

Supplementary Information – Experimental and Computational Details

Palladium-Catalyzed Synthesis of β -Hydroxy Compounds via a Strained 6,4-Palladacycle from Directed C–H Activation of Anilines and C–O Insertion of Epoxides

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General remarks

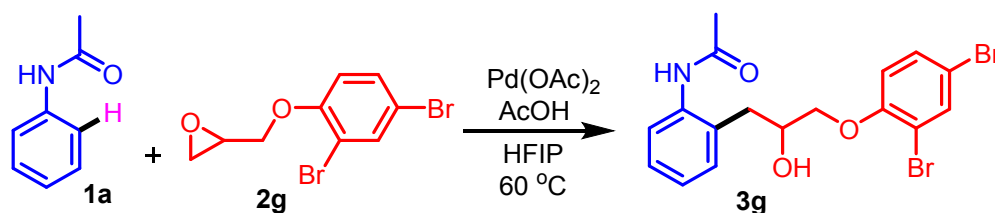
All experiments were carried out under nitrogen, unless stated otherwise. Solvents and reagents were purchased from Sigma Aldrich and TCI chemicals and used without further purification. Merck precoated silica gel plates (Art. 5554) treated with a fluorescent indicator were used for analytical thin layer chromatography (TLC). Column chromatography was performed using silica gel 9385 (Merck) and ethyl acetate/hexane (1:1) were used as eluents. Melting points are uncorrected and were determined using Fisher-Johns Melting Point Apparatus after the recrystallization with ethanol. ^1H NMR and ^{13}C NMR spectra were recorded on VNS (600 and 150 MHz) spectrometer at the core research support center for natural products and medical materials of Yeungnam University. The NMR spectra recorded in CDCl_3 using $\delta = 7.24$ and 77.00 ppm as the solvent chemical shifts. All chemical shifts (δ) are expressed in units of ppm and J values are given in Hz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, and dd = doublet of doublets. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum TwoTM IR spectrometer with frequencies expressed in cm^{-1} , and high-resolution mass spectrometry (HRMS) was carried out using a JEOL JMS-700 spectrometer at the Korea Basic Science Institute. The substituted acetanilides were prepared by following the reported procedure. High Performance Liquid Chromatography (HPLC) was recorded on Shimadzu spectrometer (chiral column: CHIRALCELL OJ-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm).

General procedure for the synthesis of 3-6

A mixture of acetanilide **1** (1 mmol), epoxide **2** (1 mmol), $\text{Pd}(\text{OAc})_2$ (10 mol%), and AcOH (3 mmol) was stirred in HFIP (3 mL) under nitrogen atmosphere at $60\text{ }^\circ\text{C}$ for described time. When the reaction was complete as indicated by TLC, the volatiles were removed in vacuo and the residue was purified by silica gel column chromatography (EtOAc/Hexane=1:1) to obtain the desired products.

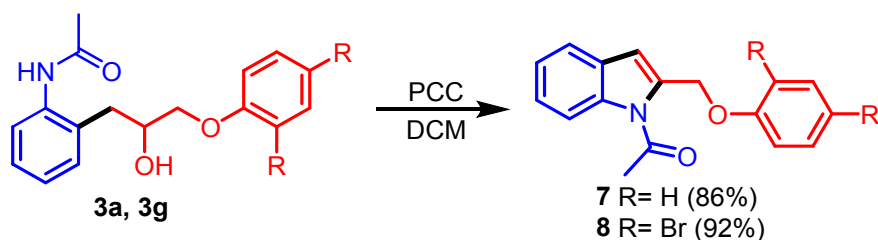
Additional experiments:

i) Gram scale experiment for synthesis of compound **3g**



A mixture of acetanilide **1** (10 mmol, 1.35g), epoxide **2** (10 mmol, 3.08g), $\text{Pd}(\text{OAc})_2$ (10 mol%) and AcOH (30 mmol) was stirred in HFIP (30 mL) under nitrogen atmosphere at 60 °C for described time. When the reaction was complete as indicated by TLC, the volatiles were removed in vacuo and the residue was purified by silica gel column chromatography (EtOAc/Hexane) to obtain the desired products **3g** (3.03g, 68%).

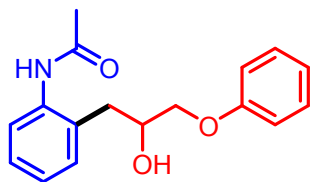
ii) Further transformations of the synthesized compound **3a** and **3g** into **7** and **8**



Procedure 1: Oxidation/cyclization of **3a or **3g** with PCC:** In a 50 mL round-bottomed flask fitted with a reflux condenser was suspended pyridinium chlorochromate (PCC) (1 equiv.) in dry CH_2Cl_2 (7 mL). Alcohol **3a** or **3g** (0.2 mmol) in CH_2Cl_2 (5mL) was added drop-wise to the magnetically stirred solution. After 2h CH_2Cl_2 (20 mL) was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly with dry CH_2Cl_2 (3 X 20 mL). The combined organic solution was evaporated by using rotatory evaporator. The residue was diluted with diethyl ether (25 mL) and filtered through a cotton plug to remove the insoluble chromium salts. The ether layer was washed with 1M NaOH (10 mL), brine (10 mL), and then dried over anhydrous MgSO_4 . Further purification by column chromatography (EtOAc/Hexane=1:4) afforded indole **7** or **8** as a solid.

Characterization data of synthesized compounds

N-(2-(2-Hydroxy-3-phenoxypropyl)phenyl)acetamide (3a)

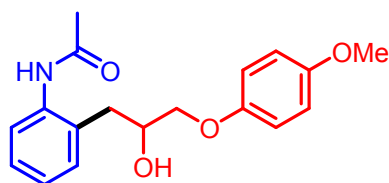


The title compound was prepared according to the general procedure.

The product was obtained as a white solid. R_f = 0.2 (50% EtOAc/ Hexane); Yield: 79% (226 mg); mp 114-116 °C. ^1H NMR (600 MHz, CDCl_3) δ 9.23 (1H, s), 7.80 (1H, d, J = 8.0 Hz), 7.27 (2H, t, J = 7.6 Hz),

7.21 (1H, t, J = 7.6 Hz), 7.13 (1H, d, J = 7.5 Hz), 7.05 (1H, t, J = 7.4 Hz), 6.96 (1H, t, J = 7.3 Hz), 6.87 (2H, d, J = 7.7 Hz), 4.25-4.24 (1H, m), 3.94 (1H, dd, J = 9.0, 3.8 Hz), 3.81 (1H, t, J = 8.4 Hz), 3.53 (1H, s), 2.91 (1H, d, J = 14.4 Hz), 2.83 (1H, dd, J = 14.5, 7.5 Hz), 2.10 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.9, 158.1, 136.7, 130.8, 129.5, 127.4, 124.9, 124.0, 121.3, 114.5, 71.8, 71.0, 35.5, 24.1; IR (ATR) 3274, 2927, 1666, 1587, 1494, 1242, 753 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3$: 285.1365. Found: 285.1361.

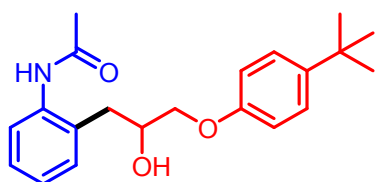
N-(2-(2-Hydroxy-3-(4-methoxyphenoxy)propyl)phenyl)acetamide (3b)



The title compound was prepared according to the general procedure. The product was obtained as a white solid. R_f = 0.2 (60% EtOAc/ Hexane); Yield: 76% (239 mg); mp 128-130 °C.

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 9.49 (1H, s), 7.48 (1H, d, J = 7.9 Hz), 7.26 (1H, d, J = 7.5 Hz), 7.18 (1H, t, J = 7.6 Hz), 7.08 (1H, t, J = 7.4 Hz), 6.87-6.83 (4H, m), 5.42 (1H, s), 4.01-3.98 (1H, m), 3.79-3.75 (2H, m), 3.69 (3H, s), 2.90 (1H, dd, J = 14.1, 4.4 Hz), 2.74 (1H, dd, J = 14.1, 7.7 Hz), 2.03 (3H, s); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 168.1, 153.3, 152.6, 136.7, 132.3, 130.8, 126.4, 125.0, 124.8, 115.4, 114.5, 72.0, 69.4, 55.3, 35.7, 23.4; IR (ATR) 3292, 2931, 1650, 1505, 1230, 754 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_4$: 315.1471. Found: 315.1473.

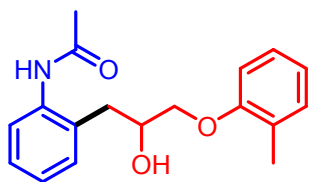
N-(2-(3-(4-(*tert*-Butyl)phenoxy)-2-hydroxypropyl)phenyl)acetamide (3c)



The title compound was prepared according to the general procedure. The product was obtained as a white solid. R_f = 0.3 (50% EtOAc/ Hexane); Yield: 78% (265 mg); mp 121-123 °C. ^1H NMR (600 MHz, CDCl_3) δ 9.06 (1H, s), 7.85 (1H, d, J = 8.0 Hz),

7.29 (2H, d, $J = 8.8$ Hz), 7.26-7.23 (1H, m), 7.13 (1H, d, $J = 7.0$ Hz), 7.06 (1H, t, $J = 7.4$ Hz), 6.81 (2H, d, $J = 8.8$ Hz), 4.30-4.26 (1H, m), 3.99 (1H, dd, $J = 9.4, 3.5$ Hz), 3.79 (1H, t, $J = 8.8$ Hz), 2.92 (1H, dd, $J = 14.5, 3.2$ Hz), 2.84 (1H, dd, $J = 14.5, 7.5$ Hz), 2.69 (1H, s), 2.12 (3H, s), 1.28 (9H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.6, 155.9, 144.3, 136.9, 130.8, 129.1, 127.6, 126.3, 124.8, 124.1, 114.1, 72.09, 71.3, 35.4, 34.1, 31.4, 24.3; IR (ATR) 3275, 2959, 1666, 1512, 1245, 755 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_3$: 341.1991. Found: 341.1992.

***N*-(2-(2-Hydroxy-3-(*o*-tolyloxy)propyl)phenyl)acetamide (3d)**

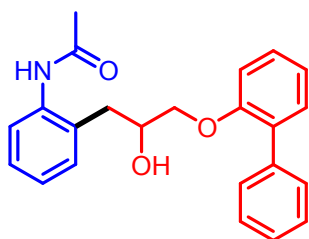


The title compound was prepared according to the general procedure.

The product was obtained as a white solid. $R_f = 0.2$ (50% EtOAc/Hexane); Yield: 77% (230 mg); mp 114-116 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.27 (1H, s), 7.79 (1H, d, $J = 8.0$ Hz), 7.21 (1H, t, $J = 7.7$ Hz),

7.13 (3H, t, $J = 8.0$ Hz), 7.06 (1H, t, $J = 7.4$ Hz), 6.88 (1H, t, $J = 7.4$ Hz), 6.75 (1H, d, $J = 8.0$ Hz), 4.28-4.26 (1H, m), 3.94 (1H, dd, $J = 9.2, 4.4$ Hz), 3.84 (1H, t, $J = 8.3$ Hz), 3.74 (1H, s), 2.91 (1H, d, $J = 12.0$ Hz), 2.86 (1H, dd, $J = 14.5, 7.6$ Hz), 2.24 (3H, s), 2.10 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.92, 156.25, 136.77, 130.8, 130.7, 129.6, 127.3, 126.8, 126.5, 124.9, 124.0, 120.9, 111.1, 72.0, 71.0, 35.6, 24.0, 16.1; IR (ATR) 3280, 2926, 1666, 1494, 1453, 1245, 752 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$: 299.1521. Found: 299.1523.

***N*-(2-(3-([1,1'-Biphenyl]-2-yloxy)-2-hydroxypropyl)phenyl)acetamide (3e)**

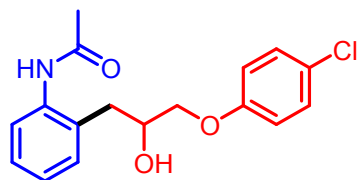


The title compound was prepared according to the general procedure.

The product was obtained as a white solid. $R_f = 0.4$ (50% EtOAc/Hexane); Yield: 79% (284 mg); mp 140-142 $^{\circ}\text{C}$. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 9.47 (1H, s), 7.60 (2H, d, $J = 7.6$ Hz), 7.52 (1H, d, $J = 8.0$ Hz), 7.42 (2H, t, $J = 7.6$ Hz), 7.36-7.30 (3H, m), 7.17 (1H, t, $J = 7.5$ Hz),

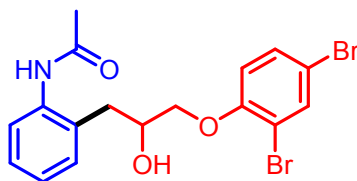
7.08 (2H, t, $J = 8.3$ Hz), 7.04 (2H, t, $J = 7.7$ Hz), 5.50 (1H, s), 4.00-3.97 (1H, m), 3.93-3.87 (2H, m), 2.81 (1H, dd, $J = 14.1, 3.7$ Hz), 2.72 (1H, dd, $J = 14.0, 8.0$ Hz), 1.99 (3H, s); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 168.0, 155.3, 138.0, 136.8, 132.0, 130.7, 130.4, 129.9, 129.3, 128.8, 127.9, 126.8, 126.4, 124.6, 120.9, 112.7, 71.7, 69.6, 35.8, 23.5; IR (ATR) 3357, 1656, 1368, 1216, 991, 755 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_3$: 361.1678. Found: 361.1679.

***N*-(2-(3-(4-Chlorophenoxy)-2-hydroxypropyl)phenyl)acetamide (3f)**



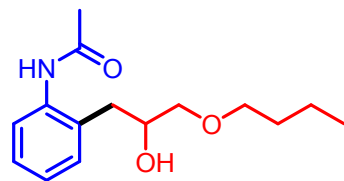
The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. $R_f = 0.2$ (50% EtOAc/ Hexane); Yield: 74 % (236 mg); ^1H NMR (600 MHz, DMSO- d_6) δ 9.49 (1H, s), 7.48 (1H, d, $J = 7.9$ Hz), 7.31 (2H, d, $J = 9.0$ Hz), 7.26 (1H, d, $J = 7.4$ Hz), 7.19 (1H, t, $J = 7.6$ Hz), 7.08 (1H, t, $J = 7.4$ Hz), 6.95 (2H, d, $J = 9.0$ Hz), 4.05-4.01 (1H, m), 3.87-3.81 (2H, m), 2.91 (1H, dd, $J = 14.0, 4.6$ Hz), 2.76 (1H, dd, $J = 14.1, 7.7$ Hz), 2.03 (3H, s); ^{13}C NMR (150 MHz, DMSO- d_6) δ 168.1, 157.4, 136.7, 132.2, 130.8, 129.1, 126.4, 125.1, 124.8, 124.2, 116.2, 71.8, 69.2, 35.6, 23.4; IR (ATR) 3284, 2928, 1665, 1491, 1244, 757 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}_3$: 319.0975. Found: 319.0975.

***N*-(2-(3-(2,4-Dibromophenoxy)-2-hydroxypropyl)phenyl)acetamide (3g)**



The title compound was prepared according to the general procedure. The product was obtained as a brown solid. $R_f = 0.2$ (50% EtOAc/ Hexane); Yield: 71% (314 mg); mp 148-150 $^{\circ}\text{C}$. ^1H NMR (600 MHz, DMSO- d_6) δ 9.50 (1H, s), 7.78 (1H, d, $J = 2.4$ Hz), 7.51-7.47 (2H, m), 7.27 (1H, d, $J = 7.4$ Hz), 7.18 (1H, t, $J = 7.6$ Hz), 7.07 (1H, t, $J = 7.4$ Hz), 7.04 (1H, d, $J = 8.9$ Hz), 5.48 (1H, s), 4.10-4.07 (1H, m), 3.97-3.91 (2H, m), 2.95 (1H, dd, $J = 14.0, 4.4$ Hz), 2.85 (1H, dd, $J = 14.1, 7.8$ Hz), 2.05 (3H, s); ^{13}C NMR (150 MHz, DMSO- d_6) δ 168.1, 154.3, 136.8, 134.5, 132.1, 131.5, 130.7, 126.4, 125.0, 124.8, 115.4, 112.2, 112.1, 72.4, 69.2, 35.6, 23.5; IR (ATR) 3283, 3028, 1739, 1663, 1477, 1368, 1216, 757 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{17}\text{Br}^{79}\text{Br}^{81}\text{NO}_3$: 442.9555. Found: 442.9556.

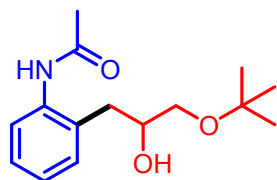
***N*-(2-(3-Butoxy-2-hydroxypropyl)phenyl)acetamide (3h)**



The title compound was prepared according to the general procedure. The product was obtained as a white solid. $R_f = 0.3$ (50% EtOAc/ Hexane); Yield: 81% (215 mg); mp 48-50 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.24 (1H, s, 1H), 7.83 (1H, d, $J = 8.1$ Hz), 7.20 (1H, d, $J = 7.2$ Hz), 7.06 (1H, d, $J = 6.8$ Hz), 7.01 (1H, t, $J = 7.4$ Hz), 4.04-4.00 (1H, m), 3.47-3.39 (3H, m),

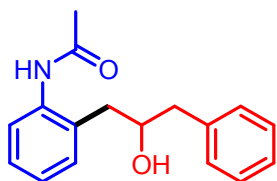
3.28 (1H, s), 3.22 (1H, t, $J = 9.0$ Hz), 2.77 (1H, dd, $J = 14.5, 3.2$ Hz), 2.70 (1H, dd, $J = 14.5, 7.3$ Hz), 2.11 (3H, s), 1.55-1.50 (2H, m), 1.36-1.30 (2H, m), 0.89 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 168.6, 136.8, 130.7, 129.4, 127.2, 124.5, 123.8, 73.8, 72.1, 71.2, 35.5, 31.6, 24.2, 19.1, 13.8; IR (ATR) 3272, 2957, 2867, 1667, 1529, 1452, 755 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_3$: 265.1678. Found: 265.1678.

***N*-(2-(3-(*tert*-Butoxy)-2-hydroxypropyl)phenyl)acetamide (3i)**



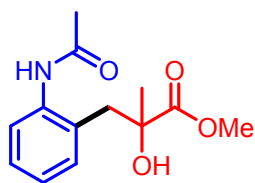
The title compound was prepared according to the general procedure. The product was obtained as a brown solid. $R_f = 0.3$ (50% EtOAc/ Hexane); Yield: 80% (212 mg); mp 76-78 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.27 (1H, s), 7.83 (1H, d, $J = 8.1$ Hz), 7.19 (1H, t, $J = 7.6$ Hz), 7.07 (1H, d, $J = 7.3$ Hz), 7.01 (1H, t, $J = 7.4$ Hz), 3.94-3.90 (1H, m), 3.37 (1H, dd, $J = 9.0, 3.7$ Hz), 3.16 (1H, t, $J = 8.8$ Hz), 2.76-2.67 (2H, m), 2.11 (3H, s), 1.16 (9H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.5, 136.8, 130.7, 129.7, 127.2, 124.4, 123.7, 73.5, 72.7, 65.0, 35.8, 27.5, 24.2; IR (ATR) 3276, 2972, 1660, 1452, 1355, 1199, 755 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_3$: 265.1678. Found: 265.1680.

***N*-(2-(2-Hydroxy-3-phenylpropyl)phenyl)acetamide (3j)**



The title compound was prepared according to the general procedure. The product was obtained as a white solid. $R_f = 0.3$ (50% EtOAc/ Hexane); Yield: 78% (210 mg); mp 173-175 $^{\circ}\text{C}$. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 9.50 (1H, s), 7.46 (1H, d, $J = 7.8$ Hz), 7.28 (2H, t, $J = 7.5$ Hz), 7.21-7.15 (5H, m), 7.07 (1H, t, $J = 7.3$ Hz), 5.19 (1H, s), 3.94-3.90 (1H, m), 2.74-2.63 (3H, m), 2.63-2.60 (1H, m), 1.96 (3H, s); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 168.0, 139.3, 136.7, 133.1, 130.8, 129.3, 128.0, 126.2, 125.8, 124.9, 124.7, 72.2, 43.5, 38.9, 23.4; IR (ATR) 3378, 3266, 1659, 1541, 992, 752 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: 269.1416. Found: 269.1413.

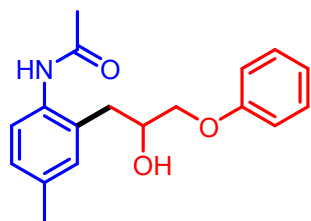
Methyl 3-(2-acetamidophenyl)-2-hydroxy-2-methylpropanoate (3k)



The title compound was prepared according to the general procedure. The product was obtained as a colourless liquid. $R_f = 0.2$ (50% EtOAc/ Hexane); Yield: 69% (173 mg); ^1H NMR (600 MHz, CDCl_3) δ 9.21 (1H, s), 7.81 (1H,

d, $J = 8.0$ Hz), 7.21-7.18 (1H, m), 7.18-6.97 (2H, m), 3.98 (1H, s), 3.74 (3H, s), 3.03-2.97 (2H, m), 2.11 (3H, s), 1.47 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 176.1, 168.4, 137.1, 131.2, 127.7, 127.1, 124.3, 123.9, 77.21, 52.9, 41.7, 26.4, 24.3; IR (ATR) 3302, 1737, 1671, 1452, 1371, 1214, 758 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4$: 251.1158. Found: 251.1157.

***N*-(2-(2-Hydroxy-3-phenoxypropyl)-4-methylphenyl)acetamide (4a)**

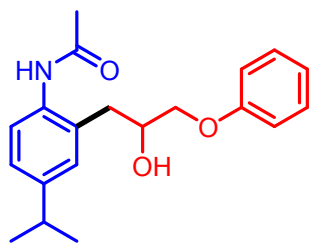


The title compound was prepared according to the general procedure.

The product was obtained as a white solid. $R_f = 0.2$ (50% EtOAc/Hexane); Yield: 79% (237 mg); mp 109-111 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.03 (1H, s), 7.63 (1H, d, $J = 8.2$ Hz), 7.29-7.25 (2H, m), 7.01 (1H, d, $J = 8.1$ Hz), 6.96 (1H, t, $J = 7.4$ Hz), 6.94 (1H, s), 6.87 (2H, d, $J = 7.9$ Hz), 4.24-4.20 (1H, m), 3.93 (1H, dd, $J = 9.3, 4.3$ Hz), 3.82 (1H, dd, $J = 9.2, 7.6$ Hz), 3.60 (1H, s), 2.85 (1H, dd, $J = 14.3, 3.2$ Hz), 2.78 (1H, dd, $J = 14.4, 7.7$ Hz), 2.26 (3H, s), 2.07 (3H, s);

^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 158.2, 134.5, 134.1, 131.3, 129.6, 129.4, 128.0, 124.1, 121.2, 114.5, 71.8, 71.1, 35.5, 24.0, 20.7; IR (ATR) 3382, 2925, 1665, 1494, 1242, 754 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$: 299.1521. Found: 299.1522.

***N*-(2-(2-Hydroxy-3-phenoxypropyl)-4-isopropylphenyl)acetamide (4b)**

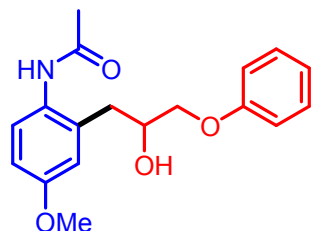


The title compound was prepared according to the general procedure.

The product was obtained as a yellow liquid. $R_f = 0.2$ (50% EtOAc/Hexane); Yield: 78 % (255 mg); ^1H NMR (600 MHz, CDCl_3) δ 8.90 (1H, s), 7.70 (1H, d, $J = 8.3$ Hz), 7.28 (2H, t, $J = 7.6$ Hz), 7.11 (1H, d, $J = 7.7$ Hz), 6.97-6.95 (2H, m), 6.88 (2H, d, $J = 8.7$ Hz), 4.30-4.28 (1H, m), 3.99 (1H, dd, $J = 9.2, 3.6$ Hz), 3.83 (1H, t, $J = 8.6$ Hz), 2.90-2.80 (3H, m), 2.50 (1H, s), 2.11 (3H, s), 1.19 (6H, d, $J = 6.9$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 168.7, 158.2, 145.6, 134.4, 129.6,

129.3, 128.7, 125.5, 124.3, 121.4, 114.5, 72.1, 71.2, 35.5, 33.5, 24.2, 24.0, 23.9; IR (ATR) 3283, 1655, 1525, 1494, 1243, 753 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_3$: 327.1834. Found: 327.1834.

***N*-(2-(2-Hydroxy-3-phenoxypropyl)-4-methoxyphenyl)acetamide (4c)**

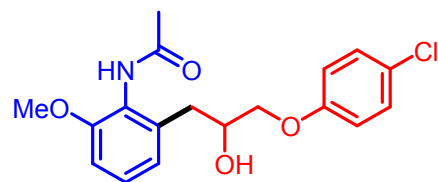


The title compound was prepared according to the general procedure.

The product was obtained as a white solid. R_f = 0.2 (60% EtOAc/Hexane); Yield: 77 % (242 mg); mp 116-118 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.85 (1H, s), 7.60 (1H, d, J = 8.8 Hz), 7.26 (2H, t, J = 7.7 Hz), 6.96 (1H, t, J = 7.4 Hz), 6.87 (2H, d, J = 8.6 Hz), 6.76 (1H, dd, J = 8.8,

2.8 Hz), 6.68 (1H, d, J = 2.7 Hz), 4.26-4.22 (1H, m), 3.94 (1H, dd, J = 9.3, 4.2 Hz), 3.83-3.80 (1H, m), 3.71 (3H, s), 3.45 (1H, s), 2.86 (1H, dd, J = 14.3, 3.3 Hz), 2.80 (1H, dd, J = 14.3, 7.6 Hz), 2.09 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 169.0, 158.1, 156.7, 131.6, 129.7, 129.5, 125.9, 121.3, 116.2, 114.5, 112.3, 71.7, 71.0, 55.3, 35.6, 23.9; IR (ATR) 3283, 2929, 1651, 1496, 1245, 755 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_4$: 315.1471. Found: 315.1473.

***N*-(2-(3-(4-Chlorophenoxy)-2-hydroxypropyl)-6-methoxyphenyl)acetamide (4d)**

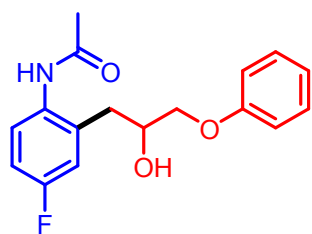


The title compound was prepared according to the general

procedure. The product was obtained as a brown solid. R_f = 0.2 (60% EtOAc/Hexane); Yield: 71 % (248 mg); mp 102-104 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.73 (1H, s), 7.17 (2H,

d, J = 7.0 Hz), 7.13 (1H, t, J = 7.9 Hz), 6.82 (1H, d, J = 7.7 Hz), 6.76-6.73 (3H, m), 4.16-4.15 (1H, m), 4.03 (1H, s), 3.80 (2H, d, J = 5.1 Hz), 3.73 (3H, s), 2.87-2.84 (1H, m), 2.75 (1H, dd, J = 13.8, 8.7 Hz), 2.11 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 170.1, 157.1, 154.4, 136.0, 129.1, 127.7, 125.6, 124.8, 122.0, 115.7, 109.5, 71.7, 70.4, 55.6, 35.2, 23.1; IR (ATR) 3263, 2933, 1657, 1490, 1242, 825 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{18}\text{H}_{20}\text{ClNO}_4$: 349.1081. Found: 349.1079.

***N*-(4-Fluoro-2-(2-hydroxy-3-phenoxypropyl)phenyl)acetamide (4e)**



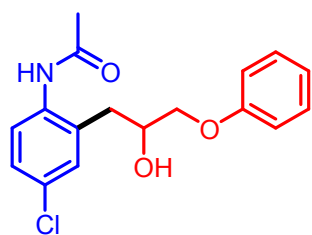
The title compound was prepared according to the general procedure.

The product was obtained as a black solid. R_f = 0.2 (50% EtOAc/Hexane); Yield: 70 % (212 mg); mp 85-87 °C. ^1H NMR (600 MHz, CDCl_3) δ 9.01 (1H, s), 7.73 (1H, dd, J = 8.8, 5.5 Hz), 7.28 (2H, t, J = 7.7 Hz), 6.97 (1H, t, J = 7.0 Hz), 6.95-6.91 (1H, m), 6.88-6.85 (3H, m),

4.29-4.26 (1H, m), 3.98 (1H, dd, J = 9.3, 3.8 Hz), 3.82 (1H, t, J = 8.7 Hz), 3.01 (1H, s), 2.88 (1H,

dd, $J = 14.4, 3.0$ Hz), 2.82 (1H, dd, $J = 14.4, 7.6$ Hz), 2.13 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 169.0, 159.5 (d, $J = 243$ Hz), 158.0, 132.7, 131.9 (d, $J = 7.35$ Hz), 129.6, 126.1 (d, $J = 8.25$ Hz), 121.5, 117.1 (d, $J = 22.2$ Hz) 114.5, 114.3 (d, $J = 21.75$ Hz), 71.8, 71.0, 35.4, 24.0; IR (ATR) 3280, 2928, 1659, 1496, 1233, 755 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{18}\text{FNO}_3$: 303.1271. Found: 303.1273.

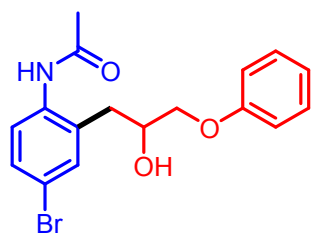
***N*-(4-Chloro-2-(2-hydroxy-3-phenoxypropyl)phenyl)acetamide (4f)**



The title compound was prepared according to the general procedure.

The product was obtained as a white solid. $R_f = 0.2$ (50% EtOAc/Hexane); Yield: 72 % (230 mg); mp 139-141 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.11 (1H, s), 7.80 (1H, d, $J = 8.7$ Hz), 7.28 (2H, dd, $J = 8.6, 7.5$ Hz), 7.20 (1H, dd, $J = 8.7, 2.4$ Hz), 7.12 (1H, d, $J = 2.4$ Hz), 6.98 (1H, t, $J = 7.4$ Hz), 6.88 (2H, d, $J = 8.6$ Hz), 4.29-4.25 (1H, m), 3.99 (1H, dd, $J = 9.3, 3.7$ Hz), 3.81 (1H, t, $J = 8.8$ Hz), 3.11 (1H, s), 2.86 (1H, dd, $J = 14.5, 3.0$ Hz), 2.80 (1H, dd, $J = 14.5, 7.6$ Hz), 2.11 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.7, 158.0, 135.5, 131.0, 130.5, 129.6, 127.5, 125.2, 121.6, 114.5, 71.9, 71.1, 35.3, 24.2; IR (ATR) 3275, 2928, 1668, 1494, 1241, 754 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}_3$: 319.0975. Found: 319.0971.

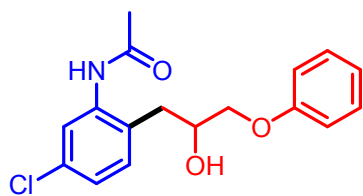
***N*-(4-Bromo-2-(2-hydroxy-3-phenoxypropyl)phenyl)acetamide (4g)**



The title compound was prepared according to the general procedure.

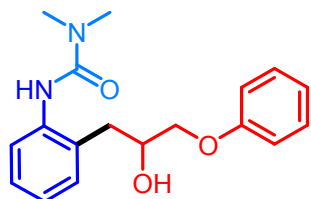
The product was obtained as a brown solid. $R_f = 0.2$ (50% EtOAc/Hexane); Yield: 74 % (268 mg); mp 146-148 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.09 (1H, s), 7.76 (1H, d, $J = 8.7$ Hz), 7.35 (1H, dd, $J = 8.6, 2.2$ Hz), 7.30-7.27 (3H, m), 6.98 (1H, t, $J = 7.4$ Hz), 6.88 (2H, d, $J = 7.9$ Hz), 4.29-4.26 (1H, m), 3.99 (1H, dd, $J = 9.3, 3.6$ Hz), 3.81 (1H, t, $J = 8.8$ Hz), 3.21 (1H, s), 2.85 (1H, dd, $J = 14.5, 3.1$ Hz), 2.80 (1H, dd, $J = 14.5, 7.6$ Hz), 2.11 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.6, 158.0, 136.1, 133.4, 131.3, 130.5, 129.6, 125.5, 121.6, 117.4, 114.5, 72.0, 71.1, 35.2, 24.3; IR (ATR) 3288, 2928, 1668, 1495, 1232, 754 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{18}\text{BrNO}_3$: 363.0470. Found: 363.0466.

***N*-(5-Chloro-2-(2-hydroxy-3-phenoxypropyl)phenyl)acetamide (4i)**



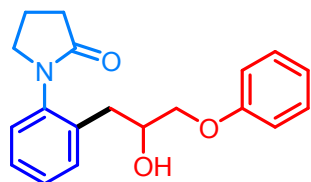
The title compound was prepared according to the general procedure. The product was obtained as a yellow solid. $R_f = 0.2$ (50% EtOAc/ Hexane); Yield: 68 % (218 mg); mp 115-117 °C. ^1H NMR (600 MHz, CDCl_3) δ 9.21 (1H, s), 7.94 (1H, s), 7.27 (2H, t, $J = 8.0$ Hz), 7.04-7.01 (2H, m), 6.97 (1H, t, $J = 7.4$ Hz), 6.86 (2H, d, $J = 7.9$ Hz), 4.29-4.26 (1H, m), 3.97 (1H, dd, $J = 9.3, 3.7$ Hz), 3.79 (1H, t, $J = 8.7$ Hz), 2.89 (1H, dd, $J = 14.6, 2.9$ Hz), 2.81 (1H, dd, $J = 14.7, 7.4$ Hz), 2.11 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.7, 158.0, 138.0, 133.0, 131.7, 129.6, 127.2, 124.6, 123.7, 121.5, 114.5, 71.9, 70.9, 35.0, 24.3; IR (ATR) 3291, 2928, 1672, 1368, 1230, 754 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}_3$: 319.0975. Found: 319.0977.

3-(2-(2-Hydroxy-3-phenoxypropyl)phenyl)-1,1-dimethylurea (5a)



The title compound was prepared according to the general procedure. The product was obtained as a colourless liquid. $R_f = 0.4$ (50% EtOAc/ Hexane); Yield: 71 % (240 mg); ^1H NMR (600 MHz, CDCl_3) δ 8.29 (1H, s), 7.65 (1H, d, $J = 8.1$ Hz), 7.26 (2H, t, $J = 7.9$ Hz), 7.17 (1H, t, $J = 7.7$ Hz), 7.07 (1H, d, $J = 7.5$ Hz), 6.98-6.94 (2H, m), 6.85 (2H, d, $J = 8.5$ Hz), 4.19-4.18 (1H, m), 3.91 (1H, dd, $J = 9.2, 4.1$ Hz), 3.78 (1H, t, $J = 8.4$ Hz), 3.66 (1H, s), 2.93 (6H, s), 2.86-2.83 (1H, m), 2.79 (1H, dd, $J = 14.4, 7.7$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 158.3, 156.5, 138.4, 130.6, 129.4, 129.4, 127.2, 124.3, 123.5, 121.1, 114.4, 71.9, 71.2, 36.3, 35.6; IR (ATR) 3288, 2925, 1638, 1527, 1493, 1244, 753 cm^{-1} ; HRMS (ESI) m/z [$\text{M}+\text{Na}$] $^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3\text{Na}$: 337.1528. Found: 337.1527.

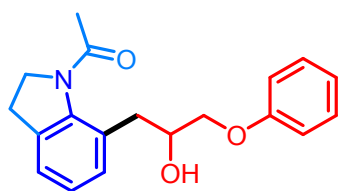
1-(2-(2-Hydroxy-3-phenoxypropyl)phenyl)pyrrolidin-2-one (5b)



The title compound was prepared according to the general procedure. The product was obtained as a yellow liquid. $R_f = 0.2$ (30% EtOAc/ Hexane); Yield: 80 % (268 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.40-7.39 (1H, m), 7.29-7.24 (4H, m), 7.13-7.11 (1H, m), 6.94 (1H, t, $J = 7.3$ Hz), 6.90 (2H, d, $J = 7.9$ Hz), 4.23-4.19 (1H, m), 3.97-3.95 (1H, m), 3.89 (1H, dd, $J = 9.3, 5.5$ Hz), 3.81-3.75 (1H, m), 3.68-3.64 (1H, m), 3.50 (1H, s), 2.97 (1H, dd, $J = 14.1, 4.0$ Hz), 2.73 (1H, dd, $J = 14.1, 8.8$ Hz), 2.56-2.50 (2H, m), 2.20-2.13 (2H, m); ^{13}C NMR (150 MHz, CDCl_3) δ 175.6, 158.4, 137.6, 135.9, 130.8, 129.3, 128.2, 127.6, 126.8, 120.8, 114.4, 71.3, 70.0, 51.6, 35.3, 31.1,

18.8; IR (ATR) 3381, 2926, 1667, 1493, 1242, 754 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{Na}$: 334.1419. Found: 334.1417.

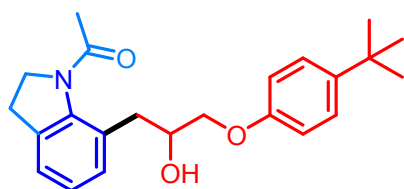
1-(7-(2-Hydroxy-3-phenoxypropyl)indolin-1-yl)ethan-1-one (5c)



The title compound was prepared according to the general procedure.

The product was obtained as a red solid. R_f = 0.3 (40% EtOAc/Hexane); Yield: 64 % (215 mg); mp 114-116 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 7.26 (2H, t, J = 7.9 Hz), 7.21-7.19 (1H, m), 7.10-7.09 (2H, m), 6.94-6.90 (3H, m), 4.32-4.29 (1H, m), 4.08 (1H, t, J = 7.5 Hz), 4.03-4.01 (1H, m), 3.95-3.90 (2H, m), 3.68-3.62 (1H, m), 3.09 (2H, dd, J = 14.6, 8.7 Hz), 2.96-2.84 (2H, m), 2.26 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 158.7, 141.2, 134.9, 129.3, 129.2, 125.8, 122.7, 120.7, 114.5, 114.4, 72.1, 69.7, 51.5, 37.0, 29.8, 24.1; IR (ATR) 3393, 2927, 1643, 1597, 1494, 1452, 1241, 755 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{Na}$: 334.1419. Found: 334.1418.

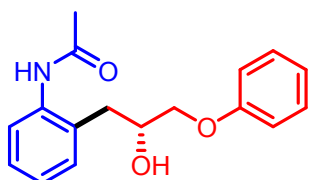
1-(7-(3-(4-(*tert*-butyl)phenoxy)-2-hydroxypropyl)indolin-1-yl)ethan-1-one (5d)



The title compound was prepared according to the general procedure. The product was obtained as a purple solid. R_f = 0.3 (30% EtOAc/Hexane); Yield: 68 % (265 mg); mp 125-127 $^{\circ}\text{C}$.

^1H NMR (600 MHz, CDCl_3) δ 7.28 (2H, d, J = 8.6 Hz), 7.20-7.19 (1H, m), 7.10-7.09 (2H, m), 6.85 (2H, d, J = 8.6 Hz), 4.31-4.28 (1H, m), 4.10-4.07 (1H, m), 4.02-3.99 (1H, m), 3.97-3.90 (2H, m), 3.13-3.06 (2H, m), 2.92 (2H, dd, J = 14.3, 9.2 Hz), 2.27 (3H, s), 1.28 (9H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 156.5, 143.4, 141.2, 134.9, 129.3, 129.1, 126.1, 125.8, 122.7, 114.0, 72.3, 69.8, 51.5, 37.1, 34.0, 31.5, 29.8, 24.1; IR (ATR) 3392, 2959, 1648, 1512, 1365, 1231, 829 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_3\text{Na}$: 390.2045. Found: 390.2044.

(*R*)-*N*-(2-(2-Hydroxy-3-phenoxypropyl)phenyl)acetamide (6a-*R*)

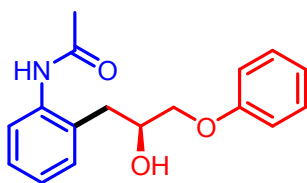


The title compound was prepared according to the general procedure.

The product was obtained as a white solid. R_f = 0.2 (50% EtOAc/Hexane); Yield: 75 % (215 mg); mp 115-117 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.32 (1H, s), 7.78 (1H, d, J = 8.0 Hz), 7.28-7.25 (2H, m), 7.19

(1H, t, $J = 7.0$ Hz), 7.12 (1H, d, $J = 6.4$ Hz), 7.05 (1H, t, $J = 7.4$ Hz), 6.96 (1H, t, $J = 7.4$ Hz), 6.87 (2H, d, $J = 7.8$ Hz), 4.24-4.20 (1H, m), 3.96 (1H, s), 3.91 (1H, dd, $J = 9.3, 4.5$ Hz), 3.80 (1H, dd, $J = 9.3, 7.4$ Hz), 2.89 (1H, dd, $J = 14.4, 3.1$ Hz), 2.82 (1H, dd, $J = 14.5, 7.6$ Hz), 2.08 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 169.0, 158.1, 136.6, 130.8, 129.6, 129.4, 127.3, 124.8, 124.0, 121.2, 114.4, 71.6, 70.9, 35.5, 24.0; IR (ATR) 3271, 2925, 1655, 1586, 1493, 1451, 752 cm^{-1} ; HRMS m/z $[\text{M}^+]$ calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3$: 285.1365. Found: 285.1367.

(S)-N-(2-(2-Hydroxy-3-phenoxypropyl)phenyl)acetamide (6b-S)

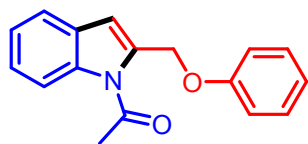


The title compound was prepared according to the general procedure.

The product was obtained as a white solid. $R_f = 0.2$ (50% EtOAc/Hexane); Yield: 76 % (217 mg); mp 117-119 $^{\circ}\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 9.30 (1H, s), 7.78 (1H, d, $J = 8.0$ Hz), 7.28-7.25 (2H, m), 7.20 (1H, t, $J = 7.7$ Hz), 7.12 (1H, d, $J = 7.5$ Hz), 7.04 (1H, t, $J = 7.4$

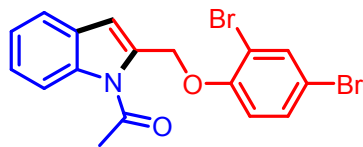
Hz), 6.96 (1H, t, $J = 7.4$ Hz), 6.87 (2H, d, $J = 7.8$ Hz), 4.24-4.21 (1H, m), 3.92 (1H, dd, $J = 9.3, 4.4$ Hz), 3.88 (1H, s), 3.80 (1H, dd, $J = 9.2, 7.5$ Hz), 2.90 (1H, dd, $J = 14.4, 3.1$ Hz), 2.82 (1H, dd, $J = 14.4, 7.5$ Hz), 2.09 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 168.9, 158.1, 136.7, 130.8, 129.5, 129.47, 127.3, 124.8, 124.0, 121.2, 114.4, 71.7, 70.9, 35.5, 24.0; IR (ATR) 3271, 2925, 1667, 1587, 1494, 1242, 753 cm^{-1} ; HRMS m/z $[\text{M}^+]$ calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3$: 285.1365. Found: 285.1367.

1-(2-(Phenoxymethyl)-1H-indol-1-yl)ethan-1-one (7)



The title compound was prepared according to the **Procedure 1**. The product was obtained as a liquid. $R_f = 0.3$ (30% EtOAc/Hexane); Yield: 86 % (50 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.77 (1H, d, $J = 8.4$ Hz), 7.47 (1H, d, $J = 7.7$ Hz), 7.24 (3H, q, $J = 7.2$ Hz), 7.19-7.17 (1H, m), 6.94 (2H, d, $J = 7.8$ Hz), 6.91 (1H, t, $J = 7.4$ Hz), 6.73 (1H, s), 5.37 (2H, s), 2.74 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 170.1, 158.3, 137.6, 136.2, 129.8, 129.5, 124.3, 123.3, 121.2, 121.1, 114.8, 114.6, 110.1, 65.5, 26.8; IR (ATR) 2923, 1699, 1597, 1300, 1212, 771, 752 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{Na}$: 288.1000. Found: 288.1001.

1-(2-((2,4-Dibromophenoxy)methyl)-1*H*-indol-1-yl)ethan-1-one (8)



The title compound was prepared according to the **Procedure 1**.

The product was obtained as a brown solid. R_f = 0.2 (30% EtOAc/Hexane); Yield: 92 % (78 mg); mp 72-74 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.74 (1H, d, J = 8.4 Hz), 7.69 (1H, d, J = 2.2 Hz), 7.57 (1H, d, J = 7.9 Hz), 7.35 (1H, dd, J = 8.7, 2.3 Hz), 7.31 (1H, t, J = 7.4 Hz), 7.27 (1H, d, J = 7.2 Hz), 6.90 (1H, s), 6.87 (1H, d, J = 8.8 Hz), 5.48 (2H, s), 2.83 (3H, s); ^{13}C NMR (150 MHz, CDCl_3) δ 170.1, 154.1, 136.9, 135.6, 131.2, 130.0, 124.3, 123.8, 123.3, 121.4, 114.7, 114.2, 113.4, 113.1, 109.8, 66.9, 27.0; IR (ATR) 3324, 2928, 1701, 1473, 1375, 1291, 1217, 743 cm^{-1} ; HRMS m/z [M^+] calcd for $\text{C}_{17}\text{H}_{13}\text{Br}^{79}\text{Br}^{81}\text{NO}_2$: 422.9293. Found: 422.9317.

Computational details:

i) Complete authorship of software packages used in this work

Gaussian 16, Revision A.03

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, **2016**.

CYLview

CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (<http://www.cylview.org>)

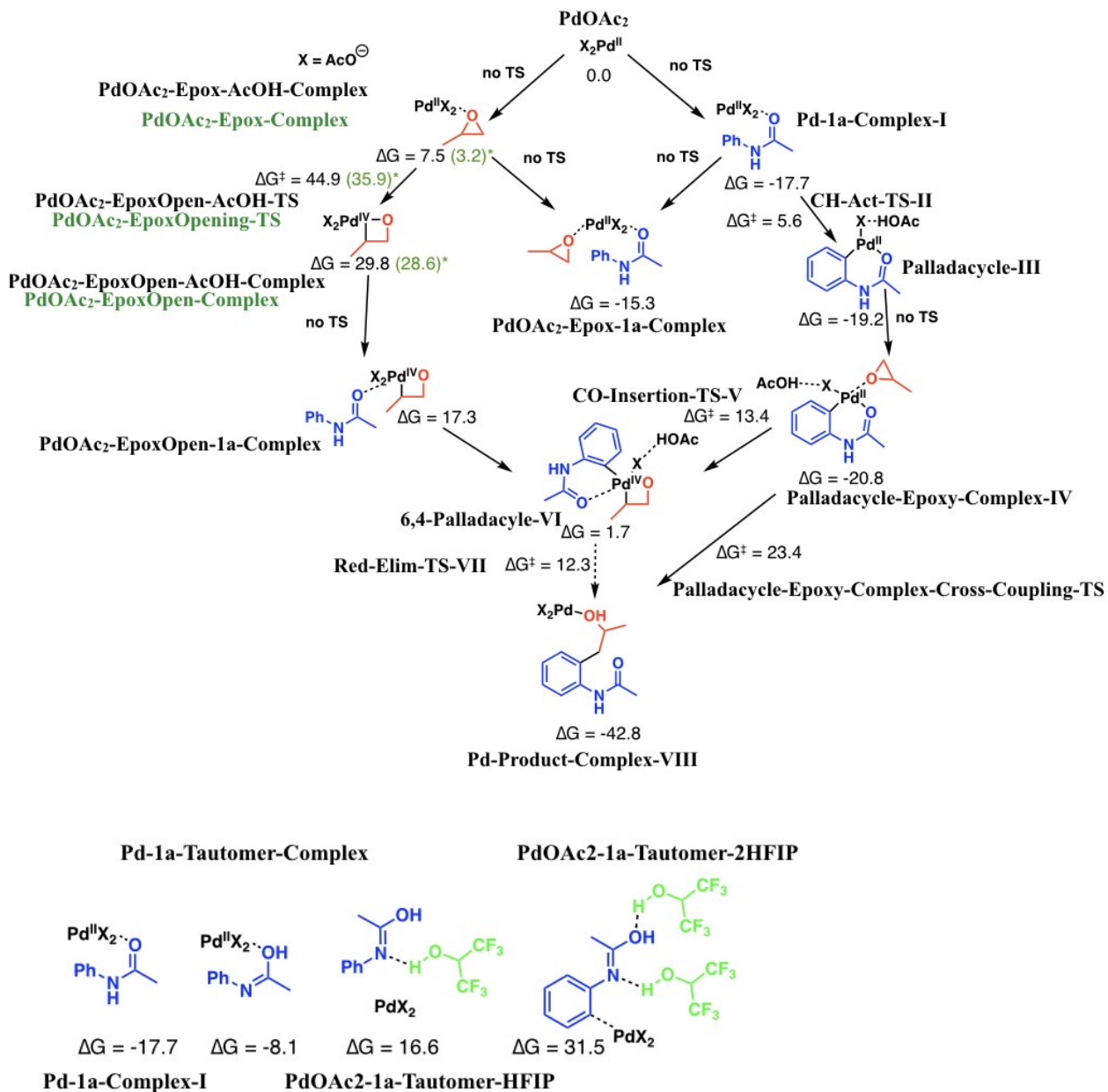
GaussView, Version 6.0.16

Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

ii) General Computational procedures

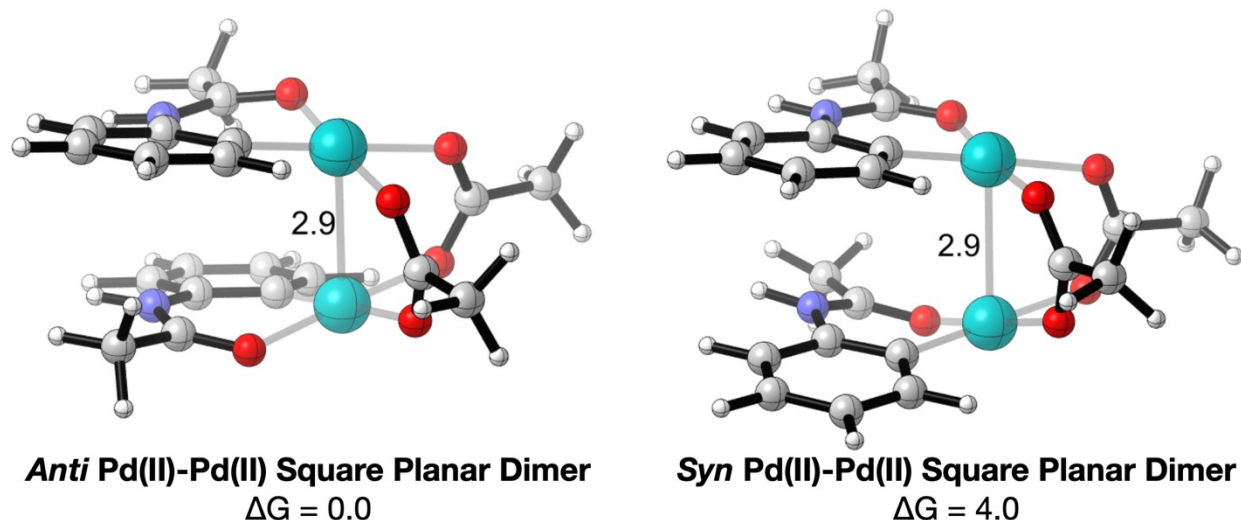
Manual conformational search was performed to locate relevant structures. All computations were performed using Density Functional Theory (DFT) using the Gaussian 16 software package (see above reference). All reactants, intermediates, and products were optimized using ω B97XD¹ functional with LANL2DZ² basis set for Pd and 6-31G*³ for all other atoms. Acetone with polarized continuum model (PCM)⁴ solvation method was used to model HFIP at 333.15 K to match experimental conditions. Images were created using CYLview (see above reference). All reported energy values are free energies in kcal/mol and all distances are in Ångströms (Å).

iii) Computed geometries and energies

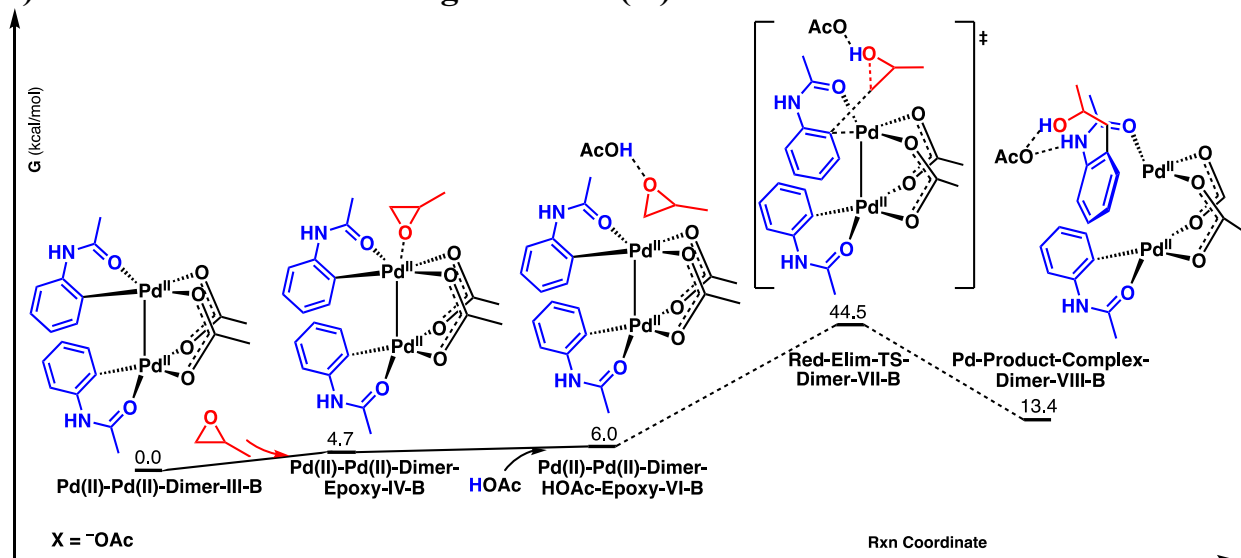


Structures from reaction coordinate diagram – Lowest energy pathway

iv) Pd(II) dimer intermediate computed geometries and energies



v) Reaction coordinate diagram of Pd(II) dimer mechanism



Pd(II) dimer structures that are analogous to literature Pd(II)-dimer species were computed. Reductive elimination barrier is 44.5 kcal/mol, prohibitively high and significantly higher than the monomer process where the rate-determining step barrier is $\Delta G^\ddagger = 30.0$ kcal/mol.

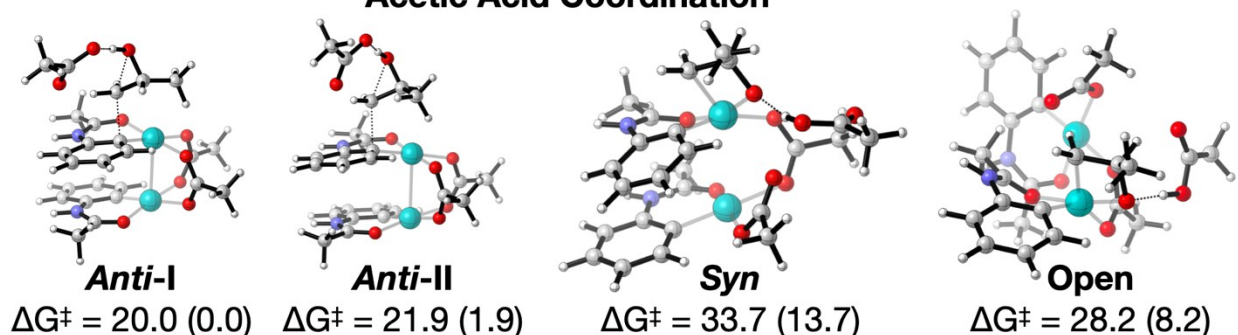
The dimer mechanism is significantly different than the monomer mechanism. The monomer mechanism proceeds via a stepwise C-O bond insertion then reductive elimination to form the C-C bond. In the dimer mechanism, despite extensive efforts to locate the stepwise pathway, the analogous transition structures were not stationary points on the potential energy surface. Rather, we discovered that the dimer mechanism proceeds via concerted C-O bond breaking and C-C bond forming reductive elimination process.

Syn- and *anti*-arrangements of the amides were explored for ground state and transition state structures. *Anti*-arrangements were revealed to be uniformly more stable than the *syn*. Both HFIP and acetic acid coordination to the forming alkoxide in the concerted reductive elimination

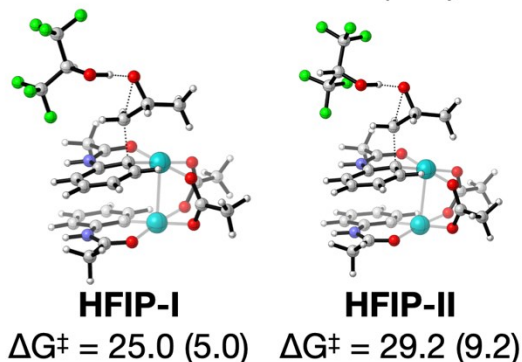
transition structures were computed. Alternate arrangements of the dimer species that are not analogous to literature precedents were also considered, and these were higher in energy than the *anti*-dimer.

vi) Pd dimer reductive elimination TS computed geometries and energies

Acetic Acid Coordination



HFIP Coordination (*Anti*)



vii) Input parameters of computed structures

Pd-1a-Complex-I

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
# wB97XD/gen pseudo=read 6D gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk Rwb97XD/ChkBas Freq
```

```
Pointgroup= C1 Stoichiometry= C12H15NO5Pd C1[X(C12H15NO5Pd)] #Atoms= 34
Charge = 0 Multiplicity = 1
```

```
SCF Energy= -1023.74662576 Predicted Change= -2.953086D-09
```

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00168	0.00180	[YES]	0.00168	0.00180	[YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	3.546463	1.586389	-0.357584
H	3.060867	2.530011	-0.132425
Pd	-1.736678	0.046523	0.337646
C	2.845040	0.388749	-0.230699
N	1.485398	0.361769	0.190064
C	0.961520	0.917346	1.280988
C	1.806453	1.693423	2.248927
H	1.367865	1.587579	3.241762
H	1.787278	2.754331	1.981490
H	2.843171	1.354651	2.256899
H	0.884630	-0.309562	-0.316252
C	3.444760	-0.822722	-0.576604
H	2.870743	-1.740827	-0.497823
C	4.759924	-0.833164	-1.027927
H	5.225595	-1.775976	-1.297013
C	5.478003	0.357113	-1.128503
H	6.506225	0.345148	-1.475757
C	4.868406	1.563348	-0.793579
H	5.415689	2.496084	-0.885405
O	-0.266195	0.814033	1.552645
C	-3.542880	1.030714	-0.970505
C	-4.682616	1.613688	-1.737314
H	-5.562183	1.649051	-1.086080
H	-4.917644	0.984374	-2.597624
H	-4.442612	2.628580	-2.057542
O	-3.388934	-0.233576	-0.874573
O	-2.700011	1.765061	-0.360519
C	-0.389372	-2.447318	0.037392
C	-0.170669	-3.907999	0.366446
H	0.215888	-4.433935	-0.507832
H	-1.092661	-4.376433	0.715501
H	0.571275	-3.977475	1.169352
O	0.242016	-1.900161	-0.879263
O	-1.236244	-1.848536	0.806756

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1023.74662576 Predicted Change= -2.953086D-09
 Zero-point correction (ZPE)= -1023.4823 0.26431
 Internal Energy (U)= -1023.4571 0.28942
 Enthalpy (H)= -1023.4561 0.29048
 Gibbs Free Energy (G)= -1023.5454 0.20115

 Frequencies -- 14.4412 32.7487 34.1042

CH-Act-TS-II

 Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

=====

```
#wB97XD/gen pseudo=read 6D scf=(maxcycle=300,direct,tight,xqc)
density=current opt=(maxcycle=250,maxstep=10,gdiis,modredundant)
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
Modredundant Input: B 1 27 F
Modredundant Input: B 27 34 F
Modredundant Input:
#wB97XD/gen pseudo=read 6D scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,nofreeze,maxstep=10,gdiis,ts,calcfc,noeigentest)
iop(1/8=18) freq=noraman SCRF=(PCM,SOLVENT=acetone) Temperature=333.15
geom=check guess=read
#N Geom=AllCheck Guess=TCHECK SCRF=Check Test GenChk RwB97XD/ChkBas Freq
```

Pointgroup= C1 Stoichiometry= C12H15NO5Pd C1[X(C12H15NO5Pd)] #Atoms= 34
 Charge = 0 Multiplicity = 1

 SCF Energy= -1023.70303834 Predicted Change= -3.275157D-08

=====

```
Optimization completed on the basis of negligible forces. {Found 3 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00000 || 0.00045 [ YES ] 0.00000 || 0.00030 [ YES ]
Displ 0.01793 || 0.00180 [ NO ] 0.01793 || 0.00180 [ NO ]
```

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	0.999918	0.900671	-0.293444
Pd	-0.223437	-0.792163	-0.476463
C	0.399076	2.074419	0.231240
N	-0.485115	2.089653	1.311551
C	-0.795050	1.095473	2.208554
C	-1.957653	1.428131	3.115897
H	-2.891434	1.253163	2.570192
H	-1.947088	2.470649	3.445725
H	-1.929938	0.770029	3.984466

H	-0.988618	2.957812	1.432551
C	0.655200	3.316775	-0.367170
H	0.202372	4.215241	0.043452
C	1.471815	3.410399	-1.482238
H	1.646840	4.384896	-1.927882
C	2.075453	2.272931	-2.025692
H	2.723696	2.352522	-2.891795
C	1.835546	1.049873	-1.428111
H	2.320695	0.159177	-1.819556
O	-0.206544	0.026271	2.256370
C	-2.656181	-0.919698	-0.937263
C	-4.128119	-0.896229	-1.214982
H	-4.623885	-0.202555	-0.531601
H	-4.551892	-1.895842	-1.112001
H	-4.293798	-0.537910	-2.235911
O	-2.025858	0.184055	-0.779837
O	-2.006917	-2.002789	-0.867072
H	1.628358	0.083652	0.548285
C	2.257115	-1.876684	0.587283
C	3.174625	-3.015164	0.945287
H	4.170529	-2.640833	1.184843
H	3.221066	-3.739565	0.131307
H	2.769827	-3.516494	1.830613
O	1.295217	-2.133111	-0.201208
O	2.472442	-0.742852	1.097694

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1023.70303834	Predicted Change=	-3.275157D-08
Zero-point correction (ZPE)=		-1023.4452	0.25780
Internal Energy (U)=		-1023.4199	0.28312
Enthalpy (H)=		-1023.4188	0.28417
Gibbs Free Energy (G)=		-1023.5084	0.19460

Frequencies -- -1353.9026 14.8606 28.0951

Palladacycle-III

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
# wB97XD/gen pseudo=read 6D gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk Rwb97XD/ChkBas Freq
```

Pointgroup= C1 Stoichiometry= C12H15NO5Pd C1[X(C12H15NO5Pd)] #Atoms= 34
 Charge = 0 Multiplicity = 1

 SCF Energy= -1023.75094127 Predicted Change= -1.420530D-08
 =====

Optimization completed.	{Found	1	times}
Item	Max Val.	Criteria	Pass? RMS Val. Criteria Pass?
Force	0.00002	0.00045	[YES] 0.00000 0.00030 [YES]
Displ	0.00358	0.00180	[NO] 0.00358 0.00180 [YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.045861	1.129727	-0.555771
Pd	0.630370	-0.618931	-1.093000
C	-1.408922	1.339511	-0.312474
N	-2.396513	0.331024	-0.442427
C	-2.295509	-0.859982	-1.041423
C	-3.506478	-1.743175	-1.038774
H	-3.376198	-2.470999	-0.231351
H	-3.559855	-2.283892	-1.984702
H	-4.434334	-1.192472	-0.875775
H	-3.310596	0.570470	-0.082299
C	-1.867943	2.594412	0.105471
H	-2.928476	2.742214	0.293271
C	-0.981622	3.647799	0.271839
H	-1.351396	4.614649	0.597243
C	0.372570	3.455503	0.011990
H	1.076261	4.273449	0.132328
C	0.830187	2.207354	-0.398887
H	1.886653	2.056090	-0.587861
O	-1.242311	-1.279404	-1.567555
C	3.072907	-0.486783	0.458002
C	4.555521	-0.201655	0.597800
H	5.094986	-0.518160	-0.298138
H	4.961774	-0.701708	1.477984
H	4.698167	0.879030	0.705483
O	2.580232	-0.160170	-0.685337
O	2.443627	-0.975393	1.409978
C	-1.005745	-1.021217	2.176395
C	-2.232299	-0.445597	2.836389
H	-2.334383	0.610746	2.571029
H	-2.127102	-0.501718	3.924198
H	-3.118818	-0.999509	2.526998
O	-1.006372	-2.033488	1.497587
O	0.076758	-0.297176	2.422575

H 0.865595 -0.654873 1.925264

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1023.75094127 Predicted Change= -1.420530D-08
 Zero-point correction (ZPE)= -1023.4865 0.26435
 Internal Energy (U)= -1023.4611 0.28978
 Enthalpy (H)= -1023.4601 0.29083
 Gibbs Free Energy (G)= -1023.5479 0.20300

Frequencies -- 31.6318 36.0375 43.8378

Palladacycle-Epoxy-Complex-IV

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

wB97XD/gen pseudo=read 6D gfprint gfinput
 scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
 SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk Rwb97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H21NO6Pd C1[X(C15H21NO6Pd)] #Atoms= 44
 Charge = 0 Multiplicity = 1

SCF Energy= -1216.79208642 Predicted Change= -7.355804D-08

Optimization completed. {Found 1 times}
 Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
 Force 0.00002 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
 Displ 0.01681 || 0.00180 [NO] 0.01681 || 0.00180 [NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-4.348632	-0.021672	-0.811677
H	-5.000835	0.631430	-1.385410
Pd	-0.264941	-0.013645	0.445876
C	-3.002984	0.323398	-0.640524
N	-2.587591	1.530860	-1.256870
C	-1.514362	2.279441	-0.985261
C	-1.386861	3.601623	-1.682750
H	-1.243825	4.378573	-0.928016
H	-2.254645	3.848761	-2.295609
H	-0.493158	3.577947	-2.312039
H	-3.249135	1.926737	-1.911262

C	-2.158193	-0.506763	0.100255
C	-2.677576	-1.672450	0.664469
H	-2.012442	-2.320208	1.223790
C	-4.016857	-2.010485	0.498261
H	-4.402187	-2.920633	0.946909
C	-4.852755	-1.183712	-0.247495
H	-5.898098	-1.437802	-0.388891
O	-0.613784	1.939559	-0.186374
C	1.455555	0.940334	2.275941
C	2.571308	1.387134	3.188332
H	3.311318	0.585549	3.275587
H	2.189100	1.640839	4.177587
H	3.076334	2.254328	2.752903
O	0.274567	0.859613	2.673245
O	1.763565	0.641931	1.065089
C	0.369751	-2.309045	-0.546079
H	-0.441236	-3.005819	-0.802831
O	0.215677	-1.876315	0.805979
C	1.718413	-2.969859	-0.758661
H	1.847253	-3.261211	-1.807137
H	1.797258	-3.868574	-0.138031
H	2.521322	-2.281195	-0.477105
C	0.186002	-0.989666	-1.278790
H	-0.620478	-0.926174	-2.006217
H	1.097644	-0.460833	-1.567660
C	4.029953	0.007808	-1.331946
C	5.270065	-0.542456	-1.985965
H	6.164634	-0.190460	-1.466028
H	5.302284	-0.246788	-3.034450
H	5.255937	-1.635164	-1.917299
O	4.032857	-0.172671	-0.016179
H	3.185401	0.183653	0.379897
O	3.115998	0.537497	-1.939207

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1216.79208642	Predicted Change=	-7.355804D-08
Zero-point correction (ZPE)=	-1216.4390	0.35307	
Internal Energy (U)=	-1216.4073	0.38476	
Enthalpy (H)=	-1216.4062	0.38582	
Gibbs Free Energy (G)=	-1216.5094	0.28260	

Frequencies -- 21.0418 29.8314 35.2479

CO-Insertion-TS-V

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
=====

wB97XD/gen pseudo=read 6D gffprint gffinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
#N Geom=AllCheck Guess=TCHECK SCRF=Check Test GenChk Rwb97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H21NO6Pd C1[X(C15H21NO6Pd)] #Atoms= 44
Charge = 0 Multiplicity = 1

SCF Energy= -1216.77122837 Predicted Change= -2.942190D-09
=====

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00000 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.00434 || 0.00180 [NO] 0.00434 || 0.00180 [YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	1.335600	0.802613	-0.380237
Pd	-0.535552	0.136890	-0.484924
C	2.432794	-0.001975	-0.714474
N	2.326971	-1.329326	-1.200666
C	1.236469	-2.043550	-1.479940
C	1.428151	-3.451594	-1.963750
H	1.067560	-4.133060	-1.187857
H	2.468807	-3.687788	-2.190751
H	0.817523	-3.604286	-2.856078
H	3.209108	-1.800636	-1.348441
C	3.743707	0.465281	-0.553594
H	4.580047	-0.176447	-0.819672
C	3.982100	1.733103	-0.048059
H	5.002727	2.080218	0.076381
C	2.905177	2.545184	0.297984
H	3.073669	3.538475	0.702770
C	1.606020	2.079039	0.126413
H	0.771681	2.709703	0.412252
O	0.067912	-1.618801	-1.355985
O	0.077571	-0.215558	3.152817
C	0.830122	-0.943399	2.533032
C	2.331306	-0.878428	2.653798
H	2.612567	-0.878093	3.709671
H	2.669321	0.066790	2.215911

H	2.818744	-1.704152	2.134187
O	0.414487	-1.862744	1.665547
C	-2.927236	-1.406875	0.331347
O	-2.208348	-1.873780	1.238438
H	-0.581646	-1.797174	1.541500
C	-4.388496	-1.818917	0.264453
H	-4.597288	-2.281972	-0.704809
H	-5.023564	-0.931345	0.345632
H	-4.635324	-2.518681	1.064185
O	-2.556741	-0.590071	-0.577285
C	-1.471087	2.041763	-1.468288
H	-0.612852	2.634918	-1.764658
H	-1.856514	1.303402	-2.166844
C	-2.274444	2.511494	-0.338210
C	-2.328216	3.986188	-0.026690
H	-1.344634	4.447042	-0.157814
H	-2.648699	4.129775	1.009750
H	-3.047467	4.485896	-0.683048
H	-3.245879	2.017327	-0.252451
O	-1.270266	1.834563	0.405045

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1216.77122837	Predicted Change=	-2.942190D-09
Zero-point correction (ZPE)=	-1216.4198	0.35142	
Internal Energy (U)=	-1216.3880	0.38319	
Enthalpy (H)=	-1216.3869	0.38424	
Gibbs Free Energy (G)=	-1216.4908	0.28035	

Frequencies -- -319.6753 19.0943 27.3565

6,4-Palladacycle-VI

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
# wB97XD/gen pseudo=read 6D gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
#N Geom=AllCheck Guess=TCHECK SCRF=Check Test GenChk Rwb97XD/ChkBas Freq
```

Pointgroup= C1 Stoichiometry= C15H21NO6Pd C1[X(C15H21NO6Pd)] #Atoms= 44
Charge = 0 Multiplicity = 1

SCF Energy=	-1216.79208642	Predicted Change=	-7.355804D-08
-------------	----------------	-------------------	---------------

Optimization completed. {Found 1 times}
 Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
 Force 0.00002 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
 Displ 0.01681 || 0.00180 [NO] 0.01681 || 0.00180 [NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-4.348632	-0.021672	-0.811677
H	-5.000835	0.631430	-1.385410
Pd	-0.264941	-0.013645	0.445876
C	-3.002984	0.323398	-0.640524
N	-2.587591	1.530860	-1.256870
C	-1.514362	2.279441	-0.985261
C	-1.386861	3.601623	-1.682750
H	-1.243825	4.378573	-0.928016
H	-2.254645	3.848761	-2.295609
H	-0.493158	3.577947	-2.312039
H	-3.249135	1.926737	-1.911262
C	-2.158193	-0.506763	0.100255
C	-2.677576	-1.672450	0.664469
H	-2.012442	-2.320208	1.223790
C	-4.016857	-2.010485	0.498261
H	-4.402187	-2.920633	0.946909
C	-4.852755	-1.183712	-0.247495
H	-5.898098	-1.437802	-0.388891
O	-0.613784	1.939559	-0.186374
C	1.455555	0.940334	2.275941
C	2.571308	1.387134	3.188332
H	3.311318	0.585549	3.275587
H	2.189100	1.640839	4.177587
H	3.076334	2.254328	2.752903
O	0.274567	0.859613	2.673245
O	1.763565	0.641931	1.065089
C	0.369751	-2.309045	-0.546079
H	-0.441236	-3.005819	-0.802831
O	0.215677	-1.876315	0.805979
C	1.718413	-2.969859	-0.758661
H	1.847253	-3.261211	-1.807137
H	1.797258	-3.868574	-0.138031
H	2.521322	-2.281195	-0.477105
C	0.186002	-0.989666	-1.278790
H	-0.620478	-0.926174	-2.006217
H	1.097644	-0.460833	-1.567660
C	4.029953	0.007808	-1.331946
C	5.270065	-0.542456	-1.985965

H	6.164634	-0.190460	-1.466028
H	5.302284	-0.246788	-3.034450
H	5.255937	-1.635164	-1.917299
O	4.032857	-0.172671	-0.016179
H	3.185401	0.183653	0.379897
O	3.115998	0.537497	-1.939207

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1216.79208642	Predicted Change=	-7.355804D-08
Zero-point correction (ZPE)=	-1216.4390	0.35307	
Internal Energy (U)=	-1216.4073	0.38476	
Enthalpy (H)=	-1216.4062	0.38582	
Gibbs Free Energy (G)=	-1216.5094	0.28260	

Frequencies -- 21.0418 29.8314 35.2479

Red-Elim-TS-VII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
#wB97XD/gen pseudo=read 6D scf=(maxcycle=300,direct,tight,xqc)
density=current opt=(maxcycle=250,modredundant) SCRF=(PCM,SOLVENT=acetone)
iop(1/8=18) Temperature=333.15
Modredundant Input: B    6    32 F
Modredundant Input:
#wB97XD/gen pseudo=read 6D scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
SCRF=(PCM,SOLVENT=acetone) Temperature=333.15 geom=check guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk Rwb97XD/ChkBas Freq
```

Pointgroup= C1 Stoichiometry= C15H21NO6Pd C1[X(C15H21NO6Pd)] #Atoms= 44
Charge = 0 Multiplicity = 1

SCF Energy= -1216.77965069 Predicted Change= -1.108515D-08

Optimization completed.		{Found 2 times}	
Item	Max Val. Criteria	Pass?	RMS Val. Criteria Pass?
Force	0.00012 0.00045	[YES]	0.00001 0.00030 [YES]
Displ	0.00324 0.00180	[NO]	0.00324 0.00180 [YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z

C	-3.317583	-2.460089	-0.556078
---	-----------	-----------	-----------

H	-3.539150	-3.516493	-0.666955
Pd	0.230018	-0.147192	-0.499209
C	-2.024295	-2.057273	-0.251220
H	-1.234909	-2.788705	-0.122148
C	-1.712025	-0.701902	-0.105235
C	-2.731056	0.246670	-0.272950
N	-2.512042	1.629079	-0.078275
C	-1.405470	2.317406	-0.382529
C	-1.410395	3.795676	-0.151351
H	-0.851176	3.979188	0.771415
H	-2.415381	4.209038	-0.053338
H	-0.885645	4.285333	-0.973083
H	-3.313348	2.168461	0.222553
C	-4.031419	-0.160456	-0.573504
H	-4.809050	0.586862	-0.700776
C	-4.324631	-1.509622	-0.712843
H	-5.338761	-1.816108	-0.946228
C	1.977154	-2.348593	0.234428
C	2.329394	-3.815216	0.056895
H	3.234526	-4.053818	0.616987
H	2.487117	-4.031890	-1.003854
H	1.503719	-4.443914	0.402500
O	2.679119	-1.583523	0.882390
O	0.859671	-2.042843	-0.371370
C	0.540407	0.458563	2.214555
H	1.498874	0.029418	1.909517
C	0.384241	0.308378	3.730231
H	-0.563810	0.741577	4.067341
H	1.202512	0.844488	4.219546
H	0.422885	-0.740739	4.038101
C	-0.619298	-0.349863	1.593735
H	-1.556908	0.079029	1.940448
H	-0.549283	-1.405921	1.846239
O	0.486687	1.828041	1.887760
C	2.733861	1.195273	-1.006525
C	4.025447	1.405372	-1.776275
H	4.534428	2.307476	-1.433333
H	3.828773	1.469676	-2.849339
H	4.679506	0.542825	-1.609962
O	2.524414	1.826344	0.038019
H	1.134571	1.949598	1.159685
O	1.954409	0.314646	-1.534890
O	-0.373299	1.785582	-0.848384

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

```
=====
SCF Energy=  -1216.77965069   Predicted Change= -1.108515D-08
Zero-point correction (ZPE)=          -1216.4261  0.35351
Internal Energy (U)=          -1216.3953  0.38430
Enthalpy (H)=          -1216.3942  0.38536
Gibbs Free Energy (G)=          -1216.4925  0.28714
=====
```

```
-----
Frequencies --  -275.2552          33.3532          36.8005
=====
```

Pd-Product-Complex-VIII

```
-----
Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
=====
```

```
=====
# wB97XD/gen pseudo=read 6D gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
#N Geom=AllCheck Guess=TCHECK SCRF=Check Test GenChk Rwb97XD/ChkBas Freq
=====
```

```
Pointgroup= C1  Stoichiometry= C15H21NO6Pd  C1[X(C15H21NO6Pd)] #Atoms= 44
Charge = 0    Multiplicity = 1
=====
```

```
SCF Energy= -1216.86858822   Predicted Change= -1.320291D-07
=====
```

```
=====
Optimization completed.      {Found      1      times}
Item   Max Val.  Criteria  Pass?   RMS Val.  Criteria  Pass?
Force   0.00013 || 0.00045 [ YES ]   0.00001 || 0.00030 [ YES ]
Displ   0.03456 || 0.00180 [ NO ]   0.03456 || 0.00180 [ NO ]
=====
```

```
-----
Atomic      Coordinates (Angstroms)
Type        X          Y          Z
-----
C          1.003144   -0.053080   -2.399070
H          2.085112   -0.088777   -2.431816
Pd          0.128585   -0.340677    0.949494
C          0.387361    0.985885   -1.702798
N          1.237625    1.996014   -1.132497
C          1.734501    2.029298    0.110259
C          2.810312    3.037727    0.388947
H          2.873250    3.816219   -0.373310
H          3.761039    2.497000    0.426974
H          2.635282    3.490814    1.365913
H          1.667344    2.630181   -1.792934
C         -1.007693    1.074167   -1.608040
C         -1.757923    0.056293   -2.204973
H         -2.839720    0.088150   -2.122691
C         -1.152609   -0.995202   -2.883386
=====
```

H	-1.765825	-1.769758	-3.333577
C	0.234193	-1.047891	-2.988884
H	0.717018	-1.861096	-3.521070
O	1.360607	1.307265	1.061665
C	2.788852	-1.461606	0.323482
C	3.693097	-2.680016	0.444859
H	3.788546	-2.979852	1.492179
H	4.678963	-2.459812	0.032481
H	3.251303	-3.520774	-0.099092
O	1.635896	-1.659926	0.893190
O	3.159378	-0.449340	-0.264337
C	-1.581217	2.223829	0.644986
H	-0.635925	2.692603	0.917475
C	-2.721235	2.996172	1.290359
H	-2.769034	4.008567	0.876694
H	-2.572265	3.066828	2.370957
H	-3.679713	2.501685	1.097639
O	-1.517974	0.916849	1.237279
C	-1.727562	2.190749	-0.889575
H	-2.792455	2.113245	-1.134728
H	-1.390034	3.164290	-1.263559
C	-2.297292	-1.993486	0.570888
C	-2.867781	-3.348531	0.214998
H	-3.951668	-3.350443	0.338392
H	-2.413479	-4.133895	0.822258
H	-2.632103	-3.555656	-0.834694
O	-3.040837	-0.992353	0.558162
H	-2.270766	0.305075	0.939223
O	-1.041076	-2.002670	0.839756

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1216.86858822 Predicted Change= -1.320291D-07

Zero-point correction (ZPE)= -1216.5128 0.35578

Internal Energy (U)= -1216.4820 0.38649

Enthalpy (H)= -1216.4810 0.38755

Gibbs Free Energy (G)= -1216.5802 0.28829

Frequencies -- 22.0756 28.6613 40.6927

Noteworthy structures

B3LYP

CH-Act-TS

```

=====
#b3lyp/gen pseudo=read 6D scf=(maxcycle=300,direct,tight,xqc)
density=current opt=(maxcycle=250,maxstep=10,gdiis,modredundant)
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
Modredundant Input: B    1    27 F
Modredundant Input: B   27   34 F
Modredundant Input:
#b3lyp/gen pseudo=read 6D scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,nofreeze,maxstep=10,gdiis,ts,calcfc,noeigentest)
iop(1/8=18) freq=noraman SCRF=(PCM,SOLVENT=acetone) Temperature=333.15
geom=check guess=read
#N Geom=AllCheck Guess=TCHECK SCRF=Check Test GenChk RB3LYP/ChkBas Freq
=====

```

```

Pointgroup= C1  Stoichiometry= C12H15NO5Pd  C1[X(C12H15NO5Pd)] #Atoms= 34
Charge = 0    Multiplicity = 1
=====

```

```

SCF Energy= -1024.00067110      Predicted Change= -5.273519D-08
=====

```

```

Optimization completed on the basis of negligible forces.      {Found    3    times}
Item  Max Val.  Criteria  Pass?  RMS Val.  Criteria  Pass?
Force  0.00000 || 0.00045 [ YES ]   0.00000 || 0.00030 [ YES ]
Displ  0.03698 || 0.00180 [ NO ]   0.03698 || 0.00180 [ NO ]
=====

```

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	1.120999	0.454437	-0.615511
Pd	-0.727133	-0.537209	-0.357629
C	1.360836	1.641971	0.138808
N	1.090038	1.791598	1.505258
C	0.700150	0.867406	2.452580
C	0.432652	1.465480	3.821922
H	-0.575156	1.897562	3.842546
H	1.144036	2.256108	4.080072
H	0.484886	0.671908	4.568732
H	1.229118	2.731812	1.855139
C	1.907184	2.774029	-0.495032
H	2.099194	3.672632	0.086730
C	2.196601	2.762850	-1.853466
H	2.610868	3.655529	-2.313674
C	1.973212	1.612386	-2.622322
H	2.215932	1.600015	-3.680492
C	1.447861	0.490060	-2.000041
H	1.299799	-0.418053	-2.579404
O	0.556844	-0.326935	2.214821

C	-3.030445	0.443876	-0.336342
C	-4.372165	1.118862	-0.358859
H	-4.349453	2.026775	0.249788
H	-5.146466	0.439656	0.003255
H	-4.611271	1.410337	-1.388250
O	-1.959493	1.153334	-0.395495
O	-2.919564	-0.820700	-0.283647
H	1.619945	-0.688105	-0.111621
C	1.247638	-2.706502	-0.020709
C	1.626710	-4.155757	0.177952
H	2.610346	-4.348950	-0.256312
H	0.878133	-4.816234	-0.261369
H	1.688283	-4.354960	1.253956
O	0.037524	-2.449618	-0.310441
O	2.153720	-1.828607	0.128656

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1024.00067110	Predicted Change=	-5.273519D-08
Zero-point correction (ZPE)=	-1023.7461	0.25447	
Internal Energy (U)=	-1023.7205	0.28009	
Enthalpy (H)=	-1023.7195	0.28115	
Gibbs Free Energy (G)=	-1023.8099	0.19069	

Frequencies --	-1314.2812	12.3656	25.7170
----------------	------------	---------	---------

CH-Act-Tautomer-TS

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
#b3lyp/gen pseudo=read 6D scf=(maxcycle=300,direct,tight,xqc)
density=current opt=(maxcycle=250,maxstep=10,gdiis,modredundant)
iop(1/8=18) Temperature=333.15 SCRF=(PCM,SOLVENT=acetone)
Modredundant Input: B   26   33 F
Modredundant Input: B    1   26 F
Modredundant Input:
#b3lyp/gen pseudo=read 6D scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,maxstep=10,gdiis,ts,calcfc,noeigentest)
iop(1/8=18) freq=noraman SCRF=(PCM,SOLVENT=acetone) Temperature=333.15
geom=check guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/ChkBas Freq
```

Pointgroup= C1 Stoichiometry= C12H15NO5Pd C1[X(C12H15NO5Pd)] #Atoms= 34
Charge = 0 Multiplicity = 1

SCF Energy= -1023.97792463 Predicted Change= -1.534914D-06

Optimization completed on the basis of negligible forces. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.75356	0.00180	[NO]	0.75356	0.00180	[NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	0.721684	0.789717	-0.752012
Pd	-0.933130	-0.421883	-0.342349
C	1.265344	1.556442	0.332874
N	1.151852	1.186319	1.667014
C	1.661468	0.187160	2.277532
C	1.404399	-0.036578	3.739961
H	0.893383	-0.994683	3.886315
H	0.793805	0.770428	4.144650
H	2.354686	-0.087762	4.282450
C	1.848947	2.809705	0.059679
H	2.261806	3.381284	0.885468
C	1.867925	3.320173	-1.232073
H	2.322886	4.290593	-1.412025
C	1.303595	2.605603	-2.302204
H	1.320237	3.016927	-3.306858
C	0.734999	1.367169	-2.054498
H	0.323833	0.790231	-2.879241
O	2.483951	-0.762579	1.780312
C	-3.226611	0.296511	0.356327
C	-4.559932	0.833134	0.792672
H	-4.478652	1.219515	1.814822
H	-5.315774	0.046221	0.764723
H	-4.858339	1.664254	0.146888
O	-2.253741	1.113360	0.147991
O	-3.021542	-0.946600	0.199277
H	1.374750	-0.348846	-0.857754
C	1.209704	-2.415997	-0.903561
C	1.730732	-3.821903	-1.060995
H	2.343492	-3.885169	-1.964820
H	0.909667	-4.537207	-1.110296
H	2.375076	-4.058833	-0.207677
O	-0.031494	-2.242490	-0.744812
O	2.062242	-1.458269	-0.937043
H	2.551320	-0.738777	0.804329

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1023.97792463 Predicted Change= -1.534914D-06
Zero-point correction (ZPE)= -1023.7243 0.25355
Internal Energy (U)= -1023.6988 0.27907
Enthalpy (H)= -1023.6977 0.28012
Gibbs Free Energy (G)= -1023.7884 0.18950

Frequencies -- -1137.0545 6.9549 18.2724

ωB97XD

PdOAc₂-Epox-1a-Complex

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

wB97XD/gen pseudo=read 6D gfpri n gfinpu t
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
#N Geom=AllCheck Guess=TChe ck SCRF=Check Test GenChk R wB97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H21NO6Pd C1[X(C15H21NO6Pd)] #Atoms= 44
Charge = 0 Multiplicity = 1

SCF Energy= -1216.81577192 Predicted Change= -2.335966D-08

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00001 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.01517 || 0.00180 [NO] 0.01517 || 0.00180 [NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-3.627542	-1.117437	0.482419
H	-2.957146	-1.969940	0.436235
Pd	1.355438	0.136801	-0.298396
C	-3.173288	0.132067	0.062639
N	-1.848189	0.289772	-0.431487
C	-1.295733	-0.389275	-1.426617
C	-2.114227	-1.292614	-2.299798
H	-3.172541	-1.030682	-2.305034
H	-2.001567	-2.315540	-1.927416
H	-1.709212	-1.253283	-3.312191
H	-1.249090	0.971763	0.067646
C	-3.985067	1.259329	0.174744
H	-3.604030	2.225174	-0.142298

C	-5.270616	1.129193	0.690928
H	-5.905219	2.005480	0.778379
C	-5.743696	-0.120872	1.085858
H	-6.749288	-0.220476	1.482377
C	-4.921064	-1.240589	0.981169
H	-5.280387	-2.212951	1.303376
O	-0.065853	-0.290274	-1.705844
C	0.745642	-2.639701	0.274615
C	1.180496	-4.093850	0.318287
H	2.035382	-4.208339	0.991479
H	1.501603	-4.415623	-0.677046
H	0.358251	-4.724828	0.658644
O	1.704421	-1.839083	-0.092556
O	-0.396984	-2.295018	0.566519
C	0.429912	2.855642	0.034791
C	0.639311	4.348891	-0.115065
H	1.577999	4.633370	0.370681
H	-0.185011	4.897366	0.342166
H	0.722659	4.613508	-1.172523
O	1.277095	2.138848	-0.620989
O	-0.484948	2.410136	0.744111
C	4.270472	0.329758	0.917454
H	4.842984	1.175910	1.287743
C	4.687191	-0.224628	-0.412090
H	5.737617	-0.526890	-0.356834
H	4.592288	0.539631	-1.189578
H	4.082953	-1.094206	-0.682656
O	2.843255	0.558689	1.133750
C	3.530015	-0.465092	1.898494
H	3.235255	-1.475036	1.631073
H	3.586941	-0.226977	2.955503

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1216.81577192	Predicted Change=	-2.335966D-08
Zero-point correction (ZPE)=		-1216.4629	0.35284
Internal Energy (U)=		-1216.4307	0.38502
Enthalpy (H)=		-1216.4296	0.38607
Gibbs Free Energy (G)=		-1216.5364	0.27930

Frequencies --	15.0607	23.2209	29.2989
----------------	---------	---------	---------

Epoxide

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```

=====
# opt=(maxcycle=250,gdiis) freq=noraman wb97xd/gen
scrf=(solvent=acetone,pcm) geom=connectivity density=current pseudo=read
scf=(maxcycle=300,direct,tight) temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/ChkBas Freq
=====

```

```

-----
Pointgroup= C1  Stoichiometry= C3H6O  C1[X(C3H6O)] #Atoms= 10
Charge = 0  Multiplicity = 1
=====

```

```

SCF Energy= -193.048584360  Predicted Change= -3.936340D-07
=====

```

```

-----
Optimization completed.      {Found      2      times}
Item  Max Val.  Criteria  Pass?  RMS Val.  Criteria  Pass?
Force  0.00028 || 0.00045 [ YES ]  0.00007 || 0.00030 [ YES ]
Displ  0.00149 || 0.00180 [ YES ]  0.00149 || 0.00180 [ YES ]
=====

```

```

-----
Atomic      Coordinates (Angstroms)
Type       X        Y        Z
-----
O          0.826092  -0.782691  -0.248831
C          -0.150497  -0.045058   0.488588
H          -0.151498  -0.273783   1.555043
C          1.038624   0.615003  -0.055770
H          1.867742   0.873733   0.601007
H          0.943559   1.226371  -0.952673
C          -1.506273   0.100394  -0.148012
H          -2.076743  -0.829872  -0.057301
H          -2.073570   0.896372   0.345644
H          -1.409349   0.346674  -1.209912
=====

```

```

-----
Statistical Thermodynamic Analysis
Temperature= 333.150 Kelvin  Pressure= 1.00000 Atm
=====

```

```

SCF Energy=   -193.048584360 Predicted Change= -3.936340D-07
Zero-point correction (ZPE)=      -192.9617  0.08682
Internal Energy (U)=      -192.9565  0.09204
Enthalpy (H)=      -192.9554  0.09309
Gibbs Free Energy (G)=      -192.9918  0.05669
=====

```

```

Frequencies --  206.3707      373.7562      420.2558
=====

```

HOAc

```

-----
Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
=====

```

```

# opt=maxcycle=250 freq=noraman wb97xd/gen scrf=(pcm,solvent=acetone)
=====

```

density=current scf=(maxcycle=300,direct,tight) Temperature=333.15
#N Geom=AllCheck Guess=TChech SCRF=Check GenChk Rwb97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C2H4O2 C1[X(C2H4O2)] #Atoms= 8
Charge = 0 Multiplicity = 1

SCF Energy= -229.013550996 Predicted Change= -1.039195D-08

Optimization completed. {Found 2 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00004 || 0.00045 [YES] 0.00001 || 0.00030 [YES]
Displ 0.00013 || 0.00180 [YES] 0.00013 || 0.00180 [YES]

Atomic Coordinates (Angstroms)
Type X Y Z

C	-0.092661	0.119777	-0.000001
O	-0.644767	1.197801	-0.000030
O	-0.774242	-1.038437	-0.000019
H	-1.720410	-0.816674	-0.000056
C	1.392784	-0.108454	0.000045
H	1.679479	-0.687565	0.882652
H	1.679525	-0.687641	-0.882497
H	1.912741	0.849025	0.000020

Statistical Thermodynamic Analysis
Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -229.013550996 Predicted Change= -1.039195D-08
Zero-point correction (ZPE)= -228.9509 0.06260
Internal Energy (U)= -228.9455 0.06798
Enthalpy (H)= -228.9445 0.06903
Gibbs Free Energy (G)= -228.9821 0.03140

Frequencies -- 61.0377 431.8958 555.9360

•OAc

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

opt=(tight,maxcycle=250) freq=noraman wb97xd/gen
scrf=(pcm,solvent=acetone) density=current scf=(maxcycle=300,direct,tight)
Temperature=333.15
#N Geom=AllCheck Guess=TChech SCRF=Check GenChk Rwb97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C2H3O2(1-) C1[X(C2H3O2)] #Atoms= 7

Charge = -1 Multiplicity = 1

SCF Energy= -228.522371771 Predicted Change= -3.579805D-13

Optimization completed. {Found 2 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00000 || 0.00001 [YES] 0.00000 || 0.00001 [YES]
Displ 0.00000 || 0.00006 [YES] 0.00000 || 0.00006 [YES]

Atomic Coordinates (Angstroms)
Type X Y Z

C	0.199690	0.000047	0.007368
O	0.798832	-1.103574	-0.001607
O	0.714536	1.146737	-0.001525
C	-1.349087	-0.040536	0.002368
H	-1.754462	0.657697	0.743520
H	-1.720698	0.284916	-0.977859
H	-1.735402	-1.044983	0.200986

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -228.522371771 Predicted Change= -3.579805D-13

Zero-point correction (ZPE)= -228.4730 0.04928

Internal Energy (U)= -228.4679 0.05440

Enthalpy (H)= -228.4669 0.05546

Gibbs Free Energy (G)= -228.5044 0.01796

Frequencies -- 44.1532 441.2363 617.9864

PdOAc₂

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current

scrf=(pcm,solvent=acetone) opt=(maxcycle=250,gdiis) freq=noraman

Temperature=333.15

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C4H6O4Pd C1[X(C4H6O4Pd)] #Atoms= 15

Charge = 0 Multiplicity = 1

SCF Energy= -583.580376402 Predicted Change= -7.319076D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01228	0.00180	[NO]	0.01228	0.00180	[NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Pd	0.000021	0.000043	-0.007103
O	-1.762992	1.083989	0.016080
C	-2.434736	-0.000017	0.021700
O	-1.762618	-1.083843	0.016199
O	1.762712	1.084115	-0.019238
C	2.434908	0.000429	-0.013627
O	1.763250	-1.083735	-0.019395
C	3.924867	0.000174	0.031002
H	4.315773	-0.874695	-0.491650
H	4.315194	0.918924	-0.409701
H	4.244648	-0.049973	1.077183
C	-3.925262	-0.000517	0.003439
H	-4.263644	0.008558	-1.038078
H	-4.306904	-0.902494	0.484813
H	-4.307524	0.893054	0.499898

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -583.580376402 Predicted Change= -7.319076D-07
Zero-point correction (ZPE)= -583.4759 0.10446
Internal Energy (U)= -583.4631 0.11718
Enthalpy (H)= -583.4621 0.11824
Gibbs Free Energy (G)= -583.5205 0.05982

Frequencies -- 48.8181 52.8669 55.3909

PdOAc₂-Epox-AcOH-Complex

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
# wb97xd/genecp pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,gdiis) freq=noraman
density=current SCRF=(PCM,SOLVENT=acetone) Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP Freq
```

Pointgroup= C1 Stoichiometry= C9H16O7Pd C1[X(C9H16O7Pd)] #Atoms= 33
Charge = 0 Multiplicity = 1

SCF Energy= -1005.67755312 Predicted Change= -9.268894D-09

Optimization completed.	{Found 1 times}		
Item	Max Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]
Displ	0.00262	0.00180	[NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z

Pd	0.297877	-1.354441	0.021392
O	-1.585600	-1.861083	0.709030
C	-2.049535	-1.750803	-0.474908
O	-1.200640	-1.525448	-1.398051
O	2.169493	-0.771197	-0.650818
C	2.578800	-0.696678	0.555787
O	1.768479	-1.093259	1.455229
C	-3.510743	-1.827069	-0.749780
H	-3.689953	-2.162320	-1.772631
H	-3.998657	-2.490495	-0.033567
H	-3.919091	-0.817660	-0.631338
C	3.906595	-0.114591	0.894635
H	4.290844	-0.550035	1.818576
H	4.609379	-0.264048	0.073279
H	3.762428	0.960945	1.045601
C	-2.645693	2.281225	0.807679
C	-1.900908	1.187035	1.431460
H	-3.732627	2.232676	0.843959
H	-0.872619	1.360204	1.740437
H	-2.425583	0.372909	1.922228
C	-2.050273	3.649168	0.624796
H	-2.350185	4.073788	-0.338549
H	-2.408822	4.314946	1.416241
H	-0.958574	3.607037	0.673066
O	-2.085616	1.222105	0.003644
C	1.189867	2.109332	-0.713283
O	1.176613	2.100135	0.506667
O	0.125360	1.827280	-1.456711
H	-0.640821	1.589905	-0.869881
C	2.408429	2.411066	-1.540844
H	2.829640	1.459384	-1.880556
H	2.148634	3.003328	-2.420880
H	3.149730	2.933362	-0.935197

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

```

=====
SCF Energy=   -1005.67755312 Predicted Change= -9.268894D-09
Zero-point correction (ZPE)=      -1005.4196  0.25793
Internal Energy (U)=      -1005.3932  0.28434
Enthalpy (H)=      -1005.3921  0.28539
Gibbs Free Energy (G)=      -1005.4826  0.19491
=====

```

```

-----
Frequencies --   31.9267           46.6959           57.9725
-----

```

PdOAc₂-Epox-Complex

```

-----
Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
=====

```

```

#wb97xd/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
scrf=(pcm,solvent=acetone) opt=(maxcycle=250,gdiis) freq=noraman
Temperature=333.15
#N Geom=AllCheck Guess=TCHECK SCRF=Check GenChk Rwb97XD/ChkBas Freq
=====

```

```

Pointgroup= C1  Stoichiometry= C7H12O5Pd  C1[X(C7H12O5Pd)] #Atoms= 25
Charge = 0  Multiplicity = 1
=====

```

```

SCF Energy= -776.642516788  Predicted Change= -1.352276D-09
=====

```

```

Optimization completed.      {Found      1      times}
Item  Max Val.  Criteria  Pass?  RMS Val.  Criteria  Pass?
Force  0.00000 || 0.00045 [ YES ]   0.00000 || 0.00030 [ YES ]
Displ  0.00911 || 0.00180 [ NO ]   0.00911 || 0.00180 [ NO ]
=====

```

```

Atomic      Coordinates (Angstroms)
Type        X          Y          Z
=====

```

```

Pd   -0.319516    0.068216    0.043872
O    -1.961997    1.308392   -0.344163
C    -2.736930    0.378814    0.049591
O    -2.188282   -0.702196    0.454078
O     0.951397   -1.353847    0.641778
C     1.015163   -2.416833   -0.116606
O     0.366547   -2.583223   -1.143865
C    -4.221908    0.521113    0.013673
H    -4.671126   -0.015183    0.851846
H    -4.500683    1.575698    0.038295
H    -4.594693    0.079563   -0.916557
C     2.005444   -3.444187    0.398203
H     1.963261   -4.346688   -0.213218
H     3.017565   -3.028341    0.362492
H     1.787731   -3.691022    1.441044

```

C	2.077069	2.022849	0.436800
C	2.702103	0.909820	-0.277802
H	1.750192	1.828207	1.455147
H	3.344655	1.113876	-1.128915
H	2.828426	-0.043732	0.223266
C	2.297761	3.457290	0.065235
H	1.385794	4.038179	0.230623
H	3.090031	3.875267	0.694018
H	2.595114	3.548475	-0.982799
O	1.315992	1.250197	-0.543820

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -776.642516788 Predicted Change= -1.352276D-09

Zero-point correction (ZPE)= -776.4496 0.19290

Internal Energy (U)= -776.4296 0.21284

Enthalpy (H)= -776.4286 0.21390

Gibbs Free Energy (G)= -776.5072 0.13522

Frequencies -- 4.6125 42.1356 43.9555

PdOAc₂-EpoxOpen-AcOH-TS

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/genecp scf=(maxcycle=300,direct,tight,yqc) density=current

scrf=(pcm,solvent=acetone) opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest)

freq=noraman

#N Geom=AllCheck Guess=TCHECK SCRF=Check GenChk Rwb97XD/GenECP Freq

Pointgroup= C1 Stoichiometry= C₉H₁₆O₇Pd C1[X(C₉H₁₆O₇Pd)] #Atoms= 33

Charge = 0 Multiplicity = 1

SCF Energy= -1005.62535621 Predicted Change= -1.113618D-07

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.03031	0.00180	[NO]	0.03031	0.00180	[NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z

O	0.702350	-1.198249	-0.502710
C	0.948216	-2.171831	0.334622

C	2.202188	-2.950448	0.002088
H	2.447824	-2.884582	-1.059452
H	3.027744	-2.519097	0.577891
H	2.082014	-3.993904	0.300060
O	0.257619	-2.421257	1.318318
O	-2.526270	-1.323195	-0.641212
C	-3.330733	-0.407720	-0.271246
C	-4.808611	-0.574354	-0.373190
H	-5.171426	-1.047406	0.545505
H	-5.056674	-1.220607	-1.216958
H	-5.291230	0.398877	-0.477487
O	-2.814346	0.654122	0.219995
Pd	-0.913978	-0.151226	0.000877
O	0.347035	1.239098	0.818845
C	0.348865	2.534608	0.211308
H	1.368894	2.923137	0.185918
C	-0.028926	1.796692	-0.997733
H	0.772411	1.345757	-1.574141
H	-1.030252	1.884425	-1.414261
C	-0.647115	3.492700	0.816270
H	-0.364914	3.716158	1.848756
H	-0.654459	4.427836	0.247426
H	-1.653129	3.062653	0.808043
C	3.526467	0.553680	-0.288758
O	3.005146	1.204323	-1.176567
O	2.917714	0.265990	0.858411
H	1.981542	0.585127	0.807701
C	4.911498	-0.027737	-0.367969
H	5.427128	0.062059	0.590692
H	4.833421	-1.093673	-0.608242
H	5.479038	0.469441	-1.154808

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1005.62535621 Predicted Change= -1.113618D-07

Zero-point correction (ZPE)= -1005.3692 0.25610

Internal Energy (U)= -1005.3475 0.27776

Enthalpy (H)= -1005.3466 0.27870

Gibbs Free Energy (G)= -1005.4230 0.20234

Frequencies -- -307.1648 30.1279 41.2897

PdOAc₂-EpoxOpening-TS

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```

=====
#wb97xd/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
scrf=(pcm,solvent=acetone) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/ChkBas Freq
=====

```

```

-----
Pointgroup= C1  Stoichiometry= C7H12O5Pd  C1[X(C7H12O5Pd)]  #Atoms= 25
Charge = 0  Multiplicity = 1
-----

```

```

=====
SCF Energy= -776.591765821  Predicted Change= -7.371991D-09
=====

```

```

-----
Optimization completed.      {Found      1      times}
Item  Max Val.  Criteria  Pass?  RMS Val.  Criteria  Pass?
Force  0.00000 || 0.00045 [ YES ]  0.00000 || 0.00030 [ YES ]
Displ  0.00977 || 0.00180 [ NO ]   0.00977 || 0.00180 [ NO ]
-----

```

```

-----
Atomic      Coordinates (Angstroms)
Type       X       Y       Z
-----
O          1.234875   0.895134   0.684170
C          1.664316   1.835461  -0.118114
C          2.896266   2.540290   0.409787
H          2.760421   2.818329   1.458016
H          3.752282   1.859654   0.354435
H          3.104485   3.427786  -0.189297
O          1.143095   2.116706  -1.191566
O          -2.003161   1.055523   0.598549
C          -2.782407   0.190708   0.081235
C          -4.263633   0.368734   0.088260
H          -4.557599   0.895070  -0.826016
H          -4.567096   0.968595   0.947898
H          -4.759630  -0.603468   0.102151
O          -2.241749  -0.826640  -0.471412
Pd          -0.350907  -0.081698  -0.032496
O          0.844490  -1.430686  -0.961366
C          1.594618  -2.314460  -0.139060
C          0.595248  -1.981587   0.883369
H          0.869223  -1.349723   1.724723
H          -0.312356  -2.572360   0.945226
C          3.024725  -1.886103   0.093631
H          3.573902  -1.904783  -0.852306
H          3.053603  -0.872901   0.502905
H          3.513472  -2.573272   0.792023
H          1.515811  -3.333380  -0.526610
-----

```

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -776.591765821 Predicted Change= -7.371991D-09
Zero-point correction (ZPE)= -776.4005 0.19125
Internal Energy (U)= -776.3813 0.21045
Enthalpy (H)= -776.3802 0.21150
Gibbs Free Energy (G)= -776.4551 0.13661

Frequencies -- -297.0504 25.6890 32.4097

PdOAc₂-EpoxOpen-AcOH-Complex

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

wb97xd/genecp pseudo=read gfprint ginput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,gdiis) freq=noraman
density=current SCRF=(PCM,SOLVENT=acetone) Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP Freq

Pointgroup= C1 Stoichiometry= C9H16O7Pd C1[X(C9H16O7Pd)] #Atoms= 33
Charge = 0 Multiplicity = 1

SCF Energy= -1005.64086646 Predicted Change= -1.611021D-07

Optimization completed on the basis of negligible forces. {Found 2 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00000 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.06001 || 0.00180 [NO] 0.06001 || 0.00180 [NO]

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z

O	0.675105	0.972134	0.851527
C	0.967471	1.987491	0.084279
C	2.131204	2.824931	0.542074
H	2.732768	2.299254	1.285130
H	2.743072	3.091003	-0.322703
H	1.748499	3.749513	0.985806
O	0.310218	2.236956	-0.929322
O	-2.601397	1.177540	0.623119
C	-3.340166	0.404354	-0.065021
C	-4.812029	0.605820	-0.175156
H	-5.013653	1.224289	-1.056151
H	-5.187527	1.123201	0.708968
H	-5.314723	-0.354237	-0.304277
O	-2.755223	-0.549618	-0.689669

Pd	-0.897201	0.112652	-0.036010
O	0.327904	-1.234612	-0.756473
C	0.248526	-2.187145	0.323873
H	1.228582	-2.246536	0.806372
C	-0.755039	-1.483929	1.222187
H	-0.388217	-1.037256	2.143929
H	-1.763374	-1.892500	1.270303
C	-0.206673	-3.535815	-0.190755
H	0.512249	-3.914903	-0.923409
H	-0.270628	-4.253757	0.634039
H	-1.188433	-3.454185	-0.668628
C	3.630293	-0.472877	-0.101857
O	3.362790	-1.240296	0.803670
O	2.775825	-0.149012	-1.068691
H	1.896910	-0.587845	-0.899155
C	4.958134	0.219447	-0.263312
H	5.379505	-0.005599	-1.247232
H	4.819144	1.303364	-0.206216
H	5.644979	-0.104195	0.518503

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1005.64086646 Predicted Change= -1.611021D-07

Zero-point correction (ZPE)= -1005.3832 0.25757

Internal Energy (U)= -1005.3574 0.28346

Enthalpy (H)= -1005.3563 0.28451

Gibbs Free Energy (G)= -1005.4470 0.19380

Frequencies -- 16.5654 22.2970 38.8871

PdOAc₂-EpoxOpen-Complex

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current

scrf=(pcm,solvent=acetone) opt=(maxcycle=250,gdiis) freq=noraman

Temperature=333.15

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C7H12O5Pd C1[X(C7H12O5Pd)] #Atoms= 25

Charge = 0 Multiplicity = 1

SCF Energy= -776.605443424 Predicted Change= -1.665211D-09

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00345	0.00180	[NO]	0.00345	0.00180	[YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
O	-1.757134	-0.253910	0.664393
C	-2.355741	-1.144932	-0.078878
C	-3.764499	-1.469725	0.347219
H	-3.754875	-1.884779	1.359334
H	-4.366479	-0.557132	0.367477
H	-4.205366	-2.191013	-0.341632
O	-1.793981	-1.673118	-1.040473
O	1.284626	-1.642469	0.715545
C	2.278535	-1.184816	0.074422
C	3.610356	-1.857363	0.080785
H	3.716544	-2.431952	-0.845235
H	3.688027	-2.535650	0.931283
H	4.406248	-1.110269	0.110164
O	2.094756	-0.118306	-0.615032
Pd	0.080829	-0.059174	-0.108507
O	-0.508271	1.605602	-0.925955
C	-0.382889	2.453421	0.218979
H	-1.373935	2.658779	0.640893
C	0.396371	1.524336	1.131013
H	-0.056151	1.209856	2.069116
H	1.478853	1.642447	1.148534
C	0.330731	3.742659	-0.134398
H	-0.244627	4.289122	-0.888214
H	0.429639	4.377947	0.752403
H	1.326848	3.530788	-0.535500

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -776.605443424 Predicted Change= -1.665211D-09
Zero-point correction (ZPE)= -776.4128 0.19262
Internal Energy (U)= -776.3935 0.21184
Enthalpy (H)= -776.3925 0.21290
Gibbs Free Energy (G)= -776.4667 0.13867

Frequencies -- 29.7261 38.6137 43.8396

PdOAc₂-EpoxOpen-1a-Complex

```

#wB97XD/gen pseudo=read 6D scf=(maxcycle=300,direct,tight,xqc)
density=current opt=(maxcycle=250,modredundant) SCRF=(PCM,SOLVENT=acetone)
iop(1/8=18) Temperature=333.15
Modredundant Input: B    20    21 F
Modredundant Input:
#wB97XD/gen pseudo=read 6D scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
SCRF=(PCM,SOLVENT=acetone) Temperature=333.15 geom=check guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk Rwb97XD/ChkBas Freq

```

```

Pointgroup= C1  Stoichiometry= C15H21NO6Pd  C1[X(C15H21NO6Pd)] #Atoms= 44
Charge = 0    Multiplicity = 1

```

```

SCF Energy= -1216.76837791      Predicted Change= -1.278843D-08

```

```

Optimization completed.      {Found    2    times}
Item  Max Val.  Criteria  Pass?  RMS Val.  Criteria  Pass?
Force  0.00001 || 0.00045 [ YES ]   0.00000 || 0.00030 [ YES ]
Displ  0.01241 || 0.00180 [ NO ]    0.01241 || 0.00180 [ NO ]

```

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	4.143117	1.210785	-0.225287
H	3.702045	2.199410	-0.151281
C	3.358286	0.077082	-0.025174
N	1.967515	0.181133	0.272061
C	1.410357	0.871547	1.261624
C	2.243761	1.644369	2.241595
H	3.241568	1.220495	2.359305
H	1.721179	1.651789	3.198738
H	2.340084	2.679536	1.900184
H	1.361518	-0.459416	-0.272436
C	3.901810	-1.198224	-0.175065
H	3.267584	-2.068721	-0.040991
C	5.246171	-1.335770	-0.503060
H	5.669953	-2.328141	-0.619104
C	6.045592	-0.207336	-0.675565
H	7.095794	-0.317919	-0.925952
C	5.491688	1.062764	-0.536930
H	6.105072	1.945607	-0.685603
O	0.158795	0.921805	1.426462
Pd	-1.394052	0.092993	0.352444
C	-0.876491	0.923298	-1.467739

H	0.183147	1.144618	-1.353504
H	-1.112086	0.126673	-2.167062
C	-1.826883	2.080784	-1.282171
C	-1.220758	3.444251	-1.548515
H	-0.302447	3.572401	-0.966162
H	-1.931223	4.225158	-1.259575
H	-0.989556	3.563789	-2.612414
H	-2.734576	1.934620	-1.880820
O	-2.115863	1.902771	0.103252
O	-2.911139	-0.679628	-0.662357
C	-4.154000	-0.645929	-0.218742
C	-4.421431	-0.036388	1.140460
H	-4.135282	1.019051	1.129957
H	-3.831734	-0.537766	1.916893
H	-5.480918	-0.132996	1.379687
O	-5.046652	-1.109384	-0.910745
C	-0.004732	-2.431834	-0.188379
C	0.034079	-3.937769	-0.053666
H	0.778658	-4.362348	-0.727815
H	-0.952336	-4.346322	-0.293836
H	0.262876	-4.215583	0.978713
O	-0.748438	-1.835401	0.678262
O	0.647183	-1.848827	-1.070387

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1216.76837791	Predicted Change=	-1.278843D-08
Zero-point correction (ZPE)=	-1216.4150	0.35337	
Internal Energy (U)=	-1216.3839	0.38441	
Enthalpy (H)=	-1216.3829	0.38546	
Gibbs Free Energy (G)=	-1216.4845	0.28384	

Frequencies --	12.2436	23.9729	36.3254
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Palladacycle-Epoxy-Complex-Cross-Coupling-TS

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
#wB97XD/gen pseudo=read 6D scf=(maxcycle=300,direct,tight,xqc)
density=current opt=(maxcycle=250,modredundant) SCRF=(PCM,SOLVENT=acetone)
iop(1/8=18) Temperature=333.15
Modredundant Input: B 12 33 F
Modredundant Input:
#wB97XD/gen pseudo=read 6D scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
```

SCRF=(PCM,SOLVENT=acetone) Temperature=333.15 geom=check guess=read
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk Rwb97XD/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H21NO6Pd C1[X(C15H21NO6Pd)] #Atoms= 44
 Charge = 0 Multiplicity = 1

SCF Energy= -1216.75783414 Predicted Change= -2.697314D-10

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00046	0.00180	[YES]	0.00046	0.00180	[YES]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	3.718559	-0.945760	-0.497607
H	4.581681	-0.439790	-0.919916
Pd	-0.403030	0.076215	-0.057223
C	2.578136	-0.184817	-0.217428
N	2.652546	1.211349	-0.460179
C	1.904719	1.883199	-1.379690
C	2.109515	3.378167	-1.384753
H	1.450762	3.798142	-0.617324
H	1.822818	3.781404	-2.356566
H	3.138160	3.667777	-1.154122
H	3.368551	1.723836	0.033478
C	1.439394	-0.819887	0.297806
C	1.479351	-2.199297	0.531184
H	0.616680	-2.692517	0.964691
C	2.621632	-2.940180	0.265342
H	2.628835	-4.006355	0.468510
C	3.752433	-2.310035	-0.250384
H	4.652442	-2.877893	-0.462500
O	1.098352	1.325846	-2.117890
C	-1.817756	-2.428171	-0.255236
C	-2.028444	-3.836363	-0.764457
H	-1.161173	-4.444229	-0.484510
H	-2.094676	-3.840596	-1.854952
H	-2.927377	-4.274759	-0.329674
O	-2.436038	-2.028956	0.755774
O	-0.956184	-1.737675	-0.901460
C	0.194744	1.447297	2.077106
C	1.379418	2.186651	2.672575
H	1.509038	1.918035	3.727026
H	1.214878	3.266845	2.608312

H	2.296607	1.941067	2.130053
H	-0.700025	1.646021	2.689405
C	0.383634	-0.065159	1.997829
H	-0.455068	-0.698354	2.290055
H	1.312917	-0.421473	2.426532
O	-0.026207	1.825088	0.737179
C	-3.284175	1.072568	-0.323348
C	-4.299763	2.121637	-0.660316
H	-5.231354	1.643603	-0.974678
H	-3.924307	2.770544	-1.450154
H	-4.515754	2.711755	0.235034
O	-3.653686	0.255806	0.625851
H	-3.031861	-0.540496	0.714450
O	-2.197314	1.012763	-0.909629

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1216.75783414 Predicted Change= -2.697314D-10

Zero-point correction (ZPE)= -1216.4066 0.35115

Internal Energy (U)= -1216.3754 0.38237

Enthalpy (H)= -1216.3744 0.38342

Gibbs Free Energy (G)= -1216.4748 0.28301

Frequencies -- -328.3307 26.3988 31.7594

Pd-1a-Tautomer-Complex

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
# wB97XD/gen pseudo=read 6D gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
SCRF=(PCM,SOLVENT=acetone) iop(1/8=18) Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk Rwb97XD/ChkBas Freq
```

Pointgroup= C1 Stoichiometry= C12H15NO5Pd C1[X(C12H15NO5Pd)] #Atoms= 34
Charge = 0 Multiplicity = 1

SCF Energy= -1023.72792133 Predicted Change= -3.075405D-05

Optimization completed.			{Found	1	times}	
Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00019	0.00045	[YES]	0.00004	0.00030	[YES]
Displ	0.28089	0.00180	[NO]	0.28089	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-2.733413	-1.262357	0.494765
H	-2.596907	-1.583782	1.522868
Pd	1.018916	-0.121306	0.225944
C	-1.918739	-0.258518	-0.028429
N	-0.894369	0.320118	0.782363
C	-1.179039	1.021463	1.823349
C	-2.552053	1.442718	2.248695
H	-2.541365	2.508971	2.494209
H	-2.845136	0.888558	3.145822
H	-3.288258	1.266290	1.466733
C	-2.056065	0.152338	-1.353890
H	-1.380206	0.905189	-1.748725
C	-3.036101	-0.433705	-2.148415
H	-3.149291	-0.114166	-3.179684
C	-3.865576	-1.427115	-1.629991
H	-4.626322	-1.882066	-2.256519
C	-3.710804	-1.841521	-0.309346
H	-4.347560	-2.620540	0.097776
O	-0.159198	1.396110	2.584520
C	2.321593	-2.189328	0.017113
C	3.115694	-3.452669	-0.079343
H	3.634170	-3.616294	0.871180
H	3.862392	-3.369791	-0.870859
H	2.454880	-4.301417	-0.263363
O	2.829214	-1.065060	-0.296860
O	1.119957	-2.200413	0.444858
C	1.180167	2.332060	-1.206257
C	1.501408	3.813979	-1.298371
H	1.362753	4.168852	-2.320565
H	2.531841	3.996195	-0.980461
H	0.845931	4.375541	-0.625478
O	0.756622	1.699518	-2.173513
O	1.395458	1.841749	-0.023093
H	-0.465299	1.958418	3.310509

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1023.72792133 Predicted Change= -3.075405D-05
Zero-point correction (ZPE)= -1023.4647 0.26314
Internal Energy (U)= -1023.4389 0.28901
Enthalpy (H)= -1023.4378 0.29007
Gibbs Free Energy (G)= -1023.5302 0.19770

Frequencies -- 7.9222 27.5432 32.7065

PdOAc₂-1a-Tautomer-HFIP

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(pcm,solvent=acetone) opt=(gdiis,maxcycle=250)
freq=noraman Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RwB97XD/GenECP/Auto Freq
```

Pointgroup= C1 Stoichiometry= C15H17F6NO6Pd C1[X(C15H17F6NO6Pd)] #Atoms= 46
Charge = 0 Multiplicity = 1

SCF Energy= -1813.30755554 Predicted Change= -8.931685D-07

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00010 || 0.00045 [YES] 0.00001 || 0.00030 [YES]
Displ 0.00965 || 0.00180 [NO] 0.00965 || 0.00180 [NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.842853	-0.837261	3.030647
C	0.149582	0.038547	2.337451
O	1.394558	-0.148086	2.784513
H	2.054774	0.213563	2.158957
N	-0.213055	0.837702	1.399085
C	0.702114	1.720046	0.778719
C	0.748907	1.765457	-0.618978
C	1.612774	2.643930	-1.263618
C	2.424906	3.504333	-0.526521
C	2.358687	3.483746	0.864932
C	1.502958	2.600517	1.517810
H	-1.362535	0.088933	0.316114
O	-1.779020	-0.474085	-0.395262
C	-3.050618	-0.033781	-0.717533
C	-3.017277	1.392078	-1.282014
F	-2.239940	1.423673	-2.372662
F	-4.236185	1.820168	-1.634272
F	-2.512190	2.264929	-0.399225
C	-3.999352	-0.177329	0.478478
F	-3.644456	0.625567	1.495956

F	-5.265620	0.106939	0.155510
F	-3.962811	-1.437826	0.932195
C	-1.299701	-3.651998	-0.585894
C	-0.038068	-2.863683	-0.566949
O	0.577747	-2.520952	-1.627827
Pd	1.942926	-1.455202	-0.485724
O	0.490896	-2.486971	0.533999
O	3.419944	-0.348765	-1.462469
C	3.819785	0.115078	-0.350743
C	4.944315	1.086361	-0.249938
O	3.224139	-0.326687	0.694671
H	-0.674106	-1.871376	2.715579
H	-0.698707	-0.781419	4.113250
H	-1.858698	-0.538955	2.777157
H	0.108979	1.102828	-1.191930
H	1.649056	2.655748	-2.348680
H	3.097580	4.190020	-1.032043
H	2.975103	4.159732	1.450126
H	1.445101	2.600635	2.602402
H	-3.445290	-0.677001	-1.509171
H	-2.087709	-3.039156	-0.140684
H	-1.567098	-3.919788	-1.608739
H	-1.178122	-4.553948	0.020197
H	4.792650	1.740656	0.609928
H	5.876921	0.529439	-0.109373
H	5.016638	1.672505	-1.166995

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1813.30755554 Predicted Change= -8.931685D-07

Zero-point correction (ZPE)= -1812.9784 0.32906

Internal Energy (U)= -1812.9409 0.36660

Enthalpy (H)= -1812.9398 0.36766

Gibbs Free Energy (G)= -1813.0577 0.24979

Frequencies -- 10.5574 20.3142 24.0256

PdOAc2-1a-Tautomer-2HFIP

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(pcm,solvent=acetone) opt=(gdiis,maxcycle=250)

freq=noraman Temperature=333.15

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UwB97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C18H19F12NO7Pd(3) C1[X(C18H19F12NO7Pd)]

#Atoms= 58

Charge = 0 Multiplicity = 3

SCF Energy= -2602.89414569 Predicted Change= -7.899290D-08
=====

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00774	0.00180	[NO]	0.00774	0.00180	[NO]

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z

C	0.852501	-2.831628	-1.018868
C	0.570987	-1.384491	-1.249780
O	-0.719782	-1.147850	-1.525310
H	-0.941267	-0.189357	-1.584167
N	1.490388	-0.502558	-1.125898
C	1.228002	0.867319	-1.267398
C	1.417636	1.700319	-0.136840
C	1.235235	3.089085	-0.256726
C	0.837134	3.642876	-1.466435
C	0.659525	2.813389	-2.574193
C	0.855256	1.436362	-2.484091
H	2.684897	-0.896411	0.107752
O	3.242430	-1.061953	0.913327
C	4.588823	-0.964100	0.602688
C	4.960602	0.461156	0.172970
F	4.574629	1.329464	1.117212
F	6.280136	0.601502	-0.000727
F	4.355783	0.815472	-0.971625
C	4.990303	-2.020505	-0.434541
F	4.334629	-1.855434	-1.594271
F	6.302469	-1.993493	-0.696789
F	4.684484	-3.239674	0.026143
C	1.375755	-0.909965	3.688323
C	0.579197	-0.092098	2.715121
O	0.383955	1.146394	2.901678
Pd	-0.765439	1.271758	0.971167
O	0.115031	-0.641095	1.667618
O	-1.958756	3.072063	0.168046
C	-2.281977	2.414925	-0.850382
C	-3.118831	3.007968	-1.946089
O	-1.898413	1.197706	-0.963504

H	0.440634	-3.113553	-0.043836
H	0.367971	-3.442486	-1.784106
H	1.926384	-3.013702	-1.016080
H	1.900258	1.288892	0.743887
H	1.414469	3.719683	0.607966
H	0.680447	4.712100	-1.553538
H	0.366642	3.243811	-3.526884
H	0.730245	0.804072	-3.357419
H	5.164186	-1.177222	1.507706
H	2.313916	-1.188946	3.198580
H	1.583226	-0.344997	4.597817
H	0.835166	-1.828792	3.929892
H	-2.594589	2.896099	-2.899576
H	-4.061378	2.456423	-2.018915
H	-3.323609	4.061475	-1.754805
H	-1.908026	-1.555195	-0.024581
O	-2.696080	-1.627308	0.539849
C	-3.777865	-1.100672	-0.163812
H	-3.474470	-0.328506	-0.878493
C	-4.692601	-0.421361	0.852453
C	-4.476314	-2.213221	-0.950486
F	-3.585627	-2.797709	-1.764783
F	-5.472357	-1.735046	-1.709544
F	-4.984541	-3.161965	-0.155032
F	-4.055411	0.611771	1.424647
F	-5.069110	-1.252516	1.829816
F	-5.797852	0.059611	0.267317

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2602.89414569 Predicted Change= -7.899290D-08

Zero-point correction (ZPE)= -2602.5008 0.39331

Internal Energy (U)= -2602.4497 0.44443

Enthalpy (H)= -2602.4486 0.44548

Gibbs Free Energy (G)= -2602.6010 0.29310

Frequencies -- 11.1439 14.8152 19.5207

Supporting Information: **Syn Pd(II)-Pd(II) Square Planar Dimer**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(pcm,solvent=acetone)

opt=(gdiis,maxcycle=250,maxstep=10) freq=noraman Temperature=333.15
#N Geom=AllCheck Guess=TCRSCRF=Check GenChk RwB97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C20H22N2O6Pd2 C1[X(C20H22N2O6Pd2)] #Atoms= 52
Charge = 0 Multiplicity = 1

SCF Energy= -1589.46218192 Predicted Change= -1.232116D-06

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00004 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.08653 || 0.00180 [NO] 0.08653 || 0.00180 [NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Pd	-0.912436	0.593573	-1.247486
Pd	-0.771558	-0.947753	1.242307
O	-0.927811	2.554949	-0.655389
O	-3.041332	0.544153	-0.765176
O	-1.094745	-1.356354	-1.973602
O	-2.845551	-0.261168	1.335323
O	-1.378745	-2.475028	-0.025640
O	-0.199535	0.615215	2.465318
C	-1.350412	-2.384674	-1.286206
C	-1.601298	-3.665315	-2.049254
H	-0.657306	-4.219304	-2.104362
H	-2.327488	-4.287733	-1.523139
H	-1.942645	-3.456152	-3.063839
C	-3.500157	0.202689	0.360289
C	-4.998418	0.345294	0.568016
H	-5.459421	0.913291	-0.241447
H	-5.448690	-0.652344	0.606550
H	-5.197987	0.832572	1.526307
C	1.029070	0.656342	-1.616441
C	1.680502	-0.444084	-2.191306
C	1.832771	1.736823	-1.230466
C	3.060151	-0.485365	-2.354980
H	1.085953	-1.297200	-2.496491
C	3.225365	1.701376	-1.384307
C	3.840490	0.591988	-1.941336
H	3.526000	-1.363262	-2.792704
H	3.825557	2.551268	-1.066918
H	4.919982	0.572420	-2.052815
N	1.324385	2.931196	-0.652436
C	0.056470	3.293256	-0.441288
C	-0.191426	4.686882	0.064472
H	0.694892	5.136667	0.516608

H	-0.511862	5.310956	-0.775834
H	-1.002880	4.661849	0.793921
C	1.092717	-1.582303	1.166067
C	2.165825	-0.717791	1.411463
C	1.398292	-2.900173	0.807444
C	3.489462	-1.141993	1.259917
C	2.713681	-3.335433	0.665653
H	0.585558	-3.592170	0.612271
C	3.765165	-2.448011	0.881479
H	4.303901	-0.445452	1.443059
H	2.914997	-4.363216	0.377440
H	4.795378	-2.769154	0.764061
N	1.992386	0.629312	1.825327
H	2.825710	1.200823	1.796790
H	2.019936	3.636756	-0.449950
C	0.908346	1.188641	2.367552
C	1.048998	2.578508	2.922286
H	1.111352	2.515580	4.013252
H	1.937435	3.093785	2.552015
H	0.156142	3.154661	2.672189

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1589.46218192 Predicted Change= -1.232116D-06

Zero-point correction (ZPE)= -1589.0587 0.40348

Internal Energy (U)= -1589.0208 0.44136

Enthalpy (H)= -1589.0197 0.44241

Gibbs Free Energy (G)= -1589.1346 0.32753

Entropy (S)= 0.00034483

Frequencies -- 11.7814 32.1135 38.6771

Supporting Information: **Anti Pd(II)-Pd(II) Square Planar Dimer (Anti-I)**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

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#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(pcm,solvent=acetone)

opt=(gdiis,maxcycle=250,maxstep=10) freq=noraman Temperature=333.15

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C20H22N2O6Pd2 C1[X(C20H22N2O6Pd2)] #Atoms= 52

Charge = 0 Multiplicity = 1

SCF Energy= -1589.46828987 Predicted Change= -2.986126D-07

=====

Optimization completed. {Found 1 times}

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Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.05899	0.00180	[NO]	0.05899	0.00180	[NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Pd	0.816909	0.823350	1.215824
Pd	-0.814287	0.825436	-1.214894
O	-0.424024	-0.400109	2.301976
O	-0.618292	2.447821	1.596113
O	2.011449	2.145621	0.168362
O	-2.004063	2.152077	-0.167532
O	0.626441	2.445144	-1.595311
C	1.660701	2.686320	-0.931228
C	2.640686	3.707483	-1.473205
H	3.538361	3.185374	-1.821015
H	2.205775	4.262547	-2.305224
H	2.945040	4.395795	-0.680743
C	-1.650813	2.693265	0.931065
C	-2.623206	3.725373	1.466263
H	-2.207897	4.241308	2.332683
H	-2.870151	4.447832	0.683873
H	-3.551651	3.222537	1.756007
C	2.068745	-0.665882	0.896007
C	3.371151	-0.429361	0.436931
C	1.691271	-2.002199	1.092147
C	4.261323	-1.468236	0.176711
H	3.681462	0.596323	0.267975
C	2.577885	-3.053171	0.824876
C	3.861004	-2.789203	0.369160
H	5.262548	-1.246063	-0.180582
H	2.259807	-4.080524	0.985391
H	4.540732	-3.610633	0.166401
N	0.407888	-2.390055	1.558100
C	-0.528032	-1.635142	2.140761
C	-1.777505	-2.312262	2.620840
H	-1.744186	-3.398187	2.518971
H	-1.939842	-2.049549	3.669031
H	-2.618199	-1.923627	2.037786
H	0.208919	-3.379571	1.506025
O	0.422044	-0.402242	-2.301586
C	0.521840	-1.637627	-2.140439
C	1.768912	-2.319037	-2.620715
H	2.611032	-1.933305	-2.037788
H	1.731883	-3.404857	-2.518885
H	1.931991	-2.056837	-3.668922
N	-0.416627	-2.389345	-1.557752

C	-2.071322	-0.659388	-0.895359
C	-3.372921	-0.418193	-0.436468
C	-1.698628	-1.997027	-1.091707
C	-4.266878	-1.453902	-0.176538
H	-3.679539	0.608602	-0.267491
C	-2.589064	-3.044830	-0.824673
C	-3.871281	-2.776271	-0.369078
H	-5.267356	-1.228170	0.180614
H	-2.274773	-4.073328	-0.985305
H	-4.553986	-3.595283	-0.166532
H	-0.221022	-3.379537	-1.505767

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1589.46828987 Predicted Change= -2.986126D-07
 Zero-point correction (ZPE)= -1589.0645 0.40374
 Internal Energy (U)= -1589.0267 0.44155
 Enthalpy (H)= -1589.0256 0.44261
 Gibbs Free Energy (G)= -1589.1410 0.32727
 Entropy (S)= 0.00034621

Frequencies -- 15.3155 18.0375 23.9807

Supporting Information: **Pd(II)-Pd(II)-Dimer-Epoxy-IV-B**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(pcm,solvent=acetone)
 opt=(gdiis,maxcycle=250,maxstep=10) freq=noraman Temperature=333.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C23H28N2O7Pd2 C1[X(C23H28N2O7Pd2)] #Atoms= 62
 Charge = 0 Multiplicity = 1

SCF Energy= -1782.52804719 Predicted Change= -5.459679D-08

Optimization completed. {Found 1 times}
 Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
 Force 0.00000 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
 Displ 0.07613 || 0.00180 [NO] 0.07613 || 0.00180 [NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z

Pd	1.002561	-0.686744	-0.140862
Pd	-1.762074	-0.895489	0.803632

O	0.601948	0.273593	-1.913969
O	0.299191	-2.541578	-1.097995
O	1.433466	-1.761028	1.575928
O	-1.891078	-2.460961	-0.539307
O	-0.693140	-2.206024	2.207841
C	0.551081	-2.303751	2.317545
C	1.107230	-3.130431	3.459713
H	1.588397	-2.461121	4.180530
H	0.314523	-3.687012	3.961030
H	1.870862	-3.818444	3.087813
C	-0.882175	-2.955187	-1.140760
C	-1.189264	-4.148969	-2.022463
H	-1.909626	-4.810118	-1.535610
H	-1.641884	-3.788395	-2.952762
H	-0.277788	-4.697030	-2.265132
C	1.591564	1.001583	0.684989
C	2.336276	1.003114	1.871098
C	1.281801	2.247909	0.122948
C	2.753955	2.184490	2.478501
H	2.582716	0.050507	2.327619
C	1.691732	3.441270	0.730438
C	2.427359	3.412412	1.905822
H	3.329586	2.145286	3.398611
H	1.442310	4.394089	0.269847
H	2.742113	4.342400	2.368336
N	0.553504	2.399119	-1.086853
C	0.287604	1.479331	-2.018542
C	-0.431975	1.920847	-3.257897
H	-0.614861	2.996048	-3.289039
H	0.156650	1.625123	-4.130007
H	-1.390170	1.394025	-3.297664
H	0.262538	3.343032	-1.301421
O	-1.630157	0.576368	2.229448
C	-1.595009	1.802322	1.989556
C	-1.018179	2.714080	3.031834
H	0.042645	2.468951	3.144104
H	-1.114919	3.771254	2.779434
H	-1.515710	2.519532	3.984994
N	-2.033509	2.351300	0.853019
C	-2.690126	0.330366	-0.433794
C	-3.364318	-0.153354	-1.562920
C	-2.671978	1.720306	-0.246537
C	-3.987725	0.697974	-2.471711
H	-3.383055	-1.224357	-1.734328
C	-3.289184	2.584242	-1.160632
C	-3.947424	2.076386	-2.270775
H	-4.498048	0.285402	-3.337084
H	-3.259588	3.658259	-0.992700

H	-4.423041	2.754239	-2.972356
H	-1.963837	3.357745	0.793780
C	3.859267	-1.089256	-2.615595
C	4.789150	-0.060859	-2.142023
H	2.802199	-0.841899	-2.703728
O	4.360648	-1.114193	-1.277571
H	4.214787	-1.894838	-3.255727
H	5.834015	-0.151883	-2.441430
C	4.327443	1.328622	-1.796511
H	3.253566	1.335753	-1.595377
H	4.846462	1.699594	-0.906032
H	4.537154	2.013548	-2.625006

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1782.52804719 Predicted Change= -5.459679D-08

Zero-point correction (ZPE)= -1782.0362 0.49176

Internal Energy (U)= -1781.9909 0.53713

Enthalpy (H)= -1781.9898 0.53819

Gibbs Free Energy (G)= -1782.1253 0.40270

Entropy (S)= 0.00040669

Frequencies -- 7.5734 15.7870 20.3032

Supporting Information: **Pd(II)-Pd(II)-Dimer-Epoxyde-HOAc-VI-B (Anti-I)**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

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#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(pcm,solvent=acetone)

opt=(gdiis,maxcycle=250,maxstep=10) freq=noraman Temperature=333.15

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C25H32N2O9Pd2 C1[X(C25H32N2O9Pd2)] #Atoms= 70

Charge = 0 Multiplicity = 1

SCF Energy= -2011.56630956 Predicted Change= -8.049783D-09

=====

Optimization completed on the basis of negligible forces. {Found 2 times}

Item Max Val. Criteria Pass? RMS Val. Criteria Pass?

Force 0.00000 || 0.00045 [YES] 0.00000 || 0.00030 [YES]

Displ 0.00543 || 0.00180 [NO] 0.00543 || 0.00180 [YES]

Atomic Coordinates (Angstroms)

Type X Y Z

Pd 0.347533 -0.927407 -0.250816

Pd	-2.486138	-0.563306	0.282536
O	0.534274	0.666247	-1.524618
O	-0.598281	-2.012147	-1.916585
O	0.152598	-2.618494	0.927776
O	-2.755176	-1.426417	-1.577380
O	-2.099434	-2.566064	1.128513
C	-0.973049	-3.082950	1.306363
C	-0.890746	-4.390251	2.068155
H	-0.275915	-5.106407	1.516669
H	-0.402753	-4.209595	3.031617
H	-1.884333	-4.805339	2.240843
C	-1.811434	-1.983329	-2.227508
C	-2.240620	-2.655446	-3.515938
H	-2.596546	-1.892084	-4.215314
H	-1.410777	-3.200018	-3.967654
H	-3.072681	-3.337515	-3.321492
C	1.222548	0.073033	1.205719
C	1.684026	-0.586551	2.353240
C	1.406530	1.461469	1.148205
C	2.291608	0.095366	3.404134
H	1.553163	-1.661683	2.417754
C	1.999000	2.157808	2.210722
C	2.444647	1.478907	3.334989
H	2.636938	-0.451346	4.276596
H	2.117173	3.237365	2.148411
H	2.906389	2.028578	4.148896
N	1.015620	2.255691	0.041567
C	0.676192	1.859619	-1.190825
C	0.460943	2.919865	-2.228236
H	-0.509458	2.752055	-2.701692
H	0.489714	3.930684	-1.817755
H	1.247943	2.813495	-2.979390
H	1.090452	3.254123	0.177244
C	3.351249	-1.683524	-2.011574
O	4.686081	-1.596149	-1.468161
C	3.581486	-1.886811	-0.583275
H	3.193545	-2.549975	-2.650017
H	2.947968	-0.736056	-2.357880
H	3.348013	-1.052058	0.075277
C	3.548050	-3.242133	0.060015
H	2.542700	-3.416643	0.459100
H	3.784999	-4.027214	-0.664524
H	4.262814	-3.296580	0.887551
H	5.053929	0.049287	-1.084416
O	5.185817	0.933344	-0.646094
C	4.292582	1.801717	-1.111357
C	4.394822	3.142451	-0.436814
H	3.682718	3.837832	-0.881608

H	4.185777	3.026826	0.631250
H	5.410413	3.536228	-0.534241
O	3.485831	1.530075	-1.981802
O	-2.257063	0.185051	2.182317
C	-2.755899	1.250281	-0.441672
C	-3.284843	1.448133	-1.723528
C	-2.367777	2.391472	0.274648
C	-3.413671	2.717987	-2.279956
H	-3.582347	0.579207	-2.300713
C	-2.486489	3.671907	-0.281145
C	-3.007622	3.837104	-1.555759
H	-3.824064	2.831534	-3.279076
H	-2.175074	4.540908	0.294106
H	-3.095143	4.833316	-1.977514
C	-1.816885	1.324493	2.447821
C	-1.233411	1.562755	3.809164
H	-0.314301	0.973577	3.890369
H	-1.002156	2.611900	4.000053
H	-1.936826	1.201280	4.562793
N	-1.823352	2.343851	1.584459
H	-1.446920	3.216509	1.928186

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2011.56630956 Predicted Change= -8.049783D-09

Zero-point correction (ZPE)= -2011.0097 0.55660

Internal Energy (U)= -2010.9576 0.60862

Enthalpy (H)= -2010.9566 0.60967

Gibbs Free Energy (G)= -2011.1053 0.46100

Entropy (S)= 0.00044626

Frequencies -- 16.4690 26.5060 27.7049

Supporting Information: **Red-Elim-TS-Dimer-VII-B (Anti-I)**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(pcm,solvent=acetone)

opt=(gdiis,maxcycle=250,maxstep=10,ts,calcfc,noeigentest) freq=noraman

Temperature=333.15

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C25H32N2O9Pd2 C1[X(C25H32N2O9Pd2)] #Atoms= 70

Charge = 0 Multiplicity = 1

SCF Energy= -2011.50178940 Predicted Change= -9.080245D-09

```

=====
Optimization completed.      {Found      1      times}
Item  Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force  0.00000 || 0.00045 [ YES ]   0.00000 || 0.00030 [ YES ]
Displ  0.01030 || 0.00180 [ NO ]    0.01030 || 0.00180 [ YES ]
=====

```

```

-----
Atomic      Coordinates (Angstroms)
Type      X      Y      Z
-----
Pd  -0.069354  -1.161682  -0.565512
Pd  -2.422059  -0.284272   0.918874
O   -0.312183   0.129585  -2.145816
O   -1.591889  -2.410443  -1.455765
O    0.149013  -2.528394   0.955635
O   -3.397762  -1.539447  -0.410403
O   -1.767960  -2.054405   2.056494
C   -0.713154  -2.702019   1.882878
C   -0.363386  -3.798493   2.866264
H   -0.041552  -4.695937   2.332404
H    0.475200  -3.461815   3.485035
H   -1.213165  -4.027891   3.510048
C   -2.824811  -2.318784  -1.235276
C   -3.754938  -3.189435  -2.052618
H   -4.182385  -2.581445  -2.857525
H   -3.214588  -4.027321  -2.494994
H   -4.578601  -3.553052  -1.434601
C    1.305691   0.040668   0.235968
C    2.023256  -0.351815   1.393921
C    1.284126   1.430712  -0.051105
C    2.734442   0.547741   2.169379
H    2.018193  -1.403725   1.658008
C    1.991477   2.342246   0.735556
C    2.719396   1.900980   1.830502
H    3.295203   0.203036   3.031430
H    1.985318   3.398262   0.481538
H    3.274336   2.620462   2.423147
N    0.605061   1.977311  -1.156456
C   -0.096287   1.356555  -2.121518
C   -0.654063   2.201898  -3.225444
H   -1.745554   2.156072  -3.161799
H   -0.335693   3.243886  -3.174451
H   -0.350014   1.772699  -4.183052
H    0.699867   2.978310  -1.264031
C    2.980667  -0.387579  -1.092509
O    4.507277  -1.413504  -1.900623
C    3.625262  -1.699134  -0.829714
H    2.371577  -0.330811  -1.988755
H    3.573112   0.485064  -0.805925

```

H	4.153393	-1.714884	0.129584
C	2.832913	-2.962826	-1.060086
H	2.134792	-3.139092	-0.237110
H	2.264356	-2.897090	-1.994266
H	3.520703	-3.811319	-1.126630
H	5.327184	-0.899617	-1.482359
O	6.458371	-0.306060	-0.796434
C	6.286213	0.878180	-0.349031
C	7.510273	1.489687	0.330914
H	7.828369	0.852772	1.163072
H	8.344767	1.535466	-0.376884
H	7.295909	2.493509	0.703680
O	5.237533	1.546728	-0.421289
O	-1.526795	0.851884	2.368201
C	-2.956992	1.326637	-0.089280
C	-3.857458	1.237275	-1.160109
C	-2.421788	2.592512	0.189896
C	-4.206013	2.345199	-1.927522
H	-4.286146	0.269759	-1.396702
C	-2.753567	3.709417	-0.589472
C	-3.645244	3.589243	-1.644160
H	-4.908494	2.234659	-2.748228
H	-2.317511	4.678203	-0.357054
H	-3.898357	4.461408	-2.238293
C	-1.177901	2.047047	2.272541
C	-0.345678	2.637997	3.373771
H	0.420883	1.916290	3.660775
H	0.129452	3.577534	3.086259
H	-0.991330	2.816994	4.239319
N	-1.525117	2.847685	1.260056
H	-1.183331	3.797514	1.316004

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

=====

SCF Energy=	-2011.50178940	Predicted Change=	-9.080245D-09
Zero-point correction (ZPE)=	-2010.9483		0.55340
Internal Energy (U)=	-2010.8970		0.60477
Enthalpy (H)=	-2010.8959		0.60583
Gibbs Free Energy (G)=	-2011.0439		0.45784
Entropy (S)=	0.00044421		

Frequencies --	-494.1358	18.1778	22.0218
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Supporting Information: **Pd-Product-Complex-Dimer-VIII-B**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
=====

```
#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(pcm,solvent=acetone,read)
opt=(gdiis,maxcycle=250,maxstep=10) freq=noraman Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq
```

```
-----
Pointgroup= C1  Stoichiometry= C25H32N2O9Pd2  C1[X(C25H32N2O9Pd2)] #Atoms= 70
Charge= 0  Multiplicity = 1
-----
```

```
SCF Energy= -2011.55932758  Predicted Change= -7.823965D-09
=====
```

```
Optimization completed.      {Found      1      times}
Item  Max Val.  Criteria  Pass?  RMS Val.  Criteria  Pass?
Force  0.00000  || 0.00045  [ YES ]   0.00000  || 0.00030  [ YES ]
Displ  0.00855  || 0.00180  [ NO ]    0.00855  || 0.00180  [ YES ]
-----
```

```
-----
Atomic      Coordinates (Angstroms)
Type      X      Y      Z
-----
Pd  -0.733306  -1.554863  -0.577785
Pd  -2.053731   0.886331   0.669670
O   0.075576  -0.321504  -1.989497
O  -2.484247  -1.633327  -1.628130
O  -1.572759  -2.695897   0.827553
O  -3.344992   0.311361  -0.854400
O  -2.603456  -0.942463   1.821959
C  -2.317120  -2.146775   1.722815
C  -2.838342  -3.122478   2.754125
H  -3.232705  -4.015993   2.264670
H  -2.005263  -3.435209   3.392448
H  -3.606419  -2.650239   3.367036
C  -3.349690  -0.709592  -1.586393
C  -4.498624  -0.844704  -2.559322
H  -4.225793  -0.325084  -3.484198
H  -4.682844  -1.893599  -2.795069
H  -5.395078  -0.375709  -2.150929
C   1.694508  -2.343766  -0.221128
C   1.634626  -3.480785   0.607830
C   1.306689  -1.093441   0.355771
C   1.293626  -3.400795   1.944803
H   1.905237  -4.440729   0.178736
C   0.982623  -1.032471   1.733199
C   0.976404  -2.164899   2.517131
H   1.281034  -4.300739   2.551203
H   0.719891  -0.075600   2.154185
H   0.713274  -2.092101   3.567055
N   1.537238   0.139694  -0.327480
C   1.011829   0.392971  -1.514752
C   1.571275   1.508717  -2.328015
-----
```

H	0.766550	2.031440	-2.847590
H	2.140303	2.196530	-1.700405
H	2.260450	1.057181	-3.049101
H	2.225853	0.829001	0.089755
C	2.328404	-2.487503	-1.585381
O	3.899435	-0.634509	-1.827768
C	3.810965	-2.022770	-1.638021
H	2.274765	-3.546812	-1.859294
H	1.787134	-1.934127	-2.356231
H	4.302537	-2.311928	-0.697030
C	4.520140	-2.711031	-2.801272
H	4.526791	-3.800501	-2.686021
H	4.019596	-2.462347	-3.744182
H	5.552076	-2.354991	-2.860352
H	4.155441	-0.200242	-0.981778
O	4.704325	0.552680	0.491005
C	4.238654	1.595117	0.981203
C	5.112866	2.445519	1.892348
H	5.035664	3.500176	1.612101
H	4.758090	2.355852	2.925853
H	6.153176	2.119764	1.847252
O	3.040356	2.014178	0.803247
O	-1.013831	1.580545	2.303553
C	-1.450610	2.448414	-0.366354
C	-2.128302	2.850763	-1.521691
C	-0.296714	3.157289	-0.007170
C	-1.663528	3.899380	-2.309561
H	-3.025981	2.317969	-1.813109
C	0.170410	4.215783	-0.795157
C	-0.504956	4.583115	-1.948082
H	-2.207356	4.180497	-3.206573
H	1.068656	4.746653	-0.490499
H	-0.132580	5.402302	-2.555031
C	0.074381	2.197786	2.221136
C	1.016344	2.200505	3.394316
H	0.736947	1.411857	4.093673
H	2.041368	2.057360	3.037629
H	0.960277	3.165483	3.908391
N	0.473340	2.872766	1.146429
H	1.480143	3.054531	1.093558

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

=====

SCF Energy= -2011.55932758 Predicted Change= -7.823965D-09

Zero-point correction (ZPE)= -2011.0006 0.55866

Internal Energy (U)= -2010.9502 0.60910

Enthalpy (H)= -2010.9491 0.61016

Gibbs Free Energy (G)= -2011.0934 0.46583
Entropy (S)= 0.00043322

Frequencies -- 7.1384 23.6673 30.2687

Supporting Information: **Anti-II**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(pcm,solvent=acetone)
opt=(gdiis,maxcycle=250,maxstep=10,ts,calcfc,noeigentest) freq=noraman
Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C25H32N2O9Pd2 C1[X(C25H32N2O9Pd2)] #Atoms= 70
Charge = 0 Multiplicity = 1

SCF Energy= -2011.50073599 Predicted Change= -8.364762D-07

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00005 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.07753 || 0.00180 [NO] 0.07753 || 0.00180 [NO]

Atomic Coordinates (Angstroms)
Type X Y Z

Pd	0.098303	-1.027581	-0.575570
Pd	-2.322598	-0.563448	1.005438
O	-0.445471	0.095962	-2.202128
O	-1.183951	-2.592501	-1.329882
O	0.640240	-2.259106	0.974982
O	-3.083745	-2.039645	-0.234143
O	-1.282165	-2.130964	2.160451
C	-0.129317	-2.564633	1.949061
C	0.477127	-3.528692	2.946214
H	1.021854	-4.321131	2.428188
H	1.194490	-2.981601	3.567686
H	-0.293156	-3.956476	3.588979
C	-2.402259	-2.728845	-1.056546
C	-3.175054	-3.794073	-1.804471
H	-2.501731	-4.556009	-2.199576
H	-3.926643	-4.249938	-1.156915
H	-3.695719	-3.318734	-2.643257
C	1.208029	0.477220	0.134280
C	1.951161	0.312633	1.331745
C	0.913533	1.813496	-0.240736

C	2.436080	1.382955	2.060648
H	2.153985	-0.696946	1.667167
C	1.407024	2.898362	0.489583
C	2.166627	2.682914	1.629170
H	3.023528	1.212627	2.956090
H	1.190763	3.913047	0.167094
H	2.543000	3.534894	2.185859
N	0.161863	2.145058	-1.383649
C	-0.437030	1.338759	-2.279278
C	-1.143568	1.988526	-3.429604
H	-2.215198	1.800268	-3.311052
H	-0.973191	3.064305	-3.487089
H	-0.814244	1.514962	-4.357130
H	0.083734	3.135737	-1.571759
C	2.887540	0.276254	-1.230498
O	4.277317	-0.641327	-2.346360
C	3.291228	-1.136758	-1.458073
H	2.368563	0.754192	-2.052926
H	3.592020	0.866461	-0.640386
H	5.171223	-0.442337	-1.818507
O	6.459601	-0.216486	-1.195555
C	6.438161	0.599690	-0.214374
C	7.793338	0.850391	0.445243
H	8.500215	1.241783	-0.293914
H	7.705217	1.557123	1.273105
H	8.205148	-0.094114	0.816419
O	5.431040	1.182407	0.233122
O	-1.626186	0.781229	2.382484
C	-3.170147	0.872203	-0.051592
C	-4.044148	0.567676	-1.104733
C	-2.875292	2.226539	0.161124
C	-4.593359	1.554053	-1.918813
H	-4.289687	-0.472026	-1.289941
C	-3.409882	3.224201	-0.665625
C	-4.268375	2.891961	-1.702087
H	-5.267433	1.276920	-2.723868
H	-3.159817	4.266614	-0.483483
H	-4.679789	3.673240	-2.333055
C	-1.530115	2.018187	2.242307
C	-0.837053	2.807834	3.315208
H	0.033650	2.247603	3.658680
H	-0.522656	3.795953	2.974483
H	-1.525883	2.926938	4.157701
N	-2.039655	2.694648	1.208119
H	-1.895038	3.695122	1.226481
C	3.809412	-1.931773	-0.278671
H	2.968597	-2.347357	0.283578
H	4.426780	-2.757701	-0.644962

H	4.412395	-1.301822	0.380579
H	2.551725	-1.703219	-2.030157

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

=====

SCF Energy= -2011.50073599 Predicted Change= -8.364762D-07
 Zero-point correction (ZPE)= -2010.9469 0.55379
 Internal Energy (U)= -2010.8958 0.60491
 Enthalpy (H)= -2010.8947 0.60597
 Gibbs Free Energy (G)= -2011.0410 0.45969
 Entropy (S)= 0.00043906

Frequencies -- -509.1853 21.8942 24.1795

Supporting Information: **HFIP-I**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

=====

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(pcm,solvent=acetone)
 opt=(gdiis,maxcycle=250,maxstep=10,ts,calcfc,noeigentest) freq=noraman
 Temperature=333.15
 #N Geom=AllCheck Guess=TCHECK SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C26H30F6N2O8Pd2 C1[X(C26H30F6N2O8Pd2)] #Atoms= 74
 Charge = 0 Multiplicity = 1

SCF Energy= -2572.06808298 Predicted Change= -7.421032D-06

=====

Optimization completed. {Found 1 times}
 Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
 Force 0.00002 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
 Displ 0.84278 || 0.00180 [NO] 0.84278 || 0.00180 [NO]

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z

Pd	-1.054215	-1.281768	-0.513869
Pd	-3.475127	0.036261	0.477007
O	-0.660636	0.101209	-1.987317
O	-2.550772	-2.127731	-1.815433
O	-1.485515	-2.715382	0.893125
O	-4.331461	-0.898471	-1.160960
O	-3.490609	-1.895027	1.539681
C	-2.575842	-2.746493	1.558782
C	-2.740111	-3.969829	2.435429
H	-2.932113	-4.840064	1.799361

H	-1.817152	-4.161124	2.988513
H	-3.573495	-3.841430	3.127014
C	-3.750334	-1.763193	-1.888680
C	-4.608997	-2.374841	-2.974610
H	-4.708799	-1.649552	-3.789491
H	-4.151867	-3.284256	-3.366340
H	-5.609903	-2.588026	-2.593022
C	0.341119	-0.441726	0.664361
C	0.606775	-1.009532	1.944524
C	0.546799	0.964744	0.549796
C	1.151123	-0.281376	2.982193
H	0.400919	-2.065867	2.075601
C	1.093909	1.705339	1.599759
C	1.404021	1.082332	2.798955
H	1.377920	-0.757838	3.929564
H	1.284749	2.767618	1.477523
H	1.837410	1.668695	3.602634
N	0.309541	1.675175	-0.636945
C	-0.219962	1.249839	-1.802345
C	-0.296695	2.242746	-2.920914
H	-1.341344	2.559235	-3.012711
H	0.329696	3.121153	-2.758763
H	-0.006763	1.749257	-3.850369
H	0.607959	2.641451	-0.625699
C	2.010041	-1.017274	-0.252460
O	3.533991	-2.271575	-0.866217
C	2.426148	-2.449398	-0.069374
H	1.731940	-0.759555	-1.270332
H	2.685092	-0.317435	0.229267
H	2.667305	-2.639255	0.993377
C	1.471092	-3.517492	-0.575823
H	0.595669	-3.625017	0.072105
H	1.131570	-3.275077	-1.590239
H	2.000558	-4.475637	-0.610911
H	4.578816	-1.650320	-0.058639
O	5.267077	-1.069533	0.466187
C	5.578588	-0.013790	-0.360305
C	6.981181	-0.207783	-0.948254
O	-2.774902	0.866085	2.211417
C	-3.416995	1.778982	-0.448495
C	-3.994754	1.936229	-1.716386
C	-2.761237	2.892916	0.095698
C	-3.921696	3.135397	-2.419410
H	-4.509769	1.090928	-2.158783
C	-2.666130	4.097530	-0.614434
C	-3.246531	4.222479	-1.867197
H	-4.384962	3.217220	-3.398121
H	-2.143901	4.943342	-0.173647

H	-3.171333	5.162010	-2.405072
C	-2.235440	1.983153	2.350057
C	-1.670434	2.342203	3.694358
H	-1.235469	1.449310	4.145098
H	-0.914351	3.127168	3.636642
H	-2.488985	2.688511	4.333768
N	-2.160787	2.902284	1.381754
H	-1.703041	3.767828	1.634497
C	5.453384	1.290415	0.429251
F	7.311406	0.765530	-1.814375
F	7.929283	-0.243974	-0.001258
F	7.028147	-1.370726	-1.612823
F	5.779072	2.365607	-0.306468
F	6.223038	1.298370	1.523770
F	4.180954	1.457402	0.833922
H	4.893509	0.071899	-1.216462

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

=====

SCF Energy= -2572.06808298 Predicted Change= -7.421032D-06

Zero-point correction (ZPE)= -2571.5139 0.55410

Internal Energy (U)= -2571.4569 0.61113

Enthalpy (H)= -2571.4558 0.61219

Gibbs Free Energy (G)= -2571.6209 0.44709

Entropy (S)= 0.00049555

Frequencies -- -515.6206 3.2540 9.0364

Supporting Information: **HFIP-II**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

=====

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(pcm,solvent=acetone)

opt=(gdiis,maxcycle=250,maxstep=10,ts,calcfc,noeigentest) freq=noraman

Temperature=333.15

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C26H30F6N2O8Pd2 C1[X(C26H30F6N2O8Pd2)] #Atoms= 74

Charge = 0 Multiplicity = 1

SCF Energy= -2572.06613481 Predicted Change= -7.967875D-09

=====

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
------	----------	----------	-------	----------	----------	-------

Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
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Displ	0.01297	0.00180	[NO]	0.01297	0.00180	[YES]
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Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Pd	-0.901488	-1.231102	-0.594042
Pd	-3.436426	-0.092795	0.345116
O	-0.457064	0.336848	-1.851888
O	-2.253820	-1.961695	-2.102318
O	-1.377939	-2.839205	0.588334
O	-4.123142	-0.868883	-1.450904
O	-3.442446	-2.138187	1.186212
C	-2.506424	-2.965945	1.174580
C	-2.669723	-4.261261	1.941178
H	-3.695520	-4.377964	2.292229
H	-2.389933	-5.108423	1.309843
H	-1.992207	-4.251648	2.801306
C	-3.457513	-1.624746	-2.226044
C	-4.207412	-2.126089	-3.441322
H	-3.709798	-2.995099	-3.873683
H	-5.239132	-2.370236	-3.179892
H	-4.230440	-1.325748	-4.189167
C	0.353580	-0.490874	0.792782
C	0.534908	-1.200120	2.016611
C	0.496309	0.926568	0.865382
C	0.951798	-0.584154	3.178091
H	0.371123	-2.271800	2.002326
C	0.917598	1.553006	2.040308
C	1.154180	0.800499	3.180420
H	1.118982	-1.163318	4.079552
H	1.063715	2.629111	2.063258
H	1.487480	1.300788	4.083966
N	0.328229	1.766919	-0.245454
C	-0.081720	1.467932	-1.495550
C	-0.101401	2.582787	-2.495365
H	-1.147963	2.853672	-2.670606
H	0.446286	3.466417	-2.165199
H	0.318852	2.219000	-3.435033
H	0.583500	2.733902	-0.094464
C	2.094540	-0.874225	-0.042569
O	3.736386	-1.961630	-0.676797
C	2.593785	-2.291332	0.011501
H	1.885141	-0.516491	-1.046151
H	2.694131	-0.202638	0.561385
H	2.772301	-2.587395	1.063195
C	1.745253	-3.347468	-0.678462
H	0.836925	-3.578946	-0.113323
H	1.459138	-3.008324	-1.681663
H	2.336075	-4.263986	-0.781805

H	4.641761	-1.261273	0.221701
O	5.196932	-0.775260	0.970030
C	5.915121	0.291586	0.490780
C	5.022900	1.412047	-0.070638
O	-2.905014	0.560124	2.209488
C	-3.386388	1.744571	-0.376122
C	-3.862490	2.020837	-1.665792
C	-2.830713	2.814864	0.340125
C	-3.784744	3.292289	-2.227088
H	-4.300056	1.212484	-2.240623
C	-2.730916	4.093444	-0.225509
C	-3.208243	4.335227	-1.504291
H	-4.167435	3.464957	-3.228532
H	-2.288340	4.903640	0.349046
H	-3.130465	5.330481	-1.929880
C	-2.444202	1.678510	2.518385
C	-2.011746	1.906086	3.938550
H	-1.532222	1.000040	4.311500
H	-1.327545	2.750631	4.040977
H	-2.902522	2.099452	4.545025
N	-2.343672	2.705466	1.668506
H	-1.957799	3.557110	2.054003
C	6.974548	-0.153443	-0.528351
F	5.723519	2.529480	-0.321053
F	4.397374	1.066964	-1.205226
F	4.074392	1.730740	0.827639
F	7.729343	0.873436	-0.955867
F	6.430979	-0.732153	-1.607968
F	7.795641	-1.048359	0.037616
H	6.470415	0.752709	1.316842

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

=====

SCF Energy= -2572.06613481 Predicted Change= -7.967875D-09

Zero-point correction (ZPE)= -2571.5116 0.55449

Internal Energy (U)= -2571.4549 0.61116

Enthalpy (H)= -2571.4539 0.61221

Gibbs Free Energy (G)= -2571.6142 0.45190

Entropy (S)= 0.0004812

Frequencies -- -511.4347 11.1806 17.9048

Supporting Information: **6,4-Palladacycle-Red-Elim-TS-Dimer-Anti-Conf-VIII-B (Open)**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

=====

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(pcm,solvent=acetone)
 opt=(gdiis,maxcycle=250,maxstep=10,ts,calcf, noeigentest) freq=noraman
 Temperature=333.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C25H32N2O9Pd2 C1[X(C25H32N2O9Pd2)] #Atoms= 70
 Charge= 0 Multiplicity = 1

SCF Energy= -2011.49458034 Predicted Change= -1.075882D-07

Optimization completed. {Found 1 times}
 Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
 Force 0.00001 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
 Displ 0.01771 || 0.00180 [NO] 0.01771 || 0.00180 [NO]

Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Pd	2.023122	0.144055	0.569844
Pd	-2.182613	-0.692807	0.062642
O	0.496849	1.543133	0.771020
O	-0.447751	0.288748	-2.243174
O	1.204546	-0.864609	2.237687
O	-1.714128	-1.502934	-1.756146
O	-0.318453	-1.620680	0.811074
C	0.146847	-1.517130	1.973073
C	-0.505777	-2.248023	3.122422
H	0.007706	-3.209010	3.240635
H	-0.401637	-1.689252	4.054589
H	-1.559130	-2.434632	2.909130
C	-0.837454	-0.868382	-2.455473
C	-0.253584	-1.686026	-3.594020
H	0.315391	-1.049656	-4.274525
H	0.410609	-2.443740	-3.163334
H	-1.042354	-2.208953	-4.141758
C	3.259443	1.634446	-0.062625
C	4.603414	1.530991	0.296948
C	2.717771	2.884391	-0.376232
C	5.411743	2.664008	0.307958
H	5.008514	0.560461	0.556467
C	3.535140	4.015472	-0.370068
C	4.880847	3.903447	-0.041334
H	6.456581	2.573729	0.586768
H	3.107688	4.984542	-0.611190
H	5.507854	4.788690	-0.042958
N	1.348794	3.048792	-0.704479
C	0.325886	2.451204	-0.074915
C	-1.064591	2.883338	-0.411920

H	-1.653538	2.934673	0.505971
H	-1.100239	3.843041	-0.930499
H	-1.484250	2.095043	-1.047320
H	1.120431	3.809224	-1.330879
C	2.621189	0.161465	-1.506520
O	3.337480	-1.283603	0.174650
C	3.333572	-1.165933	-1.252308
H	1.571003	0.125009	-1.814258
H	3.179009	0.876269	-2.104167
H	2.718576	-1.972248	-1.669184
C	4.738060	-1.252643	-1.820790
H	4.693618	-1.242945	-2.915847
H	5.361940	-0.416716	-1.491617
H	5.210205	-2.188786	-1.506077
H	2.594561	-2.718699	0.612296
O	2.087377	-3.509495	0.966264
C	1.309140	-4.021869	0.020978
C	0.303794	-4.999086	0.568870
H	-0.025590	-5.681103	-0.216023
H	0.708075	-5.556223	1.416655
H	-0.558607	-4.419708	0.916862
O	1.383929	-3.720924	-1.157130
O	-2.554601	-0.006385	1.963883
C	-3.753603	0.257404	-0.647016
C	-4.246233	-0.017960	-1.930470
C	-4.410308	1.256437	0.086752
C	-5.323210	0.676116	-2.473112
H	-3.756881	-0.788303	-2.516154
C	-5.491471	1.963675	-0.454960
C	-5.946491	1.678774	-1.733354
H	-5.671296	0.437191	-3.473917
H	-5.980957	2.735678	0.134191
H	-6.785075	2.232824	-2.143228
C	-3.227096	1.003255	2.260161
C	-3.103309	1.556300	3.651265
H	-2.078129	1.909692	3.794360
H	-3.797352	2.373905	3.852698
H	-3.280381	0.747926	4.364785
N	-4.043944	1.630650	1.408482
H	-4.538022	2.430530	1.780280

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

=====

SCF Energy= -2011.49458034 Predicted Change= -1.075882D-07

Zero-point correction (ZPE)= -2010.9392 0.55528

Internal Energy (U)= -2010.8886 0.60591

Enthalpy (H)= -2010.8876 0.60697

Gibbs Free Energy (G)= -2011.0308 0.46377
Entropy (S)= 0.00042983

Frequencies -- -258.7783 19.2564 24.4617

Supporting Information: **6,4-Palladacycle-Red-Elim-TS-Dimer-Syn-Conf-VIII-B (Syn)**

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

#wb97xd/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(pcm,solvent=acetone)
opt=(gdiis,maxcycle=250,maxstep=10,ts,calcfc,noeigentest) freq=noraman
Temperature=333.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk Rwb97XD/GenECP/Auto Freq

Pointgroup= C1 Stoichiometry= C25H32N2O9Pd2 C1[X(C25H32N2O9Pd2)] #Atoms= 70
Charge = 0 Multiplicity = 1

SCF Energy= -2011.48568301 Predicted Change= -4.837014D-08

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00001 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.00802 || 0.00180 [NO] 0.00802 || 0.00180 [NO]

Atomic Coordinates (Angstroms)
Type X Y Z

Pd	0.748462	-0.056525	-1.372297
Pd	-1.003382	-1.249640	1.222112
O	-1.200592	-0.511984	-2.009839
O	1.255207	-2.095460	-1.231768
O	2.020603	-0.296631	1.349388
O	0.521547	-2.756847	0.806263
O	0.153370	-0.274644	2.604371
O	-2.244611	-2.416237	0.063080
C	1.394986	-0.001196	2.365122
C	2.057466	0.790135	3.484151
H	3.116868	0.936675	3.266244
H	1.567606	1.766356	3.570991
H	1.940503	0.278229	4.444009
C	1.266051	-2.836825	-0.195591
C	2.321126	-3.926313	-0.204579
H	2.393051	-4.385428	-1.193671
H	3.285744	-3.455776	0.017319
H	2.110415	-4.686211	0.549802
C	0.169866	1.822109	-0.824268
C	0.943712	2.422685	0.171246

C	-1.168891	2.196966	-0.974136
C	0.394145	3.402387	0.989997
H	1.963783	2.093598	0.313813
C	-1.711088	3.186999	-0.156536
C	-0.930843	3.793994	0.817092
H	1.004141	3.854245	1.765606
H	-2.759468	3.448840	-0.260590
H	-1.368506	4.553722	1.455759
N	-2.017830	1.621032	-1.949625
C	-2.032890	0.347570	-2.368024
C	-3.096172	-0.023603	-3.361624
H	-4.050831	0.461649	-3.145807
H	-2.767261	0.290495	-4.358063
H	-3.221023	-1.105869	-3.369615
C	-2.457354	0.060761	1.543167
C	-3.632085	0.069109	0.775320
C	-2.337199	1.062729	2.515935
C	-4.605074	1.064279	0.937295
C	-3.309694	2.039362	2.703120
H	-1.438210	1.077599	3.121475
C	-4.446535	2.050614	1.898866
H	-5.498878	1.051218	0.317098
H	-3.170603	2.801347	3.464850
H	-5.209519	2.813143	2.021356
N	-3.947085	-0.918407	-0.199131
H	-4.838279	-0.790317	-0.658805
H	-2.782193	2.203865	-2.264880
C	-3.329982	-2.080503	-0.446246
C	-4.002682	-3.035925	-1.392109
H	-4.890582	-2.615903	-1.868684
H	-3.284447	-3.340918	-2.156959
H	-4.292744	-3.930249	-0.832980
C	1.163492	1.638993	-2.664546
O	2.656475	0.450732	-1.340337
C	2.652832	1.330476	-2.449325
H	0.683583	1.133616	-3.504919
H	0.908862	2.694165	-2.666734
H	3.022078	0.807882	-3.344530
C	3.513659	2.559068	-2.205471
H	3.550154	3.174887	-3.110978
H	3.117664	3.164913	-1.385244
H	4.533440	2.254445	-1.951917
H	3.781873	0.551031	-0.058214
O	4.576950	0.793120	0.490509
C	5.305023	-0.290902	0.727985
C	6.440564	-0.009621	1.680929
H	7.127639	-0.855864	1.704159
H	6.971763	0.899989	1.388591

H	6.034621	0.152578	2.685060
O	5.081660	-1.383657	0.242040

Statistical Thermodynamic Analysis

Temperature= 333.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2011.48568301 Predicted Change= -4.837014D-08

Zero-point correction (ZPE)= -2010.9305 0.55513

Internal Energy (U)= -2010.8797 0.60588

Enthalpy (H)= -2010.8787 0.60694

Gibbs Free Energy (G)= -2011.0222 0.46344

Entropy (S)= 0.00043073

Frequencies -- -323.1470 19.5172 21.8864

viii) References:

(1) Chai, J.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *J. Chem. Phys.* **2008**, *10*, 6615-6620.

(2) (a) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations – Potentials for the Transition Metal Atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270–283. (b) Wadt, W. R.; Hay, P. J. Ab Initio Effective Core Potentials for Molecular Calculations – Potentials for Main Group Elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284–298. (c) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations – Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.

(3) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian--Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257.

(4) (a) Miertuš, S.; Scrocco, E.; Tomasi, J. Electrostatic Interaction of a Solute with a Continuum. A Direct Utilization of ab initio Molecular Potentials for the Prevision of Solvent Effects. *Chem. Phys.* **1981**, *55*, 117–129. (b) Miertuš, S.; Tomasi, J. Approximate Evaluations of the Electrostatic Free Energy and Internal Energy Changes in Solution Processes. *Chem. Phys.* **1982**, *65*, 239-245. (c) Pascual-Ahuir, J. L.; Silla, E.; Tuñón, I. GEPOL: An Improved Description of Molecular-

Surfaces. 3. A New Algorithm for the Computation of a Solvent-Excluding Surface. *J. Comp. Chem.* **1994**, *15*, 1127-1138.

(5) Gutierrez, M. A.; Newkome, G. R.; Selbin, J. Cyclometallation. Palladium 2-arylpyridine complexes. *J. Organomet. Chem.* **1980**, *202*(3), 341-350.

(6) Deprez, N. R.; Sanford, M. S. Synthetic and mechanistic studies of Pd-catalyzed C–H arylation with diaryliodonium salts: evidence for a bimetallic high oxidation state Pd intermediate. *J. Am. Chem. Soc.* **2009**, *131*(31), 11234-11241.

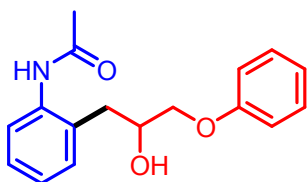
(7) Powers, D. C.; Geibel, M. A.; Klein, J. E.; Ritter, T. Bimetallic palladium catalysis: direct observation of Pd (III)– Pd (III) intermediates. *J. Am. Chem. Soc.* **2009**, *131*(47), 17050-17051.

(8) Powers, D. C.; Ritter, T. Bimetallic Pd (III) complexes in palladium-catalysed carbon–heteroatom bond formation. *Nat. Chem.* **2009**, *1*(4), 302.

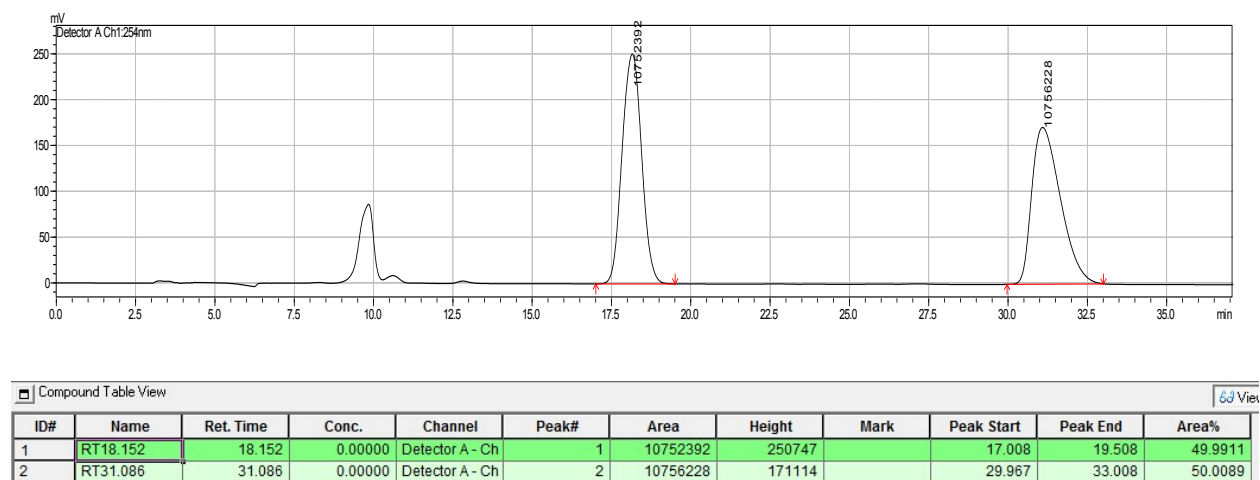
(9) Deprez, N. R.; Sanford, M. S. Synthetic and mechanistic studies of Pd-catalyzed C–H arylation with diaryliodonium salts: evidence for a bimetallic high oxidation state Pd intermediate. *J. Am. Chem. Soc.* **2009**, *131*(31), 11234-11241.

HPLC analysis of compounds **3a**, **6a-R** and **6b-S**

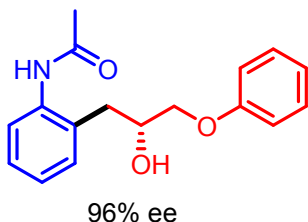
Racemic compound (**3a**):



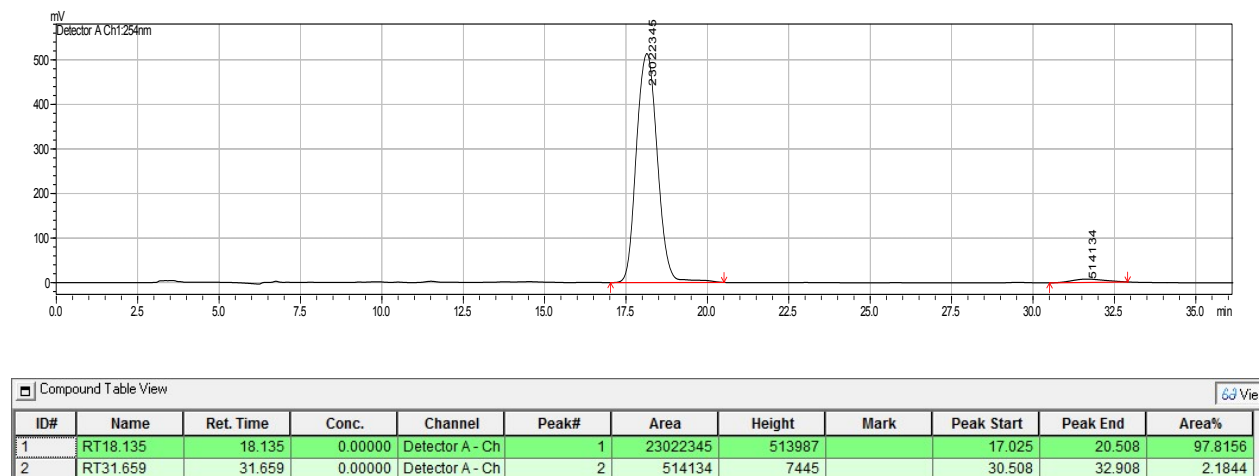
The racemic compound **3a** was analyzed by HPLC (chiral column: CHIRALCELL OJ-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm) analysis: Retention time = 18.1 min (R) and 31.0 min (S).



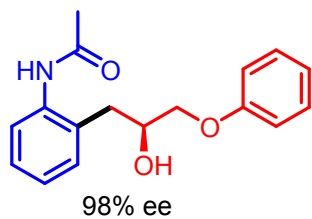
Chiral compound (**6a-R**):



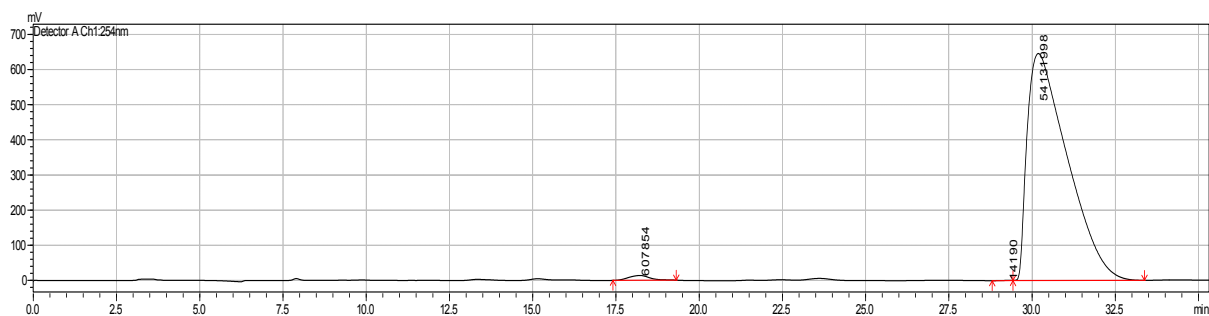
The enantiomeric excess of chiral **6a-R** was determined by HPLC (chiral column: CHIRALCELL OJ-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm) analysis: Retention time = 18.1 min (R) and 31.6 min (S).



Chiral compound (6b-S):

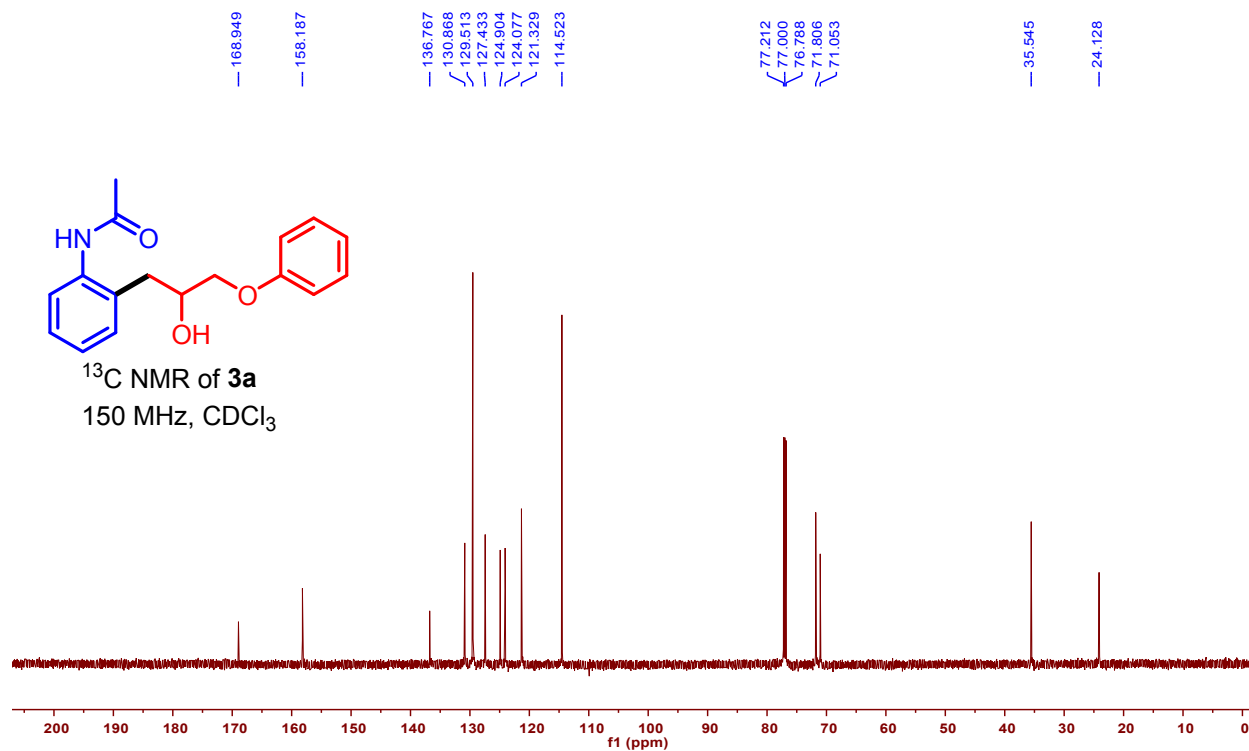
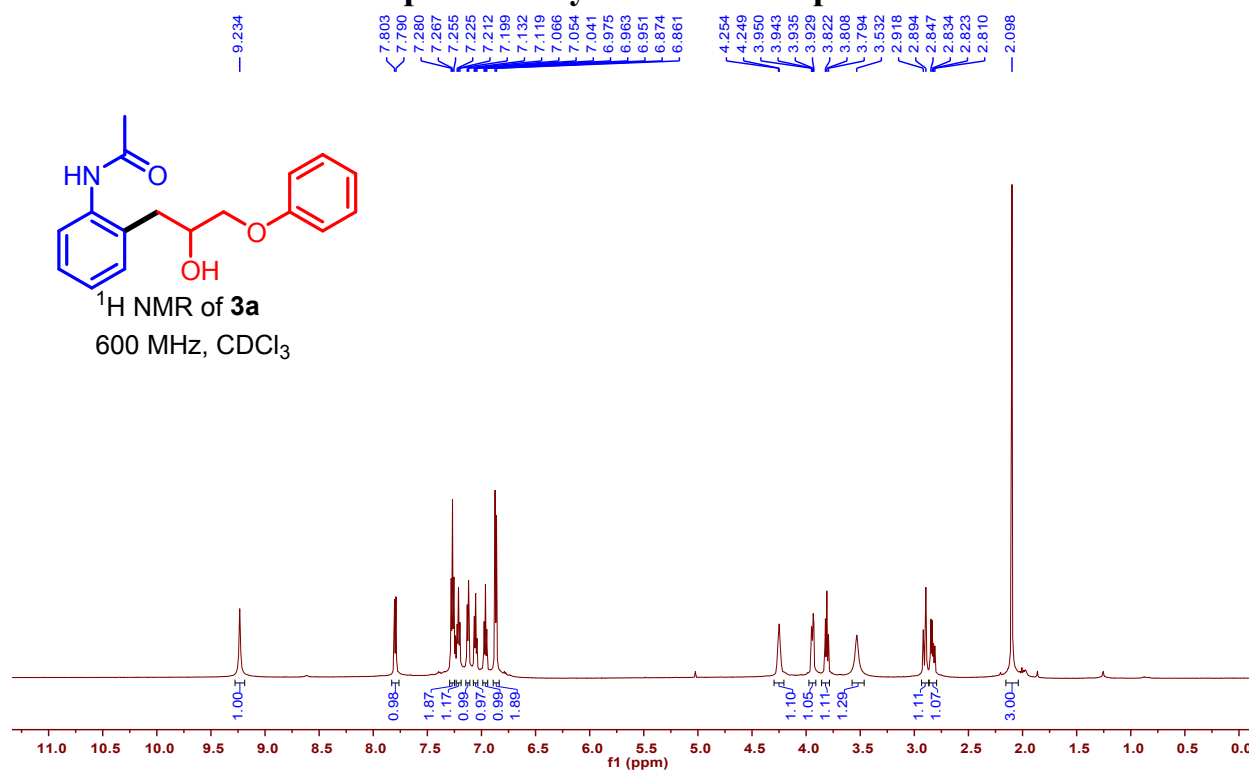


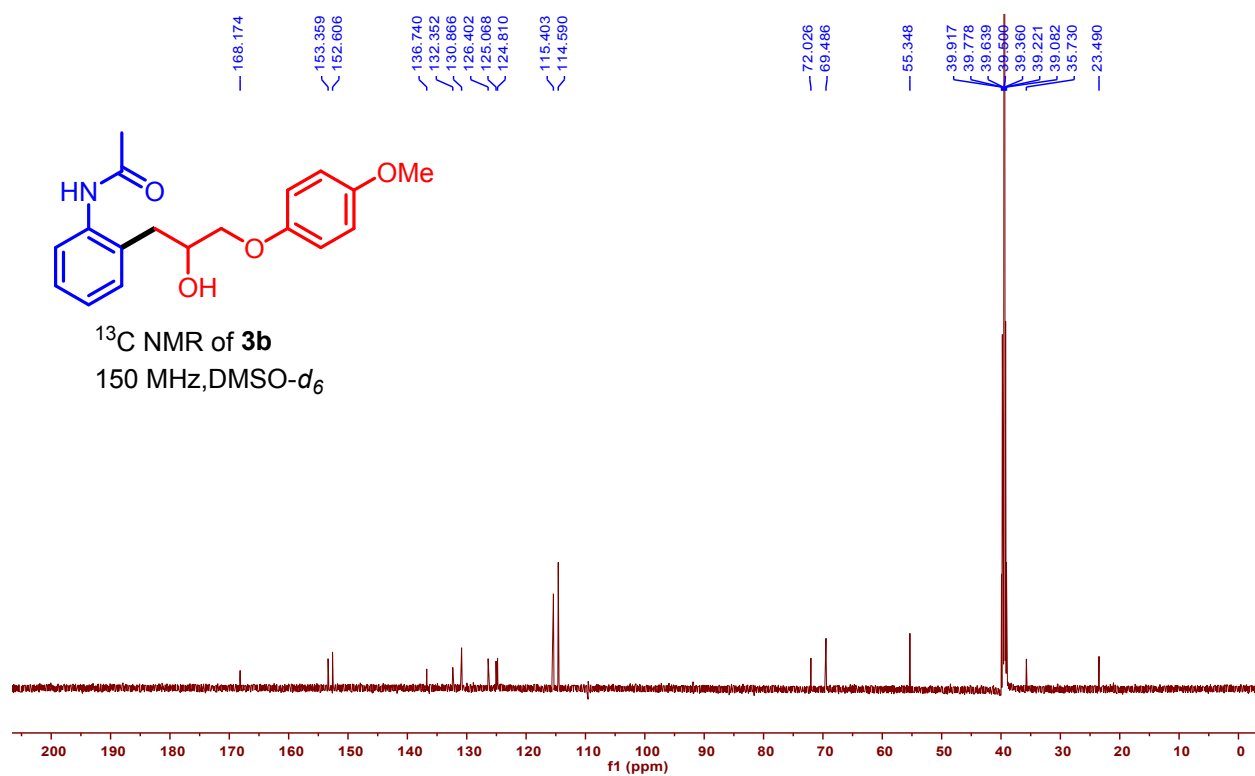
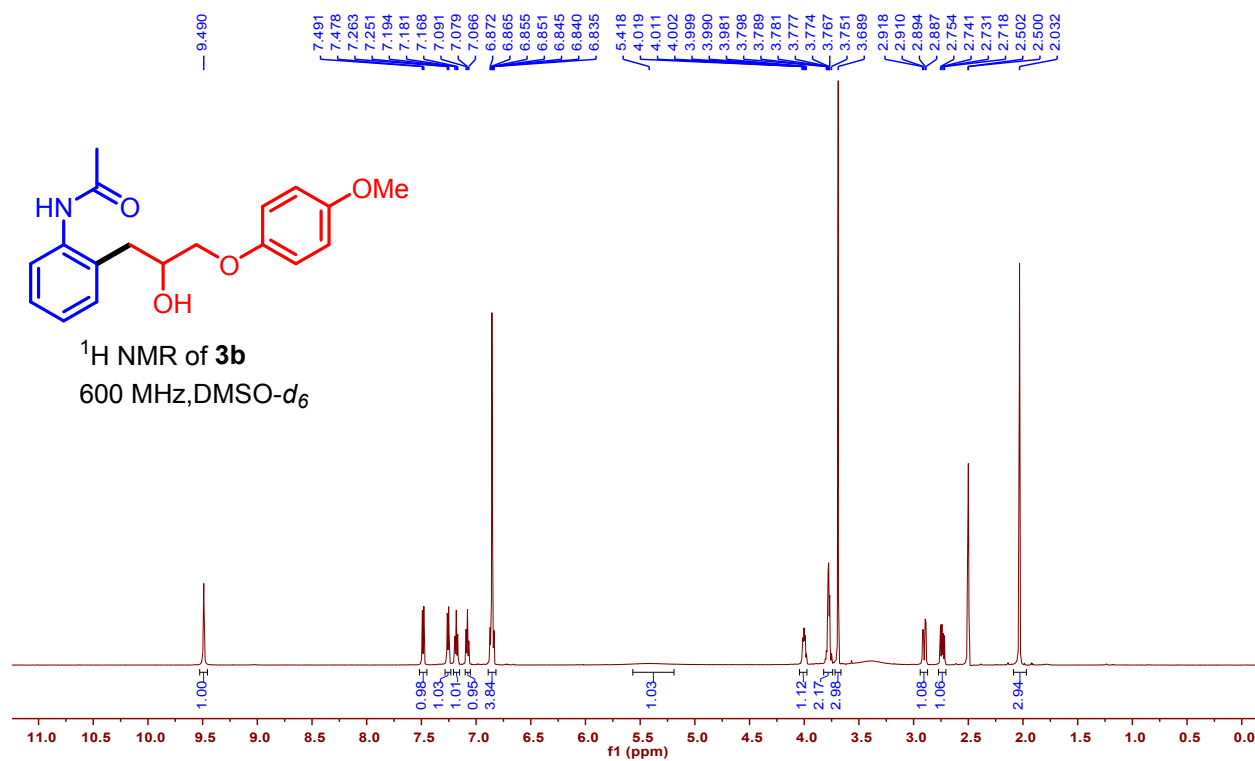
The enantiomeric excess of chiral **6b-S** was determined by HPLC (chiral column: CHIRALCELL OJ-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm) analysis: Retention time = 18.2 min (R) and 30.1 min (S).

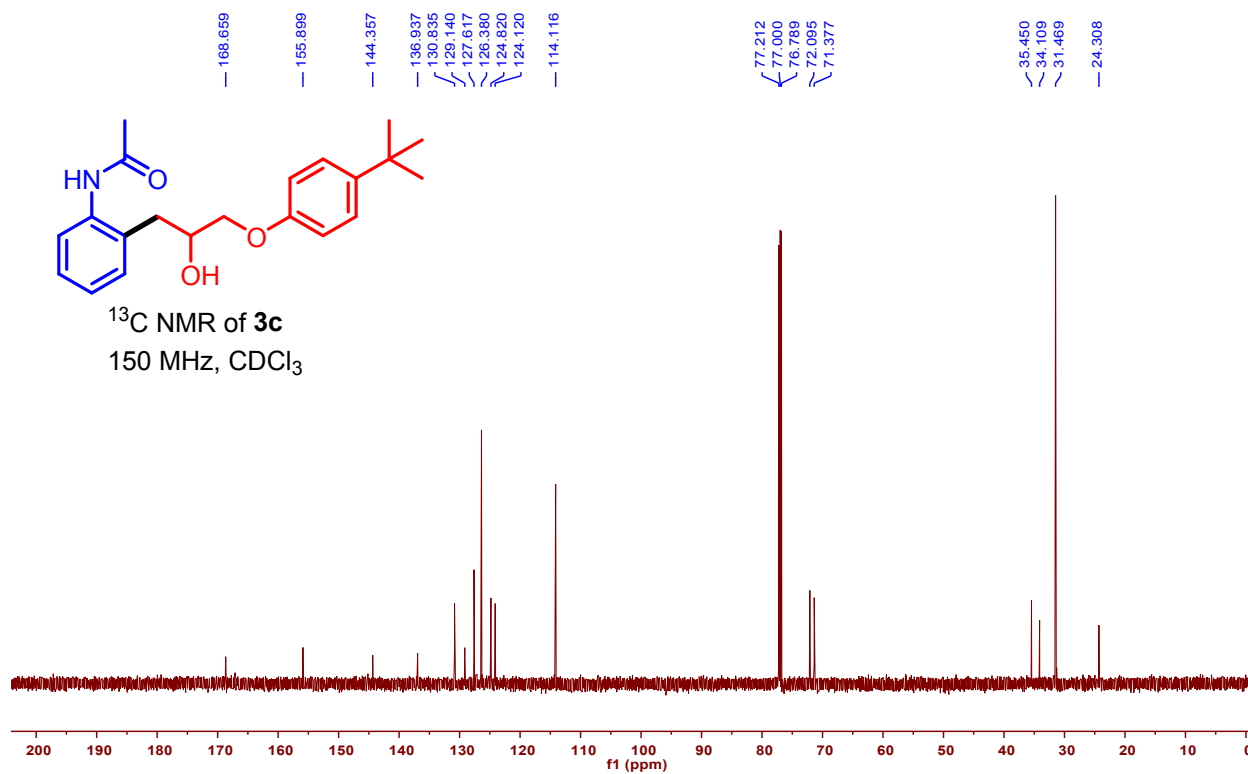
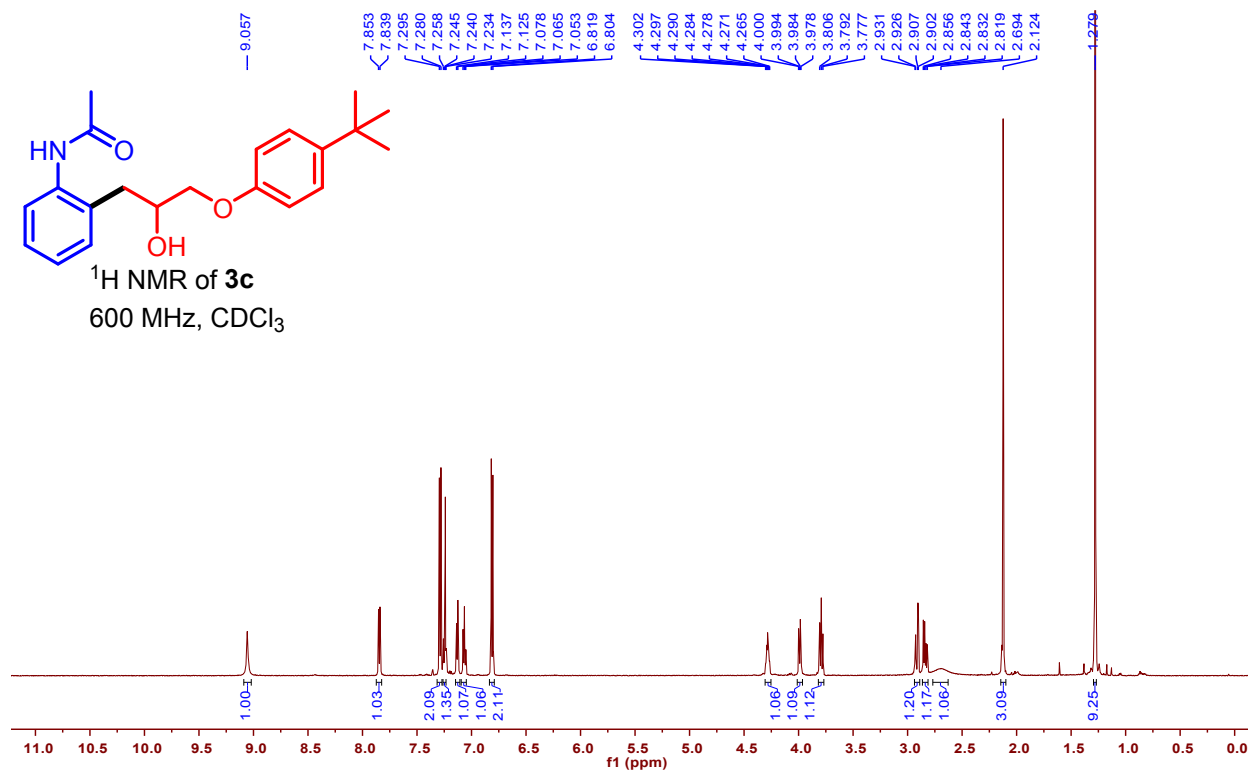


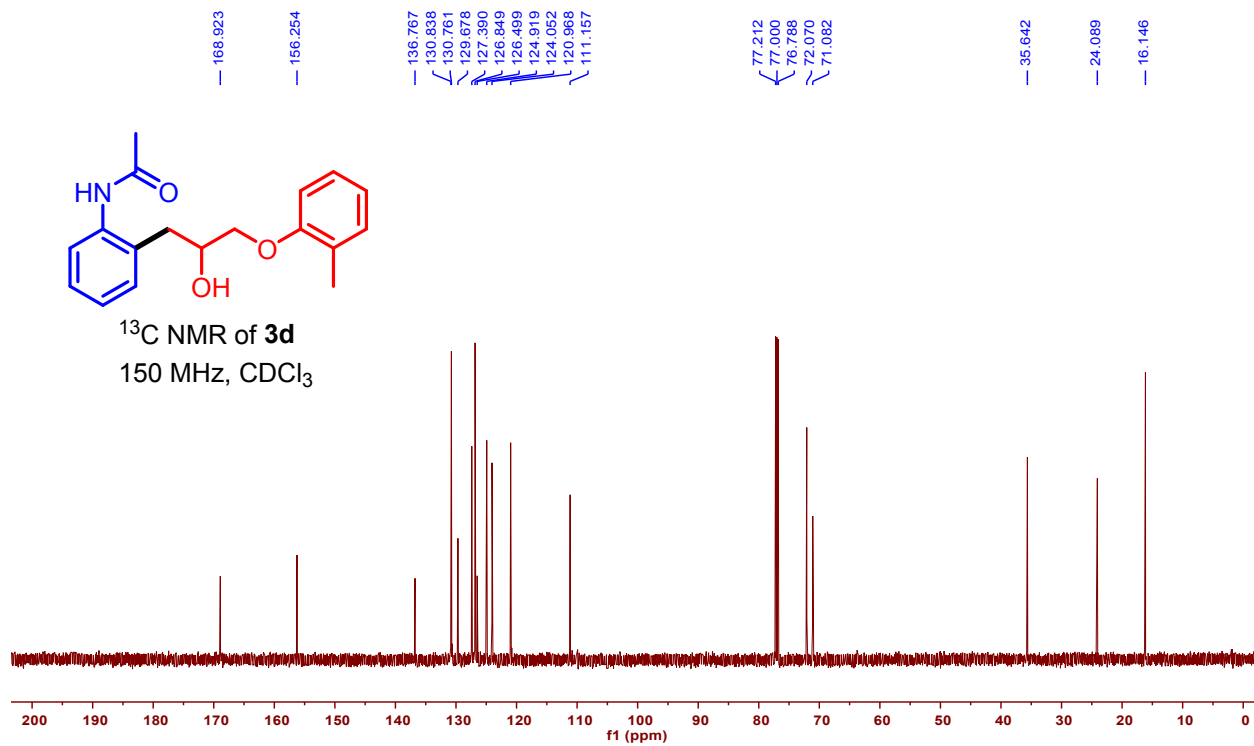
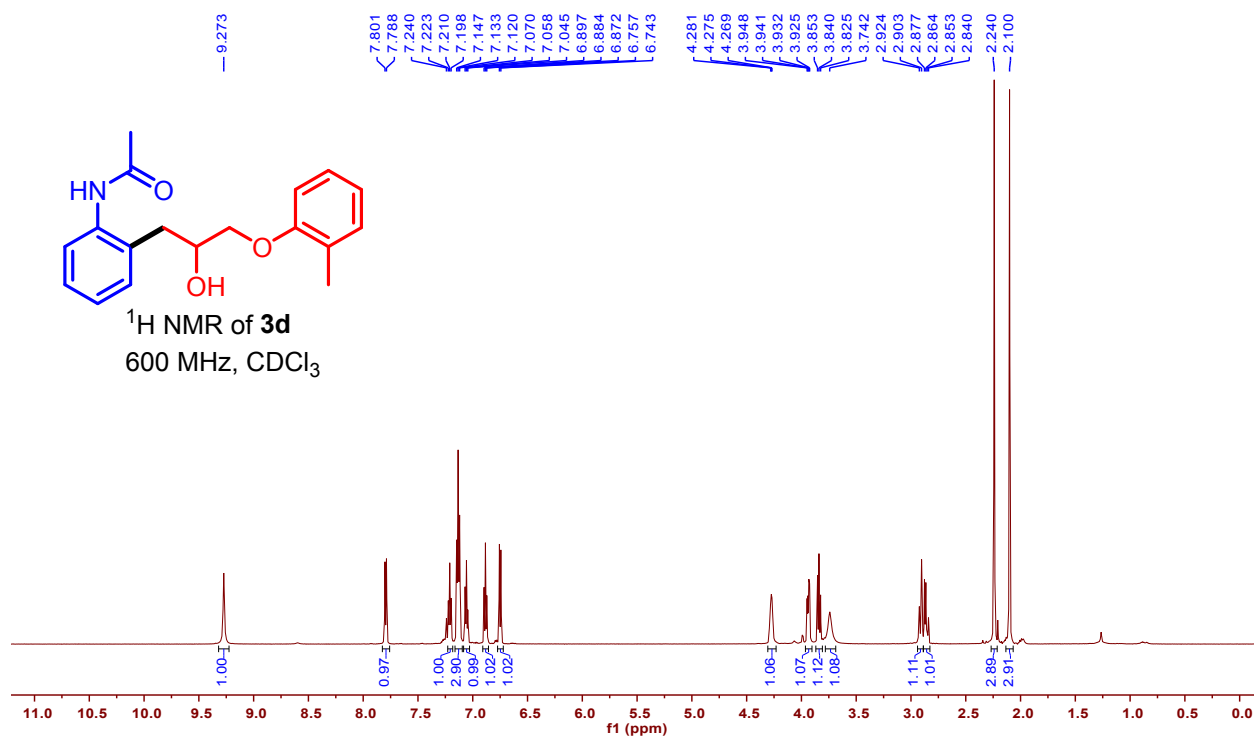
Compound Table View											
ID#	Name	Ret. Time	Conc.	Channel	Peak#	Area	Height	Mark	Peak Start	Peak End	Area%
1	RT18.217	18.217	0.00000	Detector A - Ch	1	607854	13680		17.408	19.308	1.1102
2	RT30.184	30.184	0.00000	Detector A - Ch	3	54131998	645838	V	29.425	33.375	98.8639

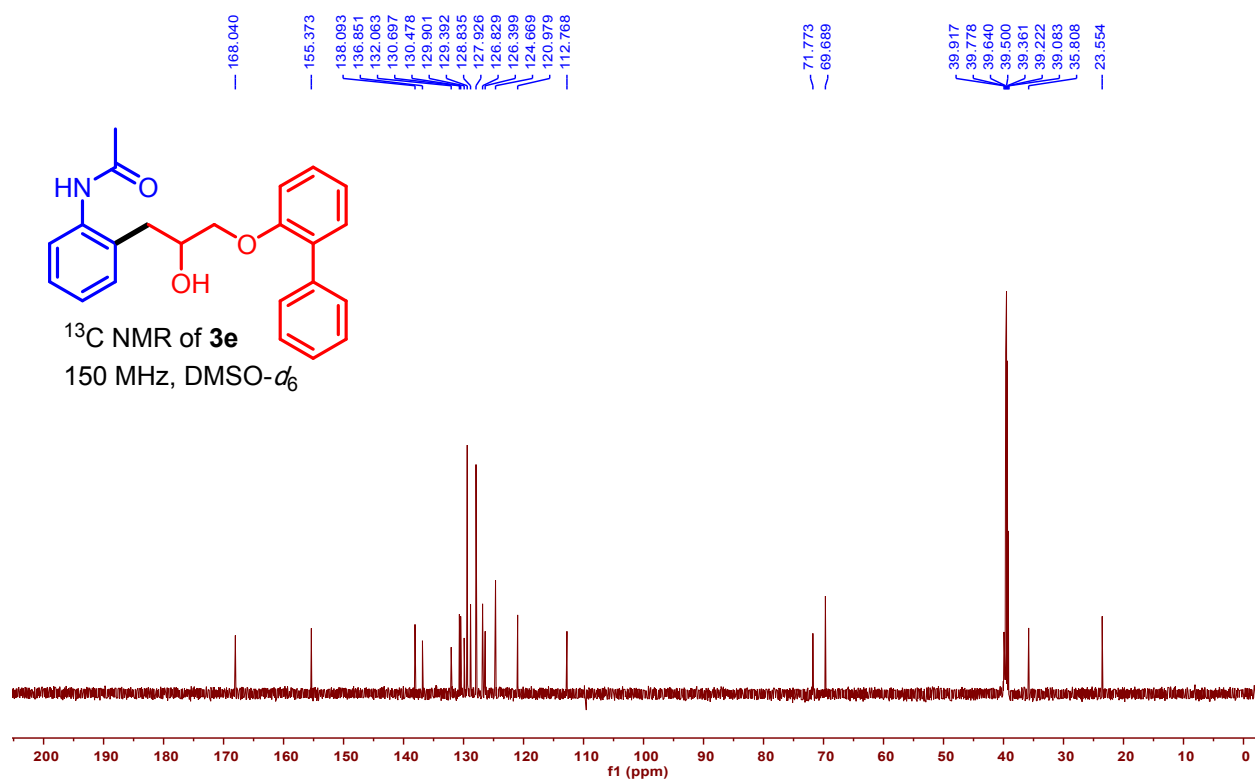
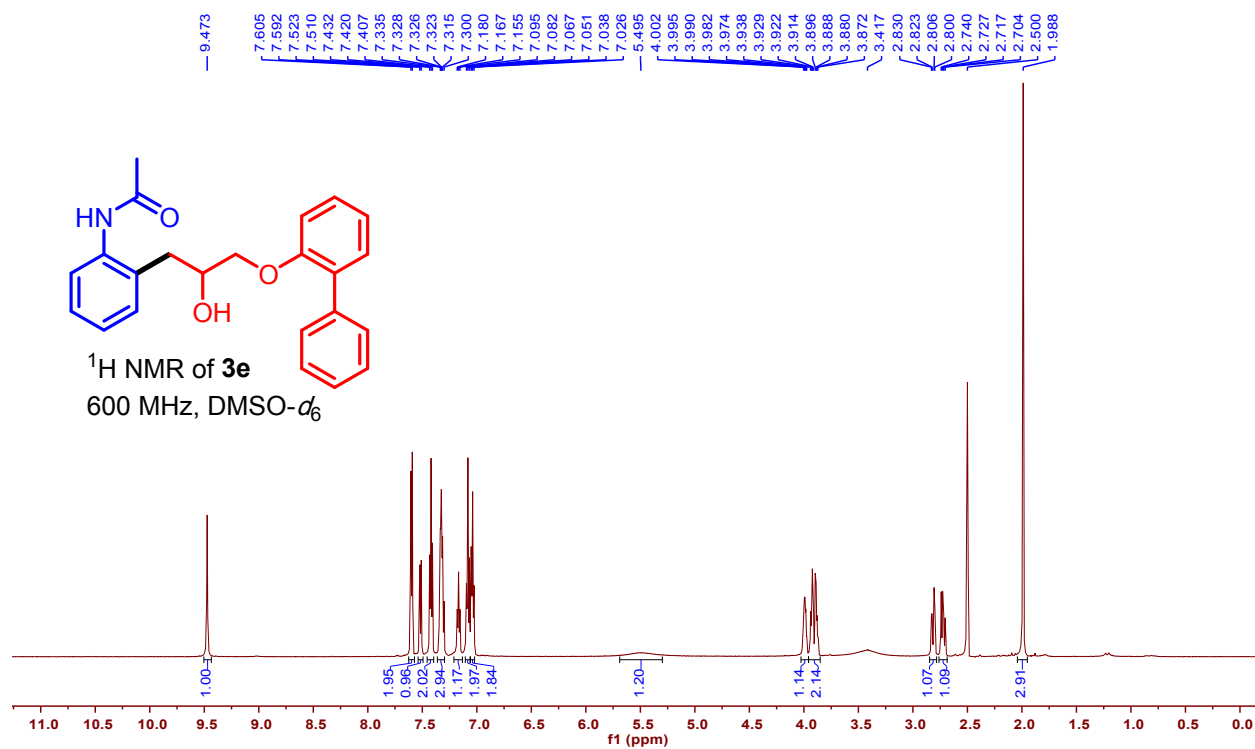
¹H NMR and ¹³C NMR spectra of synthesized compounds

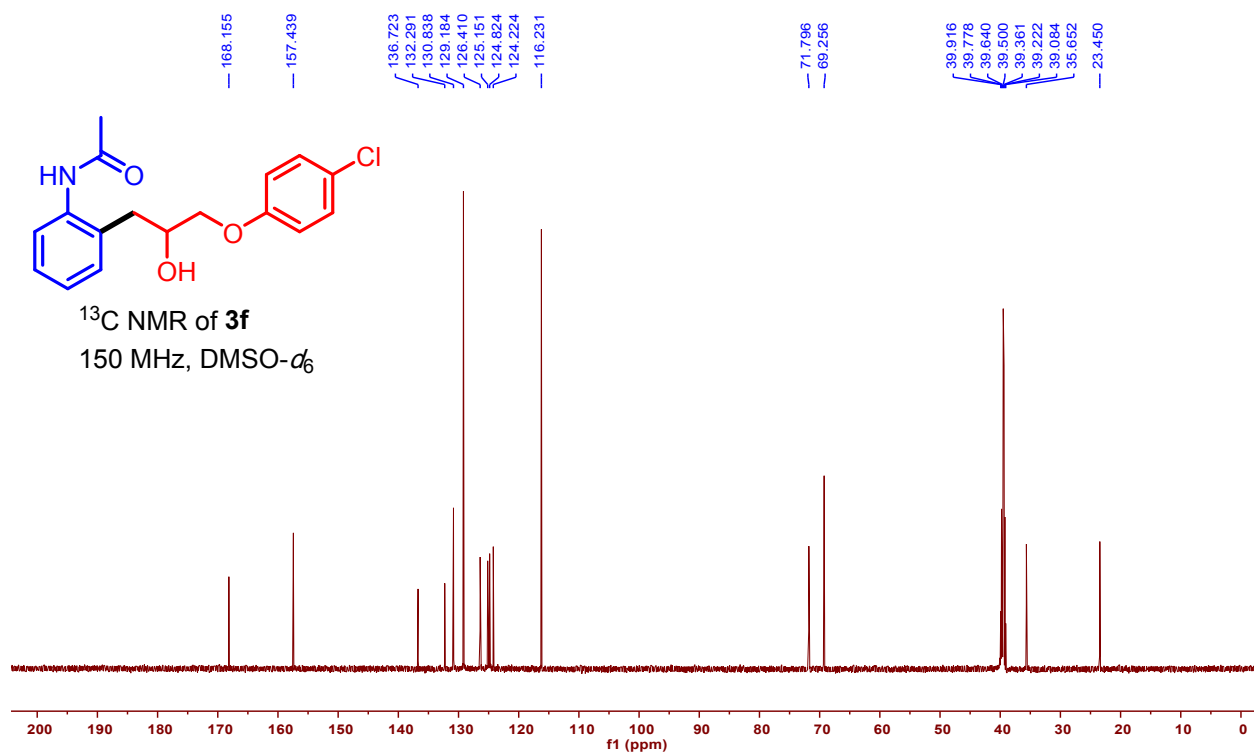
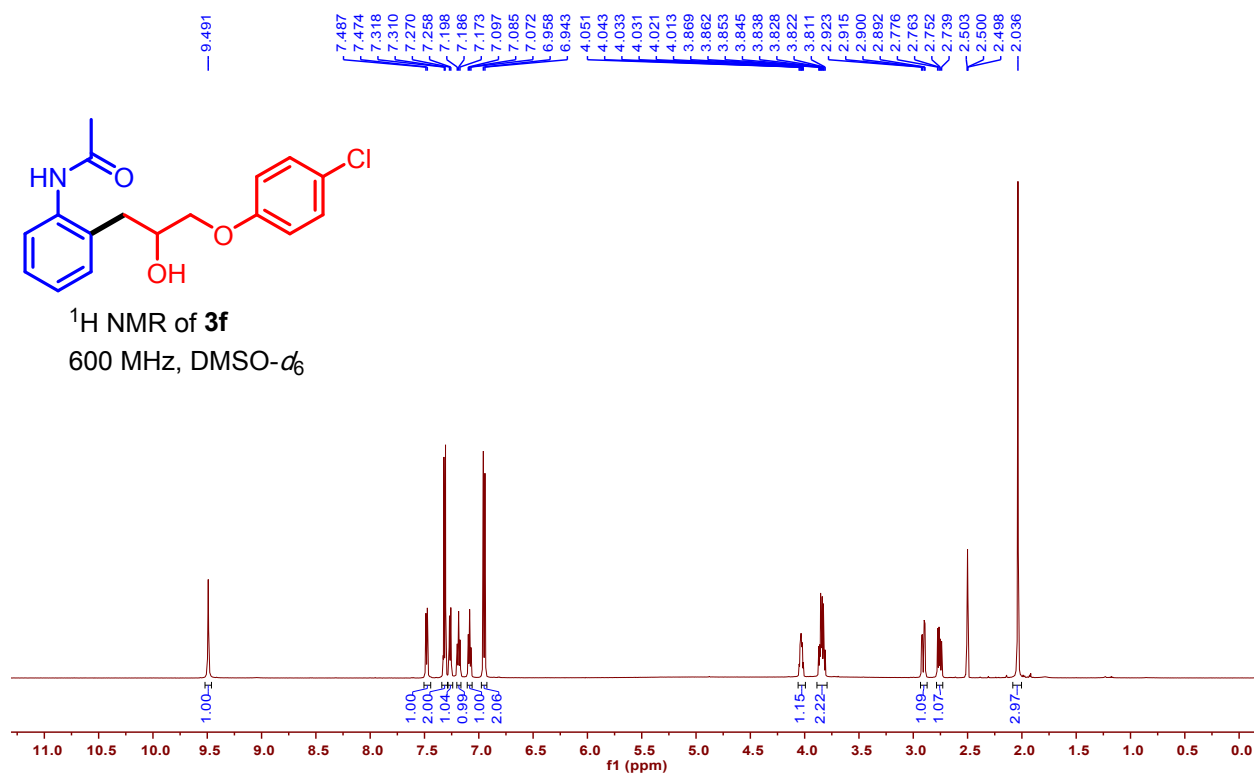


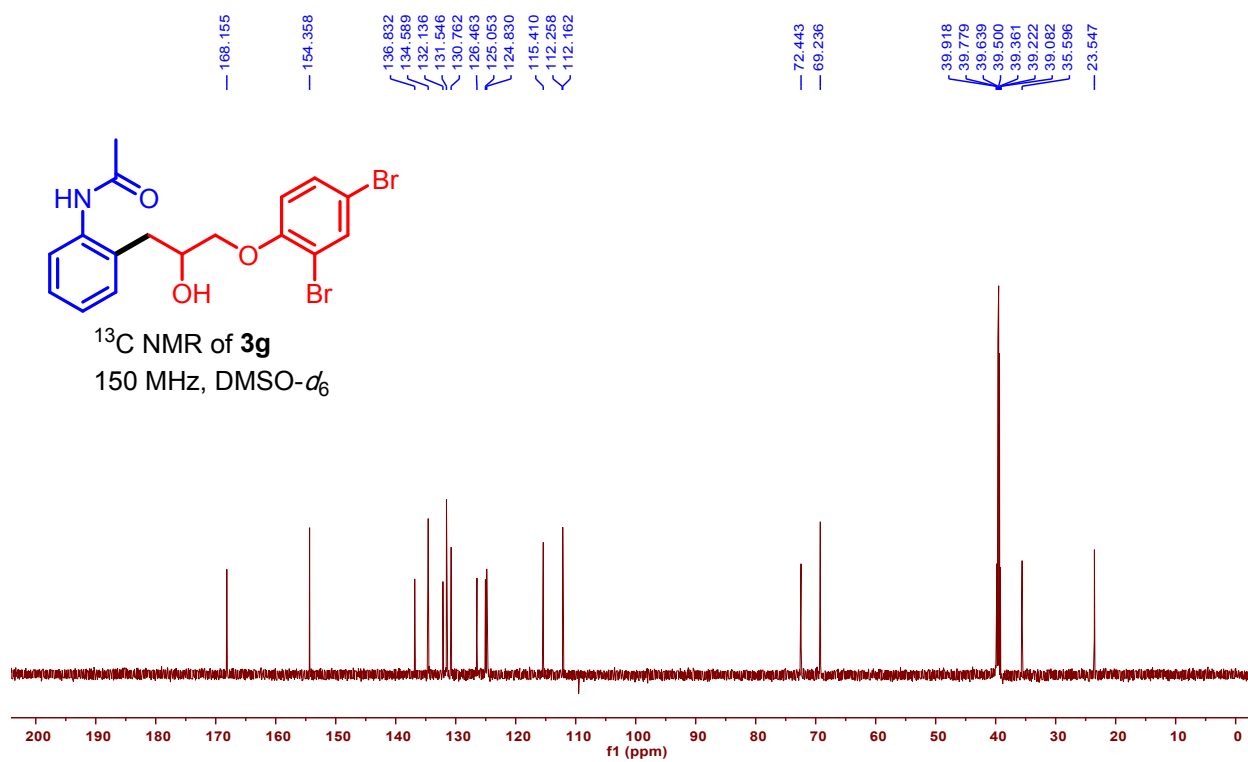
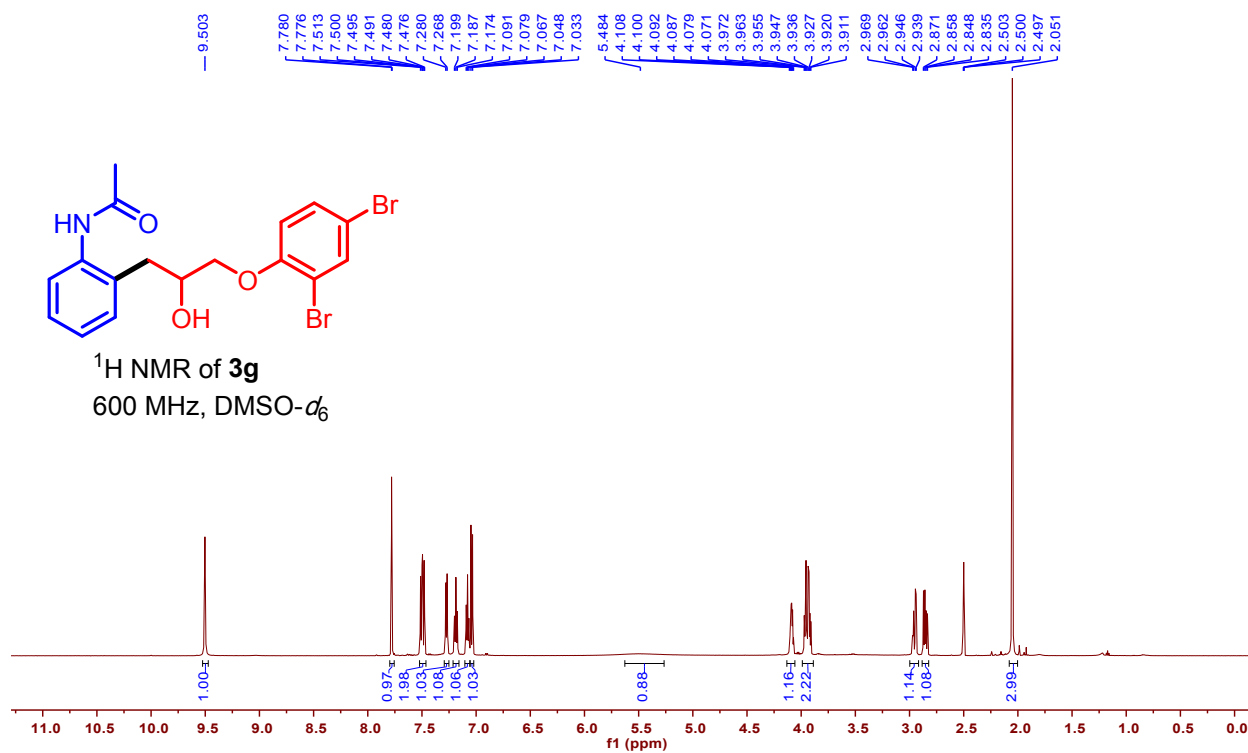


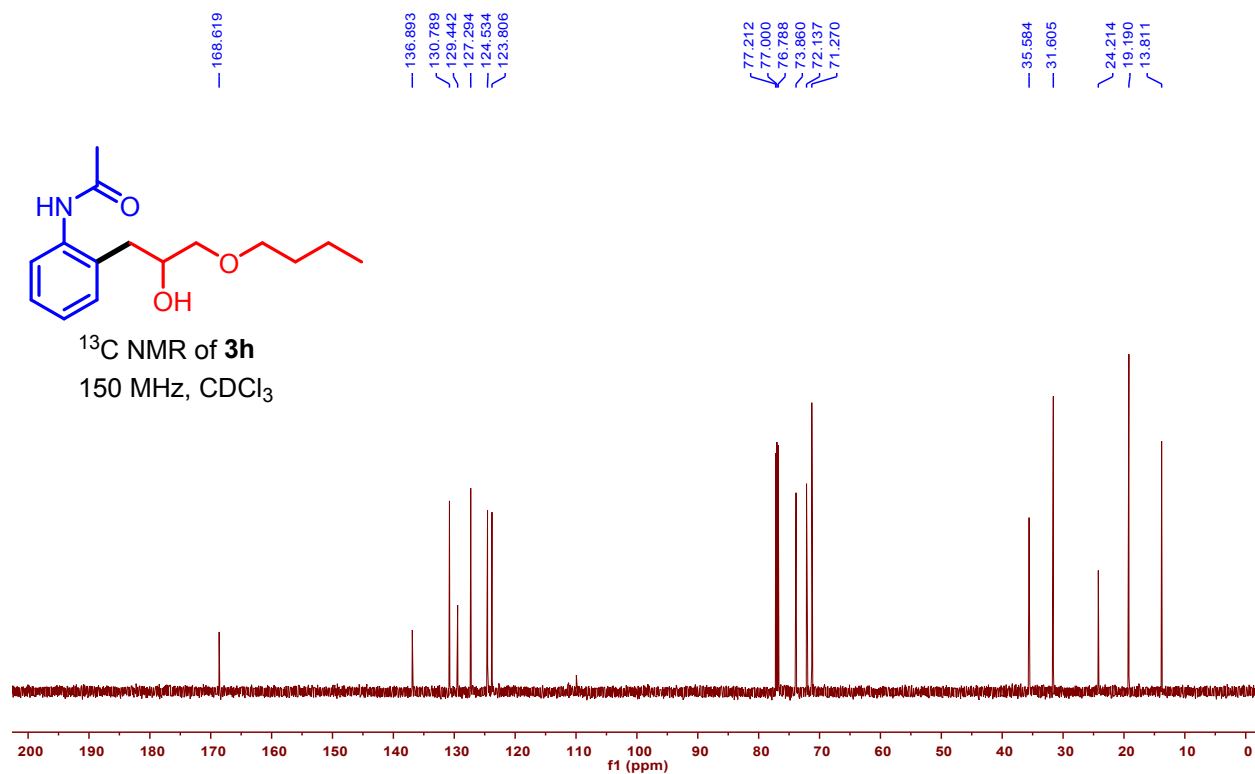
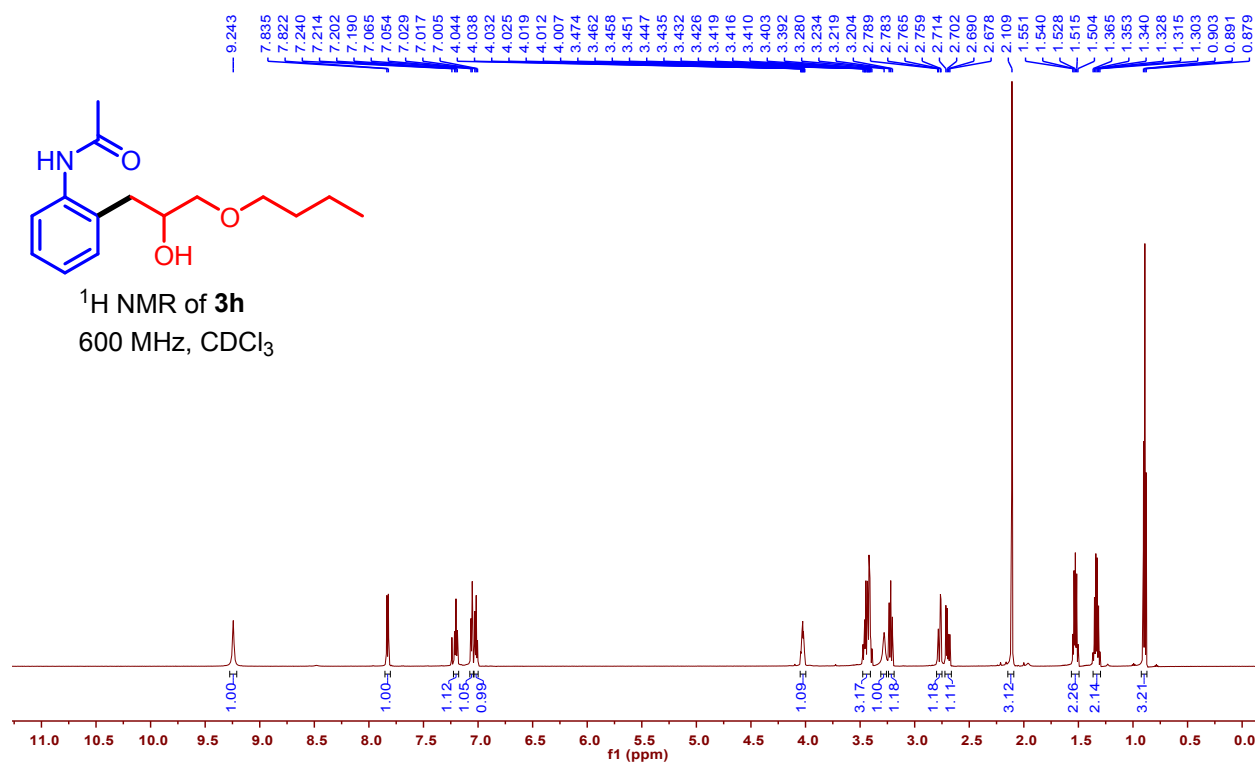


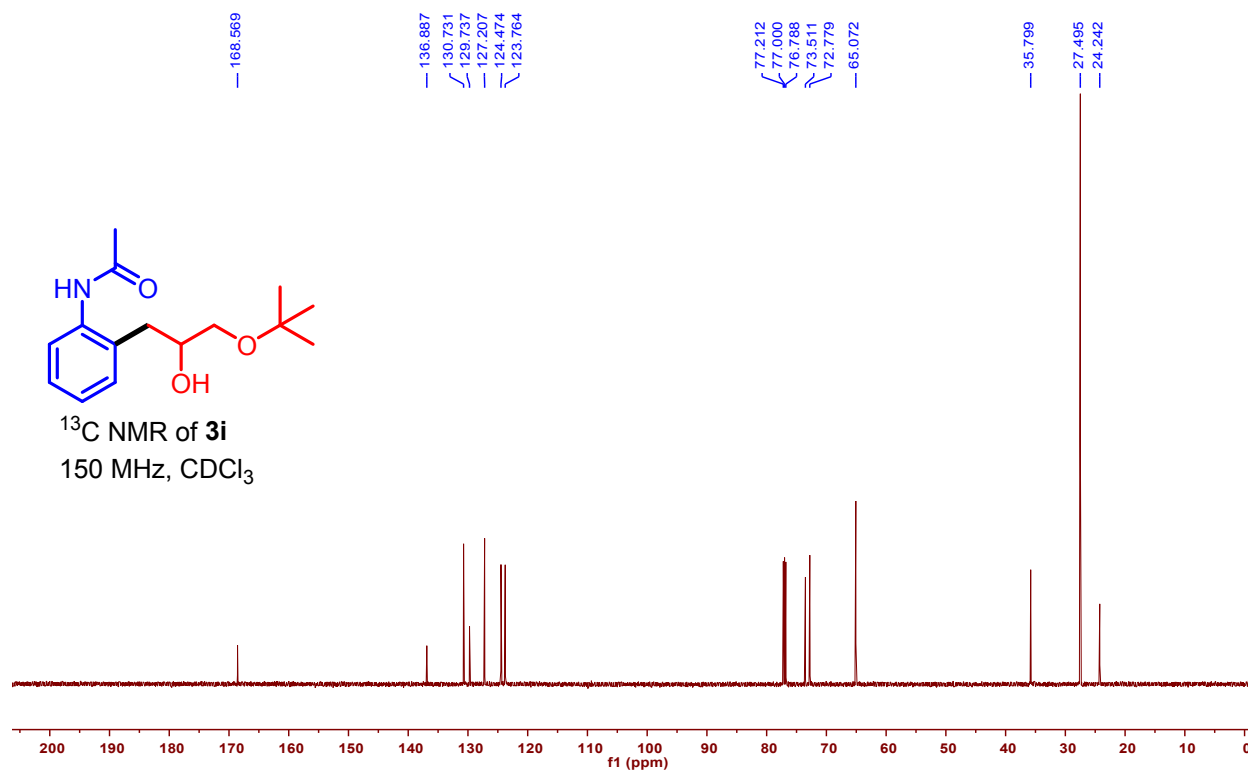
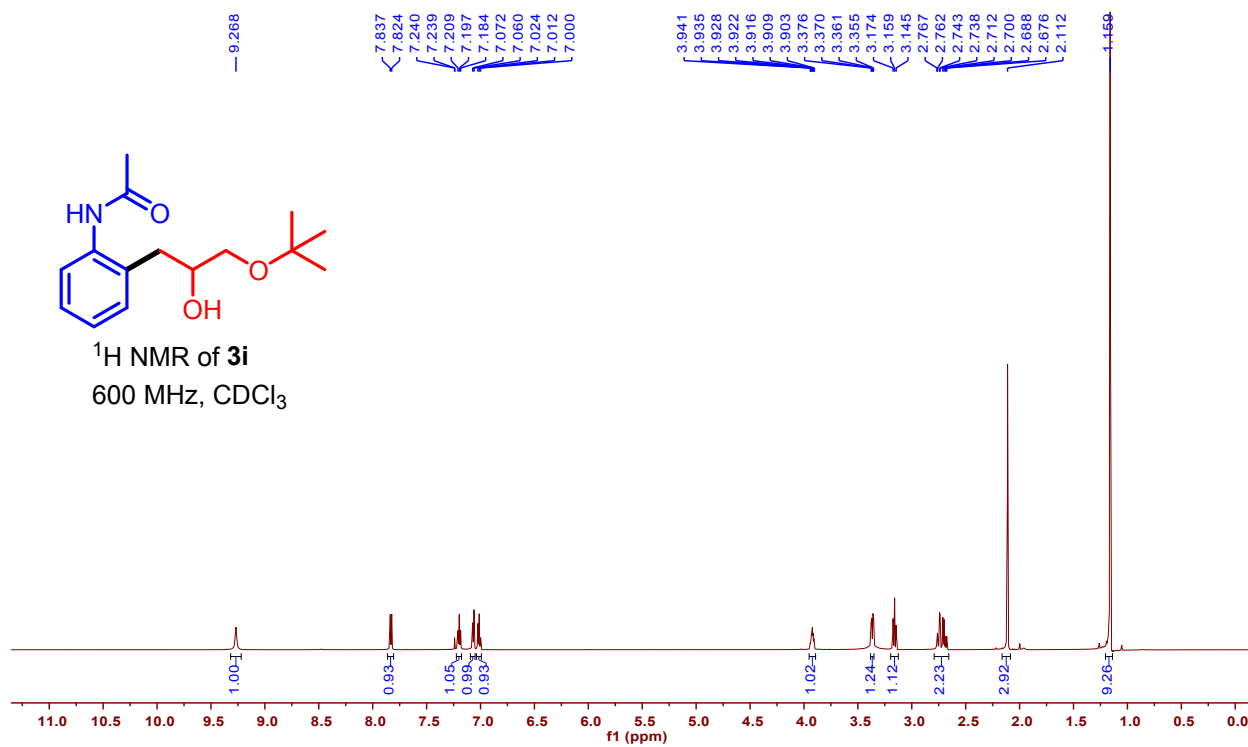


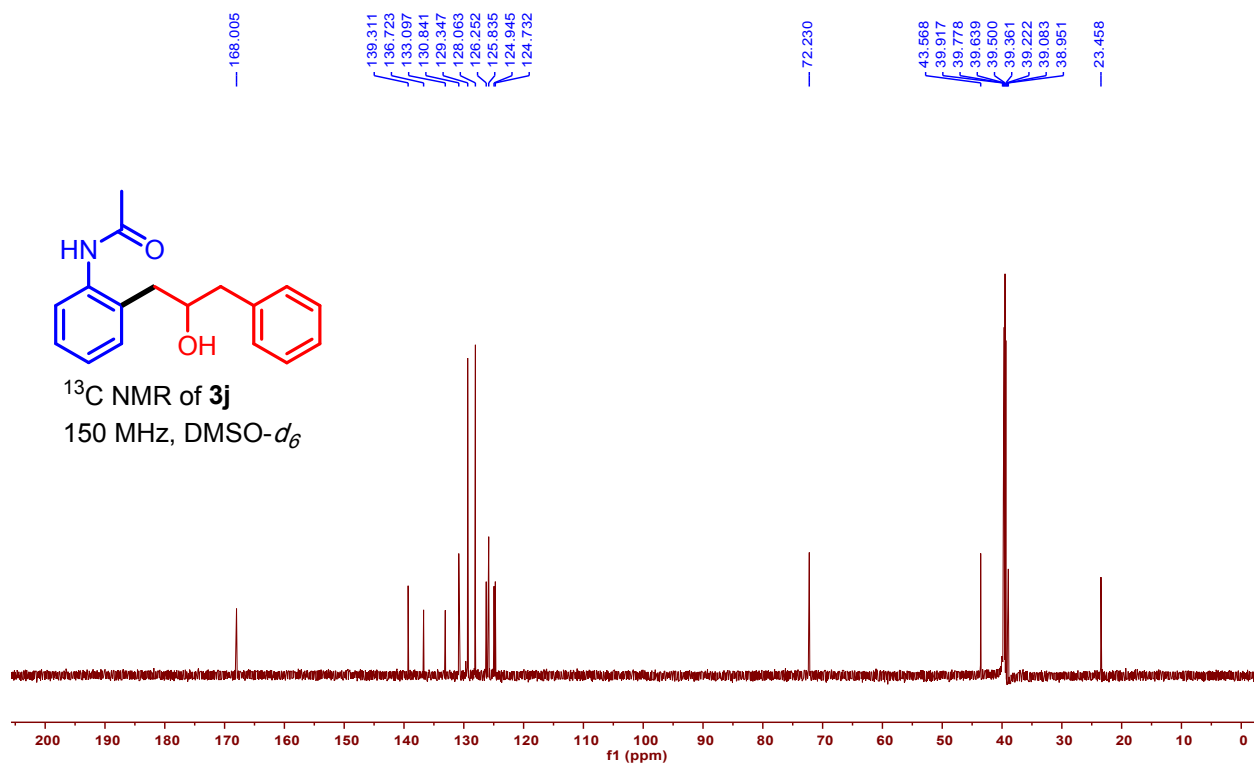
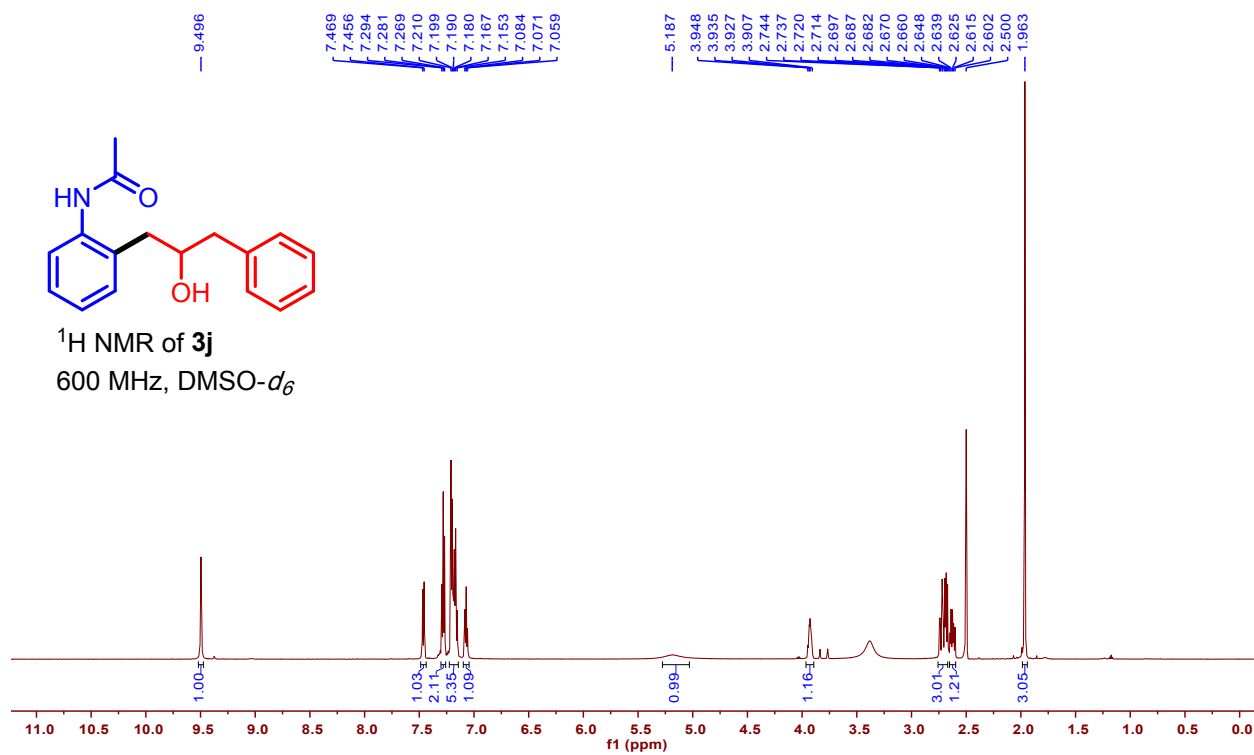


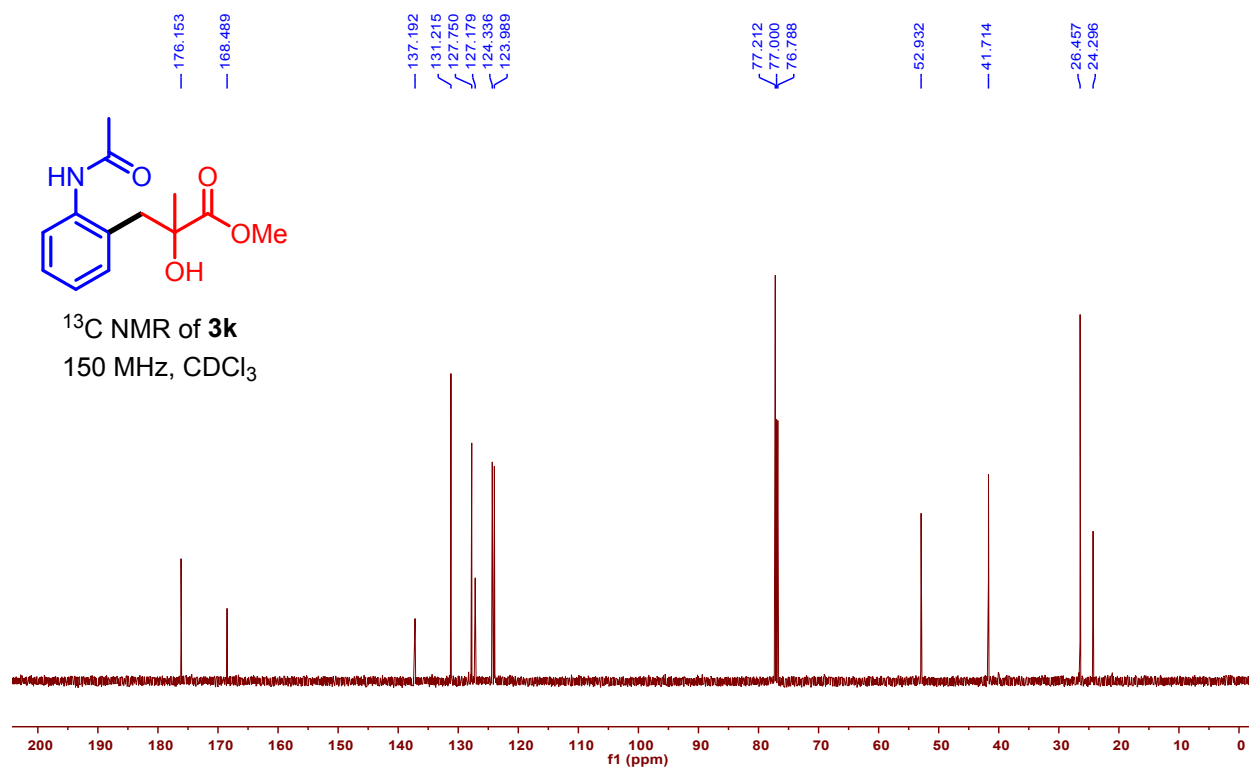
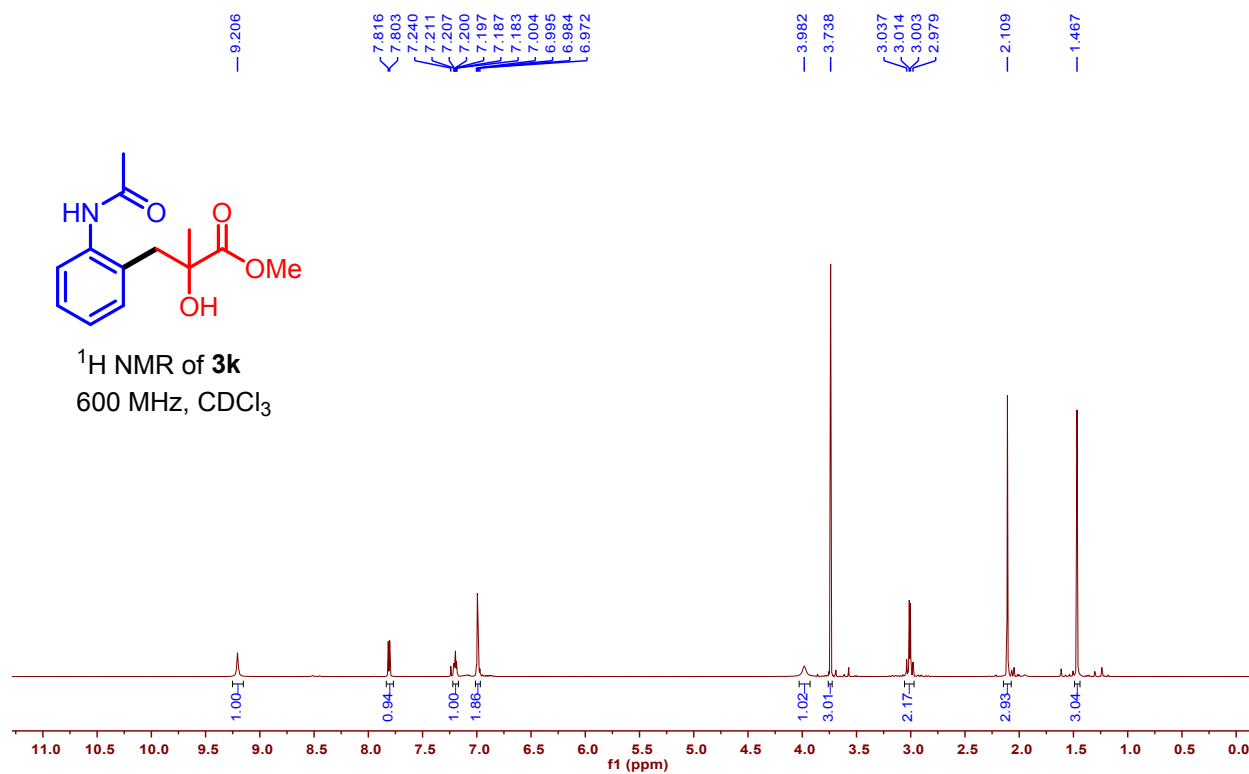


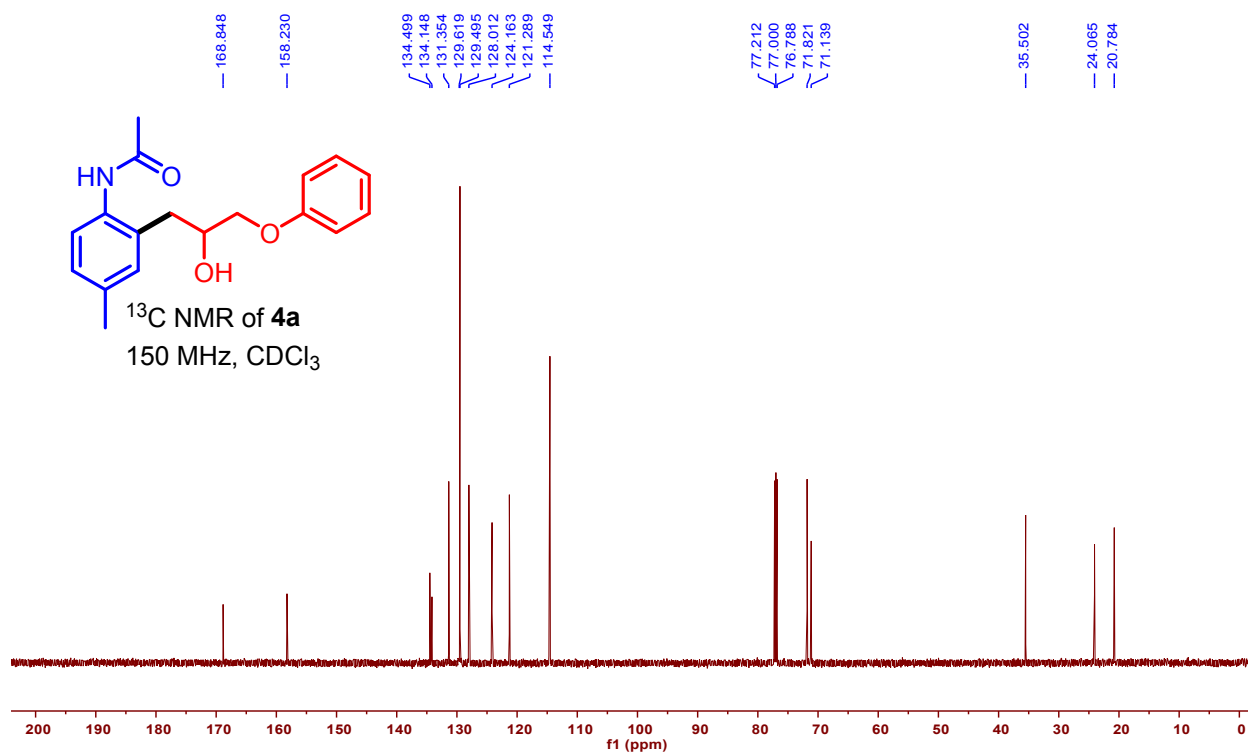
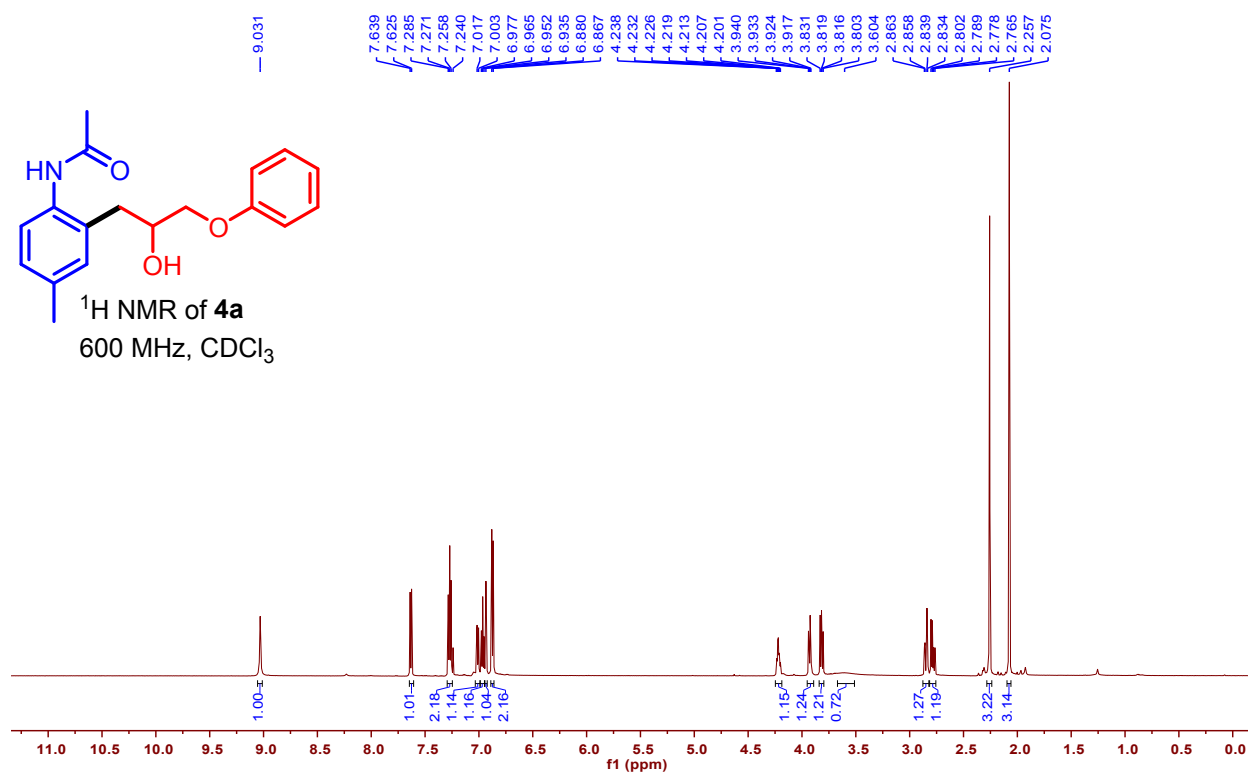


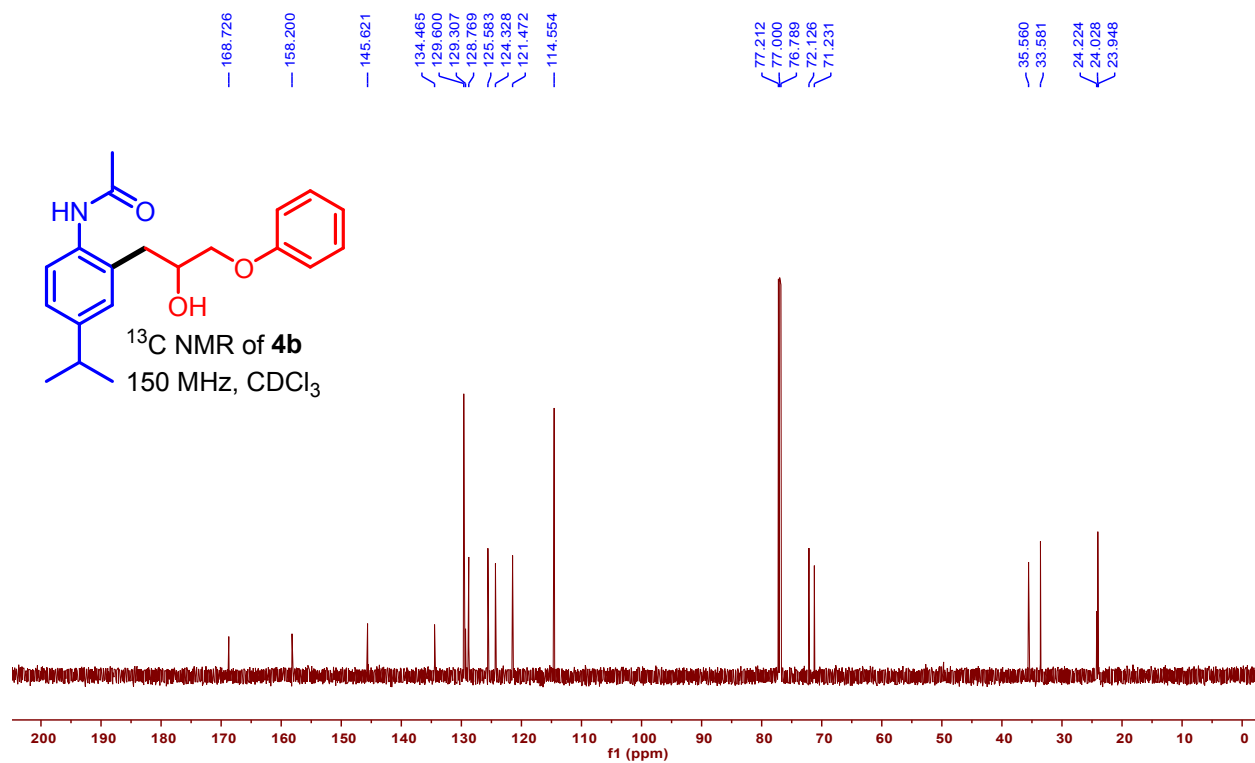
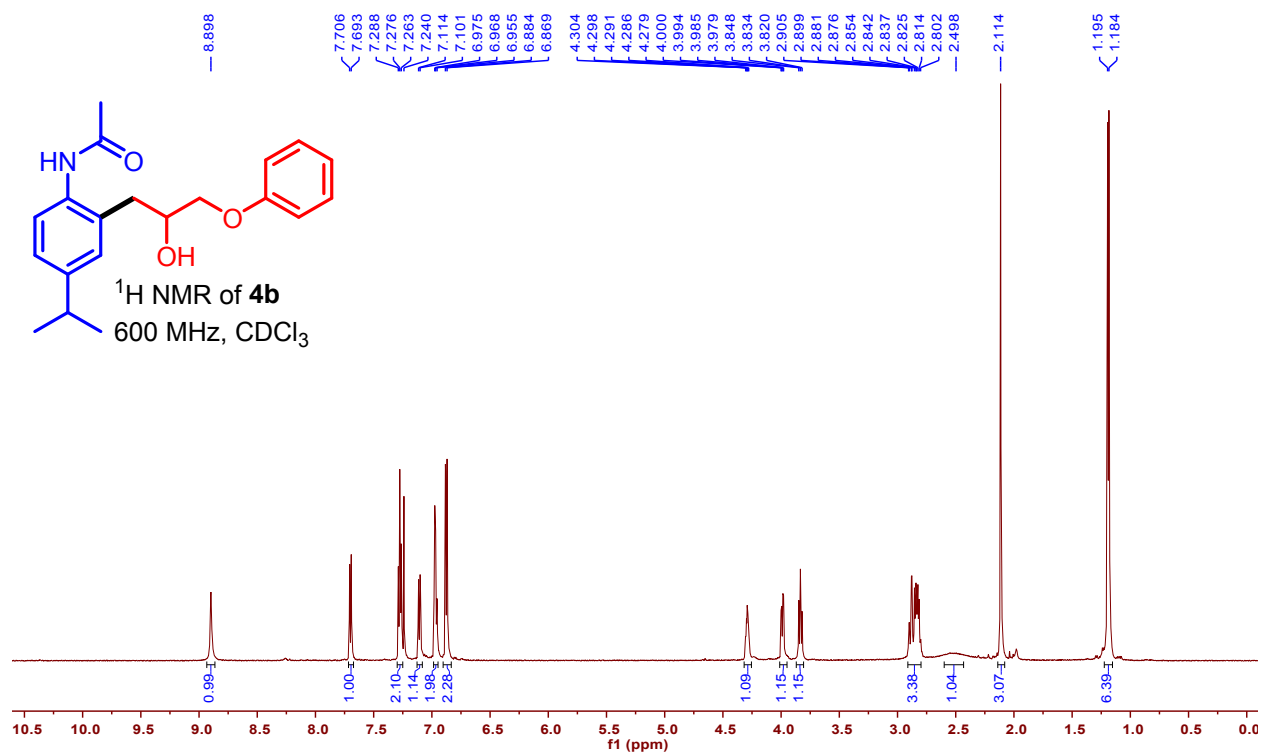


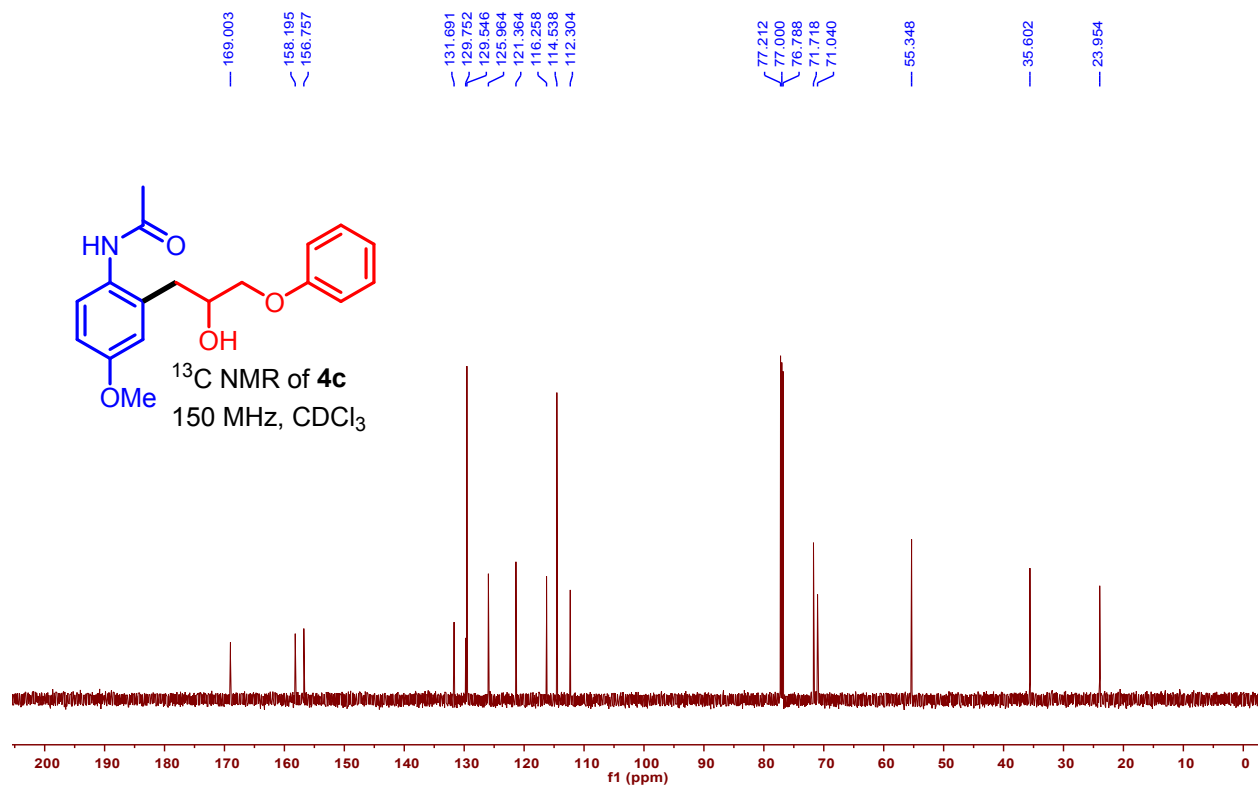
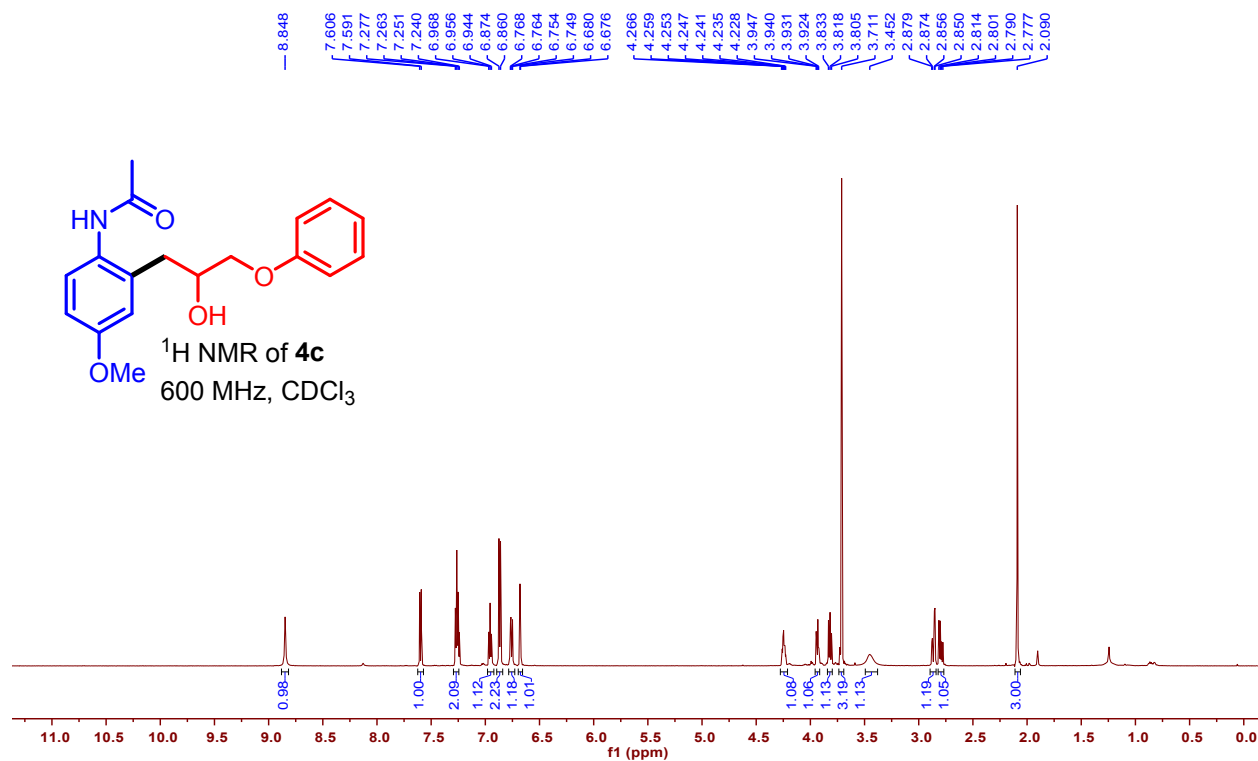


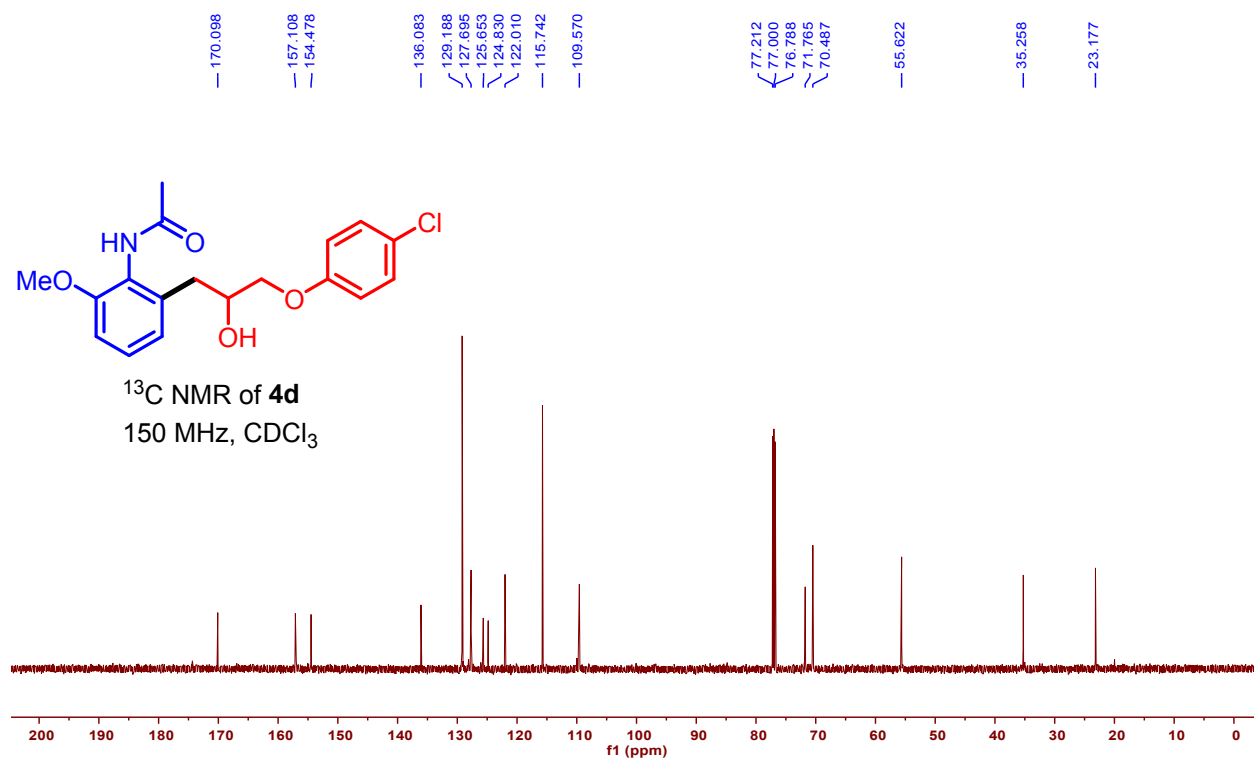


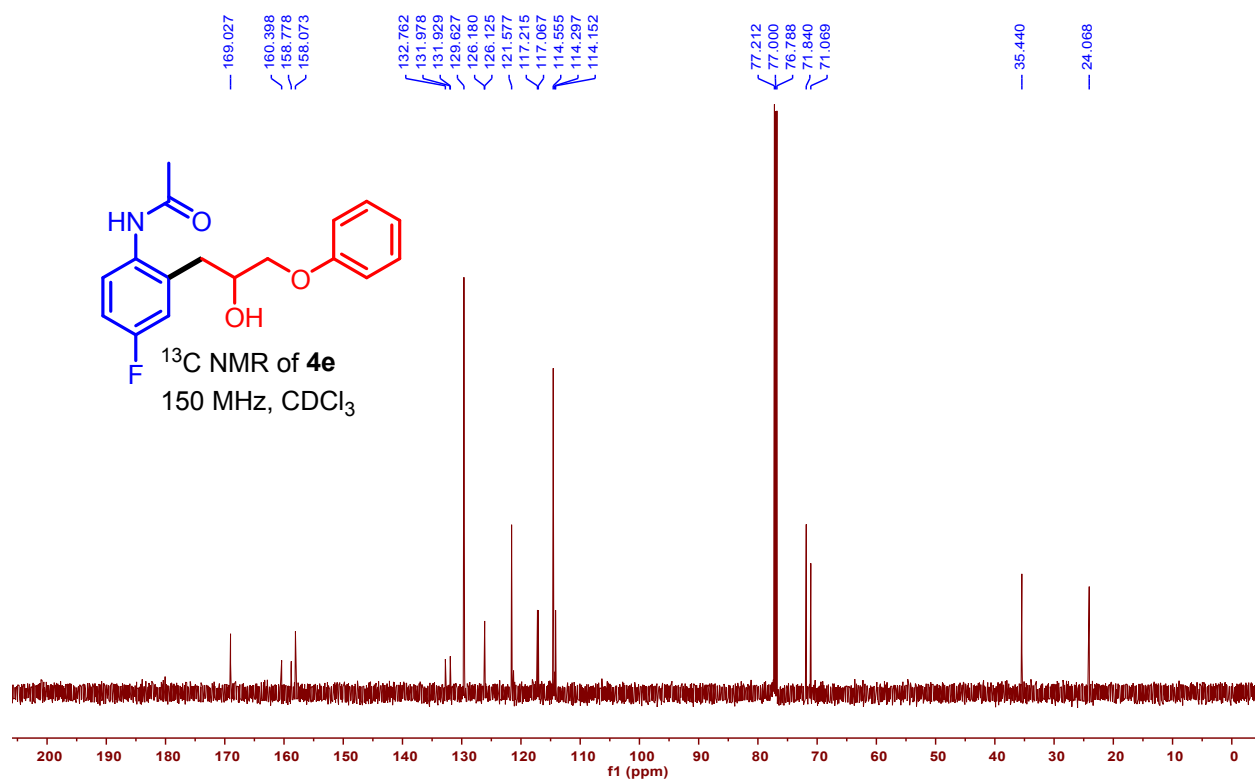
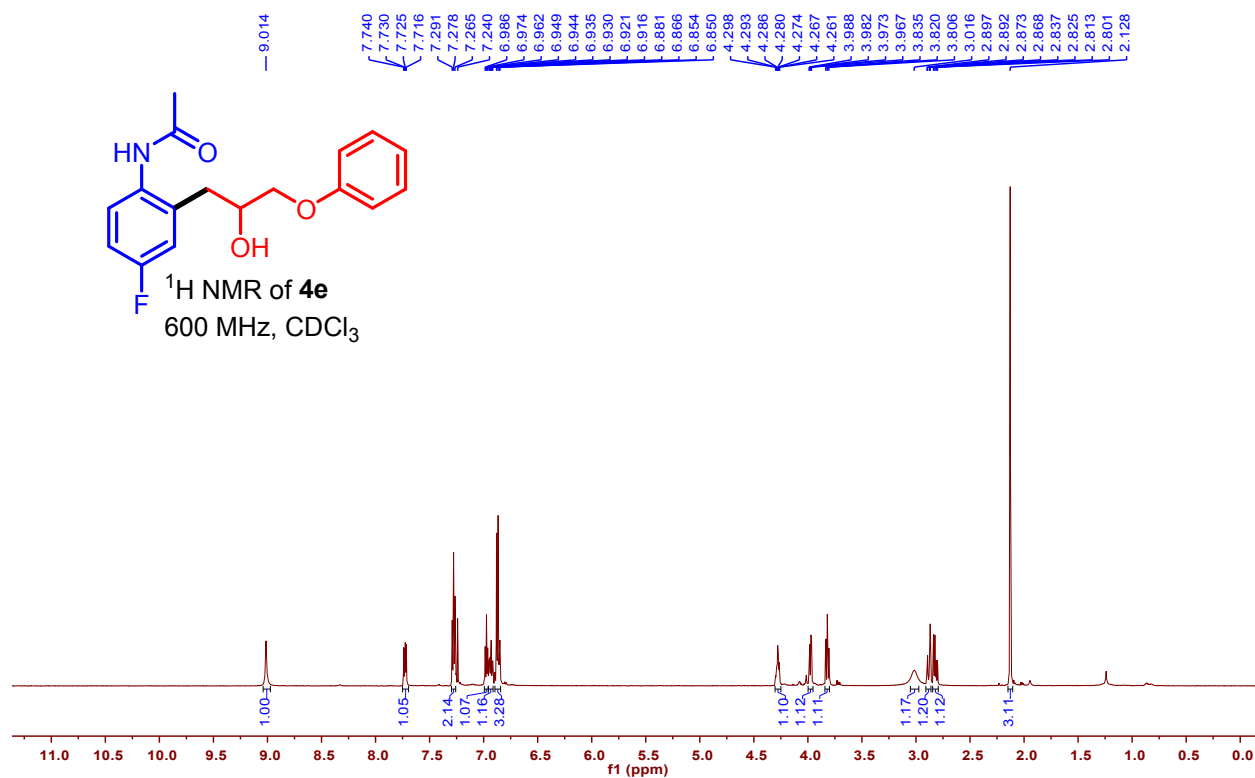


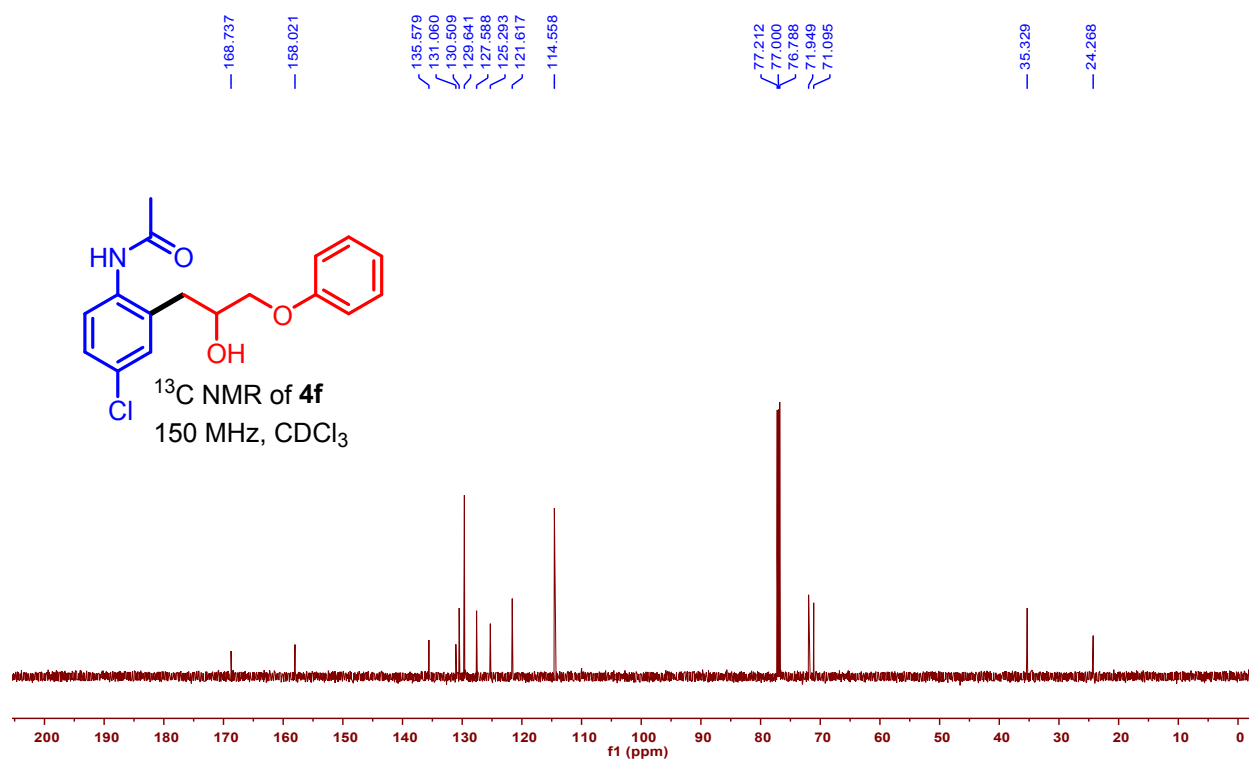
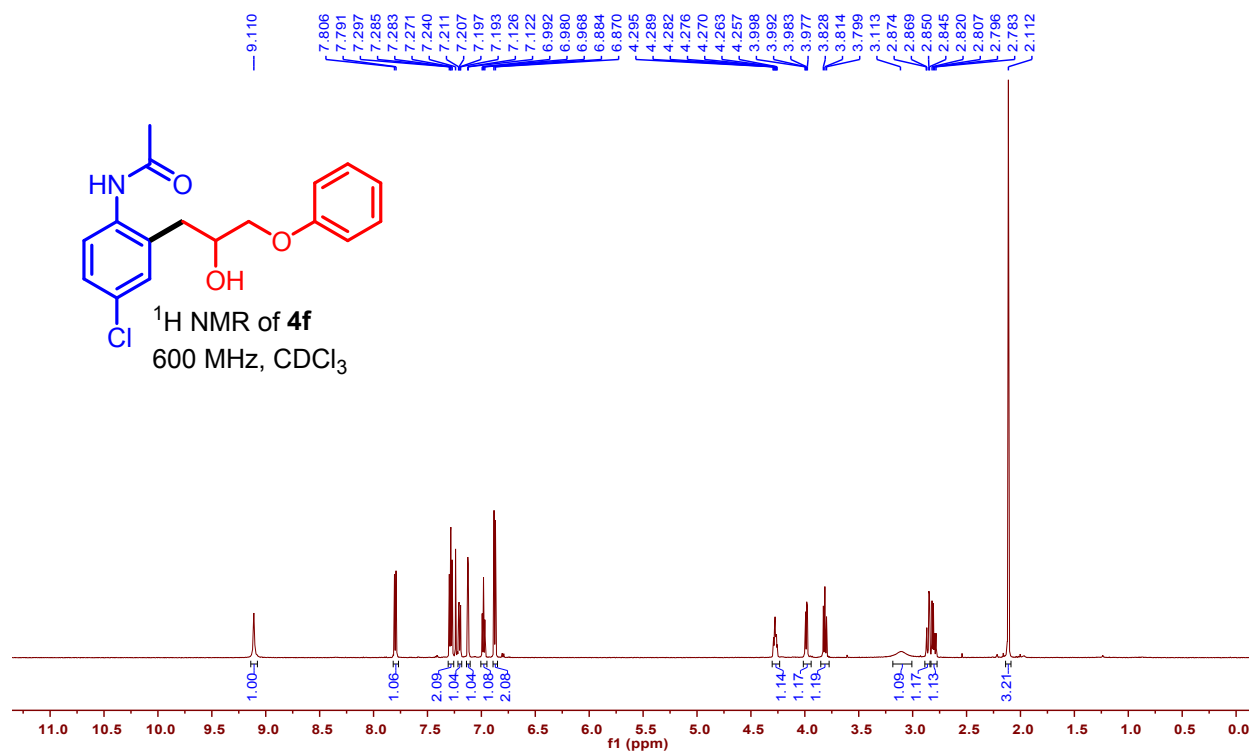


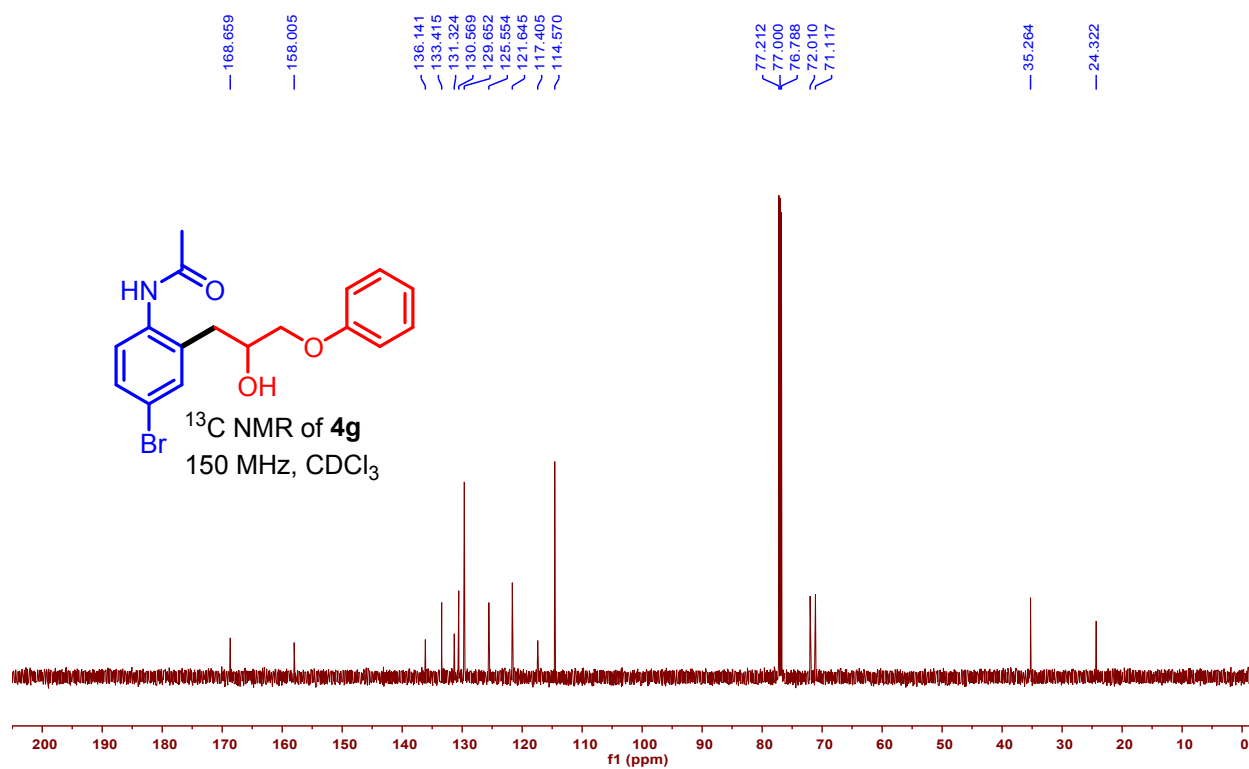
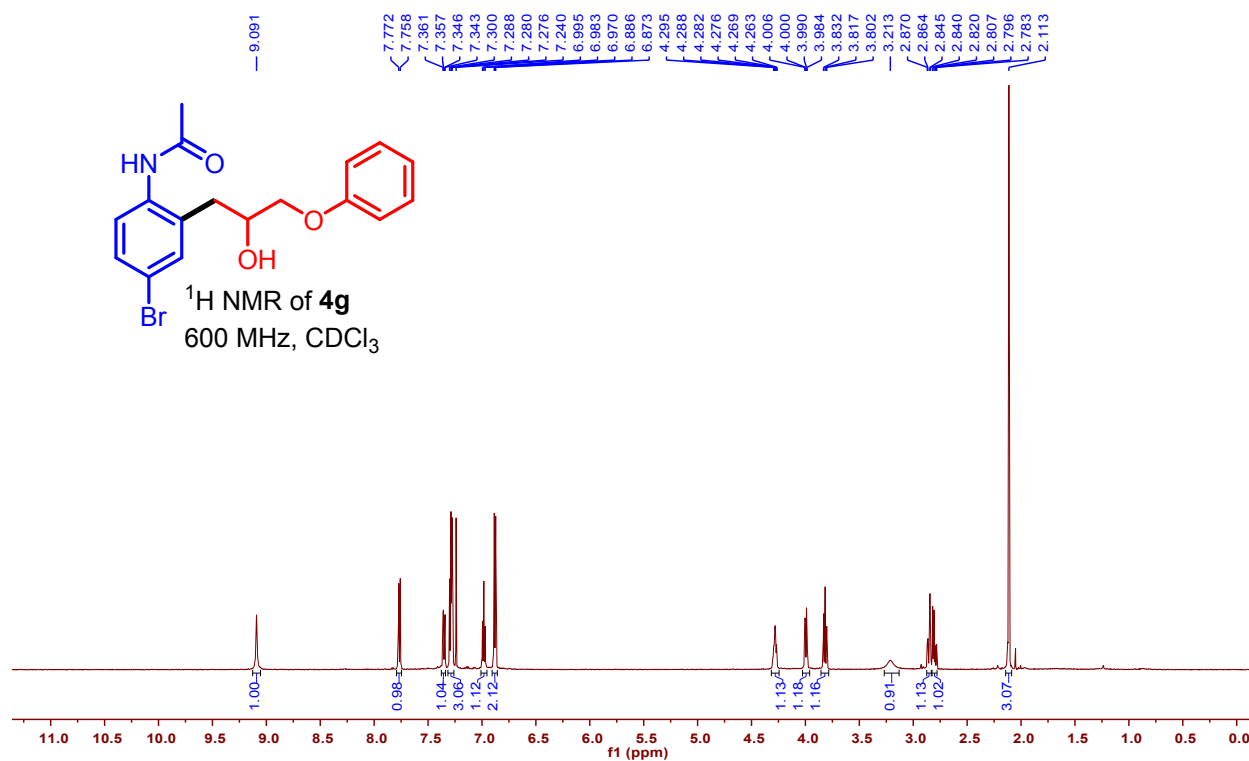


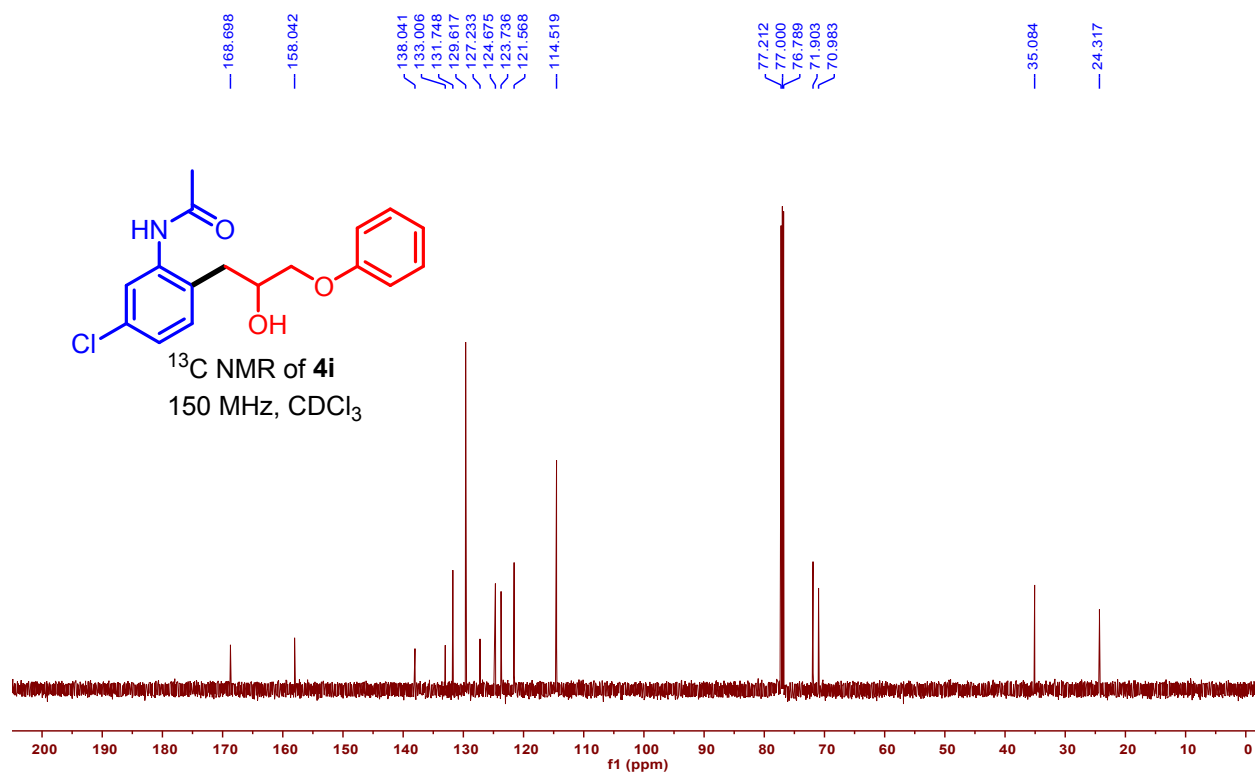
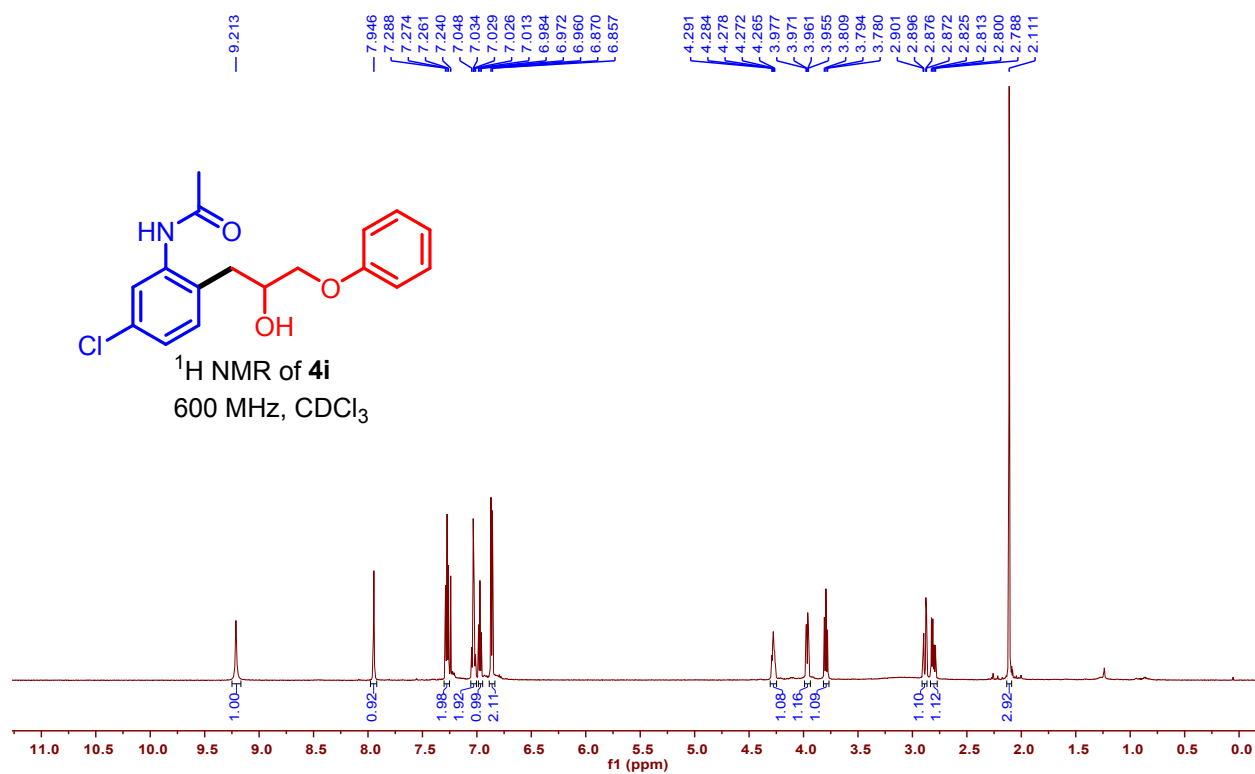


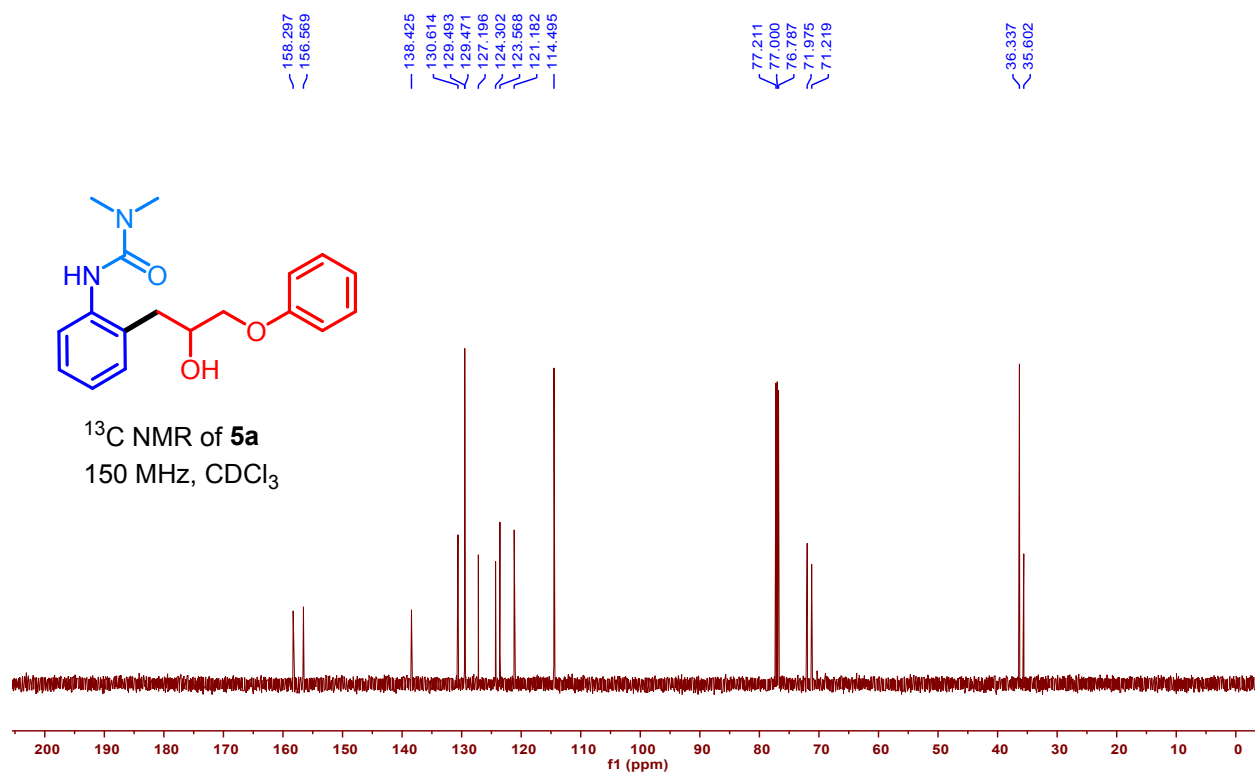
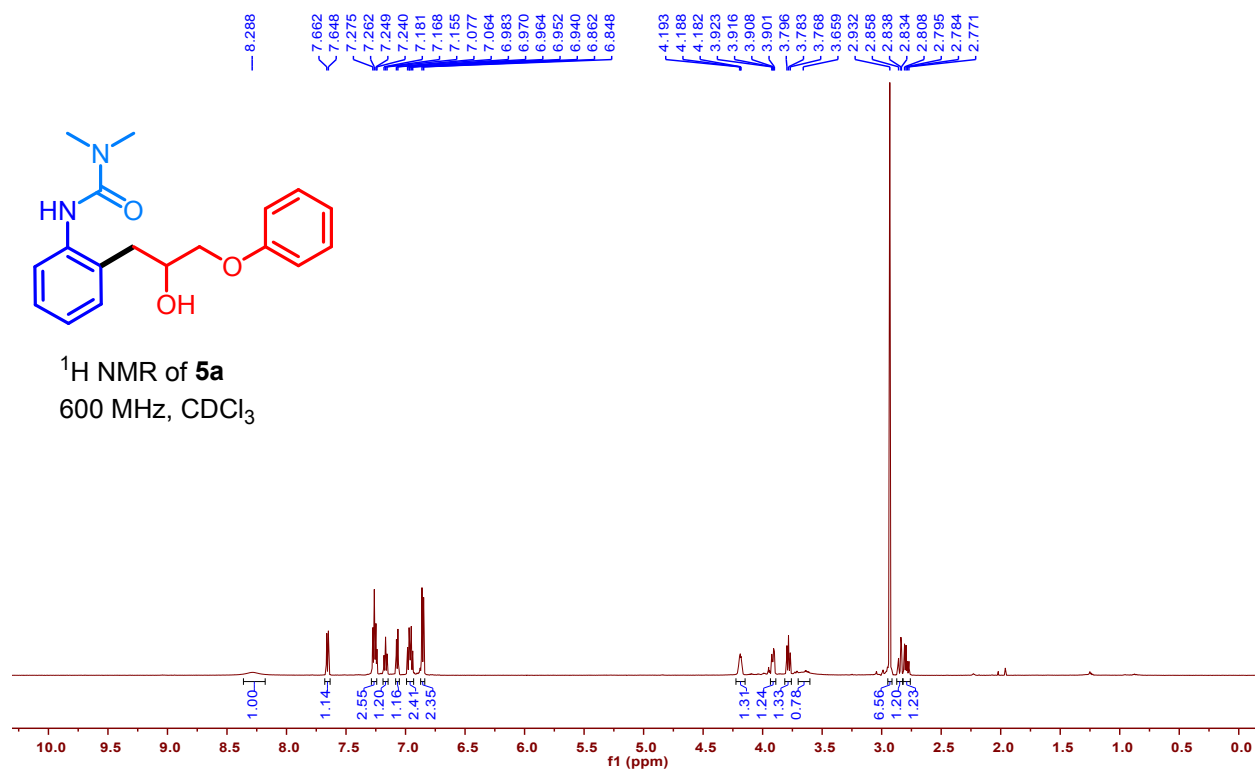


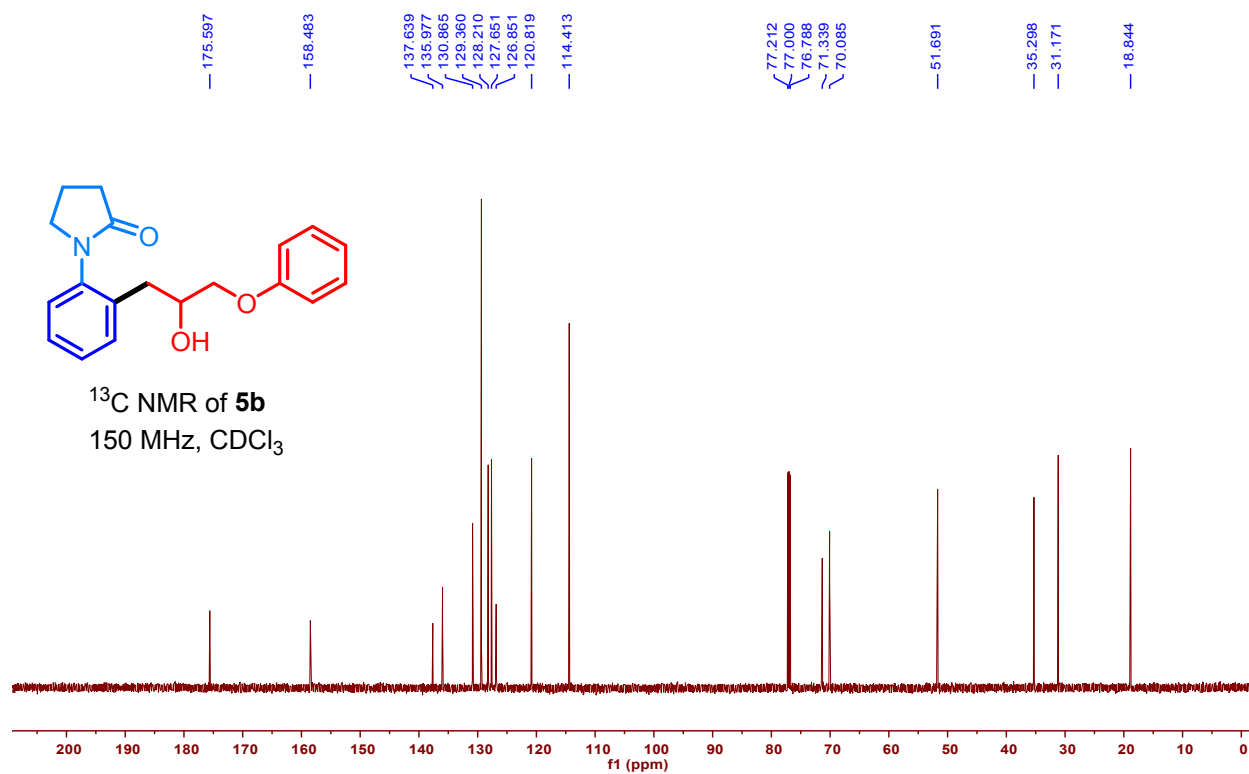
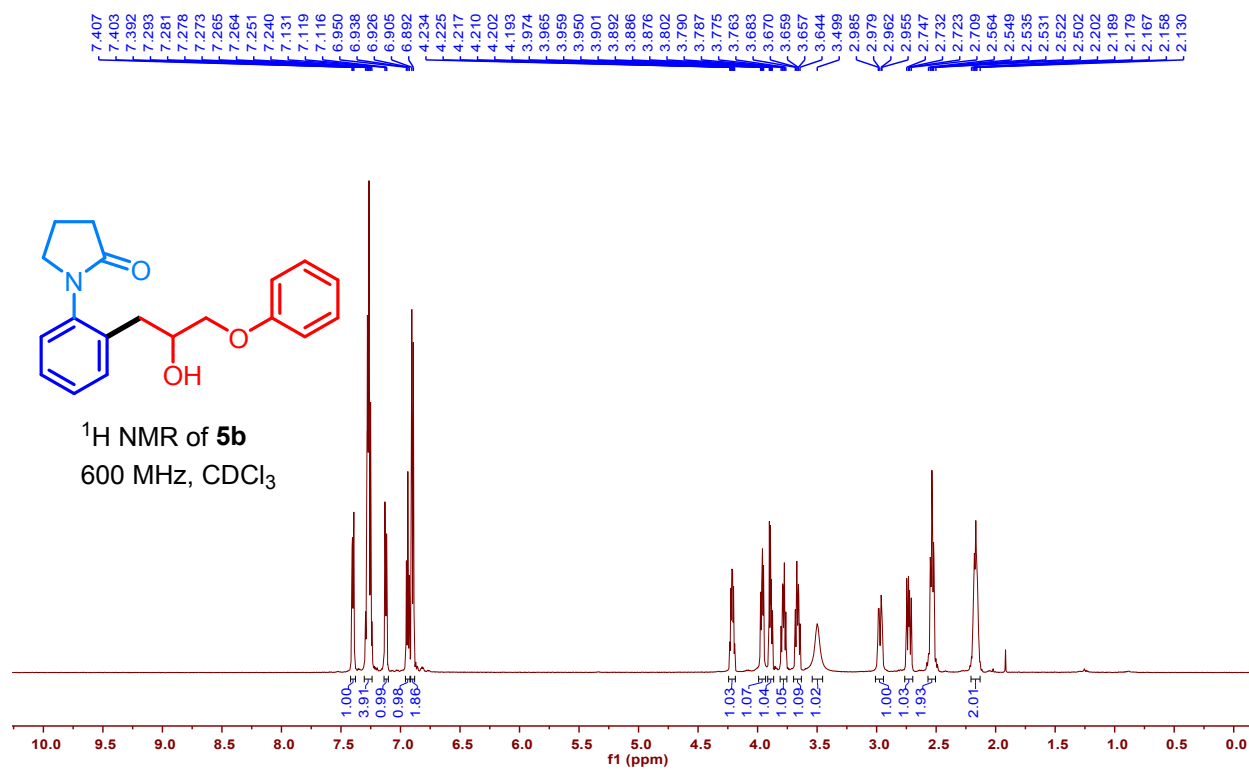


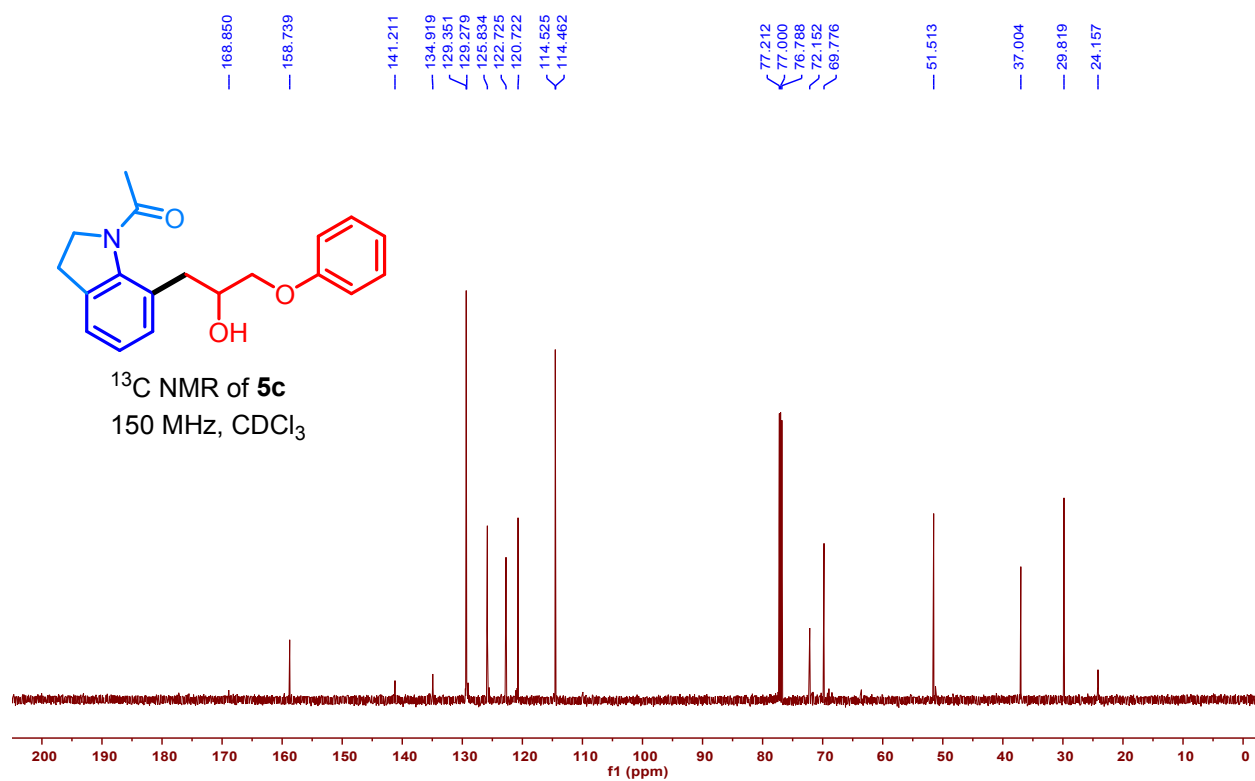
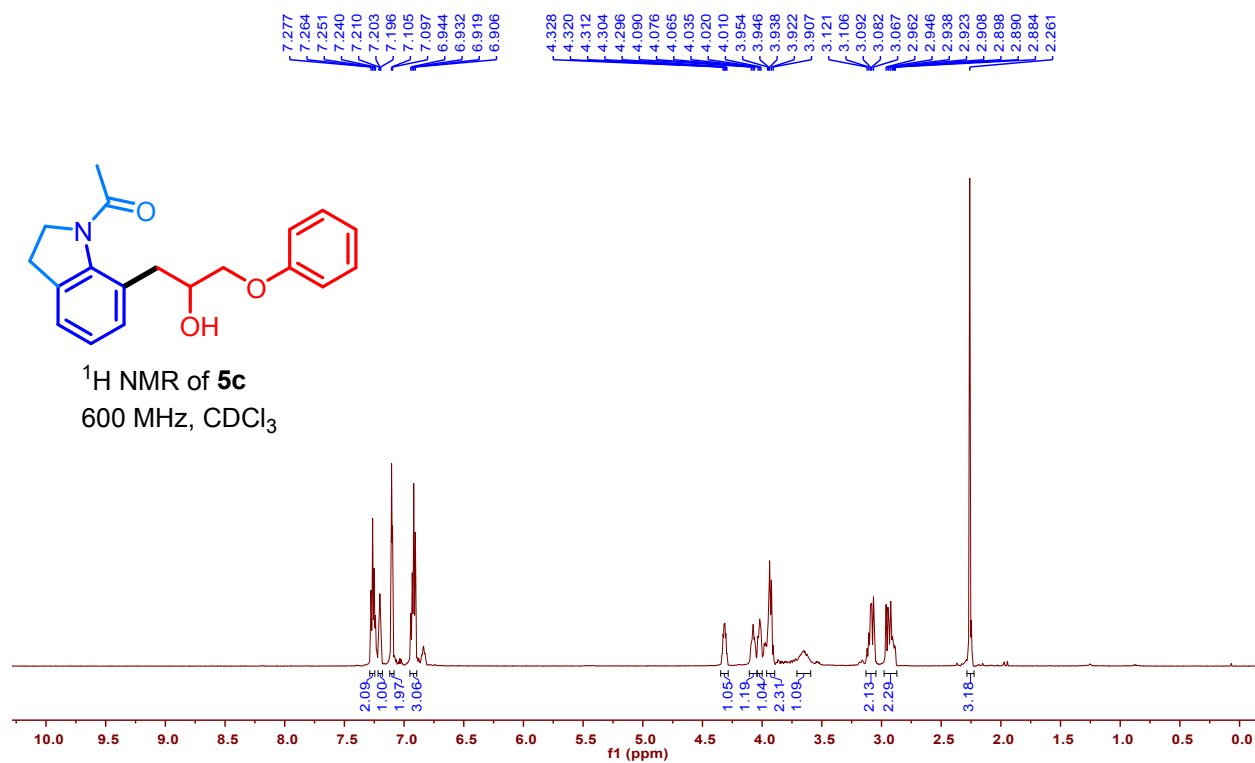


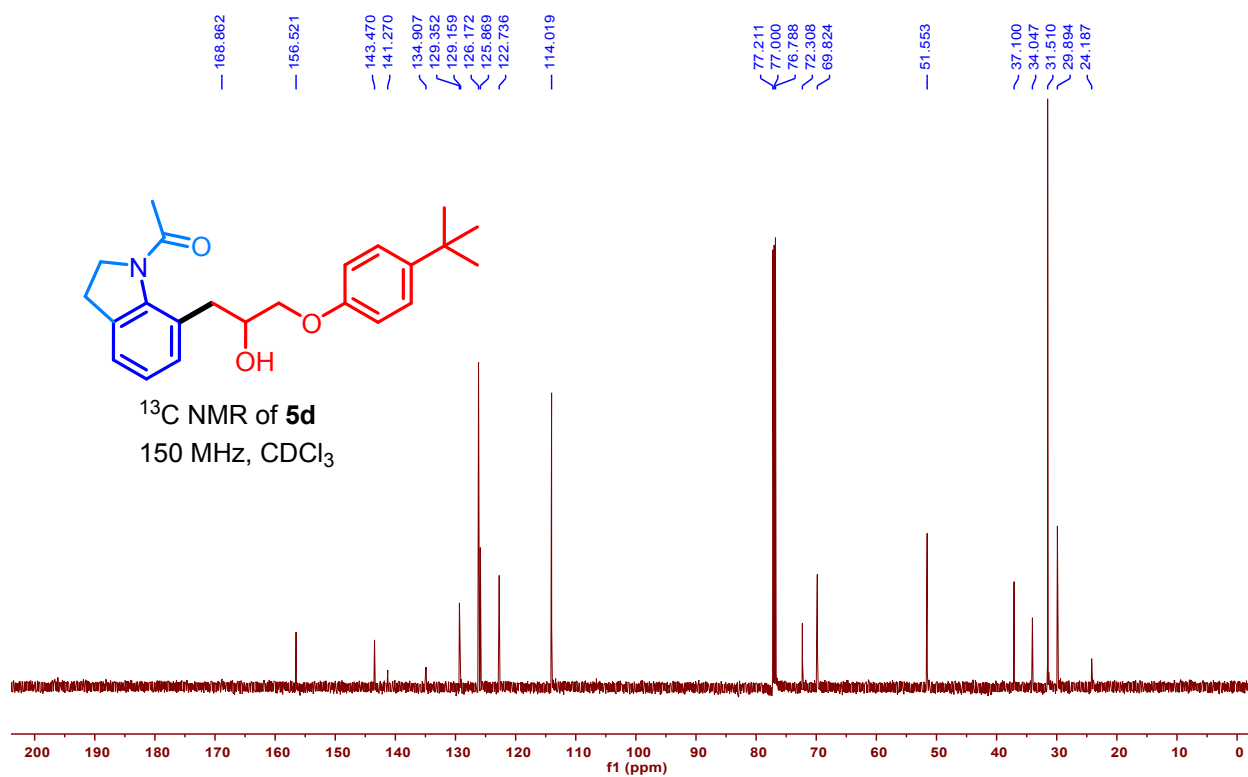
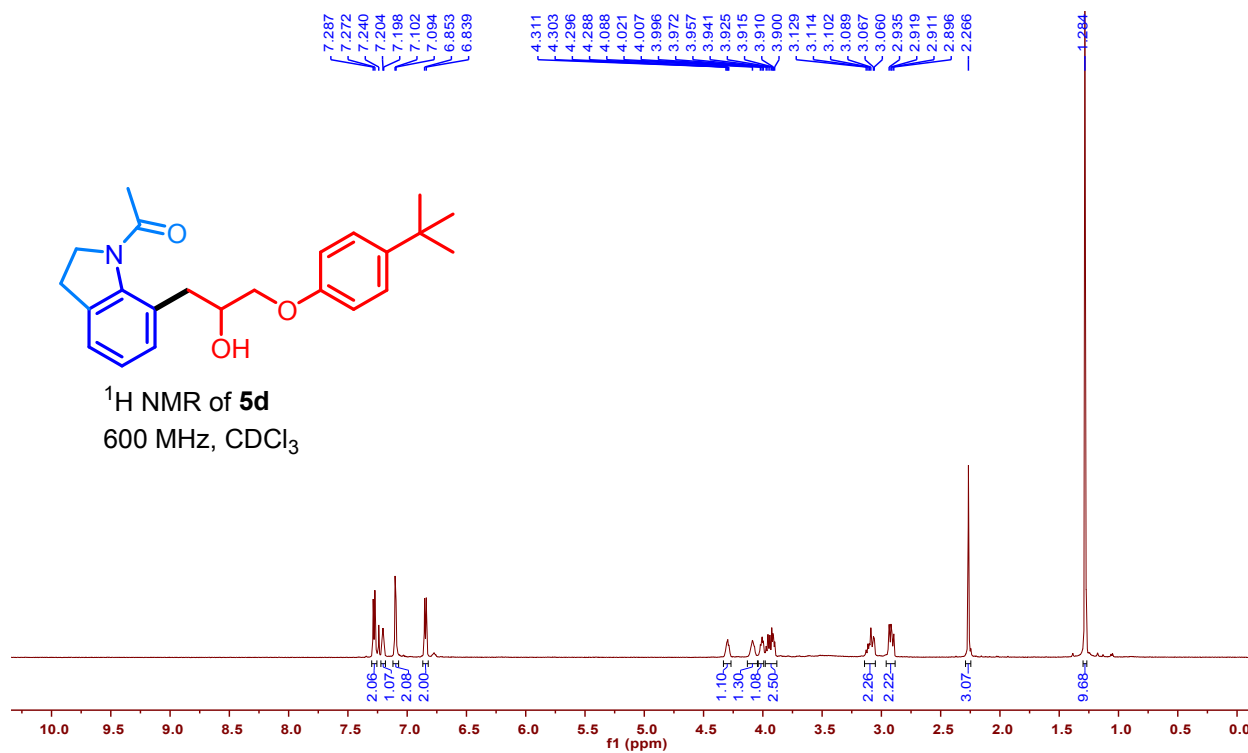


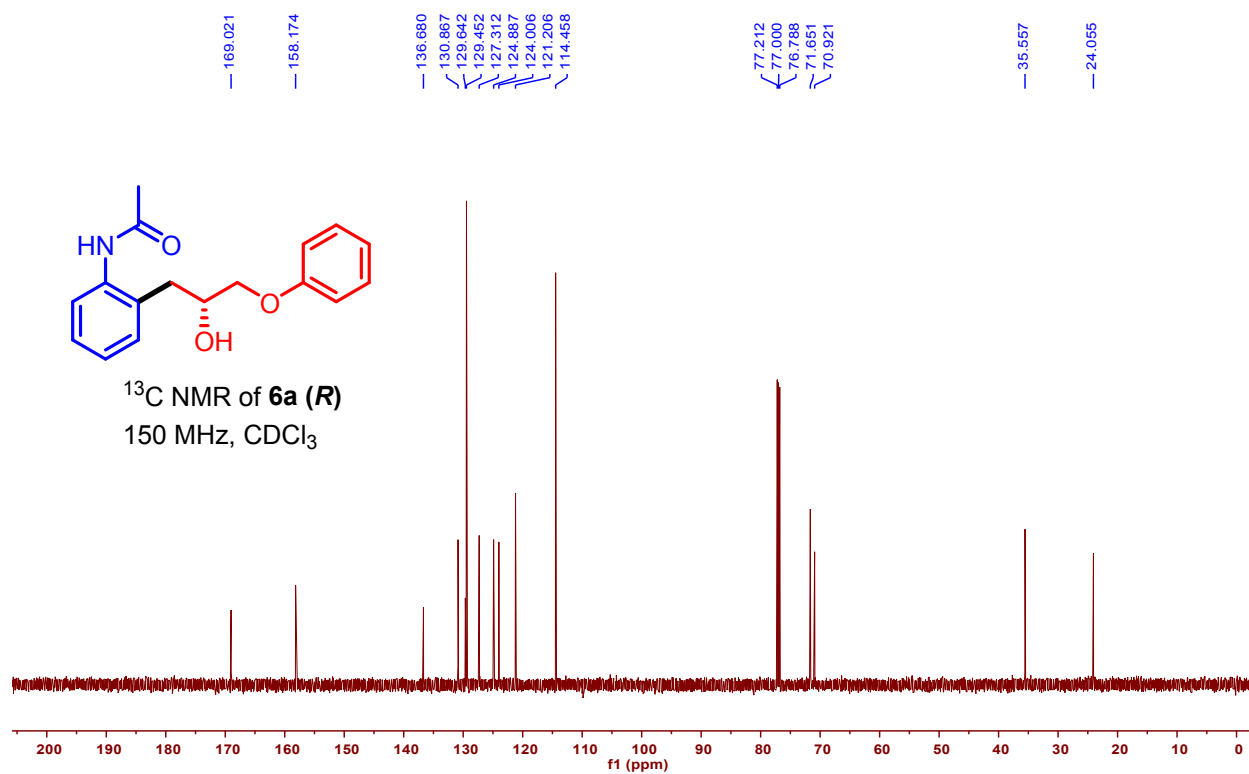
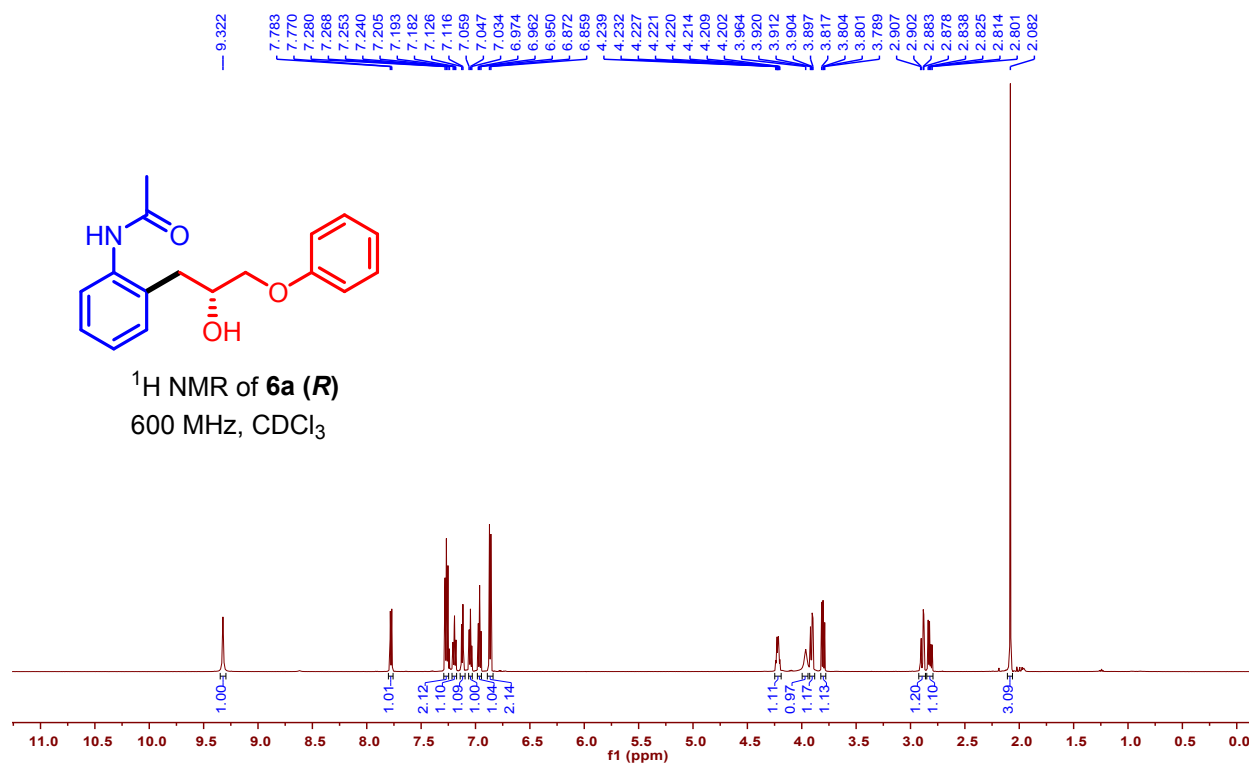


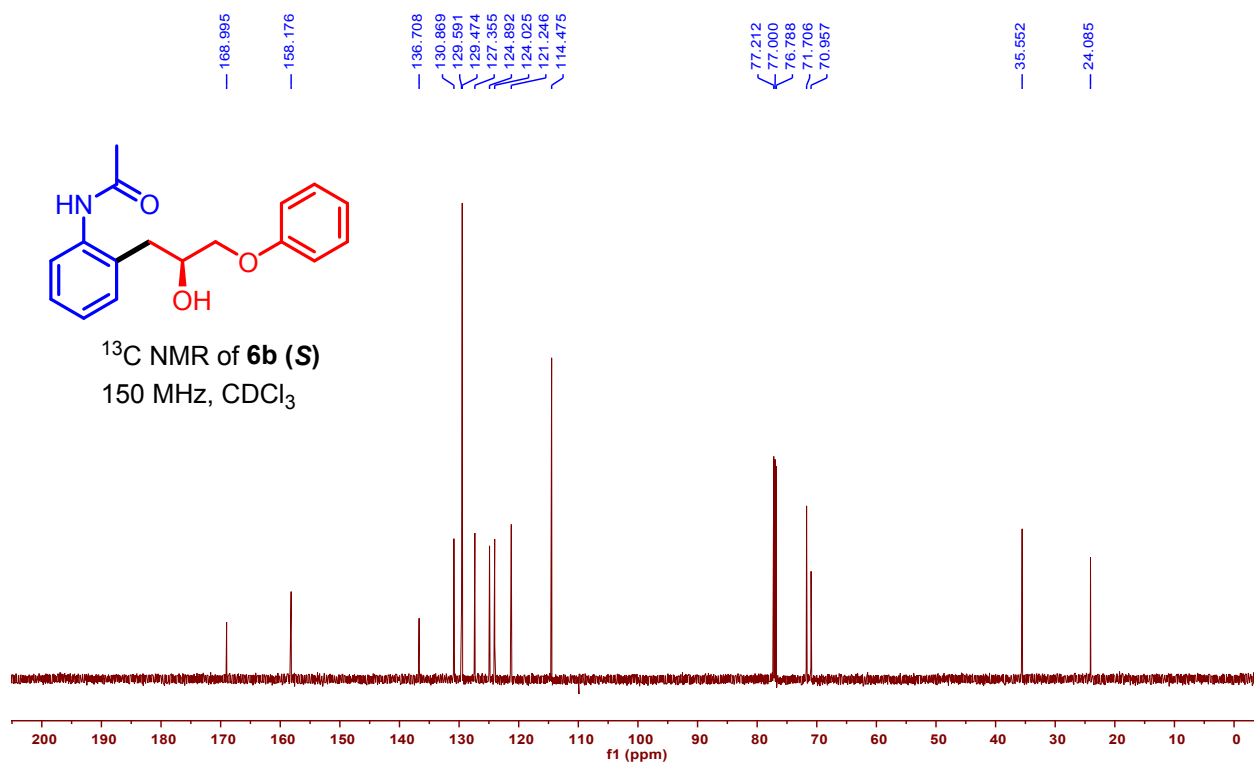
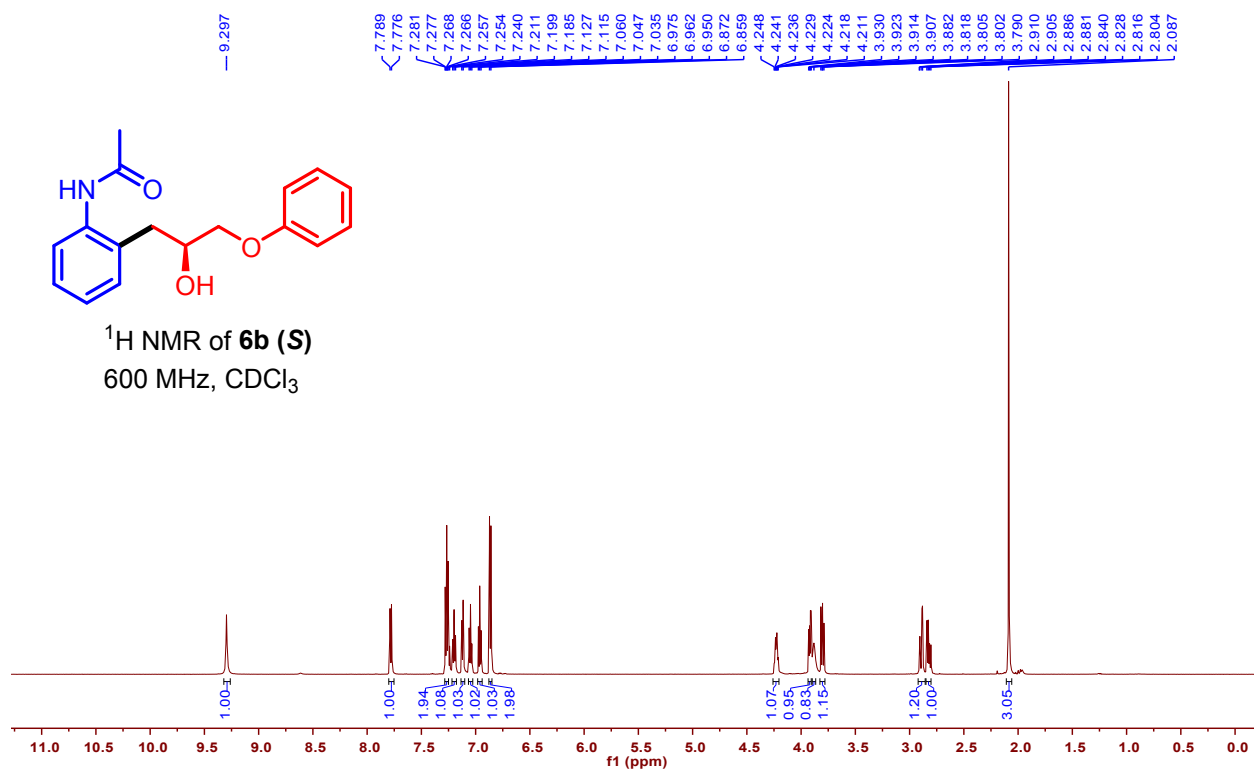


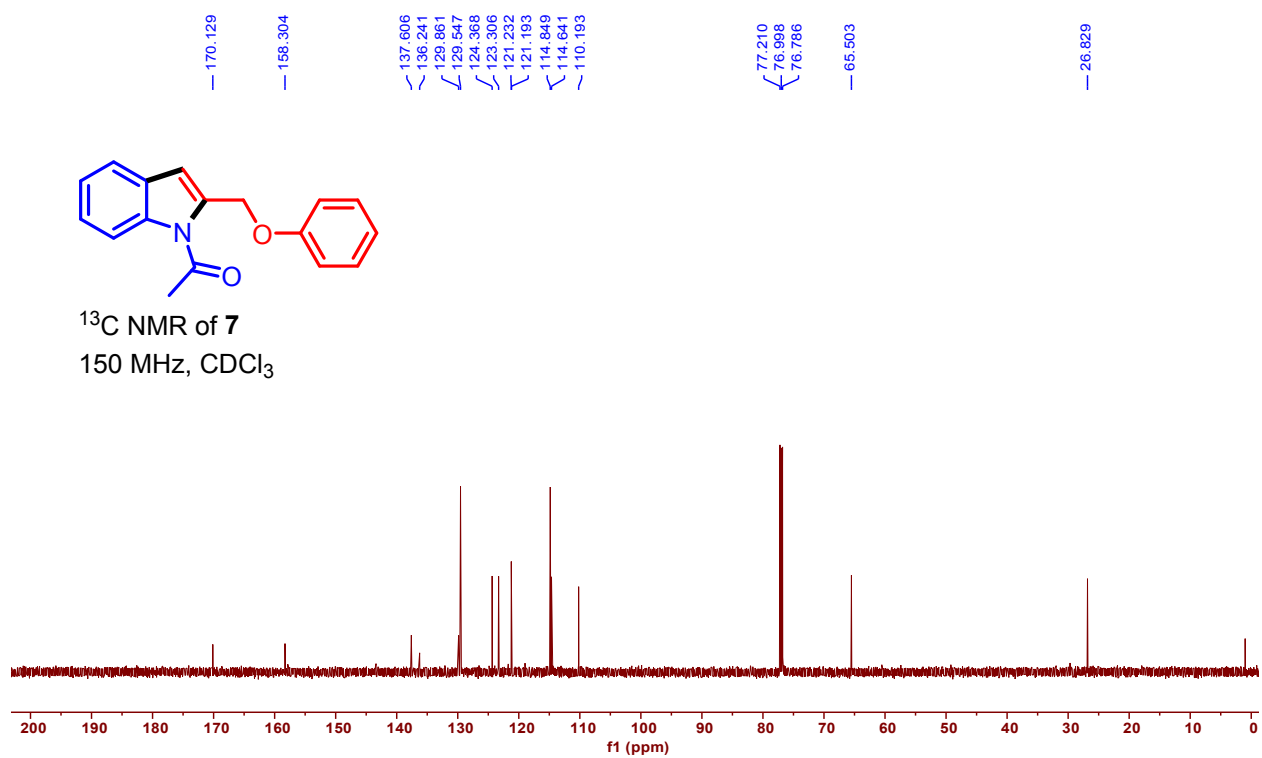
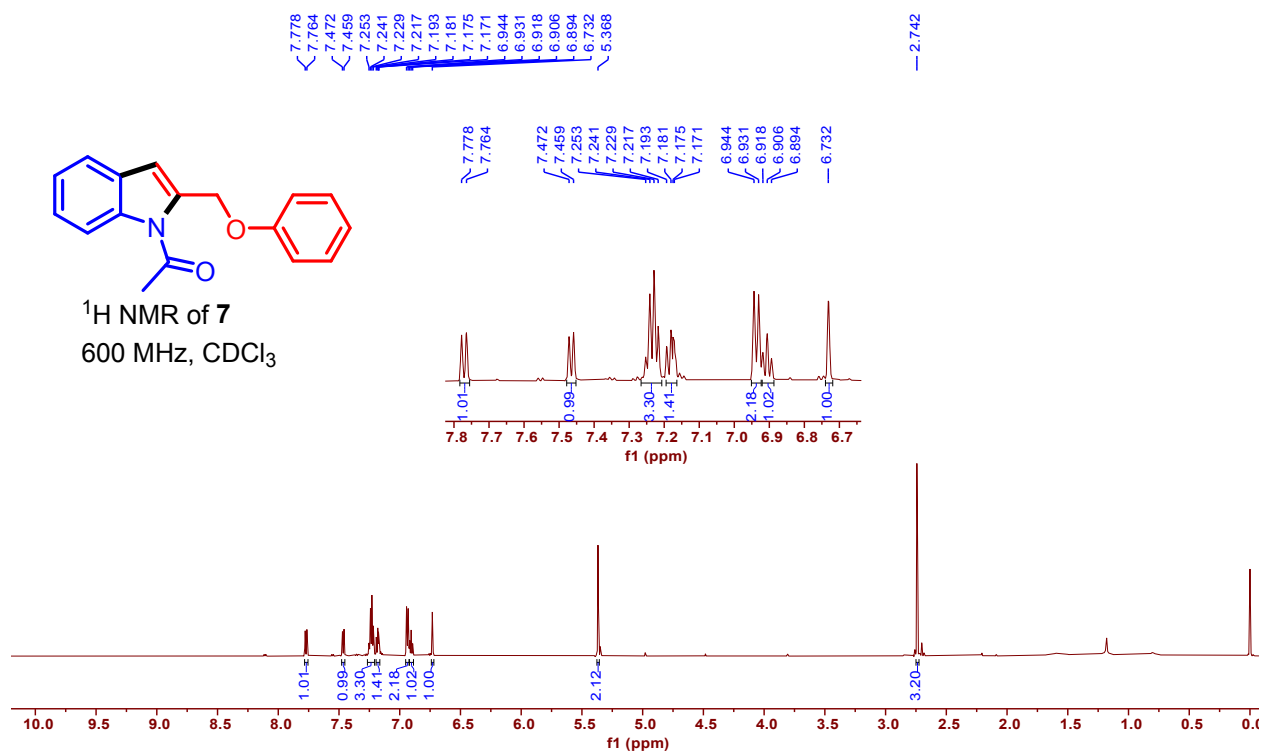


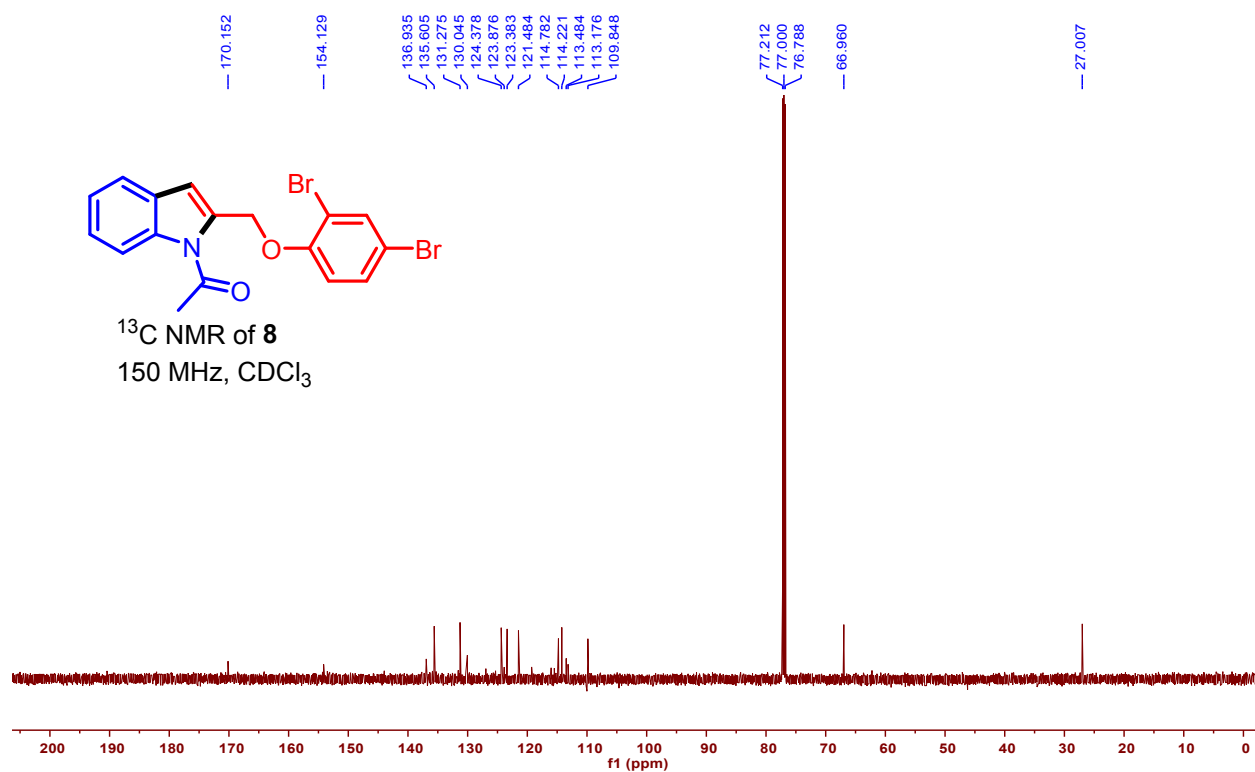
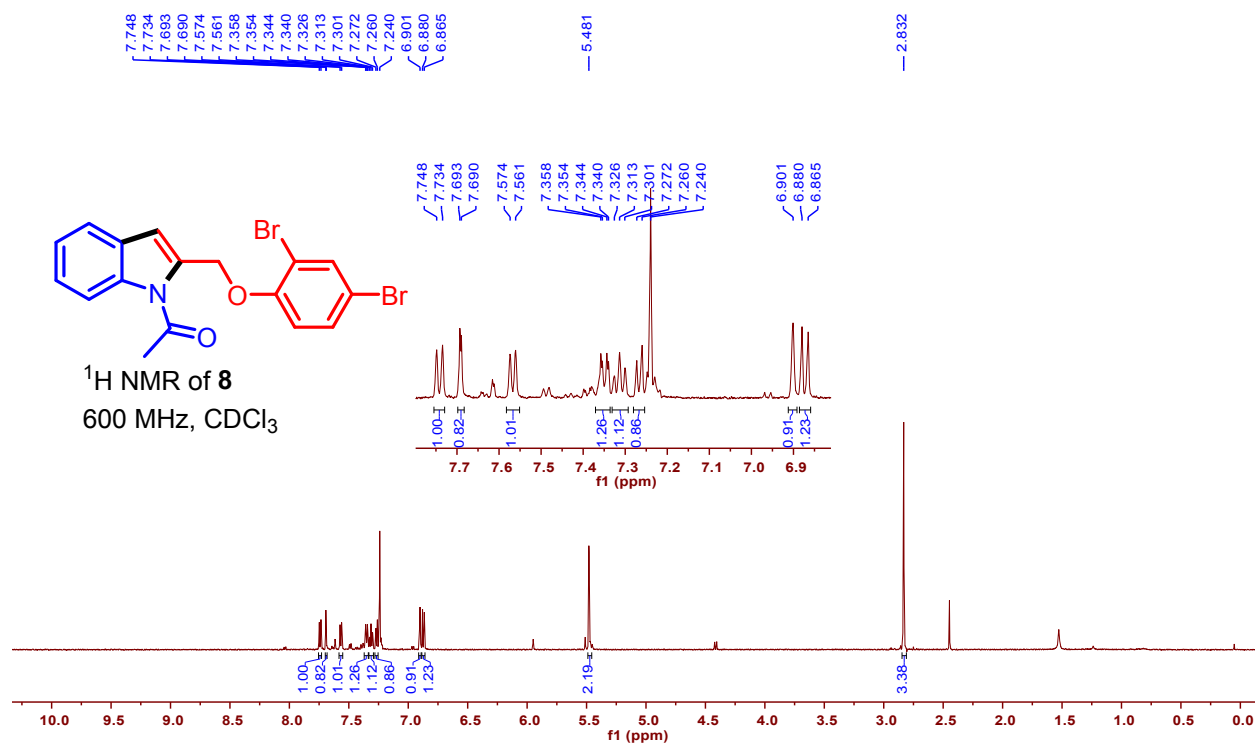












Crystal refinement data for compound 6b-S: Empirical Formula- $C_{17}H_{19}NO_3$, $M = 285.33$, Orthorhombic, Space group $P2_12_12_1$, $a = 10.2060(4) \text{ \AA}$, $b = 11.8825(5) \text{ \AA}$, $c = 12.7337(5) \text{ \AA}$, $V = 1544.25(11) \text{ \AA}^3$, $Z = 4$, $T = 223(2) \text{ K}$, $\rho_{\text{calcd}} = 1.227 \text{ Mg/m}^3$, $2\theta_{\text{max}} = 25.24^\circ$, Refinement of 202 parameters on 3821 independent reflections out of 3821 collected reflections ($R_{\text{int}} = 0.0492$) led to $R_1 = 0.0413$ [$I > 2\sigma(I)$], $wR_2 = 0.0.1283$ (all data) and $S = 1.128$ with the largest difference peak and hole of 0.192 and -0.244 $e.\text{\AA}^{-3}$ respectively. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1981280). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

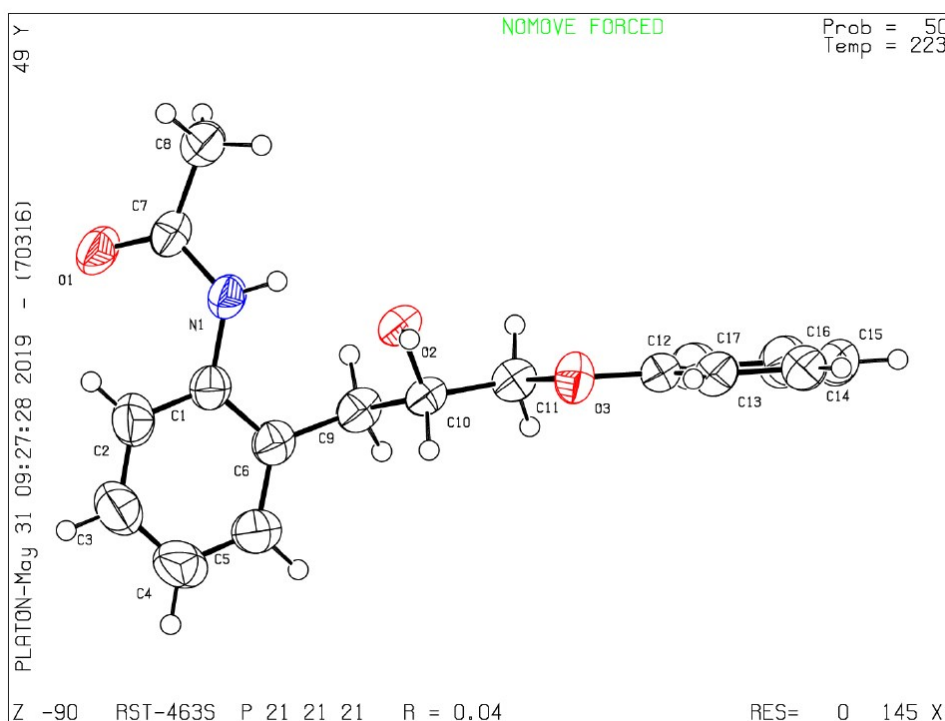


Figure S1. X-ray structure of compound **6b-S**.

Table S1. Crystal data and structure refinement for RST-463(S).

Identification code	RST-463(S)	
Empirical formula	C ₁₇ H ₁₉ N O ₃	
Formula weight	285.33	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 10.2060(4) Å	α = 90°.
	b = 11.8825(5) Å	β = 90°.
	c = 12.7337(5) Å	γ = 90°.
Volume	1544.25(11) Å ³	
Z	4	
Density (calculated)	1.227 Mg/m ³	
Absorption coefficient	0.084 mm ⁻¹	
F(000)	608	
Crystal size	0.220 x 0.160 x 0.100 mm ³	
Theta range for data collection	2.558 to 28.293°.	
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	
Reflections collected	50079	
Independent reflections	3821 [R(int) = 0.0492]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6961	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3821 / 0 / 202	
Goodness-of-fit on F ²	1.128	
Final R indices [I > 2σ(I)]	R1 = 0.0413, wR2 = 0.1085	
R indices (all data)	R1 = 0.0585, wR2 = 0.1283	
Absolute structure parameter	0.1(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.192 and -0.244 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RST-463(S). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	818(3)	-491(2)	1645(2)	47(1)
C(2)	876(4)	-1653(3)	1728(2)	64(1)
C(3)	-5(4)	-2310(3)	1172(3)	76(1)
C(4)	-934(4)	-1812(3)	537(2)	74(1)
C(5)	-984(3)	-653(3)	468(2)	58(1)
C(6)	-118(2)	35(2)	1014(2)	46(1)
N(1)	1743(2)	191(2)	2193(2)	47(1)
C(7)	2133(2)	52(2)	3190(2)	46(1)
C(8)	3166(3)	843(2)	3556(2)	54(1)
O(1)	1657(2)	-682(2)	3756(2)	62(1)
C(9)	-184(2)	1294(2)	886(2)	47(1)
C(10)	756(2)	1736(2)	49(2)	39(1)
O(2)	2070(2)	1595(2)	409(1)	42(1)
C(11)	482(2)	2947(2)	-196(2)	45(1)
O(3)	1303(2)	3256(2)	-1062(2)	51(1)
C(12)	1127(3)	4297(2)	-1495(2)	49(1)
C(13)	1915(3)	4532(3)	-2359(2)	62(1)
C(14)	1827(5)	5561(3)	-2849(3)	83(1)
C(15)	941(5)	6352(3)	-2500(3)	94(2)
C(16)	168(5)	6115(3)	-1662(3)	89(1)
C(17)	240(4)	5087(3)	-1134(3)	65(1)

Table S3. Bond lengths [Å] and angles [°] for RST-463(S).

C(1)-C(2)	1.385(4)
C(1)-C(6)	1.397(4)
C(1)-N(1)	1.426(3)
C(2)-C(3)	1.385(5)
C(2)-H(2)	0.9400
C(3)-C(4)	1.380(5)
C(3)-H(3)	0.9400
C(4)-C(5)	1.382(5)
C(4)-H(4)	0.9400
C(5)-C(6)	1.390(4)
C(5)-H(5)	0.9400
C(6)-C(9)	1.507(4)
N(1)-C(7)	1.341(3)
N(1)-H(1)	0.85(3)
C(7)-O(1)	1.231(3)
C(7)-C(8)	1.488(4)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(8)-H(8C)	0.9700
C(9)-C(10)	1.527(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(10)-O(2)#1	1.427(3)
C(10)-O(2)	1.427(3)
C(10)-C(11)	1.499(3)
C(10)-H(10)	0.98(3)
O(2)-O(2)#1	0.000(5)
O(2)-H(2A)	0.87(4)
C(11)-O(3)	1.432(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
O(3)-C(12)	1.366(3)
C(12)-C(17)	1.383(4)

C(12)-C(13)	1.392(4)
C(13)-C(14)	1.375(5)
C(13)-H(13)	0.9400
C(14)-C(15)	1.379(6)
C(14)-H(14)	0.9400
C(15)-C(16)	1.357(7)
C(15)-H(15)	0.9400
C(16)-C(17)	1.396(5)
C(16)-H(16)	0.9400
C(17)-H(17)	0.9400

C(2)-C(1)-C(6)	121.3(3)
C(2)-C(1)-N(1)	120.1(3)
C(6)-C(1)-N(1)	118.7(2)
C(3)-C(2)-C(1)	119.7(3)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(4)-C(3)-C(2)	120.3(3)
C(4)-C(3)-H(3)	119.8
C(2)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	119.3(3)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	122.1(3)
C(4)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(5)-C(6)-C(1)	117.4(3)
C(5)-C(6)-C(9)	120.1(3)
C(1)-C(6)-C(9)	122.5(2)
C(7)-N(1)-C(1)	126.1(2)
C(7)-N(1)-H(1)	117(2)
C(1)-N(1)-H(1)	117(2)
O(1)-C(7)-N(1)	121.7(3)
O(1)-C(7)-C(8)	122.9(2)
N(1)-C(7)-C(8)	115.4(2)

C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(6)-C(9)-C(10)	112.9(2)
C(6)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9A)	109.0
C(6)-C(9)-H(9B)	109.0
C(10)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
O(2)#1-C(10)-C(11)	110.8(2)
O(2)-C(10)-C(11)	110.8(2)
O(2)#1-C(10)-C(9)	109.06(18)
O(2)-C(10)-C(9)	109.06(18)
C(11)-C(10)-C(9)	111.0(2)
O(2)#1-C(10)-H(10)	110.9(16)
O(2)-C(10)-H(10)	110.9(16)
C(11)-C(10)-H(10)	108.0(15)
C(9)-C(10)-H(10)	107.0(16)
C(10)-O(2)-H(2A)	108(2)
O(3)-C(11)-C(10)	107.35(19)
O(3)-C(11)-H(11A)	110.2
C(10)-C(11)-H(11A)	110.2
O(3)-C(11)-H(11B)	110.2
C(10)-C(11)-H(11B)	110.2
H(11A)-C(11)-H(11B)	108.5
C(12)-O(3)-C(11)	117.8(2)
O(3)-C(12)-C(17)	124.5(3)
O(3)-C(12)-C(13)	115.2(3)
C(17)-C(12)-C(13)	120.3(3)
C(14)-C(13)-C(12)	120.0(4)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0

C(13)-C(14)-C(15)	120.2(4)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	119.6(3)
C(16)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2
C(15)-C(16)-C(17)	122.0(4)
C(15)-C(16)-H(16)	119.0
C(17)-C(16)-H(16)	119.0
C(12)-C(17)-C(16)	118.0(4)
C(12)-C(17)-H(17)	121.0
C(16)-C(17)-H(17)	121.0

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RST-463(S). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	49(1)	54(1)	37(1)	6(1)	4(1)	-6(1)
C(2)	82(2)	54(2)	56(2)	11(1)	1(2)	-6(2)
C(3)	103(3)	58(2)	67(2)	3(2)	4(2)	-24(2)
C(4)	86(2)	82(2)	53(2)	-2(2)	5(2)	-34(2)
C(5)	52(2)	77(2)	43(1)	3(1)	3(1)	-16(1)
C(6)	42(1)	60(2)	37(1)	6(1)	8(1)	-5(1)
N(1)	50(1)	51(1)	40(1)	12(1)	-2(1)	-4(1)
C(7)	41(1)	55(1)	42(1)	9(1)	1(1)	7(1)
C(8)	54(2)	57(2)	50(1)	4(1)	-6(1)	2(1)
O(1)	54(1)	83(1)	47(1)	26(1)	-7(1)	-13(1)
C(9)	39(1)	62(2)	40(1)	4(1)	4(1)	3(1)
C(10)	34(1)	50(1)	33(1)	1(1)	-1(1)	2(1)
O(2)	34(1)	57(1)	33(1)	3(1)	0(1)	3(1)
C(11)	41(1)	51(1)	43(1)	-2(1)	1(1)	5(1)
O(3)	47(1)	50(1)	55(1)	14(1)	6(1)	8(1)
C(12)	54(1)	44(1)	49(1)	5(1)	-15(1)	-6(1)
C(13)	71(2)	64(2)	50(1)	11(1)	-14(1)	-12(1)
C(14)	122(3)	72(2)	54(2)	16(2)	-29(2)	-38(2)
C(15)	162(4)	50(2)	69(2)	11(2)	-56(3)	-21(2)
C(16)	136(4)	44(2)	88(3)	-3(2)	-46(3)	11(2)
C(17)	78(2)	49(2)	68(2)	-5(1)	-18(2)	8(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for RST-463(S).

	x	y	z	U(eq)
H(2)	1509	-1993	2160	77
H(3)	31	-3098	1228	91
H(4)	-1528	-2258	155	89
H(5)	-1624	-319	38	69
H(1)	2080(30)	730(30)	1850(20)	54(8)
H(8A)	3401	1349	2989	80
H(8B)	2838	1276	4146	80
H(8C)	3933	421	3773	80
H(9A)	23	1651	1559	56
H(9B)	-1081	1508	696	56
H(10)	600(30)	1300(20)	-590(20)	38(7)
H(2A)	2540(40)	1360(30)	-110(30)	75(11)
H(11A)	-442	3047	-383	54
H(11B)	676	3419	415	54
H(13)	2507	3988	-2608	74
H(14)	2373	5725	-3424	99
H(15)	872	7052	-2841	113
H(16)	-434	6660	-1429	107
H(17)	-298	4937	-552	78

Table S6. Torsion angles [°] for RST-463(S).

C(6)-C(1)-C(2)-C(3)	0.4(4)
N(1)-C(1)-C(2)-C(3)	-178.3(3)
C(1)-C(2)-C(3)-C(4)	0.1(5)
C(2)-C(3)-C(4)-C(5)	-0.5(5)
C(3)-C(4)-C(5)-C(6)	0.5(5)
C(4)-C(5)-C(6)-C(1)	0.0(4)
C(4)-C(5)-C(6)-C(9)	178.1(3)
C(2)-C(1)-C(6)-C(5)	-0.4(4)
N(1)-C(1)-C(6)-C(5)	178.3(2)
C(2)-C(1)-C(6)-C(9)	-178.4(2)
N(1)-C(1)-C(6)-C(9)	0.3(3)
C(2)-C(1)-N(1)-C(7)	-44.0(4)
C(6)-C(1)-N(1)-C(7)	137.3(3)
C(1)-N(1)-C(7)-O(1)	-3.5(4)
C(1)-N(1)-C(7)-C(8)	176.8(2)
C(5)-C(6)-C(9)-C(10)	-94.2(3)
C(1)-C(6)-C(9)-C(10)	83.8(3)
C(6)-C(9)-C(10)-O(2)#1	-68.4(3)
C(6)-C(9)-C(10)-O(2)	-68.4(3)
C(6)-C(9)-C(10)-C(11)	169.2(2)
C(11)-C(10)-O(2)-O(2)#1	0.00(4)
C(9)-C(10)-O(2)-O(2)#1	0.00(2)
O(2)#1-C(10)-C(11)-O(3)	64.9(2)
O(2)-C(10)-C(11)-O(3)	64.9(2)
C(9)-C(10)-C(11)-O(3)	-173.76(19)
C(10)-C(11)-O(3)-C(12)	173.5(2)
C(11)-O(3)-C(12)-C(17)	2.3(4)
C(11)-O(3)-C(12)-C(13)	-177.5(2)
O(3)-C(12)-C(13)-C(14)	-179.3(3)
C(17)-C(12)-C(13)-C(14)	0.9(4)
C(12)-C(13)-C(14)-C(15)	-1.3(5)
C(13)-C(14)-C(15)-C(16)	0.9(5)
C(14)-C(15)-C(16)-C(17)	0.0(6)

O(3)-C(12)-C(17)-C(16)	-179.8(3)
C(13)-C(12)-C(17)-C(16)	-0.1(4)
C(15)-C(16)-C(17)-C(12)	-0.4(5)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z

Table S7. Hydrogen bonds for RST-463(S) [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1)...O(2)#1	0.85(3)	2.10(3)	2.838(3)	144(3)
O(2)-H(2A)...O(1)#2	0.87(4)	1.84(4)	2.701(3)	171(4)

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z #2 $-x+1/2, -y, z-1/2$