Supporting Information

α-Hydroxy acid as an aldehyde surrogate: Metal-free synthesis of pyrrolo[1,2-*a*]quinoxalines, quinazolinones, and other *N*-heterocycles via decarboxylative oxidative annulation reaction

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1. General Information

^{1}H NMR spectra were recorded on a Jeol RESONANCE ECZ 400S (400MHz). Chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance resulting from incomplete deuteration as the internal reference ($CDCl_3$: 7.26 ppm) or relative to TMS (δ 0.0). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, dd = doublet of doublet, td = triplet of doublet), coupling constants (Hz), number of protons. ^{13}C NMR spectra were recorded on a Jeol RESONANCE ECZ 400S (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: 77.16 ppm). High-resolution mass spectrometry was performed with on LCQ Fleet-Thermo Scientifics. All reactant or reagent was purchased from Aldrich, TCI, Alfa aesar and acros, and were directly used without further purifications. Silica gel column chromatography was performed with Silica Gel of Kieselgel ^{60} F_{254} plate (Merck).

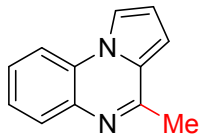
2. General Procedure for the synthesis of heterocyclic compounds

A solution of 2-(1*H*-pyrrol-1-yl)anilines (1.0 equiv.) or 2-aminobenzamides (1.0 equiv.), α-hydroxy acids (5.0 equiv.), TBHP (70% in H_2O, 4.0 equiv.) and DCE (2.0 mL) was stirred at 80 °C for particular times (see the individual substrates at the manuscript). The reaction progress was monitored by TLC. Then, 10 mL of NH_4Cl was added to the reaction mixture and extracted with EtOAc (15 mL X 3). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was then purified by flash column chromatography on silica gel by using hexanes / ethyl acetate as eluent to afford the pure product.

3. Experimental data

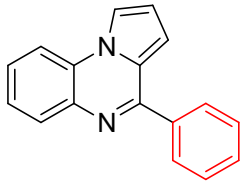
3.1 Characterization data for quinoxalines

4-methylpyrrolo[1,2-*a*]quinoxaline **3a**: [1]



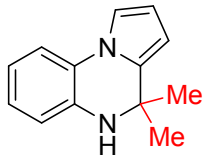
40 mg of SM afforded 35 mg of **3a**, yield 76%, Pale yellow solid. Mp: 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1H NMR (400 MHz,) δ ^{1}H NMR (400 MHz,) δ 7.97 – 7.87 (m, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.38 (m, 1H), 6.92 – 6.87 (m, 1H), 6.85 (dd, *J* = 4.7, 1.9 Hz, 1H), 2.73 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 135.9, 129.2, 127.3, 126.9, 126.2, 125.18, 114.3, 113.7, 113.5, 106.5, 22.1.

4-phenylpyrrolo[1,2-*a*]quinoxaline **3b**: [2]



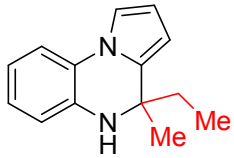
40 mg of SM afforded 34 mg of **3b**, yield 56%, Pale yellow solid. Mp: 95-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 8.03 – 7.95 (m, 3H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.43 (m, 5H), 7.00 (d, *J* = 4.0 Hz, 1H), 6.90 (dd, *J* = 4.7, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 138.4, 136.2, 130.2, 129.9, 128.7 (2C), 128.6 (2C), 127.5, 127.2, 125.4, 125.3, 114.7, 114.1, 113.7, 108.9.

4,4-dimethyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline **3c**:[2]



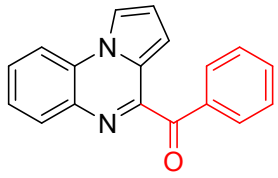
40 mg of SM afforded 21mg of **3c**, yield 42%, Pale yellow solid. Mp: 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.12 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.95 (td, *J* = 7.6, 1.3 Hz, 1H), 6.81 (td, *J* = 7.7, 1.3 Hz, 1H), 6.72 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.28 (t, *J* = 3.2 Hz, 1H), 5.98 (dd, *J* = 3.5, 1.5 Hz, 1H), 1.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 134.6, 125.3, 124.7, 119.1, 115.8, 114.6, 113.9, 109.9, 101.9, 51.5, 29.5.

4-ethyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline **3d**:[3]



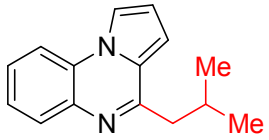
40 mg of SM afforded 20 mg of **3d**, yield 56%, brown yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz,) δ 7.27 (d, *J* = 1.0 Hz, 1H), 7.12 (dd, *J* = 2.8, 1.5 Hz, 1H), 6.93 (td, *J* = 7.7, 1.3 Hz, 1H), 6.77 (td, *J* = 7.8, 1.3 Hz, 1H), 6.70 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.28 (t, *J* = 3.2 Hz, 1H), 5.96 (dd, *J* = 3.4, 1.5 Hz, 1H), 3.75 (s, 1H), 1.81 – 1.62 (m, 2H), 1.48 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 133.3, 125.21, 124.7, 124.7, 124.6, 118.7, 115.4, 114.5, 113.8, 109.8, 103.1, 54.4, 34.5, 26.6, 8.7.

phenyl(pyrrolo[1,2-*a*]quinoxalin-4-yl)methanone **3e**: [4]



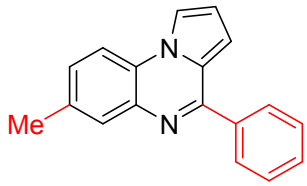
79 mg of SM afforded 88 mg of **3e**, yield 65%, yellow solid. Mp: 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.06 – 7.99 (m, 2H), 7.92 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.53 – 7.45 (m, 3H), 7.21 (dd, *J* = 4.1, 1.3 Hz, 1H), 6.96 (dd, *J* = 4.1, 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 149.9, 135.8, 134.7, 133.7, 131.1 (3C), 129.5, 128.4 (2C), 128.0, 125.6, 124.4, 115.0, 114.9, 113.9, 109.0.

4-isobutylpyrrolo[1,2-*a*]quinoxaline **3f**: [5]



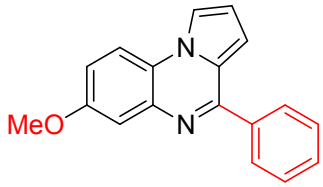
75 mg of SM afforded 42mg of **3f**, yield 41%, pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz,) δ 8.04 – 7.88 (m, 2H), 7.82 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 – 7.43 (m, 1H), 6.89 (dd, *J* = 3.9, 1.2 Hz, 1H), 6.83 (dd, *J* = 3.9, 2.7 Hz, 1H), 2.88 (d, *J* = 7.3 Hz, 2H), 2.40 (td, *J* = 13.4, 6.7 Hz, 1H), 1.02 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 135.9, 129.4, 127.2, 126.9, 126.6, 125.1, 114.2, 113.6, 113.5, 106.7, 44.6, 28.5, 22.9.

7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline **3g**: [6]



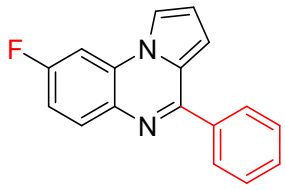
70 mg of SM afforded 51 mg of **3g**, yield 51%, brown yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.94 (dd, *J* = 2.6, 1.2 Hz, 1H), 7.85 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.56-7.50 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.96 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.85 (dd, *J* = 4.0, 2.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 138.5, 136.1, 135.1, 130.0, 129.8, 128.7 (2C), 128.6 (2C), 125.3, 125.0, 114.5, 113.8, 113.4, 108.6, 21.2.

7-methoxy-4-phenylpyrrolo[1,2-*a*]quinoxaline **3h**: [6]



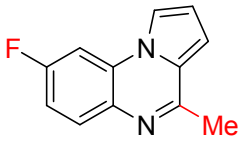
76 mg of SM afforded 68 mg of **3h**, yield 62%, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.92 (dd, *J* = 2.5, 1.2 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.56-7.51(m, 4H), 7.13 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.96 (dd, *J* = 4.1, 1.2 Hz, 1H), 6.86 (dd, *J* = 4.0, 2.7 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 154.8, 138.5, 137.4, 129.8, 128.69 (2C), 128.67 (2C), 125.2, 121.5, 116.8, 114.6, 114.3, 113.7, 111.4, 108.4, 55.8.

8-fluoro-4-phenylpyrrolo[1,2-*a*]quinoxaline **3i**: [6]



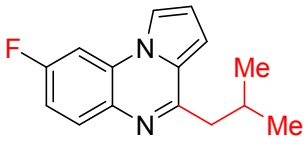
80 mg of SM afforded 72mg of **3i**, yield 61%, pale yellow solid. Mp: 152-155 °C. ^{1}H NMR (400 MHz,) δ 8.09 – 7.93 (m, 3H), 7.86-7.86 (m, 1H), 7.60 – 7.48 (m, 4H), 7.17 (tdd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 6.99 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.91 (ddd, *J* = 4.0, 2.8, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, $^{1}J_{C,F}$ = 248.3 Hz), 153.6 (d, $^{4}J_{C,F}$ = 2.8 Hz), 138.2, 132.9 (d, $^{4}J_{C,F}$ = 2.3 Hz), 132.1 (d, $^{3}J_{C,F}$ = 9.6 Hz), 129.9, 128.7 (2C), 128.6 (2C), 127.8 (d, $^{3}J_{C,F}$ = 11.3 Hz), 125.1, 114.8, 114.5, 113.2 (d, $^{2}J_{C,F}$ = 23.1 Hz), 109.0, 100.5 (d, $^{2}J_{C,F}$ = 27.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.8.

8-fluoro-4-methylpyrrolo[1,2-*a*]quinoxaline **3j**: [1]



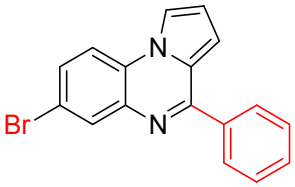
80 mg of SM afforded 61 mg of **3j**, yield 68%, pale yellow solid. Mp: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.9, 5.8 Hz, 1H), 7.76 (dd, *J* = 2.5, 1.3 Hz, 1H), 7.47 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.12 (td, *J* = 8.6, 2.7 Hz, 1H), 6.91 – 6.81 (m, 2H), 2.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, $^{1}J_{C,F}$ = 247.2 Hz), 152.8 (d, $^{4}J_{C,F}$ = 2.7 Hz), 132.5, 131.0 (d, $^{3}J_{C,F}$ = 9.6 Hz), 127.9 (d, $^{3}J_{C,F}$ = 11.6 Hz), 126.0, 114.4, 114.0, 112.9 (d, $^{2}J_{C,F}$ = 23.1 Hz), 106.8, 100.5 (d, $^{2}J_{C,F}$ = 26.9 Hz), 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.0, -110.3, -111.8.

8-fluoro-4-isobutylpyrrolo[1,2-*a*]quinoxaline **3k**:



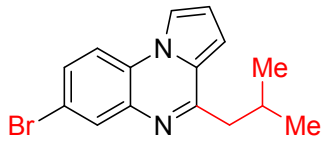
80 mg of SM afforded 51mg of **3k**, yield 46%, pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.85 (m, 1H), 7.78 (d, *J* = 1.3 Hz, 1H), 7.48 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.13 (td, *J* = 8.7, 2.7 Hz, 1H), 6.92 – 6.83 (m, 2H), 2.87 (d, *J* = 7.3 Hz, 2H), 2.38 (dp, *J* = 13.7, 6.8 Hz, 1H), 1.03 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, $^{1}J_{C,F}$ = 247.4 Hz), 156.0 (d, $^{4}J_{C,F}$ = 1.8 Hz), 131.1 (d, $^{3}J_{C,F}$ = 6.1 Hz), 127.8 (d, $^{3}J_{C,F}$ = 11.4 Hz), 126.3, 114.4, 114.0, 113.0 (d, $^{2}J_{C,F}$ = 22.5 Hz), 106.9, 100.5 (d, $^{2}J_{C,F}$ = 26.9 Hz), 44.4, 28.5, 22.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.3, -112.0, -124.0, -125.6. HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}FN_2$: 243.2973; found 243.2979

7-bromo-4-phenylpyrrolo[1,2-*a*]quinoxaline **3l**:



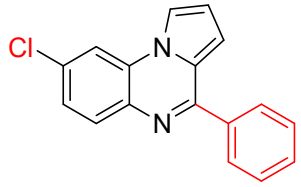
72 mg of SM afforded 64mg of **3l**, yield 65%, white solid. Mp: 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 8.19 (d, *J* = 1.6 Hz, 1H), 7.98 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.95 – 7.92 (m, 1H), 7.72 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.61 – 7.50 (m, 4H), 7.01 (d, *J* = 3.9 Hz, 1H), 6.92 – 6.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 138.1, 137.5, 132.6, 130.22, 130.20, 128.7 (4C), 126.2, 125.3, 117.9, 115.1, 115.0, 114.5, 109.5. HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{12}BrN_2$: 323.0183; found 323.0189

7-bromo-4-isobutylpyrrolo[1,2-*a*]quinoxaline **3m**:



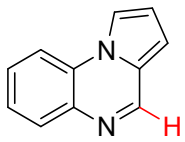
72 mg of SM afforded 43mg of **3m**, yield 47%, yellow solid. Mp: 148-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.1 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.70 – 7.63 (m, 1H), 7.53 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.90 (dd, *J* = 3.9, 0.9 Hz, 1H), 6.86 – 6.81 (m, 1H), 2.86 (d, *J* = 7.3 Hz, 2H), 2.37 (dp, *J* = 13.8, 6.8 Hz, 1H), 1.02 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 137.2, 132.0, 129.6, 126.5, 126.3, 117.6, 115.0, 114.5, 113.9, 107.2, 44.6, 28.4, 22.9. HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}BrN_2$: 303.0496; found 303.0490.

8-chloro-4-phenylpyrrolo[1,2-*a*]quinoxaline **3n**: [2]



76 mg of SM afforded 66mg of **3n**, yield 60%, yellow solid. Mp: 181-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 4H), 7.88 – 7.83 (m, 1H), 7.58 – 7.49 (m, 3H), 7.40 (ddd, *J* = 8.6, 3.4, 2.1 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.91 (dd, *J* = 3.7, 3.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 138.0, 134.7, 132.9, 131.3, 130.1, 128.71 (2C), 128.70 (2C), 127.8, 125.8, 125.3, 115.0, 114.7, 113.8, 109.5.

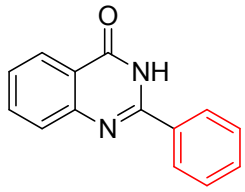
pyrrolo[1,2-*a*]quinoxaline **3o**: [7]



75 mg of SM afforded 45mg of **3o**, yield 57%, yellow solid. Mp: 135-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.95 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.50 (td, *J* = 8.0, 1.3 Hz, 1H), 7.45 – 7.40 (m, 1H), 6.91 – 6.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 135.8, 130.1, 128.0, 127.8, 126.5, 125.2, 114.2, 114.0, 113.8, 107.3.

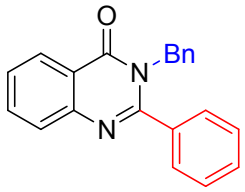
3.2 Characterization data for quinazolinones

2-phenylquinazolin-4(3*H*)-one **5a**: [8]



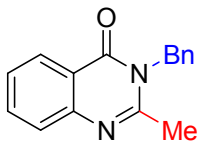
70 mg of SM afforded 96 mg of **5a**, yield 84%, white solid. Mp: 230-234 °C. ^{1}H NMR (400 MHz, DMSO d_6) δ 12.52 (s, 1H), 8.13 (t, J = 8.8 Hz, 3H), 7.81 (t, J = 7.5 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.61 – 7.44 (m, 4H); ^{13}C NMR (101 MHz, DMSO d_6) δ 162.7, 152.8, 149.2, 135.1, 133.2, 131.9, 129.1 (2C), 128.3 (2C), 127.1, 126.3, 121.5.

3-benzyl-2-phenylquinazolin-4(3*H*)-one **5b**; [9]



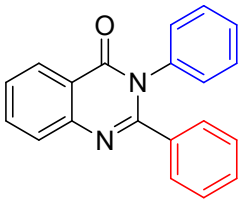
68 mg of SM afforded 64 mg of **5b**, yield 68%, white solid. Mp: 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, J = 8.7, 0.8 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.55 – 7.49 (m, 1H), 7.49 – 7.43 (m, 1H), 7.39 (dd, J = 10.3, 4.8 Hz, 2H), 7.35-7.32 (m, 2H), 7.22 – 7.16 (m, 3H), 6.95 – 6.87 (m, 2H), 5.27 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 156.5, 147.2, 136.6, 135.2, 134.6, 130.0, 128.68 (2C), 128.60 (2C), 128.0 (2C), 127.6, 127.5, 127.26, 127.20, 127.0 (2C), 120.9, 48.8.

3-benzyl-2-methylquinazolin-4(3*H*)-one **5c**: [10]



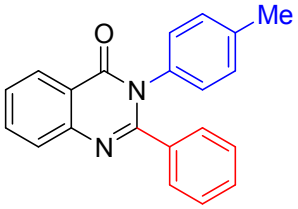
68 mg of SM afforded 50 mg of **5c**, yield 67%, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, J = 8.0, 1.5 Hz, 1H), 7.74 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.26 (m, 1H), 7.22 – 7.16 (m, 2H), 5.39 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 154.8, 147.2, 134.5, 129.0 (2C), 127.8, 127.2, 126.7, 126.69, 126.60 (2C), 120.4, 47.2, 23.4.

2,3-diphenylquinazolin-4(3*H*)-one **5d**: [10, 11]



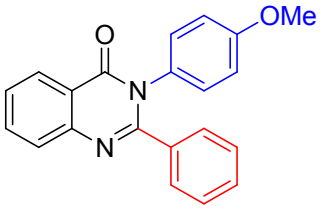
64 mg of SM afforded 68 mg of **5d**, yield 79%, white solid. Mp: 160-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.31 (m, 1H), 7.85 – 7.78 (m, 2H), 7.56 – 7.50 (m, 1H), 7.35 – 7.30 (m, 3H), 7.29-7.17 (m, 5H), 7.16 – 7.12 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 155.3, 147.5, 137.7, 135.5, 134.8, 129.4, 129.2 (2C), 129.0 (4C), 128.5, 128.0 (2C), 127.8, 127.3, 127.3, 121.0.

2-phenyl-3-(p-tolyl)quinazolin-4(3*H*)-one **5e**: [11]



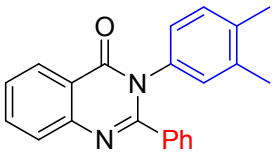
70 mg of SM afforded 67 mg of **5e**, yield 70%, white solid. Mp: 191-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.30 (m, 1H), 7.85 – 7.73 (m, 2H), 7.57 – 7.45 (m, 1H), 7.36 – 7.32 (m, 2H), 7.26 – 7.18 (m, 3H), 7.14 – 7.06 (m, 2H), 7.01 (d, J = 8.3 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 155.4, 147.5, 138.4, 135.6, 135.0, 134.7, 129.7 (2C), 129.3, 129.0 (2C), 128.8 (2C), 128.0 (2C), 127.7, 127.3, 127.2, 121.0, 21.2.

3-(4-methoxyphenyl)-2-phenylquinazolin-4(3*H*)-one **5f**: [12]



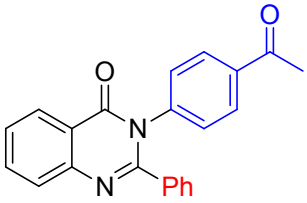
75 mg of SM afforded 73 mg of **5f**, yield 72%, white solid. Mp: 205-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.31 (m, 1H), 7.86 – 7.77 (m, 2H), 7.56 – 7.49 (m, 1H), 7.33 (dd, J = 7.7, 1.7 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.08 – 7.02 (m, 2H), 6.80 (dd, J = 6.8, 2.0 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 159.2, 155.6, 147.4, 135.5, 130.3, 130.1 (2C), 129.3, 129.0 (2C), 128.4, 128.1 (2C), 127.7, 127.3, 121.0, 114.3 (2C), 55.4.

3-(3,4-dimethylphenyl)-2-phenylquinazolin-4(3*H*)-one **5g**:



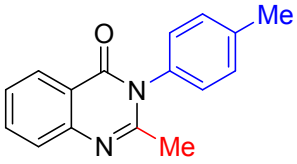
70 mg of SM afforded 65 mg of **5g**, yield 69%, champagne pink solid. Mp: 209-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.31 (m, 1H), 7.84 – 7.77 (m, 2H), 7.51 (ddd, *J* = 8.1, 6.0, 2.3 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.28 – 7.18 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.82 (dd, *J* = 7.9, 2.2 Hz, 1H), 2.18 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 155.5, 147.5, 137.5, 137.1, 135.7, 135.1, 134.7, 130.2, 129.9, 129.2, 129.0 (2C), 128.0 (2C), 127.7, 127.3, 127.2, 126.2, 121.0, 19.8, 19.6. HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{19}N_2O$: 327.1497; found 327.1517

3-(4-acetylphenyl)-2-phenylquinazolin-4(3*H*)-one **5h**: [13]



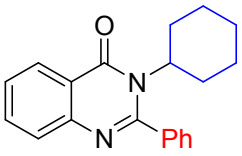
40 mg of SM afforded 36 mg of **5h**, yield 68%, white solid. Mp: 220-223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.82 (d, *J* = 3.6 Hz, 2H), 7.54 (dt, *J* = 8.1, 4.1 Hz, 1H), 7.33 (d, *J* = 4.6 Hz, 1H), 7.29 – 7.16 (m, 6H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 162.1, 154.5, 147.4, 141.9, 136.6, 135.1, 129.7, 129.5 (2C), 129.08 (2C), 129.02 (2C), 128.3 (2C), 127.9, 127.6, 127.3, 120.8, 26.7.

2-methyl-3-(p-tolyl)quinazolin-4(3*H*)-one **5i**: [14]



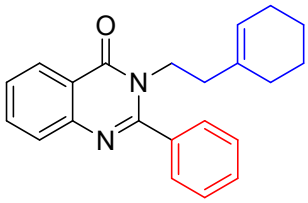
68 mg of SM afforded 61mg of **5i**, yield 81%, white solid. Mp: 153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.74 (ddd, *J* = 8.6, 7.1, 1.5 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.07 (m, 2H), 2.43 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 154.6, 147.4, 139.4, 135.1, 134.6, 130.7 (2C), 127.7 (2C), 127.1, 126.7, 126.6, 120.8, 24.4, 21.3.

3-cyclohexyl-2-phenylquinazolin-4(3*H*)-one **5j**: [15]



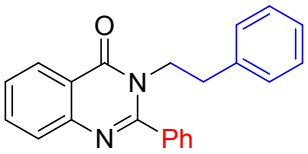
80 mg of SM afforded 72 mg of **5j**, yield 65%, pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.26 (m, 1H), 7.71 (dd, *J* = 4.2, 1.6 Hz, 2H), 7.55 – 7.45 (m, 6H), 3.88-3.82 (m, 1H), 2.81 – 2.65 (m, 2H), 1.72 (dd, *J* = 29.4, 12.4 Hz, 4H), 1.52 (d, *J* = 12.4 Hz, 1H), 1.25 – 1.17 (m, 1H), 1.00-0.90 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 157.0, 146.7, 136.4, 134.2, 129.8, 128.9 (2C), 127.2 (2C), 127.1, 127.0, 126.6, 122.2, 62.7, 28.9, 26.3, 25.0.

3-(2-(cyclohex-1-en-1-yl)ethyl)-2-phenylquinazolin-4(3*H*)-one **5k**:



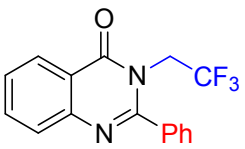
75 mg of SM afforded 77 mg of **5k**, yield 77%, white solid. Mp: 128-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 4.7, 4.0 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.57 – 7.48 (m, 6H), 5.20 (s, 1H), 4.12 – 3.99 (m, 2H), 2.22 – 2.11 (m, 2H), 1.84-1.78 (m, 2H), 1.69-1.65 (m, 2H), 1.52 – 1.40 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 156.3, 147.1, 135.5, 134.3, 133.8, 129.9, 128.8 (2C), 128.0 (2C), 127.5, 127.0, 126.8, 124.1, 121.0, 44.9, 37.0, 27.9, 25.2, 22.8, 22.1. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{22}H_{22}N_2ONa$: 353.1629; found: 353.1652

3-phenethyl-2-phenylquinazolin-4(3*H*)-one **5l**: [16]



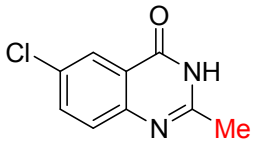
72 mg of SM afforded 68 mg of **5l**, yield 70%, white solid. Mp: 186-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.70 (m, 2H), 7.61 – 7.43 (m, 4H), 7.43 – 7.34 (m, 2H), 7.19-7.15 (m, 3H), 6.88-6.85 (m, 2H), 4.24 – 4.12 (m, 2H), 2.98 – 2.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 156.2, 147.2, 137.8, 135.4, 134.5, 129.9, 128.8 (4C), 128.6 (2C), 127.8 (2C), 127.6, 127.1, 126.8, 126.7, 121.0, 47.6, 34.7.

2-phenyl-3-(2,2,2-trifluoroethyl)quinazolin-4(3*H*)-one **5m**: [17]



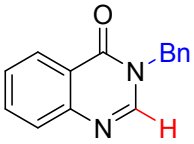
70 mg of SM afforded 68 mg of **5m**, yield 70%, pale yellow solid. Mp: 148-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.29 (m, 1H), 7.89 – 7.69 (m, 2H), 7.57 – 7.49 (m, 6H), 4.82 (q, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 155.2, 146.7, 135.3, 134.4, 130.4, 130.2, 129.1 (2C), 128.5, 128.1 (2C), 127.85, 127.83, 127.3, 124.6, 121.8, 120.3, 45.26 (q, *J* = 35.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.3.

6-chloro-2-methylquinazolin-4(3*H*)-one **5n**: [18]



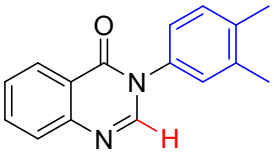
70 mg of SM afforded 25 mg of **5n**, yield 32%, white solid. Mp: 246-250 °C. ^{1}H NMR (400 MHz, DMSO d_6) δ 12.34 (s, 1H), 7.95 (d, J = 2.5 Hz, 1H), 7.74 (dd, J = 8.7, 2.5 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, DMSO d_6) δ 161.2, 155.4, 148.2, 134.8, 130.5, 129.3, 125.1, 122.4, 21.9.

3-benzylquinazolin-4(3*H*)-one **5o**:[19]



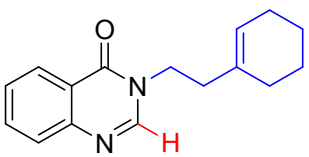
30 mg of SM afforded 21 mg of **5o**, yield 67%, pale pink solid. Mp: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (ddd, J = 6.8, 3.5, 2.8 Hz, 1H), 8.10 (s, 1H), 7.77 – 7.66 (m, 2H), 7.53 – 7.46 (m, 1H), 7.38 – 7.26 (m, 5H), 5.19 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 148.0, 146.4, 135.8, 134.4, 129.1 (2C), 128.4, 128.1 (2C), 127.5, 127.4, 126.9, 126.6, 122.2.

3-(3,4-dimethylphenyl)quinazolin-4(3*H*)-one **5p**: [19]



50 mg of SM afforded 27 mg of **5p**, yield 52%, white solid. Mp: 132-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (ddd, J = 8.0, 1.5, 0.6 Hz, 1H), 8.10 (s, 1H), 7.81 – 7.72 (m, 2H), 7.53 (ddd, J = 8.2, 6.7, 1.7 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 2.3 Hz, 1H), 7.12 (dd, J = 7.9, 2.4 Hz, 1H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 147.9, 146.4, 138.3, 138.0, 135.2, 134.5, 130.7, 128.0, 127.6, 127.5, 127.2, 124.2, 122.5, 19.9, 19.6.

3-(2-(cyclohex-1-en-1-yl)ethyl)quinazolin-4(3*H*)-one **5q**: [19]

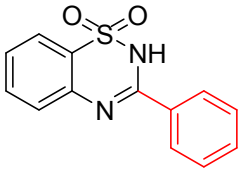


50 mg of SM afforded 29 mg of **5q**, yield 56%, white solid. Mp: 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.27 (m, 1H), 7.92 (s, 1H), 7.78 – 7.71 (m, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.48 (dd, J = 11.4, 4.4 Hz, 1H), 5.36

(s, 1H), 4.05 (t, J = 7.0 Hz, 2H), 2.38 (t, J = 7.0 Hz, 2H), 2.03 – 1.96 (m, 2H), 1.90 (d, J = 2.1 Hz, 2H), 1.65-1.60 (m, 2H), 1.57 – 1.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 148.1, 146.7, 134.1, 133.2, 127.4, 127.2, 126.7, 125.3, 122.1, 45.5, 37.4, 28.3, 25.2, 22.8, 22.2.

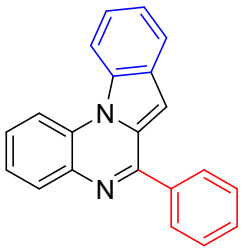
3.3 Characterization data for other heterocycles

3-phenyl-2*H*-benzo[*e*][1,2,4]thiadiazine 1,1-dioxide **6**: [20]



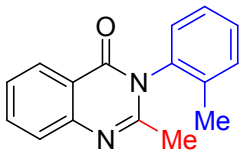
70 mg of SM afforded 38 mg of **6**, yield 37%, white solid. Mp: 310-313 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.00 (dd, J = 5.3, 3.3 Hz, 2H), 7.91 – 7.87 (m, 1H), 7.55 – 7.47 (m, 2H), 7.46-7.41 (m, 3H), 7.33 (ddd, J = 7.1, 4.3, 1.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO d_6) δ 155.4, 135.9, 133.7, 133.4, 132.2, 129.4 (2C), 128.7 (2C), 127.3, 123.8, 121.9, 118.9.

6-phenylindolo[1,2-*a*]quinoxaline **7**: [2, 6]



70 mg of SM afforded 30 mg of **7**, yield 31%, white solid. Mp: 165-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 13.8, 5.1 Hz, 2H), 8.08 (dd, J = 7.9, 1.4 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.64 – 7.51 (m, 5H), 7.44 (ddd, J = 7.1, 4.0, 1.8 Hz, 2H), 7.24 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 138.3, 136.3, 133.1, 130.6, 130.3, 130.1, 129.29, 129.21, 128.76 (2C), 128.71 (2C), 128.44, 124.45, 124.2, 122.8, 122.7, 114.7, 114.6, 102.5.

2-methyl-3-(*o*-tolyl)quinazolin-4(3*H*)-one **8**: [11, 12, 19]



70 mg of SM afforded 48 mg of **8**, yield 63%, white solid. Mp: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.0 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.47 (dd, J = 12.1, 4.2 Hz, 1H), 7.41 – 7.31 (m,

3H), 7.18 – 7.12 (m, 1H), 2.17 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 154.4, 147.7, 136.9, 135.4, 134.69, 131.64, 129.6, 128.0, 127.7, 127.2, 126.8, 126.7, 120.8, 24.0, 17.5.

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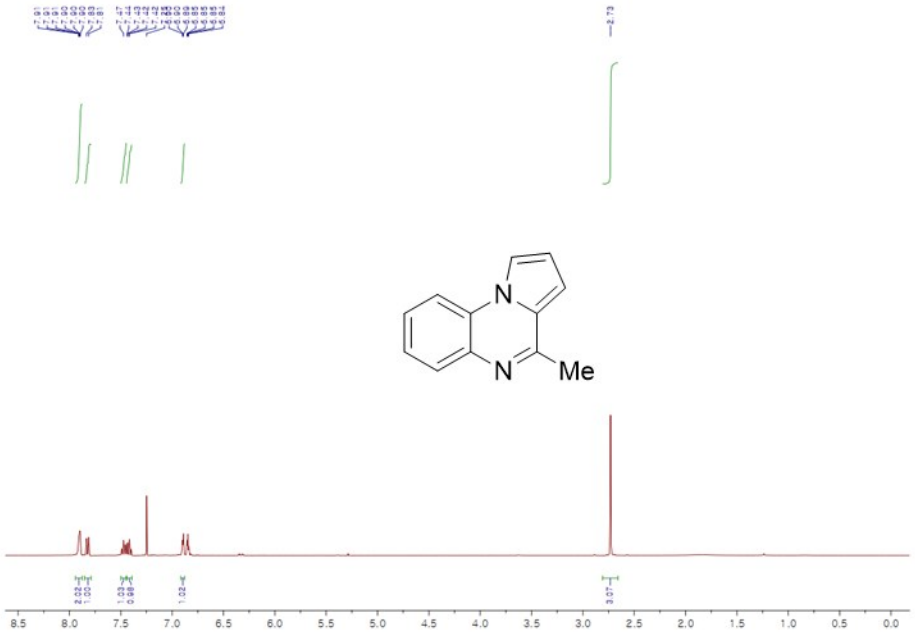
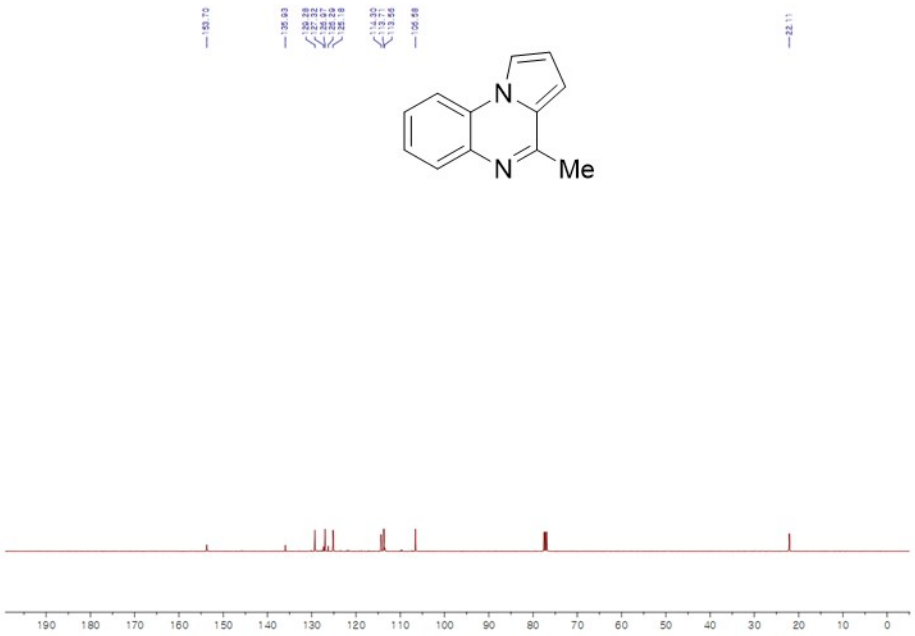
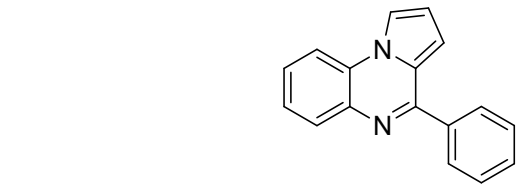
5. Copies of ^{1}H, ^{13}C, ^{19}F NMR Spectral data

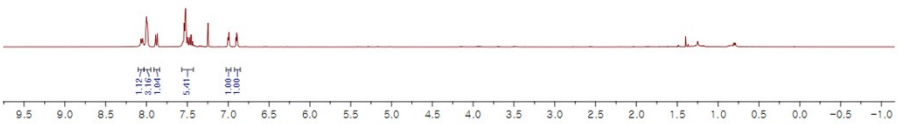
^{1}H & ^{13}C NMR of 4-methylpyrrolo[1,2-*a*]quinoxaline **3a**:

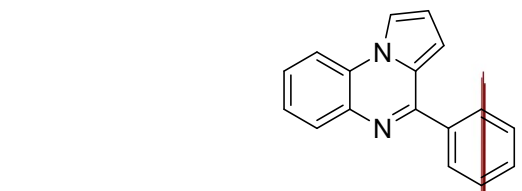


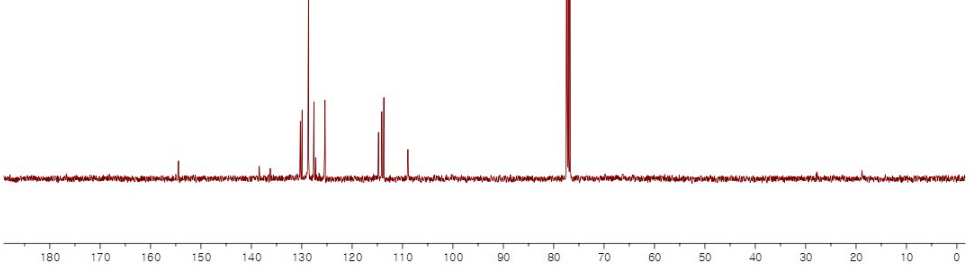


^{1}H & ^{13}C NMR of 4-phenylpyrrolo[1,2-*a*]quinoxaline **3b**

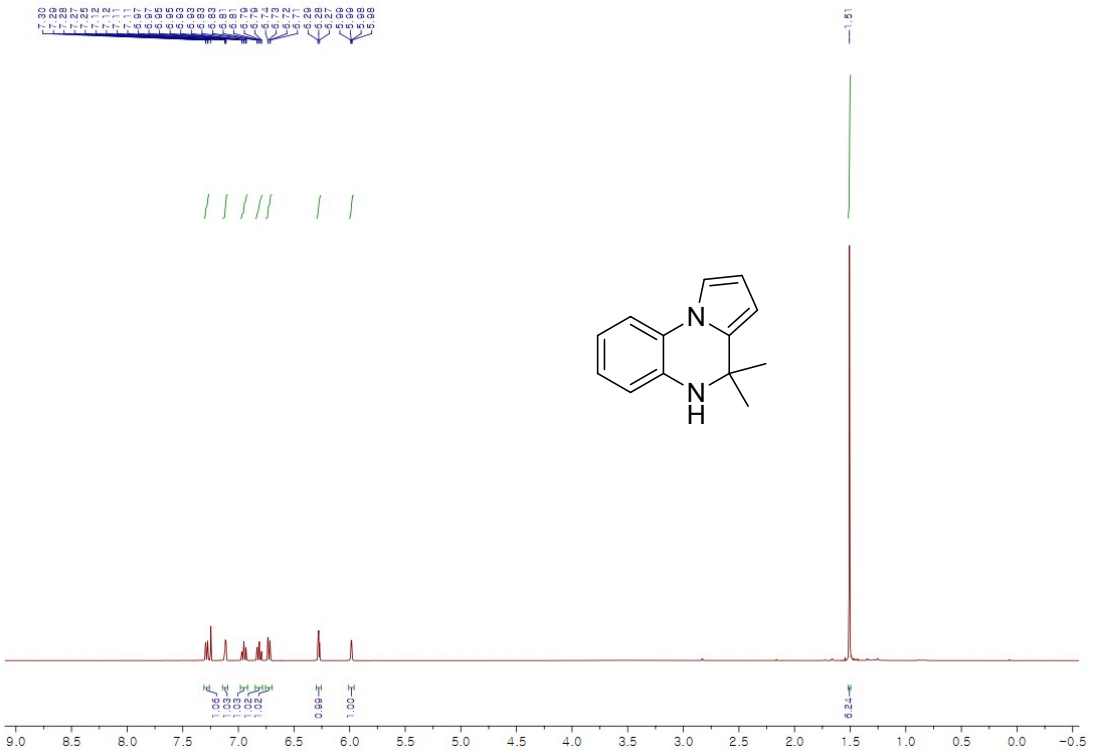


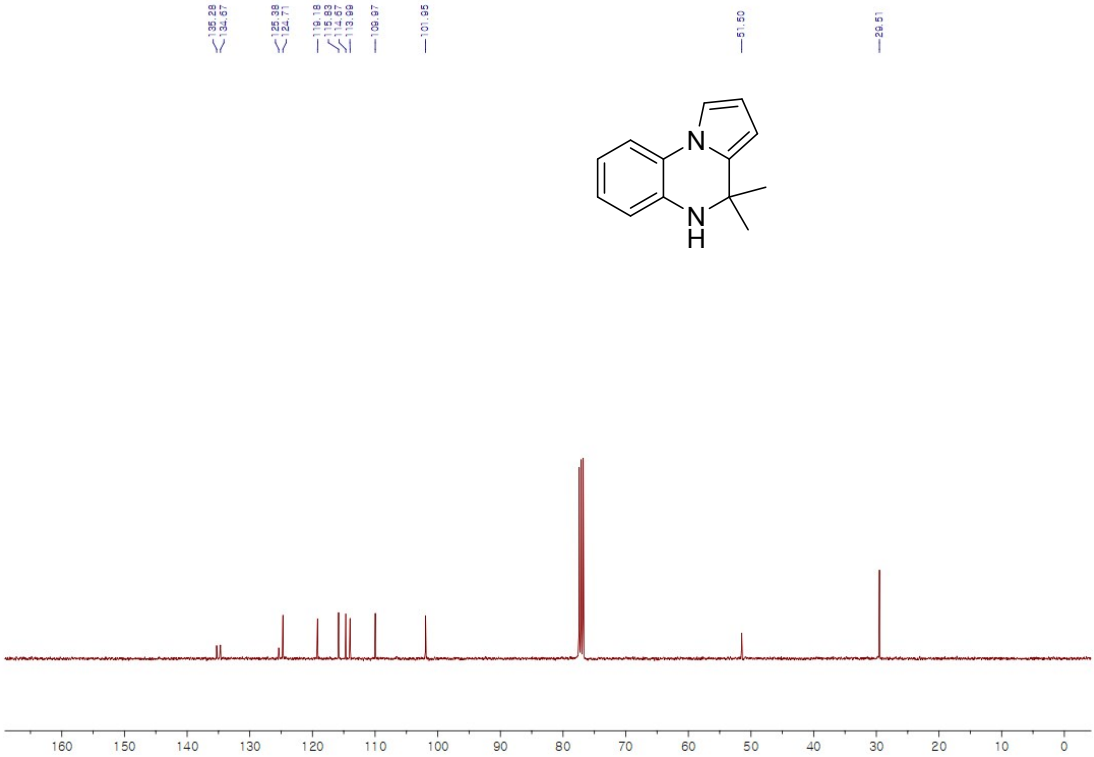




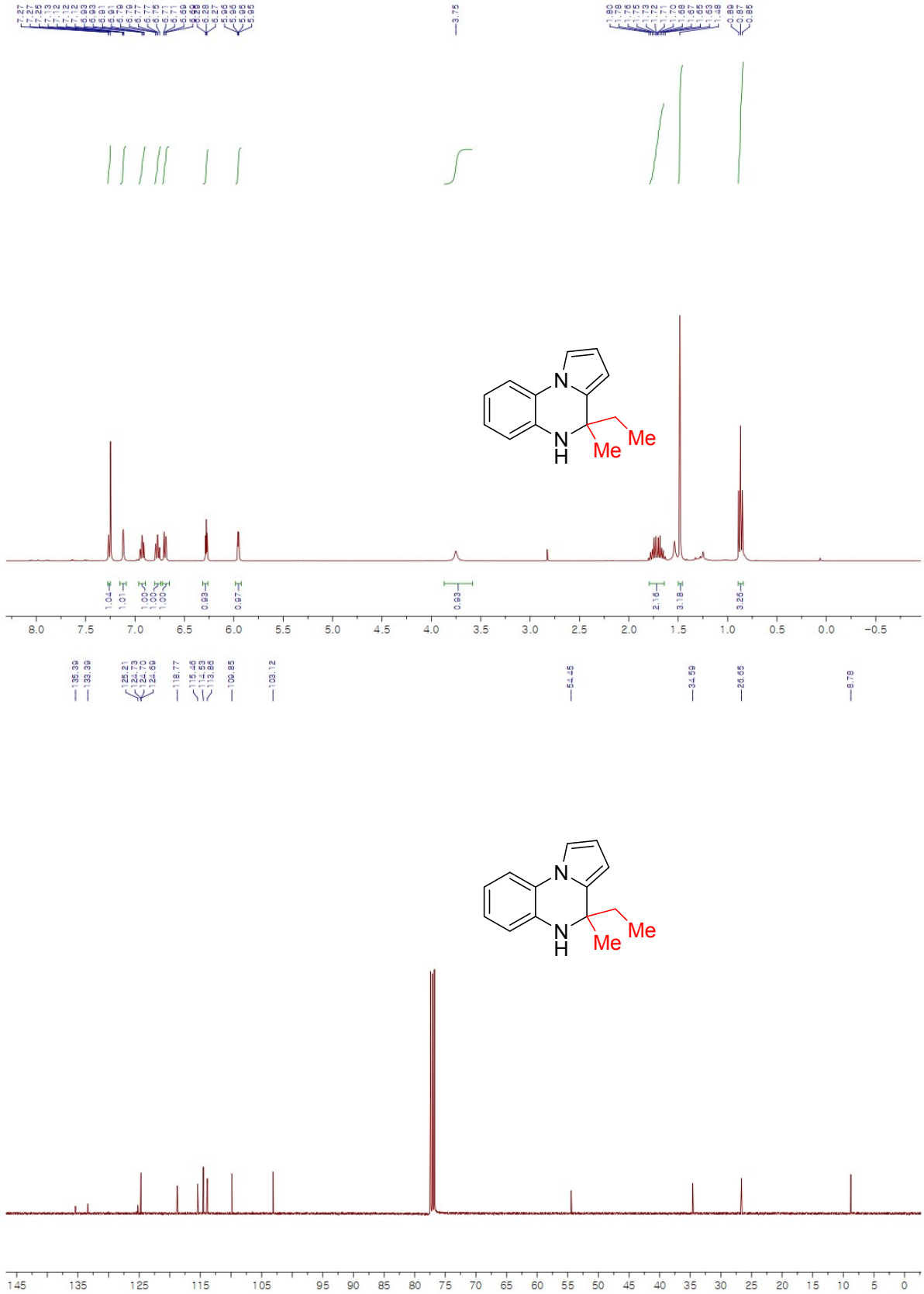


^{1}H & ^{13}C NMR of 4,4-dimethyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline **3c**

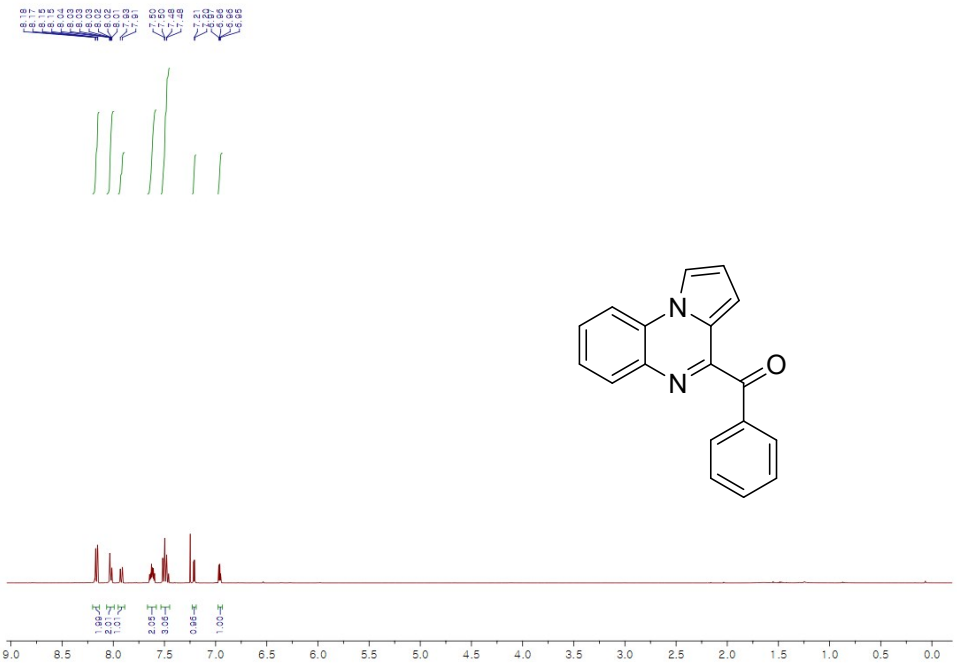


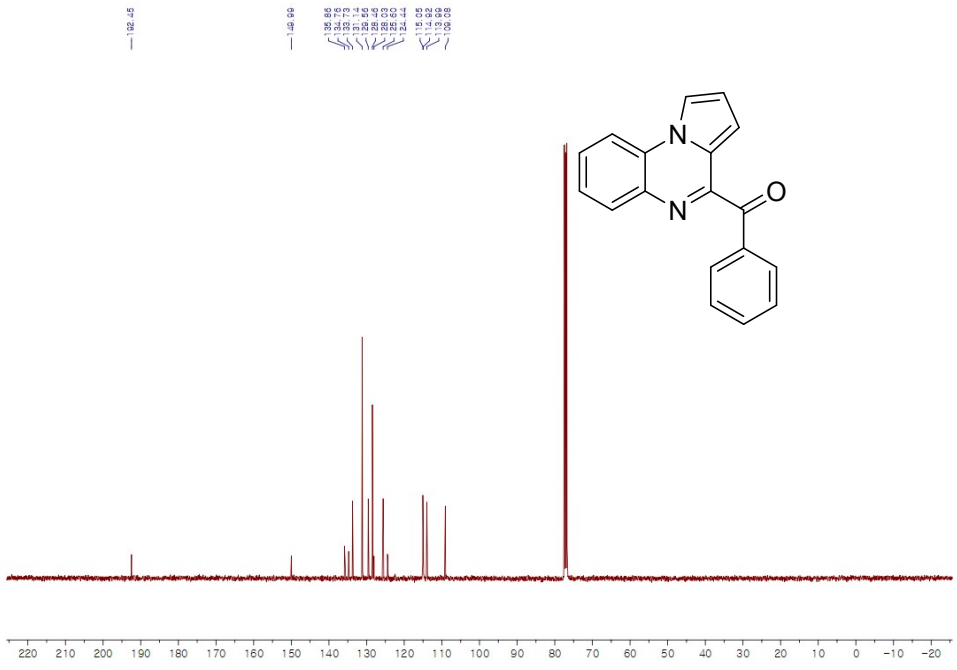


^{1}H & ^{13}C NMR of 4-ethyl-4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline **3d**

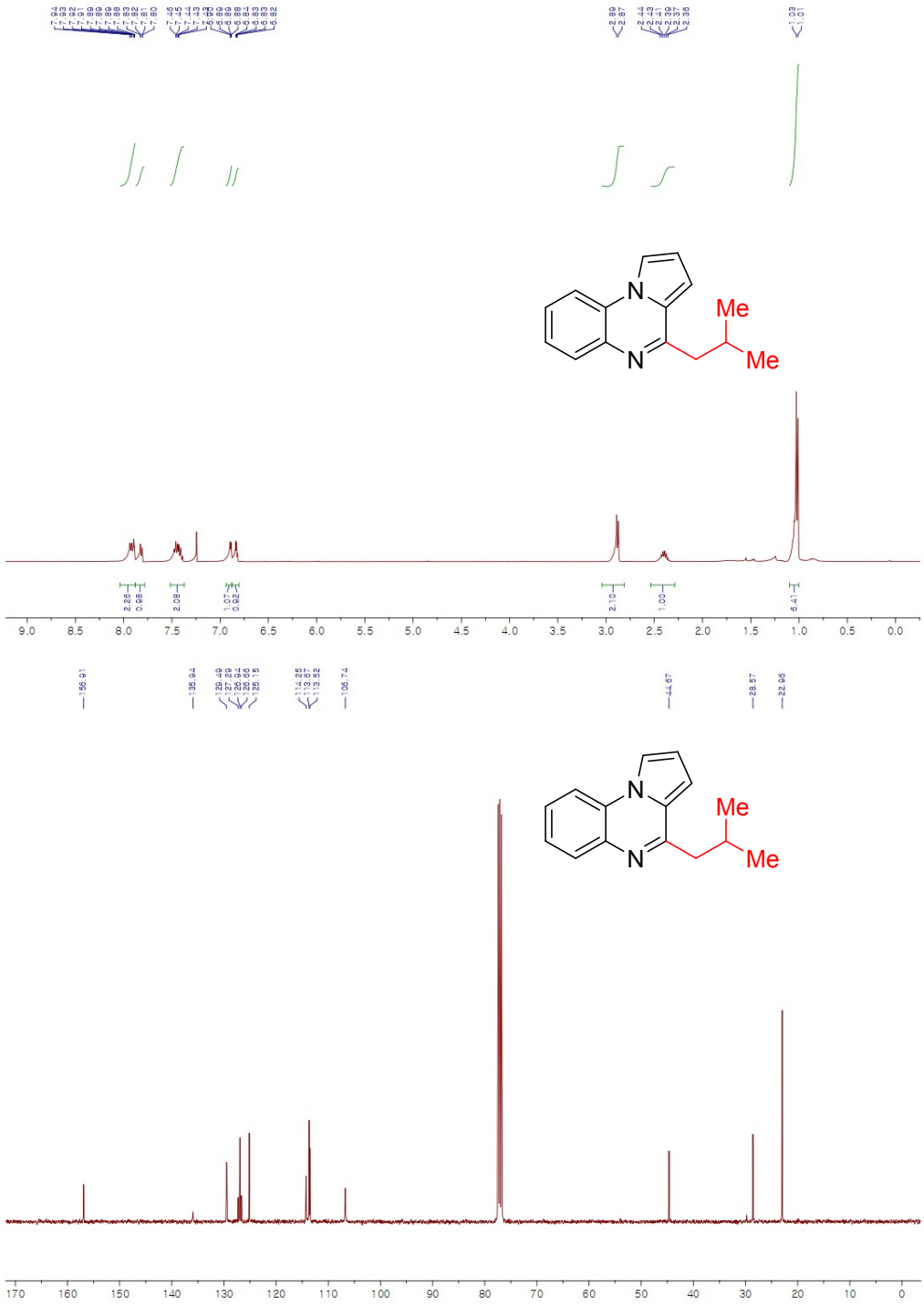


^{1}H & ^{13}C NMR of phenyl(pyrrolo[1,2-*a*]quinoxalin-4-yl)methanone **3e**

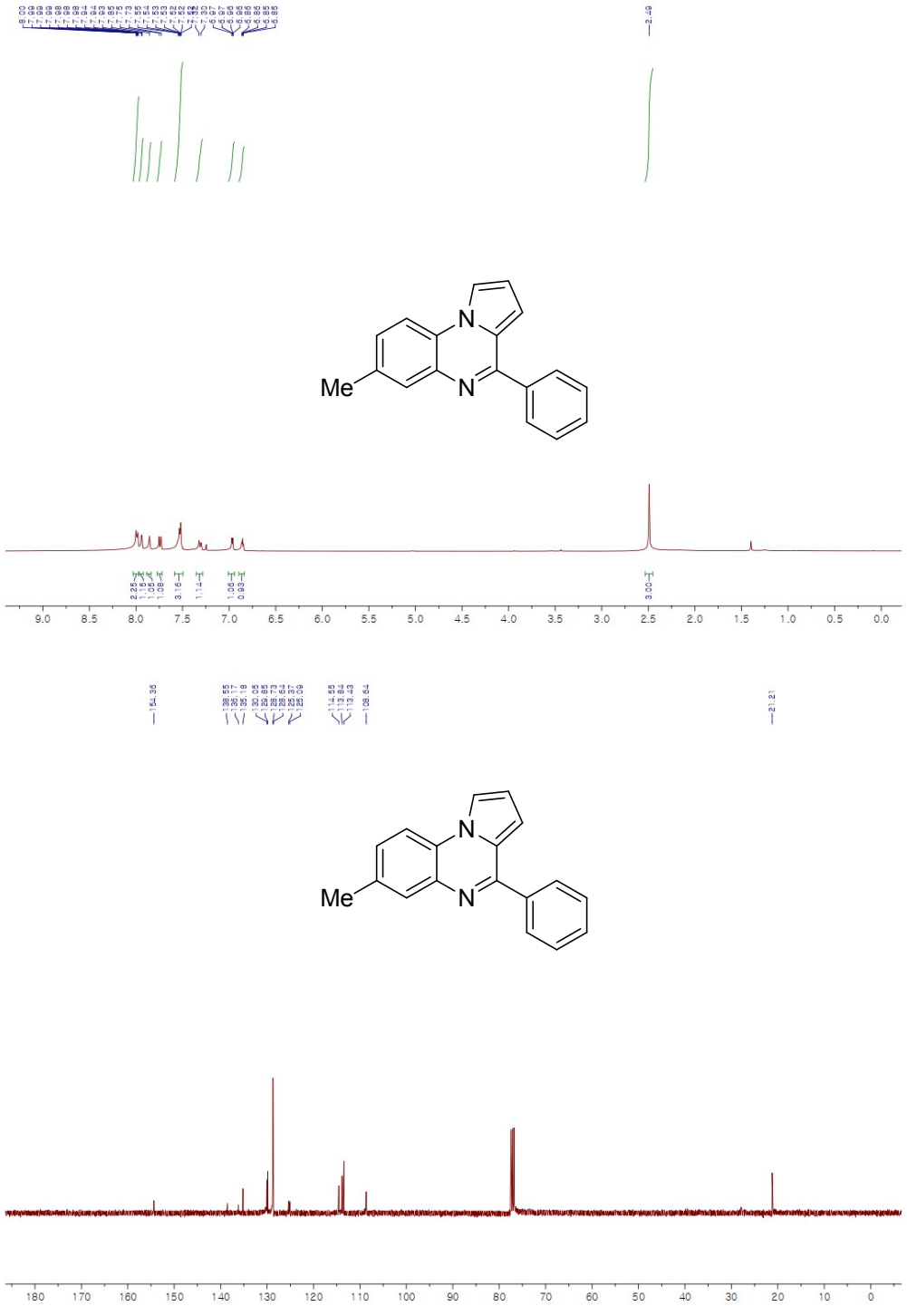




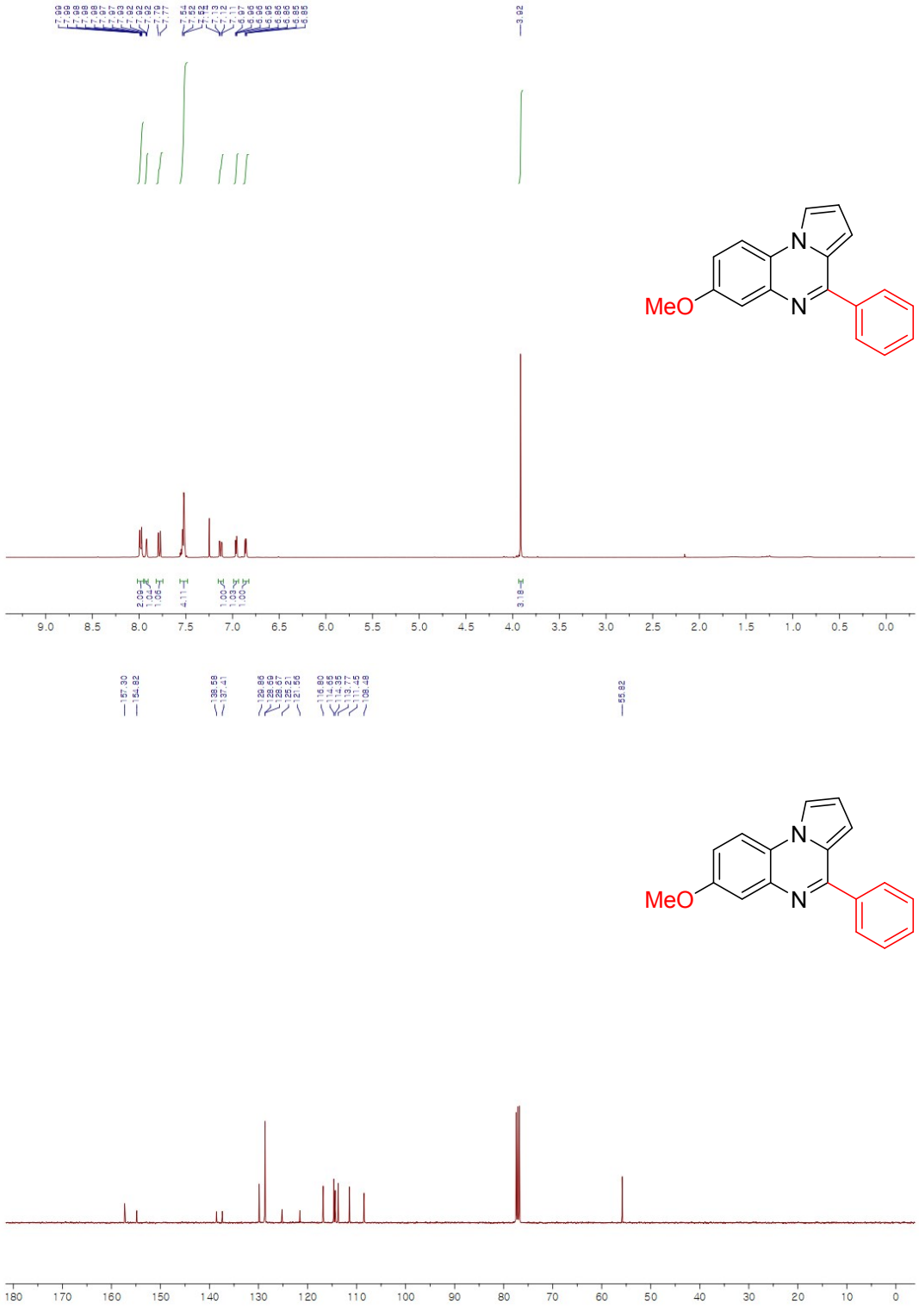
^{1}H & ^{13}C NMR of 4-isobutylpyrrolo[1,2-*a*]quinoxaline **3f**



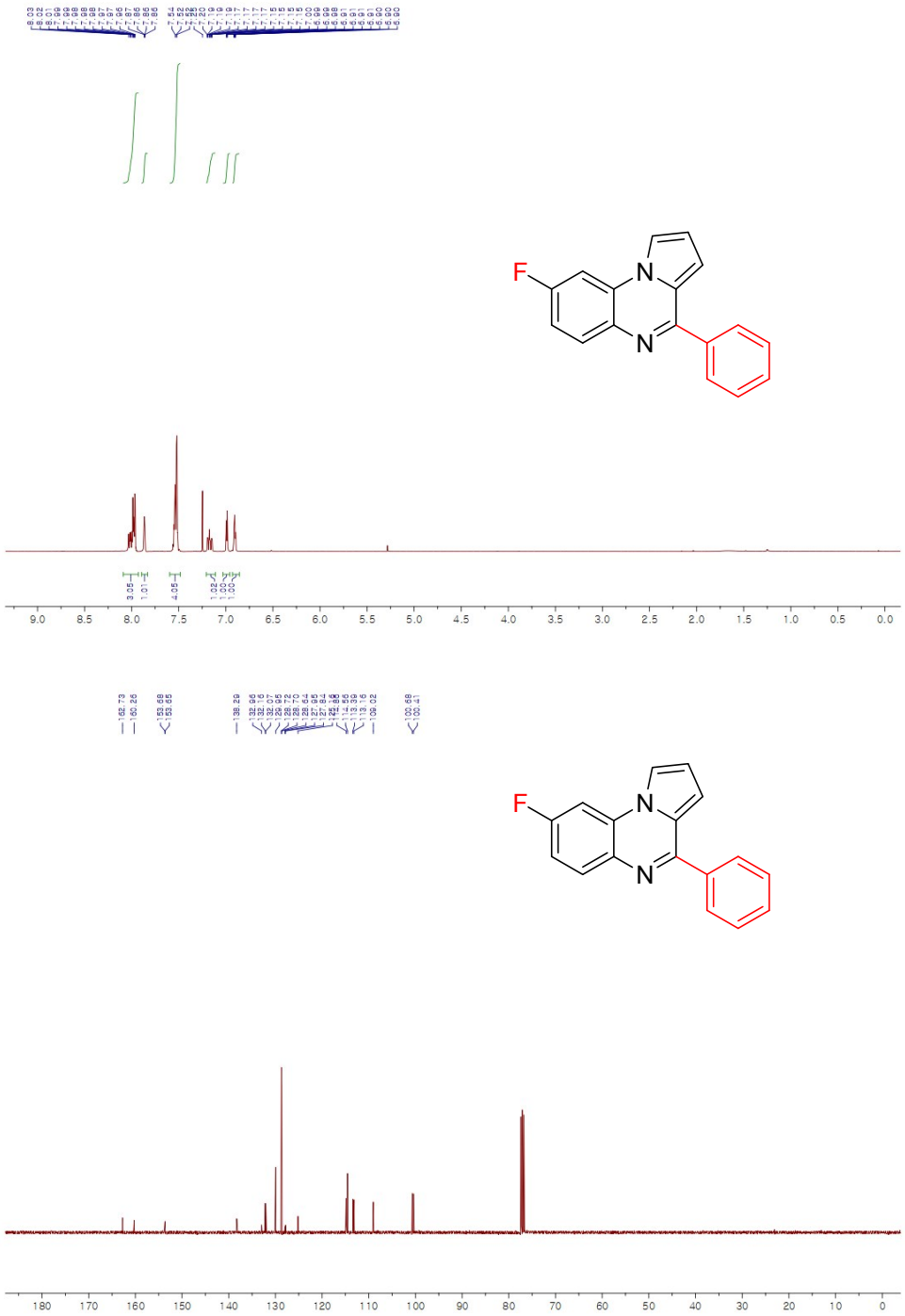
^{1}H & ^{13}C NMR of 7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline **3g**



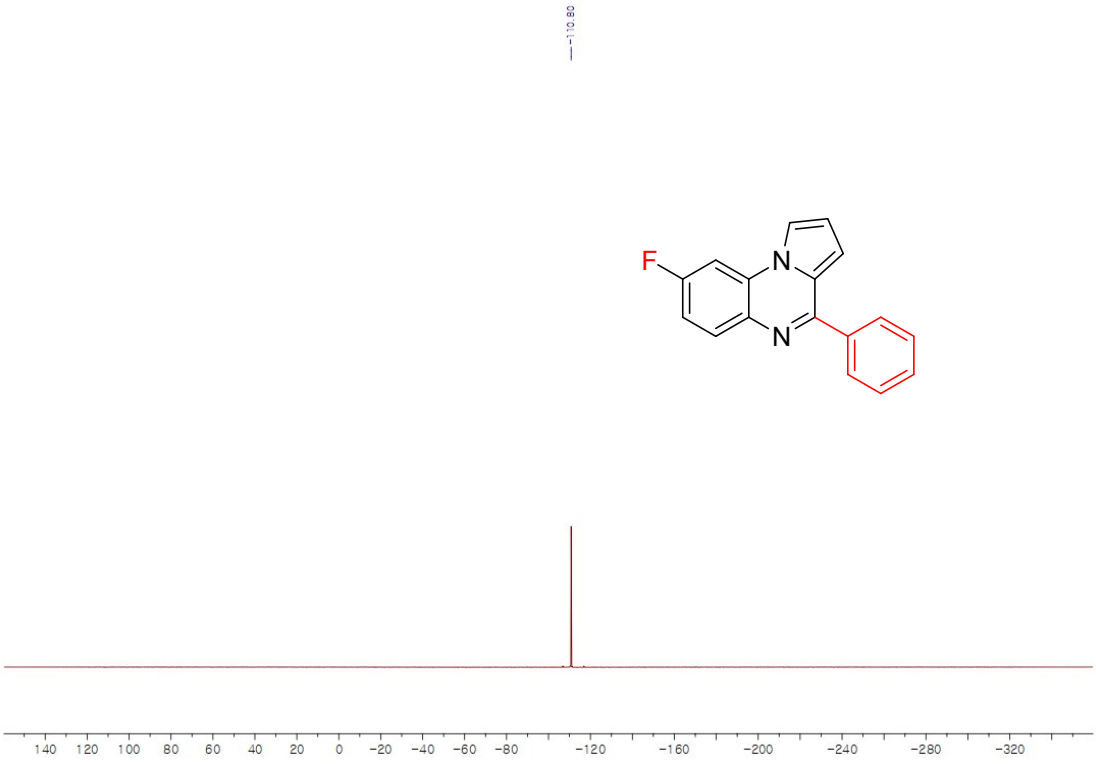
^{1}H & ^{13}C NMR of 7-methoxy-4-phenylpyrrolo[1,2-*a*]quinoxaline **3h**



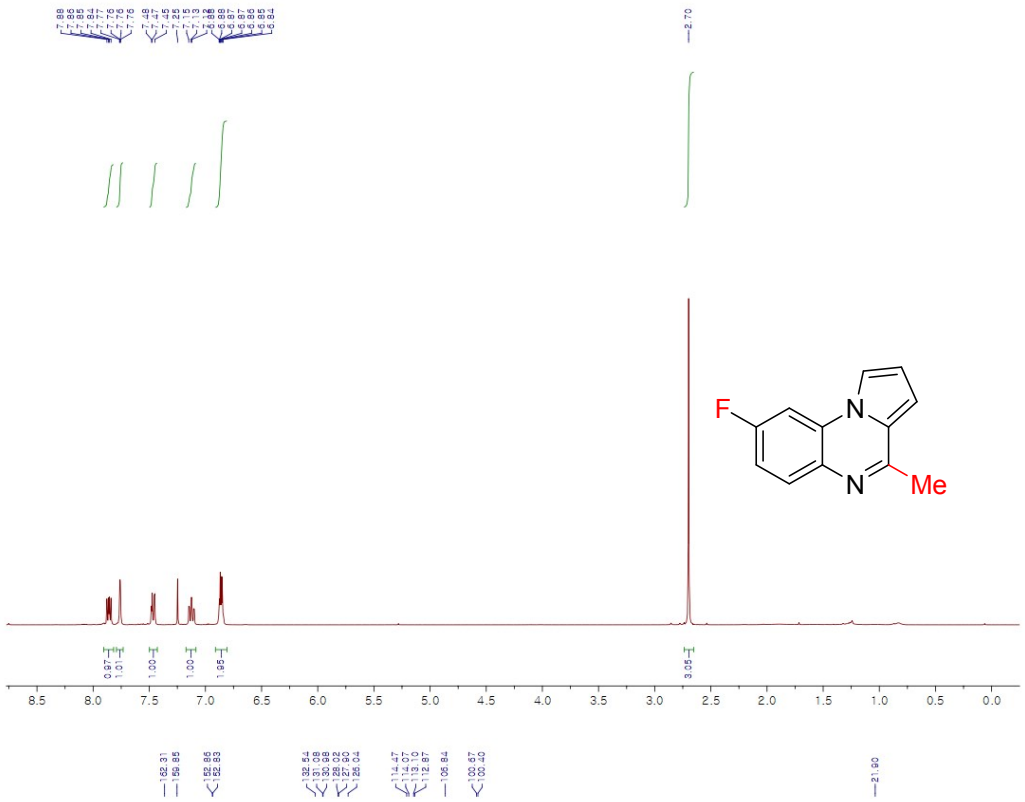
^{1}H & ^{13}C NMR of 8-fluoro-4-phenylpyrrolo[1,2-*a*]quinoxaline **3i**

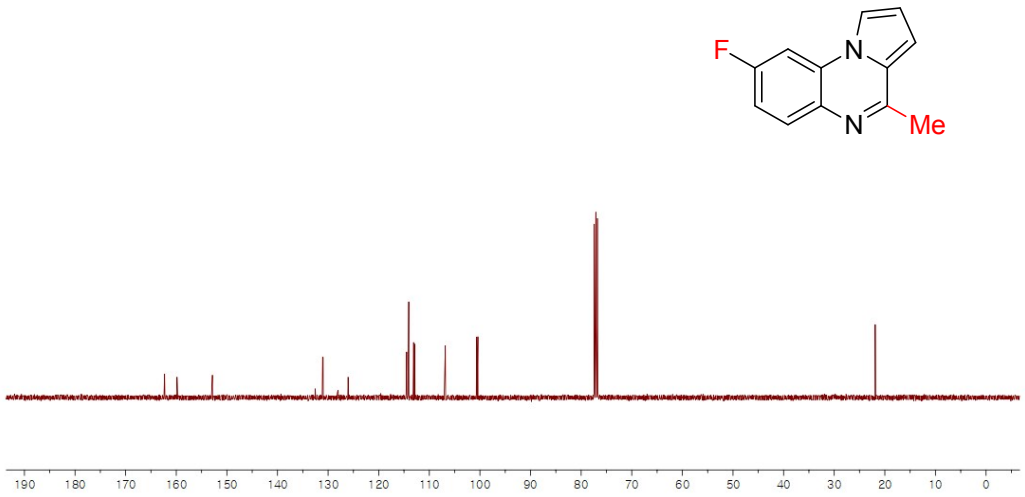


^{19}F NMR of 8-fluoro-4-phenylpyrrolo[1,2-*a*]quinoxaline **3i**

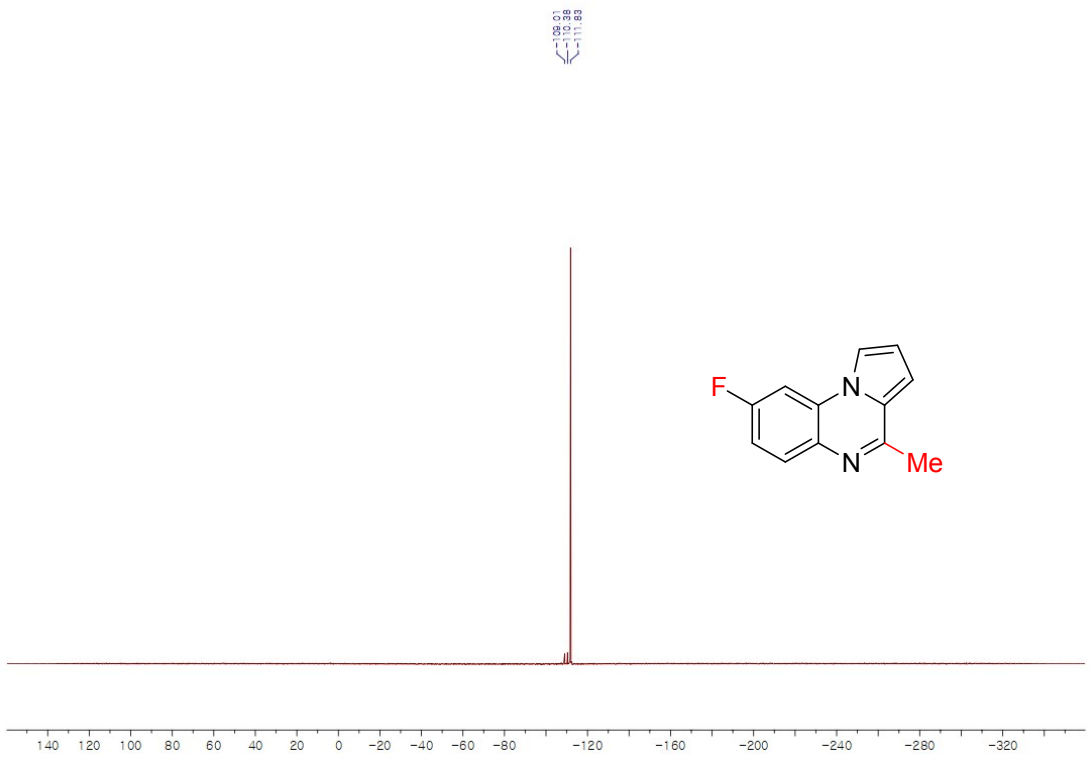


^{1}H & ^{13}C NMR of 8-fluoro-4-methylpyrrolo[1,2-*a*]quinoxaline **3j**

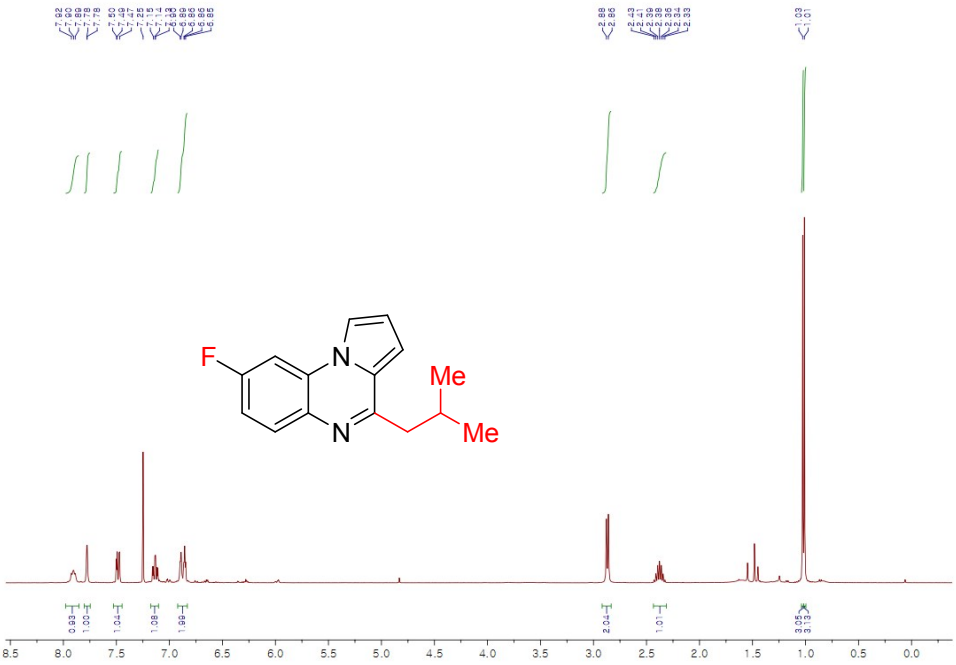


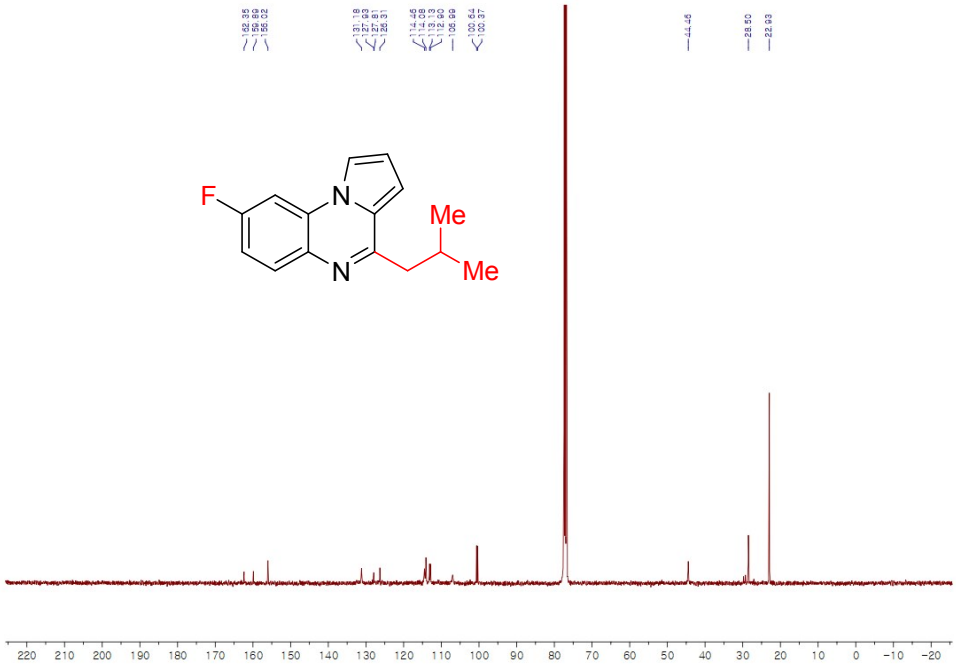


^{19}F NMR of 8-fluoro-4-methylpyrrolo[1,2-*a*]quinoxaline **3j**

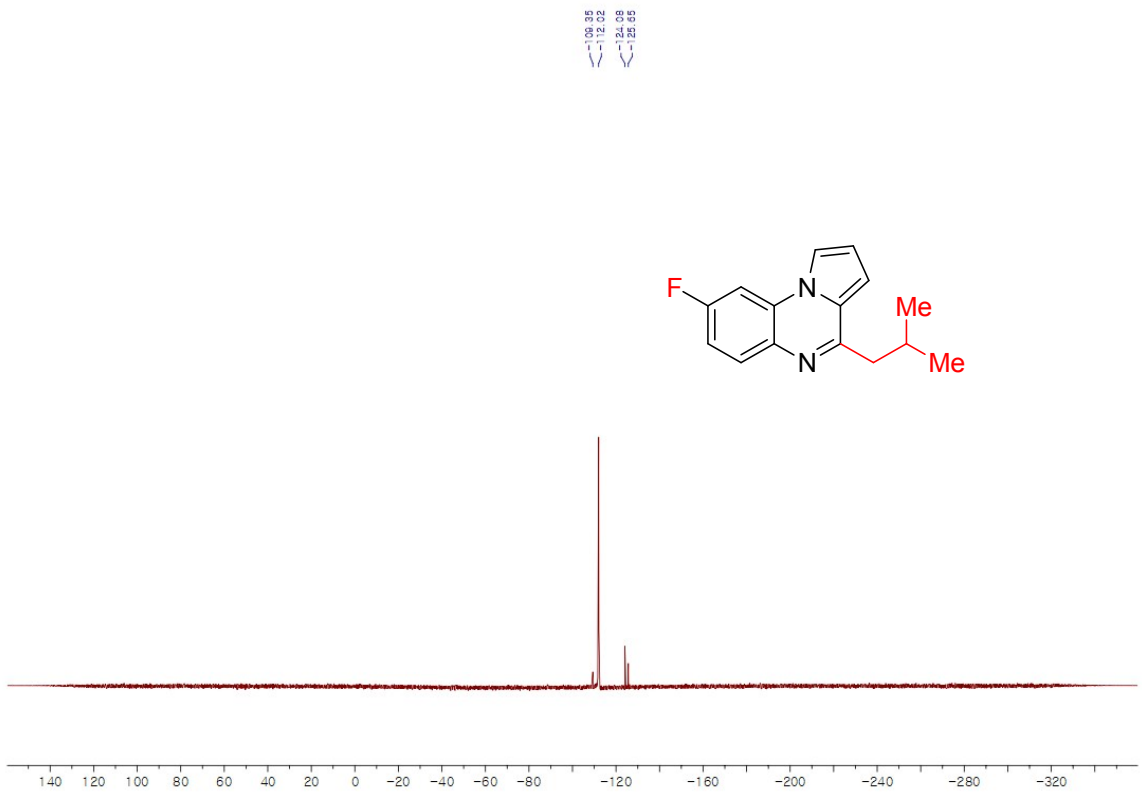


^{1}H & ^{13}C NMR of 8-fluoro-4-isobutylpyrrolo[1,2-*a*]quinoxaline **3k**

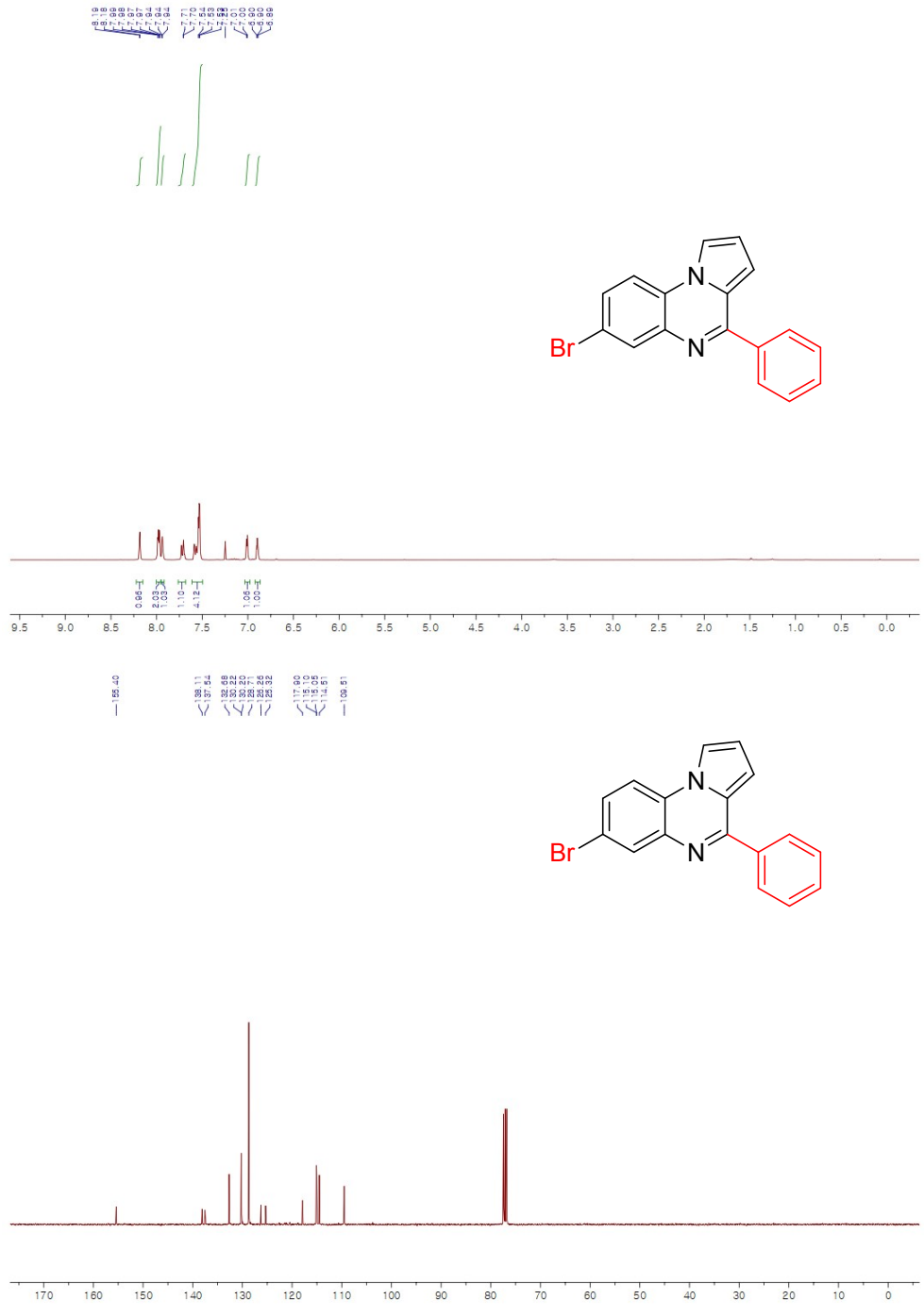




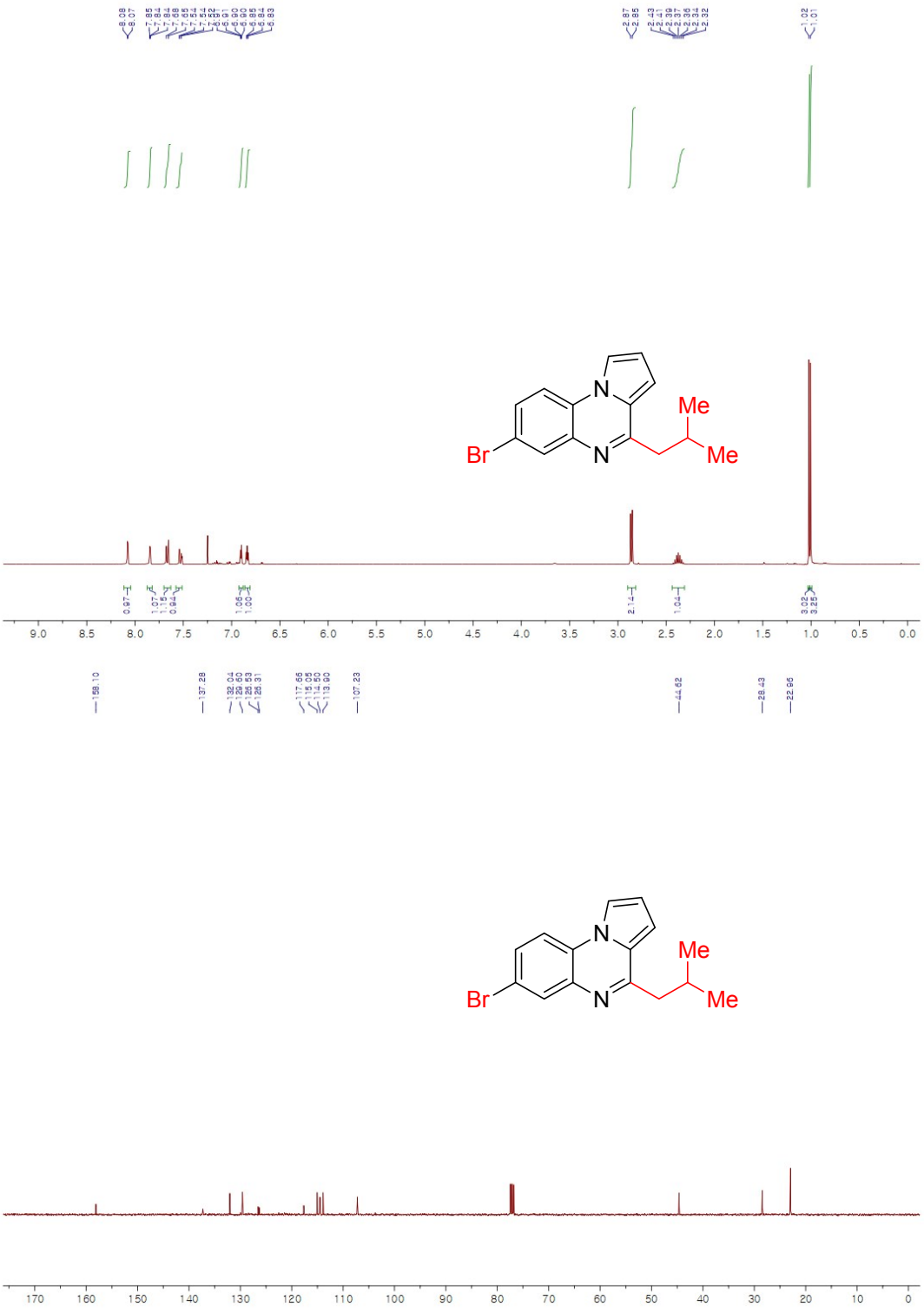
^{19}F NMR of 8-fluoro-4-isobutylpyrrolo[1,2-*a*]quinoxaline **3k**



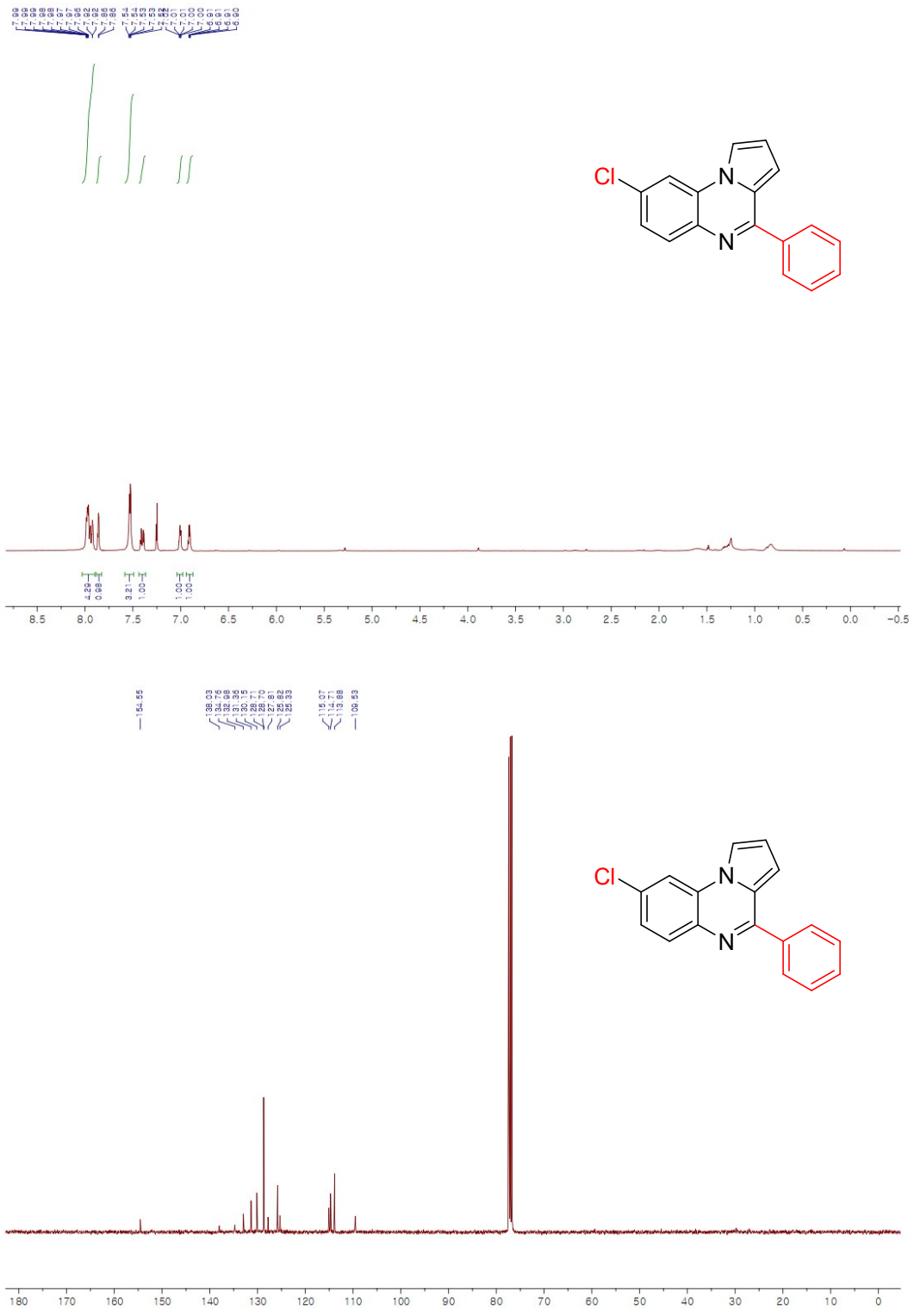
^{1}H & ^{13}C NMR of 7-bromo-4-phenylpyrrolo[1,2-*a*]quinoxaline **3l**



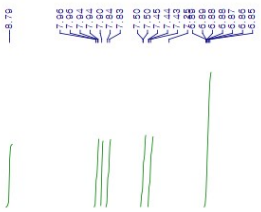
^{1}H & ^{13}C NMR of 7-bromo-4-isobutylpyrrolo[1,2-*a*]quinoxaline **3m**

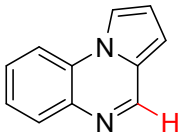


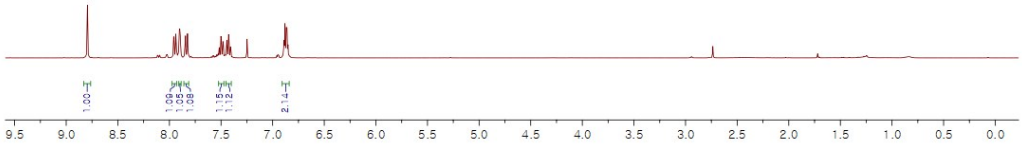
^{1}H & ^{13}C NMR of 8-chloro-4-phenylpyrrolo[1,2-*a*]quinoxaline **3n**

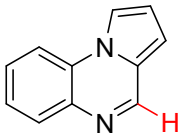


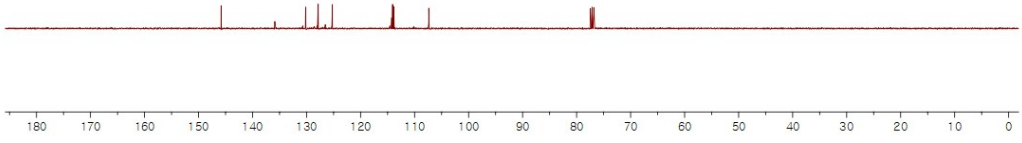
^{1}H & ^{13}C NMR of pyrrolo[1,2-*a*]quinoxaline **3o**



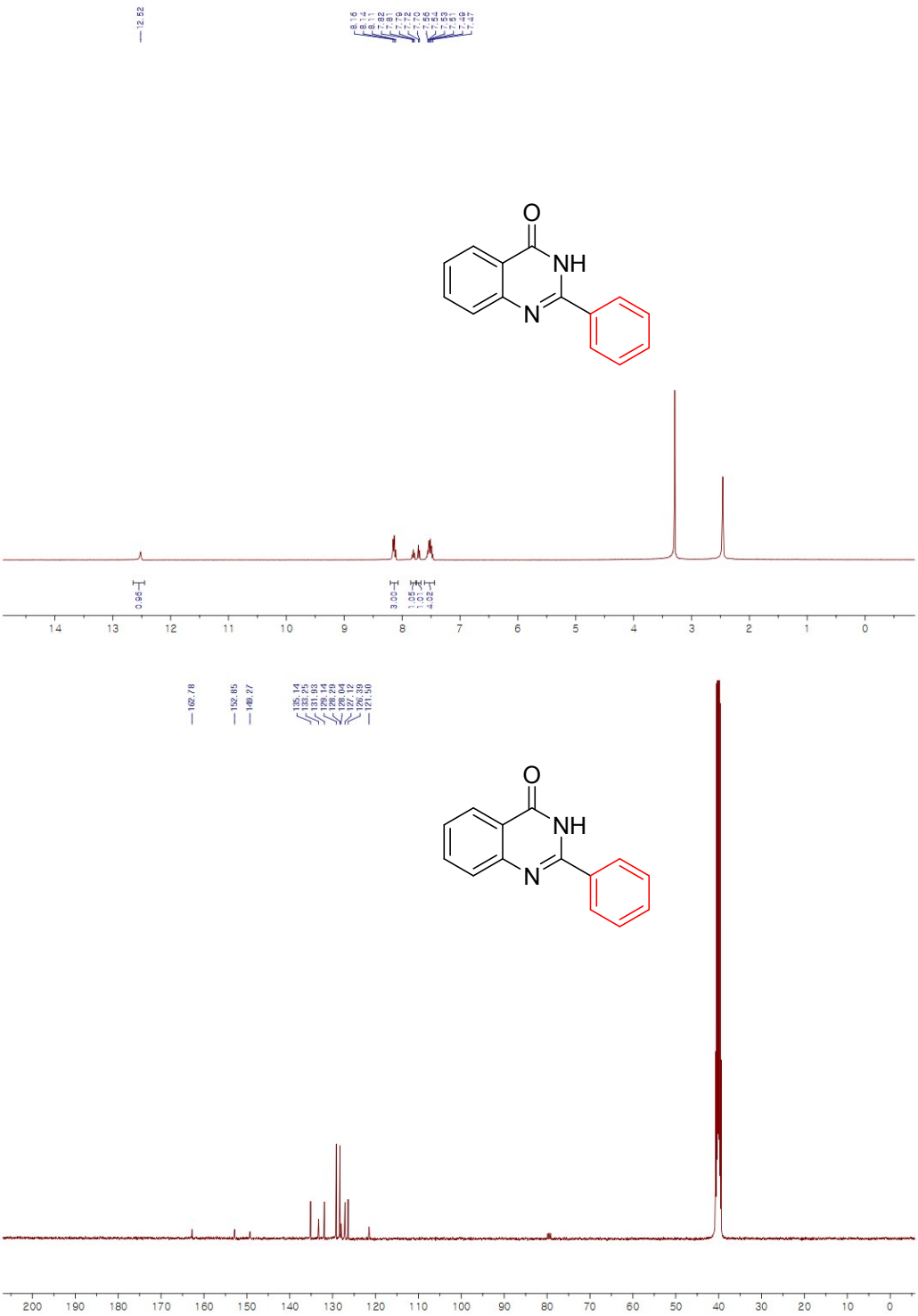




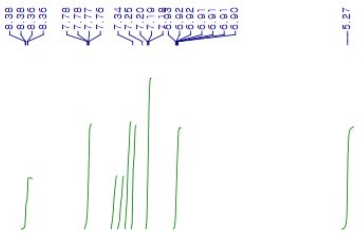


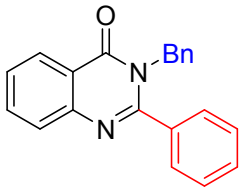


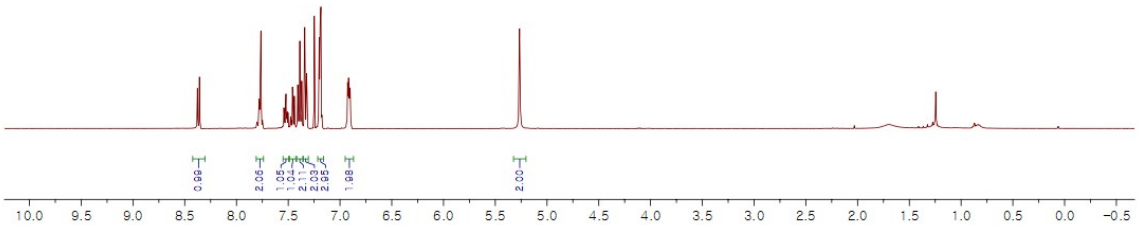
^{1}H & ^{13}C NMR of 2-phenylquinazolin-4(3*H*)-one **5a**

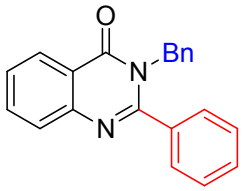


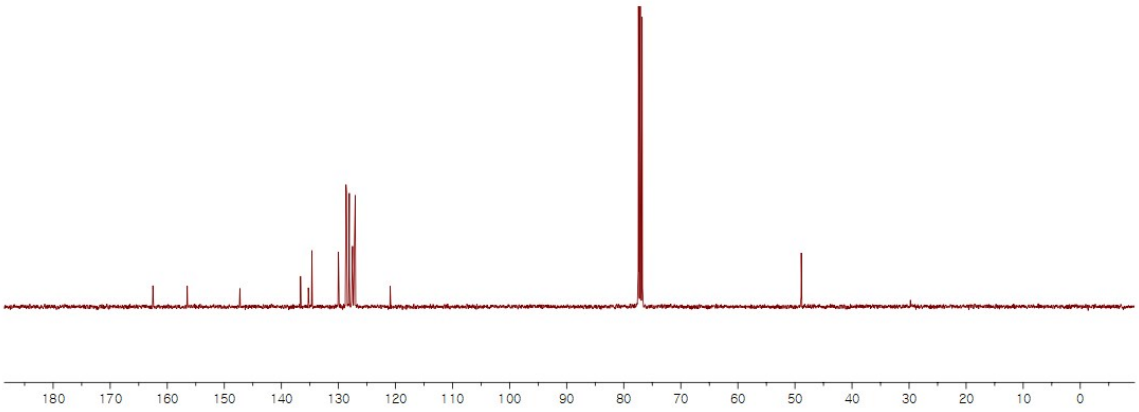
^{1}H & ^{13}C NMR of 3-benzyl-2-phenylquinazolin-4(3*H*)-one **5b**



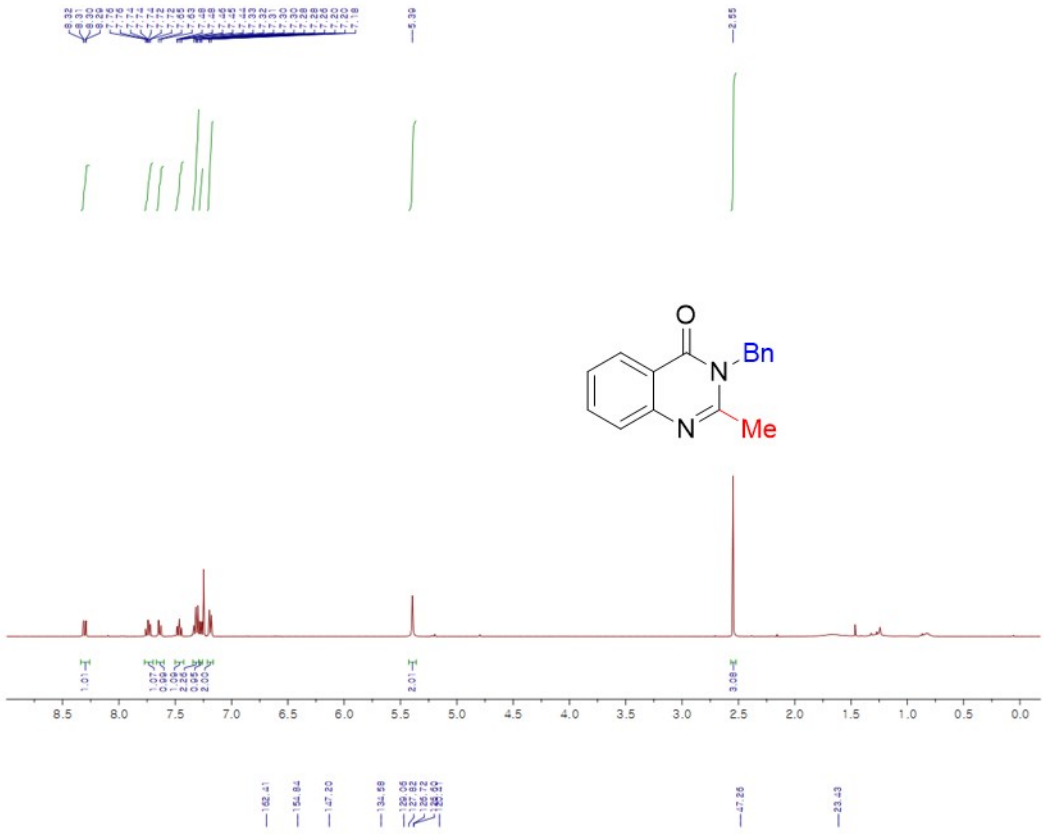


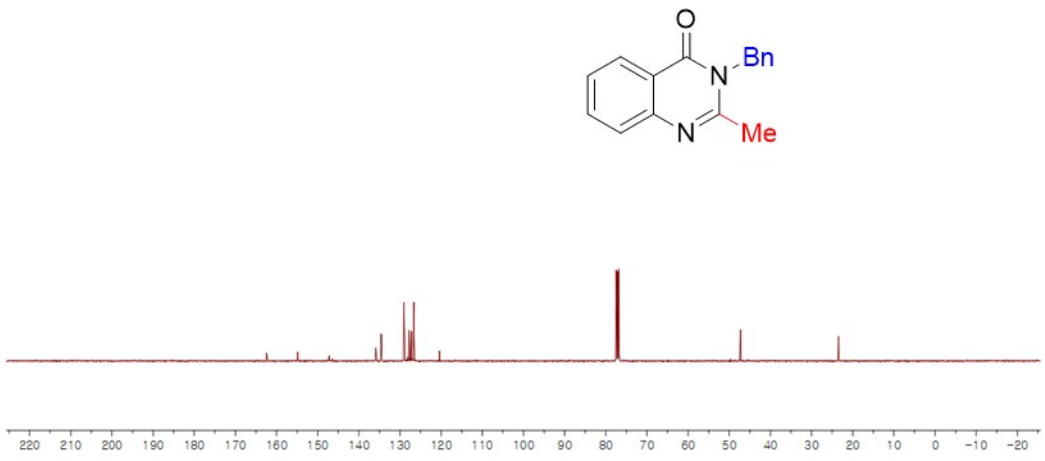




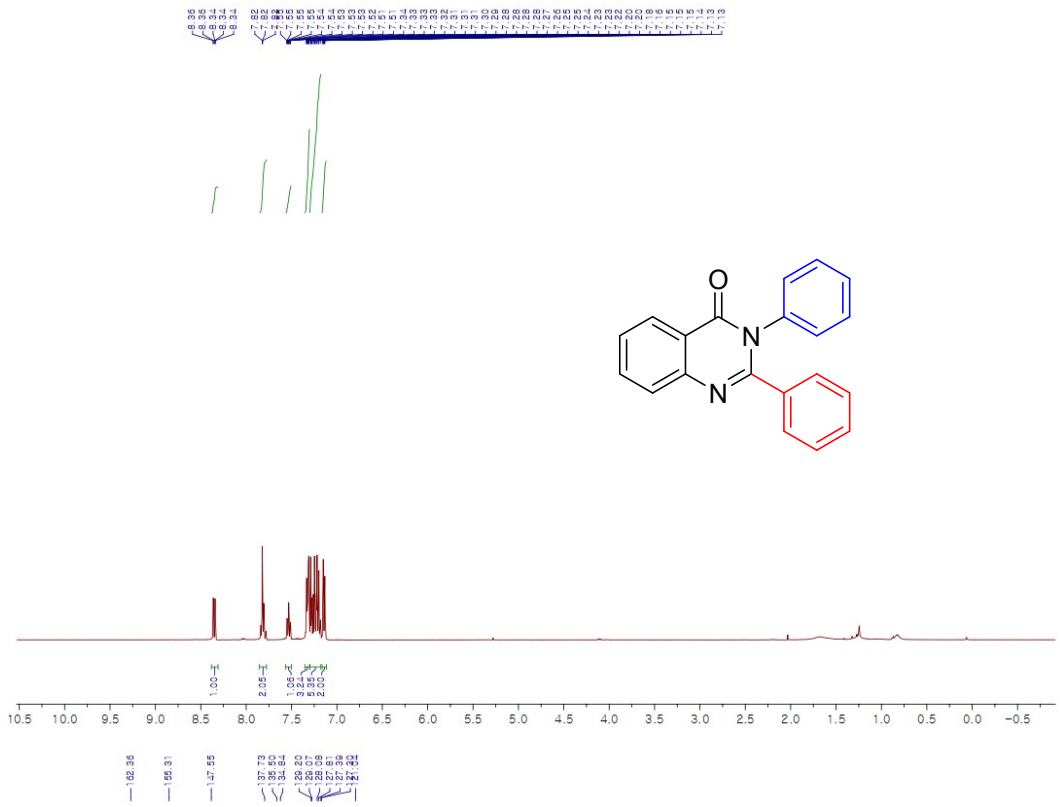


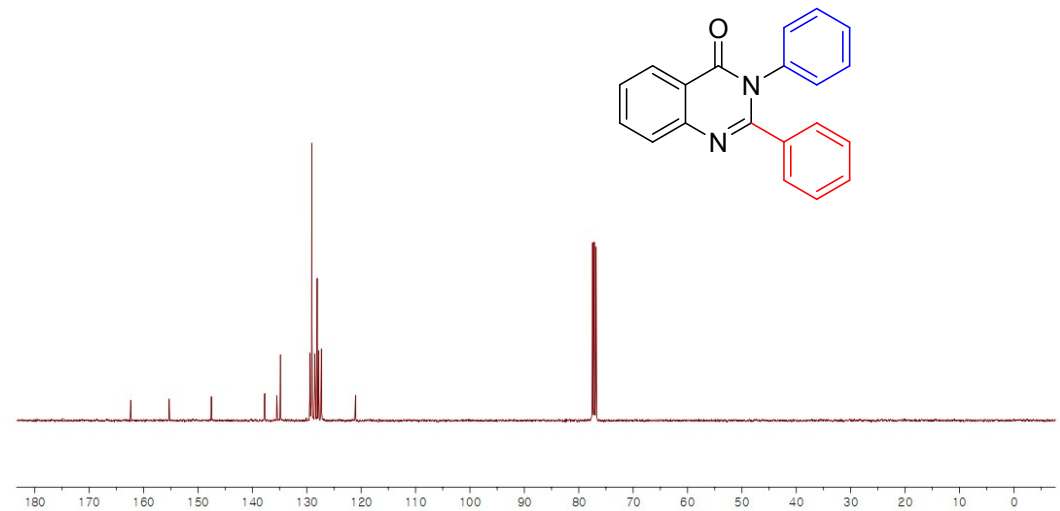
^{1}H & ^{13}C NMR of 3-benzyl-2-methylquinazolin-4(3*H*)-one **5c**



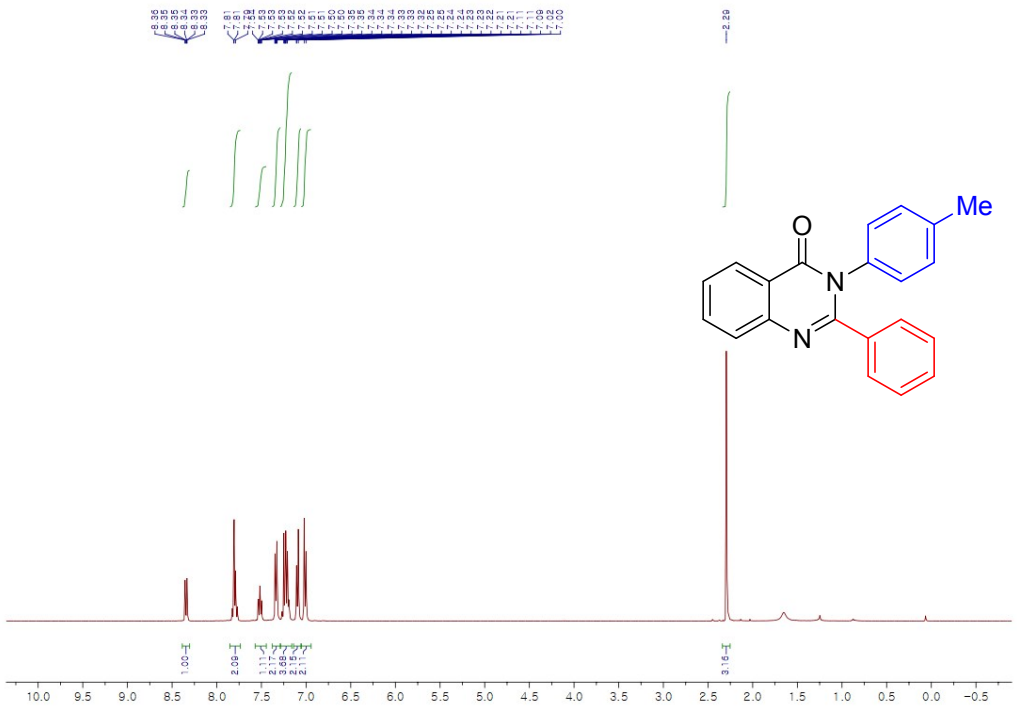


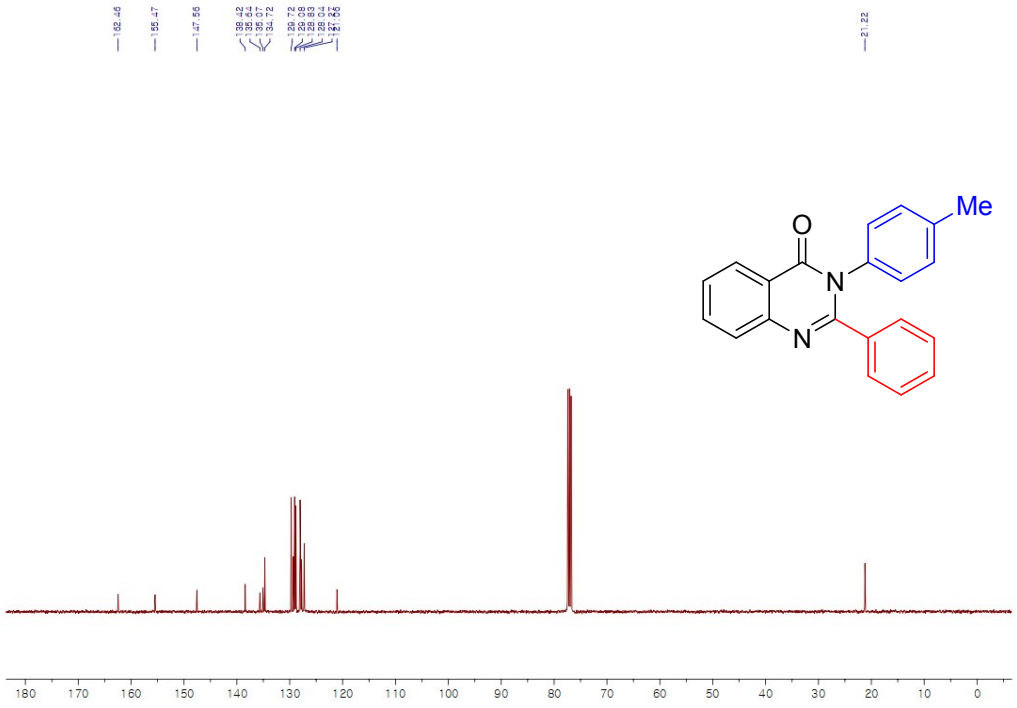
^{1}H & ^{13}C NMR of 2,3-diphenylquinazolin-4(3*H*)-one **5d**



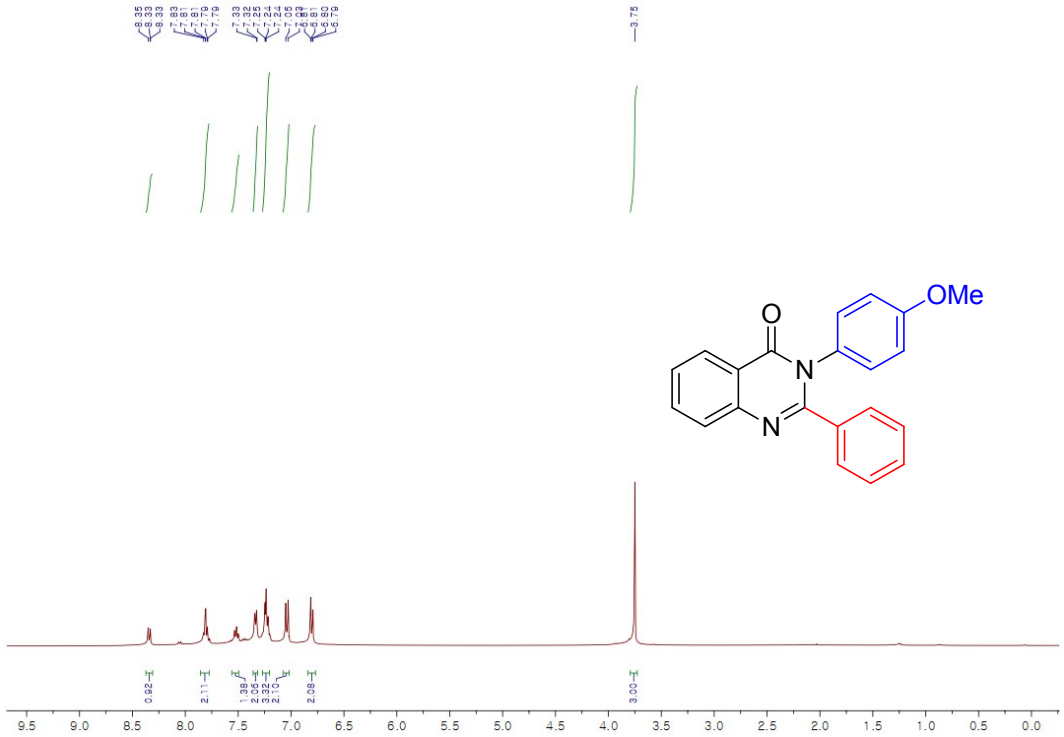


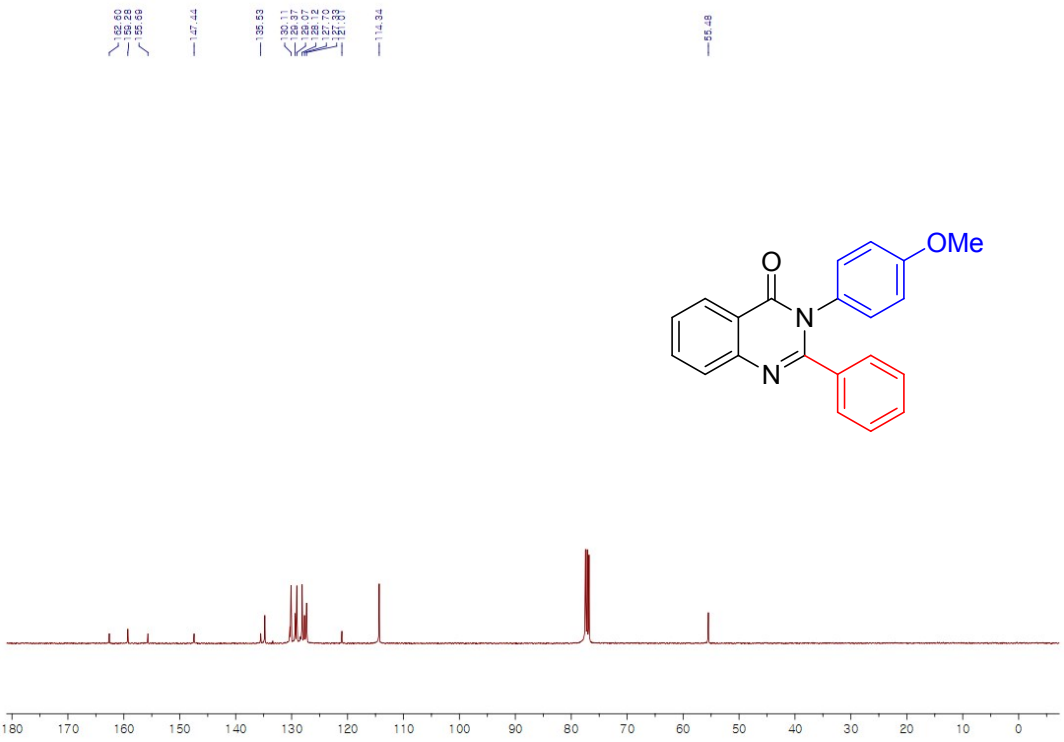
^{1}H & ^{13}C NMR of 2-phenyl-3-(*p*-tolyl)quinazolin-4(3*H*)-one **5e**



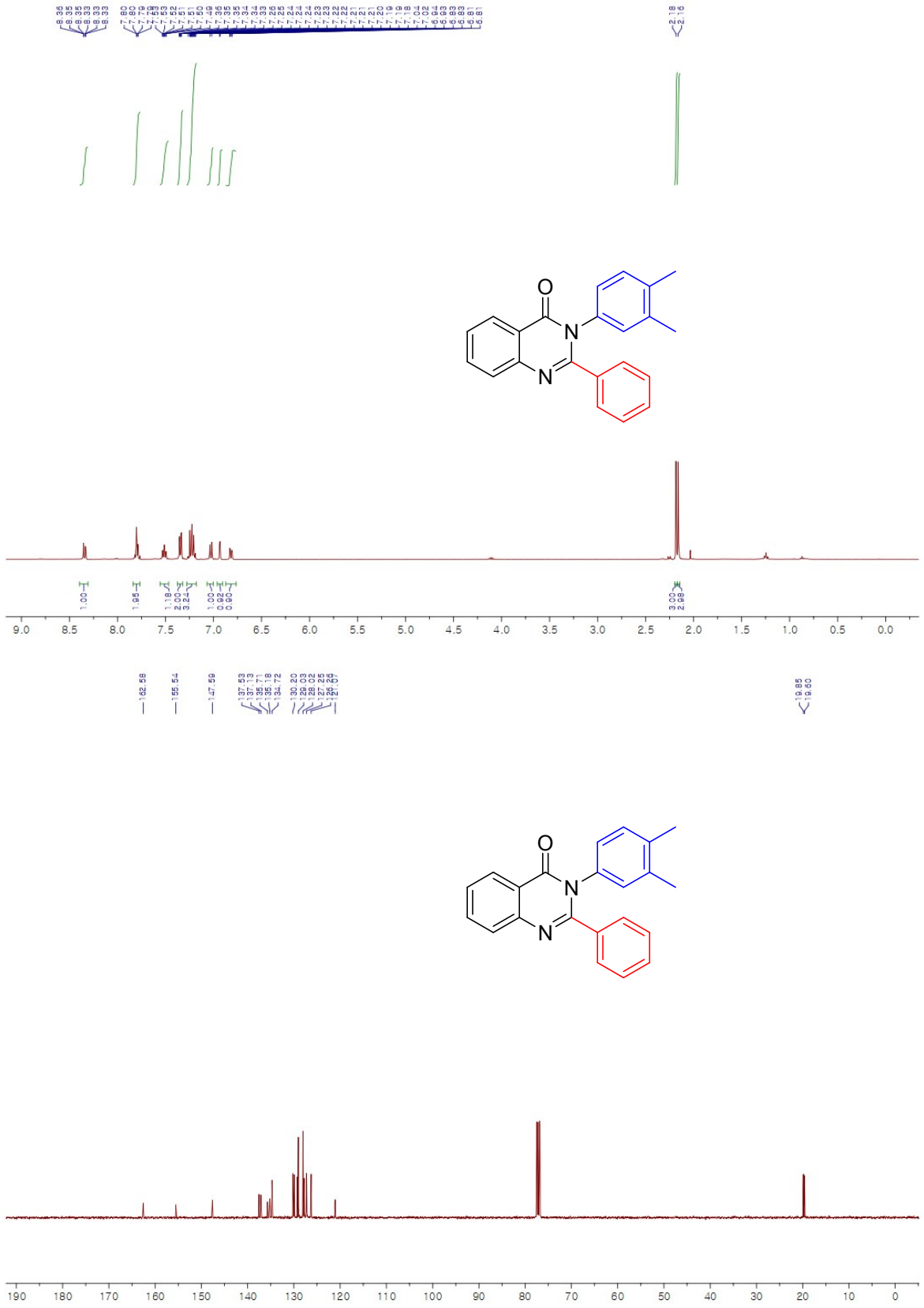


^{1}H & ^{13}C NMR of 3-(4-methoxyphenyl)-2-phenylquinazolin-4(3*H*)-one **5f**

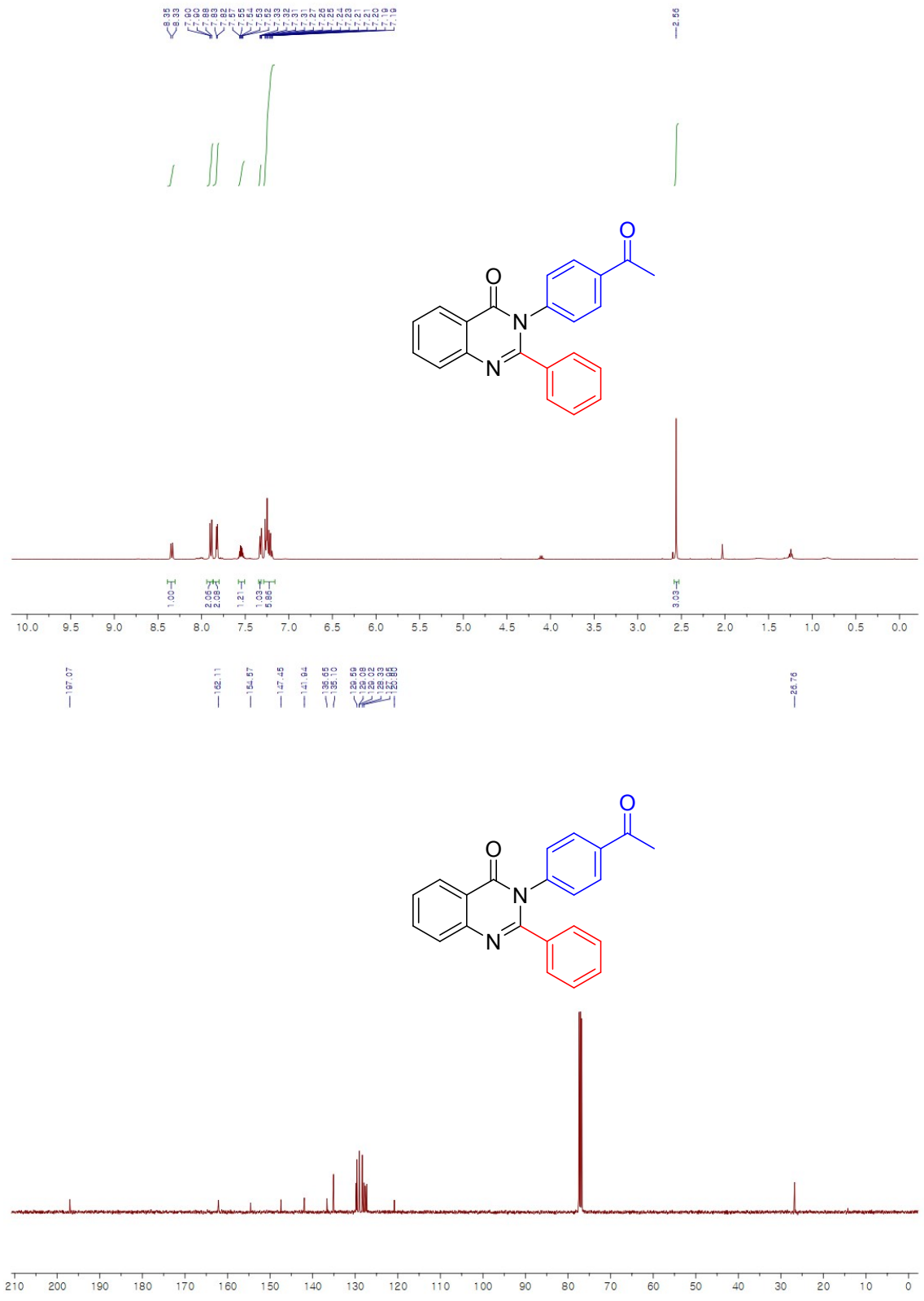




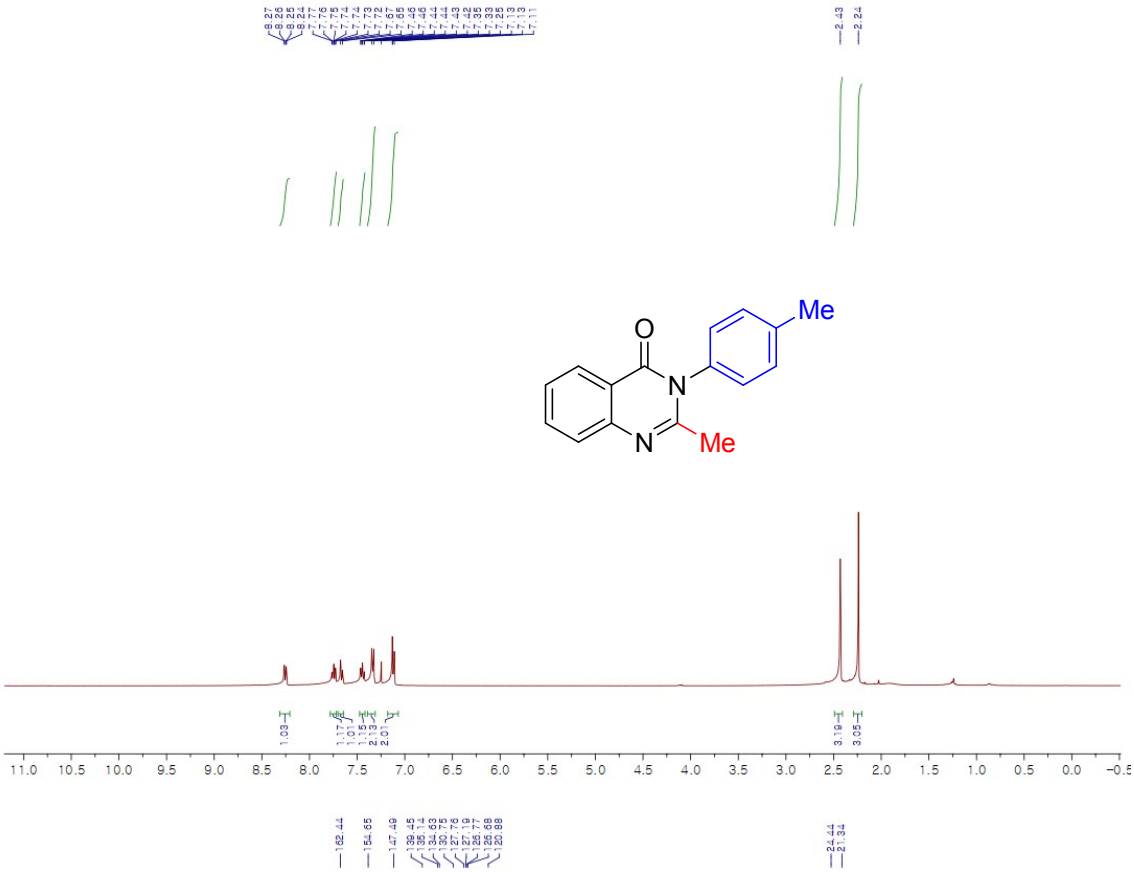
^{1}H & ^{13}C NMR of 3-(3,4-dimethylphenyl)-2-phenylquinazolin-4(3*H*)-one **5g**

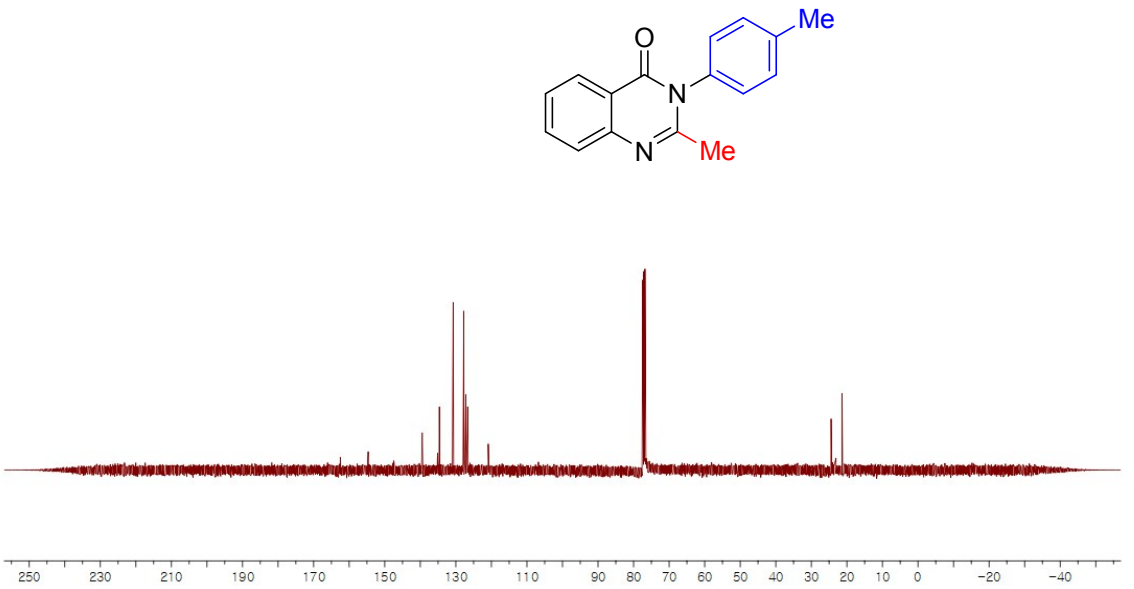


^{1}H & ^{13}C NMR of 3-(4-acetylphenyl)-2-phenylquinazolin-4(3*H*)-one **5h**

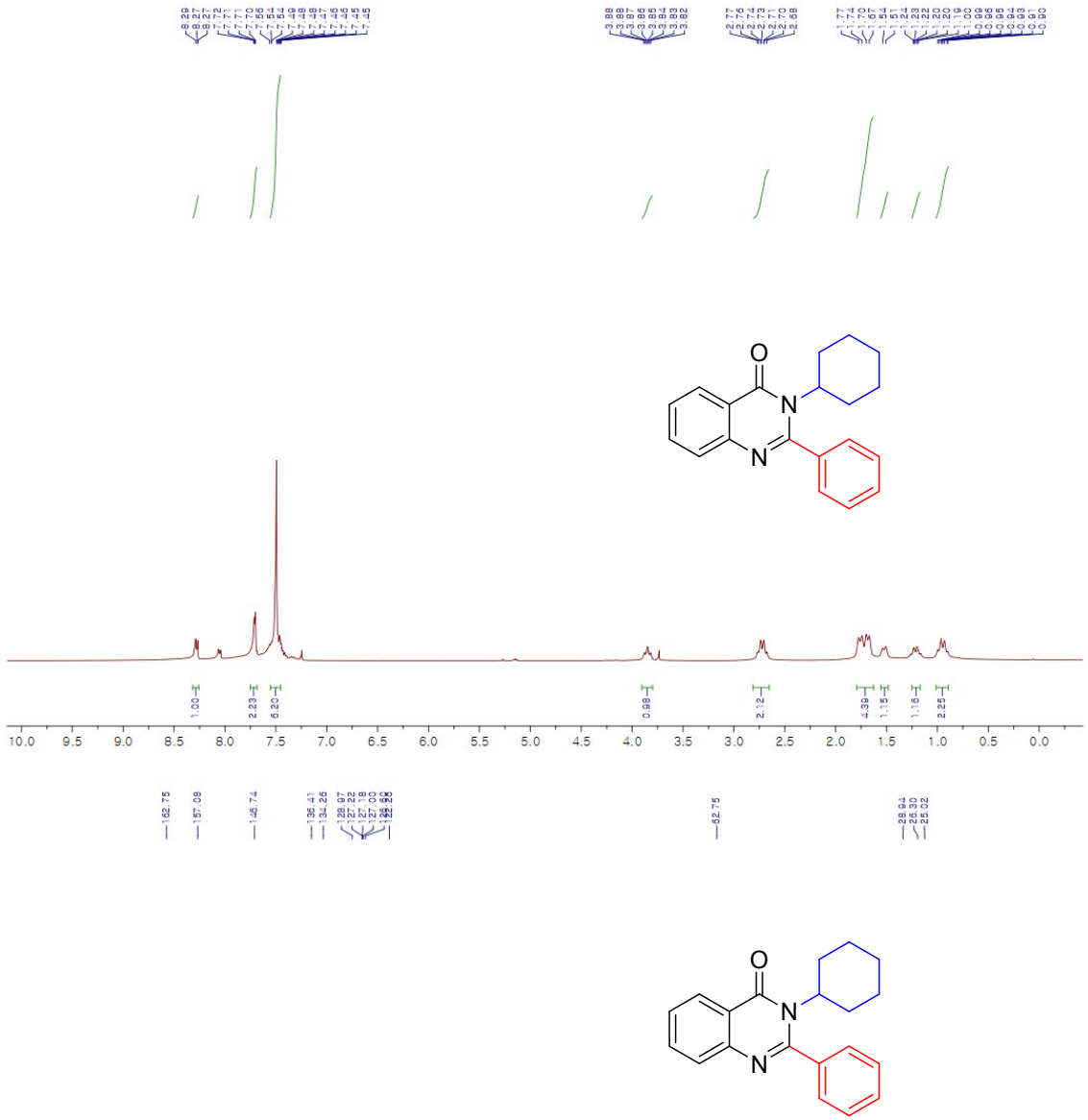


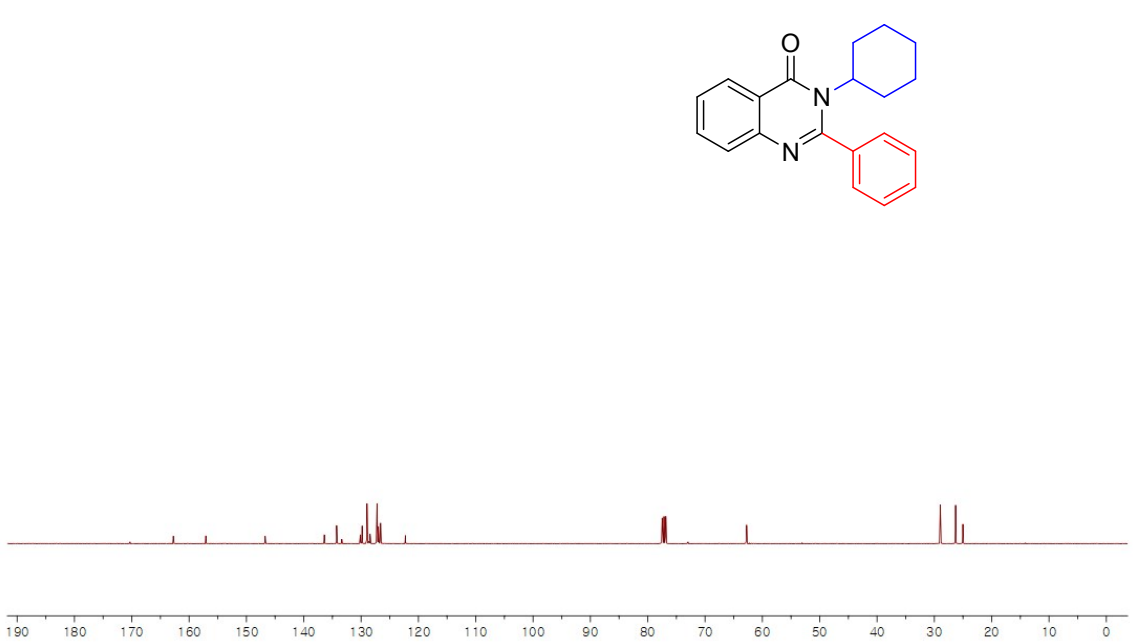
^{1}H & ^{13}C NMR of 2-methyl-3-(p-tolyl)quinazolin-4(3*H*)-one **5i**



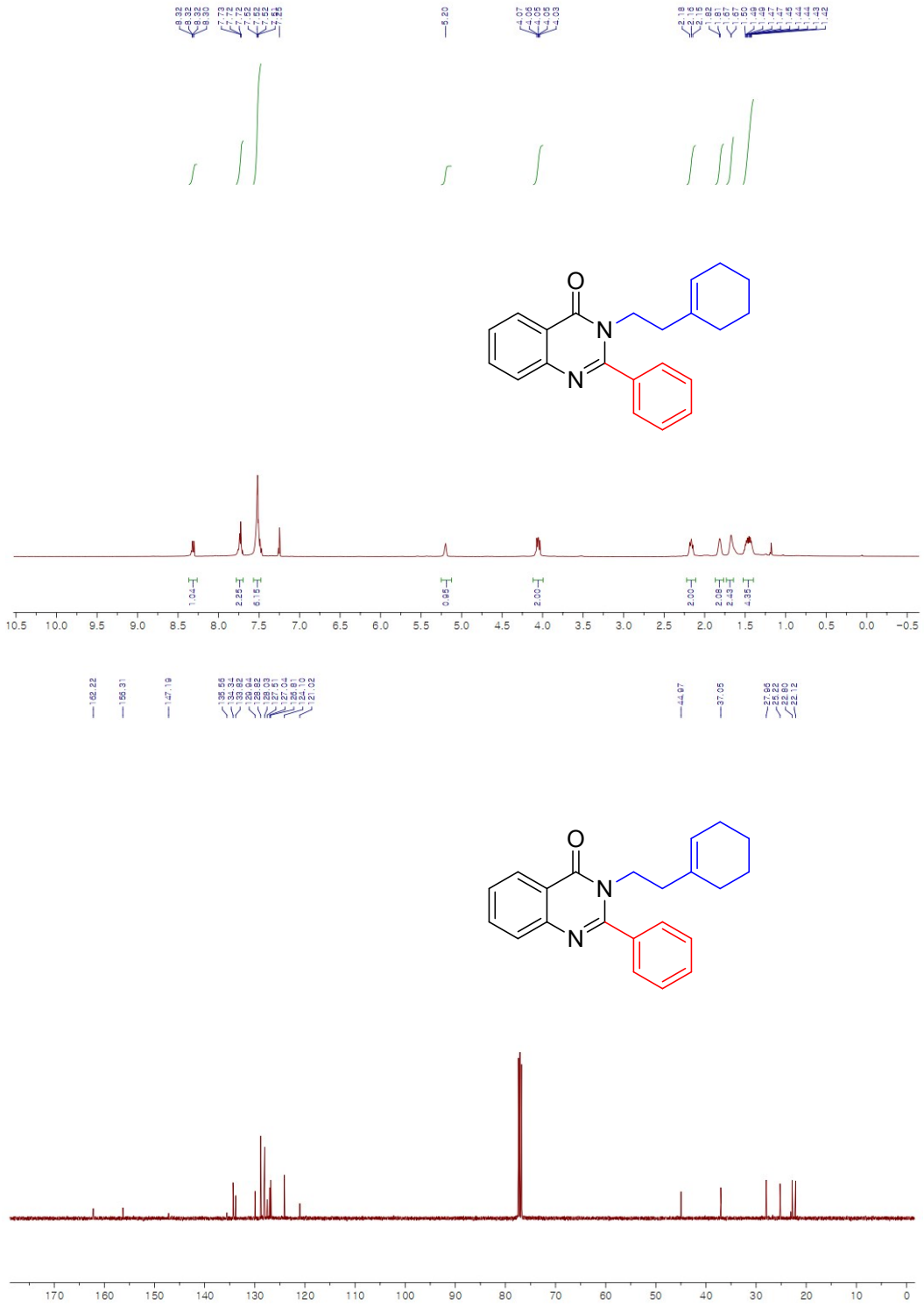


^{1}H & ^{13}C NMR of 3-cyclohexyl-2-phenylquinazolin-4(3*H*)-one **5j**

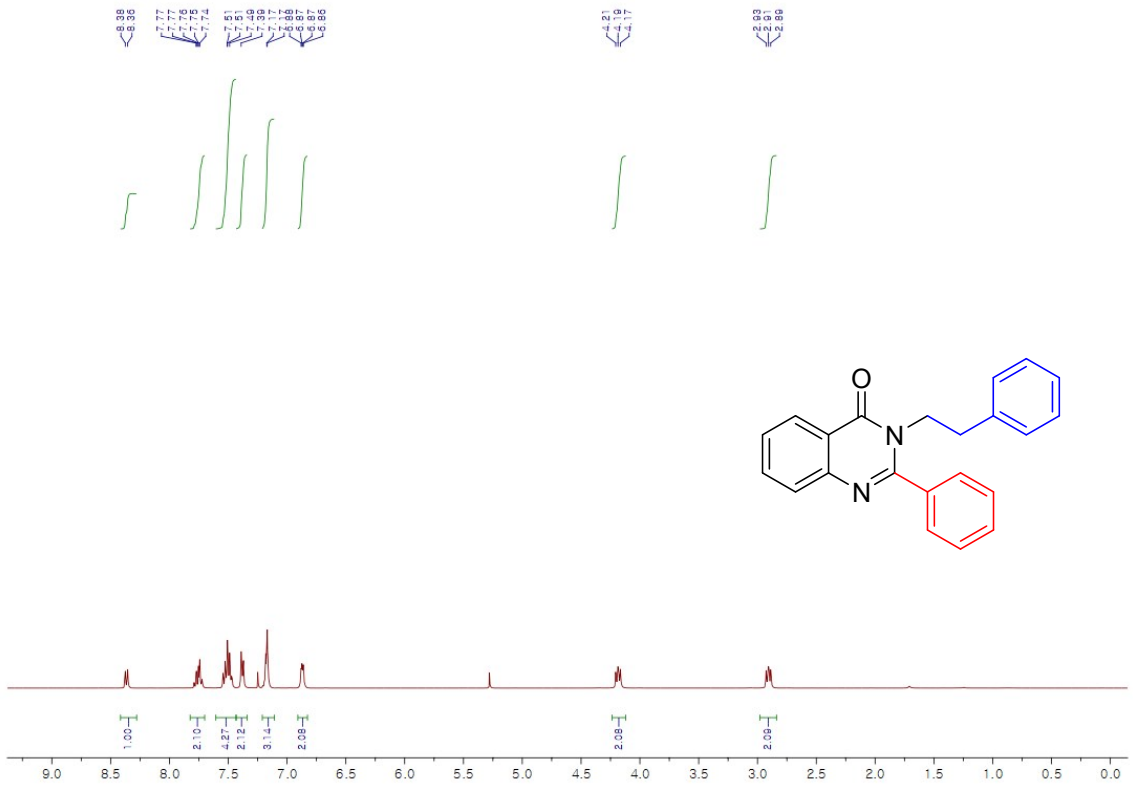


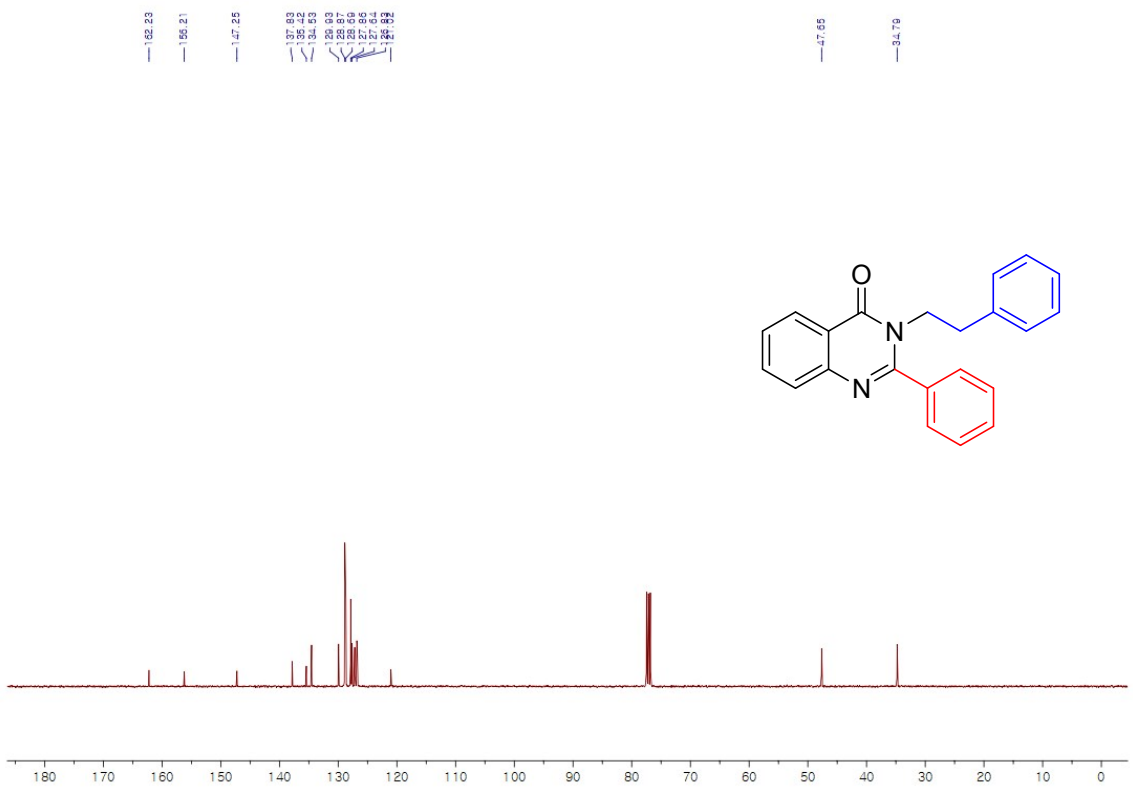


^{1}H & ^{13}C NMR of 3-(2-(cyclohex-1-en-1-yl)ethyl)-2-phenylquinazolin-4(3*H*)-one **5k**

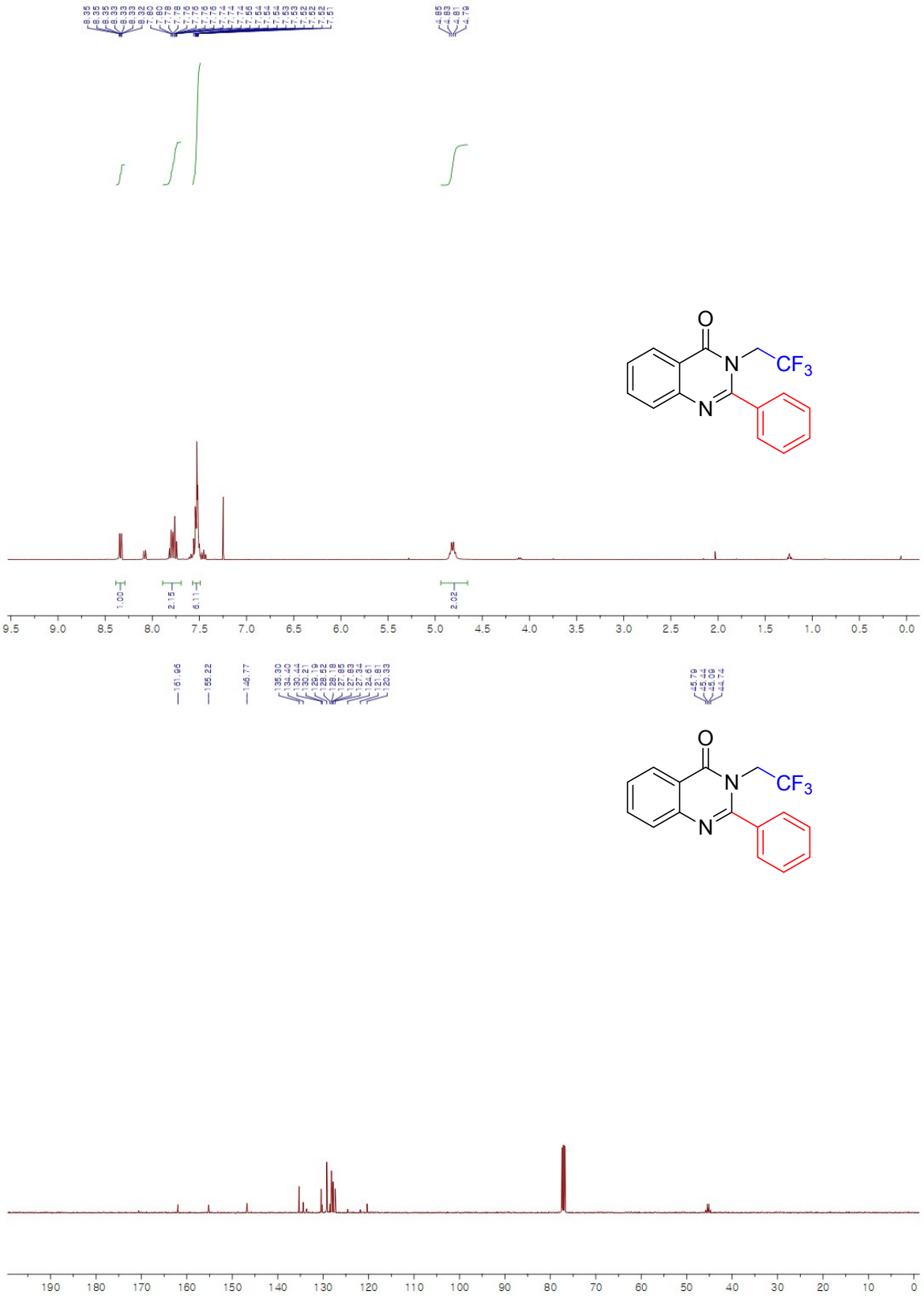


^{1}H & ^{13}C NMR of 3-phenethyl-2-phenylquinazolin-4(3*H*)-one **5l**

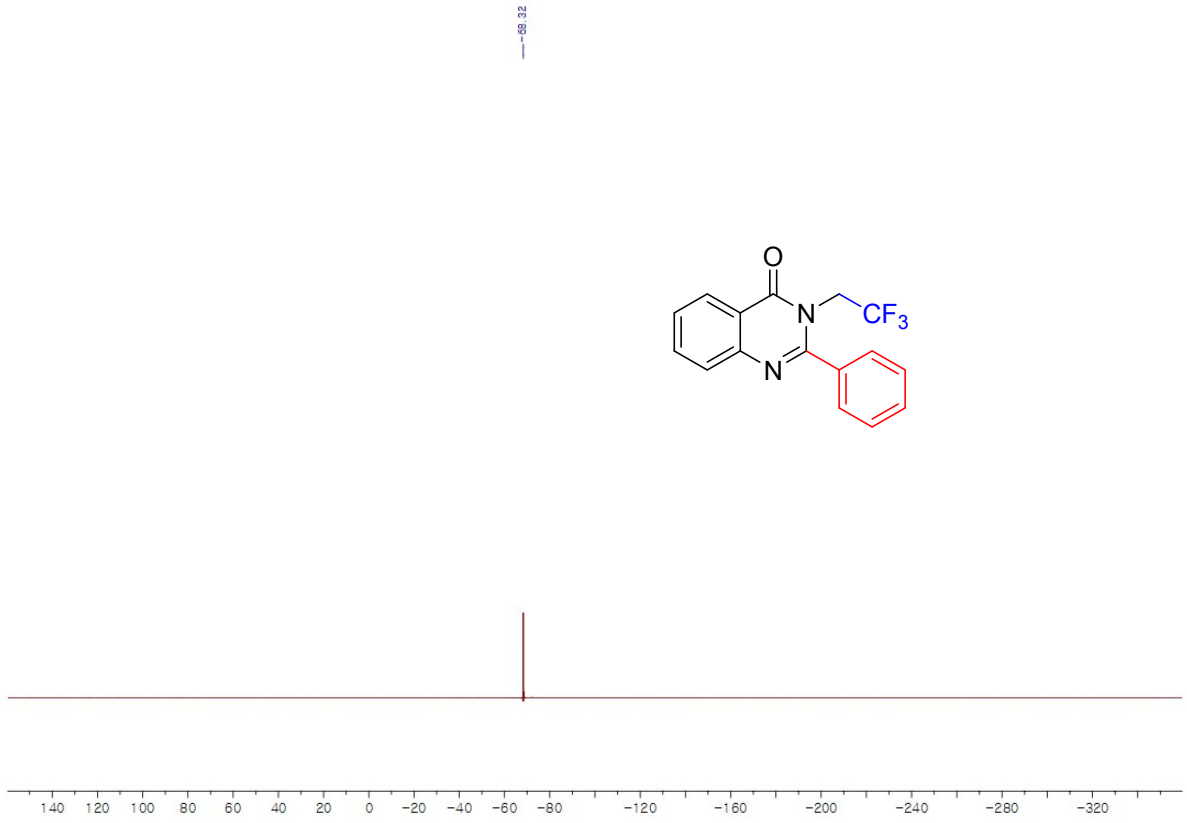




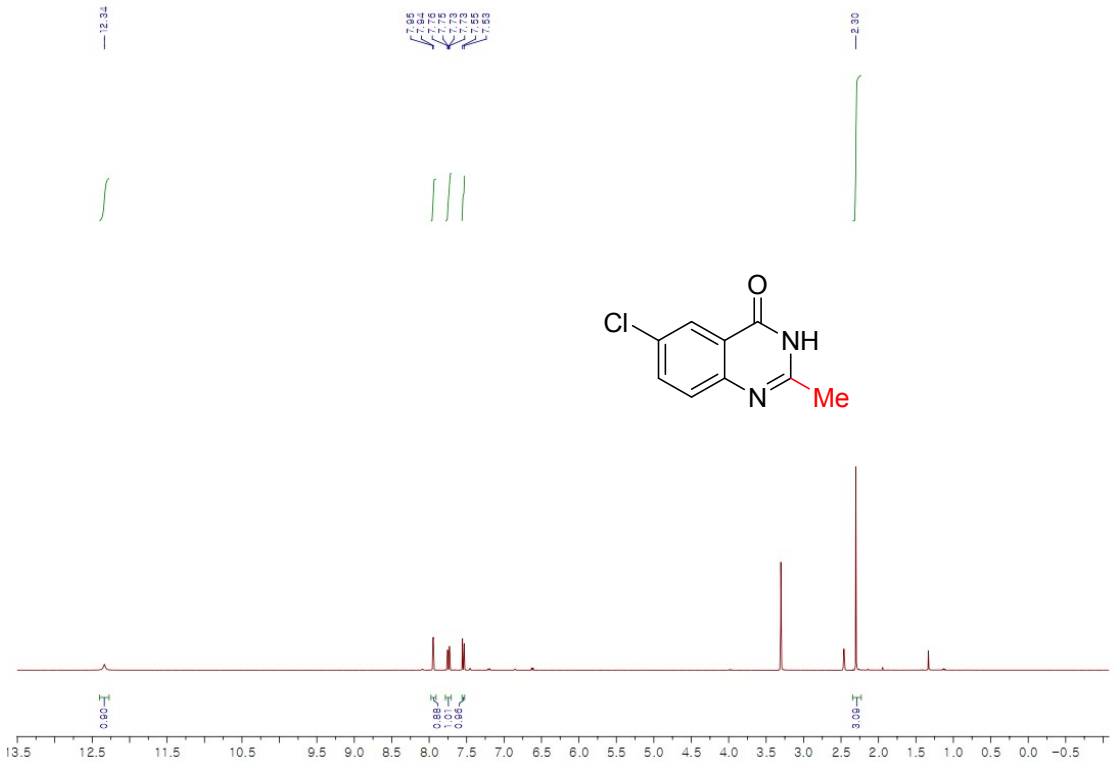
^{1}H & ^{13}C NMR of 2-phenyl-3-(2,2,2-trifluoroethyl)quinazolin-4(3*H*)-one **5m**

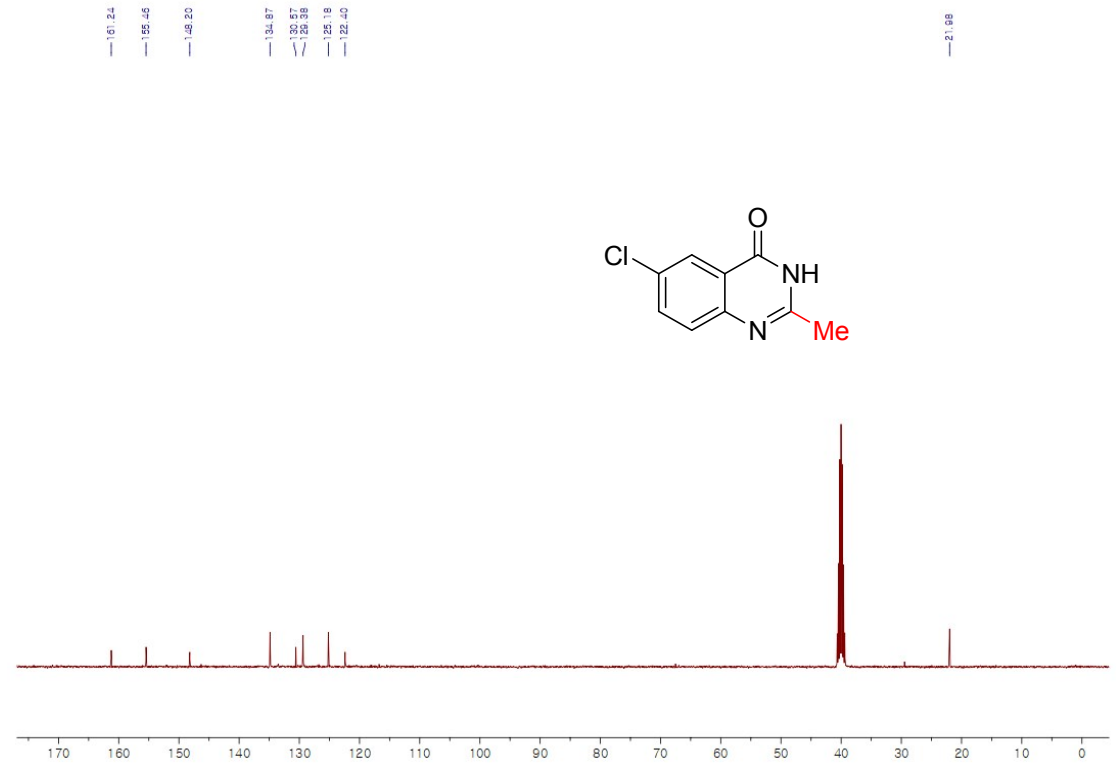


^{19}F NMR of 2-phenyl-3-(2,2,2-trifluoroethyl)quinazolin-4(3*H*)-one **5m**

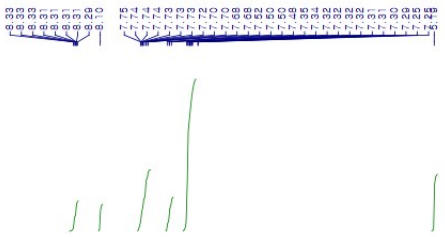


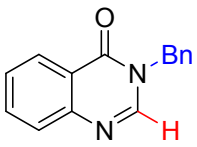
^{1}H & ^{13}C NMR of 6-chloro-2-methylquinazolin-4(3*H*)-one **5n**

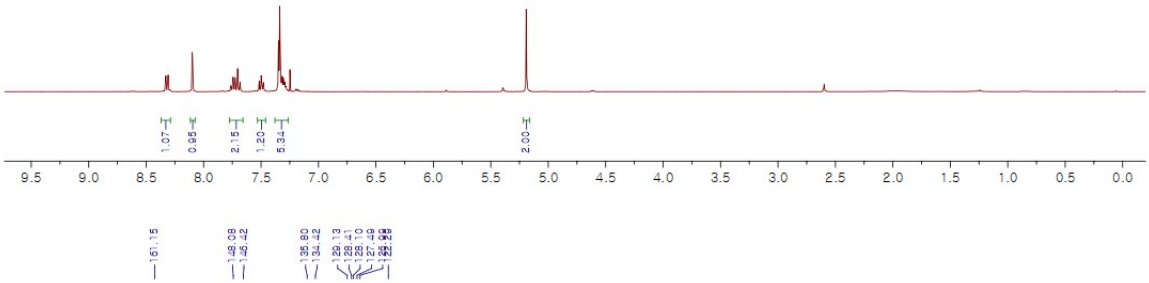


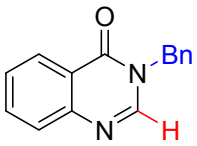


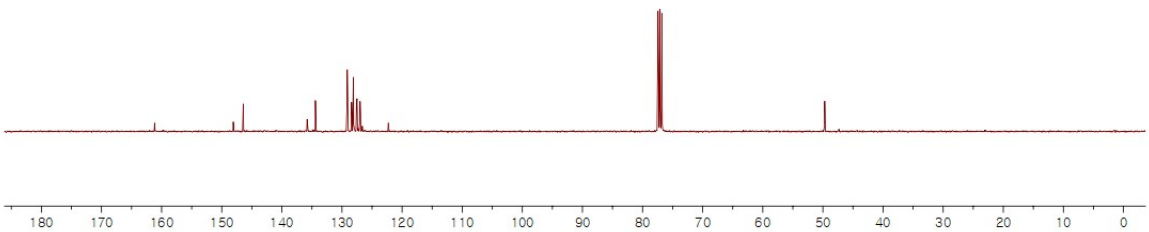
^{1}H & ^{13}C NMR of 3-benzylquinazolin-4(3*H*)-one **5o**



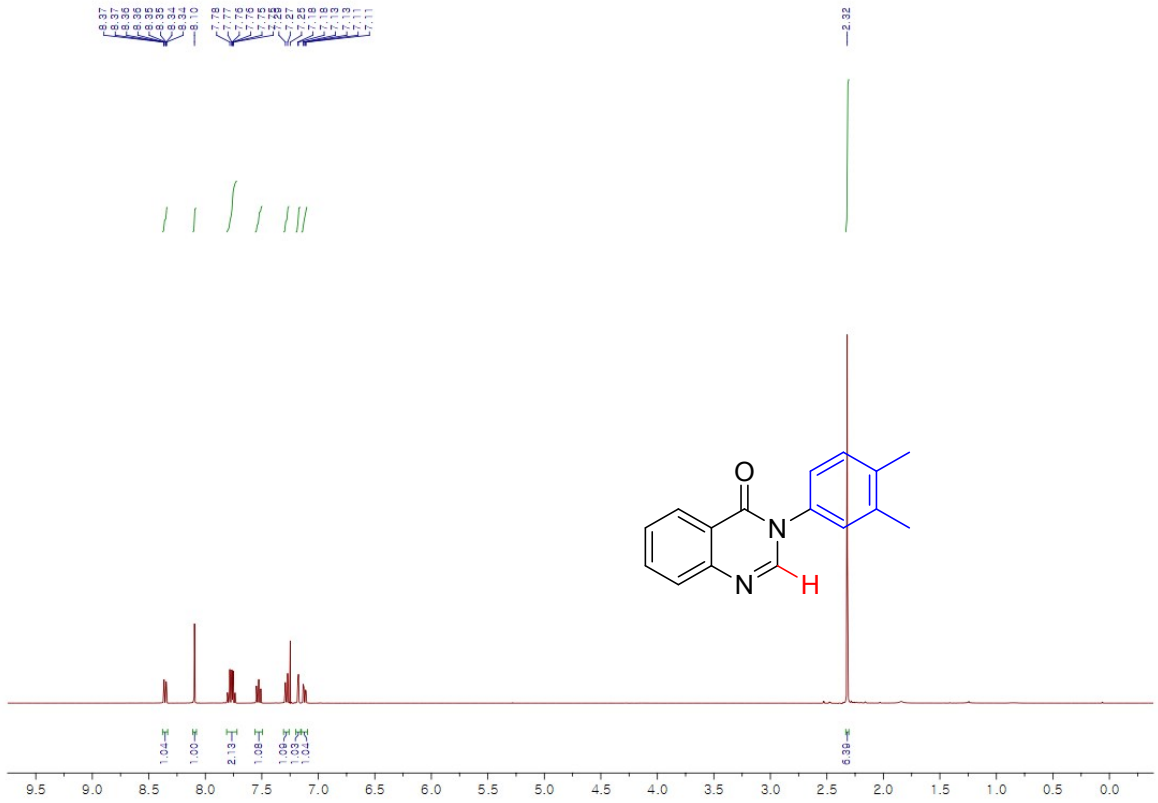


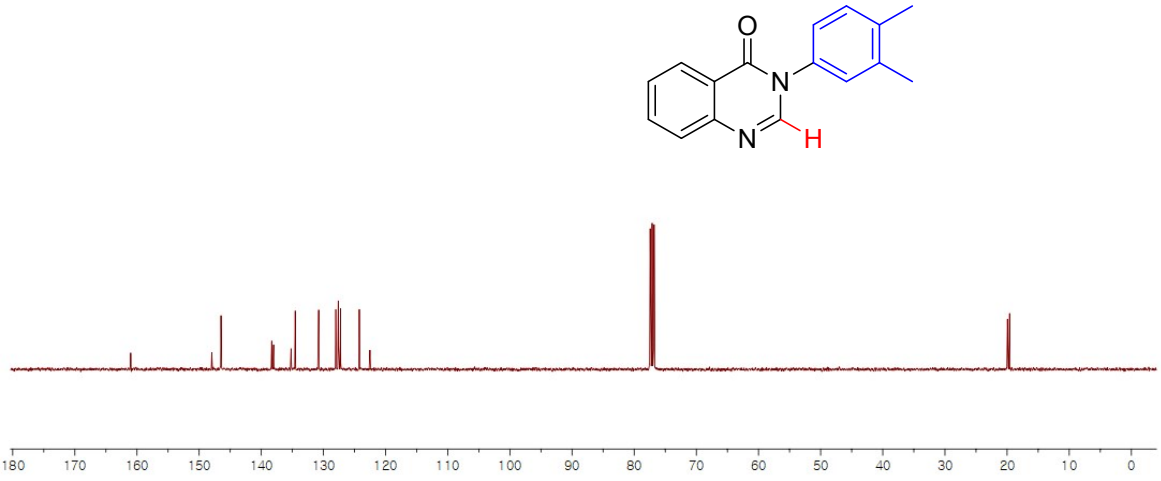




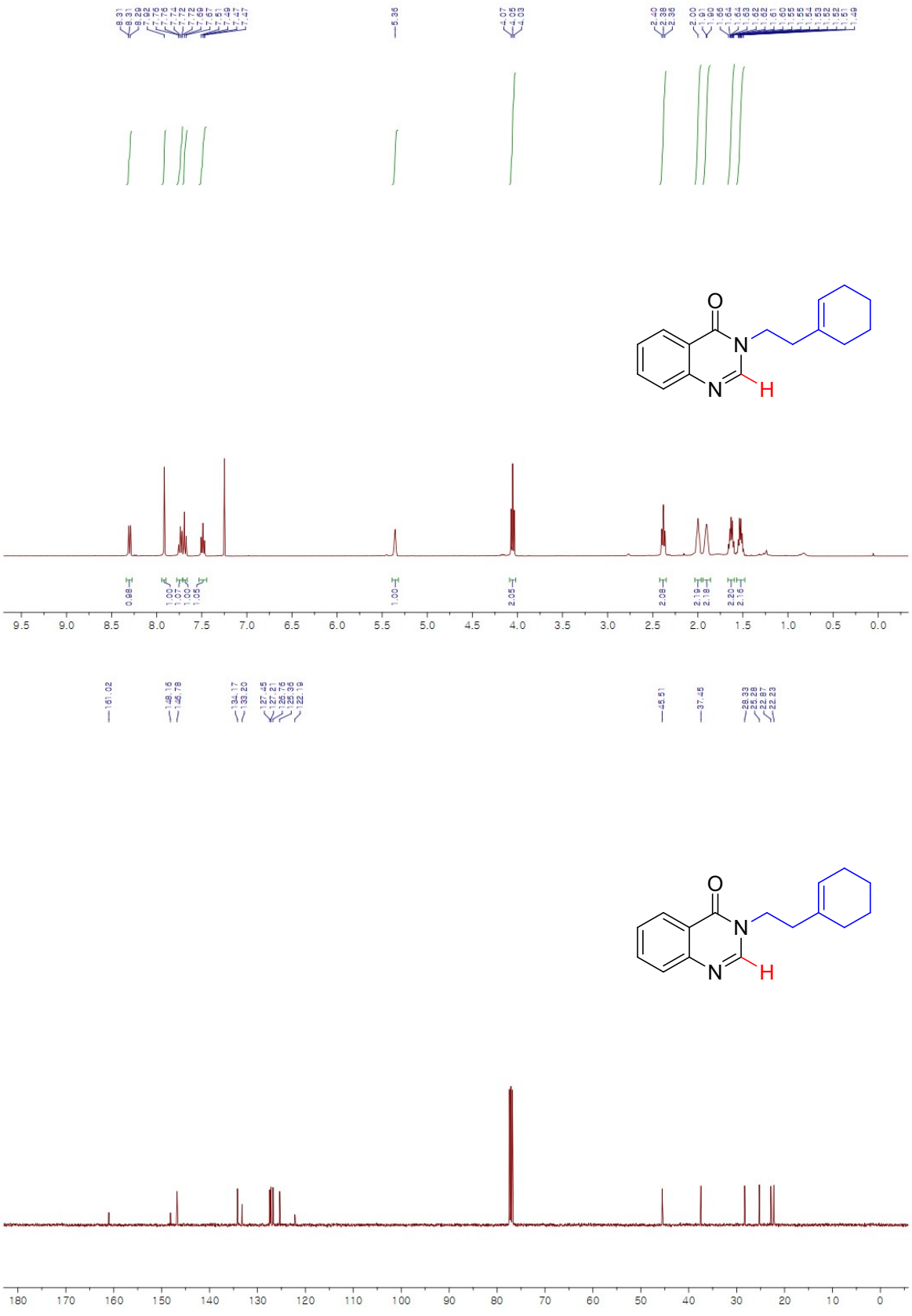


^{1}H & ^{13}C NMR of 3-(3,4-dimethylphenyl)quinazolin-4(3*H*)-one **5p**

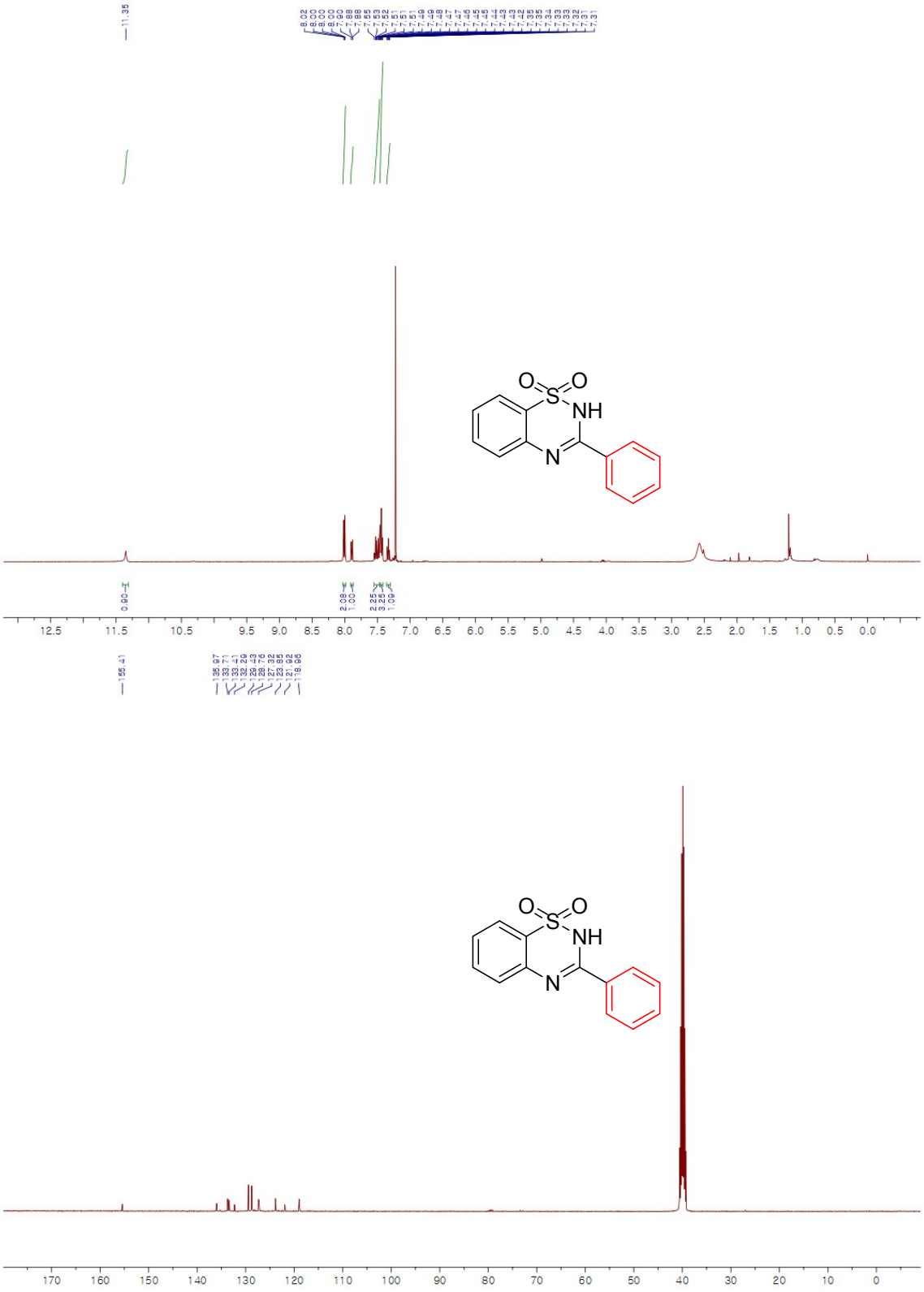




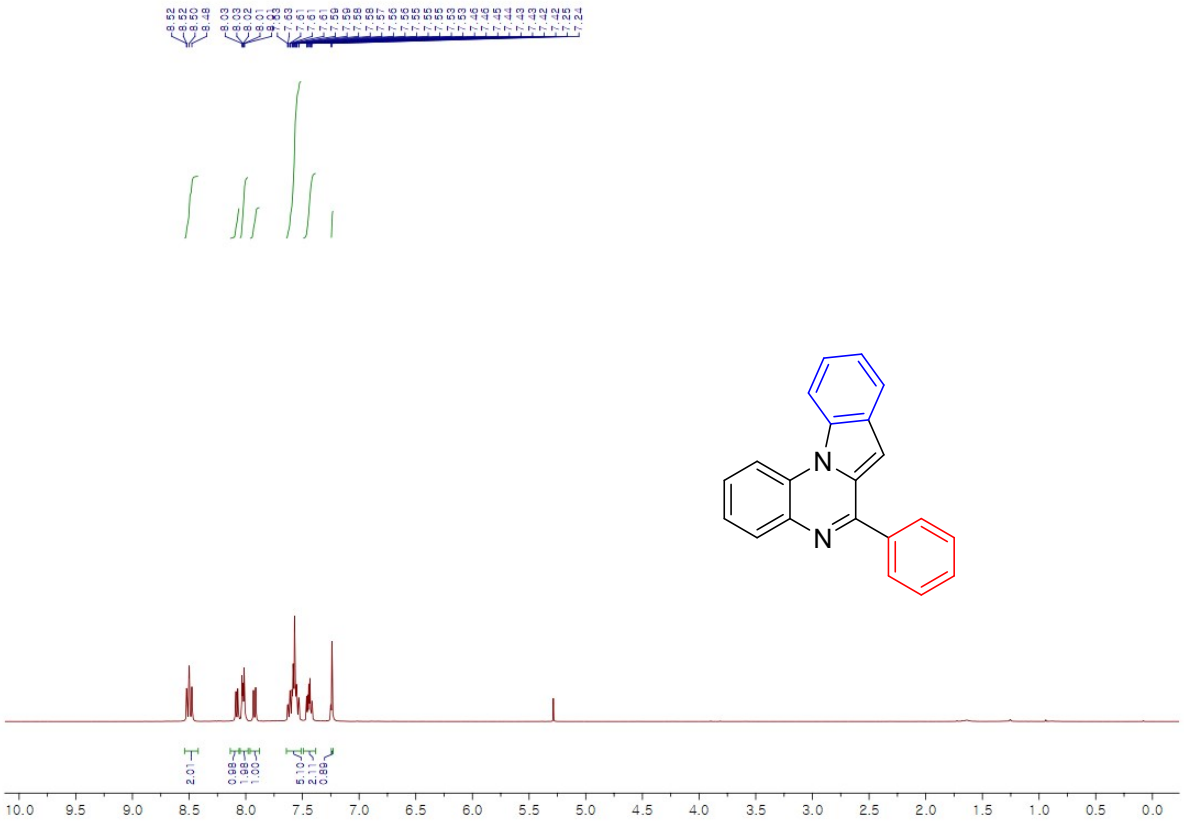
^{1}H & ^{13}C NMR of 3-(2-(cyclohex-1-en-1-yl)ethyl)quinazolin-4(3*H*)-one **5q**

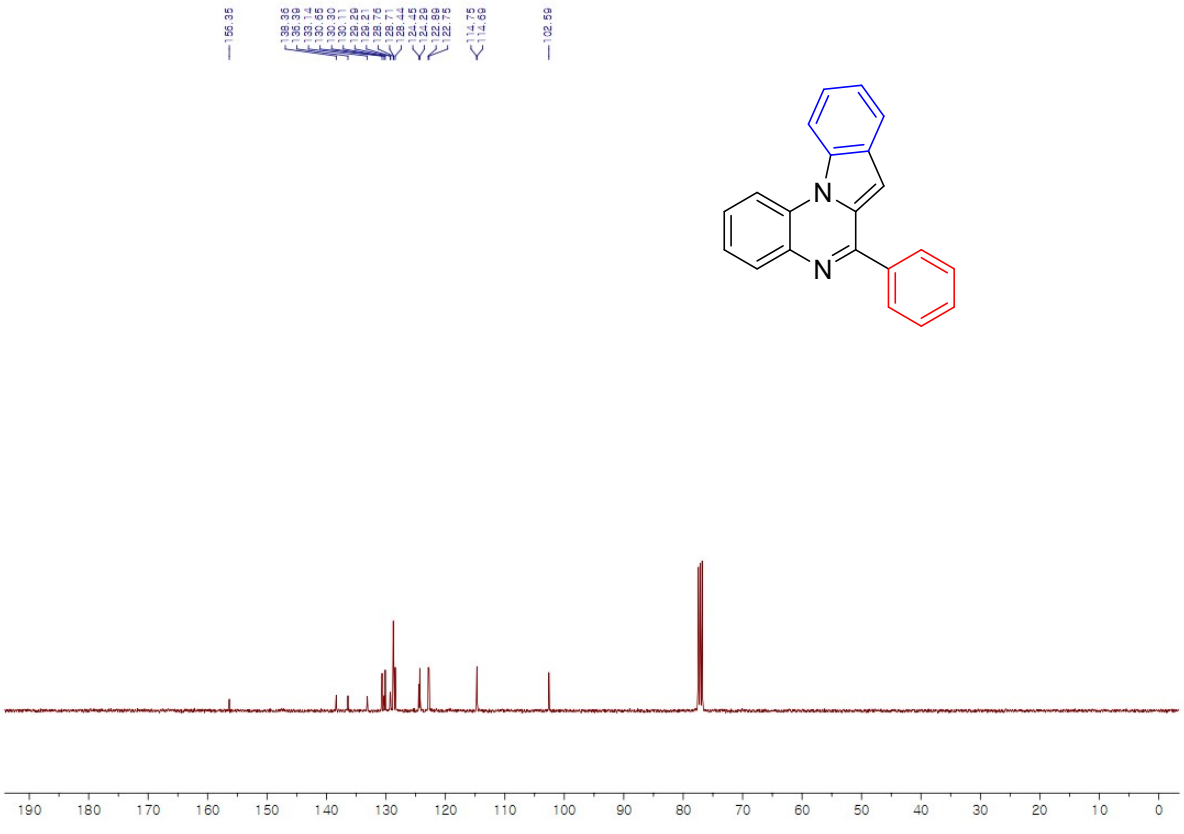


^{1}H & ^{13}C NMR of 3-phenyl-2*H*-benzo[*e*][1,2,4]thiadiazine 1,1-dioxide **6**



^{1}H & ^{13}C NMR of 6-phenylindolo[1,2-*a*]quinoxaline **7**





^{1}H & ^{13}C NMR of 2-methyl-3-(*o*-tolyl)quinazolin-4(3*H*)-one **8**