Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information

Iron catalysed nitrosation of olefins to oximes

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1. General information

All the reactions were performed in an autoclave in oven-dried glasswares under dihydrogen atmosphere, unless otherwise specified. Solvents were dried by standard procedures under argon and used immediately.[S1] Solvents were purchased from Merck, India and all other reagents and chemicals were obtained from Aldrich, USA. Only styrene substrates were purified by passing through a plug of activated alumina before use and other reagents were used as received. Column chromatography was performed by using a silica gel column (60-120 mesh, Merck India). TLC experiments were carried out on Merck silica gel 60 F_{254} pre-coated sheets and visualized by UV (254 nm) lamp.

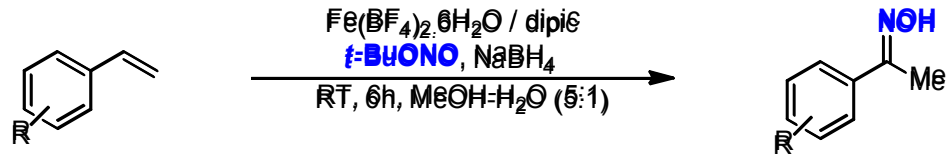
NMR spectra were recorded by 400 MHz Bruker spectrometer in $CDCl_3$. Chemical shift data are quoted as δ in ppm, coupling constants (J) are reported in Hertz (Hz) and s, d, dd, t, q, m and br represent singlet, doublet, doublet of doublet, triplet, quartet, multiplet and broad, respectively. HRMS spectra were recorded using micromass Q-TOF and BRUKER Maxis Impact mass spectrometer. GC analysis was done by Shimadzu GC-2014 gas chromatograph with a FID detector using a capillary column (112-2562 CYCLODEXB, from J & W Scientific, length 60 m, inner diameter 0.25 mm, film 0.25 μm) and GC-MS analysis was performed on an Agilent Technologies 7890A GC system coupled with 5975C inert XL EI/CI Mass Selective Detector (GCMSD) with its triple axis detector. XPS and TEM experiments were performed on MULTILAB from Thermo VG Scientific and PHILIPS CM200, respectively.

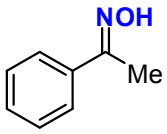
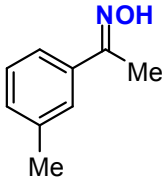
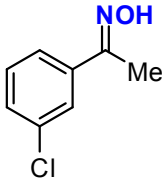
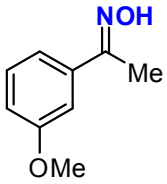
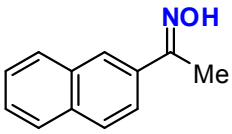
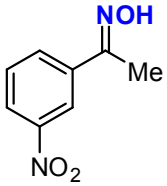
The yields of the *non-isolated products* were determined by ^{1}H NMR and/or by GC. Response factors for the alkenes and oximes were determined with respect to the internal standard, *n*-dodecane (3 mmol) for the GC-yield analysis. 1.0 μL aliquot was subjected for the analysis by GC-FID in each case. ^{1}H NMR yield was evaluated using 3 mmol of PhTMS as an internal standard which was added after the synthetic work-up i.e. just prior to the NMR analysis.

2. General procedure for the synthesis of oximes, 2a-2u

An autoclave was charged under argon atmosphere with iron(II) tetrafluoroborate hexahydrate ($Fe(BF_4)_2.6H_2O$) (10 mg, 0.03 mmol) as the transition metal catalyst in combination with 2,6-pyridinedicarboxylic acid (dipic) (5 mg, 0.03 mmol) as the co-ligand, $NaBH_4$ (170 mg, 4.5 mmol), *t*-BuONO (463.5 mg, 4.5 mmol), the corresponding olefin (3 mmol), MeOH (5 mL) and H_2O (1 mL). Then, the autoclave was filled with 10 bar of H_2 and the reaction mixture was stirred for 6h at room temperature. The mixture was then neutralized with 1N HCl and extracted with diethyl ether (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The resultant material was then passed through a silica gel column using pet ether: ethyl acetate as the eluent to isolate the desired product. The oxime products were confirmed and GC yields were calculated based on the calibration with authenticated products and GC-MS spectra were also compared. All the oximes reported in this work are previously reported in the literature (except **2f**, **2n**, **2p**, **2q** and **2s**).[S2-S12] All the reactions were performed thrice to establish the reproducibility and reliability. Moreover, products were isolated in respective cases to ensure the general applicability of the said reaction protocol (Figure S1-S36).

Table S1 A comparative study showing the difference in yields of the desired product under dihydrogen pressure and normal atmospheric conditions.[a]

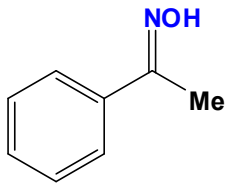


Substrate	Yield (%) (under H_2 pressure= 10bar)[b]	Yield (%) (under normal atm pressure)[b]
	99 (90)	82 (75)
	98 (89)	75
	95 (88)	78
	98 (90)	73
	98 (90)	70
	99 (92)	60

[a]Reaction conditions: 3 mmol of styrene, 1 mol% $Fe(BF_4)_2.6H_2O$, 1 mol% dipic, 1.5 equiv $NaBH_4$ and 1.5 equiv *t*-BuONO in 5 mL MeOH and 1 mL H_2O, 6h at room temperature. [b]Yields determined by GC after the reaction, isolated yield is given in parenthesis.

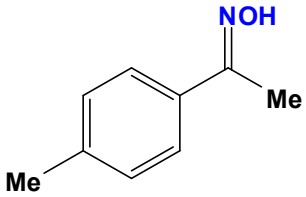
Details of product characterisation

Acetophenone oxime (2a) [S2-S7, S9]



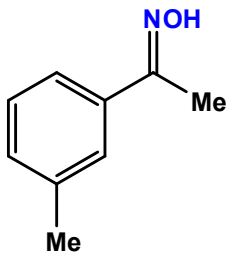
White Solid; Yield 90% ; IR υ_{max} (KBr)/cm^{-1} 3236, 3089, 2932, 1501, 1443, 1368, 1375, 1296, 1085, 1002, 925, 848, 775, 752, 685, 655 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.9 (br s, 1H), 7.70-7.60 (m, 2H), 7.45-7.25 (m, 3H), 2.30 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.2, 136.6, 129.4, 128.7, 126.2, 12.5 ; HRMS(ESI+): $C_8H_{10}NO$ m/z 136.0760 (Calcd. for $[M+H^+]$: 136.0762).

1-(4-Methylphenyl)ethanone oxime (2b) [S2-S4, S6]



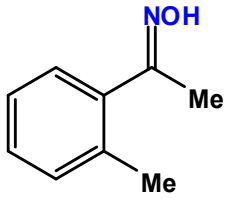
White Solid; Yield 82% ; IR υ_{max} (KBr)/cm^{-1} 3285, 3225, 3134, 3058, 3037, 2922, 1612, 1518, 1442, 1365, 1318, 1297, 1185, 1112, 1001, 927, 821, 752, 710 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (br s, 1H), 7.50 (d, J= 8.2 Hz, 2H), 7.20 (d, J= 8.2 Hz, 2H), 2.35 (s, 3H), 2.25 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.1, 139.4, 133.8, 129.3, 126.1, 21.4, 12.4 ; HRMS(ESI+): $C_9H_{12}NO$ m/z 150.0915 (Calcd. for $[M+H^+]$: 150.0918).

1-(3-Methylphenyl)ethanone oxime (2c) [S4]



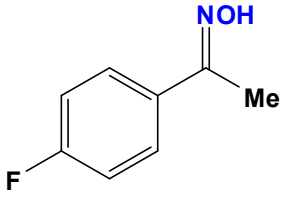
White Solid; Yield 89% ; IR υ_{max} (KBr)/cm^{-1} 3305, 3254, 3047, 2922, 2865, 1645, 1598, 1580, 1510, 1453, 1372, 1307, 1205, 1092, 1011, 945, 907, 852, 780, 751, 697, 655; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (br s, 1H), 7.40 (s, 1H), 7.25 (s, 1H), 7.15 (s, 1H), 7.05 (s, 1H), 2.35 (s, 3H), 2.25 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3, 138.2, 136.6, 130.1, 128.5, 126.8, 123.4, 21.6, 12.6 ; HRMS(ESI+): $C_9H_{12}NO$ m/z 150.0917 (Calcd. for [M+H^+]: 150.0918).

1-(2-Methylphenyl)ethanone oxime (2d) [S2-S4, S9, S11]



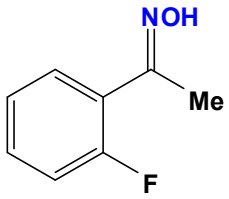
White Solid; Yield 85% ; IR υ_{max} (KBr)/cm^{-1} 3223, 3057, 3027, 2928, 1492, 1447, 1369, 1318, 1268, 1009, 927, 755, 722 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (br s, 1H), 7.35-7.20 (m, 2H), 7.20-7.10 (m, 2H), 2.35 (s, 3H), 2.20 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 137.5, 135.7, 130.7, 128.6, 128.2, 125.9, 20.1, 16.1 ; HRMS(ESI+): $C_9H_{12}NO$ m/z 150.0919 (Calcd. for [M+H^+]: 150.0918).

1-(4-Fluorophenyl)ethanone oxime (2e) [S4, S7]



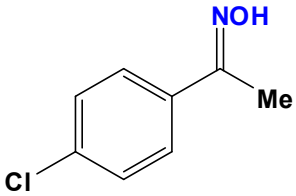
White Solid; Yield 90% ; IR υ_{max} (KBr)/cm^{-1} 3330, 3221, 3085, 2933, 1645, 1600, 1512, 1237, 1157, 1010, 927, 835, 821, 745 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (br s, 1H), 7.60 (d, J= 8.6 Hz, 2H), 7.10 (d, J= 8.6 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.8, 155.3, 132.7, 128.1, 115.8, 12.5 ; HRMS(ESI+): C_8H_9FNO m/z 154.0667 (Calcd. for [M+H^+]: 154.0668).

1-(2-Fluorophenyl)ethanone oxime (2f)



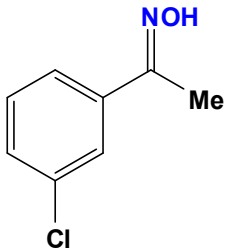
White Solid; Yield 85% ; IR υ_{max} (KBr)/cm^{-1} 3295, 3217, 3085, 2944, 1655, 1600, 1515, 1245, 1157, 1007, 921, 835, 827, 755 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.9 (br s, 1H), 7.50-7.40 (m, 1H), 7.35-7.25 (m, 1H), 7.20-7.10 (m, 2H) 2.30 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.3, 154.2, 130.9, 129.5, 125.3, 124.4, 116.5, 14.9 ; HRMS(ESI+): C_8H_9FNO m/z 154.0665 (Calcd. for $[M+H^+]$: 154.0668).

1-(4-Chlorophenyl)ethanone oxime (2g)[S2-S3, S6-S8, S9]



White Solid; Yield 82% ; IR υ_{max} (KBr)/cm^{-1} 3285, 3224, 3220, 3207, 3057, 2937, 1601, 1495, 1385, 1369, 1309, 1095, 1009, 925, 827 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.0 (br s, 1H), 7.55 (d, *J*= 8.8 Hz, 2H), 7.35 (d, *J*= 8.7 Hz, 2H), 2.30 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3, 135.4, 135.0, 128.8, 127.5, 12.3 ; HRMS(ESI+): C_8H_9ClNO m/z 170.0373 (Calcd. for $[M+H^+]$: 170.0372).

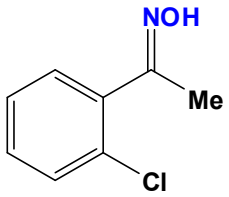
1-(3-Chlorophenyl)ethanone oxime (2h)[S2, S12]



White Solid; Yield 88% ; IR υ_{max} (KBr)/cm^{-1} 3295, 3237, 3065, 2925, 1685, 1520, 1421, 1370, 1295, 1095, 1012, 945, 885, 784, 721, 685 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (br s, 1H),

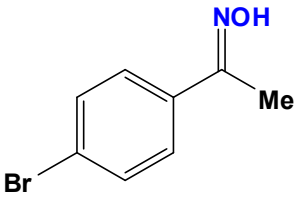
7.45-7.15 (m, 4H), 2.25 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 136.7, 132.7, 130.1, 129.8, 128.2, 127.0, 15.9 ; HRMS(ESI+): C_8H_9ClNO m/z 170.0371 (Calcd. for [M+H$^+$]: 170.0372).

1-(2-Chlorophenyl)ethanone oxime (2i)[S2-S3, S9]



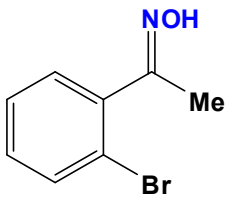
White Solid; Yield 91% ; IR υ_{max} (KBr)/cm^{-1} 3294, 3238, 3145, 3092, 3072, 3055, 2932, 1575, 1435, 1368, 1315, 1025, 925, 745, 721 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (br s, 1H), 7.50-7.20 (m, 4H), 2.25 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.1, 136.8, 132.7, 130.1, 127.0, 15.9 ; HRMS(ESI+): C_8H_9ClNO m/z 170.0373 (Calcd. for [M+H$^+$]: 170.0372).

1-(4-Bromophenyl)ethanone oxime (2j)[S2, S6]



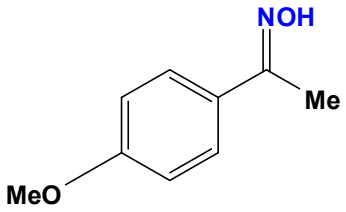
White Solid; Yield 78% ; IR υ_{max} (KBr)/cm^{-1} 3285, 3097, 2925, 1605, 1485, 1388, 1365, 1312, 1009, 928, 825, 765, 754 ; ^{1}H NMR (400 MHz, $CDCl_3$): 9.50 (br, s), 7.60-7.40 (m, 4H), 2.25 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.4, 135.6, 131.8, 127.7, 123.7, 12.1 ; HRMS(ESI+): C_8H_9BrNO m/z 213.9865 (Calcd. for [M+H$^+$]: 213.9867).

1-(2-Bromophenyl)ethanone oxime (2k)[S3, S9]



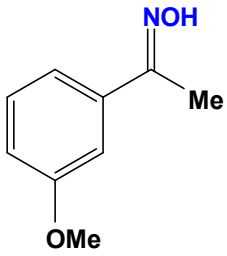
White Solid; Yield 88% ; IR υ_{max} (KBr)/cm^{-1} 3290, 3088, 2924, 1610, 1512, 1389, 1375, 1310, 1007, 925, 822, 765, 754; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (br s, 1H), 7.35-7.15 (m, 4H), 2.25 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$):155.5, 138.8, 137.3, 133.2, 130.2, 127.5, 121.8, 16.19 ; HRMS(ESI+): C_8H_9BrNO m/z 213.9867 (Calcd. for [M+H^+]: 213.9867).

1-(4-Methoxyphenyl)ethanone oxime (2l)[S2-S4, S6, S9]



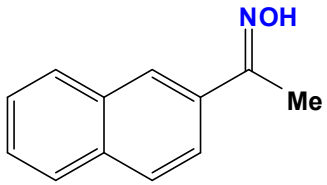
White Solid; Yield 81% ; IR υ_{max} (KBr)/cm^{-1} 3209, 3085, 2997, 2965, 2938, 2845, 1612, 1515, 1287, 1242, 1175, 1021, 925, 822, 745 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (br s, 1H), 7.55 (d, *J*= 8.8 Hz, 2H), 6.85 (d, *J*= 8.8 Hz, 2H),3.85 (s, 3H), 2.25 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): 160.6, 155.6 129.2, 127.5, 114.0, 55.4, 12.3 ; HRMS(ESI+): $C_9H_{12}NO_2$ m/z 166.0862 (Calcd. for [M+H^+]: 166.0868).

1-(3-Methoxyphenyl)ethanone oxime (2m)[S10]



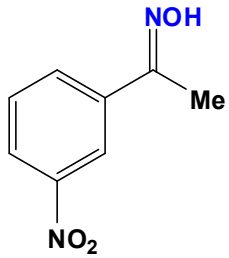
White Solid; Yield 90% ; IR υ_{max} (KBr)/cm^{-1} 3228, 3070, 3055, 3010, 2975, 2938, 2836, 1585, 1427, 1295, 1176, 1032, 925, 827, 735; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (br s, 1H), 7.30 (s, 1H), 7.20 (m, 2H), 6.90 (m,1H), 3.8 (s, 3H), 2.30 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): 159.7, 156.1, 138.0, 129.6, 118.7, 115.2, 111.5, 55.4, 12.6 ; HRMS(ESI+): $C_9H_{12}NO_2$ m/z 166.0867 (Calcd. for [M+H^+]: 166.0868).

1-(naphthalen-2-yl)ethanone oxime (2n)



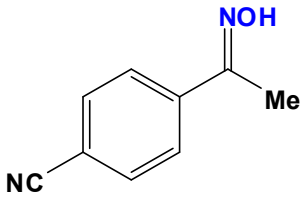
White Solid; Yield 90% ; IR υ_{max} (KBr)/cm^{-1} 3254, 3057, 2965, 1610, 1514, 1495, 1421, 1365, 1353, 1210, 1150, 1065, 988, 908, 897, 810, 727, 625, 610 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (br s, 1H), 8.05 (m, 1H), 7.85 (m, 4H), 7.45 (m, 2H), 2.40 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$):156.1, 133.9, 133.8, 133.2, 128.6, 128.3, 127.8, 126.8, 126.5, 126.1, 123.4, 12.3 ; HRMS(ESI+): $C_{12}H_{12}NO$ m/z 186.0915 (Calcd. for [M+H^+]: 186.0918).

1-(3-Nitrophenyl)ethanone oxime (2o)[S3, S8-S9]



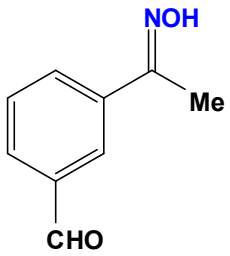
White Solid; Yield 92% ; IR υ_{max} (KBr)/cm^{-1} 3265, 3070, 2965, 2870, 1645, 1610, 1605, 1577, 1518, 1505, 1444, 1385, 1350, 1260, 1155, 925, 828, 735 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.5 (s, 1H), 8.25 (d, *J*= 8.3Hz, 1H), 8.0 (d, *J*= 8.3Hz, 1H), 7.55 (t, *J*= 7.5Hz, 1H), 2.35 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.3, 138.3, 131.9, 129.6, 124.0, 121.2, 12.1 ; HRMS(ESI+): $C_8H_9N_2O_3$ m/z 181.061 (Calcd. for [M+H^+]: 181.061).

1-(4-Cyanophenyl)ethanone oxime (2p)



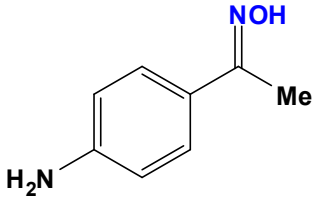
White Solid; Yield 48% ; IR υ_{max} (KBr)/cm^{-1} 3264, 2960, 2875, 2205, 1648, 1610, 1597, 1574, 1514, 1501, 1434, 1385, 1262, 928, 817, 721 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (br s, 1H), 7.75 (d, *J*= 8.2 Hz, 2H), 7.65 (d, *J*= 8.2 Hz, 2H), 2.30 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5, 140.8, 132.4, 126.7, 118.6, 112.6, 11.8 ; HRMS(ESI+): $C_9H_9N_2O$ m/z 161.0712 (Calcd. for $[M+H^+]$: 161.0714).

3-(1-hydroxyiminoethyl)benzaldehyde (2q)



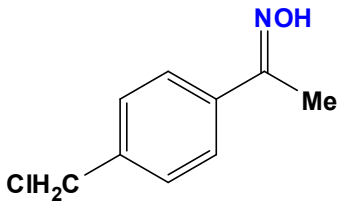
White Solid; Yield 34% ; IR υ_{max} (KBr)/cm^{-1} 3257, 3077, 2967, 2720, 2874, 1715, 1642, 1618, 1601, 1585, 1510, 1498, 1440, 1362, 1265, 877, 815, 715 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.5 (br s, 1H), 9.5 (s, 1H), 8.20 (m, 2H), 8.05 (m, 1H), 7.71 (m, 1H), 2.35 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.0, 155.2, 137.0, 134.5, 134.0, 129.1, 129.3, 12.3 ; HRMS(ESI+): $C_9H_{10}NO_2$ m/z 164.0710 (Calcd. for $[M+H^+]$: 164.0711).

1-(4-Aminophenyl)ethanone oxime (2r)[S8]



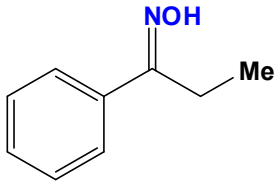
White Solid; Yield 32% ; IR υ_{max} (KBr)/cm^{-1} 3410, 3335, 3215, 3065, 2954, 2880, 1905, 1610, 1512, 1455, 1410, 1325, 1264, 1165, 1107, 1008, 925, 857, 788, 722, 685, 654, 623; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.5 (br s, 1H), 7.40 (d, *J*= 8.4 Hz, 2H), 6.60 (d, *J*= 8.4 Hz, 2H), 5.32 (br s, 2H), 2.35 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.2, 150.7, 130.0, 126.8, 114.3, 12.3; HRMS(ESI+): $C_8H_{11}N_2O$ m/z 151.0874 (Calcd. for $[M+H^+]$: 151.0871).

1-(4-Choloromethylphenyl)ethanone oxime (2s)



White Solid; Yield 92%, IR υ_{max} (KBr)/cm^{-1} 3265, 2924, 2855, 1642, 1612, 1605, 1580, 1510, 1495, 1437, 1365, 1258, 924, 822, 755, 720 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (br s, 1H), 7.60 (d, *J*= 8.5 Hz, 2H), 7.40 (d, *J*= 8.5 Hz, 2H), 4.55 (s, 2H), 2.30 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.6, 138.5, 136.6, 128.8, 126.5, 45.8, 12.5 ; HRMS(ESI+): $C_9H_{11}NOCl$ m/z 184.0527 (Calcd. for $[M+H^+]$: 184.0529).

Propiophenone oxime (2t-2u)[S2, S4]



White Solid; Yield 62% (substrate: trans-β-methyl styrene), 58% (substrate: cis-β-methyl styrene); IR υ_{max} (KBr)/cm^{-1} 3294, 3185, 2985, 2945, 2885, 1465, 1455, 1348, 1288, 1097, 1075, 1047, 975, 920, 764, 685 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (br s, 1H), 7.65-7.55 (m, 2H), 7.45-7.25 (m, 3H), 2.8 (q, *J*= 7.2Hz, 2H), 1.3 (t, *J*= 7.2Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0, 135.7, 129.3, 128.7, 126.4, 19.8, 11.1 ; HRMS(ESI+): $C_9H_{12}NO$ m/z 150.0915 (Calcd. for $[M+H^+]$: 150.0918).

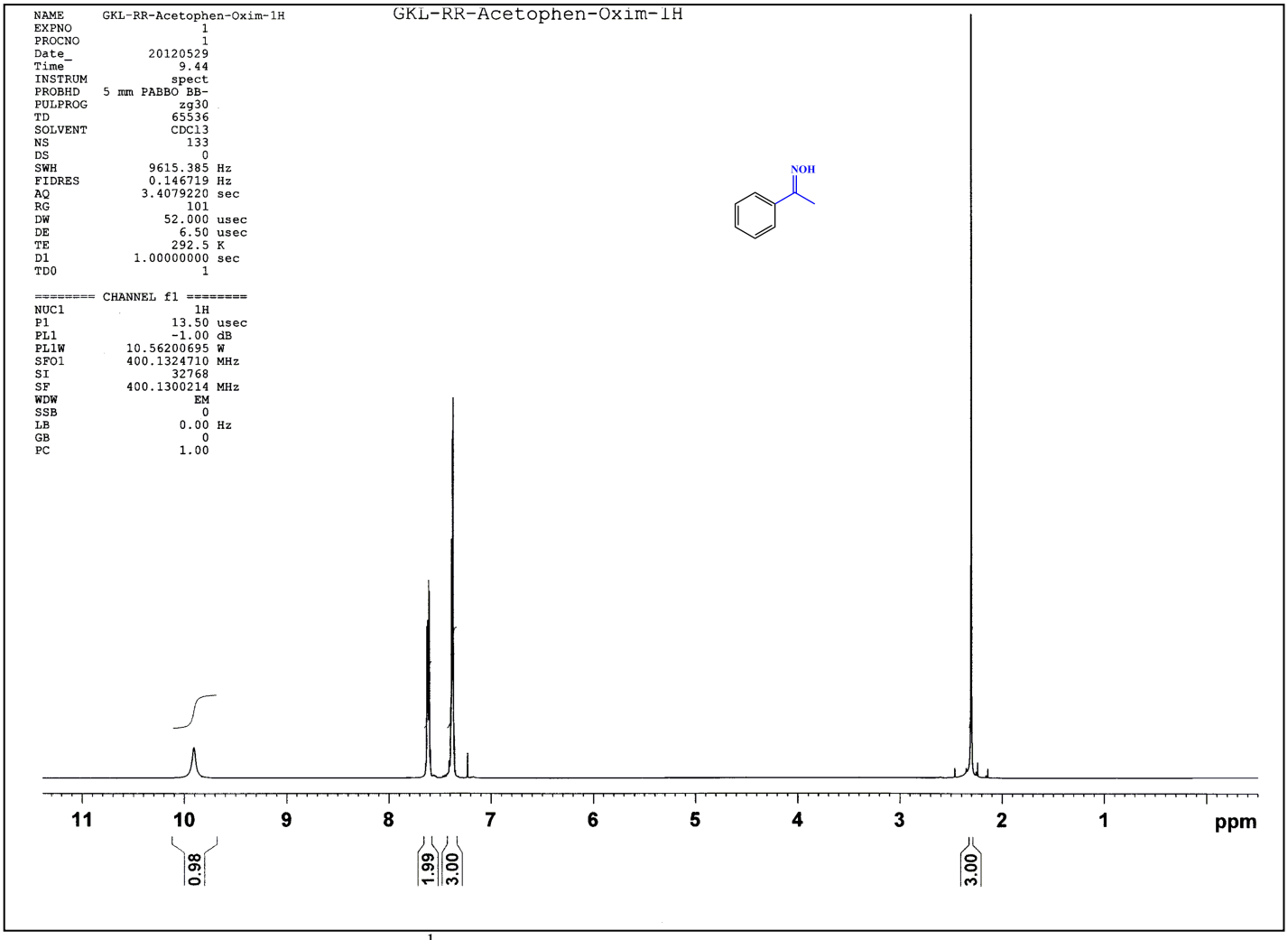


Figure S1. ^{1}H NMR spectrum of Acetophenone oxime (**2a**).

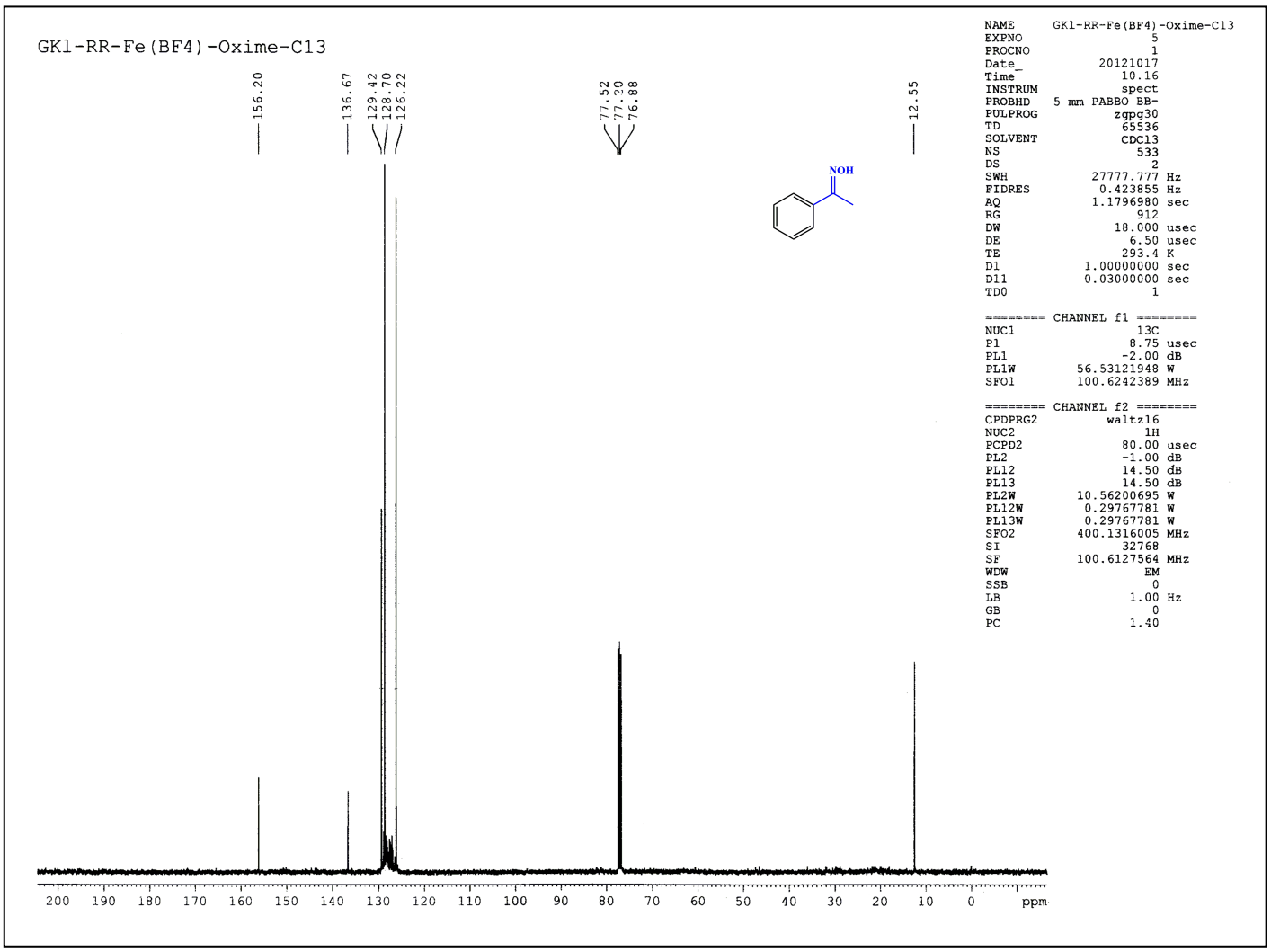


Figure S2. ^{13}C NMR spectrum of Acetophenone oxime (**2a**).

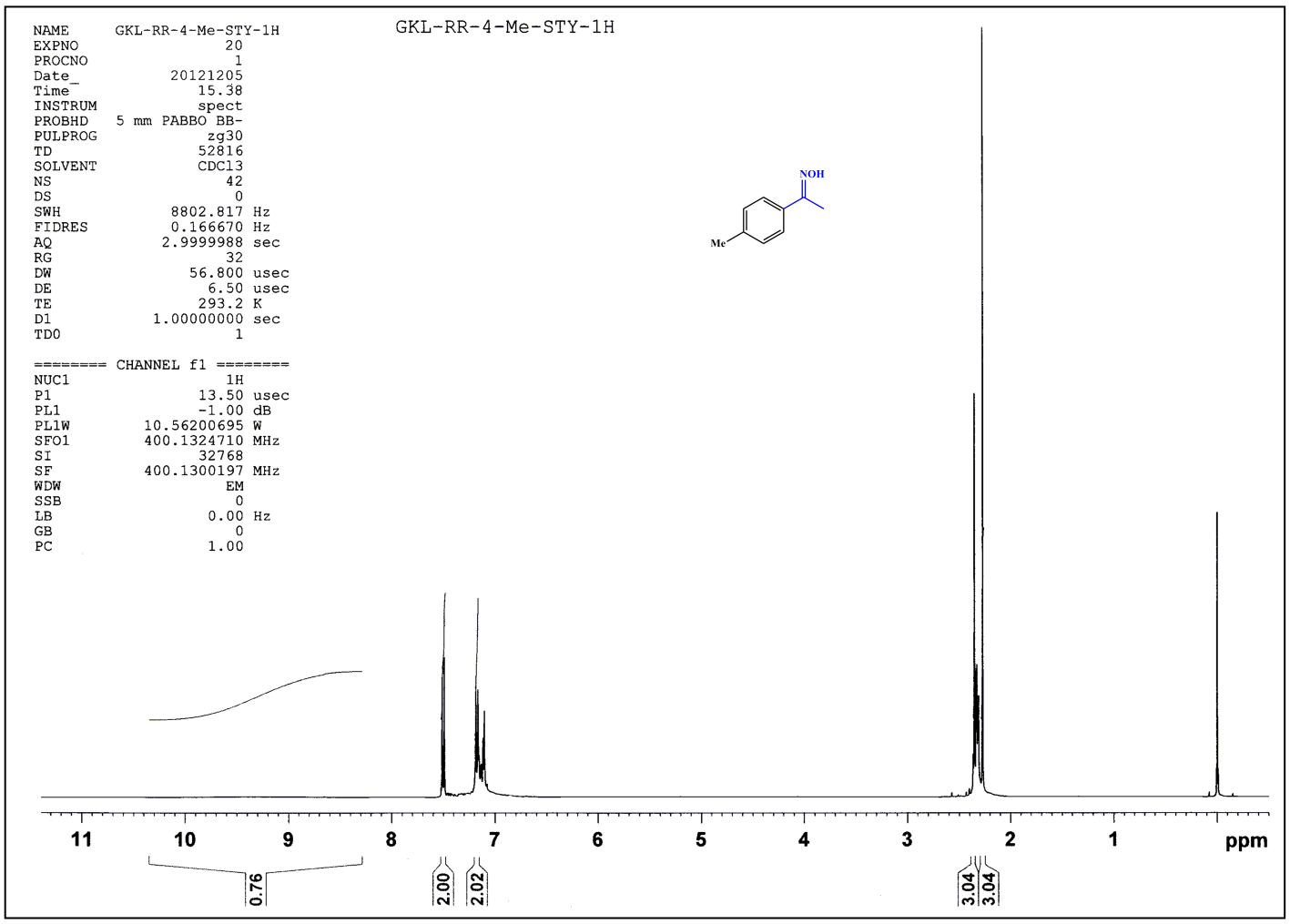


Figure S3. ^{1}H NMR spectrum of 1-(4-Methylphenyl)ethanone oxime (**2b**).

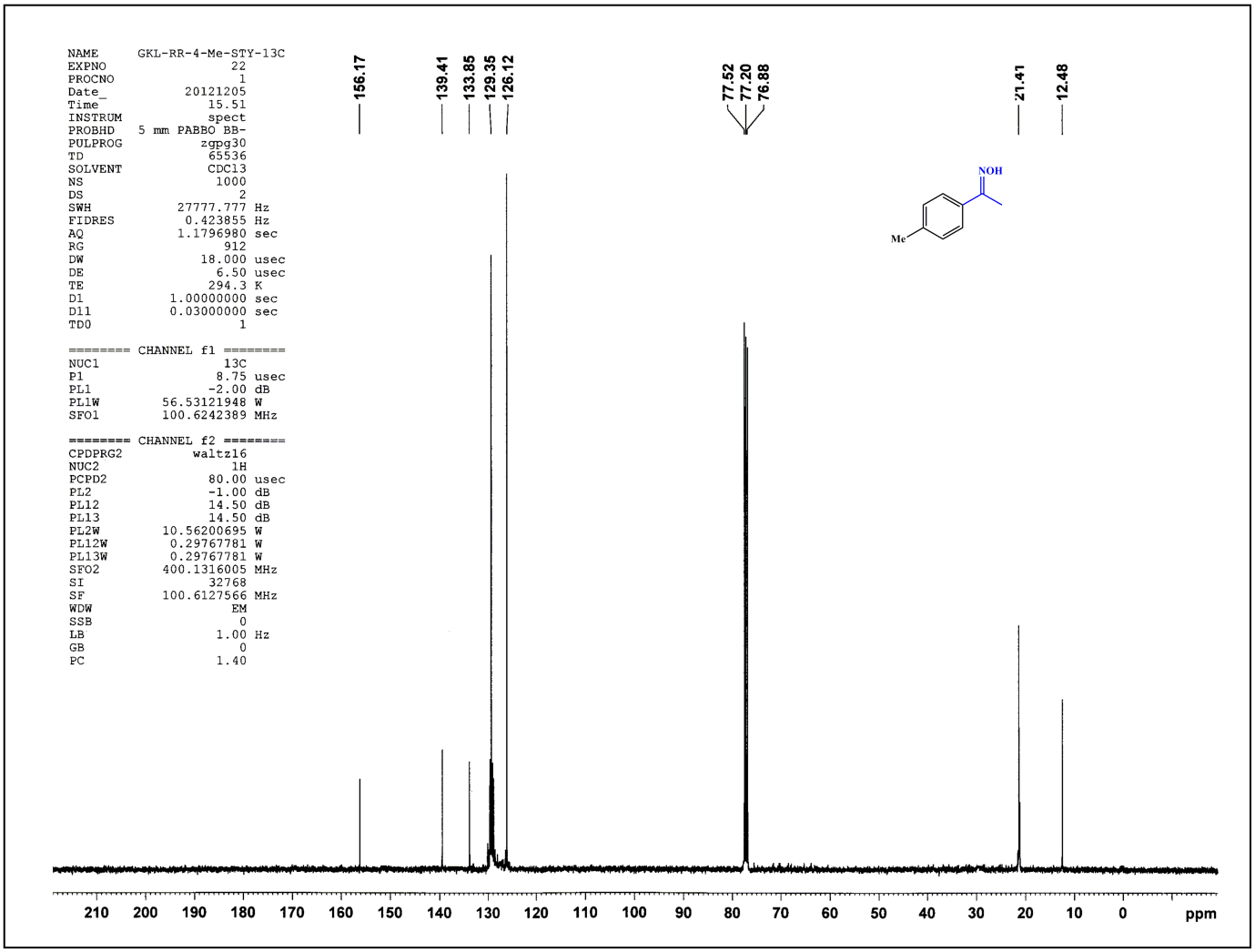


Figure S4. ^{13}C NMR spectrum of 1-(4-Methylphenyl)ethanone oxime (**2b**).

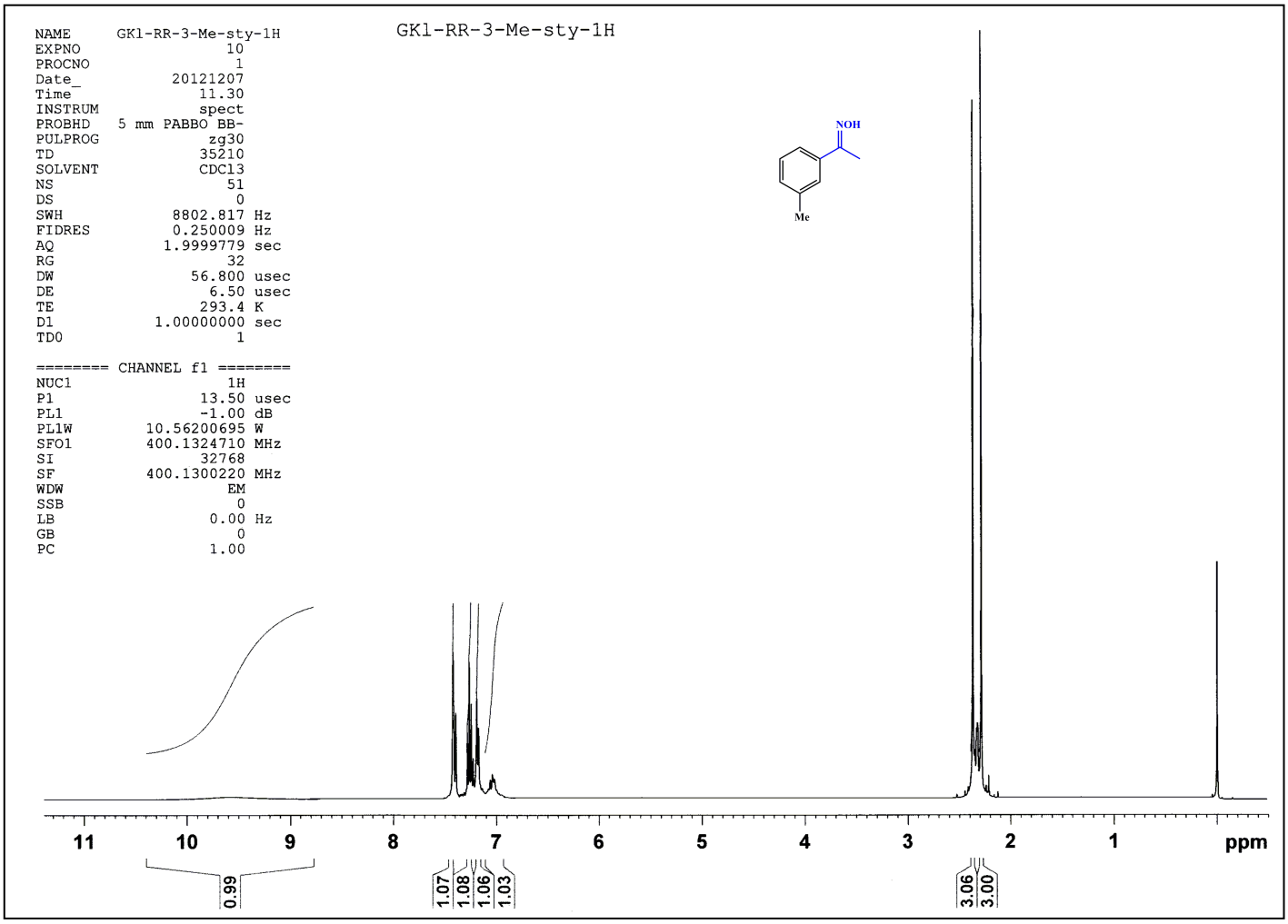


Figure S5. ^{1}H NMR spectrum of 1-(3-Methylphenyl)ethanone oxime (**2c**).

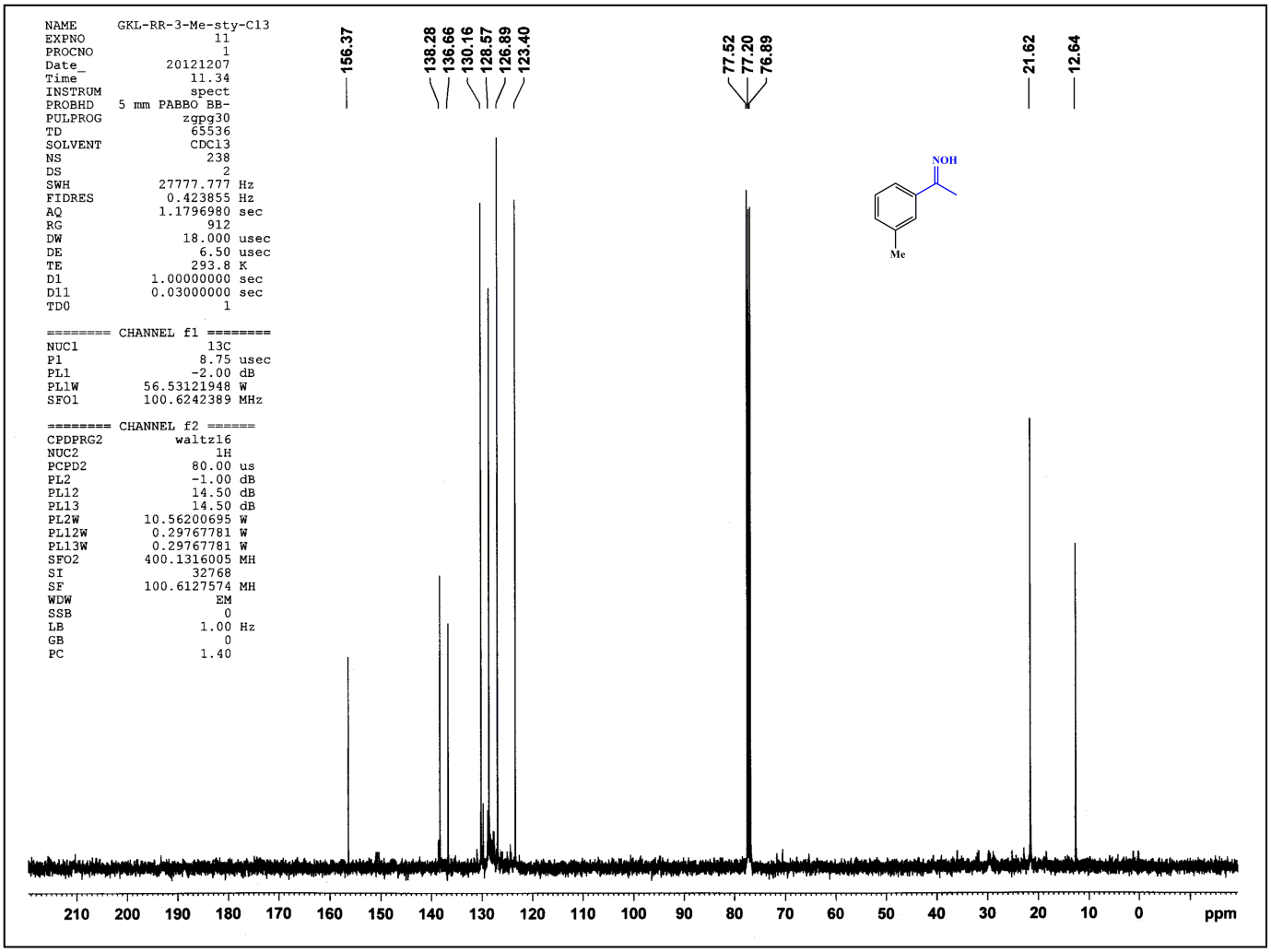


Figure S6. ^{13}C NMR spectrum of 1-(3-Methylphenyl)ethanone oxime (**2c**).

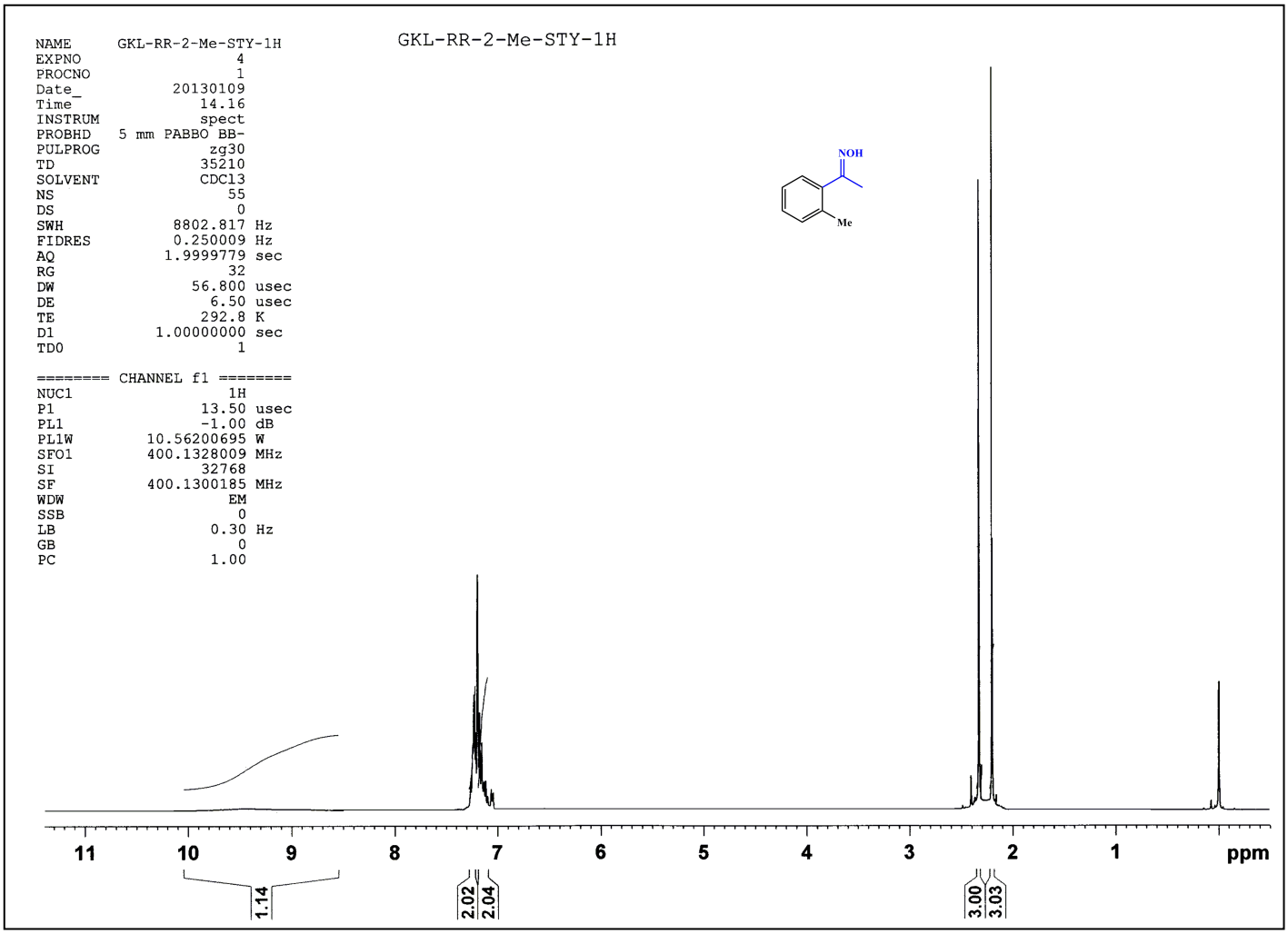


Figure S7. ^{1}H NMR spectrum of 1-(2-Methylphenyl)ethanone oxime (**2d**).

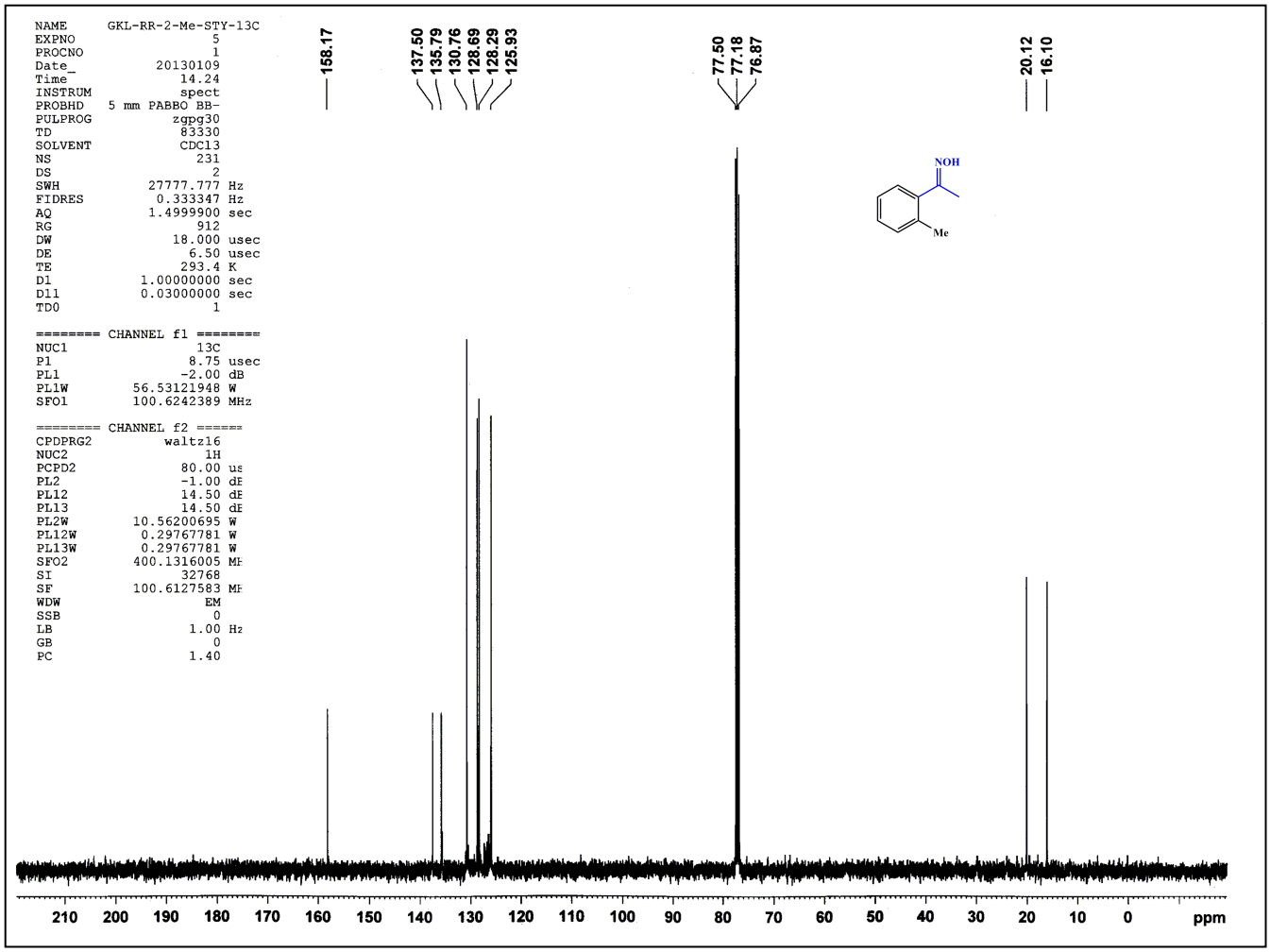


Figure S8. ^{13}C NMR spectrum of 1-(2-Methylphenyl)ethanone oxime (**2d**).

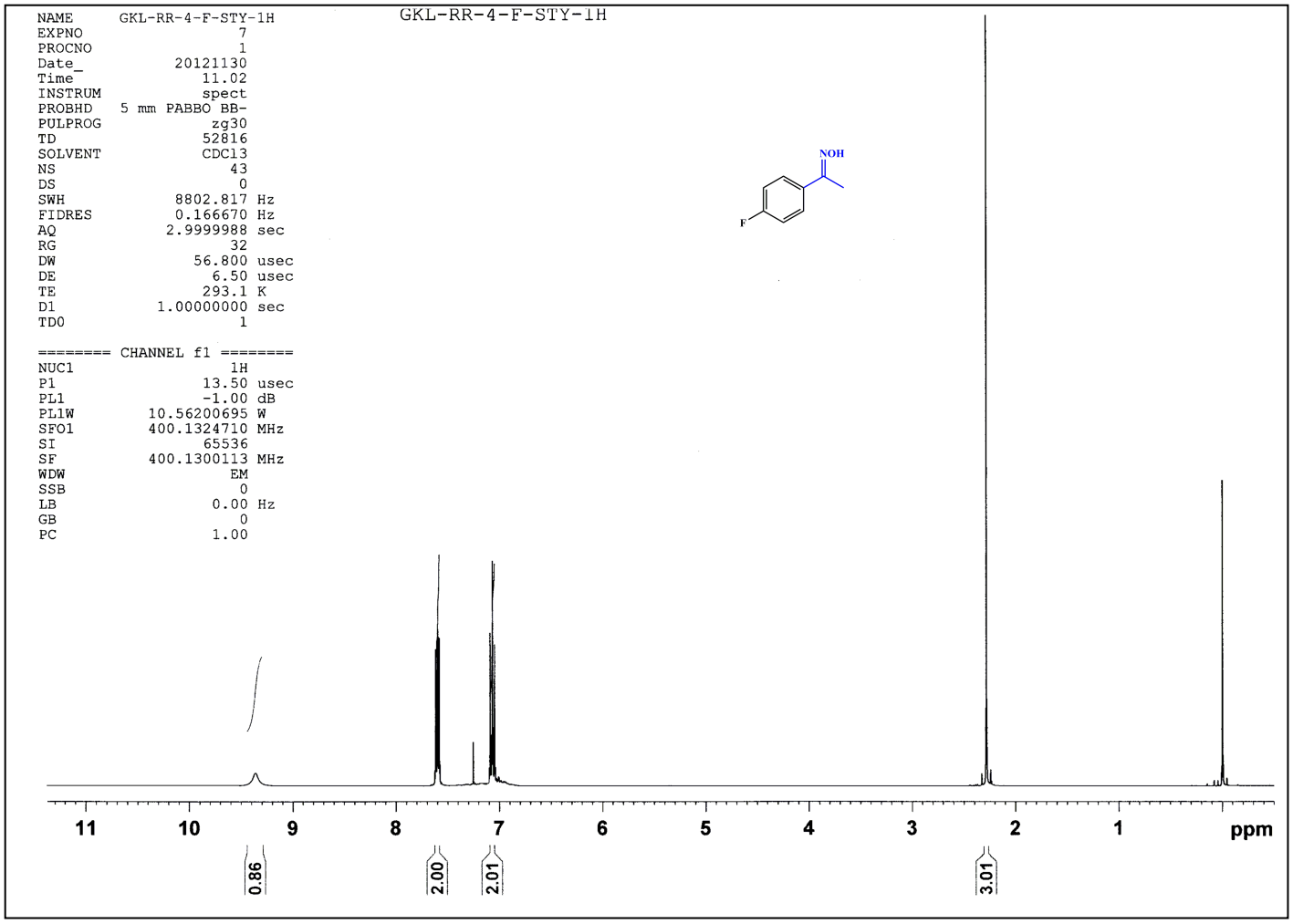


Figure S9. ^{1}H NMR spectrum of 1-(4-Fluorophenyl)ethanone oxime (**2e**).

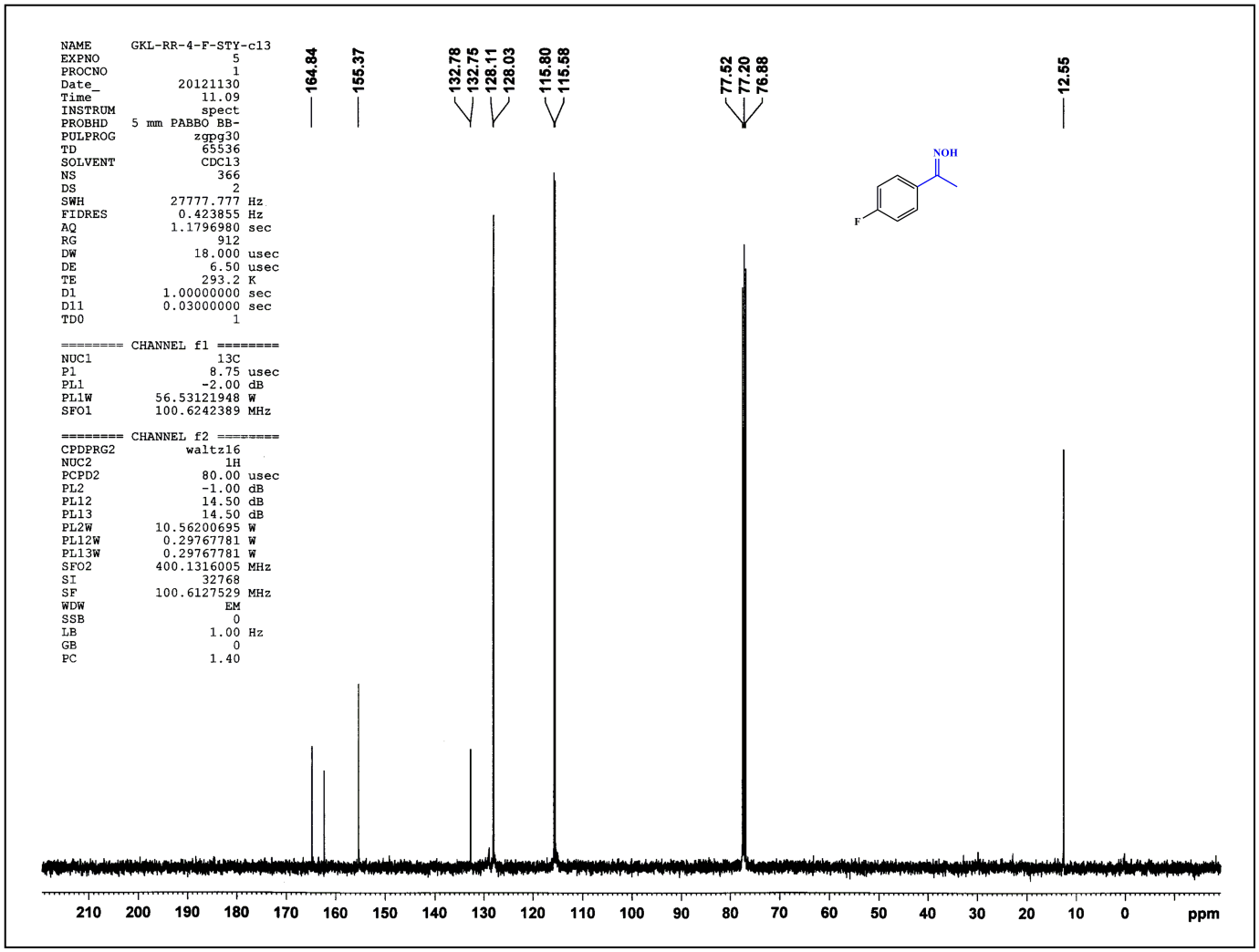


Figure S10. ^{13}C NMR spectrum of 1-(4-Fluorophenyl)ethanone oxime (**2e**).

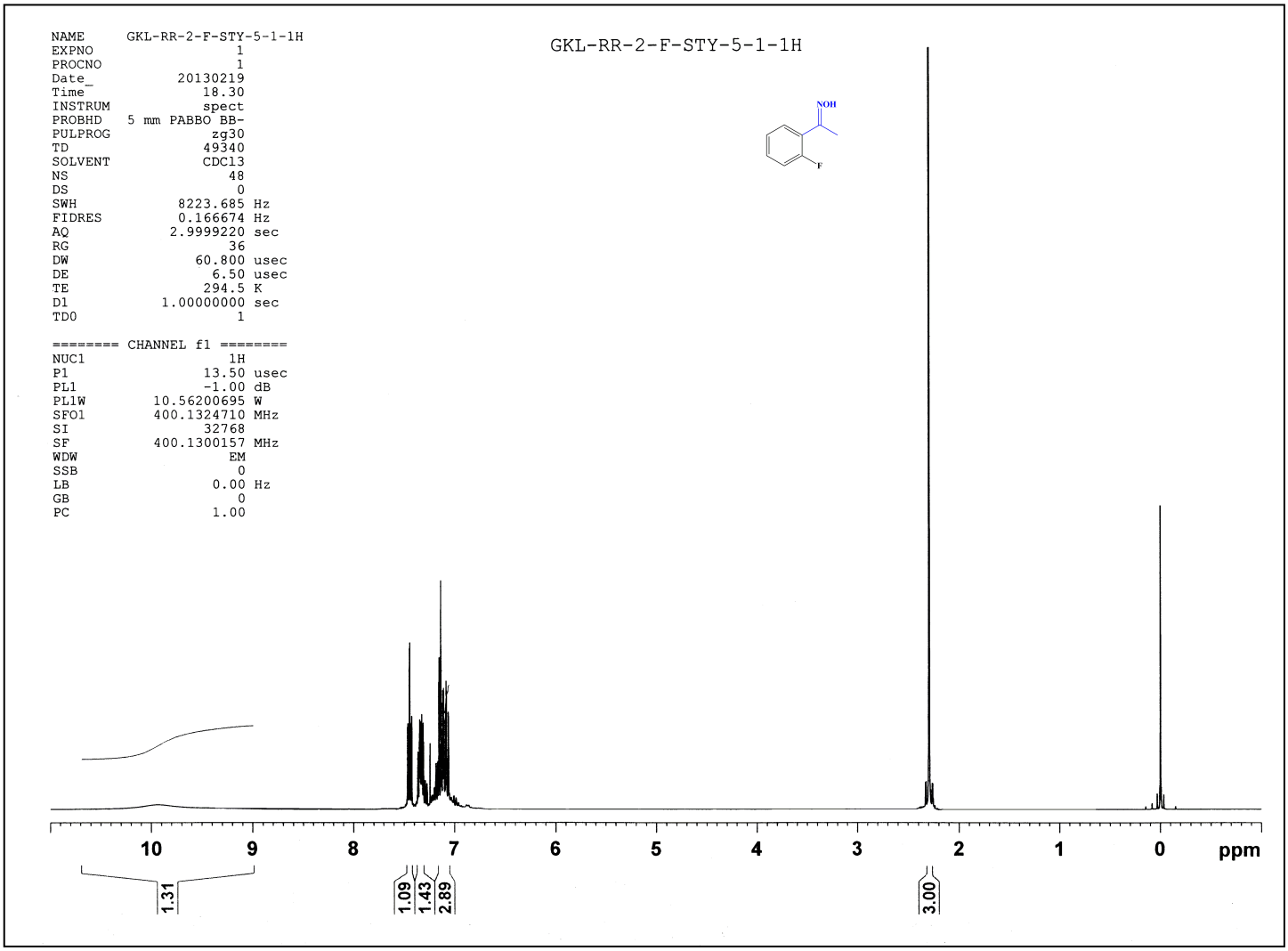


Figure S11. ^{1}H NMR spectrum of 1-(2-Fluorophenyl)ethanone oxime (**2f**).

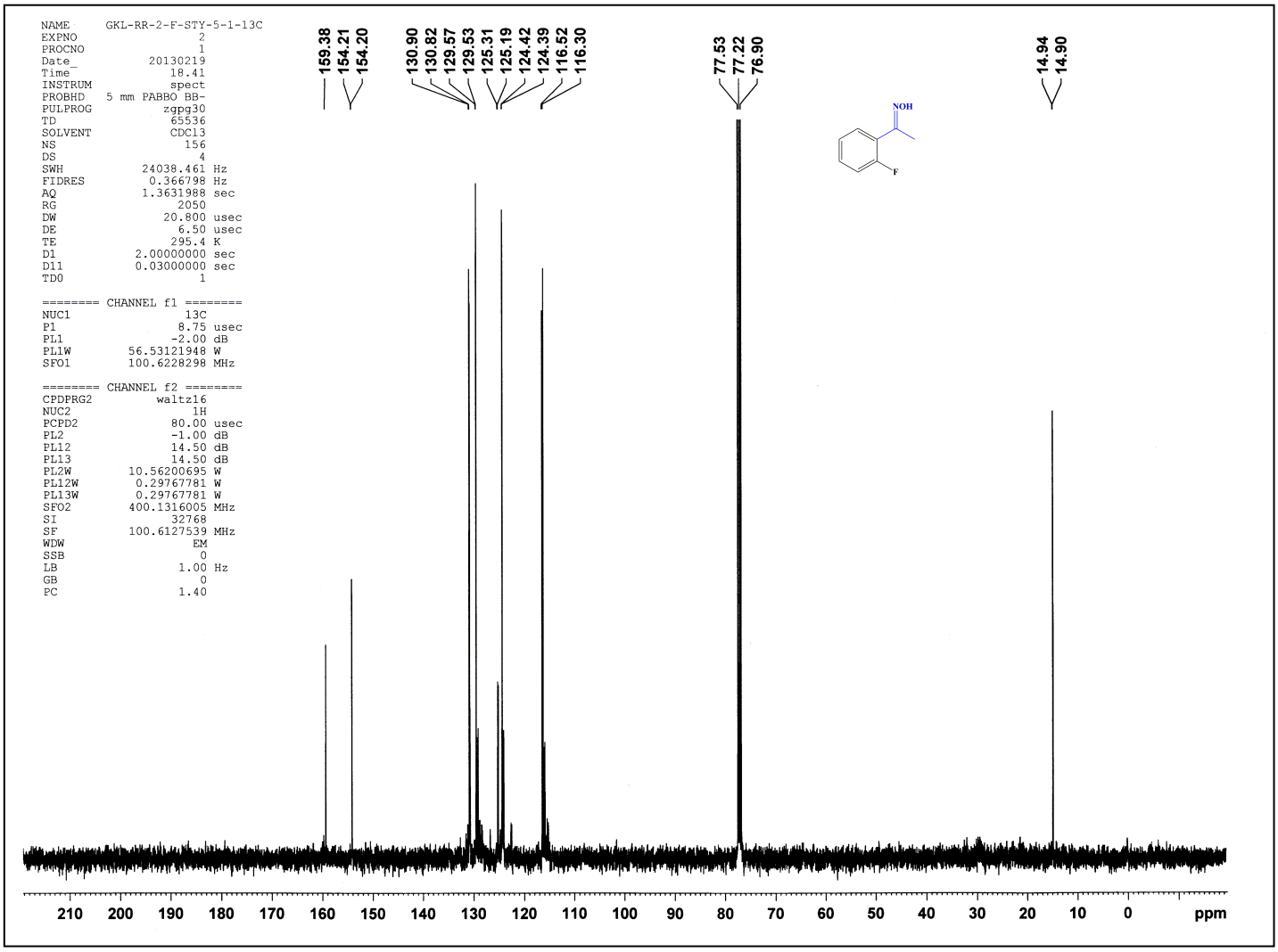


Figure S12. ^{13}C NMR spectrum of 1-(2-Fluorophenyl)ethanone oxime (**2f**).

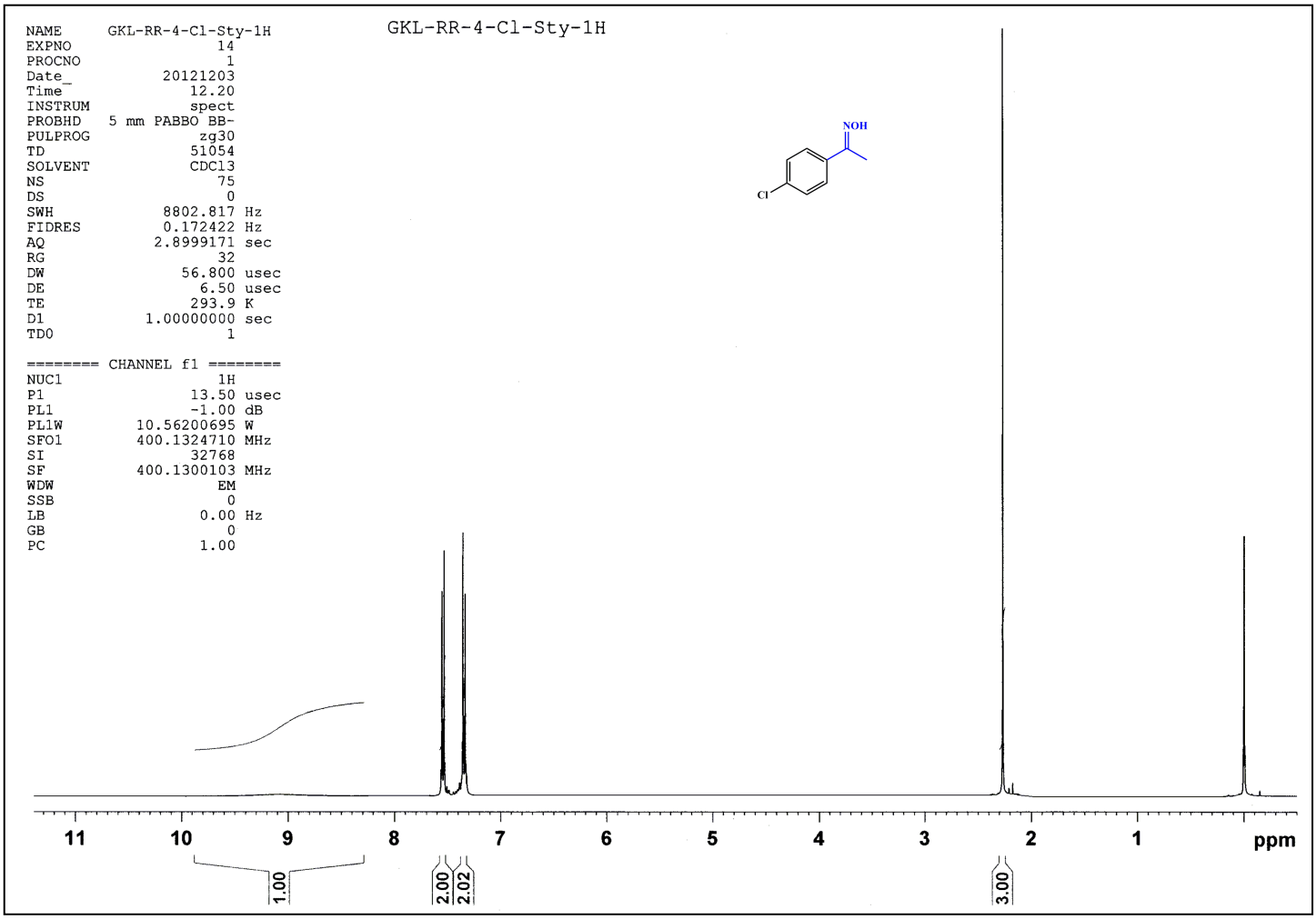


Figure S13. ^{1}H NMR spectrum of 1-(4-Chlorophenyl)ethanone oxime (**2g**).

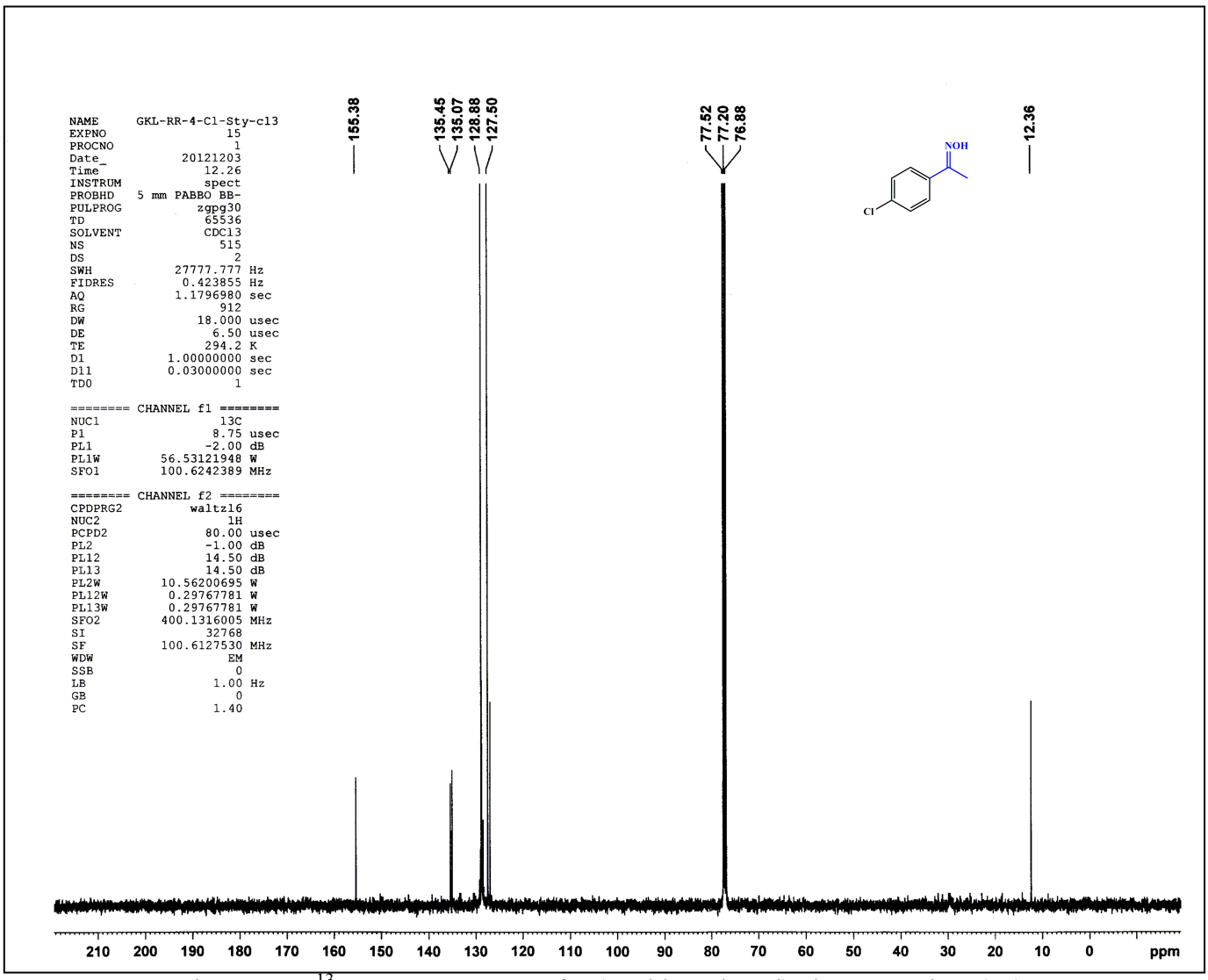


Figure S14. ^{13}C NMR spectrum of 1-(4-Chlorophenyl)ethanone oxime (**2g**).

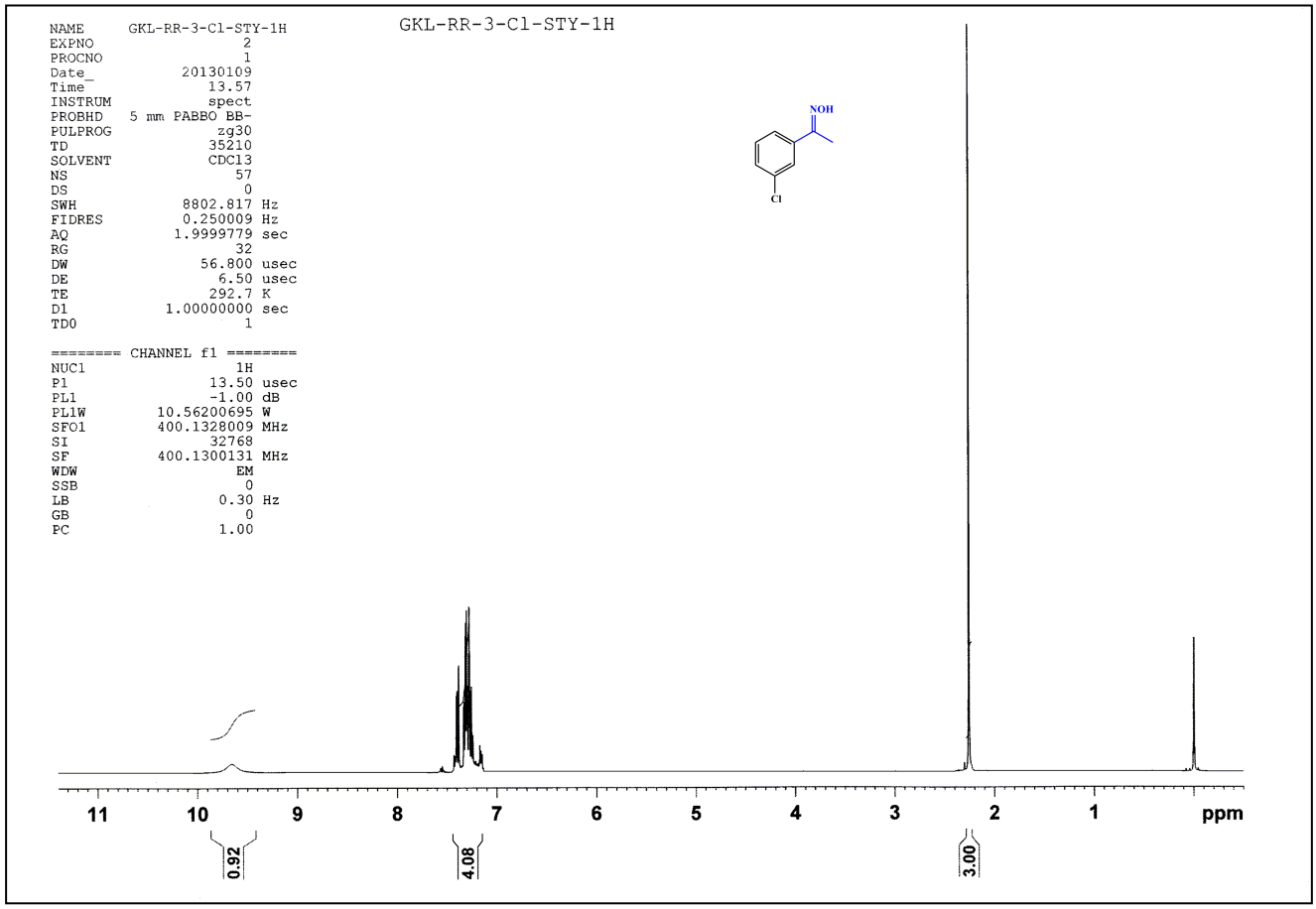


Figure S15. ^{1}H NMR spectrum of 1-(3-Chlorophenyl)ethanone oxime (**2h**).

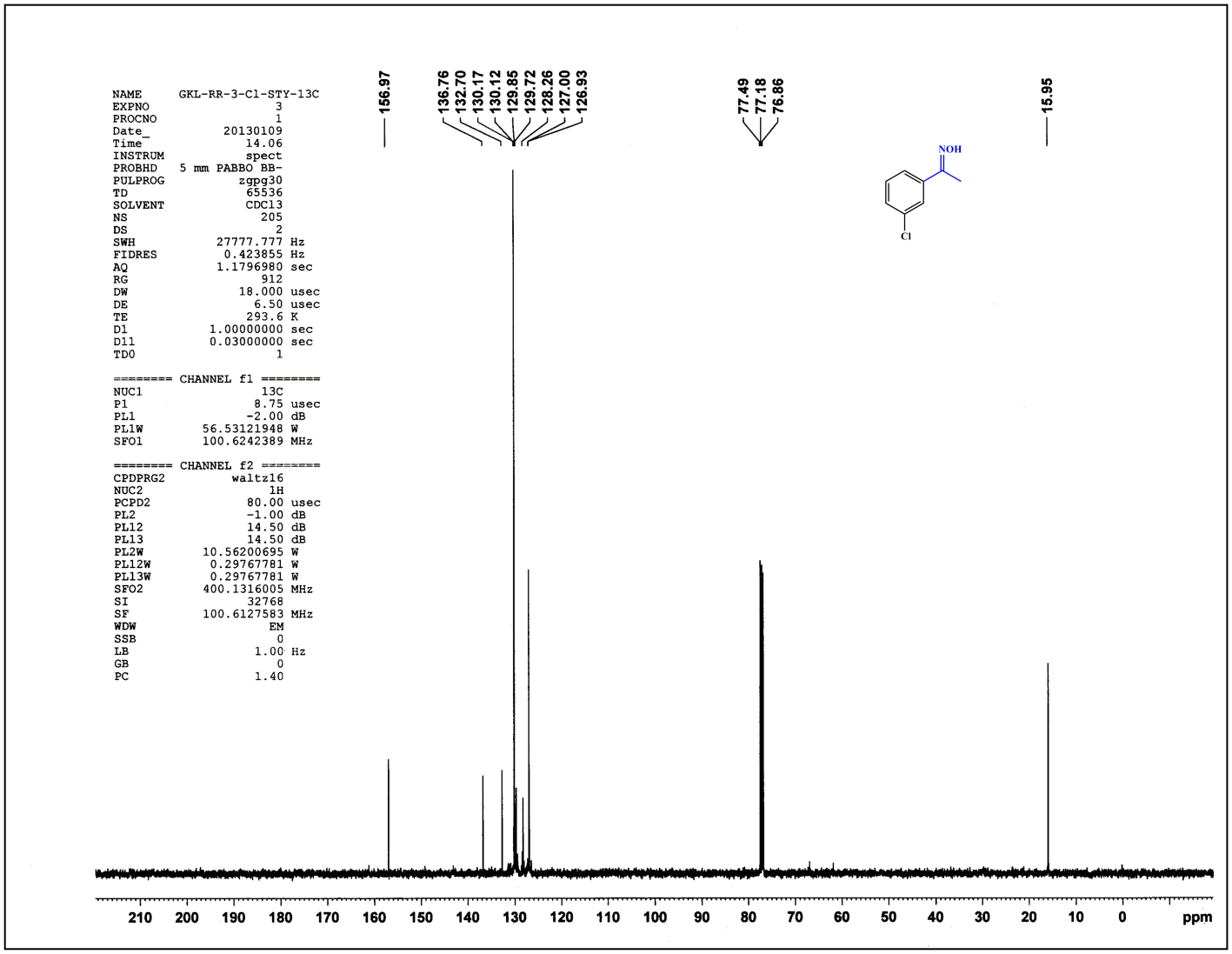


Figure S16. ^{13}C NMR spectrum of 1-(3-Chlorophenyl)ethanone oxime (**2h**).

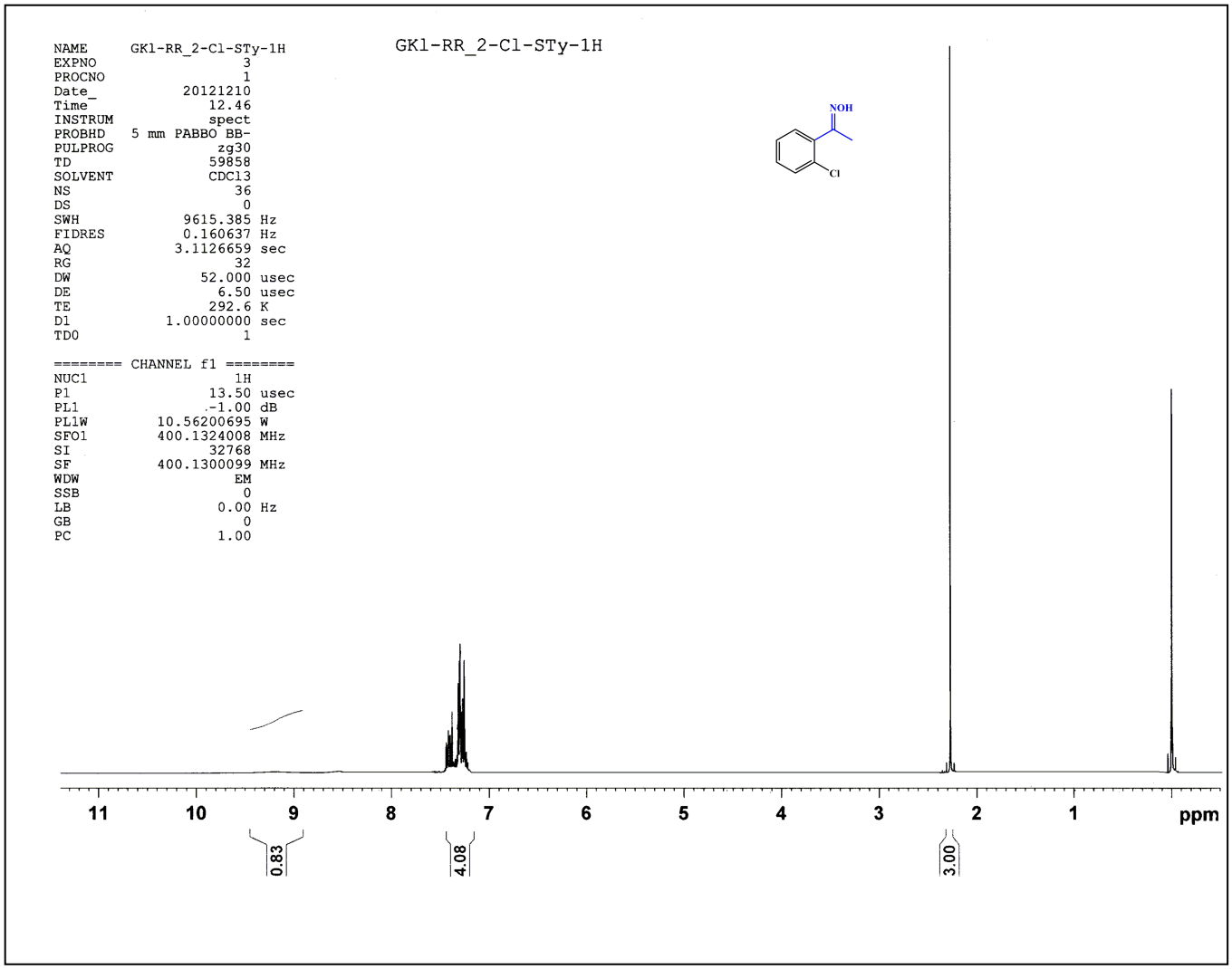


Figure S17. ^{1}H NMR spectrum of 1-(2-Chlorophenyl)ethanone oxime (**2i**).

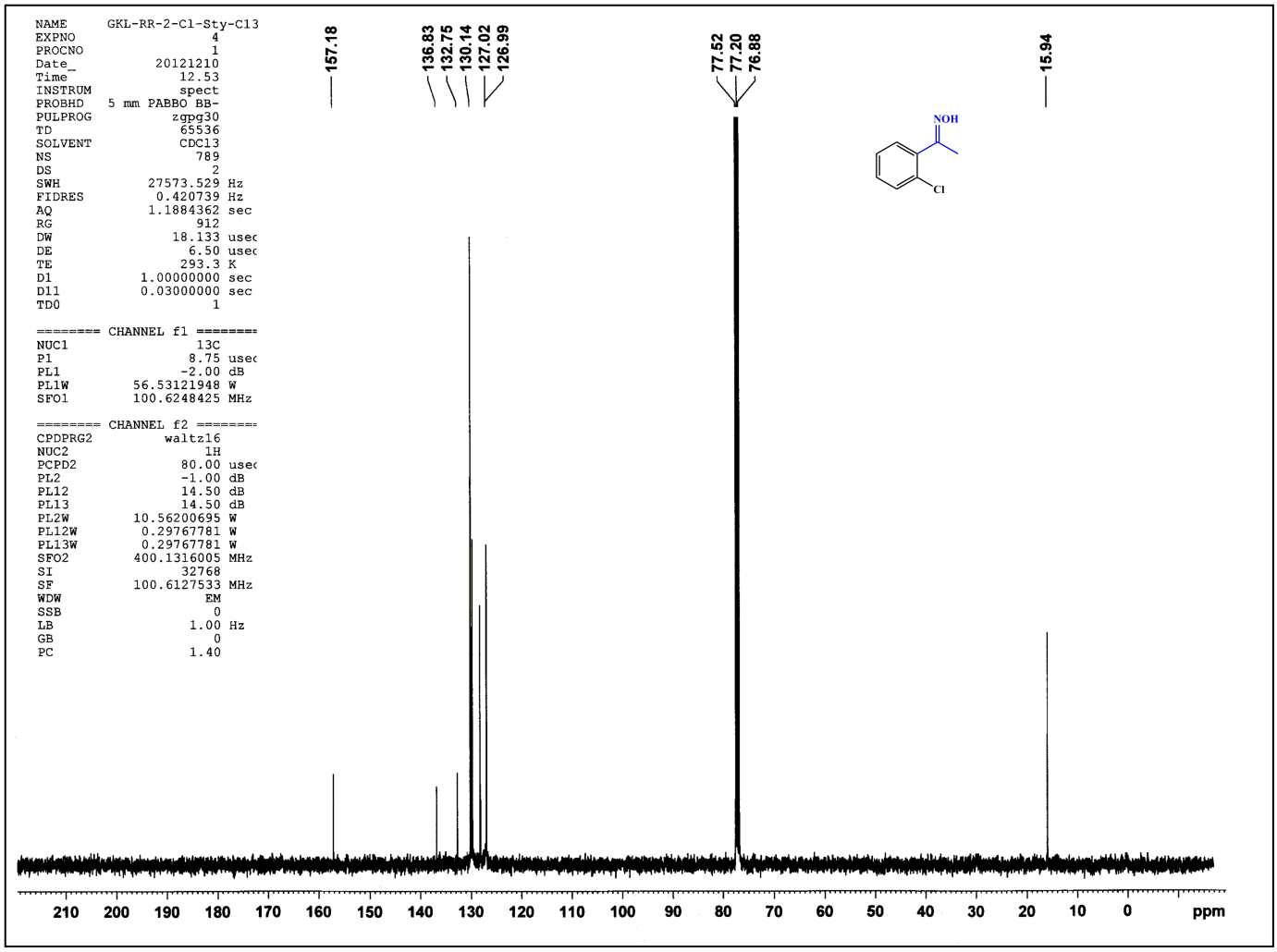


Figure S18. ^{13}C NMR spectrum of 1-(2-Chlorophenyl)ethanone oxime (**2i**).

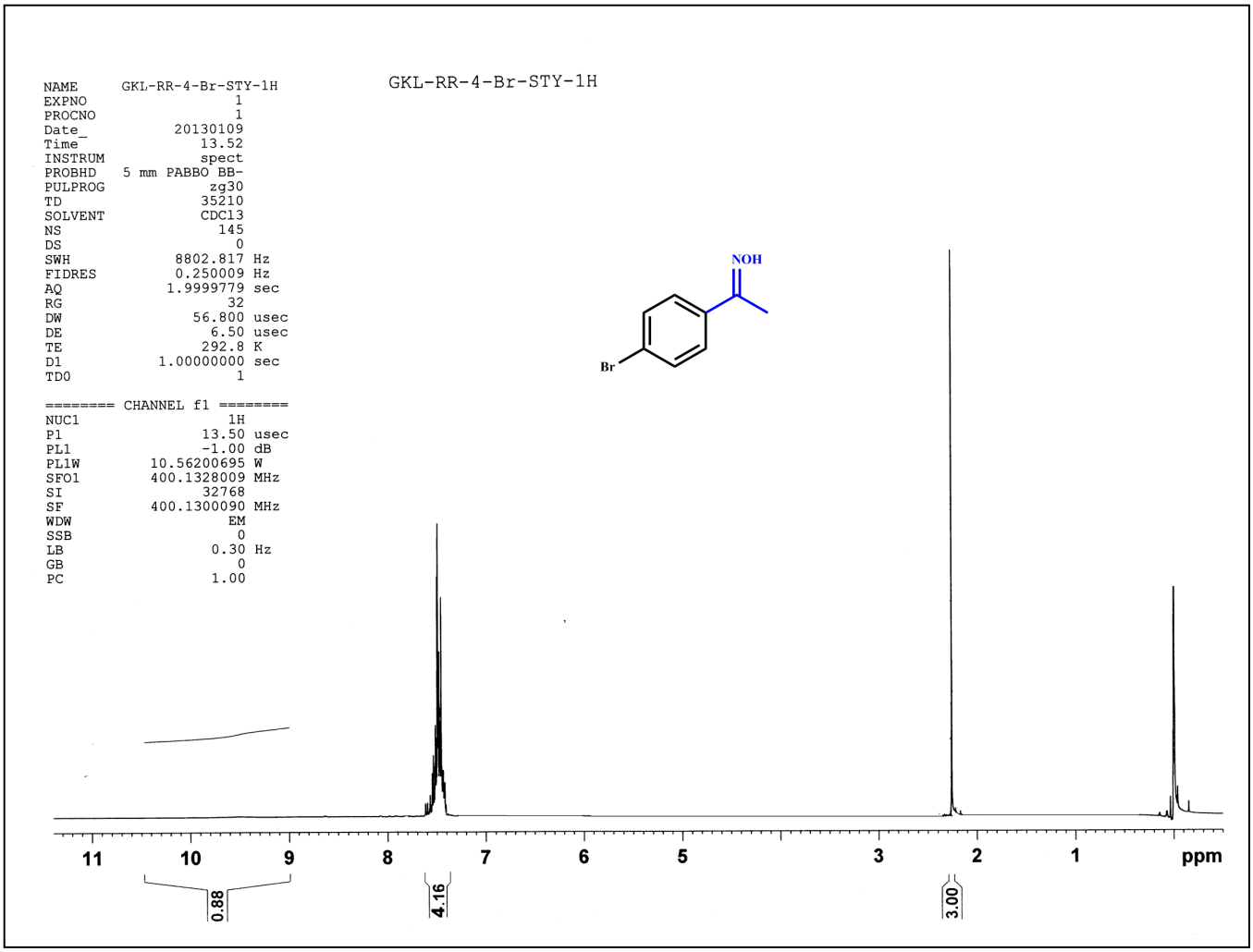


Figure S19. ^{1}H NMR spectrum of 1-(4-Bromophenyl)ethanone oxime (**2j**).

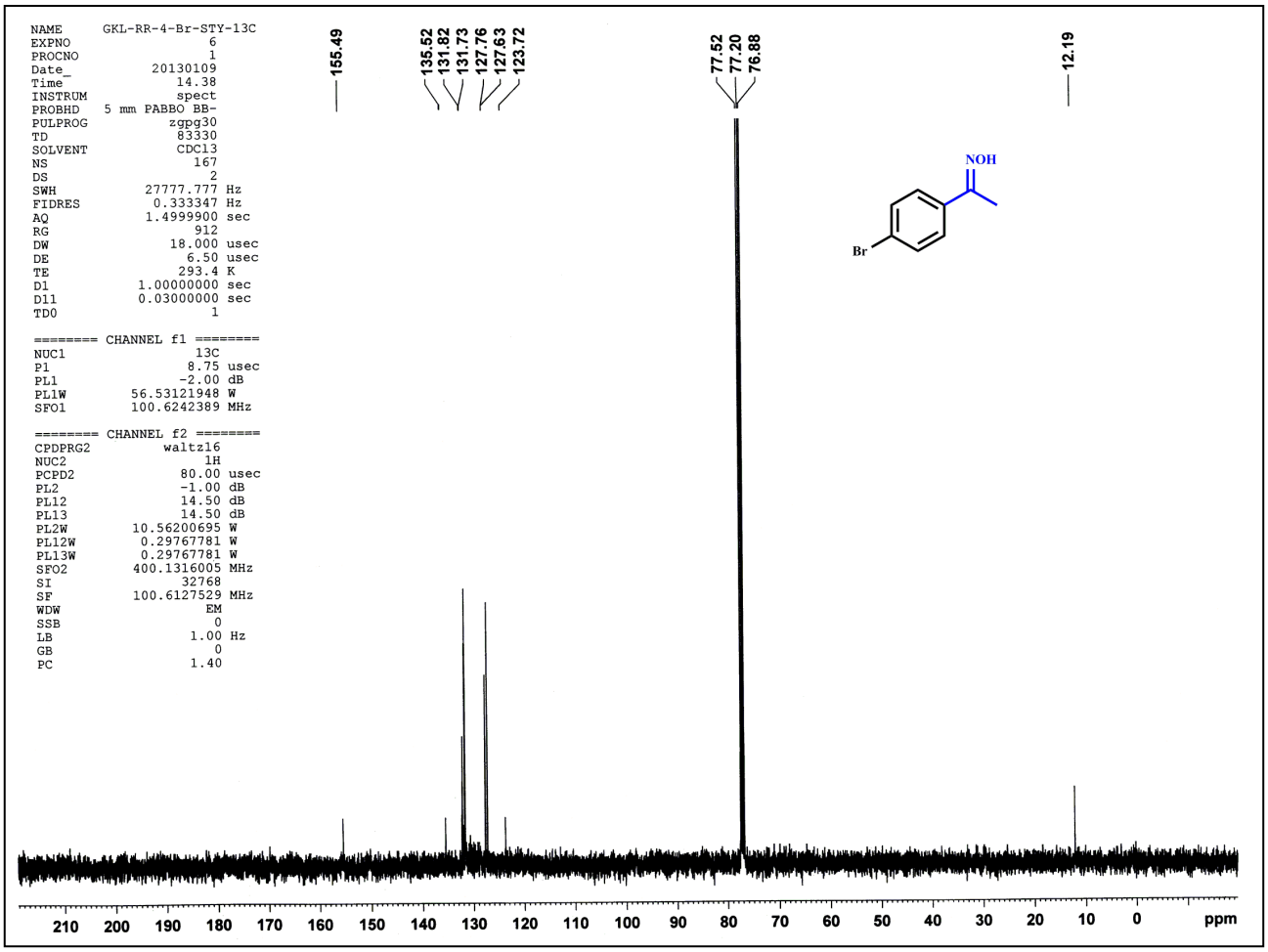


Figure S20. ^{13}C NMR spectrum of 1-(4-Bromophenyl)ethanone oxime (**2j**).

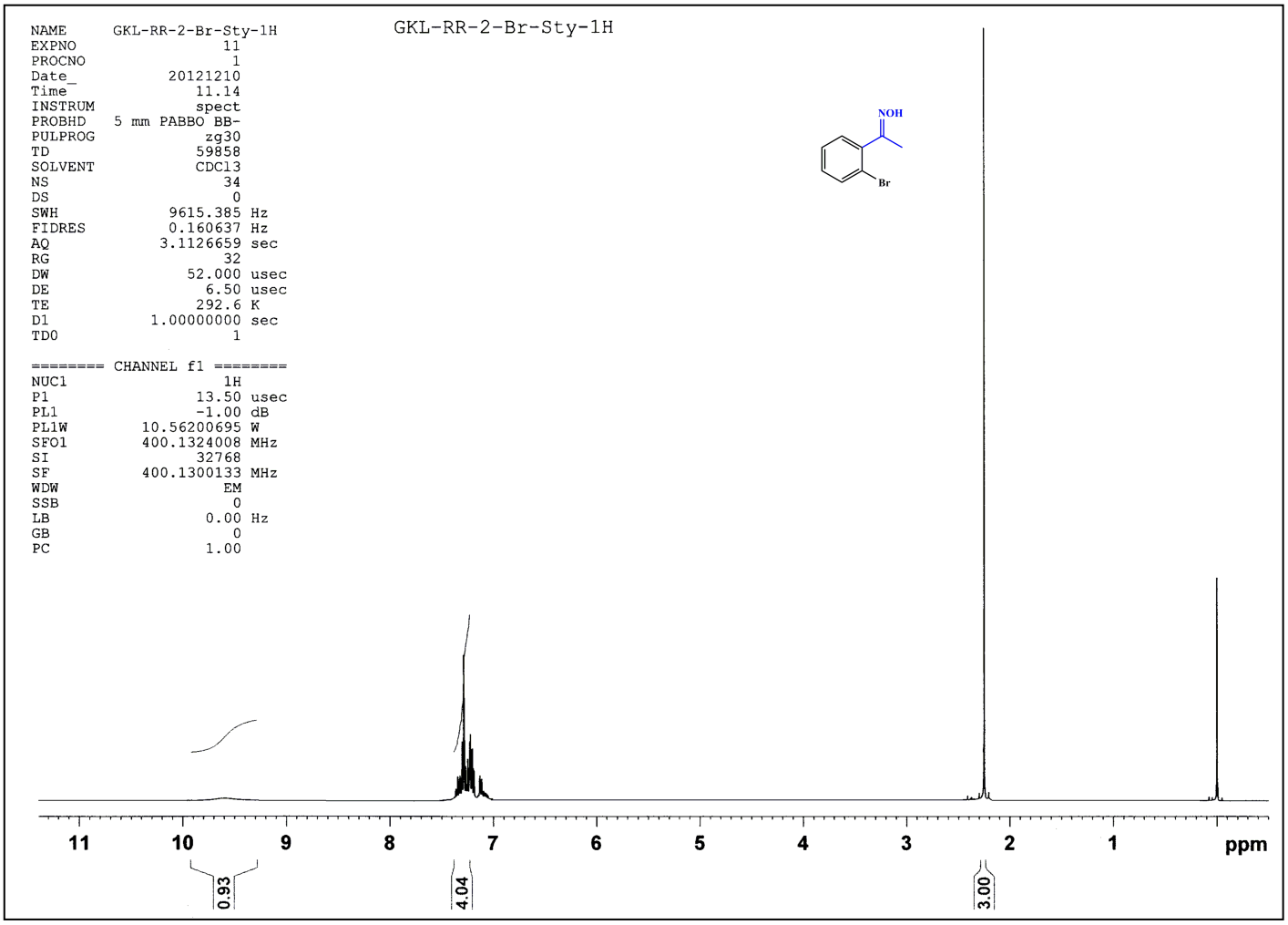


Figure S21. ^{1}H NMR spectrum of 1-(2-Bromophenyl)ethanone oxime (**2k**).

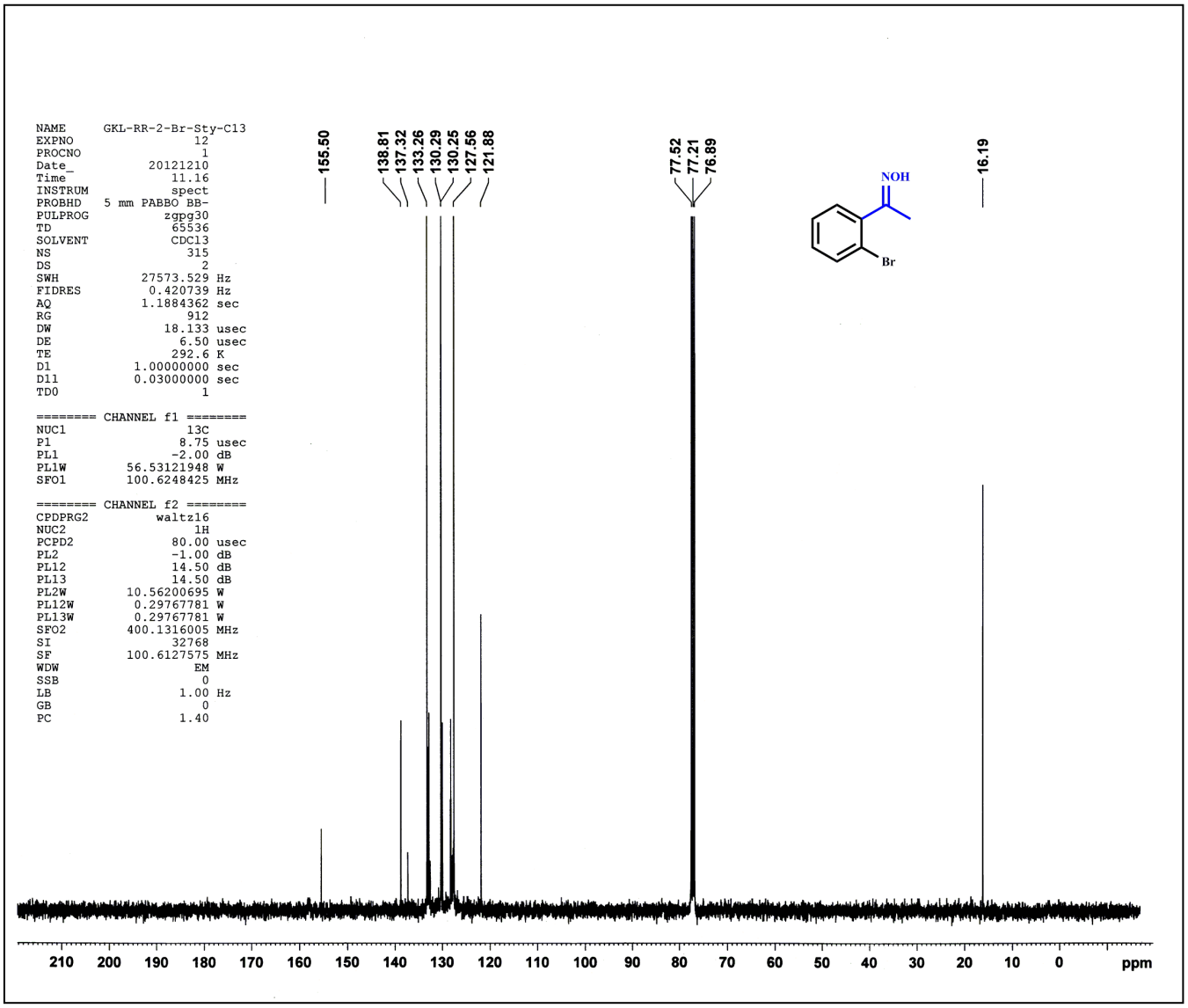


Figure S22. ^{13}C NMR spectrum of 1-(2-Bromophenyl)ethanone oxime (**2k**).

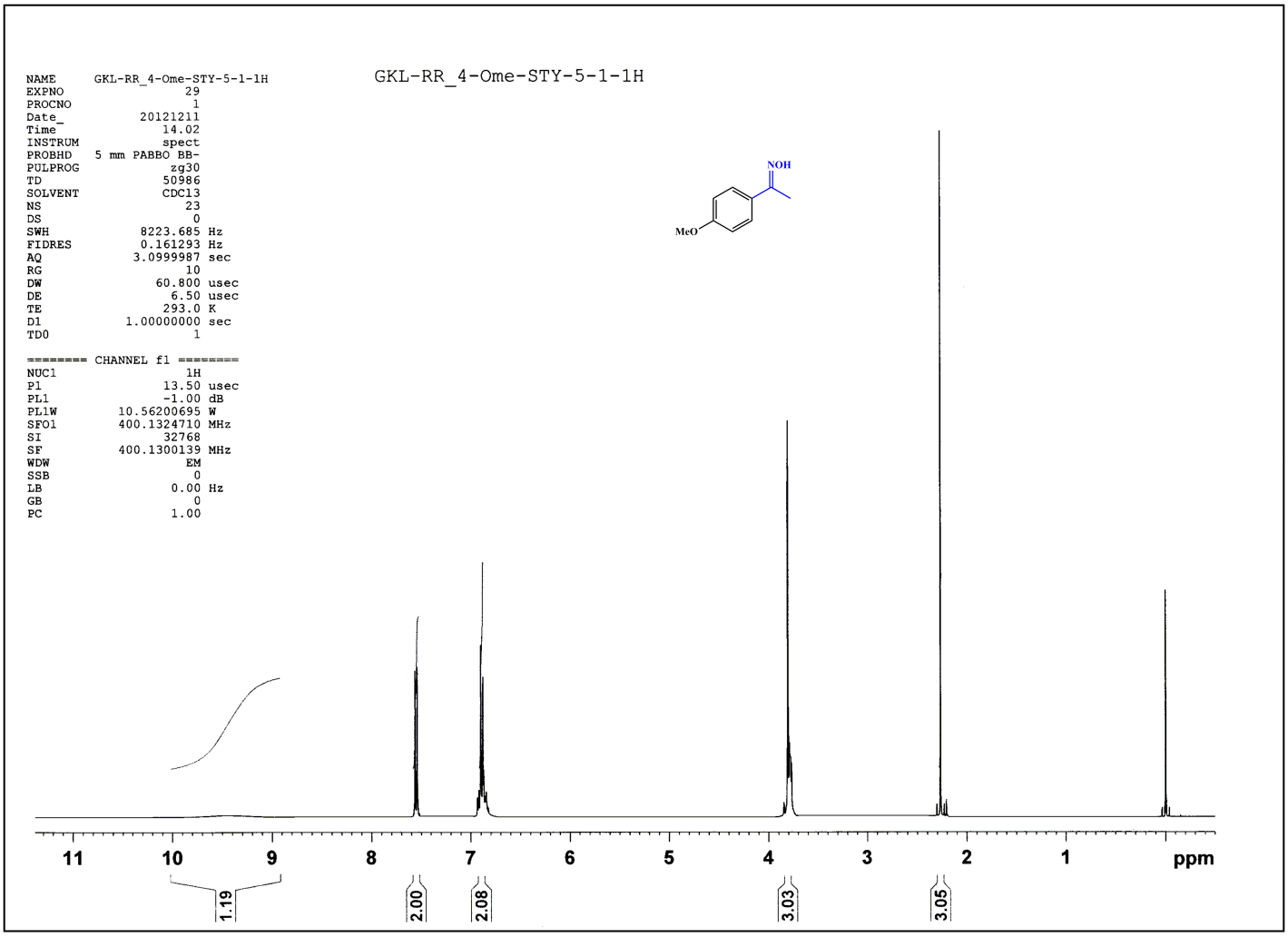


Figure S23. ^{1}H NMR spectrum of 1-(4-Methoxyphenyl)ethanone oxime (**2l**).

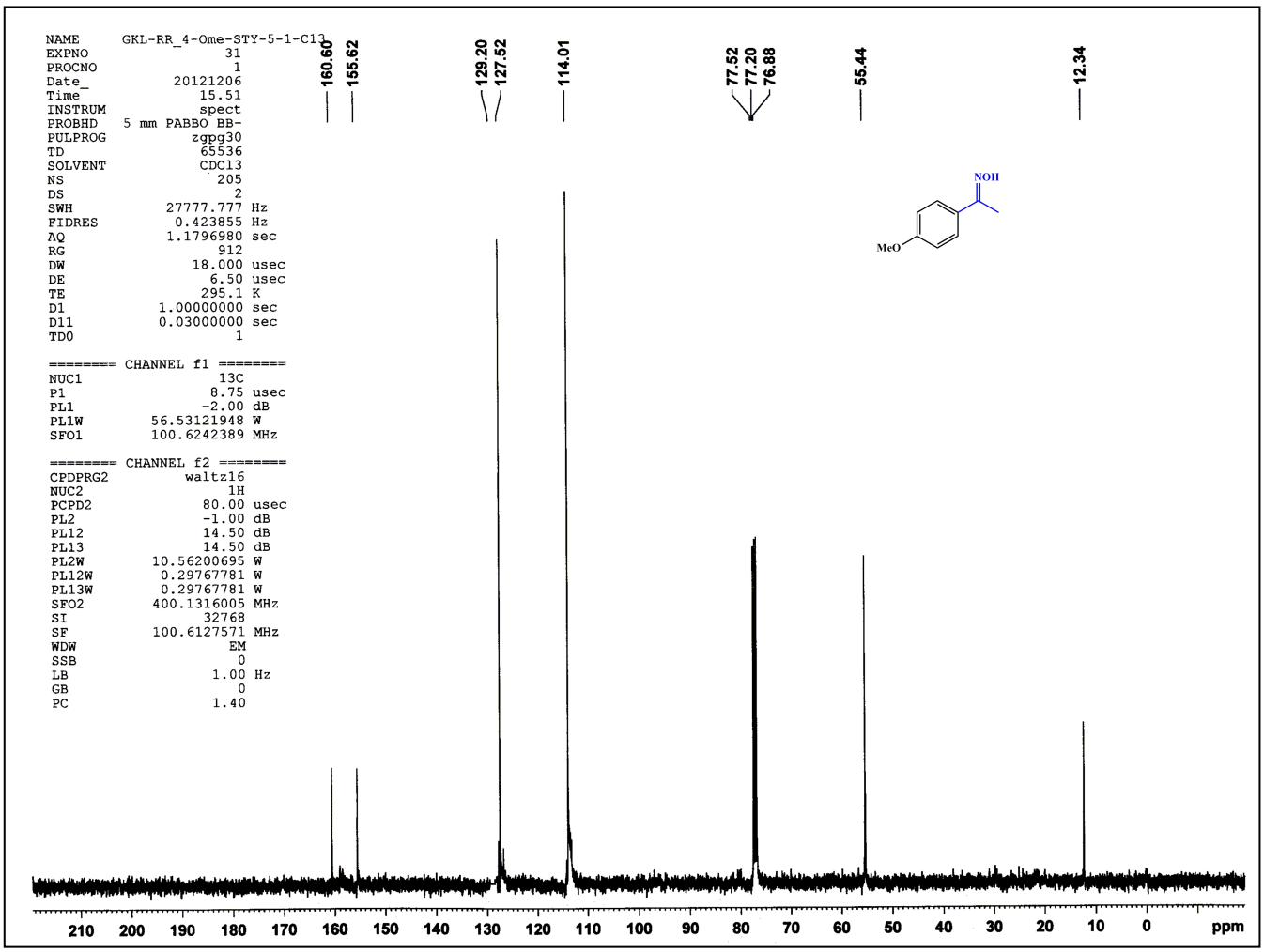


Figure S24. ^{13}C NMR spectrum of 1-(4-Methoxyphenyl)ethanone oxime (**2l**).

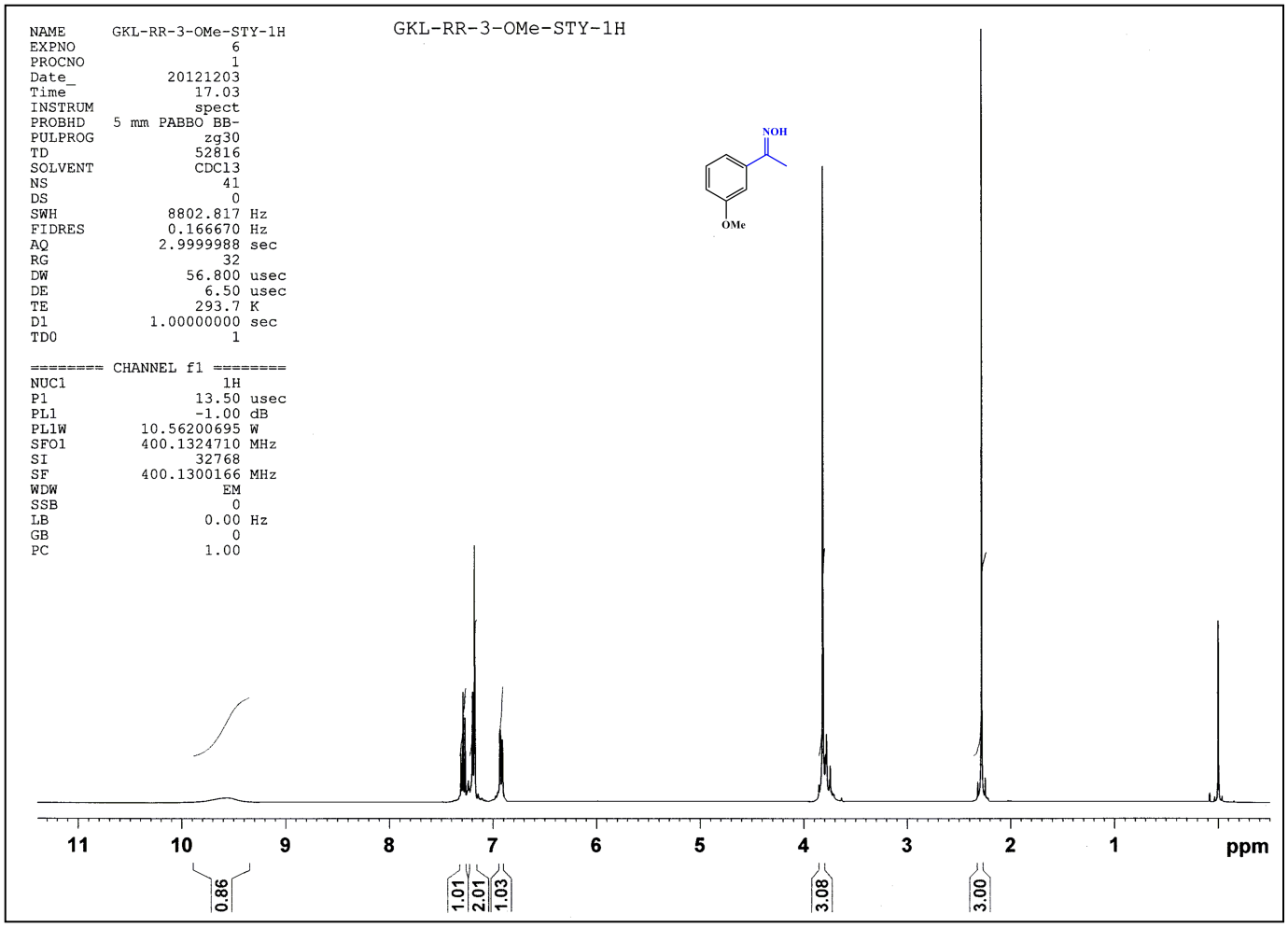


Figure S25. ^{1}H NMR spectrum of 1-(3-Methoxyphenyl)ethanone oxime (**2m**).

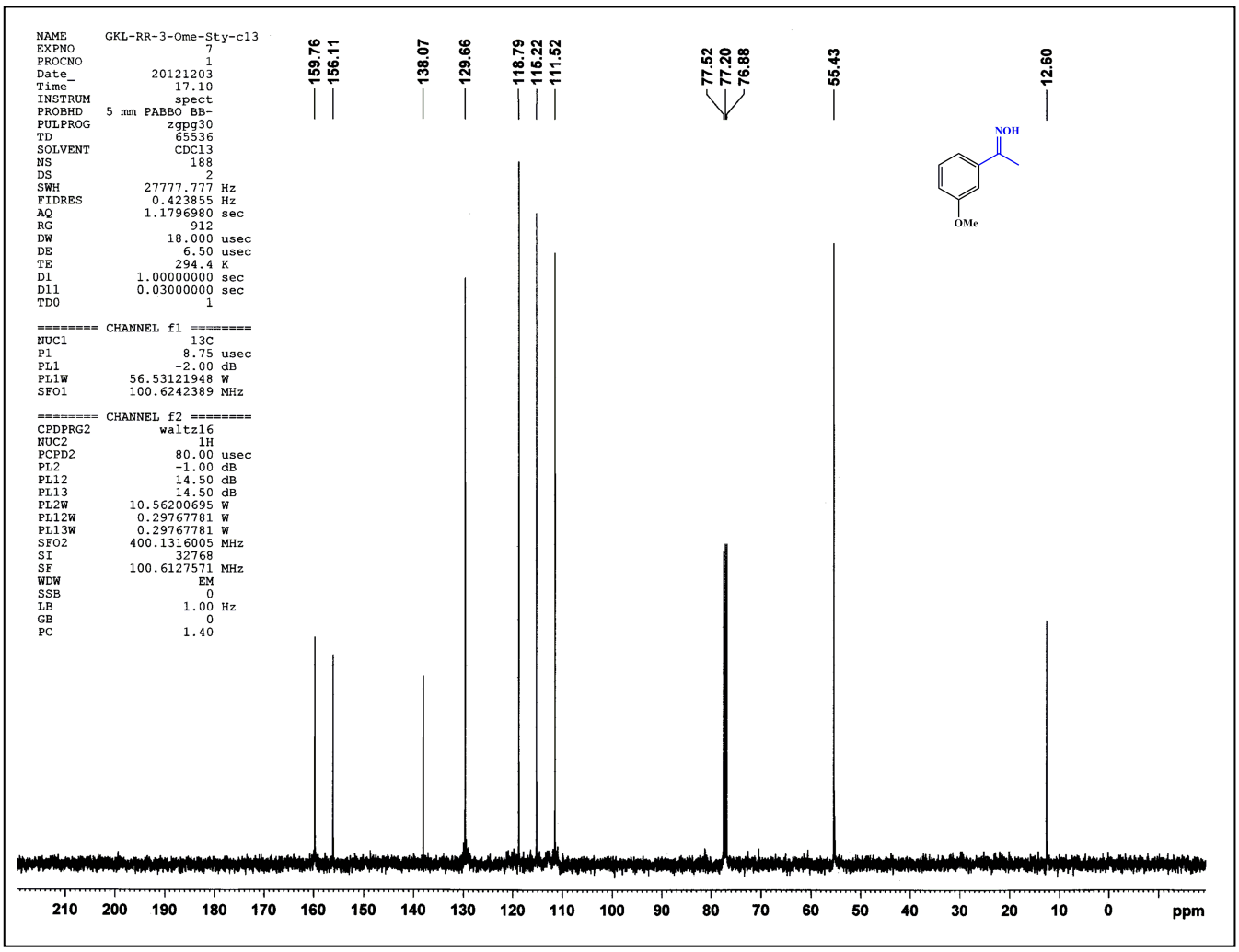
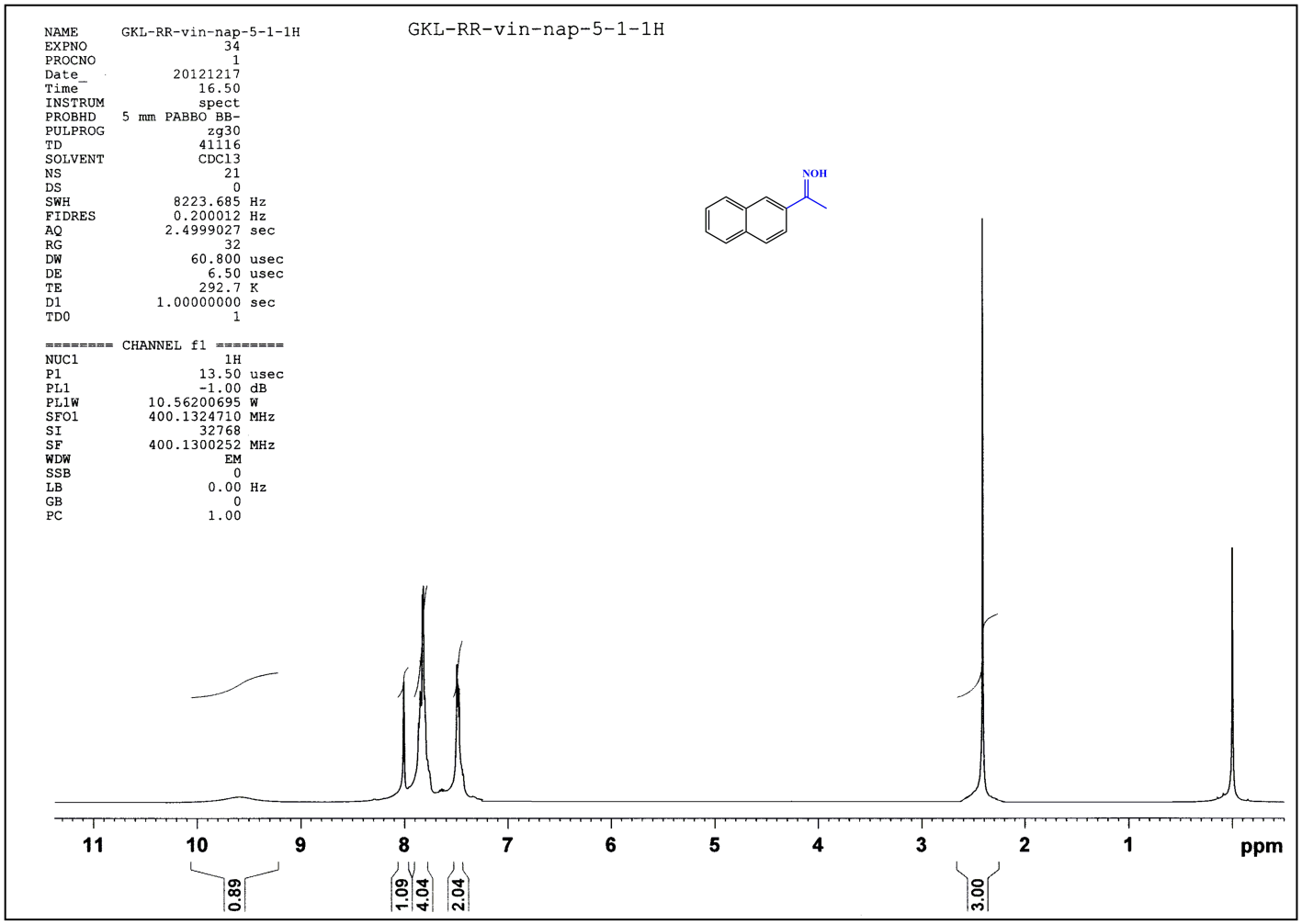


Figure S26. ^{13}C NMR spectrum of 1-(3-Methoxyphenyl)ethanone oxime (**2m**).

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DE                    6.50 usec
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D1                1.00000000 sec
TD0                      1

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PL1                   -1.00 dB
PL1W            10.56200695 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1300252 MHz
WDW                      EM
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LB                     0.00 Hz
GB                        0
PC                     1.00
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Figure S27. ^{1}H NMR spectrum of 1-(Naphthalen-2-yl)ethanone oxime (**2n**).

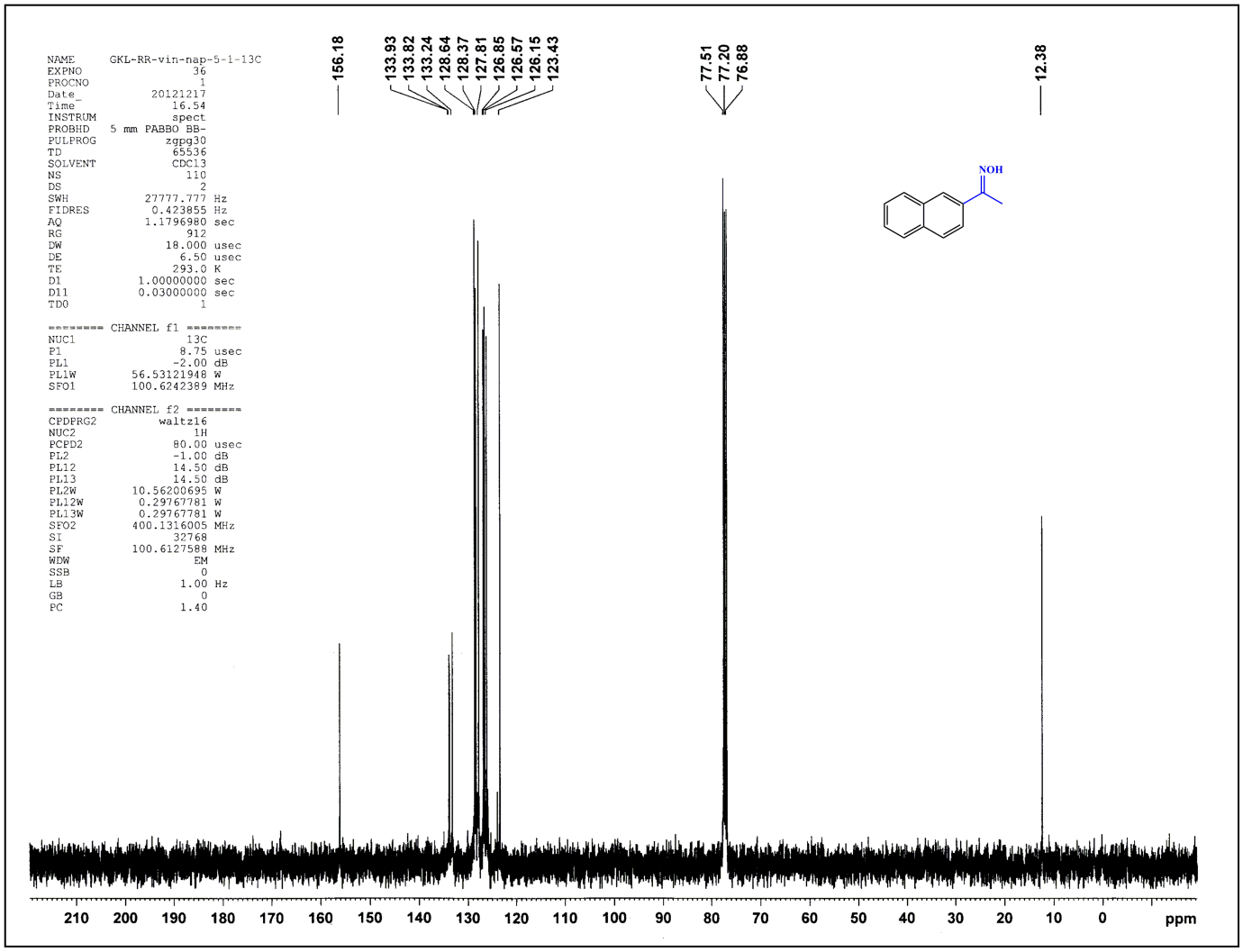

Figure S28. ^{13}C NMR spectrum of 1-(Naphthalen-2-yl)ethanone oxime (**2n**).

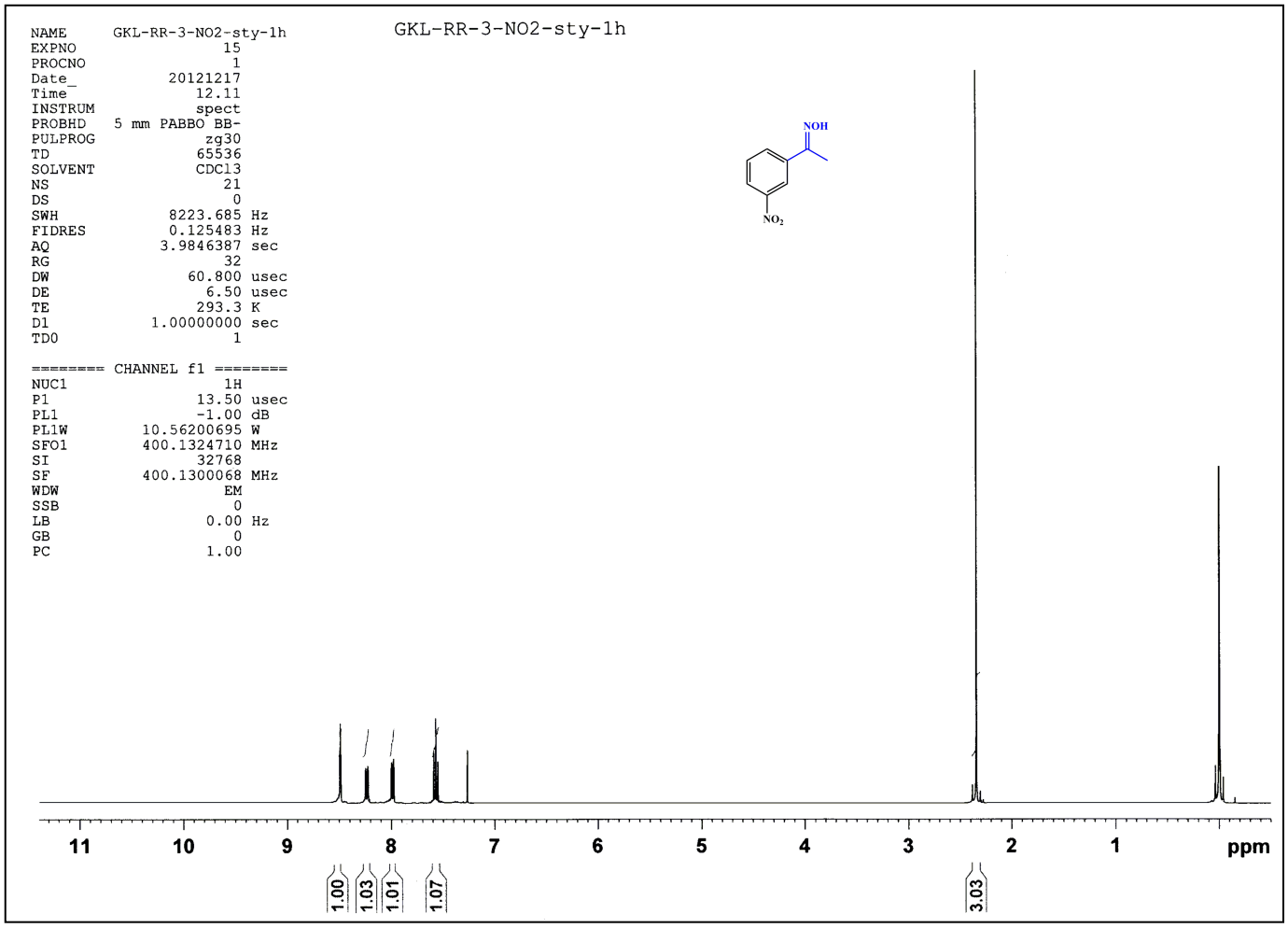

Figure S29. ^{1}H NMR spectrum of 1-(3-Nitrophenyl)ethanone oxime (**2o**).

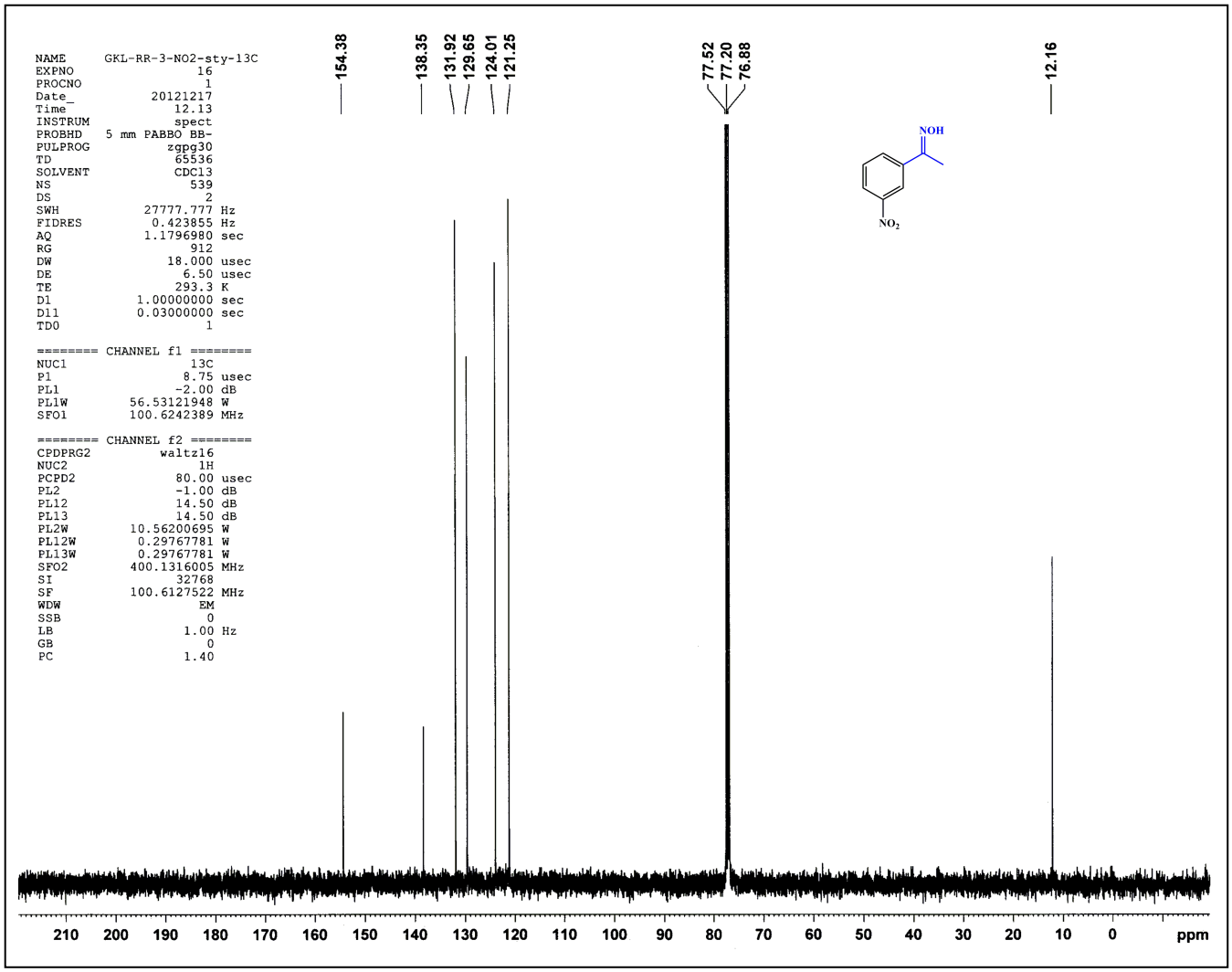

Figure S30. ^{13}C NMR spectrum of 1-(3-Nitrophenyl)ethanone oxime (**2o**).

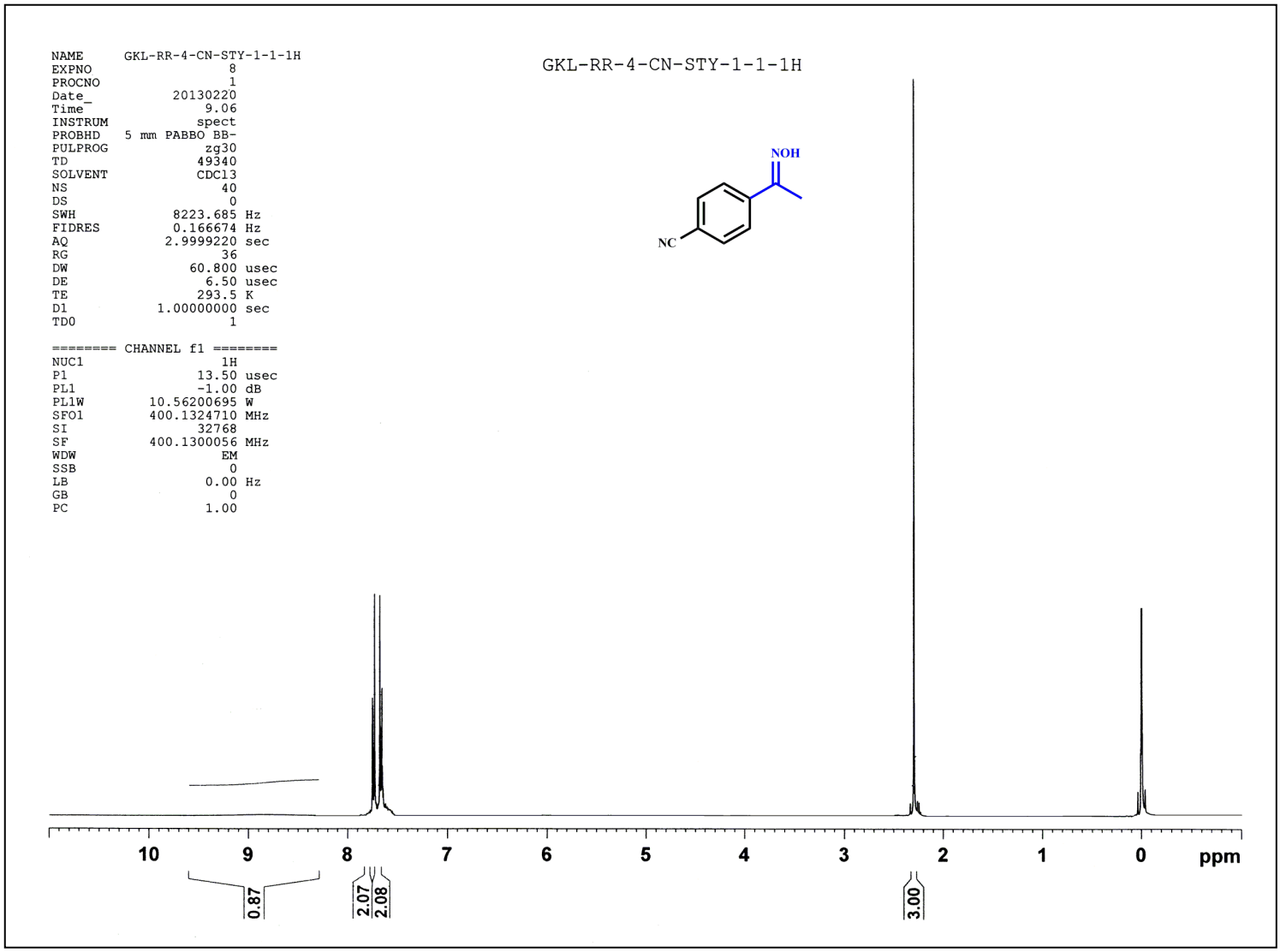

Figure S31. ^{1}H NMR spectrum of 1-(4-Cyanophenyl)ethanone oxime (**2p**).

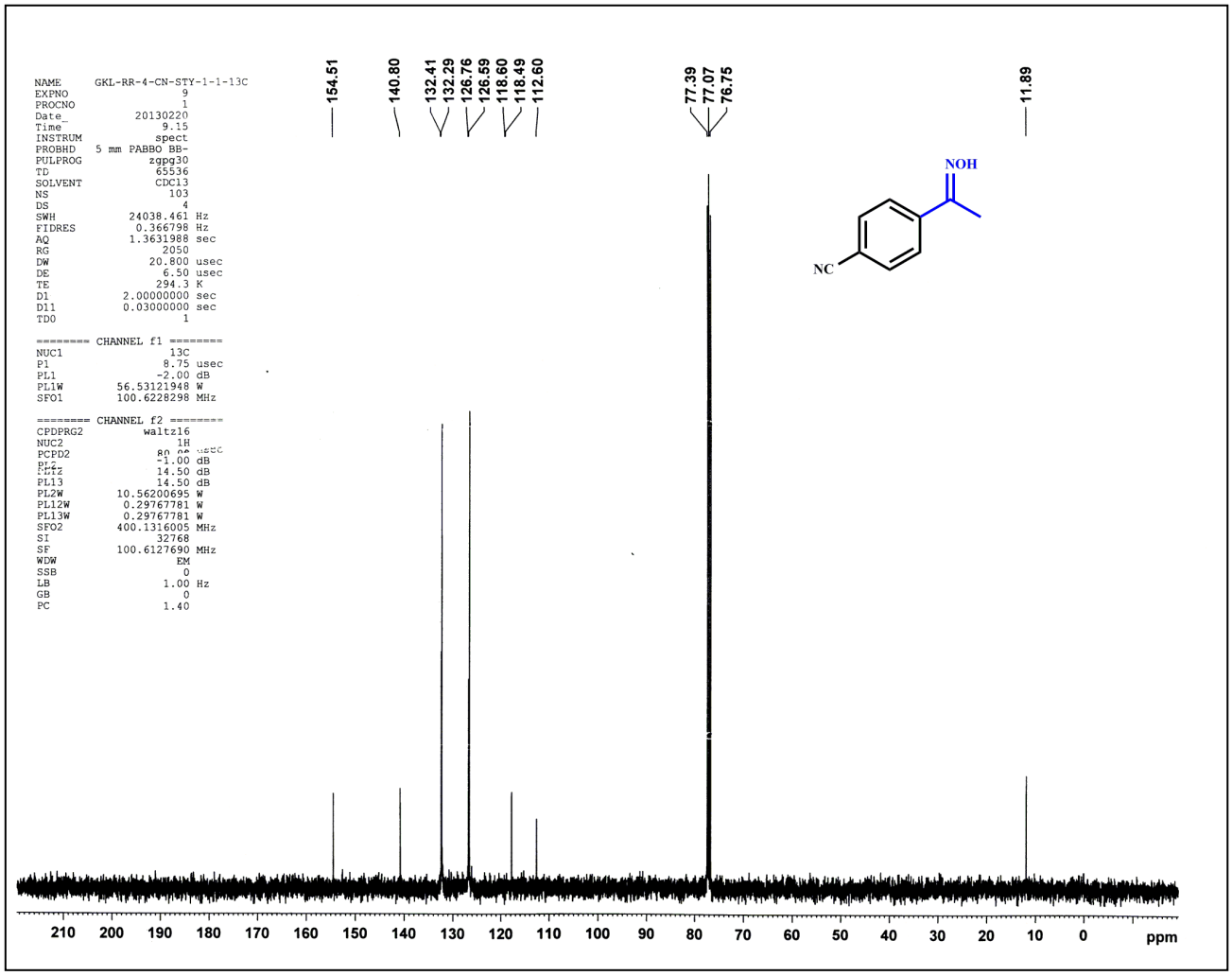

Figure S32. ^{13}C NMR spectrum of 1-(4-Cyanophenyl)ethanone oxime (**2p**).

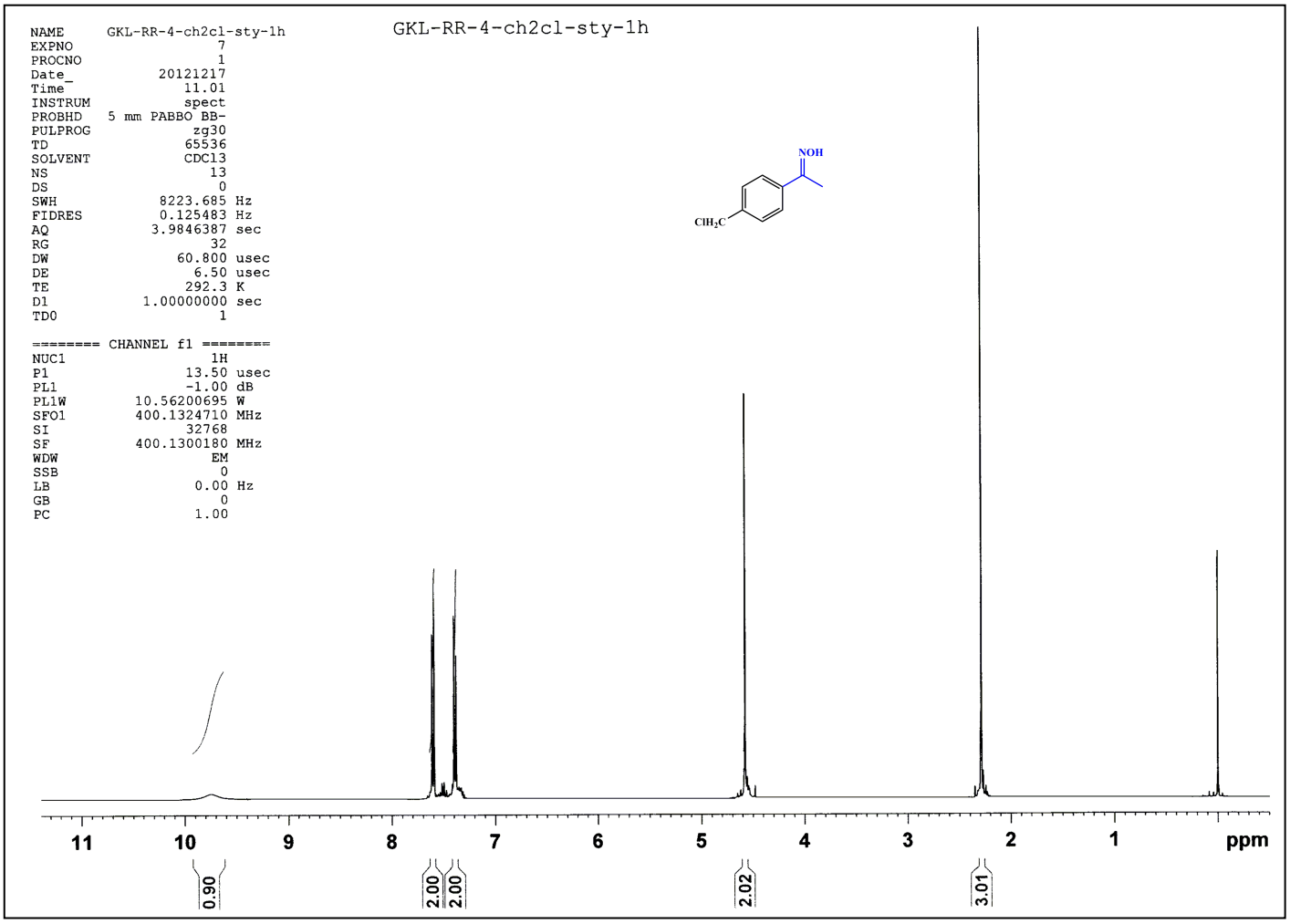

Figure S33. ^{1}H NMR spectrum of 1-(4-Cholоromethylphenyl)ethanone oxime (**2s**).

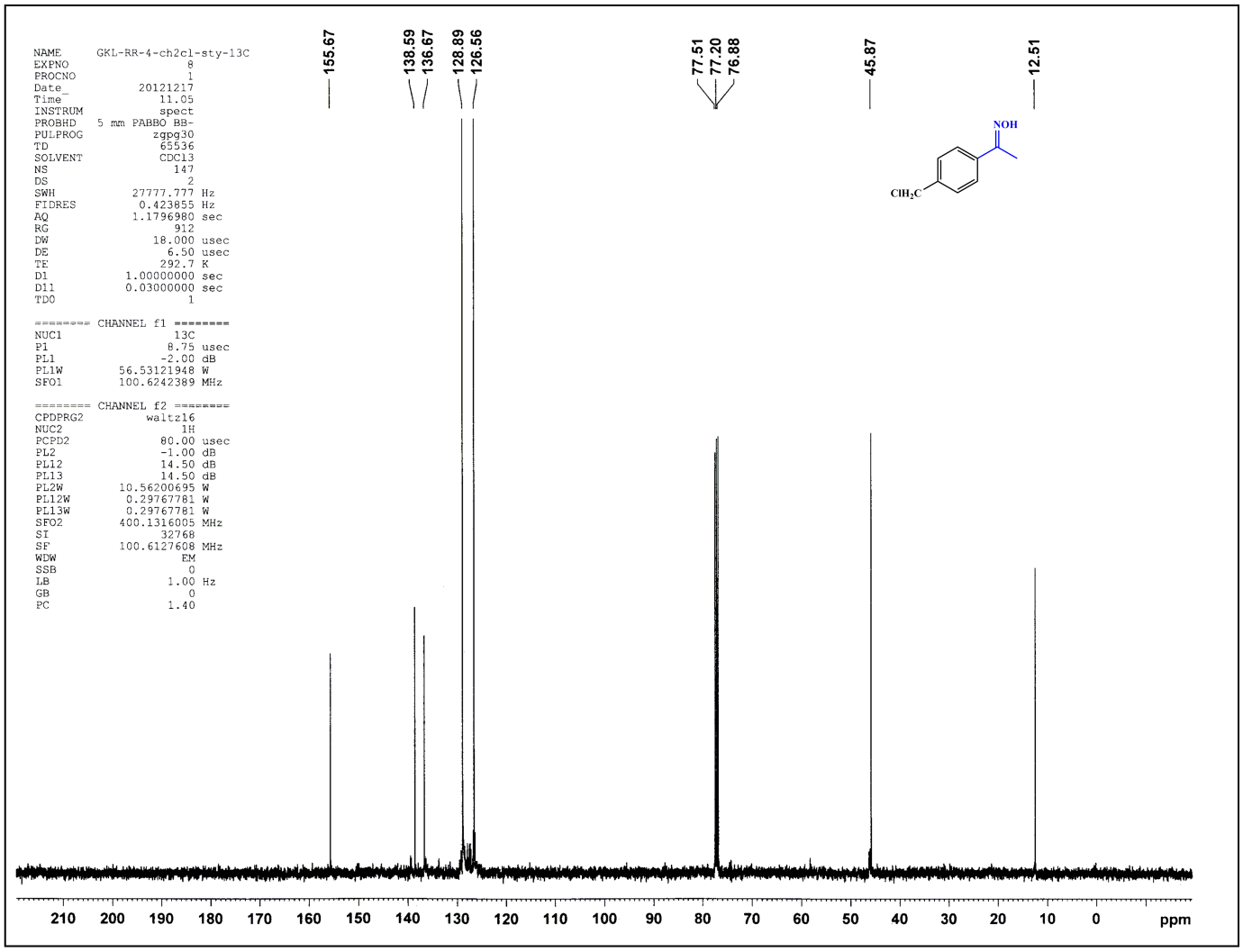

Figure S34. ^{13}C NMR spectrum of 1-(4-Cholоromethylphenyl)ethanone oxime (**2s**).

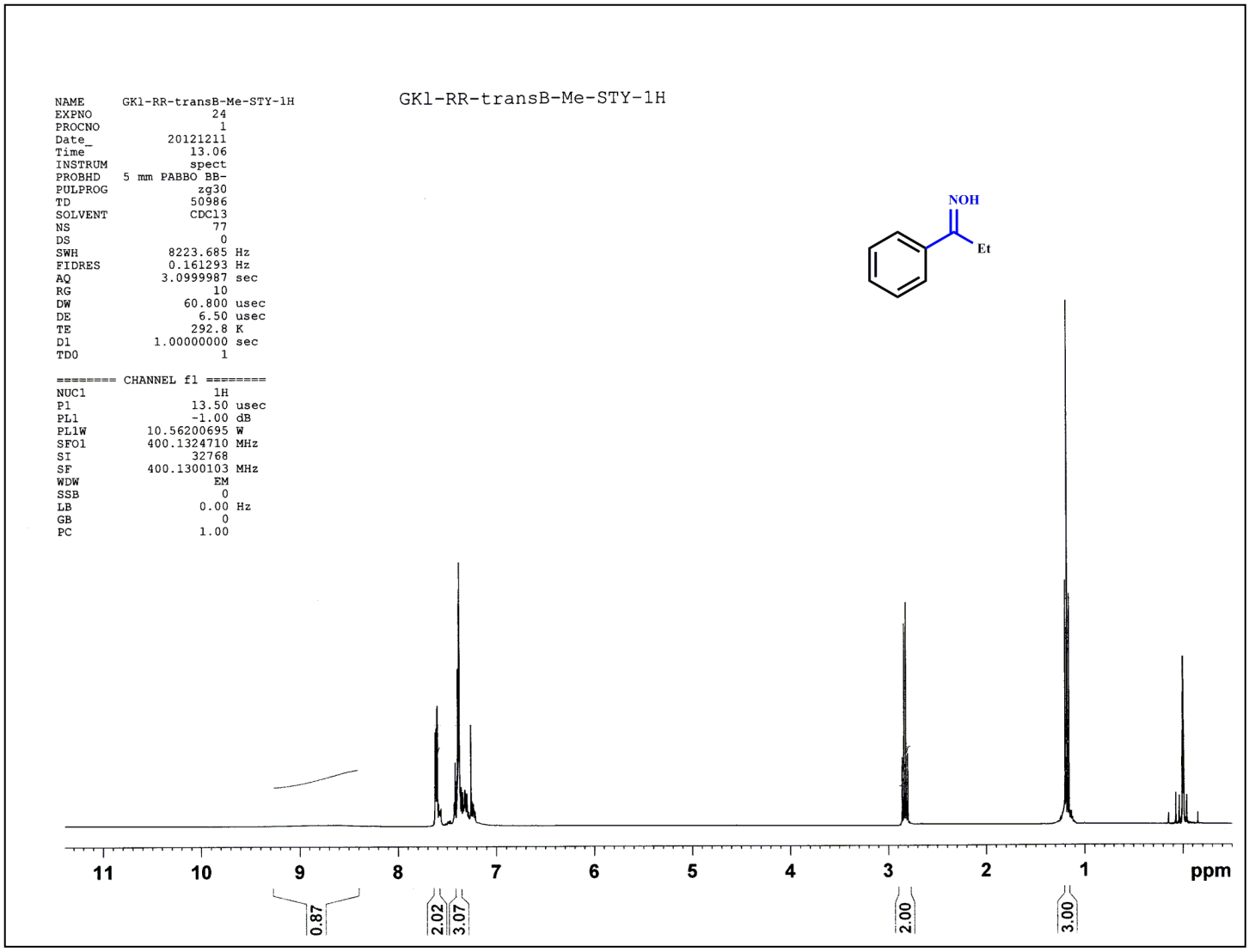

Figure S35. ^{1}H NMR spectrum of Propiophenone oxime (**2t-2u**).

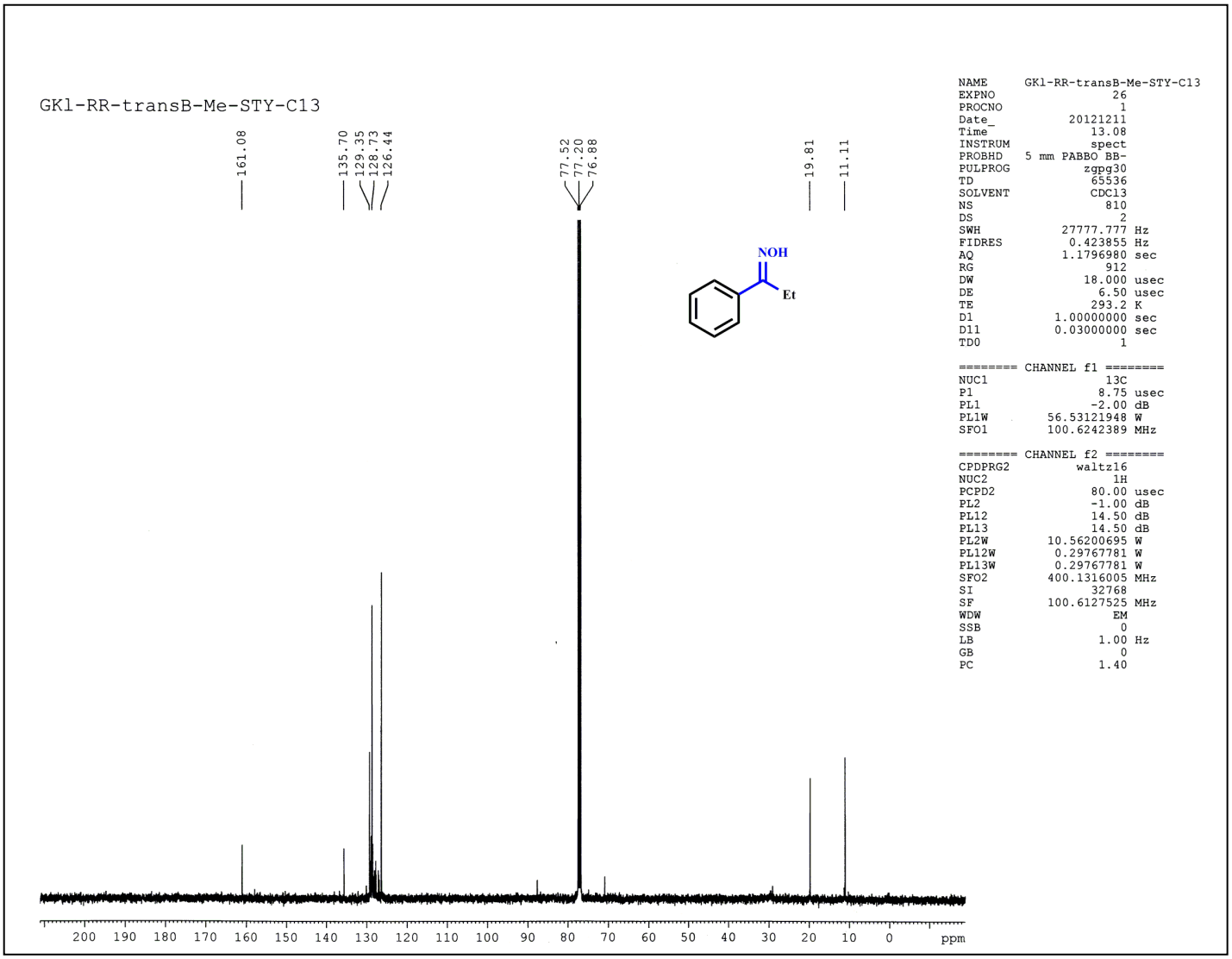

Figure S36. ^{13}H NMR spectrum of Propiophenone oxime (**2t-2u**).

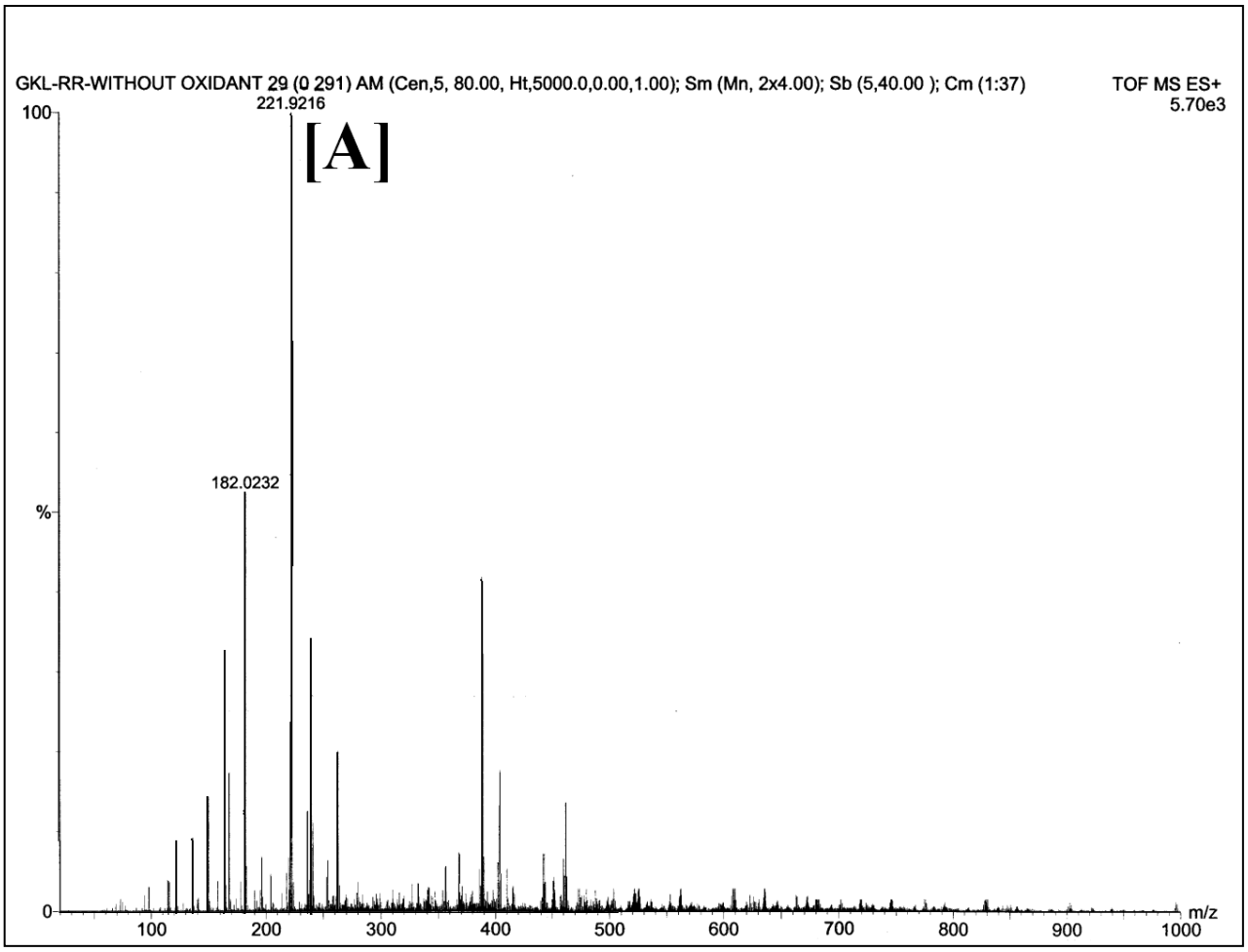

Figure S37. ESI(+)-MS of (1:1) solution of $Fe(BF_4)_2.6H_2O$ and pyridine-2,6-dicarboxylic acid (dipic) in methanol (*m/z* Calcd. for [Fe(dipic)]+H^+ **[A]** is 221.95). It shows that iron is co-ordinated to *one* dianionic tridentate dipic ligand in its pre-catalytic form.

Characterisation of the catalyst

The catalyst was characterised using TEM and XPS.

a. Characterisation by TEM: The morphology of the catalyst is analysed by transmission electron microscopy (Figure S38). The TEM images of the catalyst at the end of the reaction exhibited the presence of only micrometer size particles and presence of any iron-nanoclusters was not observed. Further, the EDX analysis of the used catalyst also revealed the presence of Fe on the surface.

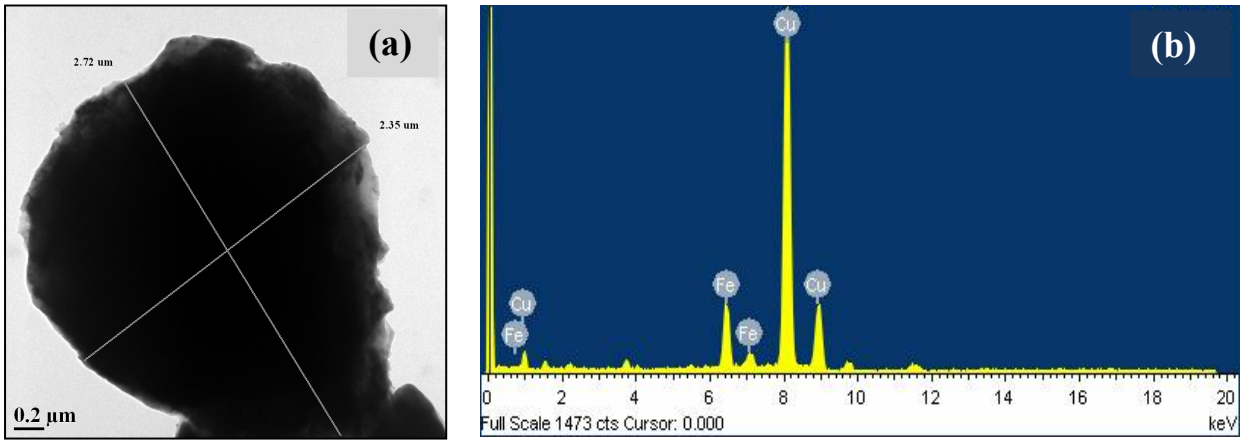

Figure S38. **(a)** FETEM image of the used catalyst at 0.2 µm resolution and **(b)** EDX spectrum of the used catalyst.

a. Characterisation by XPS study:

X-ray photoelectron spectroscopic (XPS) study of the used catalyst was carried out to determine the oxidation state of iron. XPS analysis of the used catalyst indeed revealed the absence of any iron in its zero oxidation state. However, in the used catalyst, signals for Fe 2p $_{3/2}$ and core levels at a characteristic binding energy (BE) of Fe^{+2} (Fe 2p $_{3/2}$) and Fe^{+3} (Fe 2p $_{3/2}$) are clearly seen.

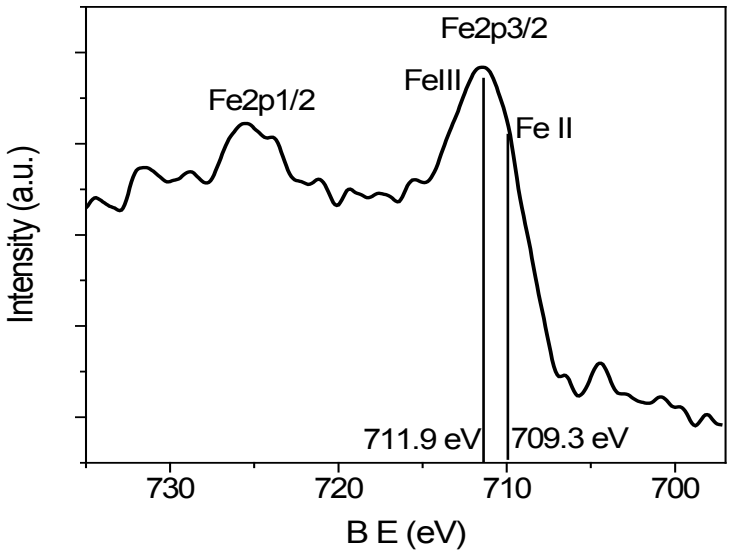

Figure S39. XPS spectra of Fe 2p $_{3/2}$ core level for the used catalyst.

Control Experiment Showing the Present Catalyst was not Poisoned by Hg(0):

Hg(0) poisoning experiment

Hg(0) poisoining test, which is a widely used test of homogeneous vs heterogeneous catalysis was performed. An autoclave was charged under argon atmosphere with iron (II) tetrafluoroborate hexahydrate ($Fe(BF_4)_2.6H_2O$) (10 mg, 0.03 mmol) as the transition metal catalyst in combination with 2,6-pyridinedicarboxylic acid (dipic) (5 mg, 0.03 mmol) as the co-ligand, $NaBH_4$ (170 mg, 4.5 mmol), *t*-BuONO (463.5 mg, 4.5 mmol), the corresponding olefin (3 mmol), MeOH (5 mL) and H_2O (1 mL). Then, the autoclave was filled with 10 bar of H_2 and the reaction mixture was stirred for 2h at room temperature. Then the reaction was stopped and Hg(0) ~100 equiv. was added to the reaction mixture and again autoclaved under 10 bar dihydrogen pressure for 5 h. The yield of the product was found to be 85% at the end of the reaction. The same reaction was carried out without addition of Hg(0) and the conversion was found to be ~30% after 2 h. This proves that the active catalytic species was not poisoned by Hg(0) under the present reaction conditions.

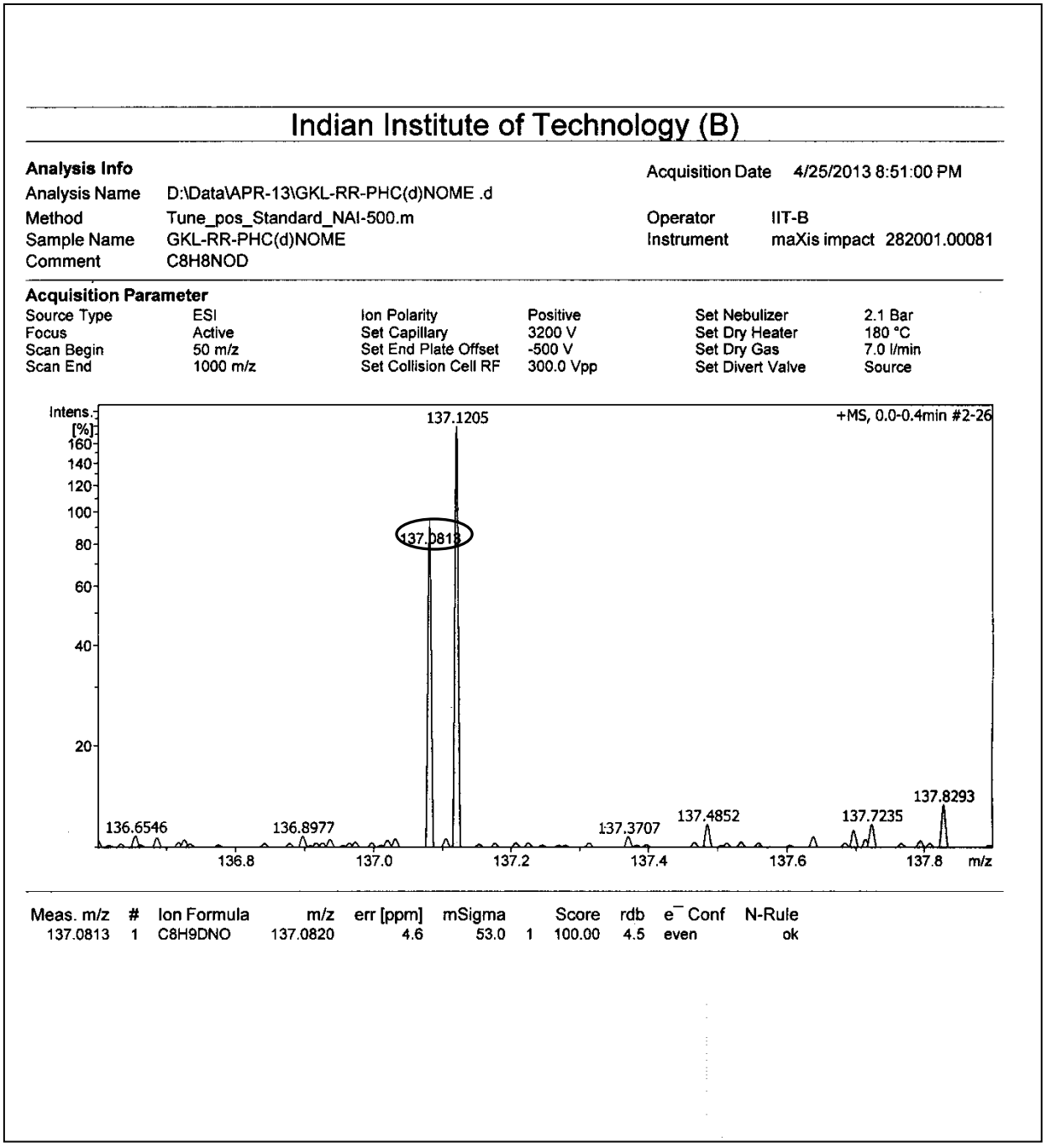

Figure S40. HRMS (ESI+) spectrum of the deuterated acetophenone oxime [PhC(D)(NO)Me] (Mass **[B]**)[where calcd. m/z ($M+H^+$) = 137.082] , the product after the work-up of the catalytic reaction in MeOH-D_2O (5:1) solvent (instead of MeOH-H_2O) under identical reaction conditions.

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