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Supporting Information

Synthesis of (NHC)Pd(salicylaldimine)Cl complexes through template-directed *ortho*-aromatic metaloxylation of NHC-palladacycles derived from arylimines

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Table S1. Selected ^{1}H, and ^{13}C NMR spectral data for complexes 1a–1d and 2a–2d

Complex	^{1}H NMR[a]	^{13}C NMR[a]	^{13}C NMR[a]	^{13}C NMR[a]
	δ C*H*=N	δ *C*H=N	δ Pd–$C_{carbene}$	δ Pd–C_{phenyl}
1a	7.73	175.8	158.7	175.9
1b	7.78	175.2	159.3	175.8
1c	7.70	176.1	159.8	178.0
1d	7.75	175.7	160.2	177.7
2a	7.44	163.0	160.3	--
2b	7.51	162.6	160.5	--
2c	7.52	163.0	162.8	--
2d	7.50	163.0	162.5	--

[a] ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 298 K (δ in ppm)

Table S2. Selected bond lengths [Å] and angles [deg] for complexes 1a−1d and 2a−2d

	1a	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**
Pd–$C_{carbene}$	1.993(3)	1.981(4)	1.986(3)	1.9773(19)	1.977(2)	1.979(3)	1.999(2) 1.995(2)	2.007(6)
Pd–Cl	2.4016(11)	2.3818(15)	2.3600(10)	2.3625(7)	2.2801(6)	2.2545(10)	2.2982(8) 2.3011(9)	2.2946(19)
Pd–N	2.095(2)	2.089(4)	2.089(2)	2.0980(17)	2.0521(17)	2.054(2)	2.061(2) 2.061(2)	2.102(5)
Pd–C_{phenyl}	2.014(3)	1.992(4)	1.988(3)	2.015(2)				
Pd–O					2.0084(15)	1.996(2)	2.0217(17), 2.024(2)	2.043(4)
$C_{carbene}$–Pd–Cl	90.75(8)	92.25(13)	91.42(8)	93.53(6)	85.80(6)	89.40(9)	88.43(7) 85.78(7)	85.10(14)
N–Pd–Cl	93.04(7)	91.44(10)	92.52(7)	92.75(5)	92.60(5)	92.26(7)	91.44(6) 91.28(7)	92.70(13)
$C_{carbene}$–Pd–C_{phenyl}	95.30(11)	95.21(17)	94.78(11)	92.86(8)				
$C_{(phenyl)}$–Pd–N	80.93(10)	81.11(16)	81.22(11)	80.87(8)				
C–Pd–O					90.40(7)	86.52(10)	87.95(8) 91.66(9)	92.18(18)
O–Pd–N					91.32(7)	91.87(9)	92.17(8) 91.38(8)	90.04(17)
PdC_2NCl/carbene dihedral angle	68.05	72.04	67.45	77.88				
PdCONCl/carbene dihedral angle					72.35	81.50	76.41 86.63	78.74

Table S3 Crystallographic data for complexes **1a**−**1d** and **2a**−**2d**

Compound	**1a**	**1b**	**1c**	**1d**
formula	$C_{37}H_{40}ClN_3Pd$	$C_{40}H_{46}ClN_3Pd$	$C_{43}H_{52}ClN_3Pd$	$C_{46}H_{58}ClN_3Pd$
fw	668.57	710.65	752.73	794.80
crystal system	Monoclinic	Monoclinic	Trigonal	Monoclinic
space group	*P*2(1)*/n*	*P*2(1)*/c*	*R-3*	*P*2(1)*/n*
a /Å	10.524(5)	16.381(10)	43.759(13)	13.430(2)
b /Å	17.000(9)	14.070(9)	43.759(13)	15.494(3)
c /Å	20.028(10)	17.588(11)	10.790(3)	21.236(3)
□ α /deg	90.00	90.00	90.00	90.00
□ β /deg	103.973(7)	93.854(11)	90.00	106.812(2)
□ γ /deg	90.00	90.00	120.00	90.00
V /Å^3	3477(3)	4045(5)	17893(9)	4230.1(12)
Z	4	4	18	4
D_{calc}/g cm^{-3}	1.277	1.167	1.257	1.248
F(000)	1384	1480	7092	1672
μ /mm^{-1}	0.638	0.552	0.566	0.535
GOF	1.023	1.005	1.084	1.034
reflections collected	17378	17439	30254	21212
independent reflections (R_{int})	6113 (0.0342)	6878 (0.0472)	6988 (0.0347)	7432 (0.0208)
observed reflections [$I > 2\sigma(I)$]	5023	5367	5689	6207
refined parameters	388	416	444	472
$R1$ [$I > 2\sigma(I)$]	0.0308	0.0539	0.0316	0.0261
$wR2$ (all data)	0.0786	0.1755	0.0988	0.0699

Compound	**2a**	**2b**	**2c**	**2d**
formula	$C_{37}H_{40}ClN_3OPd$	$C_{40}H_{46}ClN_3OPd$	$C_{43}H_{52}ClN_3OPd$	$C_{46}H_{58}ClN_3OPd$
fw	684.57	726.65	768.73	810.80
crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
space group	*P-1*	*Pbca*	*P*2(1)*/c*	*P*-1
a /Å	8.7837(11)	18.812(2)	25.435(6)	11.632(7)
b /Å	10.6465(13)	20.016(3)	15.222(3)	12.701(7)
c /Å	18.771(2)	20.045(3)	21.271(5)	16.240(10)
□α /deg	89.854(2)	90.00	90.00	84.326(11)
□β /deg	86.654(2)	90.00	90.092(4)	69.130(9)
□γ /deg	73.432(2)	90.00	90.00	81.438(10)
V /Å^3	1679.5(4)	7547.5(17)	8235(3)	2214(2)
Z	2	8	8	2
D_{calc}/g cm^{-3}	1.354	1.279	1.240	1.216
F(000)	708	3024	3216	852
μ /mm^{-1}	0.664	0.595	0.549	0.514
GOF	1.036	1.032	1.015	1.026
reflections collected	8604	36800	41278	10993
independent reflections (R_{int})	5856 (0.0136)	6642 (0.0639)	14473 (0.0261)	7670 (0.0442)
observed reflections [$I > 2\sigma(I)$]	5433	5133	11431	4910
refined parameters	397	425	905	481
$R1$ [$I > 2\sigma(I)$]	0.0255	0.0339	0.0302	0.0672
$wR2$ (all data)	0.0702	0.0975	0.0836	0.1821

Characterization data for the products for 1a−1d and 2a−2d

Complex 1a: Yield: 120 mg (90%), pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (s, 1H), 7.21–7.17 (m, 3H), 7.00–6.97 (m, 4H), 6.86 (s, 3H), 6.76 (s, 2H), 2.41 (s, 6H), 2.30 (s, 12H), 2.20 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.9, 175.8, 158.7, 146.8, 145.1, 138.5, 138.3, 137.5, 135.8, 134.7, 133.5, 130.0, 129.6, 129.3, 128.4, 127.9, 127.6, 123.3, 123.1, 20.9, 20.8, 20.1, 19.6, 18.2. IR (KBr, cm^{-1}): 3131, 2964, 2916, 1611, 1602, 1483, 1438, 1401, 1377, 1287, 1269, 1258, 1198, 1147, 1041, 899. HRMS: calcd for $C_{37}H_{40}N_3Pd$ [M–Cl$^-$]$^+$ 632.2257; found 632.2262. Anal. Calc. for $C_{37}H_{40}ClN_3Pd$: C, 66.47; H, 6.03; N, 6.28%. Found: C, 66.70; H, 6.27; N, 6.18%.

Complex 1b: Yield: 125 mg (88%), pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1H), 7.17 (s, 2H), 7.13–7.09 (m, 1H), 7.05–6.99 (m, 4H), 6.94 (s, 2H), 6.91–6.90 (m, 1H), 6.87 (s, 2H), 3.02 (sept, J = 6.8 Hz, 2H), 2.44 (s, 6H), 2.34 (s, 6H), 2.30 (s, 3H), 1.10 (d, J = 6.8 Hz, 6H), 1.05 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 175.2, 159.3, 146.7, 144.9, 140.5, 138.5, 138.1, 137.5, 135.8, 133.5, 129.4, 128.4, 127.6, 126.2, 123.2, 123.0, 122.3, 28.1, 24.0, 22.5, 20.9, 20.3, 19.6. IR (KBr, cm^{-1}): 3118, 3067, 2965, 2927, 2866, 1614, 1578, 1479, 1465, 1444, 1432, 1407, 1383, 1363, 1331, 1307, 1269, 1207, 1182, 1119, 1068, 1021, 911. HRMS: calcd for $C_{40}H_{46}N_3Pd$ [M–Cl$^-$]$^+$ 674.2727; found 674.2734. Anal. Calc. for $C_{40}H_{46}ClN_3Pd$: C, 67.60; H, 6.52; N, 5.91%. Found: C, 67.43; H, 6.74; N, 6.07%.

Complex 1c: Yield: 128 mg (85%), pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.30–7.27 (m, 4H), 7.21–7.16 (m, 3H), 7.02–6.96 (m, 2H), 6.78 (d, J = 7.2 Hz, 1H), 6.71 (s, 2H), 3.37 (sept, J = 6.8 Hz, 2H), 3.21 (sept, J = 6.8 Hz, 2H), 2.18 (s, 3H), 1.90 (s, 6H), 1.37 (d, J = 6.4 Hz, 6H), 1.19 (d, J = 6.8 Hz, 6H), 0.98 (d, J = 6.8 Hz, 6H), 0.89 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.0, 176.1, 159.8, 147.7, 147.1, 145.2, 144.7, 136.6, 135.8, 134.6, 130.7, 130.0, 129.6, 127.9, 127.5, 124.6, 124.1, 123.6, 122.8, 28.9, 28.4, 26.2, 26.2, 22.9, 22.7, 20.9, 18.3. IR (KBr, cm^{-1}): 3178, 3141, 3065, 2967, 2927, 2866, 1614, 1590, 1556, 1462, 1440, 1397, 1382, 1362, 1327, 1289, 1230, 1199, 1145, 1117, 1057, 937. HRMS: calcd for $C_{43}H_{52}N_3Pd$ [M–Cl$^-$]$^+$ 716.3196; found 716.3199. Anal. Calc. for $C_{43}H_{52}ClN_3Pd$: C, 68.61; H, 6.96; N, 5.58%. Found: C, 68.34; H, 6.81; N, 5.79%.

Complex 1d: Yield: 137 mg (86%), pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.30–7.21 (m, 7H), 7.10–7.08 (t, J = 7.6 Hz, 1H), 7.04–6.99 (m, 4H), 6.89 (d, J = 6.8 Hz, 1H), 3.34 (sept, J = 6.8 Hz, 4H), 2.94 (sept, J = 6.8 Hz, 2H), 1.35 (d, J = 6.4, 6H), 1.21 (d, J = 6.8, 6H), 0.99–0.92 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 175.7, 160.2, 147.9, 147.0, 145.0, 144.8, 140.7, 136.8, 135.8,

130.8, 129.6, 127.7, 126.3, 124.6, 124.1, 123.5, 122.8, 122.2, 28.8, 28.5, 27.9, 26.3, 26.2, 24.1, 22.9, 22.5, 22.4. IR (KBr, cm^{-1}): 3062, 2953, 2862, 1610, 1554, 1459, 1440, 1397, 1384, 1360, 1334, 1269, 1255, 1223, 1199, 1181, 1059, 935. HRMS: calcd for $C_{46}H_{58}N_3Pd$ $[M–Cl^–]^+$ 758.6666; found 758.6674. Anal. Calc. for $C_{46}H_{58}ClN_3Pd$: C, 72.75; H, 7.70; N, 5.53%. Found: C, 72.49; H, 7.87; N, 5.77%.

Complex 2a: Yield: 90 mg (88%), yellow powder. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 1H), 7.30–7.27 (m, 1H), 7.11 (s, 2H), 7.03–7.01 (m, 5H), 6.79–6.76 (m, 3H), 6.52 (t, J = 7.2 Hz, 1H), 2.38 (s, 12H), 2.28 (s, 6H), 2.23 (s, 3H), 1.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 163.0, 160.3, 147.8, 138.7, 136.5, 136.2, 135.3, 135.1, 134.3, 134.3, 130.4, 129.0, 128.7, 127.9, 123.1, 120.6, 119.5, 113.6, 21.0, 20.9, 18.7, 18.3, 17.8. IR (KBr, cm^{-1}): 3436, 3160, 2918, 1616, 1531, 1484, 1463, 1444, 1408, 1378, 1354, 1338, 1279, 1231, 1180, 1142, 1127, 1029, 926. HRMS: calcd for $C_{37}H_{41}ClN_3OPd$ $[M+H^+]^+$ 684.1973; found 684.1936 and calcd for $C_{37}H_{40}N_3OPd$ $[M–Cl^–]^+$ 648.2206; found 648.2218. Anal. Calc. for $C_{37}H_{40}ClN_3OPd$: C, 64.91; H, 5.89; N, 6.14%. Found: C, 65.11; H, 5.78; N, 6.23%.

Complex 2b: Yield: 92 mg (84%), yellow powder. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.30–7.28 (m, 1H), 7.10–7.08 (m, 4H), 7.03–7.01 (m, 6H), 6.80 (d, J = 8.4 Hz, 1H), 6.53 (t, J = 7.2 Hz, 1H), 2.91 (sept, J = 6.8 Hz, 2H), 2.38–2.37 (m, 12H), 2.26 (s, 6H), 1.03 (d, J = 6.4 Hz, 6H), 0.97 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 162.6, 160.5, 147.4, 140.8, 138.5, 136.5, 136.2, 135.3, 135.2, 134.3, 128.9, 128.7, 125.9, 123.0, 122.3, 120.7, 118.9, 113.5, 28.1, 24.2, 22.4, 21.0, 18.7, 17.8. IR (KBr, cm^{-1}): 3445, 3156, 3128, 2956, 2923, 1609, 1527, 1486, 1464, 1441, 1410, 1384, 1324, 1232, 1171, 1151, 1099, 1031, 929. HRMS: calcd for $C_{40}H_{47}ClN_3OPd$ $[M+H^+]^+$ 726.2442; found 726.2459 and calcd for $C_{40}H_{46}N_3OPd$ $[M–Cl^–]^+$ 690.2676; found 690.2699. Anal. Calc. for $C_{40}H_{46}ClN_3OPd$: C, 66.11; H, 6.38; N, 5.78%. Found: C, 66.42; H, 6.57; N, 5.54%.

Complex 2c: Yield: 95 mg (82%), yellow powder. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (t, J = 7.6 Hz, 2H), 7.37–7.34 (m, 5H), 7.17 (s, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 6.71 (s, 2H), 6.47 (t, J = 7.6 Hz, 1H), 3.40 (br, 2H), 2.94 (br, 2H), 2.21 (s, 3H), 1.85 (s, 6H), 1.26 (d, J = 6.0 Hz, 6H), 1.13 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 163.0, 162.8, 147.8, 135.3, 134.8, 134.2, 133.7, 130.5, 129.7, 127.8, 124.4, 123.8, 123.7, 122.0, 119.4, 113.6, 28.4, 26.2, 23.2, 20.9, 18.3. IR (KBr, cm^{-1}): 3448, 2962, 2926, 2866, 1618, 1534, 1465, 1445, 1411, 1383, 1346, 1324, 1279, 1208, 1181, 1142, 1127, 926. HRMS: calcd for $C_{43}H_{53}ClN_3OPd$ $[M+H^+]^+$ 728.2912; found 728.2928 and calcd for $C_{43}H_{52}N_3OPd$ $[M–Cl^–]^+$ 732.3145; found 732.3163. Anal. Calc. for $C_{43}H_{52}ClN_3OPd$: C, 67.18; H, 6.82; N, 5.47%. Found: C, 67.44; H, 6.54; N, 5.61%.

Complex 2d: Yield: 98 mg (81%), yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.45 (m, 3H), 7.31–7.27 (m, 4H), 7.24–7.22 (m, 1H), 7.15 (s, 2H), 7.09–7.05 (m, 1H), 6.99–6.95 (m, 3H), 6.77 (d, J = 8.8 Hz, 1H), 6.47 (t, J = 7.2 Hz, 1H), 3.54 (br, 2H), 2.89 (sept, J = 6.8 Hz, 2H), 2.76 (br, 2H), 1.20–1.06 (m, 24H), 0.89 (d, J = 7.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 163.0, 162.5, 147.5, 146.5, 140.9, 135.3, 135.0, 133.8, 129.7, 126.0, 124.5, 123.7, 122.3, 122.2, 118.5, 113.6, 28.0, 26.3, 23.9, 22.5. IR (KBr, cm^{-1}): 3445, 2957, 2924, 2864, 1613, 1588, 1529, 1464, 1445, 1409, 1382, 1359, 1345, 1165, 1147, 1127, 1121, 1104, 927. HRMS: calcd for $C_{46}H_{59}ClN_3OPd$ $[M+H^+]^+$ 810.3381; found 810.3390 and calcd for $C_{46}H_{58}N_3OPd$ $[M–Cl^–]^+$ 774.3615; found 774.3626. Anal. Calc. for $C_{46}H_{58}ClN_3OPd$: C, 68.14; H, 7.21; N, 5.18%. Found: C, 68.37; H, 7.45; N, 5.03%.

Characterization data for arylimines and salicylaldimines

***N*-benzylideneaniline**: White solid, mp: 52.1–52.5 °C. ^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 8.50 (s, 1H), 7.96–7.94 (m, 2H), 7.52–7.51 (m, 3H), 7.46–7.42 (m, 2H), 7.30–7.26 (m, 3H). ^{13}C NMR (100M Hz): δ (ppm) 160.3, 152.0, 136.2, 131.3, 129.1, 128.8, 128.7, 125.9, 120.8. HRMS: calcd for $C_{13}H_{12}N$ $[M+H^+]^+$ 182.0970; found 182.0957.

***N*-benzylidene-2,4,6-trimethylaniline**: Pale-yellow solid, mp: 39.2–39.5 °C. ^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 8.26 (s, 1H), 7.97–7.96 (m, 2H), 7.55–7.53 (m, 3H), 6.95 (s, 2H), 2.34 (s, 3H), 2.18 (s, 6H). ^{13}C NMR (100M Hz): δ (ppm) 162.7, 148.7, 136.1, 132.9, 131.3, 128.7, 128.7, 128.4, 127.0, 20.7, 18.2. HRMS: calcd for $C_{16}H_{18}N$ $[M+H^+]^+$ 224.1439; found 224.1451.

***N*-benzylidene-2,6-diisopropylaniline**: Pale-yellow solid, mp: 56.2–56.8 °C. ^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 8.29 (s, 1H), 8.01–8.00 (m, 2H), 7.58–7.57 (m, 3H), 7.26–7.24 (m, 2H), 7.20 (t, J = 8.4 Hz, 1H), 3.08 (sept, J = 6.8 Hz, 1H), 2.18 (d, J = 6.8 Hz, 12H). ^{13}C NMR (100M Hz): δ (ppm) 162.0, 149.2, 137.5, 136.0, 131.4, 128.8, 128.5, 124.1, 123.0, 27.9, 23.4. HRMS: calcd for $C_{19}H_{24}N$ $[M+H^+]^+$ 266.1909; found 266.1921.

***N*-(4-Chlorobenzylidene)aniline**: White solid, mp: 62.2–63.5 °C. ^{1}H NMR (500M Hz, $CDCl_3$): δ (ppm) 8.39 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.46–7.42 (m, 2H), 7.24–7.19 (m, 3H). ^{13}C NMR (125M Hz): δ (ppm) 158.7, 151.6, 137.3, 134.6, 129.9, 129.2, 129.0, 126.2, 120.8. HRMS: calcd for $C_{13}H_{11}ClN$ $[M+H^+]^+$ 216.0580; found 216.0591.

***N*-(4-Methoxybenzylidene)aniline**: White solid, mp: 56.0–56.8 °C. ^{1}H NMR (500M Hz, $CDCl_3$): δ (ppm) 8.39 (s, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.41–7.38 (m, 2H), 7.24–7.20 (m, 3H), 6.99 (d, J = 8.5 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (125M Hz): δ (ppm) 162.2, 159.7, 152.3, 130.5, 129.2, 129.1, 125.5, 120.8, 114.1, 55.4. HRMS: calcd for $C_{14}H_{14}NO$ $[M+H^+]^+$ 212.1075; found 212.1088.

***N*-(4-Nitrobenzylidene)aniline**: Pale-yellow solid, mp: 88.0–89.0 °C. ^{1}H NMR (500M Hz, $CDCl_3$): δ (ppm) 8.55 (s, 1H), 8.32 (br, 2H), 8.07 (br, 2H), 7.43 (br, 2H), 7.27 (br, 3H). ^{13}C NMR (125M Hz): δ (ppm) 157.3, 150.9, 149.2, 141.5, 129.4, 129.3, 127.0, 124.0, 120.9. HRMS: calcd for $C_{13}H_{11}N_2O_2$ $[M+H^+]^+$ 227.0821; found 227.0834.

2-((Phenylimino)methyl)phenol: Yellow solid, mp: 50.0–51.0 °C. ^{1}H NMR (500M Hz, $CDCl_3$): δ (ppm) 13.3 (br, 1H), 8.62 (s, 1H), 7.46–7.38 (m, 4H), 7.33–7.29 (m, 3H), 7.06 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H). ^{13}C NMR (125M Hz): δ (ppm) 162.6, 161.1, 148.4, 133.1, 132.2, 129.3, 126.8, 121.1, 119.1, 119.0, 117.2. HRMS: calcd for $C_{13}H_{12}NO$ $[M+H^+]^+$ 198.0919; found 198.0922.

2-((2,4,6-Trimethylphenylimino)methyl)phenol: Yellow solid, mp: 46.2–46.9 °C. ^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 13.3 (br, 1H), 8.38 (s, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 7.02–6.99 (m, 3H), 2.37 (s, 3H), 2.24 (s, 6H). ^{13}C NMR (100M Hz): δ (ppm) 166.6, 161.2, 145.6, 134.4, 133.0, 132.0, 129.0, 128.1, 118.8, 118.8, 117.2, 20.7, 18.4.

HRMS: calcd for $C_{16}H_{18}NO$ $[M+H^+]^+$ 240.1388; found 240.1397.

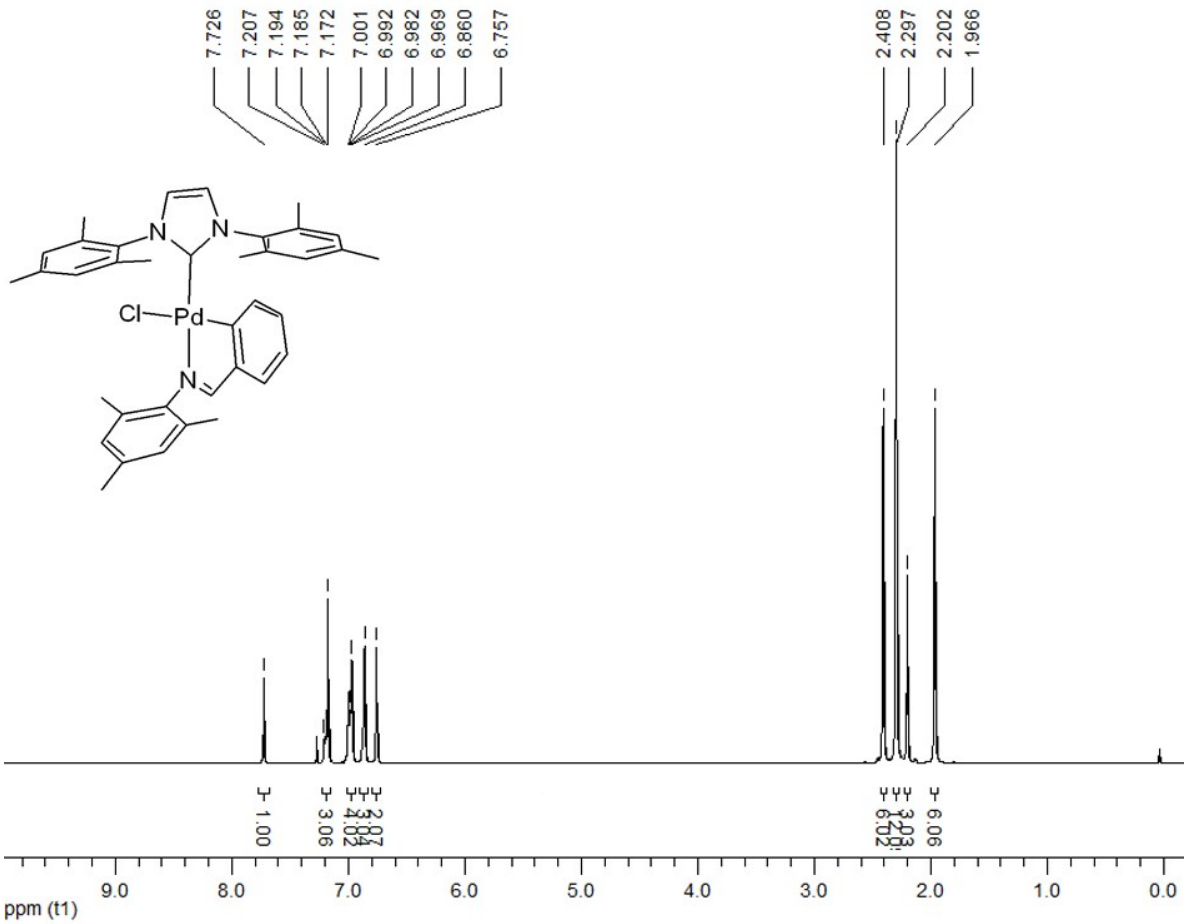
2-((2,6-diisopropylphenylimino)methyl)phenol: Yellow solid, mp: 57.5–58.5 °C. ^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 13.1 (br, 1H), 8.33 (s, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.21 (br, 3H), 7.09 (d, J = 8.4 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 3.00 (sept, J = 7.2 Hz, 1H), 1.20 (d, J = 7.2 Hz, 12H). ^{13}C NMR (100M Hz): δ (ppm) 166.6, 161.2, 146.1, 138.7, 133.2, 132.2, 125.4, 123.2, 119.0, 118.7, 117.3, 28.1, 23.5. HRMS: calcd for $C_{19}H_{24}NO$ $[M+H^+]^+$ 282.1858; found 282.1871.

5-Chloro-2-((phenylimino)methyl)phenol: Deep yellow solid, mp: 107.0–107.8 °C. ^{1}H NMR (500M Hz, $CDCl_3$): δ (ppm) 13.3 (br, 1H), 8.54 (s, 1H), 7.43 (br, 2H), 7.35–7.28 (m, 5H), 6.97–6.96 (m, 1H). ^{13}C NMR (125M Hz): δ (ppm) 161.2, 159.7, 147.9, 132.9, 131.2, 129.5, 127.3, 123.6, 121.1, 119.9, 118.8. HRMS: calcd for $C_{13}H_{11}ClNO$ $[M+H^+]^+$ 232.0529; found 232.0544.

5-Methoxy-2-((phenylimino)methyl)phenol: Yellow solid, mp: 66.2–66.9 °C.^{1}H NMR (500M Hz, $CDCl_3$): δ (ppm) 13.8 (br, 1H), 8.50 (s, 1H), 7.40–7.38 (m, 2H), 7.24 (br, 4H), 6.50–6.47 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (125M Hz): δ (ppm) 164.0, 161.4, 148.3, 133.5, 129.3, 126.3, 123.6, 120.9, 113.1, 107.1, 101.0, 55.4. HRMS: calcd for $C_{14}H_{14}NO_2$ $[M+H^+]^+$ 228.1025; found 228.1041.

5-Nitro-2-((phenylimino)methyl)phenol: Deep yellow solid, mp: 144.7–146.3 °C. ^{1}H NMR (500M Hz, $CDCl_3$): δ (ppm) 13.7 (br, 1H), 8.72 (s, 1H), 7.83–7.76 (m, 2H), 7.56–7.34 (m, 6H). ^{13}C NMR (125M Hz): δ (ppm) 161.5, 160.7, 150.1, 147.2, 132.8, 129.6, 128.1, 123.5, 121.3, 113.5, 112.7. HRMS: calcd for $C_{13}H_{11}N_2O_3$ $[M+H^+]^+$ 243.0770; found 243.0785.

^{1}H NMR and ^{13}C NMR spectra 1a−1d and 2a−2d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Pd
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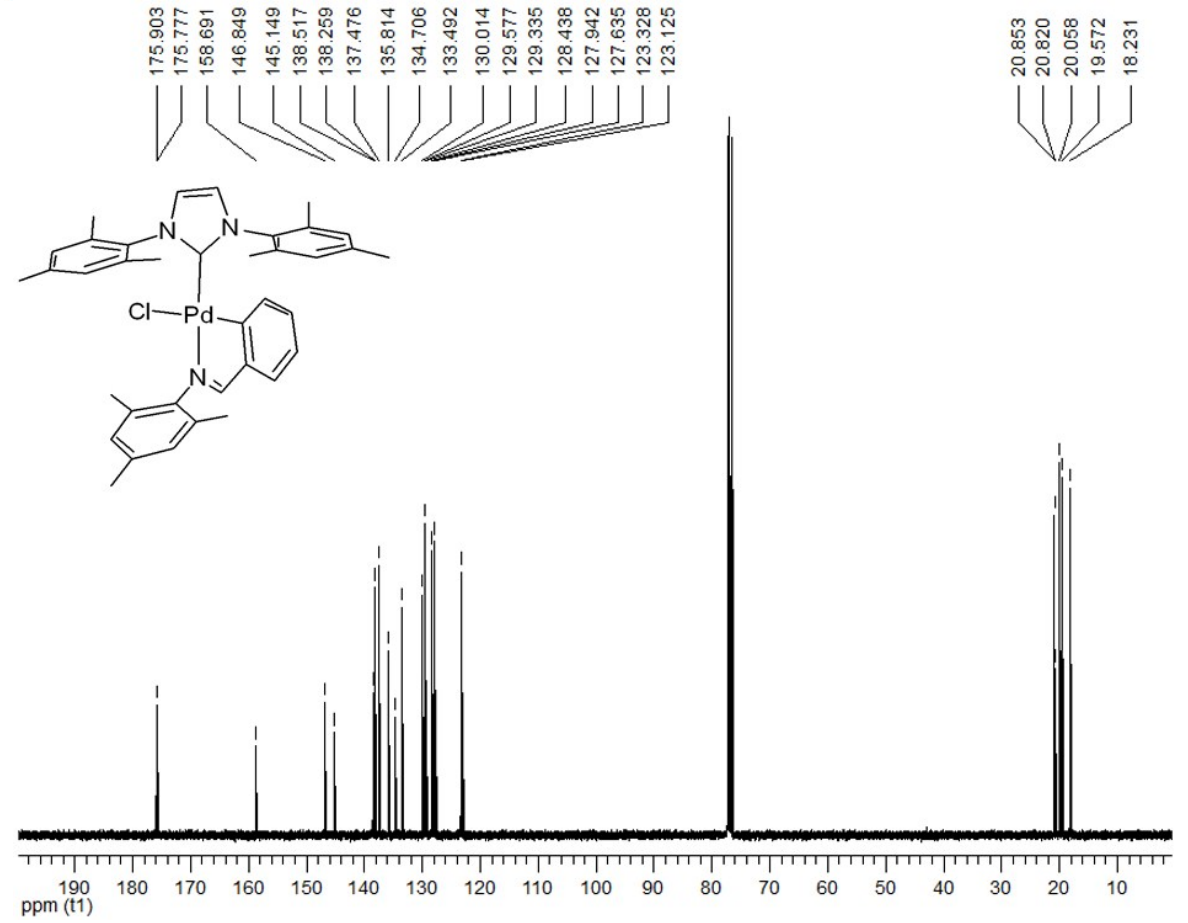
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128.438
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127.635
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123.125
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20.820
20.058
19.572
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Cl
Pd
N
190
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100
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30
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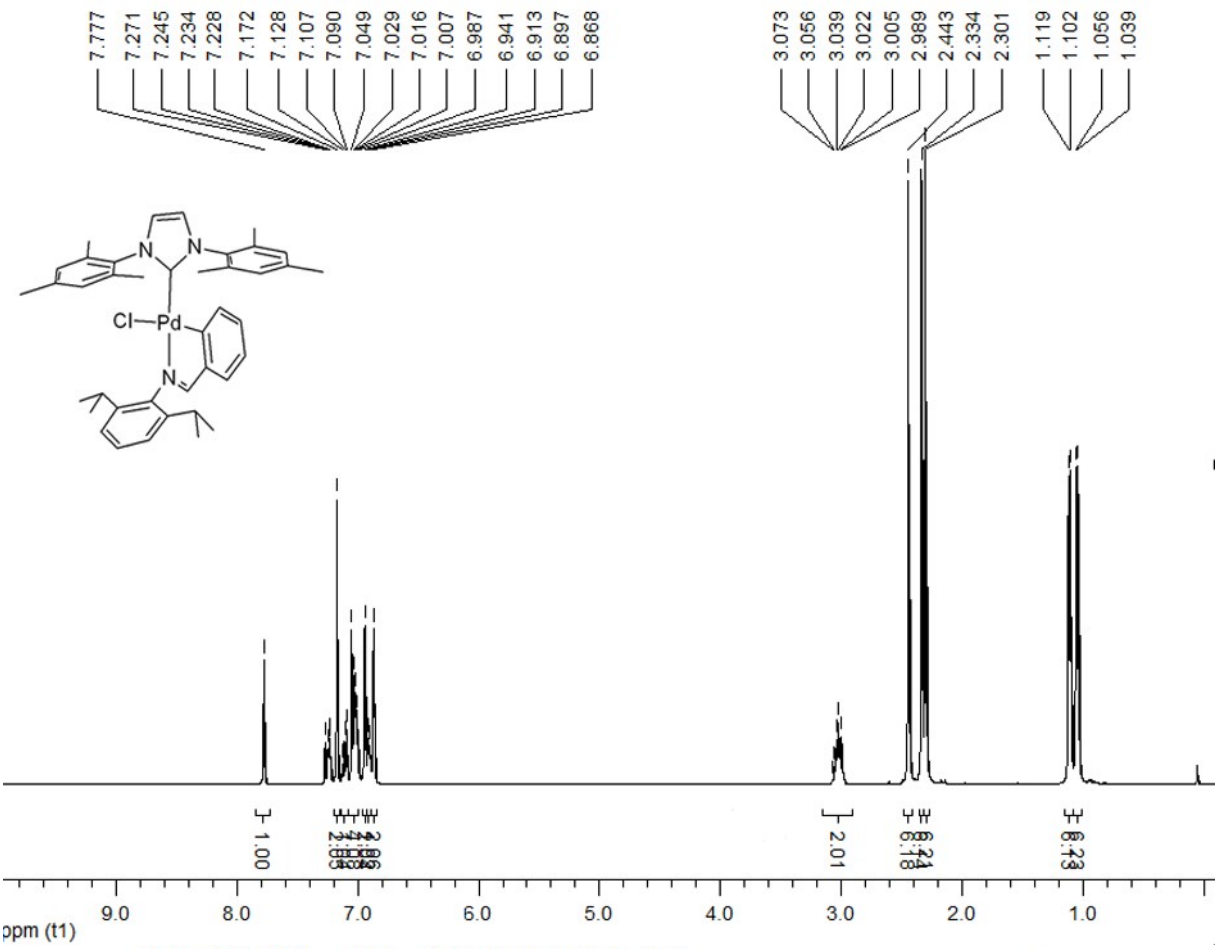
ppm (t1)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6.941
6.913
6.897
6.868
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3.056
3.039
3.022
3.005
2.989
2.443
2.334
2.301
1.119
1.102
1.056
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Cl
Pd
N
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2.01
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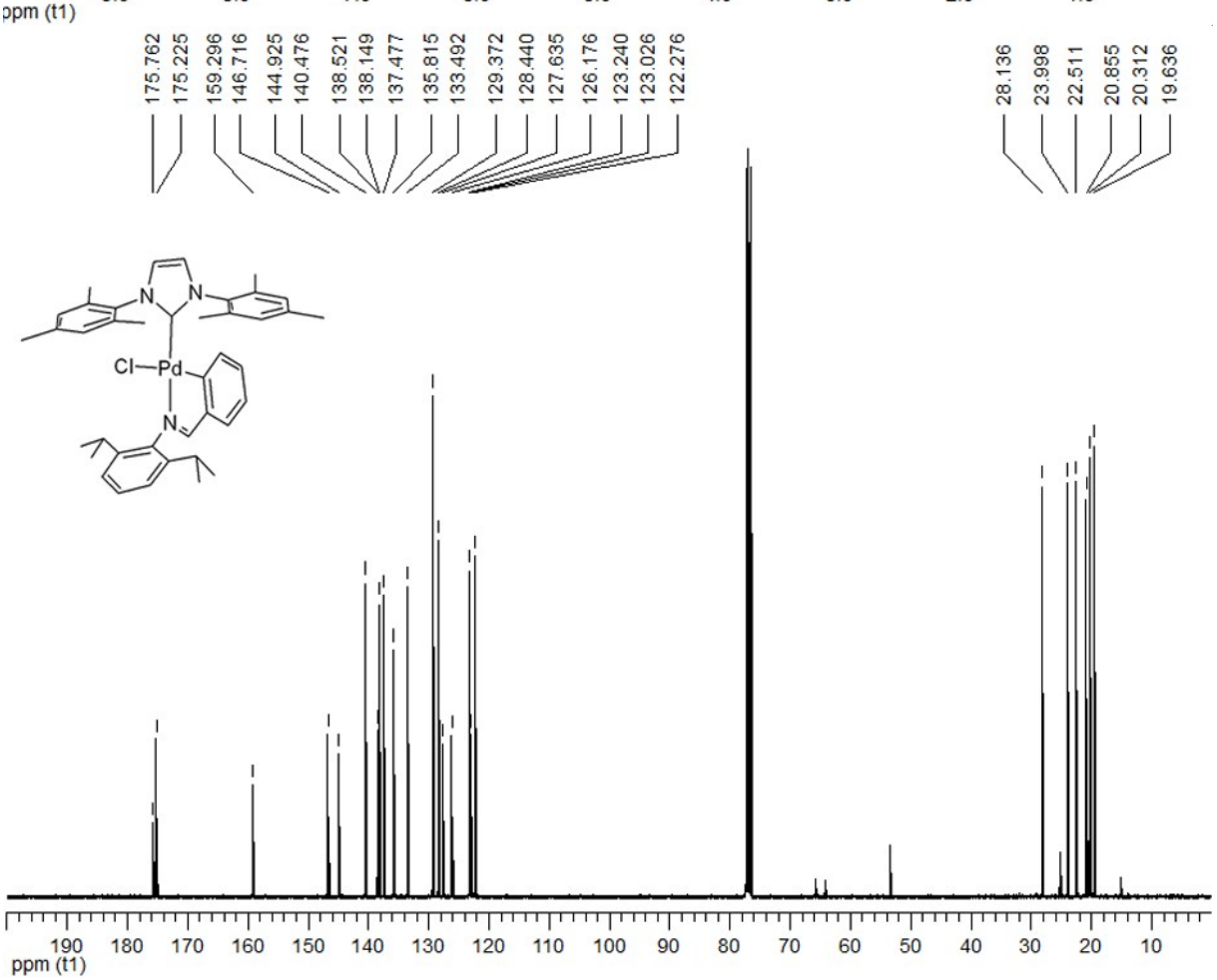
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126.176
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Cl
Pd
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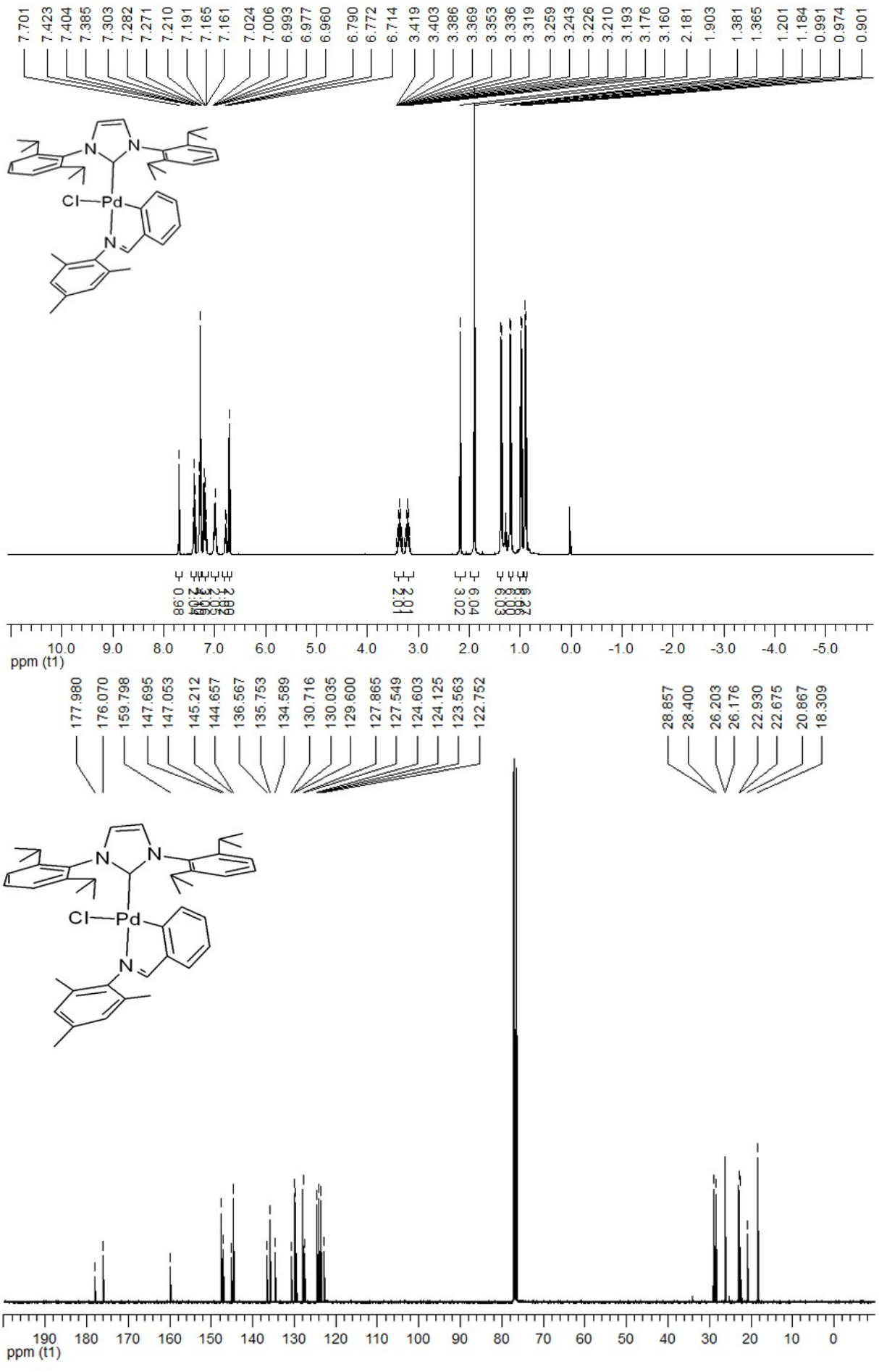
ppm (t1)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6.977
6.960
6.790
6.772
6.714
3.419
3.403
3.386
3.369
3.353
3.336
3.319
3.259
3.243
3.226
3.210
3.193
3.176
3.160
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1.365
1.201
1.184
0.991
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0.901
Cl
Pd
N
ppm (t1)
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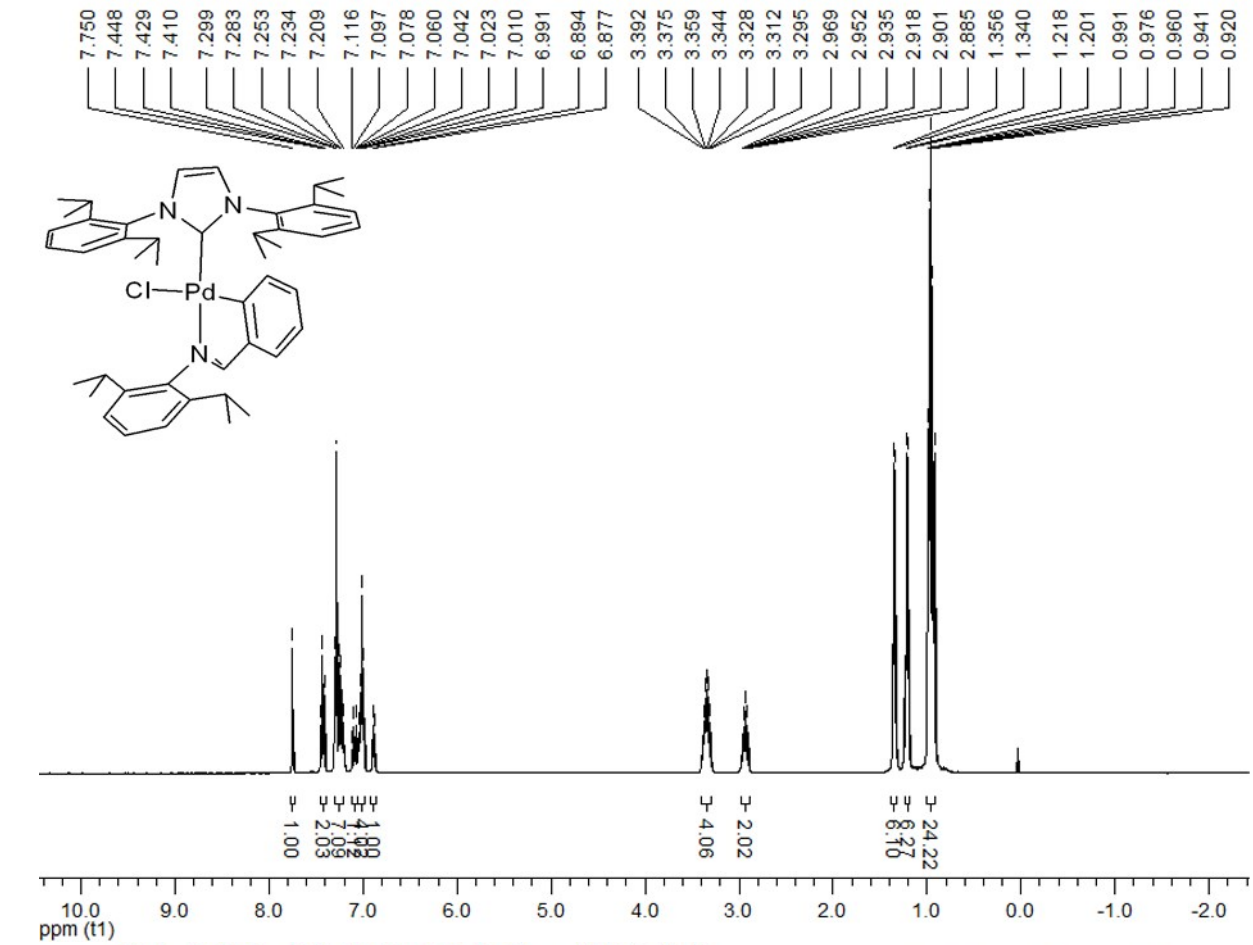
20.867
18.309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7.010
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6.894
6.877
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3.375
3.359
3.344
3.328
3.312
3.295
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2.952
2.935
2.918
2.901
2.885
1.356
1.340
1.218
1.201
0.991
0.976
0.960
0.941
0.920
Cl—Pd
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4.06
2.02
9.10
24.22
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9.0
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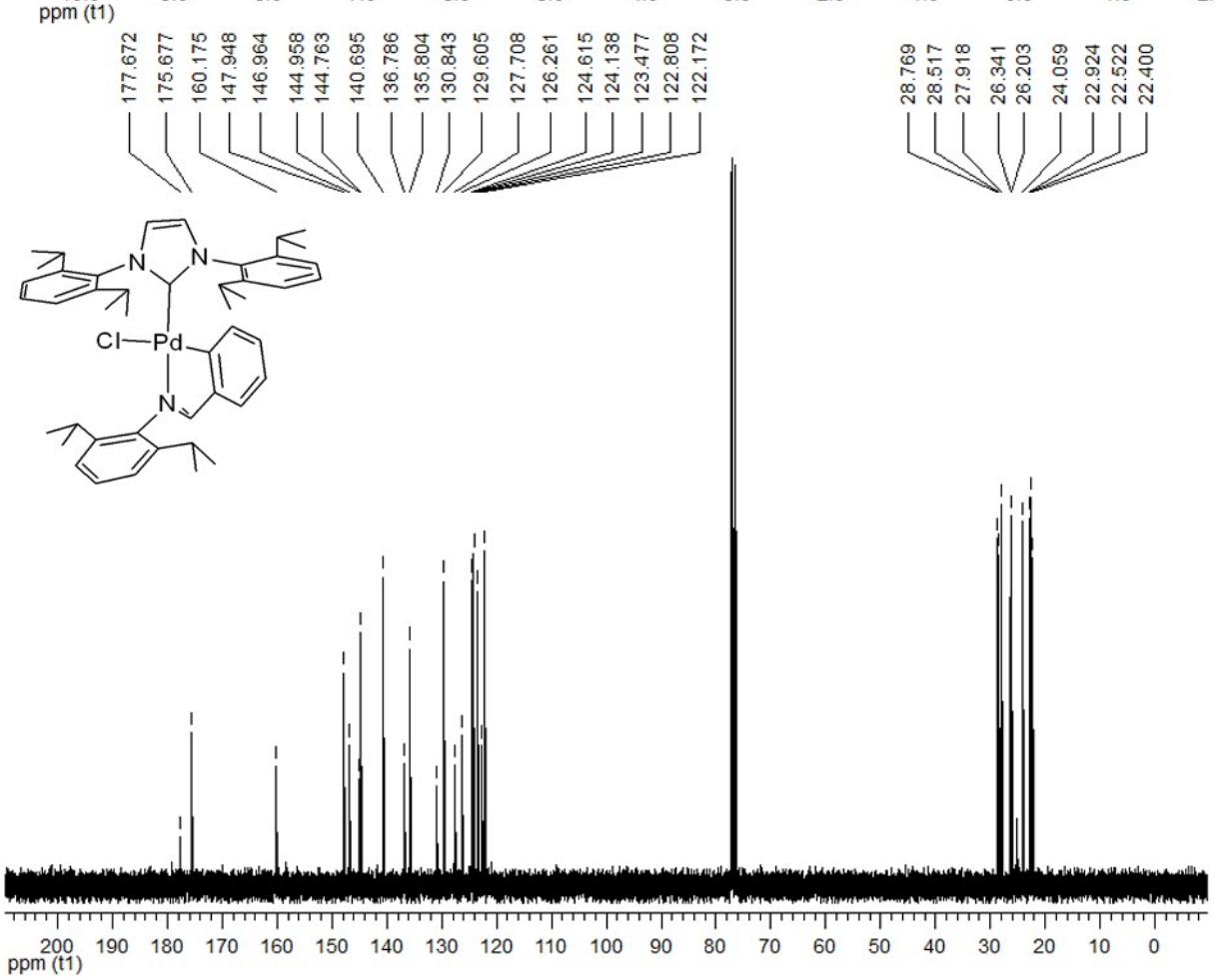
ppm (t1)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22.522
22.400
Cl—Pd
N
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190
180
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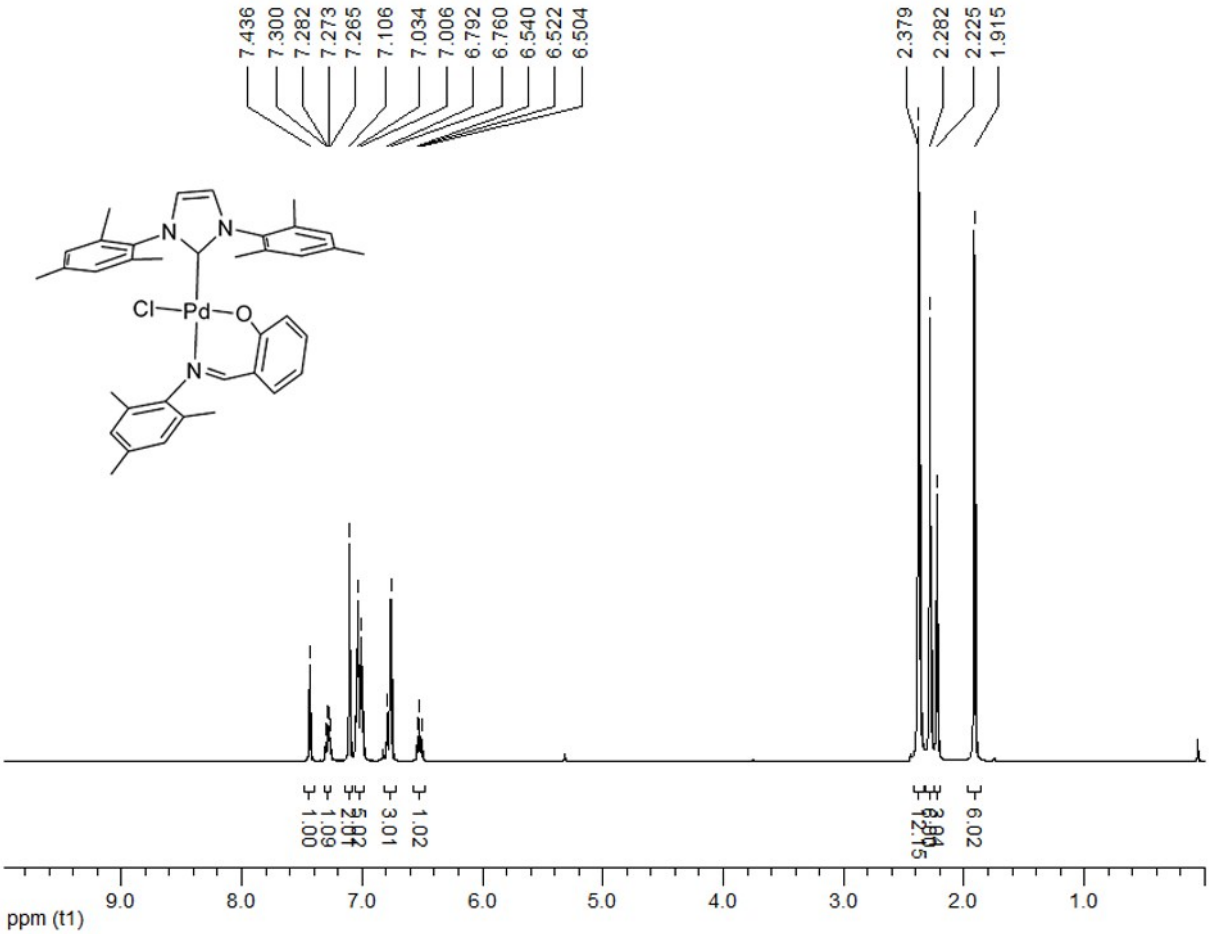
ppm (t1)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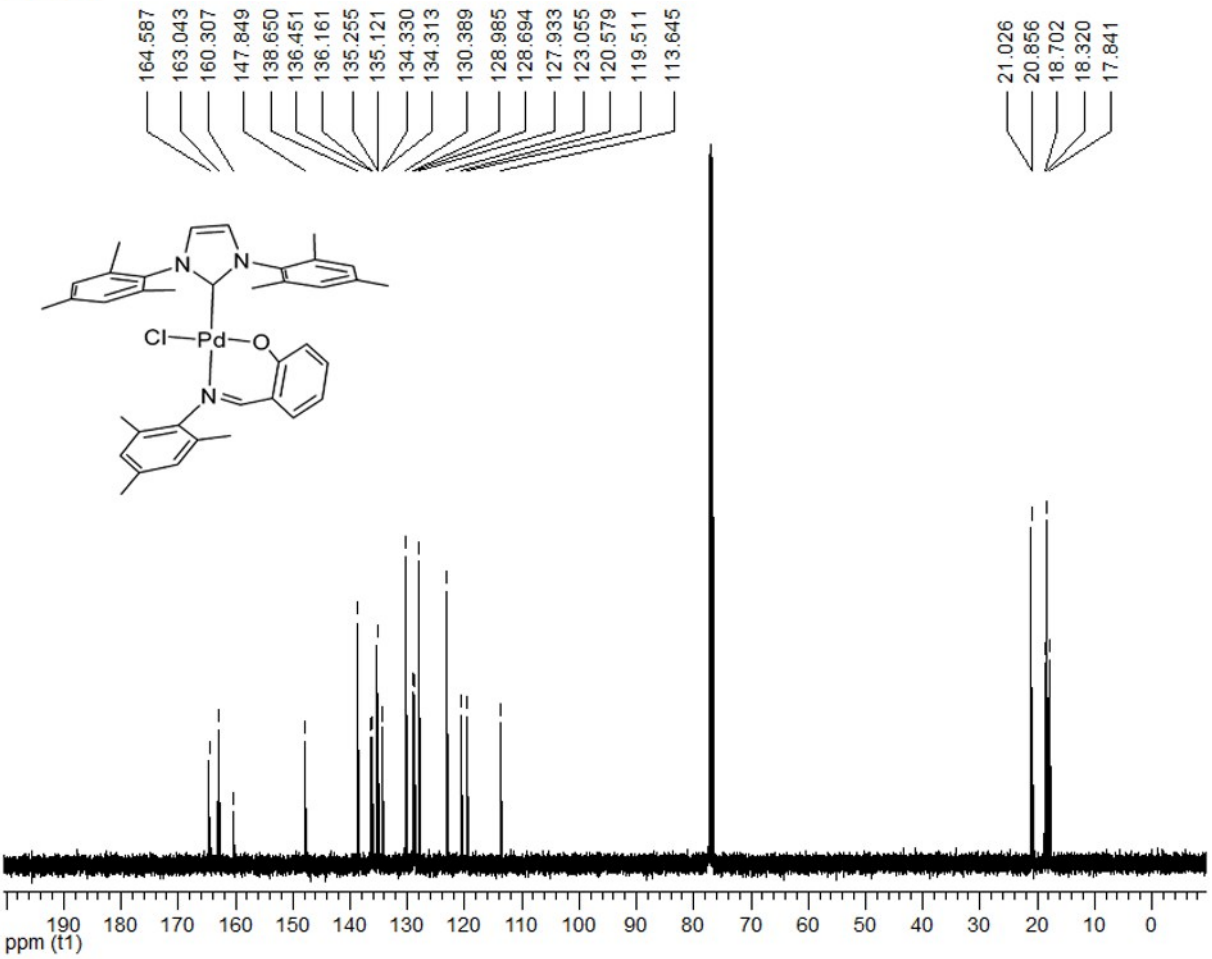
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123.055
120.579
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113.645
21.026
20.856
18.702
18.320
17.841
Cl
Pd
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N
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180
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50
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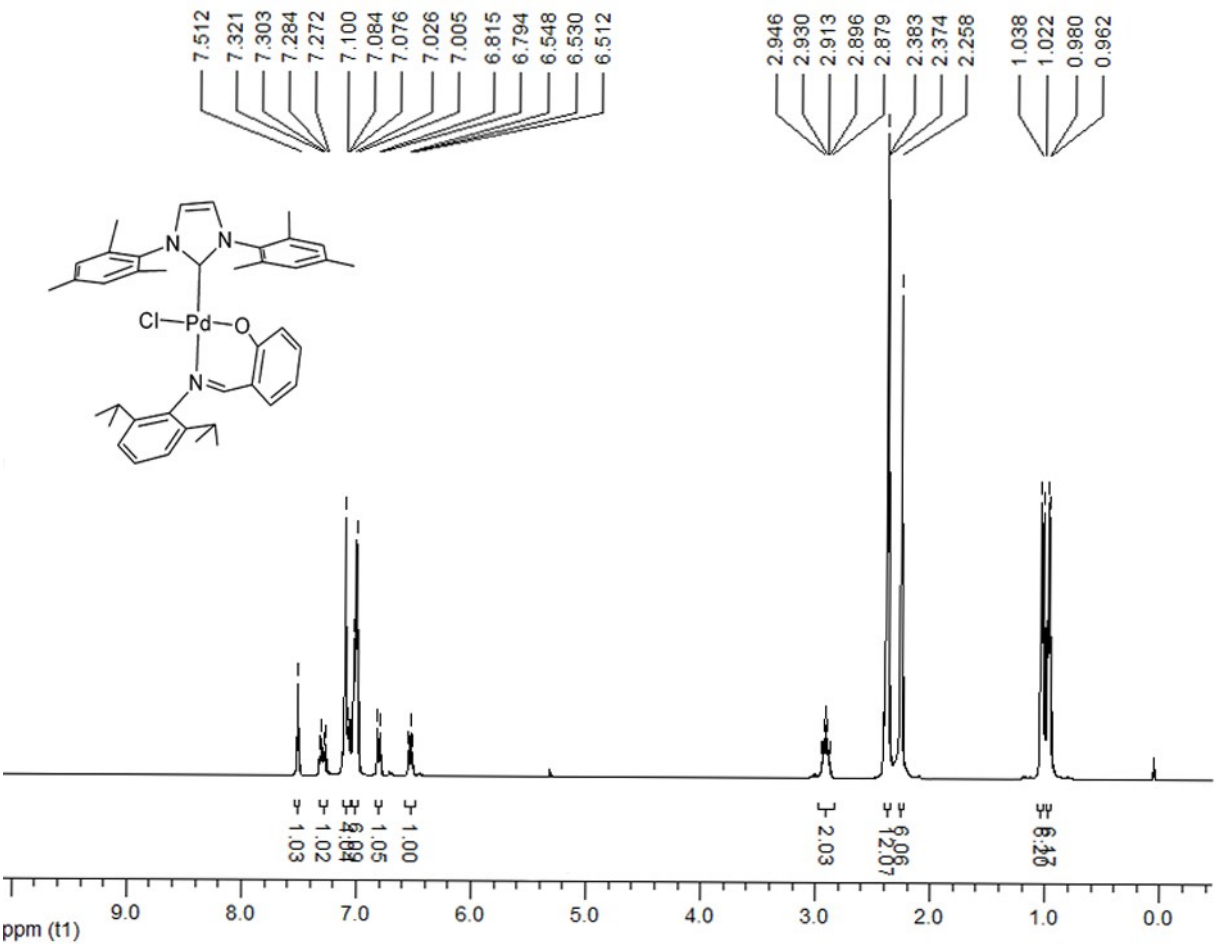
ppm (t1)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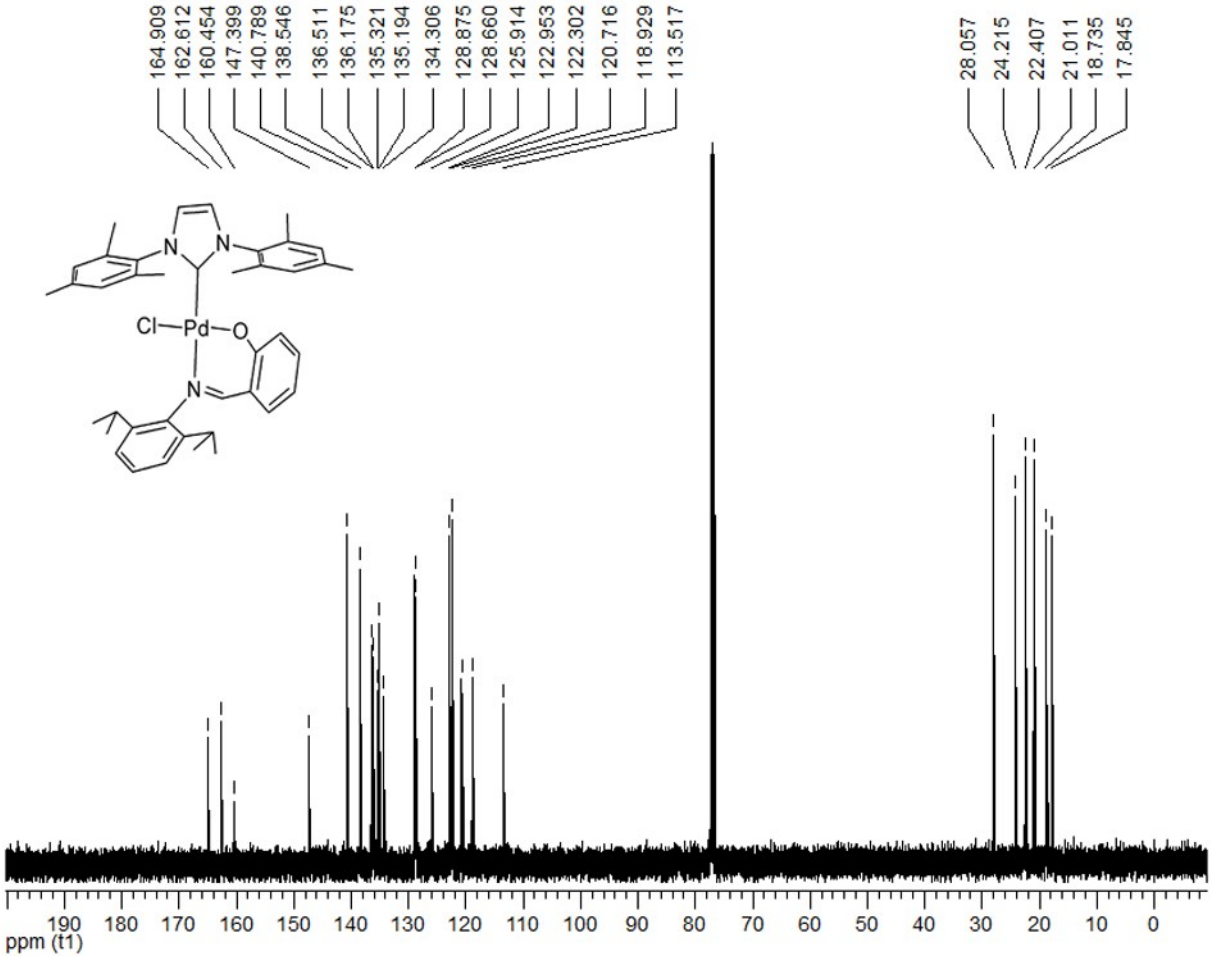
ppm (t1)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122.302
120.716
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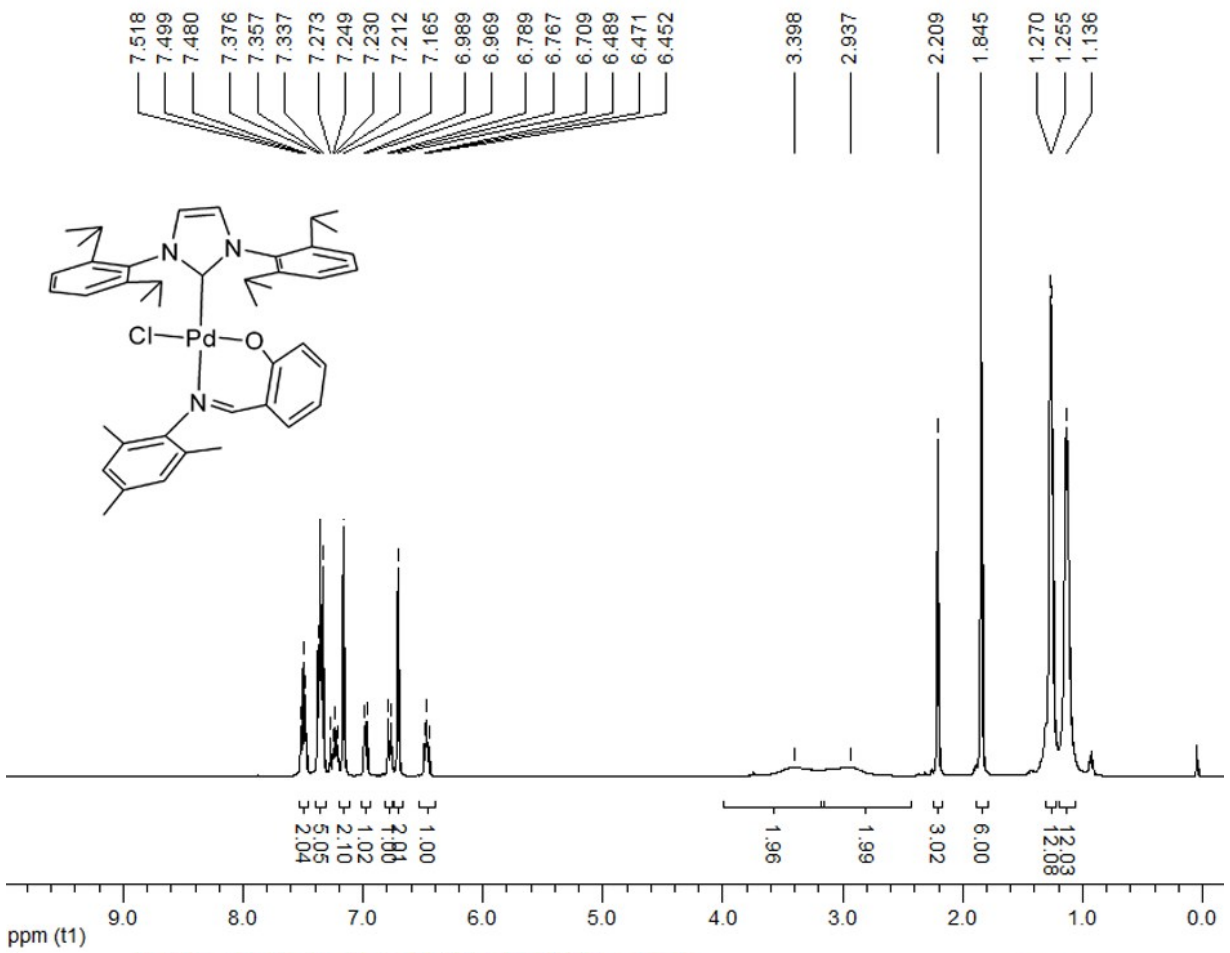
Pd
O
N
ppm (t1)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1.136
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Pd
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1.02
4.00
1.00
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1.99
3.02
6.00
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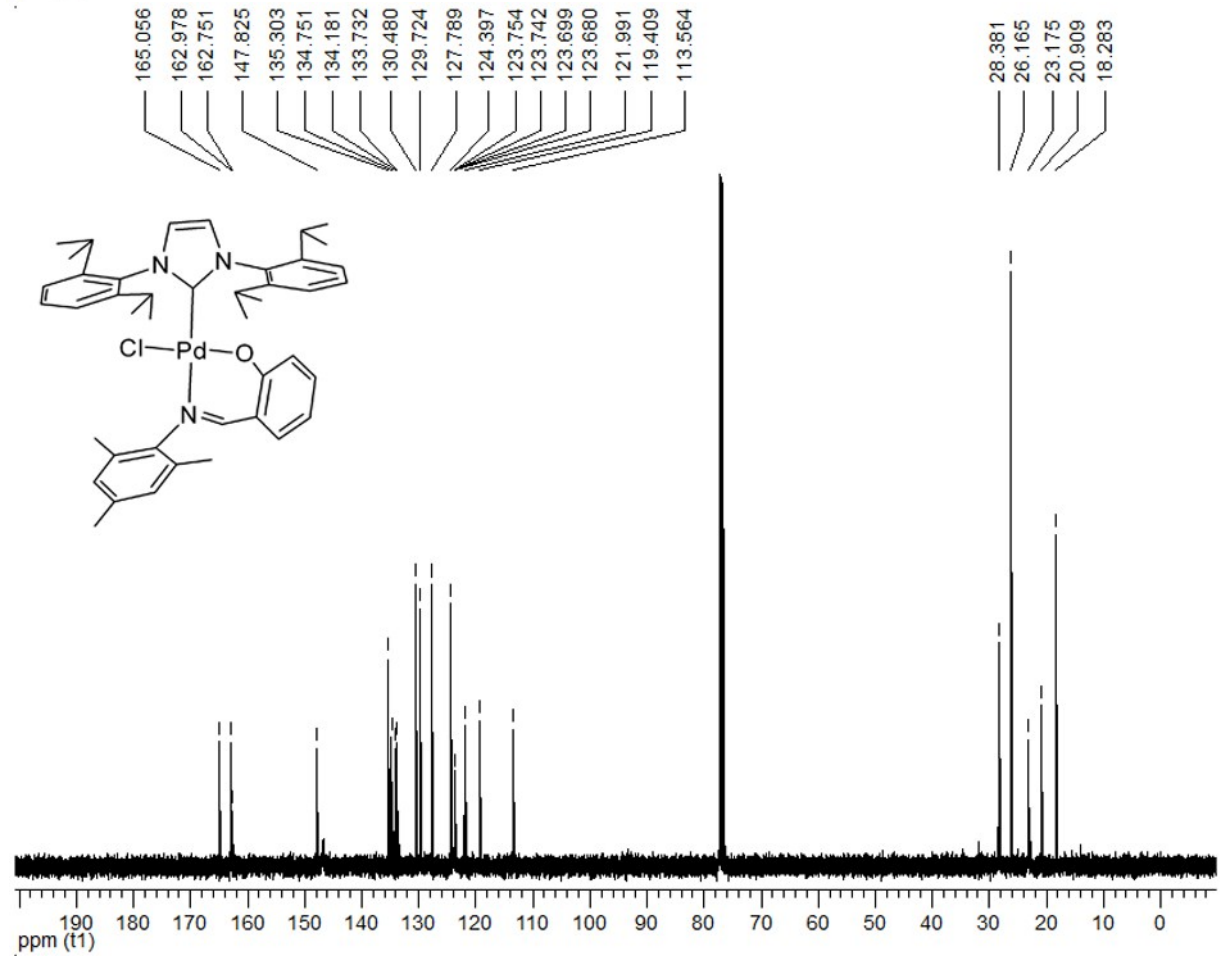
ppm (t1)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Cl
Pd
O
N
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180
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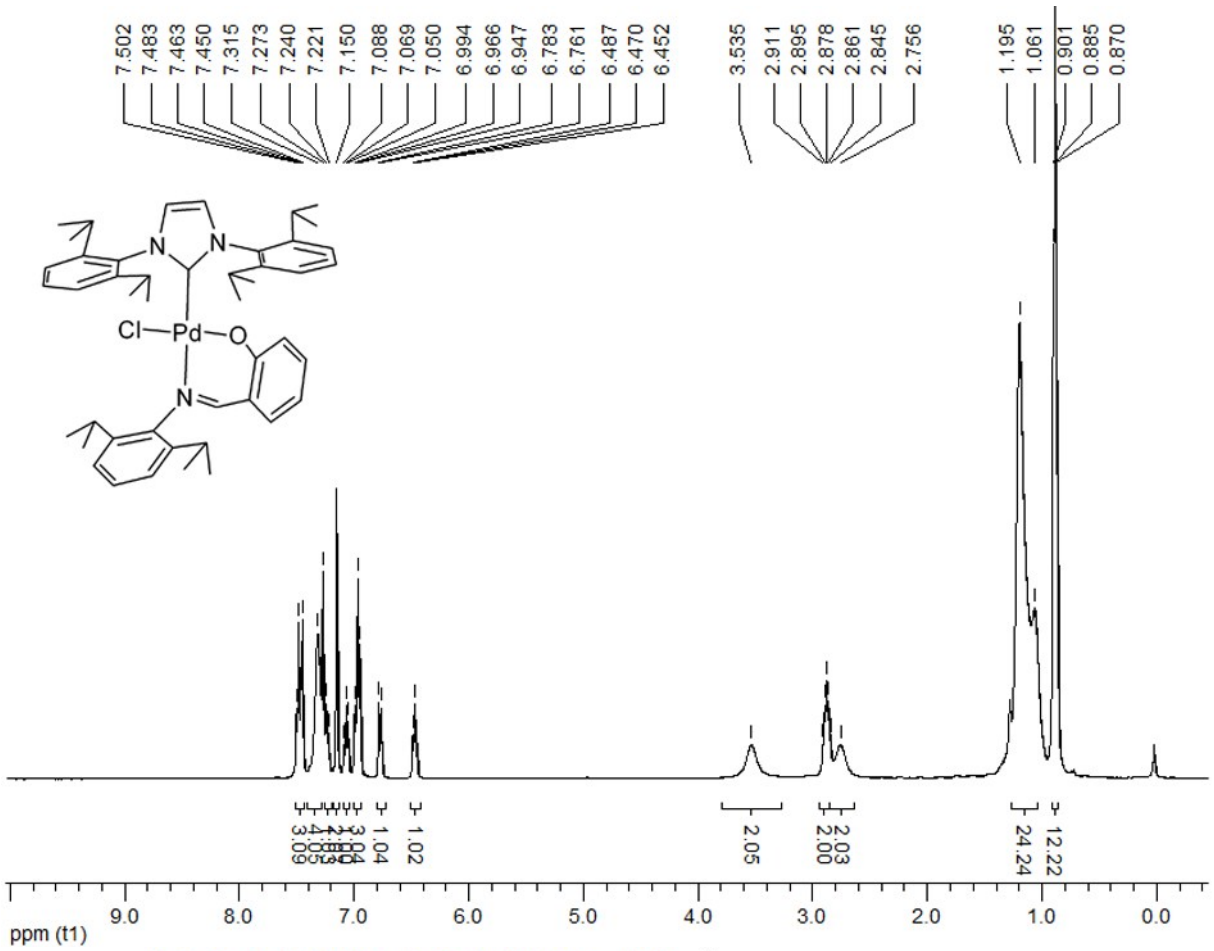
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Pd
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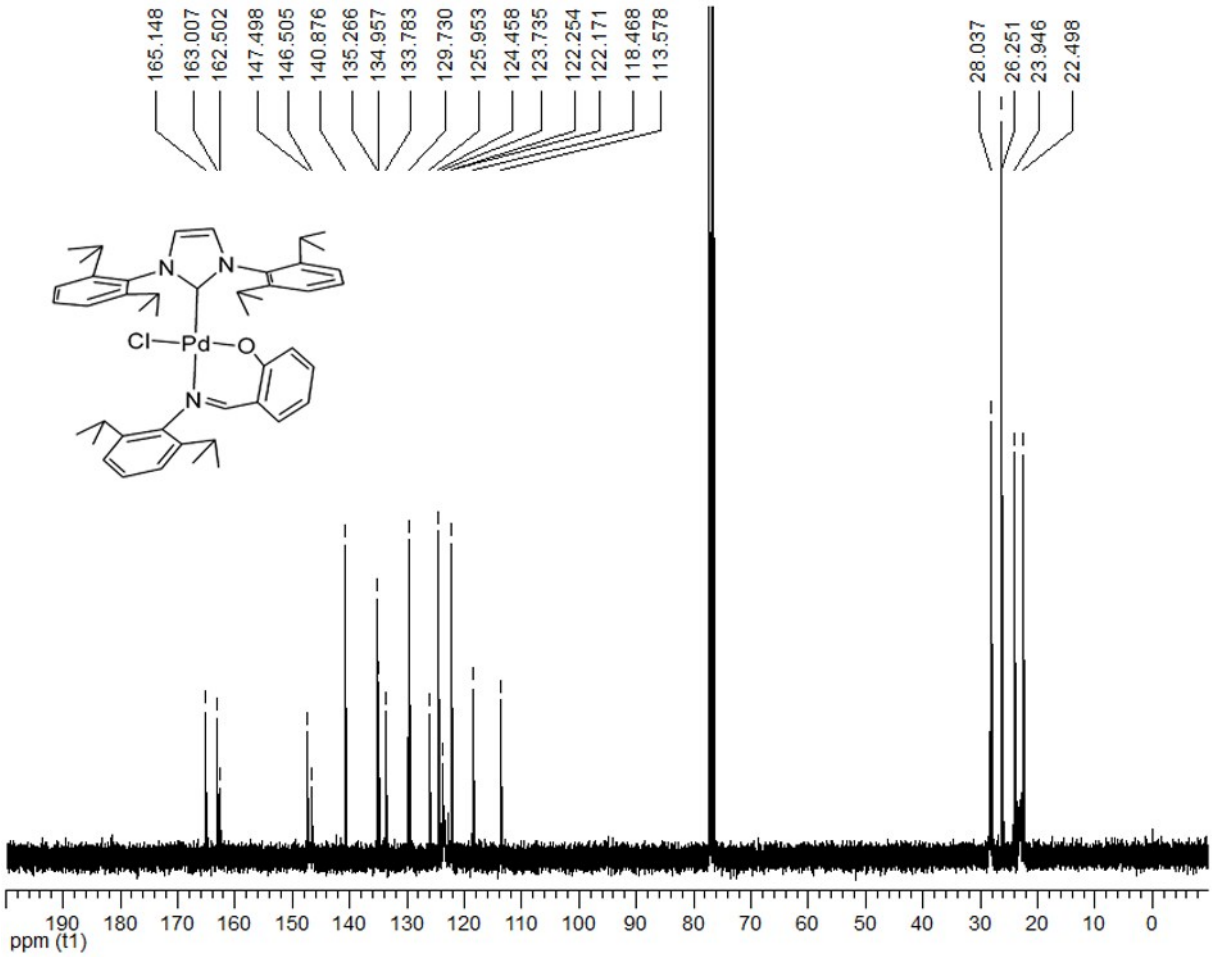
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100
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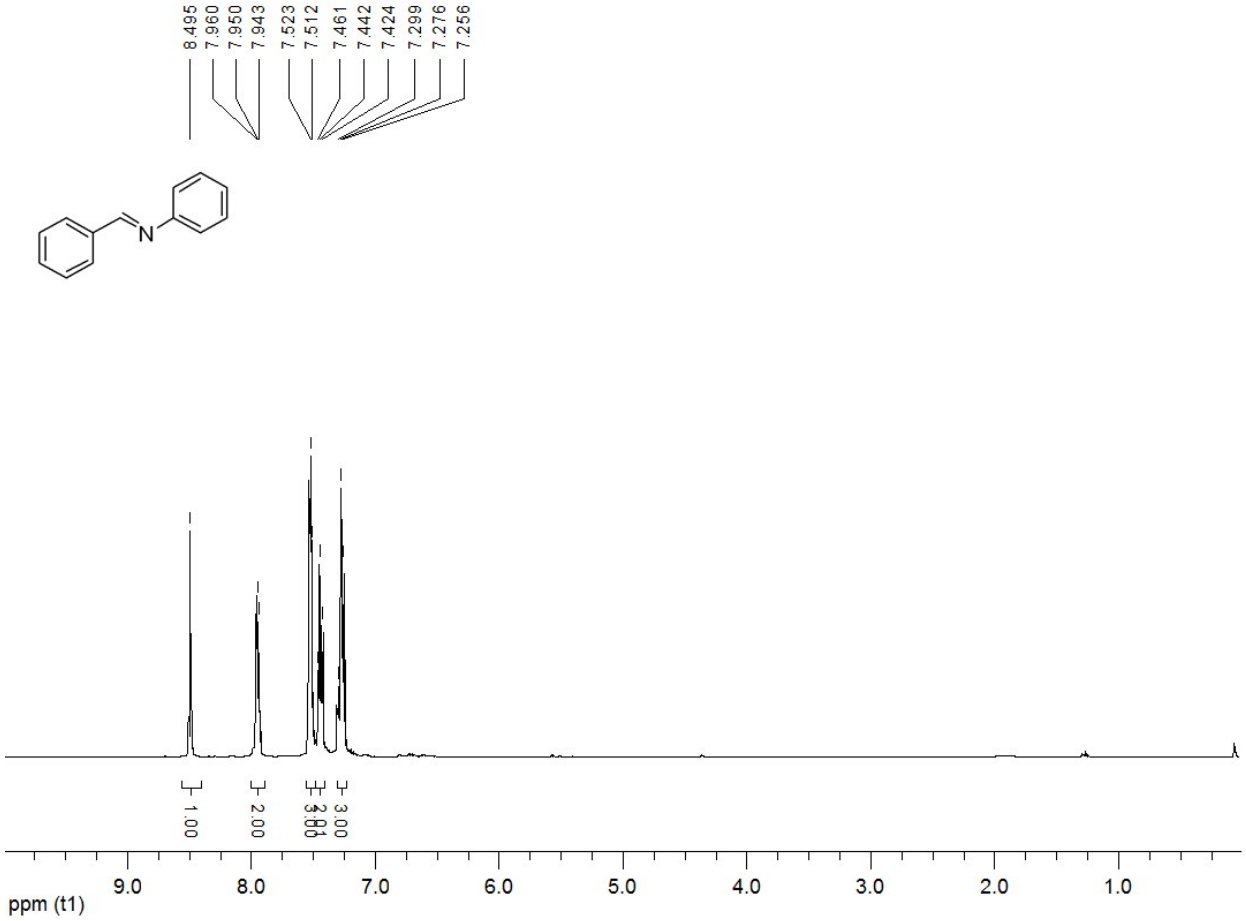
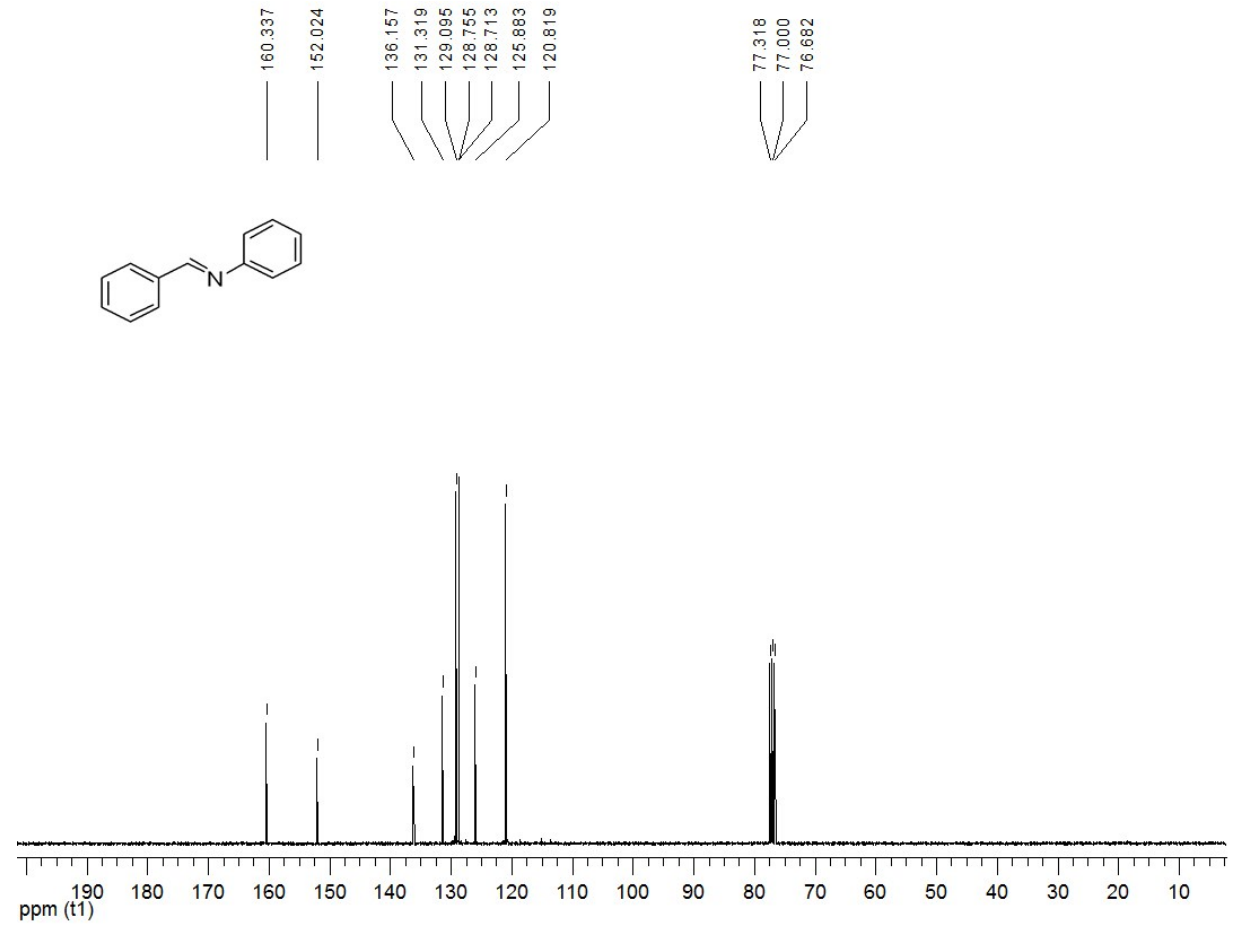
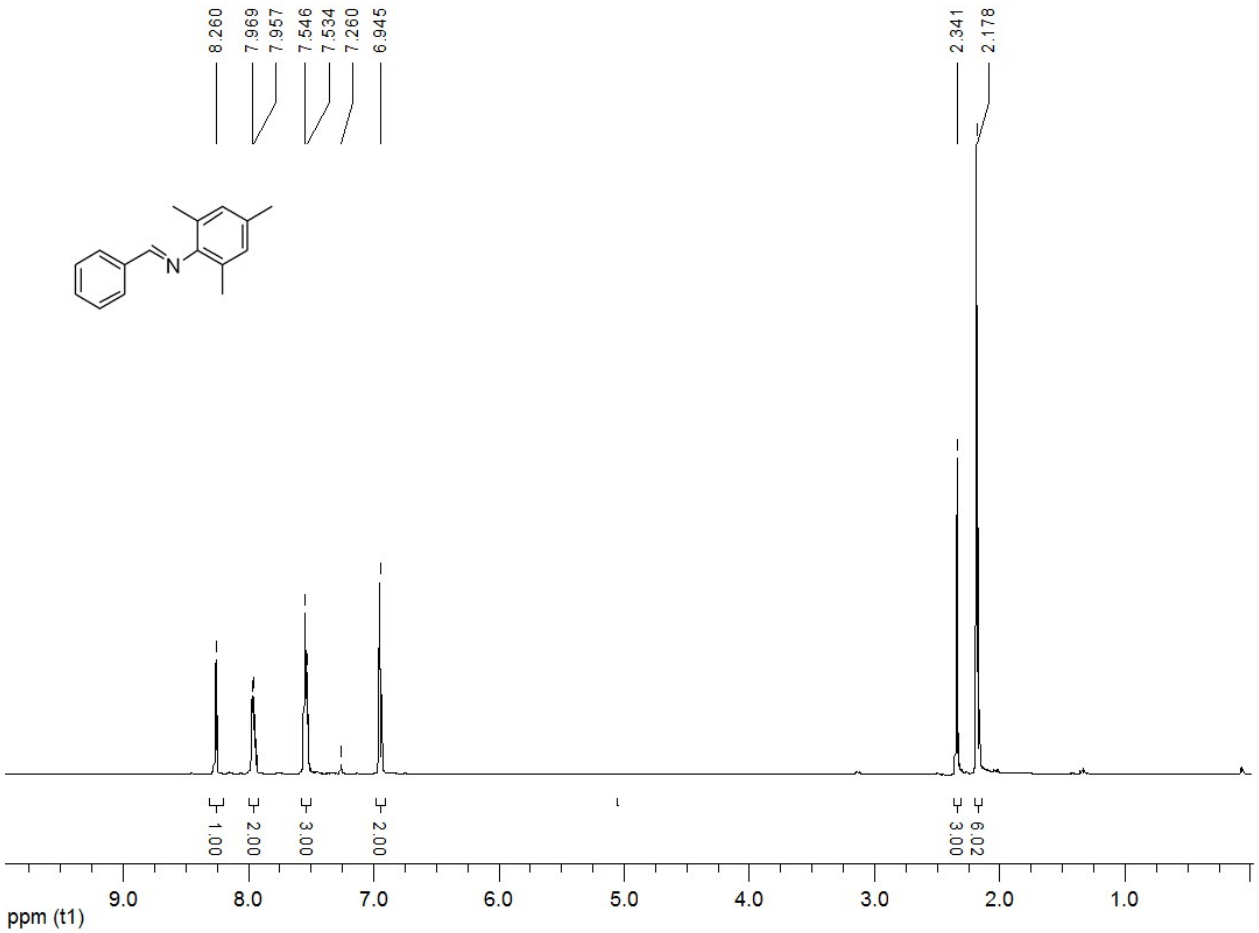
ppm (t1)

^{1}H and ^{13}C NMR spectra of arylimines and salicylaldimines



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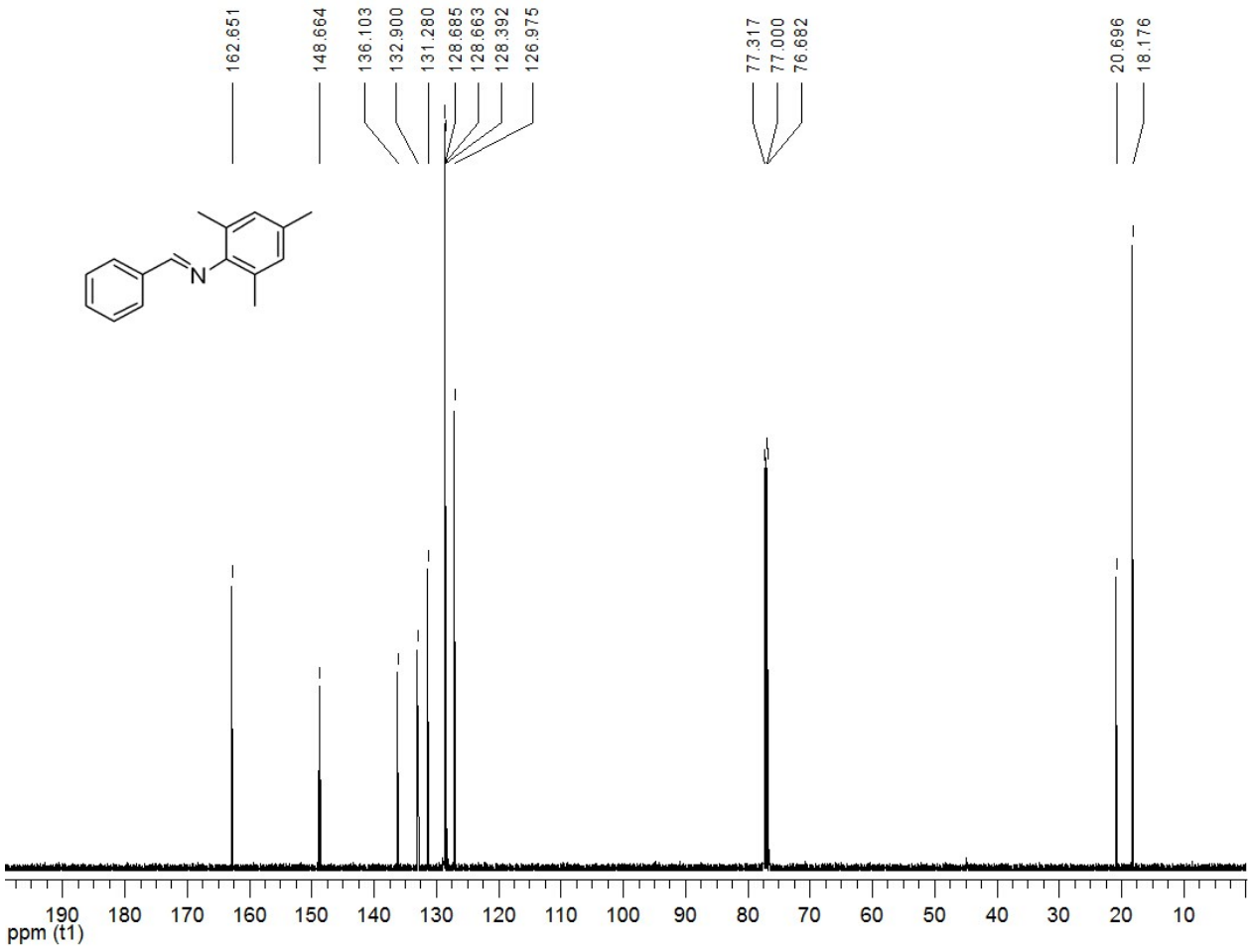
ppm (t1)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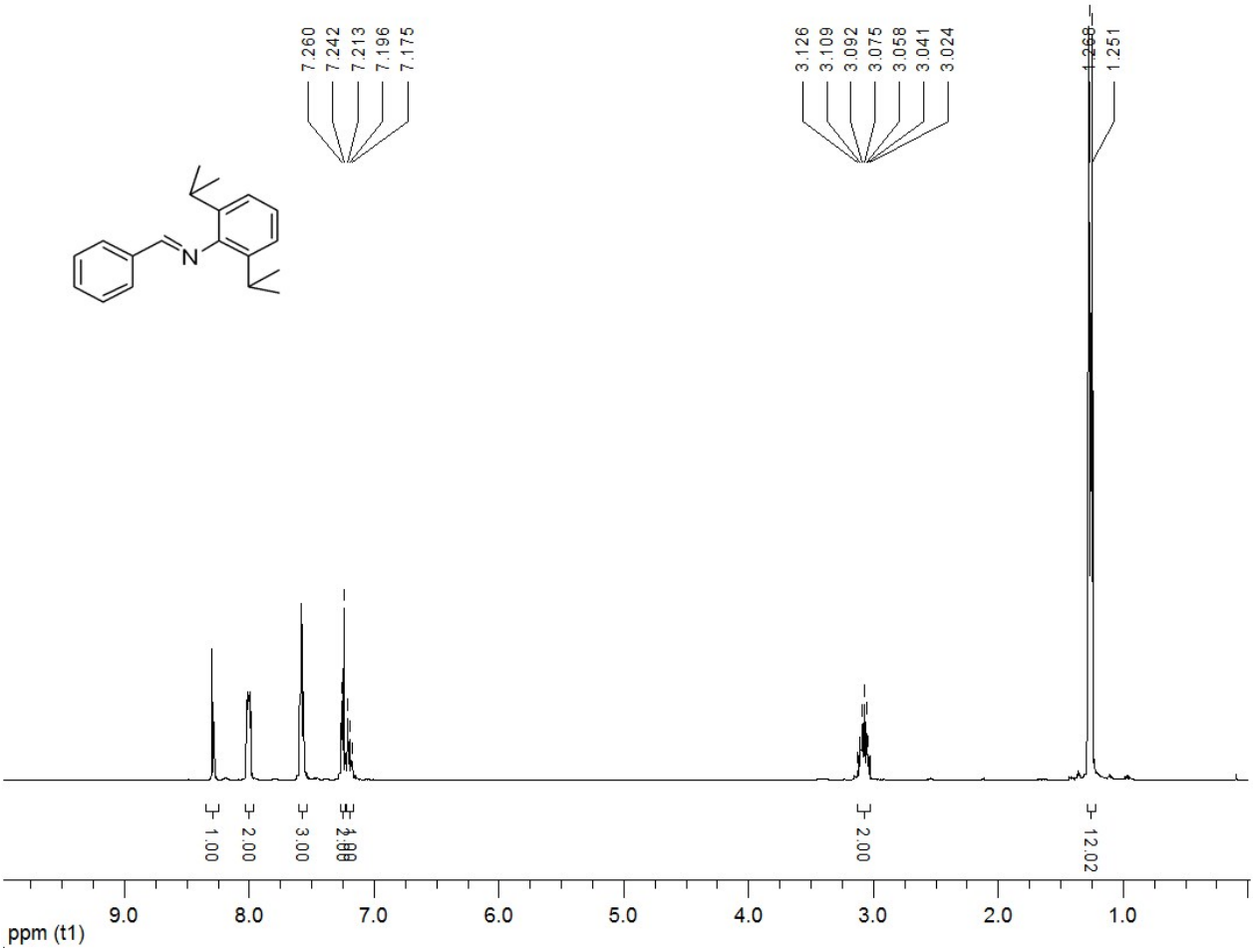
ppm (t1)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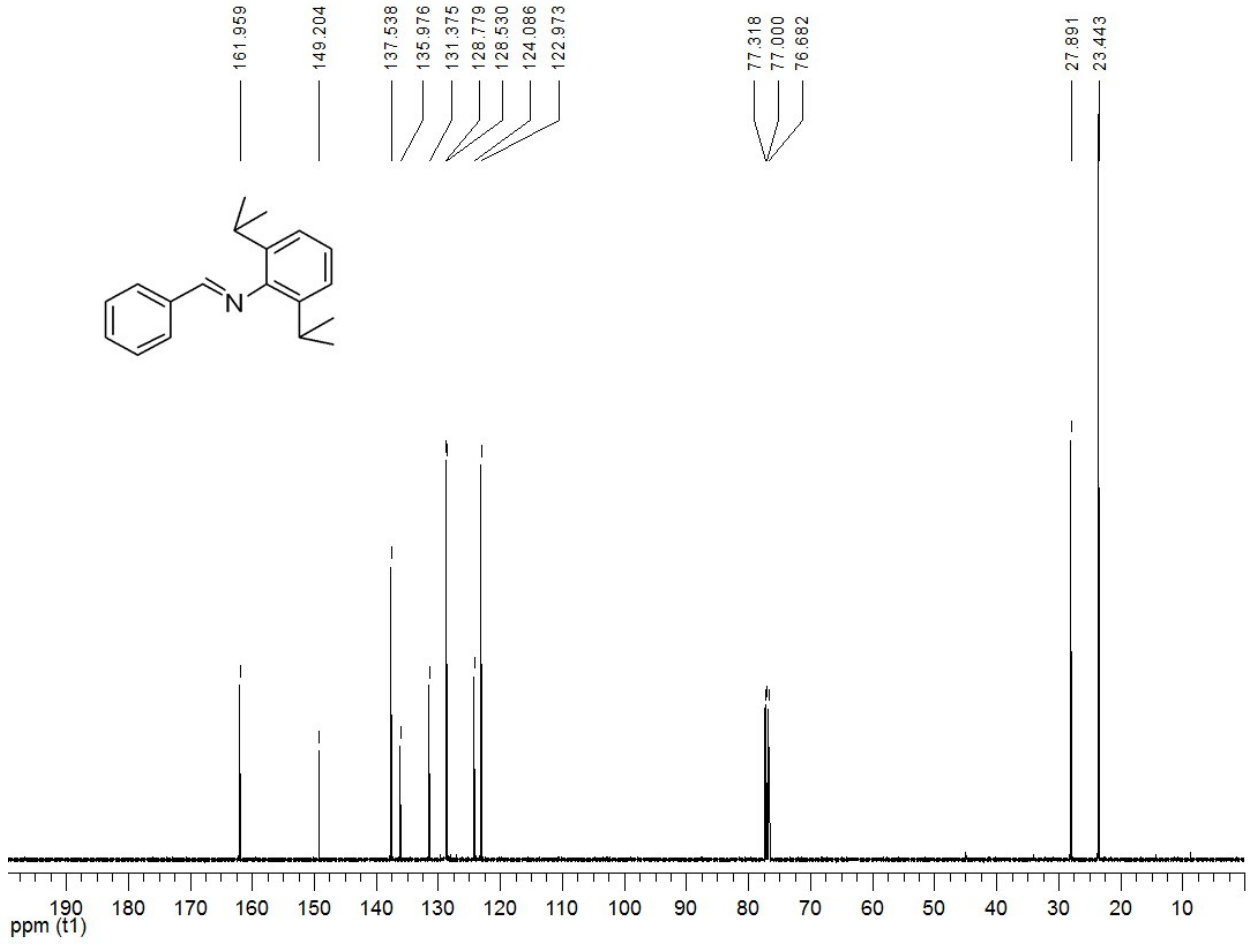
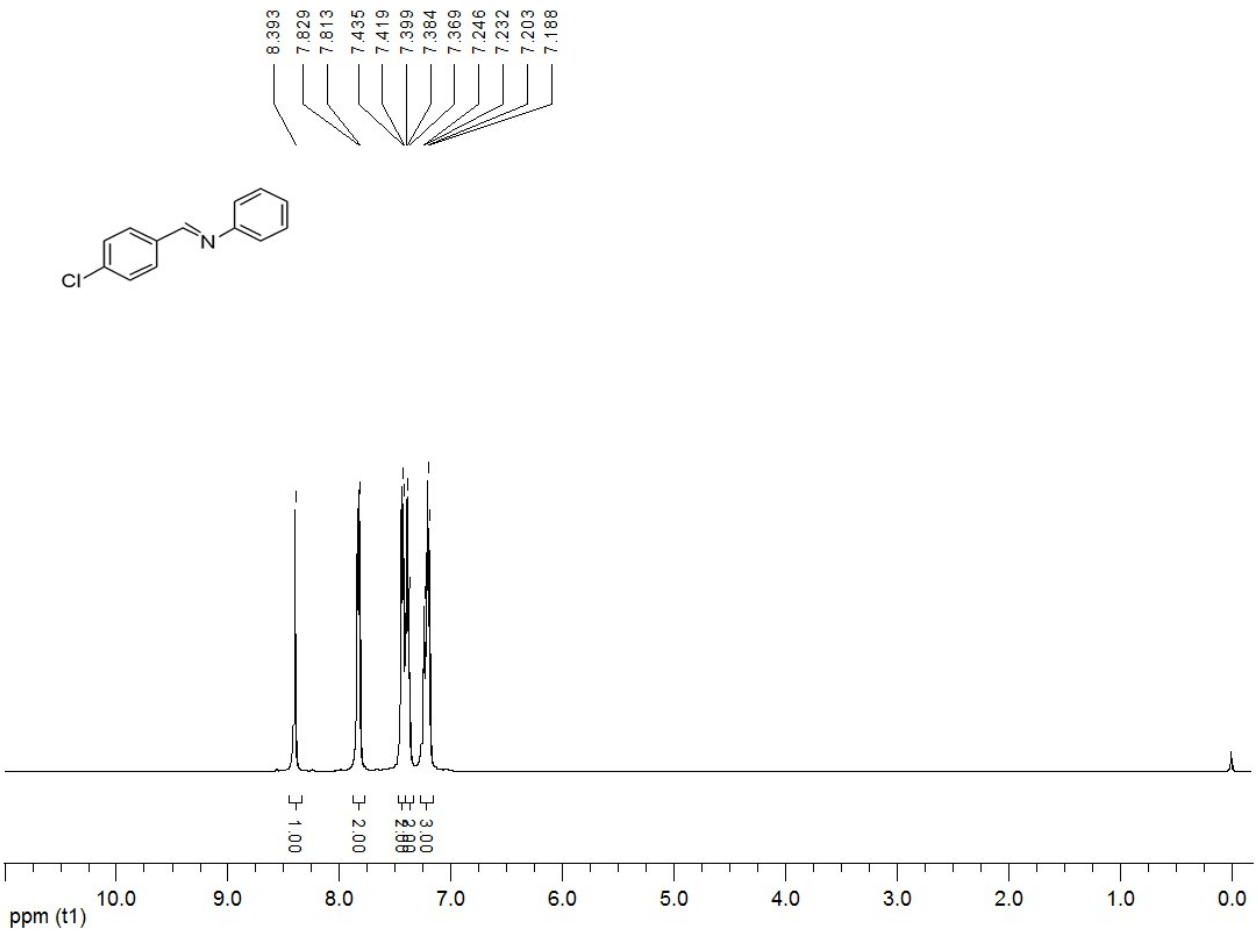
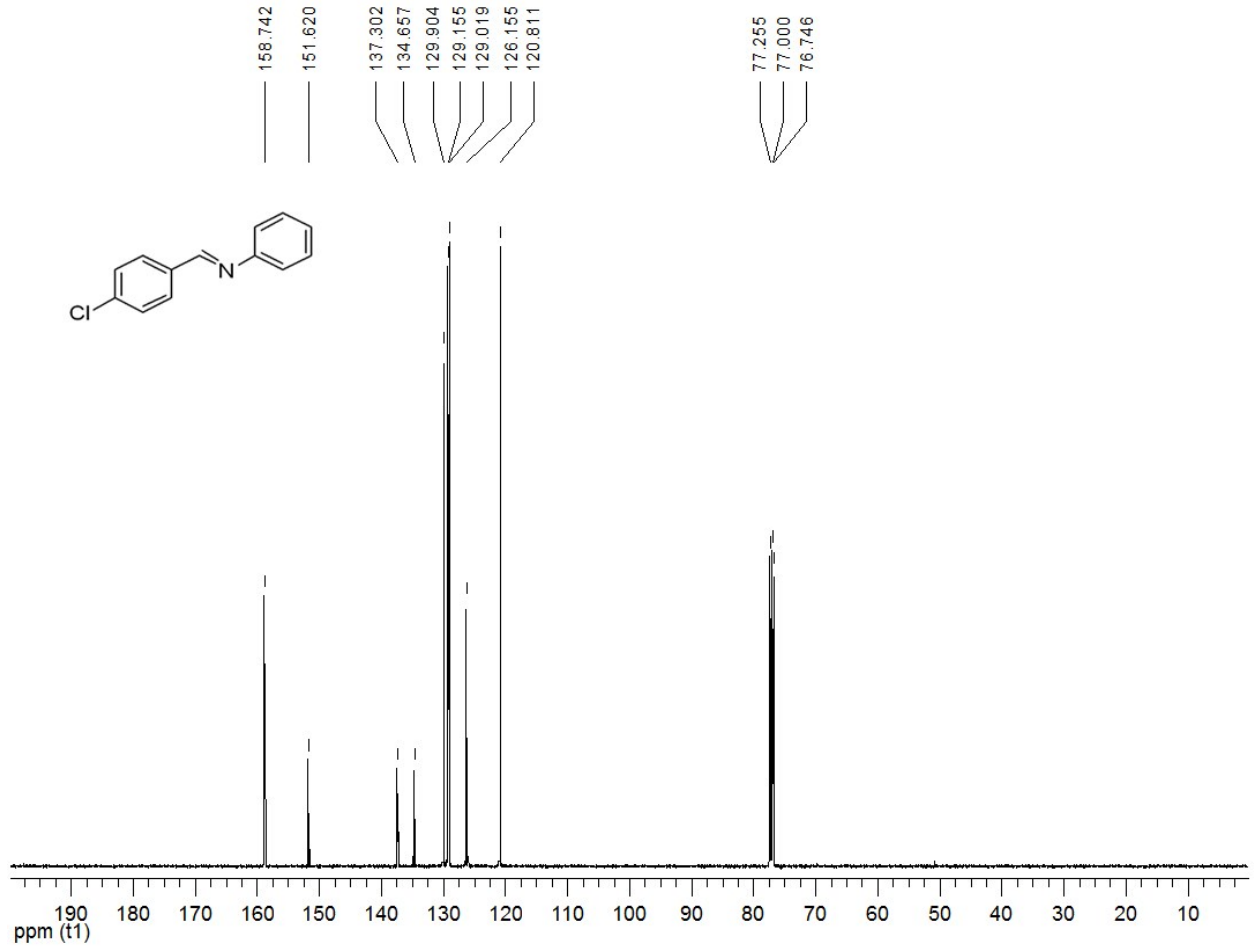
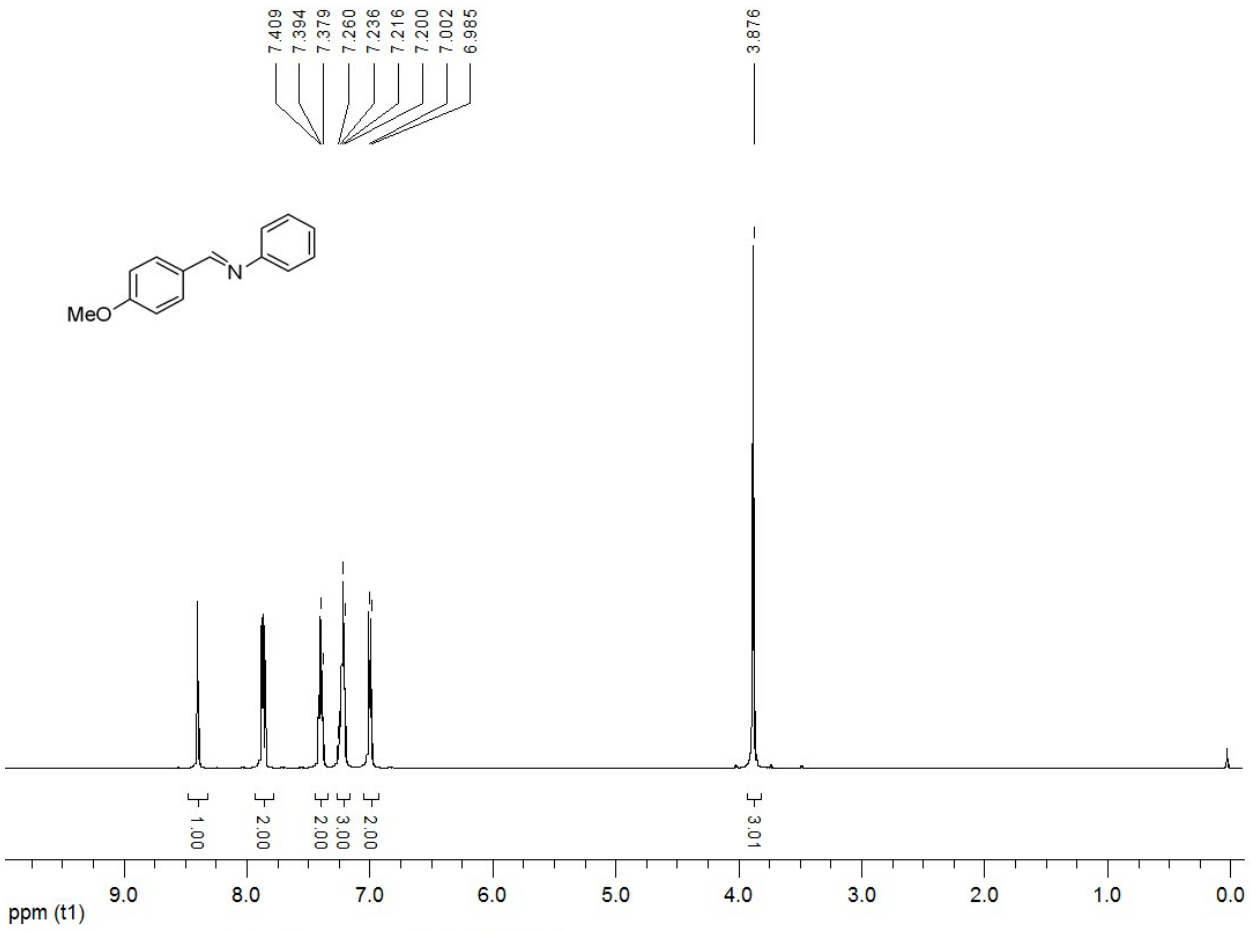
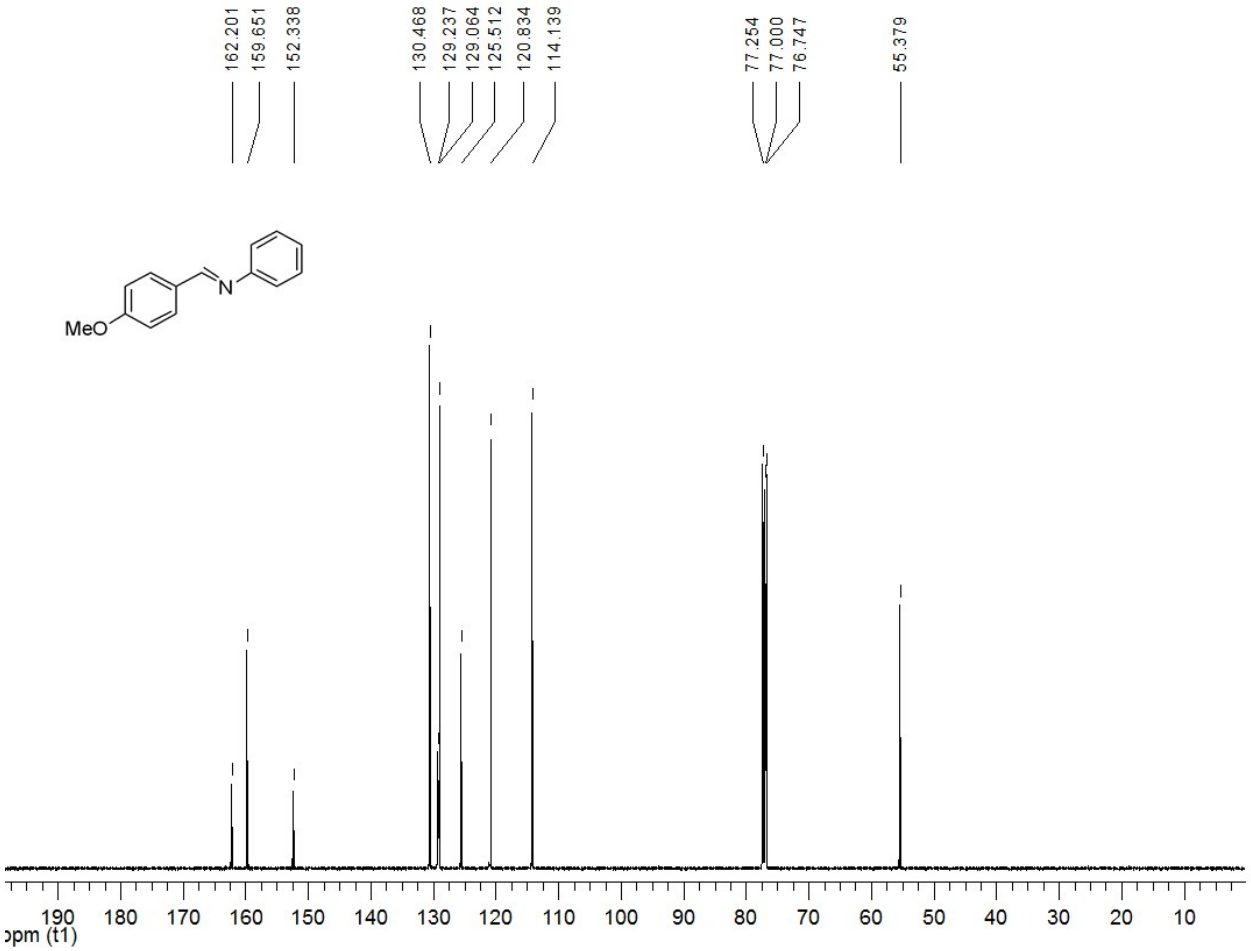
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

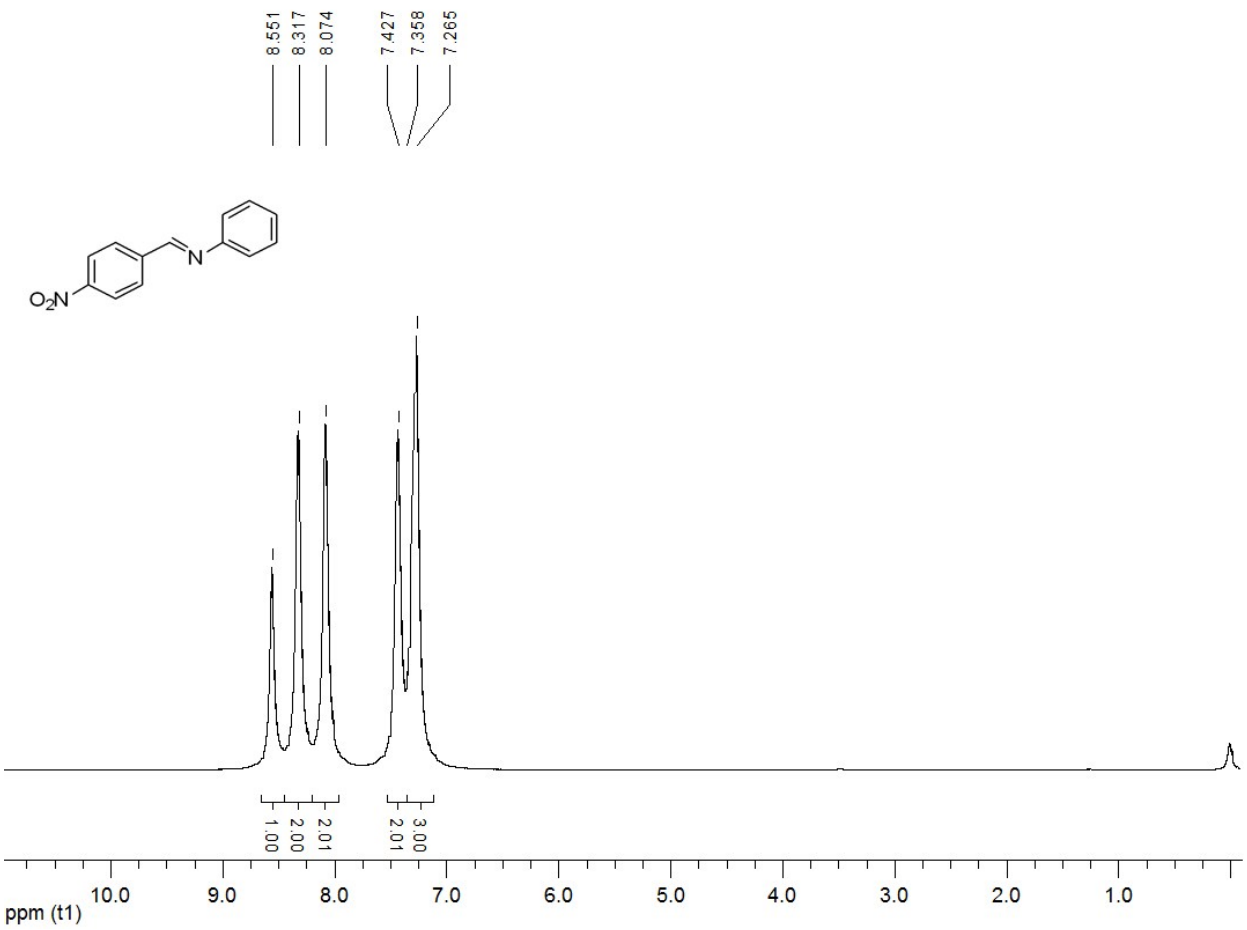

161.959
149.204
137.538
135.976
131.375
128.779
128.530
124.086
122.973
77.318
77.000
76.682
27.891
23.443
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

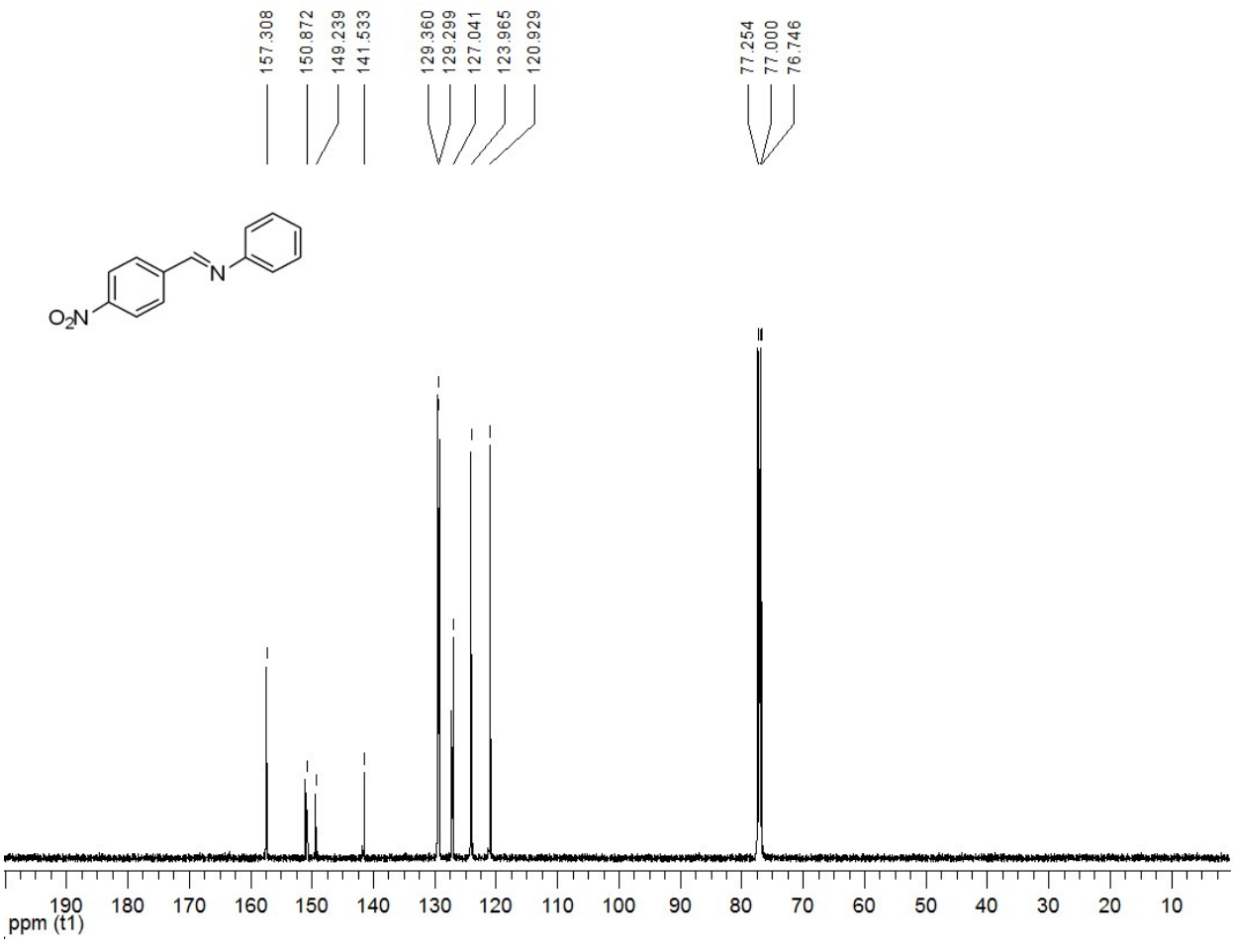

8.393
7.829
7.813
7.435
7.419
7.399
7.384
7.369
7.246
7.232
7.203
7.188
Cl
N
1.00
2.00
3.00
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

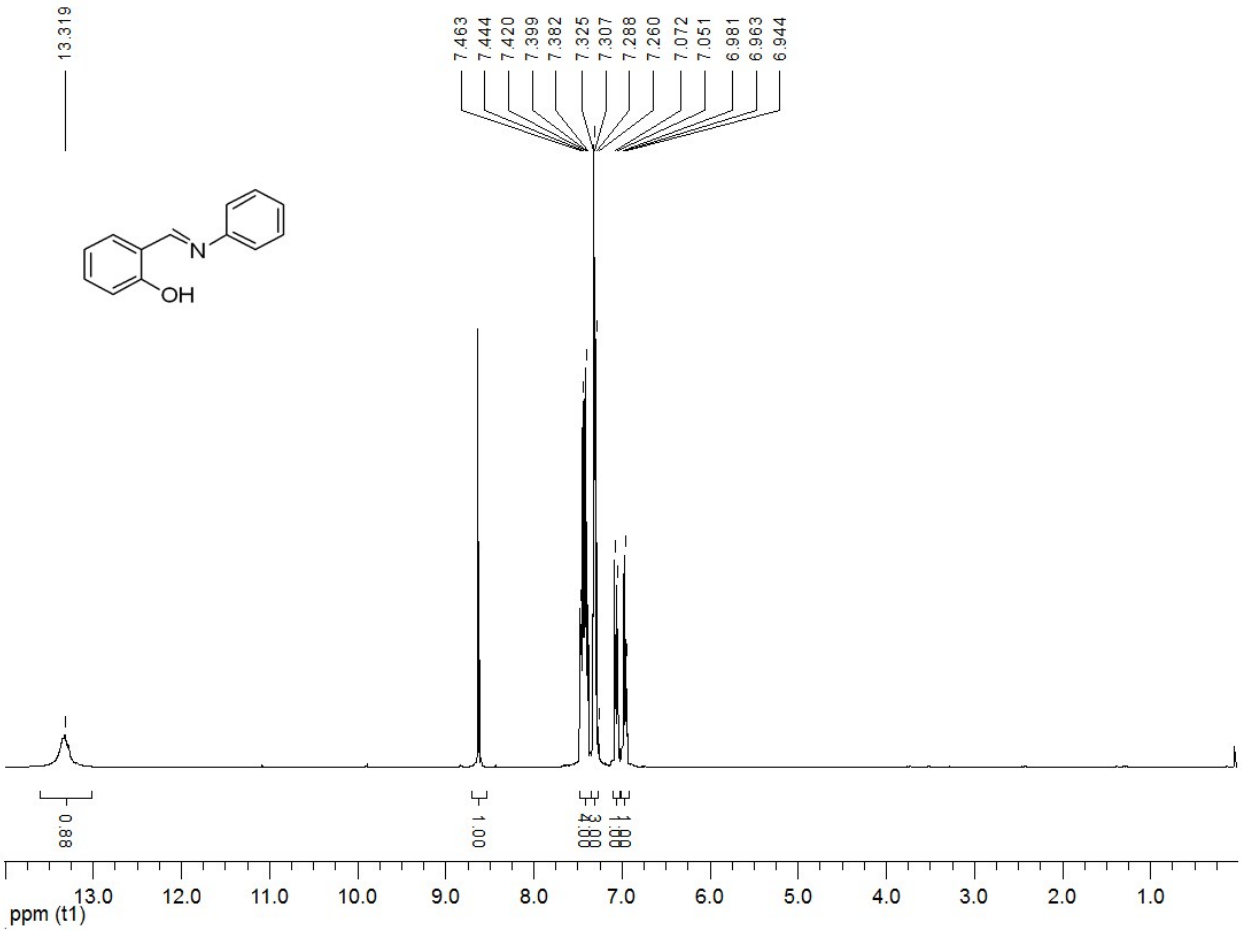

158.742
151.620
137.302
134.657
129.904
129.155
129.019
126.155
120.811
77.255
77.000
76.746
Cl
N
ppm (t1)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

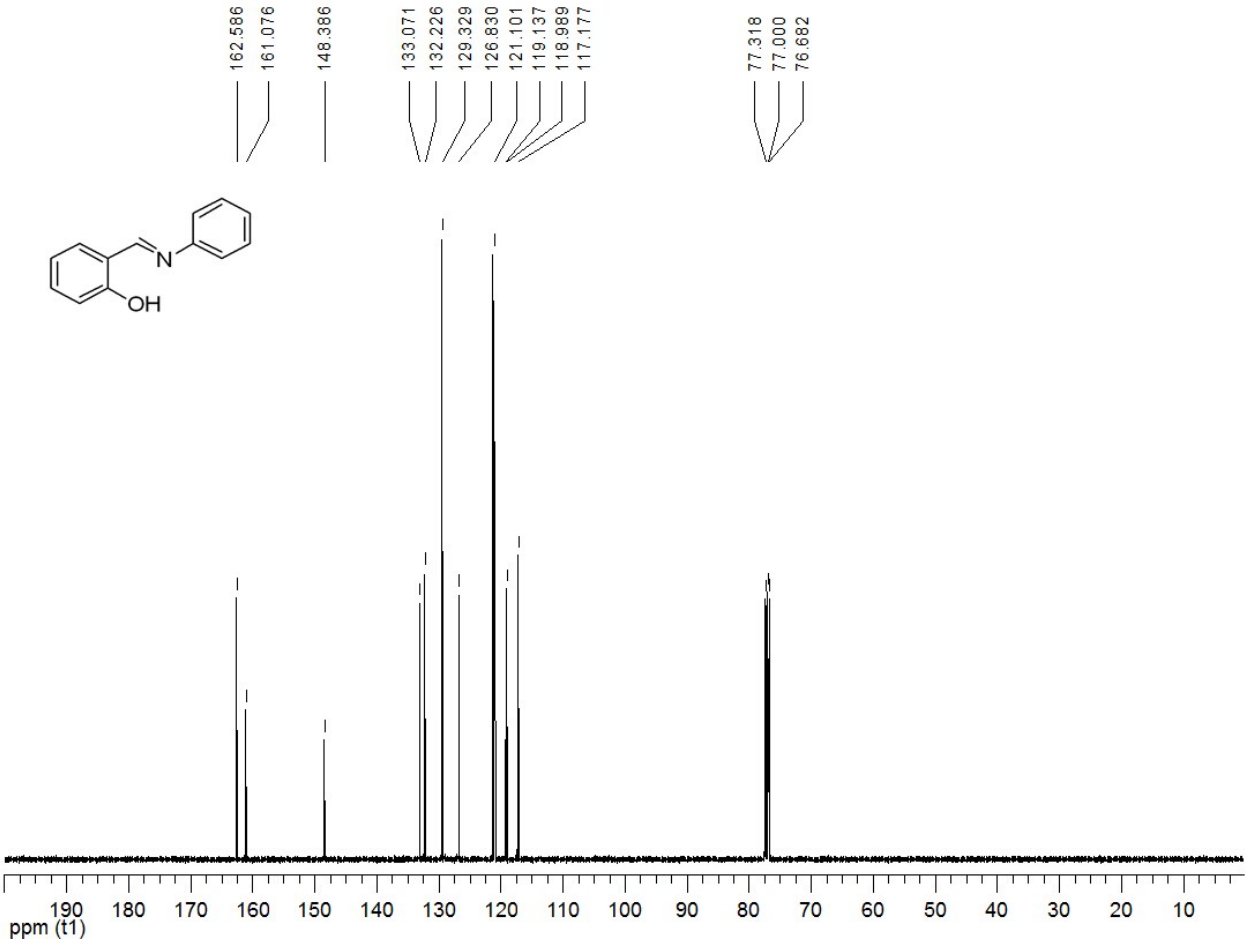

7.409
7.394
7.379
7.260
7.236
7.216
7.200
7.002
6.985
3.876
MeO
N
1.00
2.00
2.00
3.00
2.00
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

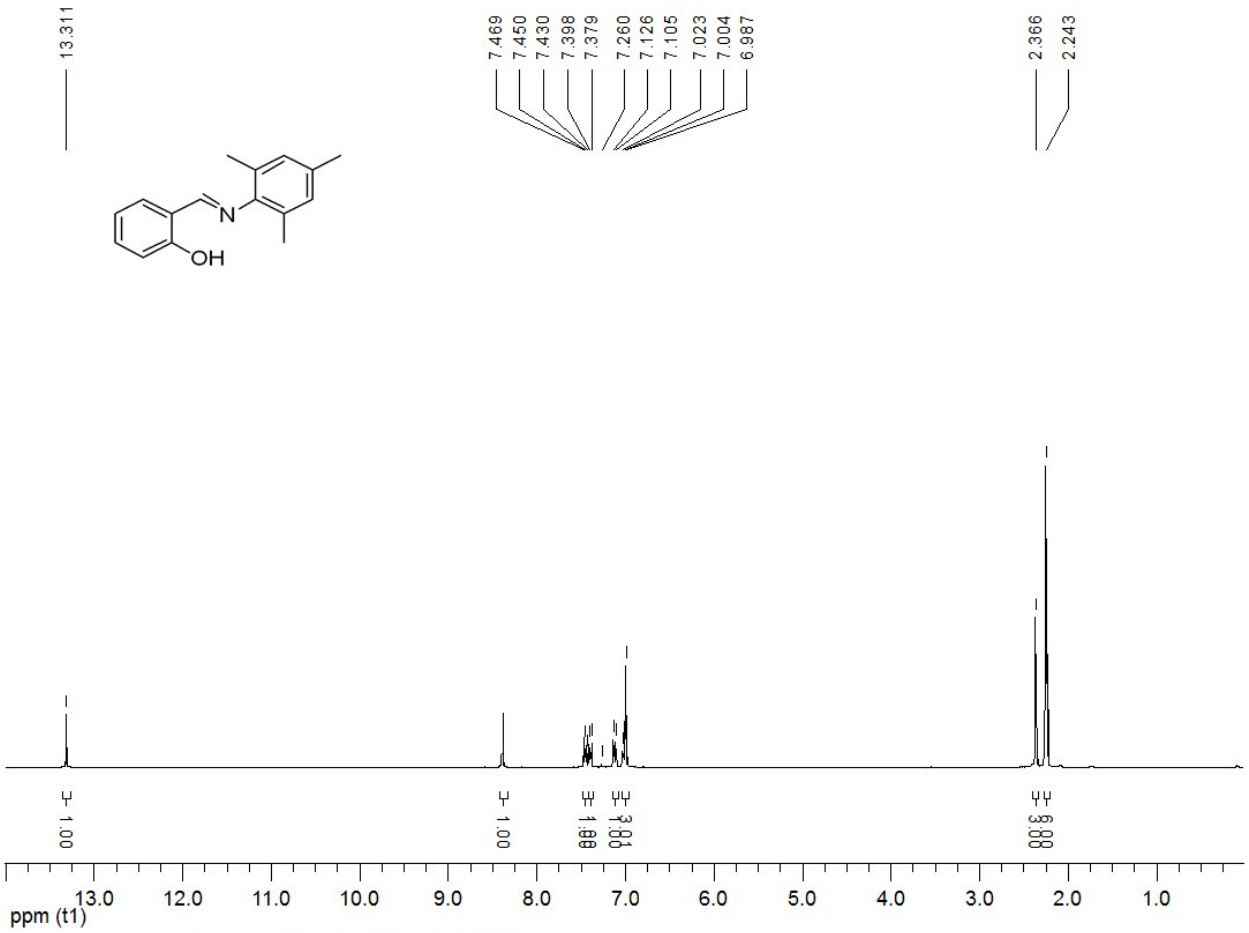

162.201
159.651
152.338
130.468
129.237
129.064
125.512
120.834
114.139
77.254
77.000
76.747
55.379
MeO
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

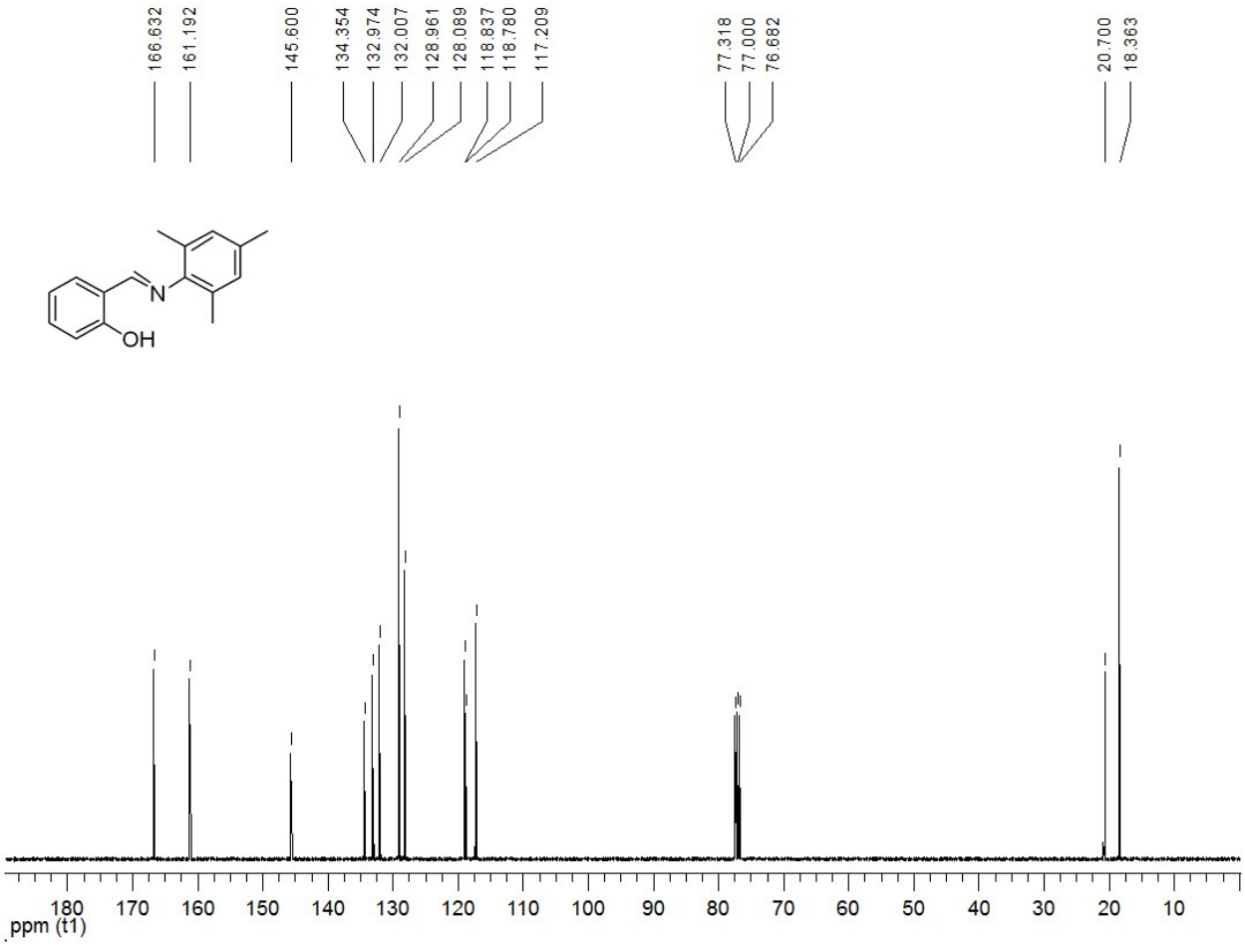

8.551
8.317
8.074
7.427
7.358
7.265
1.00
2.00
2.01
2.01
3.00
ppm (t1)

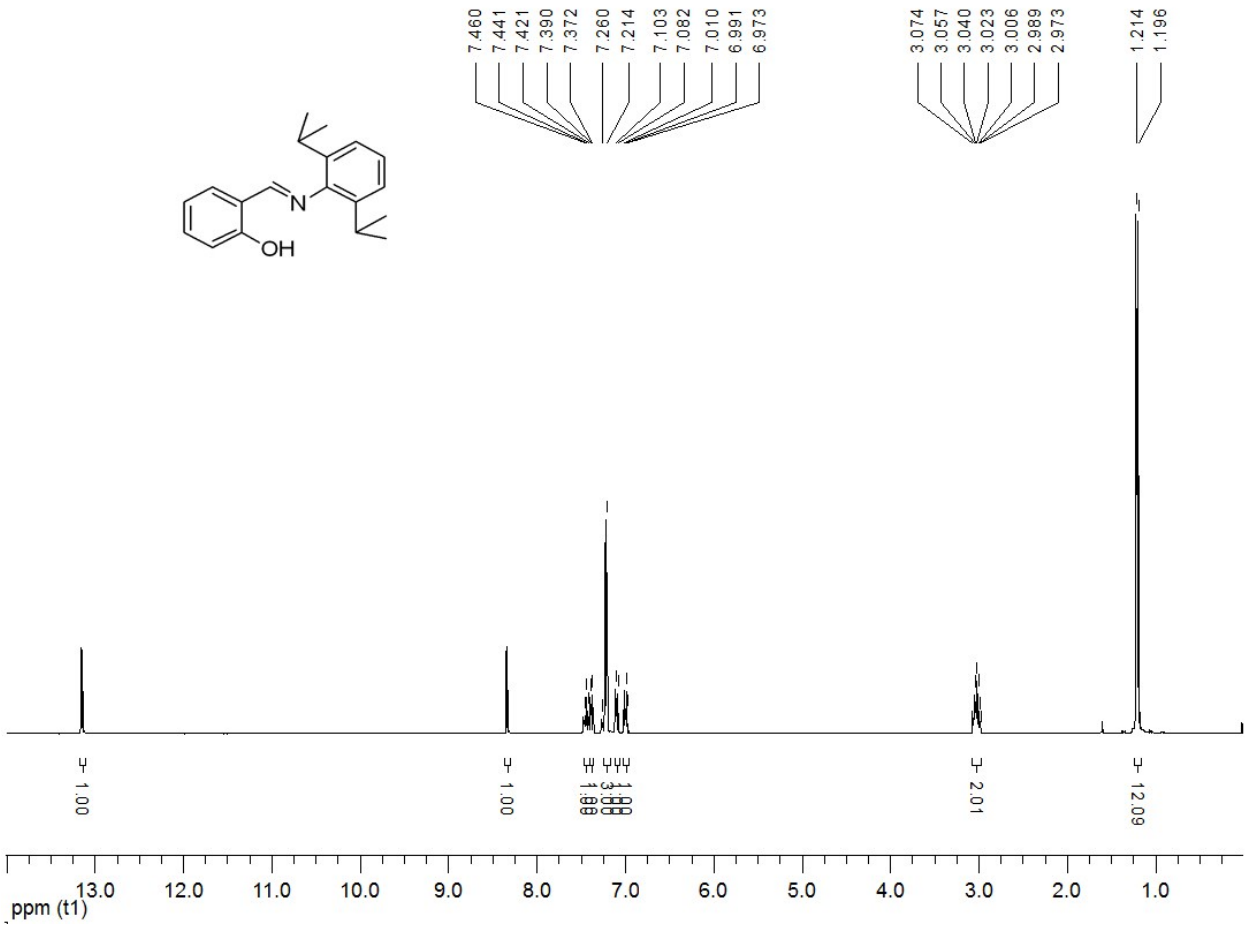

157.308
150.872
149.239
141.533
129.360
129.299
127.041
123.965
120.929
77.254
77.000
76.746
ppm (t1)

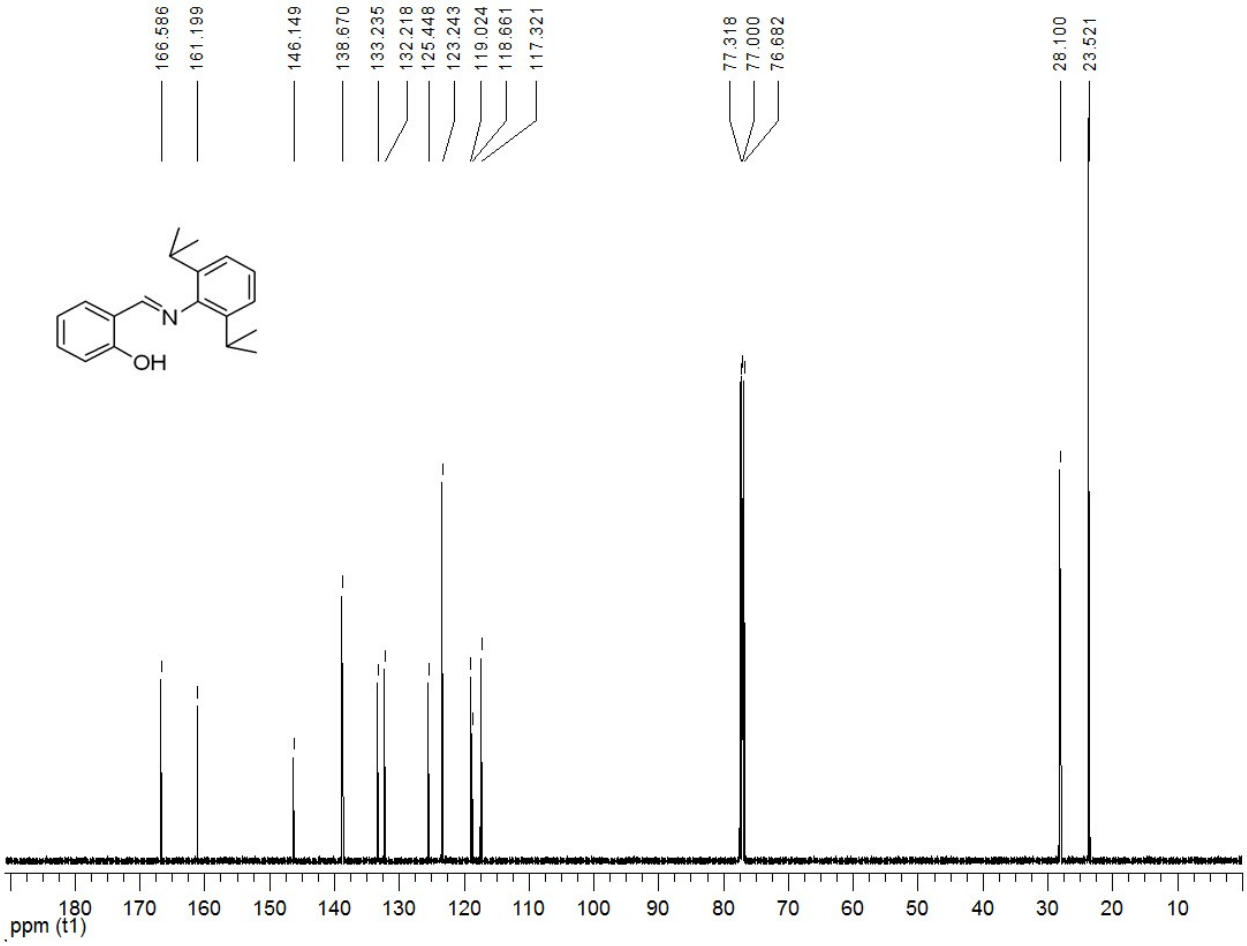

13.319
7.463
7.444
7.420
7.399
7.382
7.325
7.307
7.288
7.260
7.072
7.051
6.981
6.963
6.944
OH
0.88
1.00
2.88
1.88
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

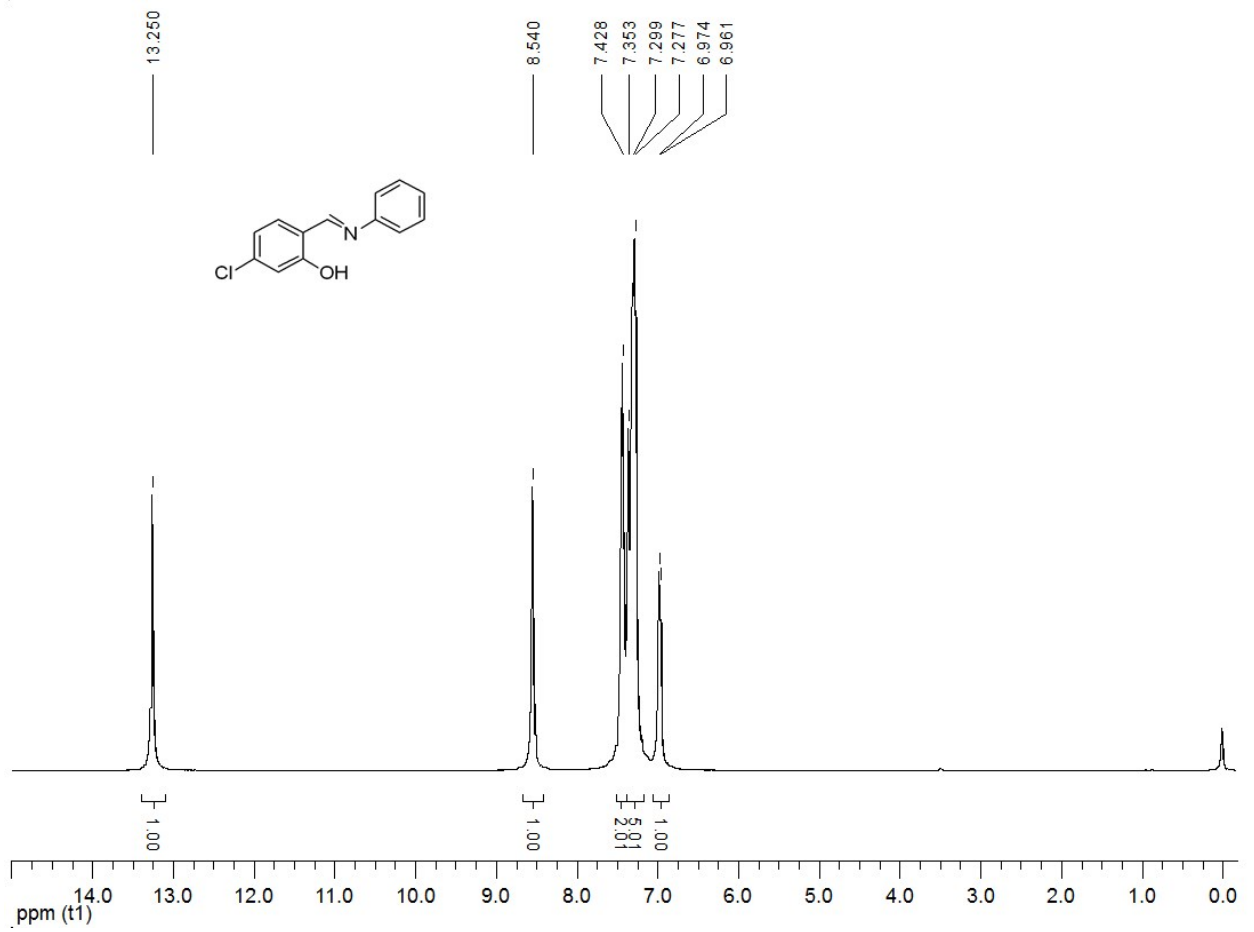

162.586
161.076
148.386
133.071
132.226
129.329
126.830
121.101
119.137
118.989
117.177
77.318
77.000
76.682
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

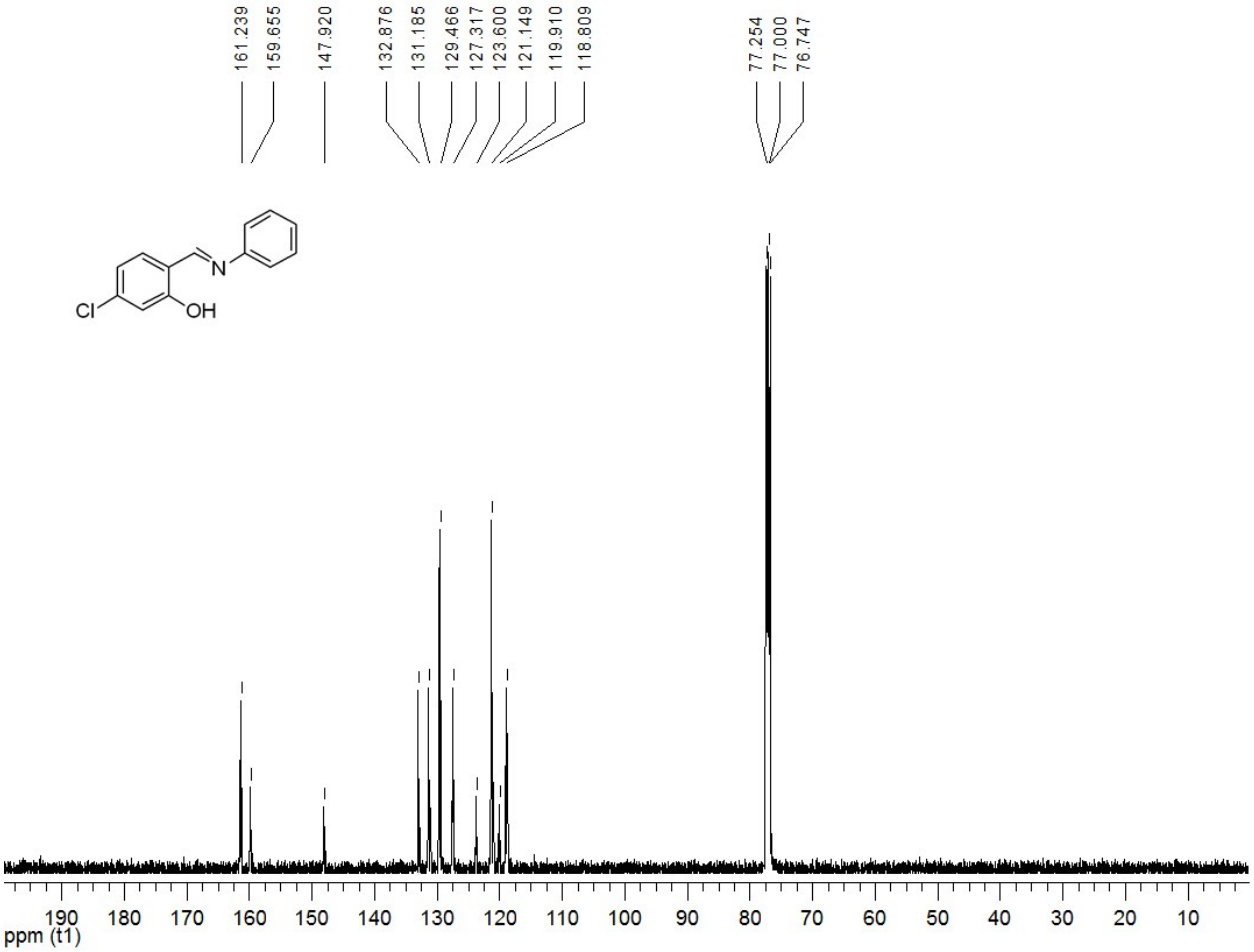

13.311
7.469
7.450
7.430
7.398
7.379
7.260
7.126
7.105
7.023
7.004
6.987
2.366
2.243
N
OH
1.00
1.00
1.98
3.04
8.08
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

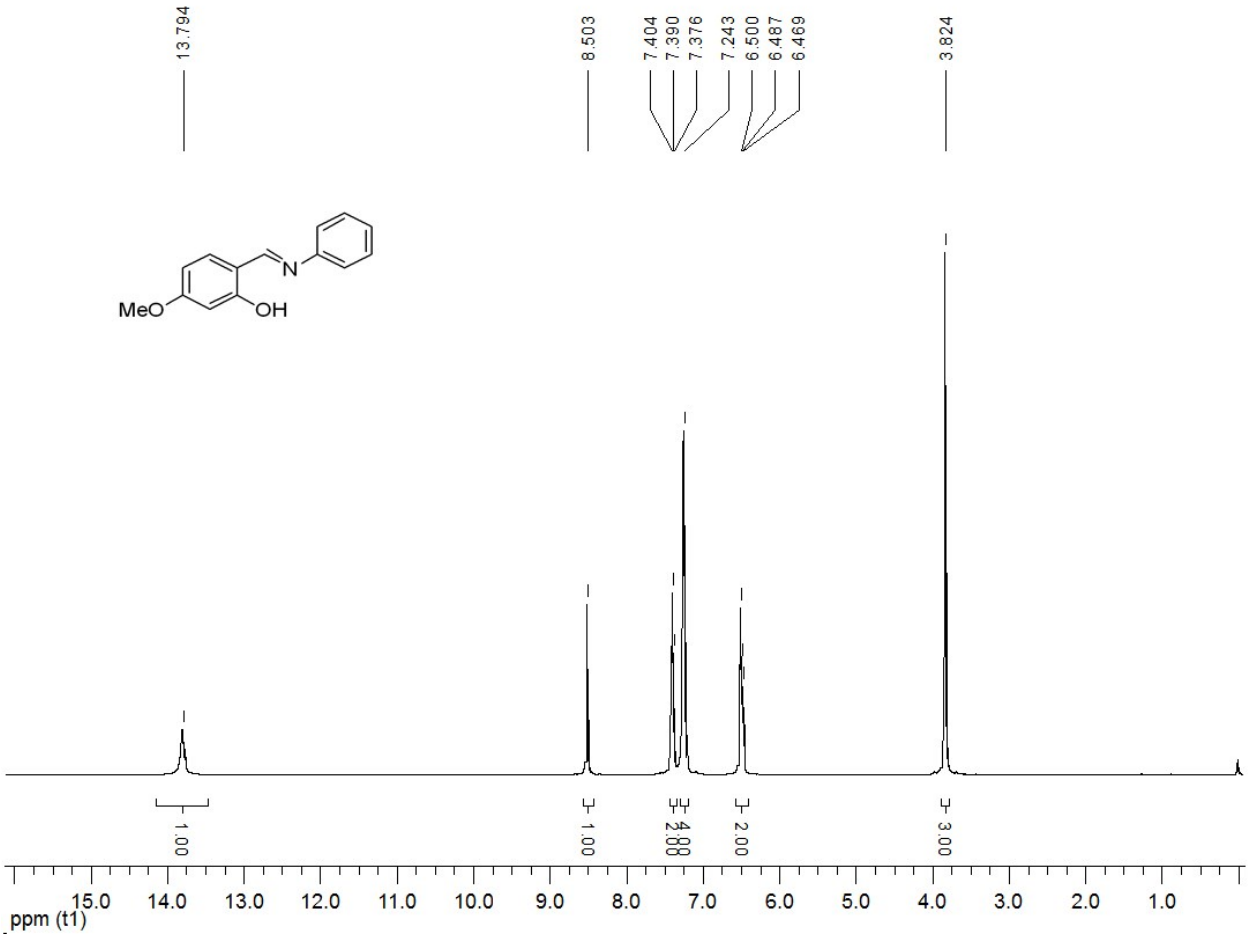

166.632
161.192
145.600
134.354
132.974
132.007
128.961
128.089
118.837
118.780
117.209
77.318
77.000
76.682
20.700
18.363
N
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

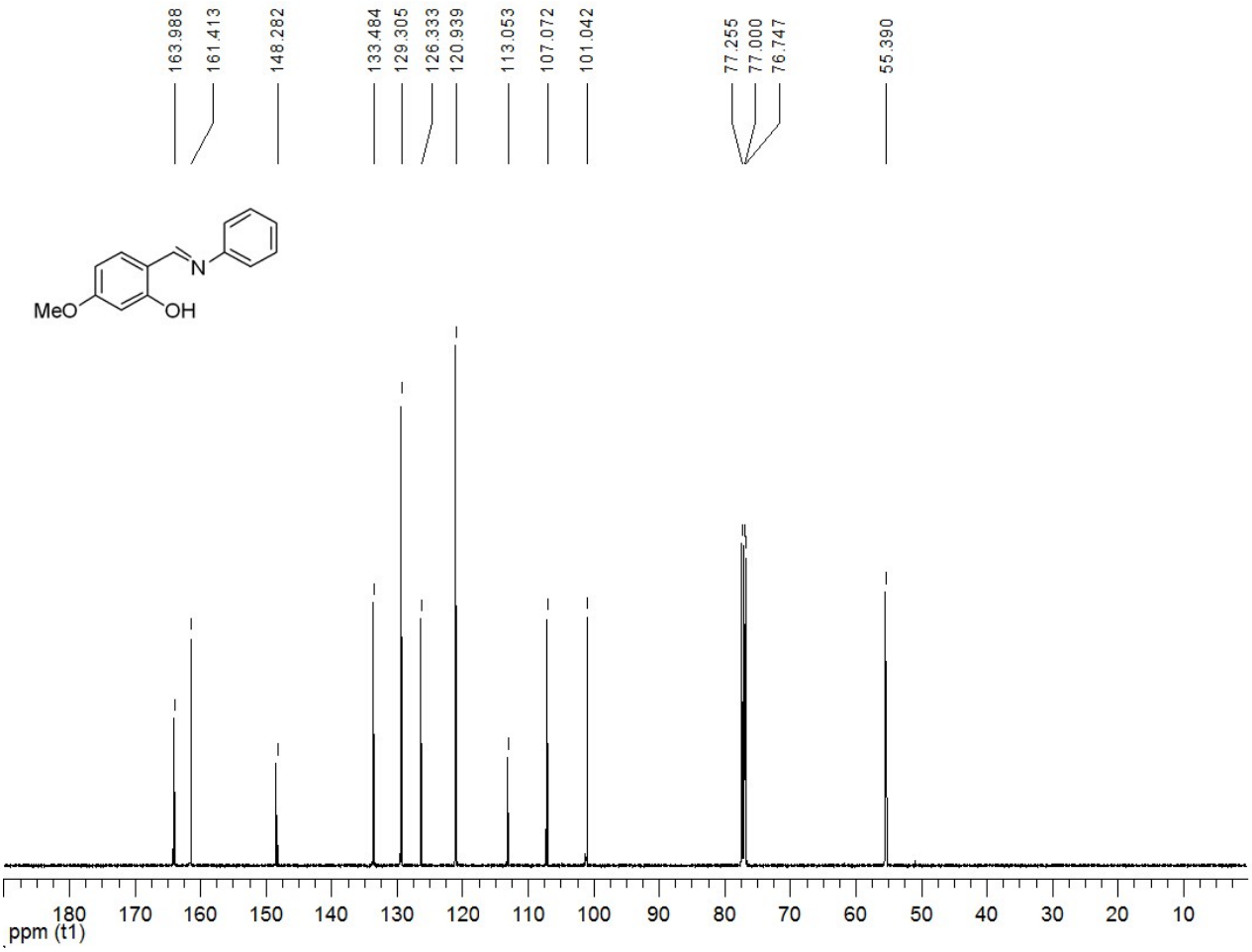

7.460
7.441
7.421
7.390
7.372
7.260
7.214
7.103
7.082
7.010
6.991
6.973
3.074
3.057
3.040
3.023
3.006
2.989
2.973
1.214
1.196
1.00
1.00
3.00
1.00
2.01
12.09
N
OH
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

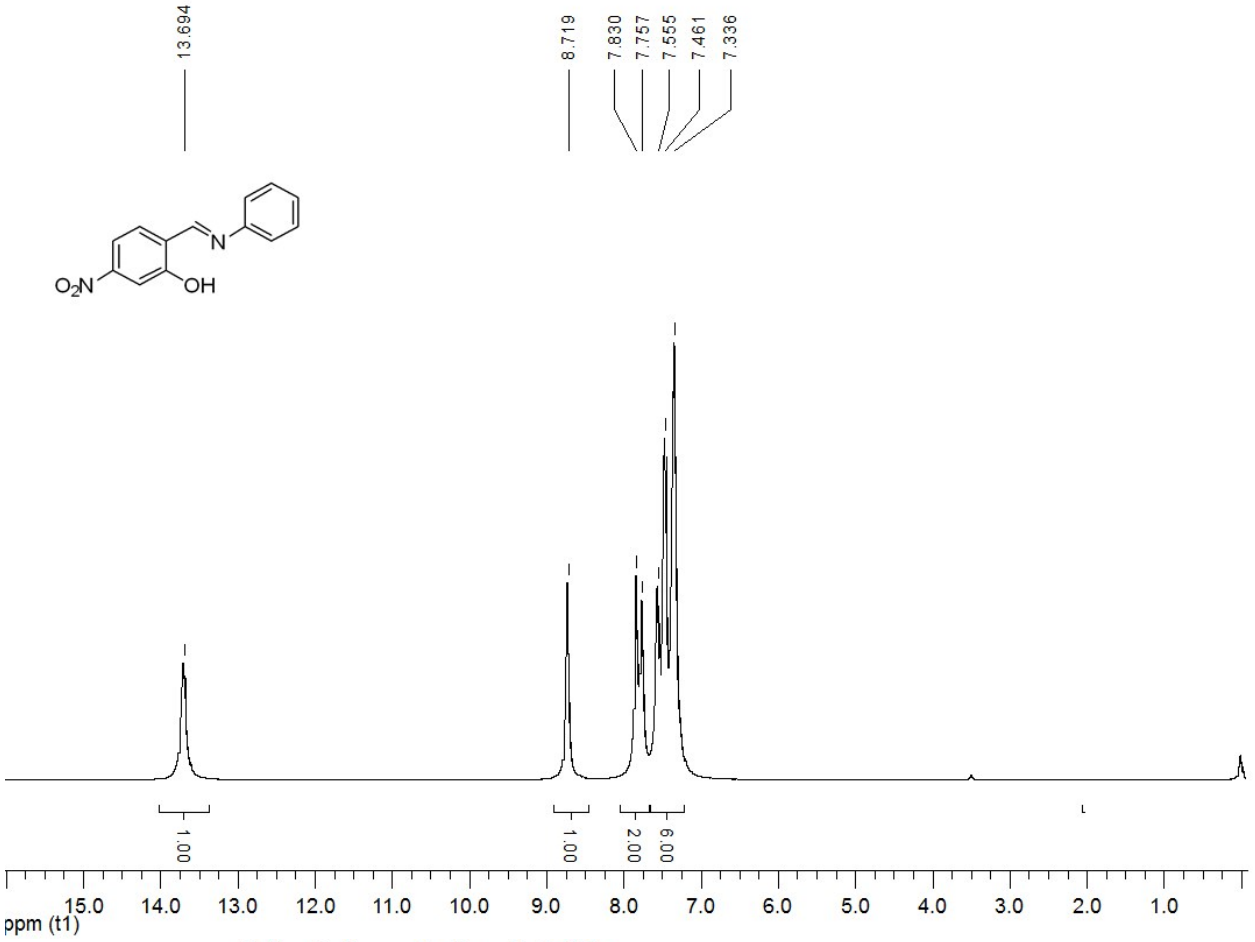

166.586
161.199
146.149
138.670
133.235
132.218
125.448
123.243
119.024
118.661
117.321
77.318
77.000
76.682
28.100
23.521
N
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

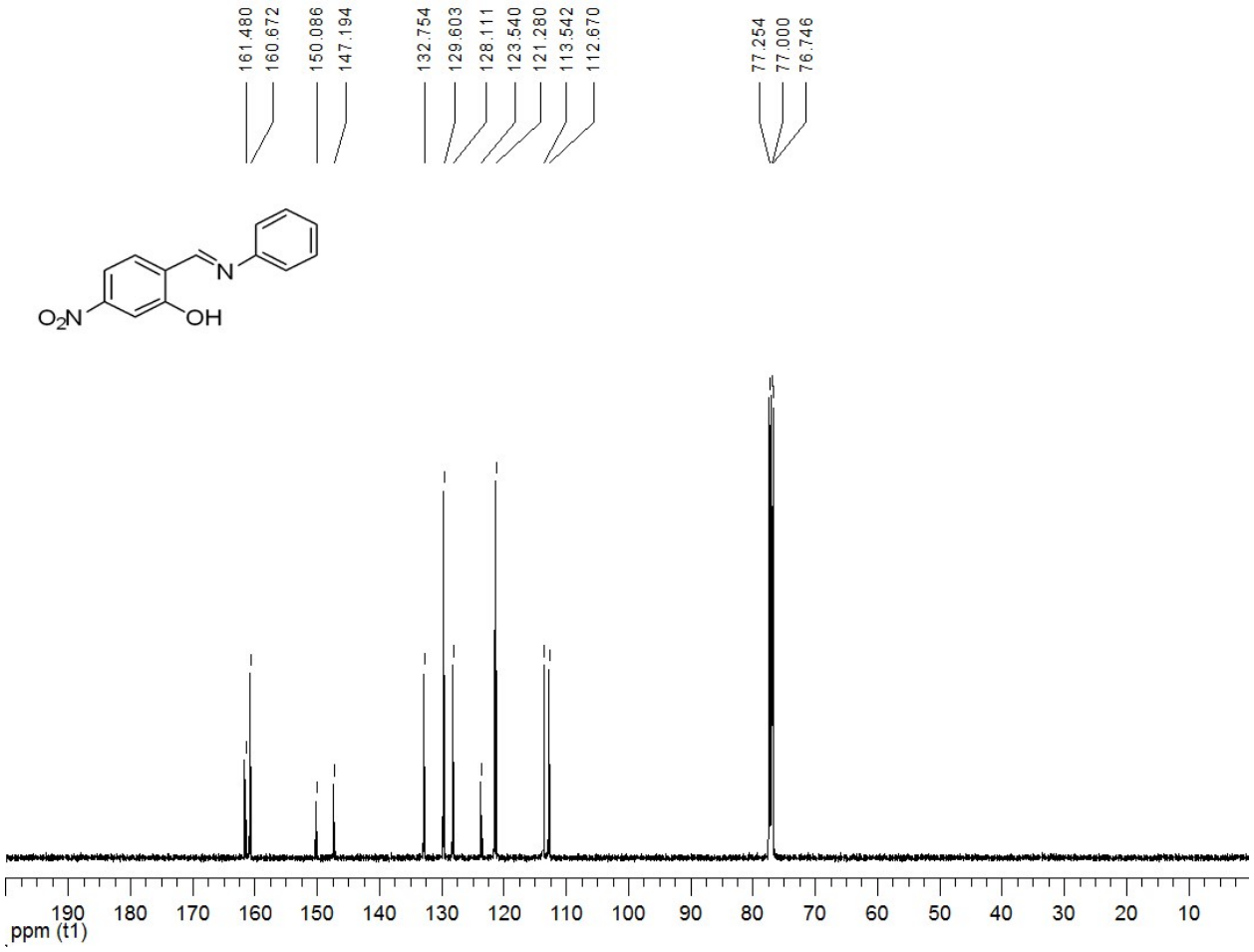

13.250
8.540
7.428
7.353
7.299
7.277
6.974
6.961
Cl
OH
N
1.00
1.00
2.01
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


161.239
159.655
147.920
132.876
131.185
129.466
127.317
123.600
121.149
119.910
118.809
77.254
77.000
76.747
Cl
OH
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


13.794
8.503
7.404
7.390
7.376
7.243
6.500
6.487
6.469
3.824
MeO
OH
1.00
1.00
4.08
2.00
3.00
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


163.988
161.413
148.282
133.484
129.305
126.333
120.939
113.053
107.072
101.042
77.255
77.000
76.747
55.390
MeO
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


13.694
8.719
7.830
7.757
7.555
7.461
7.336
O2N
OH
N
1.00
1.00
2.00
6.00
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


161.480
160.672
150.086
147.194
132.754
129.603
128.111
123.540
121.280
113.542
112.670
77.254
77.000
76.746
O2N
OH
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)