Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

NaH-mediated direct C–H arylation in the presence of 1,10-phenthroline

Kanako Nozawa-Kumada,* Yuki Iwakawa, So Onuma, Masanori Shigeno, and Yoshinori Kondo*
Graduate School of Pharmaceutical Sciences, Tohoku University, 6-3, Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan
*E-mail: kumada@m.tohoku.ac.jp, ykondo@m.tohoku.ac.jp

1. General comments

Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU IRAffinity. ^{1}H-NMR spectra were recorded on a JEOL JNM-AL400 (400 MHz) spectrometer or a JEOL ECA600 (600 MHz) spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in hertz (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 7.26 ppm, DMSO-d_6: 2.49 ppm, CD_3OD: 3.31 ppm). ^{13}C NMR spectra were referenced to a solvent signal ($CDCl_3$: 77.0 ppm, DMSO-d_6: 39.5 ppm, CD_3OD: 49.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, m = multiplet, and br.s. = broad singlet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer. Inductively coupled plasma-mass spectrometry (ICP-MS) was performed with a Agilent 8800 instrument at Technical Division of School of Engineering, Tohoku University. EPR data were recorded on a BRUKER FLEXSYS E580.

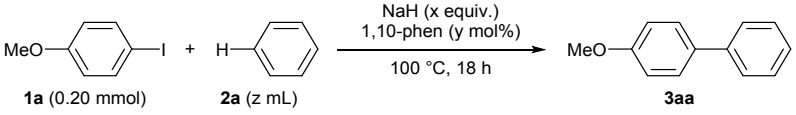
2. Materials

Dry NaH was purchased from Aldrich Inc. and used as received. Other materials such as haloarenes and unactivated arenes were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and purified by distillation or recrystallization prior to use. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70−230 mesh). **1k**,[1] and **1n**[2] were prepared according to the literature procedures.

3. Representative procedure for the biaryl coupling reaction (Table 1, entry 1)

In a glove box, a mixture of dry NaH (10.1 mg, 0.40 mmol), 1,10-phenanthroline (10.8 mg, 0.060 mmol), 4-iodoanisole (46.8 mg, 0.20 mmol) in benzene (1.5 mL) was sealed in a pressure tube. The mixture was heated to 100 °C for 18 h. The reaction mixture was quenched with 1 M HCl and extracted with diethyl ether (30 mL × 3). The combined organic layer was washed by water (30 mL × 2) and brine (30 mL), and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: hexane to hexane/AcOEt = 10/1) to give the biaryl product.

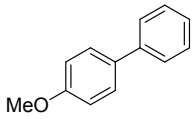
Table S1. Reaction conditions of the coupling reaction of **1a** with benzene (**2a**)



Entry	x (equiv.)	y (mol%)	z (mL)	Yield (%)[a]
1	1.5	30	1.5	53
2	2.0	30	1.5	72(72)[b]
3	2.0	20	1.5	40
4	2.0	30	1.0	62

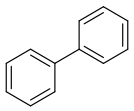
[a] Determined by ^{1}H-NMR using 1,1,2-trichloroethane as an internal standard. [b] Isolated yield in parentheses.

4-Methoxylbiphenyl (3aa)



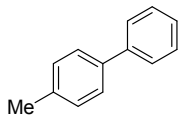
Obtained as colorless prisms, 27.6 mg (72%) (Table 1, entry 1), 25.9 mg (70%) (Table 2, entry 15), recrystallized by hexane, mp 84–85 °C; IR (neat, cm^{-1}): 3003, 2837, 1605, 1522, 1484, 1439, 1250, 1200, 833, 716; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.56–7.51 (4H, m), 7.41 (2H, t, J = 7.8 Hz), 7.30 (1H, t, J = 7.1 Hz), 6.99–6.96 (2H, m), 3.84 (3H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; LRMS (EI, *m*/*z*): 184 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{13}H_{12}O$: 184.0888, found: 184.0899.

Biphenyl (3ba)



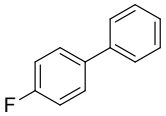
Obtained as colorless prisms in 74% yield (23.3 mg), recrystallized by hexane, mp 66–67 °C; IR (neat, cm^{-1}): 3064, 3034, 2923, 1569, 1479, 1429, 1345, 1170, 1006, 904; ^{1}H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 7.59 (4H, dd, J = 8.3, 1.4 Hz), 7.44 (4H, t, J = 8.3 Hz), 7.35–7.33 (2H, m); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 141.2, 128.7, 127.2, 127.1. LRMS (EI, *m*/*z*): 154.1 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_{10}$: 154.0783, found: 154.0783.

4-Methylbiphenyl (3ca)



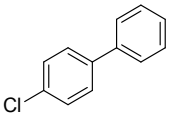
Obtained as yellow oil in 48% yield (14.9 mg); IR (neat, cm^{-1}): 3032, 2916, 2857, 1486, 1377, 1201, 1039, 1006, 821, 736; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.57 (2H, d, J = 7.8 Hz), 7.49 (2H, d, J = 7.8 Hz), 7.42 (2H, t, J = 7.8 Hz), 7.31 (1H, t, J = 7.6 Hz), 7.24 (2H, d, J = 7.8 Hz), 2.39 (3H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 141.2, 138.4, 137.0, 129.5, 128.7, 126.99, 126.97, 126.95, 21.1; LRMS (EI, *m*/*z*): 168.1 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{13}H_{12}$: 168.0939, found:168.0941.

4-Fluorobiphenyl (3da)



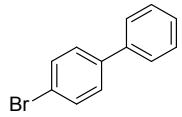
Obtained as colorless prisms in 69% yield (23.5 mg), mp 70–71°C; IR (neat, cm^{-1}): 2924, 1596, 1518, 1483, 1452, 1234, 1194, 1164, 836, 818; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.54–7.52 (4H, m), 7.43 (2H, t, J = 7.6 Hz), 7.34 (1H, t, J = 7.3 Hz), 7.12 (2H, t, J = 8.5 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 162.5 (d, J_{FC} = 247.7 Hz), 140.3, 137.3 (d, J_{FC} = 4.3 Hz), 128.8, 128.7 (d, J_{FC} = 8.6 Hz), 127.2, 127.0, 115.6 (d, J_{FC} = 21.6 Hz); LRMS (EI, *m*/*z*): 172 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_9F$: 172.0688, found: 172.0682.

4-Chlorobiphenyl (3ea)



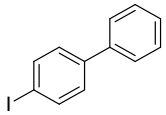
Obtained as yellow prisms, 28.8 mg (76%) (Table 2, entry 4), 22.8 mg (59%) (Table 2, entry 16), mp 70–71 °C; IR (neat, cm^{-1}): 2924, 2853, 1593,1476, 1450, 1399, 1096, 1004, 831, 739; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.55–7.50 (4H, m), 7.45–7.33 (5H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 140.0, 139.7, 133.4, 128.89, 128.86, 128.4, 127.6, 127.0; LRMS (EI, *m*/*z*): 188 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_9{}^{35}Cl$: 188.0393, found: 188.0395.

4-Bromobiphenyl (3fa)



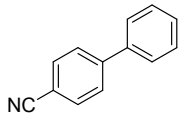
Obtained as colorless prisms in 80% yield (37.9 mg), recrystallized by hexane, mp 85–87 °C; IR (neat, cm^{-1}): 3313, 3066, 3028, 1641, 1545, 1476, 1449, 1393, 1002, 751; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 7.57–7.54 (4H, m), 7.46–7.42 (4H, m), 7.35 (1H, t, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 140.1, 140.0, 131.8, 128.9, 128.7, 127.6, 126.9, 121.5; LRMS (EI, *m*/*z*): 232 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_9{}^{79}Br$: 231.9888, found: 231.9871.

4-Iodobiphenyl (3ga)



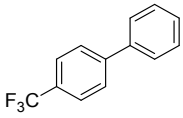
Obtained as colorless prisms in 47% yield (25.6 mg), mp 108–109 °C; IR (neat, cm^{-1}): 3062, 3034, 1581, 1473, 1389, 1275, 1067, 998, 827; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.76 (2H, d, J = 8.8 Hz), 7.55 (2H, d, J = 7.3 Hz), 7.44 (2H, t, J = 7.3 Hz), 7.38–7.32 (3H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 140.7, 140.1, 137.8, 129.0, 128.9, 127.7, 126.9, 93.0; LRMS (EI, *m*/*z*): 280 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_9I$: 279.9749, found: 279.9743.

4-Cyanobiphenyl (3ha)



Obtained as yellow prisms, 24.7 mg (69%) (Table 2, entry 7), 29.4 mg (81%) (Table 2, entry 17), mp 82–84 °C; IR (neat, cm^{-1}): 2924, 2226, 1606, 1511, 1484, 1397, 1285, 1008, 844, 722; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.74–7.67 (4H, m), 7.60–7.58 (2H, m), 7.51–7.46 (2H, m), 7.44–7.42 (1H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 145.6, 139.1, 132.5, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9; LRMS (EI, *m*/*z*): 179 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{13}H_9N$: 179.0735, found: 179.0737.

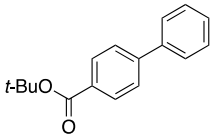
4-Trifluoromethylbiphenyl (3ia)



Obtained as yellow prisms in 40% yield (18.0 mg), mp 82–84 °C; IR (neat, cm^{-1}): 2924, 2854, 1614, 1325, 1112, 1071, 1006, 843, 767, 727; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 7.69 (4H, s), 7.61–7.59 (2H, m), 7.47 (2H, t, J = 7.6 Hz), 7.42–7.39 (1H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 144.7, 139.8, 129.4 (q, J_{FC} = 32.6 Hz), 129.0, 128.2, 127.4, 127.3, 125.7 (q, J_{FC} = 3.4 Hz), 124.3 (q, J_{FC} = 273.1 Hz); LRMS (EI, *m*/*z*): 222 (M^+); HRMS (EI, *m*/*z*): Calcd. for

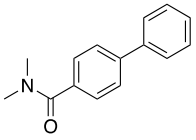
$C_{13}H_9F_3$: 222.0656, found: 222.0652.

Biphenyl-4-carboxylic acid *t*-butyl ester (3ja)



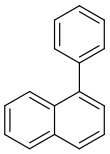
Obtained as colorless oil in 58% yield (26.9 mg); IR (neat, cm^{-1}): 2978, 1707, 1608, 1368, 1296, 1164, 1114, 1008, 849, 746; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.06 (2H, d, J = 8.3 Hz), 7.63 (4H, t, J = 7.8 Hz), 7.46 (2H, t, J = 7.8 Hz), 7.38 (1H, t, J = 7.8 Hz), 1.62 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 165.7, 145.1, 140.2, 130.8, 129.9, 128.9, 128.0, 127.3, 126.9, 81.0, 28.2; LRMS (EI, *m*/*z*): 254 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{17}H_{18}O_2$: 254.1307, found: 254.1310.

***N, N*-Dimethyl [1,1'-biphenyl]-4-carboxamide (3ka)**



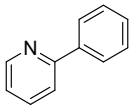
Obtained as colorless prisms in 43% yield (18.2 mg), mp 103–105 °C; IR (neat, cm^{-1}): 2927, 1618, 1485, 1395, 1266, 1089, 1007, 848, 778, 744; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.61 (4H, t, J = 8.5Hz), 7.51–7.44 (4H, m), 7.39–7.35 (1H, m), 3.13–3.04 (6H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 171.4, 142.4, 140.3, 135.1, 128.8, 127.7, 127.6, 127.1, 127.0, 39.6, 35.3; LRMS (EI, *m*/*z*): 225 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{15}H_{15}NO$: 225.1154, found: 225.1170.

1-Phenylnaphthalene (3la)



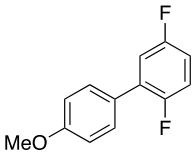
Obtained as colorless oil in 58% yield (23.7 mg); IR (neat, cm^{-1}): 3057, 3032, 1592, 1507, 1493, 1396, 1030, 800, 760, 738; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 7.90–7.88 (2H, m), 7.85 (1H, d, J = 8.2 Hz), 7.53–7.47 (6H, m), 7.43–7.41 (3H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 140.7, 140.2, 133.8, 131.6, 130.1, 128.7, 128.2, 127.6, 127.2, 127.1, 126.9, 126.0, 125.7, 125.3; LRMS (EI, *m*/*z*): 204 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{16}H_{12}$: 204.0939, found: 204.0926.

2-Phenylpyridine (3ma)



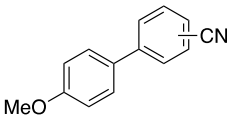
Obtained as brown oil in 64% yield (20.9 mg); IR (neat, cm^{-1}): 3065, 3008, 1587, 1580, 1468, 1450, 1424, 1020, 738; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.70 (1H, d, J = 4.9 Hz), 8.00 (2H, d, J = 7.3 Hz), 7.76–7.71 (2H, m), 7.50–7.39 (3H, m), 7.25–7.19 (1H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 157.4, 149.6, 139.4, 136.7, 128.9, 128.7, 126.9, 122.0, 120.5; LRMS (EI, *m*/*z*): 155 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{11}H_9N$: 155.0735, found: 155.0722.

2,5-Difluoro-4'-methoxybiphenyl (3ab)



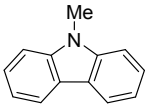
Obtained as colorless prisms in 64% yield (26.8 mg), mp 55–56 °C; IR (neat, cm^{-1}): 2839, 1610, 1520, 1490, 1253, 1175, 1040, 831, 811, 761; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 7.47 (2H, dd, J = 8.9, 1.6 Hz), 7.12–7.06 (2H, m), 6.99–6.97 (2H, m), 6.96–6.92 (1H, m), 3.85 (3H, s); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 159.6, 158.8 (d, J_{FC} = 244.8 Hz), 155.7 (d, J_{FC} = 241.9 Hz), 130.05 (dd, J_{FC} = 15.8, 8.6 Hz), 130.04 (d, J_{FC} = 2.9 Hz), 127.2, 117.0 (dd, J_{FC} = 25.9, 8.6 Hz), 116.5 (dd, J_{FC} = 24.5, 2.9 Hz), 114.5 (dd, J_{FC} = 24.5, 8.6 Hz), 114.0, 55.3; LRMS (EI, *m*/*z*): 220 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{13}H_{10}F_2O$: 220.0700, found: 220.0706.

Cyano-4'-methoxybiphenyl (3ac)



Purified by silica gel column chromatography to give **3ac** as a mixture of regioisomers (76% yield, 32.6 mg, C-2/C-3/C-4 = 56/19/25).

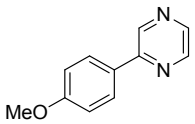
***N*-Methylcarbazole (3n)**



In a glove box, a mixture of dry NaH (9.7 mg, 0.40 mmol), 1,10-phenanthroline (10.8 mg, 0.060 mmol), *N*-2-bromophenyl-*N*-phenylaminomethane (**1n**, 52.5 mg, 0.20 mmol) in benzene (1.0 mL)

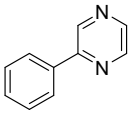
was sealed in a pressure tube. The mixture was heated to 120 °C for 18 h. The reaction mixture was quenched with water and extracted with diethyl ether (30 mL × 3). The combined organic layer was washed by brine (30 mL), and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give **3n**.
Obtained as colorless prisms in 96% yield (34.8 mg), recrystallized by hexane, mp 85–86 °C; IR (neat, cm^{-1}): 3051, 2931, 1598, 1467, 1323, 1247, 1151, 1116, 852, 745, 719; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 8.11–8.09 (2H, m), 7.49–7.47 (2H, m), 7.41 (2H, d, J = 8.3 Hz), 7.25–7.22 (2H, m), 3.86 (3H, s); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 141.0, 125.6, 122.8, 120.3, 118.8, 108.4, 29.0; LRMS (EI, *m*/*z*): 181 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{13}H_{11}N$: 181.0891, found: 181.0884.

2-(4-Methoxyphenyl)pyrazine (5aa)



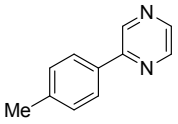
Obtained as yellow prisms in 76% yield (29.5 mg), recrystallized by hexane, mp 82–83 °C; IR (neat, cm^{-1}): 2940, 2839, 1605, 1516, 1425, 1249, 1180, 1035, 1015, 818; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.98 (1H, s), 8.58 (1H, s) 8.43 (1H, d, J = 2.4 Hz), 7.98 (2H, d, J = 8.5 Hz), 7.03 (2H, d, J = 8.5 Hz), 3.88 (3H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 161.2, 152.5, 144.0, 142.1, 141.6, 128.9, 128.3, 114.5, 55.4; LRMS (EI, *m*/*z*): 186 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{11}H_{10}N_2O$: 186.0793, found: 186.0797.

2-Phenylpyrazine (5ba)



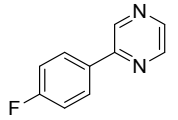
Obtained as colorless plates in 66% yield (20.6 mg), recrystallized by hexane, mp 68–69 °C; IR (neat, cm^{-1}): 3051, 3037, 1521, 1474, 1404, 1329, 1301, 1146, 1082, 1018; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 9.03 (1H, d, J = 1.4 Hz), 8.64–8.63 (1H, m), 8.51 (1H, d, J = 2.8 Hz), 8.02–8.01 (2H, m), 7.53–7.48 (3H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 152.8, 144.1, 142.9, 142.2, 136.3, 129.9, 129.0, 126.9; LRMS (EI, *m*/*z*): 156 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{10}H_8N_2$: 156.0687, found: 156.0684.

2-(4-Methylphenyl)pyrazine (5ca)



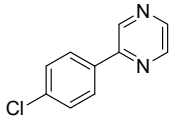
Obtained as colorless prisms in 71% yield (24.3 mg), mp 48–50 °C; IR (neat, cm^{-1}): 2914, 1476, 1414, 1376, 1330, 1146, 1080, 1017, 1013, 859; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 9.01 (1H, s), 8.60 (1H, s) 8.47 (1H, d, J = 2.4 Hz), 7.91 (2H, d, J = 8.3 Hz), 7.32 (2H, d, J = 8.3 Hz), 2.42 (3H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 152.8, 144.0, 142.5, 142.0, 140.1, 133.5, 129.8, 126.8, 21.3; LRMS (EI, *m*/*z*): 170 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{11}H_{10}N_2$: 170.0844, found: 170.0843.

2-(4-Fluorophenyl)pyrazine (5da)



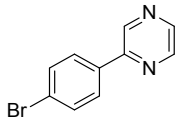
Obtained as colorless prisms in 65% yield (22.5 mg), recrystallized by hexane, mp 82–83 °C; IR (neat, cm^{-1}): 1607, 1598, 1516, 1476, 1424, 1297, 1241, 1161, 1016, 829; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 8.99 (1H, s), 8.62–8.61 (1H, m), 8.50 (1H, d, J = 2.8 Hz), 8.03–8.00 (2H, m), 7.20 (2H, t, J = 8.6 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 164.0 (d, J_{FC} = 251.9 Hz), 151.8, 144.1, 142.9, 141.9, 132.5, 128.8 (d, J_{FC} = 8.6 Hz), 116.1 (d, J_{FC} = 21.6 Hz); LRMS (EI, *m*/*z*): 174 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{10}H_7FN_2$: 174.0593, found: 174.0593.

2-(4-Chlorophenyl)pyrazine (5ea)



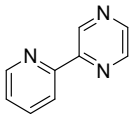
Obtained as colorless plates in 52% yield (19.9 mg), recrystallized by hexane, mp 92–93 °C; IR (neat, cm^{-1}): 1468, 1414, 1159, 1150, 1096, 1079, 1015, 1011, 786, 715; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 9.01 (1H, d, J = 1.4 Hz), 8.63 (1H, d, J = 1.4 Hz), 8.52 (1H, d, J = 2.7 Hz), 7.97 (2H, dd, J = 6.8, 2.1 Hz), 7.49 (2H, dd, J = 6.8, 2.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 151.6, 144.2, 143.2, 141.9, 136.2, 134.8, 129.3, 128.2; LRMS (EI, *m*/*z*): 190 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{10}H_7{}^{35}ClN_2$: 190.0298, found: 190.0295.

2-(4-Bromophenyl)pyrazine (5fa)



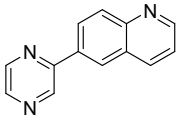
Obtained as colorless plates in 62% yield (29.2 mg), recrystallized by hexane, mp 104–105 °C; IR (neat, cm^{-1}): 1591, 1469, 1411, 1327, 1160, 1149, 1079, 1008, 782, 712; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 9.01 (1H, d, J = 1.4 Hz), 8.63–8.62 (1H, m), 8.52 (1H, d, J = 2.7 Hz), 7.90 (2H, d, J = 8.6 Hz), 7.64 (2H, d, J = 8.6 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 151.7, 144.2, 143.2, 141.9, 135.2, 132.2, 128.4, 124.6; LRMS (EI, *m*/*z*): 234 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{10}H_7{}^{79}BrN_2$: 233.9793, found: 233.9791.

2-(Pyridin-2-yl)pyrazine (5ma)



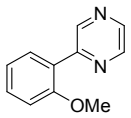
Obtained as colorless prisms in 34% yield (10.8 mg), mp 55–56 °C; IR (neat, cm^{-1}): 2957, 2926, 2855, 1727, 1587, 1453, 1389, 1155, 1034, 1016; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 9.64 (1H, d, J = 1.5 Hz), 8.73 (1H, d, J = 3.9 Hz), 8.61 (2H, dd, J = 6.8, 2.0 Hz), 8.37 (1H, d, J = 7.8 Hz), 7.85 (1H, td, J = 7.8, 1.5 Hz), 7.39–7.35 (1H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 154.2, 151.1, 149.5, 144.4, 143.5, 143.4, 137.1, 124.4, 121.4; LRMS (EI, *m*/*z*): 157 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_9H_7N_3$: 157.0640, found: 157.0638.

6-(Pyrazin-2-yl)quinoline (5oa)



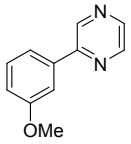
Obtained as yellow blocks in 47% yield (19.7 mg), recrystallized by hexane, mp 98 °C; IR (neat, cm^{-1}): 3870, 3650, 1653, 1560, 1507, 1462, 1124, 1014, 838, 804; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 9.20 (1H, s), 8.99–8.98 (1H, m), 8.71 (1H, s), 8.58 (1H, s), 8.52 (1H, s), 8.40–8.38 (1H, m), 8.30–8.24 (2H, m), 7.50–7.46 (1H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 152.0, 151.5, 148.9, 144.3, 143.3, 142.4, 136.8, 134.4, 130.5, 128.3, 127.7, 126.6, 121.8; LRMS (EI, *m*/*z*): 207 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{13}H_9N_3$: 207.0797, found: 207.0802.

2-(2-Methoxyphenyl)pyrazine (5pa)



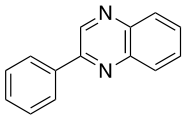
Obtained as yellow oil in 38% yield (14.2 mg); IR (neat, cm^{-1}): 2944, 2838, 1601, 1496, 1460, 1394, 1242, 1076, 1018, 751; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 9.15 (1H, d, *J* = 2.0 Hz), 8.65 (1H, t, *J* = 2.0 Hz), 8.46 (1H, d, *J* = 2.0 Hz), 7.82 (1H, dd, *J* = 7.5, 1.4 Hz), 7.45–7.42 (1H, m), 7.12 (1H, t , *J* = 7.6 Hz), 7.04 (1H, d, *J* = 8.2 Hz), 3.90 (3H, s); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 157.1, 152.0, 146.5, 144.1, 142.1, 131.2, 131.0, 125.8, 121.3, 111.4, 55.6; LRMS (EI, *m*/*z*): 186 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{11}H_{10}N_2O$: 186.0793, found: 186.0808.

2-(3-Methoxyphenyl)pyrazine (5qa)



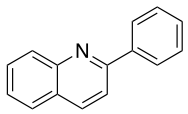
Obtained as yellow oil in 64% yield (24.2 mg); IR (neat, cm^{-1}): 3059, 2835, 1601, 1496, 1464, 1397, 1312, 1228, 1014, 783; ^1H NMR (600 MHz, $CDCl_3$/TMS) δ (ppm): 9.03 (1H, d, *J* = 1.4 Hz), 8.63 (1H, t, *J* = 2.1Hz), 8.51 (1H, d, *J* = 2.0 Hz), 7.60–7.57 (2H, m), 7.43 (1H, t, *J* = 7.9 Hz), 7.03 (1H, dd, *J* = 7.9, 2.4 Hz), 3.90 (3H, s); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 160.3, 152.6, 144.1, 143.0, 142.4, 137.8, 130.1, 119.2, 116.0, 112.1, 55.4; LRMS (EI, *m*/*z*): 186 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{11}H_{10}N_2O$: 186.0793, found: 186.0799.

2-Phenylquinoxaline (5bb)



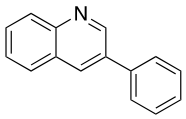
Obtained as colorless prisms in 43% yield (17.4 mg), recrystallized by hexane, mp 64–65 °C; IR (neat, cm^{-1}): 2927, 1539, 1488, 1313, 1208, 1123, 1048, 1029, 956, 764; ^1H NMR (600 MHz, CD_3OD) δ (ppm): 9.35 (1H, s), 8.22 (2H, dd, *J* = 8.3, 1.4 Hz), 8.11 (1H, dd, *J* = 8.3, 1.4 Hz), 8.06 (1H, d, *J* = 8.3 Hz), 7.83–7.77 (2H, m), 7.57–7.53 (3H, m); $^{13}C\{^1H\}$ NMR (150 MHz, CD_3OD) δ (ppm): 153.3, 144.5, 143.4, 142.4, 137.7, 131.7, 131.4, 131.0, 130.4, 130.1, 129.6, 128.6; LRMS (EI, *m*/*z*): 206 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{14}H_{10}N_2$: 206.0844, found: 206.0862.

2-Phenylquinoline (5bc-C2)



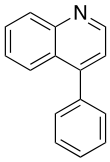
Obtained as brown oil in 7% yield (2.9 mg); IR (neat, cm^{-1}): 2924, 1598, 1507, 1490, 1262, 1125, 1075, 1024, 828, 766; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.23 (1H, dd, *J* = 8.5, 1.7 Hz), 8.19–8.16 (3H, m), 7.89 (1H, dd, *J* = 8.5, 2.2 Hz), 7.84 (1H, d, *J* = 8.3 Hz), 7.75–7.71 (1H, m), 7.56–7.52 (3H, m), 7.48–7.45 (1H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 157.4, 148.3, 139.7, 136.8, 129.8, 129.6, 129.3, 128.8, 127.6, 127.5, 127.2, 126.3, 119.0; LRMS (EI, *m*/*z*): 205 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{15}H_{11}N$: 205.0892, found: 205.0906.

3-Phenylquinoline (5bc-C3)



Obtained as yellow oil in 8% yield (3.5 mg); IR (neat, cm^{-1}): 3059, 2927, 1493, 1026, 953, 903, 786, 761, 749; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 9.20 (1H, d, *J* = 1.9 Hz), 8.32 (1H, d, *J* = 1.4 Hz), 8.15 (1H, d, *J* = 8.8 Hz), 7.89 (1H, d, *J* = 8.3 Hz), 7.75–7.72 (3H, m), 7.61–7.52 (3H, m), 7.47–7.43 (1H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 150.0, 147.4, 137.9, 133.9, 133.2, 129.4, 129.3, 129.2, 128.1, 128.05, 128.01, 127.5, 127.0; LRMS (EI, *m*/*z*): 205 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{15}H_{11}N$: 205.0892, found: 205.0888.

4-Phenylquinoline (5bc-C4)



Obtained as yellow oil in 18% yield (7.5 mg); IR (neat, cm^{-1}): 3052, 1594, 1493, 1465, 1445, 1383, 1031, 964, 794, 752; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 8.96–8.95 (1H, m), 8.20 (1H, d, *J* = 8.3 Hz), 7.83 (1H, d, *J* = 8.3 Hz), 7.75–7.69 (3H, m), 7.60 (1H, d, *J* = 7.6 Hz), 7.50 (2H, t, *J* = 7.6 Hz), 7.43–7.39 (2H, m); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$/TMS) δ (ppm): 150.3, 146.1, 140.9, 139.6, 136.2, 130.6, 130.3, 128.7, 128.0, 127.5, 127.4, 126.3, 121.0; LRMS (EI, *m*/*z*): 205 (M^+); HRMS (EI, *m*/*z*): Calcd. for $C_{15}H_{11}N$: 205.0892, found: 205.0882.

4. Results of ICP-MS

Quantitative elemental analyses of **1a**, **4a**, NaH, and 1,10-phenthroline were carried out for the detection of transition metals such as Fe, Ni, Cu, Ru, Rh, Pd, Pt, Au, and Ag. The values are expressed in ppm (μg/g).

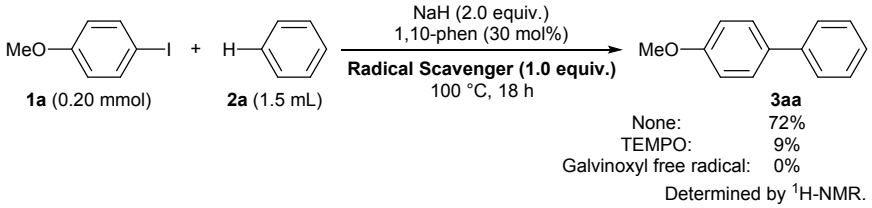
Table S2. Data of ICP-MS

μg/g	Fe	Ni	Cu	Ru	Rh	Pd	Pt	Au	Ag
1a	0.555	0.072	0.351	0.002	0.001	BDL	BDL	4.830	0.013
4a	3.925	0.093	0.376	0.003	0.002	1.515	0.065	0.758	0.032
NaH	9.910	0.214	0.352	0.002	0.001	0.015	0.012	0.017	0.366
1,10-phen	0.504	0.023	0.246	0.002	0.001	0.647	BDL	0.716	0.067

BDL = below detection limit

5. Radical scavenging experiment

Scheme S1. Radical scavenging experiment of **1a**



6. EPR analysis

Representative procedure (Figure S1, (a)).

In a glove box under an Ar atmosphere, a mixture of NaH (4.8 mg, 0.20 mmol) and 1,10-phenanthroline (18.0 mg, 0.10 mmol) in toluene (2.0 mL) was stirred at 100 °C for 2 h. After that, the mixture was analyzed by EPR. EPR spectra was recorded at 373K on EPR spectrometer operated at 9.5 GHz.

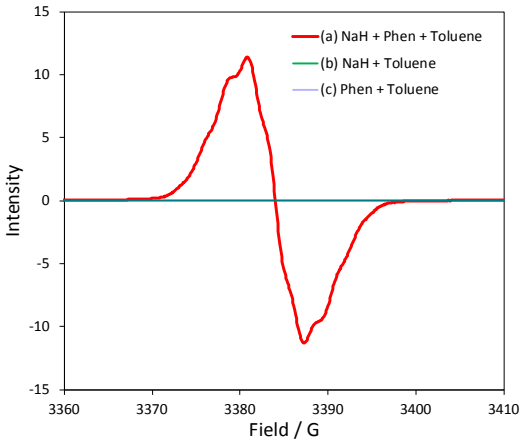
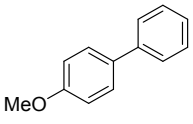
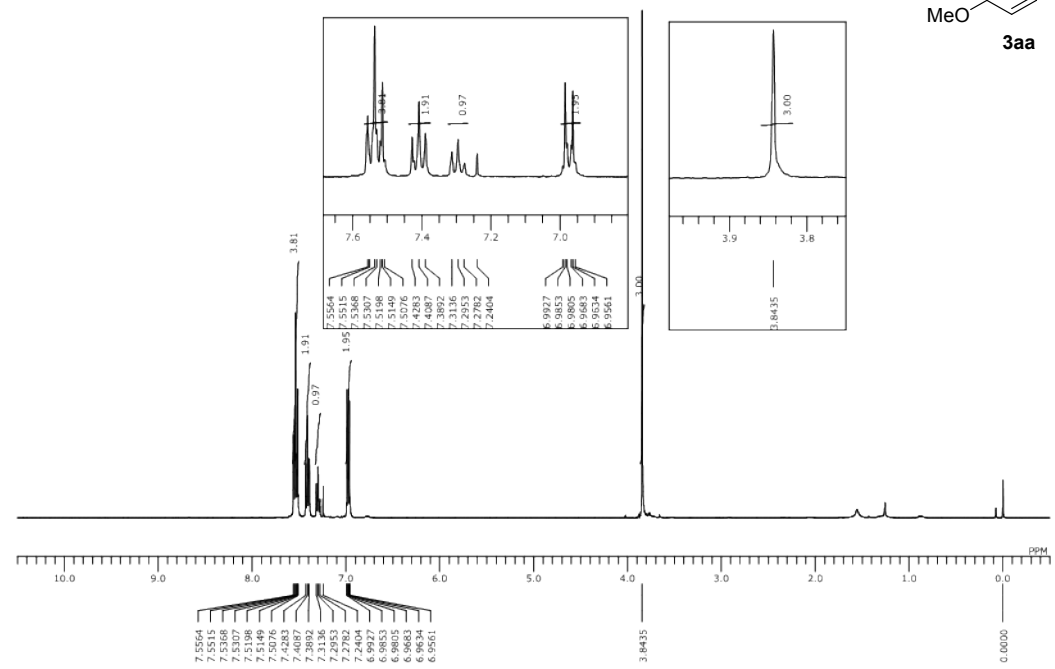


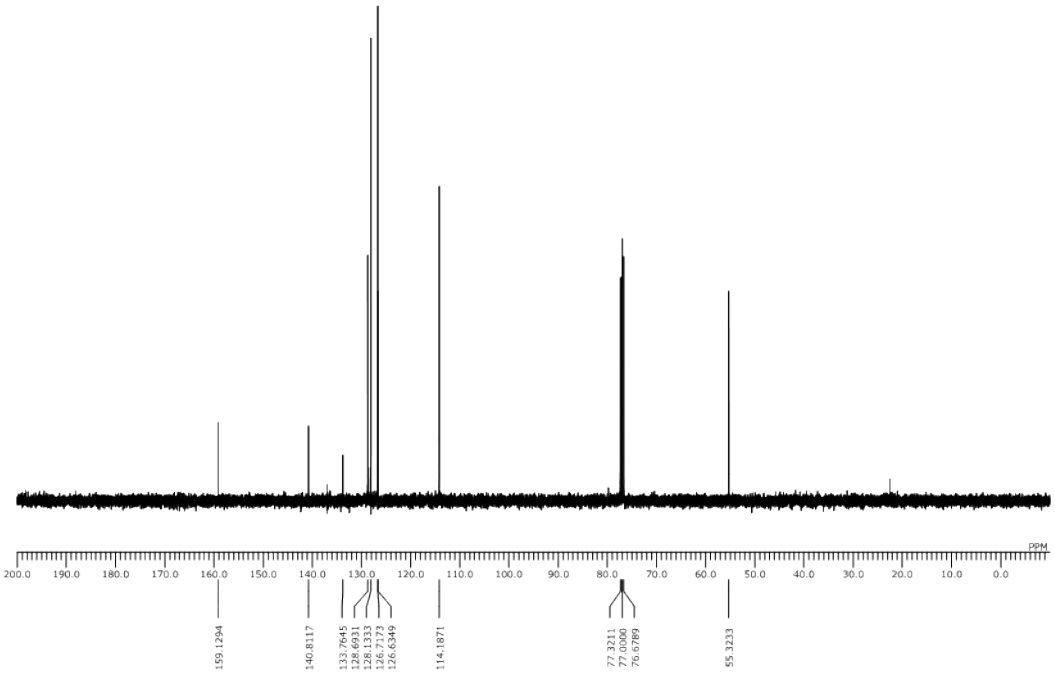
Figure S1. EPR spectra (9.5 GHz, 373 K) of solutions (a) NaH (0.20 mmol), 1,10-phenanthroline (0.10 mmol), and toluene (2.0 mL); (b) NaH (0.2 mmol) and toluene (2.0 mL); (c) 1,10-phenanthroline (0.10 mmol) and toluene (2.0 mL). The spectra were obtained at 373 K after heating at 373 K for 2 h.

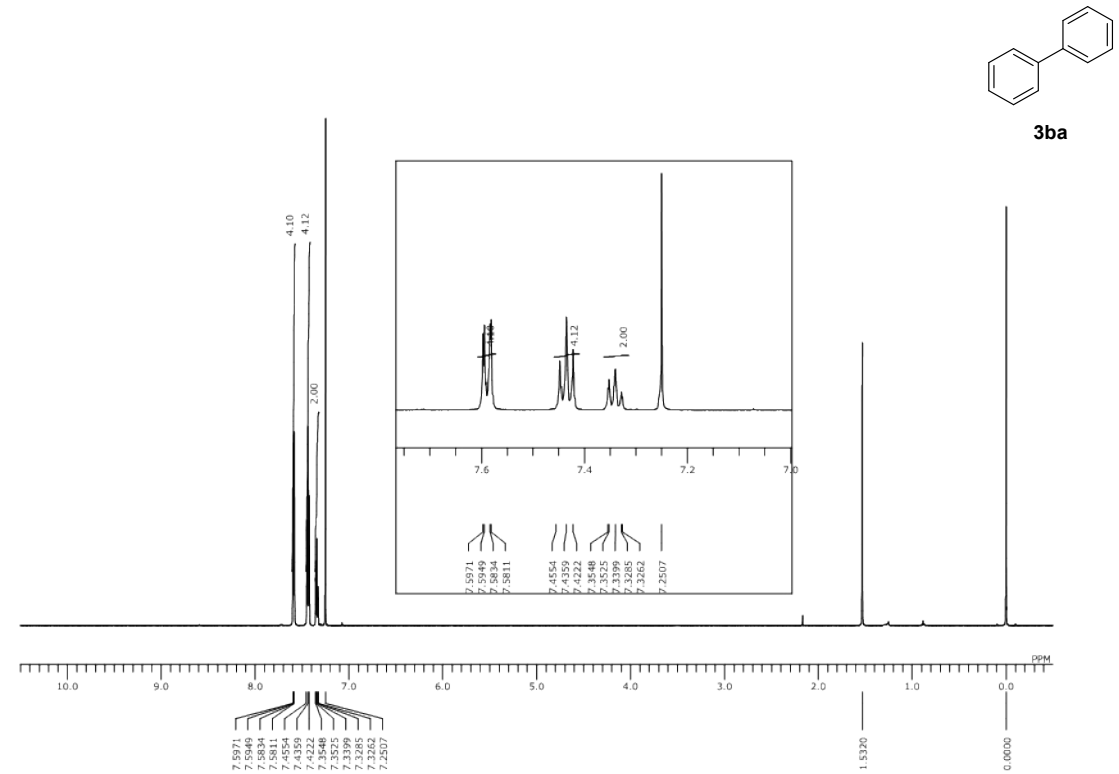
7. ^{1}H- and ^{13}C-NMR spectra



3aa

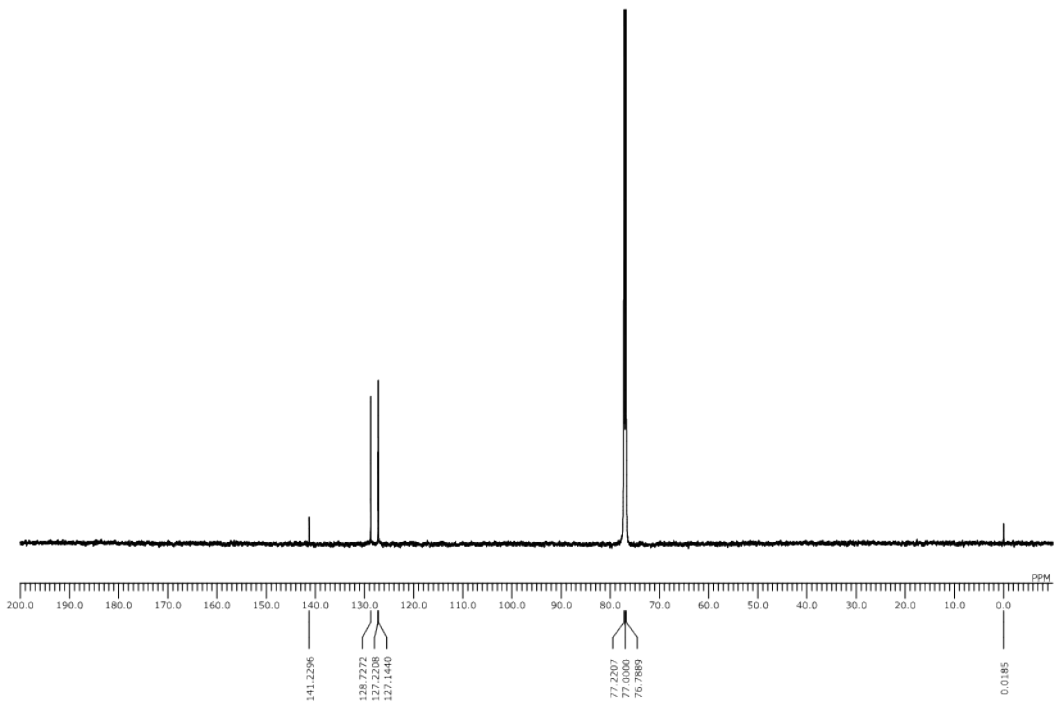






3ba

4.10
4.12
2.00
7.6
7.4
7.2
7.0
7.5971
7.5949
7.5834
7.5811
7.4554
7.4359
7.4222
7.3548
7.3525
7.3399
7.3285
7.3262
7.2507
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.5320
0.0000


PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
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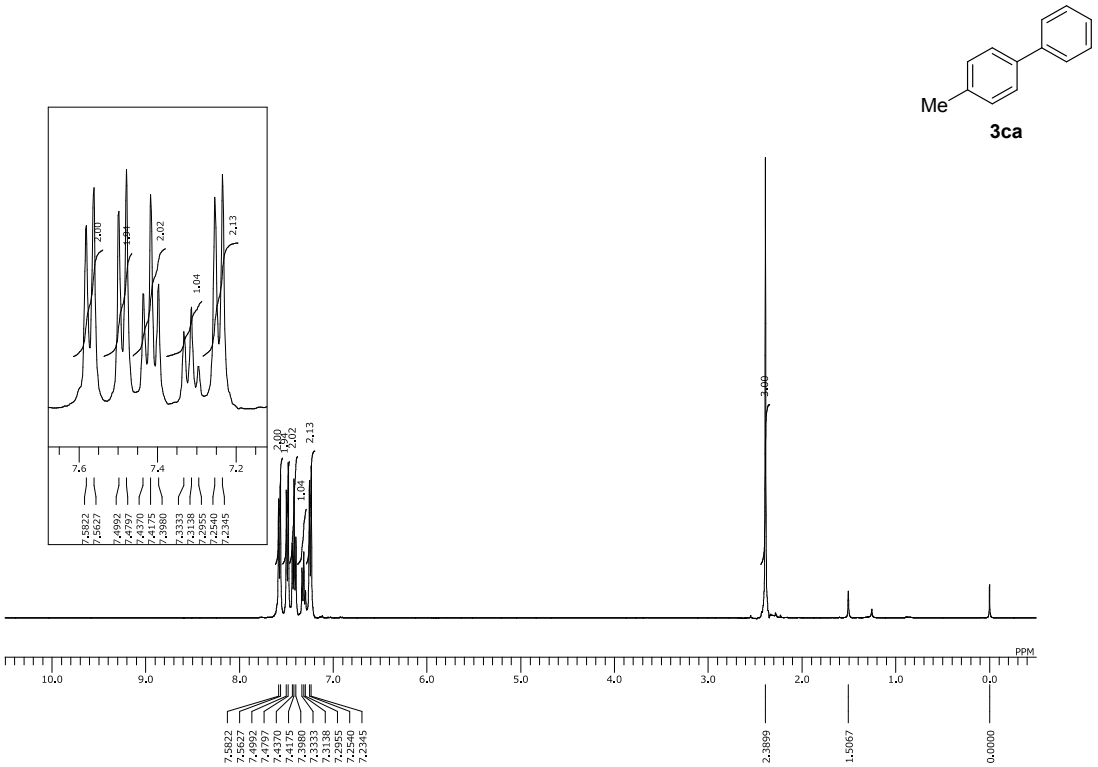
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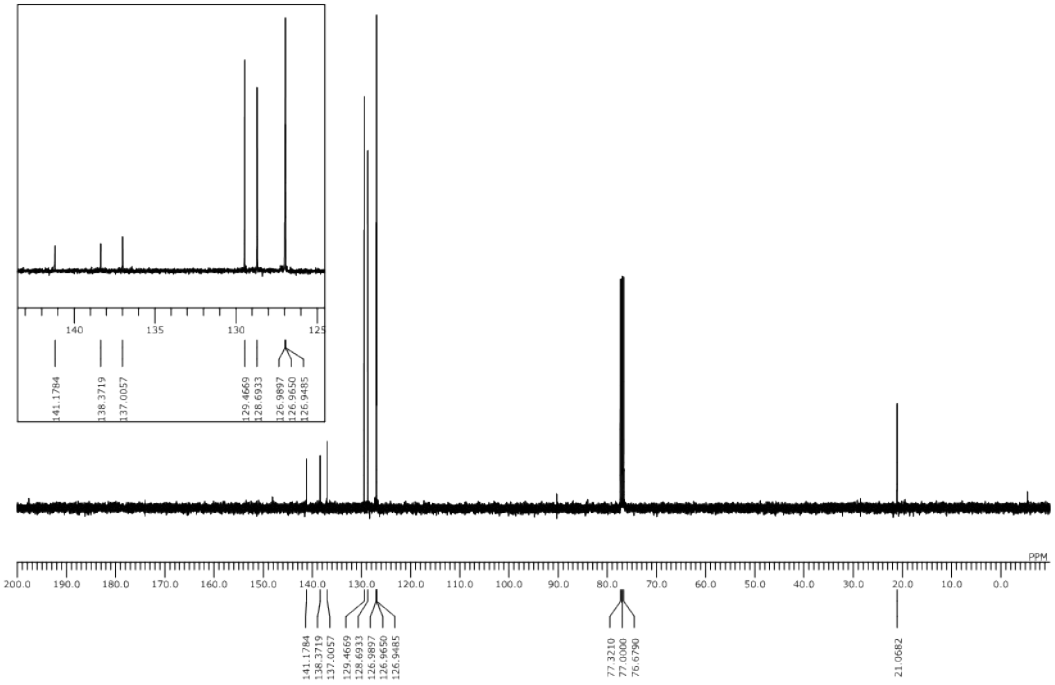
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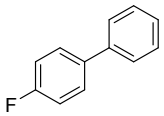
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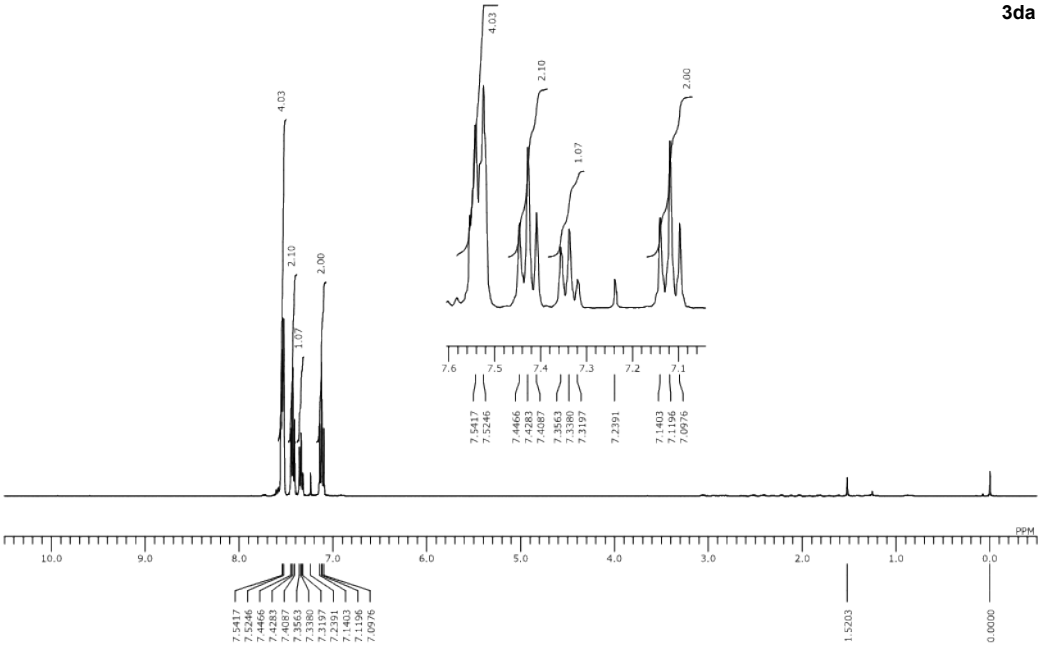
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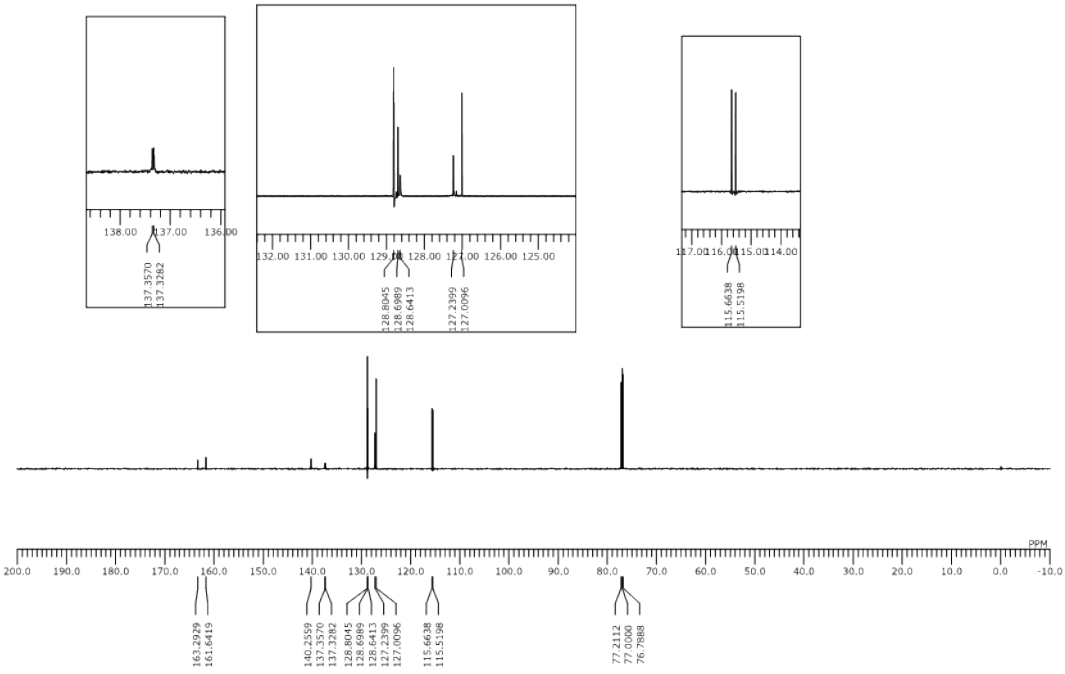
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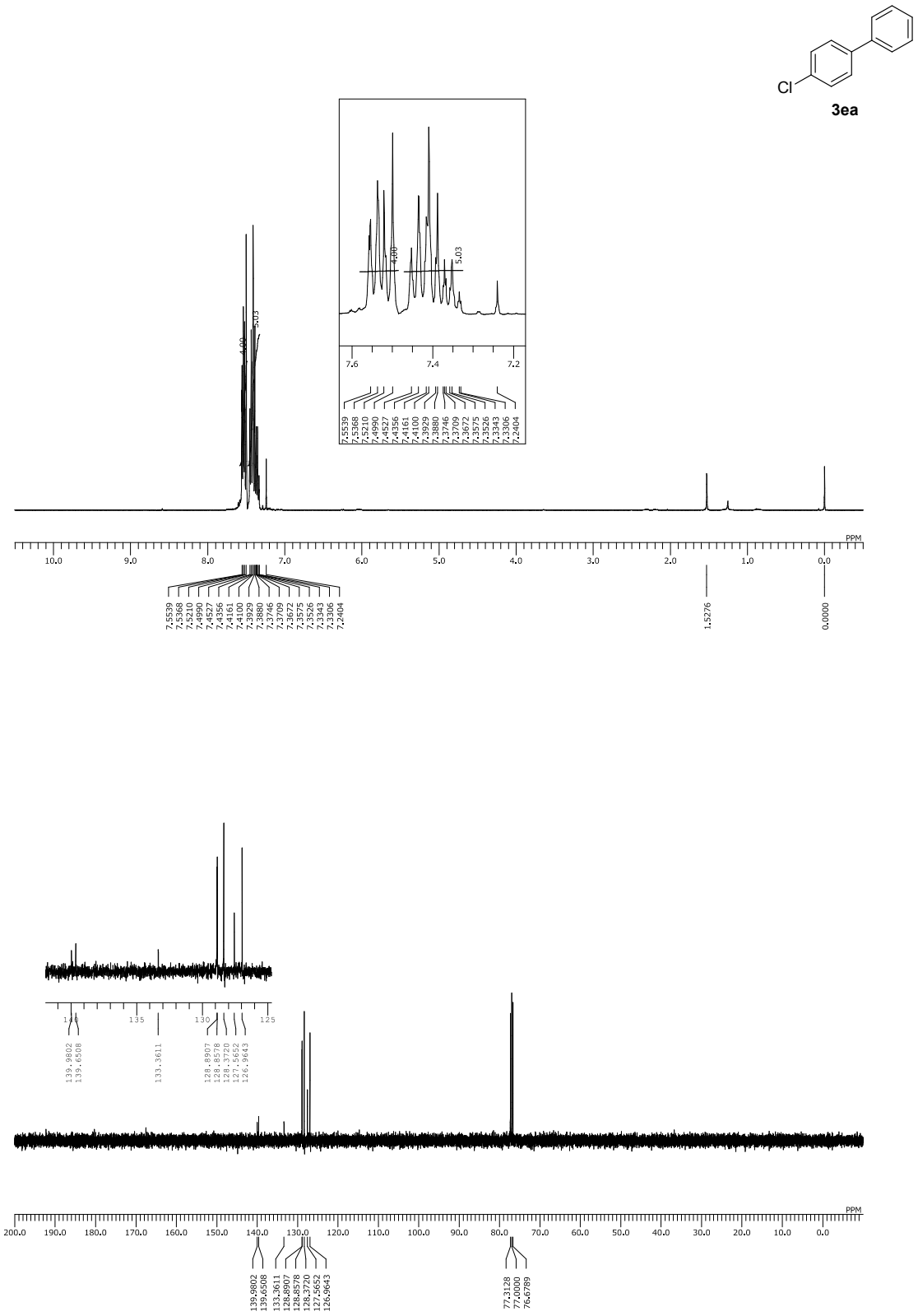
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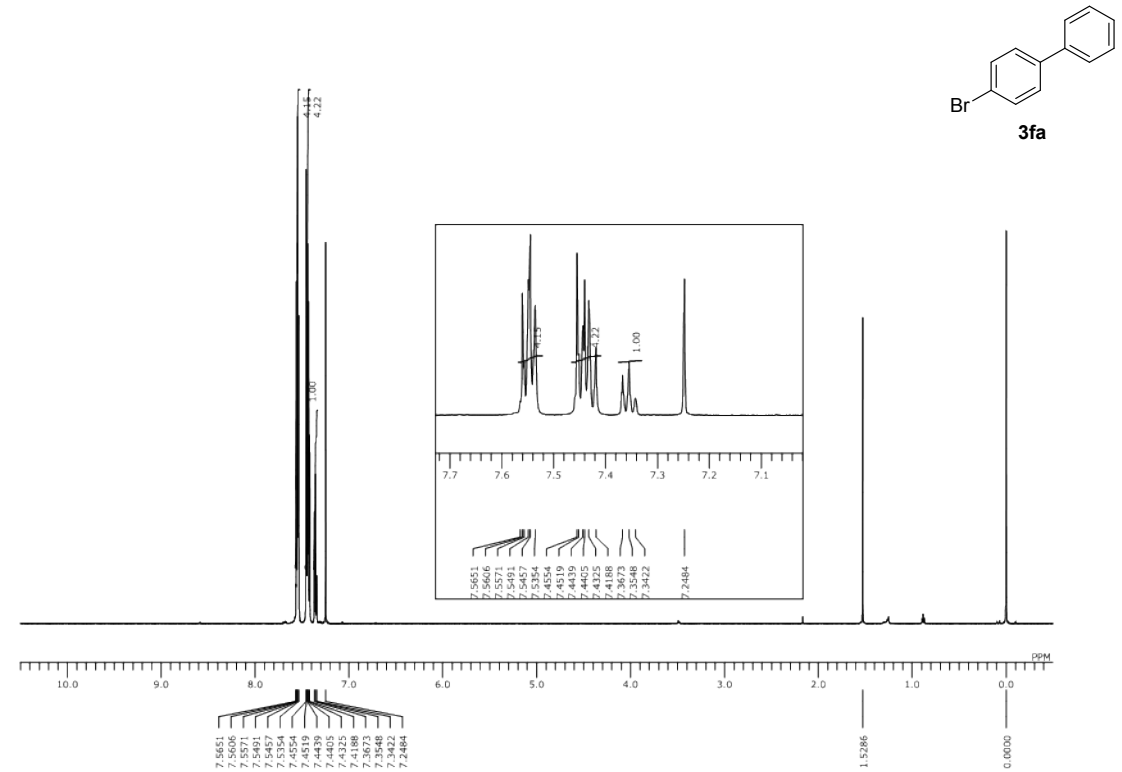
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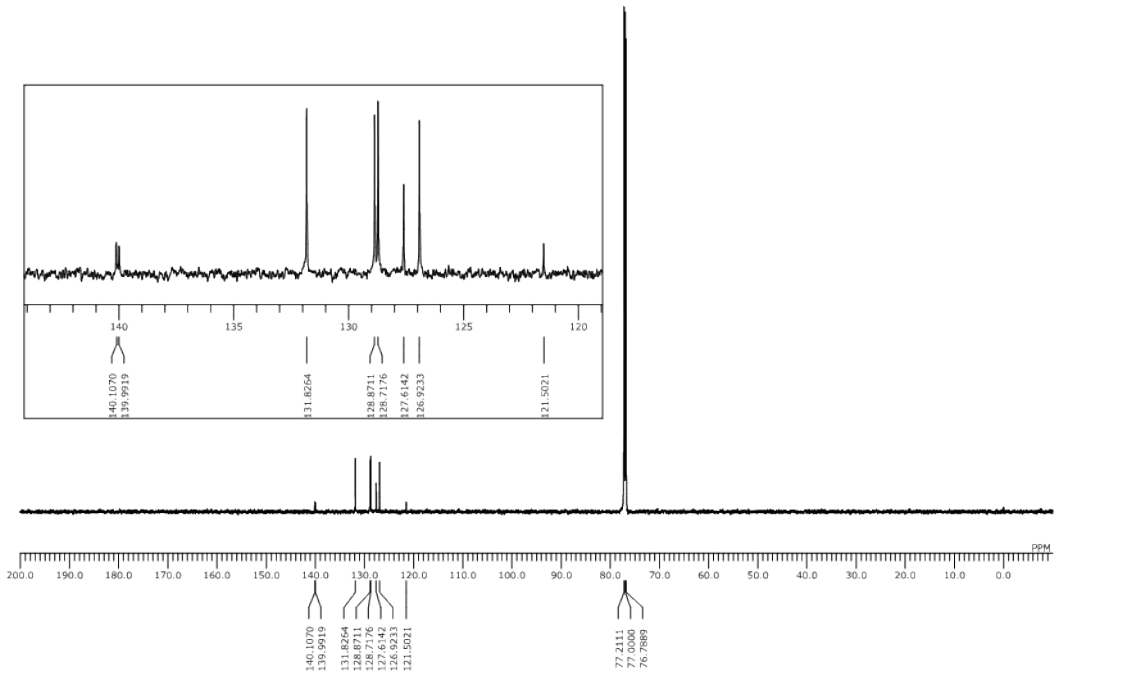
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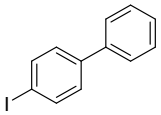

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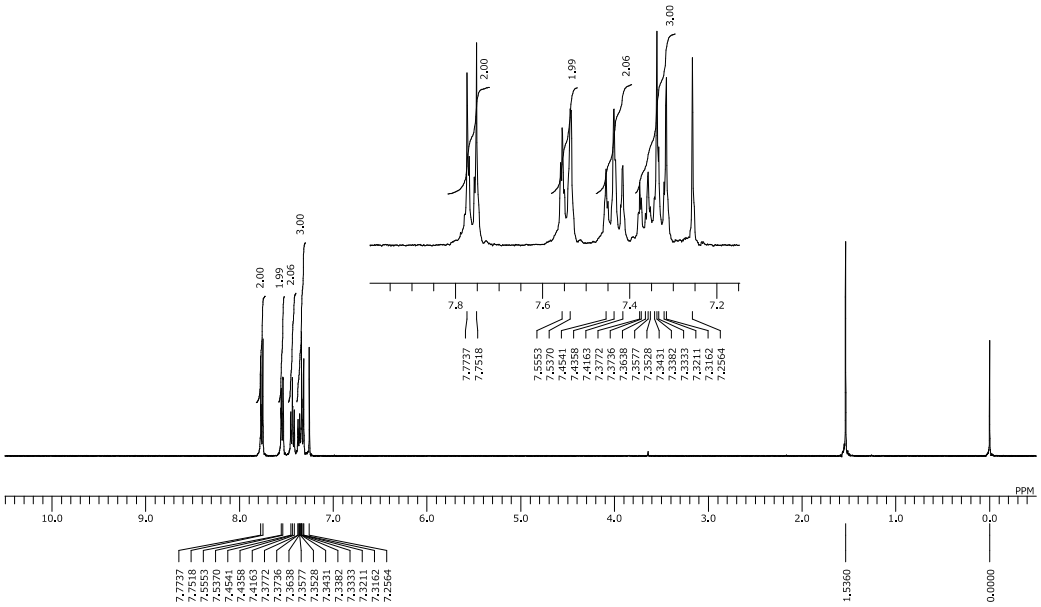
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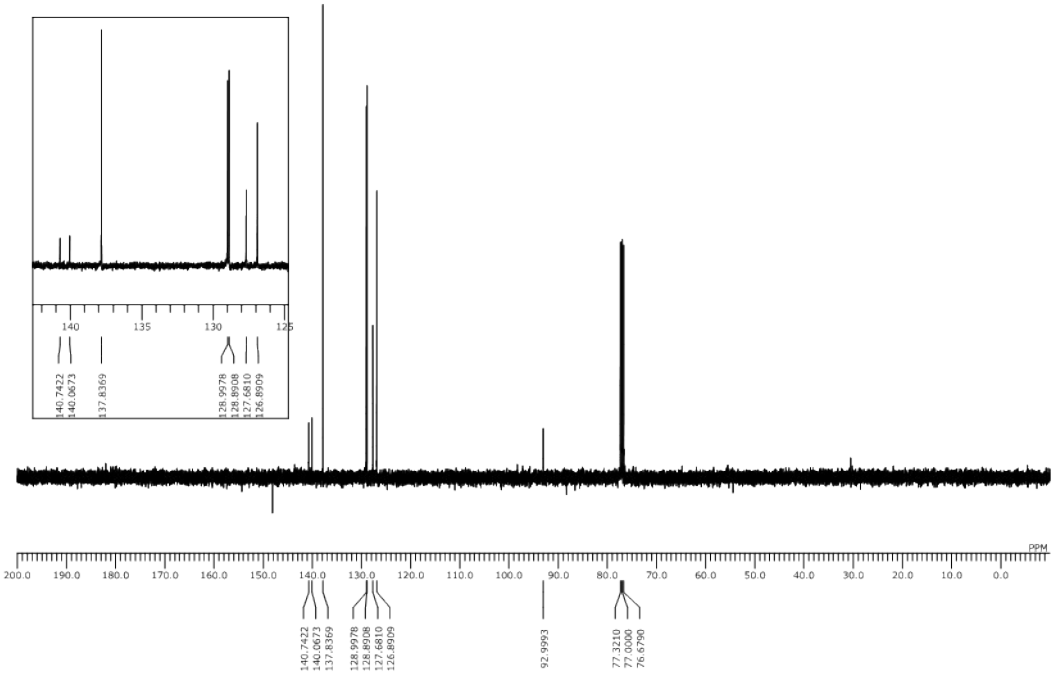
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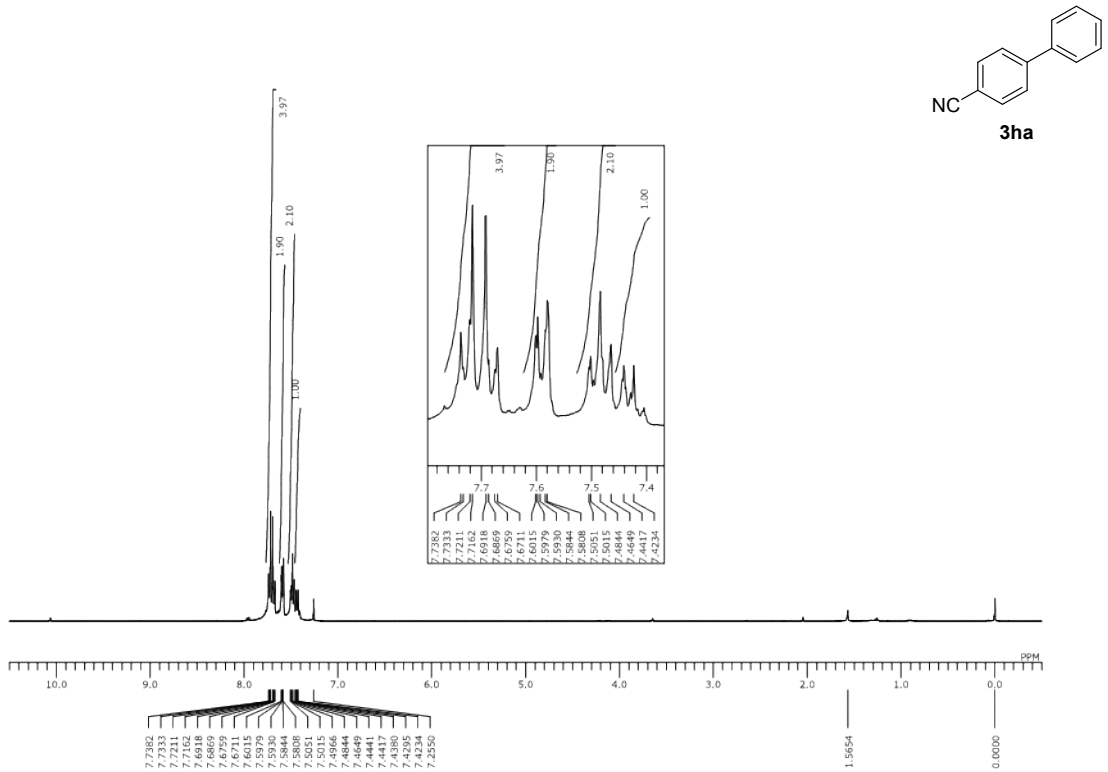
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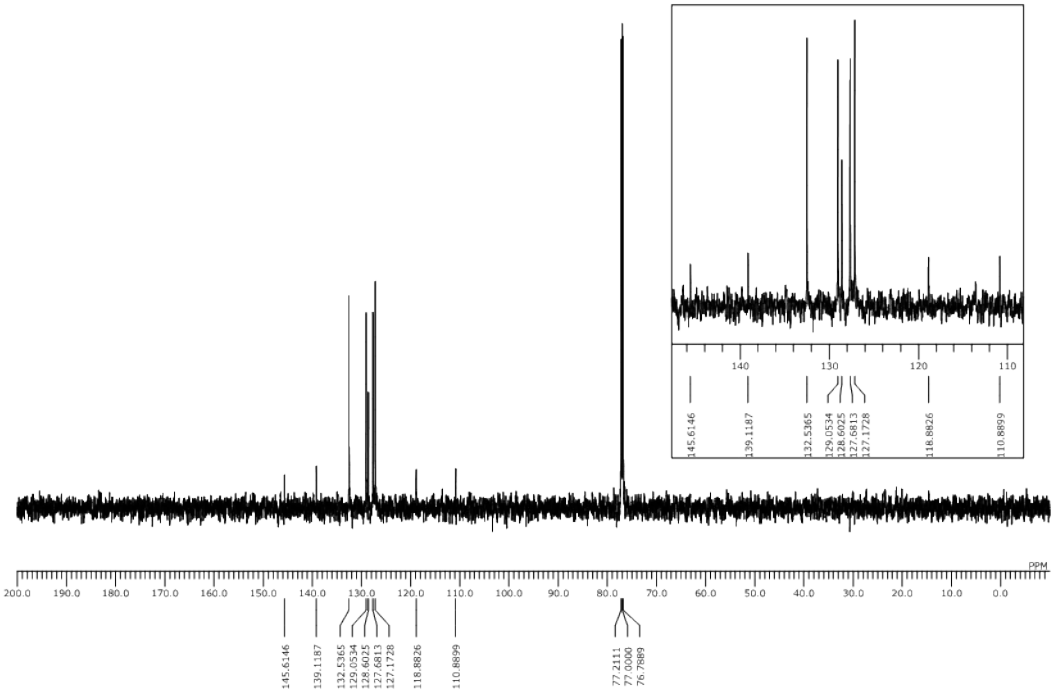
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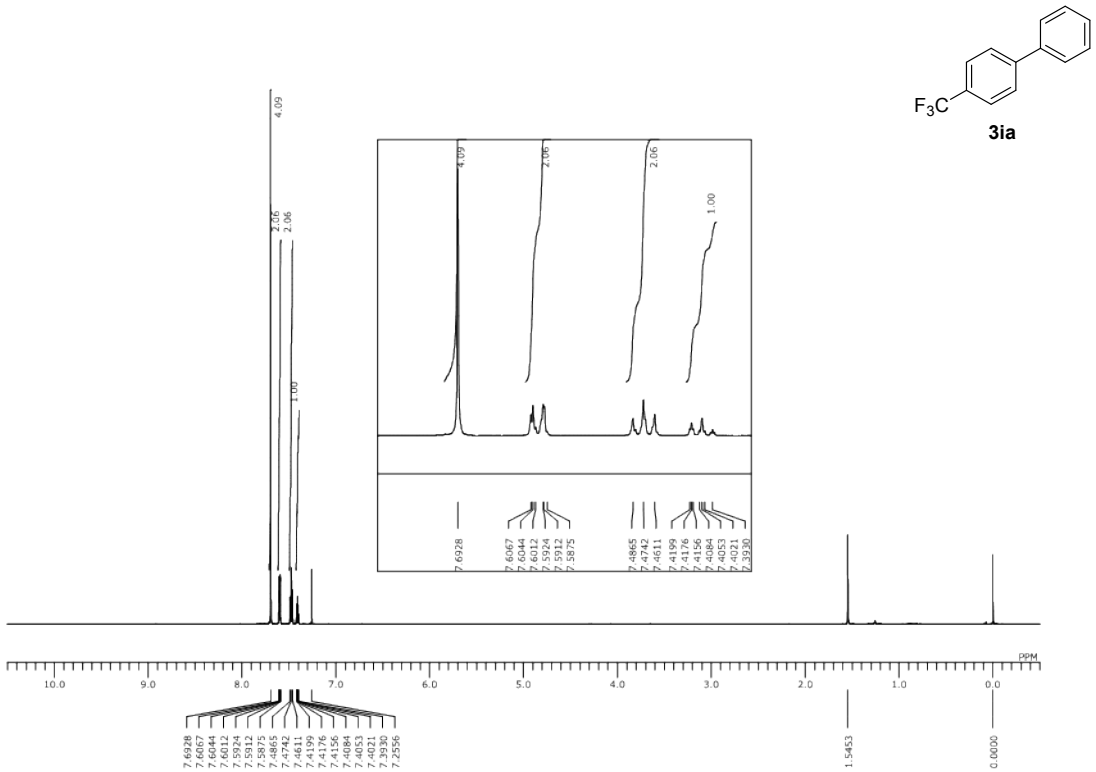
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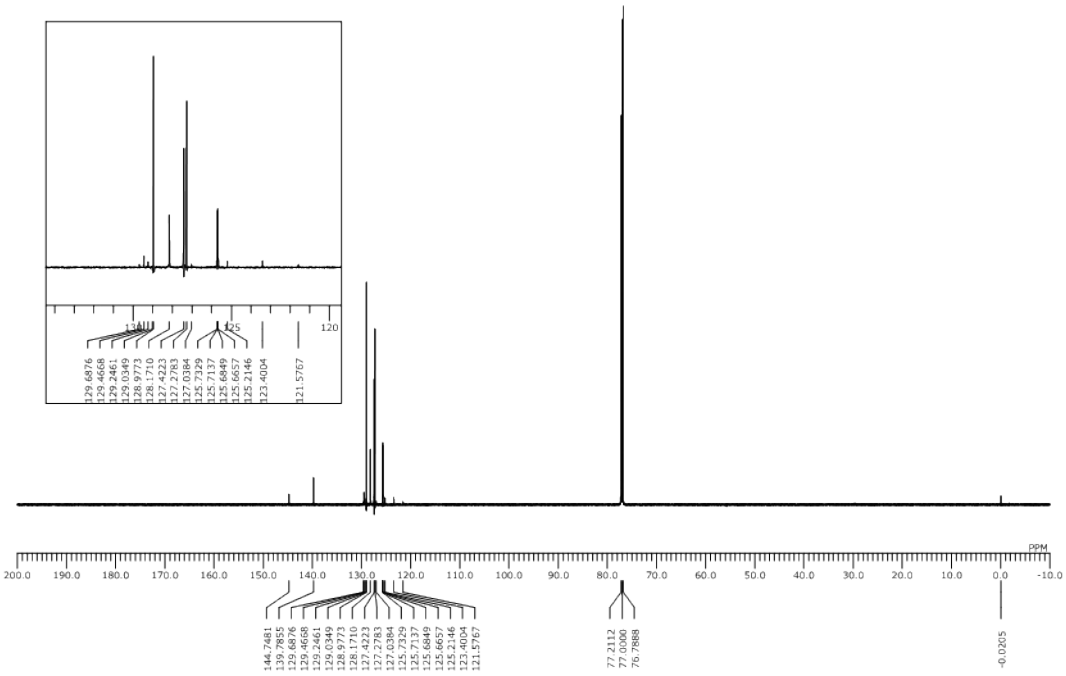
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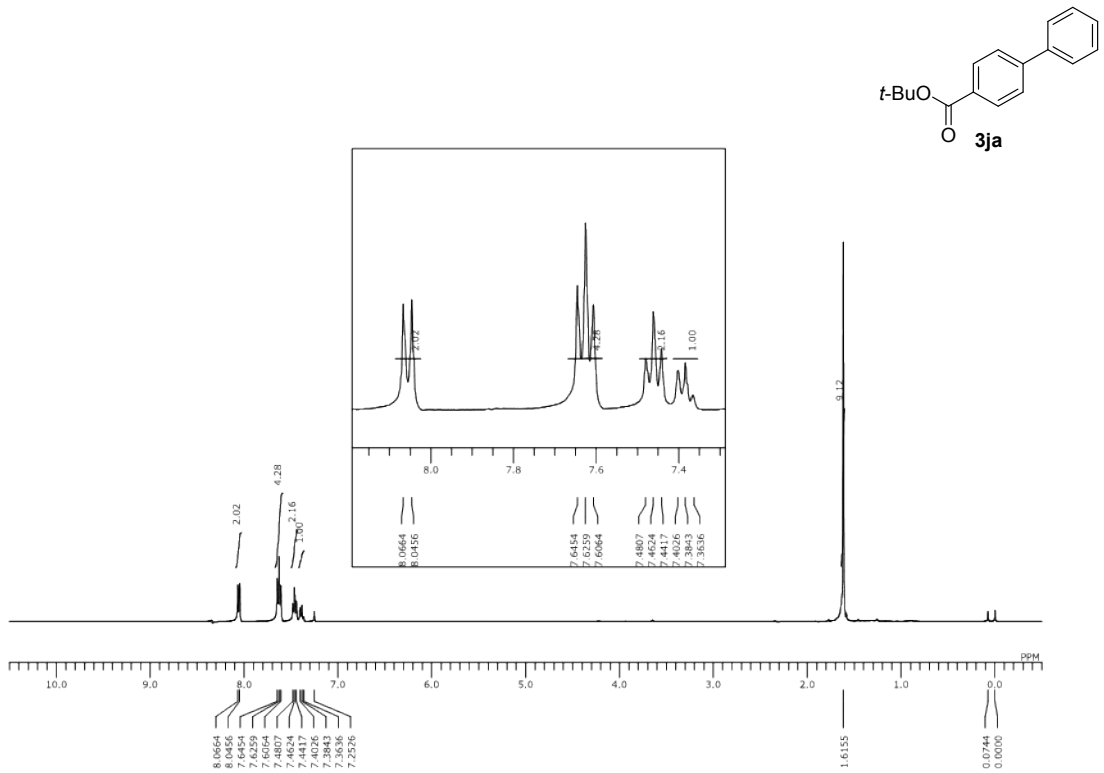
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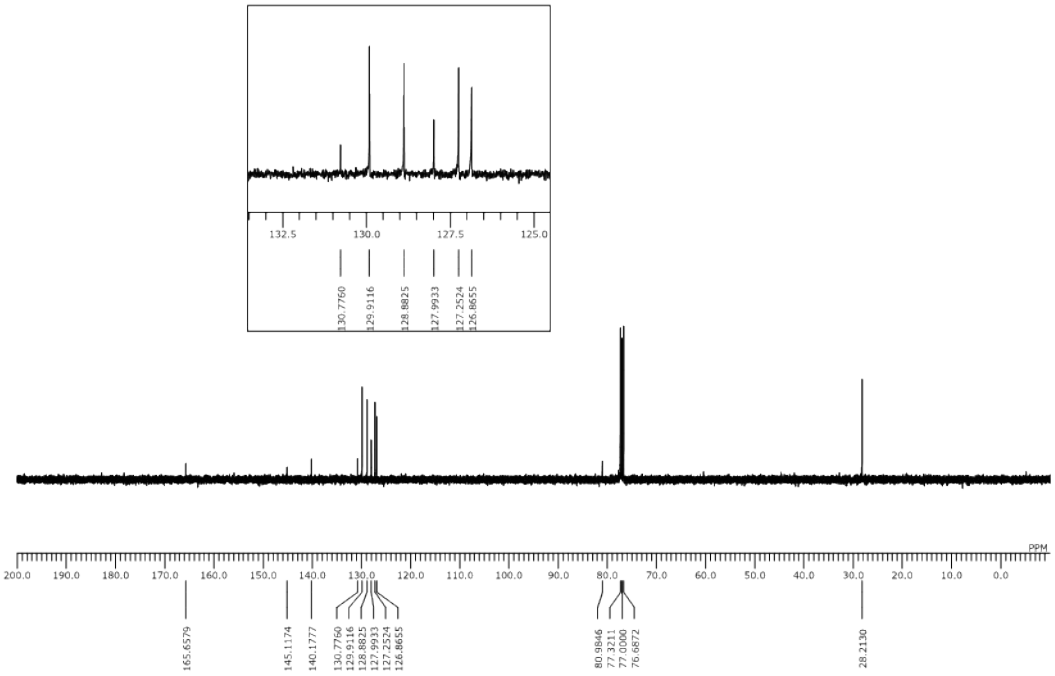
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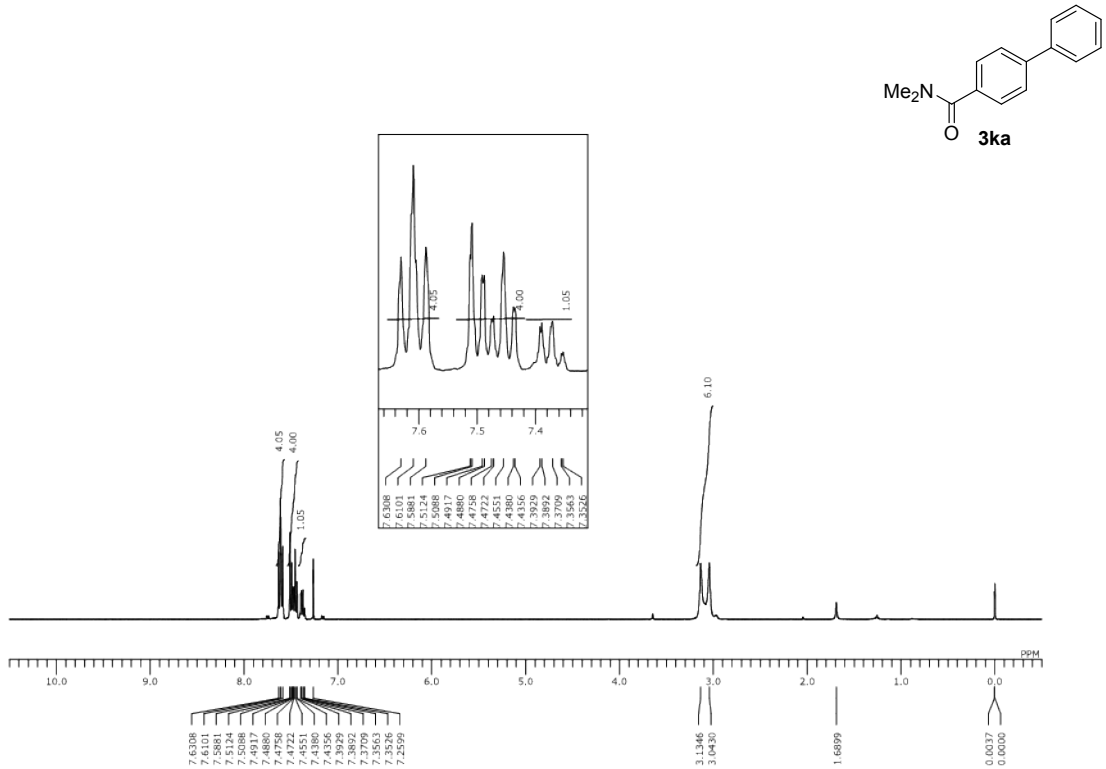
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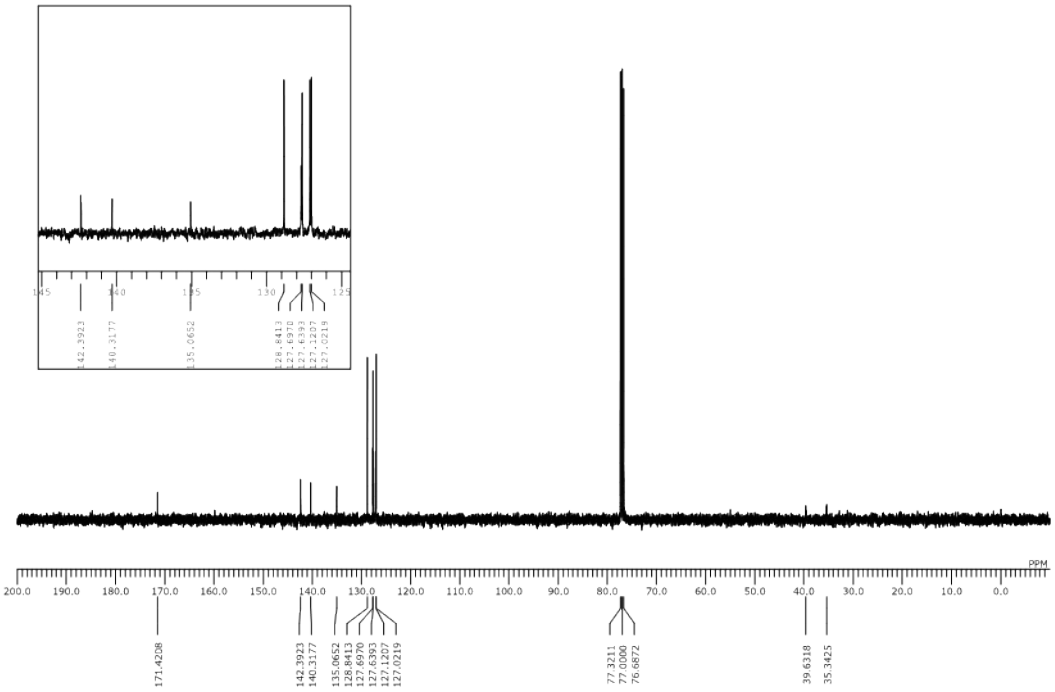

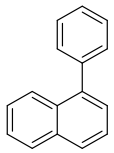

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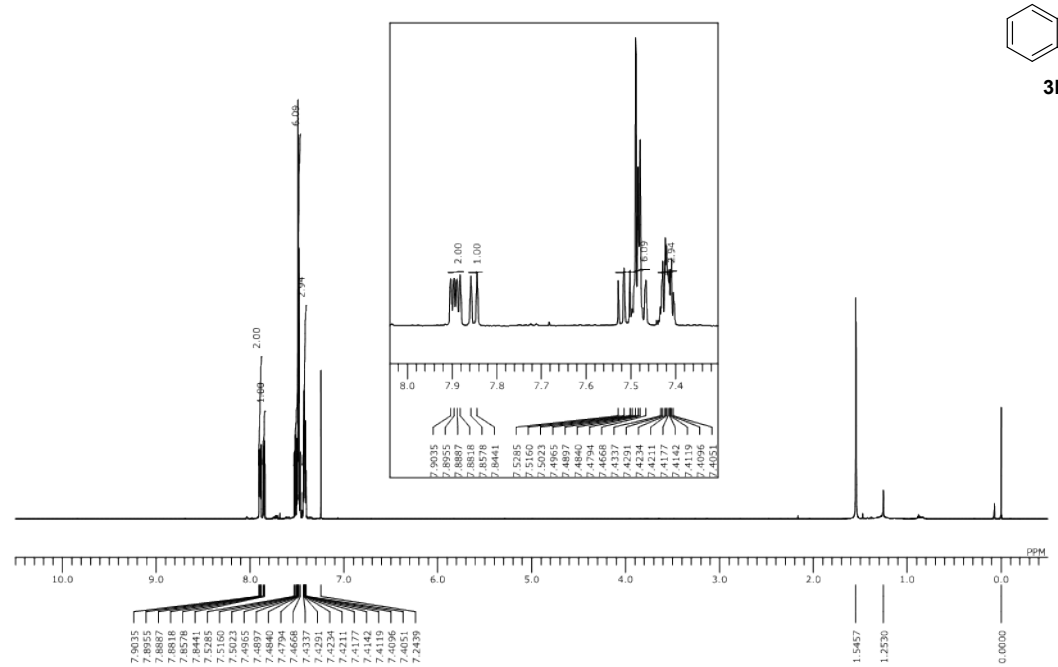

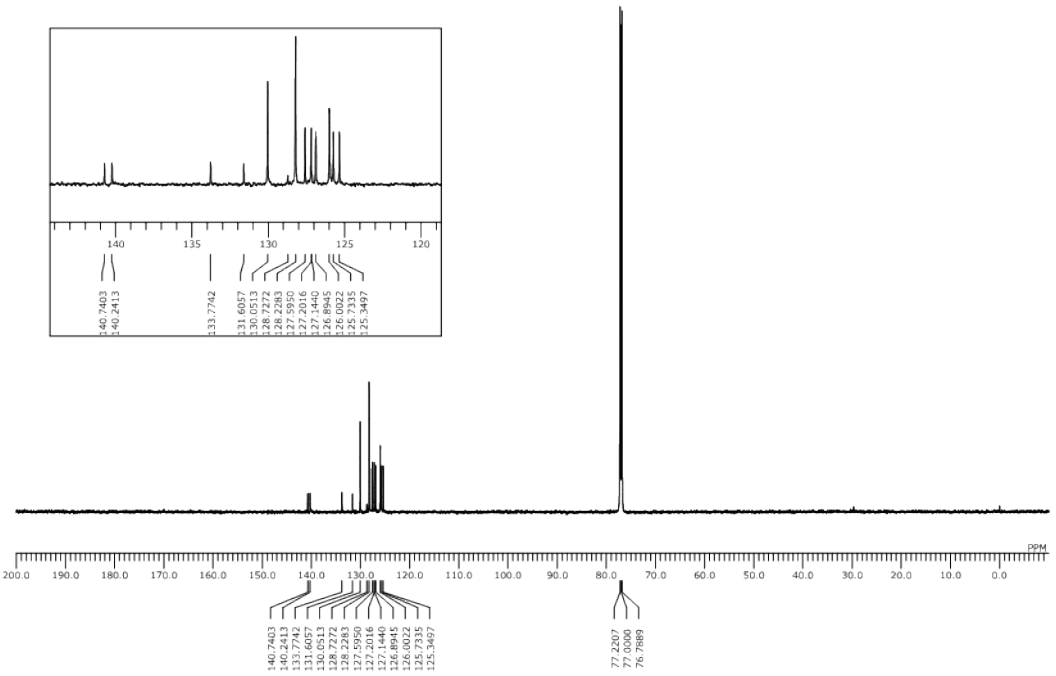

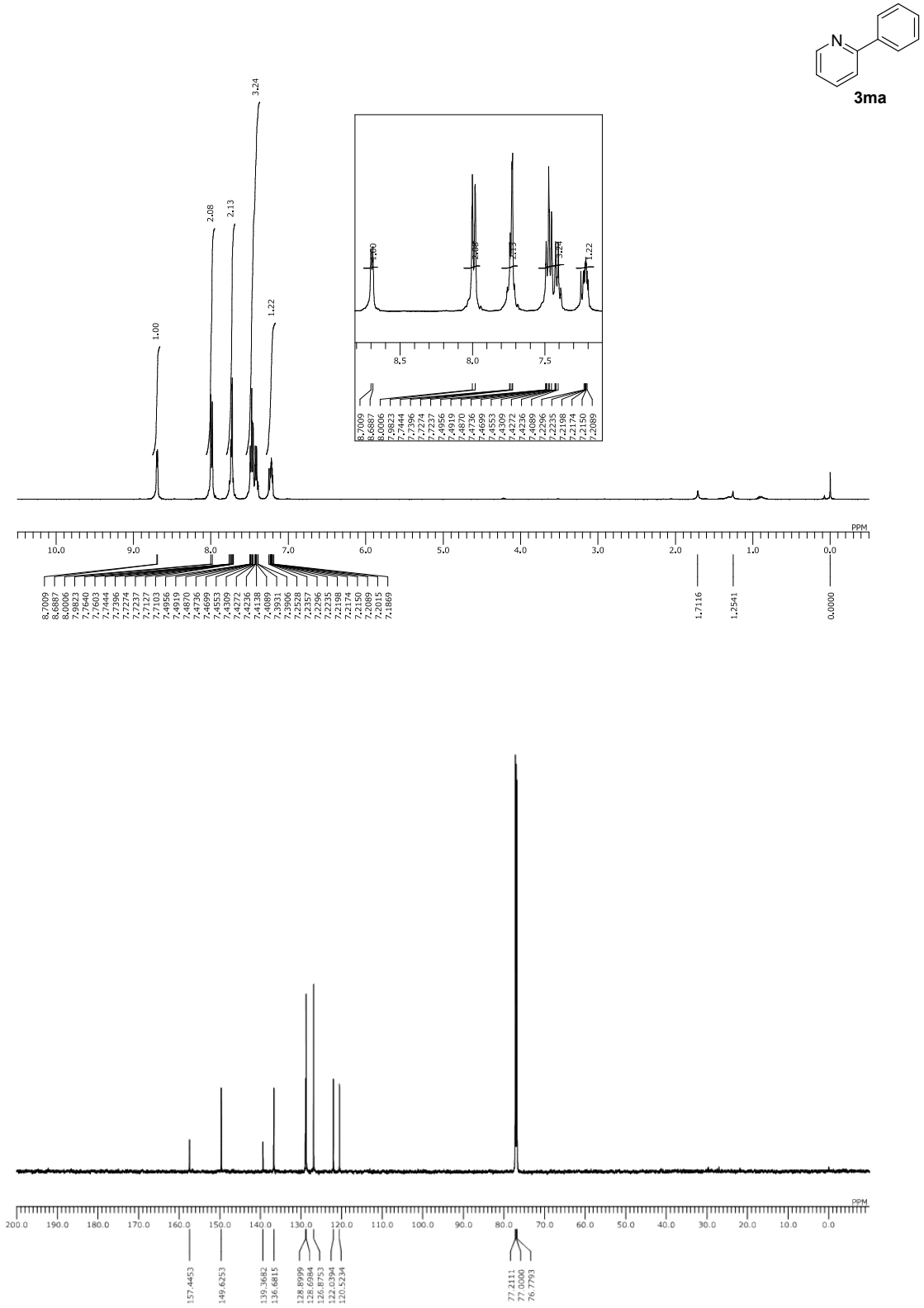
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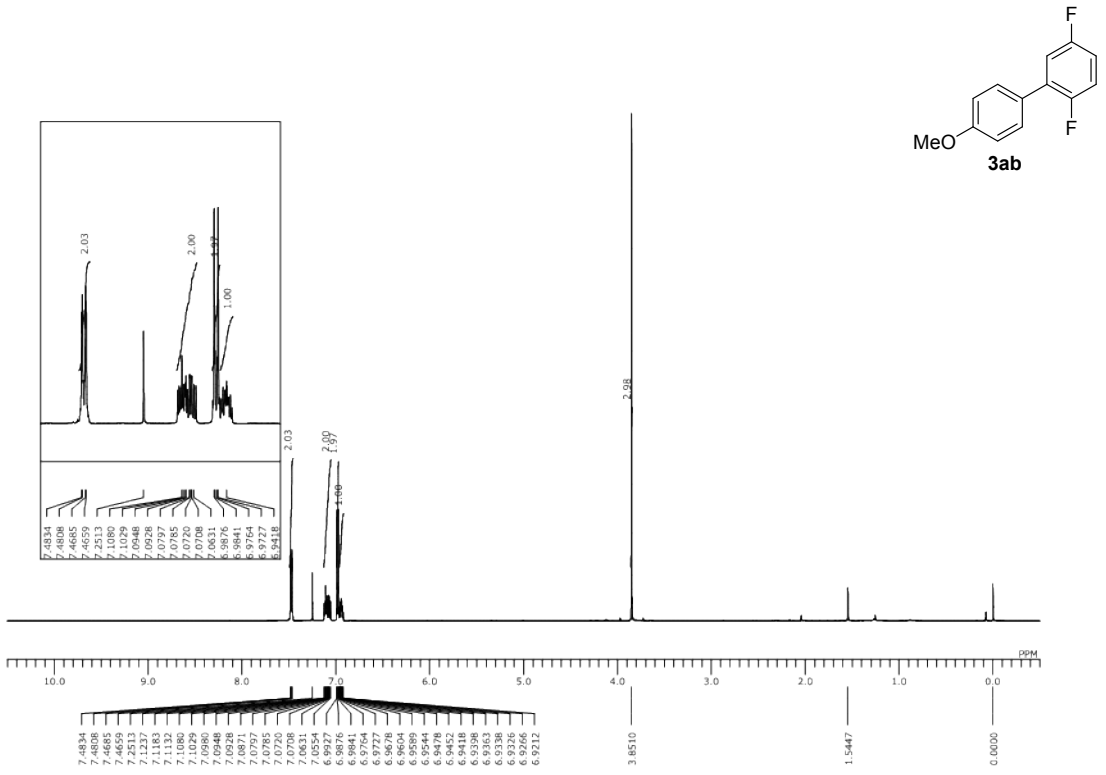
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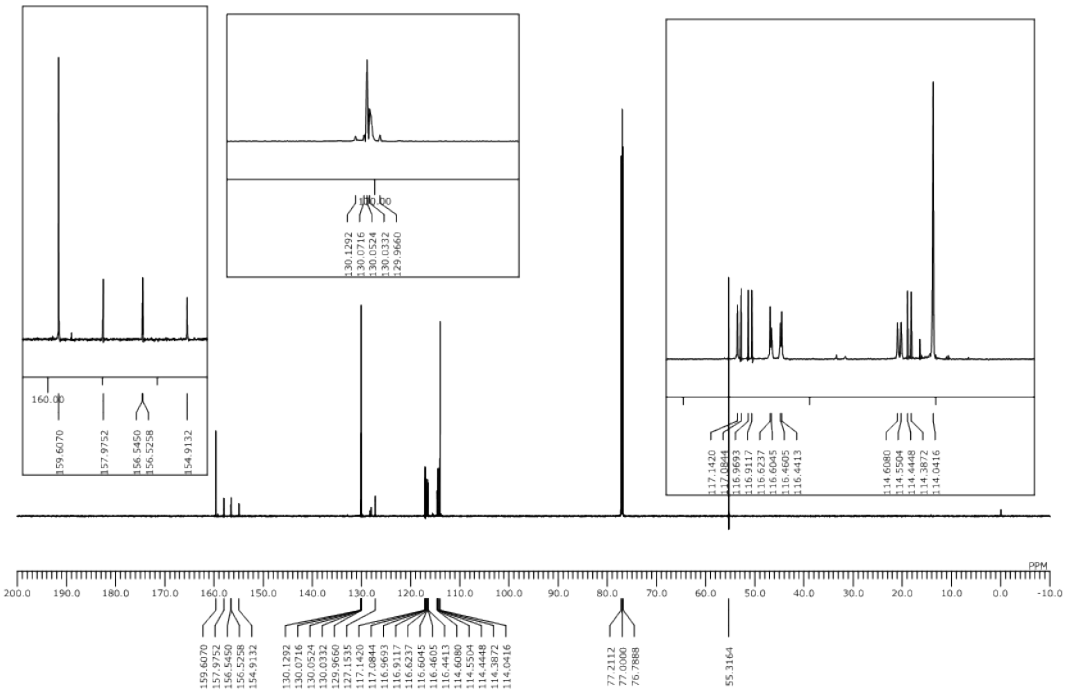
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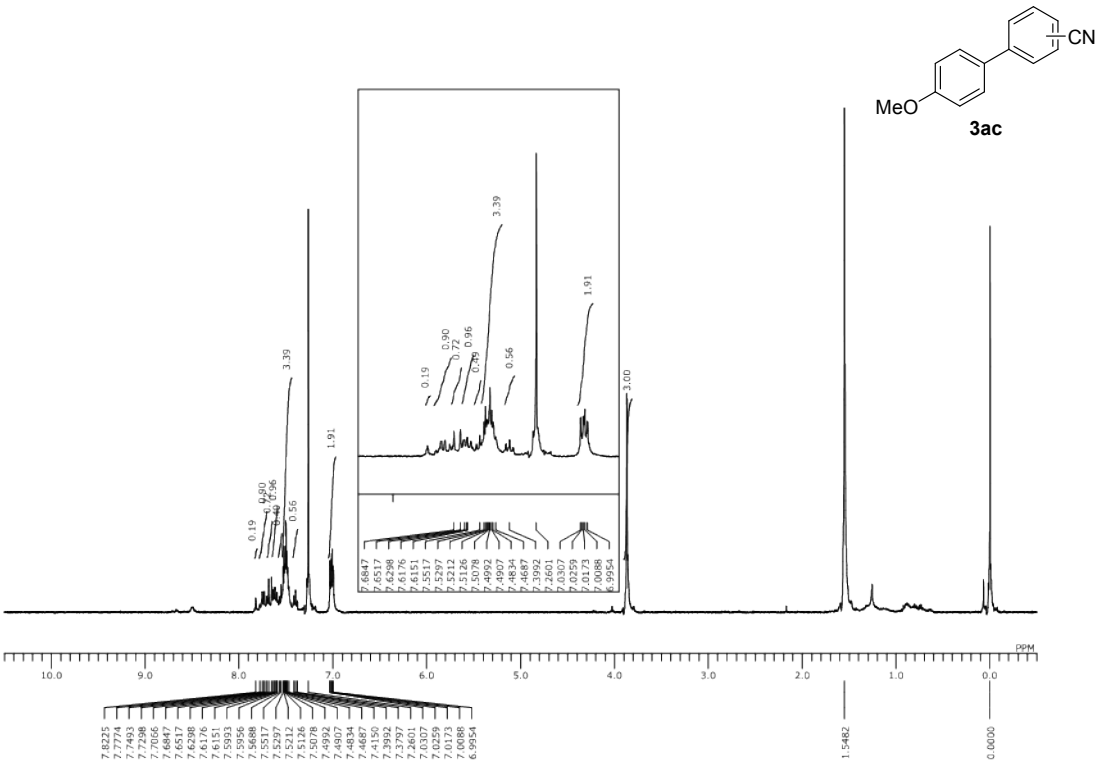
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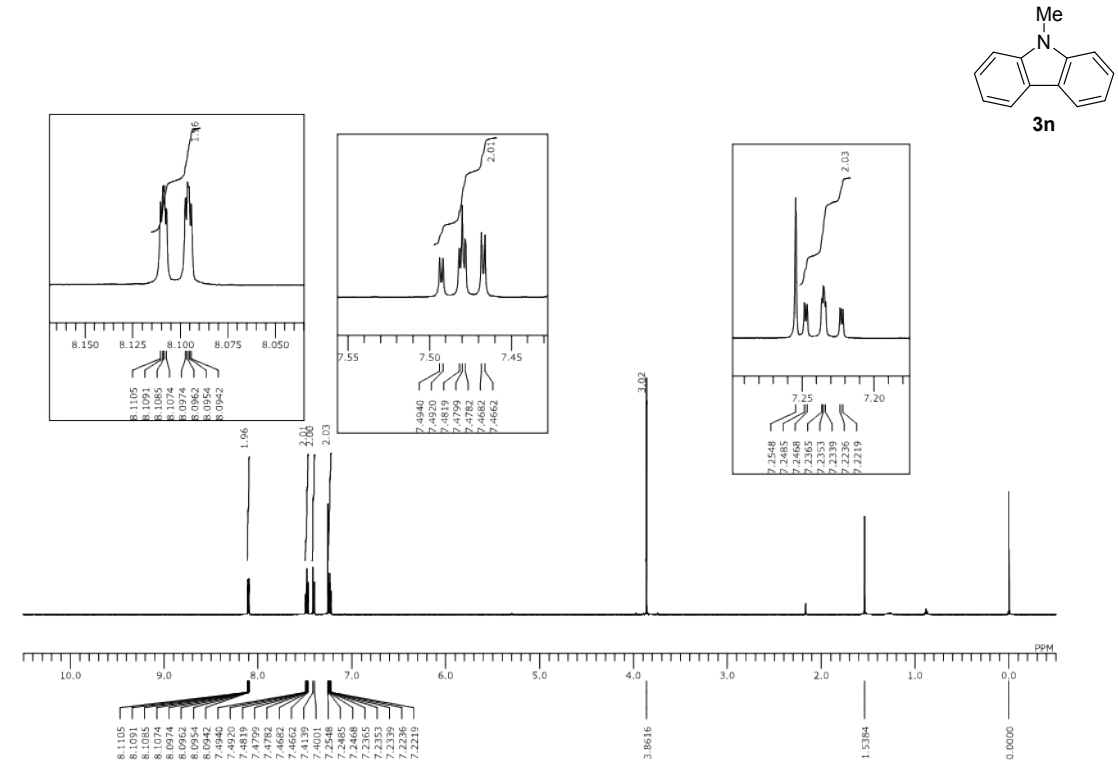
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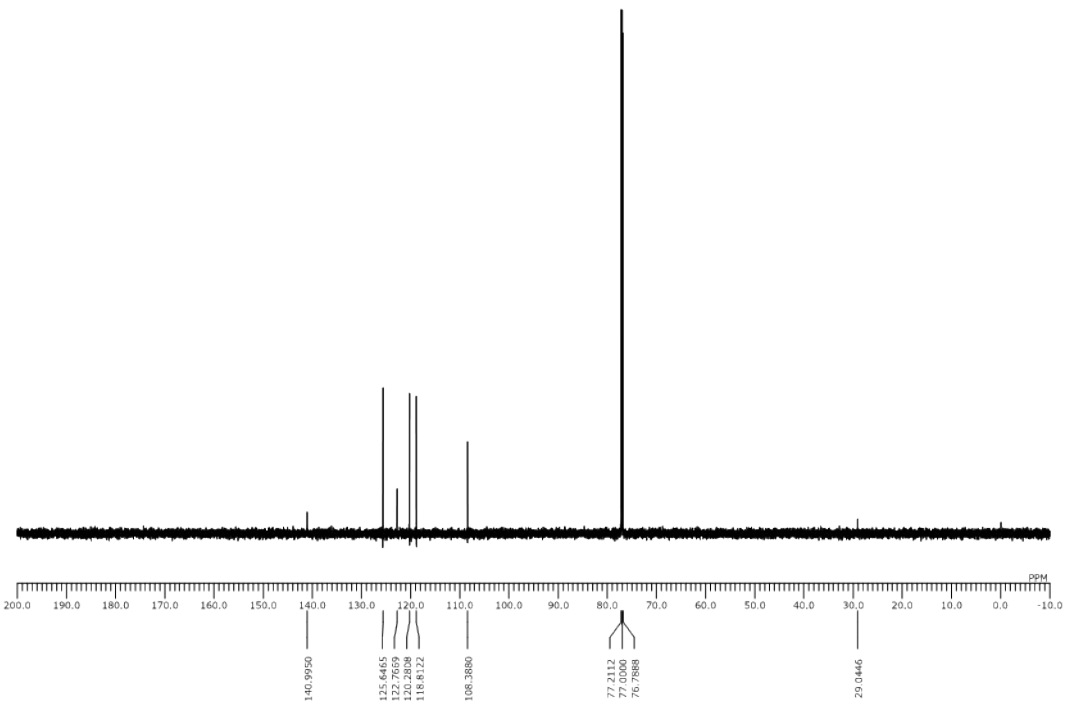
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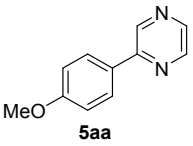
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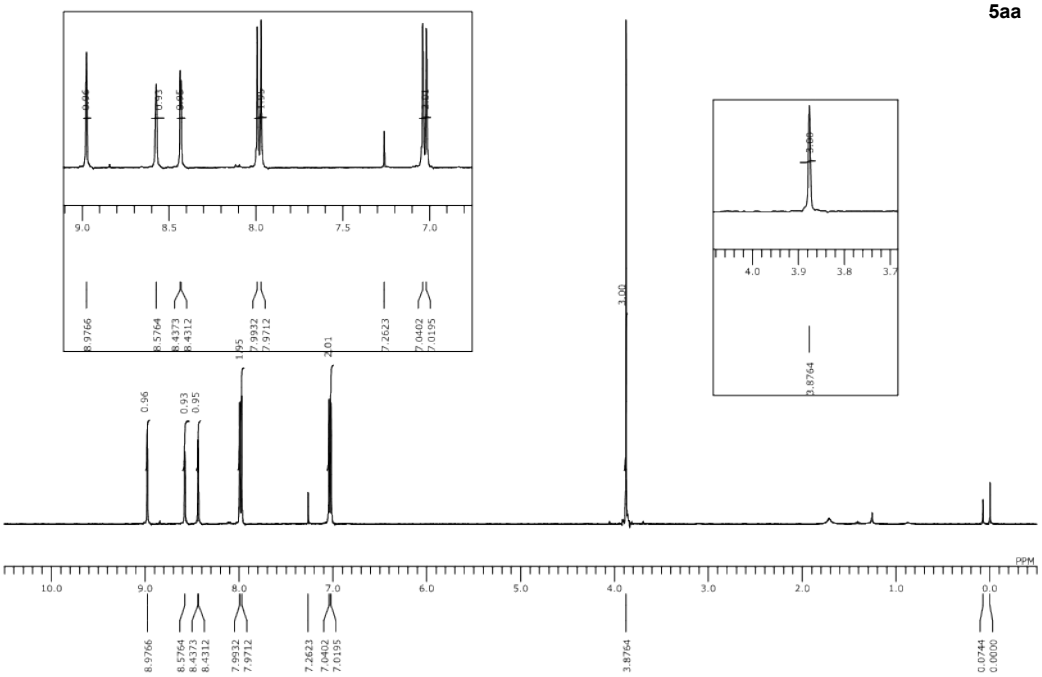
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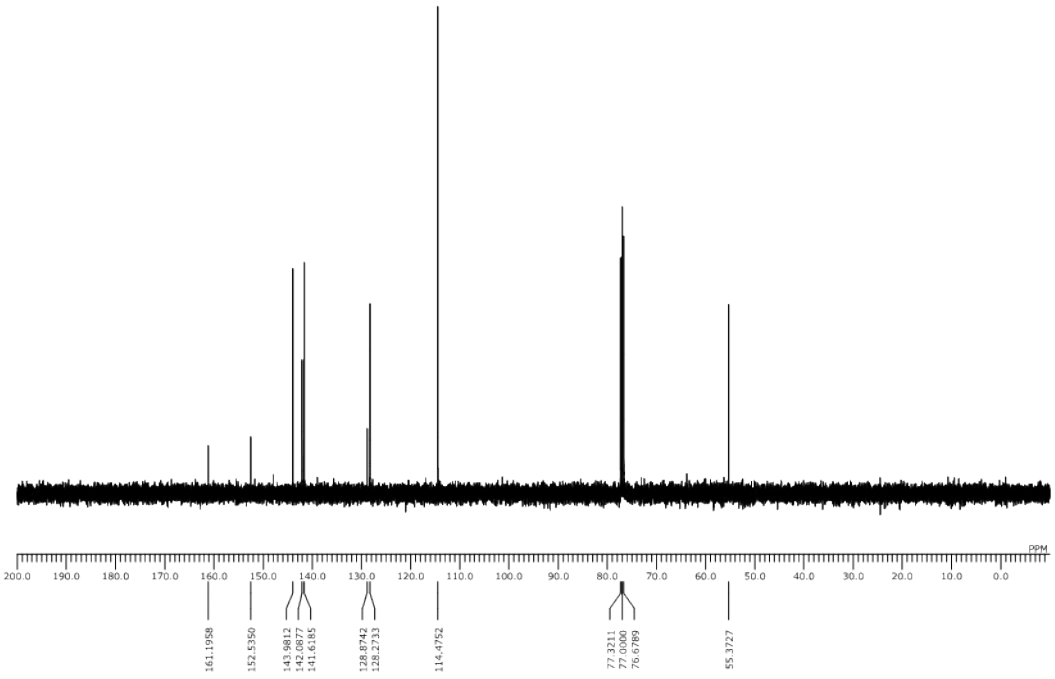
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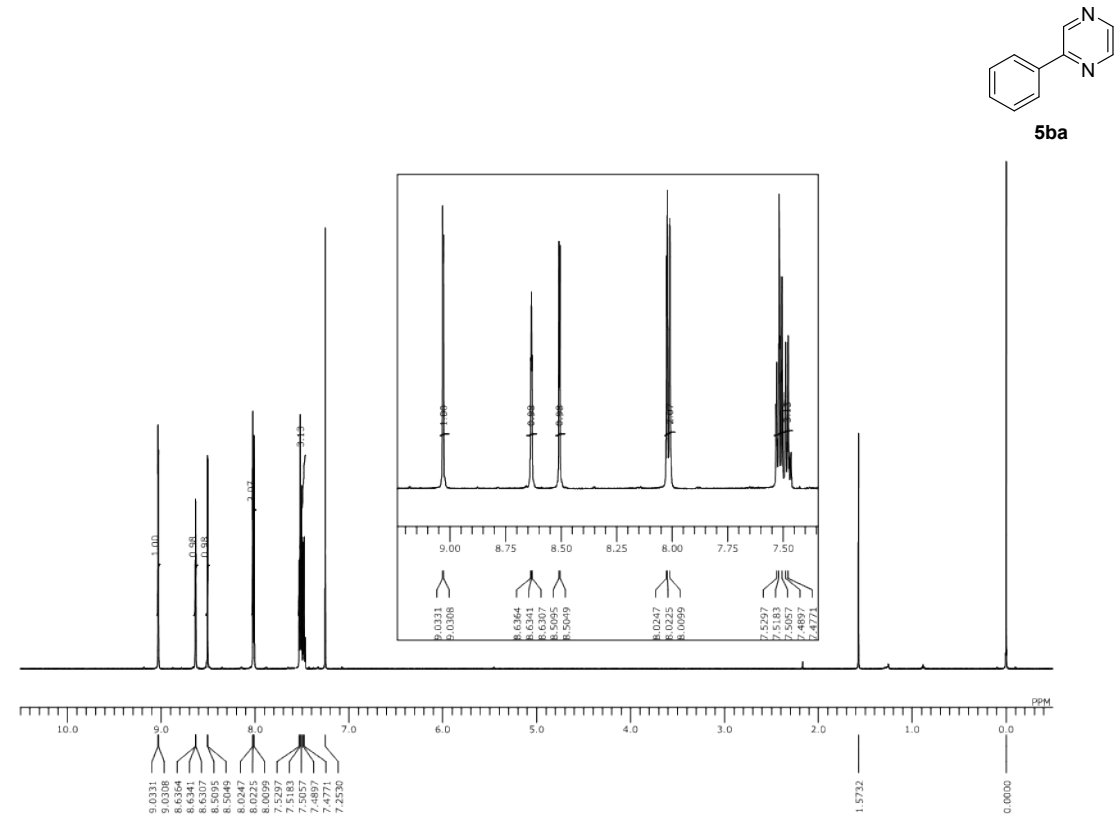

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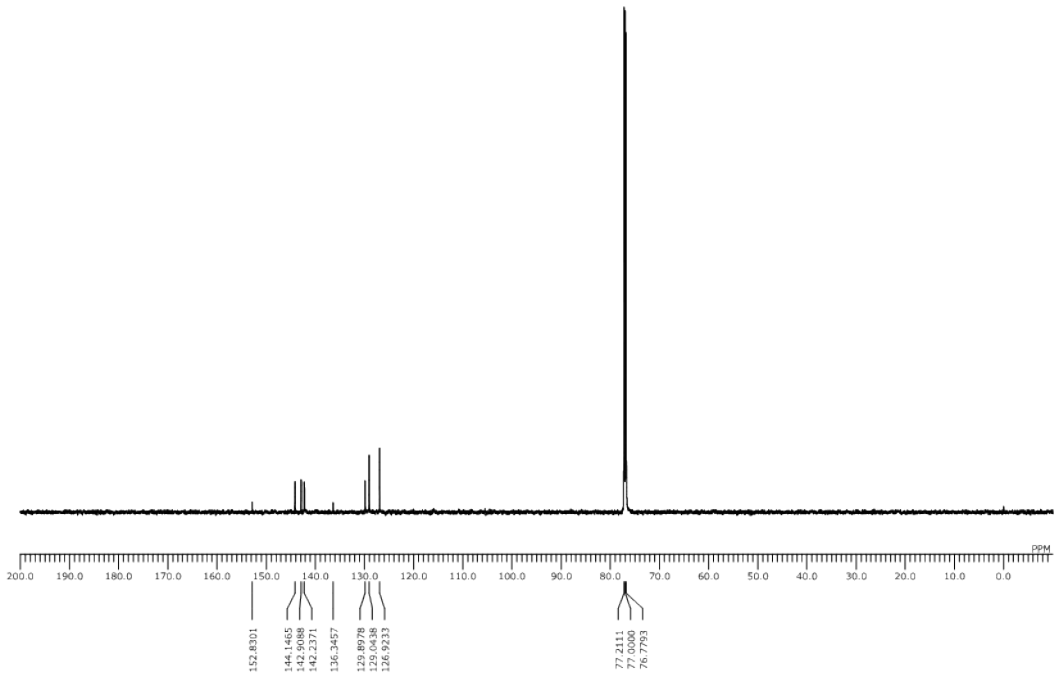

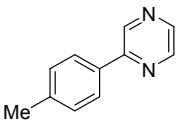
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N
Me

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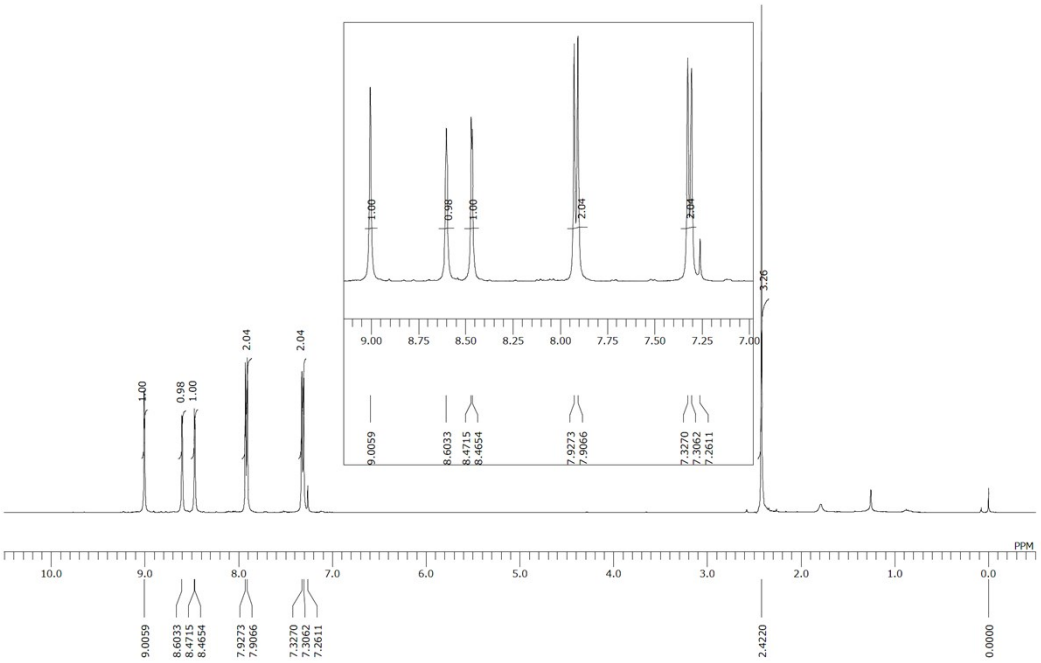
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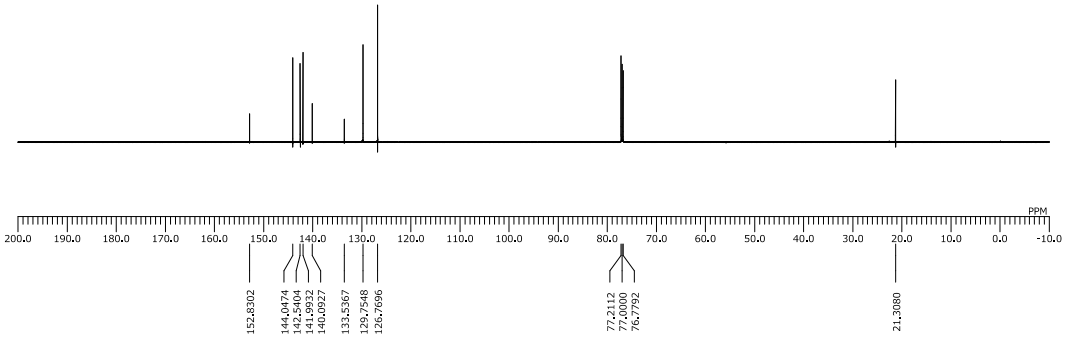
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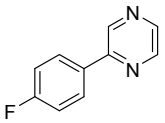
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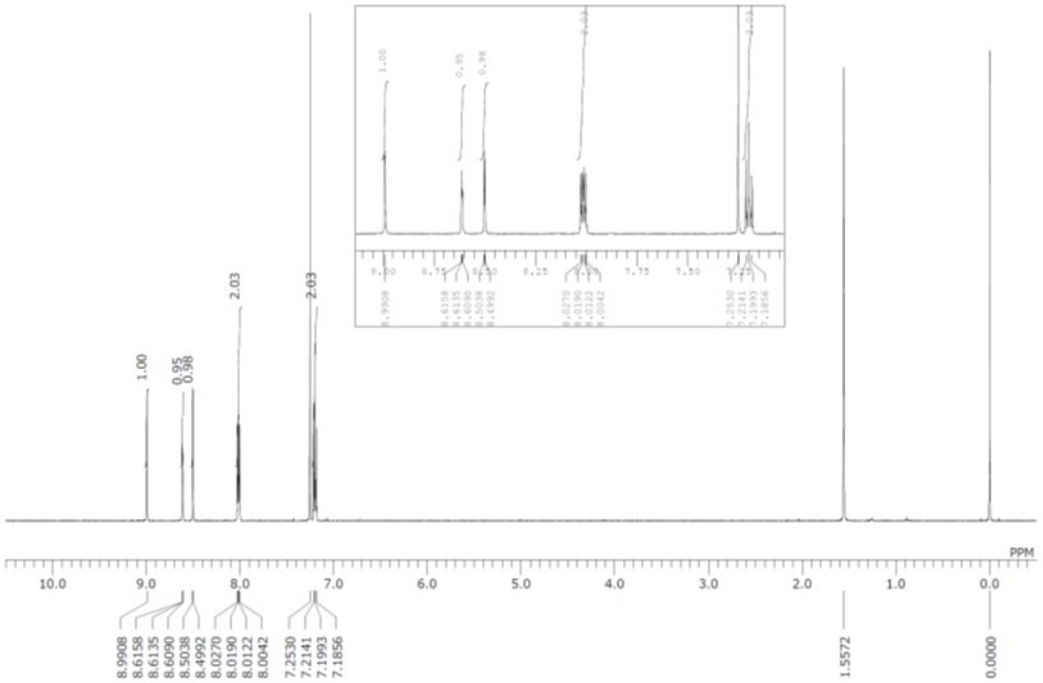
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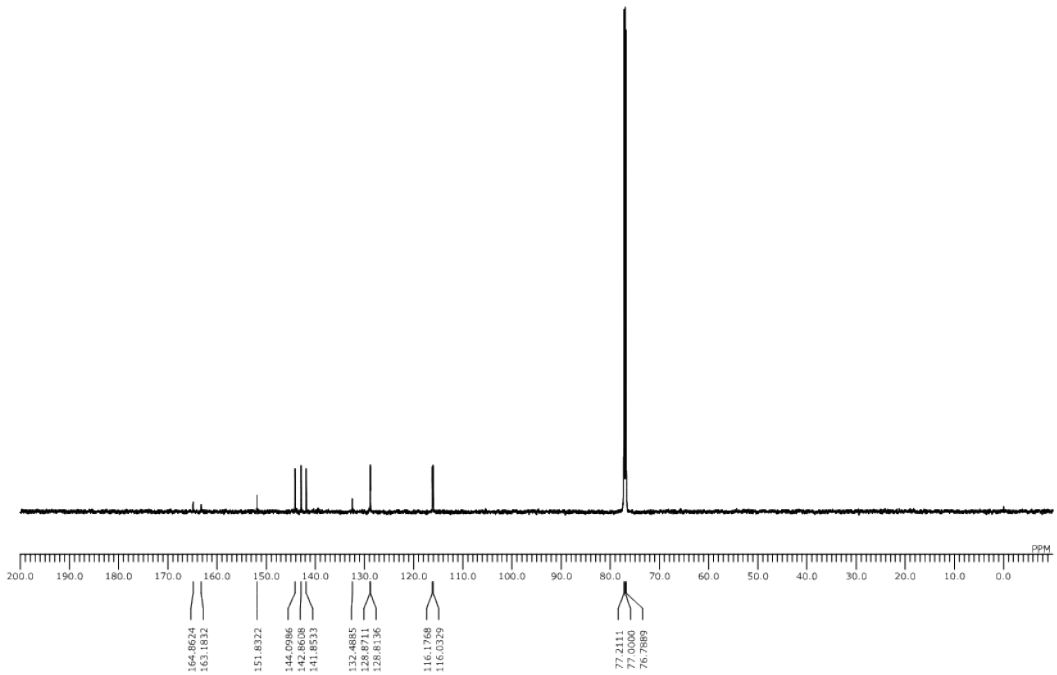
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30.0
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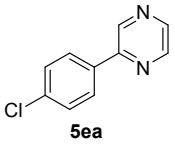
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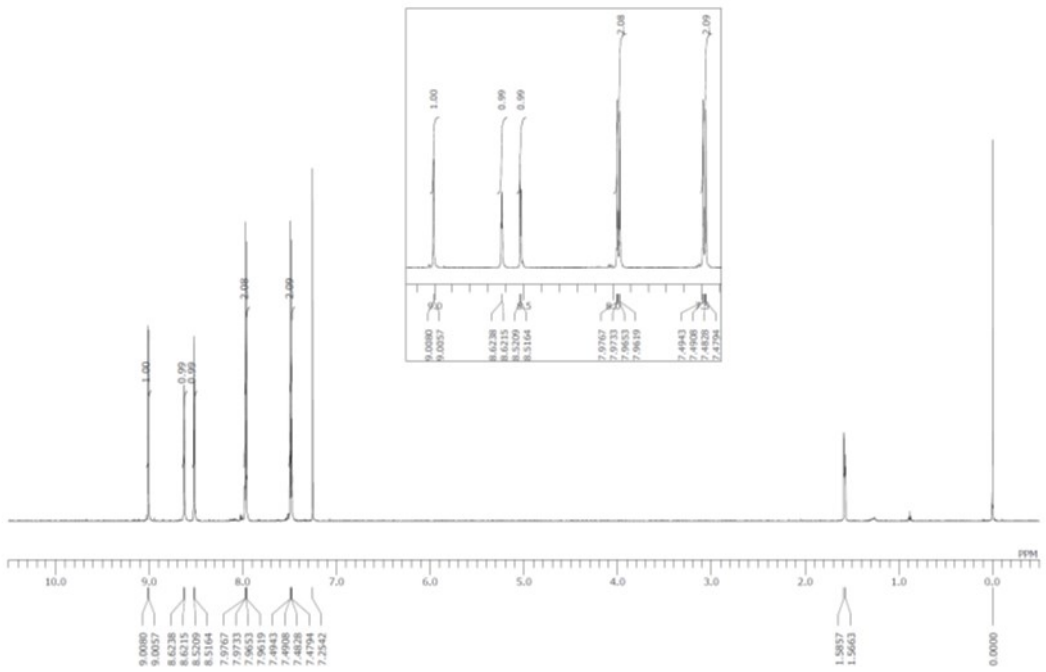
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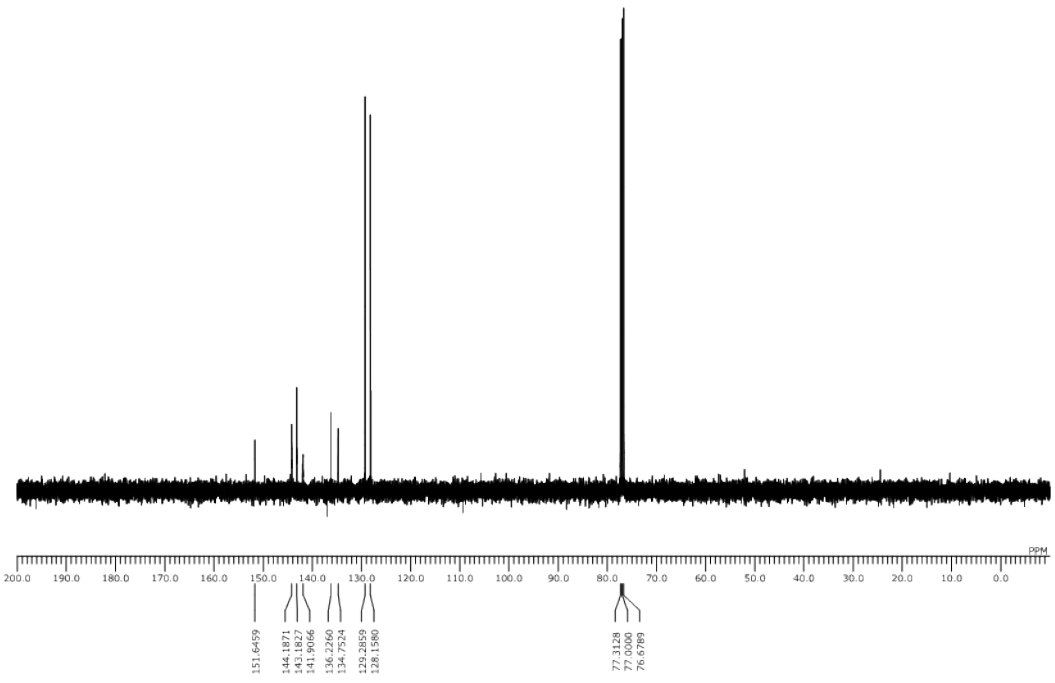
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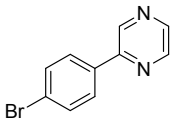
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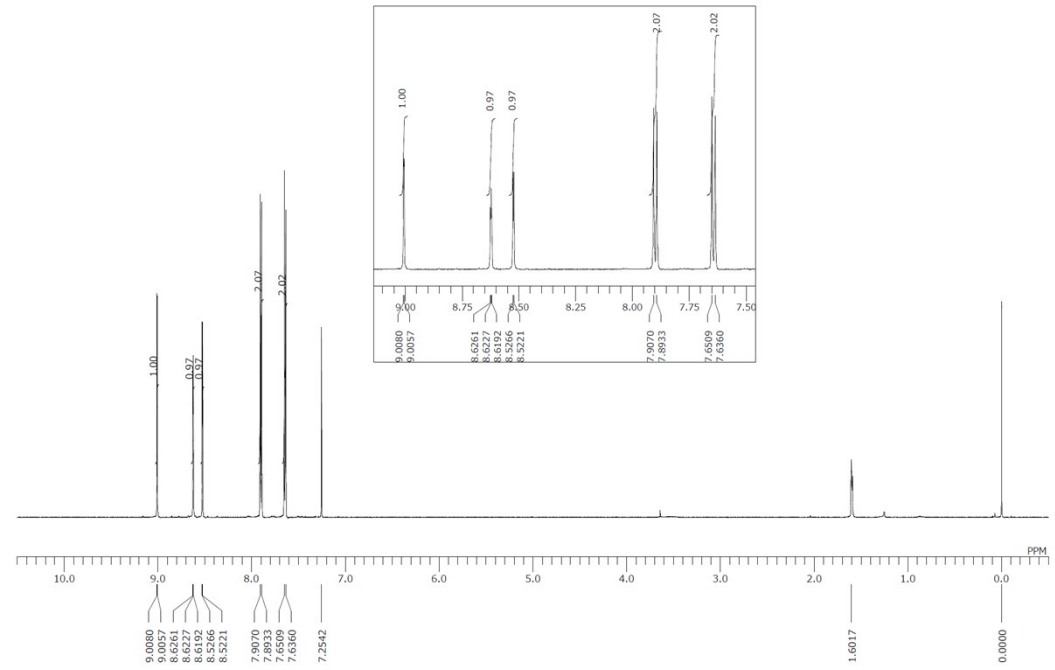
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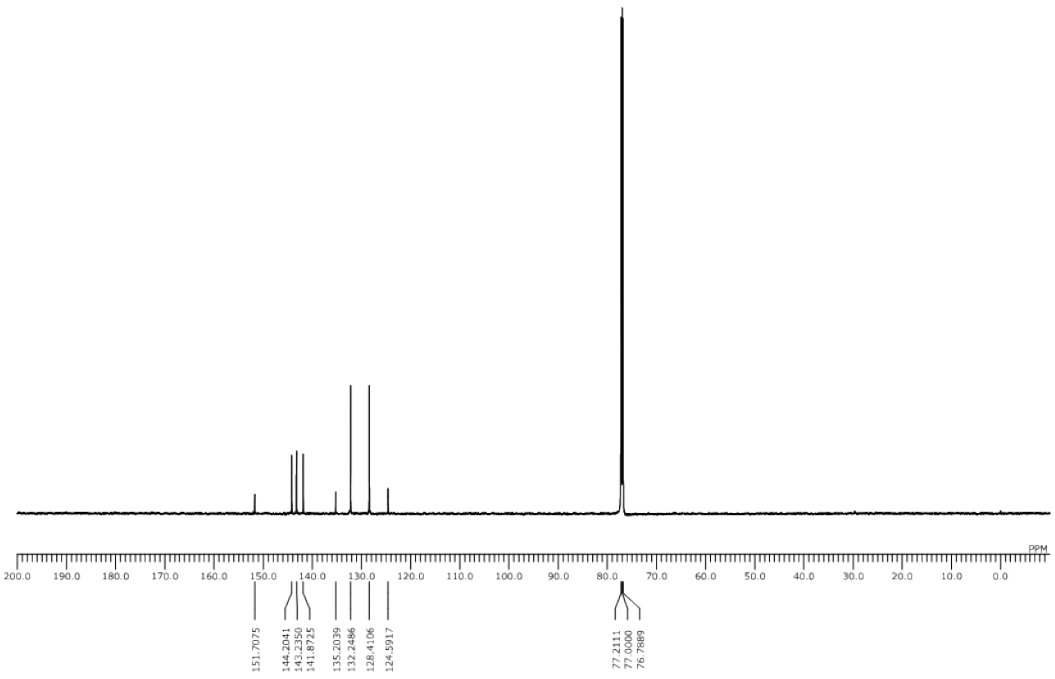
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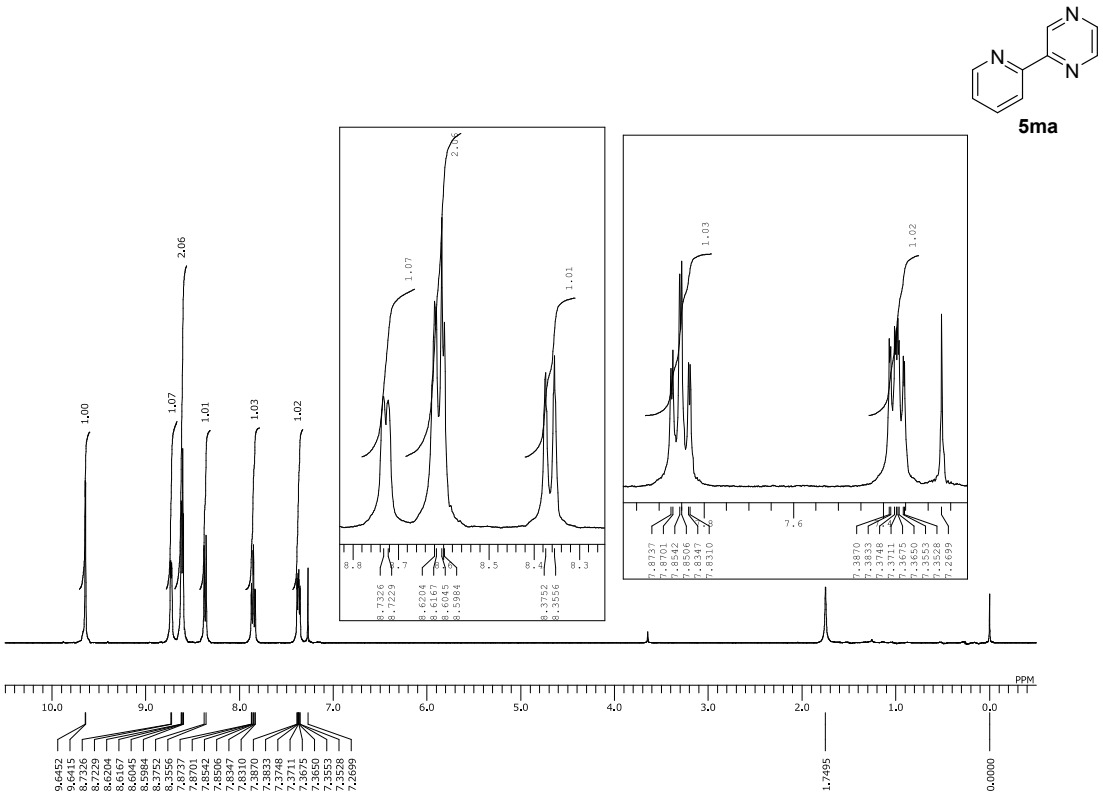
PPM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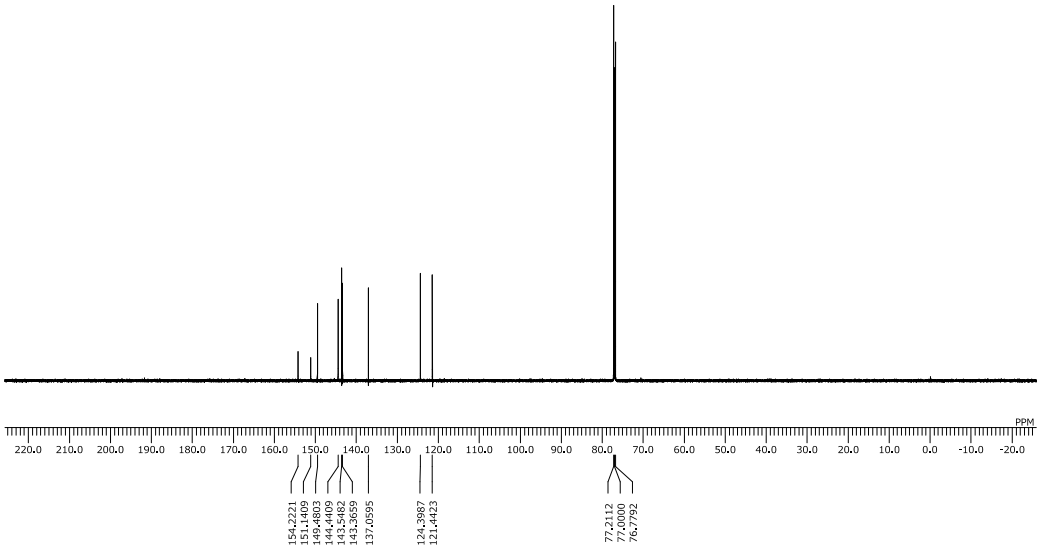
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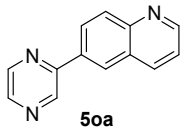

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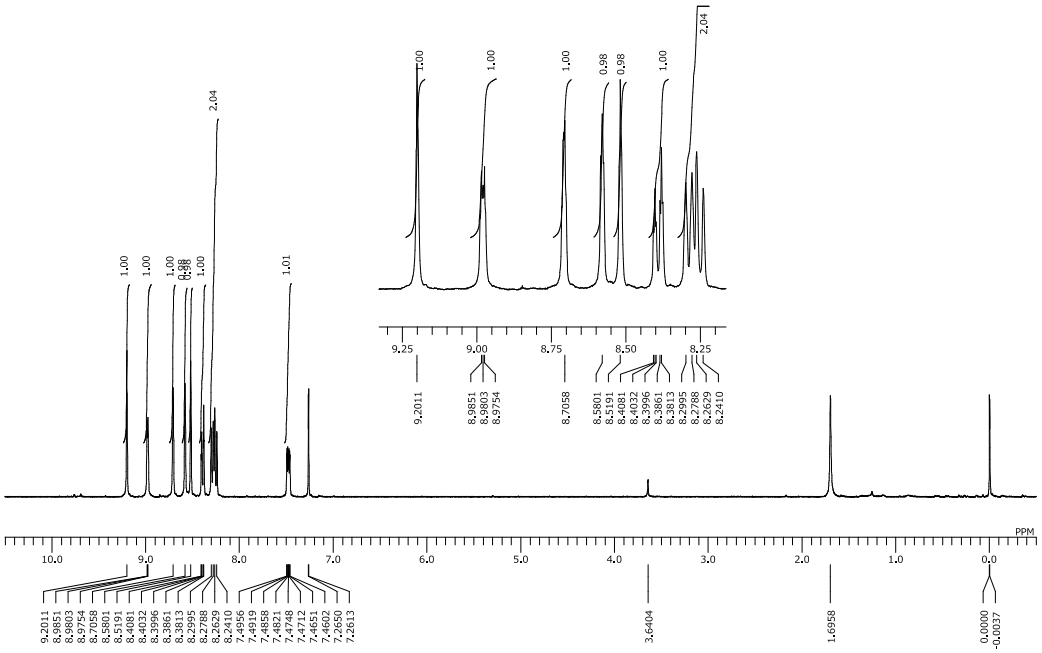

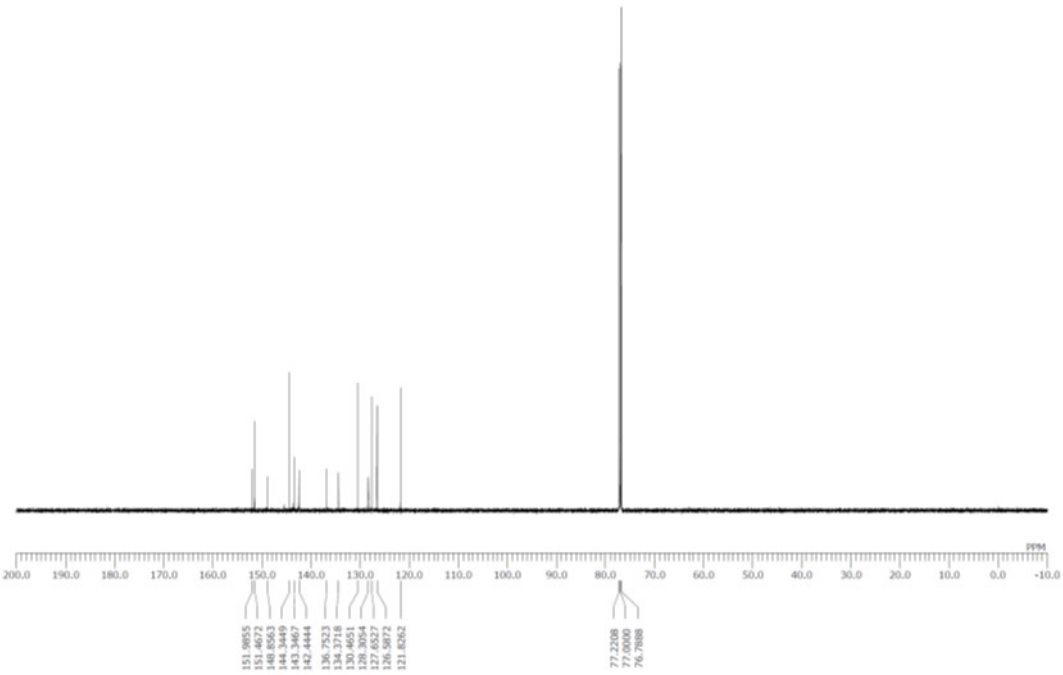

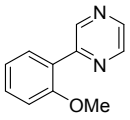
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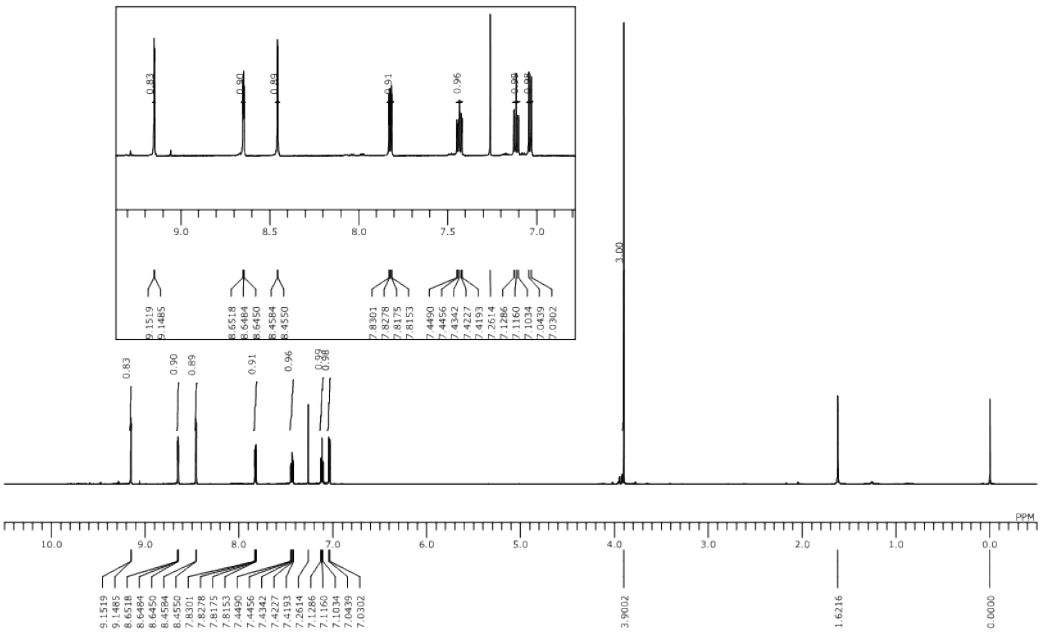
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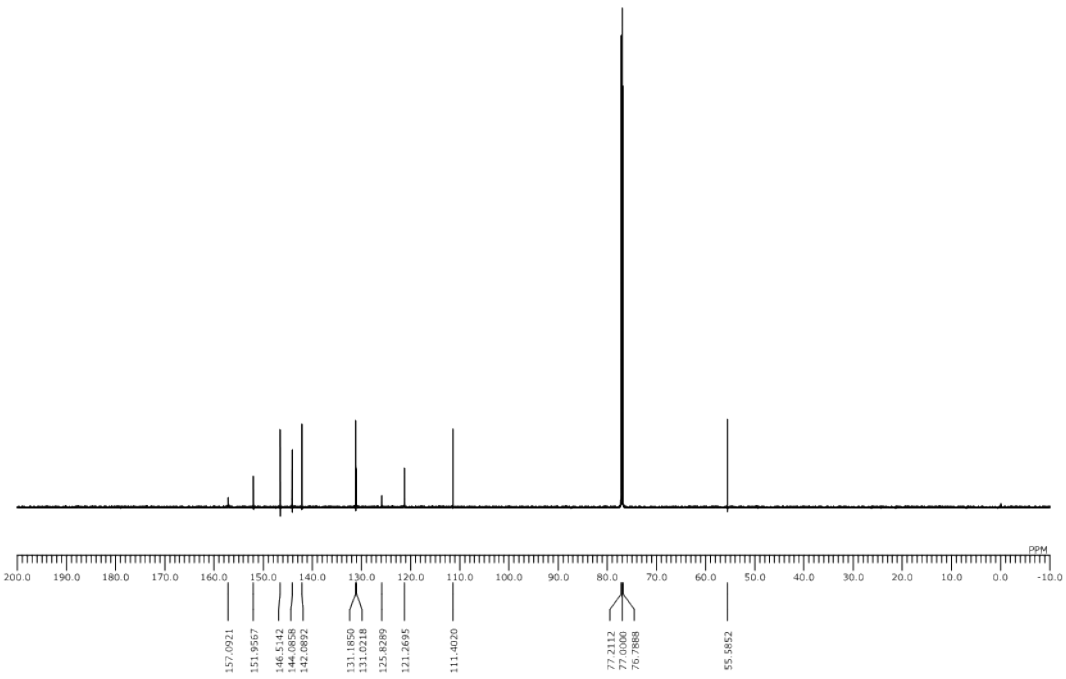
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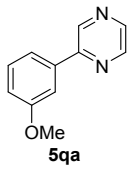
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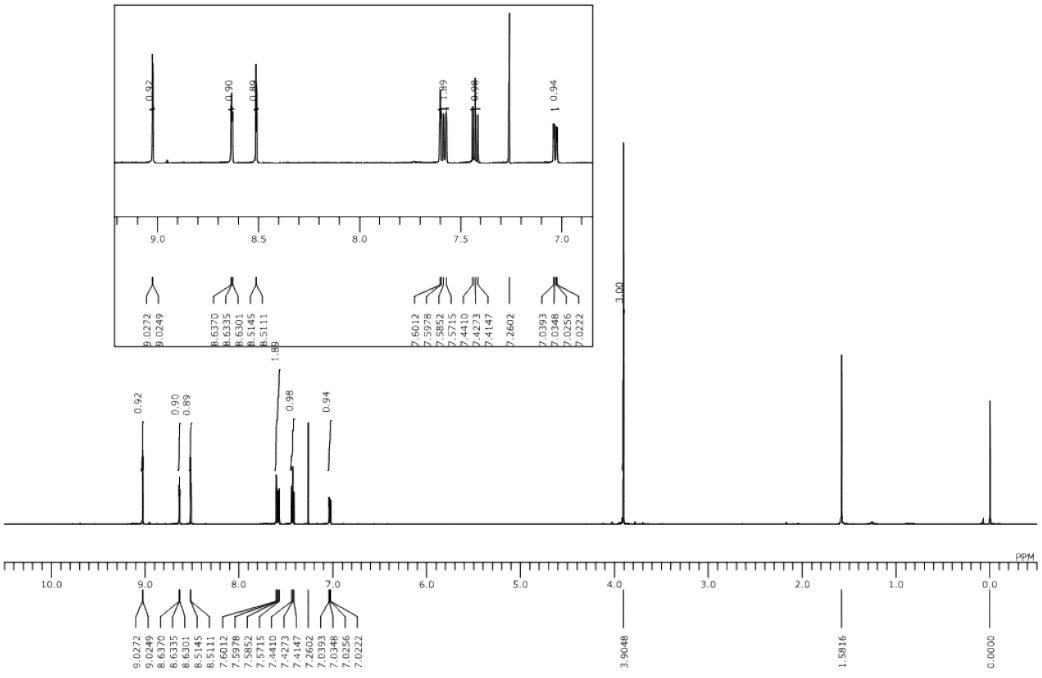
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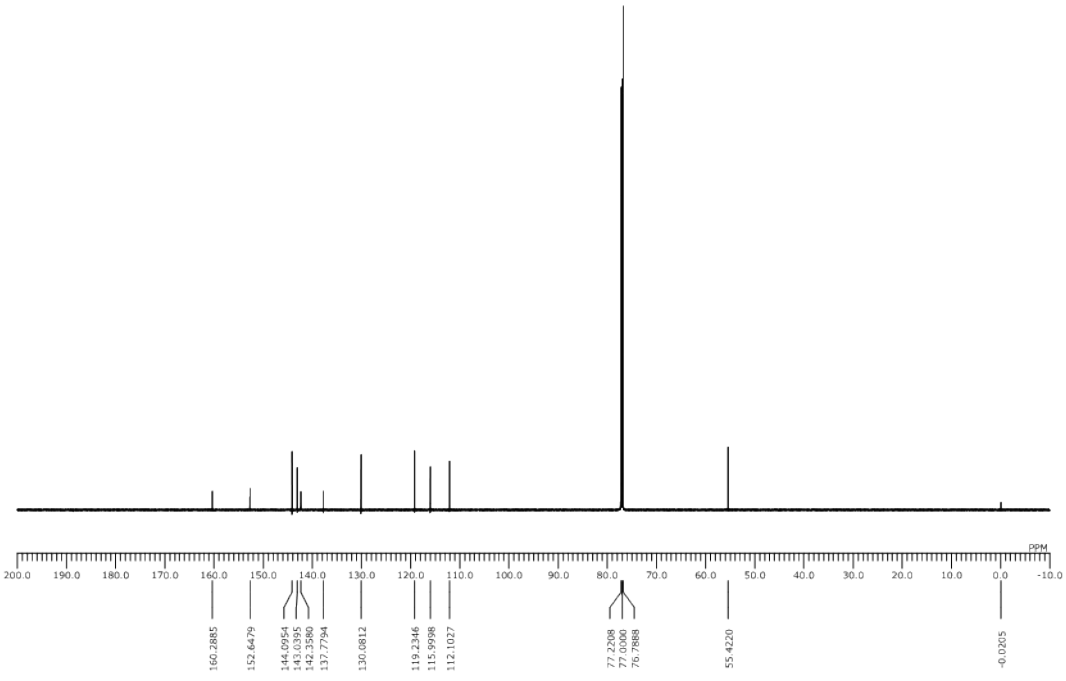
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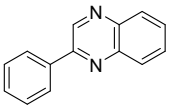

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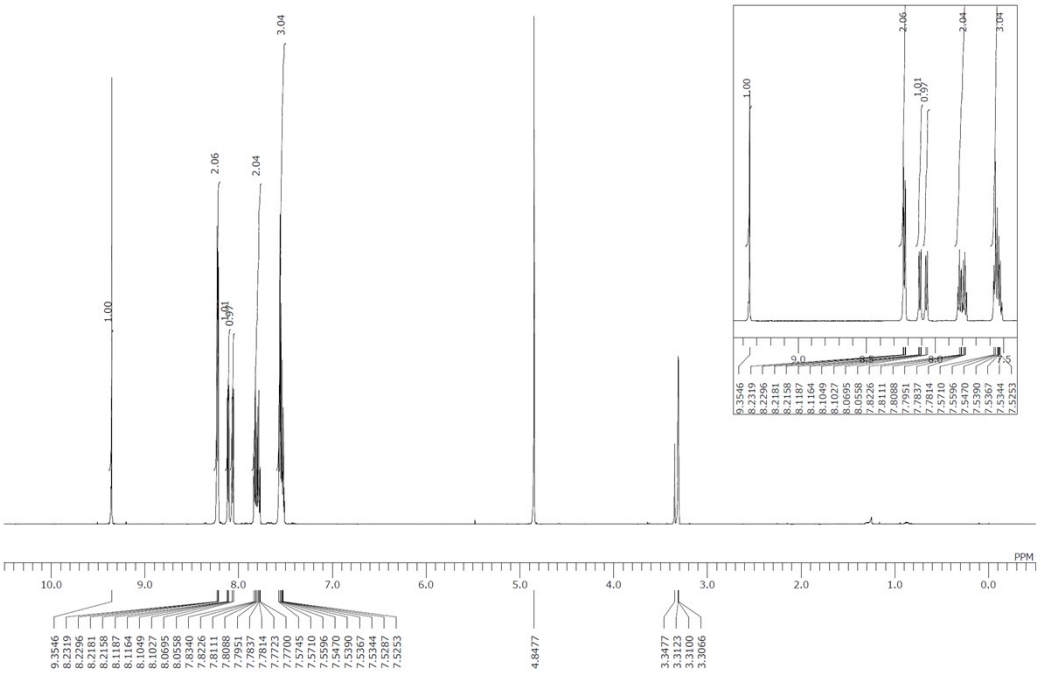
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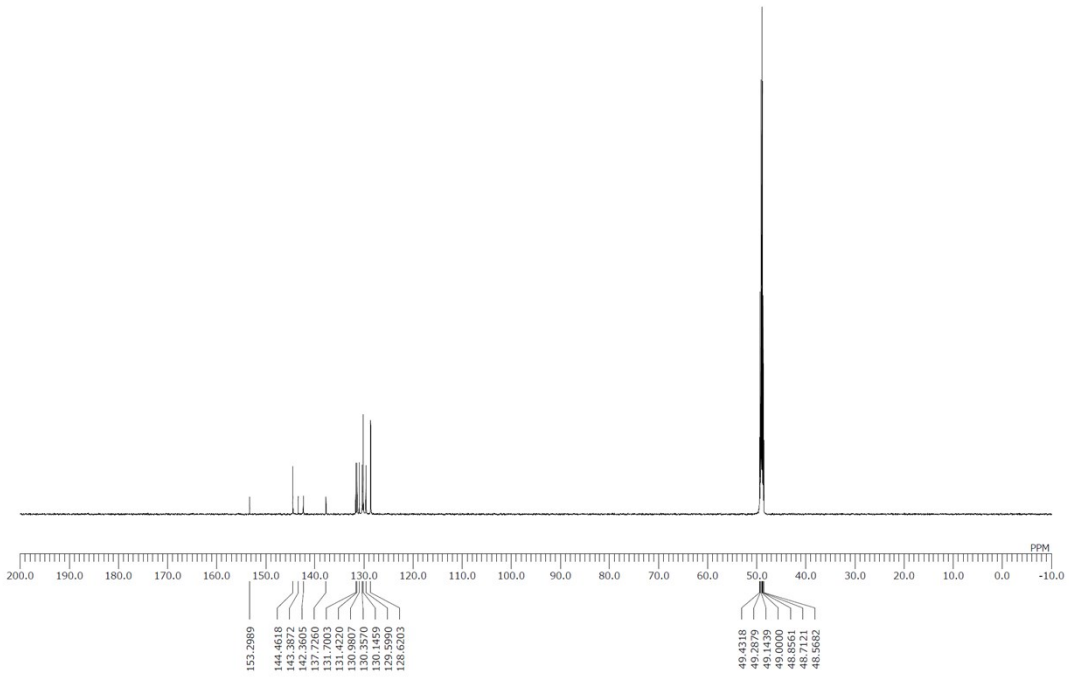
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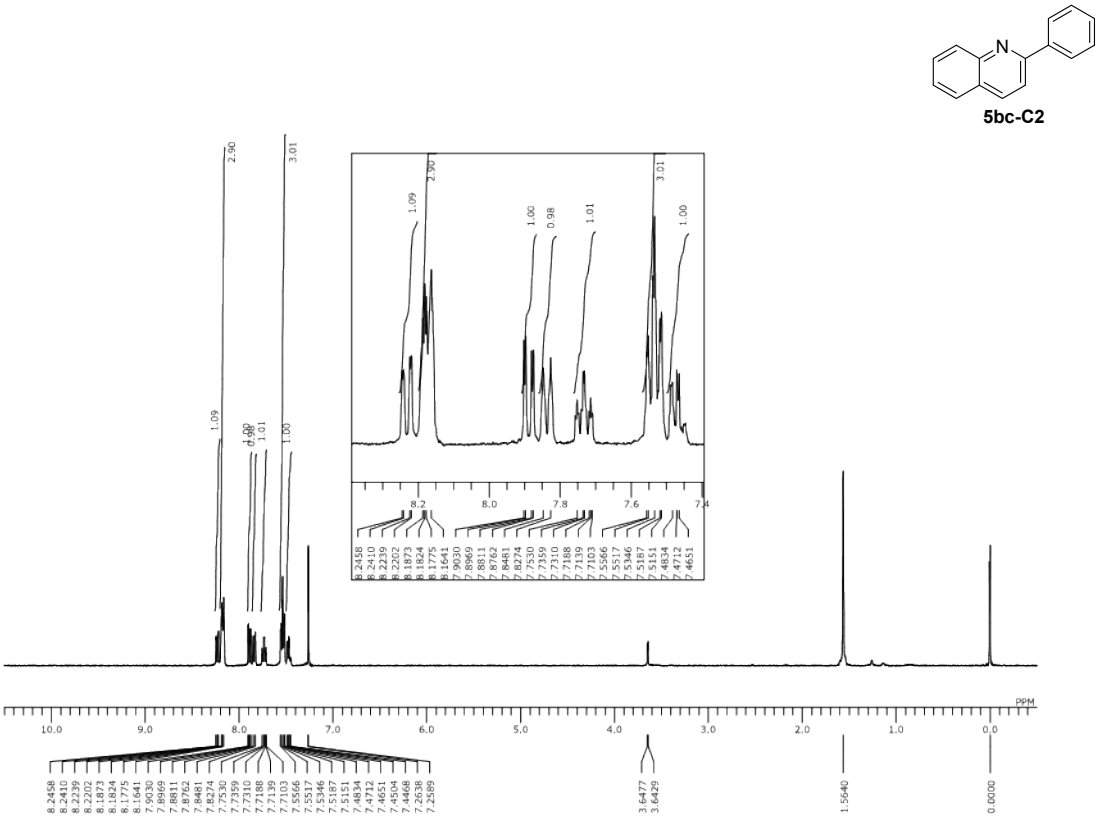
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1.00
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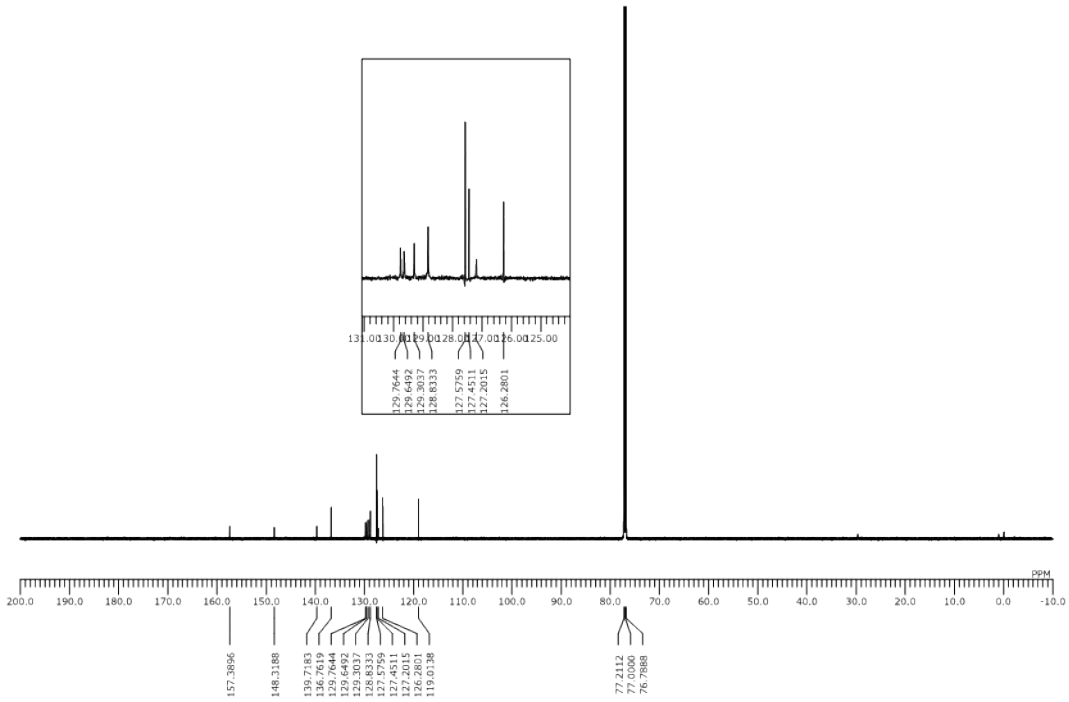
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126.2801
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
157.3896
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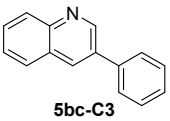

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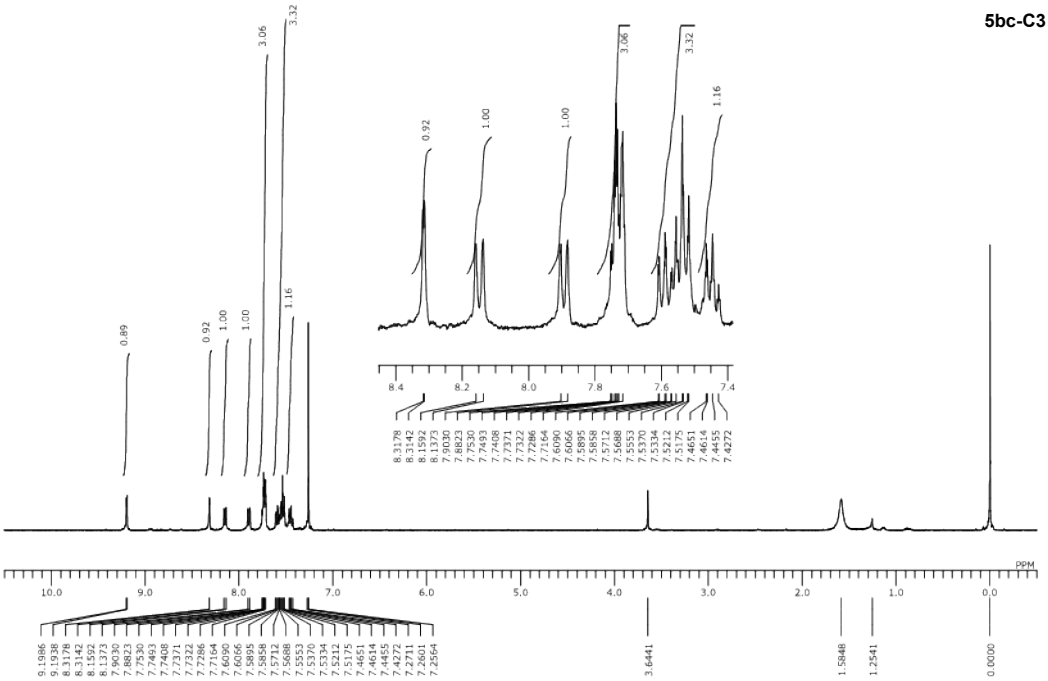

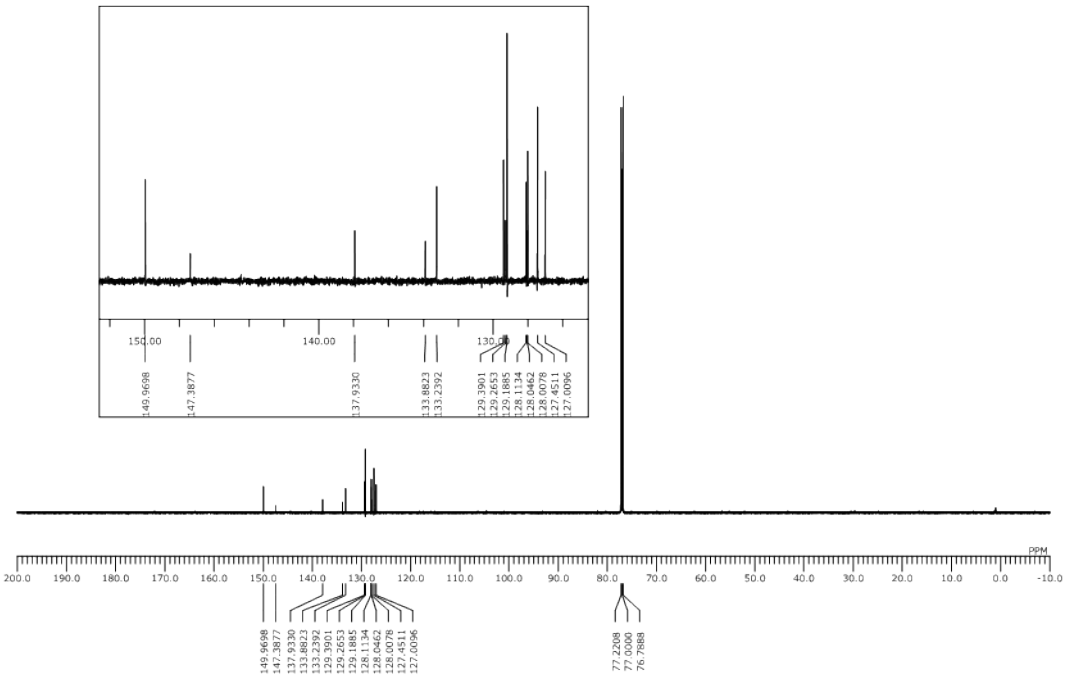

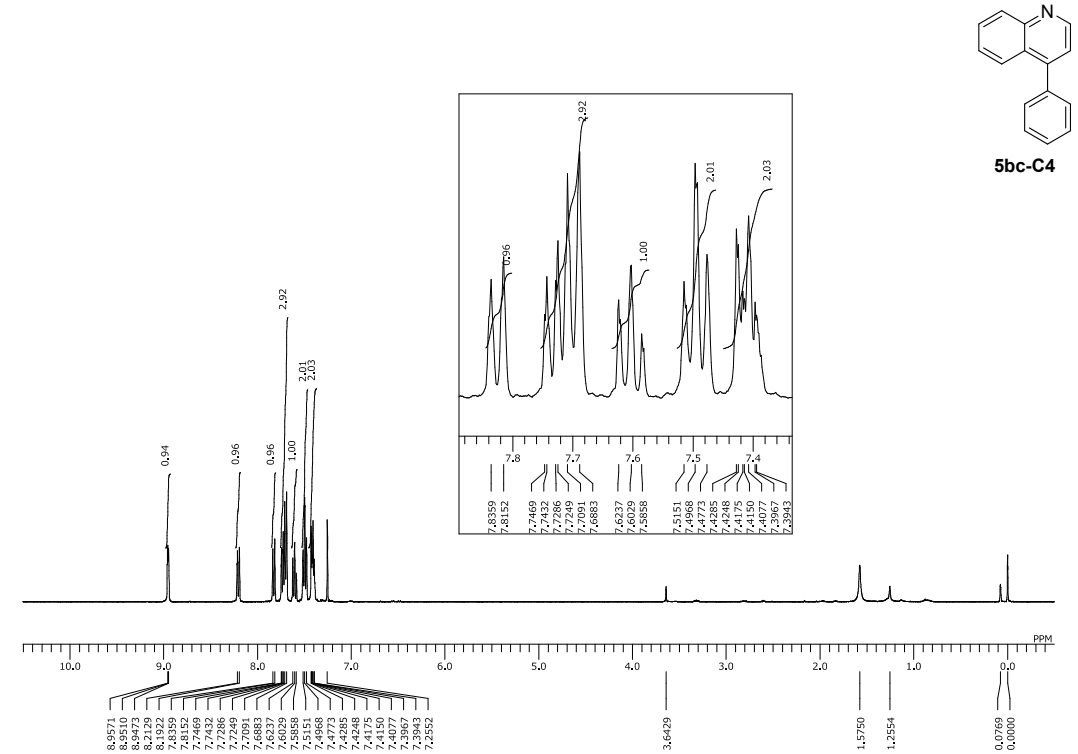
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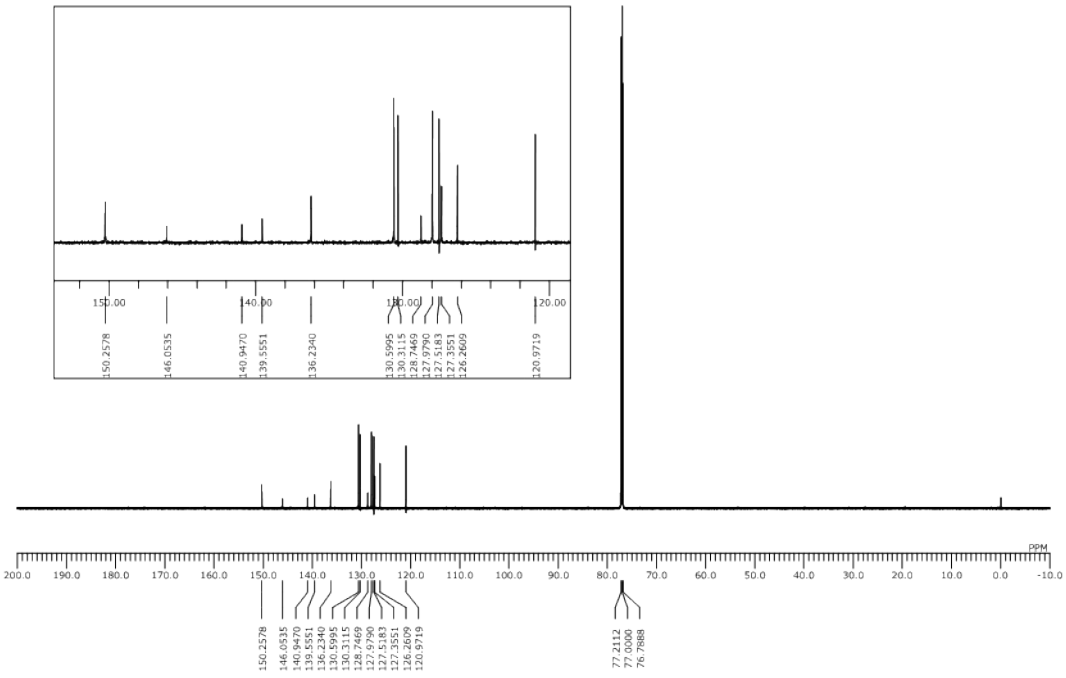

8. References

(1) L.-G. Xie and D. J. Dixon, *Chem. Sci.*, 2017, **8**, 7492.

(2) T. Torigoe, T. Ohmura and M. Suginome, *Angew. Chem., Int. Ed.*, 2017, **56**, 14272.