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Supporting Information

69451 Weinheim, Germany

Rhodium-Catalyzed Cycloisomerization: Formation of Indoles, Benzofurans, and Enol Lactones

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Experimental

1. General

Melting points were recorded using a Thomas Hoover Capillary Melting Point Apparatus, and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Paragon 500 FT-IR spectrometer. ^{1}H NMR spectra were recorded on one of the following spectrometers: Varian Gemini GEM-300 (300 MHZ), Varian Mercury Merc-400 (400 MHz) or Varian Innova UI-500 (500 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (acetone: δ 2.05 ppm, chloroform: δ 7.26 ppm, dimethylsulfoxide: δ 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sep = septet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR spectra were recorded on one of the following spectrometers: Varian Gemini GEM-300 (75 MHZ), Varian Mercury Merc-400 (100 MHz), or Varian Innova UI-500 (125 MHz) with complete proton decoupling. Chemical shifts are reported in ppm with the solvent as the internal standard (acetone: δ 206.0 ppm, chloroform: δ 77.0 ppm, dimethylsulfoxide: δ 39.5 ppm). Analytical thin layer chromatography was performed on pre-coated EM silica gel 60-F_{254} plates. Flash chromatography employed ICN silica gel (Kieselgel 60, 230-400 mesh). Solvents for extraction and chromatography were used as received. Unless otherwise noted, all reactions were conducted in flame-dried glassware with magnetic stirring under an inert atmosphere of dry nitrogen. ***The solvent for the rhodium catalyzed cycloisomerization reaction was deoxygenated by bubbling Ar (from a balloon) through for 20 min***. Acetone, diisopropylamine, and methanol were distilled from the appropriate drying agents. Benzene, dichloromethane, diethyl ether, dimethylformamide (DMF), dimethylsulfoxide, dioxane, hexane, tetrahydrofuran (THF), toluene and triethylamine were passed through activated alumina columns. All other reagents were used as received. The iodinating agent benzyltrimethylammonium iodine dichloride (BTMA·ICl_2) was prepared and used according to a literature procedure.[1] The iodination of 4-nitroaniline was carried out using iodine and hydrogen peroxide according to a literature procedure.[2] The complex $[Rh(COD)Cl]_2$ was prepared according to a literature procedure.[3] Tris(4-fluorophenyl)phosphine was purchased from Aldrich. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. High resolution mass spectra (HRMS) were obtained from the Mass Spectrometry Resource, School of Pharmacy, University of California-San Francisco on a Kratos MS9 spectrometer. HRMS data are reported with accurate mass for the molecular ion (M^+) or suitable fragments.

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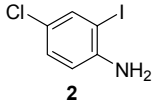
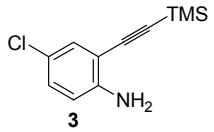
[1] Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S. & Okamoto, T. *Bull. Chem. Soc. Jpn*. **1988**. *21* (2), 600-602.
[2] Wescott, L. D. & Mattern, D. L. *J. Org. Chem*. **2003**. *68*, 10058-10066.
[3] Giordano, G. & Crabtree, R. H. *Inorg. Synth*. **1990**. *28*, 88-90.

2. Synthesis of Substrates



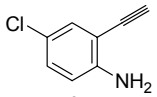
2

4-Chloroaniline (**1**, 2.56 g, 20.0 mmol) was dissolved in methylene chloride (140 mL). To this was added methanol (60 mL), followed by BTMA·ICl_2 (7.66 g, 22.0 mmol) and calcium carbonate (2.60 g, 26.0 mmol). The reaction mixture was stirred 16 hours at 25 ^oC and then filtered through a Buchner funnel. The filtrate was evaporated *in vacuo*, and then extracted from freshly prepared 5 wt% $NaHSO_3$ (aq., 100 mL) with diethyl ether (3 x 50 mL). The combined organic extracts were washed with 5 wt% $NaHSO_3$ (aq., 100 mL), dried with $MgSO_4$ (anh.), filtered, and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (pet ether / diethyl ether 3:1) to give the product **2** as a non-volatile, clear, dark red-brown oil that solidified upon standing. Yield: 4.65 g (92%). IR ($CHCl_3$): 3462, 3372, 1614, 1580, 1559, 1475, 1391, 1297, 1252, 1152, 1107, 1067, 1024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.59 (d, J = 2.4 Hz, 1H), 7.09 (dd, J = 2.4, 8.5 Hz, 1H), 6.64 (d, J = 8.5 Hz, 1H), 4.08 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.5, 137.7, 129.2, 123.1, 114.9, 83.5.



3

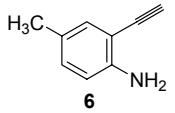
The iodoaniline **2** (1.00 g, 3.94 mmol) was dissolved in diethylamine (4.0 mL). To this was added trimethylsilylacetylene (1.26 mL, 11.8 mmol), followed by $PdCl_2(PPh_3)_2$ (0.055 g, 0.079 mmol) and cuprous iodide (0.030 g, 0.158 mmol). The resulting mixture was stirred 3 hours at 25 ^oC. The reaction was then extracted from $NaHCO_3$ (sat., aq., 30 mL) with diethyl ether (3 x 20 mL). The combined organic extracts were dried with $MgSO_4$ (anh.), filtered, and evaporated *in vacuo*. Purification by flash column chromatography over silica gel (pet ether / diethyl ether 95:5 -> 83:17) gave the product **3** as a clear, dark-red oil. Yield: 0.857 g (97%). IR ($CHCl_3$): 3484, 3387, 2960, 2899, 2152, 1615, 1592, 1487, 1408, 1304, 1250, 1148, 1088 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.25 (d, J = 2.4 Hz, 1H), 7.05 (dd, J = 2.4, 8.7 Hz, 1H), 6.59 (d, J = 8.7 Hz, 1H), 4.22 (bs, 2H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.8, 131.4, 129.8, 121.9, 115.2, 109.0, 101.0, 100.3, 0.0.



4

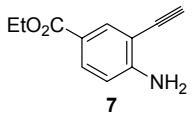
The silyl-protected alkyne **3** (1.53 g, 6.81 mmol) was dissolved in methanol (6.8 mL). Potassium carbonate (1.04 g, 7.49 mmol) was added, and the mixture was stirred 2 hours at 25 ^oC. The reaction was extracted from water (100 mL) with diethyl ether (3 x 30 mL). The combined organic extracts were washed with $NaHCO_3$ (sat., aq., 30 mL), dried with $MgSO_4$ (anh.), filtered, and evaporated *in vacuo*. Purification by flash column chromatography over silica gel (pet ether / diethyl ether 3:1) gave the product **4** as a brown solid. Yield: 1.02 g (99%). MP: 57-58 ^oC. IR ($CHCl_3$): 3477, 3384, 3288, 2102, 1616, 1592, 1561, 1487, 1407, 1304, 1250, 1186, 1150, 1087 cm^{-1}. ^1H NMR (400 MHz,

$CDCl_3$): 7.27 (d, J = 2.5 Hz, 1H), 7.08 (dd, J = 2.5, 8.7 Hz, 1H), 6.60 (d, J = 8.7 Hz, 1H), 4.24 (bs, 2H), 3.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.1, 131.7, 130.1, 121.9, 115.4, 107.8, 83.4, 79.3. HRMS. Calcd. For C_8H_6ClN: 151.0189; Found: 151.0188.



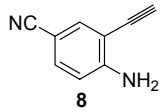
6

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 75:25) gave **6** as a clear orange oil. Yield: 78%. IR ($CHCl_3$): 3466, 3376, 3287, 3023, 2922, 2860, 2096, 1625, 1571, 1504, 1458, 1409, 1303, 1257, 1208, 1156, 1041, 1000 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 7.14 (d, J = 1.7 Hz, 1H), 6.96 (dd, J = 2.1, 8.2 Hz, 1H), 6.62 (d, J = 8.2 Hz, 1H), 4.10 (bs, 2H), 3.36 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 146.1, 132.5, 130.9, 126.9, 114.4, 106.5, 82.1, 80.7, 20.1. HRMS. Calcd. For C_9H_9N: 131.0735; Found: 131.0735.



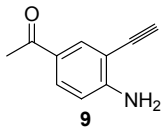
7

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 75:25 -> 50:50) gave **7** as an off-white solid. Yield: 88%. MP: 112-113 ^oC. IR ($CHCl_3$): 3497, 3465, 3402, 3360, 3305, 3261, 2986, 2254, 1702, 1618, 1570, 1505, 1477, 1446, 1429, 1392, 1367, 1286, 1259, 1214, 1183, 1146, 1101, 1024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.04 (d, J = 2.0 Hz, 1H), 7.82 (dd, J = 2.0, 8.5 Hz, 1H), 6.67 (d, J = 8.5 Hz, 1H), 4.74 (bs, 2H), 4.31 (q, J = 7.2 Hz, 2H), 3.41 (s, 1H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 152.1, 134.7, 131.7, 119.4, 113.2, 105.6, 82.9, 79.5, 60.4, 14.3. HRMS. Calcd. For $C_{11}H_{11}NO_2$: 189.0790; Found: 189.0788.



8

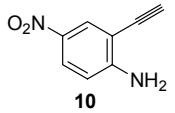
Purification by flash column chromatography over silica gel (pet ether / diethyl ether 50:50 -> 33:66) gave **8** as pale yellow crystals. Yield: 95%. MP: 104-105 ^oC. IR ($CHCl_3$): 3497, 3474, 3404, 3362, 3302, 3273, 2222, 1620, 1560, 1500, 1417, 1379, 1324, 1275, 1239, 1163, 1135 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.57 (d, J = 1.8 Hz, 1H), 7.36 (dd, J = 1.8, 8.5 Hz, 1H), 6.70 (d, J = 8.5 Hz, 1H), 4.89 (bs, 2H), 3.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.8, 136.7, 133.5, 119.3, 113.9, 106.5, 99.3, 84.2, 78.1. HRMS. Calcd. For $C_9H_6N_2$: 142.0531; Found: 142.0534.



9

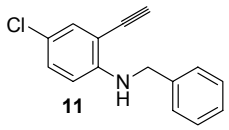
Purification by flash column chromatography over silica gel (pet ether / diethyl ether 50:50 -> 25:75) gave **9** as a pale tan solid. Yield: 96%. MP: 77-78.5 ^oC. IR ($CHCl_3$): 3467, 3346, 3277, 2101, 1655, 1619, 1588, 1560, 1507, 1415, 1259, 1321, 1299, 1268, 1154, 1076, 1021 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 7.96 (d, J = 2.1 Hz, 1H), 7.77 (dd,

J = 2.2, 8.6 Hz, 1H), 6.69 (d, J = 8.6 Hz, 1H), 4.94 (bs, 2H), 3.44 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 195.8, 152.5, 134.1, 130.7, 126.8, 113.2, 105.3, 83.0, 79.4, 25.9. HRMS. Calcd. For $C_{10}H_9NO$: 159.0684; Found: 159.0688.



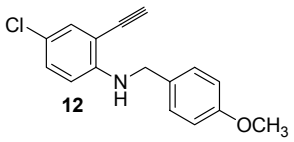
10

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 25:75) gave **10** as yellow crystals. Yield: 99%. MP: 116-118 ^{o}C (Dec.). IR ($CHCl_3$): 3475, 3408, 3370, 3302, 3247, 2254, 1620, 1571, 1493, 1430, 1334, 1322, 1183, 1147, 1090 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d6): 8.03 (d, J = 2.7 Hz, 1H), 7.96 (dd, J = 2.7, 9.2 Hz, 1H), 6.87 (bs, 2H), 6.77 (d, J = 9.2 Hz, 1H), 4.52 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d6): 155.8, 135.6, 128.9, 126.3, 113.0, 104.0, 86.8, 78.5. HRMS. Calcd. For $C_8H_6N_2O_2$: 162.0429; Found: 162.0429.



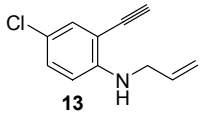
11

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 95:5 -> 90:10) gave **11** as a clear, pale brown oil. IR ($CHCl_3$): 3416, 3289, 3064, 3030, 2857, 2098, 1598, 1571, 1506, 1469, 1454, 1404, 1360, 1321, 1298, 1266, 1176, 1134, 1096, 1066, 1028 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.24 (m, 6H), 7.06 (dd, J = 2.4, 8.8 Hz, 1H), 6.43 (d, J = 8.8 Hz, 1H), 5.06 (t, J = 5.8 Hz, 1H), 4.35 (d, J = 5.8 Hz, 2H), 3.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.9, 138.4, 131.8, 130.3, 128.7, 127.3, 127.0, 120.7, 111.0, 107.5, 84.0, 79.4, 47.6. HRMS. Calcd. For $C_{15}H_{12}ClN$: 241.0658; Found: 241.0648.



12

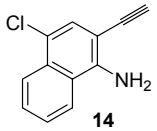
Purification by flash column chromatography over silica gel (pet ether / diethyl ether 95:5 -> 90:10) gave **12** as a pale yellow solid. MP: 70.5-72.0 ^{o}C. IR ($CHCl_3$): 3407, 3287, 3000, 2835, 1612, 1596, 1585, 1570, 1509, 1466, 1441, 1421, 1404, 1359, 1320, 1302, 1247, 1174, 113, 1110, 1069, 1034 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.29 (d, J = 2.4 Hz, 1H), 7.25 (d, J = 8.8 Hz, 2H), 7.09 (dd, J = 2.4, 9.0 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 9.0 Hz, 1H), 4.98 (t, J = 5.4 Hz, 1H), 4.30 (d, J = 5.4 Hz, 2H), 3.79 (s, 3H), 3.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.9, 147.9, 131.8, 130.3, 130.3, 128.4, 120.6, 114.1, 111.0, 107.5, 84.0, 79.4, 55.2, 47.1.



13

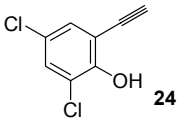
Purification by flash column chromatography over silica gel (pet ether / diethyl ether 99:1 -> 98:2 -> 97:3) gave **13** as a slightly volatile, clear brown oil. Yield: 82%. IR ($CHCl_3$): 3414, 3292, 3083, 3009, 2983, 2916, 2848, 2098, 1645, 1598, 1572, 1508, 1464, 1444,

1405, 1358, 1318, 1278, 1258, 1243, 1176, 1144 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.29 (d, J = 2.5 Hz, 1H), 7.14 (dd, J = 2.5, 8.8 Hz, 1H), 6.50 (d, J = 8.8 Hz, 1H), 5.97-5.88 (m, 1H), 5.30-5.25 (m, 1H), 5.21-5.17 (m, 1H), 4.79 (bs, 1H), 3.85-3.81 (m, 2H), 3.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.9, 134.3, 131.8, 130.2, 120.5, 116.4, 111.0, 107.4, 83.9, 79.4, 45.9. HRMS. Calcd. For $C_{11}H_{10}ClN$: 191.0502; Found: 191.0496.



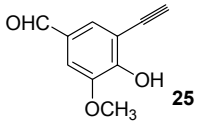
14

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 85:15 -> 80:20 -> 75:25 -> 66:33) gave **14** as an amorphous brown solid. Yield: 70%. MP: 77-79.5 ^{o}C. IR ($CHCl_3$): 3493, 3395, 3304, 2253, 2097, 1618, 1503, 1452, 1425, 1387, 1334, 1273, 1220 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.20-8.18 (m, 1H), 7.79-7.77 (m, 1H), 7.61-7.57 (m, 1H), 7.54-7.49 (m, 1H), 7.46 (s, 1H), 4.87 (bs, 2H), 3.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.0, 131.2, 128.0, 127.8, 126.1, 125.1, 123.2, 121.3, 120.2, 100.6, 83.8, 80.3. HRMS. Calcd. For $C_{12}H_8ClN$: 201.0345; Found: 201.0346.



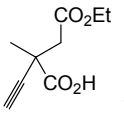
24

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 90:10 -> 80:20) gave **24** as a pale brown solid. Yield: 75%. MP: 75-76 ^{o}C. IR ($CHCl_3$): 3518, 3300, 2254, 1566, 1459, 1400, 1325, 1264, 1231, 1213, 1163, 1092 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.33 (d, J = 2.4 Hz, 1H), 7.29 (d, J = 2.4 Hz, 1H), 6.00 (s, 1H), 3.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.9, 130.8, 130.4, 125.0, 120.9, 111.0, 85.1, 76.7. Anal. Calcd. For $C_8H_4Cl_2O$: C, 51.38; H, 2.16; Found: C, 51.18; H, 2.39.



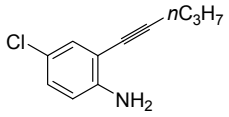
25

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 66:33 -> 50:50 -> 25:75 -> 0:100) gave **25** as chocolate-smelling brown crystals. Yield: Quant. MP: 150-153 ^{o}C. IR (CH_2Cl_2): 3266, 3055, 2987, 1671, 1586, 1495, 1466, 1446, 1422, 1402, 1368, 1294, 1266, 1209, 1188, 1144, 1078 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d6): 10.53 (s, 1H), 9.77 (s, 1H), 7.57 (d, J = 1.7 Hz, 1H), 7.41 (d, J = 1.7 Hz, 1H), 4.32 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6): 190.8, 154.4, 148.2, 129.9, 128.2, 110.0, 109.5, 85.0, 79.2, 56.1. HRMS. Calcd. For $C_{10}H_8O_3$: 176.0473; Found: 176.0473.



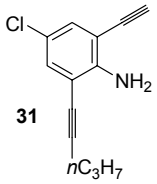
26

Prepared in a manner similar to a literature procedure.[4] Purification by flash column chromatography over silica gel (pet ether / diethyl ether 50:50 -> 0:100) gave **26** as a viscous, clear oil. IR ($CHCl_3$): 3500-2400, 3290, 2987, 2942, 1738, 1716, 1458, 1410, 1372, 1345, 1299, 1203, 1098, 1029 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 11.89 (bs, 1H), 4.17 (q, J = 7.3 Hz, 2H), 2.96-2.81 (m, 2H), 2.38 (s, 1H), 1.61 (s, 3H), 1.26 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 178.2, 169.8, 83.1, 71.8, 60.9, 43.7, 40.0, 25.5, 13.9. HRMS. Calcd. For $C_9H_{12}O_4$: 184.0736; Found: 184.0736.



30

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 90:10 -> 75:25) gave **30** as a clear orange oil. IR ($CHCl_3$): 3477, 3382, 2963, 2933, 2903, 2872, 2835, 2232, 1613, 1591, 1488, 1462, 1429, 1410, 1380, 1339, 1327, 1302, 1249, 1149, 1089 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.20 (d, J = 2.4 Hz, 1H), 7.01 (dd, J = 2.4, 8.5 Hz, 1H), 6.59 (d, J = 8.5 Hz, 1H), 4.15 (bs, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.64 (sex., J = 7.3 Hz, 2H), 1.05 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.2, 131.3, 128.7, 122.0, 115.1, 110.3, 96.7, 76.1, 22.2, 21.5, 13.5. HRMS. Calcd. For $C_{11}H_{12}ClN$: 193.0658; Found: 193.0663.



31

Purification by flash column chromatography over silica gel (pet ether / diethyl ether 98:2 -> 97:3 -> 95:5) gave **31** as a clear yellow oil. IR ($CHCl_3$): 3486, 3386, 3305, 3029, 2965, 2933, 2872, 2248, 2100, 1613, 1587, 1465, 1380, 1340, 1306, 1271, 1244, 1181 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.07 (s, 2H), 4.62 (bs, 2H), 3.36 (s, 1H), 2.44 (t, J = 7.3 Hz, 2H), 2.17 (s, 3H), 1.64 (sex, J = 7.3 Hz, 2H), 1.06 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.3, 133.3, 132.3, 126.0, 108.5, 105.8, 95.7, 82.2, 80.5, 76.7, 22.3, 21.5, 20.0, 13.5. HRMS. Calcd. For $C_{14}H_{15}N$: 197.1204; Found: 197.1214.

3. Rhodium-Catalyzed Cycloisomerization Reactions

The following three procedures were used. Yields represent the average of 2 runs.

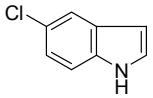
Method A: *N,N*-dimethylformamide (2.50 mL) was degassed (Ar balloon) for 20 min. This was then added *via* cannula to a mixture of substrate (0.50 mmol), $[Rh(COD)Cl]_2$

[4] Stevens, R. V.; Beaulieu, N.; Chan, W. H.; Daniewski, A. R.; Takeda, T.; Waldner, A.; Williard, P. G. & Zutter, U. *J. Am. Chem. Soc*. **1986**. *108*, 1039-1049.

(2.5 mg, 0.0050 mmol), and triphenylphosphine (5.2 mg, 0.020 mmol). The solution was stirred for 2 hours at 85 ^{o}C under Ar. The homogeneous solution turned from pale yellow to dark orange during this time. The mixture was then cooled to 25 ^{o}C and extracted from $NaHCO_3$ (sat., aq., 50 mL) with diethyl ether or ethyl acetate (3 x 10 mL). The combined organic extracts were washed with $NaHCO_3$ (sat., aq., 10 mL), dried with $MgSO_4$ (anh.), filtered, and evaporated *in vacuo*. Purification by flash column chromatography over silica gel gave the product.

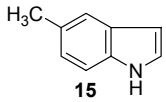
Method B: *N,N*-dimethylformamide (2.50 mL) was degassed (Ar balloon) for 20 min. This was then added *via* cannula to a mixture of substrate (0.50 mmol), $[Rh(COD)Cl]_2$ (12.3 mg, 0.025 mmol), and tris(4-fluorophenyl)phosphine (79 mg, 0.30 mmol). The solution was stirred for 2 hours at 85 ^{o}C under Ar. The homogeneous solution turned from pale yellow to dark orange during this time. The mixture was then cooled to 25 ^{o}C and extracted from $NaHCO_3$ (sat., aq., 50 mL) with diethyl ether or ethyl acetate (3 x 10 mL). The combined organic extracts were washed with $NaHCO_3$ (sat., aq., 10 mL), dried with $MgSO_4$ (anh.), filtered, and evaporated *in vacuo*. Purification by flash column chromatography over silica gel gave the product.

Method C: *N,N*-dimethylformamide (2.50 mL) was degassed (Ar balloon) for 20 min. This was then added *via* cannula to a mixture of substrate (0.50 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.0050 mmol), and tris(4-fluorophenyl)phosphine (6.3 mg, 0.020 mmol). The solution was stirred for 2 hours at 85 ^{o}C under Ar. The homogeneous solution turned from pale yellow to dark orange during this time. The mixture was then cooled to 25 ^{o}C and extracted from $NaHCO_3$ (sat., aq., 50 mL) with diethyl ether or ethyl acetate (3 x 10 mL). The combined organic extracts were washed with $NaHCO_3$ (sat., aq., 10 mL), dried with $MgSO_4$ (anh.), filtered, and evaporated *in vacuo*. Purification by flash column chromatography over silica gel gave the product.



5

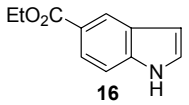
Method A was used to provide **5** as pale tan crystals. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 90:10:3 -> 50:50:3 -> 25:75:3). Yield: 58 mg (77%). MP: 71.5-72 ^{o}C. IR ($CHCl_3$): 3476, 2252, 1721, 1569, 1458, 1447, 1413, 1338, 1315, 1265, 1242, 1196, 1094, 1068 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (bs, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.24 (d, J = 8.6 Hz, 1H), 7.17 (t, J = 2.9 Hz, 1H), 7.13 (dd, J = 2.0, 8.6 Hz, 1H), 6.48-6.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 134.0, 128.8, 125.5, 125.3, 122.2, 120.0, 112.0, 102.3. HRMS. Calcd. For C_8H_6ClN: 151.0189; Found: 151.0183.



15

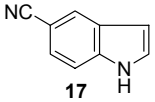
Method C was used to provide **15** as pale green crystals. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 90:10:3 -> 50:50:3). Yield: 47 mg (72%). MP: 59.5-60.5 ^{o}C. IR ($CHCl_3$): 3408, 3105, 3016, 2916,

2858, 1579, 1510, 1476, 1459, 1416, 1340, 1320, 1280, 1248, 1228, 1140, 1092, 1065, 1037 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.89 (bs, 1H), 7.42 (m, 1H), 7.23-7.18 (m, 1H), 7.08 (t, J = 2.8 Hz, 1H), 7.02-7.00 (m, 1H), 6.45 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 134.0, 128.9, 128.0, 124.2, 123.5, 120.3, 110.6, 102.0, 21.4. HRMS. Calcd. For C_9H_9N: 131.0735; Found: 131.0732.



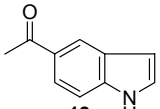
16

Method A was used to provide **16** as pale yellow crystals. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 90:10:3 -> 50:50:3 -> 25:75:3). Yield: 79 mg (84%). MP: 96.5-97.5 ^{o}C. IR ($CHCl_3$): 3414, 3335, 2982, 2937, 2903, 1688, 1617, 1580, 1514, 1465, 1422, 1390, 1368, 1350, 1329, 1304, 1288, 1269, 1245, 1190, 1128, 1100, 1021 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.43 (m, 1H), 8.35 (bs, 1H), 7.92 (dd, J = 1.7, 8.7 Hz, 1H), 7.41 (dt, J = 0.8, 8.5 Hz, 1H), 7.29-7.27 (m, 1H), 6.67-6.65 (m, 1H), 4.40 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.1, 138.4, 127.4, 125.7, 123.6, 123.1, 121.8, 110.8, 103.6, 60.6, 14.3. HRMS. Calcd. For $C_{11}H_{11}NO_2$: 189.0790; Found: 189.0783.



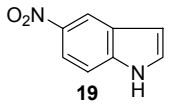
17

Method A was used to provide **17** as pale yellow crystals. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 90:10:3 -> 25:75:3 -> 0:100:3). Yield: 64 mg (90%). MP: 104.5-106.5 ^{o}C. IR ($CHCl_3$): 3471, 3345, 2253, 2224, 1615, 1471, 1419, 1347, 1323, 1284, 1250, 1222, 1126, 1091, 1068 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.49 (bs, 1H), 8.01 (s, 1H), 7.48-7.42 (m, 2H), 7.36-7.34 (m, 1H), 6.66-6.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 137.5, 127.5, 126.7, 126.1, 124.4, 121.1, 112.1, 102.9, 101.8. HRMS. Calcd. For $C_9H_6N_2$: 142.0531; Found: 142.0531.



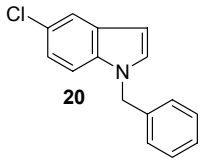
18

Method A was used to provide **18** as pale green crystals. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 90:10:3 -> 50:50:3 -> 25:75:3 -> 0:100:3). Yield: 61 mg (77%). MP: 75-76 ^{o}C. IR ($CHCl_3$): 3306, 2998, 1659, 1611, 1576, 1513, 1480, 1457, 1421, 1350, 1326, 1304, 1270, 1252, 1240, 1185, 1142, 1130, 1098, 1057, 1020 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 9.26 (bs, 1H), 8.34 (s, 1H), 7.87 (dd, J = 1.7, 8.5 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.28-7.26 (t, J = 2.8 Hz, 1H), 6.65-6.64 (m, 1H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 199.2, 138.6, 129.5, 127.3, 126.1, 123.1, 121.9, 111.2, 103.9, 26.6. HRMS. Calcd. For $C_{10}H_9NO$: 159.0684; Found: 159.0685.



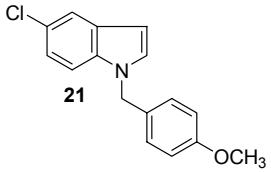
19

Method A was used to provide **19** as brilliant canary-yellow crystals. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 90:10:3 -> 50:50:3 -> 25:75:3 -> 0:100:3). Yield: 66 mg (81%). MP: 137.5-139.5 ^{o}C. IR (CH_2Cl_2): 3459, 3055, 2987, 1523, 1480, 1422, 1341, 1332, 1265, 1070 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d6): 11.83 (bs, 1H), 8.58 (d, J = 2.4 Hz, 1H), 7.99 (dd, J = 2.4, 9.0 Hz, 1H), 7.62 (d, J = 3.0 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 6.73 (d, J = 3.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6): 140.6, 139.1, 129.3, 127.0, 117.3, 116.4, 111.8, 103.9. HRMS. Calcd. For $C_8H_6N_2O_2$: 162.0429; Found: 162.0425.



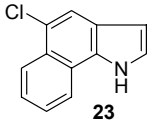
20

Method A was used to provide **20** as a viscous, non-volatile, pale brown oil. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 95:5:3 -> 90:10:3). Yield: 74 mg (61%). MP: 61-62.5 ^{o}C. IR ($CHCl_3$): 3088, 3064, 3030, 2924, 1606, 1586, 1564, 1508, 1496, 1471, 1454, 1443, 1396, 1355, 1331, 1300, 1286, 1250, 1196, 1183, 1092, 1079, 1065, 1047, 1029 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 7.60 (d, J = 2.0 Hz, 1H), 7.30-7.22 (m, 3H), 7.16-7.04 (m, 5H), 6.48 (dd, J = 0.7, 3.1 Hz, 1H), 5.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 137.0, 134.6, 129.7, 129.6, 128.8, 127.7, 126.6, 125.2, 121.9, 120.3, 110.7, 101.3, 50.2. HRMS. Calcd. For $C_{15}H_{12}ClN$: 241.0658; Found: 241.0655.



21

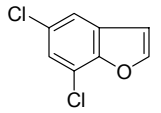
Method C was used to provide **21** as a pale tan solid. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 95:5:3 -> 90:10:3 -> 80:20:3). Yield: 100 mg (74%). MP: 65-66 ^{o}C. IR ($CHCl_3$): 3102, 3063, 3033, 3001, 2956, 2932, 2836, 1613, 1586, 1564, 1514, 1471, 1443, 1422, 1396, 1352, 1331, 1304, 1280, 1249, 1197, 1176, 1111, 1090, 1065, 1034 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, J = 2.0 Hz, 1H), 7.21-7.07 (m, 3H), 7.01 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 6.44 (dd, J = 0.8, 3.2 Hz, 1H), 5.18 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.1, 134.5, 129.7, 129.4, 128.9, 128.1, 125.1, 121.8, 120.2, 114.1, 110.7, 101.1, 55.2, 49.7.



23

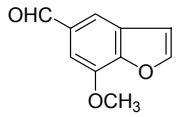
Method A was used to provide **23** as a yellow solid. Purification by flash column chromatography over silica gel (pet ether / diethyl ether / triethylamine 50:50:3 ->

25:75:3). Yield: 60 mg (59%). MP: 79-81 ^{o}C. IR ($CHCl_3$): 3435, 3062, 1626, 1589, 1524, 1493, 1466, 1445, 1390, 1367, 1298, 1250, 1171, 1159, 1117, 1082, 1067, 1038 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.81 (bs, 1H), 8.37-8.34 (m, 1H), 7.94-7.91 (m, 1H), 7.84 (s, 1H), 7.58-7.51 (m, 2H), 7.23-7.21 (m, 1H), 6.64-6.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 129.4, 127.1, 126.2, 125.7, 124.7, 123.9, 123.3, 122.9, 122.2, 120.8, 119.6, 103.9. Anal. Calcd. For $C_{12}H_8ClN$: C, 71.47; H, 4.00; N, 6.95; Found: C, 71.53; H, 4.26; N, 6.71.



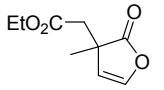
27

Method B was used to provide **27** as pungent, moderately volatile white crystals. Purification by flash column chromatography over silica gel (pet ether). Yield: 72 mg (77%). MP: 56.5-57 ^{o}C. IR ($CHCl_3$): 3156, 3127, 3084, 2253, 1610, 1579, 1497, 1445, 1408, 1321, 1265, 1171, 1126, 1076, 1033 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 7.71 (d, J = 2.2 Hz, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.32 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 149.4, 146.9, 129.7, 128.6, 124.5, 119.5, 117.4, 107.0. HRMS. Calcd. For $C_8H_4Cl_2O$: 185.9639; Found: 185.9640.



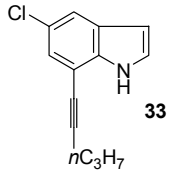
28

Method B was used to provide **28** as non-volatile white crystals. Purification by flash column chromatography over silica gel (pet ether / diethyl ether 90:10 -> 66:33). Yield: 66 mg (75%). MP: 83.5-84 ^{o}C. IR ($CHCl_3$): 3148, 3119, 3010, 2942, 2844, 2785, 2718, 1694, 1614, 1594, 1544, 1474, 1431, 1403, 1370, 1345, 1304, 1232, 1213, 1143, 1100, 1028 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 10.02 (s, 1H), 7.75 (d, J = 1.3 Hz, 1H), 7.74 (d, J = 2.2 Hz, 1H), 7.39 (d, J = 1.3 Hz, 1H), 6.91 (d, J = 2.2 Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 191.7, 147.8, 146.4, 146.1, 133.3, 128.9, 119.7, 107.5, 104.0, 56.0. Anal. Calcd. For $C_{10}H_8O_3$: C, 68.18; H, 4.58; Found: C, 67.91; H, 4.71.



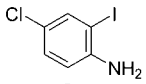
29

Method B was used to provide **29** as a clear, pale red oil. Purification by flash column chromatography over silica gel (pet ether / diethyl ether 75:25 -> 50:50). Yield: 75 mg (81%). IR ($CHCl_3$): 3121, 2981, 2935, 2876, 1794, 1737, 1618, 1590, 1498, 1452, 1411, 1370, 1340, 1291, 1228, 1201, 1153, 1133, 1088, 1068, 1031, 1007 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 6.84 (d, J = 3.6 Hz, 1H), 5.64 (d, J = 3.6 Hz, 1H), 4.18-4.06 (m, 2H), 2.81-2.62 (m, 2H), 1.36 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 180.7, 169.4, 142.2, 114.1, 60.9, 44.2, 41.5, 23.4, 13.9. Anal. Calcd. For $C_9H_{12}O_4$: C, 58.69; H, 6.57; Found: C, 58.76; H, 6.35.



33

Method A was used to provide **33** as a clear, pale brown oil. Purification by flash column chromatography over silica gel (pet ether / diethyl ether 97.5:2.5 -> 95:5 -> 90:10). Yield: 80 mg (81%). IR ($CHCl_3$): 3432, 2962, 2932, 2871, 1590, 1478, 1463, 1419, 1406, 1380, 1343, 1319, 1302, 1274, 1255, 1124, 1082, 1055, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.30 (bs, 1H), 7.36 (s, 1H), 7.17-7.16 (m, 1H), 7.11 (s, 1H), 6.47-6.45 (m, 1H), 2.48 (t, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.68 (sex, J = 7.2 Hz, 2H), 1.08 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 135.0, 128.9, 127.5, 126.5, 124.1, 120.5, 106.5, 102.5, 93.9, 76.9, 22.4, 21.6, 21.2, 13.6. Anal. Calcd. For $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10; Found: C, 85.00; H, 7.67; N, 6.89.



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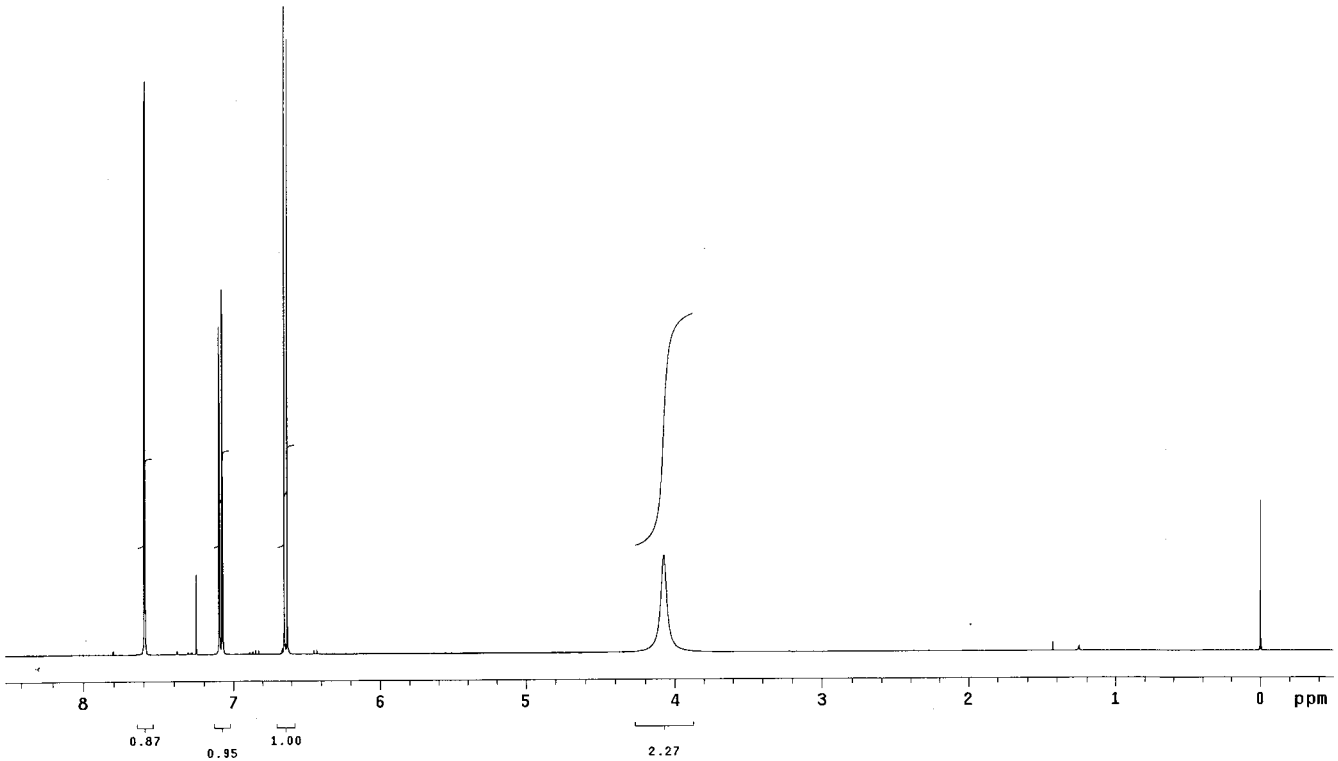
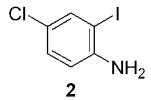
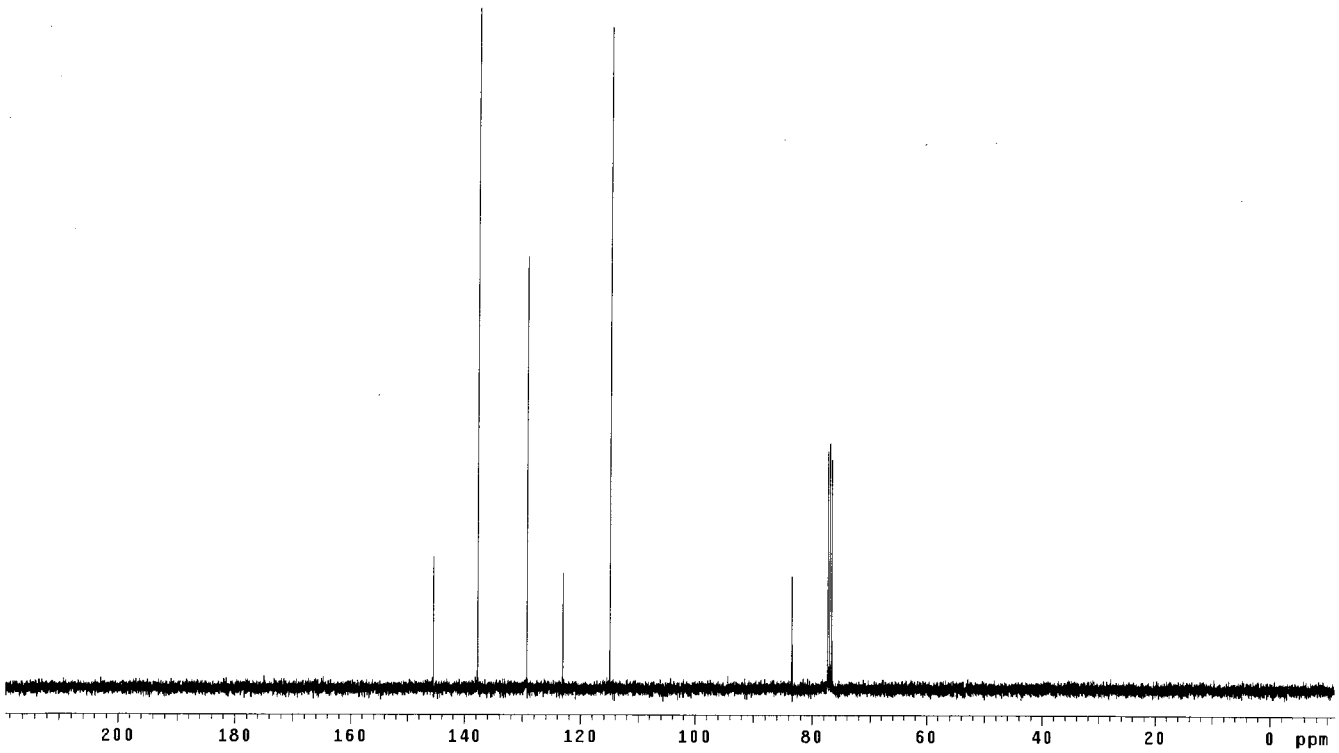
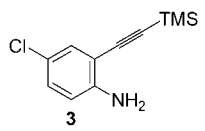




2





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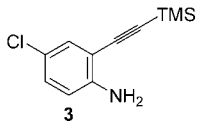

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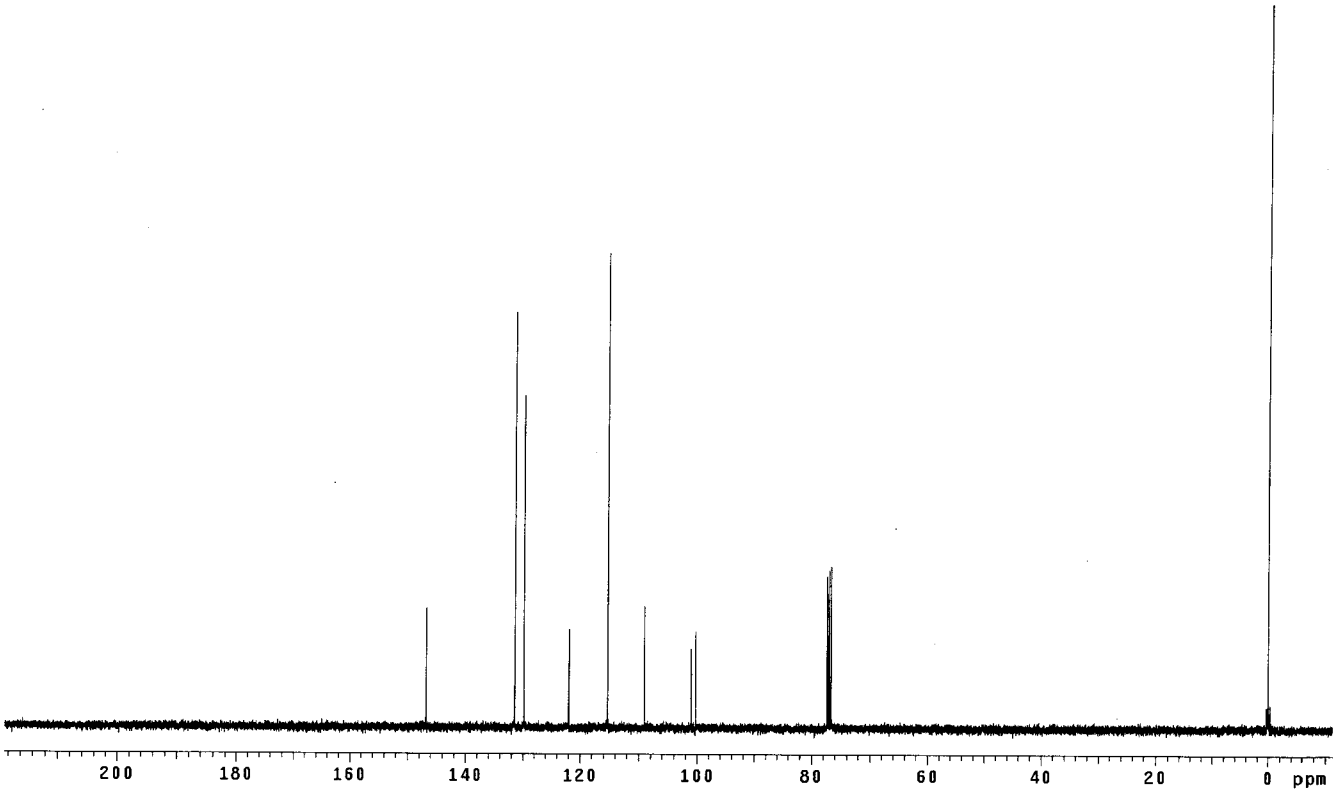

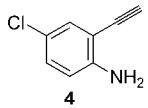

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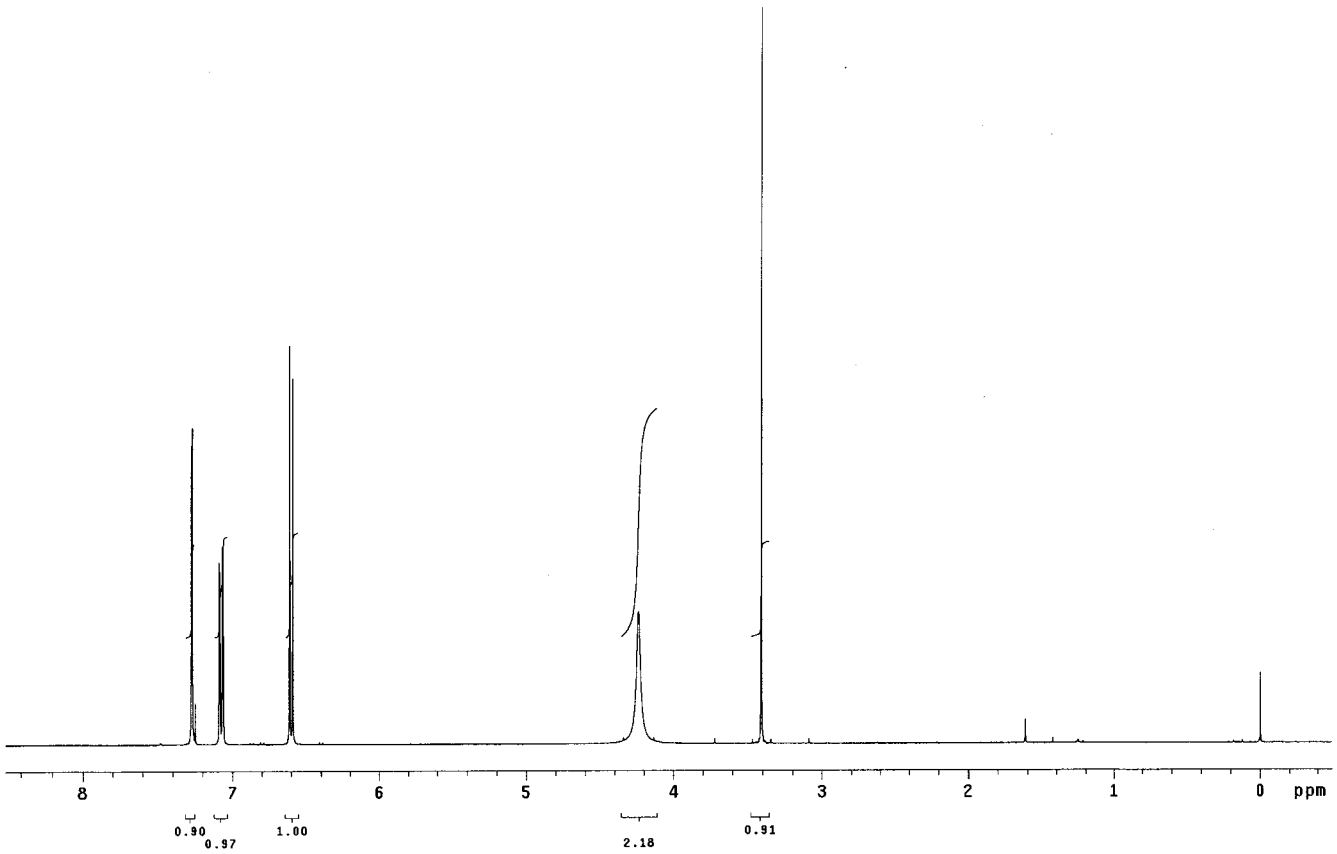

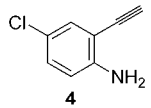

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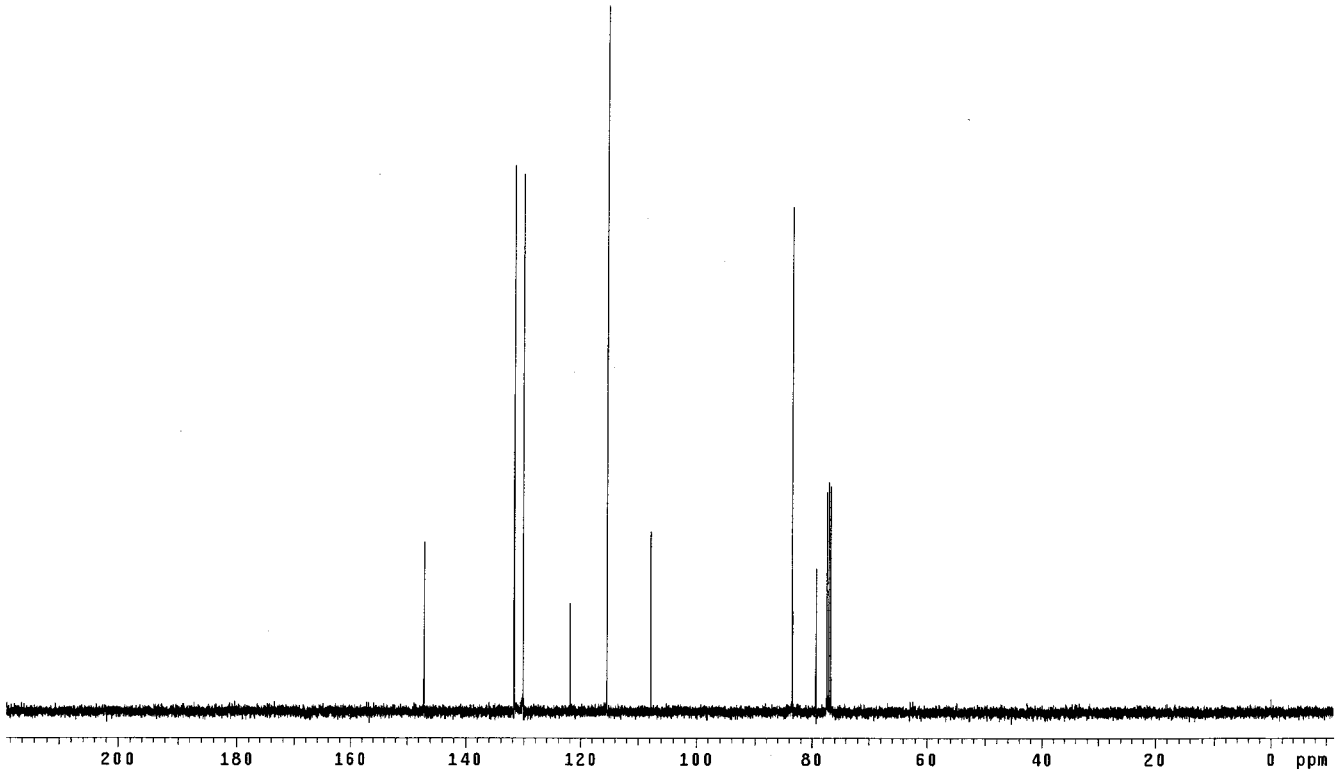

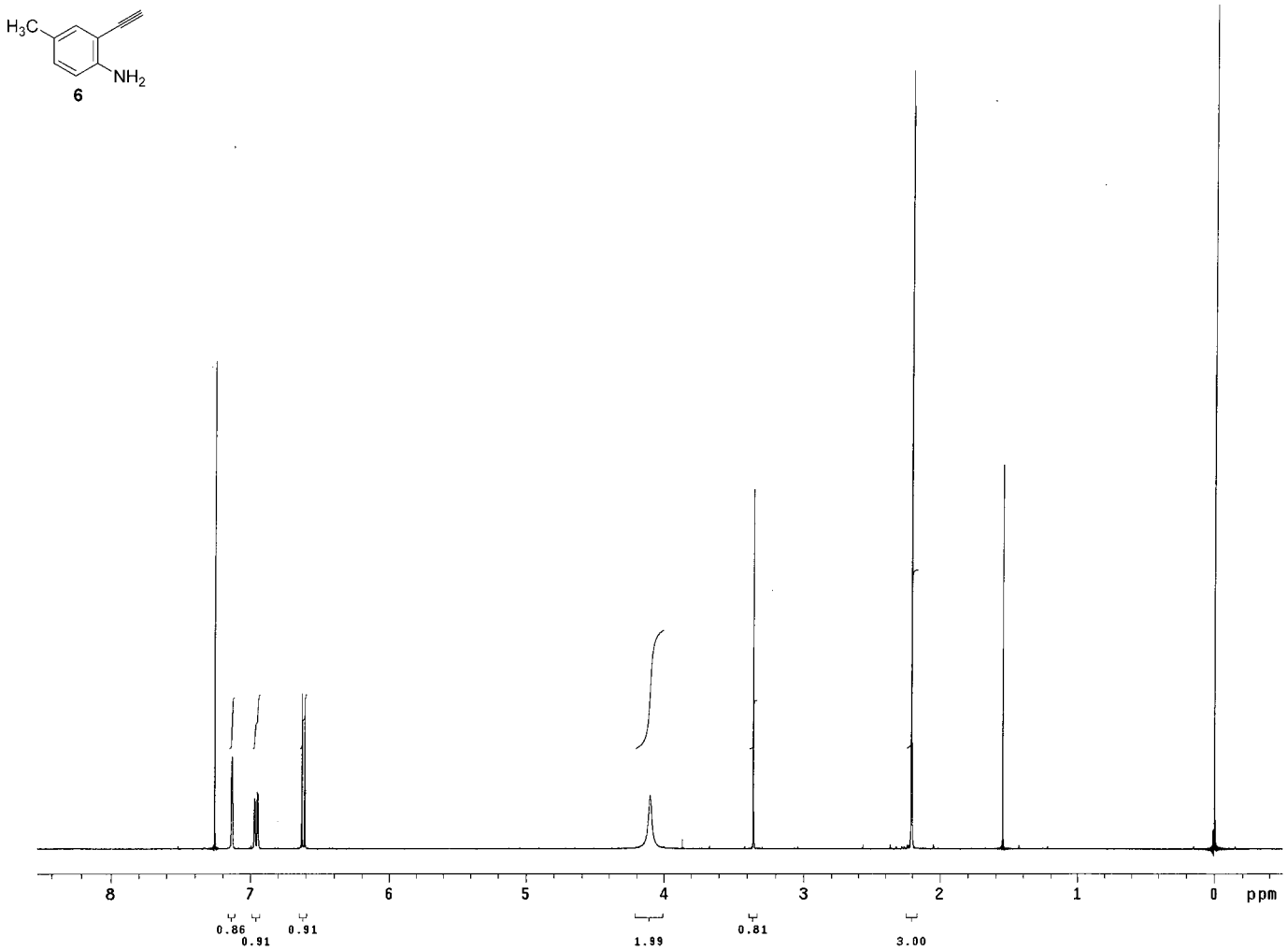
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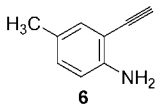

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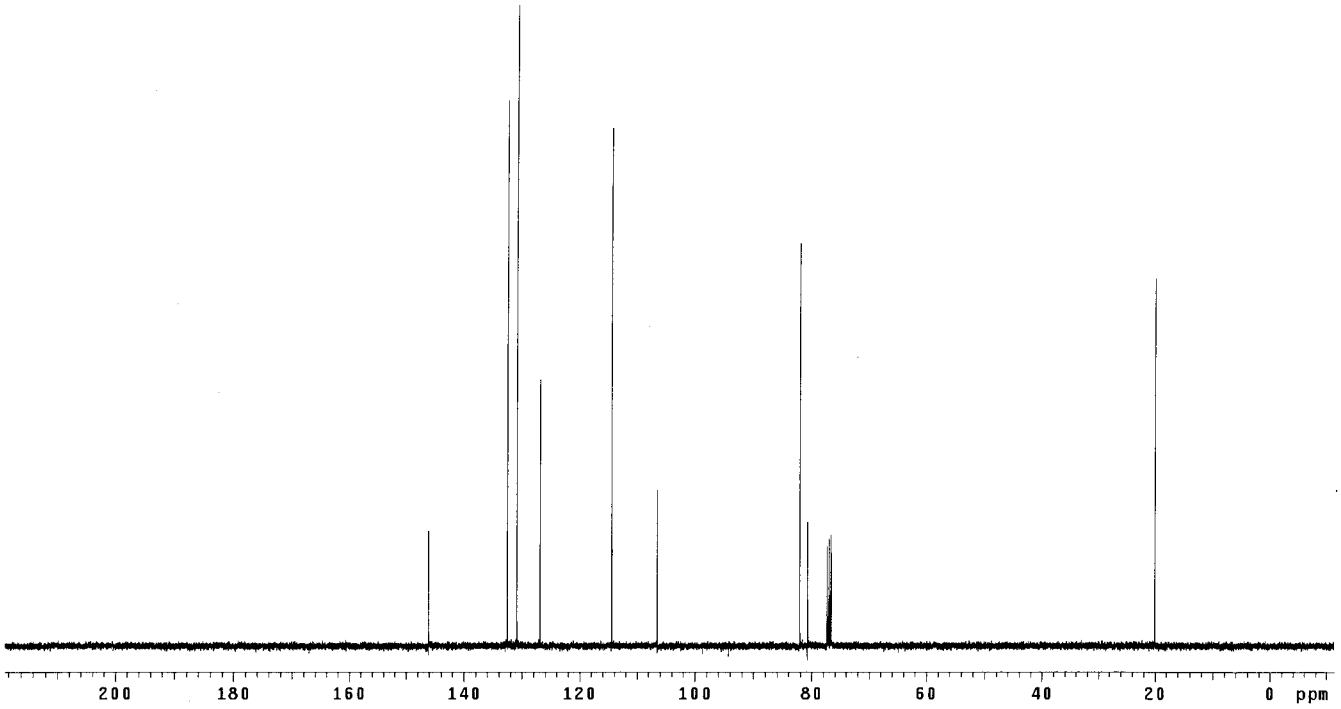

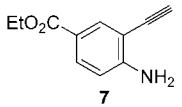

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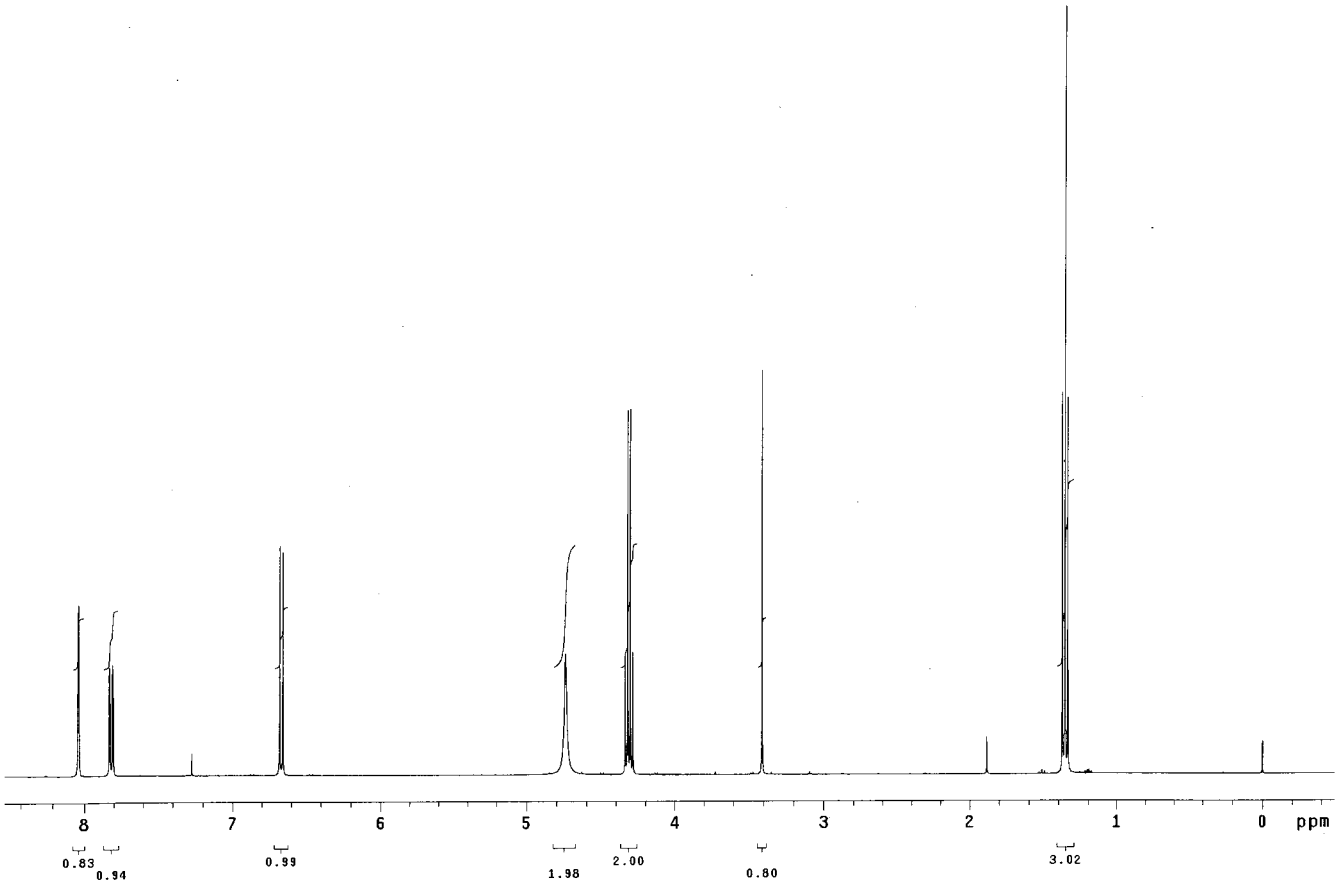

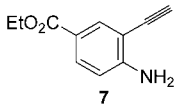

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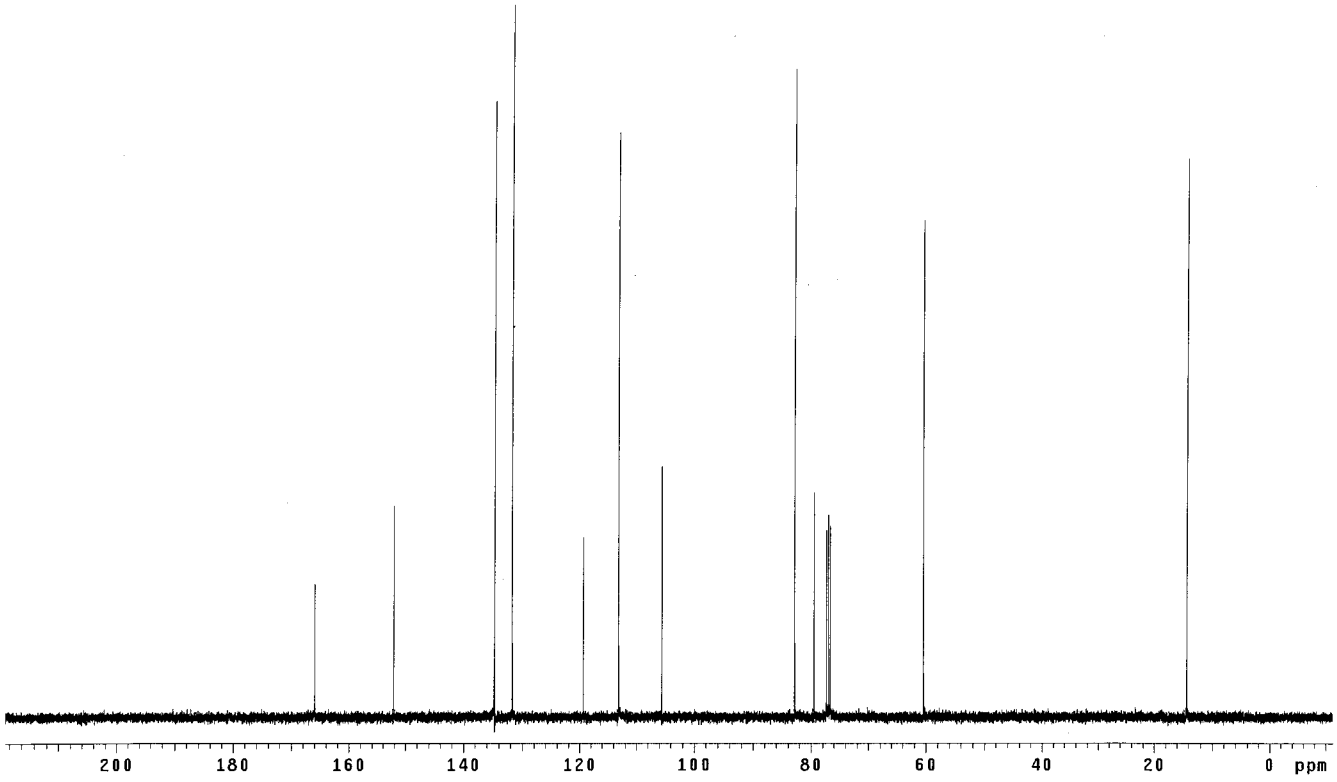

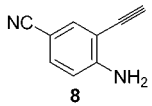

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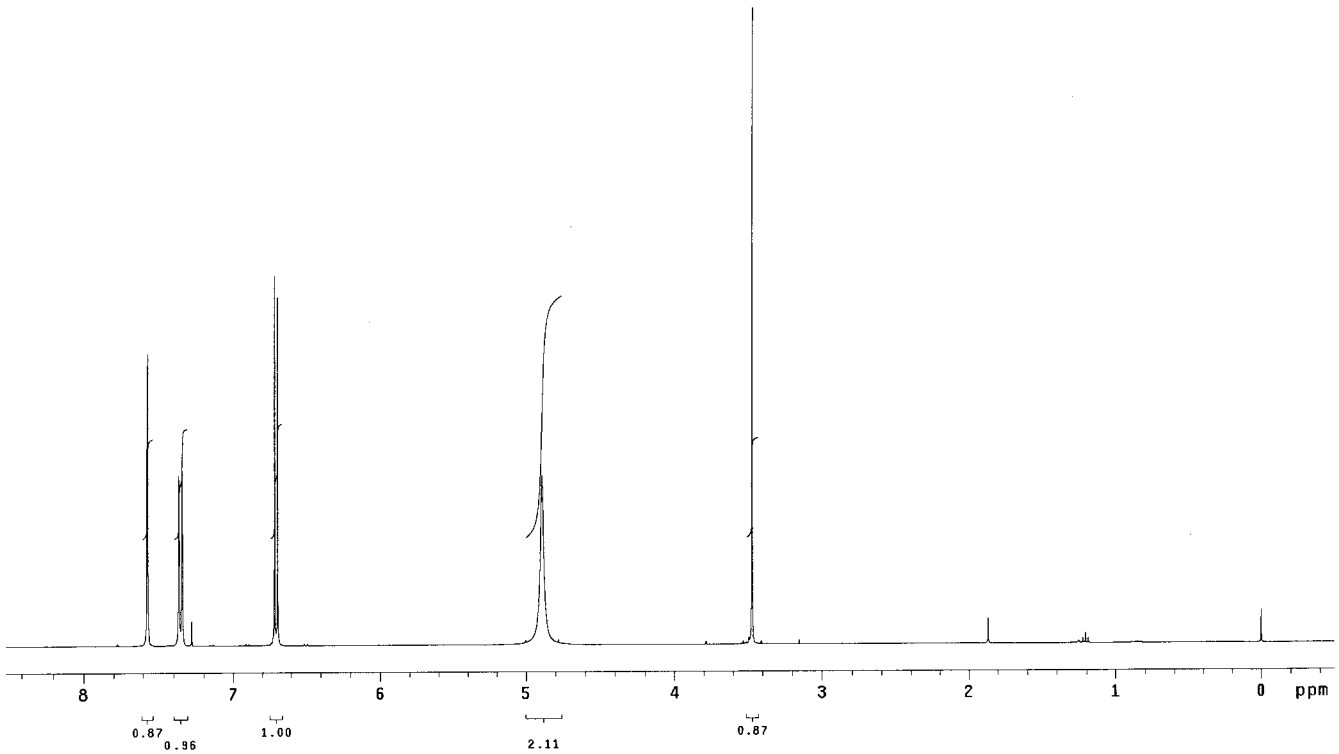

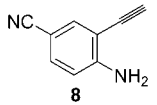

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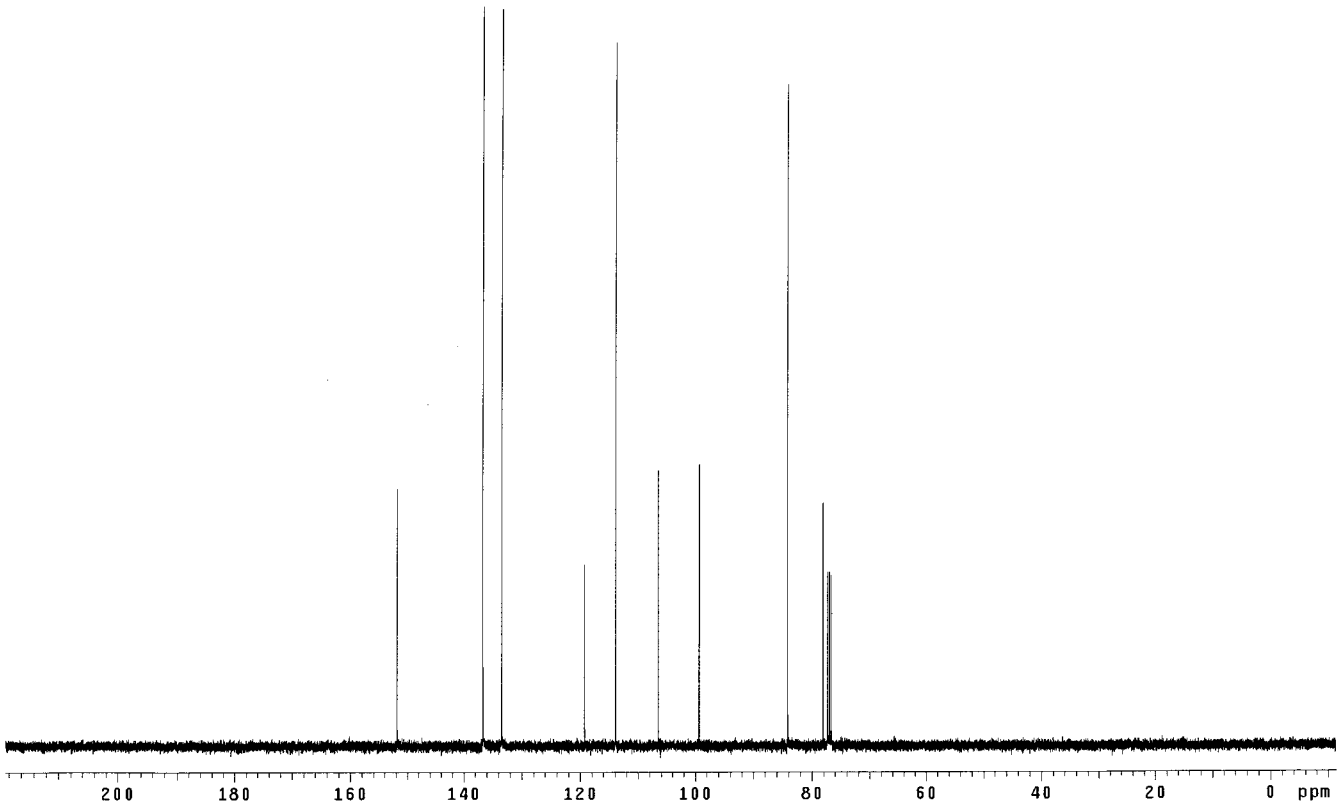

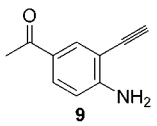

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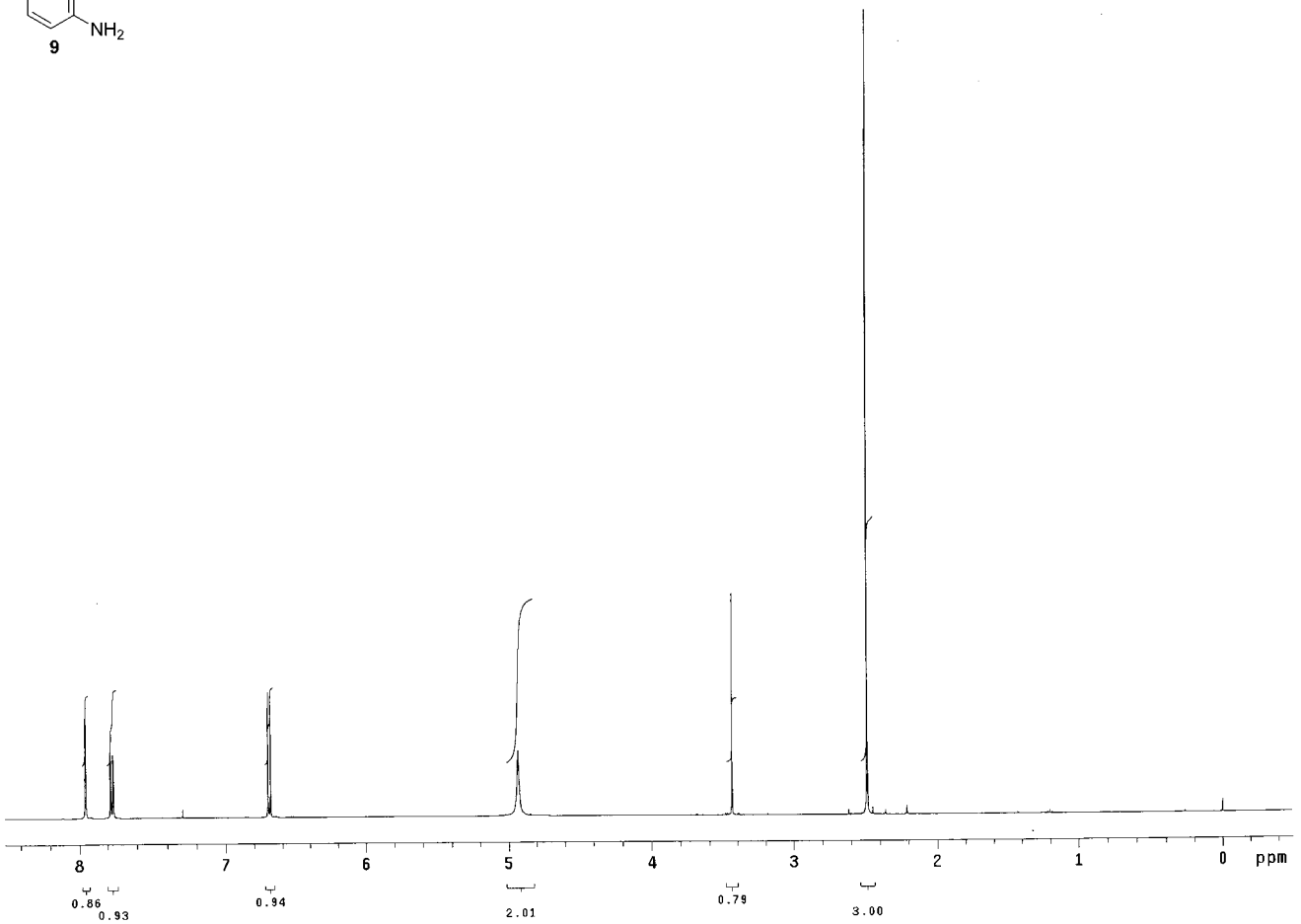

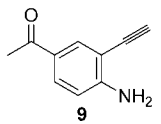

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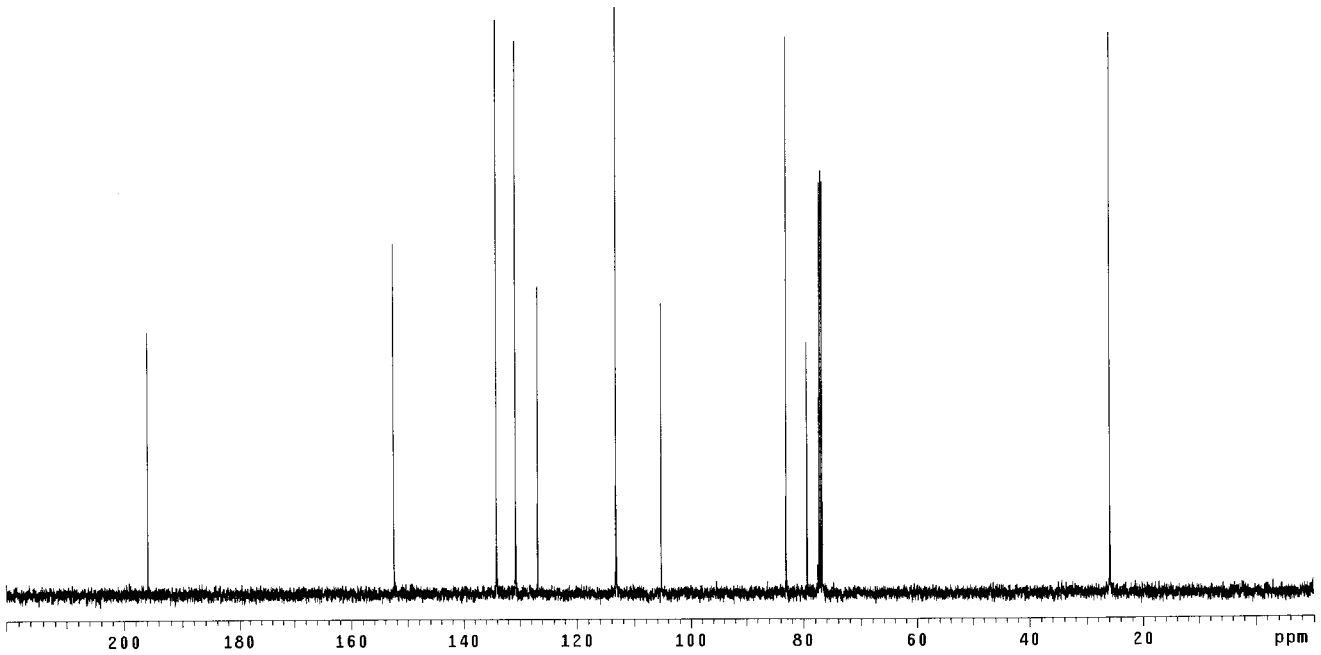

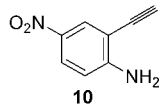

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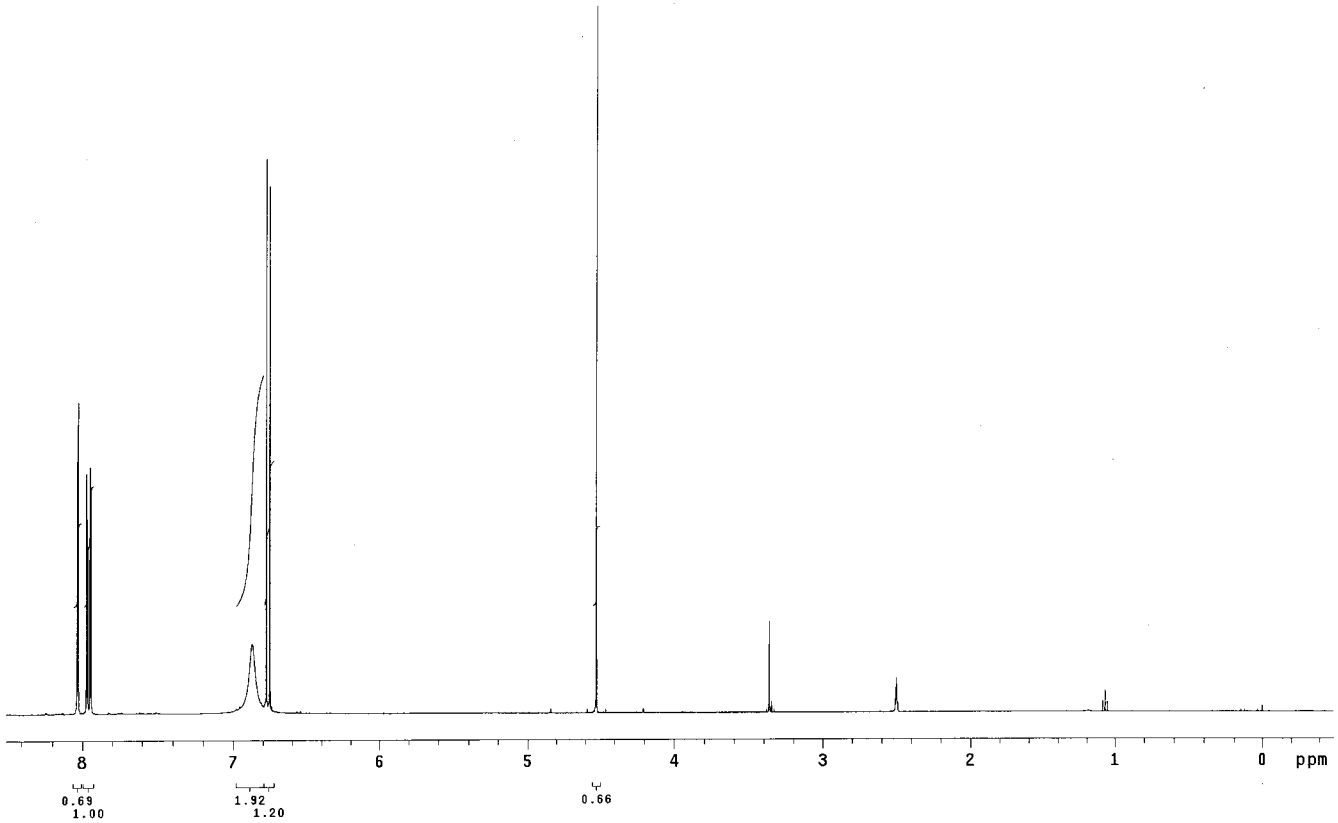

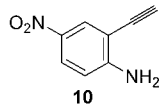

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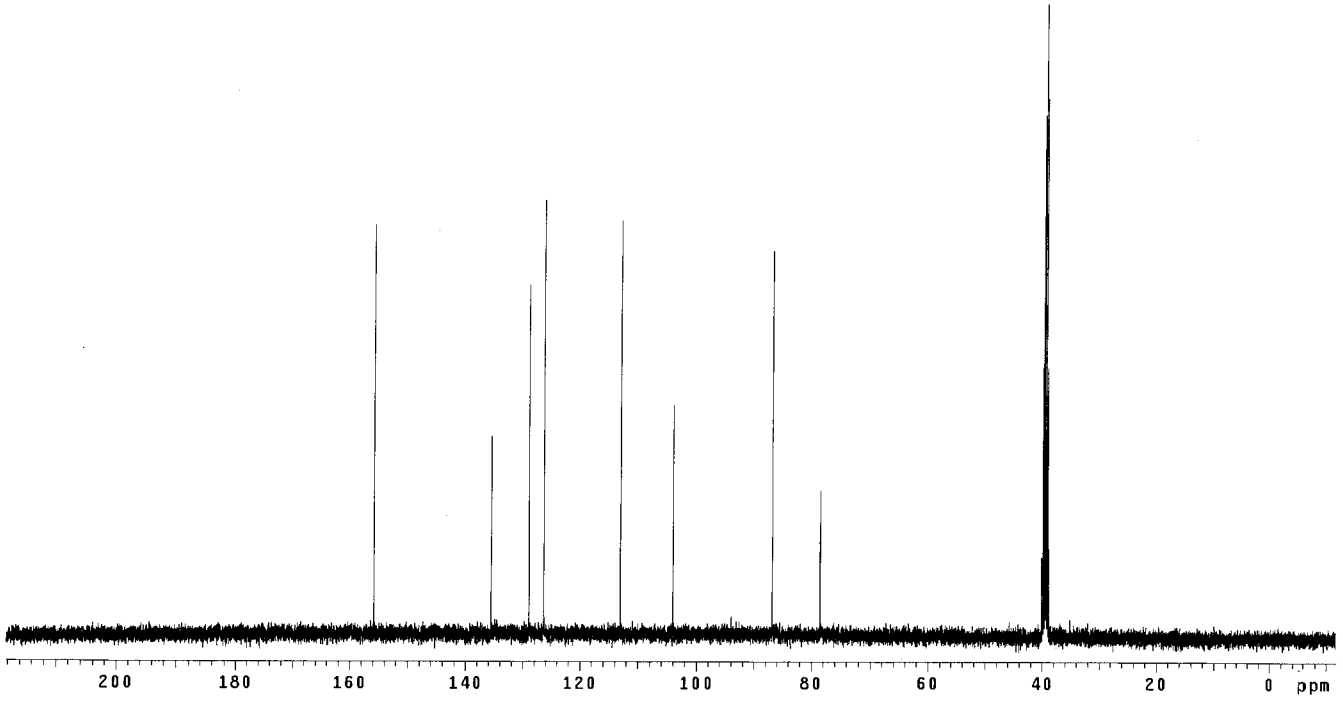

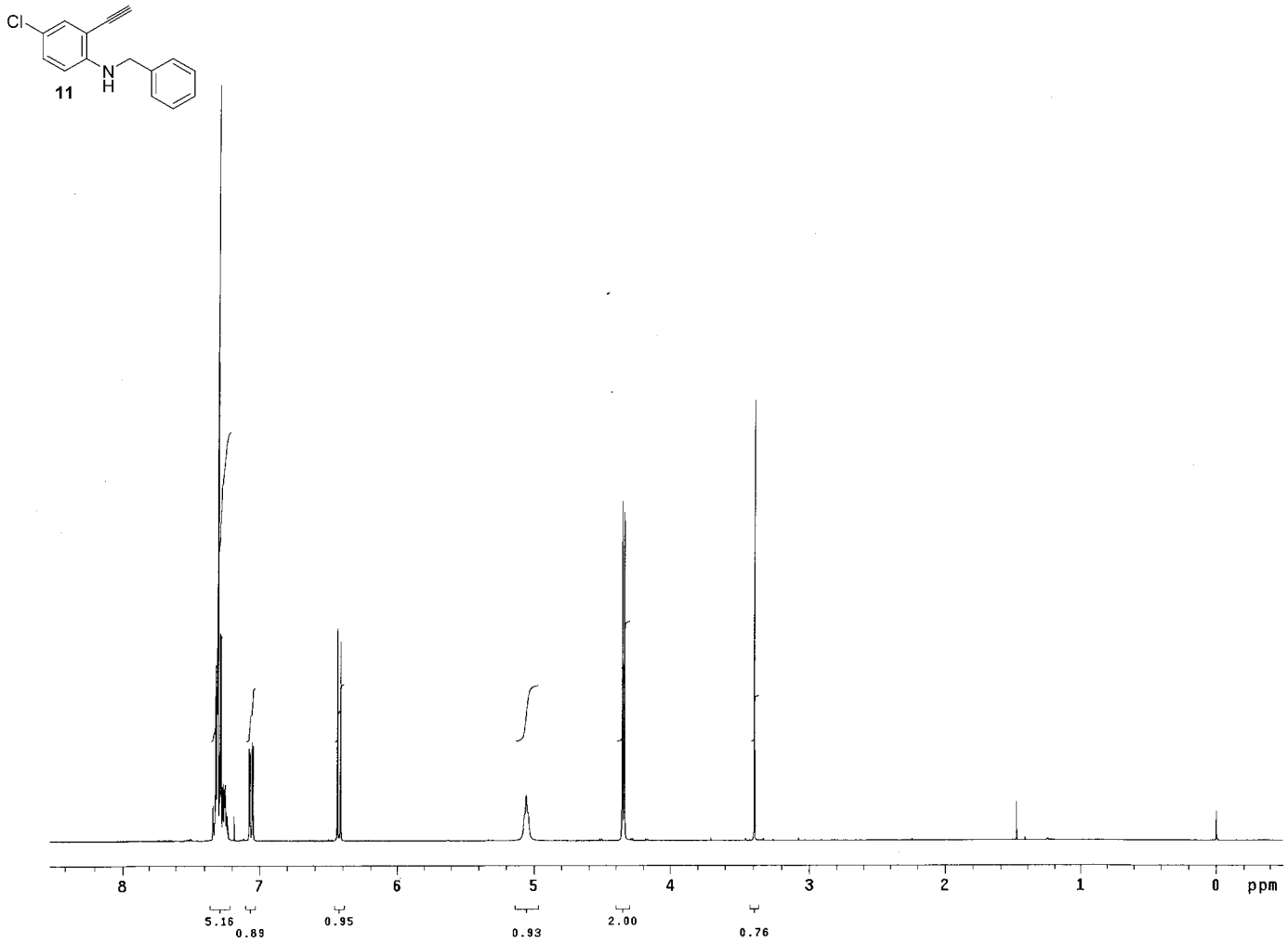
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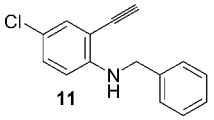

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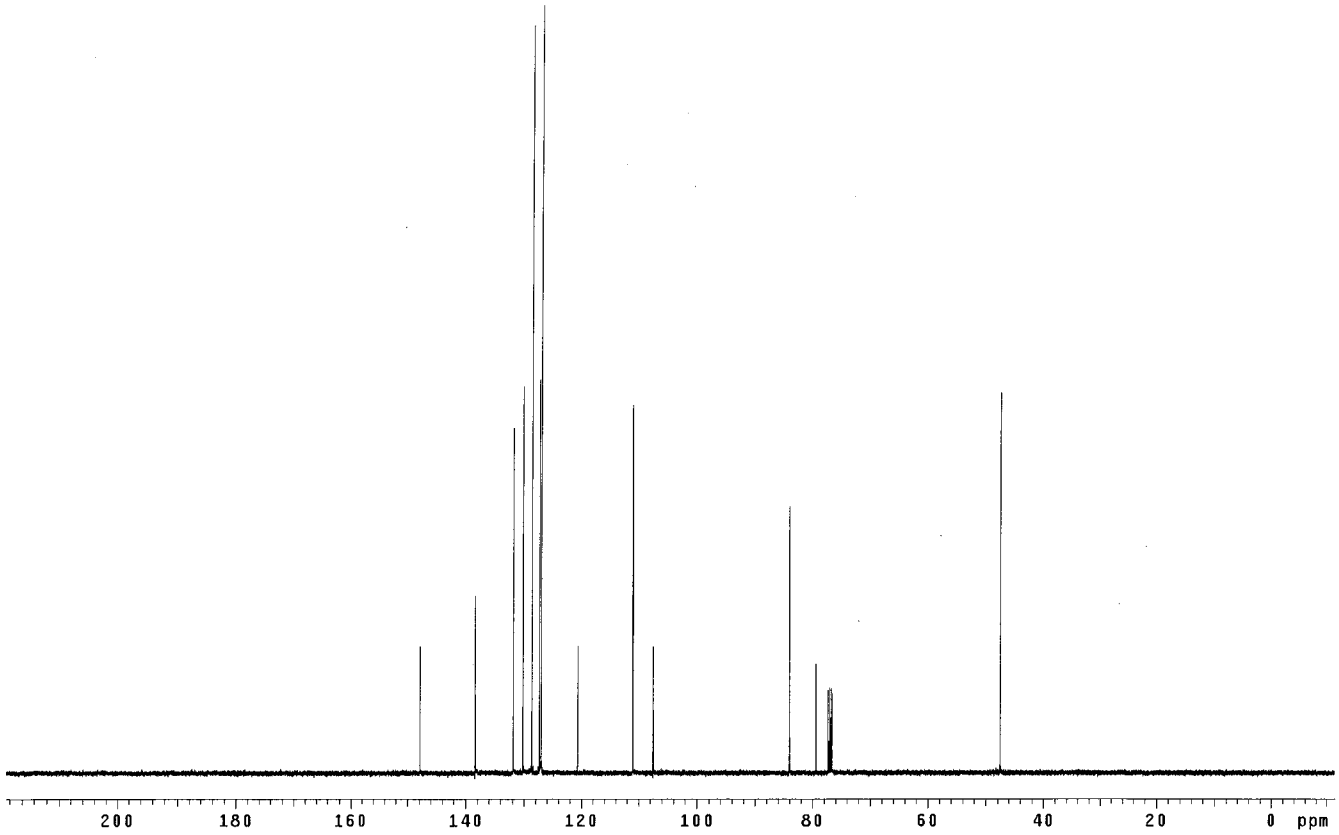

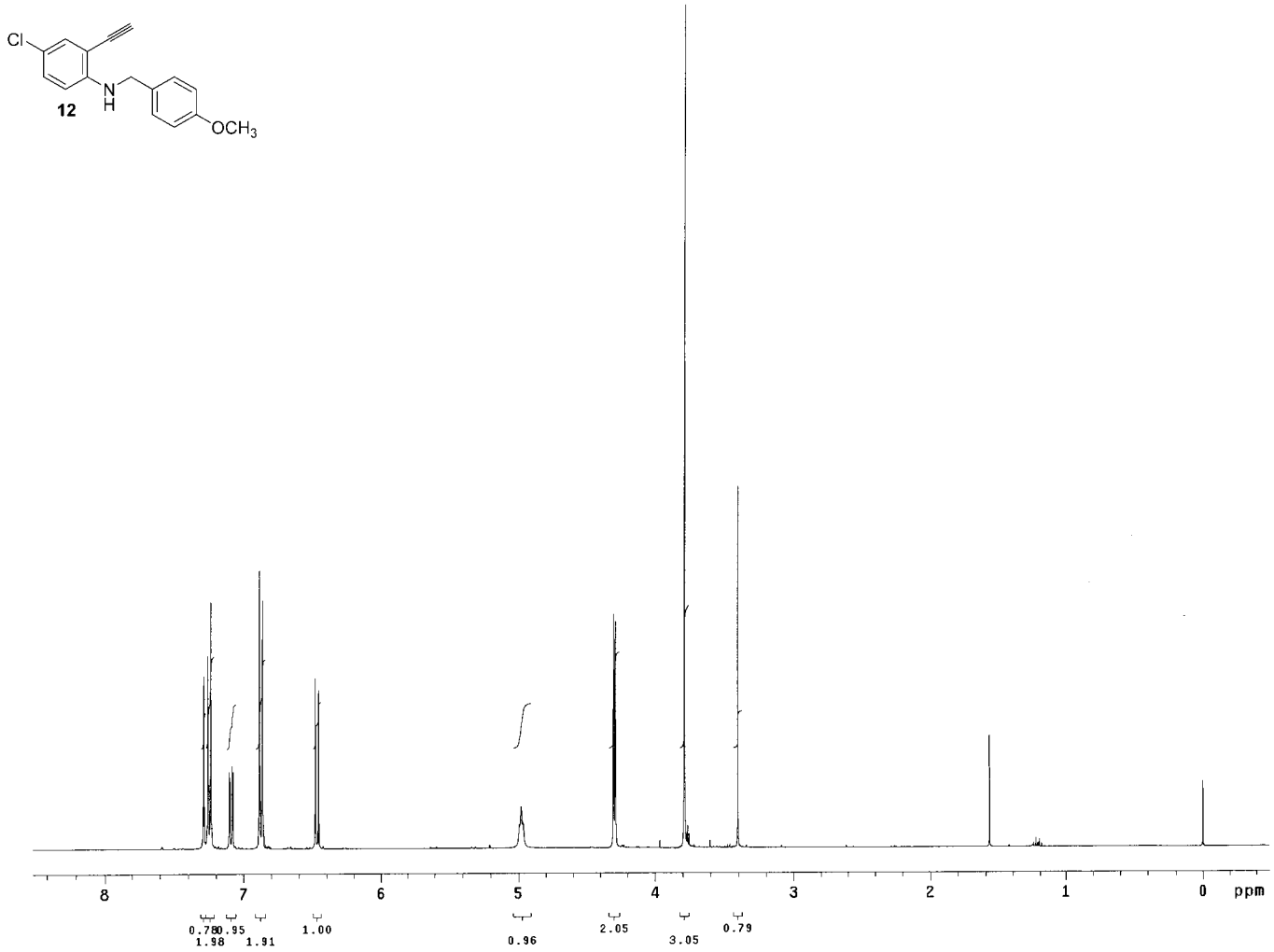
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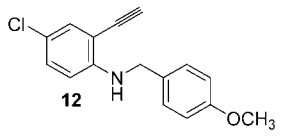

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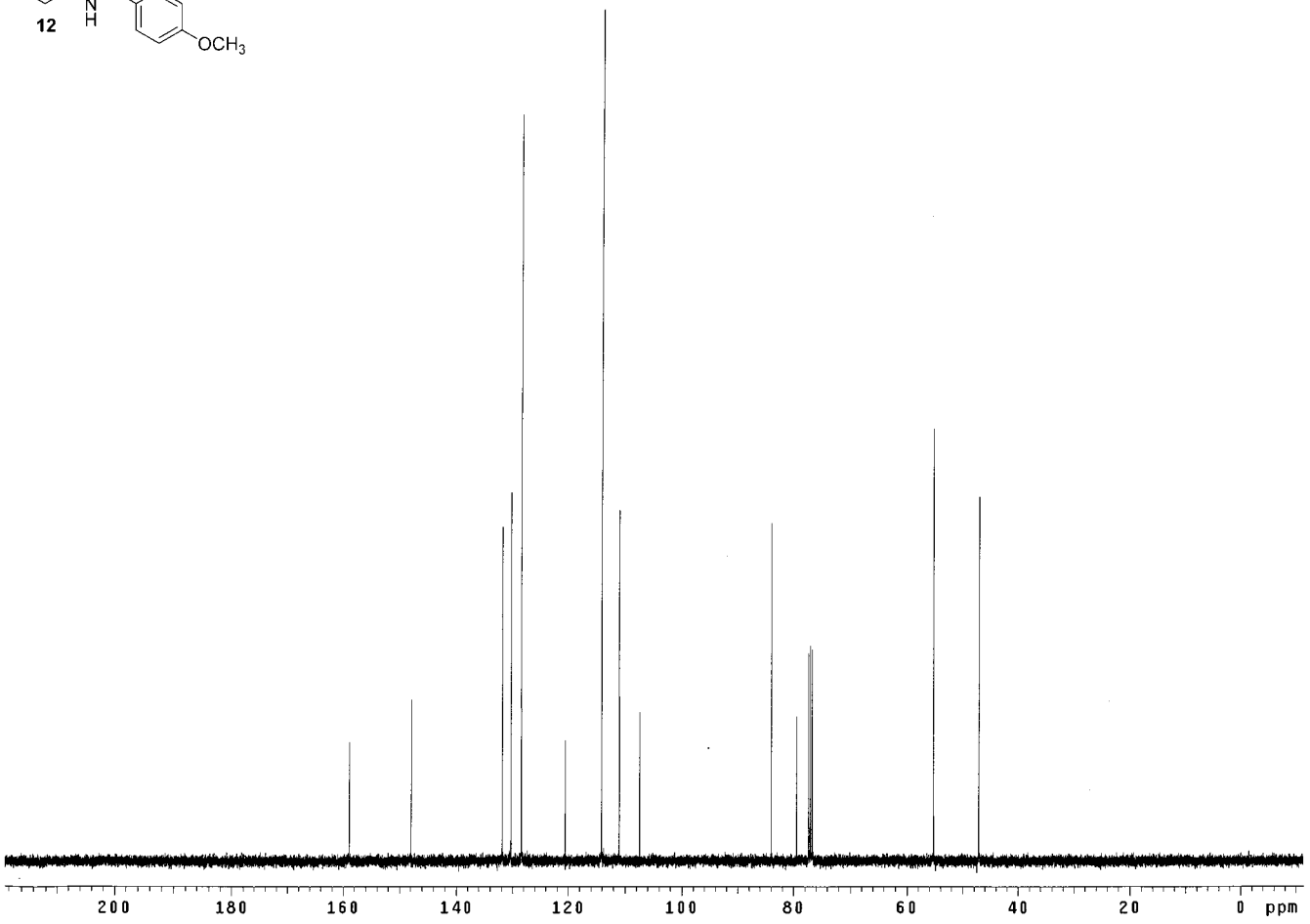

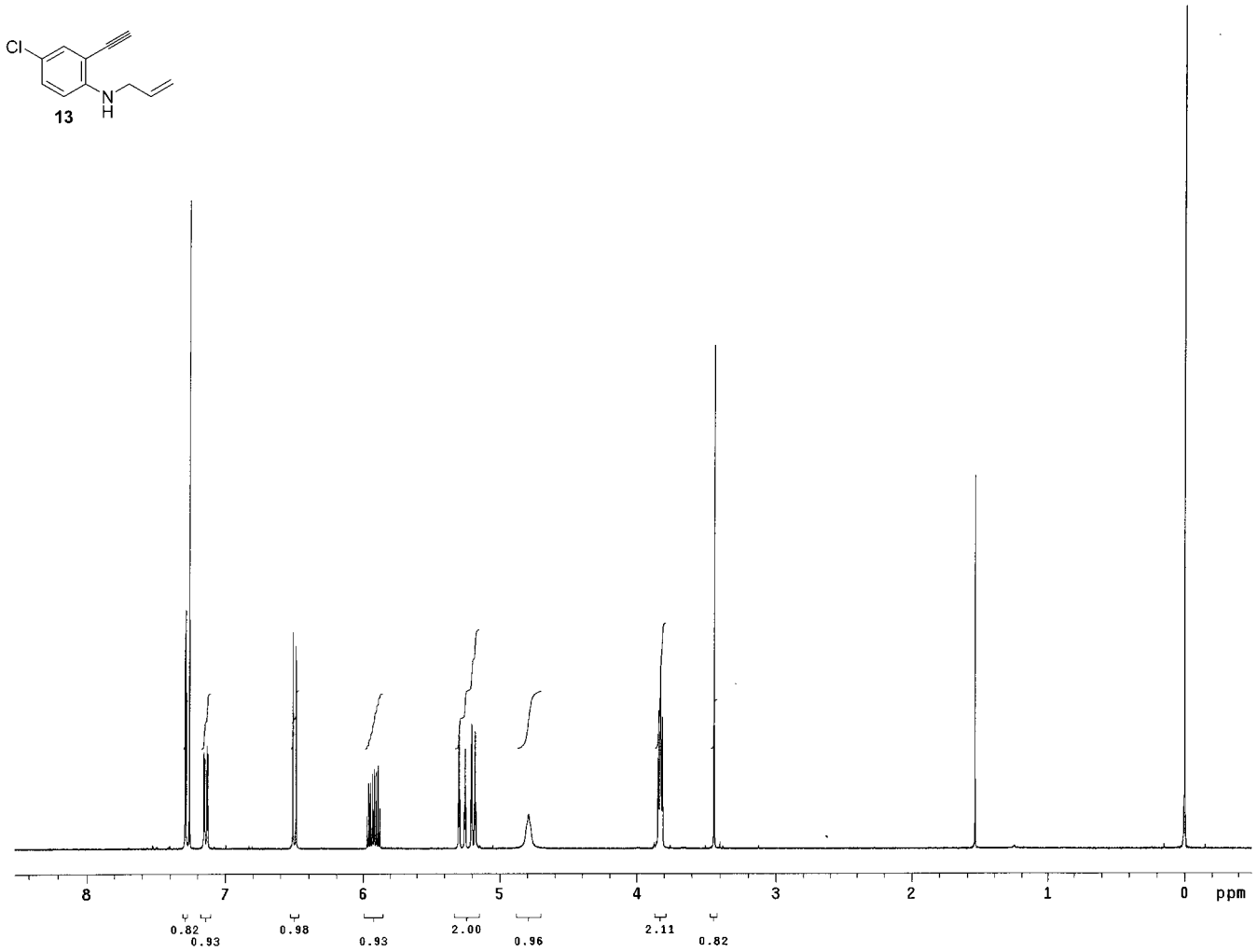
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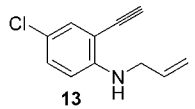

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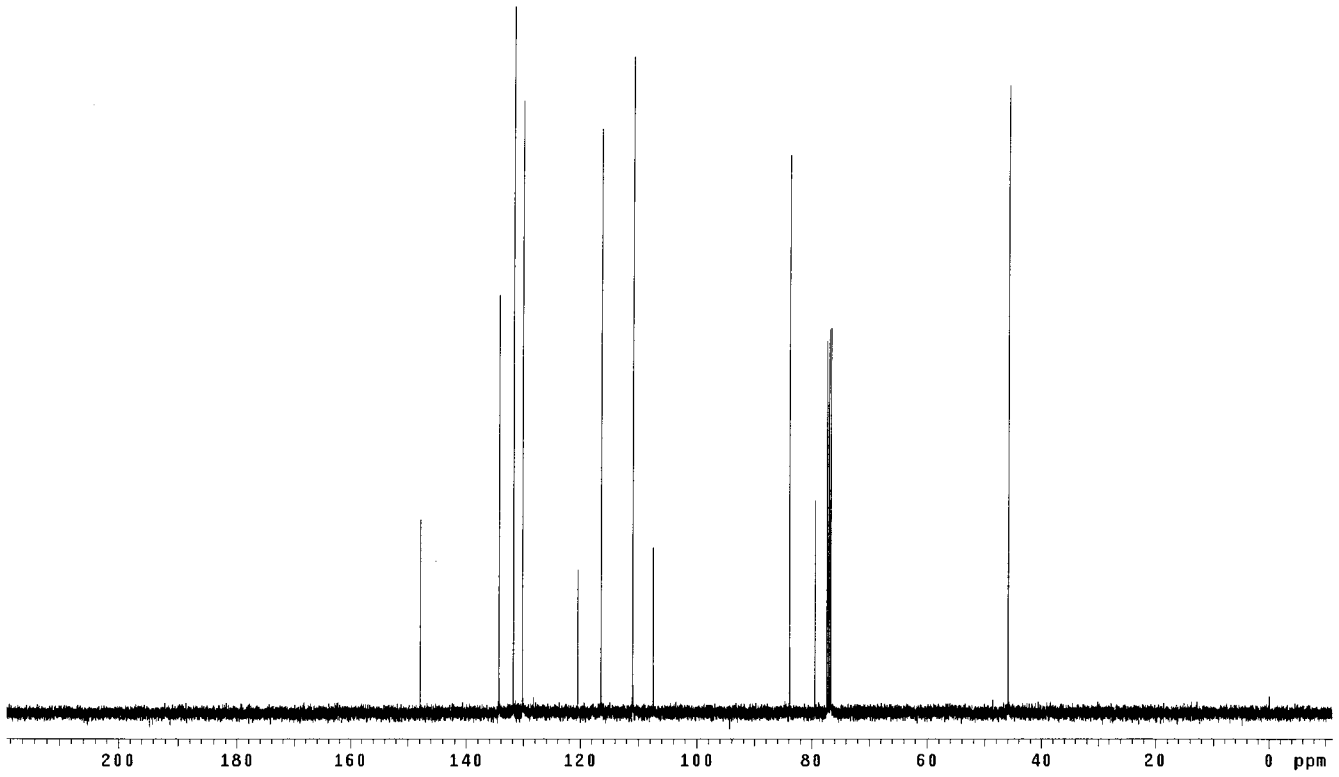

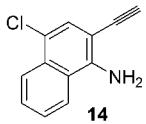

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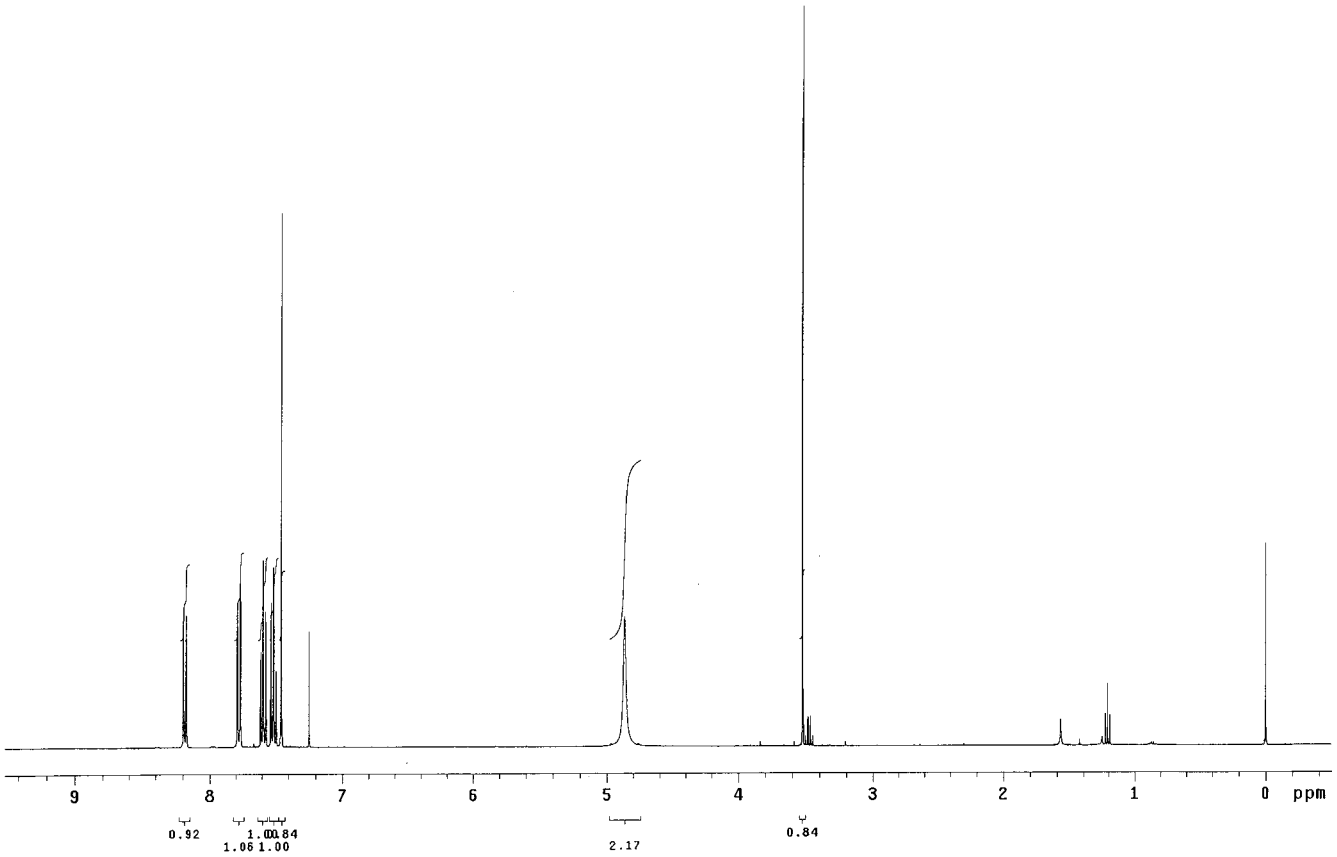

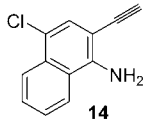

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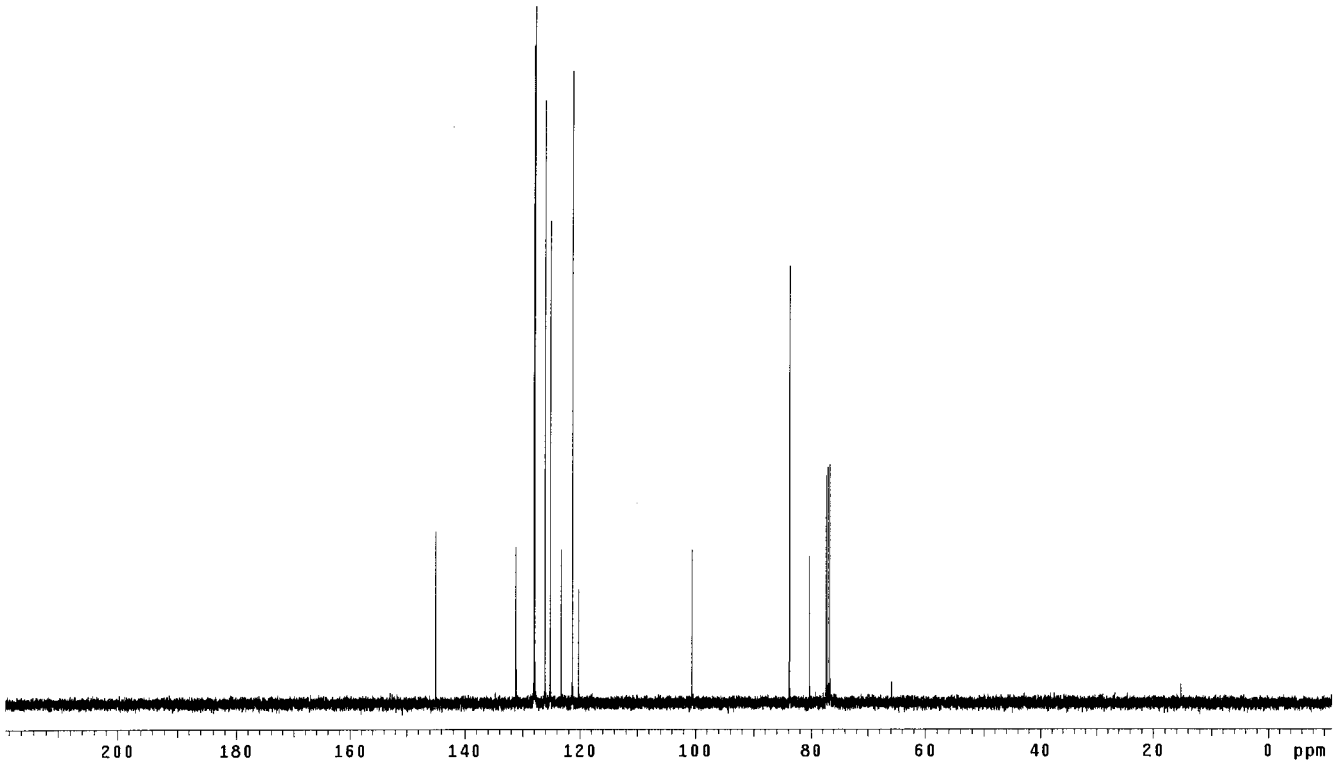

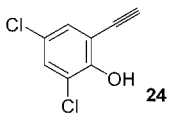

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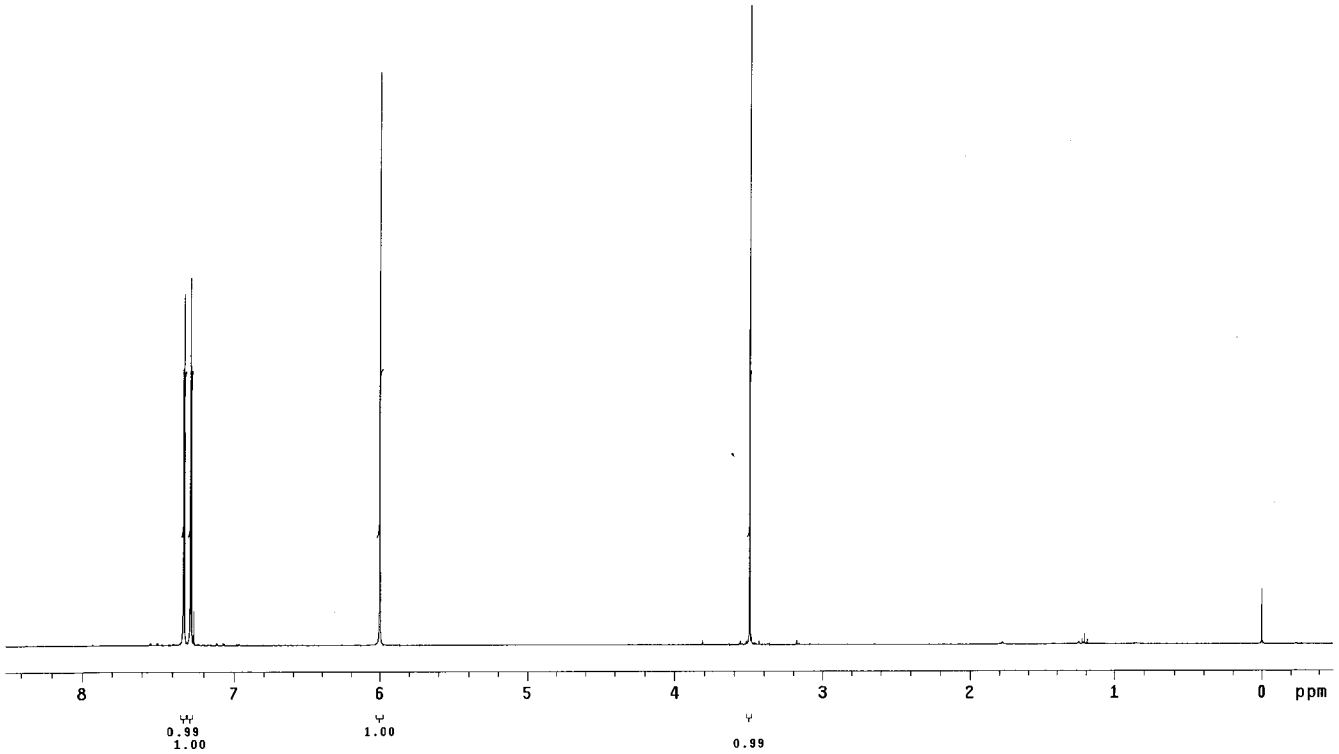

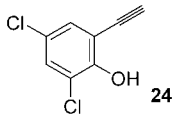

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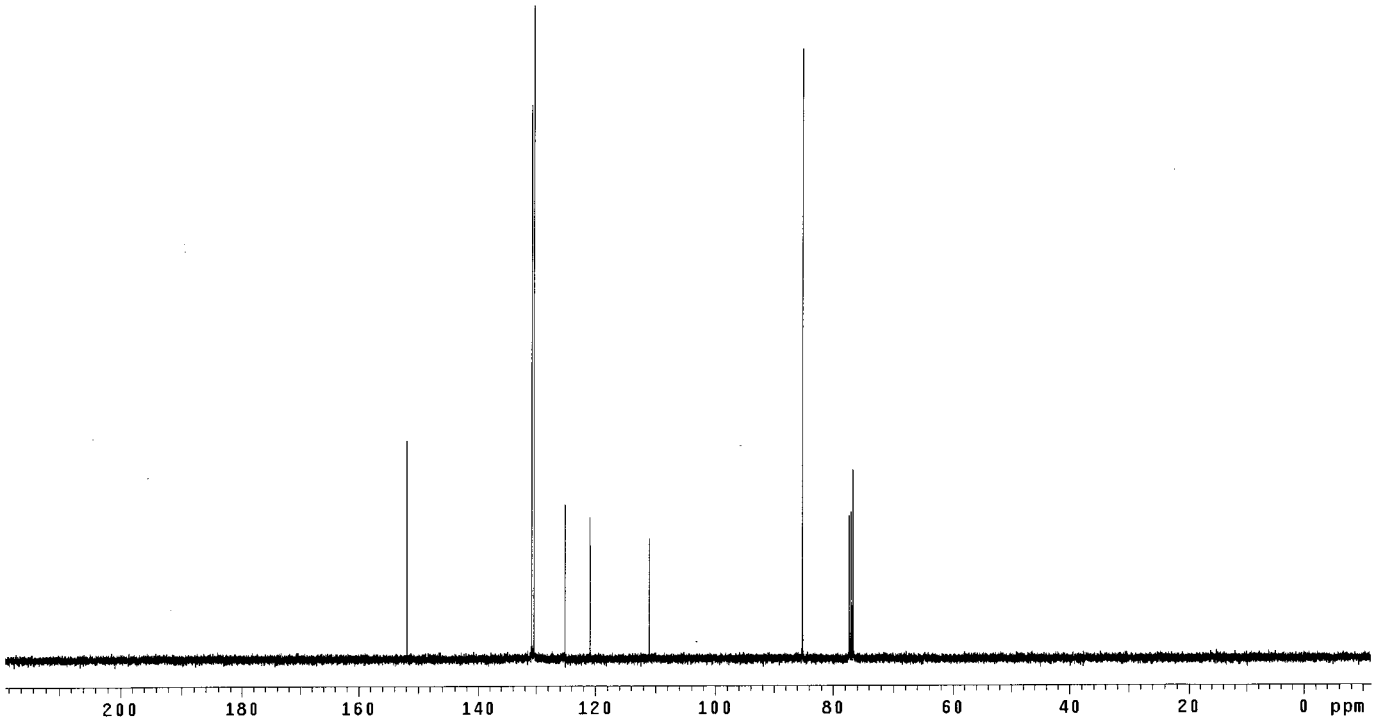

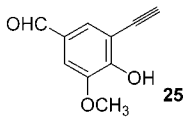

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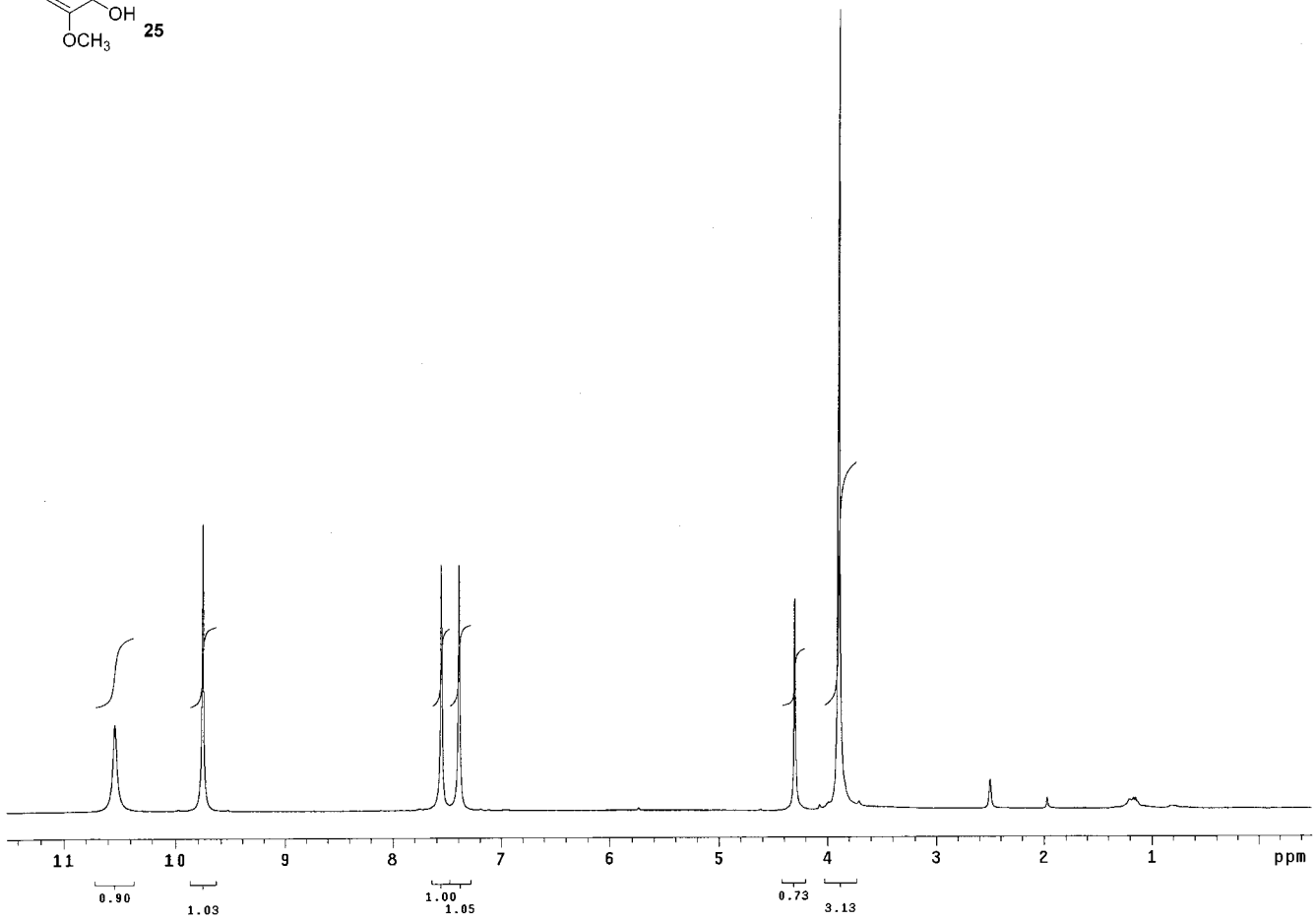

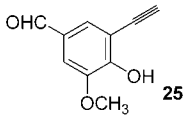

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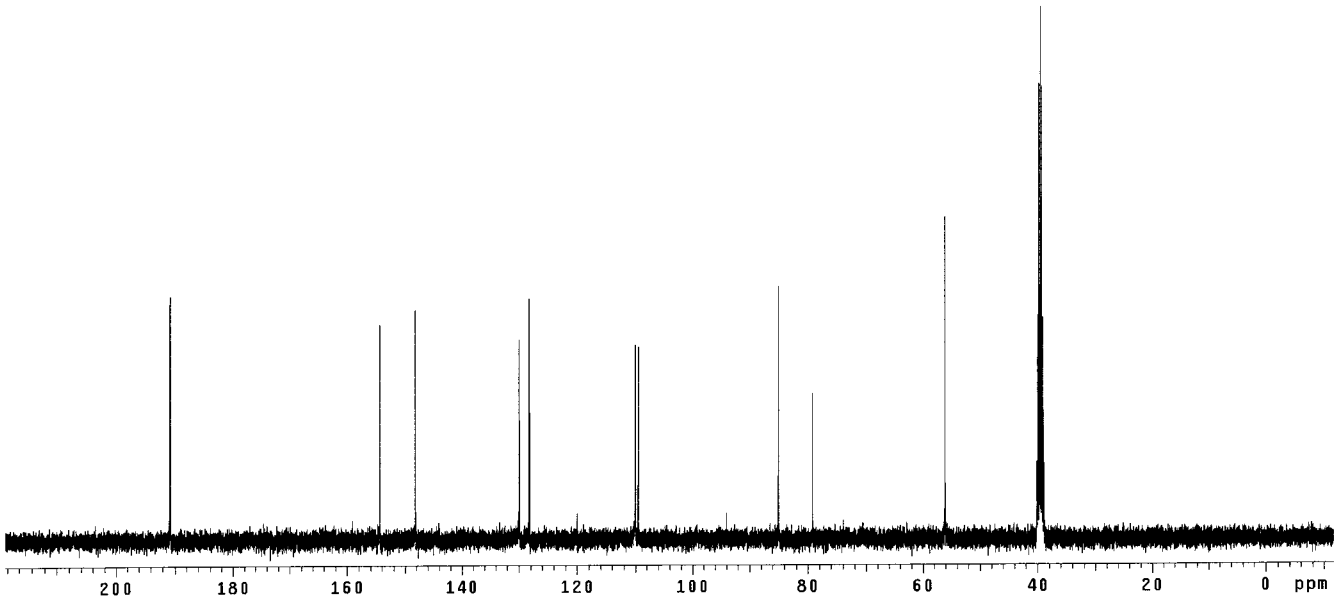

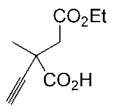

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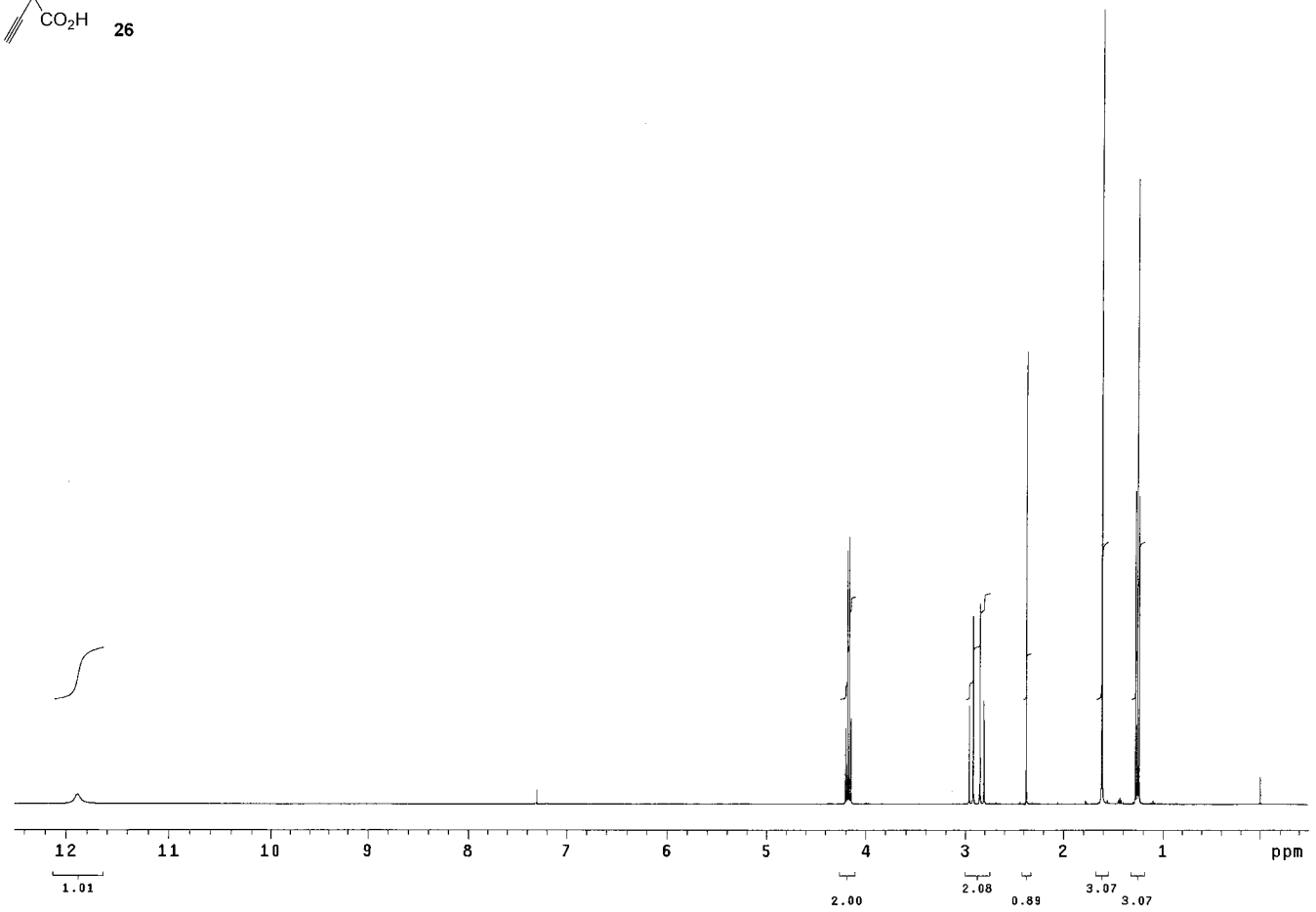

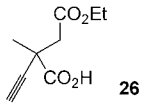

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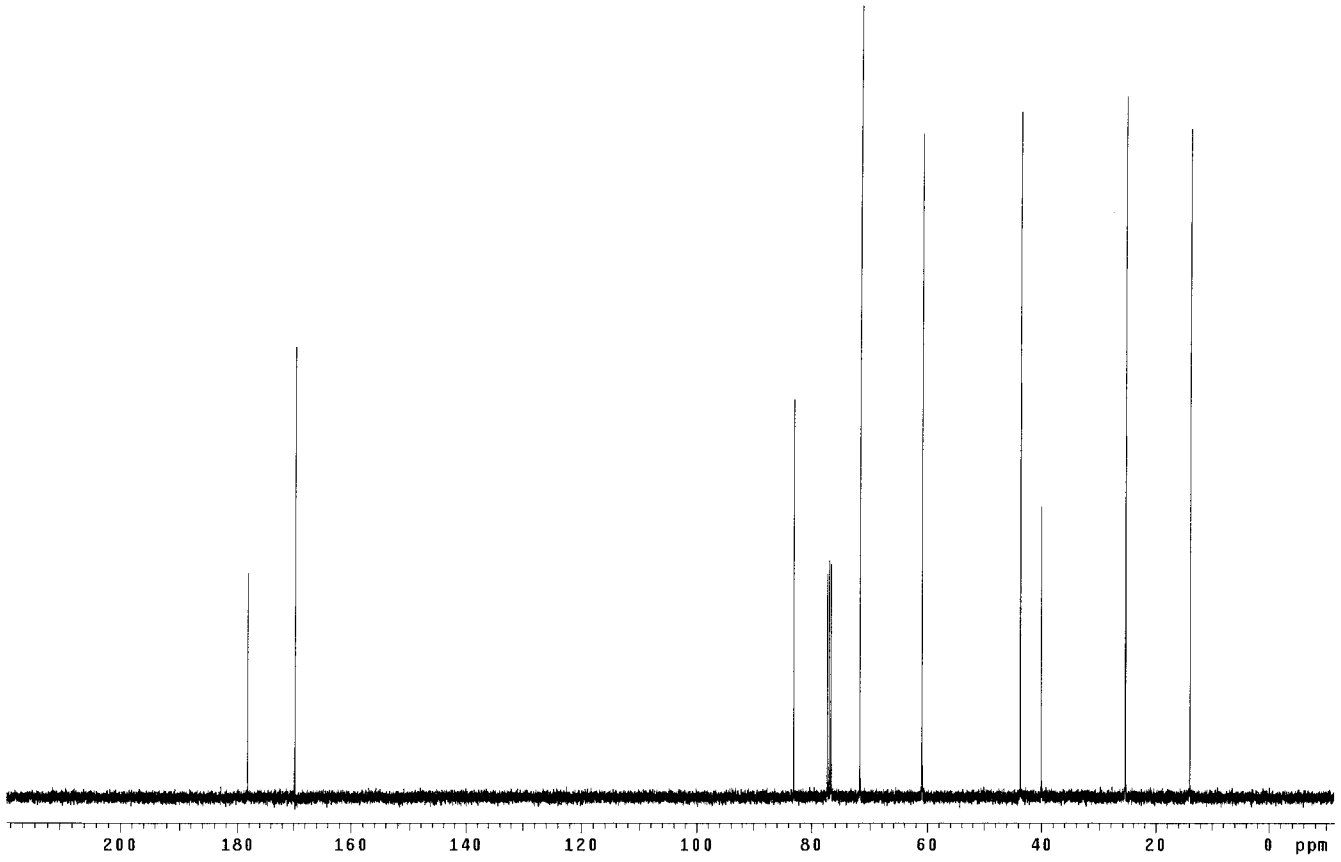

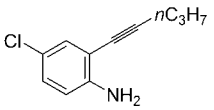

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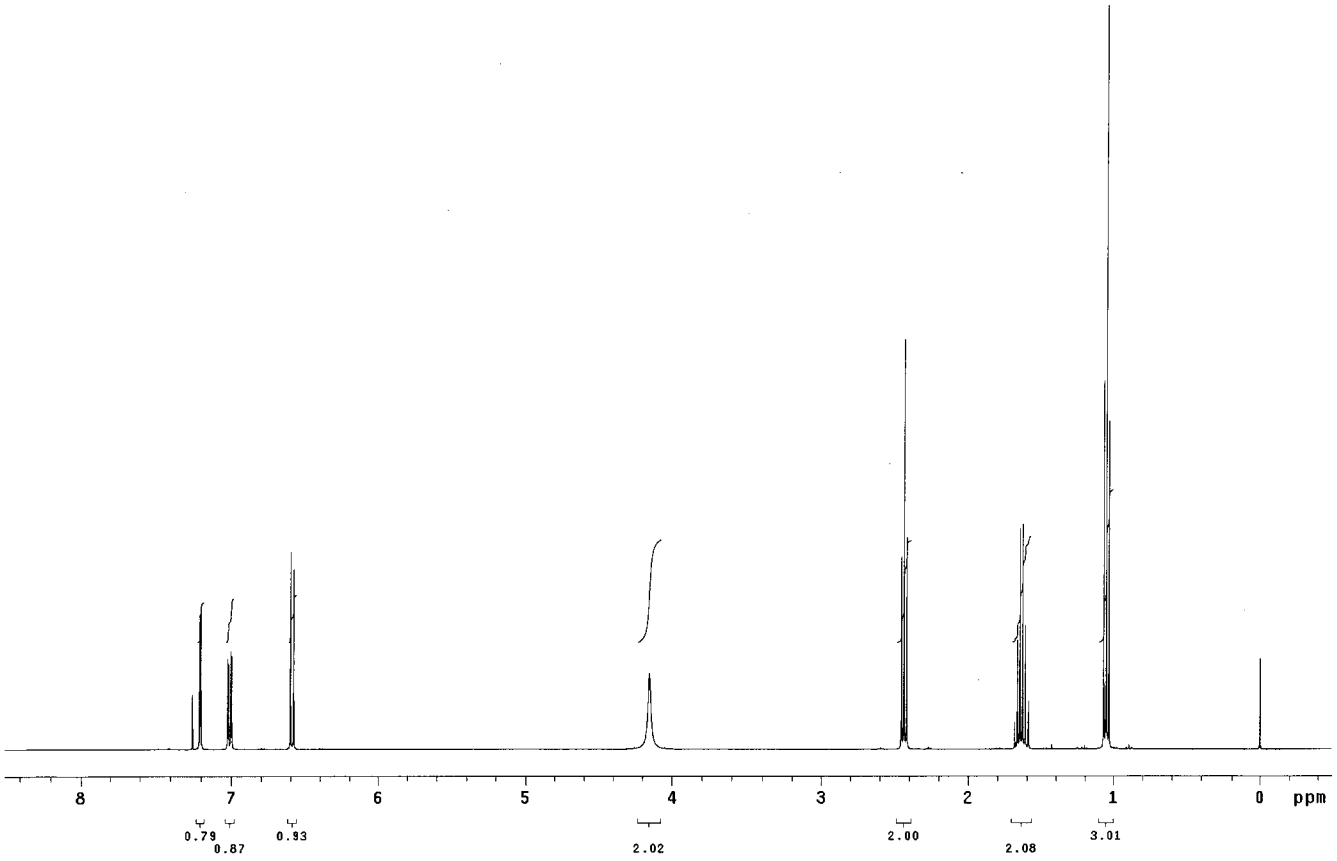

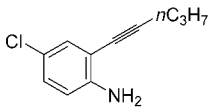

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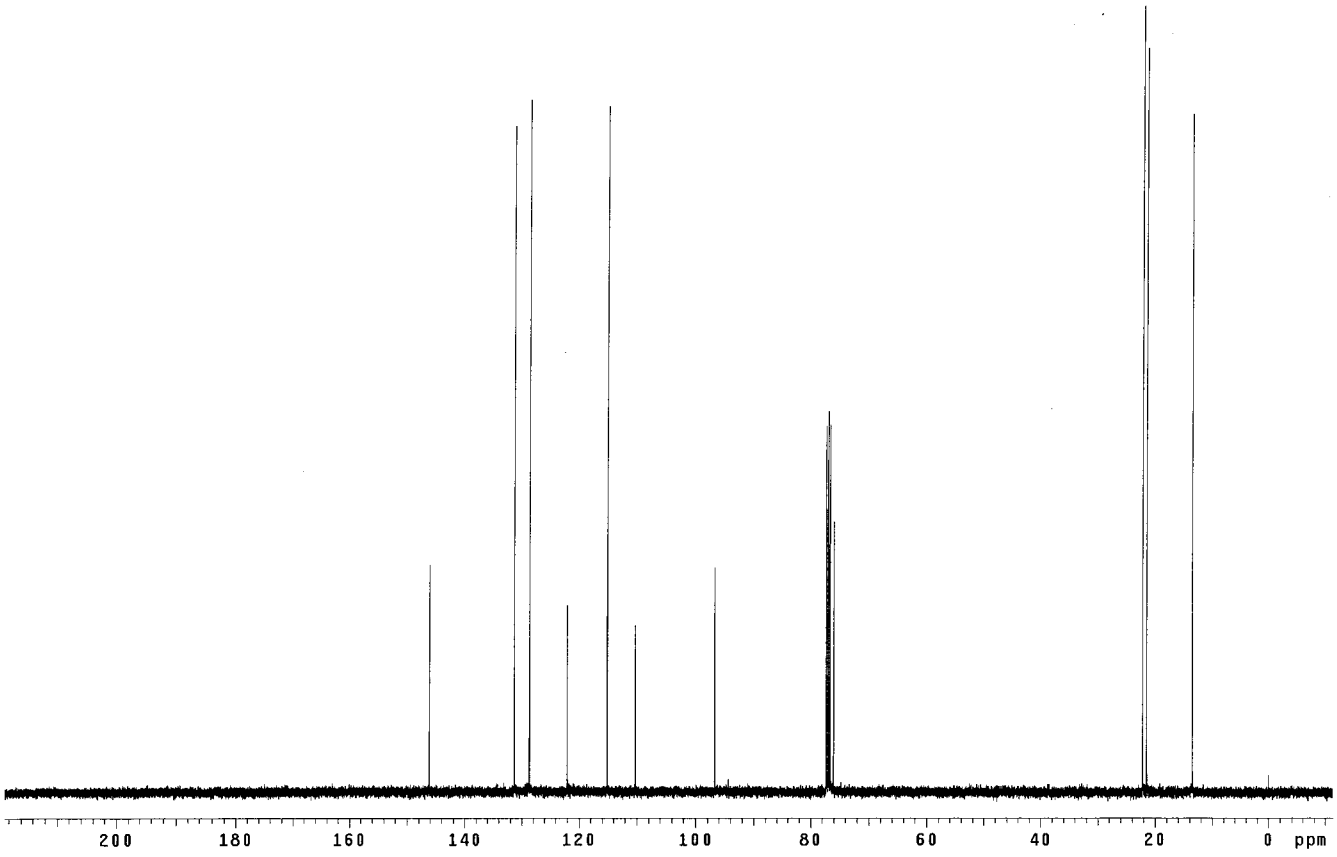

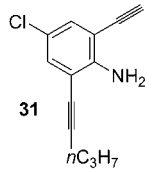

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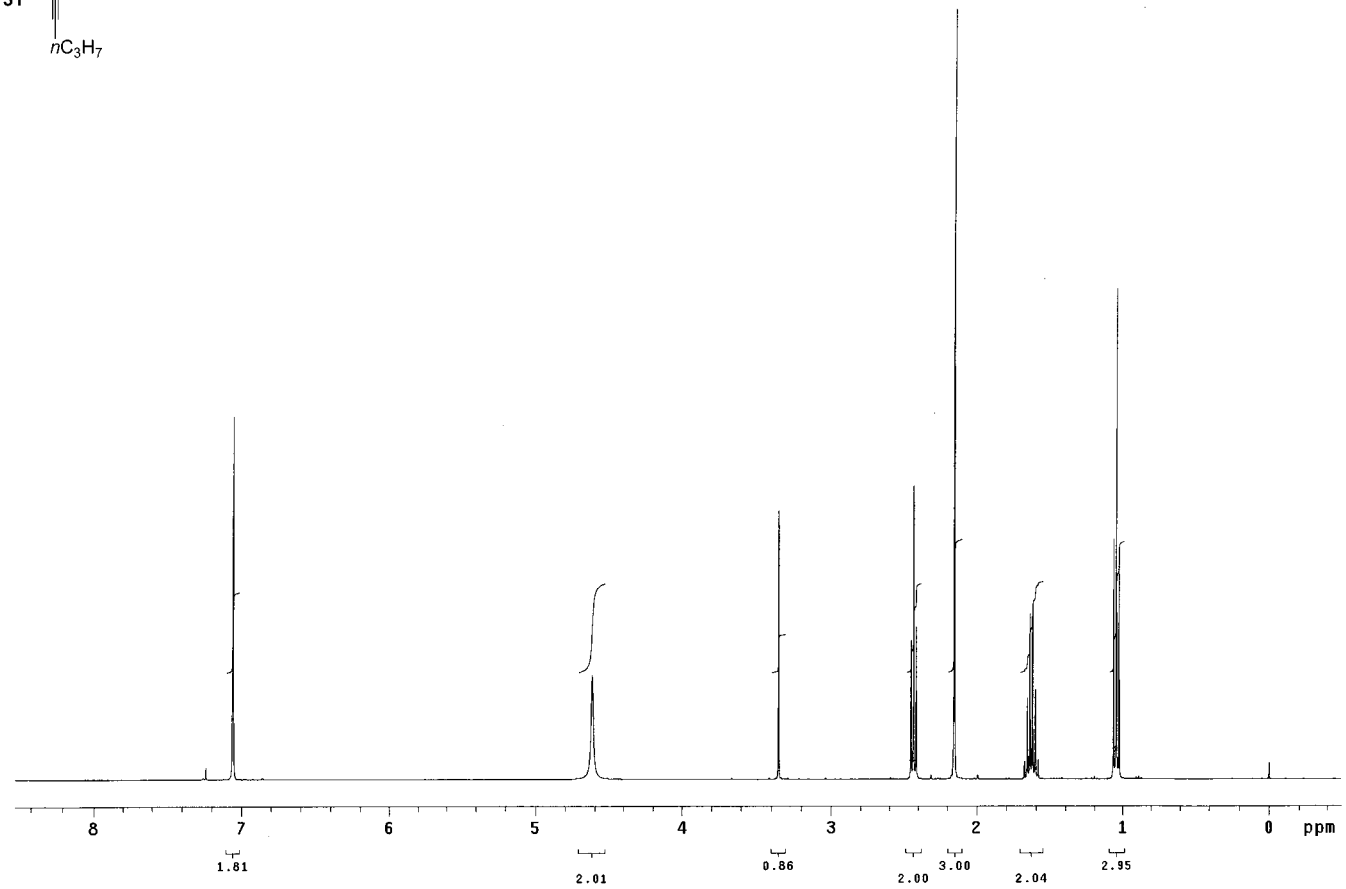

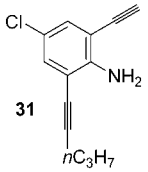

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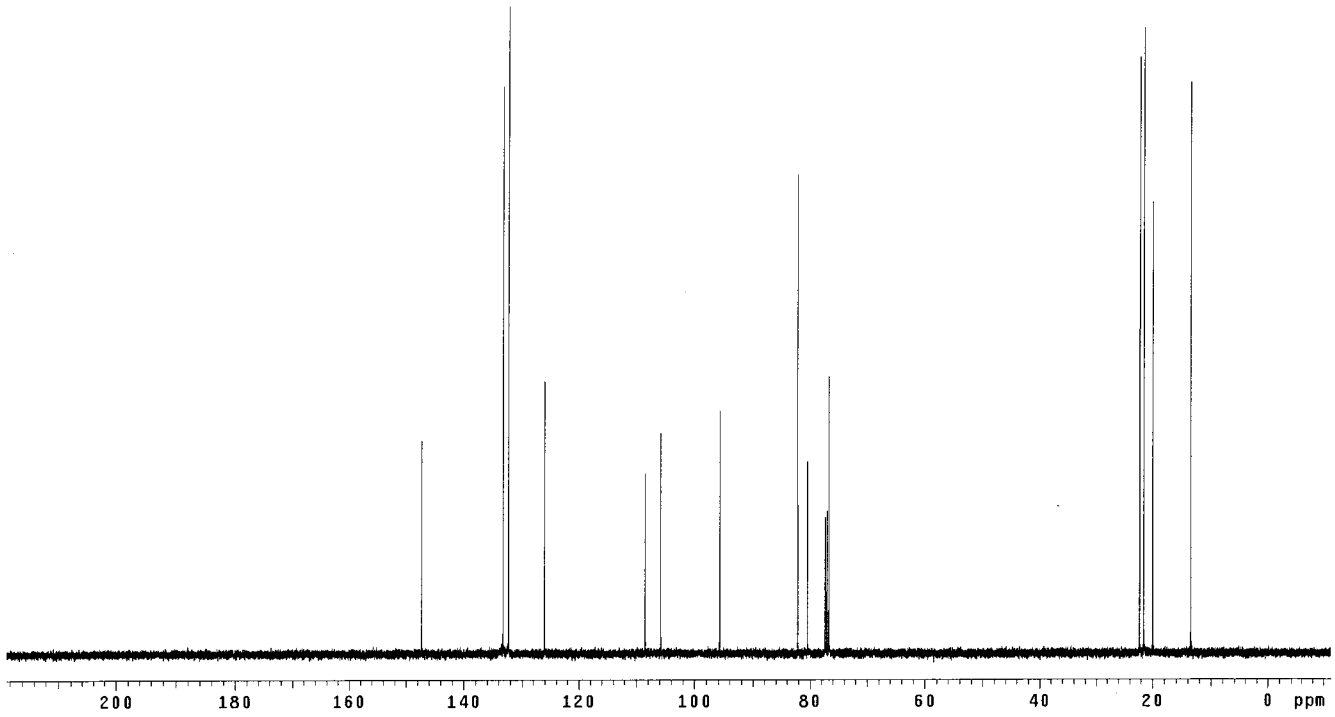

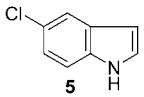

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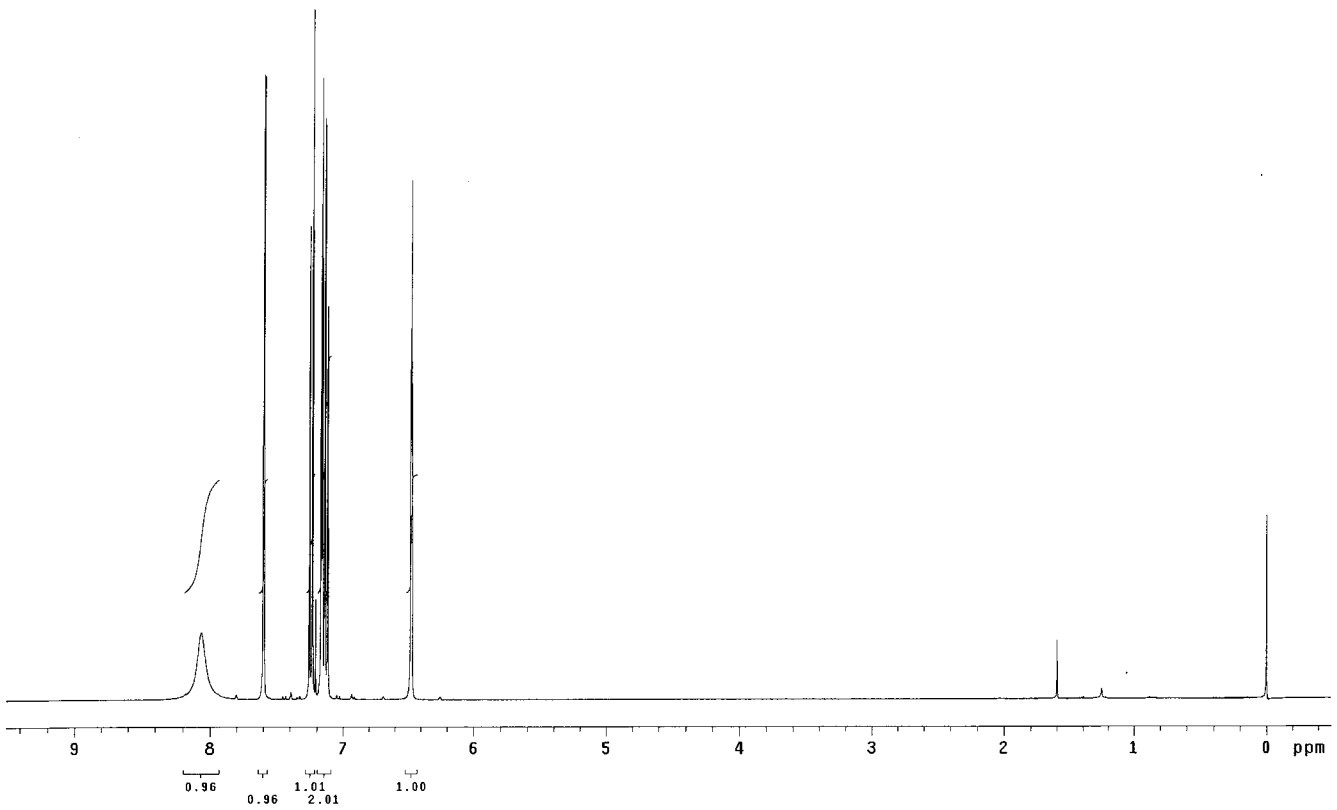

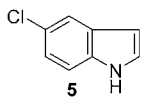

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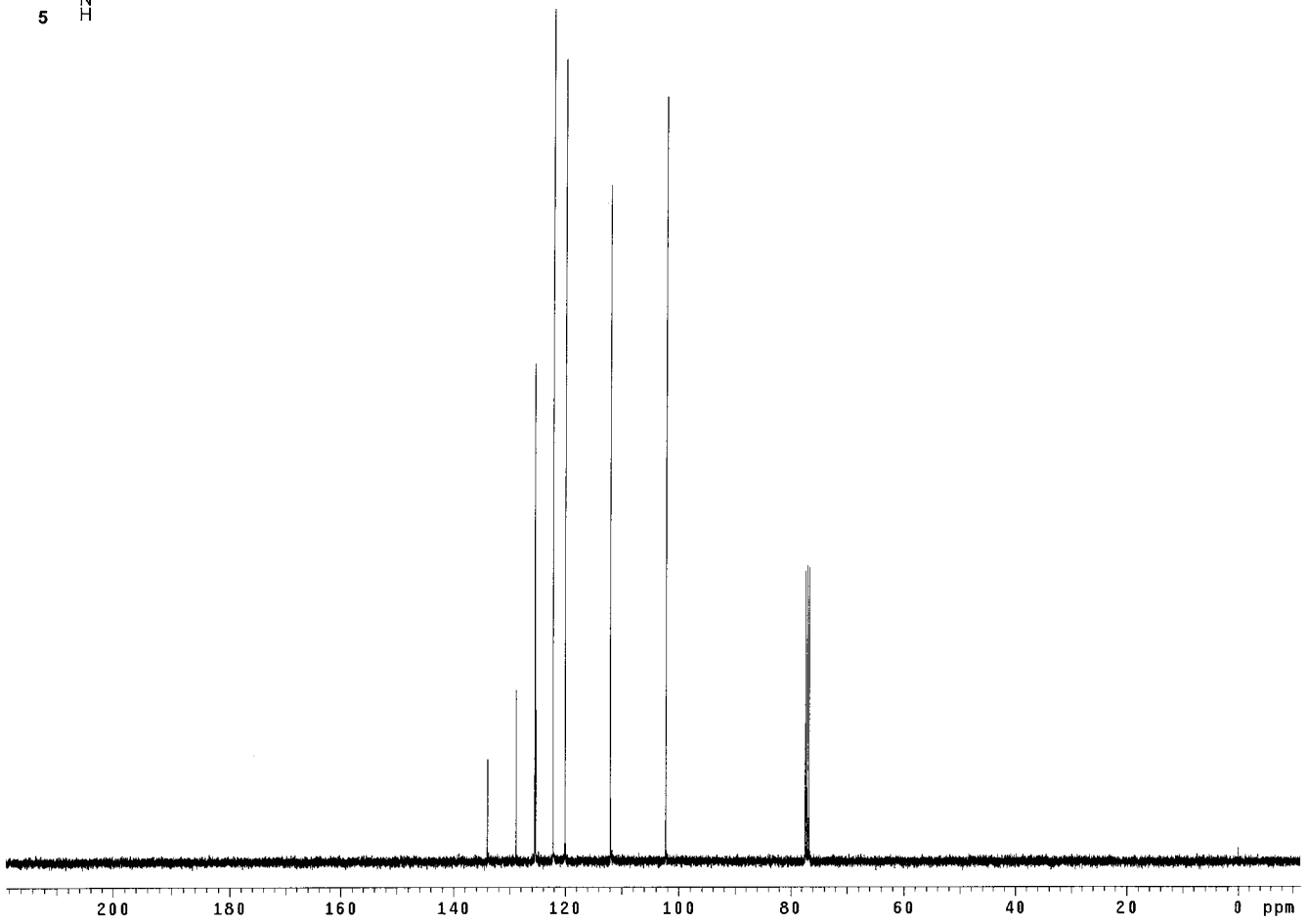

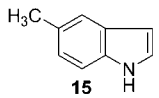

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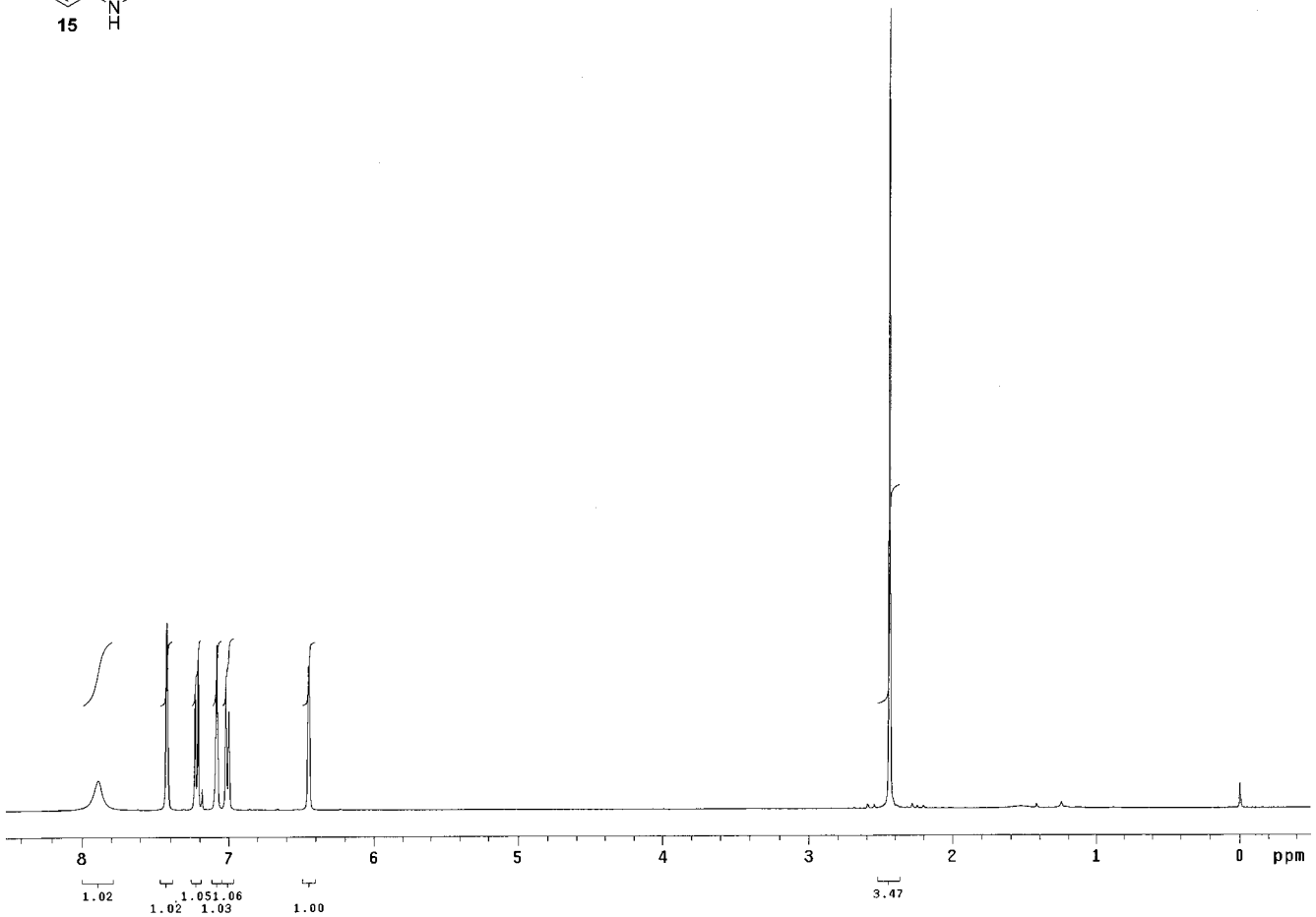

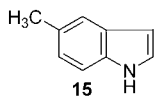

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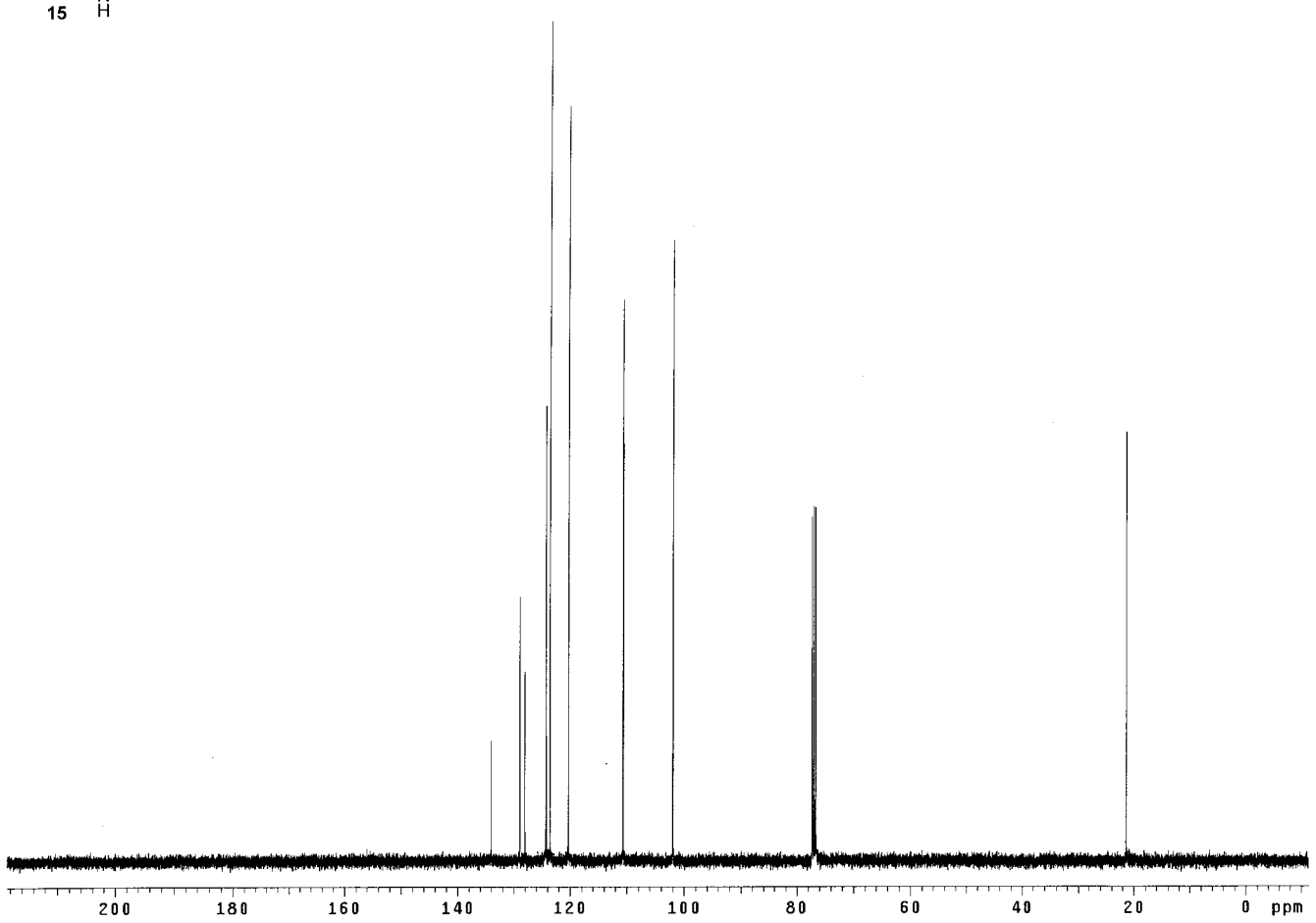

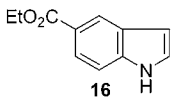

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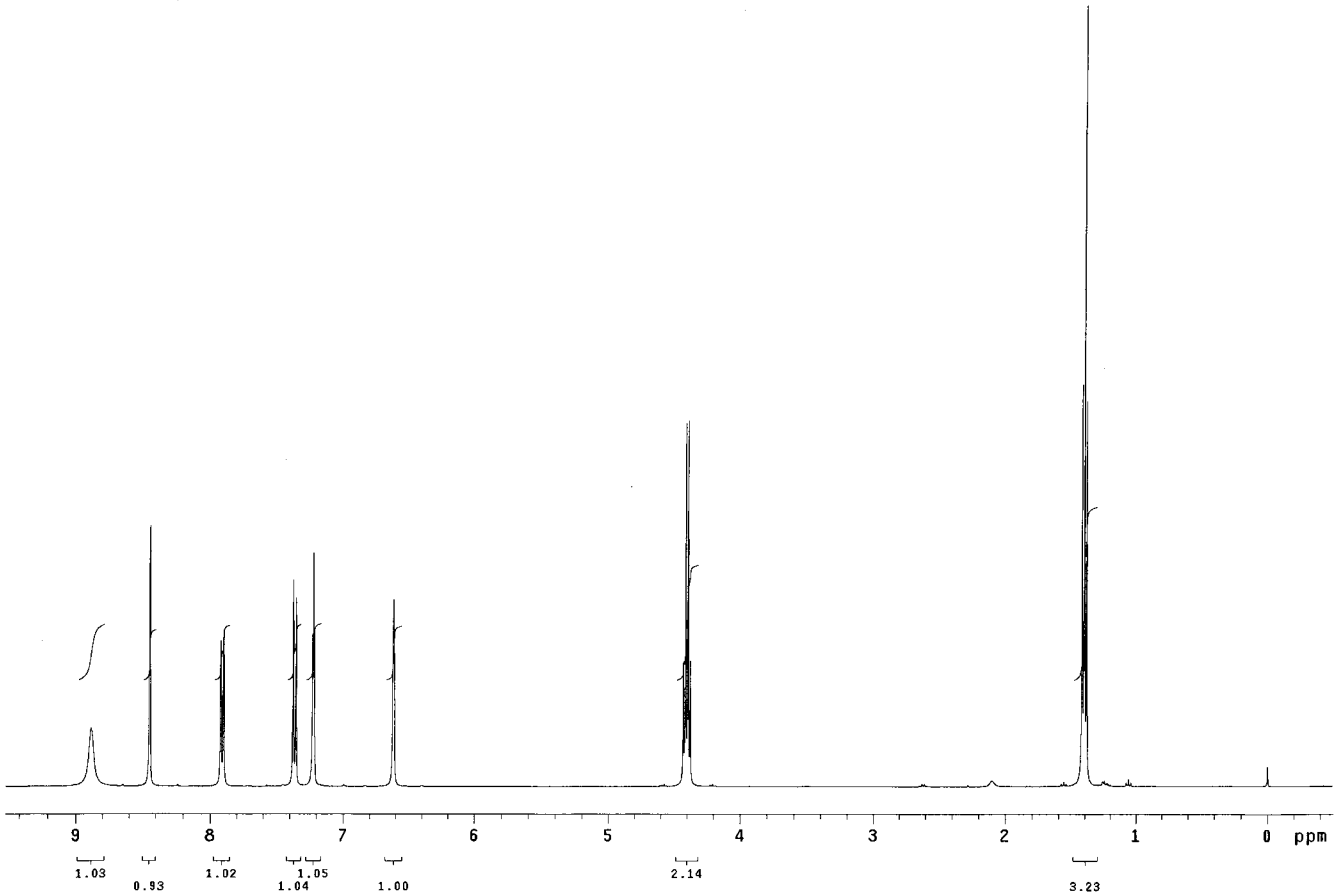

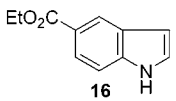

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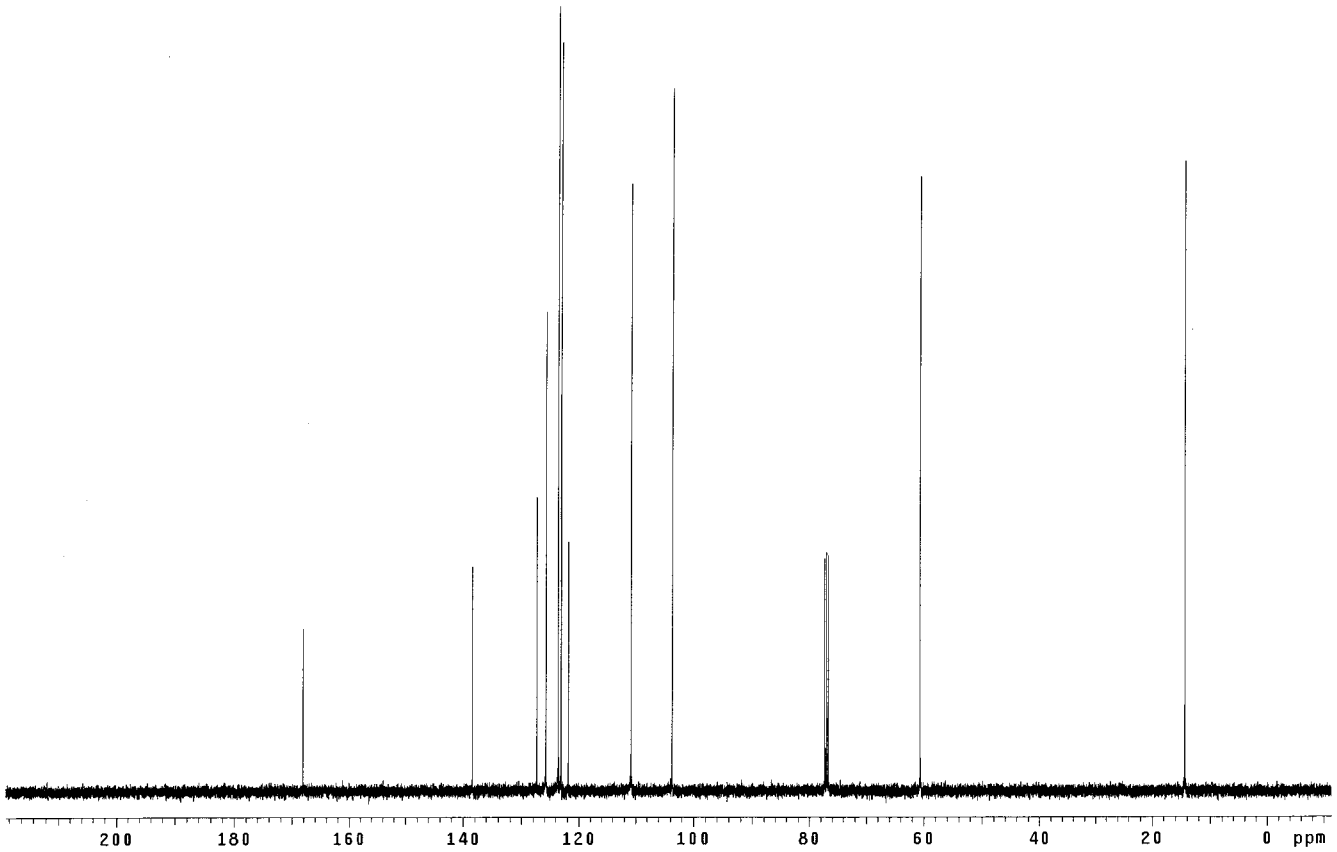

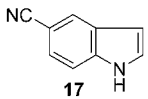

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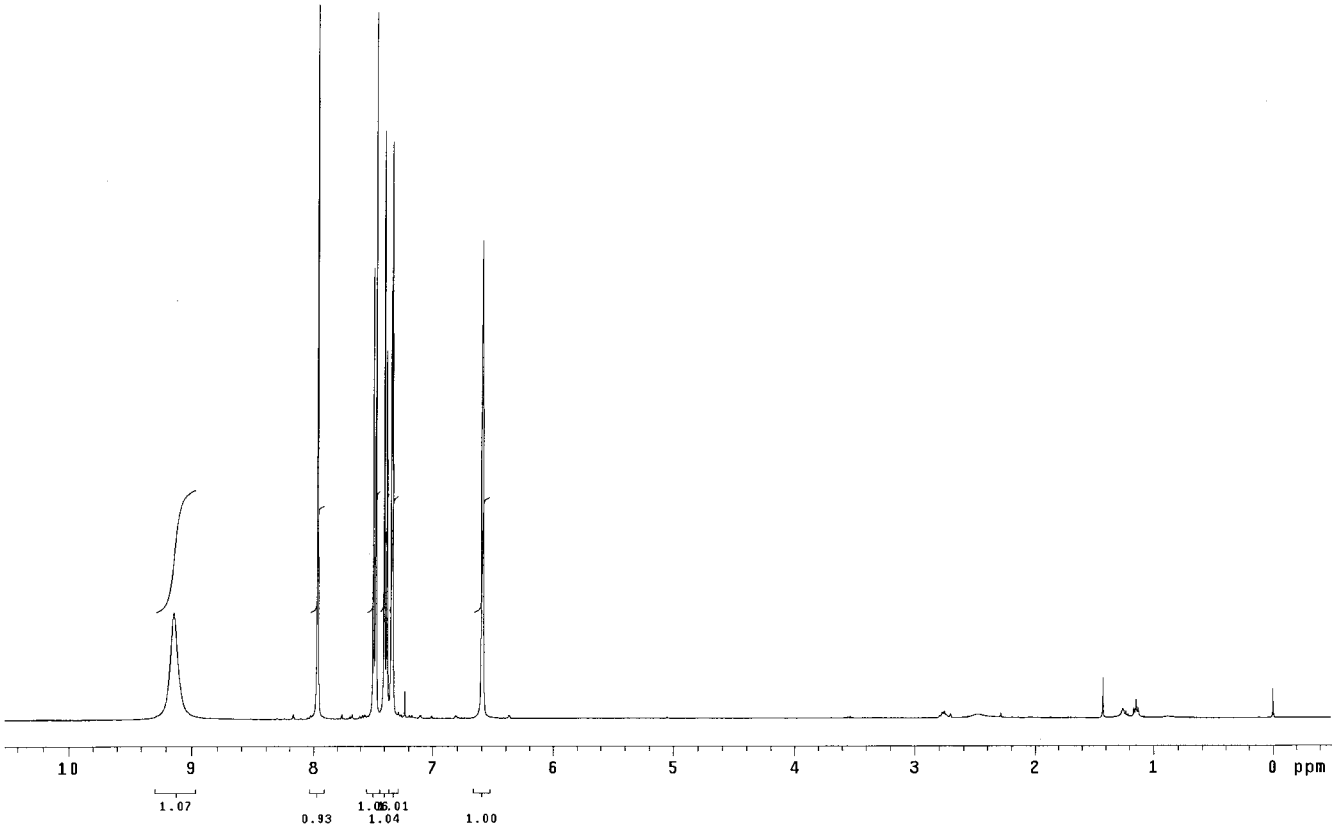

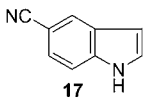

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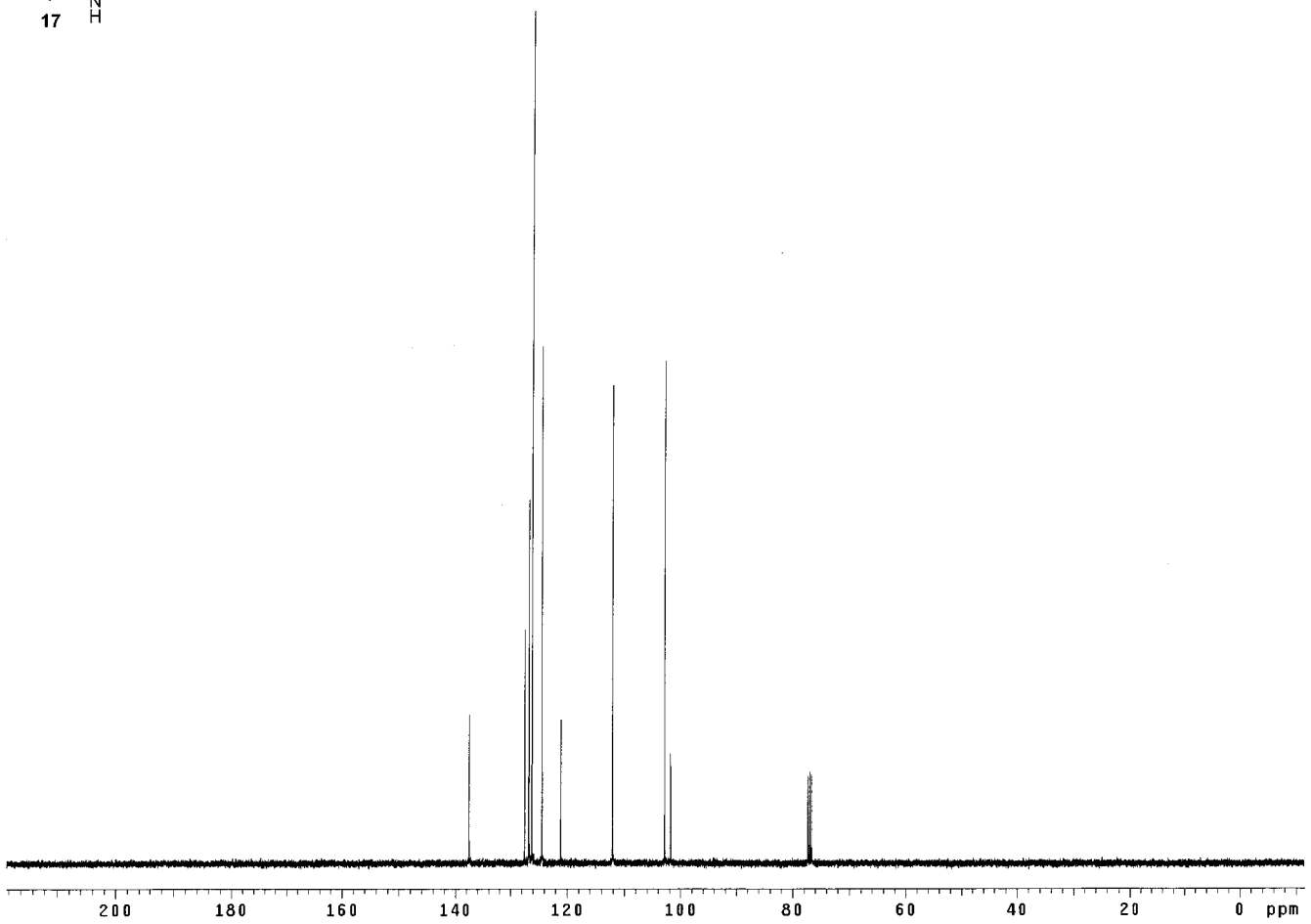

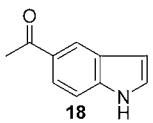

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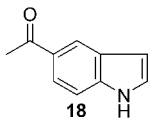

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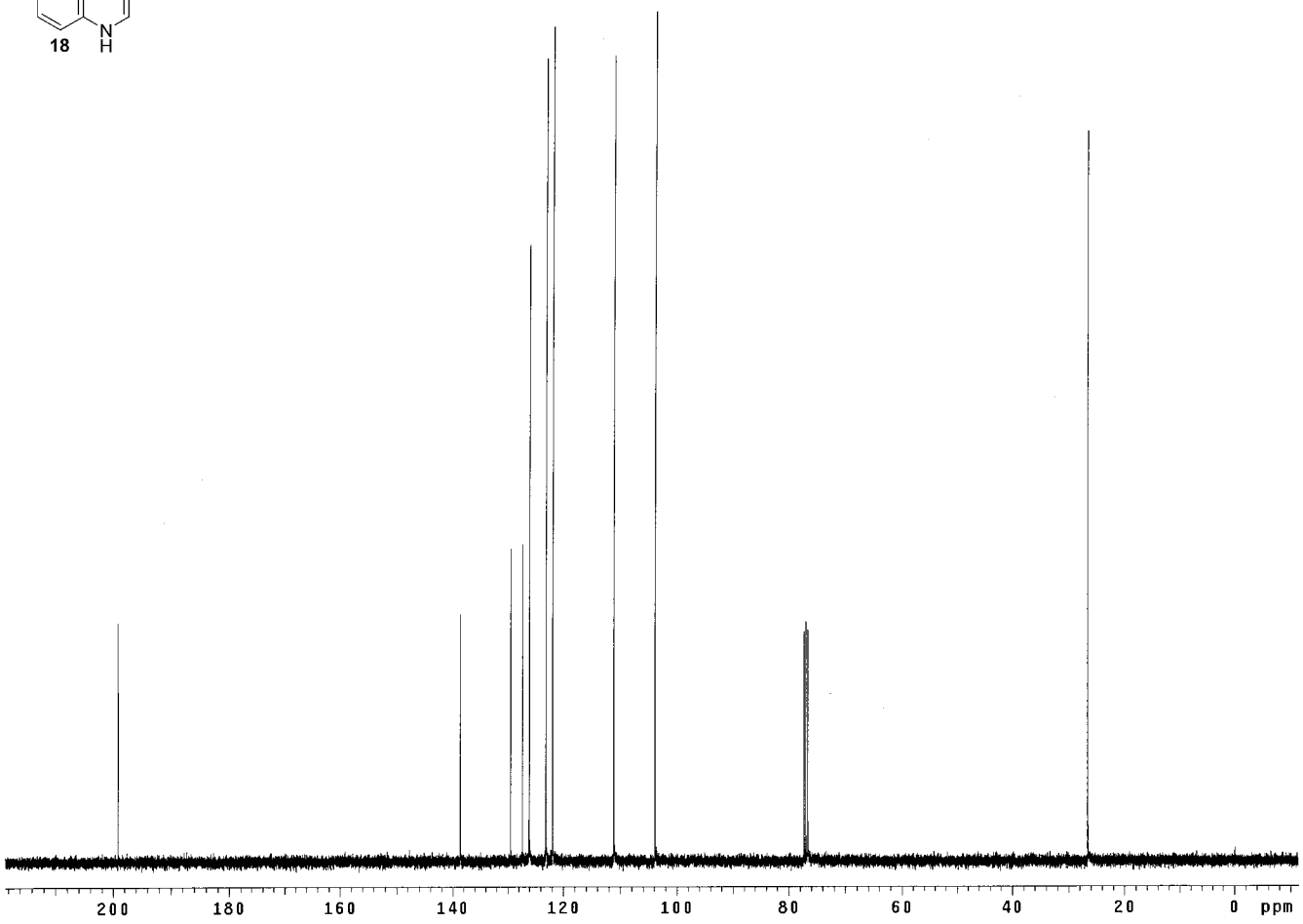

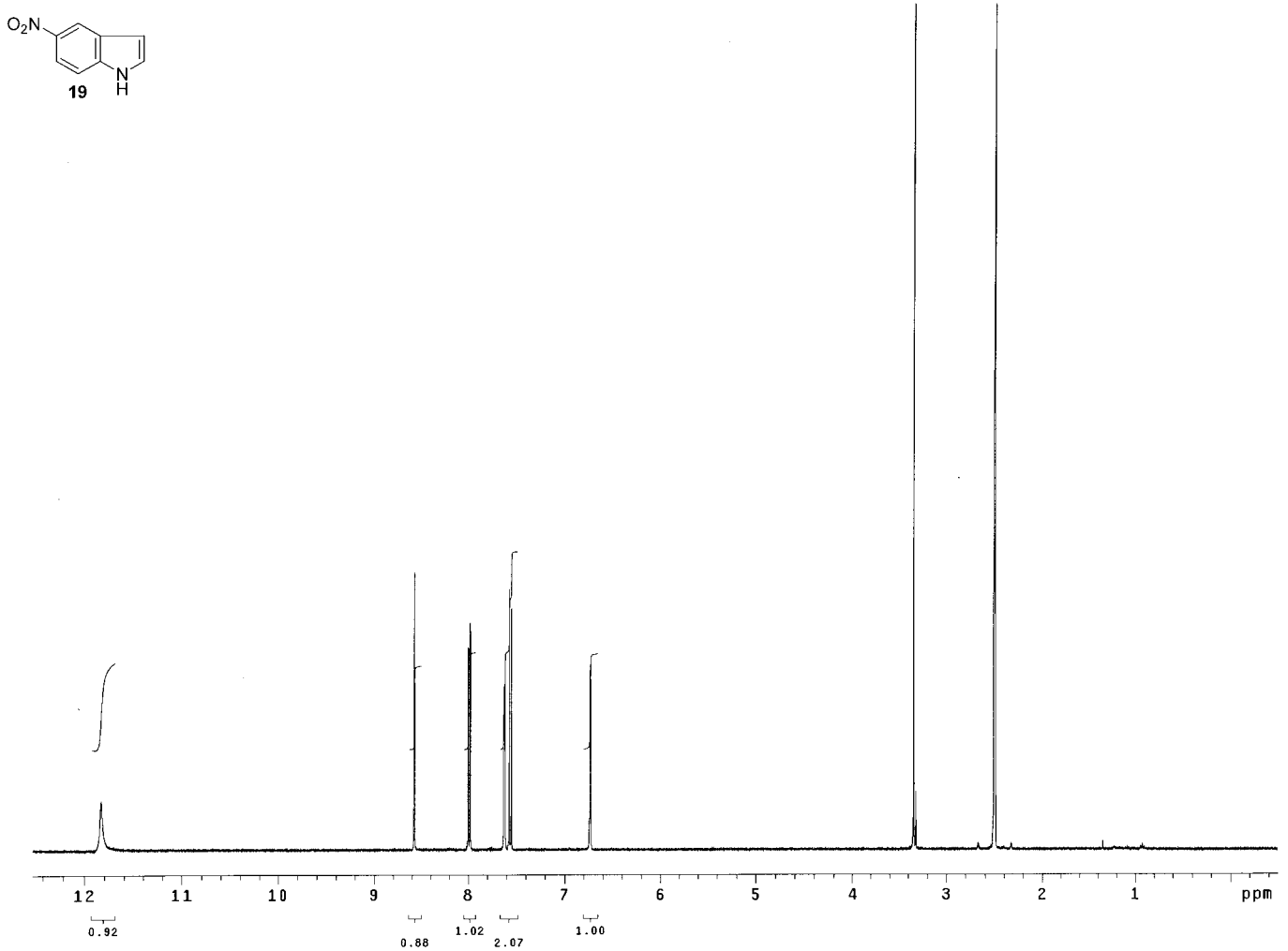
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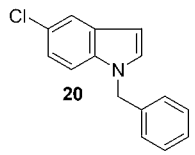

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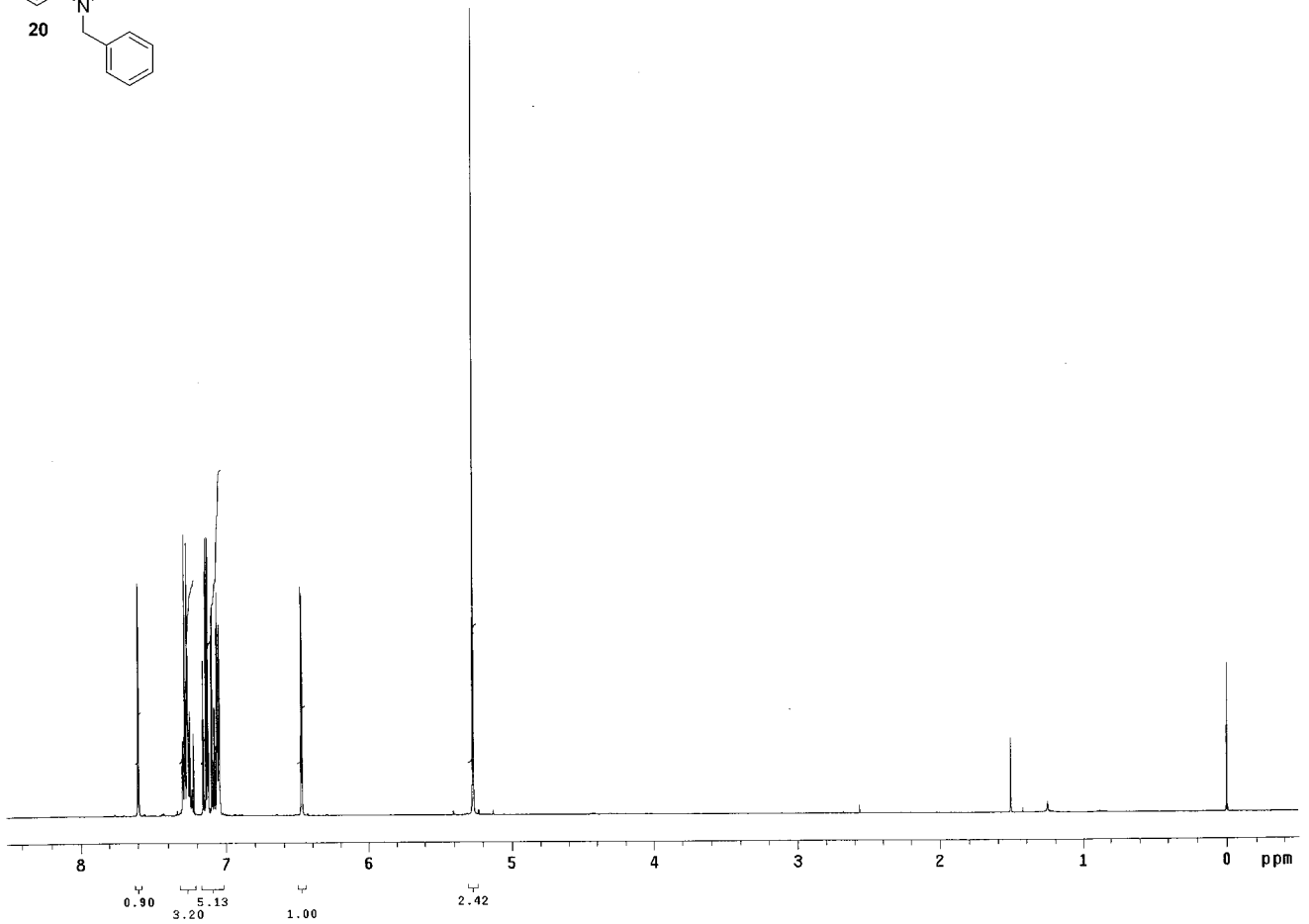

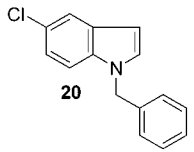

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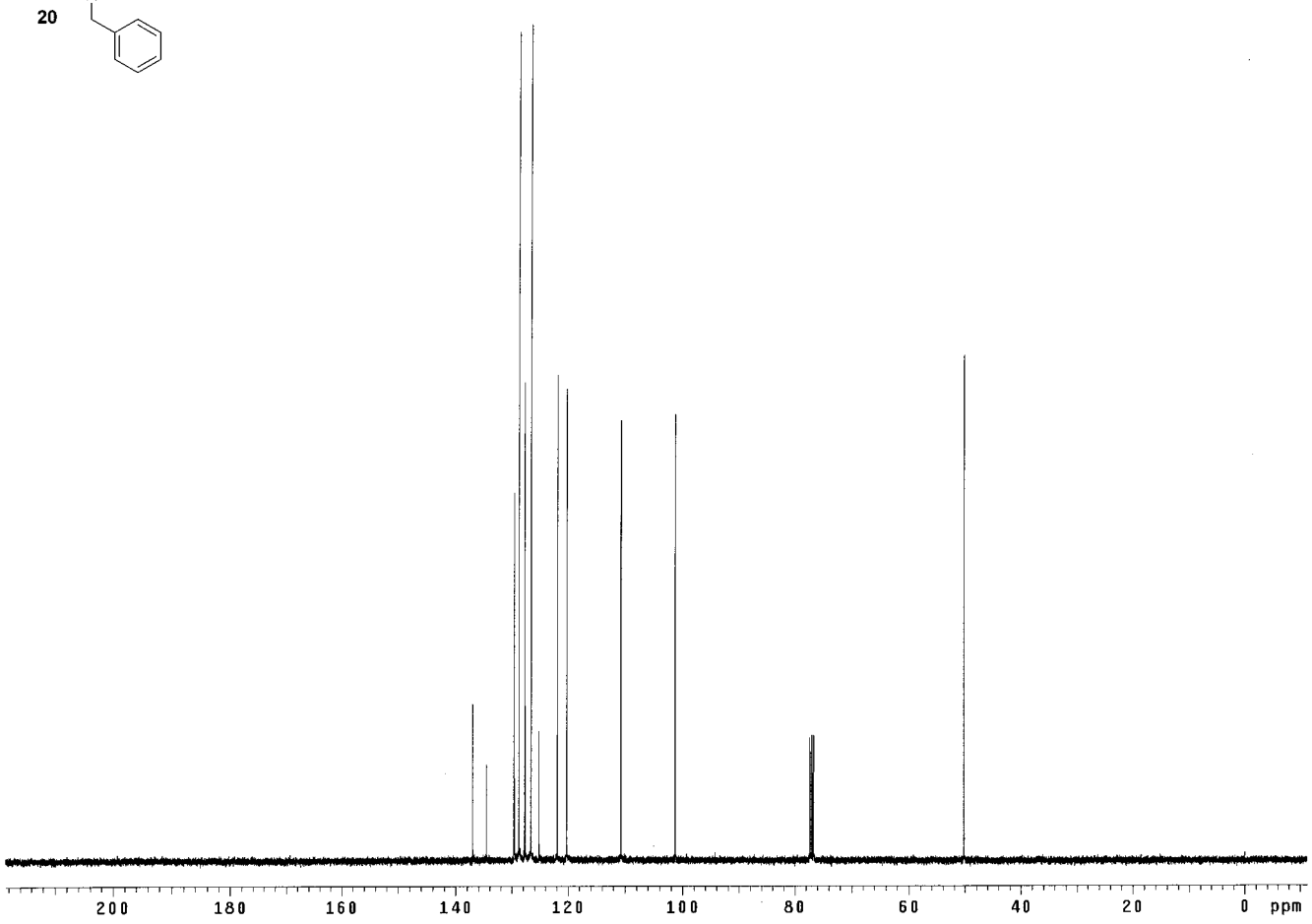

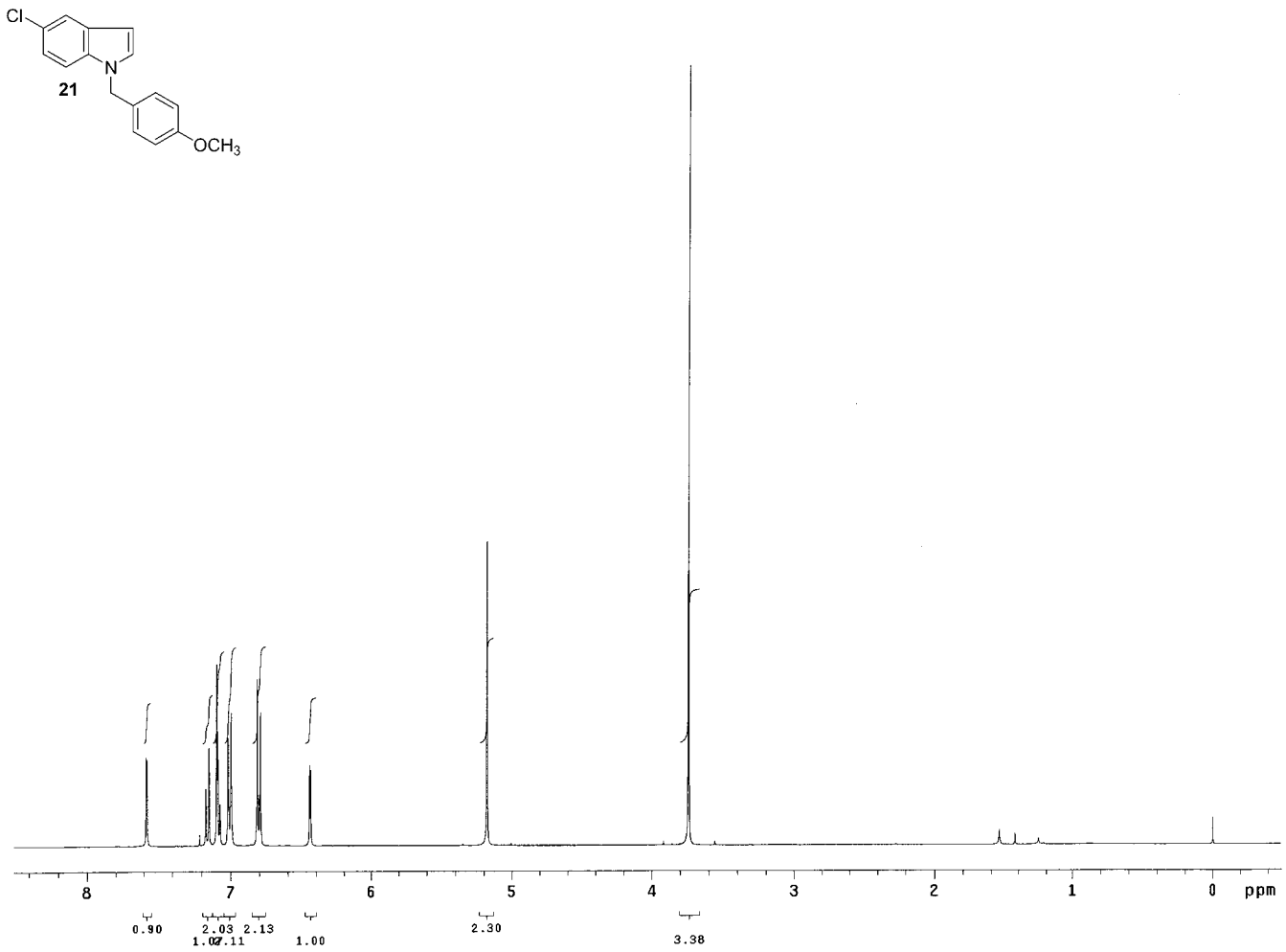
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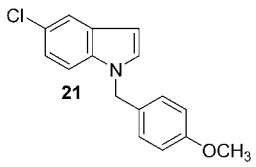

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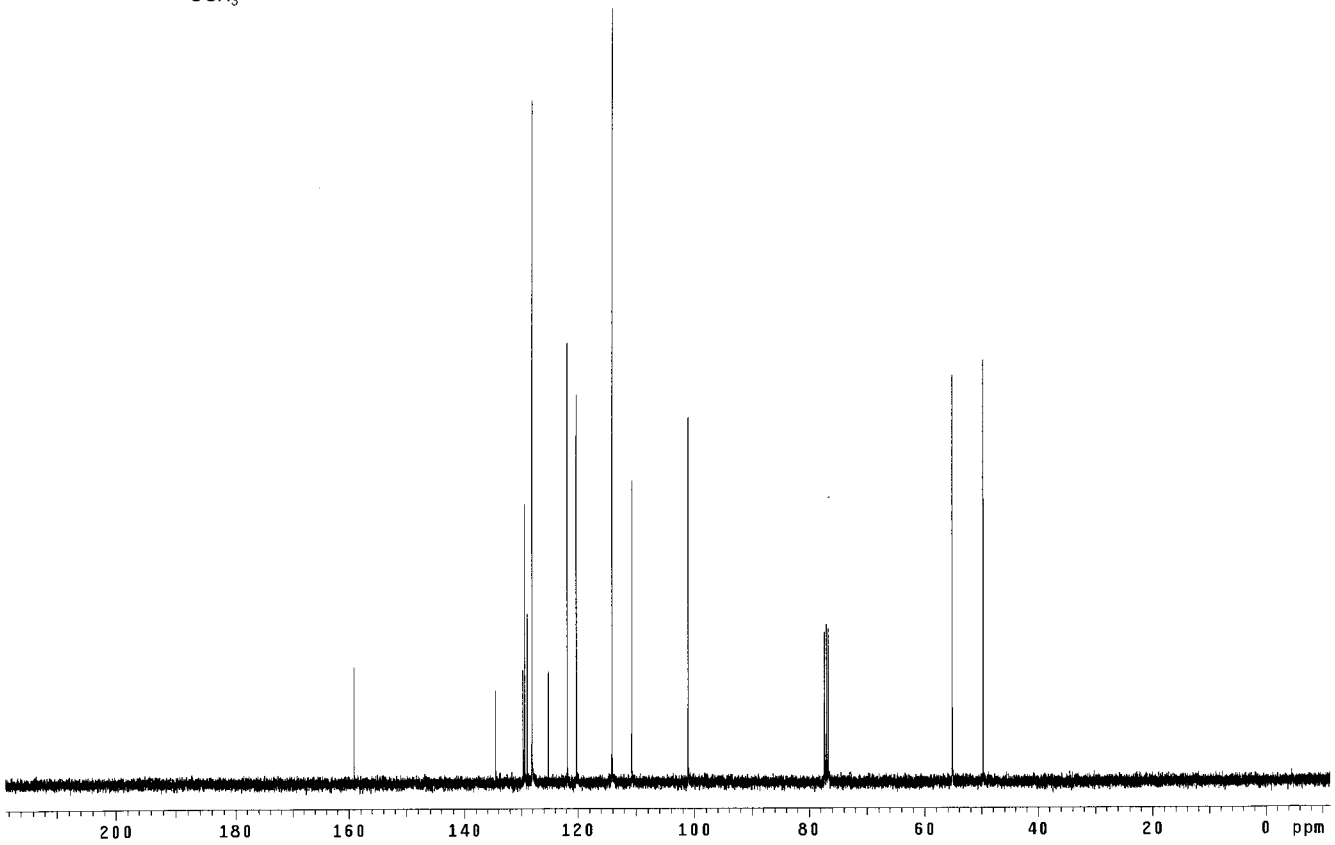

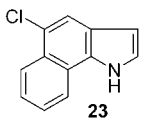

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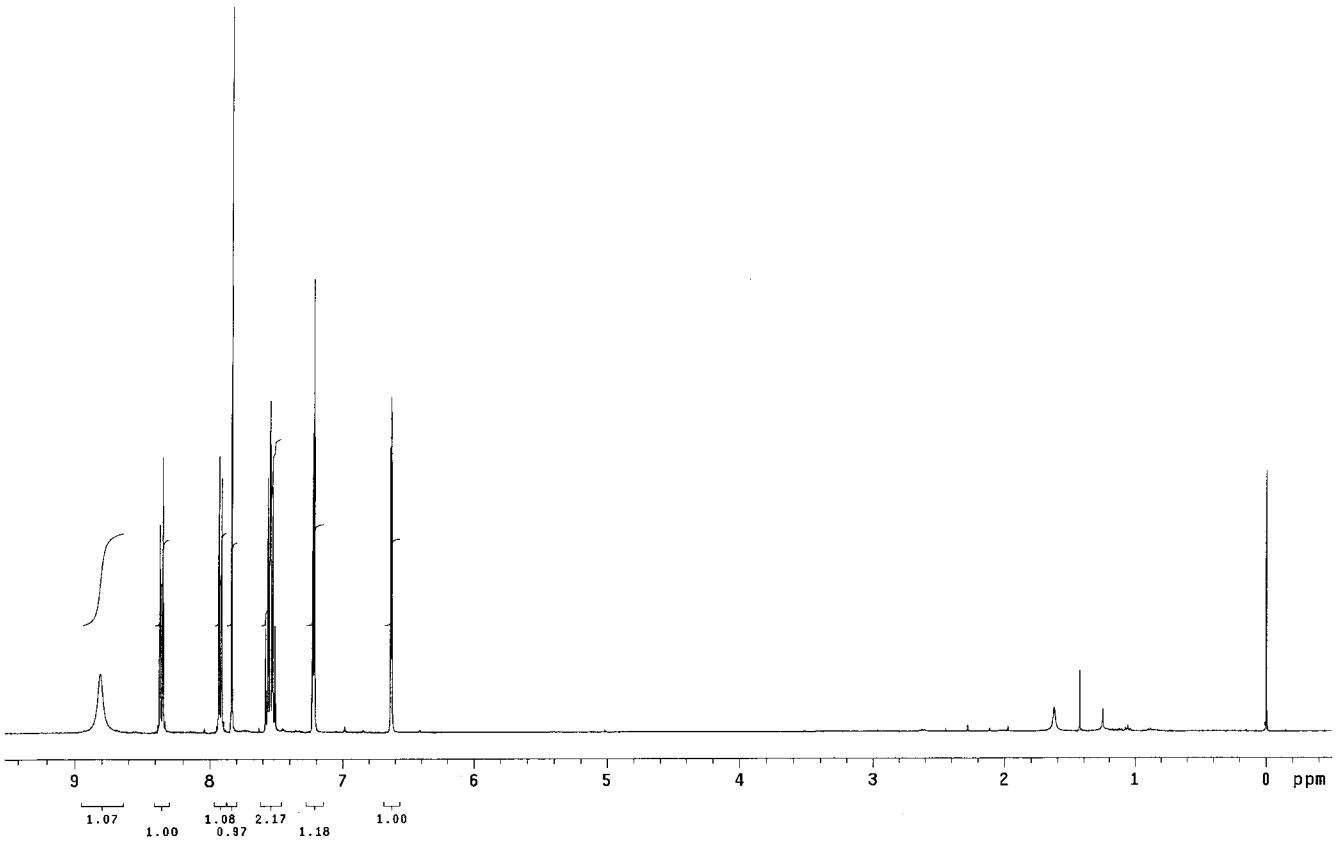

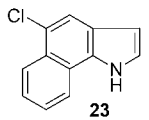

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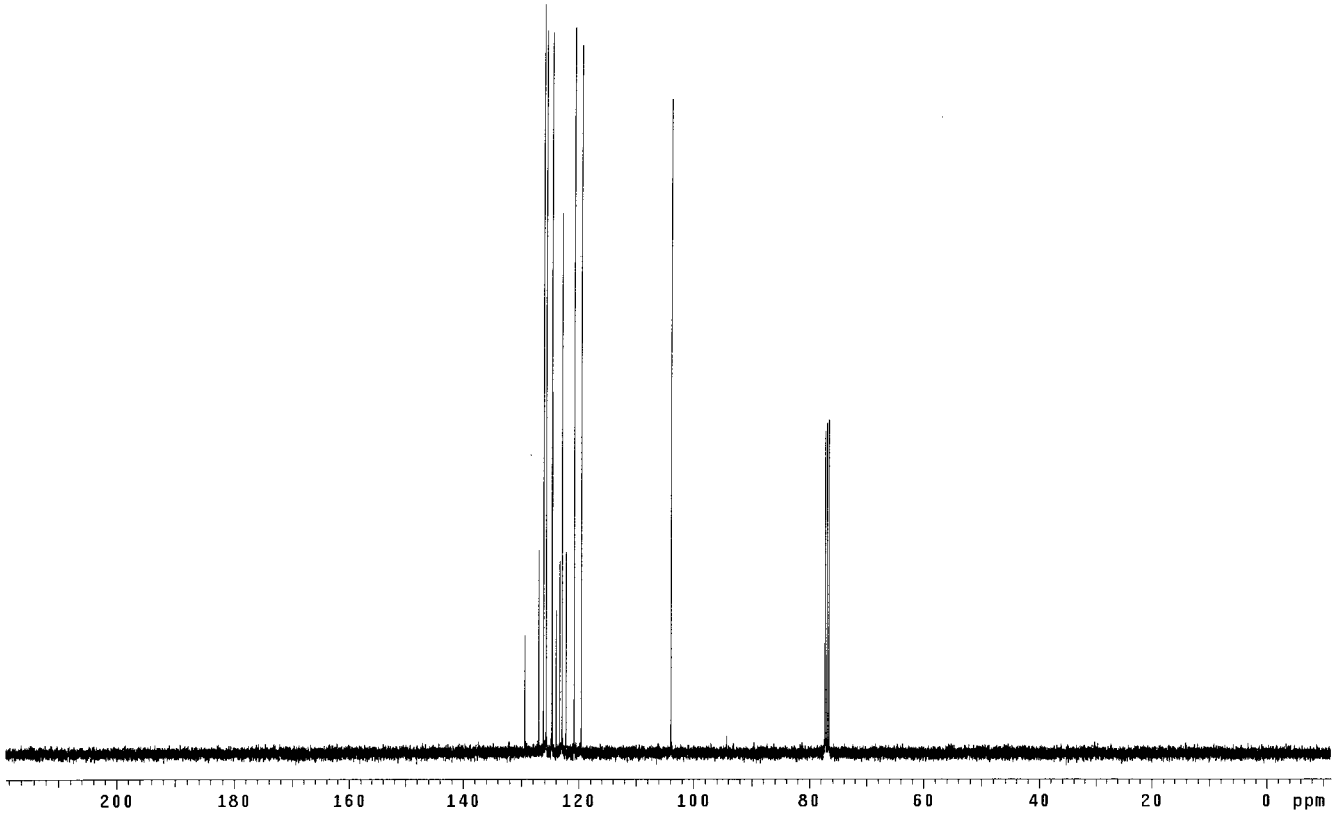

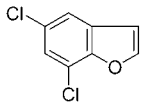

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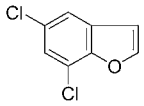

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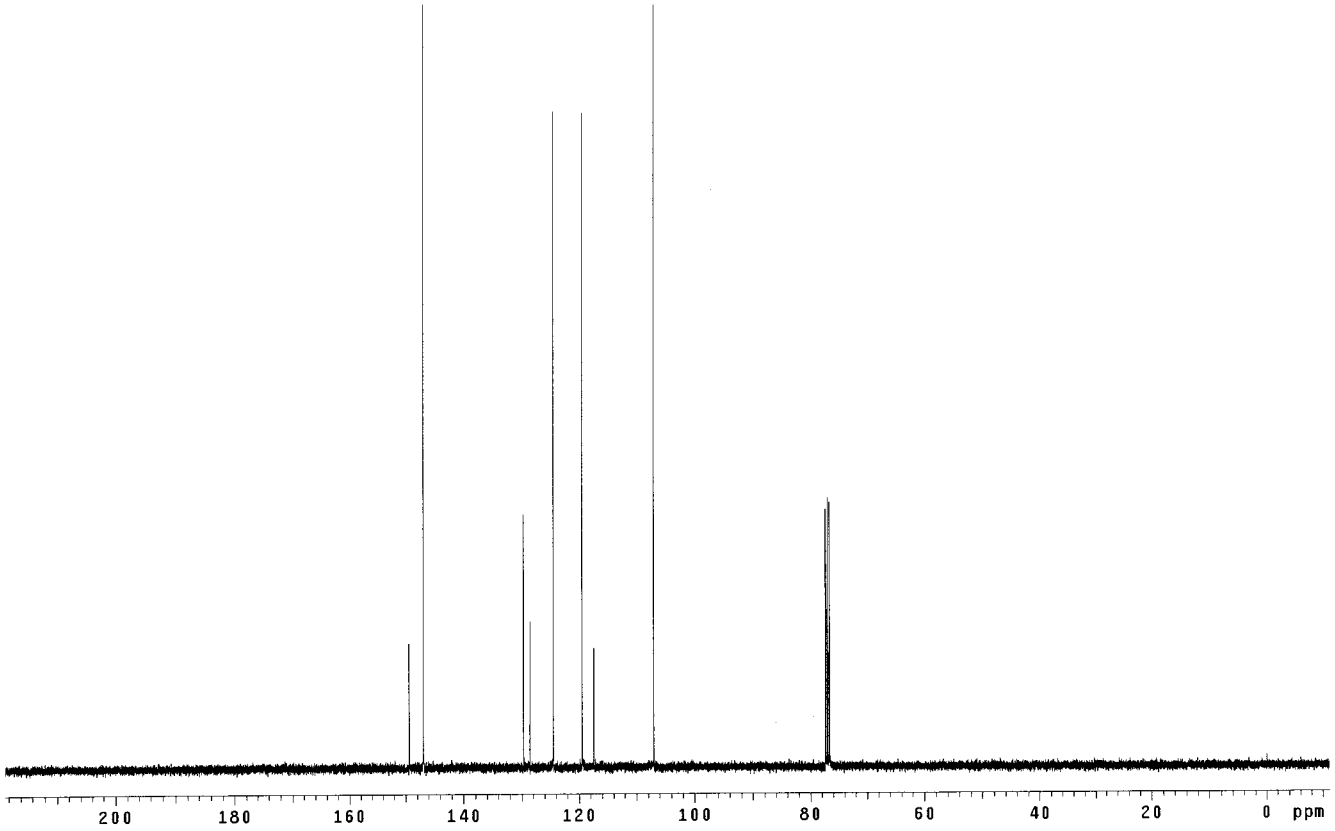

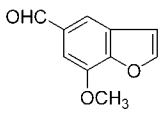

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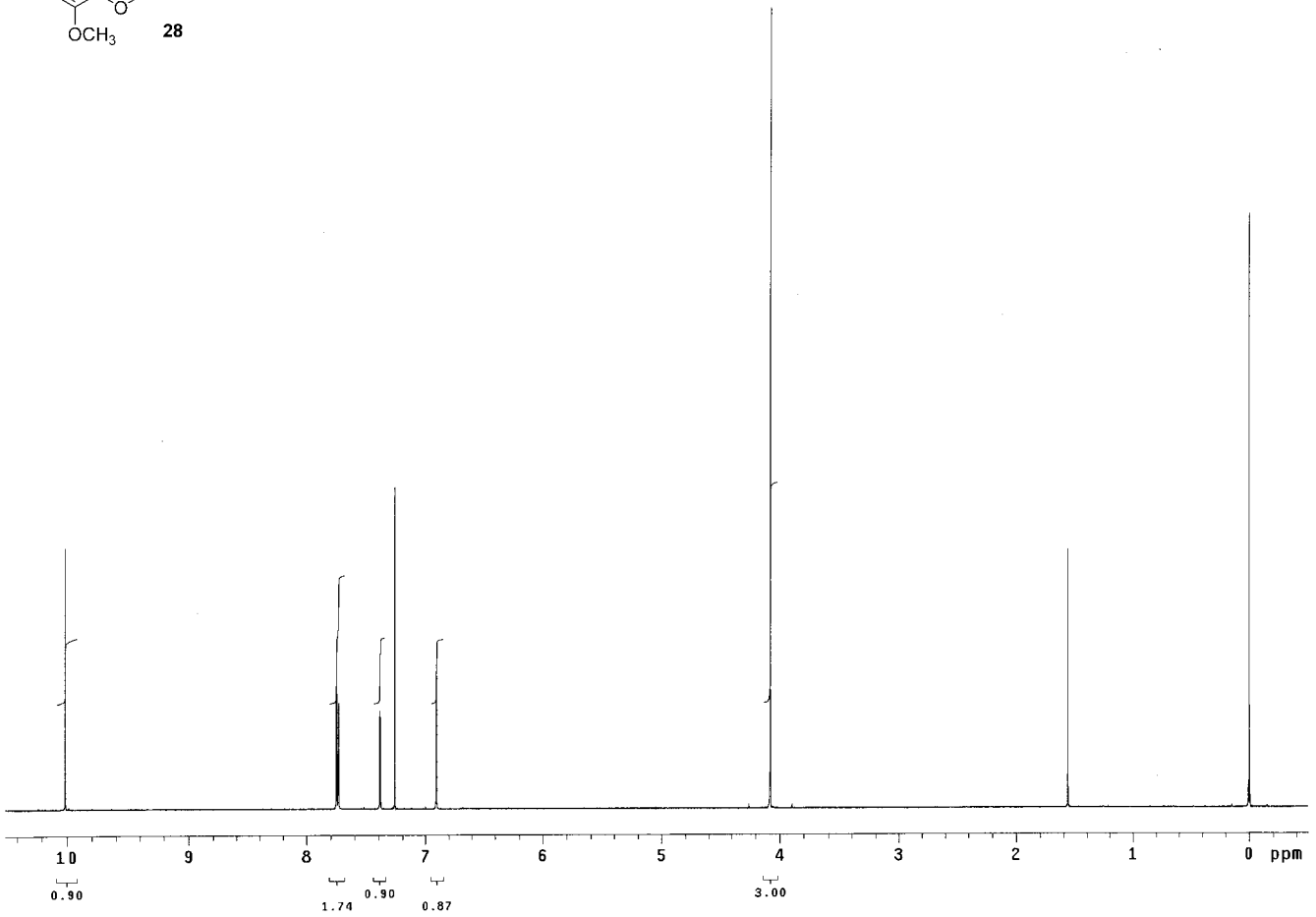

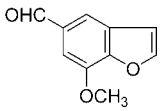

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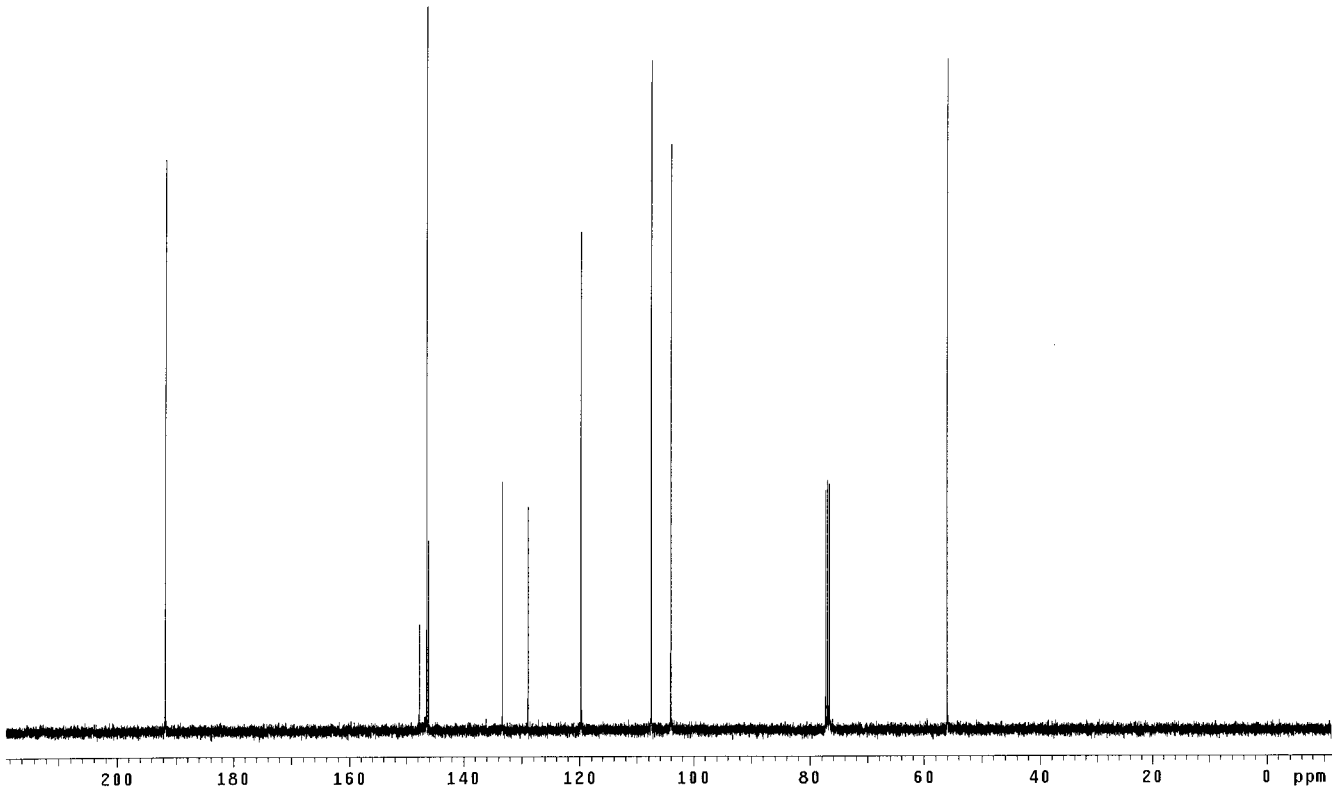

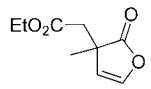

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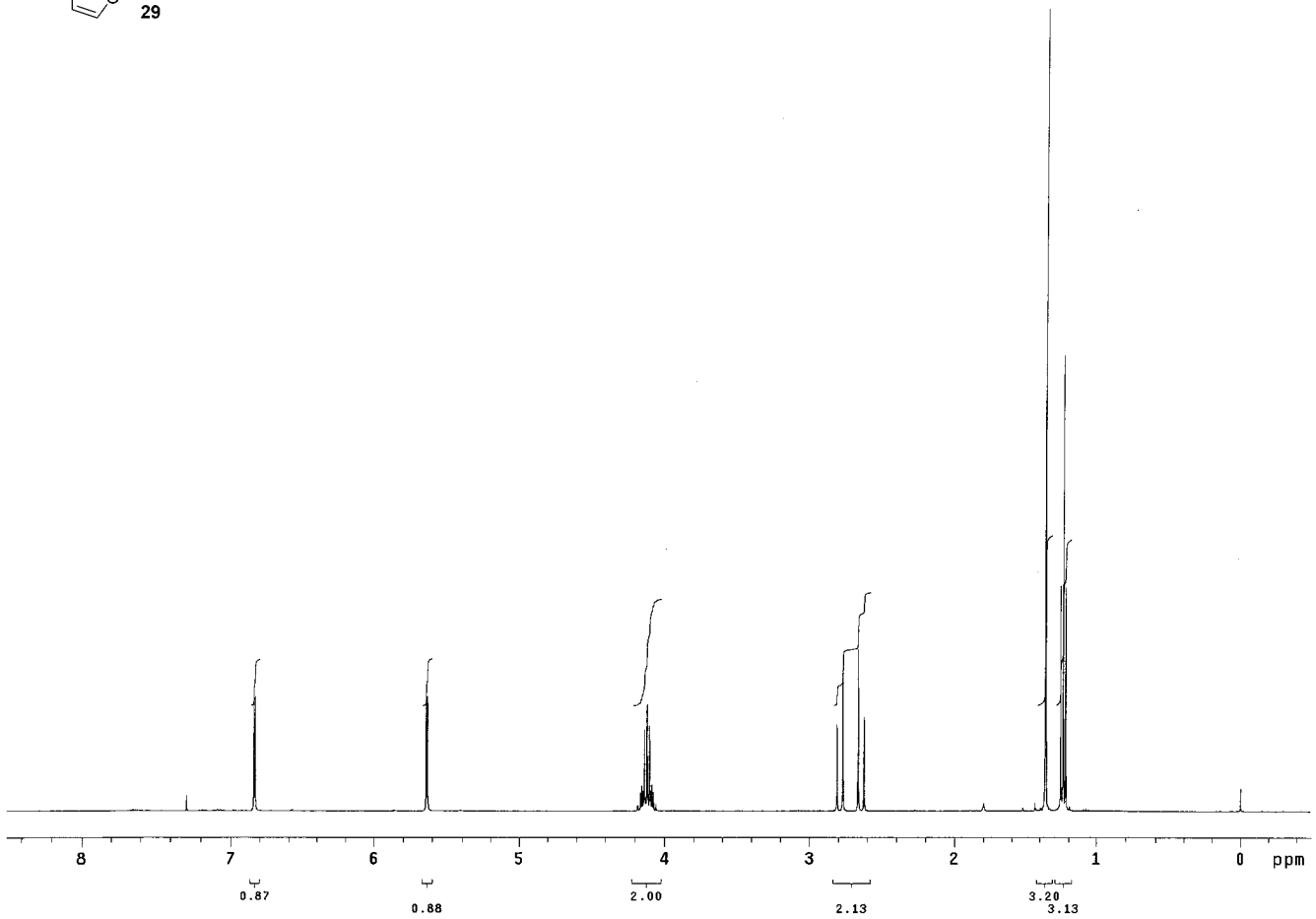

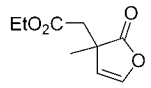

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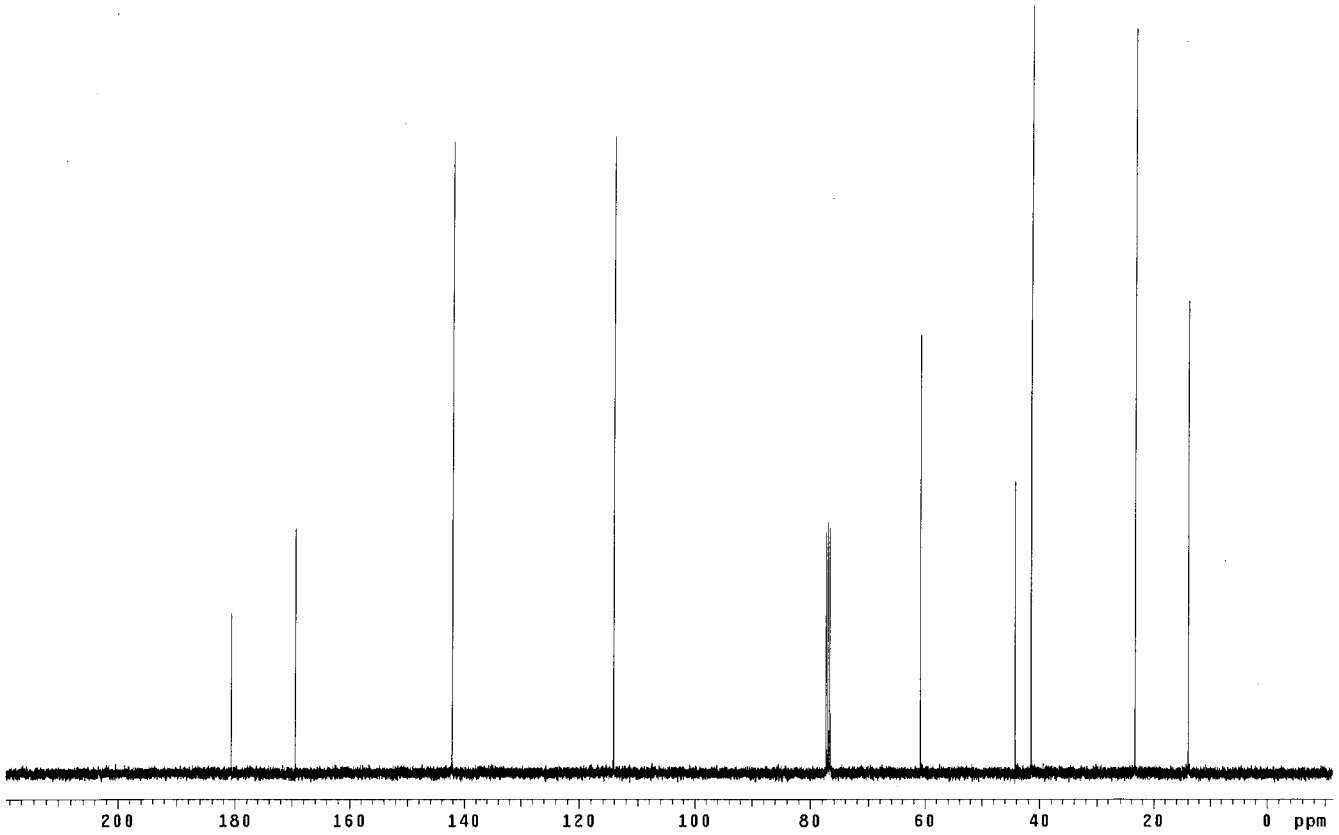

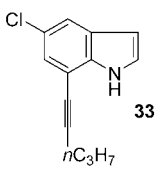

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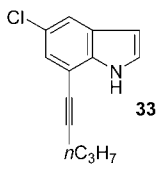

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