Supporting Information

Pyrazole based palladacycle for the synthesis of β-aminoketones by redox coupling of allyl alcohols and anilines

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General Information: All chemicals were used as received from commercially available sources such as Sigma-Aldrich, Alfa-aesar, TCI, and Spectrochem, and used without further purification. 1,2-dichloroethane was distilled from CaH_2. THF was distilled from Na/Benzophenone prior to use. All reactions were carried out in open air unless notified. NMR spectra were recorded on Bruker ARX 400 and Bruker Advance 700 spectrometer at room temperature. ^1H (400 MHz or 700MHz) and ^{13}C (100 MHz or 176MHz) NMR chemical shifts in ppm were referenced internally to its proton resonance of incomplete deuterated solvent signals. ^{31}P NMR (81 MHz) spectra were externally reference to H_3PO_4 in D_2O ($\delta = 0$). High-resolution mass spectra (HRMS) were recorded on a Bruker microTOF-QII mass spectrometer.

General procedure for synthesis of β-aminoketones: To a screw cap scintillation vial aryl amine (0.5 mmol), allyl alcohol (2.0 mmol), catalyst (0.0125 mmol) and BINOL phosphoric acid (0.025 mmol) were charged in open air and 1 mL DCE was added to it. The reaction mixture was allowed to stir at room temperature for 48 hours. The reaction mixture was diluted with dichloromethane (3 x 5 mL), and concentrated under vacuum. The crude mixture was subjected to column chromatography on silica gel using ethyl acetate and n-hexanes mixtures to afford the β-aminoketones as pure product.

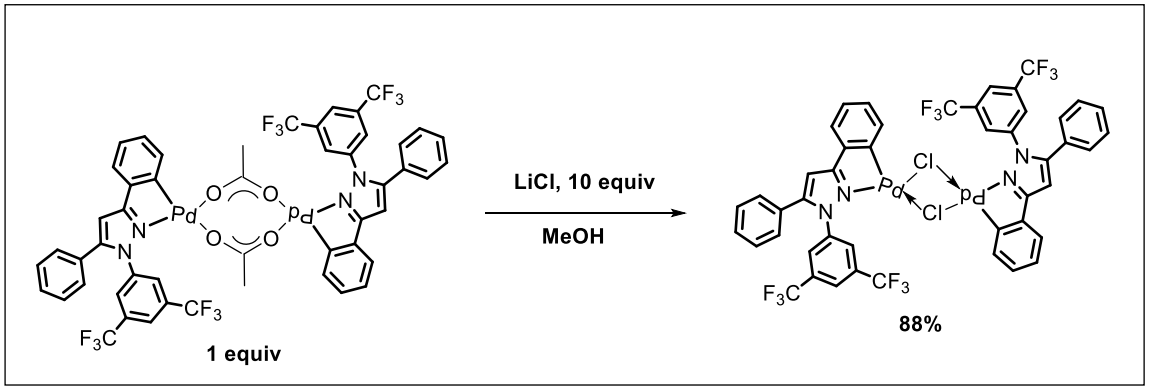
Synthesis of BINOL phosphoric acid: (S)-BINOL (1.0 g, 3.5 mmol) was dissolved in pyridine (10 mL). Phosphorous oxychloride (0.65 mL, 7 mmol) was added dropwise at room temperature with rapid stirring and the resulting solution was stirred at 60 °C for 12 hours. Water (10 mL) was added and the resulting biphasic suspension was stirred at 50 °C for a further 2 hours. The reaction mixture was diluted with CH_2Cl_2 and pyridine was extracted by washing with 1N HCl aq. The combined organic phase was dried over Na_2SO_4 and concentrated. The crude solid was purified by flash silica gel chromatography (5% MeOH in CH_2Cl_2) to yield the product as ivory-white solid (1.08g, 90%).

Synthesis of Palladacycle II (Scheme S1): Palladacycle **I** (1.0g, 0.83 mmol) was taken in a 100 mL Round bottomed flask and was dissolved in methanol. LiCl (0.35g, 8.3 mmol) was added to it and was stirred overnight at RT. Then, excess amount of water was added to it which resulted in precipitation. The reaction mixture was filtered and the residue was washed with excess water to remove any lithium salt. The residue was dried and dissolved in chloroform and was layered with hexane for crystallisation at low temperature. Yellow crystals were obtained in 88% (0.83g) yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.77 (s, 4H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 4H), 7.24 (dd, *J* = 7.4, 1.6 Hz, 2H), 7.11 (d, *J* = 6.9 Hz, 4H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.83 (t, *J* = 7.7 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 2H). ^{19}F decoupled $^{13}C\{^1H, ^{19}F\}$ NMR (101 MHz, $CDCl_3$) δ 160.97, 147.94, 144.58, 137.80, 136.08, 133.19, 132.95, 130.05, 129.22, 129.09, 129.05, 128.03, 127.26, 125.29, 123.65, 123.30, 102.38. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.72. Elemental analysis calcd (%) for $C_{46}H_{26}Cl_2F_{12}N_4Pd_2$: C 48.19, H 2.29, N 4.89. Found: C 49.12, H 2.68, N 4.66. HRMS (ESI): calculated for $C_{46}H_{26}Cl_2F_{12}N_4Pd_2$ ($[M + H]^+$) : 1144.9656, found : 1144.9118.

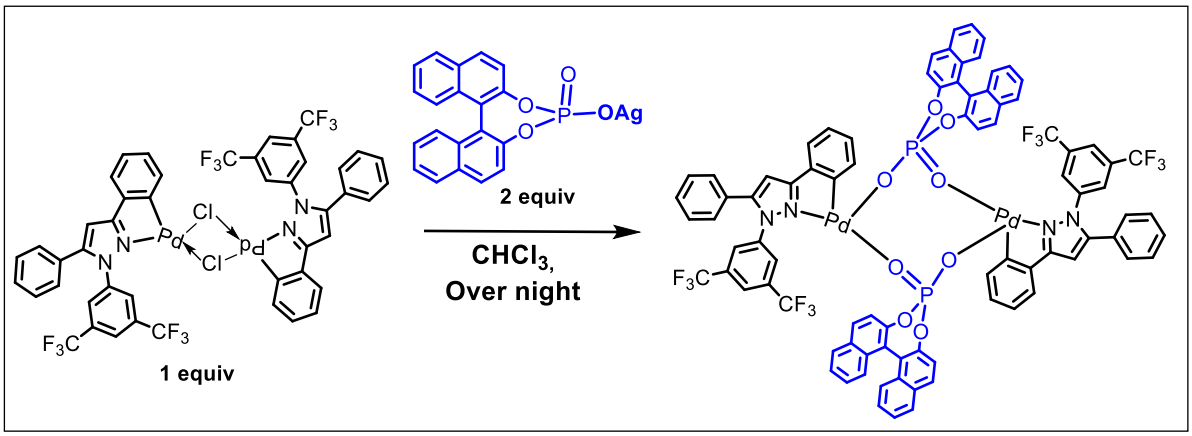
Synthesis of Palladacycle III (Scheme S2): Palladacycle S2 (0.5g, 0.437 mmol) was dissolved in chloroform. Silver BINOL phosphate (0.39g, 0.874 mmol) was added to it. The reaction was ran for overnight with vigorous stirring. After a fast celite filtration, the solvent was evaporated under vacuum, yellow solid was obtained. The compound was dissolved in DME and layered with hexane for crystallisation at low temperature. Yellow crystals were obtained in 76% (0.58g) yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 16.2, 8.5 Hz, 4H), 7.81 (d, *J* = 8.1

Hz, 2H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.50 – 7.41 (m, 8H), 7.40 – 7.35 (m, 7H), 7.35 – 7.33 (m, 3H), 7.32 (d, *J* = 2.7 Hz, 3H), 7.28 (d, *J* = 7.2 Hz, 4H), 7.25 – 7.22 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.92 (s, 2H), 6.90 – 6.86 (m, 4H), 6.40 (s, 2H). ^{19}F decoupled ^{13}C{^{1}H, ^{19}F} NMR (101 MHz, $CDCl_3$) δ 160.25, 148.40, 147.80, 145.86, 143.83, 136.92, 136.04, 132.67, 132.19, 131.70, 131.48, 130.83, 130.41, 129.73, 129.13, 128.77, 128.50, 128.39, 127.52, 126.60, 126.16, 125.82, 125.67, 125.04, 124.64, 122.62, 122.16, 121.52, 121.11, 120.88, 103.08. ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.69, -62.70. Elemental analysis calcd (%) for $C_{86}H_{50}F_{12}N_4O_8P_2Pd_2$: C 58.35, H 2.85, N 3.17. Found: C 57.86, H 3.00, N 3.26. HRMS (ESI): calculated for $C_{86}H_{50}F_{12}N_4O_8P_2Pd_2$ ($[M + H]^+$) : 1791.0878, found : 1791.0872.

Scheme S1



Scheme S2



Experimental procedure for controlled reactions

Scheme 2.a

To a screw cap scintillation vial 1-penten-3-ol (0.172 g, 2.0 mmol), palladacycle **1** (0.0125 mmol), and BINOL phosphoric acid (0.025 mmol) were charged in open air and 1 mL of DCE was added to it. The reaction mixture was allowed to stir at room temperature for 24h. Crude reaction mixture was analysed for ^{1}H and ^{13}C analysis.

Scheme 2.b

To a screw cap scintillation vial *p*-anisidine (0.061g, 0.5 mmol), 1-penten-3-one (0.168g ml, 2.0 mmol), palladacycle **1** (0.0125 mmol), and BINOL phosphoric acid (0.025 mmol) were charged in open air and 1 mL of DCE was added to it. The reaction mixture was allowed to stir at room temperature for 24h. The reaction mixture was diluted with dichloromethane (3 x 5 mL) and concentrated under vacuum. The crude mixture was subjected to column chromatography on silica gel using ethyl acetate and n-hexanes mixtures to afford the β-aminoketones as pure product.

Scheme 2.c

To a screw cap scintillation vial *p*-anisidine (0.061g, 0.5 mmol), pentan-3-one (0.172g, 2.0 mmol), palladacycle **1** (0.0125 mmol), and BINOL phosphoric acid (0.025 mmol) were charged in open air and 1 mL of DCE was added to it. The reaction mixture was allowed to stir at room temperature for 24h. The reaction mixture was monitored through TLC. No β-aminoketone product was observed.

Scheme 2.d.

To a screw cap scintillation vial *p*-anisidine (0.061g, 0.5 mmol), 1-penten-3-ol (0.172g, 2.0 mmol), and palladacycle **3** (0.022g, 0.0125 mmol) were charged in open air and 1 mL of DCE was added to it. The reaction mixture was allowed to stir at room temperature for 24h. The reaction mixture was diluted with dichloromethane (3 x 5 mL), and concentrated under vacuum. The crude mixture was subjected to column chromatography on silica gel using ethyl acetate and n-hexanes mixtures to afford the β-aminoketones (0.094g, 91%) as pure product.

Analytical data for β-aminoketones:

4-((4-methoxyphenyl)amino)butan-2-one (Table 2, product 1)[1] : prepared from *p*-anisidine (0.061g, 0.5 mmol) and 3-buten-2-ol (0.144g ml, 2.0 mmol). After purification by column chromatography, the compound was isolated as brown liquid (0.081g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.77 (d, *J* = 8.9, 2H), 6.59 (d, *J* = 8.9, 2H), 3.74 (s, 3H), 3.35 (t, *J*=6.1, 2H), 2.72 (t, *J*=6.1, 2H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.32, 152.57, 141.81, 115.03, 114.84, 55.88, 42.72, 39.76, 30.38. HRMS (ESI): calculated for $C_{11}H_{15}NO_2$ ($[M + H]^+$) : 194.1176, found : 194.1182

4-((2-methoxyphenyl)amino)butan-2-one (Table 2, product 2)[2] : prepared from *o*-anisidine (0.061g, 0.5 mmol) and 3-buten-2-ol (0.144g, 2.0 mmol). After purification by column chromatography, the compound was isolated as brown liquid (0.0878g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.75 – 6.64 (m, 2H), 3.83 (s, 3H), 3.44 (t, *J* = 6.3 Hz, 2H), 2.80 (t, *J* = 6.3, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)) δ 207.87, 147.39, 137.32, 117.36, 110.43, 109.78, 55.55, 42.91, 38.56, 30.39. HRMS (ESI): calculated for $C_{11}H_{15}NO_2$ ($[M + H]^+$) : 194.1176, found : 194.1202.

4-((3-methoxyphenyl)amino)butan-2-one (Table 2, product 3)[1] : prepared from *m*-anisidine (0.061g, 0.5 mmol) and 3-buten-2-ol (0.144g, 2.0 mmol). After purification by column chromatography, the compound was isolated as brown liquid (0.06g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J = 8.1 Hz, 1H), 6.27 (d, J = 8.1Hz, 1H), 6.21 (d, J = 8.0 Hz, 1H), 6.15 (m, 1H), 3.76 (s, 3H), 3.39 (t, J = 6.1 Hz, 2H), 2.73 (t, J = 6.1 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.23, 160.90, 149.15, 130.11, 106.16, 102.73, 98.99, 55.14, 42.59, 38.36, 30.35. HRMS (ESI): calculated for $C_{11}H_{15}NO_2$ ($[M + H]^+$) : 194.1176, found : 194.1201

4-(phenylamino)butan-2-one (Table 2, product 4)[1] : prepared from aniline (0.046g, 0.5 mmol) and 3-buten-2-ol (0.144g, 2.0 mmol). After purification by column chromatography, the compound was isolated as brown liquid (0.052g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 6.9 Hz, 2H), 6.73 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 2H), 3.41 (d, *J* = 8.2 Hz, 2H), 2.75 (t, *J* = 8.1 Hz, 2H), 2.16 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 208.19, 147.39, 129.47, 118.15, 113.46, 42.60, 38.77, 30.44. HRMS (ESI): calculated for $C_{10}H_{13}NO$ ($[M + H]^+$) : 164.1070, found : 164.1100

4-(p-tolylamino)butan-2-one (Table 2, product 5)[1] : prepared from *p*-toluidine (0.053g, 0.5 mmol) and 3-buten-2-ol (0.144g, 2.0 mmol). After purification by column chromatography, the compound was isolated as yellow liquid (0.065g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 (d, *J*=8.2, 2H), 6.55 (d, *J*=8.3, 2H), 3.39 (t, *J*=6.1, 2H), 2.74 (t, *J*=6.1, 2H), 2.23 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 208.35, 145.60, 129.95, 127.02, 113.45, 42.79, 38.93, 30.47, 20.54. HRMS (ESI): calculated for $C_{11}H_{15}NO$ ($[M+H]^+$): 178.1226, found: 178.1221

4-(o-tolylamino)butan-2-one (Table 2, product 6) : prepared from *o*- toluidine (0.053g, 0.5 mmol) and 3-buten-2-ol (0.144g, 2.0 mmol). After purification by column chromatography, the compound was isolated as yellow liquid **(**0.0788g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.47 (t, *J* = 6.1 Hz, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.17 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.30, 145.68, 130.35, 127.16, 122.66, 117.30, 109.75, 77.48, 77.16, 76.84, 42.65, 38.44, 30.38, 17.51. HRMS (ESI): calculated for $C_{11}H_{15}NO$ ($[M + H]^+$): 178.1226, found: 178.1254.

4-((4-(trifluoromethyl)phenyl)amino)butan-2-one (Table 2, product 7) : prepared from 4-(trifluoromethyl)aniline (0.080g, 0.5 mmol) and 3-buten-2-ol (0.144g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellowish white solid (0.1098g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, *J*=8.5, 2H), 6.62 (d, *J*=8.5, 2H), 3.45 (t, *J*=6.0, 2H), 2.77 (t, *J*=6.0, 2H), 2.18 (s, 3H). ^{19}F decoupled ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.94, 150.33, 126.71, 118.85, 111.97, 42.26, 37.82, 30.29. HRMS (ESI): calculated for $C_{11}H_{12}F_3NO$ ($[M + H]^+$) : 232.0944, found : 232.0958

1-((4-methoxyphenyl)amino)pentan-3-one (Table 2, product 8)[2] : prepared from *p*-anisidine (0.061g, 0.5mmol) and 1-penten-3-ol (0.172g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow solid (0.099g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.78 (d, *J*=8.8, 2H), 6.59 (d, *J*=8.8, 2H), 3.74 (s, 3H), 3.37 (t, *J*=6.1, 2H), 2.71 (t, *J*=6.1, 2H), 2.44 (q, *J* = 7.3, 2H), 1.05 (t, *J*=7.3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.04, 152.50, 141.93, 115.02, 114.77, 55.87, 41.40, 39.85, 36.41, 7.77. HRMS (ESI): calculated for $C_{12}H_{17}NO_2$ ($[M + H]^+$) : 208.1332, found : 208.1349.

1-((2-methoxyphenyl)amino)pentan-3-one (Table 2, product 9) : prepared from *o*-anisidine (0.061g, 0.5 mmol) and 1-penten-3-ol (0.172g, 2.0 mmol). After purification by column chromatography, the product was isolated as brown liquid (0.098g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 (t, *J*=8.1, 1H), 6.77 (d, *J*=7.9, 1H), 6.71 – 6.60 (m, 2H), 3.83 (s, 3H), 3.45 (t, *J*=6.4, 2H), 2.75 (t, *J*=6.4, 2H), 2.45 (q, *J*=7.3, 2H), 1.06 (t, *J*=7.3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.55, 147.13, 137.71, 121.26, 116.76, 109.88, 109.59, 55.42, 41.61, 38.32, 36.35, 7.70. HRMS (ESI): calculated for $C_{12}H_{17}NO_2$ ($[M+Na]^+$): 230.1151, found: 230.1166

1-(phenylamino)pentan-3-one (Table 2, product 10)[3] : prepared from aniline (0.046g, 0.5 mmol) and 1-penten-3-ol (0.1722g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow liquid (0.073g, 83%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.18 (t, J = 7.8 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 7.7 Hz, 2H), 3.43 (t, J = 6.1 Hz, 2H), 2.73 (t, J = 5.9 Hz, 2H), 2.44 (q, J = 7.3 Hz, 2H), 1.06 (t, J = 7.3 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 210.97, 129.45, 117.80, 113.22, 41.40, 38.81, 36.47, 7.80. HRMS (ESI): calculated for $C_{11}H_{15}NO$ ($[M + H]^+$) : 178.1226, found : 178.1253

1-(p-tolylamino)pentan-3-one (Table 2, product 11)[3] : prepared from *p*-toluidine (0.053g, 0.5 mmol) and 1-penten-3-ol(0.1722g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow solid (0.083g, 87%). ^{1}H NMR (700 MHz, $CDCl_3$) δ = 6.99 (d, *J*=8.1, 2H), 6.57 (d, *J*=8.4, 2H), 3.40 (t, *J*=6.2, 2H), 2.72 (t, *J*=6.2, 2H), 2.43 (q, *J*=7.3, 2H), 2.24 (s, 3H), 1.05 (t, *J*=7.3, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 211.02, 145.18, 129.94, 127.42, 113.72, 41.33, 39.33, 36.44, 20.52, 7.78. HRMS (ESI): calculated for $C_{12}H_{17}NO$ ($[M + H]^+$) : 192.1383, found : 192.1382

1-(o-tolylamino)pentan-3-one (Table 2, product 12)[4] : prepared from *o*- toluidine (0.053g, 0.5 mmol) and 1-penten-3-ol (0.1722g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow liquid (0.087g, 91%). ^{1}H NMR (700 MHz, $CDCl_3$) δ = 7.13 (t, *J*=7.7, 1H), 7.06 (d, *J*=7.3, 1H), 6.67 (t, *J*=7.3, 1H), 6.63 (d, *J*=8.0, 1H), 3.48 (t, *J*=6.2, 2H), 2.76 (t, *J*=6.2, 2H), 2.45 (q, *J*=7.3, 2H), 2.12 (s, 3H), 1.07 (t, *J*=7.3, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 211.14, 145.75, 130.35, 127.18, 122.68, 117.28, 109.79, 41.33, 38.63, 36.46, 17.55, 7.76. HRMS (ESI): $C_{12}H_{17}NO$ ($[M+Na]^+$): 214.1202, found: 214.1205.

1-((4-(trifluoromethyl)phenyl)amino)pentan-3-one (Table 2, product 13) : prepared from 4-(trifluoromethyl)aniline (0.080g, 0.5 mmol) and 1-penten-3-ol (0.1722g, 2.0 mmol). After purification by column chromatography, the product was isolated as brown solid (0.116g, 95%). ^{1}H NMR (700 MHz, Chloroform-*d*) δ = 7.40 (d, *J*=8.5, 2H), 6.62 (d, *J*=8.5, 2H), 3.46 (t, *J*=6.1, 2H), 2.74 (t, *J*=6.0, 2H), 2.50 – 2.38 (m, 2H), 1.06 (t, *J*=7.3, 3H)· ^{19}F decoupled ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.73, 150.34, 126.77, 118.97, 112.03, 40.99, 38.01, 36.45, 7.72. HRMS (ESI): calculated for $C_{12}H_{14}F_3NO$ ($[M + H]^+$) : 246.1100, found : 246.1100.

1-((4-fluorophenyl)amino)pentan-3-one (Table 2, product 14)[5] : prepared from 4-fluoroaniline (0.055g, 0.5 mmol) and 1-penten-3-ol (0.1722g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow solid (0.079g, 81%). ^{1}H NMR (700 MHz, $CDCl_3$) δ = 6.88 (m, 2H), 6.57 – 6.51 (m, 2H), 3.89 (s, 1H), 3.37 (t, *J*=6.1, 2H), 2.71 (t, *J*=6.1, 2H), 2.44 (q, *J*=7.3, 2H), 1.06 (t, *J*=7.3, 3H). ^{19}F decoupled ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.01, 144.18, 115.85, 114.19, 41.24, 39.44, 36.48, 7.79. HRMS (ESI): calculated for $C_{11}H_{14}FNO$ ($[M + H]^+$) : 196.1132, found : 196.1159.

1-((4-methoxyphenyl)amino)hexan-3-one (Table 2, product 15) : prepared from *p*-anisidine (0.061g, 0.5mmol) and 1-hexen-3-ol (0.2g, 2.0 mmol). After purification by column chromatography, the product was isolated as brown liquid (0.07g, 64%). ^{1}H NMR (700 MHz, $CDCl_3$) δ = 6.78 (d, *J*=8.8, 2H), 6.63 (d, *J*=8.4, 2H), 3.75 (s, 3H), 3.37 (t, *J*=6.2, 2H), 2.71 (t, *J*=5.9, 2H), 2.39 (t, *J*=7.3, 2H), 1.60 (h, *J*=7.4, 2H), 0.90 (t, *J*=7.4, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 210.64, 152.83, 141.47, 115.18, 115.07, 55.92, 45.24, 41.67, 40.15, 17.31, 13.84. HRMS (ESI): calculated for $C_{13}H_{19}NO_2$ ($[M + H]^+$) : 222.1489, found : 222.1494

1-((2-methoxyphenyl)amino)hexan-3-one (Table 2, product 16) : prepared from o-anisidine (0.061g, 0.5mmol) and 1-hexen-3-ol (0.2g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow liquid (0.064g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.0 Hz, 1H), 6.68 (t, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H), 3.44 (t, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 6.3 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 1.61 (sextet, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.21, 147.19, 137.72, 121.30, 116.83, 109.97, 109.63, 55.46, 45.20, 42.00, 38.33, 17.23, 13.77. HRMS (ESI): calculated for $C_{13}H_{19}NO_2$ ($[M + H]^+$) : 222.1489, found : 222.1499

1-(methyl(phenyl)amino)hexan-3-one (Table 2, product 17)[6] : prepared from N-methylaniline (0.053g, 0.5mmol) and 1-hexen-3-ol (0.2g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow liquid (0.078g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 2H), 6.76 – 6.68 (m, 3H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.92 (s, 3H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 1.59 (sextet, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.42, 148.67, 129.40, 116.94, 112.61, 47.66, 45.60, 39.43, 38.72, 17.25, 13.82. HRMS (ESI): Calculated for $C_{13}H_{19}NO$ ($[M+H]^+$): 206.1539, found: 206.1553

1-((2-methoxy-4-nitrophenyl)amino)hexan-3-one (Table 2, product 18) : prepared from 2-methoxy-4-nitroaniline (0.084g, 0.5mmol) and 1-hexen-3-ol (0.2g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow solid (0.11g, 83%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 1H), 7.61 (s, 1H), 6.54 (d, *J* = 8.9 Hz, 1H), 3.91 (s, 3H), 3.54 (t, *J* = 6.2 Hz, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 1.62 (sextet, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 209.56, 145.65, 143.54, 137.64, 119.91, 106.87, 105.01, 77.34, 77.16, 76.98, 56.06, 45.26, 41.33, 37.76, 17.29, 13.80. HRMS (ESI): calculated for $C_{13}H_{18}N_2O_4$ ($[M + Na]^+$) : 289.1159, found : 289.1187

1-((4-chlorophenyl)amino)hexan-3-one (Table 2, product 19) : prepared from 4-chloroaniline (0.063g, 0.5mmol) and 1-hexen-3-ol (0.2g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow solid (0.08g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 3.39 (t, *J* = 6.1 Hz, 2H), 2.72 (t, *J* = 6.1 Hz, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.60 (sextet, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.28, 145.51, 129.35, 115.06, 45.25, 41.26, 39.45, 17.30, 13.82. HRMS (ESI): calculated for $C_{12}H_{16}ClNO$ ($[M + Na]^+$) : 248.0813, found : 248.0818

1-((2-chlorophenyl)amino)hexan-3-one (Table 2, product 20) : prepared from 2-chloroaniline (0.063g, 0.5mmol) and 1-hexen-3-ol (0.2g, 2.0 mmol). After purification by column chromatography, the product was isolated as yellow liquid (0.095g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 3.48 (t, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 6.4 Hz, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 1.61 (sextet, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ 209.96, 143.66, 129.40, 127.90, 119.68, 117.60, 111.33, 45.33, 41.74, 38.37, 17.29, 13.81. HRMS (ESI): calculated for $C_{12}H_{16}ClNO$ ($[M + Na]^+$) : 248.0813, found : 248.0814

1-((4-bromo-2-nitrophenyl)amino)hexan-3-one (Table 2, product 21) : prepared from 4-bromo-2-nitroaniline (0.108g, 0.5mmol) and 1-hexen-3-ol (0.2g, 2.0 mmol). After purification by column chromatography, the product was isolated as orange solid (0.072g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 6.79 (d, *J* = 9.2 Hz, 1H), 3.59 (m, 2H), 2.81 (t, *J* = 6.6 Hz, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 1.63 (dq, *J* = 14.7, 7.1 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.65, 144.16, 139.14, 132.52, 129.15, 115.39, 106.75, 45.31, 41.51, 37.65, 17.29, 13.81. HRMS (ESI): calculated for $C_{12}H_{15}BrN_2O_3$ ($[M+H]^+$): 315.0339, found: 315.0353

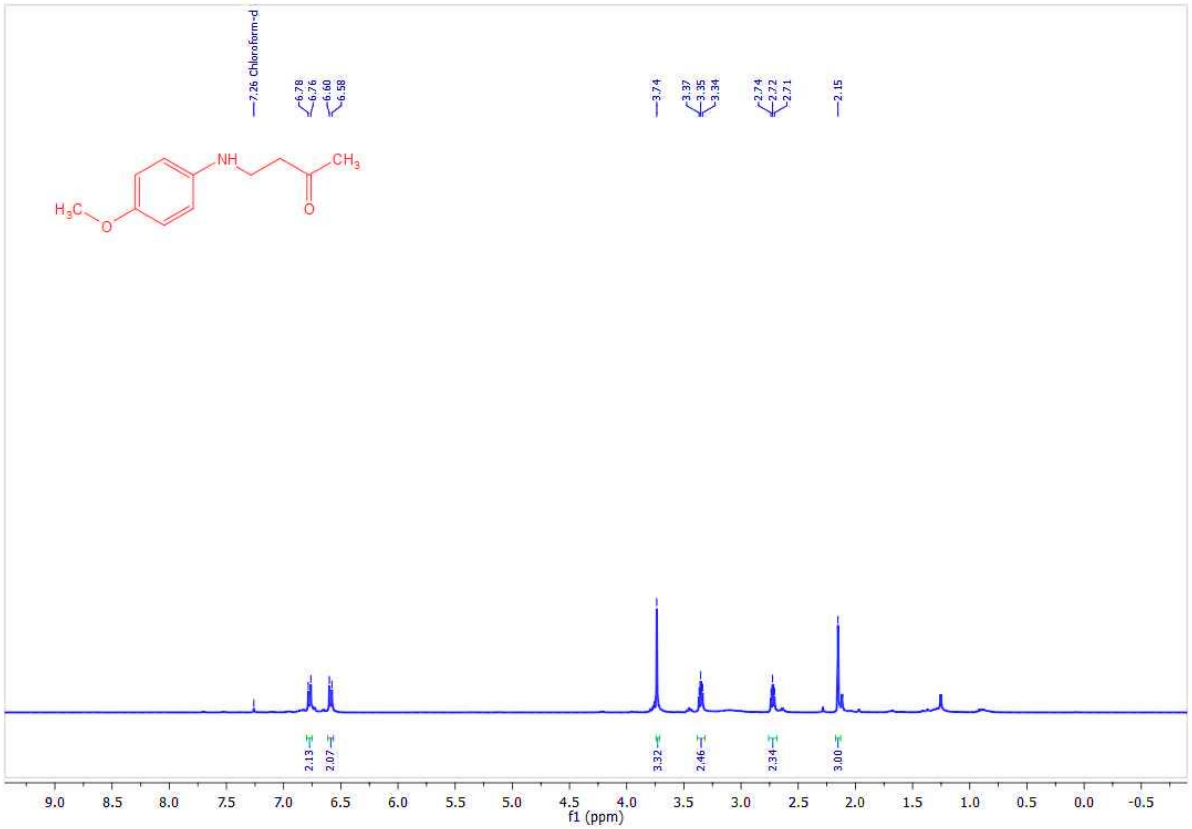


Figure S1: ^{1}H NMR spectrum of product 1

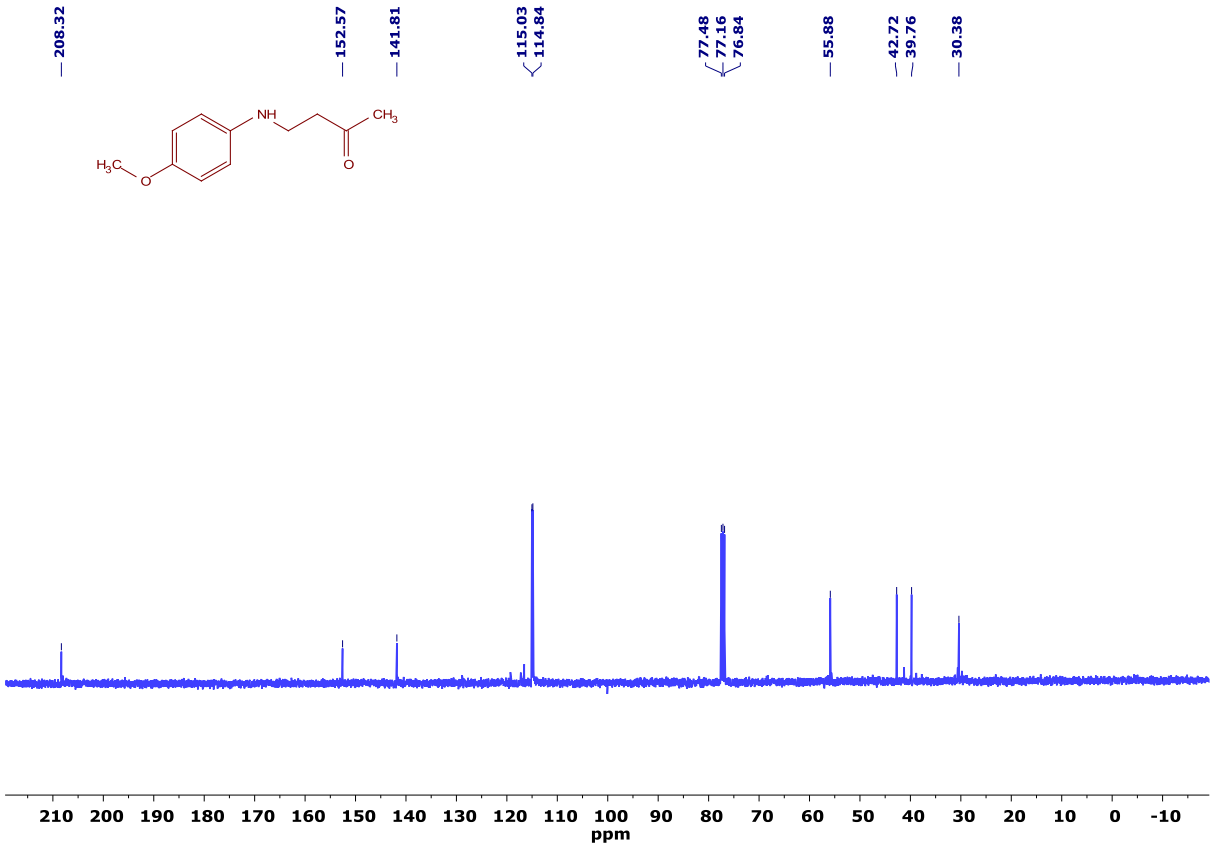


Figure S2: ^{13}C NMR spectrum of spectrum of product 1

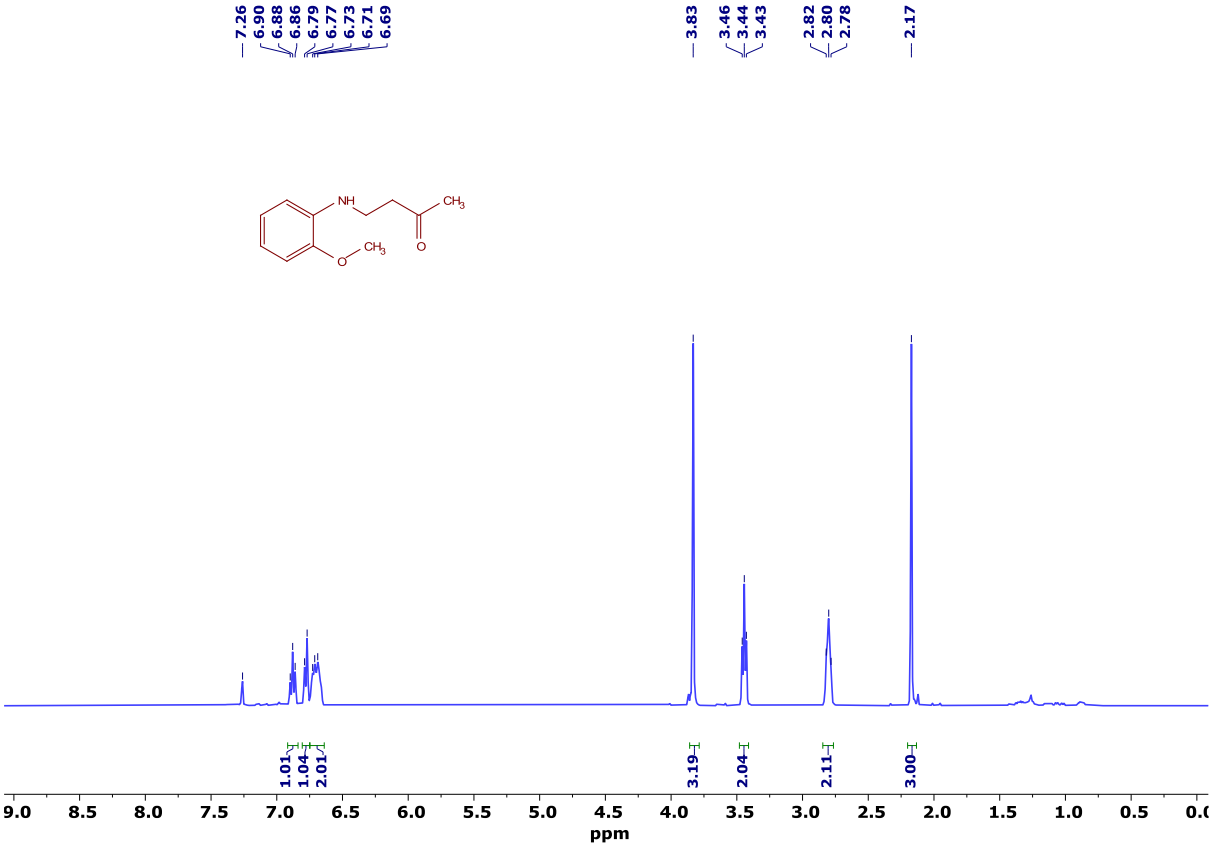


Figure S3: ^{1}H NMR spectrum of product 2

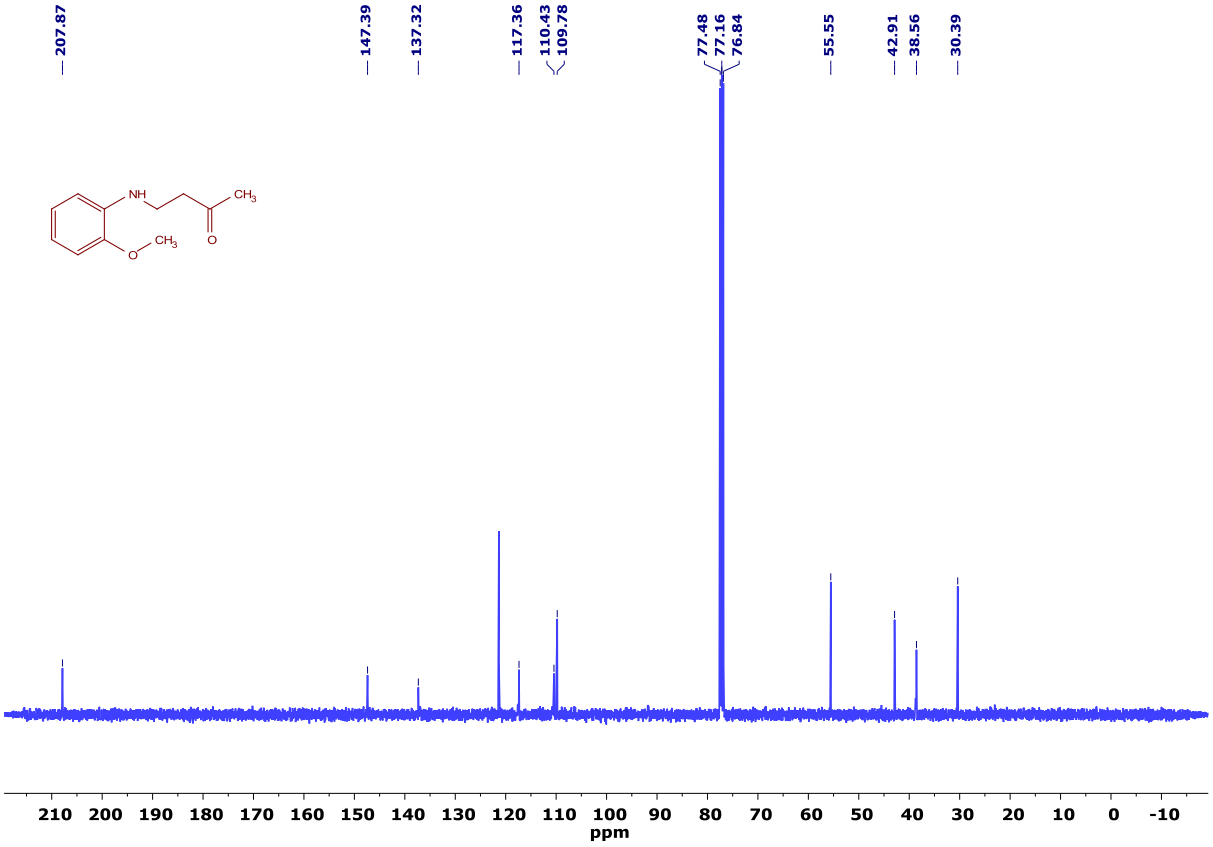


Figure S4: ^{13}C NMR spectrum of product 2

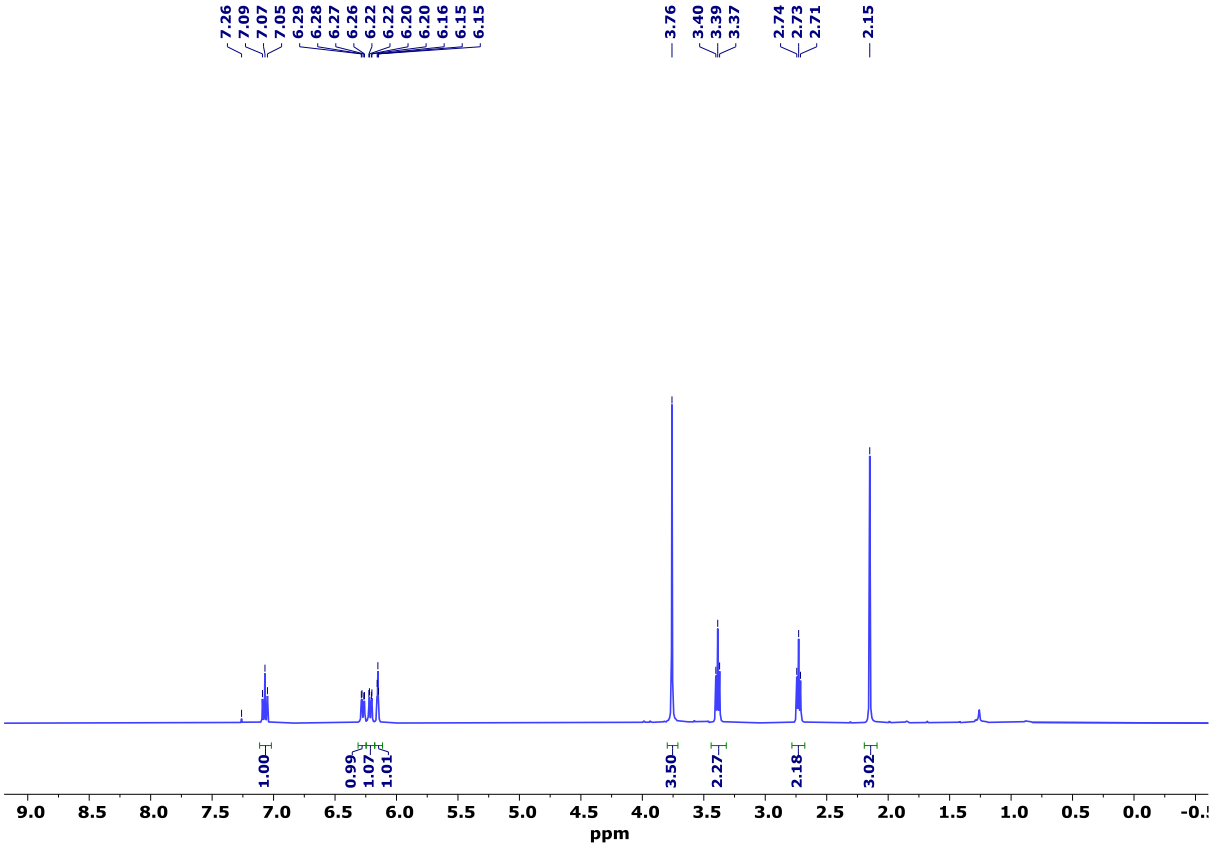


Figure S5: ^{1}H NMR spectrum of product 3

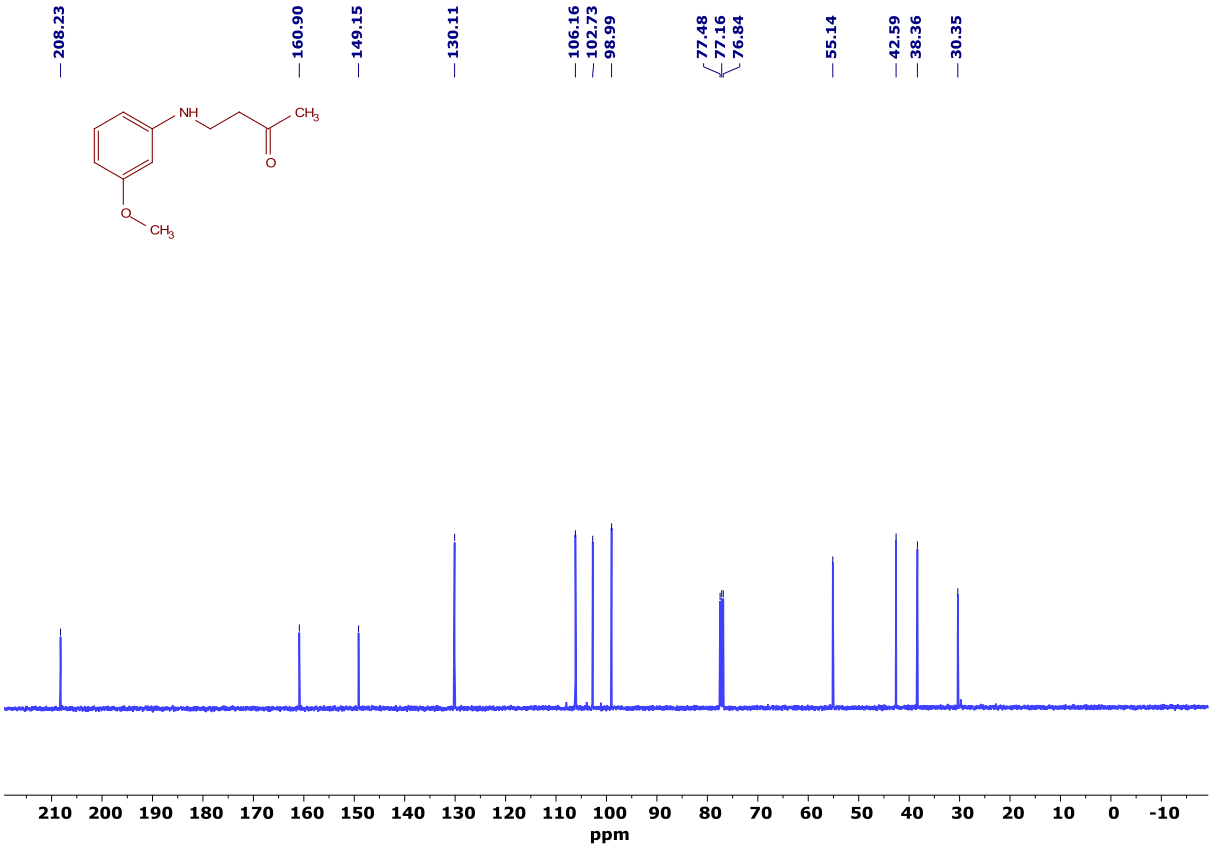


Figure S6: ^{13}C NMR spectrum of product 3

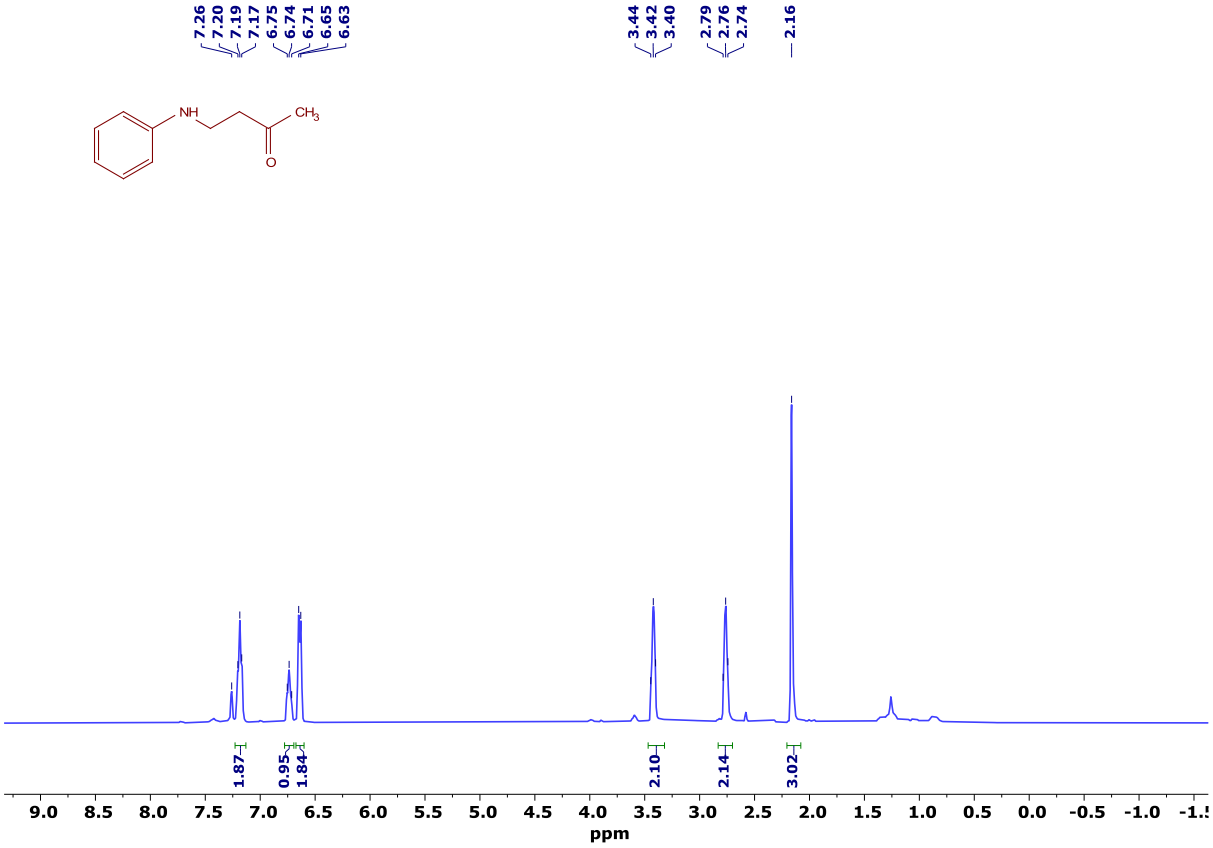


Figure S7: ^{1}H NMR spectrum of product 4

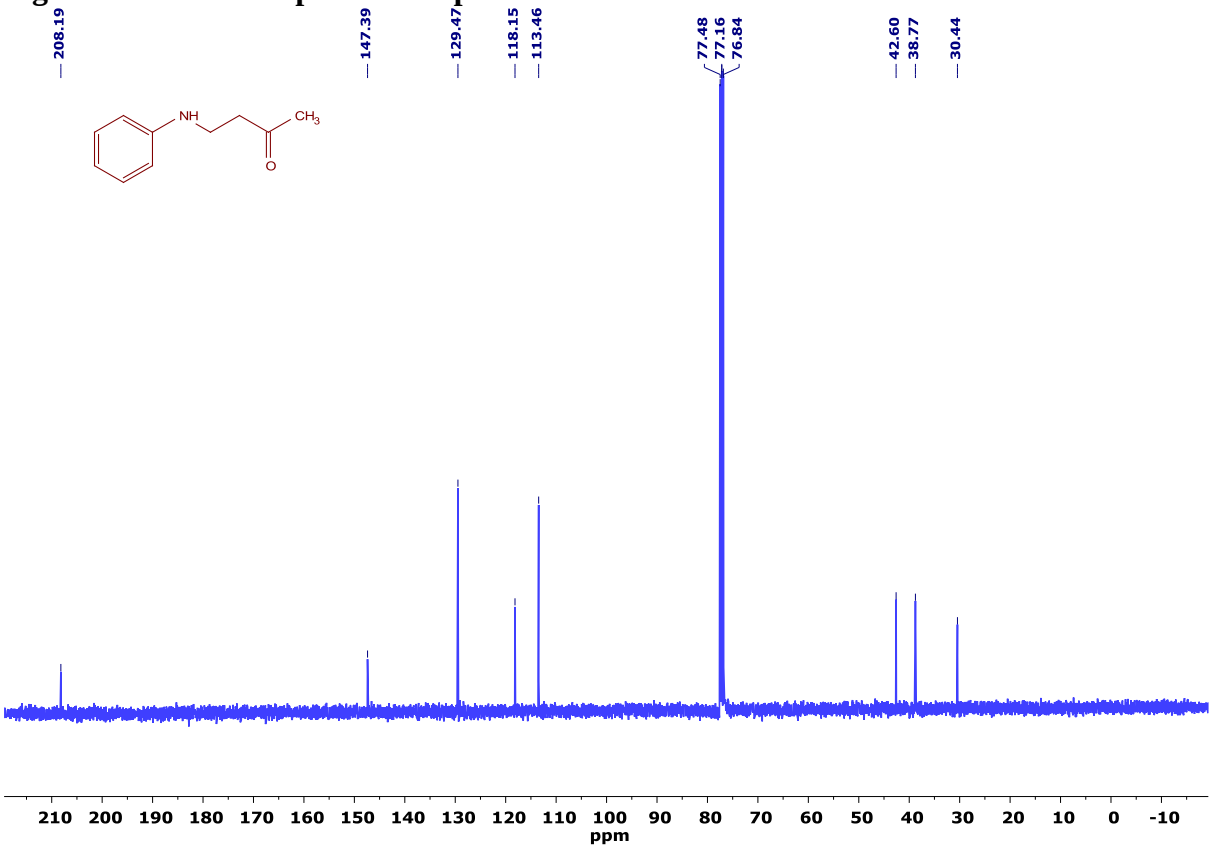


Figure S8: ^{13}C NMR spectrum of product 4

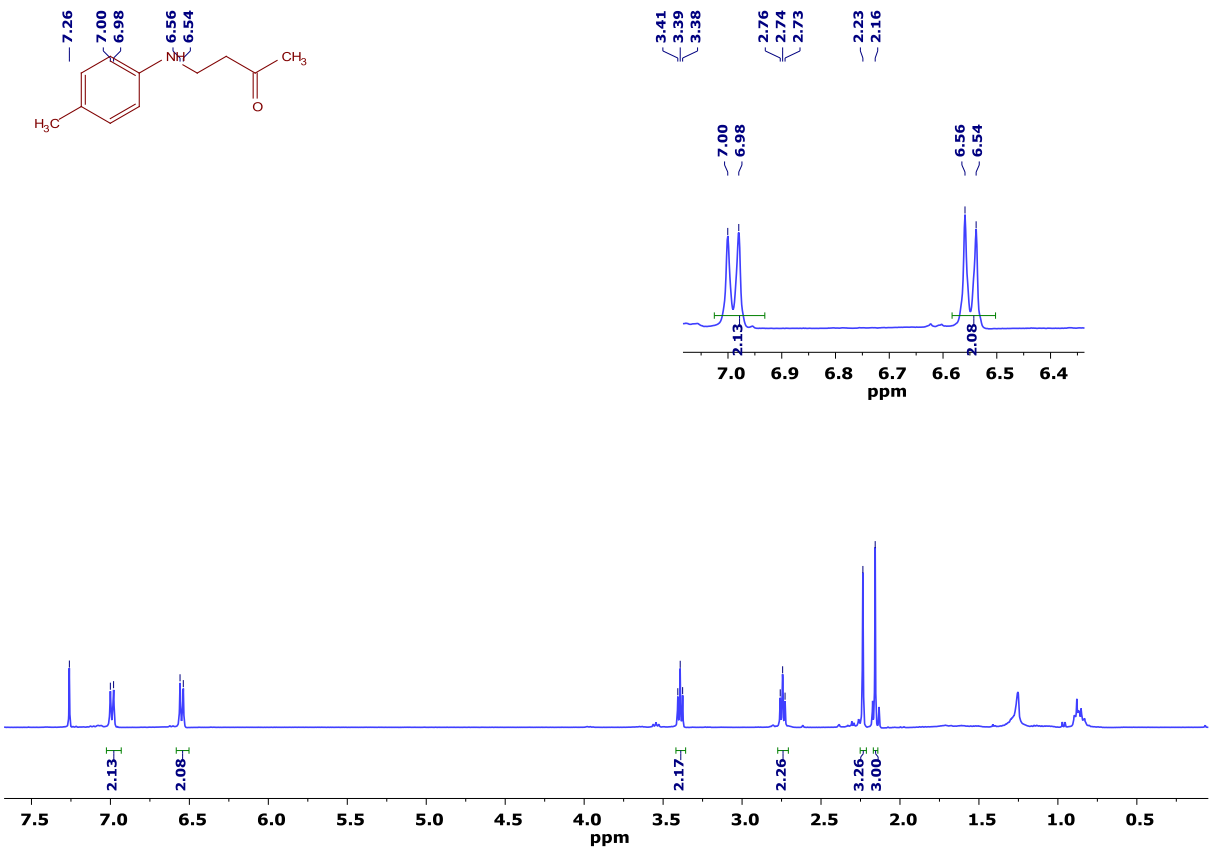
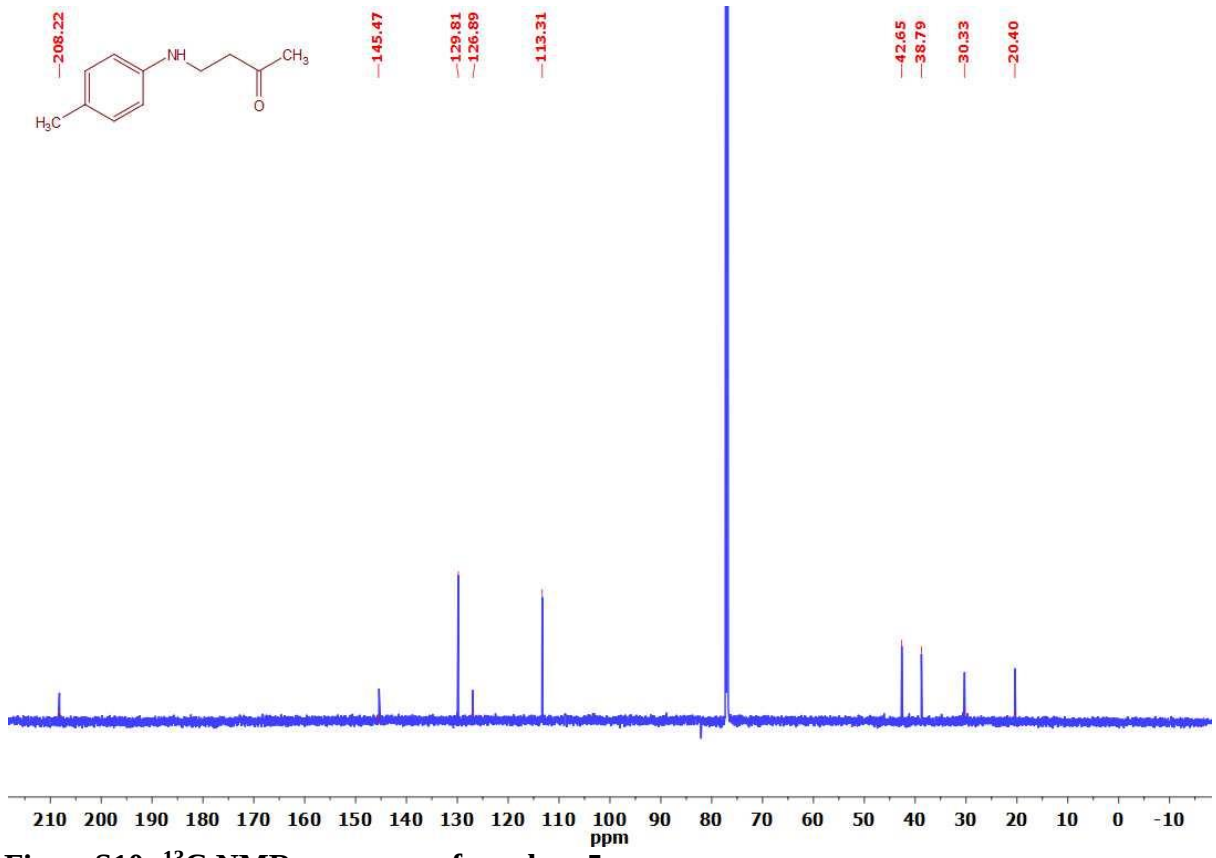


Figure S9: ^{1}H NMR spectrum of product 5



FigureS10: ^{13}C NMR spectrum of product 5

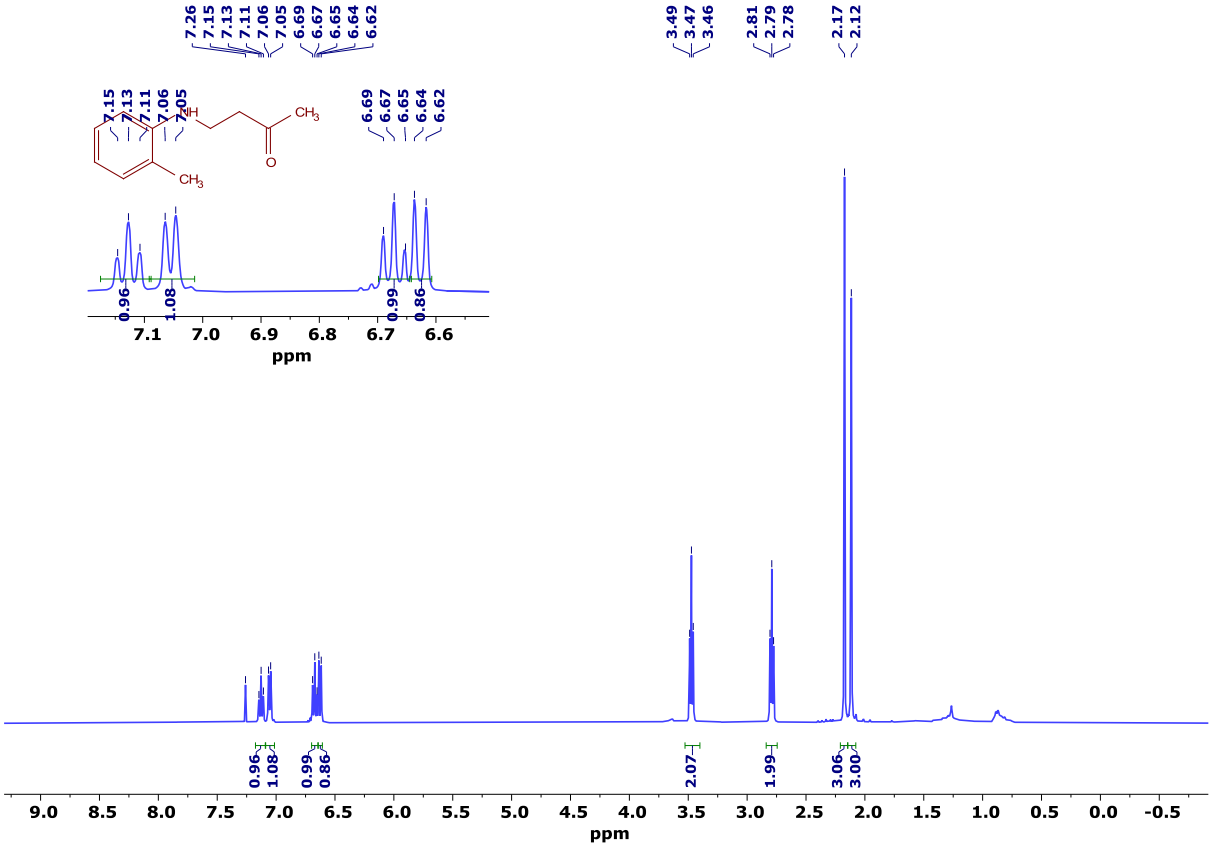


Figure S11: ^{1}H NMR spectrum of product 6

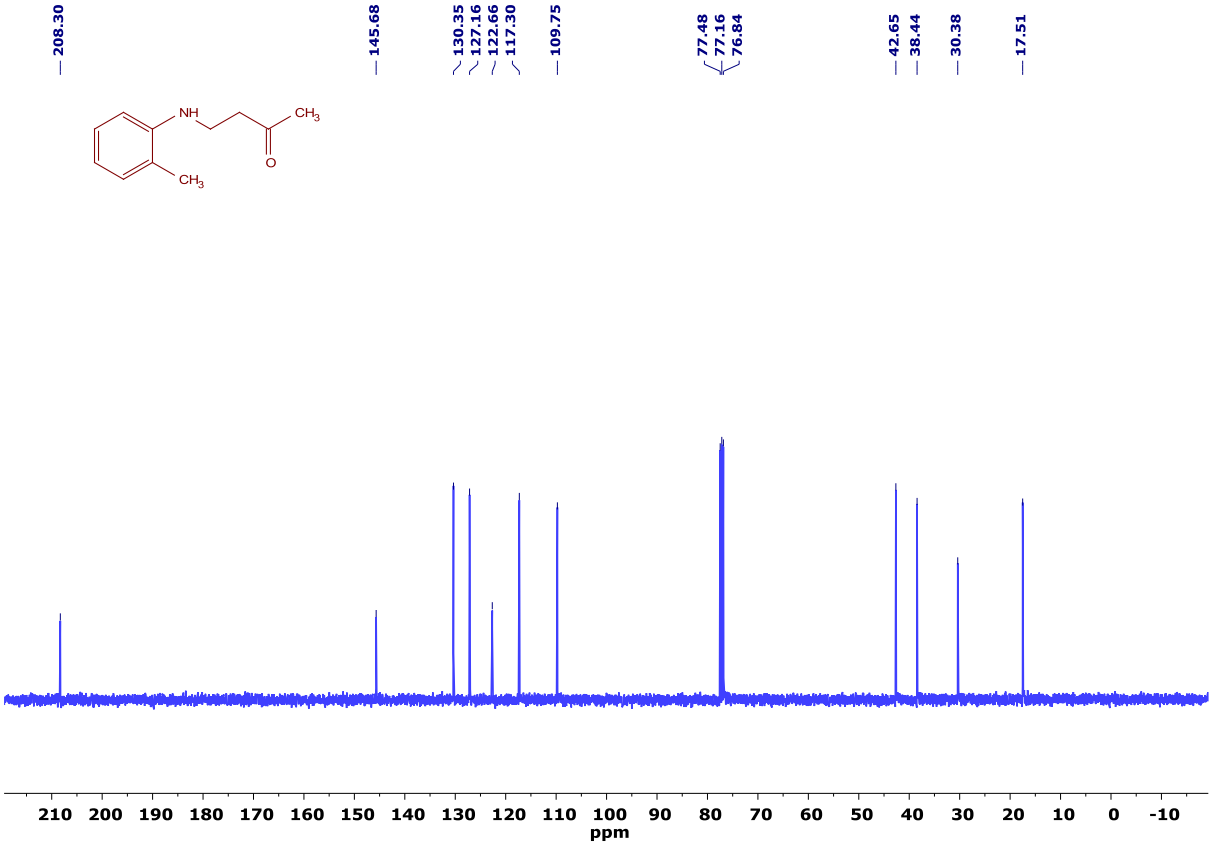


Figure S12: ^{13}C NMR spectrum of product 6

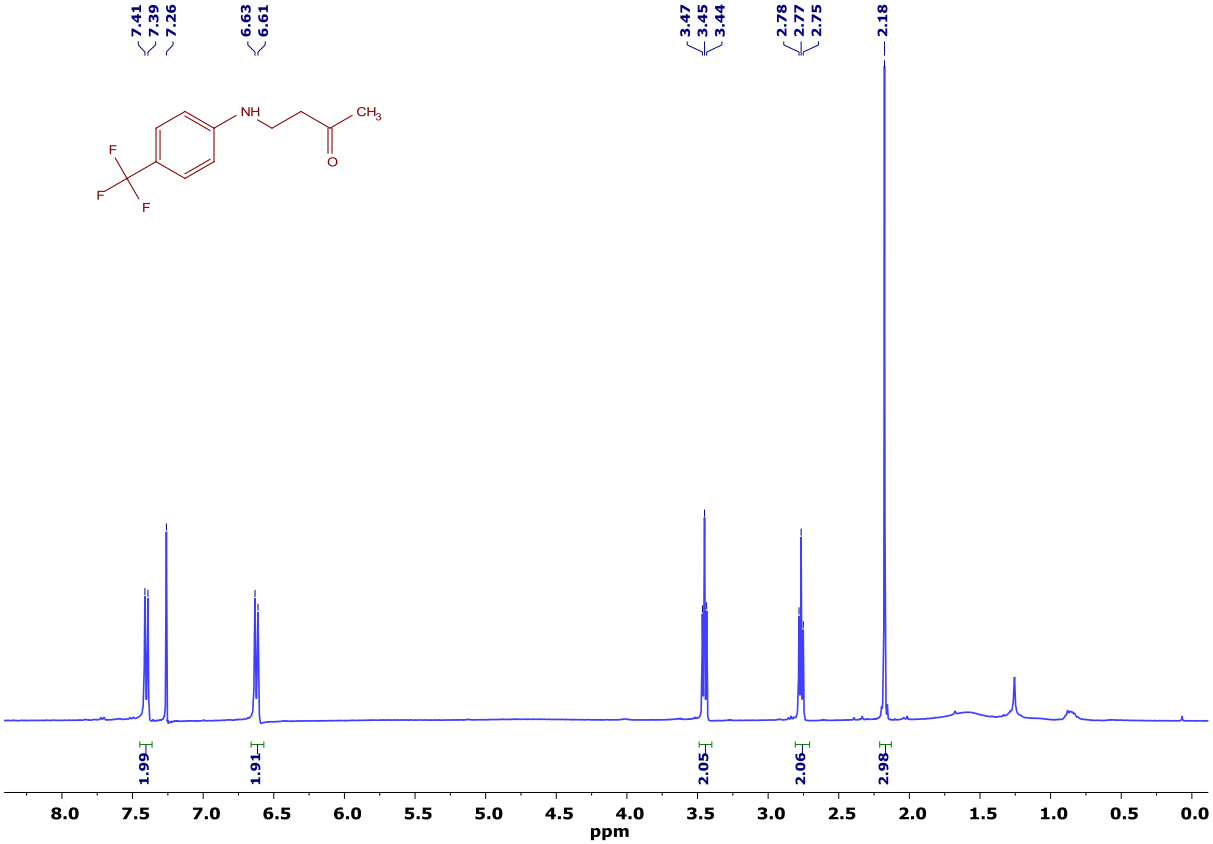


Figure S13: ^{1}H NMR spectrum of product 7

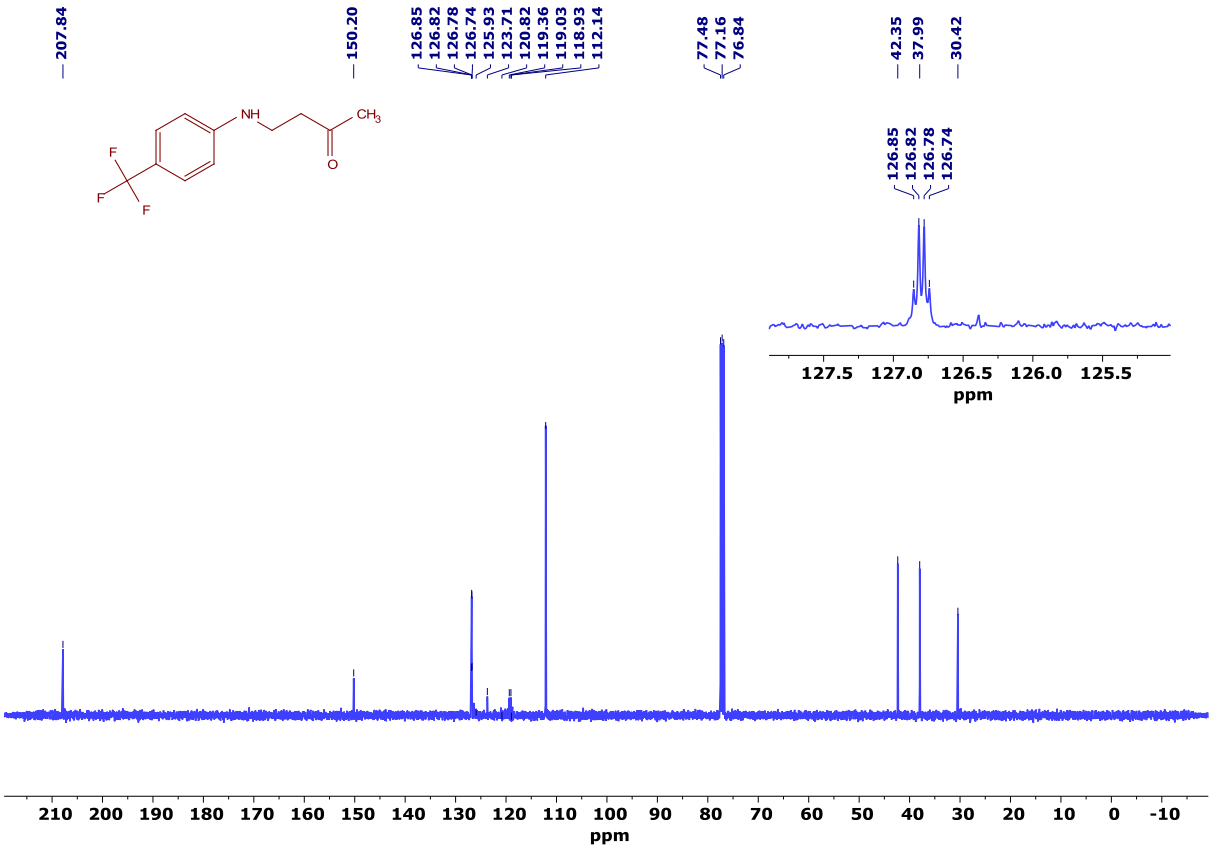


Figure S14: ^{13}C NMR spectrum of product 7

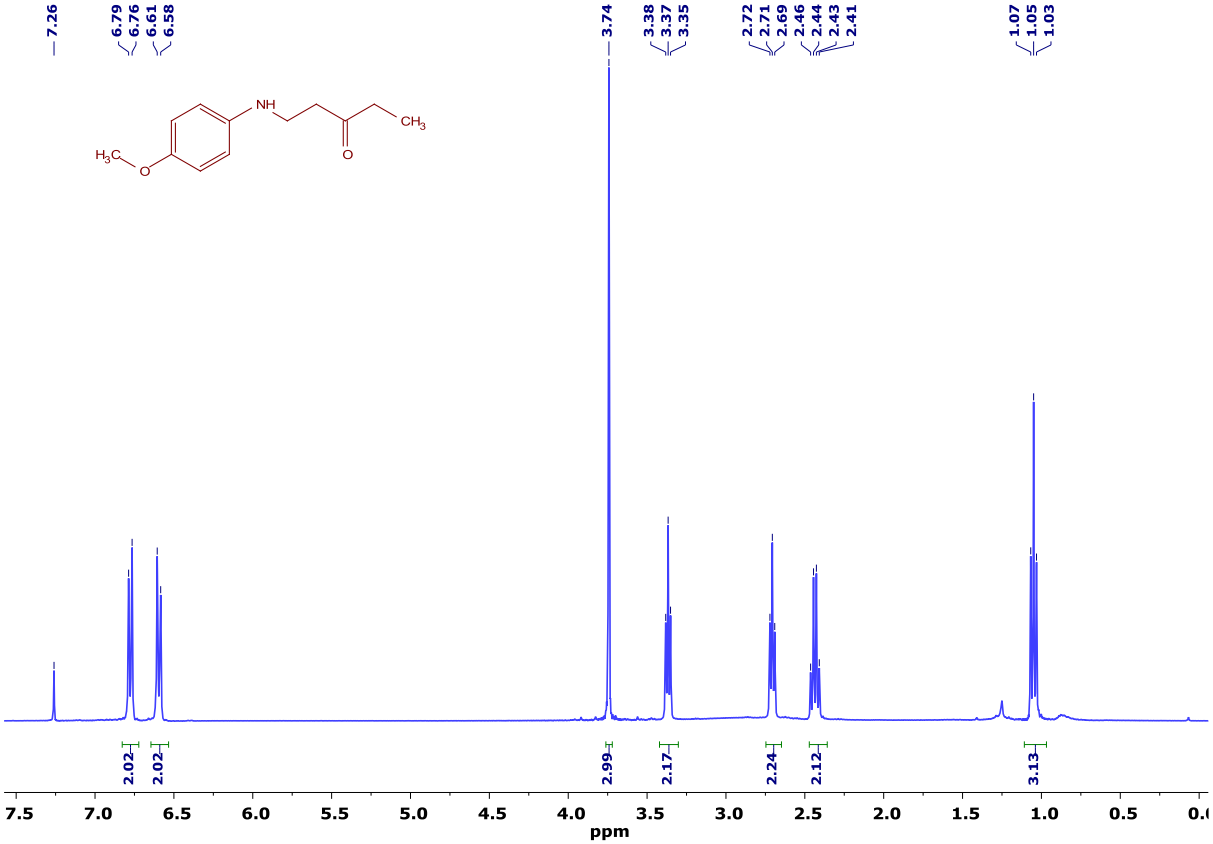


Figure S15: ^{1}H NMR spectrum of product 8

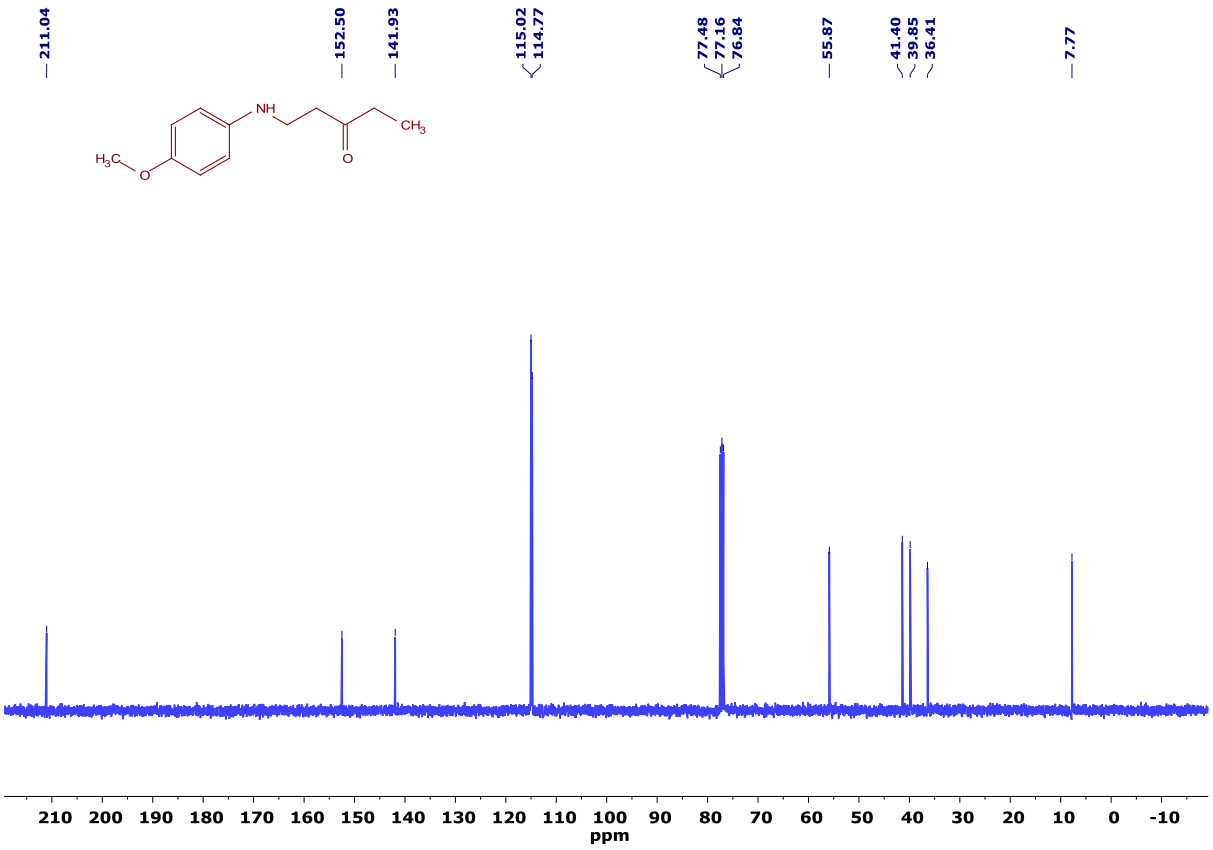


Figure S16: ^{13}C NMR spectrum of product 8

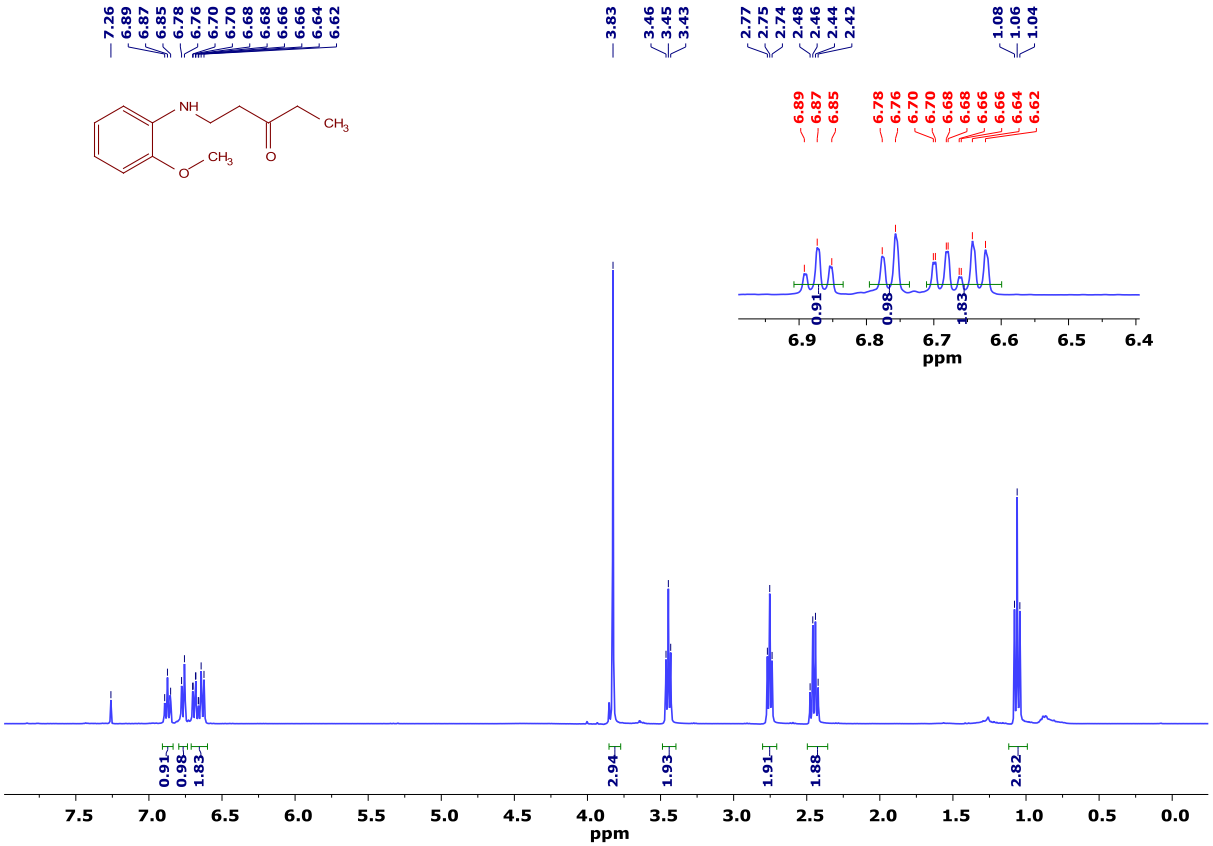


Figure S17: ^{1}H NMR spectrum of product 9

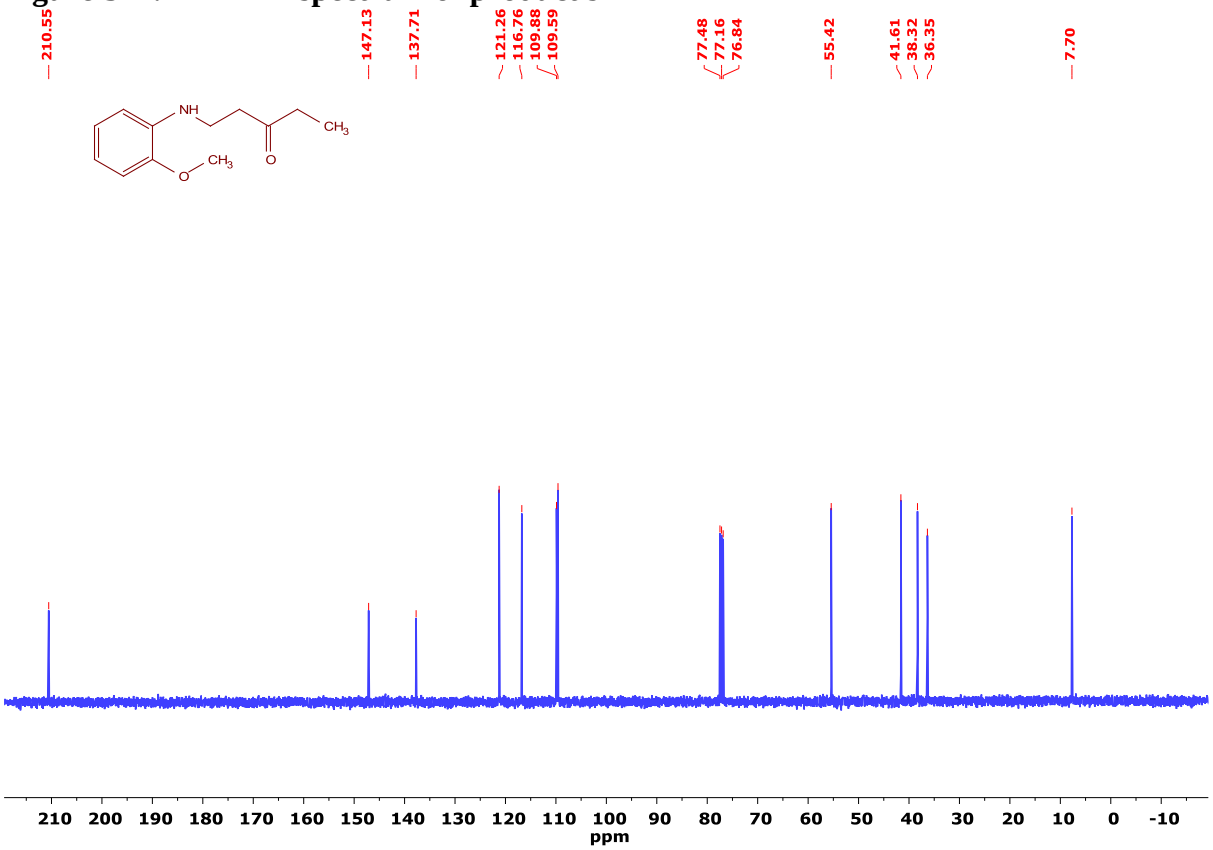


Figure S18: ^{13}C NMR spectrum of product 9

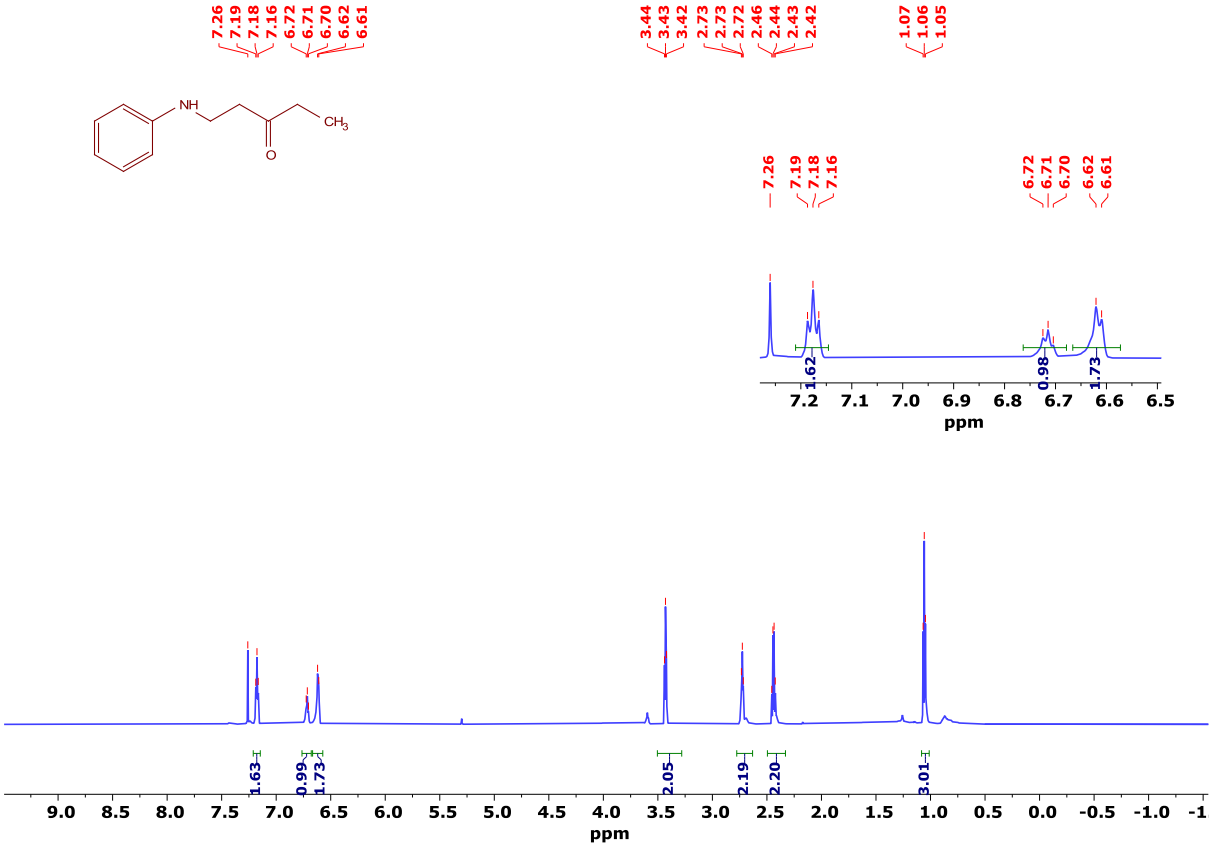


Figure S19: ^{1}H NMR spectrum of product 10

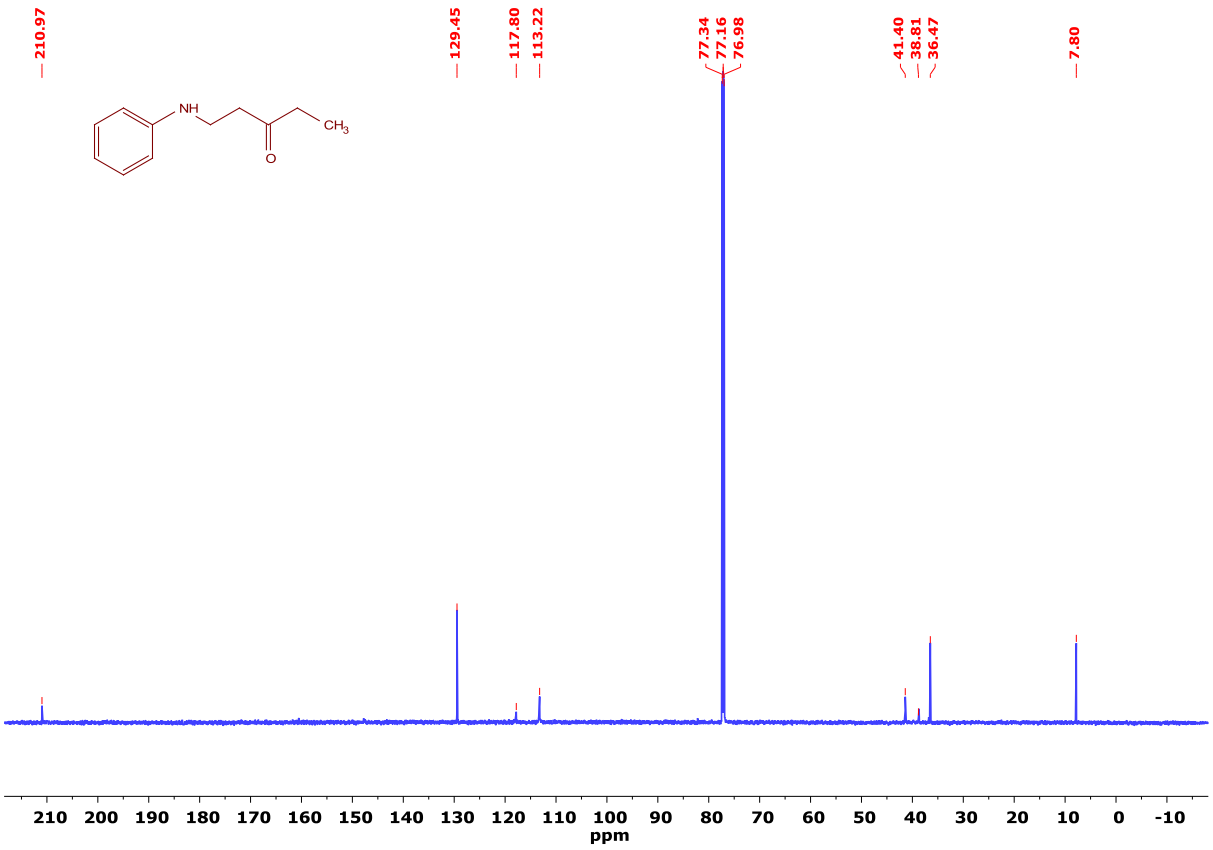


Figure S20: ^{13}C NMR spectrum of product 10

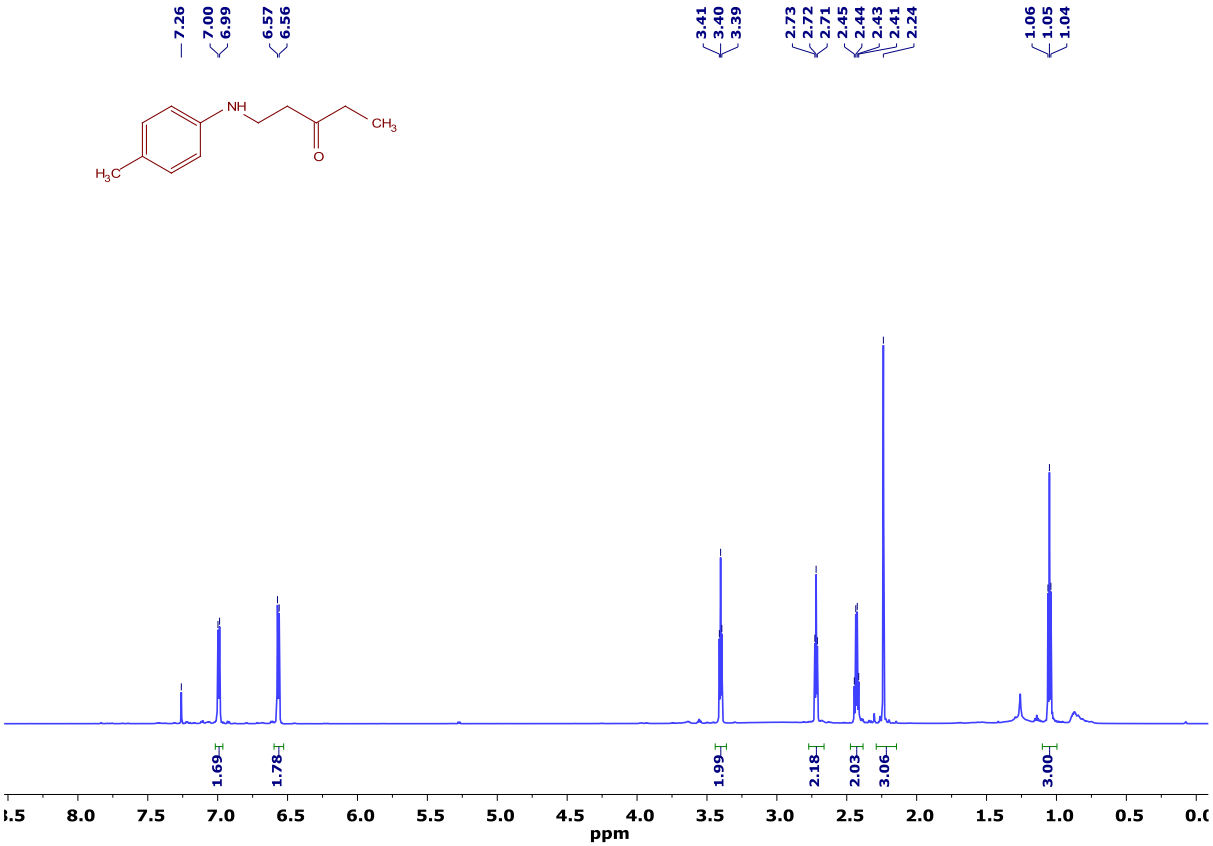


Figure S21: ^{1}H NMR spectrum of product 11

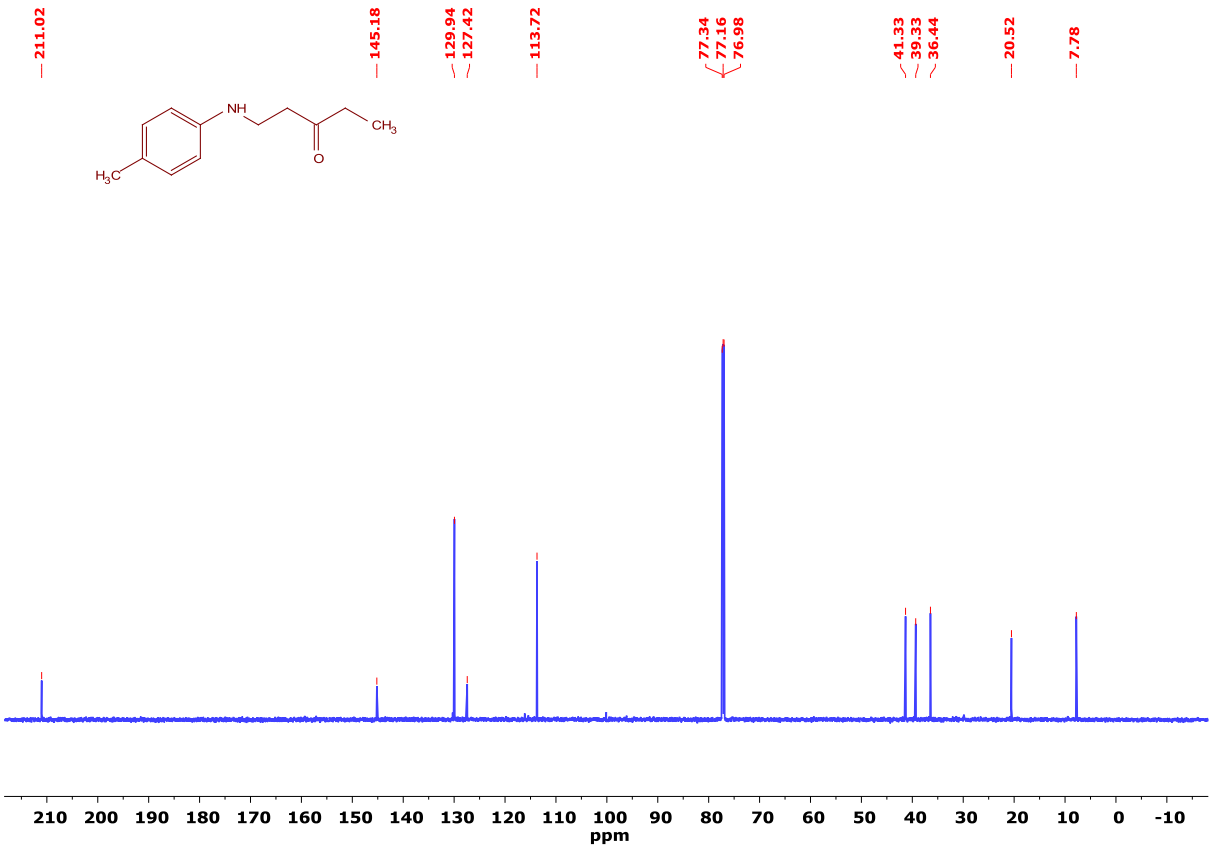


Figure S22: ^{13}C NMR spectrum of product 11

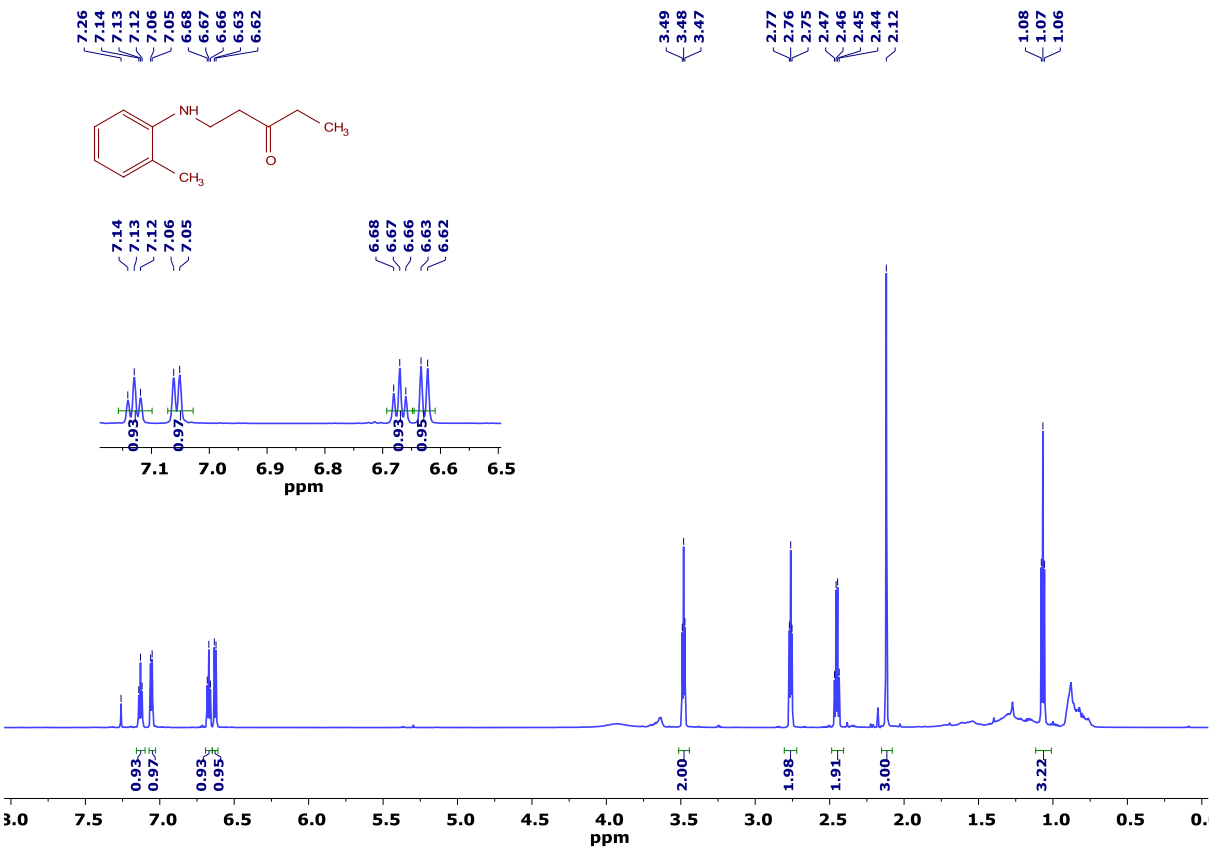


Figure S23: ^{1}H NMR spectrum of product 12

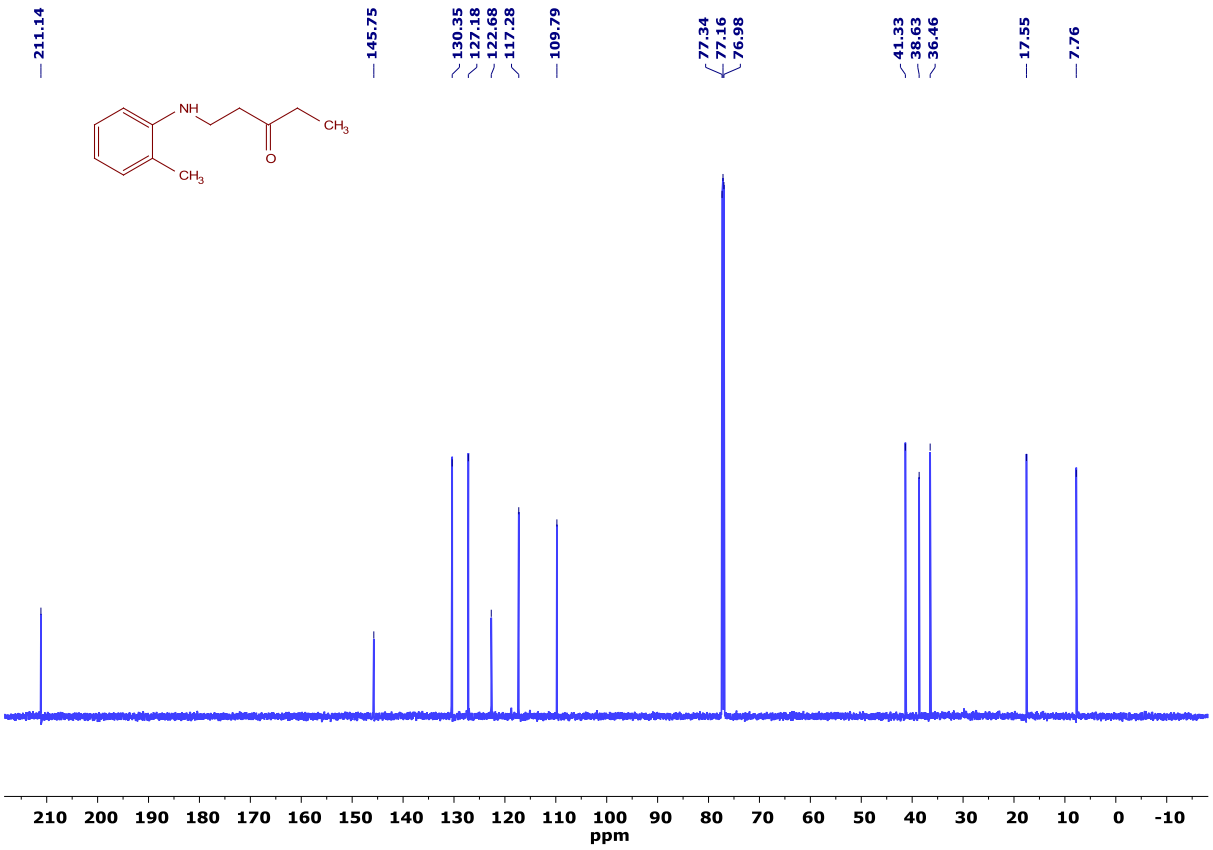


Figure S24: ^{13}C NMR spectrum of product 12

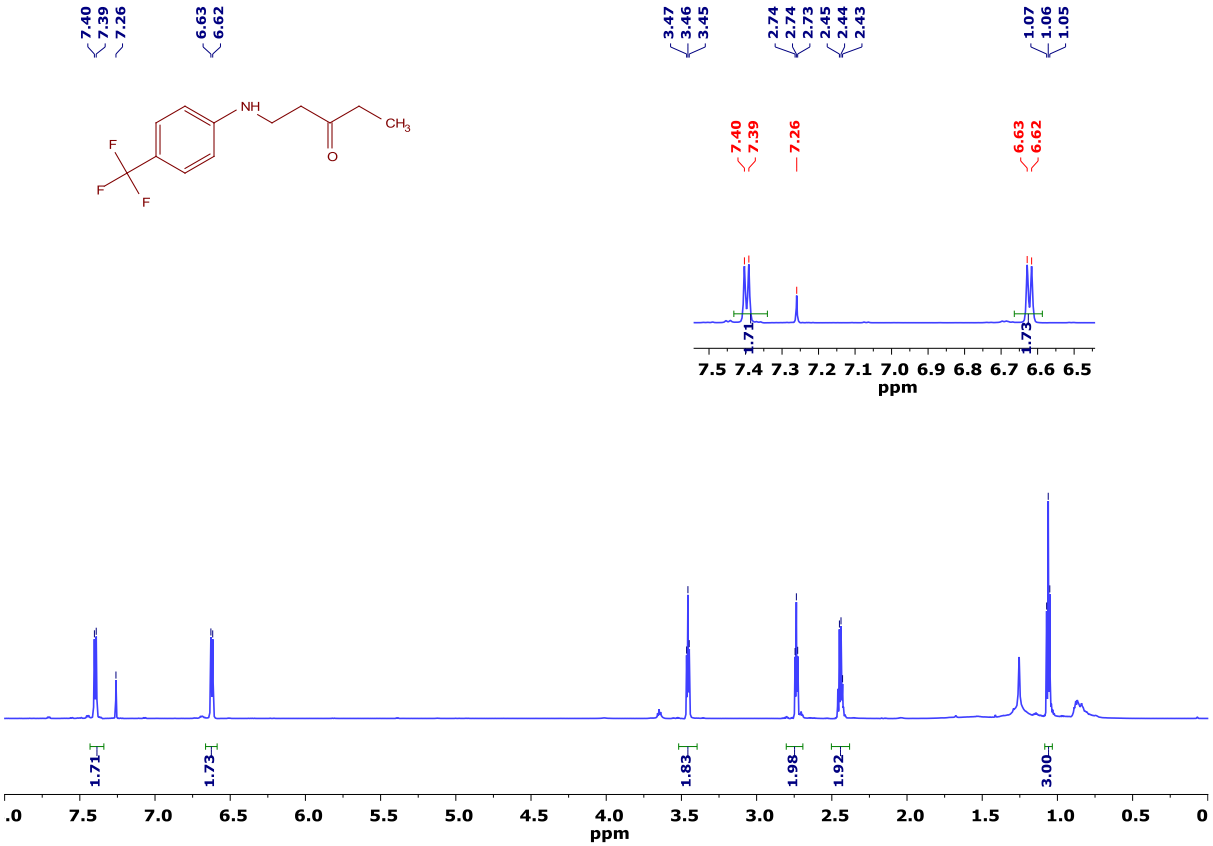


Figure S25: ^{1}H NMR spectrum of product 13

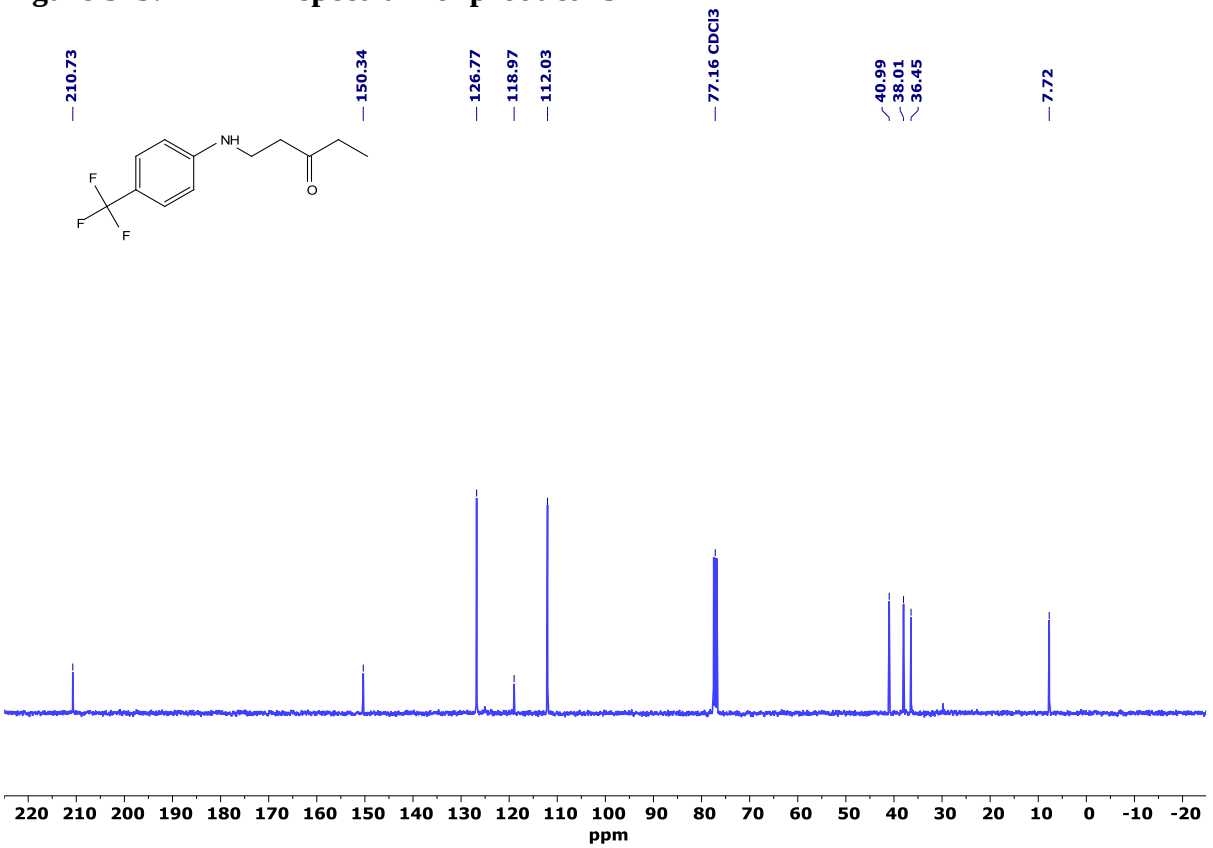


Figure S26: {^{19}F}{^{1}H}^{13}C NMR spectrum of product 13

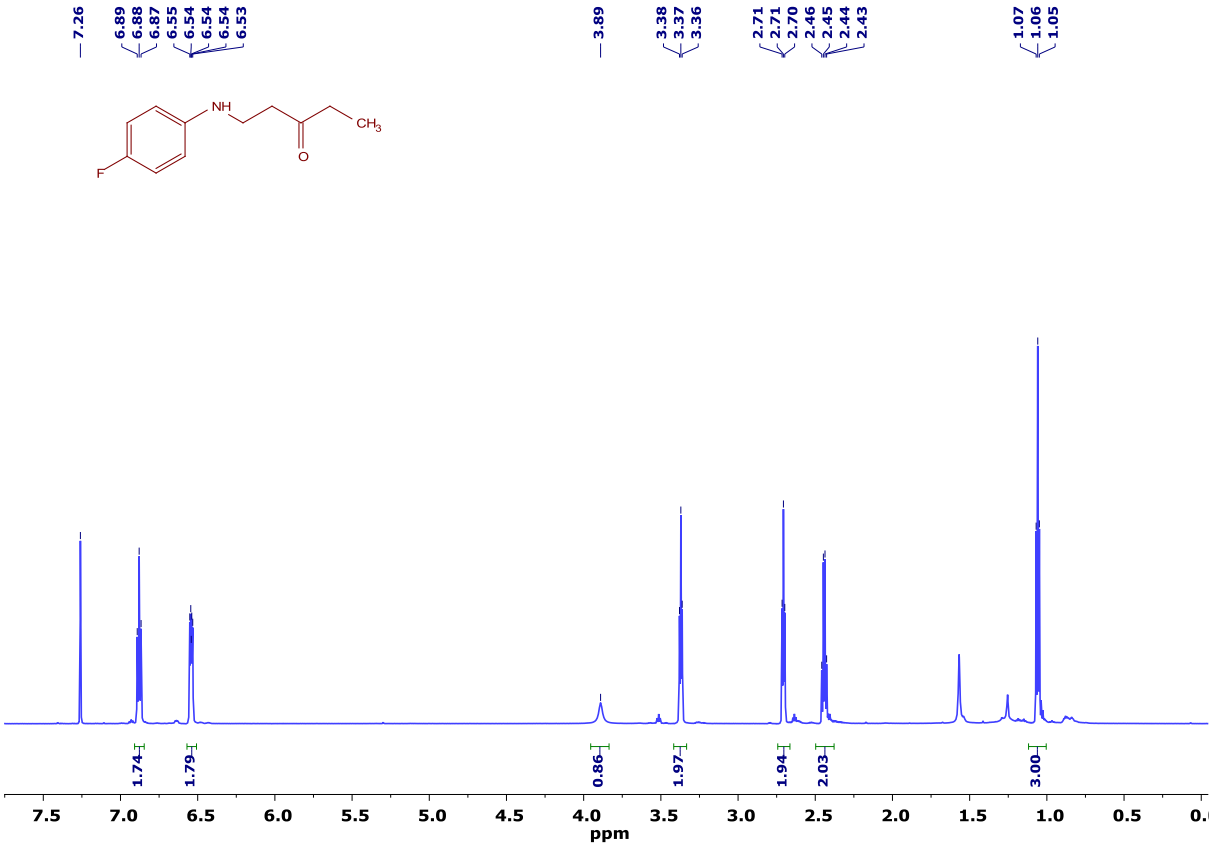


Figure S27: ^{1}H NMR spectrum of product 14

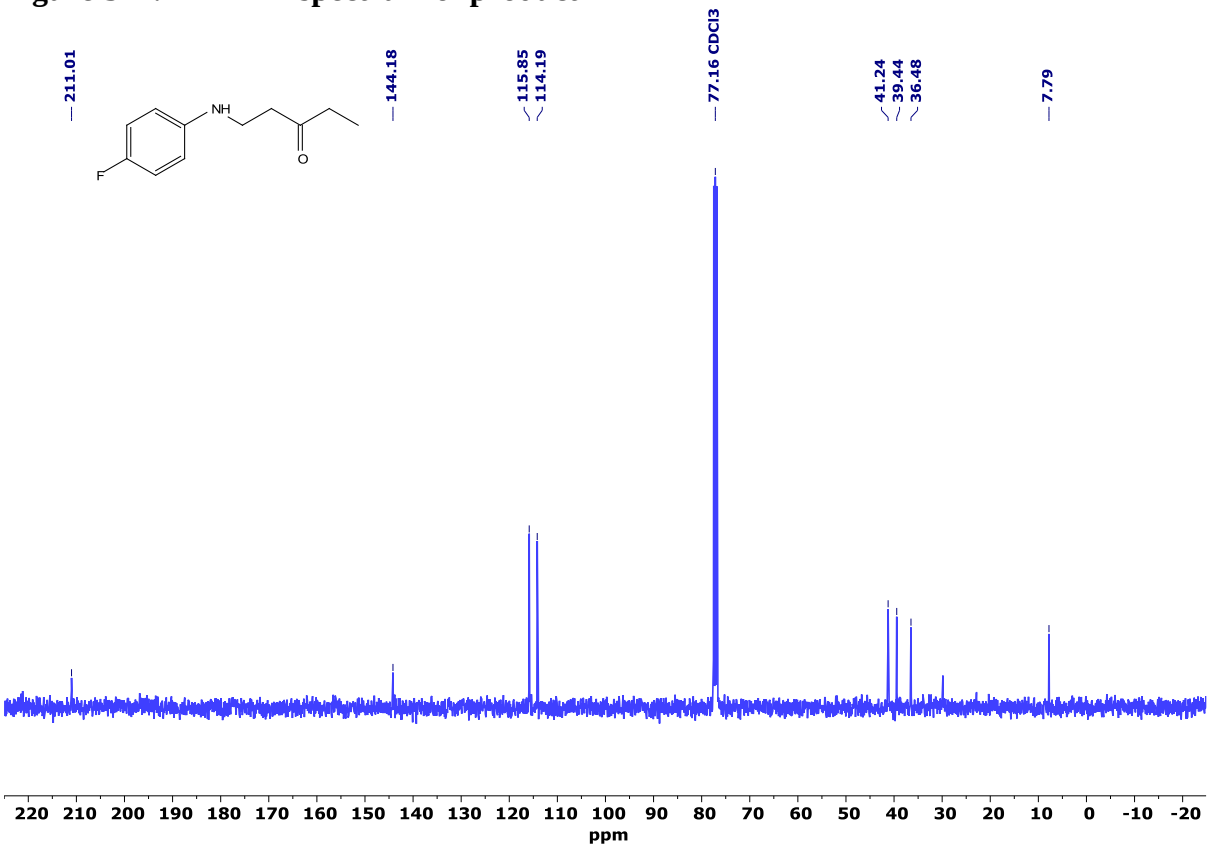


Figure S28: {^{19}F}{^{1}H}^{13}C NMR spectrum of product 14

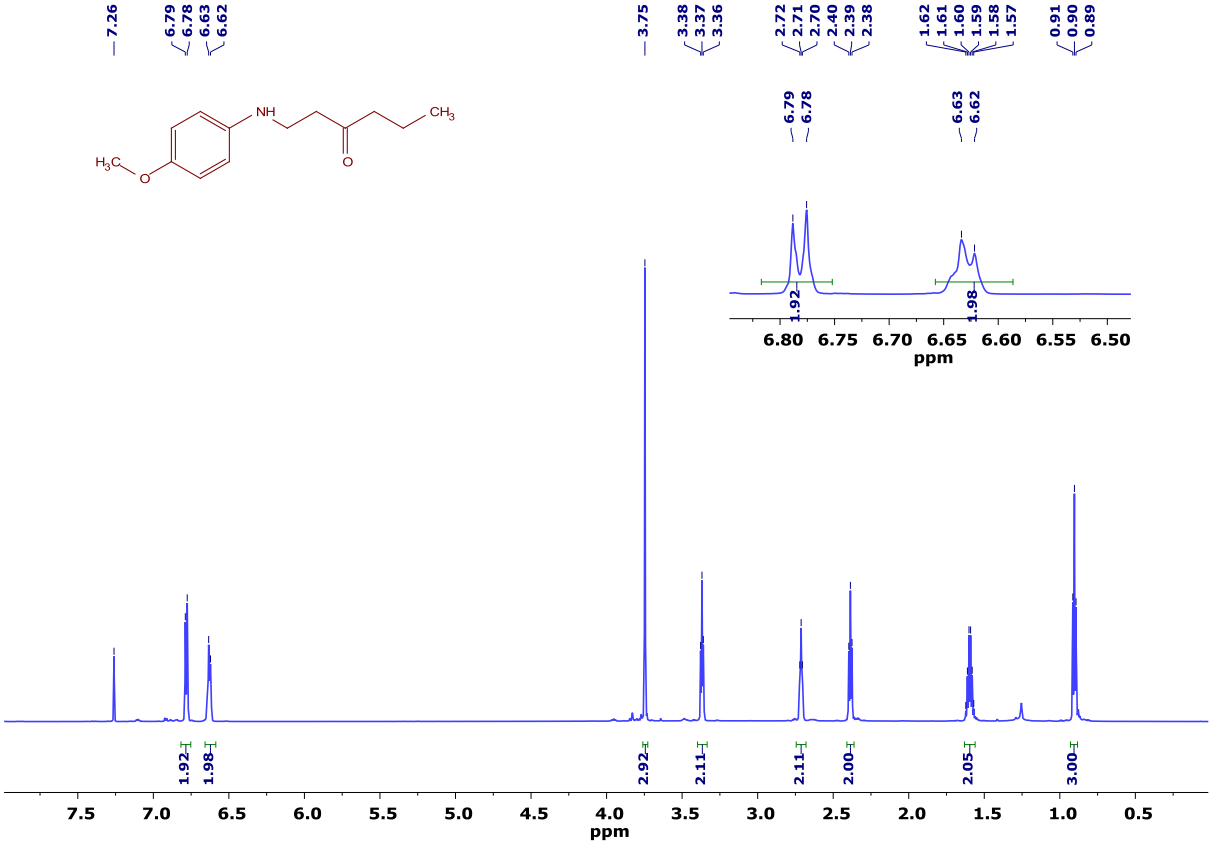


Figure S29: ^{1}H NMR spectrum of product 15

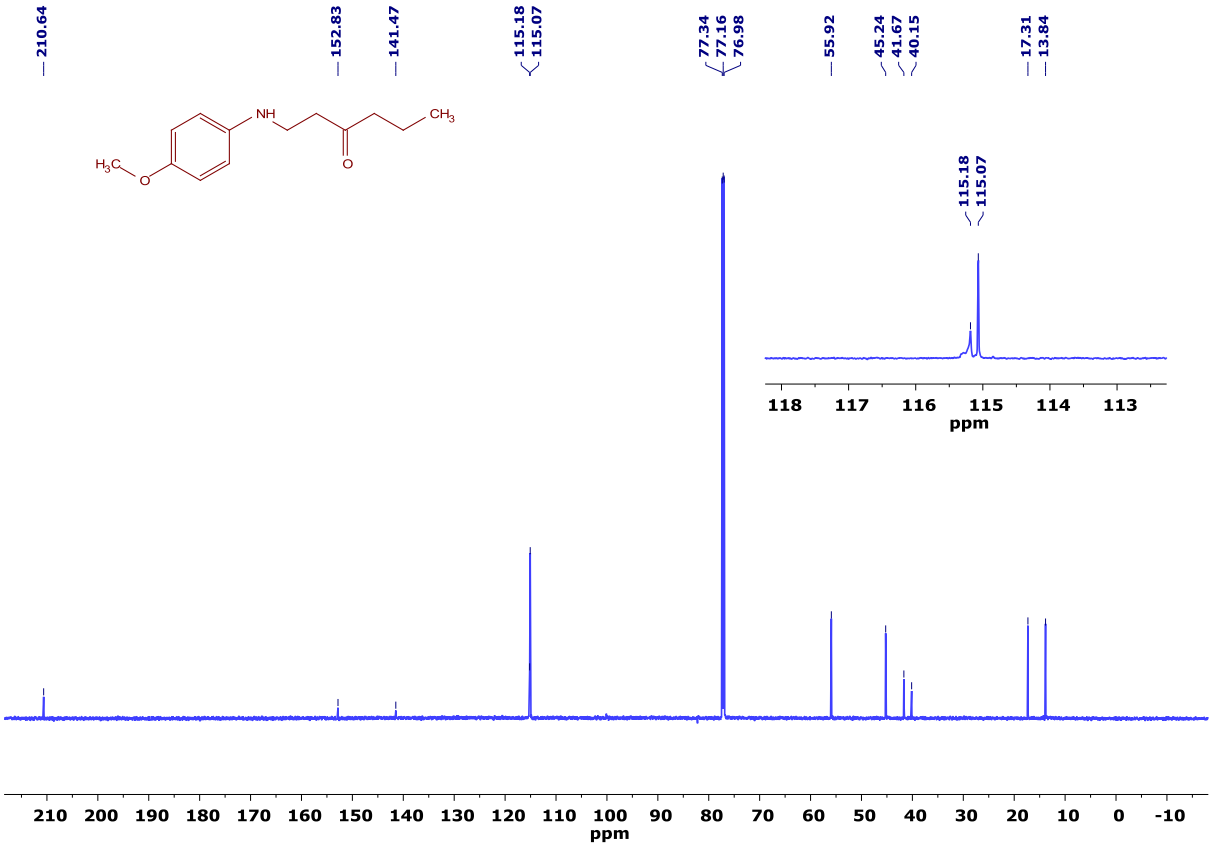


Figure S30: ^{13}C NMR Spectrum of product 15

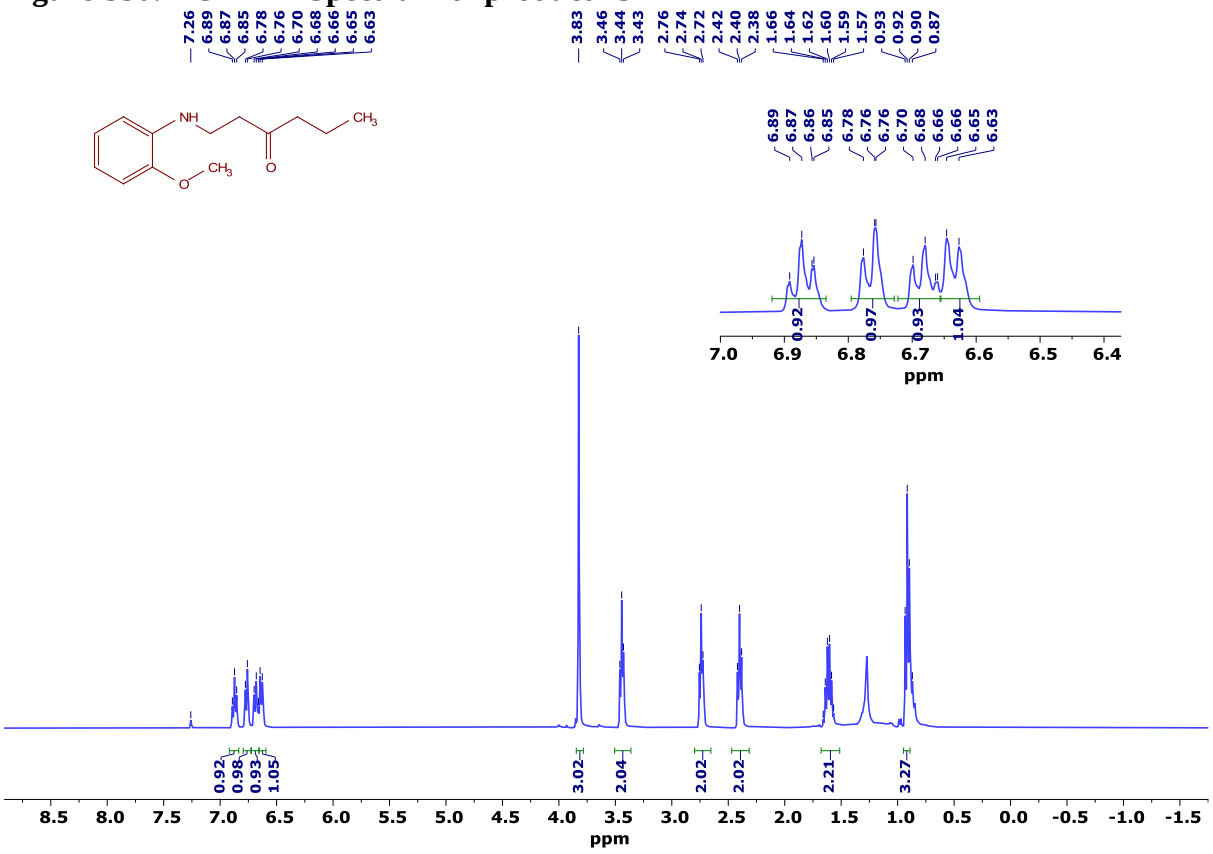


Figure S31: ^{1}H NMR spectrum of product 16

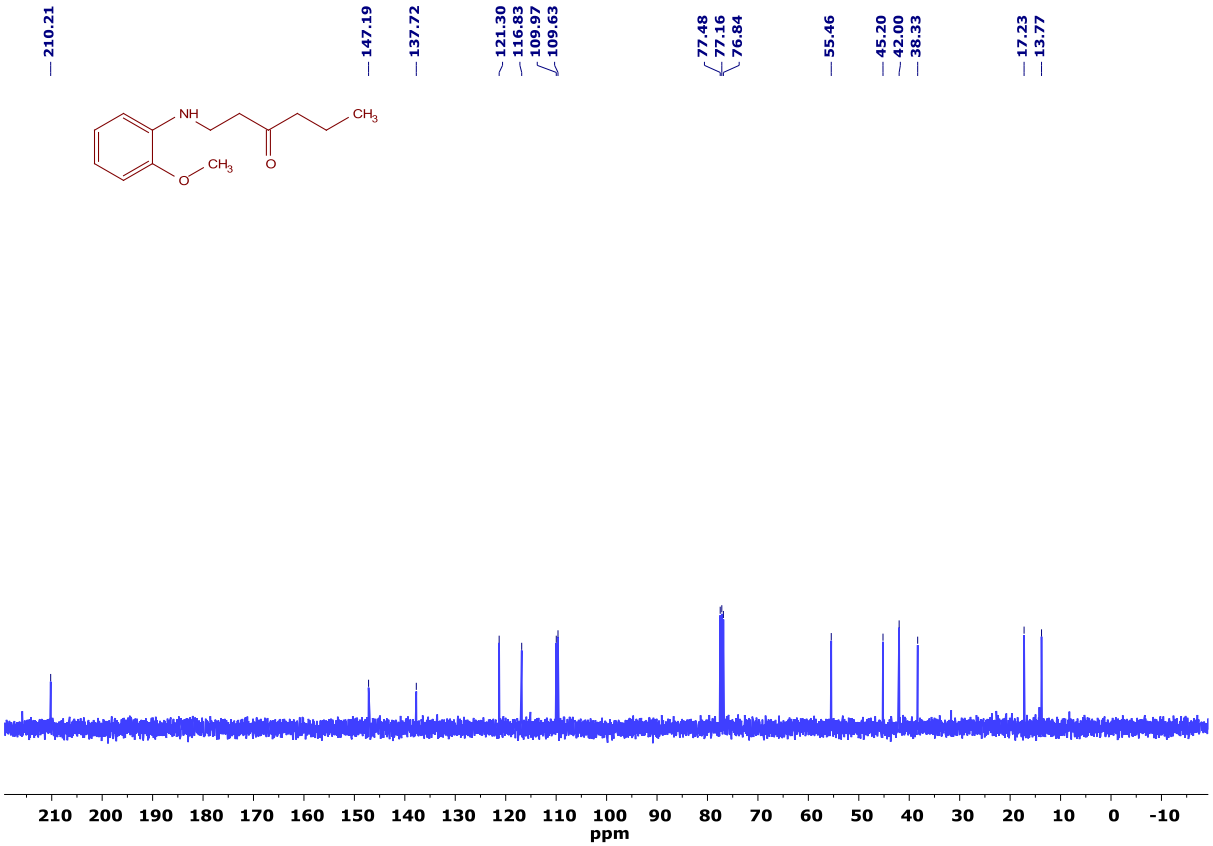


Figure S32: ^{13}C NMR spectrum of product 16

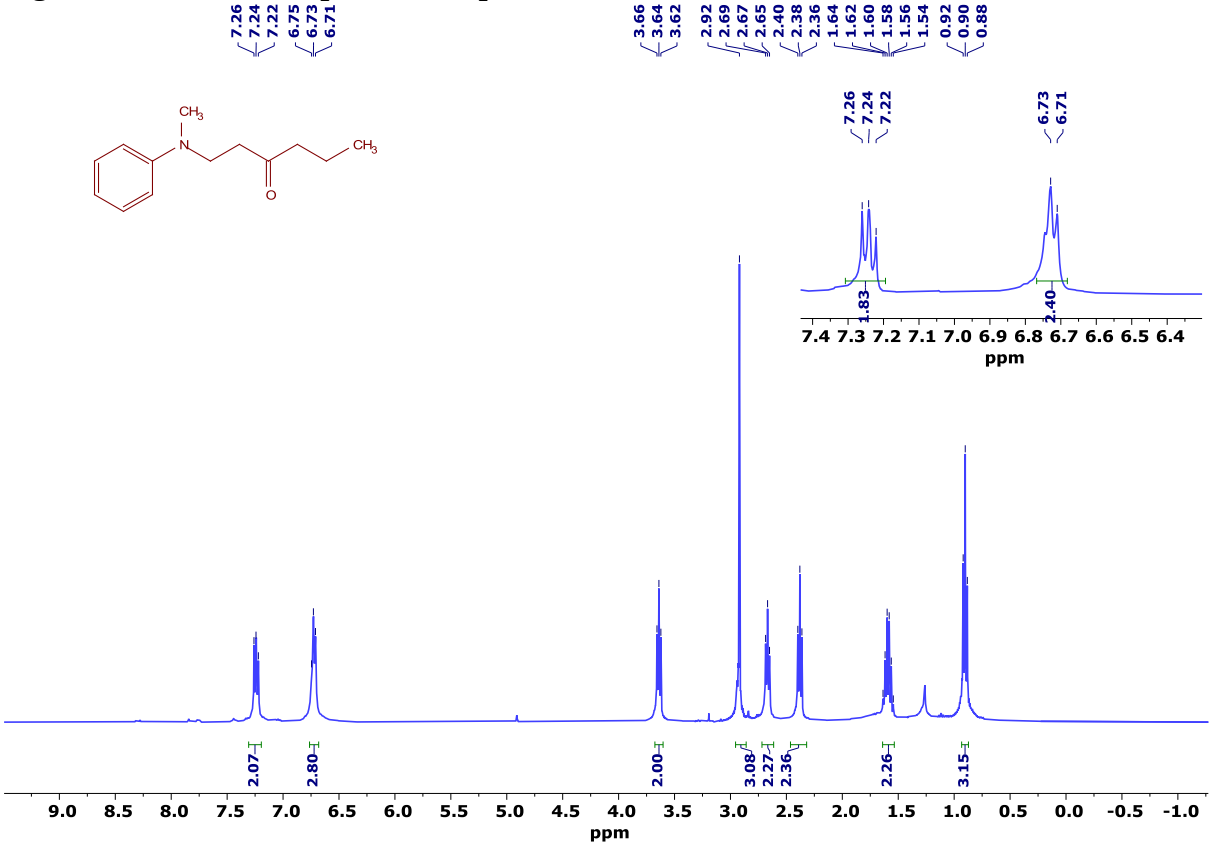


Figure S33: ^{1}H NMR spectrum of product 17

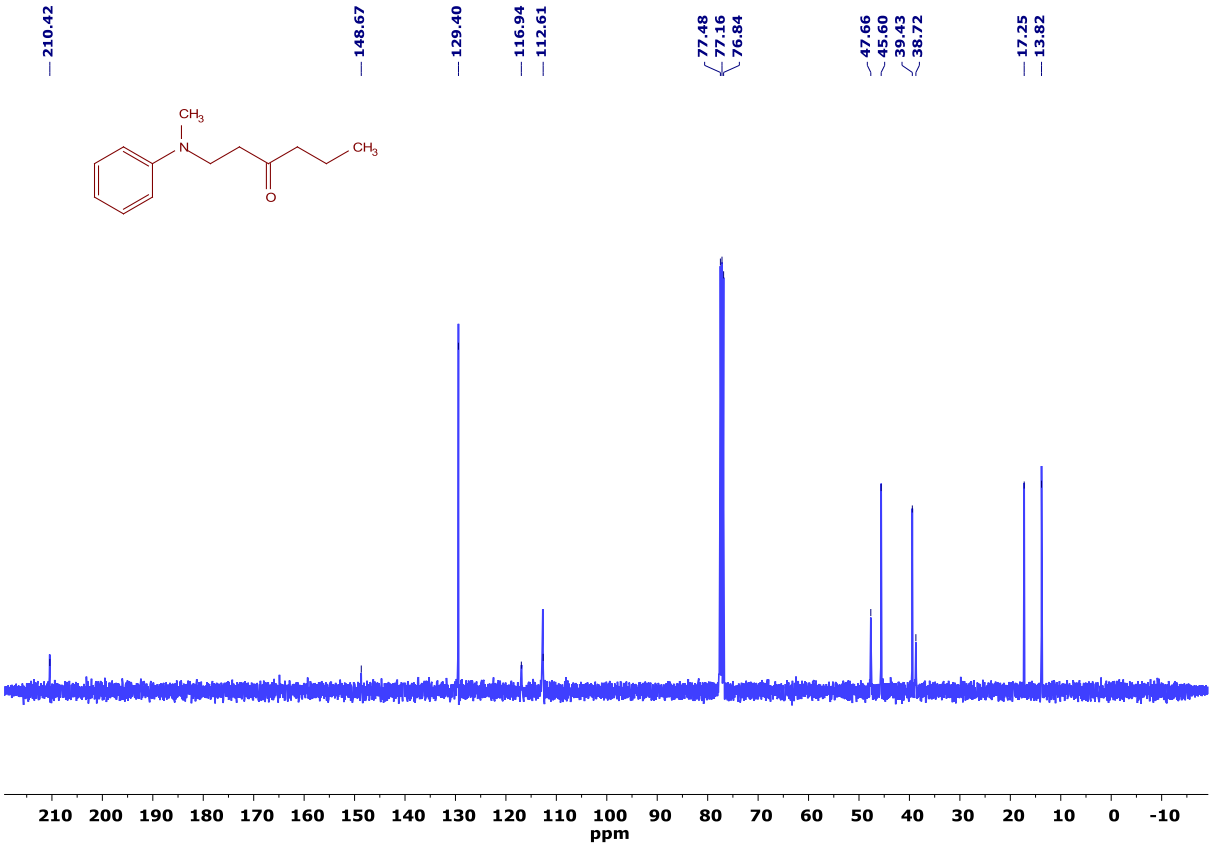


Figure S34: ^{13}C NMR spectrum of product 17

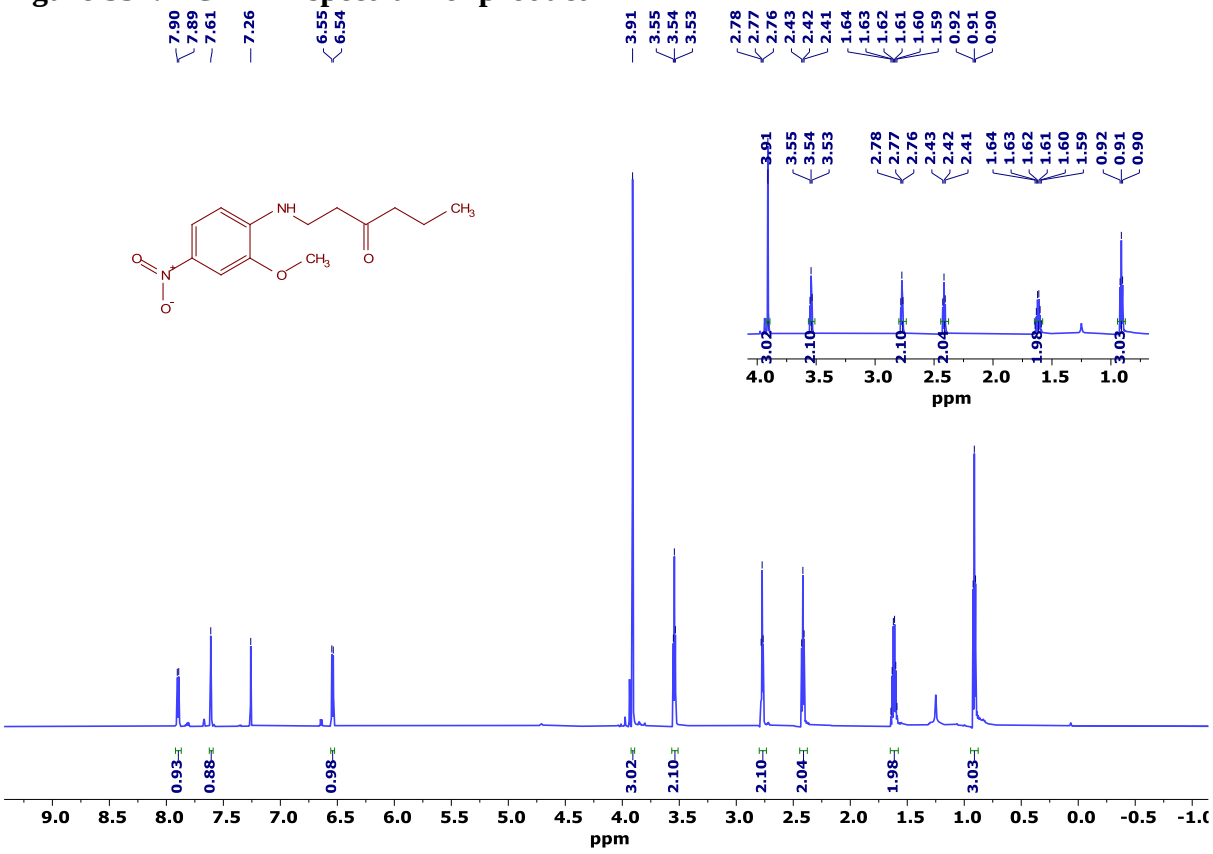


Figure S35: ^{1}H NMR spectrum of product 18

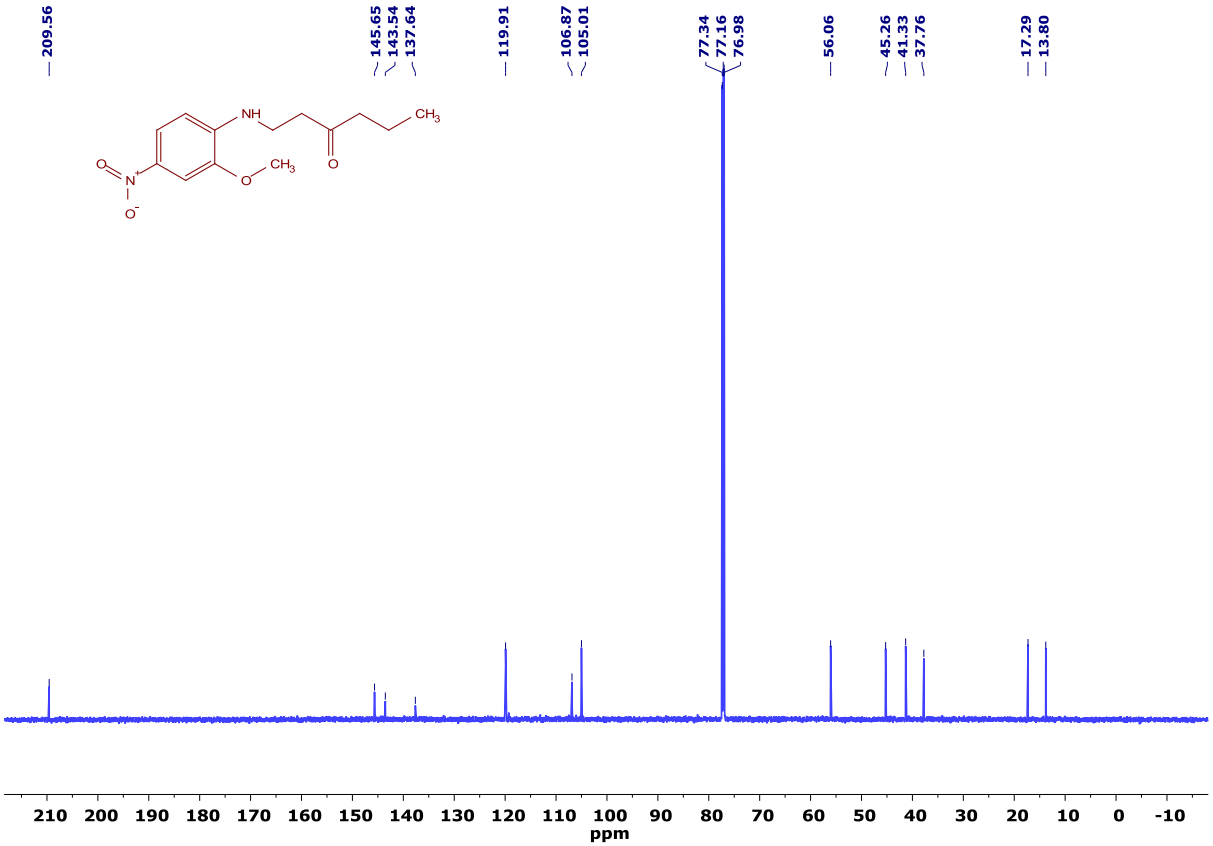


Figure S36: ^{13}C NMR spectrum of product 18

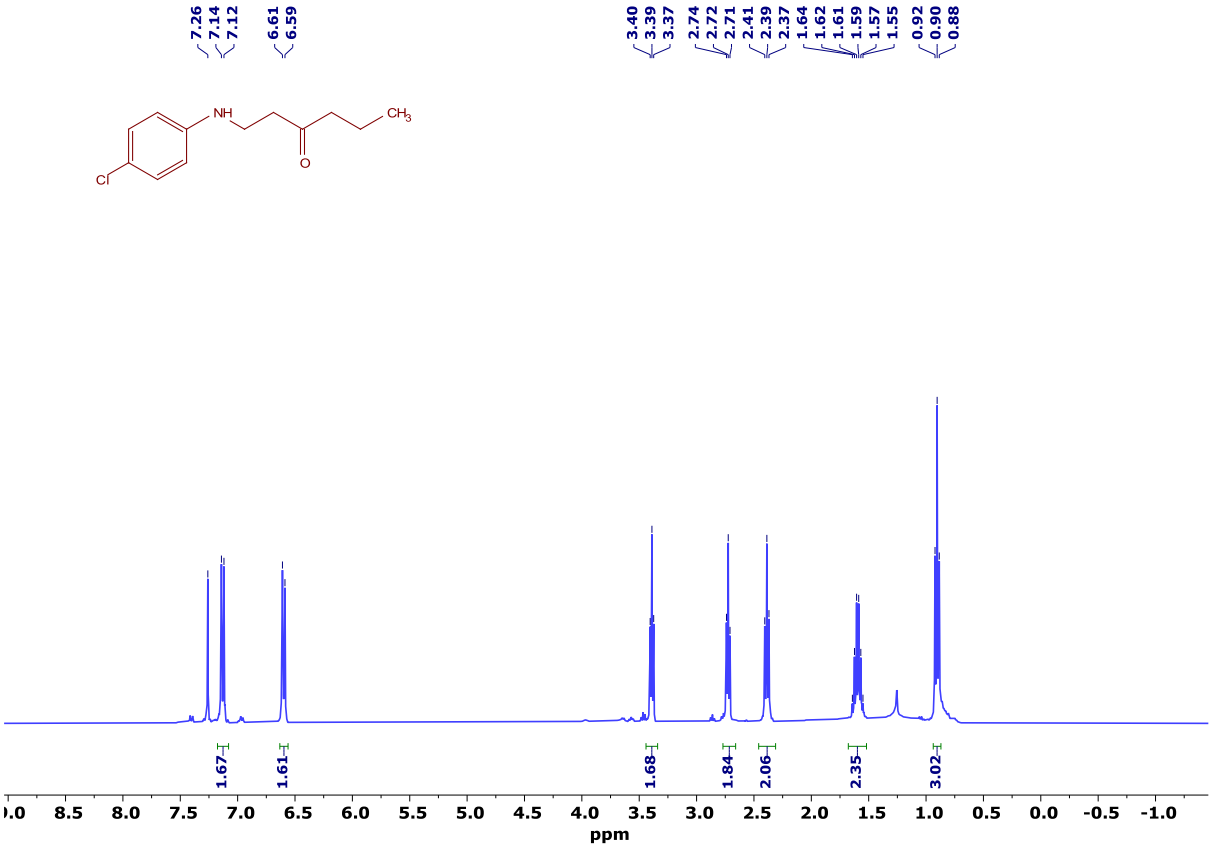


Figure S37: ^{1}H NMR spectrum of product 19

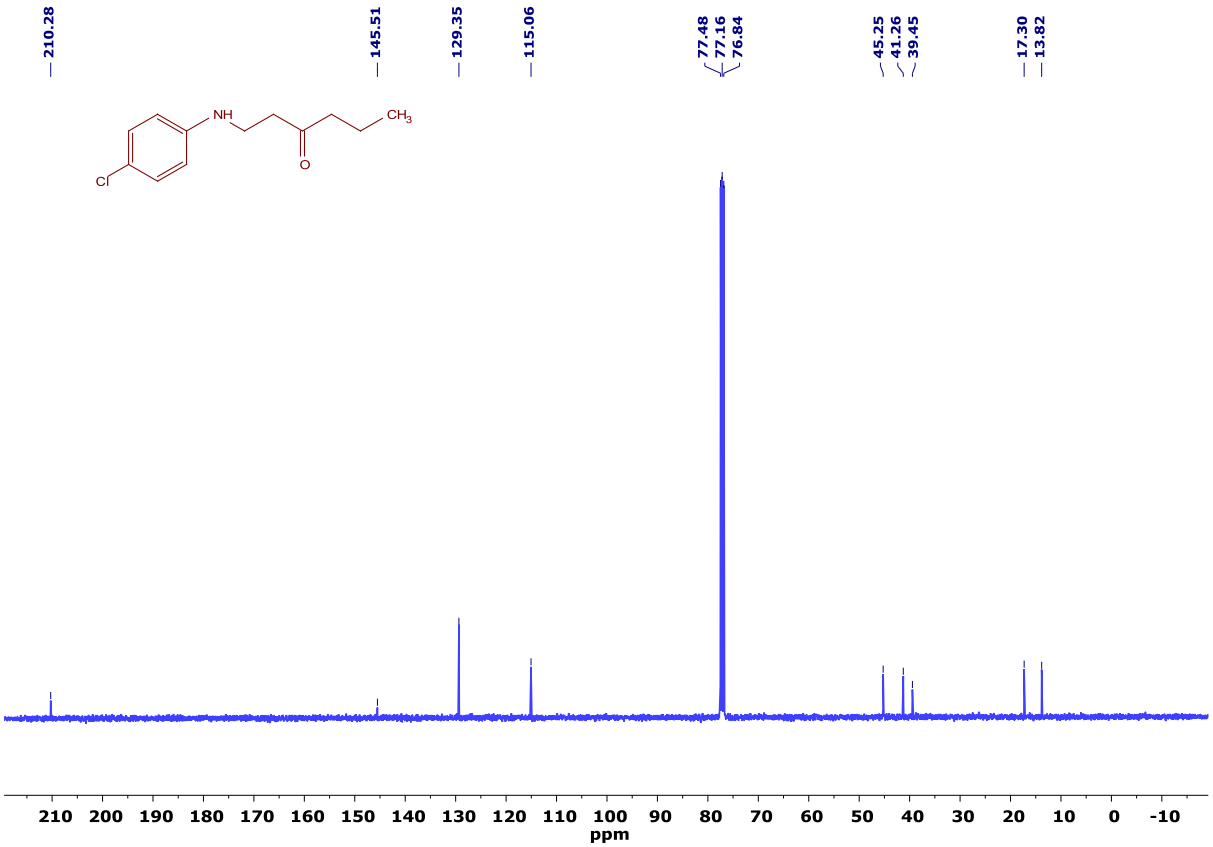


Figure S38: ^{13}C NMR spectrum of product 19

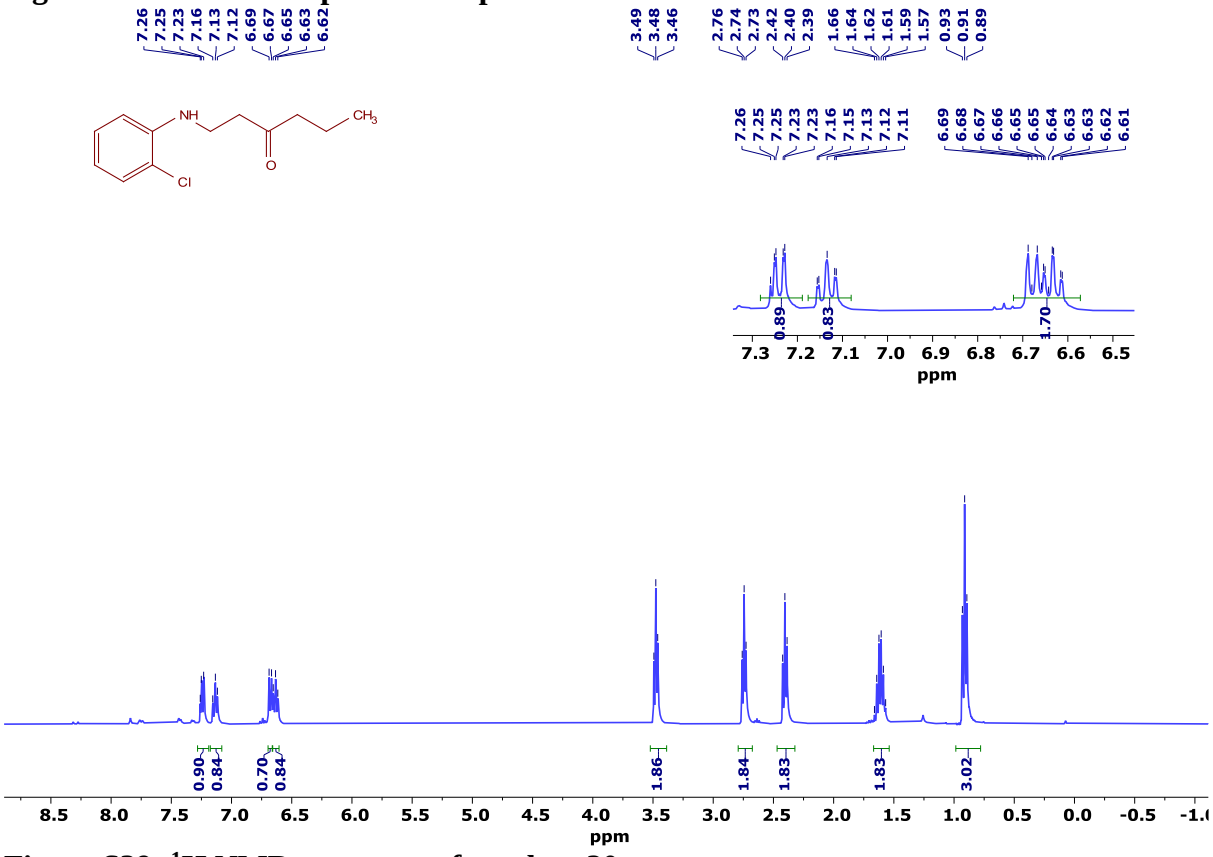


Figure S39: ^{1}H NMR spectrum of product 20

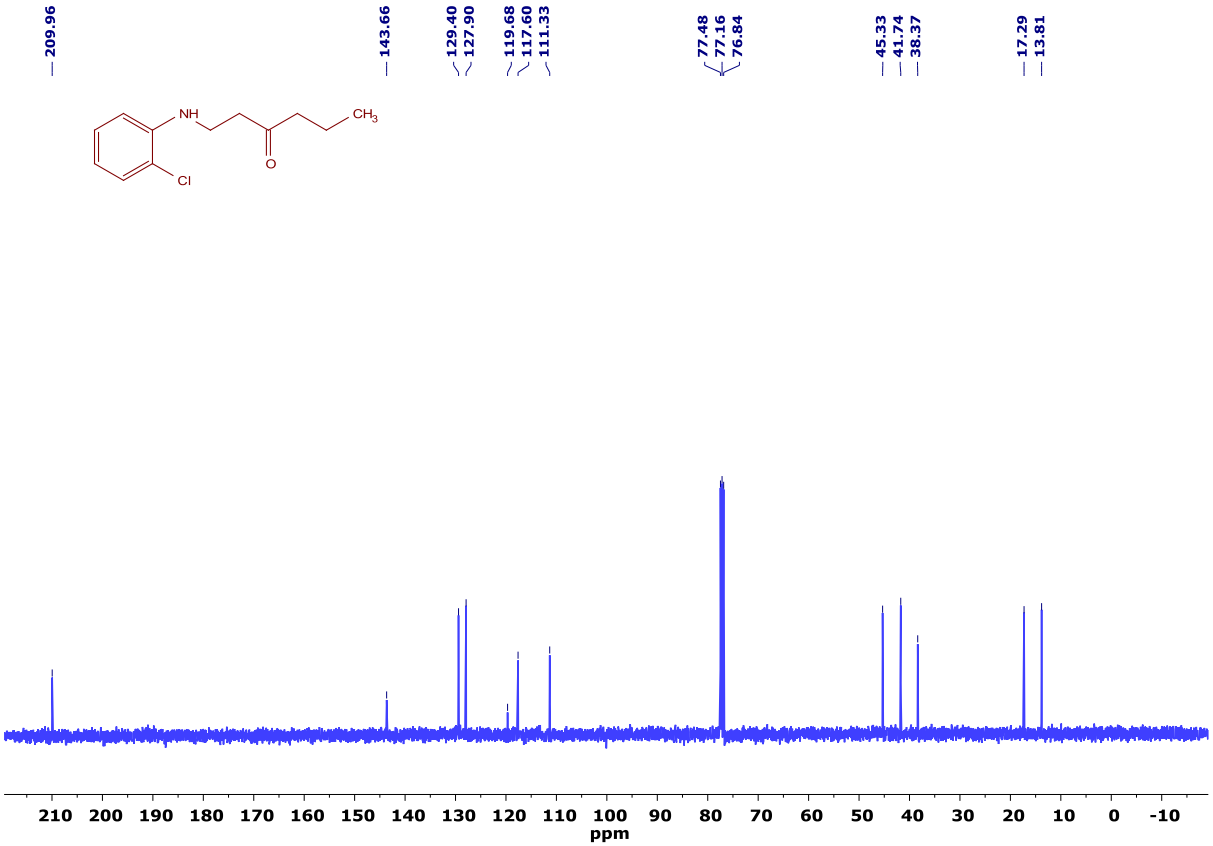


Figure S40: ^{13}C NMR spectrum of product 20

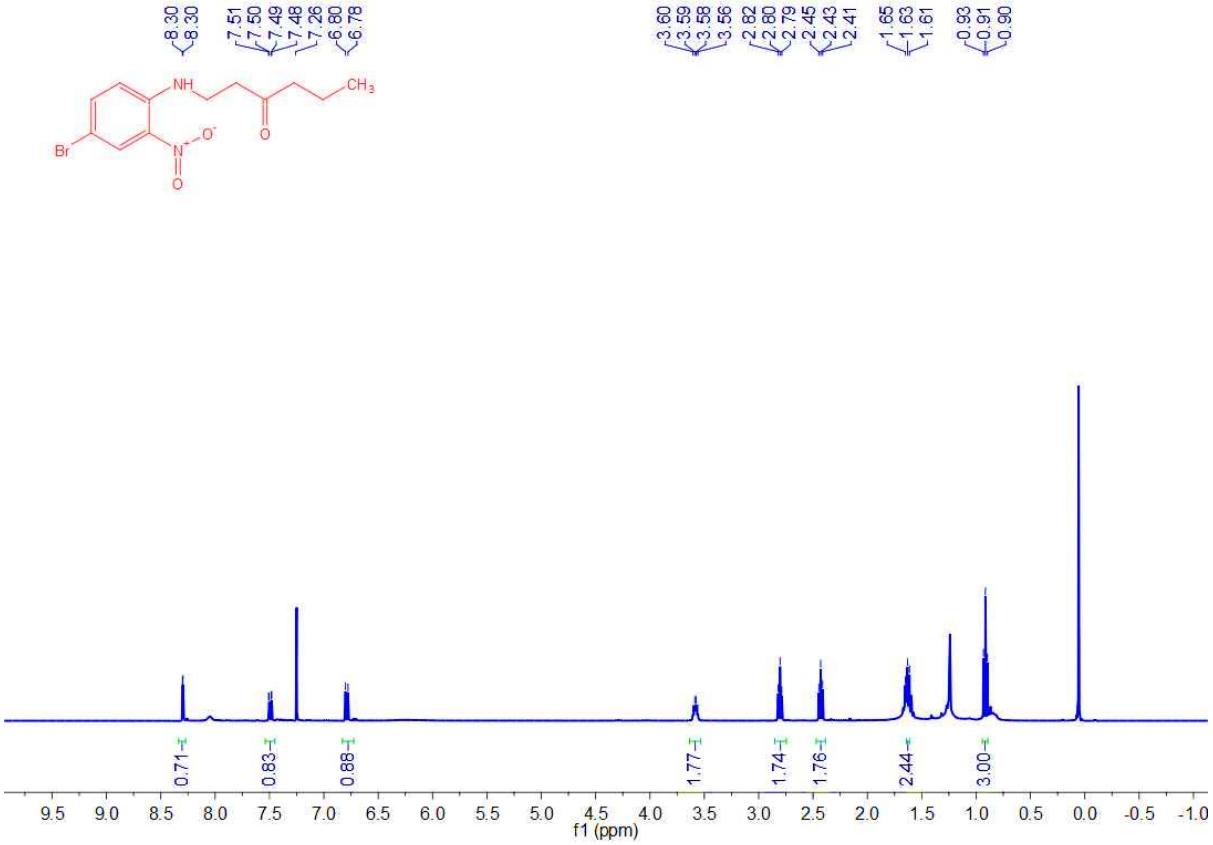


Figure S41: ^{1}H NMR spectrum of product 21

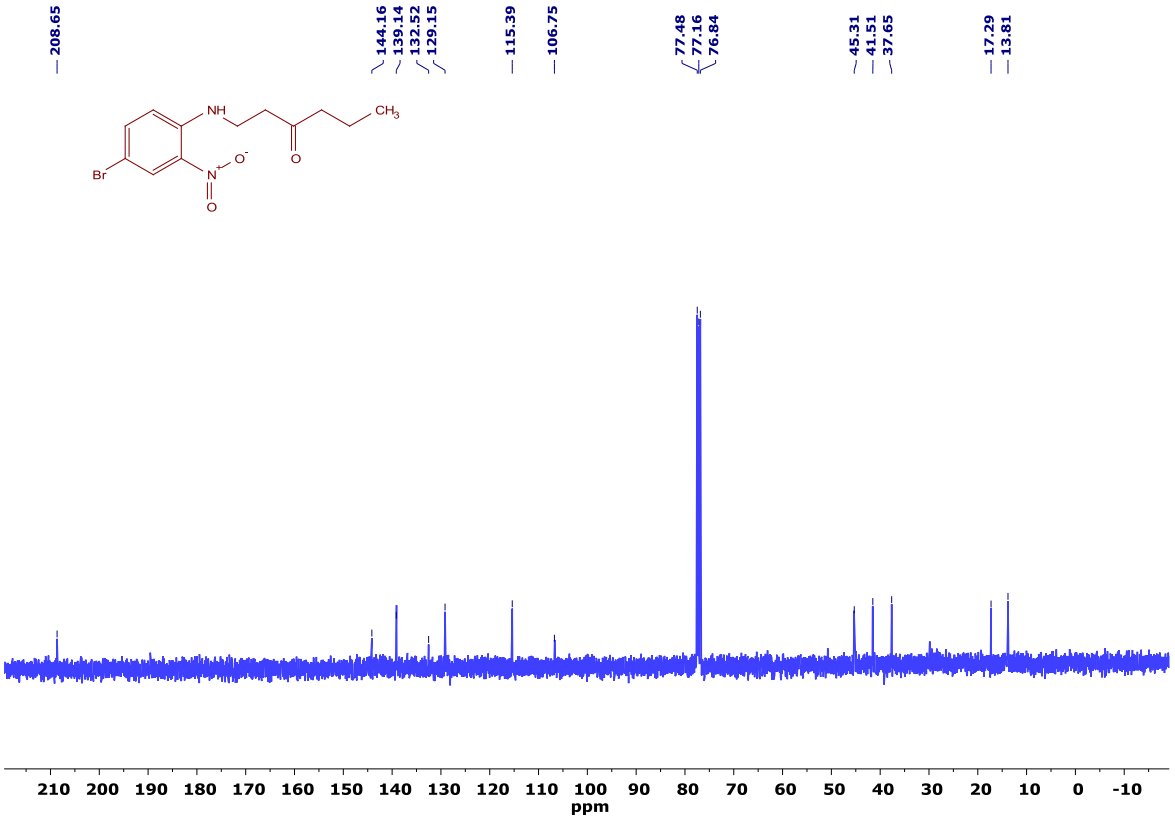


Figure S42: ^{13}C NMR spectrum of product 21

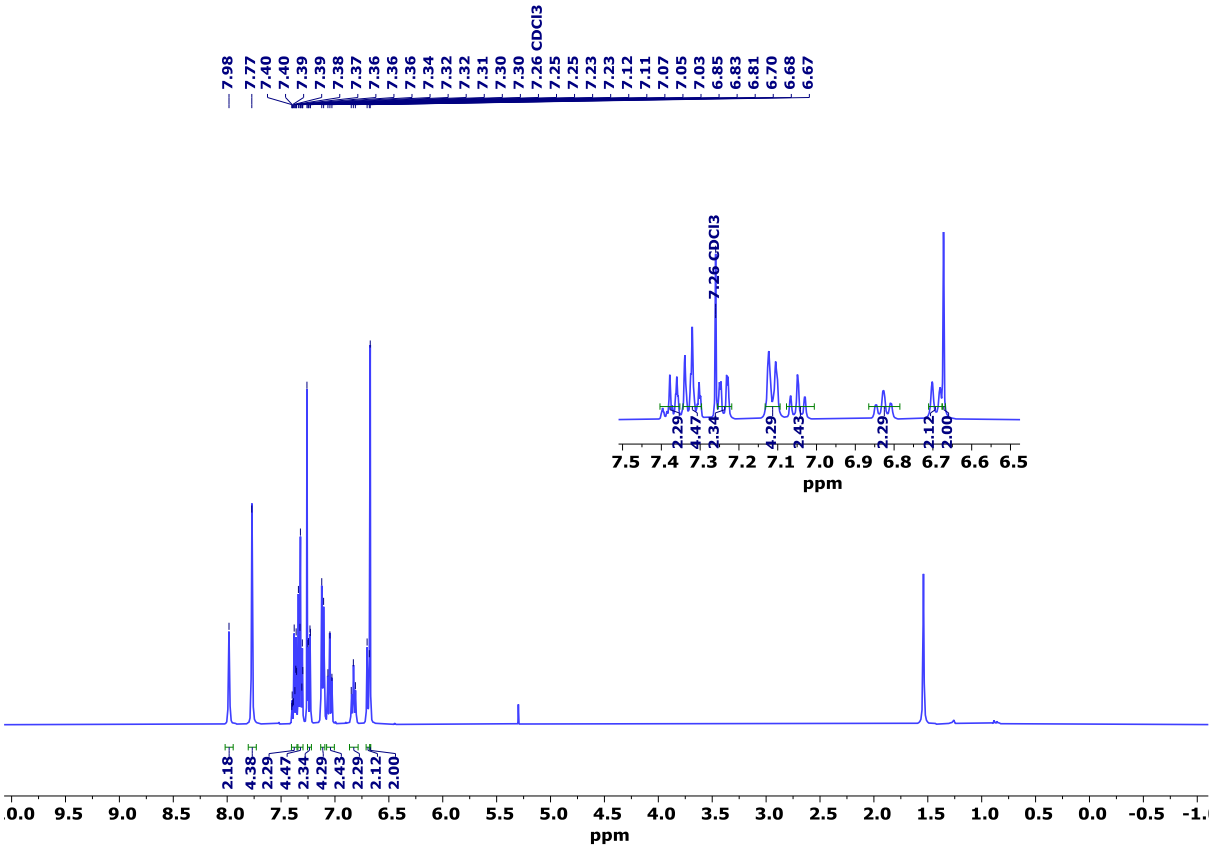


Figure S43: ^{1}H NMR spectrum of palladacycle II

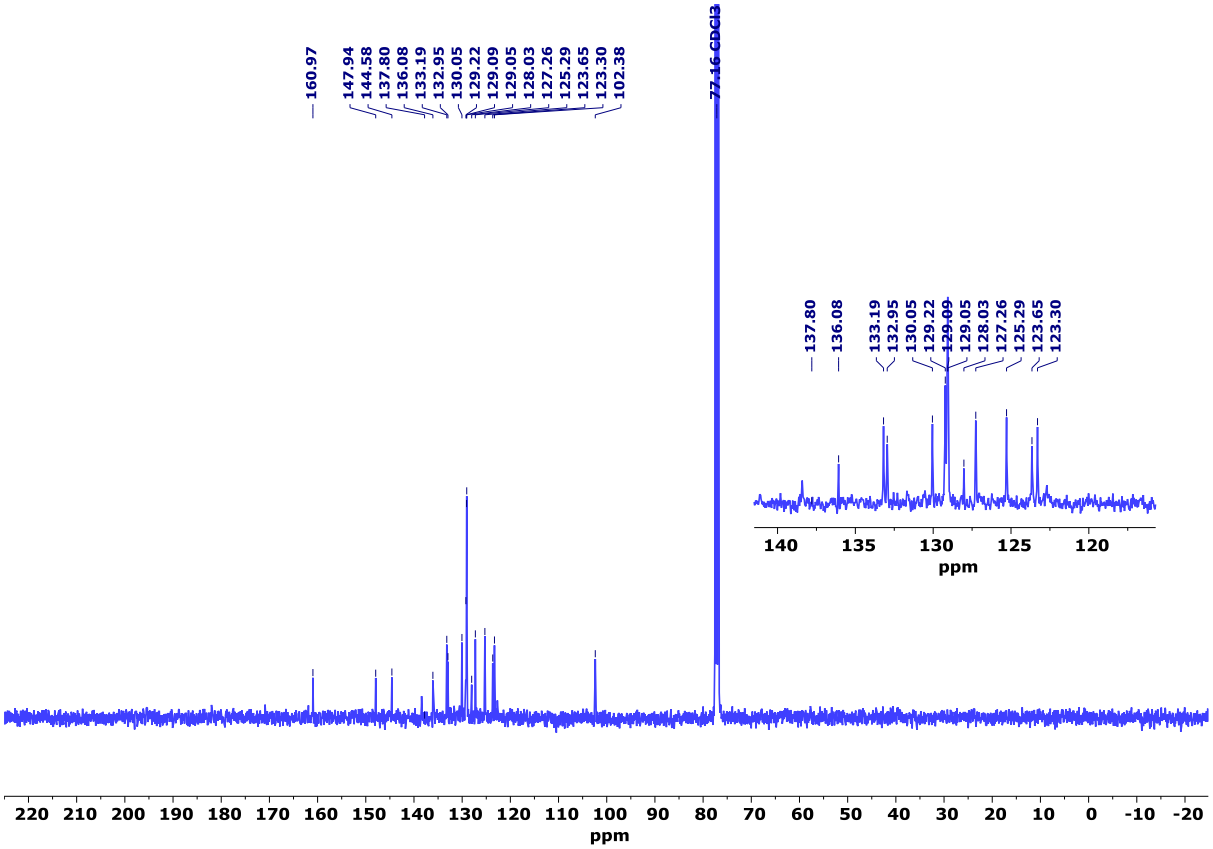


Figure S44: ^{19}F decoupled ^{13}C NMR spectrum of palladacycle II

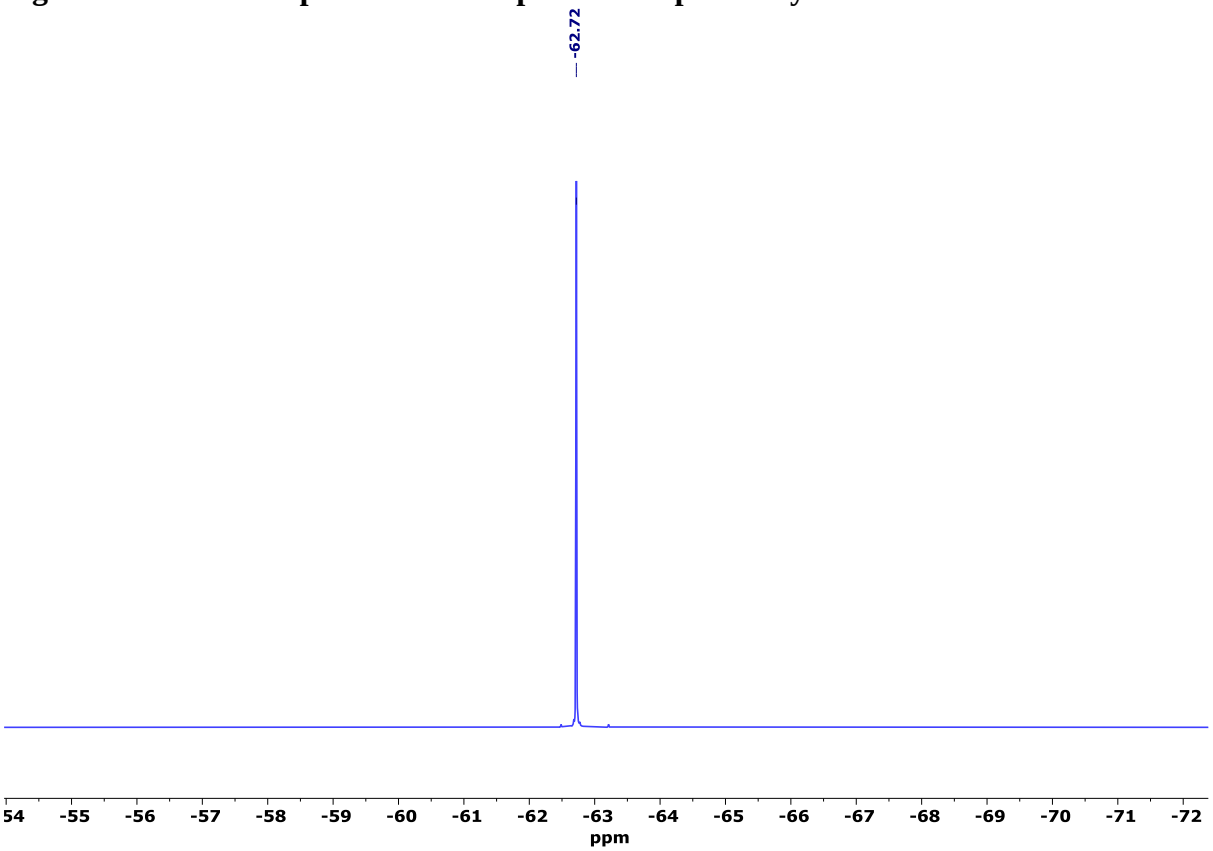


Figure S45: ^{19}F NMR spectrum of palladacycle II

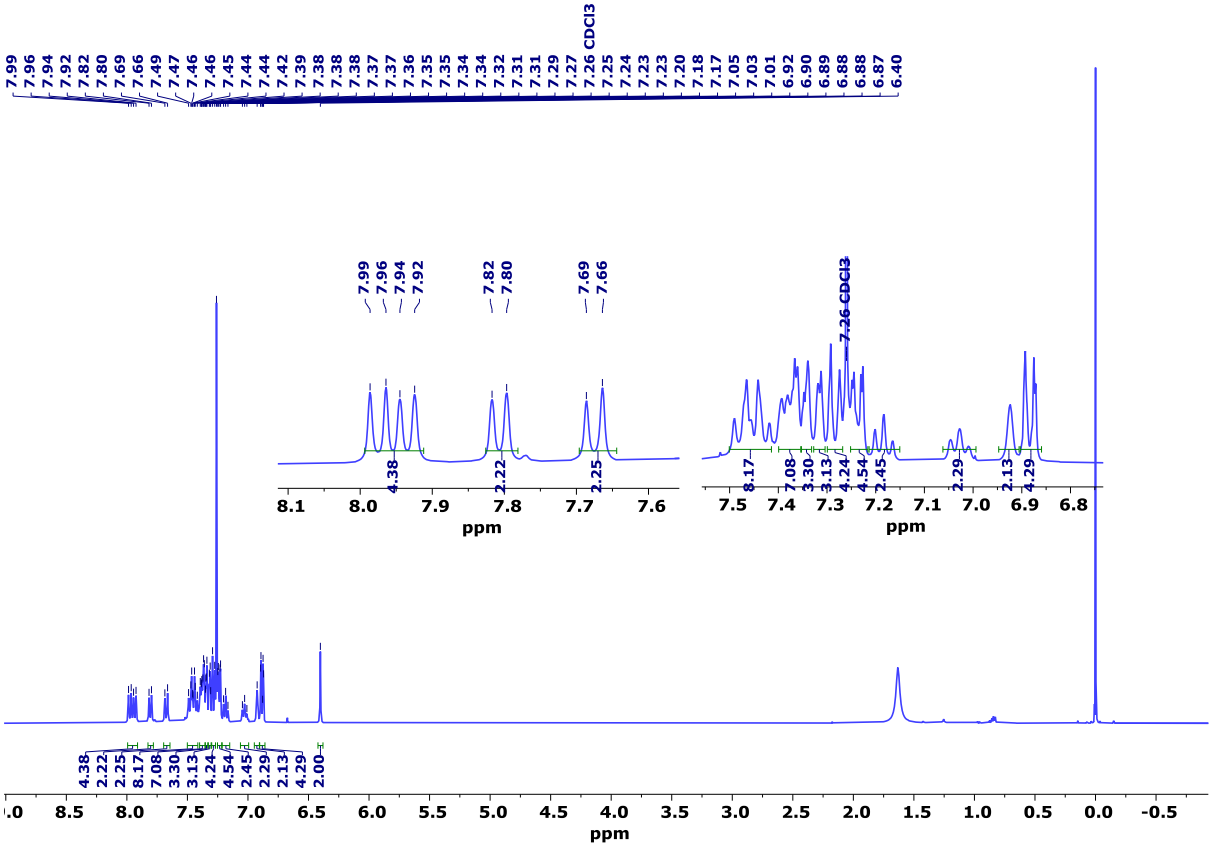


Figure S46: ^{1}H NMR spectrum of palladacycle III

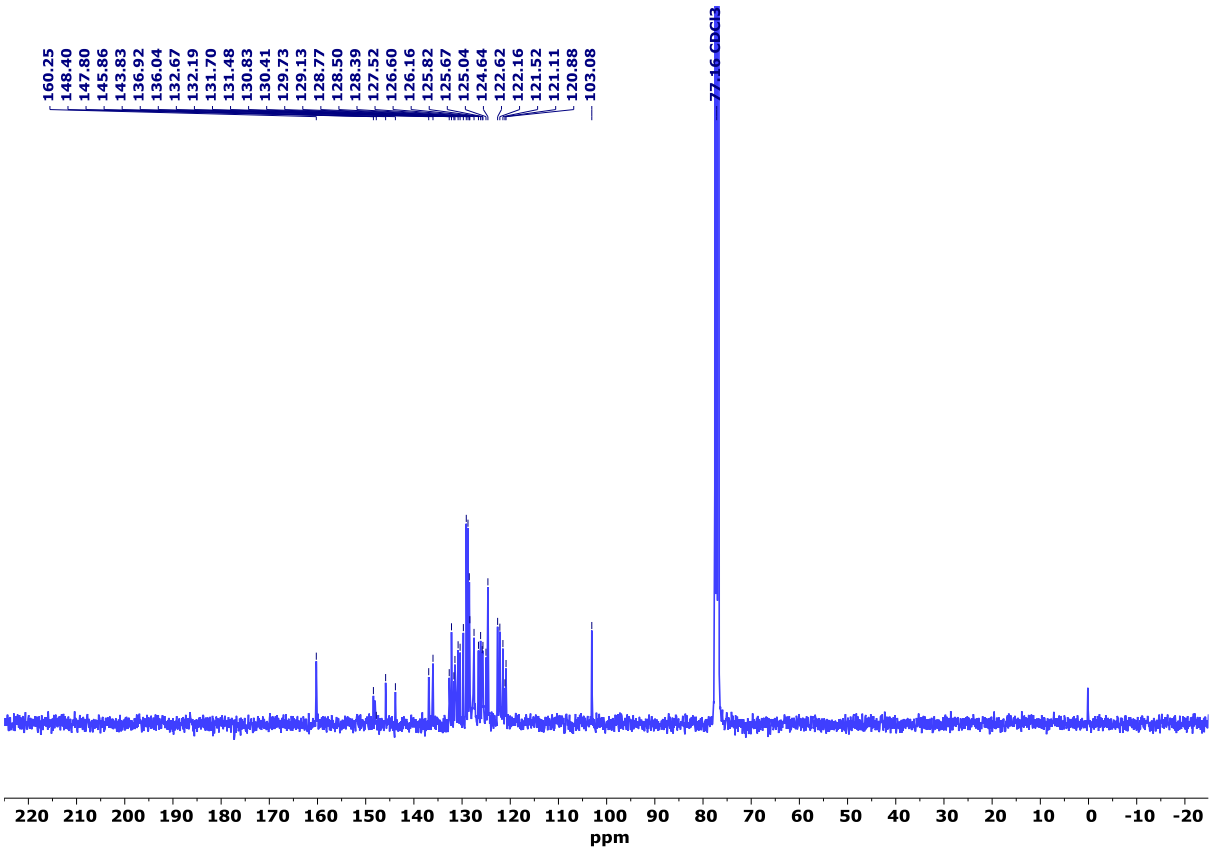


Figure S47: ^{19}F decoupled ^{13}C NMR spectrum of palladacycle III

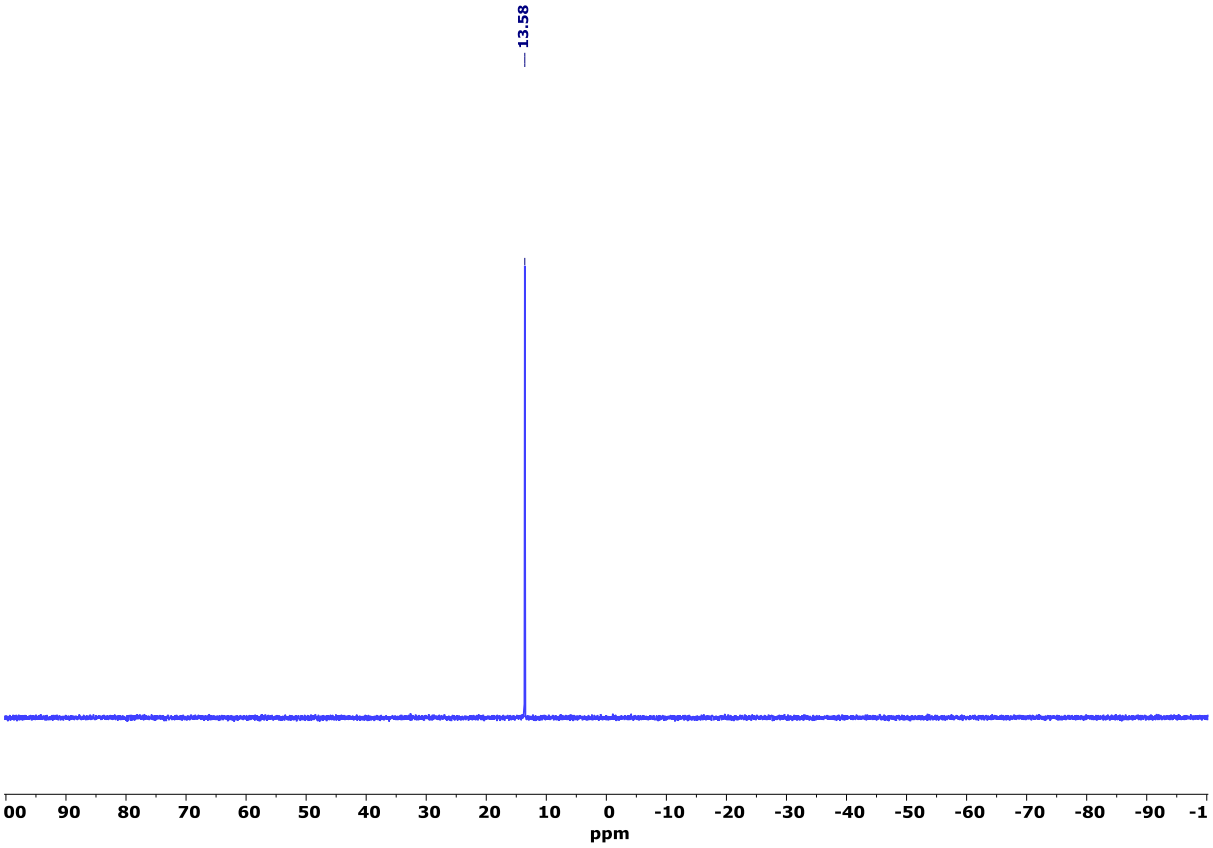


Figure S48: ^{31}P NMR spectrum of Palladacycle III

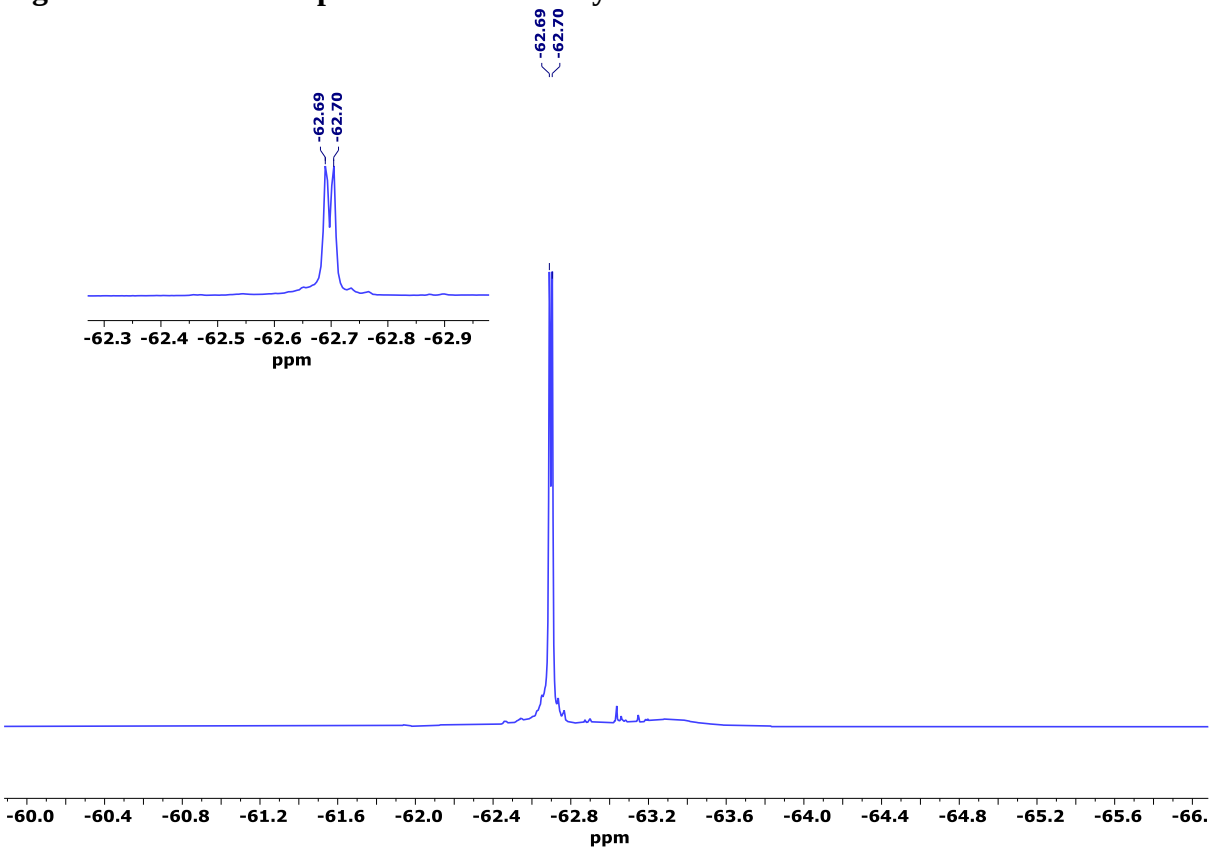


Figure S48: ^{19}F NMR spectrum of Palladacycle III

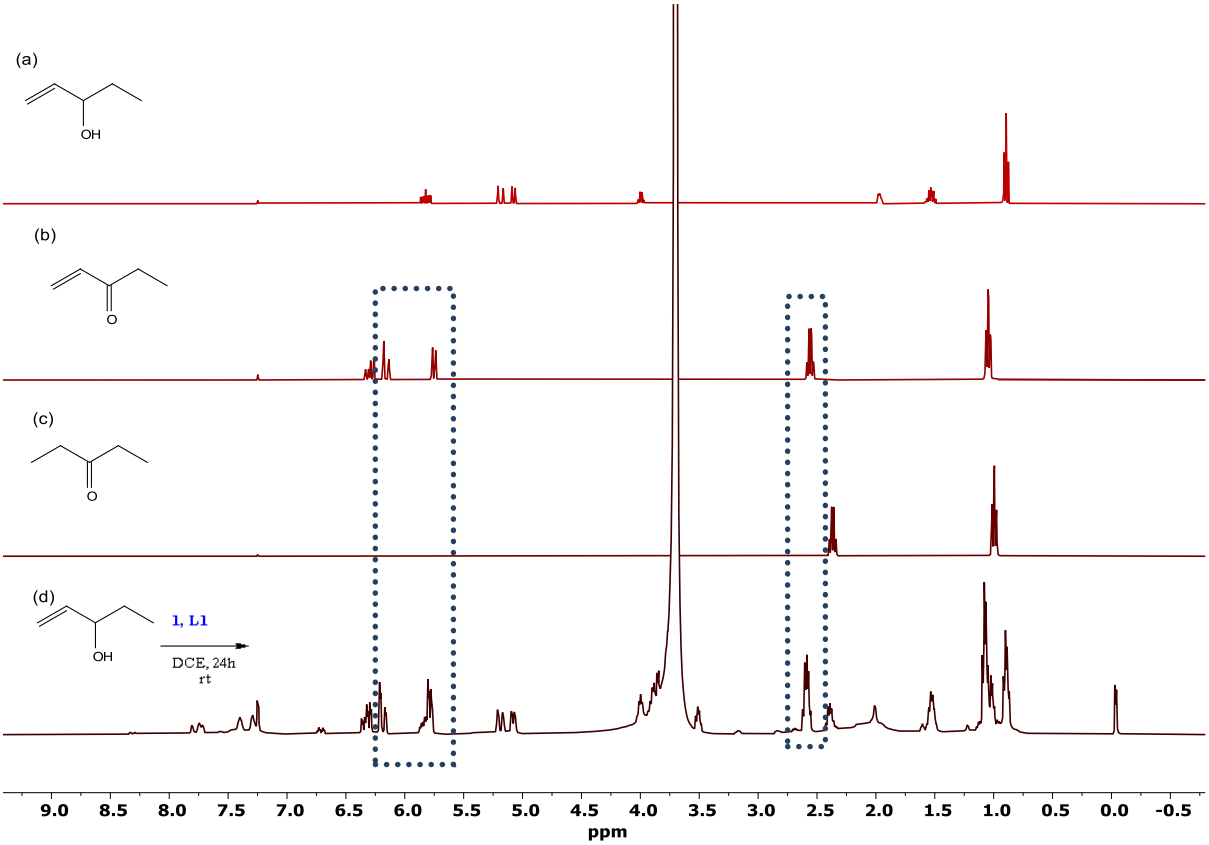


Figure S49: Stacking of ^{1}H NMR of (a) 1-penten-3-ol, (b) 1-penten-3-one, (c) 3-pentanone and (d) crude reaction mixture of 1-penten-3-ol at optimised condition after 24h

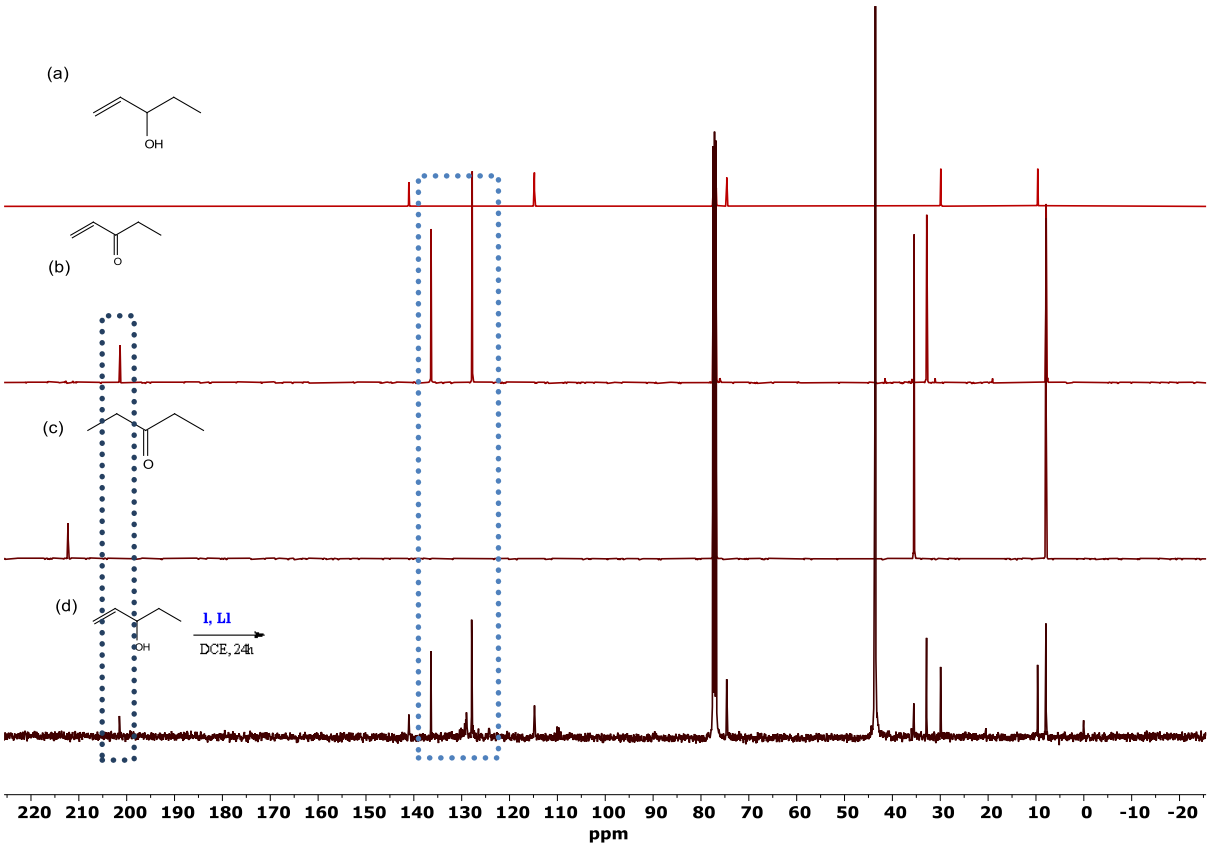


Figure S50: Stacking of ^{13}C NMR of (a) 1-penten-3-ol, (b) 1-penten-3-one, (c) 3-pentanone and (d) crude reaction mixture of 1-penten-3-ol at optimised condition after 24h

Table S1: Crystal data and structure refinement parameters for the palladacycle II & III

Identification code	**Palladacycle II**	**Palladacycle III**
Empirical formula	$C_{46}H_{26}Cl_2F_{12}N_4Pd_2$	$C_{90}H_{60}F_{12}N_4O_{10}P_2Pd_2$
Formula weight	1146.41	1860.16
Temperature/K	107(10)	112.2(4)
Crystal system	trigonal	monoclinic
Space group	R-3	$P2_1$
a/Å	27.7832(6)	14.2159(5)
b/Å	27.7832(6)	19.6780(4)
c/Å	15.2098(4)	15.4208(5)
α/°	90	90
β/°	90	115.902(4)
γ/°	120	90
Volume/Å^3	10167.6(5)	3880.5(2)
Z	9	2
ρ_{calc}g/cm^3	1.685	1.592
μ/mm^{-1}	8.294	4.948
F(000)	5076.0	1876.0
Crystal size/mm^3	0.17 × 0.13 × 0.12	0.17 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.876 to 133.162	6.912 to 155.518
Index ranges	$-31 \le h \le 30$, $-33 \le k \le 34$, $-10 \le l \le 18$	$-18 \le h \le 17$, $-24 \le k \le 24$, $-19 \le l \le 19$
Reflections collected	14690	52529
Independent reflections	3906 [R_{int} = 0.1140, R_{sigma} = 0.0687]	15378 [R_{int} = 0.0986, R_{sigma} = 0.0708]
Data/restraints/parameters	3906/69/325	15378/1/1084
Goodness-of-fit on F^2	1.338	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.1006, wR_2 = 0.2893	R1 = 0.0922, wR2 = 0.2250
Final R indexes [all data]	R_1 = 0.1038, wR_2 = 0.2945	R_1 = 0.1108, wR_2 = 0.2359
Largest diff. peak/hole / e Å^{-3}	2.96/-2.71	5.31/-1.68
Flack parameter		-0.025(15)

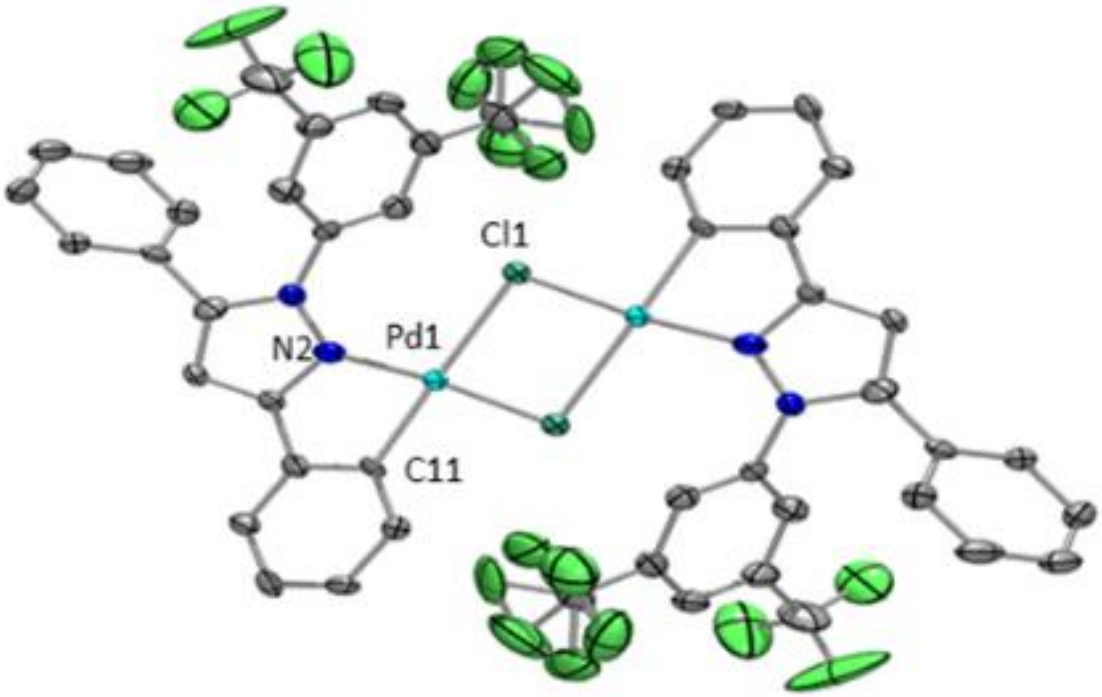


Figure S51. Molecular structure of palladacycle **II** (Thermal ellipsoids at 50% probability). Selected bond lengths (Å) and bond angles (°): Pd1-N2 2.039(6), Pd1-Cl1 2.322(2), Pd1-C11 1.985(7), N2-Pd1-Cl1 173.7(2), N2-Pd1-C11 80.9(3), C11-Pd1-Cl1 93.1(2). (CCDC No. 2373260).

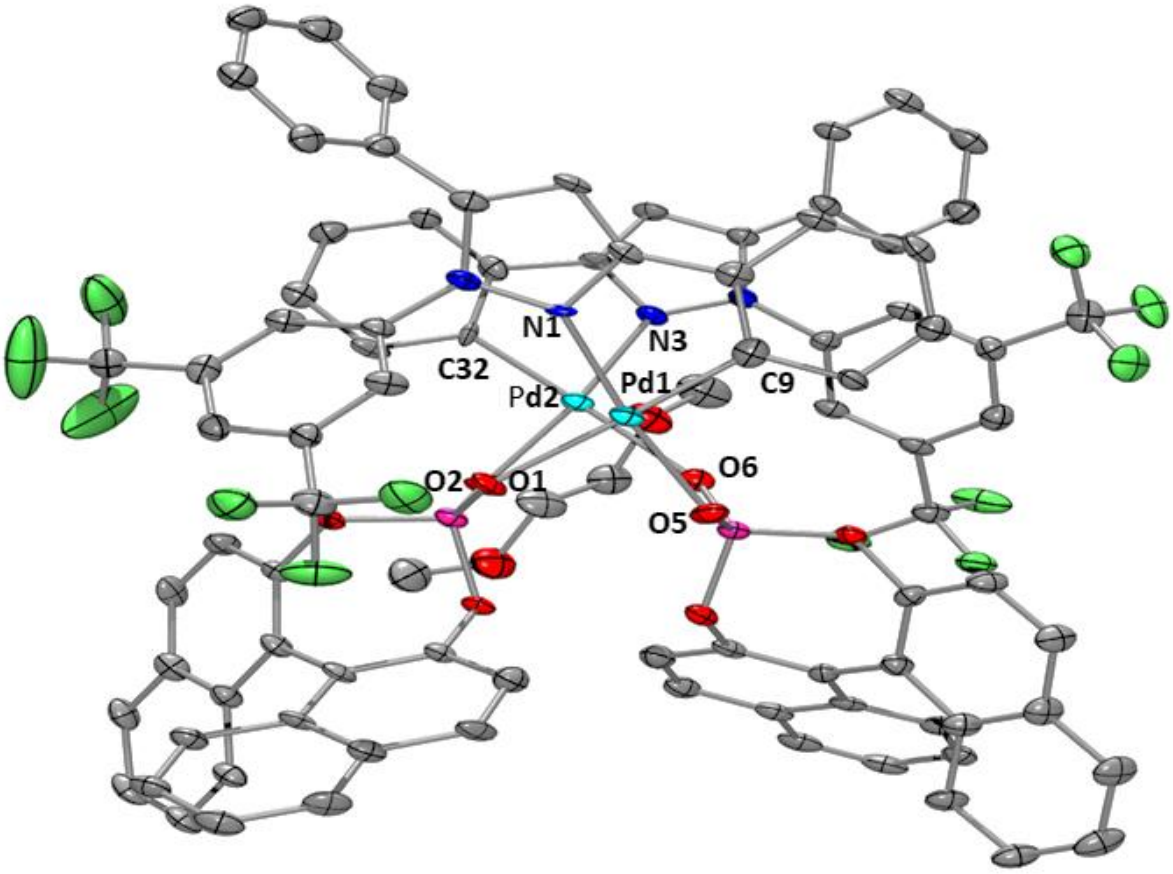


Figure S52. Molecular structure of palladacycle **III** (Thermal ellipsoids at 30% probability). Selected bond lengths (Å) and bond angles (°): Pd2-N3 2.033(12), Pd2-C32 1.968(13), Pd2-O6 2.171(12), Pd2-O2 2.051(10), Pd1-O1 2.153(10), Pd1-O5 2.058(11), Pd1-N1 2.046(11), Pd1-C9 1.954(2), Pd1-Pd2 3.226(1), O2-Pd2-O6 87.7(4), O2-Pd2-C32 91.5(6), C32-Pd2-N3 80.4(6), N3-Pd2-O6 100.1(5), C9-Pd1-O5 92.6(6), O1-Pd1-O5 88.5(5), N1-Pd1-O1 98.8(5), N1-Pd1-C9 80.1(6). (CCDC No. 2373261).

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