Supporting Information

For

"Pd-catalyzed decarboxylative ortho-acylation of *O*-methyl oximes with phenylglyoxylic acids"

Zhiyong Yang,[a] Xiang chen,[a] Jidan Liu,[a] Qingwen Gui,[a] Kai Xie,[a] Miaomiao Li,[a] Ze Tan,*[a]

[a] State Key Laboratory of Chemo/Biosensing and Chemometrics ,College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China. Tel: +86-731 88822400; E-mail: ztanze@gmail.com[b]

Supporting information

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I. General Information

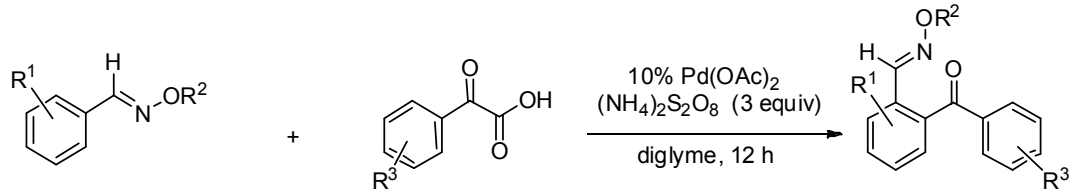
^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ at room temperature on the spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The chemical-shifts scale is based on internal TMS. Data for ^{1}H NMR and ^{13}C NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz).

II. Experimental Section

Preparation of starting materials:

Preparation for oximes and α-oxocarboxylic acids. *O*-methyl (*O*-phenyl) oximes were prepared by reacting the corresponding aldehydes or ketones with $MeONH_2 \cdot HCl$ ($BnONH_2 \cdot HCl$) in EtOH in for about 5 h.[1] All the desired oximes were purified by flash column chromatography. α-oxocarboxylic acids (**2a**, **2g)** were purchased from Alfa Aesar. Other α-oxocarboxylic acids were prepared from oxidation of corresponding methyl ketones with SeO_2 according to the reported procedure.[2]

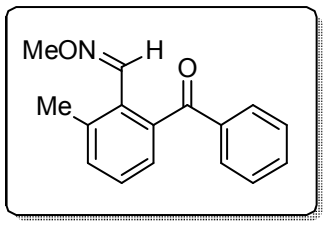
General procedure for the decarboxylative acylation recations



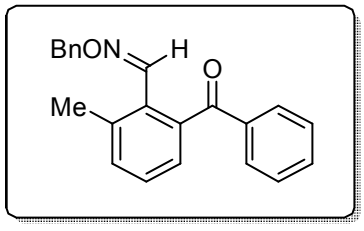
1 **2** **3** or **4**

A 25-mL round bottom flask was charged with *O*-methyl (*O*-phenyl) oximes (**1**, 0.5 mmol), phenylglyoxylic acids (**2**, 1.0 mmol), $Pd(OAc)_2$ (0.05 mmol), $(NH_4)_2S_2O_8$ (1.5 mmol) and diglyme (5 mL). The reaction flask was then stirred at 35 °C under N_2 for 12 h (monitored by TLC). Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short silica gel column to remove the deposition with ethyl acetate (100 ml). Then the ethyl acetate was washed with water (30 ml×3), and then with brine, dried over Mg_2SO_4, and filtered. The solvents were removed via vacuum evaporation. The crude products were purified with flash chromatography (silica gel, gradient eluent of EtOAc in n-pentane: 1%, v/v) to yield the product **3** or **4** as a yellow or colorless solid (oil). The appropriate eluent for each product is referred to the detail information as below.

Data of new compounds

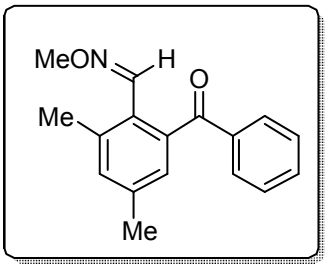


(3a) 2-benzoyl-6-methylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.40 (petroleum ether/ ethyl acetate, 12/1); Yield: 71%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 3.66 (s, 3H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.34 (t, *J* = 6.4 Hz, 1H), 7.35 (d, *J* = 6.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 8.18 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.25, 61.85, 126.33, 128.26 (2C), 128.59, 128.83, 129.45 (2C), 132.16, 132.68, 137.55, 137.84, 139.68, 145.33, 197.94; IR (neat) 2945, 2906, 1725, 1641, 1518, 1483, 1272, 1052, 798, 696 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{15}NO_2$: 253.1103, found 253.1105; Anal. Calcd. for $C_{16}H_{15}NO_2$: Elemental Analysis: C, 75.87; H, 5.97; N, 5.53; Found: C, 75.97; H, 6.05; N, 5.39.

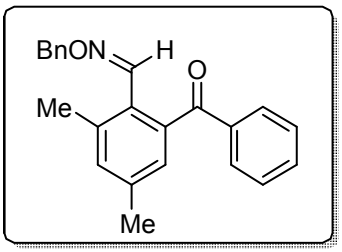


(3b) 2-benzoyl-6-methylbenzaldehyde *O*-benzyl oxime. TLC R_f = 0.44 (petroleum ether/ ethyl acetate, 12/1); Yield: 65%; colorless solid; m.p.: 78.5-79.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 4.85 (s, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.24-7.25 (m, 3H), 7.30 (d, *J* = 4.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 8.26 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.52, 76.57, 126.34, 128.08, 128.47 (2C), 128.51 (2C), 128.67 (2C), 128.78, 129.01, 129.79 (2C), 132.30, 132.91, 137.26, 137.90, 137.94, 139.99, 146.07, 197.97; IR (neat) 2920, 1725, 1602, 1536, 1483, 1370, 1317, 833, 759, 696 cm^{-1}; HRMS (EI) m/z calcd. for $C_{22}H_{19}NO_2$: 329.1416, found

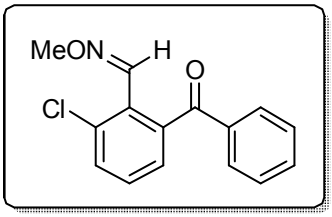
329.1418; Anal. Calcd. for $C_{22}H_{19}NO_2$: Elemental Analysis: C, 80.22; H, 5.81; N, 4.25; Found: C, 80.31; H, 5.91; N, 4.07.



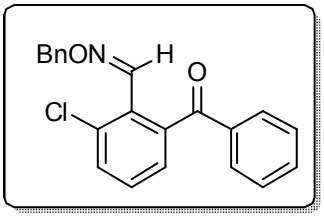
(3c) 2-benzoyl-4,6-dimethylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.45 (petroleum ether/ ethyl acetate, 12/1); Yield: 75%; colorless solid; m.p.: 79.4-81.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.41 (s, 3H), 3.63 (s, 3H), 7.05 (s, 1H), 7.15 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.13 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.83, 21.24, 61.93, 126.34, 128.42, 129.49 (2C), 129.70 (2C), 130.52, 132.70, 136.29, 137.95, 138.17, 140.00, 146.08, 197.96; MS (m/z) 267 (M^+). Anal. Calcd. for $C_{17}H_{17}NO_2$: Elemental Analysis: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.47; H, 6.48; N, 5.09.



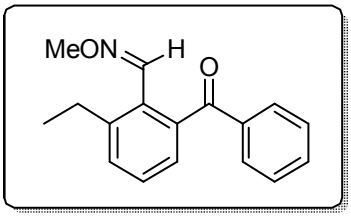
(3d) 2-benzoyl-4,6-dimethylbenzaldehyde *O*-benzyl oxime. TLC R_f = 0.45 (petroleum ether/ ethyl acetate, 12/1); Yield: 73%; colorless solid; m.p.: 97.3-98.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.38 (s, 3H), 4.83 (s, 2H), 7.02 (s, 1H), 7.11-7.14 (m, 3H), 7.25-7.26 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 8.22 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.45, 21.35, 76.48, 125.89, 126.90, 128.05, 128.47 (2C), 128.49 (2C), 128.69 (2C), 129.76 (2C), 132.85, 133.05, 137.33, 137.76, 138.00, 139.31, 140.02, 145.94, 198.22; MS (m/z) 343 (M^+). Anal. Calcd. for $C_{23}H_{21}NO_2$: Elemental Analysis: C, 80.44; H, 6.16; N, 4.08; Found: C, 80.47; H, 6.18; N, 4.11.



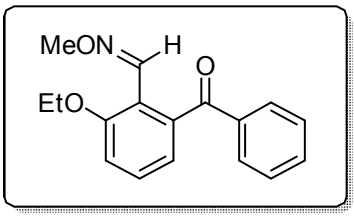
(3e) 2-benzoyl-6-chlorobenzaldehyde *O*-methyl oxime. TLC R_f = 0.50 (petroleum ether/ ethyl acetate, 12/1); Yield: 49%; yellow solid; m.p.: 106.1-107.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.60 (s, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 3H), 7.53 (d, *J* = 6.8 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 8.29 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 62.32, 127.13, 128.28, 128.62 (2C), 129.46 (2C), 130.37, 131.25, 133.12, 134.60, 137.57, 141.21, 143.94, 196.52; HRMS (EI) m/z calcd. for $C_{15}H_{12}ClNO_2$: 273.0557, found 273.0559; Anal. Calcd. for $C_{15}H_{12}ClNO_2$: Elemental Analysis: C, 65.82; H, 4.42; N, 5.12; Found: C, 65.97; H, 4.51; N, 5.00.



(3f) 2-benzoyl-6-chlorobenzaldehyde *O*-benzyl oxime. TLC R_f = 0.46 (petroleum ether/ ethyl acetate, 12/1); Yield: 43%; yellow solid; m.p.: 87.6-89.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.78 (s, 2H), 7.05-7.08 (m, 2H), 7.25-7.27 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 8.39 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 76.89, 126.86, 128.19, 128.49 (2C), 128.60, 128.64 (2C), 128.68 (2C), 129.55(2C), 130.31, 131.12, 133.10, 134.69, 136.87, 137.36, 141.19, 144.44, 196.30; MS (m/z) 349 (M^+). Anal. Calcd. for $C_{21}H_{16}ClNO_2$: Elemental Analysis: C, 72.10; H, 4.61; N, 4.00; Found: C, 72.07; H, 4.64; N, 3.92.

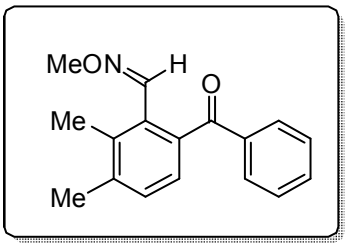


(3g) 2-benzoyl-6-ethylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.40 (petroleum ether/ ethyl acetate, 12/1); Yield: 70%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.6 Hz, 3H), 2.78 (q, *J* = 7.6 Hz, 2H), 3.65 (s, 3H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.35-7.42 (m, 4H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 8.20 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 15.80, 26.76, 62.00, 126.60, 128.26, 128.46 (2C), 129.29, 129.62 (2C), 130.84, 132.81, 138.18, 140.11, 143.91, 145.26, 198.19; MS (m/z) 267 (M^+). Anal. Calcd. for $C_{17}H_{17}NO_2$: Elemental Analysis: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.43; H, 6.45; N, 5.14.

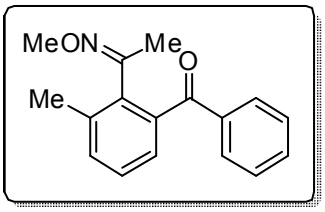


(3h) 2-benzoyl-6-ethoxybenzaldehyde *O*-methyl oxime. TLC R_f = 0.35 (petroleum ether/ ethyl acetate, 12/1); Yield: 79%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, *J* = 7.6 Hz, 3H), 3.56 (s, 3H), 4.09 (q, *J* = 6.8 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.26-7.42 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 2H), 8.28 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 14.87, 61.85, 64.50, 113.08, 118.80, 120.40, 128.34 (2C), 129.35 (2C), 130.71, 132.66, 137.92, 140.31, 142.85, 157.19, 197.62; IR (neat) 2924, 1725, 1644, 1254, 1044, 773, 696 cm^{-1}; MS (m/z) 283 (M^+). Anal. Calcd. for

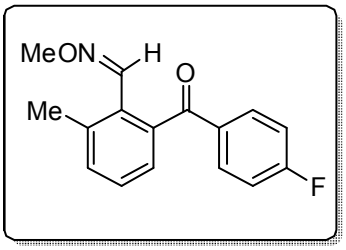
$C_{17}H_{17}NO_3$: Elemental Analysis: C, 72.07; H, 6.05; N, 4.94; Found: C, 72.17; H, 6.08; N, 4.91.



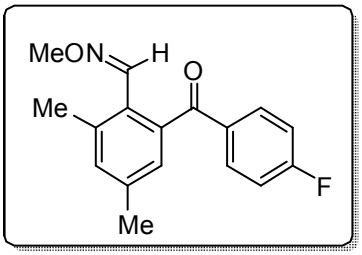
(3i) 6-benzoyl-2,3-dimethylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.40 (petroleum ether/ ethyl acetate, 12/1); Yield: 73%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3H), 2.29 (s, 3H), 3.59 (s, 3H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 8.17 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 16.11, 20.83, 61.97, 126.53, 128.43, 129.49 (2C), 129.70 (2C), 130.52, 132.70, 136.29, 137.95, 138.51, 139.79, 146.75, 198.13; MS (m/z) 267 (M^+). Anal. Calcd. for $C_{17}H_{17}NO_2$: Elemental Analysis: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.37; H, 6.48; N, 5.19.



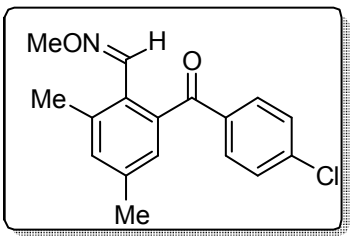
(3j) (2-(1-(methoxyimino)ethyl)-3-methylphenyl)(phenyl)methanone. TLC R_f = 0.43 (petroleum ether/ ethyl acetate, 12/1); Yield: 35%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H), 2.35 (s, 3H), 3.72 (s, 3H), 7.27-7.29 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR(100 MHz, CDC l_3): δ 17.56, 19.78, 61.74, 126.72, 127.90, 128.38 (2C), 130.22 (2C), 132.89, 132.95, 136.96, 137.21, 138.32, 139.80, 156.76, 198.11; MS (m/z) 267 (M^+). Anal. Calcd. for $C_{17}H_{17}NO_2$: Elemental Analysis: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.44; H, 6.48; N, 5.17.



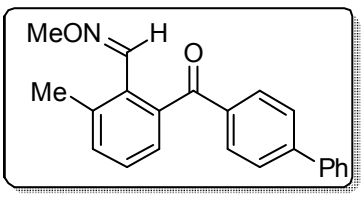
(4a) 2-(4-fluorobenzoyl)-6-methylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.42 (petroleum ether/ ethyl acetate, 12/1); Yield: 63%; colorless solid; m.p.: 107.5-110.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 3.66 (s, 3H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.33-7.38 (m, 2H), 7.74-7.77 (m, 2H), 8.18 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.83, 62.05, 115.59 (d, $J_{C\text{-}F}$ = 21.8 Hz, 2C), 128.82 (d, $J_{C\text{-}F}$ = 34.3 Hz, 1C), 129.10, 131.07, 132.18 (d, $J_{C\text{-}F}$ = 9.1 Hz, 2C), 132.52, 134.51, 137.87, 139.59, 145.39, 165.14 (d, $J_{C\text{-}F}$ = 252.9 Hz, 1C), 196.57; MS (m/z) 271 (M^+). Anal. Calcd. for $C_{16}H_{14}FNO_2$: Elemental Analysis: C, 70.84; H, 5.20; N, 5.16; Found: C, 70.77; H, 5.27; N, 5.09.



(4b) 2-(4-fluorobenzoyl)-4,6-dimethylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.41 (petroleum ether/ ethyl acetate, 12/1); Yield: 65%; colorless solid; m.p.: 107.9-109.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.42 (s, 3H), 3.64 (s, 3H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.07 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 7.15 (s, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 8.14 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.29, 21.31, 61.94, 115.52 (d, $J_{C\text{-}F}$ = 21.8 Hz, 2C), 125.78, 126.90, 132.19, 133.14 (d, $J_{C\text{-}F}$ = 9.2 Hz, 2C), 134.58 (d, $J_{C\text{-}F}$ = 2.6 Hz, 1C), 137.73, 139.41, 139.62, 145.29, 165.61 (d, $J_{C\text{-}F}$ = 252.7 Hz, 1C), 196.76; IR (neat) 2923, 2853, 1725, 1644, 1254, 1044, 773 cm^{-1}; HRMS (EI) m/z calcd. for $C_{17}H_{16}FNO_2$: 285.1165, found 285.1162; Anal. Calcd. for $C_{17}H_{16}FNO_2$: Elemental Analysis: C, 71.56; H, 5.65; N, 4.91; Found: C, 71.67; H, 5.77; N, 4.77.

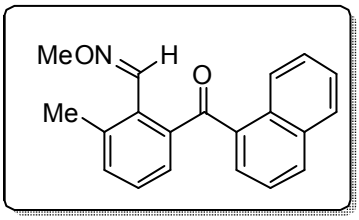


(4c) 2-(4-chlorobenzoyl)-4,6-dimethylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.41 (petroleum ether/ ethyl acetate, 12/1); Yield: 69%; colorless solid; m.p.: 111.5-113.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.41 (s, 3H), 3.64 (s, 3H), 7.02 (s, 1H), 7.15 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 8.13 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.26, 21.38, 62.04, 125.84, 127.01, 128.81 (2C), 130.96 (2C), 133.29, 136.65, 137.75, 139.14, 139.42, 139.54, 145.22, 197.13; MS (m/z) 301 (M^+). Anal. Calcd. for $C_{17}H_{16}ClNO_2$: Elemental Analysis: C, 67.66; H, 5.34; N, 4.64; Found: C, 67.57; H, 5.38; N, 4.69.

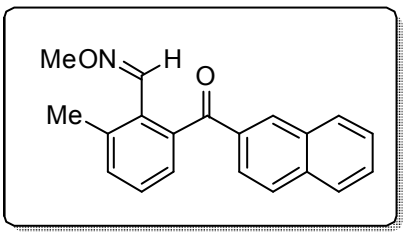


(4d) 2-([1,1'-biphenyl]-4-carbonyl)-6-methylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.40 (petroleum ether/ ethyl acetate, 12/1); Yield: 72%; colorless solid; m.p.: 87.1-89.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 3.69 (s, 3H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.34-7.40 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.61-7.64 (m, 4H), 7.81 (d, *J* = 7.6 Hz, 2H), 8.22 (s, 1H); ^{13}C NMR

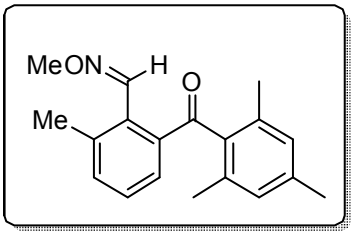
(100 MHz, $CDCl_3$): δ 20.54, 62.09, 126.47, 127.13 (2C), 127.43 (2C), 128.34, 128.82, 129.01 (2C), 129.10, 130.31 (2C), 132.38, 136. 81, 137.85, 140.04, 140.11, 145.54, 145.66, 197.68; MS (m/z) 329 (M^+). Anal. Calcd. for $C_{22}H_{19}NO_2$: Elemental Analysis: C, 80.22; H, 5.81; N, 4.25; Found: C, 80.27; H, 5.84; N, 4.19.



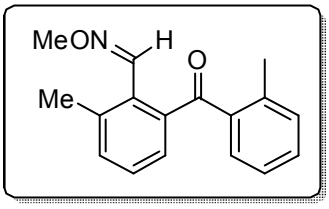
(4e) 2-(1-naphthoyl)-6-methylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.40 (petroleum ether/ ethyl acetate, 12/1); Yield: 70%; colorless solid; m.p.: 138.2-141.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.45 (s, 3H), 7.31-7.43 (m, 5H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.96 (t, *J* = 8.0 Hz, 1H), 8.14 (s, 1H), 8.88 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.33, 61.88, 124.31, 126.64, 126.78, 127.94, 127.95, 128.50, 129.02, 129.68, 130.00, 131.47, 132.93, 133.11, 134.06, 136.10, 137.96, 141.46, 146.40, 199.56; IR (neat) 2920, 1666, 1529, 1448, 1268, 1019, 973, 748, 696 cm^{-1}; HRMS (EI) m/z calcd. for $C_{20}H_{17}NO_2$: 303.1259, found 303.1263.



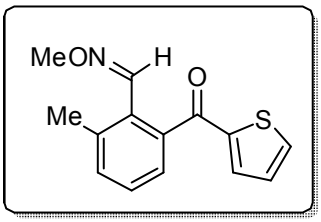
(4f) 2-(2-naphthoyl)-6-methylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.40 (petroleum eth er/ ethyl acetate, 12/1); Yield: 67%; colorless solid; m.p.: 117.0-119.1 °C; ^{1}H NMR (400 M Hz, $CDCl_3$): δ 2.48 (s, 3H), 3.63 (s, 3H), 7.31 (d, *J* = 4.8 Hz, 1H), 7.33-7.41 (m, 2H), 7.5 0 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.82-7.89 (m, 3H), 7.97 (d, *J* = 8.4 Hz, 1 H), 8.07 (s, 1H), 8.20 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.50, 62.05, 125.17, 126.59, 126.77, 127.96, 128.41, 128.49, 128.92, 129.02, 129.68, 131.58, 132.41, 132.58, 135.59, 135. 61, 137.88, 140.08, 145.56, 198.14; MS (m/z) 303 (M^+). Anal. Calcd. for $C_{20}H_{17}NO_2$: Eleme ntal Analysis: C, 79.19; H, 5.65; N, 4.62; Found: C, 79.22; H, 5.59; N, 4.61.



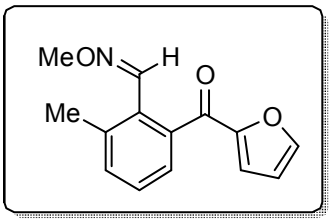
(4g) 2-methyl-6-(2,4,6-trimethylbenzoyl)benzaldehyde *O*-methyl oxime. TLC R_f = 0.42 (petrol eum ether/ ethyl acetate, 12/1); Yield: 85%; colorless solid; m.p.: 89.5-90.3 °C; ^{1}H NMR (400 M Hz, $CDCl_3$): δ 2.09 (s, 6H), 2.31 (s, 3H), 2.50 (s, 3H), 3.95 (s, 3H), 6.86 (s, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 6.8 Hz, 1H), 8.53 (s, 1H); ^{13}CNMR(100 M Hz, $CDCl_3$): δ 19.81 (2C), 21.29, 21.33, 61.99, 128.76 (4C), 129.27, 131.34, 134.98, 135.29, 137. 47, 138.78, 139.02, 139.09, 149.02, 201.57; IR (neat) 2955, 2815, 1659, 1609, 1602, 1455, 1265, 1051, 914, 850 cm^{-1}; MS (m/z) 295 (M^+). Anal. Calcd. for $C_{19}H_{21}NO_2$: Elemental Analysis: C, 77.26; H, 7.17; N, 4.74; Found: C, 7 7.27; H, 7.21; N, 4.70.



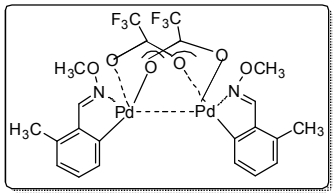
(4h) 2-methyl-6-(2-methylbenzoyl)benzaldehyde *O*-methyl oxime. TLC R_f = 0.41 (petroleum et her/ ethyl acetate, 12/1); Yield: 68%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 2.58 (s, 3H), 3.77 (s, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.28-7.33 (m, 2H), 7.3 4 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 8.19 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20. 54, 21.55, 62.00, 125.48, 127.64, 128.97, 129.57, 130.08, 130.71, 131.62, 131.76, 132.97, 138.03, 1 39.63, 141.11, 146.89, 199.75; MS (m/z) 267 (M^+). Anal. Calcd. for $C_{17}H_{17}NO_2$: Elemental Analysis: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.42; H, 6.44; N, 5.21.



(4i) 2-methyl-6-(thiophene-2-carbonyl)benzaldehyde *O*-methyl oxime. TLC R_f = 0.37 (petroleum ether/ ethyl acetate, 12/1); Yield: 64%; yellow solid; m.p.: 83.8-86.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 3.76 (s, 3H), 7.05 (t, *J* = 4.4 Hz, 1H), 7.30-7.35 (m, 4H), 7.66 (d, *J* = 4.8 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.76, 62.18, 126.17, 128.12, 128.68, 128.84, 132.66, 134.35, 134.66, 138.11, 139.71, 145.29, 145.83, 190.19; IR (neat) 2945, 2906, 1641, 1602, 1518, 1483, 1377, 1314, 1272, 1052, 798, 696 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{13}NO_2S$: 259.0667, found 259.0669; Anal. Calcd. for $C_{14}H_{13}NO_2S$: Elemental Analysis: C, 64.84; H, 5.05; N, 5.40; Found: C, 64.95; H, 5.17; N, 5.27.



(4j) 2-(furan-2-carbonyl)-6-methylbenzaldehyde *O*-methyl oxime. TLC R_f = 0.38 (petroleum ether / ethyl acetate, 12/1); Yield: 60%; yellow solid; m.p.: 75.5-78.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 3.74 (s, 3H), 6.51 (d, *J* = 4.0 Hz, 1H), 6.97 (d, *J* = 3.6 Hz, 1H), 7.26-7.34 (m, 3 H), 7.60 (t, *J* = 1.2 Hz, 1H), 8.27 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.63, 62.22, 112.44, 1 19.46, 126.57, 128.97, 132.98, 1337.15, 137.98, 138.85, 145.88, 146.85, 153.13, 185.28; MS (m/z) 243 (M^+). Anal. Calcd. for $C_{14}H_{13}NO_3$: Elemental Analysis: C, 69.12; H, 5.39; N, 5.76; Found: C, 69.22; H, 5.48; N, 5.69.



$C_{22}H_{20}F_6N_2O_6Pd_2$ was prepared according to the method reported by Chien-Hong Cheng.[3] To a suspension of palladium acetate (1 mmol, 0.224 g) in 5 mL TFA was added a solution of 2-methylbenzaldehyde *O*-methyl oxime (1 mmol, 0.149 g) in 5 mL TFA; the mixture was then kept at 50 °C for at least 5 h and concentrated via vacuum evaporation. After the residue was washed with MeOH several times, the crude product was isolated in 48% yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 3.71 (s, 3H), 6.80-6.87 (m, 3H), 7.36 (s, 1H).

III. References and notes:

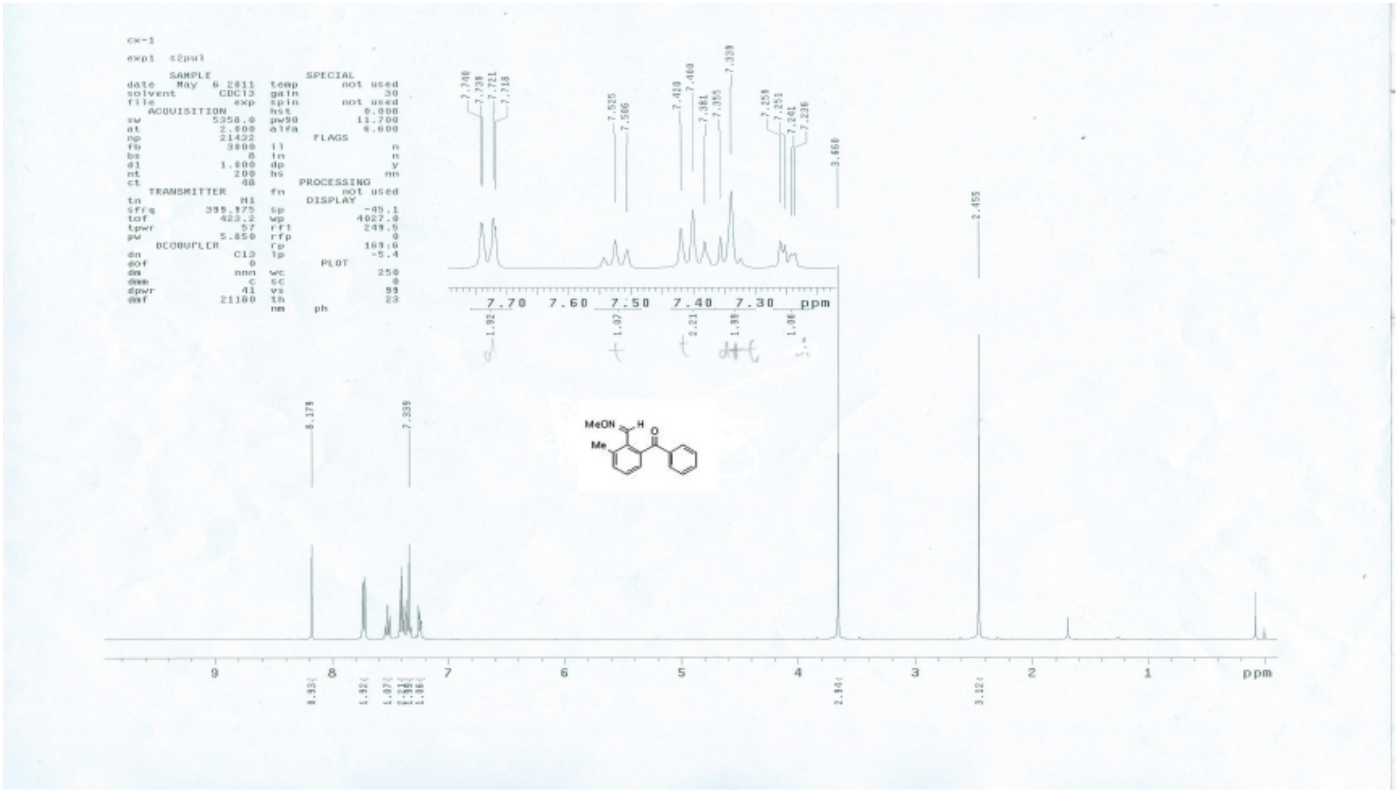
1. C. J. MacNevin, R. L. Moore and D. C. Liotta, *J. Org. Chem.*, 2008, **73**, 1264.

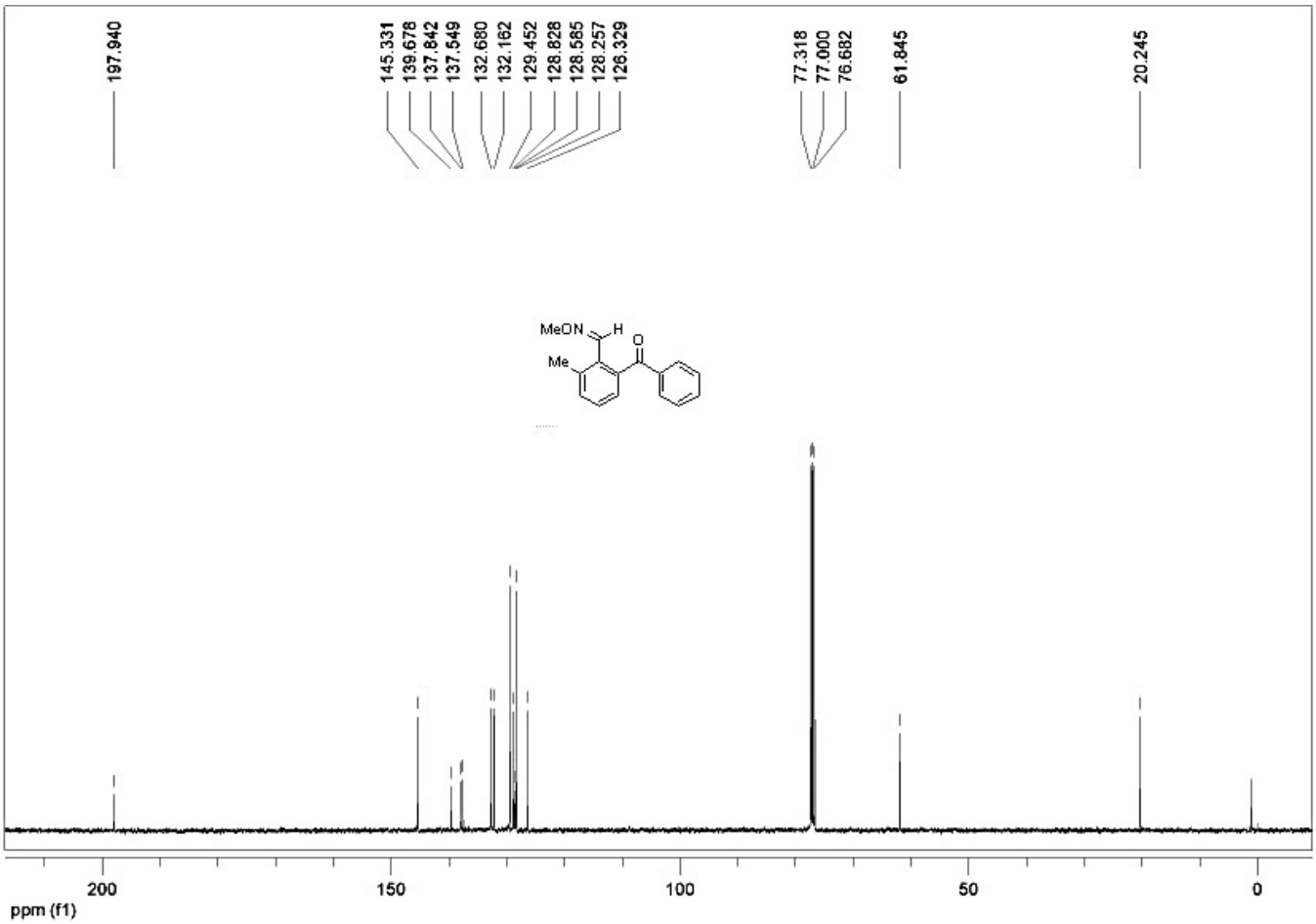
2. K. Wadhwa, C. X. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Syn. Comm.*, 2008, **38**, 4434.

3. V. S. Thirunavukkarasu and C.-H. Cheng, *Chem.-Eur. J.* 2011, **17**, 14723.

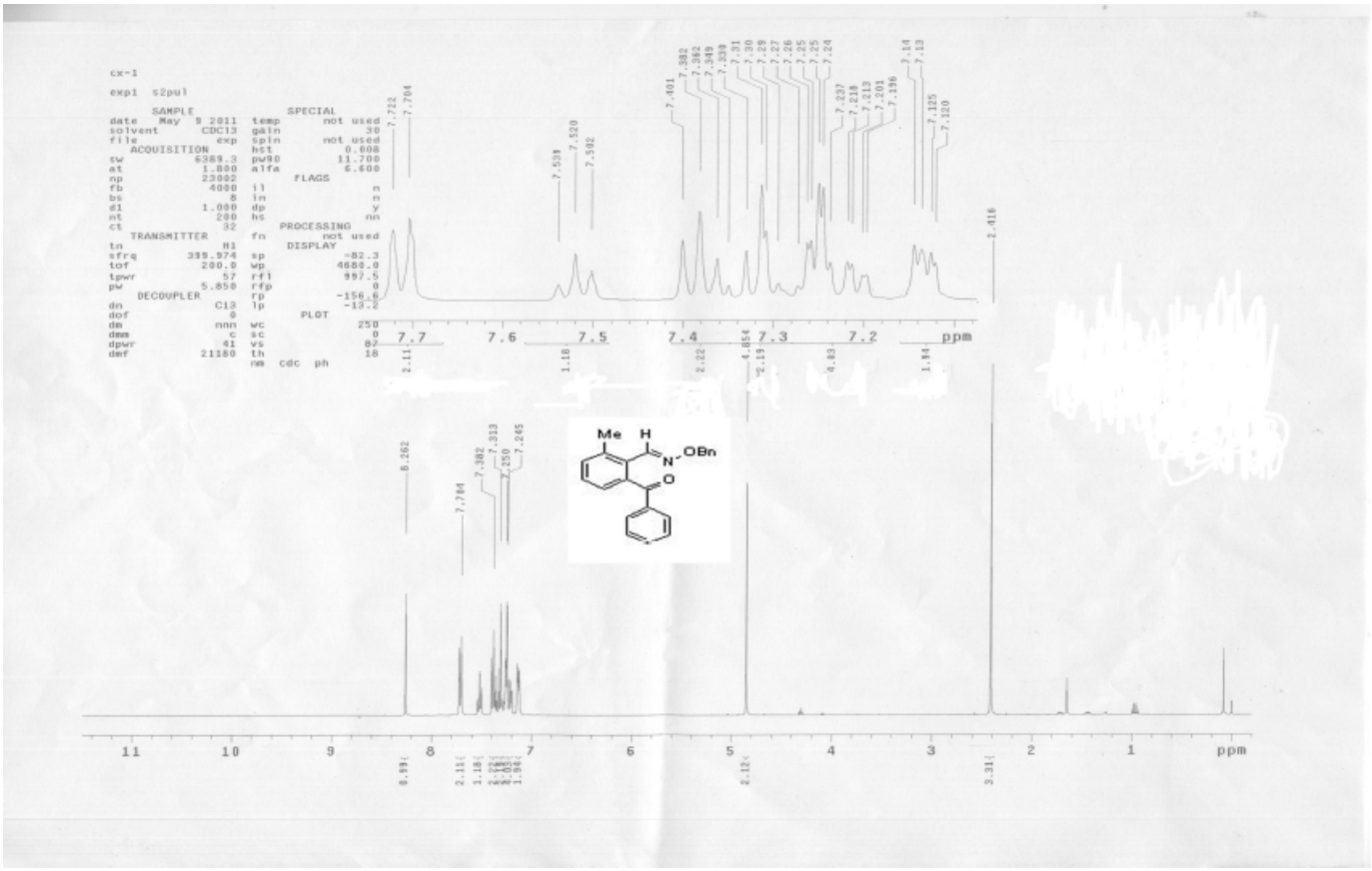
IV. ^{1}H and ^{13}C NMR Spectra

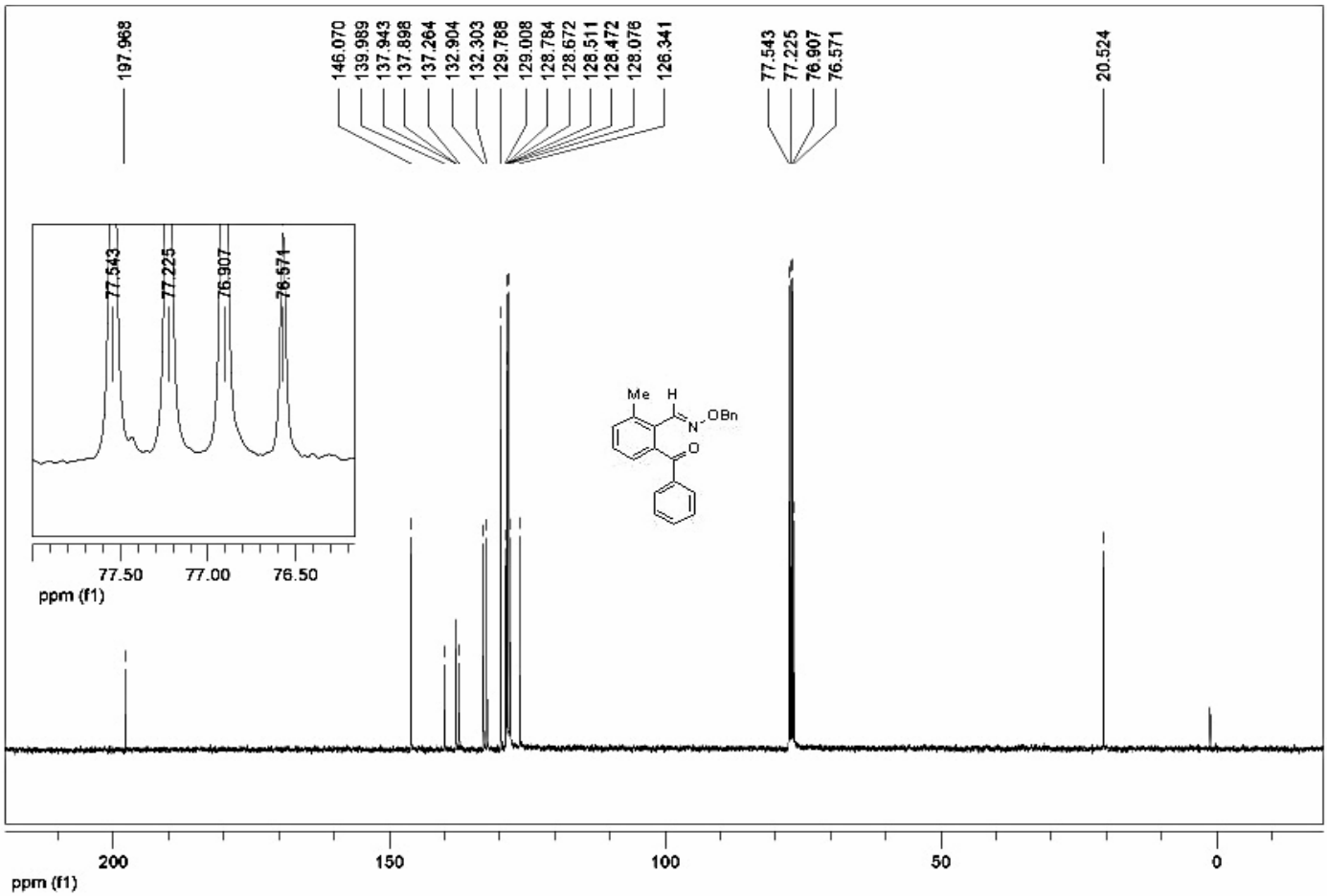
^{1}H and ^{13}C NMR Spectra for **3a**



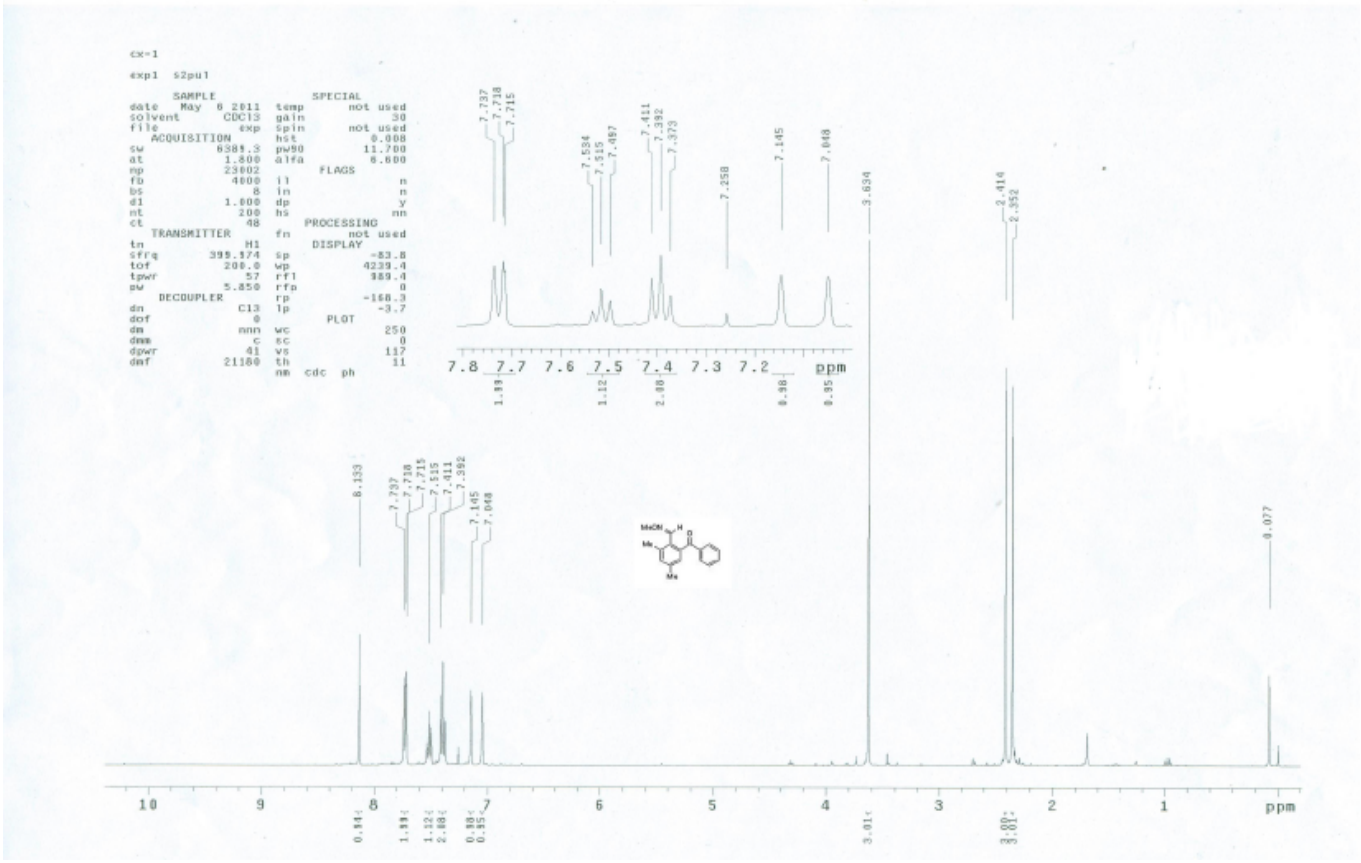


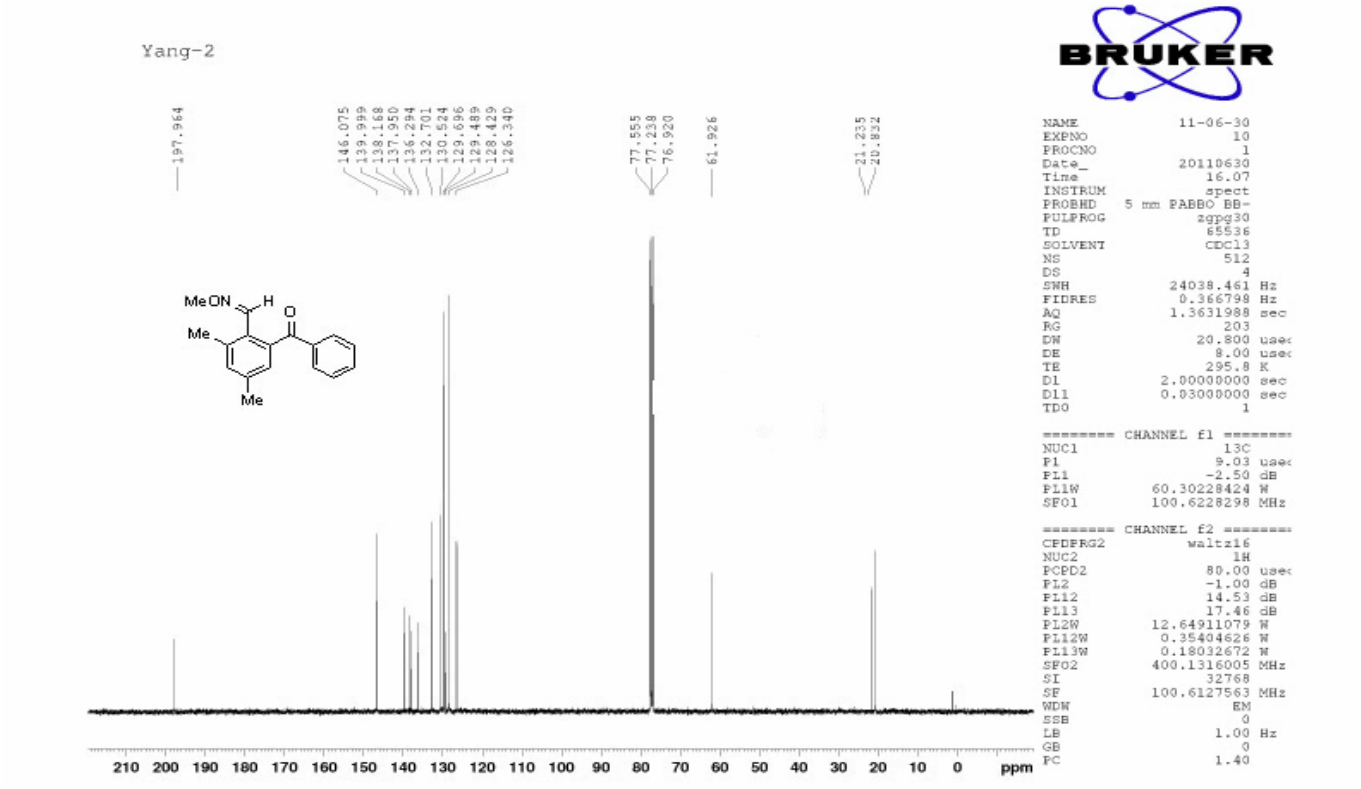
^{1}H and ^{13}C NMR Spectra for **3b**



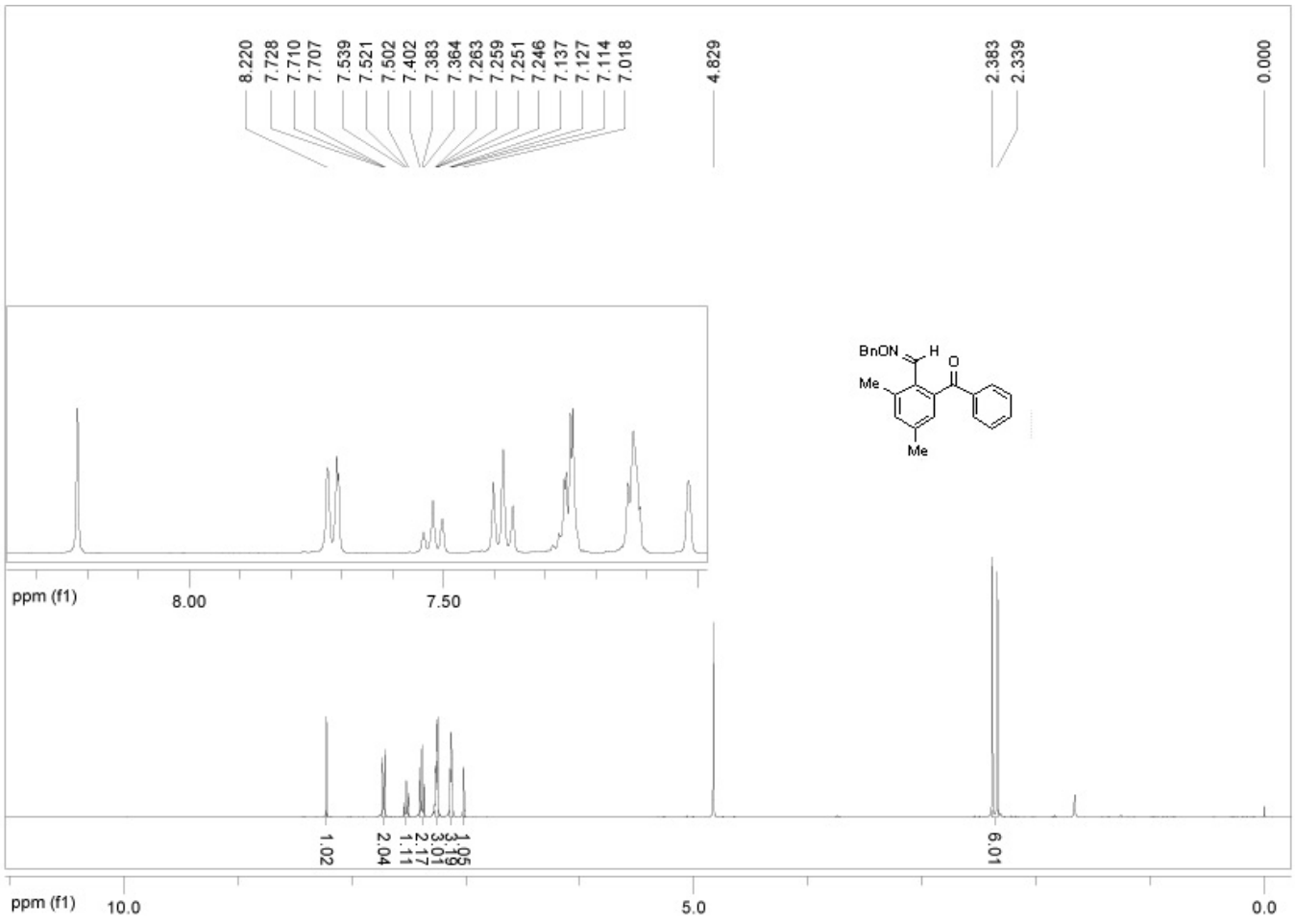


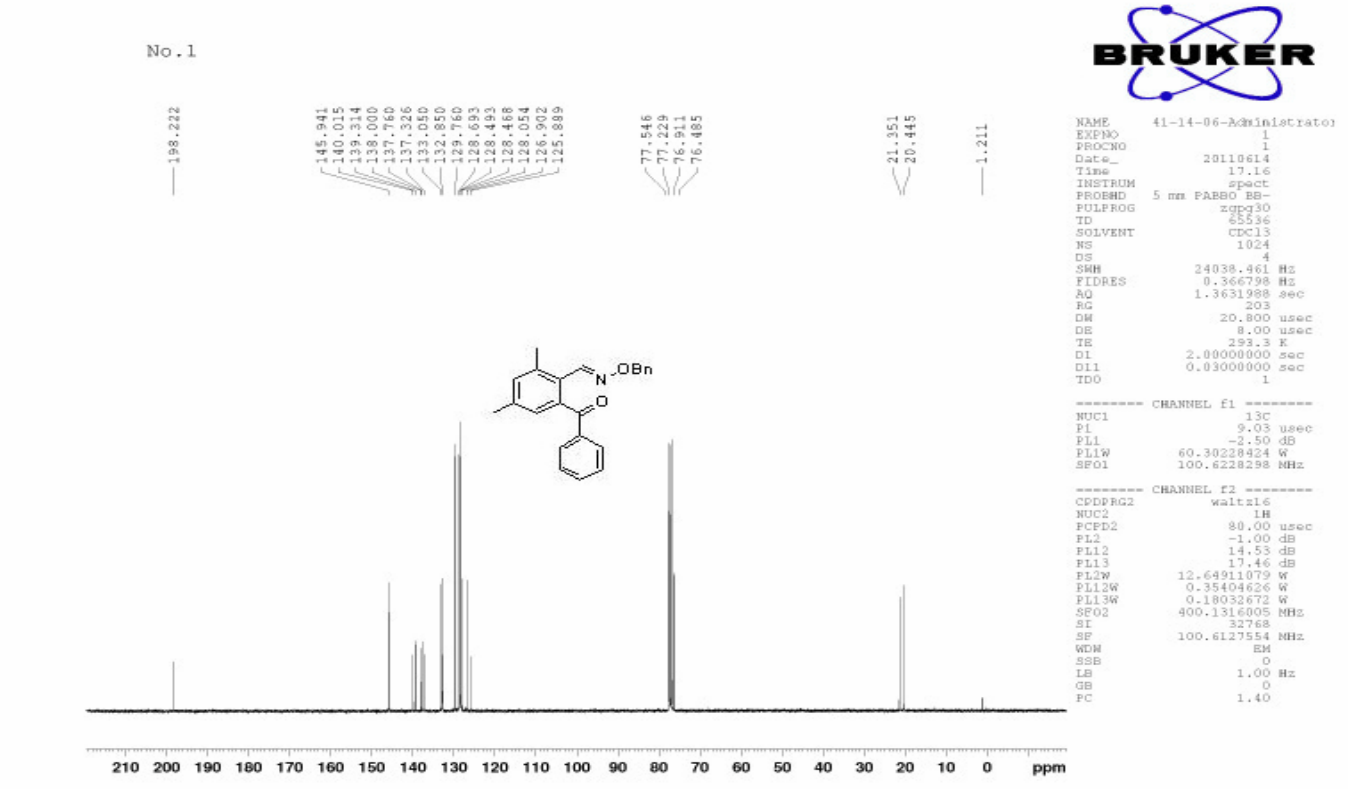
^{1}H and ^{13}C NMR Spectra for **3c**



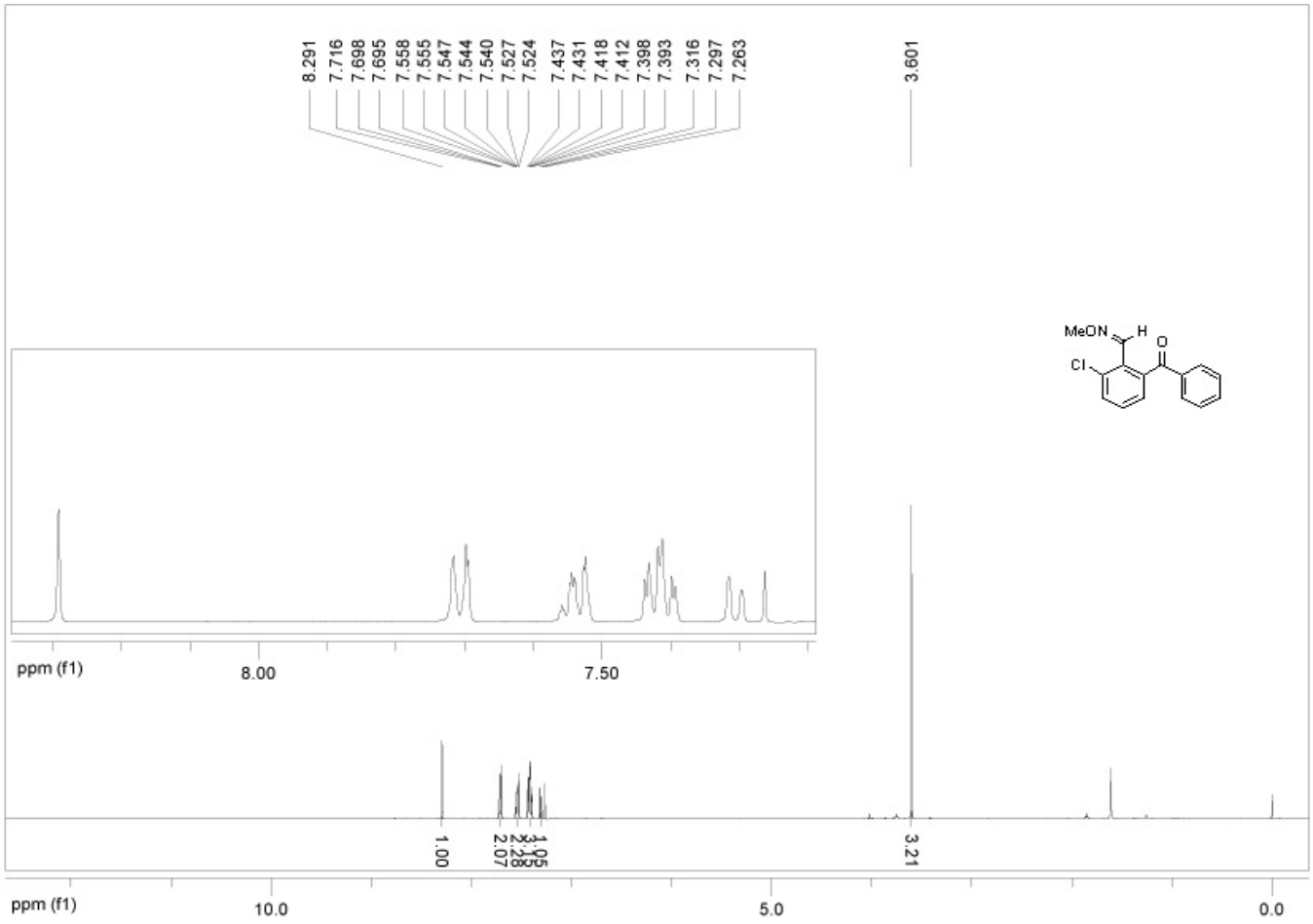


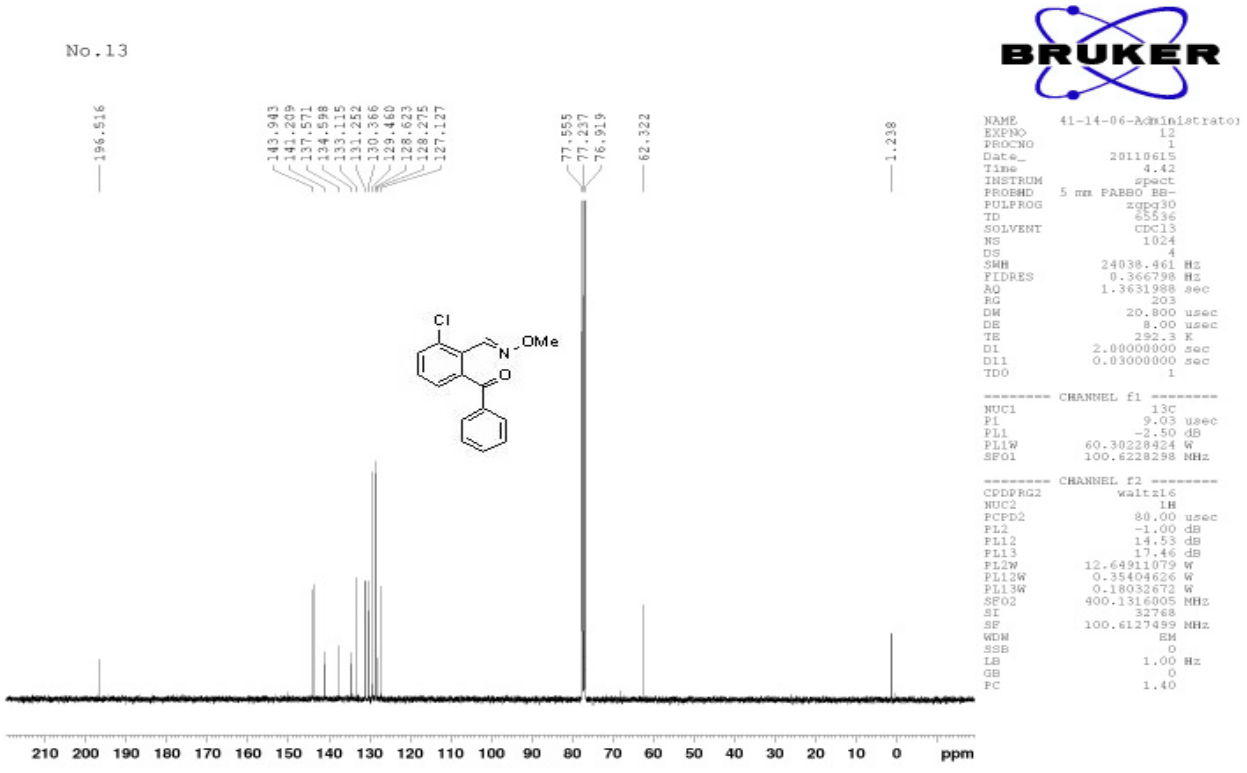
^{1}H and ^{13}C NMR Spectra for **3d**



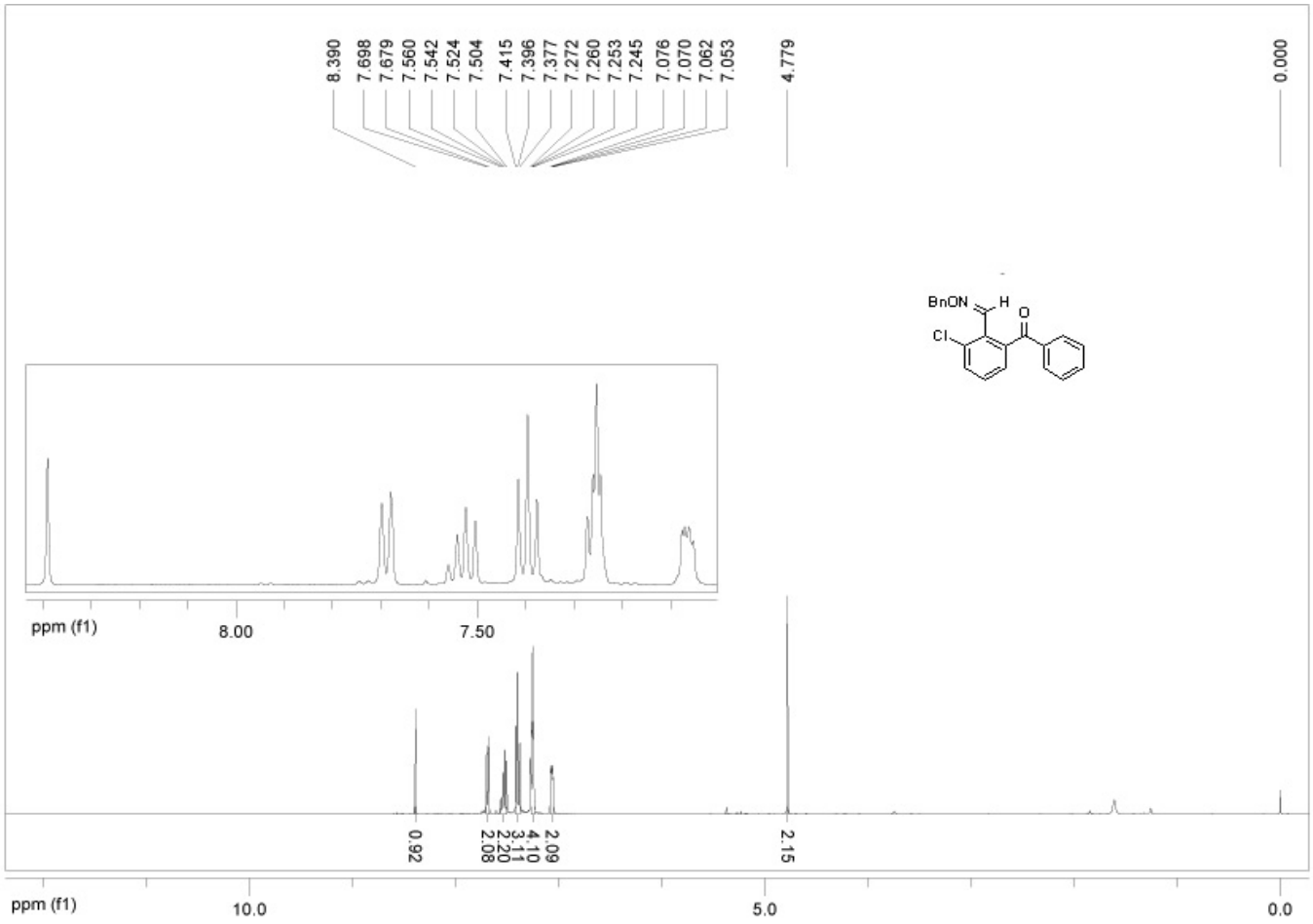


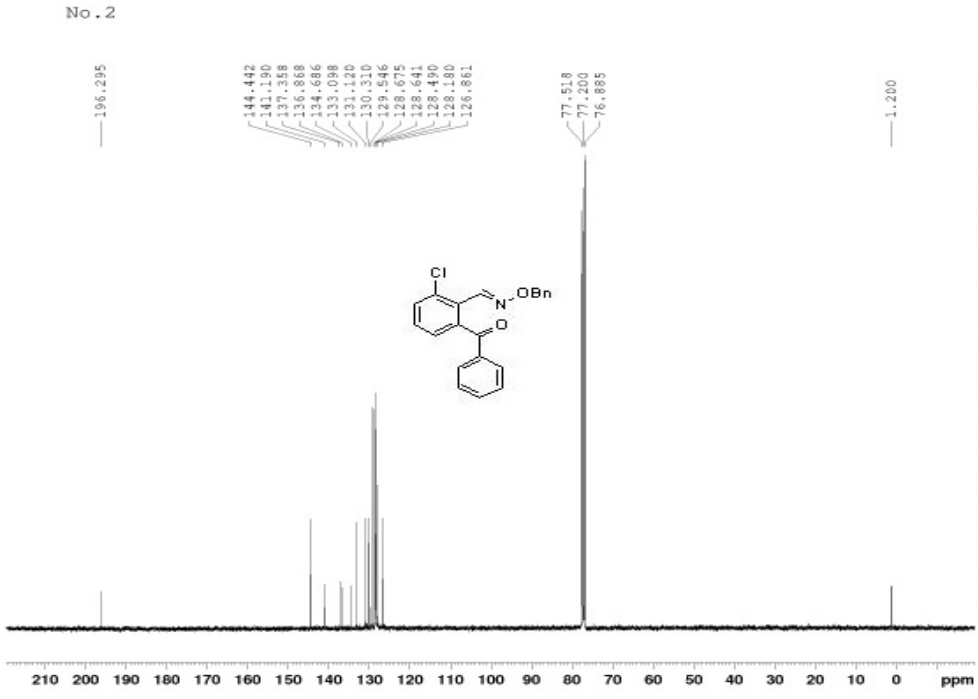
^{1}H and ^{13}C NMR Spectra for **3e**

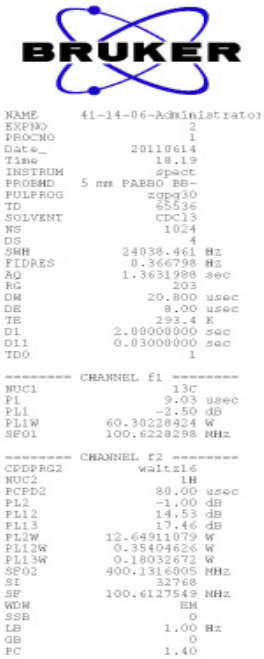




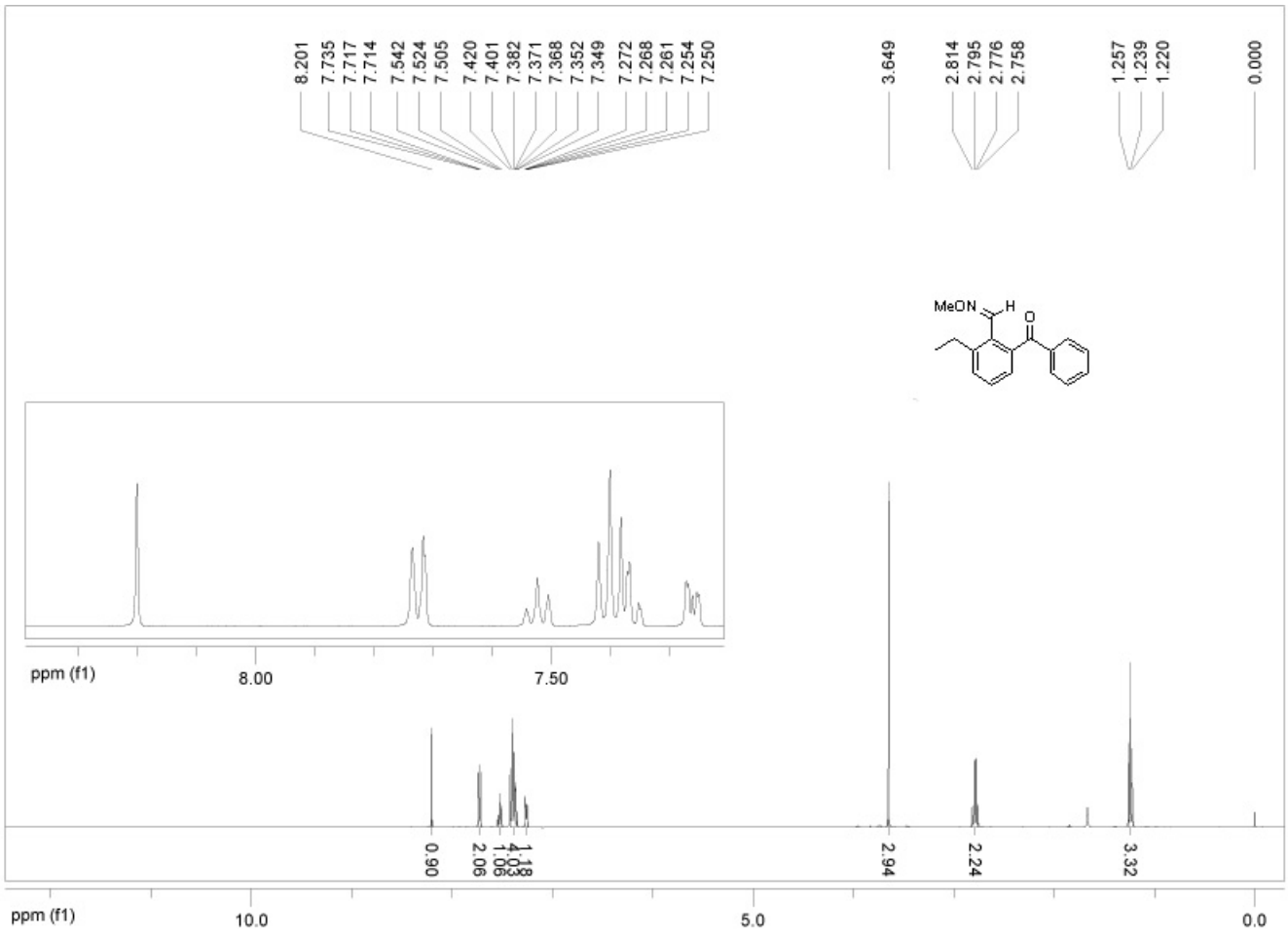
^{1}H and ^{13}C NMR Spectra for **3f**

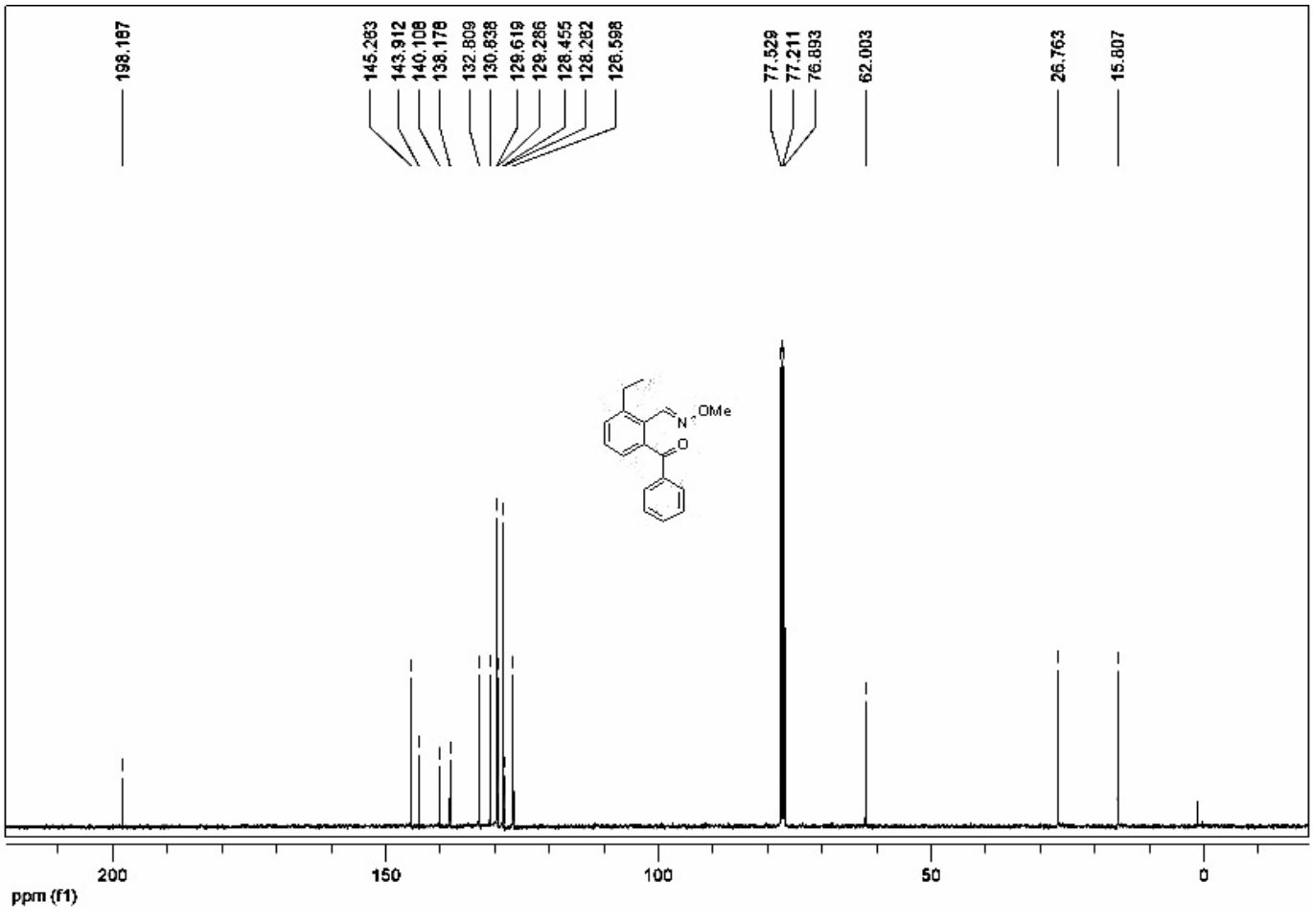




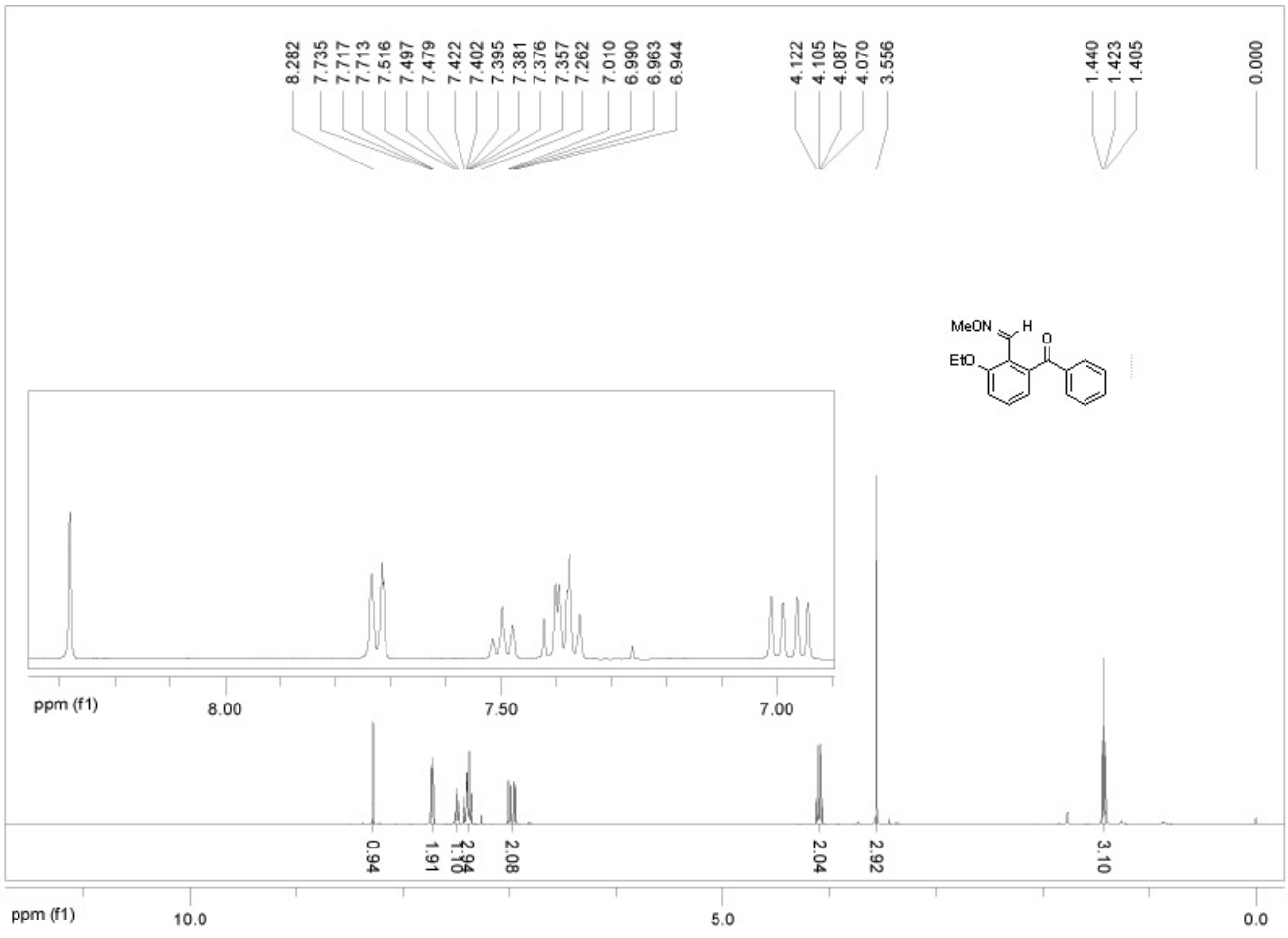


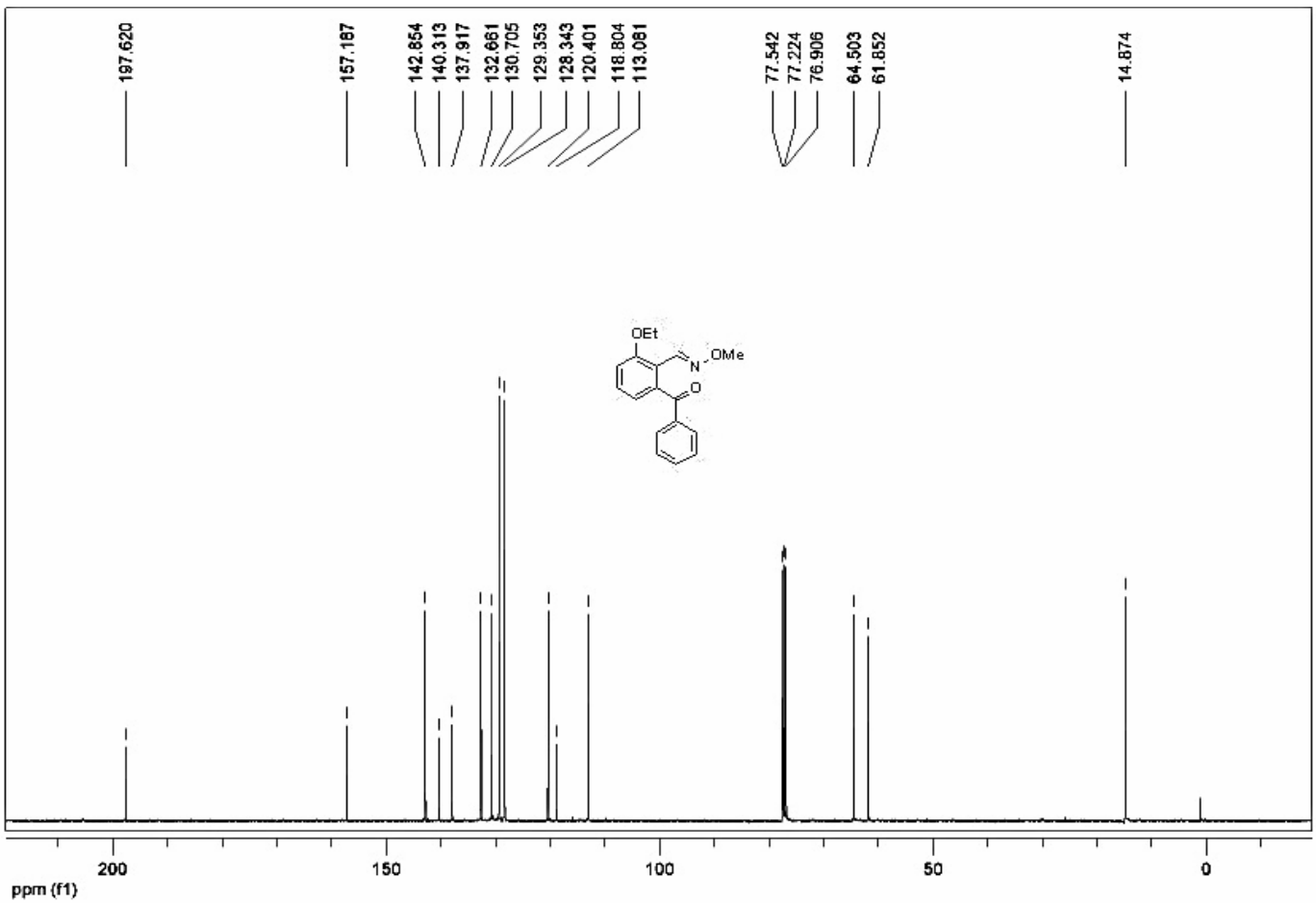
^{1}H and ^{13}C NMR Spectra for **3g**



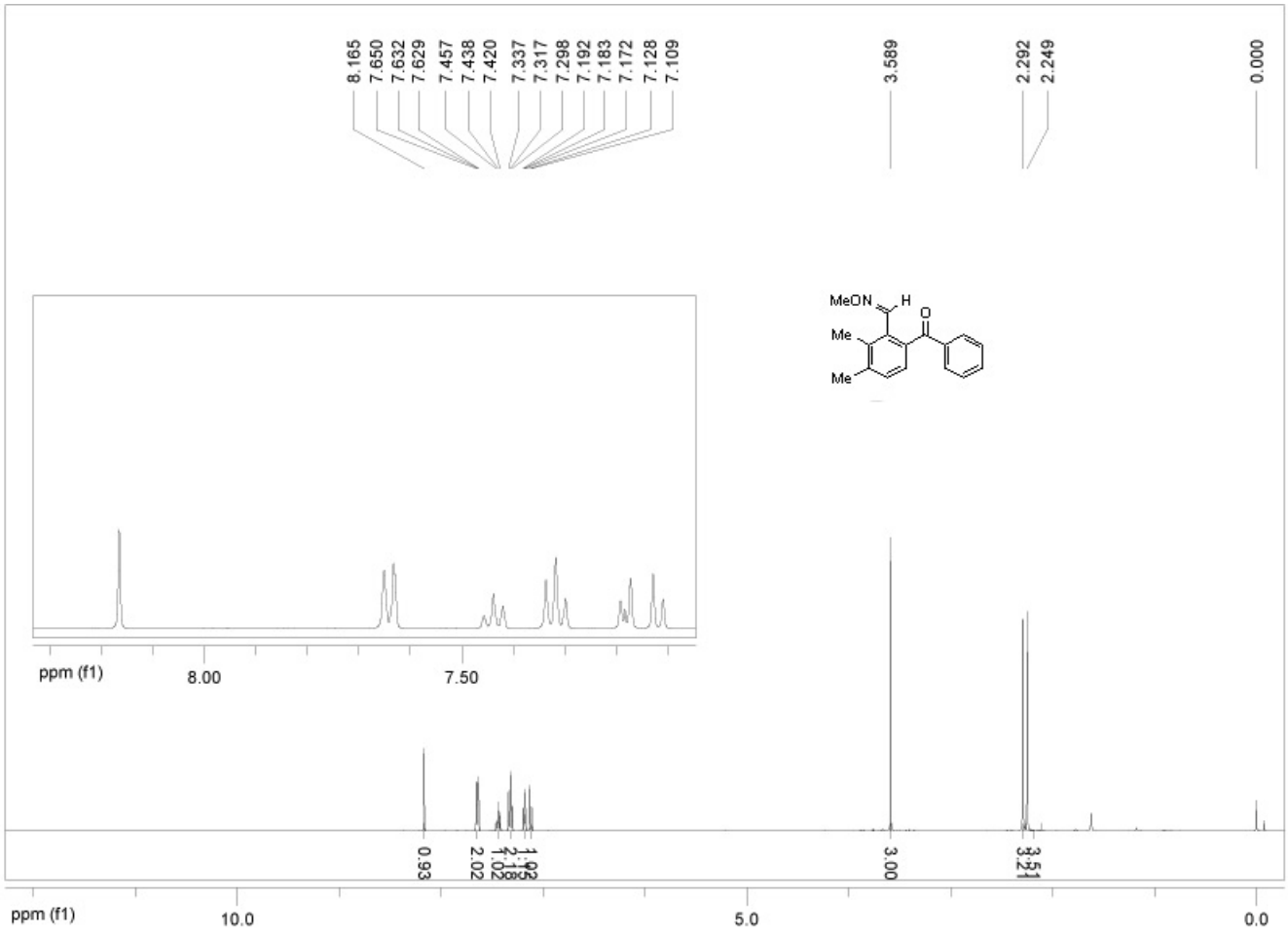


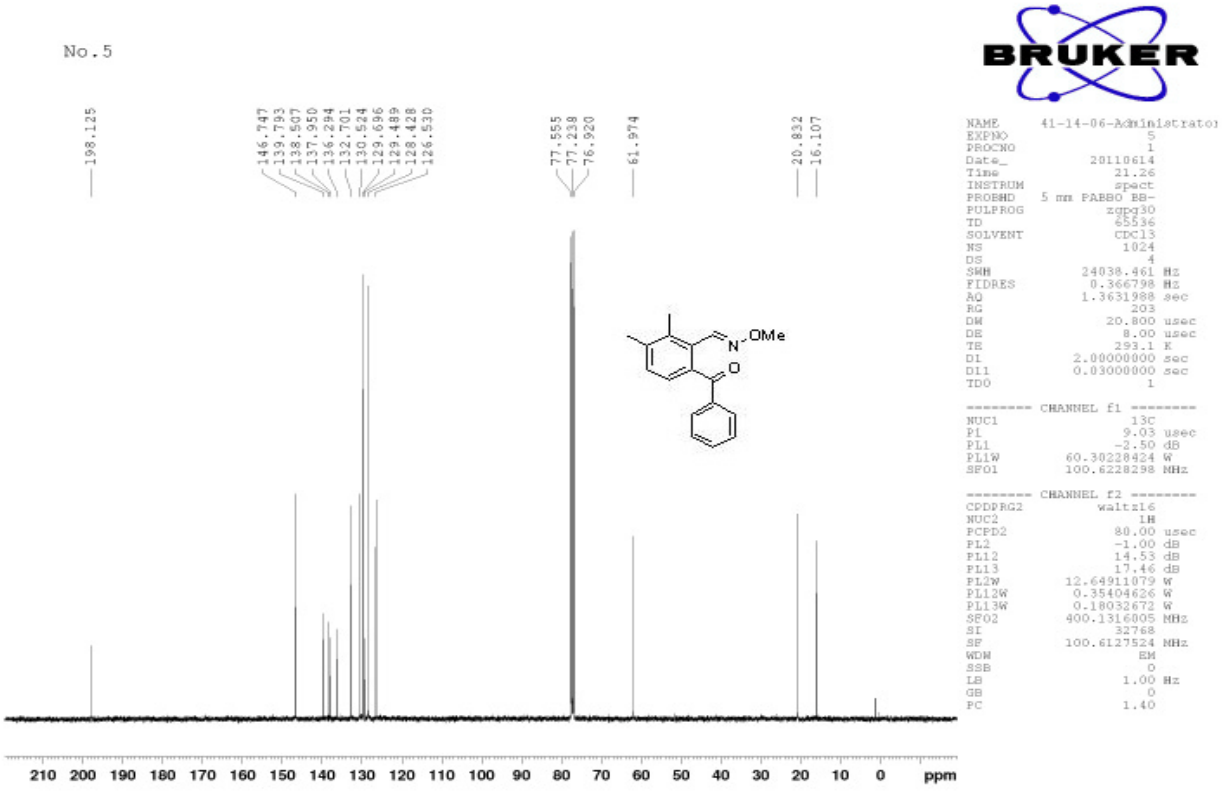
^{1}H and ^{13}C NMR Spectra for **3h**



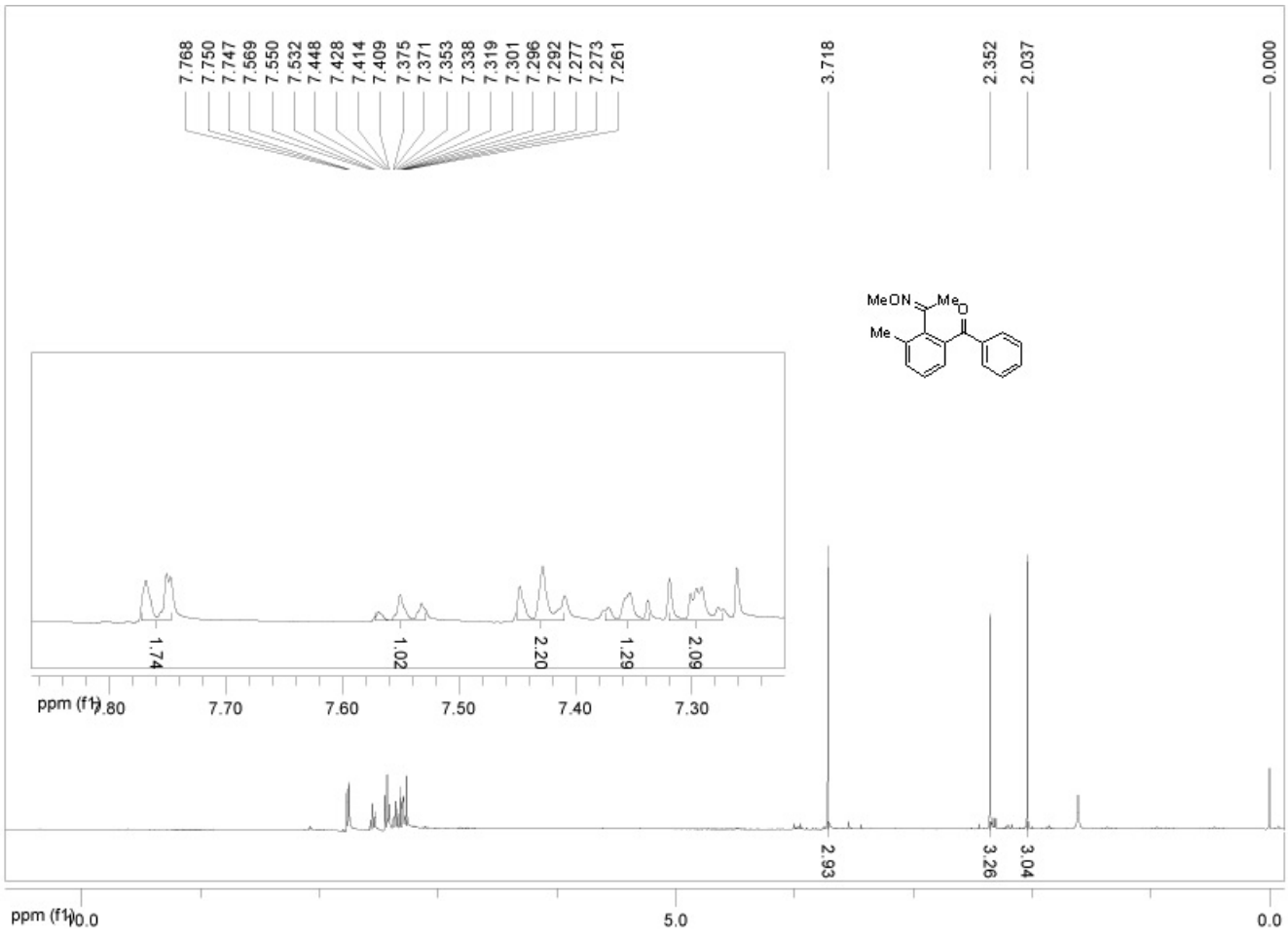


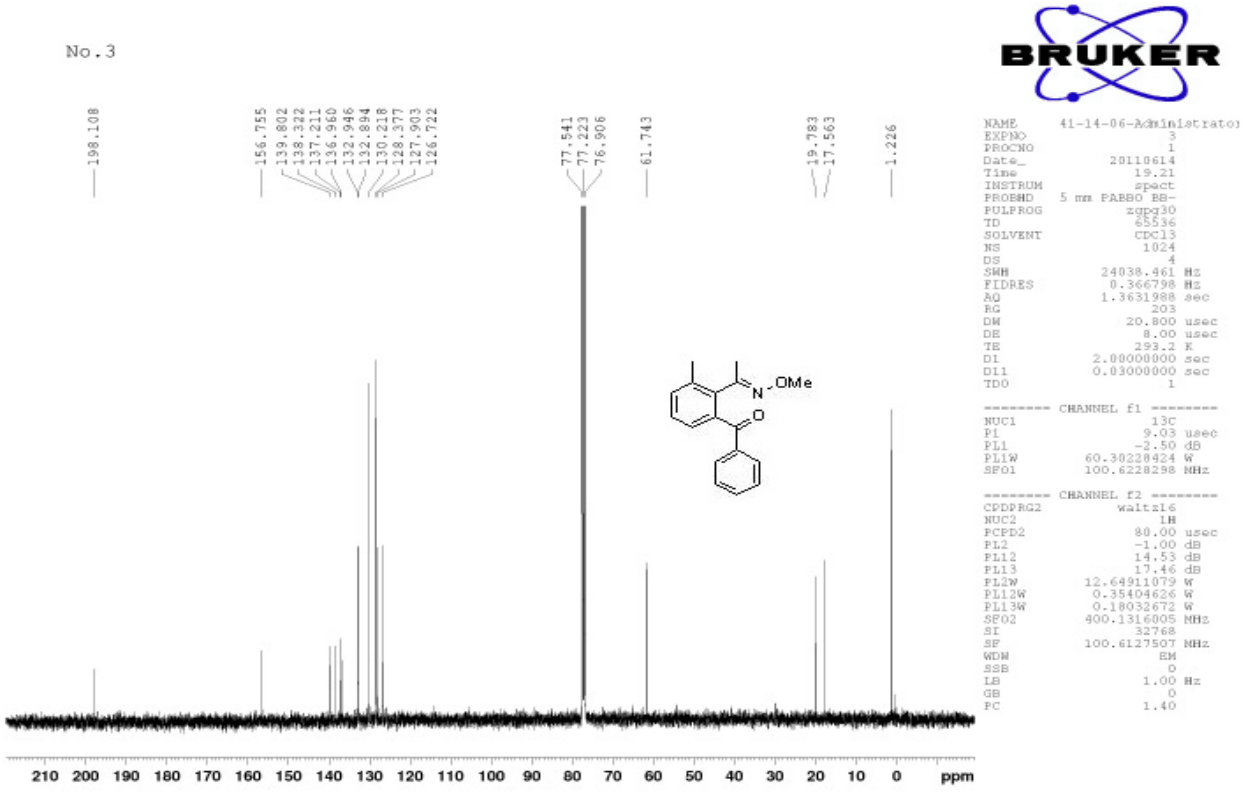
^{1}H and ^{13}C NMR Spectra for **3i**



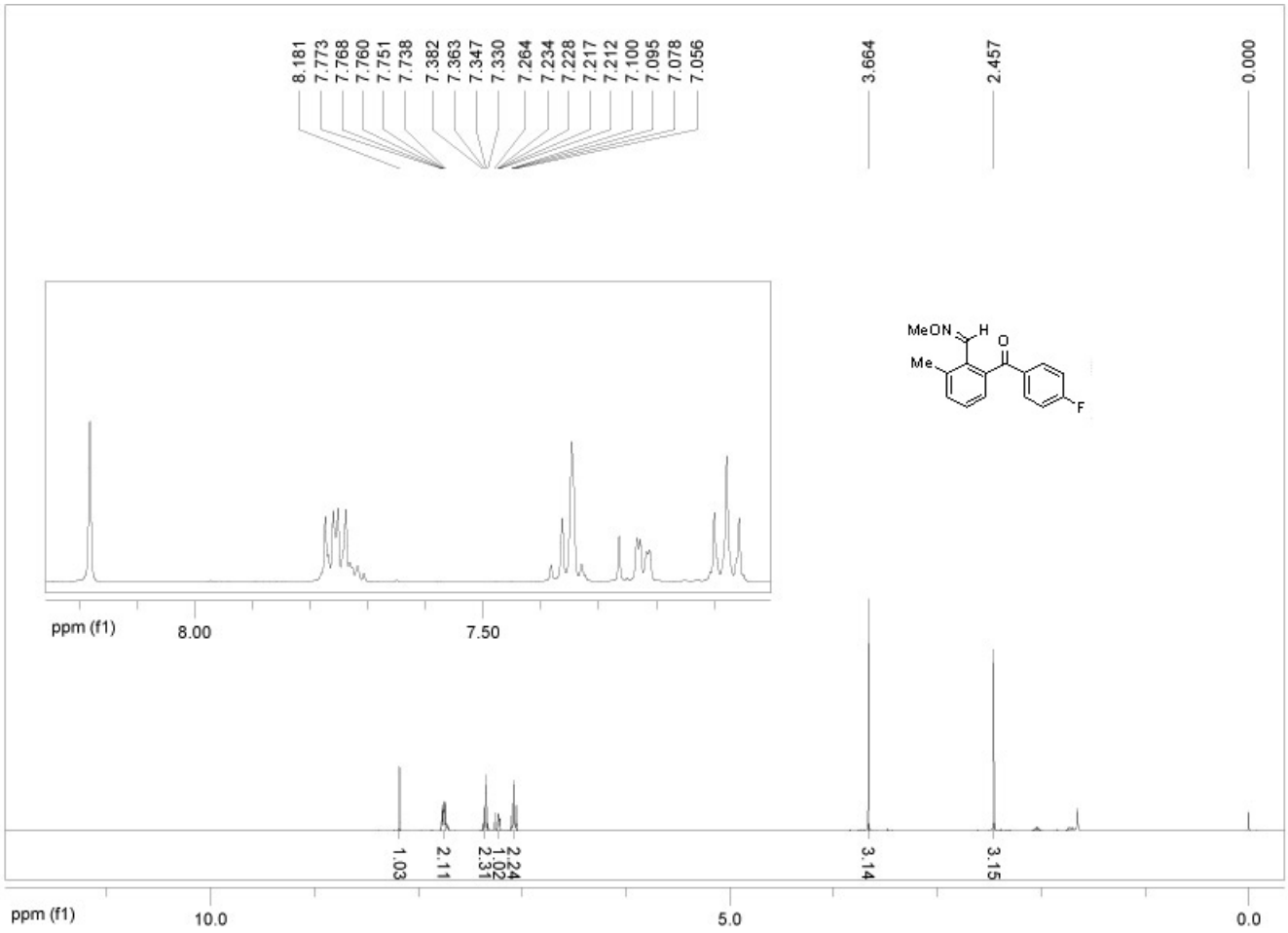


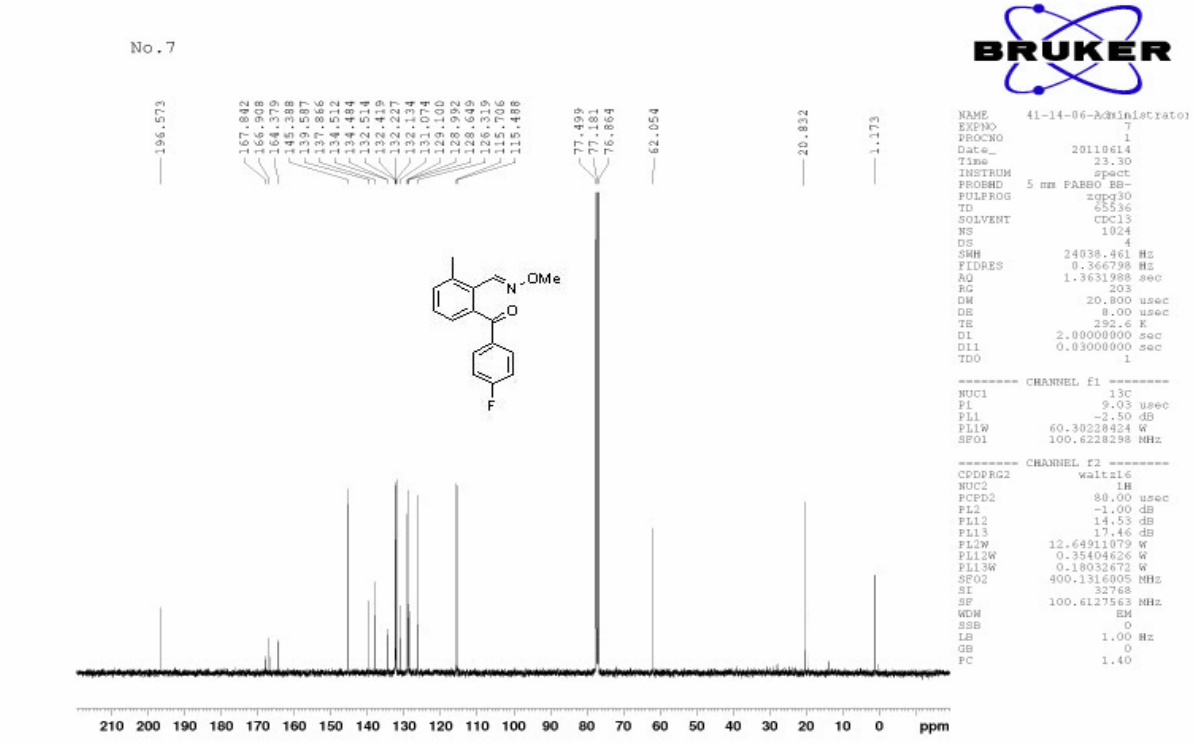
^{1}H and ^{13}C NMR Spectra for **3j**





^{1}H and ^{13}C NMR Spectra for **4a**





BRUKER

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======== CHANNEL f1 ========
NUC1                13C
P1                9.03 usec
PL1              -2.50 dB
PL1W        60.30228424 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             14.53 dB
PL13             17.46 dB
PL2W        12.64911079 W
PL12W        0.35404626 W
PL13W        0.18032672 W
SFO2       400.1316005 MHz
SI                32768
SF         100.6127563 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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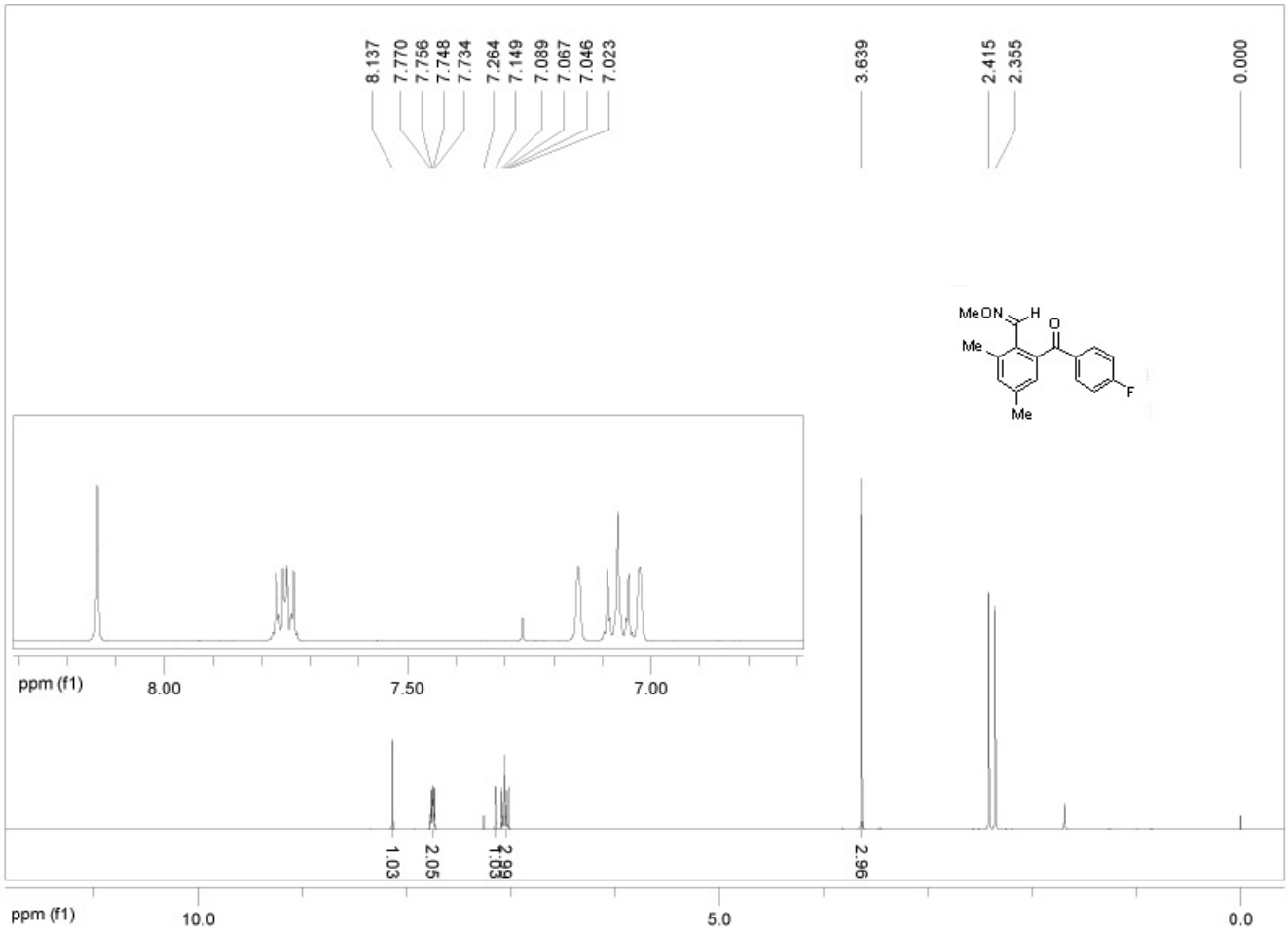
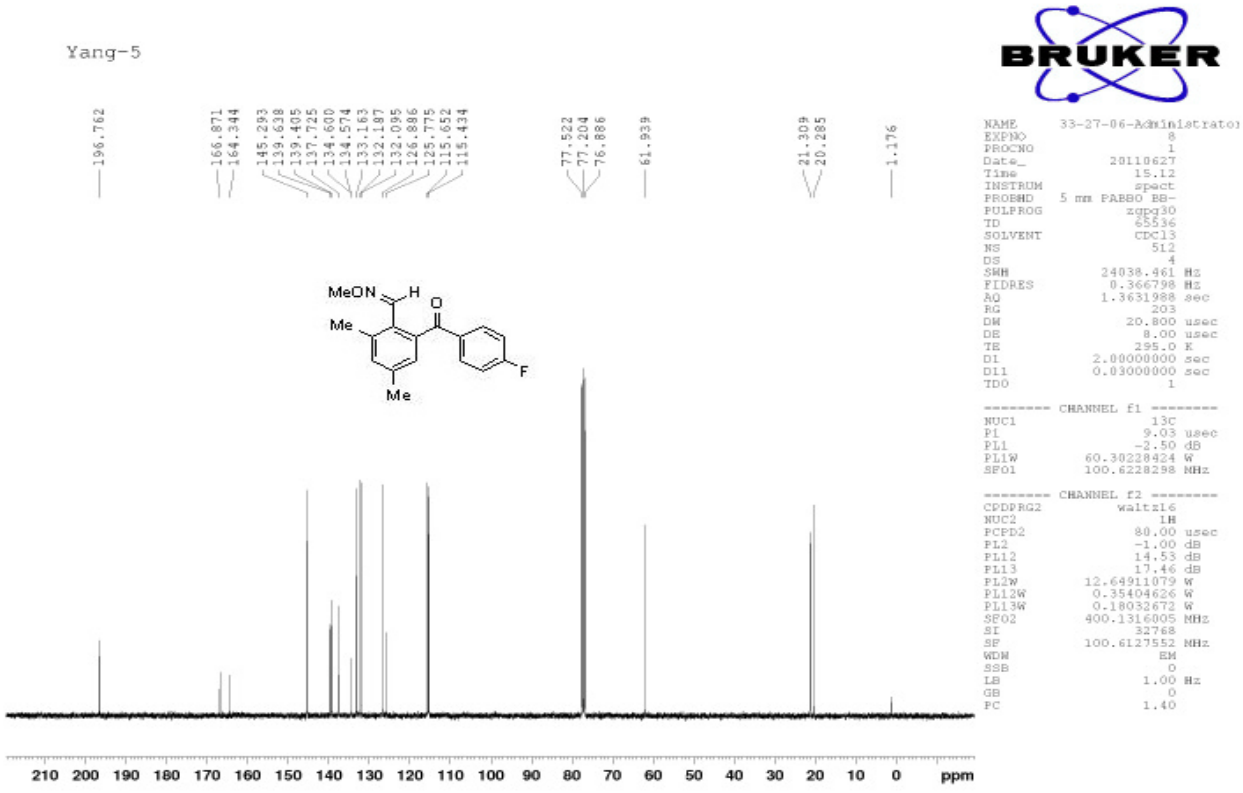
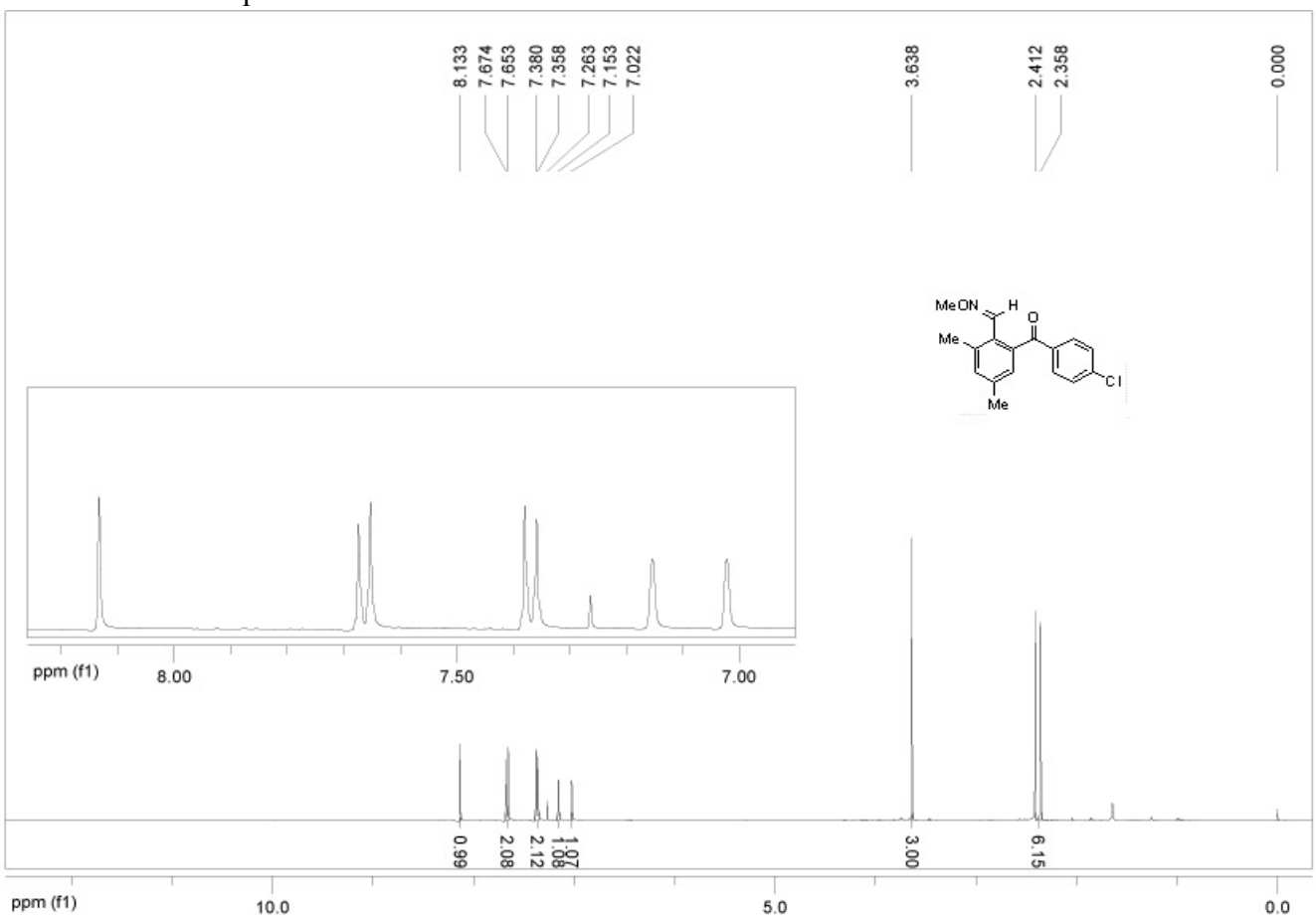
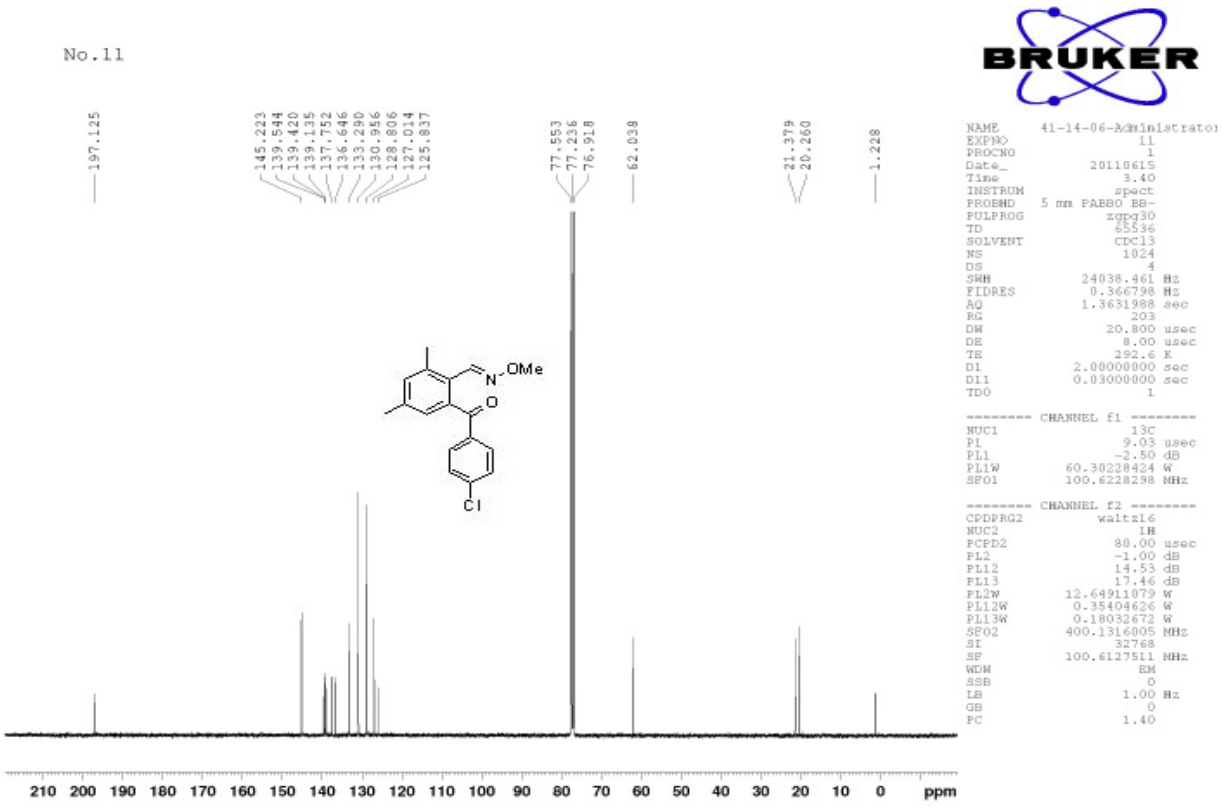
^{1}H and ^{13}C NMR Spectra for **4b**



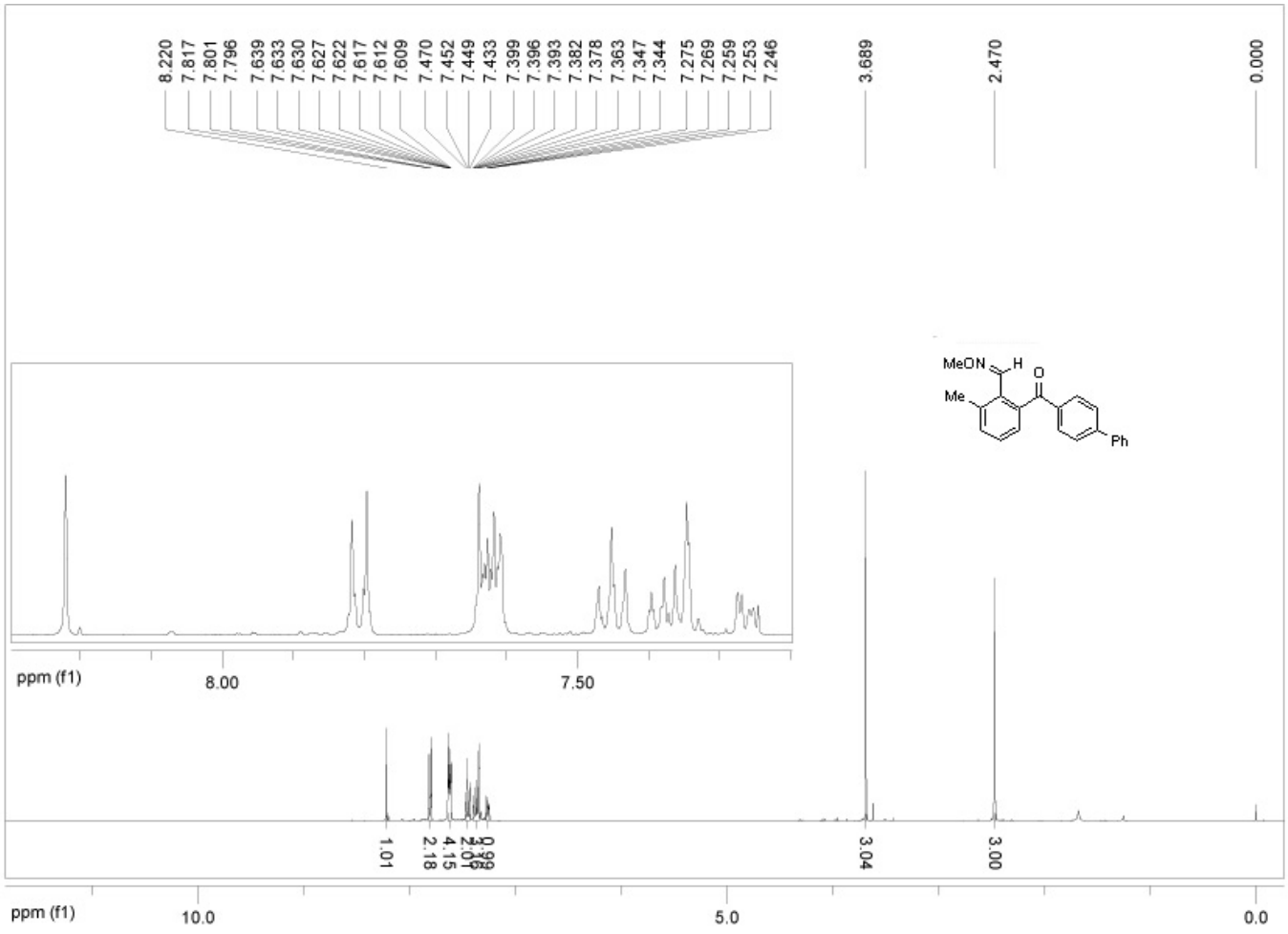


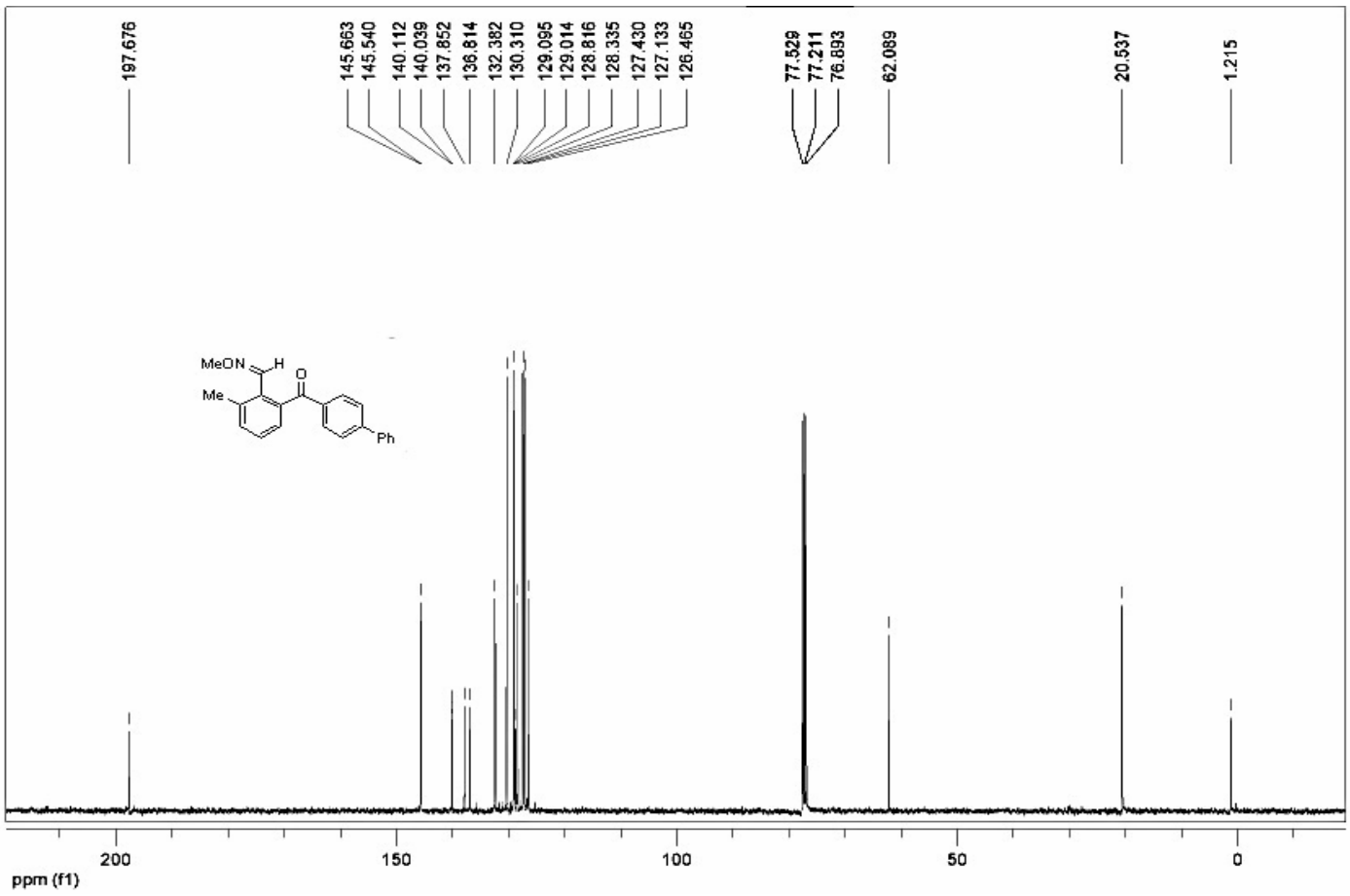
^{1}H and ^{13}C NMR Spectra for **4c**



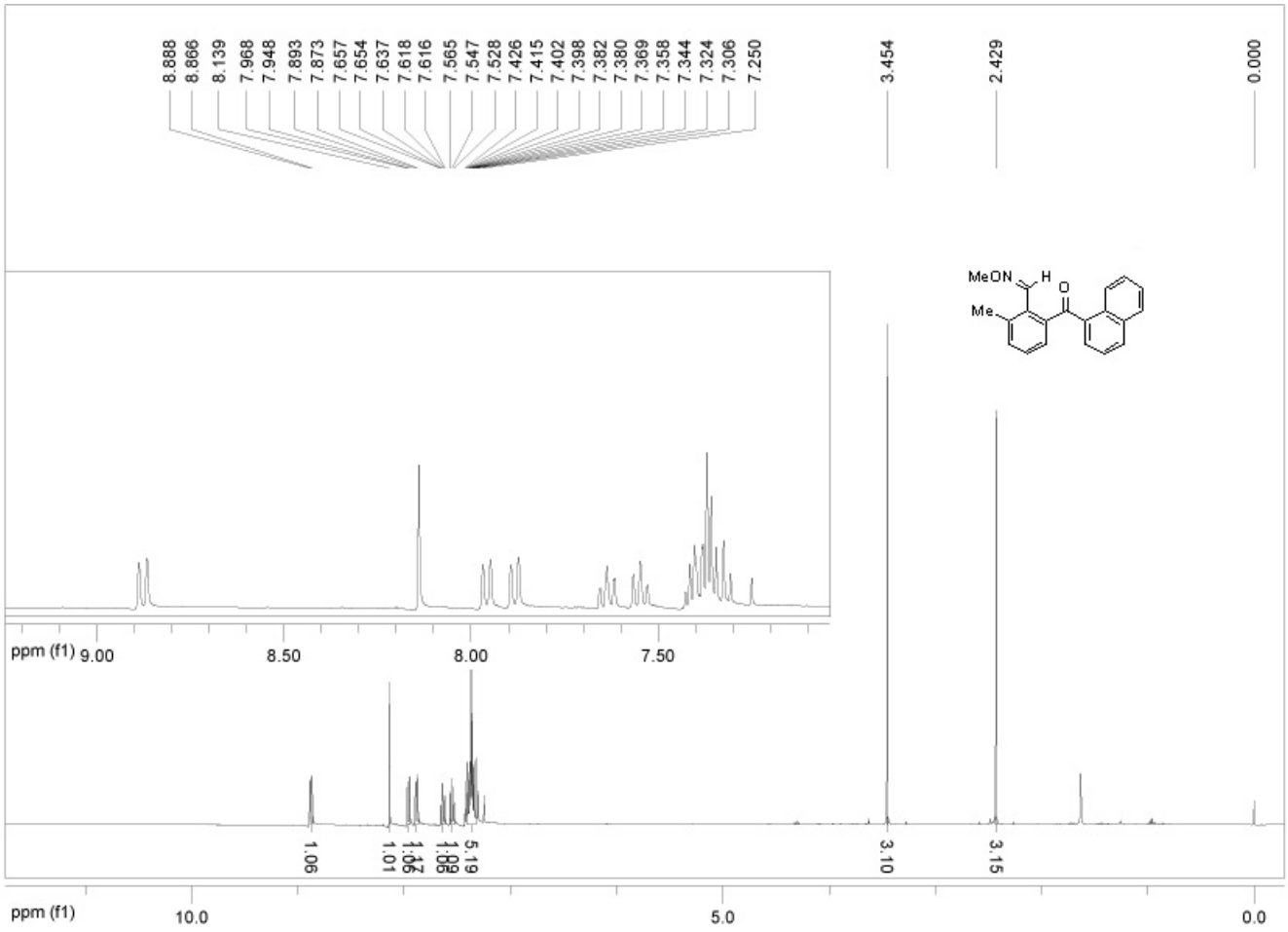


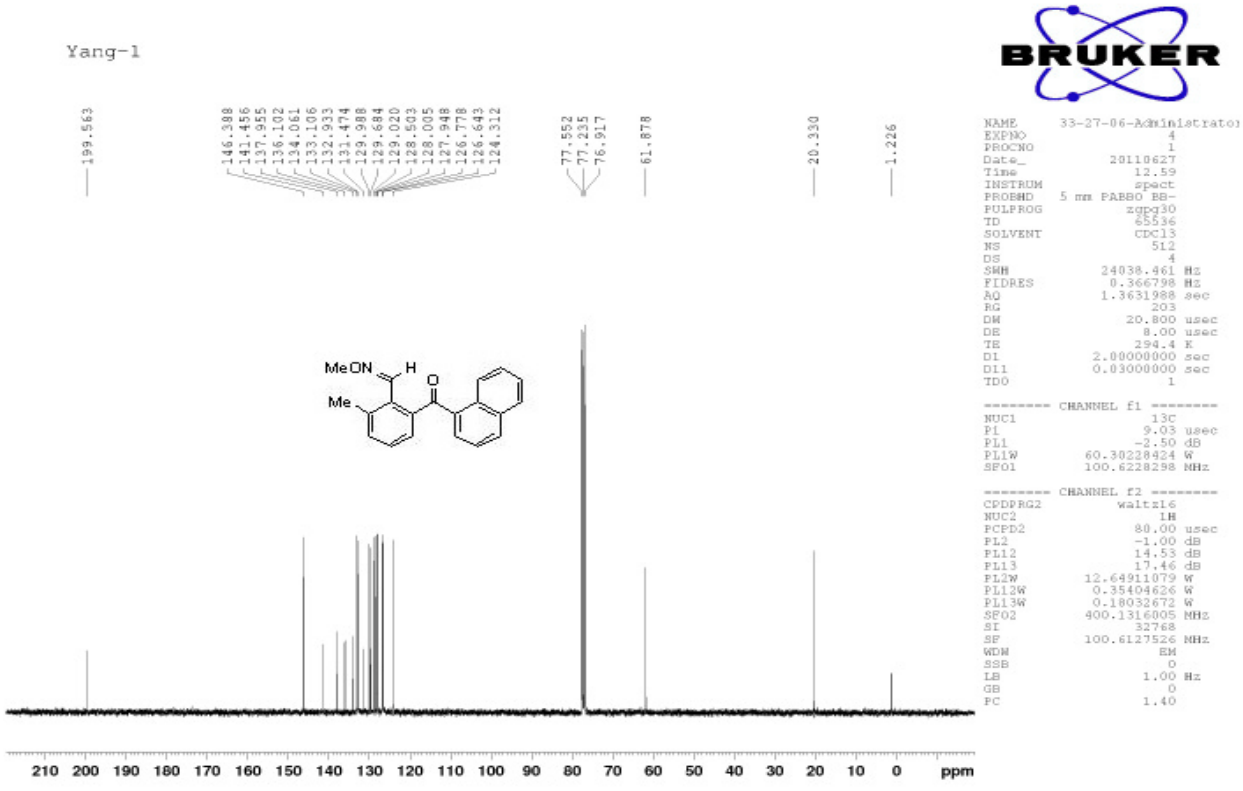
^{1}H and ^{13}C NMR Spectra for **4d**





^{1}H and ^{13}C NMR Spectra for **4e**



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PROCNO                   1
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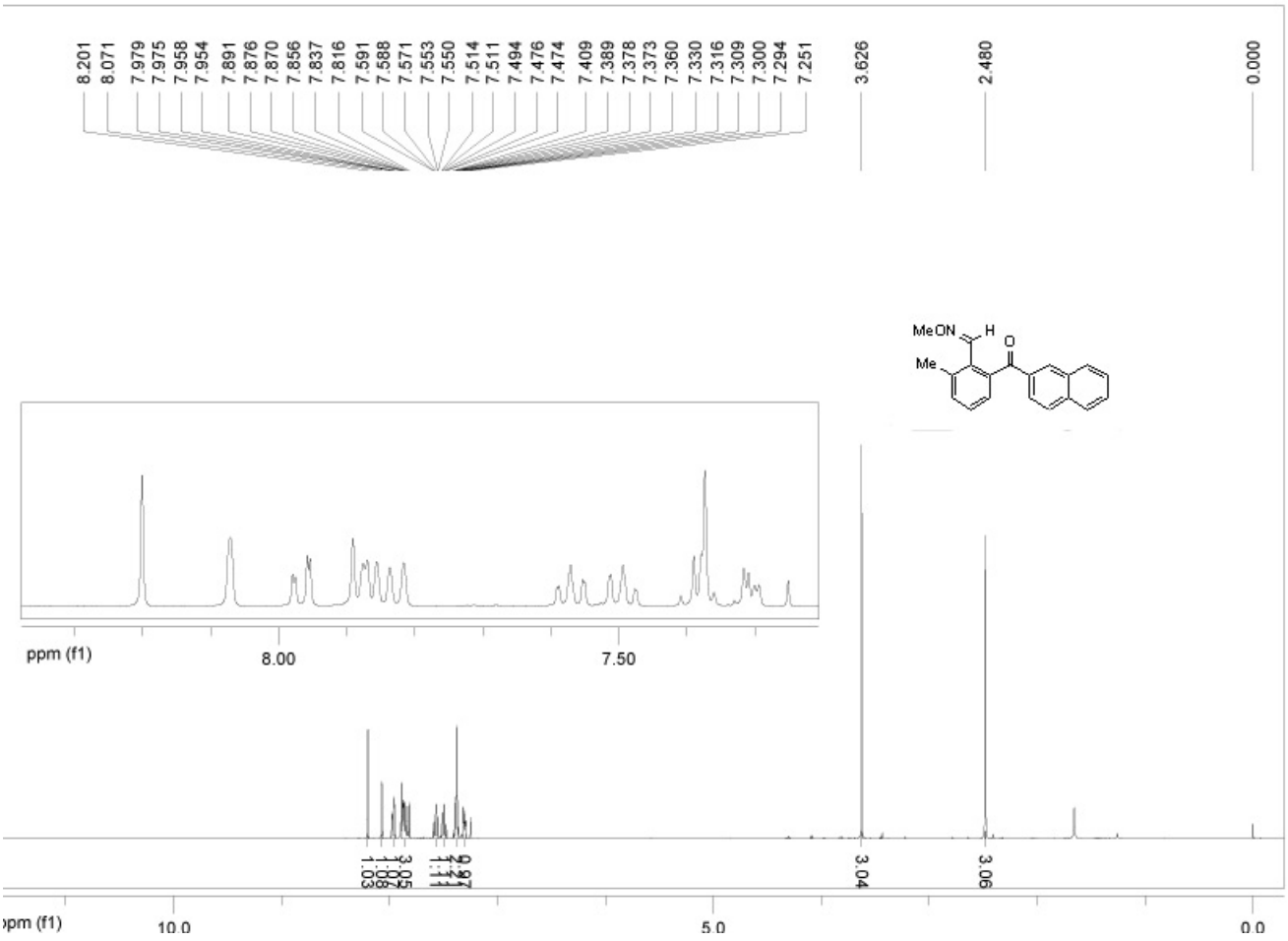
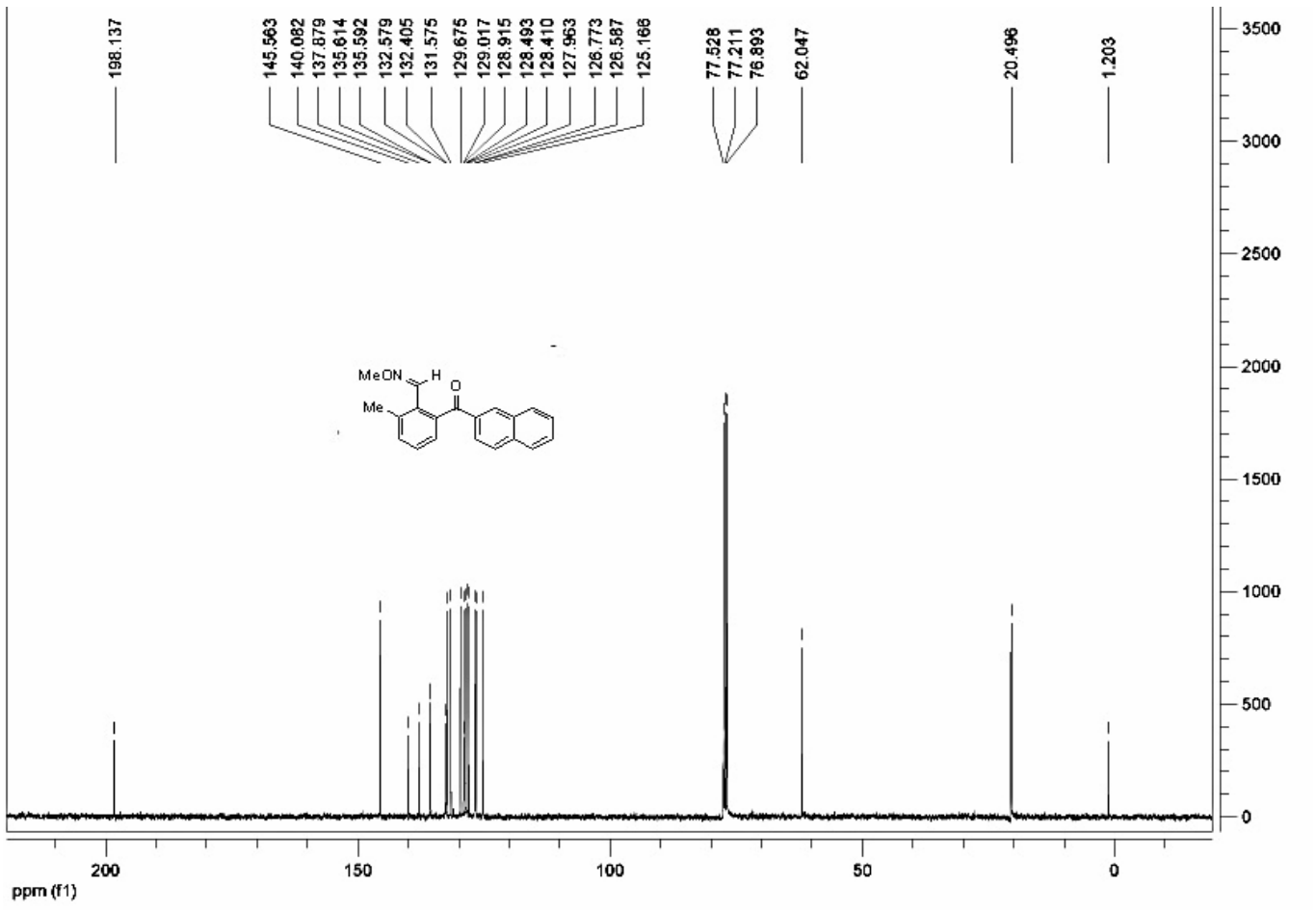
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  203
DW                20.800 usec
DE                 8.00 usec
TE                294.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.03 usec
PL1               -2.50 dB
PL1W        60.30228424 W
SFO1       100.6228298 MHz

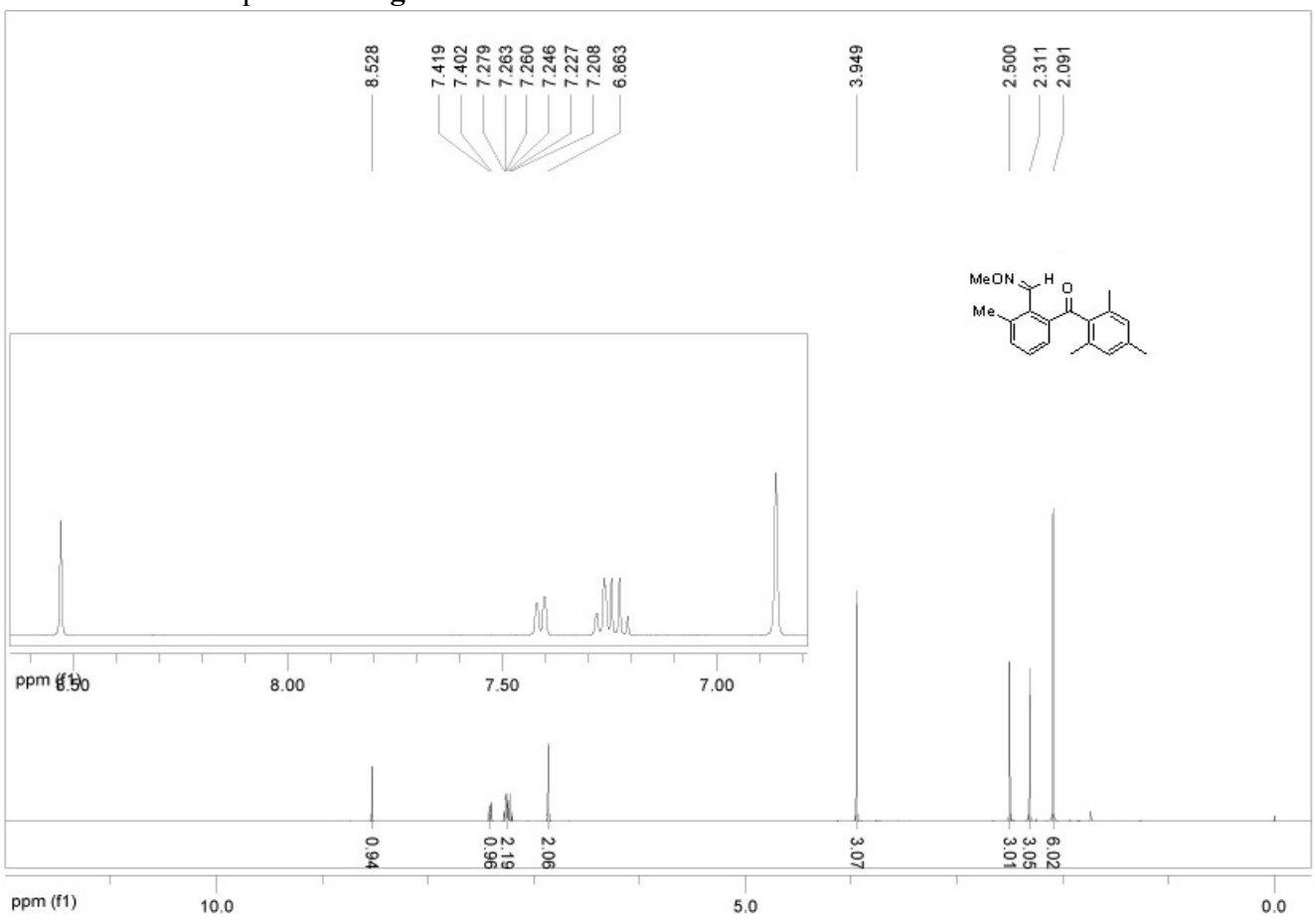
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              14.53 dB
PL13              17.46 dB
PL2W        12.649110790 W
PL12W        0.35404626 W
PL13W        0.18032672 W
SFO2       400.1316005 MHz
SI                32768
SF         100.6127526 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

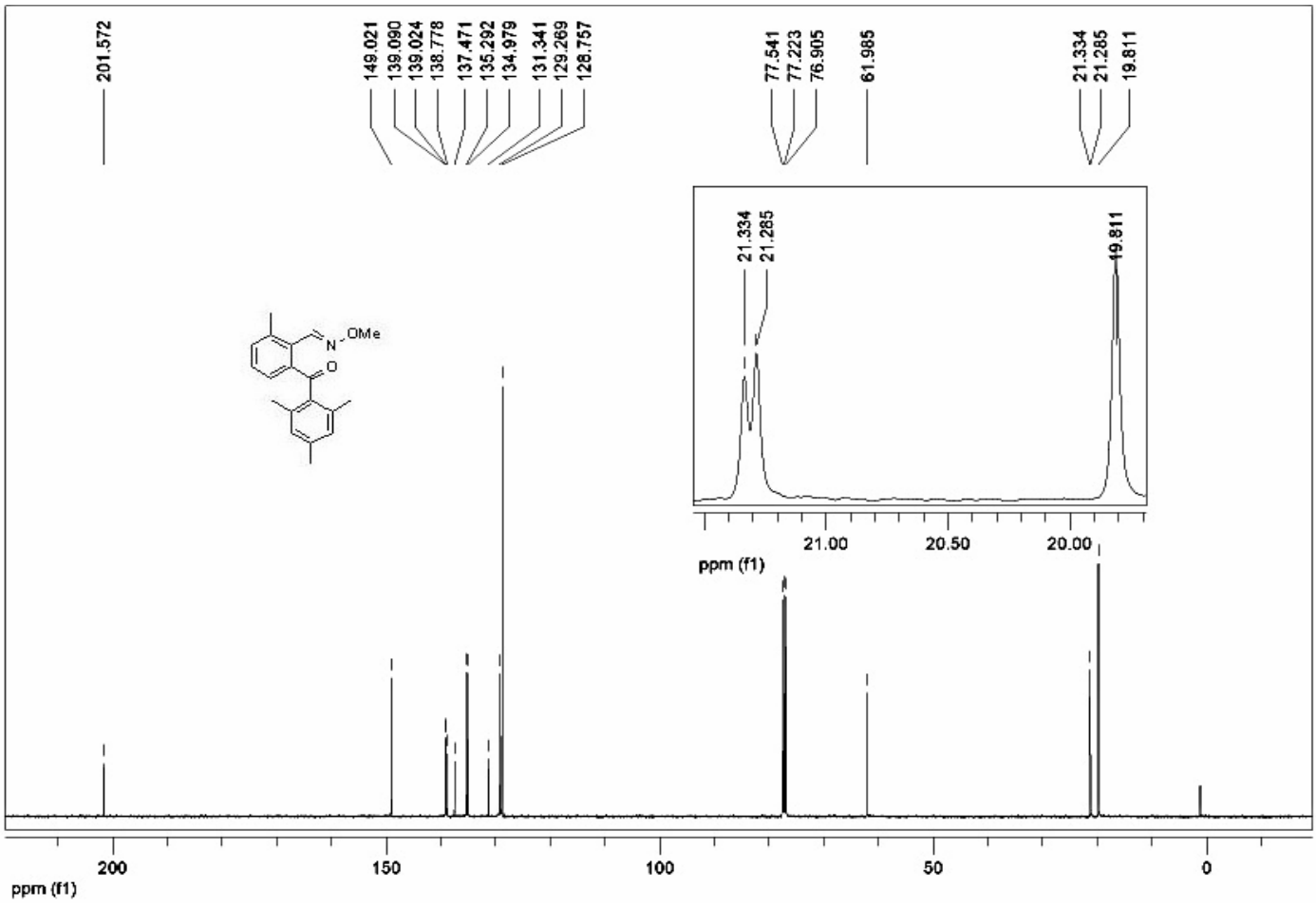
^{1}H and ^{13}C NMR Spectra for **4f**



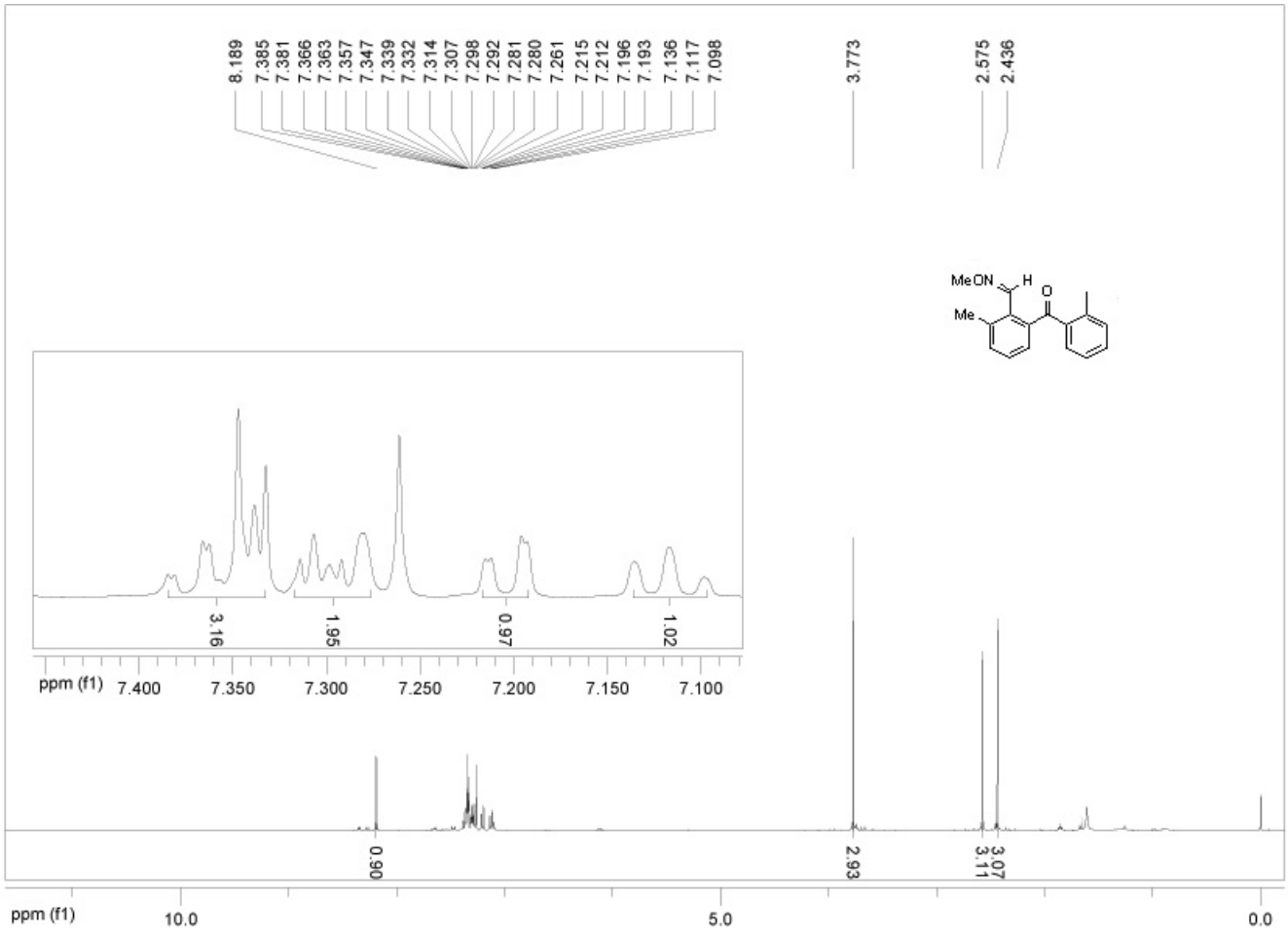


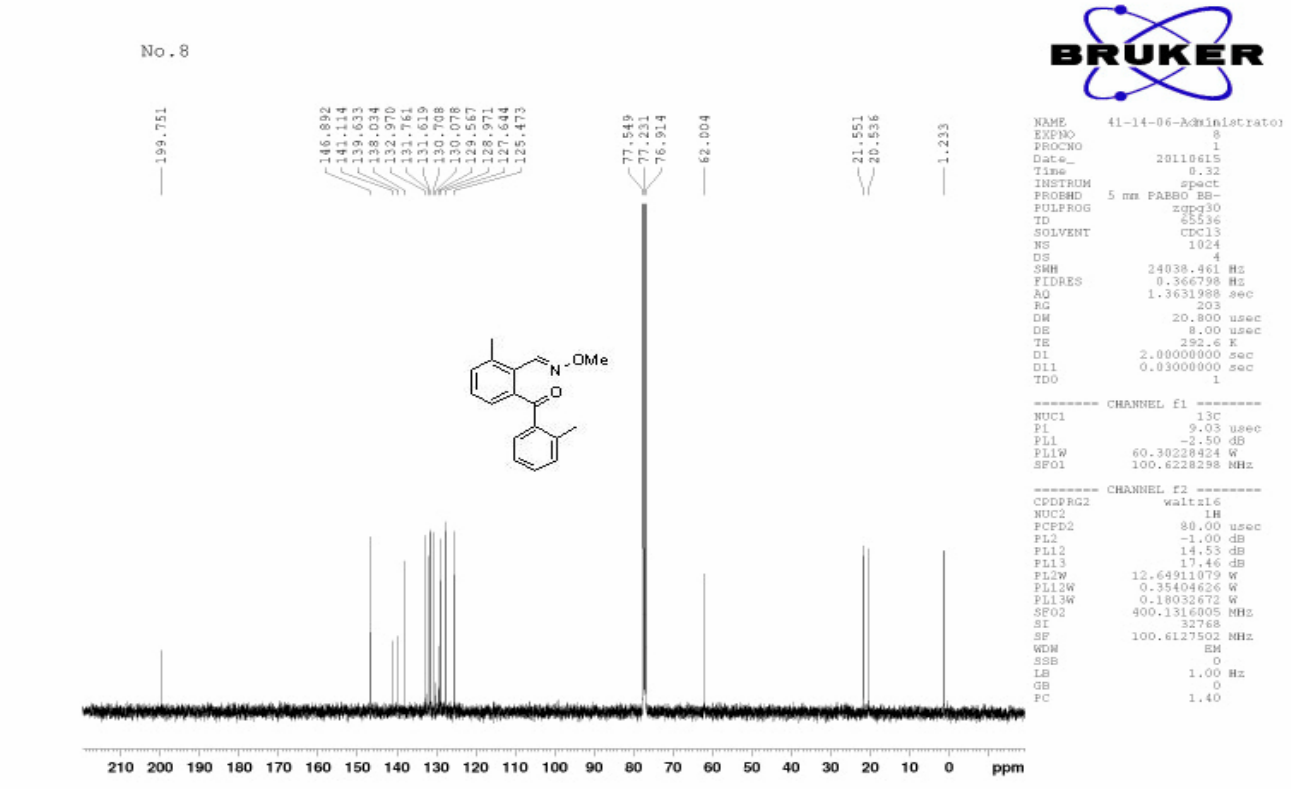
^{1}H and ^{13}C NMR Spectra for **4g**



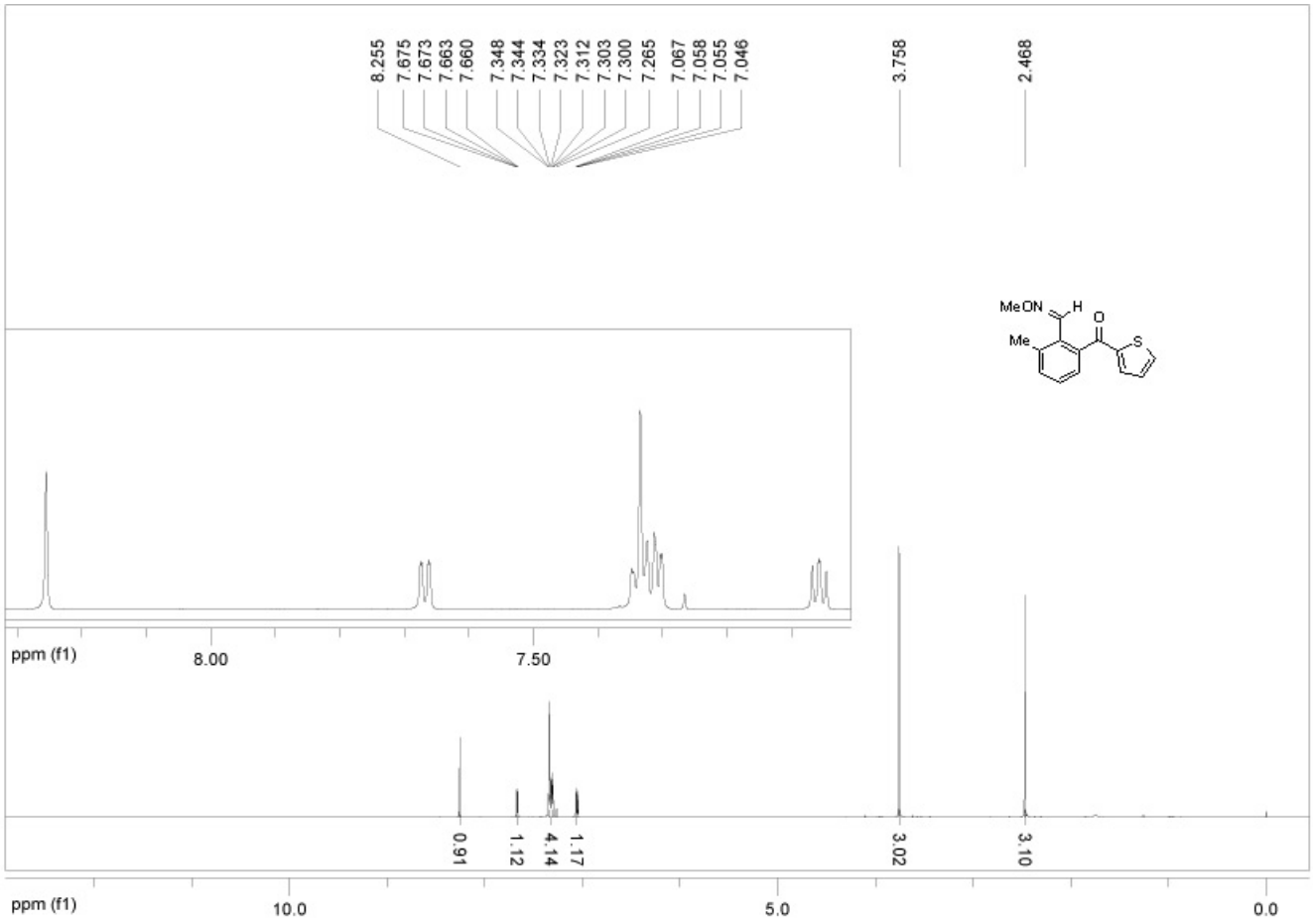


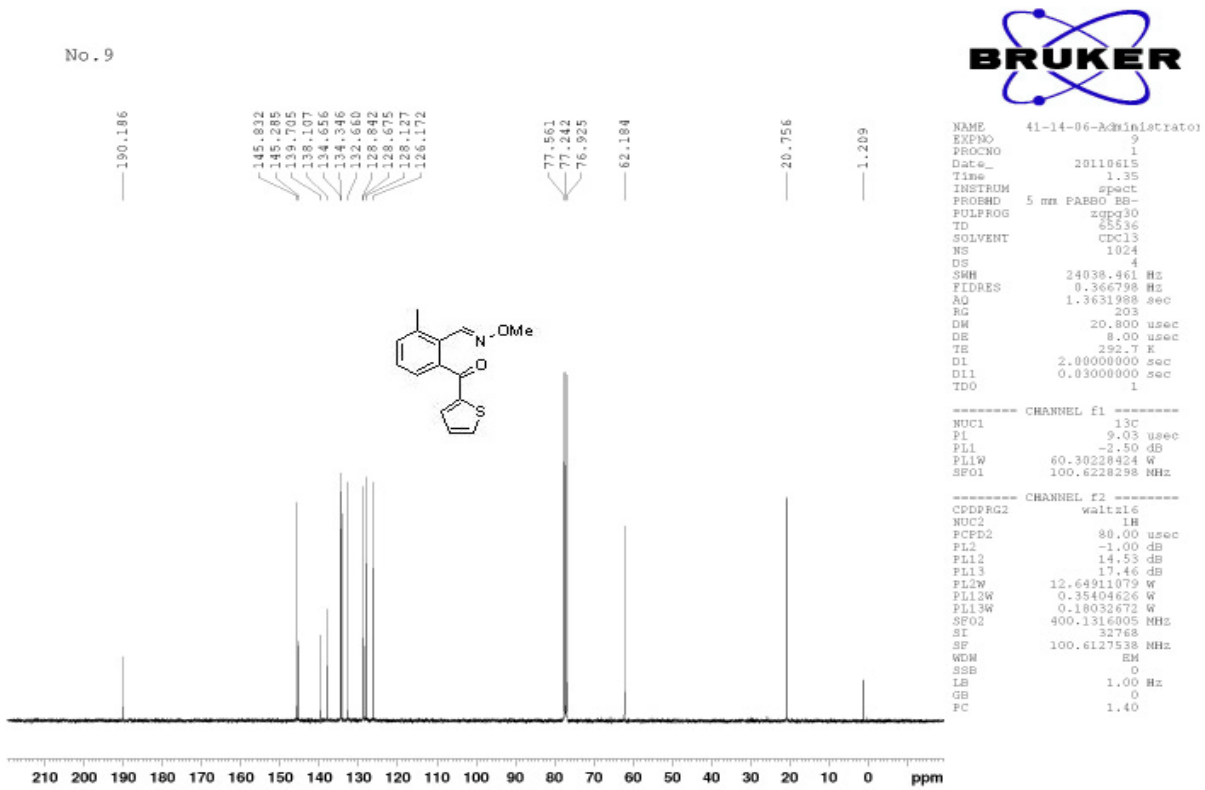
^{1}H and ^{13}C NMR Spectra for **4h**



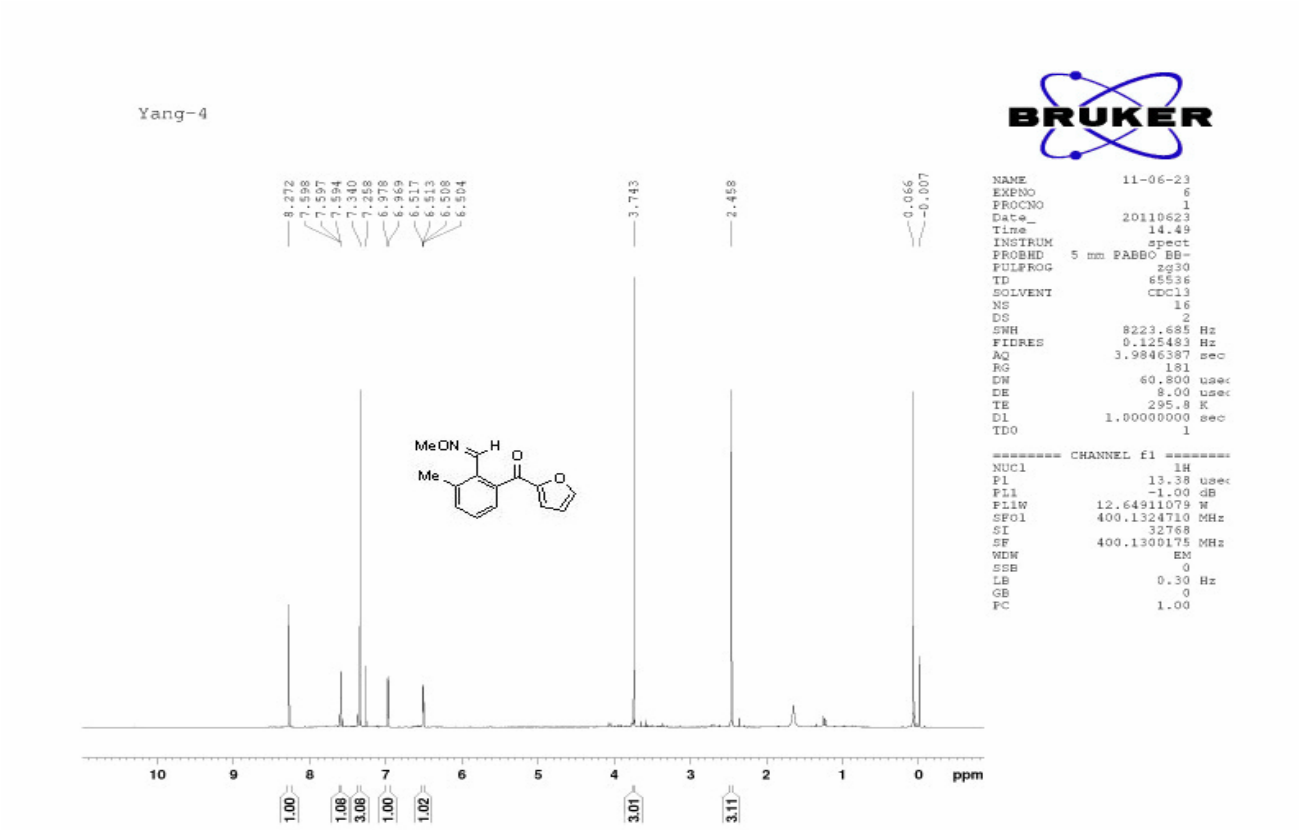


^{1}H and ^{13}C NMR Spectra for **4i**





^{1}H and ^{13}C NMR Spectra for **4j**



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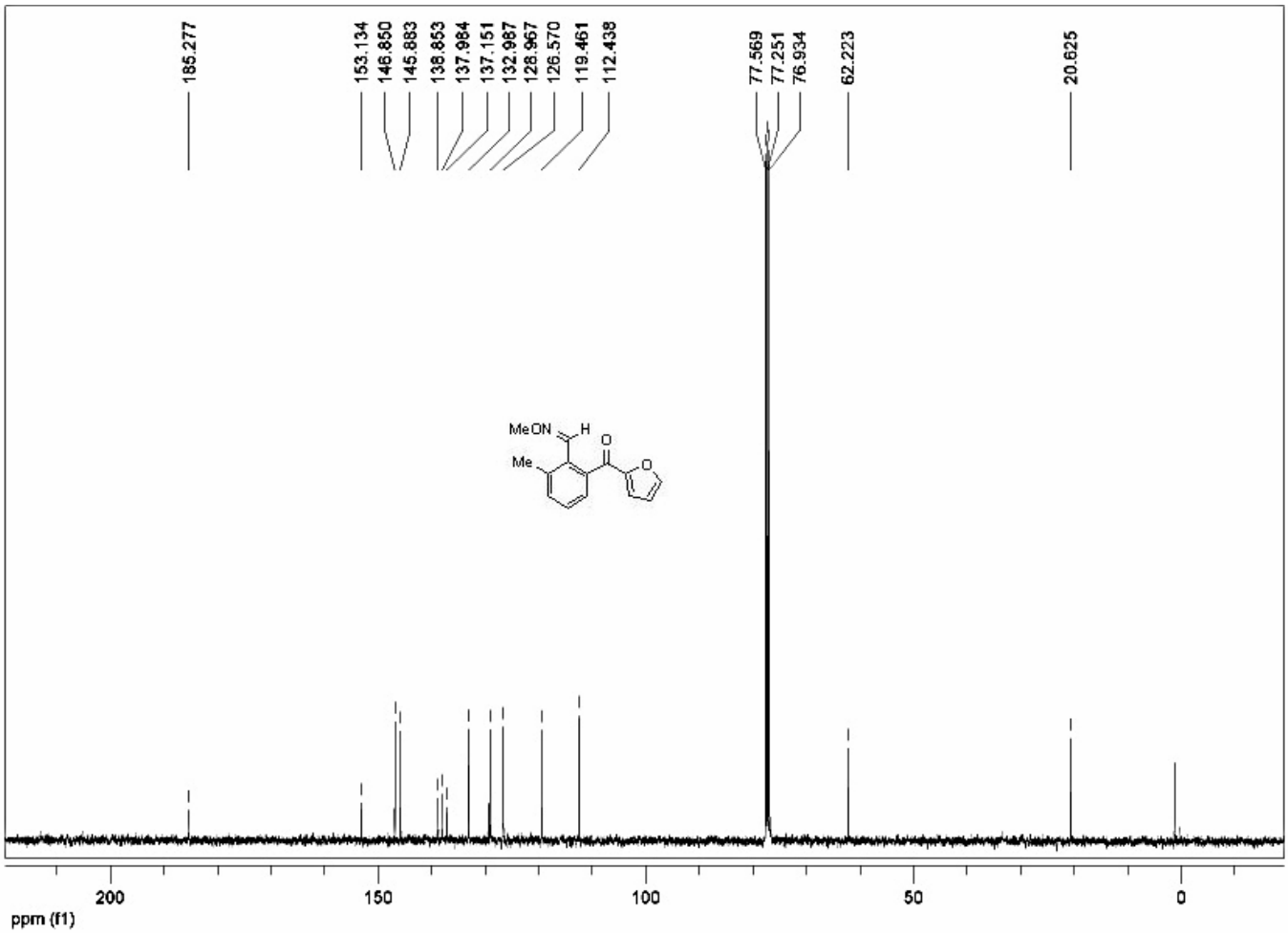
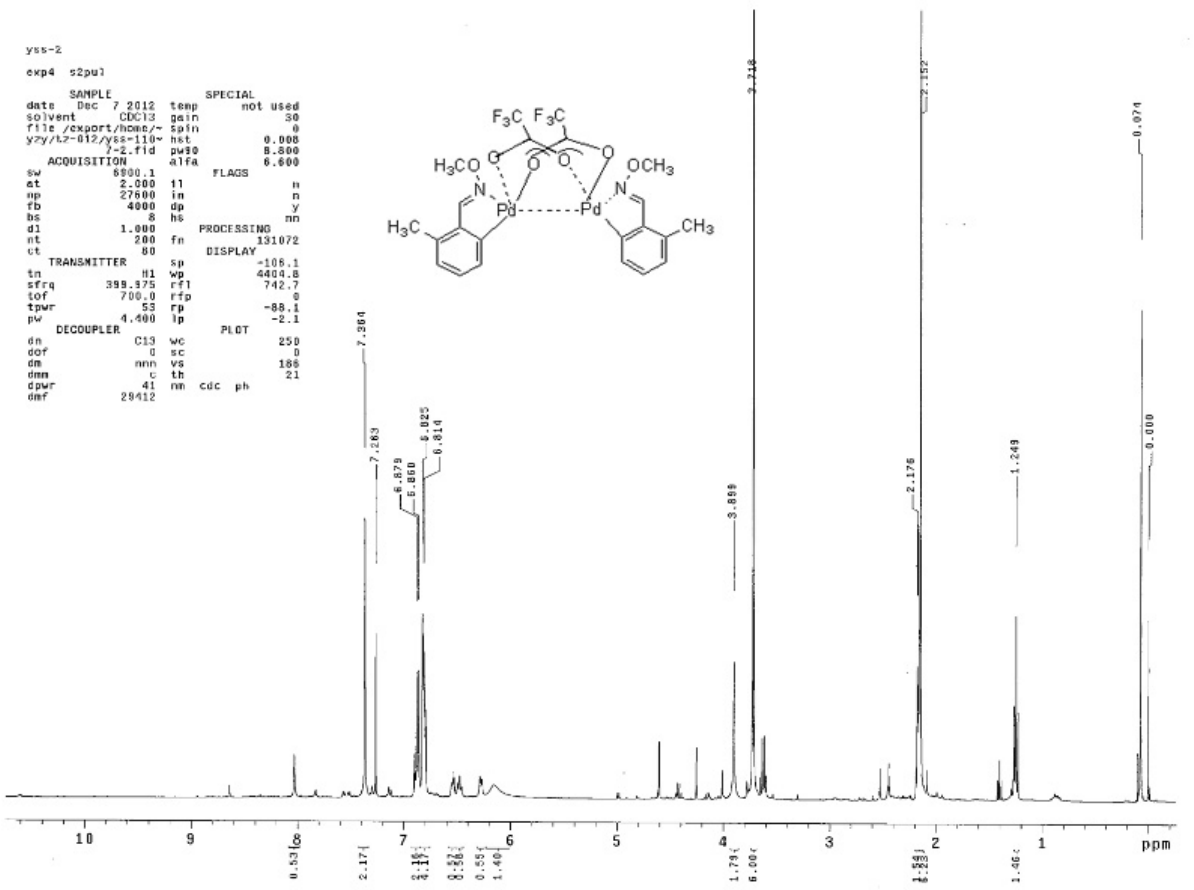
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	181
DW	60.800 usec
DE	8.00 usec
TE	295.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	13.38 usec
PL1	-1.00 dB
PL1W	12.64911079 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300175 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



^{1}H NMR for crude **$C_{22}H_{20}F_6N_2O_6Pd_2$**



^{1}H NMR for purified **$C_{22}H_{20}F_6N_2O_6Pd_2$**