Supporting Information

Organocatalytic Modified Guareschi−Thorpe Type Regioselective Synthesis: A Unified Direct Access to 5,6,7,8-Tetrahydroquinolines and Other Alicyclic[*b*]-fused Pyridines

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1. Experimental Details & Characterization Data

1.1 General experimental

All glass apparatus were oven dried prior to use. Melting points were taken in open capillaries on complab melting point apparatus and are presented uncorrected. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrum 2 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on ECS 400 MHz (JEOL) NMR spectrometer using $CDCl_3$, and CD_3SOCD_3 as solvent and tetramethylsilane as internal reference. Electrospray ionization mass spectrometry (ESI-MS) and HRMS were recorded on Xevo G2-S QTof (Waters, USA) Spectrometer. Column chromatography was performed over Merck silica gel (particle size: 60-120 Mesh) procured from Qualigens™ (India), flash silica gel (particle size: 230-400 Mesh). All chemicals and reagents were obtained from Sigma Aldrich (USA), Merck (India) or Spectrochem (India) and were used without further purification.

1.2 General Procedures

1.2.1 General procedure for the Synthesis of methyl-2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate 22a (Table 1- Optimization study):

To a solution of the NH_4OAc **20** (0.3 mmol; 1.5 eq.) in EtOH (2.0 mL) was added freshly distilled cyclohexanone **21b** (0.3 mmol; 1.5 eq.) and the reaction mixture was stirred under N_2 atmosphere at room temperature for 25 min. Methyl 2,4-dioxo-4-phenylbutanoate **19a** (0.20 mmol; 1eq.) and specified organocatalysts (30 mol%, entry 2-10; Table 1) were added and the reaction mixture was further heated under N_2 atmosphere at 80 ˚C temperature for 4h. The progress of the reaction was checked by TLC using 9:1 Hexane/ethyl acetate as an eluent. After completion of reaction, the reaction mixture was quenched with distilled water and evaporated under reduced pressure, which afforded the crude product. The crude product was dissolved in distilled water (10 ml) and extracted with ethyl acetate (3 × 25 ml). The organic layers were combined, dried over anhydrous Na_2SO_4 and removed under reduced pressure to give the final crude product. The crude product were purified by using flash column chromatography method over silica gel using 9.5:0.5 to 9:1 hexane/ethyl acetate as an eluent; which afforded the pure desired methyl 2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate **22a** (yield = 21-65%) and methyl-4-hydroxy-2-oxo-4-phenylbut-3-enoate **19aa** (yield = 32-92%) as shown in Table 1 (entry 1-10).

1.2.2 General procedure for the Synthesis of methyl-2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate 22a (Table 2 study):

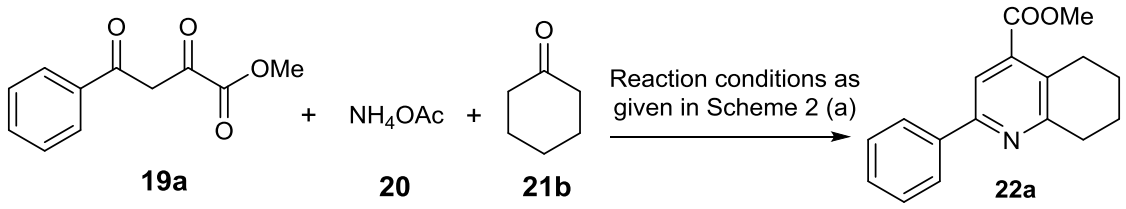
To a solution of the NH_4OAc **20** (0.3 mmol; 1.5 eq.) in EtOH (2.0 mL) was added freshly distilled cyclohexanone **21b** (0.3 mmol; 1.5 eq.), and the reaction mixture was stirred at room

temperature under N_2 atmosphere for 45 min. Methyl 2,4-dioxo-4-phenylbutanoate **19a (**0.20 mmol; 1eq.) and chitosan (as given in entry 1-16, Table 2) was added and the reaction mixture was heated under N_2 atmosphere at given temperature for specified time (as shown in entry 1-16, Table 2). The progress of the reaction was checked by TLC using 9:1 hexane/ethyl acetate as an eluent. After that, the reaction mixture was quenched with distilled water and evaporated under reduced pressure, which afforded the crude product. The crude product was dissolved in distilled water (10 ml) and extracted with ethyl acetate (3 × 10 ml). The organic layers were combined, dried over anhydrous Na_2SO_4 and removed under reduced pressure to give the crude product. The crude product were purified by using flash column chromatography method over silica gel using 9.5:0.5 to 9:1 hexane/ethyl acetate as an eluent which afforded the pure desired methyl 2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate **22a** and **19aa**. Further, the recovered **19aa** (0.10 mmol; 1eq.) was again subjected with **20** (0.15 mmol; 1.5 eq.) and **21** (0.15 mmol; 1.5 eq.) under same reaction procedure, which afforded pure methyl-2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate **22a** (yield = 20 - 87%, after 2 repeated steps), as shown in table 2.

1.2.3 General procedure for the Synthesis of 2-aryl/heteroaryl/alicyclic substituted tetrahydroquinoline pyridines and Alicyclic[*b*]-fused pyridines 22-31:

To a solution of the NH_4OAc **20** (0.3 mmol; 1.5 eq.) in 1,4-dioxane (2.0 mL) was added freshly distilled ketone **21a-21fb** (0.3 mmol; 1.5 eq.; as shown in scheme 2), or **21a-c** (0.3 mmol; 1.5 eq.; as shown in scheme 4) and the reaction mixture was stirred at room temperature under N_2 atmosphere for 45 min. Substituted diketo-ester **19a-n (**0.20 mmol; 1eq.; as shown in scheme 2) and chitosan (15 wt% with respect to **19a-n**, respectively) was added and the reaction mixture was heated under N_2 atmosphere at given temperature for 10-18h (as shown in Scheme 2 and 4). The progress of the reaction was checked by TLC using 9:1 hexane/ethyl acetate as an eluent. The reaction mixture was allowed to cool at room temperature. The reaction mixture was quenched with distilled water (1.0 mL) and the organic solvent was removed under reduced pressure afforded the crude residue. Then, the crude residue was dissolved in distilled water (10.0 ml) and extracted with ethyl acetate (3 × 50 ml). The organic layers were combined, dried over anhydrous Na_2SO_4 and removed under reduced pressure to give the crude product, which was purified through flash column chromatography over silica gel (230-400 mesh) using 9.5:0.5 to 9:1 hexane/ethyl acetate as an eluent afforded the pure product **22-31** (yield = upto 89%, after 2 repeated steps, as mentioned in table 2 study).

1.2.4 General procedure for the study of control experiment (synthesis of methyl-2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate 22a as representative product):

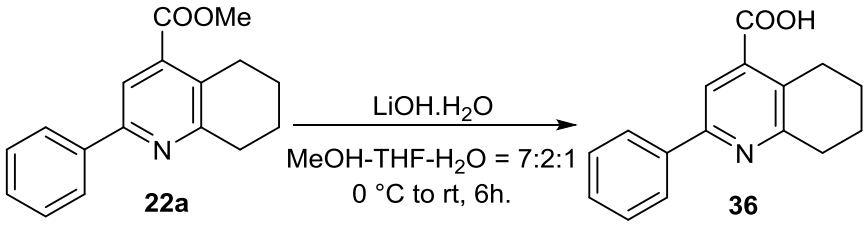


19a 20 21b 22a

Free-Radical Scavenger	Yield of **22a** (%)
(i) Tempo (30 mol%)	84
(ii) Tempo (100 mol%)	81
(iii) BHT (30 mol%)	79

The similar reaction procedures, as mentioned in Table 2 study, was followed using TEMPO (30 mol% and 100 mol%) and BHT (30 mol%) for the synthesis of methyl-2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate **22a** (yield = 79-84%).

1.2.5 Synthesis of 2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylic acid 36



22a 36

To a solution of methyl-2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate **22a** (60.0 mg, 0.22 mmol, 1eq.) in MeOH : THF : H_2O (10 ml, 7 : 2 : 1), added $LiOH.H_2O$ (14.1 mg, 0.33 mmol, 1.3 eq.) at 0 °C, and stirred for 6h at room temperature. The progress of the reaction was monitored by TLC using DCM/MeOH (98:02) as an eluent. After complete disappearance of starting material, the reaction mixture was quenched by saturated aq. NH_4Cl (2.0 mL) and evaporated the organic solvent under reduced pressure, afforded the crude residue. The residue was acidified with saturated aq. NH_4Cl (10.0 mL), diluted with distilled water (10.0 mL) and extracted with ethyl acetate (3 × 20 mL) followed by with brine (20 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure followed by recrystalization using EtOAc/Hexane (v/v = 10:90) furnished the pure 2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylic acid **36** as a white solid.

2. Characterization data of 2-aryl/heteroaryl/alicyclic substituted alicyclic[*b*]-fused pyridines 19aa, 22-31 and 36:

(Z)-methyl 4-hydroxy-2-oxo-4-phenylbut-3-enoate 19aa

Solid; yield: 32-92 % (As given in table 1), R_f (EtOAc/hexane; 05:95) = 0.45; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (7:3) as an eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.57 – 7.42 (m, 3H), 7.03 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 169.6, 162.6, 133.7, 132.4, 129.4, 129.2, 129.1, 97.9, 53.4; HRMS (ESI) calcd. for $C_{11}H_{11}O_4$ $[M+H]^+$: 207.0652; found 207.0656.

Methyl-2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylate 22a

Solid; yield: 87 % (46.6 mg) and gram scale yield: 79% [2.11 g; procedure was same as shown in section 2.2.4 under using NH_4OAc **20** (3.0 mmol), freshly distilled cyclohexanone **21a** (3.0 mmol) and methyl 2,4-dioxo-4-phenylbutanoate **19a** (2.0 mmol)**,** as shown in scheme 4]; R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 40-42 °C; FT-IR (KBr, νmax/cm^{-1}) 3436, 2920, 1732, 1590, 1437, 1247; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 7.88 (s, 1H), 7.51-7.37 (m, 3H), 3.94 (s, 3H), 3.07 (t, *J* = 6.0 Hz, 4H), 1.94 – 1.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 159.3, 154.8, 139.1, 138.2, 134.0, 128.9, 128.1, 126.9, 118.0, 52.5, 33.8, 27.0, 22.8, 22.7; HRMS (ESI) calcd. for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332; found 268.1337.

Methyl-2-(p-tolyl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 22b

Solid; yield: 81 % (45.6 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 55-60 °C; FT-IR (KBr, νmax/cm^{-1}) 3439, 2933, 1730, 1551, 1436, 1255; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (t, *J* = 8.4 Hz, 3H), 7.25 – 7.24 (m, 2H), 3.92 (s, 3H), 3.04 (t, *J* = 6.8 Hz, 4H), 2.39 (s, 3H), 1.92 – 1.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 159.2, 154.7, 138.9, 138.1, 136.3, 130.1, 129.6, 126.8, 117.6, 52.4, 33.8, 29.8, 26.9, 22.8, 22.7, 21.4; HRMS (ESI) calcd. for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1489; found 282.1487.

Methyl-2-(4-methoxyphenyl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 22c

Solid; yield: 76 % (45.2 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 53-55 °C; FT-IR (KBr, νmax/cm^{-1}) 3431, 2929, 1729, 1606, 1550, 1436, 1250; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.82 (s, 1H), 6.99 – 6.97 (m, 2H), 3.93 (s, 3H), 3.86 (s, 3H), 3.06 – 3.03 (m, 4H), 1.92 –

1.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 160.5, 159.0, 154.4, 138.1, 131.8, 129.7, 128.2, 117.3, 114.2, 55.5, 52.4, 33.8, 29.8, 26.9, 22.9, 22.7; HRMS (ESI) calcd. for $C_{18}H_{20}NO_3$ $[M+H]^+$: 298.1438; found 298.1434.

Methyl-2-(4-chlorophenyl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 22d

Solid; yield: 75 % (45.1 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 48-50 °C; FT-IR (KBr, νmax/cm^{-1}) 3407, 2925, 1711, 1545,1436, 1245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.84 (s, 1H), 7.43 - 7.40 (m, 2H), 3.94 (s, 3H), 3.05 (q, *J* = 6.0 Hz, 4H), 1.94 – 1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 159.5, 153.4, 138.2, 137.5, 135.1, 130.9, 129.0, 128.2, 117.7, 52.5, 33.8, 29.8, 27.0, 22.8; HRMS (ESI) calcd. for $C_{17}H_{17}ClNO_2$ $[M+H]^+$: 302.0942; found 302.0948.

Methyl-2-(4-fluorophenyl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 22e

Solid; yield: 78 % (44.3 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 48-50 °C; FT-IR (KBr, νmax/cm^{-1}) 3434, 2929, 1711, 1603, 1548, 1403, 1232; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.83 (s, 1H), 7.16 – 7.11 (m, 2H), 3.94 (s, 3H), 3.05 – 3.04 (m, 4H), 1.93 – 1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 164.8, 162.4, 159.4, 153.7, 138.3, 135.2, 130.6, 128.8, 128.7, 117.7, 115.9, 115.6, 52.5, 33.8, 29.8, 26.9, 27.8, 22.7; HRMS (ESI) calcd. for $C_{17}H_{17}FNO_2$ $[M+H]^+$: 286.1238; found 286.1234.

Methyl-2-(4-bromophenyl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 22f

Solid; yield: 83 % (57.2 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 40-42 °C; FT-IR (KBr, νmax/cm^{-1}) 3438, 2926, 1731, 1590, 1550, 1444, 1245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 3H), 7.59 – 7.56 (m, 2H), 3.94 (s, 3H), 3.06 – 3.03 (m, 4H), 1.92-1.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 159.5, 153.4, 138.3, 137.9, 131.9, 131.3, 128.5, 123.4, 117.7, 52.5, 33.8, 29.8, 27.1, 22.8, 22.7; HRMS (ESI) calcd. for $C_{17}H_{17}BrNO_2$ $[M+H]^+$: 346.0437; found 346.0443.

Methyl-2-(2,4-dichlorophenyl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 22g

Solid; yield: 80 % (53.7 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 72-74 °C; FT-IR (KBr, νmax/cm^{-1}) 3433, 2925, 1736, 1629, 1461, 1379, 1258; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.53

– 7.48 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.11 – 3.03 (m, 4H), 1.93 – 1.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 159.5, 153.0, 137.5, 137.4, 134.9, 133.1, 132.5, 131.5, 129.9, 127.6, 122.0, 52.6, 33.6, 27.0, 22.7, 22.6; HRMS (ESI) calcd. for $C_{17}H_{16}Cl_2NO_2$ $[M+H]^+$: 336.0553; found 336.0559.

Methyl-2-phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 23a

Solid; yield: 89 % (44.9 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 70-72 °C; FT-IR (KBr, νmax/cm^{-1}) 3430, 2926, 1723, 1573,1432, 1384, 1245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.99 (m, 3H), 7.49-7.38 (m, 3H), 3.96 (s, 3H), 3.31 (t, *J* = 8.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.22-2.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 166.8, 156.8, 139.3, 136.4, 134.1, 128.9, 128.8, 127.0, 117.8, 52.5, 34.5, 31.7, 22.9; HRMS (ESI) calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.1176; found 254.1171.

Methyl-2-(p-tolyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 23b

Solid; yield: 86 % (46.1 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 80-81 °C; FT-IR (KBr, νmax/cm^{-1}) 3430, 2948, 1788, 1573, 1435, 1384, 1245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 3.96 (s, 3H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.22-2.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 166.9, 156.8, 138.9, 136.4, 136.0, 134.1, 129.6, 126.9, 117.4, 52.5, 34.5, 31.7, 22.9, 21.4; HRMS (ESI) calcd. for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332; found 268.1339.

Methyl-2-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 23c

Solid; yield: 81 % (45.9 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 103-105°C; FT-IR (KBr, νmax/cm^{-1}) 3424, 2961, 1717, 1607, 1568, 1362, 1270; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 3H), 3.86 (s, 3H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.21 - 2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 166.9, 160.5, 156.5, 135.5, 134.1, 131.9, 128.3, 117.0, 114.2, 55.5, 52.4, 34.5, 31.7, 22.9; HRMS (ESI) calcd. for $C_{17}H_{18}NO_3$ $[M+H]^+$: 284.1281; found 284.1286.

Methyl-2-(4-chlorophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 23d

Solid; yield: 83 % (47.5 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 80-81 °C; FT-IR (KBr, νmax/cm^{-1})

3422, 2945, 1718, 1614, 1576, 1493, 1397, 1270; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.84 (m, 3H), 7.44-7.41 (m, 2H), 3.96 (s, 3H), 3.30 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 2.20 - 2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 166.6, 155.5, 137.7, 136.8, 135.1, 134.2, 129.1, 128.3, 117.5, 52.5, 34.5, 31.7, 22.9; HRMS (ESI) calcd. for $C_{16}H_{15}ClNO_2$ $[M+H]^+$: 288.0786; found 288.0781.

Methyl-2-(4-fluorophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 23e

Solid; yield: 86 % (45.2 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 77-79 °C; FT-IR (KBr, νmax/cm^{-1}) 3429, 2922, 1728, 1513, 1383, 1240; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 3H), 7.17-7.12 (m, 2H), 3.96 (s, 3H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 2.21-2.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 166.7, 155.8, 136.4, 134.2, 128.9, 128.8, 117.5, 115.9, 115.7, 52.5, 34.5, 31.7, 22.9; HRMS (ESI) calcd. for $C_{16}H_{15}FNO_2$ $[M+H]^+$: 272.1081; found 272.1087.

Methyl-2-(4-bromophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 23f

Solid; yield: 80 % (53.2 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 90-92 °C; FT-IR (KBr, νmax/cm^{-1}) 3411, 1716, 1574,1438, 1395, 1204; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 2.22-2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7,166.6, 155.5, 138.1, 136.9, 134.2, 132.0, 128.6, 123.4, 117.5, 52.5, 34.5, 31.7, 22.9; HRMS (ESI) calcd. for $C_{16}H_{15}BrNO_2$ $[M+H]^+$: 332.0281; found 332.0289.

Methyl-2-(2,4-dichlorophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 23g

Solid; yield: 77 % (49.8 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 83-85°C; FT-IR (KBr, νmax/cm^{-1}) 3441, 2918, 1715, 1611, 1590, 1434, 1364,1270; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.54-7.49 (m, 2H), 7.35-7.33 (m, 1H), 3.95 (s, 3H), 3.34 (t, *J* = 7.2 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 2H), 2.24-2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.4, 154.7, 137.6, 137.3, 134.9, 133.5, 133.2, 132.5, 129.9, 127.5, 121.8, 52.6, 34.4, 31.8, 22.8; HRMS (ESI) calcd. for $C_{16}H_{14}Cl_2NO_2$ $[M+H]^+$: 322.0396; found 322.0391.

Methyl-2-phenyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine-4-carboxylate 24a

Sticky solid; yield: 76 % (42.8 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over

silica gel using hexane/ethyl acetate (9:1) as an eluent; FT-IR (KBr, νmax/cm^{-1}) 3450, 2922, 1729, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.99 (m, 2H), 7.73 (s, 1H), 7.47 – 7.36 (m, 3H), 3.94 (s, 3H), 3.22 – 3.19 (m, 2H), 3.04 – 3.01 (m, 2H), 1.91– 1.87(m, 2H), 1.78–1.72(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 165.4, 154.0, 139.0, 135.1, 128.9, 128.8, 126.9, 117.2, 52.6, 39.6, 32.3, 29.8, 27.4, 26.6.; HRMS (ESI) calcd. for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1489; found 282.1497.

Methyl-2-(4-methoxyphenyl)-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine-4-carboxylate 24b

Sticky solid; yield: 71 % (44.3 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; FT-IR (KBr, νmax/cm^{-1}) 3445, 2924, 1704, 1580, 1426, 1235; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.66 (s, 1H), 6.97 (d, *J* = 9.2 Hz, 2H), 3.93 (s, 3H), 3.84 (s, 3H), 3.19 – 3.16 (m, 2H), 3.01 – 3.98 (m, 2H), 1.88 – 1.87 (m, 2H), 1.75 – 1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 165.2, 160.4, 153.7, 138.8, 134.3, 131.7, 128.1, 116.4, 114.2, 55.5, 52.6, 39.6, 32.3, 29.7, 27.5, 26.6; HRMS (ESI) calcd. for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594; found 312.1599.

Methyl-2-phenyl-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridine-4-carboxylate 25

Solid; yield: 72 % (42.4 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 55-56 °C; FT-IR (KBr, νmax/cm^{-1}) 3437, 2925, 1727, 1581, 1494, 1331, 1230; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.85 (s, 1H), 7.48 – 7.45 (m, 2H), 7.41 – 7.38 (m, 1H), 3.95 (s, 3H), 3.15 – 3.07 (m, 4H), 1.88 – 1.79 (m, 4H), 1.50 – 1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 163.6, 154.8, 139.1, 138.3, 133.3, 128.9, 128.8, 126.9, 118.1, 55.5, 35.8, 31.3, 31.1, 27.5, 26.7, 26.0; HRMS (ESI) calcd. for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1645; found 296.1652.

Methyl-2-([1,1'-biphenyl]-4-yl)-6,7-dihydro-5H-cyclopenta[b]pyridine-4-carboxylate 26a

Solid; yield: 83 % (54.5 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 117-119 °C; FT-IR (KBr, νmax/cm^{-1}) 3428, 2953, 1604, 1727, 1573, 1487, 1244; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.07 (m, 3H), 7.72-7.65 (m, 4H), 7.46-7.35 (m, 3H), 3.97 (s, 3H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.17 (t, *J* = 8.0 Hz, 2H), 2.24-2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 166.8, 156.3, 141.7, 140.8, 138.2, 136.5, 134.2, 128.9, 127.6 (2-C), 127.4, 127.3, 117.7, 52.5, 34.6, 31.7, 22.9; HRMS (ESI) calcd. for $C_{22}H_{20}NO_2$ $[M+H]^+$: 330.1489; found 330.1482.

Methyl-2-([1,1'-biphenyl]-4-yl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 26b

Solid; yield: 85 % (58.5 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 65-67 °C; FT-IR (KBr, νmax/cm^{-1}) 3423, 2945, 1720, 1570, 1352, 1245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.94 (s, 1H), 7.71 - 7.65 (m, 4H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.39 - 7.35 (m, 1H), 3.95 (s, 3H), 3.09 (t, *J* = 6.0 Hz, 4H), 1.94-1.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 159.4, 154.2, 141.7, 140.8, 138.2, 137.9, 130.6, 128.9, 127.6, 127.5, 127.3, 127.2, 117.8, 52.5, 33.8, 27.0, 22.8, 22.7; HRMS (ESI) calcd. for $C_{23}H_{22}NO_2$ $[M+H]^+$: 344.1645; found 344.1651.

Methyl-2-(4-cyclohexylphenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 27a

Solid; yield: 79 % (52.8 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 80-82 °C; FT-IR (KBr, νmax/cm^{-1}) 3434, 2922, 1614, 1727, 1573, 1440, 1349, 1243; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93 - 7.91 (m, 2H), 7.32-7.29 (m, 2H), 3.95 (s, 3H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 2.58 - 2.53 (s, 1H), 2.22-2.14 (m, 2H), 1.92 - 1.75 (m, 5H), 1.51 - 1.23 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 166.9, 156.9, 149.1, 136.9, 135.9, 134.0, 127.4, 126.9, 117.5, 52.4, 44.5, 34.5 (2-c), 31.7, 27.0, 26.3, 22.9; HRMS (ESI) calcd. for $C_{22}H_{26}NO_2$ $[M+H]^+$: 336.1958; found 336.1954.

Methyl-2-(4-cyclohexylphenyl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 27b

Solid; yield: 74 % (51.7 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 62-64 °C; FT-IR (KBr, νmax/cm^{-1}) 3430, 2930, 1725, 1607, 1444, 1245; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 3.07 – 3.03 (m, 4H), 2.58 – 2.55 (m, 1H), 1.90 – 1.74 (m, 9H), 1.50 – 1.26 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 159.2, 154.9, 149.1, 138.1, 136.8, 130.1, 127.4, 126.9, 117.7, 52.4, 44.5, 34.5, 33.8, 27.0, 26.3, 22.9, 22.7; HRMS (ESI) calcd. for $C_{23}H_{28}NO_2$ $[M+H]^+$: 350.2115; found 350.2120.

Methyl 2-(naphthalen-2-yl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-4-carboxylate 28a

Solid; yield: 81 % (49.3 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 93-95 °C; FT-IR (KBr, νmax/cm^{-1}) 3426, 2952, 1717, 1575, 1430, 1387, 1248; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.17 - 8.14 (m, 2H), 7.95 - 7.86 (m, 3H), 7.51 - 7.49 (m, 2H), 3.99 (s, 3H), 3.33 (t, *J* = 7.6 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 2H), 2.25 - 2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 166.8,

156.6, 136.5, 134.2, 133.6, 133.5, 128.8, 128.6, 127.8, 126.6, 126.4, 126.3, 124.7, 118.0, 52.5, 34.5, 31.7, 22.9; HRMS (ESI) calcd. for $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1332; found 304.1339.

Methyl-2-(naphthalen-2-yl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 28b

Solid; yield: 77 % (48.9 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 65-67 °C; FT-IR (KBr, νmax/cm^{-1}) 3435, 2925, 1728, 1636, 1432, 1147; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.16 – 8.14 (m, 1H), 8.03 (s, 1H), 7.94 – 7.92 (m, 3H), 7.51 – 7.49 (m, 2H), 3.96 (s, 3H), 3.11 – 3.09 (m, 4H), 1.95 – 1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 159.4, 154.6, 138.3, 136.4, 133.8, 133.7, 130.7, 128.8, 128.6, 127.8, 126.6, 126.4, 126.2, 124.7, 118.2, 52.5, 33.9, 29.8, 27.1, 22.9, 22.8; HRMS (ESI) calcd. for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1489; found 318.1480.

Methyl-2-(1-benzyl-1*H*-indol-3-yl)-5,6,7,8-tetrahydroquinoline-4-carboxylate 29

Solid; yield: 43 % (34.5 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 120-122 °C; FT-IR (KBr, νmax/cm^{-1}) 3436, 2935, 1704, 1590, 1448, 1380, 1231; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41– 8.39 (m, 1H), 7.82 (s, 1H), 7.72 (s, 1H), 7.31– 7.19 (m, 6H), 7.15–7.13 (m, 2H), 5.37 (s, 2H), 3.92 (s, 3H), 3.07– 3.01(m, 4H), 1.94–1.80 (m, 4H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 158.9, 152.2, 137.8, 137.5, 137.1, 128.9, 128.3, 128.0, 127.9, 126.9, 126.4, 122.5, 121.7, 120.9, 117.7, 116.2, 110.1, 52.4, 50.4, 33.9, 26.9, 23.0, 22.8; HRMS (ESI) calcd. for $C_{26}H_{25}N_2O_2$ $[M+H]^+$: 397.1911; found 397.1918.

Methyl-2-(furan-2-yl)-5, 6, 7, 8-tetrahydroquinoline-4-carboxylate 30

Solid; yield: 41 % (21.2 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; m.p. 60-62 °C; FT-IR (KBr, νmax/cm^{-1}) 3438, 2936, 1720, 1607, 1550, 1437,1327, 1242; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.52 (s, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 6.52 – 6.50 (m, 1H), 3.92 (s, 3H), 3.02 (q, *J* = 6.4 Hz, 4H), 1.91 – 1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 159.3, 153.2, 146.7, 143.4, 138.0, 130.5, 116.3, 112.0, 108.5, 52.5, 33.7, 27.0, 22.7, 22.6; HRMS (ESI) calcd. for $C_{15}H_{16}NO_3$ $[M+H]^+$: 258.1125; found 258.1129.

Methyl-2-cyclopropyl-5,6,7,8-tetrahydroquinoline-4-carboxylate 31

Sticky solid; yield: 72 % (33.4 mg, procedure was same as **22a**), R_f (EtOAc/hexane; 05:95) = 0.80; Purification of crude product was done by flash column chromatography method over silica gel using hexane/ethyl acetate (9:1) as an eluent; FT-IR (KBr, νmax/cm^{-1}) 3442, 2936,

1730, 1555, 1408, 1289; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 3.87 (s, 3H), 2.94 (t, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 12.8 Hz, 2H), 2.03 – 1.97 (m, 1H), 1.85 – 1.73 (m, 4H), 0.97 – 0.89 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 159.9, 158.4, 137.5, 128.3, 117.3, 52.3, 33.6, 26.7, 22.8, 22.7, 17.0, 14.2, 9.5; HRMS (ESI) calcd. for $C_{14}H_{18}NO_2$ $[M+H]^+$: 232.1332; found 232.1338.

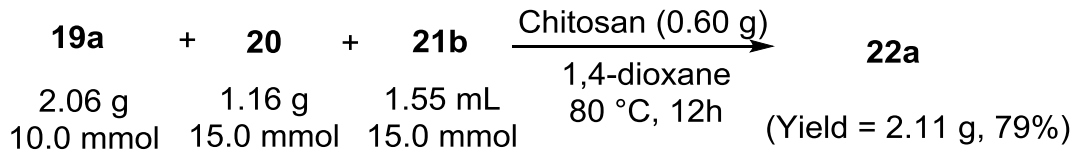
2-phenyl-5,6,7,8-tetrahydroquinoline-4-carboxylic acid 36

Solid; Yield: 94 % (53.5 mg), R_f (DCM/MeOH; 98:02) = 0.30; m.p. 180-182 °C; FT-IR (KBr, νmax/cm^{-1}) 3431, 2934, 1731, 1585, 1435, 1246; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 1H) 7.49 – 7.39 (m, 3H), 2.96 – 2.92 (m, 4H), 1.83 – 1.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 158.4, 153.2, 140.3, 138.1, 129.5, 129.2, 128.9, 126.5, 116.8, 33.1, 26.4, 22.3 (2-C); HRMS (ESI) calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.1176; found 254.1179.

3. Table S1. Reusability of chitosan catalyst.

Entry	Reusability	Time (h)	Yield (%)
1	Fresh Chitosan	10	87
2	First cycle	10	86
3	Second cycle	10	83
4	Third cycle	12	81
5	Fourth cycle	12	78

4. Gram Scale Synthesis of representative compound 22a.



General procedure for the gram scale synthesis of representative alicyclic[*b*]-fused pyridines 22a:

To a solution of the NH_4OAc **20** (15.0 mmol; 1.5 eq.) in 1,4-dioxane (40.0 mL) was added freshly distilled ketone **21b** (15.0 mmol; 1.5 eq.), and the reaction mixture was stirred at room temperature under N_2 atmosphere for 90 min. Substituted diketo-ester **19a** (10.0 mmol; 1 eq.) and chitosan (15 wt% with respect to **19a**) was added and the reaction mixture was heated under N_2 atmosphere at given temperature for 12h. The progress of the reaction was checked by TLC using 9:1 hexane/ethyl acetate as an eluent. The reaction mixture was allowed to cool at room temperature. The reaction mixture was quenched with distilled water (20 mL) and the organic solvent was removed under reduced pressure afforded the crude residue. Then, the crude residue was dissolved in distilled water (100 mL) and extracted with ethyl acetate (3 × 100 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and removed under reduced pressure to give the crude product, which was purified through

flash column chromatography over silica gel (230-400 mesh) using 9.5:0.5 to 9:1 hexane/ethyl acetate as an eluent afforded the pure product **22a** (yield = 2.11 g; 79%; after 2 repeated steps, as mentioned in table 2 study).

5 (a). The 5,6,7,8-tetrahydroquinoline analogues **29**, **30** and **31** were assessed for their *in vitro* antifungal activity against *Aspergillus Niger* and *Candida Albicans* fungal strains. **29** was found twice active compared to standard drug ketoconazole; While **31** was found equally active compared to ketoconazole in *Aspergillus Niger* fungal strain. However, **31** was also found equally active to ketoconazole in *Candida albicans* fungal strain (Table 2).

Table S2. *In vitro* antifungal activity evaluation of **29**, **30** and **31**.

S. No.	Compound name	[a]Fungal Strains (MIC in µg/mL)	
		AN[b]	***CA***[b]
1	**29**	6.25	50
2	**30**	25	100
3	**31**	12.5	25
4	**KET**[c]	12.5	25

[a]MIC of all compounds were measured at the range from 6.25-100 µg/mL.
[b]Fungi: AN, *Aspergillus Niger* (ATCC 9029); CA, *Candida Albicans* (ATCC 10231); [c]KET: Ketoconazole

5 (b). Material and method of antifungal activity evaluation protocol

The *in vitro* antifungal activities of selected tetrahydroquinoline analogues **29**, **30** and **31** were tested against the pathogenic fungus, namely, *Aspergillus Niger* and *Candida Albicans* species cultured on potato dextrose agar medium [prepared by taking 11 ml of distilled water followed by the addition of following ingredients: mycological peptone (10 g), dextrose (30 g), and agar (12 g)]. The pH of the solution was maintained to 5.7 and boiling was continued until complete dissolution. After that, the solution was sterilized under autoclave at 15 lb pressure (120 °C for 20 min) by diffusion method and further incubated at 28 °C for 3 days. Test solutions of different concentrations (microgram per litre) were prepared in DMSO solution.

6. Characterization spectra (^{1}H and ^{13}C NMR) of 2-aryl/heteroaryl/alicyclic substituted alicyclic[*b*]-fused pyridines 19aa, 22-31 and 36:

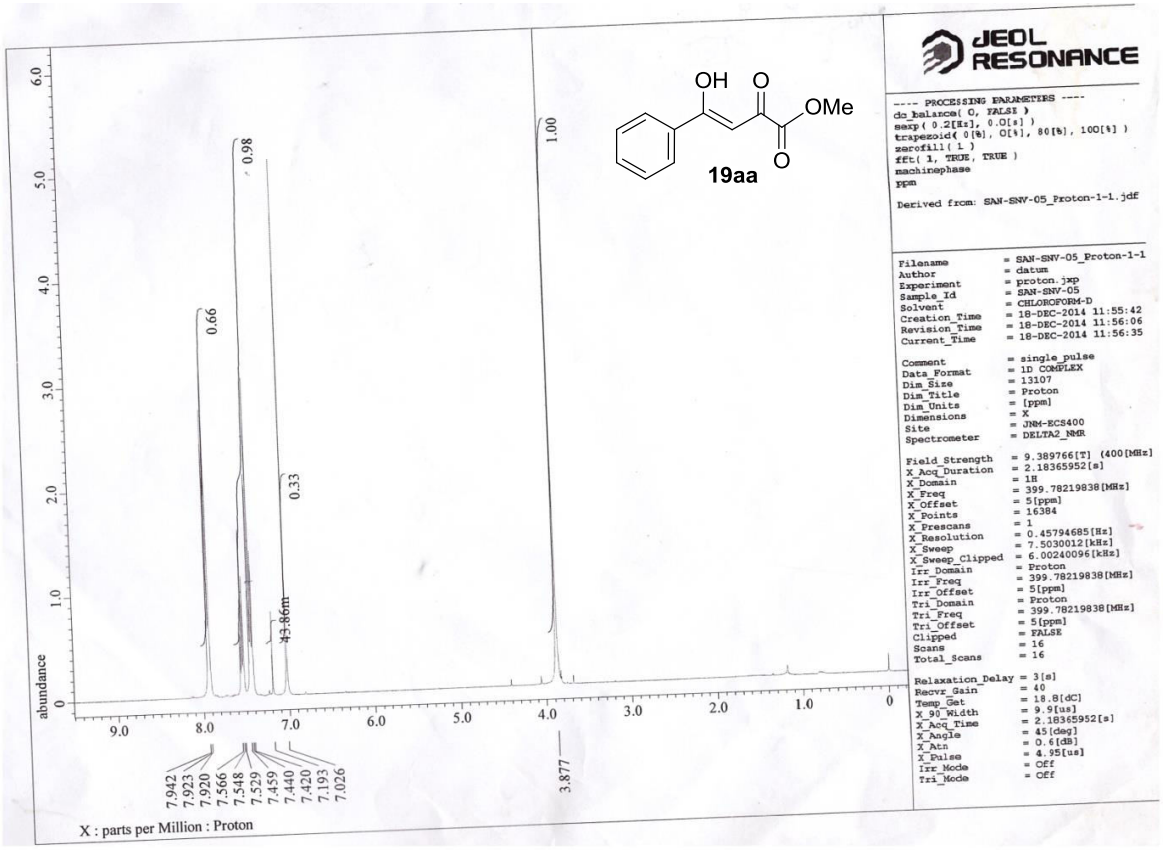


Figure 1. ^{1}H NMR Spectra of Compound **19aa**.

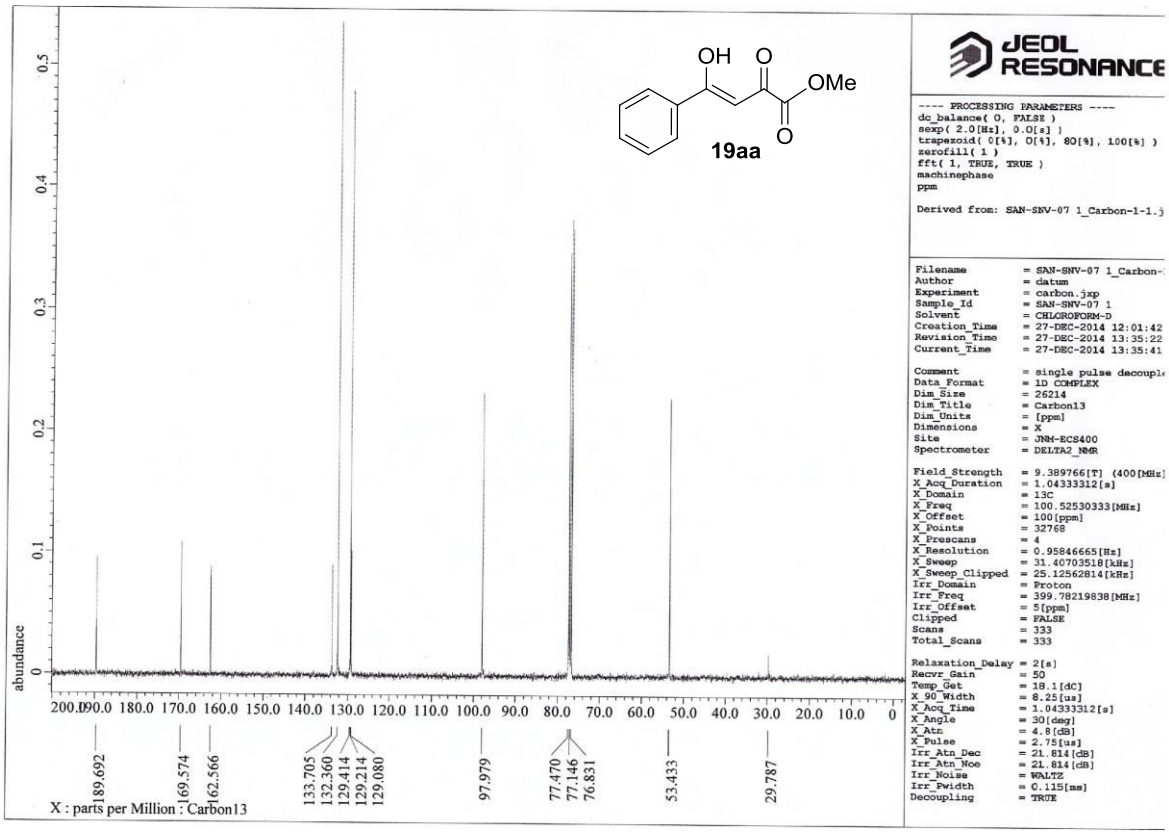


Figure 2. ^{13}C NMR Spectra of Compound **19aa**.

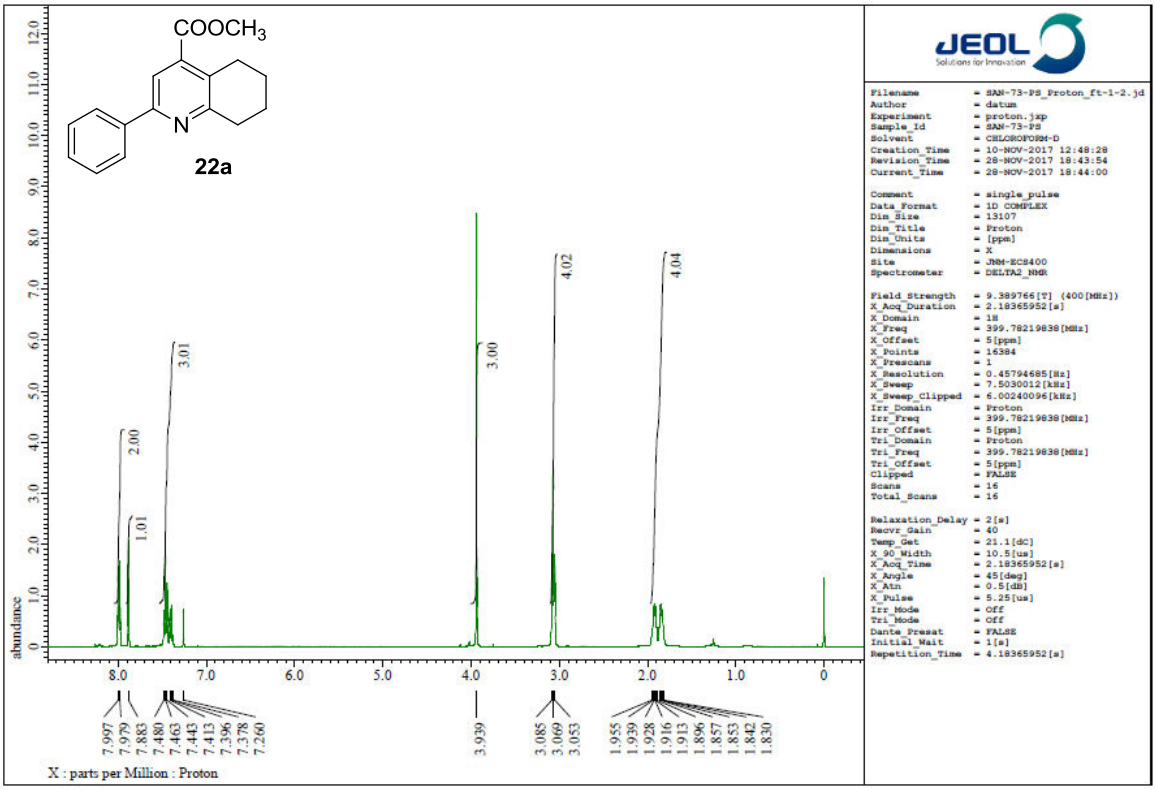


Figure 3. ^{1}H NMR Spectra of Compound **22a**.

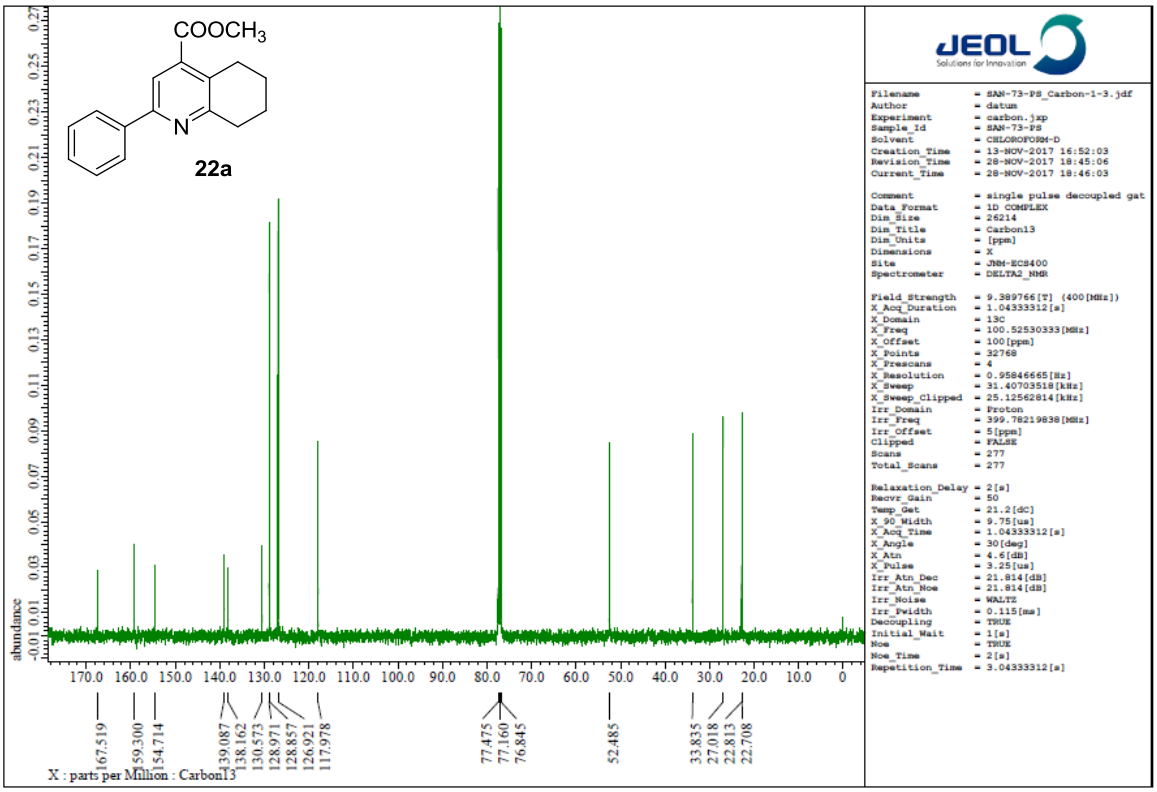


Figure 4. ^{13}C NMR Spectra of Compound **22a.**

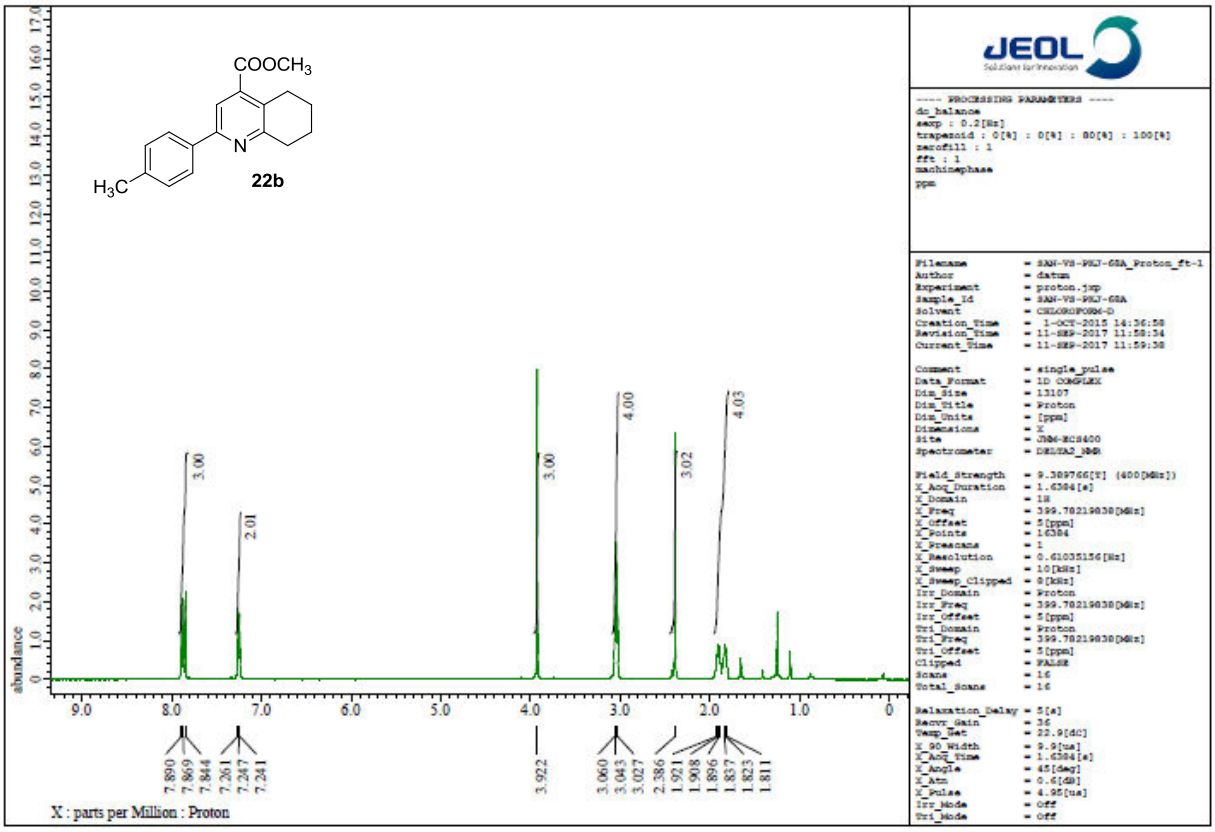


Figure 5. ^{1}H NMR Spectra of Compound **22b**.

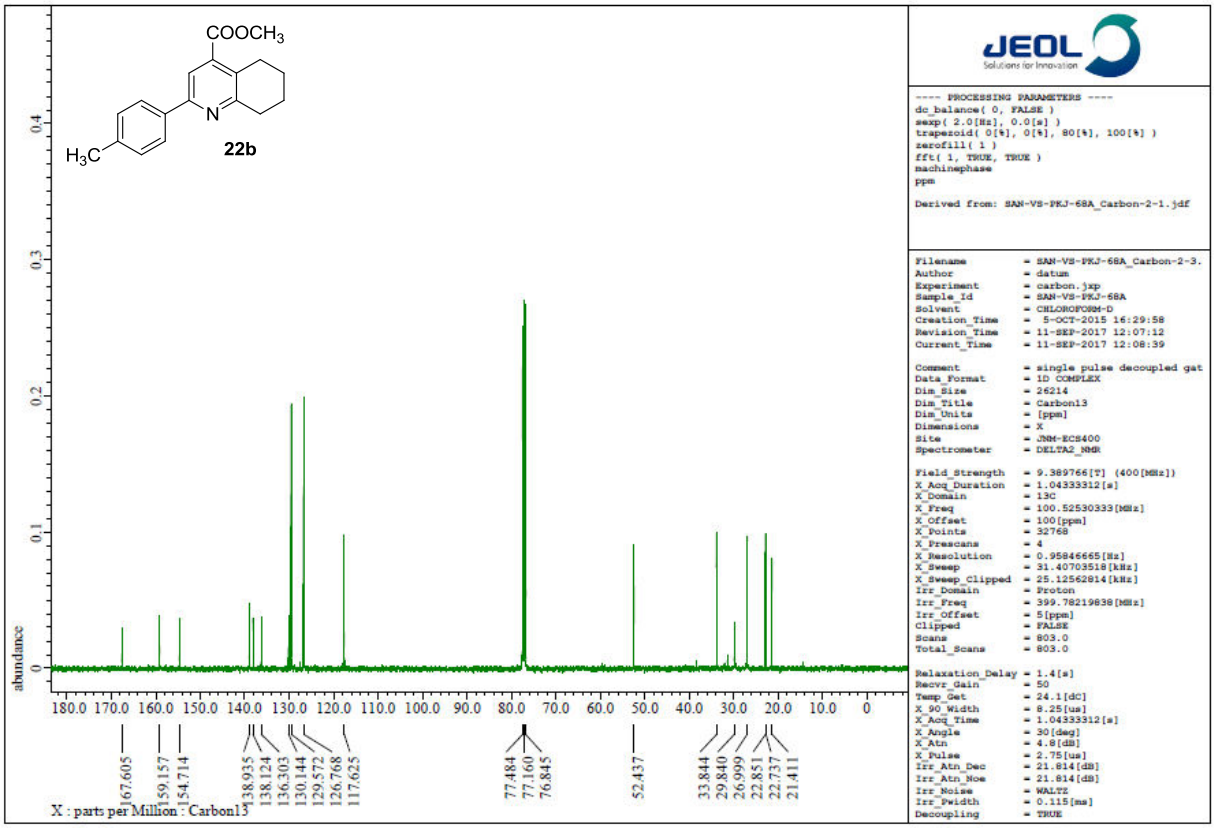


Figure 6. ^{13}C NMR Spectra of Compound **22b.**

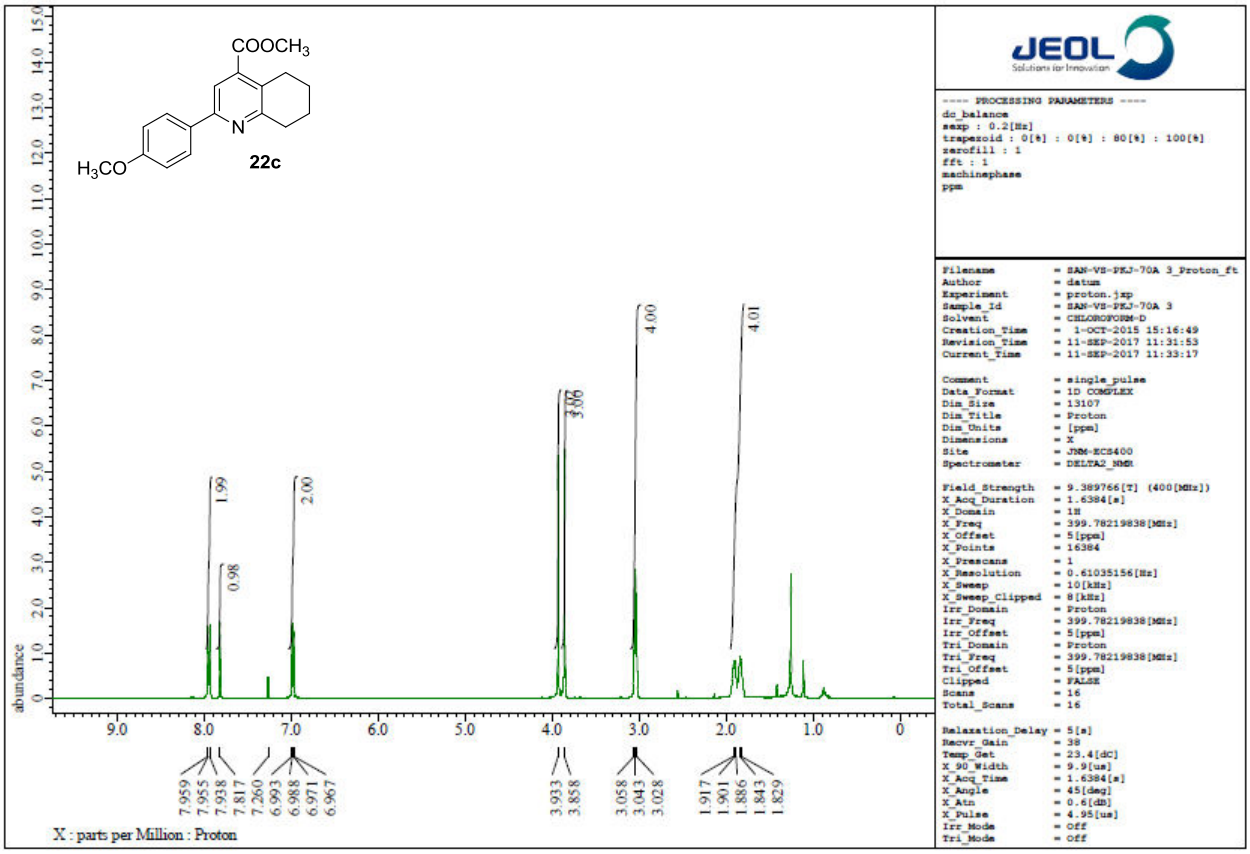


Figure 7. ^{1}H NMR Spectra of Compound **22c**.

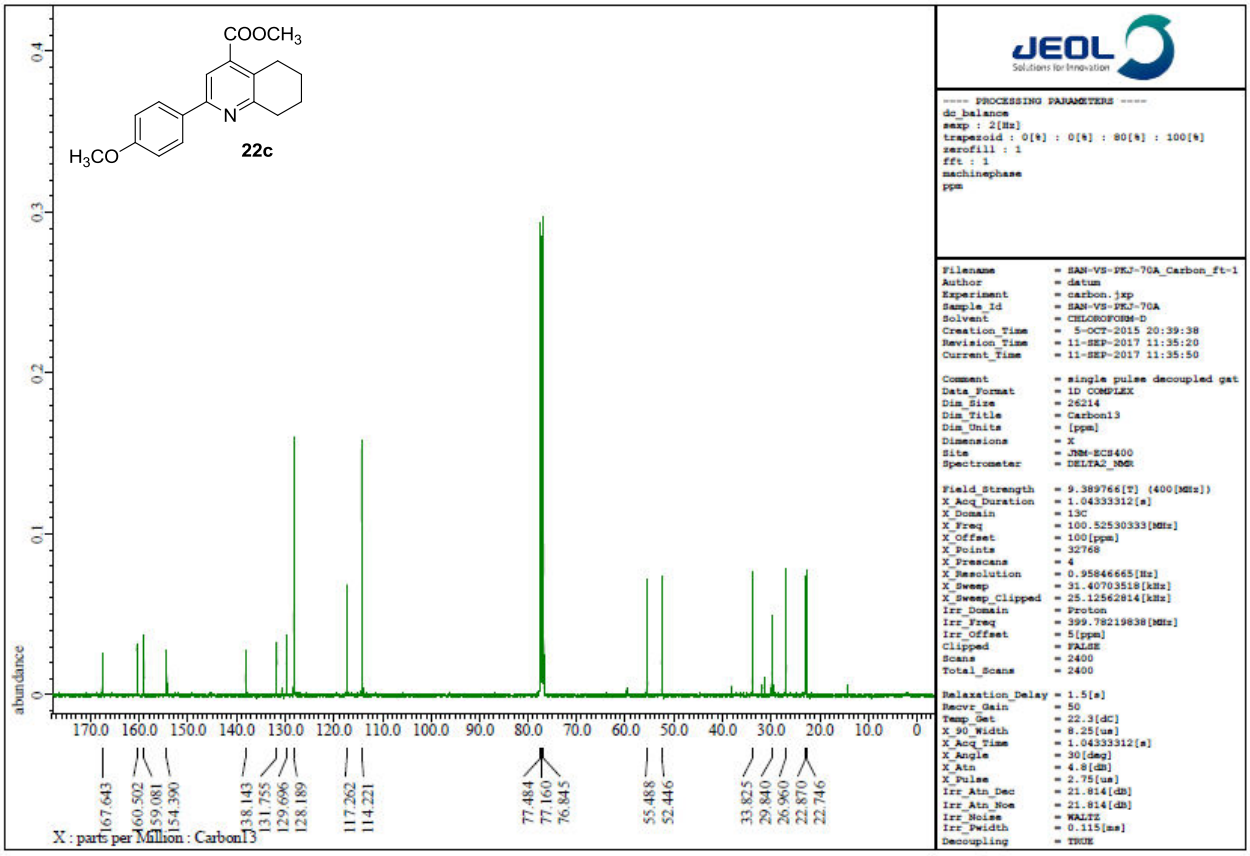


Figure 8. ^{13}C NMR Spectra of Compound **22c.**

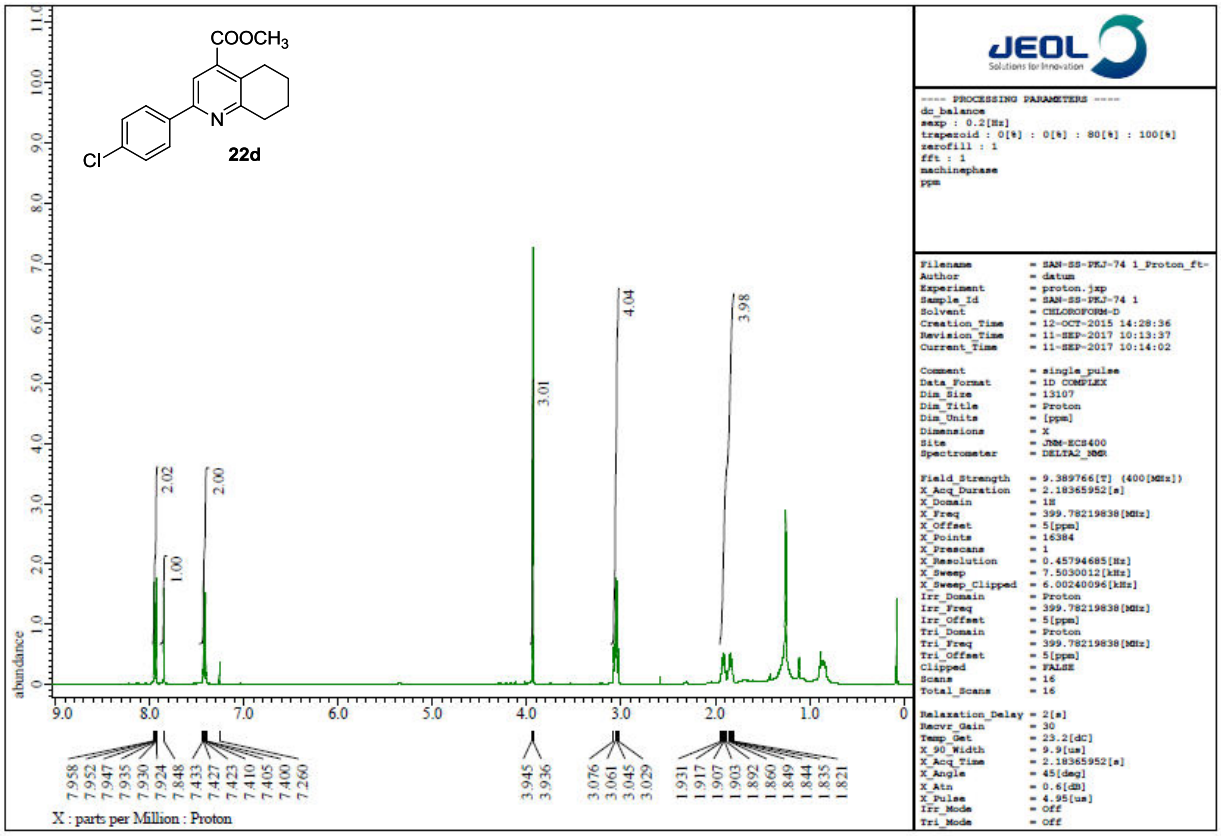


Figure 9. ^{1}H NMR Spectra of Compound **22d**.

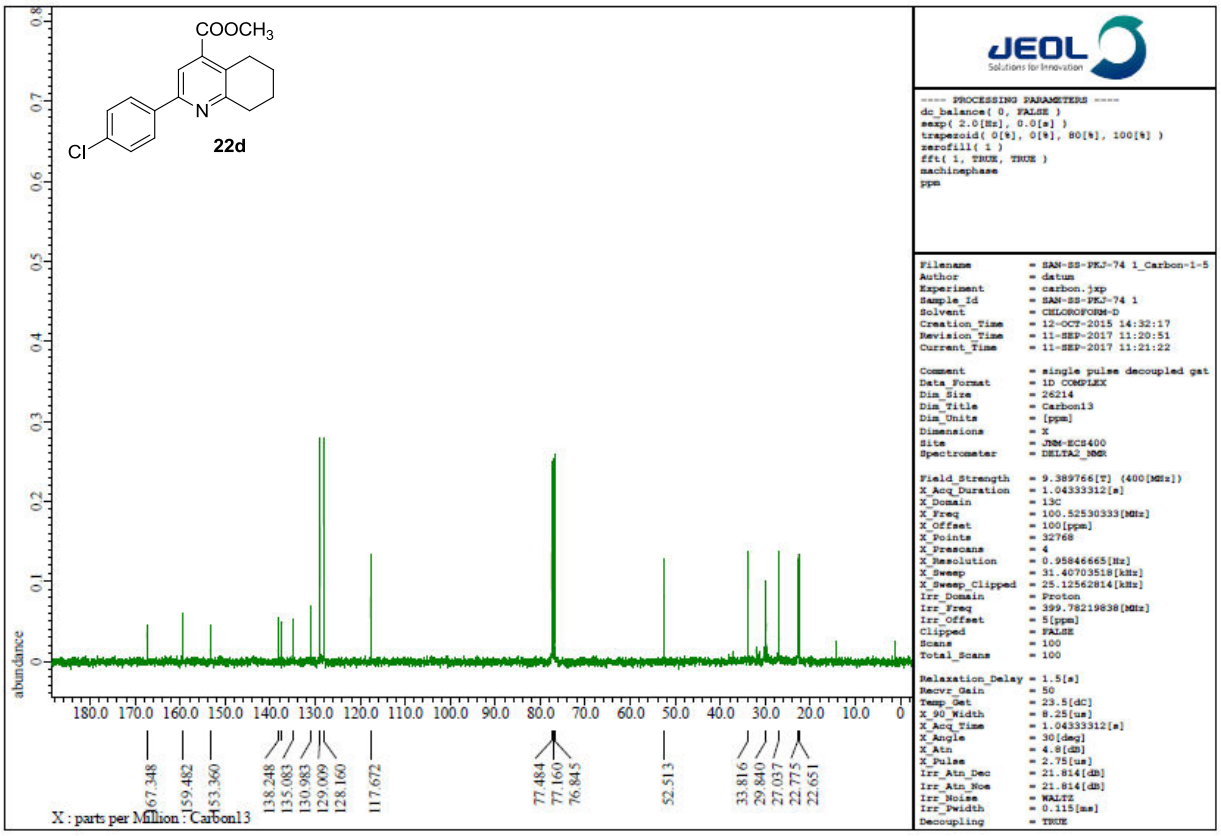


Figure 10. ^{13}C NMR Spectra of Compound **22d**.

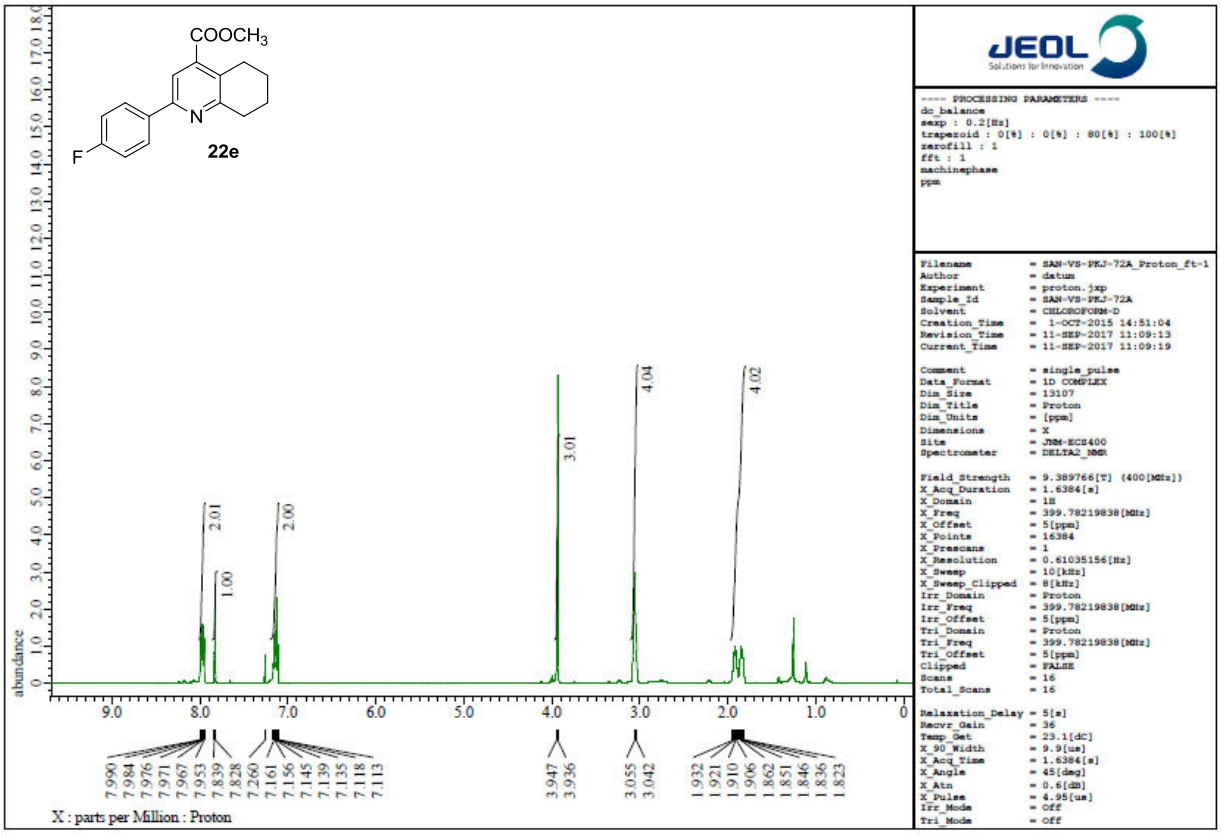


Figure 11. ^{1}H NMR Spectra of Compound **22e**.

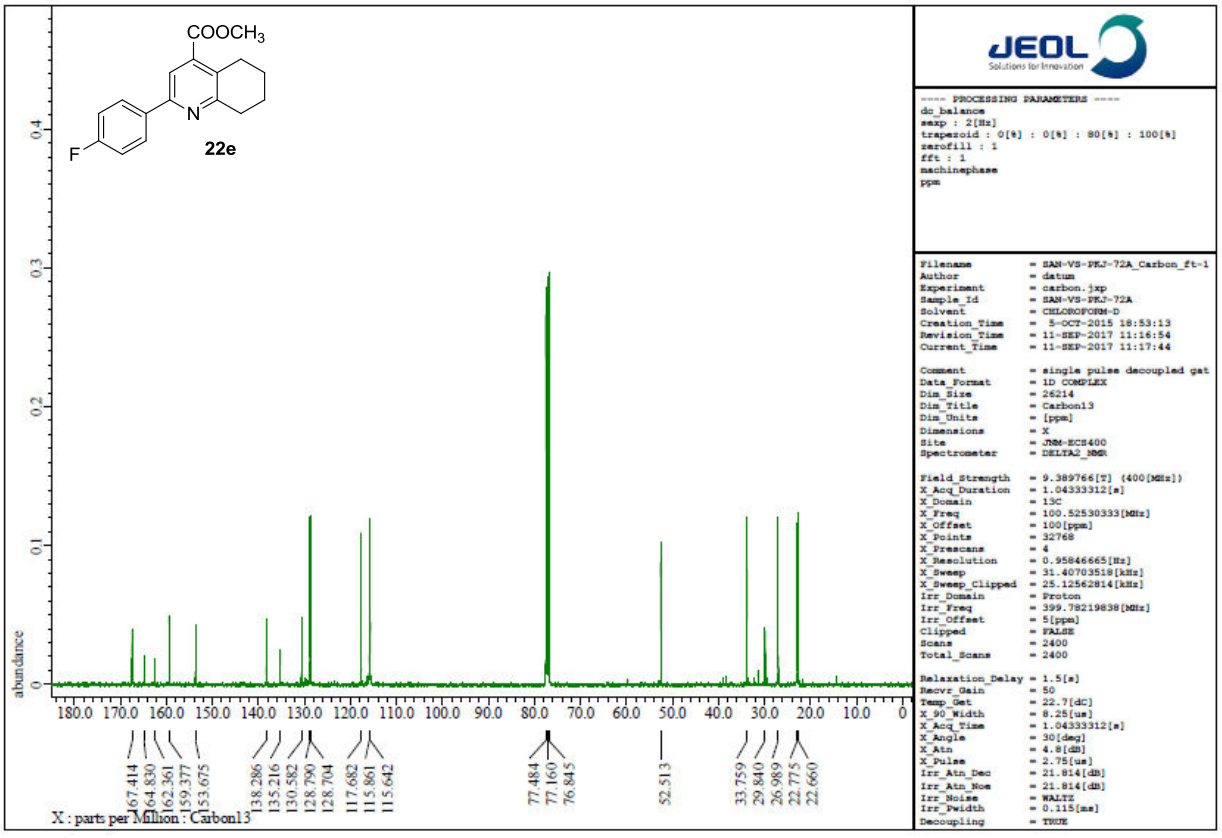


Figure 12. ^{13}C NMR Spectra of Compound **22e**.

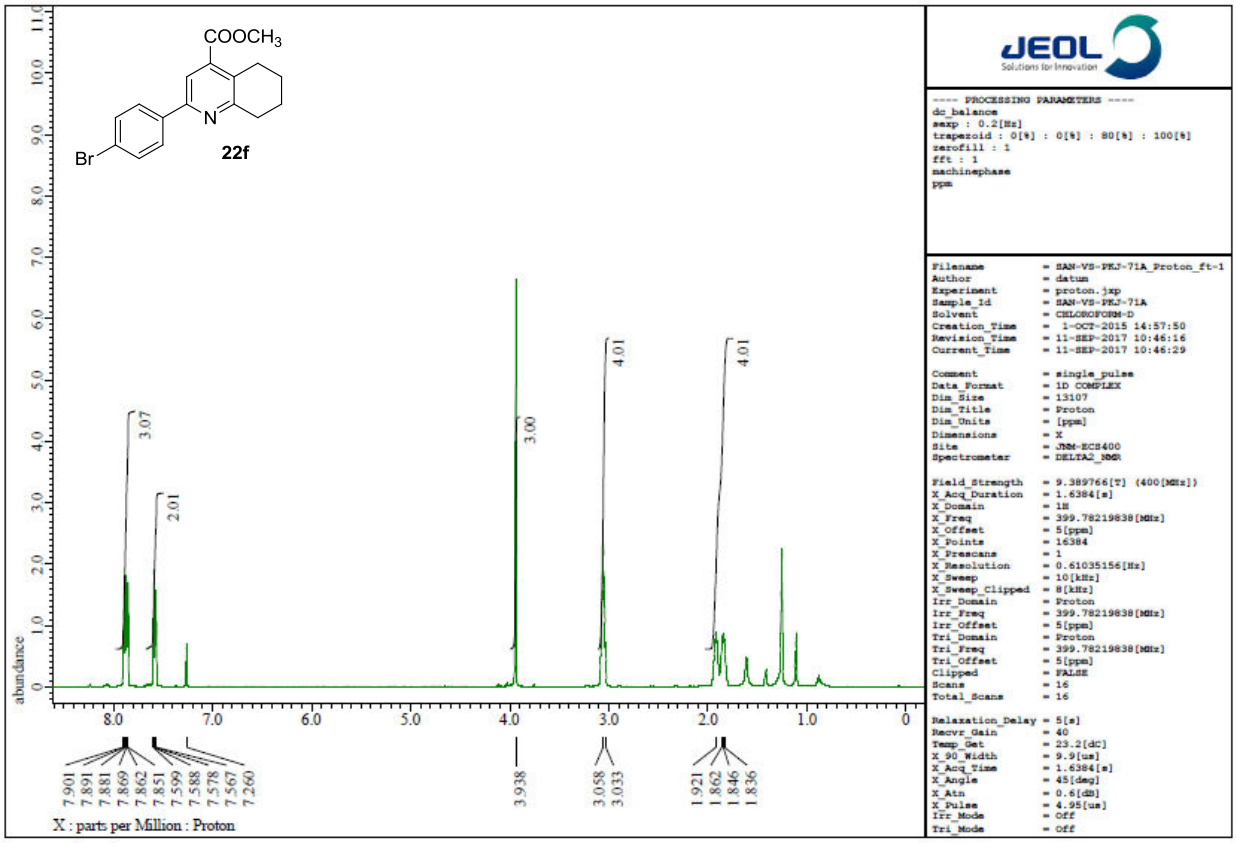


Figure 13. [1]H NMR Spectra of Compound **22f**.

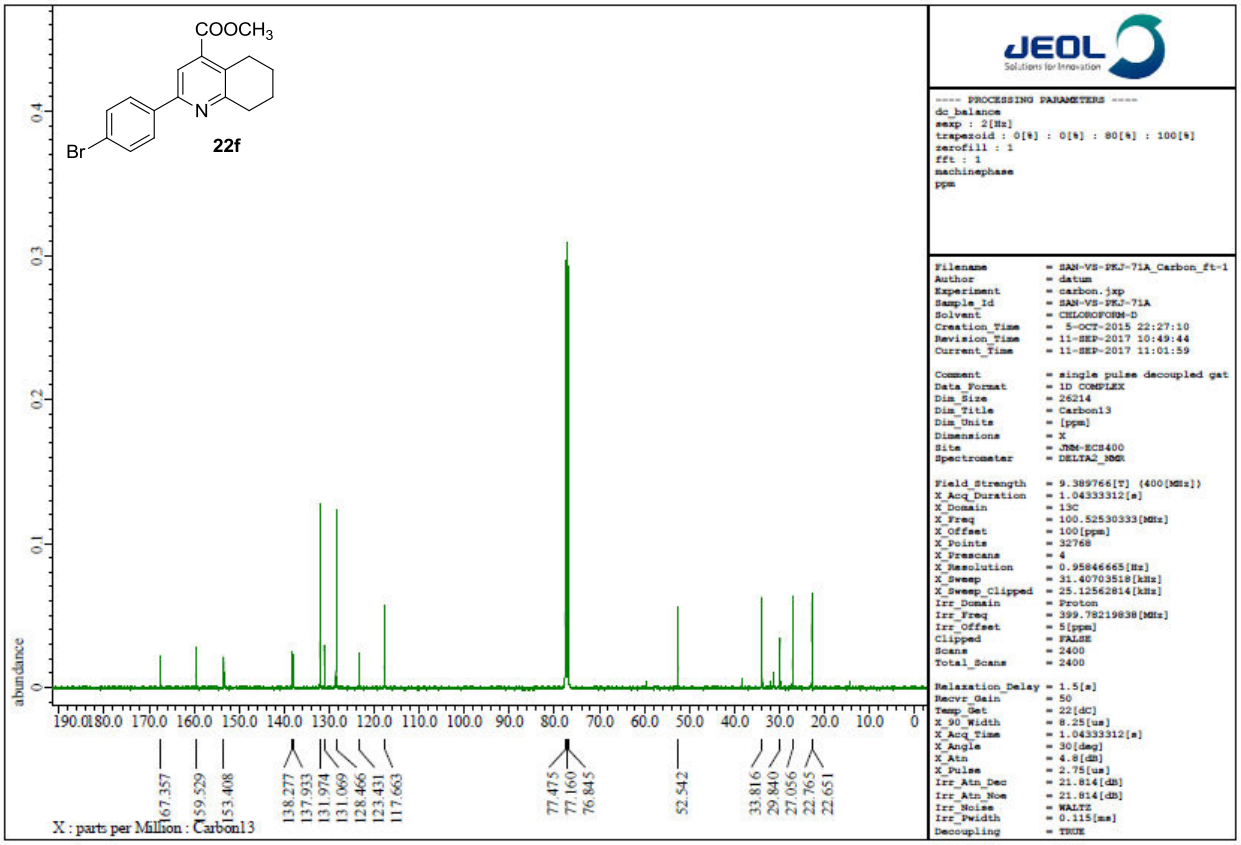


Figure 14. [13]C NMR Spectra of Compound **22f**.

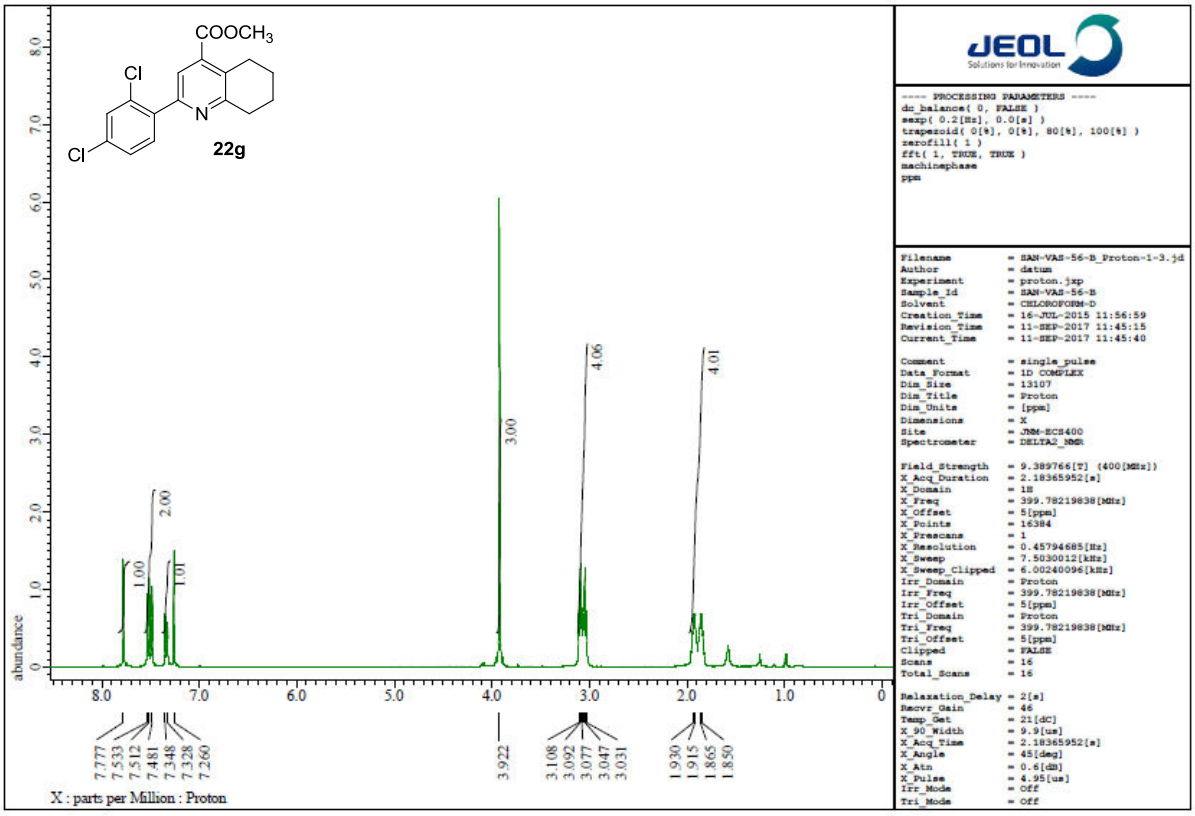


Figure 15. ^{1}H NMR Spectra of Compound **22g**.

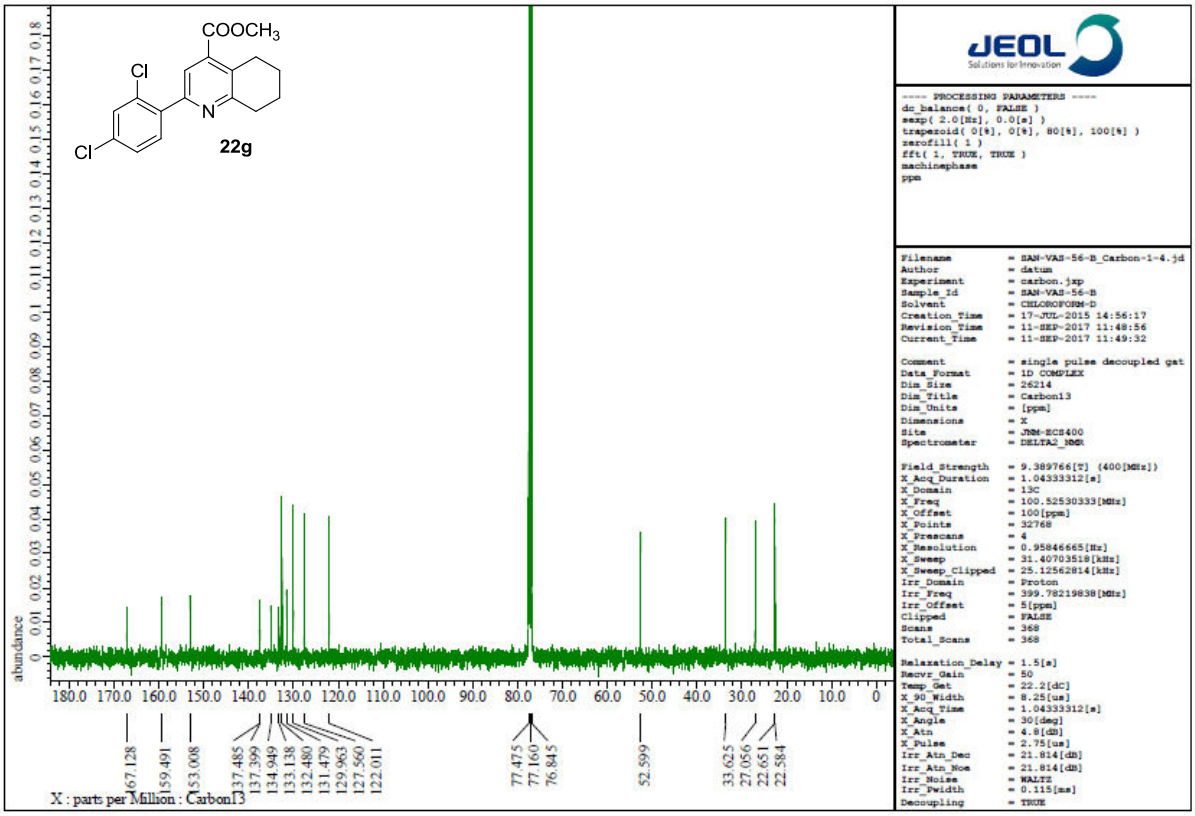


Figure 16. ^{13}C NMR Spectra of Compound **22g**.

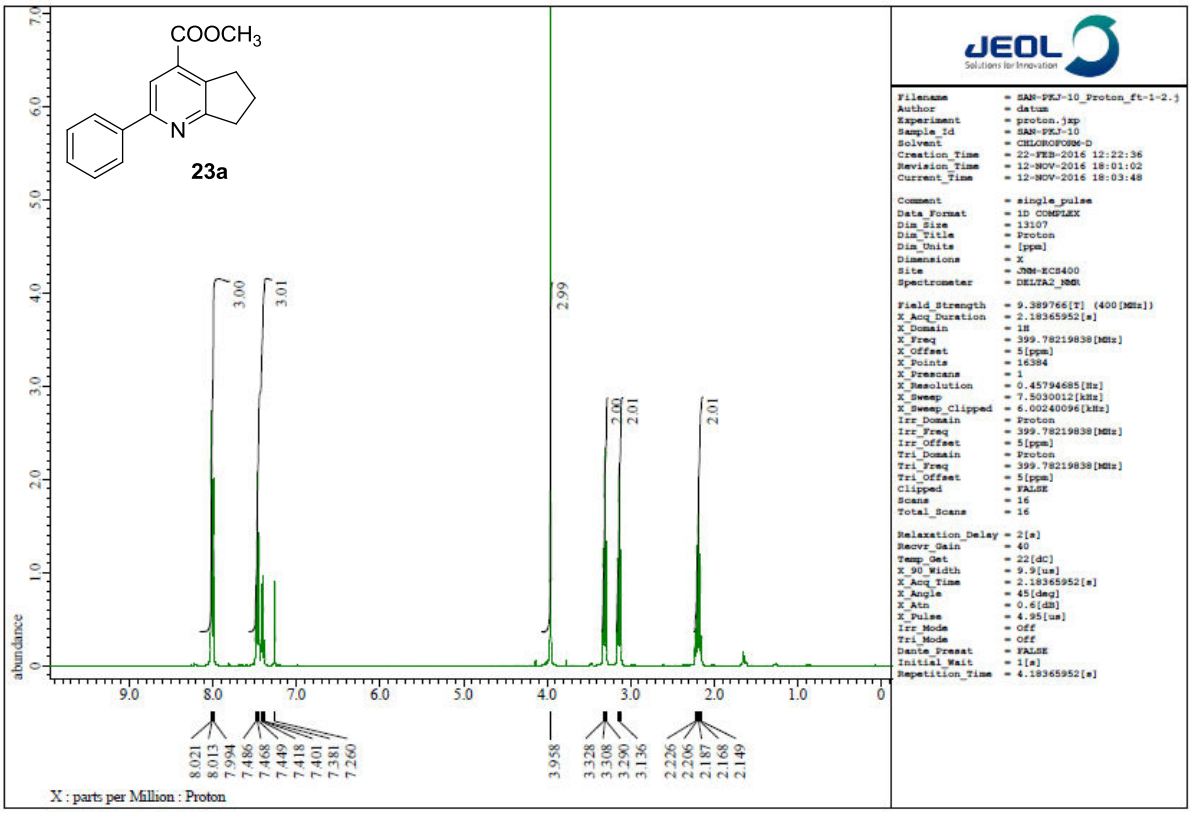


Figure 17. ^{1}H NMR Spectra of Compound **23a.**

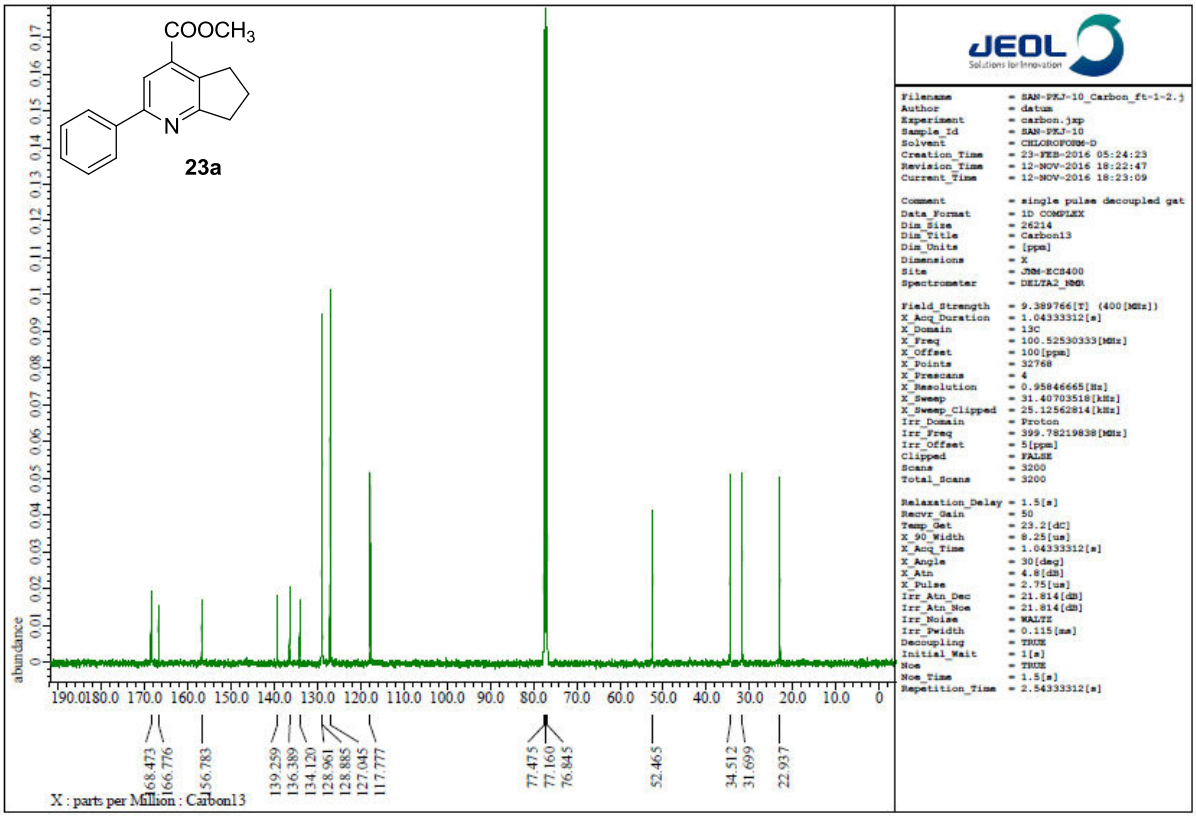


Figure 18. ^{13}C NMR Spectra of Compound **23a.**

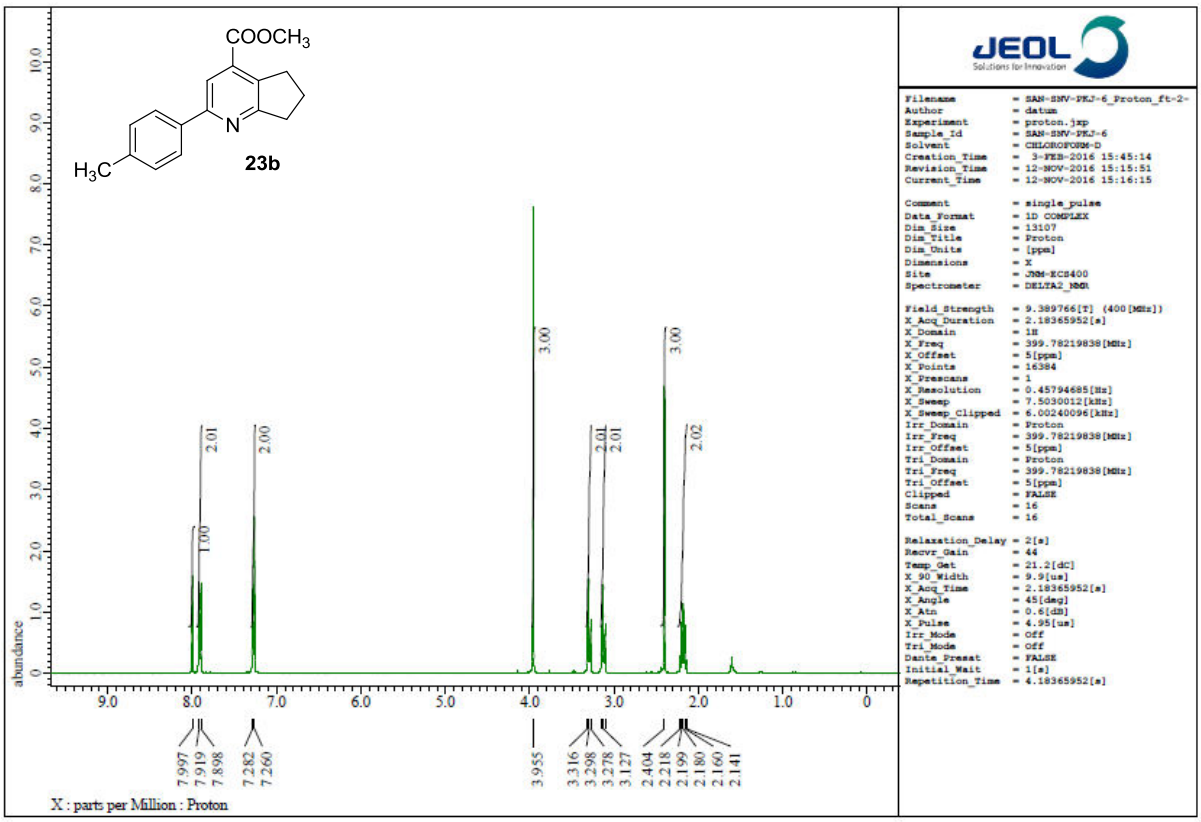


Figure 19. ^{1}H NMR Spectra of Compound **23b.**

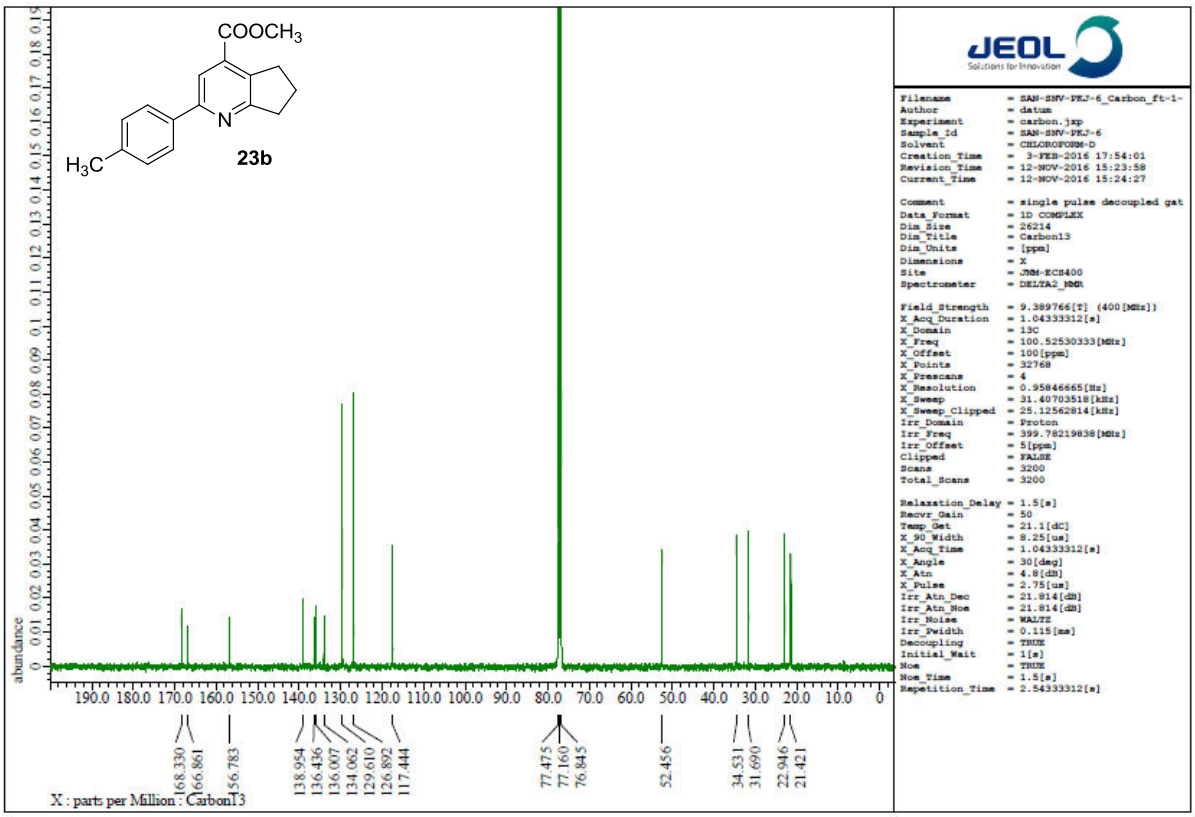


Figure 20. ^{13}C NMR Spectra of Compound **23b.**

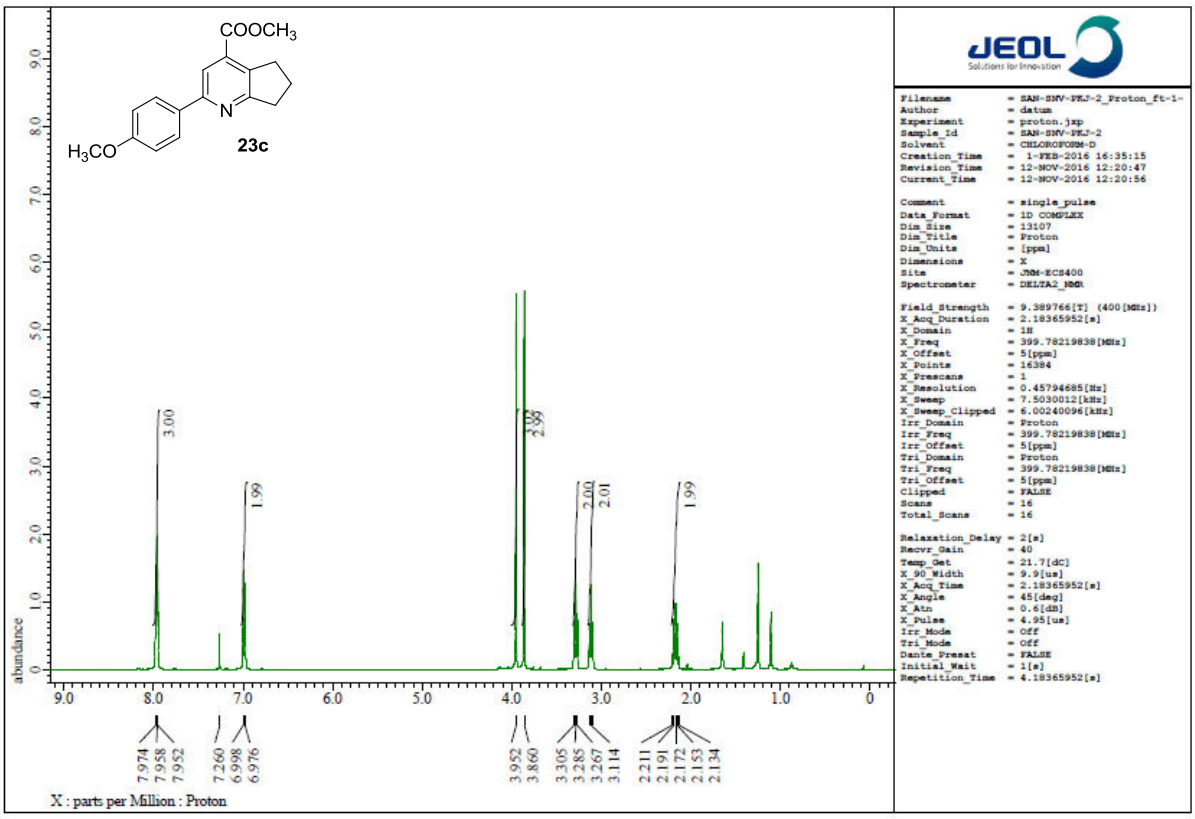


Figure 21. ^{1}H NMR Spectra of Compound **23c.**

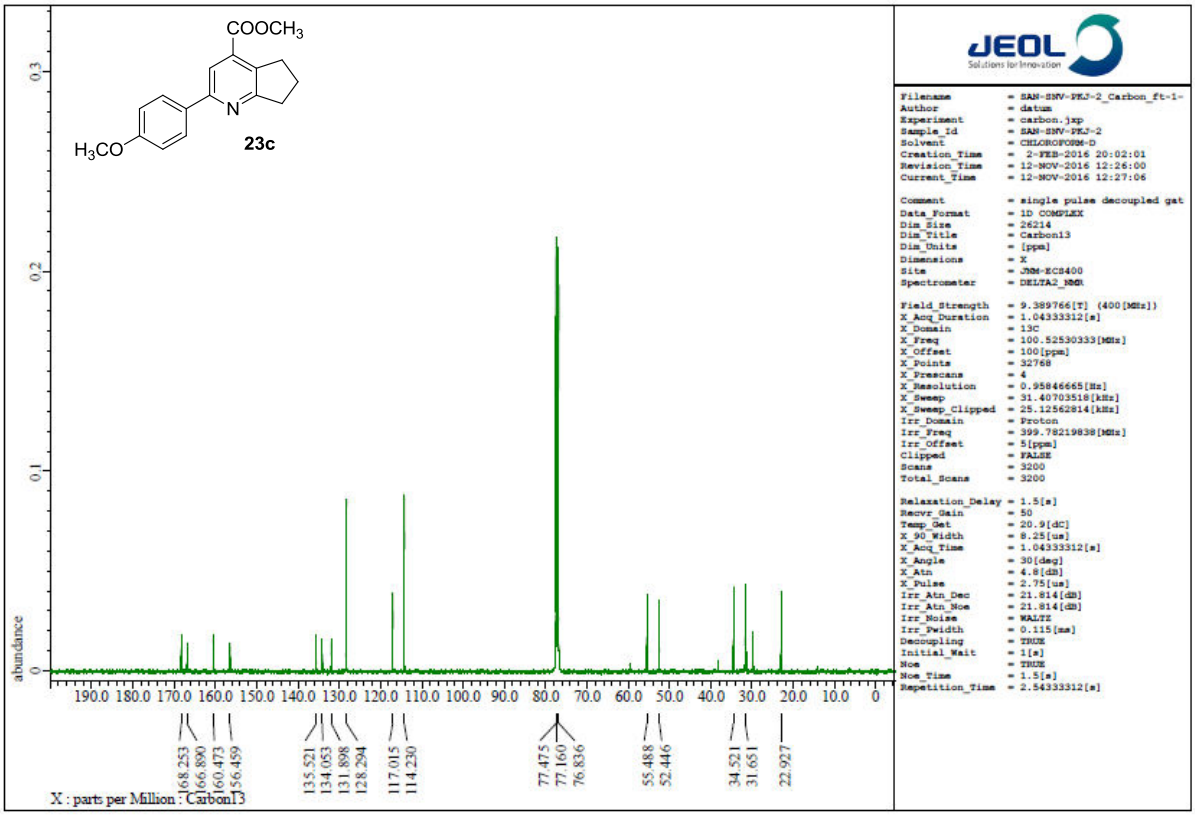


Figure 22. ^{13}C NMR Spectra of Compound **23c.**

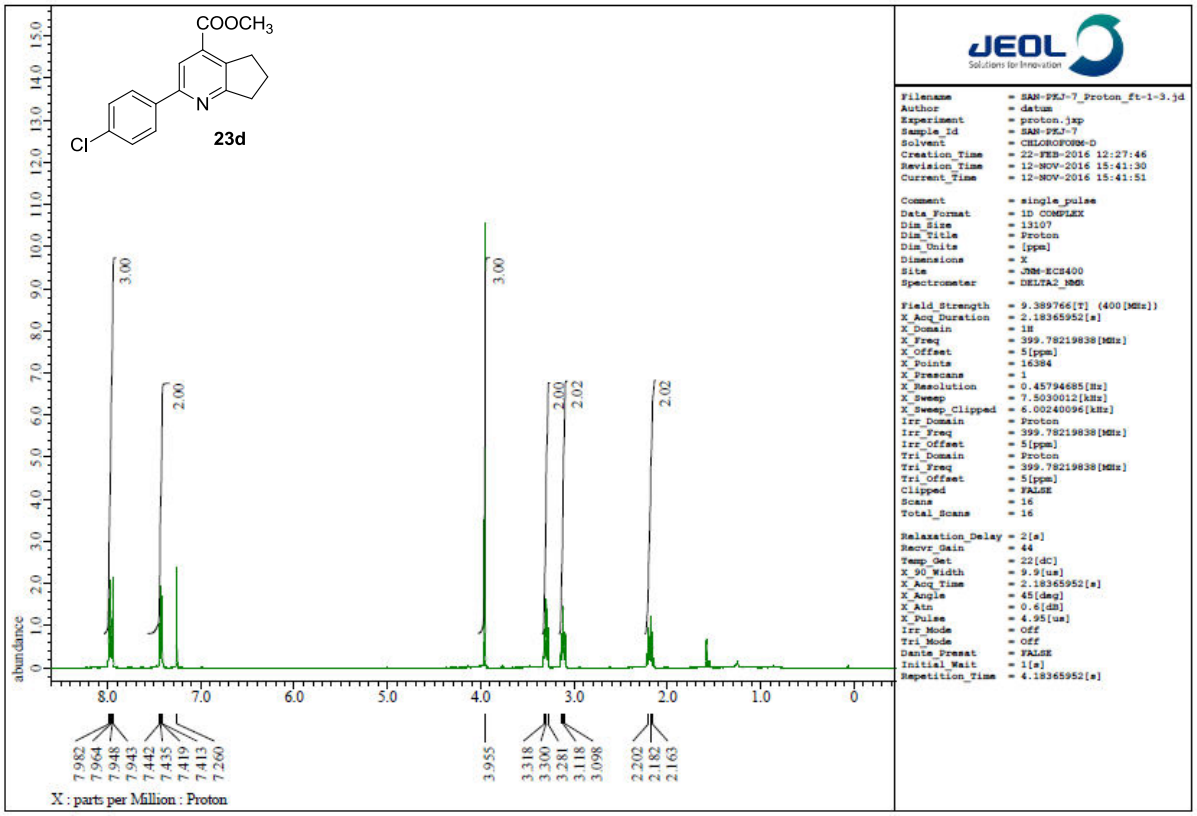


Figure 23. ^{1}H NMR Spectra of Compound **23d.**

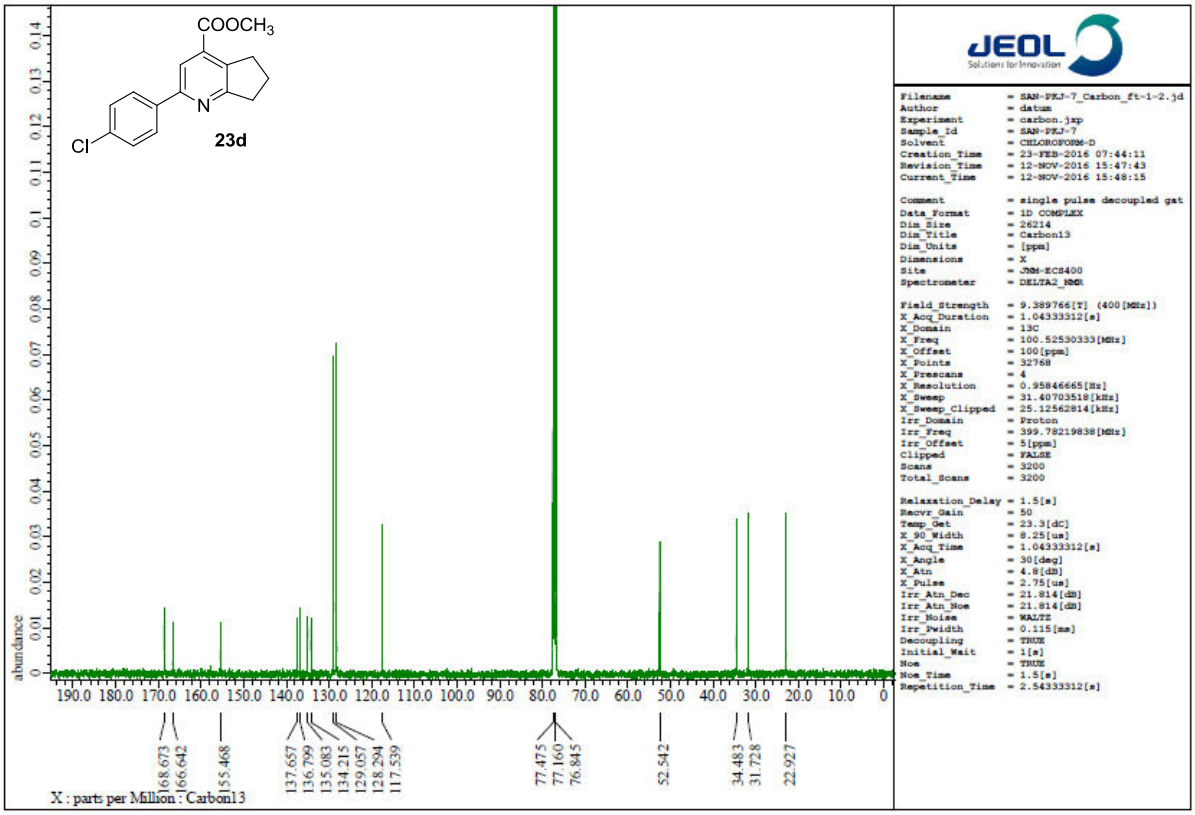


Figure 24. ^{13}C NMR Spectra of Compound **23d.**

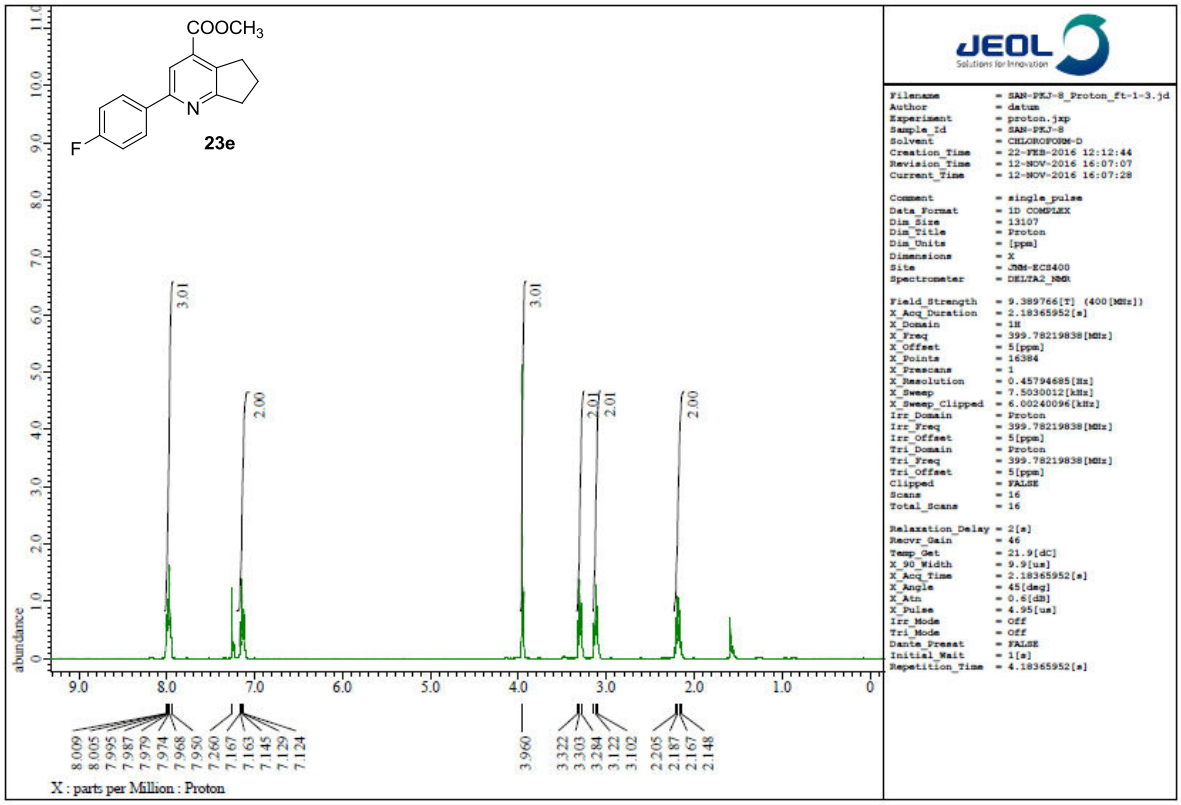


Figure 25. ^{1}H NMR Spectra of Compound **23e.**

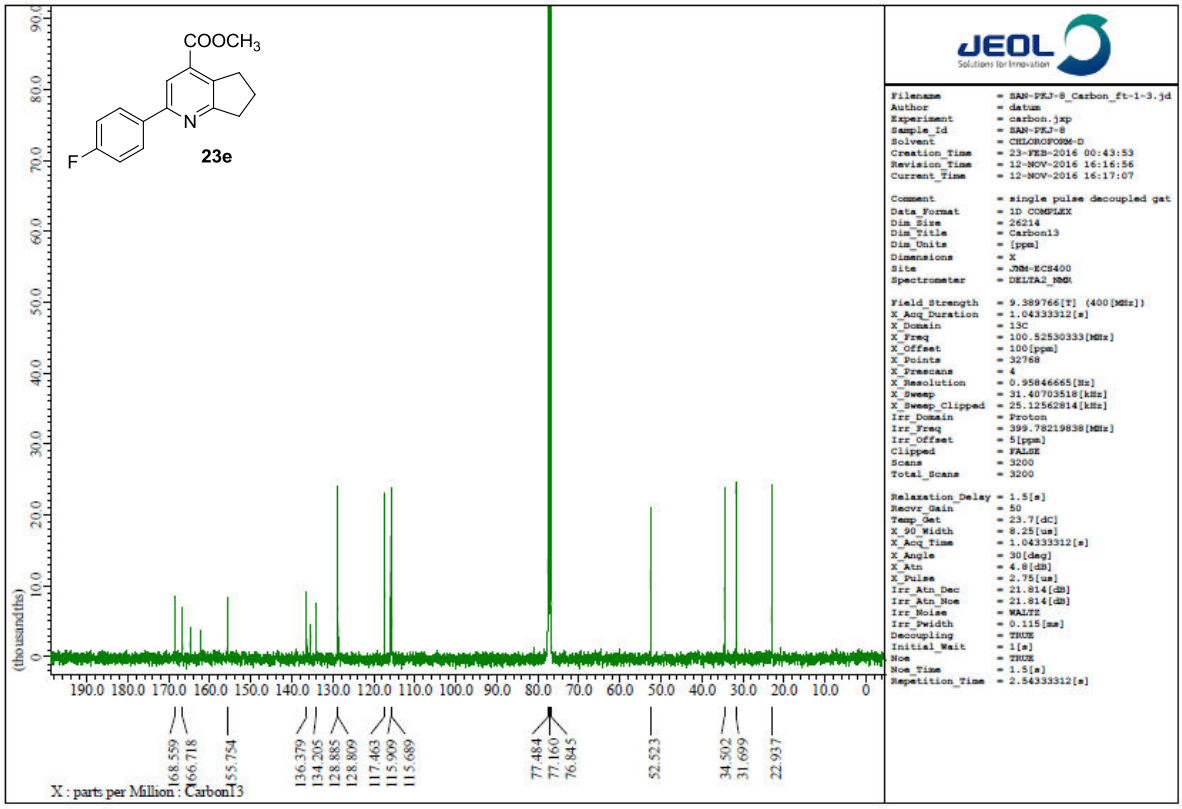


Figure 26. ^{13}C NMR Spectra of Compound **23e.**

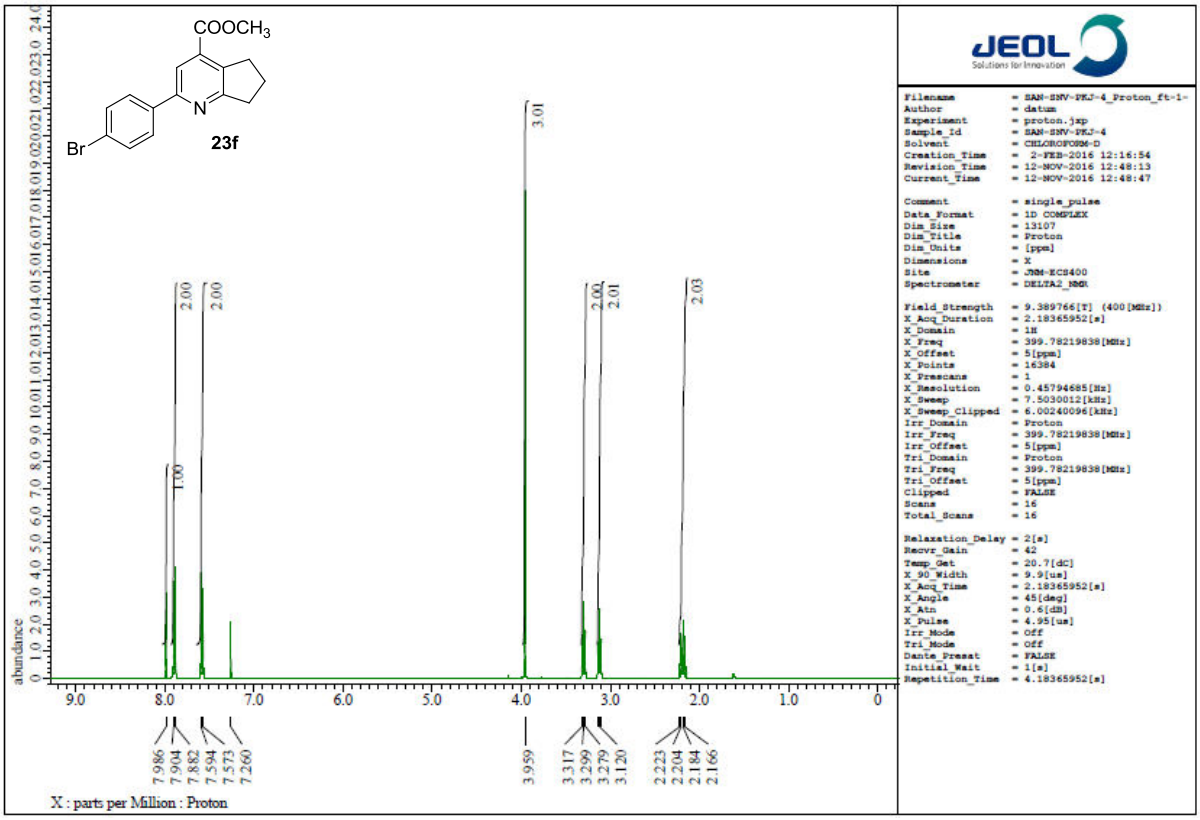


Figure 27. ^{1}H NMR Spectra of Compound **23f.**

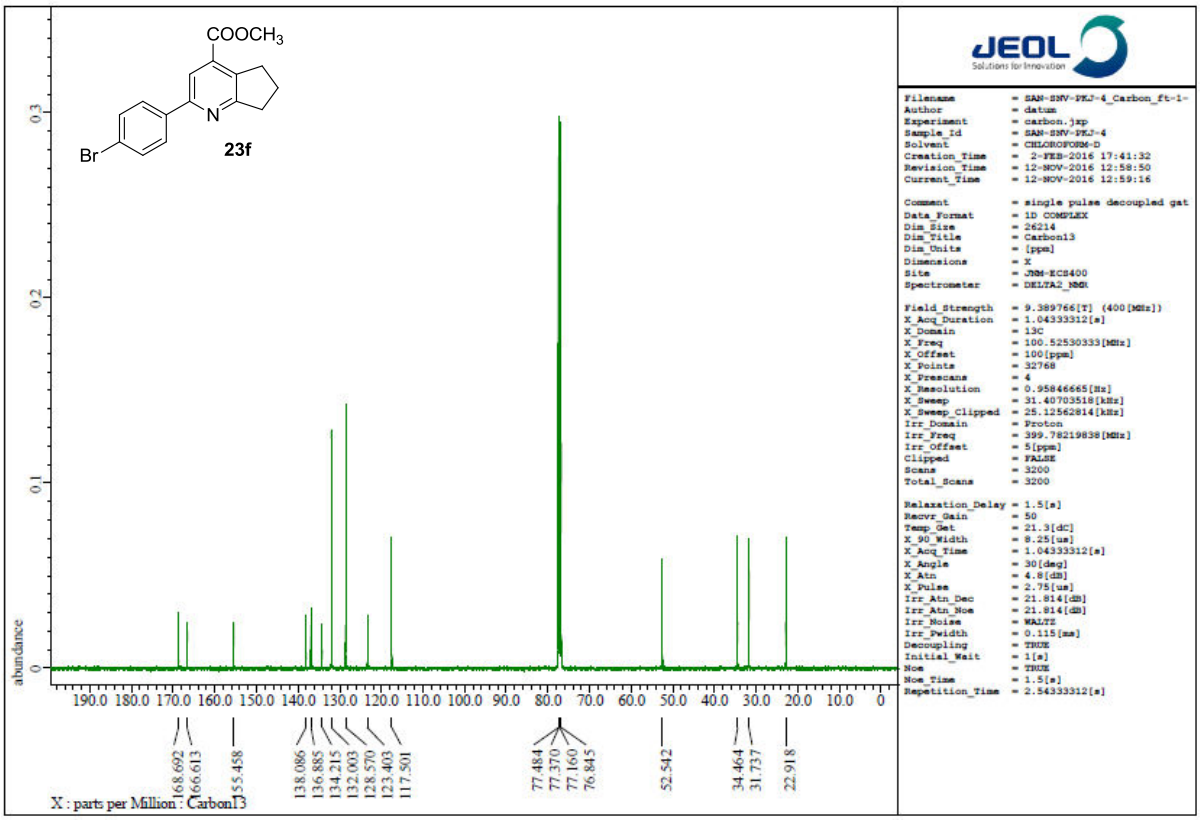


Figure 28. ^{13}C NMR Spectra of Compound **23f.**

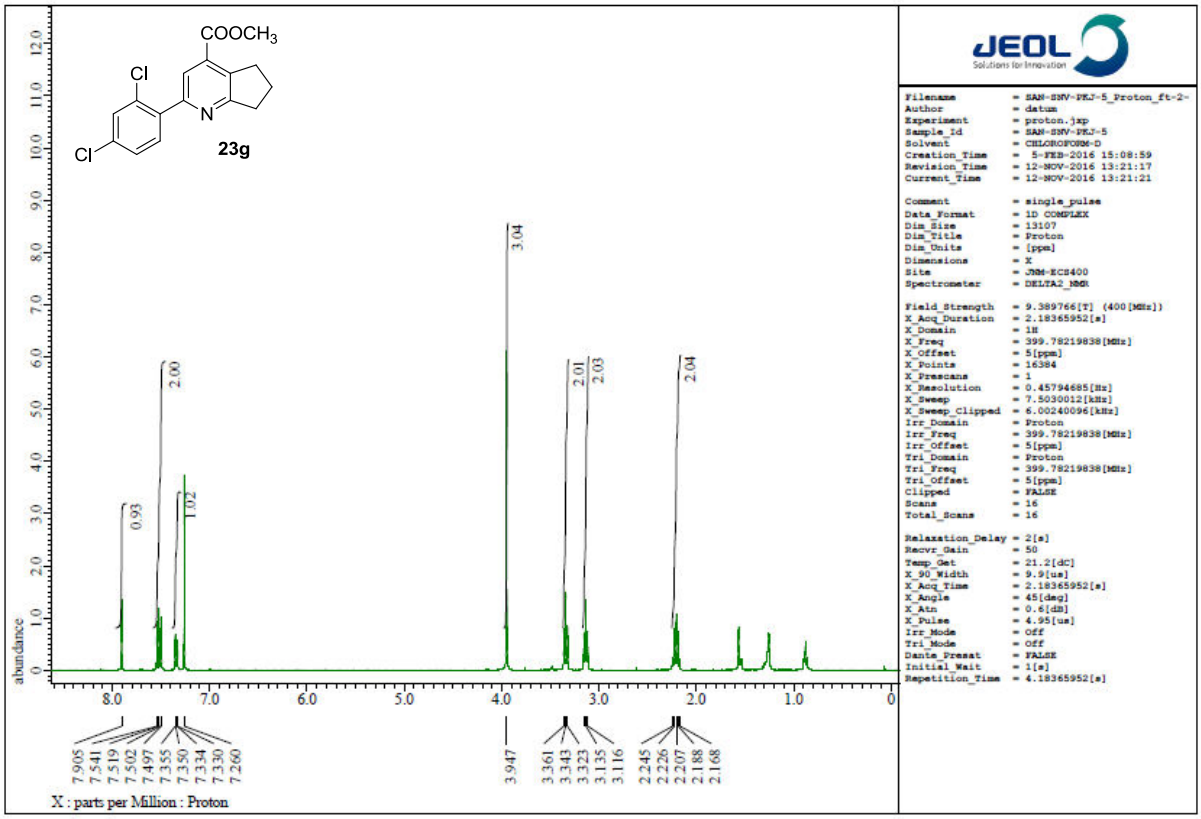


Figure 29. ^{1}H NMR Spectra of Compound **23g.**

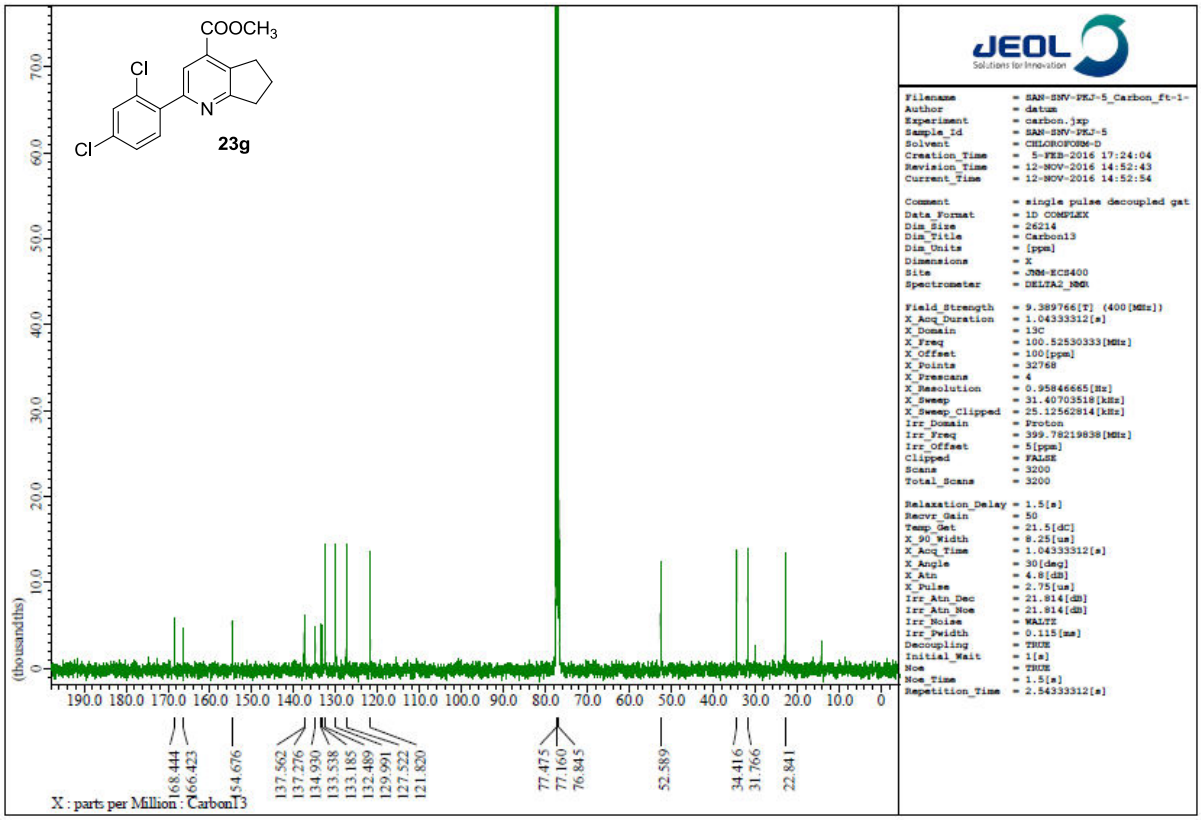


Figure 30. ^{13}C NMR Spectra of Compound **23g.**

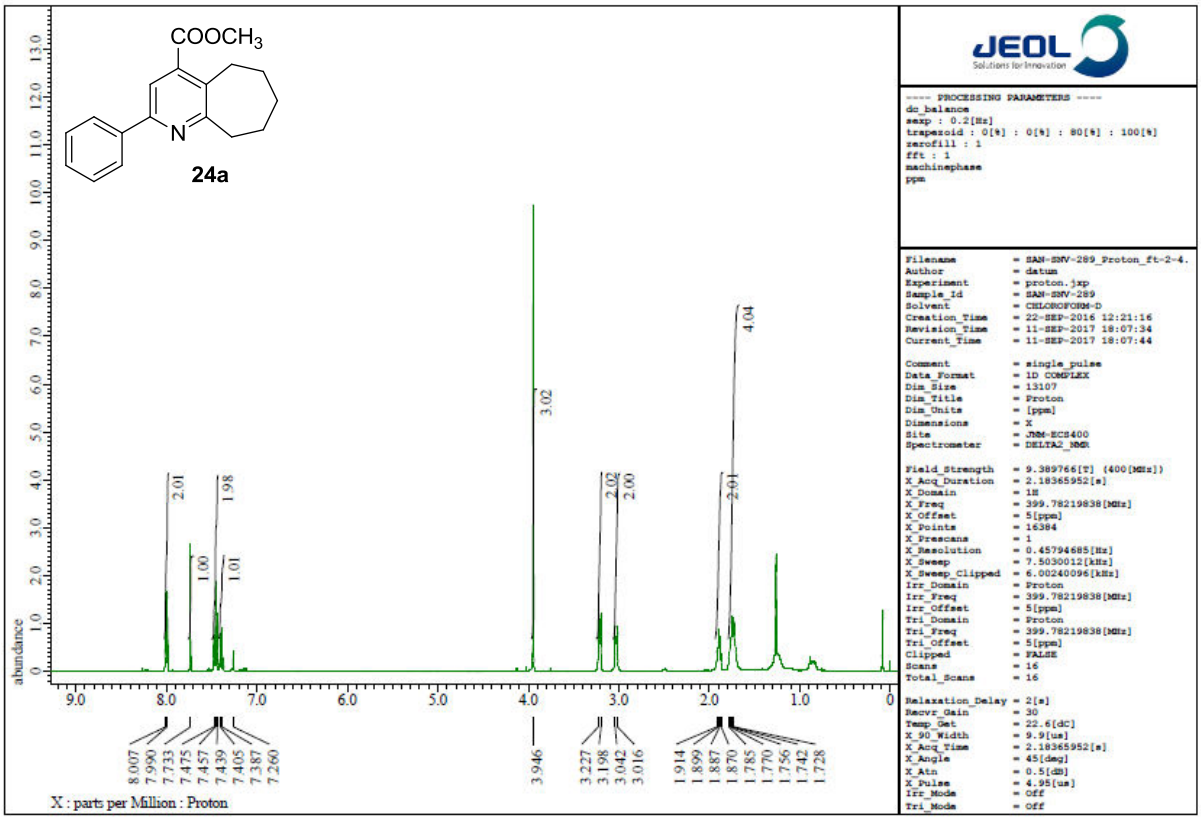


Figure 31. [1]H NMR Spectra of Compound **24a.**

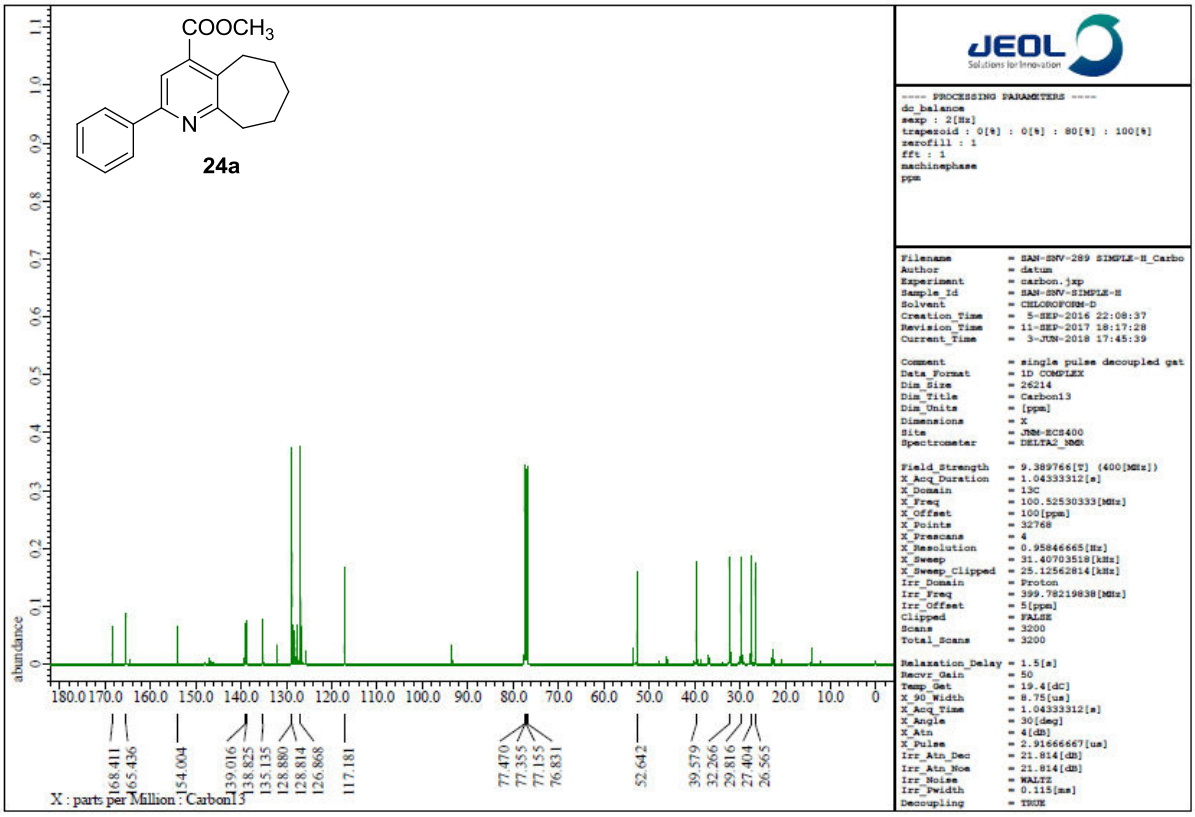


Figure 32. [13]C NMR Spectra of Compound **24a.**

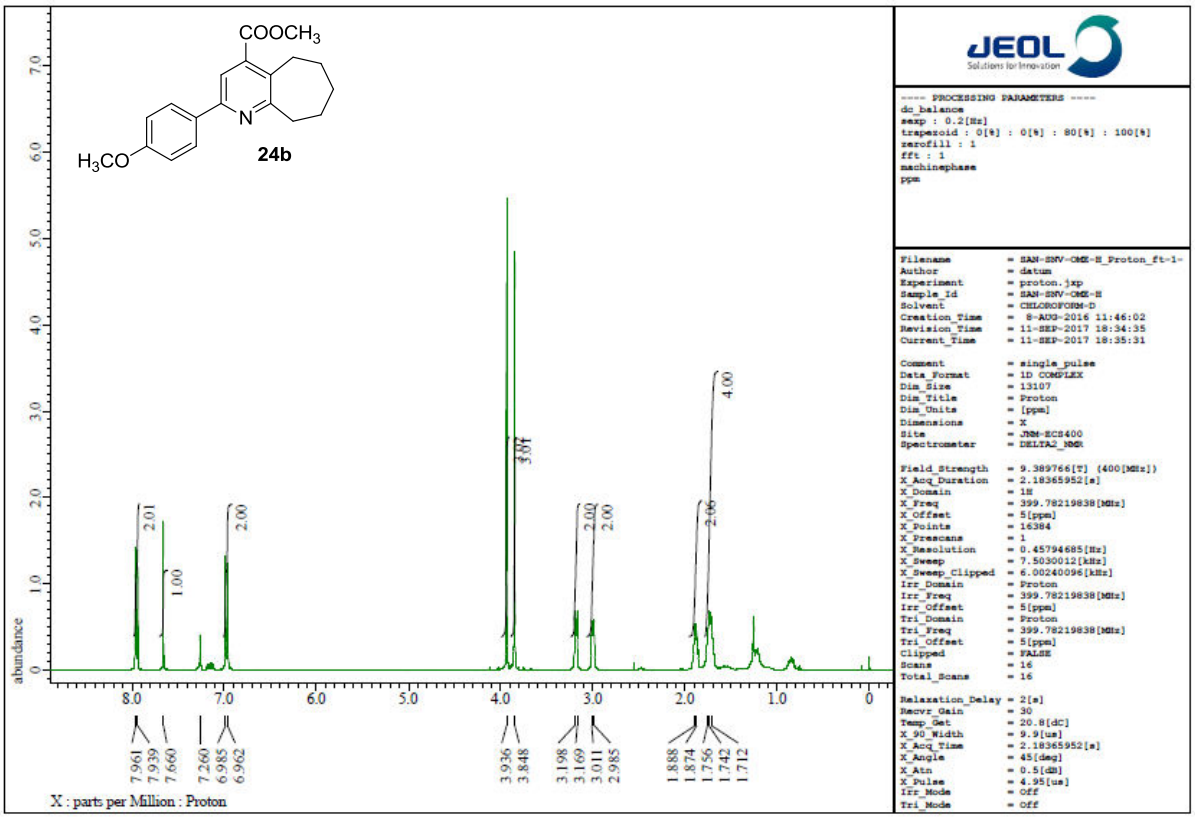


Figure 33. ^{1}H NMR Spectra of Compound **24b.**

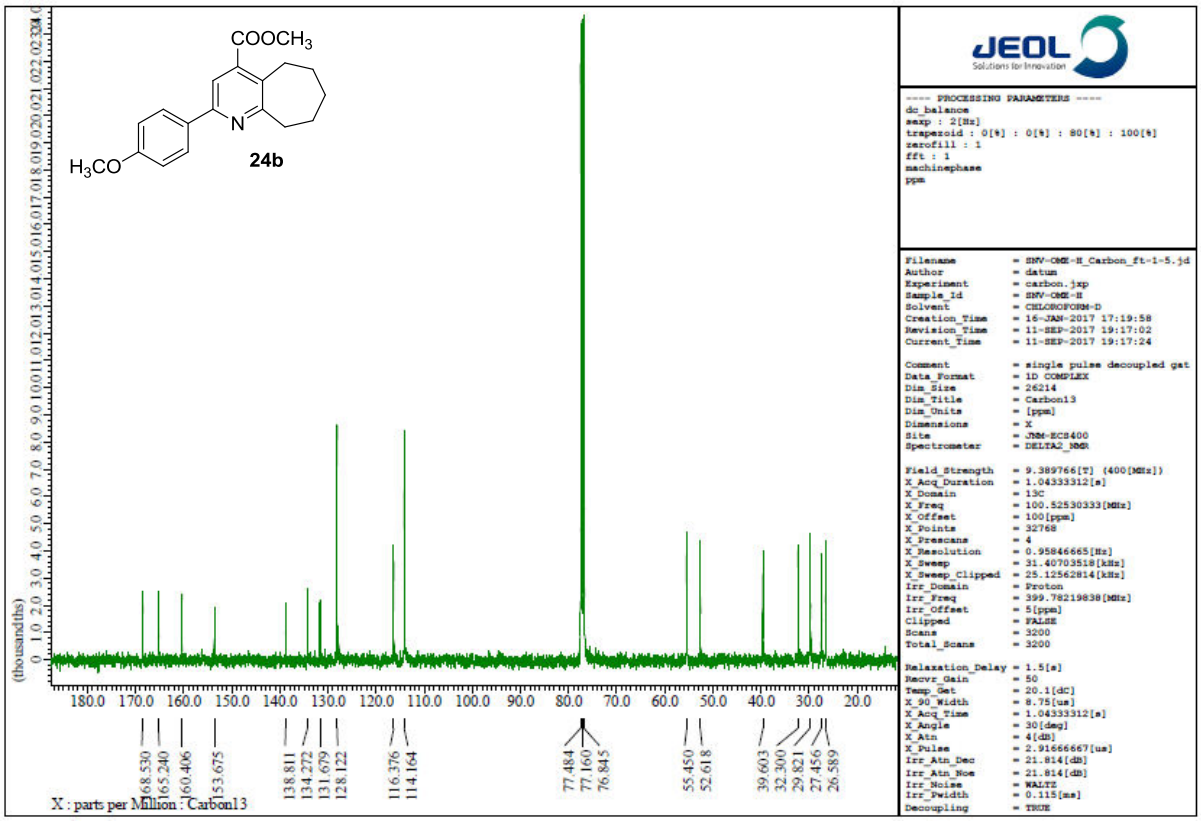


Figure 34. ^{13}C NMR Spectra of Compound **24b.**

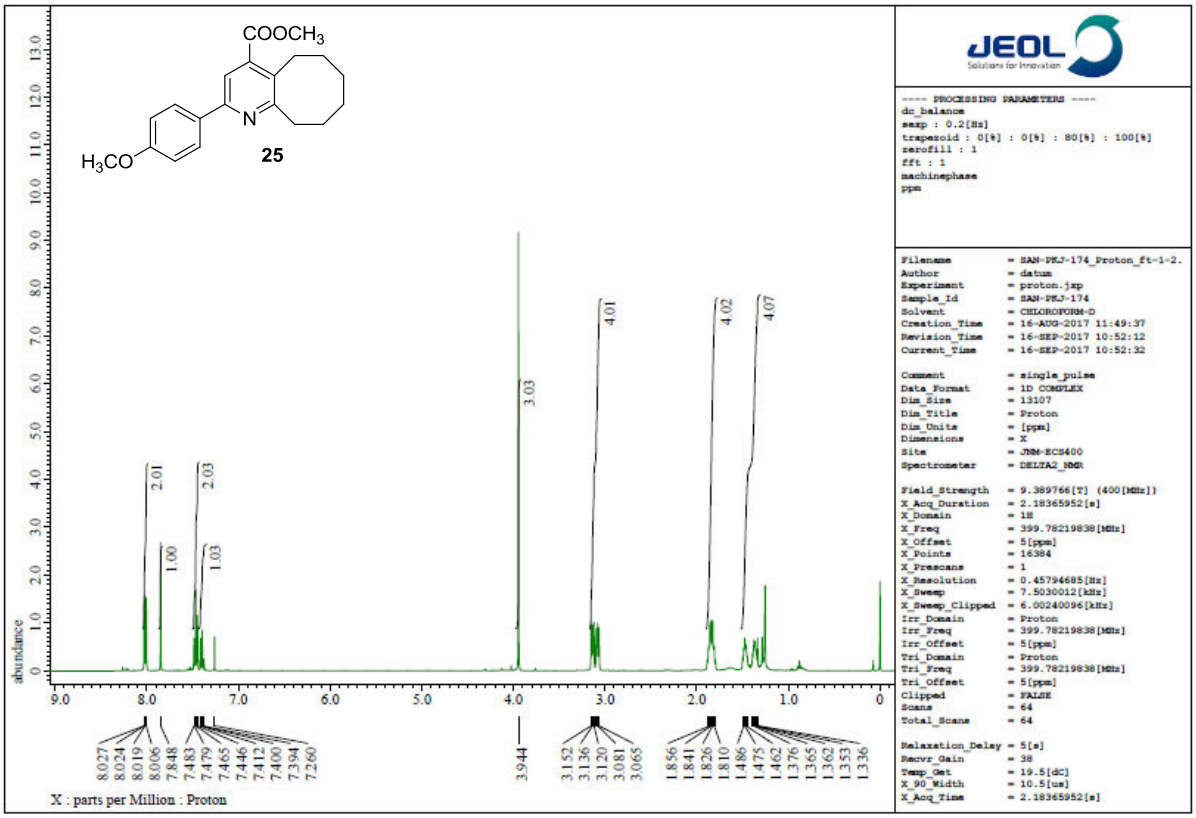


Figure 35. ^{1}H NMR Spectra of Compound **25.**

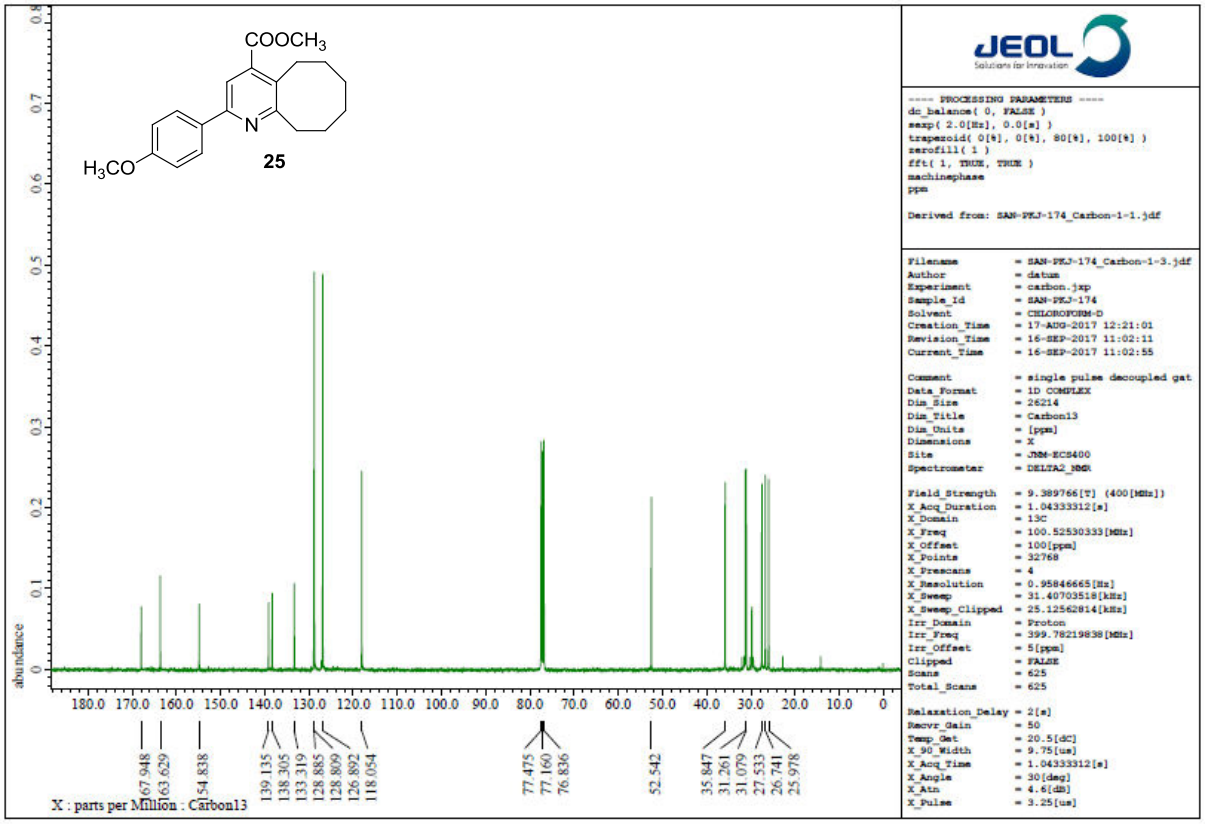


Figure 36. ^{13}C NMR Spectra of Compound **25**.

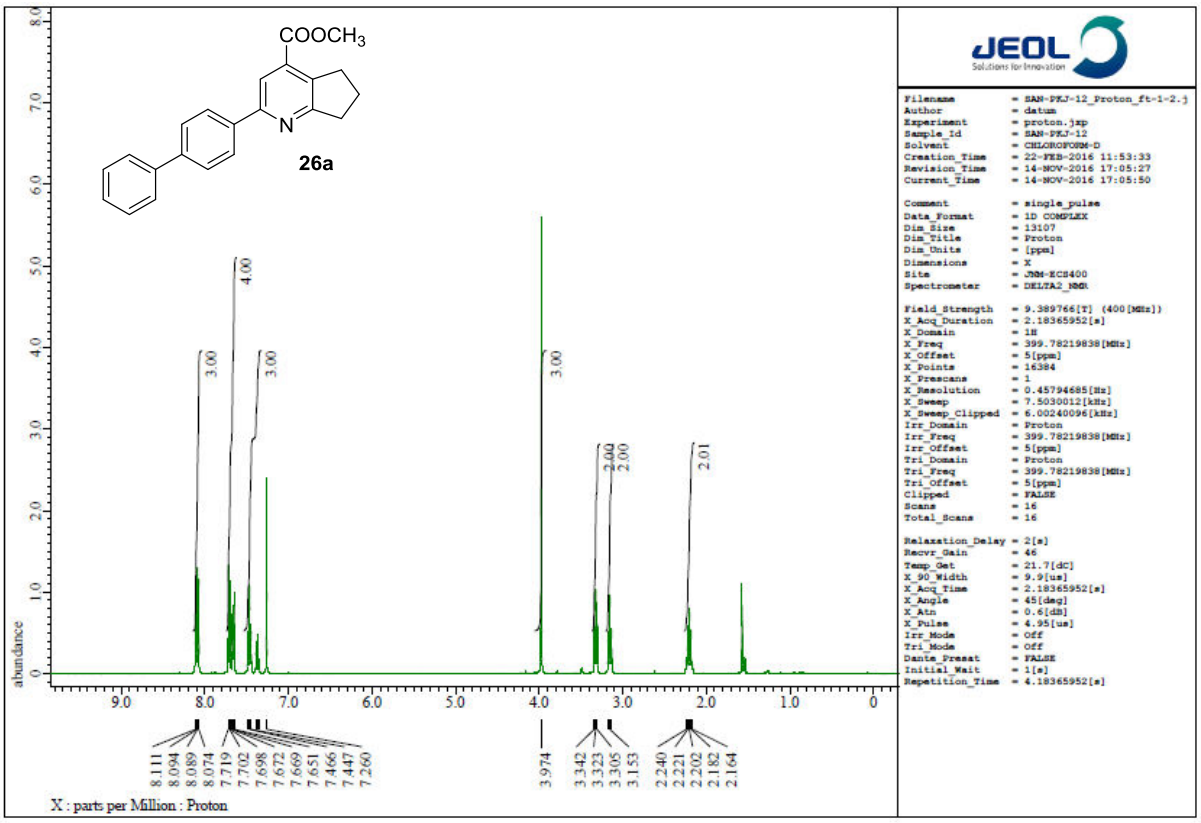


Figure 37. ^{1}H NMR Spectra of Compound **26a.**

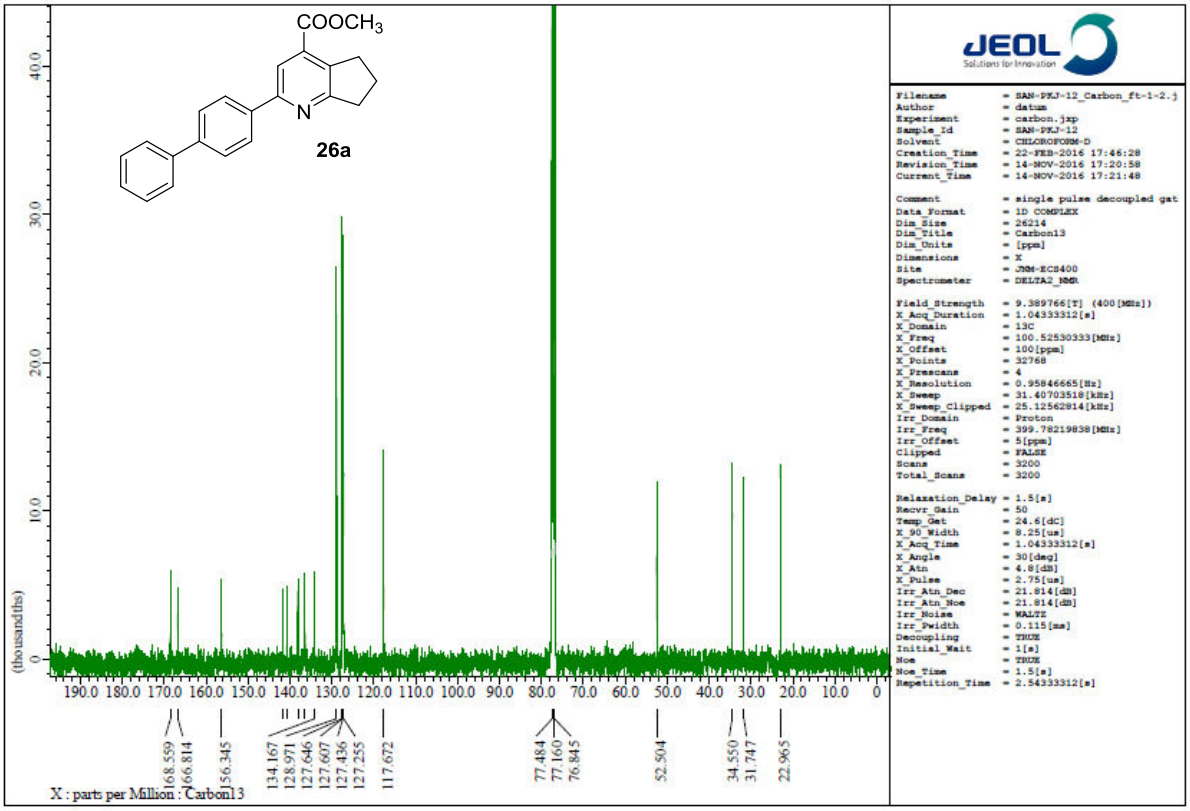


Figure 38. ^{13}C NMR Spectra of Compound **26a.**

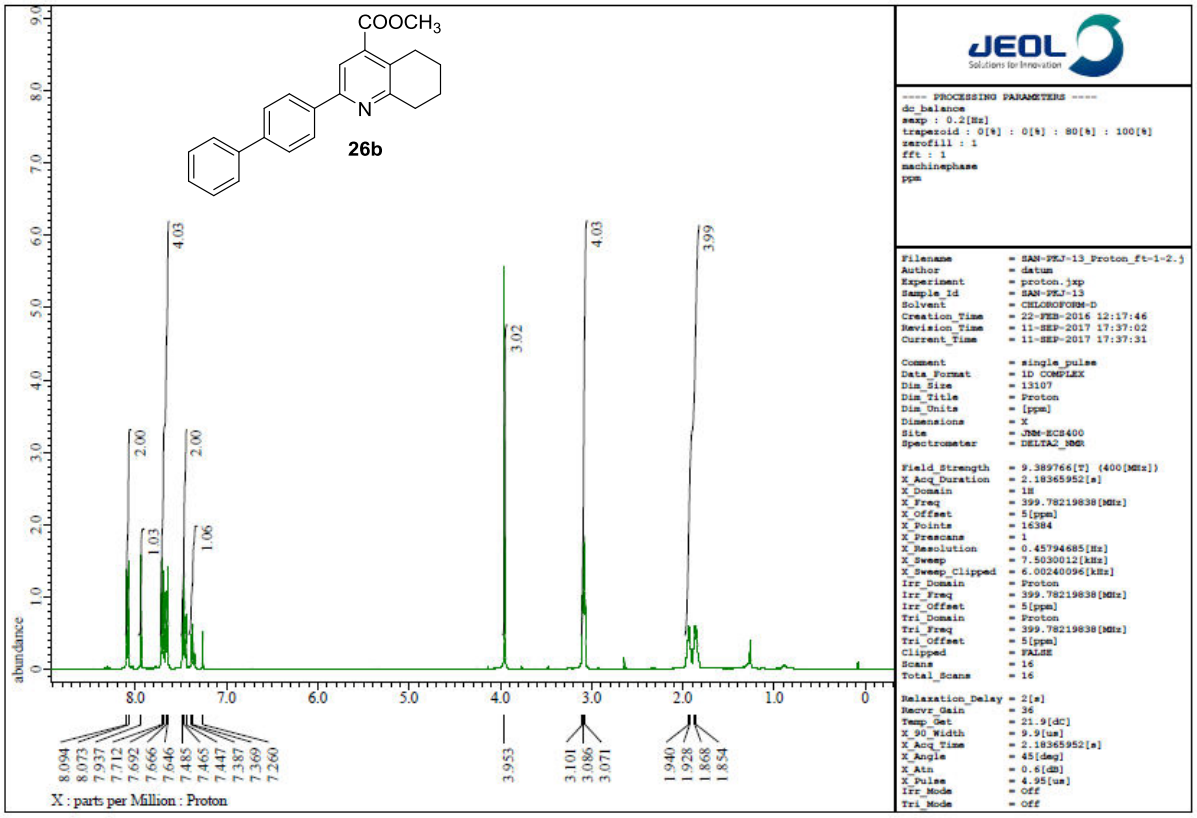


Figure 39. ^{1}H NMR Spectra of Compound **26b.**

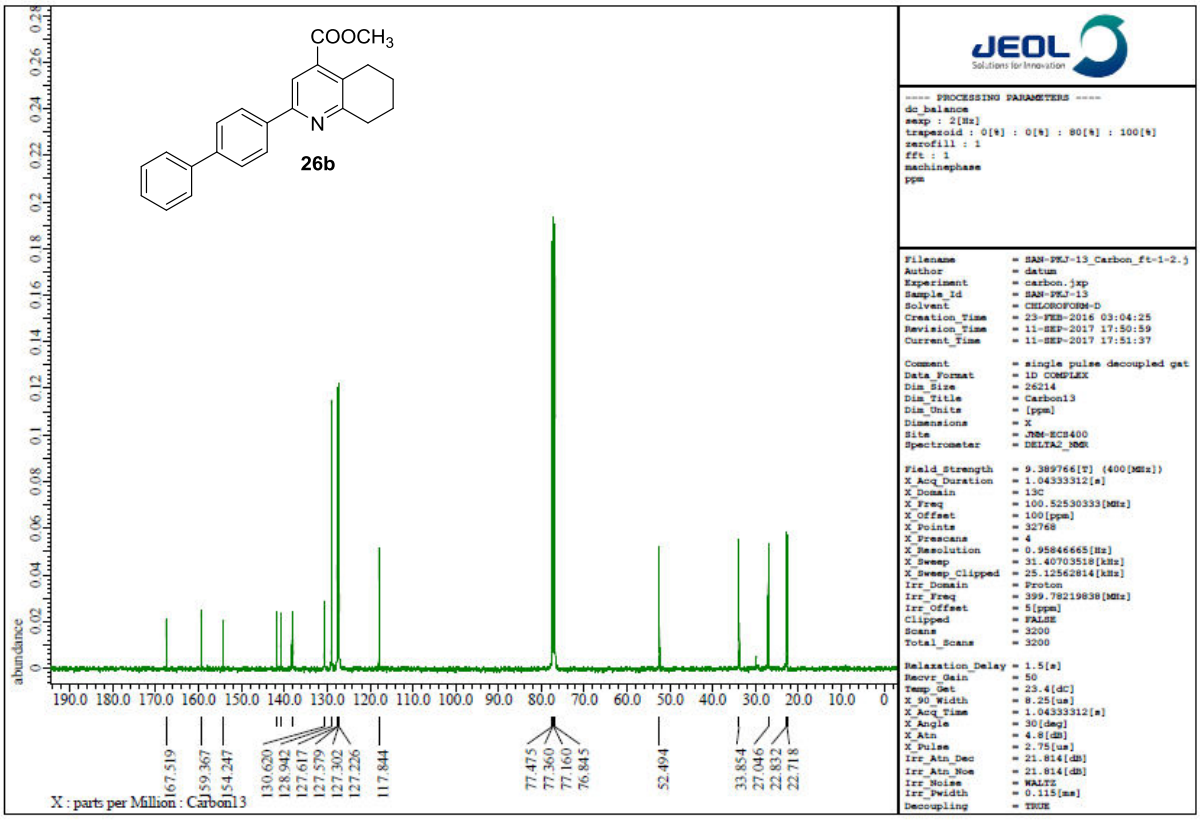


Figure 40. ^{13}C NMR Spectra of Compound **26b.**

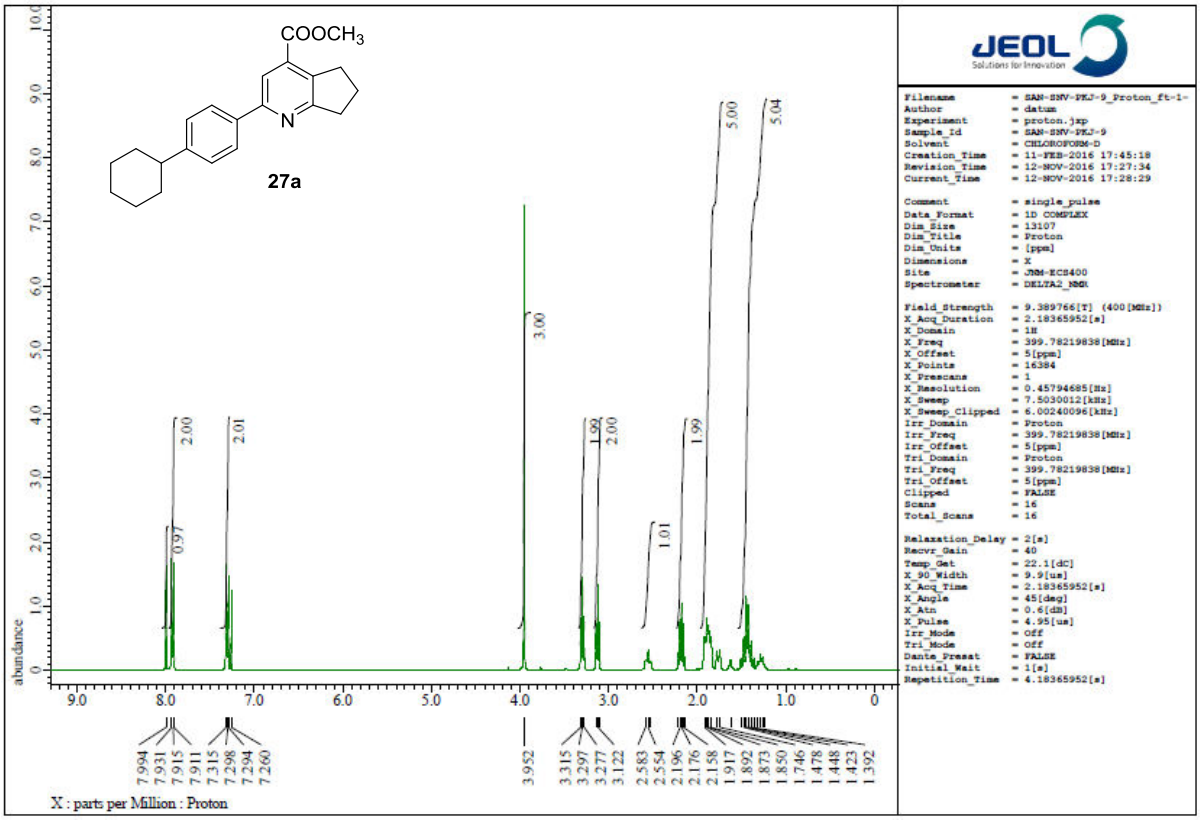


Figure 41. ^{1}H NMR Spectra of Compound **27a.**

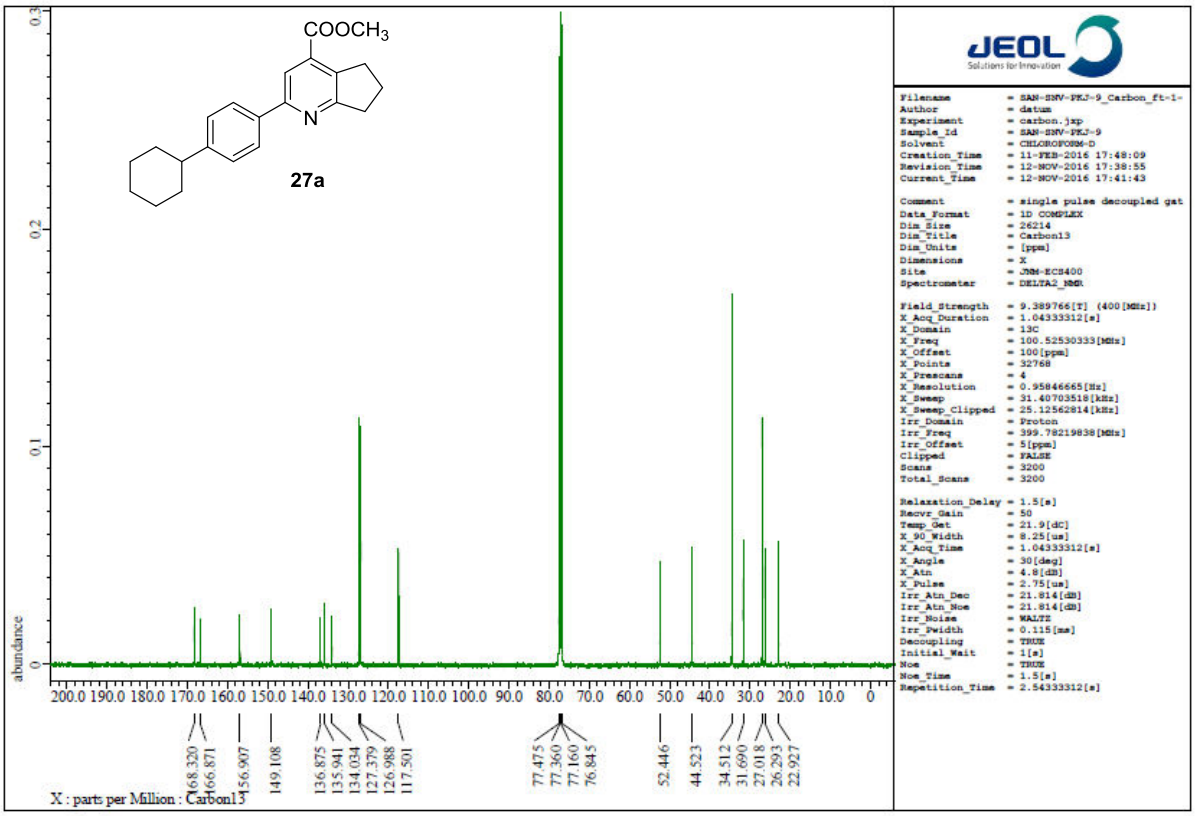


Figure 42. ^{13}C NMR Spectra of Compound **27a.**

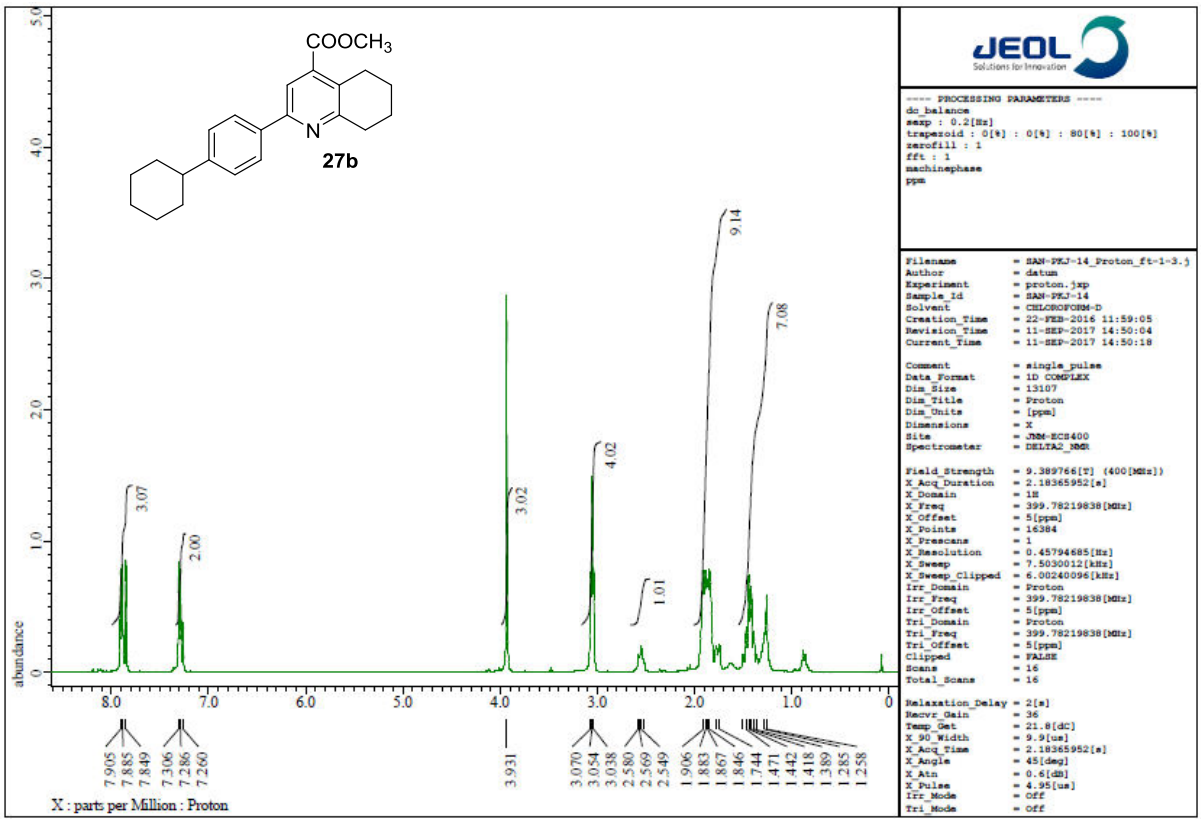


Figure 43. ^{1}H NMR Spectra of Compound **27b.**

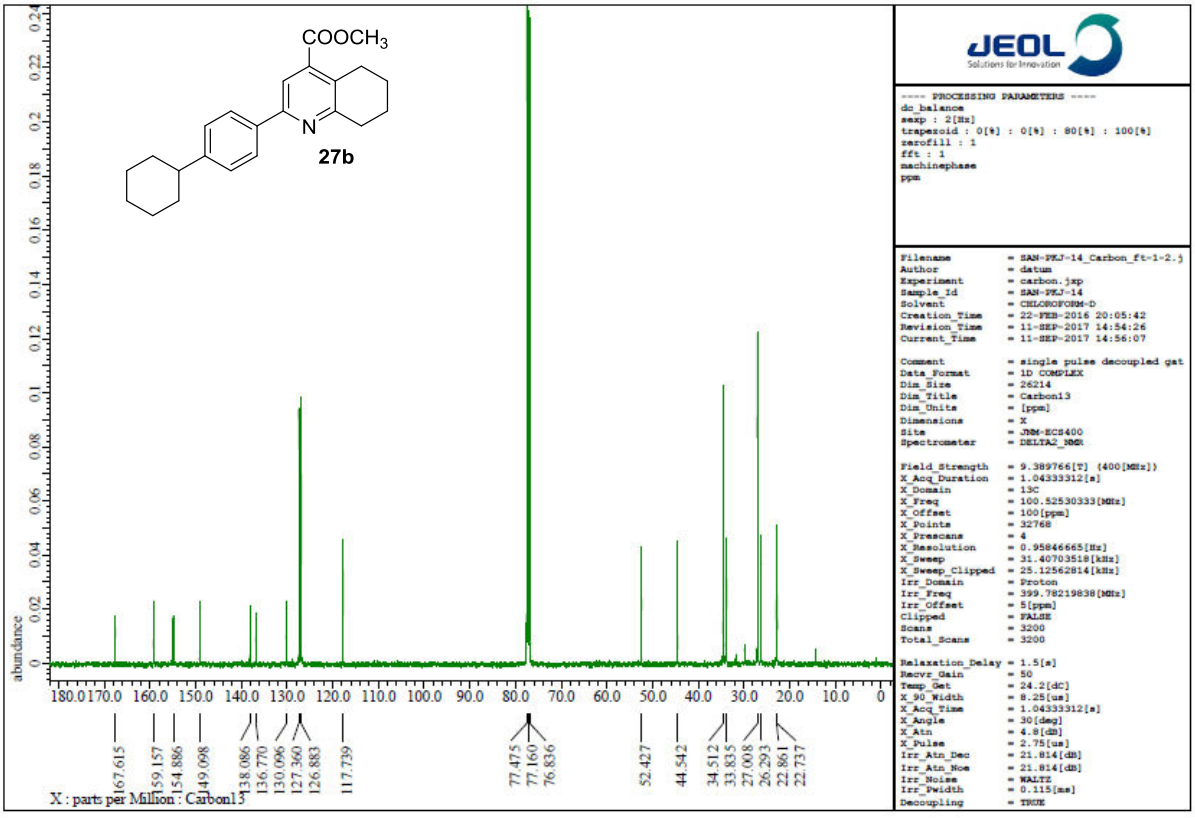


Figure 44. ^{13}C NMR Spectra of Compound **27b.**

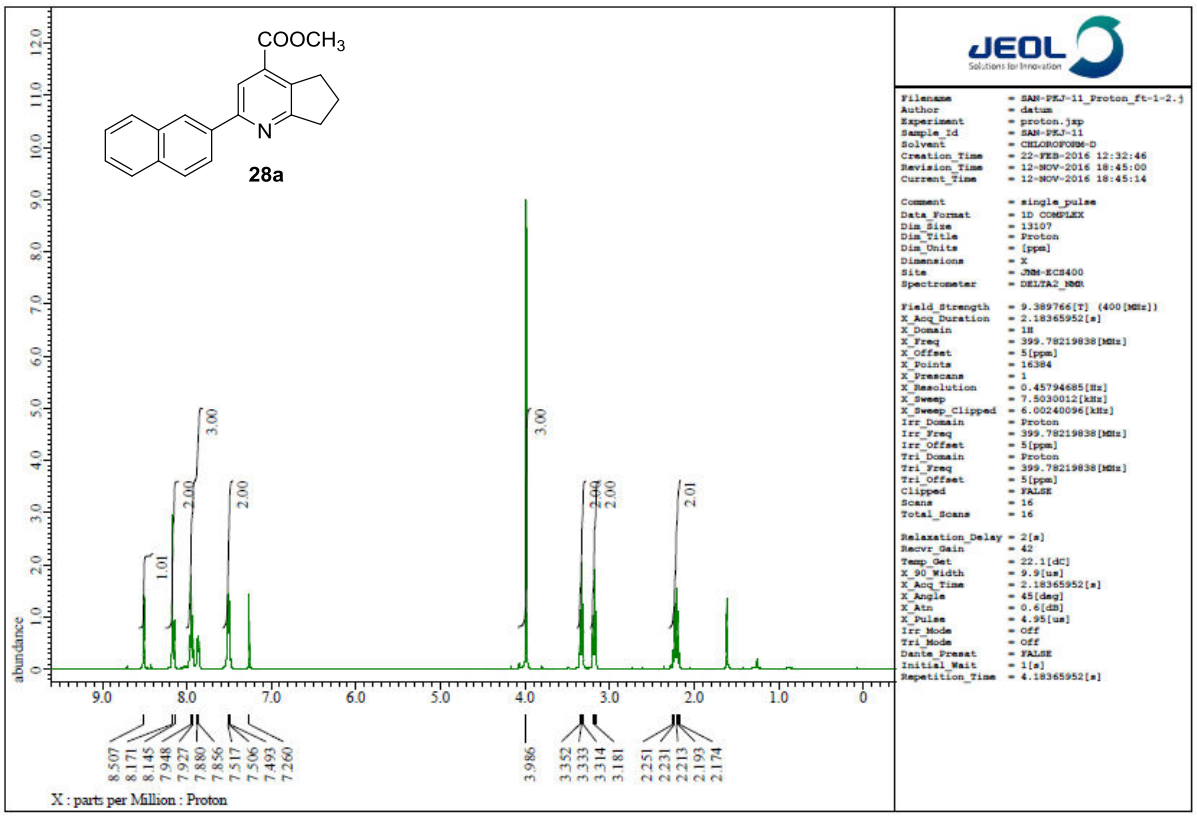


Figure 45. ^{1}H NMR Spectra of Compound **28a.**

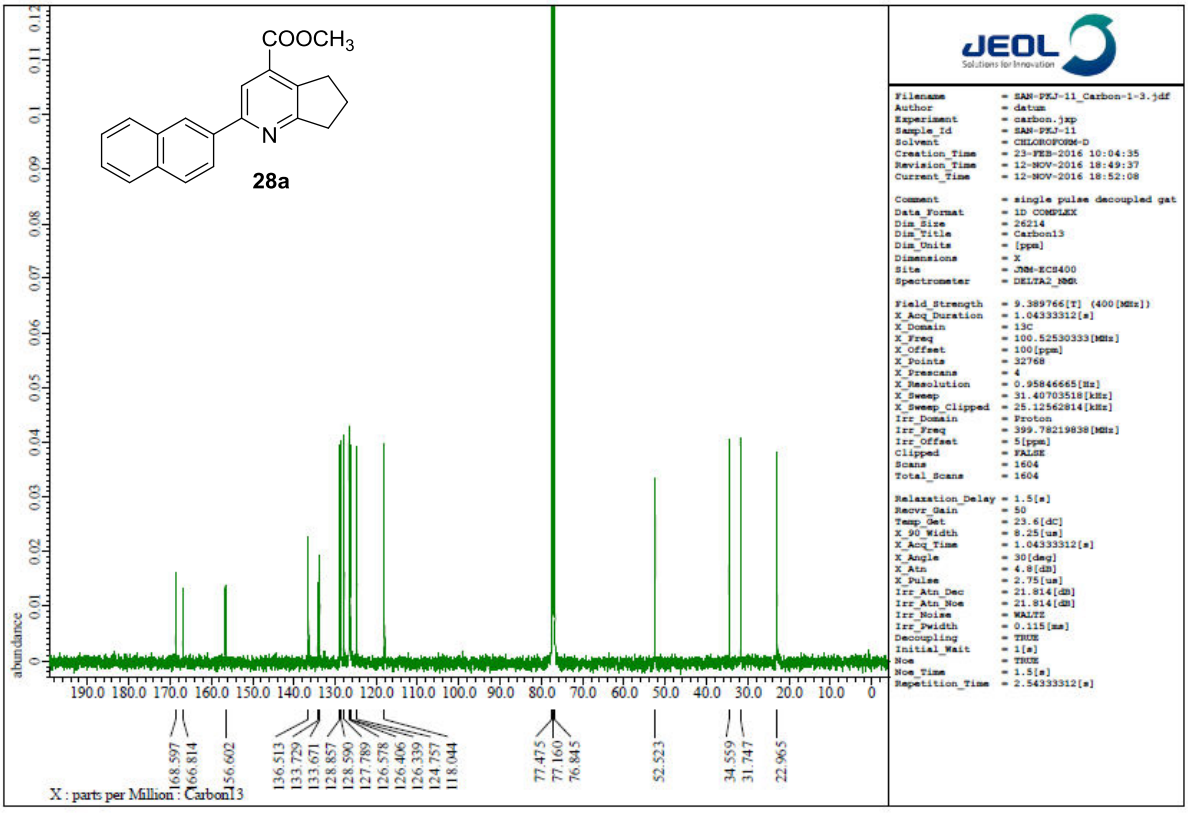


Figure 46. ^{13}C NMR Spectra of Compound **28a.**

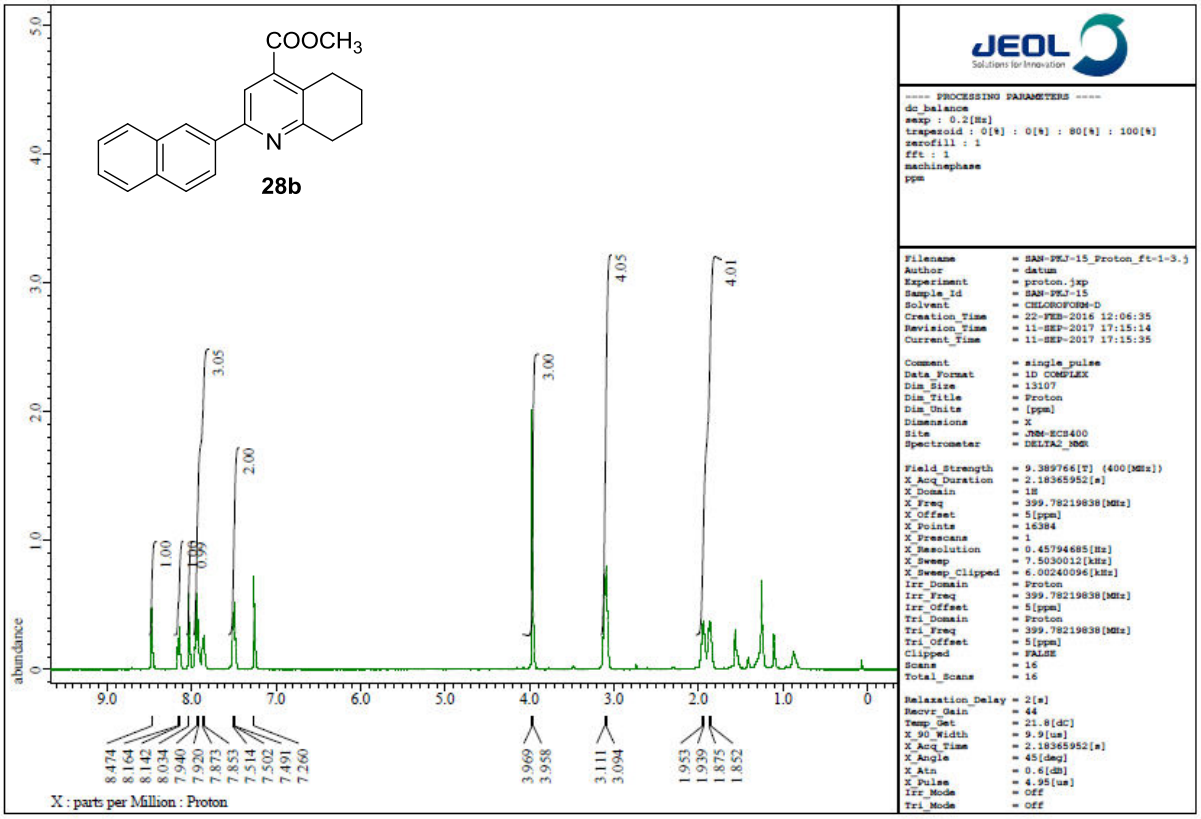


Figure 47. ^{1}H NMR Spectra of Compound **28b.**

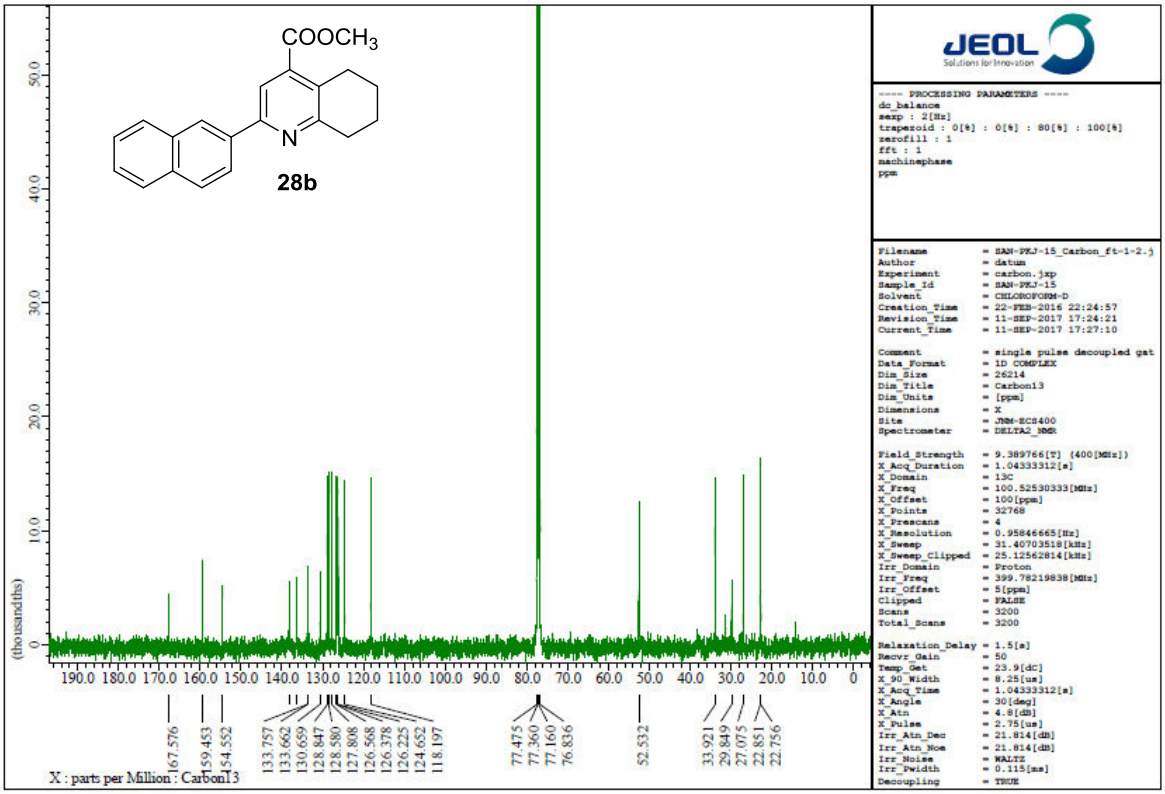


Figure 48. ^{13}C NMR Spectra of Compound **28b.**

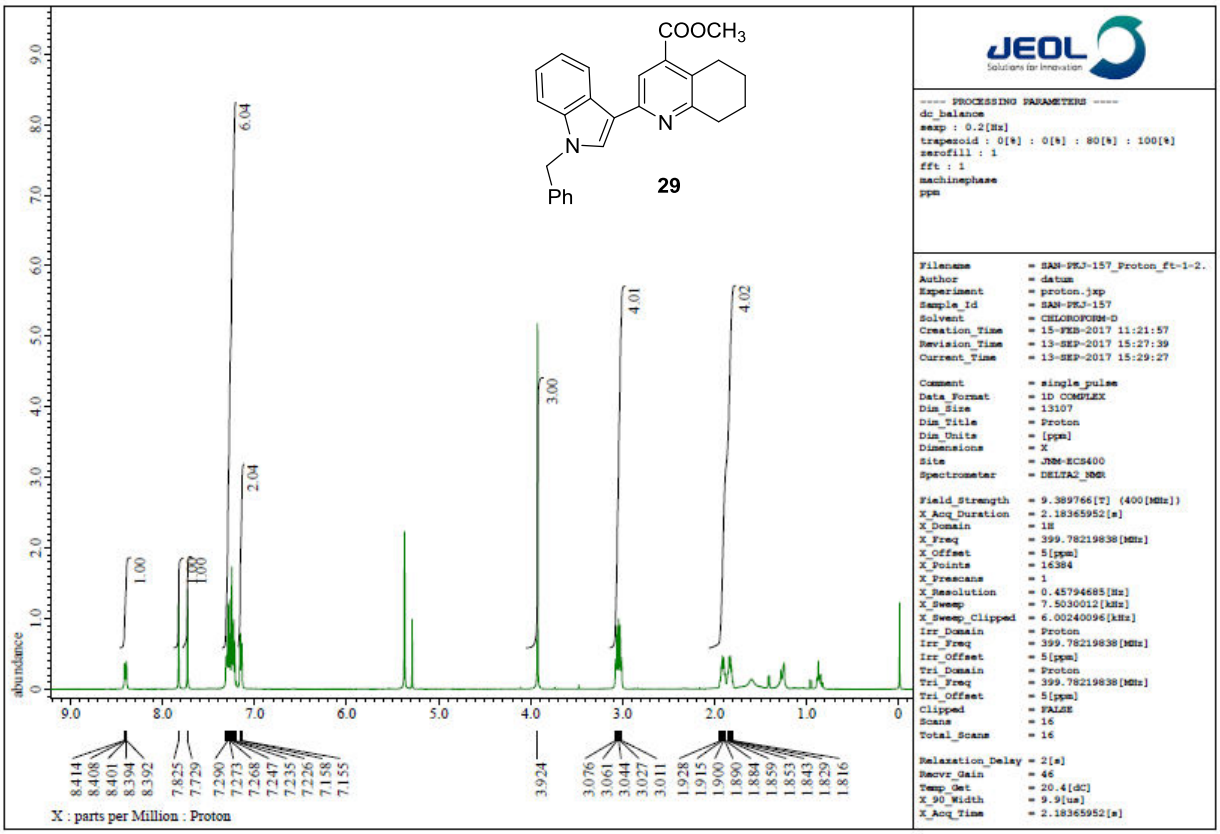


Figure 49. ^{1}H NMR Spectra of Compound **29.**

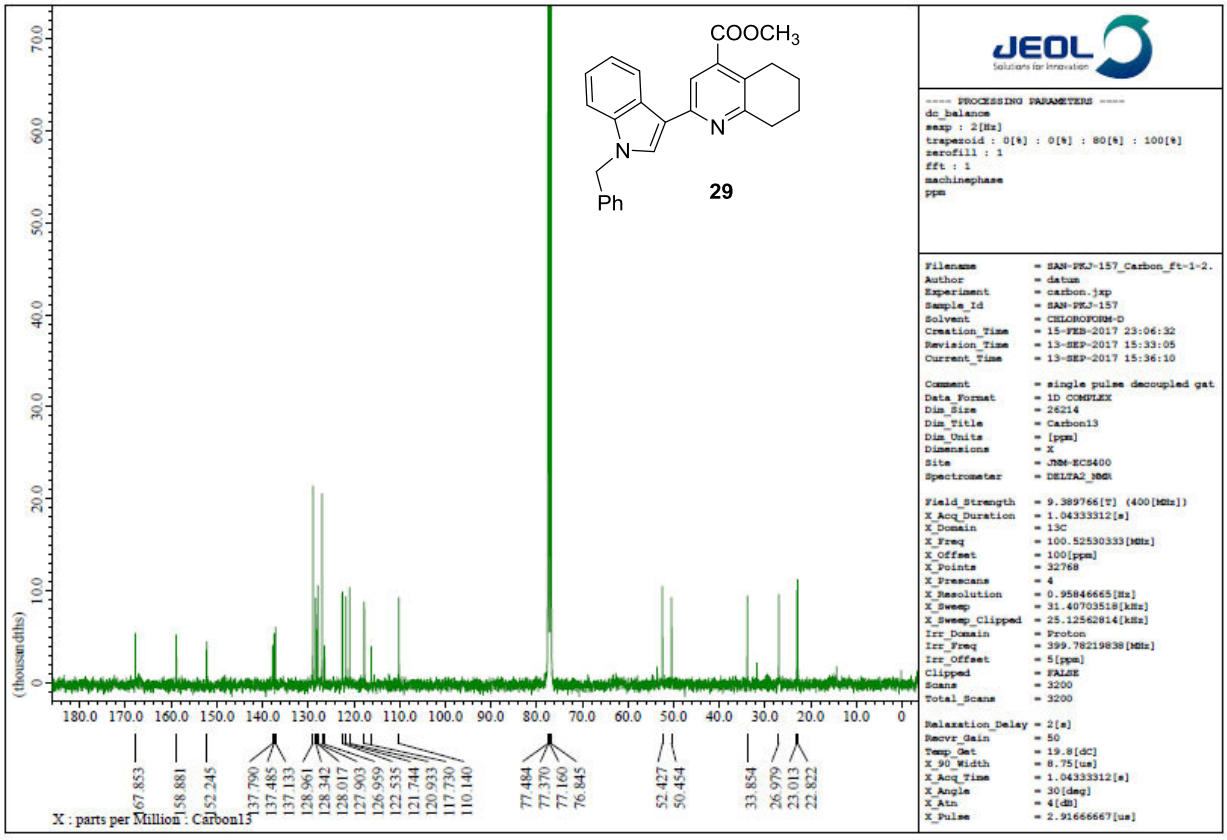


Figure 50. ^{13}C NMR Spectra of Compound **29.**

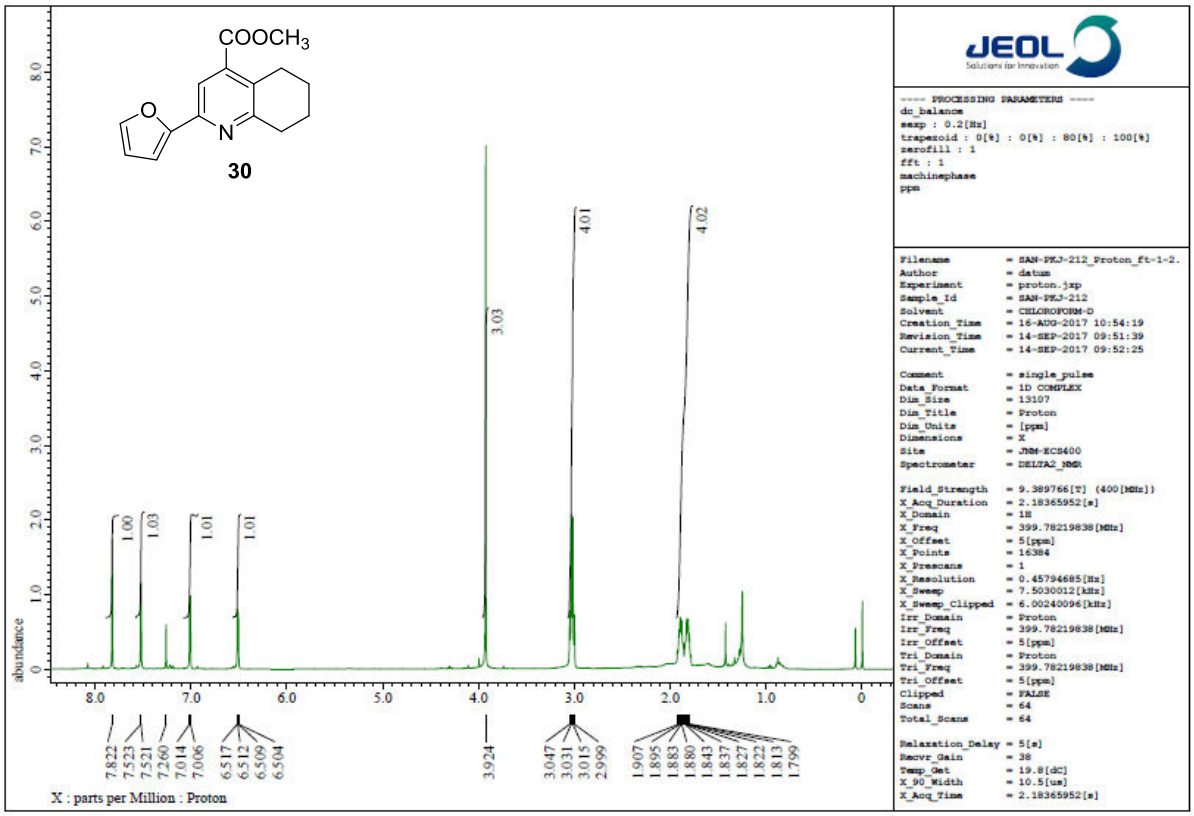


Figure 51. ^{1}H NMR Spectra of Compound **30.**

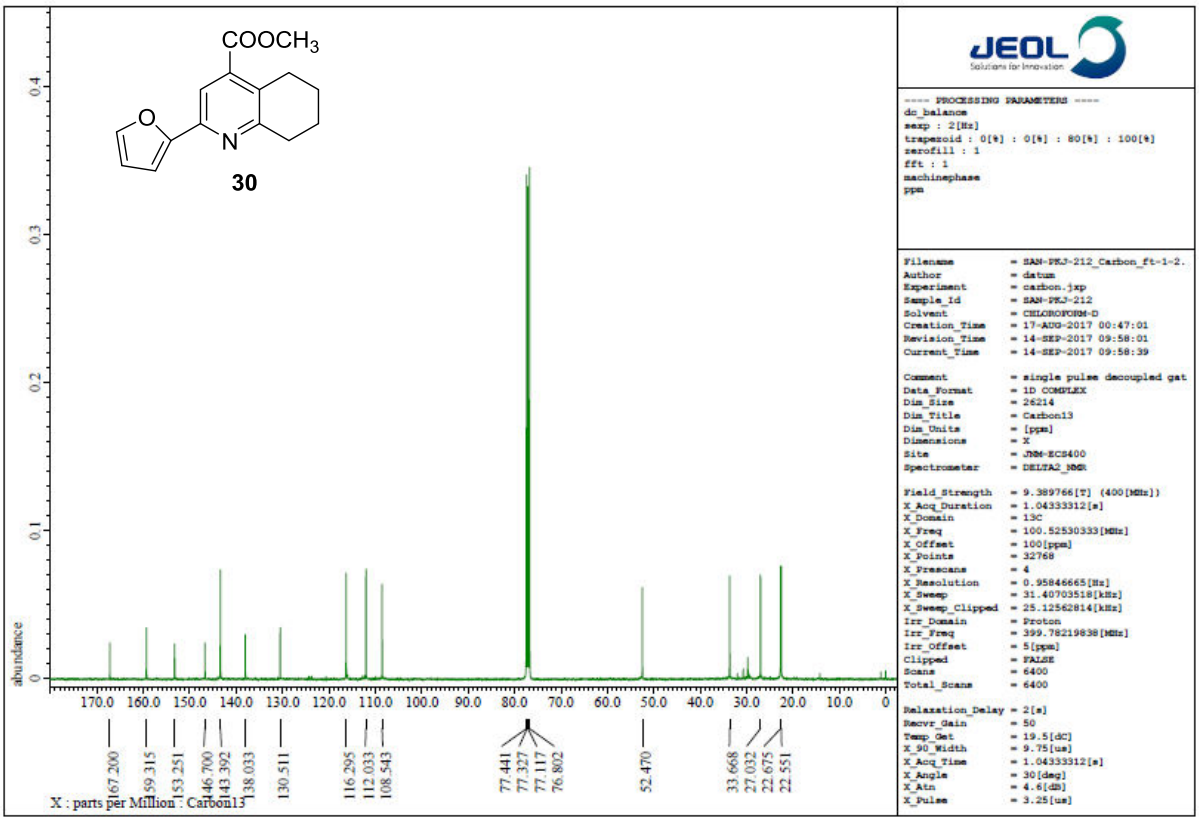


Figure 52. ^{13}C NMR Spectra of Compound **30.**

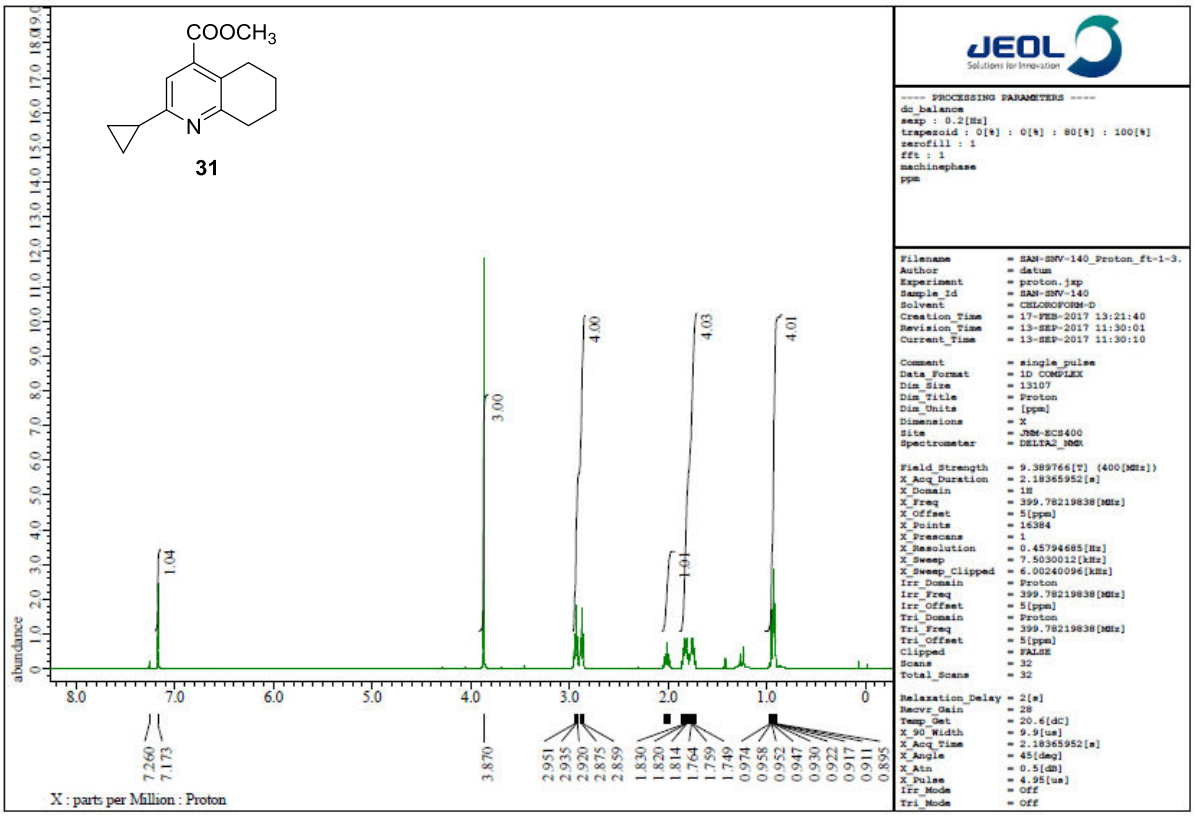


Figure 53. ^{1}H NMR Spectra of Compound **31.**

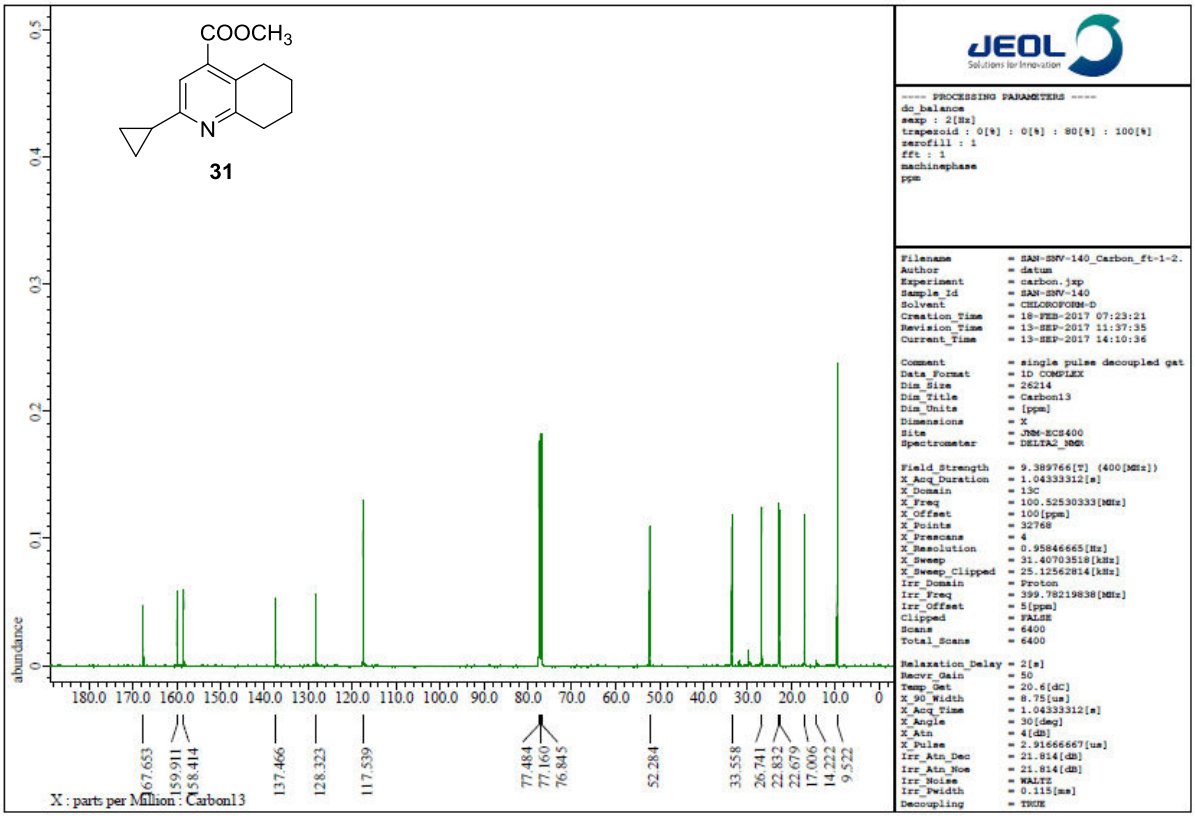


Figure 54. ^{13}C NMR Spectra of Compound **31.**

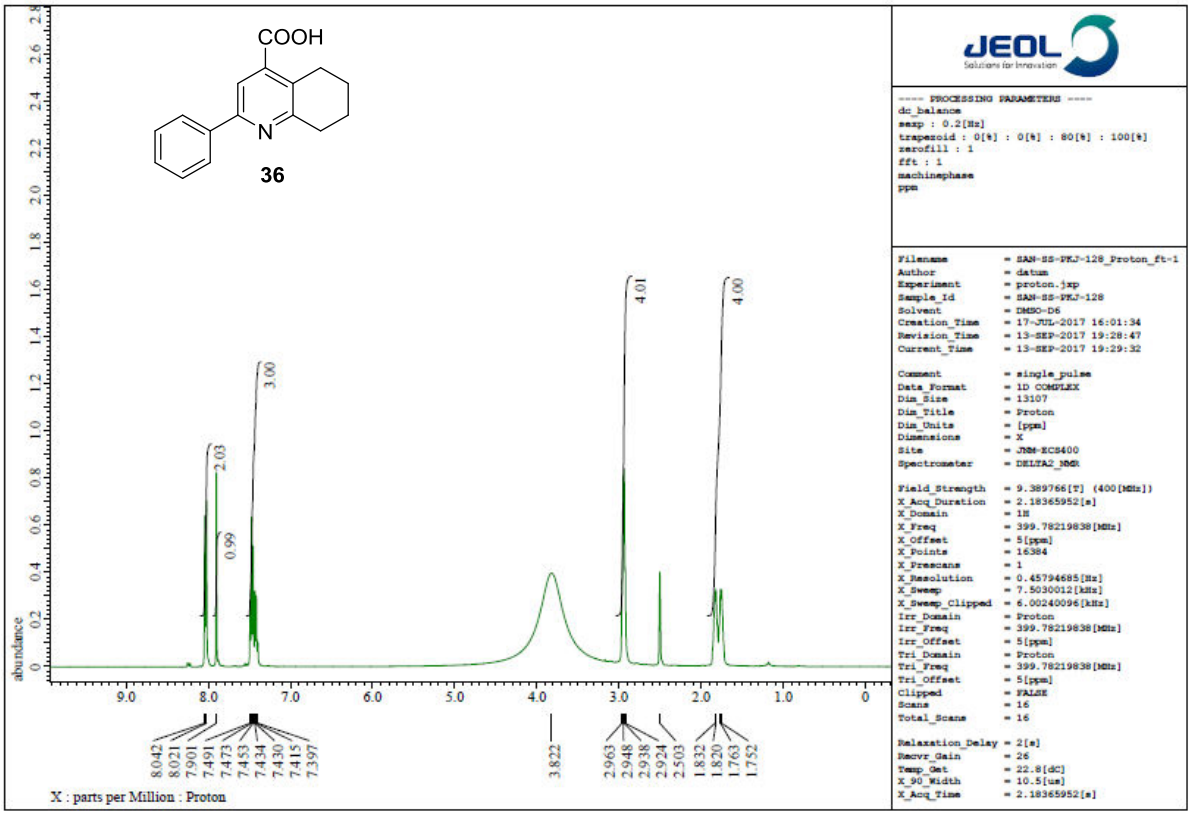


Figure 55. ^{1}H NMR Spectra of Compound **36**.

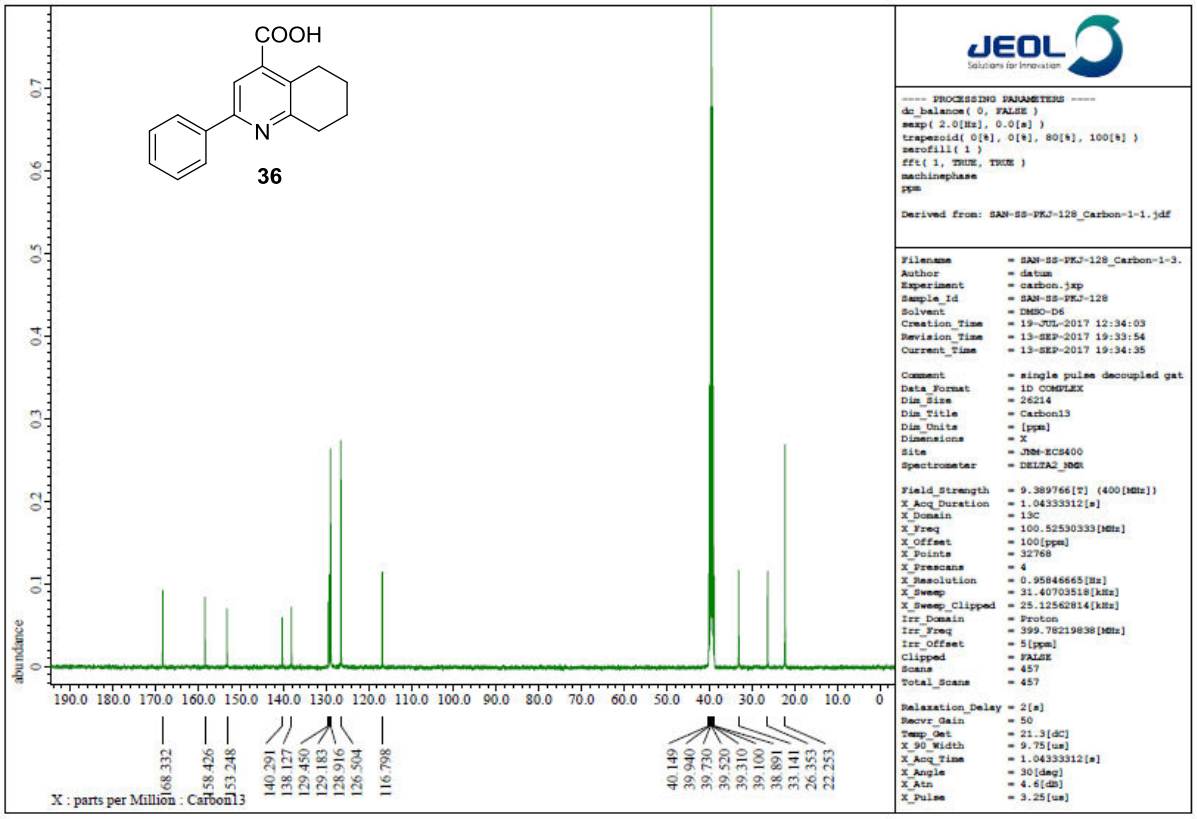


Figure 56. ^{13}C NMR Spectra of Compound **36**.