Supporting Information

Lewis Acid-Catalyzed Indole Synthesis via Intramolecular Nucleophilic Attack of Phenyldiazoacetates to Iminium Ions

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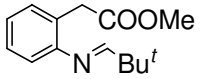
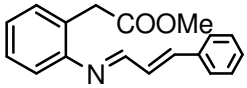
General. Reactions were performed in oven-dried (140 °C) or flame-dried glassware under an atmosphere of dry N_2. Dichloromethane (DCM) was passed through a solvent column prior to use and was not distilled. Methanol and acetonitrile were not distilled. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F_{254} plates. The developed chromatogram was analyzed by UV lamp (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (230-400 mesh). Melting points were measured by electrothermal MEL-TEMP 3.0. Metal triflate salts, boron trifluoride etherate and metal chloride salts were purchased from Aldrich and used as received. Methyl *o*-aminophenylacetate was prepared according to reported procedures.[1,2] *p*-Nitrobenzenesulfonyl azide (PNBSA) was prepared according to reported procedures.[3]

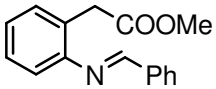
General Procedure for Synthesis of Imines (1). To a flame-dried vial under nitrogen atmosphere were added methyl *o*-aminophenylacetate (0.62 g, 3.8 mmol), aldehydes (1.0 eq.) and 5 mL of methanol. The mixture was stirred at room temperature for 16 h. After removal of methanol, crude imine was purified by flash column chromatography on silica gel to give pure imine **1** in quantitative yield.



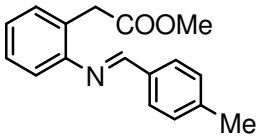
1a. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.25-6.75 (m, 4H), 3.68 (s, 2H), 3.62 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 151.2, 130.2, 128.6, 127.4, 125.2, 118.1, 51.7, 37.3, 37.0, 26.6; HRMS (ESI) for $C_{18}H_{18}NO_2$ $[M+H]^+$ calcd: 234.1494; found: 234.1506; IR (neat): 2959, 2929, 1736, 1651, 1474, 1435 cm^{-1}.



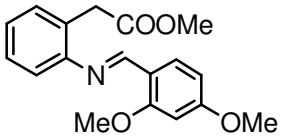
1b. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, 1H, J = 8Hz), 7.23-7.58 (m, 9H), 7.18(t, 1H, J = 8Hz), 6.93 (d, 1H, J = 8Hz), 3.79 (s, 2H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 161.9, 151.0, 144.0, 135.6, 130.4, 129.6, 129.1, 128.9, 128.7, 128.4, 127.5, 126.0, 117.8, 51.9, 37.1; HRMS (ESI) for $C_{18}H_{18}NO_2$ $[M+H]^+$ calcd: 280.1338; found: 280.1356; IR (neat): 3026, 2950, 1736, 1676, 1627 cm^{-1}.



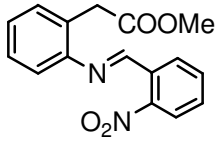
1c. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.02-7.90 (m, 9H), 3.82 (s, 2H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 159.9, 150.5, 136.3, 131.4, 130.4, 129.0, 128.8, 128.7, 128.4, 126.1, 117.6, 51.8, 37.5; HRMS (ESI) for $C_{16}H_{16}NO_2$ $[M+H]^+$ calcd: 254.1181; found: 254.1200; IR (neat): 3058, 1732, 1631, 1620, 1577 cm^{-1}.



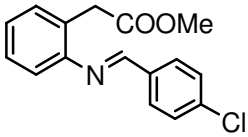
1d. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.00-7.78 (m, 8H), 3.81 (s, 2H), 3.59 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 159.8, 150.7, 141.9, 133.8, 130.4, 129.5, 128.9, 128.8, 128.4, 125.9, 117.6, 51.8, 37.5, 21.6; HRMS (ESI) for $C_{17}H_{18}NO_2$ $[M+H]^+$ calcd: 268.1338; found: 268.1348; IR (neat): 3024, 2949, 1735, 1627 cm^{-1}.



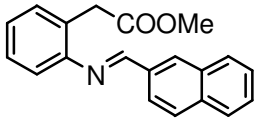
1e. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 6.42-8.11 (m, 7H), 3.85 (s, 6H), 3.80 (s, 2H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 163.7, 160.9, 155.3, 151.5, 130.2, 129.1, 128.9, 128.3, 125.3, 118.3, 117.9, 105.7, 97.9, 55.5, 51.8, 37.6; HRMS (ESI) for $C_{18}H_{20}NO_4$ $[M+H]^+$ calcd: 314.1392; found: 314.1400; IR (neat): 2968, 2947, 1735, 1604, 1462 cm^{-1}.



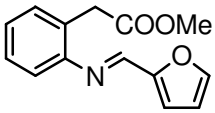
1f. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 7.12-8.29 (m, 8H), 3.84 (s, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 155.6, 133.6, 131.2, 130.6, 129.9, 129.3, 128.6, 127.1, 124.5, 117.9, 51.9, 37.7; HRMS (ESI) for $C_{16}H_{15}N_2O_4$ $[M+H]^+$ calcd: 299.1032; found: 299.1047; IR (neat): 2949, 1732, 1523, 1341 cm^{-1}.



1g. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.01-7.83 (m, 8H), 3.81 (s, 2H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 158.4, 150.1, 137.4, 134.8, 130.5 130.0, 129.2, 129.0, 128.5, 126.4, 117.4, 51.9, 37.5; HRMS (ESI) for $C_{16}H_{15}ClNO_2$ $[M+H]^+$ calcd: 288.0791; found: 288.0807; IR (neat): 2949, 1734, 1627, 1593, 1569, 1491 cm^{-1}.

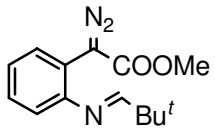


1h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.08-7.94 (m, 11H), 3.87 (s, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 159.9, 150.5, 135.0, 134.1, 133.1, 131.5, 130.5, 129.2, 128.8, 128.7, 128.5, 127.9, 127.6, 126.6, 126.2, 123.8, 117.6, 51.9, 37.6; HRMS (ESI) for $C_{20}H_{18}NO_2$ $[M+H]^+$ calcd: 304.1338; found: 304.1342; IR (neat): 3058, 2949, 1733, 1620, 1594 cm^{-1}.

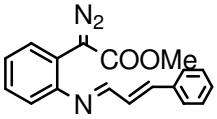


1i. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 6.52-7.59 (m, 7H), 3.82 (s, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 152.4, 150.6, 148.1, 145.6, 130.4, 128.8, 128.4, 126.1, 117.6, 115.7, 112.1, 51.8, 37,2; HRMS (ESI) for $C_{14}H_{14}NO_3$ $[M+H]^+$ calcd: 244.0974; found: 244.0987; IR (neat): 2987, 2950, 1733, 1625, 1472 cm^{-1}.

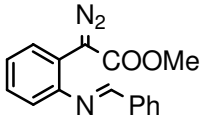
General Procedure for Synthesis of Dizao Compound (2) (Table 2). To a stirred solution of **1** (1 mmol) and PNBSA (2-3 mmol) in MeCN (5 mL) was added DBU (4-6 mmol) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 12 h, the reaction mixture was quenched with aq. NH_4Cl, extracted with diethyl ether, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel to give the corresponding diazo compound **2**. The diazo carbon was not observed in ^{13}C NMR.



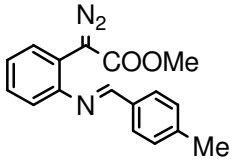
2a (R = Bu^t). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.25-6.79 (m, 4H), 3.81 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 151.2, 148.8, 129.5, 128.3, 127.4, 125.8, 118.8, 52.0, 37.4, 26.6; HRMS (ESI) for $C_{18}H_{16}N_3O_2$ $[M+H]^+$ calcd: 260.1399; found: 260.1411; IR (neat): 2959, 2098, 1700, 1650, 1489 cm^{-1}.



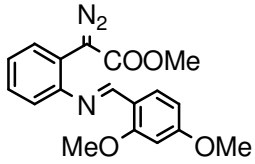
2b (R = PhCH=CH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, 1H, *J* = 8Hz), 7.23-7.52 (m, 9H), 7.18 (t, 1H, *J* = 8Hz), 6.97 (d, 1H, *J* = 8Hz), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 161.3, 148.4, 144.0, 135.6, 130.4, 129.6, 129.1, 128.9, 128.7, 128.4, 127.5, 126.0, 119.9, 118.0, 52.0; HRMS (ESI) for $C_{18}H_{16}N_3O_2$ $[M+H]^+$ calcd: 306.1243; found: 306.1261; IR (neat): 2987, 2095, 1692, 1623, 1453 cm^{-1}.



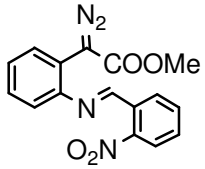
2c (R = Ph). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.88-7.92 (m, 2H), 7.64-7.67 (m, 1H), 7.45-7.52 (m, 3H), 7.24-7.29 (m, 2H), 7.03-7.05 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 159.9, 148.3, 136.2, 131.9, 129.7, 129.3, 129.0, 128.9, 128.5, 126.7, 120.2, 118.2, 52.2; HRMS (ESI) for $C_{16}H_{14}N_3O_2$ $[M+H]^+$ calcd: 280.1086; found: 280.1105; IR (neat): 2952, 2095, 1696, 1626, 1486, 1451 cm^{-1}.



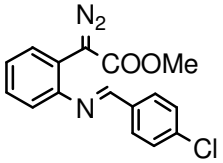
2d (R = *p*-MePh). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.00-7.81 (m, 8H), 3.82 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 159.8, 150.7, 141.9, 133.8, 130.4, 129.5, 128.9, 128.8, 128.4, 125.9, 120.0, 118.0, 52.0, 21.7; HRMS (ESI) for $C_{17}H_{16}N_3O_2$ $[M+H]^+$ calcd: 294.1243; found: 294.1253; IR (neat): 2950, 2098, 1692, 1626, 1500, 1453 cm^{-1}.



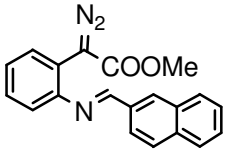
2e (R = 2,4-DiMeOPh). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 6.41-8.13 (m, 7H), 3.84 (s, 6H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 163.7, 160.9, 155.3, 151.5, 130.2, 129.1, 128.9, 128.3, 125.3, 118.3, 117.9, 105.9, 97.9, 55.6, 55.5, 51.9; HRMS (ESI) for $C_{18}H_{18}N_3O_4$ $[M+H]^+$ calcd: 340.1297; found: 340.1305; IR (neat): 2967, 2097, 1677, 1604, 1578, 1456 cm^{-1}.



2f (R = *o*-NO_2Ph). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.11-8.34 (m, 8H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 155.5, 133.6, 131.5, 131.2, 130.6, 129.9, 129.3, 128.6, 127.5, 127.1, 124.5, 118.5, 117.9, 52.1; HRMS (ESI) for $C_{16}H_{13}N_4O_4$ $[M+H]^+$ calcd: 325.0937; found: 325.0952; IR (neat): 2952, 2095, 1698, 1620, 1523, 1437 cm^{-1}.

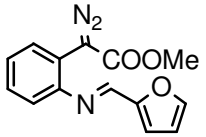


2g (R = *p*-ClPh). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.00-7.84 (m, 8H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 158.4, 150.1, 147.7, 137.4, 134.8, 130.5 130.0, 129.2, 129.0, 128.5, 126.4, 122.2, 120.2, 52.0; HRMS (ESI) for $C_{16}H_{13}ClN_3O_2$ $[M+H]^+$ calcd: 314.0696; found: 314.0712; IR (neat): 2951, 2098, 1700, 1527, 1444 cm^{-1}.



2h (R = 2-Naphthyl). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.08-8.18 (m, 11H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 159.9, 150.5, 135.0, 134.1,

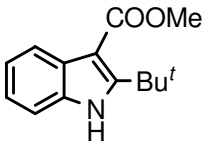
133.1, 131.5, 130.5, 129.2, 128.8, 128.7, 128.5, 127.9, 127.6, 126.6, 126.2, 123.8, 120.2, 118.0, 52.0; HRMS (ESI) for $C_{20}H_{16}N_3O_2$ $[M+H]^+$ calcd: 330.1243; found: 330.1247; IR (neat): 2952, 2099, 1694, 1623, 1444 cm^{-1}.



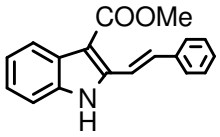
2i (R = 2-Fural). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 6.54-7.66 (m, 7H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 152.3, 150.6, 148.1, 145.6, 130.4, 128.8, 128.4, 126.1, 117.6, 115.7, 112.3, 110.9, 51.9; HRMS (ESI) for $C_{14}H_{12}N_3O_3$ $[M+H]^+$ calcd: 270.0879; found: 270.0892; IR (neat): 2951, 2097, 1697, 1528, 1438 cm^{-1}.

Cyclization of Methyl *N*-Phenyliminophenyldiazoacetate (2c) Catalyzed by Lewis Acids: Screening of Lewis Acids (Table 1). To a stirred solution of **2c** (0.25 mmol) in DCM (5 mL) was added metal chloride salts, boron trifluoride etherate, or metal triflate salts (1.0 mol%) at room temperature. The yellow reaction mixture was stirred for 1 h, during which the reaction was monitored by TLC in every 5 min till the completion of the reaction. The mixture was then passed through a silica gel plug to remove the catalyst. After evaporation of the solvent, pure indole **3c** was obtained as a light yellow solid. (TLC R_f = 0.25 in 5:1 hexanes/ethyl acetate)

General Procedure for Synthesis of Indoles (3) (Table 2). To a stirred solution of **2** (0.25 mmol) in DCM (5 mL) was added boron trifluoride etherate or zinc triflate (1.0 mol%) at room temperature. The yellow reaction mixture was stirred until it turned pale yellow or colorless within 10-30 min. The mixture was then passed through a silica gel plug to remove the catalyst. After evaporation of the solvent, pure indole **3** was obtained as a light yellow solid in quantitative yield. NMR spectral data suggest the presence of rotamers in indoles with 3-aryl groups having an ortho substituent.

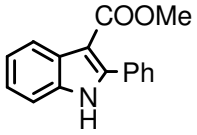


3a. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.09-8.11 (m, 1H), 7.16-7.35 (m, 3H), 3.93 (s, 3H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 154.7, 133.1, 128.6, 122.5, 122.1, 110.9, 103.7, 51.1, 33.9, 28.7; HRMS (ESI) for $C_{18}H_{16}NO_2$ $[M+H]^+$ calcd: 232.1338; found: 232.1362; IR (neat): 2949, 1669, 1575, 1455 cm^{-1}. Mp: 77.2-78.5 °C.

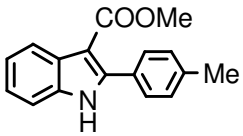


3b. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.05-7.56 (m, 11H), 3.97 (s, 3H); ^{13}C

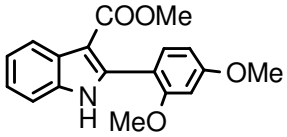
NMR (100 MHz, $CDCl_3$): δ 152.9, 141.6, 136.2, 135.6, 131.4, 131.3, 129.1, 128.8, 128.6, 128.5, 127.4, 127.0, 123.9, 122.1, 122.0, 118.0, 110.7, 51.1; HRMS (ESI) for $C_{18}H_{16}NO_2$ $[M+H]^+$ calcd: 278.1181; found: 278.1181; IR (neat): 3322, 2949, 1664, 1577, 1449 cm^{-1}. Mp: 102.7-103.9 °C.



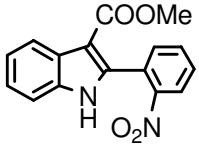
3c. ^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.19-8.21 (m, 1H), 7.62-7.64 (m, 2H), 7.41-7.44 (m, 3H), 7.34-7.37 (m, 1H), 7.24-7.29 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 144.8, 135.3, 132.2, 129.8, 129.7, 129.4, 128.4, 127.7, 123.5, 122.4, 122.3, 111.2, 51.1; HRMS (ESI) for $C_{16}H_{14}NO_2$ $[M+H]^+$ calcd: 252.1025; found: 252.1040; IR (neat): 3322, 1688, 1548, 1452 cm^{-1}. Mp: 137.6-139.0 °C.



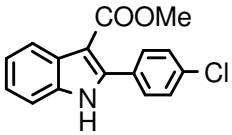
3d. ^1H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.17 (m, 1H), 7.52 (m, 2H), 7.32 (m, 1H), 7.20-7.28 (m, 4H), 3.82 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 144.9, 139.3, 135.1, 129.4, 128.9, 127.6, 123.1, 122.1, 122.0, 111.0, 50.8, 21.4; HRMS (ESI) for $C_{17}H_{16}NO_2$ $[M+H]^+$ calcd: 266.1181; found: 266.1187; IR (neat): 3325, 1678, 1500, 1455, 1439 cm^{-1}. Mp: 148.0-148.8 °C.



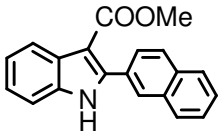
3e. NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.16 (m, 1H), 7.52 (m, 1H), 7.33 (m, 1H), 7.10-7.25 (m, 2H), 6.51-6.57 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 161.8, 158.1, 141.5, 134.9, 133.7, 130.8, 127.1, 122.7, 121.8, 121.6, 112.8, 110.8, 105.7, 104.4, 98.7, 55.5, 50.8; HRMS (ESI) for $C_{18}H_{18}NO_4$ $[M+H]^+$ calcd: 312.1236; found: 312.1236; IR (neat): 3318, 1681, 1579, 1454 cm^{-1}. Mp: 140.5-141.2 °C.



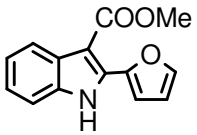
3f. ^1H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 8.05-8.15 (m, 2H), 7.24-7.63 (m, 6H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 149.3, 139.5, 135.4, 132.7, 132.2, 130.1, 127.5, 126.5, 124.4, 123.6, 122.3, 122.0, 111.3, 105.8, 51.0; HRMS (ESI) for $C_{16}H_{13}N_2O_4$ $[M+H]^+$ calcd: 297.0875; found: 297.0878; IR (neat): 3321, 1679, 1527, 1452 cm^{-1}. Mp: 164.7-165.7 °C.



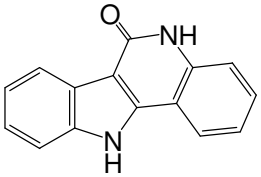
3g. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.18 (m, 1H), 7.55 (m, 2H), 7.33-7.39 (m, 3H), 7.24-7.29 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 152.4, 143.2, 135.4, 135.1, 130.8, 130.3, 128.4, 127.4, 123.5, 122.3, 122.2, 111.0, 51.0; HRMS (ESI) for $C_{16}H_{13}ClNO_2$ $[M+H]^+$ calcd: 286.0635; found: 286.0641; IR (neat): 3301, 1678, 1531, 1444 cm^{-1}. Mp: 166.2-167.2 °C.



3h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.21 (m, 1H), 8.01 (s, 1H), 7.83-7.88 (m, 3H), 7.73 (m, 1H), 7.47-7.54 (m, 2H), 7.37 (m, 1H), 7.24-7.29 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 144.4, 135.2, 133.4, 132.8, 129.5, 128.6, 128.5, 128.3, 127.9, 127.8, 127.6, 127.3, 126.9, 126.5, 123.3, 122.2, 111.0, 104.8, 50.9; HRMS (ESI) for $C_{20}H_{16}NO_2$ $[M+H]^+$ calcd: 302.1181; found: 302.1183; IR (neat): 3302, 1678, 1537, 1444 cm^{-1}. Mp: 139.9-141.0 °C.



3i. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.16 (m, 1H), 7.85 (m, 1H), 7.51 (m, 1H), 7.36 (m, 1H), 7.25 (m, 2H), 6.57 (m, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 145.5, 142.7, 134.7, 133.9, 127.3, 123.5, 122.4, 122.1, 114.6, 112.8, 110.9, 102.9, 51.0; HRMS (ESI) for $C_{14}H_{12}NO_3$ $[M+H]^+$ calcd: 242.0817; found: 242.0831; IR (neat): 3321, 1679, 1528, 1455, 1438 cm^{-1}. Mp: 115.6-116.9 °C.



Synthesis of Indolo-quinolin-2(1*H*)-one (4) (Scheme 4). Indole **3f** (300 mg) in 50 mL of ethyl acetate was hydrogenated over 10% palladium on carbon (50 mg) at room temperature under an atmospheric pressure of hydrogen for 10 h to give a light yellow solution. After filtration of Pd/C and removal of solvent under reduced pressure, a yellow solid was obtained. The solid was then redissolved in MeOH (10 mL) and the resultant mixture was stirred at room temperature for 1 h, during which some white solid precipitated. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel using 1:2 hexanes:EtOAc as eluent to give compound **4** as white solid (215 mg, 90.7%). All analytical data are identical to the literature reported data.[4]

(1) Mishra, J. K.; Panda, G. *J. Comb. Chem.* **2007**, *9*, 321–338.
(2) Katayama, S.; Ae, N.; Kodo, T.; Masumoto, S.; Hourai, S.; Tamamura, C.; Tanaka, H.; Nagata, R. *J. Med. Chem.* **2003**, *4*6, 691–701.
(3) (a) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693–11712. (b) Ruppel, J. V.; Jones, J. E.; Huff, C. A.; Kamble, R. M.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2008**, *10*, 1995–1998.
(4) Chen, Y. L.; Chung, C. H.; Chen, I. L.; Chen, P. H.; Jeng, H. Y. *Bioorganic Medicinal Chemistry* **2002**, *10*, 2705–2712.

NMR spectra of Imines (1), Diazo Imines (2), and Indoles (3)

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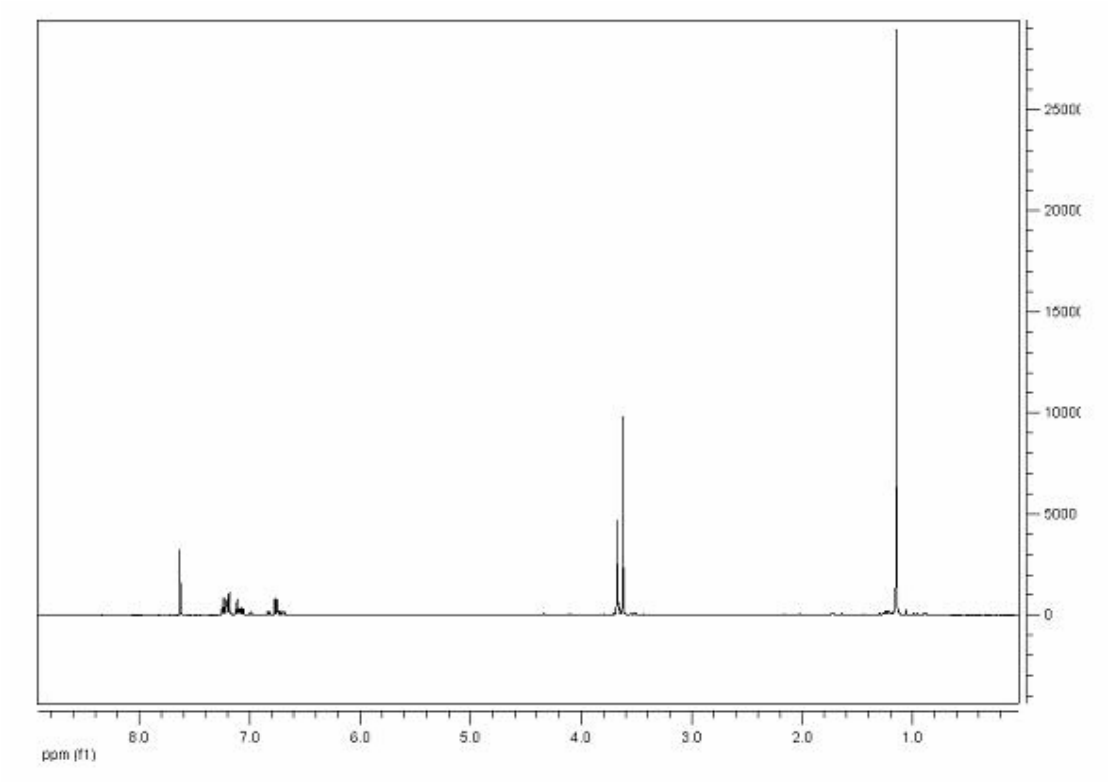

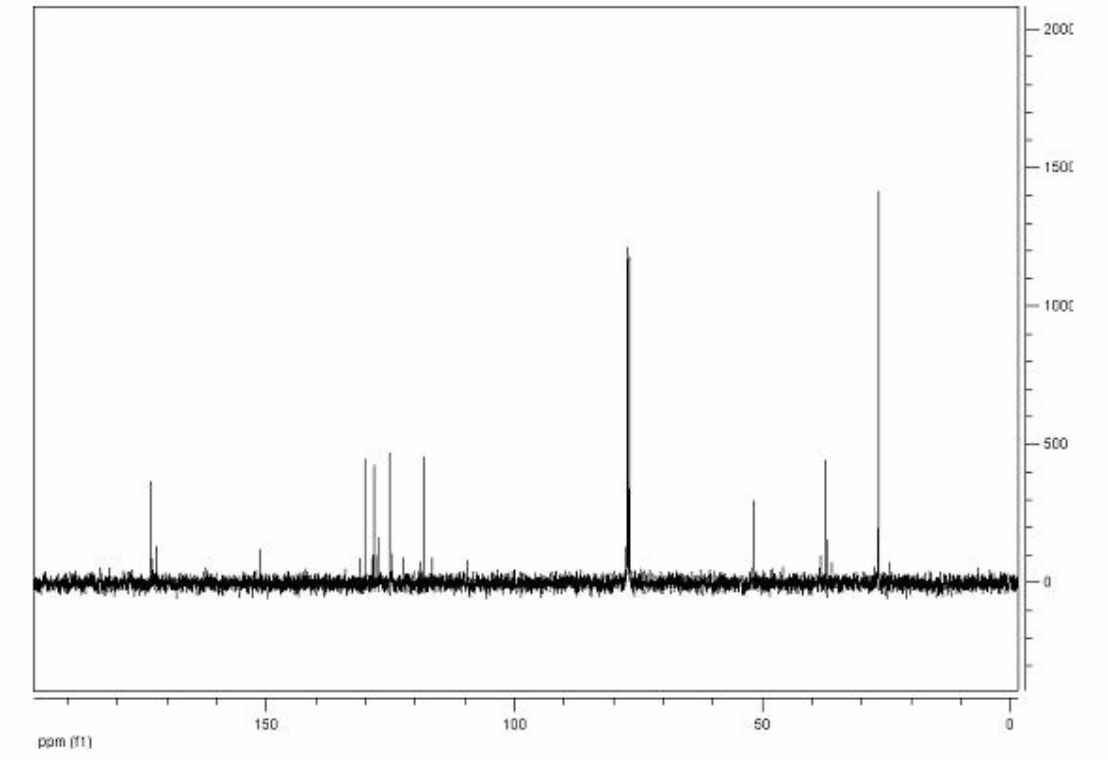

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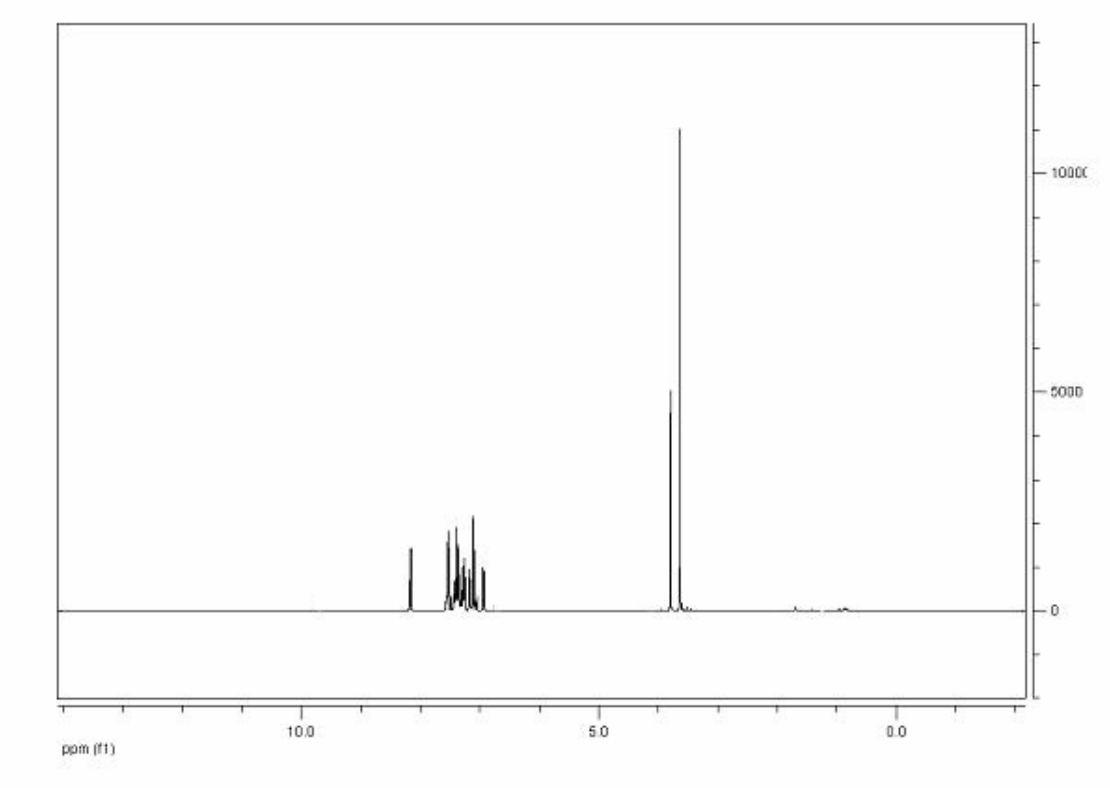
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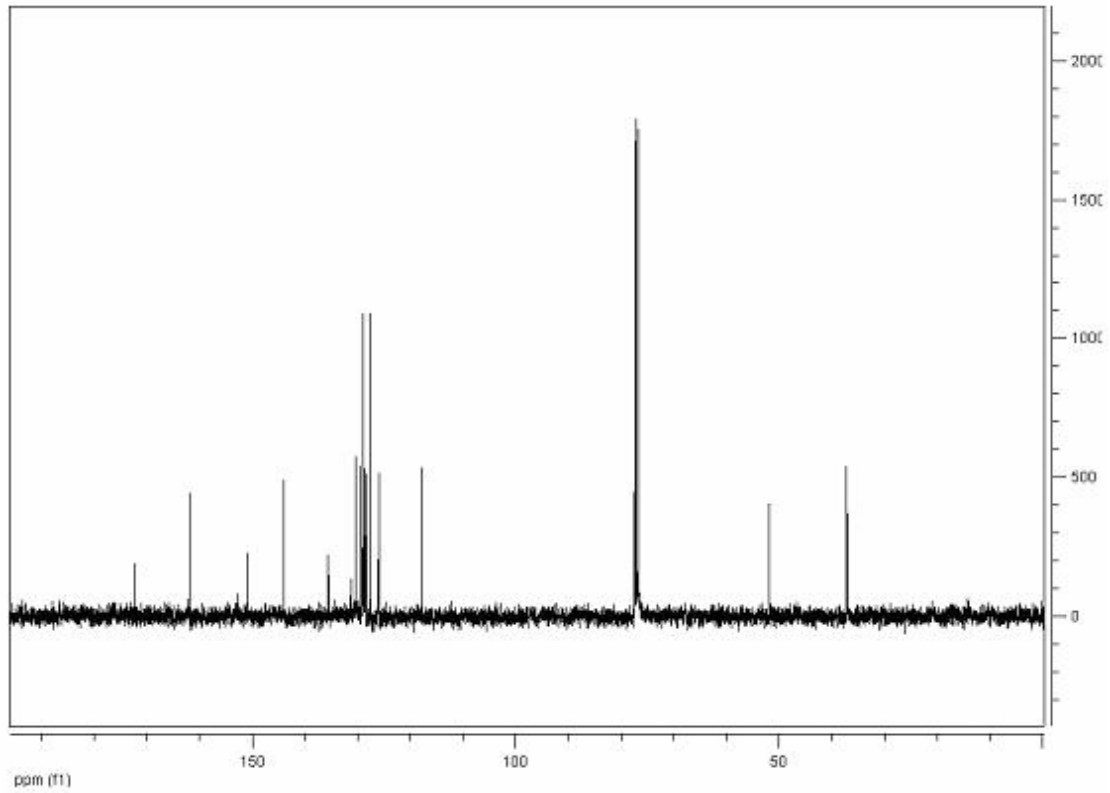
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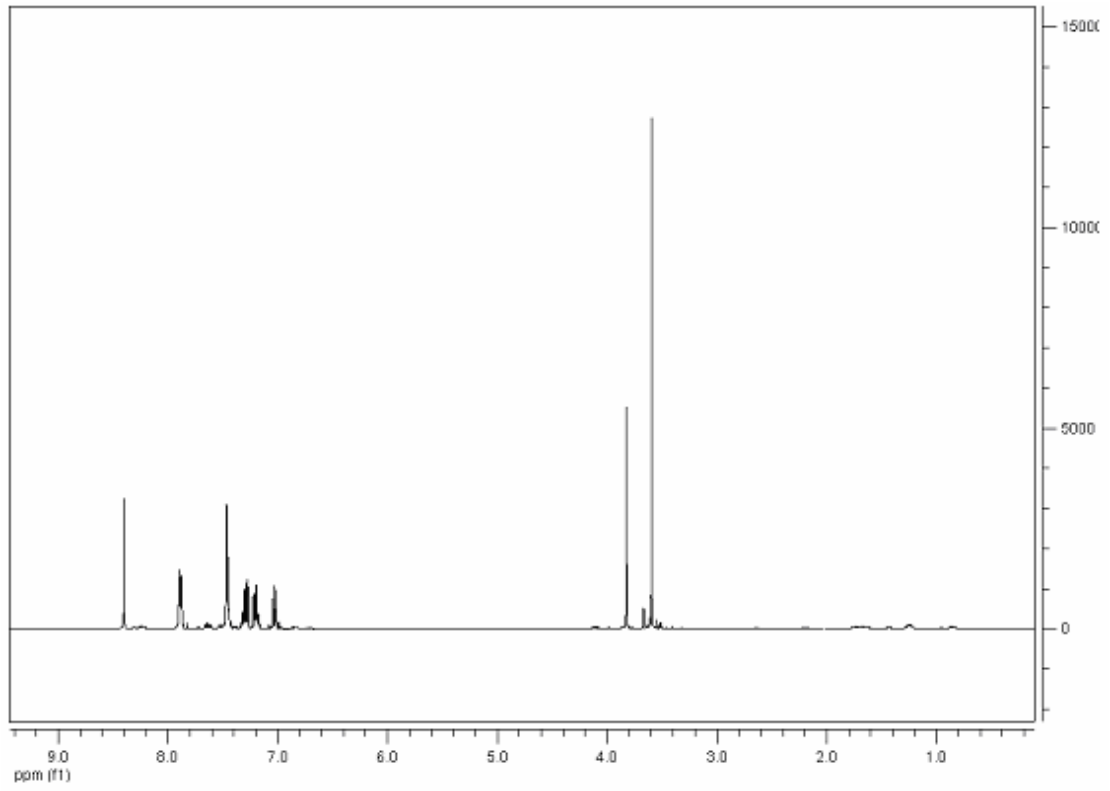
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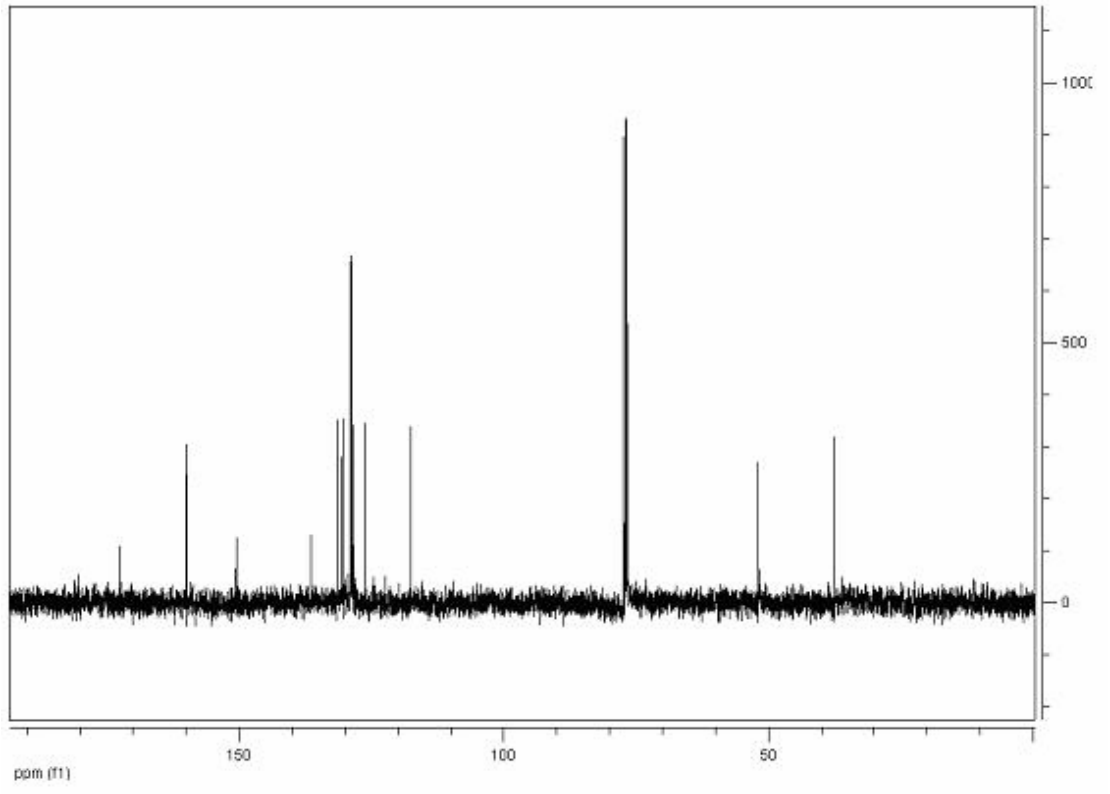
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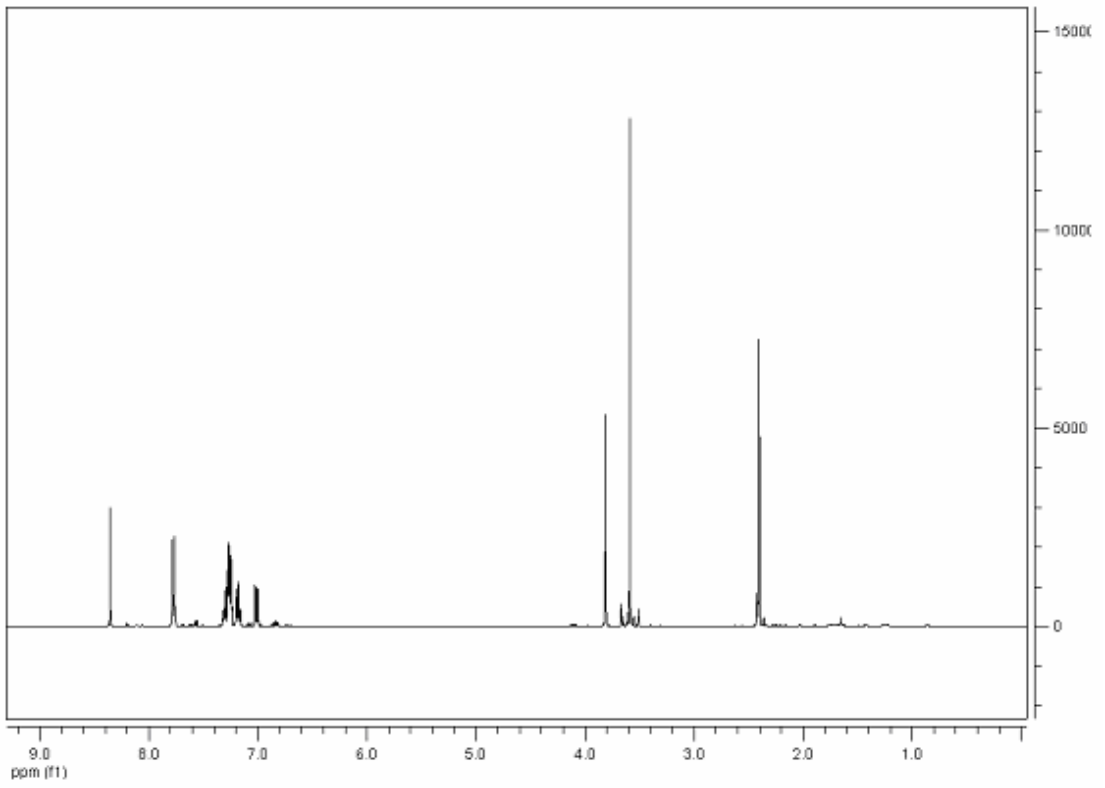
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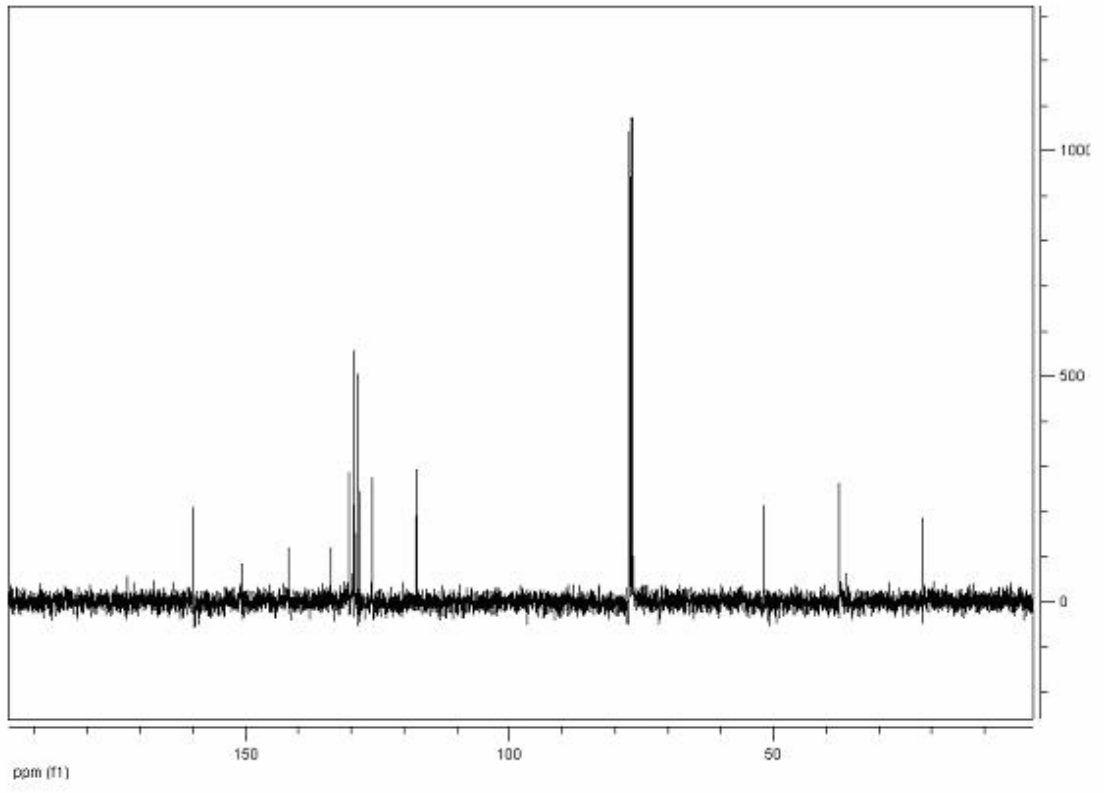
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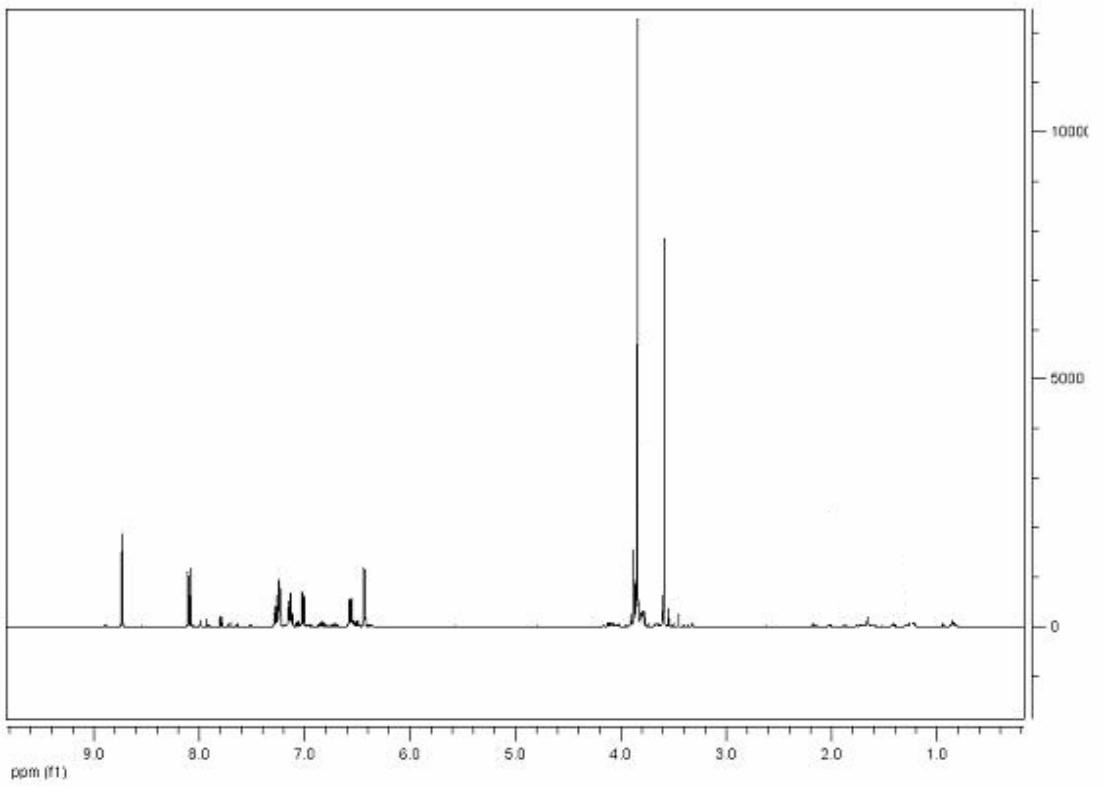
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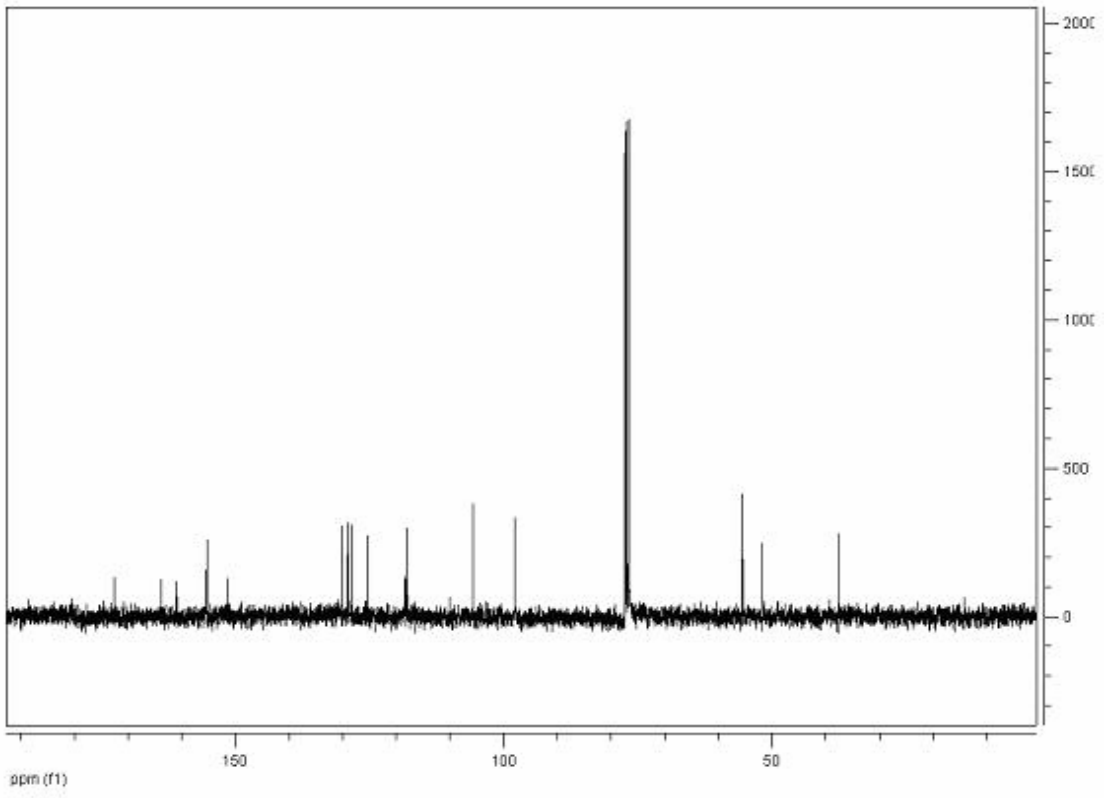
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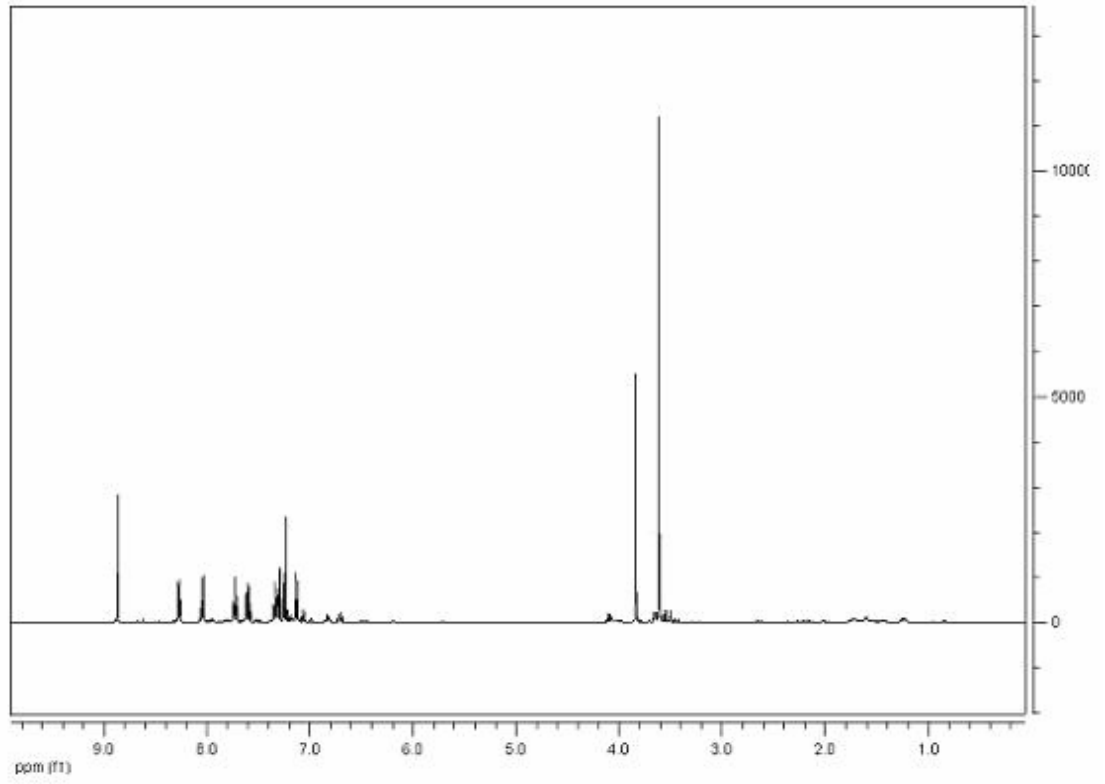
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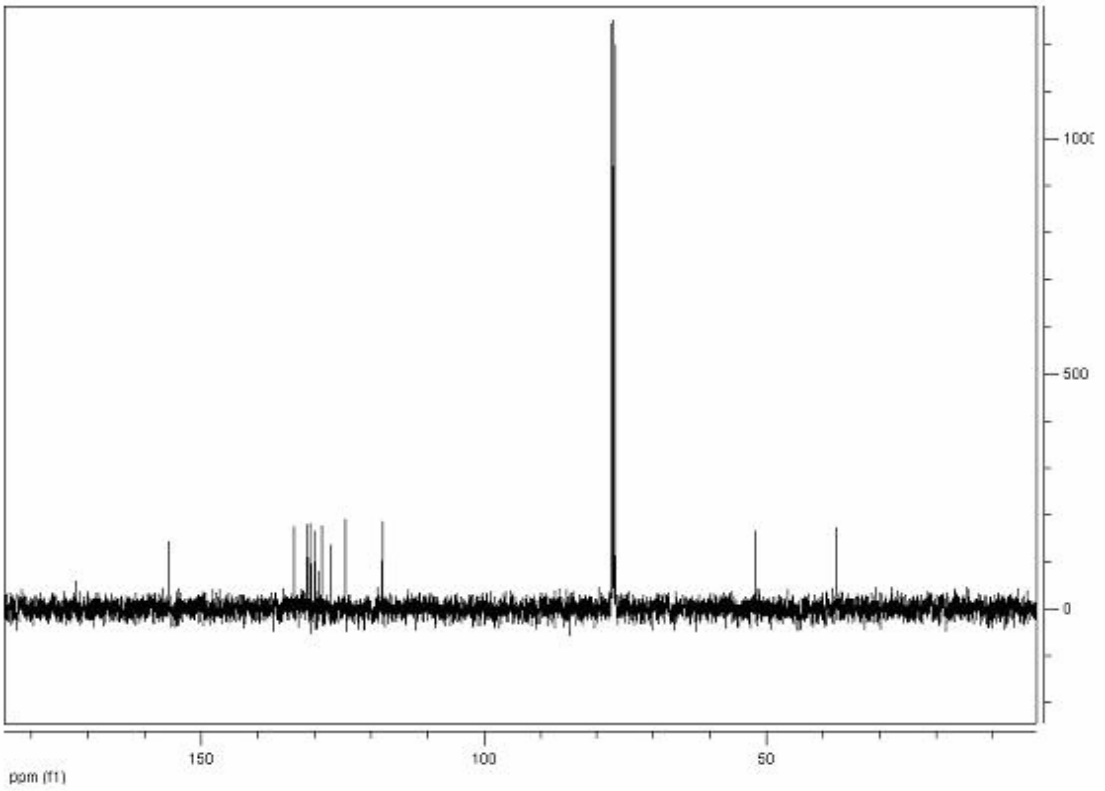
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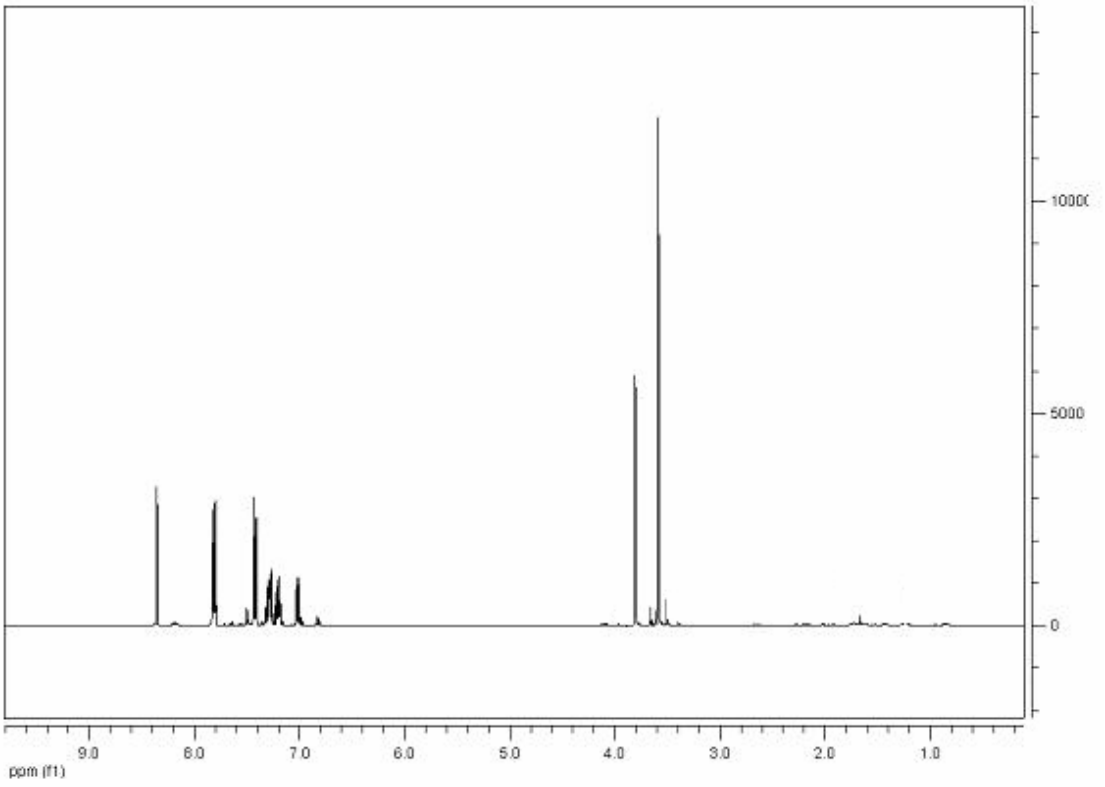
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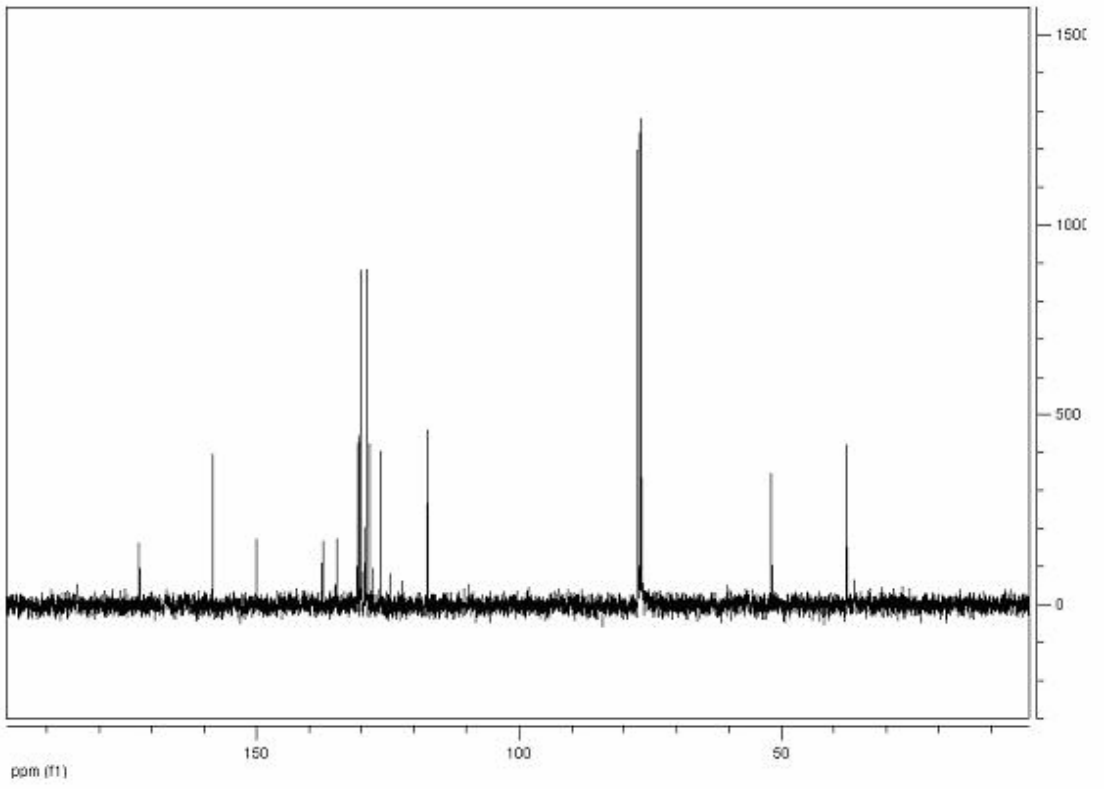
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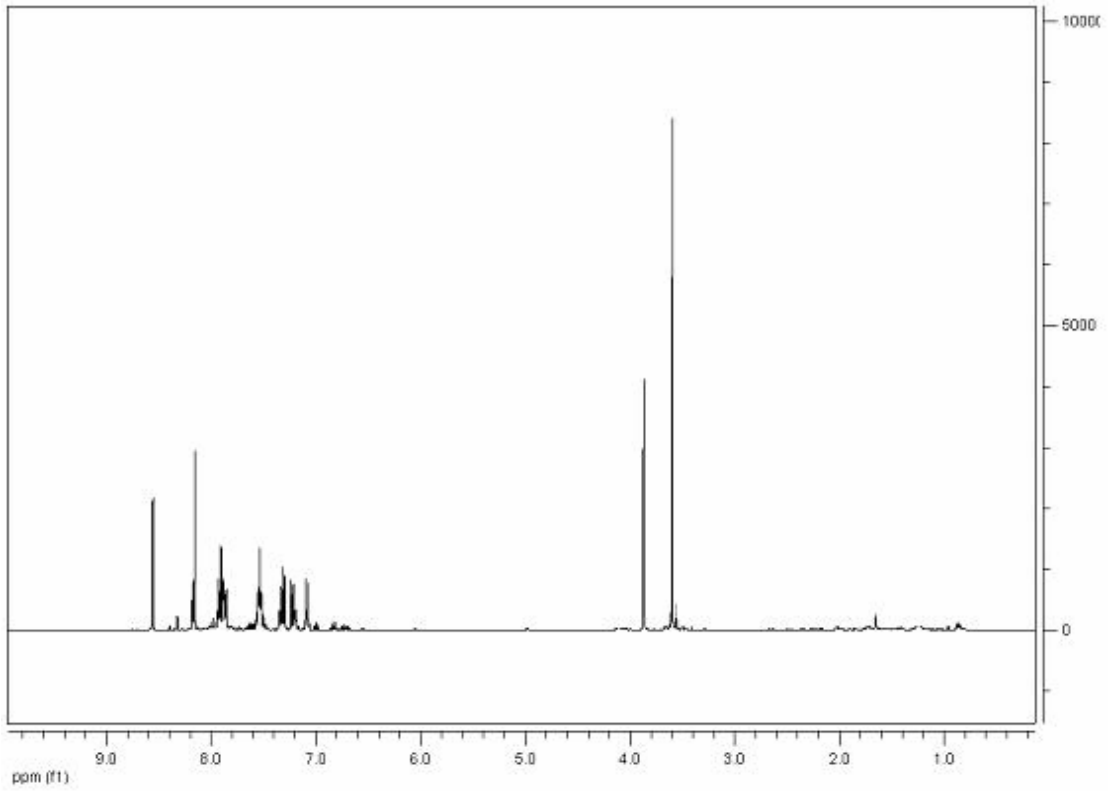
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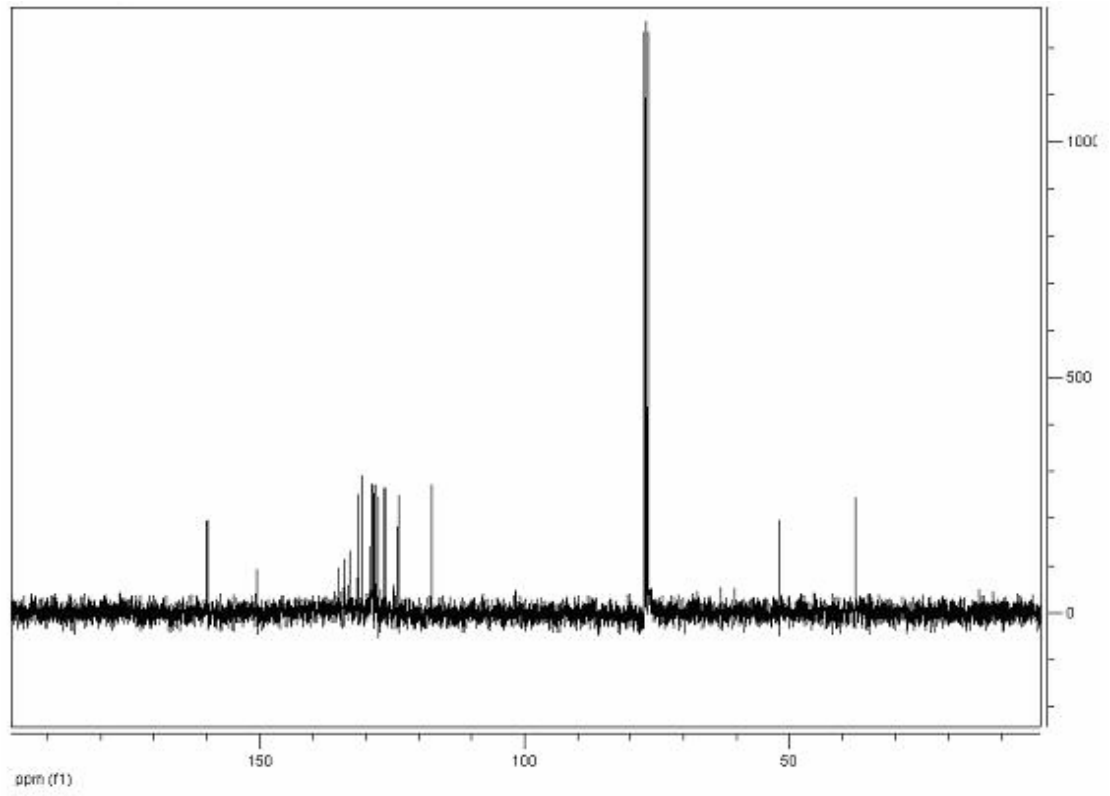
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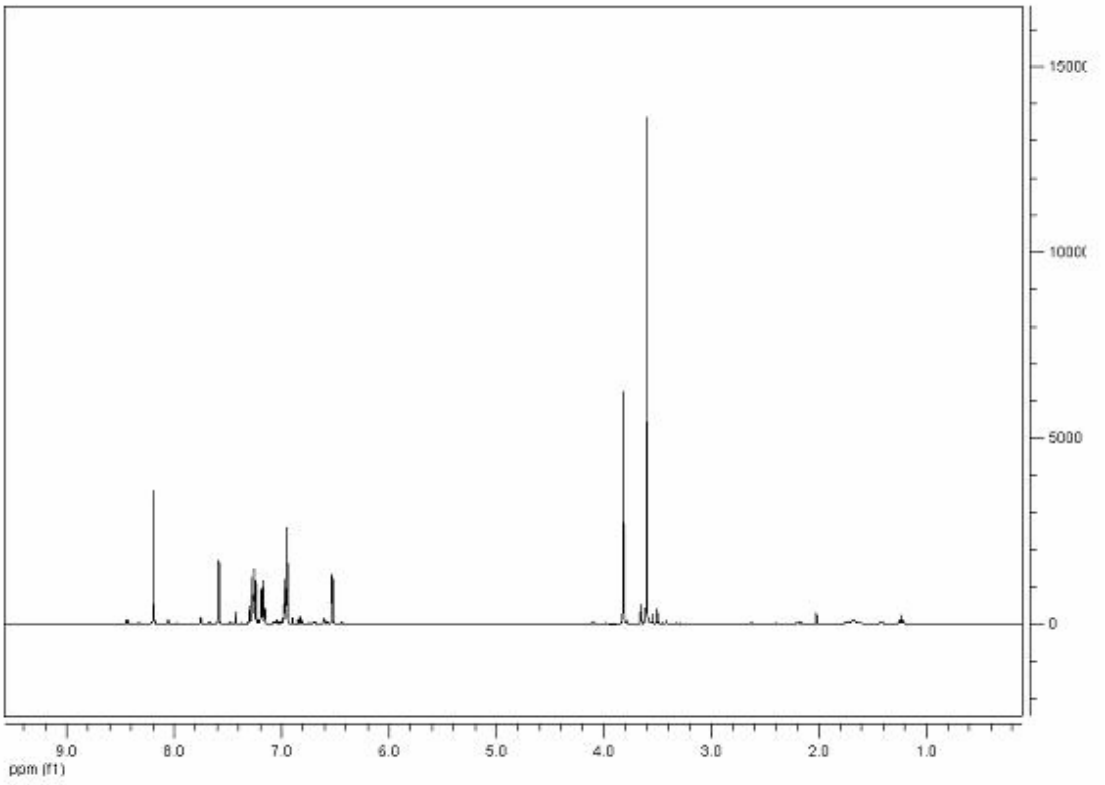
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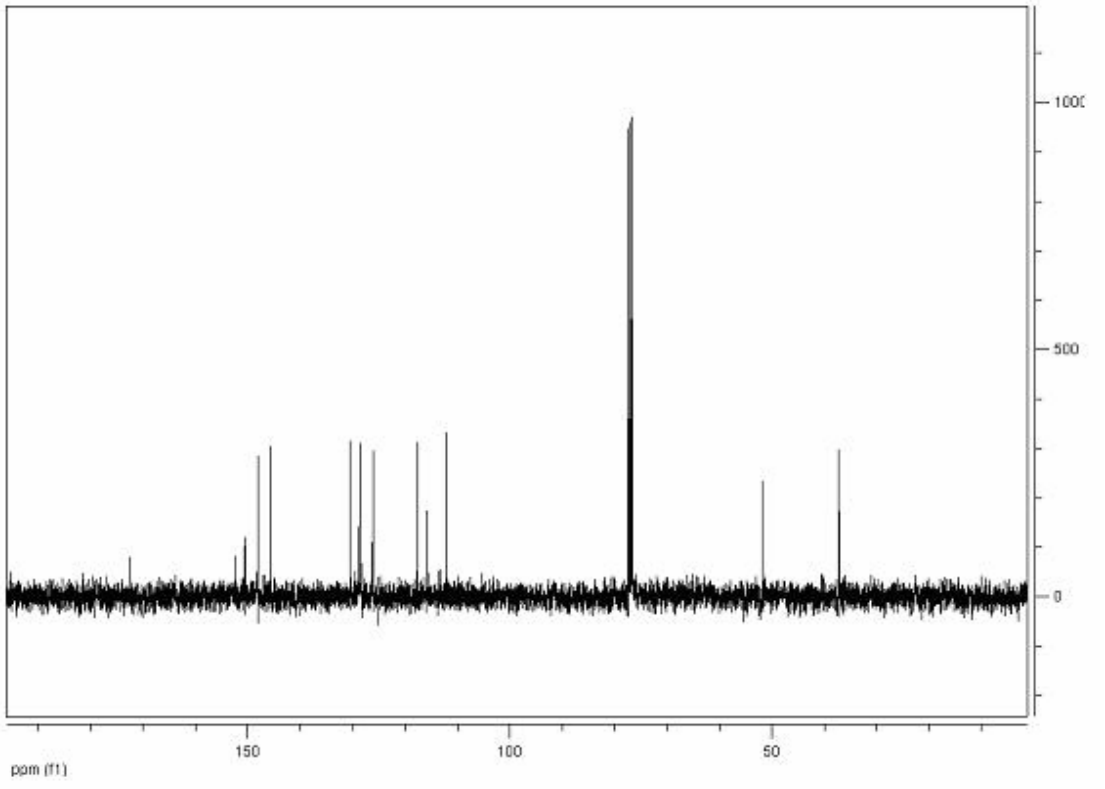
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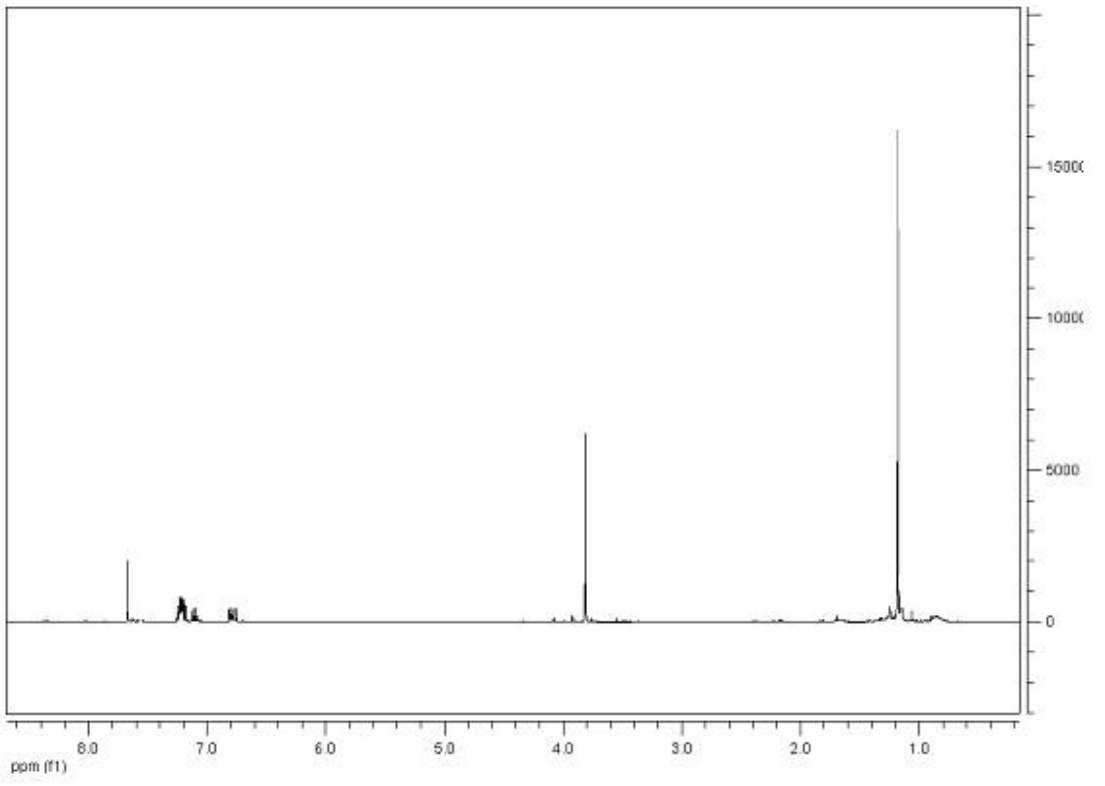
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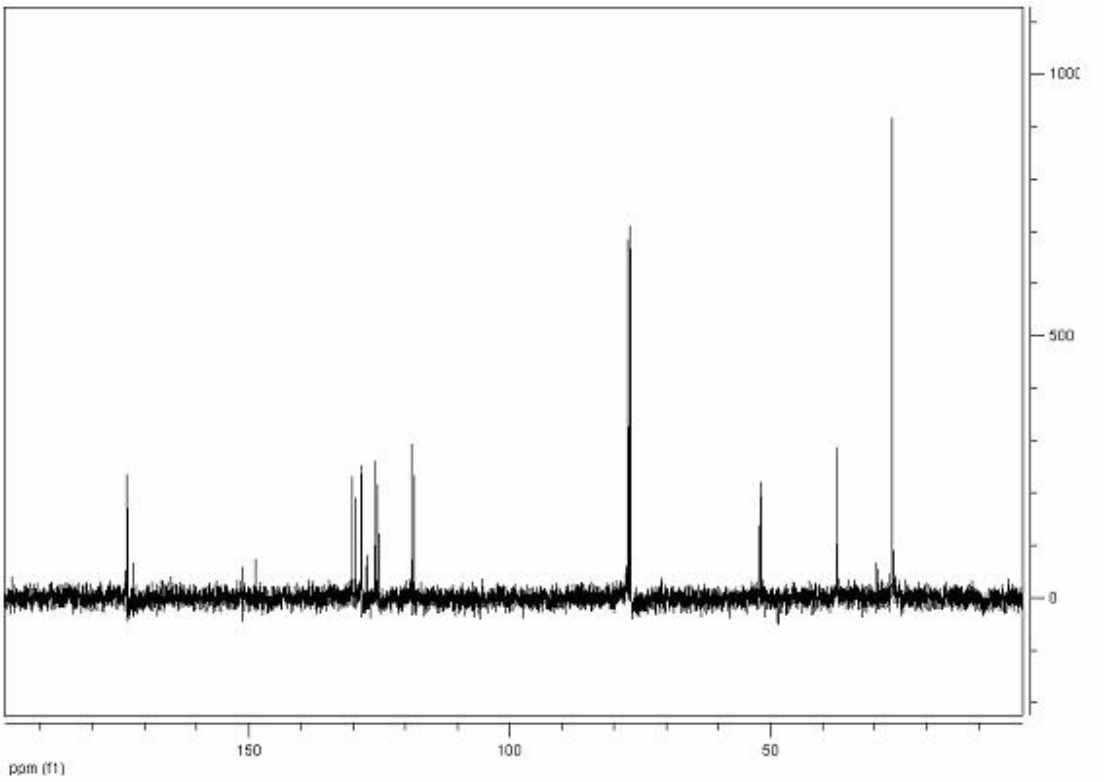
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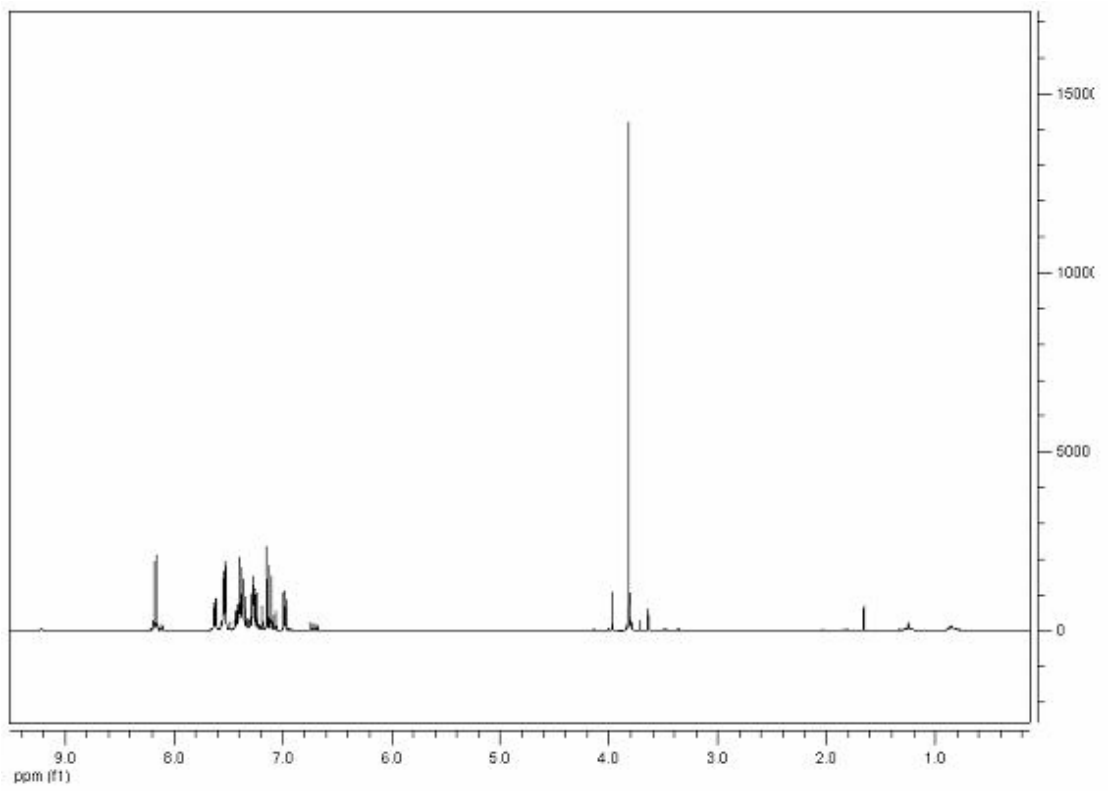
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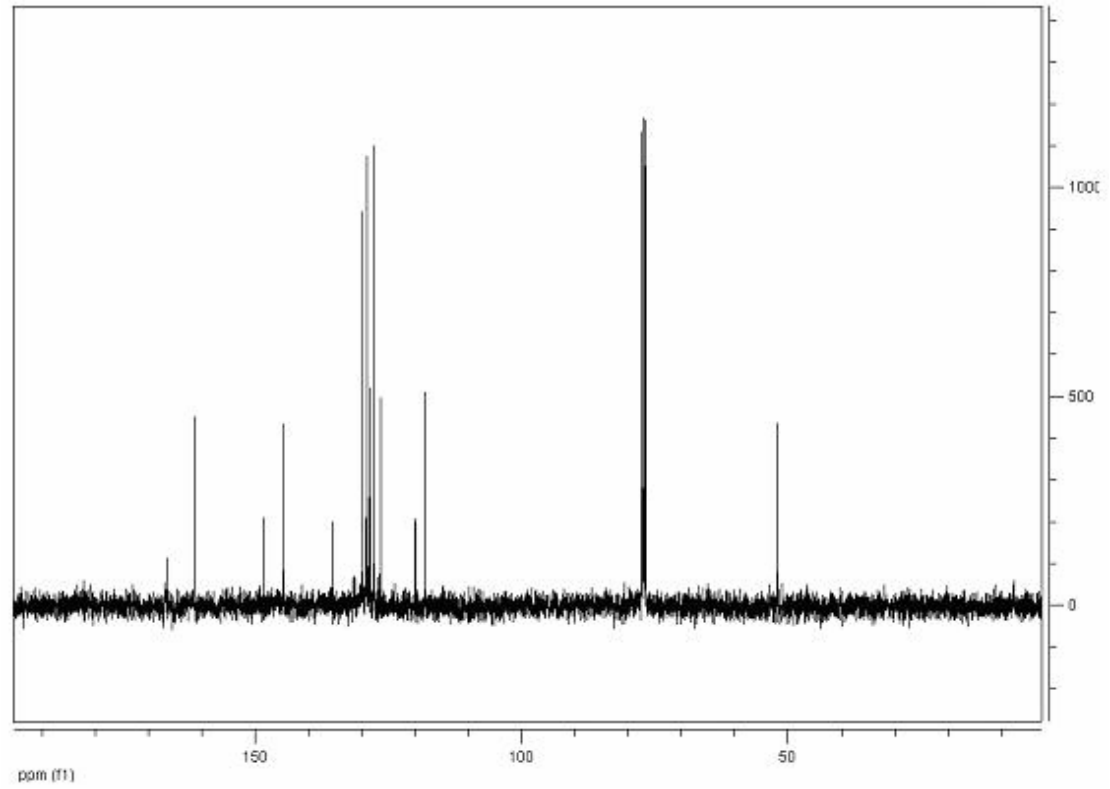
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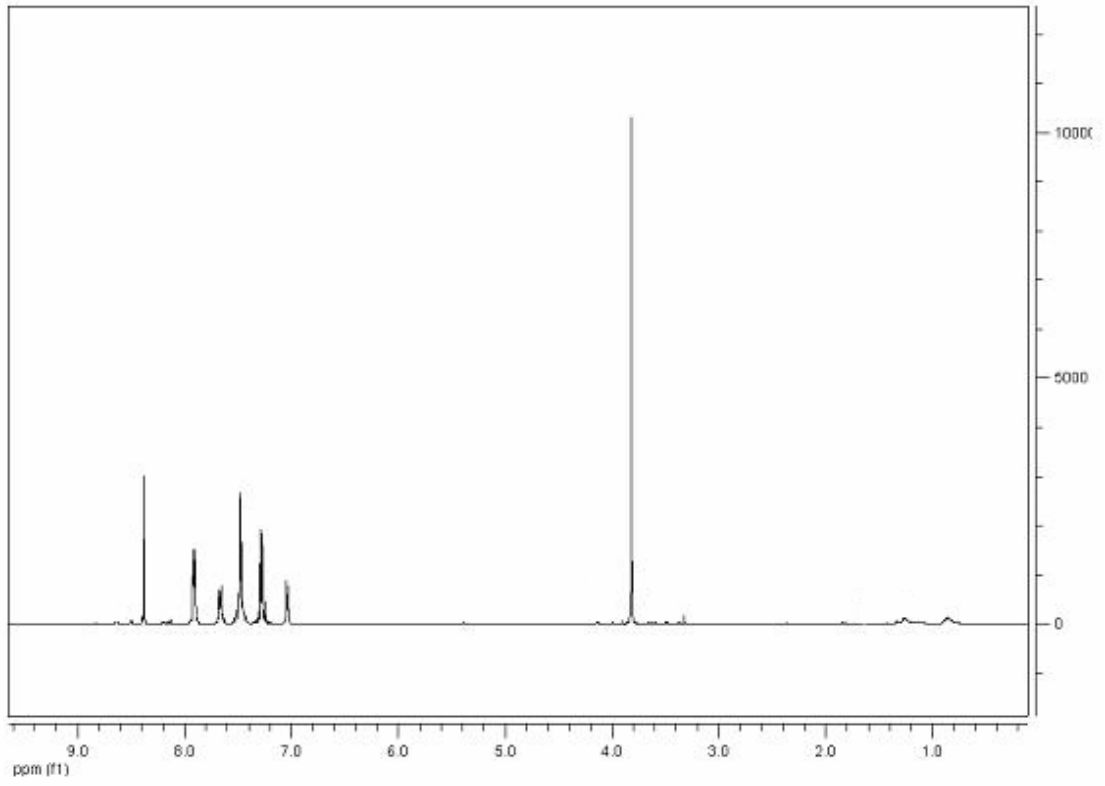
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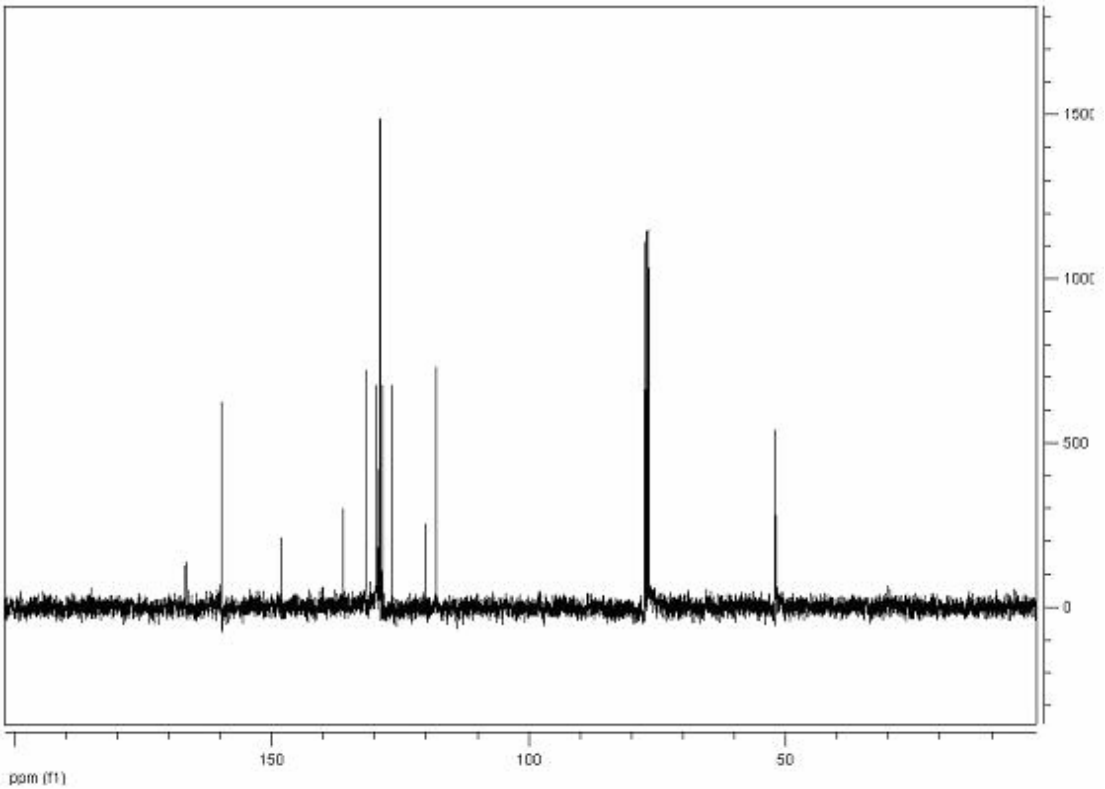
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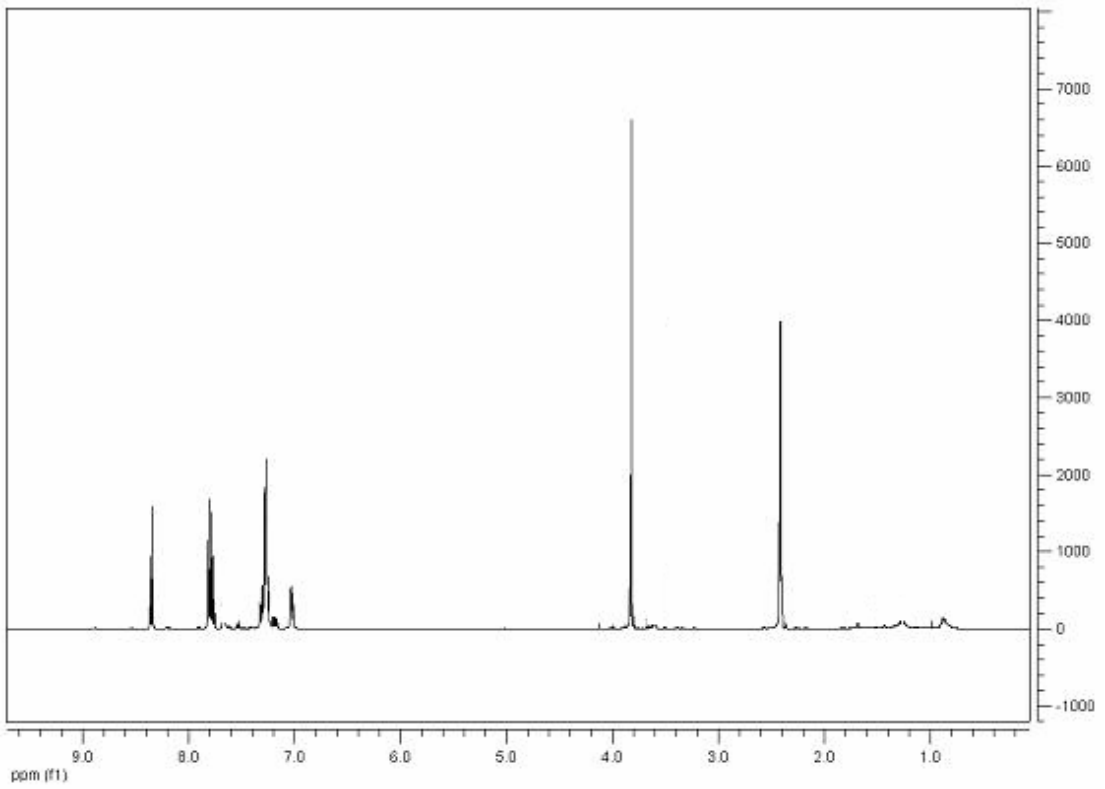
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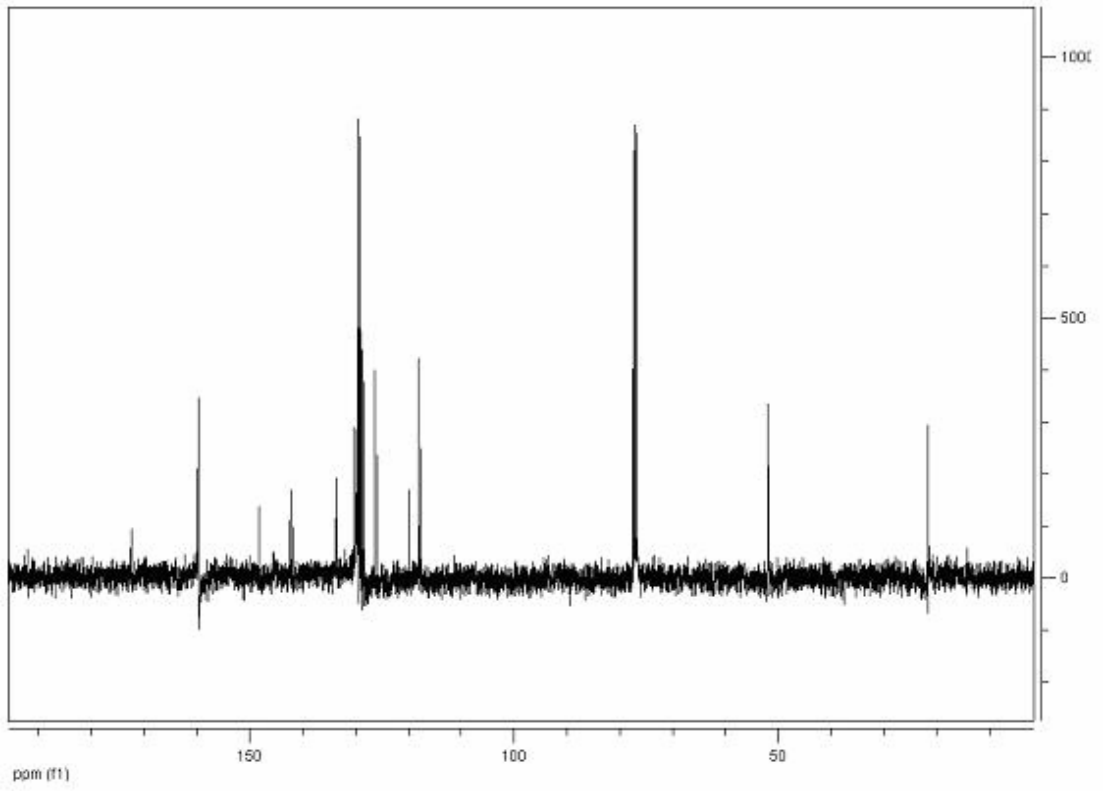
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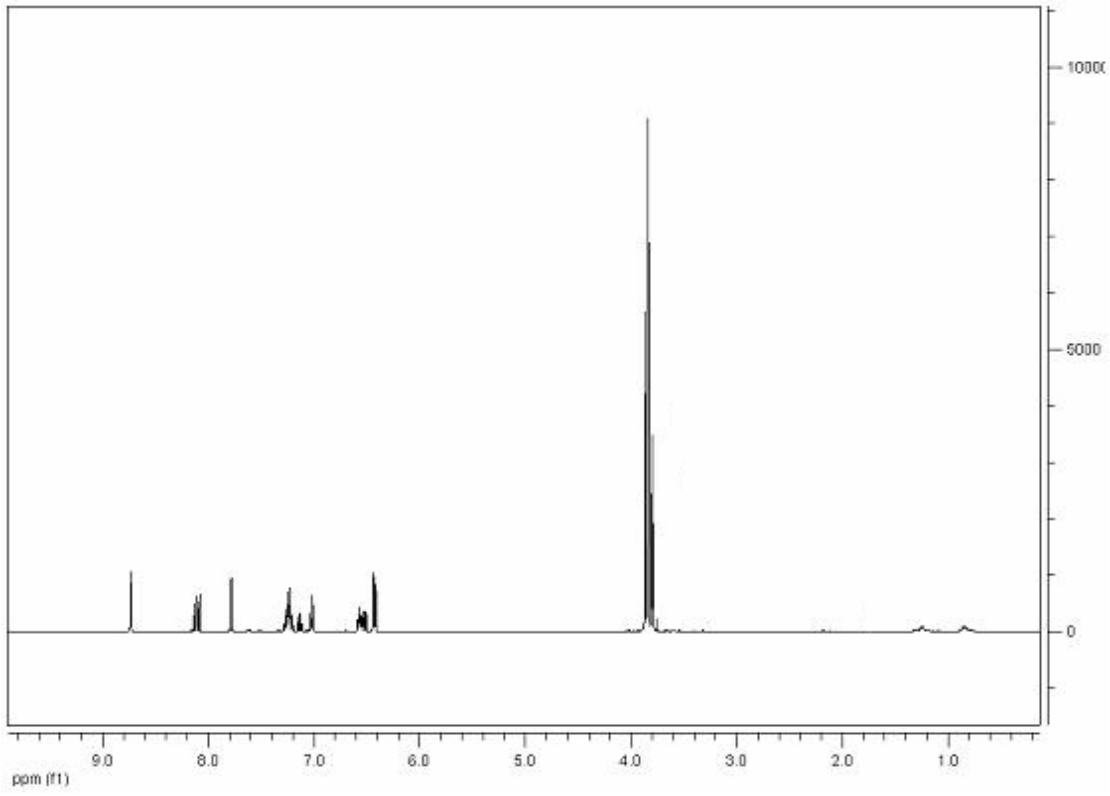
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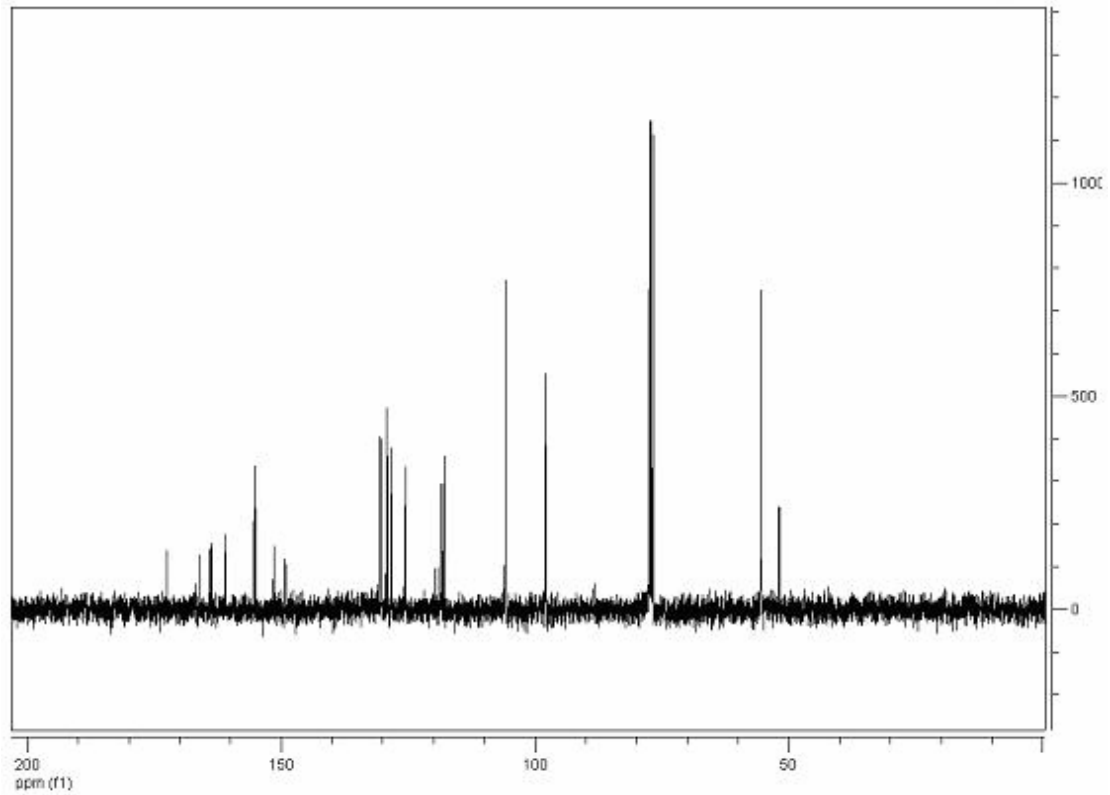
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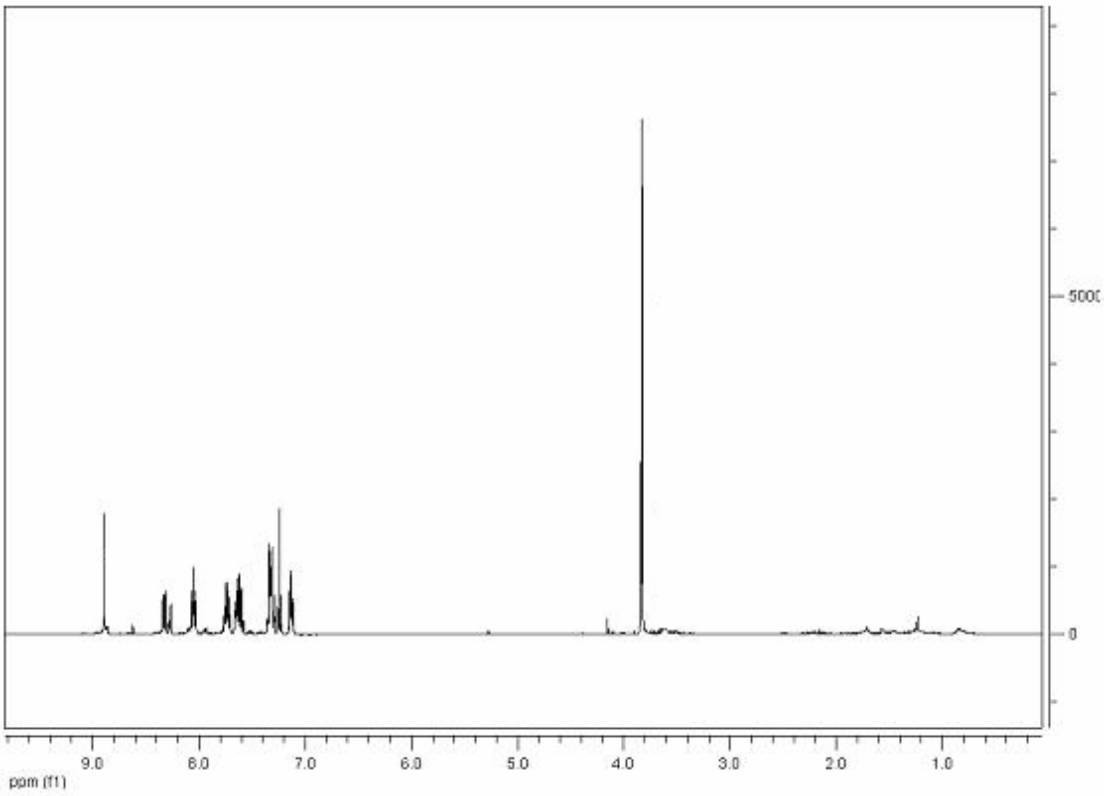
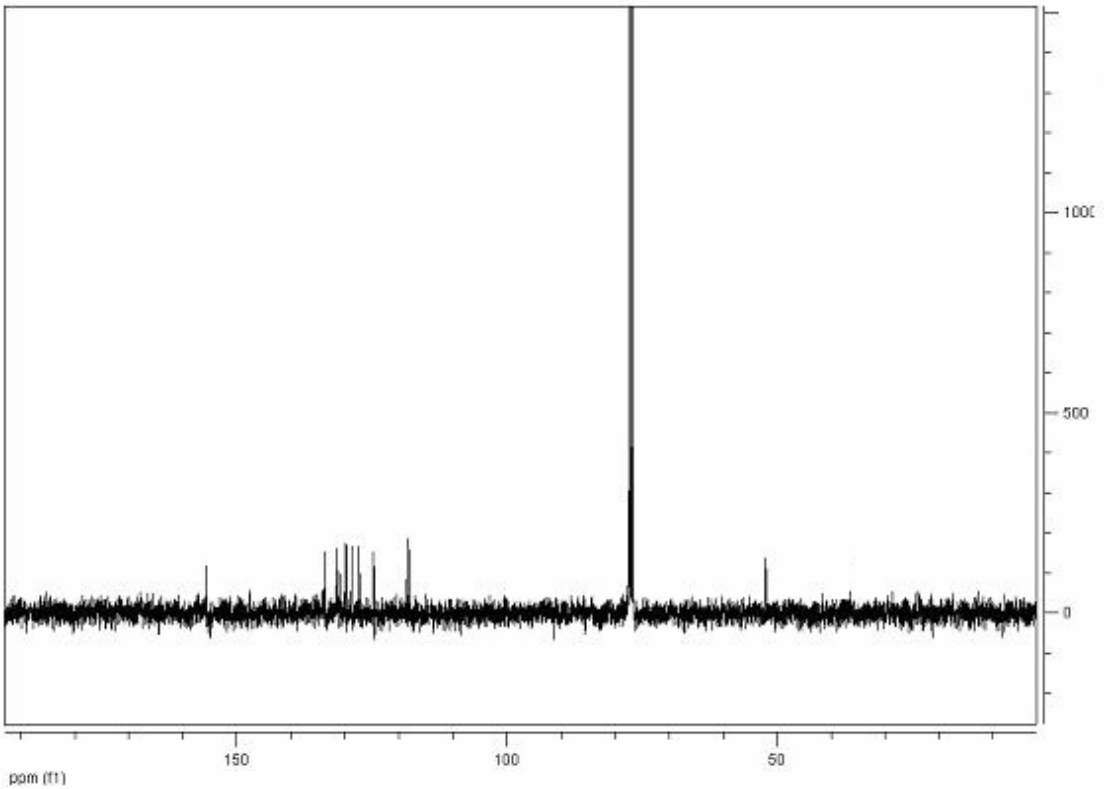
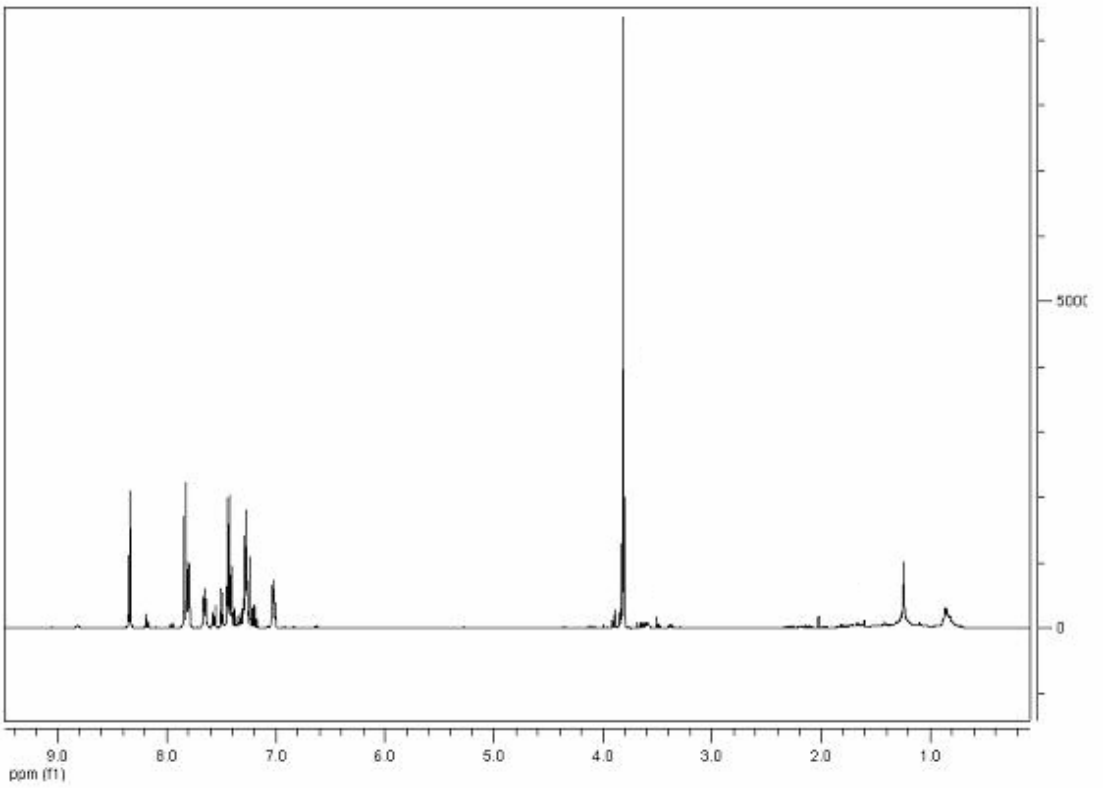
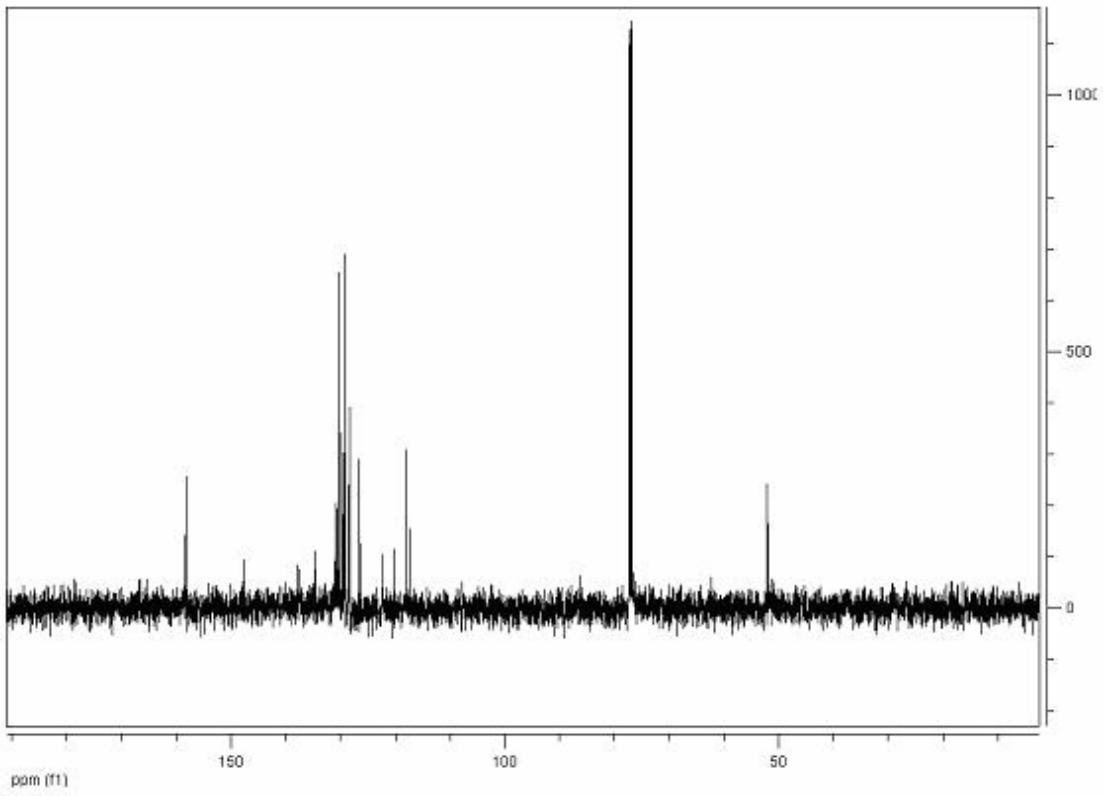


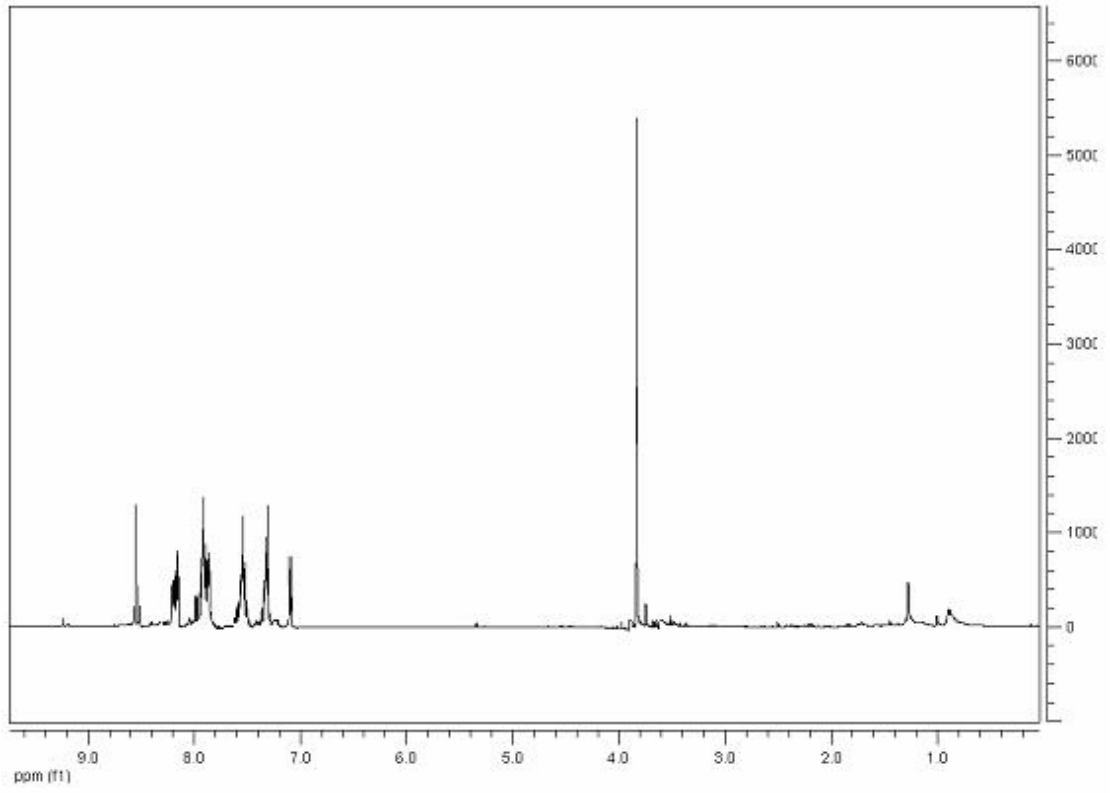


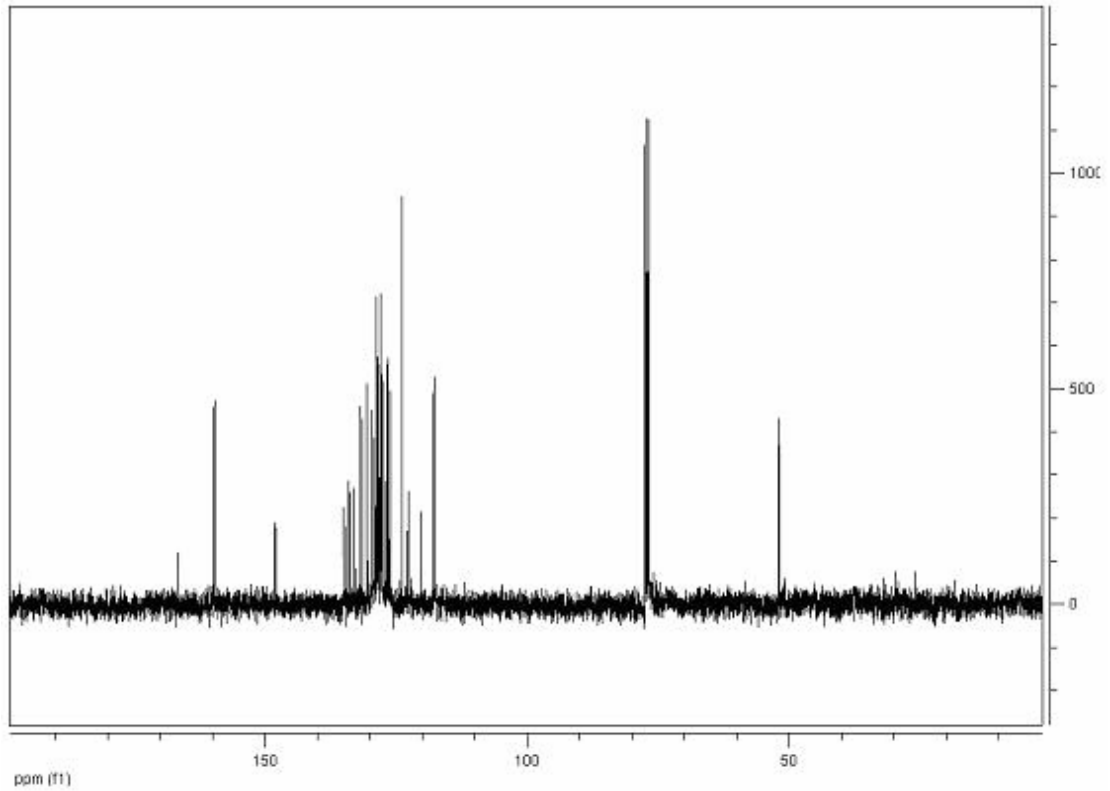
2g



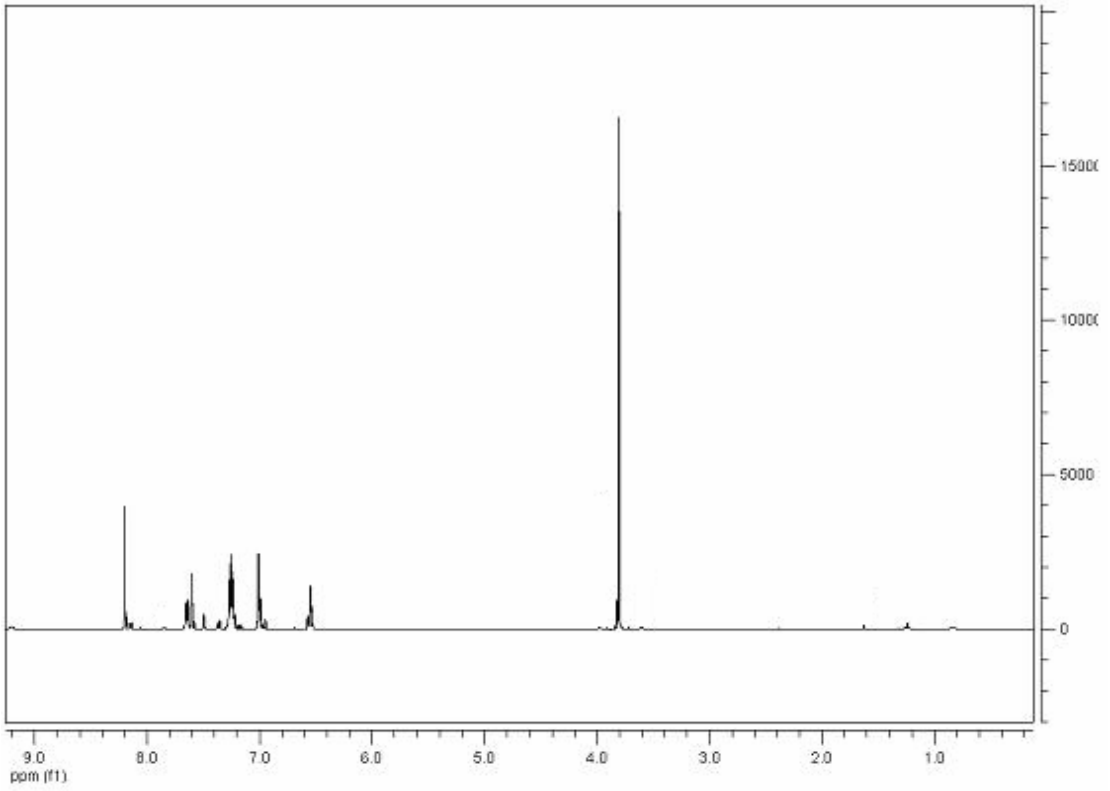


2h





2i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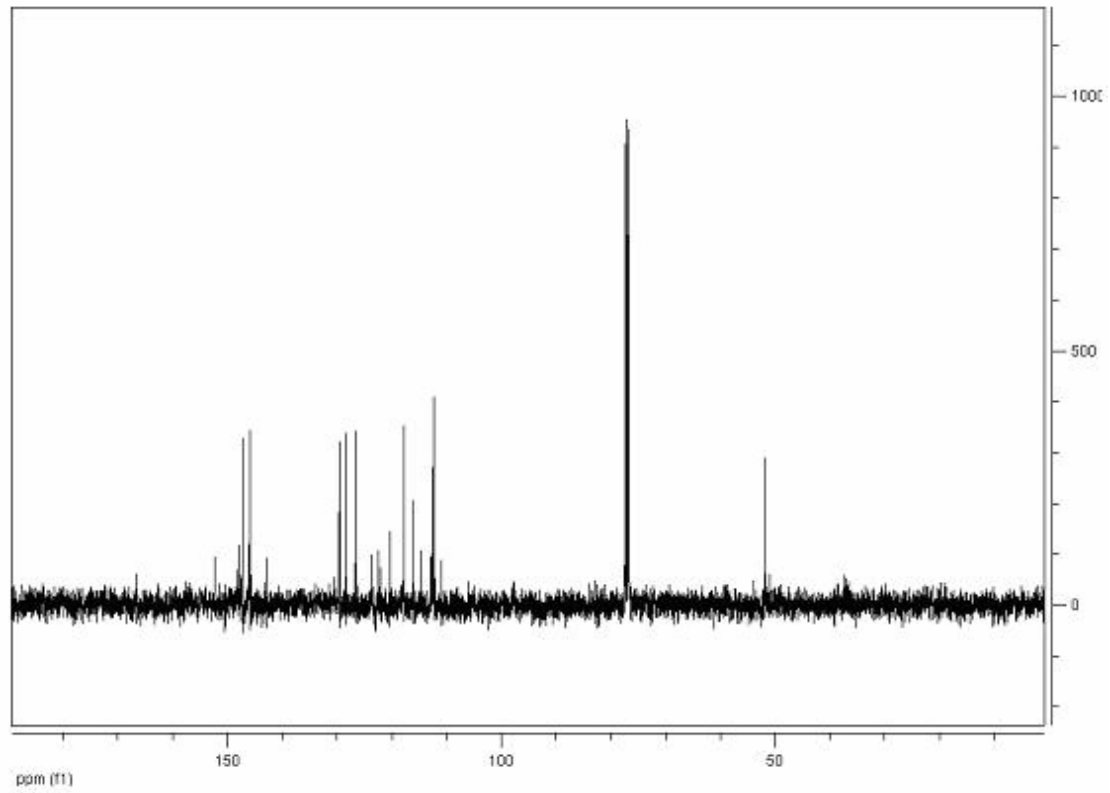
2.0
1.0
ppm (f1)


1000
500
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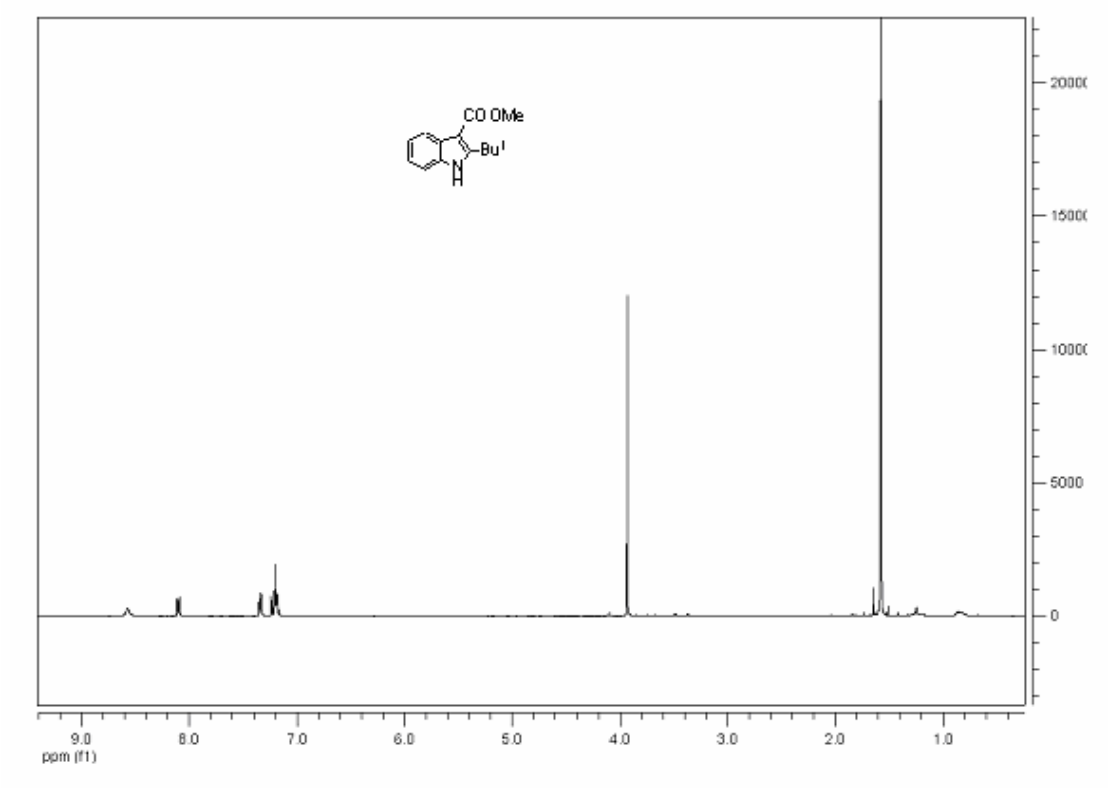
150
100
50
ppm (f1)

3a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Bu^t
N
H
20000
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6.0
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3.0
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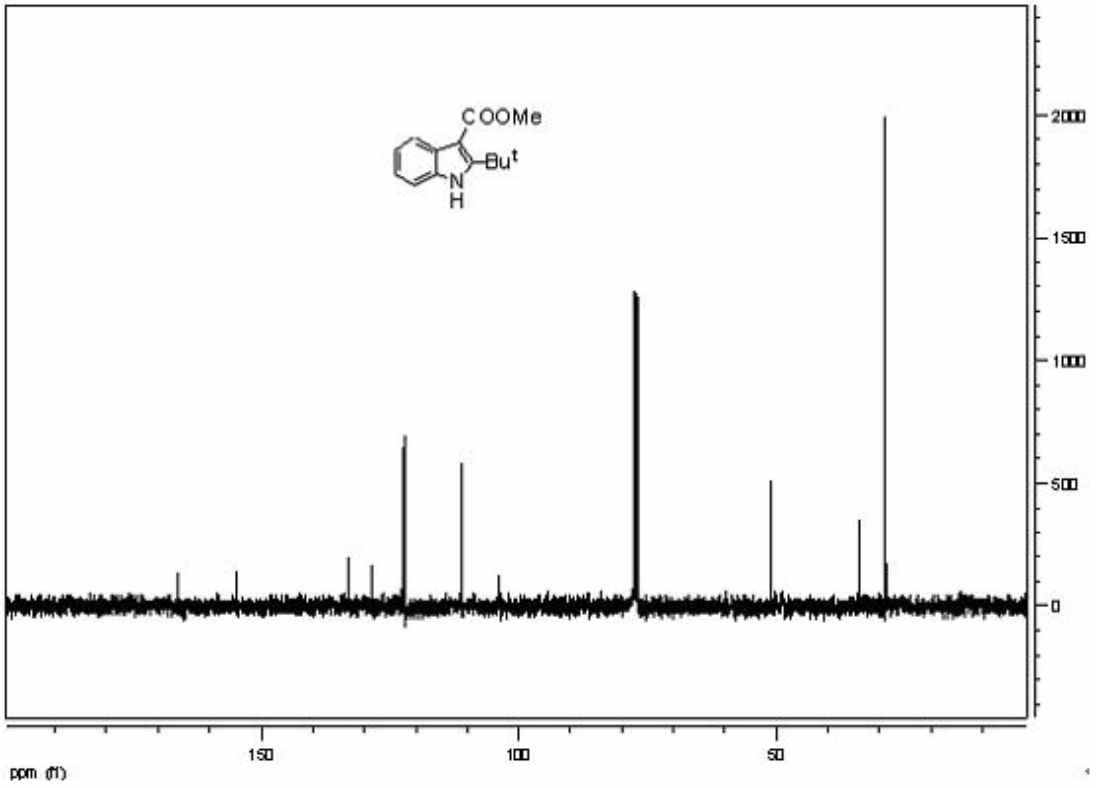
1.0
ppm (f1)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Bu^t
N
H
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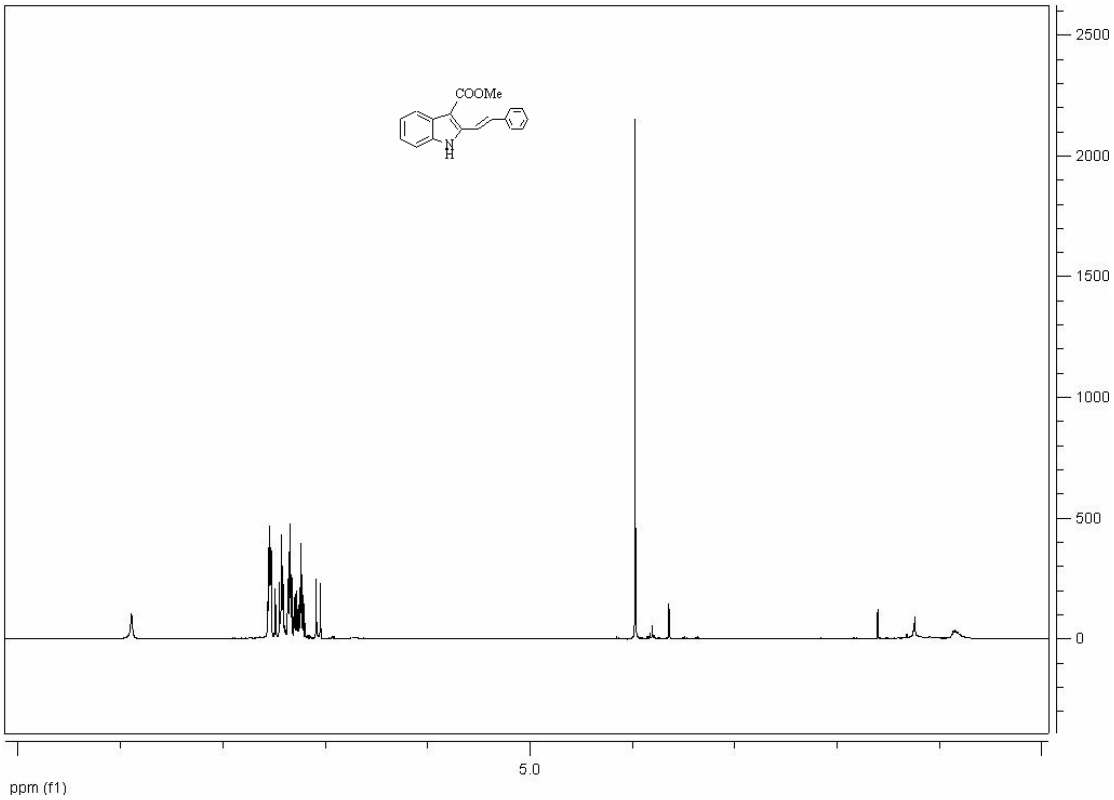
1500
1000
500
0
150
100
50
ppm (f1)

3b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H
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2000
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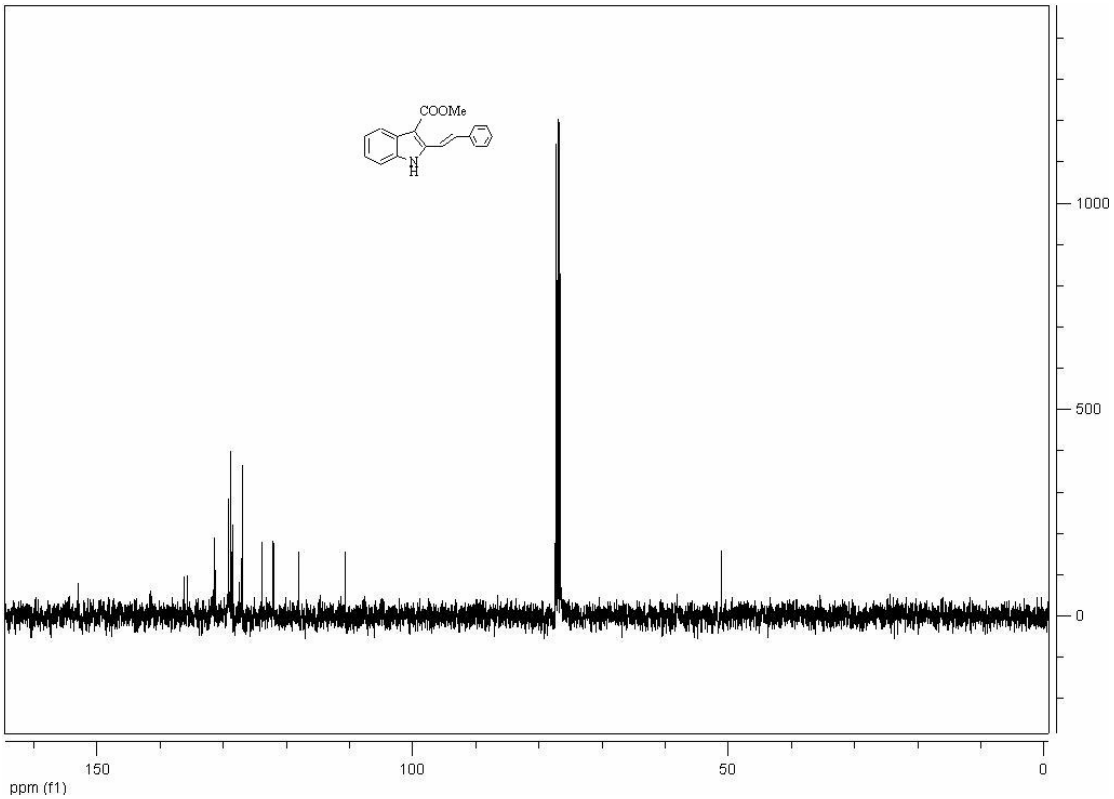
ppm (f1)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H
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500
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150
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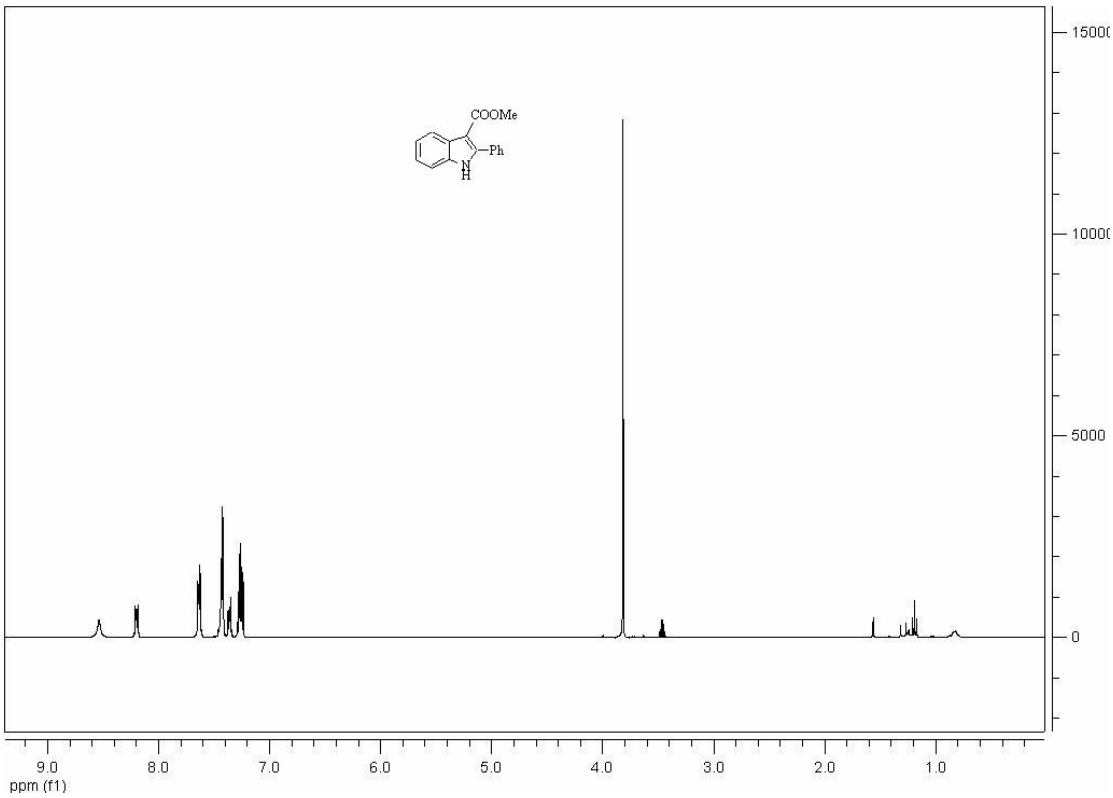
50
0
ppm (f1)

3c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Ph
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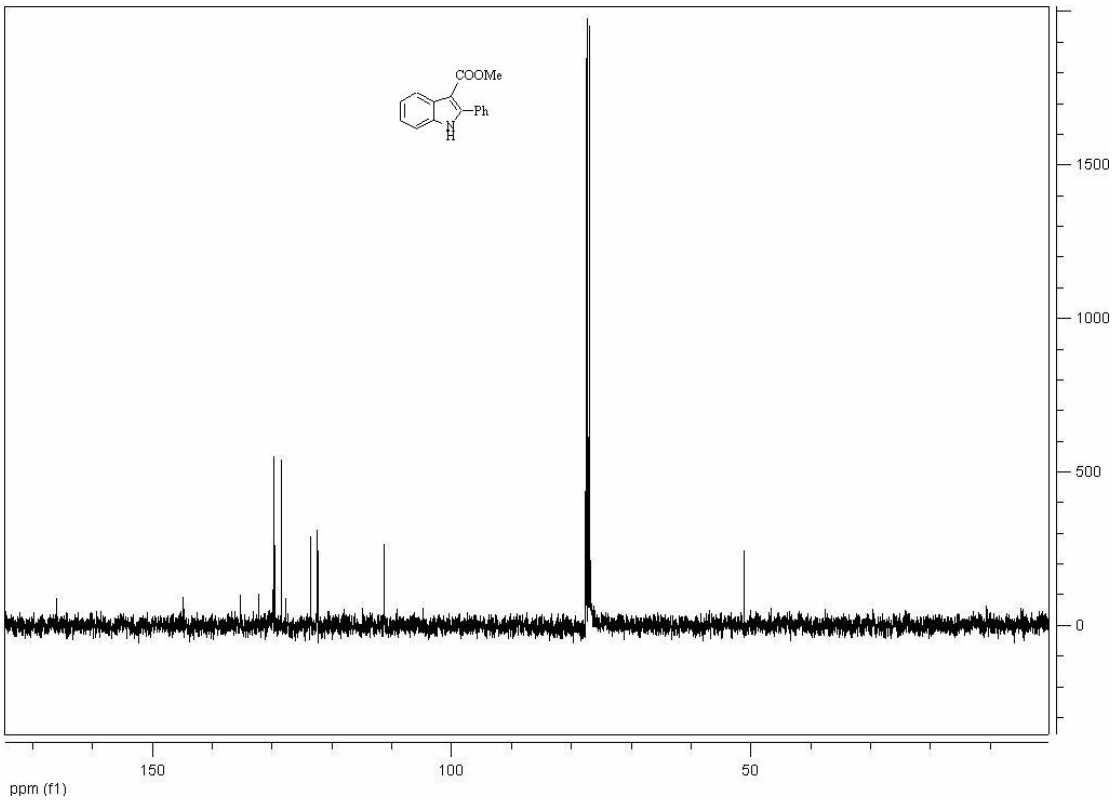
1.0
ppm (f1)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Ph
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H
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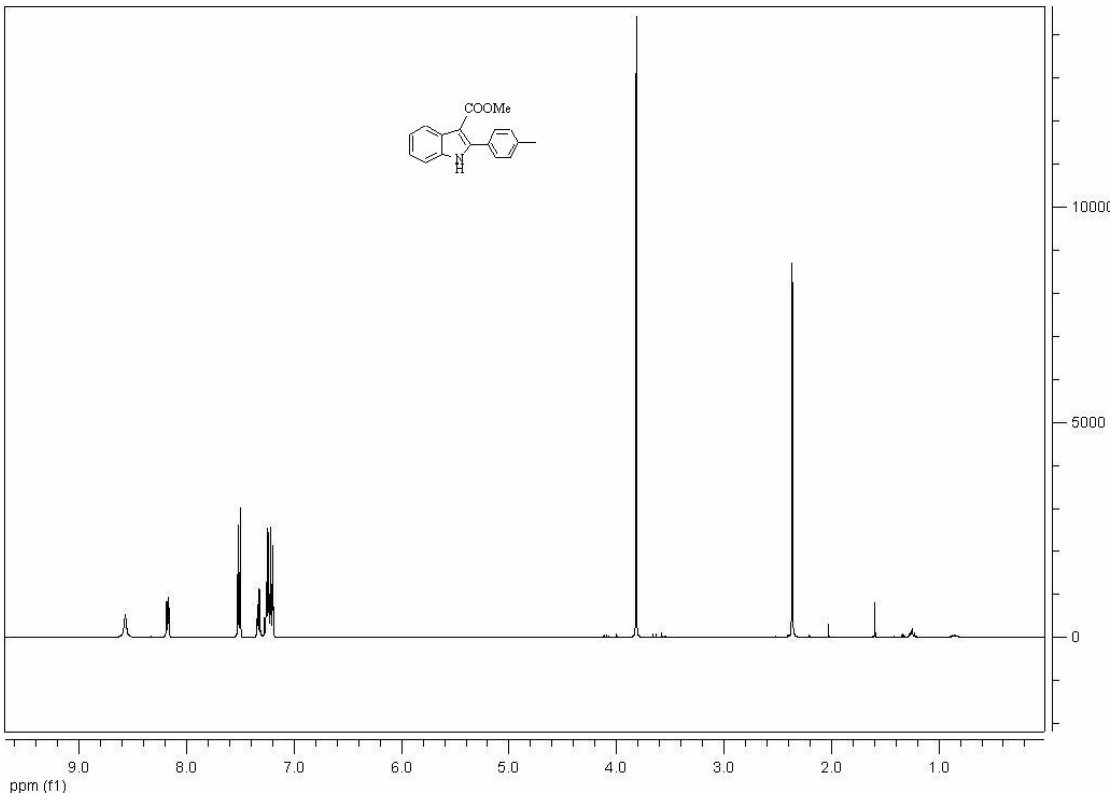
150
100
50
ppm (f1)

3d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N
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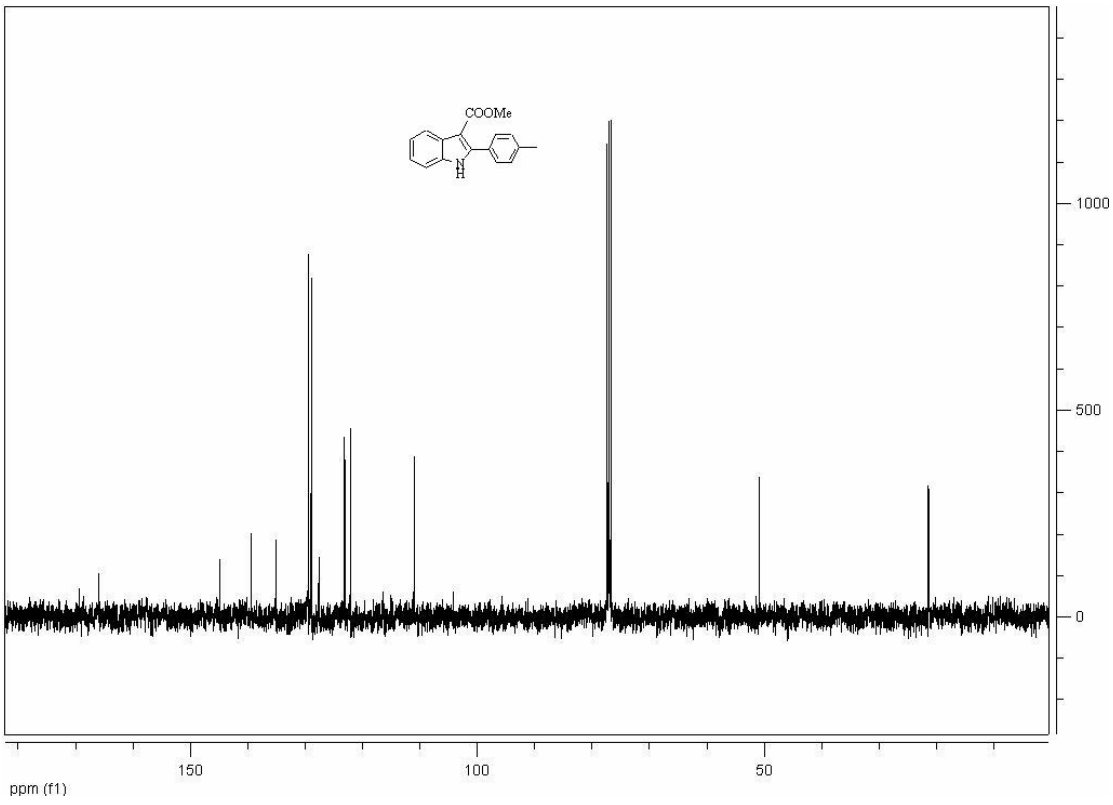
1.0
ppm (f1)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N
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500
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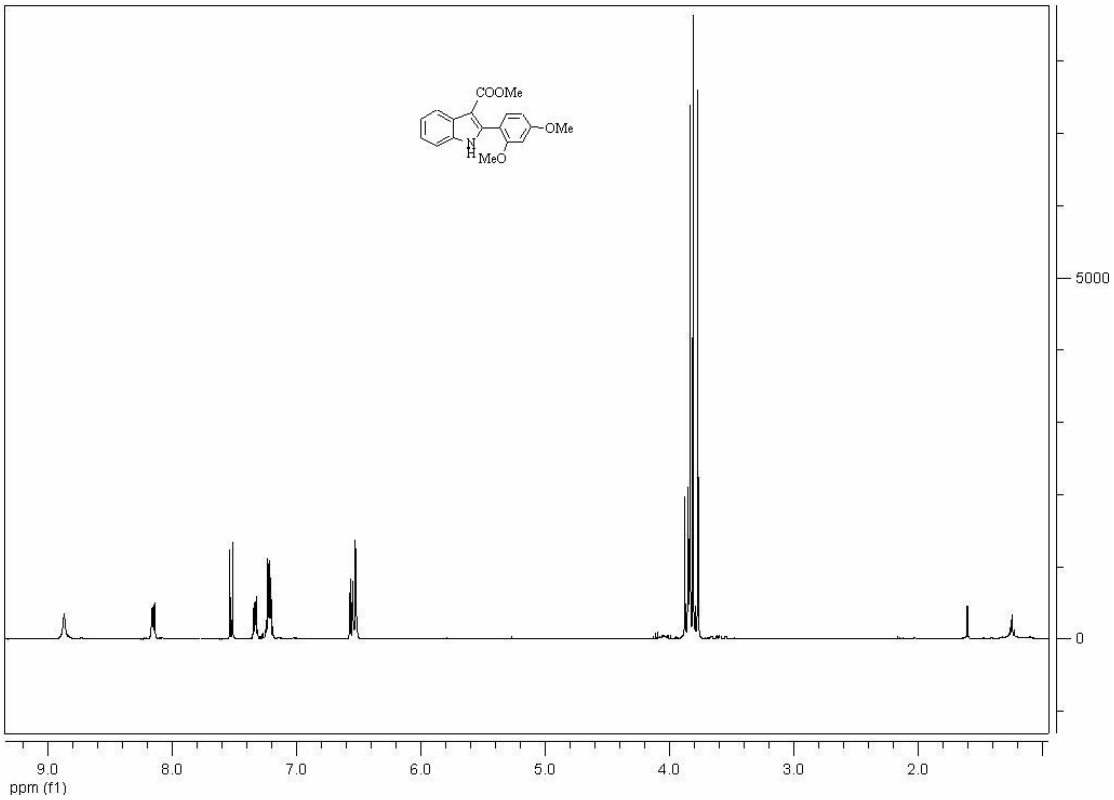
150
100
50
ppm (f1)

3e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OMe
MeO
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7.0
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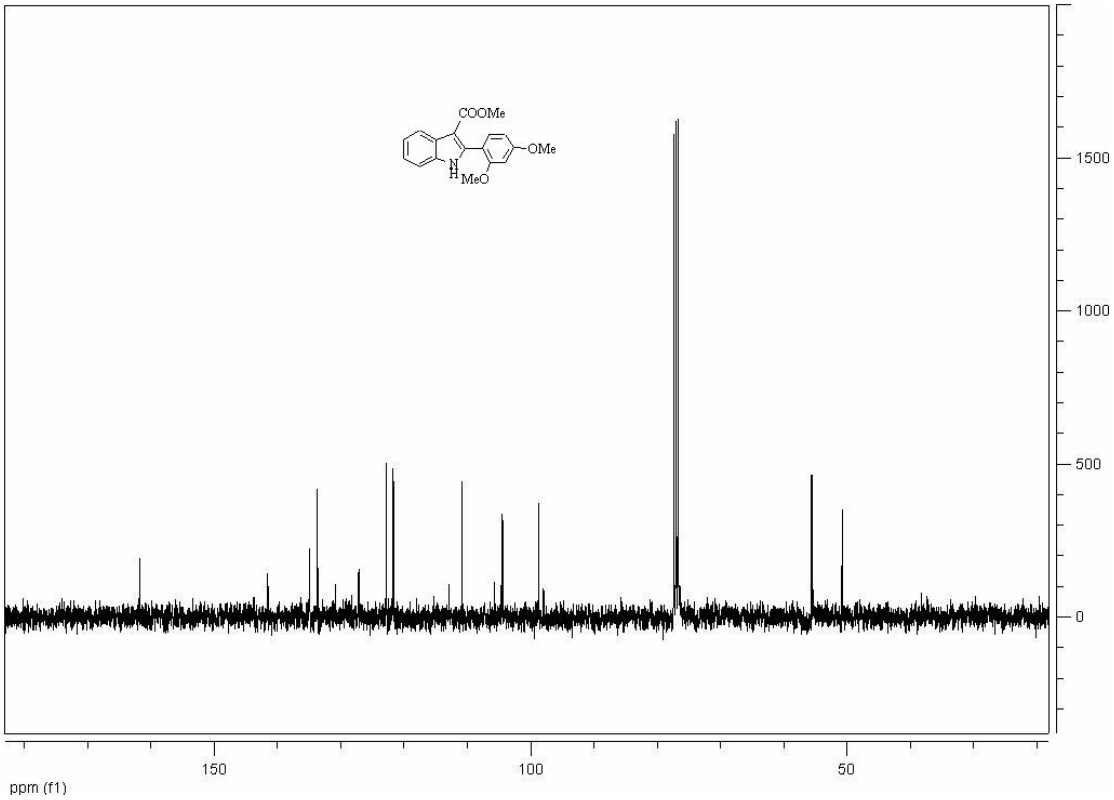
3.0
2.0
ppm (f1)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OMe
MeO
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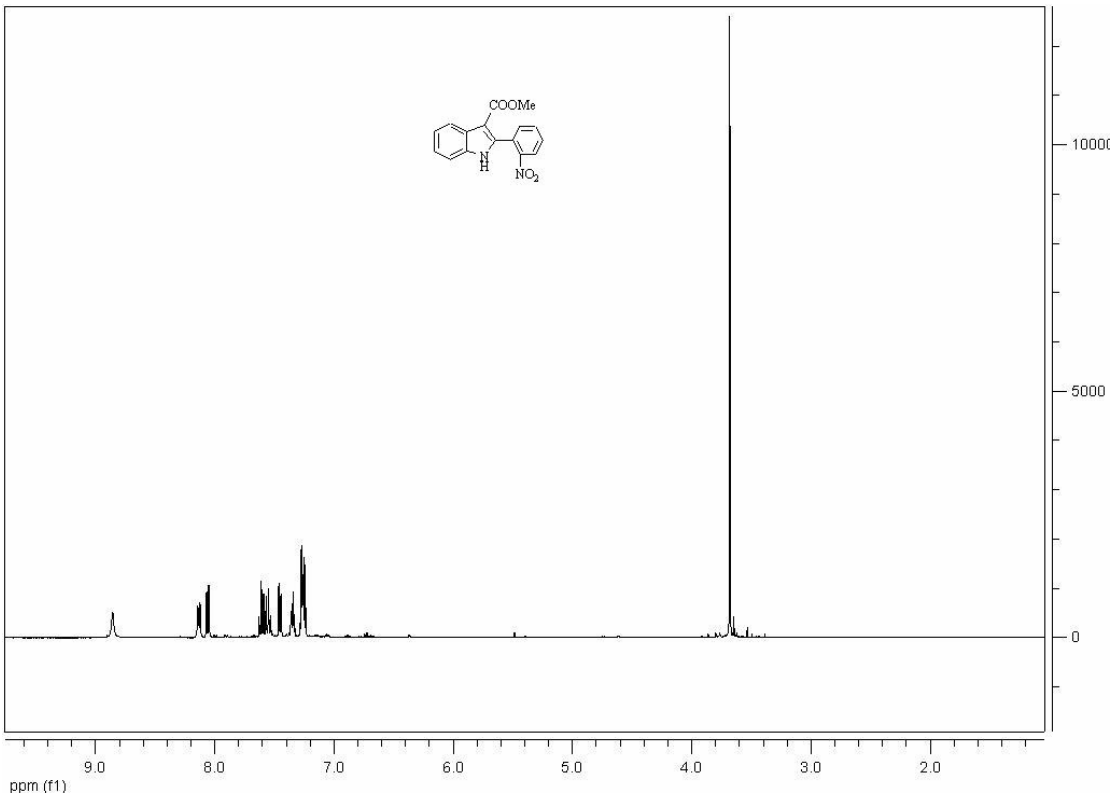
1000
500
0
150
100
50
ppm (f1)

3f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7.0
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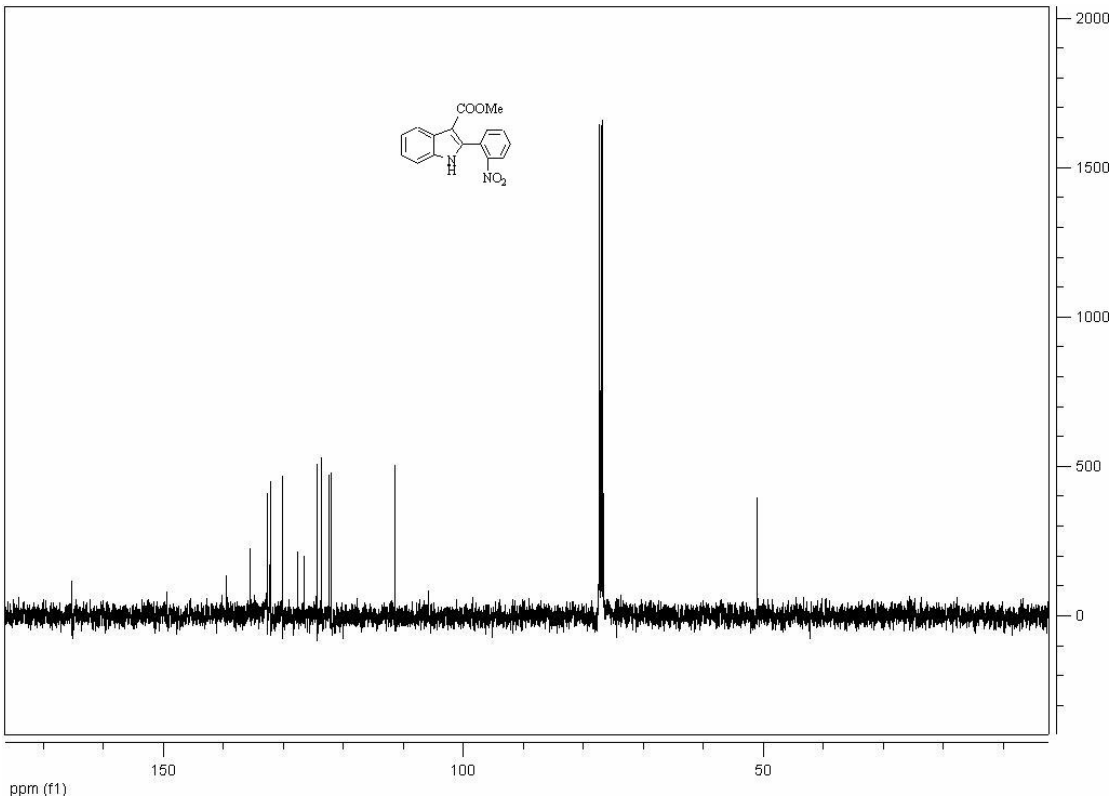
2.0
ppm (f1)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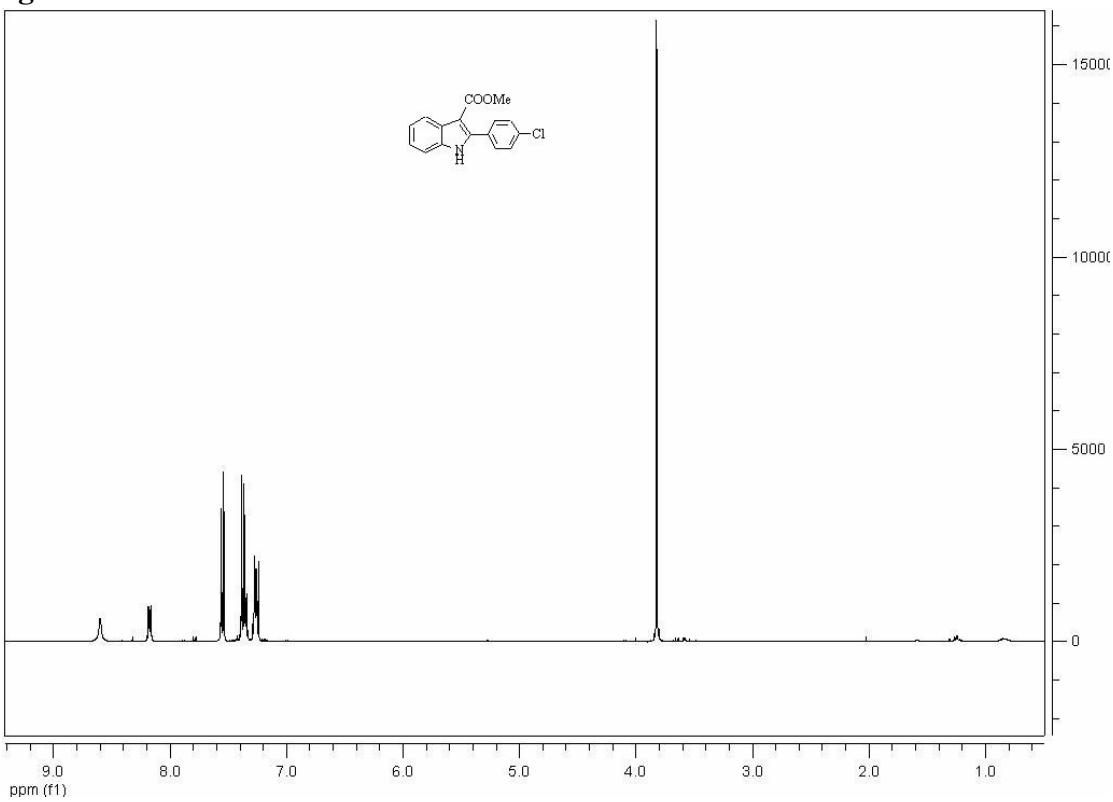
150
100
50
ppm (f1)

3g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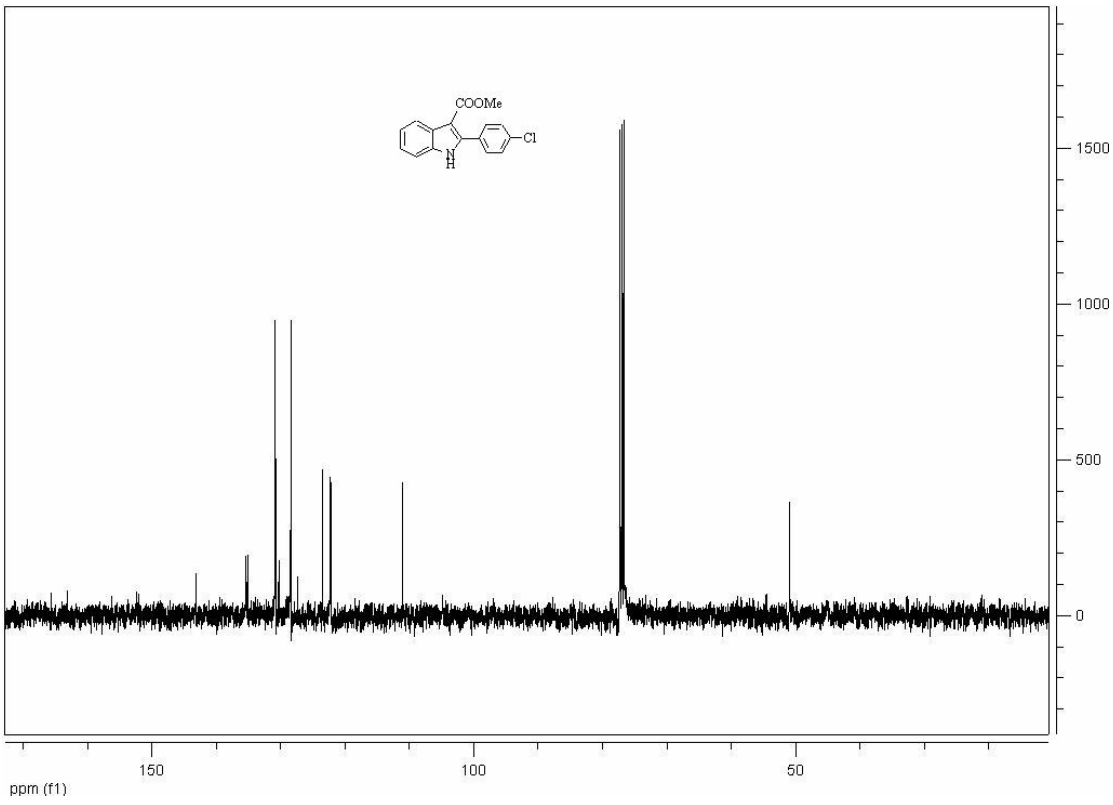
ppm (f1)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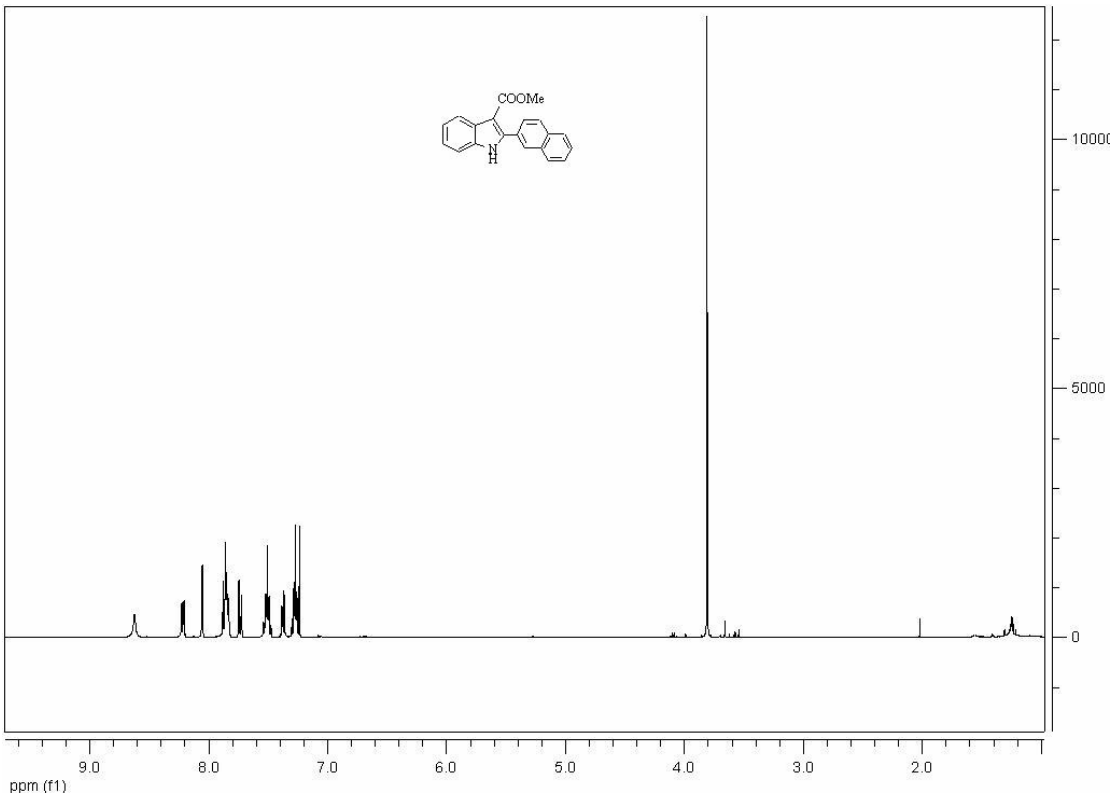
ppm (f1)

3h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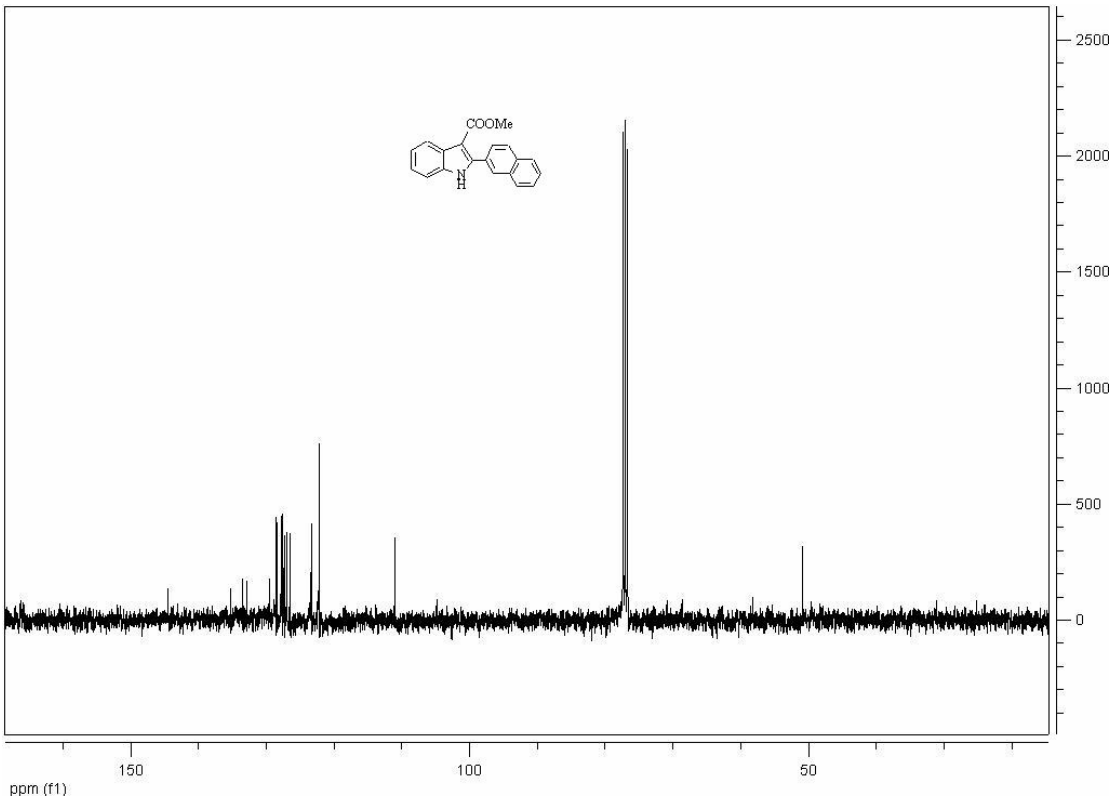
2.0
ppm (f1)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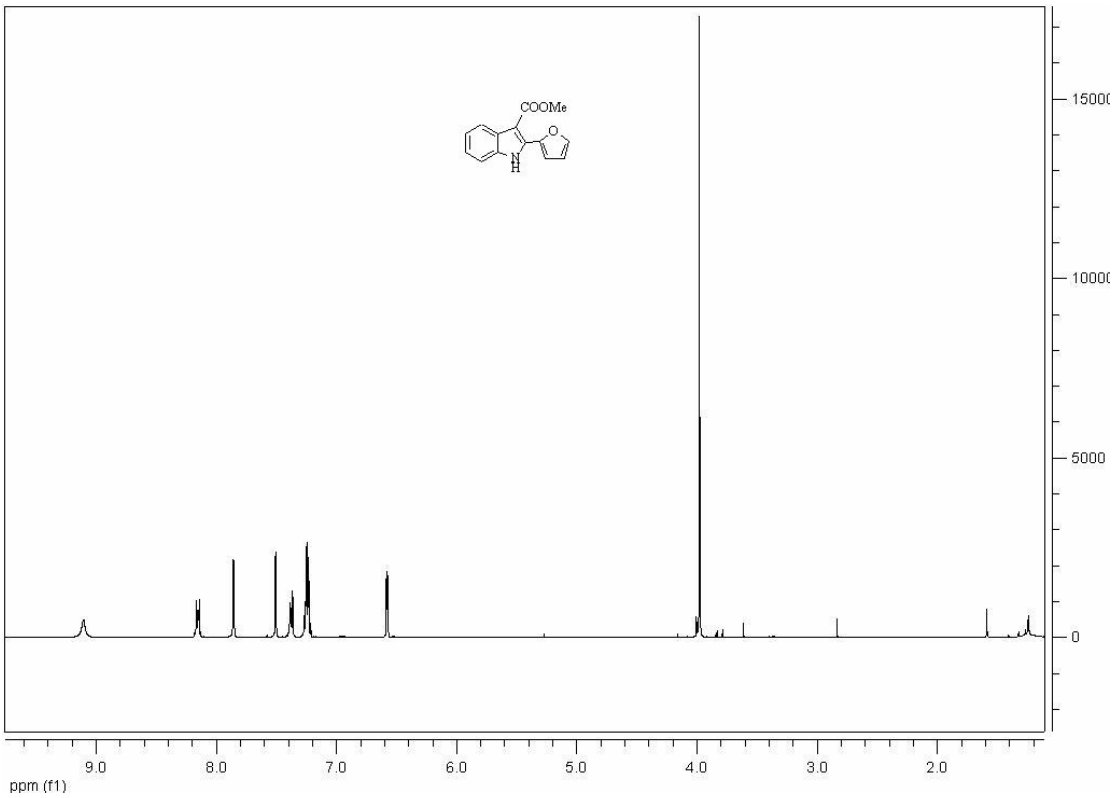
50
ppm (f1)

3i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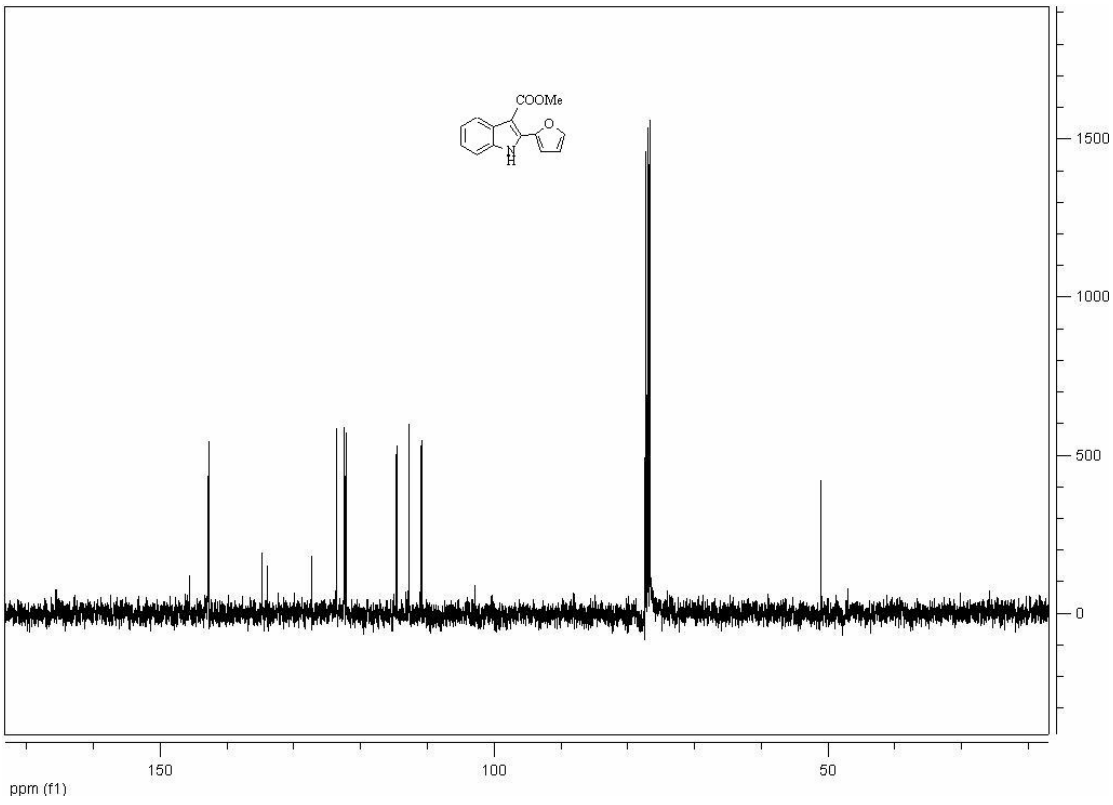
2.0
ppm (f1)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100
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ppm (f1)