Supporting Information

$[Cp^*RhCl_2]_2$-Catalyzed *ortho*-C-H Bond Amination of *O*-Methyl Aectophenone Oximes with Primary *N*-Chloroalkylamines. A Convenient Synthesis of *N*-Alkyl-2-acylanilines

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1. General Information:

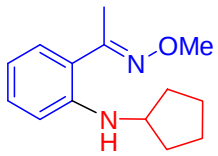
General. All the amination reactions were performed in amber 8 mL-vials equipped with Teflon® liner caps under an atmosphere of nitrogen. Thin layer chromatography was performed on silica gel plates. Flash column chromatography was performed on 230-400 mesh silica gel (NA Chemical). GC-MS analyses were performed on a 6890N-GC (Agilent Technology) with 5973Network-MS (Agilent Technology). ^{1}H, ^{13}C, DEPT 135^{o} NMR analyses were performed on a Bruker (400 MHz) spectrometer. COSY and NOSY NMR analyses were performed on a Bruker (500 MHz) spectrometer. Chemical shifts (δ) were given in ppm, and the signals were referenced with the solvent residual peak(s). NMR yields and conversions were determined with dibromomethane (0.1 mmol) as the internal standard, which has a singlet signal (2H) at 4.9 ppm (in *d*-chloroform). IR spectra were obtained by a Nicolet-380 FT-IR spectrometer. Melting points were recorded on a BÜCHI-B-545 instrument and were uncorrected. High resolution mass spectra were obtained using a VG MICROMASS Fison VG platform and with an electrospray ionization mode.

Materials. All reagents were purchased commercially and were used as received. *O*-methyloximes were prepared from the corresponding ketones with methoxyamine hydrochloride in 1:1 methanol: H_2O (for reaction with ethyl 4-acetylbenzoate, 1:1 ethanol: H_2O) under reflux and stirred overnight (~18 h). (Products were purified by vacuum distillation for liquid oximes, and flash column chromatography for solid oximes). 4-(4-Methoxyphenyl)acetophenone was prepared by Suzuki-coupling with $Pd(OAc)_2$ and triphenylphosphine as the catalyst in toluene, 100 °C for 18 h. $[Cp^*RhCl_2]_2$[1] and **4** ([Cp*RhCl(2-phenylpyridine)])[2] were prepared according to the literature procedures. All the solvents were distilled or purified according to literature procedures.[3]

2. Experimental Procedures and Characterizations:

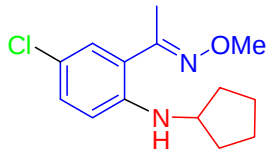
2.1 General Procedures for the Rh-Catalyzed C-H Aminations of Oxime

To an amber 8 mL-vial (vial **A**), $[Cp^*RhCl_2]_2$ (5 mol %, 6.2 mg), CsOAc (1.3 equiv, 49.7 mg) and $AgSbF_6$ (1.5 equiv, 103 mg) were added, and the vial was sealed with a Teflon® liner cap. To another amber 4-mL vial (vial **B**), *N*-chlorosuccinimide (2.2 equiv, 58.7 mg) was added, and the vial was sealed with a Teflon® liner cap. Both vials were evacuated and back filled with N_2 for three times. Freshly distilled THF (1 mL) was added to the vial **A**, followed by the addition of the oxime (0.2 mmol) with a 50-μL syringe. Vial **A** was pre-heated at 40°C. THF (1 mL) and primary amine (2.2 equiv) were added to the vial **B**, and they were mixed and stirred for 10 min. The mixture in Vial **B** was taken up by a 2.5-mL syringe equipped with a long needle (L 6 in, size 22 gauge), and it was then fitted onto a syringe-pump. The THF solution of *N*-chloroamine was added dropwise to the reaction (vial **A**) over 1 h in dark, and the reaction was stirred at 40 °C for 2 h. After cooling to room temperature, the reaction was quenched by 30% aqueous ammonia (2 mL) and was extracted by EtOAc (5 mL). The organic layer was collected, and the aqueous layer was washed with EtOAc (5 mL x 2). The combined organic fractions were dried over Na_2SO_4 and then filtered through a short plug of Celite®. Solvents were removed by rotary evaporation, and the residue was re-dissolved in a small amount of dichloromethane (DCM). The dissolved mixture was subjected to flash column chromatography with silica gel as the column stationary phase / preparative TLC for isolation by a gradient elution with hexane/DCM.



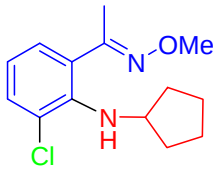
3aa

3aa was isolated as a yellowish green oil (37.1 mg, 80%) by flash column chromatography followed by high vacuum evacuation overnight (0.5 mmHg, ~18 h, for removal of **1a** residue). R_f = 0.2 (2% Et_2O in hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ_H 7.87 (bs, 1H), 7.38 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.20 (td, J = 8.0 Hz, 1.6 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 6.64 (t, J = 8.0 Hz, 1H), 3.98 (s, 3H), 3.90 (bs, 1H), 2.30 (s, 3H), 2.04-2.01 (m, 2H), 1.79-1.77 (m, 2H), 1.68-1.60 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 157.48 (C), 146.72 (C), 129.70 (CH), 128.96 (CH), 116.87 (C), 114.40 (CH), 111.55 (CH), 61.74 (CH_3), 53.99 (CH), 33.46 (CH_2), 23.99 (CH_2), 12.76 (CH_3); IR (thin-film, cm^{-1}): 3293, 2955, 2869, 1734, 1604, 1568, 1521, 1453, 1337, 1272, 1184, 1052, 900, 743; HRMS m/z (ESI): calculated for $C_{14}H_{21}N_2O^+$: 233.1654, found: 233.1647.



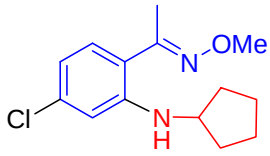
3ma

3ma was isolated as a lightly brown oil (23.4 mg, 44%) by flash column chromatography followed by high vacuum evacuation overnight (0.5 mmHg, ~18 h, for removal of **1m** residue) R_f = 0.3 (2% Et_2O in hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ_H 7.88 (bs, 1H), 7.31 (d, J = 2.4 Hz, 1H), 7.12 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 6.64 (d, J = 9.4 Hz, 1H), 3.97 (s, 3H), 3.84 (bs, 1H), 2.25 (s, 3H), 2.03-1.98 (m, 2H), 1.76-1.74 (m, 2H), 1.67-1.64 (m, 2H), 1.60-1.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.54 (C), 145.25 (C), 129.32 (CH), 128.41 (CH), 119.04 (C), 118.01 (C), 112.76 (CH), 61.88 (CH_3), 54.13 (CH), 33.33 (CH_2), 23.95 (CH_2), 12.67 (CH_3); IR (thin-film, cm^{-1}): 3290, 2956, 2869, 1735, 1600, 1566, 1512, 1449, 1409, 1325, 1262, 1183, 1040, 913, 804; HRMS m/z (ESI): calculated for $C_{14}H_{20}N_2OCl^+$: 267.1264, found: 267.1266.



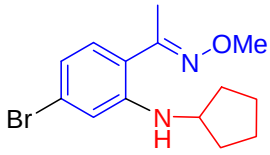
3ma'

3ma' was isolated as a light brown oil (5.4 mg, 10% yield) (*chlorination product of **3aa**)* by flash column chromatography. R_f = 0.1 (2% Et_2O in hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ_H 7.29 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.15 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 6.82 (t, J = 8.0 Hz, 1H), ~5.3 (bs, 1H), 3.98 (s, 3H), 3.89-3.84 (m, 1H), 2.20 (s, 3H), 1.80-1.77 (m, 2H), 1.70-1.66 (m, 2H), 1.58-1.54 (m, 2H), 1.46-1.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.75 (C), 143.18 (C), 130.04 (CH), 128.66 (C), 128.38 (CH), 125.70 (C), 120.43 (CH), 61.82 (CH_3), 58.96 (CH), 33.39 (CH_2), 23.36 (CH_2), 14.48 (CH_3); IR (thin-film, cm^{-1}): 3360, 3313, 2957, 2870, 1592, 1453, 1439, 1253, 1079, 1048, 891, 779, 743; HRMS m/z (ESI): calculated for $C_{14}H_{20}N_2OCl^+$: 267.1264, found: 267.1262.



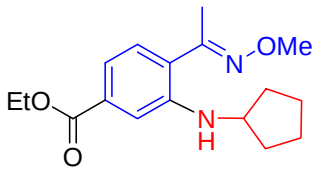
3ba

3ba was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as a light brown oil (40.5 mg, 76% yield) (with 1.3 equiv of CsOAc, ^1H NMR yield = 48%) by preparative TLC. R_f = 0.4 (10% DCM in hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ_H 8.13 (bs, 1H), 7.27 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 1.6 Hz, 1H), 6.59 (dd, J = 8.4 Hz, 2 Hz, 1H), 3.96 (s, 3H), 3.86-3.82 (bm, 1H), 2.25 (s, 3H), 2.06-1.99 (m, 2H), 1.78-1.75 (m, 2H), 1.68-1.64 (m, 2H) 1.62-1.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.85 (C), 147.45 (C), 135.62 (C), 130.02 (CH), 115.48 (C), 114.50 (CH), 111.22 (CH), 61.82 (CH_3), 54.11 (CH), 33.24 (CH_2), 23.91 (CH_2), 12.69 (CH_3); IR (thin-film, cm^{-1}): 3289, 2957, 2869, 1600, 1512, 1409, 1325, 1262, 1183, 1046, 913, 804; HRMS m/z (ESI): calculated for $C_{14}H_{20}N_2OCl^+$: 267.1264, found: 267.1257.



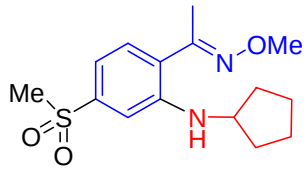
3ca

3ca was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as a light brown oil (48.5 mg, 78% yield) (with 1.3 equiv of CsOAc, ^1H NMR yield = 52%) by preparative TLC. R_f = 0.4 (10% DCM in hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ_H 8.08 (bs, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 2 Hz, 1H), 6.72 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 3.96 (s, 3H), 3.83-3.82 (bm, 1H), 2.24 (s, 3H), 2.05-2.00 (m, 2H), 1.76-1.75 (m, 2H), 1.68-1.65 (m, 2H), 1.61-1.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.93 (C), 147.57 (C), 130.19 (CH), 124.15 (C), 117.34 (CH), 115.80 (C), 114.13 (CH), 61.84 (CH_3), 54.05 (CH), 33.25 (CH_2), 23.91 (CH_2), 12.66 (CH_3); IR (thin-film, cm^{-1}): 3275, 2956, 2869, 1597, 1563, 1509, 1425, 1273, 1061, 1044, 905; HRMS m/z (ESI): calculated for $C_{14}H_{20}N_2OBr^+$: 311.0759, found: 311.0763.



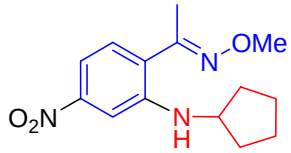
3da

3da was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as a brown oil (49.2 mg, 81% yield) (with 1.3 equiv of CsOAc, ^1H NMR yield = 43%) by preparative TLC. R_f = 0.55 (50% DCM in hexane); ^1H NMR ($CDCl_3$, 400 MHz): δ_H 7.95 (bs, 1H), 7.41-7.39 (m, 2H), 7.257 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 3.99-3.97 (m, 4H), 2.23 (s, 3H), 2.09-2.05 (m, 2H), 1.77-1.75 (m, 2H), 1.69-1.65 (m, 2H), 1.60-1.56 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 166.86 (C), 156.97 (C), 146.43 (C), 131.05 (C), 128.77 (CH), 120.47 (C), 115.20 (CH), 112.65 (CH), 61.91 (CH_3), 60.75 (CH_2), 54.08 (CH), 33.39 (CH_2), 23.96 (CH_2), 14.24 (CH_3), 12.76 (CH_3); IR (thin-film, cm^{-1}): 3294, 2957, 2870, 1716, 1597, 1561, 1435, 1306, 1248, 1111, 1045, 901, 763; HRMS m/z (ESI): calculated for $C_{17}H_{25}N_2O_3^+$: 305.1865, found: 305.1852.



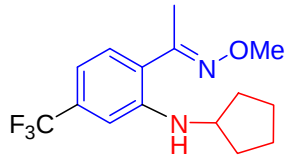
3ea

3ea was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as a yellow oil (47.7 mg, 77% yield) (with 1.3 equiv of CsOAc, ^{1}H NMR yield = 32%) by preparative TLC (30% EtOAc in hexane) followed by flash column chromatography (30% hexane in DCM). R_f = 0.5 (10% hexane in DCM); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.22 (bs, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.20 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 4.00 (s, 3H), 3.94-3.92 (bm, 1H), 3.04 (s, 3H), 2.29 (s, 3H), 2.09-2.04 (m, 2H), 1.78-1.68 (m, 4H), 1.59-1.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.48 (C), 146.91 (C), 140.75 (C), 129.79 (CH), 120.86 (C), 112.05 (CH), 109.59 (CH), 62.11 (CH_3), 54.07 (CH), 44.31 (CH_3), 33.21 (CH_2), 23.85 (CH_2), 12.88 (CH_3); IR (thin-film, cm^{-1}): 3280, 2957, 2870, 1597, 1561, 1517, 1429, 1310, 1279, 1154, 1058, 1043, 899, 760, 546; HRMS m/z (ESI): calculated for $C_{15}H_{23}N_2O_3S^+$: 311.1429, found: 311.1417.



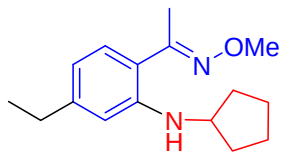
3fa

3fa was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as an orange solid (50.9 mg, 92% yield) (with 1.3 equiv of CsOAc, ^{1}H NMR yield = 23%) by flash column chromatography. R_f = 0.25 (20% DCM in hexanes); mp = 99.0-100.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.25 (bs, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.41 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 4.01 (s, 3H), 3.95-3.92 (bm, 1H), 2.30 (s, 3H), 2.12-2.07 (m, 2H), 1.80-1.68 (m, 4H), 1.62-1.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.38 (C), 148.45 (C), 147.01 (C), 129.47 (CH), 121.83 (C), 108.71 (CH), 105.79 (CH), 61.18 (CH_3), 54.19 (CH), 33.20 (CH_2), 23.91 (CH_2), 12.92 (CH_3); IR (KBr, cm^{-1}): 3256, 2956, 2934, 1621, 1527, 1505, 1434, 1342, 1284, 1056, 1042, 907; HRMS m/z (ESI): calculated for $C_{14}H_{20}N_3O_3^+$: 278.1505, found: 278.1495.



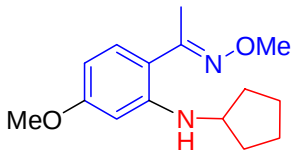
3ga

3ga was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as a pale yellow oil (48.6 mg, 81% yield) (with 1.3 equiv of CsOAc, ^{1}H NMR yield = 28%) by preparative TLC. R_f = 0.4 (10% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.10 (bs, 1H), 7.44 (d, J = 8.4 Hz, 1H), 6.90 (s, 1H), 6.84 (d, J = 8.0 Hz, 1H), 4.00 (s, 3H), 3.91 (bs, 1H), 2.29 (s, 3H), 2.08-2.03 (m, 2H), 1.78-1.69 (m, 4H), 1.62-1.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.72 (C), 146.62 (C), 131.72, 131.41, 131.09, 130.77 (q, J = 31 Hz, C), 129.26 (CH), 128.35, 125.61, 122.90, 120.24 (q, J = 266 Hz, C), 110.54, 110.50, 110.46, 110.43 (q, J = 4 Hz, CH), 107.93, 107.89, 107,85, 107.81 (q, J = 4 Hz, CH), 61.94 (CH_3), 53.97 (CH), 33.28 (CH_2), 23.91 (CH_2), 12.75 (CH_3); IR (thin-film, cm^{-1}): 3285, 2959, 2872, 1619, 1600, 1569, 1535, 1444, 1338, 1278, 1168, 1123, 1097, 1060, 1045, 923, 853, 803; HRMS m/z (ESI): calculated for $C_{15}H_{20}N_2OF_3^+$: 301.1528, found: 301.1540.



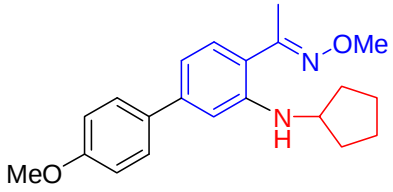
3ha

3ha was isolated as a pale yellow oil (33.3 mg, 64% yield) by flash column chromatography. R_f = 0.15 (10% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.88(bs, 1H), 7.30 (d, J = 8.0 Hz, 1H), 6.56-6.51 (bm, 2H), 3.95 (s, 3H), 3.93-3.89 (m, 1H), 2.60 (q, J = 7.6 Hz, 2H), 2.27 (s, 3H), 2.04-2.00 (m, 2H), 1.78-1.76 (m, 2H), 1.67-1.64 (m, 4H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 157.38 (C), 146.19 (C), 128.99 (CH), 114.27 (C), 110.91 (C), 61.68 (CH_3), 54.07 (CH), 33.39 (CH_2), 29.03 (CH_2), 23.95 (CH_2), 15.32 (CH_3), 12.67 (CH_3) (2 CH signals missing); IR (thin-film, cm^{-1}): 3292, 2959, 2869, 1612, 1596, 1562, 1438, 1274, 1062, 1045, 894; HRMS m/z (ESI): calculated for $C_{16}H_{25}N_2O^+$: 261.1955, found: 261.1967.



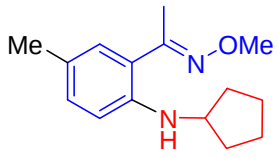
3ia

3ia was isolated as a brown oil (18.8 mg, 36% yield) by flash column chromatography. R_f = 0.2 (20% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.10 (bs, 1H), 7.30 (d, J = 8.4 Hz, 1H), 6.23-6.21 (m, 2H), 3.94 (s, 3H), 3.84-3.81 (m, 4H), 2.25 (s, 3H), 2.04-2.00 (m, 2H), 1.78-1.77 (m, 2H), 1.67-1.58 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 160.95 (C), 157.18 (C), 130.36 (CH), 61.61 (CH_3), 55.01 (CH_3), 54.28 (CH), 33.24 (CH_2), 23.98 (CH_2), 12.62 (CH_3) (2 CH, 2 C signals missing); IR (thin-film, cm^{-1}): 3285, 2954, 2869, 1613, 1567, 1528, 1463, 1288, 1222, 1050, 894; HRMS m/z (ESI): calculated for $C_{15}H_{23}N_2O_2^+$: 263.1760, found: 263.1748.



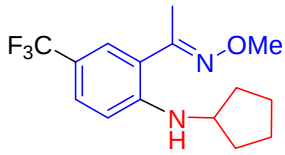
3ja

3ja was isolated as a light brown solid (33.1 mg, 49% yield) by flash column chromatography. R_f = 0.3 (30% DCM in hexanes); mp = 73.2-75.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.01 (bs, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.90-6.83 (bm, 2H), 3.99 (m, 4H), 3.86 (s, 3H), 2.31 (s, 3H), 2.07-2.06 (bm, 2H), 1.80 (bs, 2H), 1.67 (bs, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 159.23 (C), 157.28 (C), 142.01 (C), 133.90 (C), 129.38 (CH), 128.11 (2CH), 114.04 (2CH), 113.48 (C), 109.73 (C), 61.78 (CH_3), 55.29 (CH_3), 54.13 (CH), 33.41 (CH_2), 24.01 (CH_2), 12.70 (CH_3) (2 CH signals missing); IR (KBr, cm^{-1}): 3268, 2952, 2933, 1594, 1556, 1506, 1436, 1285, 1246, 1179, 1049, 1027, 912, 827; HRMS m/z (ESI): calculated for $C_{21}H_{27}N_2O_2^+$: 339.2073, found: 339.2074.



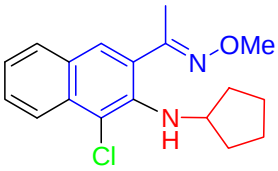
3ka

3ka was isolated as a light brown oil (27.0 mg, 55% yield) by flash column chromatography followed by high vacuum evacuation overnight (0.5 mmHg, ~18 h, for removal of **1k** residue). R_f = 0.2 (2% Et_2O in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.58 (bs, 1H), 7.17 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.68 (bs, 1H), 3.96 (s, 3H), 3.86-3.85 (bm, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.02-1.96 (m, 2H), 1.77-1.74 (bm, 2H), 1.66-1.60 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 157.29 (C), 130.45 (CH), 129.27 (CH), 112.59 (bs, C), 61.76 (CH_3), 54.48 (bs, CH), 33.25 (CH_2), 23.95 (CH_2), 20.42 (CH_3), 12.87 (CH_3) (1 CH, 2 C signals missing); IR (thin-film, cm^{-1}): 3300, 2954, 2868, 1620, 1521, 1325, 1273, 1182, 1047, 925, 879, 805; HRMS m/z (ESI): calculated for $C_{15}H_{23}N_2O^+$: 247.1810, found: 247.1800.



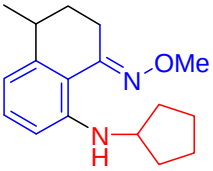
3la

3la was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as a light brown oil (46.8 mg, 78% yield) (with 1.3 equiv of CsOAc, ^{1}H NMR yield = 46%) by preparative TLC. R_f = 0.45 (10% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.37 (bs, 1H), 7.59 (s, 1H), 7.39 (d, J = 8.8 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 3.99 (s, 3H), 3.92-3.91 (bm, 1H), 2.31 (s, 3H), 2.06-2.02 (m, 2H), 1.78-1.76 (m, 2H), 1.70-1.66 (m, 2H), 1.64-1.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.82 (C), 148.81 (C), 129.08, ~126.4, 123.71, 121.03 (q, J = 268 Hz, C), 126.49-126.37 (m, CH), 126.23, 126.19, 126.15, 126.11 (q, J = 4 Hz, CH), 116.37, 116.06, 115.73, 115.40 (q, J = 33 Hz, C), 116.06 (C), 111.01 (CH), 61.89 (CH_3), 53.96 (CH), 33.28 (CH_2), 23.91 (CH_2), 12.52 (CH_3); IR (thin-film, cm^{-1}): 3273, 2959, 2873, 1619, 1599, 1535, 1337, 1317, 1269, 1108, 1047, 898, 814, 647; HRMS m/z (ESI): calculated for $C_{15}H_{20}N_2OF_3^+$: 301.1528, found: 301.1519.



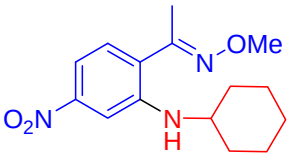
3na-3Cl

3na-3Cl was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as a brown oil (27.2 mg, 43% yield) by preparative TLC. R_f = 0.2 (20% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.10 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 4.81 (bs, 1H), 4.03 (s, 3H), 3.90-3.85 (m, 1H), 2.28 (s, 3H), 1.84-1.78 (m, 2H), 1.74-1.71 (m, 2H), 1.59-1.57 (m, 2H), 1.49-1.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 157.23 (C), 140.87 (C), 131.41 (C), 129.70 (C), 128.89 (C), 128.39 (CH), 128.34 (CH), 127.72 (CH), 124.11 (CH), 123.15 (CH), 119.71 (C), 61.88 (CH_3), 59.32 (CH), 33.46 (CH_2), 23.44 (CH_2), 14.73 (CH_3); IR (thin-film, cm^{-1}): 3358, 2858, 2870, 1625, 1473, 1438, 1047, 884, 747; HRMS m/z (ESI): calculated for $C_{18}H_{22}N_2OCl^+$: 317.1421, found: 317.1420.



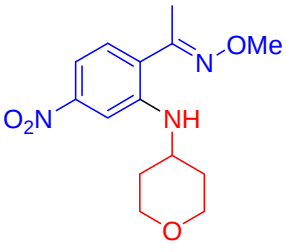
3oa

3oa was as a greenish brown semi-solid (32.6 mg, 60% yield) by preparative TLC. R_f = 0.6 (20% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.37 (bs, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.48 (d, J = 8 Hz, 1H), 3.97 (s, 3H), 3.89 (bs, 1H), 2.91-2,80 (m, 3H), 2.04-2.01 (m, 2H), 1.87-1.82 (m, 1H), 1.78 (bs, 2H), 1.67-1.62 (m, 5H), 1.24 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 158.26 (C), 147.39 (C), 146.63 (C), 129.68 (CH), 113.81 (CH), 110.93 (CH), 109.44 (C), 61.75 (CH_3), 54.11 (CH), 34.06 (CH), 33.51 (CH_2), 33.48 (CH_3), 27.53 (CH_2), 24.02 (CH_2), 21.63 (CH_2), 20.67 (CH_3); IR (thin-film, cm^{-1}): 3277, 2956, 2866, 1593, 1519, 1464, 1335, 1181, 1053, 900, 790, 741; HRMS m/z (ESI): calculated for $C_{17}H_{25}N_2O^+$: 273.1967, found: 273.1955.



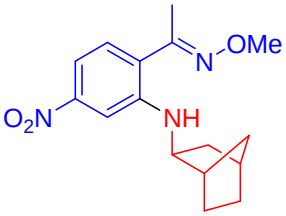
3fb

3fb was synthesized using the general procedure with 1.1 equiv of CsOAc and it was isolated as an orange solid (50.0 mg, 86% yield) by preparative TLC. R_f = 0.35 (30% DCM in hexanes); mp = 98.2-99.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.20 (bs, 1H), 7.48-7.45 (m, 2H), 7.38 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 4.02 (s, 3H), 3.50 (bs, 1H), 2.30 (s, 3H), 2.06-2.03 (m, 2H), 1.78-1.74 (m, 2H), 1.66-1.62 (m, 1H), 1.52-1.46 (m, 2H), 1.44-1.35 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.44 (C), 148.55 (C), 146.51 (C), 129.66 (CH), 121.80 (C), 108.52 (CH), 105.46 (CH), 62.22 (CH_3), 50.81 (CH), 32.42 (CH_2), 25.77 (CH_2), 24.25 (CH_2), 13.01 (CH_3); IR (KBr, cm^{-1}): 3269, 2930, 2856, 1621, 1531, 1510, 1342, 1283, 1058, 1043, 903, 857; HRMS m/z (ESI): calculated for $C_{15}H_{22}N_3O_3^+$: 292.1661, found: 292.1653.



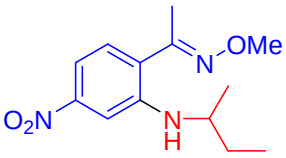
3fc

3fc was synthesized using the general procedure with 1.1 equiv of CsOAc and it was isolated as an orange solid (38.7 mg, 66% yield) by flash column chromatography. R_f = 0.2 (50% DCM in hexanes); mp = 151.5-153.5 °C ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.29 (bd, J = 6.0 Hz, 1H), 7.50-7.48 (m, 2H), 7.43 (d, J = 8.4 Hz, 1H), 4.02-3.97 (m, 5H), 3.73-3.72 (bm, 1H), 3.62 (t, J = 10 Hz, 2H), 2.31 (s, 3H), 2.12-2.09 (m, 2H), 1.65-1.57 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.47 (C), 148.51 (C), 146.20 (C), 129.80 (CH), 122.13 (C), 109.14 (CH), 105.23 (CH), 66.20 (CH_2), 62.28 (CH), 48.08 (CH_3), 32.65 (CH_2), 13.03 (CH_3); IR (KBr, cm^{-1}): 3225, 2937, 2861, 1531, 1504, 1434, 1340, 1135, 1035, 909, 859, 824; HRMS m/z (ESI): calculated for $C_{14}H_{19}N_3O_4^+$: 294.1454, found: 294.1455.



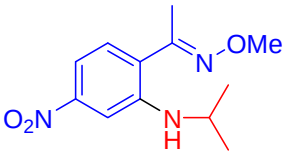
3fd

3fd was synthesized using the general procedure with 1.1 equiv of CsOAc and it was isolated as an orange gum (45.6 mg, 75% yield) by preparative TLC. R_f = 0.3 (20% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.18 (bd, J = 4.0 Hz, 1H), 7.47-7.39 (m, 3H), 4.01 (s, 3H), 3.39 (bs, 1H), 2.35-1.96 (m, 5H), 1.93-1.91 (m, 1H), 1.64-1.52 (m, 3H), 1.32-1.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.36 (C), 148.44 (C), 146.59 (C), 129.44 (CH), 121.76 (C), 108.65 (CH), 105.61 (CH), 62.20 (CH), 56.15 (CH), 41.49 (CH_3), 40.90 (CH_2), 35.74 (CH), 35.68 (CH_2), 28.39 (CH_2), 26.30 (CH_2), 12.87 (CH_3); IR (thin-film, cm^{-1}): 3281, 2953, 2870, 1618, 1538, 1434, 1345, 1284, 1060, 1044, 904, 857, 818, 742; HRMS m/z (ESI): calculated for $C_{16}H_{22}N_3O_3^+$: 304.1661, found: 304.1667.



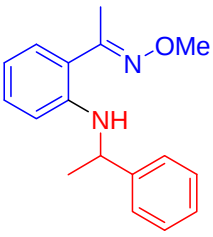
3fe

3fe was synthesized using the general procedure with 1.1 equiv of CsOAc and it was isolated as an orange solid (45.1 mg, 85% yield) by preparative TLC. R_f = 0.35 (30% DCM in hexanes); mp = 62.8-64.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.14 (bs, 1H), 7.48-7.45 (m, 2H), 7.39 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 4.01 (s, 3H), 3.62-3.57 (m, 1H), 2.31 (s, 3H), 1.69-1.60 (m, 2H), 1.26 (d, J = 6.4 Hz, 3H) 1.01 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.42 (C), 148.56 (C), 146.84 (C), 129.63 (CH), 121.87 (C), 108.56 (CH), 105.44 (CH), 62.16 (CH_3), 49.55 (CH), 29.26 (CH_2), 19.75 (CH_3), 12.99 (CH_3) 10.10 (CH_3); IR (KBr, cm^{-1}): 3251, 2963, 2930, 1621, 1531, 1506, 1436, 1342, 1283, 1062, 1045, 901, 863, 819; HRMS m/z (ESI): calculated for $C_{13}H_{20}N_3O_3^+$: 266.1513, found: 266.1505.



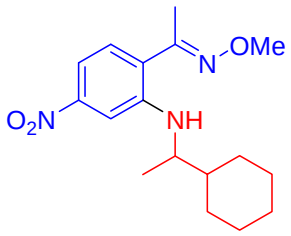
3ff

3ff was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as an orange solid (42.2 mg, 84% yield) by flash column chromatography. R_f = 0.4 (30% DCM in hexanes); mp = 79.5-81.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.12 (bs, 1H), 7.47-7.45 (m, 2H), 7.40 (d, J = 8.8 Hz, 1H), 4.02 (s, 3H), 3.79-3.76 (bm, 1H), 2.30 (s, 3H), 1.30 (d, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.34 (C), 148.54 (C), 146.59 (C), 129.62 (CH), 121.83 (C), 108.63 (CH), 105.43 (CH), 62.17 (CH_3), 43.96 (CH), 22.52 (CH_3), 13.01 (CH_3); IR (KBr, cm^{-1}): 3255, 2977, 2966, 2928, 1621, 1536, 1512, 1436, 1342, 1284, 1060, 1044, 902; HRMS m/z (ESI): calculated for $C_{12}H_{18}N_3O_3^+$: 252.1348, found: 252.1336.



3ag

3ag was isolated as a yellow solid (35.4 mg, 66% yield) by flash column chromatography. R_f = 0.3 (20% DCM in hexanes); mp = 71.0-72.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.35 (bd, J = 3.2, 1H), 7.42-7.38 (m, 3H), 7.35-7.31 (m, 2H), 7.26-7.22 (m, 1H), 7.05 (t, J = 7.2 Hz, 1H), 6.63 (t, J = 7.2 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.65-4.59 (m, 1H), 4.03 (s, 3H), 2.36 (s, 3H), 1.60 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 157.62 (C), 146.15 (C), 145.40 (C), 129.67 (CH), 128.83 (CH), 128.56 (CH), 126.71 (CH), 125.79 (CH), 117.07 (C), 114.97 (CH), 112.22 (CH), 61.86 (CH_3), 53.14 (CH), 24.98 (CH_3), 12.85 (CH_3); IR (KBr, cm^{-1}): 3275, 2962, 2930, 1598, 1521, 1450, 1275, 1049, 1036, 899, 762, 740, 702; HRMS m/z (ESI): calculated for $C_{17}H_{21}N_2O^+$: 269.1654, found: 269.1653.

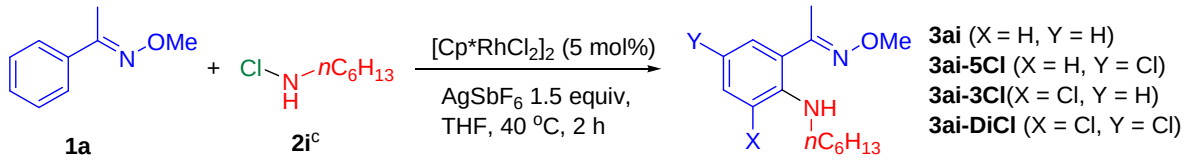


3fh

3fh was synthesized using the general procedure with 1.0 equiv of CsOAc and it was isolated as an orange oil (26.8 mg, 42% yield) by flash column chromatography. R_f = 0.4 (30% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.20 (bd, J = 6.4 Hz, 1H), 7.47-7.45 (m, 2H), 7.37 (d, J = 8.4 Hz, 1H), 4.01 (s, 3H), 3.53-3.49 (bm, 1H), 2.31 (s, 3H), 1.92-1.89 (m, 1H), 1.77-1.68 (m, 4H), 1.57-1.52 (m, 1H), 1.25-1.13 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.62 (C), 148.62 (C), 147.16 (C), 129.69 (CH), 121.60 (C), 108.16 (CH), 105.15 (CH), 62.18 (CH_3), 52.91 (CH), 43.28 (CH), 29.24 (CH_2), 28.91 (CH_2), 26.47 (CH_2), 26.35 (CH_2), 26.26 (CH_2), 17.13 (CH_3), 12.92 (CH_3); IR (thin-film, cm^{-1}): 3281, 2929, 2852, 1618, 1533, 1437, 1344, 1281, 1059, 1044, 906, 821; HRMS m/z (ESI): calculated for $C_{17}H_{26}N_3O_3^+$: 320.1974, found: 320.1976.

3. Amination Reactions with *N*-Chlorohexylamine and Charaterizations

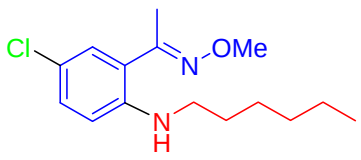
3.1 Condition Examination for the Reaction with *N*-Chlorohexylamine



entry	CsOAc (equiv)	Additive (equiv)	yield% **3ai**	yield% **3ai-3Cl**	yield% **3ai-5Cl**	yield% **3ai-DiCl**
1	1.3	--	--	--	trace	--
2	0.3	--	trace	17	20	trace
3[d]	--	--	trace	(20)[e]	(10)	(12%)

[a]Reaction conditions: **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (1.5 equiv), CsOAc, THF (1 mL) at 40 °C, 2 h, **2i** (2.2 equiv, in 1 mL THF) was added dropwise using a syringe pump at a rate of 2.2 equiv / h. [b]Yields were determined by ^{1}H NMR. [c]**2i** were freshly prepared by stirring *N*-Chlorosuccinimide and *n*-hexylamine (1:1) in THF (1 mL) for 10 min. [d]$[Cp^*Rh(OAc)_2]$ (10 mol%) was used instead. [e]Isolated yields in parentheses.

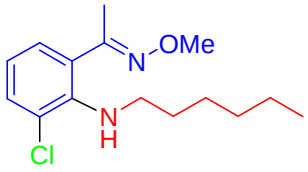
3.2 Product Characterizations



3mi

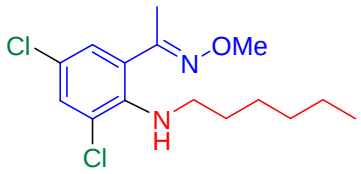
3mi was synthesized using the general procedure with **1a** as substrate, $[Cp^*Rh(OAc)_2]$ (10 mol%) and without CsOAc, and it was isolated as a white solid (9.6 mg, 17% yield) by flash column chromatography. R_f = 0.3 (20% DCM in hexanes); mp = 52.0-53.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.68 (bs, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.13 (dd, J = 8.8 Hz,

2.4 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 3.98 (s, 3H), 3.17-3.12 (m, 2H), 2.26 (s, 3H), 1.68 (p, J = 7.2 Hz, 2H), 1.48-1.44 (m, 2H), 1.36-1.32 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.60 (C), 145.84 (C), 129.44 (CH), 128.35 (CH), 119.16 (C), 118.03 (C), 111.87 (CH), 61.92 (CH_3), 43.37 (CH_2), 31.57 (CH_2), 29.01 (CH_2), 26.97 (CH_2), 22.57 (CH_2), 13.96 (CH_3), 12.73 (CH_3); IR (KBr, cm^{-1}): 3284, 2953, 2928, 2855, 1602, 1560, 1516, 1412, 1251, 1045, 916, 798; HRMS m/z (ESI): calculated for $C_{15}H_{24}N_2OCl^+$: 283.1577, found: 283.1579.



3mi'

3mi' was synthesized using the general procedure with **1a** as substrate, [Cp*Rh(OAc)$_2$] (10 mol%) and without CsOAc, and it was isolated as an colourless oil (11.3 mg, 20% yield) by flash column chromatography. R_f = 0.1 (20% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.28 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.12 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.78 (t, J = 8.0 Hz, 1H), 4.96 (bs, 1H), 3.98 (s, 3H), 3.09 (t, J = 7.2 Hz, 2H), 2.19 (s, 3H), 1.52-1.49 (m, 2H), 1.34-1.25 (bm, 6H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 156.66 (C), 144.02 (C), 129.99 (CH), 128.46 (CH), 127.75 (C), 124.90 (C), 119.97 (CH), 61.80 (CH_3), 48.19 (CH_2), 31.49 (CH_2), 30.66 (CH_2), 26.50 (CH_2), 22.51 (CH_2), 14.68 (CH_3), 13.92 (CH_3); IR (thin-film, cm^{-1}): 3377, 3306, 2956, 2929, 2856, 1593, 1492, 1456, 1441, 1365, 1253, 1048, 889, 779, 741; HRMS m/z (ESI): calculated for $C_{15}H_{24}N_2OCl^+$: 283.1577, found: 283.1584.

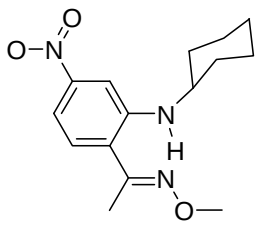


3ai-DiCl

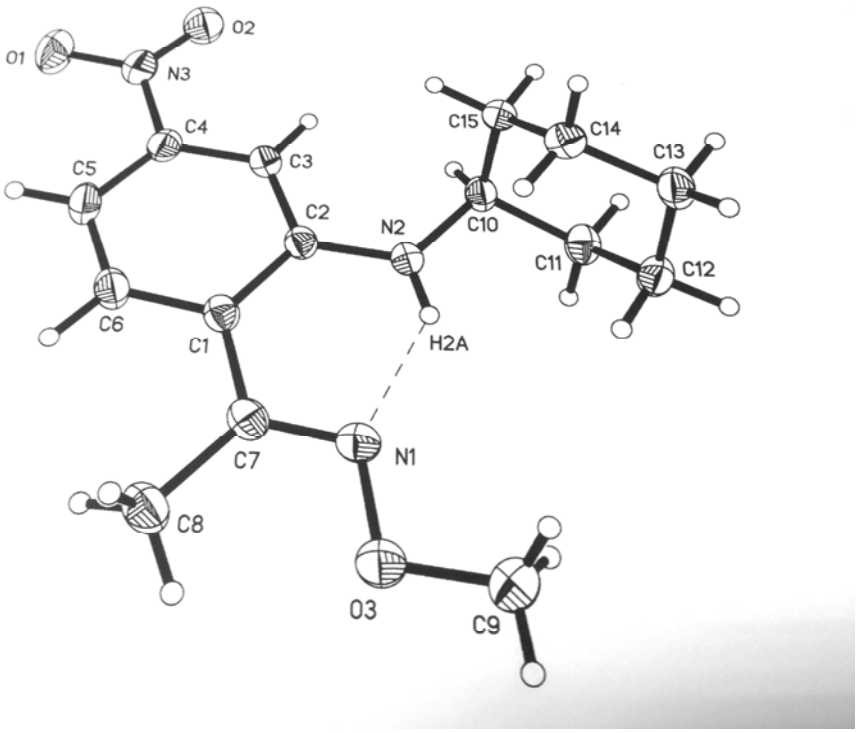
3ai-DiCl was synthesized using the general procedure with **1a** as substrate, [Cp*Rh(OAc)$_2$] (10 mol%) and without CsOAc, and it was isolated as an white paste (6.3 mg, 12% yield) by flash column chromatography followed by high vacuum evacuation overnight (0.5 mmHg, ~18 h, for removal of **1a** residue). R_f = 0.2 (20% DCM in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.28 (d, J = 2.4 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 4.95 (bs, 1H), 3.98 (s, 3H), 3.07 (t, J = 6.8 Hz, 2H), 2.17 (s, 3H), 1.51-1.47 (m, 2H), 1.33-1.27 (m, 6H), 0.87 (t, J = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 155.62 (C), 142.84 (C), 129.42 (CH), 128.34 (CH), 125.30 (C), 124.11 (C), 61.96 (CH_3), 48.14 (CH_2), 31.45 (CH_2), 30.60 (CH_2), 26.45 (CH_2), 22.50 (CH_2), 14.50 (CH_3), 13.91 (CH_3); IR (thin-film, cm^{-1}): 3379, 3306, 2956, 2930, 2856, 1479, 1466, 1440, 1366, 1242, 1050, 863, 817, 743; HRMS m/z (ESI): calculated for $C_{15}H_{23}N_2OCl_2^+$: 317.1187, found: 317.1181.

4. Preparation of 3fb Crystal for X-ray Diffraction Analysis and the X-ray Structure

3fb (0.1 mmol) was dissolved in distilled acetonitrile (1 mL) in an 8-mL vial, and it was loosely covered by a Teflon® liner cap. After slow evaporation over 48 h, orange crystals formed and they were collected for X-ray diffraction analysis.

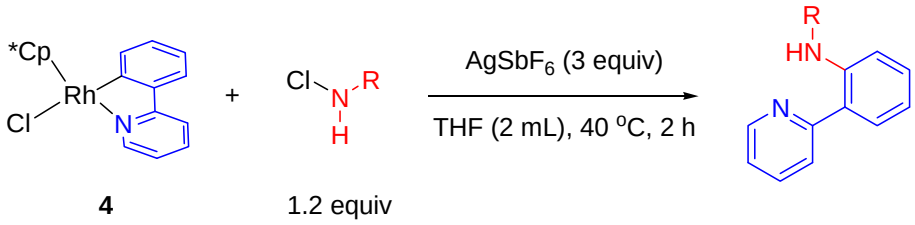


3fb



5. Stoichiometric Reactions and Characterizations

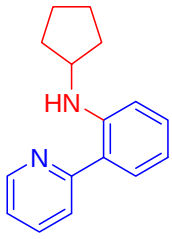
5.1 Procedure for Aminations of Cyclorhodated Complex 4



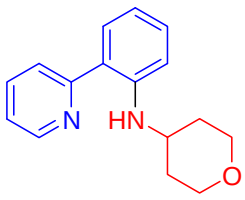
4 1.2 equiv

To an amber 8 mL-vial (vial **A**), **4** (0.05 mmol, 21.4 mg) and $AgSbF_6$ (3 equiv, 51.45 mg) were added, and the vial was sealed with a Teflon® liner cap. To another amber 4-mL vial (vial **B**), *N*-chlorosuccinimide (1.5 equiv, 10.0 mg) was added, and the vial was sealed with a Teflon® liner cap. Both vials were evacuated and back filled with N_2 for three times. Freshly distilled THF (1 mL) was added to the vial **A**, the mixture was pre-heated and stirred at 40 °C for 10 min. THF (1 mL) and primary amine (1.2 equiv) were added to the vial **B**, and they were mixed and stirred for 10 min. The mixture in Vial **B** was transferred to the reaction (vial **A**) in one portion, and stirred at 40 °C for 2 h. To work-up, 30% aqueous ammonia (2 mL) and EtOAc (5 mL) were added. The organic layer was collected, and the aqueous layer was washed with EtOAc (5 mL x 2). The combined organic fractions were dried over Na_2SO_4 and then filtered through a short plug of silica gel. Solvents were removed by rotary evaporation, and the residue was re-dissolved in a small amount of dichloromethane (DCM). The dissolved mixture was subjected to flash column chromatography with silica gel as the column stationary phase / preparative TLC for isolation by a gradient elution with hexane/Et_2O.

5.2 Product Characterizations

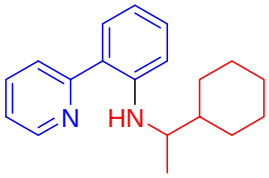


***N*-Cyclopentyl-2-(pyridin-2-yl)aniline;** The title compound was isolated by preparative TLC as a pale yellow oil (9.4 mg, 79% yield). R_f = 0.7 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.57 (d, J = 4.4 Hz, 1H), 8.18 (bs, 1H), 7.74 (t, J = 7.2 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H) 7.53 (d, J = 7.6 Hz, 1H), 7.27-7.24 (m, 1H), 7.16 (td, J = 6.0 Hz, 1H), 6.81 (bd, 1H), 6.71-6.69 (bm, 1), 3.87 (bt, J = 5.2 Hz, 1H), 2.06-2.03 (m, 2H), 1.75-1.73 (m, 2H), 1.64-1.58 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 159.61 (C), 147.22 (CH), 136.80 (CH), 130.16 (CH), 129.34 (CH), 122.22 (CH), 121.45 (C), 120.69 (CH), 115.82 (bs, CH), 115.27 (C), 112.85 (bs, CH), 54.54 (CH), 33.27 (CH_2), 24.04 (CH_2); IR (thin-film, cm^{-1}): 3291, 2954, 2867, 1604, 1584, 1515, 1478, 1442, 1332, 1240, 745; HRMS m/z (ESI): calculated for $C_{16}H_{19}N_2^+$: 239.1538, found: 239.1548.

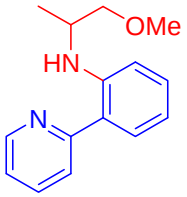


Tetrahydro-*N*-(2-(pyridin-2-yl)phenyl)-2*H*-pyran-4-amine; The title compound was isolated by preparative TLC as a yellow semi-solid (11.6 mg, 93% yield). R_f = 0.55 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.58 (d, J = 4.8 Hz, 1H),7.77 (t, J = 7.2 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H) 7.27 (t, J = 7.6 Hz, 1H), 7.19 (t, J = 6.0 Hz, 1H), 6.87 (bs, 1H), 6.78

(bs, 1H), 4.00-3.95 (m, 2H), 3.66-3.63 (m, 1H), 3.58-3.52 (m, 2H), 2.09-2.04 (m, 2H), 1.66-1.57 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 159.36 (C), 147.21 (CH), 136.94 (CH), 130.24 (CH), 129.59 (CH), 122.25 (CH), 121.72 (bs, C), 120.86 (CH), 116.37 (bs, CH), 112.68 (bs, CH), 66.37 (CH_2), 48.38 (bs, CH), 32.77 (CH_2) (1 arene-C missing); IR (thin-film, cm^{-1}): 3276, 2952, 2847, 1604, 1584, 1518, 1478, 1443, 1422, 1329, 1259, 1239, 1160, 1138, 1087, 748; HRMS m/z (ESI): calculated for $C_{16}H_{19}N_2O^+$: 255.1497, found: 255.1494.



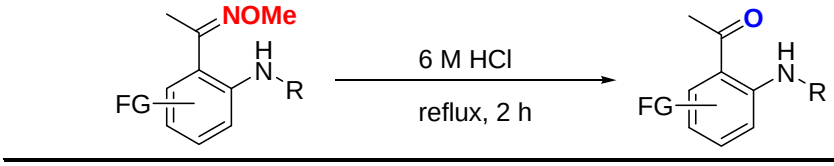
***N*-(1-Cyclohexylethyl)-2-(pyridin-2-yl)benzenamine;** The title compound was isolated by preparative TLC as a pale yellow oil (11.4 mg, 81% yield). R_f = 0.5 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.57 (d, J = 4.4 Hz, 1H), 7.74 (t, J = 7.2 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H) 7.24 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 6.0 Hz, 1H), 6.81 (bs, 1H), 6.68 (bm, 1H), 3.46-3.43 (m, 1H), 1.87-1.57 (m, 6H), 1.26-1.15 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 159.64 (C), 147.11 (CH), 136.70 (CH), 130.23 (CH), 129.58 (C), 129.45 (CH), 122.08 (CH), 121.06 (bs, C), 120.52 (CH), 115.15 (bs, CH), 112.17 (bs, CH), 53.06 (bs, CH), 42.93 (CH), 29.48 (CH_2), 28.60 (CH_2), 26.67 (CH_2), 26.54 (CH_2), 26.37 (CH_2), 16.97 (CH); IR (think-film, cm^{-1}): 3302, 2924, 2850, 1605, 1584, 1518, 1478, 1445, 1330, 1163, 744; HRMS m/z (ESI): calculated for $C_{19}H_{25}N_2^+$: 281.2018, found: 281.2010.

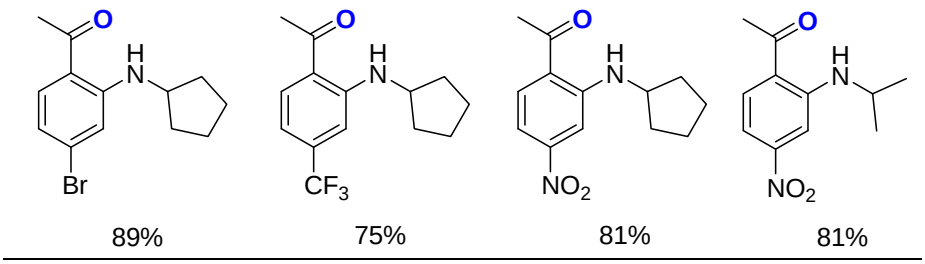


***N*-(1-Methoxypropan-2-yl)-2-(pyridin-2-yl)aniline;** The title compound was isolated by flash column chromatography as a pale yellow oil (10.45 mg, 86% yield). R_f = 0.3 (60% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.58 (d, J = 4.8 Hz, 1H), 8.17 (bs, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H) 7.53 (d, J = 7.6 Hz, 1H), 7.27-7.24 (m, 1H), 7.16 (t, J = 76.0 Hz, 1H), 6.84 (bs, 1H), 6.72 (bs, 1H), 3.77-3.73 (m, 1H), 3.58-3.54 (m, 1H), 3.39-3.32 (m, 4H), 1.29 (d, J = 6.4); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 157.37 (C), 147.29 (CH), 139.56 (C), 136.78 (CH), 130.20 (CH), 129.58 (CH), 123.63 (C), 122.29 (CH), 120.74 (CH), 115.78 (CH), 77.14 (CH), 59.04 (CH_3), 17.91 (CH_3) (1 arene-CH, 1 alkyl-CH_2 missing); IR (thin-film, cm^{-1}): 3270, 2973, 2924, 1064, 1585, 1517, 1478, 1443, 1389, 1239, 1168, 1110, 747; HRMS m/z (ESI): calculated for $C_{15}H_{19}N_2O^+$: 243.1497, found: 243.1508.

6. *O*-Methyloxime Arylamine Product Deprotection and Characterizations

6.1 Procedure for Deprotection of the *O*-Methyloxime Arylamine Products

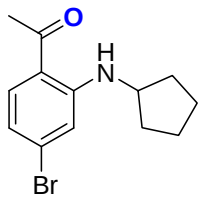




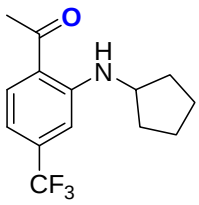
89% 75% 81% 81%

To an 8-mL vial containing *O*-methyloxime arylamine product (0.1 mmol), 6 M HCl (0.5 mL) was added, and the vial was tightly sealed with a Teflon® liner cap. The mixture was stirred vigorously at reflux (oil bath temp. = 120 ° C) for 2 h. To work-up, the solution was diluted with DI water (5 mL) and it was neutralized with saturated $NaHCO_3$ solution followed by the addition ethyl acetate (10 mL). The organic fraction was collected, and the aqueous fraction was washed with ethyl acetate (10 mL) twice. The combined organic fractions were washed with brine, dried over Na_2SO_4, and filtered through a short plug of Celite®. The solution was dried using a rotary evaporator, and the resulting residue was dissolved in a small amount of dichloromethane followed by a flash column chromatography using silica gel as the stationary phase for isolation of the 2-acetyl-*N*-alkylaniline products.

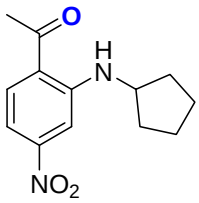
6.2 Product Characterizations



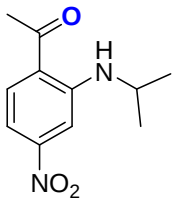
1-(4-bromo-2-(cyclopentylamino)phenyl)ethanone isolated as a yellow oil (25.0 mg, 89% yield) by flash column chromatography. R_f = 0.35 (10% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.99 (bs, 1H), 7.50 (d, J = 8.8 Hz, 1H), 6.87 (d, J = 2.0 Hz, 1H), 6.65 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 3.84-3.79 (m, 1H), 2.52 (s, 3H), 2.06-1.78 (m, 2H), 1.77-1.75 (m, 2H), 1.66-1.63 (m, 2H), 1.62-1.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 199.98 (C), 151.20 (C), 133.88 (CH), 129.91 (C), 116.69 (CH), 116.12 (C), 115.06 (CH), 53.50 (CH), 33.26 (CH_2), 27.79 (CH_3), 23.92 (CH_2); IR (thin-film, cm^{-1}): 3284, 2958, 2869, 1639, 1594, 1563, 1504, 1439, 1358, 1239, 954; HRMS m/z (ESI): calculated for $C_{13}H_{17}NOBr^+$: 282.0494, found: 282.0506.



1-(2-(cyclopentylamino)-4-(trifluoromethyl)phenyl)ethanone isolated as a yellow oil (20.3 mg, 75% yield) by flash column chromatography. R_f = 0.35 (10% DCM in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 9.04 (bs, 1H), 7.81 (d, J = 8.4 Hz, 1H), 6.94 (s, 1H), 6.75 (d, J = 8.4 Hz, 1H), 3.91-3.87 (m, 1H), 2.59 (s, 3H), 2.08-2.04 (m, 2H), 1.79-1.76 (m, 2H), 1.68-1.65 (m, 2H), 1.64-1.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 200.39 (C), 150.21 (C), 136.22-135.24 (q, J = 31 Hz, C), 133.31 (CH), 127.70-119.77 (q, J = 260 Hz, CF_3), 118.91 (C), 109.43-109.28 (m, CH) (1 CH missing); IR (thin-film, cm^{-1}): 3297, 2960, 2872, 1650, 1577, 1524, 1464, 1337, 1240, 1171, 1128, 1089, 962; HRMS m/z (ESI): calculated for $C_{14}H_{17}NOF_3^+$: 272.1262, found: 272.1253.



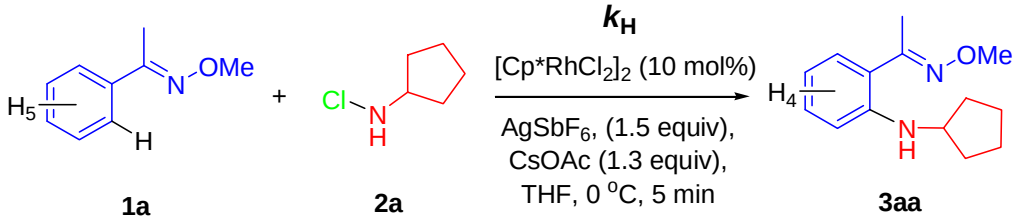
1-(2-(cyclopentylamino)-4-nitrophenyl)ethanone isolated as an orange solid (20.1 mg, 81% yield) by flash column chromatography. R_f = 0.20 (20% DCM in hexanes); mp = 66.0-68.5 ° C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 9.07 (bs, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.24 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 3.95-3.89 (m, 1H), 2.62 (s, 3H), 2.12-2.08 (m, 2H), 1.79-1.77 (m, 2H), 1.71-1.67 (m, 2H), 1.62-1.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 200.21 (C), 151.52 (C), 150.67 (C), 133.79 (CH), 120.43 (C), 107.28 (CH), 53.80 (CH), 33.22 (CH_2), 28.28 (CH_3), 23.92 (CH_2) (1 CH missing); IR (KBr, cm^{-1}): 3305, 2960, 2872, 1650, 1537, 1350, 1264, 1232; HRMS m/z (ESI): calculated for $C_{13}H_{17}N_2O_3^+$: 249.1239, found: 249.1243.



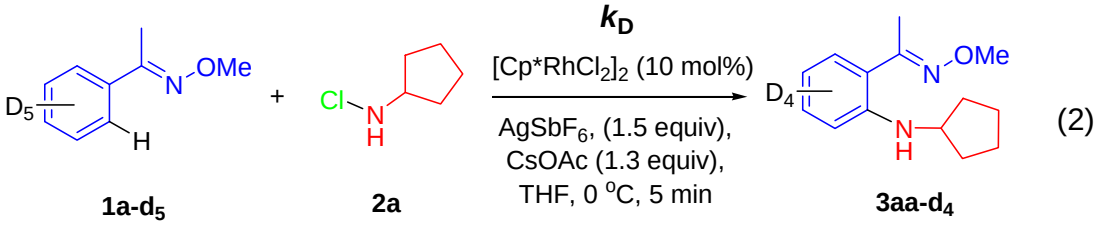
1-(2-(isopropylamino)-4-nitrophenyl)ethanone isolated as an orange solid (20.1 mg, 81% yield) by flash column chromatography. R_f = 0.35 (30% DCM in hexanes); mp = 54.0-55.0 ° C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.98 (bs, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 7.30 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 3.83-3.74 (m, 1H), 2.62 (s, 3H), 1.31 (d, J = 6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 200.26 (C), 151.65 (C), 150.24 (C), 133.94 (CH), 120.36 (C), 107.21 (CH), 106.84 (CH), 43.71 (CH), 28.33 (CH_3), 22.46 (CH_3); IR (KBr, cm^{-1}): 3287, 2983, 2928, 1647, 1529, 1346, 1231, 1169, 1130; HRMS m/z (ESI): calculated for $C_{11}H_{15}N_2O_3^+$: 223.1083, found: 223.1080.

7. Kinetic Isotope Effect Experiments

7.1 Experimental Procedures for Two Parallel Reactions



(1)



1a-d$_5$ **2a** **3aa-d$_4$** (2)

To an amber 8 mL-vial (vial **A**), $[Cp^*RhCl_2]_2$ (10 mol %, 6.2 mg), CsOAc (1.3 equiv, 24.8 mg) and $AgSbF_6$ (1.5 equiv, 51.5 mg) were added, and the vial was sealed with a Teflon® liner cap. To another amber 4-mL vial (vial **B**), *N*-chlorosuccinimide (2.2 equiv, 58.7 mg) was added, and the vial was sealed with a Teflon® liner cap. Both vials were evacuated and back filled with N_2 for three times. Freshly distilled THF (1 mL) was added to the vial **A**, followed by the addition of the H_5-acetophenone-*O*-methyloxime (0.1 mmol) using a 50-μL syringe. Vial **A** was pre-cooled at 0°C. THF (1 mL) and cyclopentylamine (2.2 equiv, 22 μL) were added to the vial **B**, and they were mixed and stirred for 10 min. The mixture in Vial **B** was taken up by a 1-mL syringe, and added to the reaction (vial **A**) in one portion, and the reaction was stirred at 0 °C for 5 min. The reaction was quenched by adding 30% aqueous ammonia (2 mL). EtOAc (5 mL) were added for extraction. The organic layer was collected, and the aqueous layer was washed with EtOAc (5 mL x 2). The combined organic fractions were dried over Na_2SO_4 and then filtered through a short plug of Celite®. Solvent was removed by rotary evaporation, and the residue was subjected to ^1H NMR analysis to determine the substrate conversions. *(singlet signal at 2.20 ppm, 3H, was used as the marker peak with reference to the singlet signal at 4.9 ppm, 2H, from dibromomethane (0.1 mmol) as internal standard.)*

A parallel reaction was run at the same time with d_5-acetophenone-*O*-methyloxime as substrate. The pair of reactions was duplicated.

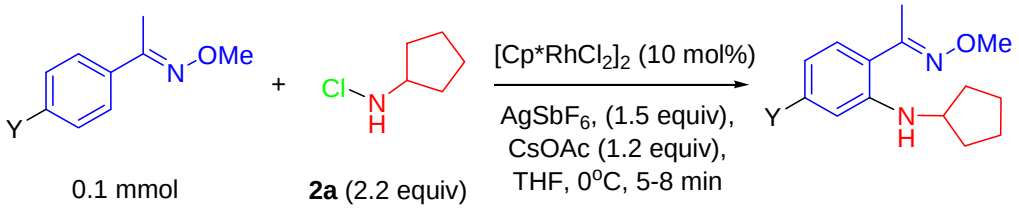
7.2 Experimental Data & Calculated KIE

Table S1: Data for Kinetic Isotope Effect

runs	Conversion for **1a**	Conversion For **1a-d$_5$**	reaction time	ratio of the remaining **1a/1a-d$_5$** (mmol/mmol)	ratio of the consumed **1a/1a-d$_5$** (mmol/mmol)	k_H / k_D
1st run	21%	9.6%	5 min	0.0790/0.0904	0.0210/0.0096	2.19
2nd run	22%	12%	5 min	0.078/0.088	0.022/0.012	1.83
					average	2.01

8. Hammett Correlation Studies

8.1 Experimental Procedures



0.1 mmol **2a** (2.2 equiv)

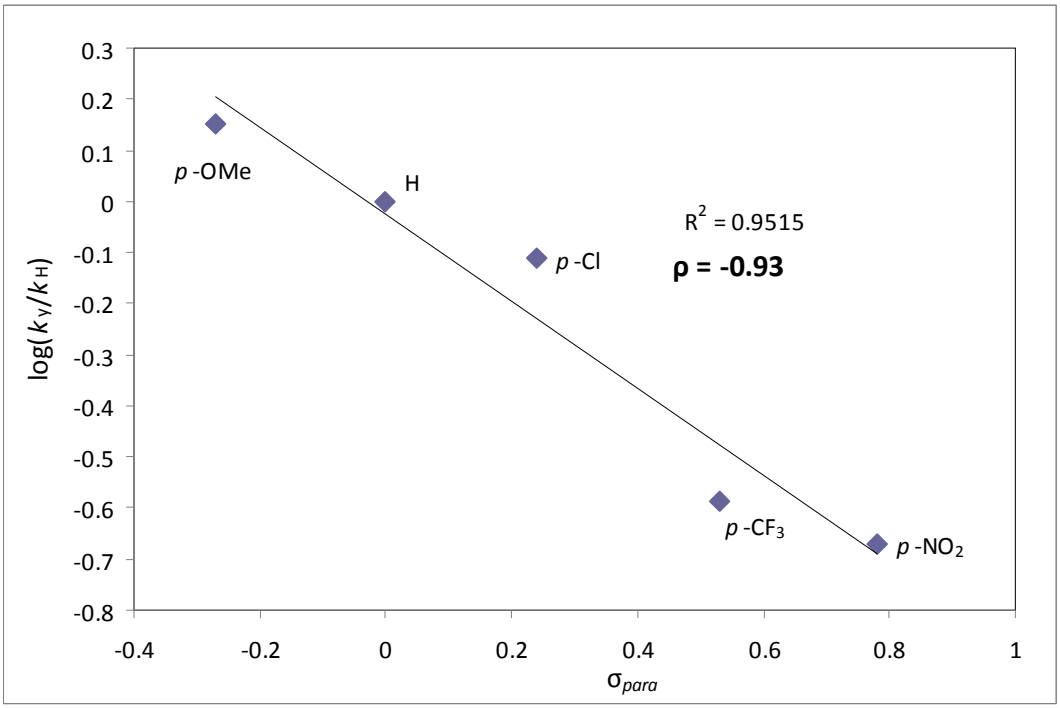
To an amber 8 mL-vial (vial **A**), $[Cp^*RhCl_2]_2$ (10 mol %, 6.2 mg), CsOAc (1.3 equiv, 24.8 mg) and $AgSbF_6$ (1.5 equiv, 51.5 mg) were added, and the vial was sealed with a Teflon® liner cap. To another amber 4-mL vial (vial **B**), *N*-chlorosuccinimide (2.2 equiv, 58.7 mg) was added, and the vial was sealed with a Teflon® liner cap. Both vials were evacuated and back filled with N_2 for three times. Freshly distilled THF (1 mL) was added to the vial **A**, followed by the addition of a suitable *para*-substituted acetophenone *O*-methyloxime (0.1 mmol) using a 50-µL syringe. Vial **A** was pre-cooled at 0°C. THF (1 mL) and cyclopentylamine (2.2 equiv, 22 µL) were added to the vial **B**, and they were mixed and stirred for 10 min. The mixture in Vial **B** was taken up by a 1-mL syringe, and added to the reaction (vial **A**) in one portion, and the reaction was stirred at 0 °C for 5 - 8 min. The reaction was quenched by adding 30% aqueous ammonia (2 mL). EtOAc (5 mL) were added for extraction. The organic layer was collected, and the aqueous layer was washed with EtOAc (5 mL x 2). The combined organic fractions were dried over Na_2SO_4 and then filtered through a short plug of Celite®. Solvent was removed by rotary evaporation, and the residue was subjected to ^1H NMR analysis to determine the substrate conversions. *(Dibromomethane (0.1 mmol) was used as internal standard, singlet signal at 4.9 ppm.)* All reactions were duplicated.

8.2 Experimental Data & Hammett Plot

Table S2: Data for Hammett Correlation

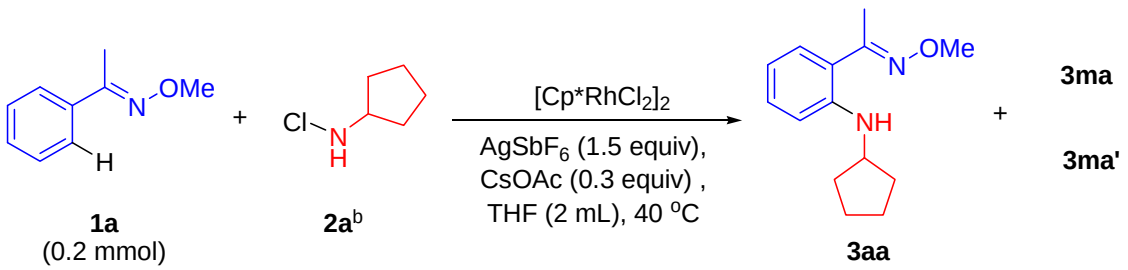
runs	Y	Marker peak in ^1H NMR	σ_{para} [4]	t (min)	substrate remained (mmol)	substrate consumed (mmol)	k_X (average) (k_H for H) (mmol / min)	$\log(k_X / k_H)$
1st	OMe	7.57, 2H,	-0.27	5	0.06932	0.03068	0.006158	0.1525
2nd	OMe	d		5	0.06910	0.03090		
1st	H	7.65-7.62,	0	5	0.07877	0.02123	0.004318	0
2nd	H	2H, m		5	0.07805	0.02195		
1st	Cl	7.57, 2H,	0.24	5	0.08327	0.01673	0.003341	-0.1114
2nd	Cl	d		5	0.08332	0.01668		
1st	CF_3	7.75, 2H,	0.53	8	0.09158	0.00842	0.001117	-0.5873
2nd	CF_3	d		8	0.09055	0.00945		
1st	NO_2	8.18, 2H,	0.78	8	0.09392	0.00608	0.000092	-0.6706
2nd	NO_2	d		8	0.09133	0.00867		

Figure S1: Hammett Free Energy Correlation



9. Reaction Optimization

Table S3: Preliminary Results.[a]

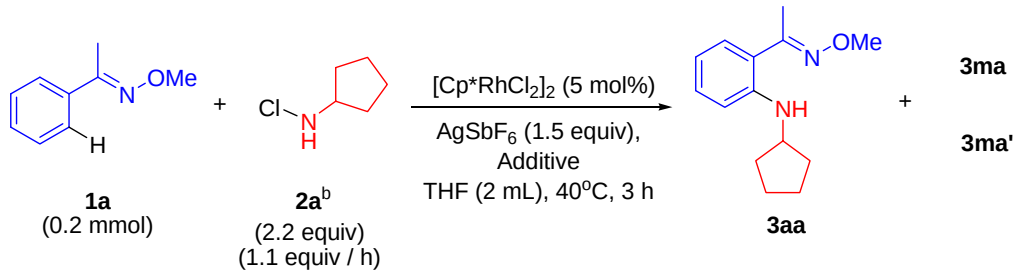


entry	$[Cp^*Rh(Cl)_2]_2$ (mol%)	addition of **2a** (equiv)	time	conv. (%)[c]	**3aa** (%)[c]	**3ma'** (%)[c]	**3ma** (%)[c]
1	2.5	one-pot (1.1)	1 h	50	10	10	25
2	--	one-pot (1.1)	1 h	<5	--	--	--
3[d]	5	1.1 equiv / h (1.1)	2 h	60	33	6	15

4[d]	5	1.1 equiv / h (2.2)	3 h	90	(28)[e]	(22)[e]	(40)[e]

[a]Reaction conditions: **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$, $AgSbF_6$ (1.5 equiv), CsOAc (0.3 equiv), **2a**, THF (2 mL), at 40 °C. [b]**2a** was freshly prepared by mixing cyclopentylamine and *N*-chlorosuccinimide (1:1), and stirred at rt for 10 min. [c]Yields and conversions were determined by ^{1}H NMR. [d]**2a** was added slowly via a syringe pump. [e]Isolated yields in parentheses.

Table S4: Effect of Additives[a]



1a (0.2 mmol)

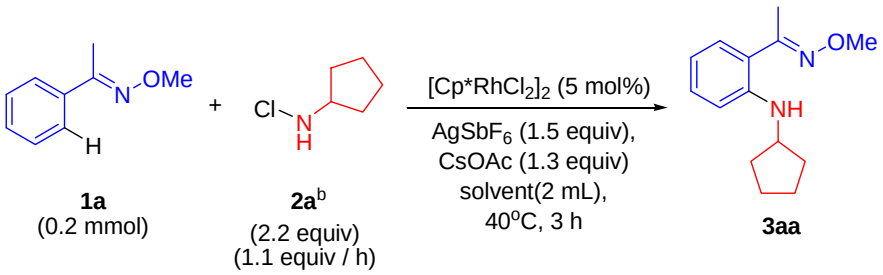
2a[b] (2.2 equiv) (1.1 equiv / h)

3aa

entry	base (equiv)	CsOAc (equiv)	conv. (%)[c]	**3aa** (%)[c]	**3ma** (%)[c]	**3ma'** (%)[c]
1	KO*t*Bu 1.3	0.3	10	<5	--	--
2	K_2CO_3 1.3	0.3	50	35	--	--
3	$KHCO_3$ 1.3	0.3	42	28	--	--
4	K_3PO_4 1.3	0.3	48	33	trace	--
5	K_2HPO_4 1.3	0.3	52	18	17	8
6	KOAc 1.3	--	79	77	trace	--
7[d]	AgOAc 1.5	--	<5	<5	--	--
8	--	1.3	77	73	trace	--
9	--	0.6	74	20	25	17
10	--	0.3	90	(28)[e]	(22)[e]	(40)[e]
11	--	2.0	30	18	--	--

[a]Reaction conditions: **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (1.5 equiv), CsOAc, THF (1 mL), at 40 °C for 3 h and **2a** (2.2 equiv in 1 mL THF) was added slowly via a syringe pump at a rate of 1.1 equiv / h [b]**2a** was freshly prepared by mixing cyclopentylamine and *N*-chlorosuccinimide (1:1) and stirred at rt for 10 min. [c]Yields and conversions were determined by ^{1}H NMR. [d]No $AgSbF_6$ was added. [e]Isolated yields in parentheses.

Table S5: Solvent Effect[a]

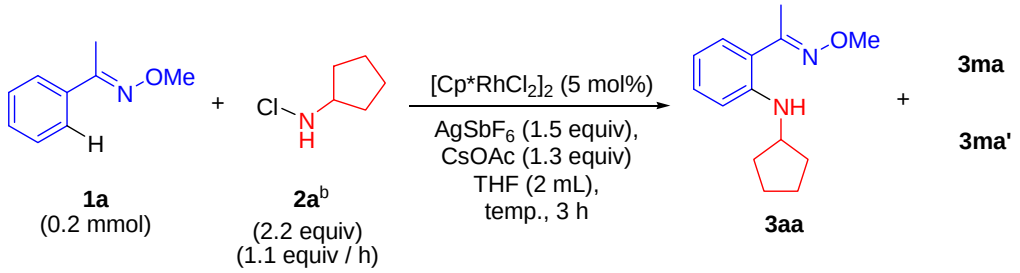


1a (0.2 mmol) + **2a**[b] (2.2 equiv) (1.1 equiv / h) → **3aa**

entry	Solvent	**3aa** (%)[c]
1	THF	73
2	*tert*-amylOH	< 5
3	1,2-dichloroethane	9
4	toluene	--
5	1,4-dioxane	< 5

[a]Reaction conditions: **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (1.5 equiv), CsOAc (1.3 equiv), solvent (1 mL), at 40 °C for 3 h and **2a** (2.2 equiv in 1 mL solvent) was added slowly via a syringe pump at a rate of 1.1 equiv / h [b]**2a** was freshly prepared by mixing cyclopentylamine and *N*-chlorosuccinimide (1:1) and stirred at rt for 10 min. [c]Yields were determined by ^{1}H NMR.

Table S6: Effect of Temperature[a]

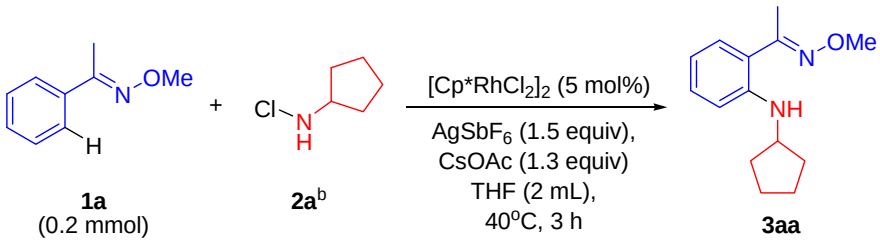


1a (0.2 mmol) + **2a**[b] (2.2 equiv) (1.1 equiv / h) → **3aa** + **3ma** + **3ma'**

entry	temp.	conv. (%)[c]	**3aa** (%)[c]	**3ma'** (%)[c]	**3ma** (%)[c]
1	rt	83	76	--	trace
2	40°C	77	73	--	trace
3	60°C	66	27	5	10

[a]Reaction conditions: **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (1.5 equiv), CsOAc (1.3 equiv), THF (1 mL) for 3 h and **2a** (2.2 equiv in 1 mL THF) was added slowly via a syringe pump at a rate of 1.1 equiv / h [b]**2a** was freshly prepared by mixing cyclopentylamine and *N*-chlorosuccinimide (1:1) and stirred at rt for 10 min. [c]Yields and conversions were determined by ^{1}H NMR.

Table S7: Effect of **2a** amount and the addition rate.[a]



1a (0.2 mmol) + **2a**[b] → **3aa**

entry	**2a** (equiv)	rate of **2a** addition	time	conv. (%)[c]	**3aa** (%)[c]
1	2.2	0.7 equiv / h	5 h	66	65
2	2.2	1.1 equiv / h	3 h	77	73
3	2.2	2.2 equiv / h	2 h	83	(80)[d]
4	2.5	2.2 equiv / h	2 h	64	65
5	3	3 equiv / h	2 h	55	43
6	1.8	1.8 equiv / h	2 h	61	59
7[e]	2.2	2.2 equiv / h	2 h	68	45

[a]Reaction conditions: **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (1.5 equiv), CsOAc (1.3 equiv), THF (1 mL) for 3 h and **2a** (in 1 mL THF) was added slowly via a syringe pump. [b]**2a** was freshly prepared by mixing cyclopentylamine and *N*-chlorosuccinimide (1:1) and stirred at rt for 10 min. [c]Yields and conversions were determined by ^{1}H NMR. [d]Isolated yield in parentheses. [e]**2a** was individually synthesized using NaOCl (aq. ~14%) instead of prepared freshly.

10. References

1. Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc*. **1969**, *91*, 5970.

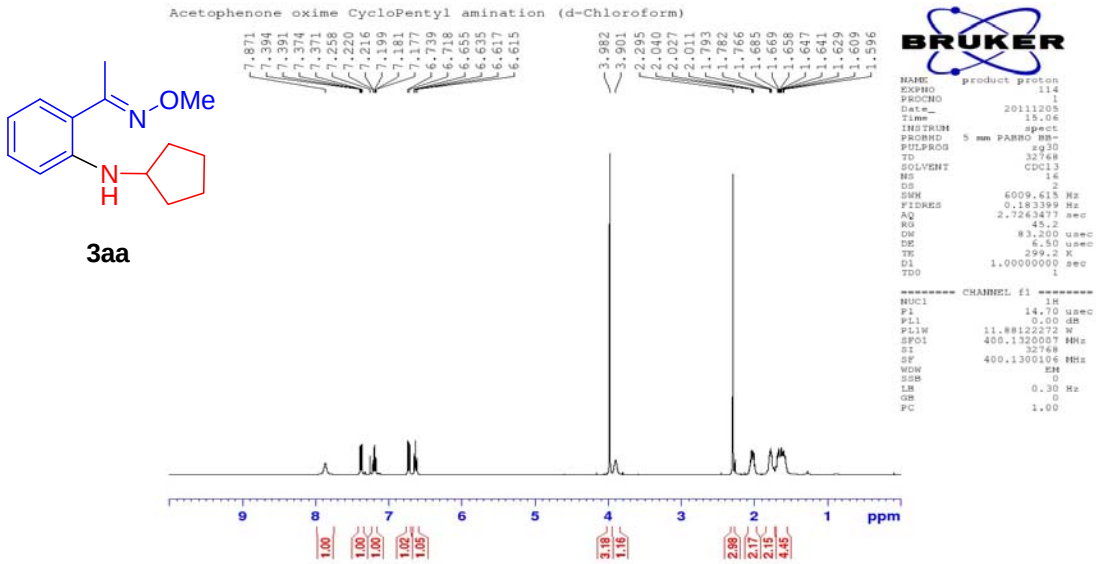
2. Li, L.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2009**, *28*, 3492.

3. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: London, England, 1996.

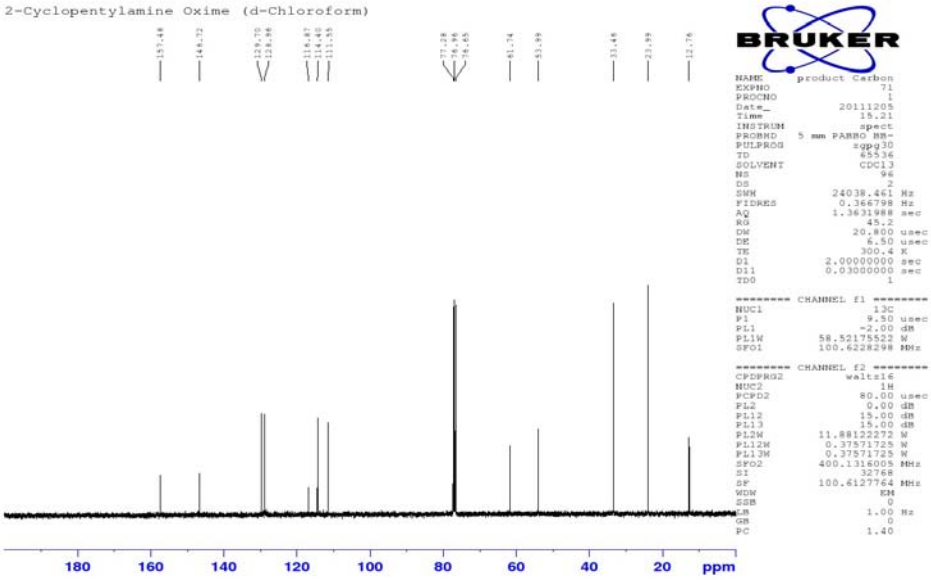
4. Isaacs, N. S. *Physical Organic Chemistry*, 2nd ed.; Longman Scientific & Technical: UK,, 1995..

11. ^{1}H NMR and ^{13}C NMR Spectra (COSY & NOSY for 3na-3Cl)

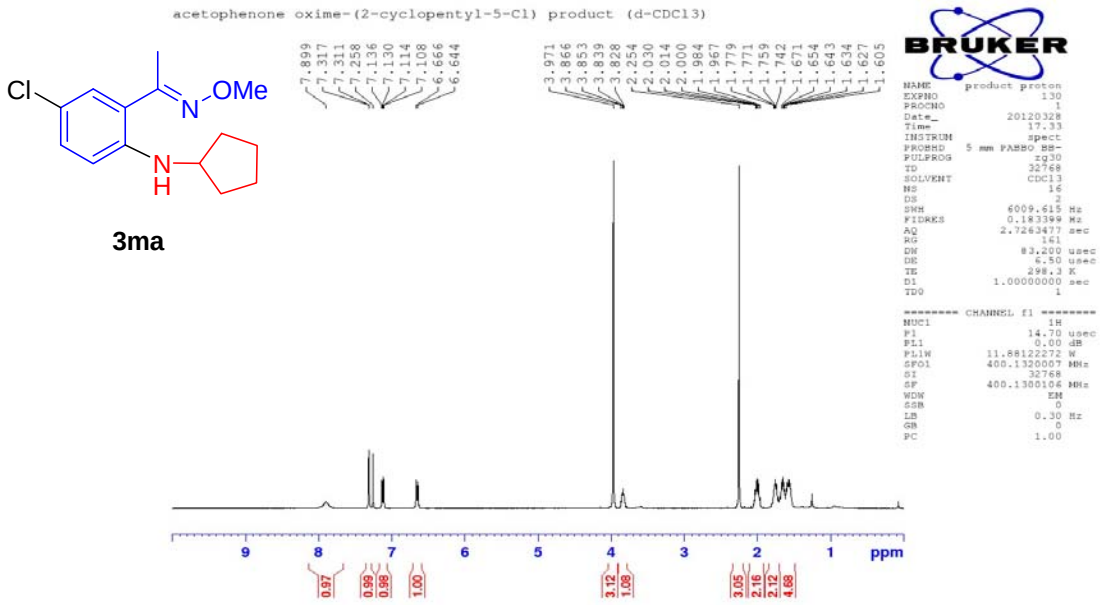
^{1}H NMR spectrum of **3aa**



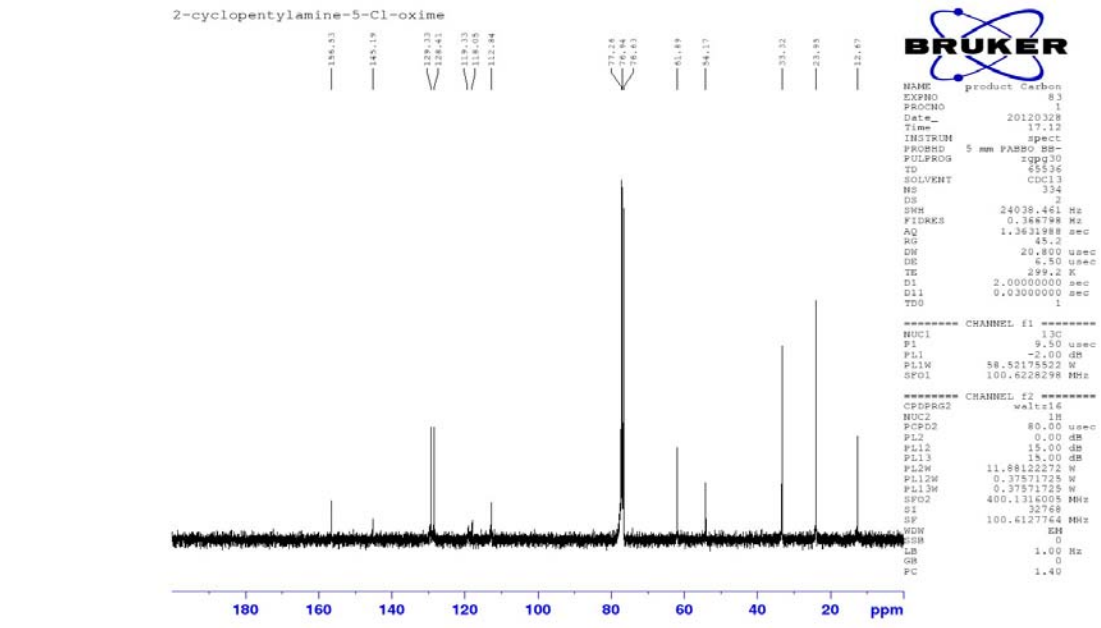
^{13}C NMR spectrum of **3aa**



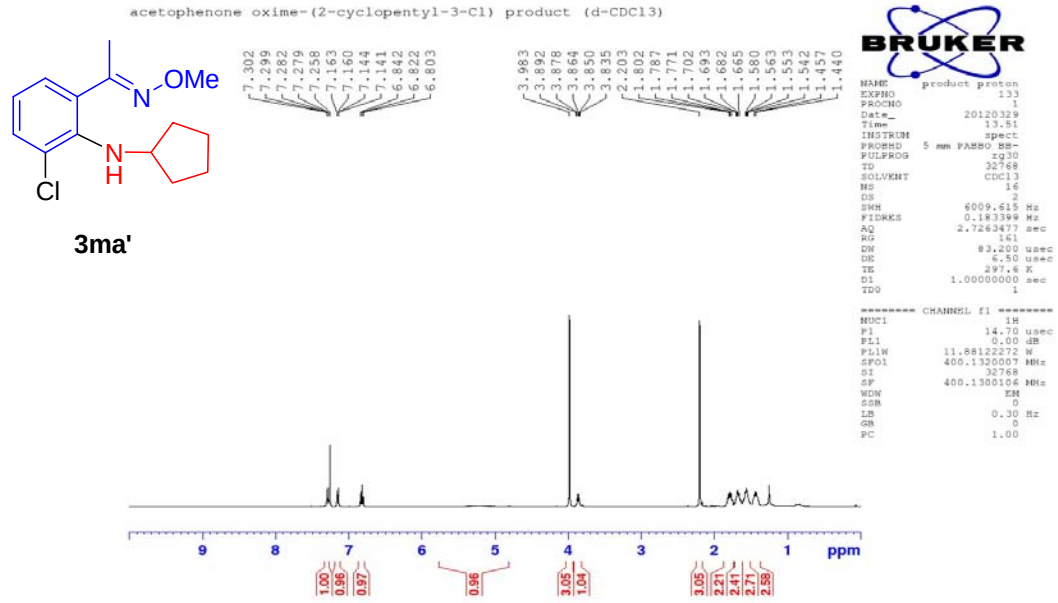
^{1}H NMR spectrum of **3ma**



^{13}C NMR spectrum of **3ma**

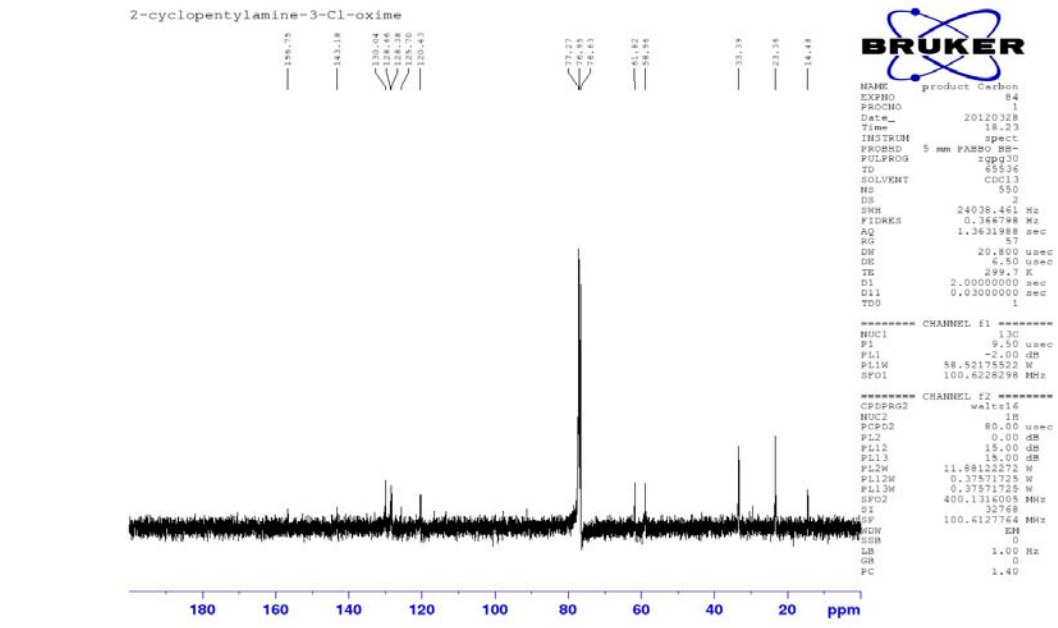


^{1}H NMR spectrum of **3ma'**

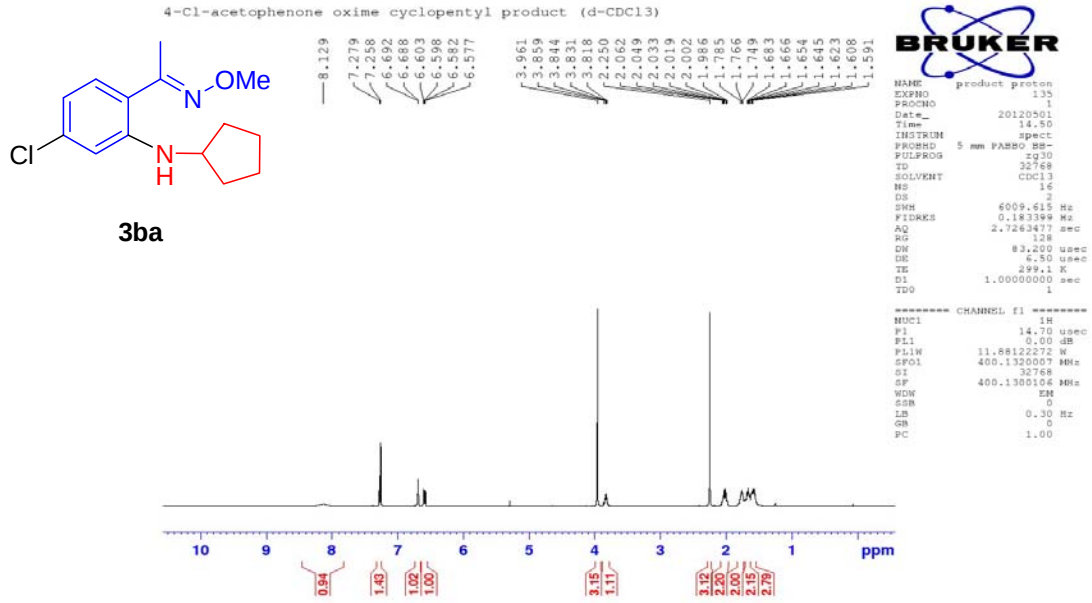


3ma'

^{13}C NMR spectrum of **3ma'**

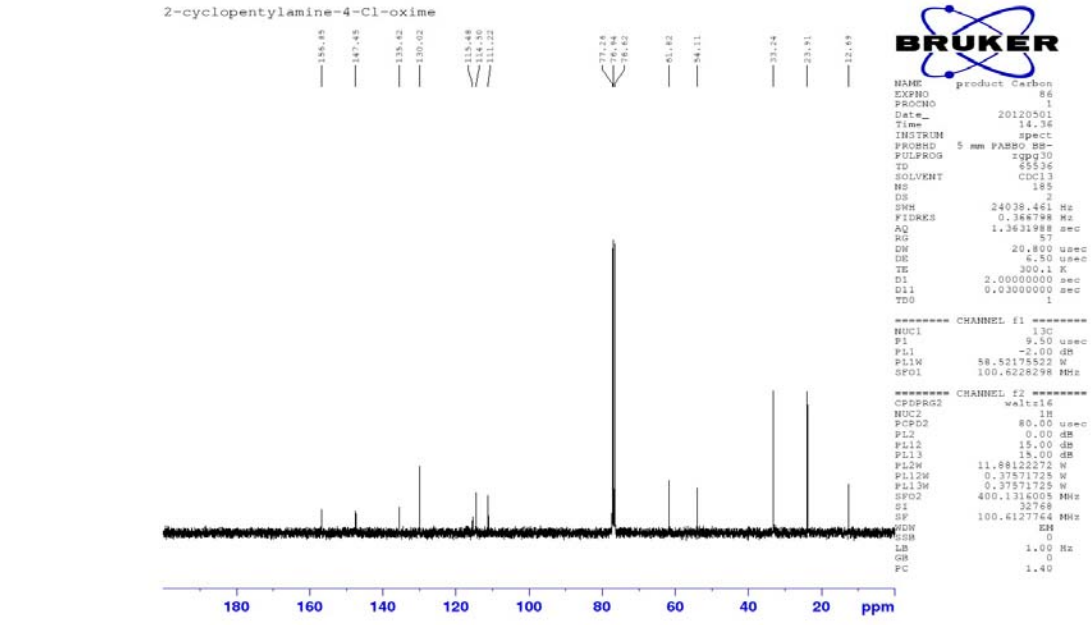


^{1}H NMR Spectrum of **3ba**

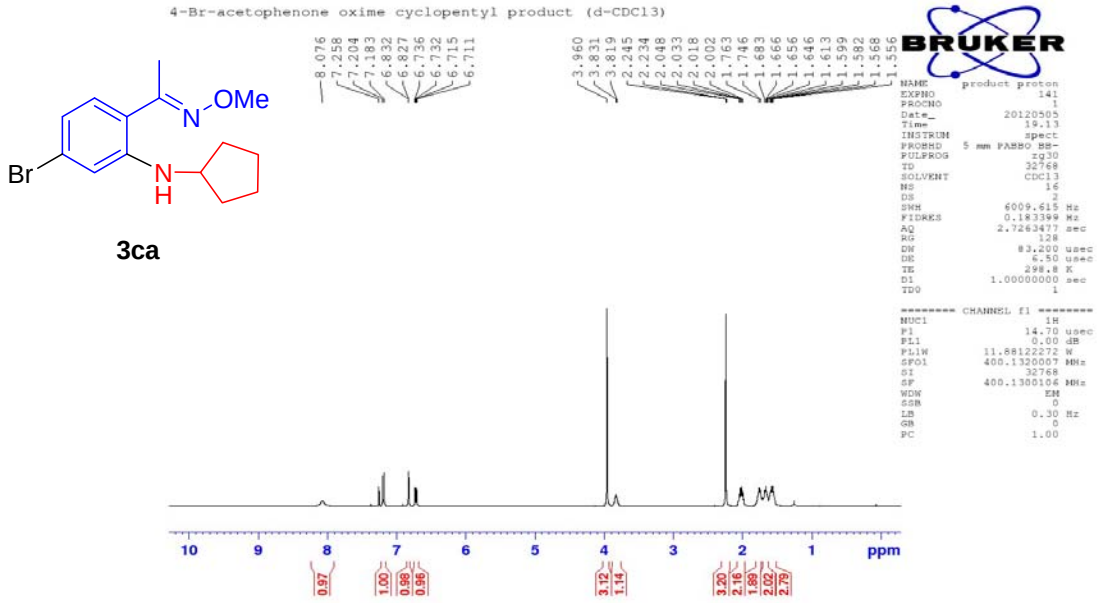


3ba

^{13}C spectrum of **3ba**

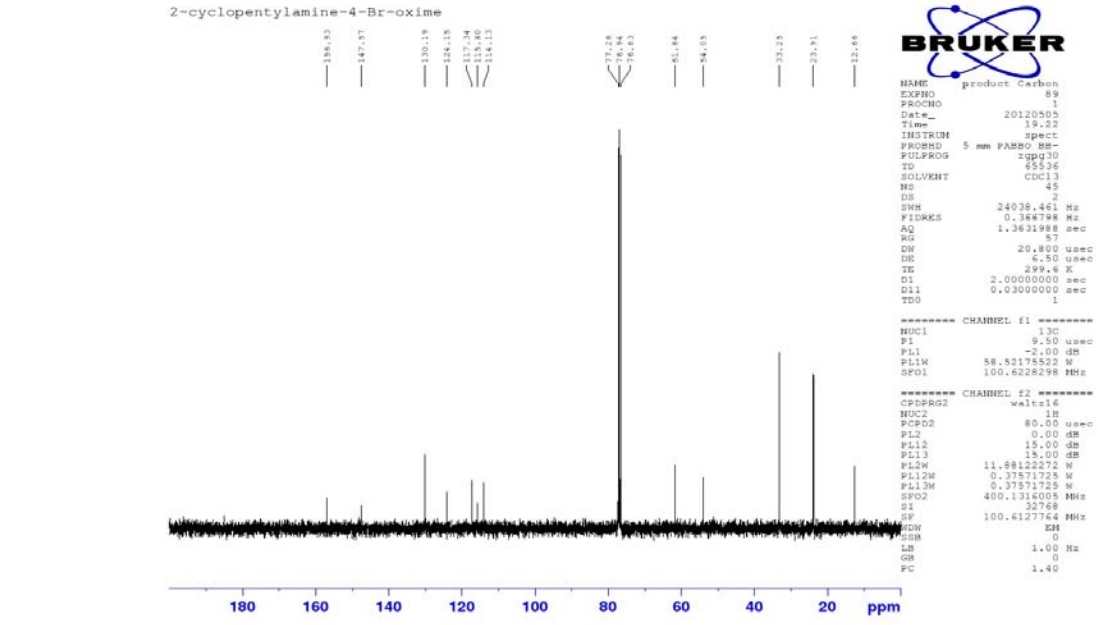


^{1}H NMR spectrum of **3ca**

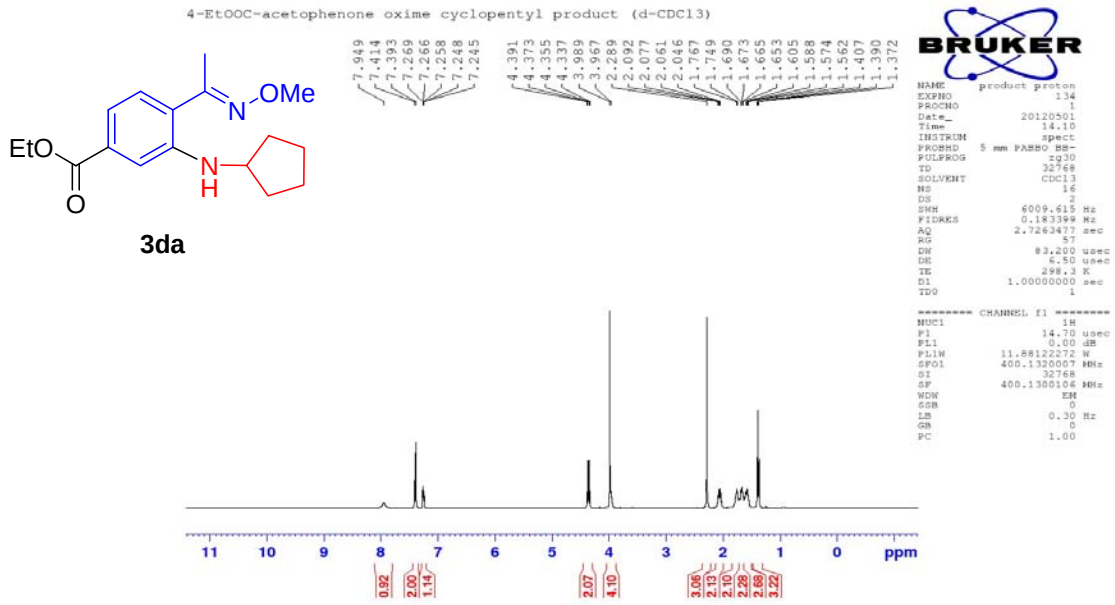


3ca

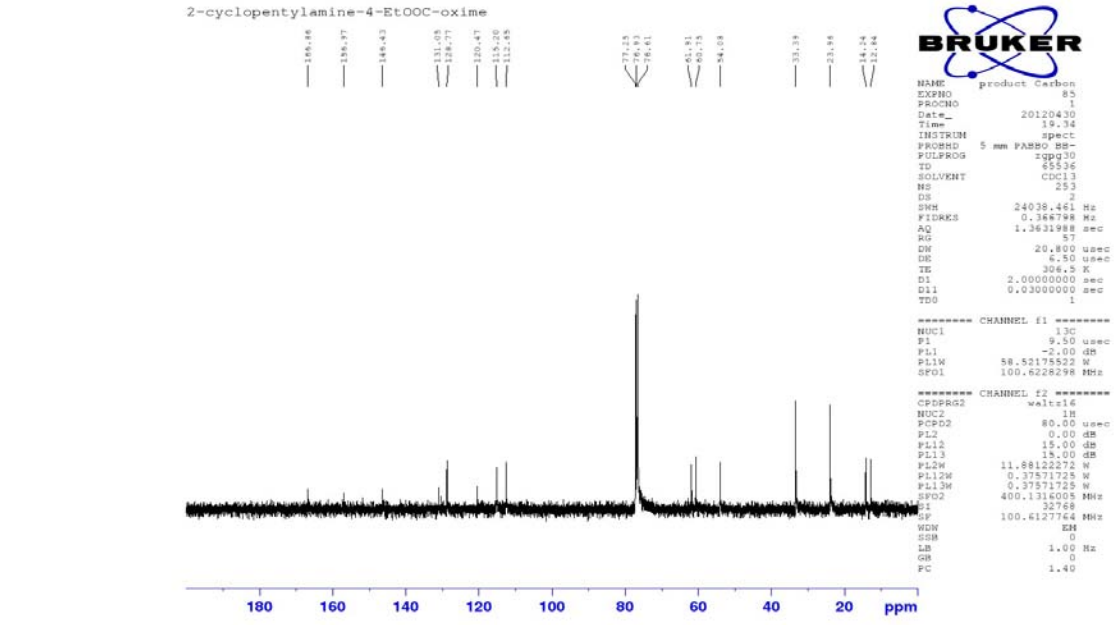
^{13}C NMR spectrum of **3ca**



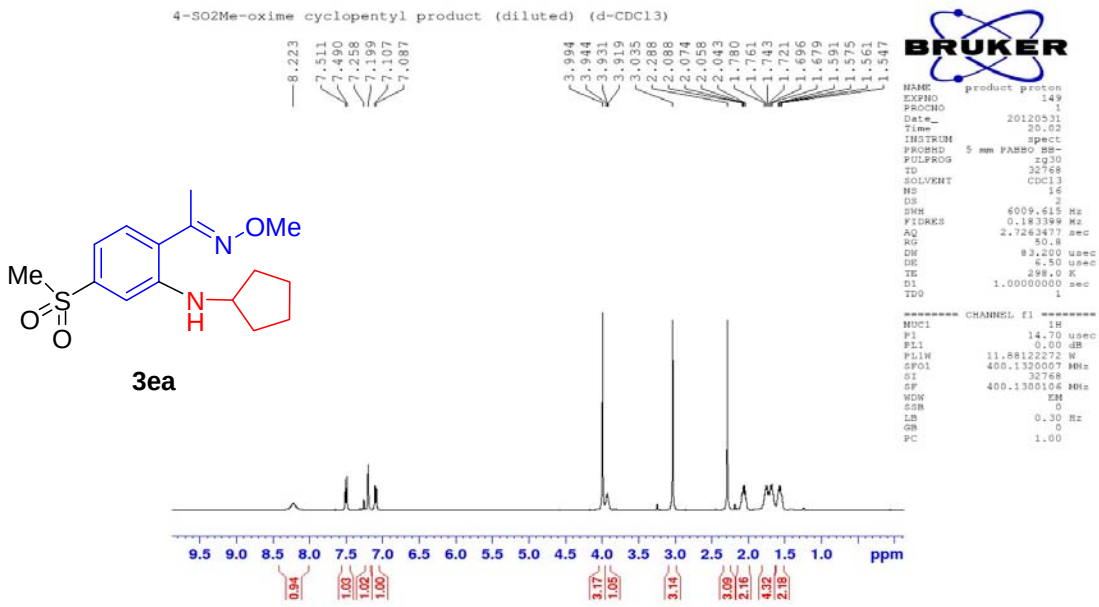
^{1}H NMR spectrum of **3da**



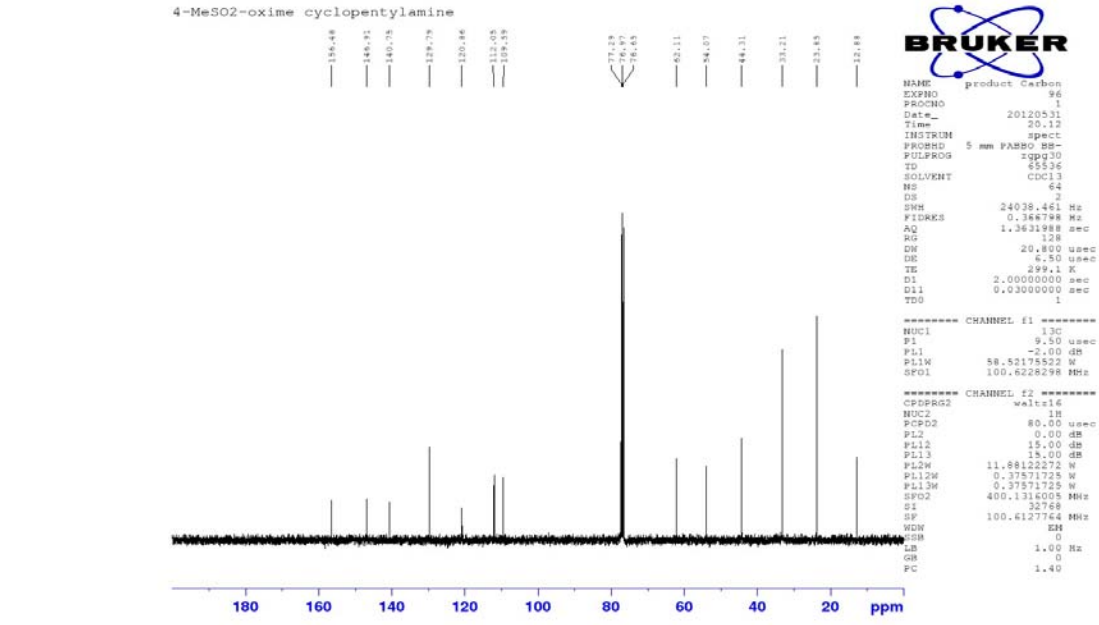
^{13}C NMR spectrum of **3da**



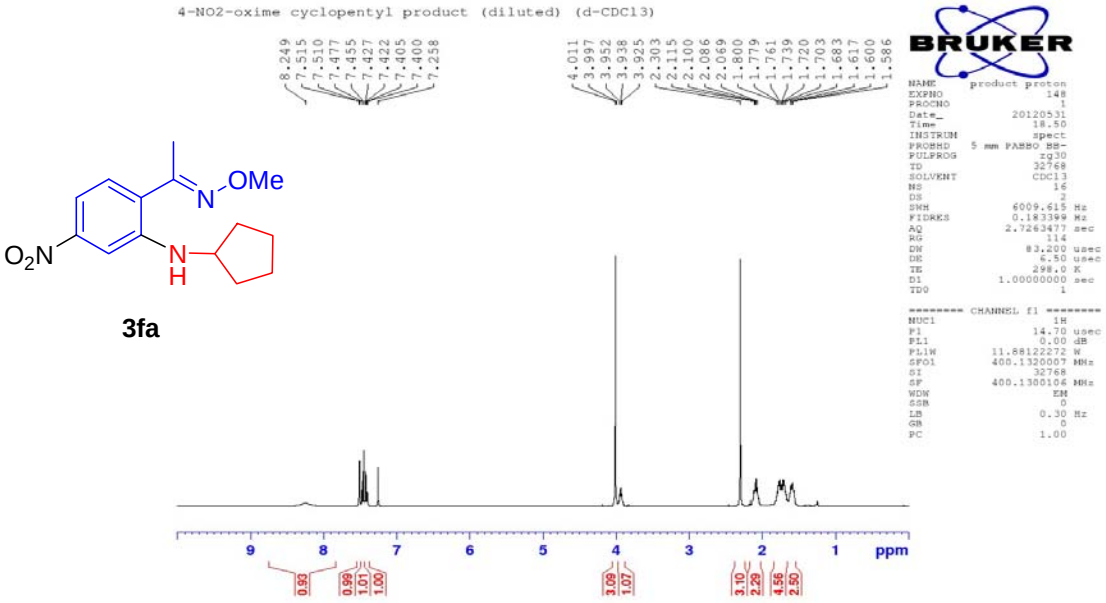
^{1}H NMR spectrum of **3ea**



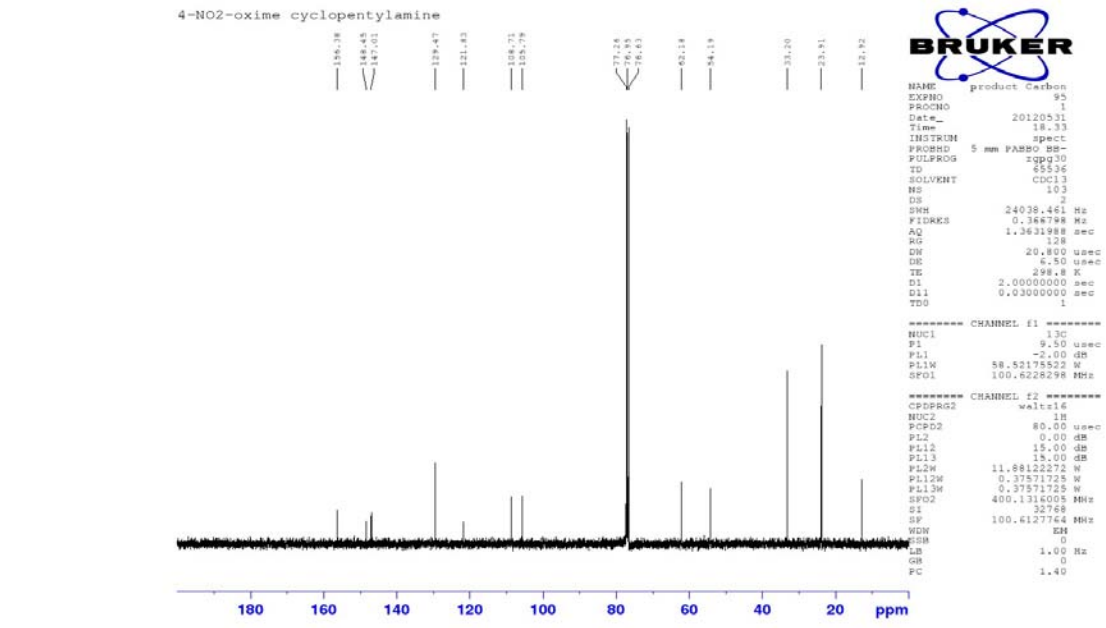
^{13}C NMR spectrum of **3ea**



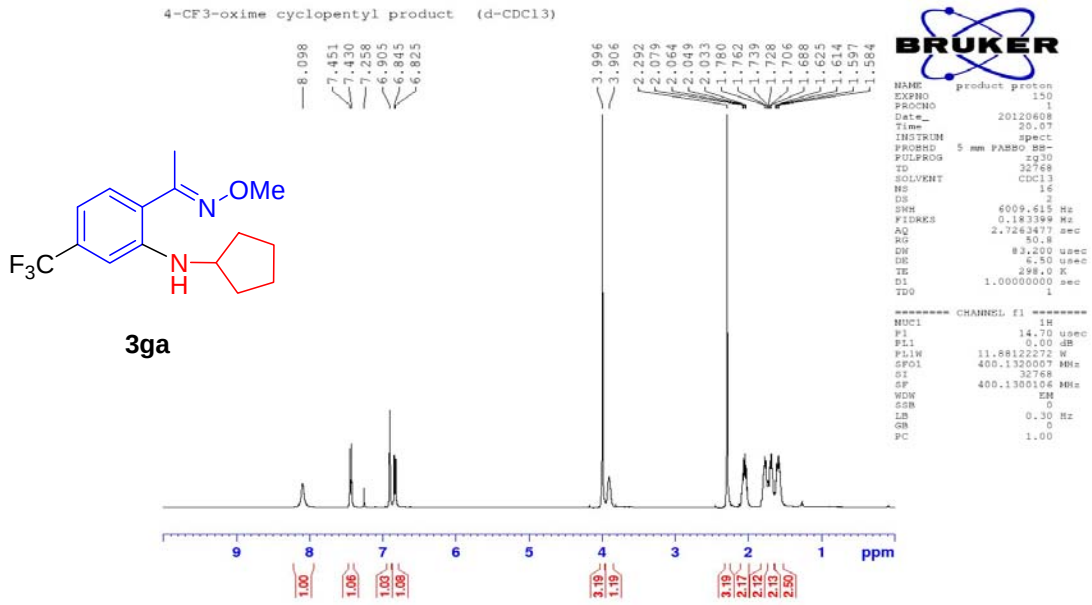
^{1}H NMR spectrum of **3fa**



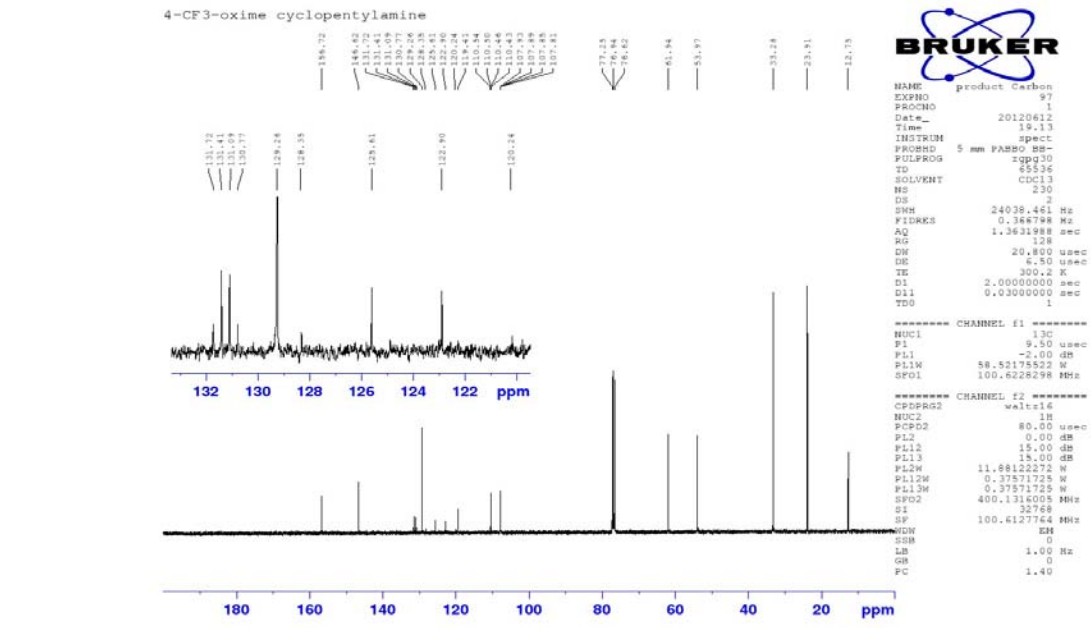
^{13}C NMR spectrum of **3fa**



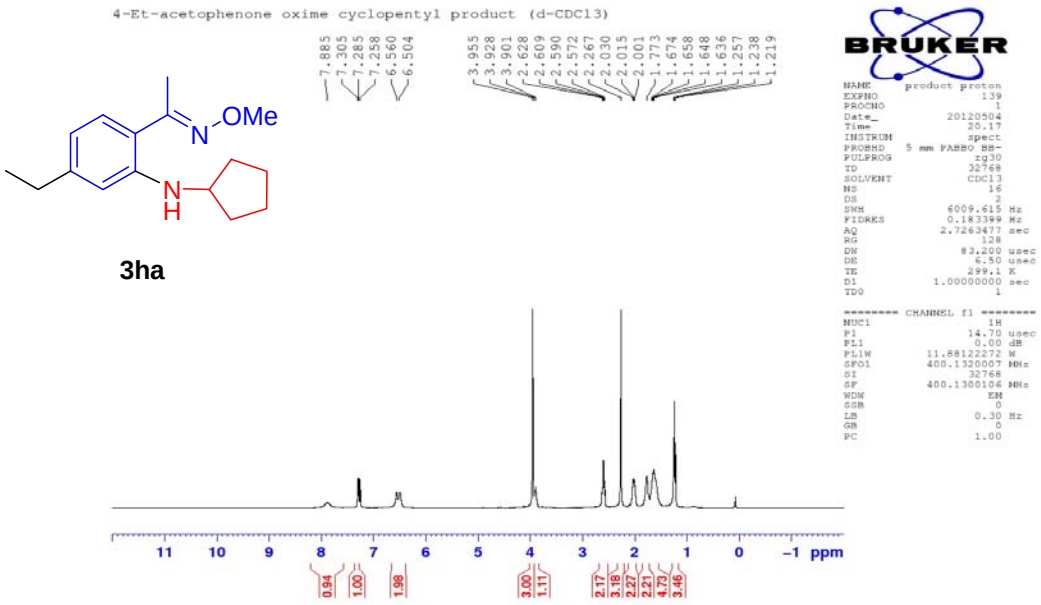
^{1}H NMR spectrum of **3ga**



^{13}C NMR spectrum of **3ga**

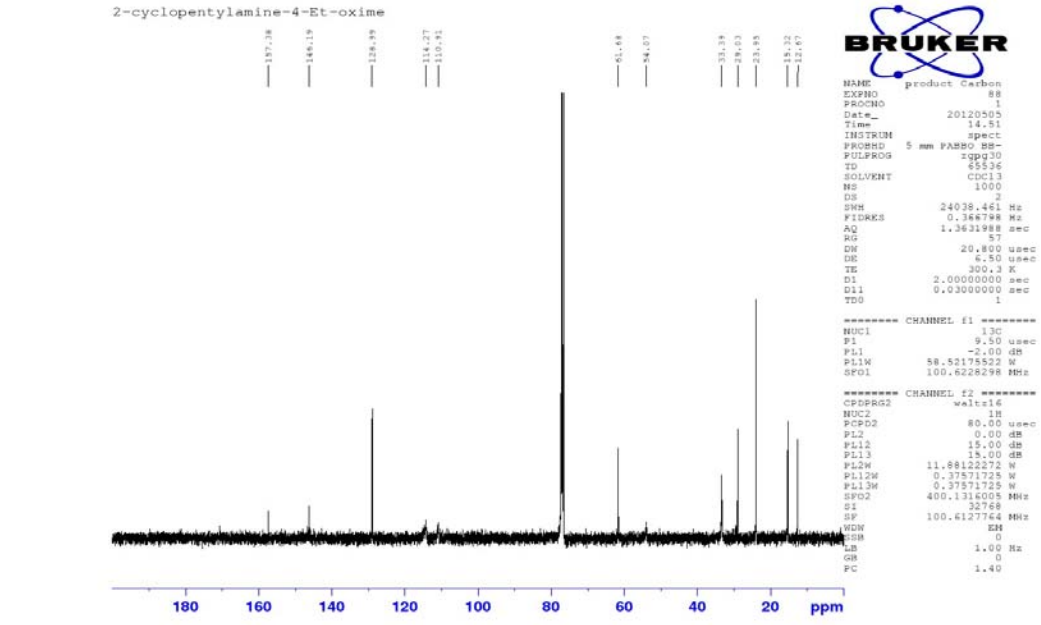


^{1}H NMR spectrum of **3ha**

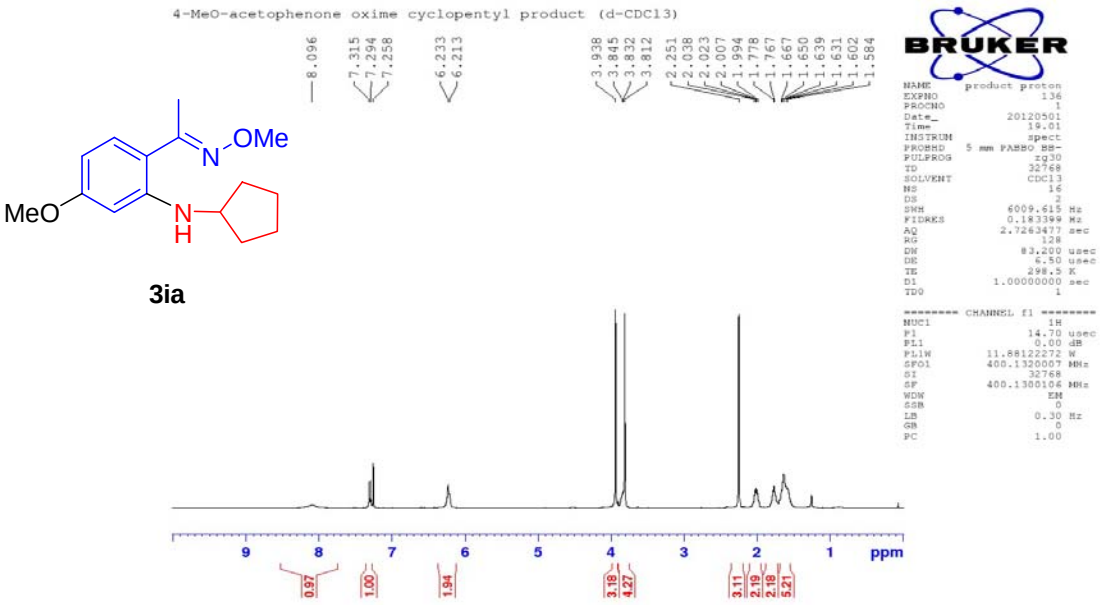


3ha

^{13}C NMR spectrum of **3ha**

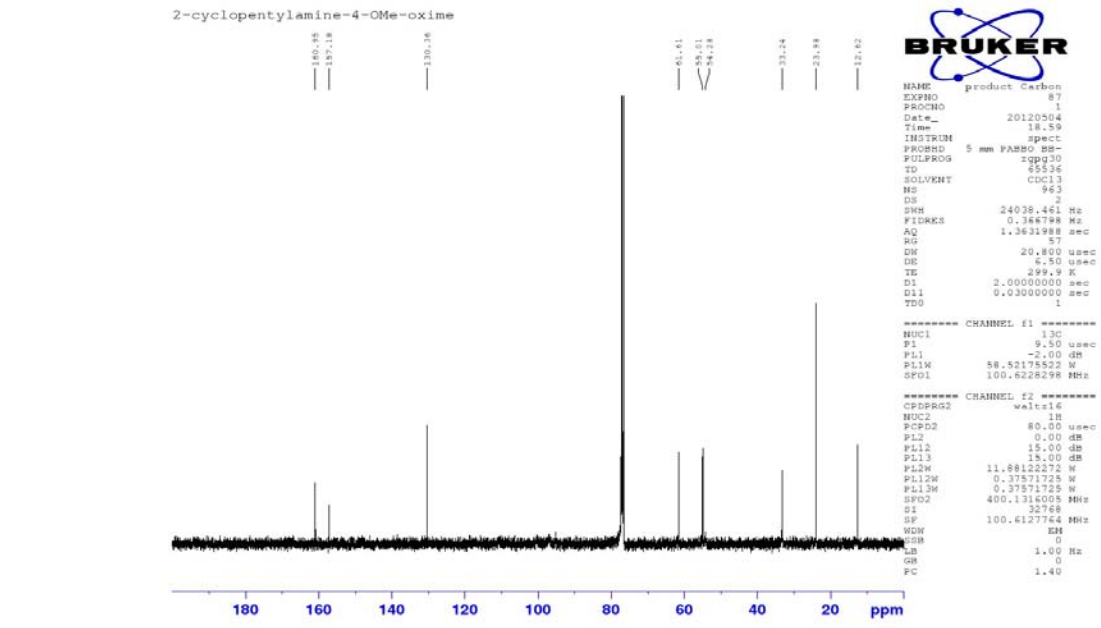


^{1}H NMR spectrum of **3ia**

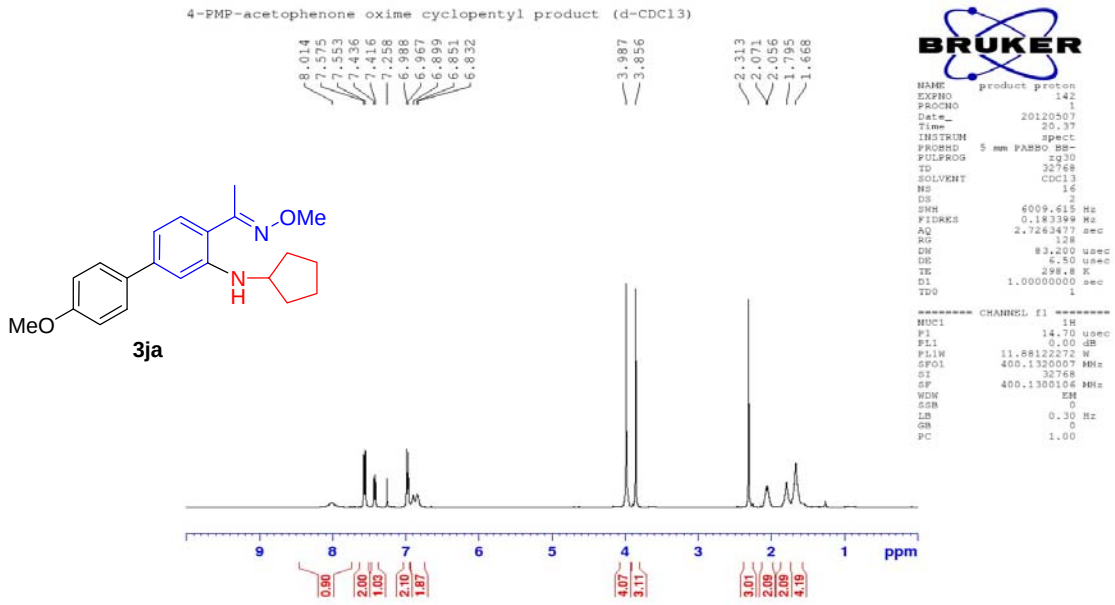


3ia

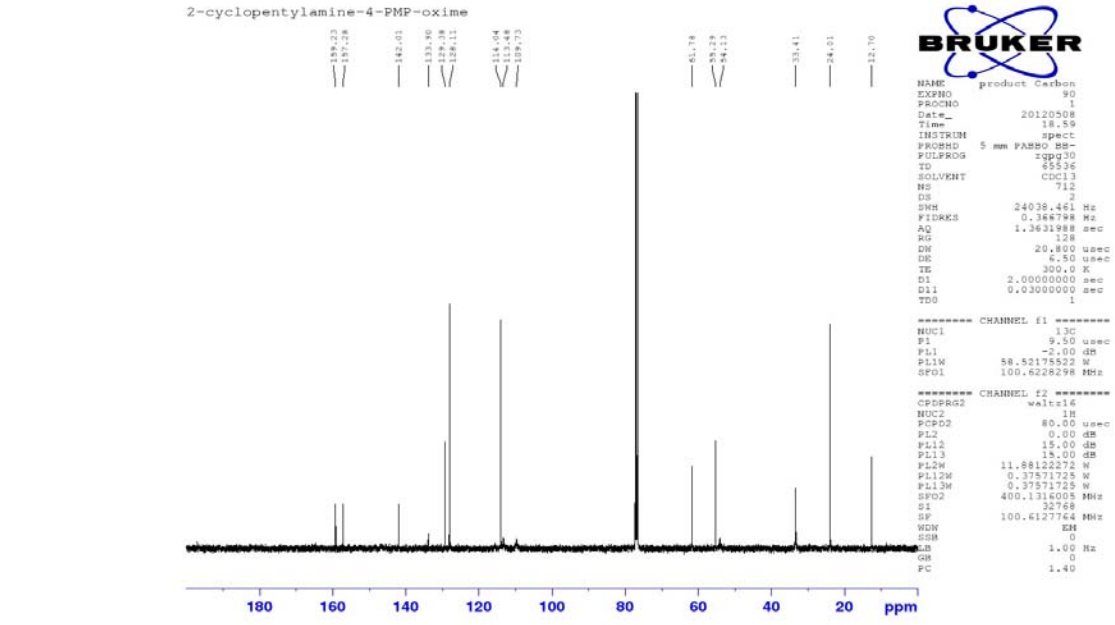
^{13}C NMR spectrum of **3ia**



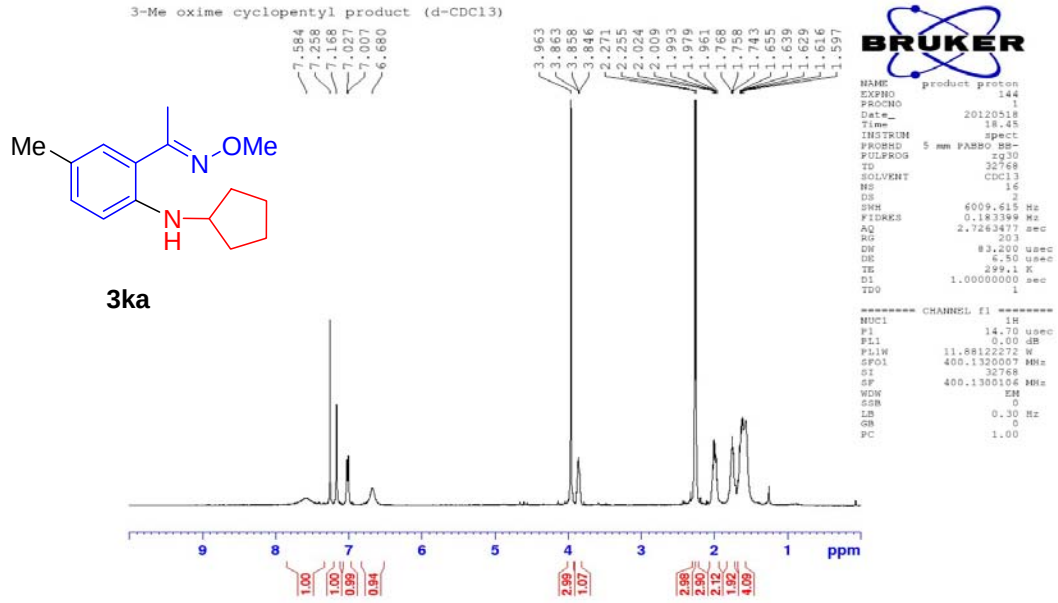
^{1}H NMR spectrum of **3ja**



^{13}C NMR spectrum of **3ja**

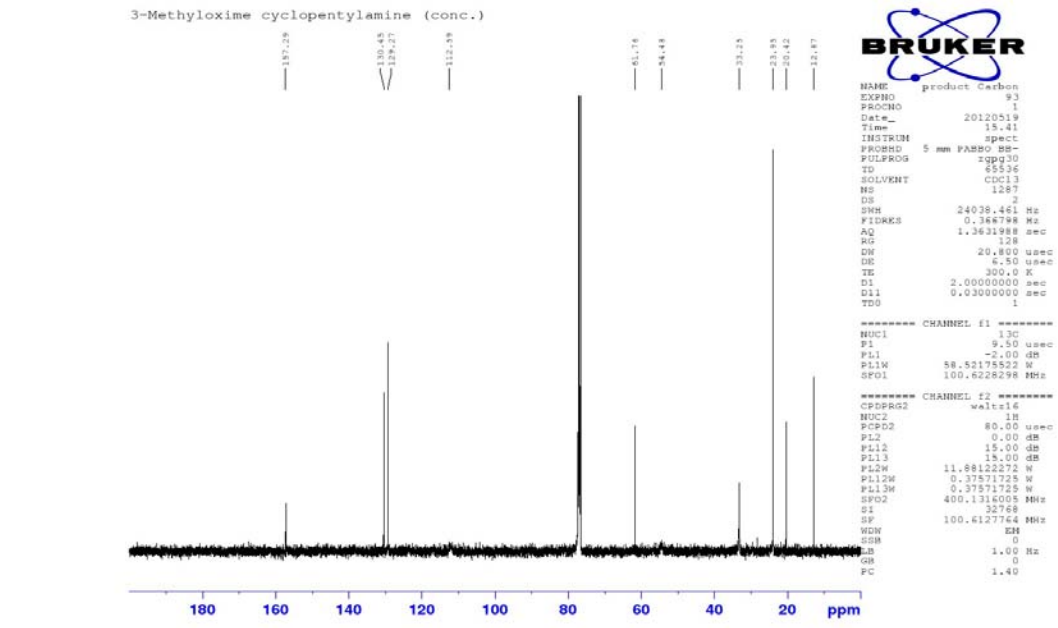


^{1}H NMR spectrum of **3ka**

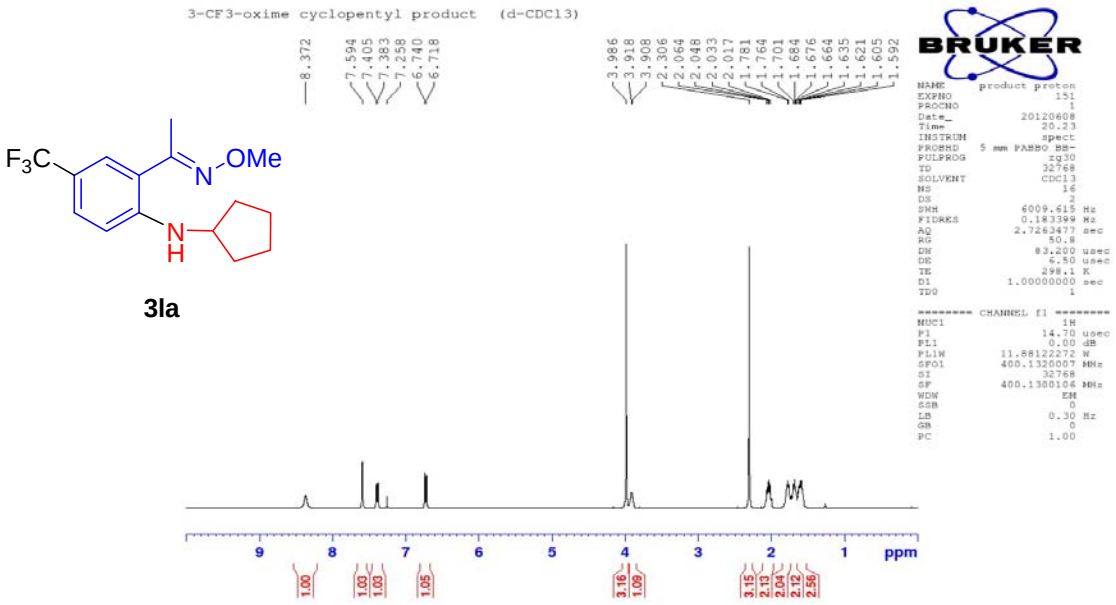


3ka

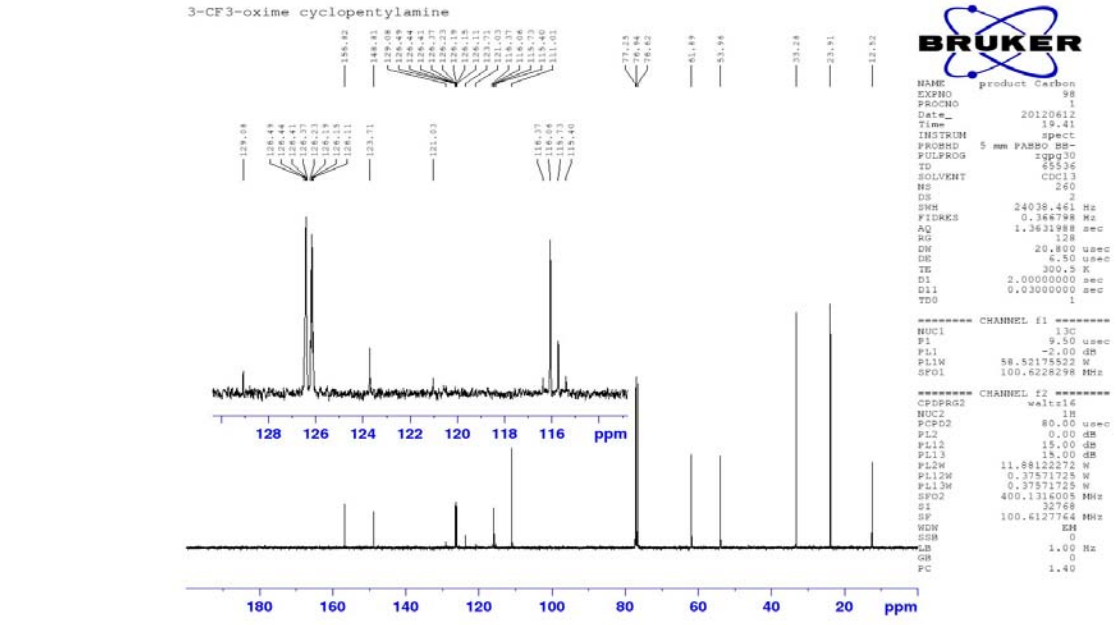
^{13}C NMR spectrum of **3ka**



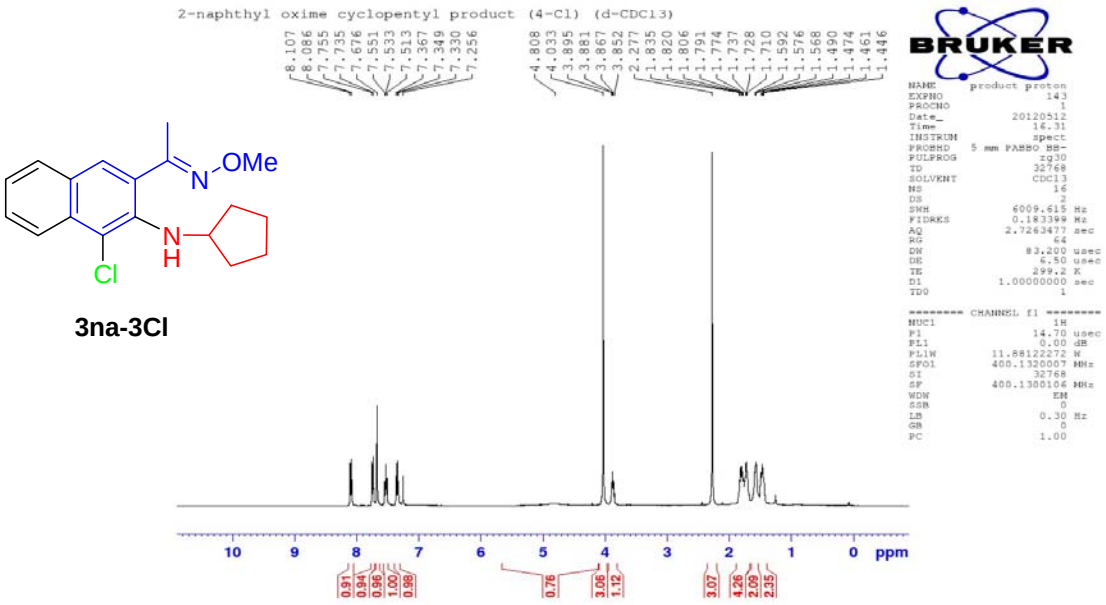
^{1}H NMR spectrum of **3la**



^{13}C NMR spectrum of **3la**

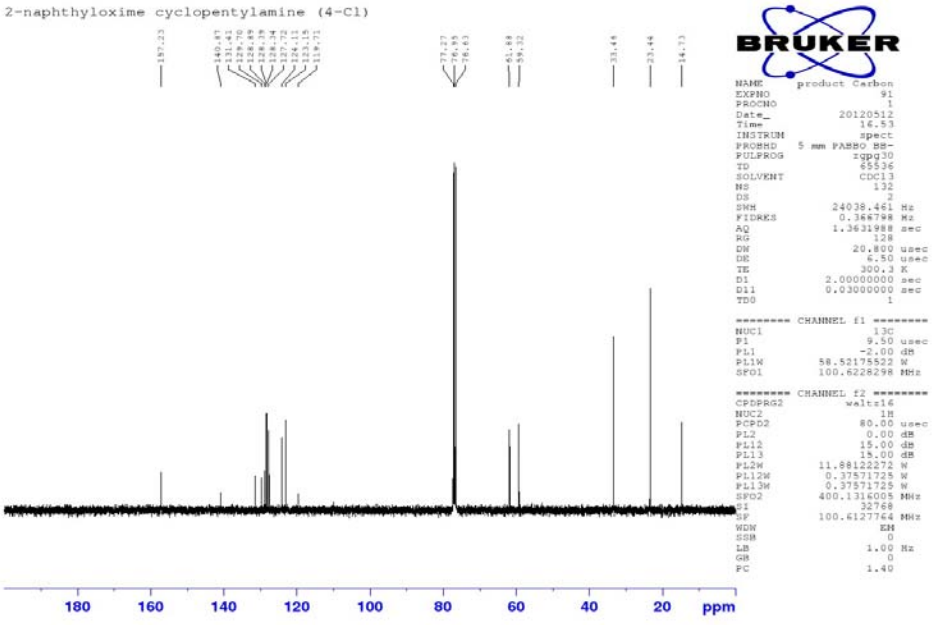


^{1}H NMR spectrum of **3na-3Cl**

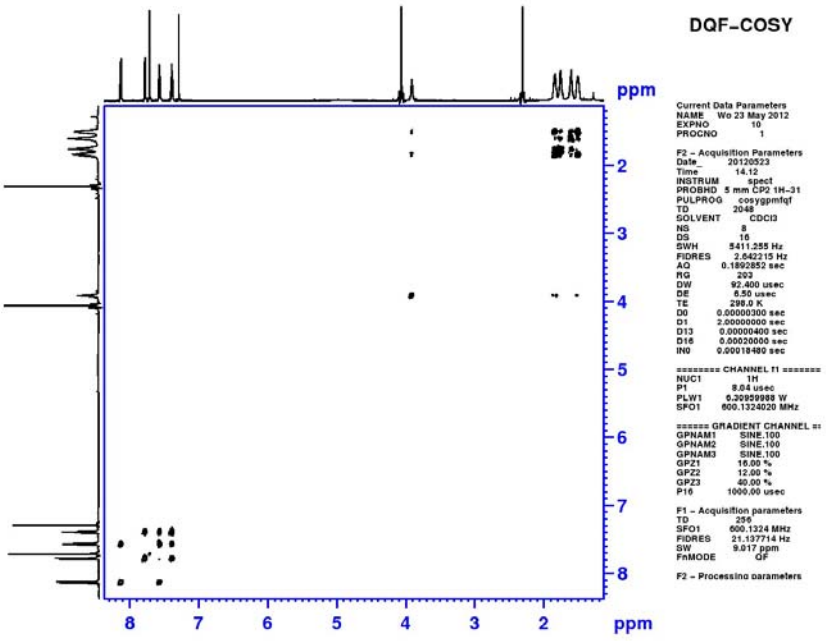


3na-3Cl

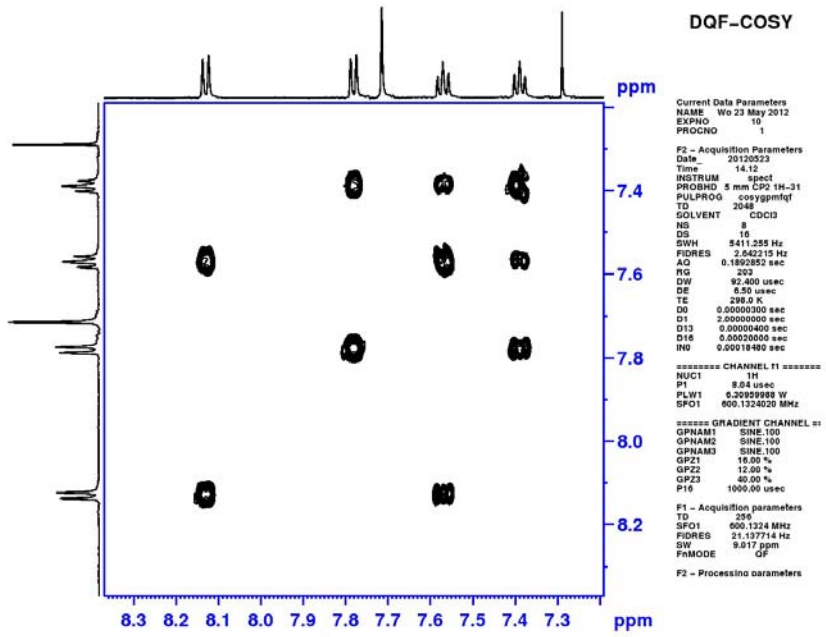
^{13}C NMR spectrum of **3na-3Cl**



COSY NMR spectra of **3na-3Cl**

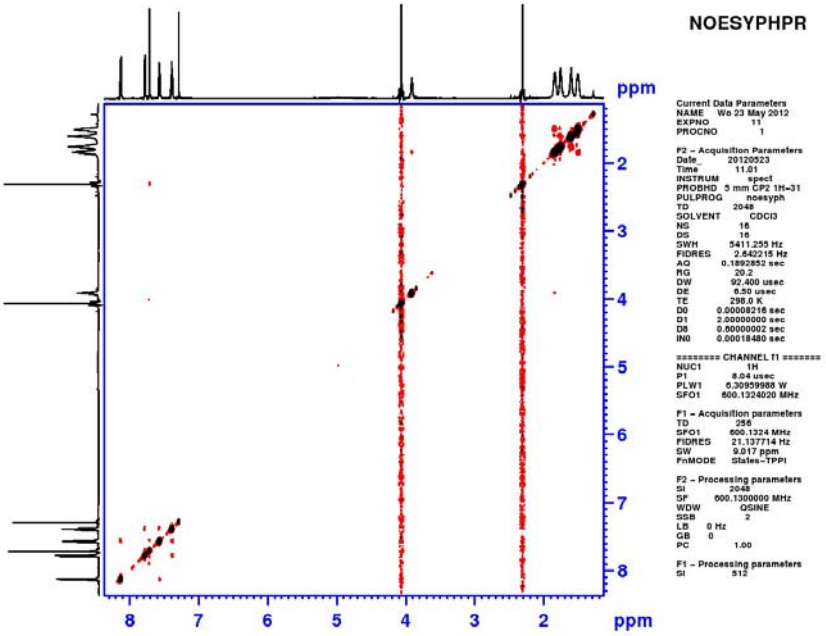


(Original)

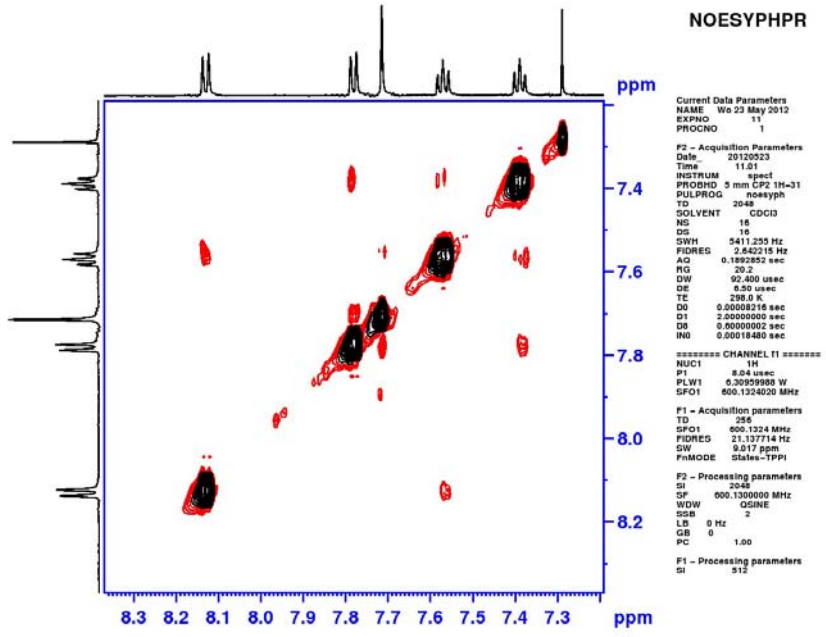


(Magnified at 8.4-7.2 ppm)

NOSY NMR spectrum of **3na-3Cl**

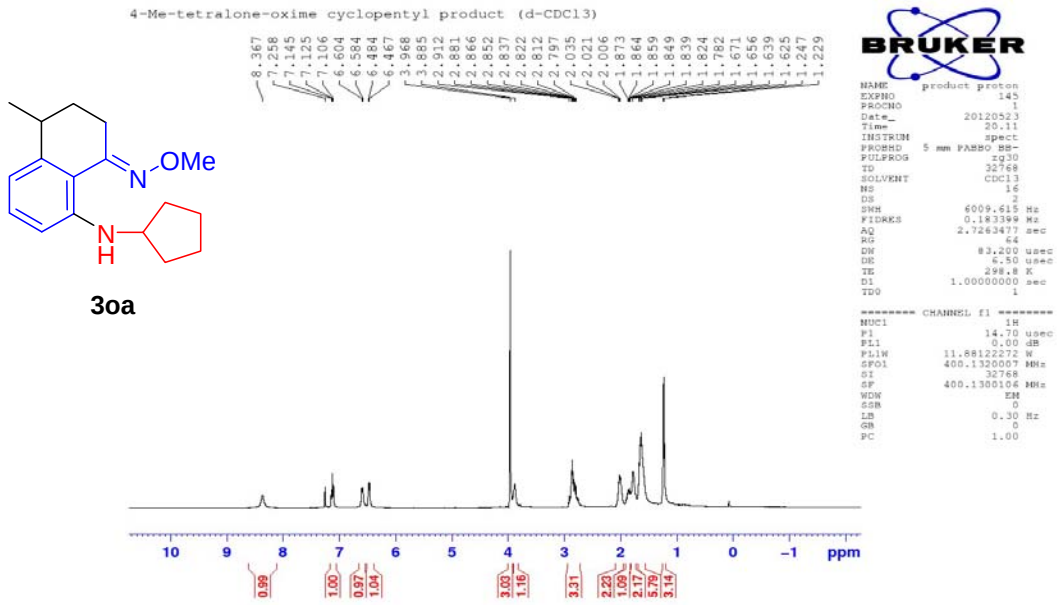


(Original)



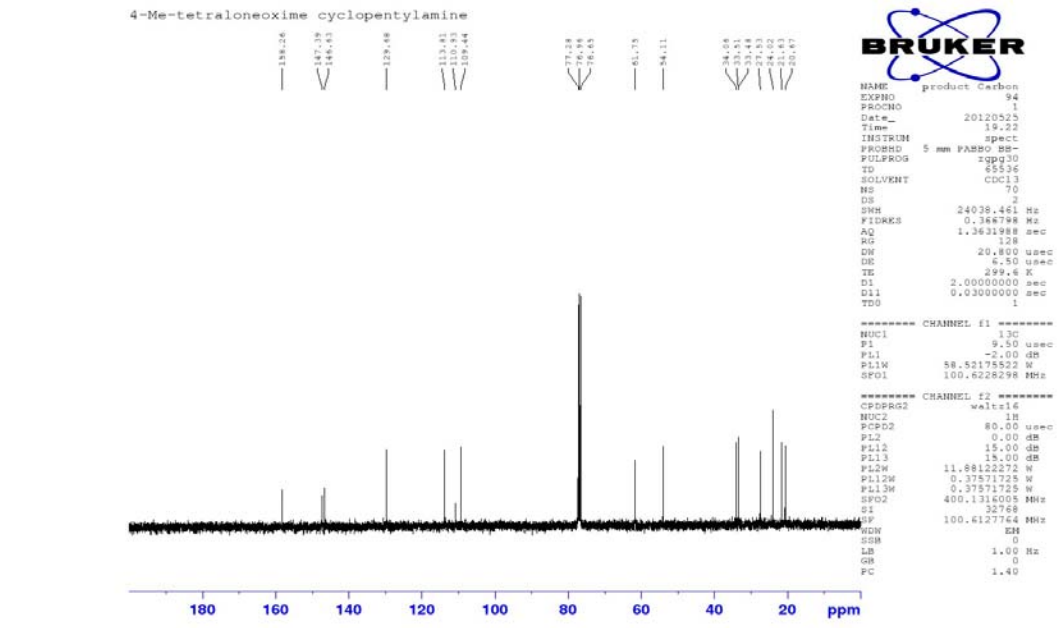
(Magnified at 8.4-7.2 ppm)

^{1}H NMR spectrum of **3oa**

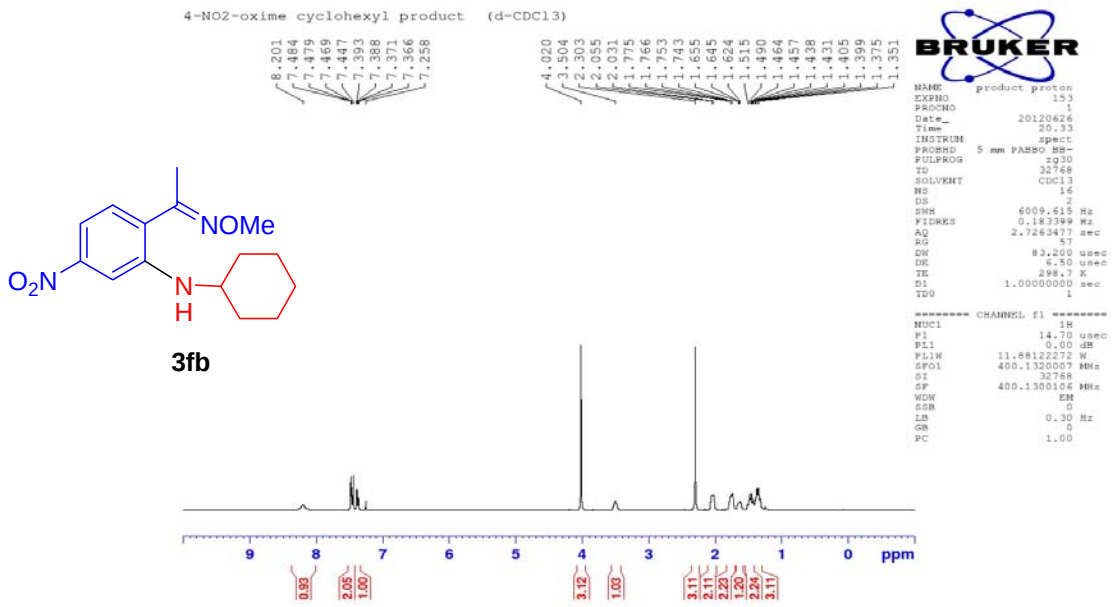


3oa

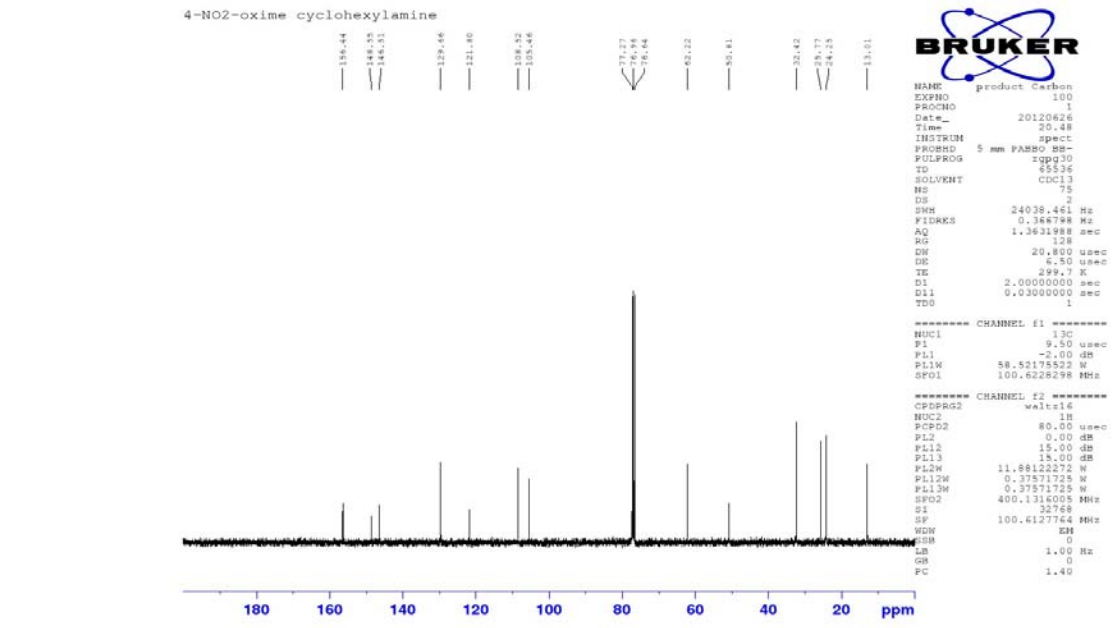
^{13}C NMR spectrum of **3oa**



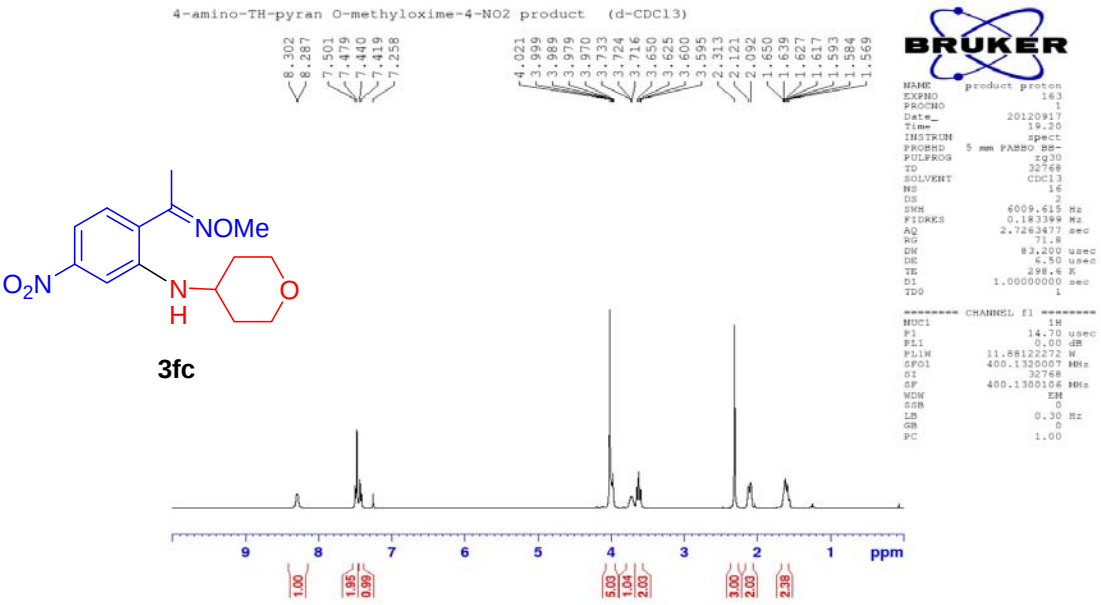
^{1}H NMR spectrum of **3fb**



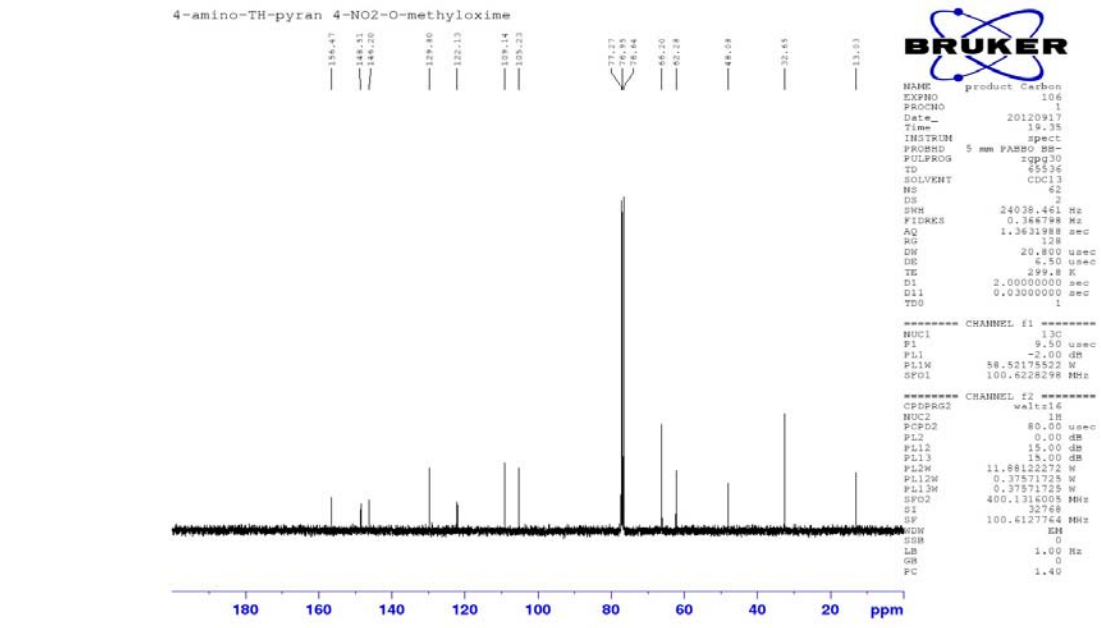
^{13}C NMR spectrum of **3fb**



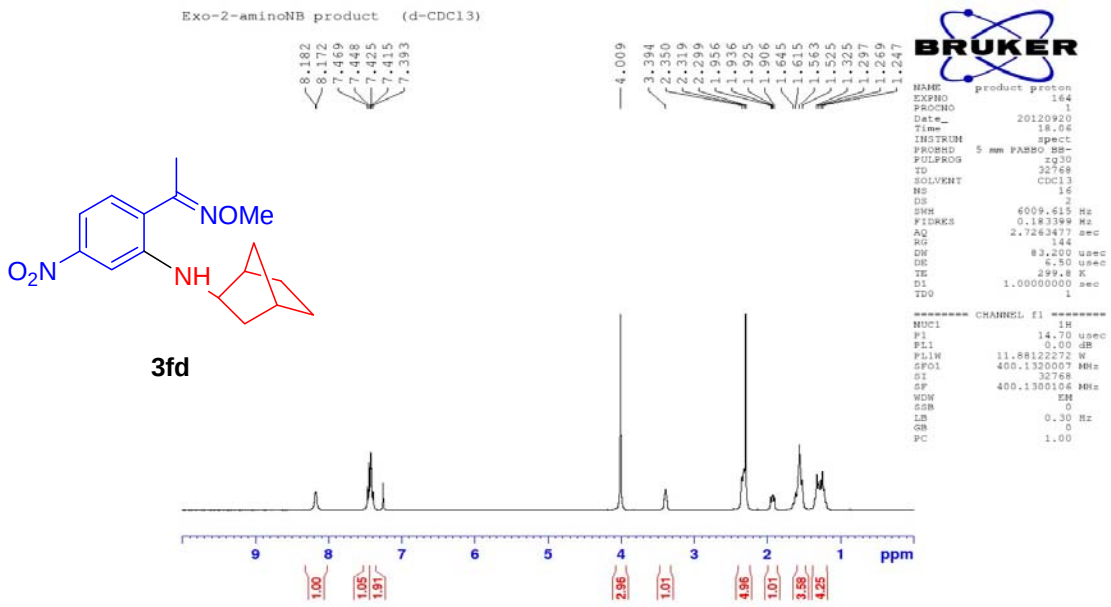
^{1}H NMR spectrum of **3fc**



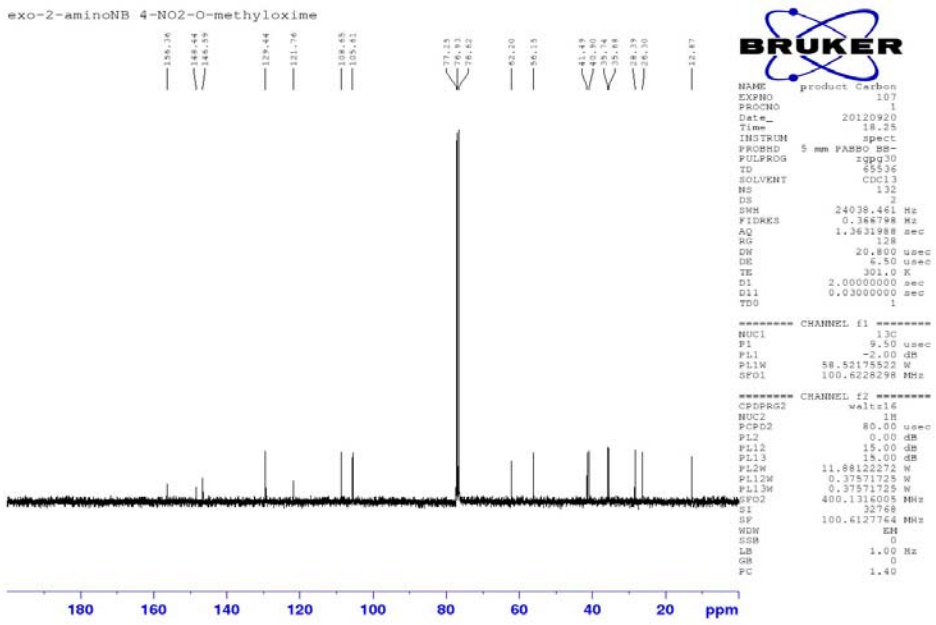
^{13}C NMR spectrum of **3fc**



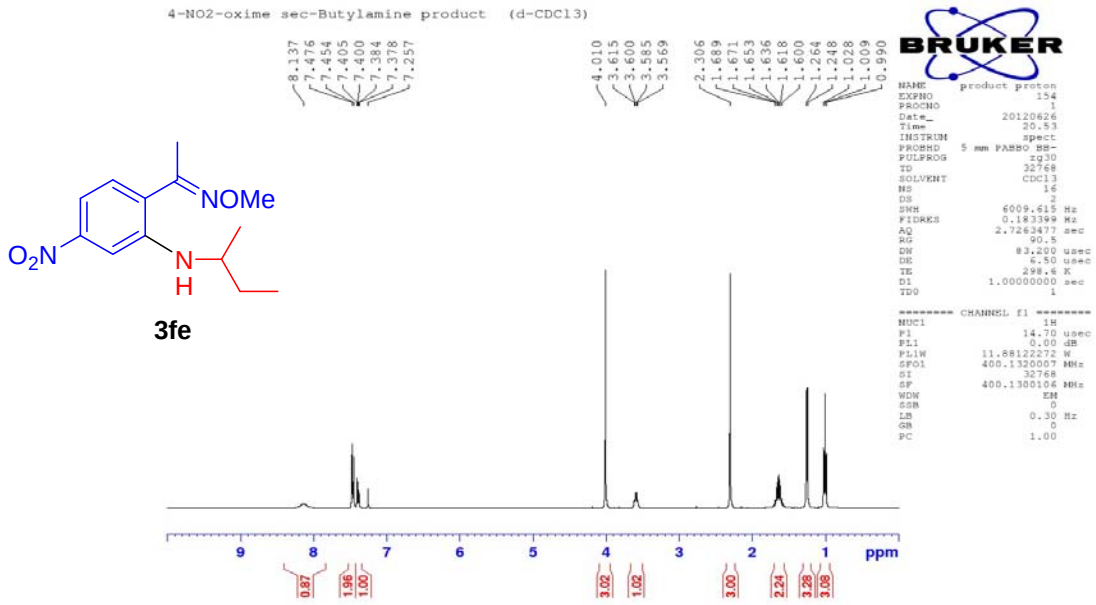
^{1}H NMR spectrum of **3fd**



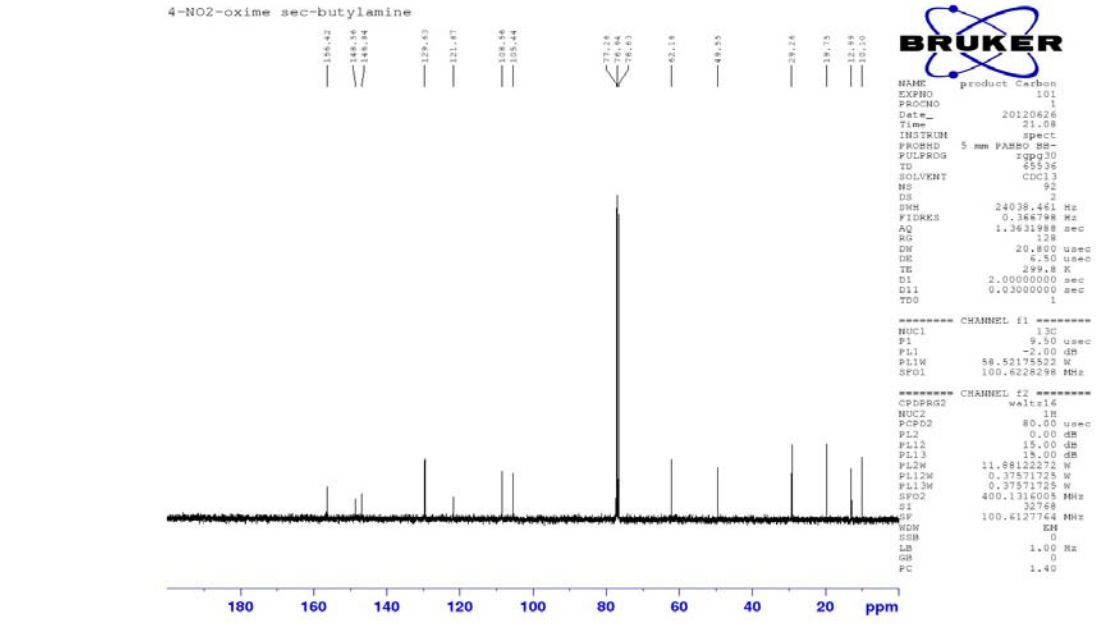
^{13}C NMR spectrum of **3fd**



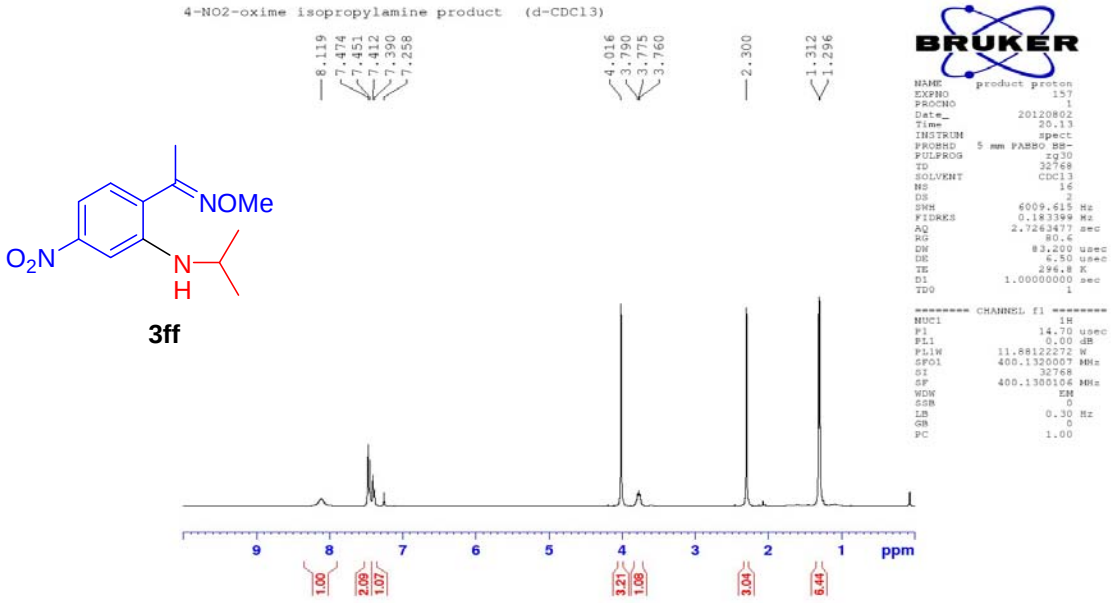
^{1}H NMR spectrum of **3fe**



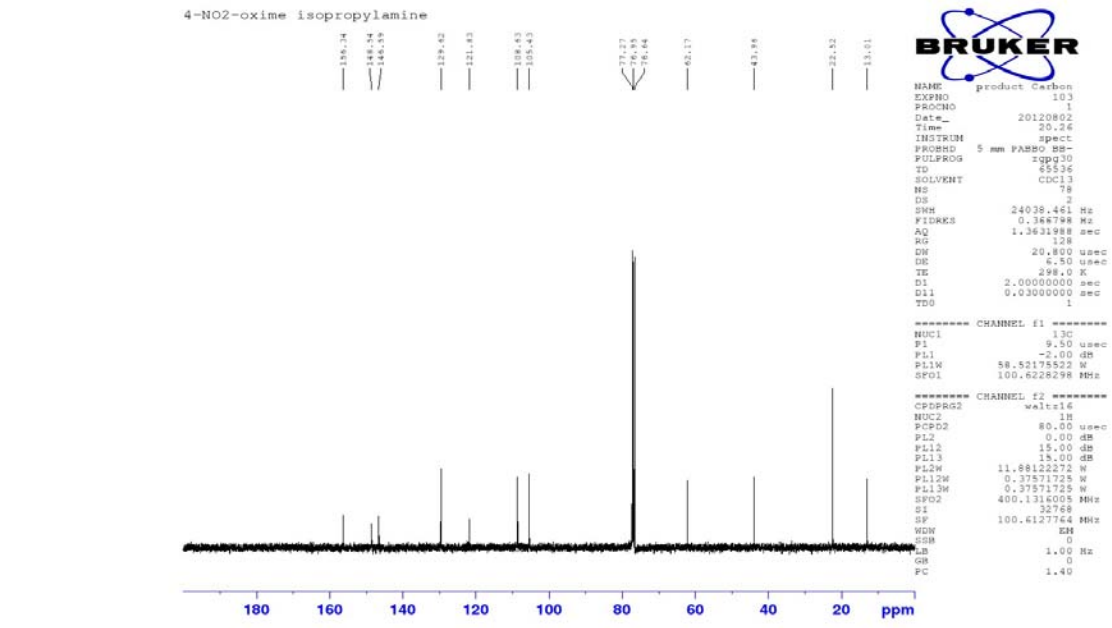
^{13}C NMR spectrum of **3fe**



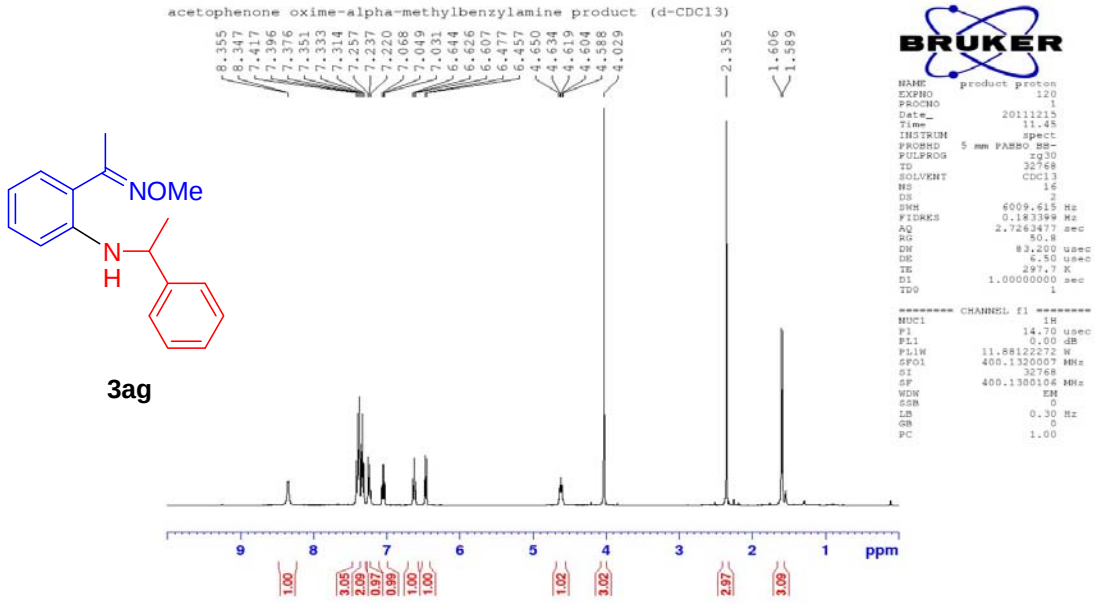
^{1}H NMR spectrum of **3ff**



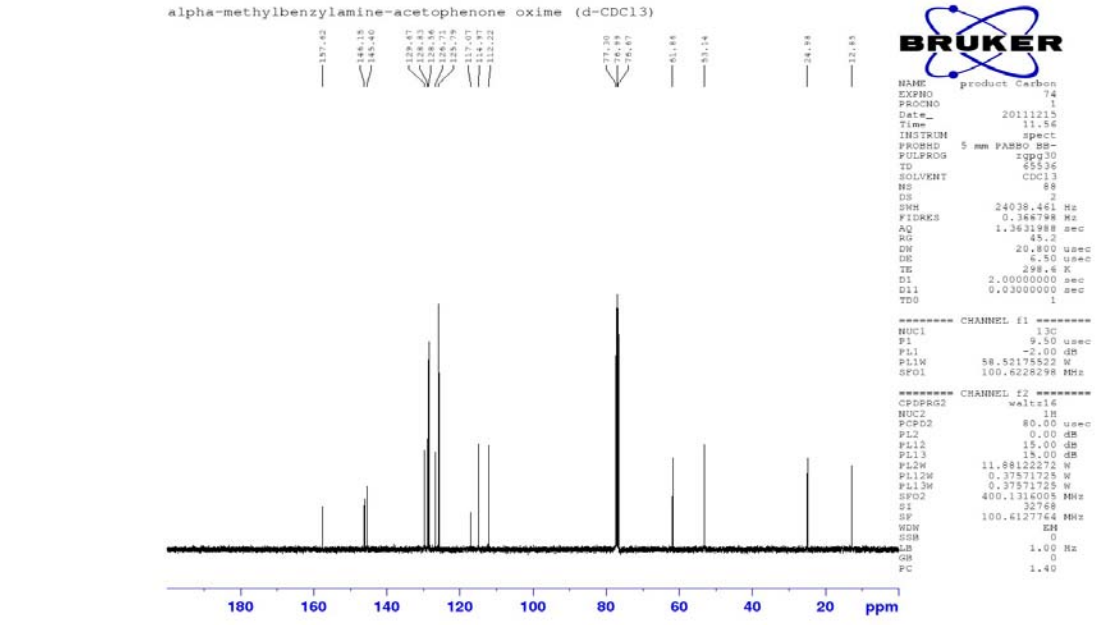
^{13}C NMR spectrum of **3ff**



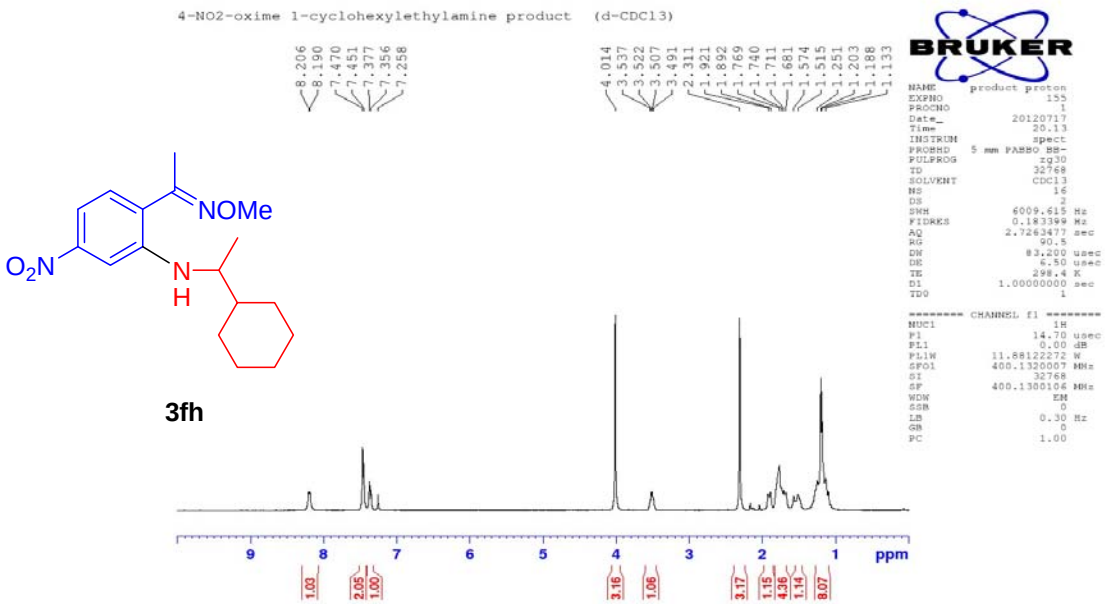
^{1}H NMR spectrum of **3ag**



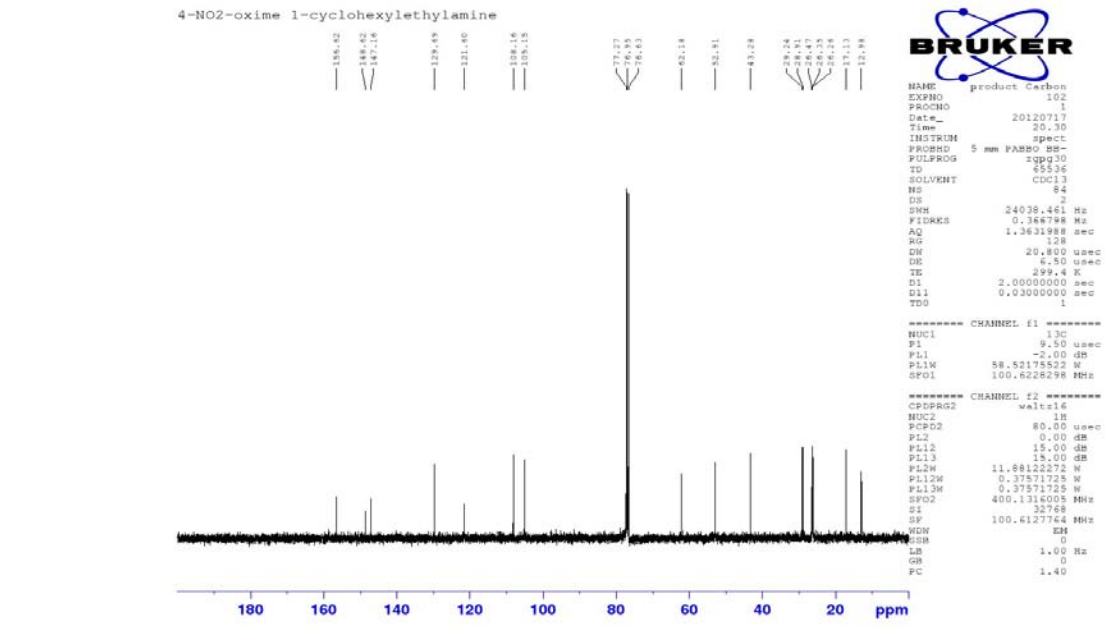
^{13}C NMR spectrum of **3ag**



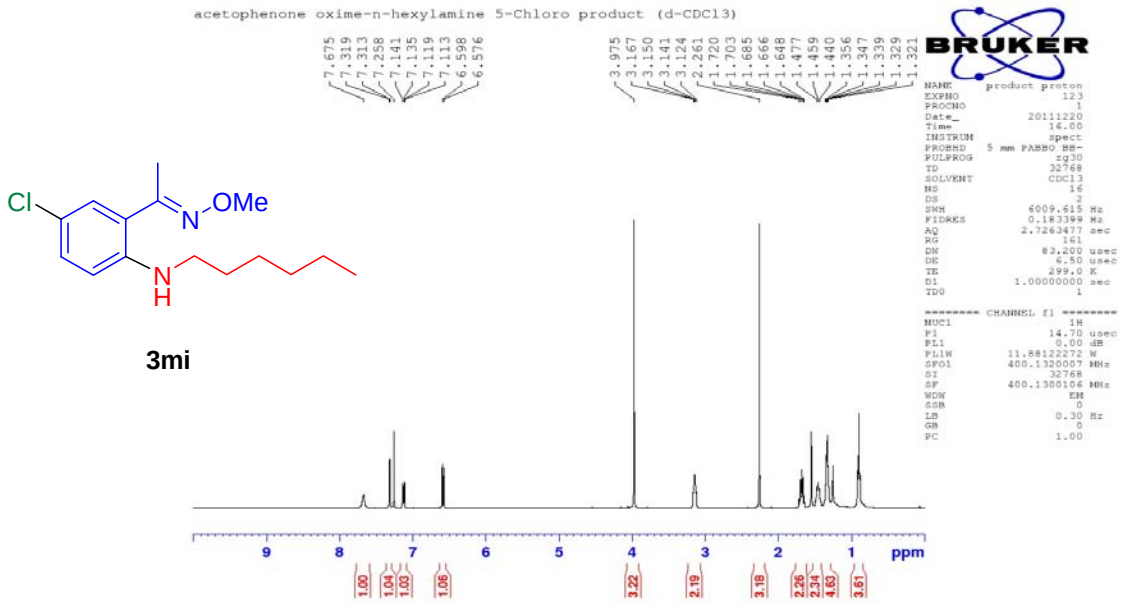
^{1}H NMR spectrum of **3fh**



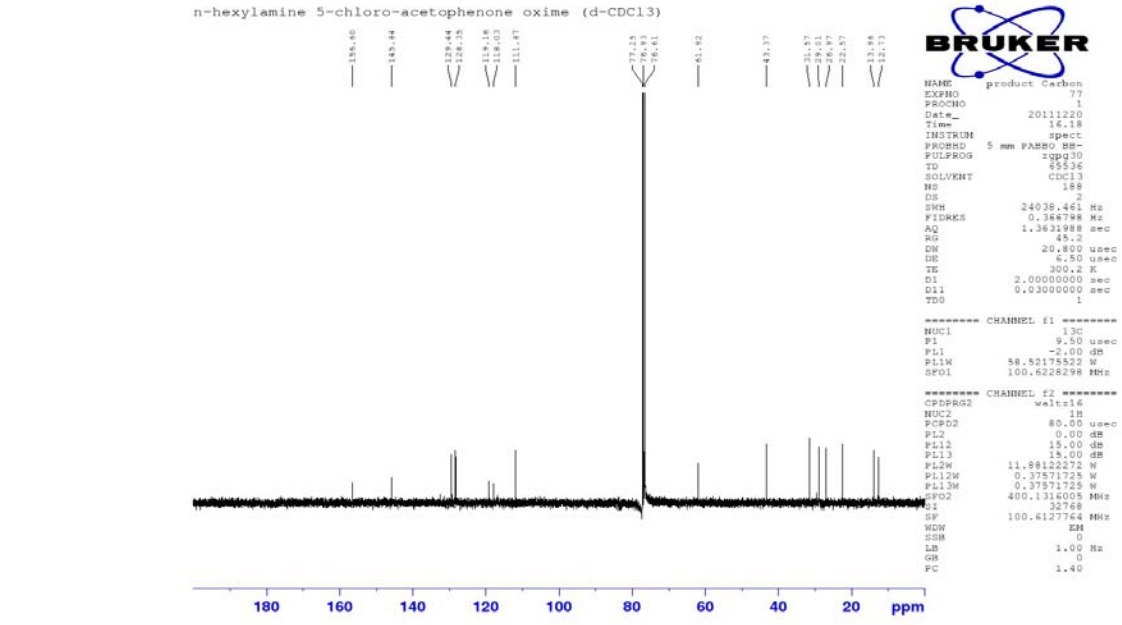
^{13}C NMR spectrum of **3fh**



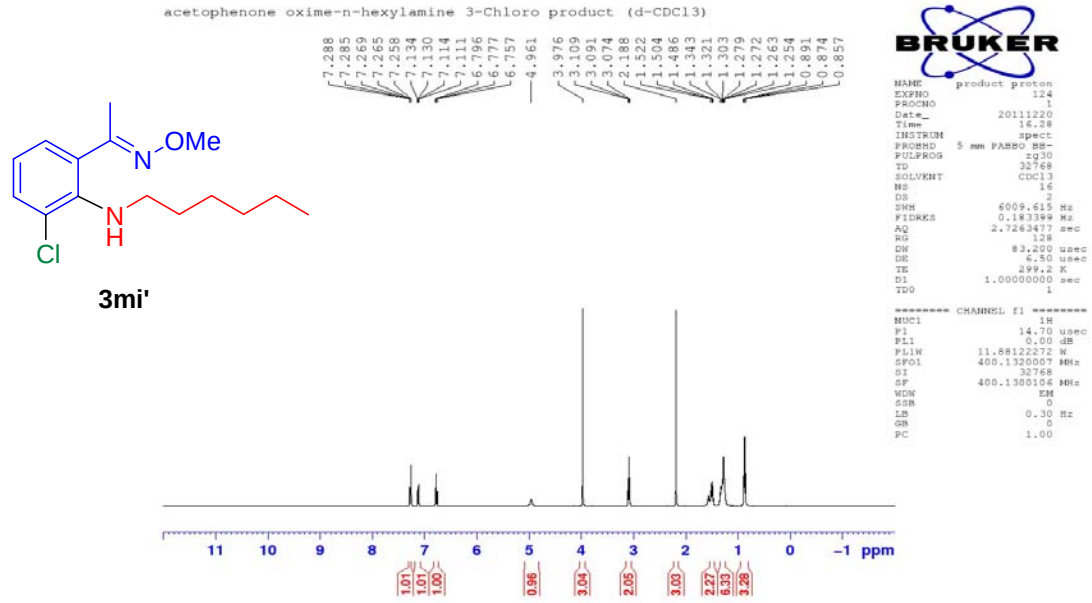
^{1}H NMR spectrum of **3mi**



^{13}C NMR spectrum of **3mi**

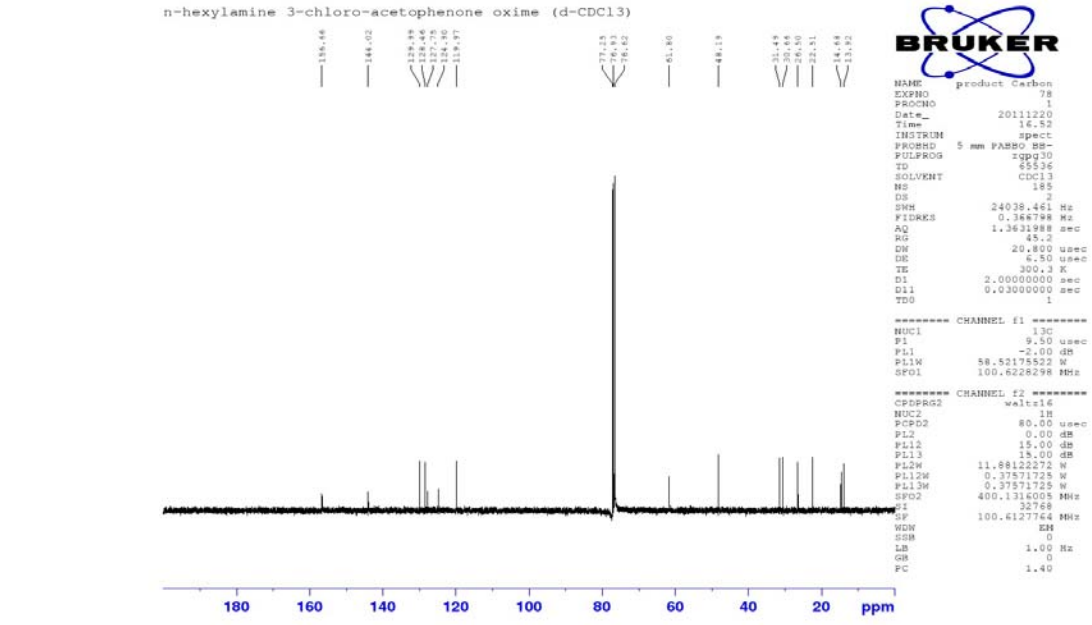


^{1}H NMR spectrum of **3mi'**

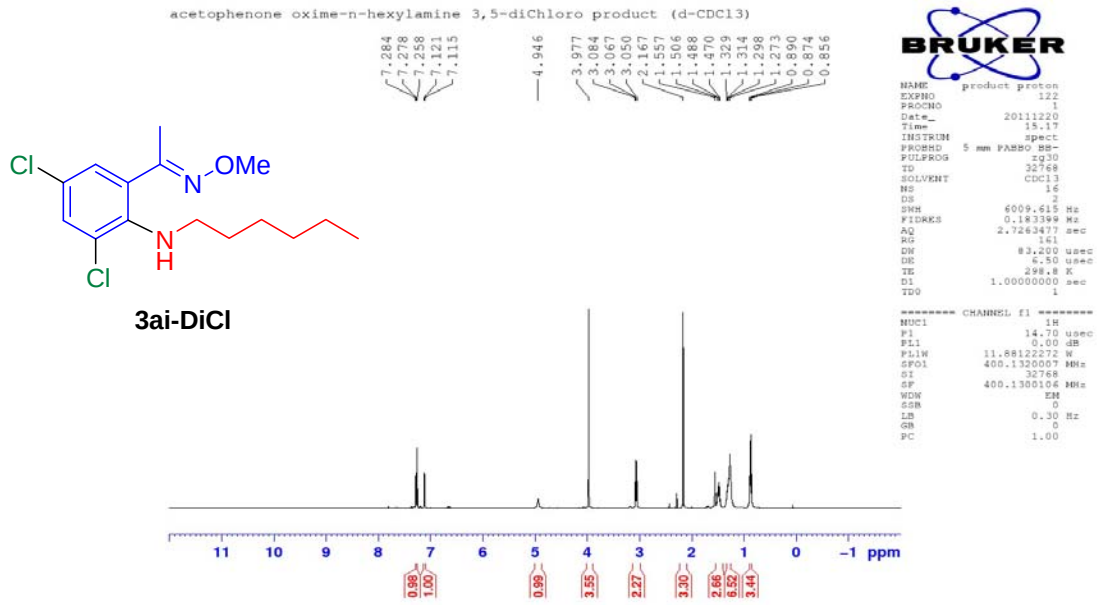


3mi'

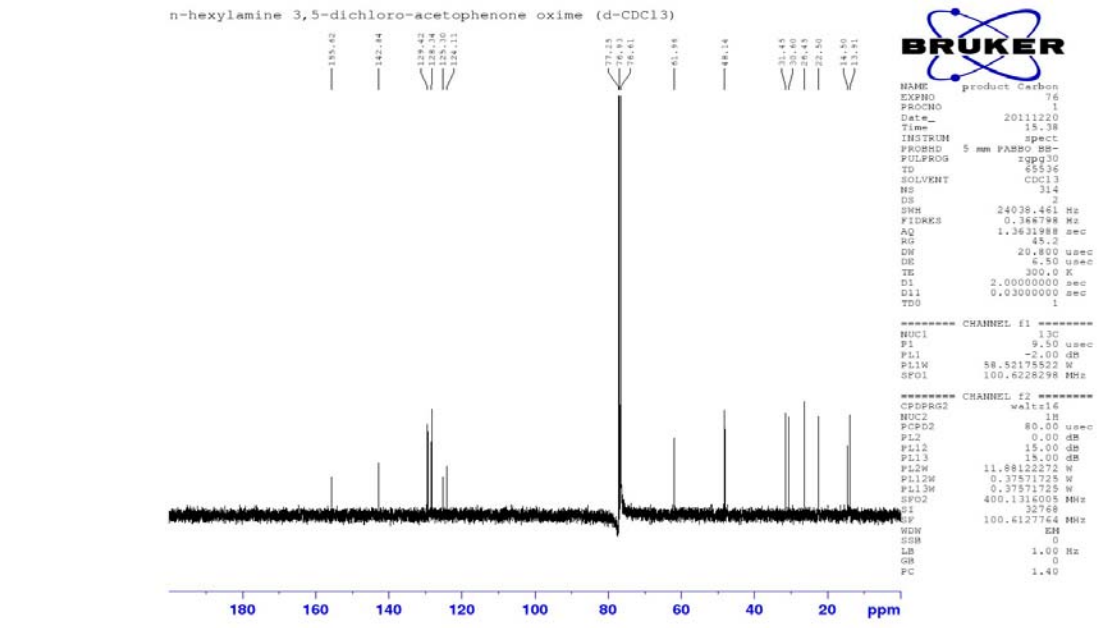
^{13}C NMR spectrum of **3mi'**



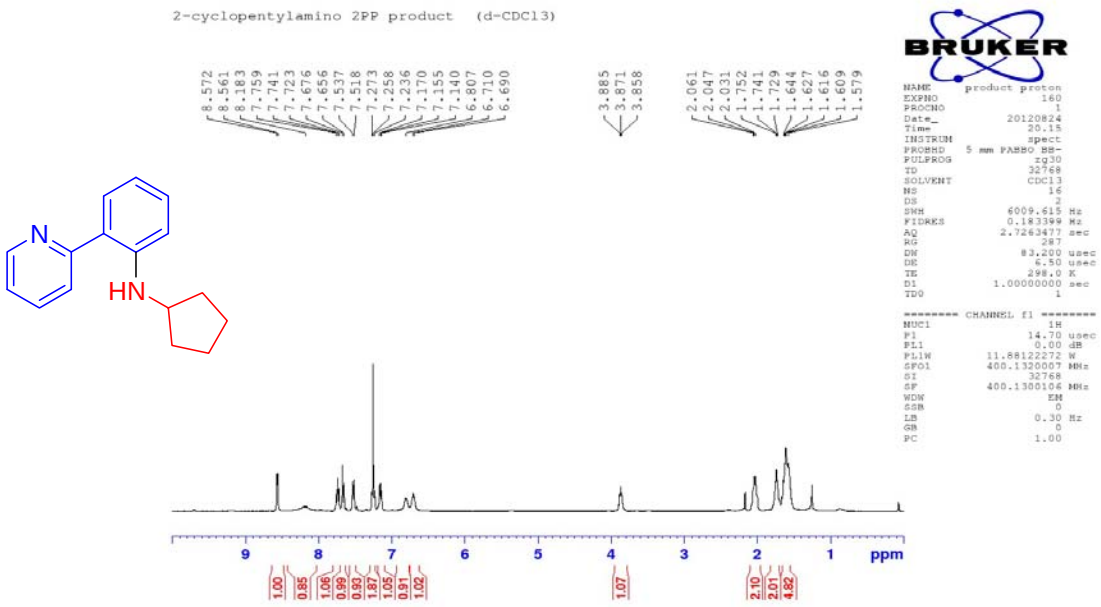
^{1}H NMR spectrum of **3ai-DiCl**



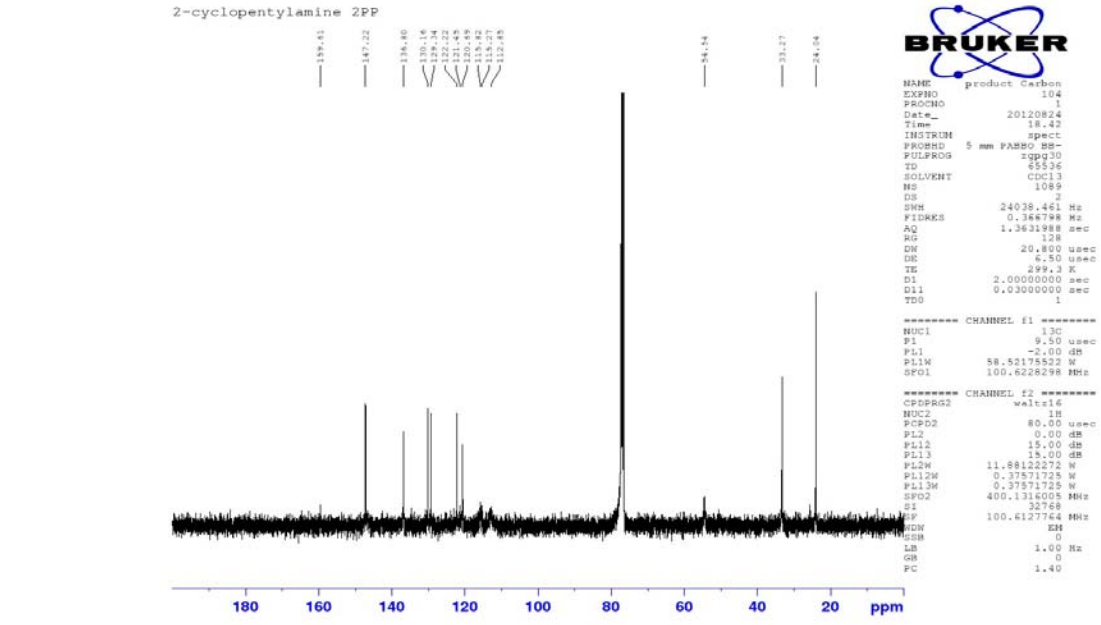
^{13}C NMR spectrum of **3ai-DiCl**



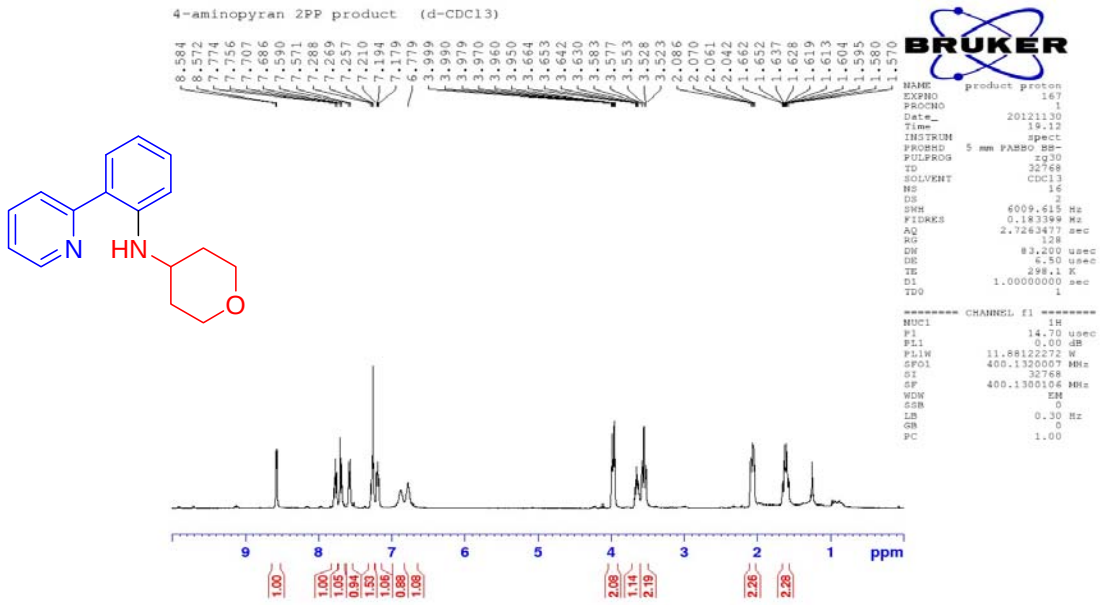
^{1}H NMR spectrum of ***N*-cyclopentyl-2-(pyridin-2-yl)aniline**



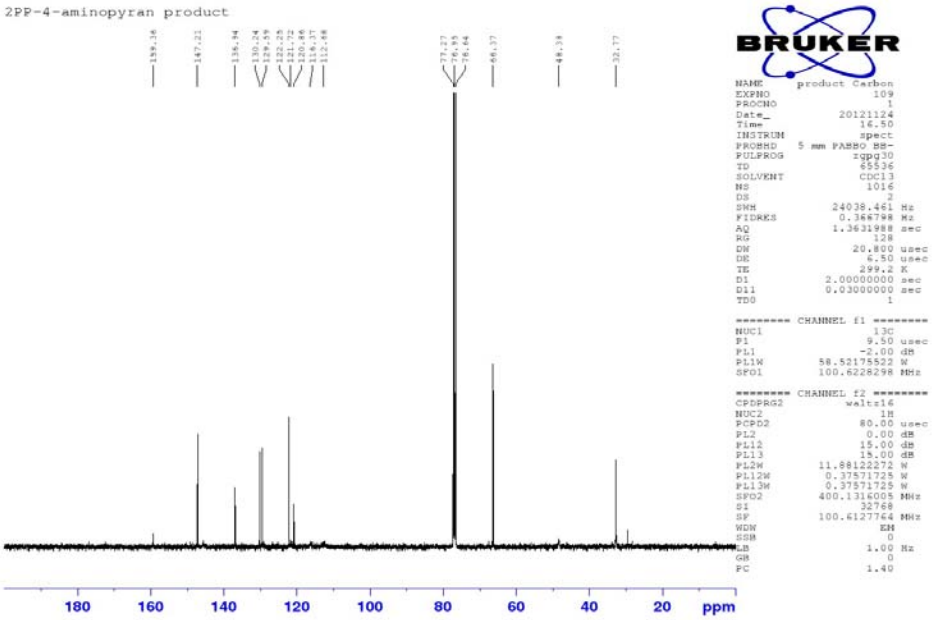
^{13}C NMR spectrum of ***N*-cyclopentyl-2-(pyridin-2-yl)aniline**



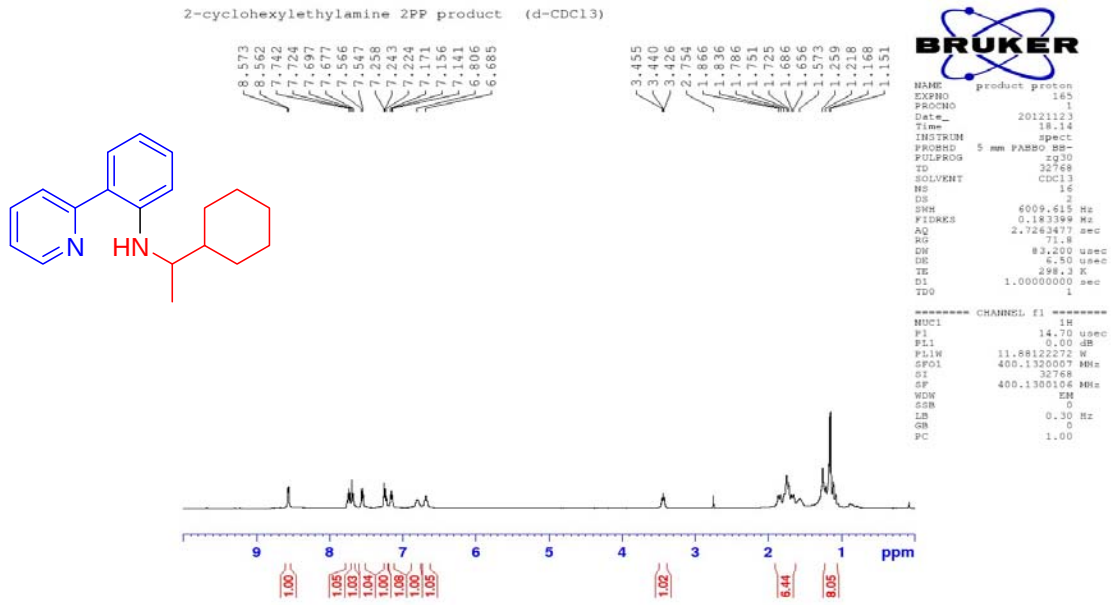
^{1}H NMR spectrum of **tetrahydro-*N*-(2-(pyridin-2-yl)phenyl)-2H-pyran-4-amine**



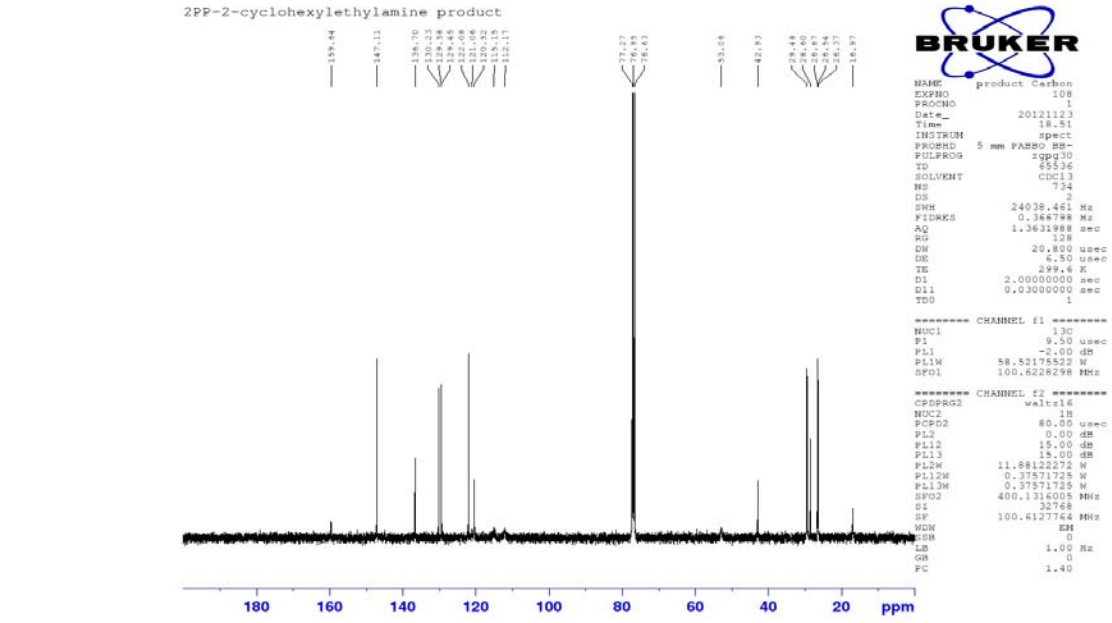
^{13}C NMR spectrum of **tetrahydro-*N*-(2-(pyridin-2-yl)phenyl)-2H-pyran-4-amine**



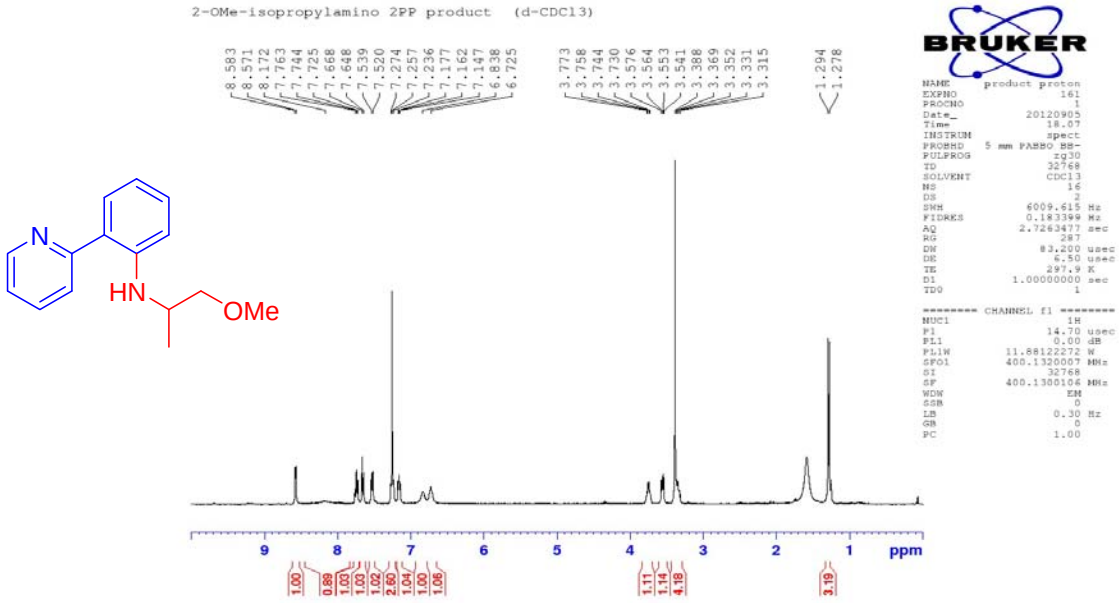
^{1}H NMR spectrum of ***N*-(1-cyclohexylethyl)-2-(pyridin-2-yl)benzenamine**



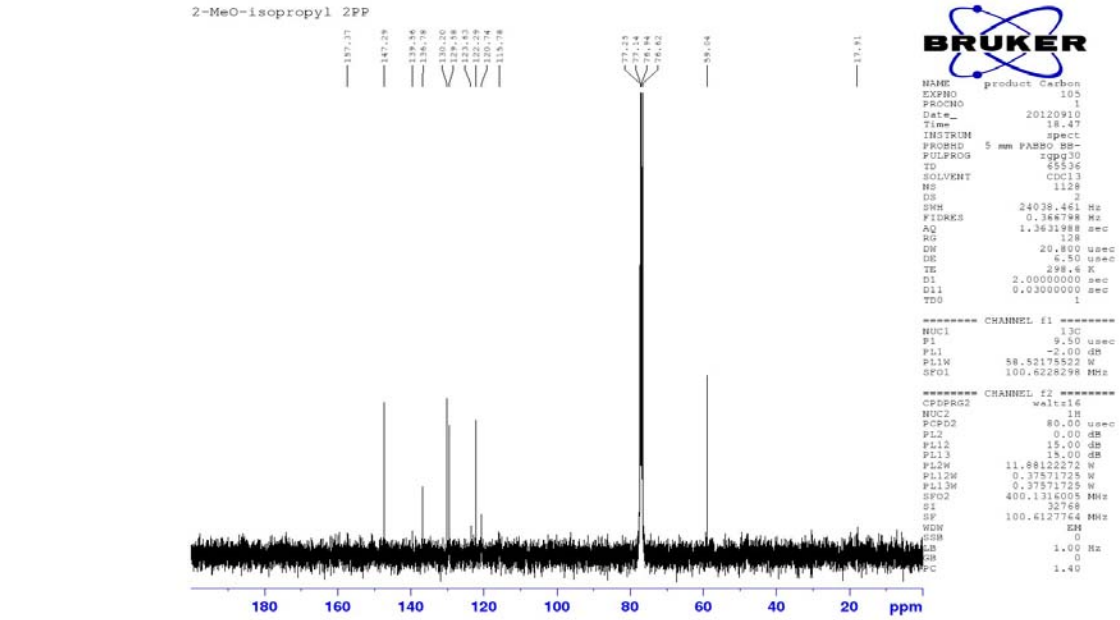
^{13}C NMR spectrum of ***N*-(1-cyclohexylethyl)-2-(pyridin-2-yl)benzenamine**



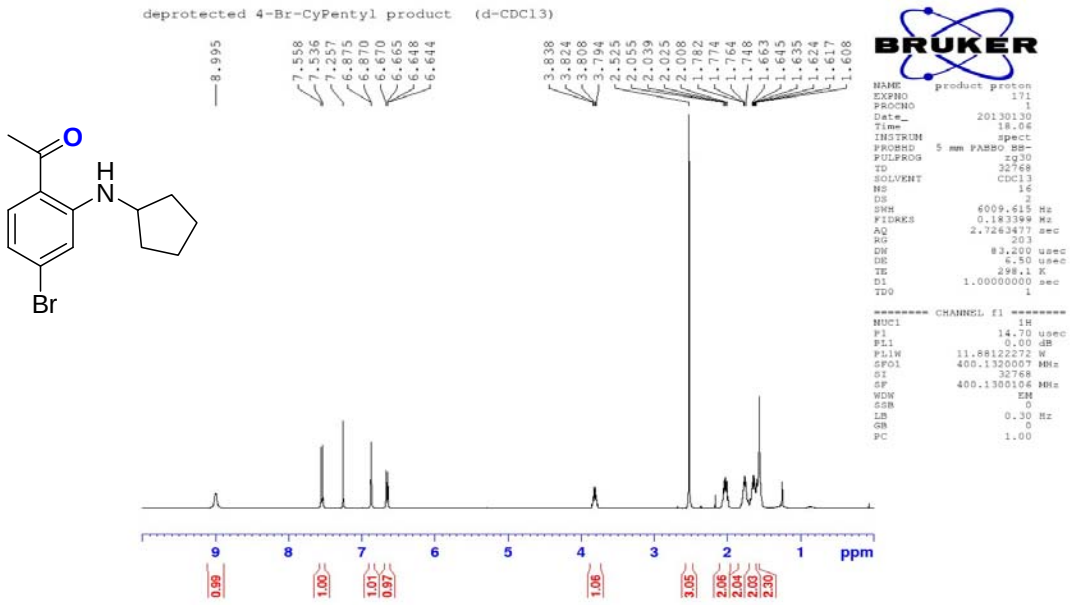
^{1}H NMR spectrum of ***N*-(1-methoxypropan-2-yl)-2-(pyridin-2-yl)aniline**



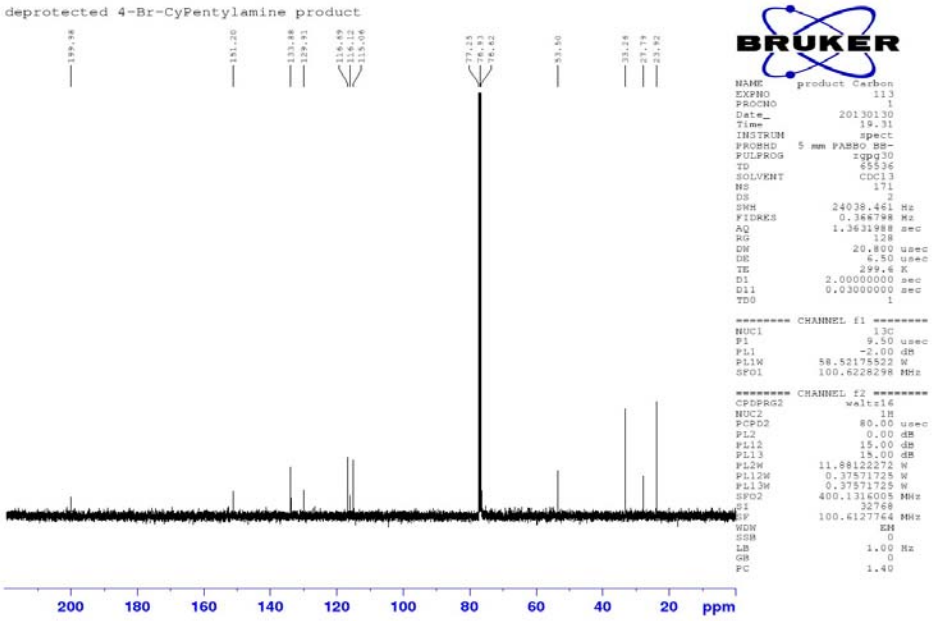
^{13}C NMR spectrum of ***N*-(1-methoxypropan-2-yl)-2-(pyridin-2-yl)aniline**



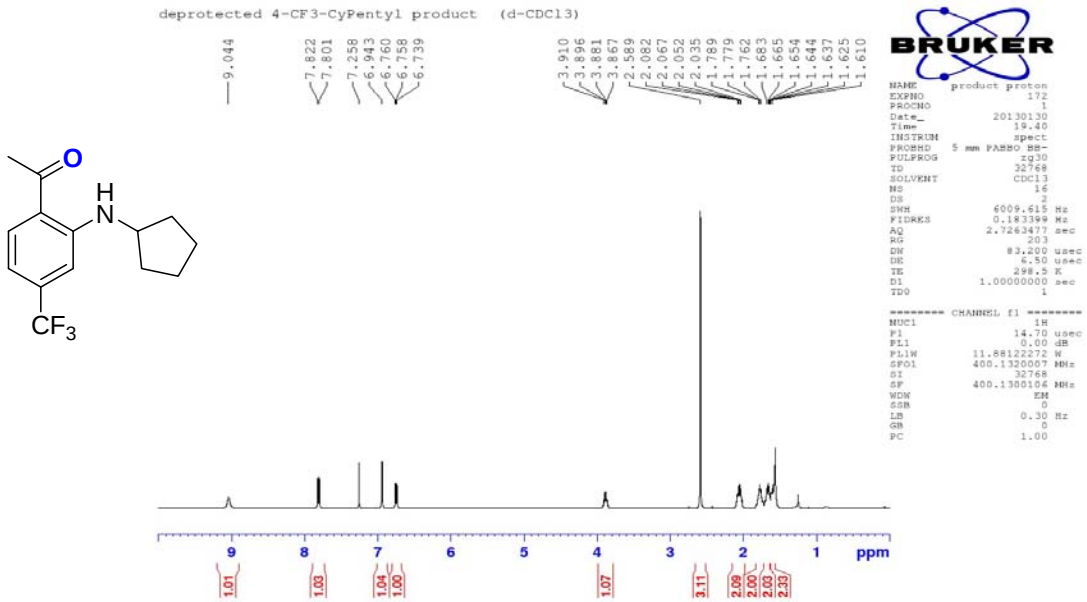
^{1}H NMR spectrum of **1-(4-bromo-2-(cyclopentylamino)phenyl)ethanone**



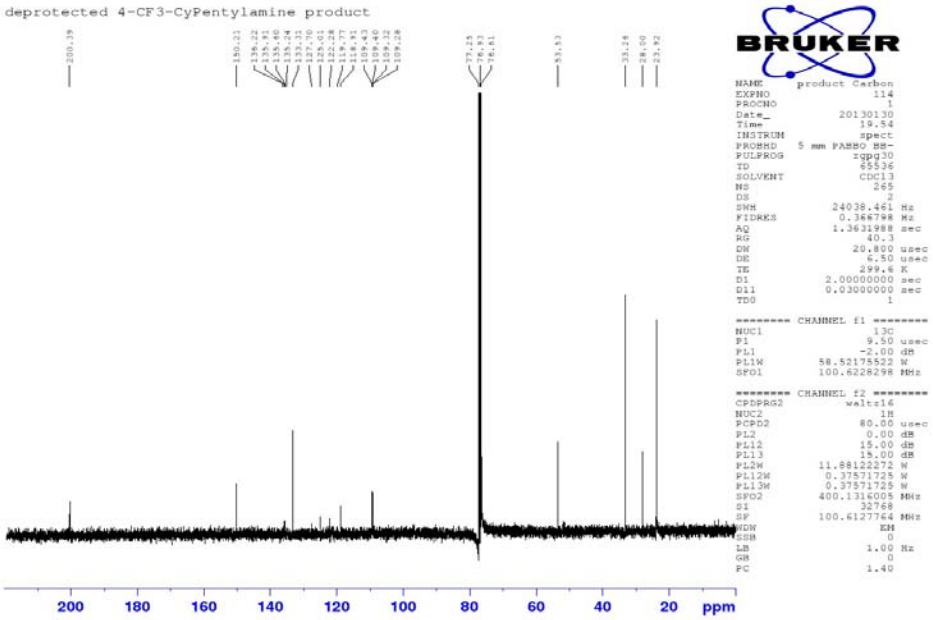
^{13}C NMR spectrum of **1-(4-bromo-2-(cyclopentylamino)phenyl)ethanone**



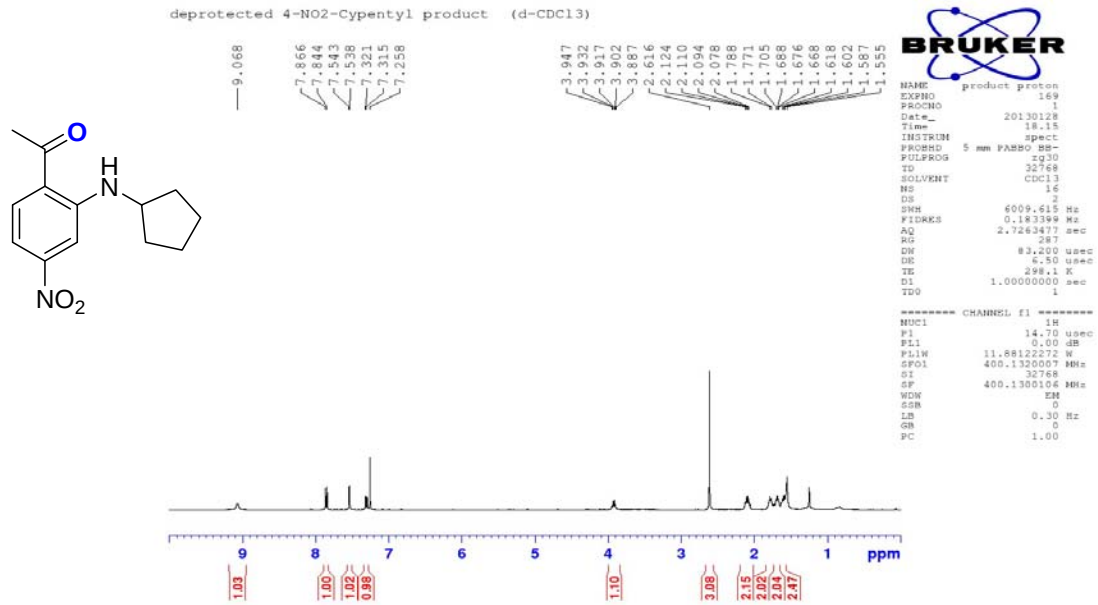
^{1}H NMR spectrum of **1-(2-(cyclopentylamino)-4-(trifluoromethyl)phenyl)ethanone**



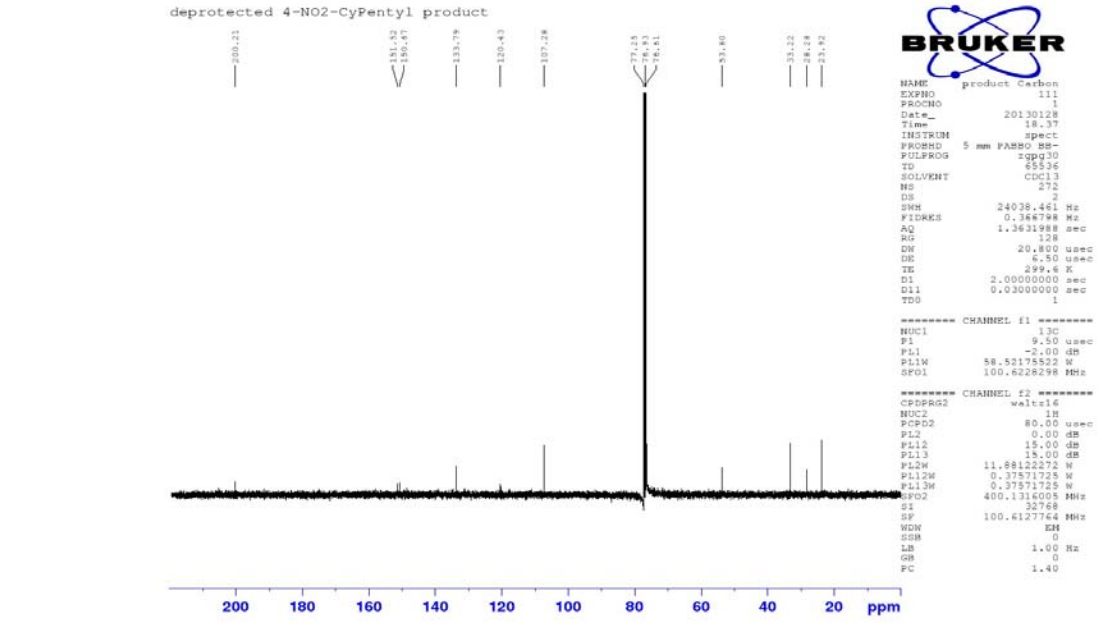
^{13}C NMR spectrum of **1-(2-(cyclopentylamino)-4-(trifluoromethyl)phenyl)ethanone**



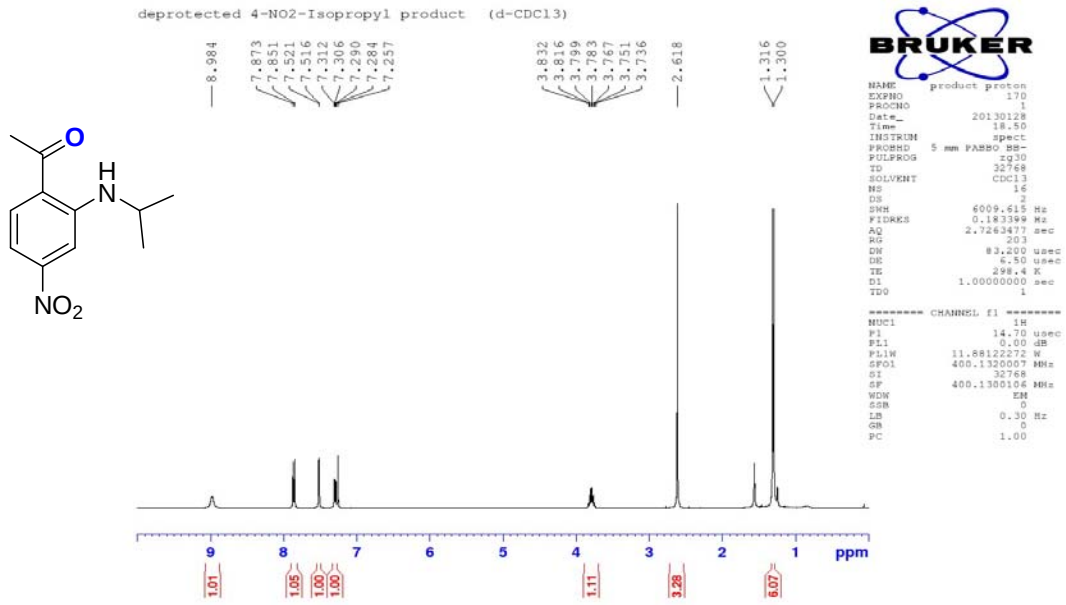
^{1}H NMR spectrum of **1-(2-(cyclopentylamino)-4-nitrophenyl)ethanone**



^{13}C NMR spectrum of **1-(2-(cyclopentylamino)-4-nitrophenyl)ethanone**



^{1}H NMR spectrum of **1-(2-(isopropylamino)-4-nitrophenyl)ethanone**



^{13}C NMR spectrum of **1-(2-(isopropylamino)-4-nitrophenyl)ethanone**