Supplementary Information

Synthesis of *N*-heterocyclic compounds using *N,N*-dialkylacetamide as an electrophilic carbon source

Dayoung Chun,[a†] Seok Beom Lee,[b†] Simin Chun,[a] Seung Hyun Choi,[a] Junhwa Hong,[a] Honghui Lee,[a] Jinwoo Lee,[a] and Suckchang Hong[a,b]*

[a] Research Institute of Pharmaceutical Sciences, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea

[b] Natural Products Research Institute, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea

†D.C. and S.B.L. contributed equally to this work.

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

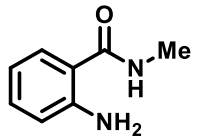
List of the Contents

1. General information

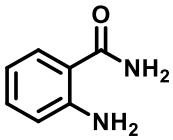
All commercially available reagents and solvents (purchased from Sigma-Aldrich, TCI, Alfa-Aesar, Acros, Combi-block) were used without further purification unless otherwise noted. All reactions were carried out in oven-dried round bottom flask or Borosilicate Glass Tubes. Borosilicate Glass Tubes were purchased from Fisher Scientific (Fisherbrand^{TM} Disposable Borosilicate Glass Tubes with Threaded End). Reactions were monitored by thin layer chromatography on silica gel 60 F254 plate (Merck, Darmstadt, Germany) using UV illumination at 254 nm (VL-4.LC, Vilber Lourmat, Eberhardzell, Germany). Column chromatography was performed on silica gel (230~400 mesh; Zeochem, Lake Zurich, Switzerland), using mixture of hexane and EtOAc as eluents. Melting points were measured on a Büchi B-540 melting point apparatus and were not corrected. Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) spectra were measured on JEOL JNM-ECZ400s [400 MHz (^{1}H), 100 MHz (^{13}C), 376 MHz (^{19}F)] spectrometer. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; for $^{13}C\{^{1}H\}$ NMR: $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm. Coupling constants (*J*) are expressed in hertz (Hz). IR spectra were recorded on a JASCO, FT/IR-4200 Infrared spectrophotometer and are reported as cm^{-1}. All high-resolution mass spectra (HR-MS) were acquired using fast atom bombardments (FAB) ionization method on a double-focusing magnetic sector mass spectrometer, JMS-700 MStation mass spectrometer (JEOL, Tokyo, Japan).

2. List of substrates

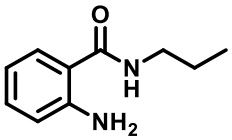
2-1. 2-Amino-benzamide substrates



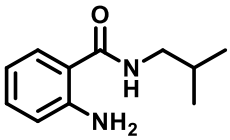
1a



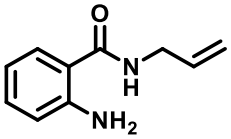
1b



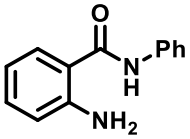
1c



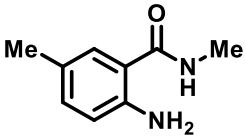
1d



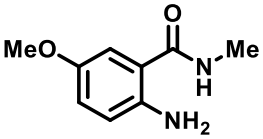
1e



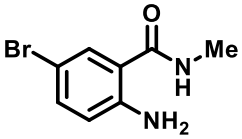
1f



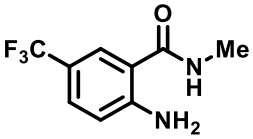
1g



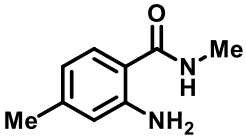
1h



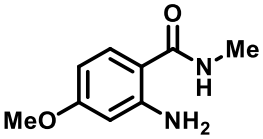
1i



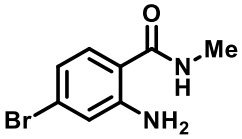
1j



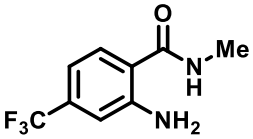
1k



1l

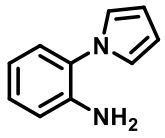


1m

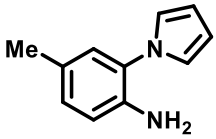


1n

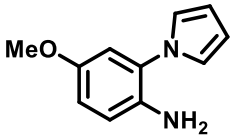
2-2. 1-(2-aminophenyl)pyrrole substrates



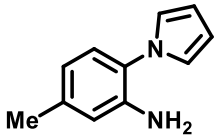
4a



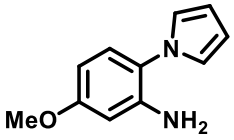
4b



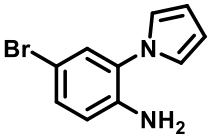
4c



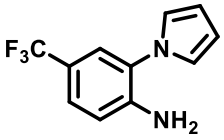
4d



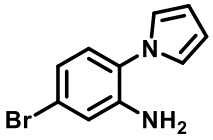
4e



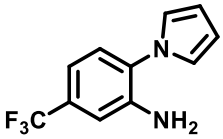
4f



4g

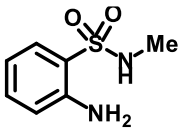


4h

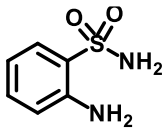


4i

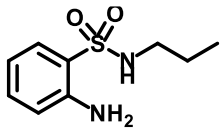
2-3. 2-Amino-*N*-substituted benzenesulfonamide substrates



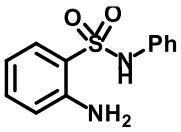
6a



6b



6c

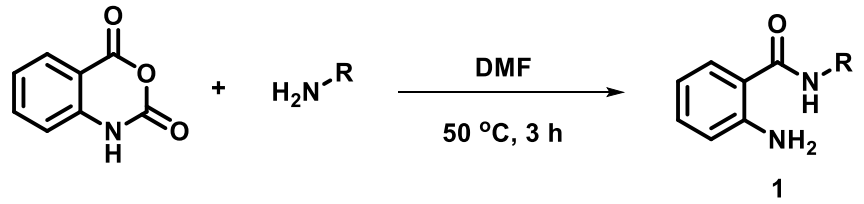


6d

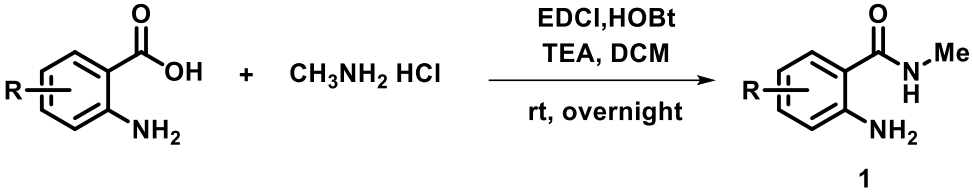
3. Synthesis of substrates

3-1. Synthesis of 2-aminobenzamide substrates (1d-1e, 1g-1h, 1j-1k, 1m-1n)

Procedure A



Procedure B



Substrates **1a** and **1b** are commercially available. **1c**, **1f**, **1i** and **1l** were synthesized through known procedures and characterization data were consistent with the literature.[1] Other substrates were synthesized following below procedures.

Procedure A. Isatoic anhydride (1.00 equiv.) and alkylamine (1.10 equiv.) were dissolved with anhydrous DMF (0.20 M) in a round bottom flask. The mixture was stirred at 50 °C for 3 h. Once the reaction was completed, the mixture was diluted with EtOAc (125 mL), and then washed with brine solution several times. The organic layer was then dried over anhydrous $MgSO_4$, concentrated, and finally purified by using flash column chromatography on silica gel to afford the desired substrate **1**.

Procedure B. The corresponding 2-aminobenzoic acid (1.00 equiv.), methylamine hydrochloride (1.20 equiv.), EDCI (1.20 equiv.), HOBt (1.20 equiv.), and TEA (3.00 equiv.) were dissolved with DCM (0.20 M) in a round bottom flask. The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the mixture was washed with saturated NH_4Cl solution. The organic layer was then dried over anhydrous $MgSO_4$, concentrated, and then finally purified by flash column chromatography on silica gel to afford the desired substrate **1**.

*2-Amino-N-isobutylbenzamide (**1d**).* Following the procedure A using isatoic anhydride (815.7 mg, 5.00 mmol, 1.00 equiv.) and isobutylamine (0.55 mL, 5.50 mmol, 1.10 equiv.) as starting materials, **1d** was obtained as a white solid (807.3 mg, 84% yield). mp: 110-112 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (t, J = 5.5 Hz, 1H), 7.47 (dd, J = 8.0, 1.6 Hz, 1H), 7.14-7.09 (m, 1H), 6.67 (dd, J = 8.2, 1.4 Hz, 1H), 6.52-6.48 (m, 1H), 6.33 (s, 2H), 3.02 (dd, J = 6.9, 5.9 Hz, 2H), 1.87-1.77 (m, 1H), 0.87 (d, J = 6.4 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 168.8, 149.5, 131.4, 128.0, 116.2, 115.2, 114.5, 46.3, 28.1, 20.2; IR (neat) ν 3421, 3303, 2957, 1620, 1588, 1536, 1308, 1269, 1158, 746, 695 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_{17}N_2O$ [M+H]: 193.1341, found: 193.1342.

*N-Allyl-2-aminobenzamide (**1e**).* Following the procedure A with isatoic anhydride (815.7 mg, 5.00 mmol, 1.00 equiv.) and allylamine hydrochloride (514.5 mg, 5.50 mmol, 1.10 equiv.) as starting materials, **1e** was obtained as a white solid (834.4 mg, 95% yield). mp: 95-96 ºC; ^{1}H NMR (400 MHz, $CDCl_3$-d) δ 7.33 (dd, J = 7.8, 1.4 Hz, 1H), 7.23-7.19 (m, 1H), 6.69-6.63 (m, 2H), 6.11 (br s, 1H), 5.98-5.89 (m, 1H), 5.52 (br s, 2H), 5.30-5.24 (m, 1H), 5.18 (dq, J = 10.1, 1.4 Hz, 1H), 4.05 (tt, J = 5.7, 1.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-d) δ 169.3, 148.9, 134.4, 132.5, 127.2, 117.5, 116.7, 116.7, 116.0, 42.2; IR (neat) ν 3420, 3296, 1620, 1588, 1531, 1303, 1262, 1157, 749 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_{13}N_2O$ [M]: 177.1028, found: 177.1032.

*2-Amino-N,5-dimethylbenzamide (**1g**).* Following the procedure B using 2-amino-5-methylbenzoic acid (453.5 mg, 3.00 mmol, 1.00 equiv.) and methylamine chloride (243.1 mg, 3.60 mmol, 1.20 equiv.) as starting materials, **1g** was obtained as a white solid (398.0 mg, 81% yield). mp: 128-129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$-d) δ 7.10 (d, J = 1.4 Hz, 1H), 7.02 (dd, J = 8.2, 1.8 Hz, 1H), 6.60 (d, J = 8.2 Hz, 1H), 6.09 (br s, 1H), 5.29 (br s, 2H), 2.95 (d, J = 5.0 Hz, 3H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-d) δ 170.2, 146.2, 133.1, 127.3, 126.0, 117.6, 116.6, 26.6, 20.5; IR (neat) ν 3419, 3295, 1636, 1588, 1542, 1298, 1261, 1223, 1158, 822 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_{12}N_2O$ [M+H]: 165.1028, found: 165.1024.

*2-Amino-5-methoxy-N-methylbenzamide (**1h**).* Following the procedure B using 2-amino-5-methoxybenzoic acid (501.5 mg, 3.00 mmol, 1.00 equiv.) and methylamine chloride (243.1 mg, 3.60 mmol, 1.20 equiv.) as starting materials, **1h** was obtained as a white solid (389.6 mg, 72% yield).

mp: 117-118 ºC; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.18 (d, *J* = 4.1 Hz, 1H), 7.02 (d, *J* = 2.7 Hz, 1H), 6.82 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.65 (d, *J* = 8.7 Hz, 1H), 6.03 (s, 2H), 3.67 (s, 3H), 2.72 (d, *J* = 4.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 169.0, 149.3, 143.7, 119.3, 117.7, 115.1, 111.8, 55.5, 25.9; IR (neat) ν 3421, 3299, 1638, 1587, 1541, 1497, 1242, 1160, 1043, 824 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_{12}N_2O_2$ [M]: 180.0899, found: 180.0896.

2-Amino-N-methyl-5-(trifluoromethyl)benzamide ***(1j)***. Following the procedure B using 2-amino-5-(trifluoromethyl)benzoic acid (615.4 mg, 3.00 mmol, 1.00 equiv.) and methylamine hydrochloride (243.1 mg, 3.60 mmol, 1.20 equiv.) as starting materials, **1j** was obtained as a white solid (515.1mg, 79% yield). mp: 127-128 ºC; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.44 (d, *J* = 3.7 Hz, 1H), 7.81 (s, 1H), 7.40 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.07 (s, 2H), 6.82 (d, *J* = 8.7 Hz, 1H), 2.73 (d, *J* = 4.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 168.3, 152.5, 128.1 (q, $C_{C\text{-}F}$, *J* = 3.9 Hz), 125.7 (q, $C_{C\text{-}F}$, *J* = 3.9 Hz), 125.0 (q, $C_{C\text{-}F}$, *J* = 269.3 Hz), 116.4, 114.4 (q, $C_{C\text{-}F}$, *J* = 31.6 Hz), 113.5, 26.0; ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -59.0; IR (neat) ν 3430, 3353, 1636, 1590, 1547, 1411, 1301, 1265, 1147, 1108, 914, 834 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_{10}F_3N_2O$ [M+H]: 219.0745, found: 219.0749.

2-Amino-N,4-dimethylbenzamide ***(1k)***. Following the procedure B using 2-amino-4-methylbenzoic acid (453.5 mg, 3.00 mmol, 1.00 equiv.) and methylamine chloride (243.1 mg, 3.60 mmol, 1.20 equiv.) as starting materials, **1k** was obtained as a pale-yellow solid (108.5 mg, 22% yield). mp: 96-97 ºC; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.18 (d, *J* = 8.3 Hz, 1H), 6.49 (s, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.04 (s, 1H), 5.50 (s, 2H), 2.94 (d, *J* = 5.1 Hz, 3H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 170.1, 148.9, 142.8, 127.1, 117.9, 117.7, 113.6, 77.5, 77.2, 76.8, 26.6, 21.5; IR (neat) ν 3347, 2942, 1633, 1587, 1537, 1317, 1260, 1175, 821, 771 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_{12}N_2O$ [M+H]: 165.1028, found: 165.1031.

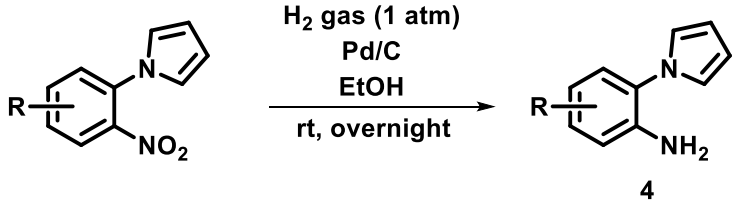
2-Amino-4-bromo-N-methylbenzamide ***(1m)***. Following the procedure B using 2-amino-4-bromobenzoic acid (273.2 mg, 1.27 mmol, 1.00 equiv.) and methylamine hydrochloride (102.5 mg, 1.52 mmol, 1.20 equiv.) as starting materials, **1m** was obtained as a white solid (243.9 mg, 84% yield). mp: 111-112 ºC; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.24 (d, *J* = 4.1 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.1 Hz, 3H), 2.70 (d, *J* = 4.6 Hz, 3H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 168.6, 151.0, 129.8, 124.9, 118.1, 117.0, 113.7, 26.0; IR (neat) ν 3339, 1607, 1571, 1541, 1487, 1256, 1168, 890, 765 cm^{-1}; HRMS (FAB) m/z calcd for $C_8H_{10}BrN_2O$ [M+H]: 228.9976, found: 228.9972.

*2-Amino-N-methyl-4-(trifluoromethyl)benzamide (**1n**)*. Following the procedure B using 2-amino-4-(trifluoromethyl)benzoic acid (615.4 mg, 3.00 mmol, 1.00 equiv.) and methylamine chloride (243.1 mg, 3.60 mmol, 1.20 equiv.) as starting materials, **1n** was obtained as a white solid (454.6 mg, 69% yield). mp: 126-127 ºC; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.38 (d, *J* = 8.2 Hz, 1H), 6.90 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.09 (s, 1H), 5.67 (s, 2H), 2.99 (d, *J* = 5.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 169.2, 148.6, 133.9 (q, C_{C-F}, *J* = 31.7 Hz), 127.9, 123.7 (q, C_{C-F}, *J* = 271.5 Hz), 118.8, 113.8 (q, C_{C-F}, *J* = 3.8 Hz), 112.8 (q, C_{C-F}, *J* = 3.8 Hz), 26.7; ^{19}F NMR (376 MHz, $CDCl_3$-*d*) δ -63.5; IR (neat) ν 3504, 3330, 1638, 1596, 1540, 1439, 1411, 1335, 1257, 1167, 1125, 877, 781, 750 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_{10}F_3N_2O$ [M+H]: 219.0745, found: 219.0755.

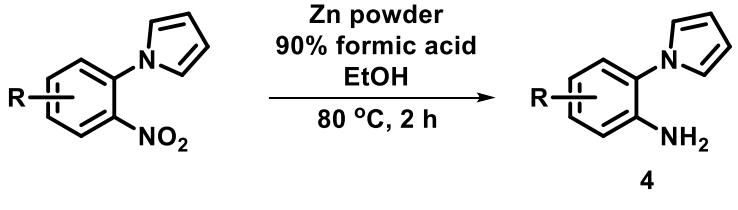
3-2. Synthesis of 1-(2-aminophenyl)pyrrole substrates (**4f**-**4h**)

Procedure C



4

Procedure D



4

Substrate **4a** is commercially available. **4b**-**4e** and **4i** were synthesized through known procedures and characterization data were consistent with the literature.[2] Other substrates were synthesized following below procedures.

Procedure C. The corresponding 1-(2-nitrophenyl)-1*H*-pyrrole (1.00 equiv.) was dissolved in ethanol (0.3 M) and then, Pd/C (10 mol% activated Pd, 0.15 equiv.) was added to the mixture. The mixture was stirred overnight under H_2 gas (1 atm) at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was filtered over Celite, and then the solvent was removed under reduced pressure thoroughly. The resulting residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent. The desired products **4** were obtained by recrystallization using dichloromethane and hexane.

Procedure D. The corresponding 1-(2-nitrophenyl)-1*H*-pyrrole (1.00 equiv.) was dissolved in ethanol (0.3 M) and, powdered zinc (10.2 equiv.) was added to the vigorously stirred solution. 90% formic acid (11.8 equiv.) was slowly added to the reaction mixture while stirring vigorously. After refluxing at 80 ^{o}C for 2 h, the reaction mixture was cooled down to room temperature and filtrated the reaction mixture over Celite. After removing the solvent under reduced pressure thoroughly, the reaction mixture was poured into water (100 mL) and extracted with EtOAc three times. The residue was purified by flash column chromatography using hexane/EtOAc as the eluent to afford the desired substrate **4**.

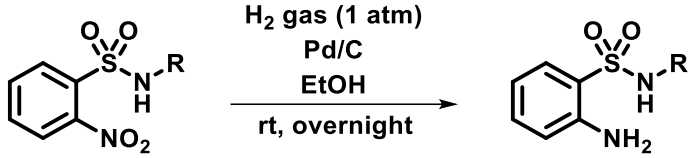
*4-Bromo-2-(1H-pyrrol-1-yl)aniline (**4f**)*. Following the procedure D using 1-(5-bromo-2-ni trophenyl)-1*H*-pyrrole (1000.0 mg, 3.74 mmol, 1.00 equiv.) as a starting material, **4f** was obtained as a needle-like pale white solid (461.5 mg, 52% yield). mp: 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.29-7.24 (m, 2H), 6.81 (t, *J* = 2.1 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 1H), 6.34 (t, *J* = 2.1 Hz, 2H), 3.75 (s, 2H*)*; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 141.3, 131.4, 129.9, 128.5, 121.6, 117.4, 110.0, 109.3; IR (neat) ν 3376, 3307, 1629, 1577, 1500, 1415, 1328, 1281, 1062, 1016, 834, 814, 739 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_9BrN_2$ [M] 235.9949, found: 235.9941.

*2-(1H-pyrrol-1-yl)-4-(trifluoromethyl)aniline (**4g**)*. Following the procedure C using 1-(2-nitro-5-(trifluoromethyl)phenyl)-1*H*-pyrrole (1100.0 mg, 4.29 mmol, 1.00 equiv.) as a starting material, **4g** was obtained as a needle-like white solid (673.9 mg, 69% yield). mp: 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.41 (d, *J* = 6.9 Hz, 2H), 6.85-6.82 (m, 3H), 6.38 (t, *J* = 2.1 Hz, 2H), 4.05 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 145.3, 126.7, 125.8 (q, $C_{C\text{-}F}$, *J* = 3.8 Hz), 124.7 (q, $C_{C\text{-}F}$, *J* = 3.9 Hz), 124.4 (q, $C_{C\text{-}F}$, *J* = 269.5 Hz), 121.6, 120.3 (q, $C_{C\text{-}F}$, *J* = 33.5 Hz), 115.6, 110.2;

^{19}F NMR (376 MHz, $CDCl_3$-*d*) δ -61.2; IR (neat) ν 3388, 3319, 3211, 1632, 1588, 1523, 1488, 1344, 1287, 1164, 1112, 1074, 1022, 912, 828, 740, 692 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_9F_3N_2$ [M] 226.0718, found: 226.0712.

*5-Bromo-2-(1H-pyrrol-1-yl)aniline (**4h**).* Following the procedure D using 1-(4-bromo-2-nitrophenyl)-1*H*-pyrrole (1000.0 mg, 3.74 mmol, 1.00 equiv.) as a starting material, **4h** was obtained as a white solid (538.7 mg, 61% yield). mp: 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.00 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 1.8 Hz, 1H), 6.89 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 2H), 6.34 (t, *J* = 2.1 Hz, 2H), 3.78 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 143.5, 128.5, 126.5, 122.0, 121.7, 121.3, 118.6, 109.9; IR (neat) ν 3477, 3378, 1617, 1506, 1421, 1327, 1264, 1108, 925, 800, 739 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_9BrN_2$ [M] 235.9949, found: 235.9952.

3-3. Synthesis of 2-amino-*N*-substituted benzenesulfonamide substrates (**6a**, **6c-6d**)



6

Substrate **6b** is commercially available. Other substrates were synthesized by following procedures. The corresponding *N*-alkyl-2-nitrobenzenesulfonamide (1.00 equiv.) was dissolved in ethanol (0.3 M) and then, Pd/C (10 mol% activated Pd, 0.25 equiv.) was added to the mixture. The mixture was stirred under H_2 gas (1 atm) at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was filtered over Celite, and then the solvent was removed under reduced pressure thoroughly. The resulting residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent. The desired products **6** were obtained by recrystallization using dichloromethane and hexane.

*2-Amino-N-methylbenzenesulfonamide (**6a**).* Following above procedure using *N*-methyl-2-nitrobenzenesulfonamide (152.4 mg, 0.75 mmol, 1.00 equiv.), **6a** was obtained as light greenish-yellow oil (130.9 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.32-

7.28 (m, 1H), 6.80-6.75 (m, 2H), 4.97 (s, 1H), 4.91 (s, 2H), 2.53 (dd, *J* = 5.5, 1.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 145.3, 134.3, 130.0, 120.1, 117.9, 117.7, 29.4; IR (neat) ν 3479, 3378, 1621, 1601, 1484, 1455, 1399, 1317, 1154, 1088, 843, 755, 696 cm^{-1}; HRMS (FAB) m/z calcd for $C_7H_{11}N_2O_2S$ [M+H] 187.0541, found: 187.0539.

*2-Amino-N-propylbenzenesulfonamide (**6c**)*. Following above procedure using 2-nitro-*N*-propylbenzenesulfonamide (900.0 mg, 3.68 mmol, 1.00 equiv.), **6c** was obtained as a light yellow oil (763.4 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.34-7.30 (m, 1H), 6.83-6.75 (m, 2H), 4.77 (d, *J* = 50.1 Hz, 3H), 2.83 (q, *J* = 6.9 Hz, 2H), 1.45 (td, *J* = 14.7, 7.4 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 145.1, 134.2, 129.8, 122.0, 118.1, 117.8, 45.1, 22.9, 11.2; IR (neat) ν 3480, 3379, 2967, 1620, 1568, 1484, 1455, 1318, 1154, 1076, 842, 754, 695 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_{15}N_2O_2S$ [M+H] 215.0854, found: 215.0862.

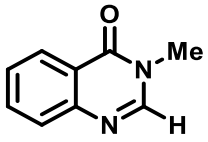
*2-Amino-N-phenylbenzenesulfonamide (**6d**)*. Following above procedure using 2-nitro-*N*-phenylbenzenesulfonamide (880.0 mg, 3.16 mmol, 1.00 equiv.), **6d** was obtained as a white solid (719.1 mg, 92% yield). mp: 121-123 ºC; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.48 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.28-7.18 (m, 4H), 7.12-7.08 (m, 1H), 7.05-7.02 (m, 2H), 6.81 (s, 1H), 6.74 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.69-6.65 (m, 1H), 4.86 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 145.1, 136.4, 134.6, 130.1, 129.3, 126.0, 122.9, 121.0, 118.0, 117.8; IR (neat) ν 3484, 3384, 3272, 1621, 1600, 1483, 1454, 1410, 1319, 1143, 1083, 920, 752, 697 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_{13}N_2O_2S$ [M+H] 249.0698, found: 249.0700.

4. Synthesis of *N*-heterocyclic compounds

4-1. General synthetic procedure for *N*-heterocyclic compounds.

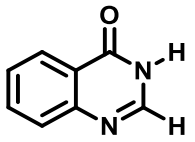
To a mixture of a substrate (0.3 mmol, 1.00 equiv.) and $FeCl_3 \cdot 6H_2O$ (0.03 mmol, 0.10 equiv.) in 2.00 mL of DMAc, DTBP (0.30-0.90 mmol, 1.00-3.00 equiv.) was added in a Borosilicate Glass Tube. The tube was capped with a rubber septum. A pink 18/24 gage needle was inserted through the septum to allow for airflow. The reaction mixture was stirred at a temperature range of 90-110 ºC for 20 h. After stirring for 20 h, the reaction mixture was cooled down to room temperature and diluted with 5 mL of EtOAc. The organic phase was extracted three times with 5 mL of EtOAc.

The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent.



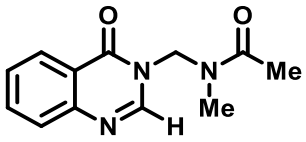
3aa

*3-Methylquinazolin-4(3H)-one (**3aa**).* Following the general procedure, **1a** (46.0 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 3:1), **3aa** was obtained as a white solid (43.1 mg, 90% yield). mp: 103-105 ^oC; ^1H NMR (400 MHz, $CDCl_3$-*d*) δ 8.30 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.05 (s, 1H), 7.76-7.68 (m, 2H), 7.51-7.47 (m, 1H), 3.59 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 161.6, 148.3, 146.9, 134.3, 127.5, 127.4, 126.7, 122.1, 34.*2*; IR (neat) ν 1670, 1612, 1472, 1340, 1322, 1294, 1264, 772, 695 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_9N_2O$ [M+H] 161.0715, found: 161.0716.



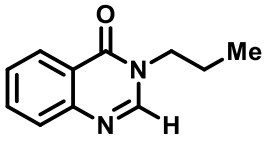
3ba

*Quinazolin-4(3H)-one (**3ba**).* Following the general procedure, **1b** (41.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:2), **3ba** was obtained as a white solid (15.2 mg, 35% yield). mp: 222-224 ^oC; ^1H NMR (400 MHz, $CDCl_3$-*d*) δ 12.22 (s, 1H), 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.09 (s, 1H), 7.81 (td, *J* = 7.8, 1.4 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.54-7.50 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 160.7, 148.7, 145.4, 134.3, 127.2, 126.7, 125.8, 122.6; IR (neat) ν 3165, 2929, 1705, 1664, 1495, 1399, 1351, 1262, 1245, 1112, 1128, 1030, 780, 694 cm^{-1}; HRMS (FAB) m/z calcd for $C_8H_7N_2O$ [M+H] 147.0558, found: 147.0564.



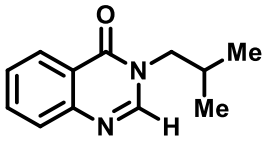
3ba'

N-Methyl-N-((4-oxoquinazolin-3(4H)-yl)methyl)acetamide ***(3ba′)****.* Following the general procedure, **1b** (41.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:10), **3ba′** was obtained as a white solid (17.8 mg, 26% yield). mp: 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.51 (s, 1H), 8.28 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.78-7.70 (m, 2H), 7.51-7.47 (m, 1H), 5.49 (s, 2H), 3.30 (s, 3H), 2.11 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 173.0, 162.1, 148.3, 147.8, 134.7, 127.8, 127.4, 126.8, 122.1, 57.9, 37.7, 21.9; IR (neat) ν 3525, 2925, 1679, 1611, 1474, 1377, 1350, 1277, 1254, 1170, 1147, 1030, 775, 695 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_{14}N_3O_2$ [M+H] 232.1086, found: 232.1084.



3ca

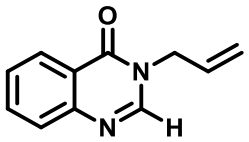
3-Propylquinazolin-4(3H)-one ***(3ca)****.* Following the general procedure, **1c** (53.5 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 2:1), **3ca** was obtained as a white solid (45.0 mg, 80% yield). mp: 83-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.31 (dd, *J* = 7.5, 1.1 Hz, 1H), 8.02 (s, 1H), 7.77-7.68 (m, 2H), 7.52-7.47 (m, 1H), 3.89-4.04 (2H), 1.83 (td, *J* = 14.8, 7.5 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 161.2, 148.3, 146.7, 134.2, 127.5, 127.3, 126.8, 122.3, 48.7, 22.8, 11.3; IR (neat) ν 2965, 1676, 1613, 1473, 1367, 1241, 768, 696 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_{13}N_2O$ [M+H] 189.1028, found: 189.1031.



3da

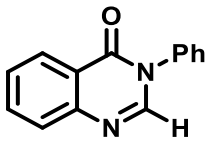
3-Isobutylquinazolin-4(3H)-one ***(3da)****.* Following the general procedure, **1d** (57.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc =

3:1), **3da** was obtained as a pale-yellow solid (49.1 mg, 81% yield). mp: 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.29 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.97 (s, 1H), 7.75-7.67 (m, 2H), 7.50-7.46 (m, 1H), 3.79 (d, *J* = 7.3 Hz, 2H), 2.20 (tt, *J* = 20.7, 6.8 Hz, 1H), 0.97 (d, *J* = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 161.3, 148.2, 147.0, 134.2, 127.5, 127.3, 126.9, 122.3, 54.2, 28.2, 20.0; IR (neat) ν 2961, 1679, 1610, 1473, 1377, 775, 696 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_{15}N_2O$ [M+H] 203.1184, found: 203.1186.



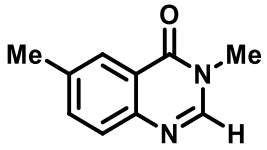
3ea

*3-Allylquinazolin-4(3H)-one (**3ea**).* Following the general procedure, **1e** (52.9 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:2), **3ea** was obtained as a white solid (47.2 mg, 84% yield). mp: 62-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.31 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.01 (s, 1H), 7.78-7.69 (m, 2H), 7.52-7.48 (m, 1H), 6.04-5.94 (m, 1H), 5.32-5.24 (m, 2H), 4.63 (td, *J* = 3.5, 2.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 160.9, 148.2, 146.3, 134.4, 132.0, 127.6, 127.5, 126.9, 122.2, 119.0, 48.5; IR (neat) ν 3053, 1678, 1607, 1474, 1362, 1323, 1239, 1105, 932, 770, 697 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_{11}N_2O$ [M+H] 187.0871, found: 187.0869.



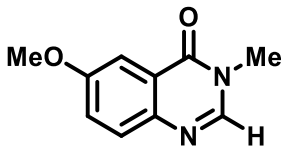
3fa

*3-Phenylquinazolin-4(3H)-one (**3fa**).* Following the general procedure, **1f** (63.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 5:1), **3fa** was obtained as a white solid (55.6 mg, 83% yield). mp: 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.31-8.40 (1H), 8.09-8.16 (1H), 7.82-7.75 (m, 2H), 7.57-7.46 (m, 4H), 7.44-7.41 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 13C-NMR (101 MHz, CHLOROFORM-D) δ 160.8, 148.0, 146.2, 137.6, 134.7, 129.7, 129.2, 127.7, 127.7, 127.3, 127.1, 122.5; IR (neat) ν 3840, 3738, 1681, 1611, 1592, 1495, 1473, 1323, 1290, 1262, 770, 751, 691 cm^{-1}; HRMS (FAB) m/z calcd for $C_{14}H_{11}N_2O$ [M+H] 223.0871, found: 223.0869.



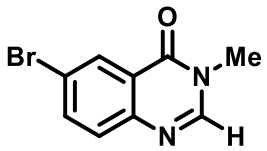
3ga

*3,6-Dimethylquinazolin-4(3H)-one (**3ga**).* Following the general procedure, **1g** (49.3 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:5), **3ga** was obtained as a pale-yellow solid (47.2 mg, 91% yield). mp: 73-76 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.06 (t, *J* = 0.9 Hz, 1H), 7.97 (s, 1H), 7.58-7.51 (m, 2H), 3.56 (s, 3H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 161.6, 146.4, 146.1, 137.6, 135.7, 127.3, 126.0, 121.8, 34.1, 21.4; IR (neat) ν 3840, 3738, 3566, 2924, 1671, 1608, 1490, 1338, 1281, 1263, 1122, 1059, 830, 795 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_{11}N_2O$ [M+H] 175.0871, found: 175.0885.



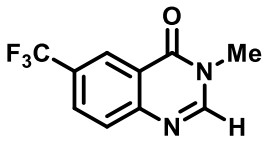
3ha

*6-Methoxy-3-methylquinazolin-4(3H)-one (**3ha**).* Following the general procedure, **1h** (54.1 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:5), **3ha** was obtained as a pale-yellow solid (51.6 mg, 90% yield). mp: 110-112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.94 (s, 1H), 7.65 (d, *J* = 2.7 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.33 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.91 (s, 3H), 3.58 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 161.6, 158.9, 144.8, 143.0, 129.2, 124.5, 122.9, 106.0, 56.0, 34.2; IR (neat) ν 2962, 1666, 1620, 1607, 1491, 1354, 1338, 1281, 1237, 1026, 829, 801, 785 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_{11}N_2O$ [M+H] 191.0821, found: 191.0829.



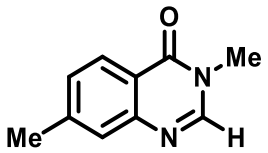
3ia

*6-Bromo-3-methylquinazolin-4(3H)-one (**3ia**).* Following the general procedure, **1i** (68.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:4), **3ia** was obtained as a white solid (61.1 mg, 85% yield). mp: 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.39 (d, *J* = 2.3 Hz, 1H), 8.02 (s, 1H), 7.78 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 3.57 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 160.4, 147.2, 137.4, 129.4, 129.2, 123.4, 121.0, 34.3; IR (neat) ν 3566, 3076, 2924, 1674, 1610, 1464, 1338, 1319, 1266, 1119, 1061, 833, 789, 776 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_8BrN_2O$ [M+H] 238.9820, found: 238.9815.



3ja

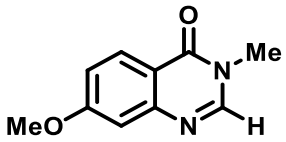
*3-Methyl-6-(trifluoromethyl)quinazolin-4(3H)-one (**3ja**).* Following the general procedure, **1j** (65.5 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:3), **3ja** was obtained as a white solid (48.7 mg, 71% yield). mp: 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.57 (d, *J* = 1.4 Hz, 1H), 8.11 (s, 1H), 7.92 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 160.9, 150.5, 148.7, 130.4 (q, $C_{C\text{-}F}$, *J* = 2.9 Hz), 129.3 (q, $C_{C\text{-}F}$, *J* = 33.5 Hz), 128.6, 124.6 (q, $C_{C\text{-}F}$, *J* = 3.8 Hz), 123.7 (q, $C_{C\text{-}F}$, *J* = 271.5 Hz), 122.0, 34.3; ^{19}F NMR (376 MHz, $CDCl_3$-*d*) δ -62.3; IR (neat) ν 3060, 1686, 1607, 1565, 1497, 1354, 1337, 1310, 1272, 1257, 1120, 1062, 839, 794 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_7F_3N_2O$ [M+H] 229.0589, found: 229.0590.



3ka

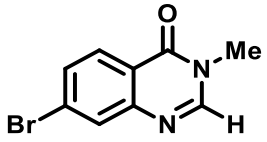
*3,7-Dimethylquinazolin-4(3H)-one (**3ka**).* Following the general procedure, **1k** (49.3 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:3), **3ka** was obtained as a pale white solid (35.4 mg, 68% yield). mp: 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.17 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 7.47 (s, 1H), 7.30 (dd,

J = 8.2, 1.4 Hz, 1H), 3.56 (s, 3H), 2.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 161.6, 148.5, 147.0, 145.3, 129.0, 127.3, 126.5, 119.7, 34.1, 22.0; IR (neat) ν 2948, 1666, 1623, 1608, 1481, 1333, 1298, 1188, 1058, 832, 784, 698 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_{11}N_2O$ [M+H] 175.0871, found: 175.0879.



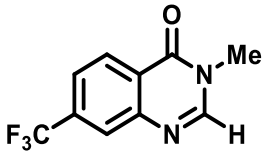
3la

*7-Methoxy-3-methylquinazolin-4(3H)-one (**3la**).* Following the general procedure, **1l** (54.1 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:3), **3la** was obtained as a white solid (19.4 mg, 34% yield). mp: 132-134 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.20 (dd, *J* = 7.5, 1.6 Hz, 1H), 8.01 (s, 1H), 7.06 (dd, *J* = 8.0, 2.1 Hz, 2H), 3.91 (s, 3H), 3.56 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 164.5, 161.3, 150.7, 147.6, 128.2, 117.4, 115.7, 108.3, 55.8, 34.1; IR (neat) ν 3525, 2944, 2842, 1671, 1612, 1563, 1488, 1447, 1347, 1245, 1156, 1057, 1025, 840, 781, 698 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_{11}N_2O$ [M+H] 191.0821, found: 191.0823.



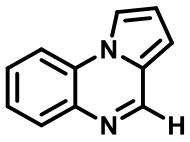
3ma

*7-Bromo-3-methylquinazolin-4(3H)-one (**3ma**).* Following the general procedure, **1m** (68.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:3), **3ma** was obtained as a white solid (60.1 mg, 84% yield). mp: 159-161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.15 (d, *J* = 8.7 Hz, 1H), 8.03 (s, 1H), 7.87 (d, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.58 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-*d*) δ 161.2, 149.4, 148.0, 130.8, 130.4, 129.0, 128.2, 120.9, 34.3; IR (neat) ν 3050, 1668, 1611, 1599, 1463, 1332, 1317, 1184, 1156, 808, 779, 696 cm^{-1}; HRMS (FAB) m/z calcd for $C_9H_8BrN_2O$ [M+H] 238.9820, found: 238.9827.



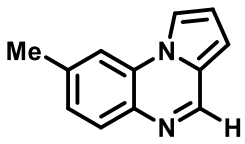
3na

*3-Methyl-7-(trifluoromethyl)quinazolin-4(3H)-one (**3na**).* Following the general procedure, **1n** (65.5 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 1:1), **3na** was obtained as a white solid (62.9 mg, 92% yield). mp: 143-145 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.39 (d, *J* = 8.2 Hz, 1H), 8.10 (s, 1H), 7.95 (s, 1H), 7.67 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 160.8, 148.4, 148.1, 135.9 (q, $C_{C\text{-}F}$, *J* = 32.7 Hz), 127.8, 125.2 (q, $C_{C\text{-}F}$, *J* = 3.8 Hz), 124.3, 123.5 (q, $C_{C\text{-}F}$, *J* = 272.4 Hz), 123.4 (q, $C_{C\text{-}F}$, *J* = 2.9 Hz),, 34.3; ^{19}F NMR (376 MHz, $CDCl_3$-*d*) δ -63.1; IR (neat) ν 3087, 2371, 1686, 1615, 1567, 1446, 1397, 1336, 1317, 1153, 1119, 1049, 912, 900, 857, 794, 700 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_7F_3N_2O$ [M+H] 229.0589, found: 229.0595.



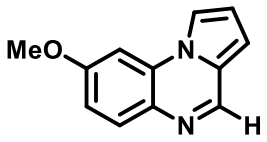
5aa

*Pyrrolo[1,2-a]quinoxaline (**5aa**).* Following the general procedure, **4a** (47.5 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 5:1), **5aa** was obtained as a light-yellow solid (35.8 mg, 71% yield). mp: 135-137 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.82 (s, 1H), 8.00-7.95 (m, 2H), 7.88 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.54 (td, *J* = 7.8, 1.4 Hz, 1H), 7.48-7.44 (m, 1H), 6.94-6.89 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 145.9, 135.9, 130.2, 128.1, 127.9, 126.5, 125.3, 114.3, 114.1, 113.9, 107.5; IR (neat) ν 3091, 3059, 1614, 1589, 1549, 1478, 1452, 1421, 1364, 1338, 1295, 1242, 1034, 867, 744 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_9N_2$ [M+H] 169.0766, found: 169.0770.



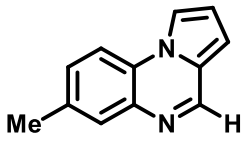
5ba

*8-Methylpyrrolo[1,2-a]quinoxaline (**5ba**).* Following the general procedure, **4b** (51.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 5:1), **5ba** was obtained as a yellow solid (29.1 mg, 53% yield). mp: 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.75 (s, 1H), 7.87-7.82 (m, 2H), 7.64 (s, 1H), 7.26-7.23 (m, 1H), 6.87-6.84 (m, 2H), 2.54 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 145.0, 138.4, 133.9, 129.9, 127.9, 126.6, 126.5, 113.9, 107.0, 22.0; IR (neat) ν 3738, 3094, 1747, 1622, 1548, 1488, 1459, 1419, 1357, 1339, 1291, 1038, 874, 815, 731 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_{11}N_2$ [M+H] 183.0922, found: 183.0928.



5ca

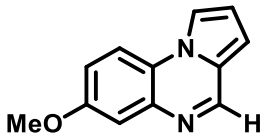
*8-Methoxypyrrolo[1,2-a]quinoxaline (**5ca**).* Following the general procedure, **4c** (56.5 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 10:1), **5ca** was obtained as a yellowish brown solid (33.4 mg, 56% yield). mp: 111-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.69 (s, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.80 (t, *J* = 1.4 Hz, 1H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.02 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.85 (qd, *J* = 4.0, 2.0 Hz, 2H), 3.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 159.4, 143.4, 131.4, 130.4, 128.9, 126.5, 114.1, 113.7, 112.8, 106.8, 97.7, 55.9; IR (neat) ν 3738, 3086, 2372, 1747, 1622, 1551, 1489, 1458, 1340, 1280, 1177, 1090, 1036, 873, 836, 732 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_{11}N_2O$ [M+H] 199.0871, found: 199.0876.



5da

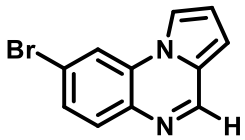
*7-Methylpyrrolo[1,2-a]quinoxaline (**5da**).* Following the general procedure, **4d** (51.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 3:1), **5da** was obtained as a bright yellow solid (27.1 mg, 50% yield). mp: 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.78 (s, 1H), 7.86 (t, *J* = 1.1 Hz, 1H), 7.74-7.71 (m, 2H), 7.31 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.87-6.83 (m, 2H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-

d) δ 145.8, 135.8, 135.1, 130.0, 129.0, 126.5, 125.9, 114.1, 113.8, 113.6, 107.1, 21.2; IR (neat) ν 3738, 3094, 3033, 1747, 1620 1594, 1549, 1492, 1455, 1424, 1336, 1036, 839, 814, 737, 673 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_{11}N_2$ [M+H] 183.0922, found: 183.0924.



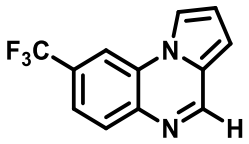
5ea

*7-Methoxypyrrolo[1,2-a]quinoxaline (**5ea**).* Following the general procedure, **4e** (56.5 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 7:1), **5ea** was obtained as a yellow solid (34.0 mg, 57% yield). mp: 97-99 ºC; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.78 (s, 1H), 7.84 (t, *J* = 1.1 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.42 (d, *J* = 2.8 Hz, 1H), 7.12 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.88-6.83 (m, 2H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 157.2, 146.2, 137.0, 126.3, 122.4, 116.9, 114.8, 114.0, 113.8, 111.6, 107.1, 55.8; IR (neat) ν 3566, 3095, 2321, 1748, 1600, 1542, 1491, 1469, 1421, 1336, 1303, 1249, 1154, 1040, 942, 843, 810, 793 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_{11}N_2O$ [M+H] 199.00871, found: 199.0873.



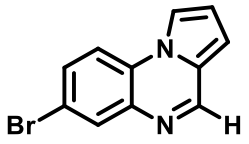
5fa

*8-Bromopyrrolo[1,2-a]quinoxaline (**5fa**).* Following the general procedure, **4f** (71.1mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 3:1), **5fa** was obtained as a bright yellow solid (49.0 mg, 66% yield). mp: 220-222 ºC; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.80 (s, 1H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.88-7.80 (m, 2H), 7.54 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.91 (qd, *J* = 4.2, 2.1 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 146.2, 134.9, 131.6, 129.0, 128.6, 126.5, 121.2, 117.1, 114.8, 114.6, 108.1; IR (neat) ν 3092, 1606, 1540, 1478, 1431, 1336, 1290, 1092, 1011, 867, 822, 785, 739 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_8BrN_2$ [M+H] 246.9871, found: 246.9873.



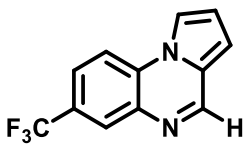
5ga

*8-(Trifluoromethyl)pyrrolo[1,2-a]quinoxaline (**5ga**).* Following the general procedure, **4g** (67.9 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 5:1), **5ga** was obtained as a light-yellow solid (50.0 mg, 71% yield). mp: 134-136 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.81 (s, 1H), 8.04 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 (t, *J* = 1.4 Hz, 1H), 7.63 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.94-6.89 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 147.7, 138.0, 130.9, 129.3 (q, C_{C-F}, *J* = 32.6 Hz), 127.8, 126.5, 123.9 (q, C_{C-F}, *J* = 270.3 Hz), 121.6 (q, C_{C-F}, *J* = 3.8 Hz), 115.1, 114.9, 111.5 (q, C_{C-F}, *J* = 3.8 Hz), 108.7; ^{19}F NMR (376 MHz, $CDCl_3$-*d*) δ -61.9; IR (neat) ν 3107, 1747, 1629, 1542, 1465, 1440, 1421, 1364, 1339, 1310, 1173, 1111, 1068, 871, 831, 740 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_8F_3N_2$ [M+H] 237.0640, found: 237.0630.



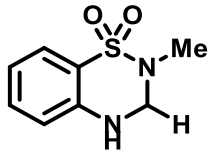
5ha

*7-Bromopyrrolo[1,2-a]quinoxaline (**5ha**).* Following the general procedure, **4h** (71.1 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 7:1), **5ha** was obtained as a white solid (41.5 mg, 56% yield). mp: 172-174 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.80 (s, 1H), 8.10 (d, *J* = 2.3 Hz, 1H), 7.90 (t, *J* = 1.1 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.61 (dd, *J* = 8.7, 1.8 Hz, 1H), 6.91 (dq, *J* = 11.3, 2.1 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 146.9, 137.2, 132.7, 130.7, 127.2, 126.5, 117.9, 115.4, 114.7, 114.6, 108.2; IR (neat) ν 3097, 1607, 1584, 1542, 1480, 1425, 1333, 1096, 1029, 932, 880, 868, 813, 739 cm^{-1}; HRMS (FAB) m/z calcd for $C_{11}H_8BrN_2$ [M+H] 246.9871, found: 246.9867.



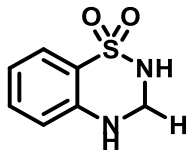
5ia

*7-(Trifluoromethyl)pyrrolo[1,2-a]quinoxaline (**5ia**).* Following the general procedure, **4i** (67.9 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 5:1), **5ia** was obtained as a pale white solid (49.5 mg, 70% yield). mp: 161-162 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 8.82 (s, 1H), 8.20 (d, *J* = 1.4 Hz, 1H), 7.93-7.88 (m, 2H), 7.71 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.95-6.92 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 147.1, 135.6, 130.2, 127.7 (q, C_{C-F}, *J* = 3.8 Hz), 127.4 (q, C_{C-F}, *J* = 32.5 Hz), 126.6, 124.3 (q, C_{C-F}, *J* = 3.8 Hz), 124.0 (q, C_{C-F}, *J* = 270.3 Hz), 115.1, 115.0, 114.6, 108.6; ^{19}F NMR (376 MHz, $CDCl_3$-*d*) δ -61.9; IR (neat) ν 3107, 1625, 1594, 1555, 1438, 1422, 1325, 1300, 1266, 1165, 1123, 1101, 905, 888, 822, 748 cm^{-1}; HRMS (FAB) m/z calcd for $C_{12}H_8F_3N_2$ [M+H] 237.0640, found: 237.0641.



7aa

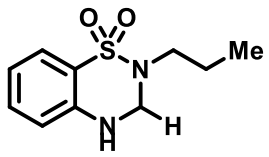
*2-Methyl-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine 1,1-dioxide (**7aa**).* Following the general procedure, **6a** (55.9 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 3:1), **7aa** was obtained as a white solid (52.9 mg, 89% yield). mp: 159-160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.64 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.32-7.28 (m, 1H), 6.86-6.82 (m, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 4.87 (d, *J* = 3.2 Hz, 2H), 4.65 (s, 1H), 2.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$- *d*) δ 141.9, 133.6, 126.1, 119.9, 118.8, 116.0, 61.8, 35.0; IR (neat) ν 3373, 1770, 1607, 1506, 1369, 1315, 1247, 1153, 1050, 905, 711 cm^{-1}; HRMS (FAB) m/z calcd for $C_8H_{11}N_2O_2S$ [M+H] 199.0541, found: 199.0541.



7ba

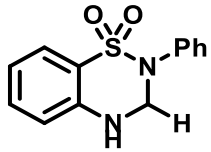
*3,4-Dihydro-2H-benzo[e][1,2,4]thiadiazine 1,1-dioxide (**7ba**).* Following the general procedure, **6b** (51.7 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 2:1), **7ba** was obtained as a white solid (42.6 mg, 77% yield). mp: 170-173 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (t, *J* = 8.2 Hz, 1H), 7.45 (dd, *J* = 7.9, 1.2

Hz, 1H), 7.29-7.25 (m, 1H), 7.09 (s, 1H), 6.76 (d, J = 8.5 Hz, 1H), 6.71-6.67 (m, 1H), 4.61 (q, J = 3.7 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO- d_6) δ 143.7, 132.8, 123.8, 121.7, 116.1, 115.9, 54.4; IR (neat) ν 3399, 3224, 2925, 2853, 1607, 1503, 1311, 1155, 1138, 750 cm^{-1}; HRMS (FAB) m/z calcd for $C_7H_9N_2O_2S$ [M+H] 185.0385, found: 185.0388.



7ca

*2-Propyl-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine 1,1-dioxide (**7ca**).* Following the general procedure, **6c** (64.3 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 5:1), **7ca** was obtained as a light-yellow solid (47.3 mg, 70% yield). mp: 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d) δ 7.61 (dd, J = 7.8, 1.4 Hz, 1H), 7.29-7.25 (m, 1H), 6.82-6.78 (m, 1H), 6.68 (dd, J = 8.2, 0.9 Hz, 1H), 4.88 (d, J = 3.2 Hz, 2H), 4.80 (s, 1H), 3.03 (t, J = 7.3 Hz, 2H), 1.63 (td, J = 14.6, 7.2 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$-d) δ 142.3, 133.4, 125.7, 120.7, 118.4, 116.0, 58.7, 47.9, 21.6, 11.3; IR (neat) ν 3384, 2966, 2933, 2875, 1607, 1503, 1323, 1173, 1153, 1137, 1073, 937, 750, 709 cm^{-1}; HRMS (FAB) m/z calcd for $C_{10}H_{15}N_2O_2S$ [M+H] 227.0854, found: 227.0860.



7da

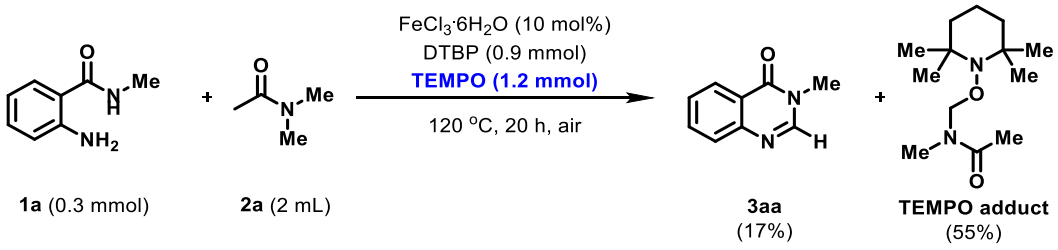
*2-Phenyl-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine 1,1-dioxide (**7da**).* Following the general procedure, **6d** (74.5 mg, 0.3 mmol) was used as a starting material. After purification by column chromatography (hexane:EtOAc = 5:1), **7da** was obtained as a white solid (47.5 mg, 61% yield). mp: 173-175 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (t, J = 3.4 Hz, 1H), 7.47 (dd, J = 8.3, 1.4 Hz, 1H), 7.39-7.24 (m, 6H), 6.90 (d, J = 7.8 Hz, 1H), 6.78-6.74 (m, 1H), 5.22 (d, J = 3.7 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 143.2, 140.6, 133.7, 129.1, 127.3, 125.9, 124.4, 119.5, 117.1, 116.3, 61.5; IR (neat) ν 3384, 1606, 1492, 1336, 1251, 1212, 1158, 1138, 1076, 749, 707, 693 cm^{-1}; HRMS (FAB) m/z calcd for $C_{13}H_{13}N_2O_2S$ [M+H] 261.0698, found: 261.0702.

5. Mechanism studies

5-1. Capturing the *N,N*-dimethylacetamide radical by TEMPO

To investigate the presence of *N,N*-dimethylacetamide (DMAc) radicals in the reaction system, we utilized a radical scavenger, TEMPO. A larger amount of TEMPO than the amount of DTBP was added since the air could potentially act as an additional oxidant in this reaction. As a result, the TEMPO adduct, which successfully captured the DMAc radical, was obtained as a white solid. The spectral data of the TEMPO adduct is consistent with the literature.[3]

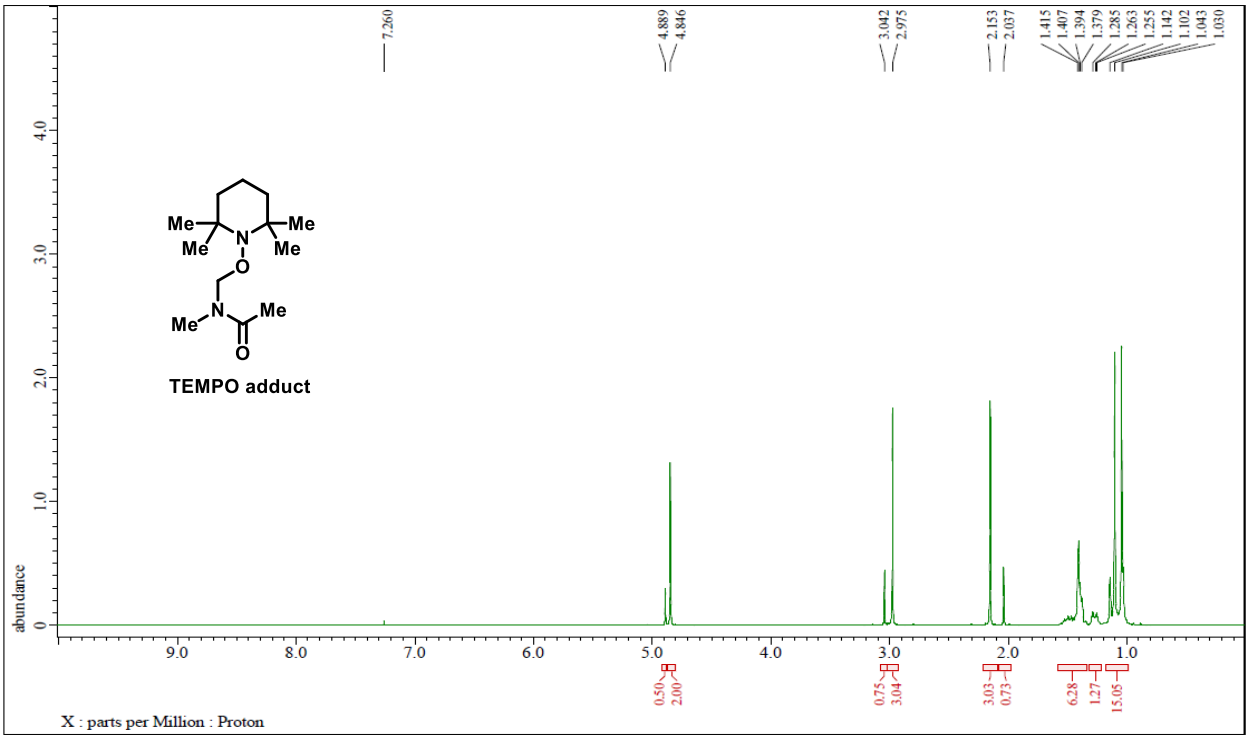
Radical trap reactions with TEMPO. Substrate **1a** (45.1 mg, 0.3 mmol, 1.0 equiv.), $FeCl_3 \cdot 6H_2O$ (8.1 mg, 10 mol%.) and TEMPO (187.5 mg, 1.2 mmol, 4.0 equiv.) were added to an oven-dried Borosilicate Glass Tube. The DMAc **2a** (2.0 mL, 21.6 mmol) and DTBP (0.16 mL, 0.9 mmol, 3.0 equiv.) were added to the reaction tube. The reaction mixture was stirred at 120 ℃ using oil bath under open system. After stirring for 20 h, the reaction mixture was cooled down to room temperature and diluted with EtOAc (10 mL) and H_2O (20 mL). The mixture was extracted with EtOAc (10 mL x 2). Combined organic phase was washed with brine solution (2 x 10 mL), dried over anhydrous $MgSO_4$, and concentrated in *vacuo*. After purification by column chromatography (hexane : EtOAc = 10:1 to 2:1), **3aa** was obtained as white solid (16.0 mg, 17% yield) and **TEMPO adduct** was obtained as white solid (103.1 mg, 55% yield).



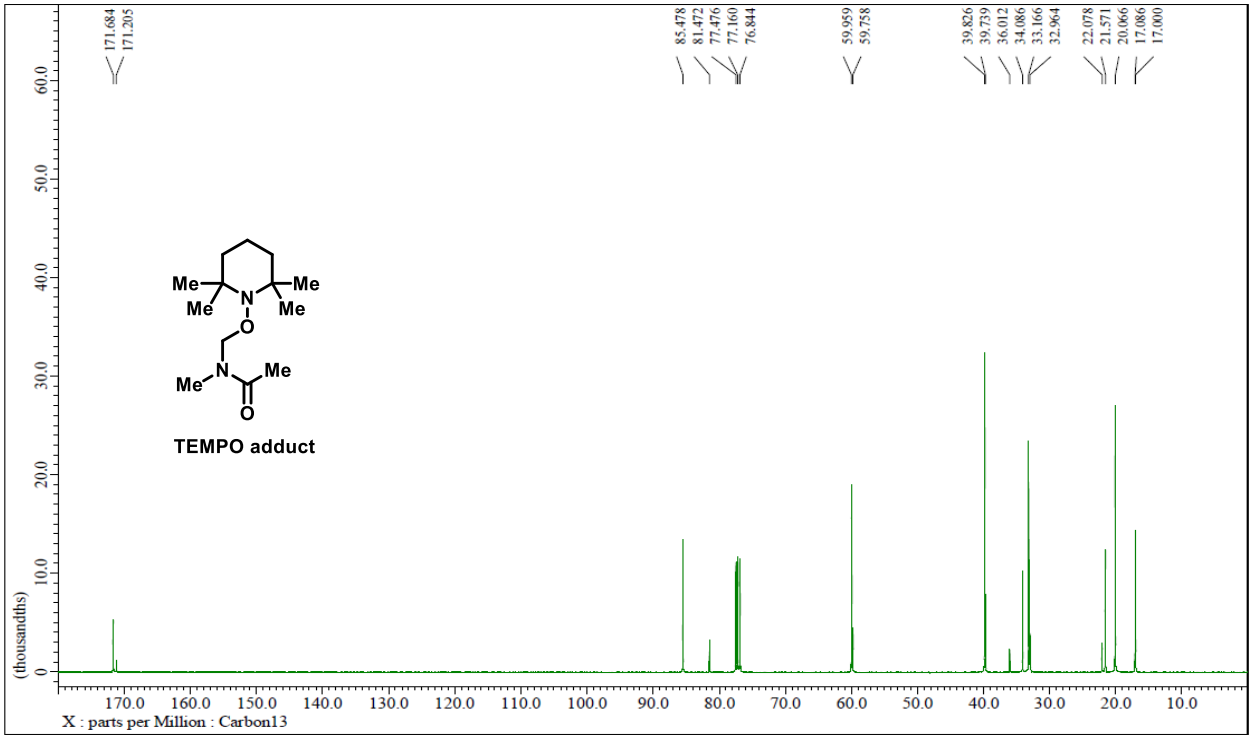
N-Methyl-N-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)acetamide ***(DMAc captured TEMPO adduct)***

mp: 56-58 ºC; Major peak = ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 4.85 (s, 2H), 2.98 (s, 3H), 2.15 (s, 3H), 1.55-1.35 (m, 5H), 1.30-1.25 (m, 1H), 1.07 (d, J = 23.6 MHz, 12H), Minor peak = ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 4.89 (s, 0.5H), 3.04 (s, 0.75H), 2.04 (s, 0.75H), 1.55-1.35 (m, 1.25H), 1.30-1.25 (m, 0.25H), 1.09 (d, J = 44.8 MHz, 3H); Major peak = ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) δ 171.7, 85.5, 60.0, 39.8, 34.1, 33.2, 21.6, 20.1, 17.0; Minor peak = ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*) minor peak = δ 171.2, 81.5, 59.8, 39.7, 36.0, 33.0, 22.1, 20.1, 17.1; HRMS (FAB) m/z calcd for $C_{13}H_{27}N_2O_2$ $[M+H]^+$: 243.2067 found: 243.2076.

^{1}H NMR (400 MHz, $CDCl_3$-*d*) of ***DMAc captured TEMPO adduct***



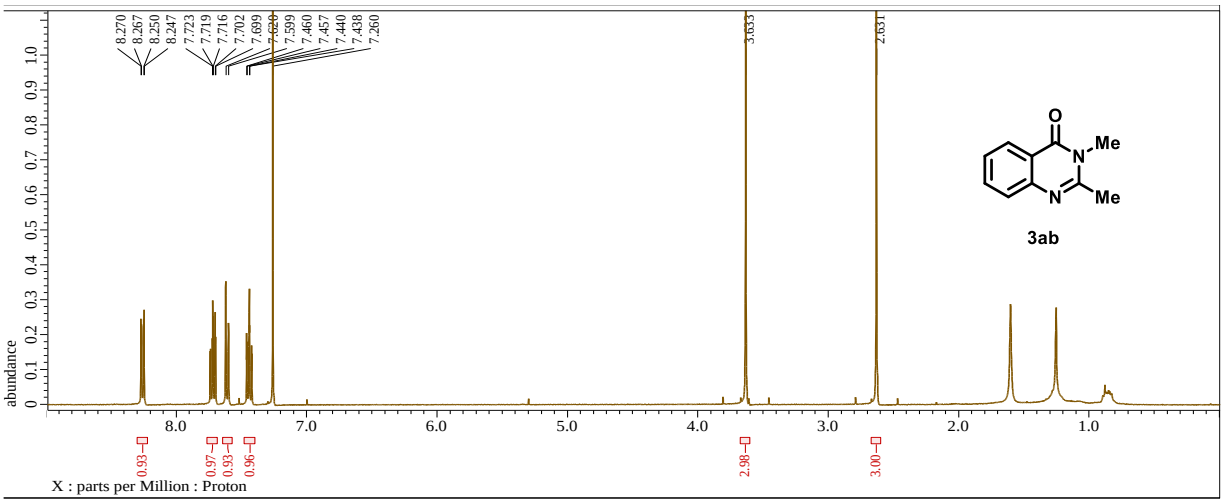
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of ***DMAc captured TEMPO adduct***

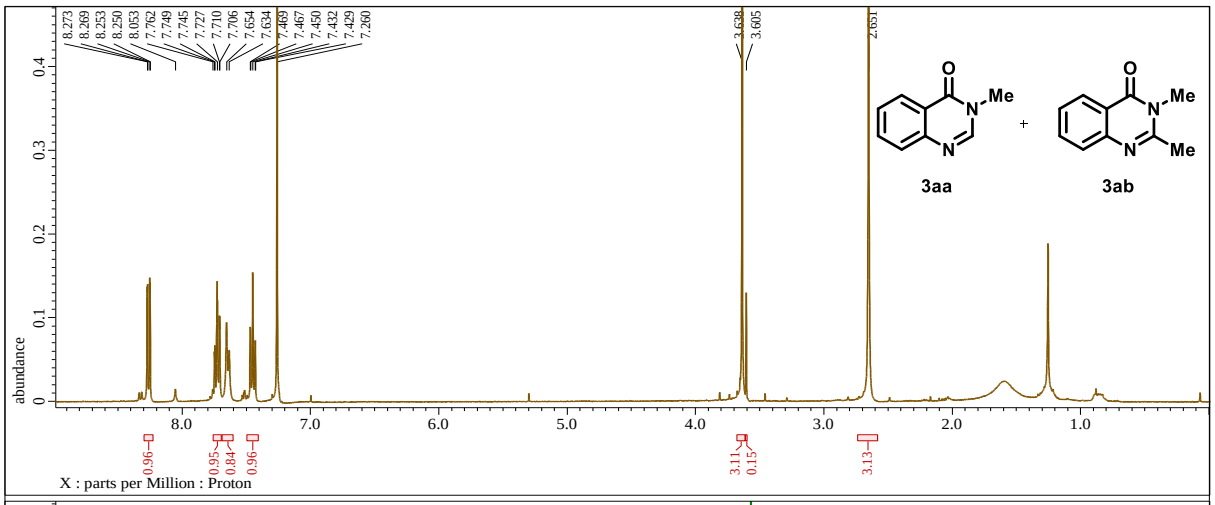


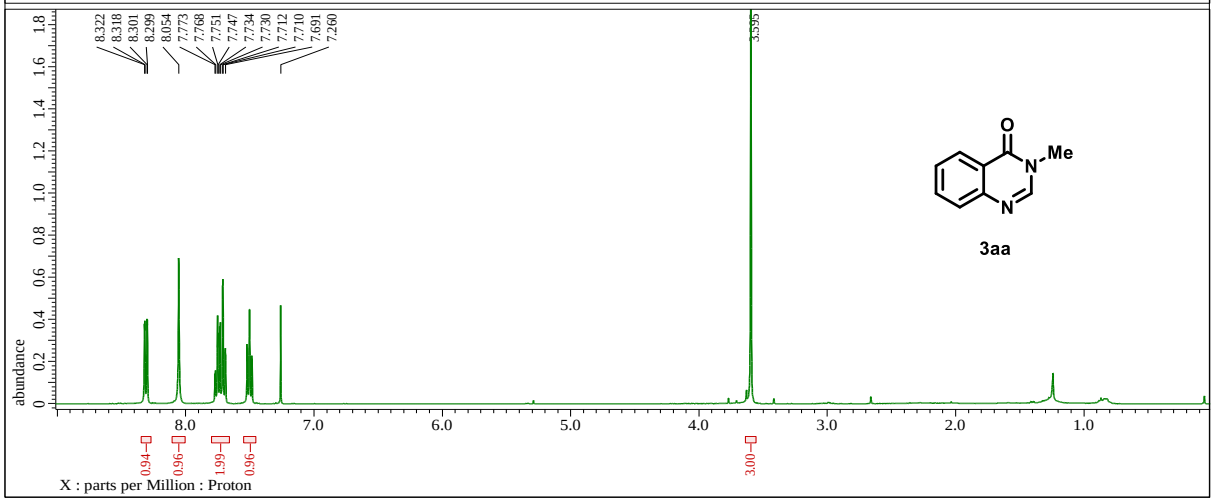
5-2. Confirming the Introduction of the Ethyl Carbon Source from the Ethyl Substituted Organic Solvents

We hypothesized that a carbon adjacent to a heteroatom in organic solvents was introduced as an electrophilic carbon source to produce a desired product. In addition to the methyl carbon source, we investigated whether ethyl-substituted organic solvents could also be introduced to this reaction system. Instead of isolating the ethyl-substituted product (**3ab**), the desired product was detected in ^{1}H NMR of a mixture, which was obtained under a given condition, as shown in ^{1}H NMR spectra below. Since they do have similar R_f values, each product could not be isolated respectively. Because the ethyl-substituted product (**3ab**) is known compound,[1] based on the ratio of their methyl peaks the NMR yield could be calculated.

Since *N,N*-diethylacetamide demonstrated an outstanding yield among the tested ethyl-substituted solvents, the NMR spectra of that mixture were exampled as shown below**.**


8.270
8.267
8.250
8.247
7.723
7.719
7.716
7.702
7.699
7.599
7.460
7.457
7.440
7.438
7.260
3.633
2.631
abundance
0.93
0.97
0.93
0.96
2.98
3.00
X : parts per Million : Proton
3ab

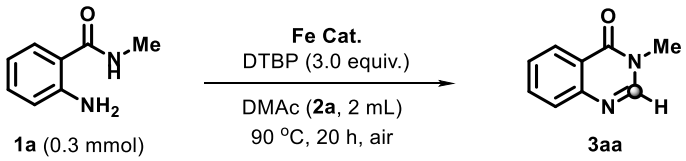

8.273
8.269
8.253
8.250
8.053
7.762
7.749
7.745
7.727
7.710
7.706
7.654
7.634
7.469
7.467
7.450
7.432
7.429
7.260
3.638
3.605
2.651
abundance
0.96
0.95
0.84
0.96
3.11
0.15
3.13
X : parts per Million : Proton
3aa
3ab


8.322
8.318
8.301
8.299
8.054
7.773
7.768
7.751
7.747
7.734
7.730
7.712
7.710
7.691
7.260
3.595
abundance
0.94
0.96
1.99
0.96
3.00
X : parts per Million : Proton
3aa

5-3. Screening of iron catalysts

We have investigated effect of various iron salts under our conditions. A noticeable decrease in yield was observed when we reduced the amount of catalyst or used $FeCl_2$. Additionally, the results from using different Fe^{III} salts show the impact of the counter anion on the reaction. Generally, reactions with halide salts performed well, while reactions with other anion salts showed little to no progress of the reaction.

Table S1. Screening of Fe catalysts



1a (0.3 mmol) → 3aa

Entry	**Fe Cat.**	mol %	Yield[a] (%)
1	$FeCl_3.6H_2O$	10	90
2	$FeCl_3.6H_2O$	5	81
3	$FeCl_2.4H_2O$	10	71
4	$FeBr_3$	10	78
5	$Fe(acac)_3$	10	trace
6	$Fe(NO_3)_3.9H_2O$	10	15
7	$Fe(ClO_4)_3$	10	9

[a] Isolated yield.

6. Reference

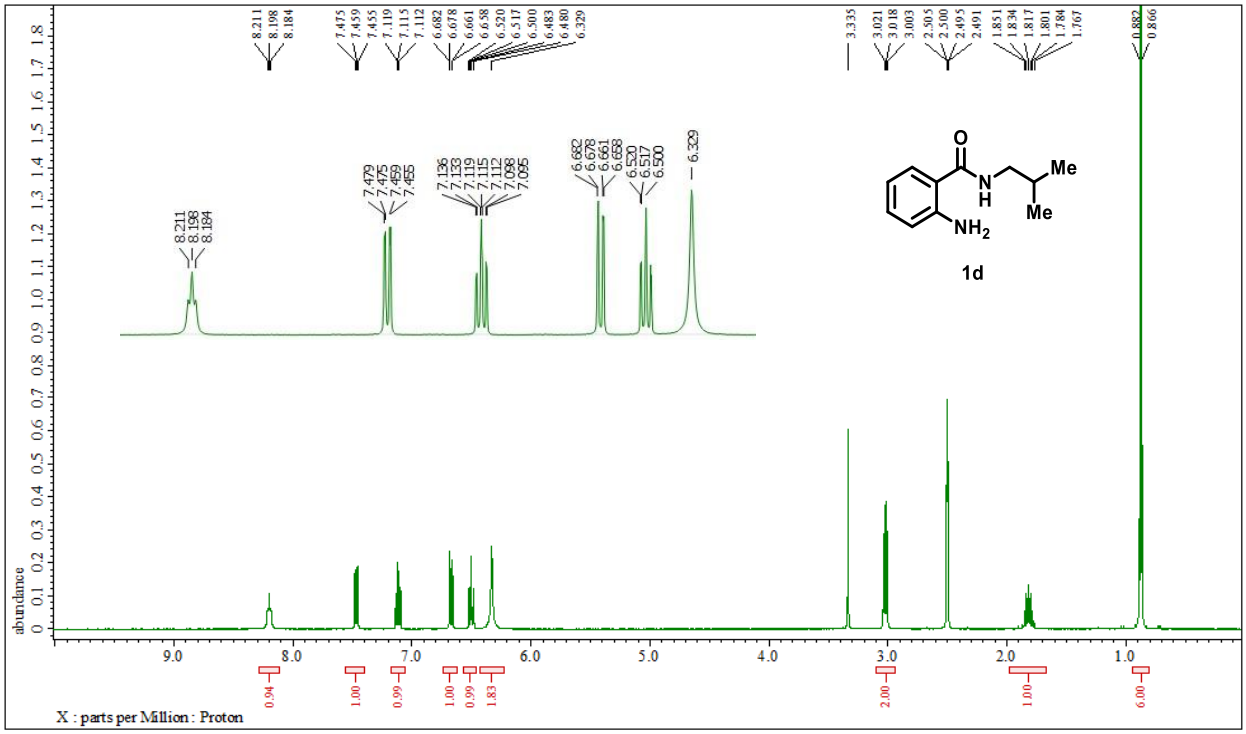
1. Jang, Y.; Lee, S. B.; Hong, J.; Chun, S.; Lee, J.; Hong, S. Synthesis of 2-aryl quinazolinones *via* iron-catalyzed cross-dehydrogenative coupling (CDC) between N–H and C–H bonds. *Org. Biomol. Chem*. **2020**, *18*, 5435-5441.

2. Ahn, J.; Lee, S. B.; Song, I.; Chun, S.; Oh, D.; Hong, S. Synthesis of 4-Aryl Pyrrolo[1,2-*α*]quinoxalines *via* Iron-Catalyzed Oxidative Coupling from an Unactivated Methyl Arene. *J. Org. Chem.* **2021**, *86*, 7390-7402.

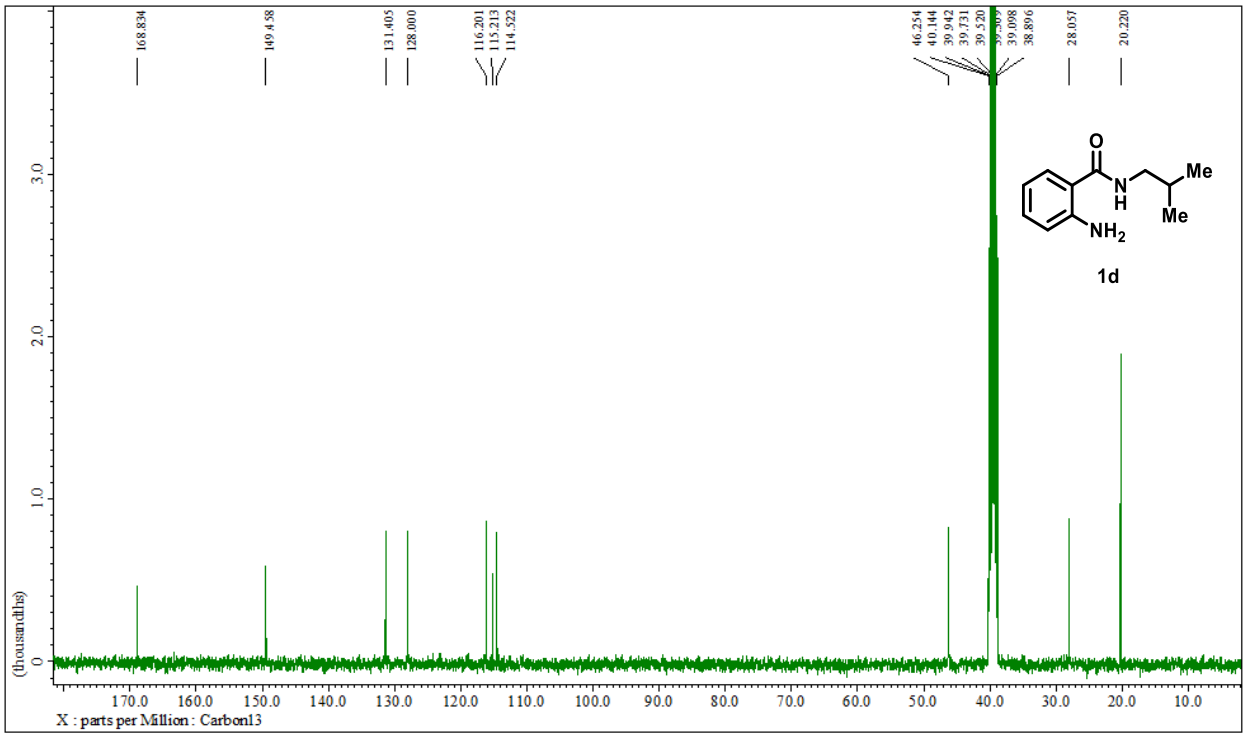
3. Lao, Z. Q.; Zhong, W. H.; Lou, Q. H.; Li, Z. J.; Meng, X. B. KI-catalyzed imidation of sp^3 C–H bond adjacent to amidenitrogen atom. *Org. Biomol. Chem.* **2012**, *10 (39)*, 7869–7871.

7. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of all compounds

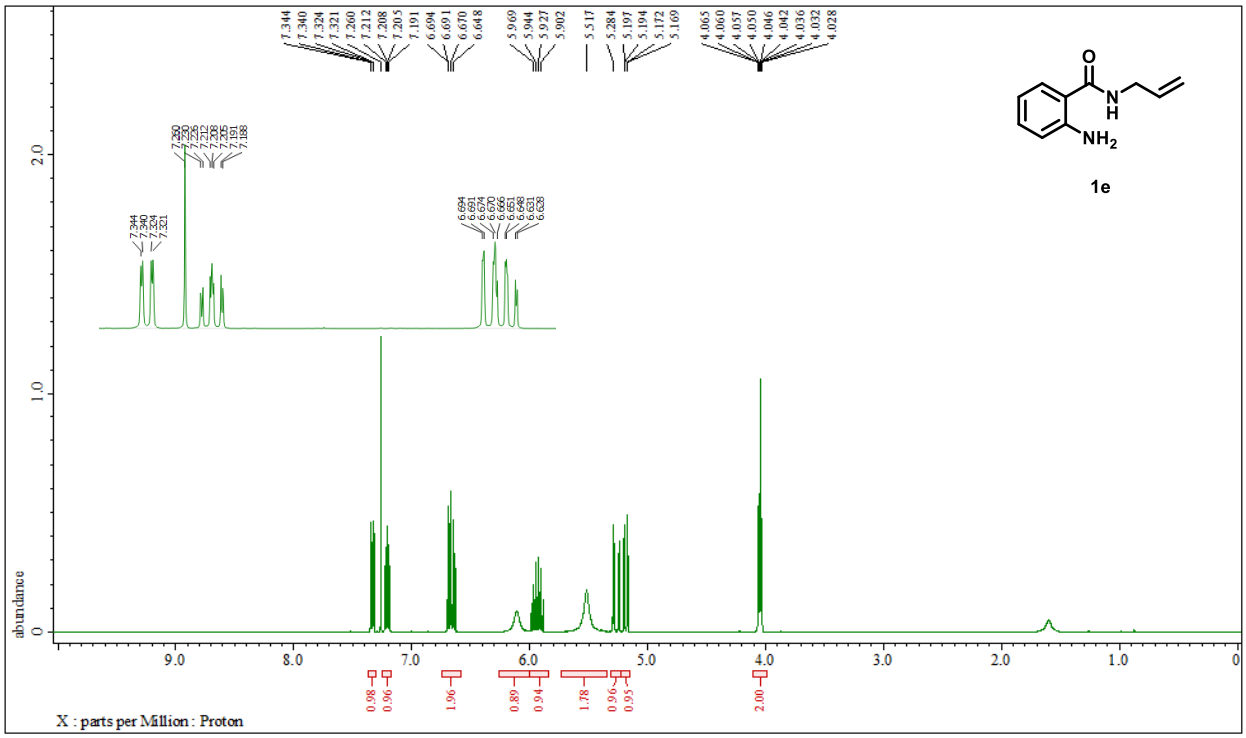
^{1}H NMR (400 MHz, DMSO-d_6) of **1d**



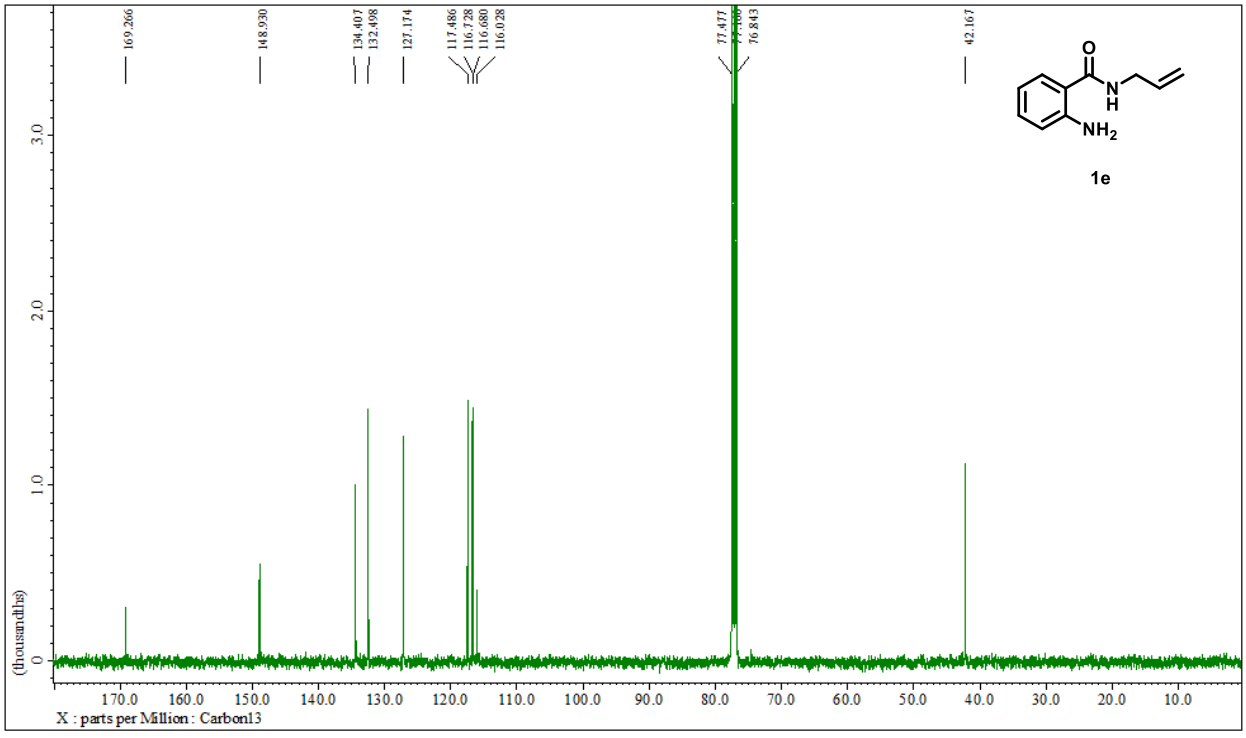
^{13}C NMR (100 MHz, DMSO-d_6) of **1d**



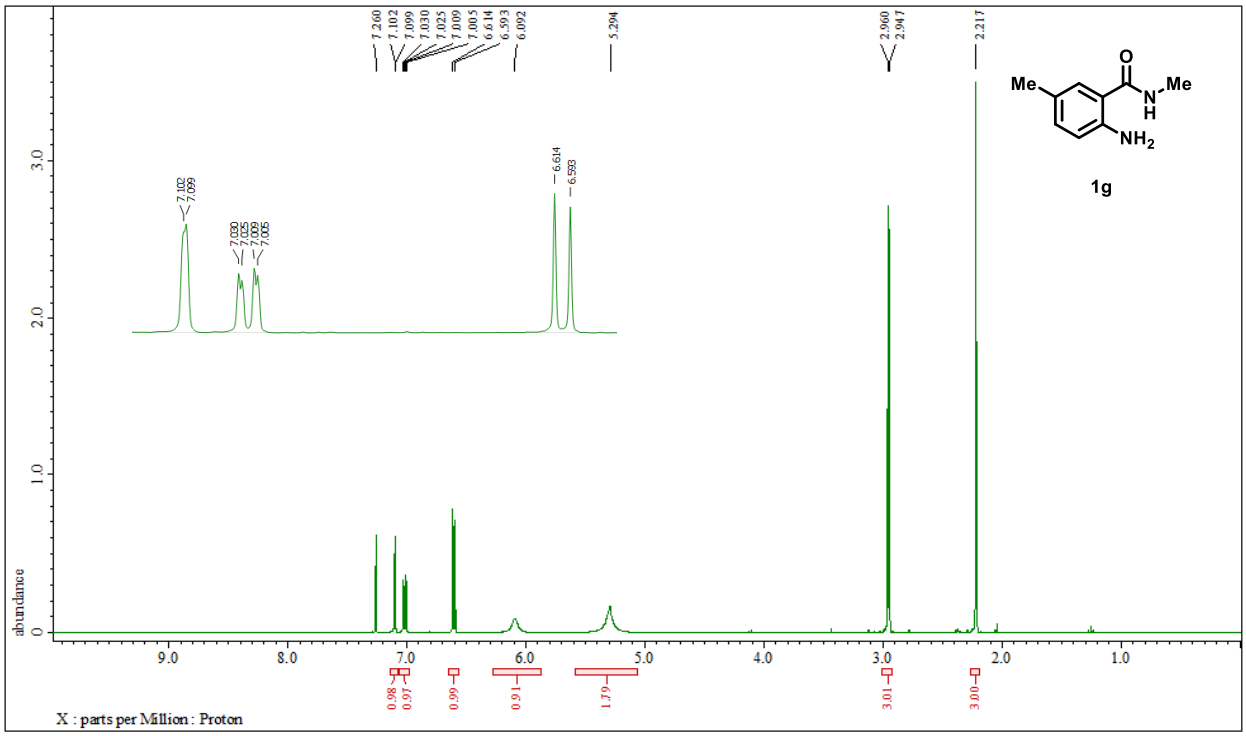
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **1e**



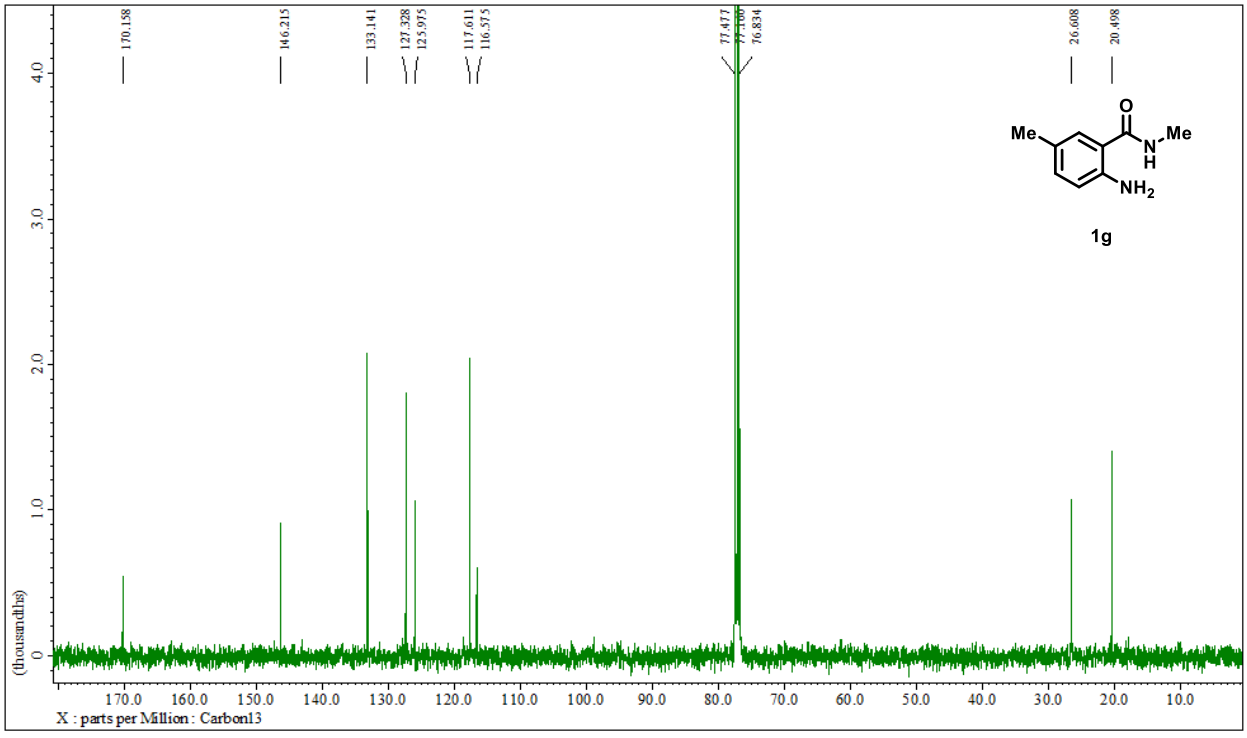
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **1e**



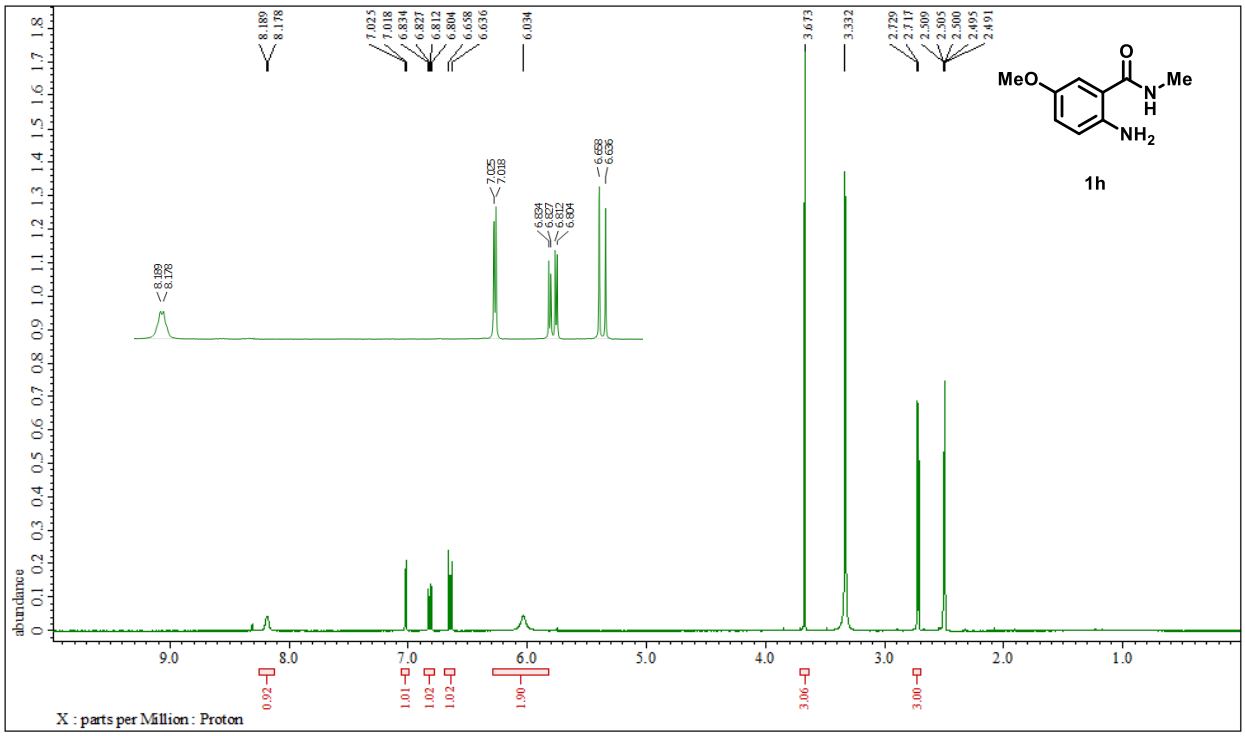
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **1g**



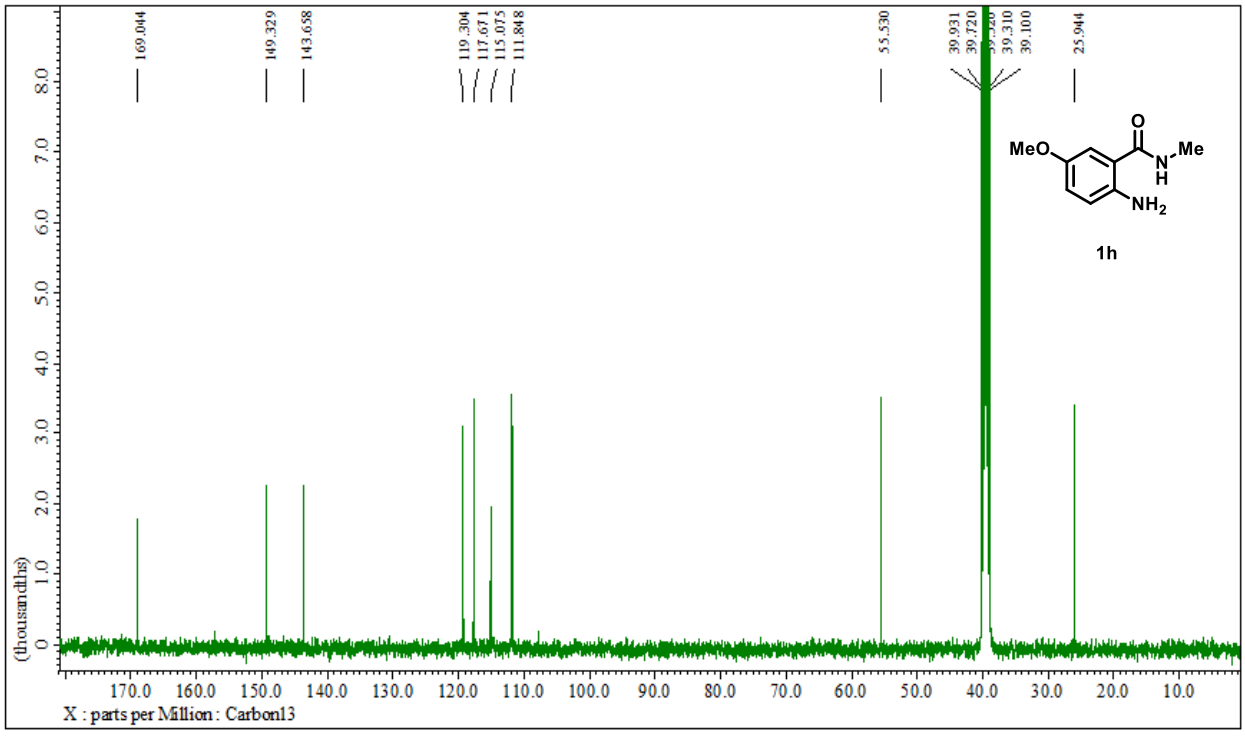
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **1g**



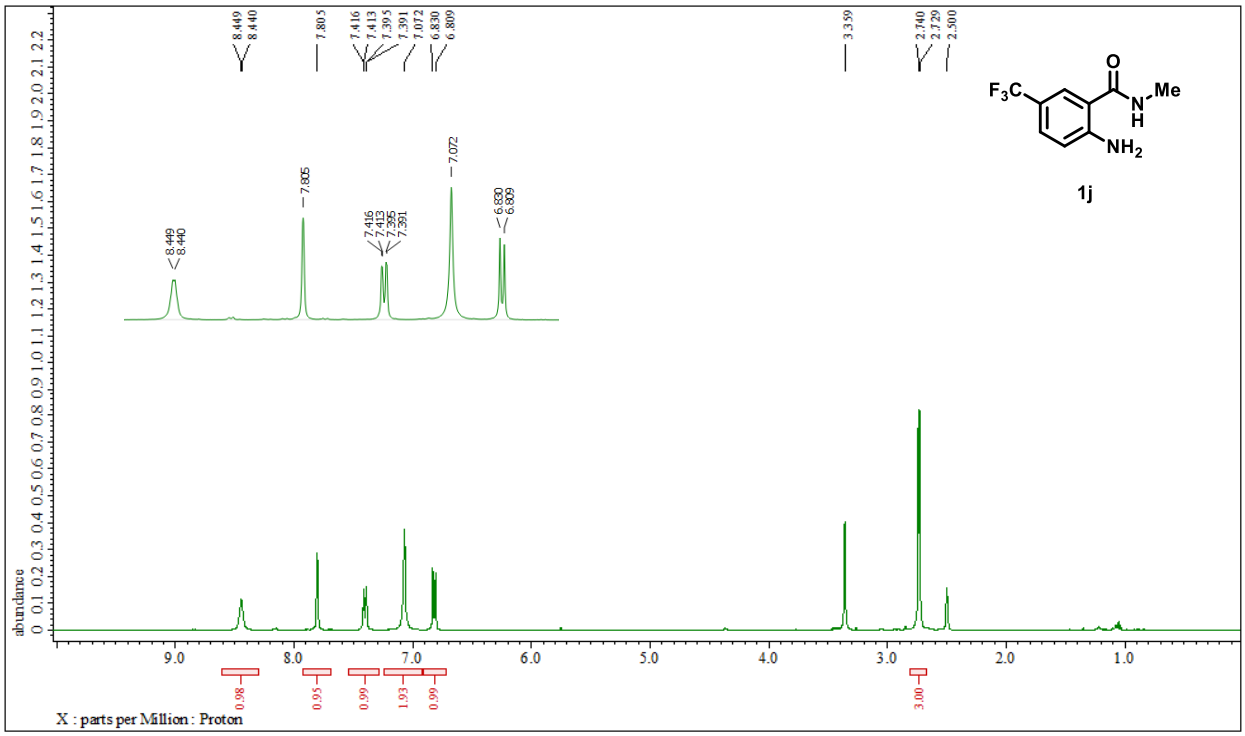
^{1}H NMR (400 MHz, DMSO-d_6) of **1h**



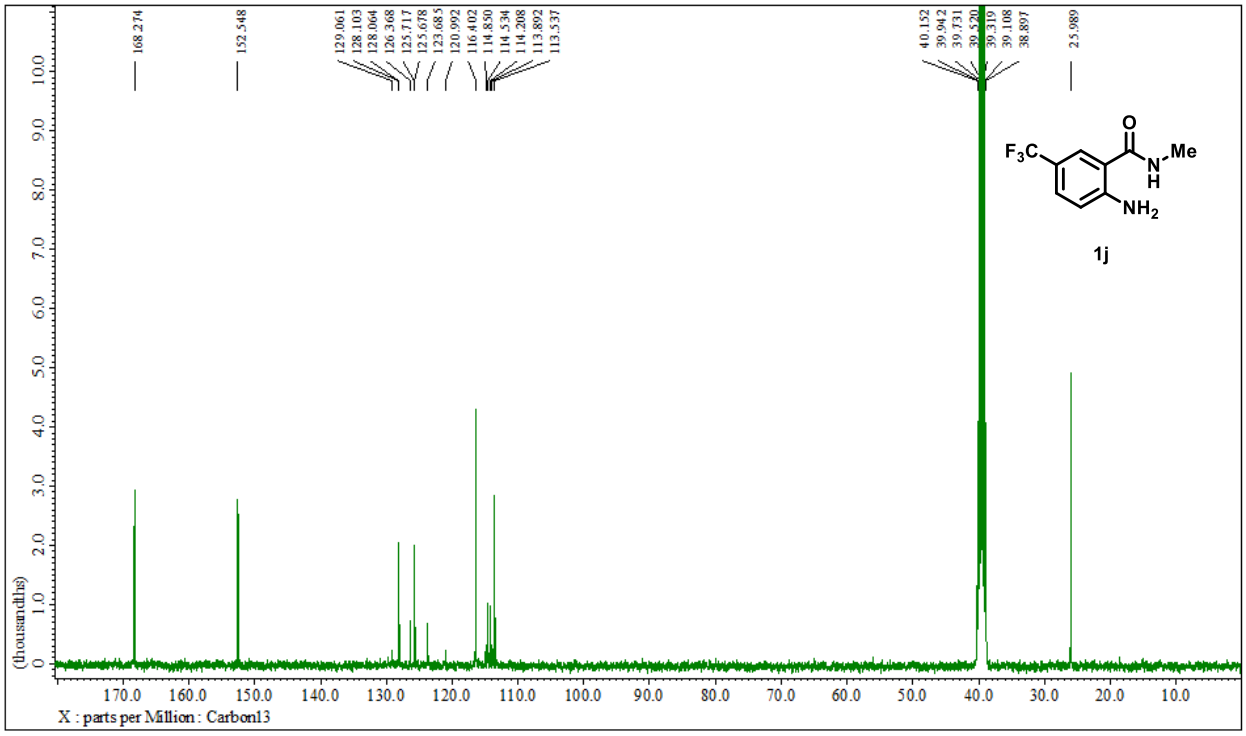
^{13}C NMR (100 MHz, DMSO-d_6) of **1h**



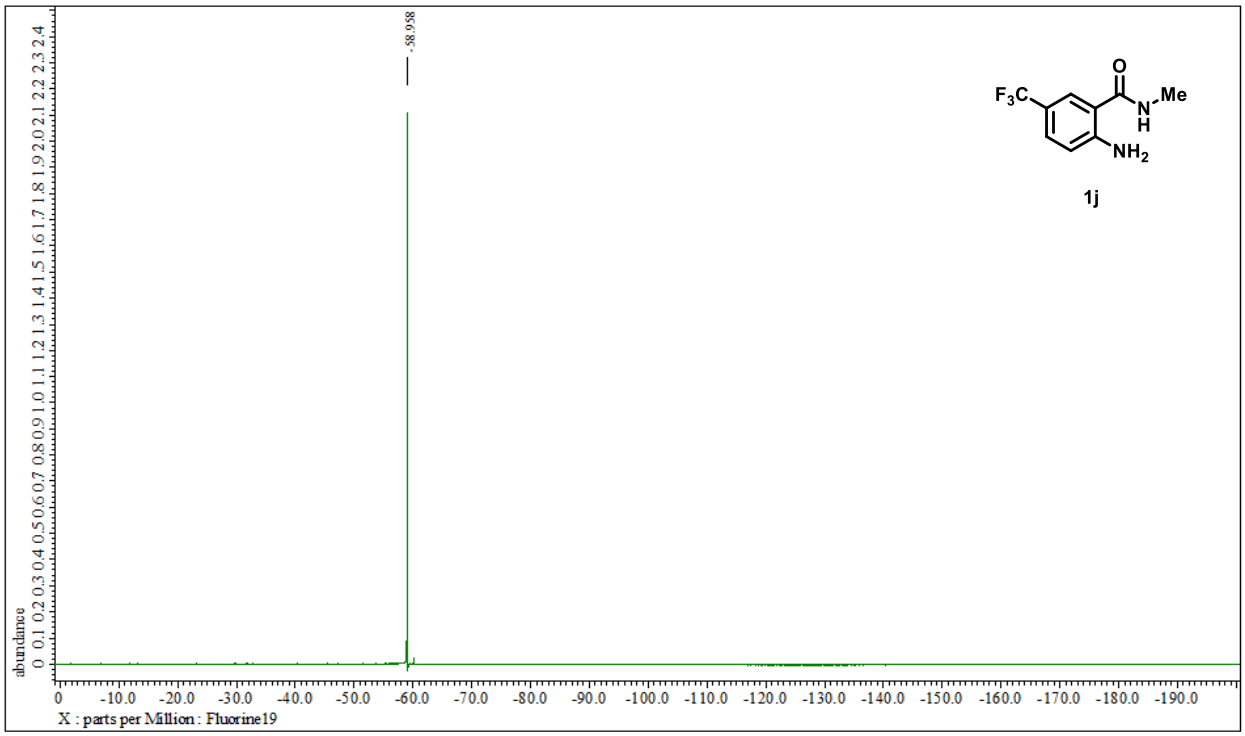
^{1}H NMR (400 MHz, DMSO-d_6) of **1j**



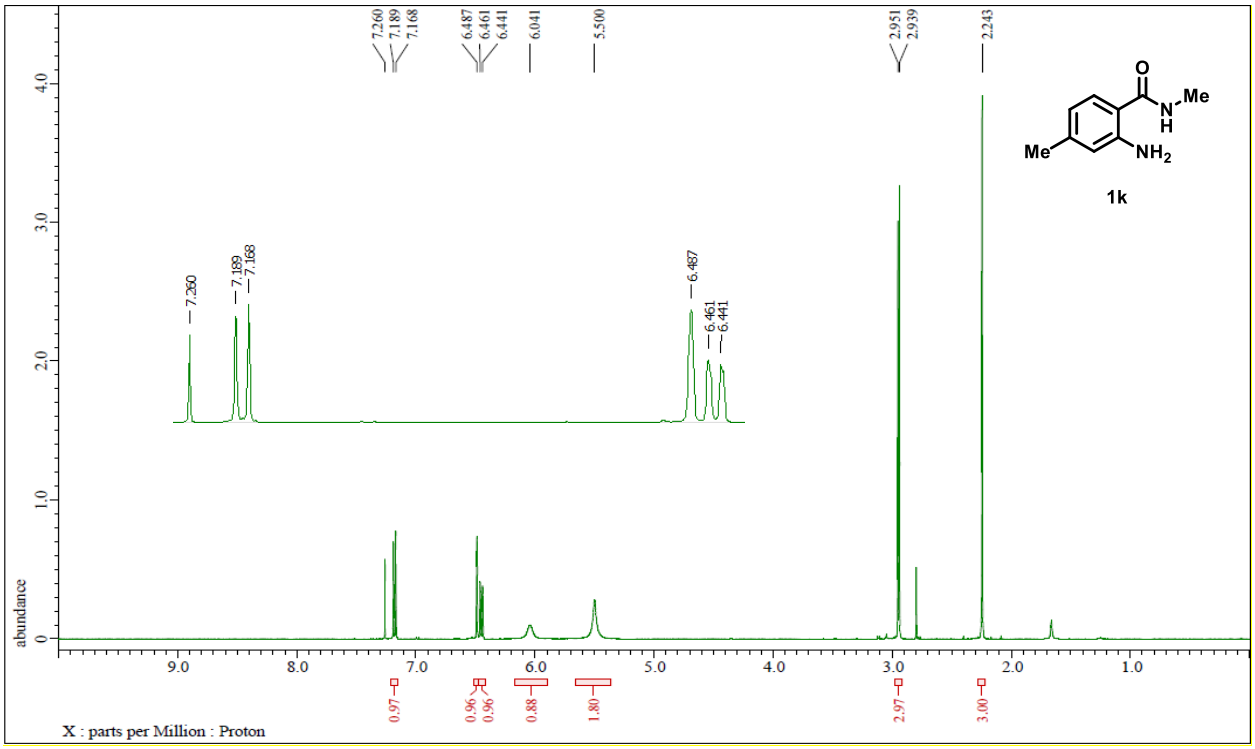
^{13}C NMR (100 MHz, DMSO-d_6) of **1j**



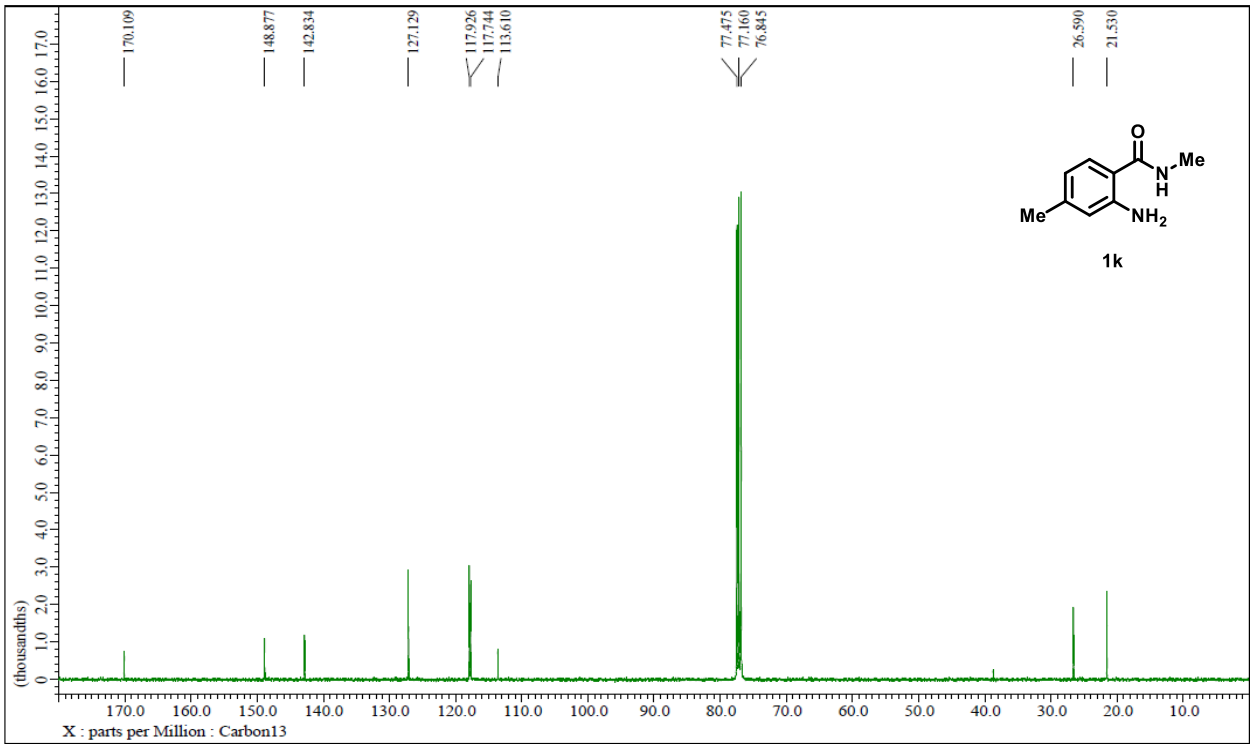
^{19}F NMR (376 MHz, DMSO-d_6) of **1j**



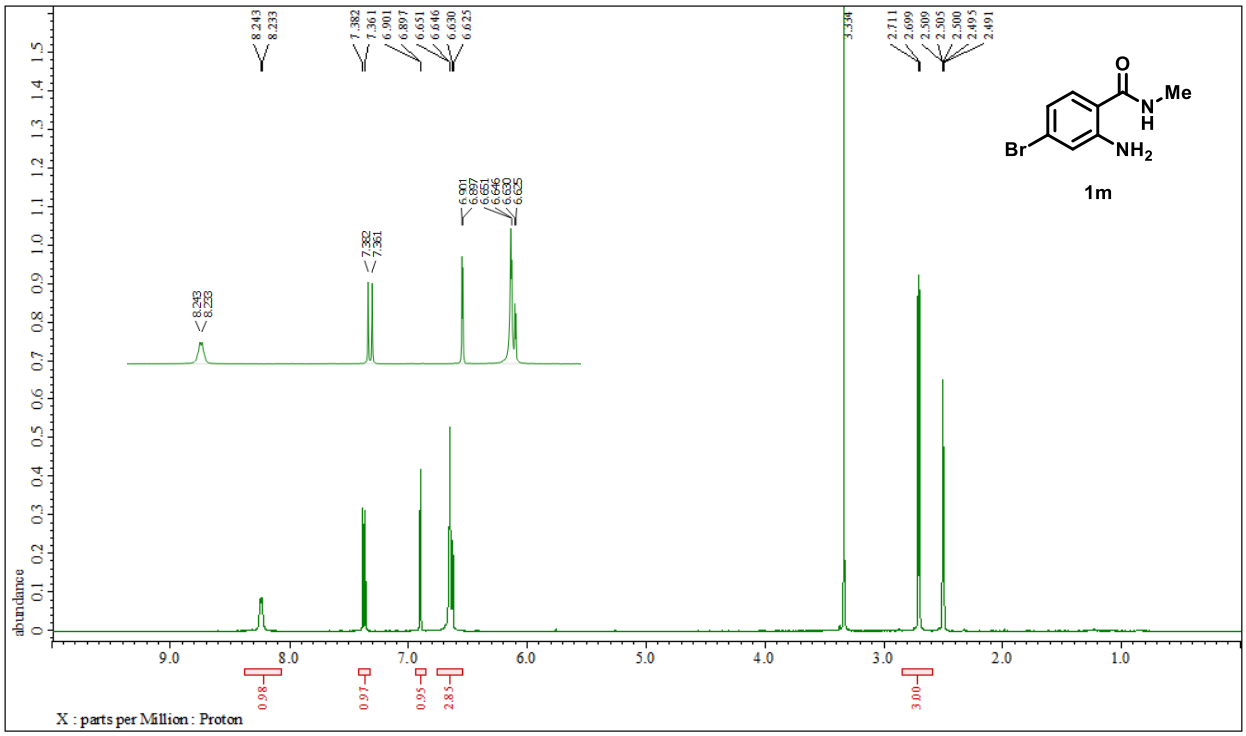
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **1k**



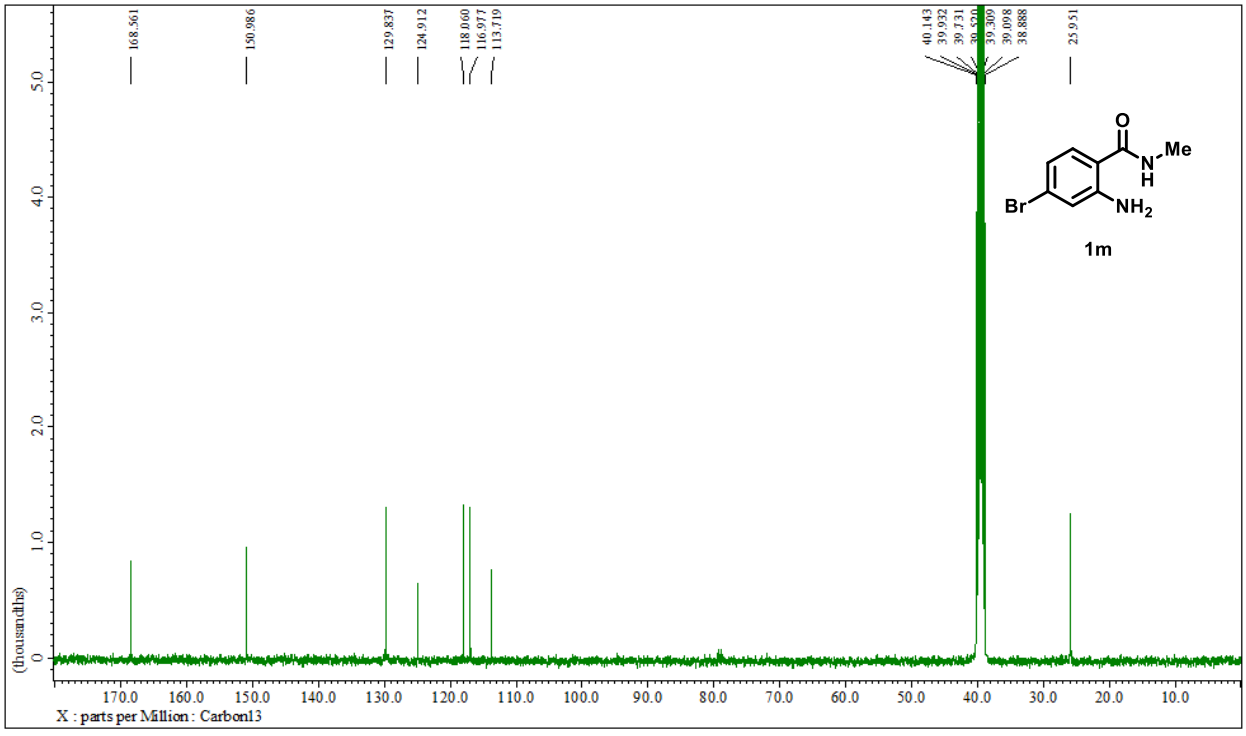
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **1k**



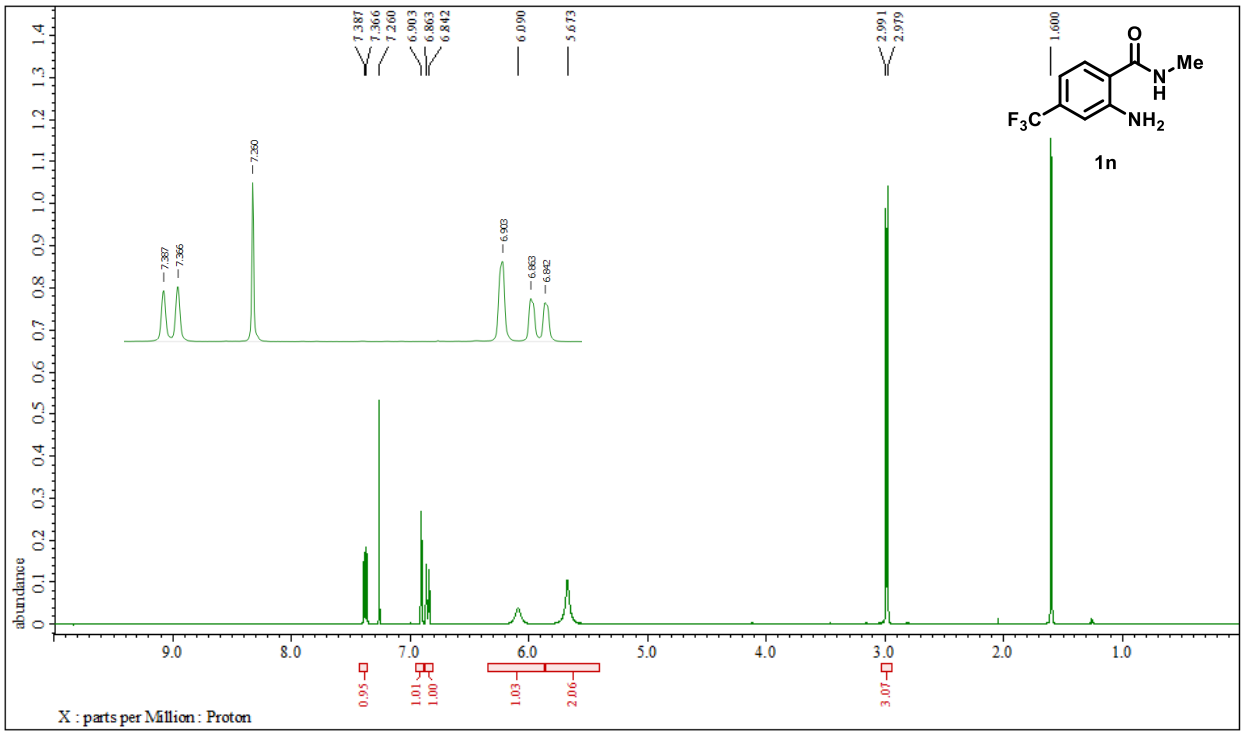
^{1}H NMR (400 MHz, DMSO-d_6) of **1m**



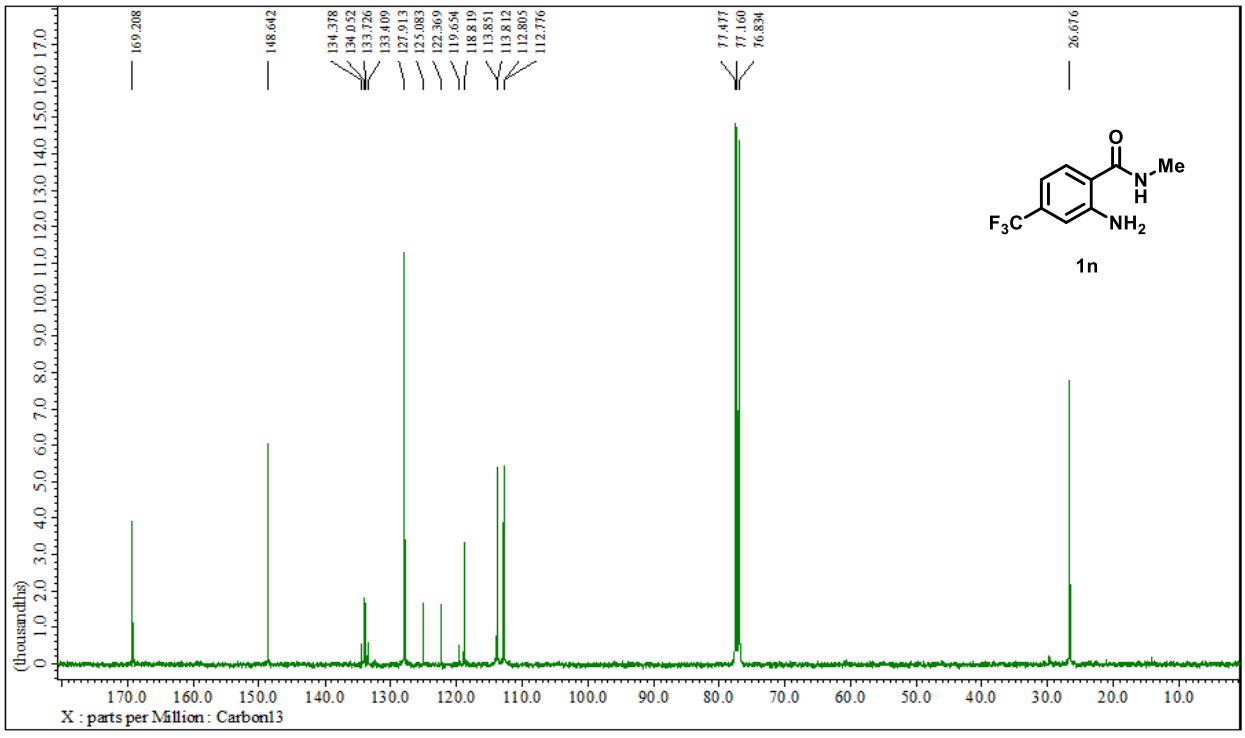
^{13}C NMR (100 MHz, DMSO-d_6) of **1m**



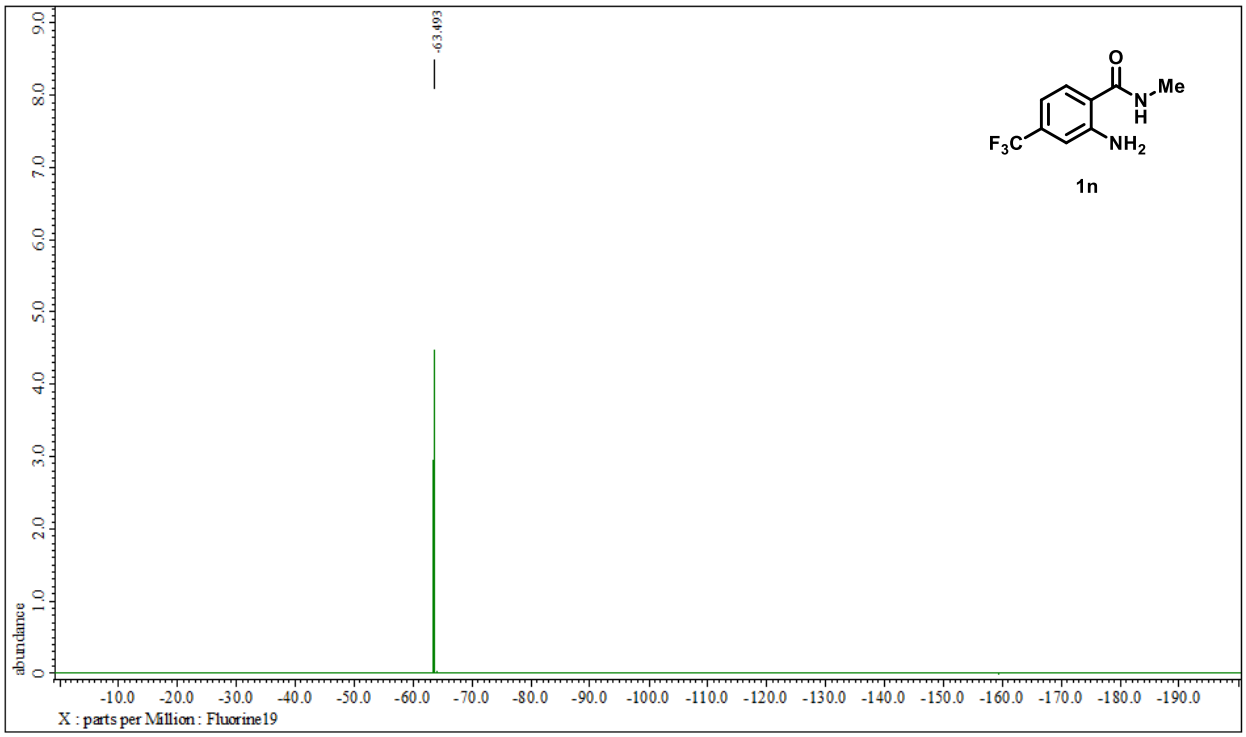
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **1n**



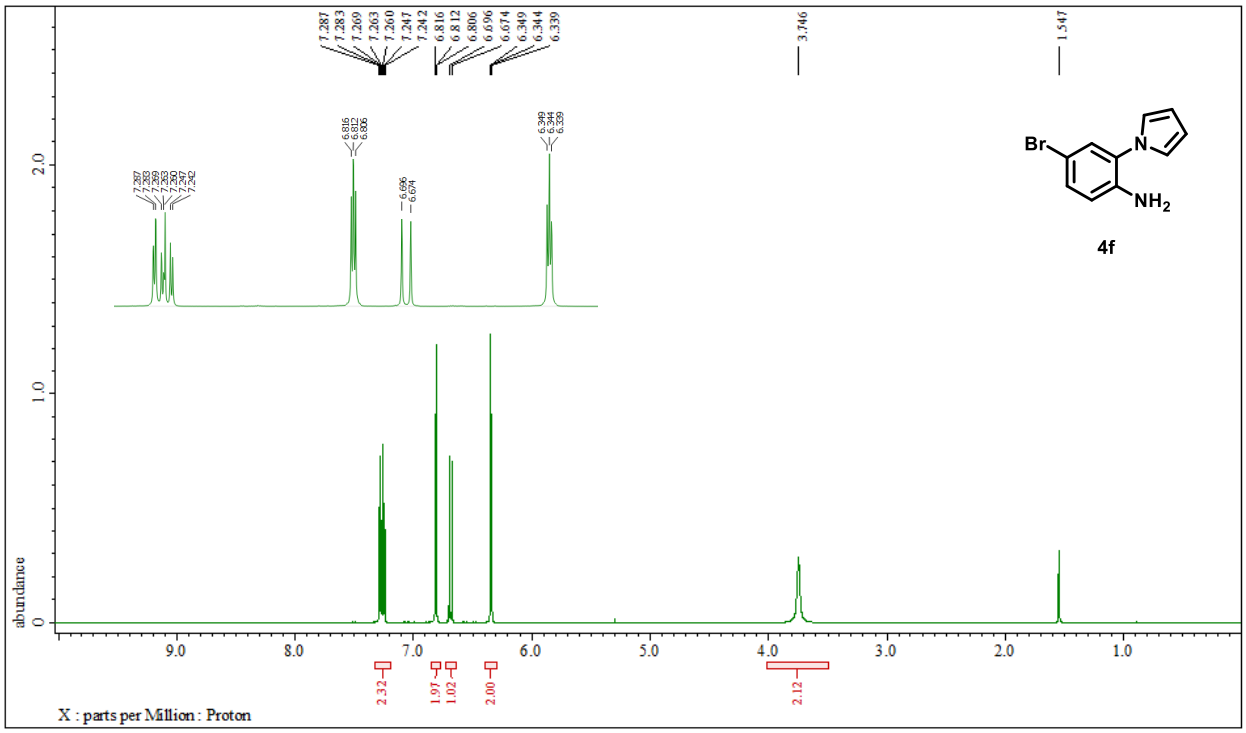
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **1n**



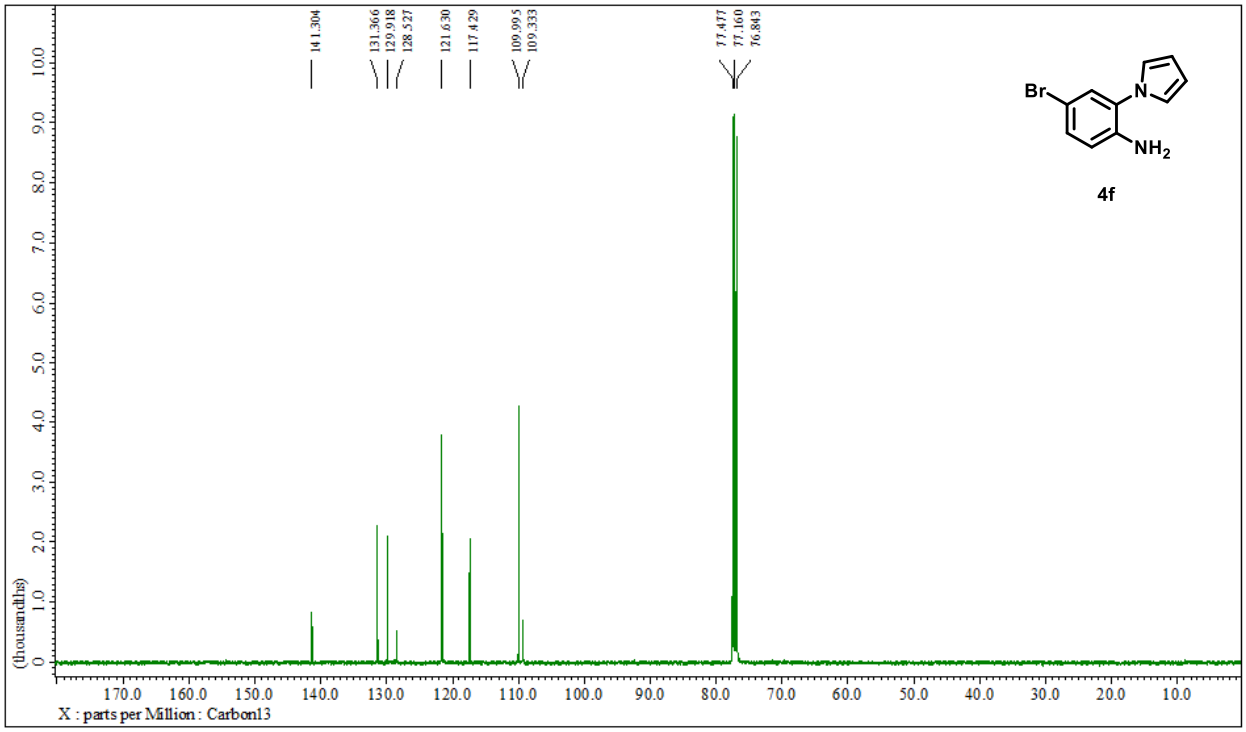
^{19}F NMR (376 MHz, $CDCl_3$-*d*) of **1n**



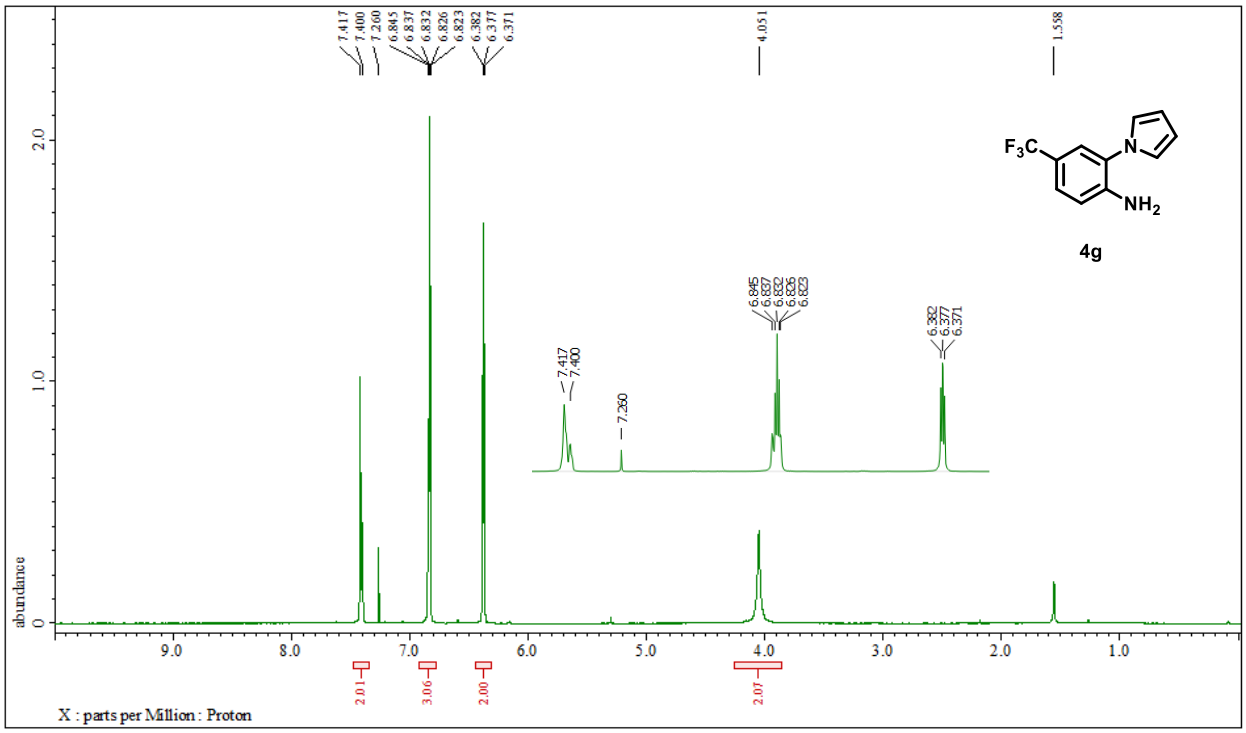
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **4f**



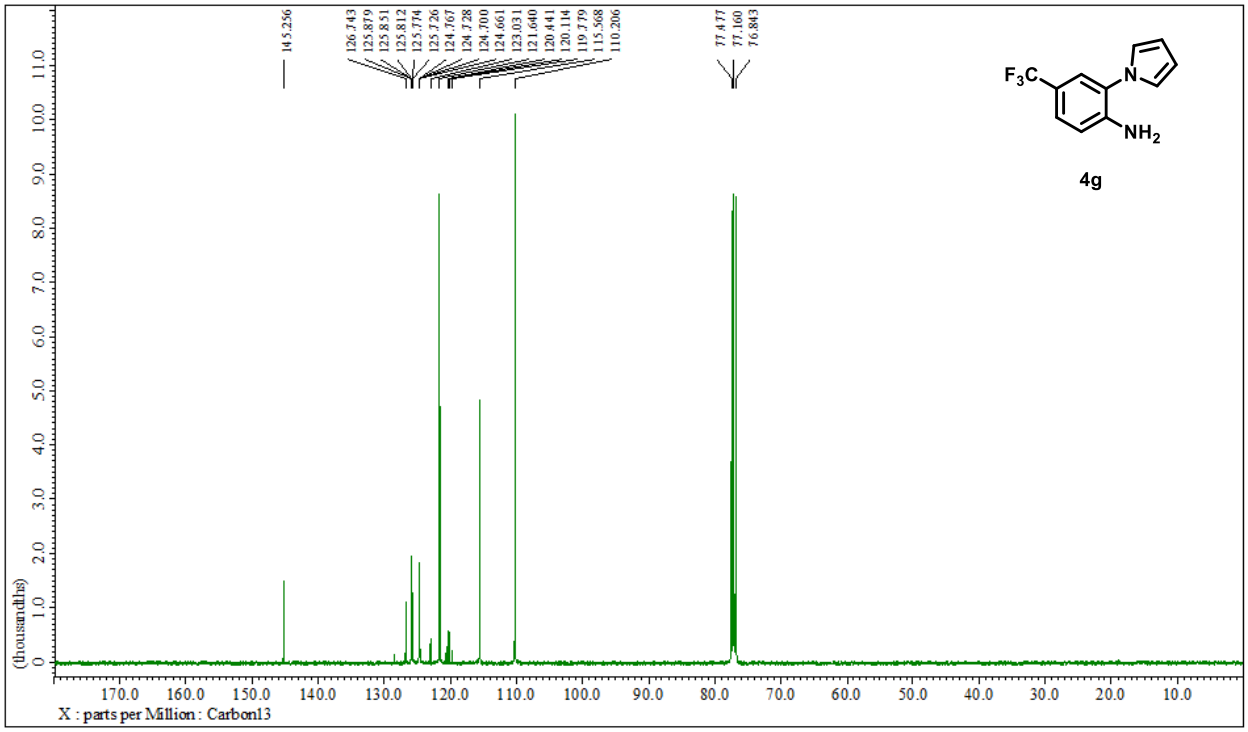
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **4f**



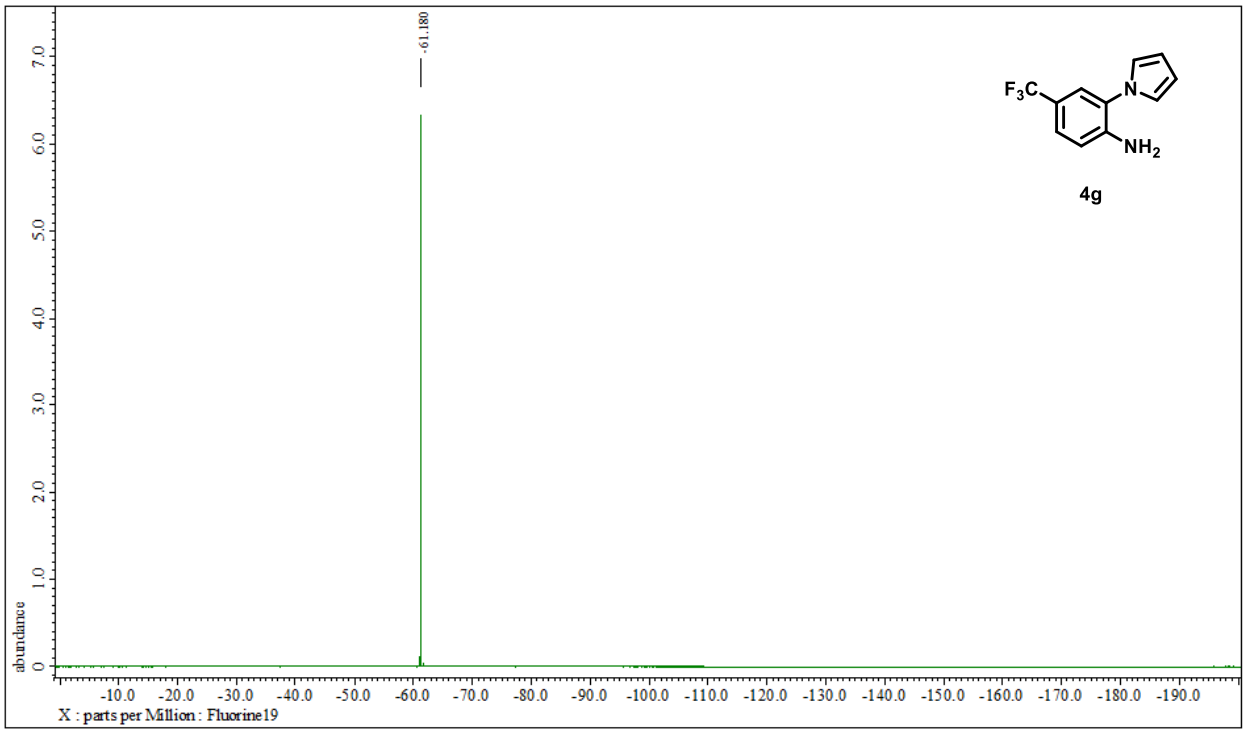
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **4g**



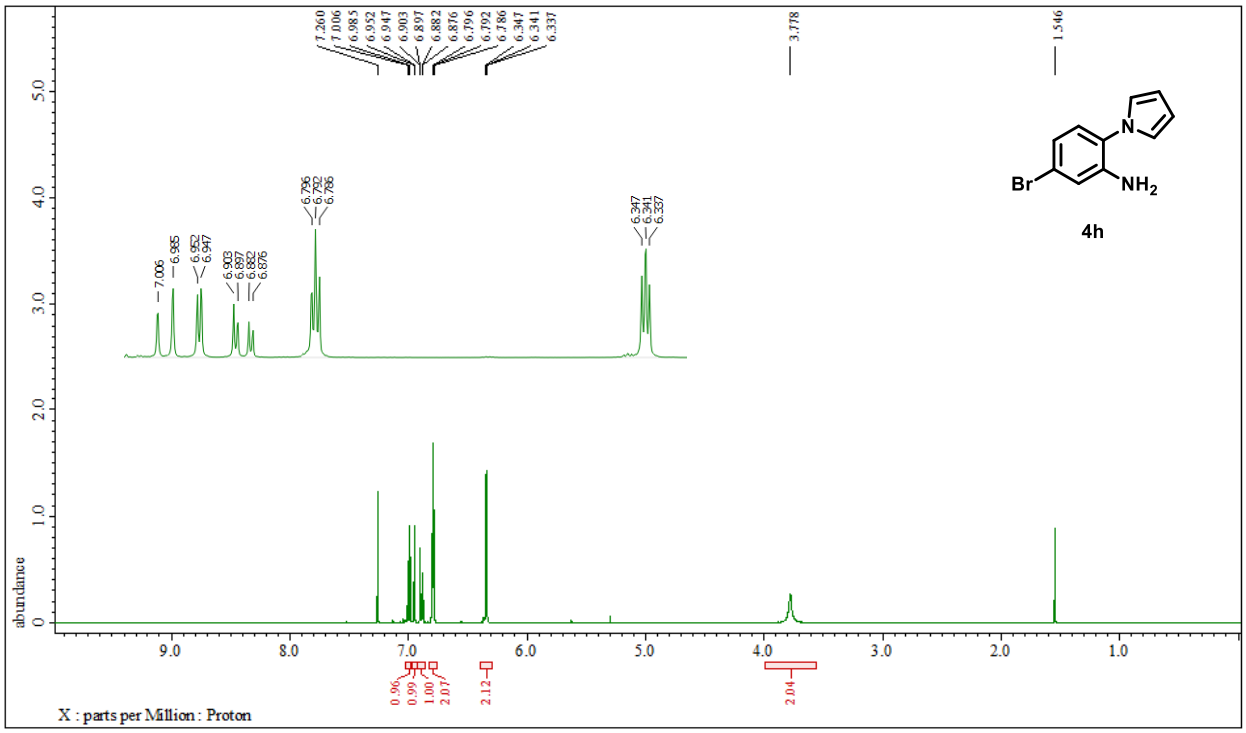
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **4g**



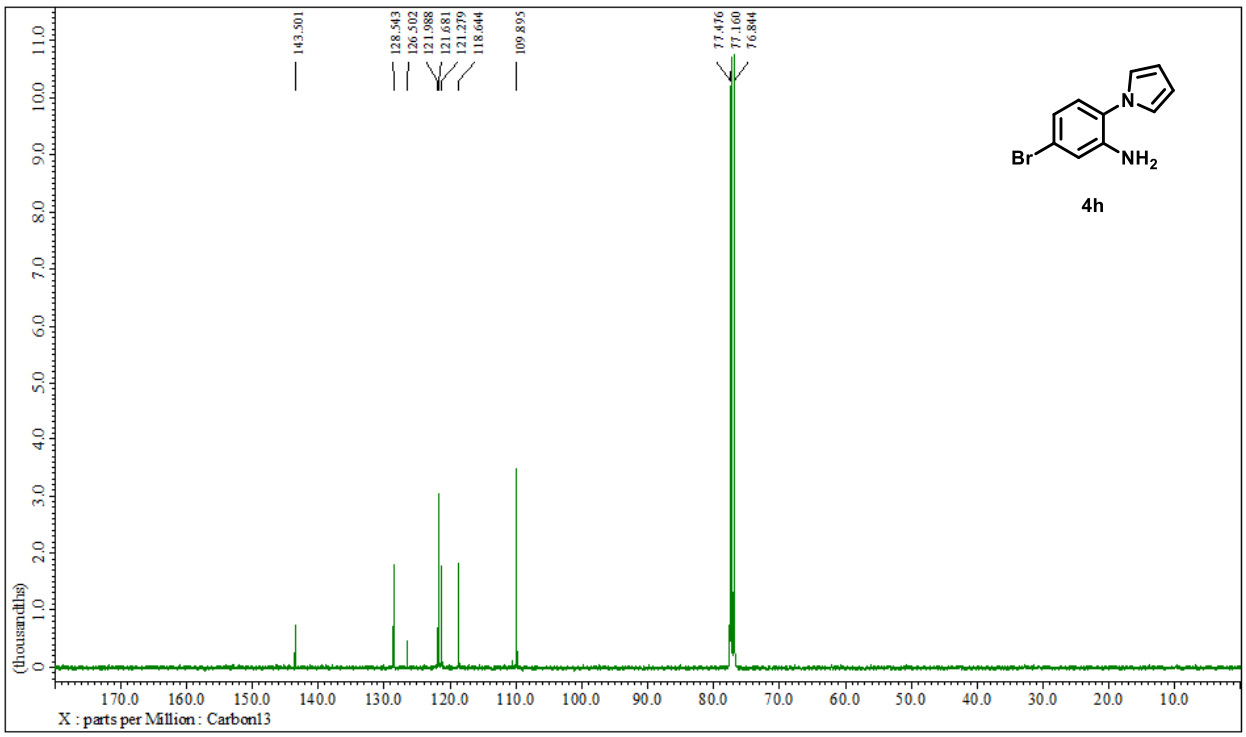
^{19}F NMR (376 MHz, $CDCl_3$-*d*) of **4g**



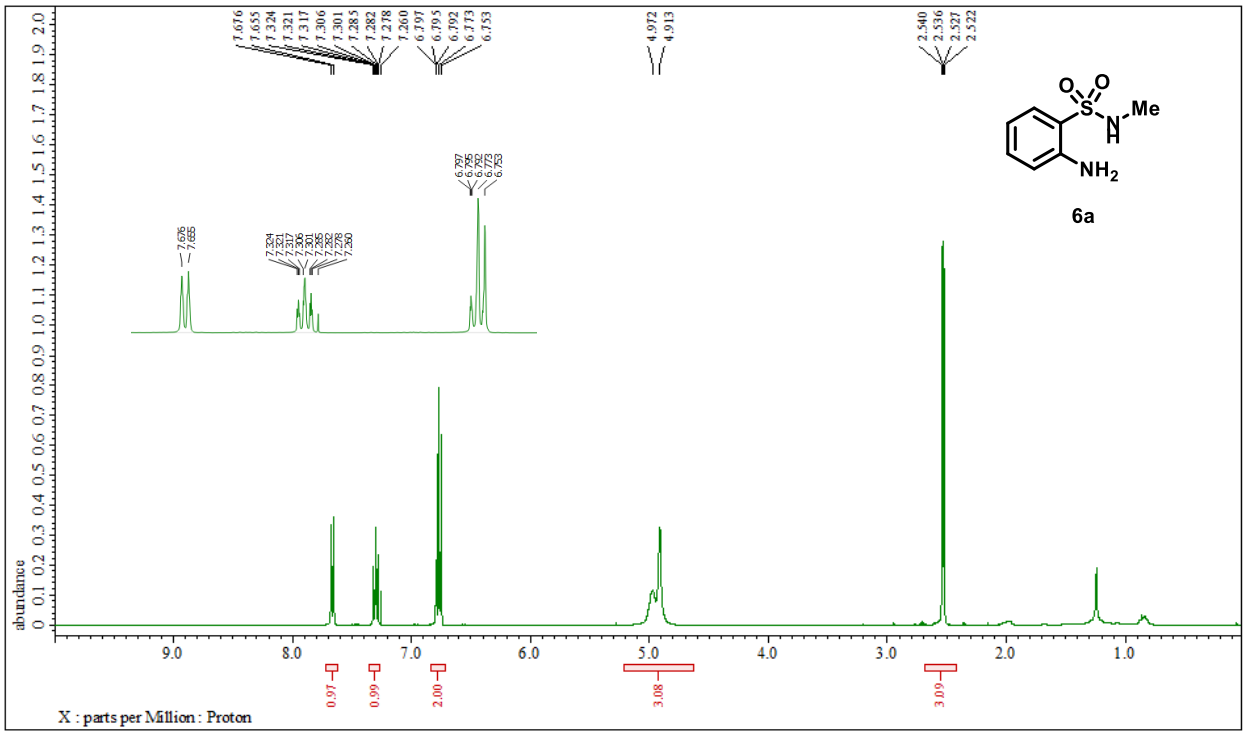
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **4h**



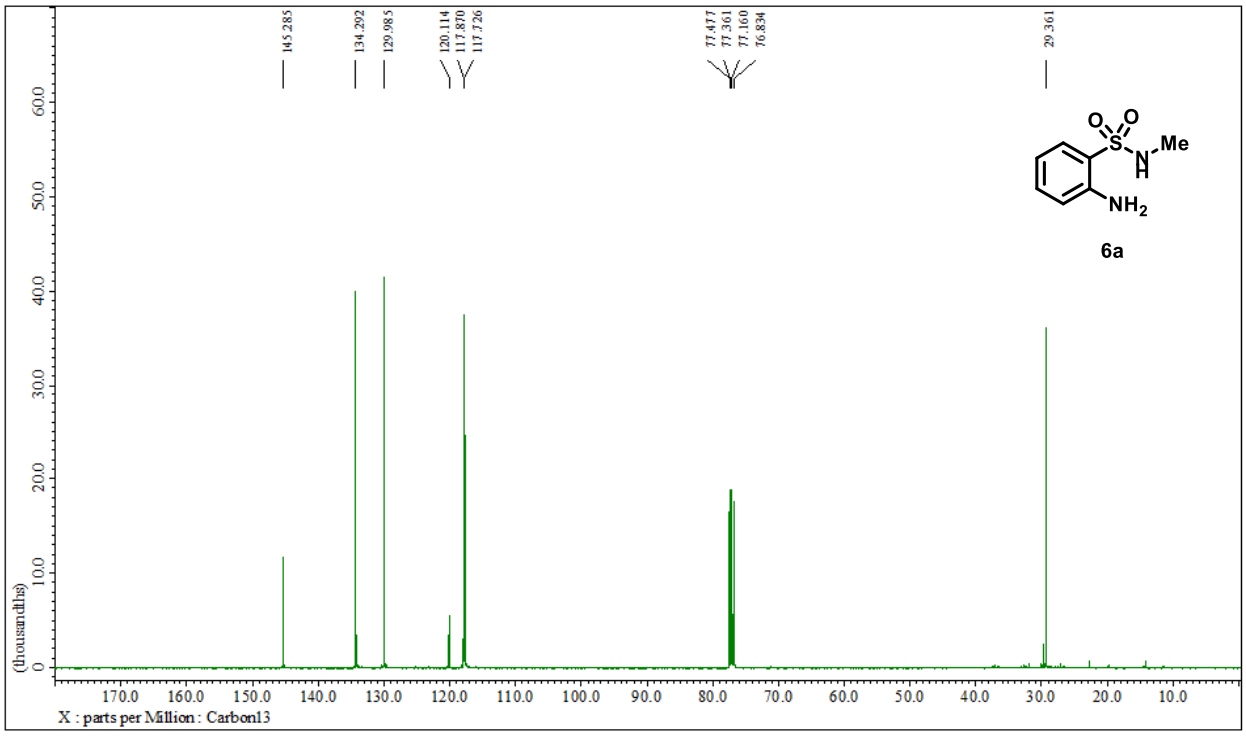
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **4h**



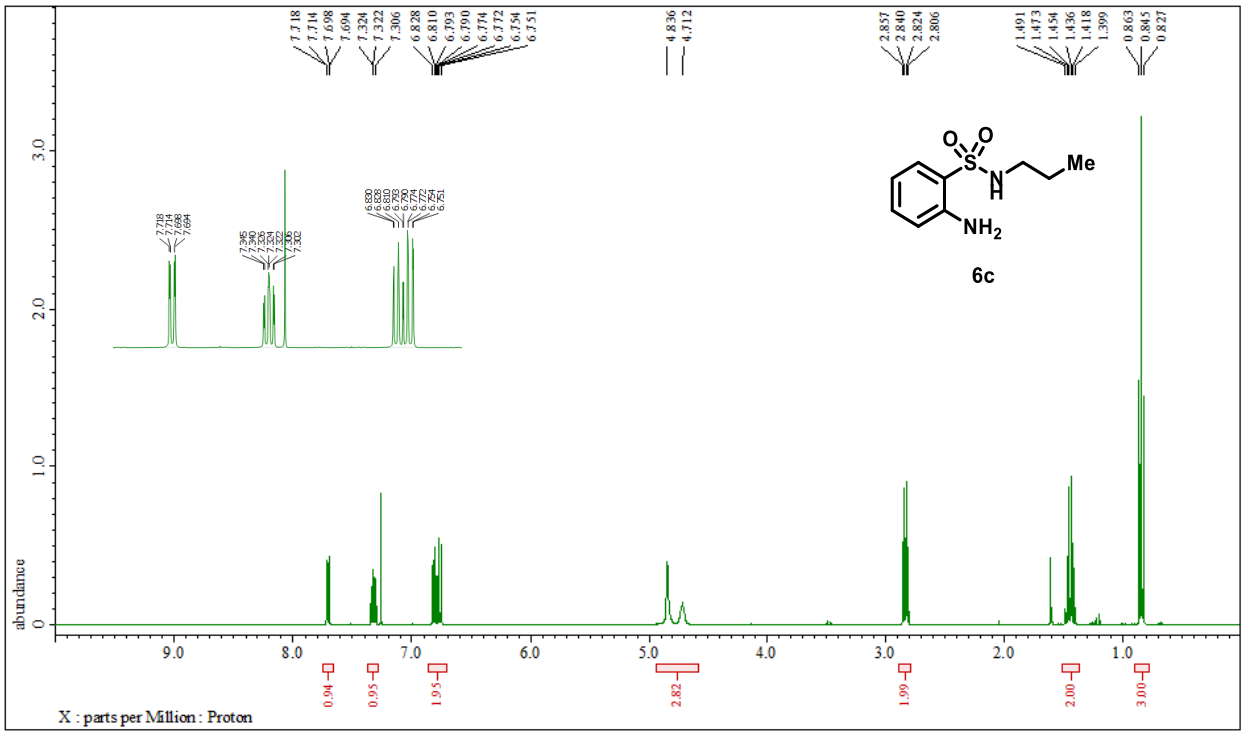
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **6a**



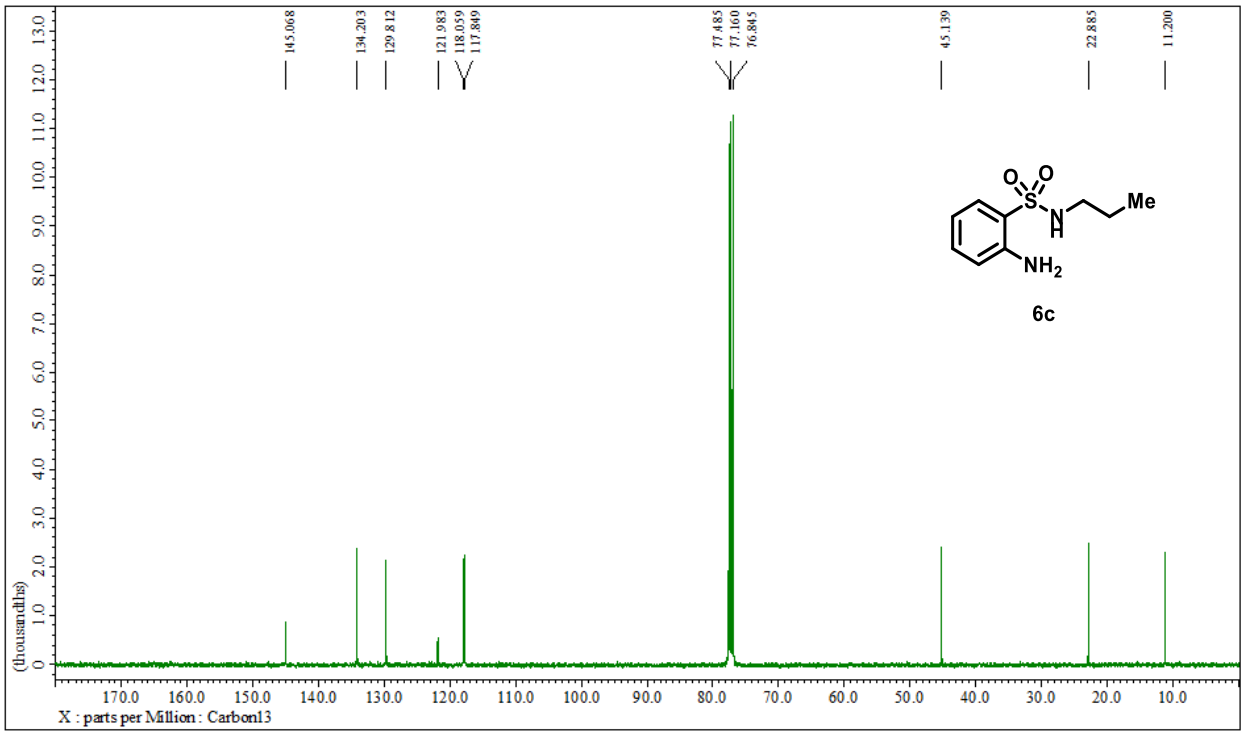
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **6a**



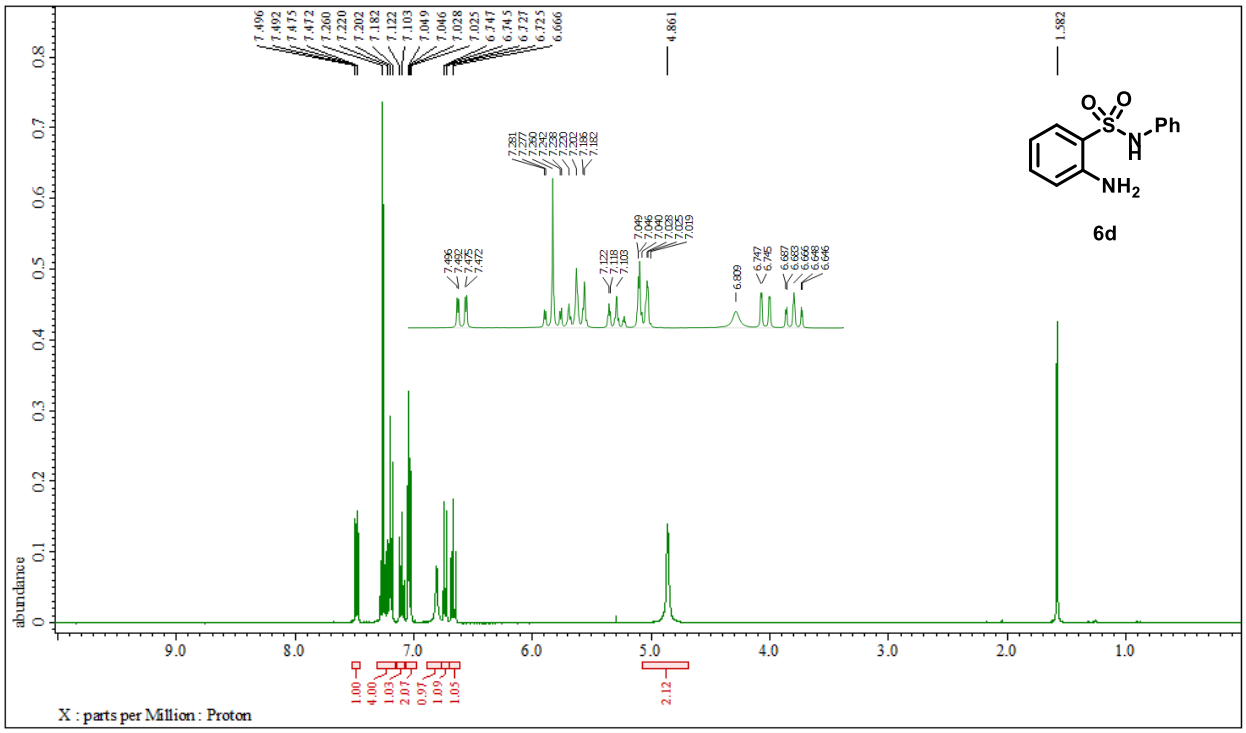
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **6c**



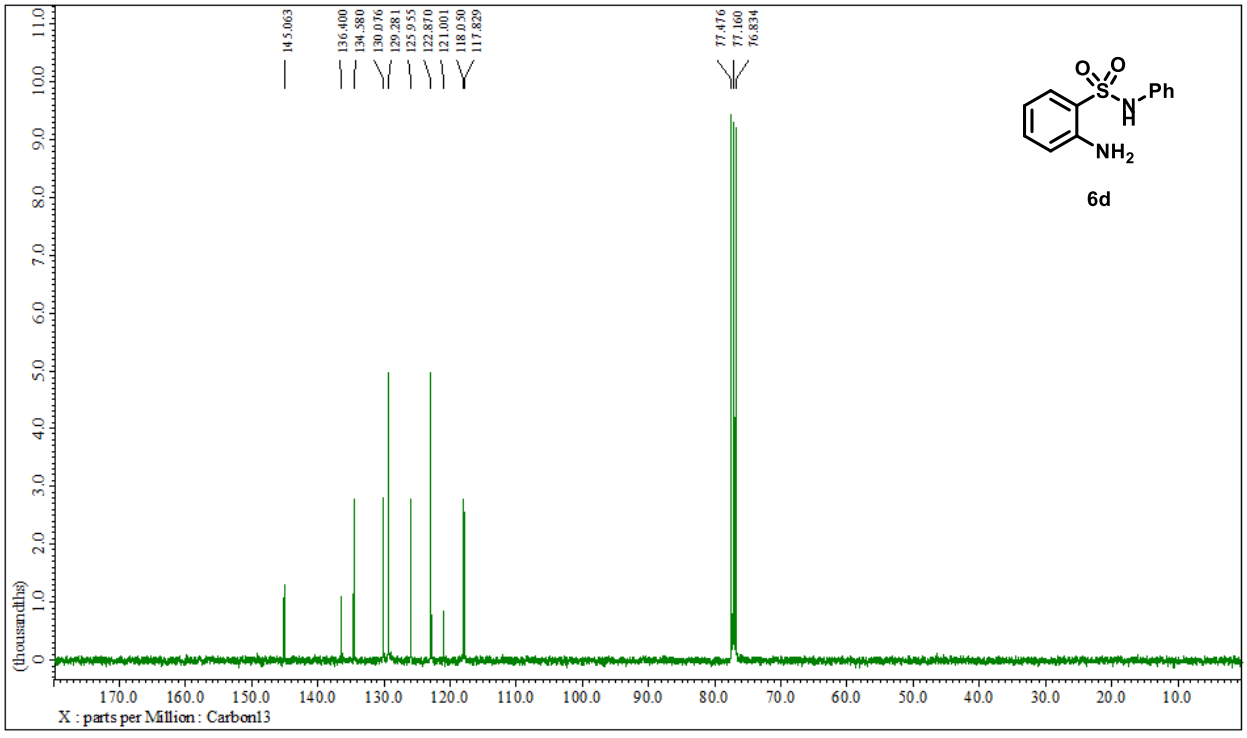
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **6c**



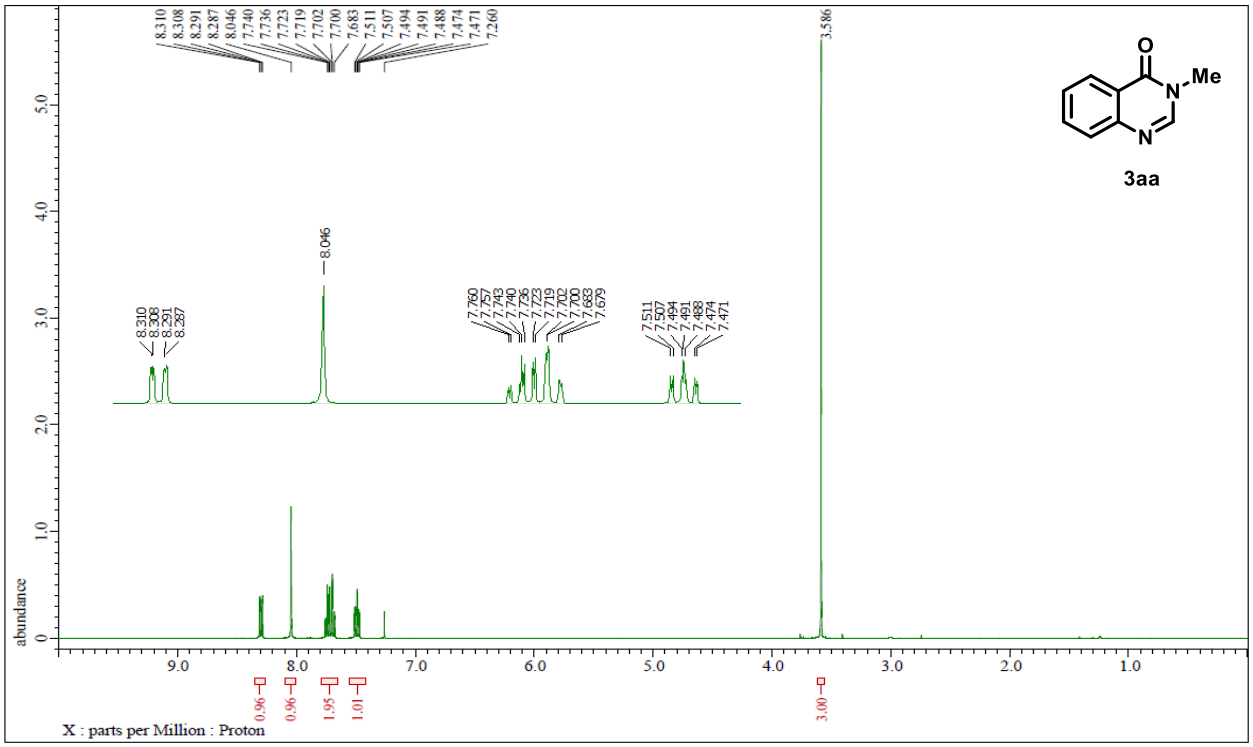
^{1}H NMR (400 MHz, $CDCl_3$-*d*) of **6d**



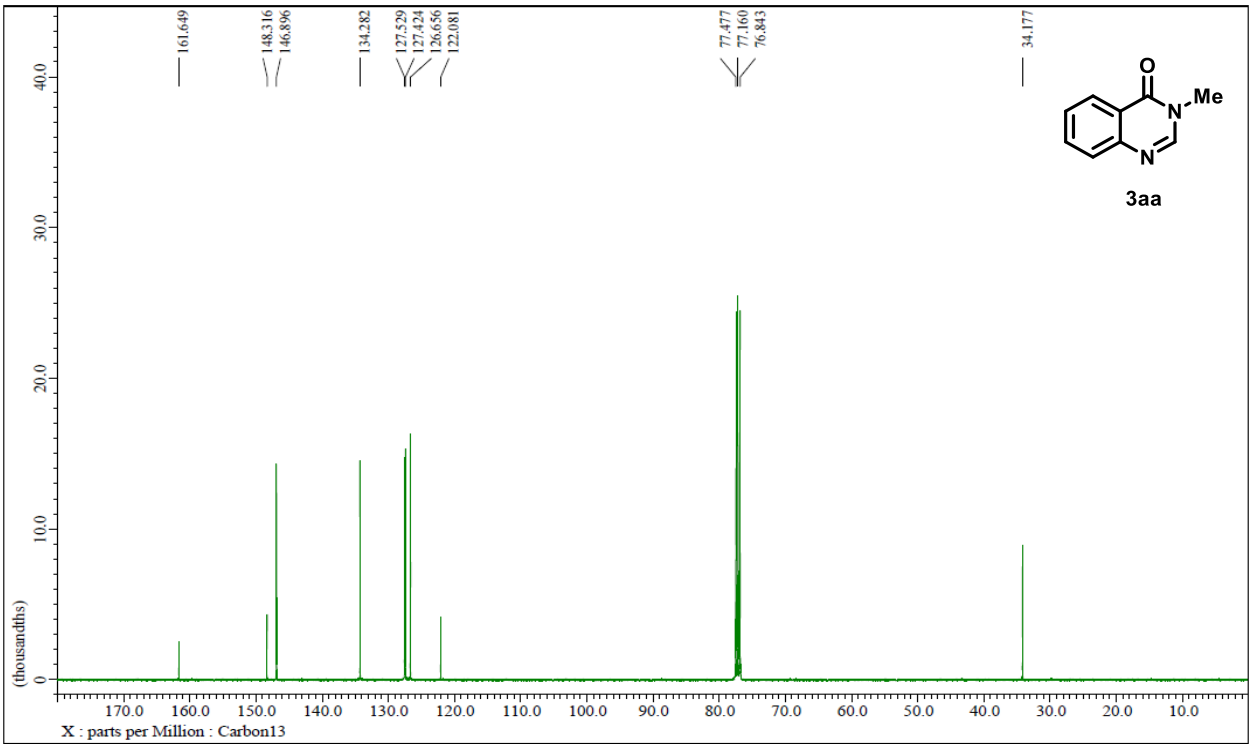
^{13}C NMR (100 MHz, $CDCl_3$-*d*) of **6d**



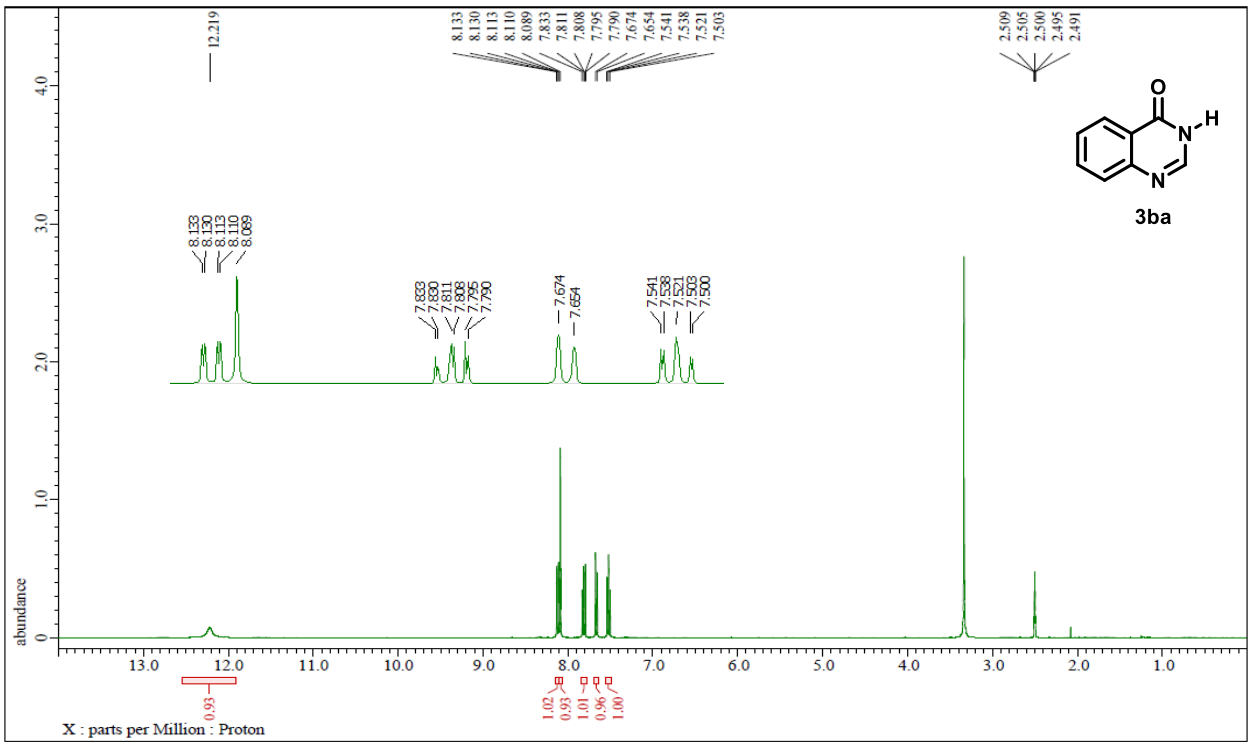
^{1}H NMR of Compound **3aa** ($CDCl_3$-*d*, 400 MHz)



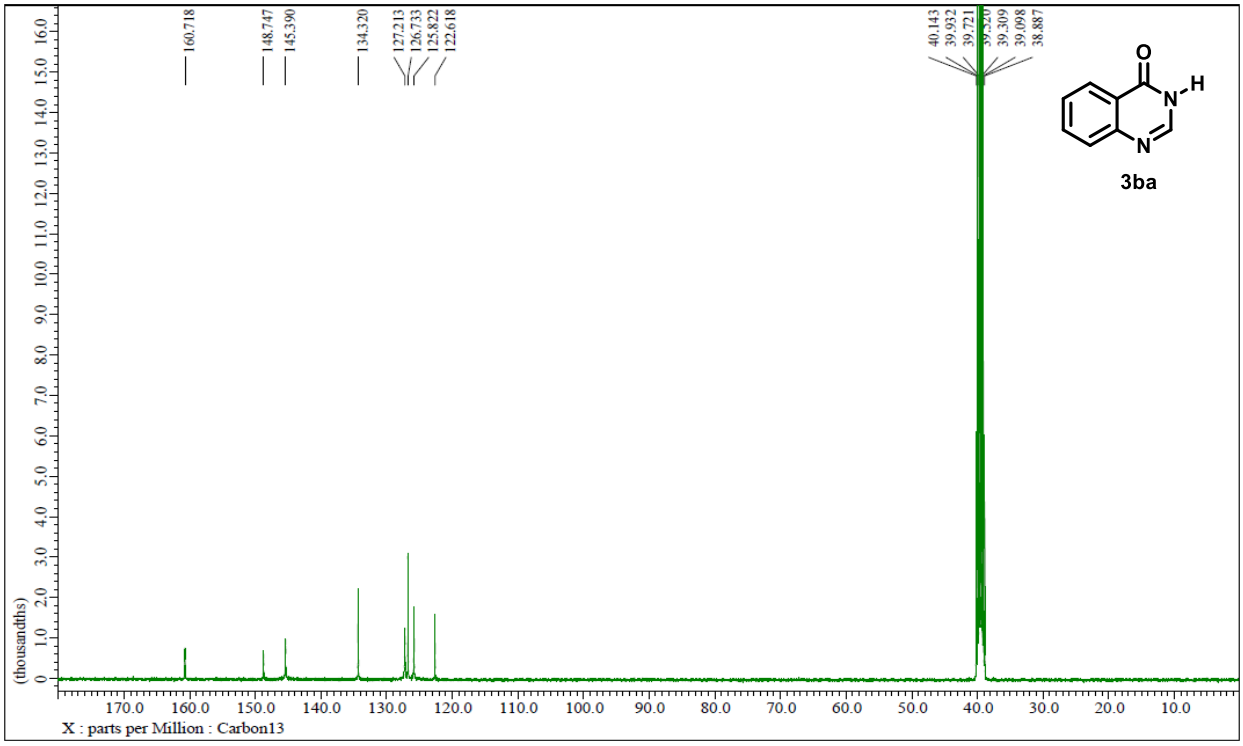
^{13}C NMR of Compound **3aa** ($CDCl_3$-*d*, 100 MHz)



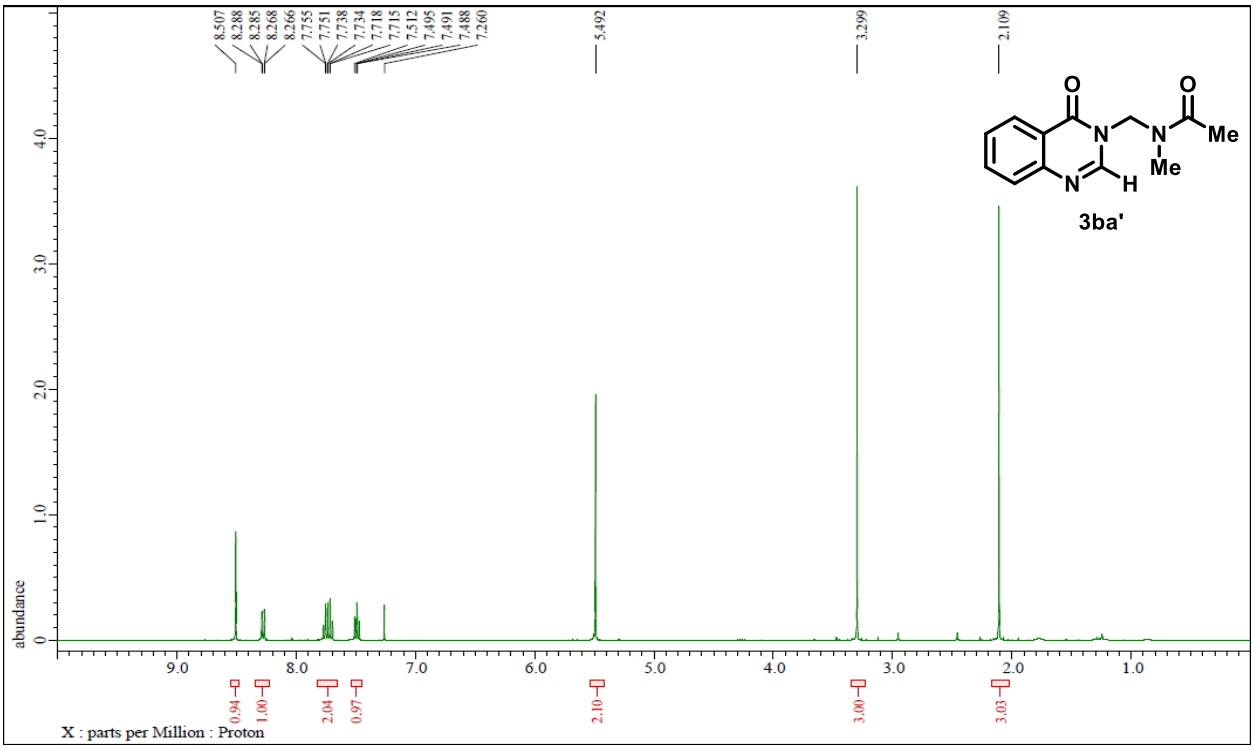
^{1}H NMR of Compound **3ba** (DMSO-d_6, 400 MHz)



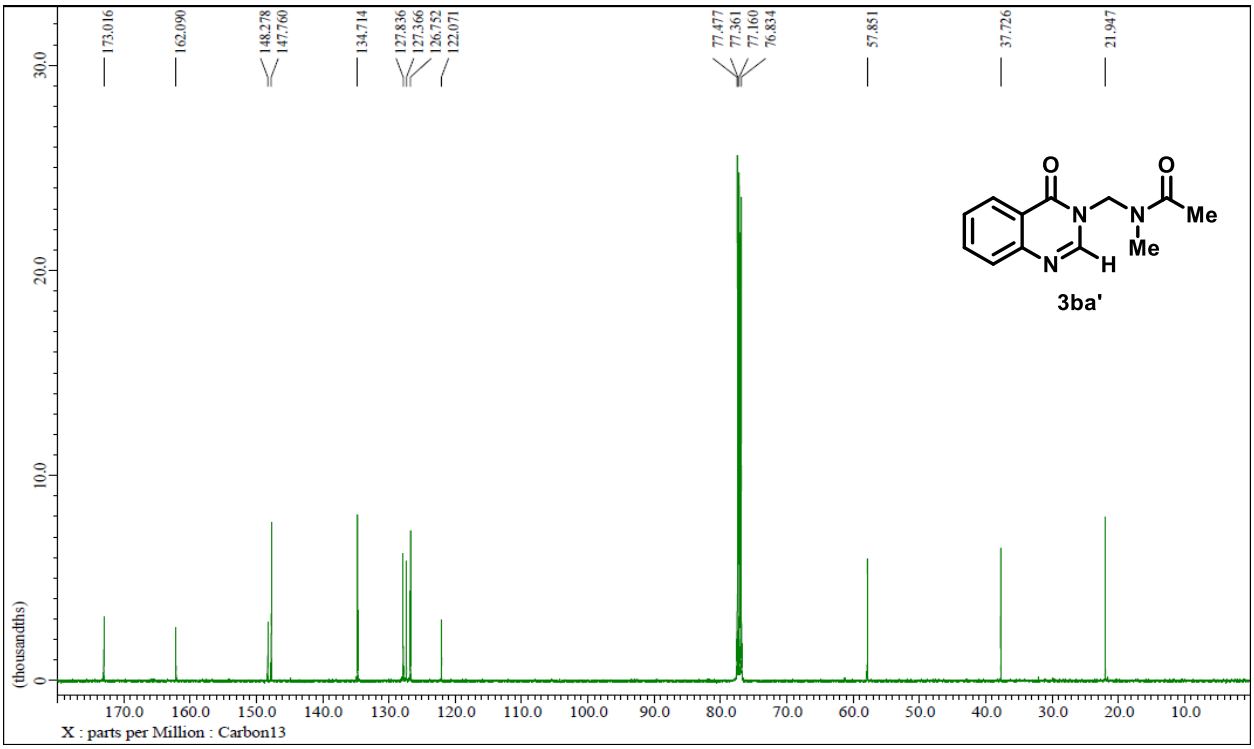
^{13}C NMR of Compound **3ba** (DMSO-d_6, 100 MHz)



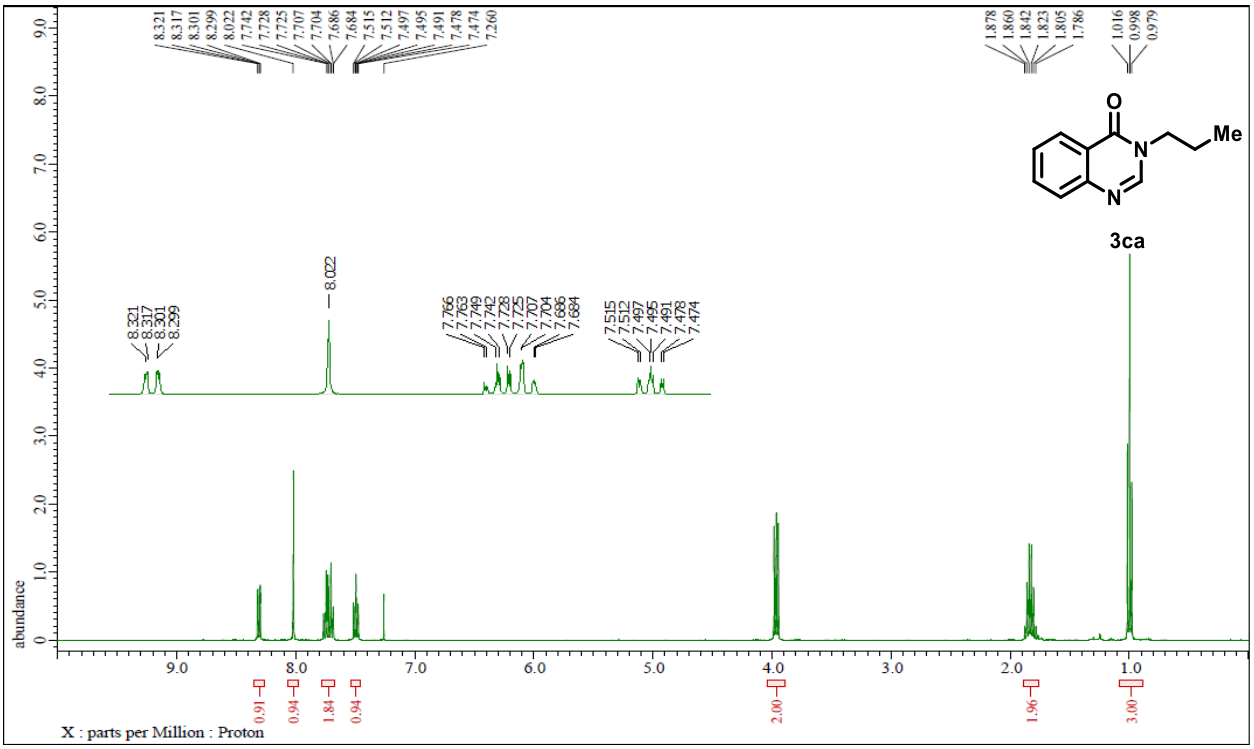
^{1}H NMR of Compound **3ba′** ($CDCl_3$-*d*, 400 MHz)



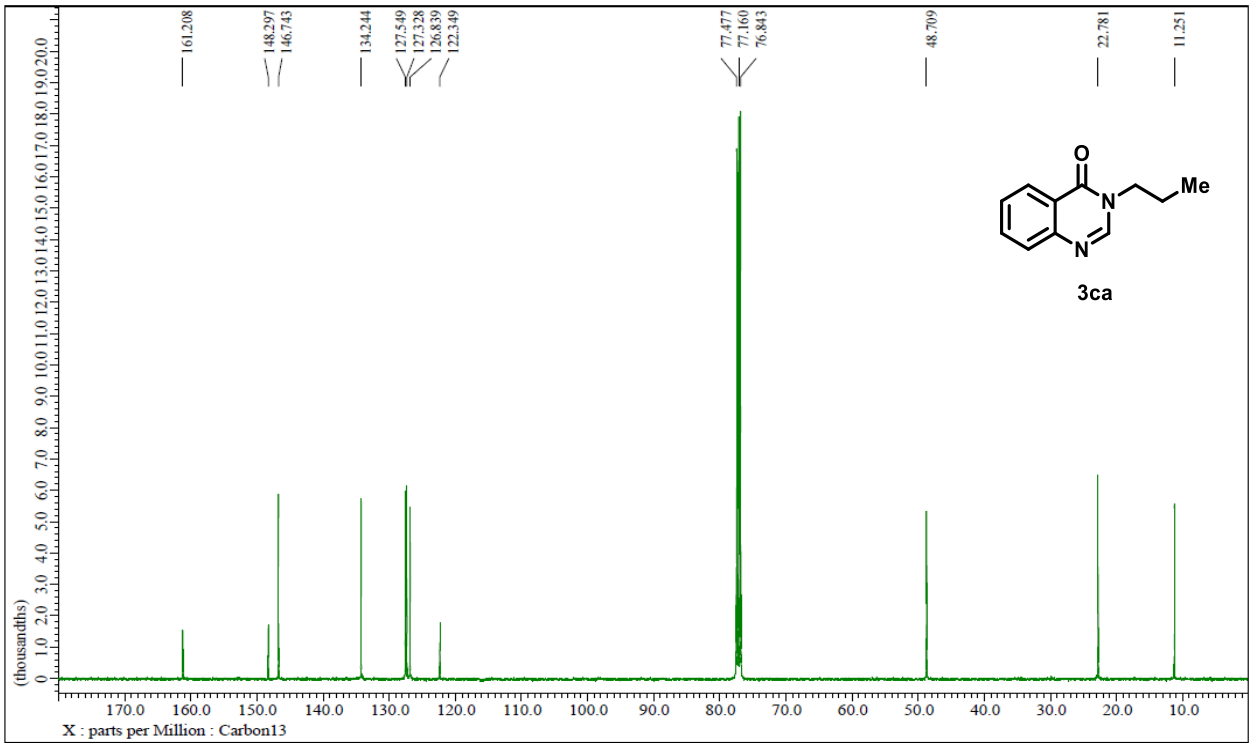
^{13}C NMR of Compound **3ba′** ($CDCl_3$-*d*, 100 MHz)



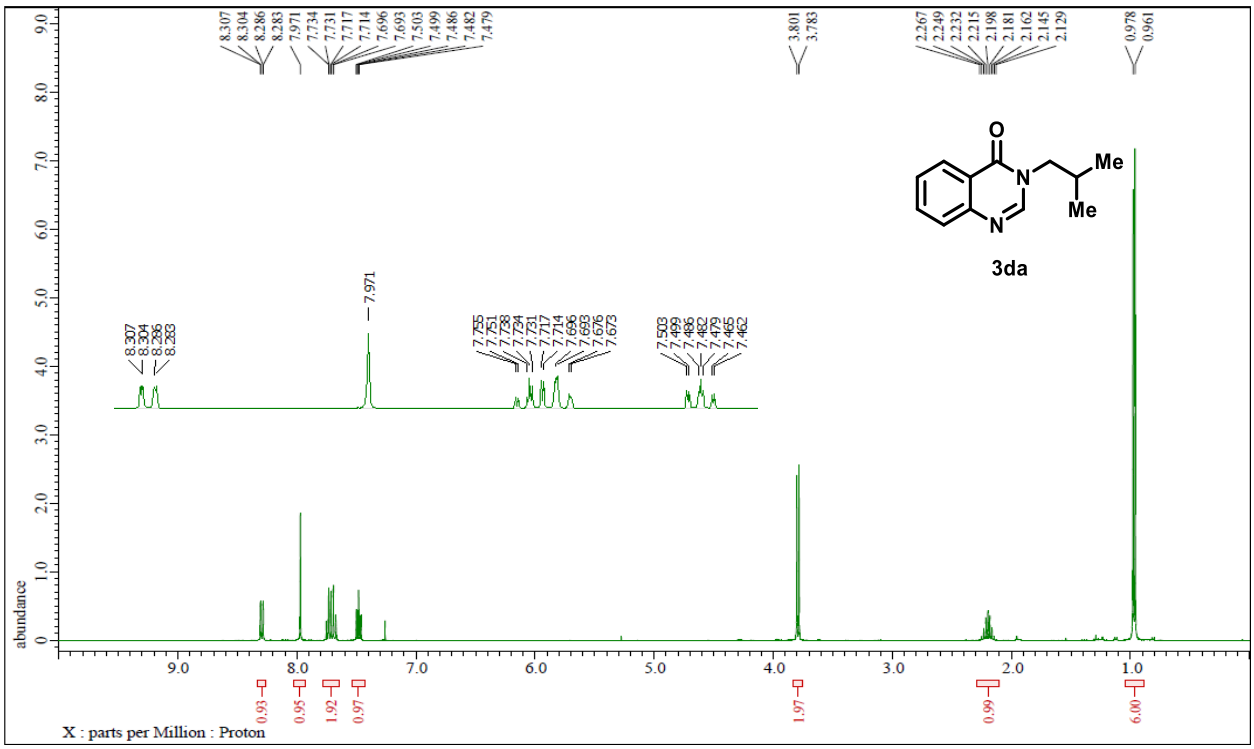
^{1}H NMR of Compound **3ca** ($CDCl_3$-*d*, 400 MHz)



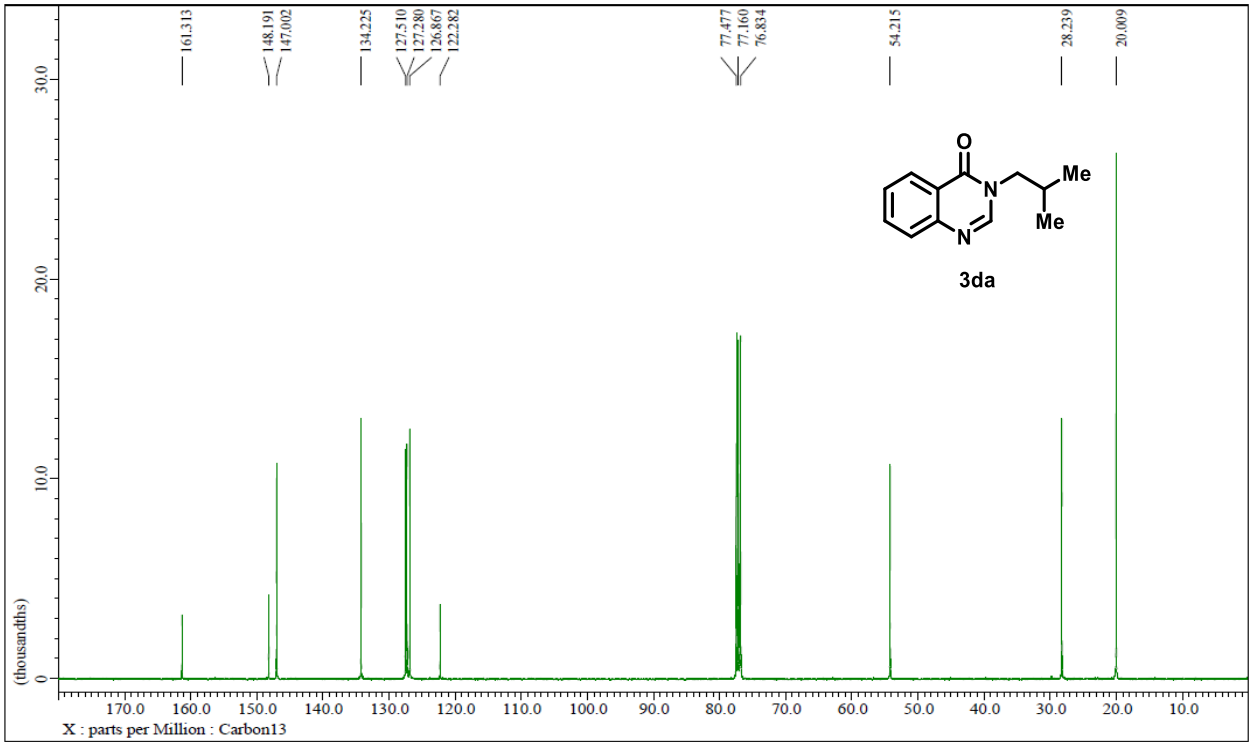
^{13}C NMR of Compound **3ca** ($CDCl_3$-*d*, 100 MHz)



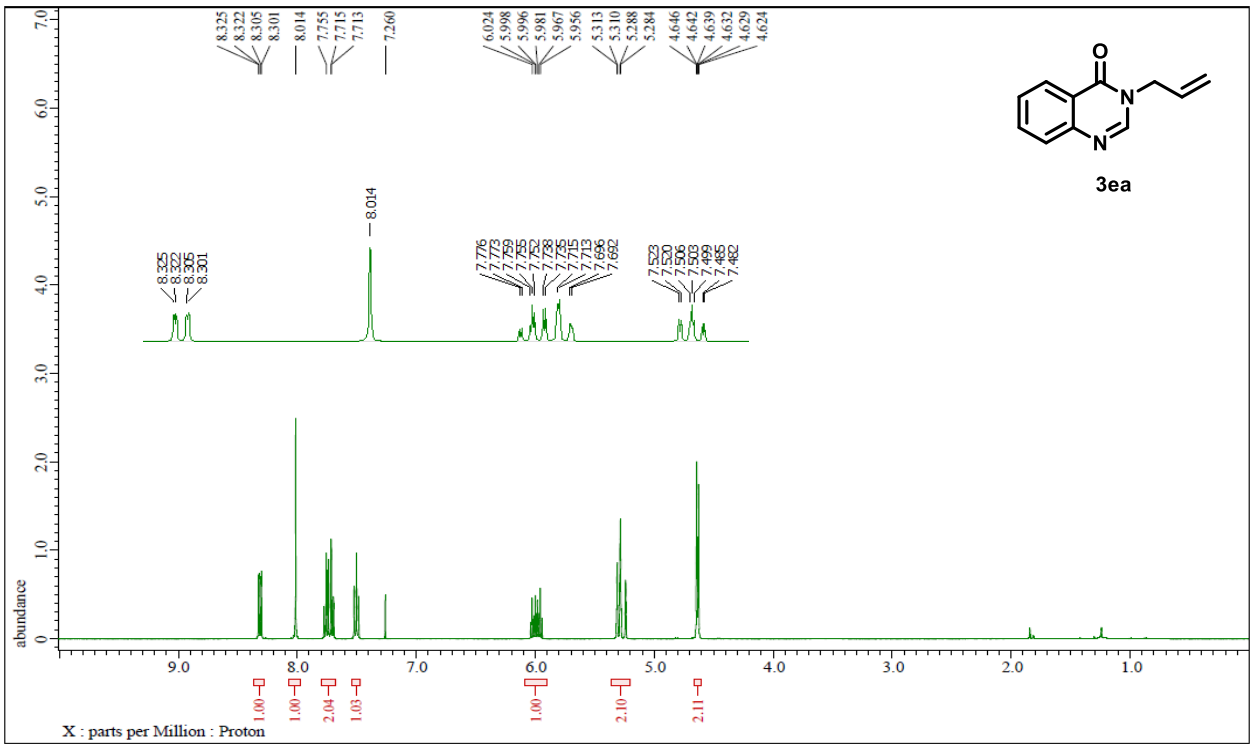
^{1}H NMR of Compound **3da** ($CDCl_3$-*d*, 400 MHz)



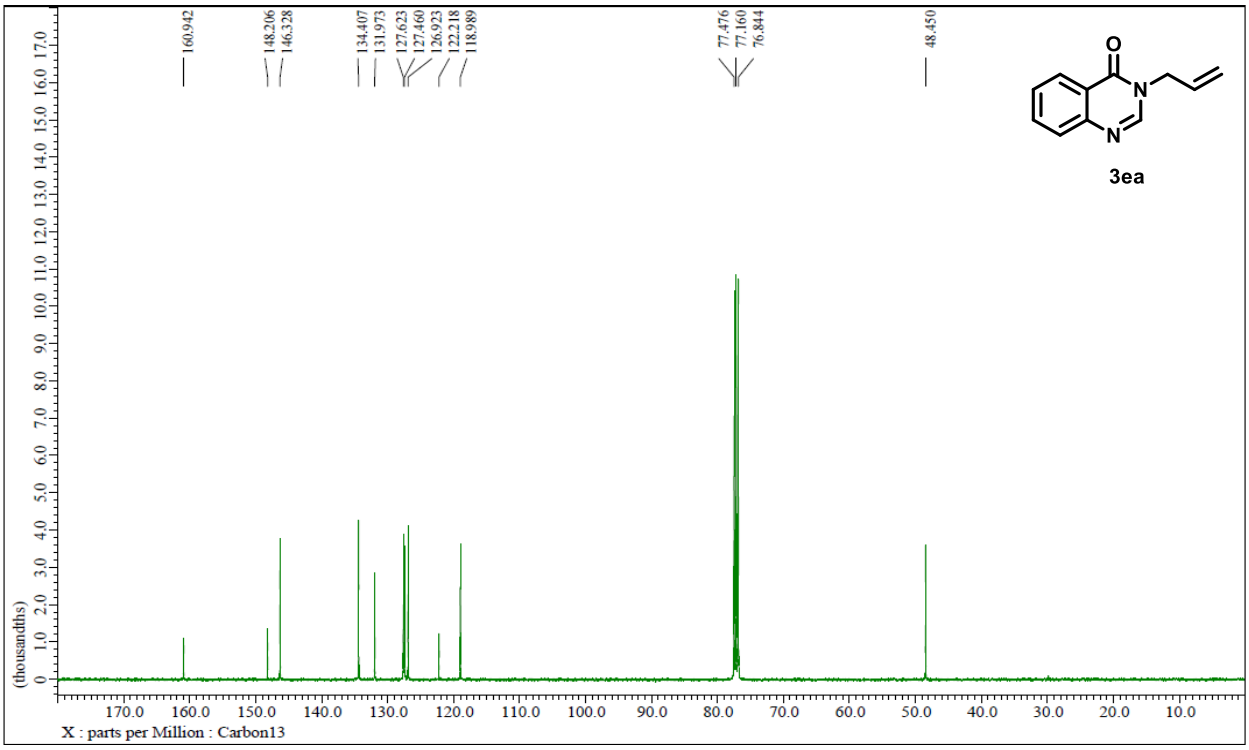
^{13}C NMR of Compound **3da** ($CDCl_3$-*d*, 100 MHz)



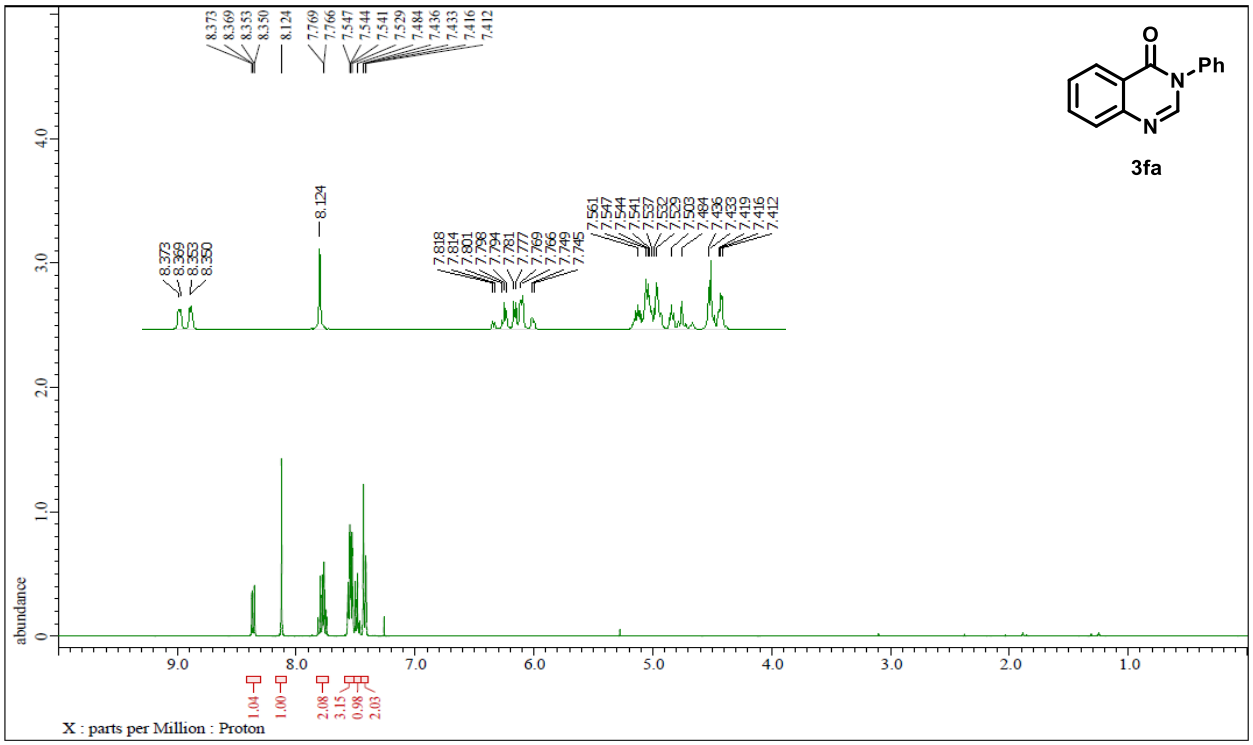
^{1}H NMR of Compound **3ea** ($CDCl_3$-*d*, 400 MHz)



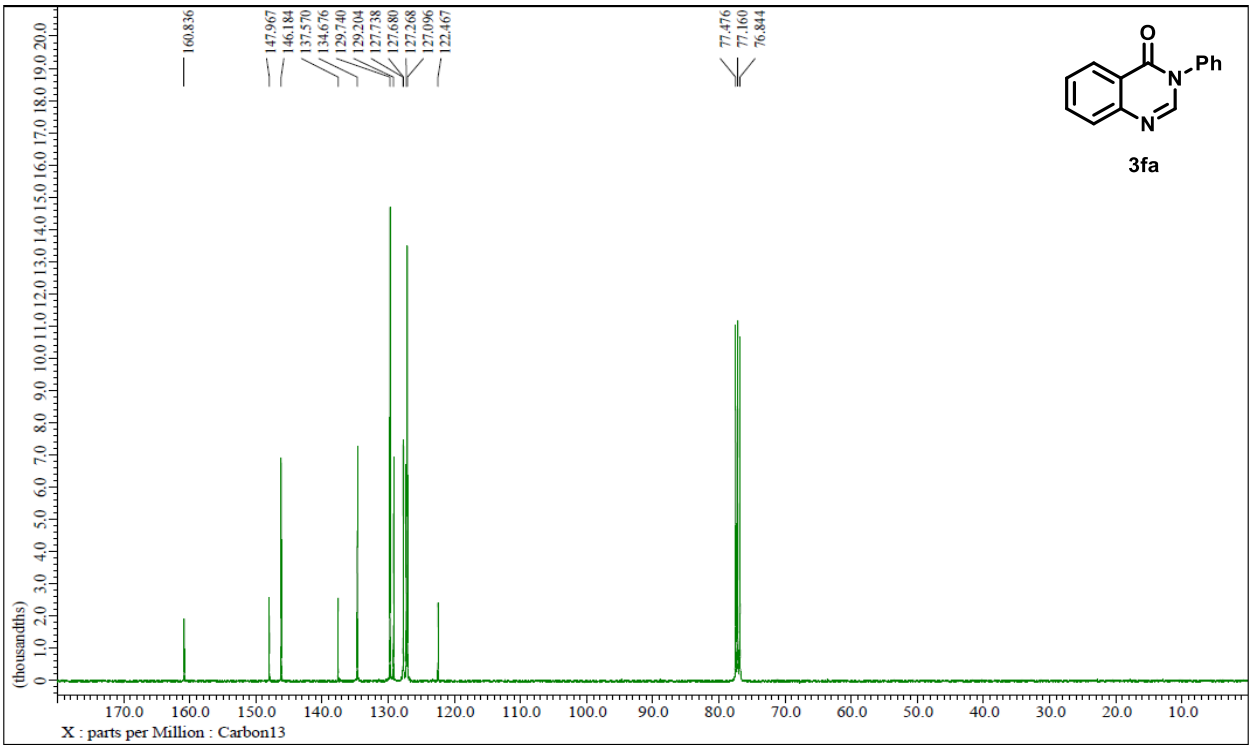
^{13}C NMR of Compound **3ea** ($CDCl_3$-*d*, 100 MHz)



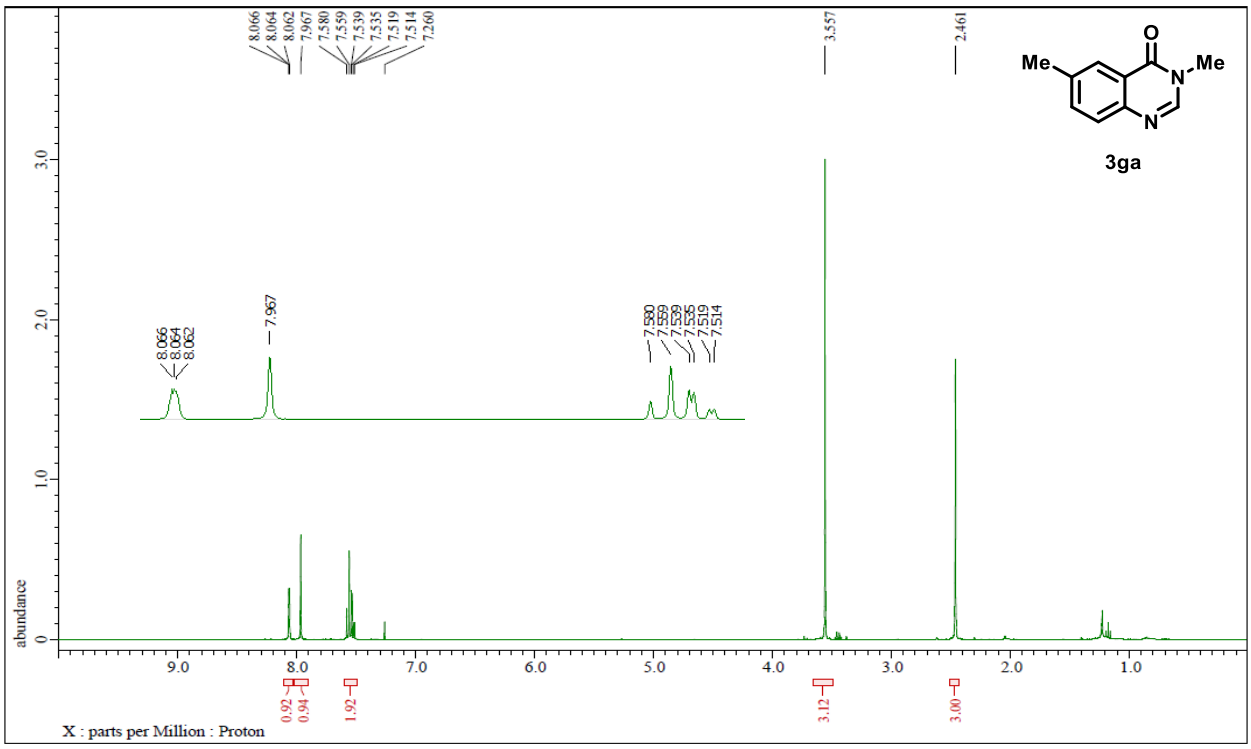
^{1}H NMR of Compound **3fa** ($CDCl_3$-*d*, 400 MHz)



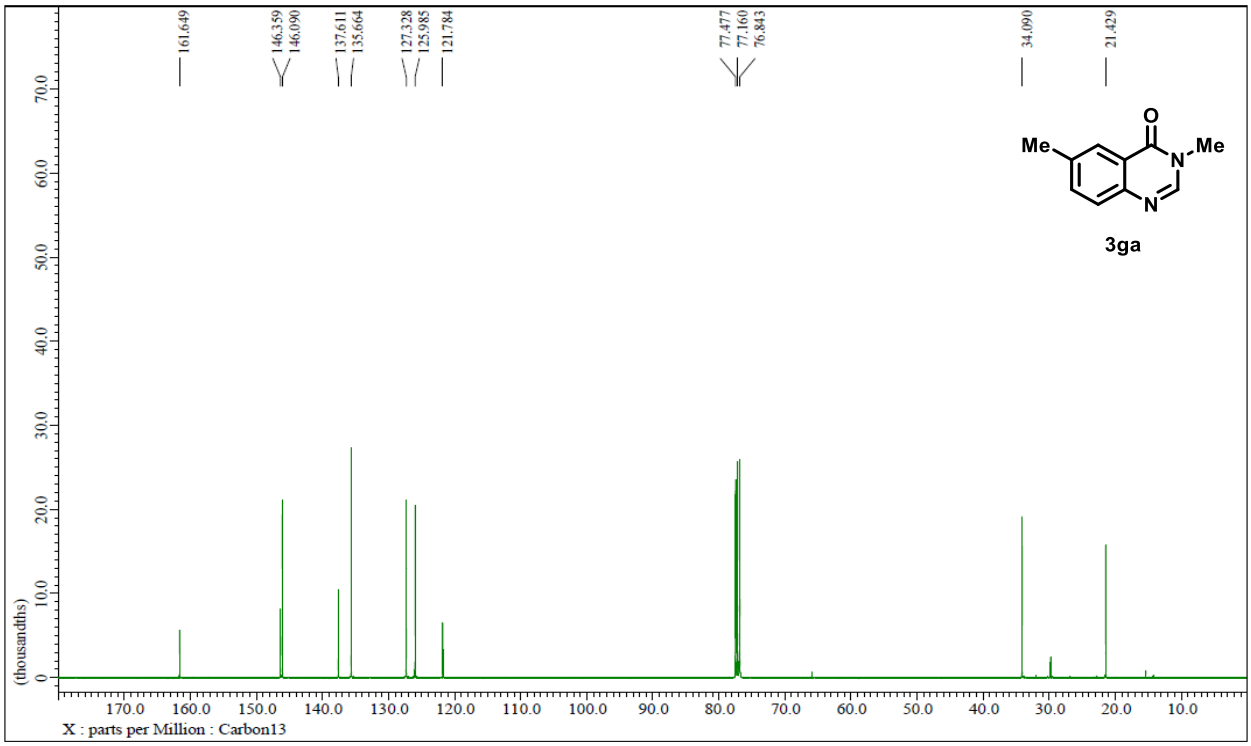
^{13}C NMR of Compound **3fa** ($CDCl_3$-*d*, 100 MHz)



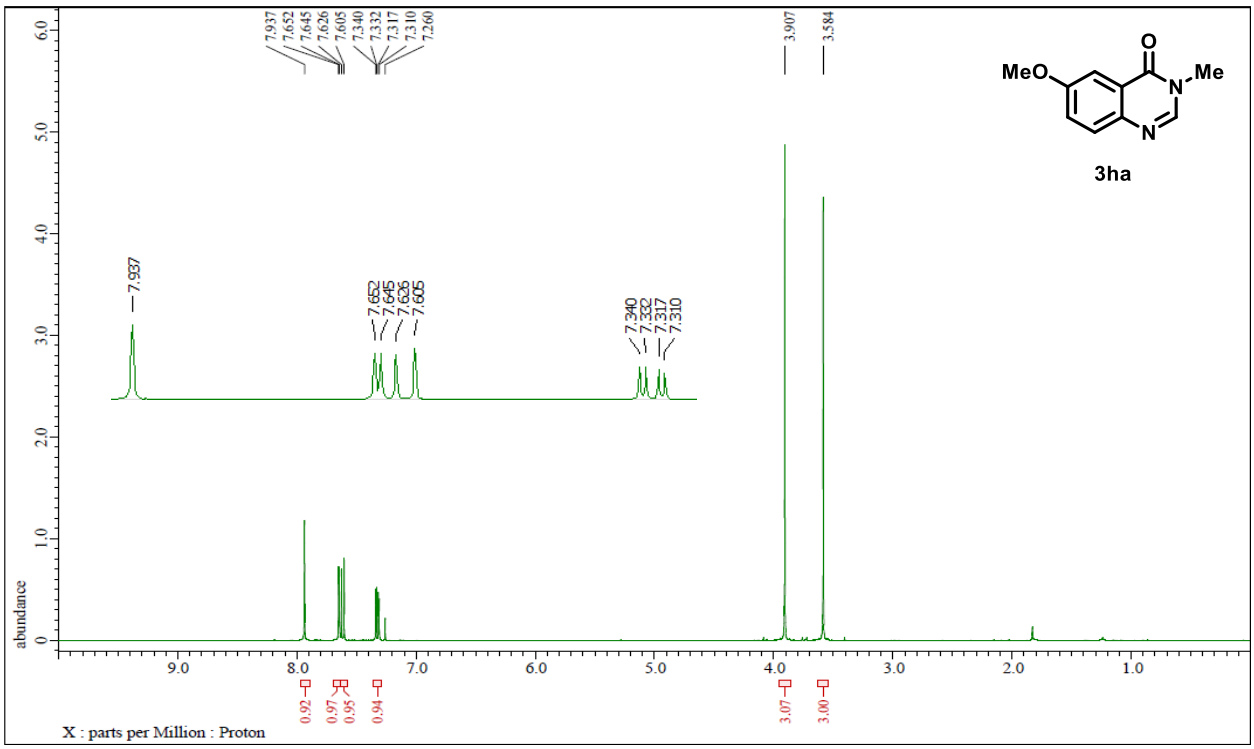
^{1}H NMR of Compound **3ga** ($CDCl_3$-*d*, 400 MHz)



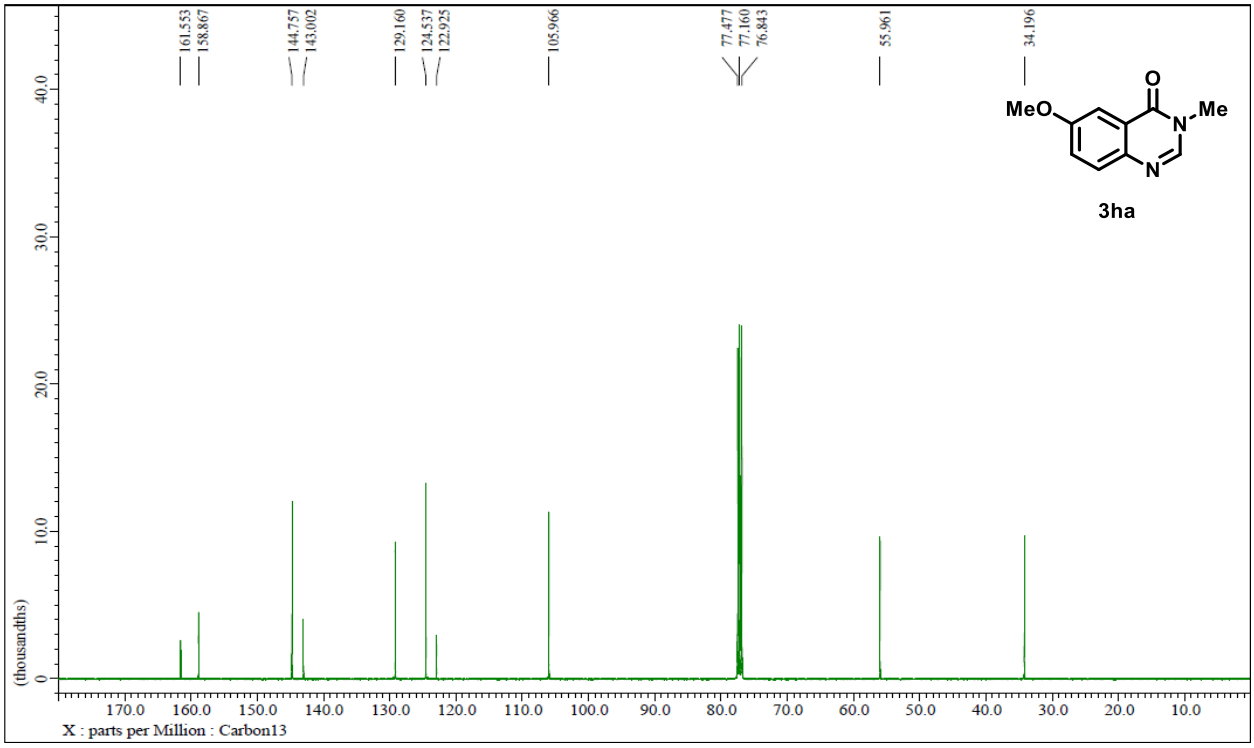
^{13}C NMR of Compound **3ga** ($CDCl_3$-*d*, 100 MHz)



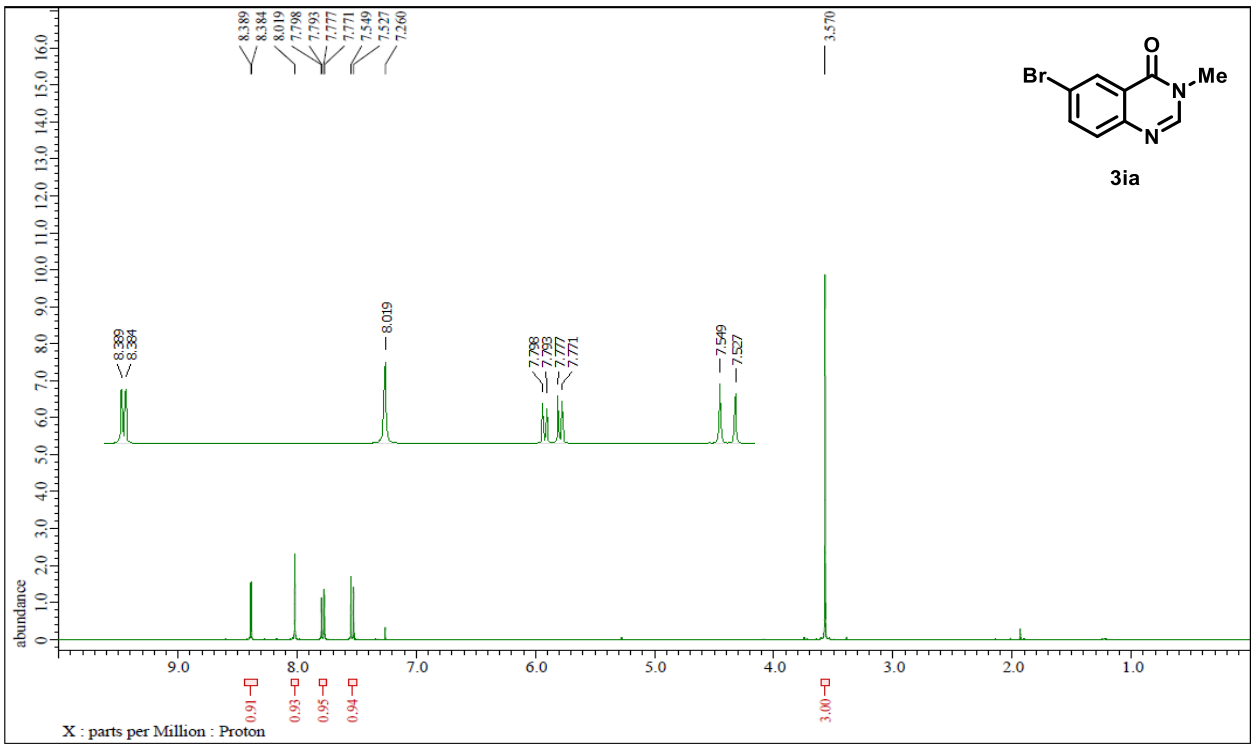
^{1}H NMR of Compound **3ha** ($CDCl_3$-*d*, 400 MHz)



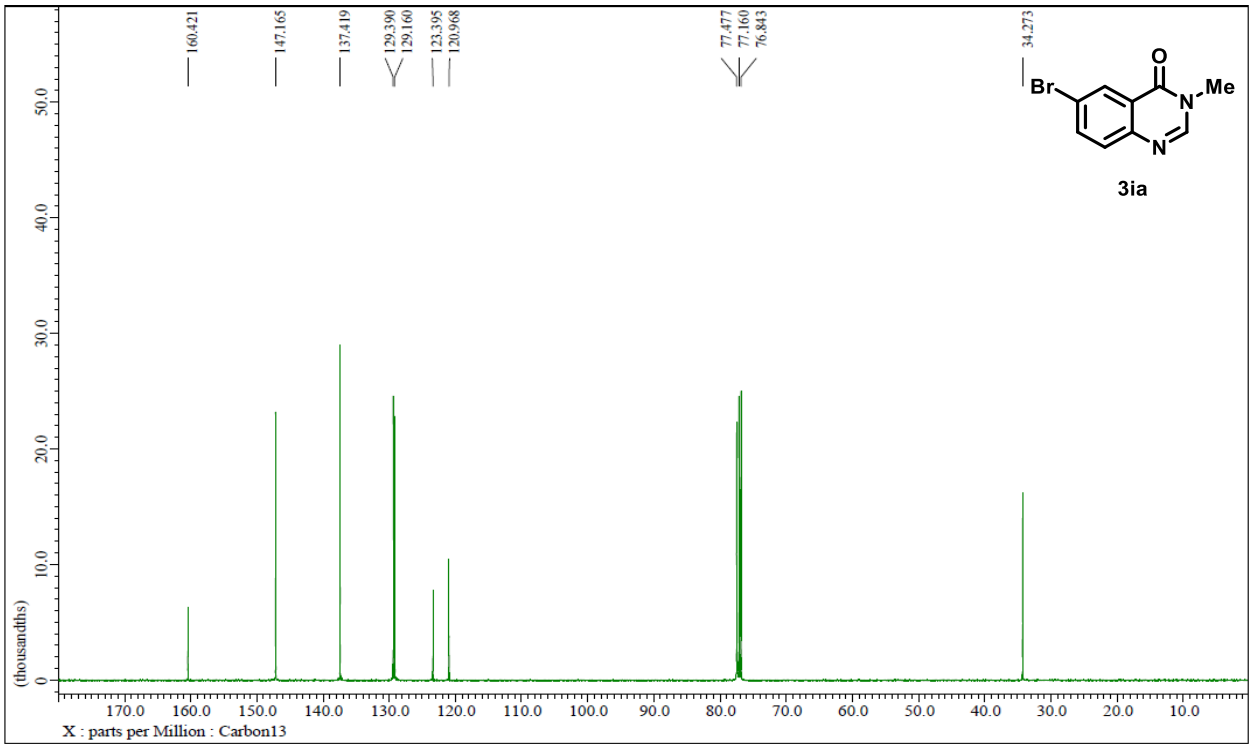
^{13}C NMR of Compound **3ha** ($CDCl_3$-*d*, 100 MHz)



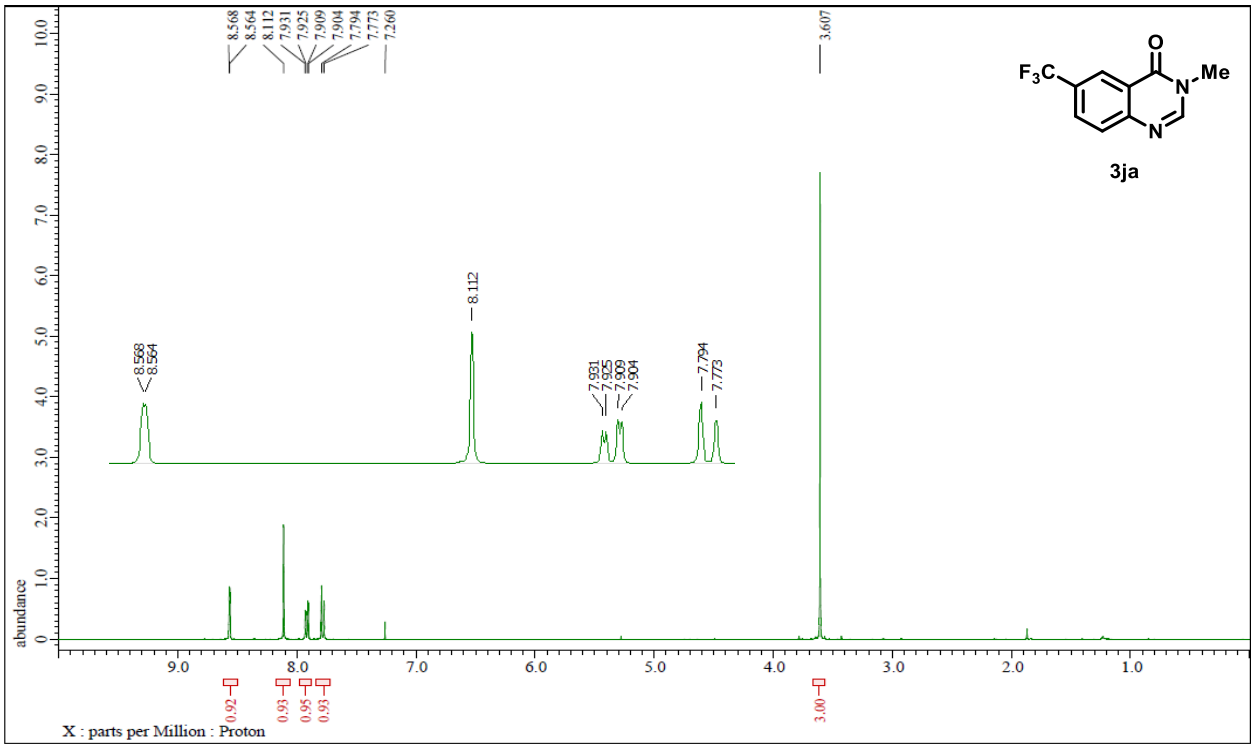
^{1}H NMR of Compound **3ia** ($CDCl_3$-*d*, 400 MHz)



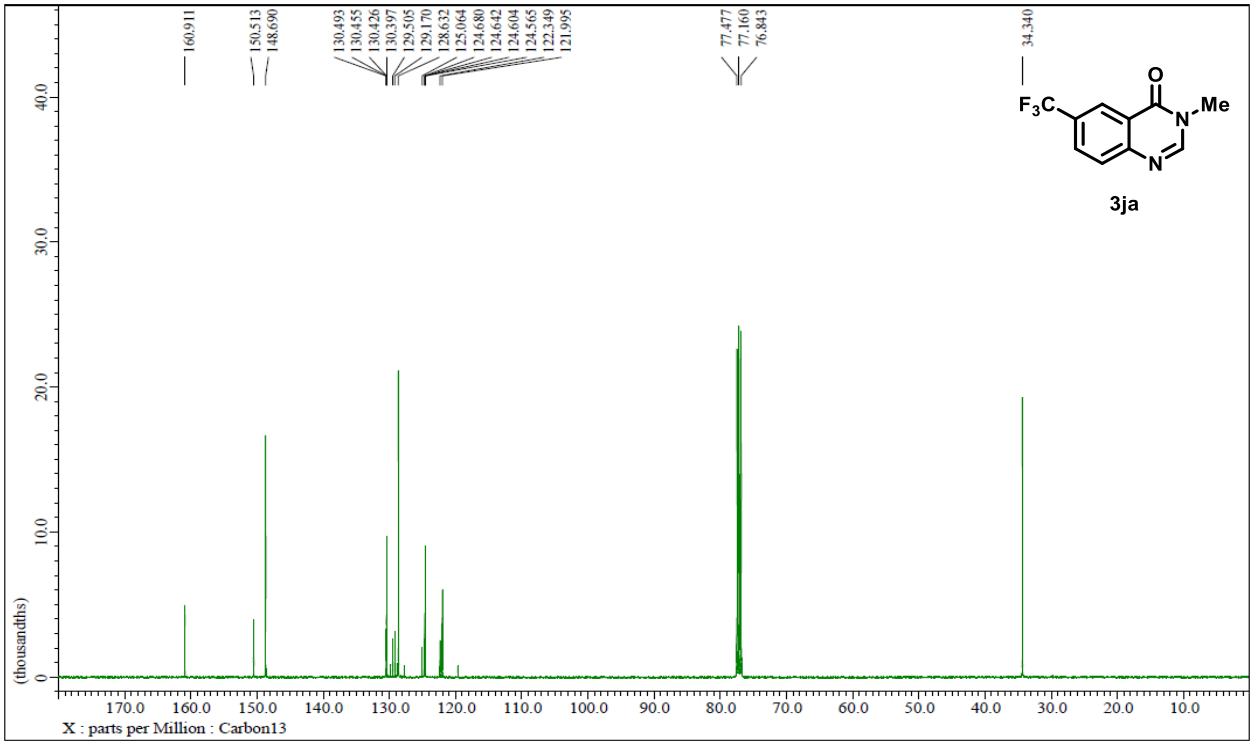
^{13}C NMR of Compound **3ia** ($CDCl_3$-*d*, 100 MHz)



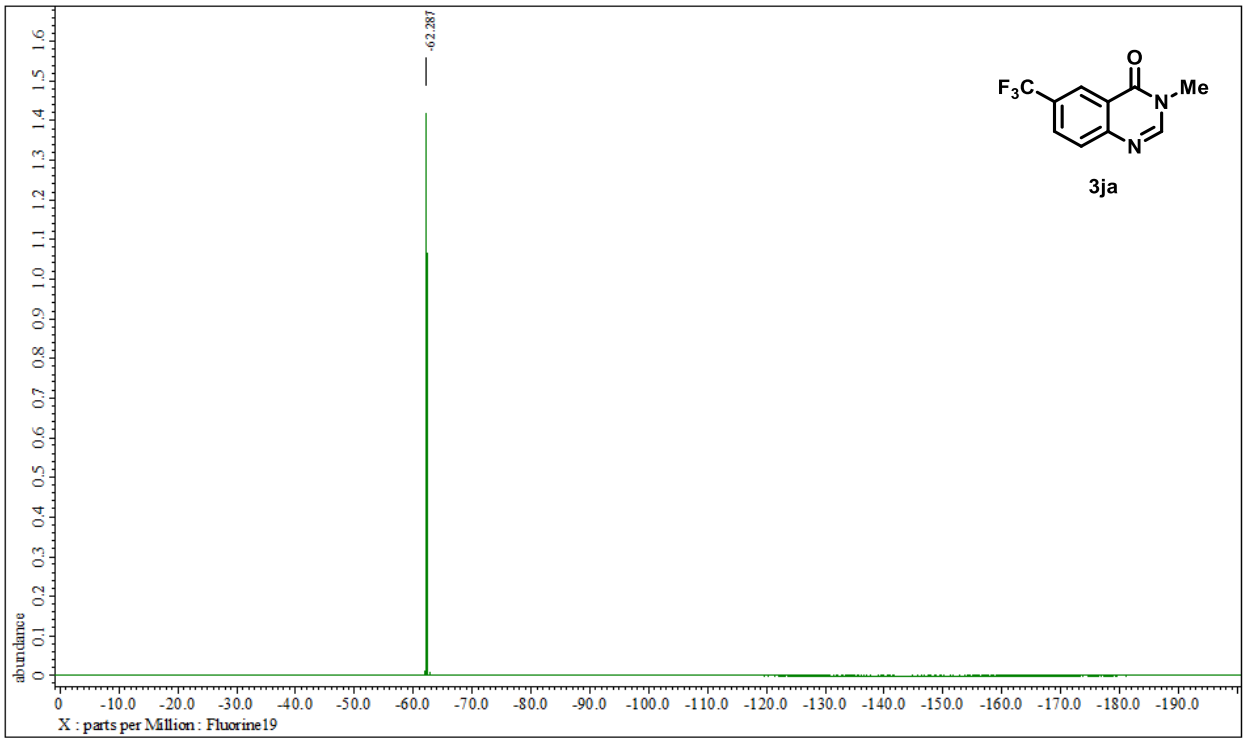
^{1}H NMR of Compound **3ja** ($CDCl_3$-*d*, 400 MHz)



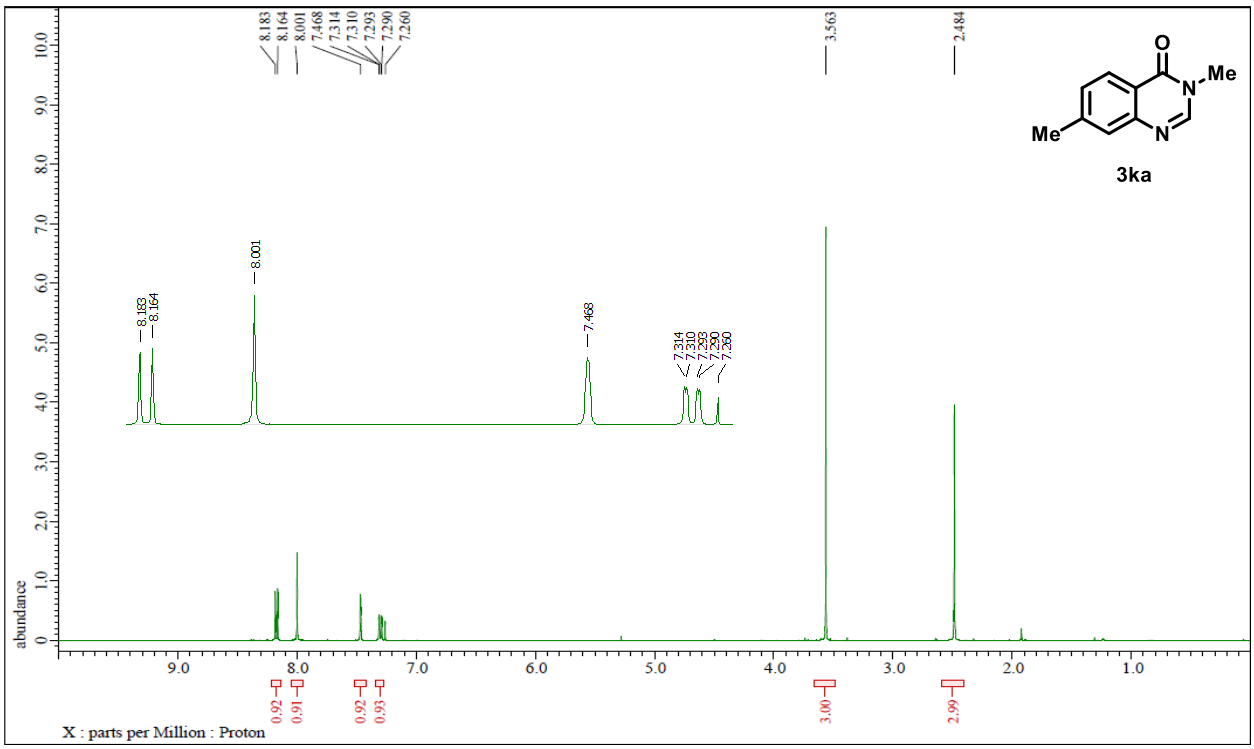
^{13}C NMR of Compound **3ja** ($CDCl_3$-*d*, 100 MHz)



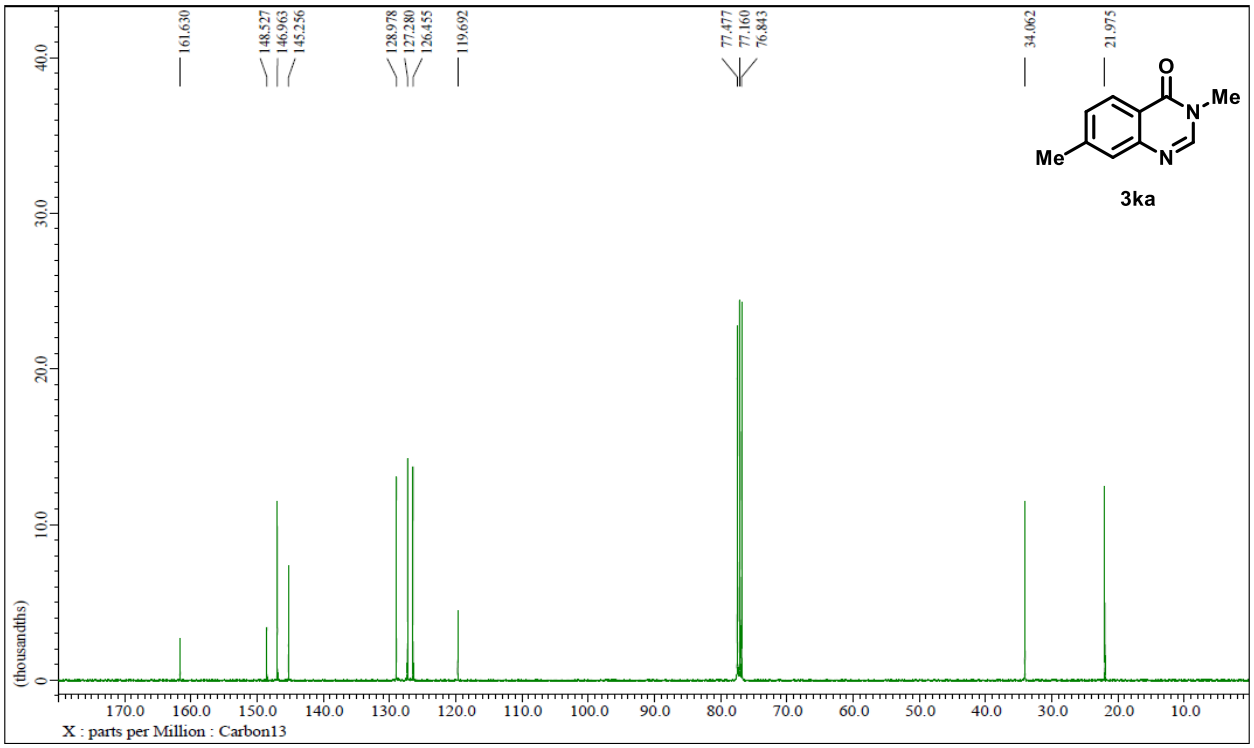
^{19}F NMR of Compound **3ja** ($CDCl_3$-*d*, 376 MHz)



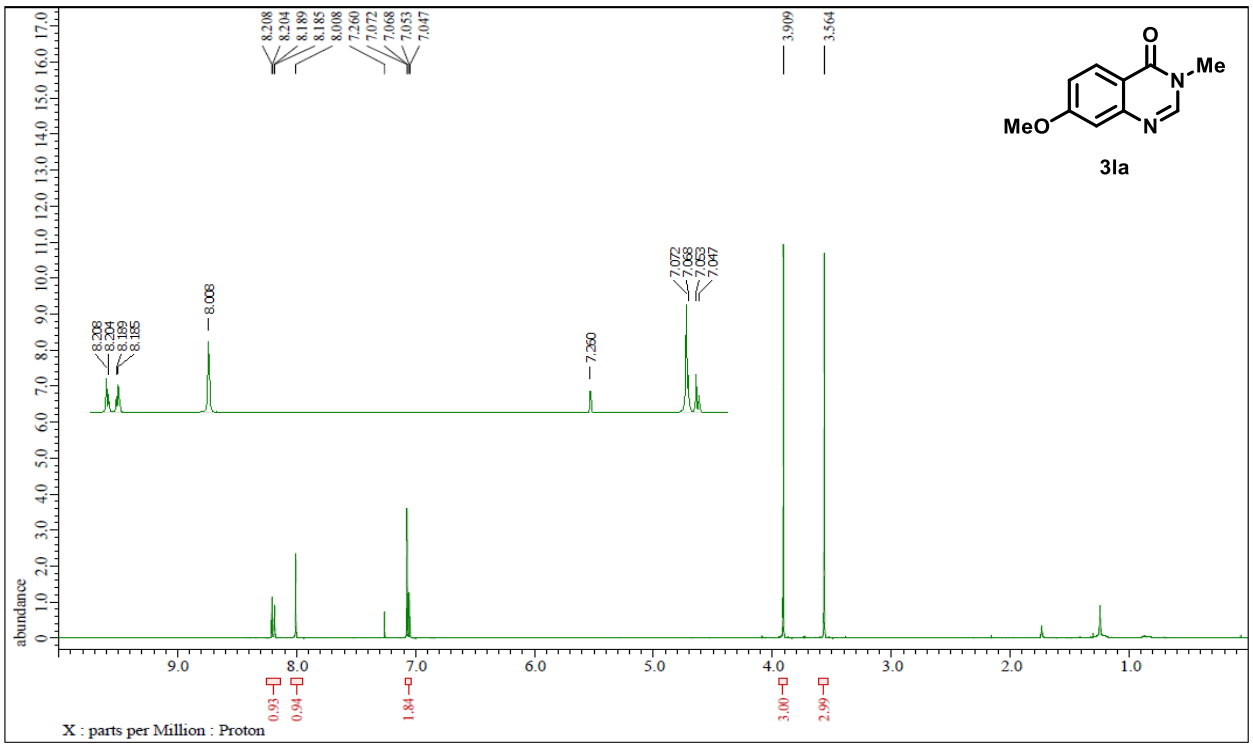
^{1}H NMR of Compound **3ka** ($CDCl_3$-*d*, 400 MHz)



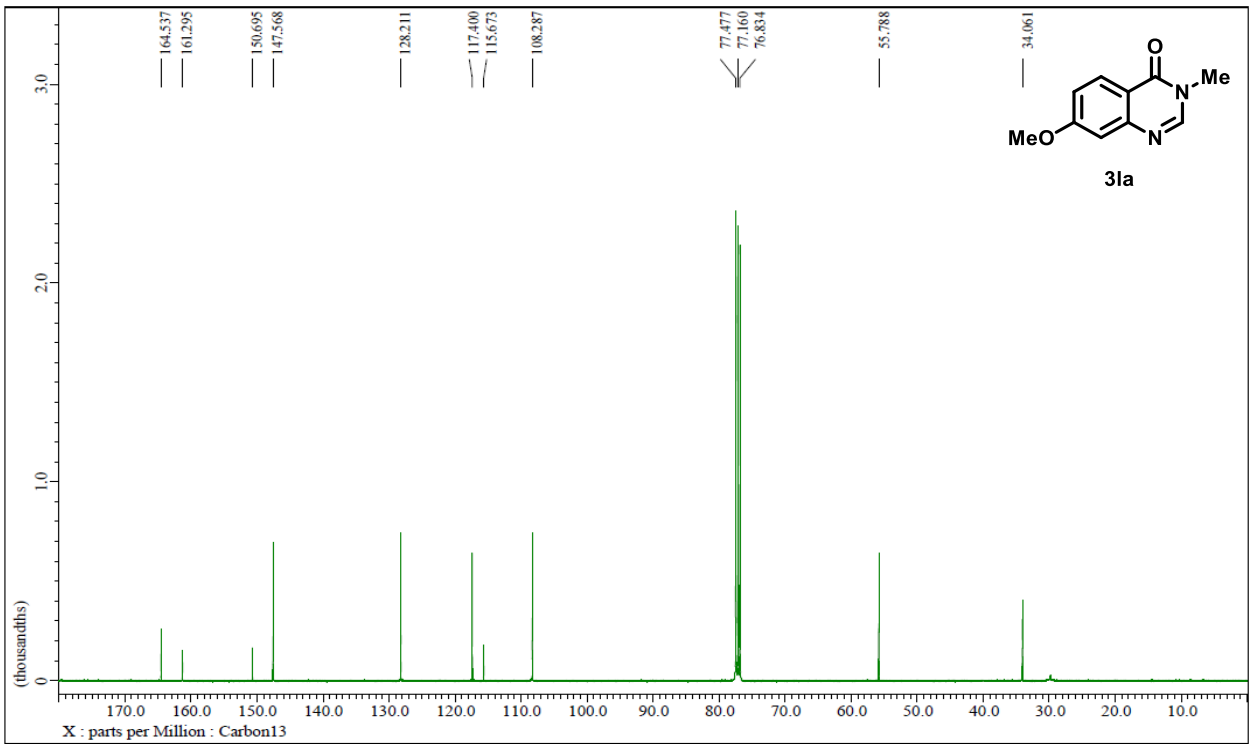
^{13}C NMR of Compound **3ka** ($CDCl_3$-*d*, 100 MHz)



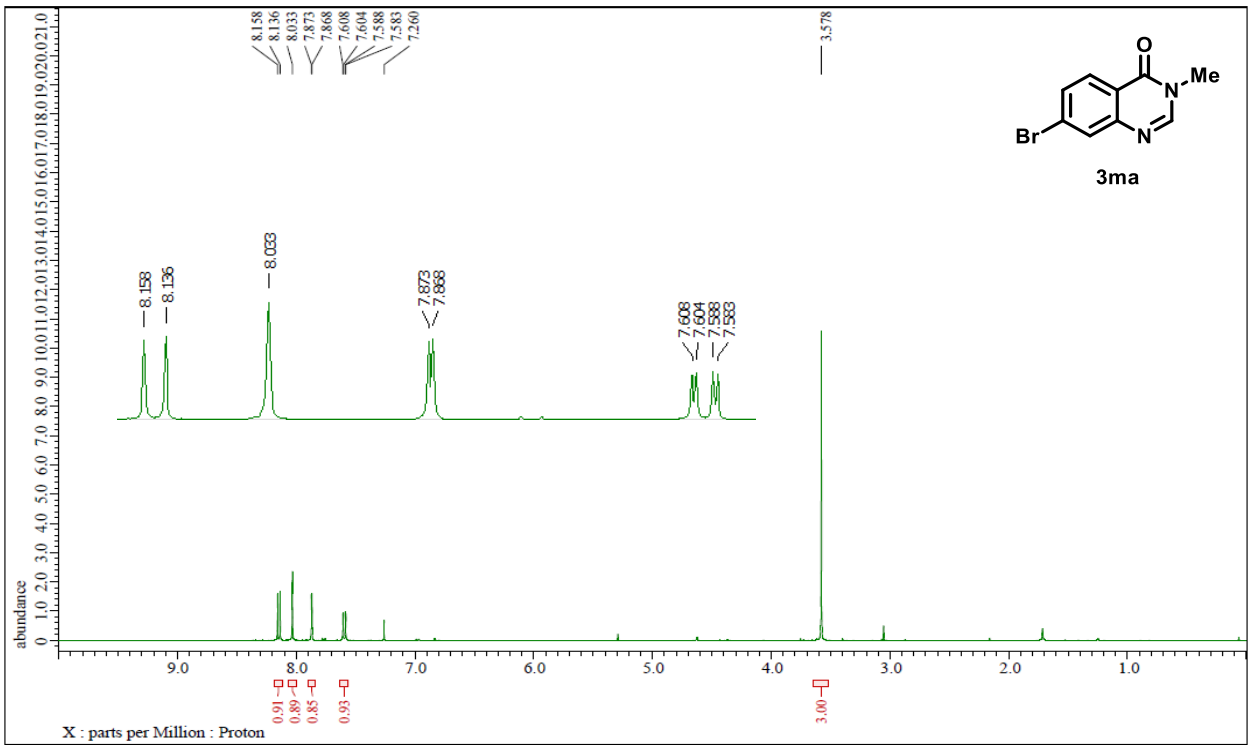
^{1}H NMR of Compound **3la** ($CDCl_3$-*d*, 400 MHz)



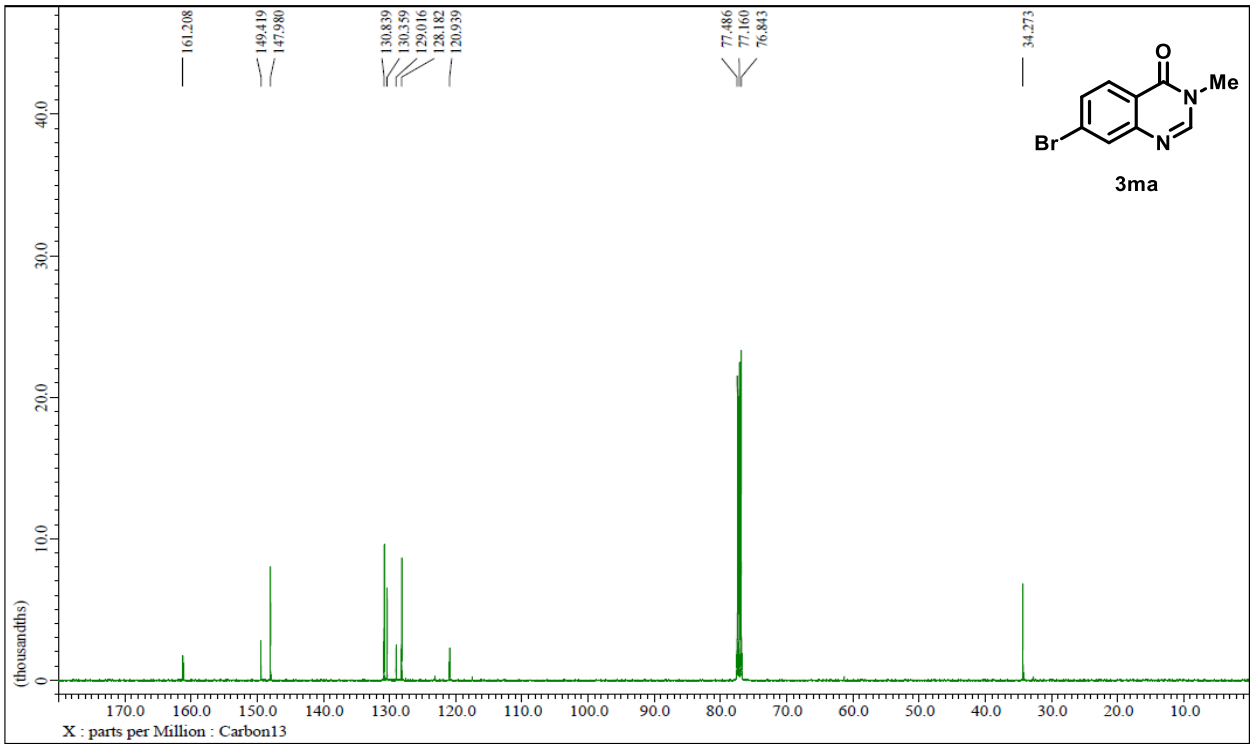
^{13}C NMR of Compound **3la** ($CDCl_3$-*d*, 100 MHz)



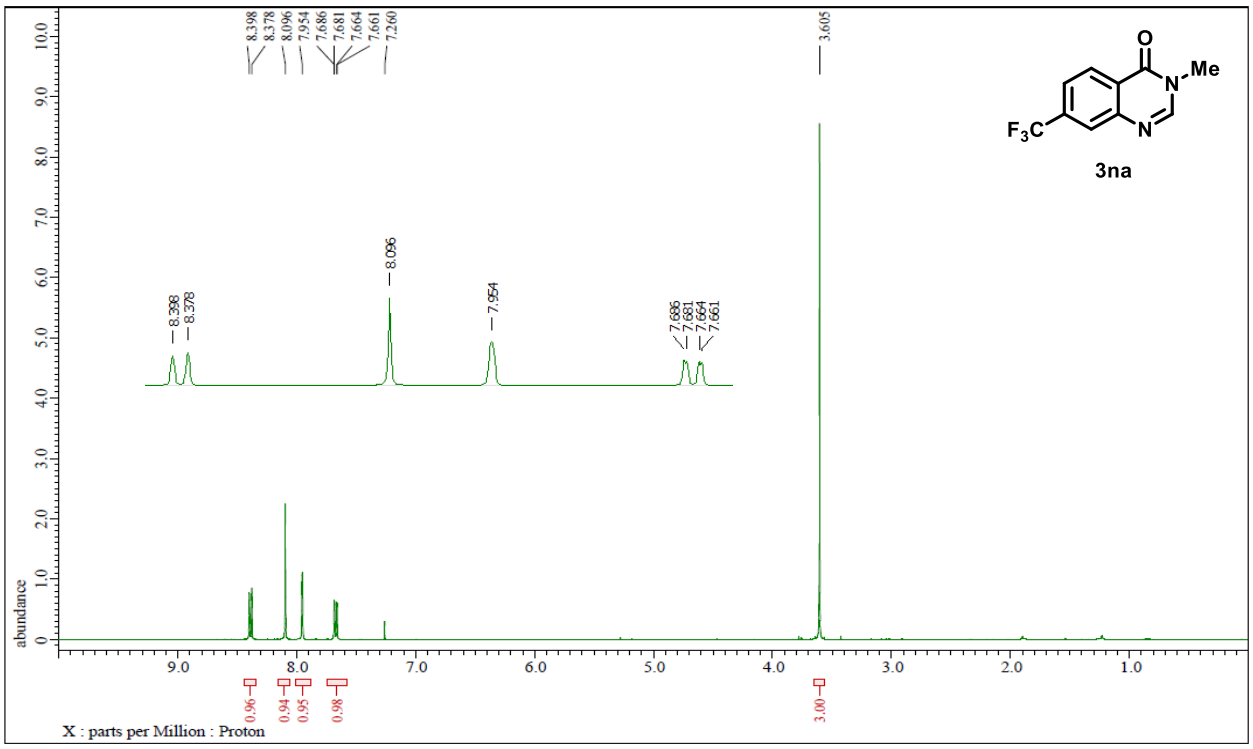
^{1}H NMR of Compound **3ma** ($CDCl_3$-*d*, 400 MHz)



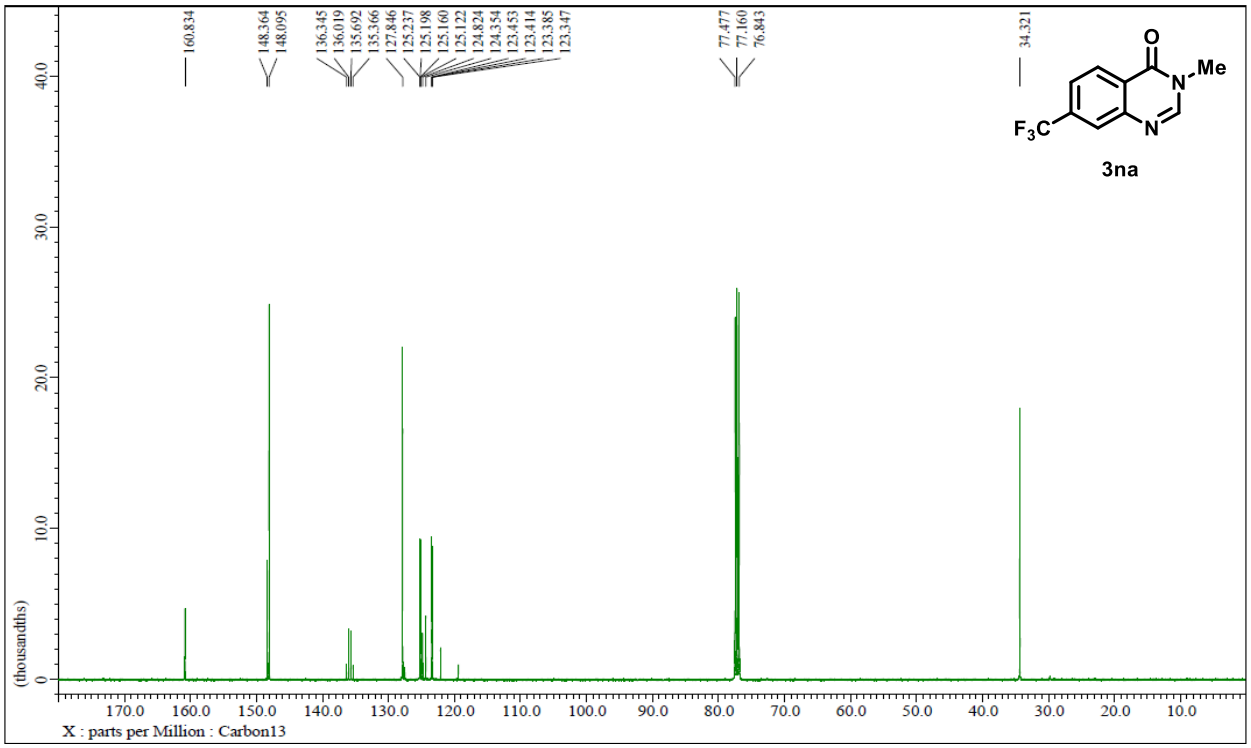
^{13}C NMR of Compound **3ma** ($CDCl_3$-*d*, 100 MHz)



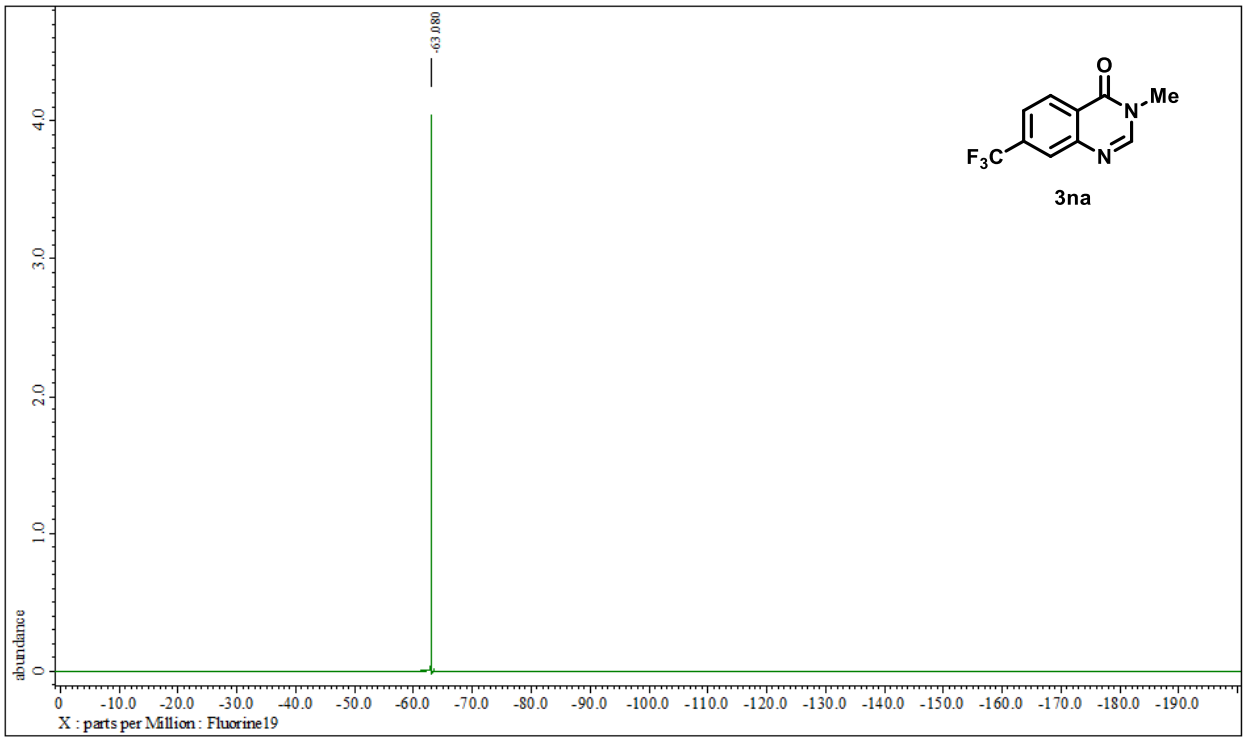
^{1}H NMR of Compound **3na** ($CDCl_3$-*d*, 400 MHz)



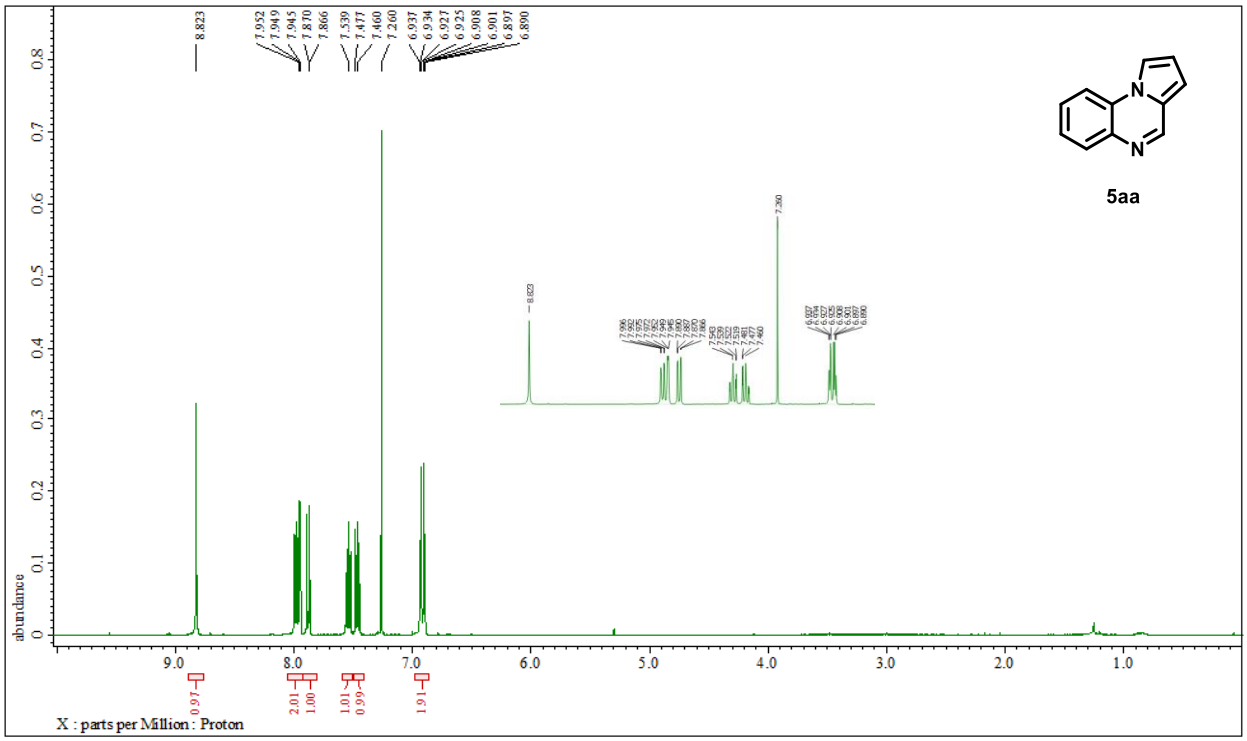
^{13}C NMR of Compound **3na** ($CDCl_3$-*d*, 100 MHz)



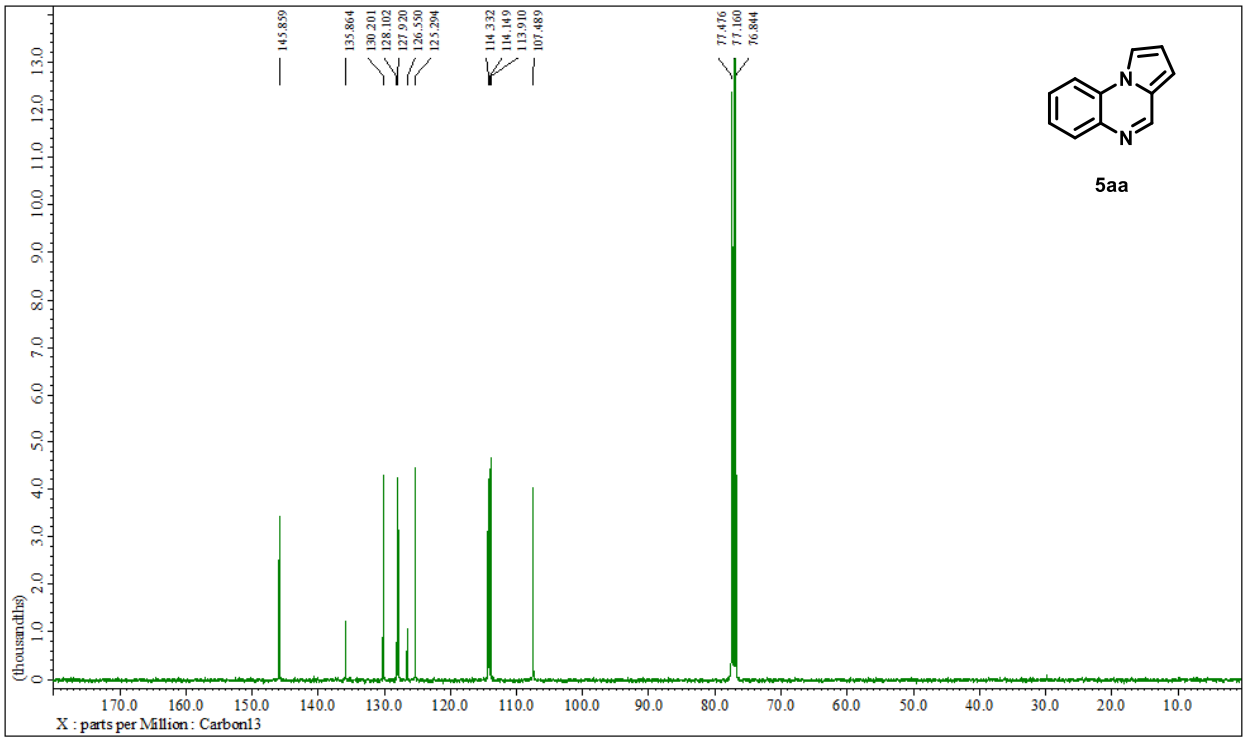
^{19}F NMR of Compound **3na** ($CDCl_3$-*d*, 376 MHz)



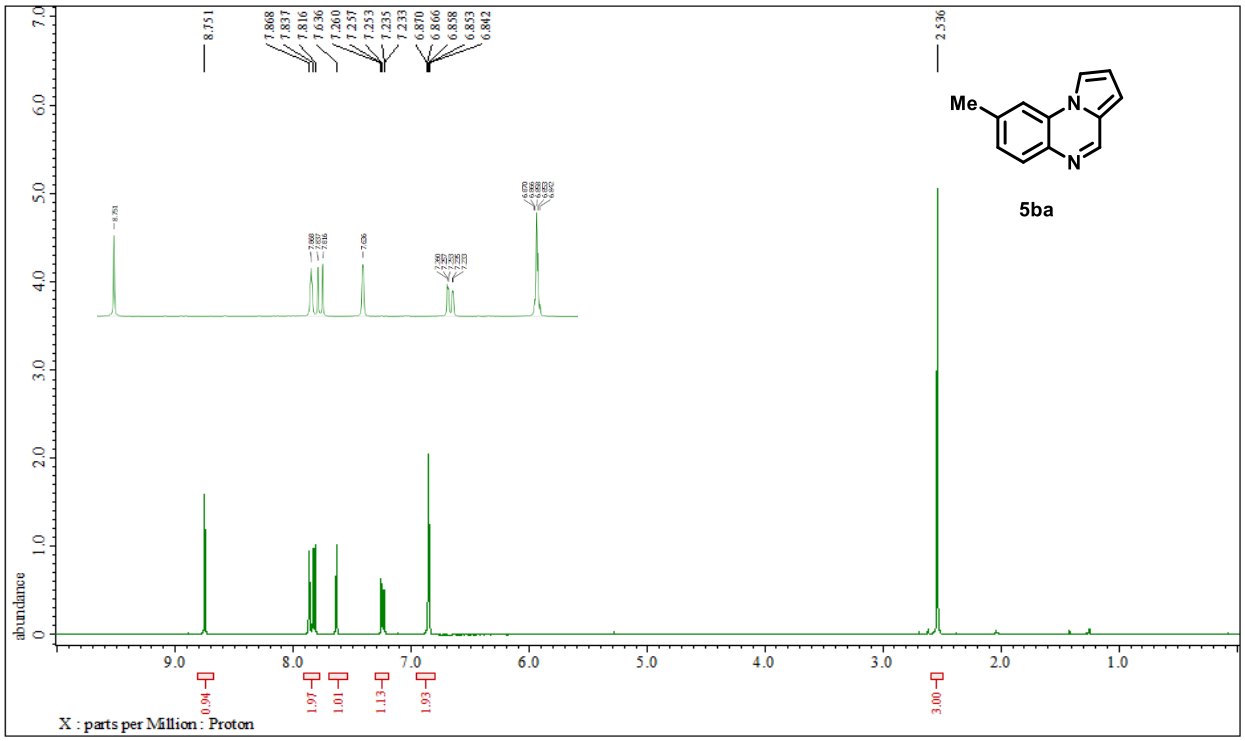
^{1}H NMR of Compound **5aa** ($CDCl_3$-*d*, 400 MHz)



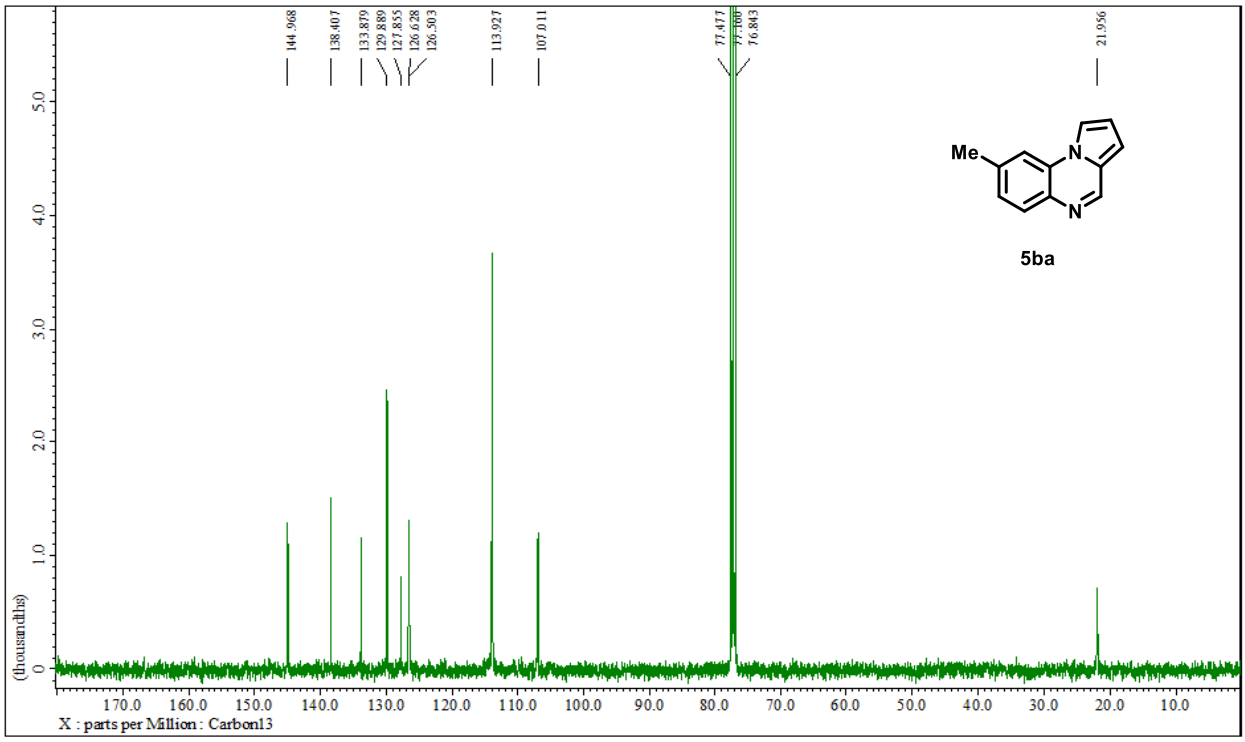
^{13}C NMR of Compound **5aa** ($CDCl_3$-*d*, 100 MHz)



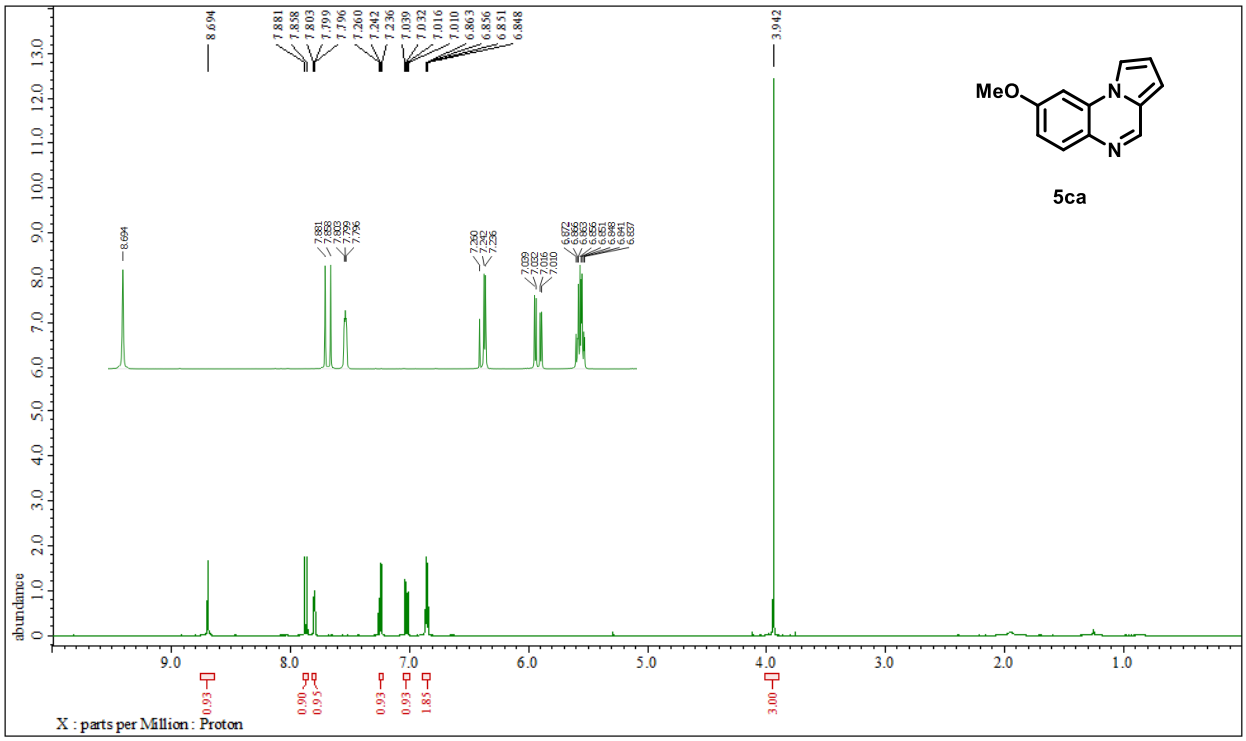
^{1}H NMR of Compound **5ba** ($CDCl_3$-*d*, 400 MHz)



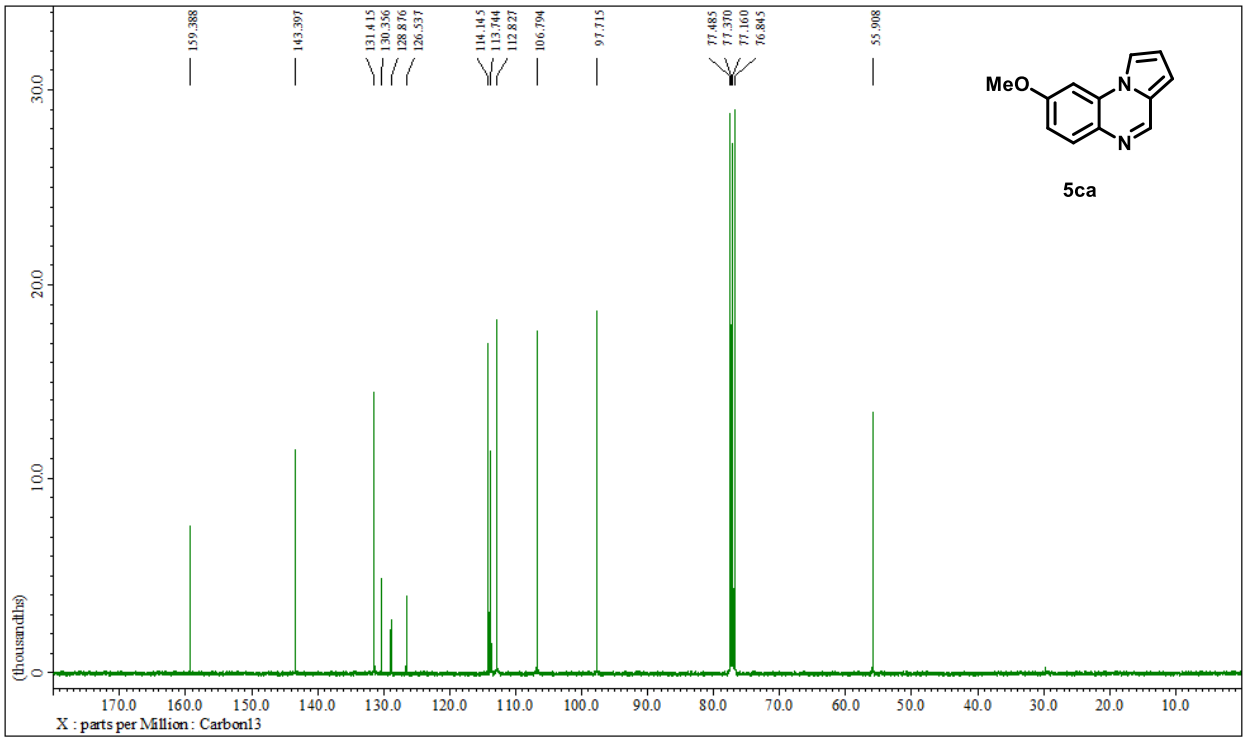
^{13}C NMR of Compound **5ba** ($CDCl_3$-*d*, 100 MHz)



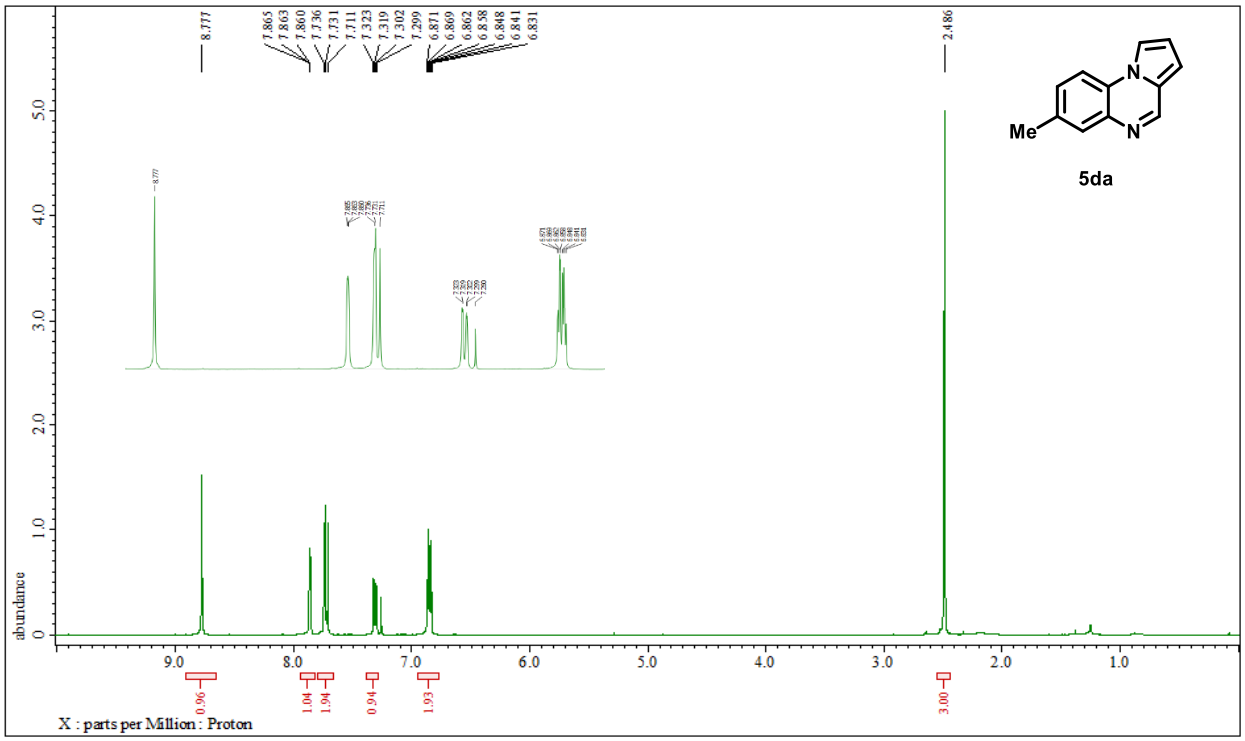
^{1}H NMR of Compound **5ca** ($CDCl_3$-*d*, 400 MHz)



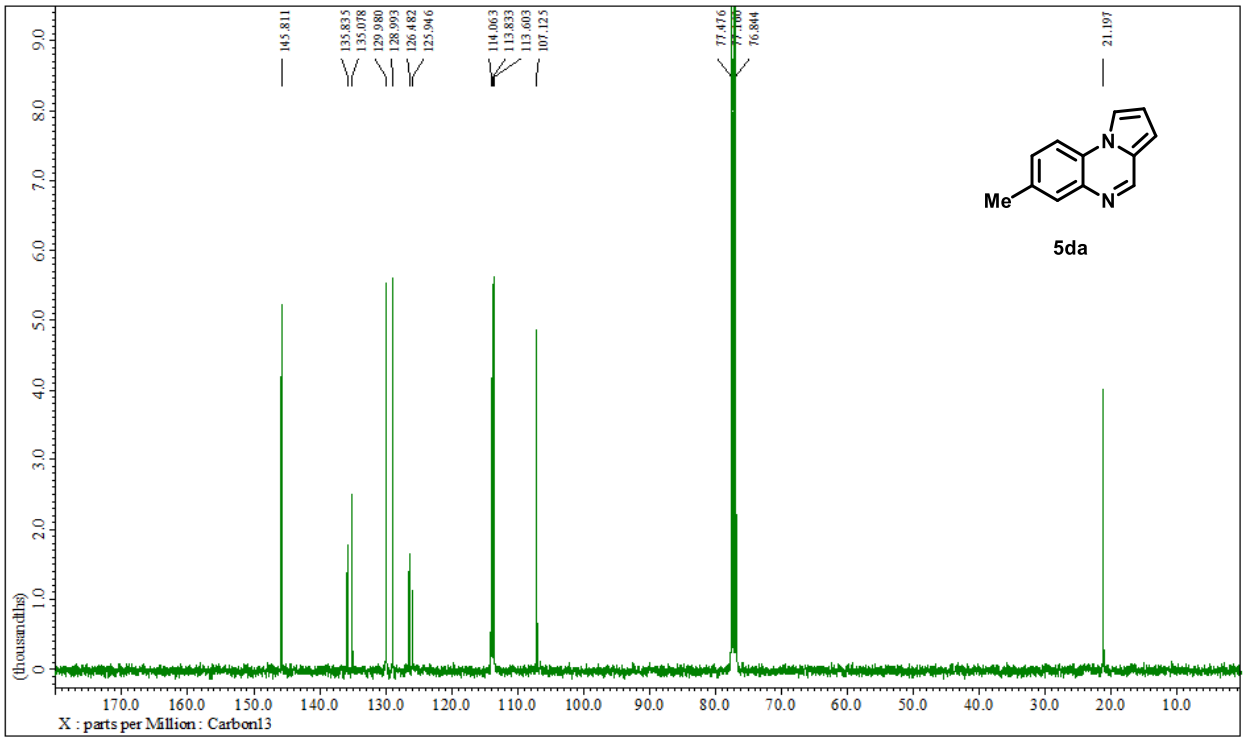
^{13}C NMR of Compound **5ca** ($CDCl_3$-*d*, 100 MHz)



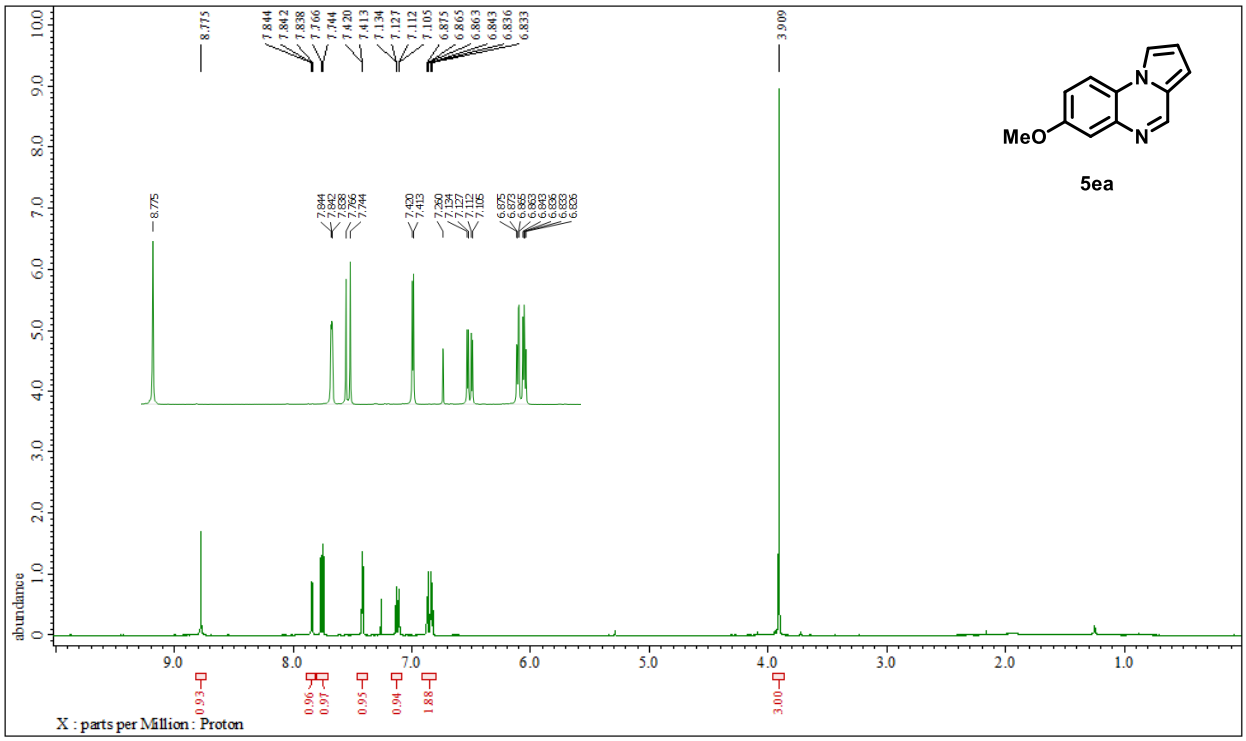
^{1}H NMR of Compound **5da** ($CDCl_3$-*d*, 400 MHz)



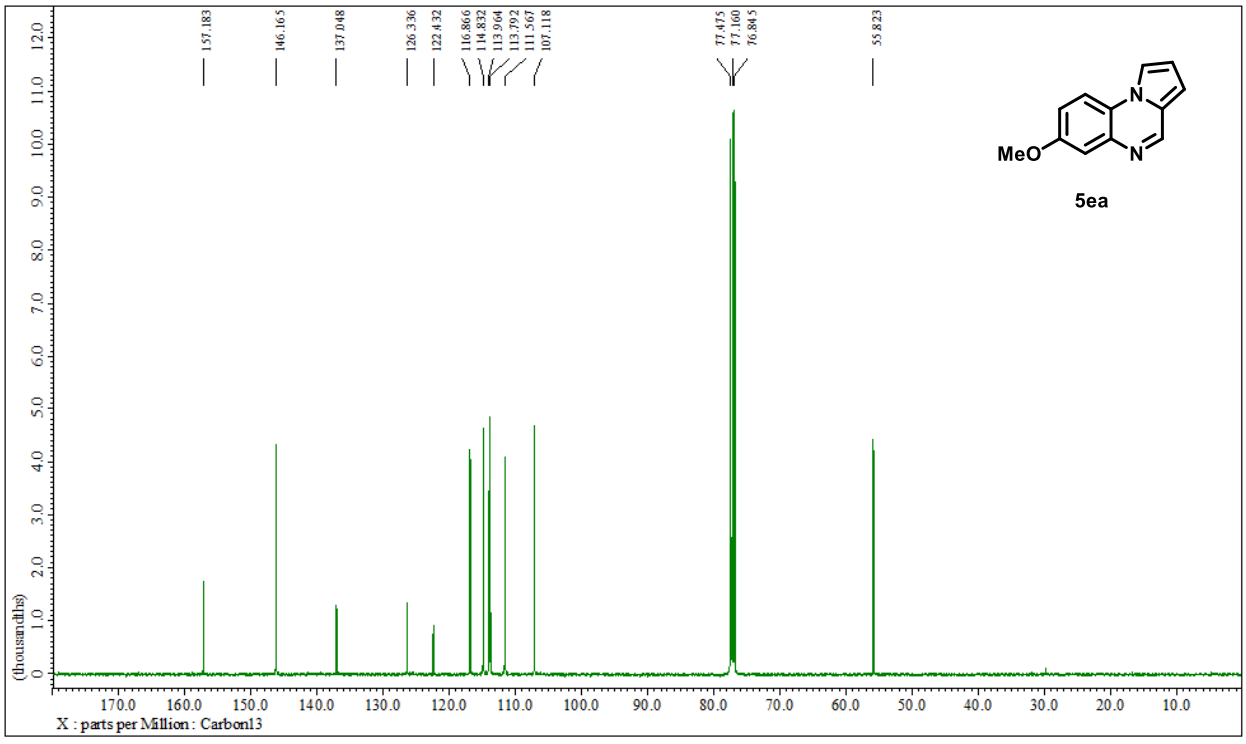
^{13}C NMR of Compound **5da** ($CDCl_3$-*d*, 100 MHz)



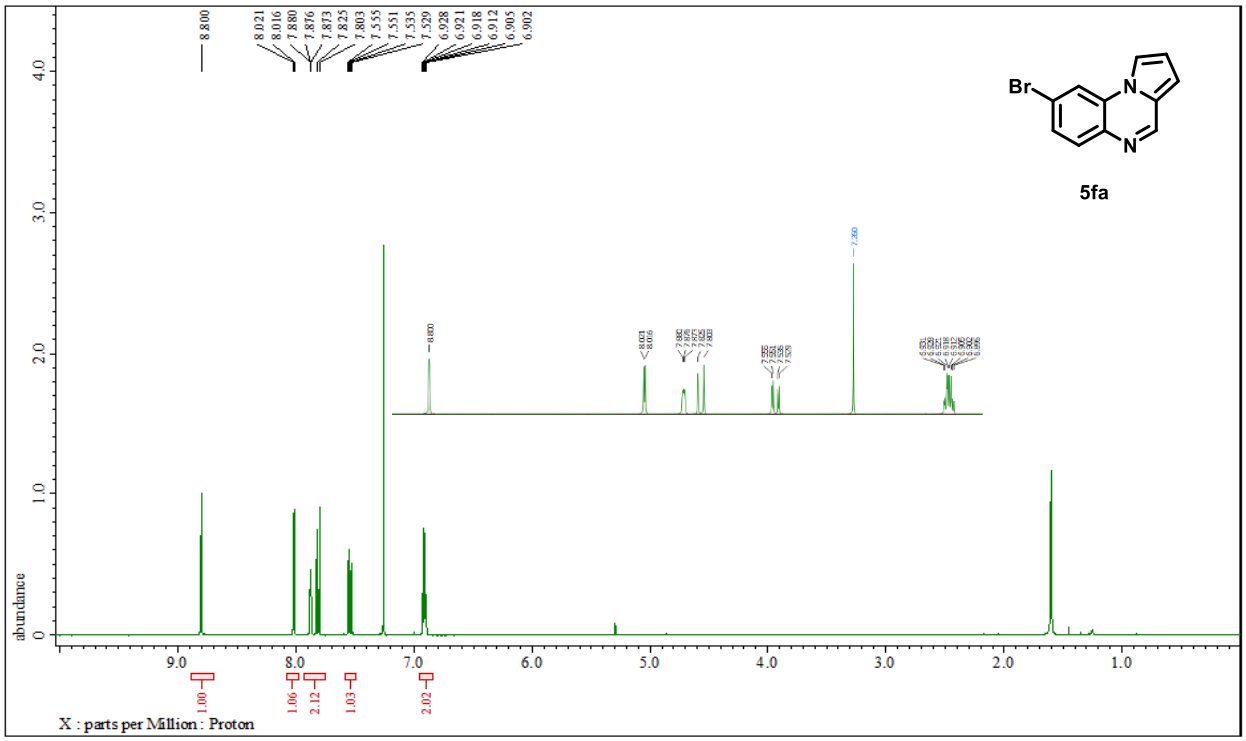
^{1}H NMR of Compound **5ea** ($CDCl_3$-*d*, 400 MHz)



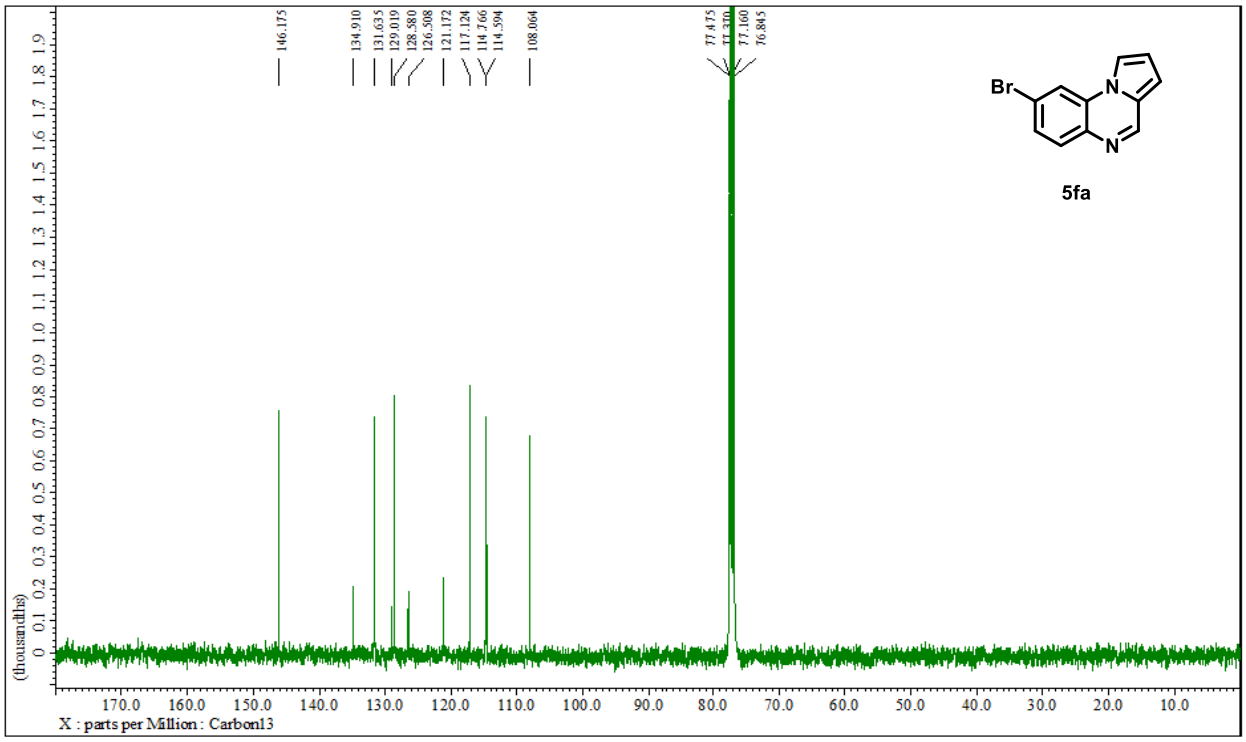
^{13}C NMR of Compound **5ea** ($CDCl_3$-*d*, 100 MHz)



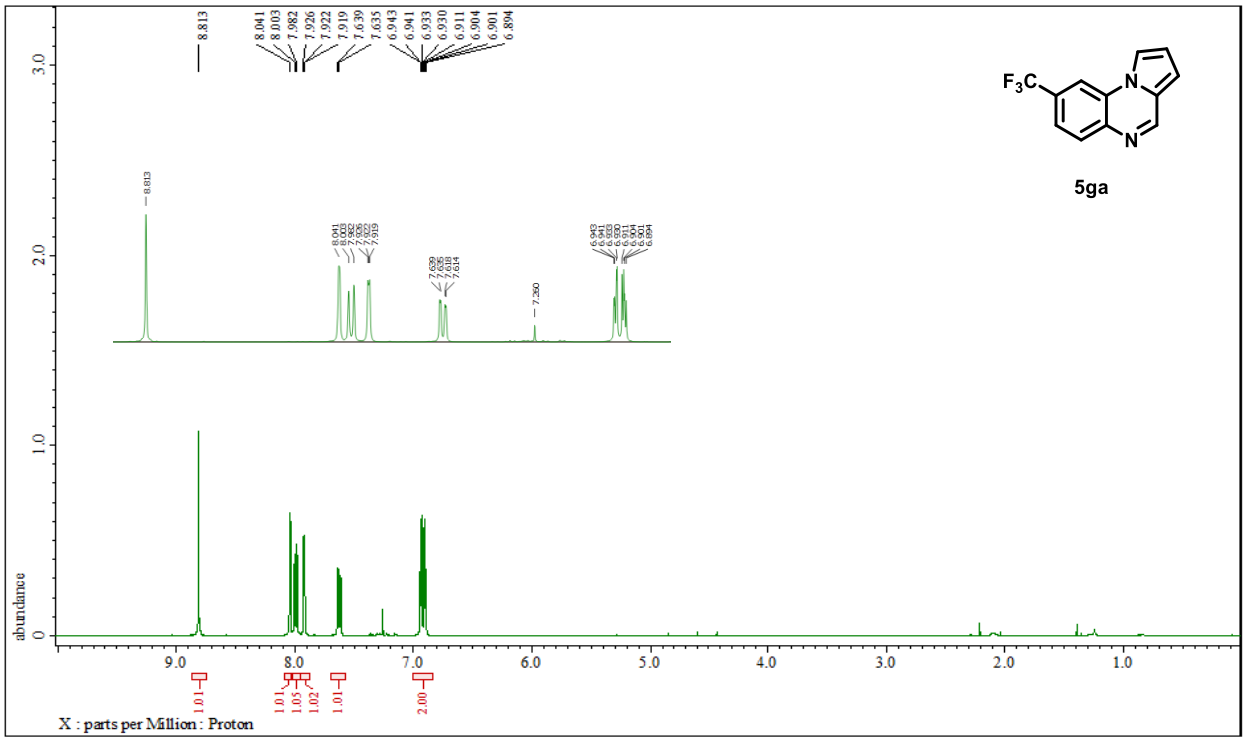
^{1}H NMR of Compound **5fa** ($CDCl_3$-*d*, 400 MHz)



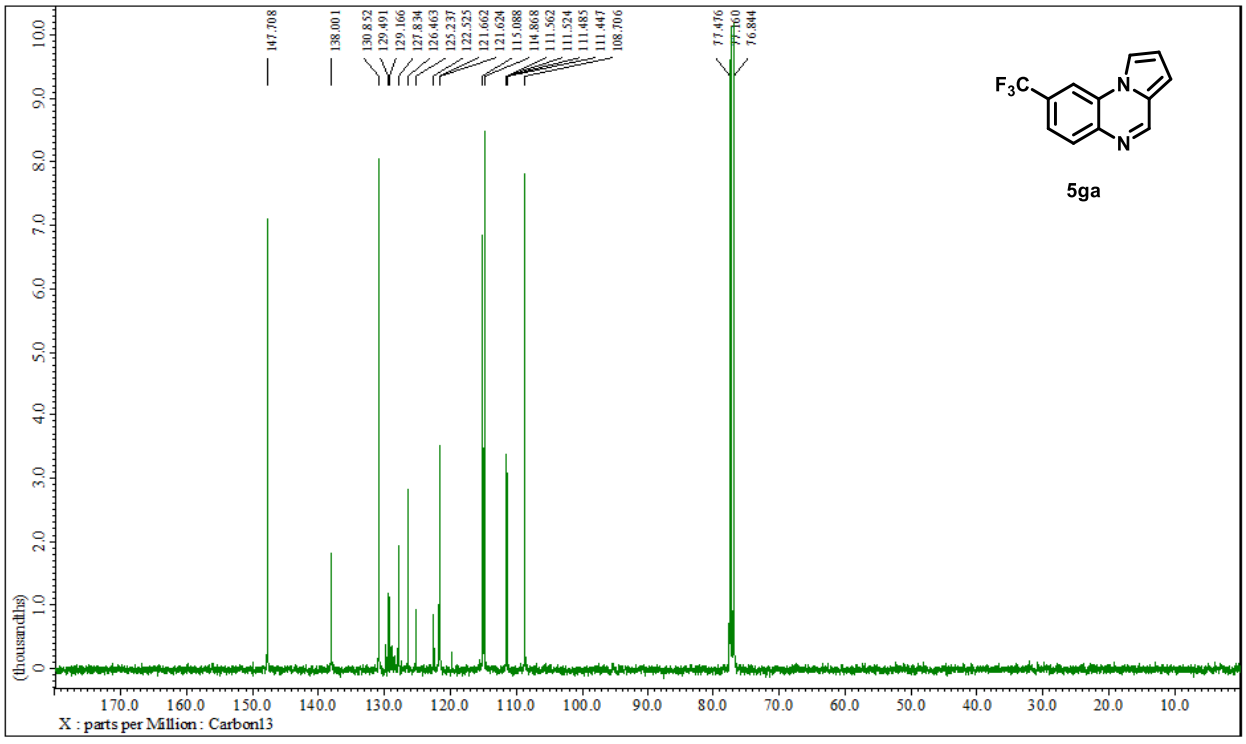
^{13}C NMR of Compound **5fa** ($CDCl_3$-*d*, 100 MHz)



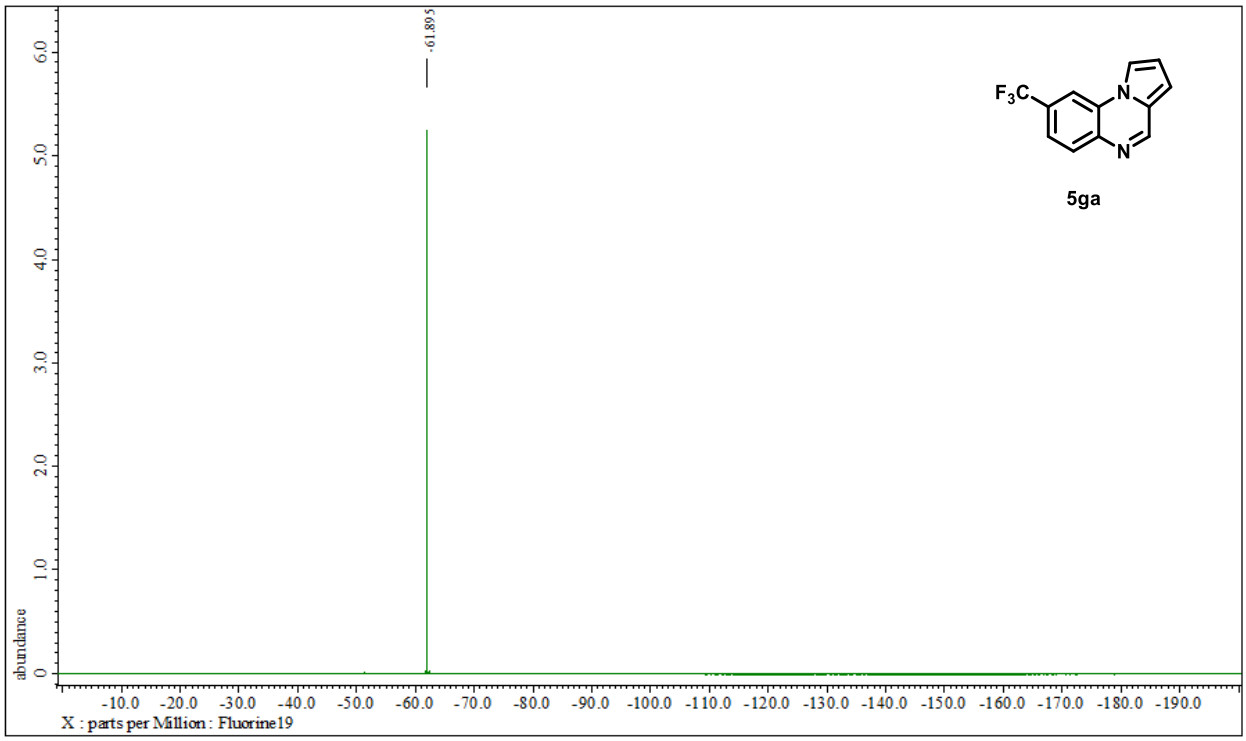
^{1}H NMR of Compound **5ga** ($CDCl_3$-*d*, 400 MHz)



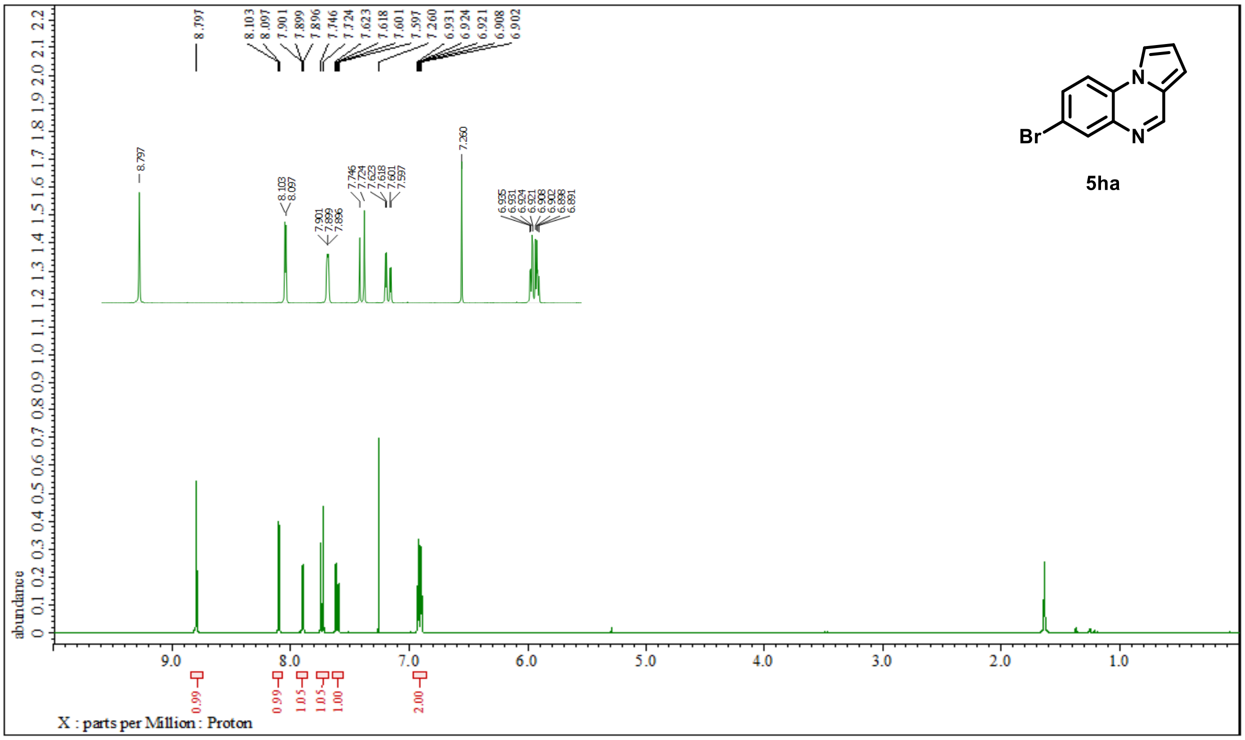
^{13}C NMR of Compound **5ga** ($CDCl_3$-*d*, 100 MHz)



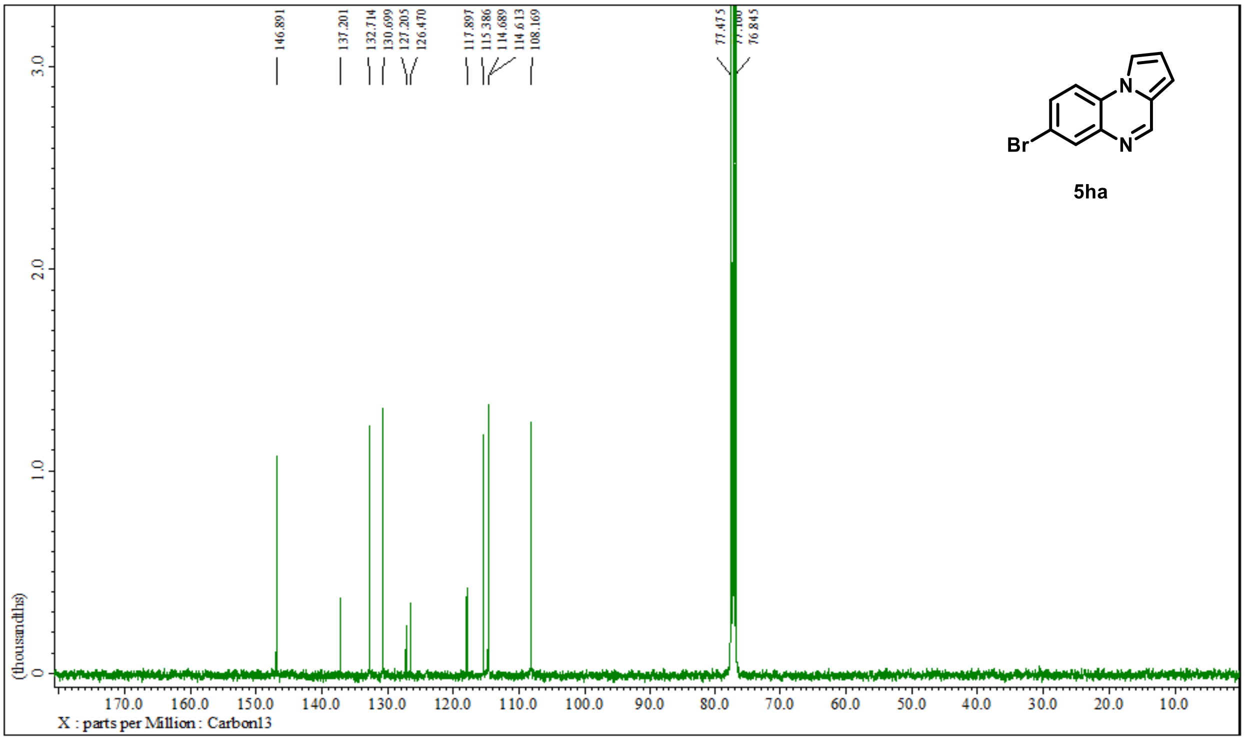
^{19}F NMR of Compound **5ga** ($CDCl_3$-*d*, 376 MHz)



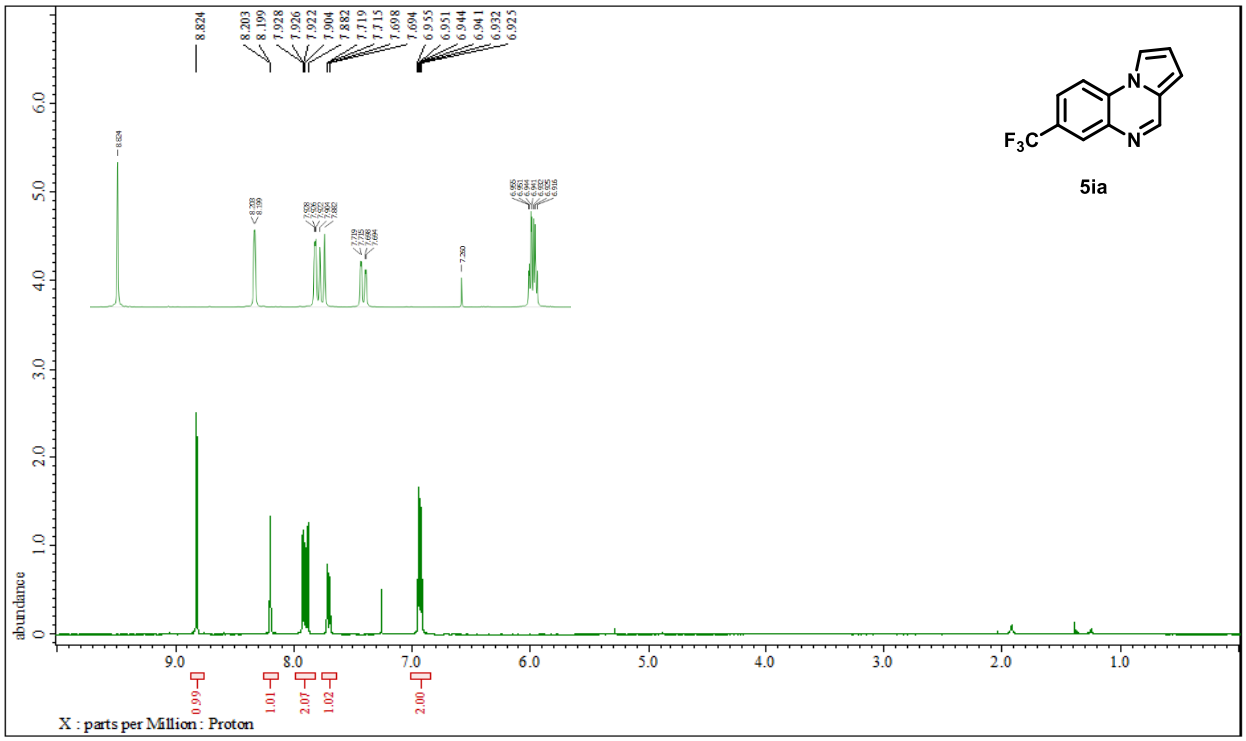
[1]H NMR of Compound **5ha** ($CDCl_3$-*d*, 400 MHz)



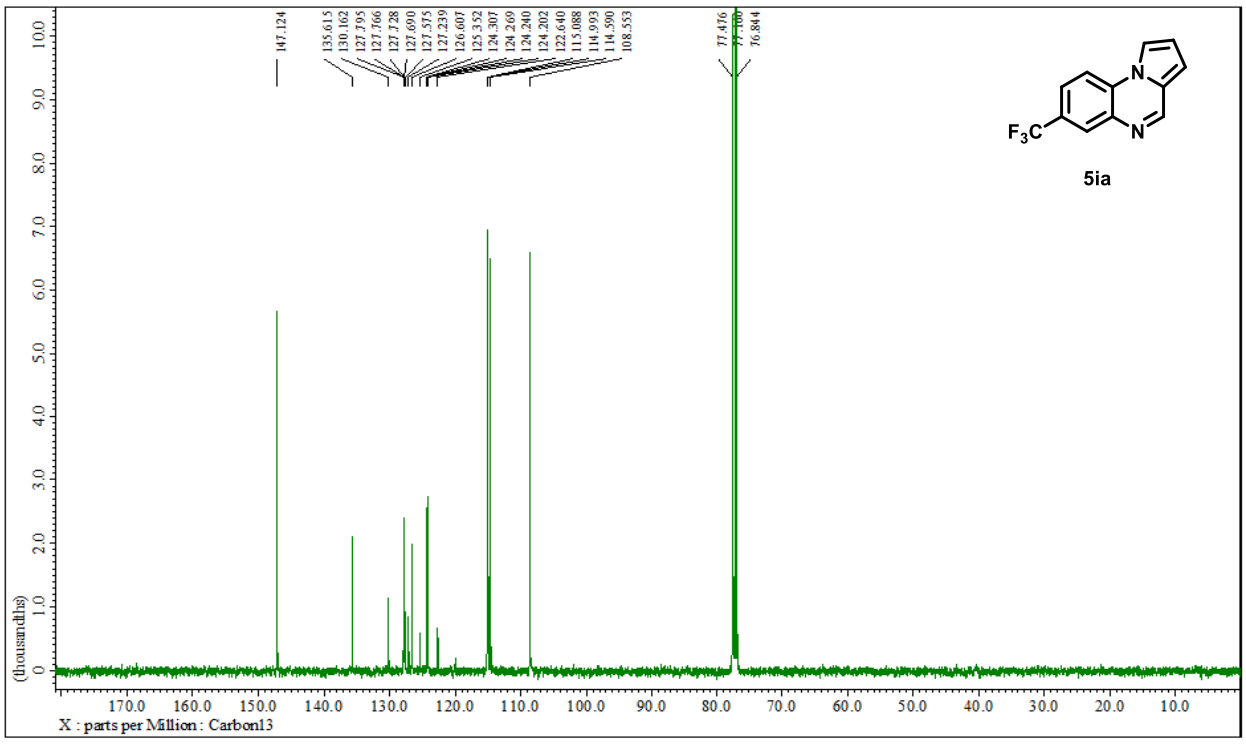
[13]C NMR of Compound **5ha** ($CDCl_3$-*d*, 100 MHz)



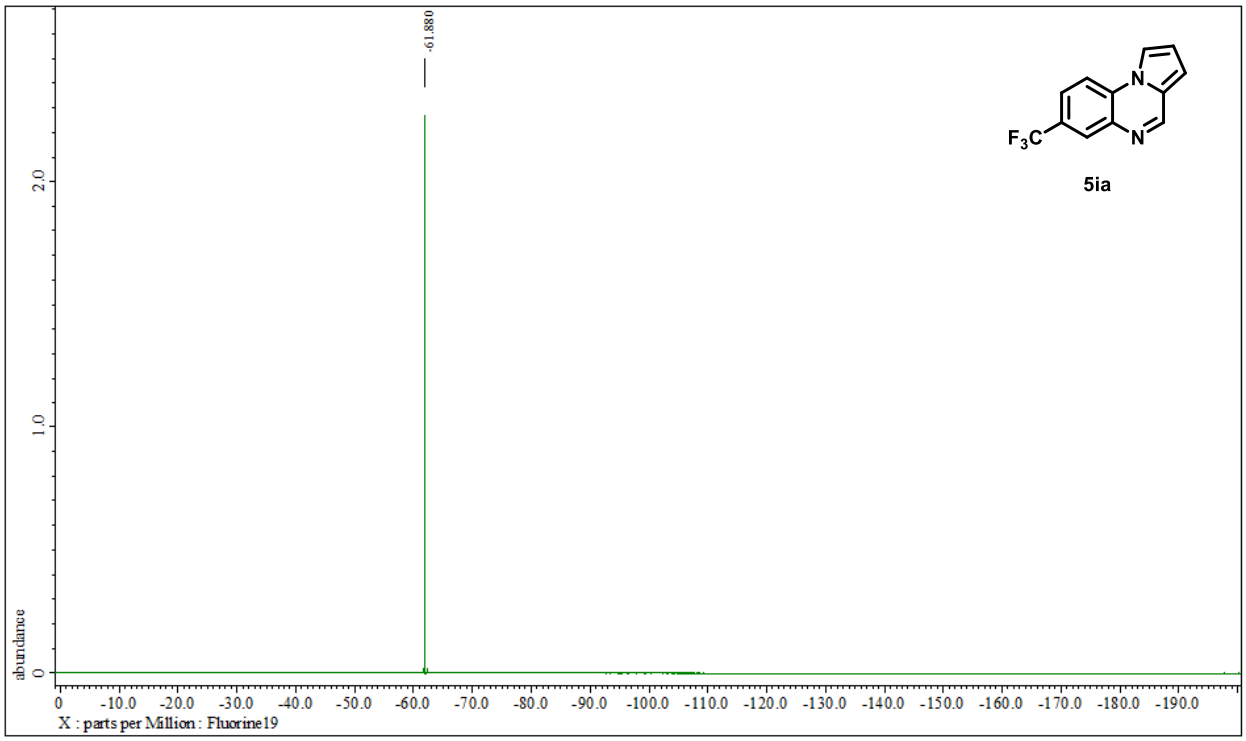
^{1}H NMR of Compound **5ia** ($CDCl_3$-*d*, 400 MHz)



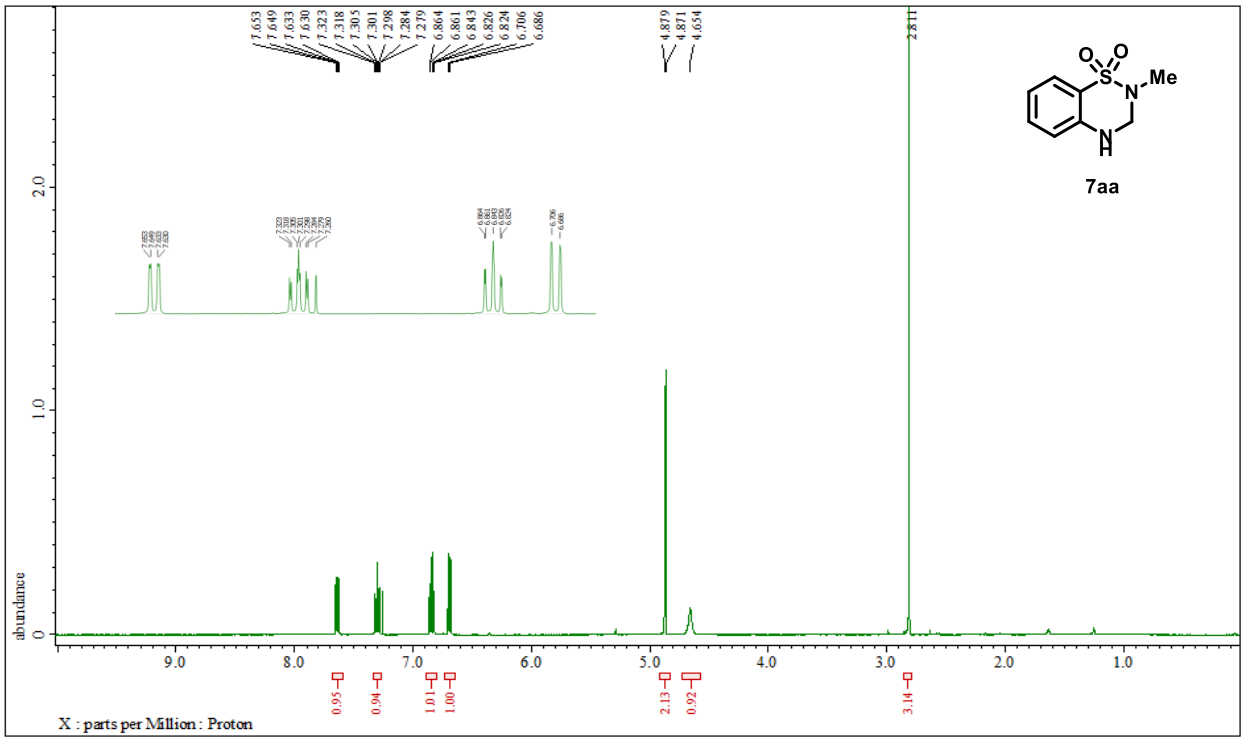
^{13}C NMR of Compound **5ia** ($CDCl_3$-*d*, 100 MHz)



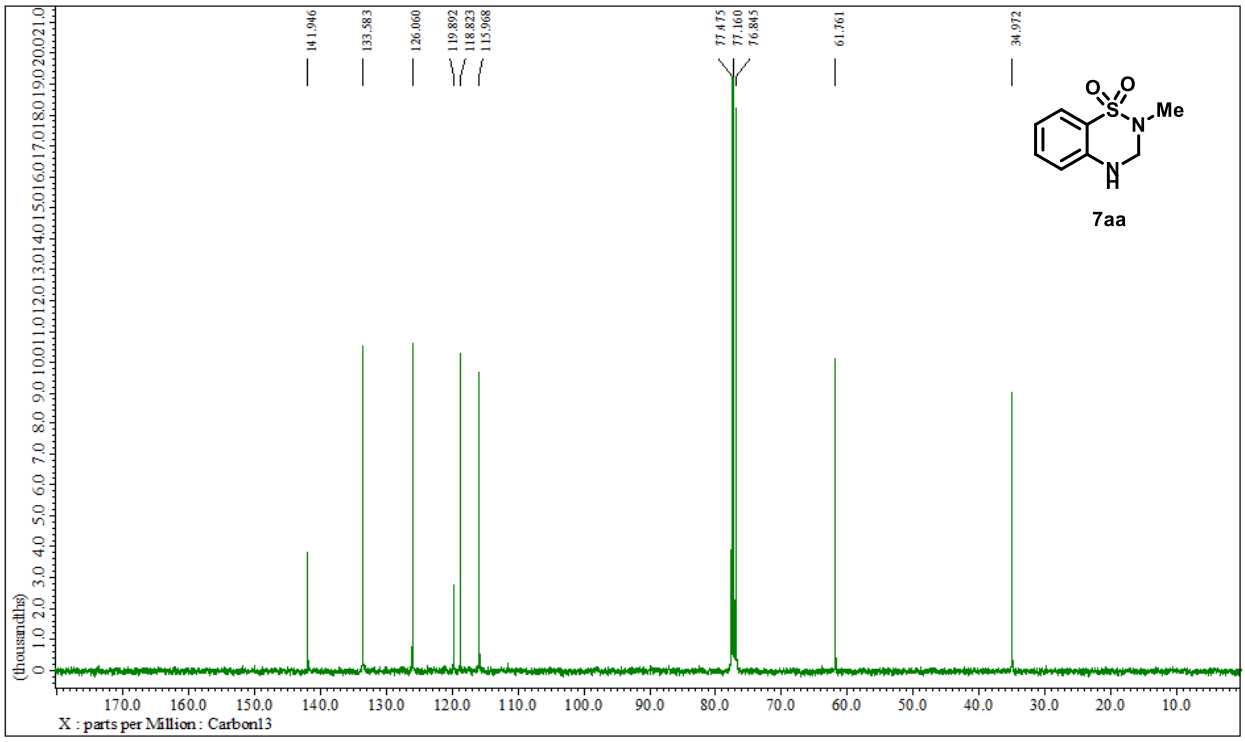
^{19}F NMR of Compound **5ia** ($CDCl_3$-*d*, 376 MHz)



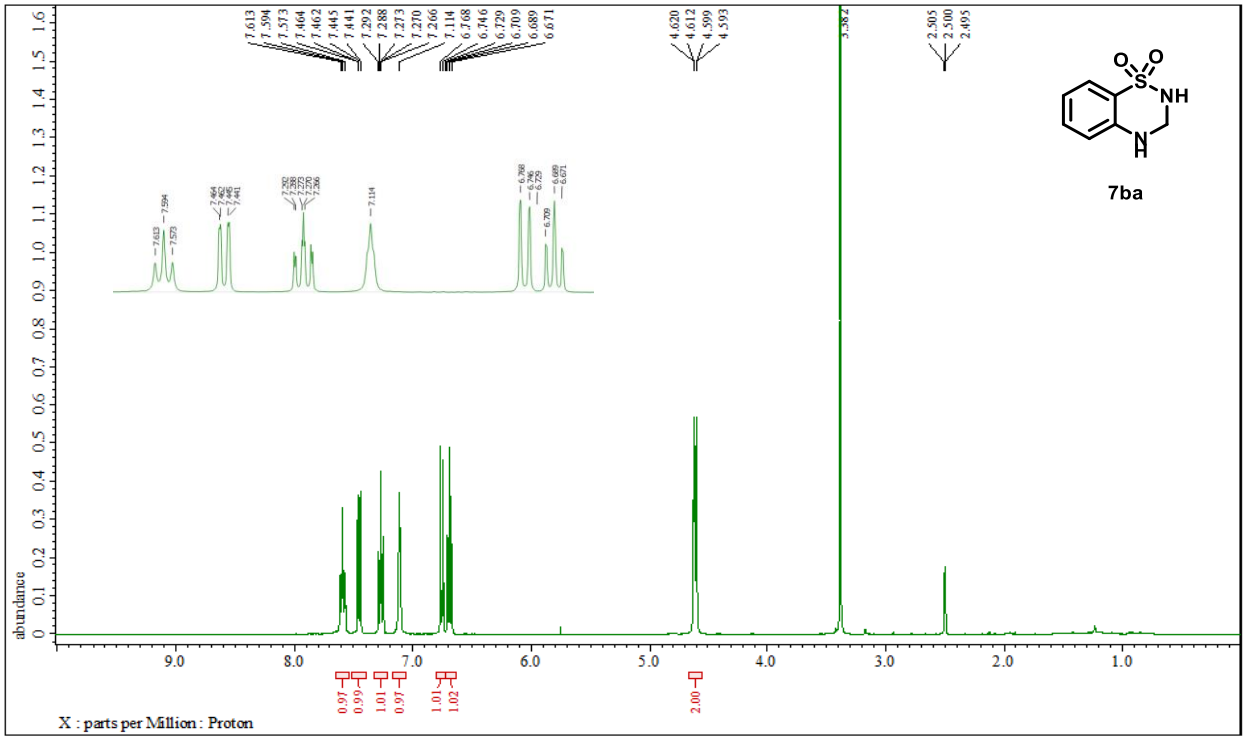
^{1}H NMR of Compound **7aa** ($CDCl_3$-*d*, 400 MHz)



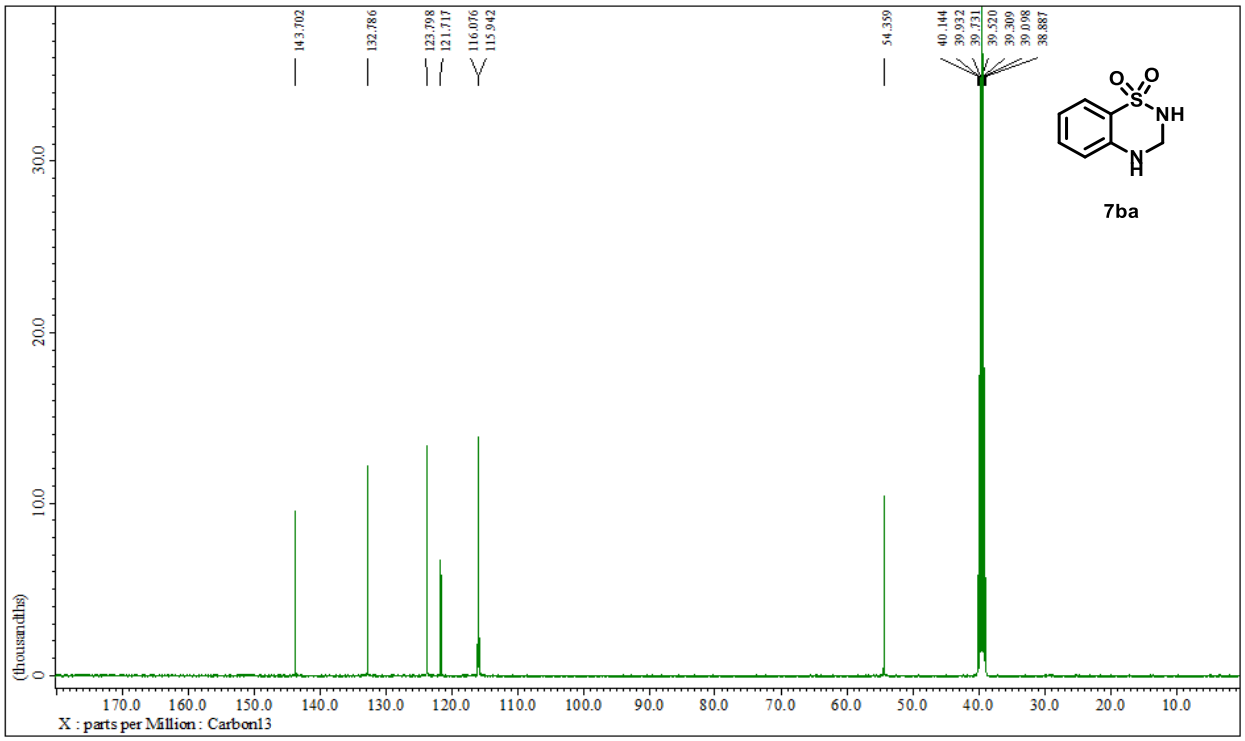
^{13}C NMR of Compound **7aa** ($CDCl_3$-*d*, 100 MHz)



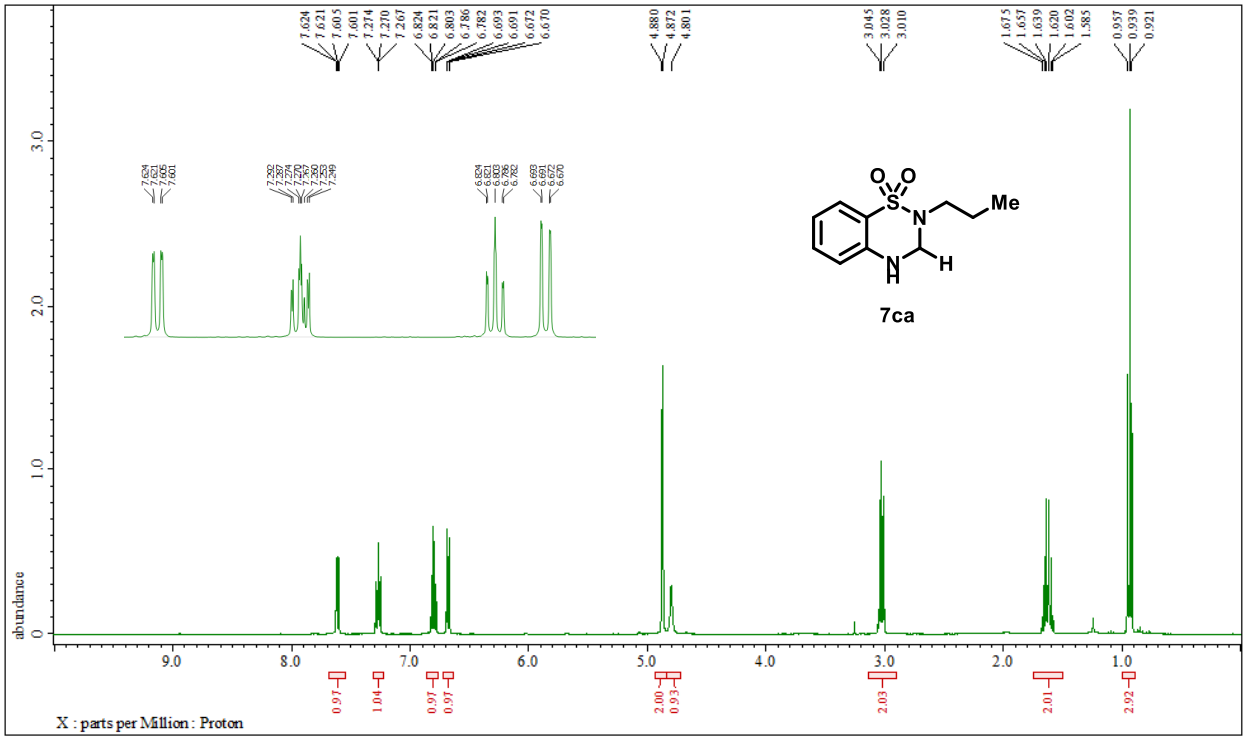
^{1}H NMR of Compound **7ba** (DMSO-d_6, 400 MHz)



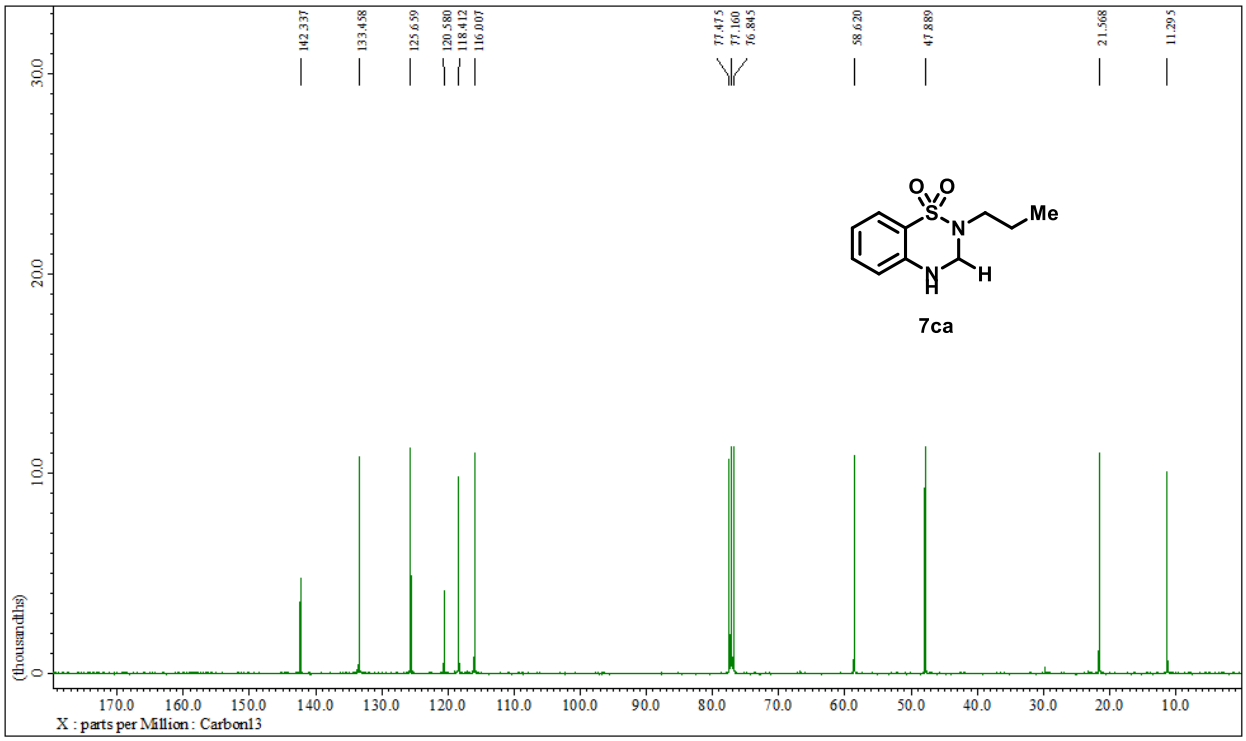
^{13}C NMR of Compound **7ba** (DMSO-d_6, 100 MHz)



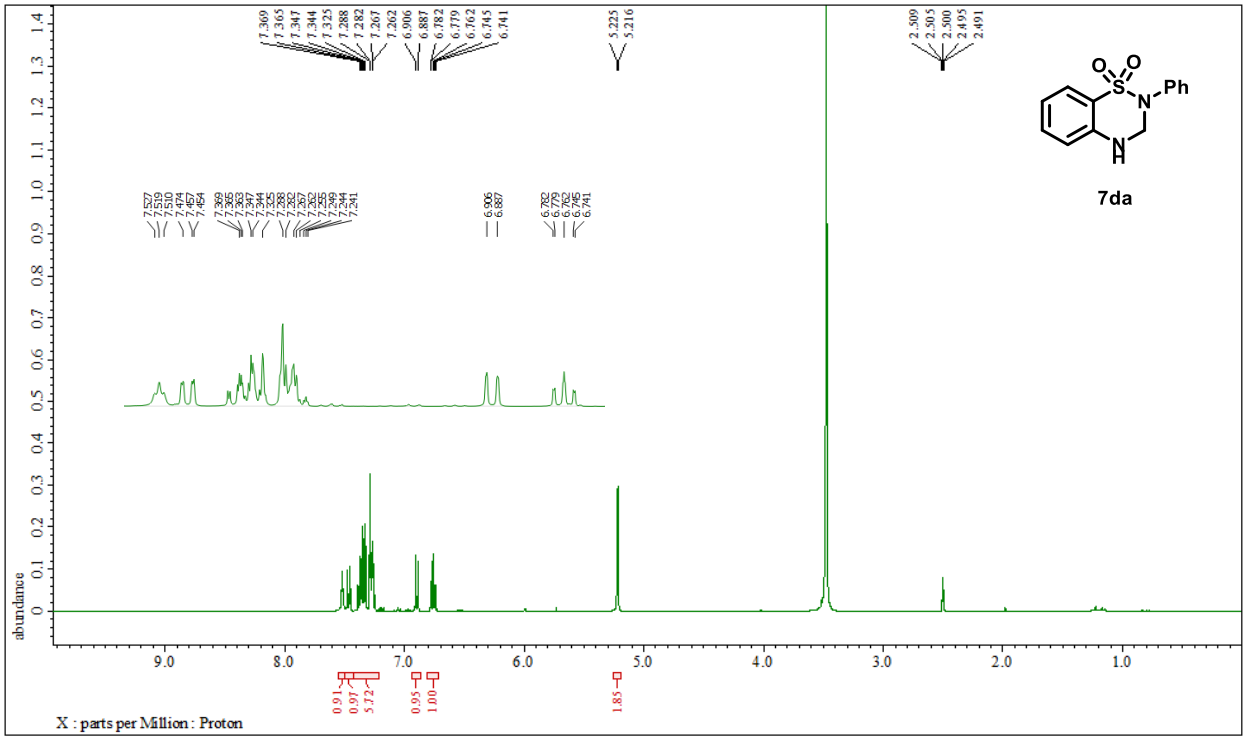
^{1}H NMR of Compound **7ca** ($CDCl_3$-*d*, 400 MHz)



^{13}C NMR of Compound **7ca** ($CDCl_3$-*d*, 100 MHz)



^{1}H NMR of Compound **7da** (DMSO-d_6, 400 MHz)



^{13}C NMR of Compound **7da** (DMSO-d_6, 100 MHz)