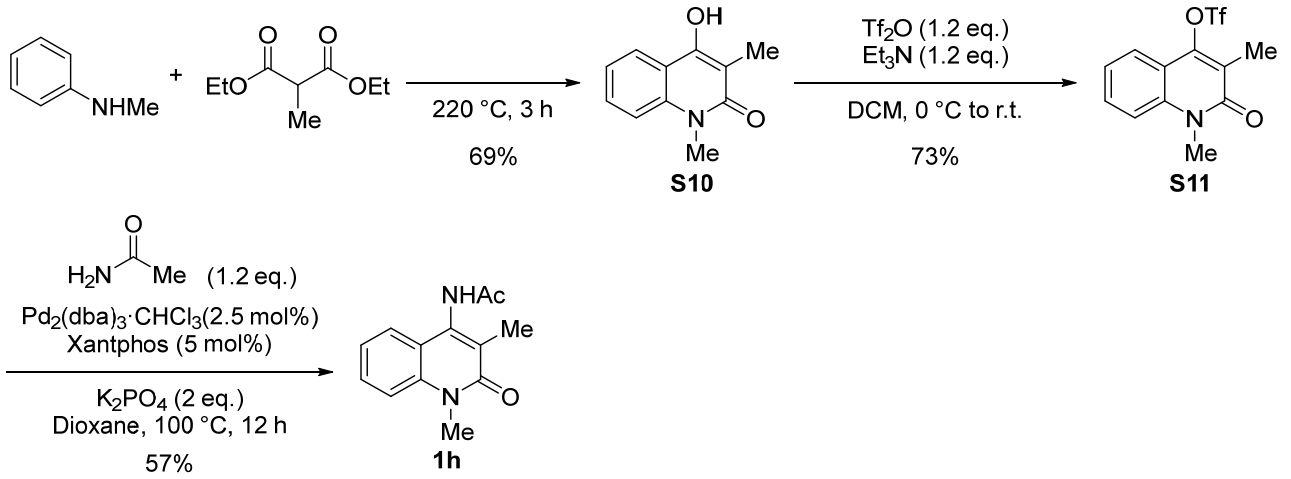
***N*-(7-Methoxy-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)acetamide (1g)**



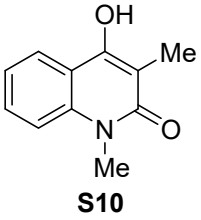
**1g**

This compound was prepared from **S8g** in 36% yield in a similar manner to the synthesis of **1c** from **S8c**. **Analytical data for 1g:** white solid (mp 251.3–253.4 °C); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.77 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.10 (s, 1H), 6.96-6.89 (m, 2H), 3.90 (s, 3H), 3.56 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 170.0, 162.0, 161.5, 142.6, 141.6, 124.9, 109.1, 108.9, 106.0, 99.1, 55.6, 28.9, 24.3; IR (KBr) 2956, 1645, 1614 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{15}N_2O_3$ 247.1083, found 247.1076.

## Synthesis and Characterization of 1h



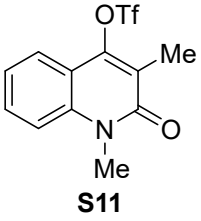

### 4-Hydroxy-1,3-dimethylquinolin-2(1*H*)-one (S10)[16]




**S10**

A mixture of diethyl methylmalonate (3.42 mL, 20.0 mmol) and *N*-methylaniline (2.16 mL, 20.0 mmol) was heated to 220 °C in a 10 mL round bottomed flask topped with a short path distillation head. After finishing the generation of EtOH, the mixture solidified upon cooling to room temperature. The crude product was washed with $H_2O$ (40 mL) and DCM (40 mL) and dried in vacuo to afford **S10** (2.59 g, 69%) as a white solid (mp 194.1–195.4 °C). **Analytical data for S10**[17]**:** $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.08 (s, 1H), 7.95 (dd, $J$ = 8.2, 1.4 Hz, 1H), 7.53 (t, $J$ = 7.8 Hz, 1H), 7.42 (d, $J$ = 8.2 Hz, 1H), 7.21 (t, $J$ = 7.6 Hz, 1H), 3.56 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 163.0, 155.9, 138.1, 130.0, 122.8, 121.2, 116.2, 114.1, 106.4, 29.1, 10.3; IR (KBr) 3165, 3090, 1644 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{12}NO_2$ 190.0868, found 190.0887.

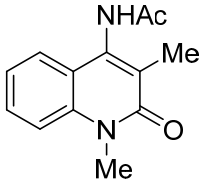
### 1,3-Dimethyl-2-oxo-1,2-dihydroquinolin-4-yl trifluoromethanesulfonate (S11)[18]




**S11**

To a solution of **S10** (1.89 g, 10.0 mmol) and $Et_3N$ (1.7 mL, 12.0 mmol) in dry DCM (100 mL) was slowly added $Tf_2O$ (2.0 mL, 12.0 mmol) at 0 °C under Ar atmosphere. The reaction mixture was gradually warmed to room temperature and kept stirring for 5 h. After concentration in vacuo, the residue was purified by silica gel column chromatography (Hexane/EtOAc = 1:1) to give **S11** (2.36g, 73%) as a yellow amorphous solid. **Analytical data for S11**[18]**:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, $J$ = 8.0, 1.1 Hz, 1H), 7.65 (ddd, $J$ = 8.5, 7.1, 1.4 Hz, 1H), 7.44 (d, $J$ = 8.7 Hz, 1H), 7.35 (dd, $J$ = 7.3, 0.9 Hz, 1H), 3.78 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.4, 149.6, 138.1, 131.3, 123.3, 122.9, 122.7, 118.5 (q, $^3J_{CF}$ = 320.1 Hz), 115.7, 114.3, 30.4, 12.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –73.7; IR (KBr) 1639 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{11}F_3NO_4S$ 322.0361, found 322.0337.

***N*-(1,3-Dimethyl-2-oxo-1,2-dihydroquinolin-4-yl)acetamide (1h)**



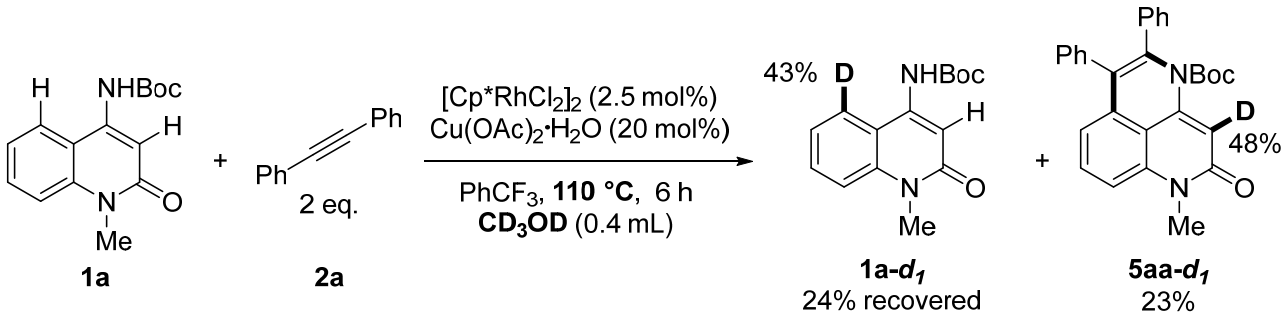
**1h**

A Schlenk tube was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (14.1 mg, 0.025 mmol, 5.0 mol%), Xantphos (14.2 mg, 0.025 mmol, 5.0 mol%), **S11** (160.5 mg, 0.50 mmol), $K_3PO_4$ (212.5 mg, 1.0 mmol), acetamide (36.1 mg, 0.60 mmol) and dry dioxane (8 mL) under Ar atmosphere. The mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with water and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with water (2 x 40 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc only) to give **1h** (65.9 mg, 57%) as a white amorphous solid; **Analytical data for 1h:** This compound was observed as a mixture of rotamers (ratio 3.75:1) at 25 ºC. $^1$H NMR (400 MHz, $CDCl_3$) discernible data for major rotamer: δ 7.60 (d, $J$ = 8.2 Hz, 1H), 7.54 (t, $J$ = 7.8 Hz, 1H), 7.38 (d, $J$ = 8.7 Hz, 1H), 7.26-7.21 (m, 1H), 7.05 (br s, 1H), 3.75 (s, 3H), 2.34 (s, 3H), 2.20 (s, 3H); discernable data for minor rotamer: δ 7.75 (d, $J$ = 7.3 Hz, 1H), 7.43 (d, $J$ = 8.7 Hz, 1H), 7.32 (t, $J$ = 7.3 Hz, 1H), 6.80 (br s, 1H), 3.79 (s, 3H), 2.29 (s, 3H), 1.84 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 168.2, 161.9, 139.6, 138.0, 130.0, 125.2, 124.4, 121.7, 118.5, 114.5, 29.6, 22.8, 13.3; IR (KBr) 3258, 1638, 1597 cm$^{-1}$; HRMS (DART) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{15}N_2O_2$ 231.1134, found 231.1122.

# 7. Mechanistic Studies

## 7-1. H/D Exchange Experiments

*H/D exchange experiment with **1a** in the presence of $CD_3OD$ at 110 °C.*




A Schlenk tube was charged with $[Cp^*RhCl_2]_2$ (3.0 mg, 0.0050 mmol, 2.5 mol%), $Cu(OAc)_2 \cdot H_2O$ (8.0 mg, 0.040 mmol, 20 mol%), **1a** (54.7 mg, 0.20 mmol), and **2a** (71.5 mg, 0.40 mmol) . $PhCF_3$ (2.0 mL) and $CD_3OD$ (0.40 mL) were added, and the mixture was stirred at 110 °C for 6 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with $CHCl_3$ to remove the metal salts. After evaporation of the solvents under reduced pressure, the residue was purified by a silica gel column chromatography (Hexane/EtOAc = 1:1) to afford a mixture of **1a-*d*$_2$** and **5aa-*d*$_1$**. This mixture was further purified by preparative HPLC to give pure **1a-*d*$_2$** (24%) and **5aa-*d*$_1$** (23%). $^1$H NMR analysis (400 MHz, $CD_3OD$ or $CDCl_3$) showed that only 43% deuterium incorporation at the C5 position was observed in **1a**. In **5aa**, 48% deuterium incorporation at the C3 position was observed.

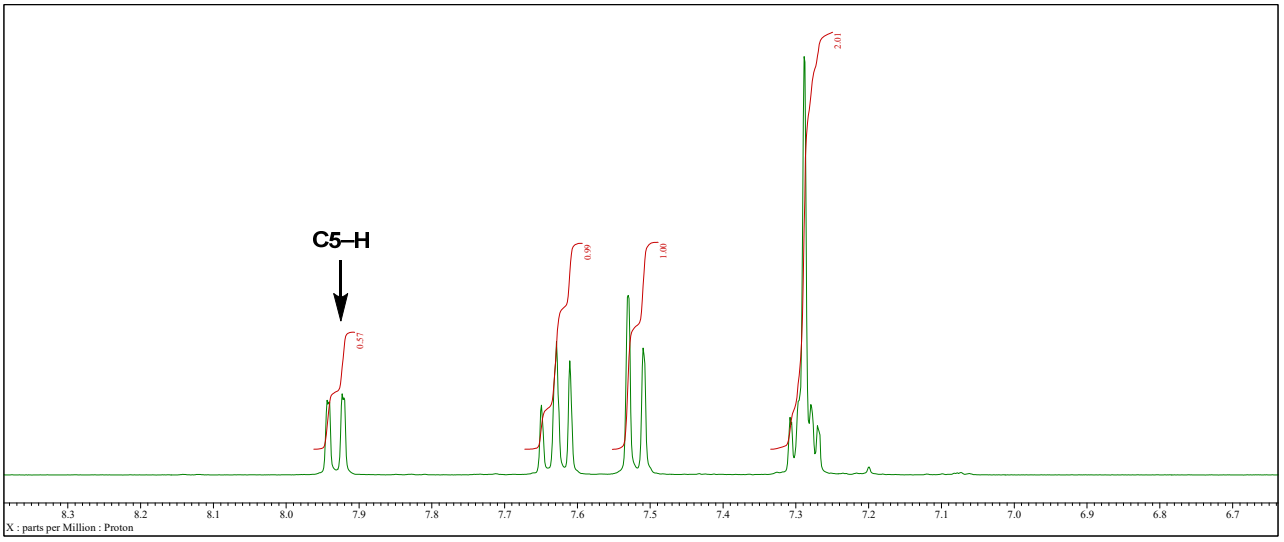



**Figure S1.** $^1$H NMR spectrum ($CD_3OD$) of **1a** after the H/D exchange experiment.

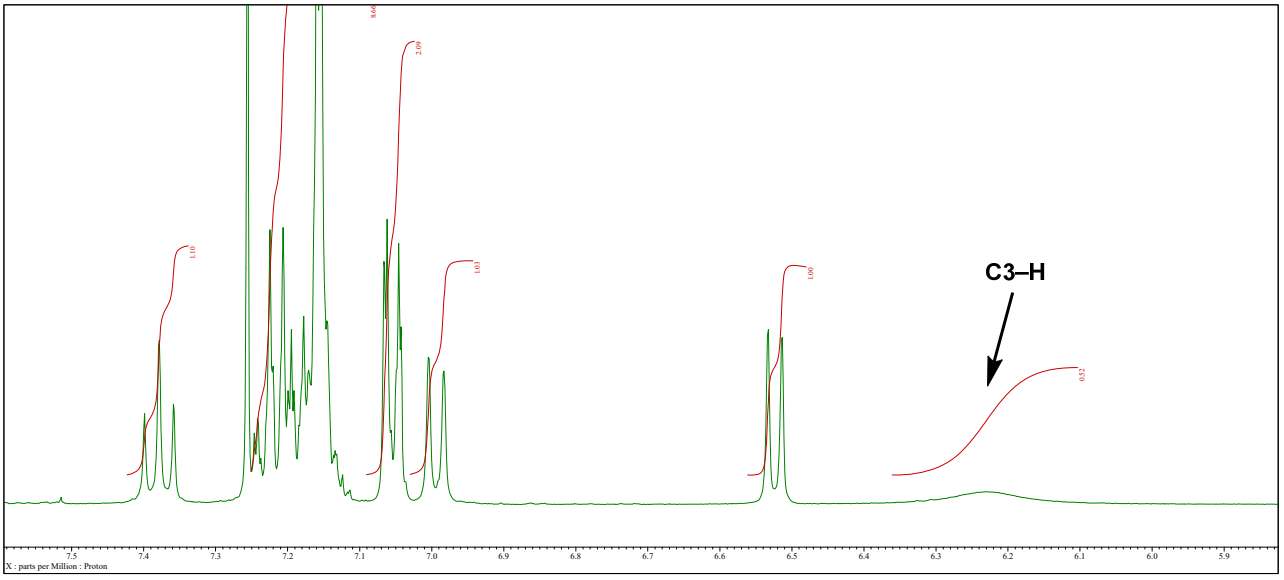
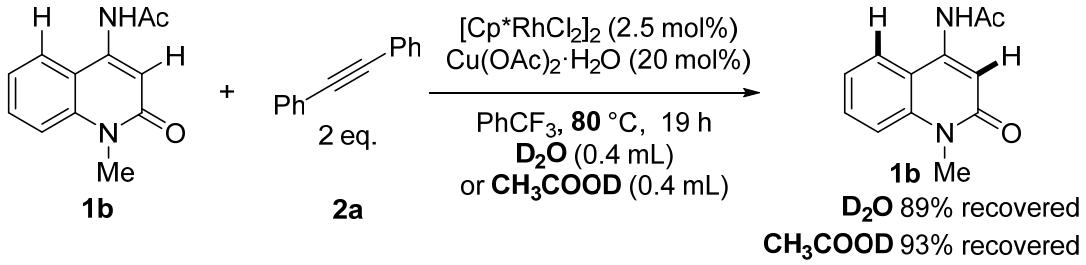


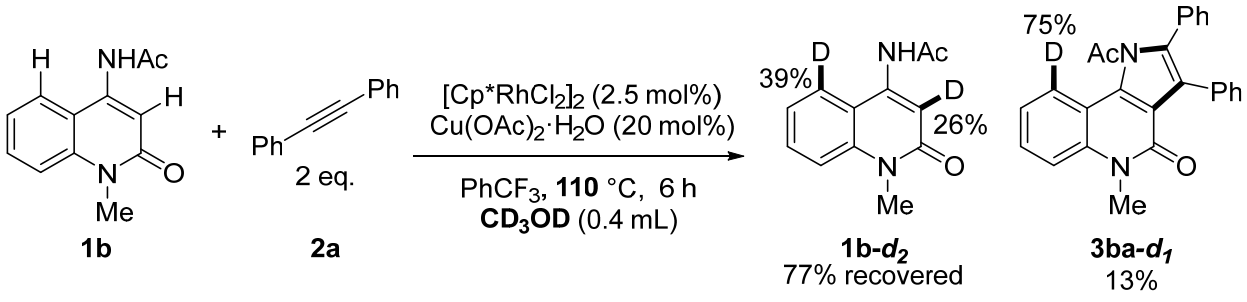

**Figure S2.** $^1$H NMR spectrum ($CDCl_3$) of **5aa** after the H/D exchange experiment.

*H/D exchange experiment with **1b** in the presence of $D_2O$ or AcOD at 80 °C.*




A Schlenk tube was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), $Cu(OAc)_2 \cdot H_2O$ (8.0 mg, 0.040 mmol, 20 mol%), **1b** (43.2 mg, 0.20 mmol), and **2a** (71.3 mg, 0.40 mmol). $PhCF_3$ (2.0 mL) and $D_2O$ (or AcOD) (0.40 mL) were added, and the mixture was stirred at 80 °C for 19 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with $CHCl_3$ to remove the metal salts. After evaporation of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (EtOAc only) to recover **1b** in 89% (or 93%) yield. $^1$H NMR analysis (400 MHz, $CD_3OD$) showed that the deuterium incorporation at the C3- and C5 positions was not observed.

*H/D exchange experiment with **1b** in the presence of $CD_3OD$ at 110 °C.*



A Schlenk tube was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), $Cu(OAc)_2 \cdot H_2O$ (8.0 mg, 0.040 mmol, 20 mol%), **1b** (43.2 mg, 0.20 mmol), and **2a** (71.3 mg, 0.40 mmol). $PhCF_3$ (2.0 mL) and $CD_3OD$ (0.40 mL) were added, and the mixture was stirred at 110 °C for 6 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with $CHCl_3$ to remove the metal salts. After evaporation of the solvents under reduced pressure, the residue was purified by a silica gel column chromatography (Hexane/EtOAc = 3:1 to EtOAc only) to afford **1b-*d*$_2$** in 77% yield and **3ba-*d*$_1$** in 13% yield. $^1$H NMR analysis (400 MHz, $CD_3OD$) showed that 26% deuterium incorporation at the C3 position and 39% deuterium incorporation at the C5 position were observed in **1b**. In **3ba**, 75% deuterium incorporation at the C5 position was observed.

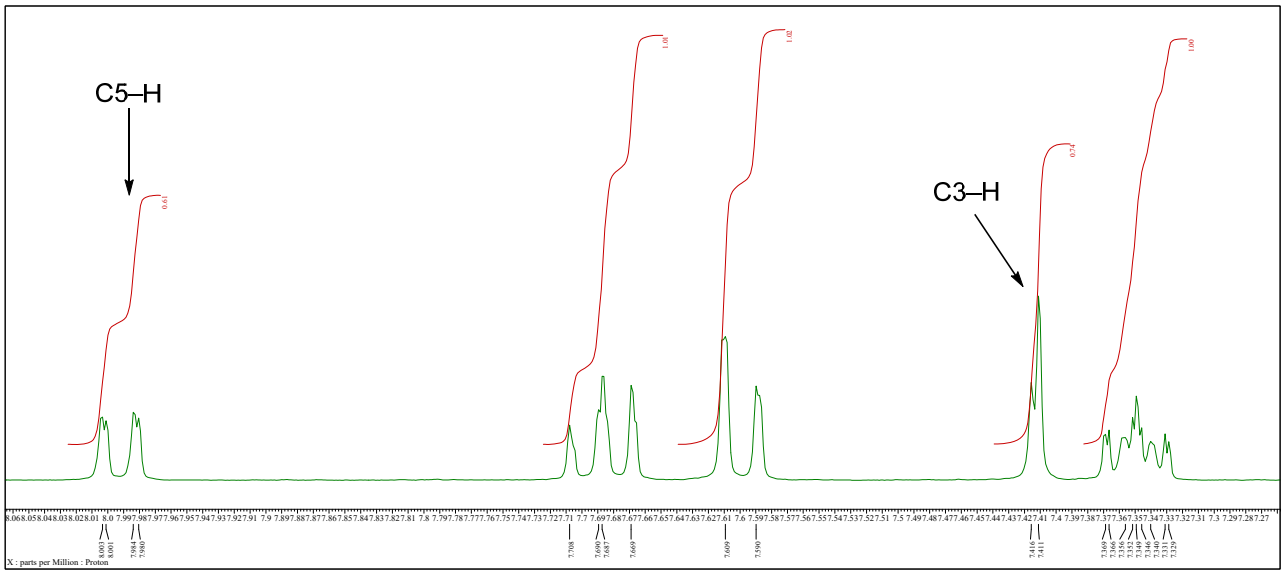



**Figure S3.** $^1$H NMR spectrum of **1b** after the H/D exchange experiment.

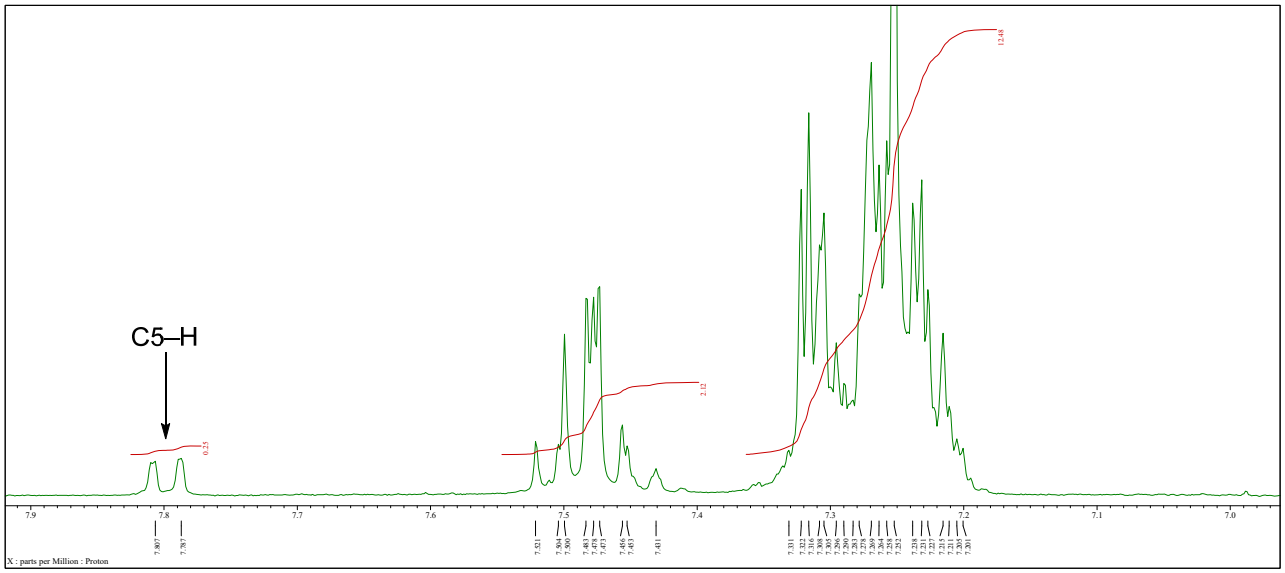
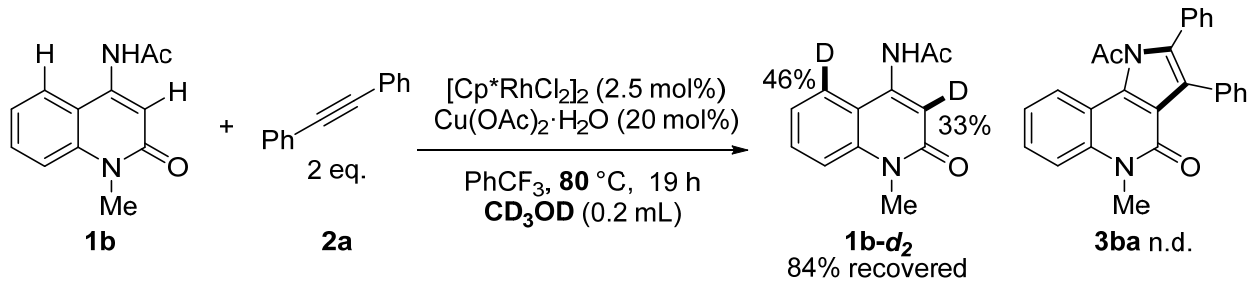



**Figure S4.** $^1$H NMR spectrum of **3ba** after the H/D exchange experiment.

*H/D exchange experiment with **1a** in the presence of $CD_3OD$ at 80 °C.*




A Schlenk tube was charged with $[Cp^*RhCl_2]_2$ (1.5 mg, 0.0025 mmol, 2.5 mol%), $Cu(OAc)_2·H_2O$ (4.0 mg, 0.020 mmol, 20 mol%), **1b** (21.3 mg, 0.10 mmol), and **2a** (36.4 mg, 0.20 mmol). $PhCF_3$ (1.0 mL) and $CD_3OD$ (0.20 mL) were added, and the mixture was stirred at 80 °C for 19 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with $CHCl_3$ to remove the metal salts. After evaporation of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (EtOAc only) to afford **1b-*d*$_2$** in 84% yield. $^1$H NMR analysis (400 MHz, $CD_3OD$)showed that the deuterium incorporation at both the C3 position (33%) and the C5 position (46%) were observed.

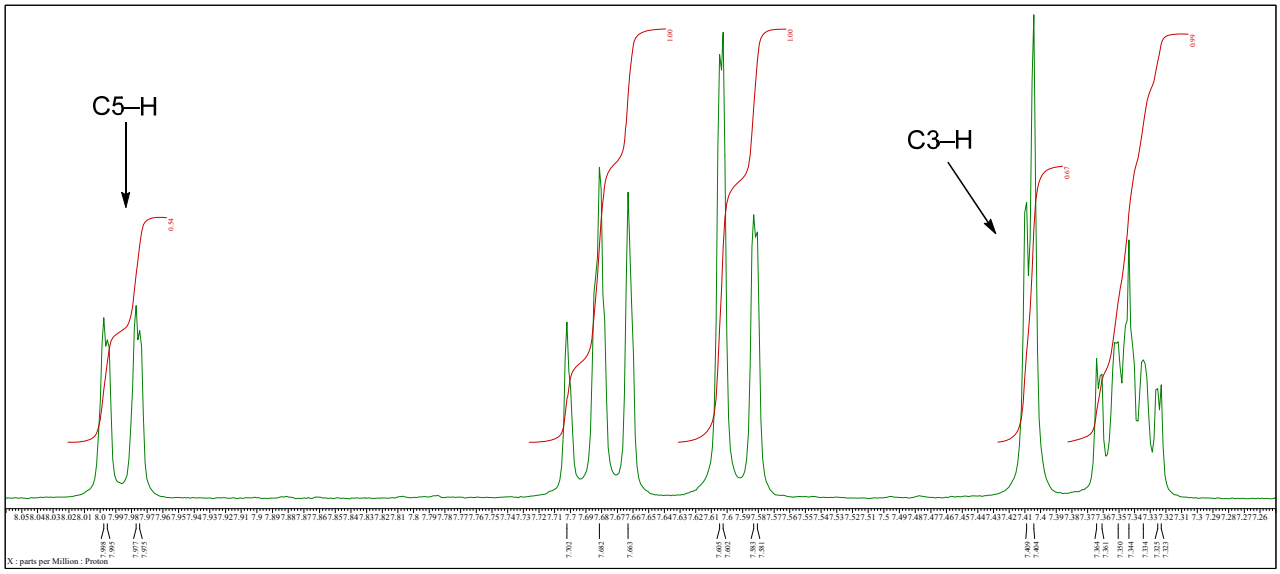
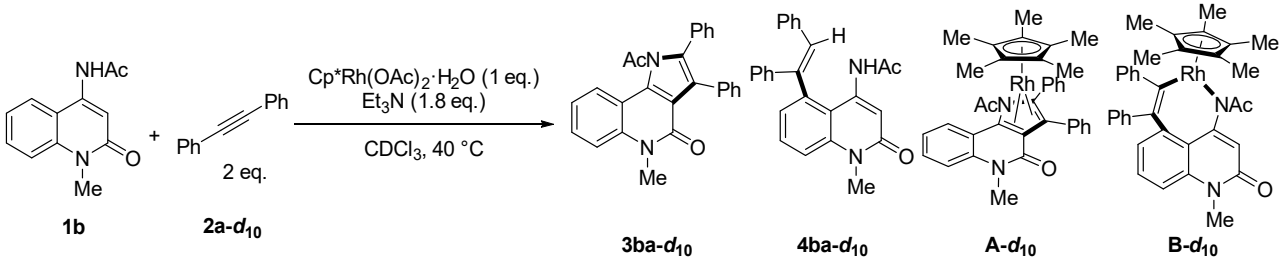



**Figure S5.** $^1$H NMR spectrum of **1b** after the H/D exchange experiment.

## 7-2. $^1$H NMR Monitoring of the Reaction




A J.Young. NMR tube was charged with Cp*Rh(OAc)$_2$·H$_2$O (3.8 mg, 0.010 mmol), **1b** (2.1 mg, 0.010 mmol), **2a** (3.7 mg, 0.020 mmol), Et$_3$N (2.5 μL (1.8 mg), 0.18 mmol), and CDCl$_3$ (0.50 mL) under Ar atmosphere. The reaction mixture was stirred at 40 °C using an oil bath and the reaction was monitored by $^1$H NMR.

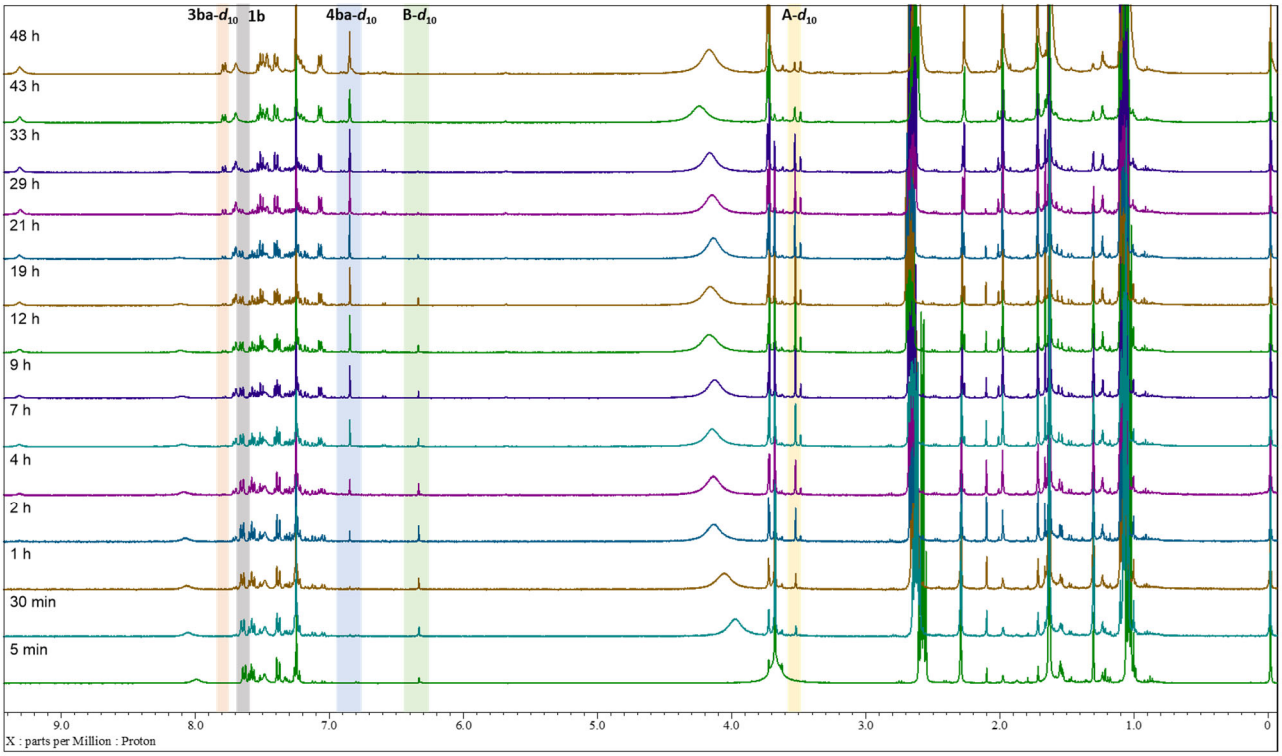
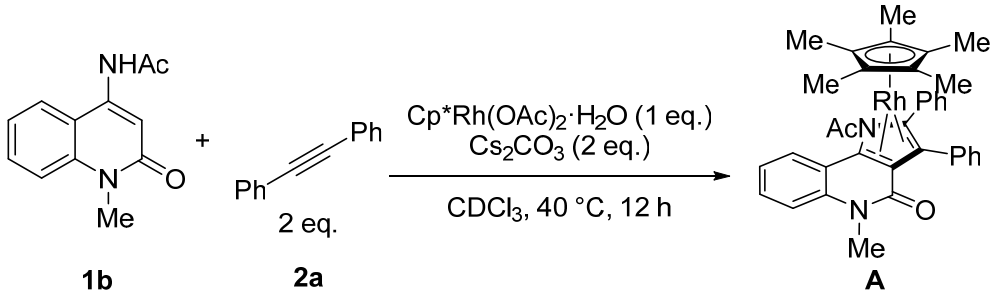



**Figure S6.** Monitoring of the reaction.

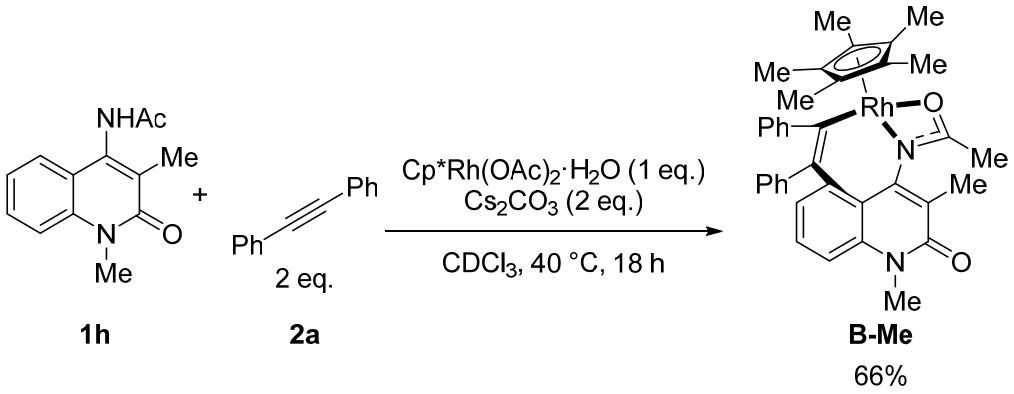
### 7-3. Isolation of Complex A




A J. Young. NMR tube was charged with Cp*Rh(OAc)$_2$·H$_2$O (11.2 mg, 0.030 mol), **1b** (6.5 mg, 0.030 mmol), **2a** (10.7 mg, 0.060 mmol), $Cs_2CO_3$ (19.5 mg, 0.060 mmol), and $CDCl_3$ (0.50 mL) under Ar atmosphere. The reaction mixture was stirred at 40 °C using an oil bath and the reaction was monitored by $^1$H NMR. After 12 h, $CDCl_3$ was removed under reduced pressure. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 1:1). Red crystals were obtained by recrystallization from $CHCl_3$ and hexane. The structure of complex **A** was determined by X-Ray diffraction analysis. Other than that, only $^1$H NMR analysis was conducted using a mixture of **A** and **3ba** because **A** was immediately converted to **3ba** in $CDCl_3$.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.77-7.65 (m, 3H), 7.53-7.37 (m, 3H), 7.35-7.28 (m, 3H), 7.20 (d, $J$ = 7.8 Hz, 1H), 7.17-7.10 (m, 2H), 7.06-6.95 (m, 2H), 3.55 (s, 3H), 1.68 (s, 3H), 1.13 (s, 15H).

### 7-4. Preparation and Characterization of Complex B-Me




A Schlenk tube was charged with Cp*Rh(OAc)$_2$·H$_2$O (11.1 mg, 0.030 mmol), **1h** (6.5 mg, 0.030 mmol), **2a** (10.7 mg, 0.060 mmol), $Cs_2CO_3$ (19.5 mg, 0.060 mmol), and $CDCl_3$ (0.50 mL) under Ar atmosphere. The reaction mixture was stirred at 40 °C using an oil bath for 12 h. The solvent was removed under reduced pressure. This crude product was treated with DCM and hexane at room temperature to form a reddish-orange solid, which was collected by filtration (12.7 mg, 66%). The obtained solid was recrystallized from diethyl ether/hexane. **Analytical data for B-Me:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 1H), 7.14 (dd, $J$ = 7.6, 6.2 Hz, 2H), 7.07-6.98 (m, 4H), 6.91-6.85 (m, 3H), 6.82-6.77(m, 1H), 6.74-6.70 (m, 2H), 3.80 (s, 3H), 2.28 (s, 3H), 1.89 (s, 3H), 1.29 (s, 15H); $^{13}$C NMR data could not be obtained due to the instability of the complex over the timescale required for the experiment; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{37}H_{37}N_2NaO_2Rh$ 667.1808, found 667.1817.

Comparison of $^{1}$H NMR spectra of **B** and **B-Me**.

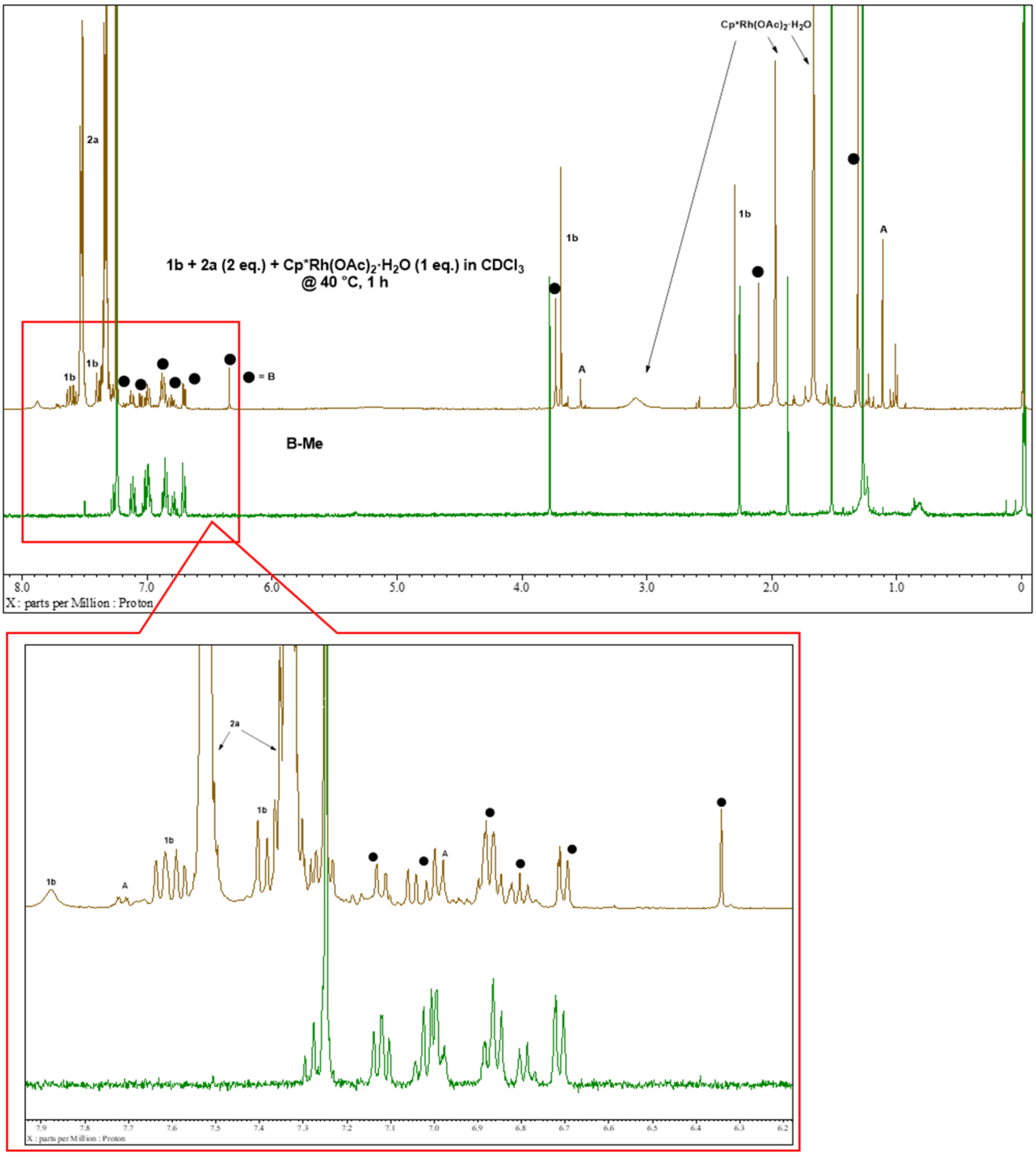
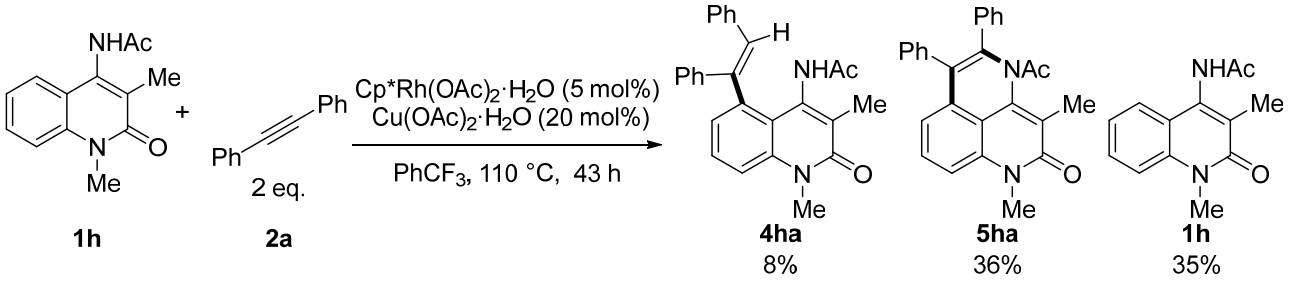



**Figure S7.** $^{1}$H NMR spectra of **B** (reaction mixture) and **B-Me** (purified).

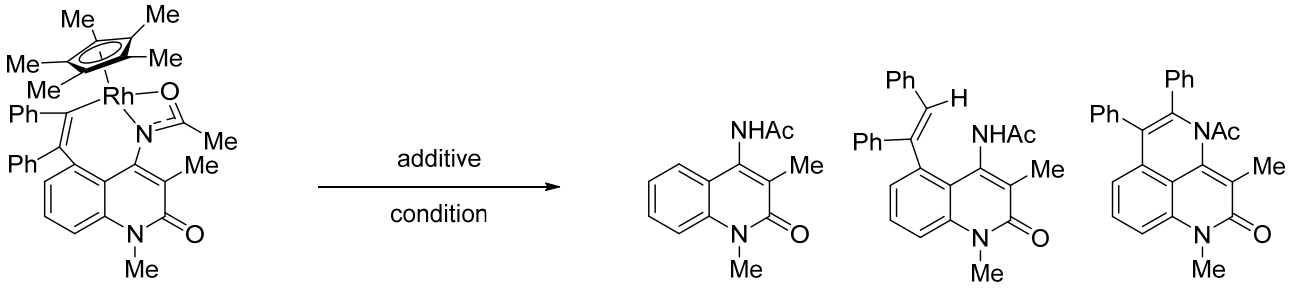
### 7-5. Catalytic Reaction with 1h




A Schlenk tube was charged with $Cp^*Rh(OAc)_2 \cdot H_2O$ (3.7 mg, 0.010 mmol, 5 mol%), $Cu(OAc)_2 \cdot H_2O$ (7.9 mg, 0.040 mmol, 20 mol%), **1h** (46.1 mg, 0.20 mmol), **2a** (71.1 mg, 0.40 mmol), and $PhCF_3$ (2.0 mL). The reaction mixture was stirred at 110 °C for 43 h under air atmosphere using an oil bath. Then, the mixture was cooled to room temperature and filtered through a pad of Celite® with $CHCl_3$ to remove the metal salts. After concentration in vacuo, the residue was purified by silica gel column chromatography (Hexane/EtOAc = 2:1 to 1:1 to EtOAc only).

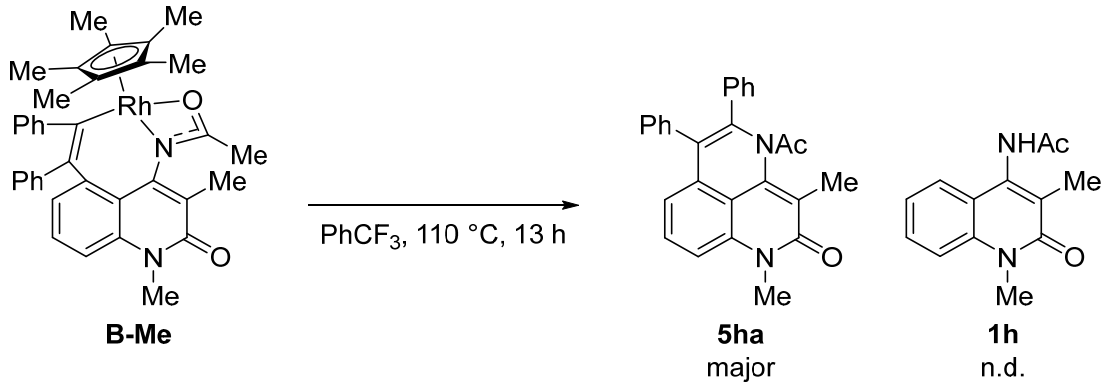
### 7-6. Experiments with B-Me

**Table S3.** Screening some additives to promote the *β*-carbon elimination.




| additive | condition | **1h** | **4ha** | **5ha** |
|---|---|---|---|---|
| - | $PhCF_3$, 110 °C, 13 h | n.d. | n.d. | major |
| AcOH-$d_4$ (1 eq.) | $CDCl_3$, 60 °C, 3 h | n.d. | major | n.d. |
| MeOH-$d_4$ (1 eq.) | $CDCl_3$, 60 °C, 4 days | n.d. | trace | major |
| **1b** (10 eq.) | $CDCl_3$, 60 °C, 4 days | n.d. | major (1 : 1) | |
| $Cu(OAc)_2 \cdot H_2O$ (1 eq.) | $PhCF_3$, 110 °C, 13 h | n.d. | n.d. | major |
| NaOAc (1 eq.) | $PhCF_3$, 110 °C, 13 h | n.d. | n.d. | major |
| **3ba** (1 eq.) | $PhCF_3$, 110 °C, 13 h | n.d. | n.d. | major |
| $Cp^*Rh(OAc)_2 \cdot H_2O$ (1 eq.) | $PhCF_3$, 110 °C, 13 h | | major (1 : 1.2 : 1.2) | |

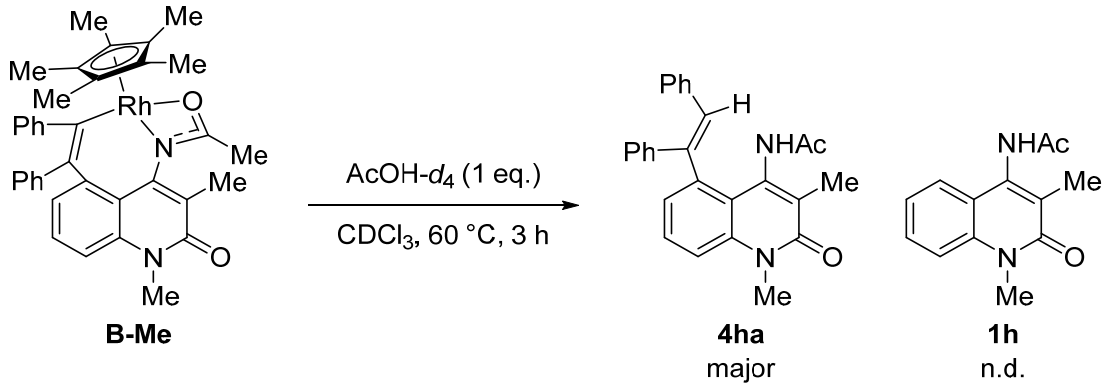
*Heating **B-Me** at 110 °C.*




**B-Me** **5ha** major **1h** n.d.

A Schlenk tube was charged with **B-Me** (0.6 mg, 0.0010 mmol) and $PhCF_3$ (1.0 mL) under Ar atmosphere. The reaction mixture was stirred at 110 °C for 13 h under Ar atmosphere using an oil bath. The resulting solution was concentrated. $^1$H NMR analysis of the crude product mixture showed that **5ha** was mainly observed while **1h** was not detected.

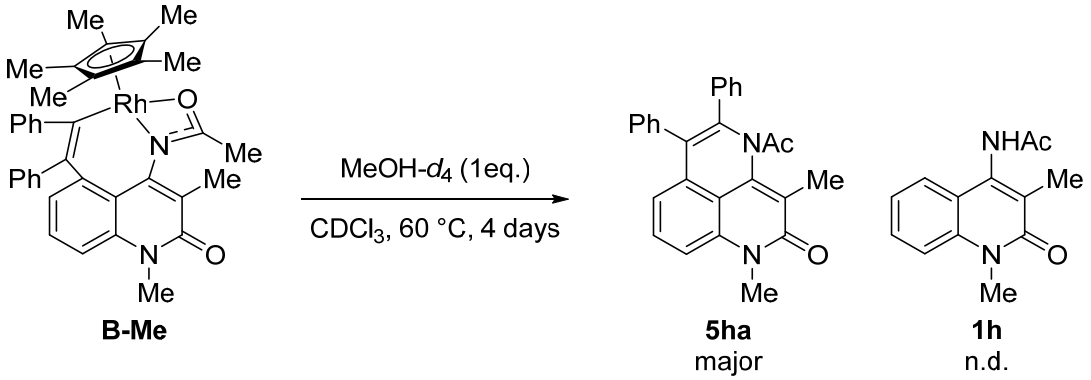
*Addition of acetic acid (1 eq.) at 60 °C.*




**B-Me** **4ha** major **1h** n.d.

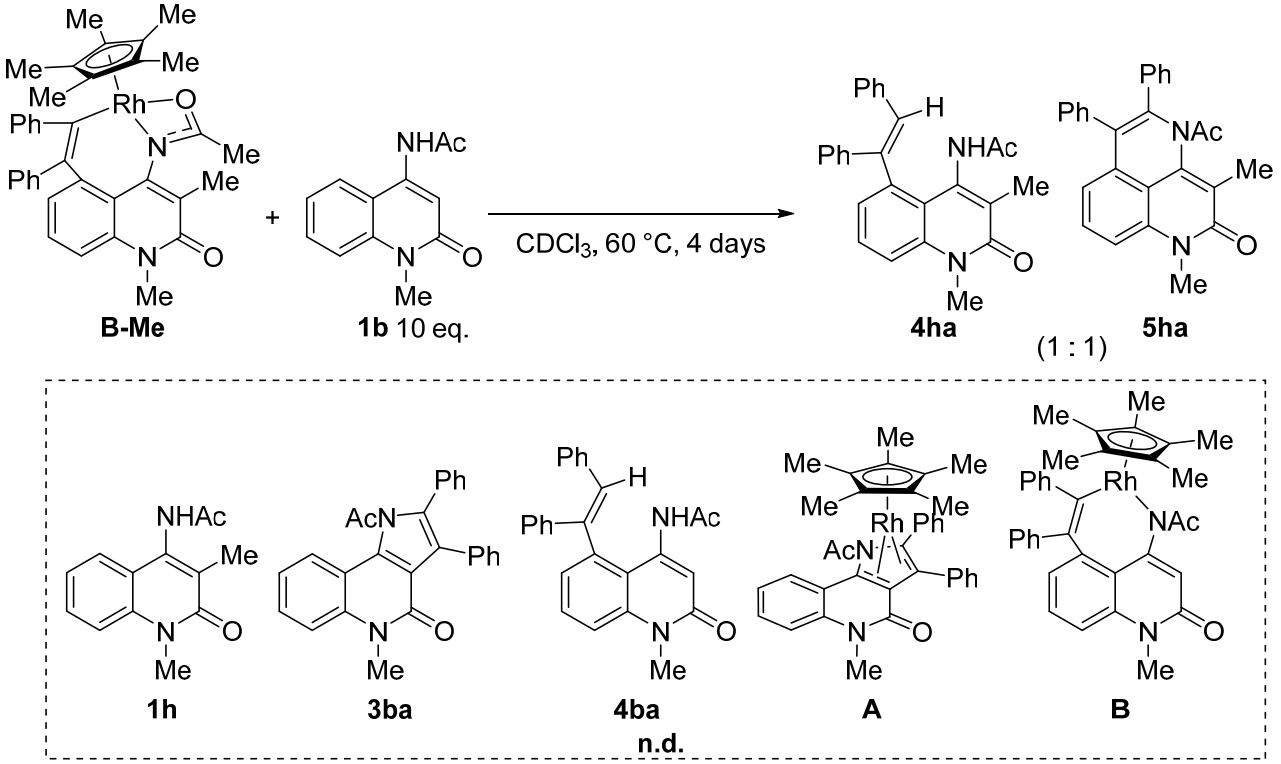
A crimp vial was loaded with AcOH-$d_4$ (6.4 mg, 0.010 mmol) and dissolved in 5 mL of $CDCl_3$ to obtain a 0.002 M AcOH-$d_4$ solution in $CDCl_3$. A J. Young NMR tube was charged with **B-Me** (0.6 mg, 0.0010 mmol) and the prepared solution (0.50 mL) under Ar atmosphere. The reaction mixture was stirred at 60 °C using an oil bath and the reaction was monitored by $^1$H NMR. After 3h at this temperature, **B-Me** was completely consumed and **4ha** was mainly observed while **1h** was not detected by $^1$H NMR.

*Addition of methanol (1 eq.) as a proton source at 60 °C.*



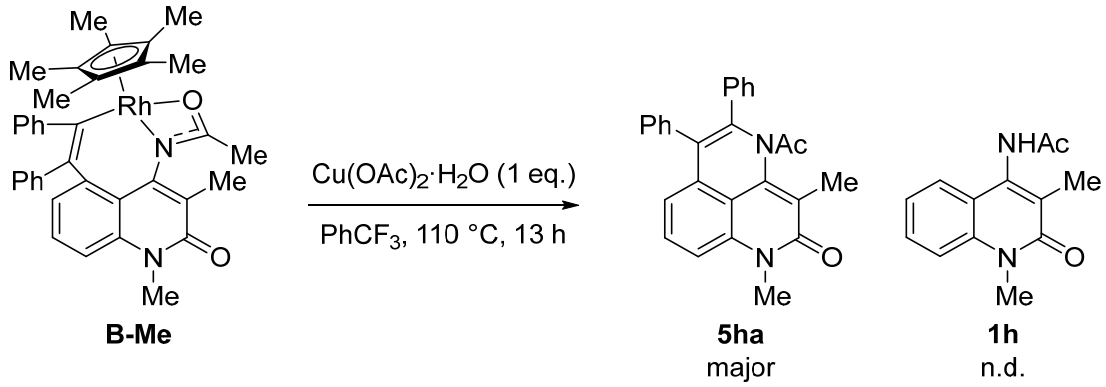

A crimp vial was loaded with MeOH-$d_4$ (3.6 mg, 0.010 mmol) and dissolved in 5 mL of $CDCl_3$ to obtain a 0.002 M MeOH-$d_4$ solution in $CDCl_3$. A J. Young NMR tube was charged with **B-Me** (0.6 mg, 0.0010 mmol) and the prepared solution (0.50 mL) under Ar atmosphere. The reaction mixture was stirred at 60 °C using an oil bath and the reaction was monitored by $^1$H NMR. After 4 days at this temperature, **B-Me** was completely consumed and **5ha** was mainly observed while **1h** was not detected by $^1$H NMR.

*Addition of **1b** (10 eq.) at 60 °C.*




A J. Young NMR tube was charged with **B-Me** (0.6 mg, 0.0010 mmol), **1b** (2.2 mg, 0.010 mmol), $CDCl_3$ (0.5 mL) under Ar atmosphere. The reaction mixture was stirred at 60 °C using an oil bath and the reaction was monitored by $^1$H NMR. After 4 days at this temperature, **4ha** and **5ha** were observed as the major products, while other products such as **1h**, **3ba**, **4ba**, **A**, and **B** were not detected in this experiment.

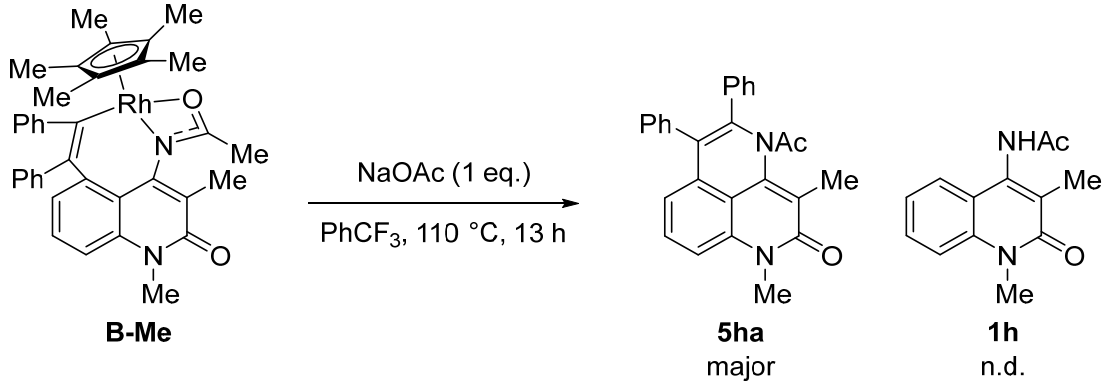
*Heating **B-Me** with $Cu(OAc)_2·H_2O$ (1 eq) at 110 °C.*




**B-Me** **5ha** major **1h** n.d.

A Schlenk tube was charged with **B-Me** (0.6 mg, 0.0010 mmol), $Cu(OAc)_2·H_2O$ (0.2 mg, 0.0010 mmol) and $PhCF_3$ (1.0 mL) under Ar atmosphere. The reaction mixture was stirred at 110 °C for 13 h under Ar atmosphere using an oil bath. The resulting solution was concentrated, and the $^1H$ NMR analysis of the crude product mixture showed that **5ha** was mainly observed while **1h** was not detected.

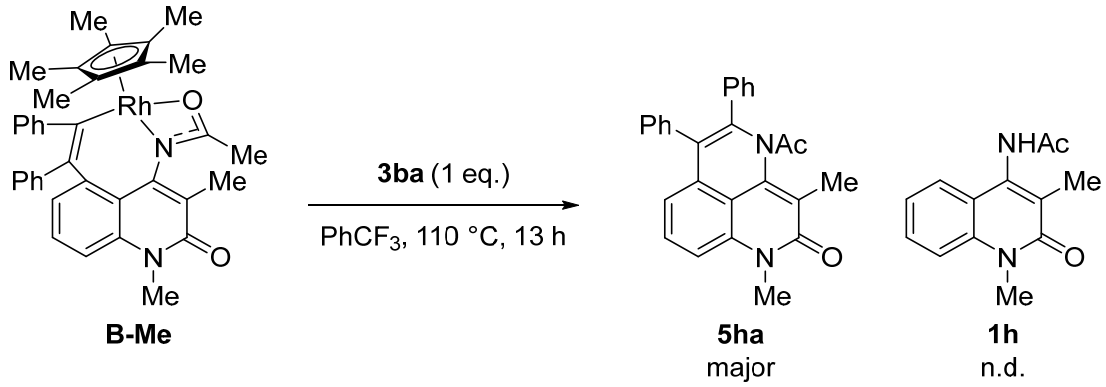
*Heating **B-Me** with NaOAc (1 eq) at 110 °C.*




**B-Me** **5ha** major **1h** n.d.

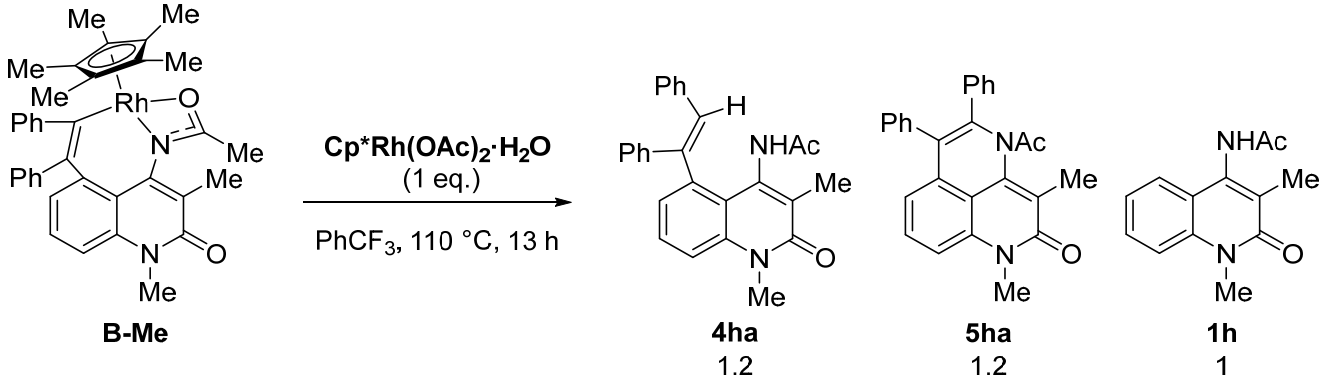
A Schlenk tube was charged with **B-Me** (0.6 mg, 0.0010 mmol), NaOAc (0.08 mg, 0.0010 mmol) and $PhCF_3$ (1.0 mL) under Ar atmosphere. The reaction mixture was stirred at 110 °C for 13 h under Ar atmosphere using an oil bath. The resulting solution was concentrated, and the $^1H$ NMR analysis of the crude product mixture showed that **5ha** was mainly observed while **1h** was not detected.

*Heating **B-Me** with **3ba** (1 eq.) at 110 °C.*




A Schlenk tube was charged with **B-Me** (0.6 mg, 0.0010 mmol), **3ba** (0.4 mg, 0.0010 mmol) and $PhCF_3$ (1.0 mL) under Ar atmosphere. The reaction mixture was stirred at 110 °C for 6 h under Ar atmosphere using an oil bath. The resulting solution was concentrated, and the $^1H$ NMR analysis of the crude product mixture showed that **5ha** was mainly observed while **1h** was not detected.

*Heating **B-Me** with Cp*Rh(OAc)$_2$·H$_2$O (1 eq.) at 110 °C.*




A Schlenk tube was charged with **B-Me** (0.6 mg, 0.0010 mmol), $Rh(OAc)_2·H_2O$ (0.4 mg, 0.0010 mmol) and $PhCF_3$ (1.0 mL) under Ar atmosphere. The reaction mixture was stirred at 110 °C for 13 h under Ar atmosphere using an oil bath. The resulting solution was concentrated, and the $^1H$ NMR analysis of the crude product mixture showed that **4ha**, **5ha**, and **1h** were obtained (**4ha**/**5ha**/**1h** = 1.2:1.2:1).

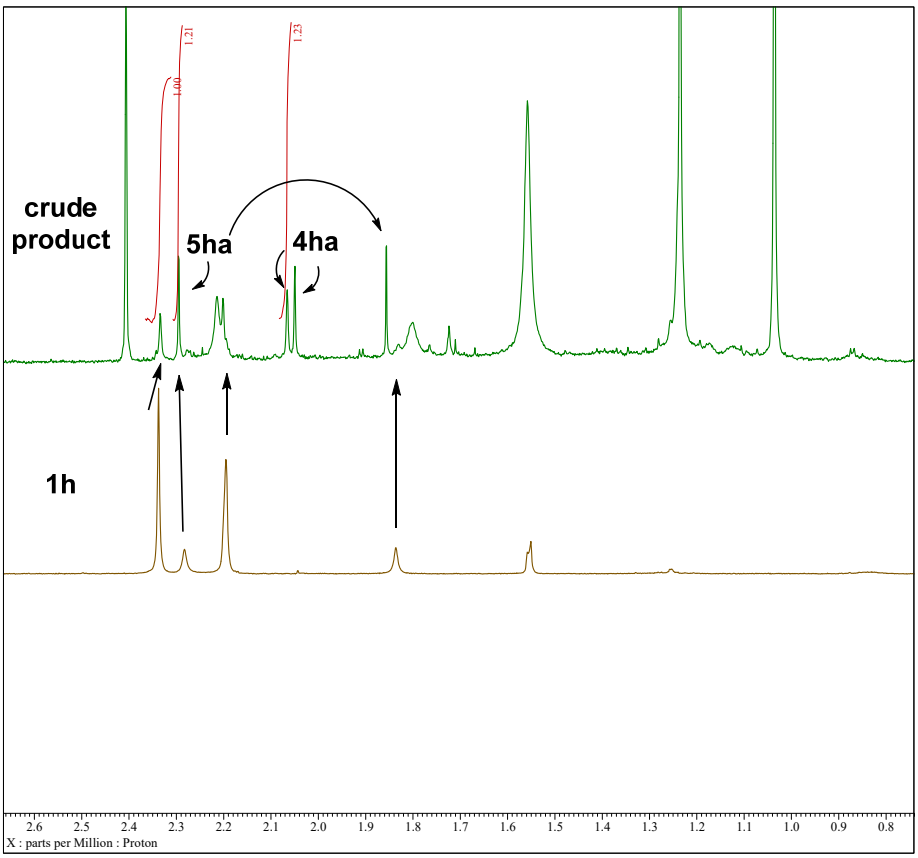
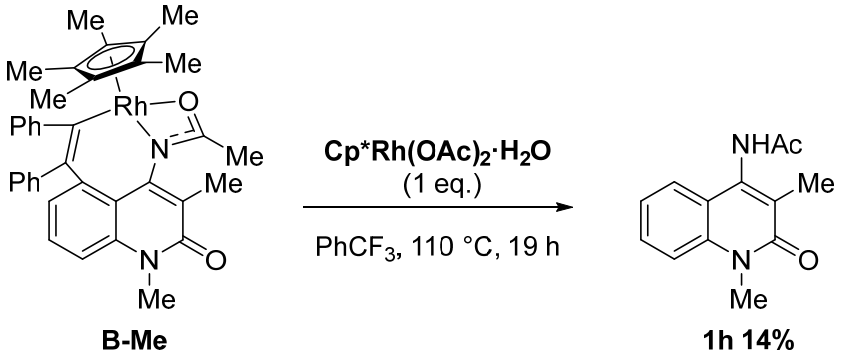



**Figure S8.** $^{1}$H NMR spectra of the crude product.

*Isolated of **1h** from the reaction of **B-Me** with Cp*Rh(OAc)$_2$·H$_2$O.*




A Schlenk tube was charged with **B-Me** (19.3 mg, 0.030 mmol), Rh(OAc)$_2$·H$_2$O (11.2 mg, 0.030 mmol) and PhCF$_3$ (30 mL) under Ar atmosphere. The reaction mixture was stirred at 110 °C for 19 h under Ar atmosphere using an oil bath. The resulting solution was concentrated and the $^{1}$H NMR analysis of the crude product mixture showed that **4ha**, **5ha**, and **1h** were obtained (**4ha**/**5ha**/**1h** =29%:38%:19%). The crude product purified by preparative TLC (Hexane/EtOAc = 1:1 to EtOAc only) to give **1h** (0.50 mg, 14%).

# 8. X-Ray Diffraction Analysis

### X-Ray Diffraction Analysis of 3ba

Diffraction data were collected in $\theta$ ranges specified in Table S4 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S4. The supplementary crystallographic data for this paper (CCDC2278040) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

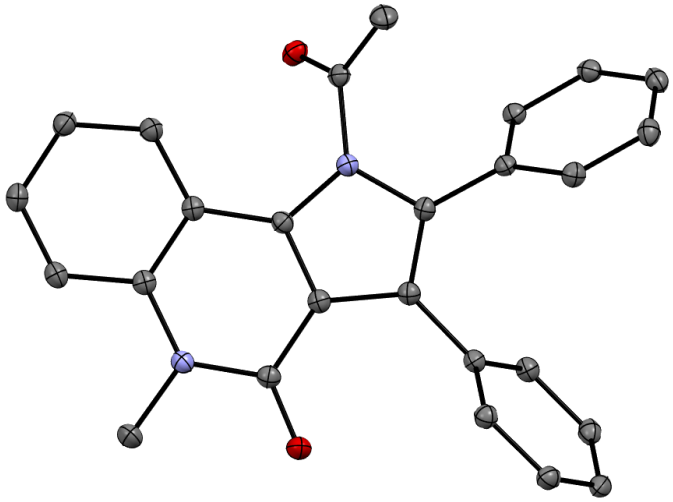


**Figure S9. ORTEP plot of 3ba**

**Table S4.** Selected crystallographic data and collection parameters for **3ba**.

| | | | |
|---|---|---|---|
| formula | $C_{26}H_{20}N_2O_2$ | crystal size, mm | 0.2 x 0.15 x 0.1 |
| FW | 392.46 | maximum 2θ, deg | 136.3 |
| crystal system | monoclinic | reflections collected | 22156 |
| space group | P21/n (#14) | independent reflections [*R*(int)] | 3536 [R(int) = 0.0272] |
| *a*, Å | 10.3174(4) | max. and min. transmission | 0.935/0.699 |
| *b*, Å | 18.8450(7) | goodness-of-fit on $F^2$ | 1.044 |
| *c*, Å | 10.3316(4) | $R_1$ [$I$ >2σ($I$)] | 0.0406 |
| volume, Å$^3$ | 1956.84(14) | $R$, $wR_2$ (all data) | 0.0433, 0.1085 |
| β, ° | 103.056(7) | Weighting scheme | $R_1 = \Sigma \lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert / \Sigma \lvert Fo\rvert$ |
| *Z* | 4 | | $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2}$ |
| *D* (calcd), Mg m$^{-3}$ | 1.332 | largest diff. peak and hole, e Å$^{-3}$ | 0.19 and –0.26 |
| $\mu$, cm$^{-1}$ | 6.763 | | |
| *F*(000) | 824.00 | | |

### X-Ray Diffraction Analysis of 3bf'·$CHCl_3$

Diffraction data were collected in $\theta$ ranges specified in Table S5 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S5. The supplementary crystallographic data for this paper (CCDC2278041) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

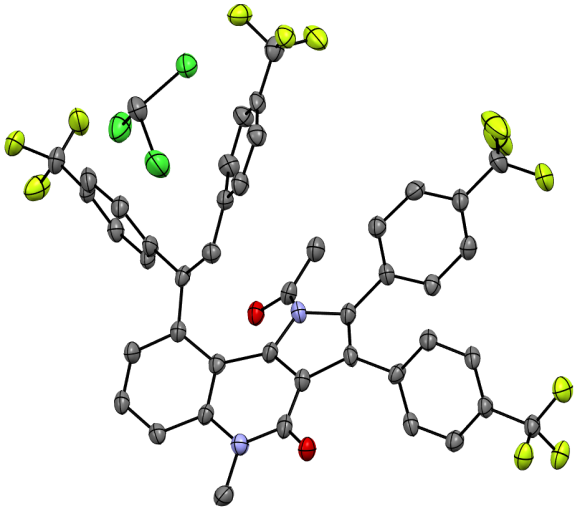


**Figure S10. ORTEP plot of 3bf'·$CHCl_3$**

**Table S5.** Selected crystallographic data and collection parameters for **3bf'·$CHCl_3$**.

| | | | |
|---|---|---|---|
| formula | $C_{45}H_{27}Cl_3F_{12}N_2O_2$ | $\mu$, $cm^{-1}$ | 29.459 |
| FW | 962.06 | $F$(000) | 972.00 |
| crystal system | triclinic | crystal size, mm | 0.3 x 0.1 x 0.05 |
| | | maximum 2θ, deg | 136.4 |
| space group | P-1 (#2) | reflections collected | 23137 |
| $a$, Å | 10.1061(11) | independent reflections [$R$(int)] | 7190 [R(int) = 0.1528] |
| $b$, Å | 14.1090(14) | max. and min. transmission | 0.863/0.329 |
| $c$, Å | 14.8443(15) | goodness-of-fit on $F^2$ | 1.072 |
| volume, $Å^3$ | 2017.9(4) | $R_1$ [$I$ >2σ($I$)] | 0.1199 |
| α, º | 85.453(6) | $R$, $wR_2$ (all data) | 0.2328, 0.4302 |
| β, º | 83.081(6) | Weighting scheme | $R_1 = \Sigma \, \|\|Fo\| - \|Fc\|\| / \Sigma \, \|Fo\|$ |
| γ, º | 74.047(5) | | $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2}$ |
| $Z$ | 2 | largest diff. peak and hole, e $Å^{-3}$ | 0.52 and –0.40 |
| $D$ (calcd), Mg $m^{-3}$ | 1.583 | | |

**X-Ray Diffraction Analysis of 4ba**

Diffraction data were collected in $\theta$ ranges specified in Table S6 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S6. The supplementary crystallographic data for this paper (CCDC2278042) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

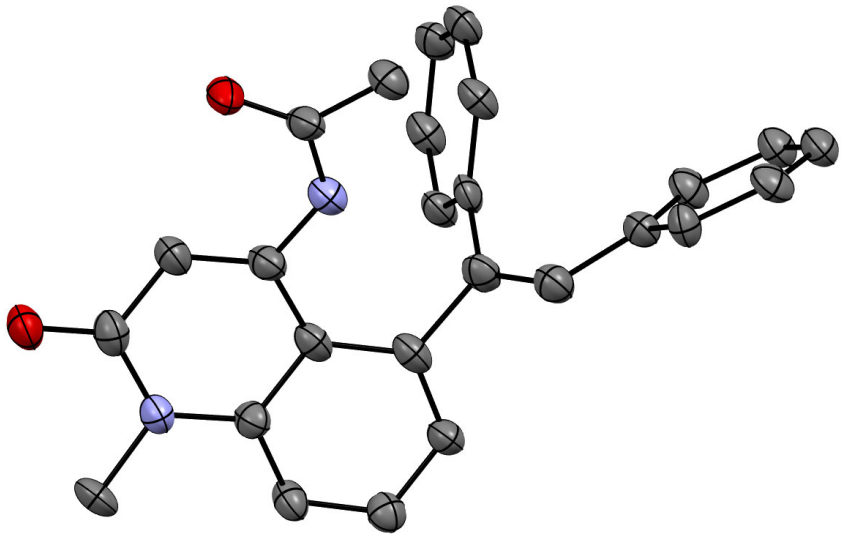


**Figure S11. ORTEP plot of 4ba**

**Table S6.** Selected crystallographic data and collection parameters for **4ba**.

| | | | |
|---|---|---|---|
| formula | $C_{26}H_{22}N_2O_2$ | crystal size, mm | 0.1 x 0.1 x 0.1 |
| FW | 394.47 | maximum 2θ, deg | 136.3 |
| crystal system | monoclinic | reflections collected | 10978 |
| space group | P21 (#4) | independent reflections [*R*(int)] | 3580 [R(int) = 0.1214] |
| *a*, Å | 11.2867(14) | max. and min. transmission | 0.937/0.538 |
| *b*, Å | 7.6954(9) | goodness-of-fit on $F^2$ | 0.991 |
| *c*, Å | 11.8213(14) | $R_1$ [$I > 2\sigma(I)$] | 0.0904 |
| volume, Å$^3$ | 1014.9(2) | *R*, $wR_2$ (all data) | 0.1934, 0.2730 |
| β, ° | 98.725(7) | Weighting scheme | $R_1 = \Sigma \, \|\|Fo\| - \|Fc\|\| / \Sigma \, \|Fo\|$ |
| *Z* | 2 | | $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2}$ |
| *D* (calcd), Mg m$^{-3}$ | 1.291 | largest diff. peak and hole, e Å$^{-3}$ | 0.18 and –0.18 |
| $\mu$, cm$^{-1}$ | 6.523 | | |
| *F*(000) | 416.00 | | |

**X-Ray Diffraction Analysis of 5ha**

Diffraction data were collected in $\theta$ ranges specified in Table S7 at 123 K on a Rigaku PILATUS200K diffractometer with graphite monochromatized MoKa radiation (λ =0.71075 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S7. The supplementary crystallographic data for this paper (CCDC2278043) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

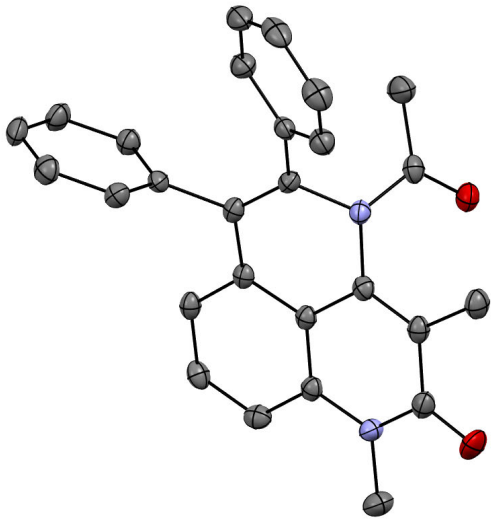


**Figure S12. ORTEP plot of 5ha**

**Table S7.** Selected crystallographic data and collection parameters for **5ha**.

| | | | |
|---|---|---|---|
| formula | $C_{27}H_{22}N_2O_2$ | crystal size, mm | 0.15 x 0.1 x 0.075 |
| FW | 406.48 | maximum 2θ, deg | 55.0 |
| crystal system | monoclinic | reflections collected | 17132 |
| space group | P21/n (#14) | independent reflections [*R*(int)] | 4658 [R(int) = 0.1149] |
| *a*, Å | 9.0396(15) Å | max. and min. transmission | 0.994/0.569 |
| *b*, Å | 21.882(4) Å | goodness-of-fit on $F^2$ | 0.824 |
| *c*, Å | 10.4133(18) Å | $R_1$ [$I > 2\sigma(I)$] | 0.0524 |
| volume, Å$^3$ | 2043.5(6) | $R$, $wR_2$ (all data) | 0.0706, 0.1152 |
| β, ° | 97.221(4) | Weighting scheme | $R_1 = \Sigma \, \|\|Fo\| - \|Fc\|\| / \Sigma \, \|Fo\|$ |
| *Z* | 4 | | $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2}$ |
| *D* (calcd), Mg m$^{-3}$ | 1.321 | largest diff. peak and hole, e Å$^{-3}$ | 0.26 and –0.27 |
| $\mu$, cm$^{-1}$ | 0.838 | | |
| *F*(000) | 856.00 | | |

### X-Ray Diffraction Analysis of A

Diffraction data were collected in $\theta$ ranges specified in Table S8 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S8. The supplementary crystallographic data for this paper (CCDC2278044) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

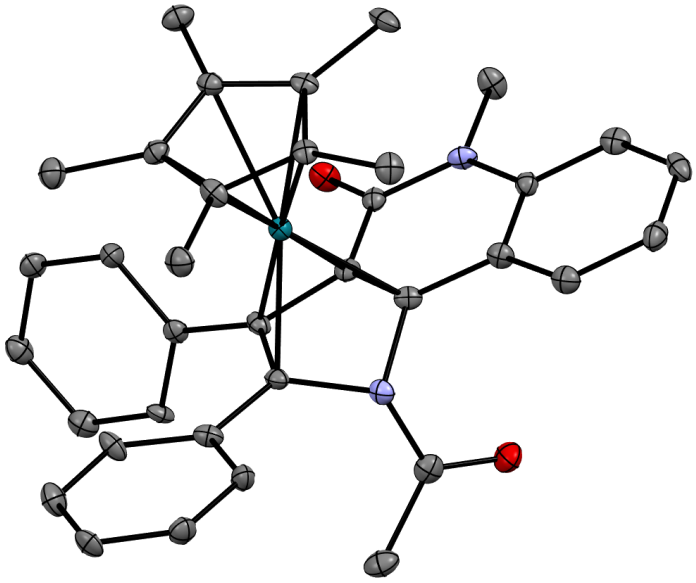


**Figure S13. ORTEP plot of A**

**Table S8.** Selected crystallographic data and collection parameters for **A**.

| | | | |
|---|---|---|---|
| formula | $C_{72}H_{70}N_4O_4Rh_2$ | crystal size, mm | 0.6 x 0.1 x 0.1 |
| FW | 1261.18 | maximum 2θ, deg | 136.3 |
| crystal system | orthorhombic | reflections collected | 51511 |
| space group | Pna21 (#33) | independent reflections [*R*(int)] | 10423 [R(int) = 0.0926] |
| *a*, Å | 21.2877(5) | max. and min. transmission | 0.600/0.262 |
| *b*, Å | 9.8400(2) | goodness-of-fit on $F^2$ | 1.029 |
| *c*, Å | 27.3069(6) | $R_1$ [$I > 2\sigma(I)$] | 0.0570 |
| volume, Å$^3$ | 5720.0(2) | $R$, $wR_2$ (all data) | 0.0728, 0.1341 |
| *Z* | 4 | Weighting scheme | $R_1 = \Sigma \lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert / \Sigma \lvert Fo\rvert$ $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2}$ |
| *D* (calcd), Mg m$^{-3}$ | 1.464 | | |
| $\mu$, cm$^{-1}$ | 51.065 | largest diff. peak and hole, e Å$^{-3}$ | 1.22 and –0.68 |
| *F*(000) | 2608.00 | | |

### X-Ray Diffraction Analysis of B-Me

Diffraction data were collected in $\theta$ ranges specified in Table S9 at 123 K on a Rigaku R-AXIS Rapid diffractometer with graphite monochromatized Cu-Ka radiation (λ = 1.54187 Å). The Lorenz polarization absorption correction was applied. The structure was solved by direct methods and refined by the full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using the riding model. Final refinement details are compiled in Table S9. The supplementary crystallographic data for this paper (CCDC2278045) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

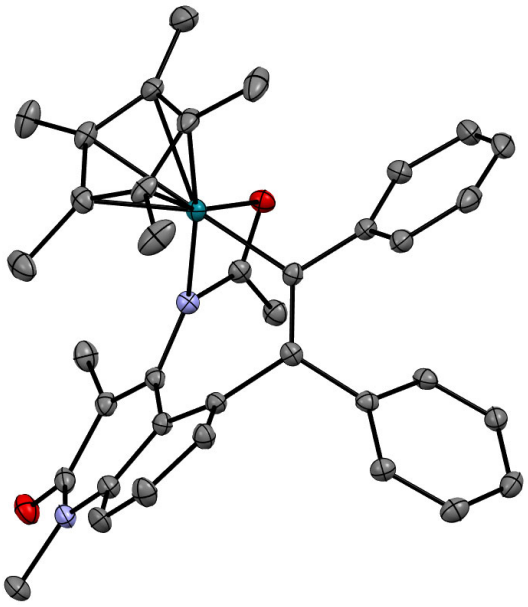


**Figure S14. ORTEP plot of B-Me**

**Table S9.** Selected crystallographic data and collection parameters for **B-Me**.

| | | | |
|---|---|---|---|
| formula | $C_{37}H_{37}N_2O_2Rh$ | crystal size, mm | 0.3 x 0.1 x 0.1 |
| FW | 644.62 | maximum 2θ, deg | 136.5 |
| crystal system | orthorhombic | reflections collected | 63038 |
| space group | Pbca (#61) | independent reflections [*R*(int)] | 5468 [R(int) = 0.0759] |
| *a*, Å | 17.6227(4) | max. and min. transmission | 0.613/0.369 |
| *b*, Å | 18.3009(4) | goodness-of-fit on $F^2$ | 1.115 |
| *c*, Å | 18.5577(4) | $R_1$ [$I > 2\sigma(I)$] | 0.0511 |
| volume, Å$^3$ | 5985.1(2) | $R$, $wR_2$ (all data) | 0.0632, 0.1233 |
| *Z* | 8 | Weighting scheme | $R_1 = \Sigma \, \|\|Fo\| - \|Fc\|\| / \Sigma \, \|Fo\|$ $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2}$ |
| *D* (calcd), Mg m$^{-3}$ | 1.431 | | |
| $\mu$, cm$^{-1}$ | 48.925 | largest diff. peak and hole, e Å$^{-3}$ | 0.98 and –0.37 |
| *F*(000) | 2672.00 | | |

## 9. DFT Calculations

The Gaussian 16 program package was used for all geometry optimizations.[19] Geometry optimization and energy calculations were performed with B3LYP[20] with GD3BJ[21] empirical dispersion along with a combined basis set. The Lanl2DZ basis set[22] with ECP was used for Rh, and the 6-31G(d) basis set[23] was used for other atoms. Thermal correction to Gibbs free energy (TCGFE) including zero-point energy were calculated at the same level of theory. Harmonic frequency calculations were performed at the same level for each stationary point to ensure that it is either an energy minimum (no imaginary frequency) or a transition state (only one imaginary frequency). The connectivity of each step was also confirmed using intrinsic reaction coordinate (IRC)[24] calculation from the transition states, followed by optimization of the resultant geometries. Final energies were obtained using the more extended 6-311+G(d,p)[25] basis set for all atoms except Rh for which SDD[26] was used. To examine the solvent effect, the above single-point energy calculations were performed using the SMD model[27] with dichloroethane as the solvent because the ε value of DiChloroEthane (10.36) is similar to that of $CF_3C_6H_5$ (9.18). The obtained energies, TCGFEs, and IF are summarized in Table S10.

**Table S10**. Summary of theoretical calculations.

| Model | TCGFE/au | Energy/au | imaginary frequency /$cm^{-1}$ |
|---|---|---|---|
| **B** | 0.551908 | -1764.175154 | |
| **C** | 0.551336 | -1764.166298 | |
| **$TS_{CD}$** | 0.548677 | -1764.126033 | 288.73i |
| **D** | 0.549077 | -1764.148695 | |
| **$TS_{BE}$** | 0.550221 | -1764.131682 | 302.52i |
| **E** | 0.550802 | -1764.135307 | |

**Cartesian coordinates**

**B**

| | | | |
|---|---|---|---|
| Rh | 1.93549 | 4.15741 | 8.45946 |
| O | 3.91833 | 5.19347 | 9.00998 |
| O | -0.41838 | 8.10964 | 13.09314 |
| N | 2.11672 | 5.26961 | 10.23063 |
| N | -1.07716 | 5.92287 | 12.79251 |
| C | 2.55771 | 2.64536 | 9.65069 |
| C | 0.38702 | 4.35022 | 11.64007 |
| C | 2.82901 | 1.76246 | 11.96937 |
| C | 2.0679 | 2.48995 | 10.90322 |
| C | 3.57198 | 1.7773 | 9.02533 |
| C | 4.22257 | -0.47351 | 8.34057 |
| H | 4.02813 | -1.54285 | 8.33959 |
| C | 1.47134 | 4.87776 | 6.29133 |
| C | 0.5634 | 2.94099 | 7.23738 |
| C | 1.20603 | 5.48624 | 11.24449 |
| C | 4.23627 | 1.85121 | 11.9734 |
| H | 4.72838 | 2.43186 | 11.2026 |
| C | 2.22745 | 1.05781 | 13.02751 |
| H | 1.14862 | 0.99938 | 13.09614 |
| C | 0.40674 | 5.28731 | 7.10623 |

| | | | |
|---|---|---|---|
| C | -0.186 | 7.00401 | 12.60591 |
| C | 4.38729 | 0.4964 | 13.97091 |
| H | 4.98345 | 0.00727 | 14.73612 |
| C | 4.70457 | 2.27653 | 8.353 |
| H | 4.88929 | 3.34437 | 8.36835 |
| C | 0.71212 | 3.00719 | 11.31253 |
| C | 5.00283 | 1.22042 | 12.94759 |
| H | 6.08556 | 1.30796 | 12.91483 |
| C | -1.7806 | 3.61728 | 12.50688 |
| H | -2.72498 | 3.82745 | 12.99061 |
| C | 1.61391 | 3.42167 | 6.39888 |
| C | 3.39194 | 5.58802 | 10.10638 |
| C | 4.21556 | 6.28123 | 11.15548 |
| H | 4.4614 | 7.29694 | 10.82593 |
| H | 5.15575 | 5.73639 | 11.2812 |
| H | 3.68953 | 6.33916 | 12.11083 |
| C | 2.99542 | 0.42886 | 14.0076 |
| H | 2.49689 | -0.11455 | 14.80609 |
| C | -0.12147 | 4.09411 | 7.76851 |
| C | -0.82945 | 4.639 | 12.32005 |
| C | 3.35014 | 0.38555 | 9.00619 |
| H | 2.48469 | -0.01012 | 9.52852 |
| C | -0.27478 | 2.03014 | 11.4777 |
| H | -0.05365 | 1.01001 | 11.181 |
| C | 5.34278 | 0.03613 | 7.6809 |
| H | 6.02398 | -0.63185 | 7.16127 |
| C | -2.29308 | 6.20134 | 13.54943 |
| H | -2.35541 | 5.55569 | 14.43143 |
| H | -3.18219 | 6.04703 | 12.92826 |
| H | -2.23829 | 7.24315 | 13.85881 |
| C | -1.51267 | 2.33716 | 12.04903 |
| H | -2.26268 | 1.55982 | 12.16502 |
| C | 5.58024 | 1.41326 | 7.69875 |
| H | 6.45469 | 1.81916 | 7.19645 |
| C | -1.32956 | 4.08808 | 8.64959 |
| H | -1.37209 | 3.19346 | 9.27218 |
| H | -2.24263 | 4.128 | 8.03963 |
| H | -1.33712 | 4.95508 | 9.31543 |
| C | 2.58245 | 2.5904 | 5.61676 |
| H | 3.54824 | 3.09445 | 5.52144 |
| H | 2.20443 | 2.39411 | 4.60375 |
| H | 2.76643 | 1.63076 | 6.10518 |
| C | 0.23179 | 1.51061 | 7.52264 |
| H | -0.22923 | 1.40314 | 8.50758 |
| H | 1.12695 | 0.88436 | 7.50096 |
| H | -0.47187 | 1.12568 | 6.77268 |
| C | 2.39523 | 5.73814 | 5.48906 |

| | | | |
|---|---|---|---|
| H | 2.26817 | 5.54854 | 4.41543 |
| H | 3.43974 | 5.52436 | 5.7399 |
| H | 2.21848 | 6.80082 | 5.67009 |
| C | -0.08645 | 6.67712 | 7.36686 |
| H | -0.16578 | 6.87037 | 8.44231 |
| H | -1.08134 | 6.83368 | 6.92991 |
| H | 0.58649 | 7.42756 | 6.94449 |
| C | 0.93899 | 6.72928 | 11.73758 |
| H | 1.50789 | 7.59366 | 11.41698 |

**C**

| | | | |
|---|---|---|---|
| Rh | 0.57209 | 0.89394 | 0.14567 |
| C | 2.13739 | 2.275 | -0.3795 |
| C | 3.12405 | 2.12769 | -1.48948 |
| C | 0.90246 | 3.07274 | -0.46032 |
| C | 0.36622 | 3.64232 | -1.73505 |
| C | 0.32454 | 3.10122 | 0.8131 |
| C | -0.98651 | 3.69938 | 1.21811 |
| C | 1.19163 | 2.33094 | 1.71947 |
| C | 0.91164 | 2.1392 | 3.17604 |
| C | 2.34885 | 1.9179 | 1.00765 |
| C | 3.55881 | 1.22968 | 1.55392 |
| H | -2.31079 | -0.17264 | 4.28009 |
| H | -0.44955 | -1.35337 | 3.1248 |
| H | 2.61399 | 1.85741 | -2.41563 |
| H | 3.85418 | 1.3473 | -1.26628 |
| H | 3.66511 | 3.07332 | -1.63579 |
| H | 0.51606 | 2.93444 | -2.55445 |
| H | 0.88543 | 4.57508 | -1.99193 |
| H | -0.70261 | 3.85878 | -1.66041 |
| H | -1.57884 | 2.98917 | 1.80659 |
| H | -1.5801 | 3.98506 | 0.34626 |
| H | -0.83925 | 4.59517 | 1.83575 |
| H | -0.13359 | 1.86107 | 3.34256 |
| H | 1.10358 | 3.06755 | 3.73055 |
| H | 1.53976 | 1.35352 | 3.60256 |
| H | 4.35105 | 1.9599 | 1.76509 |
| H | 3.95254 | 0.49685 | 0.84633 |
| H | 3.33271 | 0.69942 | 2.48251 |
| H | -4.09504 | 0.89473 | 2.97172 |
| N | -0.58423 | 0.21381 | -1.48919 |
| C | -1.88623 | 0.23703 | -1.03894 |
| C | -2.96072 | 0.72395 | -1.73282 |
| C | -4.21081 | 1.08299 | -1.10767 |
| C | -2.24721 | -0.16526 | 3.19571 |
| C | -1.19424 | -0.80807 | 2.55448 |
| C | -1.0934 | -0.81529 | 1.15185 |
| C | -2.04882 | -0.06971 | 0.39065 |

| | | | |
|---|---|---|---|
| C | -3.18964 | 0.47828 | 1.05238 |
| C | -3.25535 | 0.44718 | 2.45681 |
| H | -2.87811 | 1.00582 | -2.77391 |
| C | -0.16257 | 0.06296 | -2.77016 |
| O | 0.96448 | 0.43147 | -3.13132 |
| C | -1.05889 | -0.65793 | -3.77027 |
| H | -1.89079 | -1.19229 | -3.3077 |
| H | -1.46071 | 0.05773 | -4.49631 |
| H | -0.42778 | -1.35984 | -4.32208 |
| N | -4.22556 | 1.0224 | 0.31079 |
| O | -5.18707 | 1.51181 | -1.7209 |
| C | -5.41915 | 1.52575 | 0.97872 |
| H | -5.88833 | 0.74079 | 1.58175 |
| H | -5.17529 | 2.37647 | 1.62532 |
| H | -6.1036 | 1.84503 | 0.1952 |
| C | 1.0966 | -1.06827 | 0.20479 |
| C | -0.01605 | -1.7255 | 0.58118 |
| C | 2.43133 | -1.56977 | -0.10781 |
| C | 3.05464 | -1.29894 | -1.33976 |
| C | 3.14698 | -2.2883 | 0.86908 |
| C | 4.35242 | -1.74752 | -1.58324 |
| H | 2.5074 | -0.74106 | -2.09308 |
| C | 4.44634 | -2.72519 | 0.62246 |
| H | 2.66613 | -2.49959 | 1.81963 |
| C | 5.05591 | -2.45623 | -0.60567 |
| H | 4.81729 | -1.53949 | -2.54341 |
| H | 4.98412 | -3.27657 | 1.38919 |
| H | 6.06948 | -2.7964 | -0.79873 |
| C | -0.29104 | -3.18007 | 0.53635 |
| C | 0.47235 | -4.03172 | -0.28801 |
| C | -1.35383 | -3.75199 | 1.25978 |
| C | 0.2035 | -5.3946 | -0.35513 |
| H | 1.27116 | -3.61631 | -0.8893 |
| C | -1.62403 | -5.11799 | 1.18628 |
| H | -1.9768 | -3.12442 | 1.88747 |
| C | -0.84353 | -5.95027 | 0.38516 |
| H | 0.80907 | -6.02545 | -1.00035 |
| H | -2.45059 | -5.53009 | 1.75913 |
| H | -1.05302 | -7.01467 | 0.32849 |

**$TS_{CD}$**

| | | | |
|---|---|---|---|
| Rh | 0.72332 | -0.11015 | 0.05469 |
| C | 2.4948 | 1.33808 | 0.00925 |
| C | 3.49826 | 1.64032 | -1.05792 |
| C | 1.25523 | 2.07725 | 0.21915 |
| C | 0.72824 | 3.10472 | -0.73196 |
| C | 0.70109 | 1.69311 | 1.46931 |

| | | | |
|---|---|---|---|
| C | -0.53853 | 2.23042 | 2.11452 |
| C | 1.54314 | 0.64389 | 2.00252 |
| C | 1.39777 | -0.00394 | 3.34601 |
| C | 2.66227 | 0.46107 | 1.11678 |
| C | 3.80306 | -0.48277 | 1.34468 |
| H | -3.17012 | -1.38001 | 3.36257 |
| H | -0.78554 | -1.48605 | 2.72239 |
| H | 3.01783 | 1.69906 | -2.03483 |
| H | 4.27747 | 0.87471 | -1.09972 |
| H | 3.98988 | 2.60013 | -0.84606 |
| H | 0.89152 | 2.77667 | -1.76081 |
| H | 1.24307 | 4.06381 | -0.58534 |
| H | -0.34261 | 3.27047 | -0.59015 |
| H | -1.15365 | 1.42511 | 2.52808 |
| H | -1.15247 | 2.77452 | 1.39222 |
| H | -0.29152 | 2.92172 | 2.93109 |
| H | 0.39554 | 0.14325 | 3.75282 |
| H | 2.11296 | 0.43069 | 4.05709 |
| H | 1.59283 | -1.08036 | 3.30188 |
| H | 4.60739 | 0.00286 | 1.91307 |
| H | 4.22116 | -0.83725 | 0.39935 |
| H | 3.48009 | -1.36001 | 1.91318 |
| H | -4.91018 | -1.01344 | 1.66806 |
| N | -0.38112 | -0.06017 | -1.76811 |
| C | -1.73589 | -0.27073 | -1.63376 |
| C | -2.72111 | 0.00189 | -2.55344 |
| C | -4.12841 | -0.14867 | -2.272 |
| C | -2.87964 | -1.19925 | 2.33107 |
| C | -1.52896 | -1.21838 | 1.98178 |
| C | -1.14729 | -0.99372 | 0.65439 |
| C | -2.13918 | -0.70729 | -0.31226 |
| C | -3.51283 | -0.7467 | 0.03181 |
| C | -3.86875 | -0.99541 | 1.37386 |
| H | -2.50709 | 0.40709 | -3.53144 |
| C | 0.26942 | 0.07824 | -2.96742 |
| O | 1.35615 | 0.66003 | -3.04418 |
| C | -0.27781 | -0.58842 | -4.22438 |
| H | -1.0435 | -1.33961 | -4.02423 |
| H | -0.6908 | 0.16005 | -4.90941 |
| H | 0.57805 | -1.05042 | -4.72415 |
| N | -4.4678 | -0.5165 | -0.94204 |
| O | -5.01704 | 0.06053 | -3.09964 |
| C | -5.88484 | -0.5927 | -0.61482 |
| H | -6.13774 | -1.58213 | -0.2184 |
| H | -6.15889 | 0.16856 | 0.125 |
| H | -6.42876 | -0.41364 | -1.54057 |
| C | 1.14889 | -2.00812 | -0.59536 |

| | | | |
|---|---|---|---|
| C | 0.17313 | -2.39565 | 0.16322 |
| C | 2.17741 | -2.59034 | -1.43332 |
| C | 2.29049 | -3.99201 | -1.54215 |
| C | 3.07586 | -1.78036 | -2.14623 |
| C | 3.28939 | -4.55861 | -2.32633 |
| H | 1.59401 | -4.62598 | -1.00366 |
| C | 4.07477 | -2.35485 | -2.93013 |
| H | 2.94495 | -0.70817 | -2.11516 |
| C | 4.1898 | -3.74278 | -3.01929 |
| H | 3.36657 | -5.63993 | -2.39951 |
| H | 4.75662 | -1.71385 | -3.48188 |
| H | 4.96865 | -4.18899 | -3.63128 |
| C | -0.20753 | -3.57912 | 0.92757 |
| C | 0.77483 | -4.25791 | 1.66811 |
| C | -1.51608 | -4.08953 | 0.89444 |
| C | 0.45624 | -5.4283 | 2.35625 |
| H | 1.78487 | -3.85974 | 1.68937 |
| C | -1.82741 | -5.26089 | 1.57648 |
| H | -2.27672 | -3.55657 | 0.33416 |
| C | -0.84452 | -5.93194 | 2.31151 |
| H | 1.22274 | -5.94383 | 2.9279 |
| H | -2.8395 | -5.6532 | 1.53758 |
| H | -1.09381 | -6.84336 | 2.84732 |

**D**

| | | | |
|---|---|---|---|
| Rh | 0.6622 | 0.48886 | 0.28483 |
| C | 2.64441 | 1.80444 | 0.10701 |
| C | 3.74438 | 1.70379 | -0.9001 |
| C | 1.50061 | 2.62156 | -0.00212 |
| C | 1.14162 | 3.50933 | -1.14939 |
| C | 0.70952 | 2.47095 | 1.20782 |
| C | -0.51896 | 3.25829 | 1.54408 |
| C | 1.45425 | 1.62286 | 2.11213 |
| C | 1.14821 | 1.39795 | 3.55788 |
| C | 2.5912 | 1.14695 | 1.40691 |
| C | 3.65488 | 0.25625 | 1.96597 |
| H | -2.64571 | -1.09441 | 4.03805 |
| H | -0.37605 | -0.81402 | 3.10448 |
| H | 3.33272 | 1.62205 | -1.90881 |
| H | 4.37608 | 0.83072 | -0.72706 |
| H | 4.38634 | 2.59424 | -0.86006 |
| H | 1.59658 | 3.1583 | -2.07528 |
| H | 1.47703 | 4.53622 | -0.94949 |
| H | 0.05884 | 3.53581 | -1.29813 |
| H | -1.12565 | 2.74101 | 2.29092 |
| H | -1.14462 | 3.40636 | 0.65973 |
| H | -0.25407 | 4.24804 | 1.93972 |

| | | | |
|---|---|---|---|
| H | 0.07545 | 1.43849 | 3.75428 |
| H | 1.63323 | 2.17402 | 4.16583 |
| H | 1.51863 | 0.42941 | 3.9061 |
| H | 4.43555 | 0.85238 | 2.45771 |
| H | 4.13476 | -0.33204 | 1.18152 |
| H | 3.24651 | -0.43456 | 2.70921 |
| H | -4.64056 | -0.46117 | 2.75601 |
| N | -0.70546 | 0.66017 | -1.29239 |
| C | -2.03362 | 0.72043 | -0.89574 |
| C | -3.13 | 1.13243 | -1.6101 |
| C | -4.47498 | 1.06372 | -1.07614 |
| C | -2.52502 | -0.6788 | 3.04053 |
| C | -1.23505 | -0.50796 | 2.51793 |
| C | -1.07947 | 0.00812 | 1.23824 |
| C | -2.21984 | 0.31171 | 0.47766 |
| C | -3.52181 | 0.17722 | 1.0105 |
| C | -3.65999 | -0.32877 | 2.31657 |
| H | -3.07461 | 1.52395 | -2.61419 |
| C | -0.23525 | 0.66381 | -2.57269 |
| O | 0.96416 | 0.86682 | -2.8085 |
| C | -1.15408 | 0.33912 | -3.74317 |
| H | -1.99939 | -0.2946 | -3.46667 |
| H | -1.55064 | 1.25851 | -4.18837 |
| H | -0.54145 | -0.15611 | -4.5 |
| N | -4.61186 | 0.53716 | 0.23215 |
| O | -5.47037 | 1.41984 | -1.71093 |
| C | -5.96086 | 0.42017 | 0.76711 |
| H | -6.18884 | -0.6222 | 1.01702 |
| H | -6.07684 | 1.03378 | 1.66775 |
| H | -6.63916 | 0.77264 | -0.00785 |
| C | 1.65779 | -1.41079 | -0.64834 |
| C | 0.65189 | -1.82318 | -0.04837 |
| C | 2.9431 | -1.53637 | -1.28034 |
| C | 3.95821 | -2.20924 | -0.56902 |
| C | 3.20957 | -1.06895 | -2.57823 |
| C | 5.21574 | -2.39162 | -1.13726 |
| H | 3.74147 | -2.59014 | 0.42389 |
| C | 4.46906 | -1.26658 | -3.14011 |
| H | 2.43314 | -0.53476 | -3.11106 |
| C | 5.4767 | -1.91743 | -2.42543 |
| H | 5.98897 | -2.91016 | -0.57752 |
| H | 4.66574 | -0.90097 | -4.14397 |
| H | 6.45793 | -2.05912 | -2.86934 |
| C | -0.36196 | -2.71453 | 0.43602 |
| C | -0.09925 | -3.52832 | 1.54979 |
| C | -1.62554 | -2.766 | -0.17616 |
| C | -1.08702 | -4.375 | 2.04577 |

| | | | |
|---|---|---|---|
| H | 0.87682 | -3.47944 | 2.02259 |
| C | -2.60954 | -3.60797 | 0.33054 |
| H | -1.82662 | -2.12843 | -1.02902 |
| C | -2.346 | -4.411 | 1.44321 |
| H | -0.87675 | -5.00118 | 2.90814 |
| H | -3.58801 | -3.63177 | -0.13986 |
| H | -3.1197 | -5.06278 | 1.83859 |

**$TS_{BE}$**

| | | | |
|---|---|---|---|
| Rh | 0.88832 | 1.03578 | -1.52004 |
| C | 1.36173 | 3.23048 | -2.2542 |
| C | 1.49665 | 3.63739 | -3.68836 |
| C | 0.23758 | 3.30716 | -1.43824 |
| C | -1.13551 | 3.7987 | -1.77299 |
| C | 0.58852 | 2.69639 | -0.14532 |
| C | -0.30078 | 2.72068 | 1.05602 |
| C | 1.99917 | 2.40465 | -0.14193 |
| C | 2.78324 | 1.93067 | 1.04027 |
| C | 2.44717 | 2.59439 | -1.47678 |
| C | 3.83714 | 2.39572 | -1.99811 |
| H | -2.87094 | 0.26624 | 3.96326 |
| H | -0.69144 | -0.603 | 3.22355 |
| H | 1.91082 | 2.82334 | -4.29347 |
| H | 2.17144 | 4.49756 | -3.79386 |
| H | 0.53091 | 3.91295 | -4.11967 |
| H | -1.39892 | 4.67736 | -1.16963 |
| H | -1.88895 | 3.02784 | -1.57205 |
| H | -1.21925 | 4.07697 | -2.82661 |
| H | 0.00399 | 1.98439 | 1.80068 |
| H | -1.34062 | 2.51211 | 0.79385 |
| H | -0.26613 | 3.71485 | 1.52377 |
| H | 3.70055 | 1.41899 | 0.73485 |
| H | 2.19734 | 1.23233 | 1.64545 |
| H | 3.07124 | 2.77125 | 1.68626 |
| H | 3.82543 | 1.97325 | -3.00808 |
| H | 4.41189 | 1.72059 | -1.35789 |
| H | 4.3786 | 3.35059 | -2.04738 |
| H | -4.60929 | 0.88565 | 2.34166 |
| N | -0.6293 | -0.46157 | -1.70562 |
| C | -1.91165 | -0.13716 | -1.24722 |
| C | -2.89156 | 0.22088 | -2.13689 |
| C | -4.20509 | 0.63366 | -1.71499 |
| C | -2.66893 | 0.15714 | 2.90098 |
| C | -1.43889 | -0.32964 | 2.48906 |
| C | -1.12749 | -0.45665 | 1.11789 |
| C | -2.12812 | -0.06919 | 0.17041 |
| C | -3.40423 | 0.39234 | 0.61071 |

| | | | |
|---|---|---|---|
| C | -3.65781 | 0.5164 | 1.98562 |
| H | -2.71024 | 0.26724 | -3.20267 |
| C | -0.3215 | -0.84549 | -3.00596 |
| O | 0.73476 | -0.35904 | -3.44784 |
| C | -1.11219 | -1.89005 | -3.73725 |
| H | -2.00229 | -2.19124 | -3.18379 |
| H | -1.40506 | -1.5187 | -4.72419 |
| H | -0.45665 | -2.75578 | -3.88622 |
| N | -4.39053 | 0.71406 | -0.31653 |
| O | -5.11144 | 0.9346 | -2.49431 |
| C | -5.69719 | 1.16869 | 0.14315 |
| H | -6.17015 | 0.40789 | 0.77315 |
| H | -5.60482 | 2.09797 | 0.71614 |
| H | -6.3004 | 1.34227 | -0.74565 |
| C | 0.65564 | -0.82218 | -0.59467 |
| C | 0.13558 | -1.01727 | 0.69508 |
| C | 1.56494 | -1.87282 | -1.1535 |
| C | 1.09316 | -3.1881 | -1.26891 |
| C | 2.87063 | -1.58549 | -1.56498 |
| C | 1.91044 | -4.19423 | -1.78124 |
| H | 0.08525 | -3.41487 | -0.93383 |
| C | 3.69813 | -2.59297 | -2.05696 |
| H | 3.22841 | -0.56341 | -1.49076 |
| C | 3.21824 | -3.89933 | -2.17217 |
| H | 1.53148 | -5.20906 | -1.86486 |
| H | 4.71496 | -2.35761 | -2.35878 |
| H | 3.85966 | -4.68322 | -2.56502 |
| C | 0.87276 | -1.90838 | 1.62887 |
| C | 0.20905 | -2.93702 | 2.32417 |
| C | 2.25842 | -1.77901 | 1.82551 |
| C | 0.90109 | -3.80061 | 3.16907 |
| H | -0.8609 | -3.05966 | 2.18581 |
| C | 2.95534 | -2.64829 | 2.66299 |
| H | 2.79124 | -0.99131 | 1.30524 |
| C | 2.28109 | -3.6638 | 3.34156 |
| H | 0.36353 | -4.59155 | 3.6857 |
| H | 4.02777 | -2.52597 | 2.79044 |
| H | 2.82195 | -4.33977 | 3.99786 |

**E**

| | | | |
|---|---|---|---|
| Rh | 0.91764 | 0.95325 | -0.82584 |
| C | 1.02789 | 3.25709 | -1.31072 |
| C | 0.71436 | 3.88348 | -2.63436 |
| C | 0.18068 | 3.07603 | -0.21715 |
| C | -1.26716 | 3.42728 | -0.09295 |
| C | 0.93909 | 2.36602 | 0.83578 |
| C | 0.4211 | 2.10785 | 2.21567 |

| | | | |
|---|---|---|---|
| C | 2.30122 | 2.24656 | 0.41441 |
| C | 3.48051 | 1.84579 | 1.24555 |
| C | 2.31232 | 2.62781 | -0.96486 |
| C | 3.50739 | 2.61246 | -1.86718 |
| H | -3.50104 | 0.0286 | 4.25581 |
| H | -1.24446 | -0.78222 | 3.75676 |
| H | 1.07677 | 3.26662 | -3.46391 |
| H | 1.18682 | 4.87053 | -2.73429 |
| H | -0.36284 | 4.01548 | -2.7682 |
| H | -1.42047 | 4.20861 | 0.66328 |
| H | -1.85451 | 2.55645 | 0.22109 |
| H | -1.68053 | 3.78371 | -1.03952 |
| H | 0.89455 | 1.23129 | 2.66486 |
| H | -0.65607 | 1.93126 | 2.21533 |
| H | 0.6202 | 2.97284 | 2.86366 |
| H | 4.16347 | 1.18517 | 0.70092 |
| H | 3.16826 | 1.32667 | 2.15459 |
| H | 4.05892 | 2.72874 | 1.55432 |
| H | 3.22369 | 2.37697 | -2.89767 |
| H | 4.2434 | 1.87243 | -1.54058 |
| H | 3.99971 | 3.59487 | -1.87639 |
| H | -5.05055 | 0.71202 | 2.47436 |
| N | -0.63109 | -0.60409 | -1.08824 |
| C | -1.9465 | -0.19114 | -0.79134 |
| C | -2.7576 | 0.29123 | -1.78746 |
| C | -4.09584 | 0.74548 | -1.51685 |
| C | -3.18023 | -0.04883 | 3.22012 |
| C | -1.90822 | -0.51703 | 2.94447 |
| C | -1.44842 | -0.62464 | 1.60741 |
| C | -2.34416 | -0.19211 | 0.57417 |
| C | -3.6525 | 0.28836 | 0.87602 |
| C | -4.06806 | 0.34535 | 2.21204 |
| H | -2.42412 | 0.39854 | -2.81165 |
| C | -0.24877 | -0.91715 | -2.43529 |
| O | 0.77104 | -0.35717 | -2.82677 |
| C | -0.99814 | -1.95791 | -3.20658 |
| H | -1.99674 | -2.12475 | -2.80289 |
| H | -1.05814 | -1.67377 | -4.26011 |
| H | -0.41905 | -2.88751 | -3.13326 |
| N | -4.48726 | 0.7039 | -0.15625 |
| O | -4.86715 | 1.1637 | -2.38302 |
| C | -5.82957 | 1.17901 | 0.15309 |
| H | -6.40394 | 0.39832 | 0.66305 |
| H | -5.78858 | 2.06609 | 0.79539 |
| H | -6.30159 | 1.43235 | -0.79399 |
| C | 0.35598 | -1.03541 | -0.0587 |
| C | -0.15294 | -1.12285 | 1.26848 |

| | | | |
|---|---|---|---|
| C | 1.25133 | -2.16138 | -0.52342 |
| C | 0.72528 | -3.46081 | -0.53608 |
| C | 2.57456 | -1.96382 | -0.92362 |
| C | 1.50338 | -4.53909 | -0.95544 |
| H | -0.29531 | -3.6184 | -0.19767 |
| C | 3.36067 | -3.04152 | -1.33117 |
| H | 2.97339 | -0.95391 | -0.91178 |
| C | 2.82607 | -4.3305 | -1.35292 |
| H | 1.08235 | -5.54064 | -0.96113 |
| H | 4.39073 | -2.87379 | -1.633 |
| H | 3.43754 | -5.16955 | -1.67283 |
| C | 0.72355 | -1.74748 | 2.28004 |
| C | 0.24928 | -2.72492 | 3.17506 |
| C | 2.08828 | -1.41149 | 2.34367 |
| C | 1.09885 | -3.32511 | 4.10123 |
| H | -0.79279 | -3.02498 | 3.12617 |
| C | 2.94069 | -2.016 | 3.265 |
| H | 2.47193 | -0.67207 | 1.65208 |
| C | 2.45022 | -2.97345 | 4.15397 |
| H | 0.70716 | -4.08186 | 4.77591 |
| H | 3.9905 | -1.73512 | 3.28985 |
| H | 3.11181 | -3.44435 | 4.8755 |

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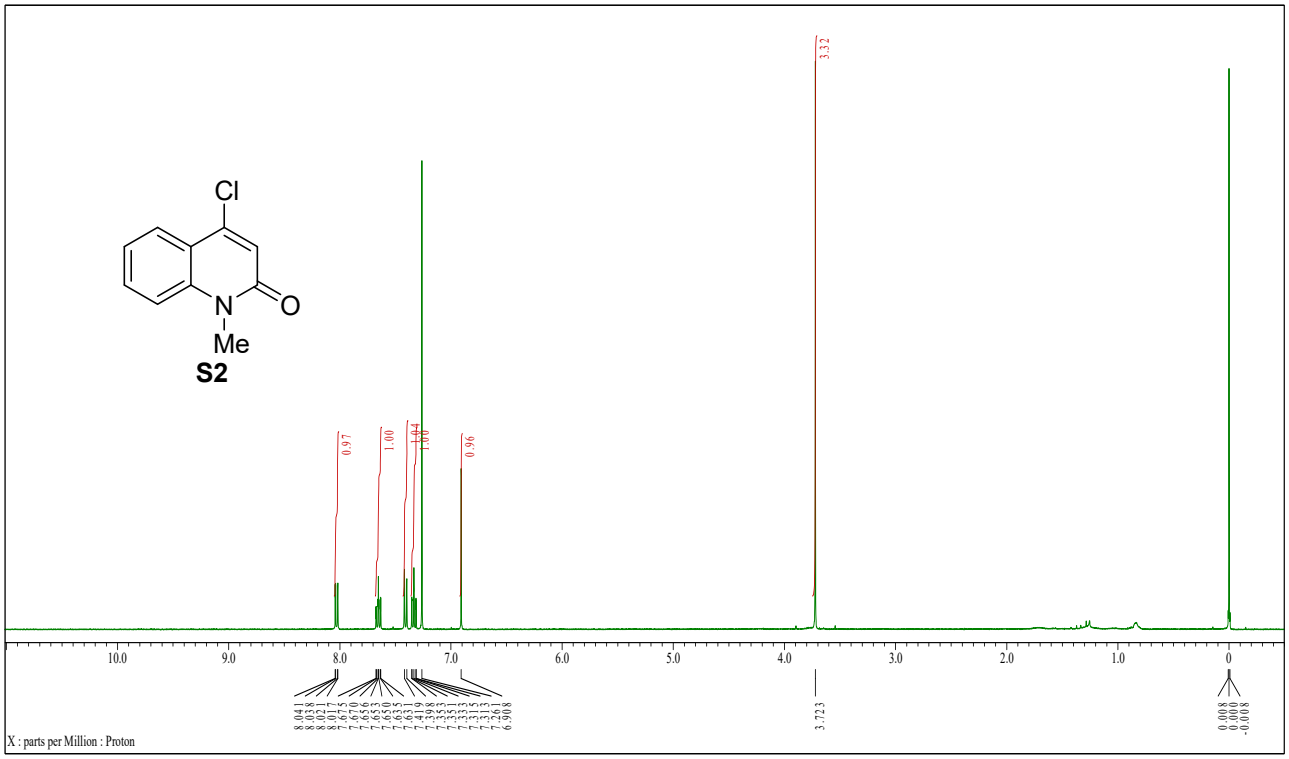
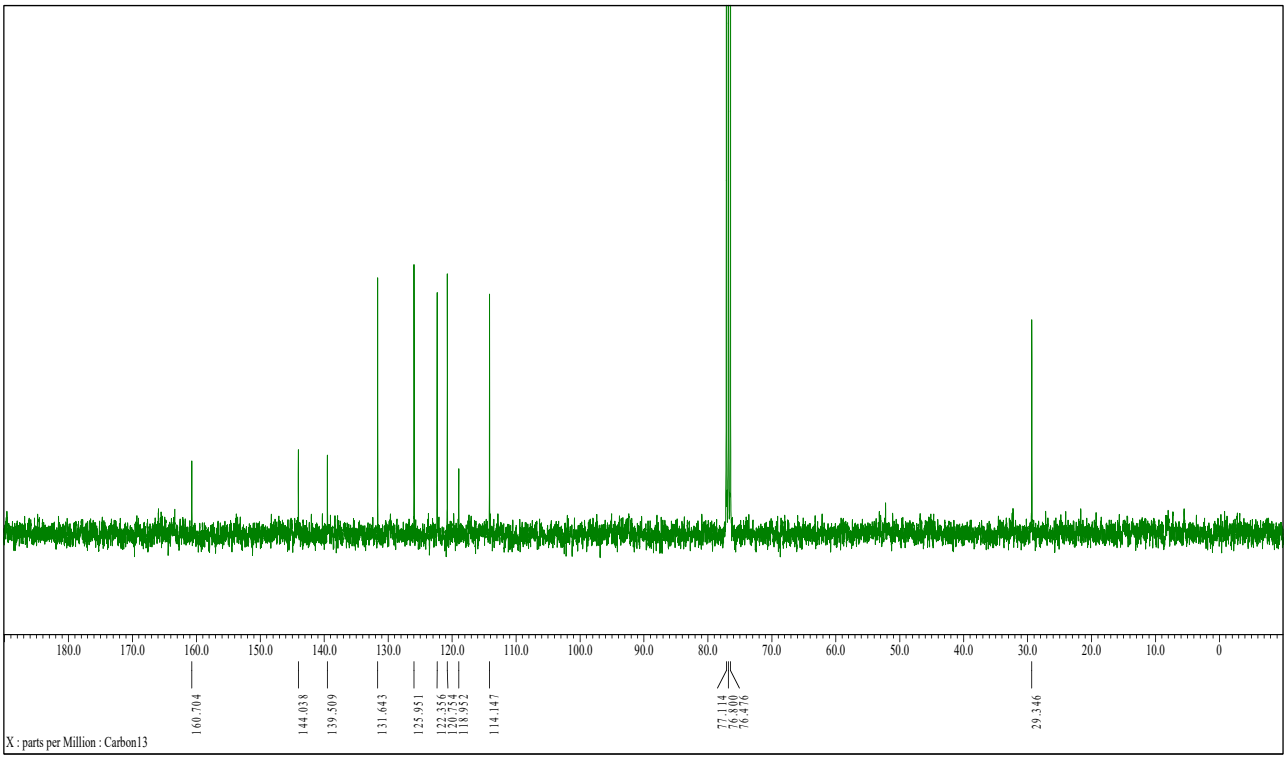
# 12. NMR Spectra

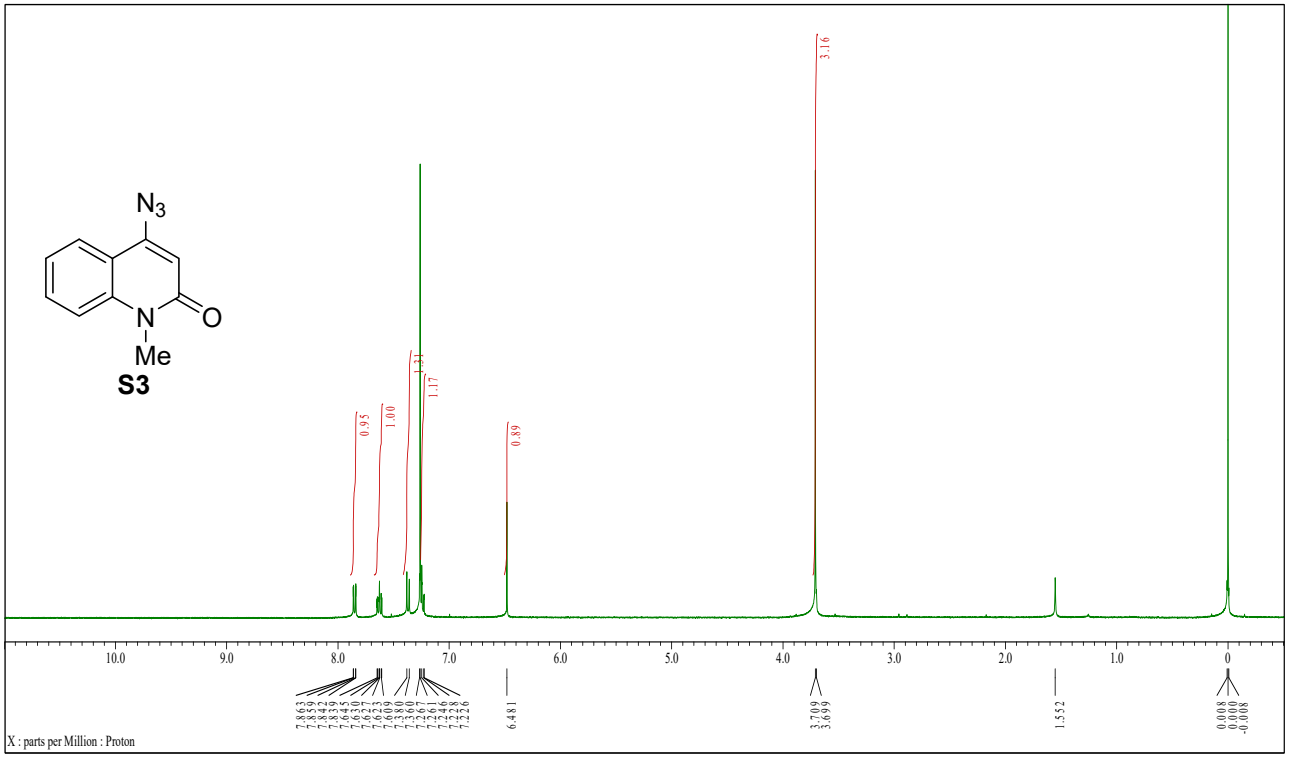
## $^{1}$H NMR (400 MHz, $CDCl_3$) of S2




## $^{13}$C NMR (100 MHz, $CDCl_3$) of S2



**$^{1}$H NMR (400 MHz, $CDCl_3$) of S3**

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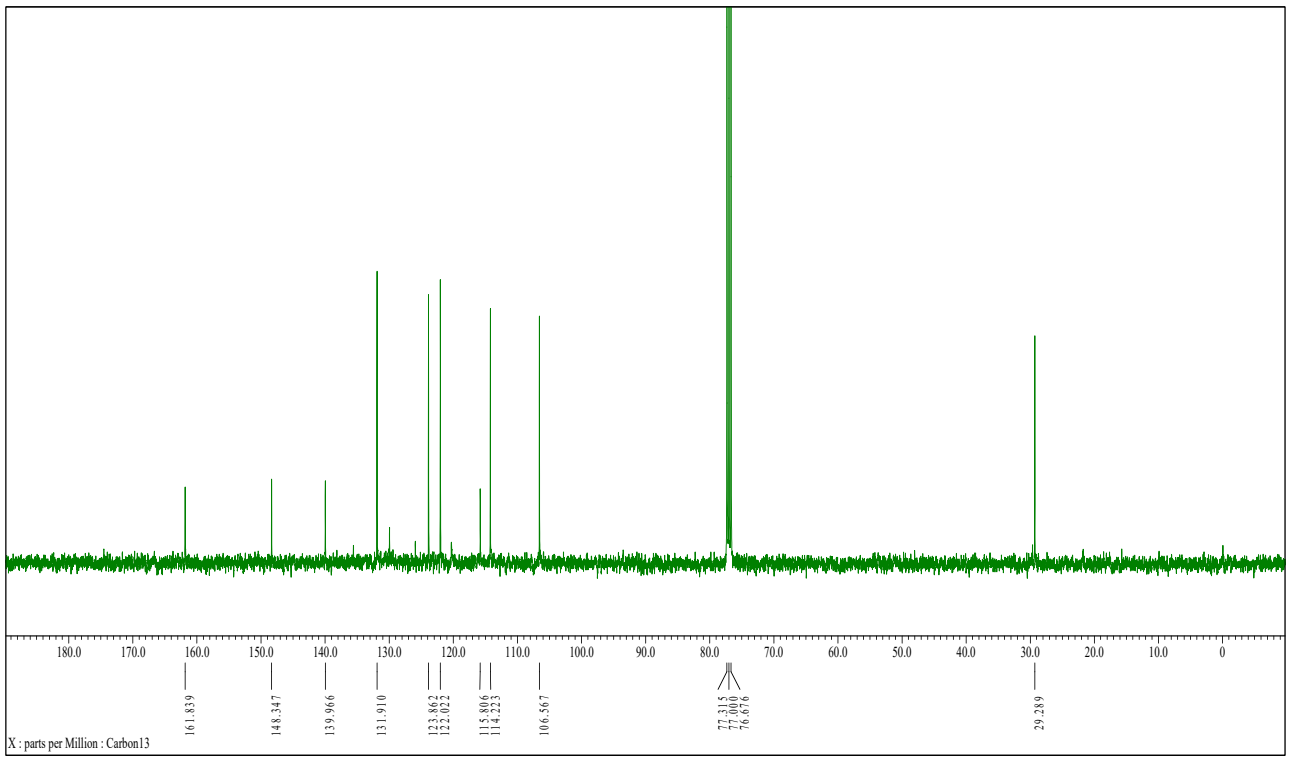
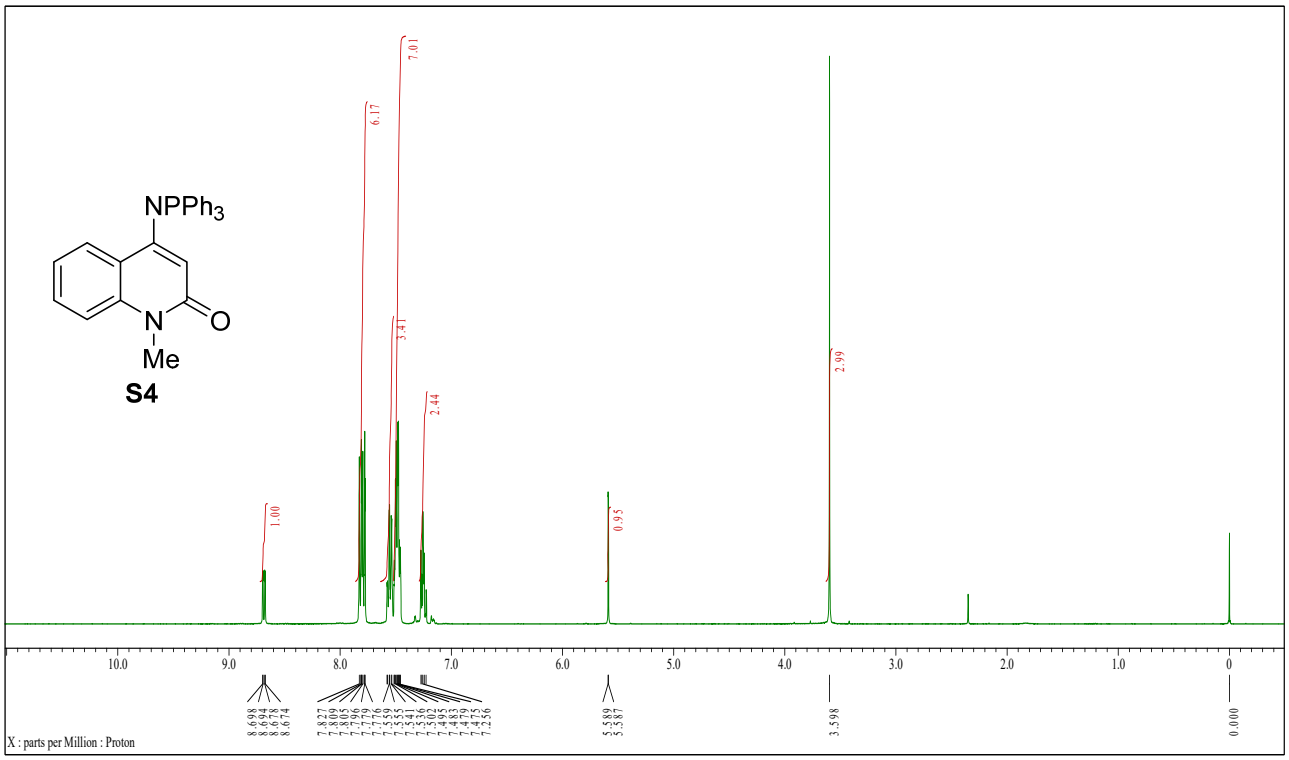


**$^{1}$H NMR (400 MHz, $CDCl_3$) of S4**

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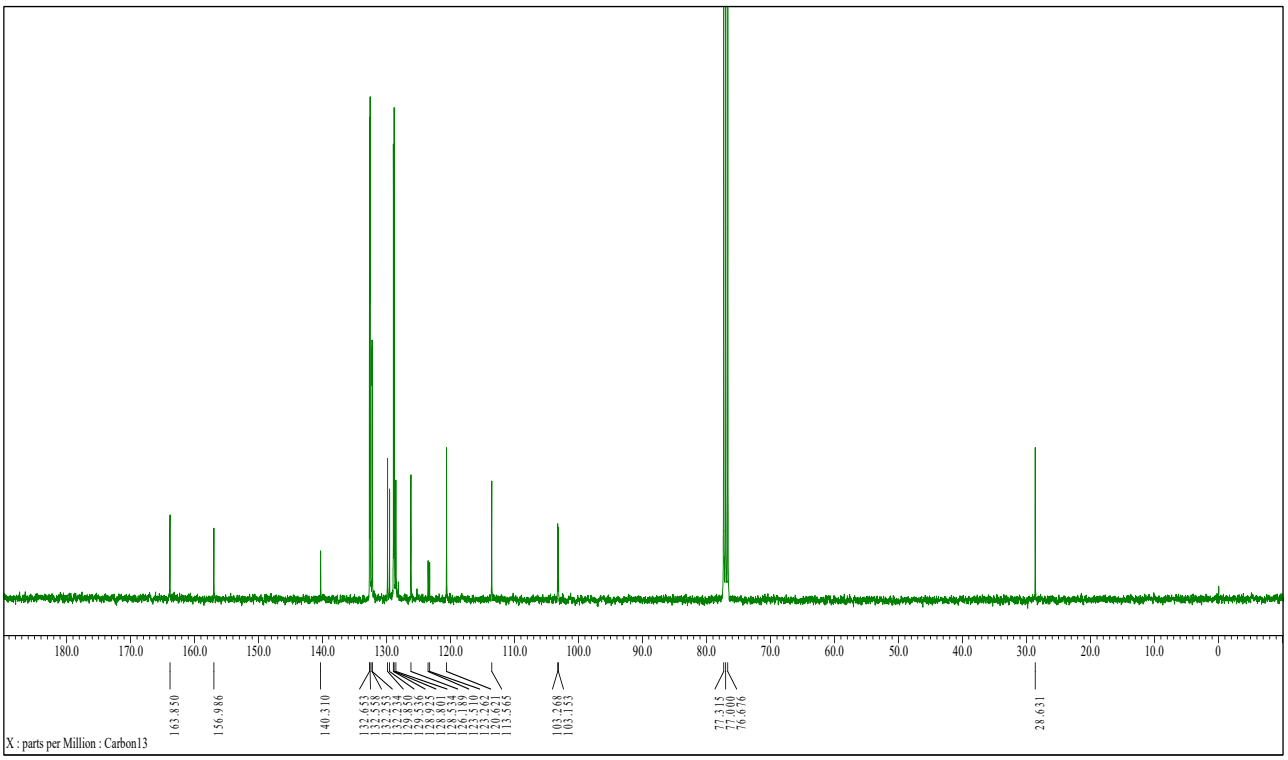
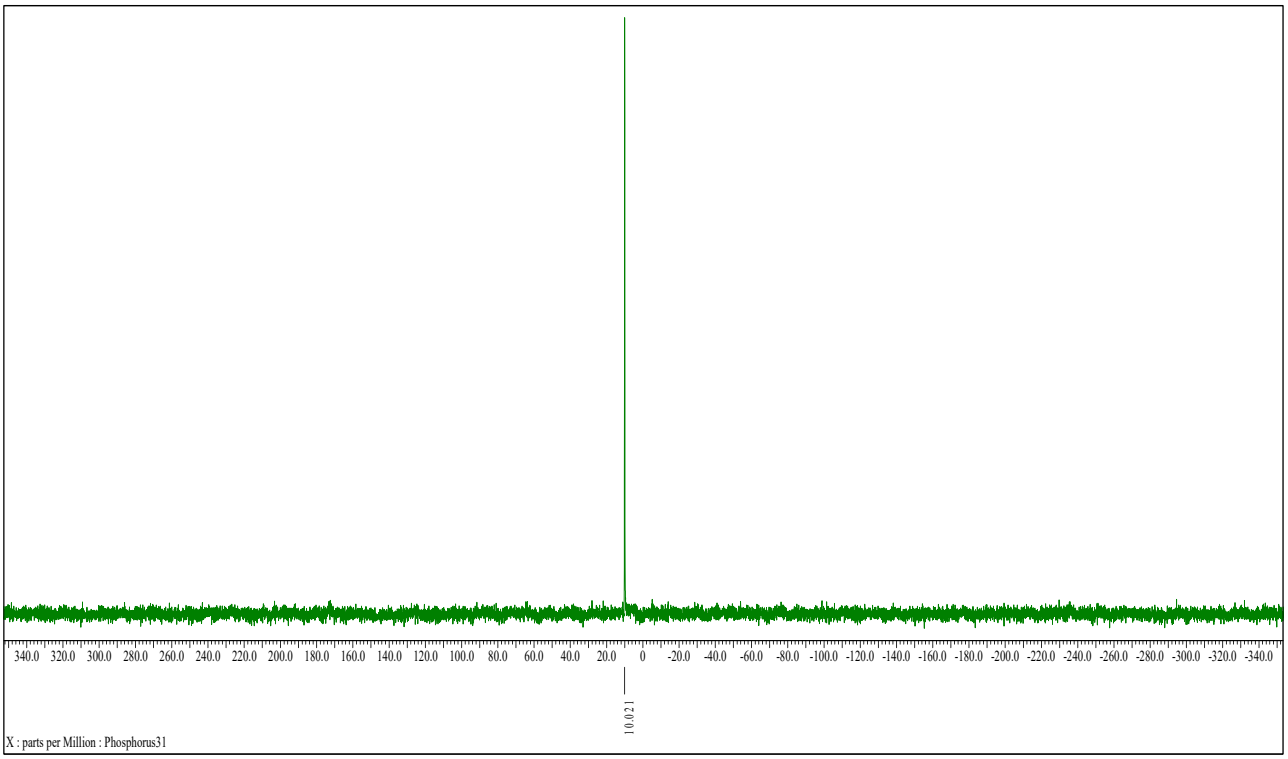
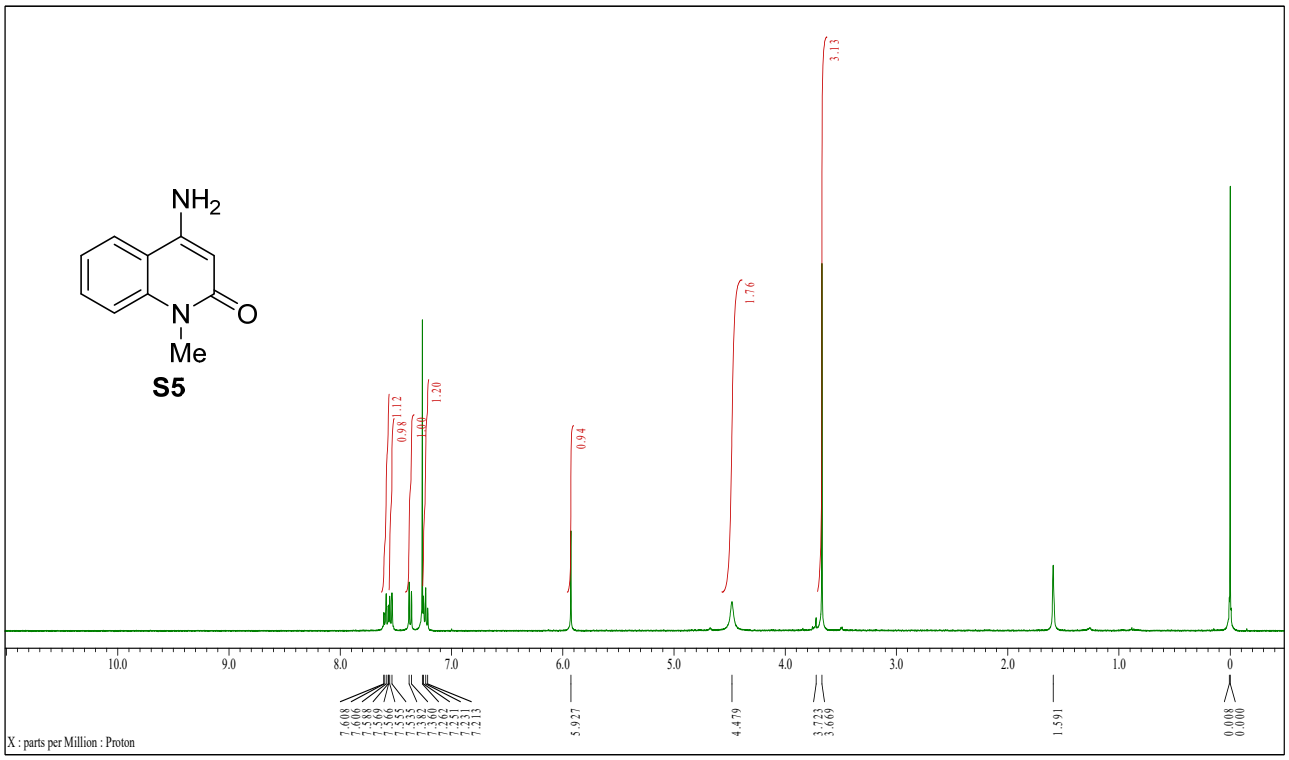


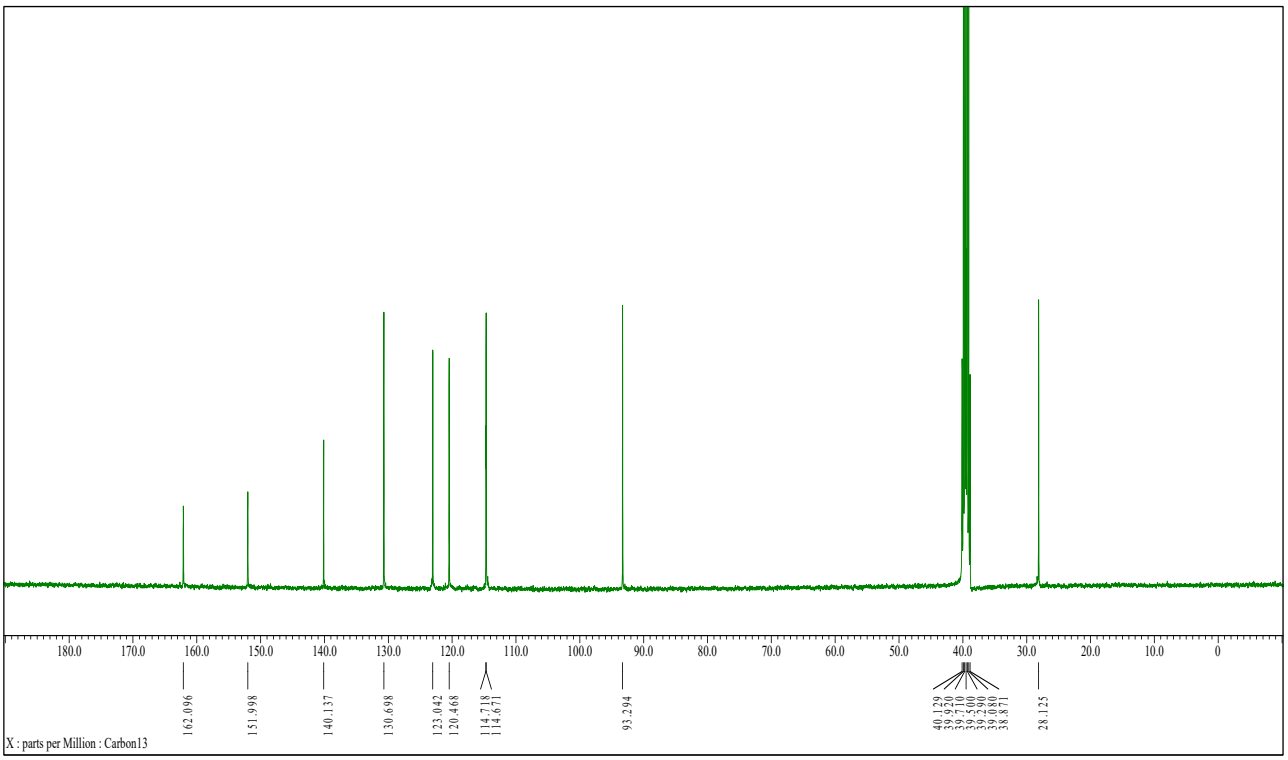
**$^{31}$P NMR (162 MHz, $CHCl_3$) of S4**



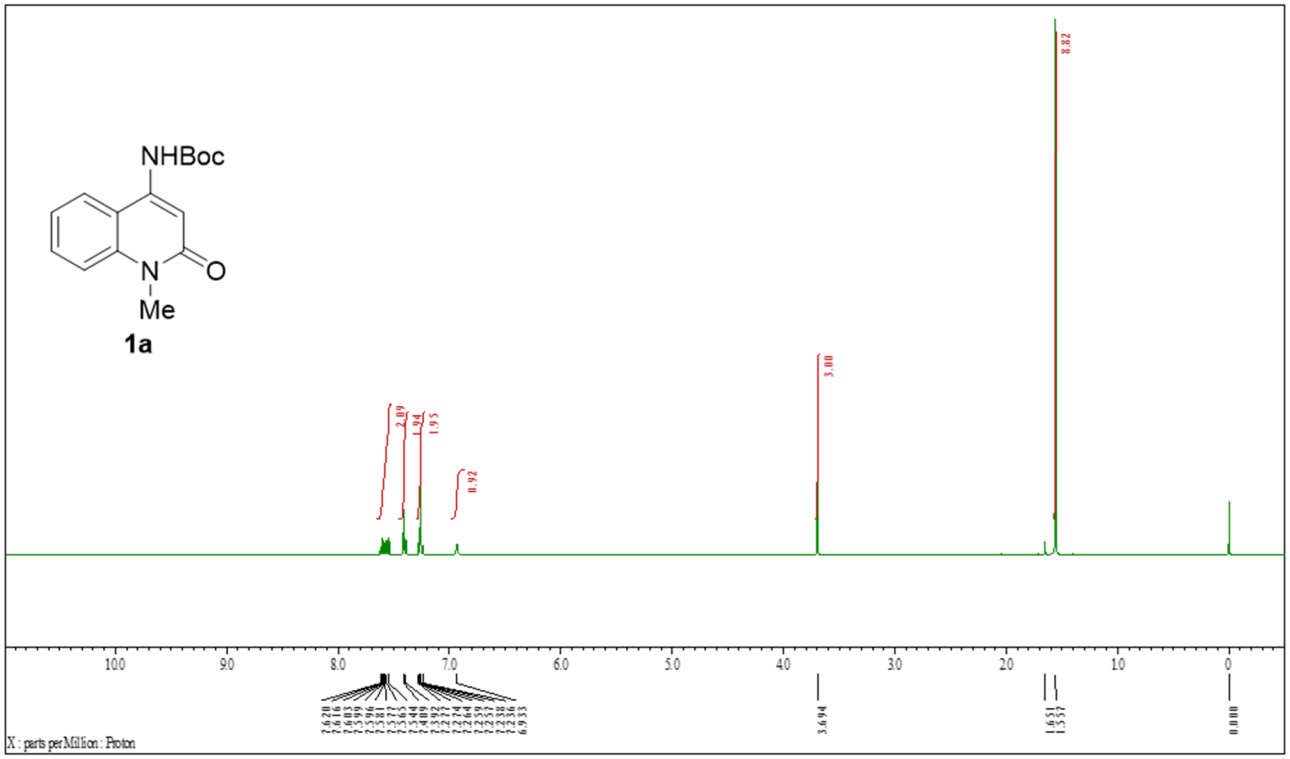
**$^1$H NMR (400 MHz, $CDCl_3$) of S5**



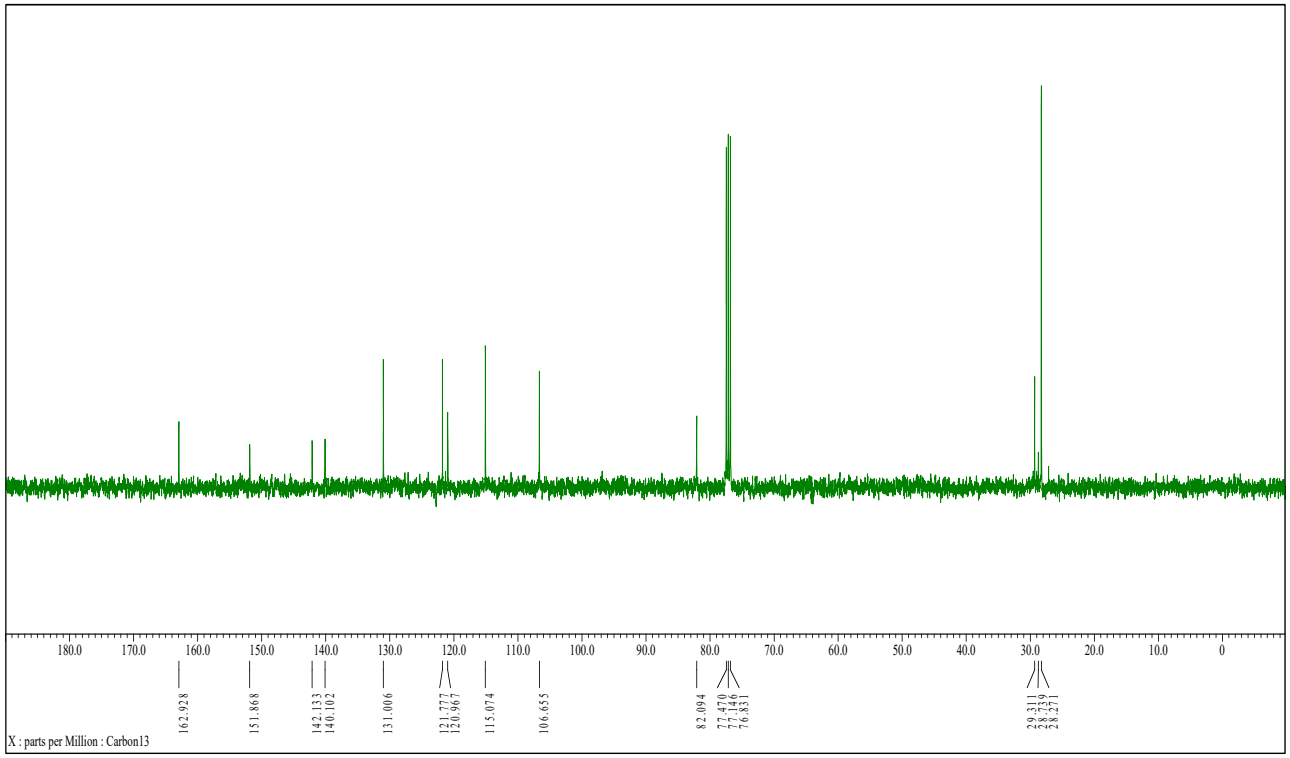

**$^{13}$C NMR (100 MHz, DMSO-$d_6$) of S5**



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




**$^{13}$C NMR (100 MHz, $CDCl_3$) of 1a**



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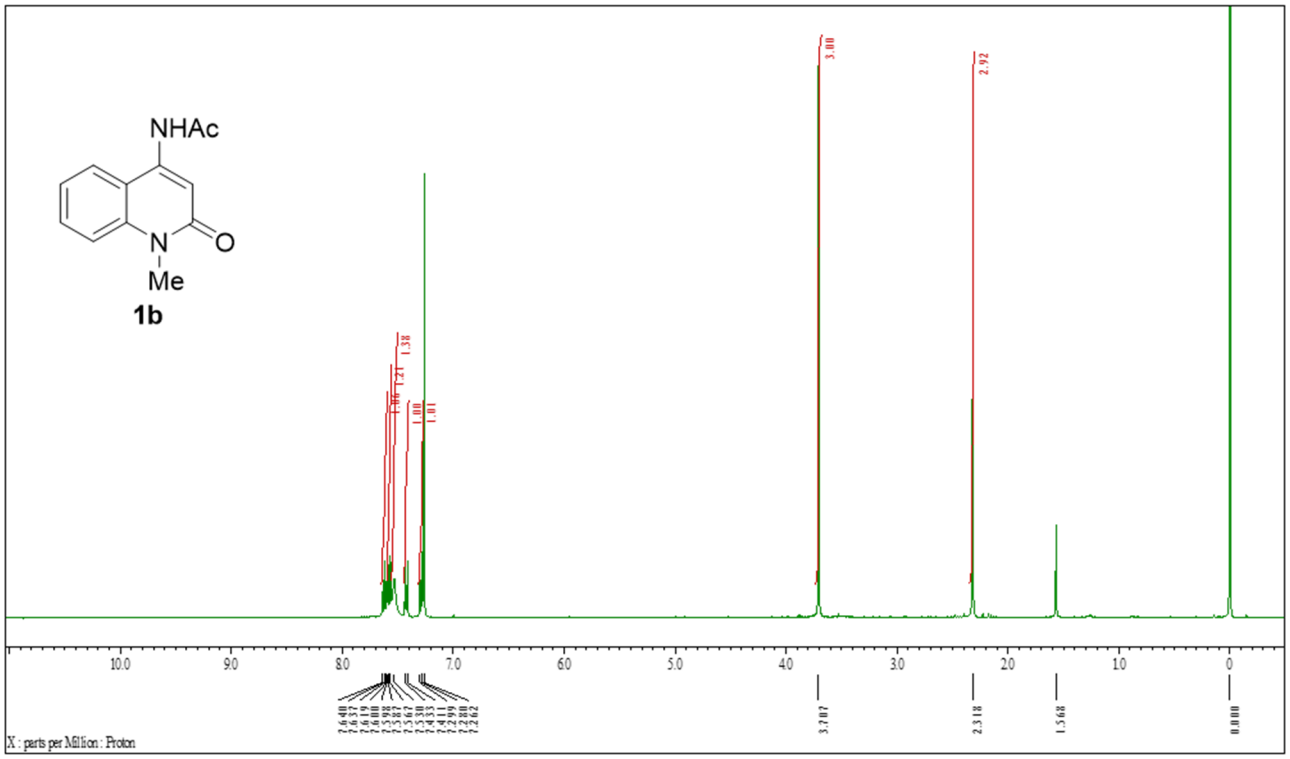


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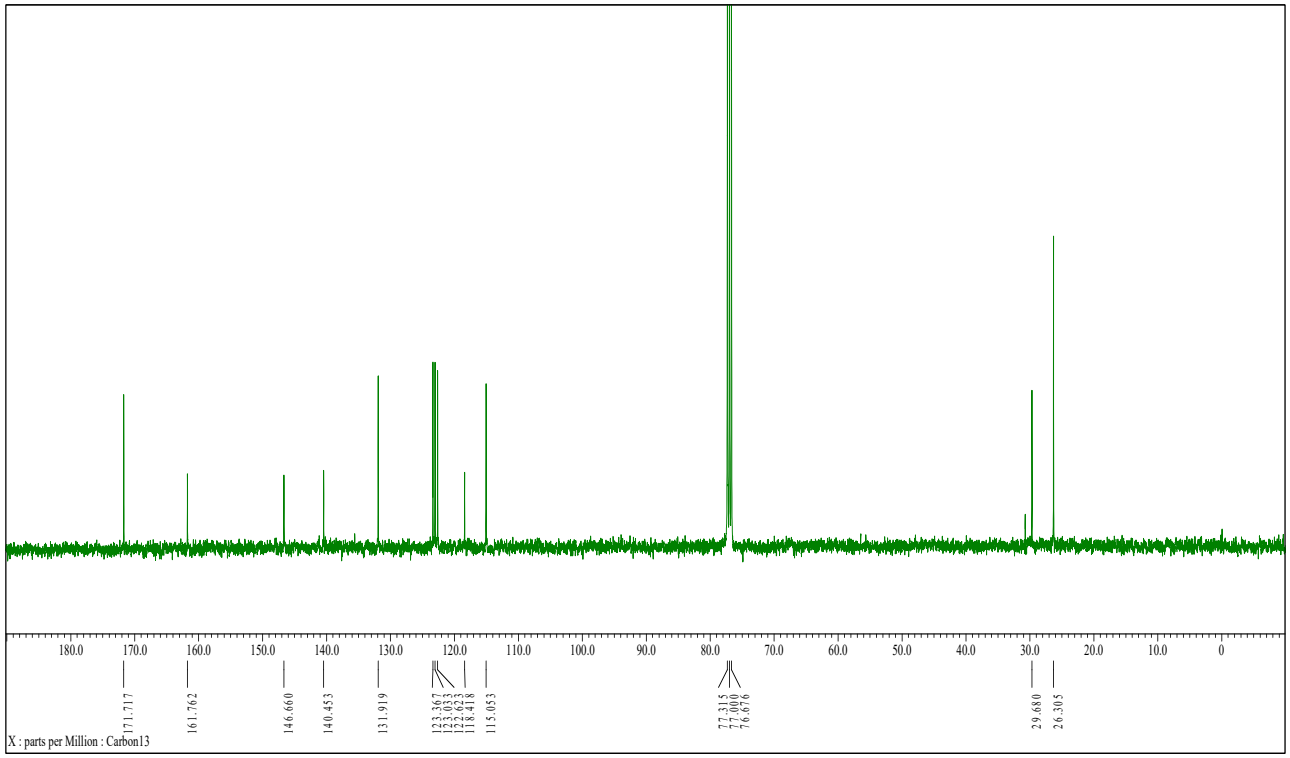
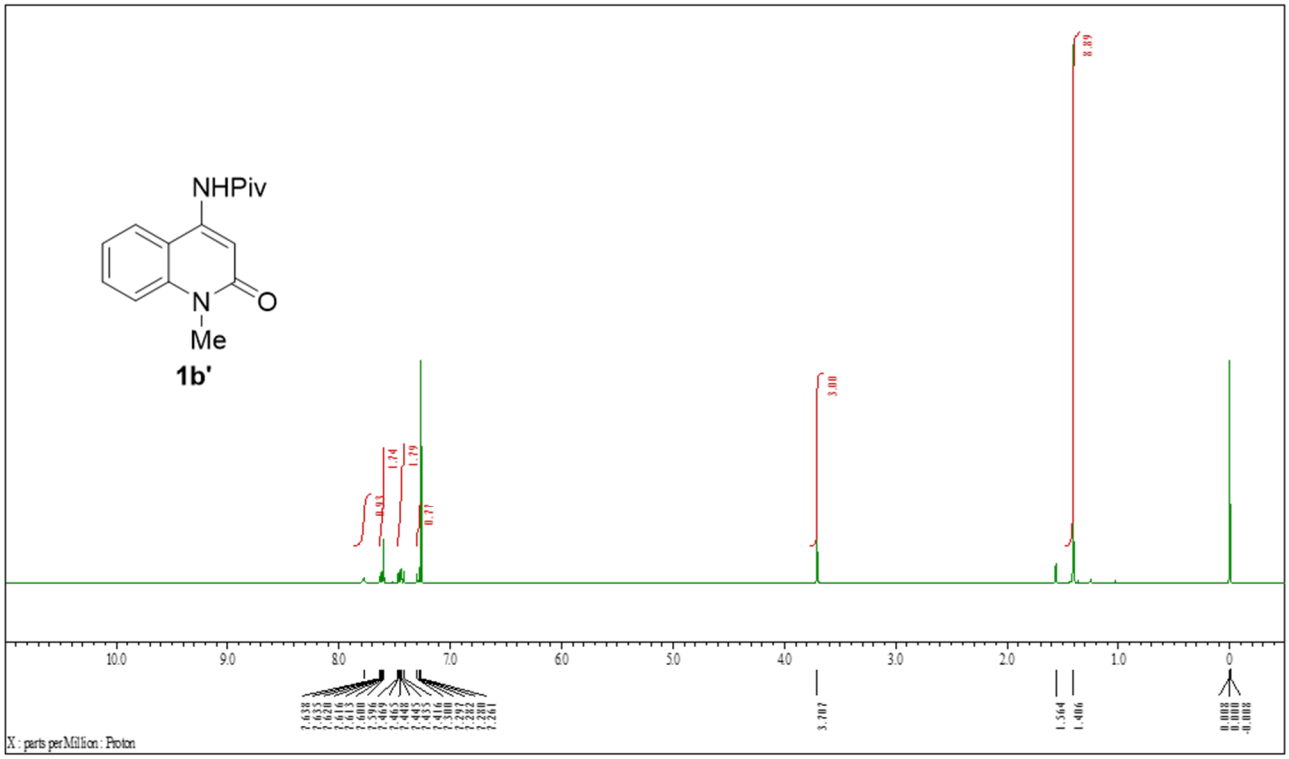
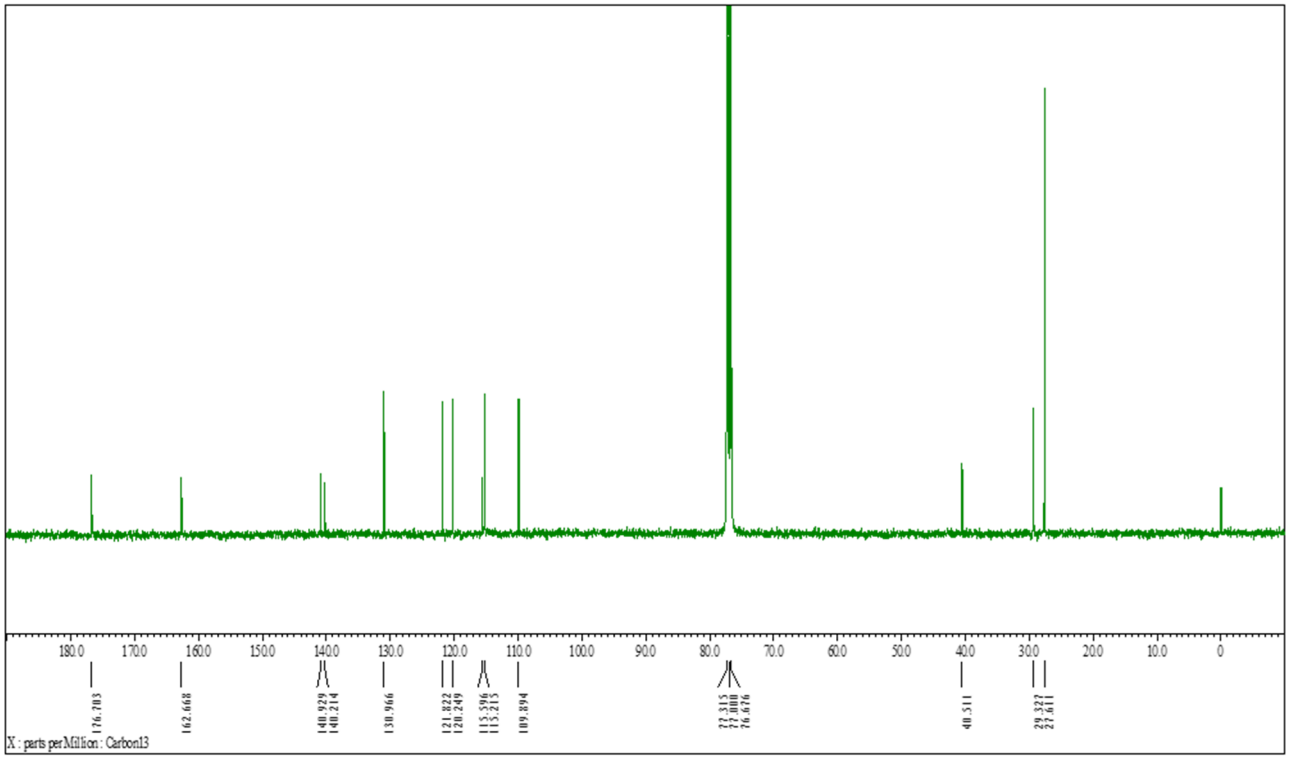


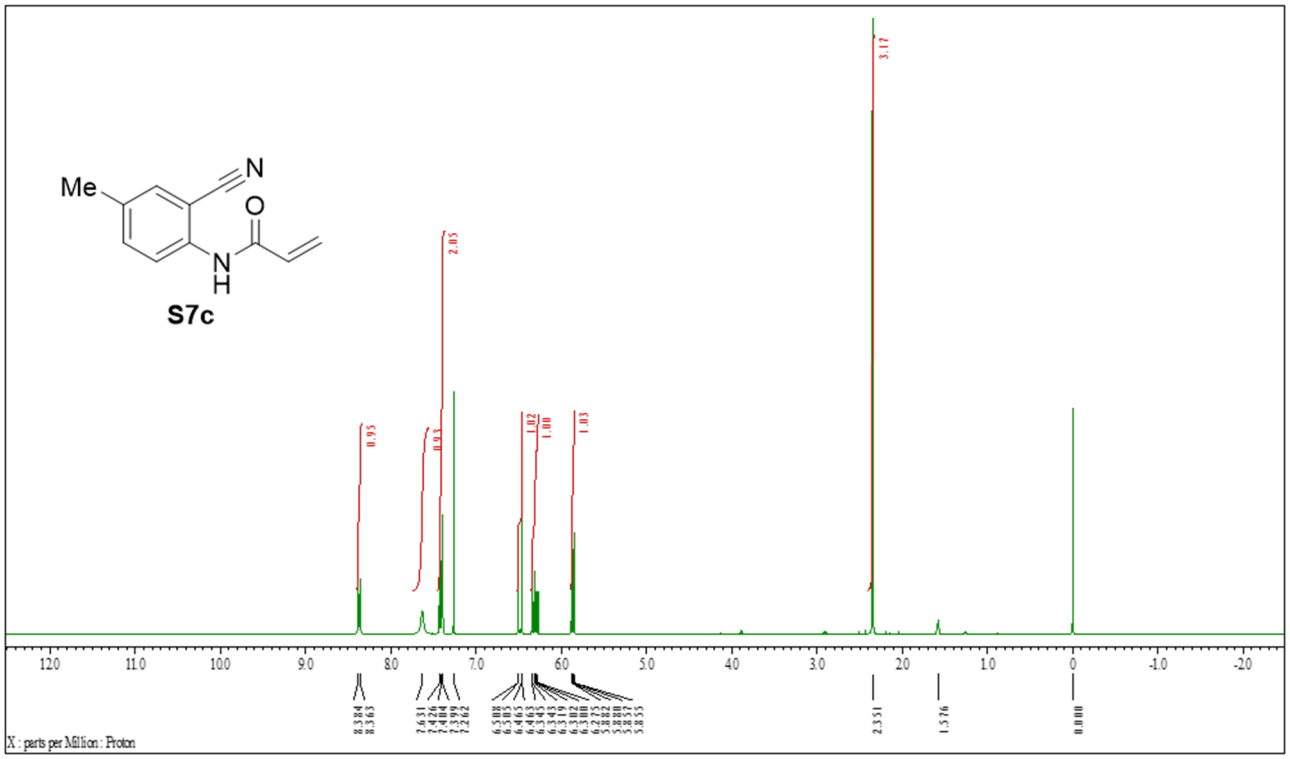
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 1b'**



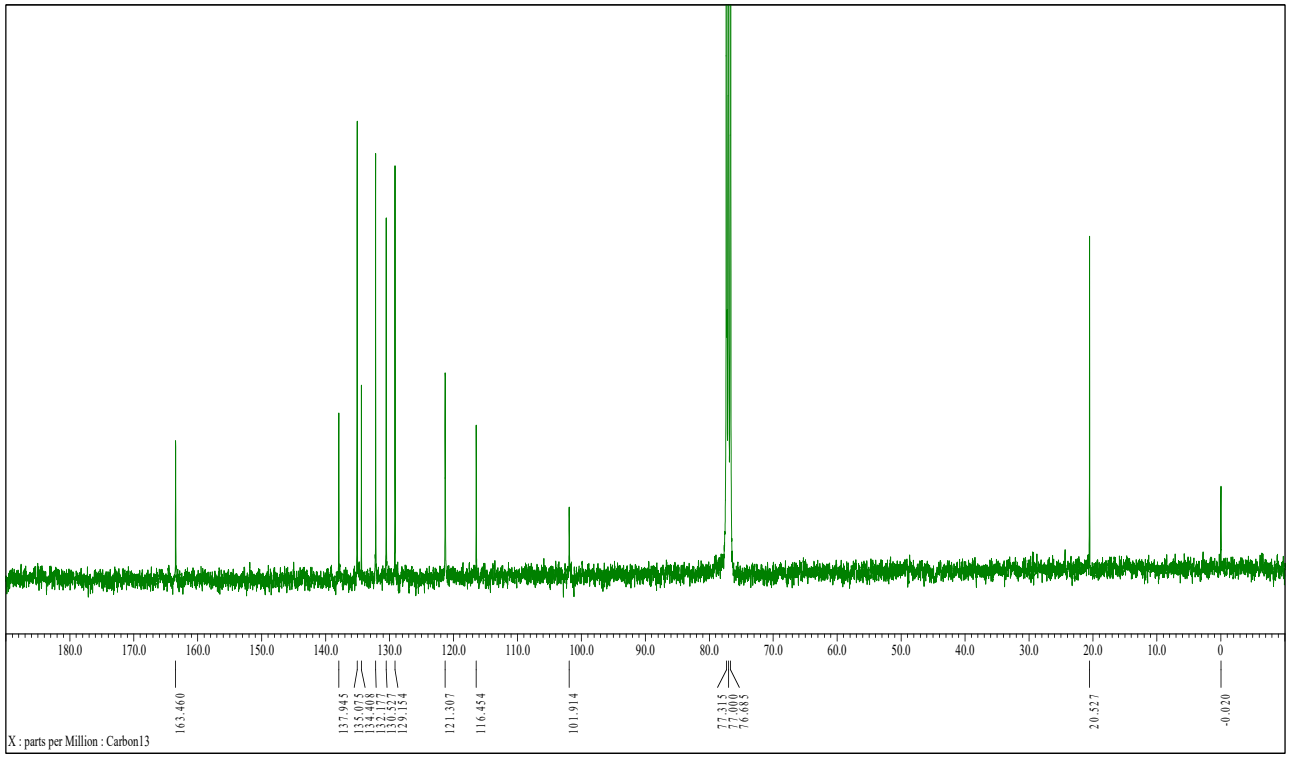

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 1b'**



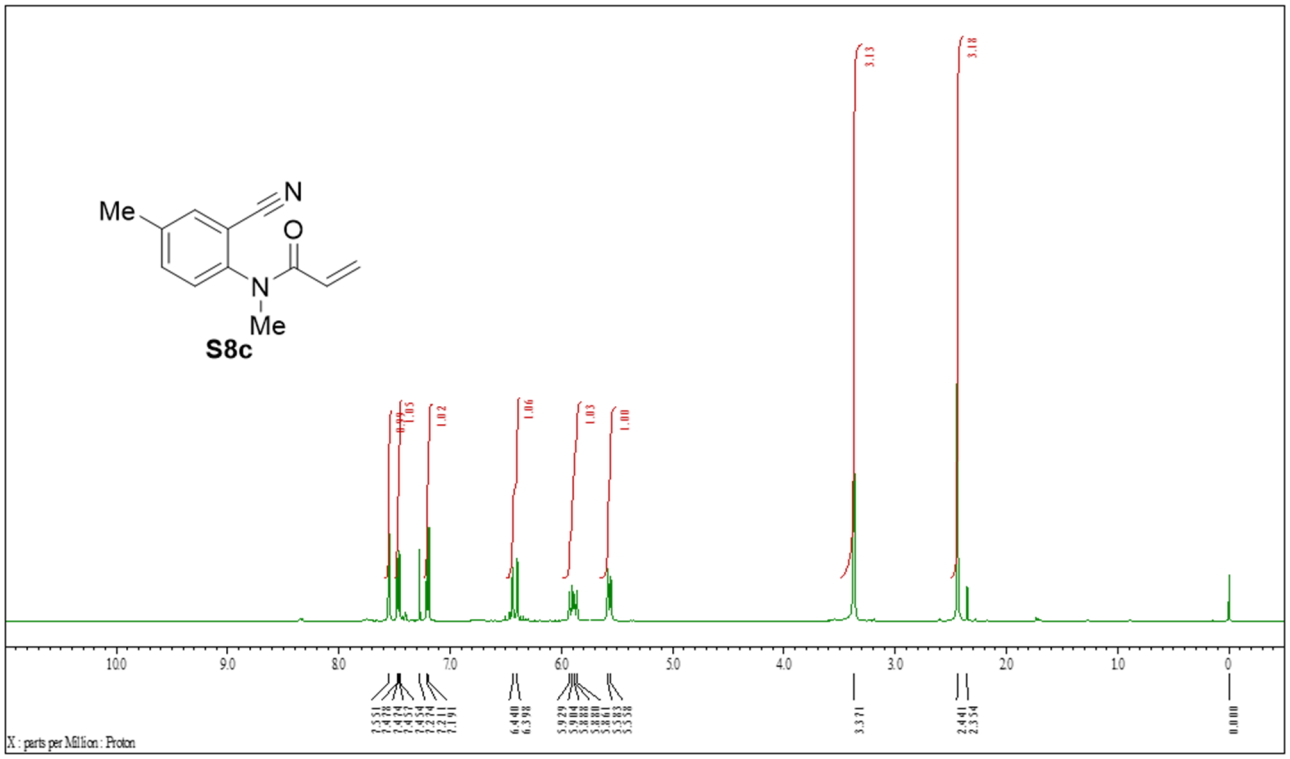
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S7c**



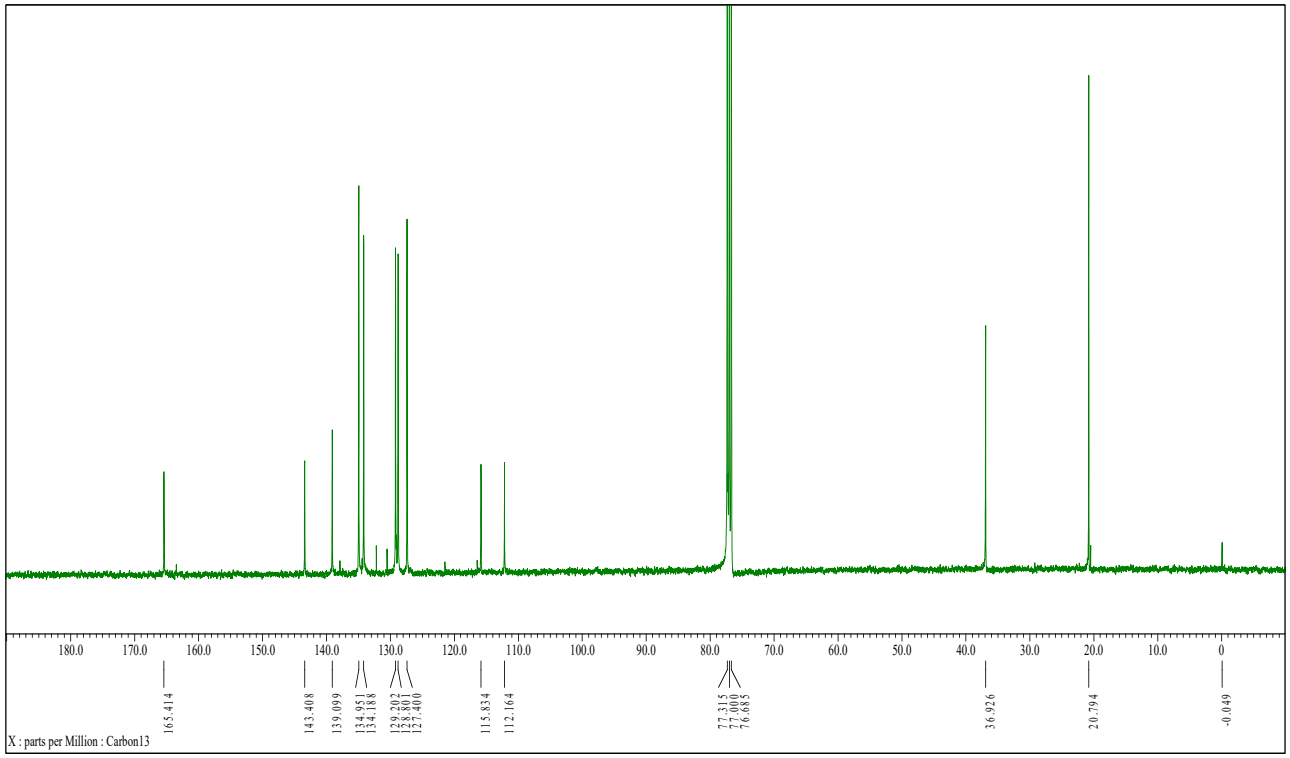

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S7c**



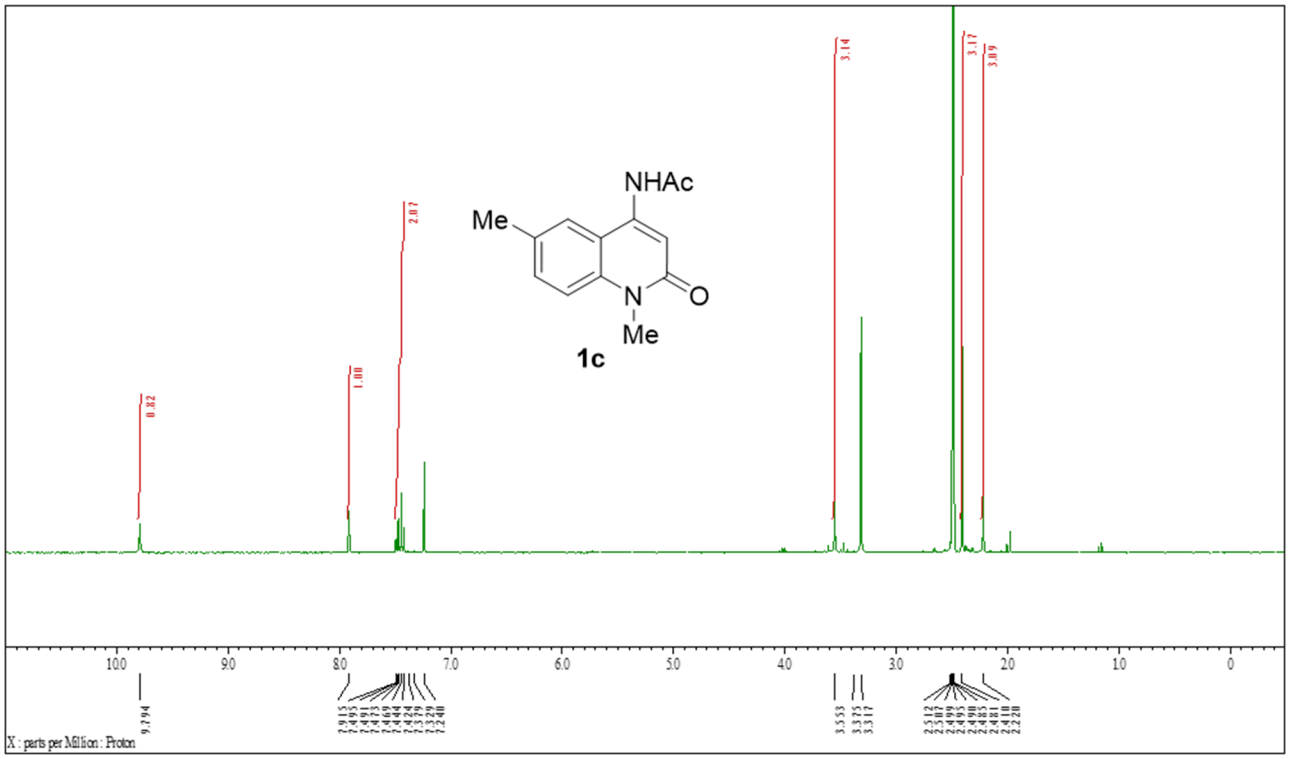
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S8c**



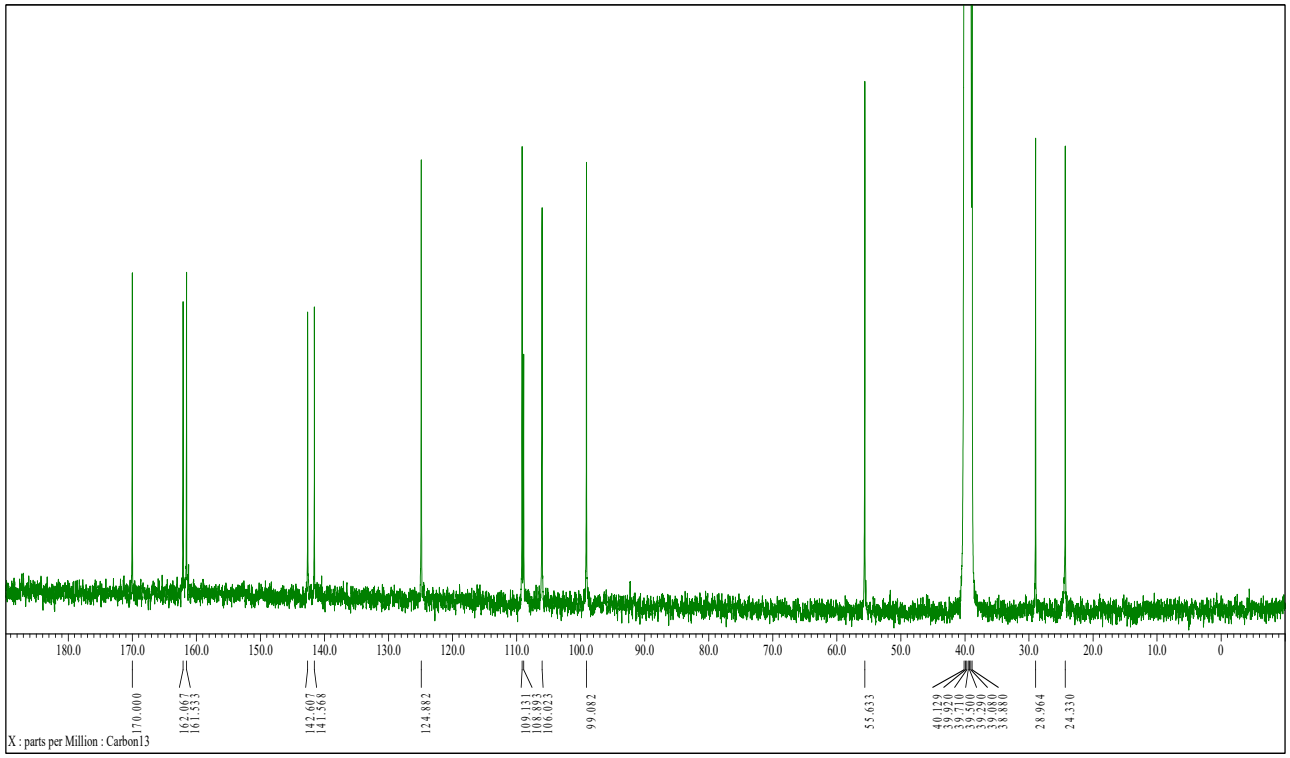

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S8c**



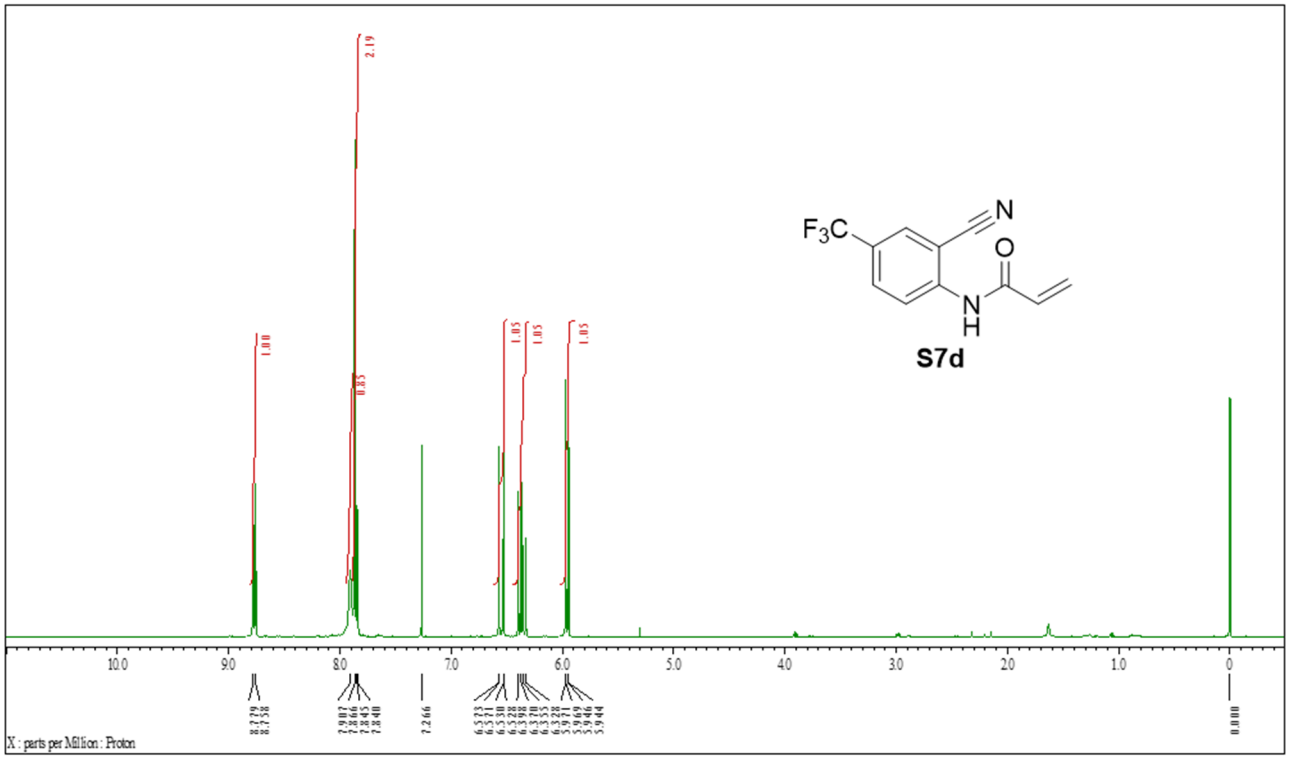
**$^{1}$H NMR (400 MHz, DMSO-$d_6$) of 1c**



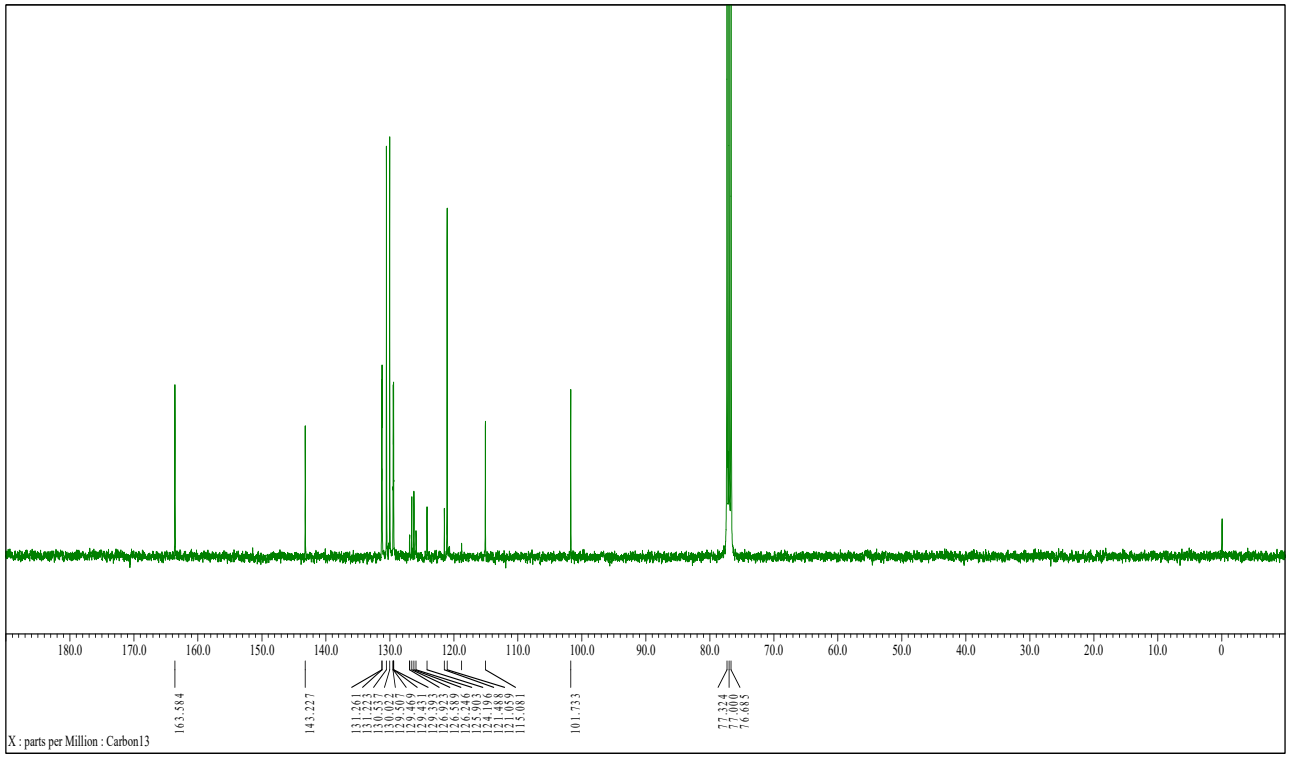

**$^{13}$C NMR (100 MHz, DMSO-$d_6$) of 1c**



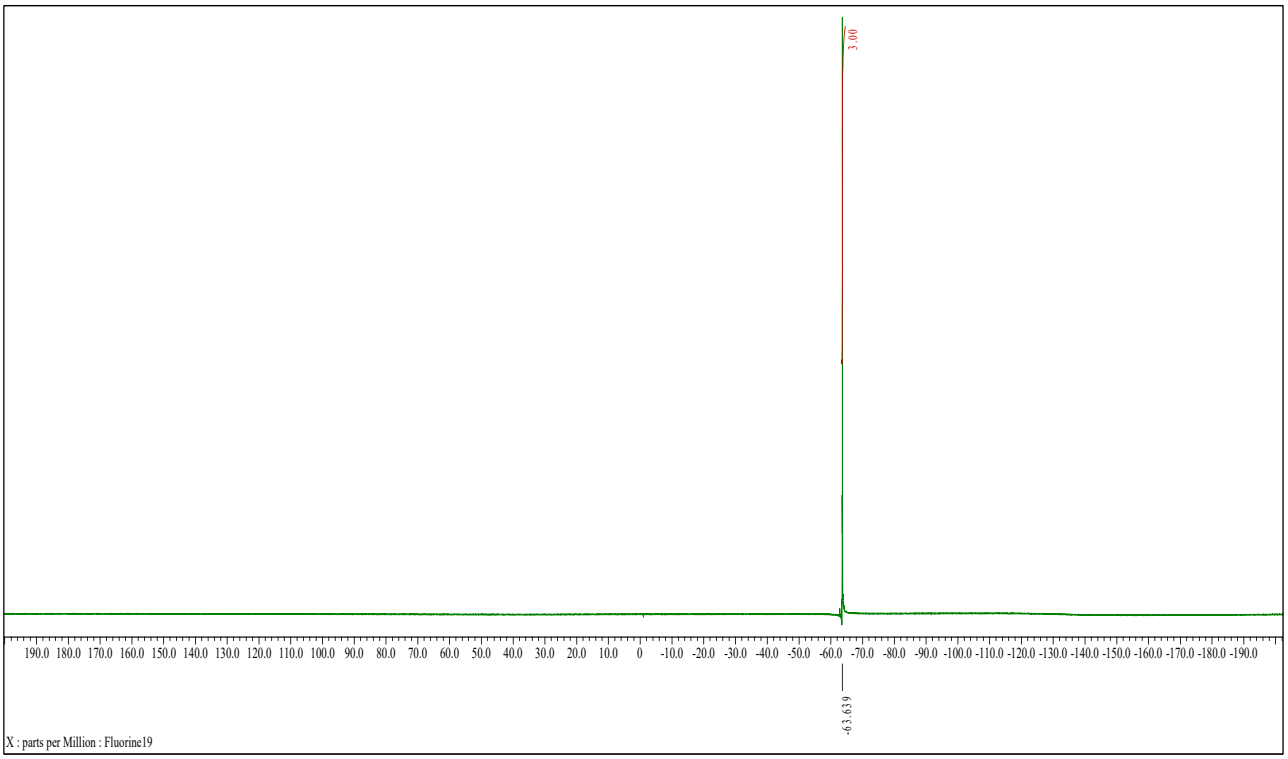
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S7d**



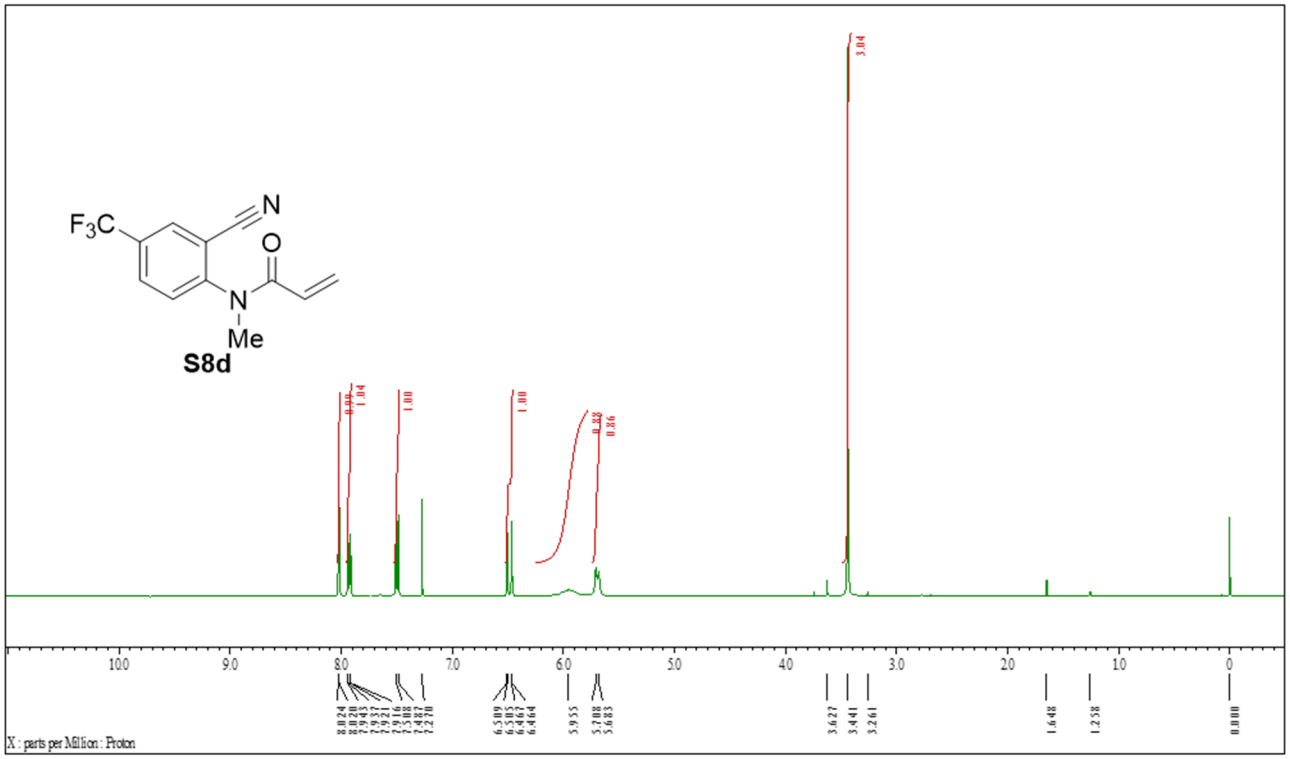

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S7d**



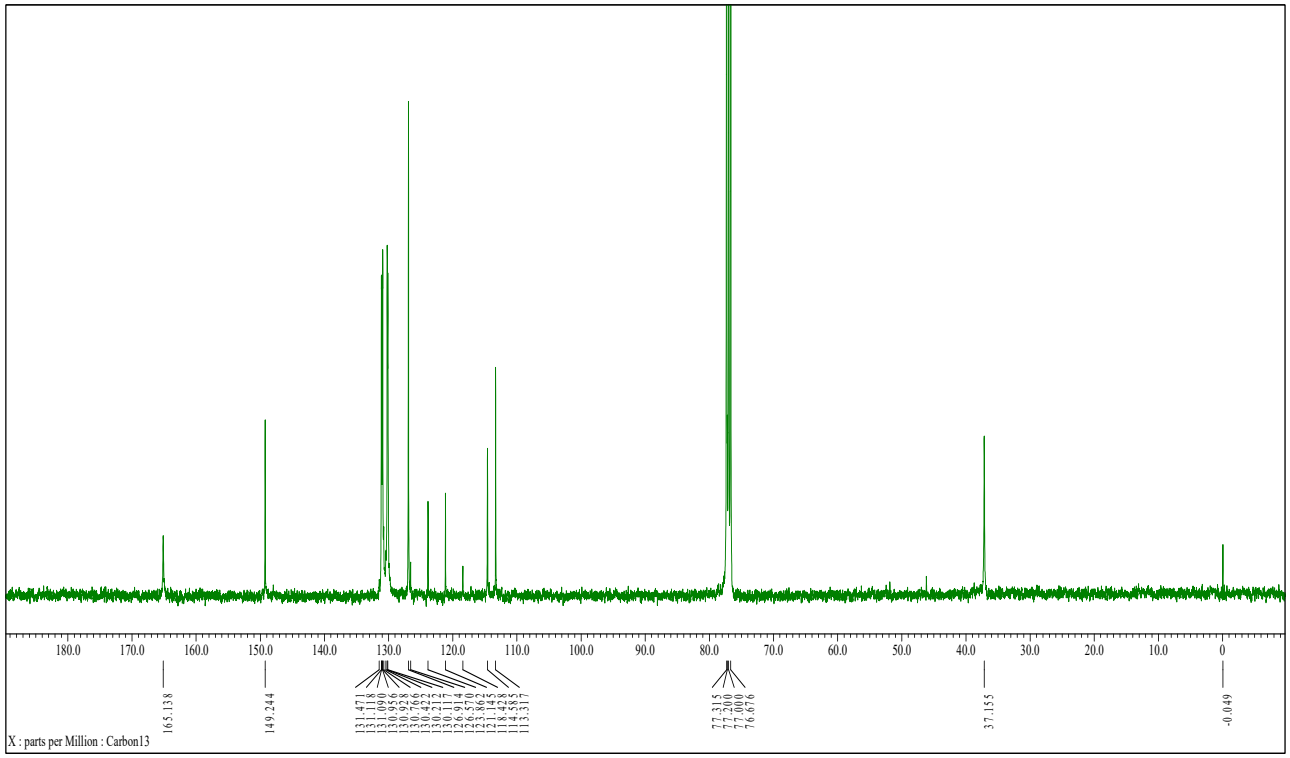
## $^{19}F$ NMR (376 MHz, $CDCl_3$) of S7d



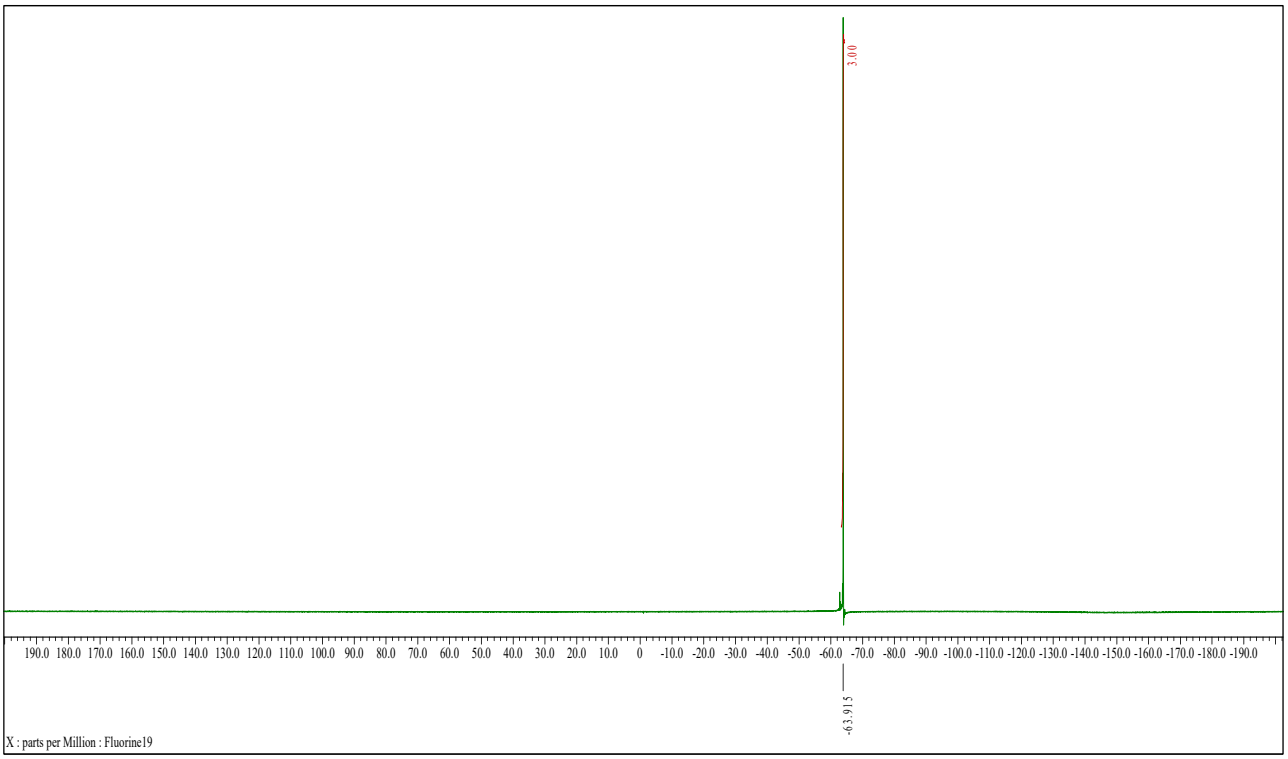
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S8d**



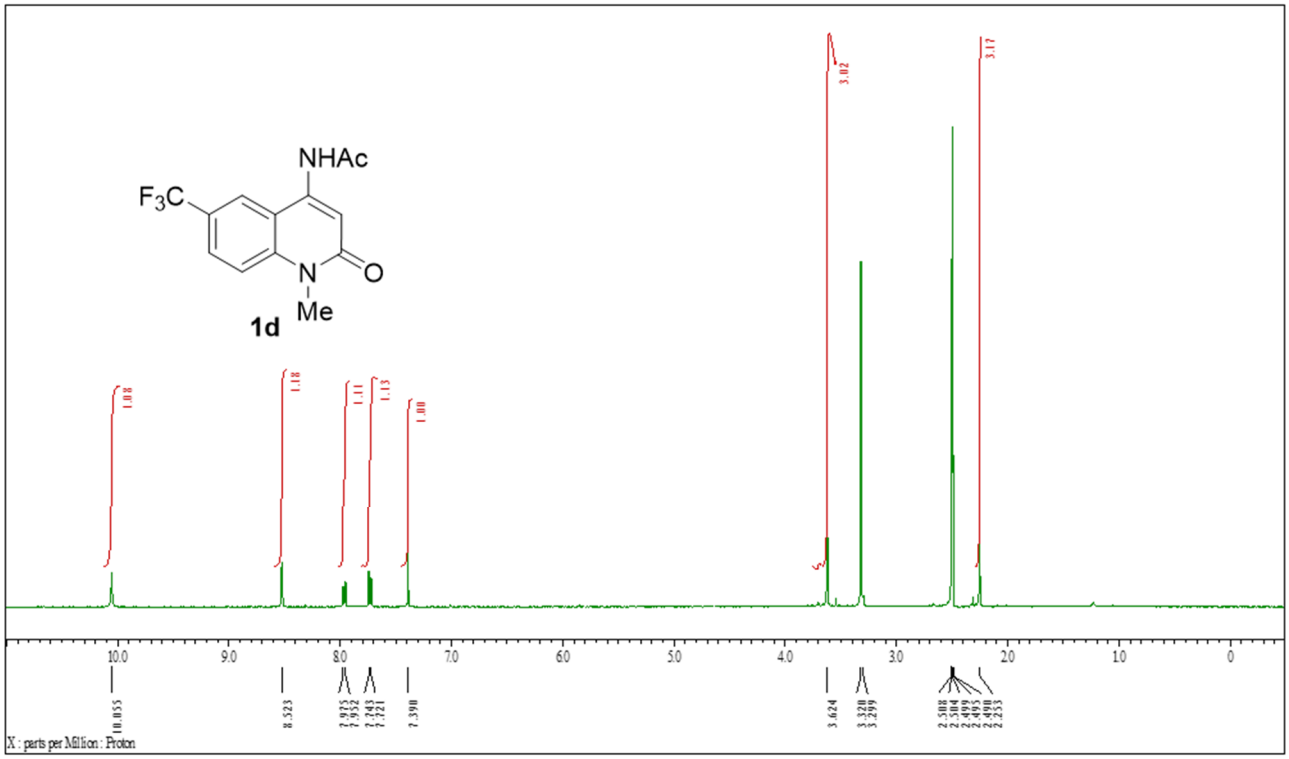

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S8d**



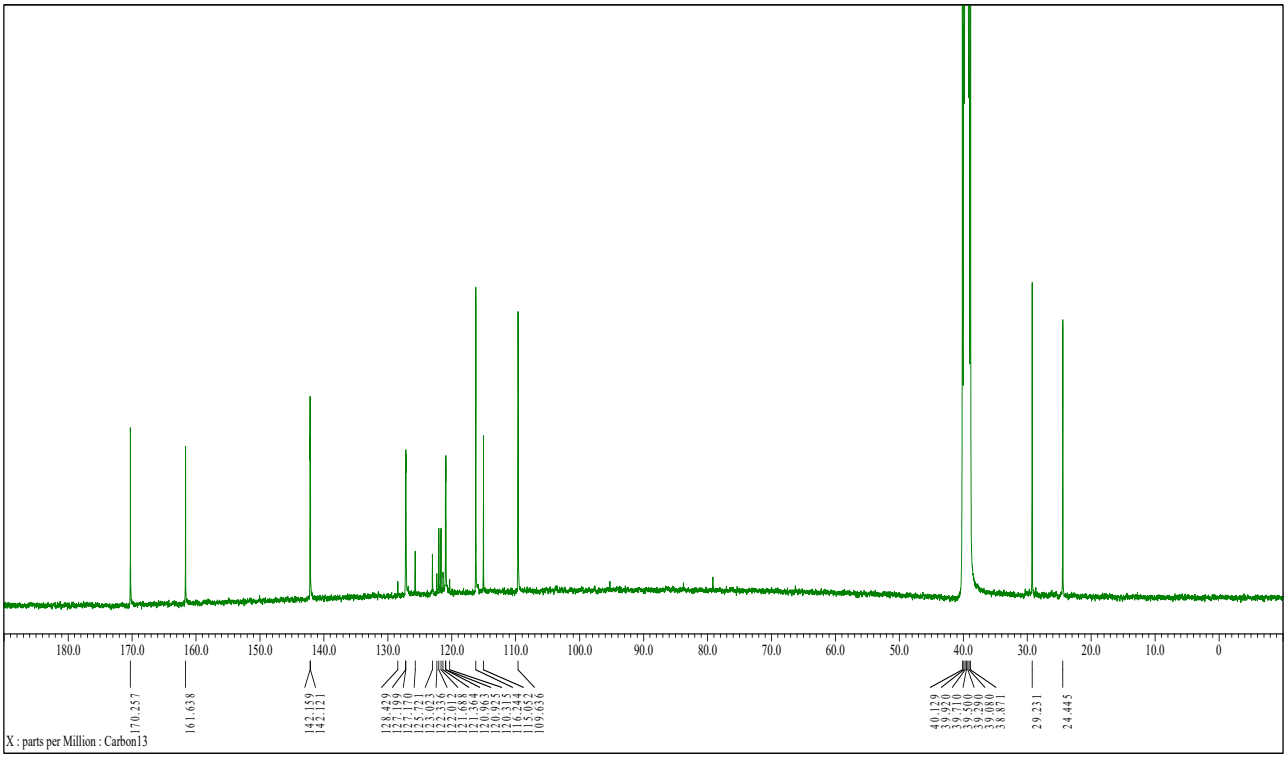
**$^{19}F$ NMR (376 MHz, $CDCl_3$) of S8d**



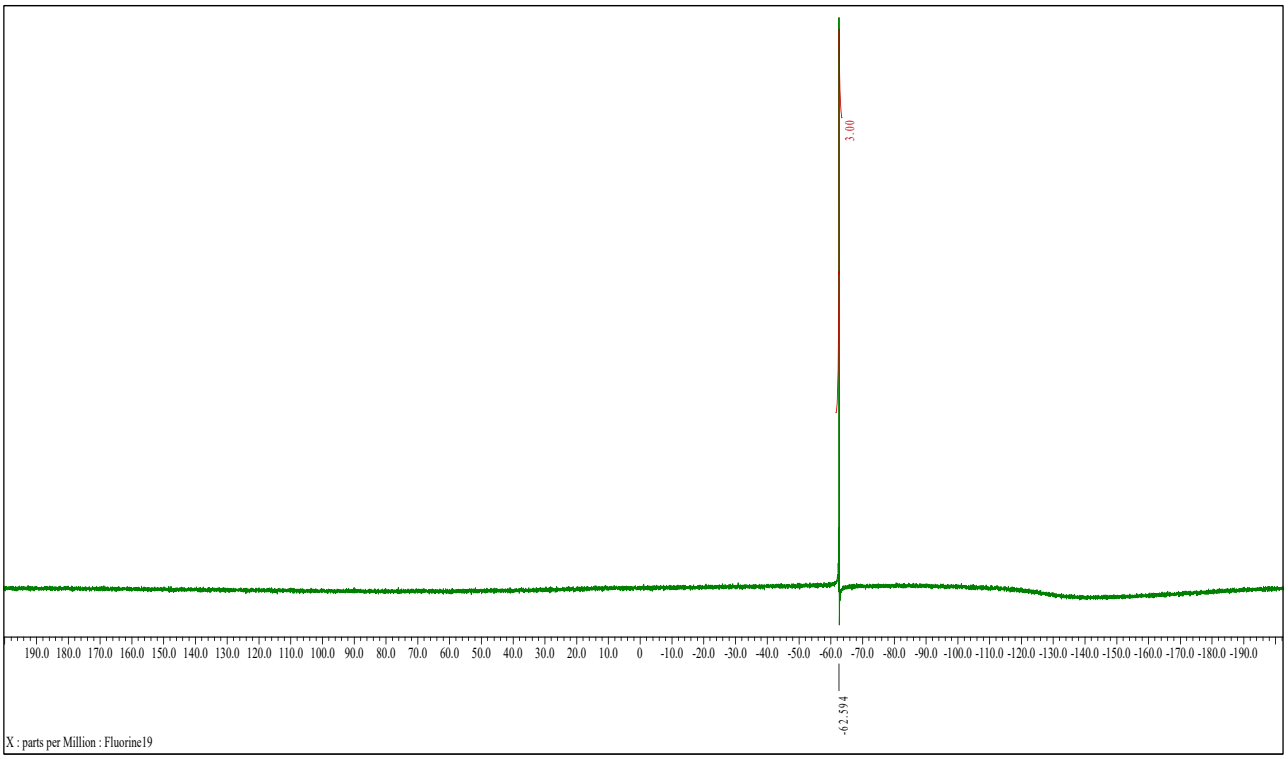
**$^{1}$H NMR (400 MHz, DMSO-$d_6$) of 1d**



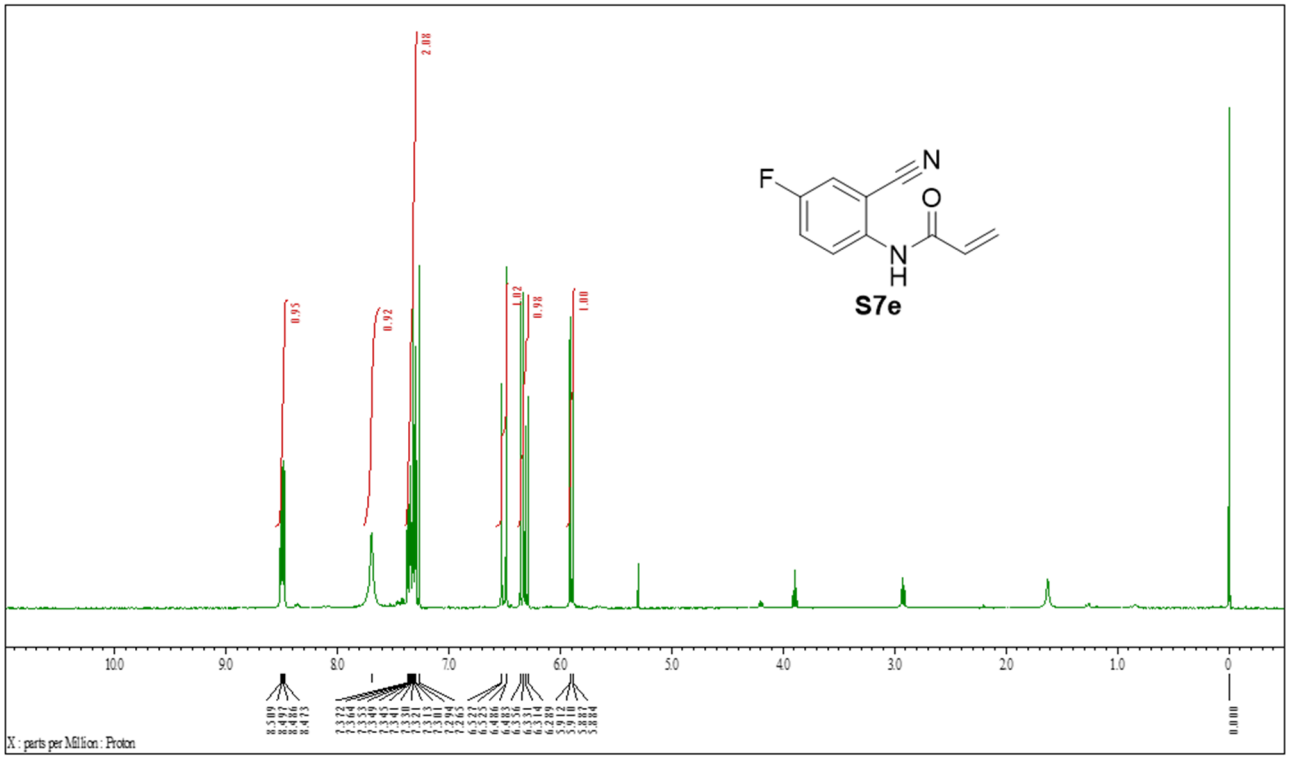

**$^{13}$C NMR (100 MHz, DMSO-$d_6$) of 1d**



**$^{19}F$ NMR (376 MHz, $CDCl_3$) of 1d**



**$^{1}$H NMR (400 MHz, $CDCl_3$) of S7e**

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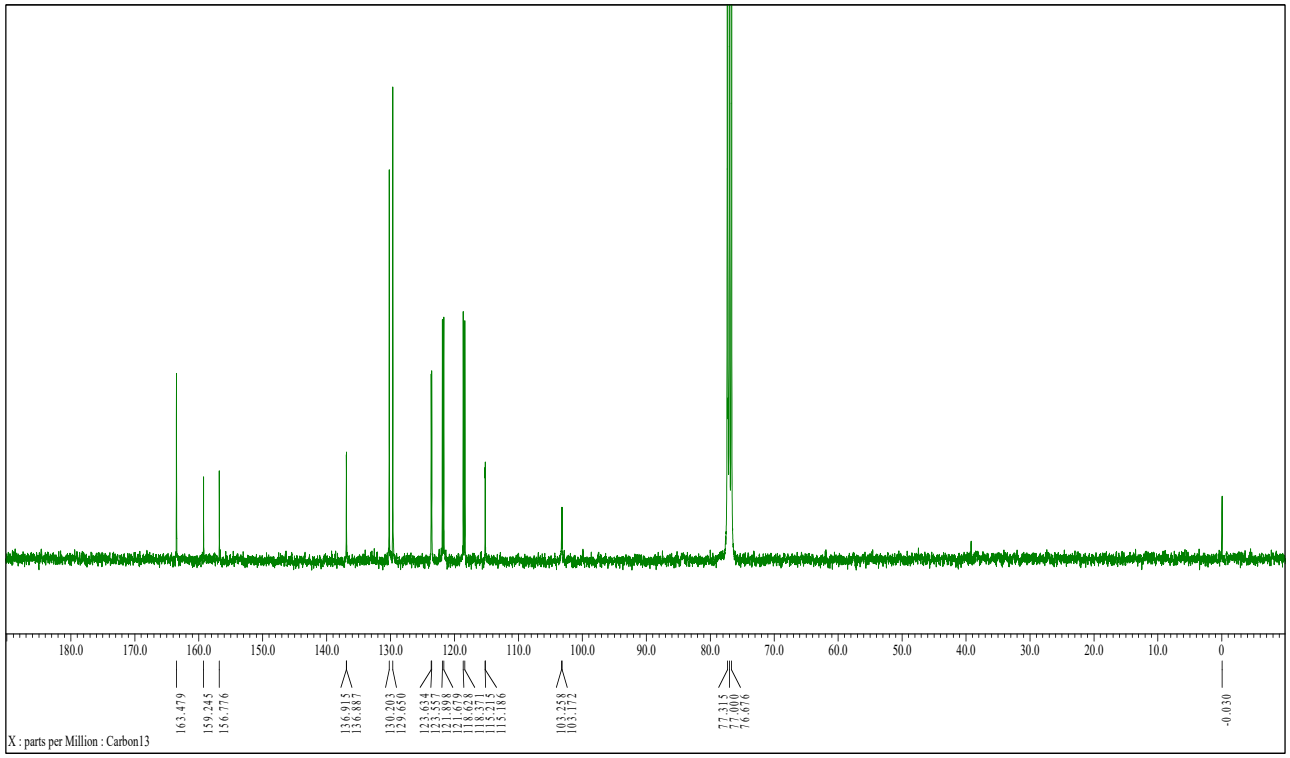
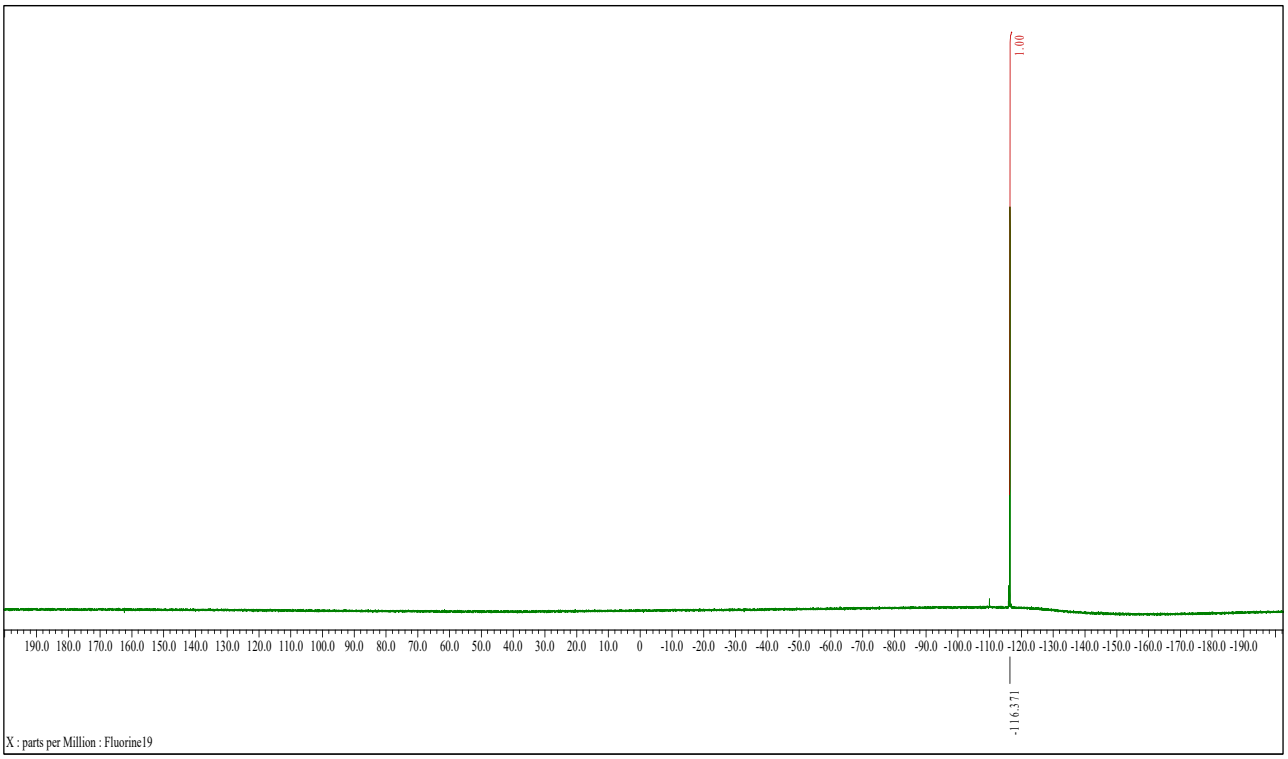
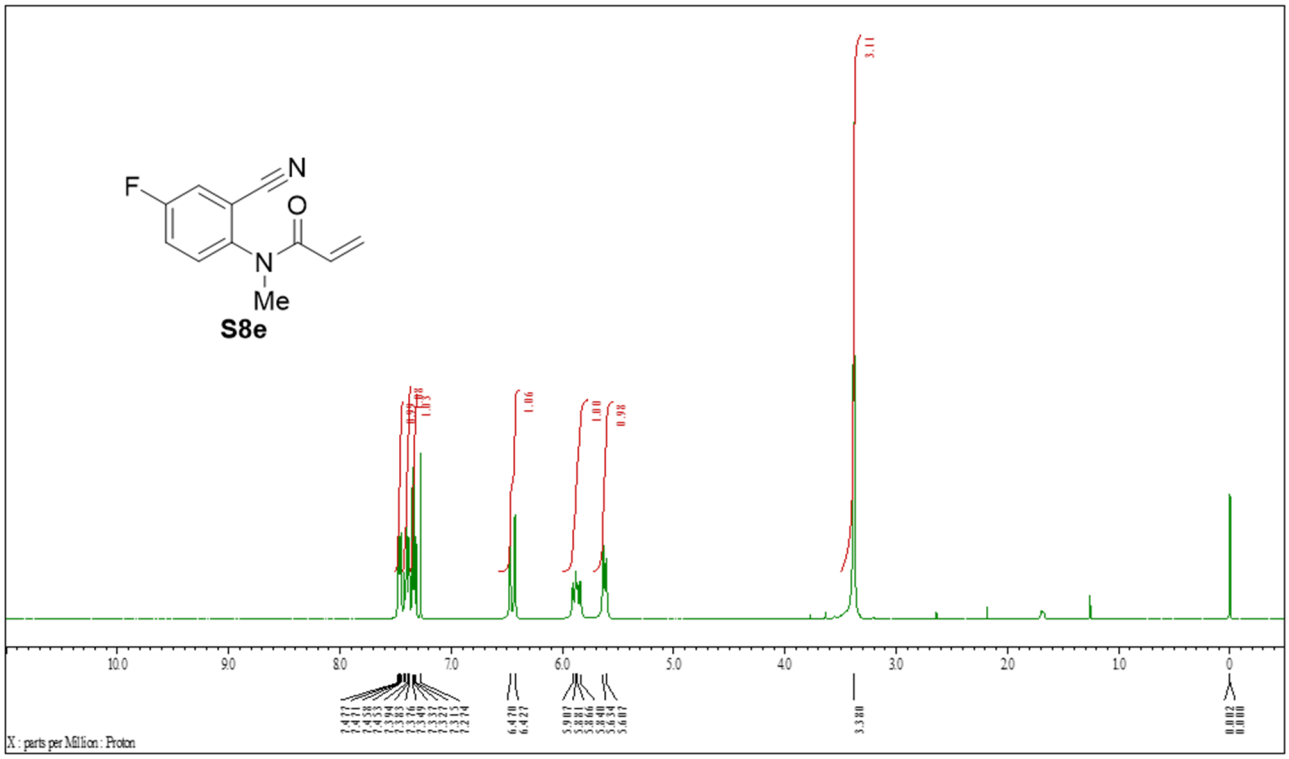


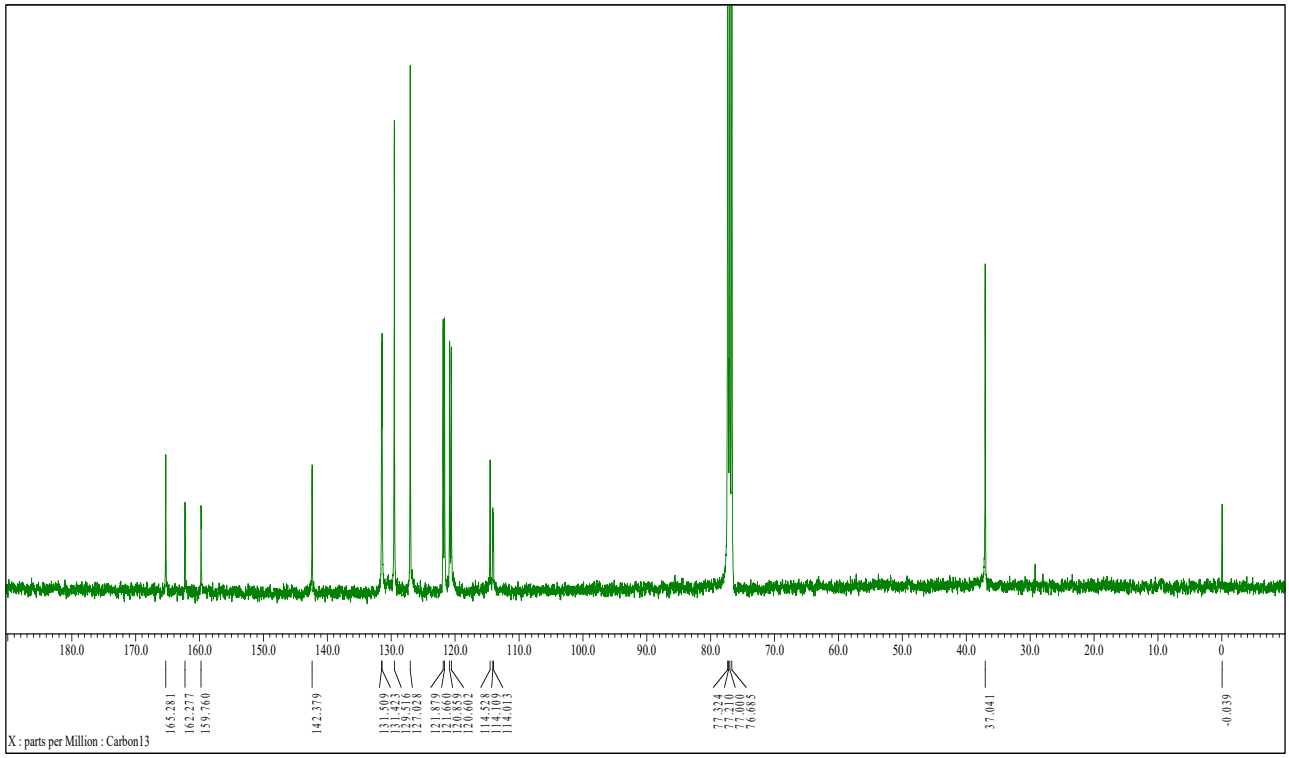
**$^{19}$F NMR (376 MHz, $CDCl_3$) of S7e**



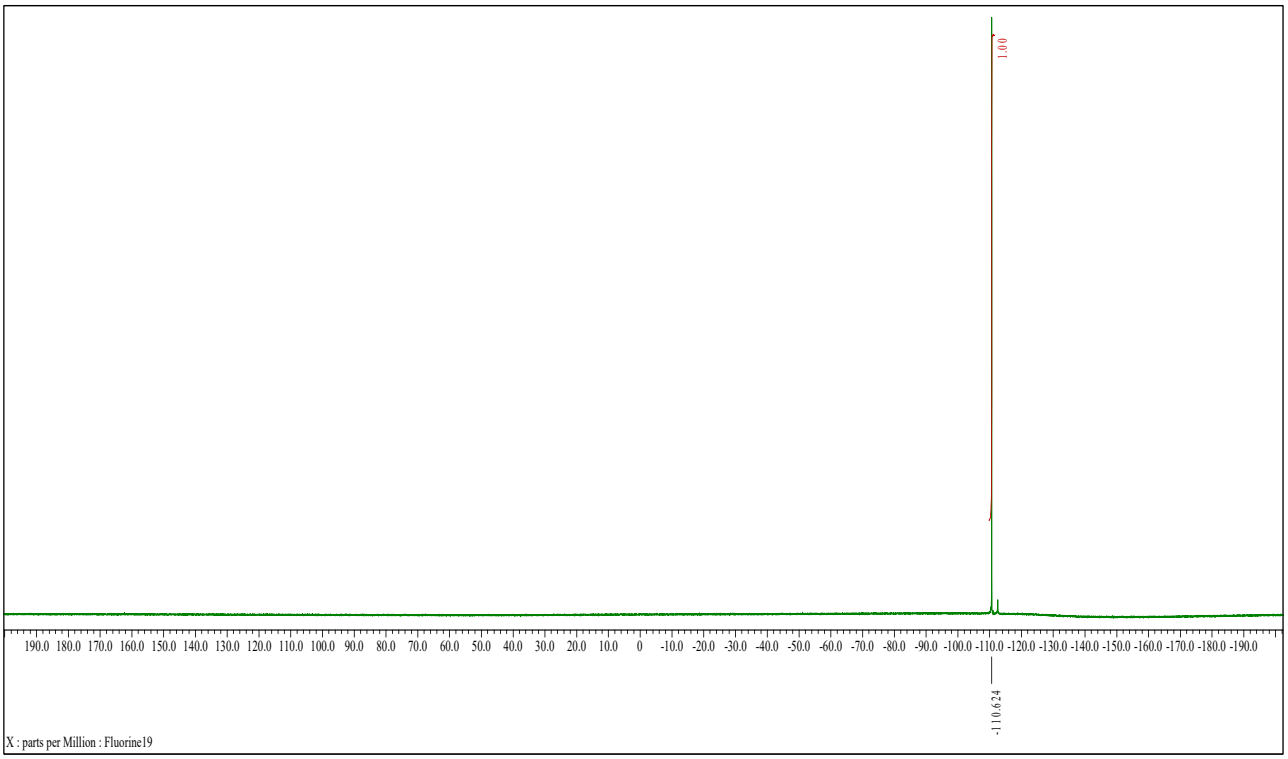
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S8e**



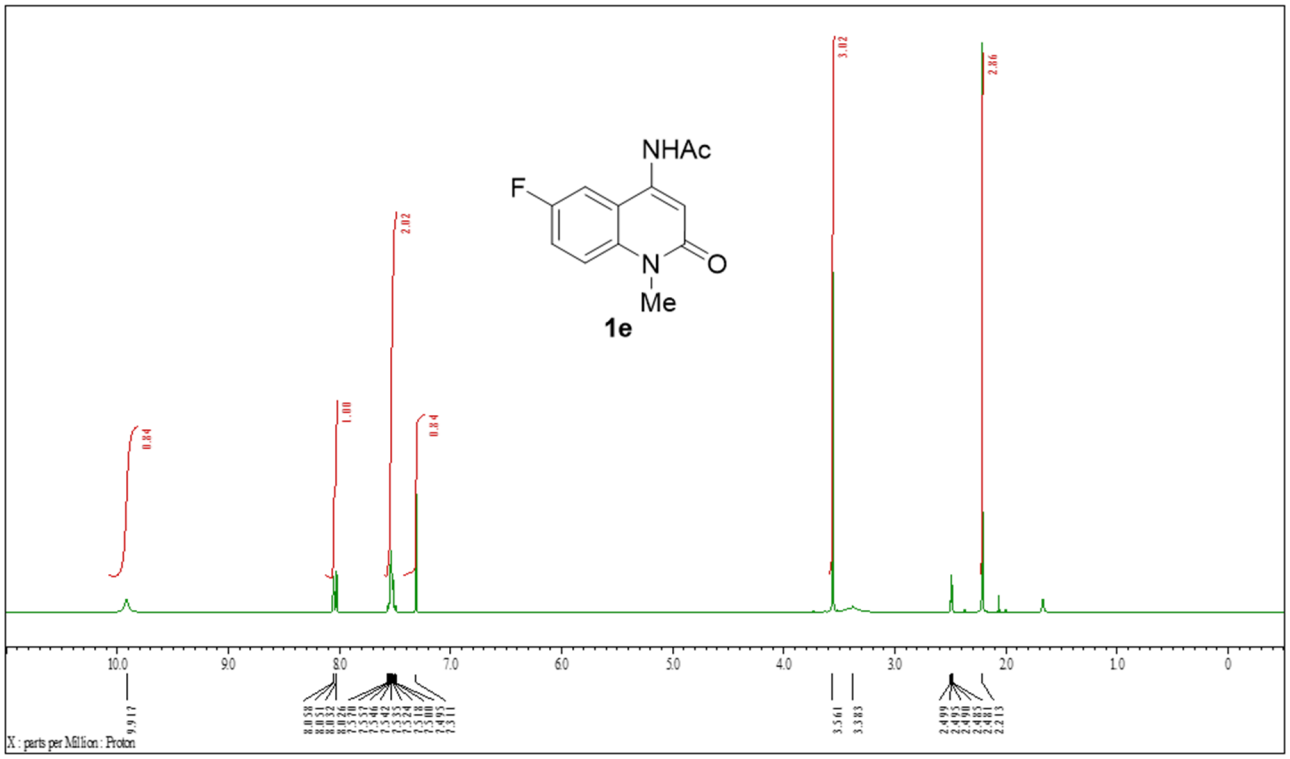

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S8e**



**$^{19}F$ NMR (376 MHz, $CDCl_3$) of S8e**



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

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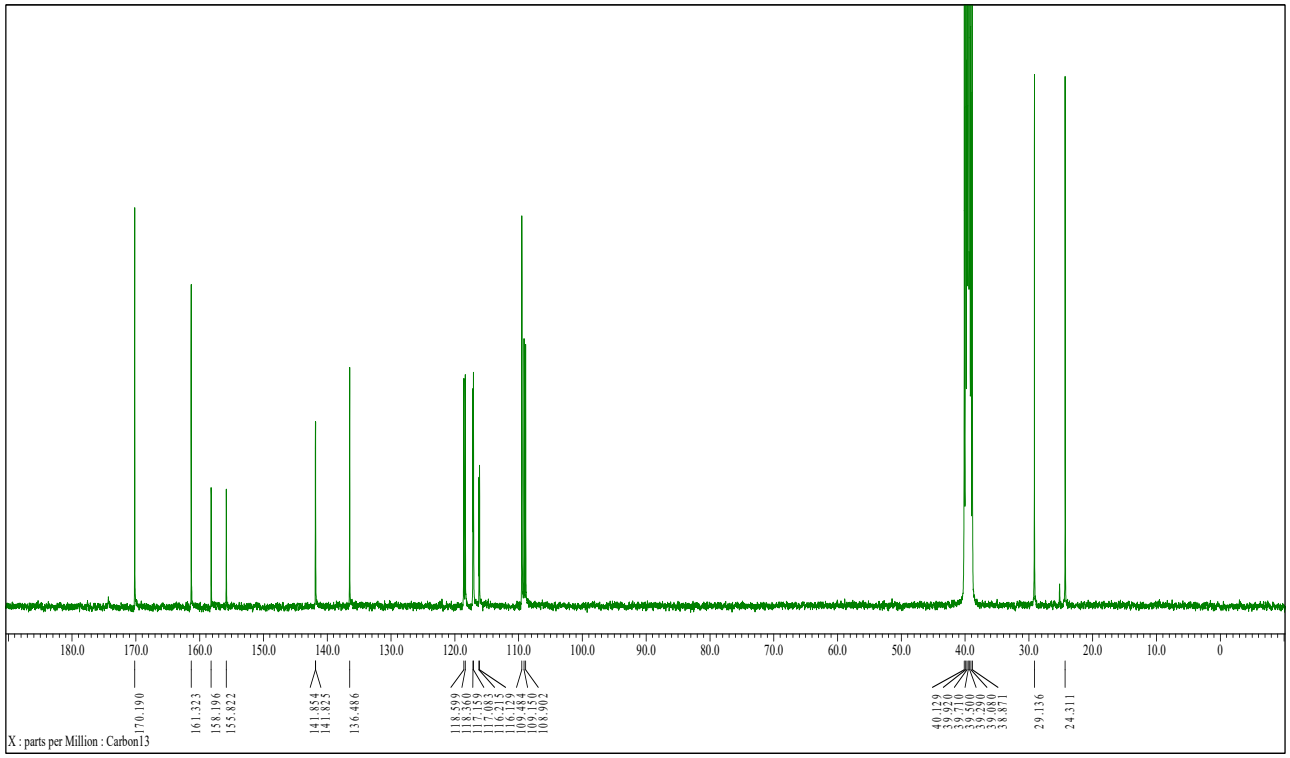
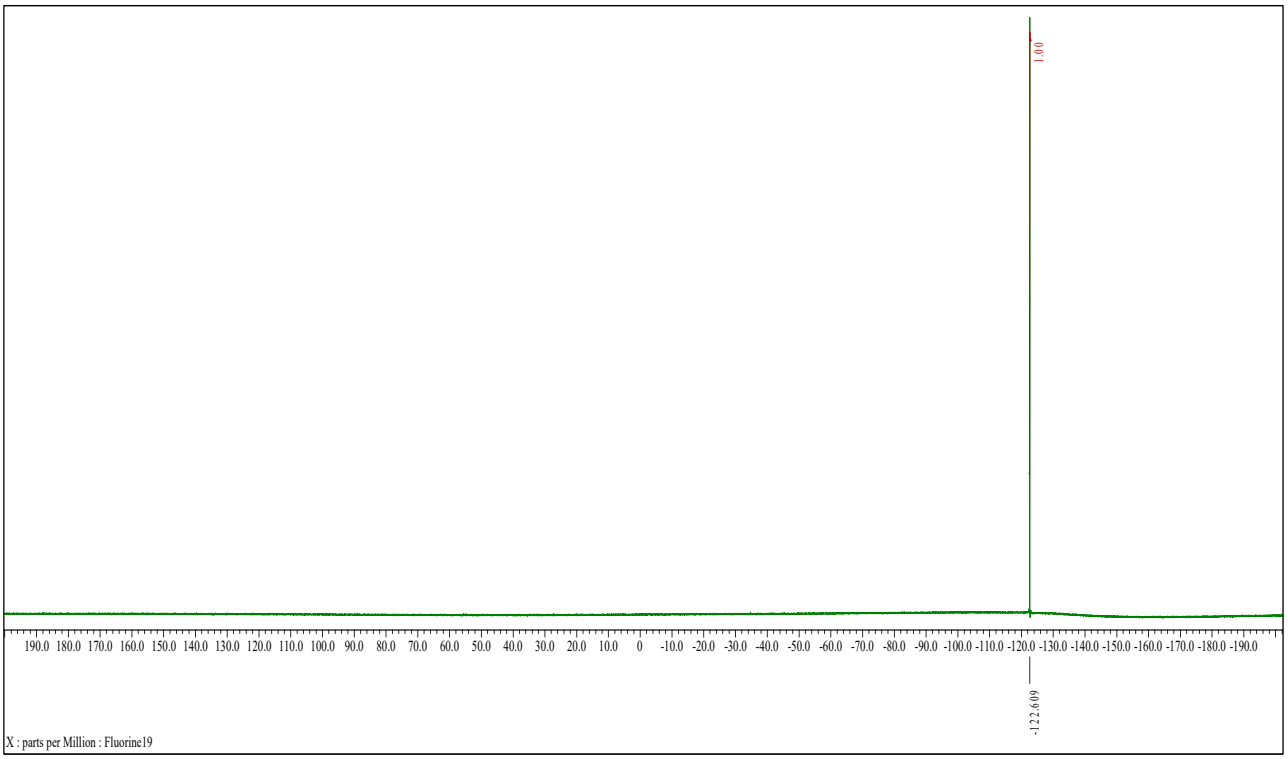
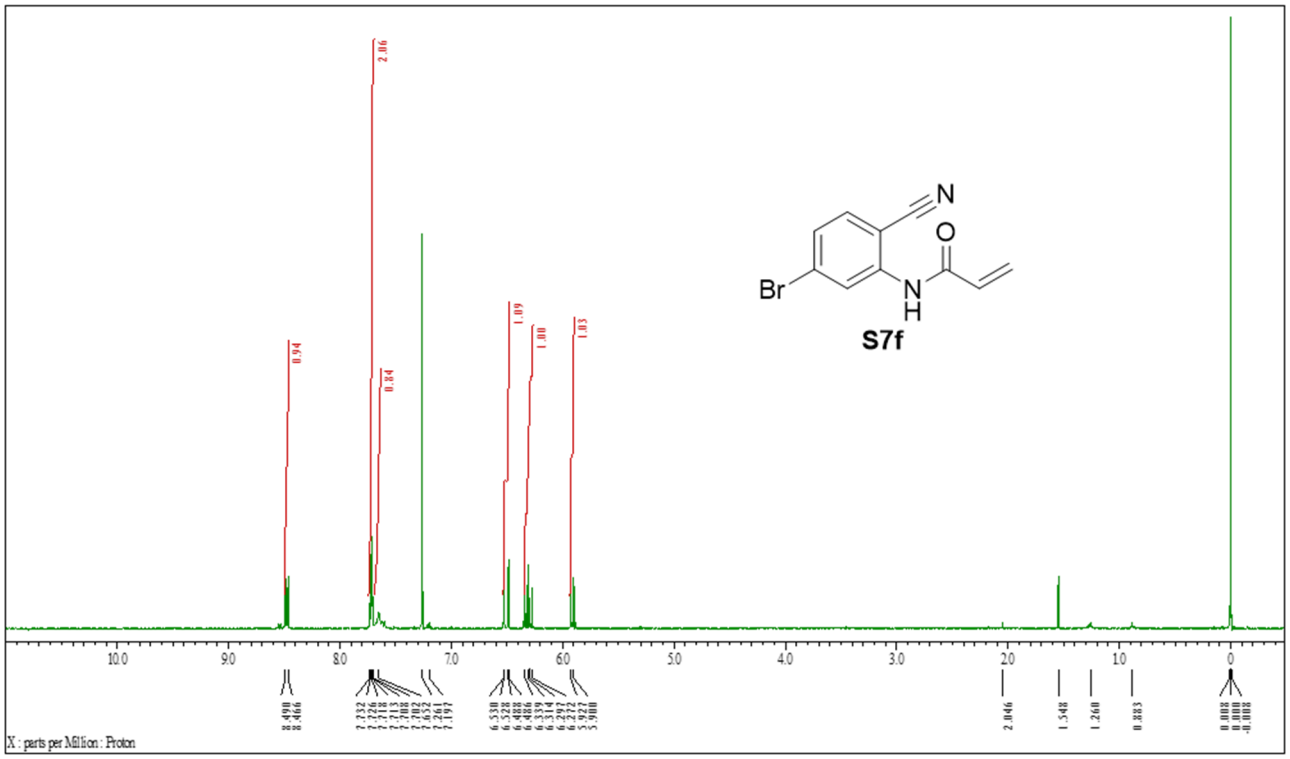


**$^{19}F$ NMR (376 MHz, $CDCl_3$) of 1e**



**$^{1}$H NMR (400 MHz, $CDCl_3$) of S7f**

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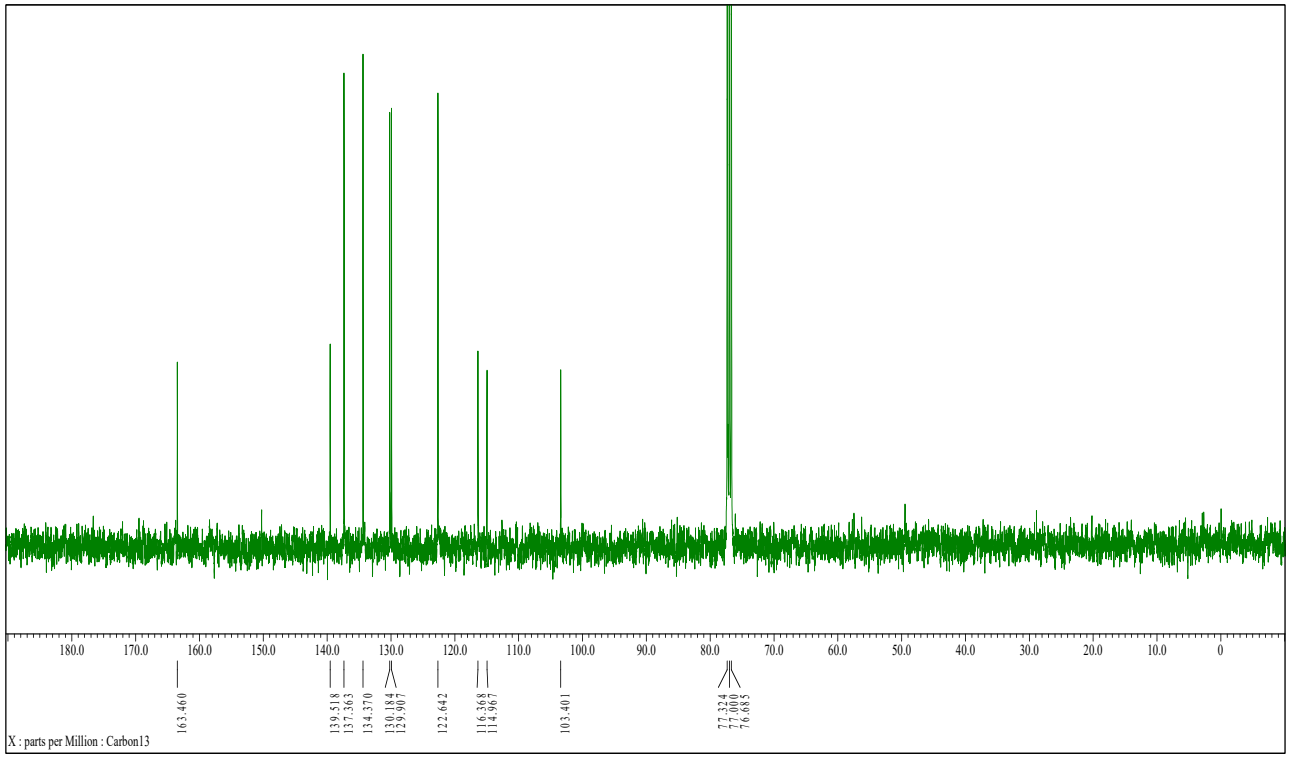
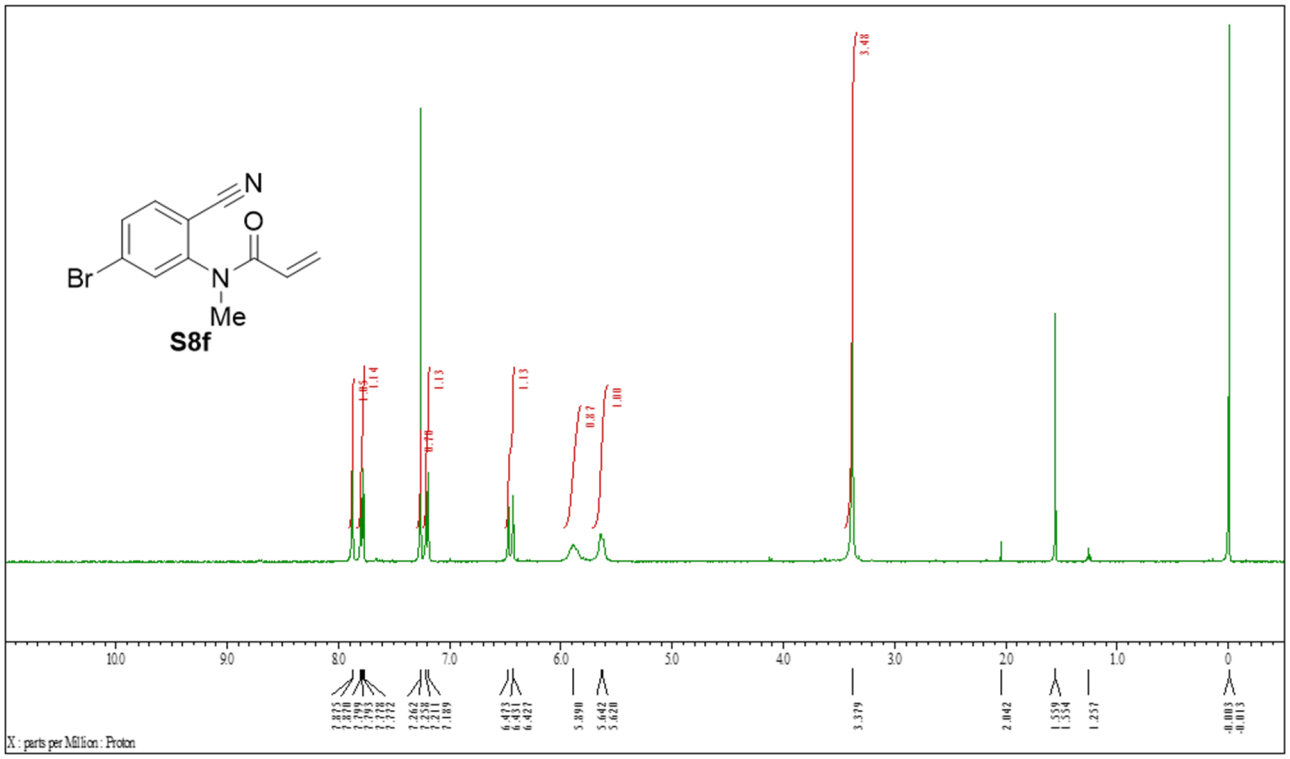
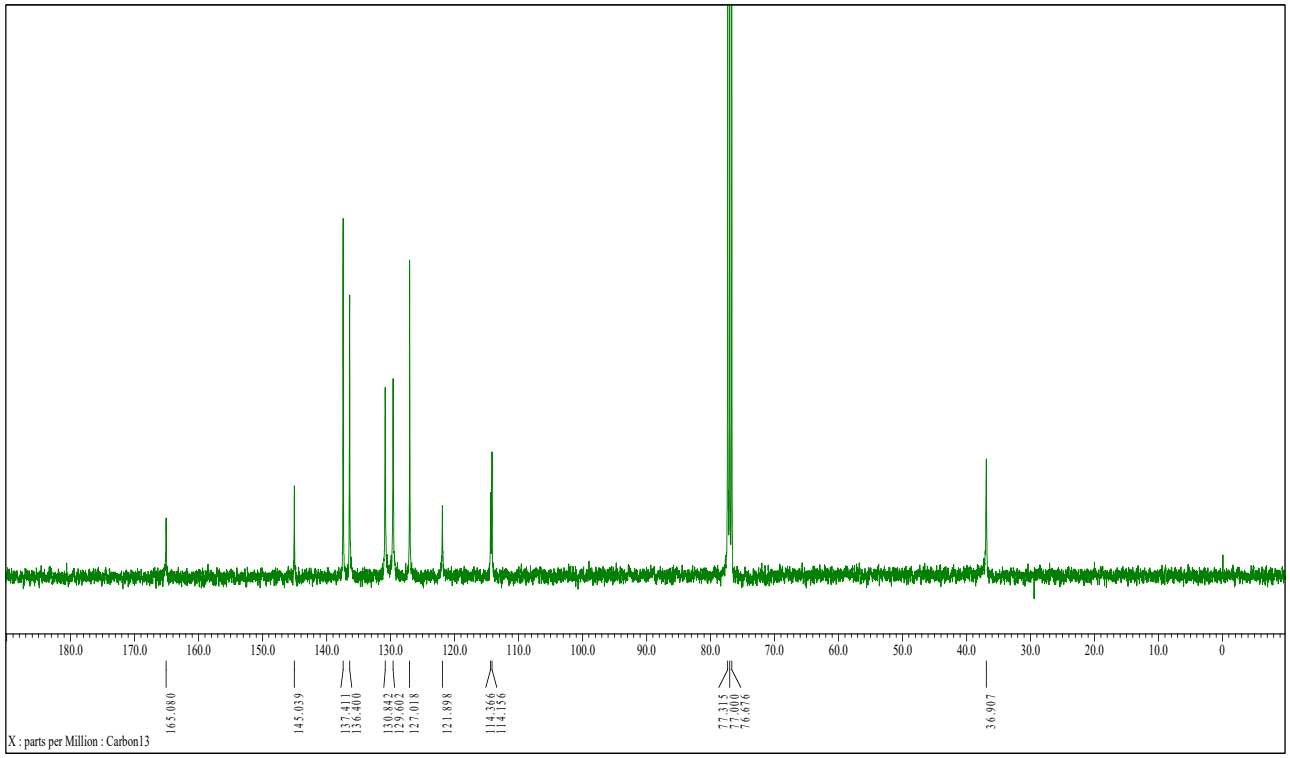


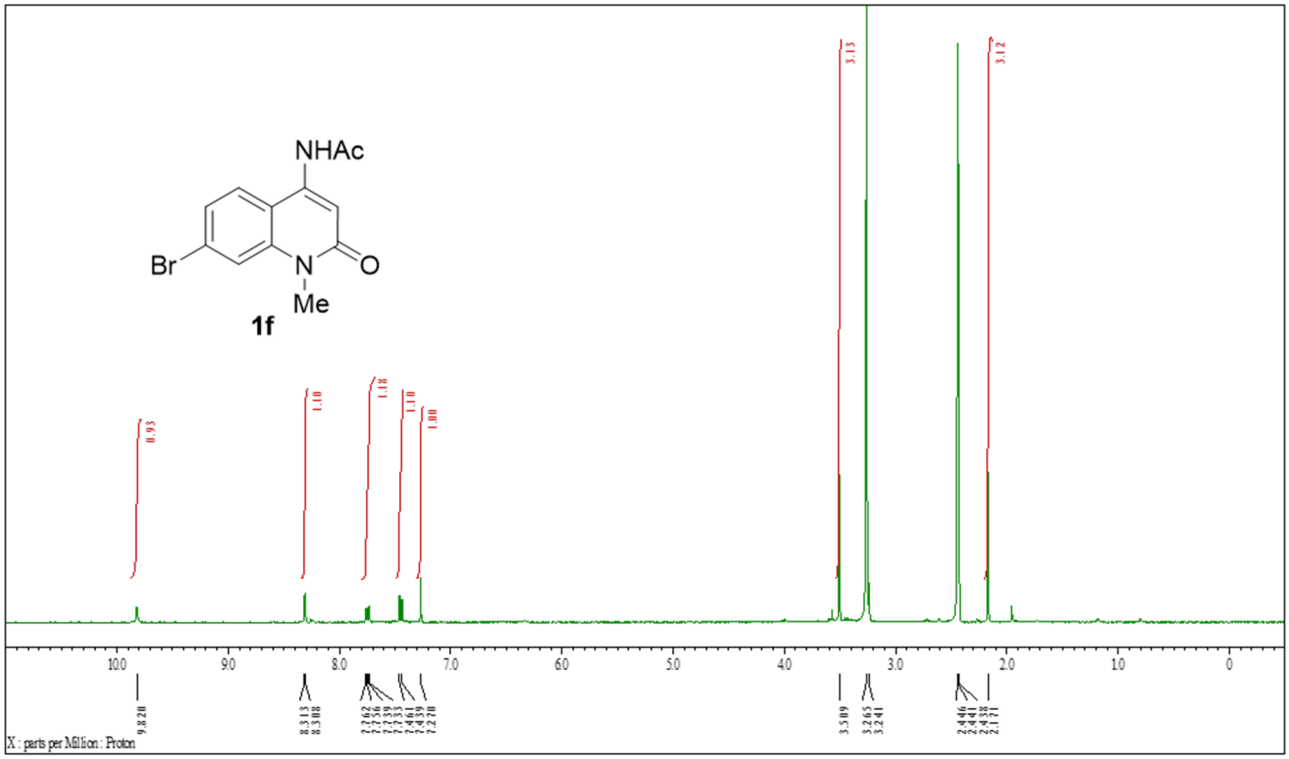
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S8f**



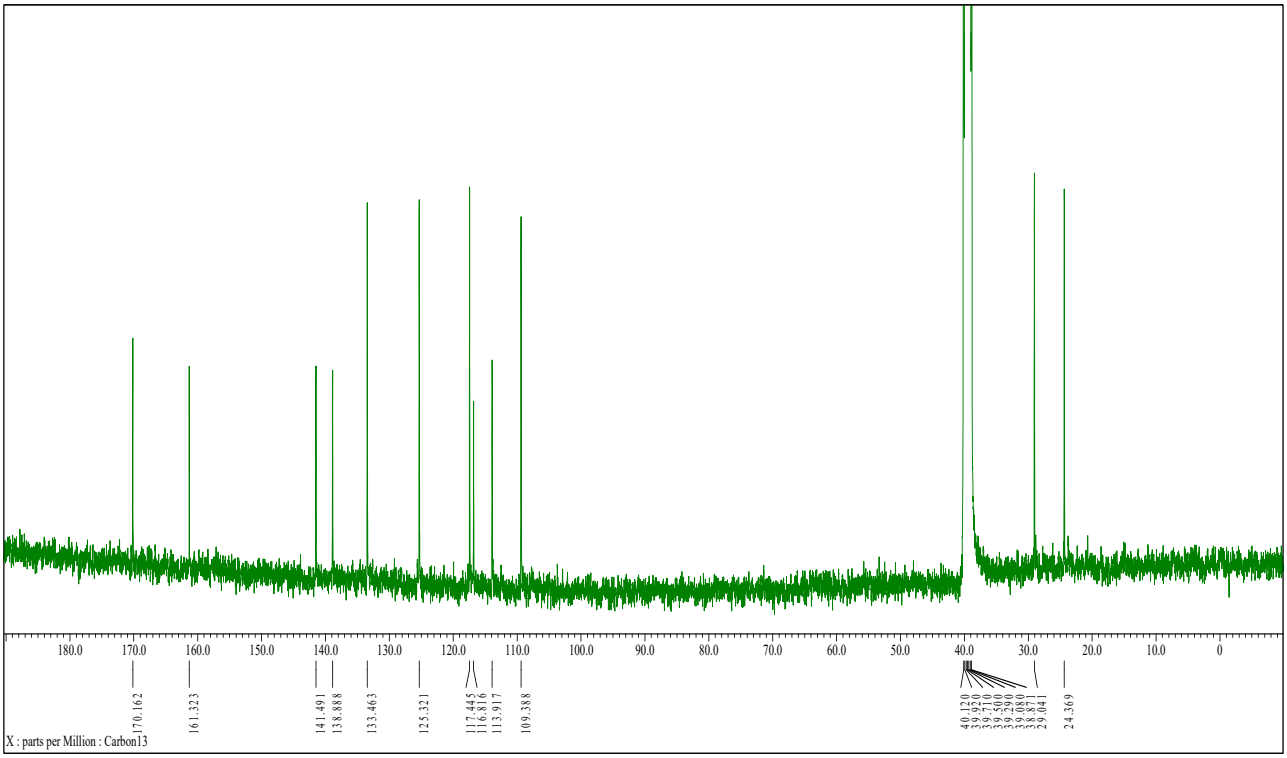

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S8f**



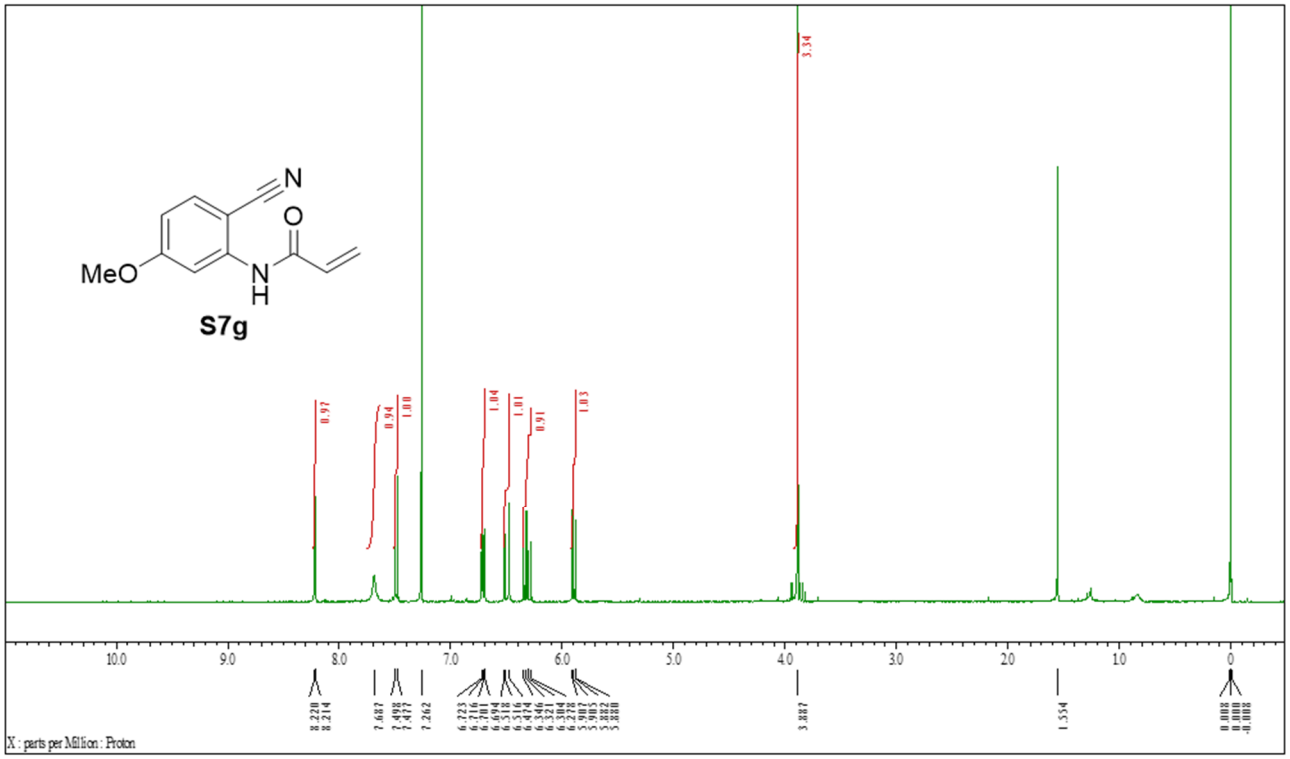
**$^{1}$H NMR (400 MHz, DMSO-$d_6$) of 1f**



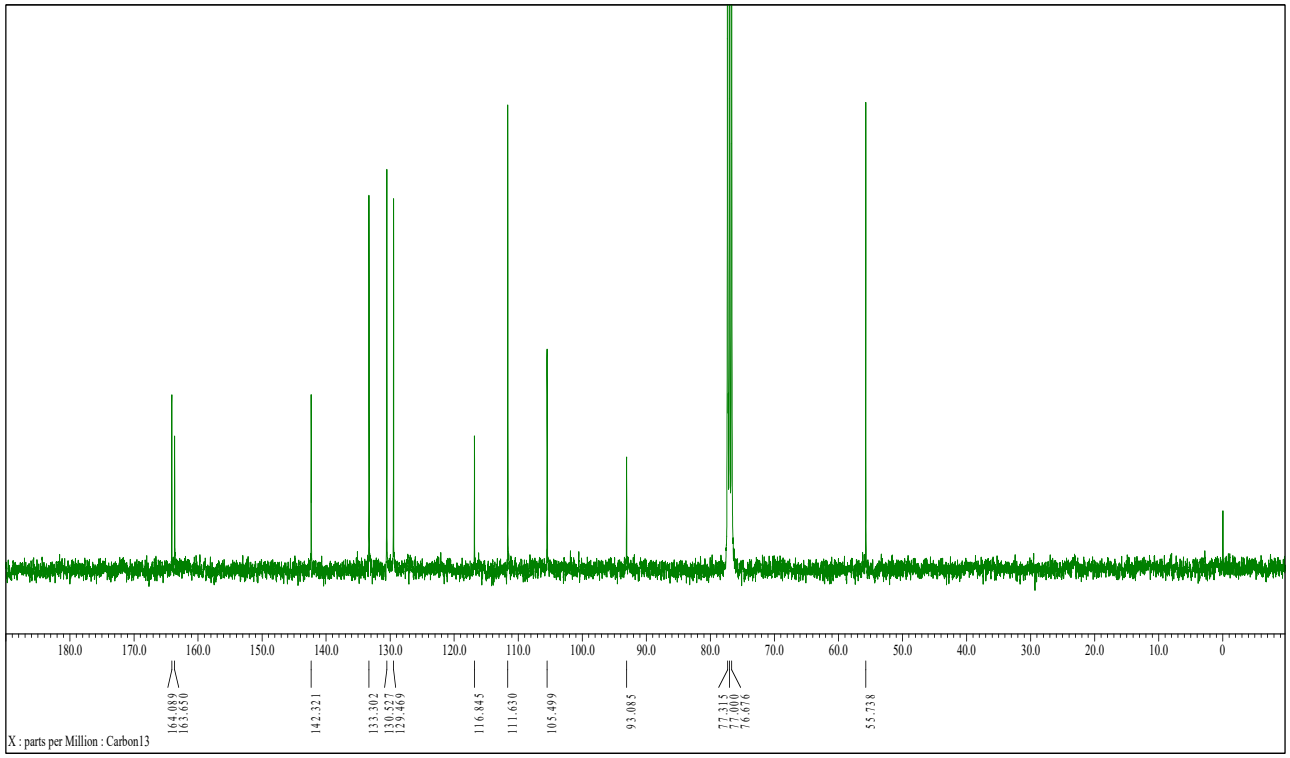

**$^{13}$C NMR (100 MHz, DMSO-$d_6$) of 1e**



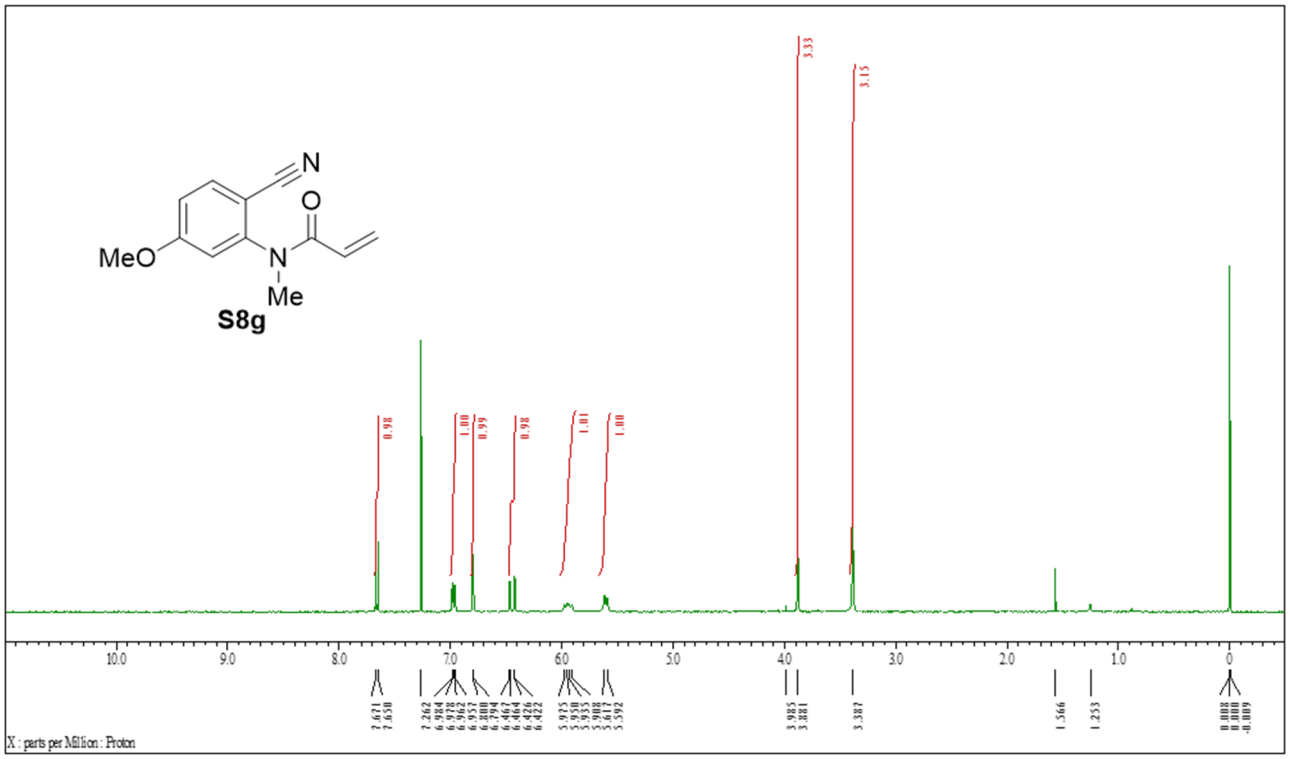
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S7g**



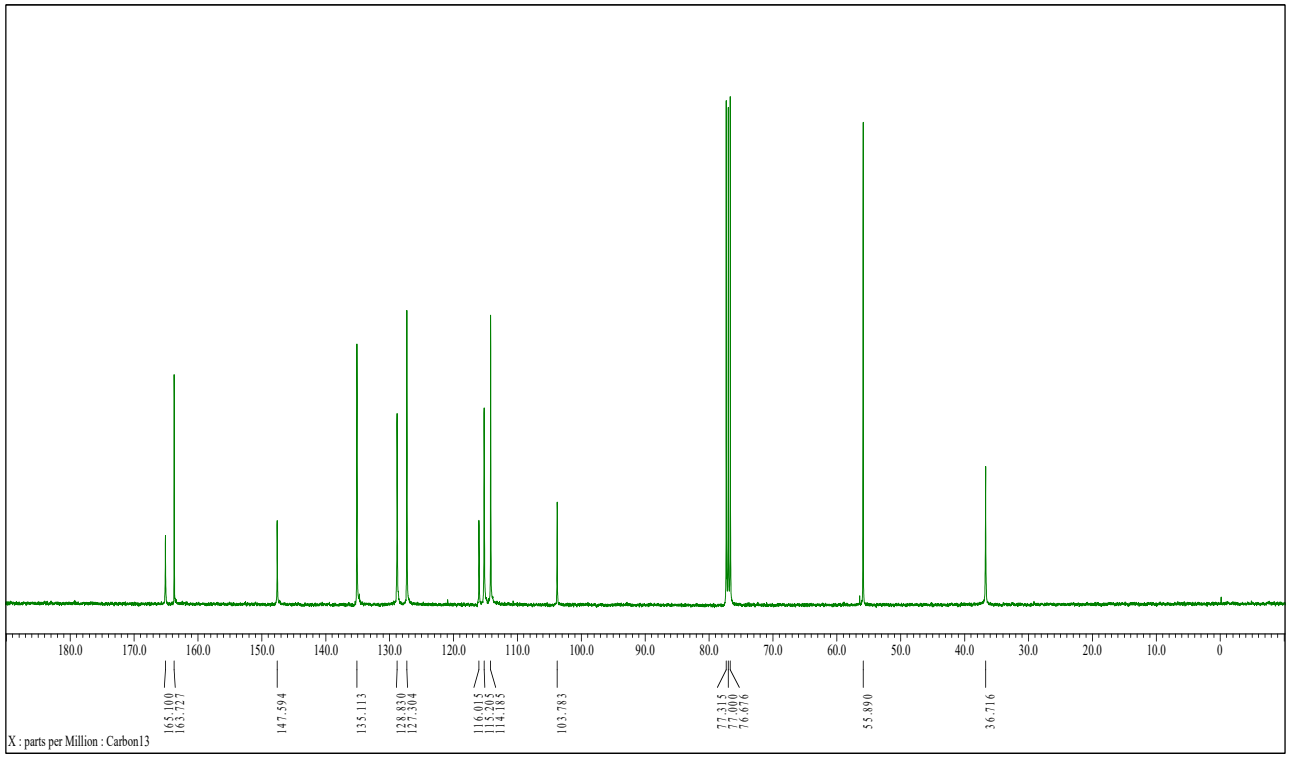

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S7g**



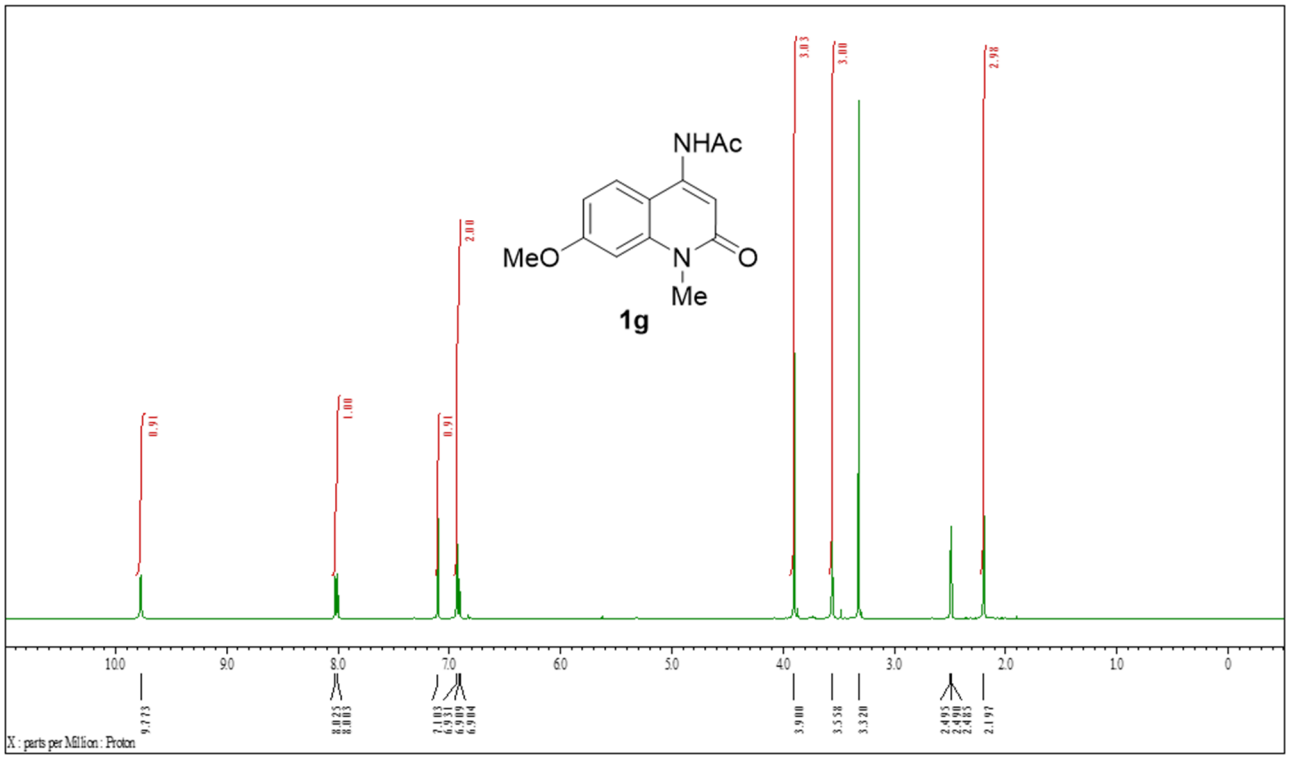
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S8g**



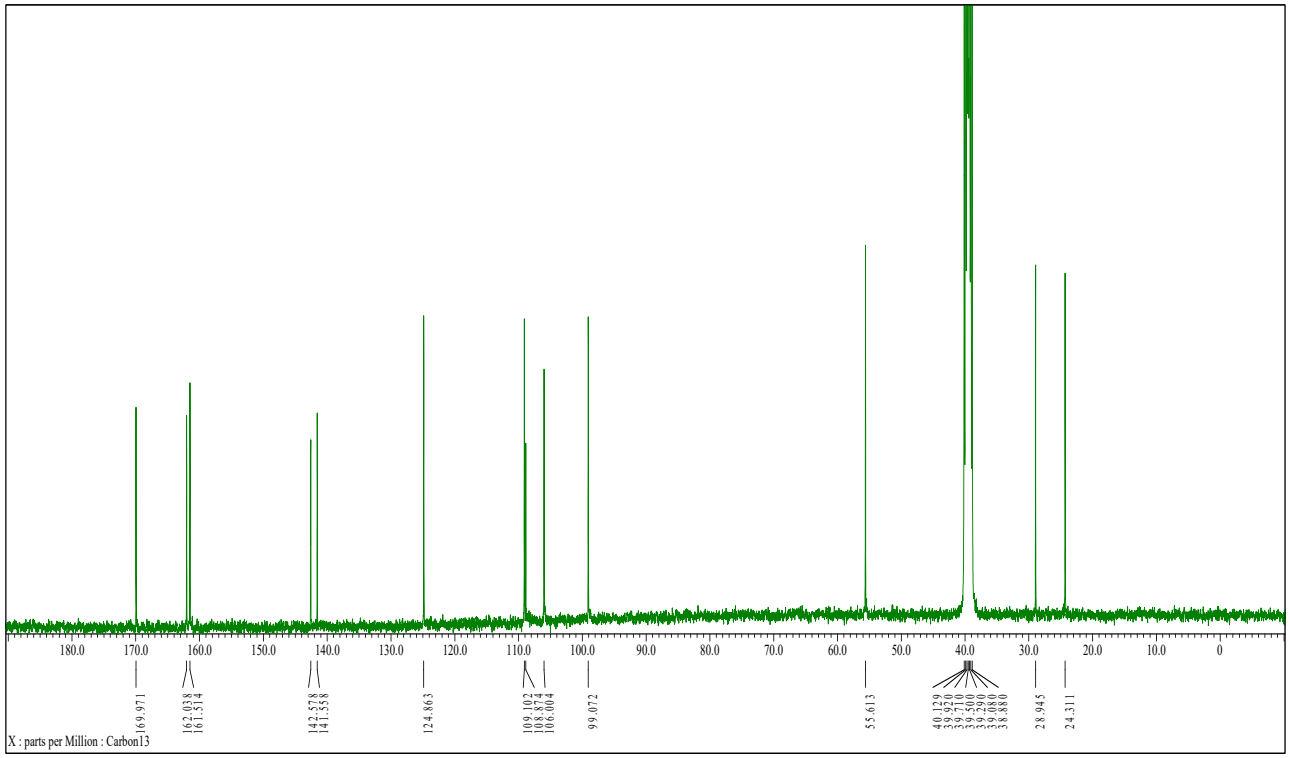

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S8g**



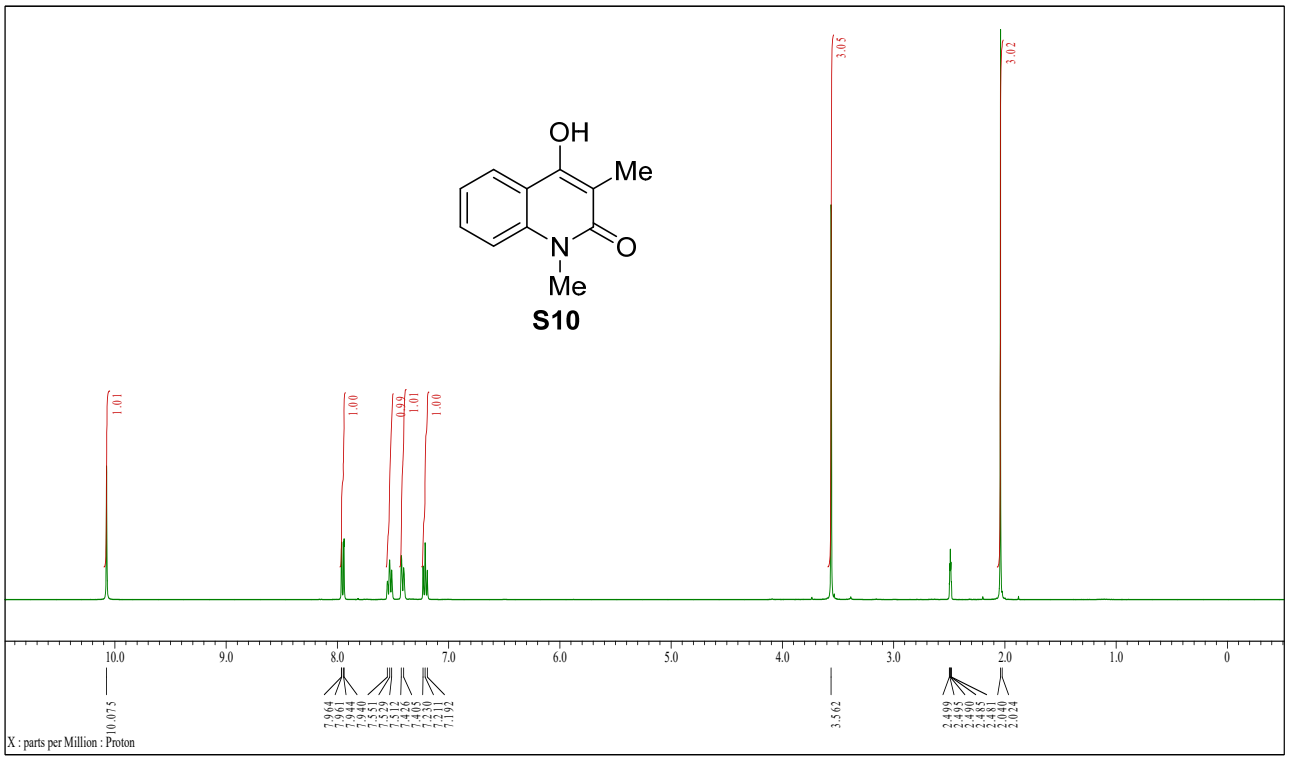
**$^{1}$H NMR (400 MHz, DMSO-$d_6$) of 1g**



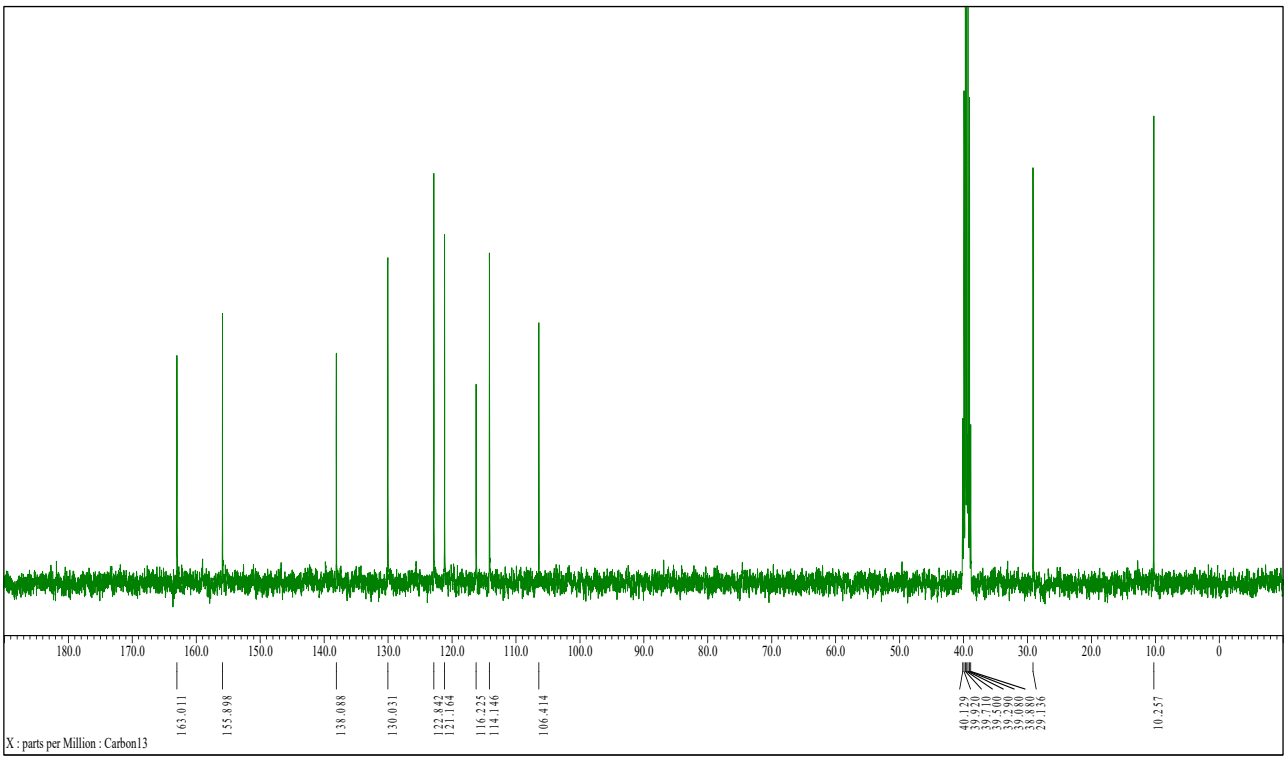

**$^{13}$C NMR (100 MHz, DMSO-$d_6$) of 1g**



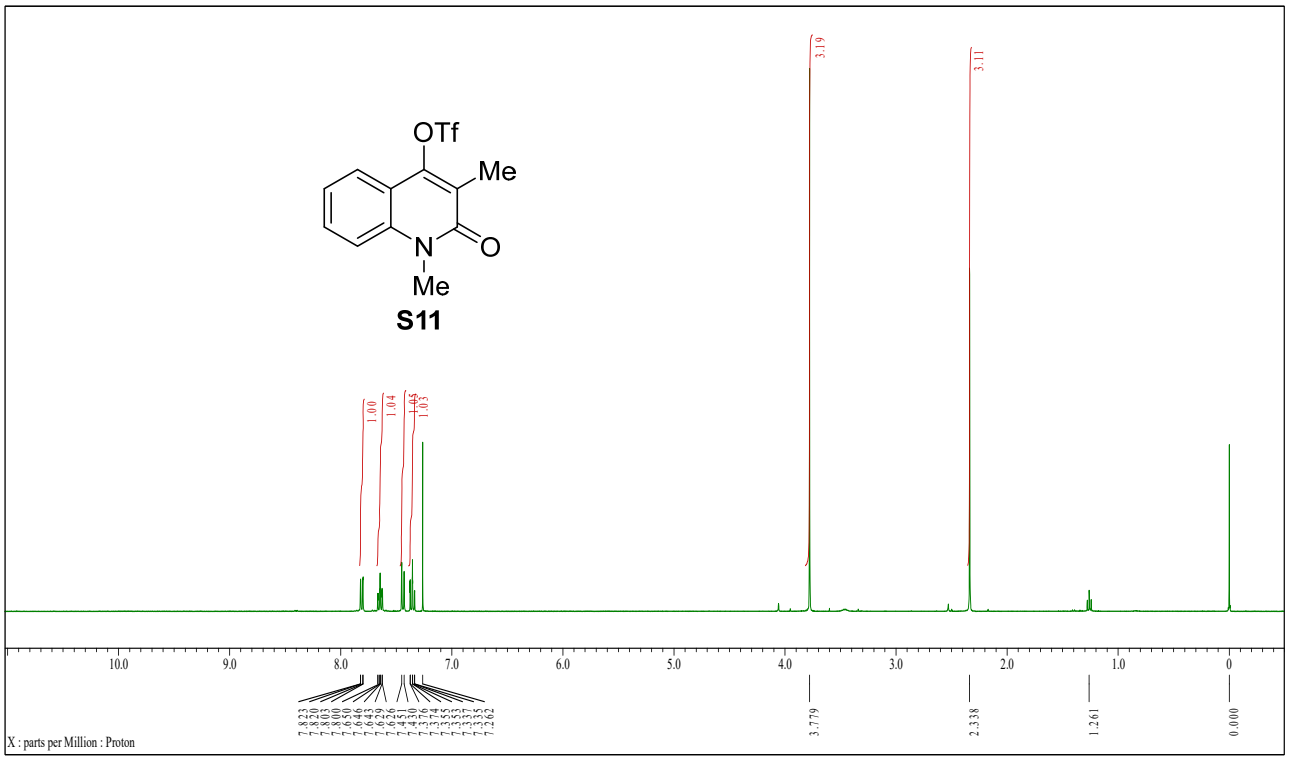
**$^{1}$H NMR (400 MHz, DMSO-$d_6$) of S10**



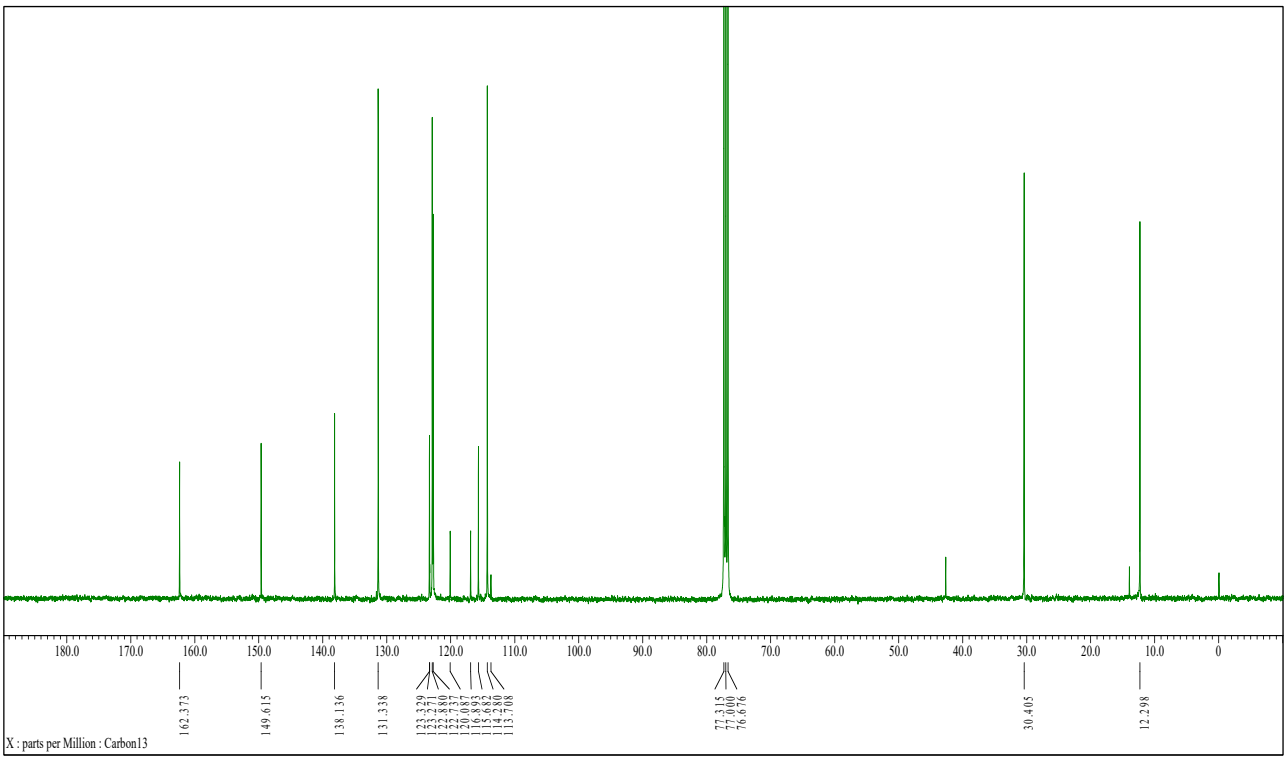

**$^{13}$C NMR (100 MHz, DMSO-$d_6$) of S10**



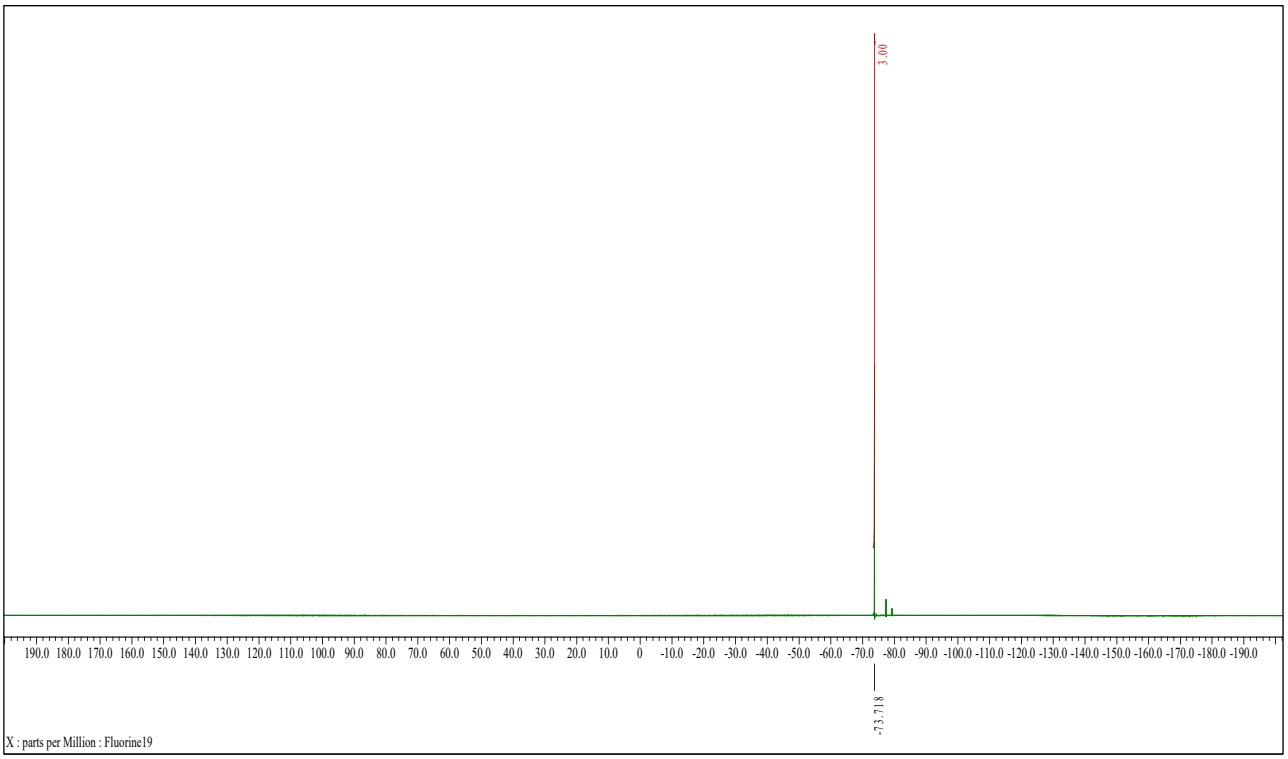
**$^{1}$H NMR (400 MHz, $CDCl_3$) of S11**



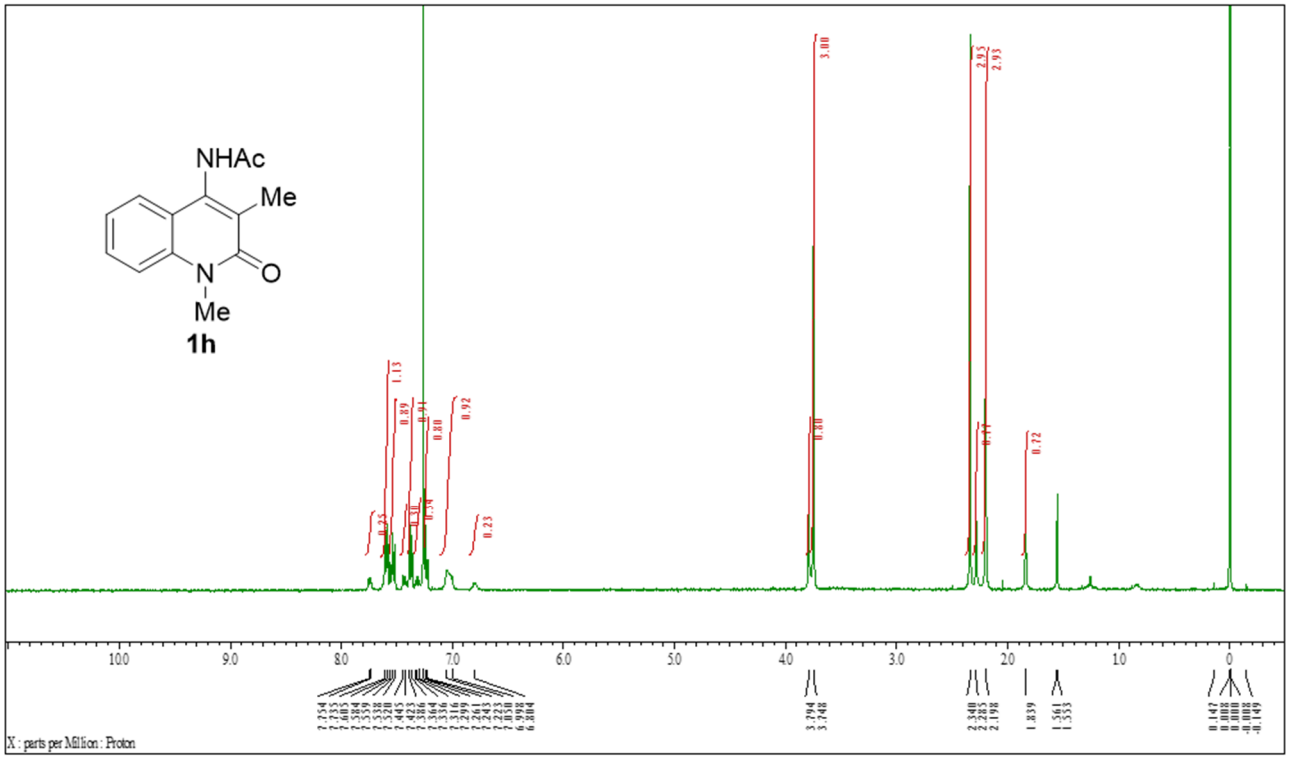

**$^{13}$C NMR (100 MHz, $CDCl_3$) of S11**



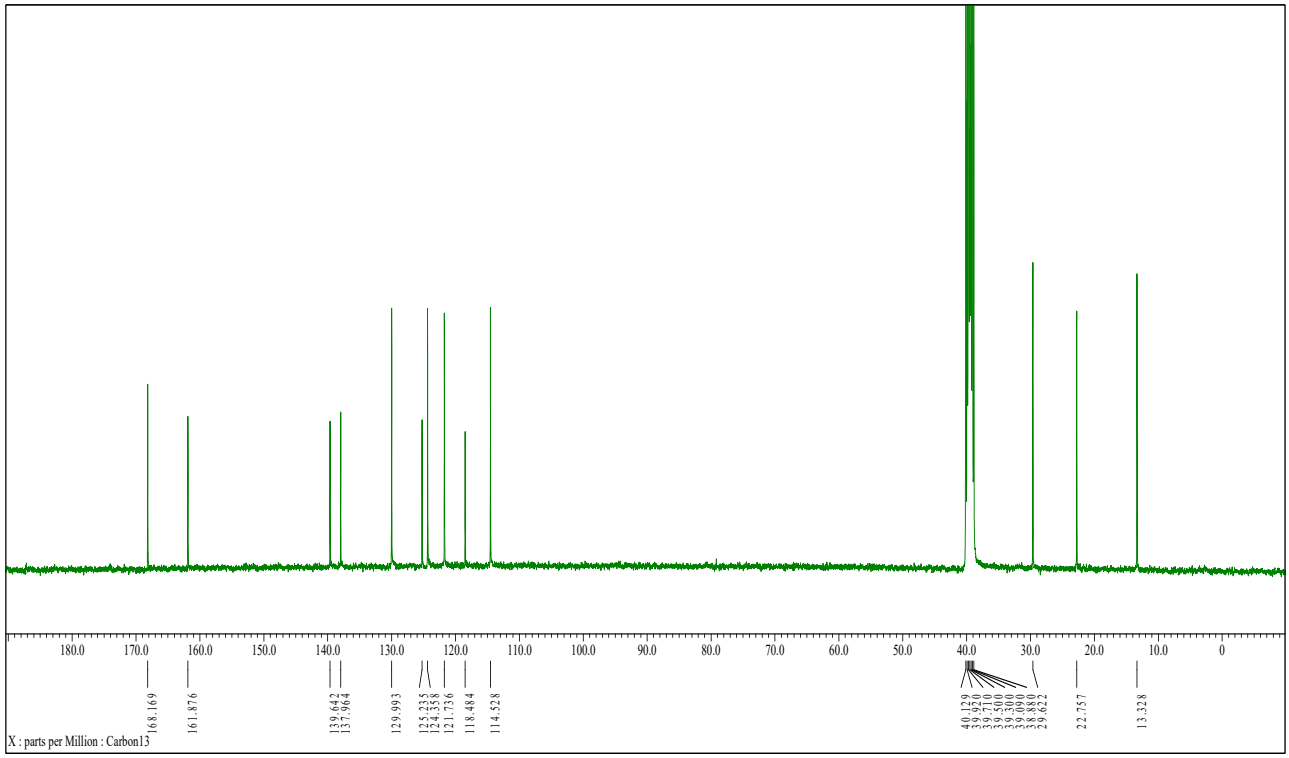
**$^{19}F$ NMR (376 MHz, $CDCl_3$) of S11**



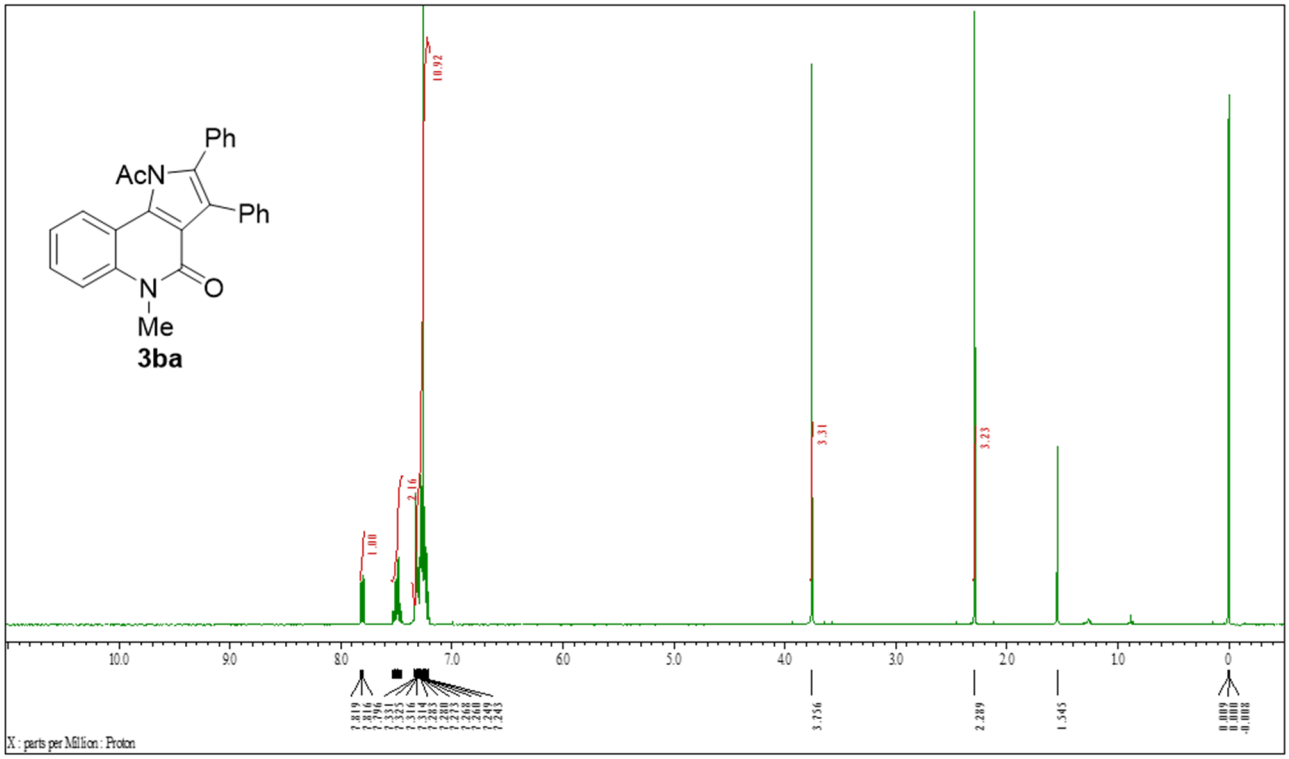
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 1h**



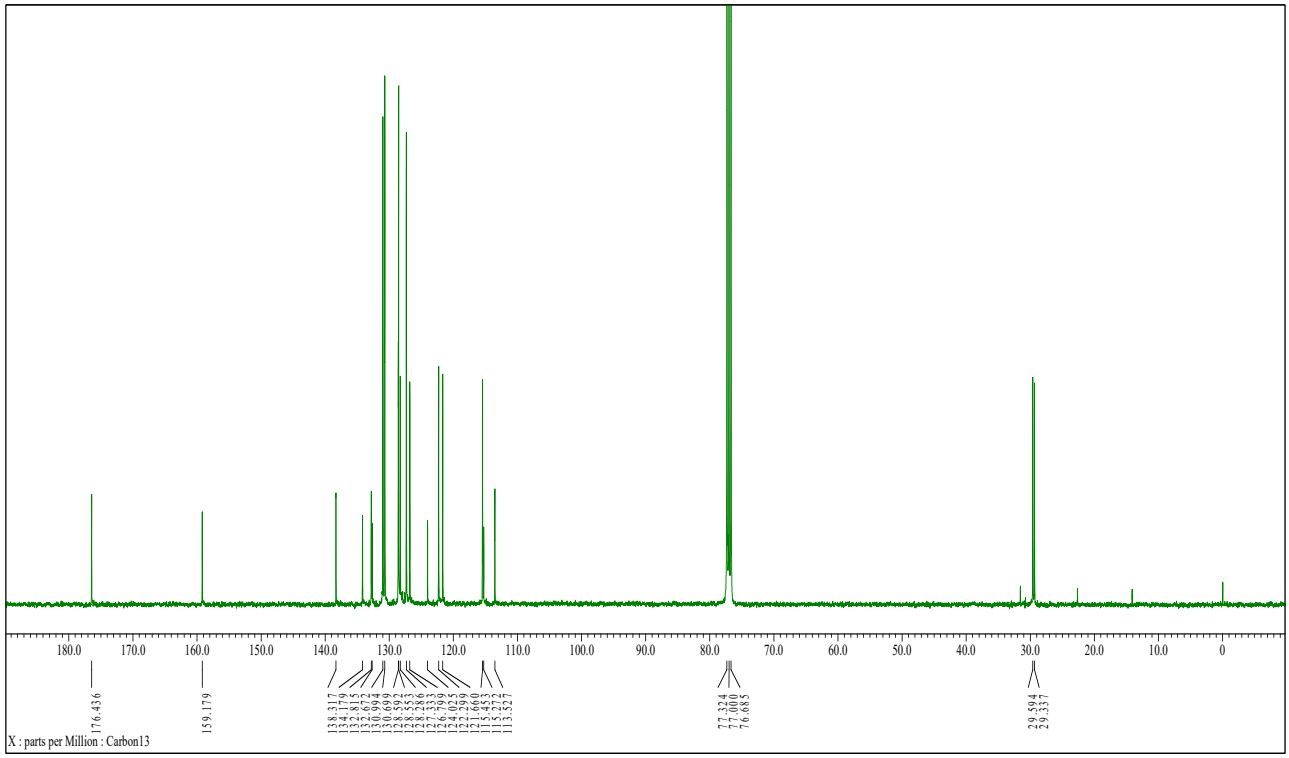

**$^{13}$C NMR (100 MHz, DMSO-$d_6$) of 1h**



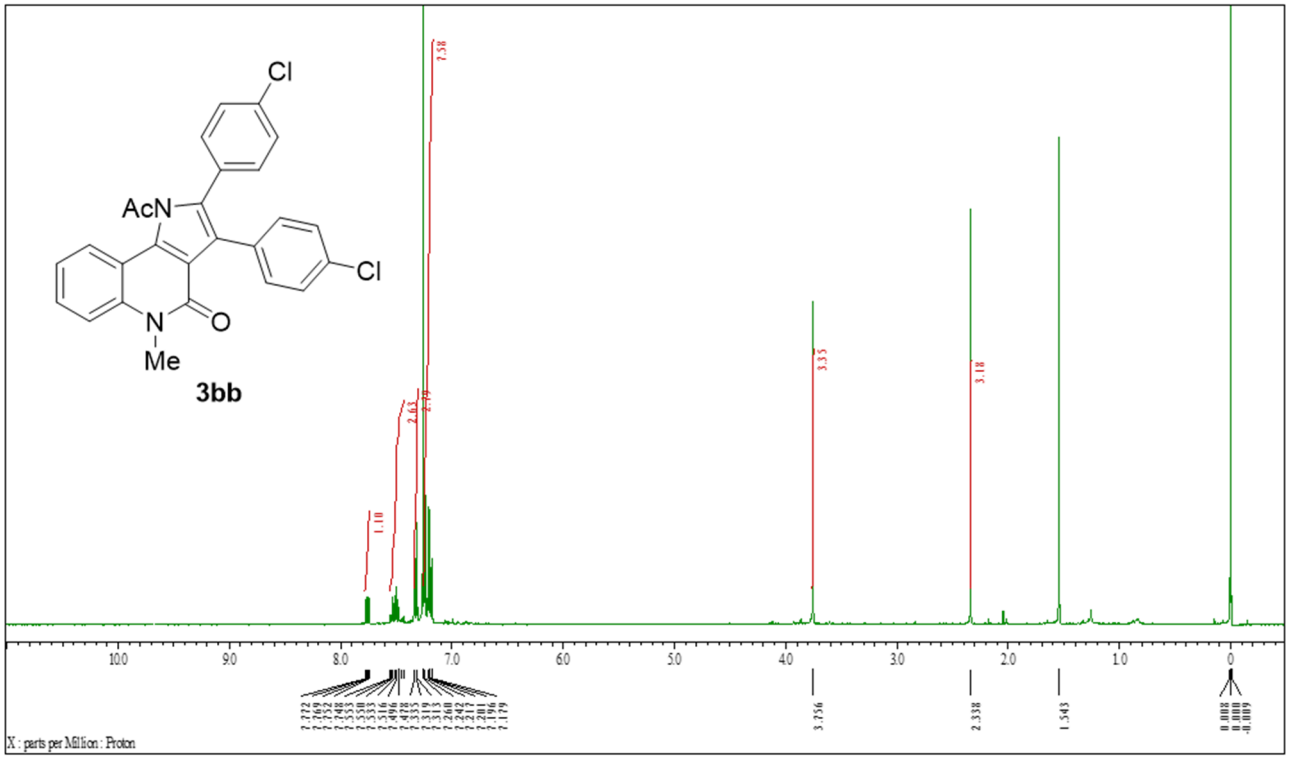
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3ba**



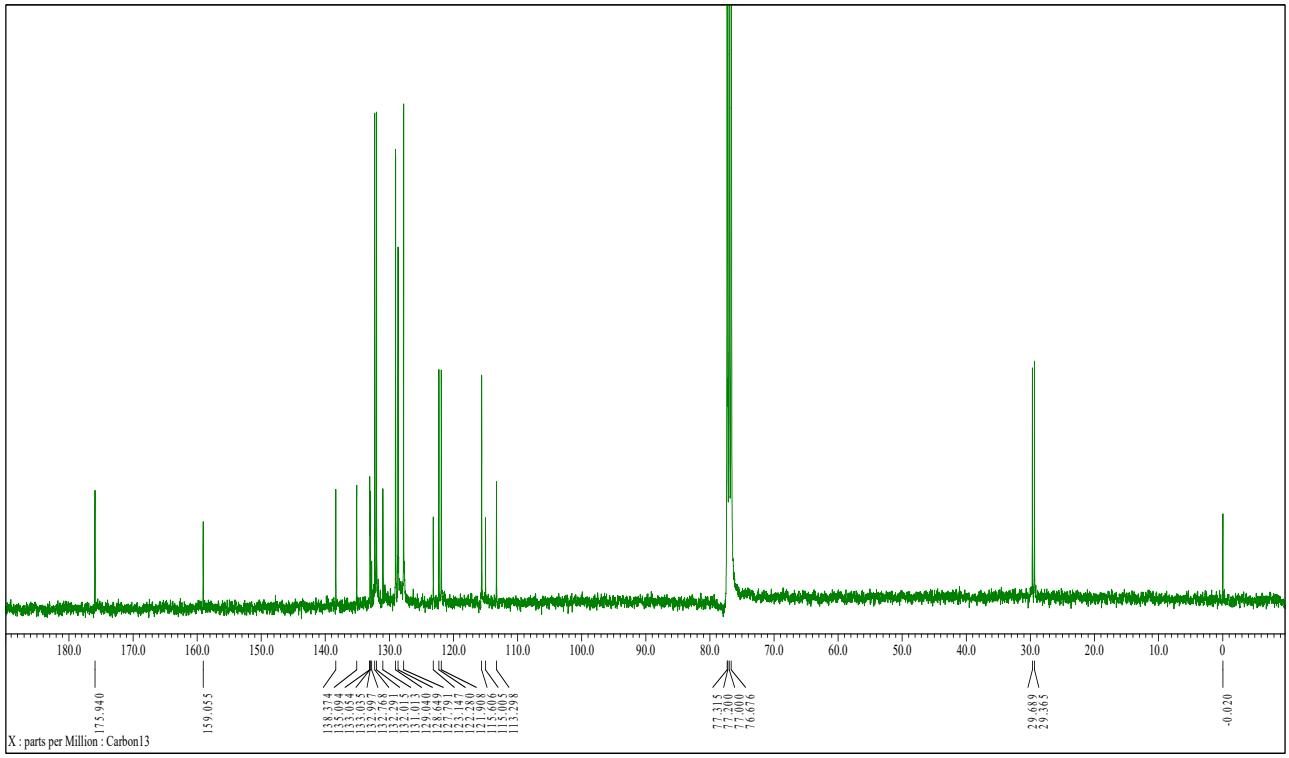

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3ba**



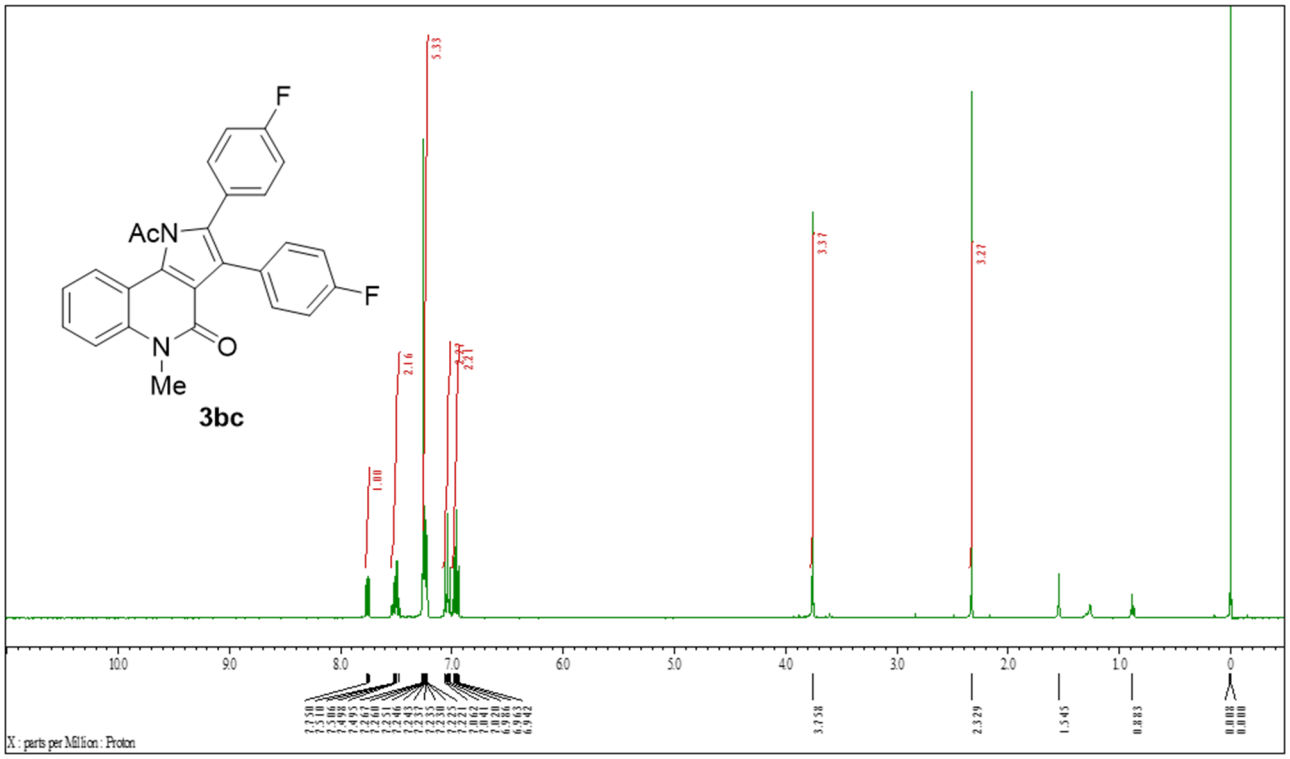
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bb**



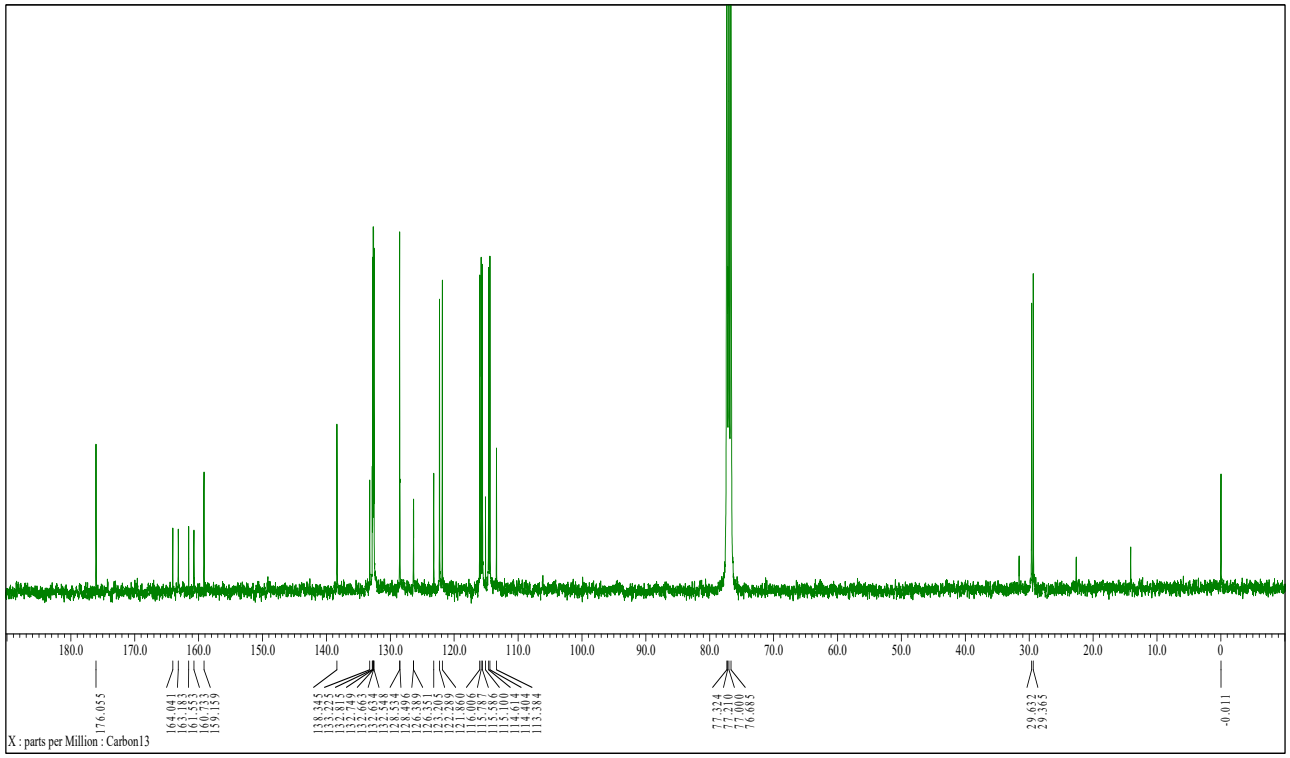

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bb**



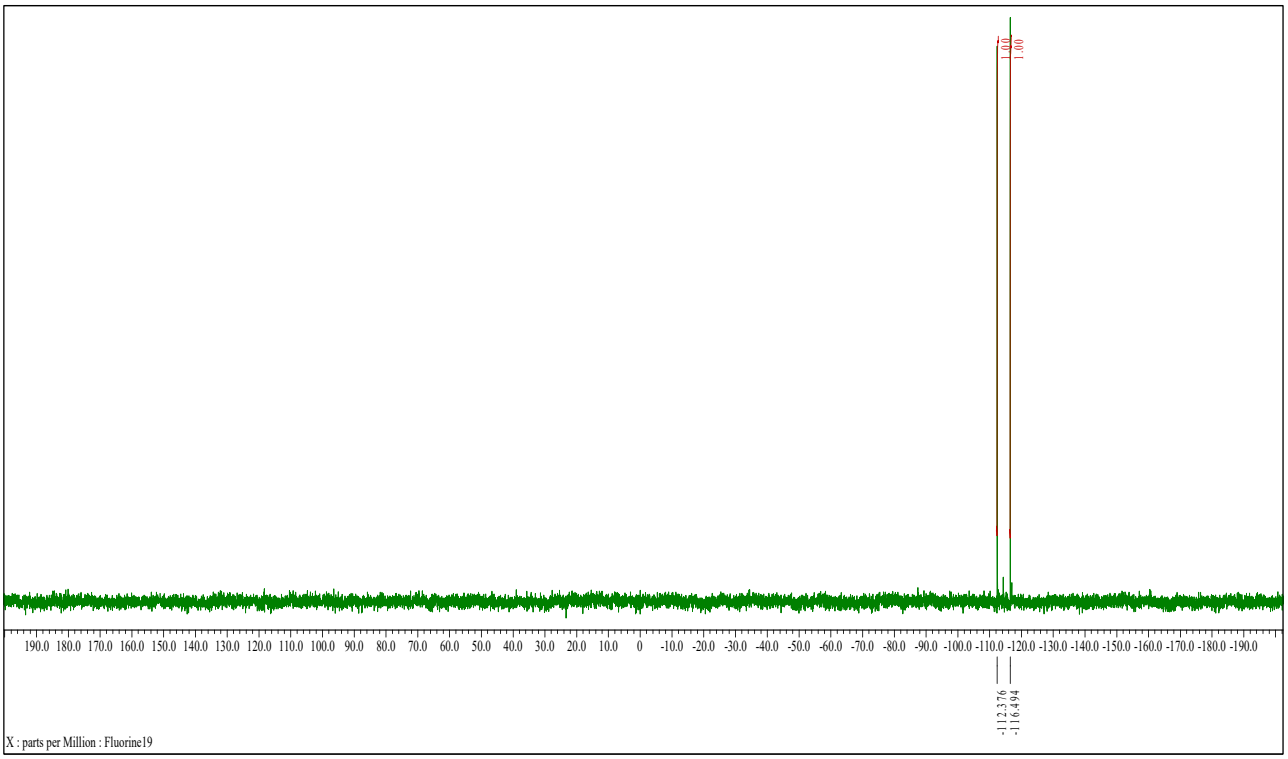
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bc**



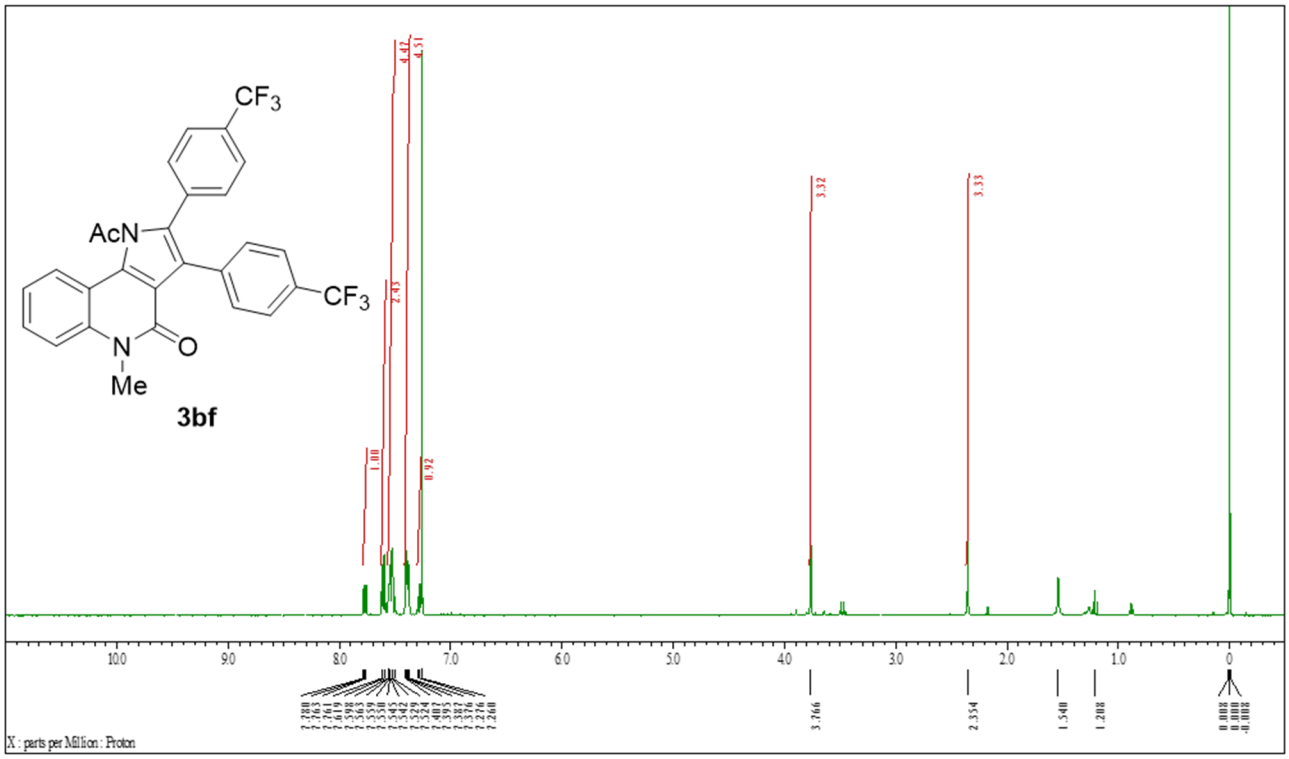

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bc**



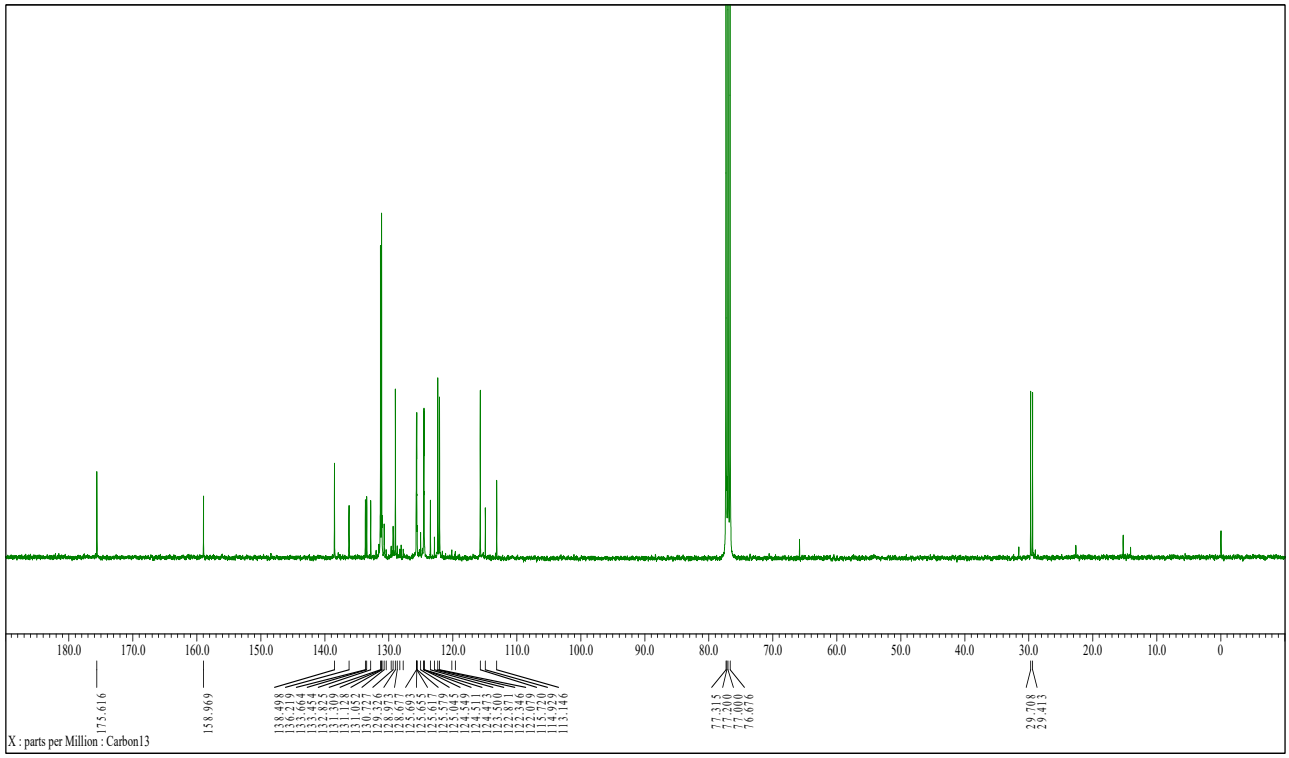
**$^{19}F$ NMR (376 MHz, $CDCl_3$) of 3bc**



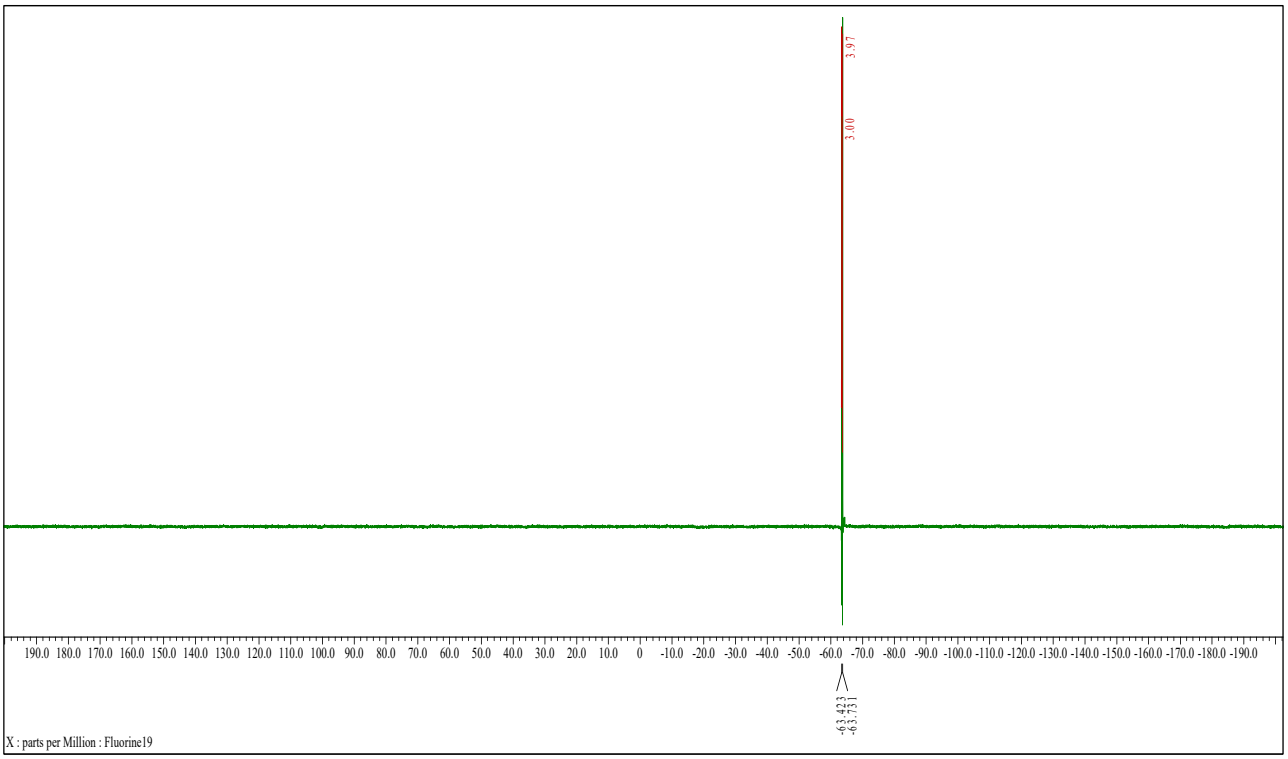
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bf**



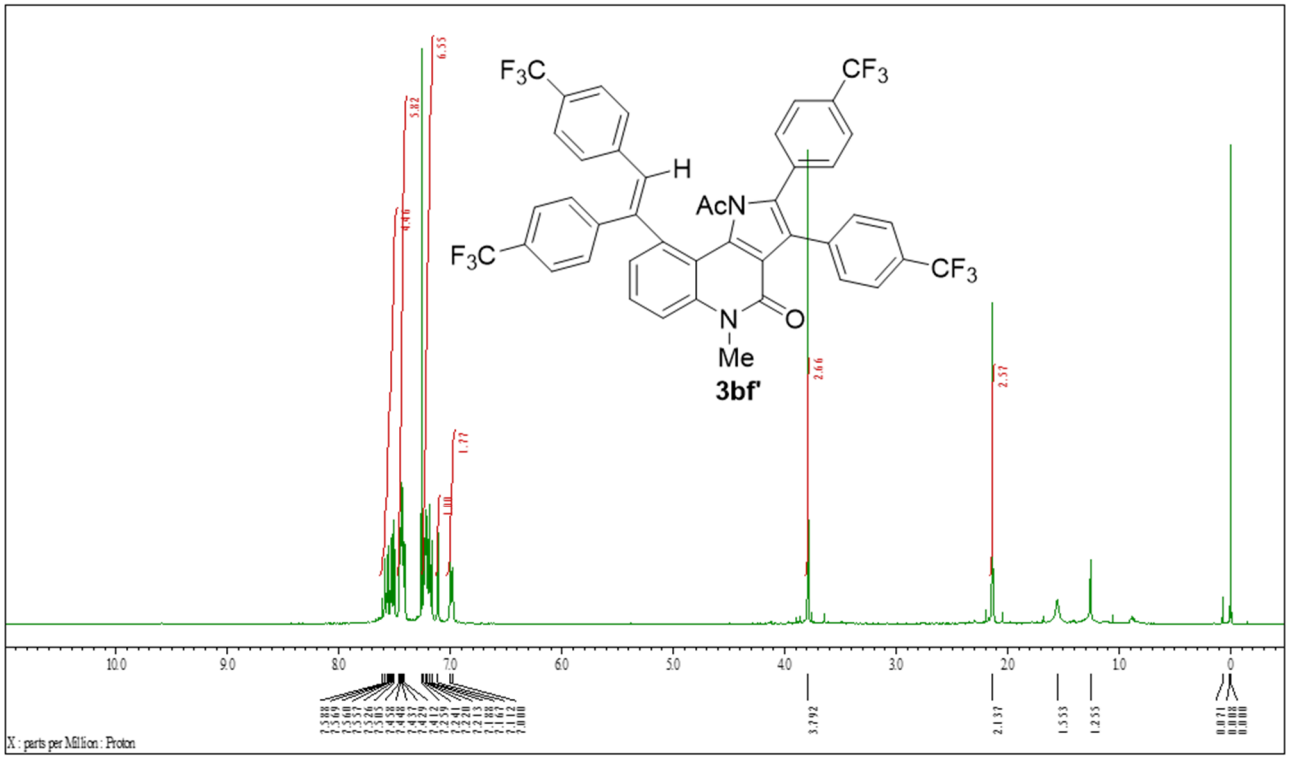

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bf**



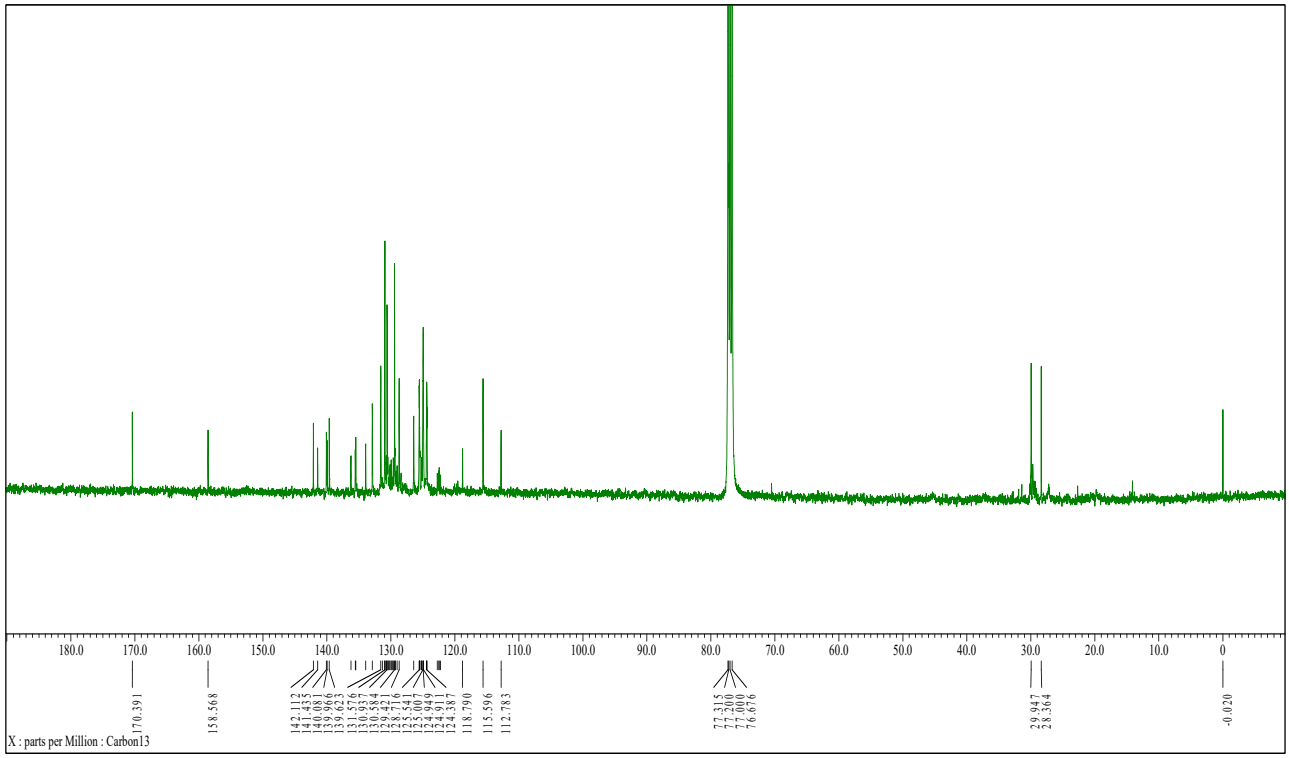
**$^{19}$F NMR (376 MHz, $CDCl_3$) of 3bf**



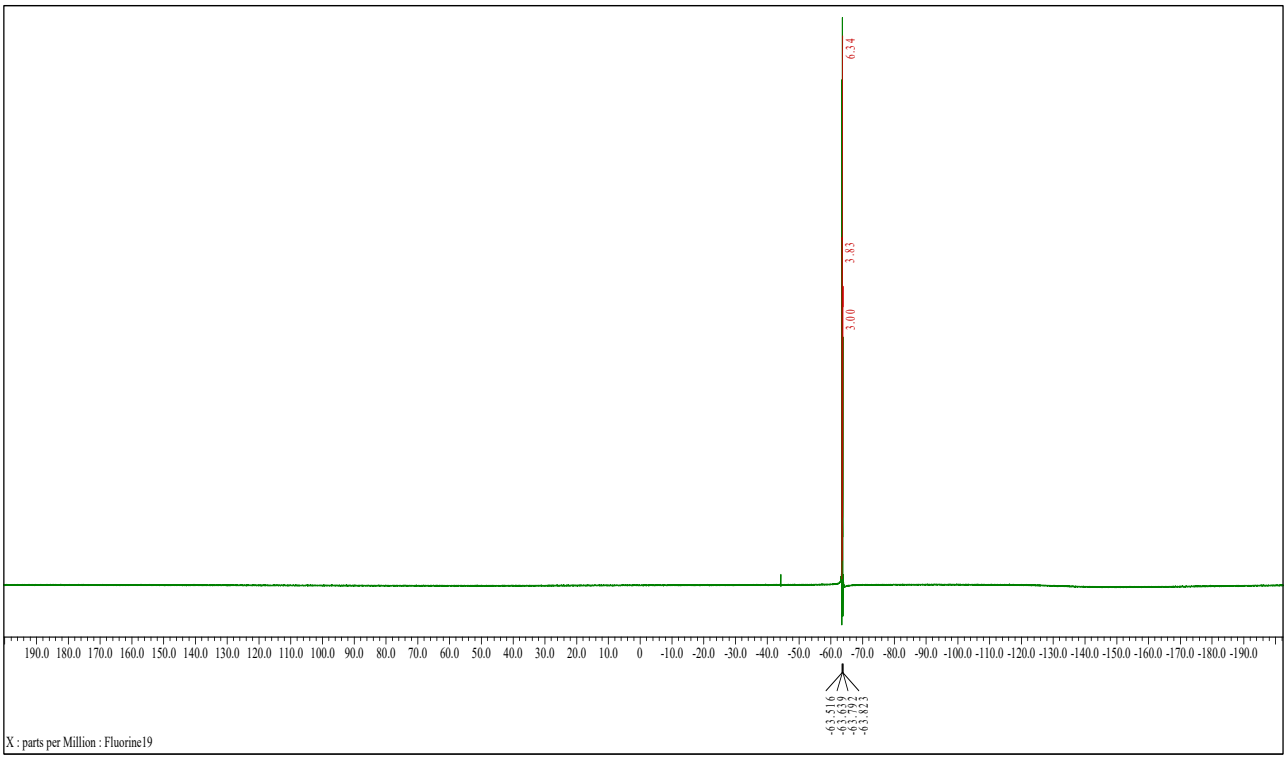
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bf'**



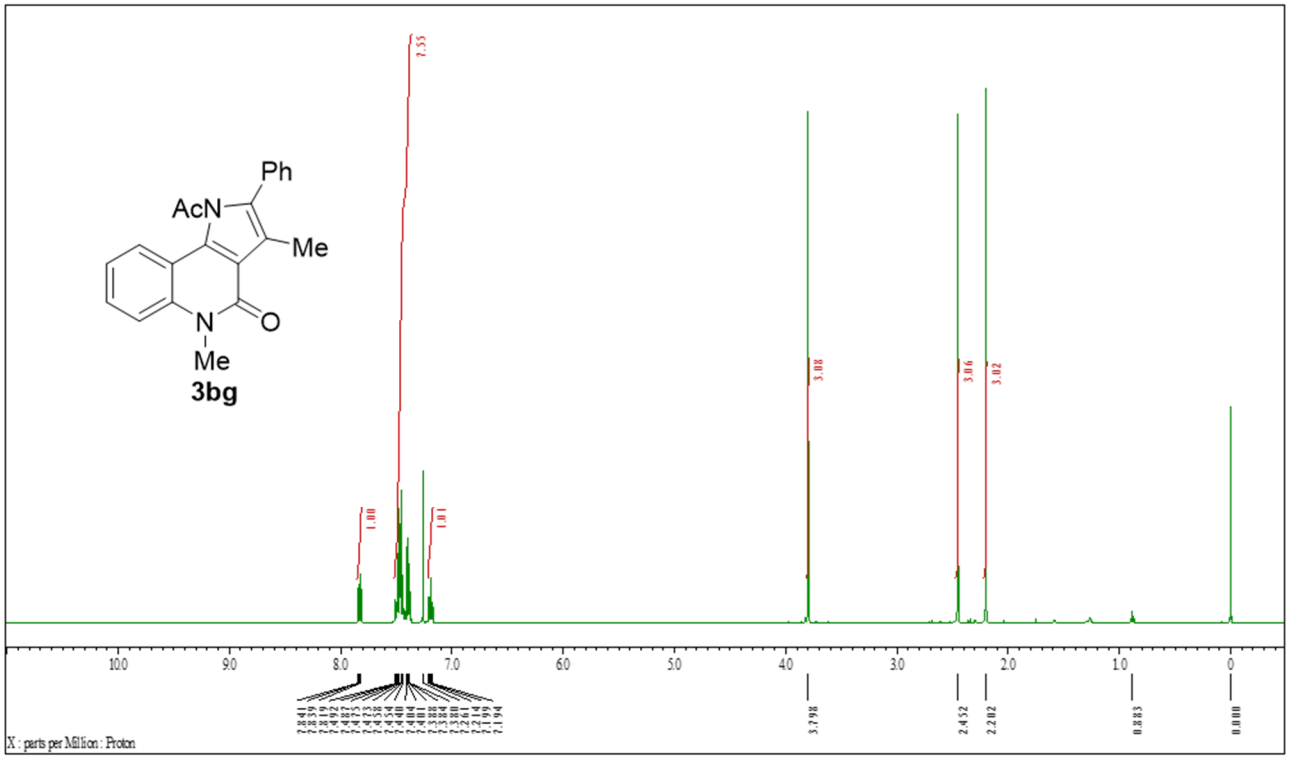

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bf'**



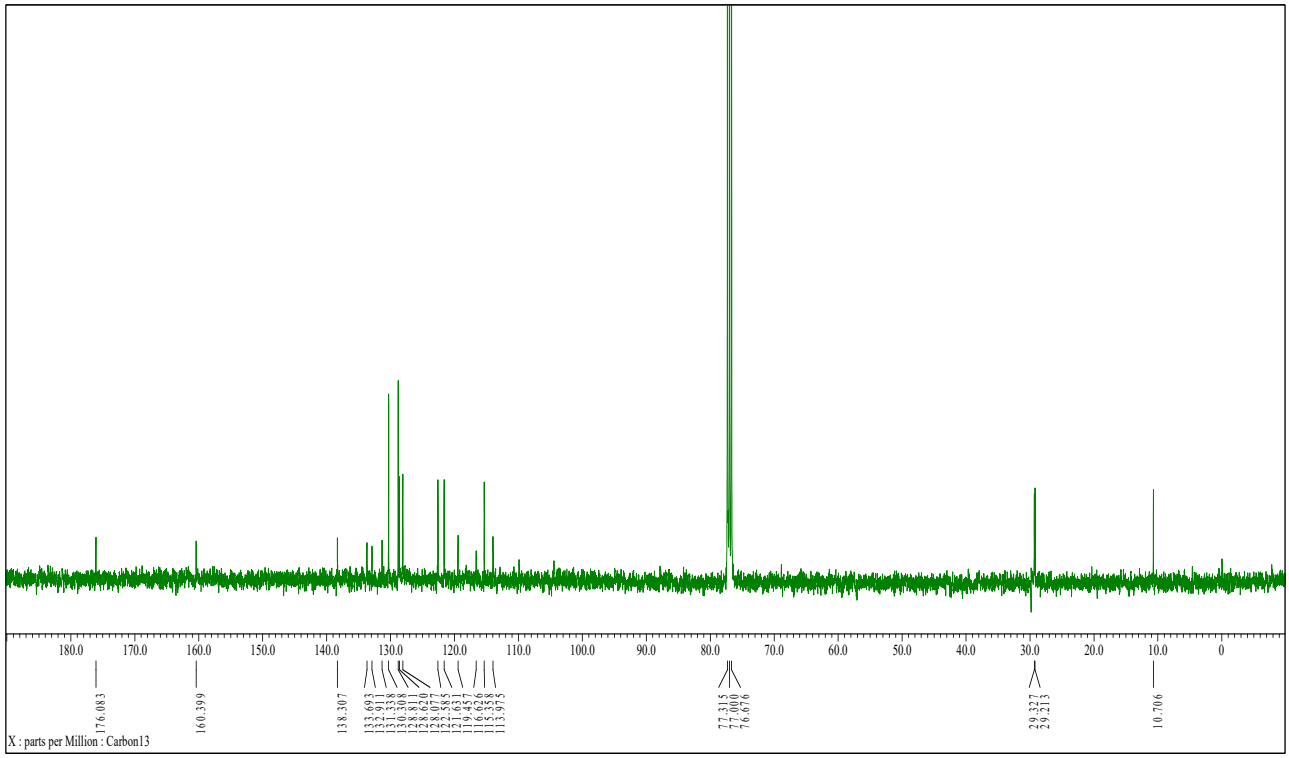
**$^{19}F$ NMR (376 MHz, $CDCl_3$) of 3bf'**



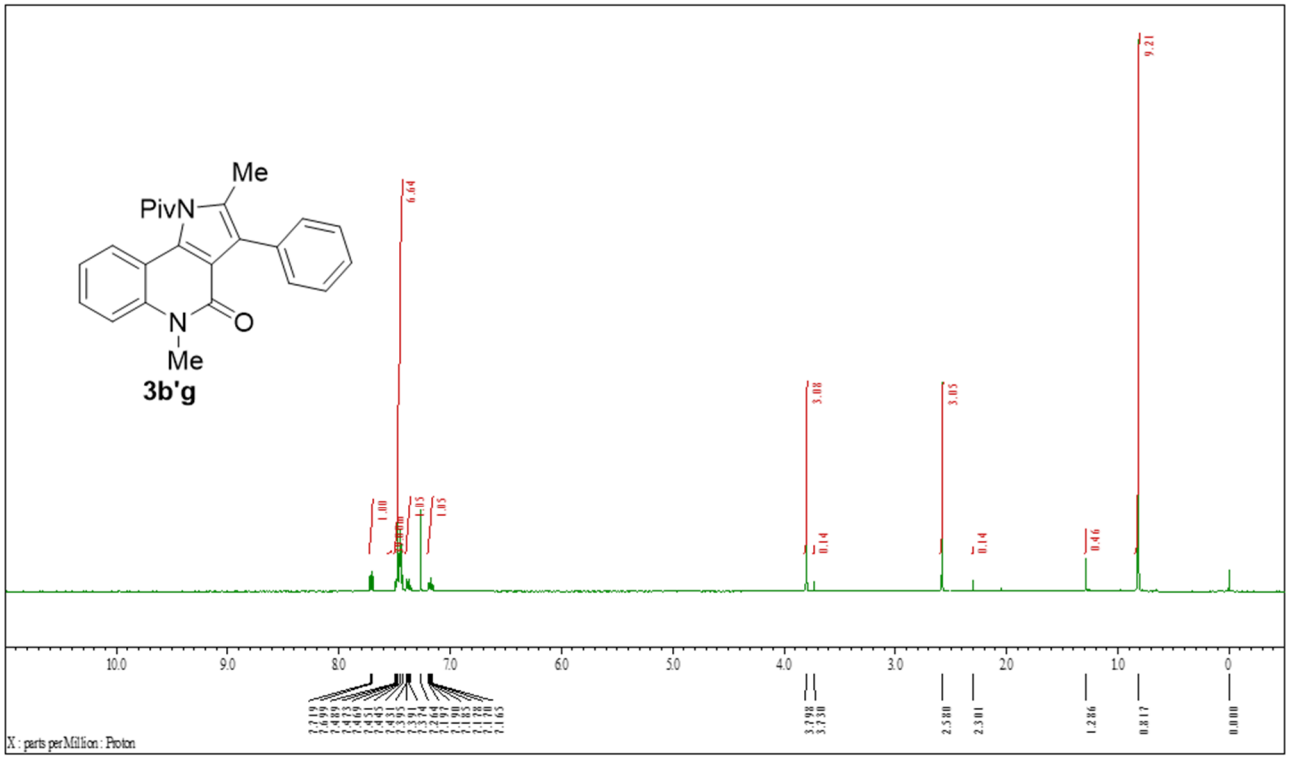
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bg**



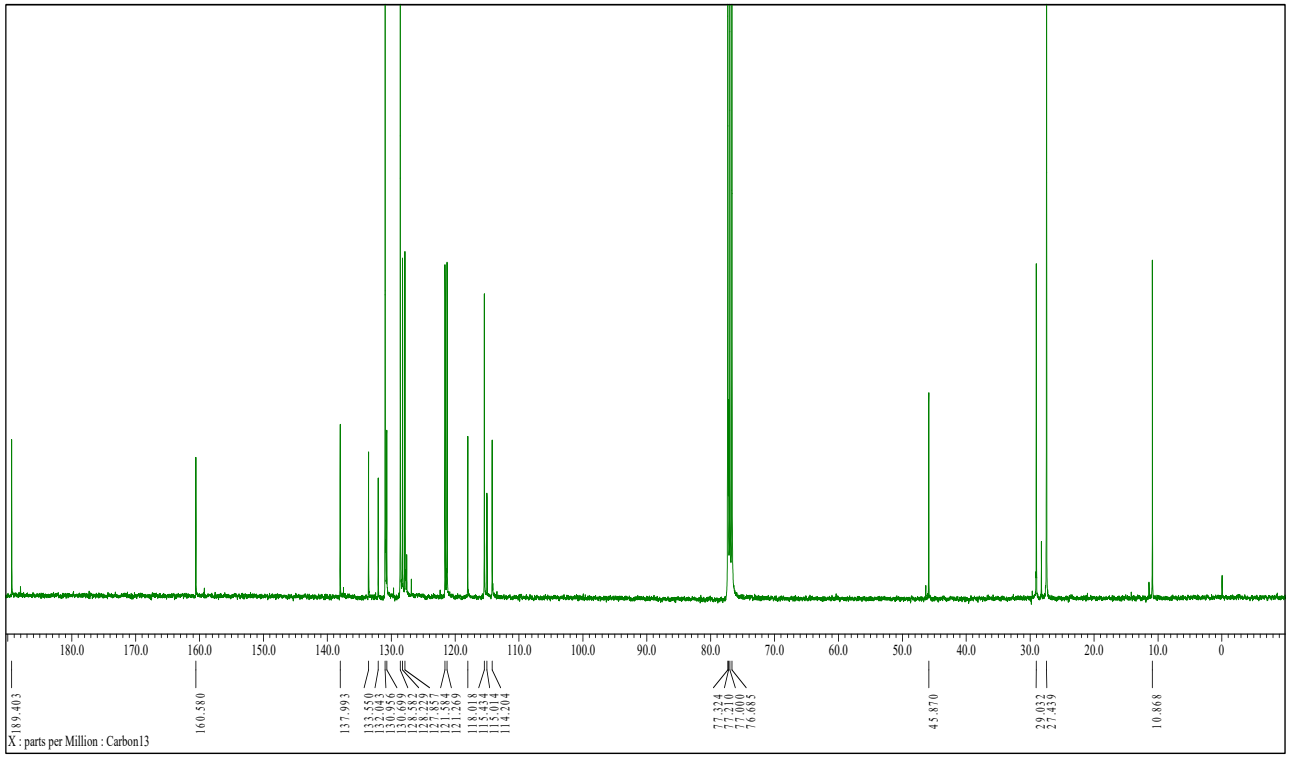

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bg**



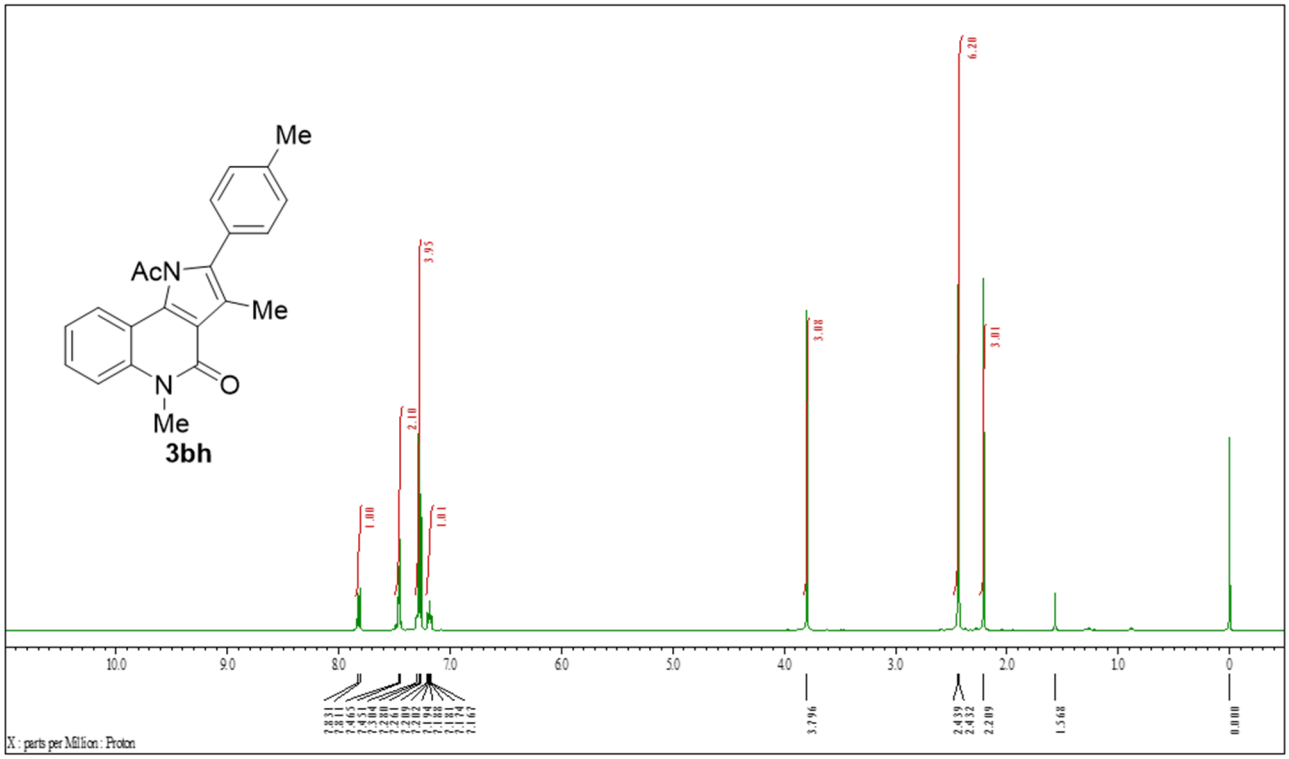
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3b'g**



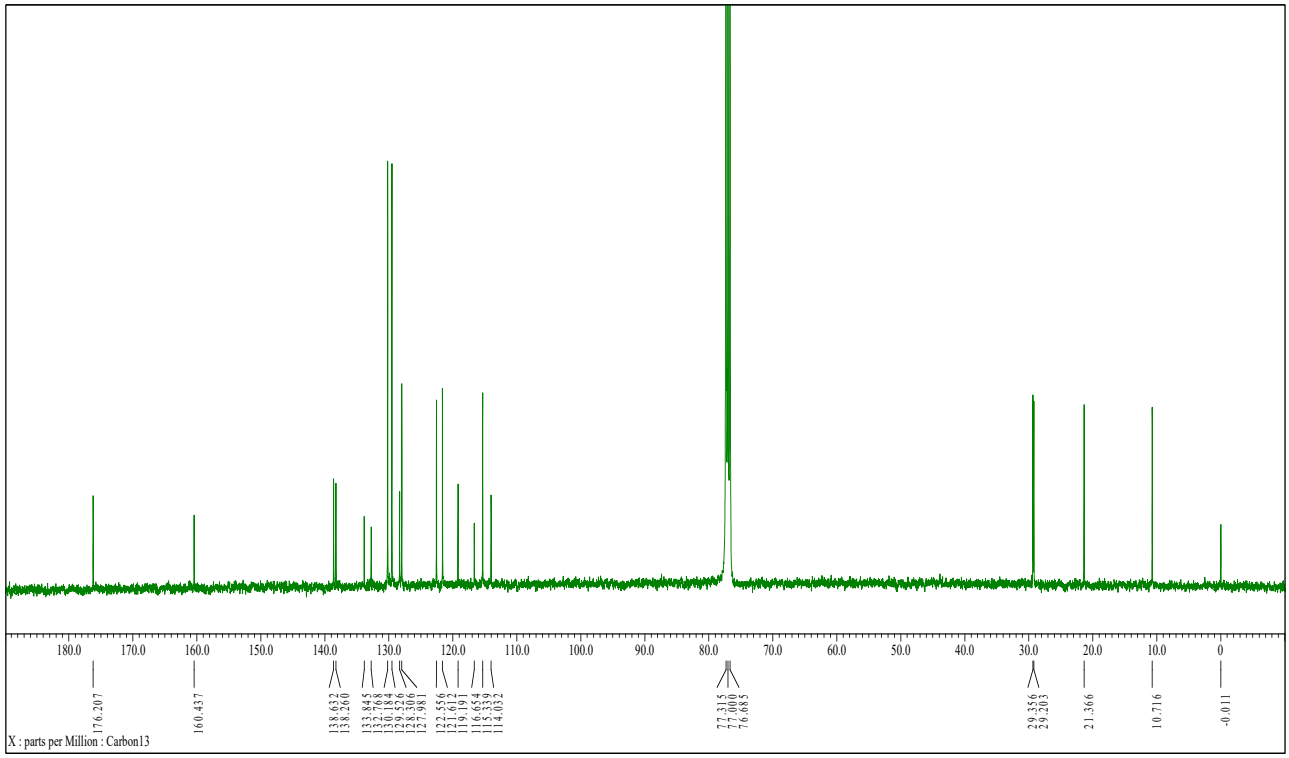

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3b'g**



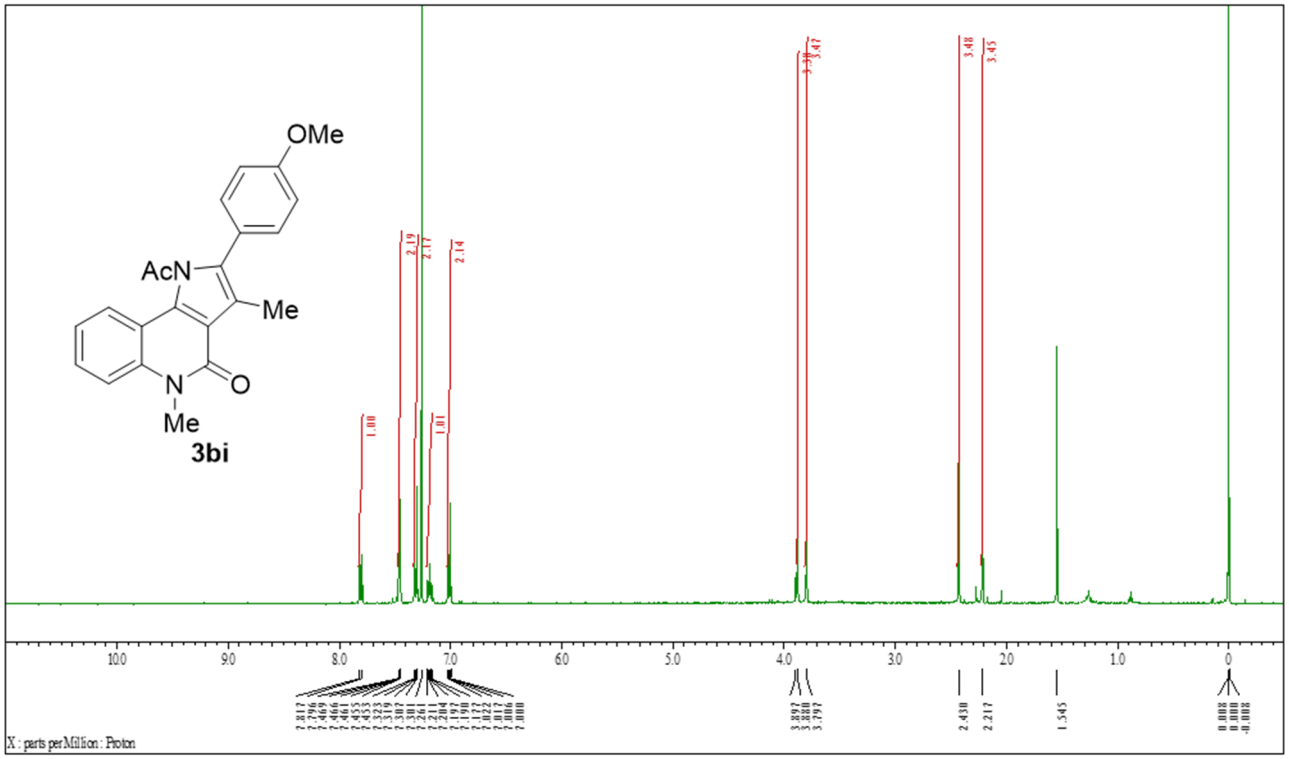
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bh**



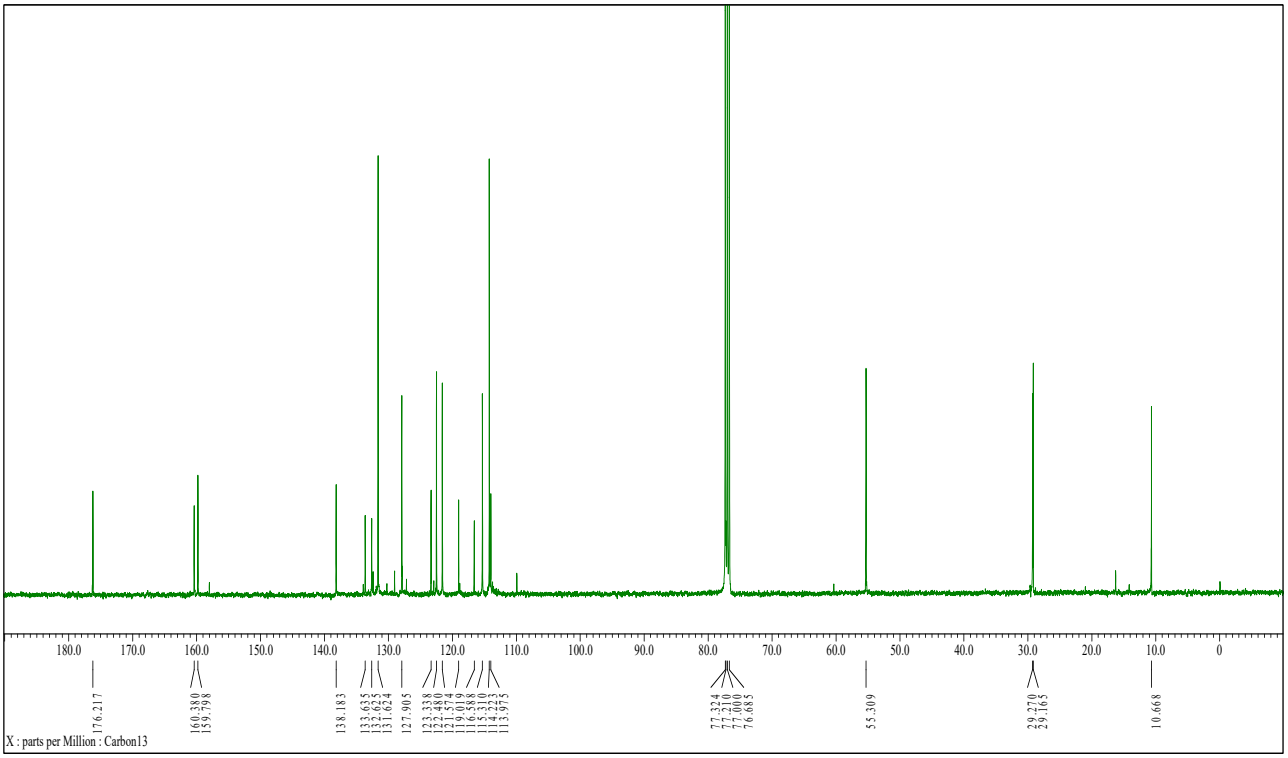

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bh**



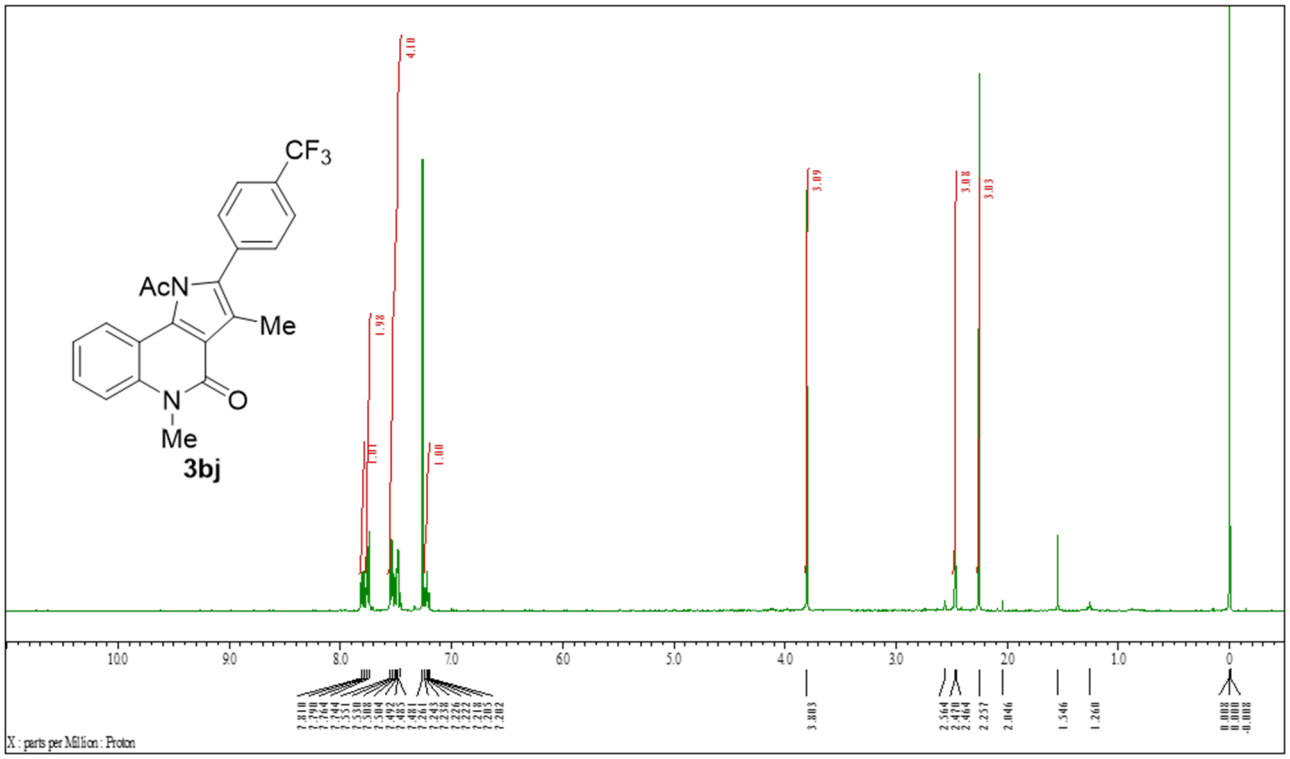
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bi**



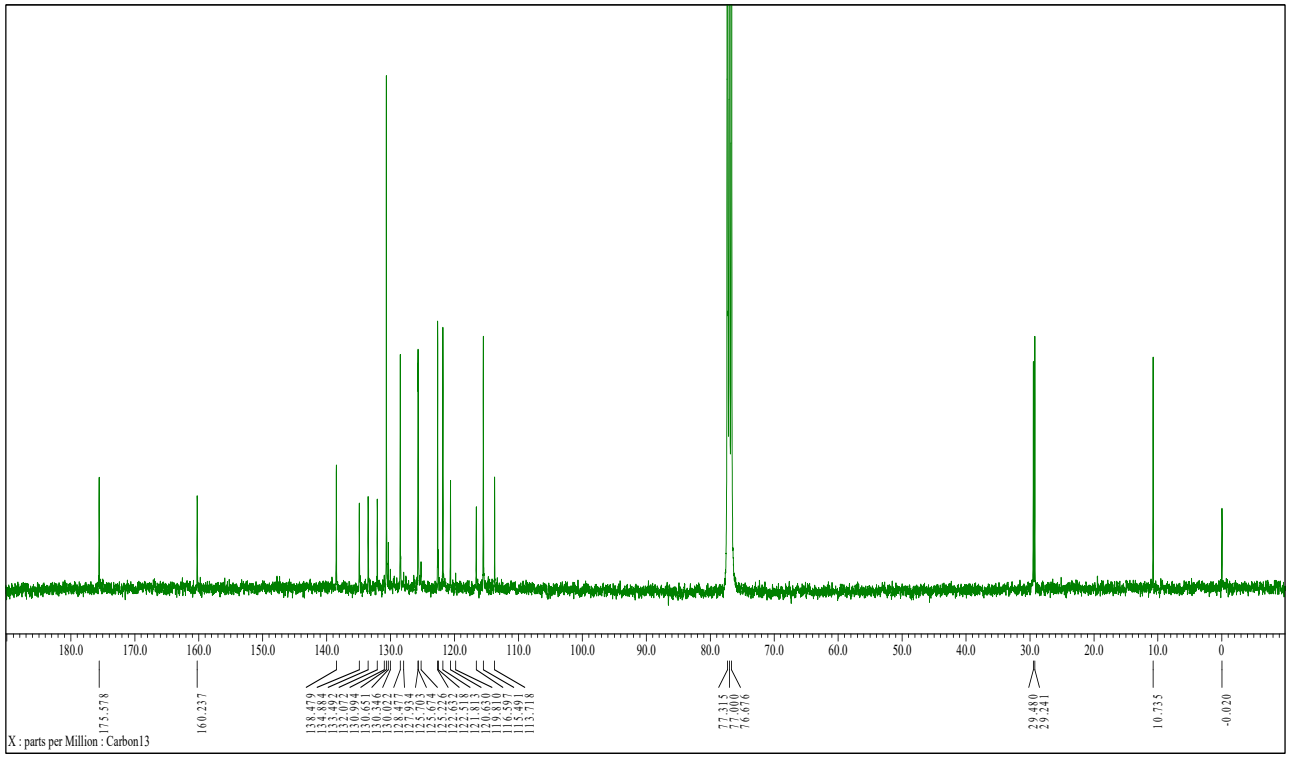

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bi**



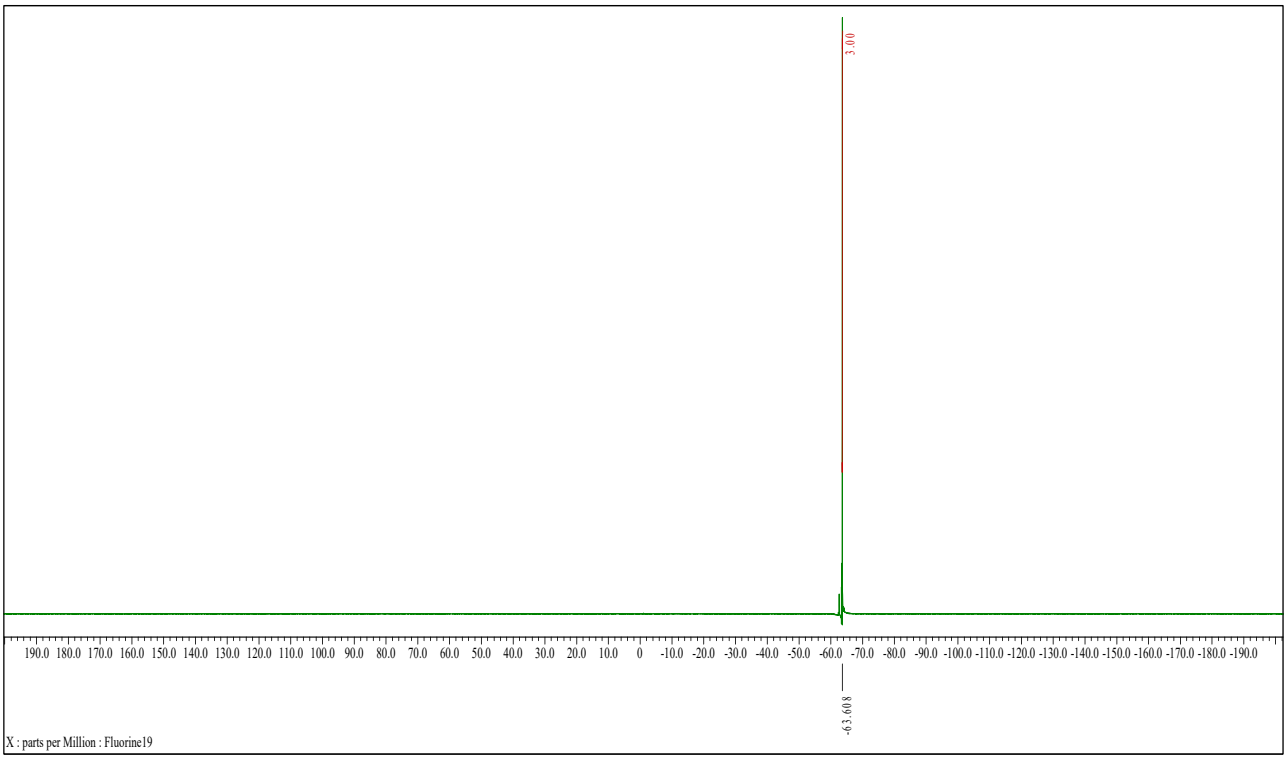
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bj**



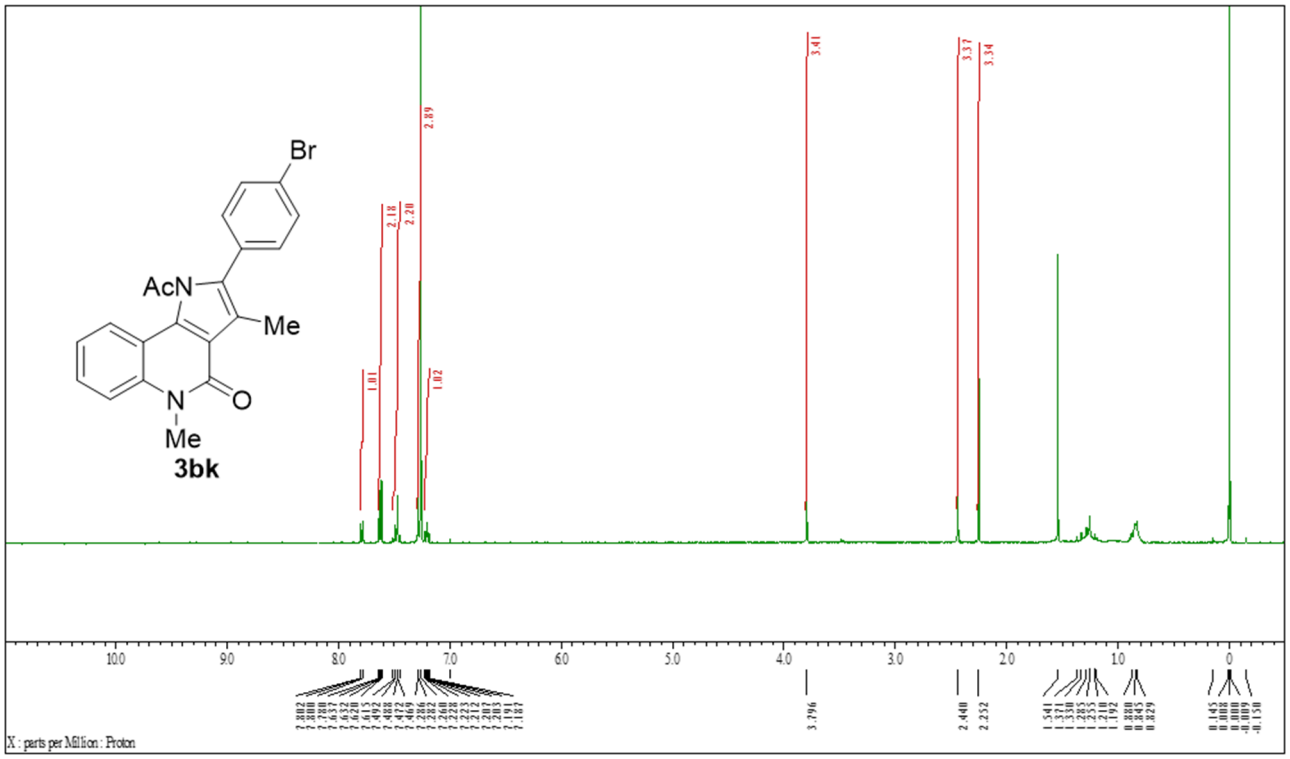

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bj**



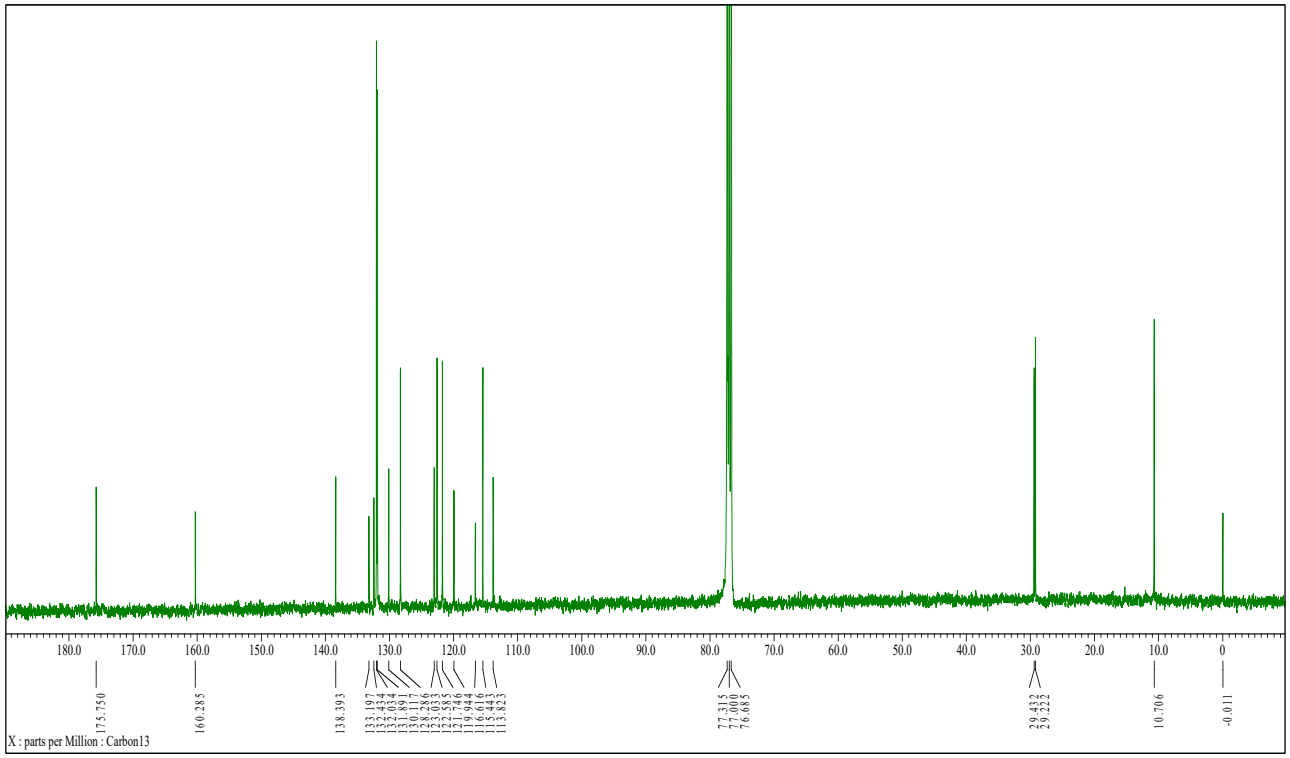
**$^{19}$F NMR (376 MHz, $CDCl_3$) of 3bj**



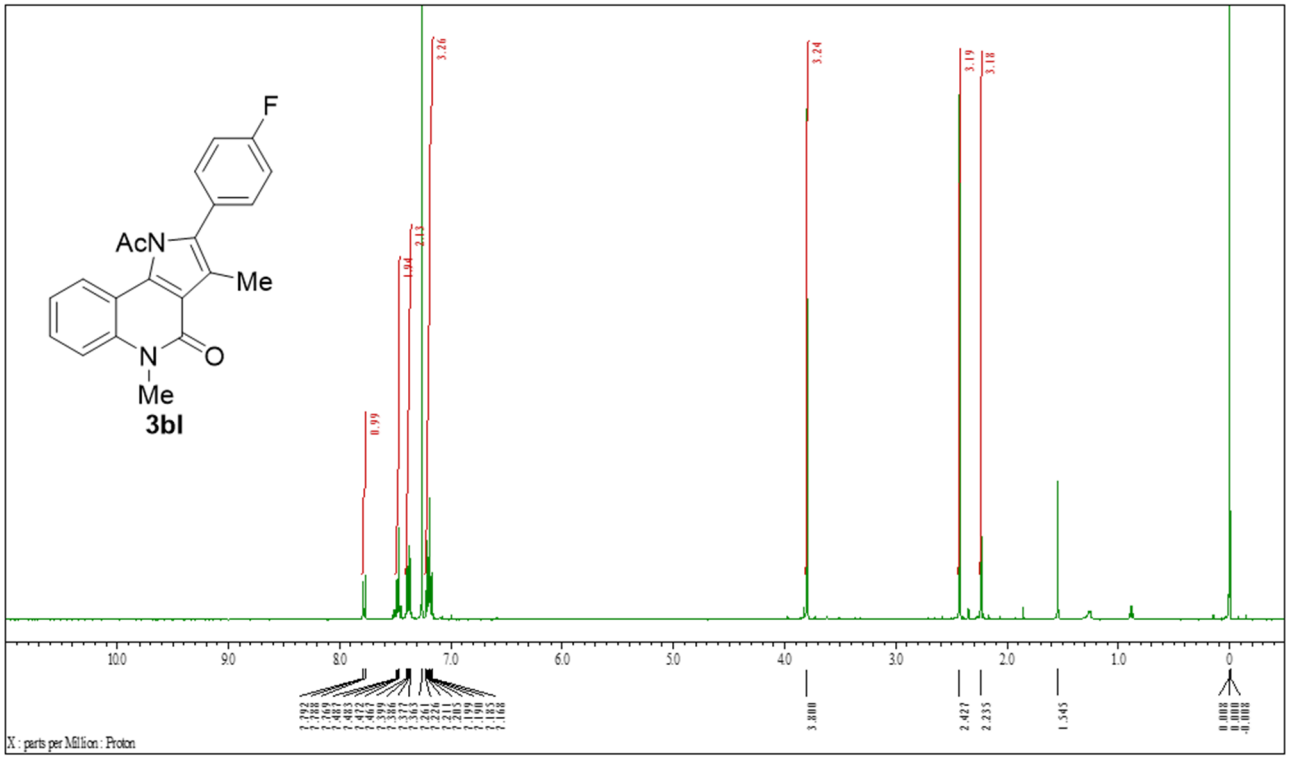
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bk**



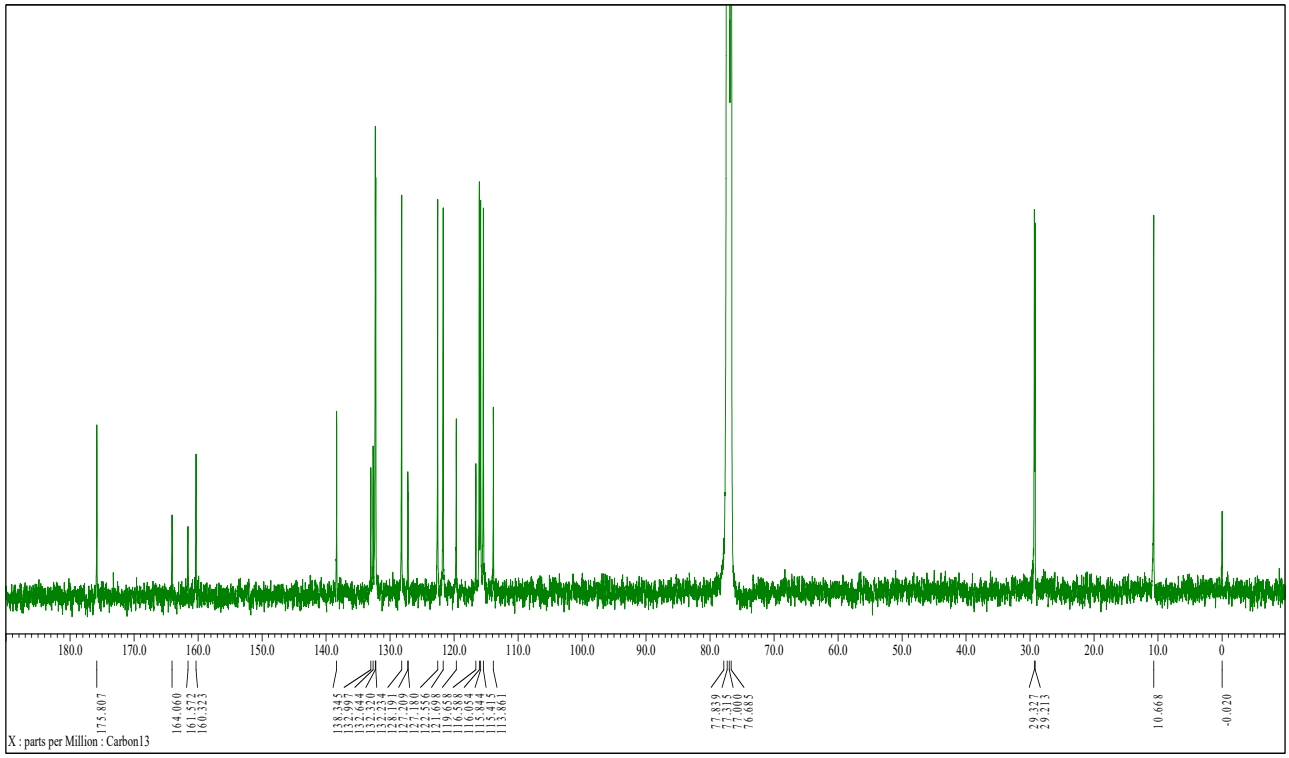

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bk**



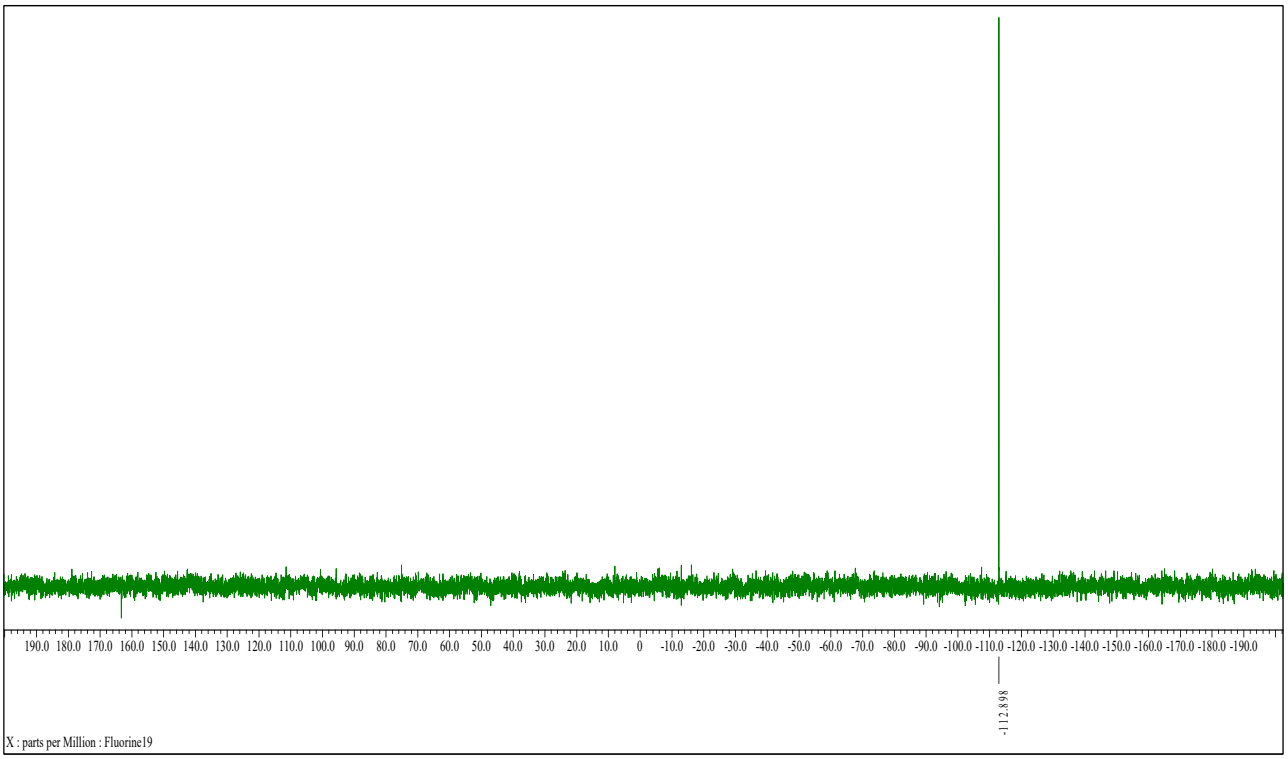
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bl**



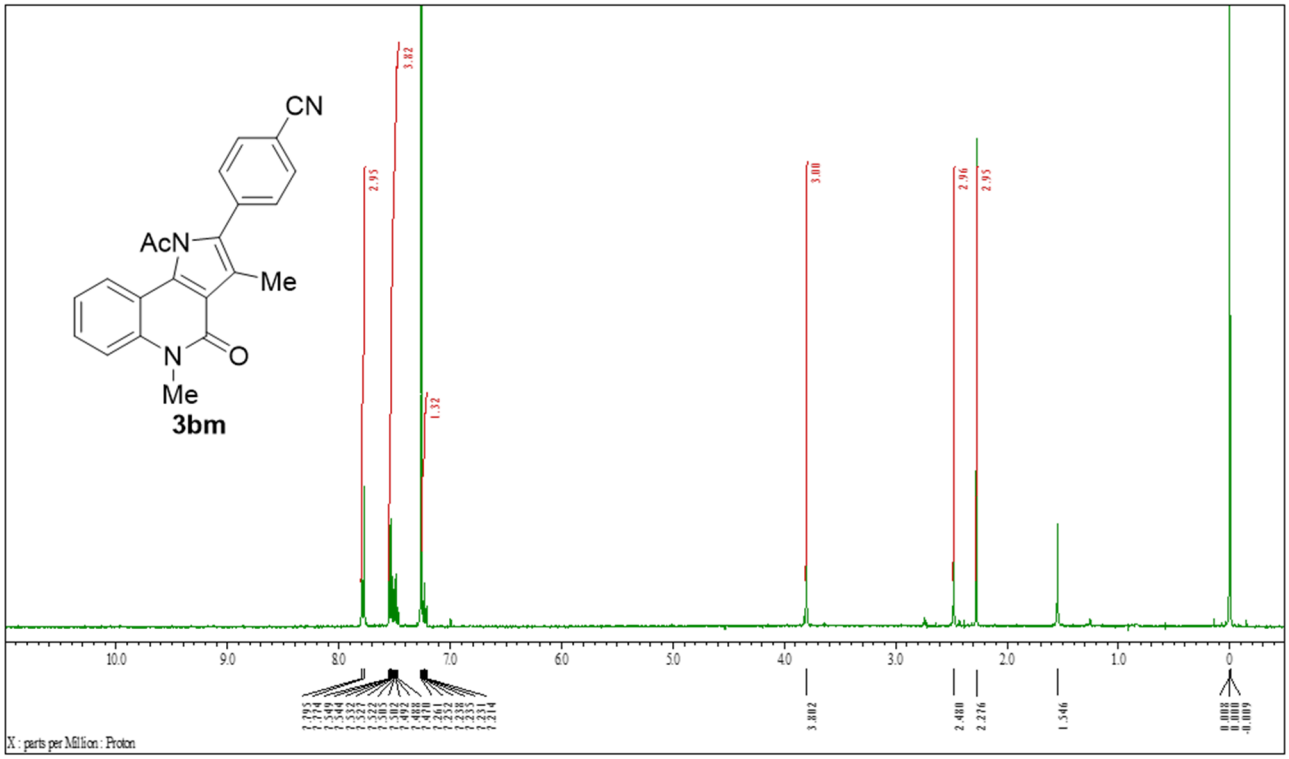

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bl**



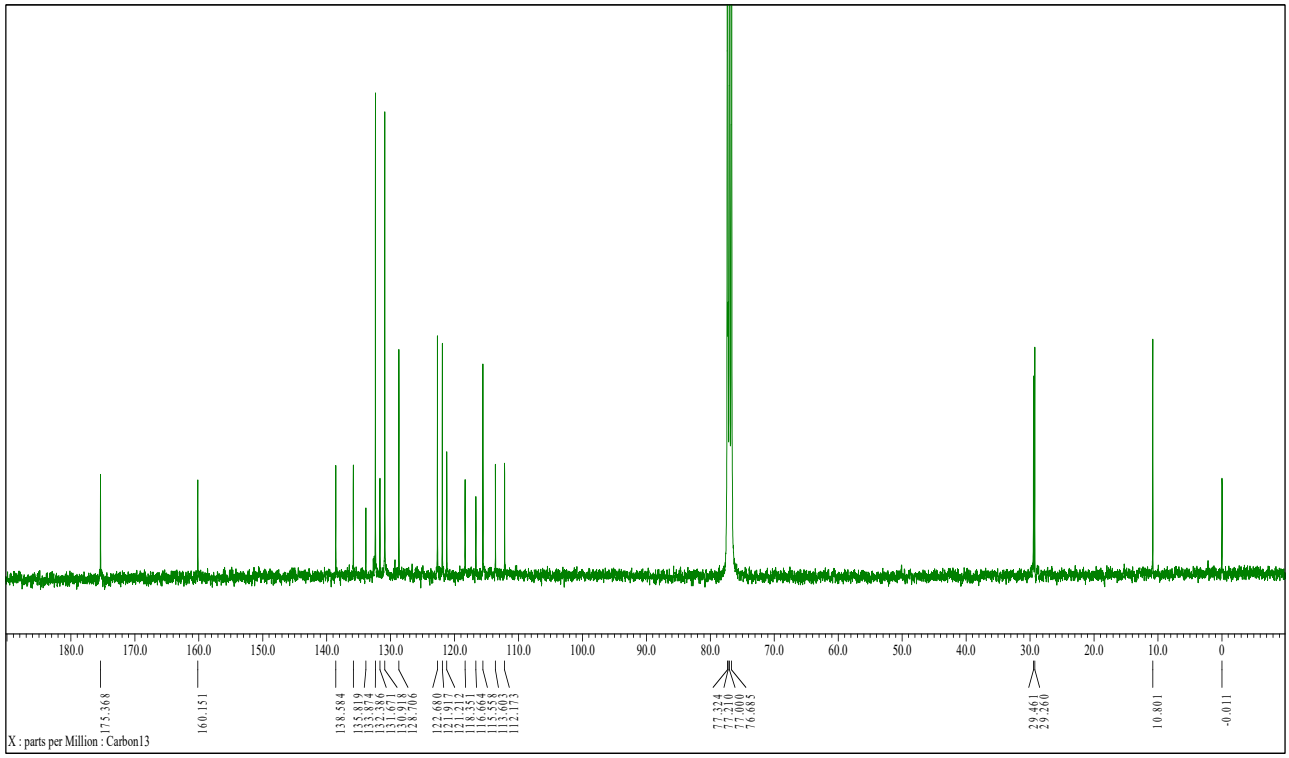
**$^{19}F$ NMR (376 MHz, $CDCl_3$) of 3bl**



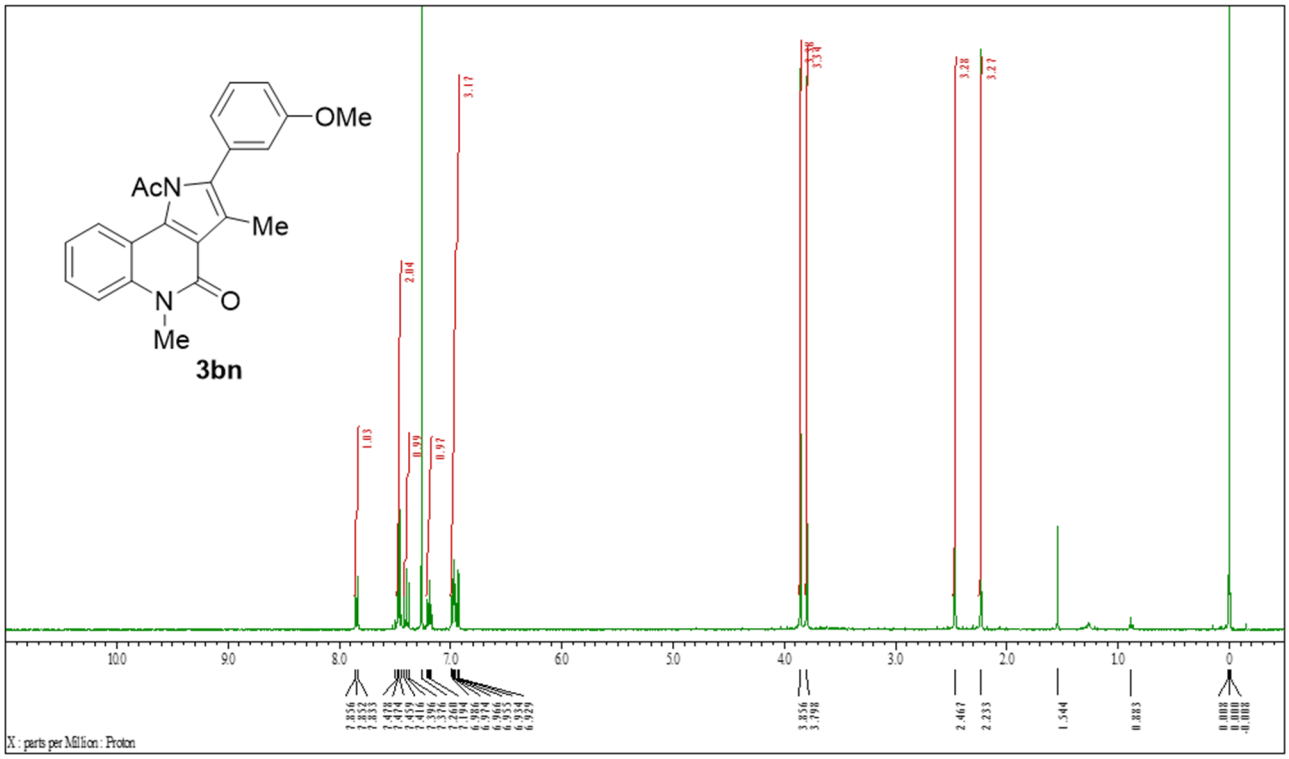
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bm**



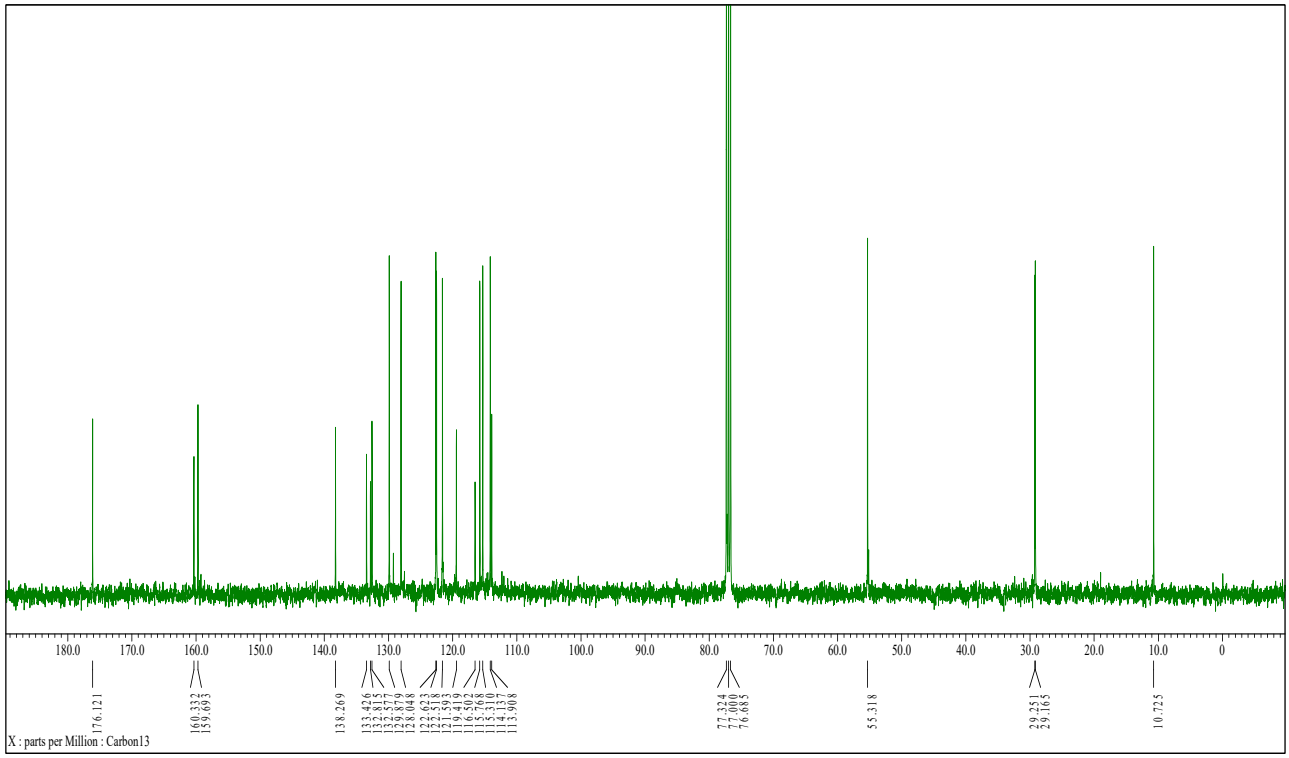

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bm**



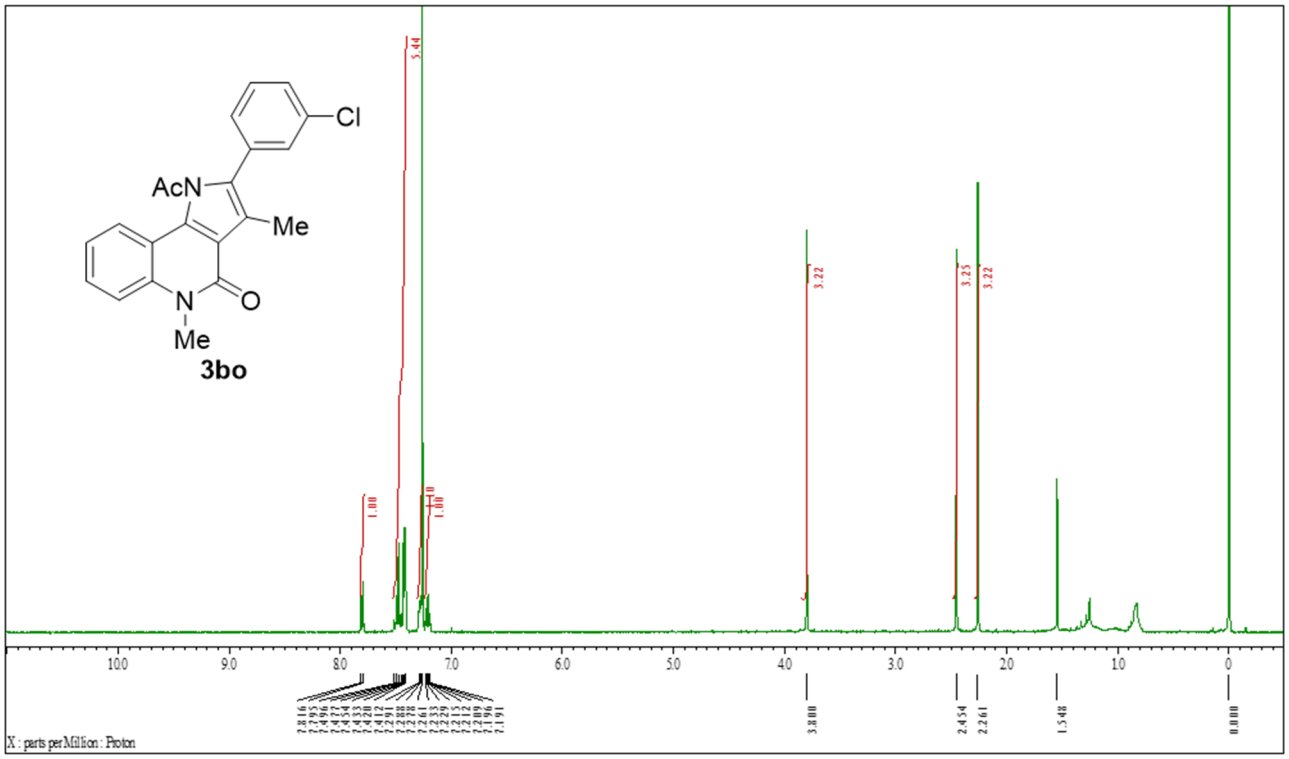
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bn**



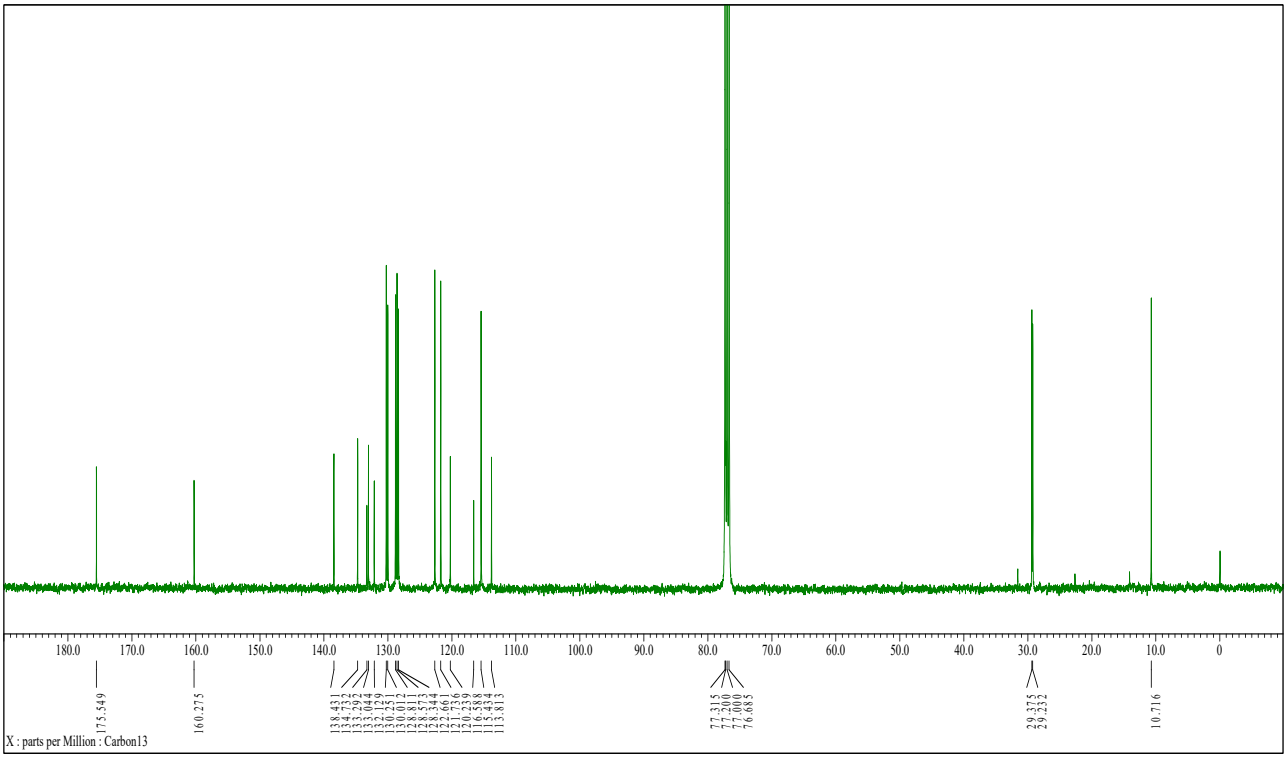

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bn**



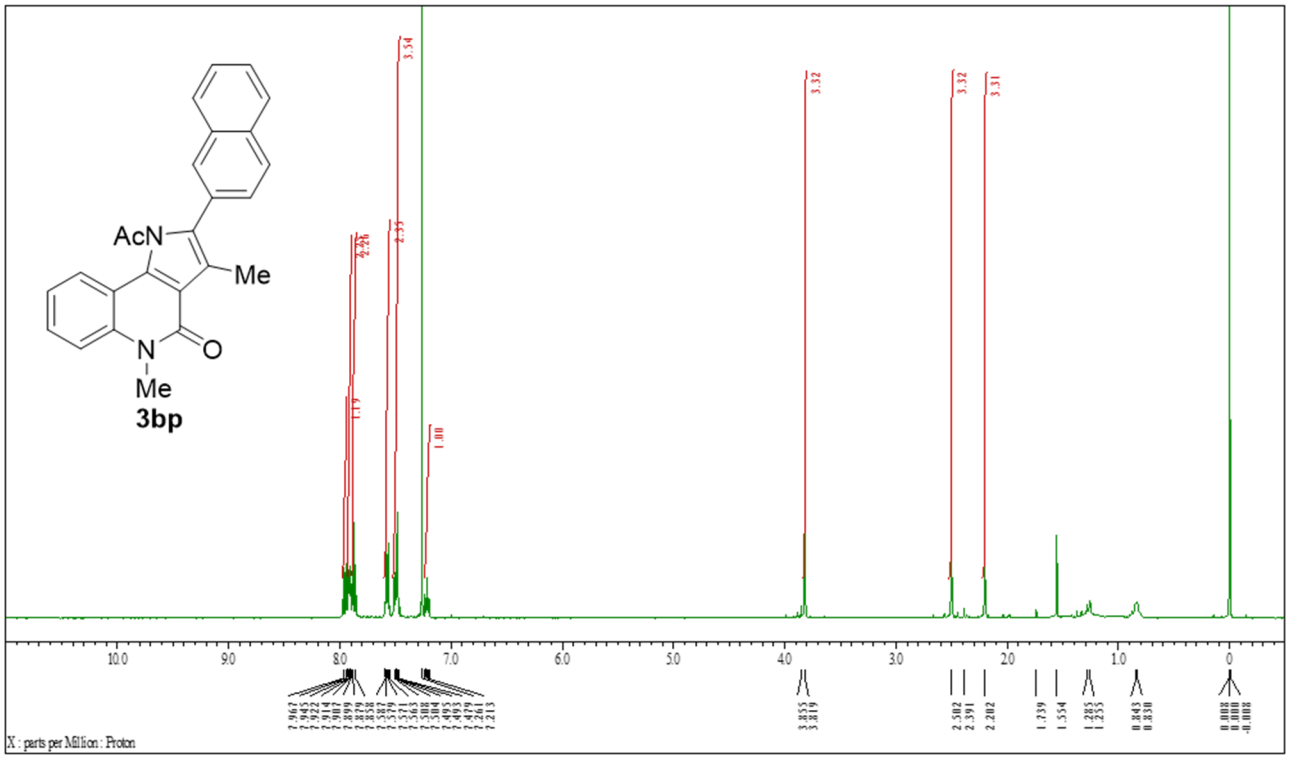
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bo**



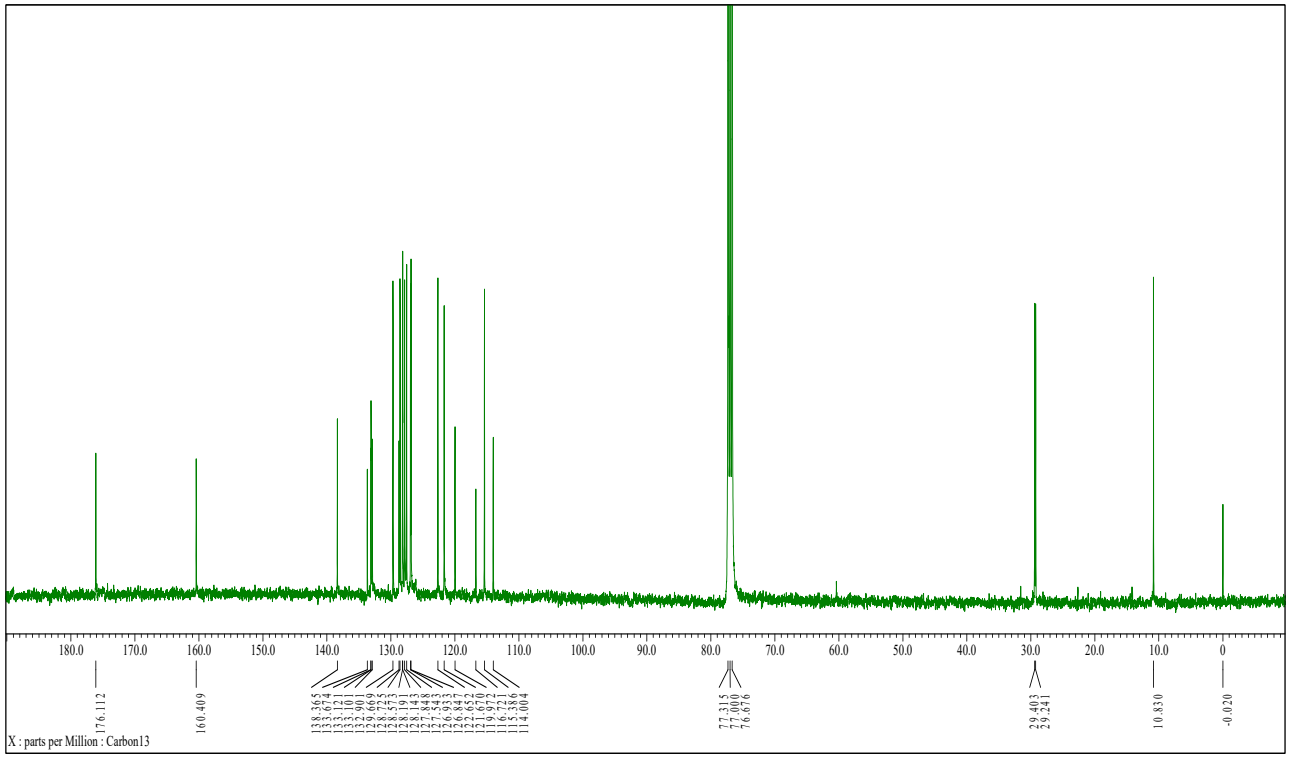

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bo**



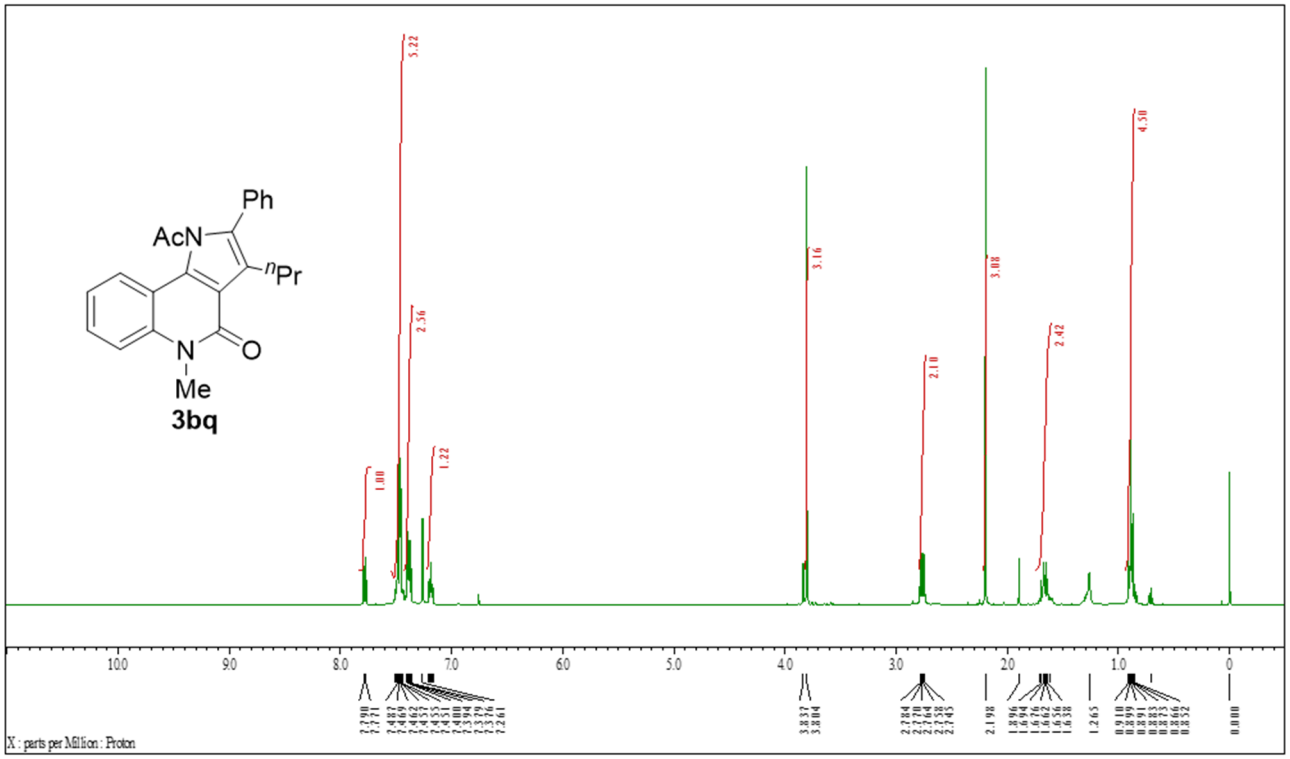
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bp**



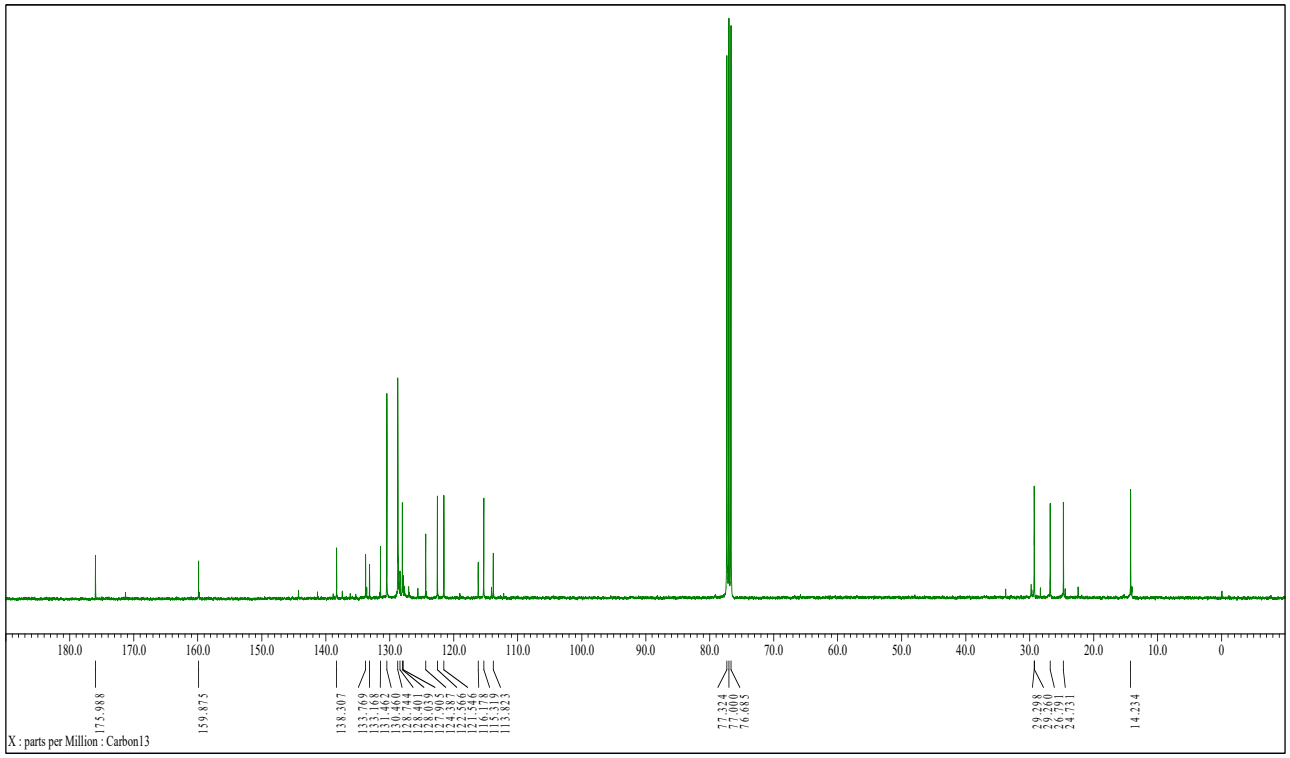

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bp**



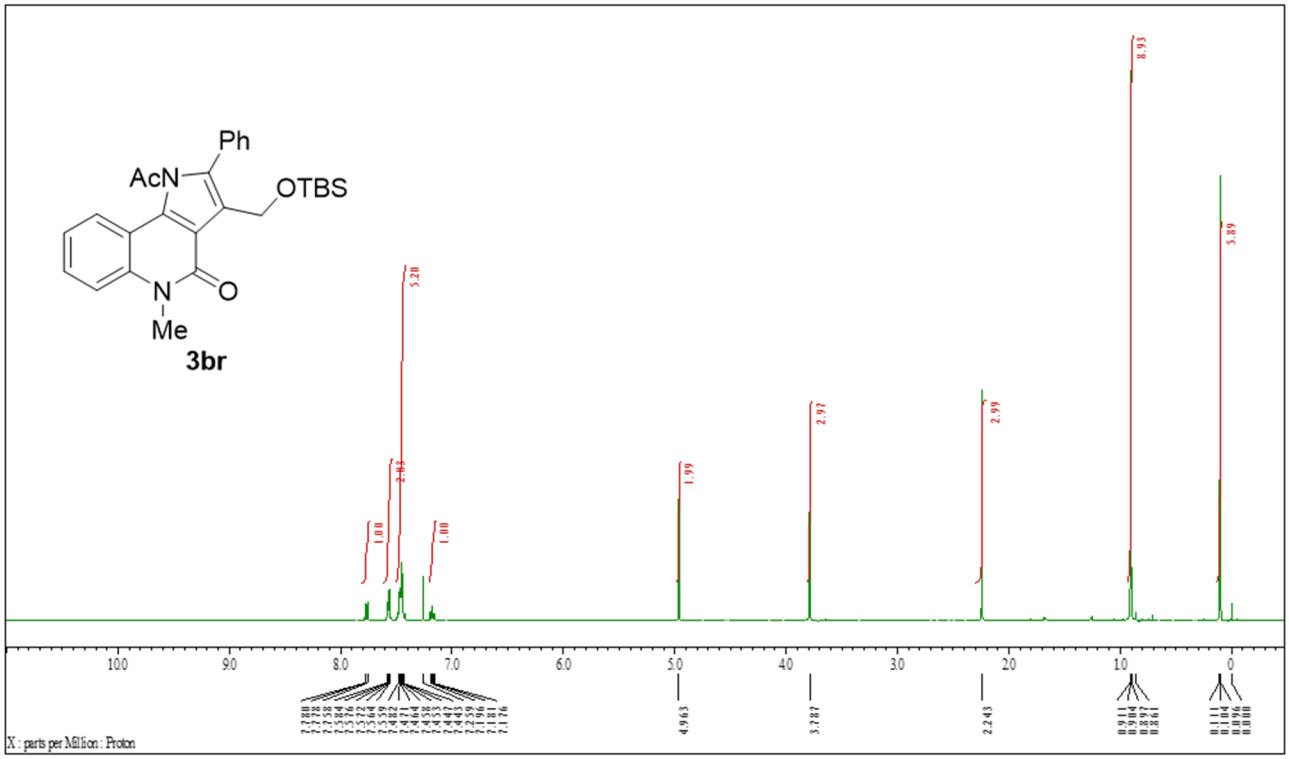
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bq**



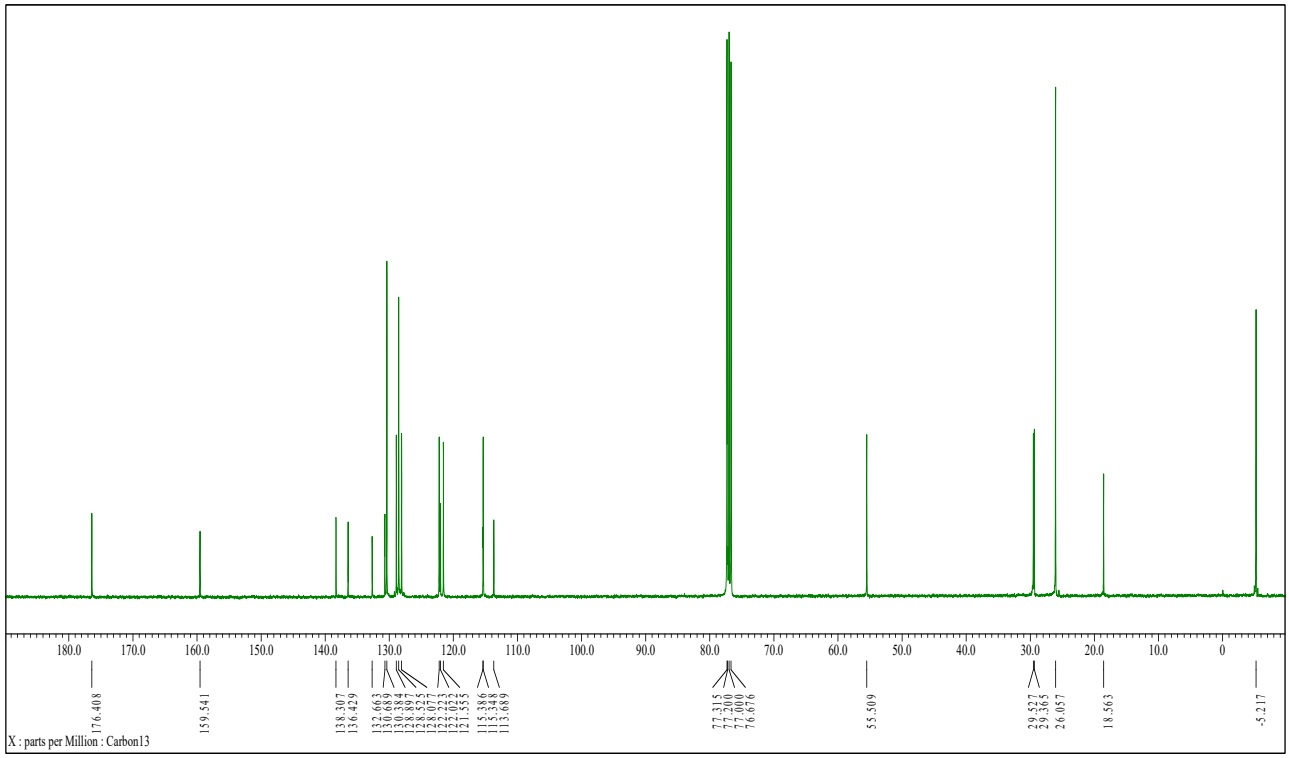

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bq**



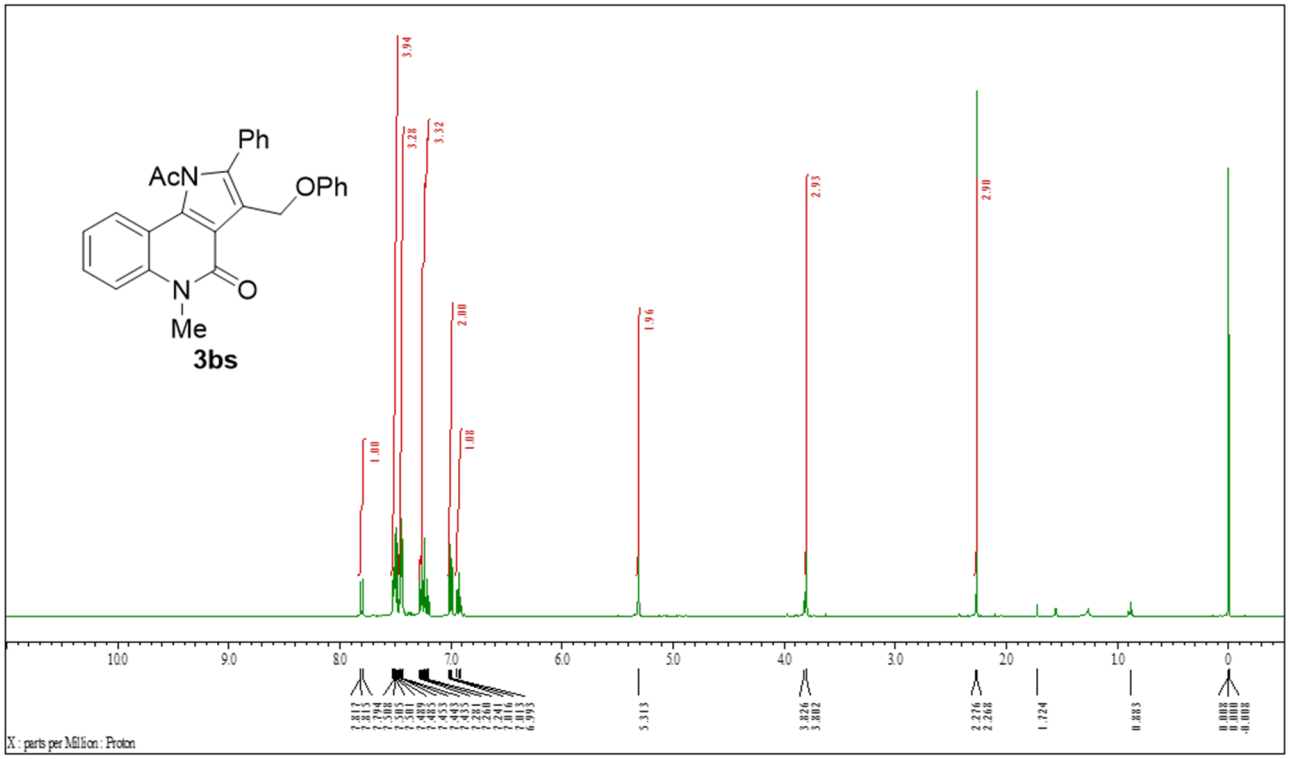
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3br**



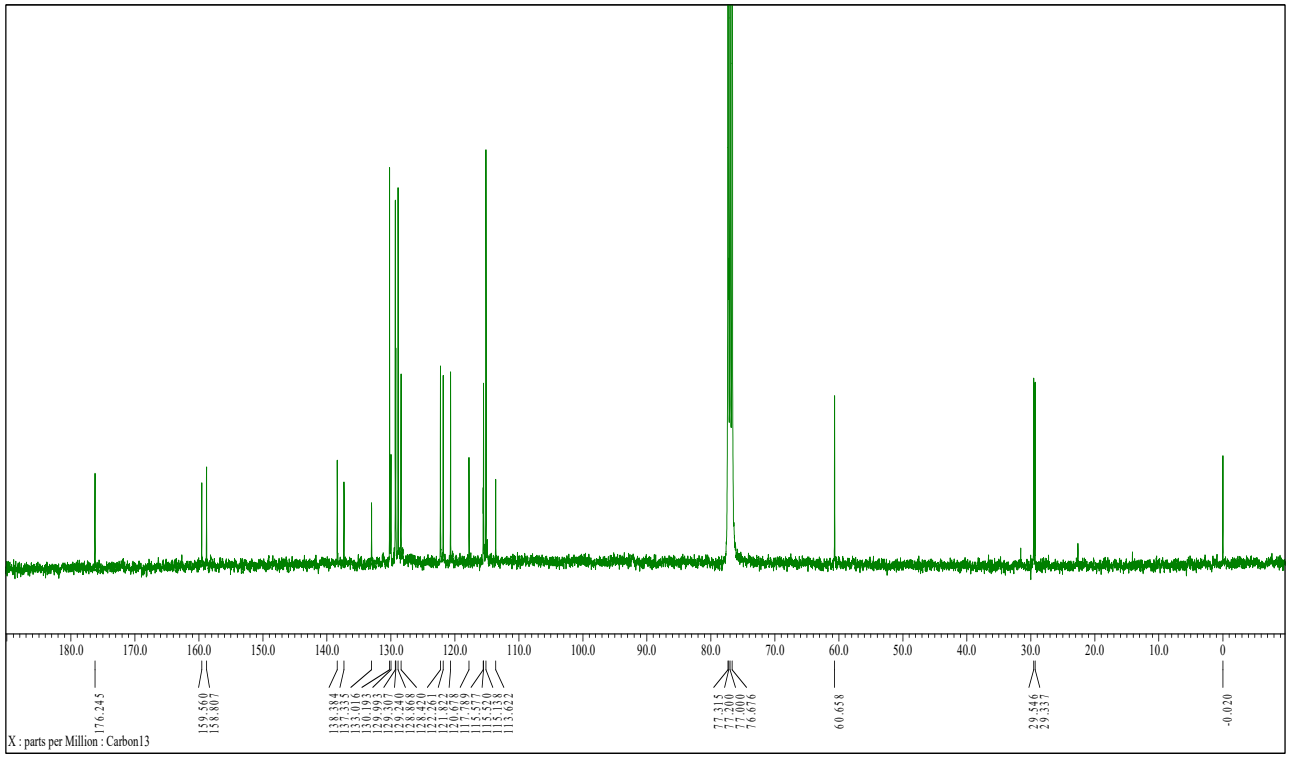

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3br**



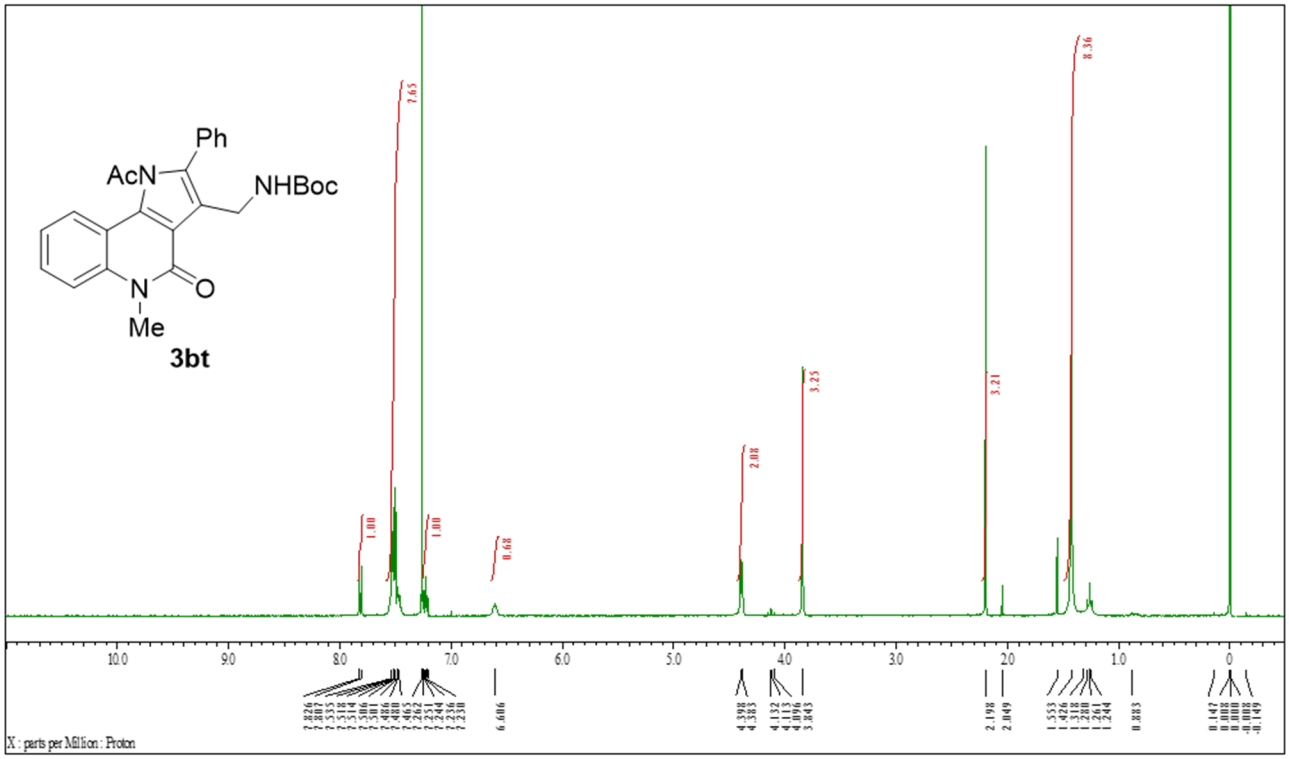
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bs**



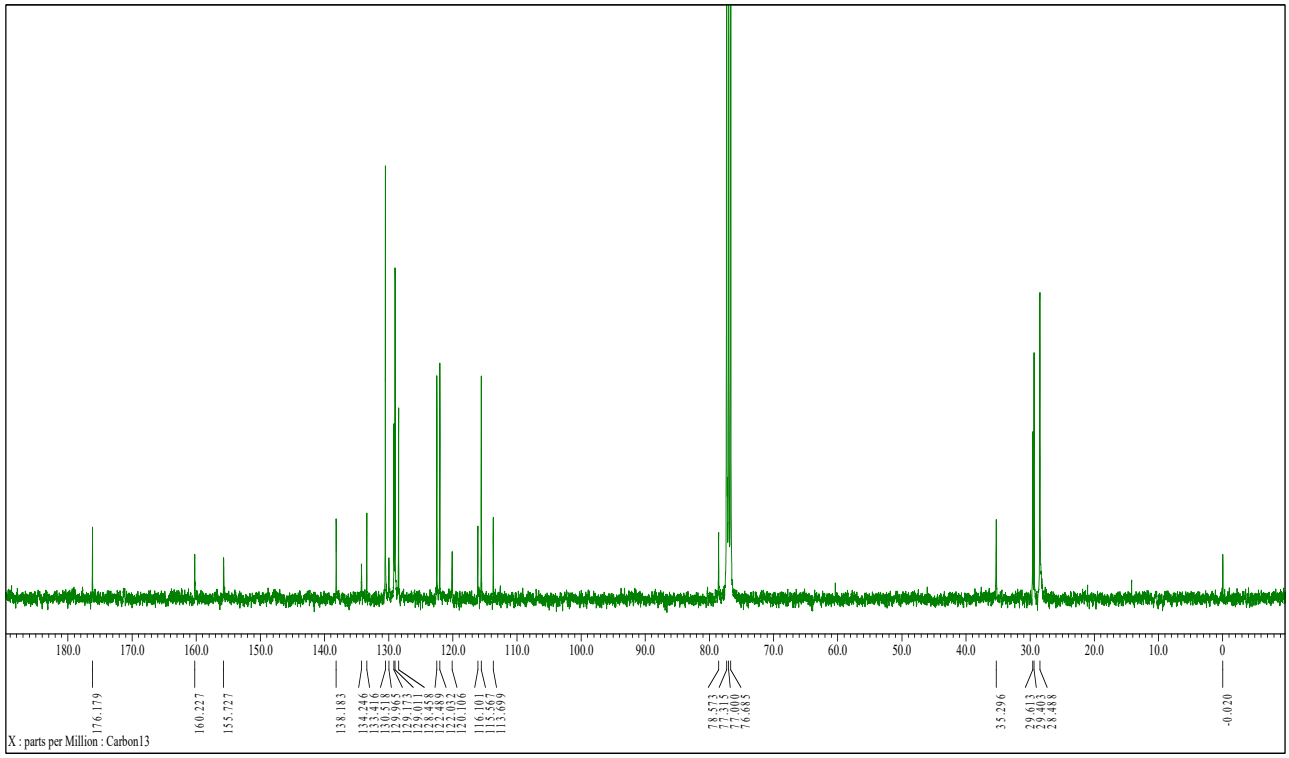

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bs**



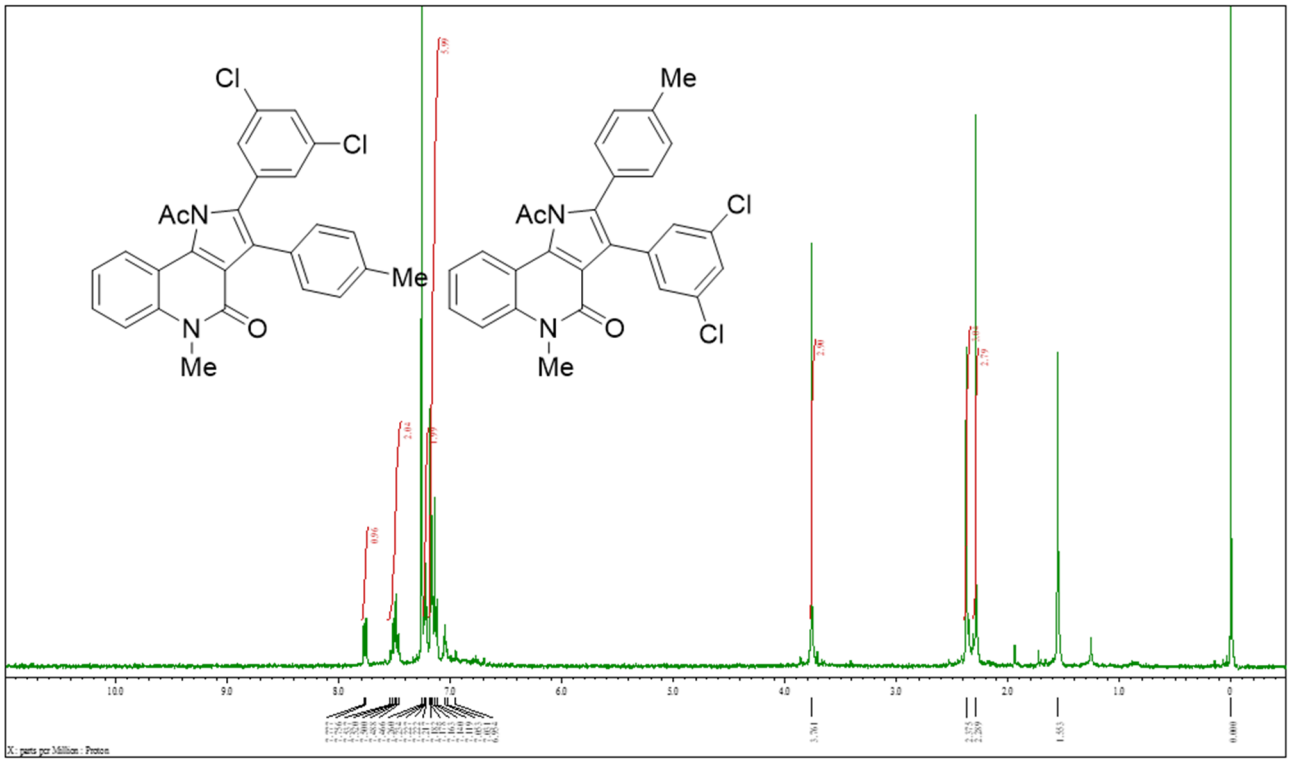
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3bt**

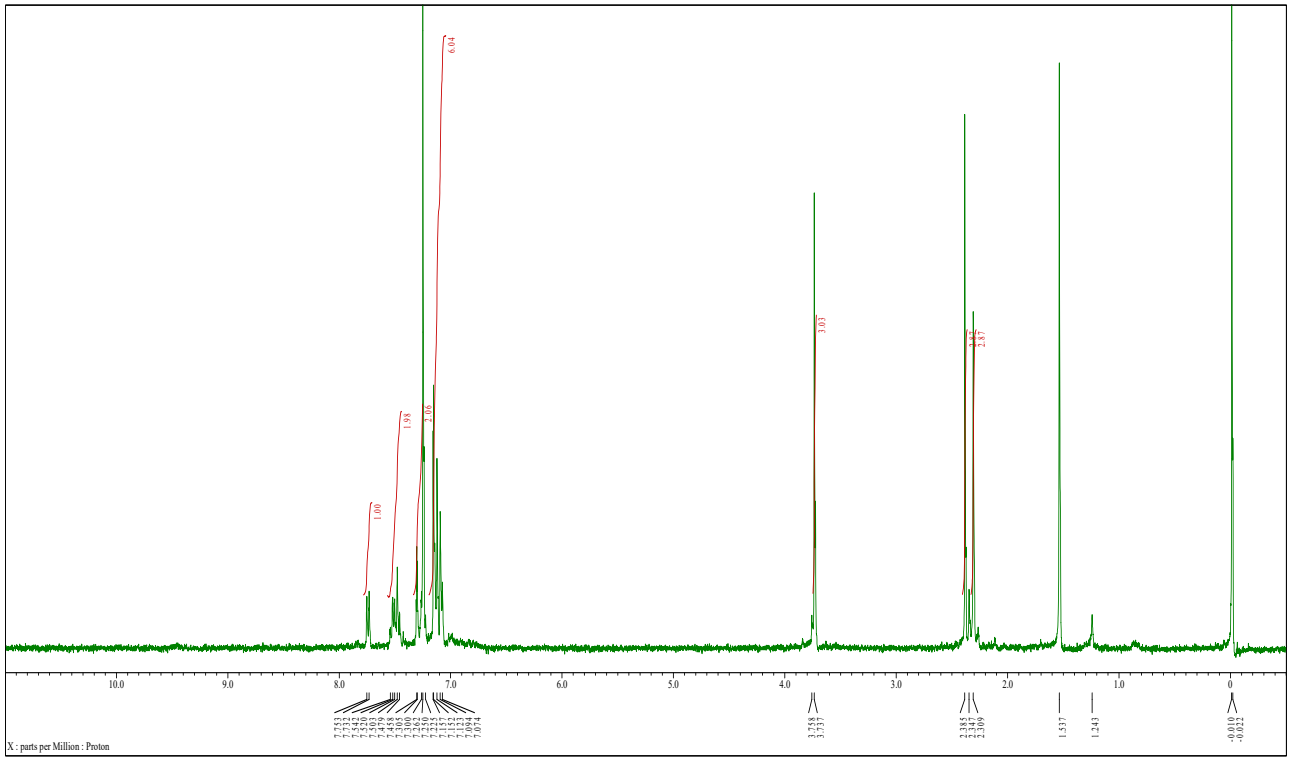



**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bt**

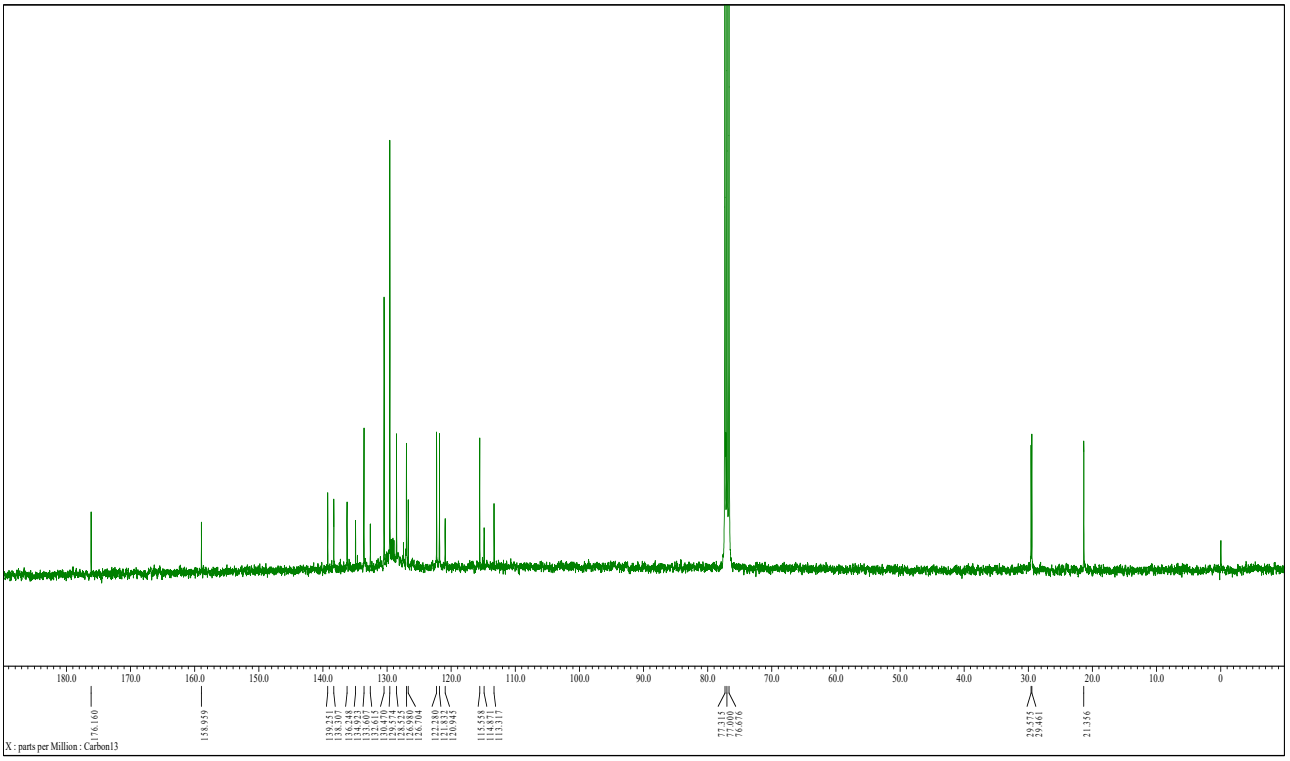


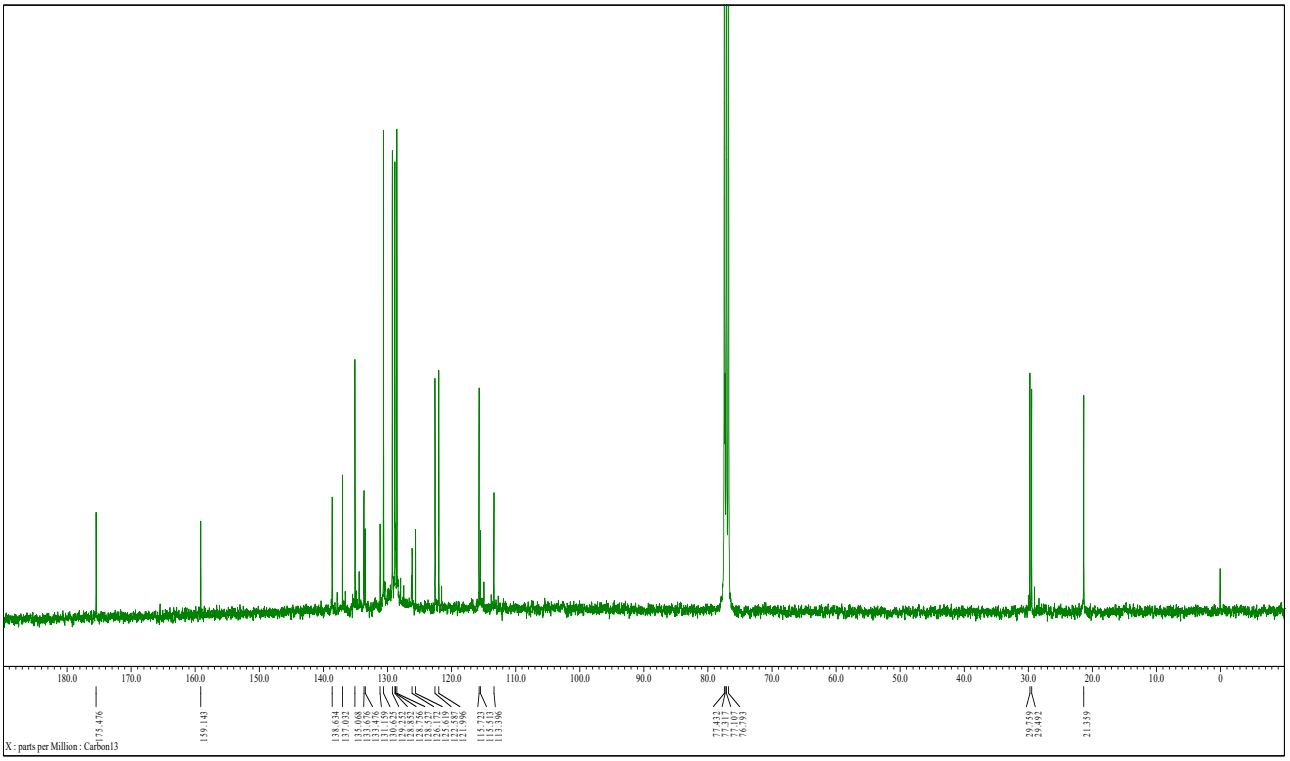
**$^1$H NMR (400 MHz, $CDCl_3$) of 3bu**



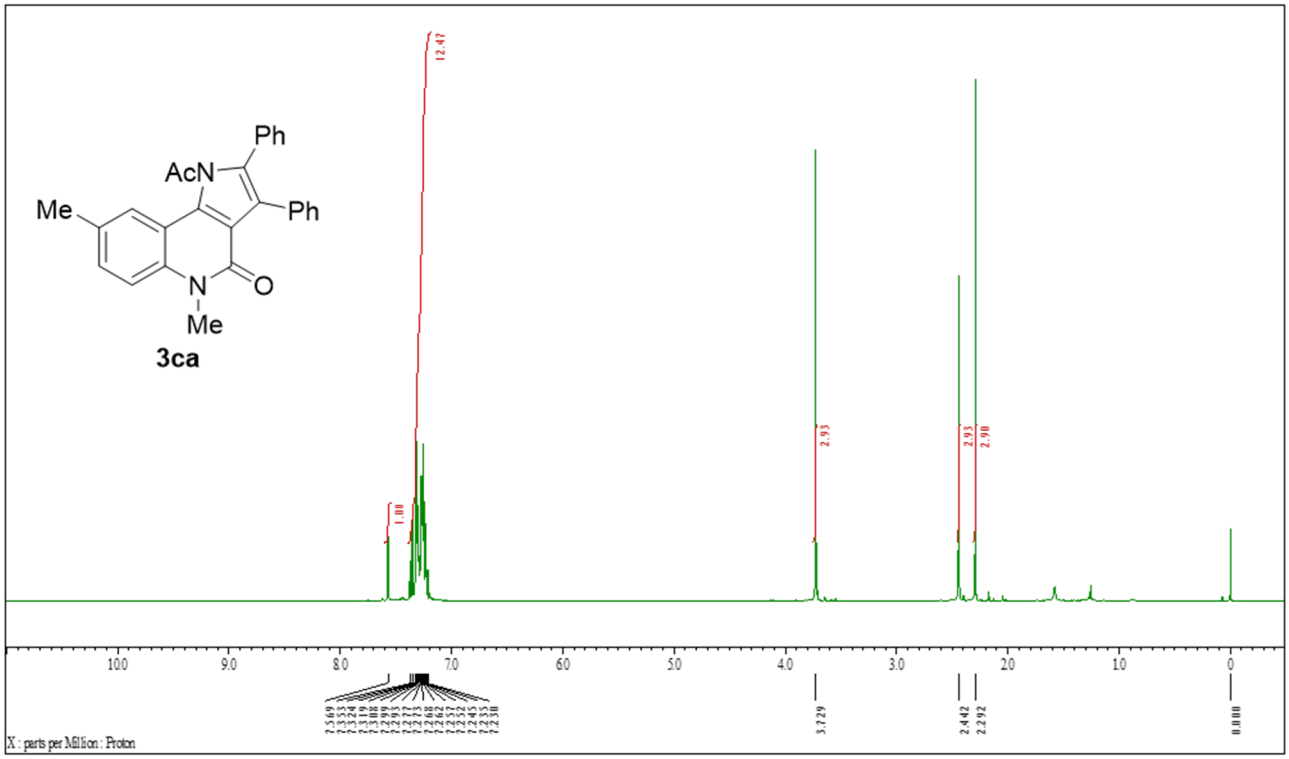



**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3bu**

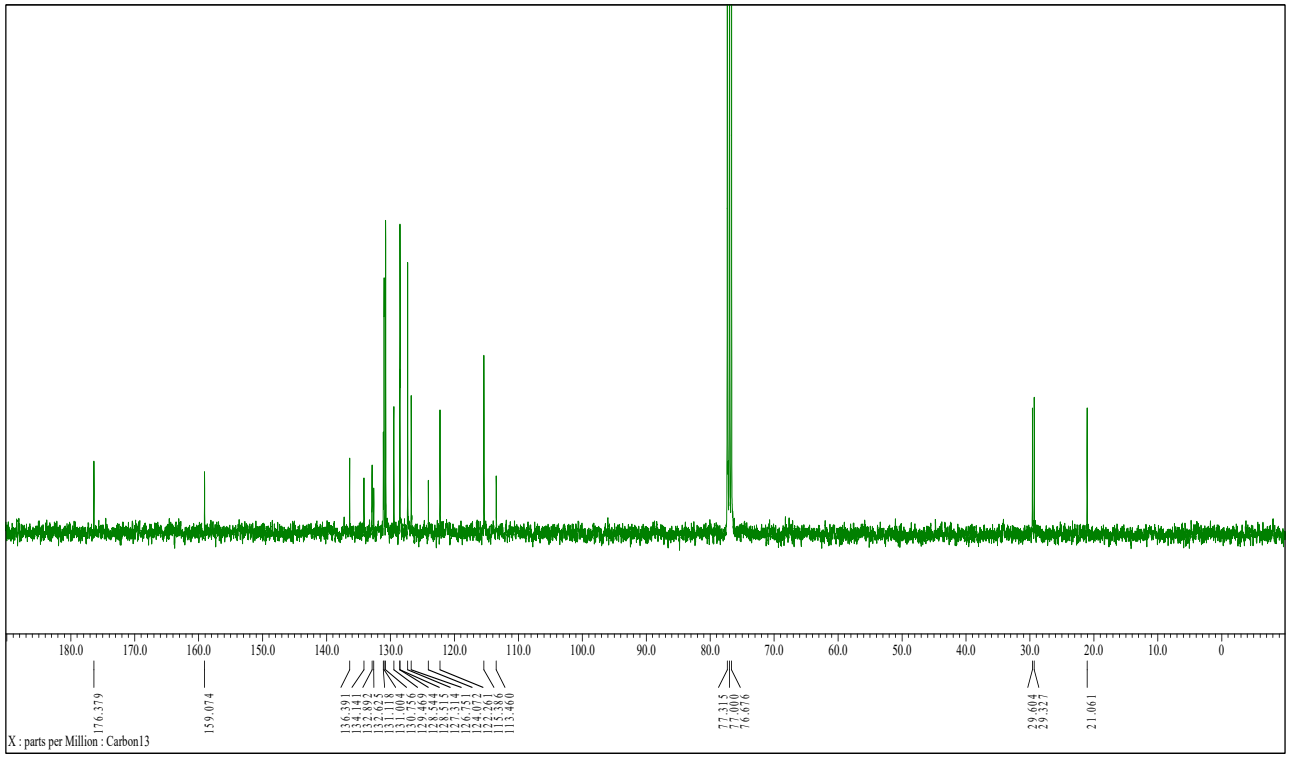


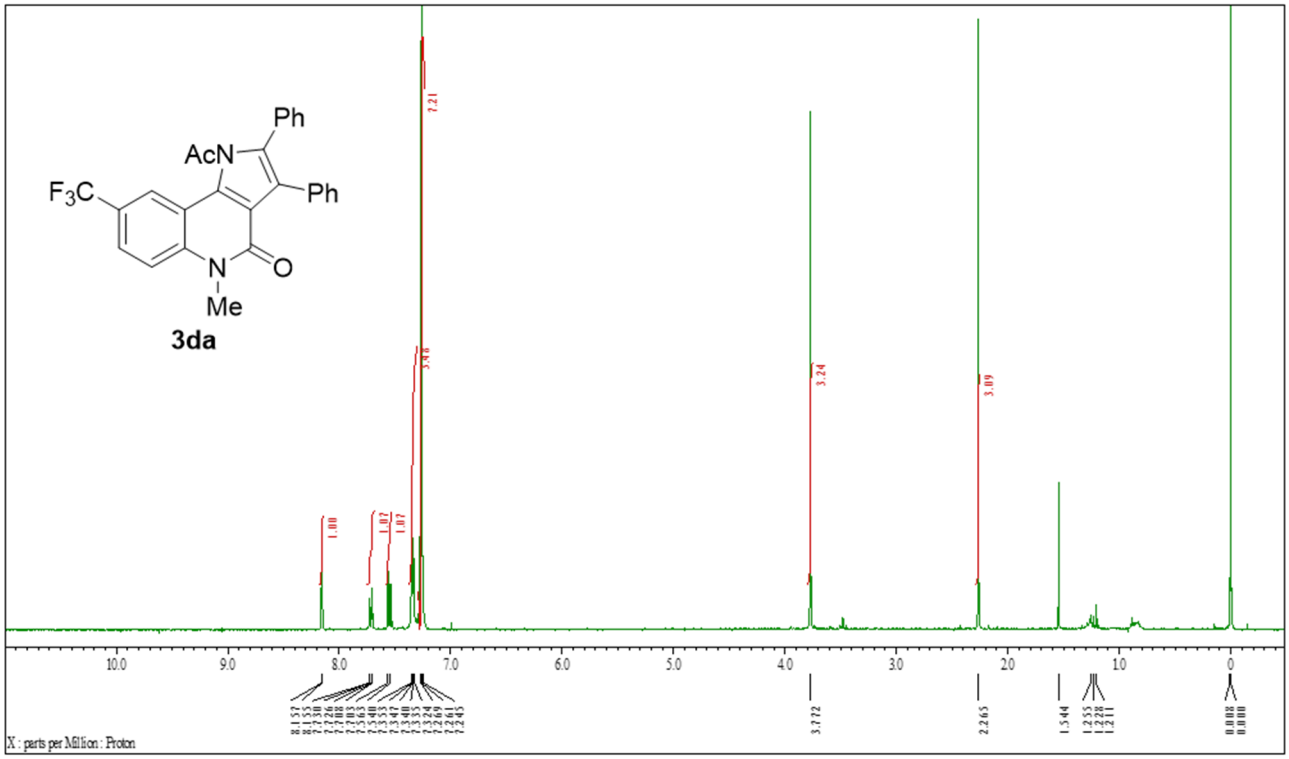
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3ca**



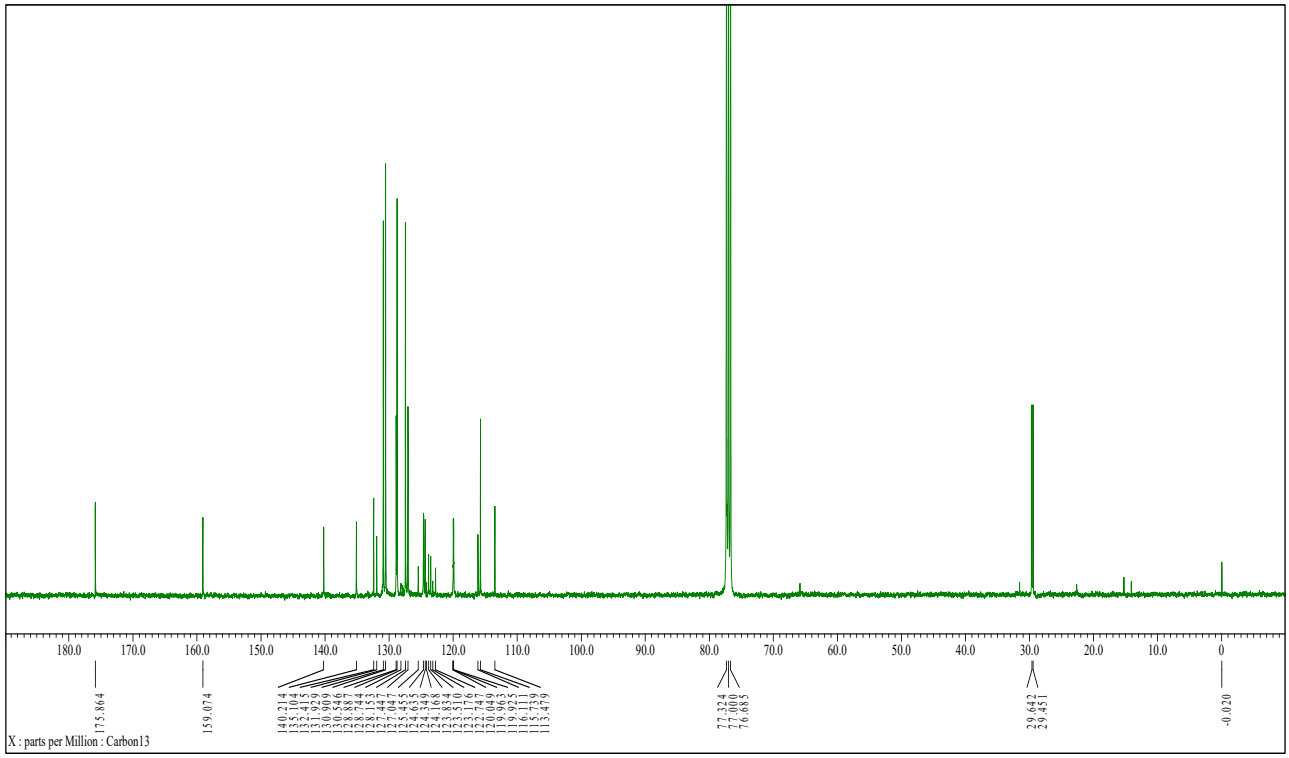

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3ca**



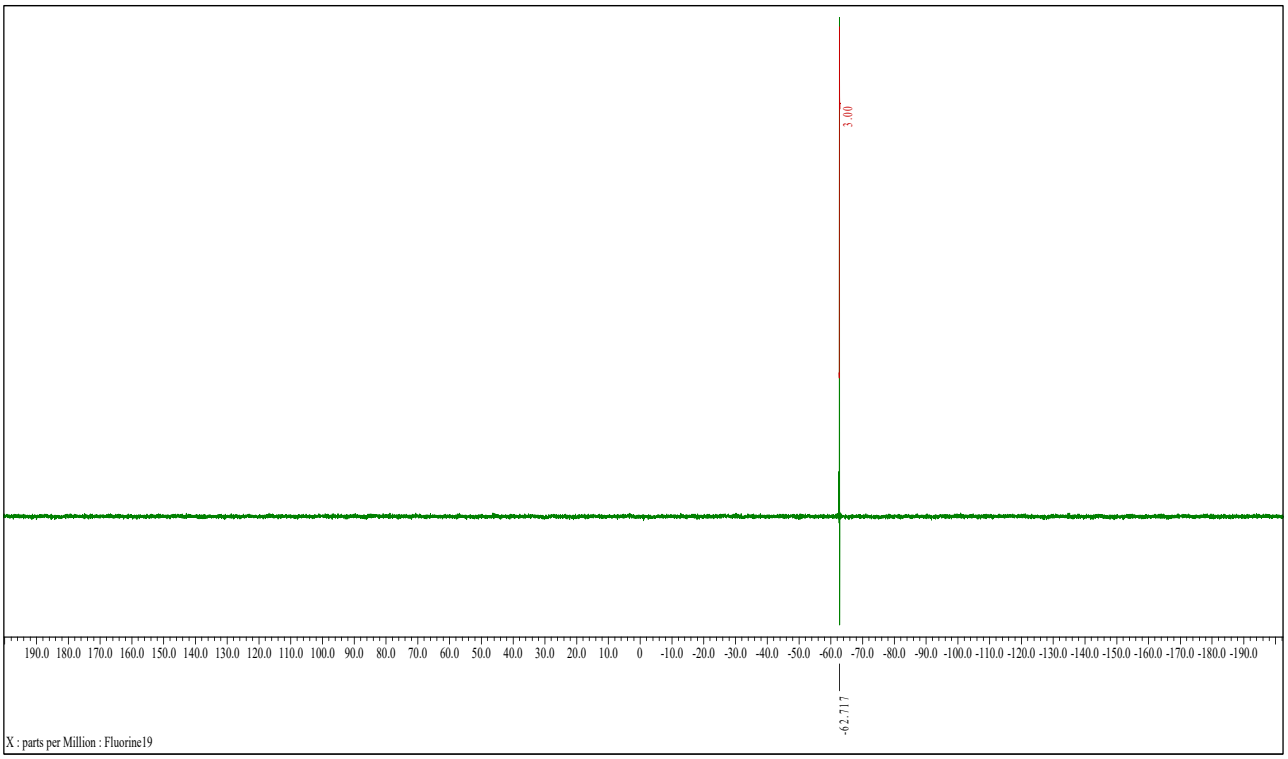
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3da**



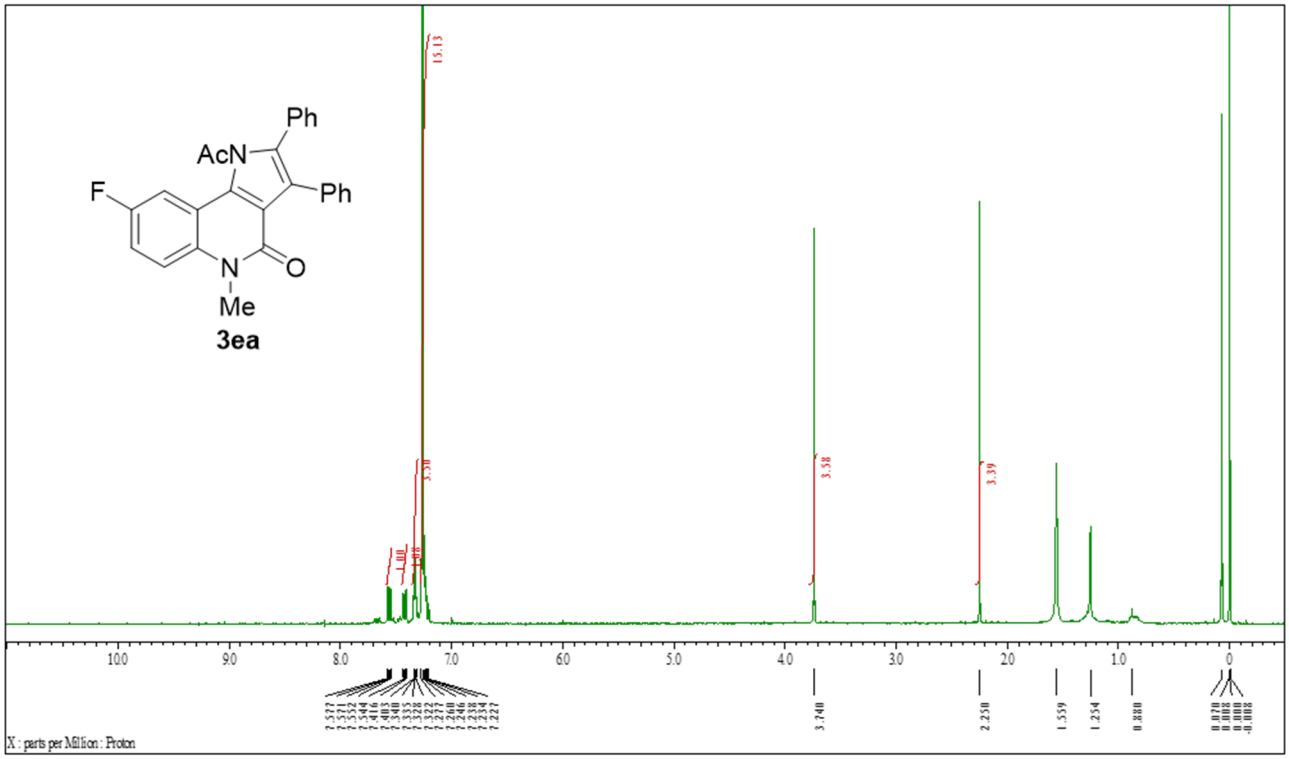

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3da**



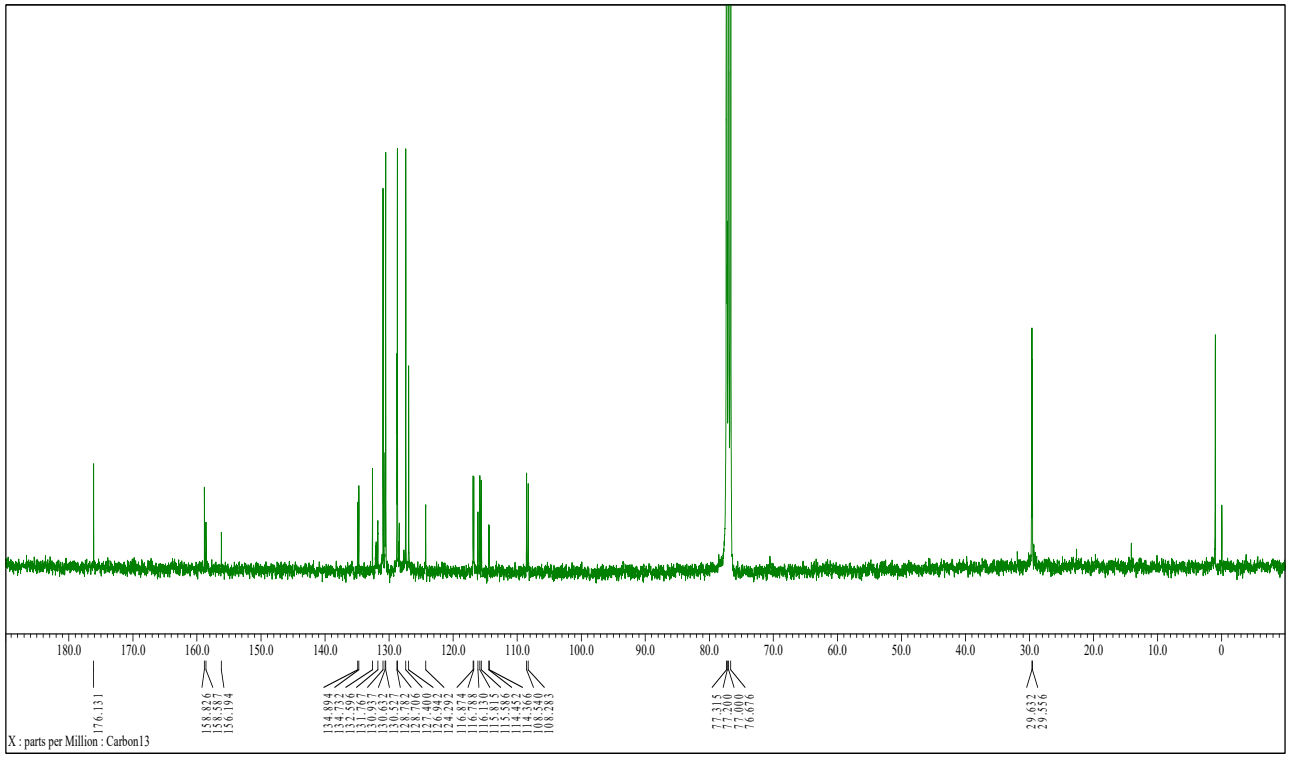
**$^{19}F$ NMR (376 MHz, $CDCl_3$) of 3da**



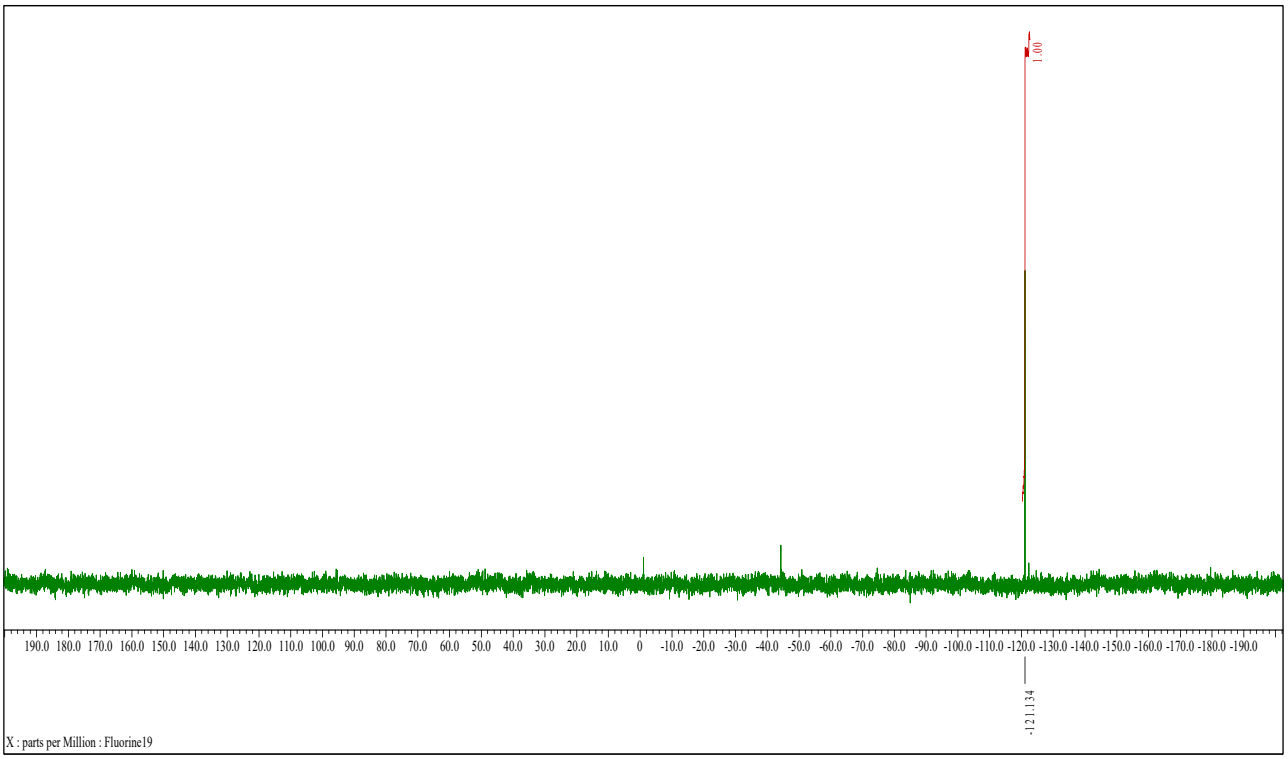
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3ea**



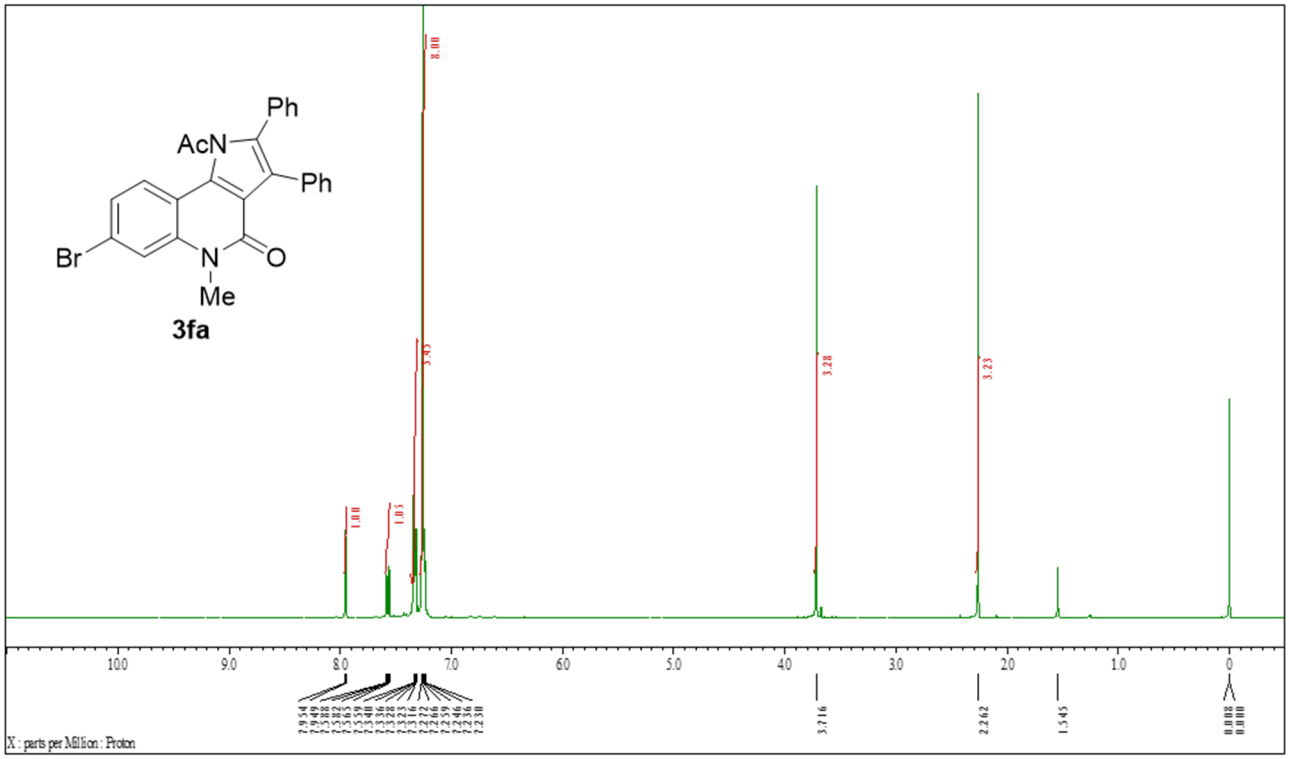

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3ea**



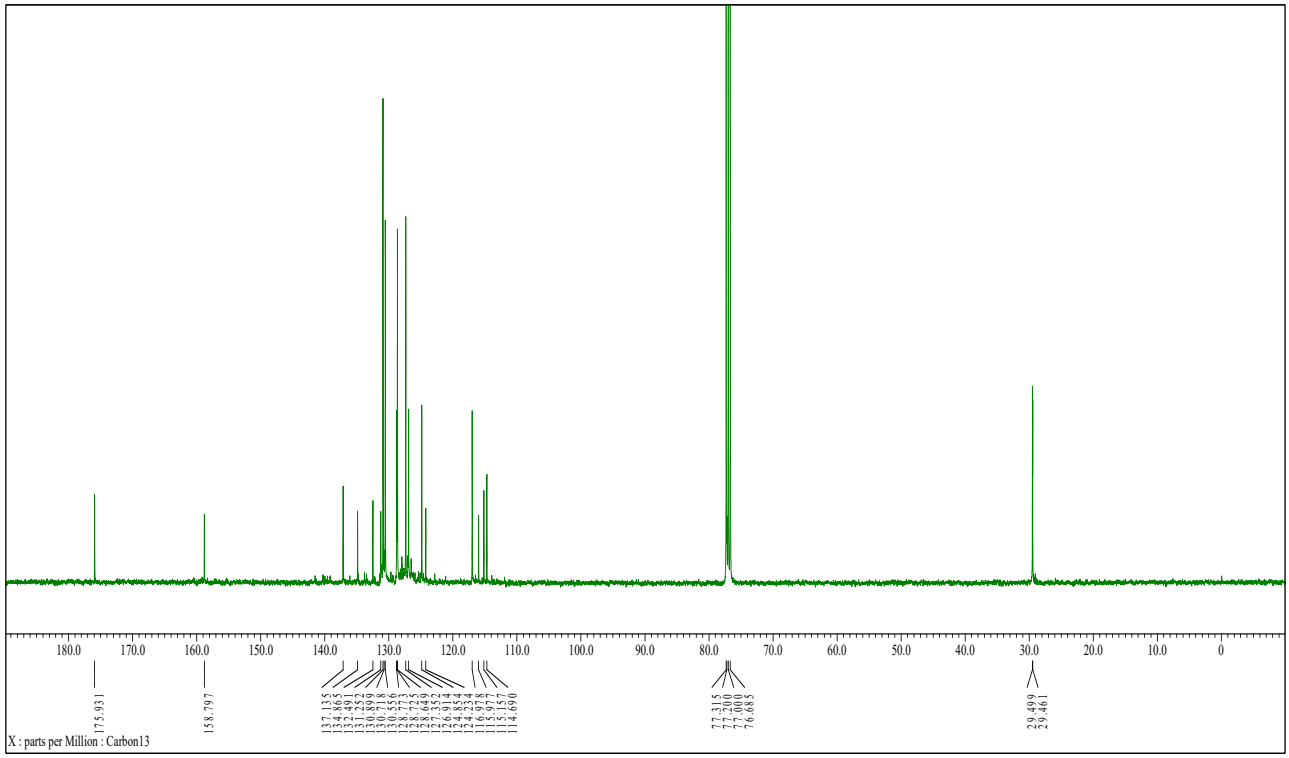
**$^{19}F$ NMR (376 MHz, $CDCl_3$) of 3ea**



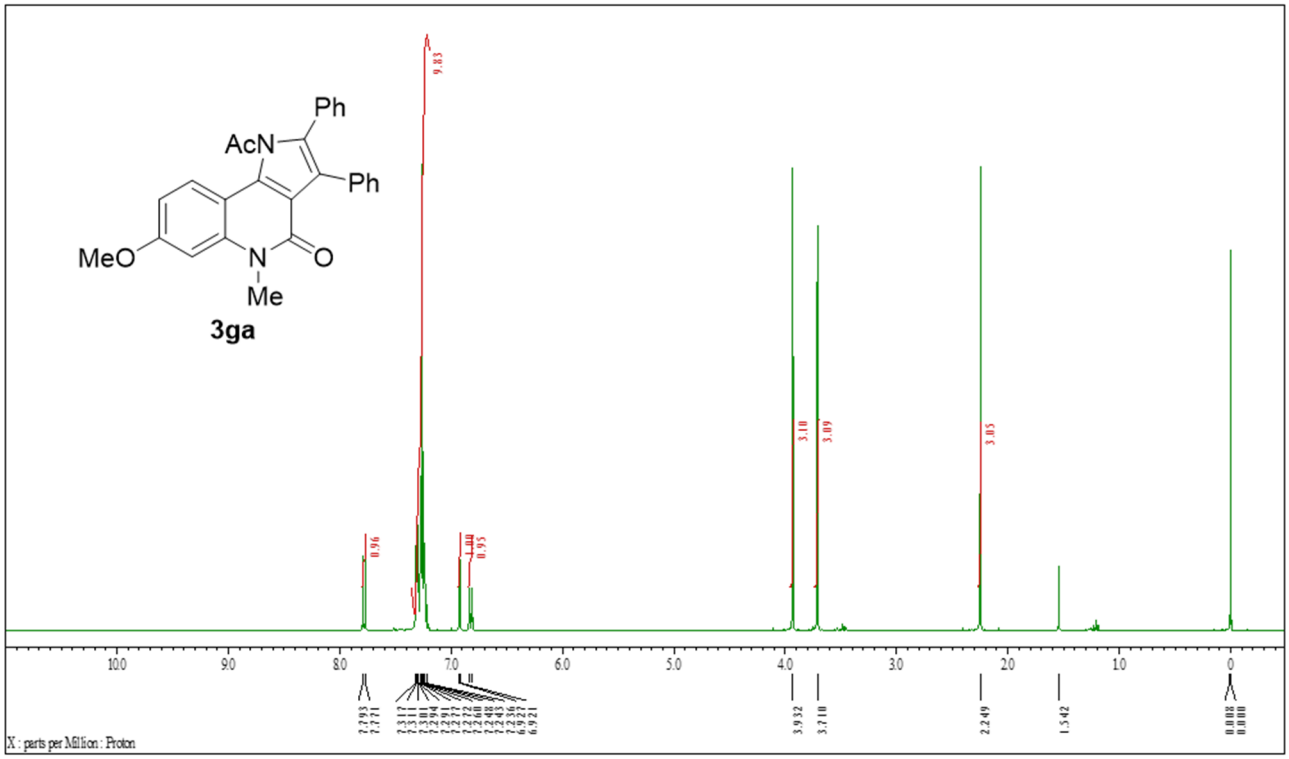
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3fa**



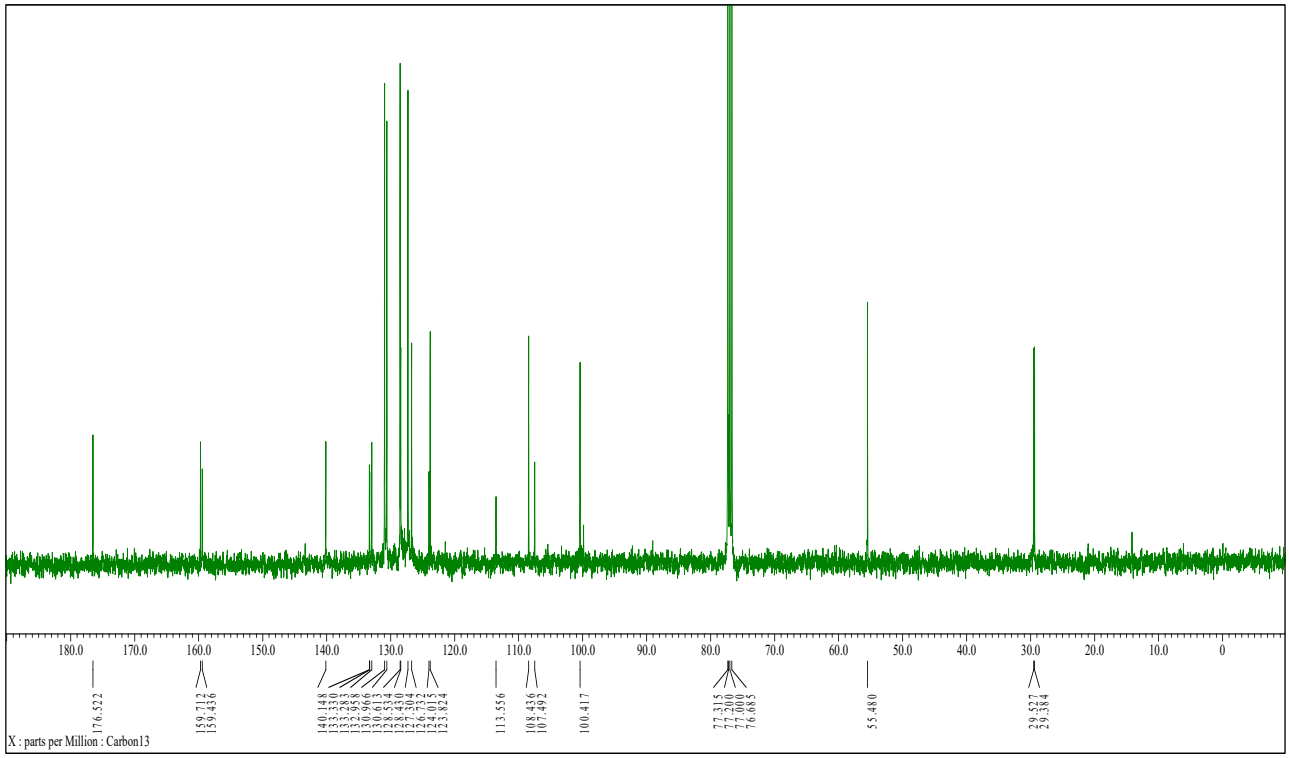

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3fa**



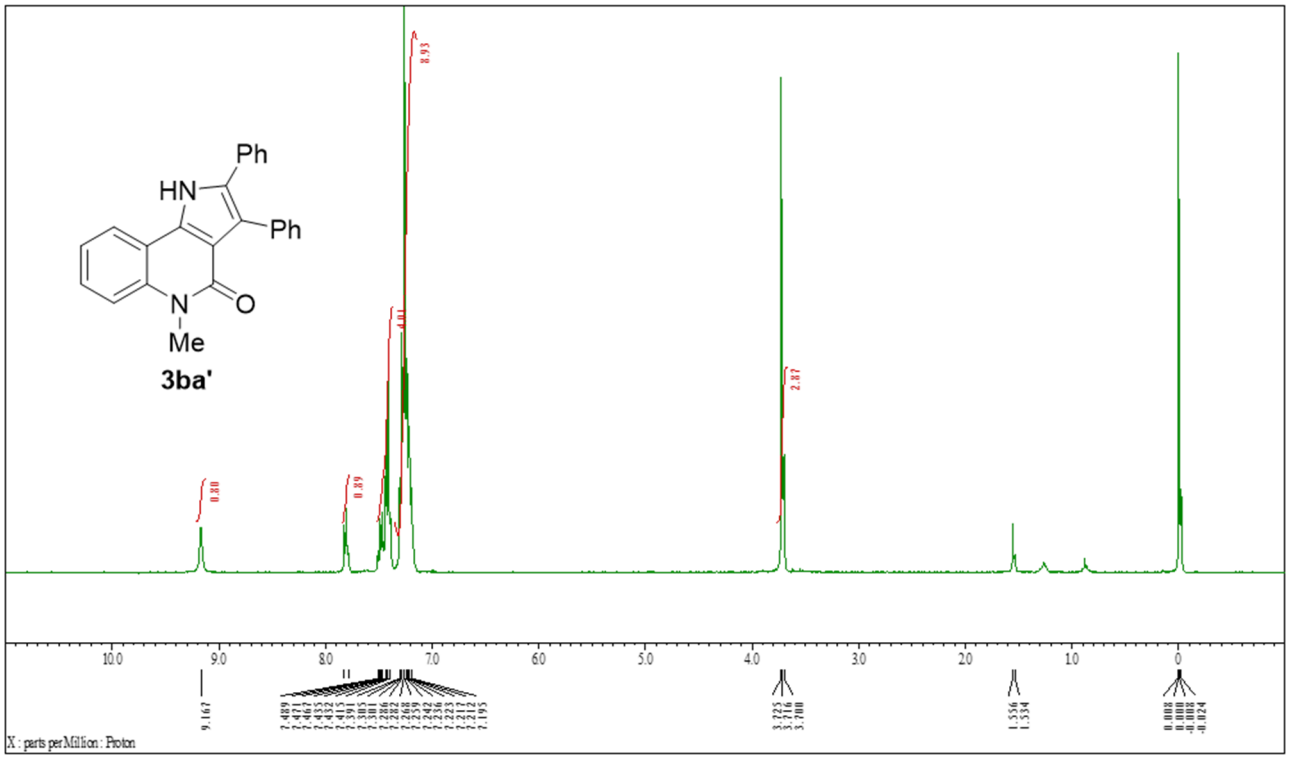
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3ga**



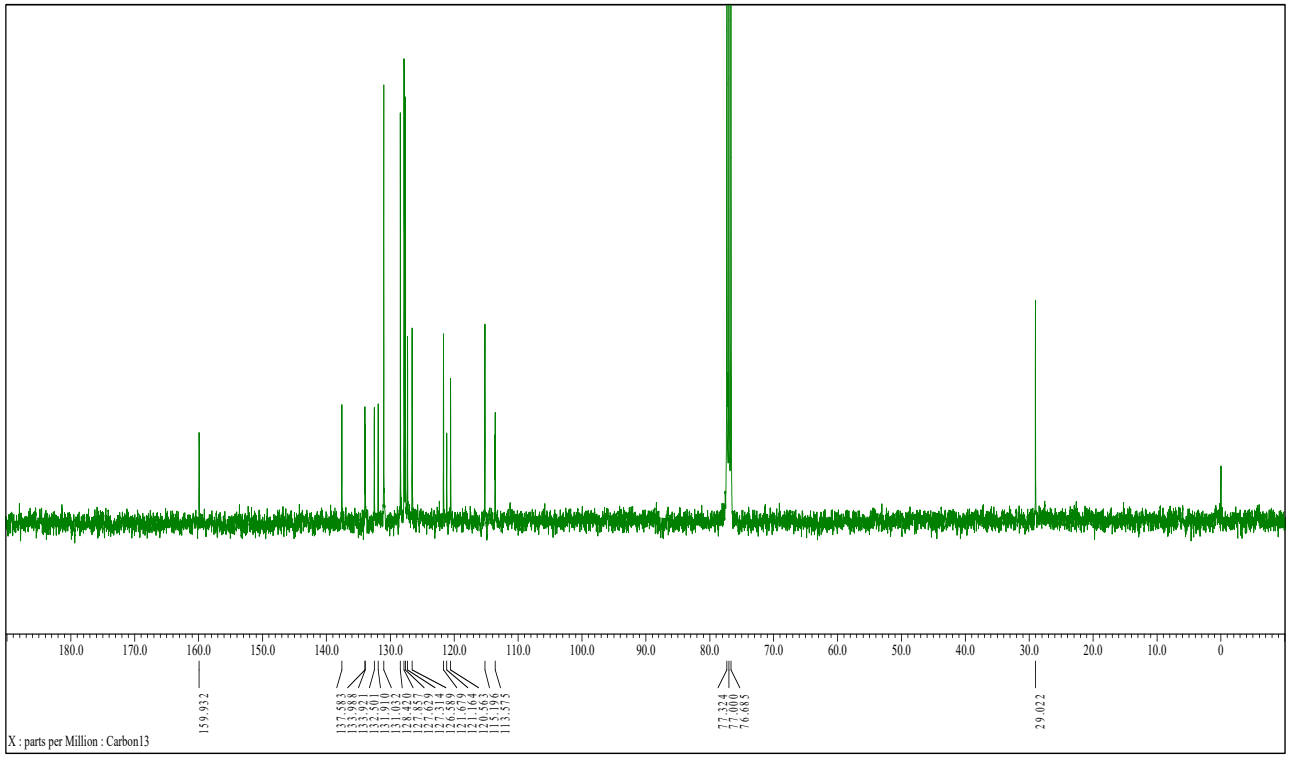

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3ga**



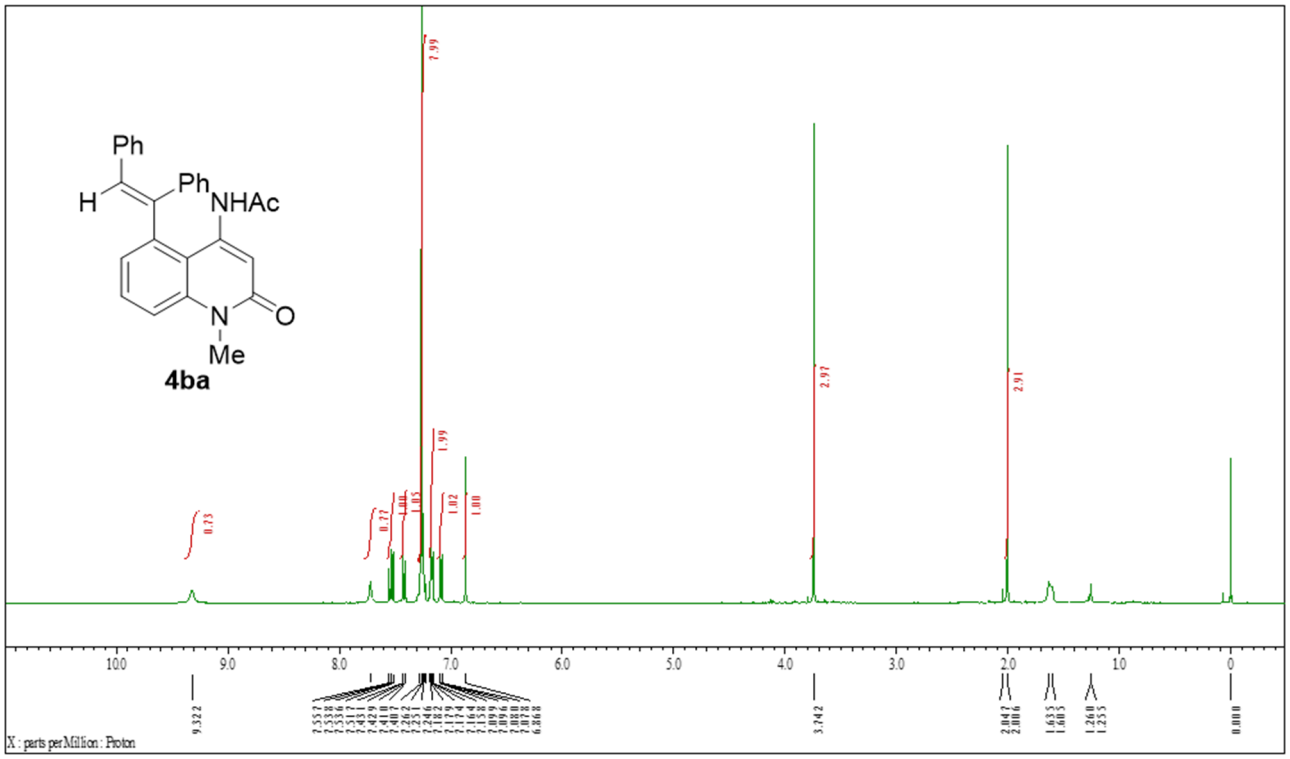
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3ba'**



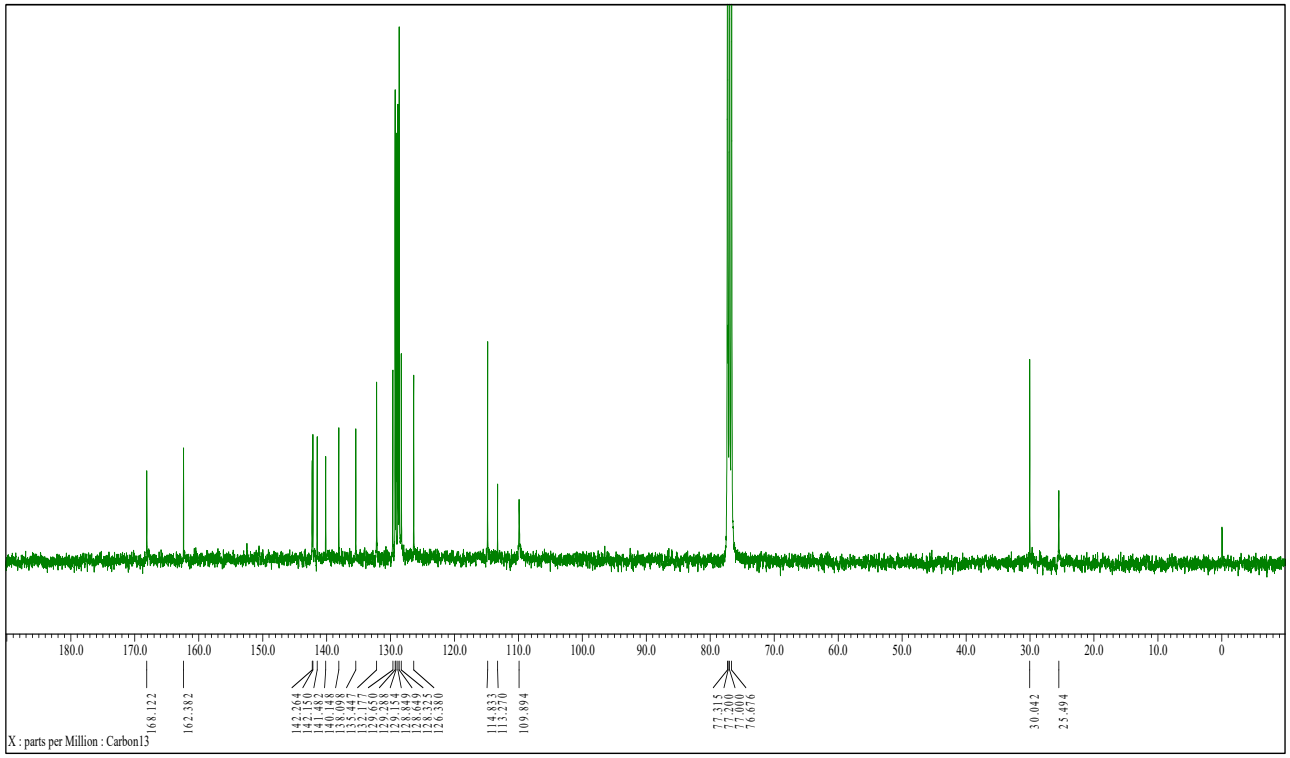

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 3ba'**



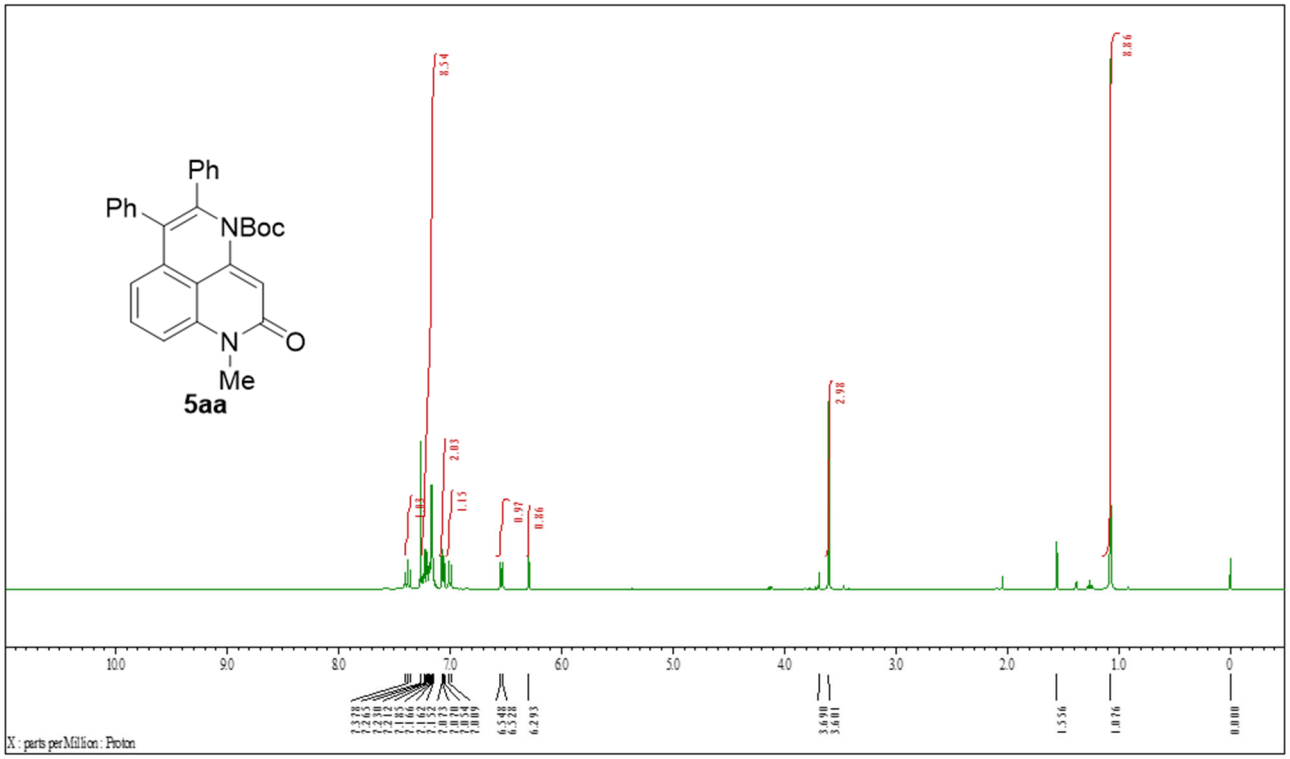
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 4ba**



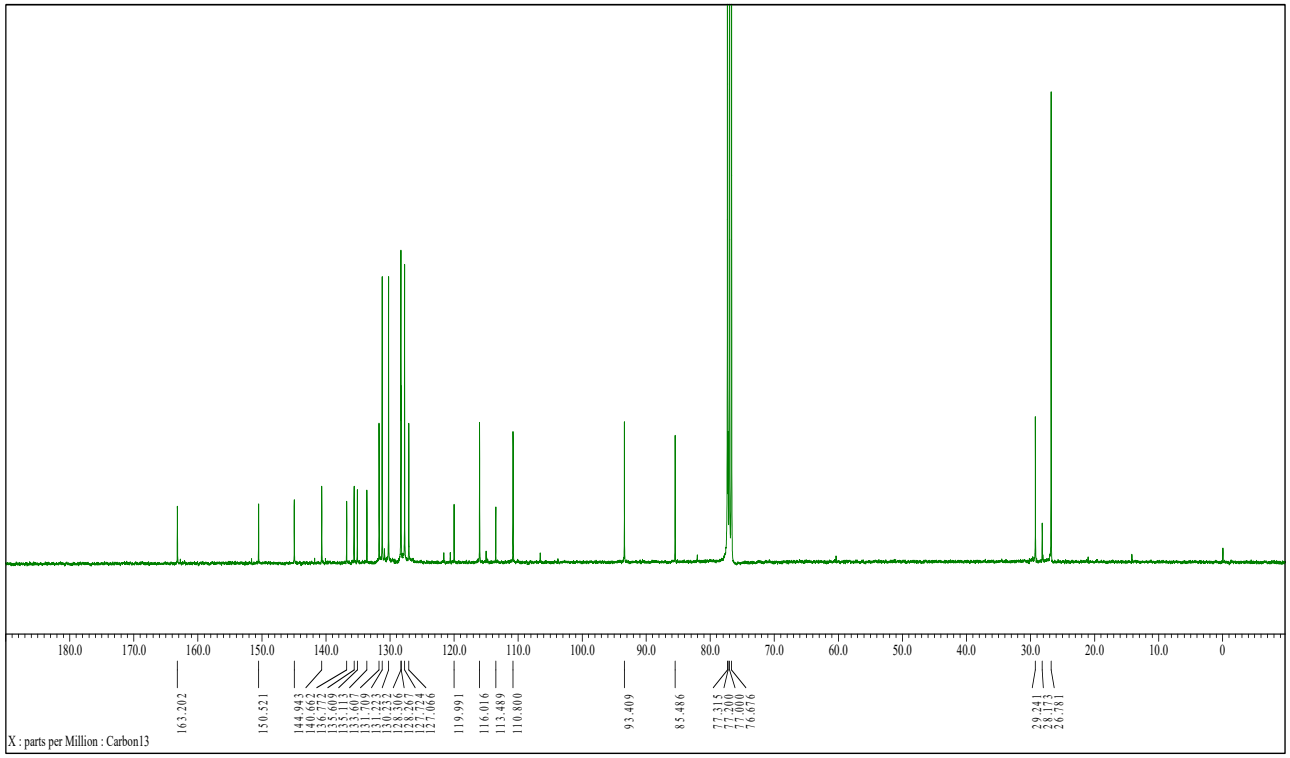

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 4ba**



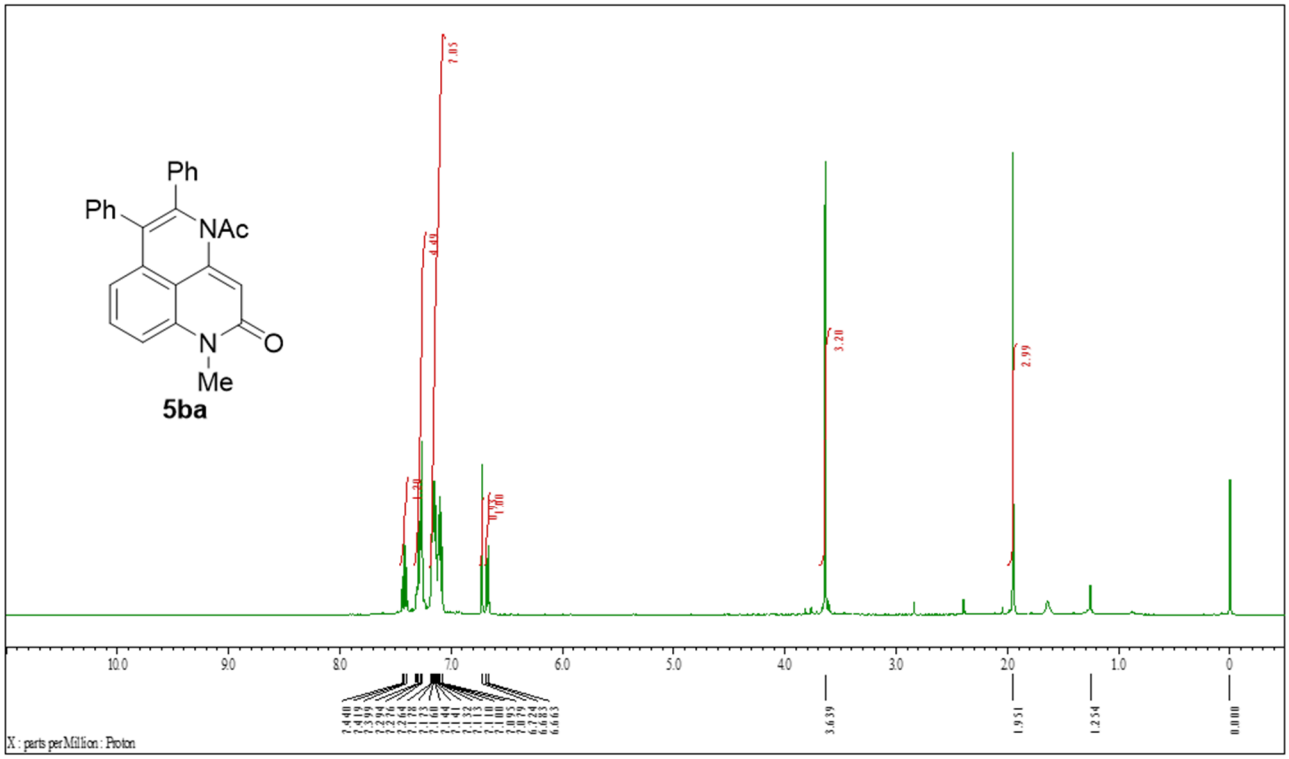
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 5aa**



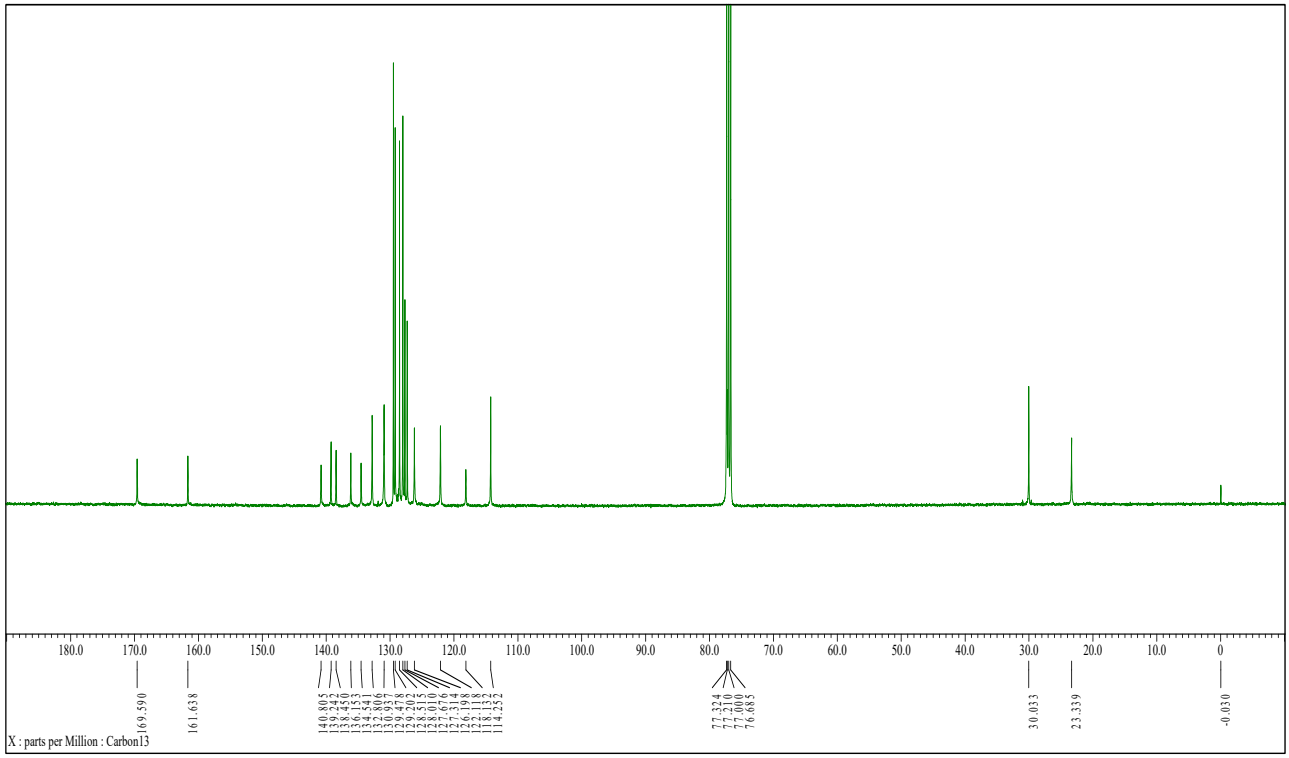

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 5aa**



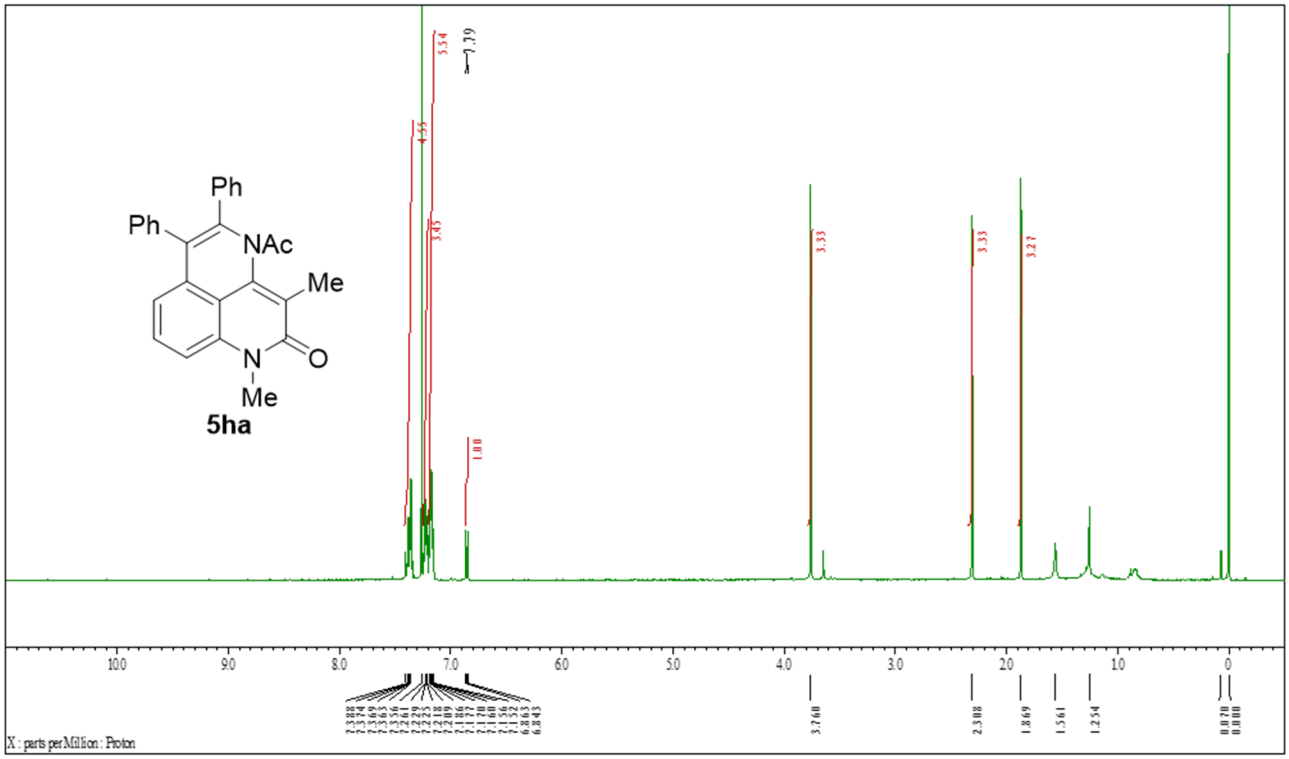
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 5ba**



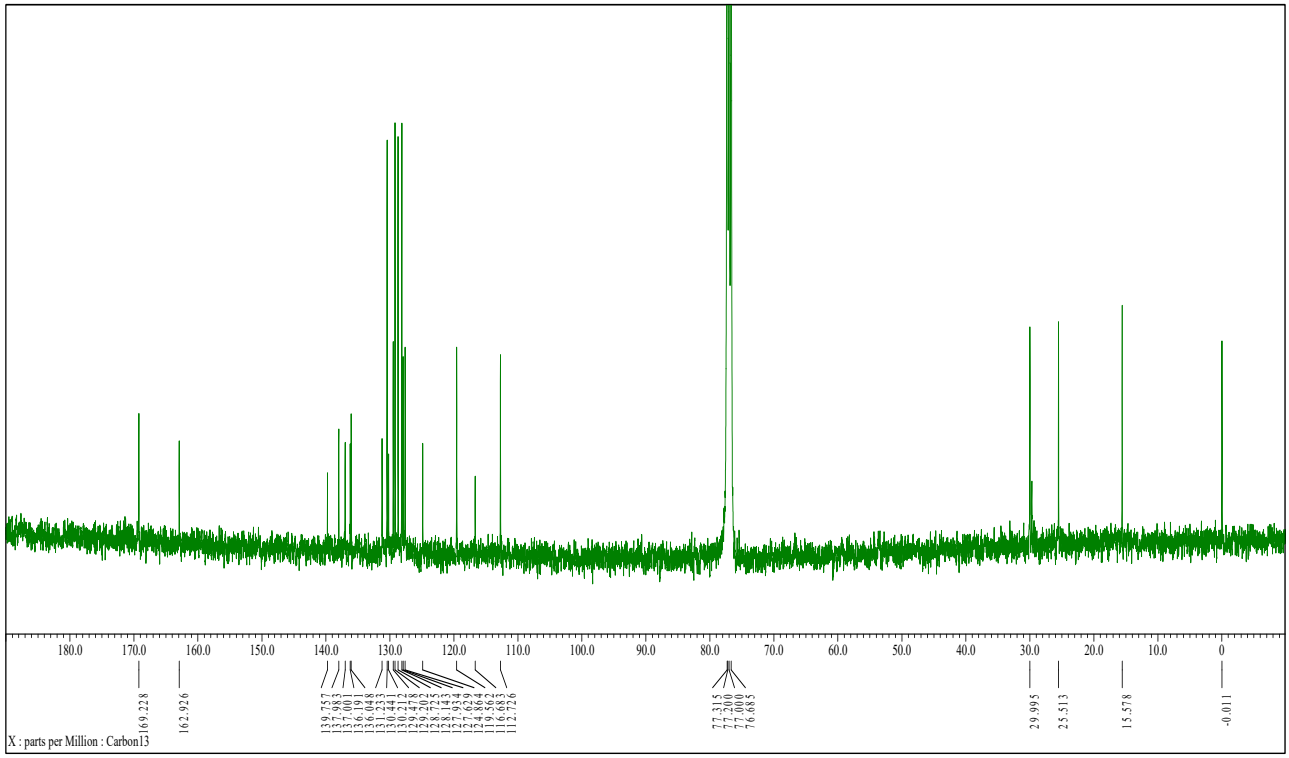

**$^{13}$C NMR (100 MHz, $CDCl_3$) of 5ba**



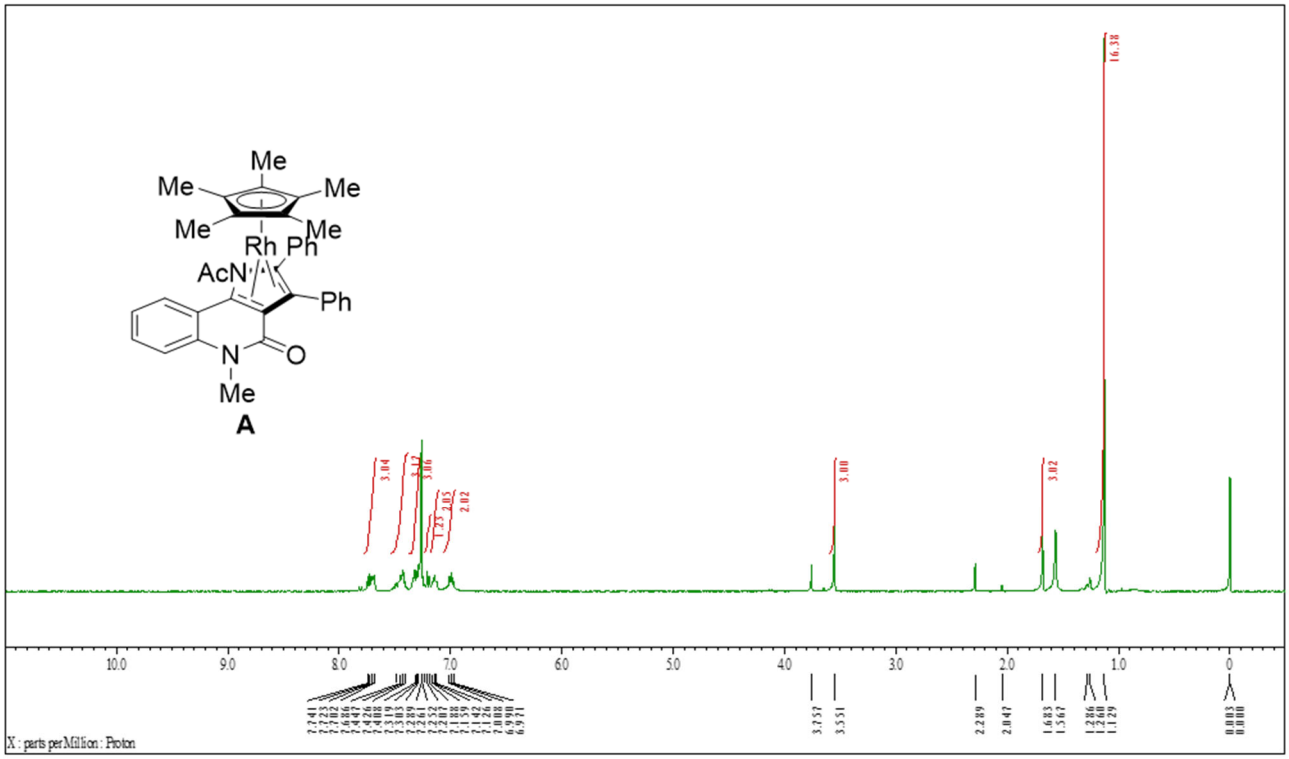
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 5ha**




**$^{13}$C NMR (100 MHz, $CDCl_3$) of 5ha**



**$^1$H NMR (400 MHz, $CDCl_3$) of A**




**$^1$H NMR (400 MHz, $CDCl_3$) of B-Me**