Oxidative Dimerization of *N*-Protected and Free Indole Derivatives toward 3,3'-Biindoles *via* Pd-Catalyzed Direct C-H Transformations

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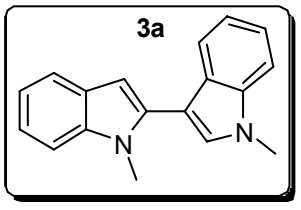
Supporting Information

General

If no special indicated, all the reactions were carried out under N_2 atmosphere. $Pd(OTFA)_2$ were purchased from Alfa Aesar and other reagents were used as commercially available and without further purification. *N*-protected indoles were prepared according to literature method.[1] DMSO was distilled under reduced pressure over CaH_2 below 90 °C. NMR Spectra were recorded on a Bruker 400, Varian 300, or Varian 200 spectrometer in the solvents indicated; Chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm/(DMSO resonance in the ^1H spectrum as 2.50 ppm) and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm/ (DMSO resonance in the ^{13}C spectrum as 39.52 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh 200-300. FTIR were performed on Fourier transform infrared spectrometer. HRMS or MS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

General procedures for syntheses of 2,3'-linked N-protected indole dimer (3).

N-methyl indole **1a** (0.5 mmol), $Pd(OTFA)_2$ (0.025 mmol), anhydrous $Cu(OAc)_2$ (0.5 mmol), and DMSO (2.0 mL) were added into an oven-dried Schlenck tube. The mixture was stirred at 90 ºC for 12 h under N_2 gas atmosphere in a Wattecs-12 Parallel Reaction Station. After that, the reaction was quenched by water (25 mL) and extracted with CH_2Cl_2 (4 x 25 mL). The combined organic layer was washed with brine (3 x 25 mL), dried over $MgSO_4$. After the evaporation, the residue was purified on silica gel chromatography with hexanes/EtOAc as eluents to afford compound **3a**



^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.39-7.27 (m, 3H), 7.25-7.11 (m, 4H), 6.62 (s, 1H), 3.82 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (75.4 MHz,$CDCl_3$): δ 137.83, 136.81, 135.02, 128.33, 128.28, 127.55, 122.24, 120.89, 120.26, 120.13, 119.93, 119.48, 109.48, 109.29, 107.16, 101.24, 32.95, 30.93; FTIR (film, cm^{-1}): 3046, 1733, 1461, 1246, 780, 744; HRMS: *m/z*: $[M + H]^+$ calculated for $C_{18}H_{17}N_2$, 261.1386; Found 261.1382.

General procedures for syntheses of 3,3'-linked N-protected indole dimer (4).

Condition A: $Pd(OTFA)_2$ (0.05 mmol) was added into a solution of N-protected indole **1** (0.5 mmol) in DMSO (2 mL) in an oven-dried Schlenk tube. Then $AgNO_3$ (0.6 mmol) was added and followed by HOAc (0.10 mmol). The reaction mixture was stirred at 30 °C for 10 h under N_2 gas atmosphere in a Wattecs-12 Parallel Reaction Station. The reaction was quenched with sat. $NaHCO_3$ solution (20 mL) and extracted with EtOAc (4 x 25 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc or hexanes/DCM/EtOAc as eluents to afford compound **4**.

Condition B: $Pd(OTFA)_2$ (0.025 mmol) was added into a solution of N-protected indole **1** (0.25 mmol) in DMSO (7 mL) in an oven-dried Schlenk tube. Then $AgNO_3$ (0.30 mmol) was added. The reaction mixture was stirred at 30 °C for 3-20 h under N_2 gas atmosphere in a Wattecs-12 Parallel Reaction Station. After the completion traced by TLC, the reaction was quenched with water (30 mL) and extracted with EtOAc (4 x 25 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc or hexanes/DCM/EtOAc as eluents to afford compound **4**.

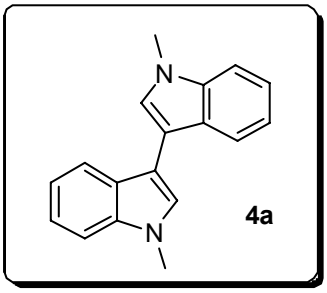
Condition C: $Pd(OTFA)_2$ (0.025 mmol) was added into a solution of N-protected indole **1** (0.25 mmol) in DMSO (1 mL) in an oven-dried Schlenk tube. Then $AgNO_3$ (0.5 mmol) was added. The reaction mixture was stirred at 60 °C for 4.5-10 h under N_2 gas atmosphere in a Wattecs-12 Parallel Reaction Station. After the completion traced by TLC, the reaction was quenched with water (20 mL) and extracted with EtOAc (4 x 25 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc or hexanes/DCM/EtOAc as eluents to afford compound **4**.

General procedures for syntheses of 3,3'-linked NH indole dimer (4).

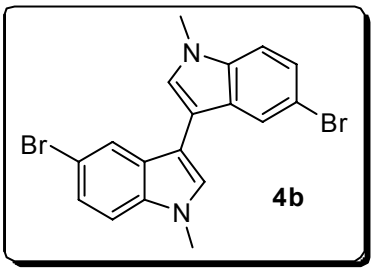
$Pd(OTFA)_2$ (0.05 mmol) was added into a solution of indole **1** (0.5 mmol) in DMSO

(4 mL) in an oven-dried Schlenk tube. Then Anhydrous $MgSO_4$ (1.5 mmol) was added and followed by $AgNO_3$ (0.6 mmol). The reaction mixture was stirred at 20 °C for 10-40 h under N_2 gas atmosphere in a Wattecs-12 Reaction Station. After the completion traced by TLC, the reaction was quenched with water (20 mL) and extracted with EtOAc (4 x 25 mL)/ DCM (4 x 25 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc or hexanes/DCM/EtOAc as eluents to afford compound **4**.

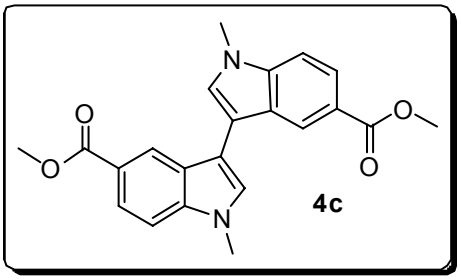
Synthesis and analytical data for the products 4a-4t



1,1'-dimethyl-1H,1'H-3,3'-biindole (**4a**): According to condition A, starting from 0.5 mmol of **1a**, 47 mg of **4a** was obtained in 72 %yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 0.6 Hz, *J* = 8.1 Hz, 2H), 7.38 (dd, *J* = 0.6 Hz, *J* = 8.1 Hz, 2H), 7.31-7.28 (m, 4H), 7.18-7.13 (m, 2H), 3.86 (s, 6H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 137.11, 127.21, 126.03, 121.77, 120.26, 119.18, 109.52, 109.25, 32.72.; FTIR (film, cm^{-1}): 2995, 2359, 1769, 1241, 739. MS: *m/z*: $[M]^+$ 260.1

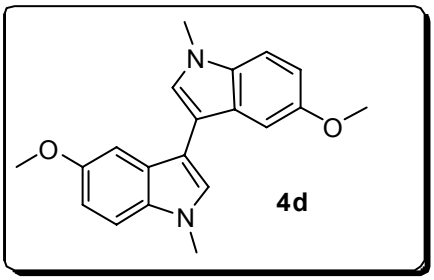


5,5'-dibromo-1,1'-dimethyl-1H,1'H-3,3'-biindole (4b): According to condition A, starting from 0.50 mmol of **1b**, 83 mg of **4b** was obtained in 79 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 1.8 Hz, 2H), 7.37-7.34 (m, 2H), 7.30-7.24 (m, 4H), 3.86 (s, 6H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 135.73, 128.72, 127.22, 124.76, 122.38, 112.91, 110.84, 108.45, 32.99. FTIR (film, cm^{-1}): 2995, 2359, 1769, 1240, 733. HRMS: *m/z*: $[M]^+$ calculated for $C_{18}H_{14}Br_2N_2$, 415.9518; Found 415.9513.

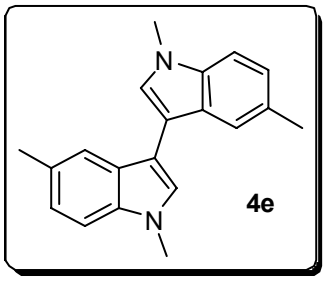


dimethyl 1,1'-dimethyl-1H,1'H-3,3'-biindole-5,5'-dicarboxylate (4c): According to condition A, starting from 0.5 mmol of **1m**, 76 mg of **1c** was obtained in 80 % yield. ^{1}H NMR

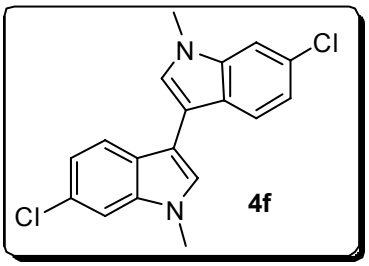
(300 MHz, $CDCl_3$): δ 8.58 (d, *J* = 1.8 Hz, 2H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.49 (s, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 6H), 3.83(s, 6H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 168.26, 139.49, 127.58, 126.67, 123.36, 122.97, 121.52, 110.36, 109.00, 51.81, 33.09. FTIR (film, cm^{-1}): 2995, 2361, 1770, 1247, 754. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{22}H_{21}N_2O_4$, 377.1496; Found 377.1492.



5,5'-dimethoxy-1,1'-dimethyl-1H,1'H-3,3'-biindole (4d): According to condition B, starting from 0.25 mmol of **1d** for 10 h, 8 mg of **4d** was obtained in 20 % yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.29-7.21 (m, 6H), 6.96 (d, *J* = 2.4 Hz, 2H), 3.84 (s, 6H), 3.82(s, 6H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 153.59, 132.14, 126.73, 126.51, 113.35, 110.46, 108.31, 101.75, 55.51, 32.56. FTIR (film, cm^{-1}): 2992, 1750, 1210, 776. HRMS: *m/z*: $[M]^+$ calculated for $C_{20}H_{20}N_2O_2$, 320.1519; Found 320.1510.

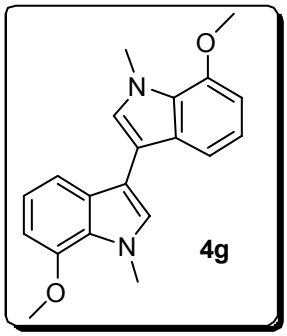


1,1',5,5'-tetramethyl-1H,1'H-3,3'-biindole (4e): According to condition B, starting from 0.25 mmol of **1e** for 3 h, 22 mg of **4e** was obtained in 61 % yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 0.6 Hz, 2H), 7.27-7.24 (m, 4H), 7.09 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H), 3.83(s, 6H), 2.46 (s, 6H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 135.58, 128.37, 127.54, 126.22, 123.35, 119.89, 109.05, 108.91, 32.81, 21.51. FTIR (film, cm^{-1}): 2995, 2359, 1769, 1242, 788. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{20}H_{21}N_2$, 289.1699; Found 289.1696.

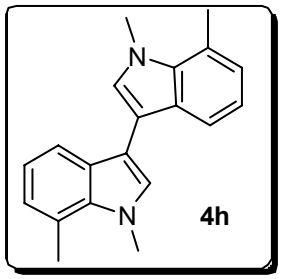


6,6'-dichloro-1,1'-dimethyl-1H,1'H-3,3'-biindole (4f): According to condition A, starting from 0.50 mmol of **1f**, 60 mg of **4f** was obtained in 73 % yield. ^1H NMR (300 MHz, $CDCl_3$): 7.67 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 1.8 Hz, 2H), 7.25 (s, 2H), 7.12 (dd, *J* = 1.8 Hz, *J* = 8.4 Hz, 2H), 3.83 (s, 6H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 137.15, 127.37,

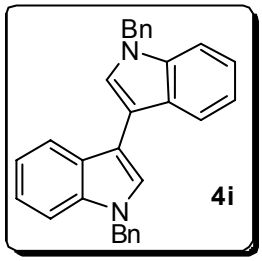
126.40, 124.77, 121.04, 119.28, 109.79, 108.36, 32.59. FTIR (film, cm^{-1}): 1769, 1234, 1068, 905, 787. HRMS: *m/z*: $[M]^+$ calculated for $C_{18}H_{14}Cl_2N_2$, 328.0529; Found 328.0523.



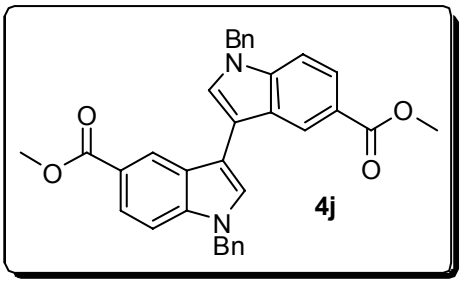
7,7'-dimethoxy-1,1'-dimethyl-1H,1'H-3,3'-biindole (4g): According to condition B, starting from 0.25 mmol of **1g** for 20 h, 29 mg of **4g** was obtained in 72 % yield. ^1H NMR (300 MHz, $CDCl_3$): 7.38 (d, *J* = 7.8 Hz, 2H), 7.13 (s, 2H), 7.01 (t, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 4.10 (s, 6H), 3.94 (s, 6H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 147.89, 129.61, 127.34, 126.78, 119.54, 113.19, 109.52, 102.58, 55.46, 36.46. FTIR (film, cm^{-1}): 2995, 2359, 1769, 1252, 732. FTIR (film, cm^{-1}): 2995, 2359, 1769, 1252, 732 . HRMS: *m/z*: $[M+H]^+$ calculated for $C_{20}H_{21}N_2O_2$, 321.1598; Found 321.1594.



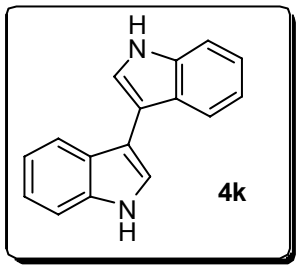
1,1',7,7'-tetramethyl-1H,1'H-3,3'-biindole (4h): According to condition B, starting from 0.25 mmol of **1h** for 10 h, 26 mg of **4h** was obtained in 72 % yield. ^1H NMR (300 MHz, $CDCl_3$): 7.61 (d, *J* = 7.5 Hz, 2H), 7.13 (s, 2H), 7.01-6.93 (m, 4H), 4.10 (s, 6H), 2.79 (s, 6H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 135.79, 128.52, 128.03, 124.43, 121.21, 119.42, 118.43, 109.18, 36.74, 19.78. FTIR (film, cm^{-1}): 2956, 2359, 1770, 1514, 1247, 778. HRMS: *m/z*: $[M]^+$ calculated for $C_{20}H_2N_2$, 288.1621; Found 288.1616.



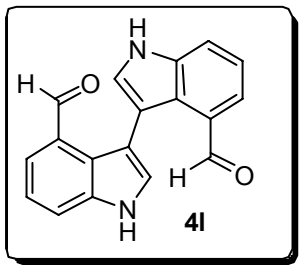
1,1'-dibenzyl-1H,1'H-3,3'-biindole (4i): According to condition C, starting from 0.25 mmol of **1i** for 4.5 h, 36 mg of **4i** was obtained in 69 %yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86-7.84 (m, 2H), 7.43 (s, 2H), 7.36-7.15 (m, 16H), 5.41(s, 4H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 137.56, 136.79, 128.76, 127.58, 127.45, 126.84, 125.51, 122.03, 120.41, 119.51, 110.15, 109.77, 50.08. FTIR (film, cm^{-1}): 2996, 2360, 1770, 1467, 1248, 732. HRMS: *m/z*: $[M]^+$ calculated for $C_{30}H_{24}N_2$, 412.1934; Found 412.1924.



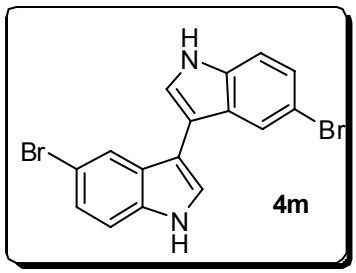
dimethyl 1,1'-dibenzyl-1H,1'H-3,3'-biindole -5,5'-dicarboxylate (4j): According to condition C, starting from 0.25 mmol of **1j** for 10 h, 52 mg of **4j** was obtained in 79 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): 8.58 (d, J = 0.9 Hz, 2H), 7.94 (dd, J = 1.5 Hz, J = 8.7 Hz, 2H), 7.57 (s, 2H), 7.37-7.19 (m, 12H), 5.45 (s, 4H), 3.91 (s, 6H); ^{13}C NMR (50 MHz,$CDCl_3$): δ 168.11, 139.16, 136.80, 128.90, 127.86, 127.07, 126.98, 126.82, 123.59, 123.11, 121.87, 110.90, 109.56, 51.81, 50.39. FTIR (film, cm^{-1}): 2359, 1770, 1247, 1059, 740. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{34}H_{29}N_2O_4$, 529.2122; Found 529.2106.



1H,1'H-3,3'-biindole (4k): According to the standard condition, starting from 0.5 mmol of **1k**, 32 mg of **4k** was obtained in 54 % yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.18 (br s, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.66 (d, J = 2.4 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.18-7.05 (m, 4H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 136.38, 126.07, 121.84, 121.20, 119.59, 118.81, 111.57, 109.74. FTIR (film, cm^{-1}): 3396, 2364, 1770, 1456, 1239, 736. MS: *m/z*: $[M]^+$ 232.1.

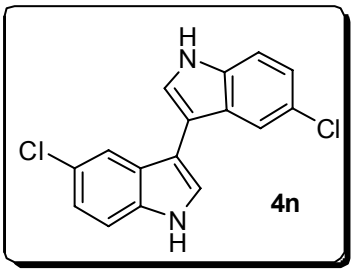


1H,1'H-3,3'-biindole-4,4'-dicarbaldehyde (4l): According to the standard condition, starting from 0.5 mmol of **1l**, 61 mg of **4l** was obtained in 84 % yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.81 (br s, 2H), 9.89 (s, 2H), 7.84 (dd, J = 0.9 Hz, J = 7.8 Hz),7.69 (d, J = 2.4 Hz, 2H), 7.60 (dd, J = 0.9 Hz, J = 7.5 Hz), 7.34 (t, J = 7.5 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 190.28, 137.92, 129.15, 128.35, 127.82, 121.11, 119.03, 118.42, 108.98. FTIR (film, cm^{-1}): 3343, 1666, 1343, 1108. HRMS: *m/z*: $[M + Na]^+$ calculated for $C_{18}H_{12}N_2$ Na O_2, 311.0791; Found 311.0792.

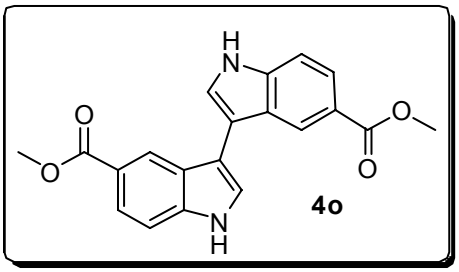


5,5'-dibromo-1H,1'H-3,3'-biindole (4m): According to the standard condition, starting from 0.50 mmol of **1m**, 77 mg of **4m** was obtained in 78 % yield. ^{1}H NMR (300

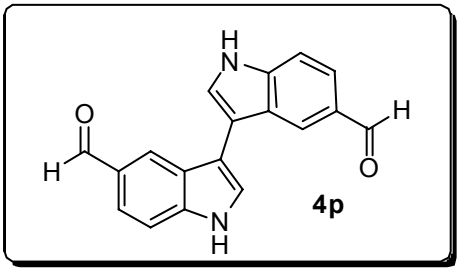
MHz, DMSO-d_6): 11.45 (br s, 2H), 7.87 (s, 2H), 7.77 (d, J = 2.1 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.27 (dd, J = 1.8 Hz, J = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 135.07, 127.75, 123.94, 123.86, 121.47, 113.68, 111.67, 108.68. FTIR (film, cm^{-1}): 3430, 1712, 1445, 1098, 793, HRMS: *m/z*: $[M + H]^+$ calculated for $C_{16}H_{11}Br_2N_2$, 388.9284; Found 388.9289.



5,5'-dichloro-1H,1'H-3,3'-biindole (4n): According to the standard condition, starting from 0.50 mmol of **1n**, 62 mg of **4n** was obtained in 82 % yield. ^{1}H NMR (300 MHz, DMSO-d_6):11.45 (br s, 2H), 7.81-7.75 (m, 4H), 7.48 (d, J = 8.7 Hz, 2H), 7.16 (dd, J = 2.1 Hz, J = 8.7 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 134.85, 127.00, 124.05, 123.70, 121.31, 118.48, 113.18, 108.83. FTIR (film, cm^{-1}): 3433, 2917, 1458, 1101, 796. HRMS: *m/z*: $[M + H]^+$ calculated for $C_{16}H_{11}Cl_2N_2$, 301.0294; Found 301.0293.

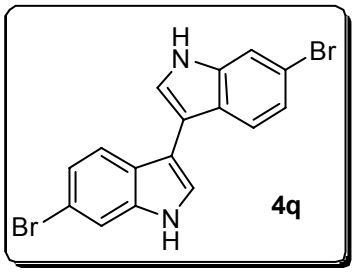


dimethyl 1H,1'H-3,3'-biindole-5,5'-dicarboxylate (4o): According to the standard condition, the reaction was stirred at 40 °C for 10 h, starting from 0.50 mmol of **1o**, 44 mg of **4o** was obtained in 50 % yield. ^{1}H NMR (300 MHz, DMSO-d_6): 11.68 (br s, 2H), 8.38 (s, 2H), 7.82-7.76 (m, 4H), 7.56 (d, J = 8.7 Hz, 2H), 3.83 (s, 6H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 167.31, 138.99, 125.91, 124.29, 122.44, 121.87, 120.58, 111.76, 110.25, 51.71. FTIR (film, cm^{-1}): 3294, 1690, 1289, 1253, 772. HRMS: *m/z*: $[M + Na]^+$ calculated for $C_{20}H_{16}N_2NaO_4$, 371.1002; Found 371.0998.

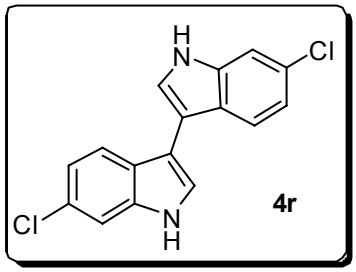


1H,1'H-3,3'-biindole-5,5'-dicarbaldehyde (4p): According to the standard condition for 24 h, starting from 0.50 mmol of **1p**, 63 mg of **4p** was obtained in 87 % yield. ^{1}H NMR (300

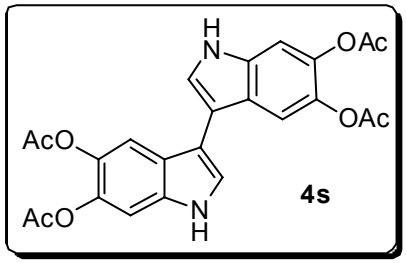
MHz, DMSO-d_6): 11.88 (br s, 2H), 10.05 (s, 2H), 8.47 (s, 2H), 7.99 (d, J = 2.1 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 192.70, 139.76, 129.11, 125.76, 125.76, 124.41, 120.93, 112.46, 110.89. FTIR (film, cm^{-1}):3245, 2916, 2359, 1672, 1472, 810. HRMS: *m/z*: [M + Na]$^+$ calculated for $C_{18}H_{12}N_2NaO_2$, 311.0791; Found 311.0791.



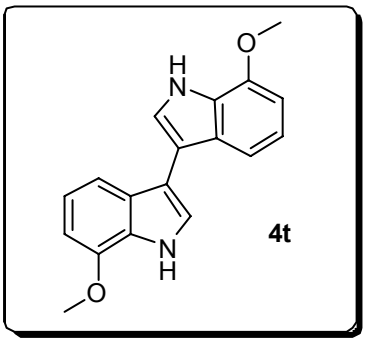
6,6'-dibromo-1H,1'H-3,3'-biindole (4q): According to the standard condition for 16 h, starting from 0.50 mmol of **1q**, 68 mg of **4q** was obtained in 69 % yield. ^{1}H NMR (300 MHz, DMSO-d_6): 11.39 (br s, 2H), 7.70-7.63 (m, 6H), 7.18 (dd, J = 1.8 Hz, J = 8.7 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 137.24, 124.94, 123.09, 121.78, 121.29, 114.14, 114.05, 109.40. FTIR (film, cm^{-1}):3394, 2919, 1609, 1452, 1101. HRMS: *m/z*: [M + H]$^+$ calculated for $C_{16}H_{11}Br_2N_2$, 388.9284; Found 388.9285.



6,6'-dichloro-1H,1'H-3,3'-biindole (4r): According to the standard condition, starting from 0.50 mmol of **1r**, 59 mg of **4r** was obtained in 78 % yield. ^{1}H NMR (300 MHz, DMSO-d_6): 11.39 (br s, 2H), 7.78-7.72 (m, 4H), 7.50 (d, J = 2.1 Hz, 2H), 7.08 (dd, J = 1.8 Hz, J = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 136.76, 126.04, 124.72, 123.16, 120.89, 119.25, 111.20, 109.42. FTIR (film, cm^{-1}): 3228, 2359. 1454, 1330, 1003, 777, 761. HRMS: *m/z*: [M + H]$^+$ calculated for $C_{16}H_{11}Cl_2N_2$, 301.0294; Found 301.0291.

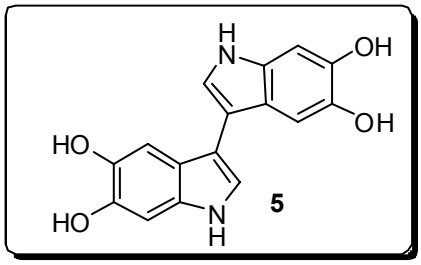


1H,1'H-3,3'-biindole-5,5',6,6'-tetrayl tetraacetate (4s): According to the standard condition for 40 h, starting from 1.50 mmol of **1s**, 279 mg of **4s** was obtained in 80 % yield. ^{1}H NMR (300 MHz, DMSO-d_6): 11.39 (br s, 2H), 7.73 (d, J = 2.4 Hz, 2H), 7.56 (s, 2H), 7.29 (s, 2H), 2.29 (s, 6H), 2.27 (s, 6H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 169.06, 168.88, 137.62, 135.91, 133.42, 123.61, 123.26, 112.82, 109.38, 105.78, 20.50, 20.45. FTIR (film, cm^{-1}): 3423, 1762, 1218, 902. HRMS: *m/z*: [M + Na]$^+$ calculated for $C_{24}H_{20}N_2NaO_8$, 487.1112; Found 487.1113.



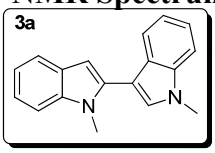
7,7'-dimethoxy-1H,1'H-3,3'-biindole (4t): According to the standard condition, starting from 0.50 mmol of **1t**, 53 mg of **4t** was obtained in 72 % yield. ^{1}H NMR (300 MHz, DMSO-d_6): 11.27 (br s, 2H), 7.48 (d, J = 2.1 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 6.99 (t, J = 7.8 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H), 3.95 (s, 6H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 146.26, 127.57, 126.44, 121.38, 119.33, 112.42, 110.34, 101.74, 55.15. FTIR (film, cm^{-1}): 3222, 2359, 1575, 1254, 780, 732. HRMS: *m/z*: $[M + H]^+$ calculated for $C_{18}H_{17}N_2O_2$, 293.1284; found, 293.1284.

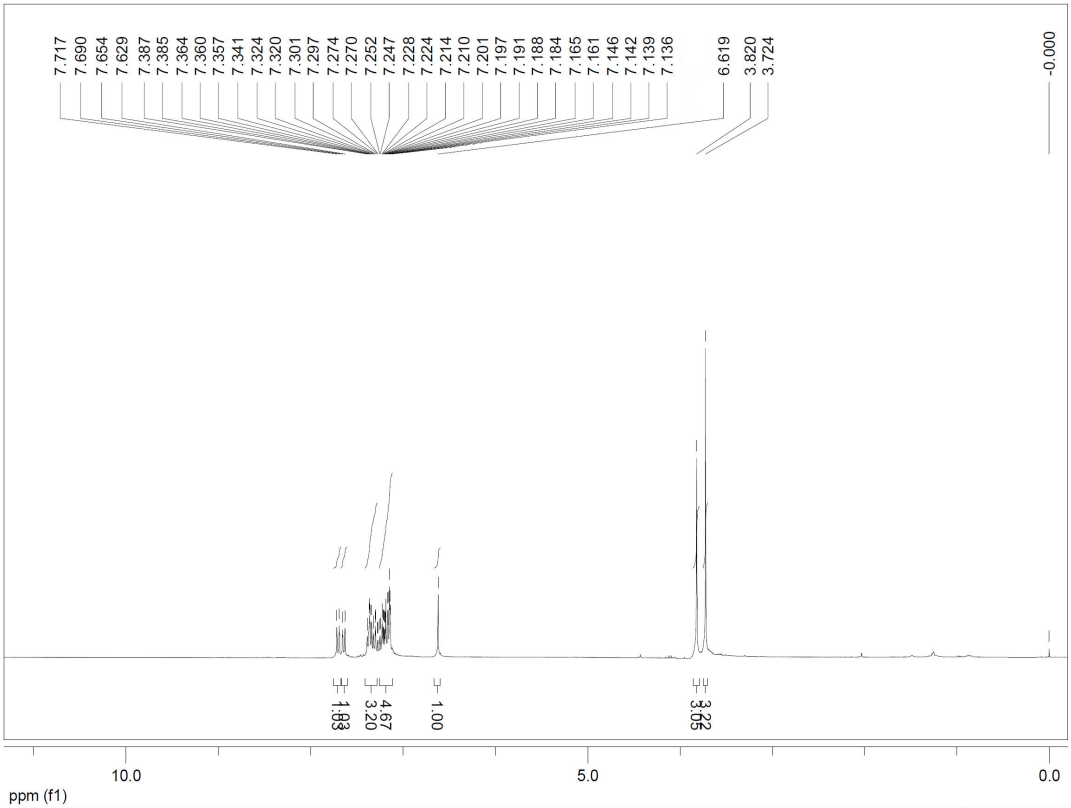
General procedures for syntheses of product 5

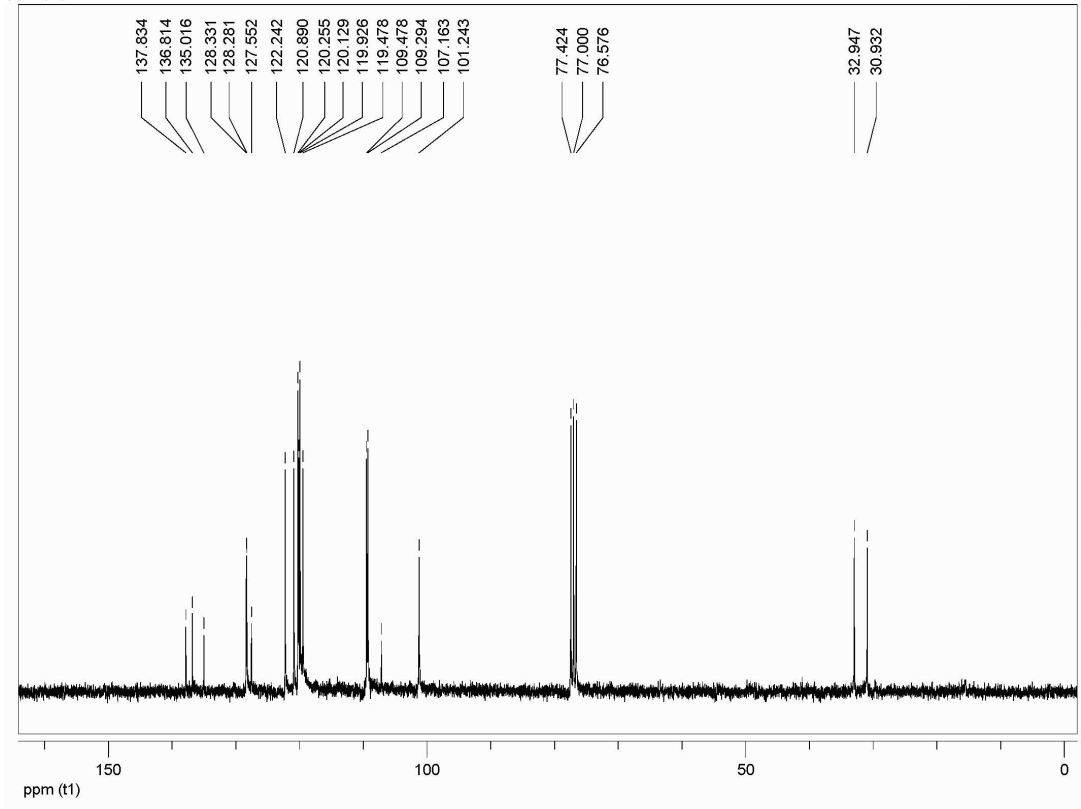


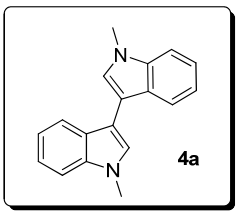
To the suspension of compound **4s** (50 mg, 0.11 mmol) in MeOH (5 mL) was added conc. HCl (0.10 mL, 1.2 mmol). The reaction mixture was stirred at 60 °C for 10 h under Ar atmospher. After cooling to rt, the solvent was removed in vacuo. Then anhydrous toluene (10 mL x 3) was added and evaportaed in vacuo to remove the remained water in reaction. After that, the compound was dried in vacuo to afford compound **5** in quantity yield. (Notice: compound **5** was very senstive to air and is easy to turn messy). ^{1}H NMR (300 MHz, DMSO-d_6): 10.42 (br s, 2H), 7.14 (d, J = 1.8 Hz, 2H), 7.02 (s, 2H), 6.76 (s, 2H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 142.68, 140.38, 130.77, 118.96, 118.76, 109.76, 104.49, 97.39. MS: *m/z*: $[M + H]^+$ 297.1.

NMR Spectrum of compound 3a and 4





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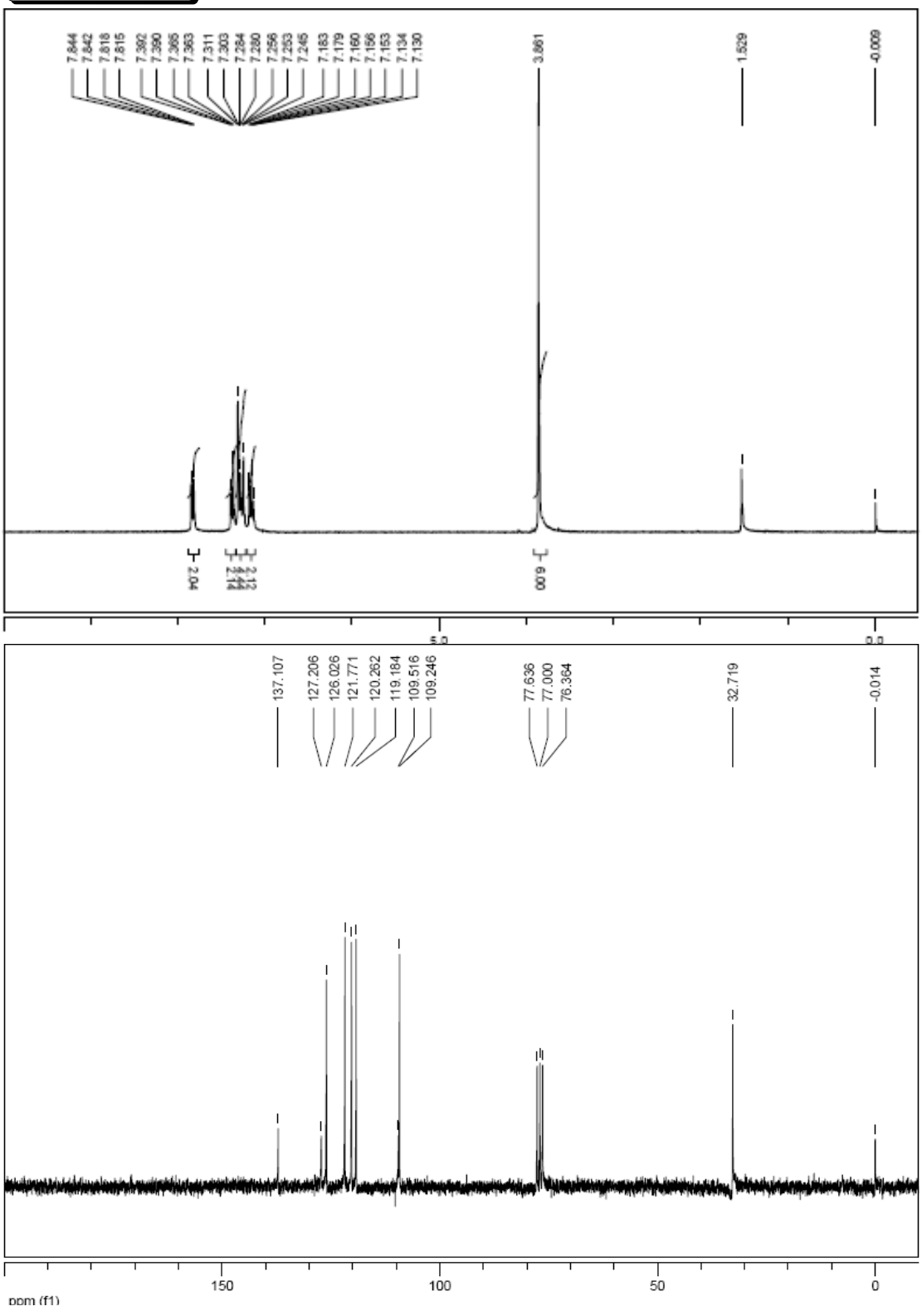
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7.253
7.245
7.183
7.179
7.160
7.156
7.153
7.134
7.130
3.861
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2.04
2.14
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6.00
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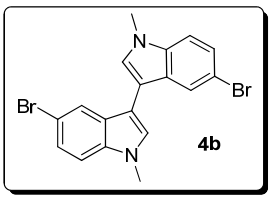
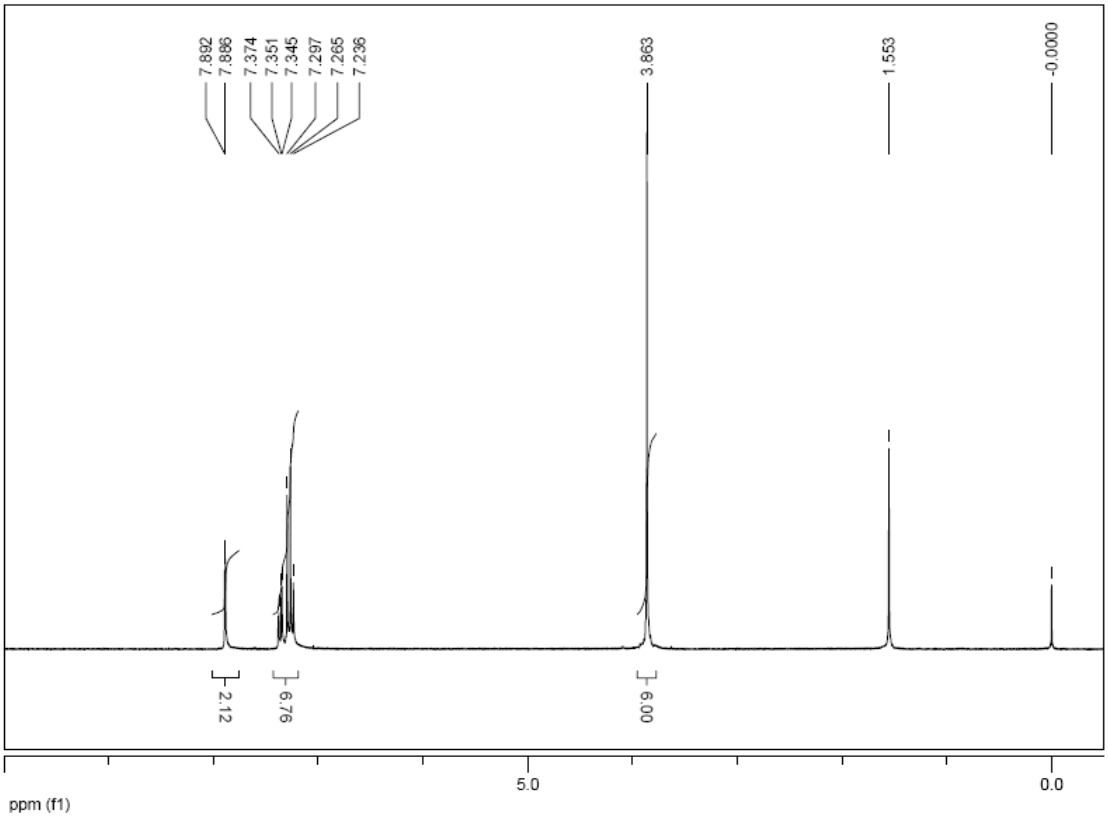

Br
Br
N
N
4b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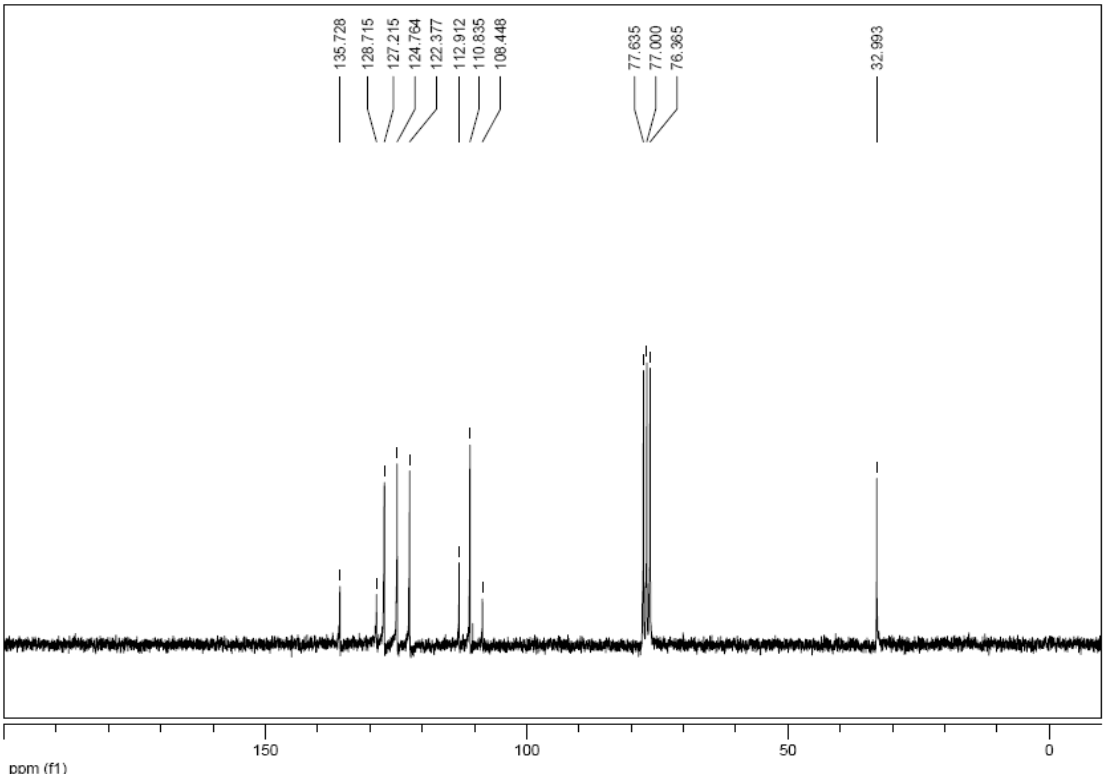
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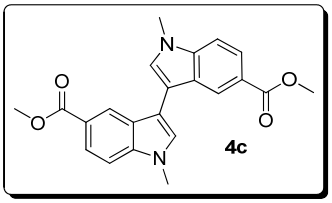
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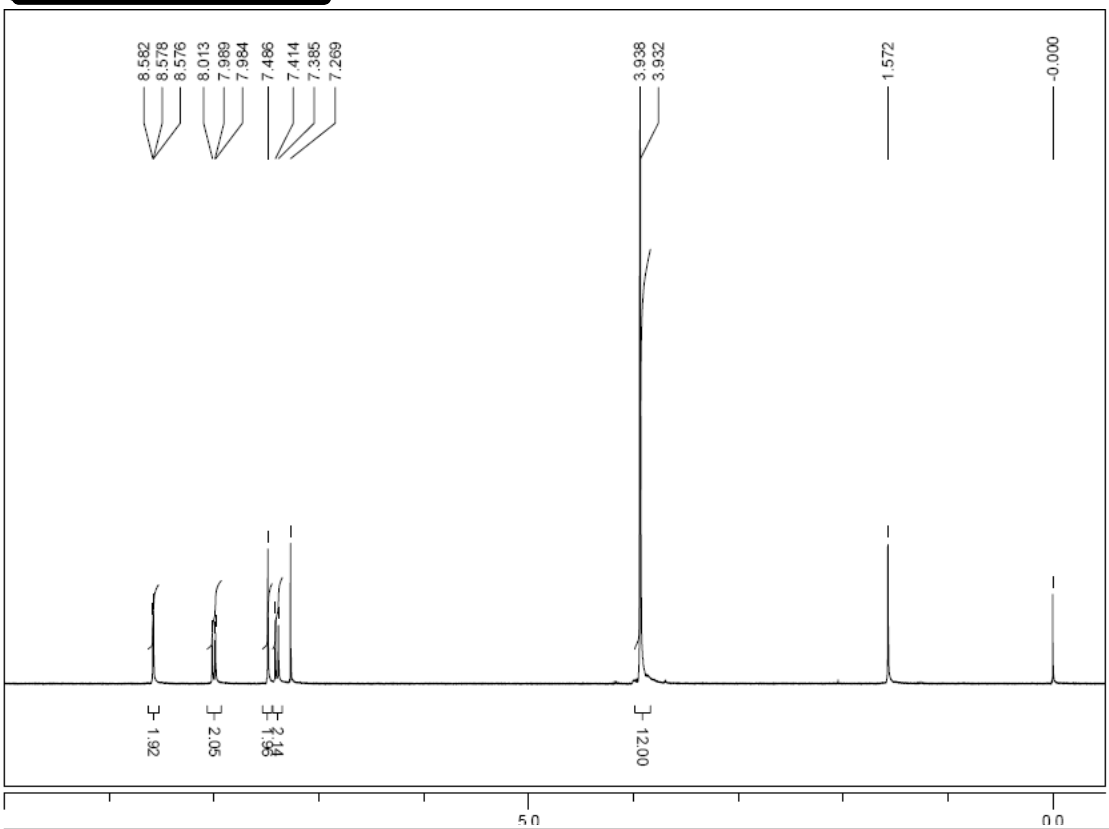
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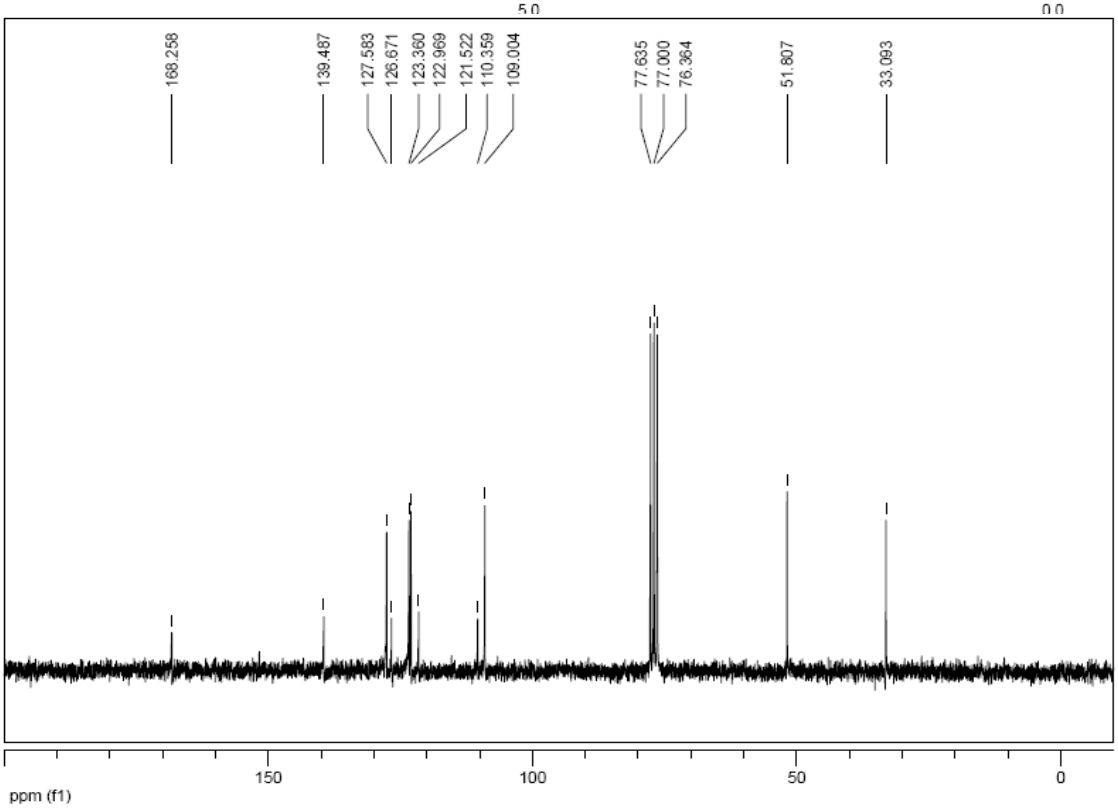
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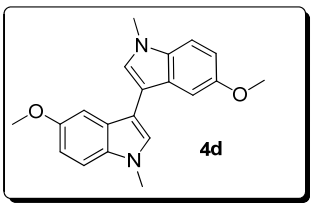
ppm (f1)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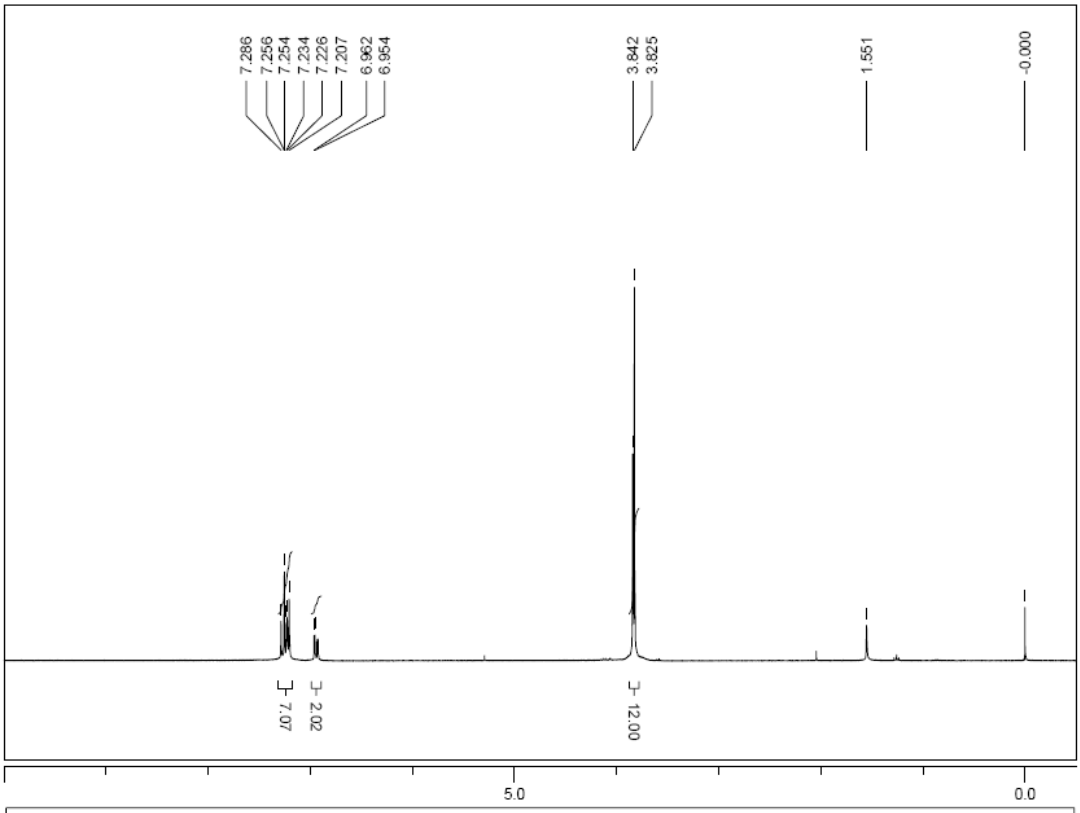
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12.00
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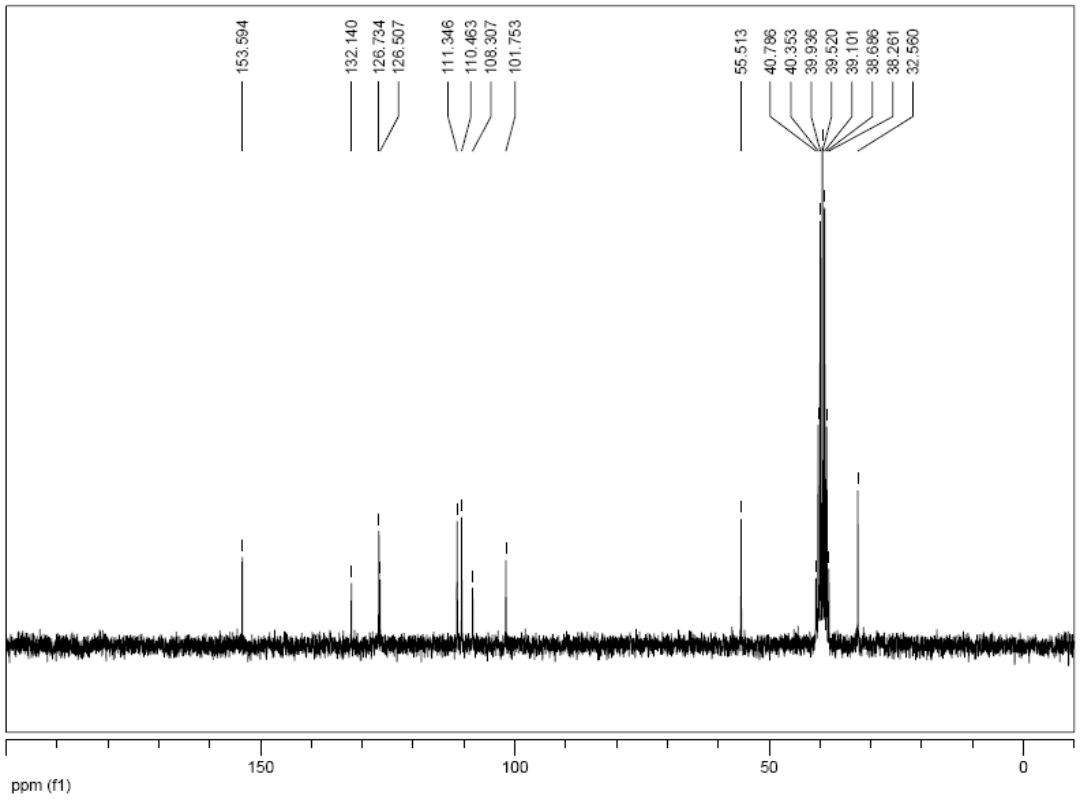
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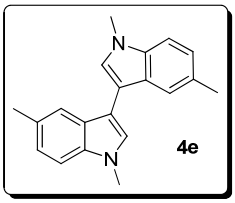
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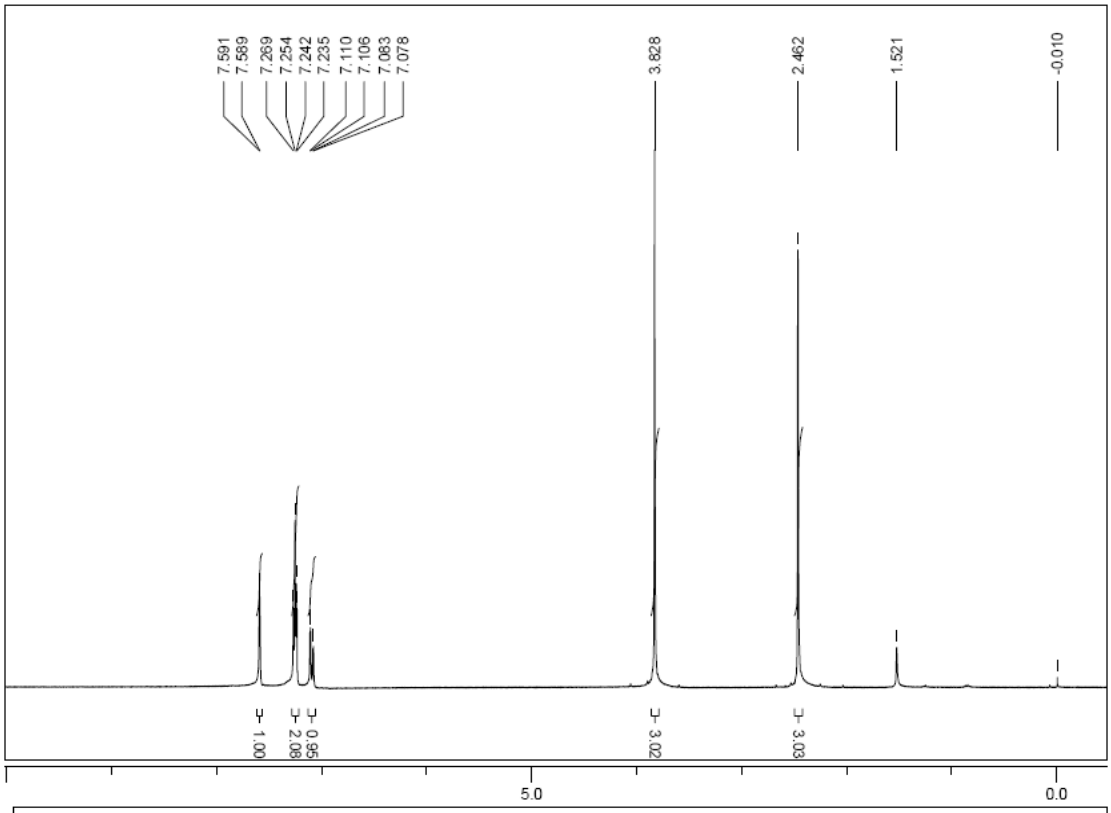
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3.03
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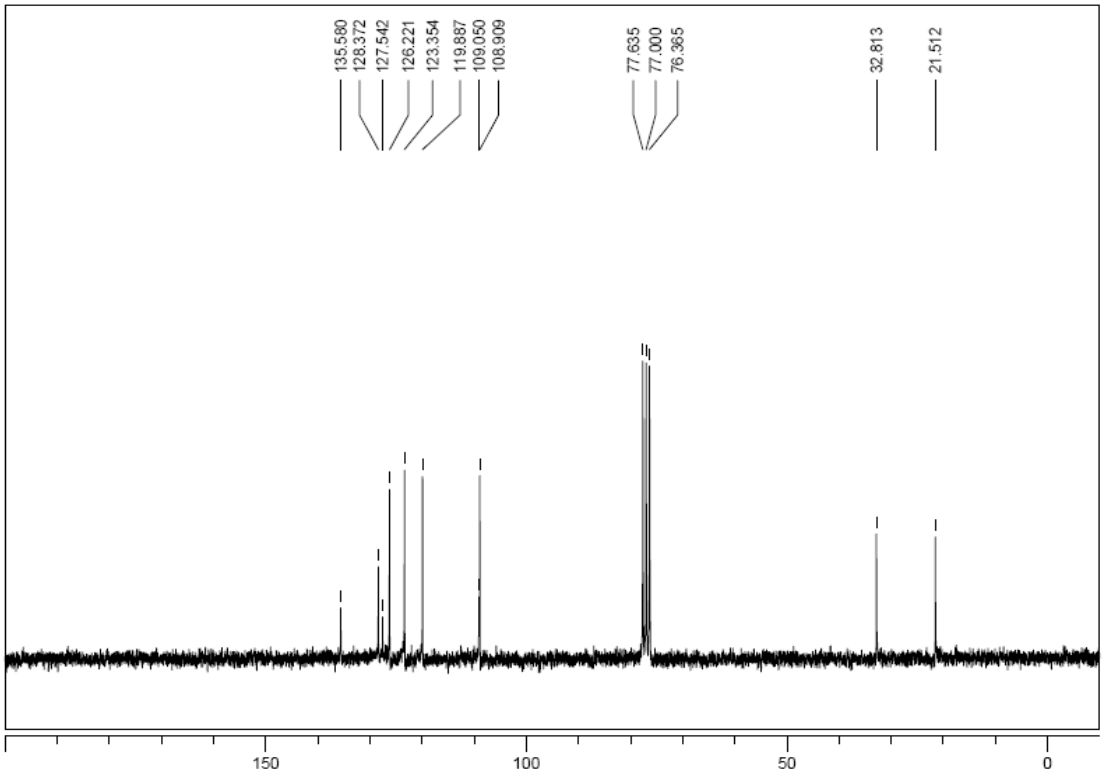
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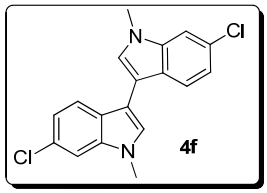
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Cl
Cl
N
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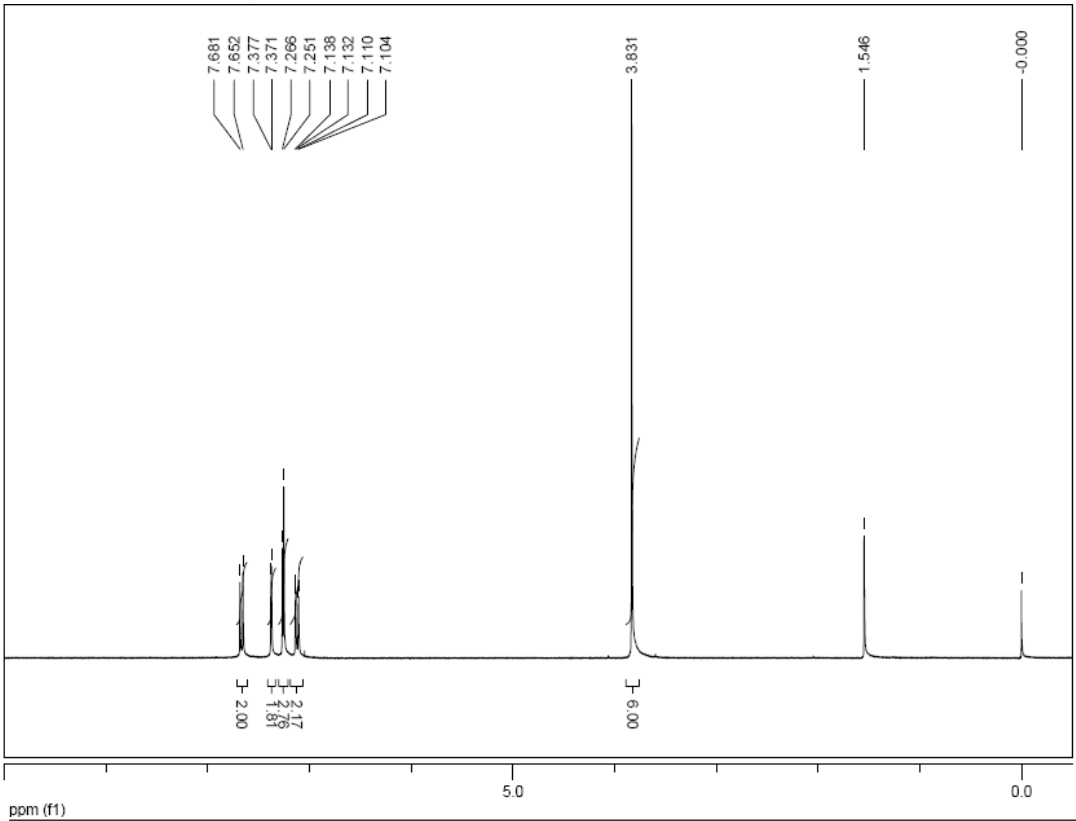
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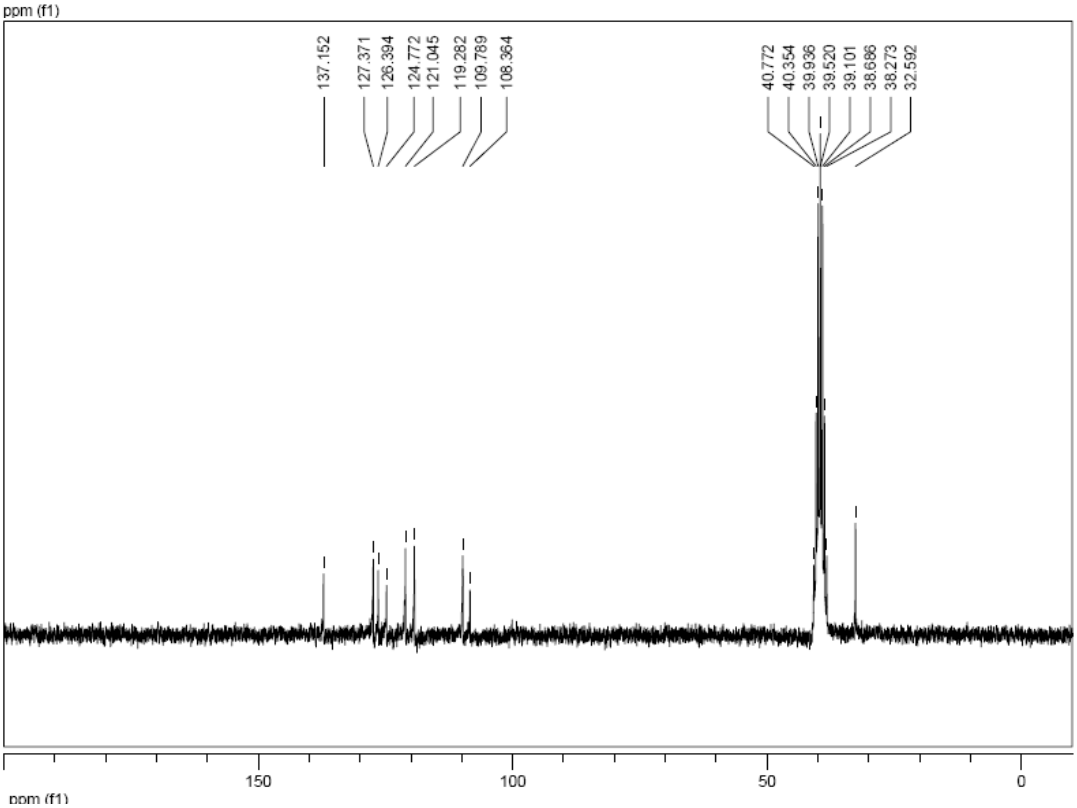
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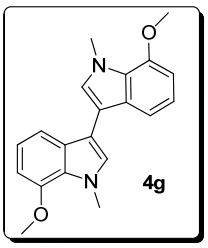
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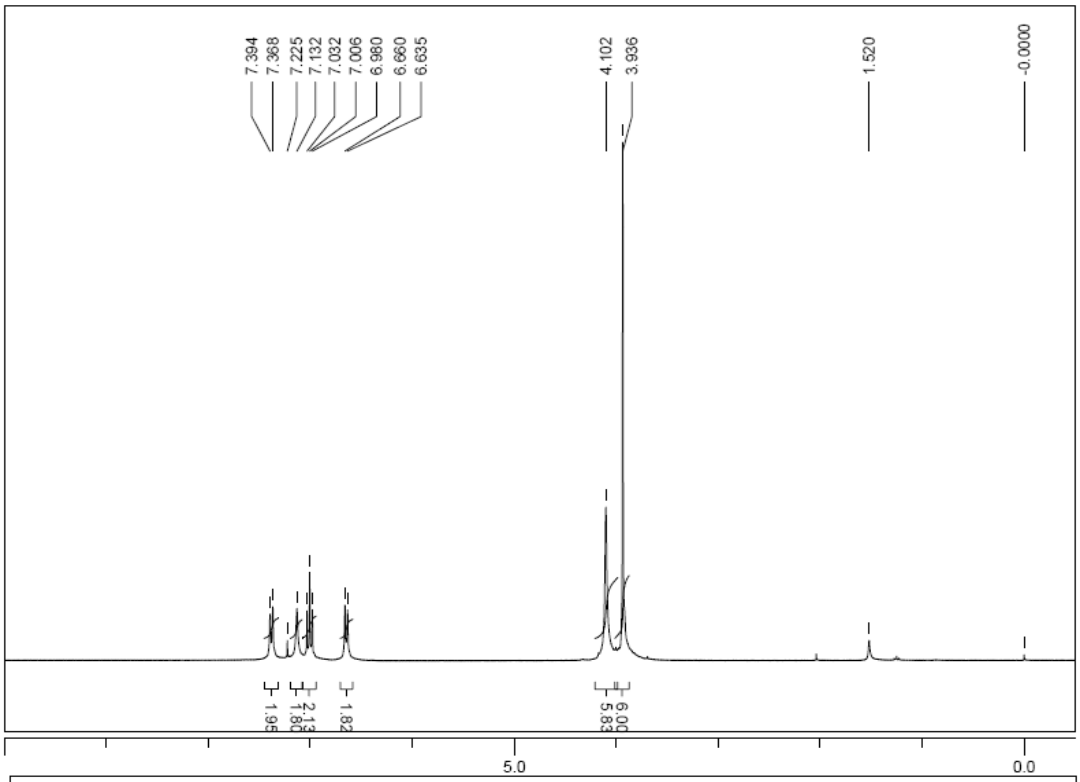
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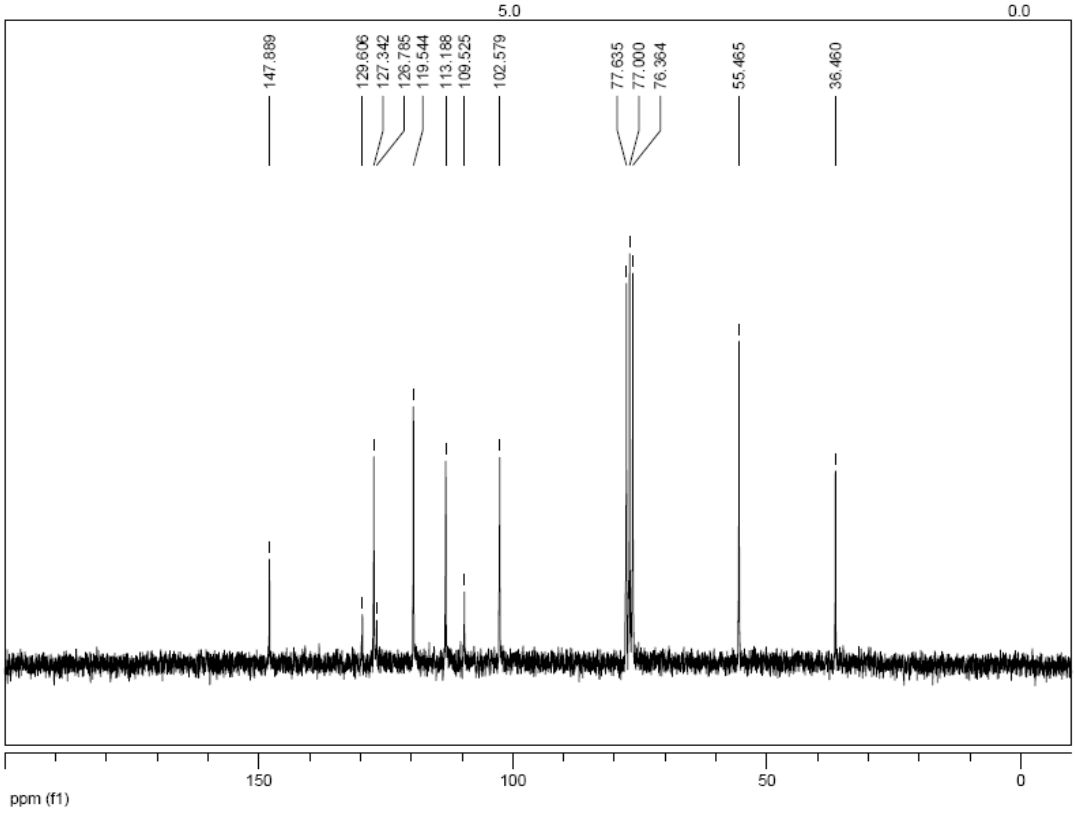
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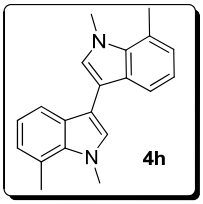
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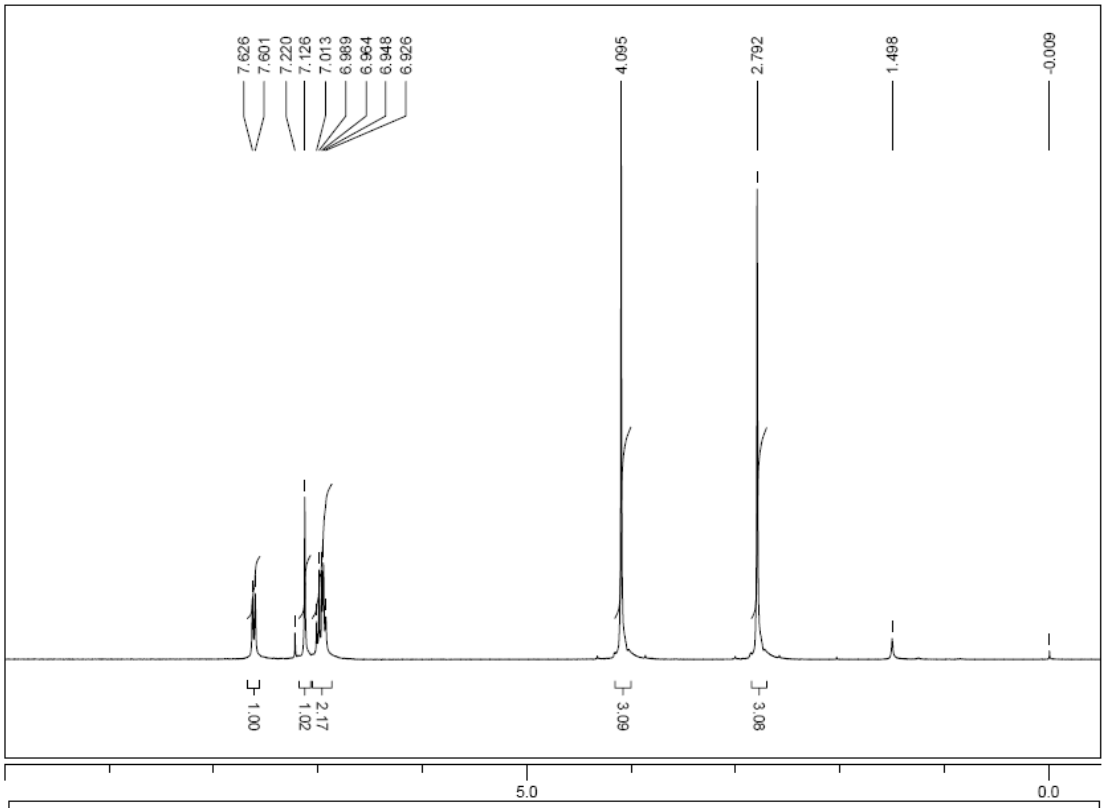
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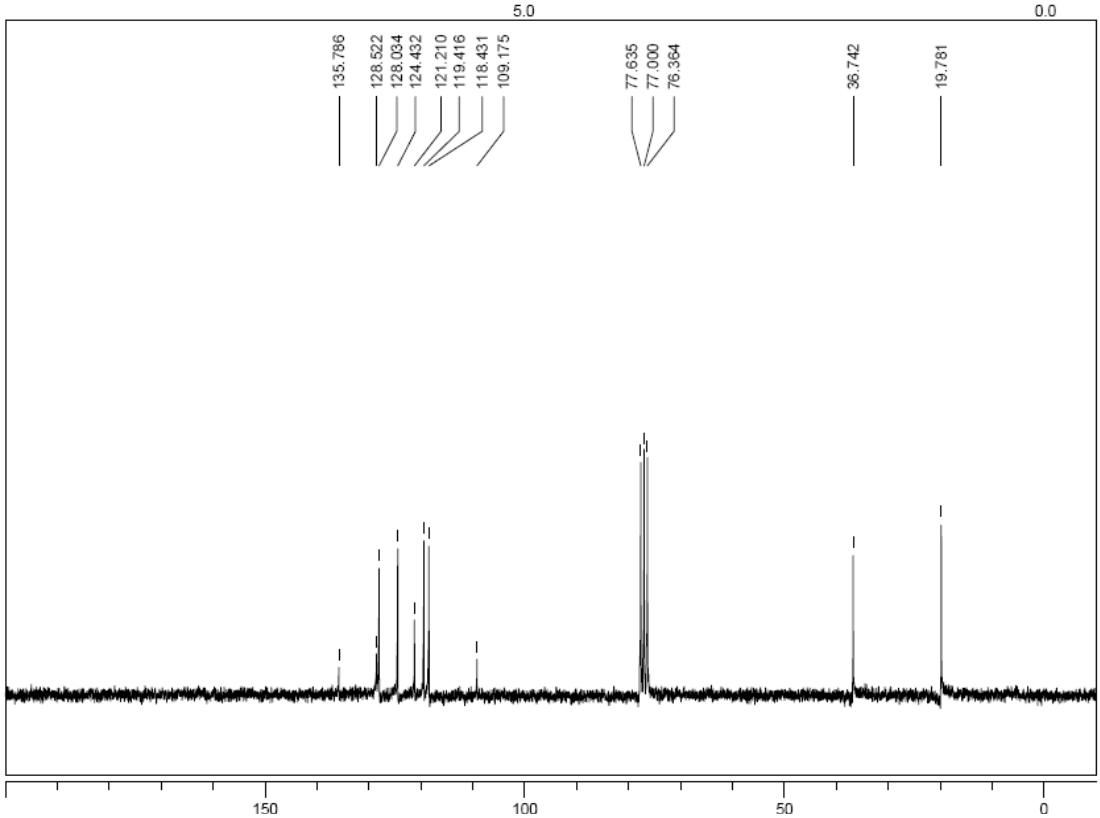
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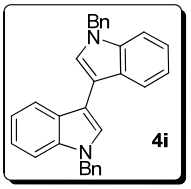
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N
Bn
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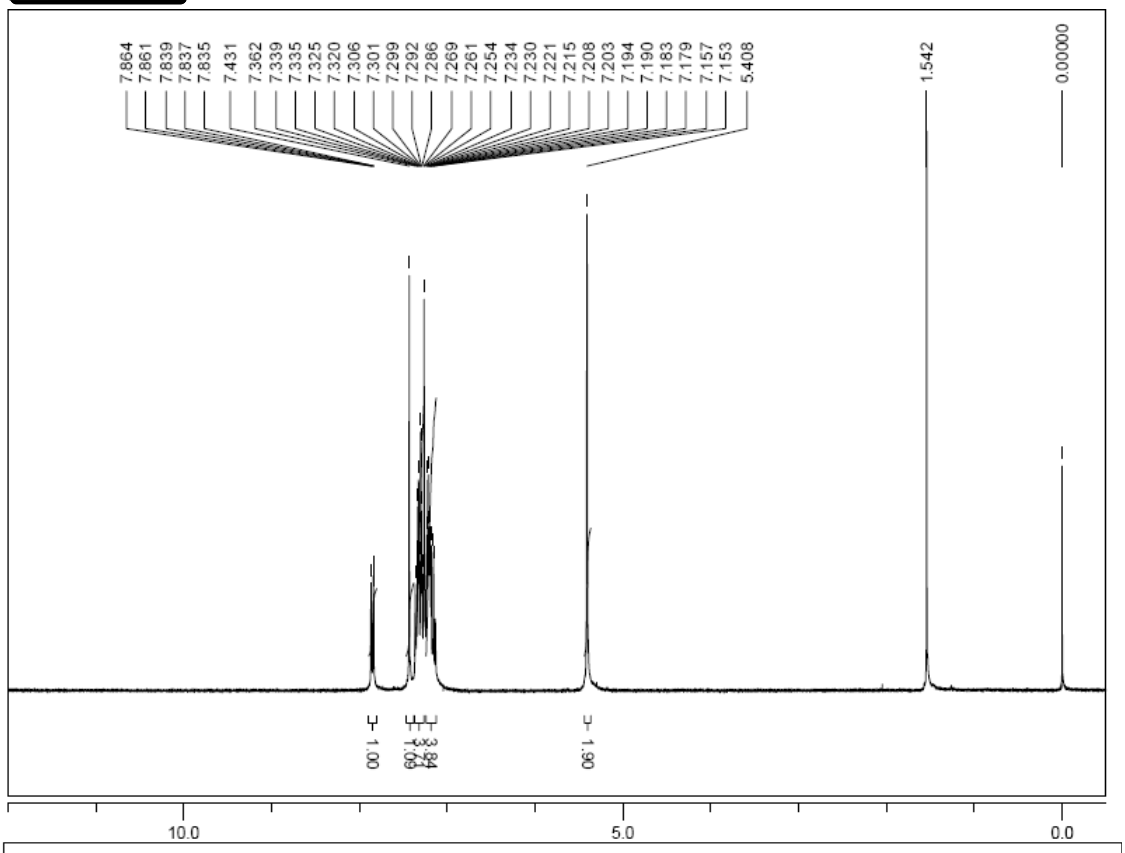
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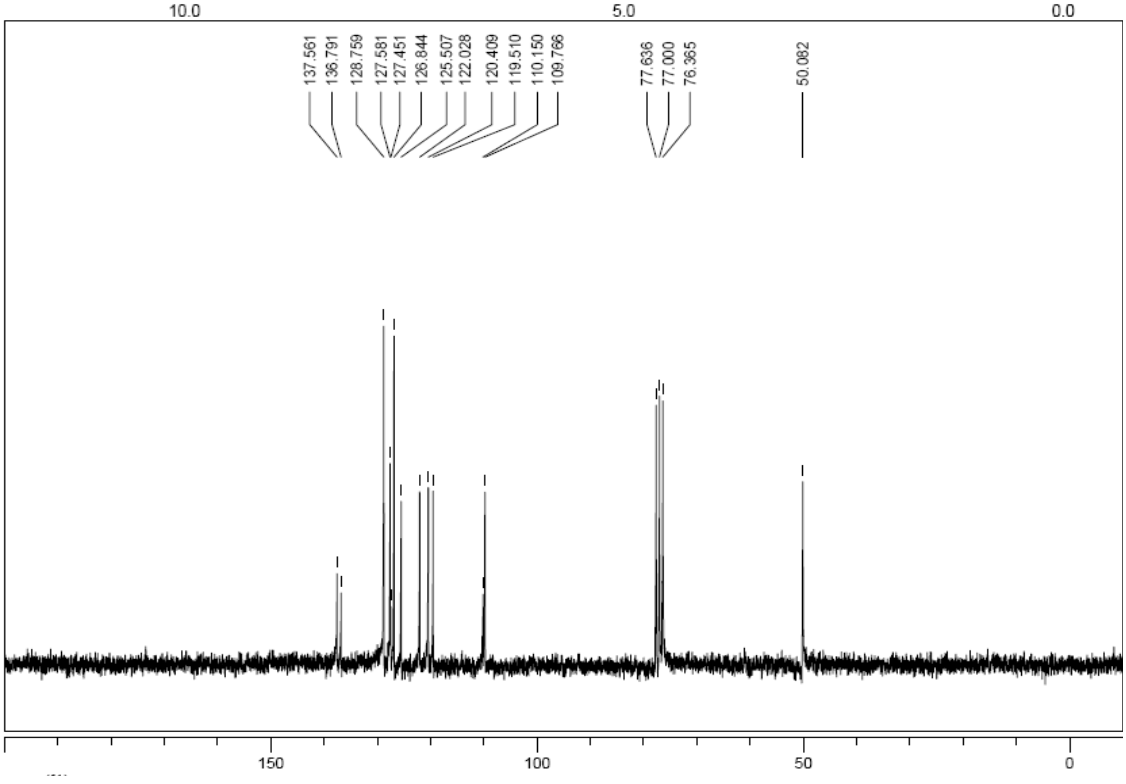
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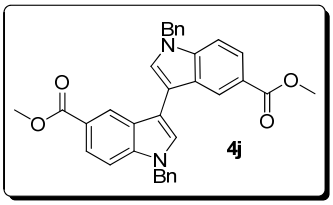
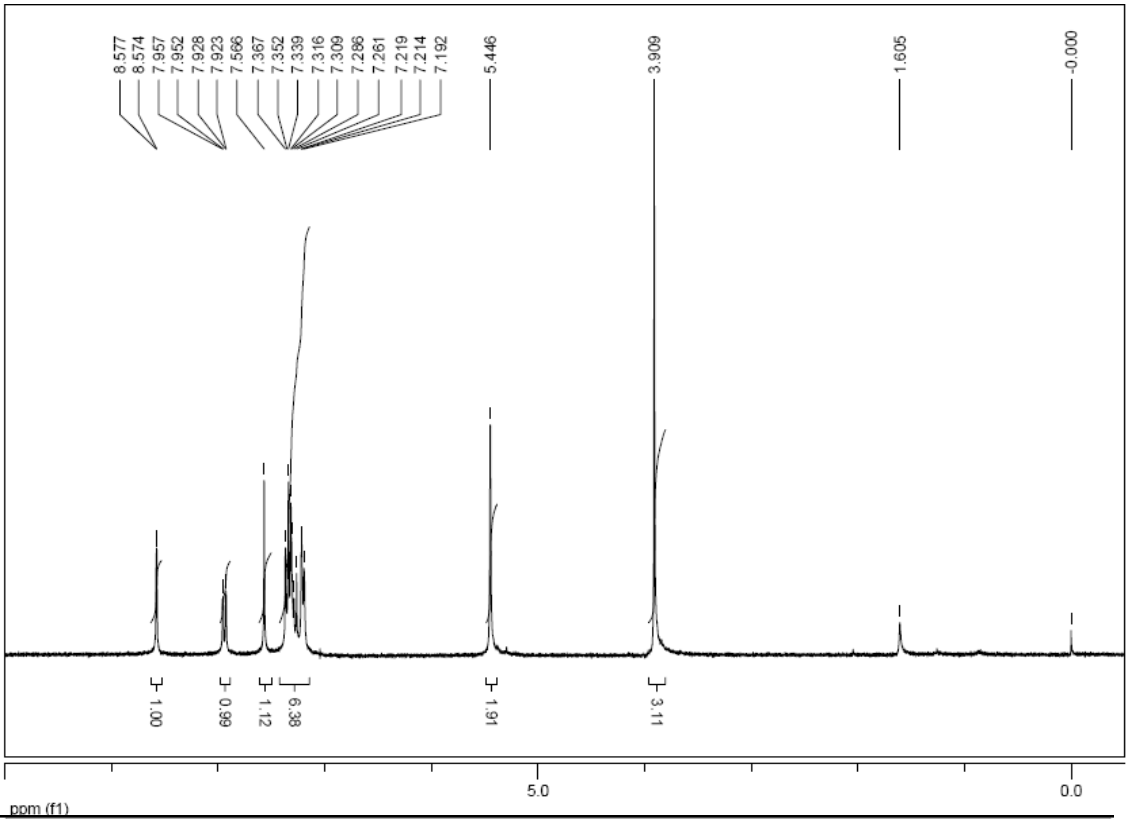

Bn
N
O
O
O
O
4j
N
Bn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8.574
7.957
7.952
7.928
7.923
7.566
7.367
7.352
7.339
7.316
7.309
7.286
7.261
7.219
7.214
7.192
5.446
3.909
1.605
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1.00
0.99
1.12
6.38
1.91
3.11
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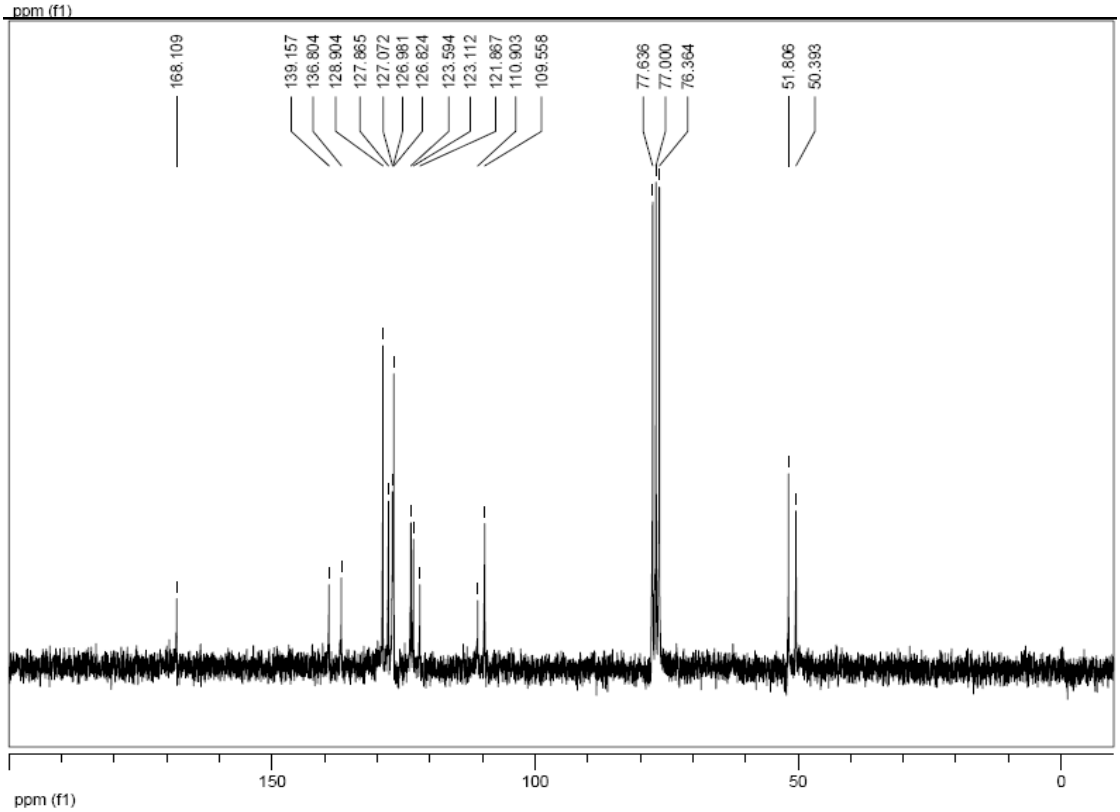
ppm (f1)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136.804
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127.072
126.981
126.824
123.594
123.112
121.867
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109.558
77.636
77.000
76.364
51.806
50.393
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50
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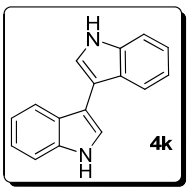
ppm (f1)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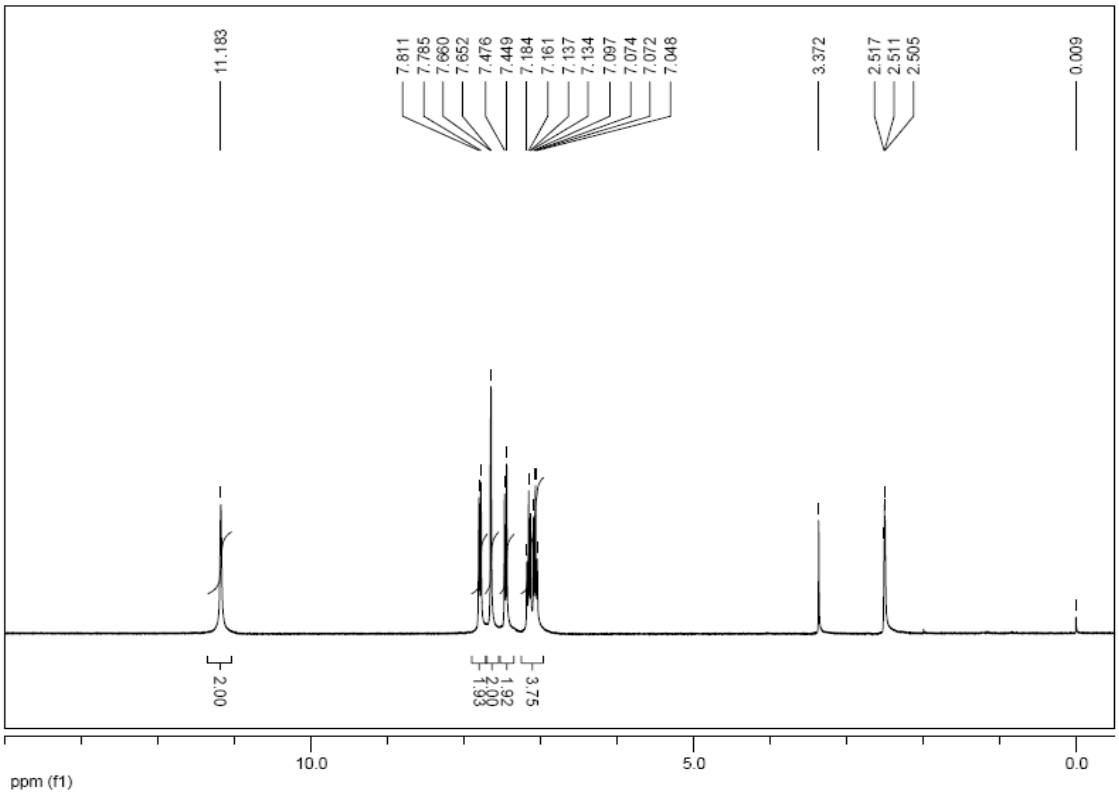
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7.476
7.449
7.184
7.161
7.137
7.134
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7.074
7.072
7.048
3.372
2.517
2.511
2.505
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2.00
1.92
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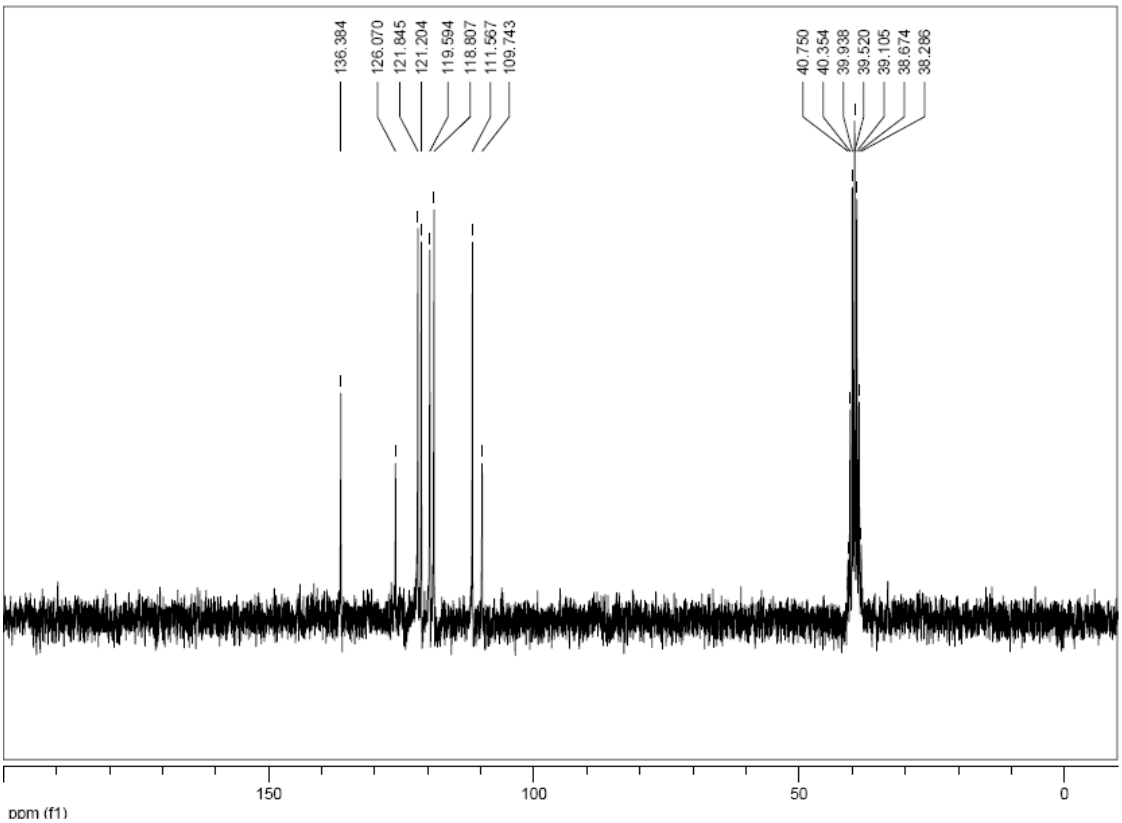
ppm (f1)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121.845
121.204
119.594
118.807
111.567
109.743
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40.354
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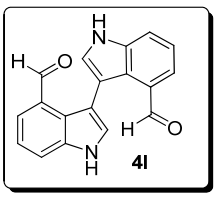
39.520
39.105
38.674
38.286
150
100
50
0
ppm (f1)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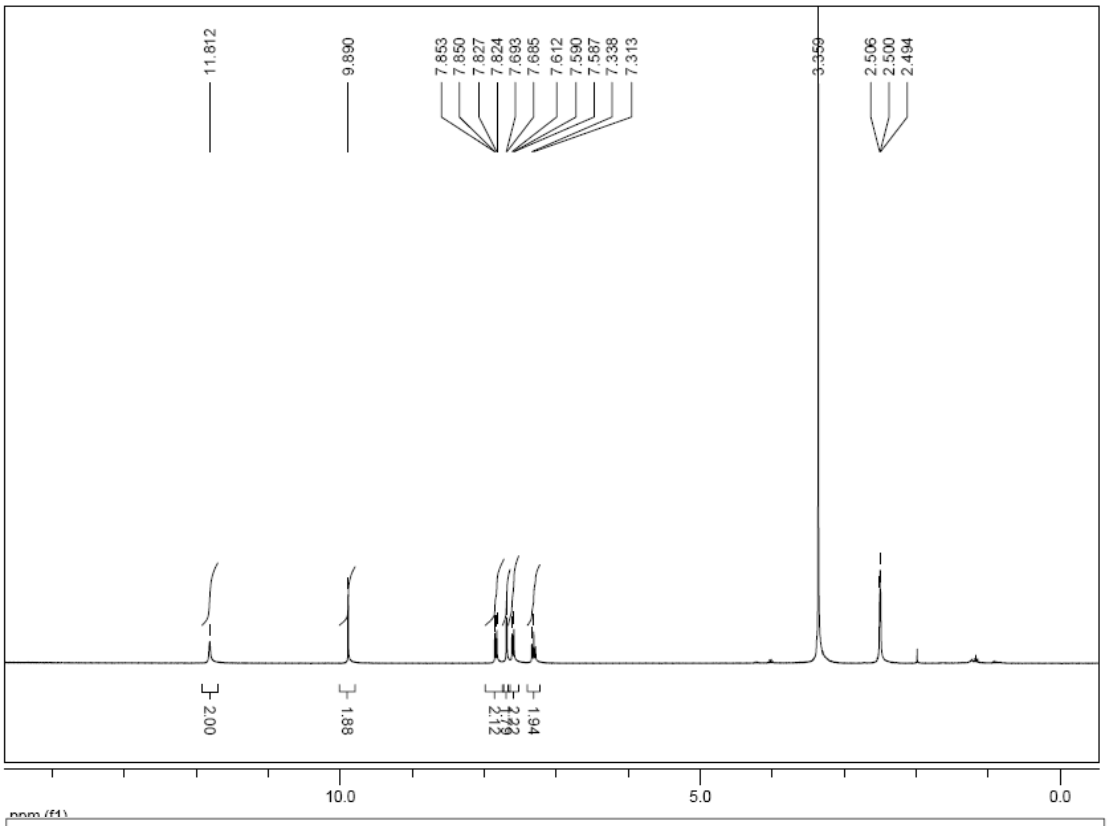
N
H
O
H
O
N
H

4l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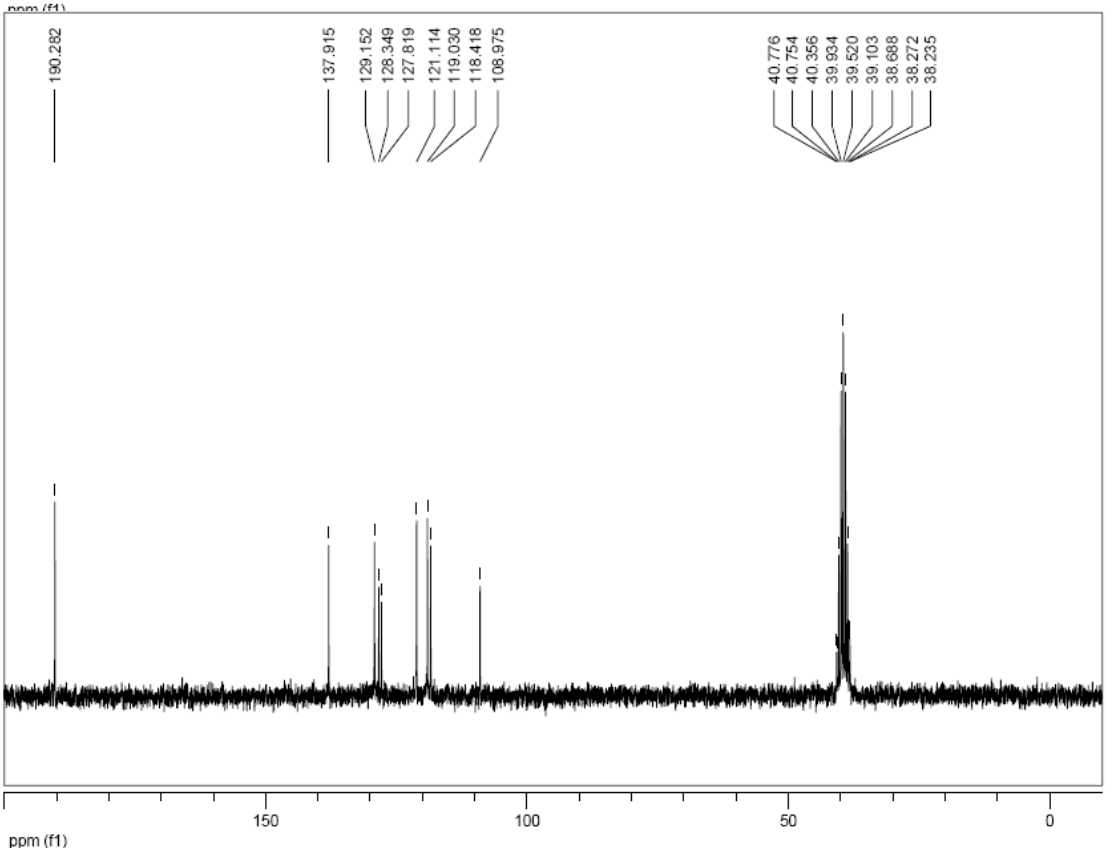
7.853
7.850
7.827
7.824
7.693
7.685
7.612
7.590
7.587
7.338
7.313
3.359
2.506
2.500
2.494
2.00
1.88
2.12
2.26
1.84
10.0
5.0
0.0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128.349
127.819
121.114
119.030
118.418
108.975
40.776
40.754
40.356
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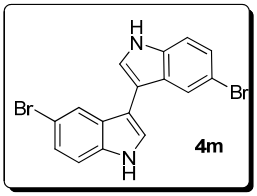
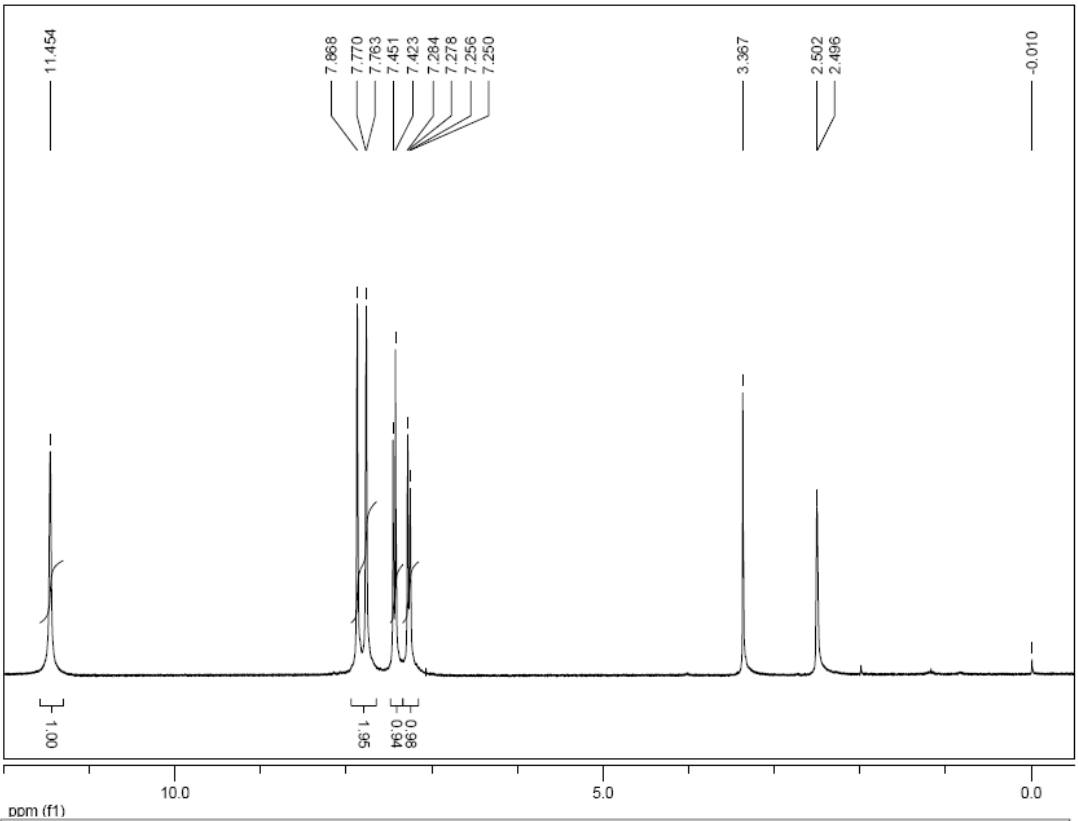
39.520
39.103
38.688
38.272
38.235
150
100
50
0
ppm (f1)


H
N
Br
Br
N
H
4m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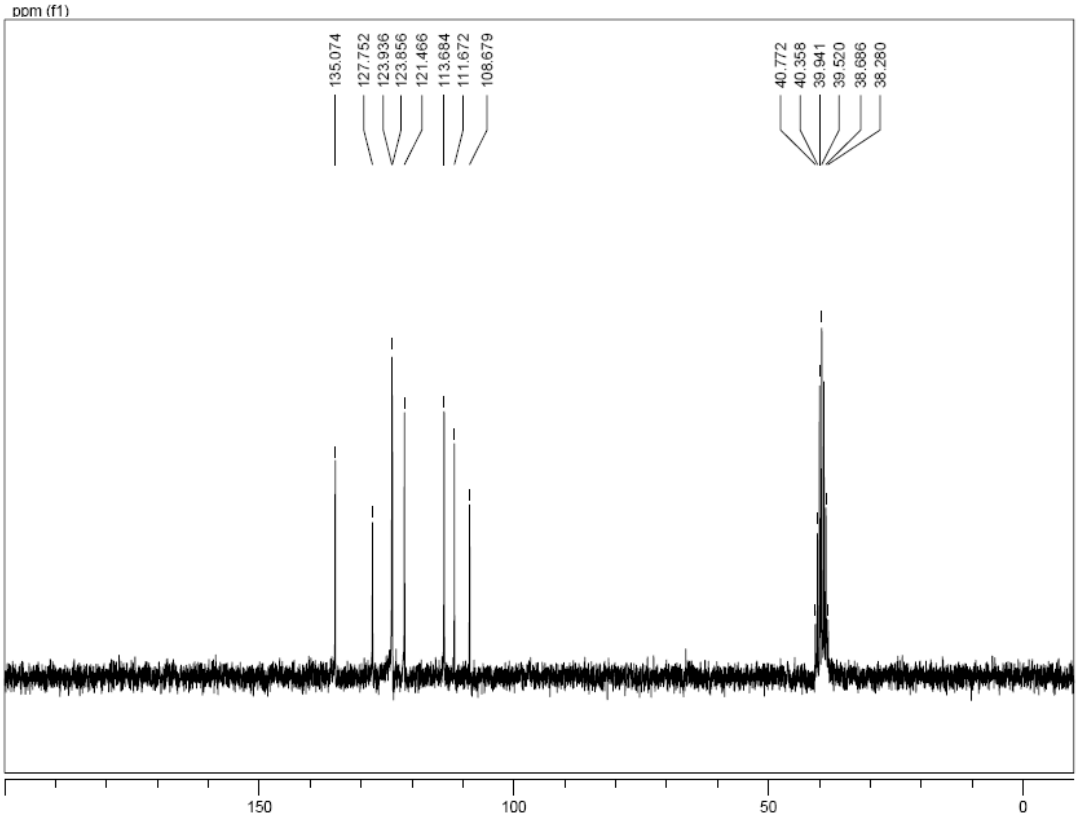
7.770
7.763
7.451
7.423
7.284
7.278
7.256
7.250
3.367
2.502
2.496
-0.010
1.00
1.96
0.94
0.98
10.0
5.0
0.0


ppm (f1)
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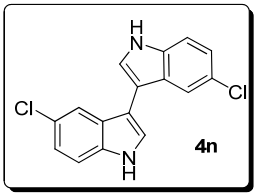
127.752
123.936
123.856
121.466
113.684
111.672
108.679
40.772
40.358
39.941
39.520
38.686
38.280
150
100
50
0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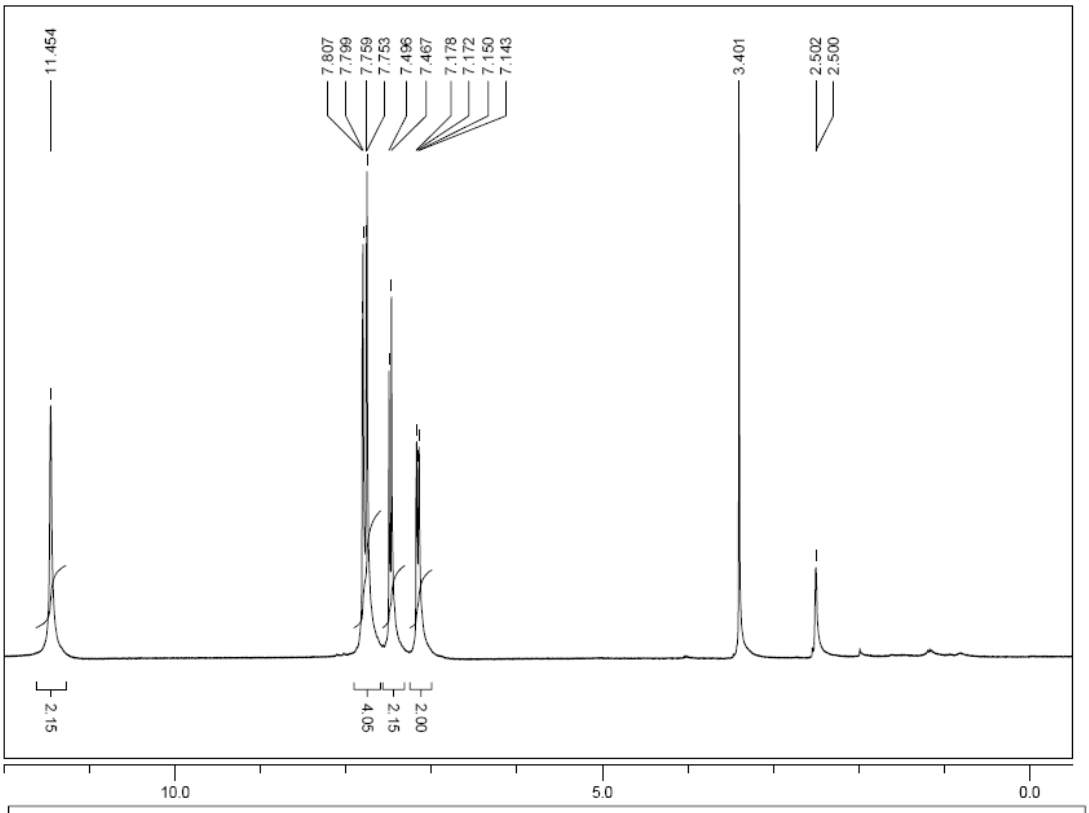
N
Cl
Cl
N
H
4n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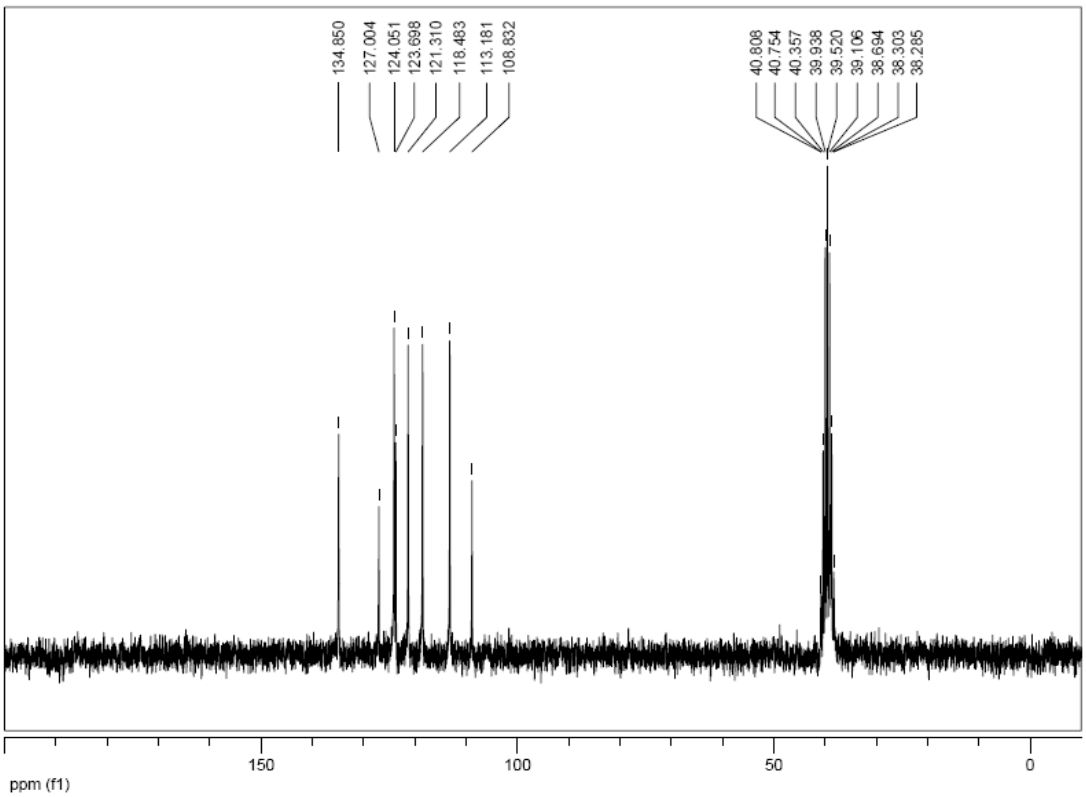
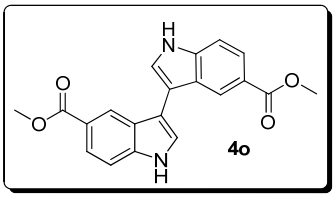
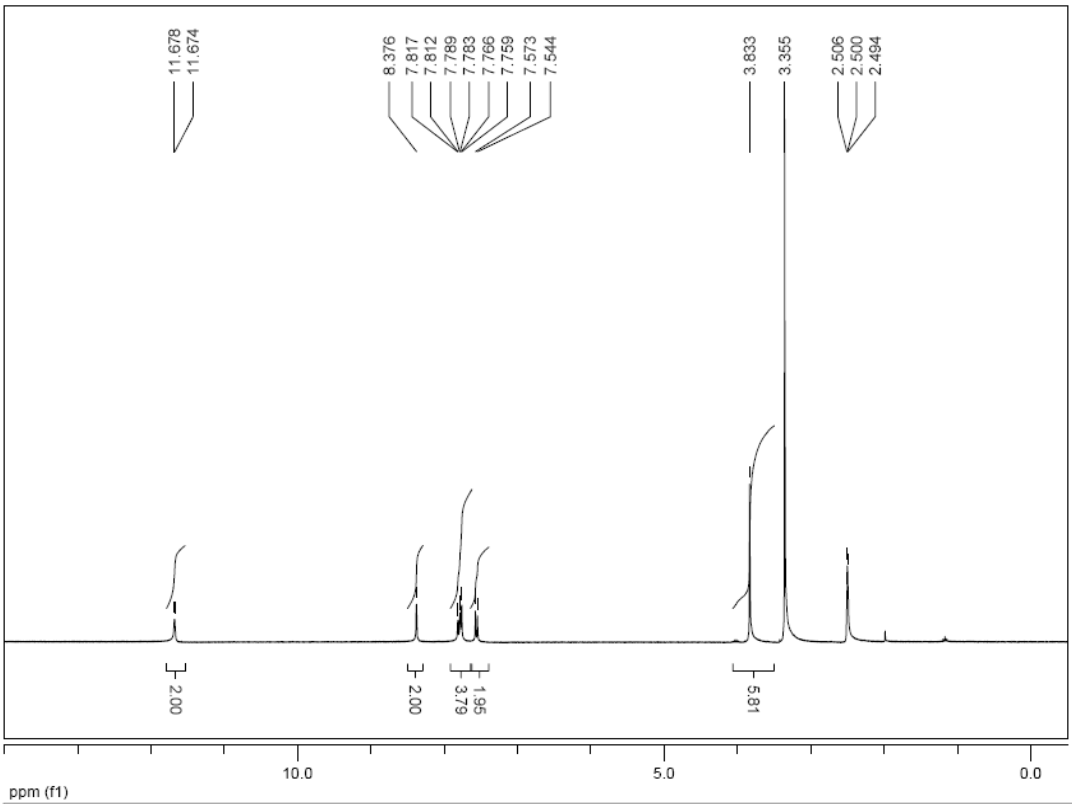
7.807
7.799
7.759
7.753
7.496
7.467
7.178
7.172
7.150
7.143
3.401
2.502
2.500
2.15
4.06
2.15
2.00
10.0
5.0
0.0


134.850
127.004
124.051
123.698
121.310
118.483
113.181
108.832
40.808
40.754
40.357
39.938
39.520
39.106
38.694
38.303
38.285
150
100
50
0
ppm (f1)


4o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11.674
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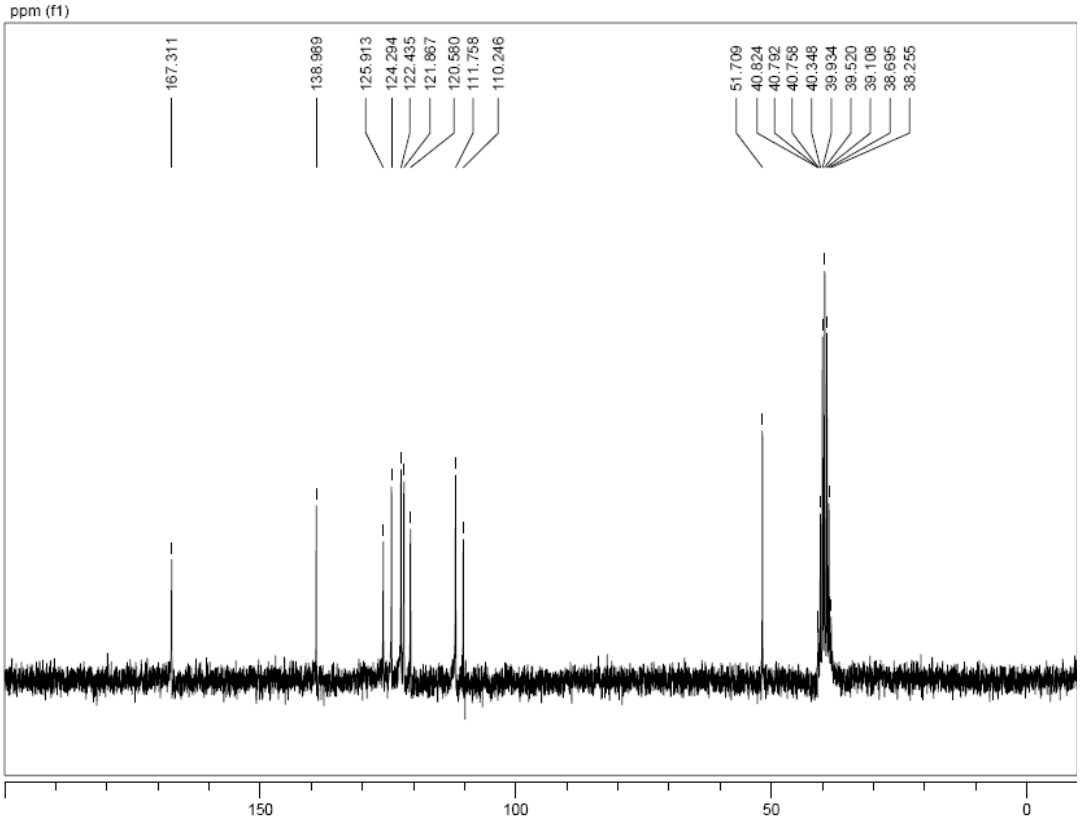
7.817
7.812
7.789
7.783
7.766
7.759
7.573
7.544
3.833
3.355
2.506
2.500
2.494
2.00
2.00
3.79
1.95
5.81
10.0
5.0
0.0


ppm (f1)
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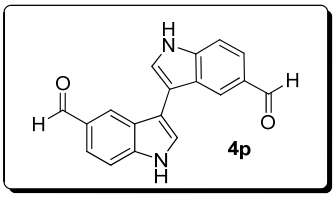
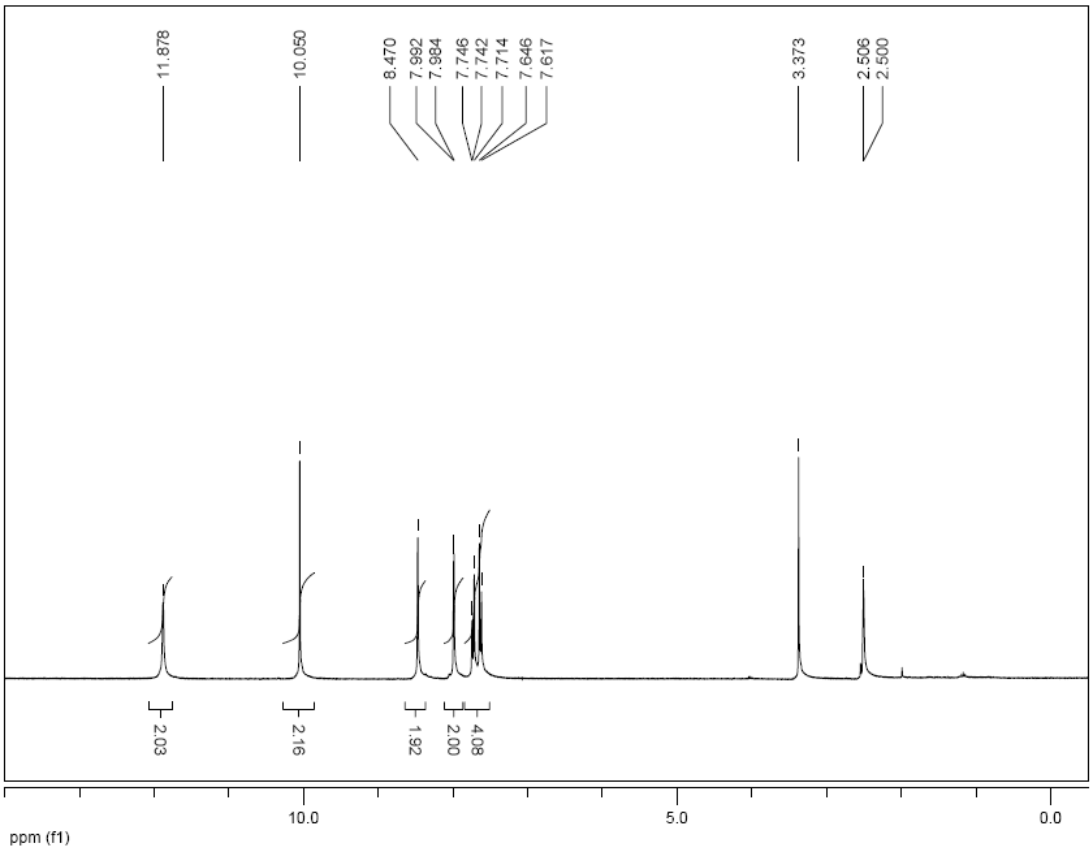
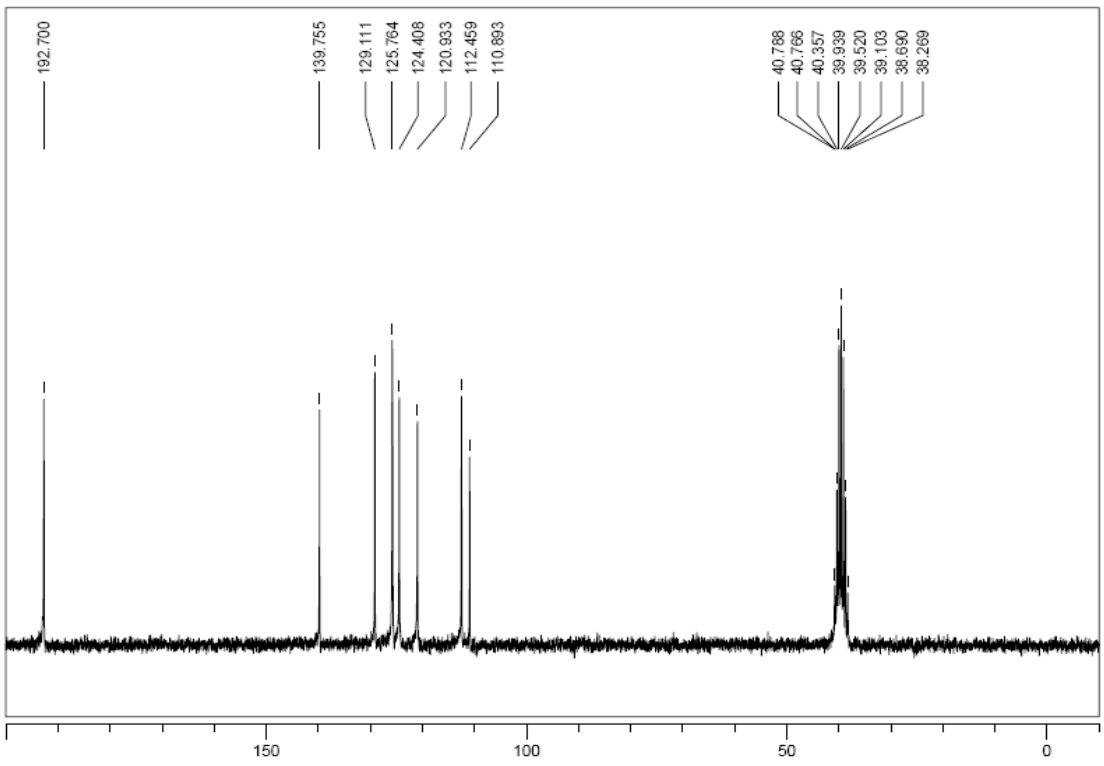
138.989
125.913
124.294
122.435
121.867
120.580
111.758
110.246
51.709
40.824
40.792
40.758
40.348
39.934
39.520
39.108
38.695
38.255
150
100
50
0


4p


11.878
10.050
8.470
7.992
7.984
7.746
7.742
7.714
7.646
7.617
3.373
2.506
2.500
2.03
2.19
1.92
2.00
4.08
10.0
5.0
0.0
ppm (f1)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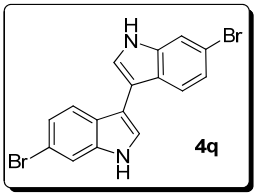
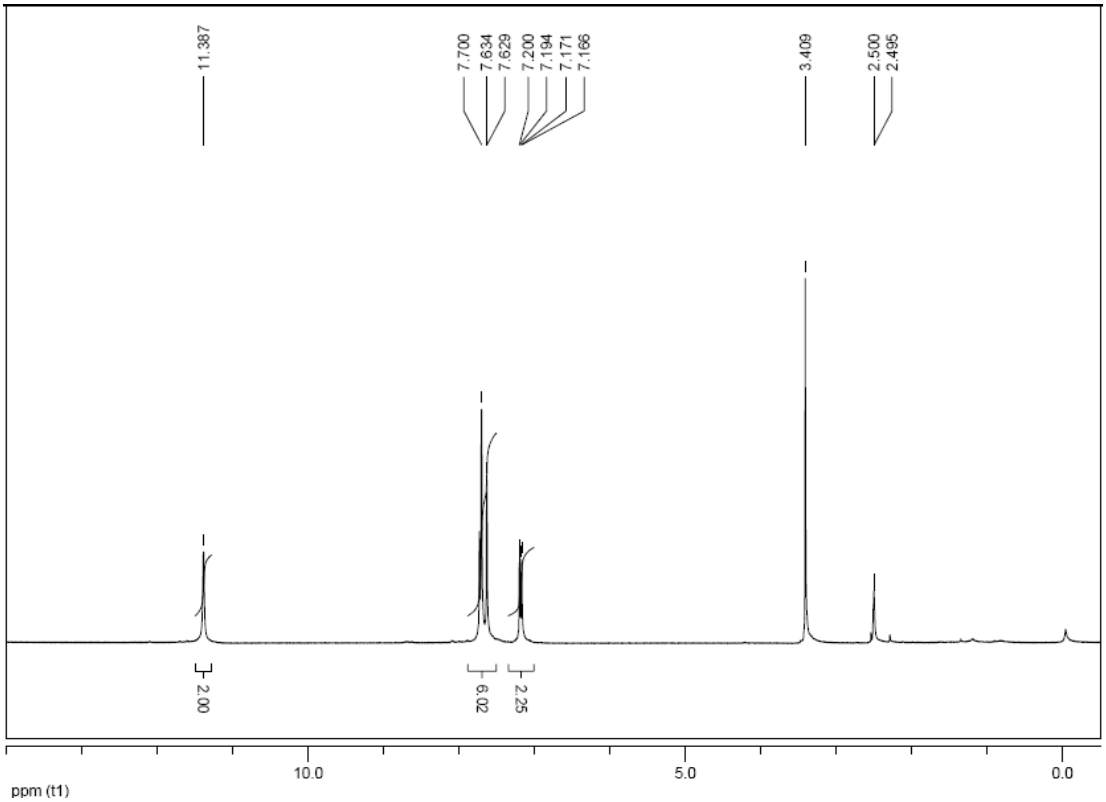
139.755
129.111
125.764
124.408
120.933
112.459
110.893
40.788
40.766
40.357
39.939
39.520
39.103
38.690
38.269
150
100
50
0


H
N
Br
Br
N
H
4q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7.634
7.629
7.200
7.194
7.171
7.166
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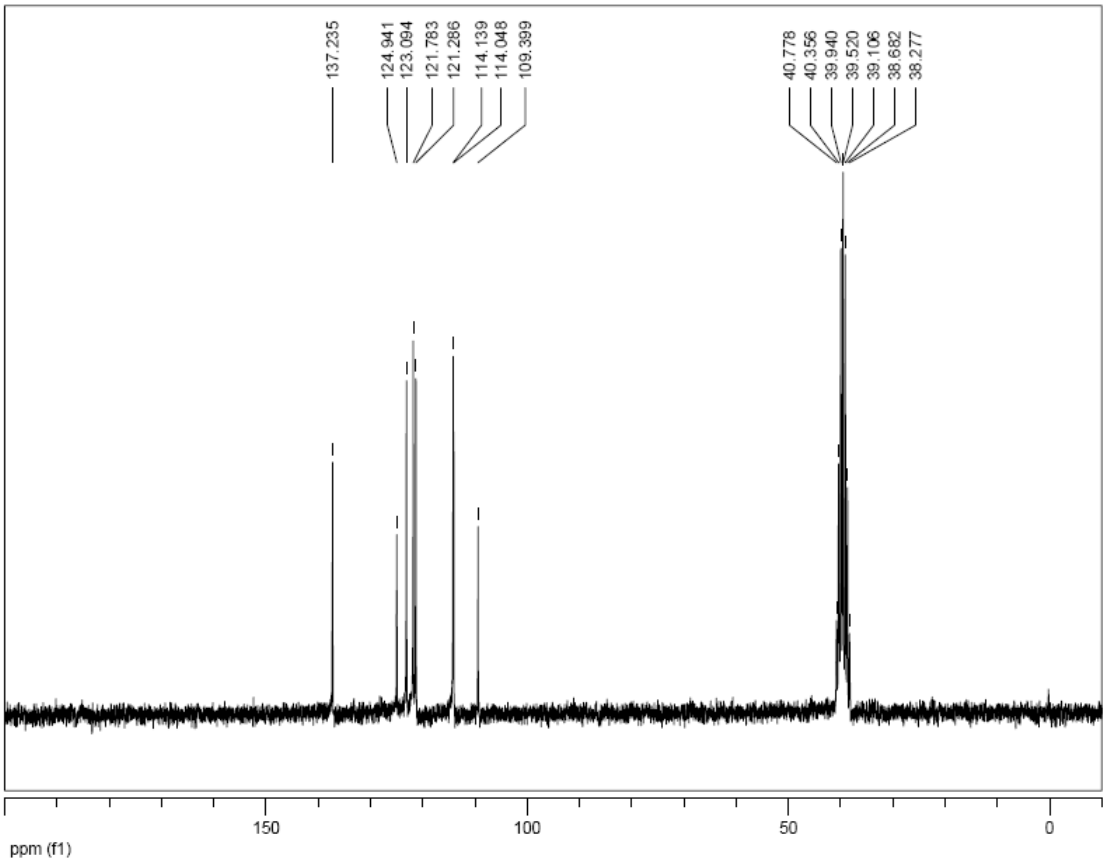
2.500
2.495
2.00
6.02
2.25
10.0
5.0
0.0
ppm (t1)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124.941
123.094
121.783
121.286
114.139
114.048
109.399
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40.356
39.940
39.520
39.106
38.682
38.277
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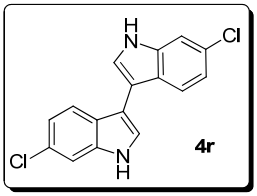
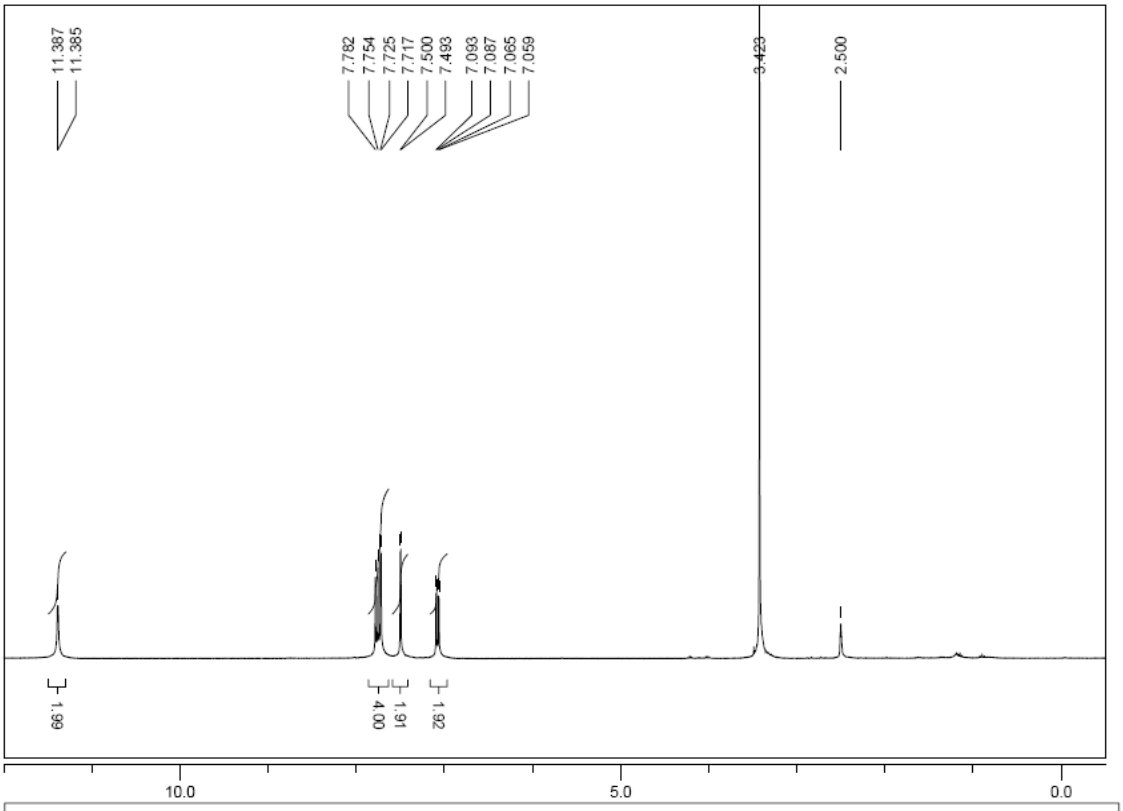
100
50
0
ppm (f1)


Cl
Cl
4r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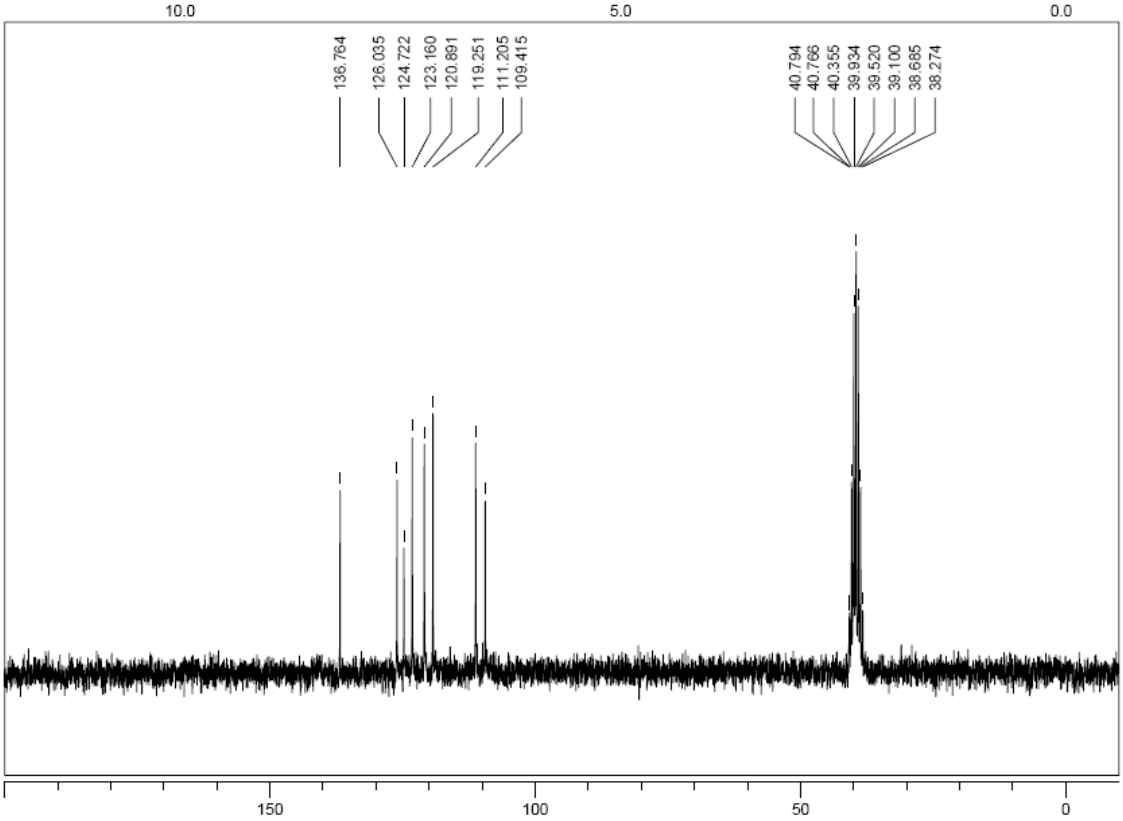
11.385
7.782
7.754
7.725
7.717
7.500
7.493
7.093
7.087
7.065
7.059
3.423
2.500
1.99
4.00
1.91
1.92
10.0
5.0
0.0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119.251
111.205
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39.520
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50
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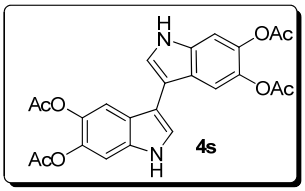
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OAc
AcO
AcO
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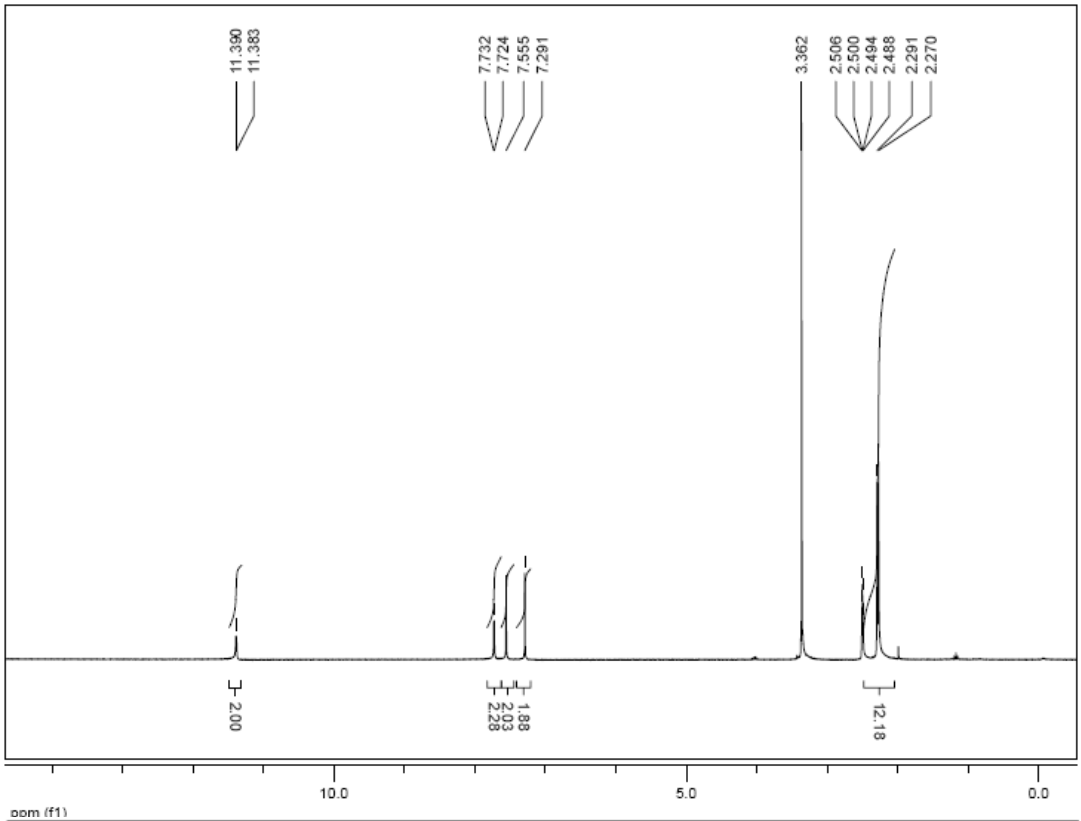
H
4s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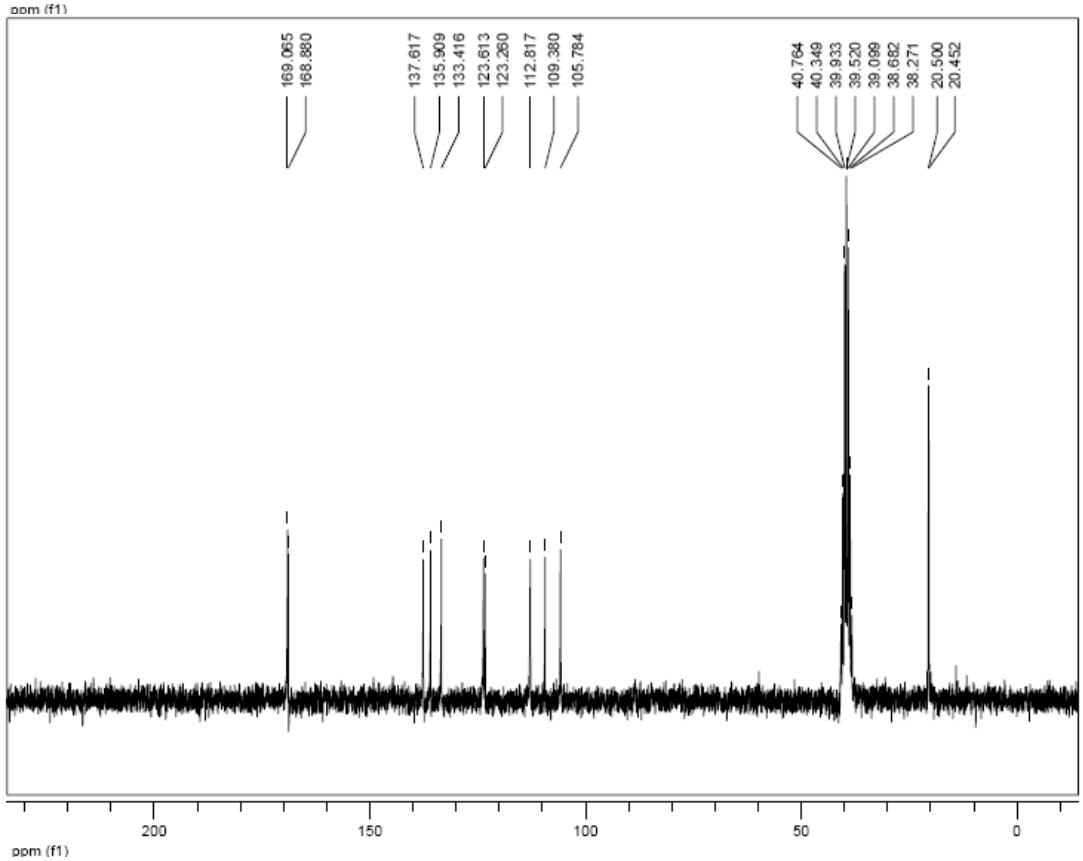
11.383
7.732
7.724
7.555
7.291
3.362
2.506
2.500
2.494
2.488
2.291
2.270
2.00
2.28
2.03
1.88
12.18
10.0
5.0
0.0
ppm (f1)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168.880
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135.909
133.416
123.613
123.260
112.817
109.380
105.784
40.764
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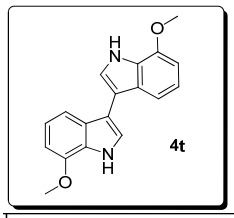
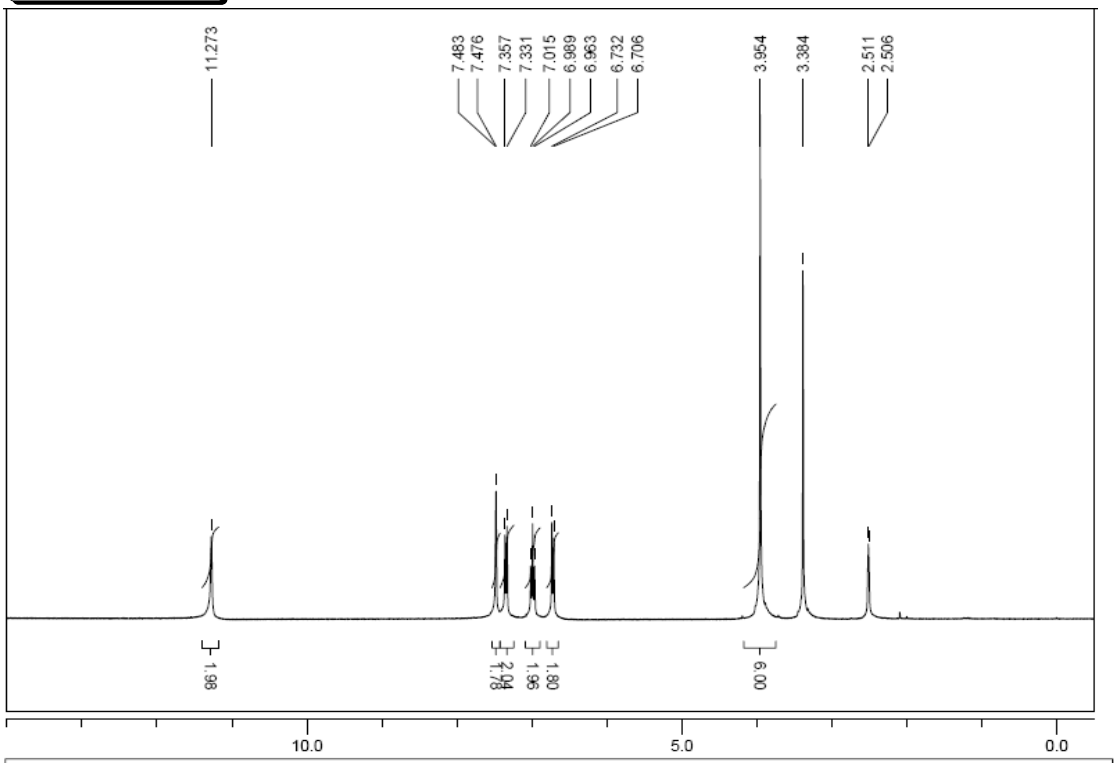
39.933
39.520
39.099
38.682
38.271
20.500
20.452
200
150
100
50
0
ppm (f1)


4t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7.331
7.015
6.989
6.963
6.732
6.706
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2.506
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2.04
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1.80
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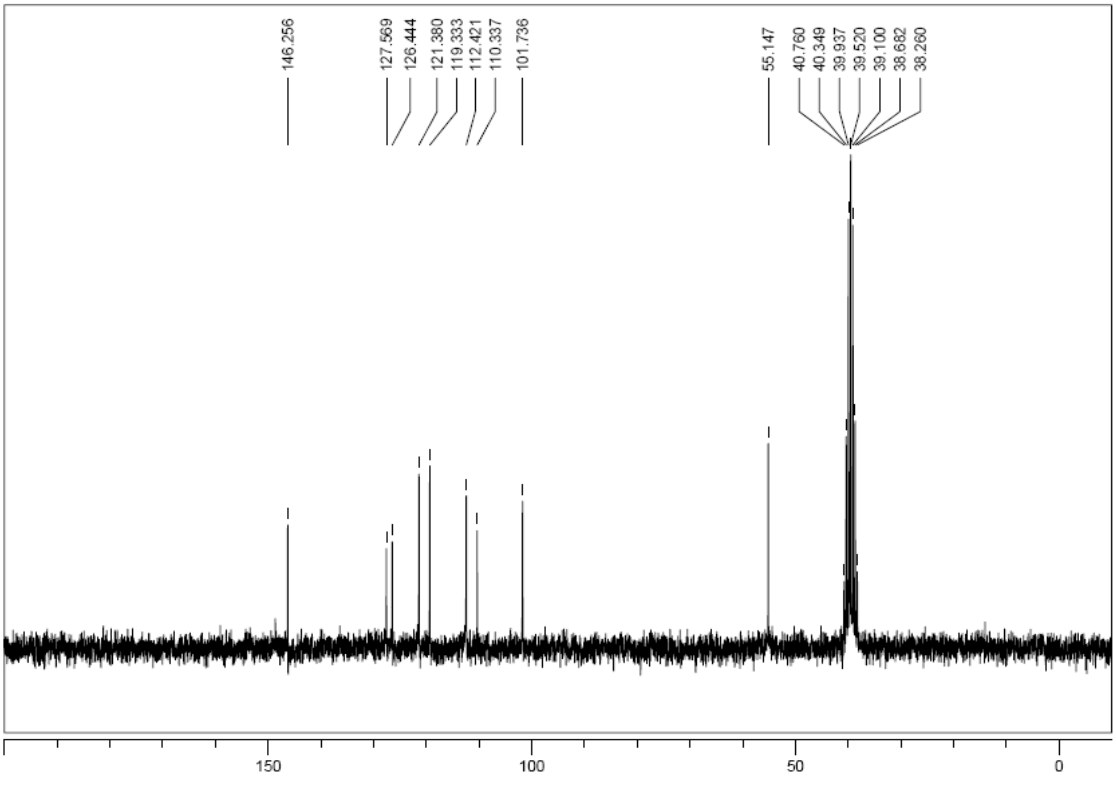
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119.333
112.421
110.337
101.736
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40.760
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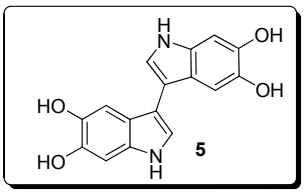
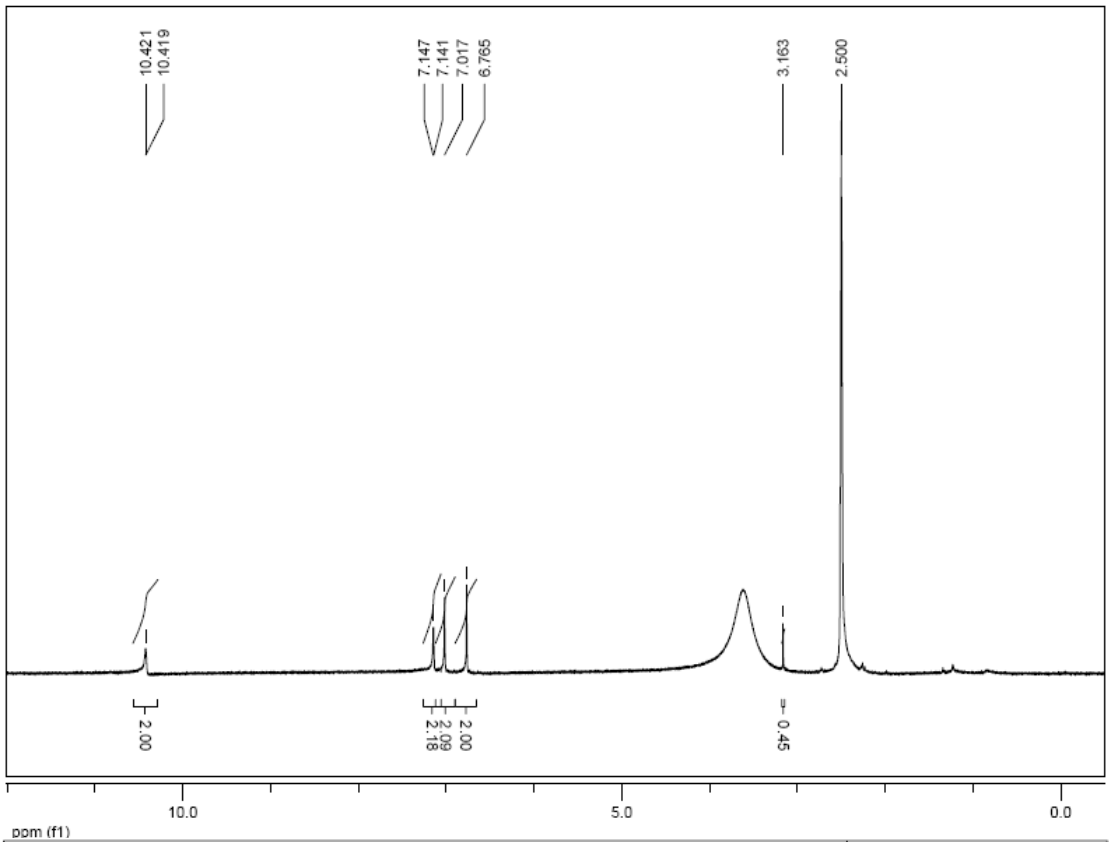
39.100
38.682
38.260
150
100
50
0


H
N
OH
OH
HO
HO
N
H
5


10.421
10.419
7.147
7.141
7.017
6.765
3.163
2.500
2.00
2.18
2.09
2.00
0.45
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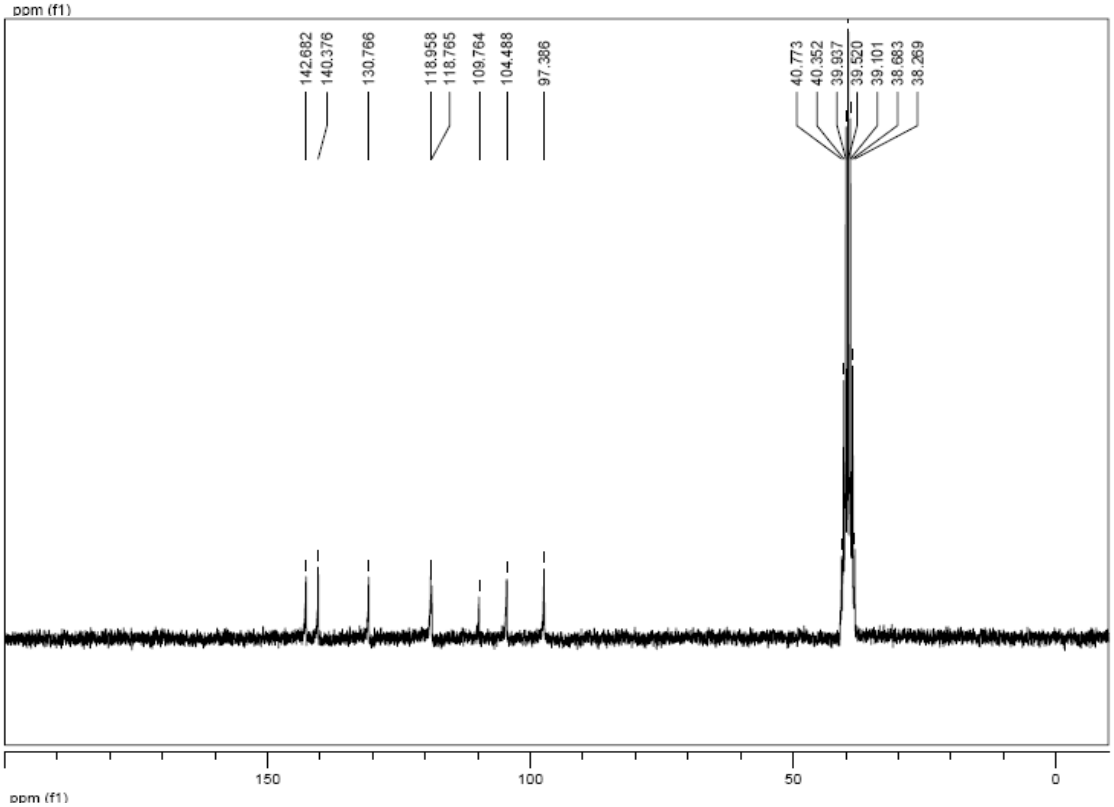
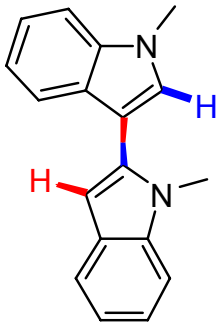
5.0
0.0
ppm (f1)


142.682
140.376
130.766
118.958
118.765
109.764
104.488
97.386
40.773
40.352
39.937
39.520
39.101
38.683
38.269
150
100
50
0
ppm (f1)

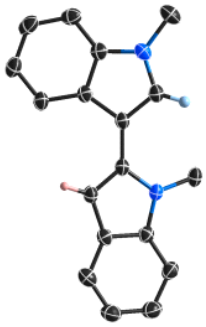
X-ray Crystal Structure Determination for compound 3a and 4a

The collections of crystallographic data of **3a** and **4a** were carried out on a Bruker Smart-1000 CCD diffractometer at 298 K, using graphite-monochromated Mo-Kα (λ = 0.71073 Å). The structures were solved by direct method and expanded using Fourier techniques with Shelxl-97 program.[1] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2.[2] The organic hydrogen atoms were generated geometrically (C–H = 0.93 Å). The detailed crystal data and structure refinement information as follows. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (**3a**, CCDC 687631; **4a** CCDC 715135). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (.44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(1) G. M. Sheldrick, SHELXS 97, *A Program for the solution of crystal structures,* University of Göttingen, **1997**.
(2) G. M. Sheldrick, *A Program for the Refinement of Crystal Structures from X-ray Data*, University of Göttingen, Germany, **1998**.



3a



X-ray structure of 3**a**

X-ray Crystal Structure of Compound 3a

Table 1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	$C_{18}H_{16}N_2$
Formula weight	260.33
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P2(1)/c*
Unit cell dimensions	*a* = 11.290(2) Å *α* = 90 °. *b* = 7.2745(15) Å *β* = 96.63(3) °. *c* = 17.151(3) Å *γ* = 90 °.
Volume	1399.2(5) Å^3
Z, Calculated density	4, 1.236 Mg/m^3
Absorption coefficient	0.073 mm^-1
F(000)	552
Crystal size	0.60 x 0.41 x 0.31 mm
Theta range for data collection	1.82 to 27.48 °..
Limiting indices	0<=h<=14, 0<=k<=9, -22<=l<=22
Reflections collected / unique	3208 / 3208 [R(int) = 0.0000]
Completeness to theta = 27.48	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3208 / 0 / 184
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1154
R indices (all data)	R1 = 0.0917, wR2 = 0.1344
Extinction coefficient	0.135(8)
Largest diff. peak and hole	0.319 and -0.416 e.Å^-3

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(2)	5542(1)	2572(2)	2197(1)	48(1)
C(3)	6747(1)	2023(2)	2104(1)	48(1)
C(10)	4570(1)	2737(2)	1570(1)	48(1)
C(12)	3456(1)	3148(2)	401(1)	54(1)
N(2)	3373(1)	2548(2)	1683(1)	50(1)
C(11)	4627(1)	3096(2)	788(1)	55(1)
C(17)	2685(1)	2810(2)	979(1)	52(1)
C(1)	5554(2)	2989(2)	2981(1)	54(1)
N(1)	6657(1)	2745(2)	3375(1)	57(1)
C(8)	7414(1)	2152(2)	2849(1)	53(1)
C(4)	7333(1)	1414(2)	1472(1)	59(1)
C(18)	2895(1)	1993(2)	2402(1)	60(1)
C(16)	1451(2)	2776(3)	800(1)	68(1)
C(13)	2950(2)	3466(3)	-374(1)	72(1)
C(7)	8614(2)	1717(3)	2976(1)	69(1)
C(9)	6981(2)	3040(3)	4212(1)	73(1)
C(5)	8525(2)	993(3)	1597(1)	73(1)
C(15)	1000(2)	3084(3)	35(1)	84(1)
C(6)	9156(2)	1140(3)	2338(1)	79(1)
C(14)	1738(2)	3432(3)	-546(1)	85(1)

Table 3. Bond lengths [Å] and angles [˚] for **3a**.

C(2)-C(1)	1.376(2)
C(2)-C(3)	1.445(2)
C(2)-C(10)	1.451(2)
C(3)-C(4)	1.405(2)
C(3)-C(8)	1.409(2)
C(10)-C(11)	1.374(2)
C(10)-N(2)	1.3945(18)
C(12)-C(13)	1.403(2)
C(12)-C(11)	1.410(2)
C(12)-C(17)	1.414(2)
N(2)-C(17)	1.372(2)
N(2)-C(18)	1.4579(18)
C(11)-H(11)	0.9300
C(17)-C(16)	1.392(2)
C(1)-N(1)	1.358(2)
C(1)-H(1)	0.9300
N(1)-C(8)	1.382(2)
N(1)-C(9)	1.456(2)
C(8)-C(7)	1.384(2)
C(4)-C(5)	1.372(2)
C(4)-H(4)	0.9300
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(16)-C(15)	1.369(3)
C(16)-H(16)	0.9300
C(13)-C(14)	1.367(3)
C(13)-H(13)	0.9300
C(7)-C(6)	1.378(3)
C(7)-H(7)	0.9300
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(5)-C(6)	1.388(2)
C(5)-H(5)	0.9300
C(15)-C(14)	1.394(3)
C(15)-H(15)	0.9300
C(6)-H(6)	0.9300
C(14)-H(14)	0.9300

C(1)-C(2)-C(3)	105.47(14)
C(1)-C(2)-C(10)	128.85(14)
C(3)-C(2)-C(10)	125.58(14)
C(4)-C(3)-C(8)	118.08(15)
C(4)-C(3)-C(2)	134.94(15)
C(8)-C(3)-C(2)	106.97(14)
C(11)-C(10)-N(2)	108.03(14)
C(11)-C(10)-C(2)	128.54(14)
N(2)-C(10)-C(2)	123.43(14)
C(13)-C(12)-C(11)	135.04(16)
C(13)-C(12)-C(17)	118.46(16)
C(11)-C(12)-C(17)	106.49(14)
C(17)-N(2)-C(10)	108.84(12)
C(17)-N(2)-C(18)	123.72(13)
C(10)-N(2)-C(18)	127.21(14)
C(10)-C(11)-C(12)	108.57(14)
C(10)-C(11)-H(11)	125.7
C(12)-C(11)-H(11)	125.7
N(2)-C(17)-C(16)	129.98(15)
N(2)-C(17)-C(12)	108.07(13)
C(16)-C(17)-C(12)	121.95(16)
N(1)-C(1)-C(2)	111.19(14)
N(1)-C(1)-H(1)	124.4
C(2)-C(1)-H(1)	124.4
C(1)-N(1)-C(8)	108.49(13)
C(1)-N(1)-C(9)	125.64(15)
C(8)-N(1)-C(9)	125.87(15)
N(1)-C(8)-C(7)	129.55(16)
N(1)-C(8)-C(3)	107.88(14)
C(7)-C(8)-C(3)	122.57(16)
C(5)-C(4)-C(3)	119.32(16)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
N(2)-C(18)-H(18A)	109.5
N(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(15)-C(16)-C(17)	117.48(18)
C(15)-C(16)-H(16)	121.3
C(17)-C(16)-H(16)	121.3
C(14)-C(13)-C(12)	119.29(18)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(6)-C(7)-C(8)	117.44(17)
C(6)-C(7)-H(7)	121.3
C(8)-C(7)-H(7)	121.3
N(1)-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(4)-C(5)-C(6)	121.14(17)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(16)-C(15)-C(14)	121.76(19)
C(16)-C(15)-H(15)	119.1
C(14)-C(15)-H(15)	119.1
C(7)-C(6)-C(5)	121.45(17)
C(7)-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
C(13)-C(14)-C(15)	121.05(19)
C(13)-C(14)-H(14)	119.5
C(15)-C(14)-H(14)	119.5

Symmetry transformations used to generate equivalent atoms

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
C(2)	52(1)	46(1)	47(1)	1(1)	13(1)	-3(1)
C(3)	50(1)	46(1)	50(1)	4(1)	11(1)	-6(1)
C(10)	47(1)	48(1)	50(1)	-2(1)	14(1)	-2(1)
C(12)	60(1)	51(1)	51(1)	-5(1)	9(1)	-1(1)
N(2)	48(1)	53(1)	52(1)	1(1)	16(1)	2(1)
C(11)	53(1)	65(1)	48(1)	1(1)	15(1)	-4(1)
C(17)	55(1)	46(1)	57(1)	-6(1)	9(1)	2(1)
C(1)	60(1)	51(1)	53(1)	1(1)	15(1)	1(1)
N(1)	68(1)	56(1)	46(1)	2(1)	7(1)	-4(1)
C(8)	55(1)	49(1)	57(1)	7(1)	9(1)	-6(1)
C(4)	57(1)	66(1)	58(1)	2(1)	19(1)	-4(1)
C(18)	58(1)	63(1)	62(1)	5(1)	26(1)	1(1)
C(16)	53(1)	73(1)	78(1)	-10(1)	10(1)	2(1)
C(13)	82(1)	80(1)	54(1)	-8(1)	5(1)	-2(1)
C(7)	59(1)	73(1)	72(1)	13(1)	0(1)	-8(1)
C(9)	101(2)	67(1)	49(1)	0(1)	3(1)	-8(1)
C(5)	57(1)	83(1)	82(1)	5(1)	28(1)	1(1)
C(15)	62(1)	97(2)	88(2)	-17(1)	-8(1)	6(1)
C(6)	49(1)	92(2)	99(2)	17(1)	14(1)	-2(1)
C(14)	83(1)	99(2)	68(1)	-12(1)	-13(1)	5(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3a**.

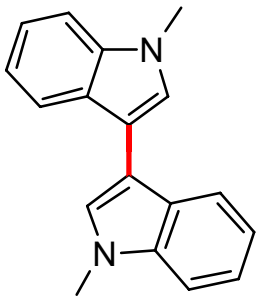
	x	y	z	U(eq)
H(11)	5321	3273	554	66
H(1)	4892	3387	3211	65
H(4)	6918	1297	973	71
H(18A)	2743	3065	2701	89
H(18B)	3462	1221	2706	89
H(18C)	2165	1328	2270	89
H(16)	953	2552	1184	81
H(13)	3435	3697	-766	86
H(7)	9039	1810	3472	82
H(9A)	6332	3623	4430	109
H(9B)	7674	3812	4291	109
H(9C)	7152	1879	4466	109
H(5)	8916	603	1178	87
H(15)	178	3061	-100	101
H(6)	9963	843	2406	95
H(14)	1400	3644	-1058	102

Table 6. Torsion angles [°] for **3a**.

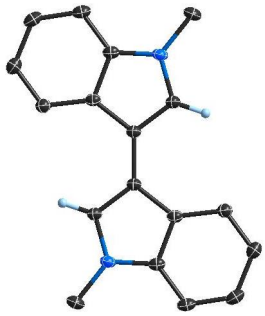
C(1)-C(2)-C(3)-C(4)	178.96(17)
C(10)-C(2)-C(3)-C(4)	-4.4(3)
C(1)-C(2)-C(3)-C(8)	-0.11(16)
C(10)-C(2)-C(3)-C(8)	176.52(14)
C(1)-C(2)-C(10)-C(11)	149.26(18)
C(3)-C(2)-C(10)-C(11)	-26.6(2)
C(1)-C(2)-C(10)-N(2)	-30.5(2)
C(3)-C(2)-C(10)-N(2)	153.64(15)
C(11)-C(10)-N(2)-C(17)	-0.76(17)
C(2)-C(10)-N(2)-C(17)	179.07(13)
C(11)-C(10)-N(2)-C(18)	173.76(15)
C(2)-C(10)-N(2)-C(18)	-6.4(2)
N(2)-C(10)-C(11)-C(12)	0.41(18)
C(2)-C(10)-C(11)-C(12)	-179.42(14)
C(13)-C(12)-C(11)-C(10)	179.12(19)
C(17)-C(12)-C(11)-C(10)	0.09(18)

C(10)-N(2)-C(17)-C(16)	-179.32(16)
C(18)-N(2)-C(17)-C(16)	5.9(3)
C(10)-N(2)-C(17)-C(12)	0.82(17)
C(18)-N(2)-C(17)-C(12)	-173.94(14)
C(13)-C(12)-C(17)-N(2)	-179.78(14)
C(11)-C(12)-C(17)-N(2)	-0.56(17)
C(13)-C(12)-C(17)-C(16)	0.3(2)
C(11)-C(12)-C(17)-C(16)	179.56(15)
C(3)-C(2)-C(1)-N(1)	0.03(17)
C(10)-C(2)-C(1)-N(1)	-176.45(14)
C(2)-C(1)-N(1)-C(8)	0.07(17)
C(2)-C(1)-N(1)-C(9)	-179.26(14)
C(1)-N(1)-C(8)-C(7)	-179.70(16)
C(9)-N(1)-C(8)-C(7)	-0.4(3)
C(1)-N(1)-C(8)-C(3)	-0.13(16)
C(9)-N(1)-C(8)-C(3)	179.19(14)
C(4)-C(3)-C(8)-N(1)	-179.11(14)
C(2)-C(3)-C(8)-N(1)	0.15(16)
C(4)-C(3)-C(8)-C(7)	0.5(2)
C(2)-C(3)-C(8)-C(7)	179.75(15)
C(8)-C(3)-C(4)-C(5)	-0.9(2)
C(2)-C(3)-C(4)-C(5)	-179.85(17)
N(2)-C(17)-C(16)-C(15)	-179.88(16)
C(12)-C(17)-C(16)-C(15)	0.0(3)
C(11)-C(12)-C(13)-C(14)	-179.21(19)
C(17)-C(12)-C(13)-C(14)	-0.3(3)
N(1)-C(8)-C(7)-C(6)	179.55(17)
C(3)-C(8)-C(7)-C(6)	0.0(2)
C(3)-C(4)-C(5)-C(6)	0.7(3)
C(17)-C(16)-C(15)-C(14)	-0.4(3)
C(8)-C(7)-C(6)-C(5)	-0.2(3)
C(4)-C(5)-C(6)-C(7)	-0.1(3)
C(12)-C(13)-C(14)-C(15)	-0.1(3)
C(16)-C(15)-C(14)-C(13)	0.5(3)

Symmetry transformations used to generate equivalent atoms



4a



X-ray Crystal Structure of Compound 4a

Table 1. Crystal data and structure refinement for **4a**.

Identification code	**4a**
Empirical formula	$C_{18}H_{16}N_2$
Formula weight	260.33
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 6.4851(13) Å alpha = 90 °. b = 13.409(3) Å beta = 109.73(3) °. c = 8.1723(16) Å gamma = 90 °.
Volume	668.9(2) Å^3
Z, Calculated density	2, 1.292 Mg/m^3
Absorption coefficient	0.077 mm^-1
F(000)	276
Crystal size	0.22 x 0.18 x 0.10 mm
Theta range for data collection	3.04 to 24.99 °.
Limiting indices	-5<=h<=7, -14<=k<=15, -9<=l<=9
Reflections collected / unique	4364 / 1160 [R(int) = 0.0346]
Completeness to theta = 24.99	98.6 %
Absorption correction	Numerical
Max. and min. transmission	0.9924 and 0.9833
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1160 / 0 / 92
Goodness-of-fit on F^2	1.154
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1141

R indices (all data)	R1 = 0.0533, wR2 = 0.1175
Largest diff. peak and hole	0.221 and -0.210 e.Å^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	-2375(2)	9886(1)	2526(2)	31(1)
C(1)	-721(3)	8412(1)	4383(2)	34(1)
C(2)	820(3)	7675(2)	4615(2)	39(1)
C(3)	2072(3)	7600(1)	3520(2)	37(1)
C(4)	1818(3)	8266(1)	2185(2)	31(1)
C(5)	286(3)	9043(1)	1914(2)	26(1)
C(6)	-402(3)	9864(1)	707(2)	26(1)
C(7)	-2011(3)	10345(1)	1148(2)	31(1)
C(8)	-977(3)	9090(1)	3028(2)	28(1)
C(9)	-3934(3)	10205(2)	3345(2)	37(1)

Table 3. Bond lengths [Å] and angles [°] for **4a**.

N(1)-C(8)	1.370(2)
N(1)-C(7)	1.372(2)
N(1)-C(9)	1.453(2)
C(1)-C(2)	1.373(3)
C(1)-C(8)	1.399(2)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.400(3)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.377(2)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.405(2)
C(4)-H(4A)	0.9500
C(5)-C(8)	1.417(2)
C(5)-C(6)	1.444(2)
C(6)-C(7)	1.375(2)
C(6)-C(6)#1	1.466(3)
C(7)-H(7A)	0.9500
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(8)-N(1)-C(7)	108.42(14)
C(8)-N(1)-C(9)	125.77(14)
C(7)-N(1)-C(9)	125.80(16)
C(2)-C(1)-C(8)	117.61(17)
C(2)-C(1)-H(1A)	121.2
C(8)-C(1)-H(1A)	121.2
C(1)-C(2)-C(3)	121.07(17)
C(1)-C(2)-H(2A)	119.5

C(3)-C(2)-H(2A)	119.5
C(4)-C(3)-C(2)	121.33(18)
C(4)-C(3)-H(3A)	119.3
C(2)-C(3)-H(3A)	119.3
C(3)-C(4)-C(5)	119.69(16)
C(3)-C(4)-H(4A)	120.2
C(5)-C(4)-H(4A)	120.2
C(4)-C(5)-C(8)	117.61(15)
C(4)-C(5)-C(6)	135.38(15)
C(8)-C(5)-C(6)	107.01(14)
C(7)-C(6)-C(5)	105.40(14)
C(7)-C(6)-C(6)#1	126.4(2)
C(5)-C(6)-C(6)#1	128.22(19)
N(1)-C(7)-C(6)	111.10(16)
N(1)-C(7)-H(7A)	124.4
C(6)-C(7)-H(7A)	124.4
N(1)-C(8)-C(1)	129.26(16)
N(1)-C(8)-C(5)	108.07(14)
C(1)-C(8)-C(5)	122.67(16)
N(1)-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **4a**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

U11	U22	U33	U23	U13	U12
N(1)	32(1)	39(1)	27(1)	2(1)	17(1)	1(1)
C(1)	36(1)	40(1)	27(1)	2(1)	12(1)	-10(1)
C(2)	43(1)	38(1)	33(1)	10(1)	10(1)	-7(1)
C(3)	40(1)	32(1)	38(1)	6(1)	11(1)	2(1)
C(4)	33(1)	31(1)	29(1)	0(1)	12(1)	-1(1)
C(5)	27(1)	29(1)	22(1)	-2(1)	9(1)	-6(1)
C(6)	28(1)	28(1)	23(1)	-1(1)	11(1)	-2(1)
C(7)	34(1)	35(1)	27(1)	4(1)	14(1)	3(1)
C(8)	29(1)	32(1)	23(1)	-2(1)	9(1)	-7(1)
C(9)	36(1)	46(1)	35(1)	-3(1)	22(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4a**.

	x	y	z	U(eq)
H(1A)	-1583	8460	5117	41
H(2A)	1041	7208	5532	46
H(3A)	3118	7079	3703	45
H(4A)	2674	8200	1450	37
H(7A)	-2772	10921	575	37
H(9A)	-4938	9655	3326	55
H(9B)	-4770	10776	2711	55
H(9C)	-3145	10398	4552	55

Table 6. Torsion angles [°] for **4a**.

C(8)-C(1)-C(2)-C(3)	-0.7(3)
C(1)-C(2)-C(3)-C(4)	0.6(3)
C(2)-C(3)-C(4)-C(5)	0.5(3)
C(3)-C(4)-C(5)-C(8)	-1.3(2)
C(3)-C(4)-C(5)-C(6)	179.14(18)
C(4)-C(5)-C(6)-C(7)	179.32(19)
C(8)-C(5)-C(6)-C(7)	-0.23(18)
C(4)-C(5)-C(6)-C(6)#1	-0.2(4)
C(8)-C(5)-C(6)-C(6)#1	-179.7(2)
C(8)-N(1)-C(7)-C(6)	0.6(2)
C(9)-N(1)-C(7)-C(6)	178.99(16)
C(5)-C(6)-C(7)-N(1)	-0.2(2)
C(6)#1-C(6)-C(7)-N(1)	179.3(2)
C(7)-N(1)-C(8)-C(1)	178.93(17)
C(9)-N(1)-C(8)-C(1)	0.5(3)
C(7)-N(1)-C(8)-C(5)	-0.70(19)
C(9)-N(1)-C(8)-C(5)	-179.12(16)
C(2)-C(1)-C(8)-N(1)	-179.85(17)
C(2)-C(1)-C(8)-C(5)	-0.3(3)
C(4)-C(5)-C(8)-N(1)	-179.07(14)
C(6)-C(5)-C(8)-N(1)	0.57(18)
C(4)-C(5)-C(8)-C(1)	1.3(2)
C(6)-C(5)-C(8)-C(1)	-179.09(15)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z

Reference

1 (*a*) L. Rout, S. Jammi, and T. Punniyamurthy, *Org. Lett.,* 2007, 9, 3397; (b) W. C. Guida, and D. J. Mathre, *J. Org. Chem.*, 1980, **45**, 3172; (c) O. Ottoni, R. Cruz, and R. Alves, *Tetrahedron*, 1998, **54**, 13915.