Metal-Free Synthesis of *N*-Fused Heterocyclic Iodides via C-H Functionalization Mediated by *tert*-Butylhydroperoxide

Krishna K. Sharma, Dhananjay I. Patel, Rahul Jain*
Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research, Sector 67, S. A. S. Nagar, Punjab, 160 062, India

Supporting Information

Contents

1. General information and materials

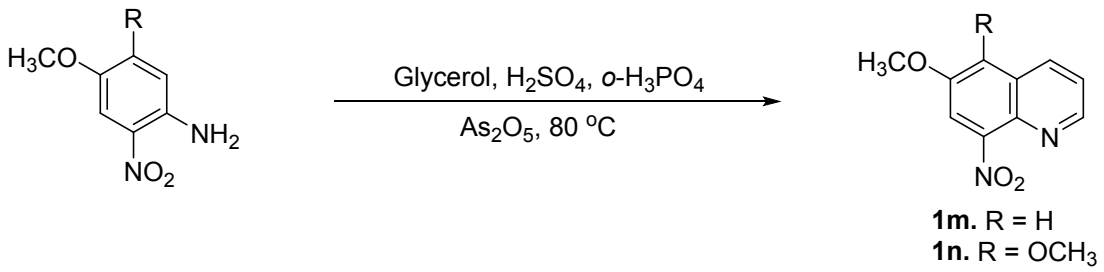
Reagents and starting material were available from commercial suppliers and used without any purification unless otherwise stated. Various heterocycles, solvent, and other reagents were purchased from commercial sources such as Sigma-Aldrich, Alfa-aesar, Merck,TCI, Avra, and Chem-Impex. Nuclear magnetic resonance spectra (NMR) were recorded on a BrukerAvance-III 400 spectrometer (^{1}H NMR, 400 MHz), (^{13}C NMR, 100 MHz). Chemical shifts of given data for ^{1}H NMR was reported as δ values and coupling constants were in hertz (Hz). The following abbreviations were used for spin multiplicity: s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet, q = quadruplet, td = triplet of doublet, dt = doublet of triplet and if

splitting patterns could not be interpreted easily are reported as multiplet (m). Chemical shifts for ^{13}C NMR were reported in ppm relative to the solvent peak. If required 5-10% v/v of CD_3OD was added in $CDCl_3$ while recording the spectra to enhance the solubility before recording of spectra. Thin layer chromatography was performed on Merck precoated silica gel plates(0.25 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm).Visualization on TLC was observed under UV light (254 nm), or staining with iodine or Dragendorff's reagent solution. Synthesized compounds were isolated by automated flash chromatography on silica gel (200−400 mesh). High resolution mass spectra (HRMS) were recorded on Bruker Maxis and IR spectra were recorded in KBr or neat.

2. Synthesis of 5-chloro-8-methoxyquinoline (1l)

Sodium hydride (60 % suspension, 3 equiv.) was washed with dry toluene in a flame dried RBF. To the resulting anhydrous NaH, was added DMF (5 mL) and 5-chloro-8-hydroxyquinoline (1 equiv., 1 mmol). Reaction mixture was allowed to stir at room temperature for 30 min, under nitrogen atmosphere. Methyl iodide (1.5 equiv.) was added, and reaction mixture was stirred for 5 h at ambient temperature.[1] Reaction was terminated by the addition of water (2 mL) and crude product was extracted with chloroform (2 x 20 mL). The combined organic layer was dried over $Na_2SO_4$and concentrated under reduced pressure. The pure compound was isolated by automated flash column chromatography on 230-400 mesh silica using a mobile phase of 60% hexanes in EtOAc.

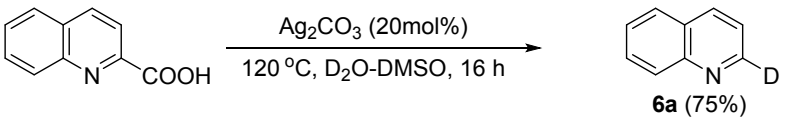
3. Procedure for the synthesis of 6-methoxy-8-nitroquinolines (1m-n)



1m. R = H
1n. R = OCH_3

Synthesized using procedure reported earlier.[2]

4. Procedure for the synthesis of quinoline-2-*d* (6a)

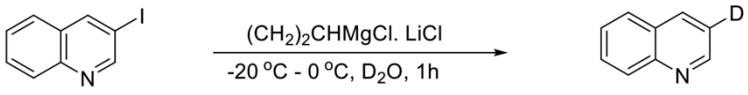


6a (75%)

Synthesized using procedure reported earlier.[3]

5. Procedure for the synthesis of quinoline-3-*d*

Under the argon atmosphere, Turbo Grignard [$(CH_3)_2CHMgCl{\cdot}LiCl$] in THF (1.1 equiv.) was added to the two neck RBF at -20 ˚C. 3-Iodoquinoline (1 equiv.) (dissolved in anhydrous THF) was added to RBF, and mixture was stirred for 10 min. The temperature of the reaction was increased to 0 ˚C and D_2O added to the reaction; stirring continued for 30 min. The product was extracted from the reaction mixture by extraction with diethyl ether and purified on automated flash purification system.



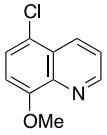
(55%)

6. General procedure for the iodination

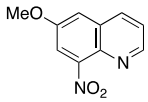
All reagents were weight under ambient conditions. To a mixture of starting material (0.25 mmol, 1 equiv.) in MeCN (4 mL) was added iodine (1.2 equiv.) and TBHP (8 equiv., 70% aq. solution) at ambient temperature. The reaction mixture was heated at 80 ˚C for the desired reaction time, as monitored by TLC. After completion of reaction, solvent was removed under reduced pressure and to the residue was added aqueous saturated sodium thiosulfate solution. The mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and solvent removed under reduced pressure to produce crude product. The pure product was isolated by flash chromatography using a mobile phase of 20-60% hexanes in EtOAc.

For the exclusive synthesis of compounds **2qb** and **2rb**, a higher amount of I_2 (2.4 equiv.) and TBHP (16 equiv.) was added in the reaction medium (8 mL), while keeping the time and temperature of the reaction same as above. The compounds **2qb** and **2rb** were obtained in 77% and 82% yields, respectively.

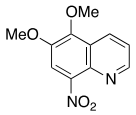
7. Characterization data of synthesized intermediates



5-Chloro-8-methoxyquinoline (1l): Synthesized from 5-chloro-8-hydroxyquinoline. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (dd, *J* = 4.2 Hz, 1.6 Hz, 1H), 8.51 (dd, *J* = 8.6 Hz, 1.68 Hz, 1H), 7.55-7.50 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 149.6, 140.5, 133.0, 126.9, 126.4, 122.4, 122.1, 107.4, 56.1; IR (neat, cm^{-1}): 1715, 1590, 1308, 1099, 927, 819, 784; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{10}H_9ClNO^+$ 193.0294, found 193.0292.

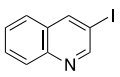


6-Methoxy-8-nitroquinoline (1m): Synthesized from 4-methoxy-2-nitroaniline. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, *J* = 4.2 Hz, 1.64 Hz, 1H), 8.15 (dd, *J* = 8.4 Hz, 1.60 Hz, 1H), 7.71 (d, *J* = 2.7 Hz, 1H), 8.50 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 7.29 (d, *J* = 2.7 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$): δ 156.1, 150.0, 134.8, 130.0, 123.0, 116.6, 109.4, 56.2; IR (neat, cm^{-1}) 3420, 1586, 1515, 1337, 1247, 1109, 1061, 758; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{11}H_{11}N_2O_4^+$ 205.0608, found 205.0602.



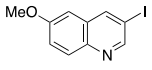
5,6-Dimethoxy-8-nitroquinoline (1n): Synthesized from 4,5-dimethoxy-2-nitroaniline. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (dd, *J* = 4.1 Hz, 1.7 Hz, 1H), 8.55 (dd, *J* = 8.7 Hz, 1.7 Hz, 1H), 8.03 (s, 1H), 7.51 (dd, *J* = 8.6 Hz, 4.1 Hz, 1H), 4.13 (s, 3H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 146.3, 146.0, 142.9, 135.8, 130.6, 124.2, 122.3, 114.4, 61.7, 57.2; IR (neat, cm^{-1}): 3417, 1593, 1525, 1324, 1259, 1116, 1064, 778; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{11}H_{11}N_2O_4^+$ 234.0641, found 234.0639.

8. Characterization data of the synthesized iodinated compounds

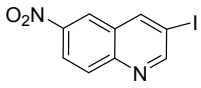


3-Iodoquinoline (2a):[4] Synthesized from quinoline (**1a**, 32 mg, 0.25 mmol). Yield: 58.6 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, *J* = 2.0 Hz, 1H), 8.51 (d, *J* = 1.7 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.75-7.67 (m, 2H), 7.57-7.53 (m, 1H); ^{13}C NMR (100 MHz, MeOD): δ 155.1, 145.5, 144.5, 130 .1, 129.8, 128.0, 127.4, 126.9, 88.7; IR (neat, cm^{-1}): 1634, 1489, 1350, 1124, 938, 887, 745;

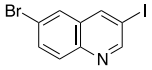
HRMS (ESI-TOF): *m/z* [(M+H)$^+$] calculated for $C_{11}H_{13}INH^+$ 255.9624, found 255.9610.



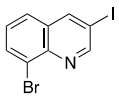
3-Iodo-6-methoxyquinoline (2b):[5] Synthesized from 6-methoxyquinoline (**1b**, 40 mg, 0.25 mmol). Yield: 60.6 mg (85%). ^{1}H NMR (400 MHz, MeOD): δ 8.79 (d, *J* = 2.0 Hz, 1H), 8.63 (d, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.40 (dd, *J* = 9.2 Hz, 2.8 Hz, 1H), 7.16 (d, *J* = 2.8 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, MeOD): δ 158.6, 152.4, 143.2, 141.6, 131.3, 129.3, 123.1, 104.2, 89.3, 54.8; IR (neat, cm^{-1}): 1615, 1456, 1160, 1027, 820, 727; HRMS (ESI-TOF): *m/z* [(M+H)$^+$] calculated for $C_{10}H_9INO^+$ 285.9729, found 285.9721.



3-Iodo-6-nitroquinoline (2c): Synthesized from 6-nitroquinoline (**1c**, 44 mg, 0.25 mmol). Yield 69 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (d, *J* = 2.1 Hz, 1H), 8.75 (d, *J* = 1.9 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.50 (dd, *J* = 9.2 Hz, 2.48 Hz, 1H), 8.22 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 148.2, 145.9,145.2, 131.5, 128.6, 123.4, 123.3, 92.0; IR (neat, cm^{-1}) 1631, 1528, 1344, 1088, 878, 777; HRMS (ESI-TOF): *m/z* [(M+H)+] calculated for $C_9H_6IN_2O_2^+$ 300.9474, found 300.9471.

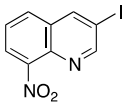


6-Bromo-3-iodoquinoline (2d): Synthesized from 6-bromoquinoline (**1d**, 52 mg, 0.25 mmol). Yield: 70 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 2.0 Hz, 1H), 8.45 (d, *J* = 1.8 Hz, 1H), 7.93 (d, *J* = 4.9 Hz, 1H), 7.87 (d, *J* = 2.1 Hz, 1H), 7.80 (dd, *J* = 8.9 Hz, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 144.9, 142.6, 133.5, 131.2, 130.7, 128.7, 121.3, 91.0; IR (neat, cm^{-1}): 1570, 1475, 1323, 1125, 938, 907, 823; HRMS (ESI-TOF): *m/z* [(M+H)$^+$] calculated for $C_9H_6BrIN^+$ 333.8728, found 333.8713

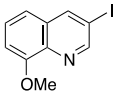


8-Bromo-3-iodoquinoline (2e): Synthesized from 8-bromoquinoline (**1e**, 52 mg, 0.25 mmol). Yield: 72 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 2.0 Hz, 1H), 8.56 (d, *J* = 2.0

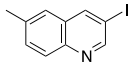
Hz, 1H), 8.08 (dd, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.70 (dd, *J* = 8.2 Hz, 2.1 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 144.1, 143.6, 133.7, 131.0, 127.9, 126.7, 124.9, 91.0; IR (neat, cm^{-1}): 1568, 1477, 1333, 1115, 942, 911, 822; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_9H_6BrIN^+$ 333.8728, found 333.8711.



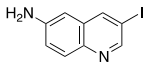
3-Iodo-8-nitroquinoline (2f): Synthesized from 8-nitroquinoline (**1f**, 44 mg, 0.25 mmol). Yield: 65 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (s, 1H), 8.66 (d, *J* = 2.0 Hz, 1H), 8.07 (dd, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.95 (dd, *J* = 8.3 Hz, 1.2 Hz, 1H), 7.66 (dd, *J* = 8.1 Hz, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 148.3, 143.7, 137.6, 130.9, 130.3, 126.4, 124.2, 92.0; IR (neat, cm^{-1}): 1638, 1522, 1350, 1078, 889, 762; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_9H_6IN_2O_2^+$ 300.9474, found 300.9477.



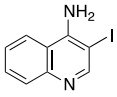
3-Iodo-8-methoxyquinoline (2g): Synthesized from 8-methoxyquinoline (**1g**, 40 mg, 0.25 mmol). Yield: 60 mg (84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, *J* = 2.1 Hz, 1H), 8.50 (d, *J* = 2.1 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.27-7.25 (m, 1H), 7.06 (dd, *J* = 7.8 Hz, 0.9 Hz, 1H), 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 154.2, 143.5, 138.3, 131.0, 127.8, 118.1, 108.1, 90.9, 56.0; IR (neat, cm^{-1}): 1559, 1484, 1376, 1260, 1118, 885, 753; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{10}H_9INO^+$ 285.9729, found 285.9725.



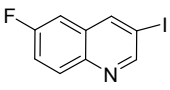
3-Iodo-6-methylquinoline (2h): Synthesized from 6-methylquinoline (**1h**, 36 mg, 0.25 mmol). Yield: 63 mg (93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.40 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.42 (s, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 144.9, 142.9, 137.4, 132.3, 129.9, 129.1, 125.5, 89.8, 21.6; IR (neat, cm^{-1}): 1636, 1489, 1336, 1258, 952, 902, 817, 749; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{10}H_9IN^+$ 269.9780, found 269.9776.



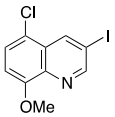
6-Amino-3-iodoquinoline (2i): Synthesized from 6-aminoquinoline (**1i**, 36 mg, 0.25 mmol). Yield: 65 mg (97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 1.5 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.36 (dd, *J* = 8.6 Hz, 4.2 Hz, 1H), 7.21 (d, *J* = 8.9 Hz, 1H), 4.63 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 146.0, 143.7, 137.9, 131.3, 130.7, 122.8, 120.1, 80.9; IR (neat, cm^{-1}): 3416, 1642, 1453, 1371, 1249, 1101, 725; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_9H_8IN_2^+$ 270.9732, found 270.9739.



4-Amino-3-iodoquinoline (2j): Synthesized from 4-aminoquinoline (**1j**, 36 mg, 0.25 mmol). Yield: 61 mg (90%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.62 (s, 1H), 7.92 (dd, *J* = 8.5 Hz, 0.8 Hz, 1H), 7.84 (dd, *J* = 8.5 Hz, 0.6 Hz, 1H), 7.66-7.61 (m, 1H), 7.47-7.42 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 155.7, 150.8, 146.8, 130.0, 128.1, 125.6, 121.2, 118.2, 73.6; IR (neat, cm^{-1}): 3390, 1639, 1464, 1363, 1264, 1085, 742; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_9H_8IN_2^+$ 270.9732, found 270.9725.

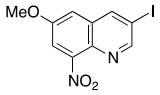


6-Fluoro-3-iodoquinoline (2k): Synthesized from 6-flouroquinoline (**1k**, 36 mg, 0.25 mmol). Yield 60 mg (89%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 2.0 Hz, 1H), 8.50 (d, *J* = 1.6 Hz, 1H), 8.07 (dd, *J* = 9.2 Hz, 5.3 Hz, 1H), 7.50 (td, *J* = 8.7 Hz, 2.8 Hz, 1H), 7.33 (dd, *J* = 8.7 Hz, 2.7 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.9, 159.4, 154.9, 142.9, 132.1, 130.4, 120.2, 109.7, 91.1; IR (neat, cm^{-1}) 1578, 1469, 1319, 1132, 945, 899, 841; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_9H_6FIN^+$ 273.9529, found 273.9522.

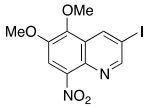


5-Chloro-3-iodo-8-methoxyquinoline (2l): Synthesized from 5-chloro-8-methoxyquinoline (**1l**, 48 mg, 0.25 mmol). Yield: 70 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, *J* = 2.0 Hz, 1H), 8.91 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.8, 140.8, 138.8, 128.4, 127.4, 120.9, 108.0, 92.1, 56.2; IR (neat, cm^{-1}): 1604, 1560, 1483, 1366, 1107, 939, 809, 742; HRMS (ESI-TOF):

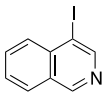
m/z [(M+H)$^+$] calculated for $C_{10}H_8ClINO^+$ 319.9339, found 319.9336.



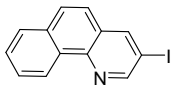
3-Iodo-6-methoxy-8-nitroquinoline (2m): Synthesized from 6-methoxy-8-nitroquinoline (**1m**, 51 mg, 0.25 mmol). Yield: 68 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (d, *J* = 1.9 Hz, 1H), 8.52 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 2.6 Hz, 1H), 7.15 (d, *J* = 2.7 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, MeOD): δ 152.8, 151.3, 144.5, 138.6, 129.5, 127.5, 113.3, 104.4, 88.5, 52.3; IR (neat, cm^{-1}): 1614, 1511, 1444, 1340, 1285, 1160, 825, 727; HRMS (ESI-TOF): *m/z* [(M+H)$^+$] calculated for $C_{10}H_8IN_2O_3^+$ 330.9580, found 330.9571.



3-Iodo-5,6-dimethoxy-8-nitroquinoline (2n): Synthesized from 5,6-dimethoxy-8-nitroquinoline (**1n**, 59 mg, 0.25 mmol). Yield: 74 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.92 (s, 1H), 8.02 (s, 1H), 4.14 (s, 3H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 151.1, 146.8, 138.4, 131.0, 125.5, 122.2, 114.6, 91.9, 61.8, 57.26; IR (neat, cm^{-1}): 1620, 1495, 1301, 1299, 1155, 838, 740; HRMS (ESI-TOF): *m/z* [(M+H)$^+$] calculated for $C_{11}H_{10}IN_2O_4^+$ 360.9685, found 360.9678.

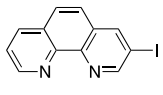


4-Iodoisoquinoline (2o):[6] Synthesized from isoquinoline (**1o**, 32 mg, 0.25 mmol). Yield: 56 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (s, 1H), 8.96 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.83-7.79 (m, 1H), 7.70-7.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 150.9, 137.1, 131.9, 130.7, 129.7, 128.3, 128.1, 96.8; IR (neat, cm^{-1}): 1561, 1484, 1372, 1209, 952, 902, 817, 749; HRMS (ESI-TOF): *m/z* [(M+H)$^+$] calculated for $C_9H_7IN^+$ 255.9624, found 255.9619.

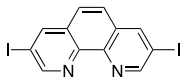


3-Iodobenzo[*h*]quinoline (2p): Synthesized from benzo[*h*]quinoline (**1p**, 45 mg, 0.25 mmol. Yield: 63 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (dd, *J* = 8.2, 1.3 Hz, 1H), 9.15 (d, *J* = 2.1 Hz, 1H), 8.54 (d, *J* = 2.1 Hz, 1H), 7.92 (dd, *J* = 6.7 Hz, 2.5 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.77-7.73 (m, 2H), 7.58 (d, *J* =

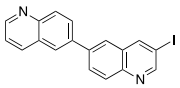
8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 145.0, 143.3, 133.5, 131.2, 128.8, 128.6, 128.1, 127.9, 127.4, 124.2, 124.1, 90.7; IR (neat, cm^{-1}): 1585, 1501, 1467, 1363, 1097, 890, 816, 783, 749; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{13}H_9IN^+$ 305.9780, found 305.9771.



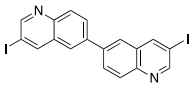
3-Iodo-1,10-phenanthroline (2qa): Synthesized from 1,10-phenanthroline (**1q**, 45 mg, 0.25 mmol). Yield: 51 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (d, *J* = 2.0 Hz, 1H), 9.17 (t, *J* = 4.3 Hz, 1H), 8.57 (d, *J* = 2.1 Hz, 1H), 8.22 (dd, *J* = 8.1 Hz, 1.7 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.64 (dd, *J* = 8.1 Hz, 4.26 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 150.5, 145.9, 144.5, 143.6, 136.1, 130.1, 128.6, 127.6, 125.3, 123.4, 92.8; IR (neat, cm^{-1}): 1701, 1494, 1405, 1267, 1117, 831, 734; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{12}H_8IN_2^+$ 306.9732, found 306.9739.



3,8-Diiodo-1,10-phenanthroline (2qb): Synthesized from 1,10-phenanthroline (**1q**, 45 mg, 0.25 mmol). Yield: 8 mg (7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (d, *J* = 2.1 Hz, 2H), 8.60 (d, *J* = 2.0 Hz, 2H), 7.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 144.4, 143.7, 130.1, 126.5, 93.2; IR (neat, cm^{-1}): 1717, 1465, 1415, 1259, 1097, 835, 729; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{12}H_7I_2N_2^+$ 432.8699, found 432.8698.

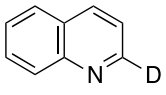


3-Iodo-6,6'-biquinoline (2ra): Synthesized from 6,6-biquinoline (**1r**, 64 mg, 0.25 mmol). Yield: 58 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (t, *J* = 2.8 Hz, 1H), 8.98 (d, *J* = 2.9 Hz, 1H), 8.65 (d, *J* = 1.9 Hz, 1H), 8.22 (dd, *J* = 8.1 Hz, 1.68 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.64 (dd, *J* = 8.1 Hz, 4.26 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 150.6, 147.5, 145.7, 144.0, 139.3, 138.0, 136.6, 130.1, 130.0, 129.8, 129.2, 126.2, 124.9, 121.8, 90.4; IR (neat, cm^{-1}): 1701, 1494, 1405, 1267, 1117, 831, 734; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{18}H_{12}IN_2^+$ 383.0045, found 383.0036.

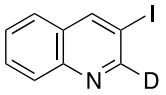


3,3'-Diiodo-6,6'-biquinoline (2rb): Synthesized from 6,6-biquinoline (**1r**, 64 mg, 0.25 mmol). Yield: 12 mg (9%); ^{1}HNMR (400 MHz, $CDCl_3$): δ 9.07 (d, *J* = 2.1 Hz, 2H), 8.63 (d, *J* = 1.9 Hz,

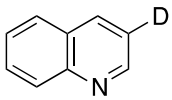
2H), 8.19 (d, *J* = 8.8 Hz, 2H), 8.08 (dd, *J* = 8.8 Hz, 2.00 Hz, 2H), 8.00 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 146.0, 144.0, 138.9, 130.2, 130.1, 129.6, 125.1; IR (neat, cm^{-1}): 1698, 1504, 1378, 1288, 1090, 801, 742; HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_{18}H_{11}I_2N_2$ 508.9006, found 508.9002.



Quinoline-2-*d* (6a): Synthesized from quinoline-2-carboxylic acid (approx. 96% deuteration). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (d, *J* = 4.3 Hz, 0.036 H), 8.13 (t, *J* = 9.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H); HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_9H_7DN^+$ 131.0719, found 131.0718.



3-Iodoquinoline-2-*d* (6b): Synthesized from quinoline-2-*d*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.75-7.69 (m, 2H), 7.56 (td, *J* = 7.5 Hz, 1.1 Hz, 1H); HRMS (ESI-TOF): *m/z* [$(M+H)^+$] calculated for $C_9H_7DIN^+$ 256.9686, found 256.9682.



Quinoline-3-*d*: Synthesized from 3-iodoquinoline (approx. 91% deuteration). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.27 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H); 7.49-7.46 (m, 0.09); HRMS (ESI-TOF): *m/z* [(M+H)+] calculated for $C_9H_7DN^+$ 131.0719, found 131.0715.

References

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(2) H. S. Mosher, W. H. Yanko, and F. C. Whitmore, *Org. Synth.,* 1947*,* **27,** 48.

(3) R. Grainger, A. Nikmal, J. Cornella and I. Larrosa, *Org. Biomol. Chem.*, 2012, **10**, 3172.

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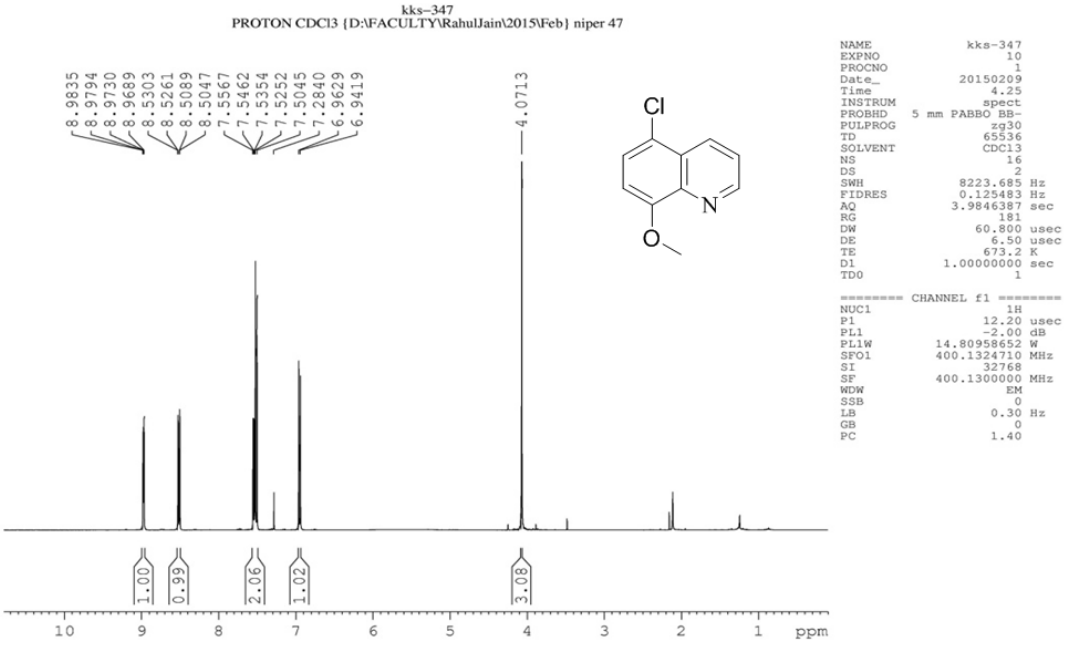
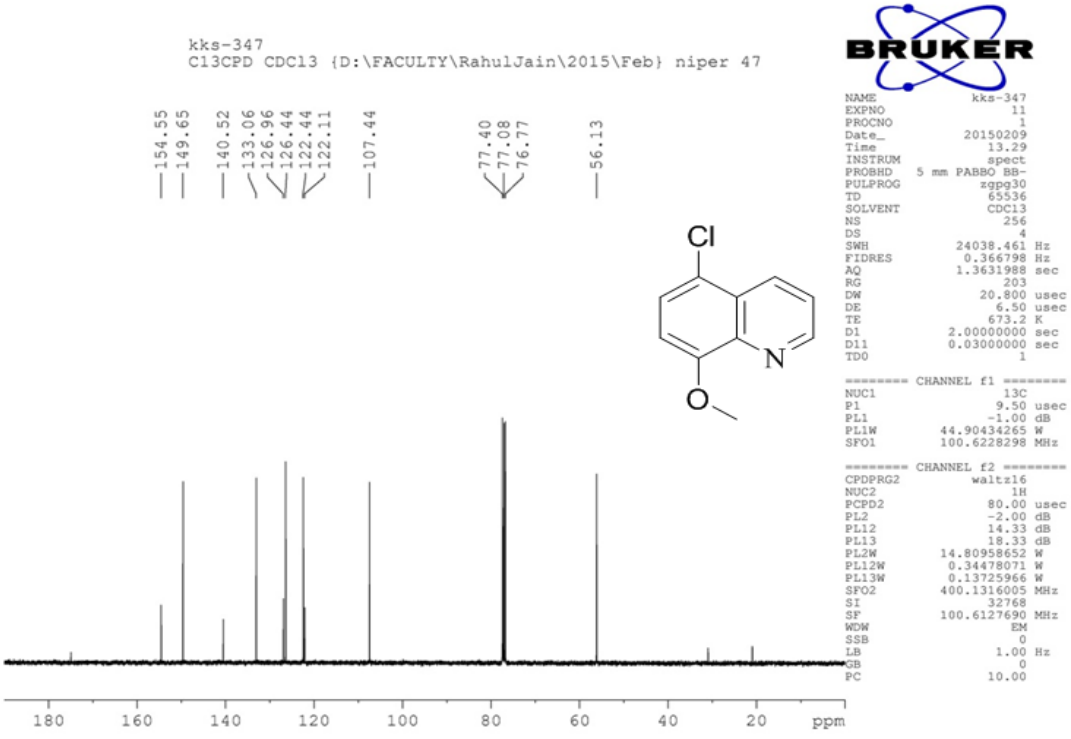
(5) B. M. Partridge and J. F. Hartwig, *Org. Lett.,* 2013, **15**, 140.

(6) B. Boganyi and J. Kaman, *Tetrahedron,* 2013, **69**, 9512.

9. ^{1}H and ^{13}C NMR Spectrum

5-Chloro-8-methoxyquinoline (1l):





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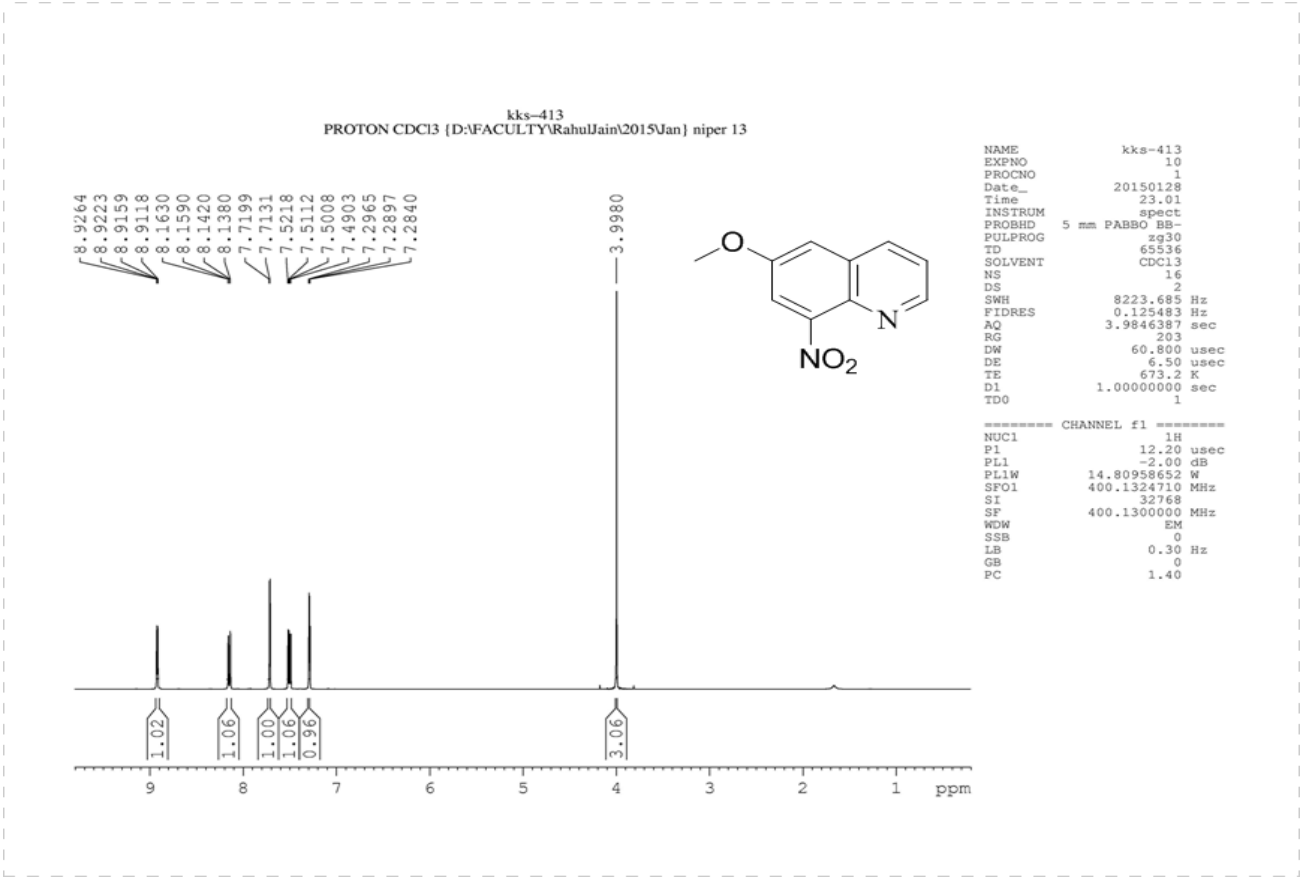

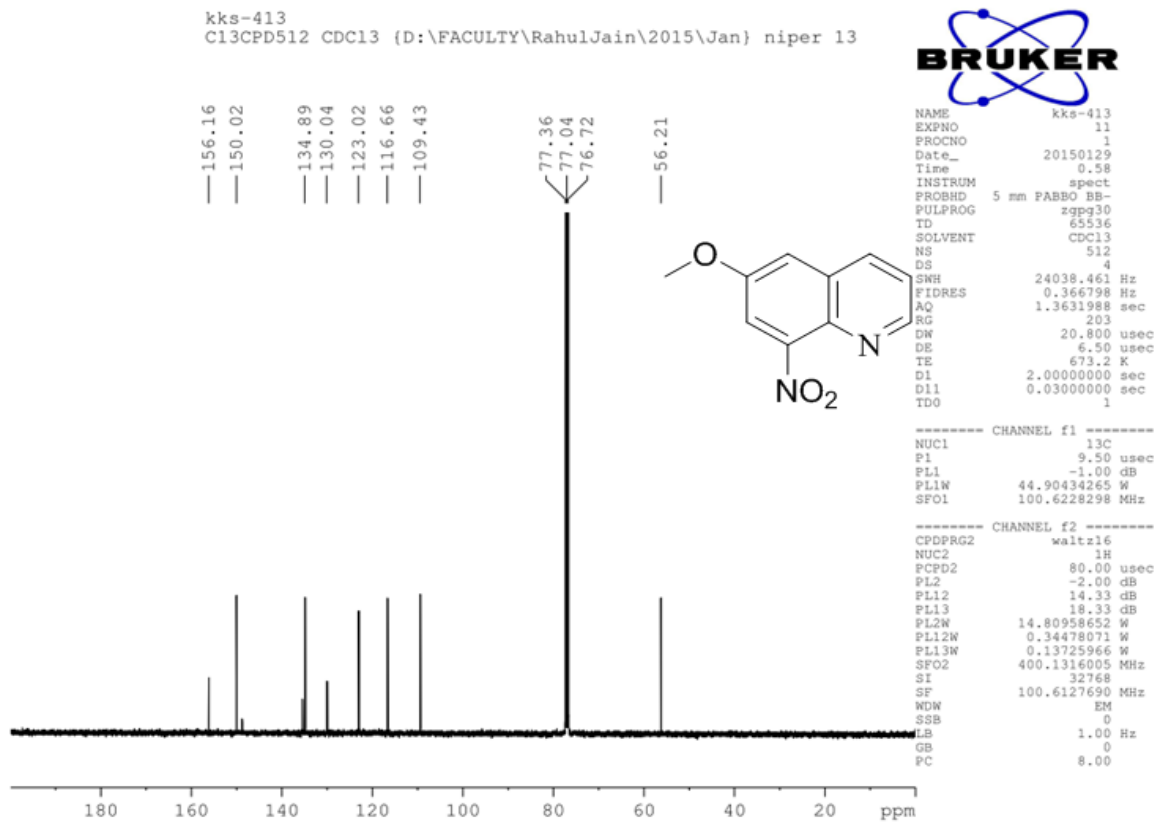
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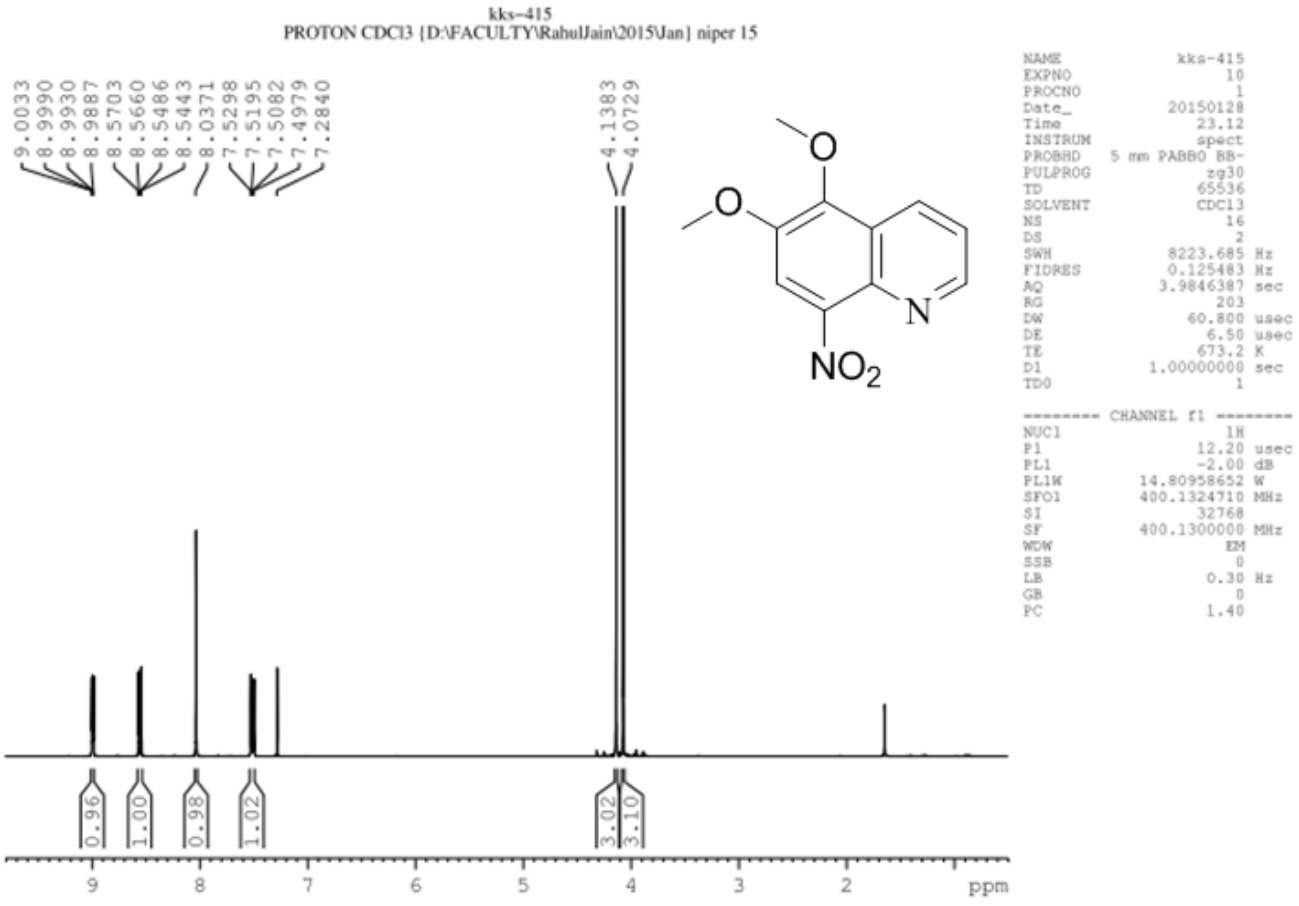

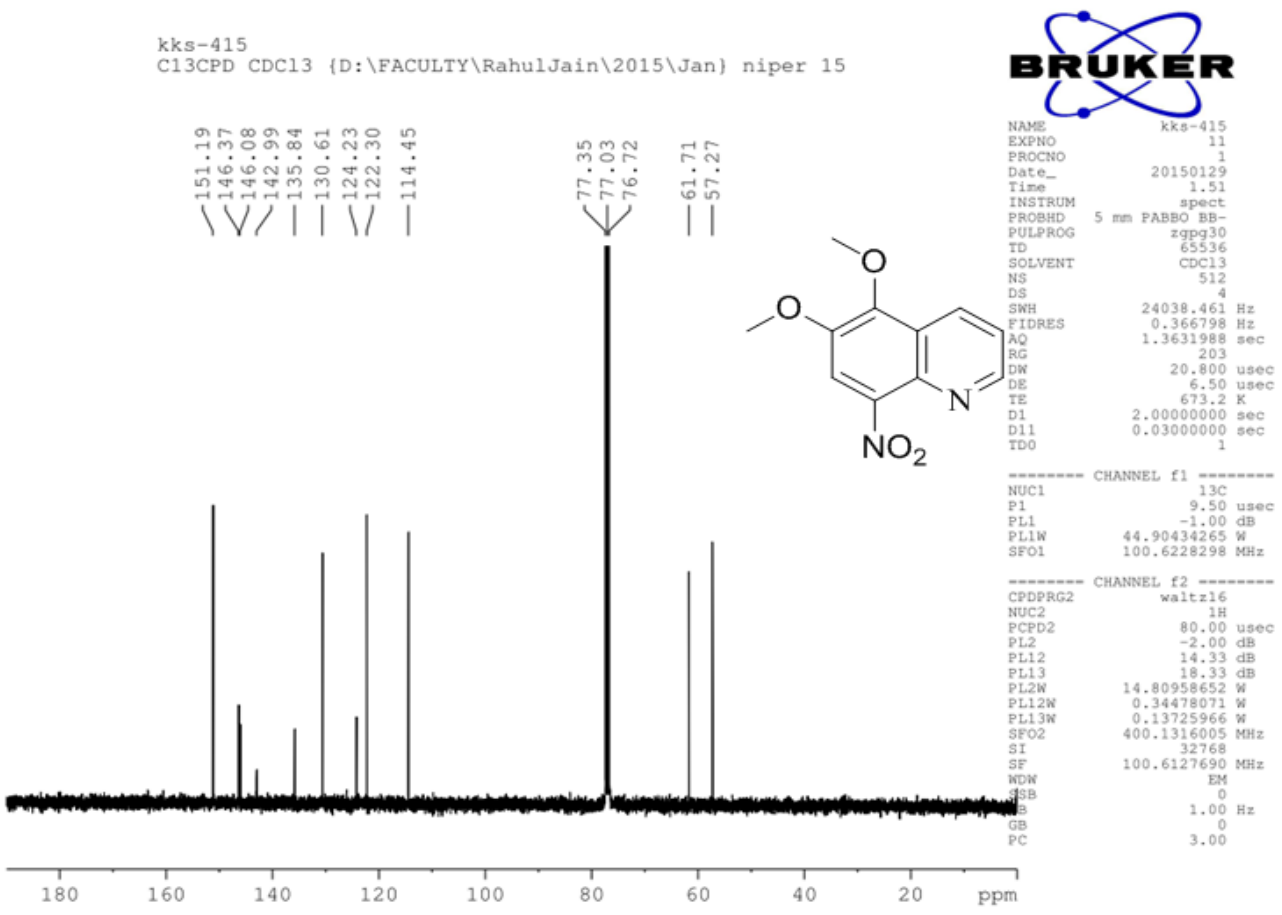
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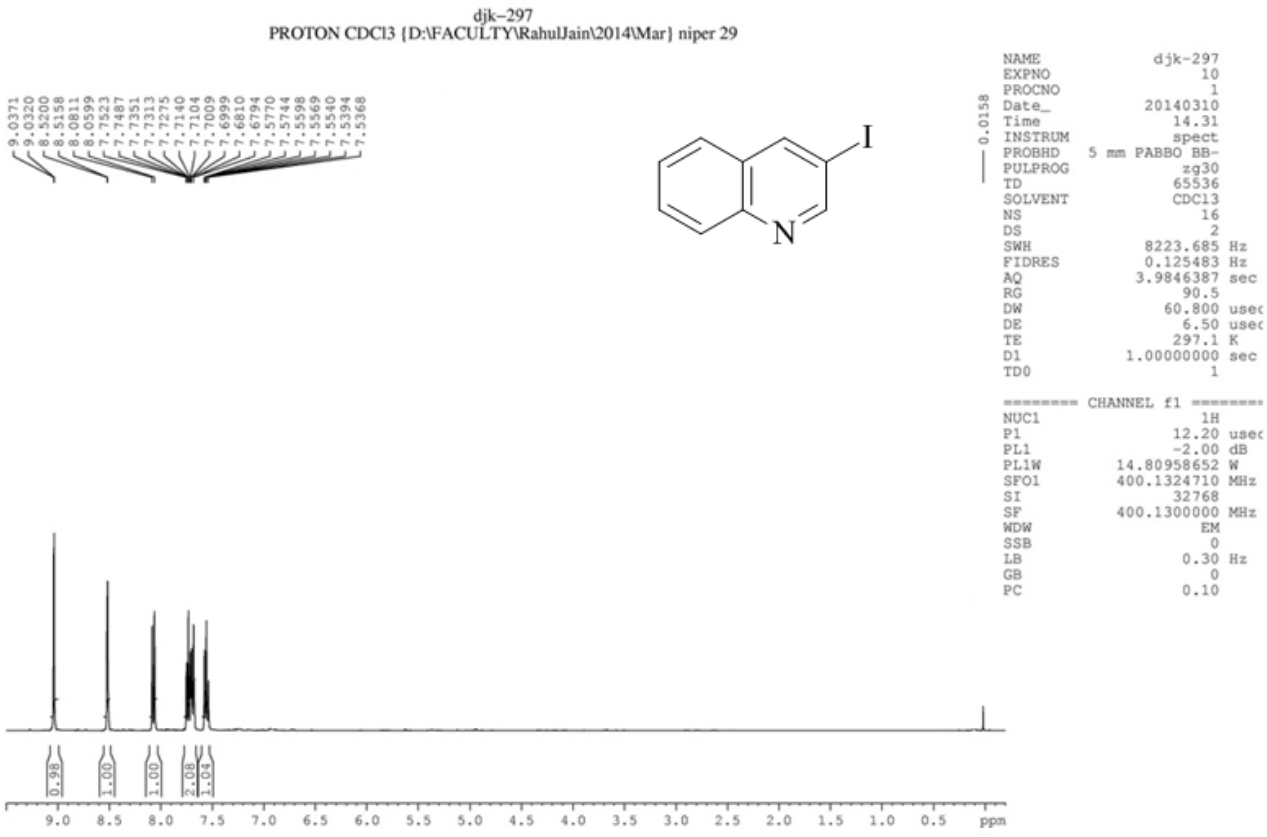
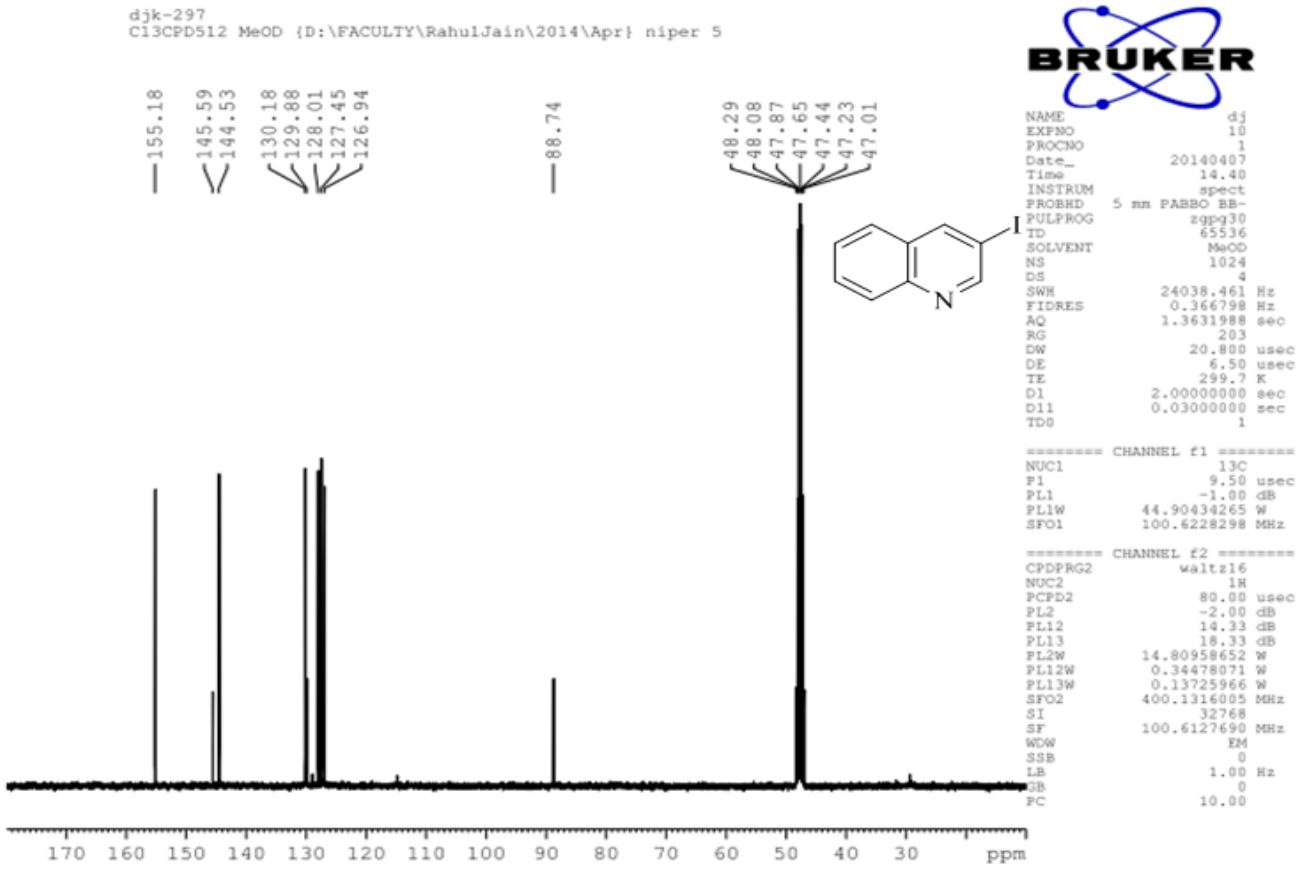
3-Iodoquinoline (2a)





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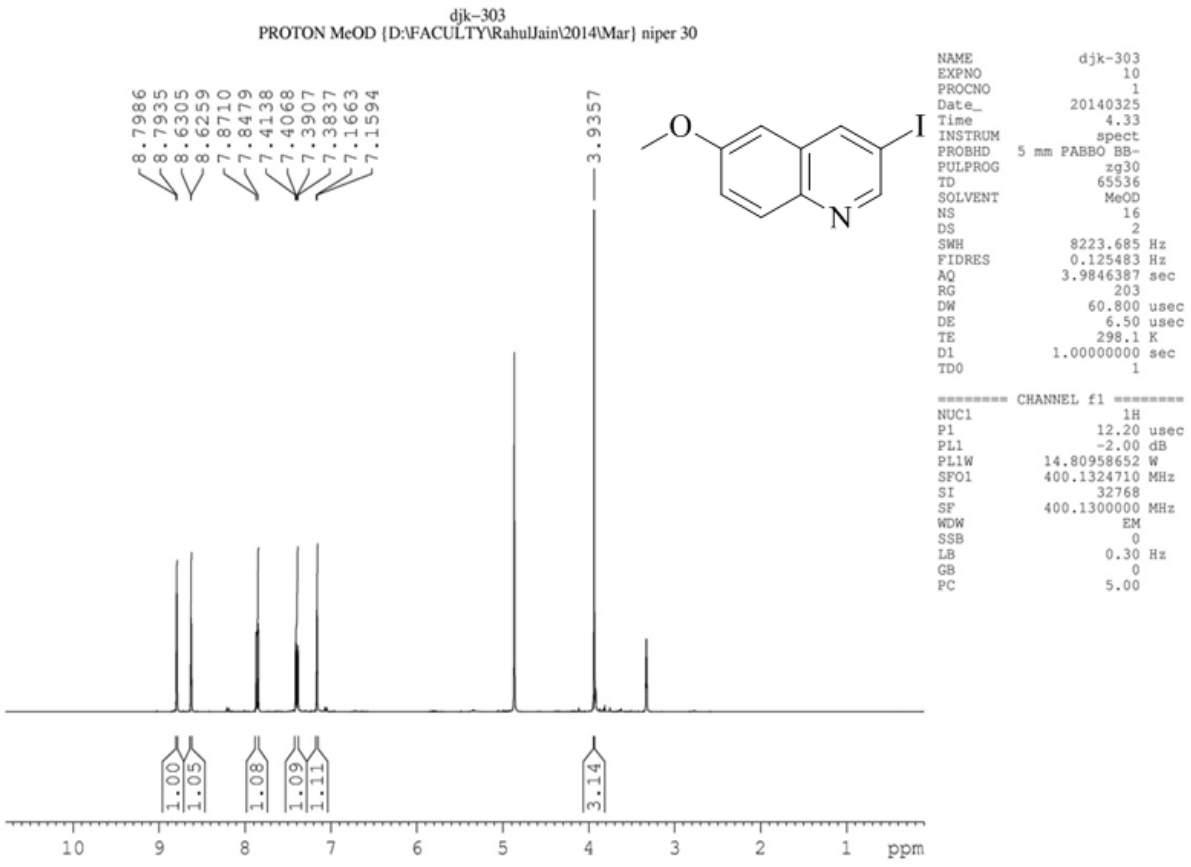

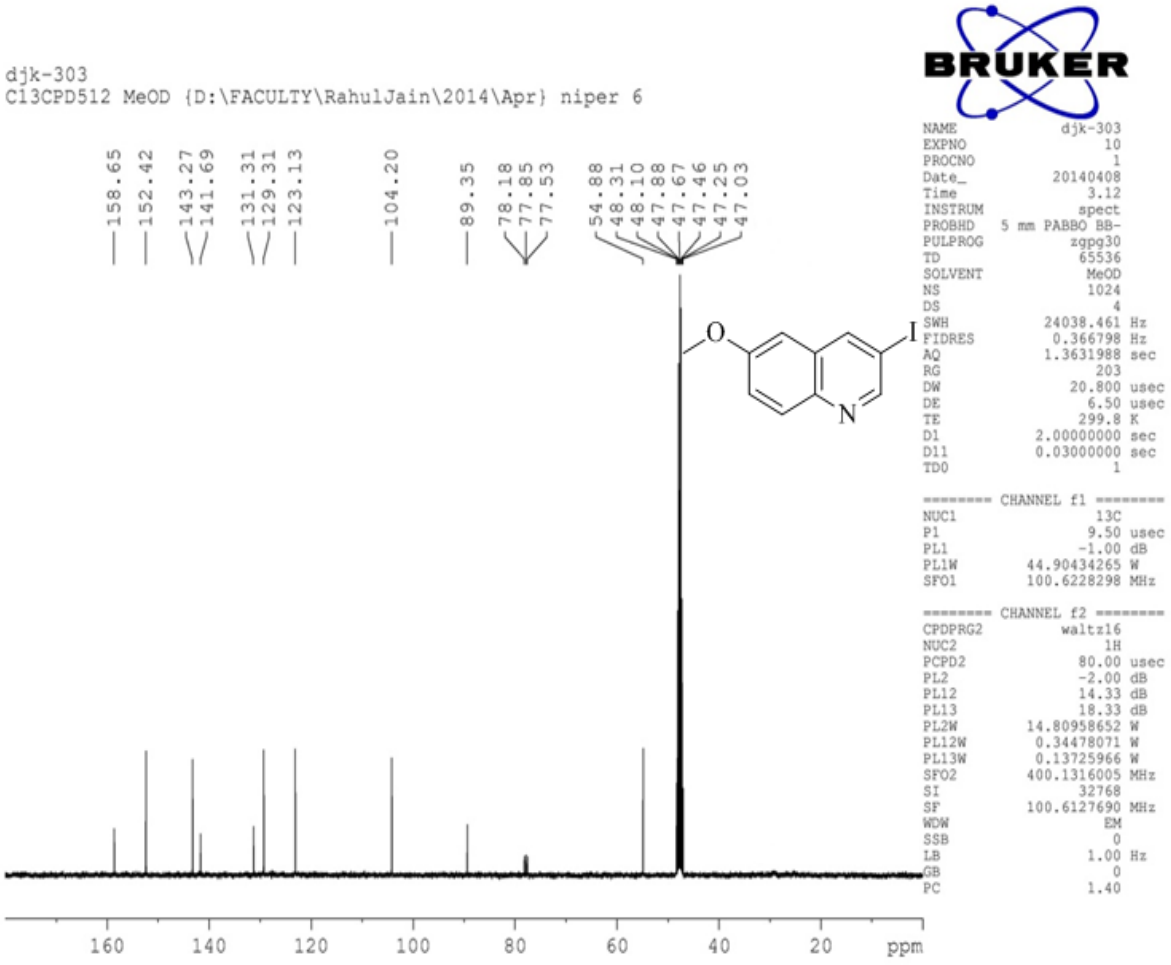

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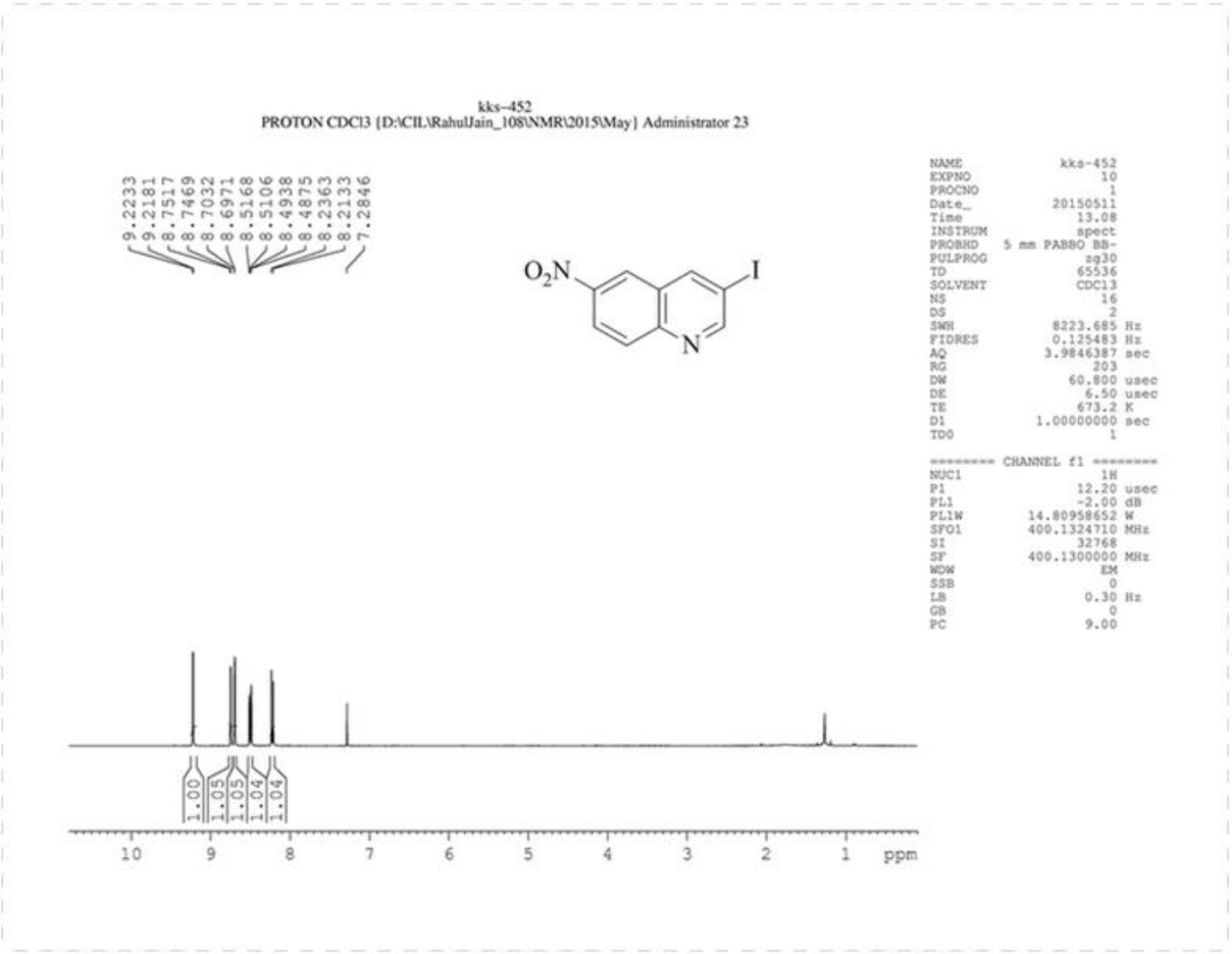
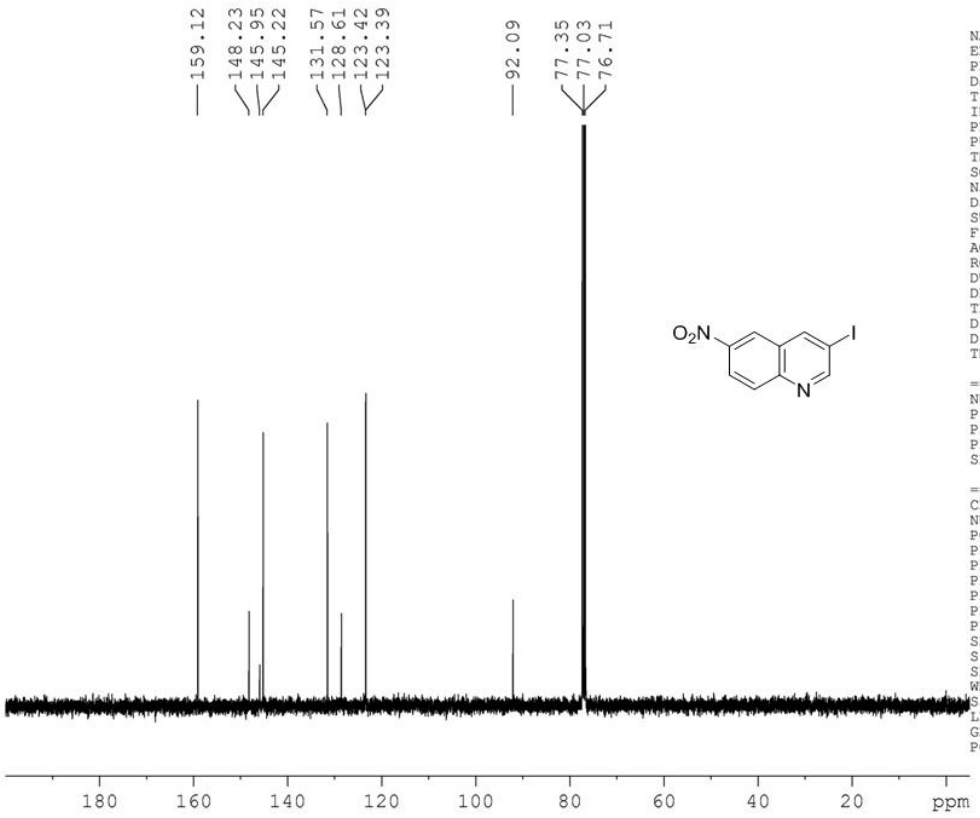
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	14.33 dB
PL13	18.33 dB
PL2W	14.80958652 W
PL12W	0.34478071 W
PL13W	0.13725966 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

3-Iodo-6-nitro-quinoline (2c):

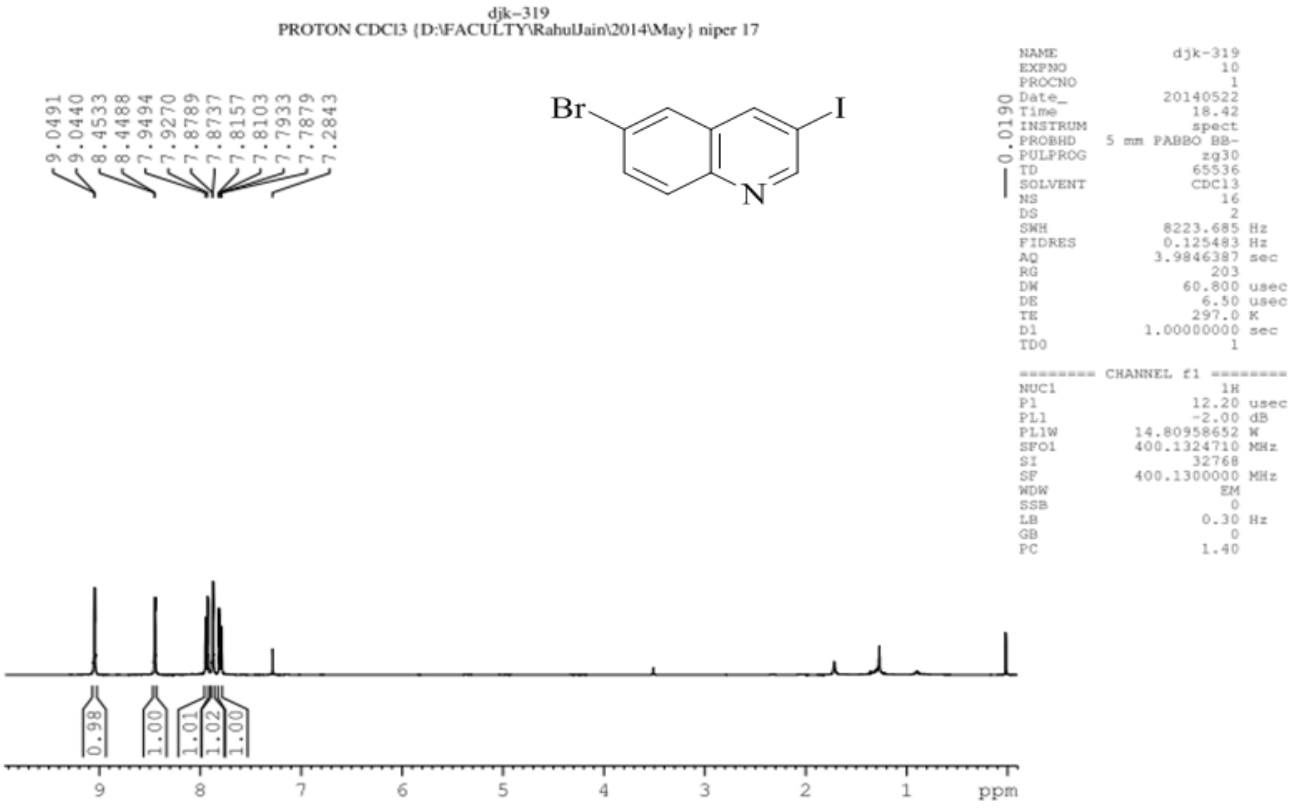


kks-452
C13CPD CDCl3 {D:\CIL\RahulJain_108\NMR\2015\May} Administrator 23

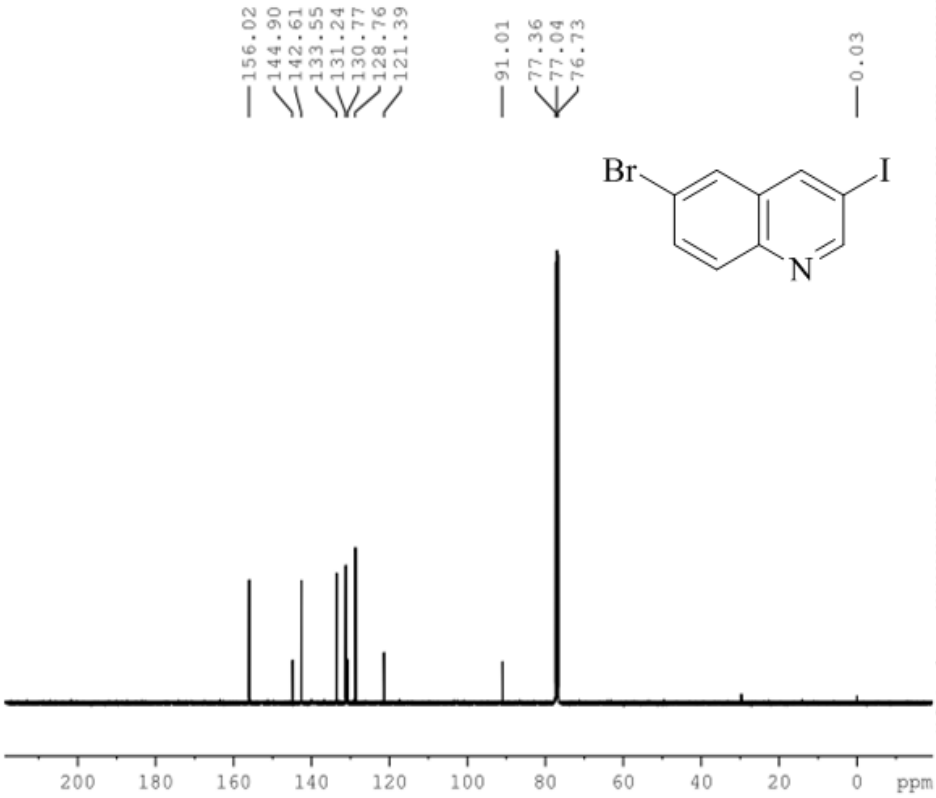


NAME	kks-452
EXPNO	11
PROCNO	1
Date_	20150511
Time	19.17
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	673.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-1.00 dB
PL1W	44.90434265 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	14.33 dB
PL13	18.33 dB
PL2W	14.80958652 W
PL12W	0.34478071 W
PL13W	0.13725966 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

6-Bromo-3-iodoquinoline (2d):

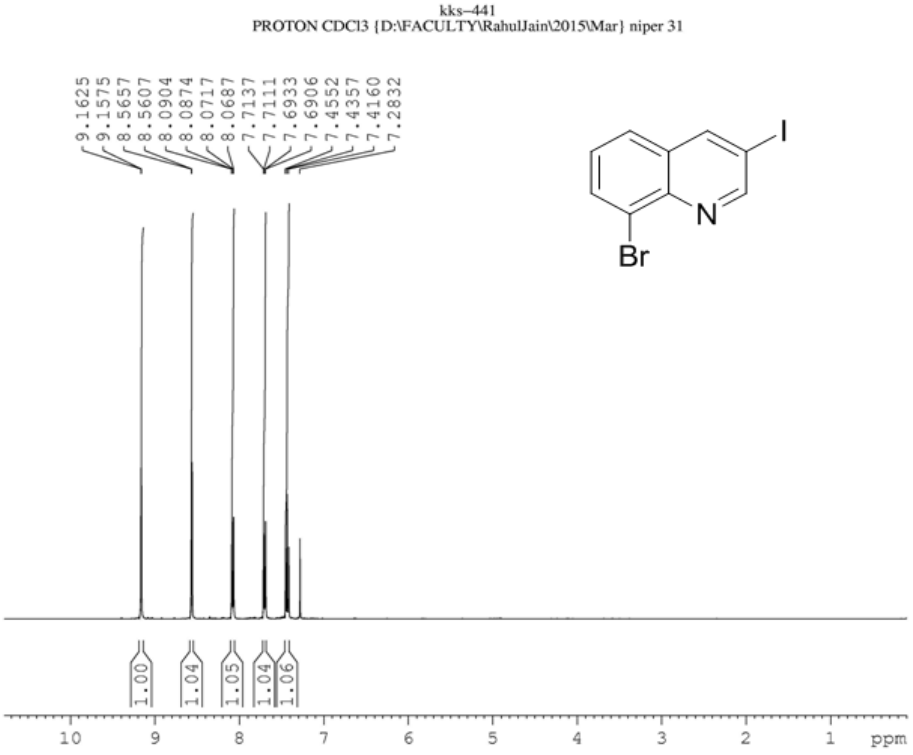


djk-319 r
C13CPD CDCl3 {D:\FACULTY\RahulJain\2014\May} niper 17



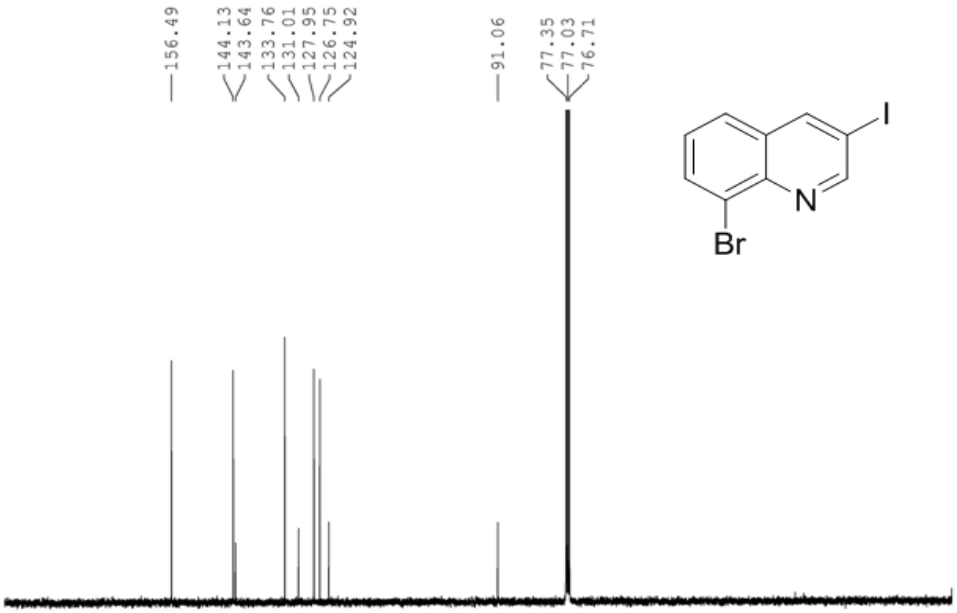
NAME	djk-319 r
EXPNO	10
PROCNO	1
Date_	20140524
Time	21.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	673.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-1.00 dB
PL1W	44.90434265 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	14.33 dB
PL13	18.33 dB
PL2W	14.80958652 W
PL12W	0.34478071 W
PL13W	0.13725966 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

8-Bromo-3-iodoquinoline (2e)



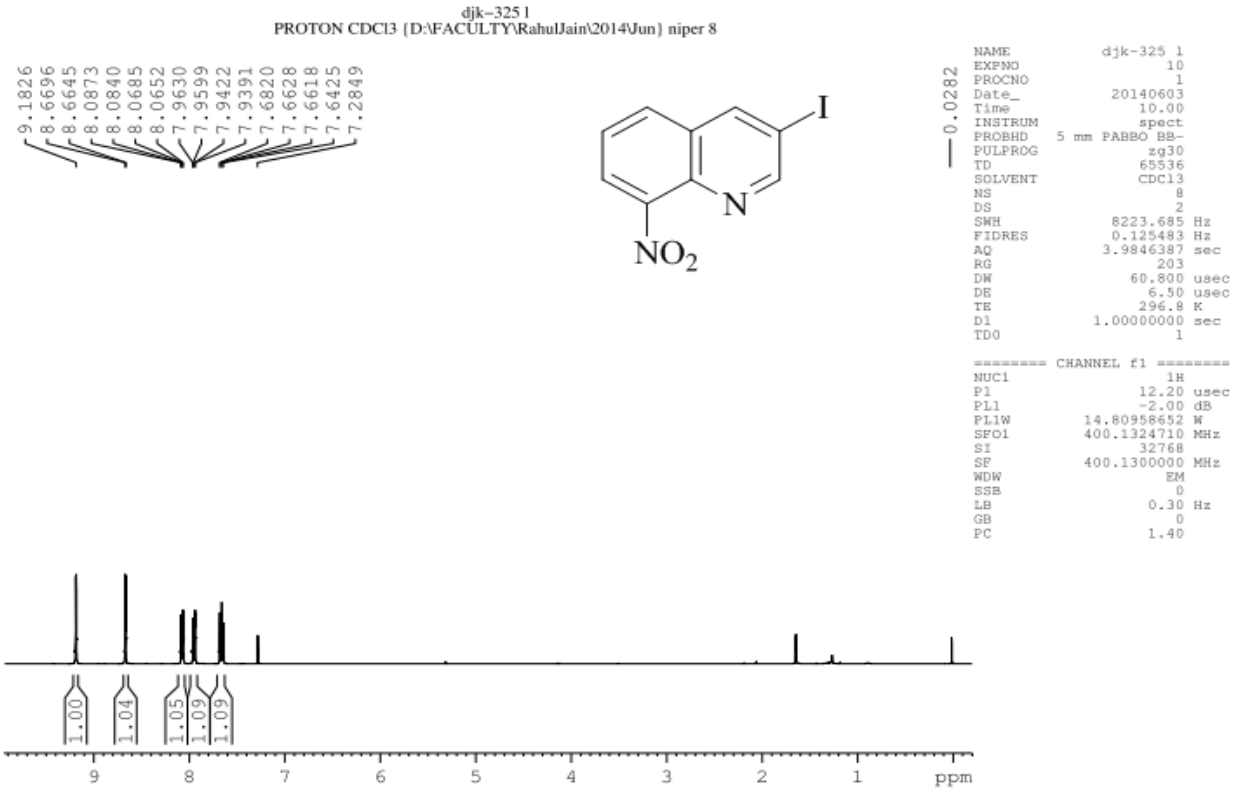
NAME	kks-441
EXPNO	10
PROCNO	1
Date_	20150305
Time	3.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	673.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.20 usec
PL1	-2.00 dB
PL1W	14.80958652 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	10.00

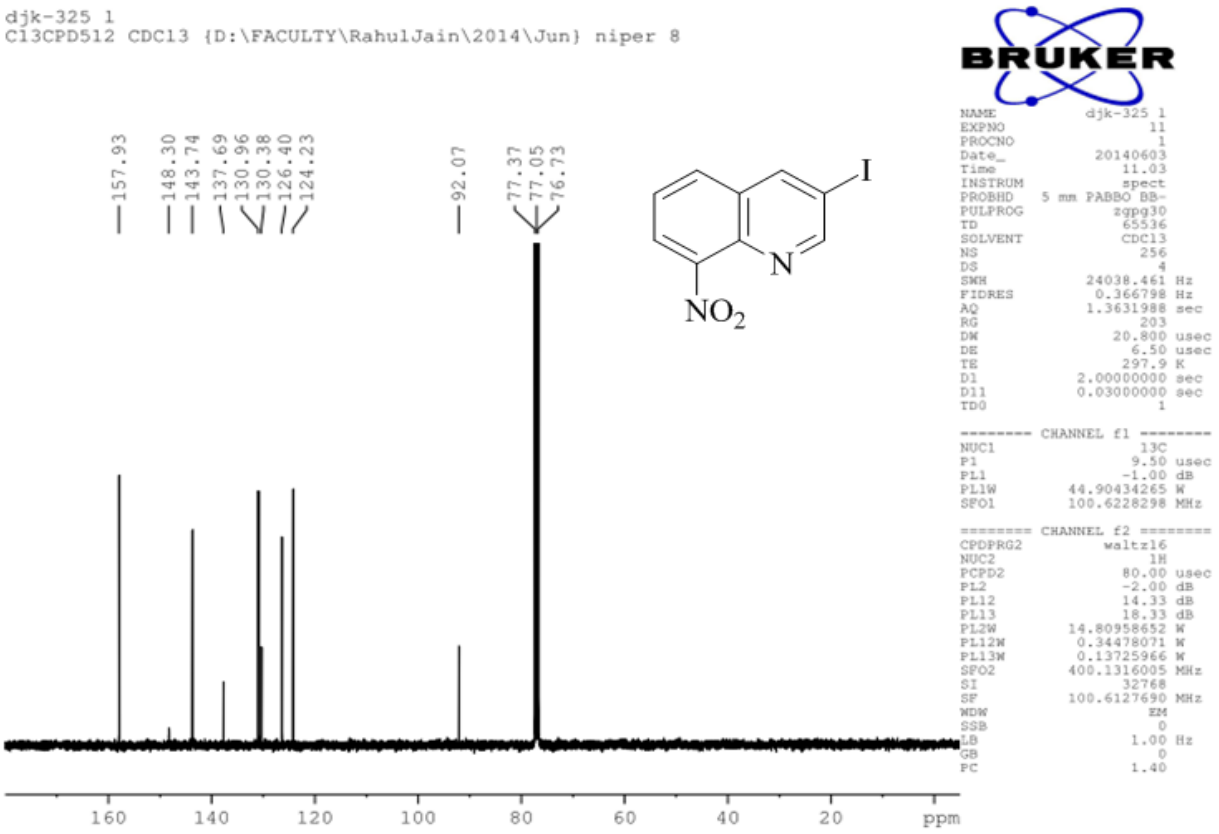
kks-441
C13CPD CDCl3 {D:\FACULTY\RahulJain\2015\Mar} niper 31



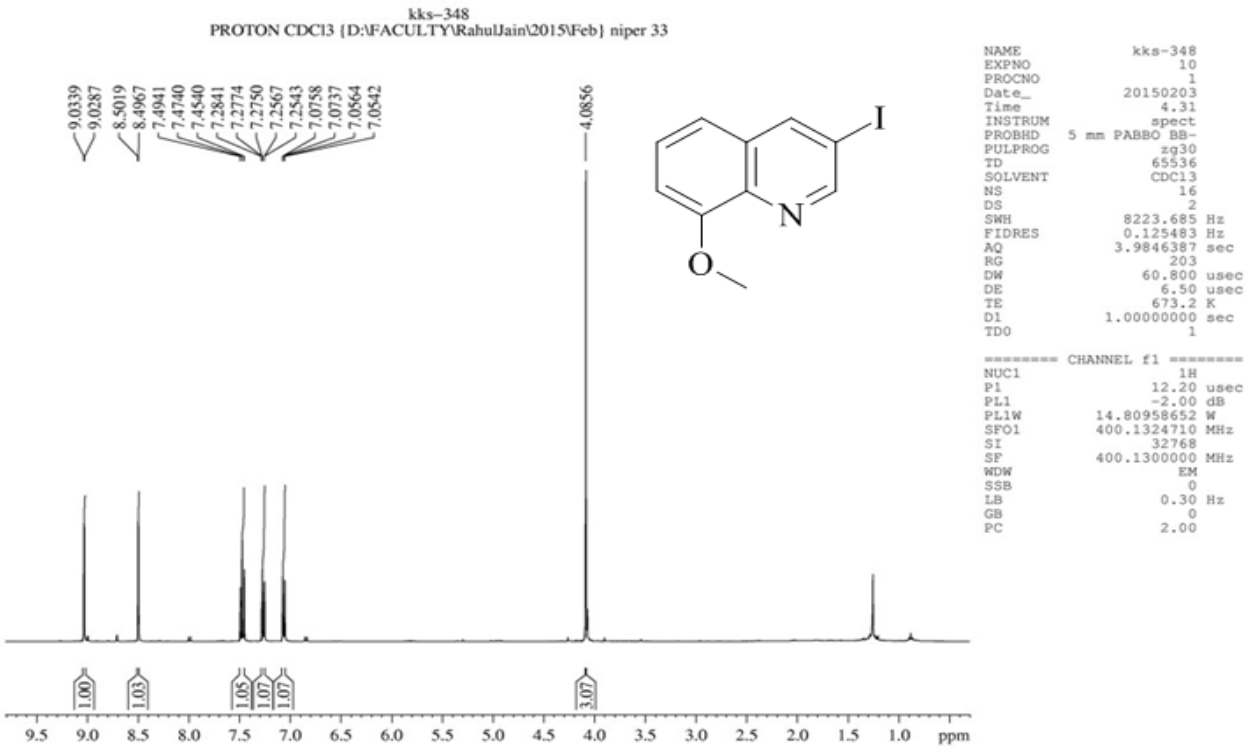
NAME	kks-441	
EXPNO	11	
PROCNO	1	
Date_	20150305	
Time	16.03	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	1024	
DS	4	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	673.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-1.00	dB
PL1W	44.90434265	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	-2.00	dB
PL12	14.33	dB
PL13	18.33	dB
PL2W	14.80958652	W
PL12W	0.34478071	W
PL13W	0.13725966	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127690	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

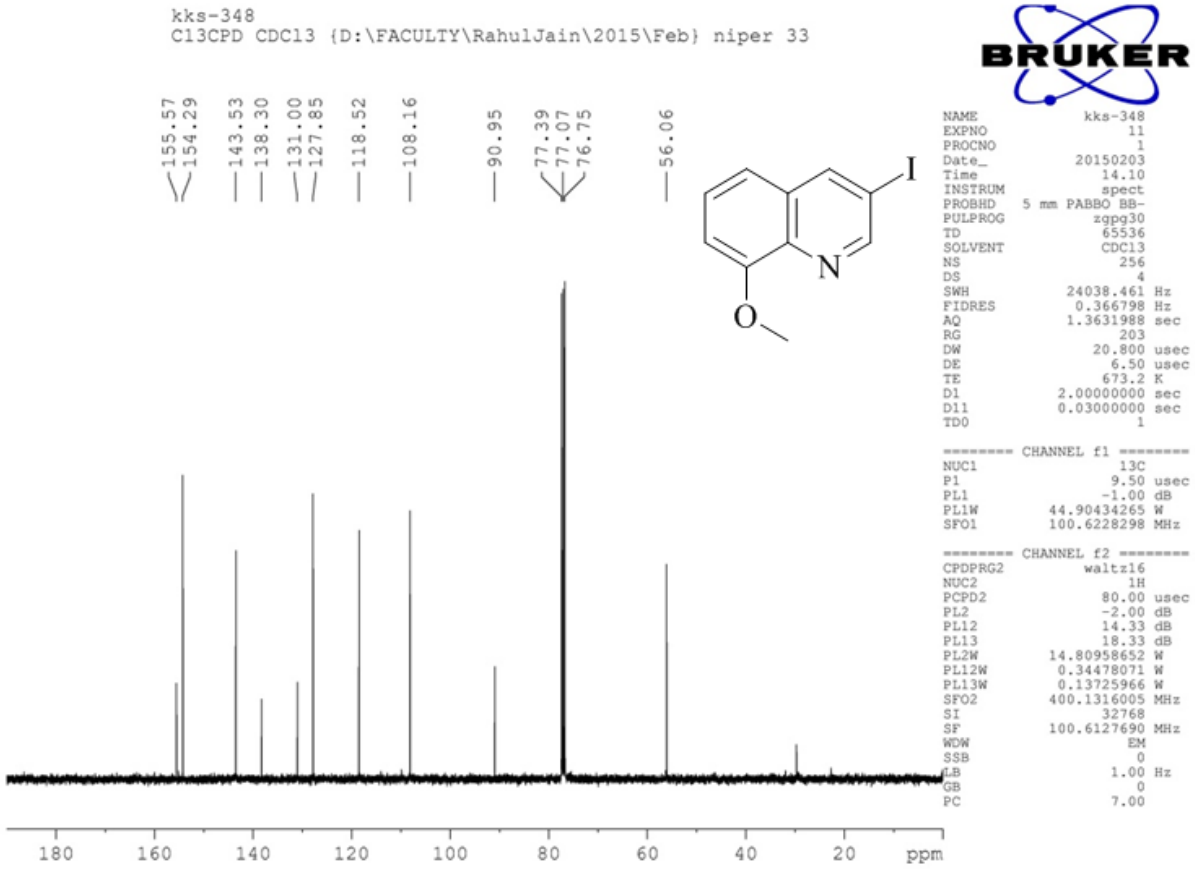
3-iodo-8-nitroquinoline (2f):



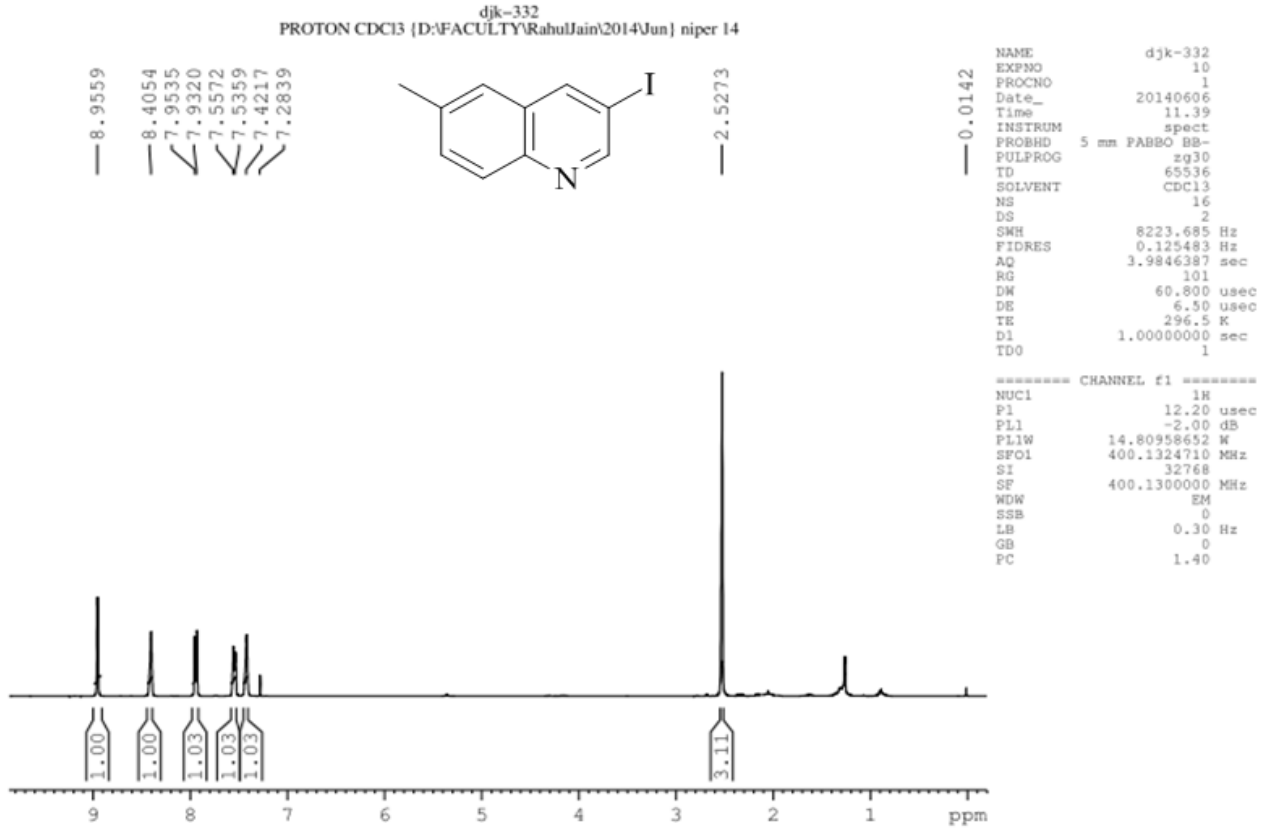

djk-325 1
C13CPD512 CDCl3 {D:\FACULTY\RahulJain\2014\Jun} niper 8
157.93
148.30
143.74
137.69
130.96
130.38
126.40
124.23
92.07
77.37
77.05
76.73
I
N
NO2
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME djk-325 1
EXPNO 11
PROCNO 1
Date_ 20140603
Time 11.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3-Iodo-8-methoxyquinoline (2g):

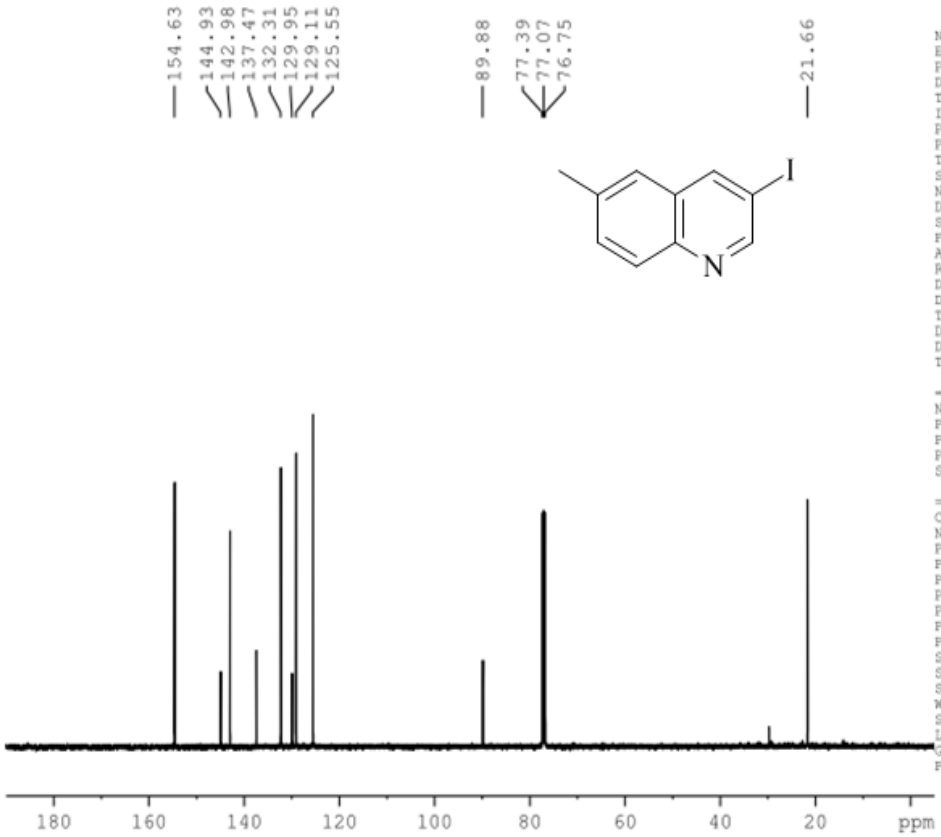



kks-348
C13CPD CDCl3 {D:\FACULTY\RahulJain\2015\Feb} niper 33
BRUKER
155.57
154.29
143.53
138.30
131.00
127.85
118.52
108.16
90.95
77.39
77.07
76.75
56.06
I
N
O
180
160
140
120
100
80
60
40
20
ppm
NAME kks-348
EXPNO 11
PROCNO 1
Date_ 20150203
Time 14.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 7.00

3-Iodo-6-methylquinoline (2h):



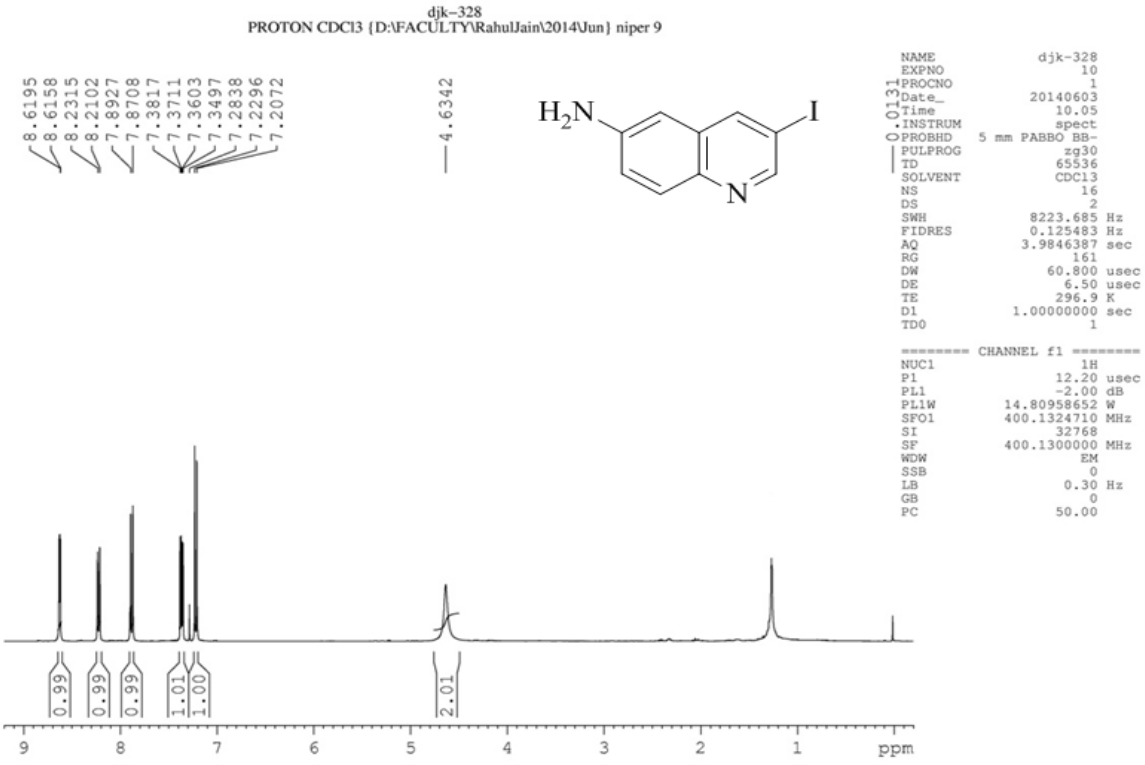
djk-332
C13CPD512 CDC13 {D:\FACULTY\RahulJain\2014\Jun} niper 14

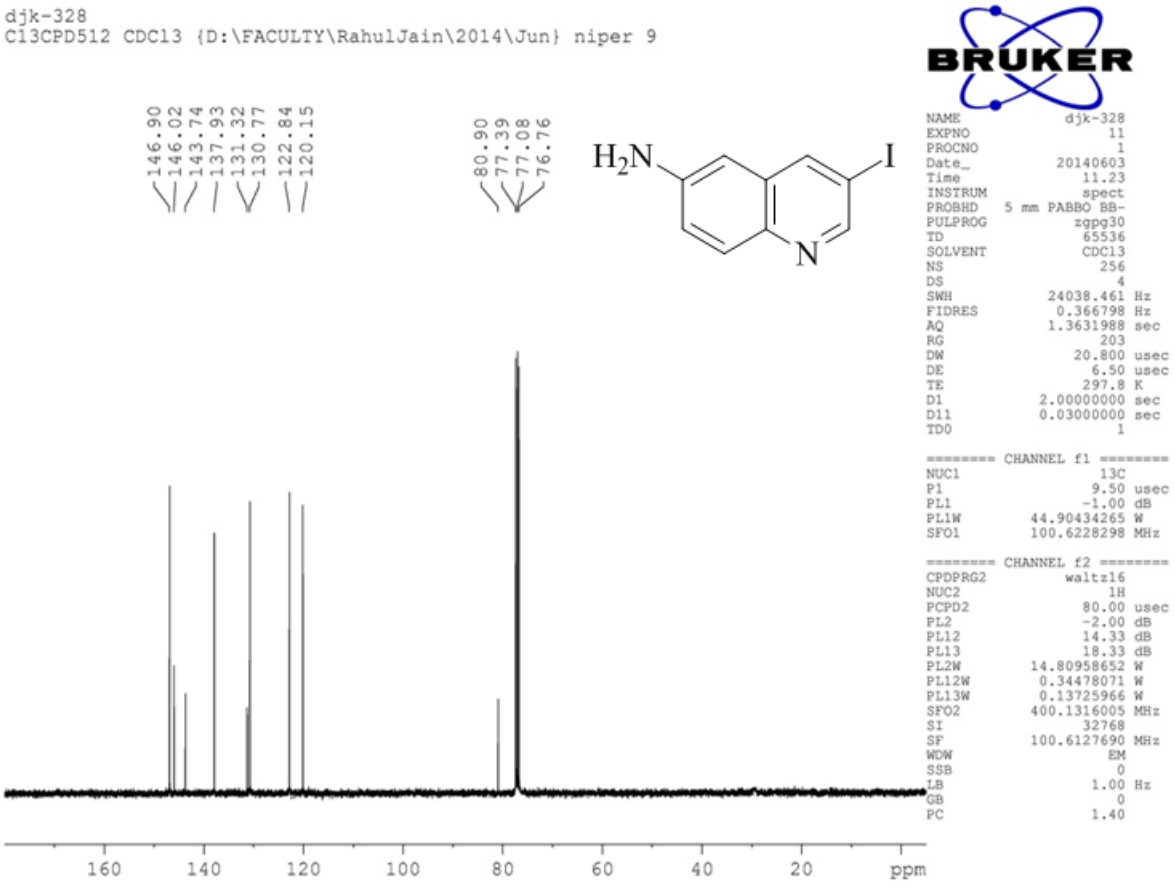


BRUKER

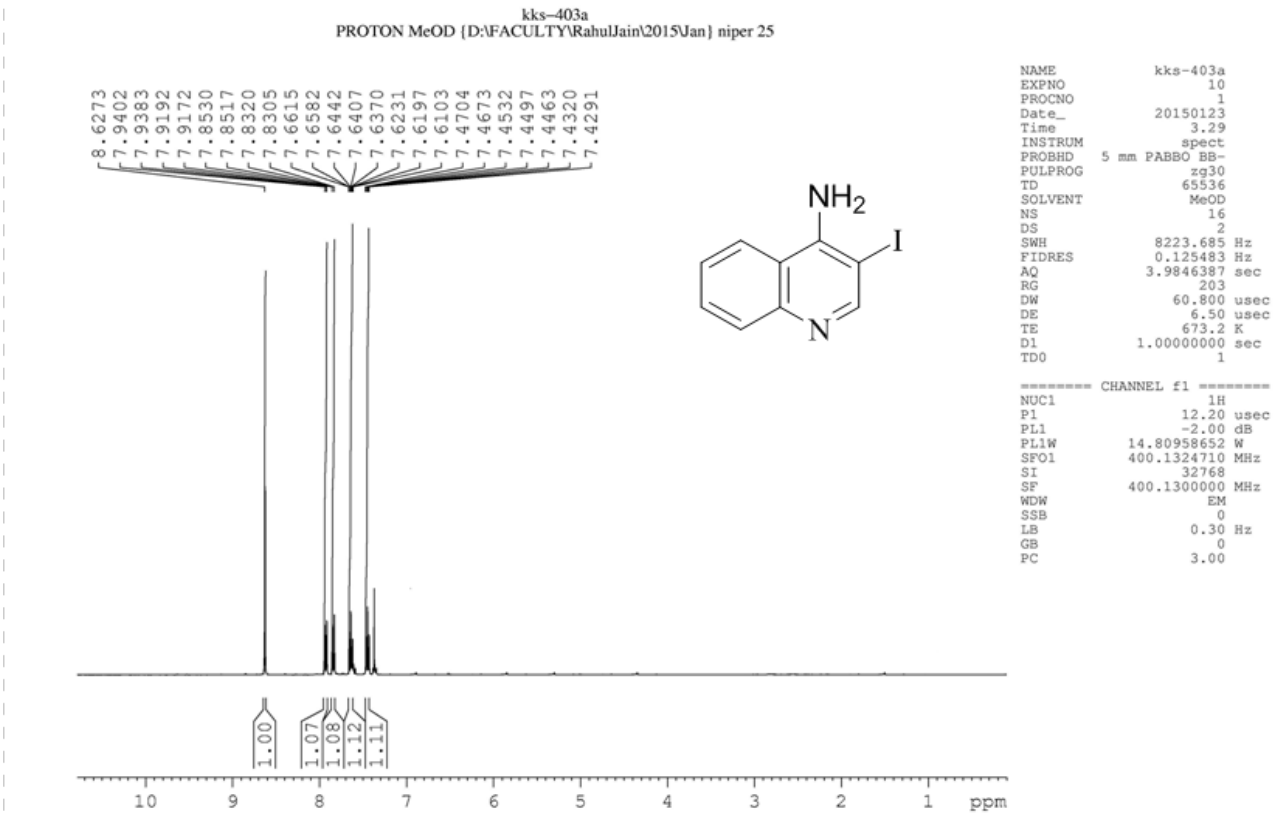
NAME	djk-332
EXPNO	11
PROCNO	1
Date_	20140606
Time	13.48
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	512
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-1.00 dB
PL1W	44.90434265 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	14.33 dB
PL13	18.33 dB
PL2W	14.80958652 W
PL12W	0.34478071 W
PL13W	0.13725966 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

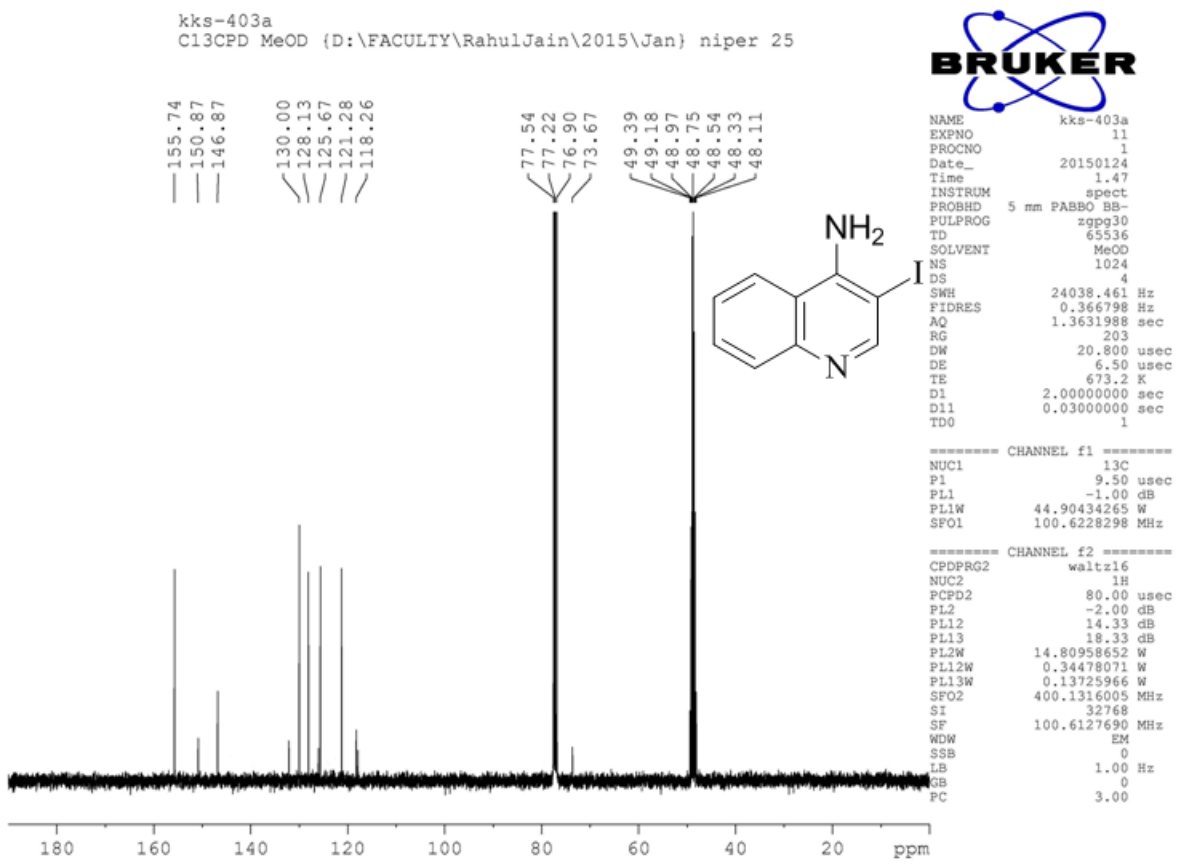
3-Iodoquinolin-6-amine (2i):



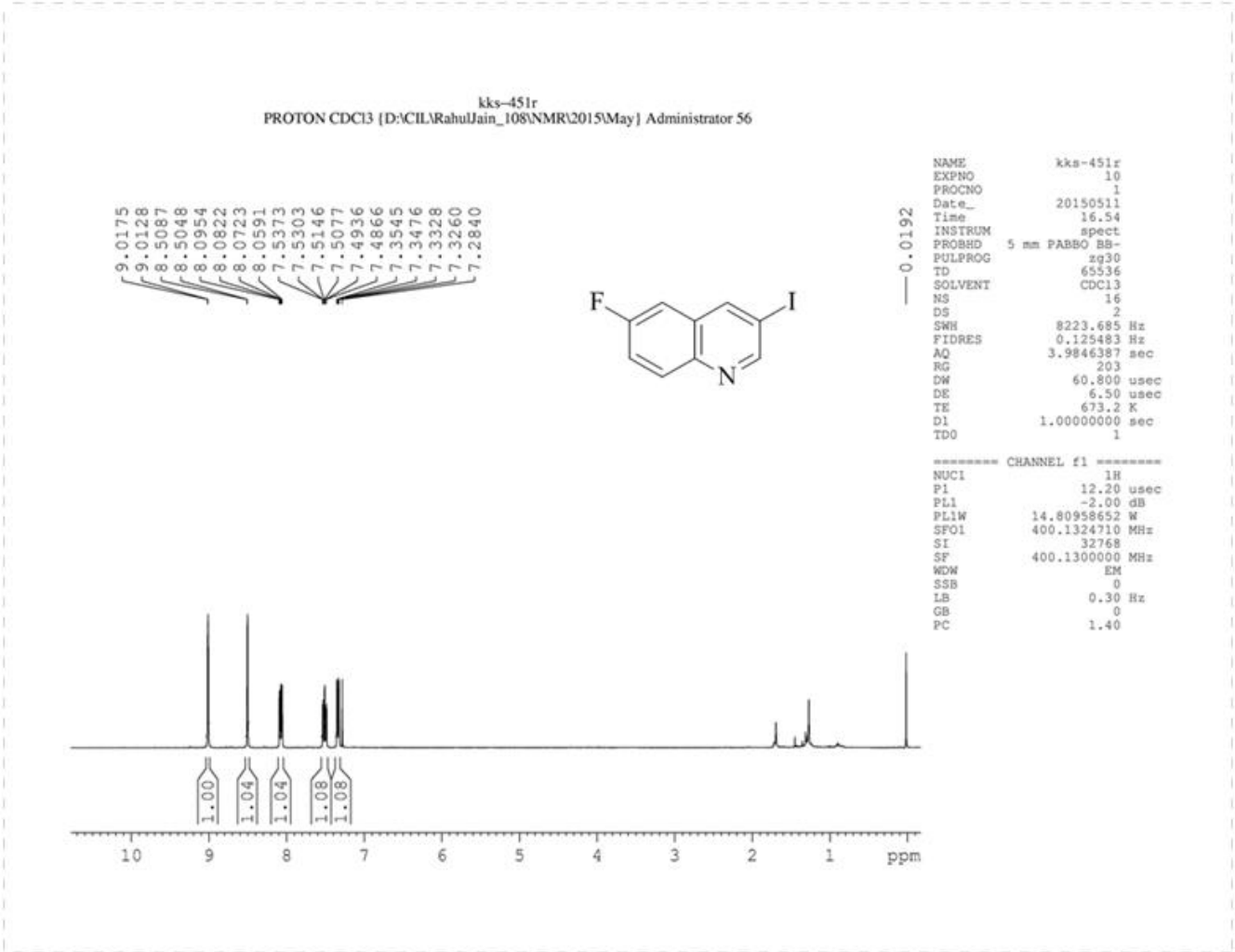

djk-328
C13CPD512 CDCl3 {D:\FACULTY\RahulJain\2014\Jun} niper 9
146.90
146.02
143.74
137.93
131.32
130.77
122.84
120.15
80.90
77.39
77.08
76.76
H2N
I
N
160
140
120
100
80
60
40
20
ppm
NAME djk-328
EXPNO 11
PROCNO 1
Date_ 20140603
Time 11.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3-Iodoquinolin-4-amine (2j):

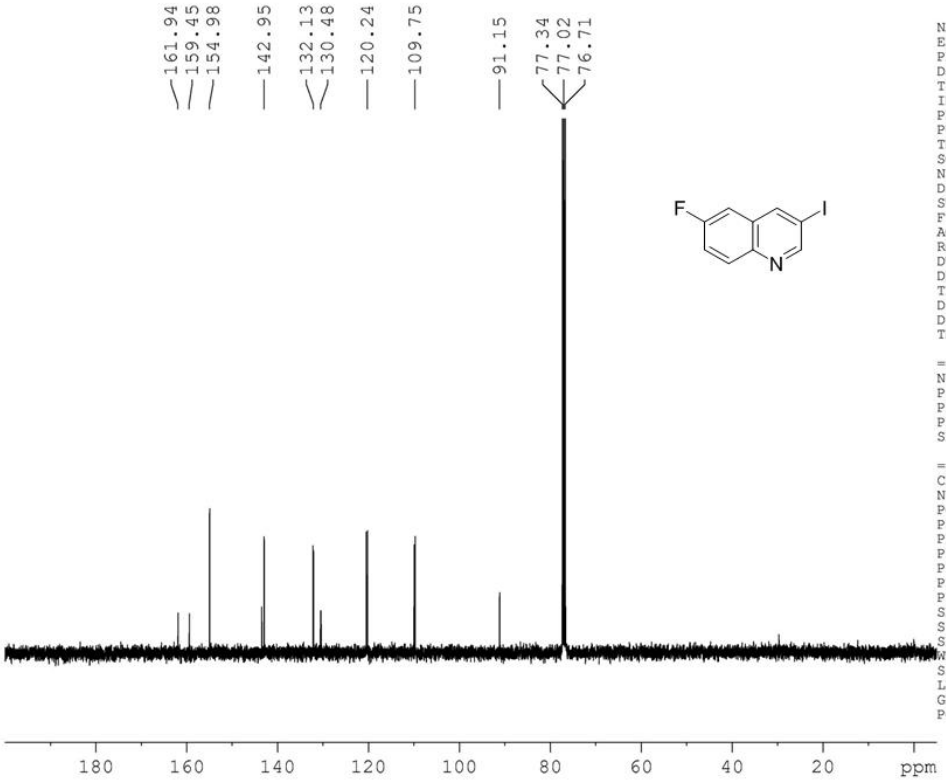



kks-403a
C13CPD MeOD {D:\FACULTY\RahulJain\2015\Jan} niper 25
155.74
150.87
146.87
130.00
128.13
125.67
121.28
118.26
77.54
77.22
76.90
73.67
49.39
49.18
48.97
48.75
48.54
48.33
48.11
NH2
I
N
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME kks-403a
EXPNO 11
PROCNO 1
Date_ 20150124
Time 1.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 3.00

6-Fluoro-3-iodoquinoline (2k):

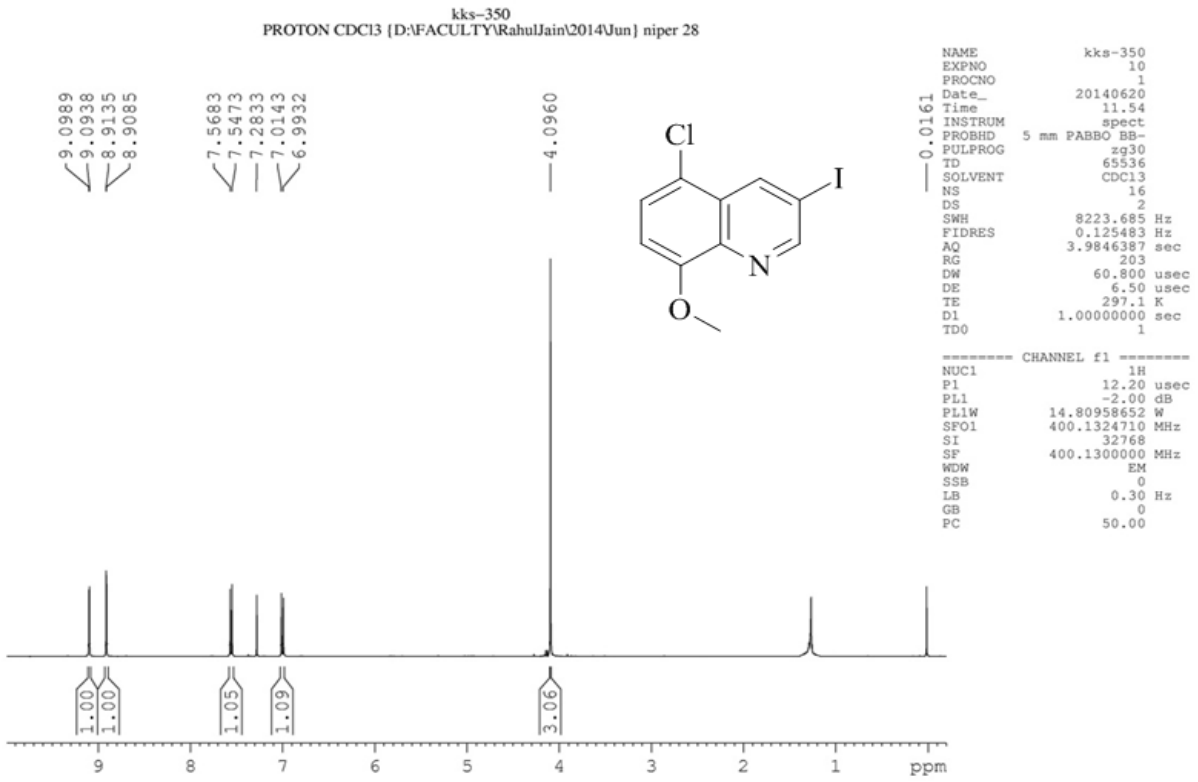


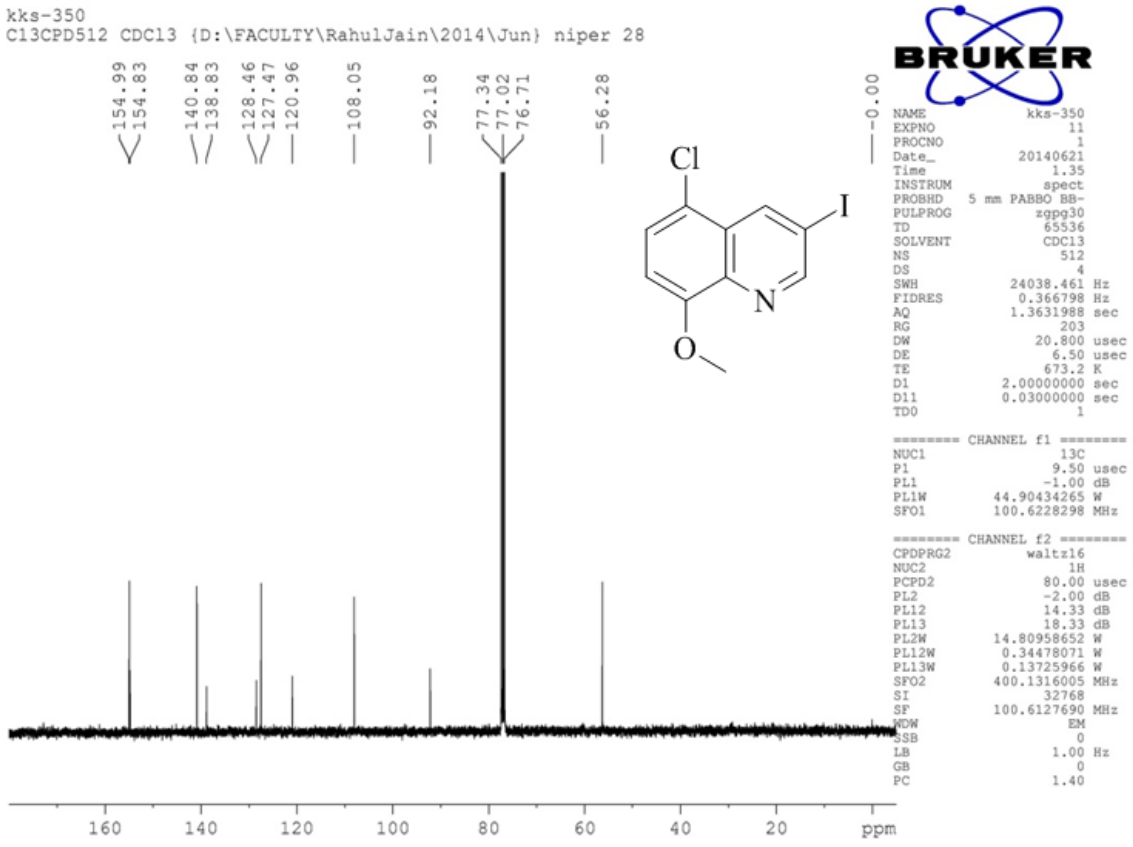
kks-451r
C13CPD CDCl3 {D:\CIL\RahulJain_108\NMR\2015\May} Administrator 56



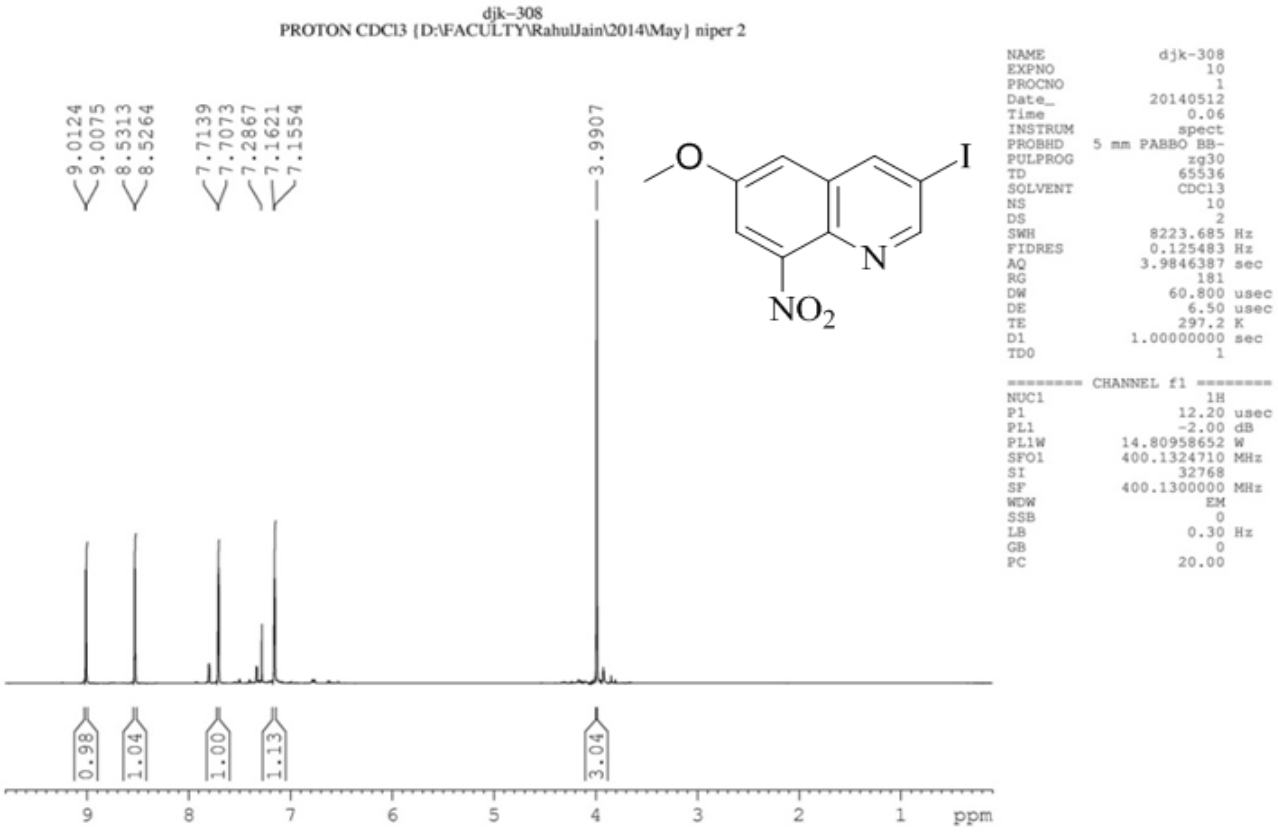
NAME	kks-451r
EXPNO	11
PROCNO	1
Date_	20150511
Time	20.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	673.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-1.00 dB
PL1W	44.90434265 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	14.33 dB
PL13	18.33 dB
PL2W	14.80958652 W
PL12W	0.34478071 W
PL13W	0.13725966 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	3.00

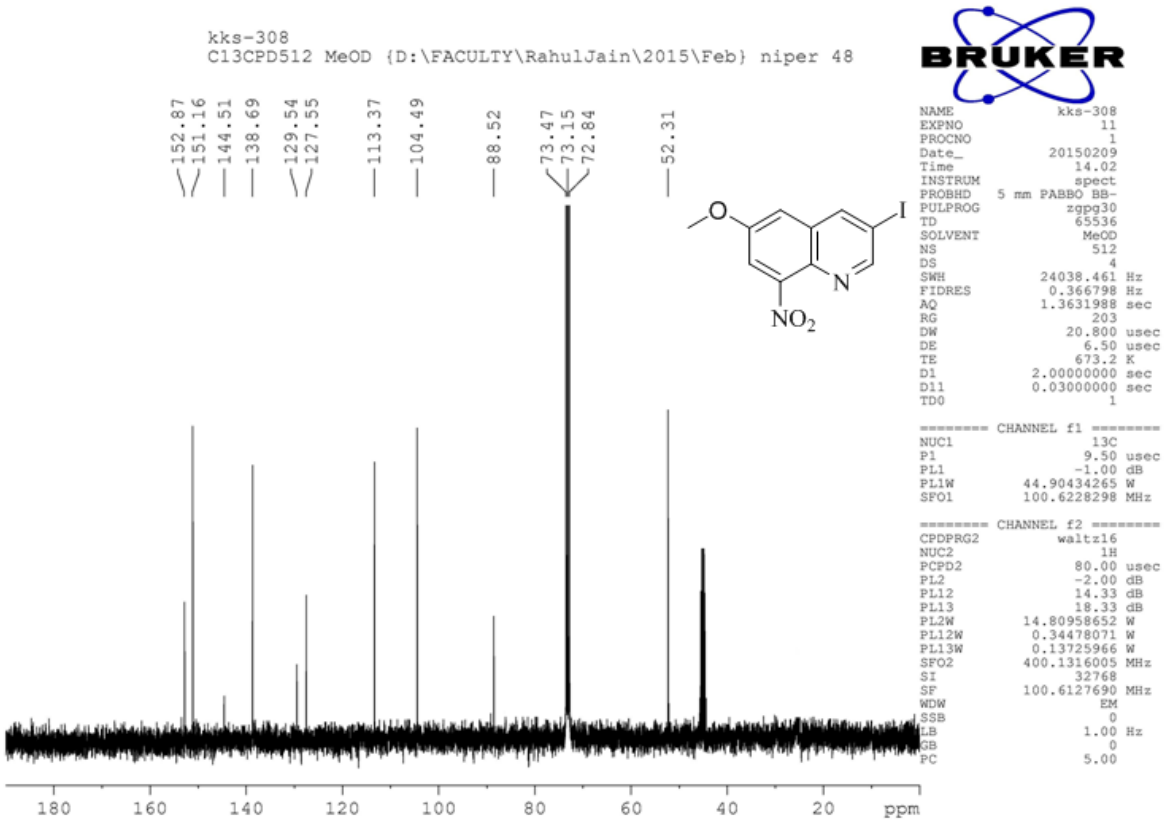
5-Chloro- 3-iodo-8-methoxyquinoline (2l):



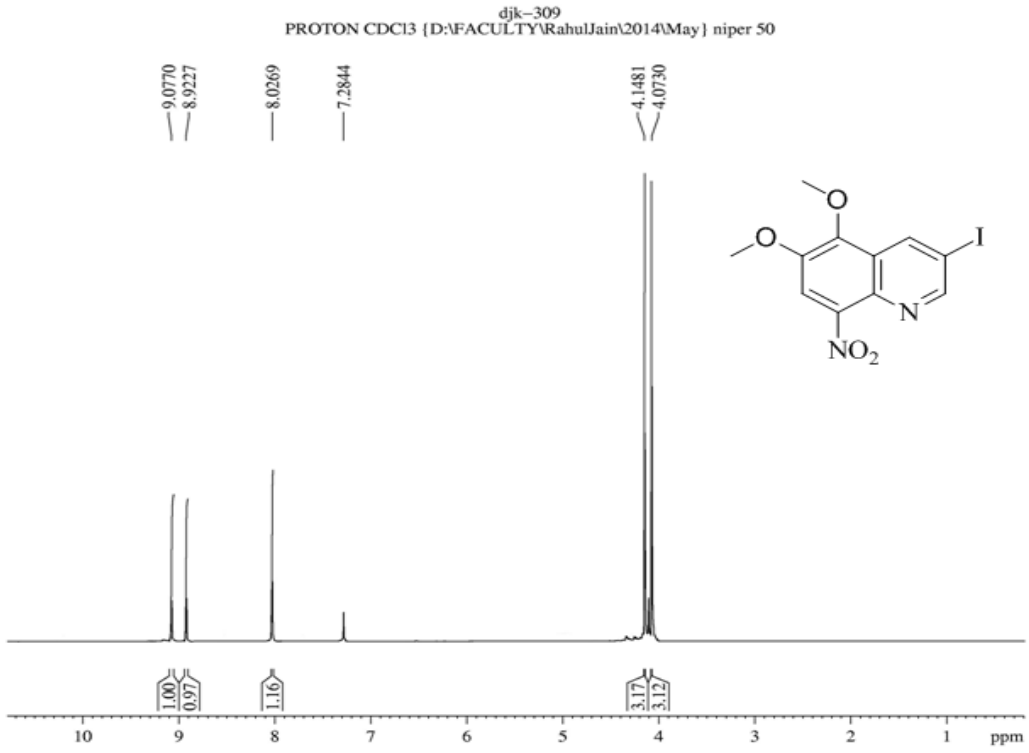

kks-350
C13CPD512 CDCl3 {D:\FACULTY\RahulJain\2014\Jun} niper 28
154.99
154.83
140.84
138.83
128.46
127.47
120.96
108.05
92.18
77.34
77.02
76.71
56.28
0.00
Cl
I
N
O
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME kks-350
EXPNO 11
PROCNO 1
Date_ 20140621
Time 1.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3-Iodo-6-methoxy-8-nitroquinoline (2m):




kks-308
C13CPD512 MeOD {D:\FACULTY\RahulJain\2015\Feb} niper 48
152.87
151.16
144.51
138.69
129.54
127.55
113.37
104.49
88.52
73.47
73.15
72.84
52.31
O
I
N
NO2
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME kks-308
EXPNO 11
PROCNO 1
Date_ 20150209
Time 14.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 5.00

3-Iodo-5,6-dimethoxy-8-nitroquinoline (2n):



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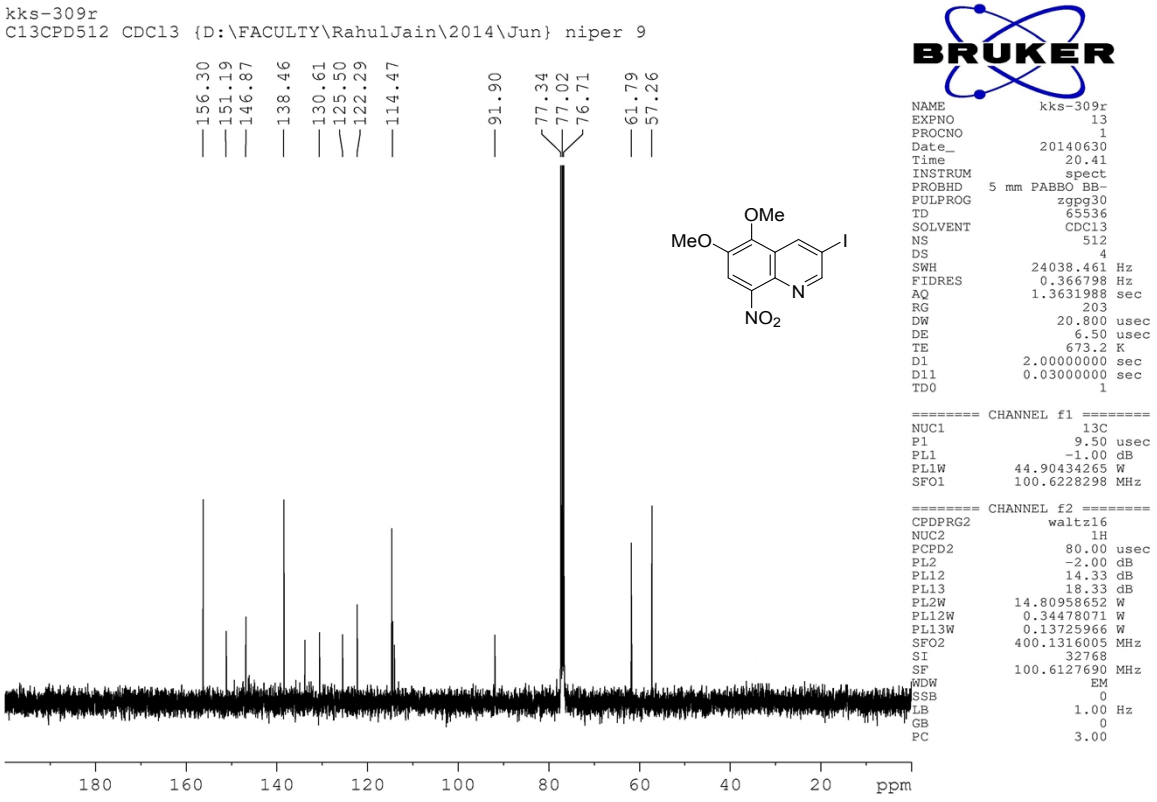
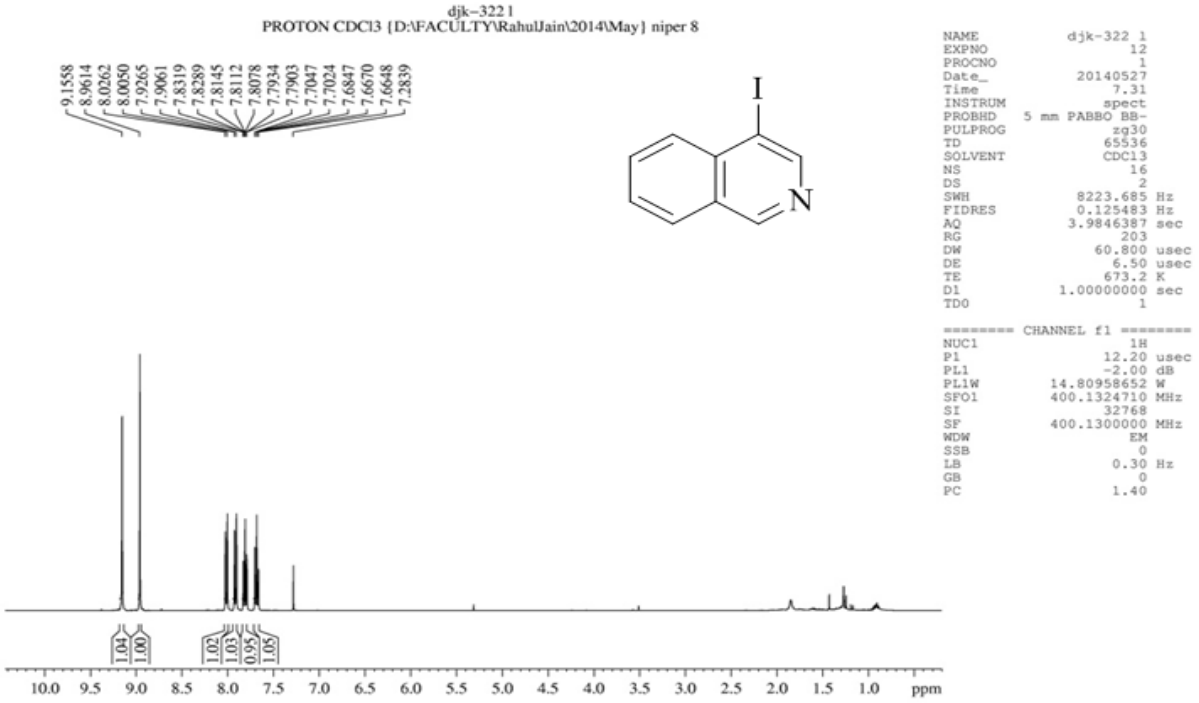
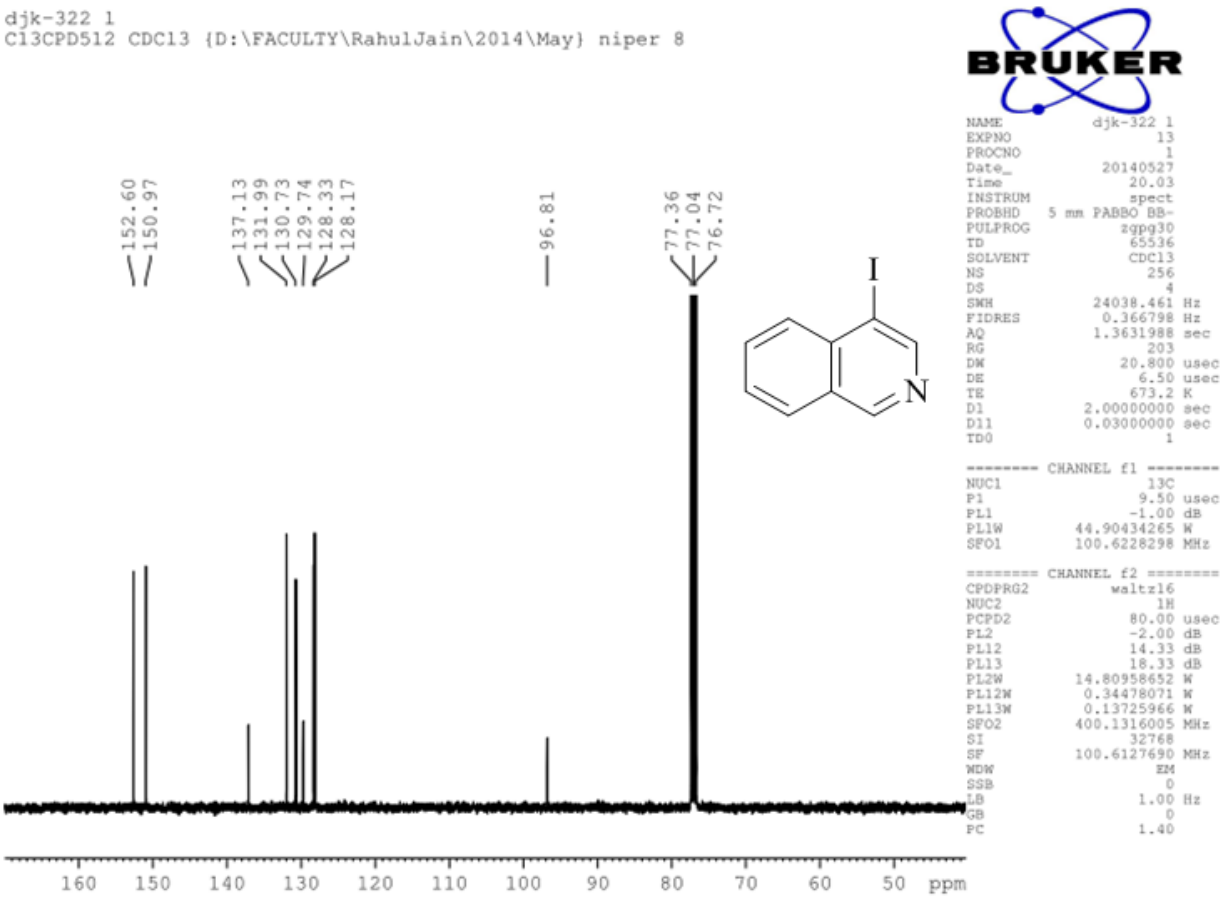
PROCNO	1	
Date_	20140522	
Time	5.34	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	8223.685	Hz
FIDRES	0.125483	Hz
AQ	3.9846387	sec
RG	181	
DW	60.800	usec
DE	6.50	usec
TE	299.4	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	12.20	usec
PL1	-2.00	dB
PL1W	14.80958652	W
SFO1	400.1324710	MHz
SI	32768	
SF	400.1300000	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	10.00	

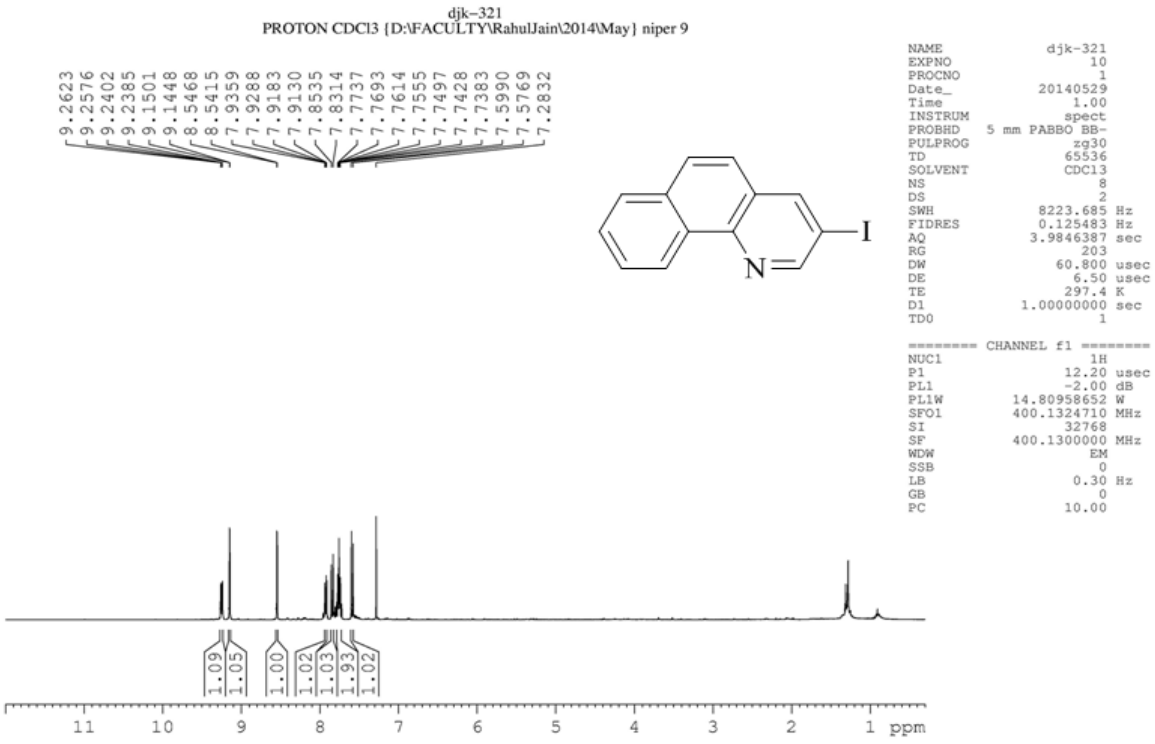

kks-309r
C13CPD512 CDCl3 {D:\FACULTY\RahulJain\2014\Jun} niper 9
156.30
151.19
146.87
138.46
130.61
125.50
122.29
114.47
91.90
77.34
77.02
76.71
61.79
57.26
OMe
MeO
I
N
NO2
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME kks-309r
EXPNO 13
PROCNO 1
Date_ 20140630
Time 20.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 3.00

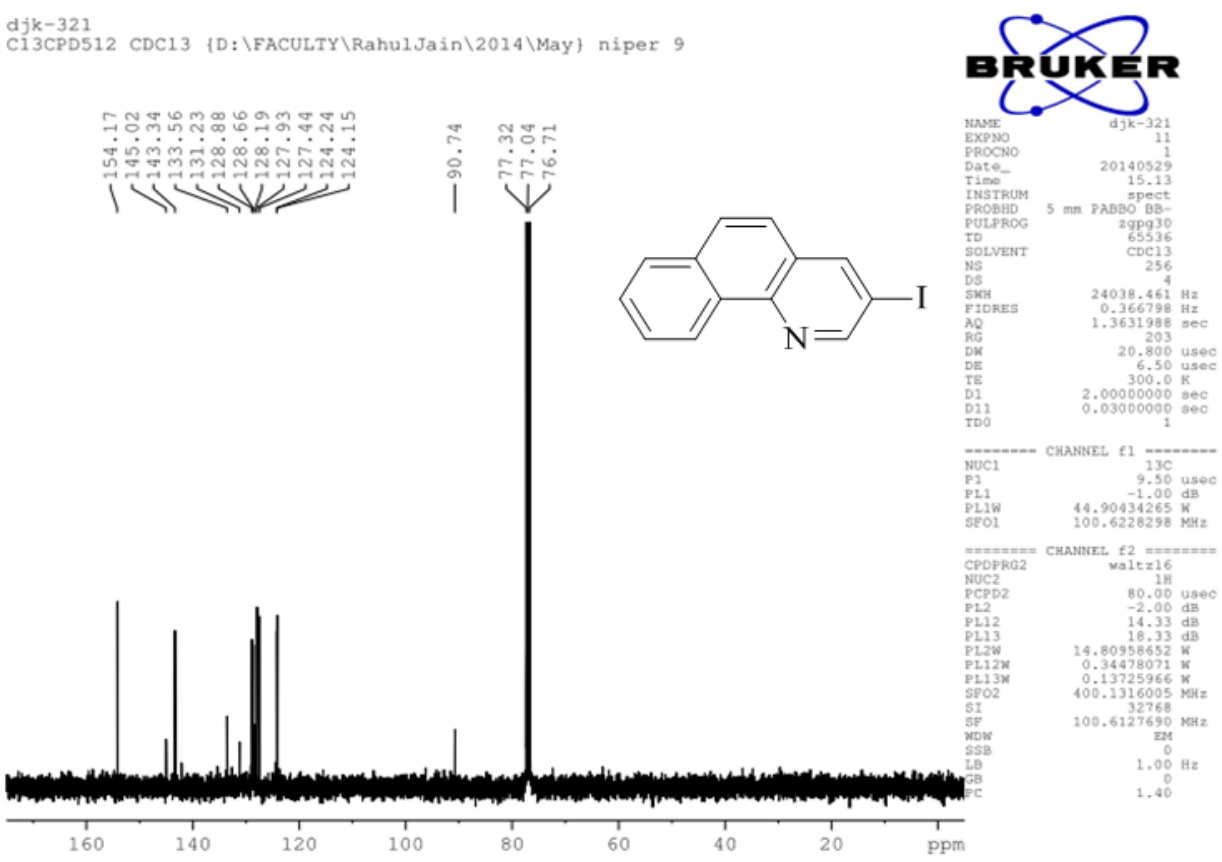
4-Iodoisoquinoline (2o):



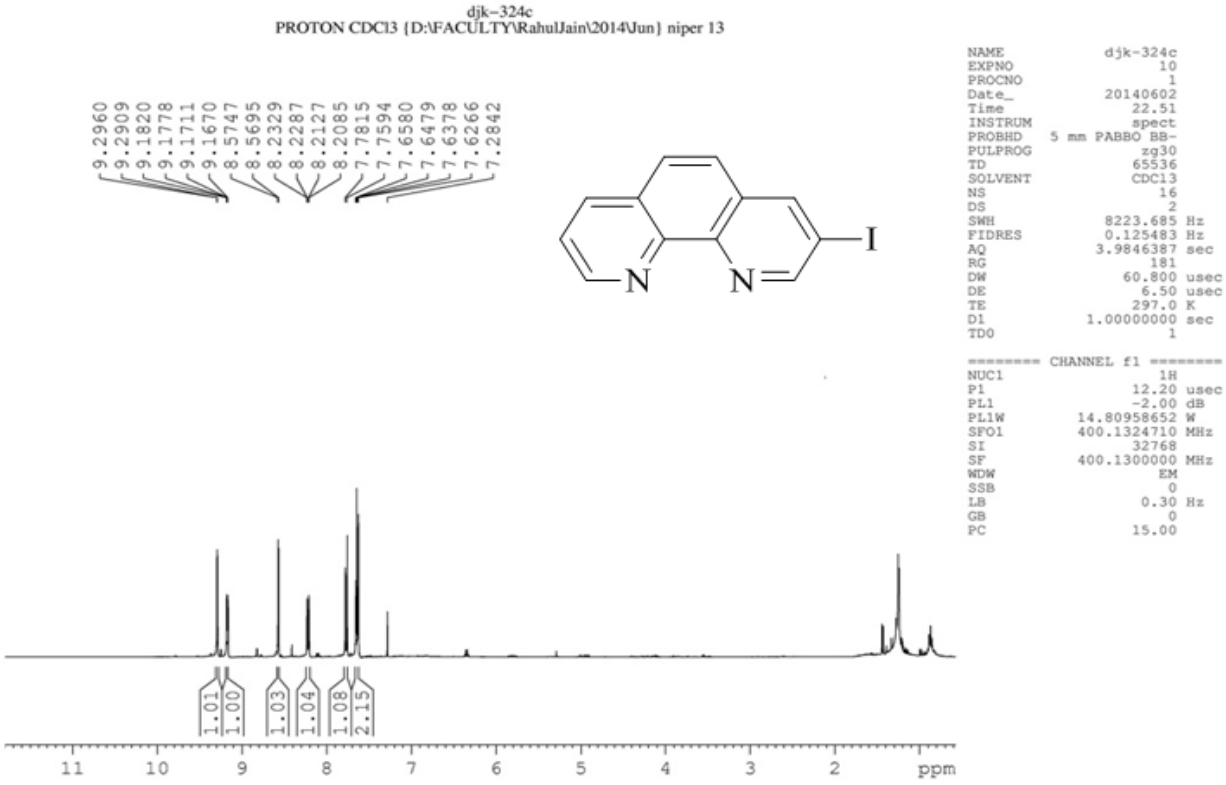

djk-322 1
C13CPD512 CDC13 {D:\FACULTY\RahulJain\2014\May} niper 8
152.60
150.97
137.13
131.99
130.73
129.74
128.33
128.17
96.81
77.36
77.04
76.72
I
N
160
150
140
130
120
110
100
90
80
70
60
50
ppm
NAME djk-322 1
EXPNO 13
PROCNO 1
Date_ 20140527
Time 20.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

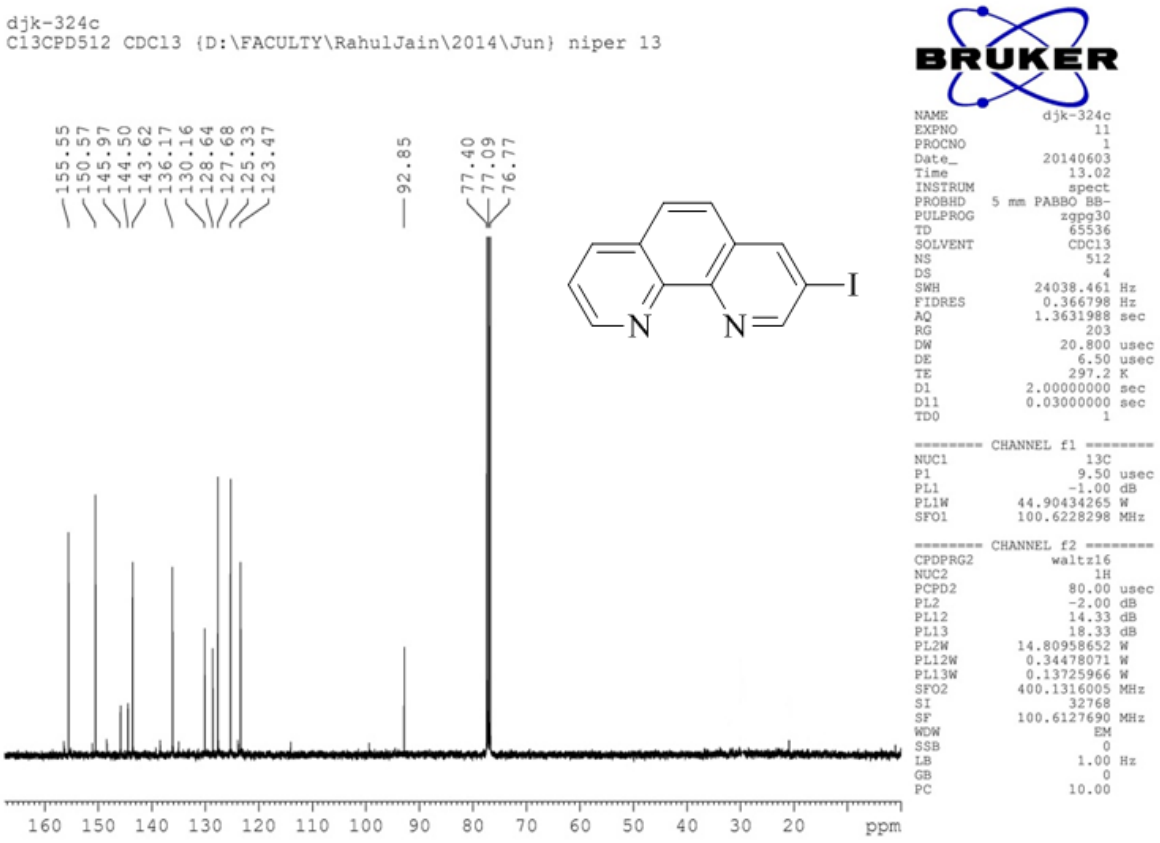
3-Iodobenzo(*h*)Quinoline (2p):




djk-321
C13CPD512 CDCl3 {D:\FACULTY\RahulJain\2014\May} niper 9
154.17
145.02
143.34
133.56
131.23
128.88
128.66
128.19
127.93
127.44
124.24
124.15
90.74
77.32
77.04
76.71
I
N
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME djk-321
EXPNO 11
PROCNO 1
Date_ 20140529
Time 15.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3-Iodo-1,10-phenanthroline (2qa):

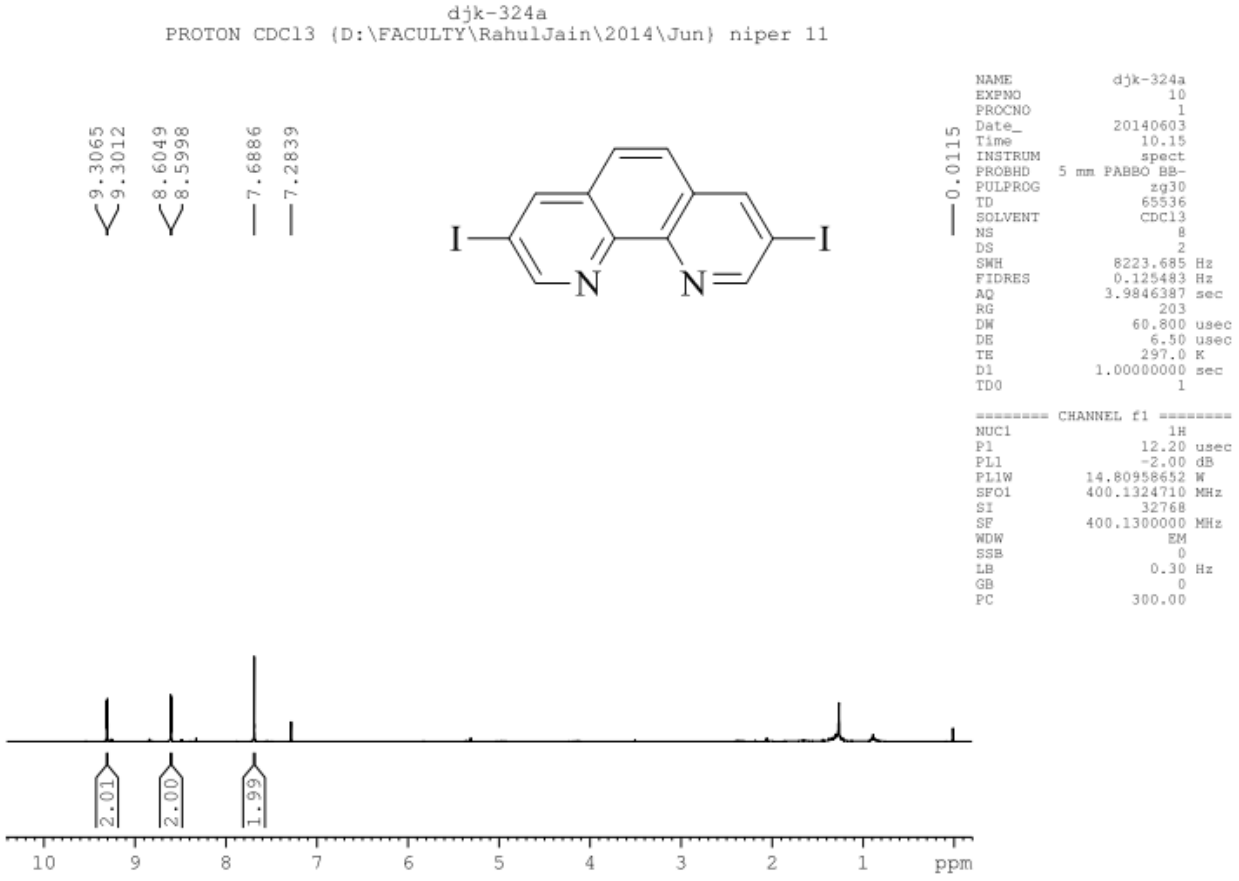


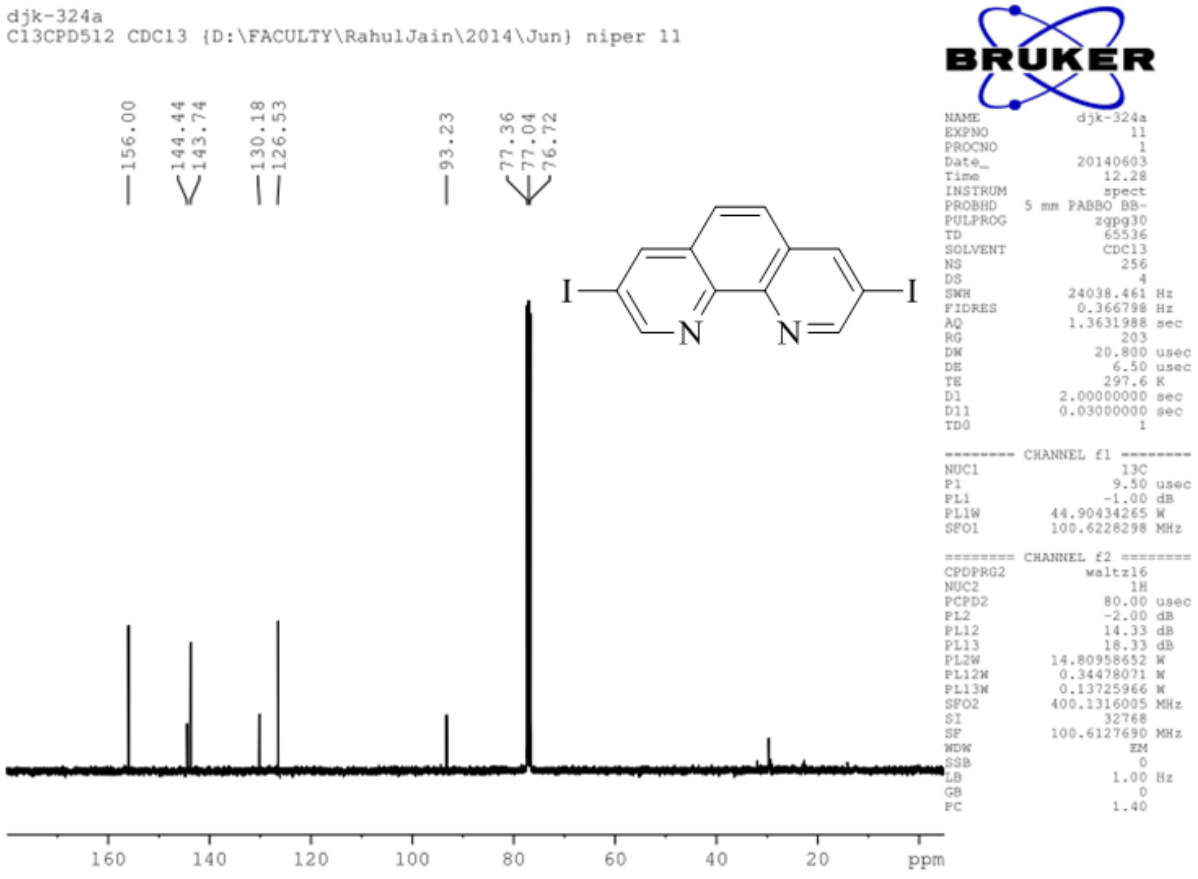


BRUKER

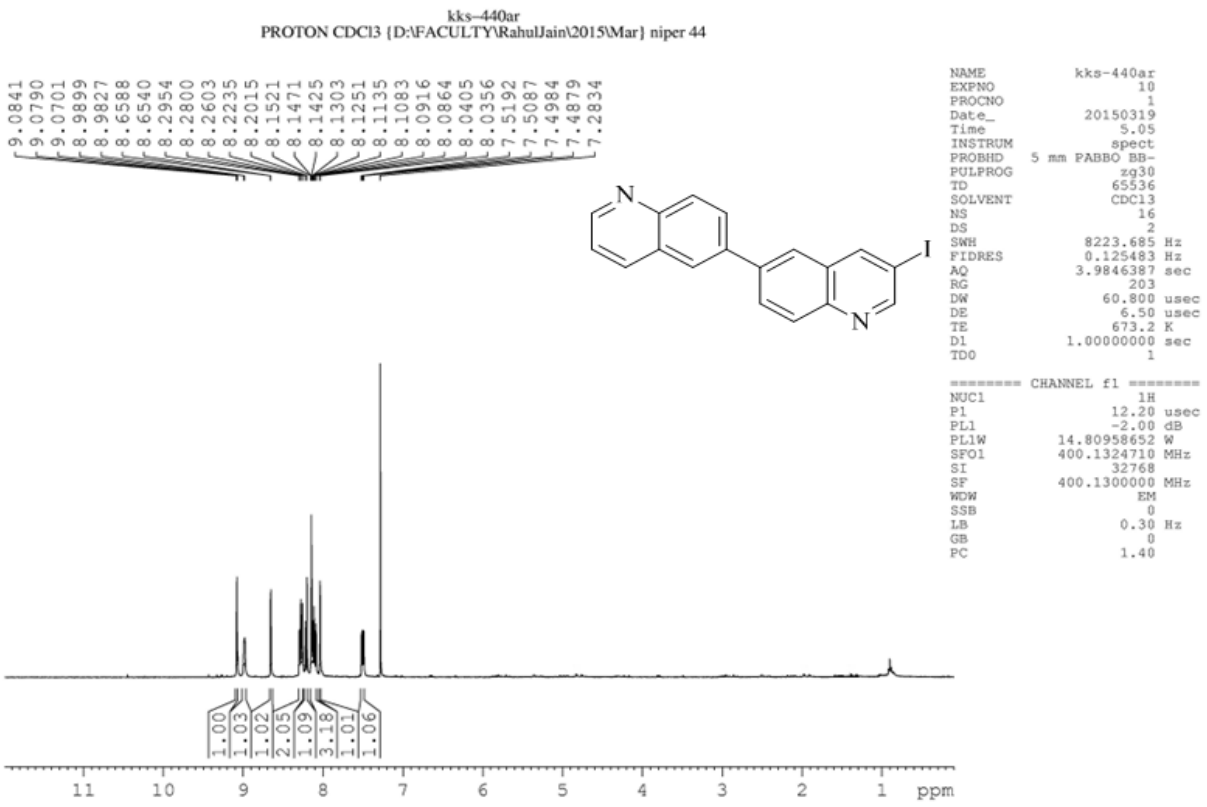
NAME	djk-324c
EXPNO	11
PROCNO	1
Date_	20140603
Time	13.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-1.00 dB
PL1W	44.90434265 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	14.33 dB
PL13	18.33 dB
PL2W	14.80958652 W
PL12W	0.34478071 W
PL13W	0.13725966 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	10.00

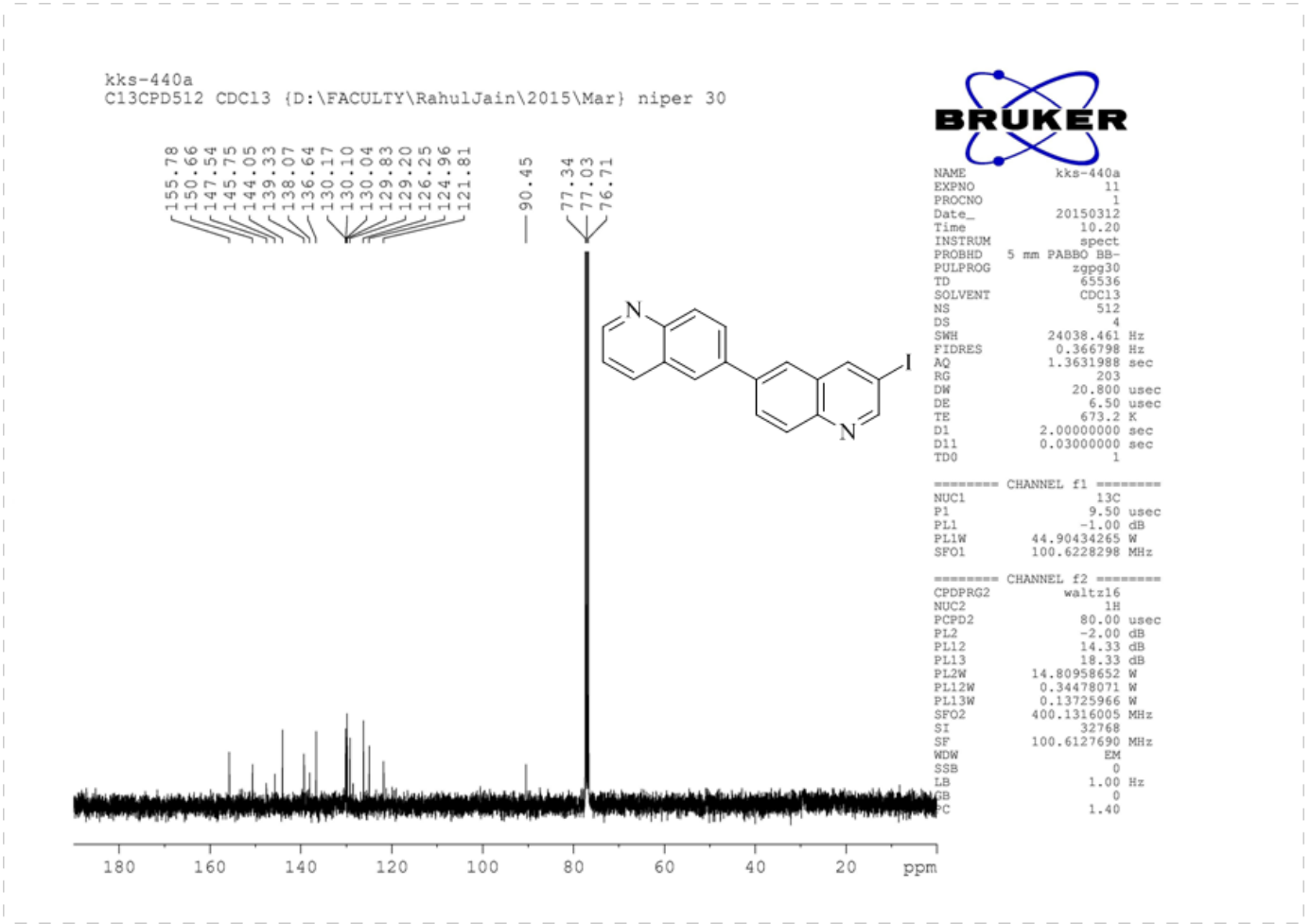
3,8-Diiodo-1,10-phenanthrolene (2qb):



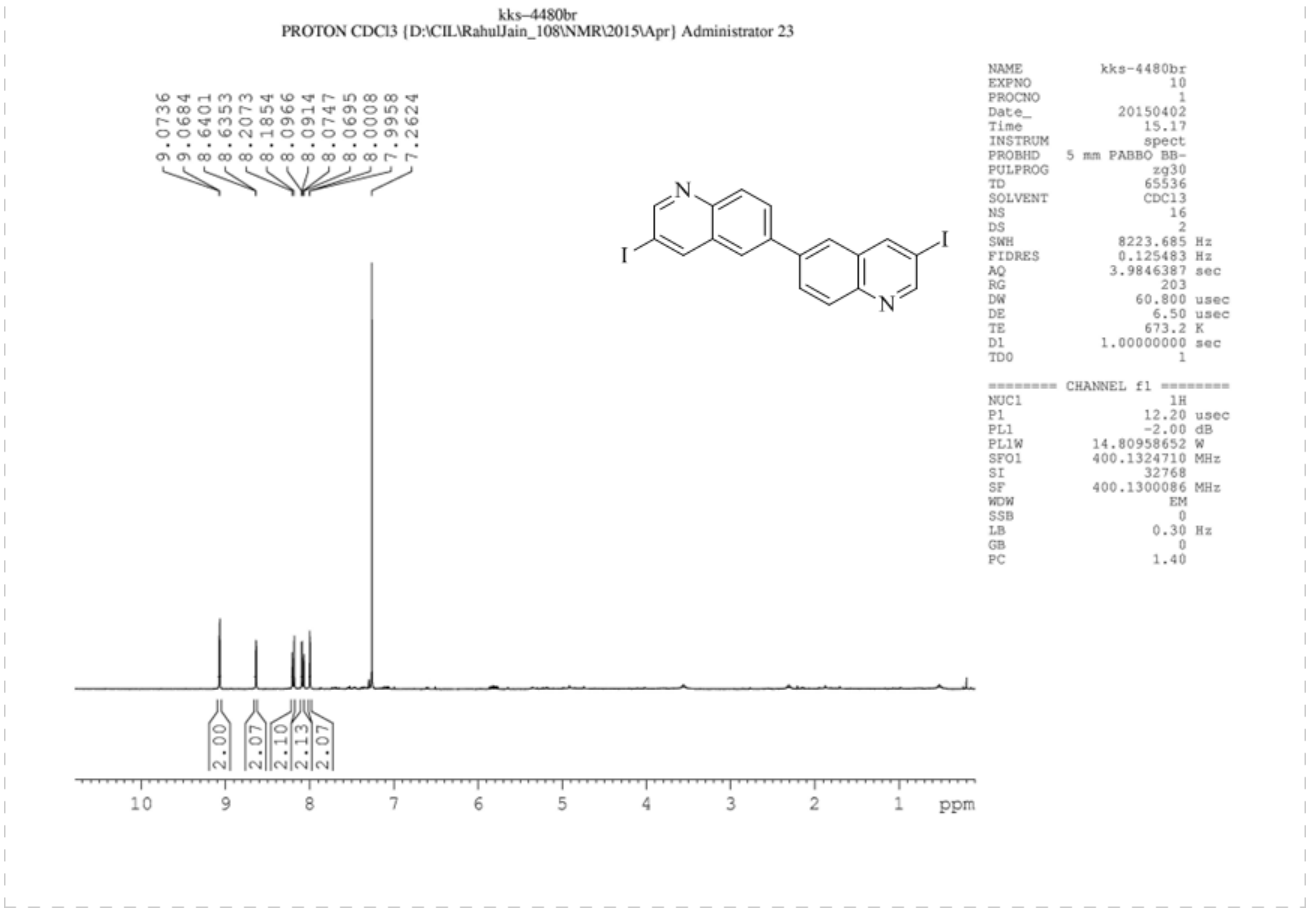

djk-324a
C13CPD512 CDC13 {D:\FACULTY\RahulJain\2014\Jun} niper 11
156.00
144.44
143.74
130.18
126.53
93.23
77.36
77.04
76.72
I
I
N
N
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME djk-324a
EXPNO 11
PROCNO 1
Date_ 20140603
Time 12.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

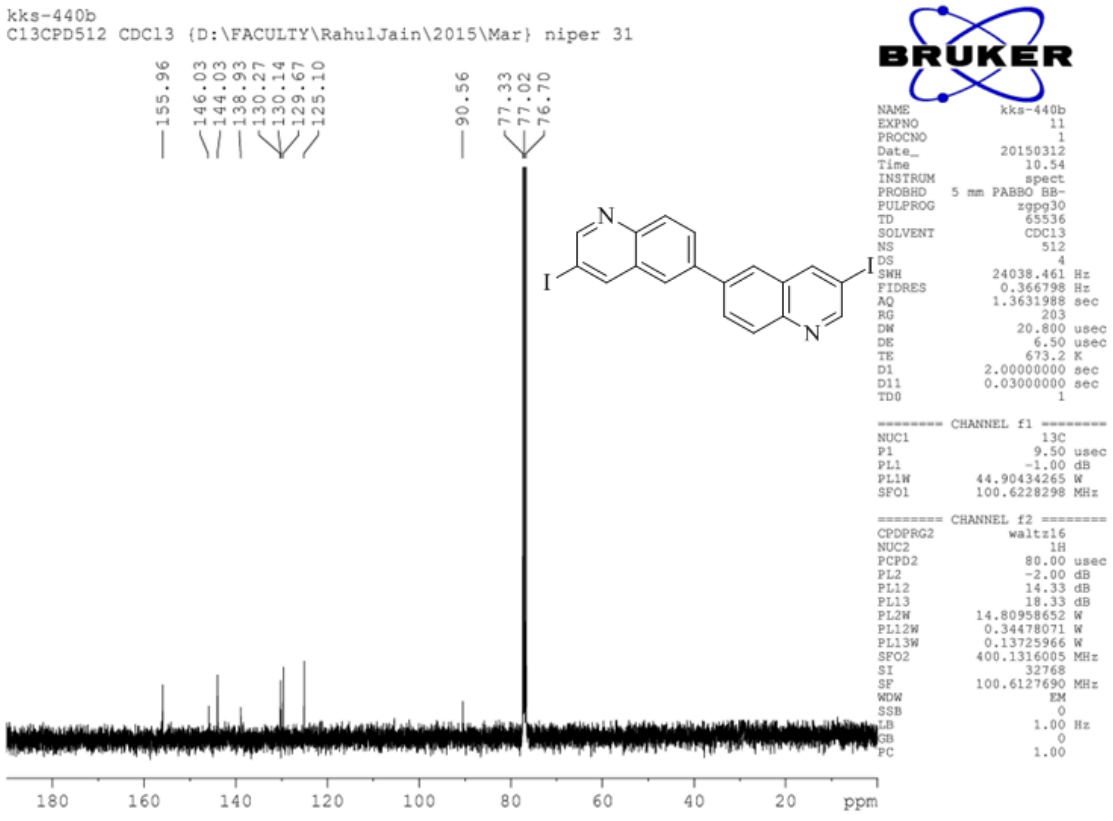
3-Iodo-6,6'-biquinoline (2ra)



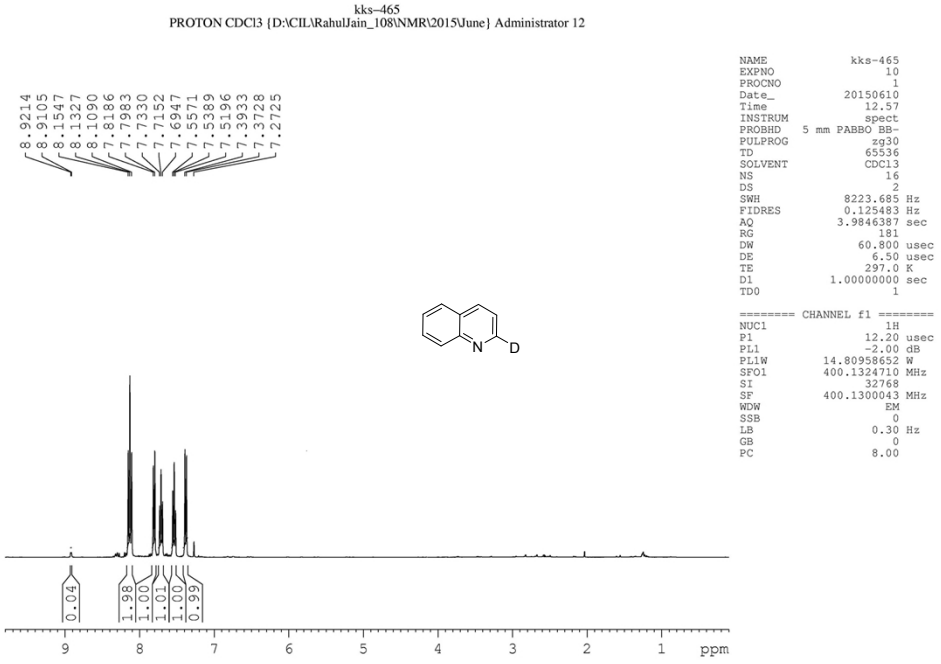

kks-440a
C13CPD512 CDCl3 {D:\FACULTY\RahulJain\2015\Mar} niper 30
155.78
150.66
147.54
145.75
144.05
139.33
138.07
136.64
136.17
130.10
130.04
129.83
129.20
126.25
124.96
121.81
90.45
77.34
77.03
76.71
N
I
N
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME kks-440a
EXPNO 11
PROCNO 1
Date_ 20150312
Time 10.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,3’-Diiodo-6,6’-biquinoline (2rb)

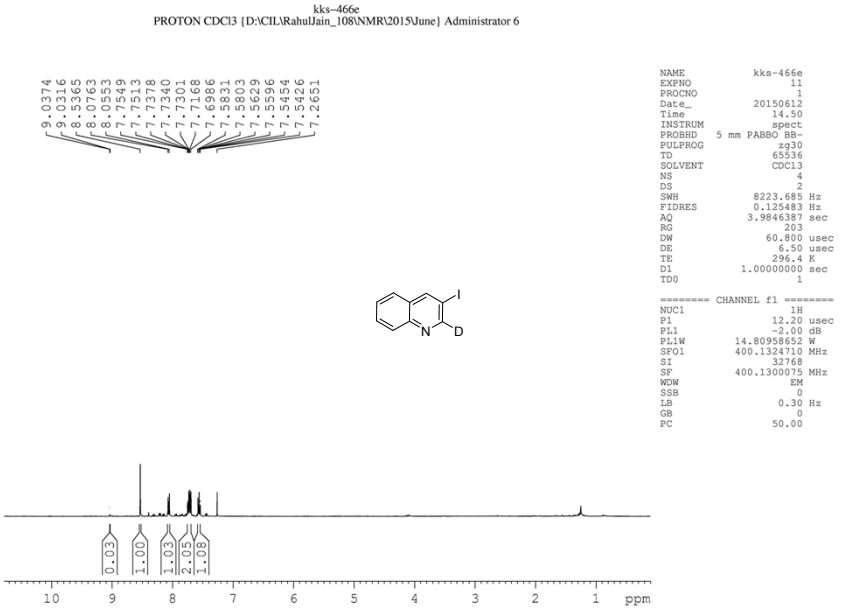



kks-440b
C13CPD512 CDCl3 {D:\FACULTY\RahulJain\2015\Mar} niper 31
155.96
146.03
144.03
138.93
130.27
130.14
129.67
125.10
90.56
77.33
77.02
76.70
N
I
I
N
BRUKER
NAME kks-440b
EXPNO 11
PROCNO 1
Date_ 20150312
Time 10.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -1.00 dB
PL1W 44.90434265 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.33 dB
PL13 18.33 dB
PL2W 14.80958652 W
PL12W 0.34478071 W
PL13W 0.13725966 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
180
160
140
120
100
80
60
40
20
ppm

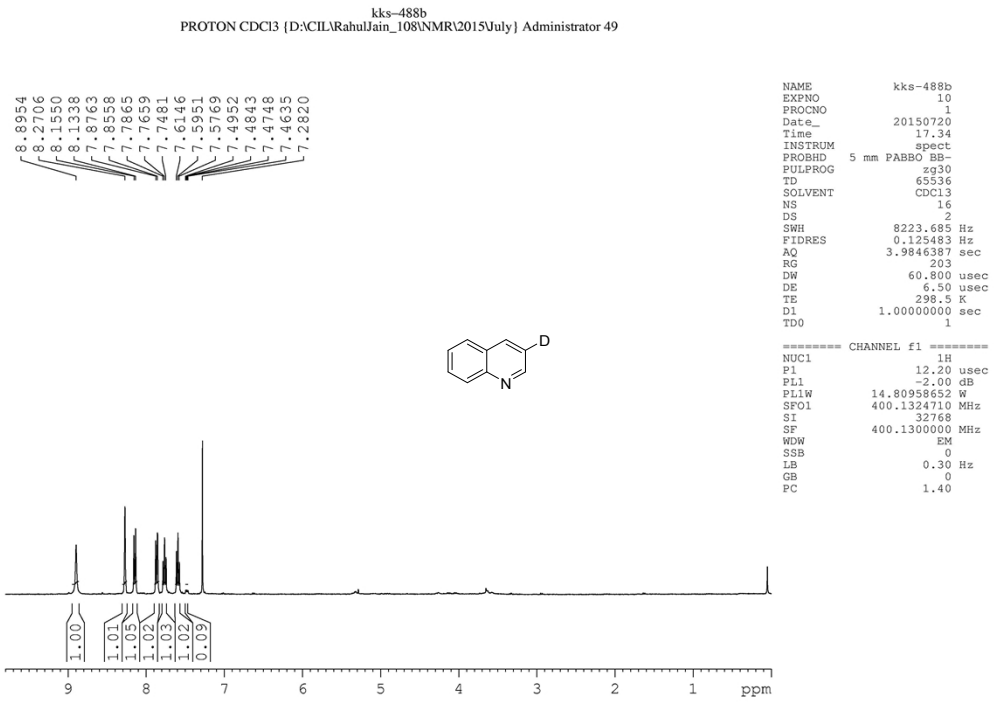
Quinoline-2-*d* (6a)



3-Iodoquinoline-2-*d* (6b)



Quinoline-3*d*



10. NMR study

Aliquots of reaction mixture were taken and concentrated under vaccum and submitted for NMR analysis.

Figure: NMR study for the iodination of substrate **1a**

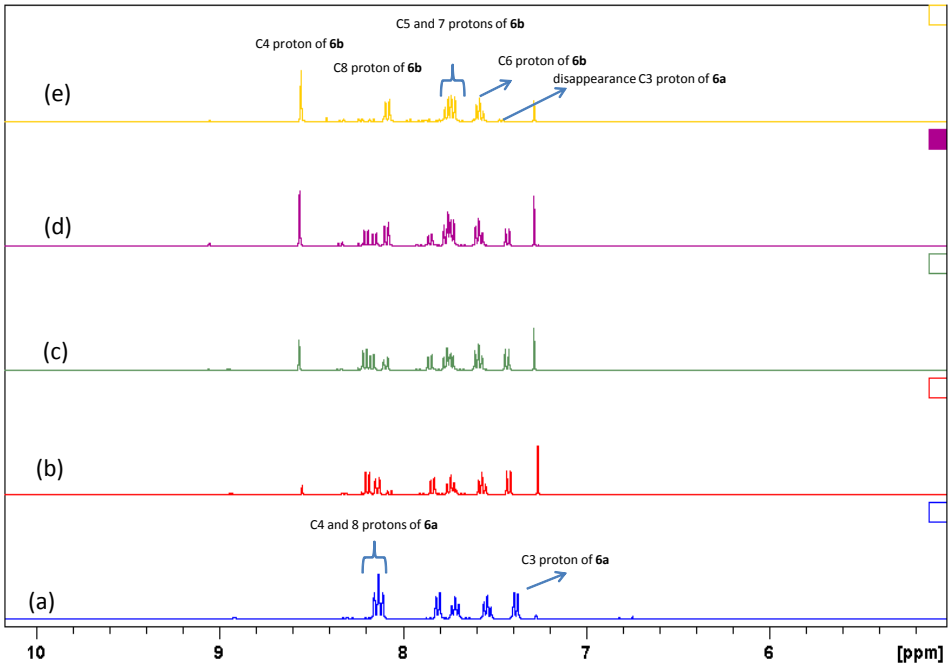


Figure: NMR study for the iodination of substrate **6a**

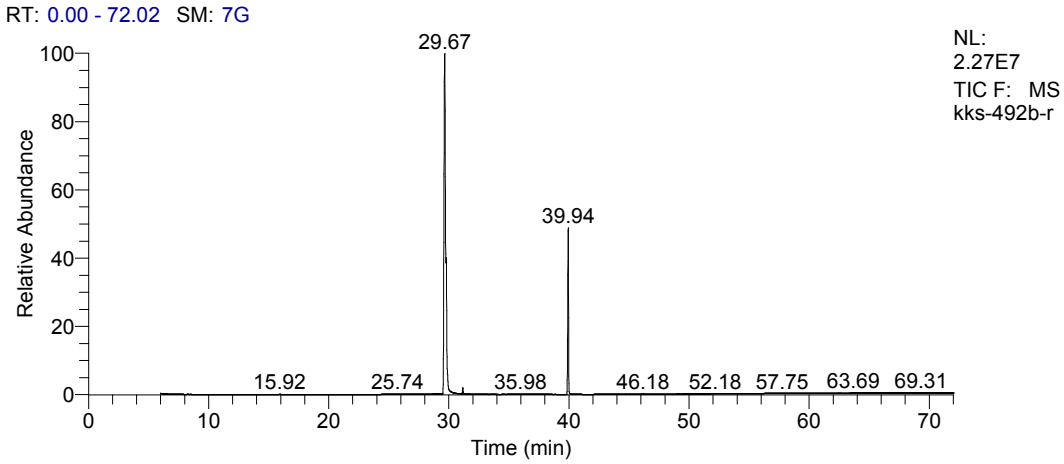
Spectrum	**Aliquots withdrawal time**
(a)	0 min
(b)	30 min
(c)	2h
(d)	6 h
(e)	12 h

11. Kinetic Isotope Effect (KIE) study

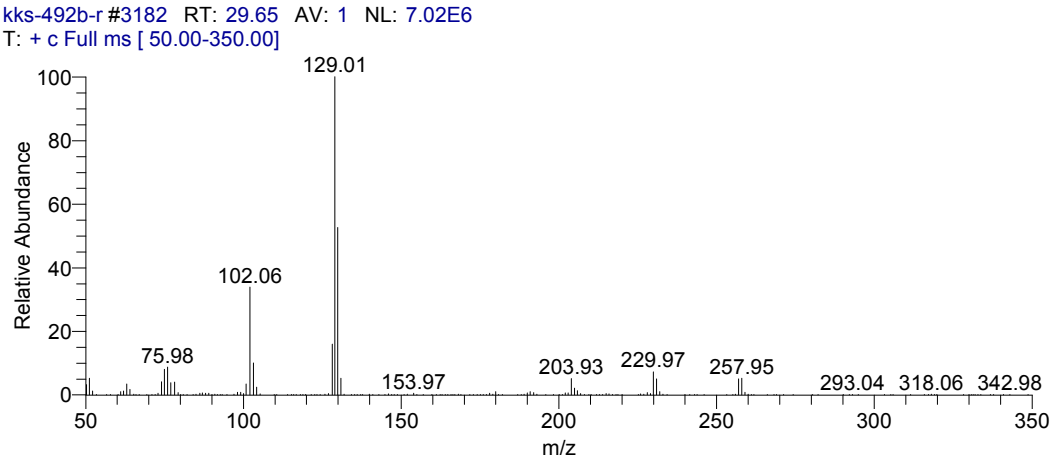
Under same conditions and optimized conditions parallel reactions (0.25 mmol) were set and aliquots of reaction mixture were taken at various time intervals and concentrated under vacuum and submitted for GCMS analysis. Mean of obtained data was used for calculation of k_H/k_D.

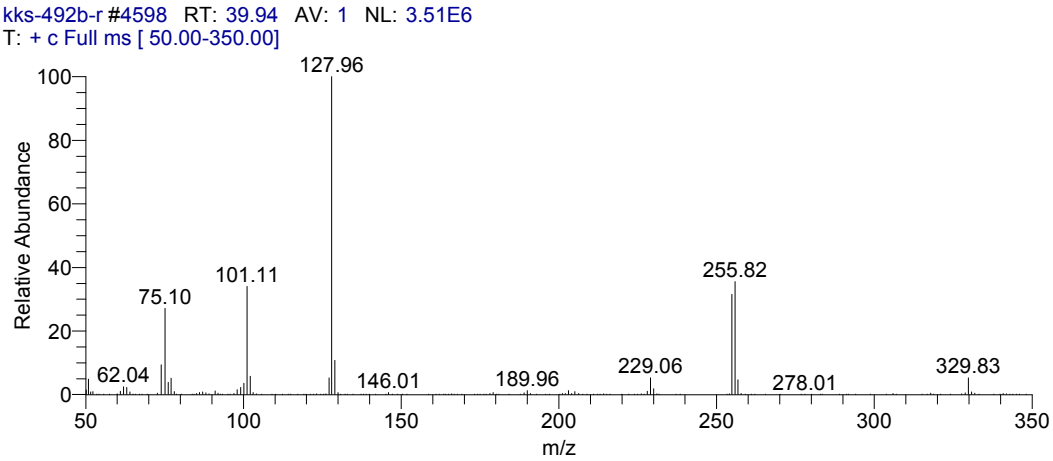
Representative data for primary KIE:

(a) GCMS data for reaction mixture of quinoline (1a):

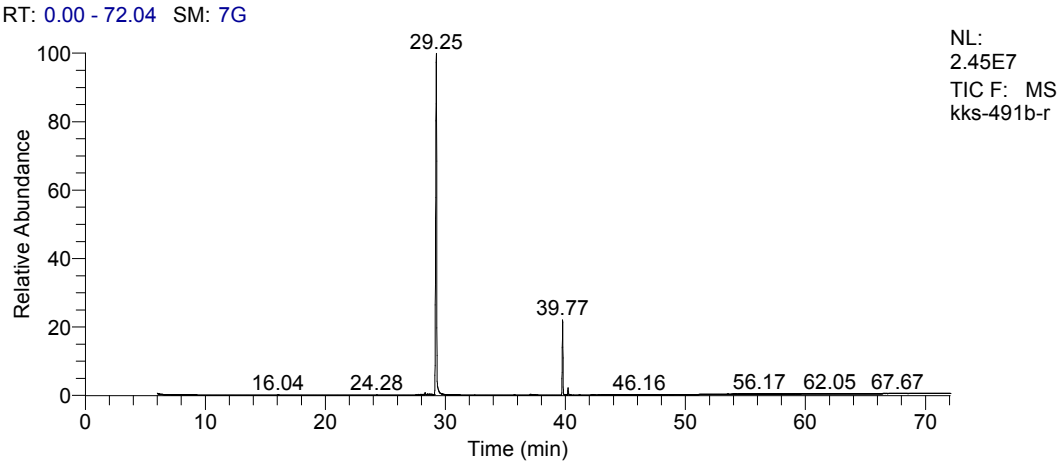


RT	Area %	Peak Area	Peak Height
29.65	70.27	84495076	14055027
39.94	29.73	35750180	9521358

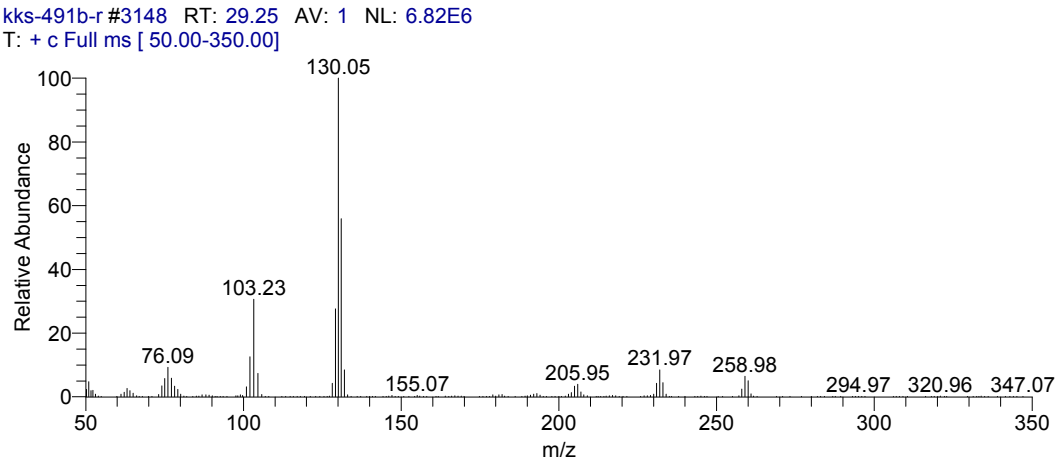


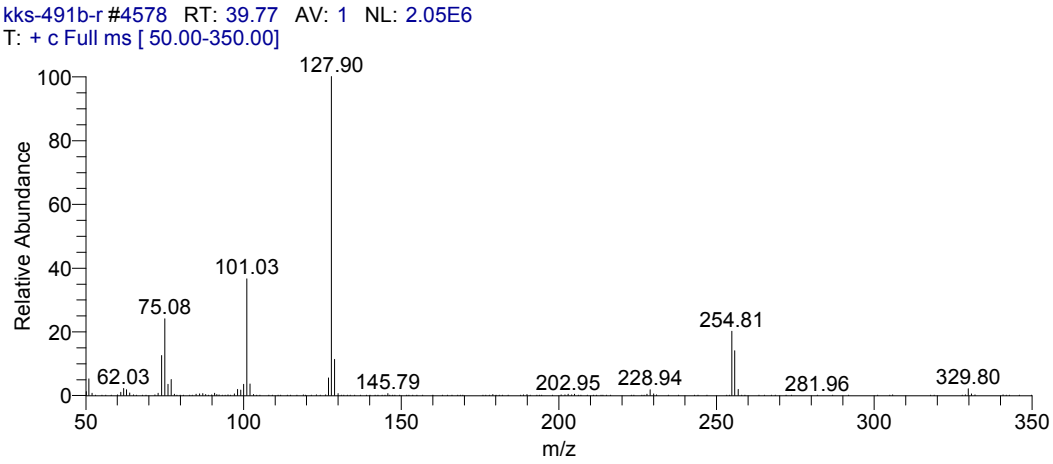


(b) GCMS data for reaction mixture of quinoline-3-*d*:



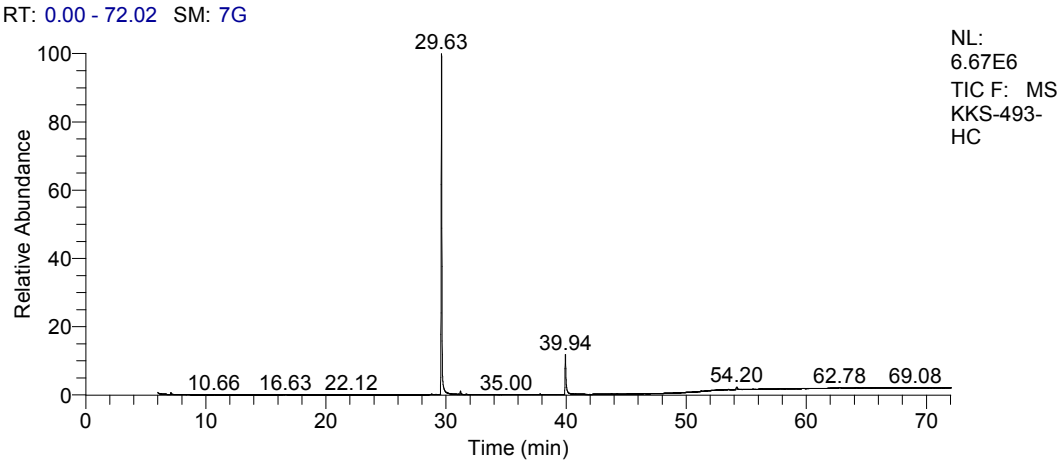
RT	Area %	Peak Area	Peak Height
29.25	86.22	94437999	19651717
39.77	13.78	15093657	4529895



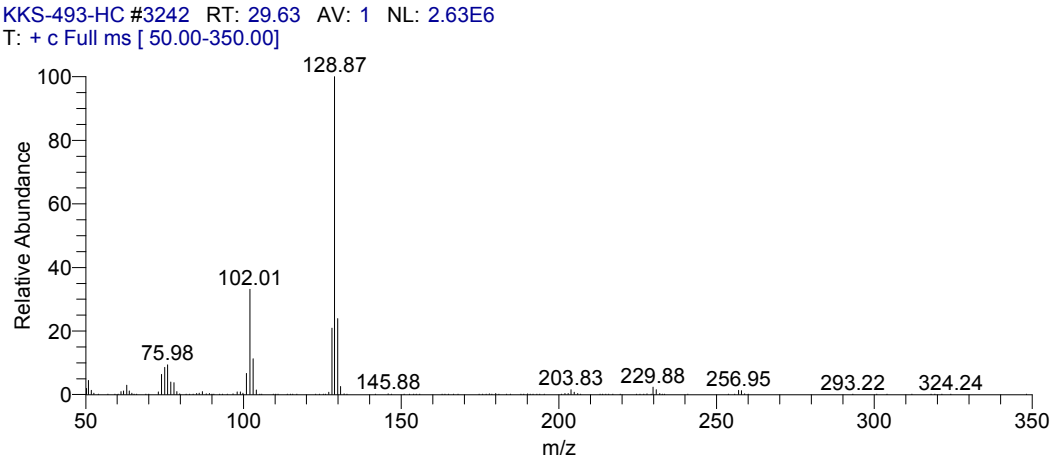


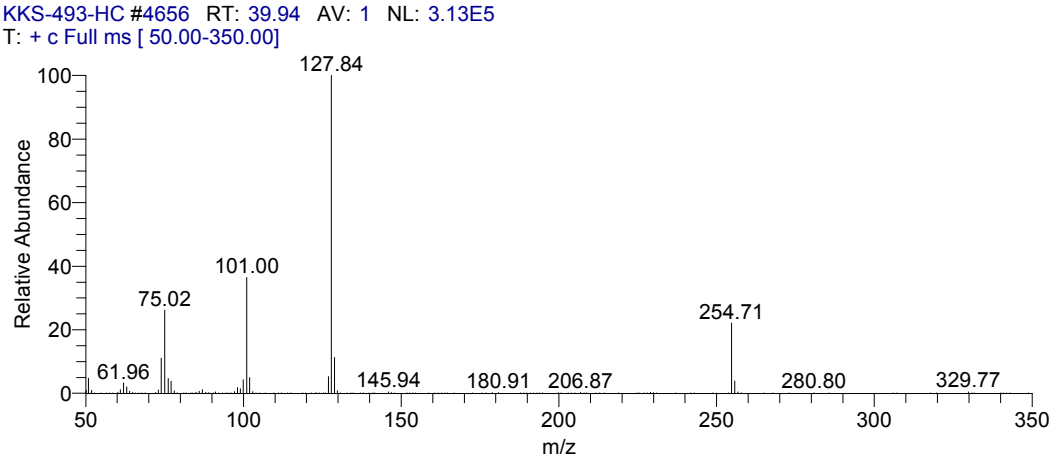
Representative data for secondary KIE:

(a) GCMS data for iodination reaction mixture of quinoline (1a):

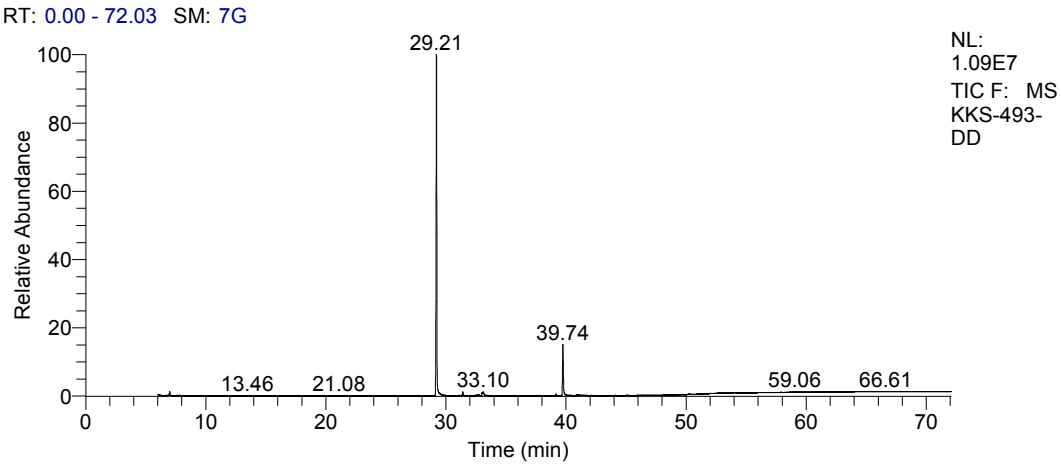


RT	Area %	Peak Area	Peak Height
29.63	88.70	16962630	5655307
39.94	11.30	2161997	614720



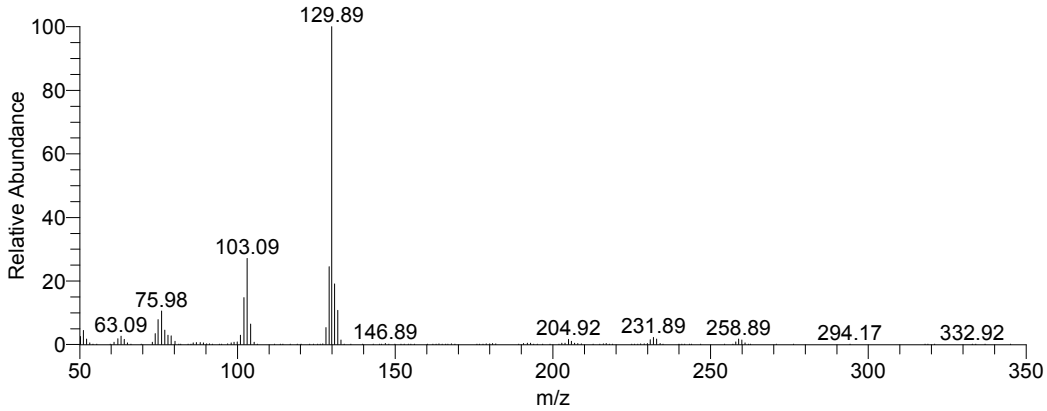


(b) GCMS data for iodination reaction mixture of quinoline-2-*d* (6a):



RT	Area %	Peak Area	Peak Height
29.22	85.96	28423761	9209008
39.74	14.04	4643984	1332652

KKS-493-DD #3165 RT: 29.22 AV: 1 NL: 3.96E6
T: + c Full ms [50.00-350.00]



KKS-493-DD #4608 RT: 39.74 AV: 1 NL: 6.12E5
T: + c Full ms [50.00-350.00]