

Supporting Information

Isolation and Characterization of Regio-isomers of Pyrazole based Palladacycle, and their use in α -Alkylation of Ketones using Alcohols

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General: All chemicals were used as received from commercially available sources. NMR spectra were recorded on Bruker ARX 400 spectrometer at room temperature. ^1H (400 MHz) and ^{13}C (100 MHz) NMR chemical shifts in ppm were referenced internally to its proton resonance of incomplete deuterated solvent signals. ^{19}F NMR spectra were externally reference to α,α,α -trifluorotoluene in CDCl_3 ($\delta = -63.73$ ppm). Electron spray ionization mass spectra were recorded on a Bruker microTOF-QII spectrometry. IR spectra were recorded with Perkin Elmer instrument. Single-crystal X-ray diffraction data were collected at 296 K using, Mo-K α radiation (0.71073 \AA). Crystallographic data for the palladacycle **1** & **2** and compound **30** and details of X-ray diffraction experiments and crystal structure refinements are given in Table S1. SADABS absorption corrections were applied in both cases. The structures were solved and refined with SHELX suite of programs. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. Crystallographic data for palladacycle **1** and **2** and compound **30** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1555731-1555733. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

General procedure for α -alkylation of ketones using alcohols:

An oven dried Schlenk tube was charged with palladacycle (1×10^{-2} mmol to 2×10^{-2} mmol), $\text{P}(2\text{-Fur})_3$ (2×10^{-2} mmol to 4×10^{-2} mmol). Under inert atmosphere LiOH (0.25 mmol), ketone (1.0 mmol), alcohol (1.2 mmol to 2.0 mmol) were added to the reaction mixture and the system was purged with nitrogen gas for 10 minutes. Then the Schlenk tube was closed with PTFE stopper and the reaction mixture was stirred at $80 - 130\text{ }^\circ\text{C}$ for 24 - 48 h. The reaction mixture was cooled to room temperature, diluted and washed with dichloromethane ($3 \times 5\text{ mL}$), and concentrated under vacuum. The crude mixture was subjected to column chromatography on silica gel using ethyl acetate and *n*-hexanes mixtures to afford the α -alkylated product in high purity.

General procedure for the synthesis of quinolines:

An oven dried Schlenk tube was charged with palladacycle (1×10^{-2} mmol), $\text{P}(2\text{-Fur})_3$ (2×10^{-2} mmol). Under inert atmosphere, LiOH (0.25 mmol), ketone (1.2 mmol), 2-aminobenzyl alcohol (1.0 mmol) were added to the reaction mixture and the system was purged with nitrogen gas for 10 minutes. Then the Schlenk tube was closed with PTFE stopper and the reaction mixture was stirred at $100\text{ }^\circ\text{C}$ for 24 h. The reaction mixture was cooled to room temperature, diluted and washed with dichloromethane ($3 \times 5\text{ mL}$), and concentrated under vacuum. The crude product was subjected to column chromatography on silica gel using ethyl acetate and *n*-hexanes mixtures to afford the corresponding quinoline derivative products in high purity.

*Synthesis of 3,5-diphenyl-1-(4-(trifluoromethyl) phenyl)-1*H*-pyrazole ¹:*

1,3-Diphenylpropane-1,3-dione (1.00 g, 4.5 mmol) and (4-(trifluoromethyl)phenyl) hydrazine (0.86 g, 4.9 mmol) were taken in 100 mL round bottom flask. To this flask, 10 mL of methanol and 10 mL of acetic acid were added and the reaction mixture was refluxed for overnight. To the cooled reaction mixture, saturated sodium carbonate solution was added and the compound was extracted using dichloromethane. The solvent was removed under vacuum and the residue was purified by column chromatography (*n*-hexane-ethyl acetate) to afford the product, 3,5-diphenyl-1-(4-(trifluoromethyl) phenyl)-1H-pyrazole (1.55 g, Yield: 95 %) as a white solid. Mp = 114 - 115 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 3H), 7.40 – 7.36 (m, 4H), 7.32 – 7.29 (m, 2H), 6.86 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 152.8, 144.9, 142.8, 132.6, 130.3, 129.0, 128.9 (2C), 128.5, 126.2 (q, *J* = 3.7 Hz), 126.0, 125.0, 106.4 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -63.29 ppm. IR (KBr): ν (cm⁻¹) = 3067 (m), 1613 (m), 1485 (m), 1411 (m), 1364 (m), 1326 (s), 1168 (s), 1126 (s), 766 (s), 698 (s). HRMS (ESI): calcd. for C₂₂H₁₅F₃N₂ ([M+H]) : 365.1260, found : 365.1245.

Cyclopalladation of 3,5-diphenyl-1-(4-(trifluoromethyl) phenyl)-1H-pyrazole:

Palladium acetate (0.31 g, 1.4 mmol) and 3,5-diphenyl-1-(4-(trifluoromethyl) phenyl)-1H-pyrazole (0.50 g, 1.4 mmol) were suspended in glacial acetic acid (5 mL), then the reaction mixture was heated in an oil bath for 1h (100 °C). The reaction mixture (hot condition) was filtered through celite (to remove palladium black) then the filtrate was concentrated. The residue was re-dissolved in dichloromethane, layered with hexane and stored at 5 °C for 24 h and filtered through celite (1 cm height) silicagel (100-200 mesh, 1 cm height) to remove palladium black traces. The solvents were removed under vacuum and the yellow product (0.65 g, Yield: 90%) was recrystallized sequentially from a mixture of dichloromethane and hexanes. First batch of recrystallization gave palladacycle **1** (0.28 g, 39.2 %) as a pale yellow solid, second batch of recrystallization gave mixture of palladacycles (0.06 g, 8.1 %) in which palladacycle **2** was major and third batch of recrystallization gave palladacycle **2** (0.31 g, 43.0 %) as a dark yellow solid.

Palladacycle 1: Mp = 216 – 219 °C (decompose). ¹H NMR (400 MHz, CDCl₃): δ = 7.66 (d, *J* = 6.7 Hz, 4H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.50 – 7.41 (m, 10H), 7.24 (s, 2H), 7.08 (d, *J* = 4.4 Hz, 4H), 6.96 (d, *J* = 9.7 Hz, 2H), 6.35 (d, *J* = 8.4 Hz, 2H), 6.06 (s, 2H), 1.22 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 182.4, 155.3, 145.8, 143.0, 134.1, 130.3, 129.7 (2C), 129.5, 129.3 (q, *J* = 3.5 Hz), 129.0 (2C), 128.4, 121.3 (q, *J* = 3.7 Hz), 111.7 (d, *J* = 160.3 Hz), 22.7 ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.41 ppm. Elemental analysis calcd (%) for C₄₈H₃₄F₆N₄O₄Pd₂.(CH₂Cl₂)_{0.5} C 52.95, H 3.21, N 5.09; found: C 52.69, H 3.67, N 5.96. The slight variation for H and N for the elemental analysis is likely due to incomplete combustion as a result of fluorine or volatile nature of dichloromethane solvent. IR (KBr): ν (cm⁻¹) = 3060 (m), 1570 (s), 1479 (m), 1417 (s), 1320 (s), 1167 (m), 1118 (s), 763 (s), 698 (s).

Palladacycle 2: Mp = 221 – 223 °C (decompose). ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (d, *J* = 8.4 Hz, 4H), 7.37 – 7.27 (m, 10H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.92 (d, *J* =

7.1 Hz, 4H), 6.82 – 6.74 (m, 4H), 6.26 (s, 2H), 1.33 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 180.4, 160.1, 146.3, 145.3, 138.8, 137.2, 131.7, 129.3, 129.0 (2C), 128.6, 128.0, 125.7 (q, J = 2.9 Hz), 123.25 (d, J = 194.0 Hz), 102.7, 23.3 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ = -63.64 ppm. Elemental analysis calcd (%) for $\text{C}_{48}\text{H}_{34}\text{F}_6\text{N}_4\text{O}_4\text{Pd}_2\cdot(\text{CH}_2\text{Cl}_2)_{0.2}$ C 53.87, H 3.23, N 5.21; found: C 53.40, H 3.36, N 5.76. The slight variation for C and N for the elemental analysis is likely due to incomplete combustion as a result of fluorine or volatile nature of dichloromethane solvent. IR (KBr): ν (cm^{-1}) = 3054 (m), 1570 (s), 1414 (s), 1325 (s), 1159 (m), 1128 (s), 758 (s), 700 (s).

Analytical data for C-alkylated products:

1,3-diphenylpropan-1-one (Table 1, entry 1)²: Prepared from acetophenone (0.12 g, 1.0 mmol) and benzyl alcohol (0.13 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.21 g, 0.9 mmol, 98 %). Mp = 72-73 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.99 (d, J = 7.1 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.35 – 7.22 (m, 5H), 3.33 (t, J = 7.7 Hz, 2H), 3.10 (t, J = 7.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 199.3, 141.4, 136.9, 133.1, 128.7, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2 ppm. HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{14}\text{ONa}$ ([M+Na]) : 233.0937, found : 233.0942.

3-phenyl-1-(*p*-tolyl)propan-1-one (Table 1, entry 2)²: Prepared from 4'-methyl acetophenone (0.13 g, 1.0 mmol) and benzyl alcohol (0.13 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.21 g, 0.9 mmol, 94 %). Mp = 68-69 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.89 (d, J = 8.2 Hz, 2H), 7.34 – 7.21 (m, 7H), 3.29 (t, J = 7.5 Hz, 2H), 3.08 (t, J = 7.5 Hz, 2H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 198.9, 143.9, 141.5, 134.5, 129.4, 128.6, 128.5, 128.3, 126.2, 40.4, 30.3, 21.7 ppm. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{16}\text{O}$ ([M+H]) : 225.1274, found : 225.1281.

1-(4-methoxyphenyl)-3-phenylpropan-1-one (Table 1, entry 3)³: Prepared from 4'-methoxy acetophenone (0.15 g, 1.0 mmol) and benzyl alcohol (0.13 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.22 g, 0.9 mmol, 92 %), Mp = 96-97 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.96 (d, J = 8.9 Hz, 2H), 7.33 – 7.20 (m, 5H), 6.93 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.26 (t, J = 7.8 Hz, 2H), 3.07 (t, J = 7.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 197.9, 163.5, 141.5, 130.4, 130.0, 128.6, 128.5, 126.1, 113.8, 55.5, 40.2, 30.4 ppm. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ ([M+H]) : 241.1223, found : 241.1233.

1-(4-ethylphenyl)-3-phenylpropan-1-one (Table 1, entry 4)³: Prepared from 4'-ethyl acetophenone (0.15 g, 1.0 mmol) and benzyl alcohol (0.13 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.22 g, 0.9 mmol, 94 %), Mp = 65-66 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.93 (d, J = 8 Hz, 2H), 7.31 – 7.22 (m, 7H), 3.31 (t, J = 8 Hz, 2H), 3.10 (t, J = 8 Hz, 2H), 2.73 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 198.9, 150.0, 141.5, 134.7, 128.6, 128.5, 128.3, 128.2,

126.2, 40.4, 30.3, 28.9, 15.3 ppm. HRMS (ESI): calcd. for $C_{17}H_{18}O$ ([M+H]) : 239.1430, found : 239.1442.

1-(naphthalen-1-yl)-3-phenylpropan-1-one (Table 1, entry 5)⁴: Prepared from 1-acetonaphthone (0.17 g. 1.0 mmol) and benzyl alcohol (0.13 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.21 g, 0.8 mmol, 82 %), Mp = 54-55 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.95 – 7.87 (m, 3H), 7.62 – 7.53 (m, 2H), 7.33 (dd, J = 11.3, 4.8 Hz, 4H), 7.25 – 7.20 (m, 1H), 3.45 (t, J = 7.6 Hz, 2H), 3.15 (t, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 141.5, 135.7, 134.3, 132.7, 129.8, 129.7, 128.7, 128.6, 127.9, 126.9, 126.3, 123.9, 40.7, 30.4 ppm. HRMS (ESI): calcd. for $C_{19}H_{16}O$ ([M+H]) : 261.1274, found : 261.1277.

3-(naphthalen-2-yl)-1-(p-tolyl)propan-1-one (Table 1, entry 6)⁴: Prepared from 4'-methyl acetophenone (0.13 g. 1.0 mmol) and 2-naphthalenemethanol (0.19 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.26 g, 0.9 mmol, 96 %), Mp = 90-91 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.74 (t, J = 4 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.41 (d, J = 4.1 Hz, 2H), 7.25 – 7.23 (m, 3H), 3.53 (t, J = 8 Hz, 2H), 3.40 (d, J = 8 Hz, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1, 144.0, 137.6, 134.5, 134.1, 131.8, 129.4, 129.1, 128.3, 127.1, 126.3, 126.2, 125.8, 125.7, 123.7, 39.8, 27.4, 21.8 ppm. HRMS (ESI): calcd. for $C_{20}H_{18}O$ ([M+H]) : 275.1430, found : 275.1426.

3-(4-fluorophenyl)-1-(p-tolyl)propan-1-one (Table 1, entry 7)⁵: Prepared from 4'-methyl acetophenone (0.13 g. 1.0 mmol) and 4-fluoro benzylalcohol (0.15 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.21 g, 0.8 mmol, 86 %), Mp = 67-68 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.2 Hz, 2H), 7.26 – 7.18 (m, 4H), 6.97 (t, J = 8.7 Hz, 2H), 3.25 (d, J = 7.6 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.84, 161.53 (d, J = 243.7 Hz), 144.07, 137.13 (d, J = 3.2 Hz), 134.49, 129.96 (d, J = 7.8 Hz), 129.44, 128.29, 115.36 (d, J = 21.1 Hz), 40.45, 29.50, 21.77 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -118.33 ppm. HRMS (ESI): calcd. for $C_{16}H_{15}FO$ ([M+H]) : 243.1180, found : 243.1171.

1-(benzo[d][1,3]dioxol-5-yl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (Table 1, entry 8)^{new}: Prepared from 3',4'-methylenedioxy acetophenone (0.16 g. 1.0 mmol) and 4-trifluoro benzylalcohol (0.21 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.29 g, 0.9 mmol, 92 %), Mp = 62-63 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.2 Hz, 3H), 7.43 (d, J = 1.7 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.2 Hz, 1H), 6.03 (s, 2H), 3.24 (t, J = 7.7 Hz, 2H), 3.11 (t, J = 7.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 152.0, 148.4, 145.6, 131.7, 129.5, 128.9, 128.6 (d, J = 32.3 Hz), 125.5 (q, J = 3.8 Hz), 124.4, 123.1, 108.0 (d, J = 8.0 Hz), 102.0, 39.7, 30.1 ppm. ^{19}F NMR (376 MHz,

CDCl₃): δ = -63.34 ppm. HRMS (ESI): calcd. for C₁₇H₁₃F₃O₃ ([M+H]) : 323.0890, found : 323.0897.

1-(naphthalen-2-yl)-3-(*p*-tolyl)propan-1-one (Table 1, entry 9) ^{new}: Prepared from 2-acetylnaphthalene (0.17 g, 1.0 mmol) and 4-methyl benzylalcohol (0.15 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.24 g, 0.8 mmol, 87 %), Mp = 108 - 109 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.46 (s, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 7.6 Hz, 2H), 7.62 - 7.53 (m, 2H), 7.17 (dd, J = 23.5, 7.8 Hz, 4H), 3.43 (t, J = 7.6 Hz, 2H), 3.10 (t, J = 7.7 Hz, 2H), 2.34 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.4, 138.4, 135.8, 135.7, 134.4, 132.7, 129.8, 129.7, 129.4, 128.6, 128.6, 128.5, 127.9, 126.9, 124.0, 40.9, 30.0, 21.2 ppm. HR-MS (ESI): calcd. for C₂₀H₁₈ONa ([M+Na]) : 297.1250, found : 297.1255.

1-(4-methoxyphenyl)-3-(*o*-tolyl)propan-1-one (Table 1, entry 10) ⁶: Prepared from 4'-methoxy acetophenone (0.15 g, 1.0 mmol) and 2-methyl benzylalcohol (0.15 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.24 g, 0.9 mmol, 94 %), Mp = 82 - 83 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.96 (d, J = 8.8 Hz, 2H), 7.21 - 7.12 (m, 4H), 6.94 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.21 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H), 2.36 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.1, 163.6, 139.7, 136.1, 130.4, 130.4, 130.1, 128.8, 126.4, 126.3, 113.9, 55.6, 38.9, 27.8, 19.5 ppm. HRMS (ESI): calcd. for C₁₇H₁₈O₂ ([M+H]) : 255.1380, found : 255.1393.

1, 5-diphenylpentan-3-one (Table 1, entry 11) ⁵: Prepared from acetone (58 mg, 1.0 mmol) and benzylalcohol (0.32 g, 3.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.22 g, 0.9 mmol, 91 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.32 - 7.27 (m, 4H), 7.24 - 7.14 (m, 6H), 2.91 (t, J = 7.6 Hz, 4H), 2.73 (t, J = 7.6 Hz, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 209.3, 141.1, 128.6, 128.4, 126.2, 44.6, 29.8 ppm. HRMS (ESI): calcd. for C₁₇H₁₈O ([M+H]) : 239.1430, found : 239.1431.

1-phenylhexan-3-one (Table 1, entry 12) ⁷: Prepared from 2-pentanone (86 mg, 1.0 mmol) and benzylalcohol (0.13 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as colourless liquid (0.13 g, 0.7 mmol, 72 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.28 (d, J = 7.5 Hz, 2H), 7.20 (t, J = 6.4 Hz, 3H), 2.91 (t, J = 7.6 Hz, 2H), 2.73 (t, J = 7.7 Hz, 2H), 2.38 (t, J = 7.3 Hz, 2H), 1.60 (dd, J = 14.8, 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 210.4, 141.3, 128.6, 128.4, 126.2, 45.1, 44.4, 29.9, 17.4, 13.8 ppm. HR-MS (ESI): calcd. for C₁₂H₁₆ONa ([M+Na]) : 199.1093, found : 199.1092.

1-(4-methoxyphenyl)-4-phenylbutan-2-one (Table 1, entry 13) ⁸: Prepared from 4-methoxyphenylacetone (0.16 g, 1.0 mmol) and benzylalcohol (0.13 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as white solid (0.17 g, 0.7

mmol, 68 %), Mp = 66-67 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.26 (t, J = 7.3 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.13 (d, J = 6.9 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.60 (s, 2H), 2.87 (t, J = 7.4 Hz, 2H), 2.76 (t, J = 7.3 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 208.0, 158.8, 141.1, 130.5, 128.6, 128.5, 126.2, 114.3, 55.4, 49.6, 43.4, 29.9 ppm. HRMS (ESI): calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$ ([M+H]) : 255.1380, found : 255.1391.

3-(2-methoxyphenyl)-1-(4-methoxyphenyl)propan-1-one (Table 1, entry 14)⁹: Prepared from 4'-methoxy acetophenone (0.15 g, 1.0 mmol) and 2-methoxy benzylalcohol (0.27 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.25 g, 0.9 mmol, 91 %). ^1H NMR (400 MHz, CDCl_3): δ = 7.97 (d, J = 8.8 Hz, 2H), 7.21 (t, J = 6.4 Hz, 2H), 6.96 – 6.83 (m, 4H), 3.86 (s, 3H), 3.84 (s, 3H), 3.21 (d, J = 7.6 Hz, 2H), 3.04 (d, J = 7.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 198.7, 163.4, 157.6, 130.5, 130.3, 130.2, 129.8, 127.6, 120.7, 113.8, 110.4, 55.6, 55.3, 38.8, 26.1 ppm. HRMS (ESI): calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_3$ ([M+H]) : 271.1329, found : 271.1339.

3-([1,1'-biphenyl]-2-yl)-1-(4-fluorophenyl)propan-1-one (Table 1, entry 15) *new*: Prepared from 4'-fluoro acetophenone (0.14 g, 1.0 mmol) and 2-biphenylmethanol (0.22 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.25 g, 0.8 mmol, 82 %). ^1H NMR (400 MHz, CDCl_3): δ = 7.71 (dd, J = 8.7, 5.4 Hz, 2H), 7.46 – 7.25 (m, 9H), 7.03 (t, J = 8.6 Hz, 2H), 3.07 – 3.04 (m, 2H), 3.00 – 2.96 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 197.9, 165.8 (d, J = 254.6 Hz), 141.9 (d, J = 34.1 Hz), 138.7, 138.5, 133.1, 130.8 (d, J = 9.3 Hz), 130.4, 129.6, 129.3, 128.7, 128.5, 128.2, 127.9, 127.2, 126.4, 115.7 (d, J = 21.8 Hz), 40.3, 28.6 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ = -106.40 ppm. HRMS (ESI): calcd. for $\text{C}_{21}\text{H}_{17}\text{FO}$ ([M+H]) : 305.1336, found : 305.1352.

3-(2-fluorophenyl)-1-phenylpropan-1-one (Table 1, entry 16)¹⁰: Prepared from acetophenone (0.12 g, 1.0 mmol) and 2-fluoro benzyl alcohol (0.25 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.15 g, 0.6 mmol, 64 %). ^1H NMR (400 MHz, CDCl_3): δ = 7.97 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 6.7 Hz, 1H), 7.23 – 7.00 (m, 3H), 3.32 (t, J = 7.6 Hz, 2H), 3.10 (t, J = 7.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 199.1, 161.4 (d, J = 244.9 Hz), 141.4, 136.9, 133.2, 131.0 (d, J = 5.0 Hz), 128.7, 128.2, 126.3, 124.2 (d, J = 3.5 Hz), 115.4 (d, J = 21.9 Hz), 38.9, 24.1 ppm. ^{19}F NMR (376 MHz, CDCl_3): δ = -119.40. HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{13}\text{FO}$ ([M+H]) : 229.1023, found : 229.1018.

1-((8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-(p-tolyl)propan-1-one (Table 1, entry 17) *new*: Prepared from β -pregnenolone (0.32 g, 1.0 mmol) and 4-methyl benzyl alcohol (0.37 g, 3.0 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.33 g, 0.8 mmol, 78 %), Mp = 116 - 117 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.10 – 7.05

(m, 4H), 5.34 (d, J = 5.1 Hz, 1H), 3.58 – 3.46 (m, 1H), 2.85 (t, J = 7.7 Hz, 2H), 2.70 – 2.64 (m, 2H), 2.49 (t, J = 8.9 Hz, 1H), 2.31 (s, 3H), 2.24 – 2.15 (m, 2H), 2.04 – 1.93 (m, 2H), 1.84 (d, J = 9.8 Hz, 2H), 1.69 – 1.36 (m, 11H), 1.27 – 1.07 (m, 3H), 1.00 (s, 3H), 0.59 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 210.8, 140.9, 138.5, 135.6, 129.2, 128.4, 121.5, 71.8, 63.2, 57.1, 50.1, 46.3, 44.4, 42.4, 39.1, 37.4, 36.6, 32.0, 31.9, 31.7, 29.5, 24.7, 23.1, 21.2, 21.1, 19.5, 13.5 ppm. HRMS (ESI): calcd. for $\text{C}_{29}\text{H}_{40}\text{O}_2\text{Na}$ ([M+Na]) : 443.2921, found : 443.2926.

3-phenyl-1-(*o*-tolyl)propan-1-one (Table 1, entry 18)³: Prepared from 2'-methyl acetophenone (0.13 g, 1.0 mmol) and benzylalcohol (0.22 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.16 g, 0.7 mmol, 72 %). ^1H NMR (400 MHz, CDCl_3): δ = 7.62 (d, J = 8.8 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.33 – 7.21 (m, 7H), 3.25 (t, J = 7.6 Hz, 2H), 3.07 (t, J = 7.6 Hz, 2H), 2.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 203.5, 141.3, 138.2, 138.0, 132.1, 131.3, 128.6, 128.5, 128.5, 126.2, 125.8, 43.3, 30.4, 21.4 ppm. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{16}\text{O}$ ([M+H]) : 225.1274, found : 225.1267.

1-(4-methoxyphenyl)hexan-1-one (Table 2, entry 19)¹¹: Prepared from 4'-methoxy acetophenone (0.15 g, 1.0 mmol) and 1-butanol (0.15 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.17 g, 0.8 mmol, 85 %). $\text{Mp} = 39$ –40 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.93 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 2.93 – 2.85 (m, 2H), 1.74 – 1.68 (m, 2H), 1.41 – 1.31 (m, 4H), 0.90 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 199.4, 163.4, 130.4, 130.3, 113.8, 55.6, 38.4, 31.7, 24.5, 22.7, 14.1 ppm. HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2$ ([M+H]) : 207.1380, found : 207.1386.

1-(4-methoxyphenyl)butan-1-one (Table 2, entry 20)¹¹: Prepared from 4'-methoxy acetophenone (0.15 g, 1.0 mmol) and ethanol (0.14 g, 3.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.13 g, 0.7 mmol, 74 %). ^1H NMR (400 MHz, CDCl_3): δ = 7.94 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 2.89 (t, J = 7.3 Hz, 2H), 1.80 – 1.71 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 199.2, 163.4, 130.4, 130.4, 113.8, 55.6, 40.3, 18.1, 14.1 ppm. HRMS (ESI): calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$ ([M+H]) : 179.1067, found : 179.1075.

1-(4-methoxyphenyl)-4-phenylbutan-1-one (Table 2, entry 21)¹²: Prepared from 4'-methoxy acetophenone (0.15 g, 1.0 mmol) and 2-phenyl ethanol (0.24 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.23 g, 0.9 mmol, 89 %), $\text{Mp} = 57$ –58 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.92 (d, J = 8.9 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.23 – 7.19 (m, 3H), 6.93 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 2.94 (t, J = 7.3 Hz, 2H), 2.73 (t, J = 7.6 Hz, 2H), 2.13 – 2.05 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 198.7, 163.4, 141.8, 130.3, 130.2, 128.6, 128.4, 125.9, 113.7, 55.5, 37.4, 35.3, 26.0 ppm. HRMS (ESI): calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$ ([M+H]) : 255.1380, found : 255.1387.

1-(4-methoxyphenyl)decan-1-one (Table 2, entry 22)¹¹: Prepared from 4'-methoxy acetophenone (0.15 g, 1.0 mmol) and 1-octanol (0.26 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.21 g, 0.8 mmol, 81 %), Mp = 46–47 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.94 – 7.91 (m, 2H), 6.93 – 6.89 (m, 2H), 3.85 (s, 3H), 2.88 (dd, *J* = 12.2, 7.7 Hz, 2H), 1.69 (dd, *J* = 12.9, 6.0 Hz, 2H), 1.33 – 1.25 (m, 12H), 0.87 (t, *J* = 5.6 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.3, 163.4, 130.4, 130.3, 113.7, 55.5, 38.4, 32.0, 29.6, 29.6, 29.5, 29.4, 24.7, 22.8, 14.2 ppm. HRMS (ESI): calcd. for C₁₇H₂₆O₂ ([M+H]) : 263.2006, found : 263.2008.

2-benzyl-3,4-dihydronaphthalen-1(2H)-one (Table 2, entry 23)²: Prepared from 1-tetralone (0.15 g, 1.0 mmol) and benzyl alcohol (0.22 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.23 g, 0.9 mmol, 96 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.08 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.25 – 7.22 (m, 4H), 3.50 (dd, *J* = 13.6, 3.9 Hz, 1H), 2.96 – 2.92 (m, 2H), 2.78 – 2.72 (m, 1H), 2.66 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.14 – 2.10 (m, 1H), 1.85 – 1.75 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.5, 144.2, 140.2, 133.4, 129.4, 128.8, 128.5, 127.7, 126.8, 126.3, 49.6, 35.8, 28.8, 27.8 ppm. HRMS (ESI): calcd. for C₁₇H₁₆O ([M+H]) : 237.1274, found : 237.1276.

2-(4-methylbenzyl)-3,4-dihydronaphthalen-1(2H)-one (Table 2, entry 24)¹³: Prepared from 1-tetralone (0.15 g, 1.0 mmol) and 4-methylbenzyl alcohol (0.24 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.23 g, 0.9 mmol, 91 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (d, *J* = 7.1 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 4H), 3.45 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.93 (m, 2H), 2.75 – 2.70 (m, 1H), 2.61 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.33 (s, 3H), 2.15 – 2.08 (m, 1H), 1.81 – 1.78 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.5, 144.2, 140.2, 133.4, 129.4, 128.8, 128.5, 127.7, 126.8, 126.3, 49.6, 35.8, 28.8, 27.8 ppm. HRMS (ESI): calcd. for C₁₈H₁₈O ([M+H]) : 251.1430, found : 251.1420.

2-benzyl-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (Table 2, entry 25)¹⁴: Prepared from 5,6-dimethoxy indanone (0.19 g, 1.0 mmol) and benzyl alcohol (0.22 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.26 g, 0.9 mmol, 92 %), Mp = 128–129 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.30 – 7.19 (m, 6H), 6.80 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.36 (dd, *J* = 13.9, 3.6 Hz, 1H), 3.08 – 2.97 (m, 2H), 2.75 (d, *J* = 16.6 Hz, 1H), 2.63 (dd, *J* = 13.8, 10.3 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 206.6, 155.7, 149.5, 149.0, 139.9, 129.3, 129.0, 128.6, 126.4, 107.5, 104.5, 56.3, 56.2, 49.2, 37.4, 32.0 ppm. HRMS (ESI): calcd. for C₁₈H₁₈O₃Na ([M+Na]) : 305.1148, found : 305.1158.

2-methyl-1,3-diphenylpropan-1-one (Table 2, entry 26)³: Prepared from propiophenone (0.13 g, 1.0 mmol) and benzyl alcohol (0.22 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.19 g, 0.8 mmol, 86 %). ¹H NMR (400 MHz,

CDCl_3): $\delta = 7.94$ (d, $J = 8.6$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.30 – 7.18 (m, 5H), 3.81 – 3.73 (m, 1H), 3.19 (dd, $J = 13.7, 6.3$ Hz, 1H), 2.71 (dd, $J = 13.7, 7.8$ Hz, 1H), 1.22 (d, $J = 6.9$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 203.8, 140.0, 136.5, 133.0, 129.2, 128.7, 128.5, 128.4, 126.3, 42.8, 39.5, 17.5$ ppm. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{16}\text{O}$ ([M+H]): 225.1274, found: 225.1277.

3-phenyl-1-(thiophen-2-yl)propan-1-one (Table 2, entry 27)³: Prepared from 2-acetylthiophene (0.13 g, 1.0 mmol) and benzyl alcohol (0.22 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.17 g, 0.8 mmol, 81 %). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.69$ (d, $J = 4.5$ Hz, 1H), 7.62 (d, $J = 4.9$ Hz, 1H), 7.33 – 7.20 (m, 5H), 7.13 – 7.10 (m, 1H), 3.24 (t, $J = 7.6$ Hz, 2H), 3.08 (t, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 192.3, 144.3, 141.1, 133.7, 131.9, 128.7, 128.5, 128.2, 126.3, 41.2, 30.5$ ppm. HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{12}\text{OS}$ ([M+H]) : 217.0682, found : 217.0684.

1-(benzo[d][1,3]dioxol-5-yl)-3-(furan-2-yl)propan-1-one (Table 2, entry 28) ^{new}: Prepared from 3,4-methylenedioxy acetophenone (0.16 g, 1.0 mmol) and 2-furylmethanol (0.19 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a yellow solid (0.19 g, 0.8 mmol, 79 %). $M_p = 95\text{--}96$ °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.57$ (dd, $J = 8.2, 1.6$ Hz, 1H), 7.45 (d, $J = 1.5$ Hz, 1H), 7.30 (d, $J = 1.3$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.28 – 6.27 (m, 1H), 6.04 (s, 3H), 3.25 (t, $J = 7.6$ Hz, 2H), 3.06 (t, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.9, 155.0, 151.9, 148.4, 141.2, 131.8, 124.4, 110.4, 108.0, 108.0, 105.4, 102.0, 36.8, 22.8$ ppm. HRMS (ESI): calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_4\text{Na}$ ([M+Na]) : 267.0628, found : 267.0632.

1-(benzo[d][1,3]dioxol-5-yl)-3-(pyridin-2-yl)propan-1-one (Table 2, entry 29)¹⁵: Prepared from 3,4-methylenedioxy acetophenone (0.16 g, 1.0 mmol) and 2-pyridinemethanol (0.22 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.21 g, 0.8 mmol, 81 %). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.53$ (d, $J = 4.5$ Hz, 1H), 7.74 (m, 1H), 7.61 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.43 (m, 2H), 7.26 – 7.20 (m, 1H), 6.83 (d, $J = 8.2$ Hz, 1H), 6.03 (s, 2H), 3.52 (t, $J = 7.1$ Hz, 2H), 3.30 (t, $J = 7.1$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 197.2, 160.2, 152.0, 148.3, 147.4, 138.4, 131.7, 124.7, 124.6, 122.0, 108.0, 102.9, 37.8, 31.4$ ppm. HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_3$ ([M+H]) : 256.0968, found : 256.0971.

(8R,9S,13S,14S)-16-benzyl-3-hydroxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (Table 2, entry 30)¹⁶: Prepared from estrone (0.27 g, 1.0 mmol) and benzyl alcohol (0.32 g, 3.0 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.28 g, 0.7 mmol, 78 %), $M_p = 231\text{--}232$ °C. ^1H NMR (400 MHz, DMSO) $\delta = 8.99$ (s, 1H), 7.28 (t, $J = 7.3$ Hz, 2H), 7.20 (d, $J = 7.4$ Hz, 3H), 7.02 (d, $J = 8.4$ Hz, 1H), 6.50 (d, $J = 8.5$ Hz, 1H), 6.43 (s, 1H), 3.03 (dd, $J = 13.4, 3.9$ Hz, 1H), 2.70 (dd, $J = 17.5, 10.9$ Hz, 3H), 2.28 (d, $J = 12.6$ Hz, 1H), 2.11 (d, $J = 9.2$ Hz, 1H), 1.92 – 1.75 (m, 3H), 1.50 – 1.21 (m, 7H), 0.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO): $\delta = 155.4, 140.2, 137.5, 130.4,$

129.4, 128.7, 126.5, 126.4, 115.4, 113.2, 50.8, 48.3, 48.3, 44.0, 37.8, 37.1, 32.1, 29.4, 27.7, 26.7, 25.9, 13.8 ppm. HRMS (ESI): calcd. for $C_{25}H_{28}O_2$ ([M+H]) : 361.2162, found : 361.2151.

2-methyl-1-phenyldodecan-1-one (Table 2, entry 31) ^{new}: Prepared from propiophenone (0.13 g, 1.0 mmol) and 1-decanol (0.32 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.20 g, 0.7 mmol, 72 %). 1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.6 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 3.47 (m, 1H), 1.84 – 1.75 (m, 1H), 1.47 – 1.39 (m, 1H), 1.29 – 1.24 (m, 16H), 1.19 (d, J = 6.8 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.7, 136.9, 132.9, 128.7, 128.4, 40.7, 33.9, 32.0, 29.9, 29.7, 29.6, 29.4, 27.5, 22.8, 17.3, 14.2 ppm. HRMS (ESI): calcd. for $C_{19}H_{30}O$ ([M+H]) : 275.2369, found : 275.2381.

(8R,9S,10R,13S,14S)-3-hydroxy-10,13-dimethyl-16-(4-methylbenzyl)-3,4,7,8,9,10,11,12,13,14,15,16-dodecahydro-1H-cyclopenta[a]phenanthren-17(2H)-one (Table 2, entry 32) ^{new}: Prepared from *trans*-dehydroandrosterone (0.29 g, 1.0 mmol) and 4-methyl benzylalcohol (0.37 g, 3.0 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.30 g, 0.7 mmol, 76 %), M_p = 168–169 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.10 – 7.05 (m, 4H), 5.34 – 5.30 (m, 1H), 3.55 – 3.47 (m, 1H), 3.16 (dd, J = 13.7, 4.1 Hz, 1H), 2.61 (dd, J = 13.7, 9.8 Hz, 1H), 2.37 (d, J = 9.4 Hz, 1H), 2.32 (s, 3H), 2.21 (d, J = 11.2 Hz, 1H), 1.95 (dd, J = 11.6, 4.3 Hz, 1H), 1.88 – 1.80 (m, 4H), 1.69 – 1.62 (m, 2H), 1.52 – 1.43 (m, 3H), 1.31 (t, J = 6.4 Hz, 3H), 1.08 (s, 1H), 1.01 (s, 3H), 0.92 – 0.86 (m, 3H), 0.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 136.9, 135.9, 129.2, 129.0, 121.1, 71.8, 51.5, 50.5, 50.4, 48.2, 42.4, 37.4, 37.3, 36.8, 32.0, 31.7, 31.1, 31.1, 28.4, 22.8, 21.2, 20.5, 19.5, 14.5, 14.3, 13.5 ppm. HRMS (ESI): calcd. for $C_{27}H_{36}O_2Na$ ([M+Na]) : 415.2608, found : 415.2615.

2-((1-benzylpiperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (Scheme 2, compound 33) ¹⁴: Prepared from 5,6-dimethoxy indanone (0.19 g, 1.0 mmol) and (1-benzylpiperidin-4-yl)methanol (0.62 g, 3.0 mmol). After purification by column chromatography, the compound was isolated as a yellow semi-liquid (0.18 g, 0.46 mmol, 46 %). 1H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.31 (m, 4H), 7.27 – 7.23 (m, 1H), 7.15 (s, 1H), 6.84 (s, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.56 (s, 2H), 3.22 (dd, J = 17.6, 8.1 Hz, 1H), 2.96 – 2.92 (m, 2H), 2.71 – 2.65 (m, 2H), 2.06 – 1.99 (m, 2H), 1.93 – 1.86 (m, 1H), 1.71 – 1.67 (m, 2H), 1.45 – 1.25 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.8, 155.6, 149.5, 148.8, 137.6, 129.5, 129.4, 128.3, 127.3, 107.4, 104.5, 63.2, 56.3, 56.2, 45.5, 38.7, 34.3, 33.5, 32.7, 31.6 ppm. HRMS (ESI): calcd. for $C_{24}H_{29}NO_3$ ([M+H]): 380.2220, found : 380.2226.

(1-benzylpiperidin-4-yl)methanol (Scheme 2, compound 34) ¹⁹: Prepared from 4-piperidinemethanol (0.50 g, 4.34 mmol) and benzyl alcohol (1.41 g, 13.02 mmol). After purification by column chromatography, the compound was isolated as a light yellow semi-liquid (0.63 g, 3.09 mmol, 71 %). 1H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.29 (m, 5H), 3.52 (d, J = 4.0

Hz, 2H), 3.50 – 3.47 (m, 2H), 2.92 (d, J = 11.2 Hz, 2H), 1.98 (t, J = 11.6 Hz, 3H), 1.71 (d, J = 12.7 Hz, 2H), 1.50 (br, 1H), 1.31 (d, J = 11.9 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 138.3, 129.4, 128.3, 127.2, 68.0, 63.5, 53.5, 38.6, 28.8 ppm. HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}$ ([M+H]): 206.1539, found : 206.1543.

2-phenylquinoline (Table 3, entry 35) ¹⁷: Prepared from 2-aminobenzyl alcohol (0.12 g, 1.0 mmol) and acetophenone (0.14 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.18 g, 0.9 mmol, 89 %), Mp = 81-82 °C. ^1H NMR (400 MHz, CDCl_3): δ = 8.25 – 8.18 (m, 4H), 7.85 (dd, J = 19.0, 8.3 Hz, 2H), 7.74 (t, J = 8.4 Hz, 1H), 7.56 – 7.46 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 157.4, 148.2, 139.6, 137.1, 129.9, 129.7, 129.5, 129.0, 127.7, 127.6, 127.3, 126.4, 119.1 ppm. HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{11}\text{N}$ ([M+H]) : 206.0964, found : 206.0975.

2-(*p*-tolyl) quinoline (Table 3, entry 36) ¹⁷: Prepared from 2-aminobenzyl alcohol (0.12 g, 1.0 mmol) and 4'-methyl acetophenone (0.16 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.20 g, 0.9 mmol, 91 %), Mp = 82-83 °C. ^1H NMR (400 MHz, CDCl_3): δ = 8.21 (d, J = 8.6 Hz, 2H), 8.08 (d, J = 8.1 Hz, 2H), 7.84 (dd, J = 18.6, 8.3 Hz, 2H), 7.73 (t, J = 7.7 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 157.4, 139.7, 137.0, 137.0, 136.7, 129.9, 129.7, 129.6, 127.7, 127.6, 127.2, 126.3, 119.1, 21.5 ppm. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{13}\text{N}$ ([M+H]) : 220.1121, found : 220.1117.

2-(4-fluorophenyl) quinoline (Table 3, entry 37) ¹⁷: Prepared from 2-aminobenzyl alcohol (0.12 g, 1.0 mmol) and 4'-fluoro acetophenone (0.16 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.19 g, 0.8 mmol, 86 %), Mp = 93-94 °C. ^1H NMR (400 MHz, CDCl_3): δ = 8.24 – 8.15 (m, 4H), 7.83 (d, J = 8.5 Hz, 2H), 7.74 (t, J = 7.0 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 8.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 163.9 (d, J = 249.3 Hz), 156.3, 137.2, 135.8 (d, J = 2.4 Hz), 130.0, 129.6 (d, J = 8.5 Hz), 129.0, 127.8, 127.6, 127.2, 126.5, 118.8, 115.9 (d, J = 21.6 Hz) ppm. ^{19}F NMR (376 MHz, CDCl_3): δ = -113.3 ppm. HRMS (ESI): calcd. for $\text{C}_{15}\text{H}_{10}\text{NF}$ ([M+H]) : 224.0870, found : 224.0869.

3-methyl-2-phenylquinoline (Table 3, entry 38) ¹⁷: Prepared from 2-aminobenzyl alcohol (0.12 g, 1.0 mmol) and propiophenone (0.16 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.18 g, 0.8 mmol, 82 %). ^1H NMR (400 MHz, CDCl_3): δ = 8.19 (d, J = 8.3 Hz, 1H), 8.04 (s, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 8.2 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.55 – 7.43 (m, 4H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 160.6, 146.6, 140.9, 137.0, 129.4, 129.3, 129.0, 128.9, 128.4, 128.3, 127.7, 126.8, 126.6, 20.7 ppm. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{13}\text{N}$ ([M+H]) : 220.1121, found : 220.1115.

3-ethyl-2-phenylquinoline (Table 3, entry 39)¹⁷: Prepared from 2-aminobenzyl alcohol (0.12 g, 1.0 mmol) and butyrophenone (0.18 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.18 g, 0.8 mmol, 78 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.25 – 8.11 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.57 – 7.44 (m, 6H), 2.81 (q, J = 7.5 Hz, 2H), 1.21 (t, J = 7.5 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = ¹³C NMR (100 MHz, CDCl₃): δ = 160.4, 145.1, 135.7, 135.5, 129.3, 128.9, 128.5, 128.5, 127.9, 127.6, 127.1, 126.8, 126.0, 26.1, 14.8 ppm. HRMS (ESI): calcd. for C₁₇H₁₅N ([M+H]) : 234.1277, found : 234.1283.

5,6-dihydrobenzo[c]acridine (Table 3, entry 40)¹⁷: Prepared from 2-aminobenzyl alcohol (0.12 g, 1.0 mmol) and 1-tetralone (0.17 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.21 g, 0.9 mmol, 91 %), Mp = 65-66 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.62 (d, J = 7.6 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.91 (s, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.28 (d, J = 7.4 Hz, 1H), 3.12 (t, J = 7.7 Hz, 2H), 3.01 (t, J = 7.7 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 147.6, 139.5, 134.7, 133.9, 130.7, 129.8, 129.4, 128.8, 128.1, 128.0, 127.4, 127.0, 126.2, 126.2, 28.9, 28.5 ppm. HRMS (ESI): calcd. for C₁₇H₁₃N ([M+H]) : 232.1121, found : 232.1122.

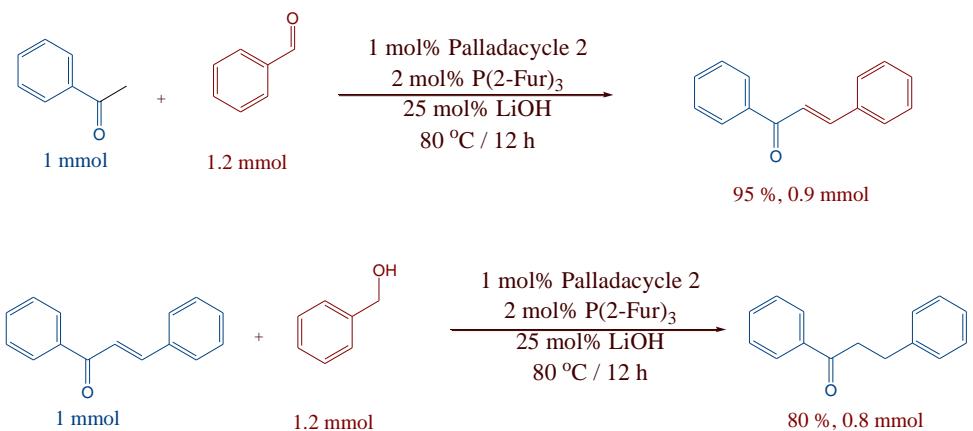
2-propylquinoline (Table 3, entry 41)¹⁸: Prepared from 2-aminobenzyl alcohol (0.12 g, 1.0 mmol) and 2-pentanone (0.10 g, 1.2 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.12 g, 0.7 mmol, 68 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.11 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.7 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 2.99 (d, J = 7.7 Hz, 2H), 1.90 – 1.81 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.0, 147.7, 136.6, 129.6, 128.7, 127.6, 126.9, 125.9, 121.5, 41.1, 23.4, 14.1 ppm. HRMS (ESI): calcd. for C₁₂H₁₃N ([M+H]): 172.1121, found: 172.1126.

Computational Details: All the calculations were performed using Gaussian 09 software²⁰. The geometries were optimized using DFT functional B3LYP^{21,22} with LANL2DZ^{23,24} basis set for Pd and 6-31G(d,p)²⁵ basis set for other atoms. The stationary points were characterized using harmonic frequencies using the same level of theory. The nature of the transition states were confirmed by intrinsic reaction coordinate (IRC)²⁶ calculations. Thermal corrections were calculated at 333.15 K, the reaction temperature.

References:

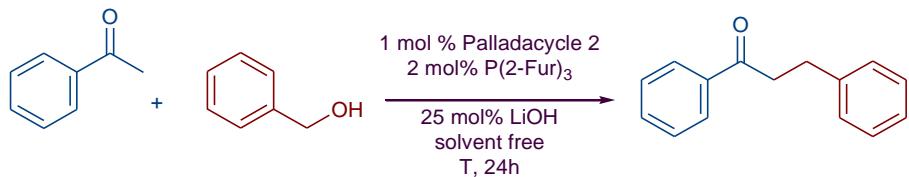
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Scheme S1: Controlled experiments

Table S1: Optimization of α -alkylation of acetophenone with benzyl alcohol using palladacycles^a



S.No.	Base	T (°C)	Yield ^b (%)
1 ^c	LiOH	50	56
2	LiOH	50	78
3	LiOH	60	82
4	LiOH	80	98
5	LiOH.H ₂ O	80	89
6	CsOH.H ₂ O	80	92
7	KO ^t Bu	80	ND
8	Cs ₂ CO ₃	80	ND
9	K ₃ PO ₄	80	ND
10	KOH	80	Trace
11	NaOH	80	Trace
12	Li ₂ CO ₃	80	21
13 ^d	LiOH	80	ND
14 ^e	LiOH	80	Trace
15 ^f	LiOH	80	ND
16 ^c	LiOH	80	91

^aReaction conditions: Acetophenone 1.0 mmol, benzyl alcohol 1.2 mmol, LiOH 0.25 mmol, palladacycle **1** 1×10^{-2} mmol, P(2-Fur)₃ 2×10^{-2} mmol. ^bIsolated yield after column chromatography. ^cPalladacycle **1** was used, ^dInstead of Palladacycle **2**, 2 mol% Pd(OAc)₂ was used. ^eInstead of Palladacycle **2**, 2 mol% PdCl₂ was used. ^fInstead of Palladacycle **2**, 1 mol% Pd₂(dba)₃ was used. ND: Not Detected.

Table S2. Energetics for both the reactions using **PP1**, **PP2**, and **PP3**.

Stationary Points (<i>k</i>)	Structures ^a	$\Delta G_k(\text{PP1})$ (kcal/mol)	$\Delta G_k(\text{PP2})$ (kcal/mol)	$\Delta G_k(\text{PP3})$ (kcal/mol)	$\Delta\Delta G_{21}^b$	$\Delta\Delta G_{31}^c$
1	PPn + Li-BA	0.0	0.0	0.0	0.0	0.0
2	PPn-Int1	-19.8	-21.8	-21.4	-2.0	-1.6
3	PPn-TS1	-10.8	-16.3	-11.9	-5.5	-1.1
4	PPn-Int2	-30.7	-41.5	-29.6	-10.8	1.1
5	PPn-Benz	-9.2	-19.8	-9.2	-10.6	0.0
6	PPn-TS2	51.1	42.4		-8.7	
7	PPn-H	-23.6	-42.2	-21.9	-18.6	1.7
8	PPn-Alko	-5.8	-16.2	-5.0	-10.4	0.8
9	Li-Alko + PPn-Benz	-23.8	-34.3	-23.8	-10.5	0.0

^a***n*=1, 2, 3**

^b $\Delta\Delta G_{21} = \Delta G_k(\text{PP2}) - \Delta G_k(\text{PP1})$

^c $\Delta\Delta G_{31} = \Delta G_k(\text{PP3}) - \Delta G_k(\text{PP1})$

Table S3: Crystal data and structure refinement parameters for the palladacycle **1**, **2** and compound **30**

	Palladacycle 1	Palladacycle 2	Compound 30
Empirical formula	C ₄₉ H ₃₆ N ₄ O ₄ F ₆ Pd ₂ Cl ₂	C ₄₉ H ₃₆ Cl ₂ F ₆ N ₄ O ₄ Pd ₂	C ₂₅ H ₂₈ O ₂ P
Mr	1142.52	1142.52	360.47
T [K]	296.15	296.15	296.15
wavelength [Å]	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	Triclinic	Orthorhombic	Monoclinic
space group	P-1	Pccn	P2 ₁
a [Å]	12.5806(4)	27.3687(6)	7.3530(2)
b [Å]	13.4047(4)	7.6079(2)	11.9596(3)
c [Å]	16.5104(8)	22.5235(5)	11.5356(3)
α [°]	110.580(2)	90	90
β [°]	106.147(2)	90	99.870(2)
γ [°]	99.622(2)	90	90
V [Å ³]	2392.68(16)	4689.81(19)	999.41(5)
Z	2	4	2
ρ _{calc} [g cm ⁻³]	1.586	1.618	1.198
μ (MoKα) [mm ⁻¹]	0.934	0.954	0.074
F (000)	1140.0	2280.0	388.0
Crystal size [mm]	0.27 × 0.22 × 0.2	0.25 × 0.22 × 0.18	0.18 × 0.15 × 0.10
θ range [°]	2.74 – 28.32	2.78 – 26.79	2.47 – 28.17
limiting indices	-16<=h<=15 -17<=k<=17 -22<=l<=22	-34 ≤ h ≤ 34, -9 ≤ k ≤ 9, -28 ≤ l ≤ 28	-9 ≤ h ≤ 9, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
reflns collected	39212	58819	11323
independent reflns	11845	5005 [R(int) = 0.0522]	4688 [R(int) = 0.0233]
absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
refinement method	Full-matrix least square on F ²	Full-matrix least square on F ²	Full-matrix least square on F ²
data / restraints / parameters	11845 / 0 / 607	5005/0/304	4688/1/248
Goodness-of-fit on F ²	1.014	1.063	1.042
final R indices	R ₁ = 0.0369	R ₁ = 0.0380	R ₁ = 0.0404
[I > 2σ(I)] [a]	wR ₂ = 0.0877	wR ₂ = 0.0873	wR ₂ = 0.0961
R indices (all data) [a]	R ₁ = 0.0568	R ₁ = 0.0536	R ₁ = 0.0503
	wR ₂ = 0.1003	wR ₂ = 0.0962	wR ₂ = 0.1025
peak _{max} /hole _{min} [e Å ⁻³]	0.83 and -0.57	0.77/-0.85	0.21/-0.20

^[a] R₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR₂ = $\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

Figure S1

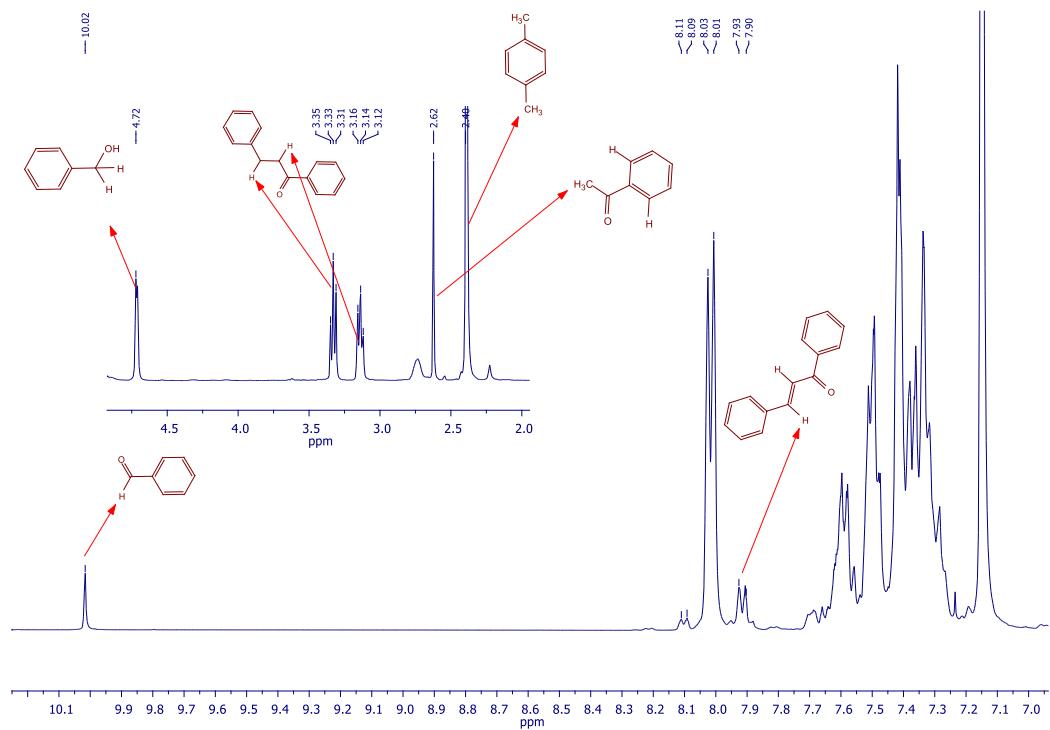
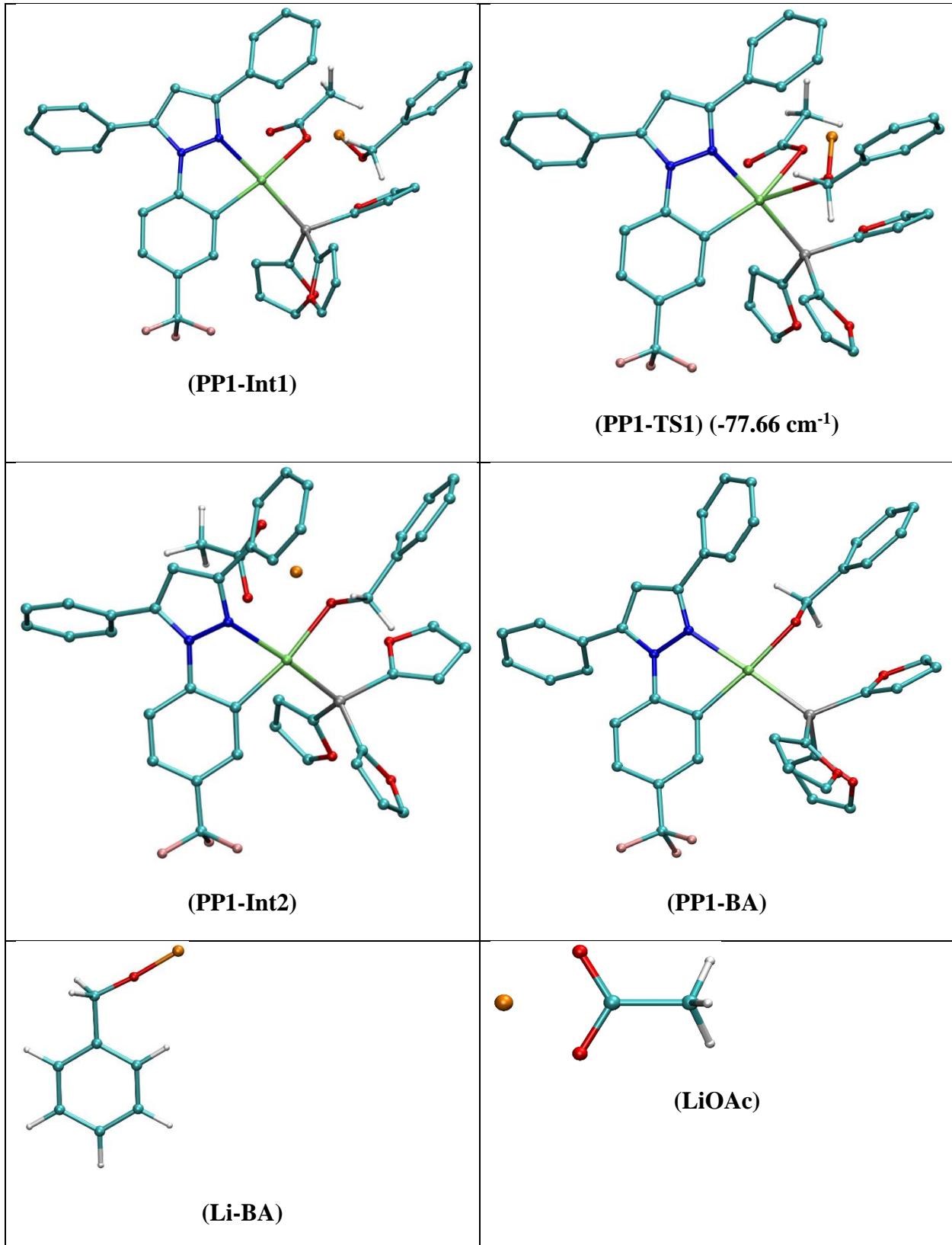


Figure S1. ^1H NMR spectrum of the reaction mixture of acetophenone using benzyl alcohol after 12 h at 60 °C.

Figure S2



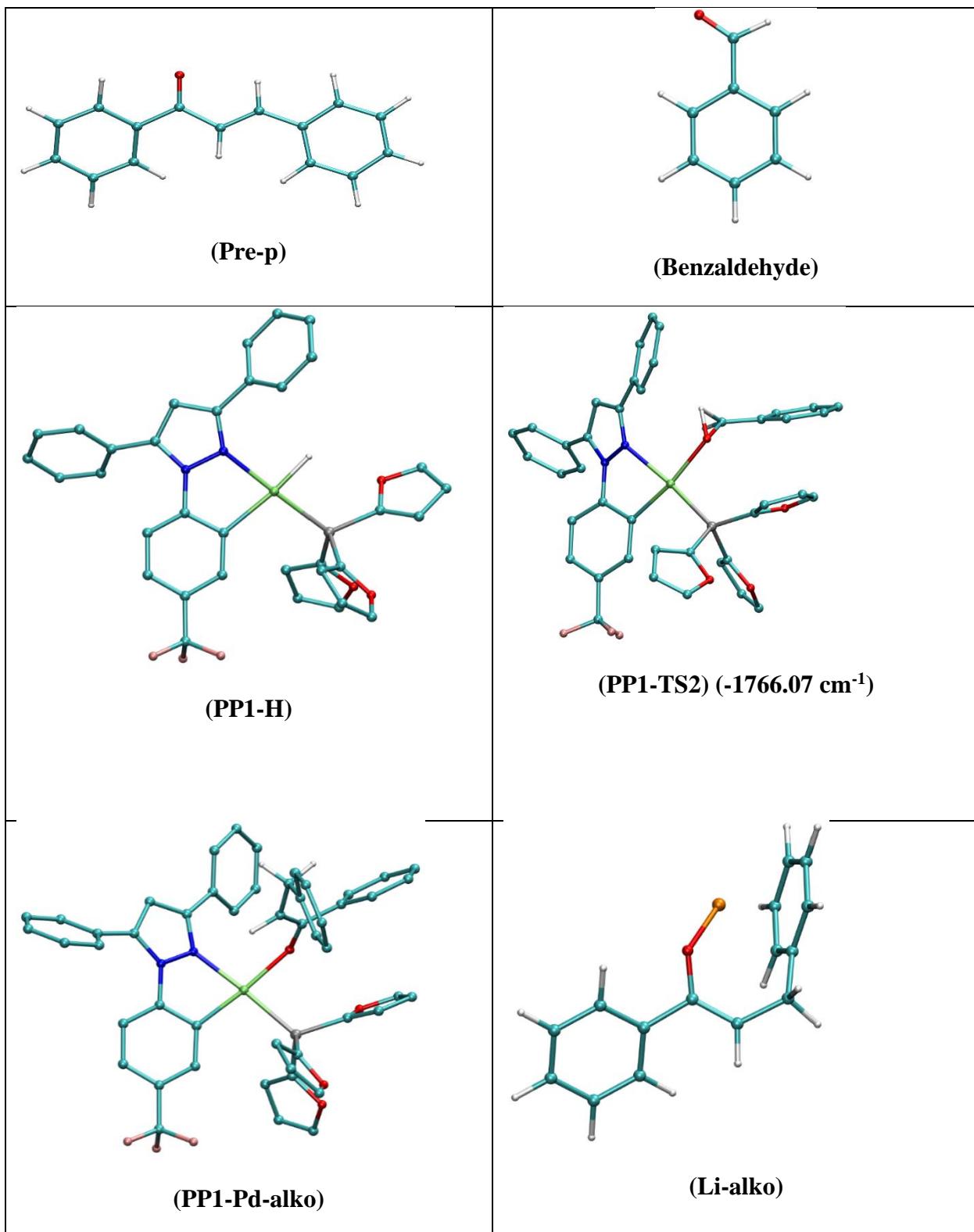
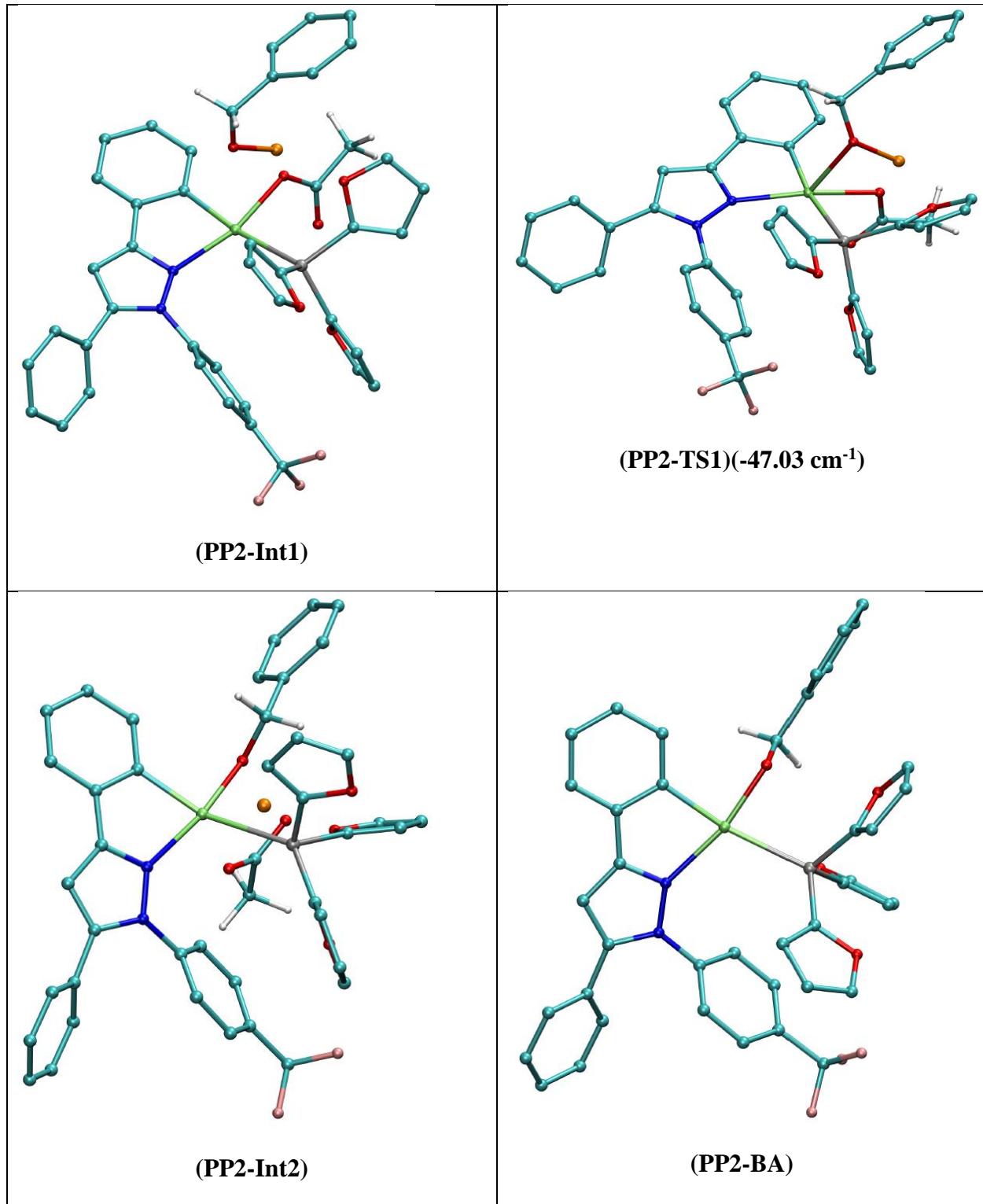


Figure S2. Optimized geometries of stationary states formed when **PP1** reacts with **Li-BA**.

Figure S3



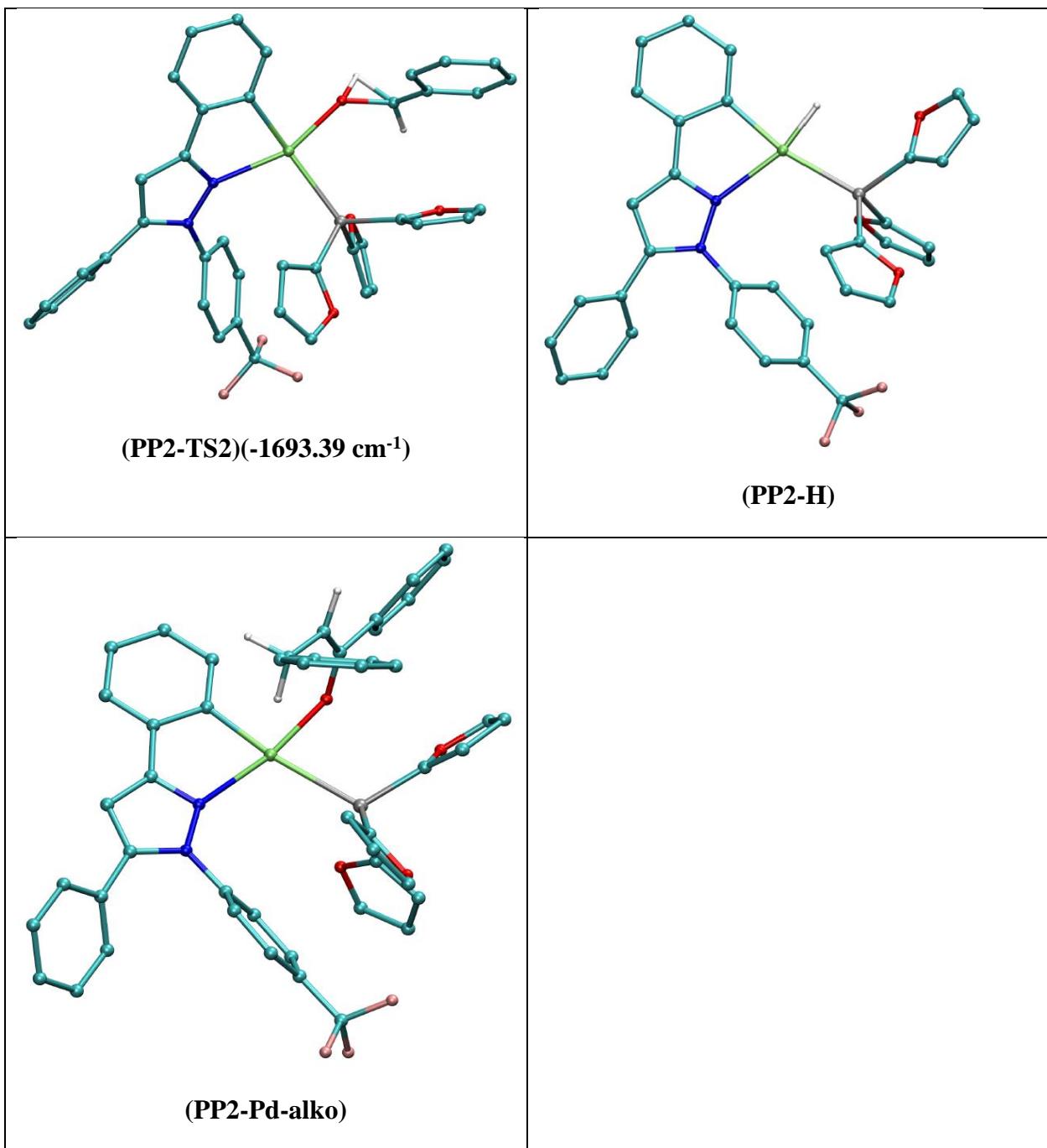


Figure S3. Optimized geometries of intermediates and transition states formed when catalyst **PP2** reacts with **Li-BA**.

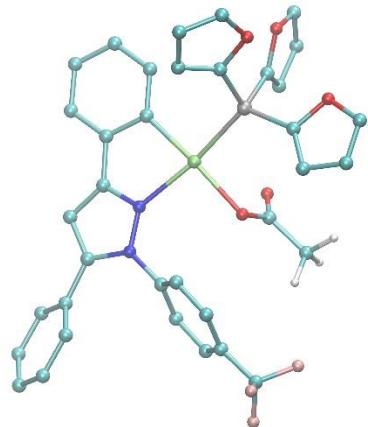
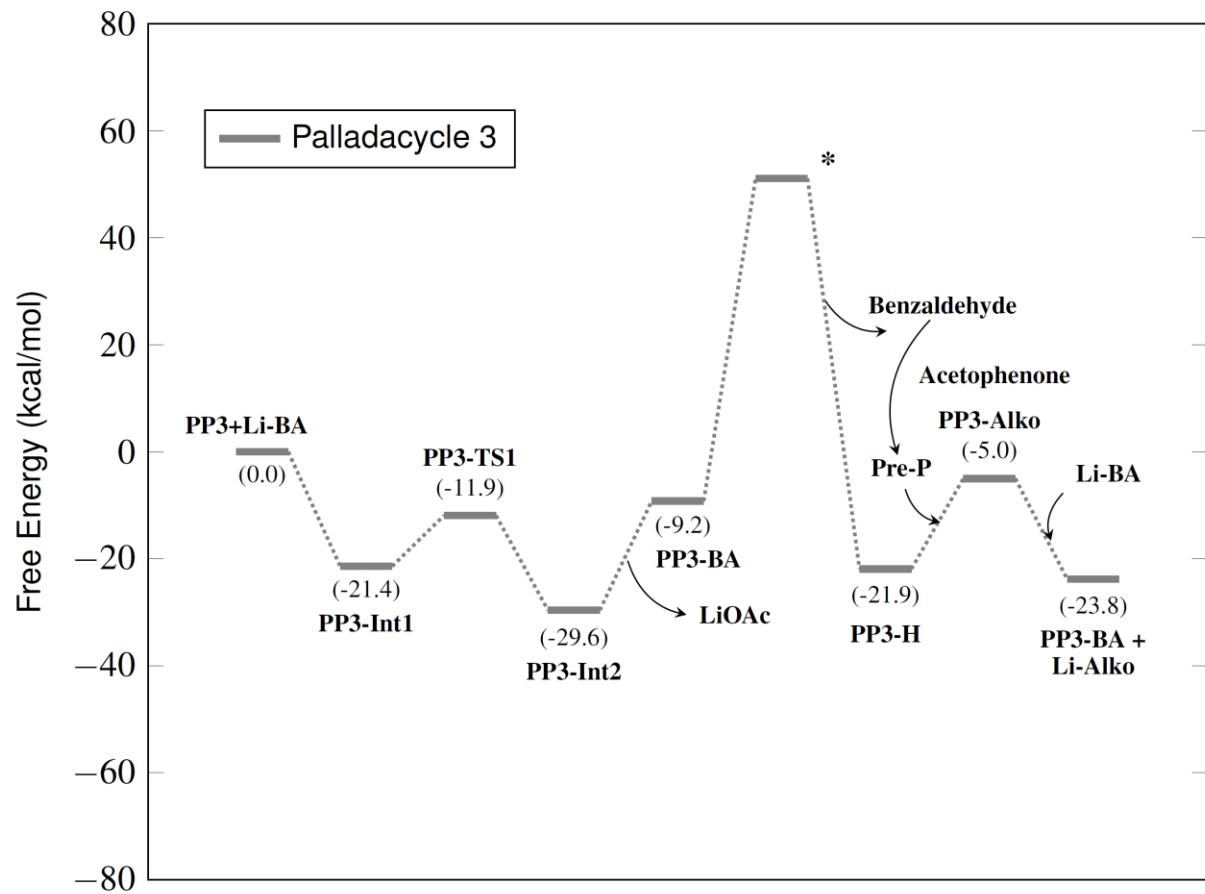


Figure S4. (top) Free energy profile for reaction between **Li-BA** with **PP3**. (*) indicates that transition state could not be optimized; (bottom) Optimized geometry of palladacycle-phosphine catalysts **2** (**PP3**). Phenyl & furyl H atoms not shown for clarity.

NMR Spectra for important and new compounds

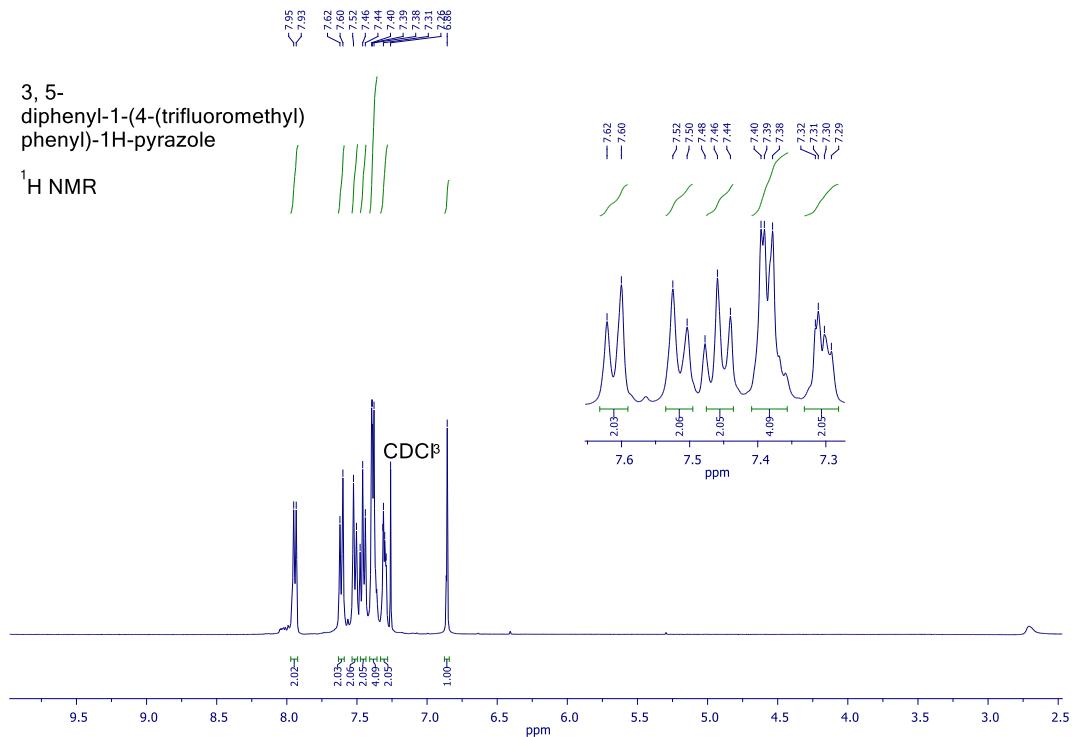


Figure S5.¹H NMR of 3, 5-diphenyl-1-(4-(trifluoromethyl) phenyl)-1H-pyrazole.

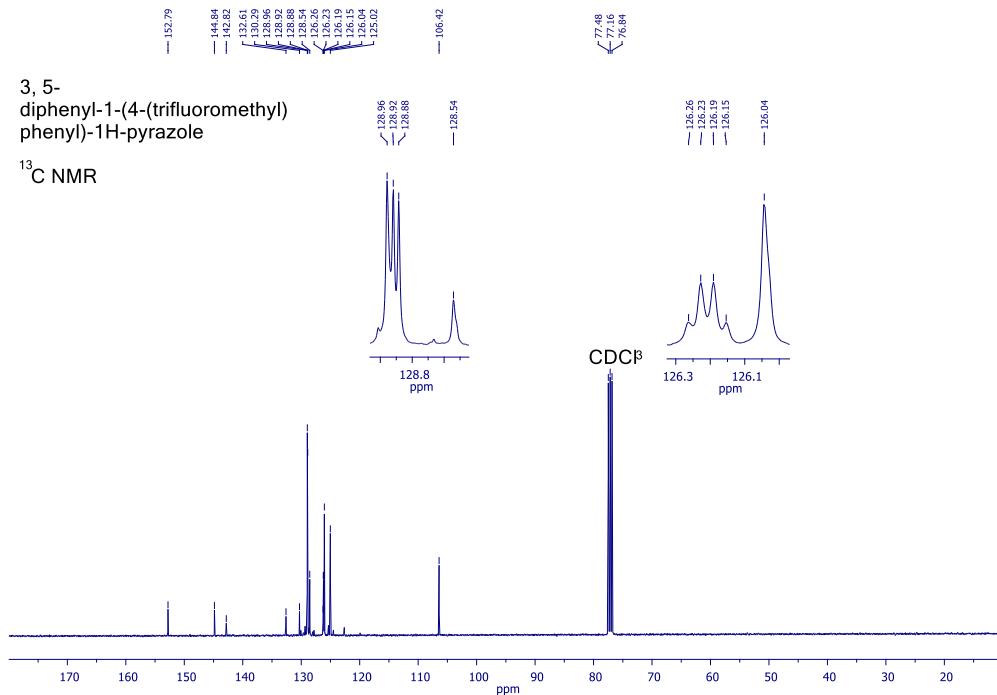


Figure S6. ^{13}C NMR of 3, 5-diphenyl-1-(4-(trifluoromethyl) phenyl)-1H-pyrazole.

3, 5-
diphenyl-1-(4-(trifluoromethyl)
phenyl)-1H-pyrazole

¹⁹F NMR

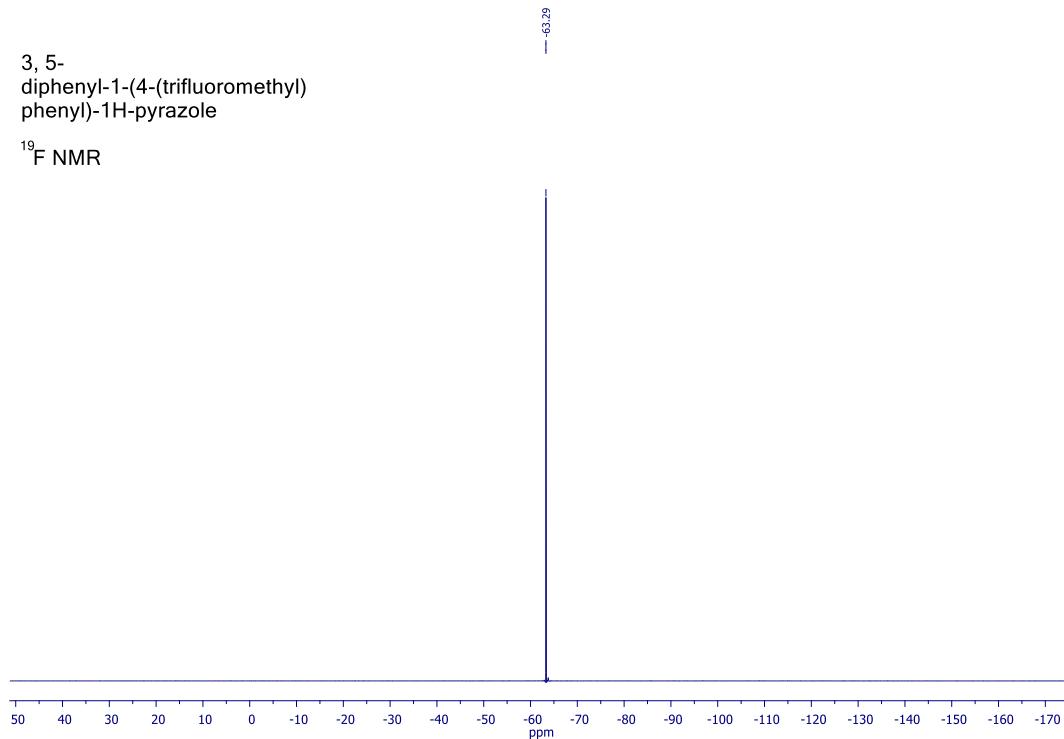


Figure S7. ^{19}F NMR of 3, 5-diphenyl-1-(4-(trifluoromethyl) phenyl)-1H-pyrazole.

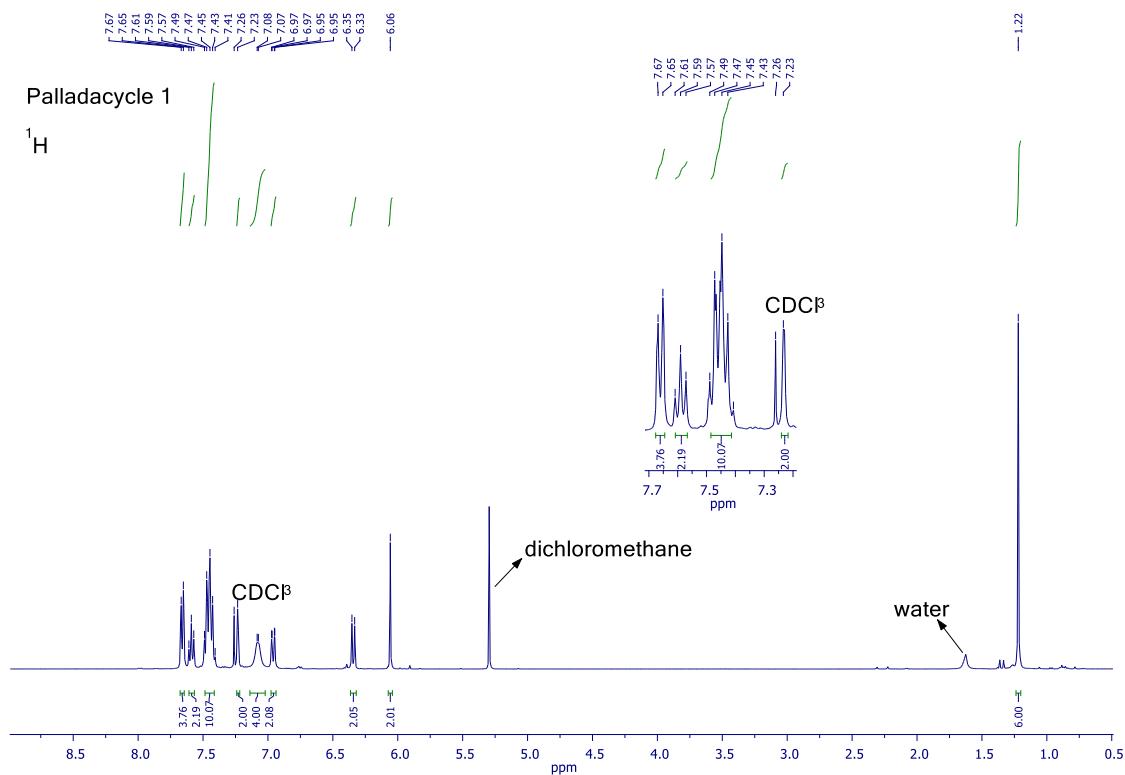


Figure S8. ^1H NMR of palladacycle **1**.

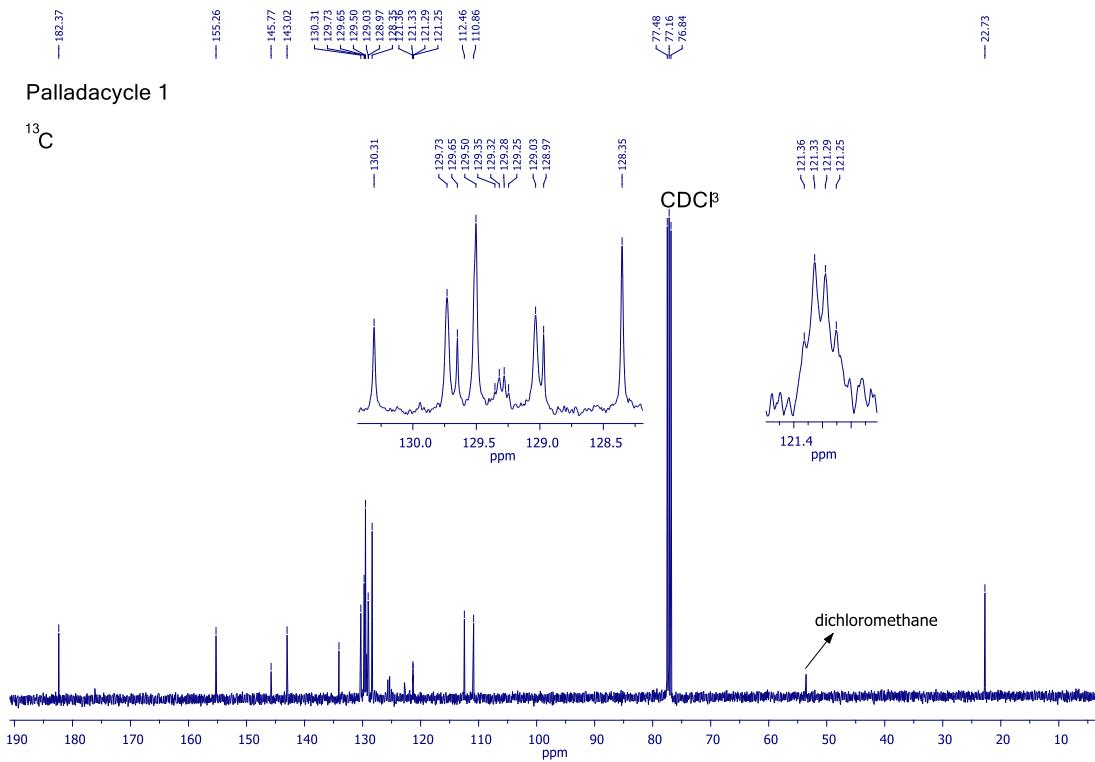


Figure S9. ^{13}C NMR of palladacycle 1.

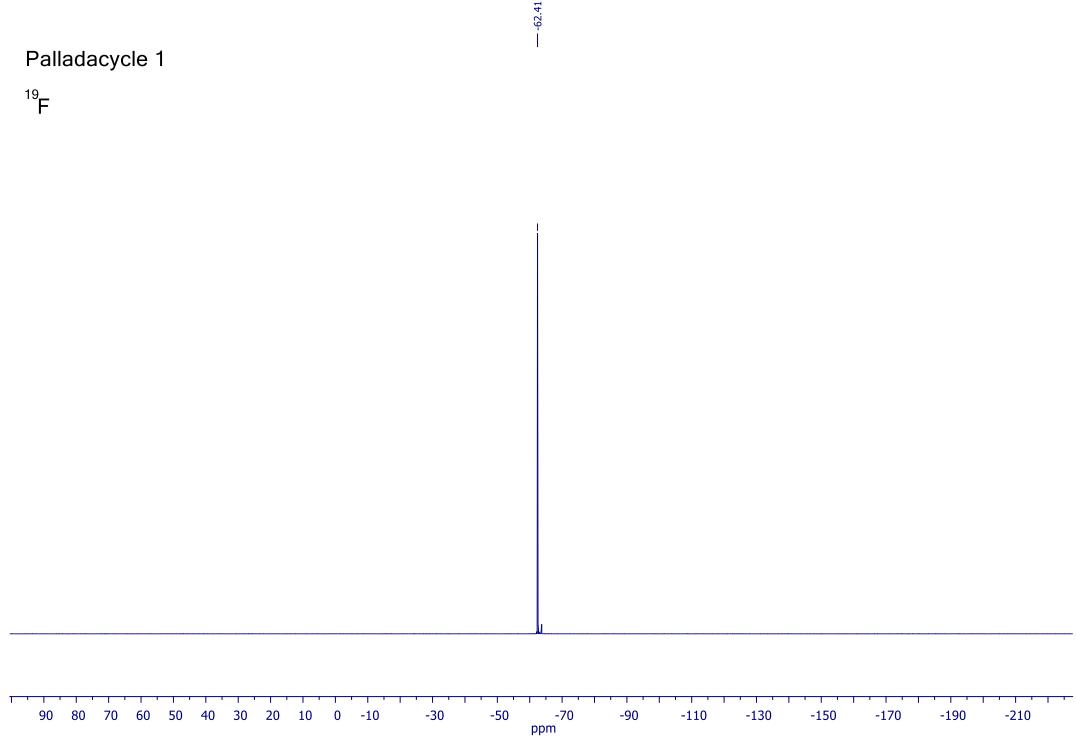


Figure S10. ^{19}F NMR of palladacycle 1.

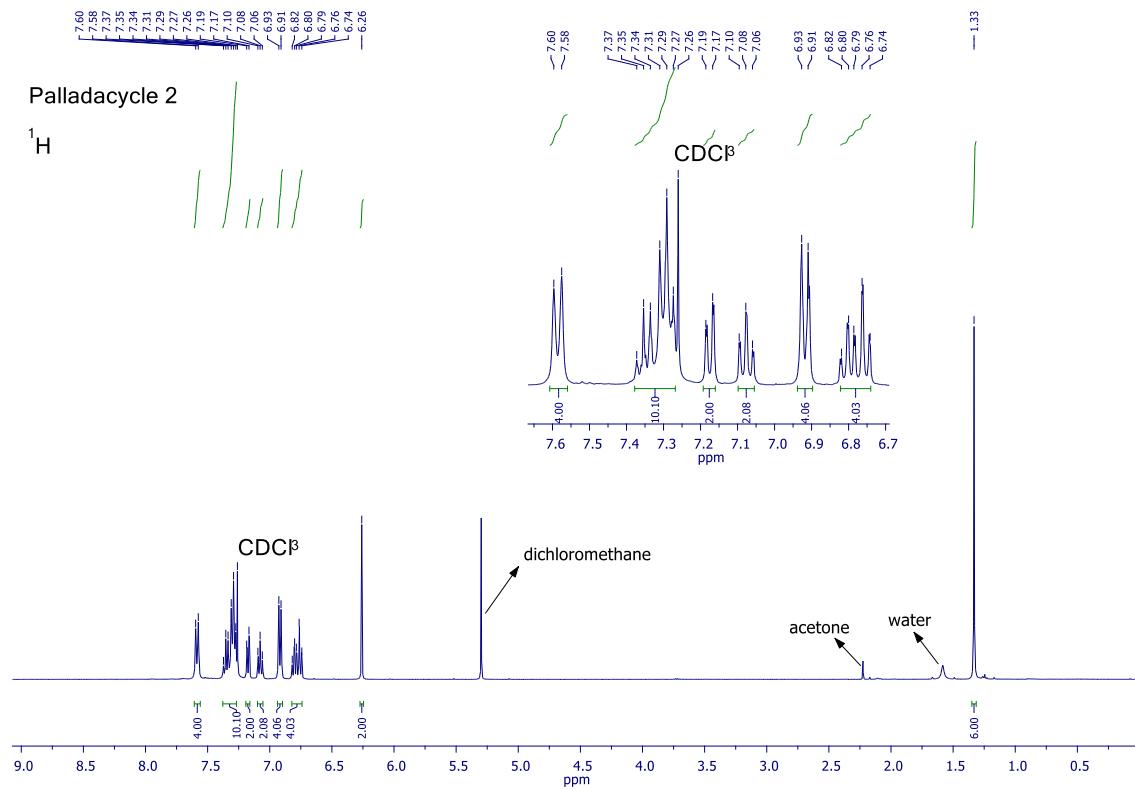


Figure S11.¹H NMR of palladacycle **2**.

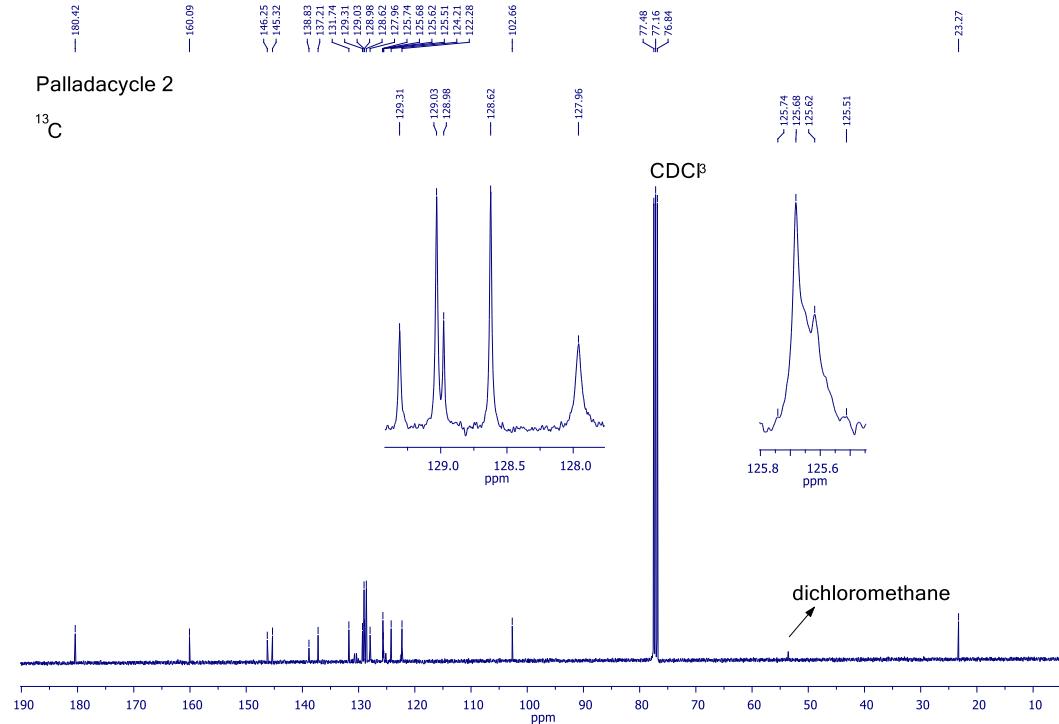


Figure S12. ^{13}C NMR of palladacycle **2**.

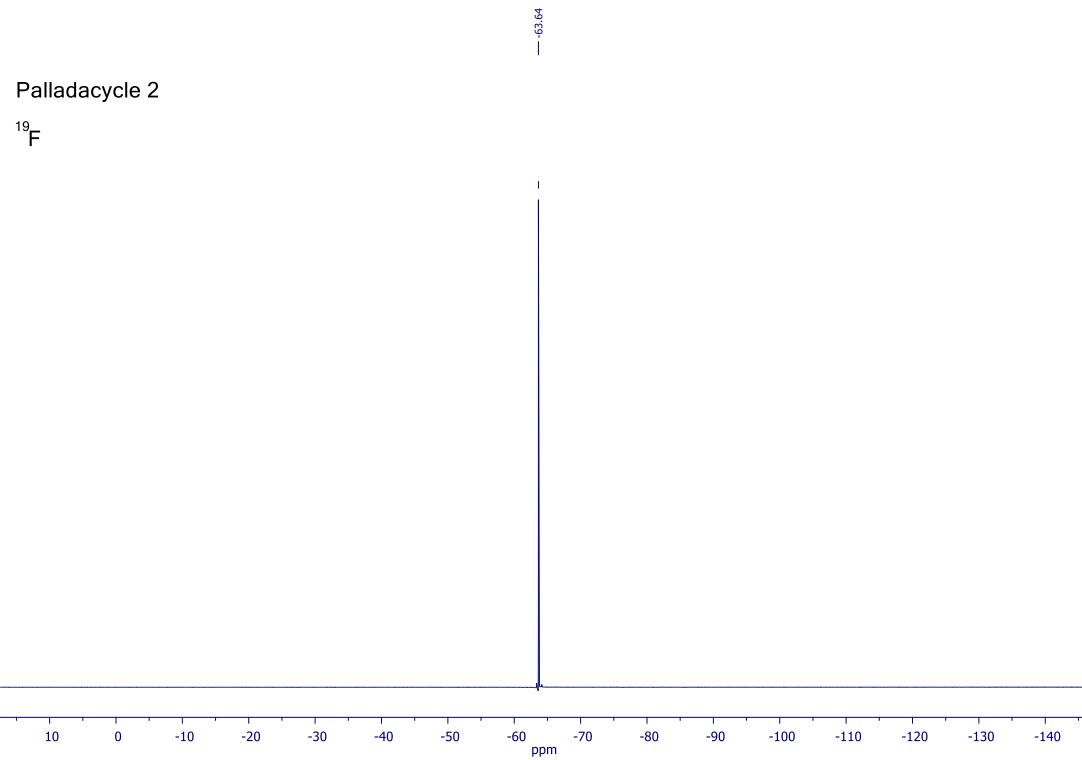


Figure S13. ^{19}F NMR of palladacycle 2.

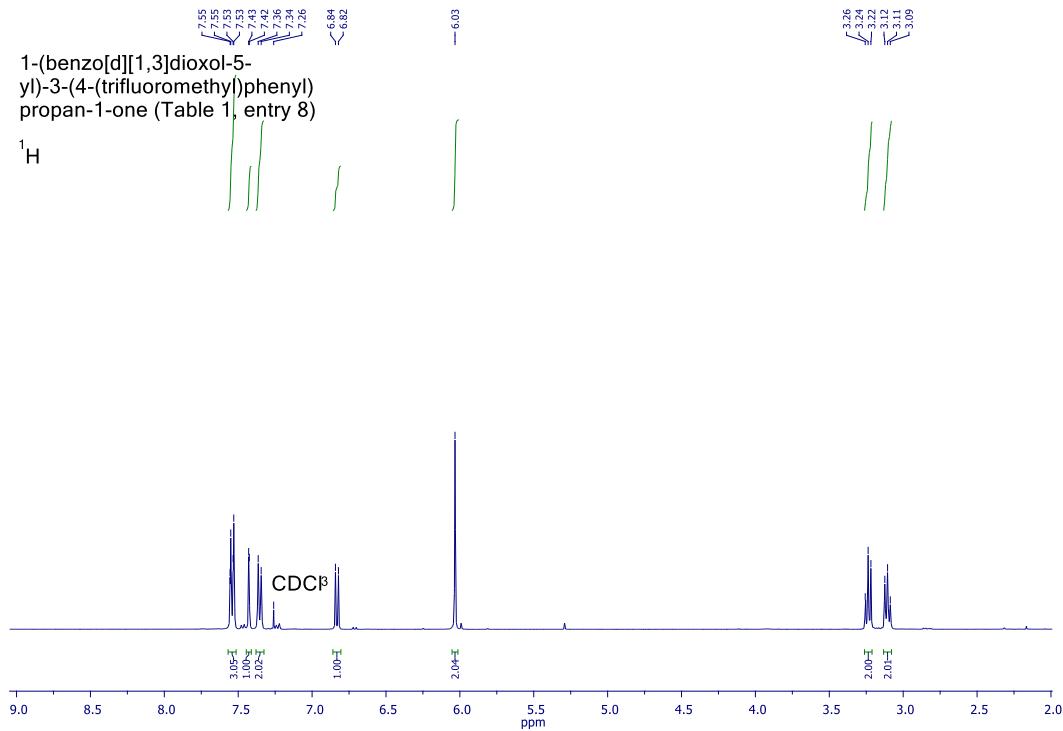


Figure S14. ^1H NMR of 1-(benzo[d][1,3]dioxol-5-yl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (Table 1, entry 8).

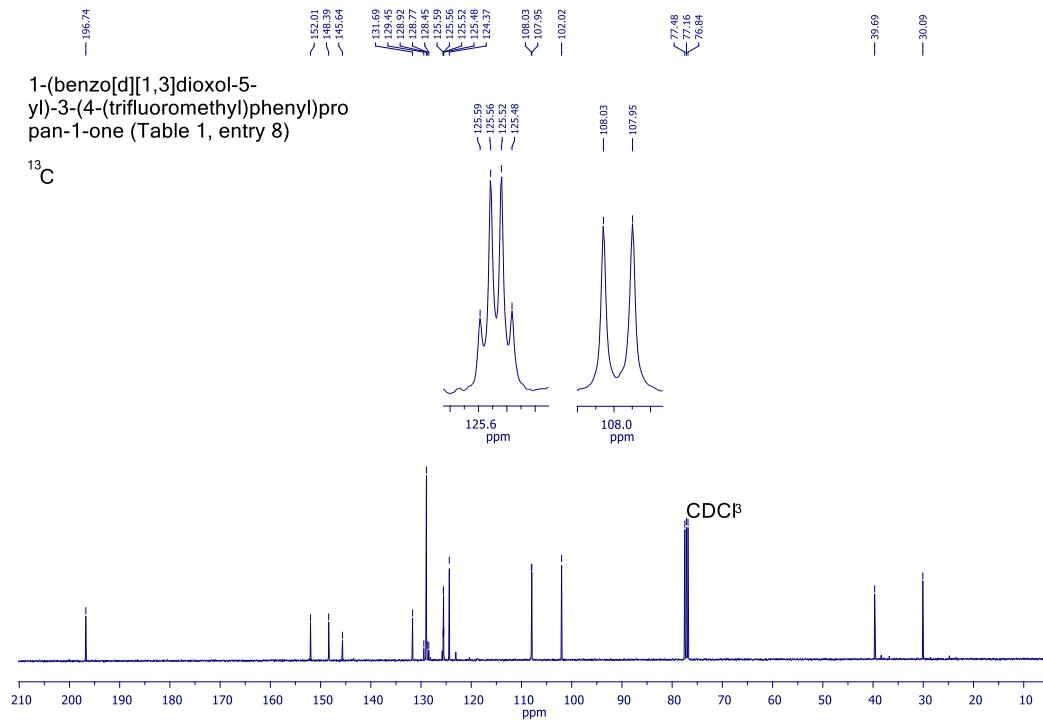


Figure S15. ¹³C NMR of 1-(benzo[d][1,3]dioxol-5-yl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (Table 1, entry 8).

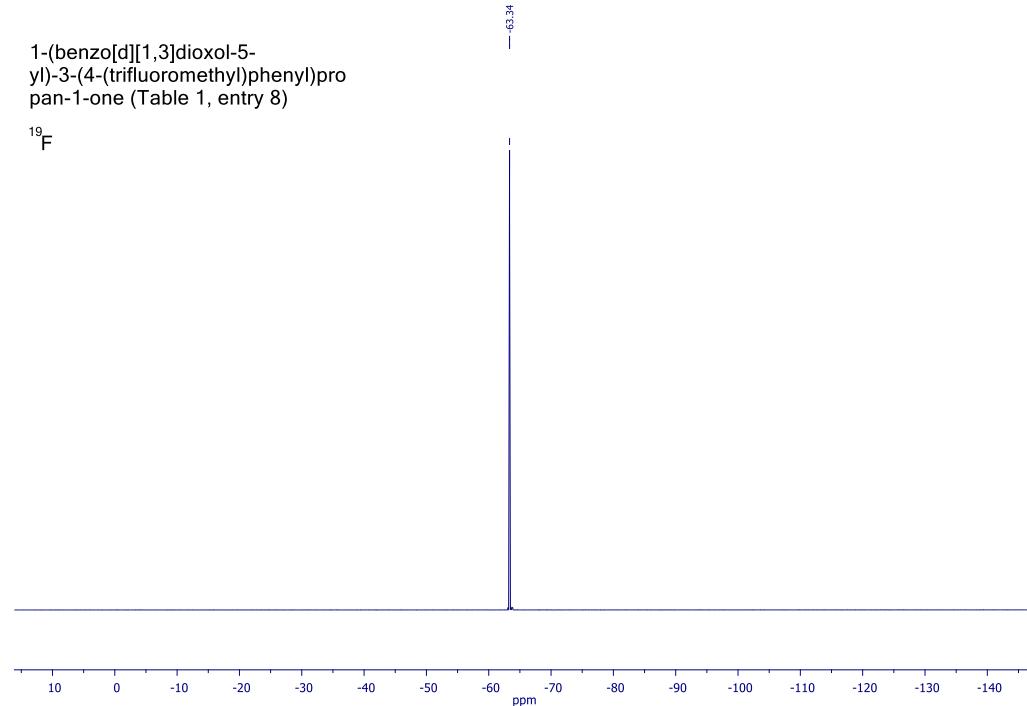


Figure S16. ¹⁹F NMR of 1-(benzo[d][1,3]dioxol-5-yl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (Table 1, entry 8).

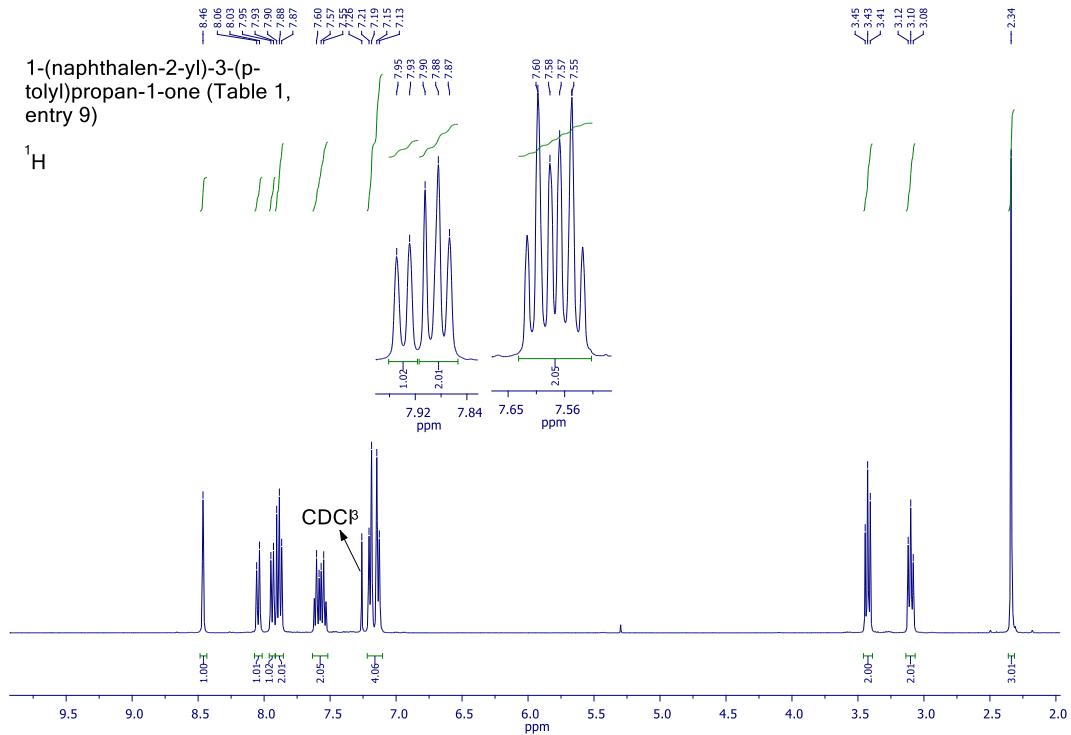


Figure S17.¹H NMR of 1-(naphthalen-2-yl)-3-(p-tolyl)propan-1-one (Table 1, entry 9).

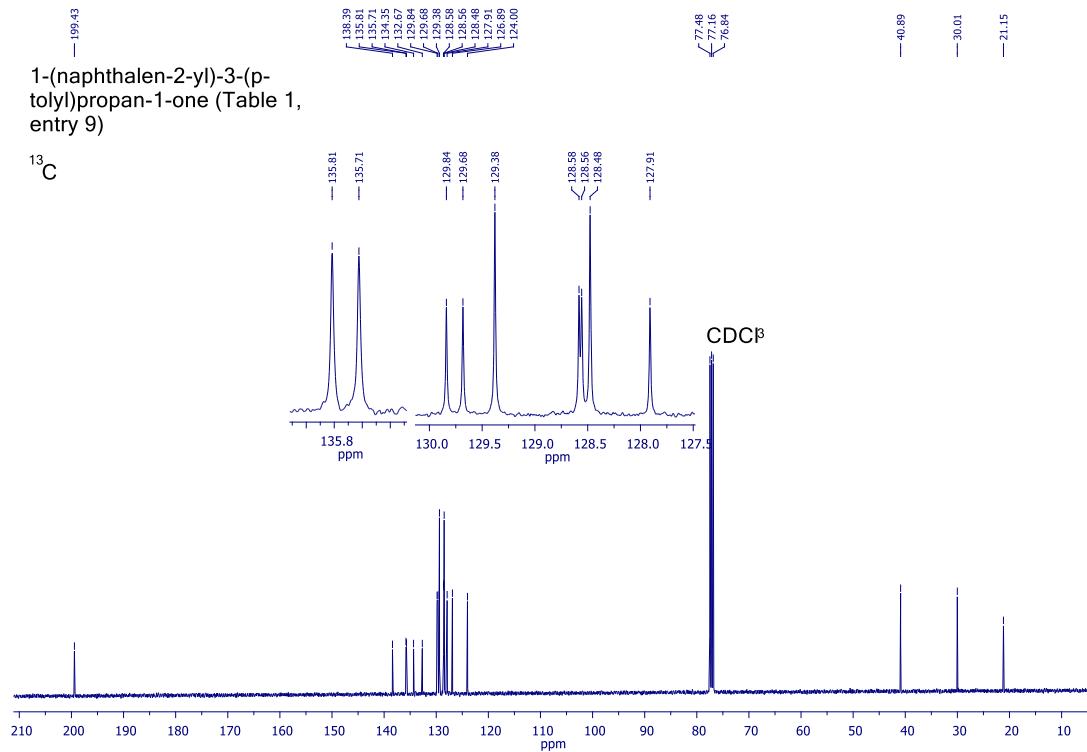


Figure S18. ^{13}C NMR of 1-(naphthalen-2-yl)-3-(p-tolyl)propan-1-one (Table 1, entry 9).

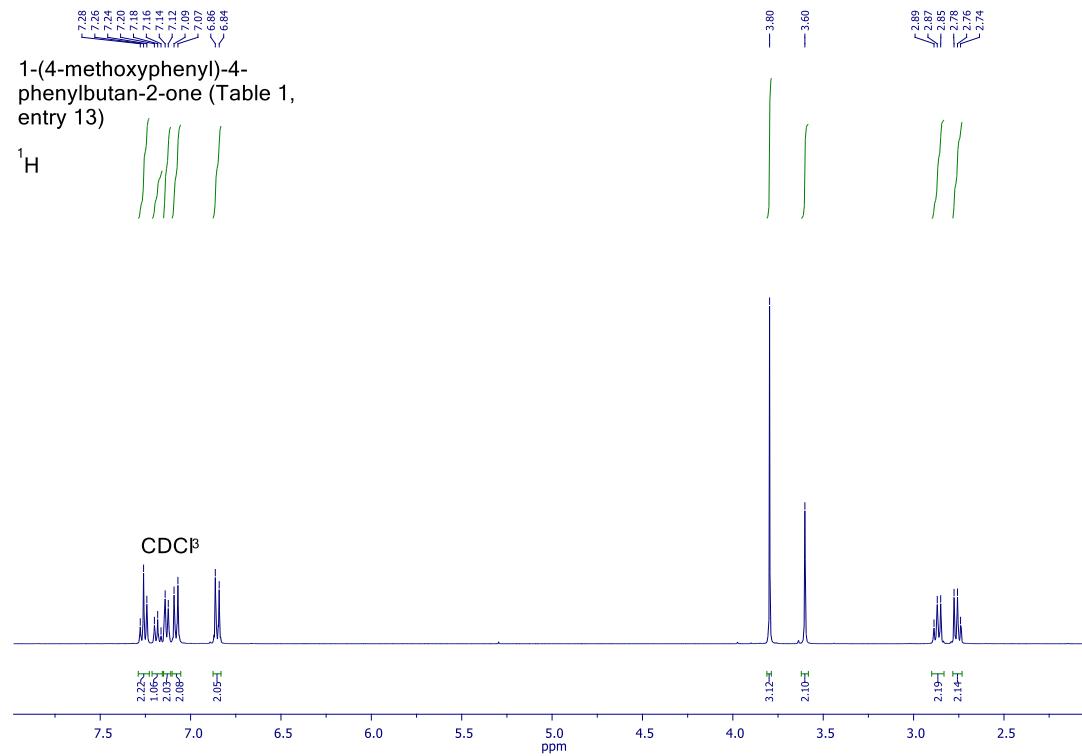


Figure S19. ¹H NMR of 1-(4-methoxyphenyl)-4-phenylbutan-2-one (Table 1, entry 13).

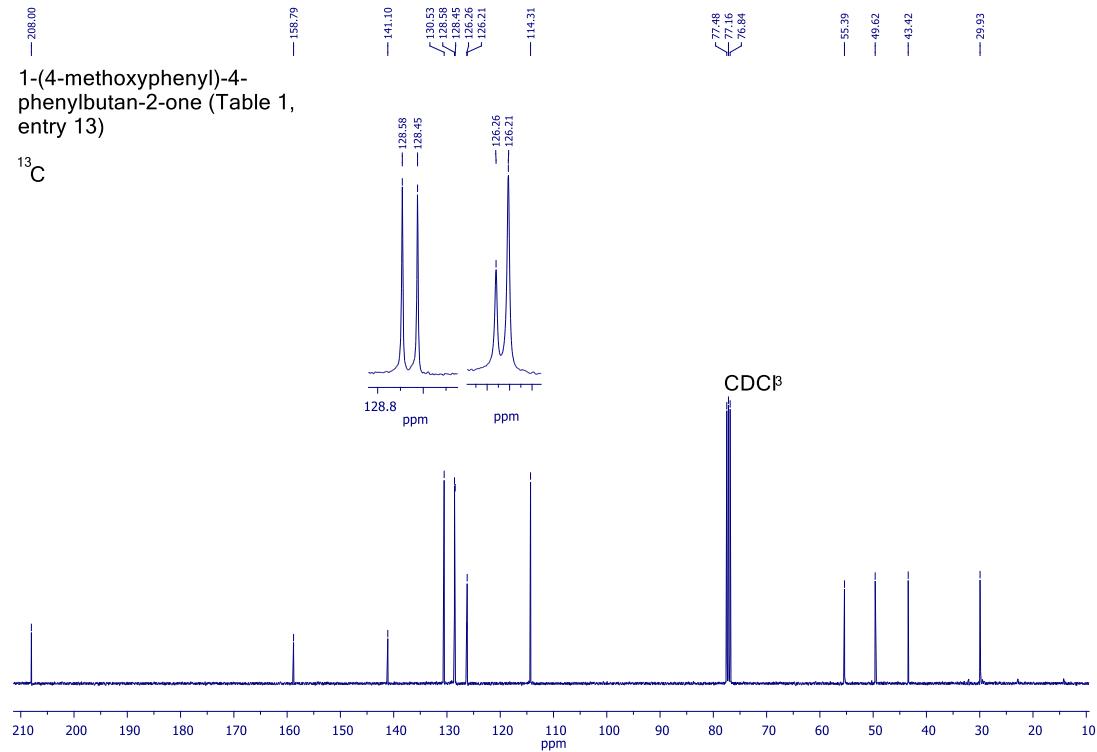


Figure S20. ¹³C NMR of 1-(4-methoxyphenyl)-4-phenylbutan-2-one (Table 1, entry 13).

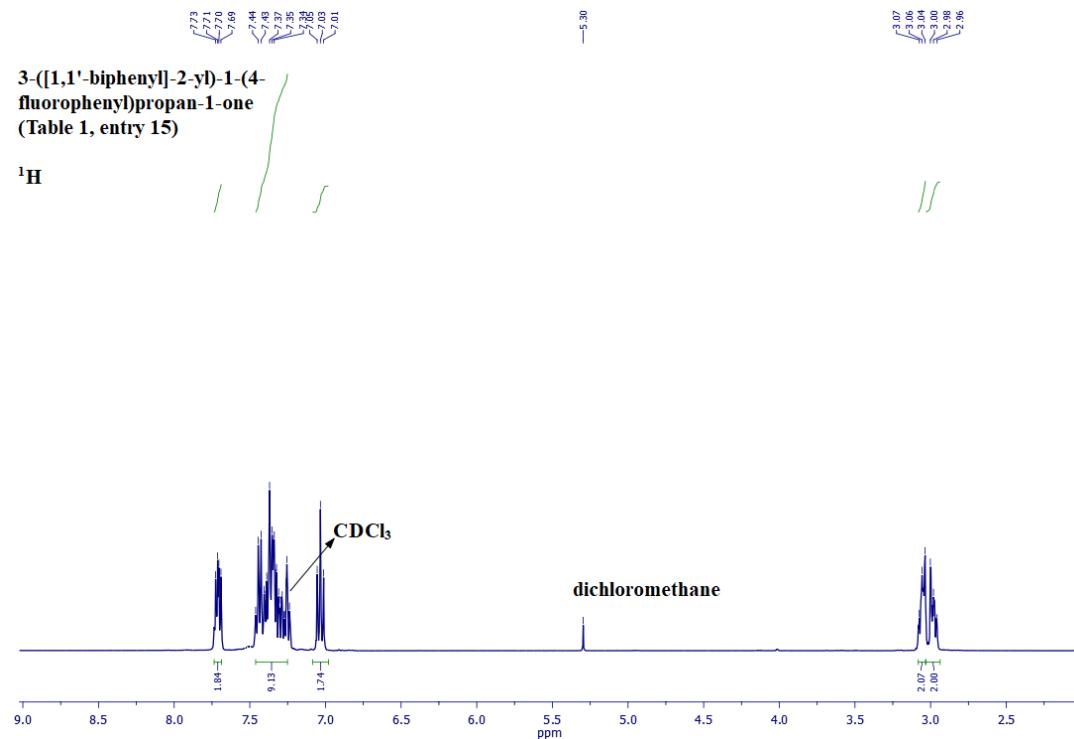


Figure S21. ^1H NMR of 3-([1,1'-biphenyl]-2-yl)-1-(4-fluorophenyl)propan-1-one (Table 1, entry 15).

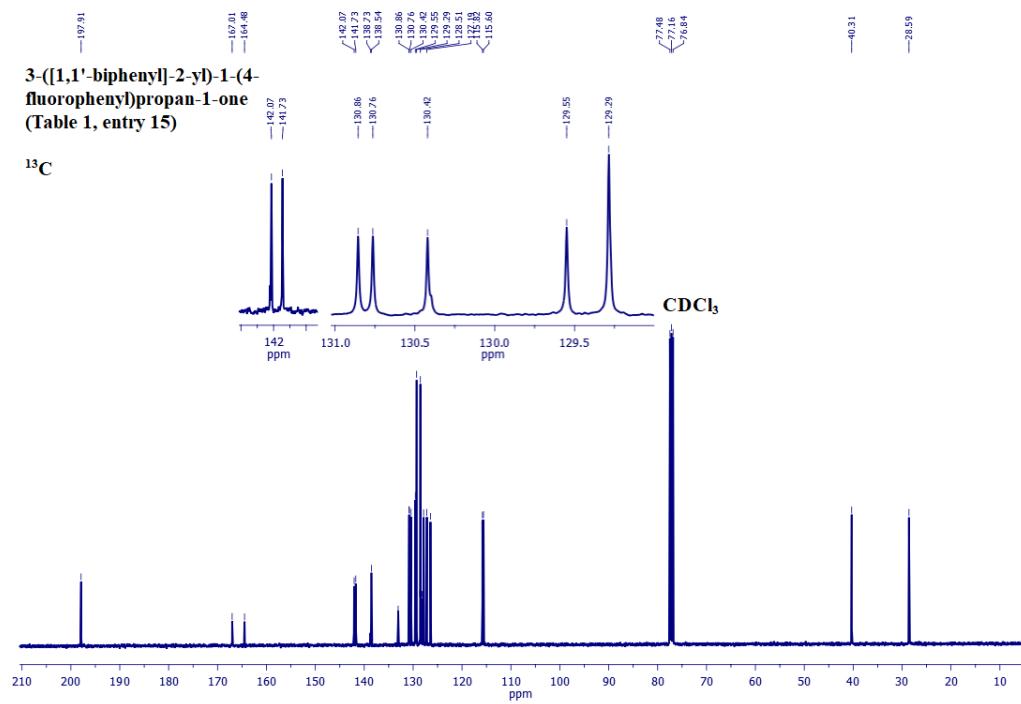


Figure S22.¹³C NMR of 3-([1,1'-biphenyl]-2-yl)-1-(4-fluorophenyl)propan-1-one (Table 1, entry 15).

3-([1,1'-biphenyl]-2-yl)-1-(4-fluorophenyl)propan-1-one
(Table 1, entry 15)

^{19}F

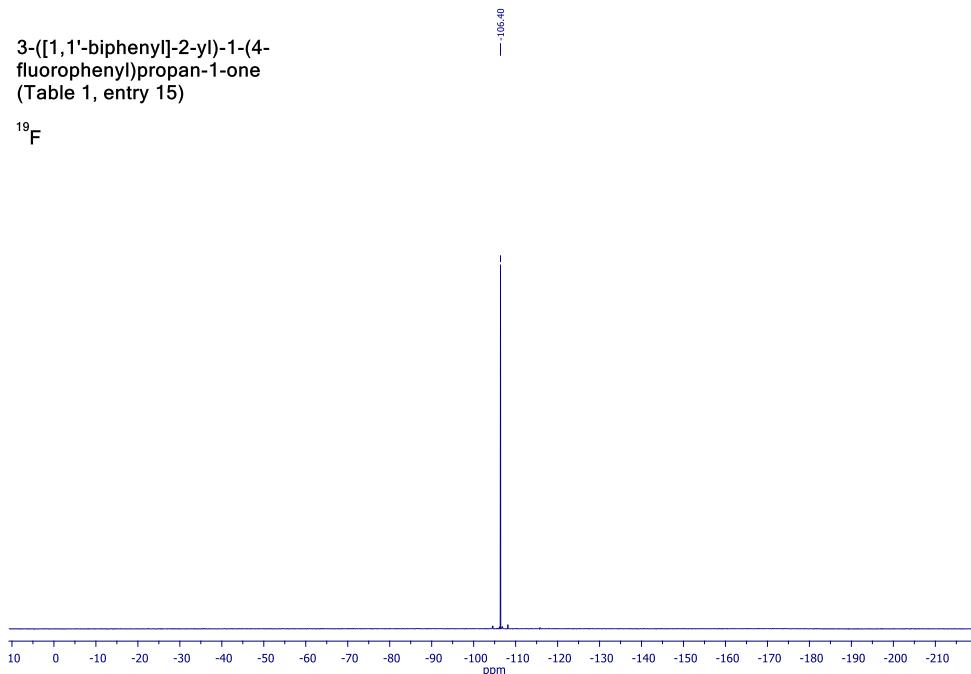


Figure S23. ^{19}F NMR of 3-([1,1'-biphenyl]-2-yl)-1-(4-fluorophenyl)propan-1-one (Table 1, entry 15).

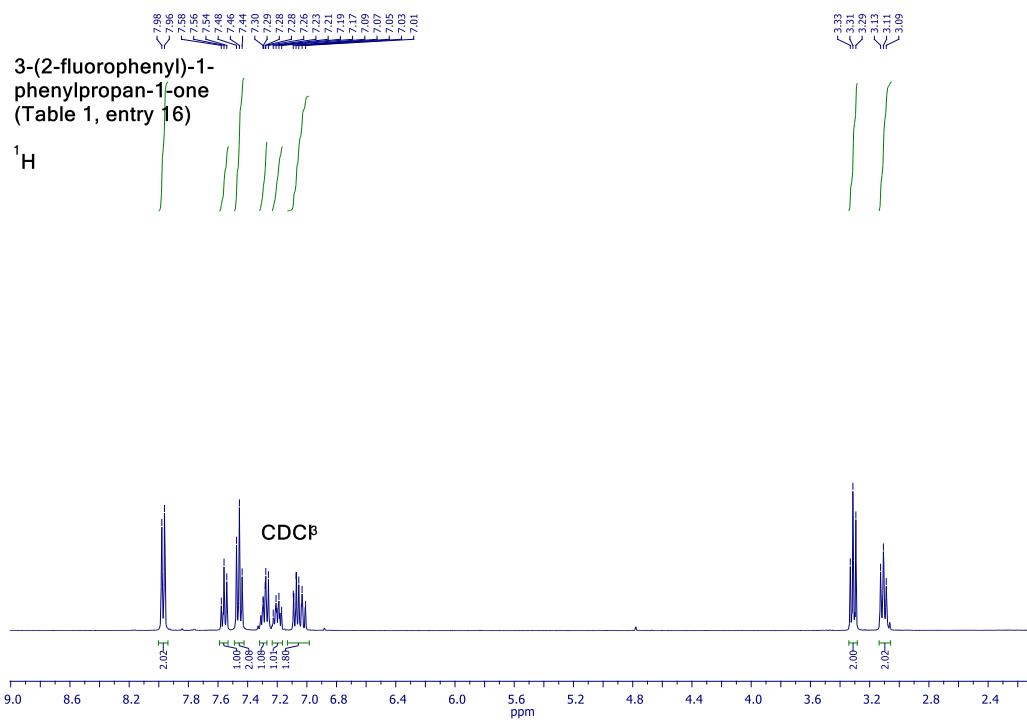


Figure S24. ^1H NMR of 3-(2-fluorophenyl)-1-phenylpropan-1-one (Table 1, entry 16).

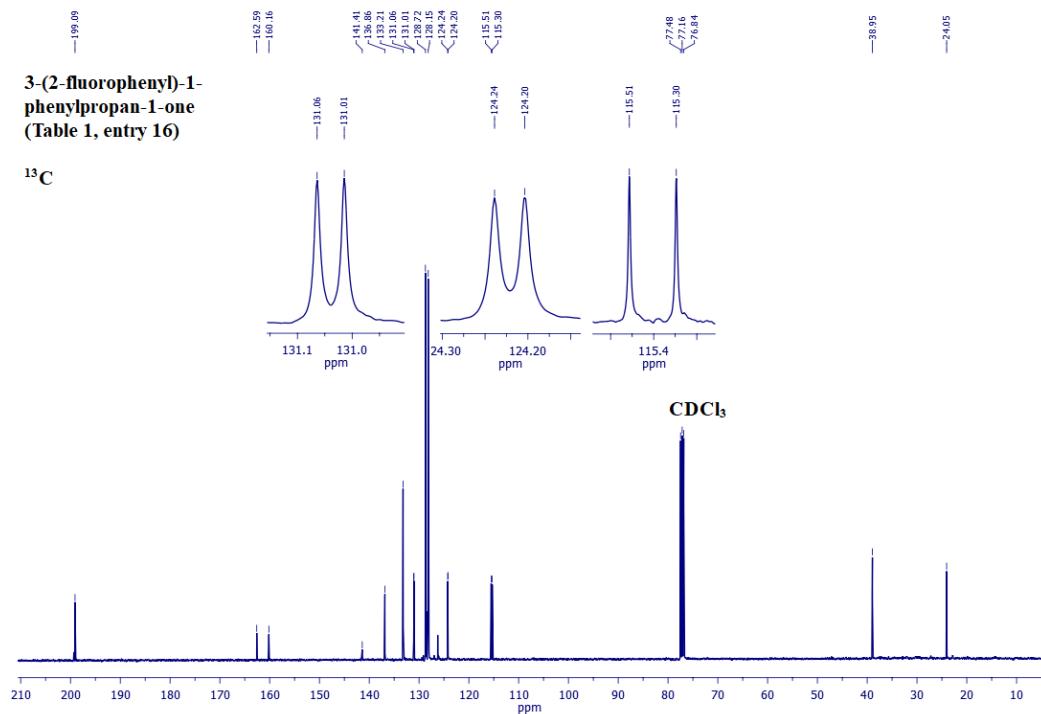


Figure S25. ¹³C NMR of 3-(2-fluorophenyl)-1-phenylpropan-1-one (Table 1, entry 16).

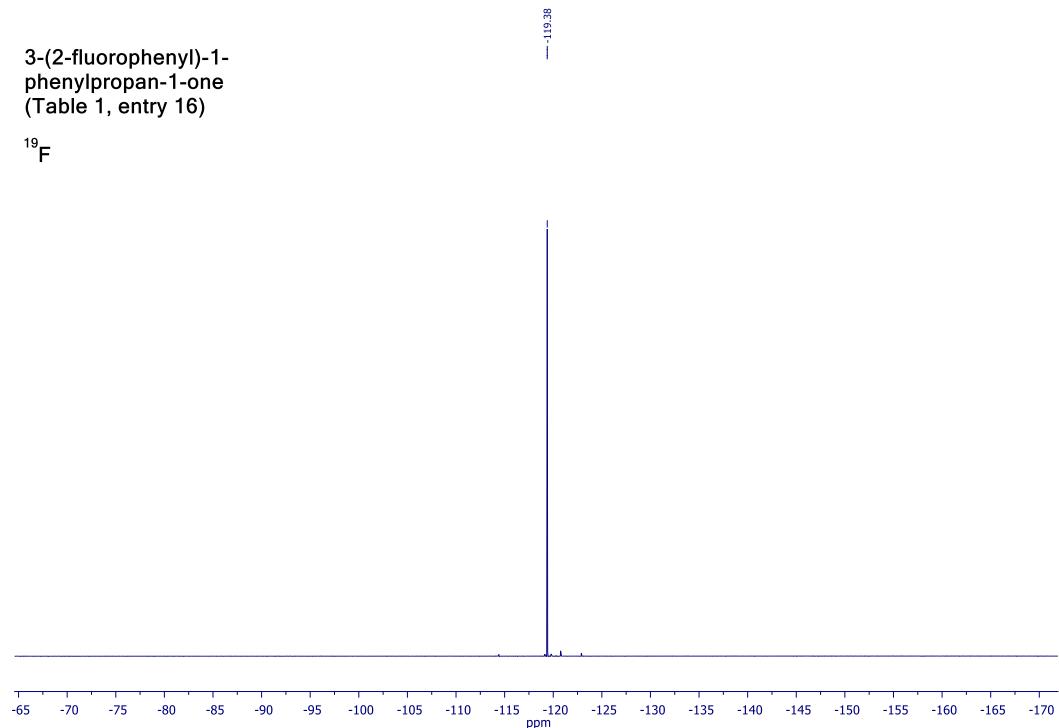


Figure S26. ¹⁹F NMR of 3-(2-fluorophenyl)-1-phenylpropan-1-one (Table 1, entry 16).

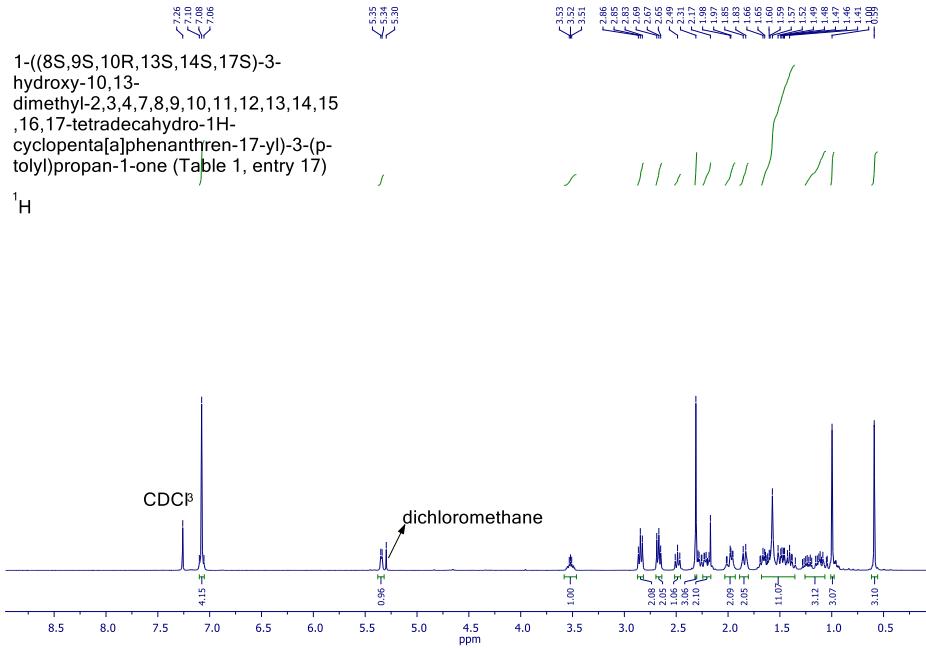


Figure S27. ¹H NMR of 1-((8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-(p-tolyl)propan-1-one (Table 1, entry 17).

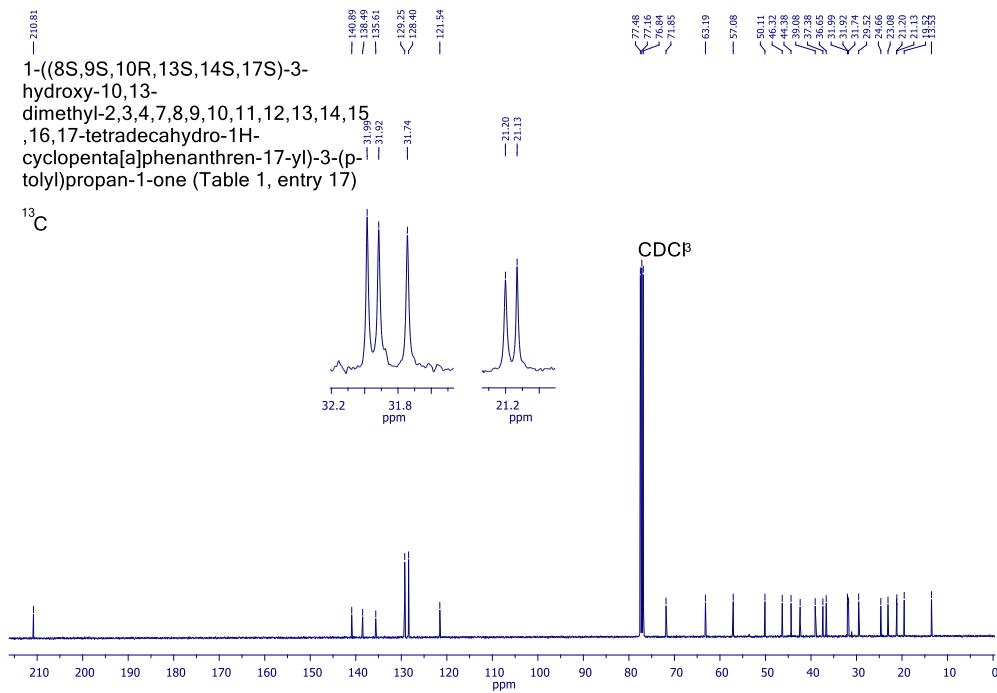


Figure S28. ¹³C NMR of 1-((8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-(p-tolyl)propan-1-one (Table 1, entry 17).

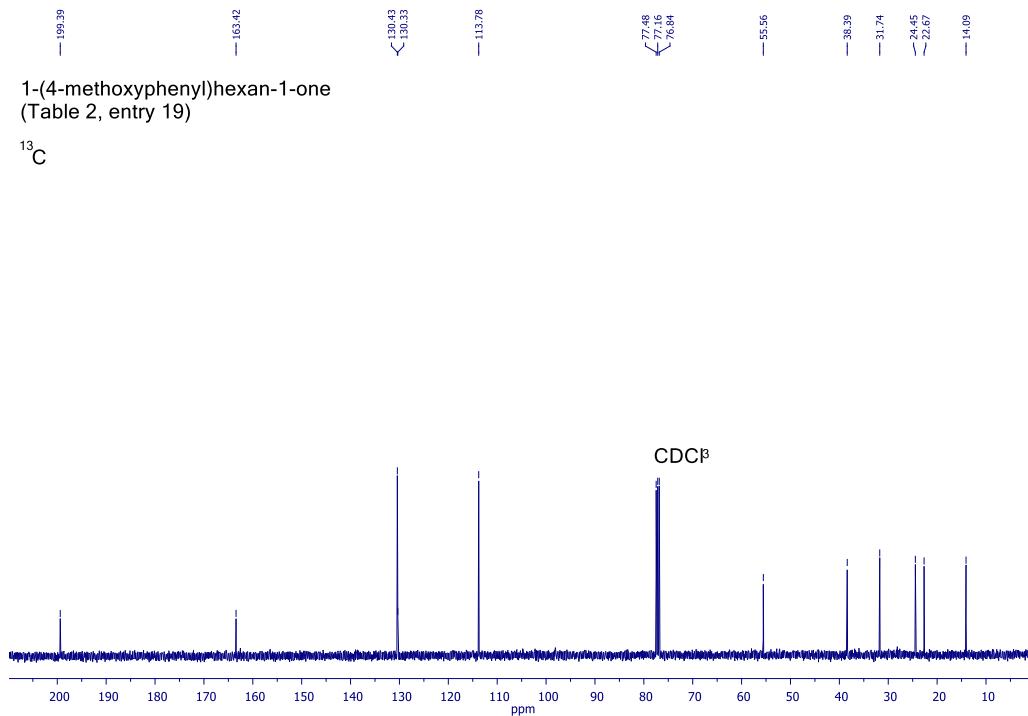
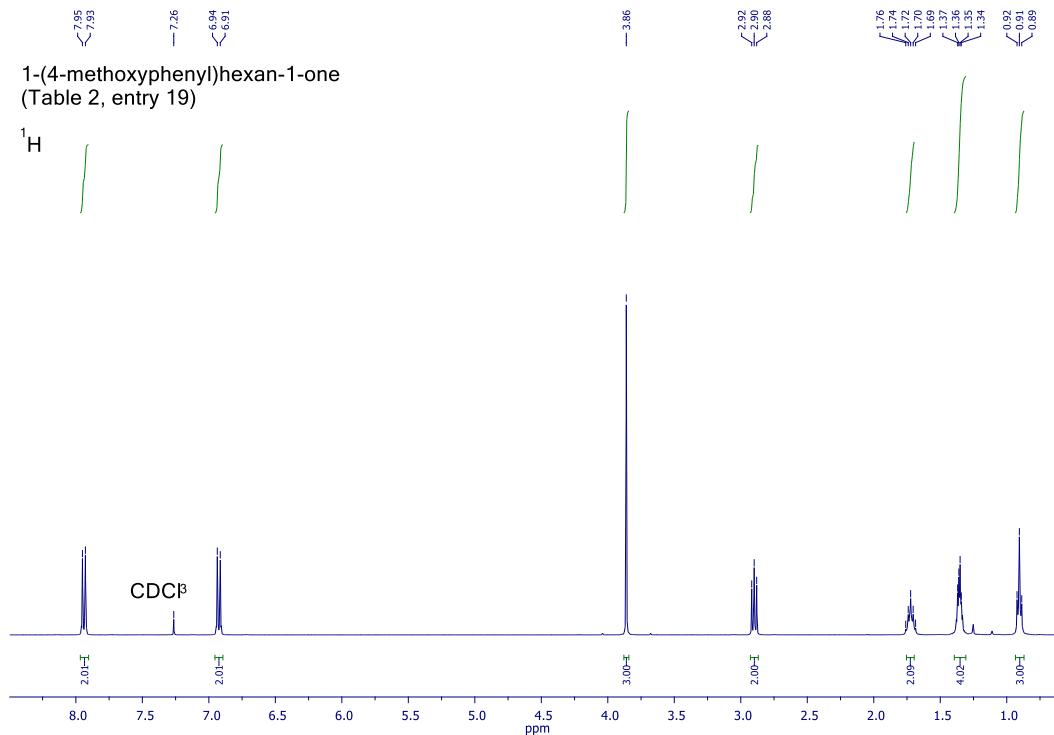


Figure S30.¹³C NMR of 1-(4-methoxyphenyl)hexan-1-one (Table 2, entry 19).

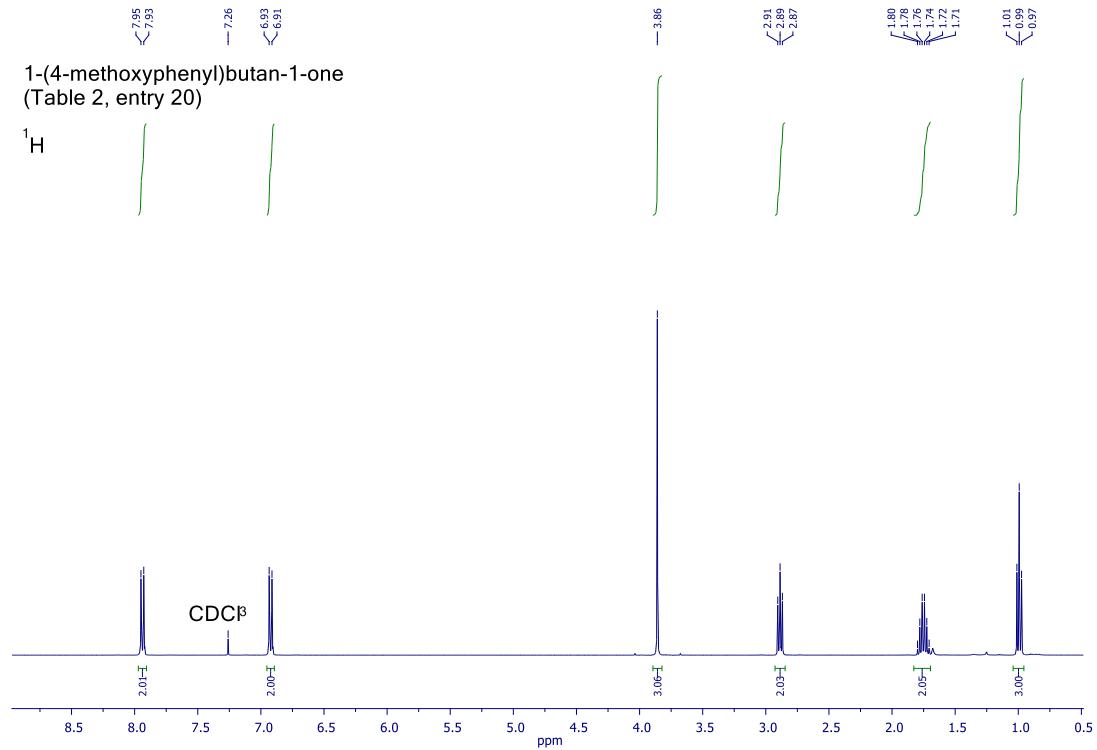


Figure S31. ¹H NMR of 1-(4-methoxyphenyl)butan-1-one (Table 2, entry 20).

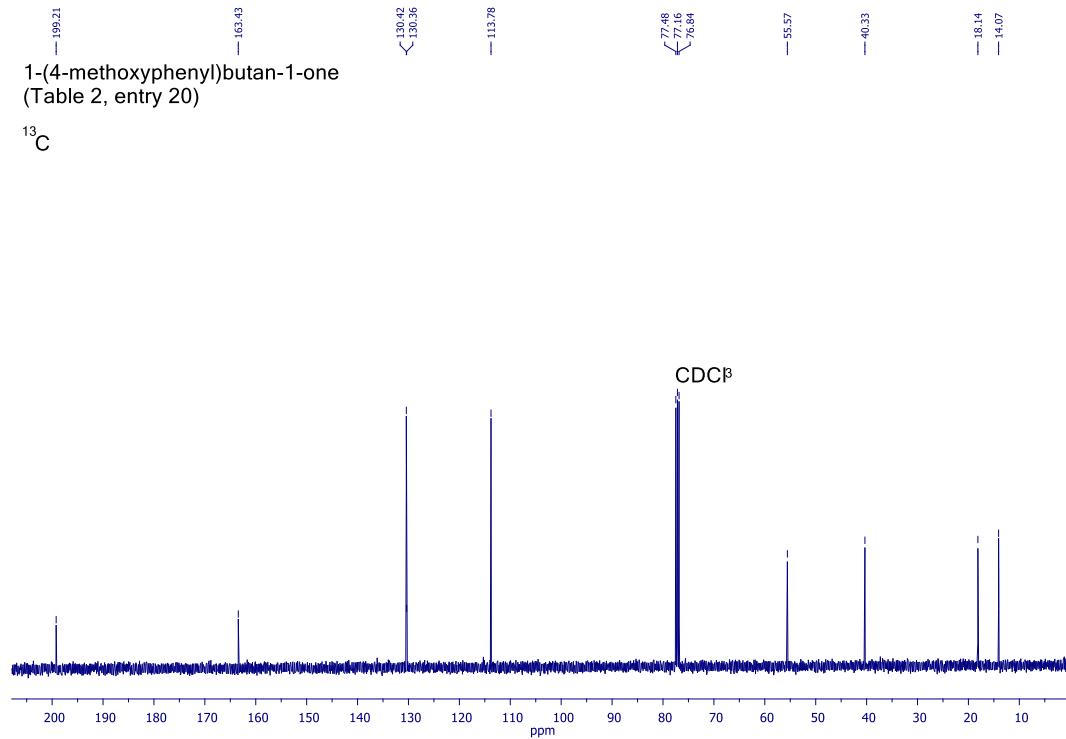


Figure S32. ¹³C NMR of 1-(4-methoxyphenyl)butan-1-one (Table 2, entry 20).

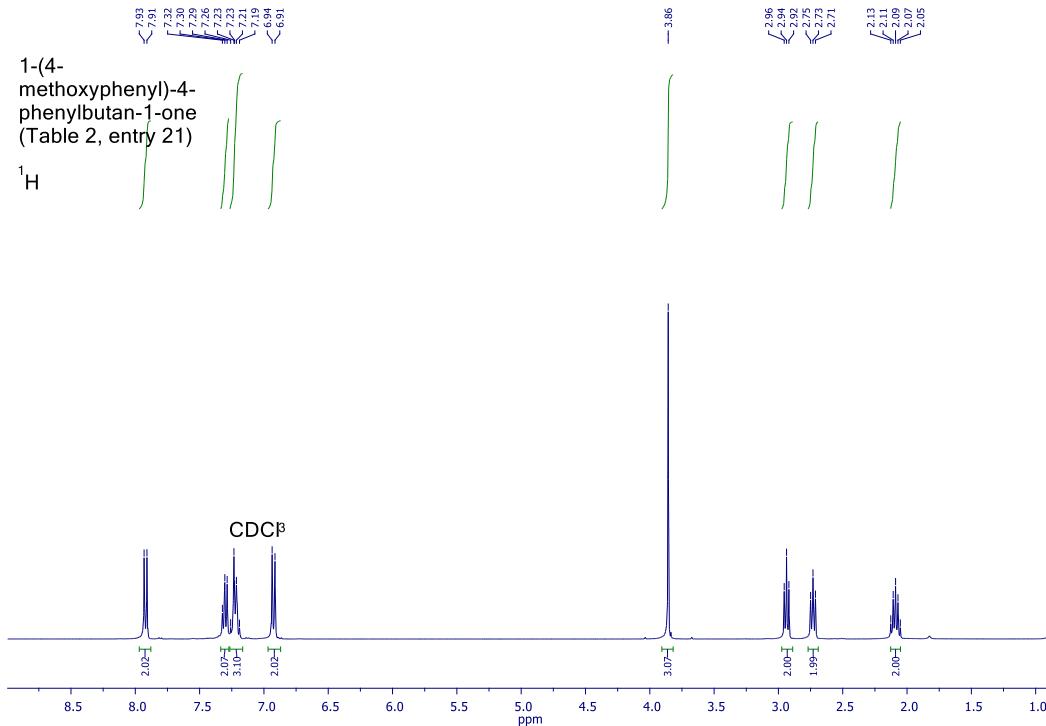


Figure S33.¹H NMR of 1-(4-methoxyphenyl)-4-phenylbutan-1-one (Table 2, entry 21).

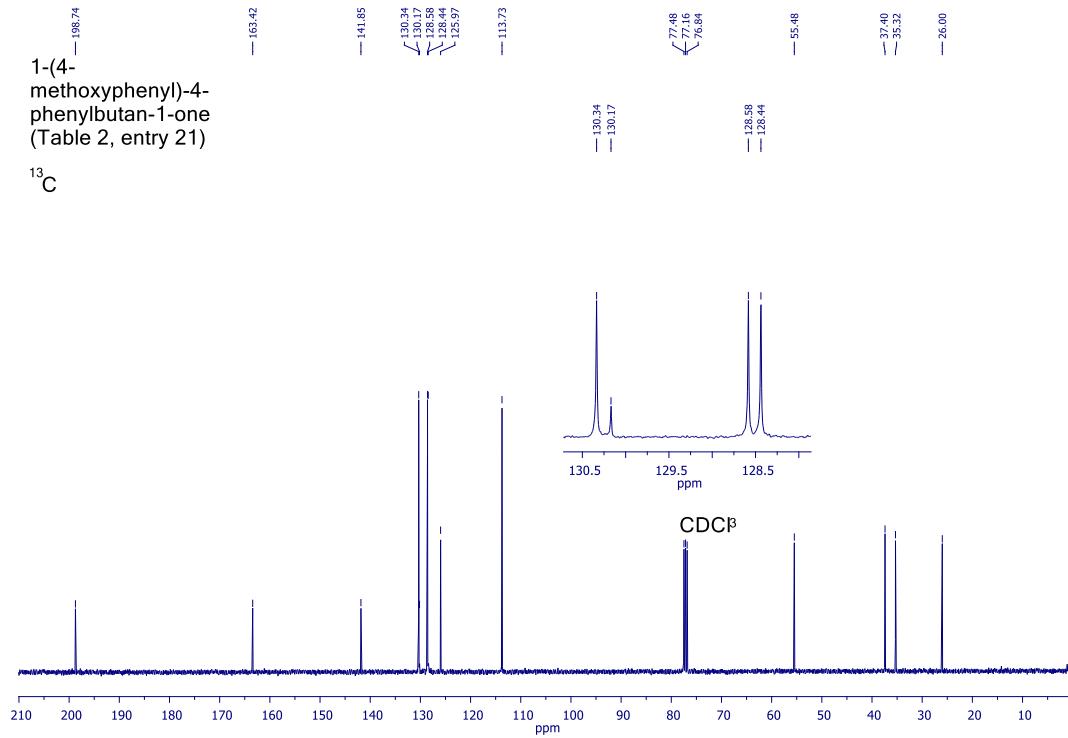


Figure S34. ^{13}C NMR of 1-(4-methoxyphenyl)-4-phenylbutan-1-one (Table 2, entry 21).

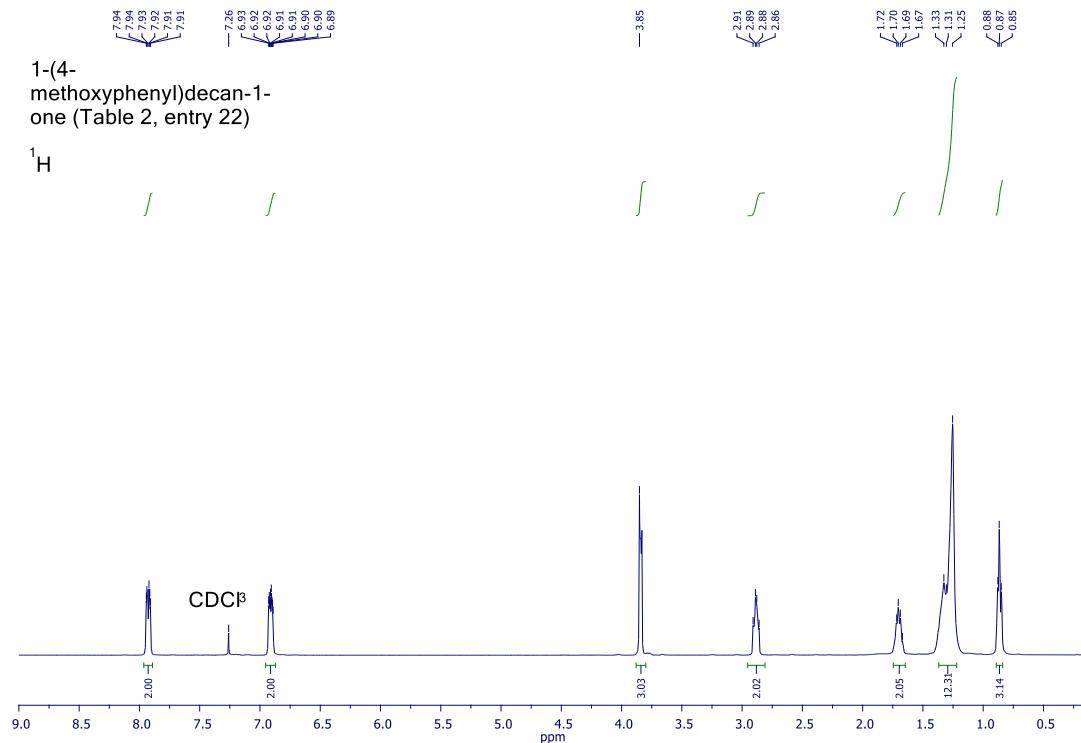


Figure S35. ^1H NMR of 1-(4-methoxyphenyl)decan-1-one (Table 2, entry 22).

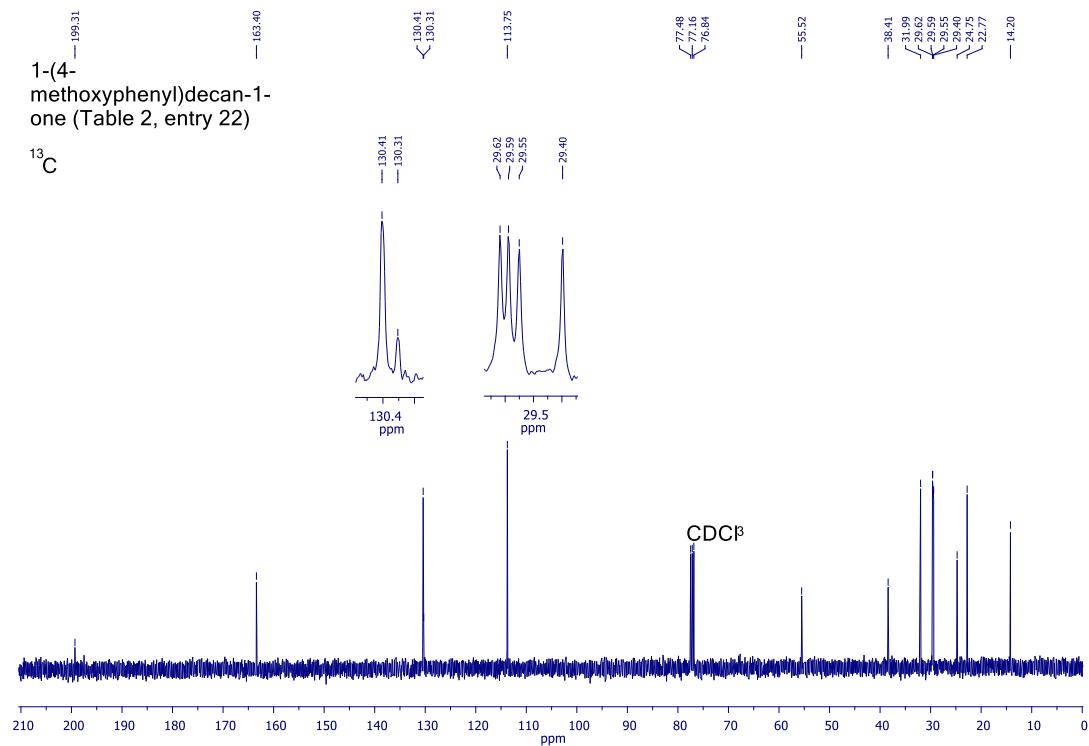


Figure S36. ^{13}C NMR of 1-(4-methoxyphenyl)decan-1-one (Table 2, entry 22).

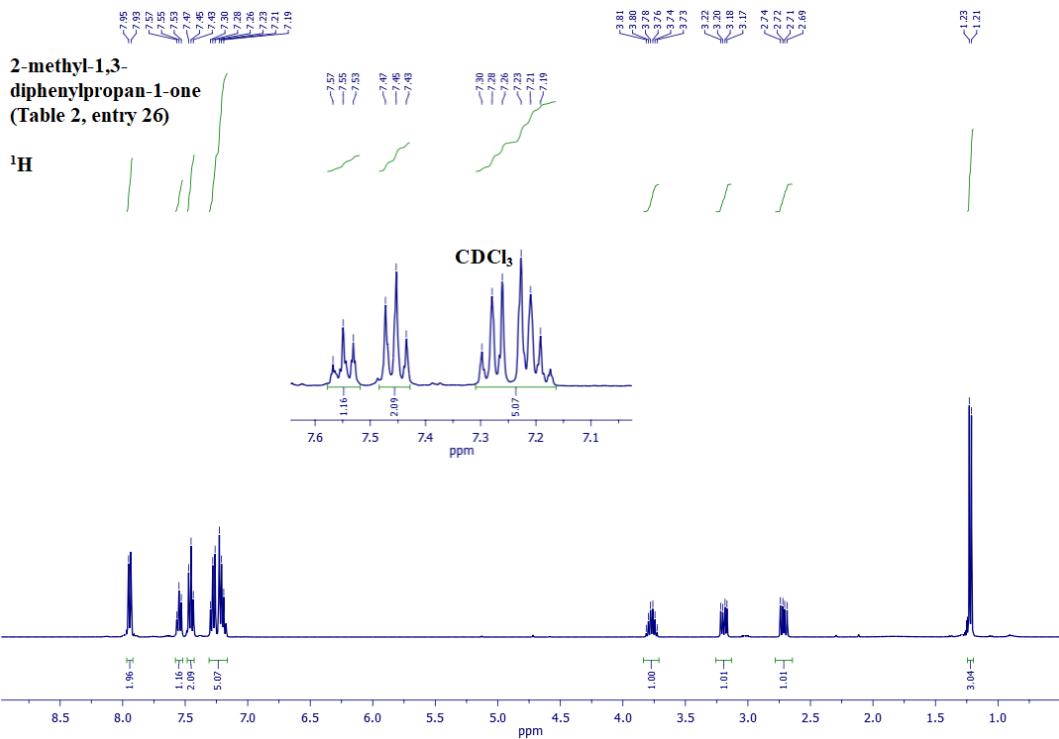


Figure S37.¹H NMR of 2-methyl-1,3-diphenylpropan-1-one (Table 2, entry 26).

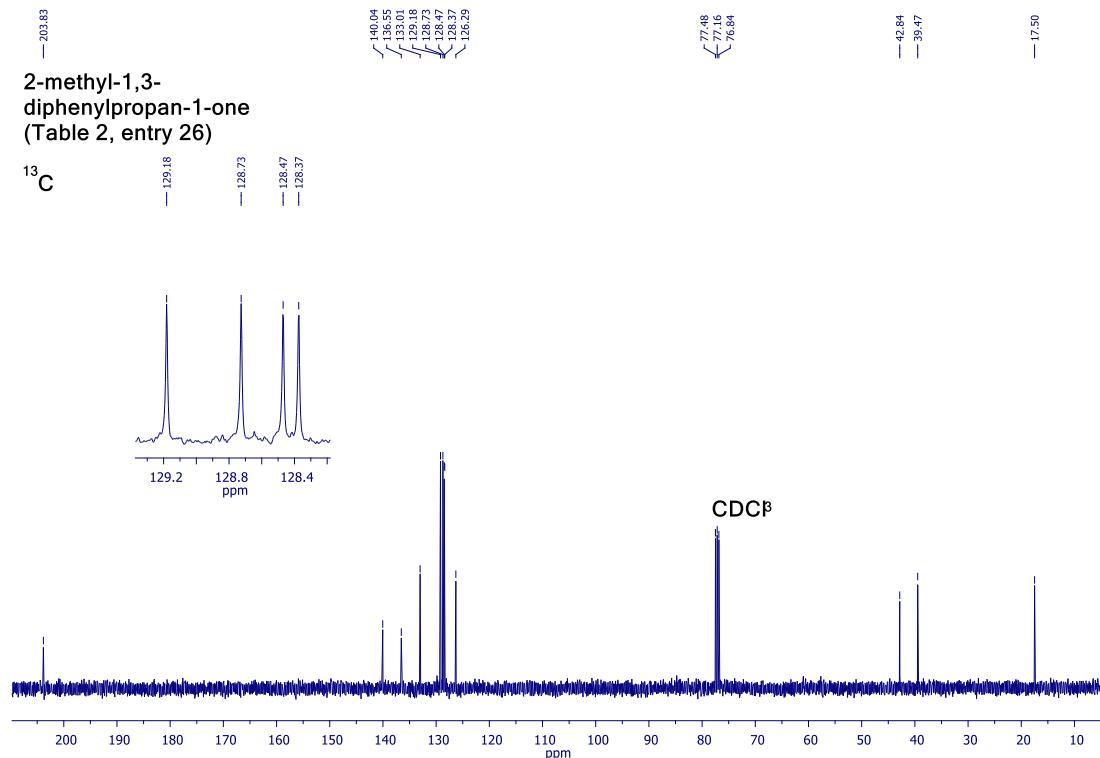


Figure S38. ^{13}C NMR of 2-methyl-1,3-diphenylpropan-1-one (Table 2, entry 26).

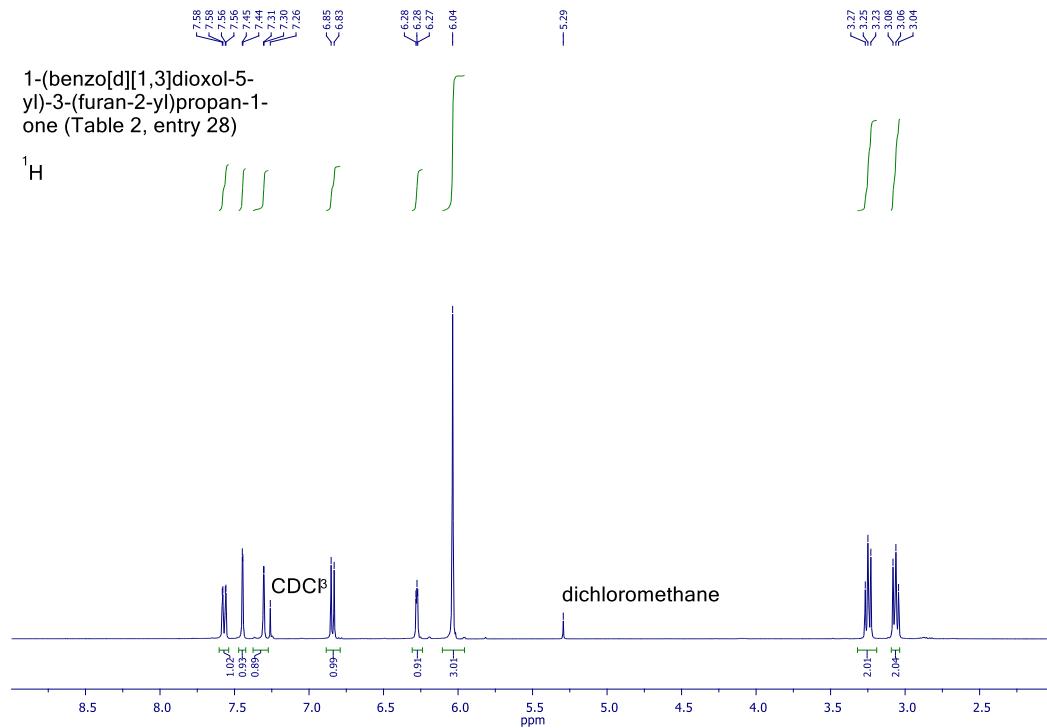


Figure S39. ¹H NMR of 1-(benzo[d][1,3]dioxol-5-yl)-3-(furan-2-yl)propan-1-one (Table 2, entry 28).

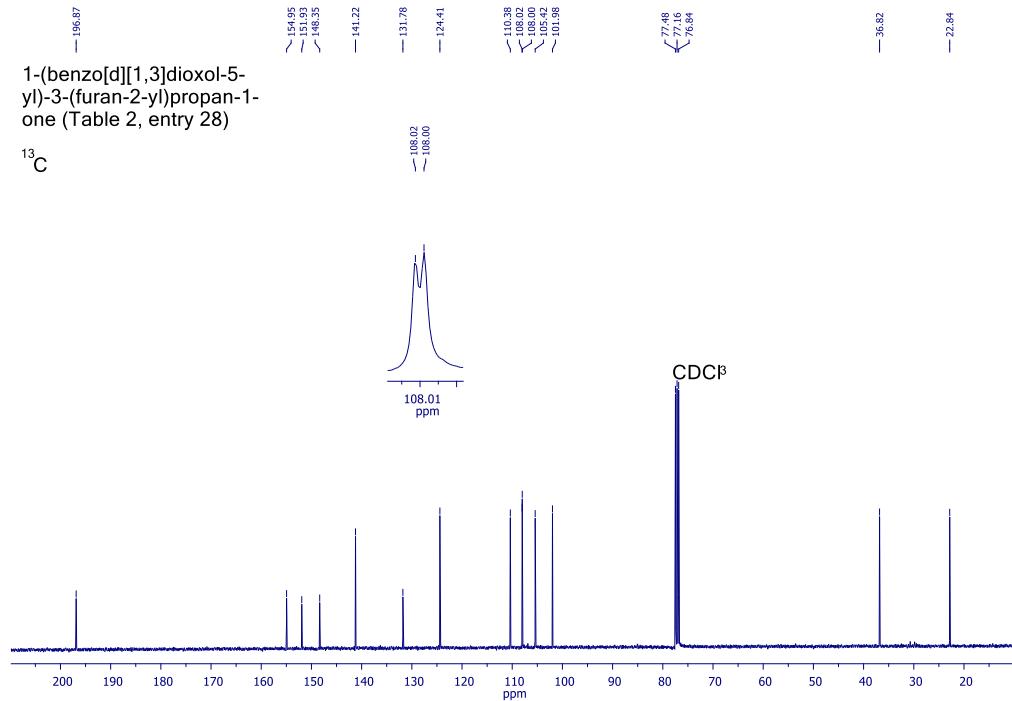


Figure S40. ¹³C NMR of 1-(benzo[d][1,3]dioxol-5-yl)-3-(furan-2-yl)propan-1-one (Table 2, entry 28).

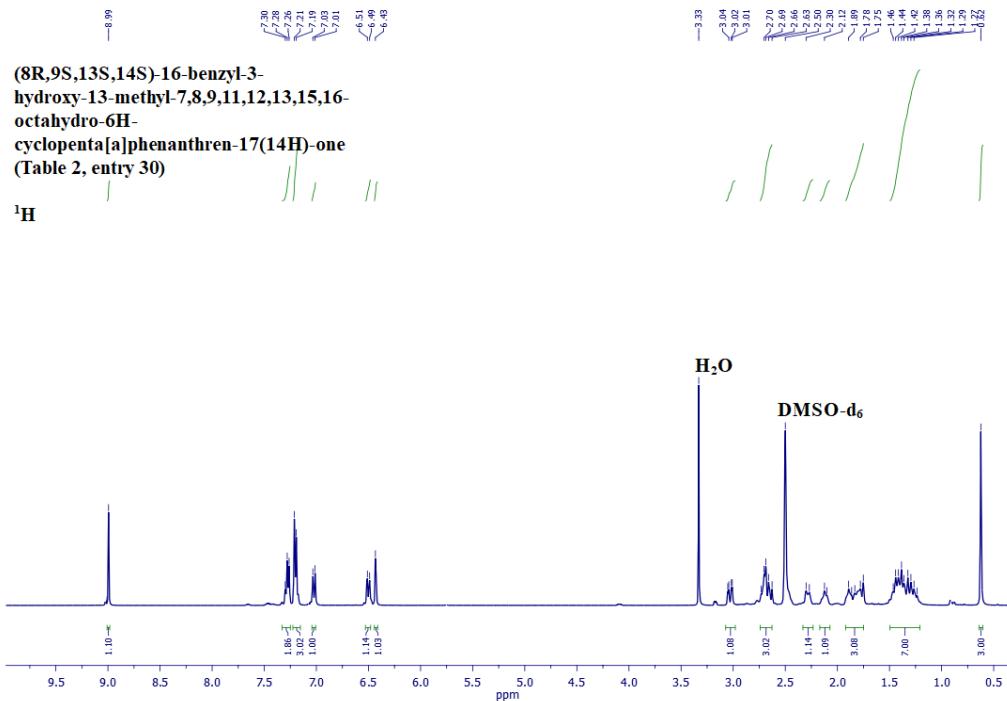


Figure S41.¹H NMR of (8R,9S,13S,14S)-16-benzyl-3-hydroxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (Table 2, entry 30).

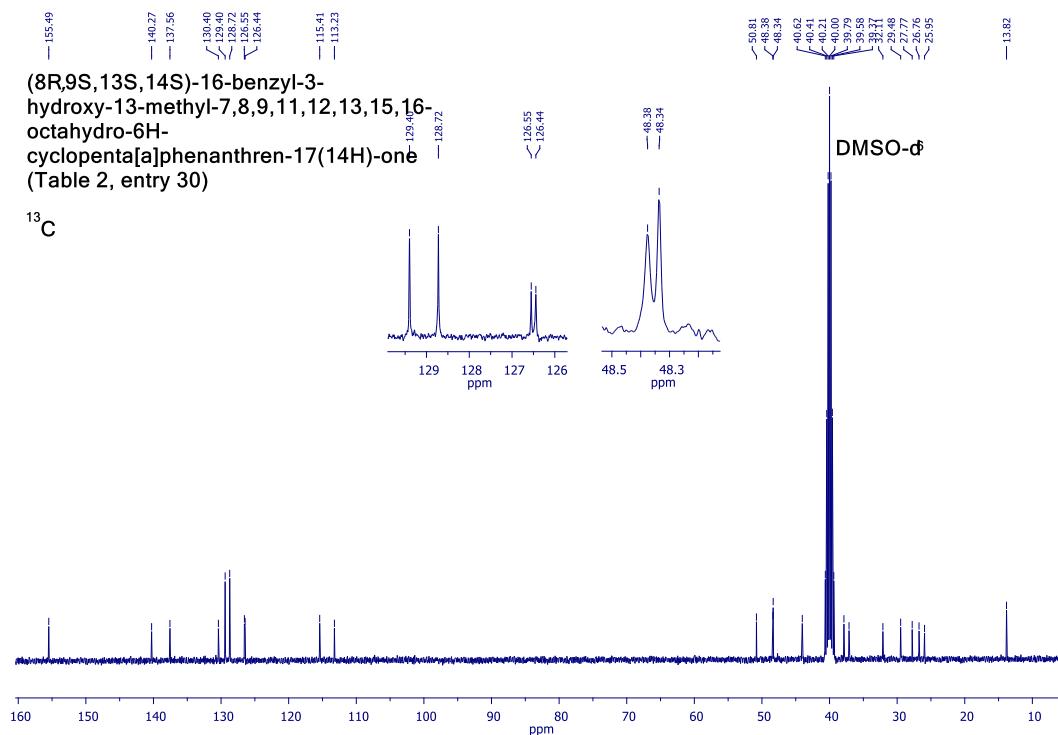


Figure S42. ^{13}C NMR of (8R,9S,13S,14S)-16-benzyl-3-hydroxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (Table 2, entry 30).

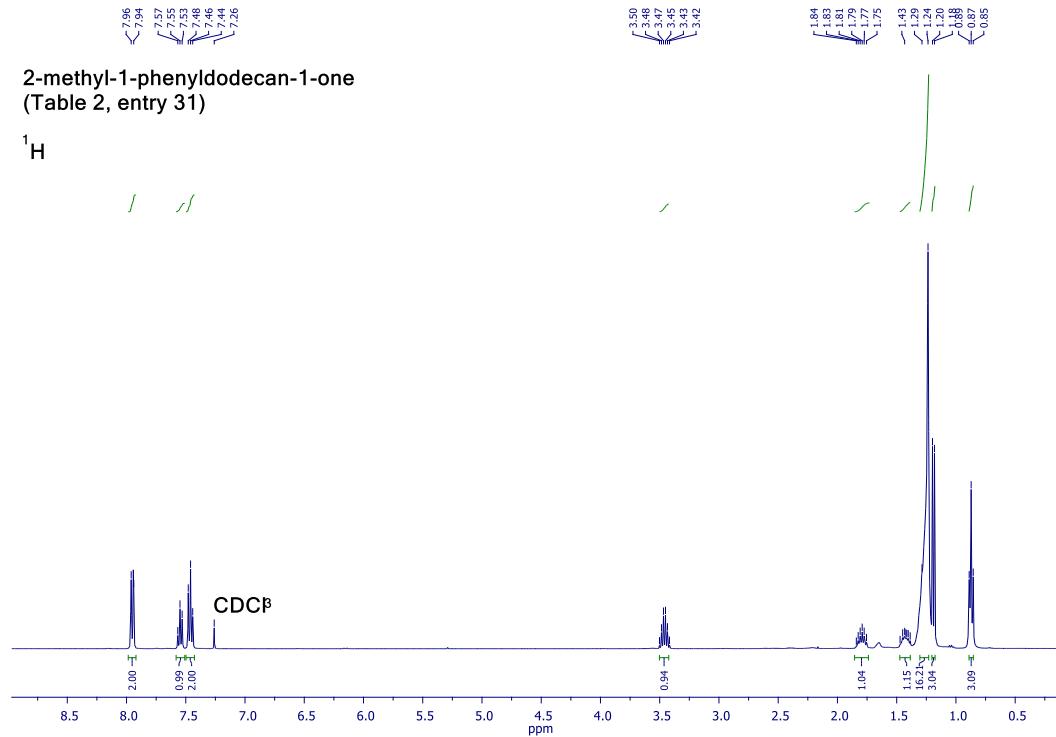


Figure S43. ^1H NMR of 2-methyl-1-phenyldodecan-1-one (Table 2, entry 31).

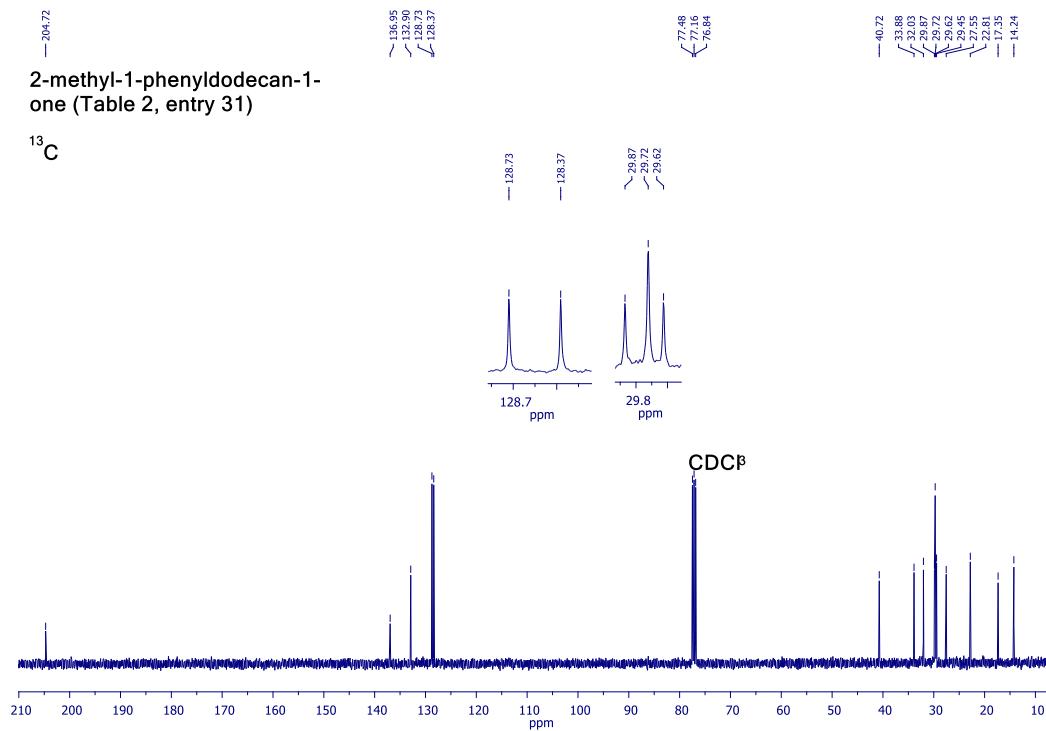


Figure S44. ^{13}C NMR of 2-methyl-1-phenyldodecan-1-one (Table 2, entry 31).

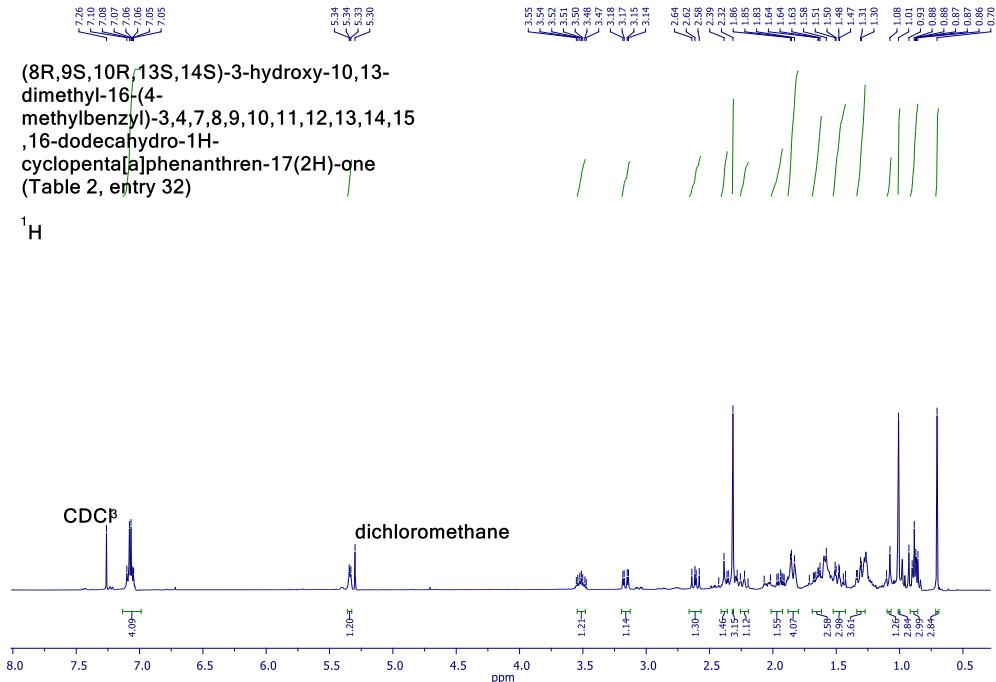


Figure S45. ^1H NMR of (8R,9S,10R,13S,14S)-3-hydroxy-10,13-dimethyl-16-(4-methylbenzyl)-3,4,7,8,9,10,11,12,13,14,15,16-dodecahydro-1H-cyclopenta[a]phenanthren-17(2H)-one (Table 2, entry 32).

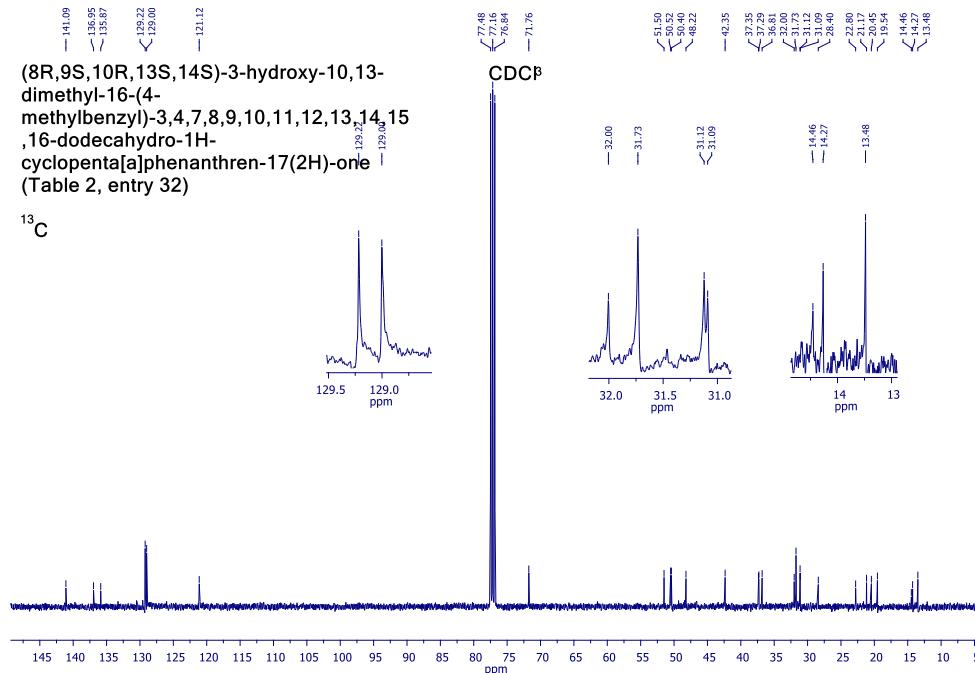


Figure S46. ^{13}C NMR of (8R,9S,10R,13S,14S)-3-hydroxy-10,13-dimethyl-16-(4-methylbenzyl)-3,4,7,8,9,10,11,12,13,14,15,16-dodecahydro-1H-cyclopenta[a]phenanthren-17(2H)-one (Table 2, entry 32).

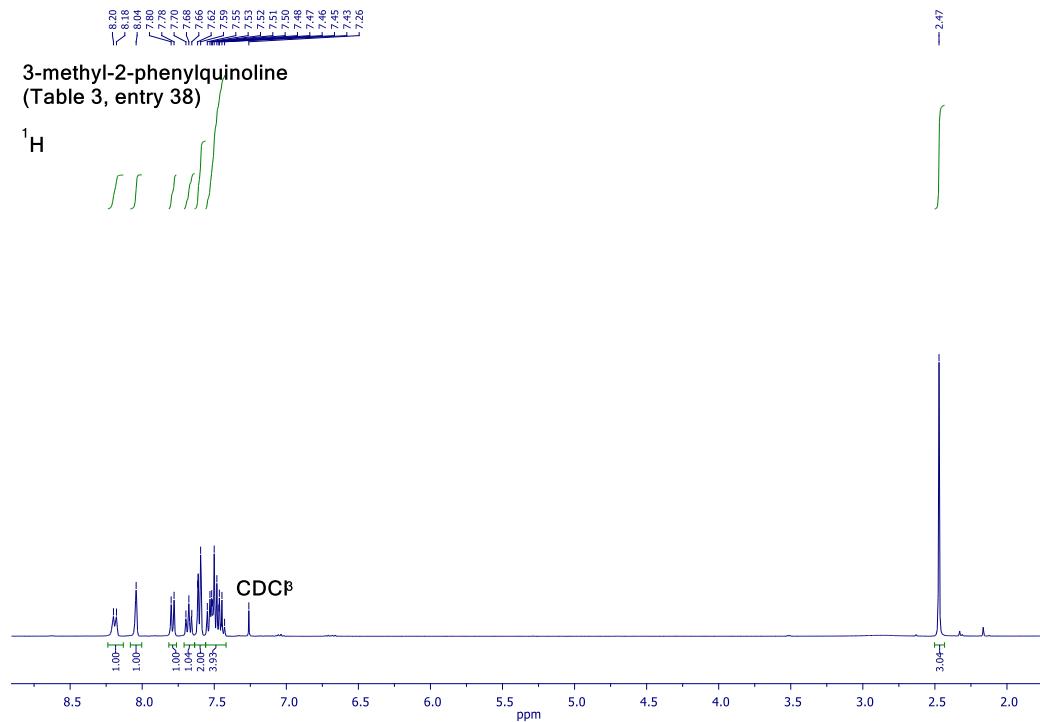


Figure S47. ^1H NMR of 3-methyl-2-phenylquinoline (Table 3, entry 38).

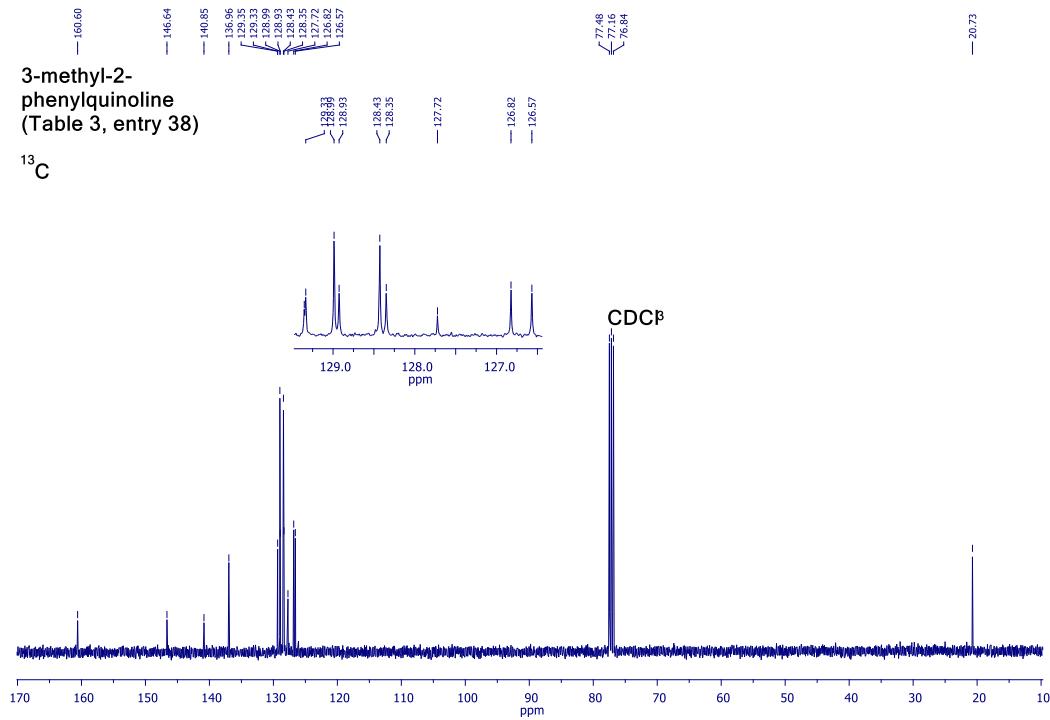


Figure S48. ^{13}C NMR of 3-methyl-2-phenylquinoline (Table 3, entry 38).

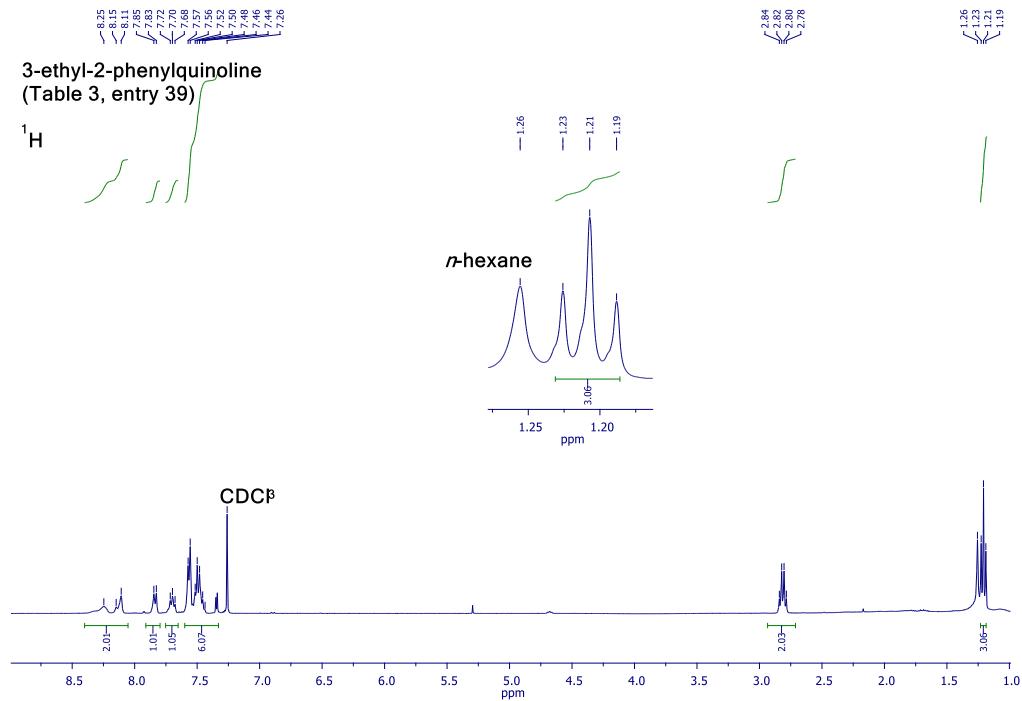


Figure S49. ¹H NMR of 3-ethyl-2-phenylquinoline (Table 3, entry 39).

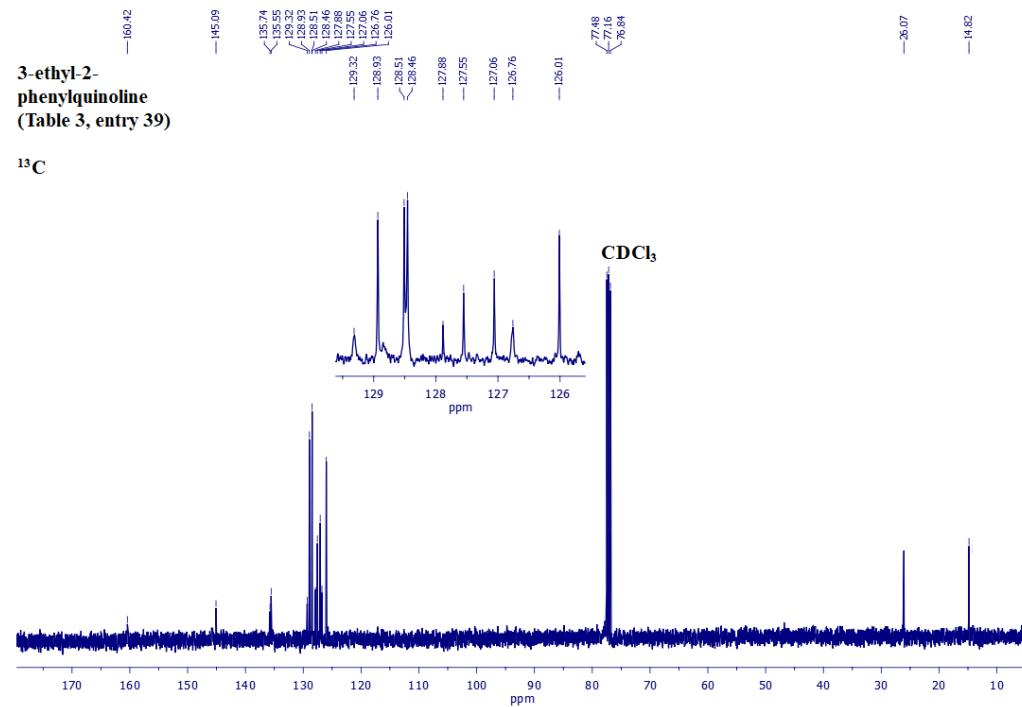


Figure S50. ¹³C NMR of 3-ethyl-2-phenylquinoline (Table 3, entry 39).

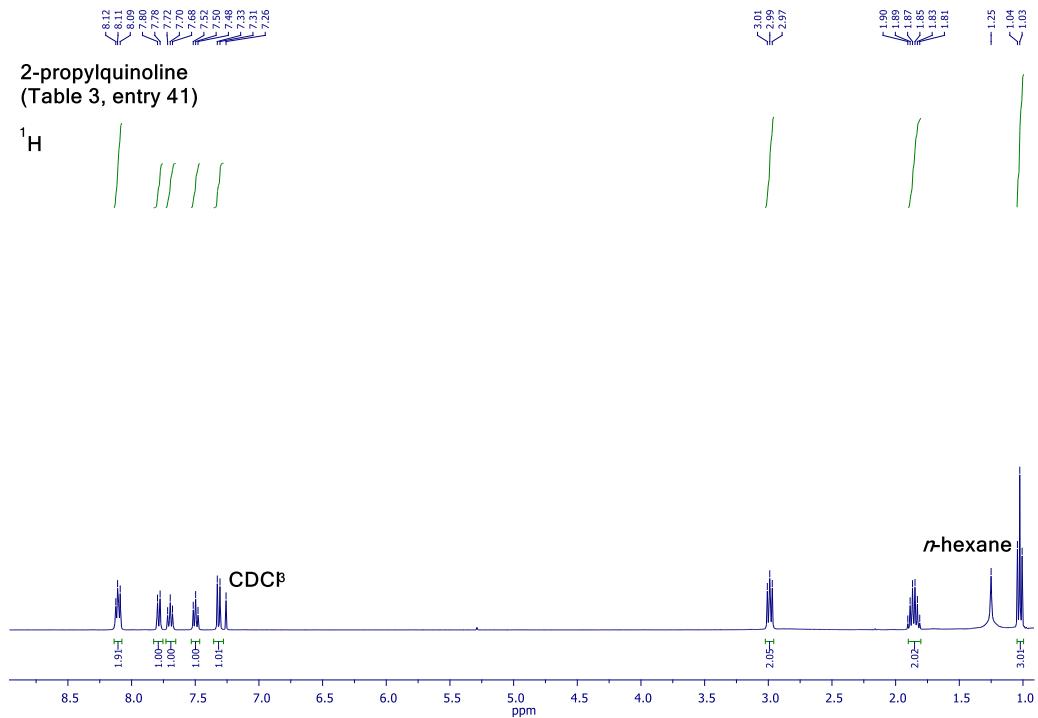


Figure S51. ¹H NMR of 2-propylquinoline (Table 3, entry 41).

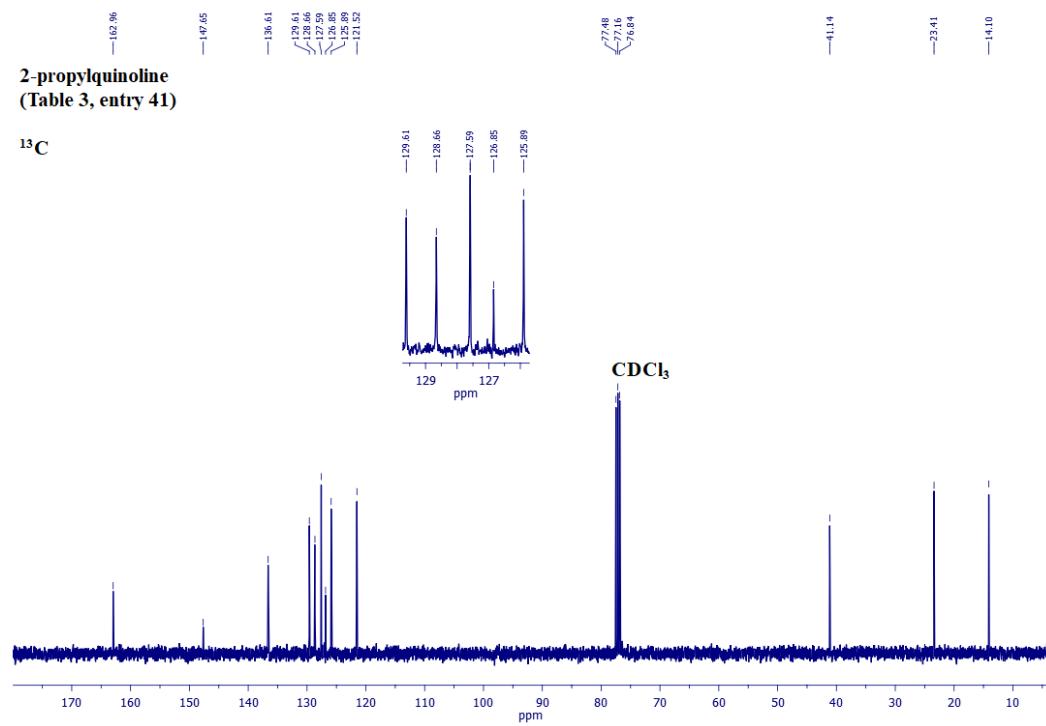


Figure S52. ¹³C NMR of 2-propylquinoline (Table 3, entry 41).

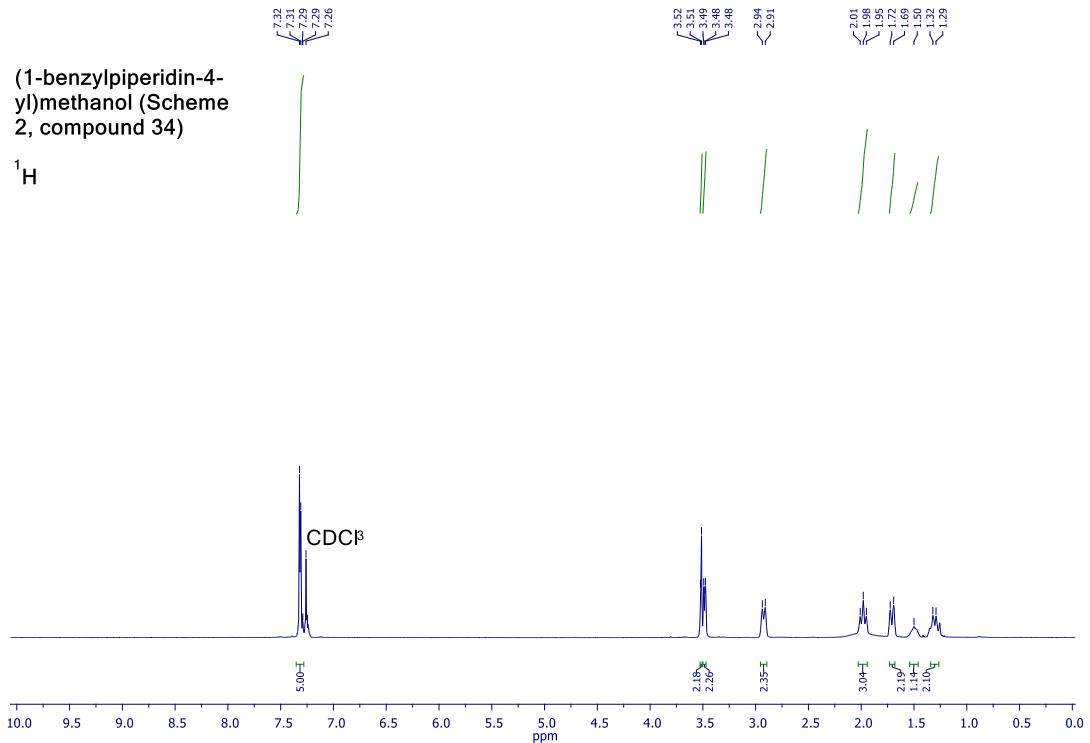


Figure S53. ¹H NMR of (1-benzylpiperidin-4-yl)methanol (Scheme 2, compound 34).

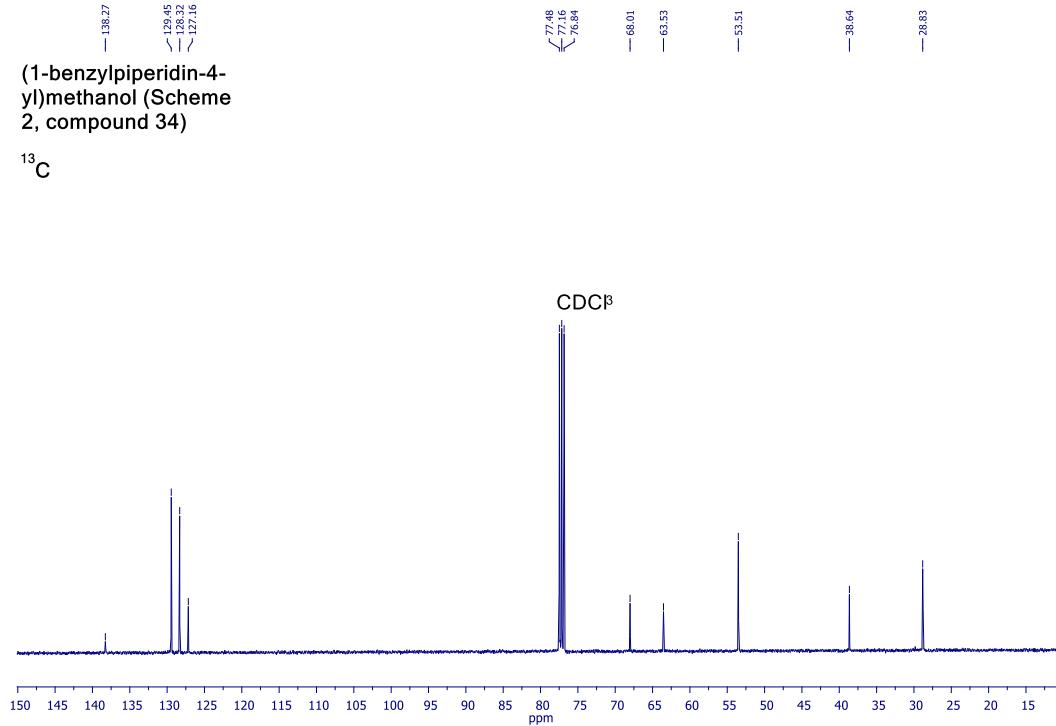


Figure S54. ¹³C NMR of (1-benzylpiperidin-4-yl)methanol (Scheme 2, compound 34).

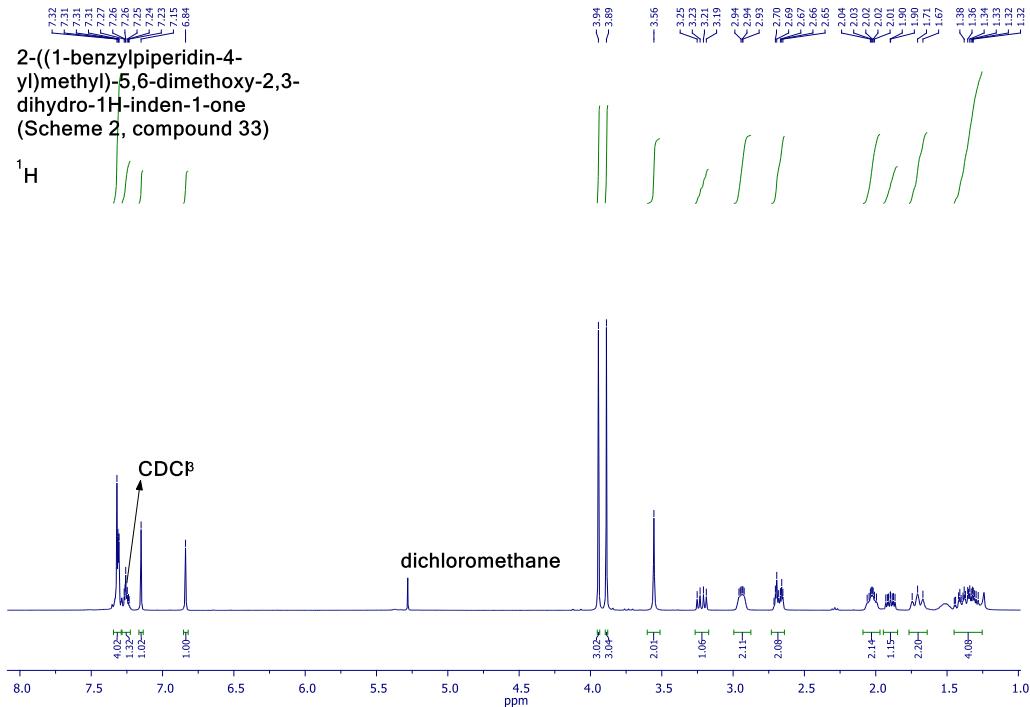


Figure S55. ¹H NMR of 2-((1-benzylpiperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (Scheme 2, compound 33).

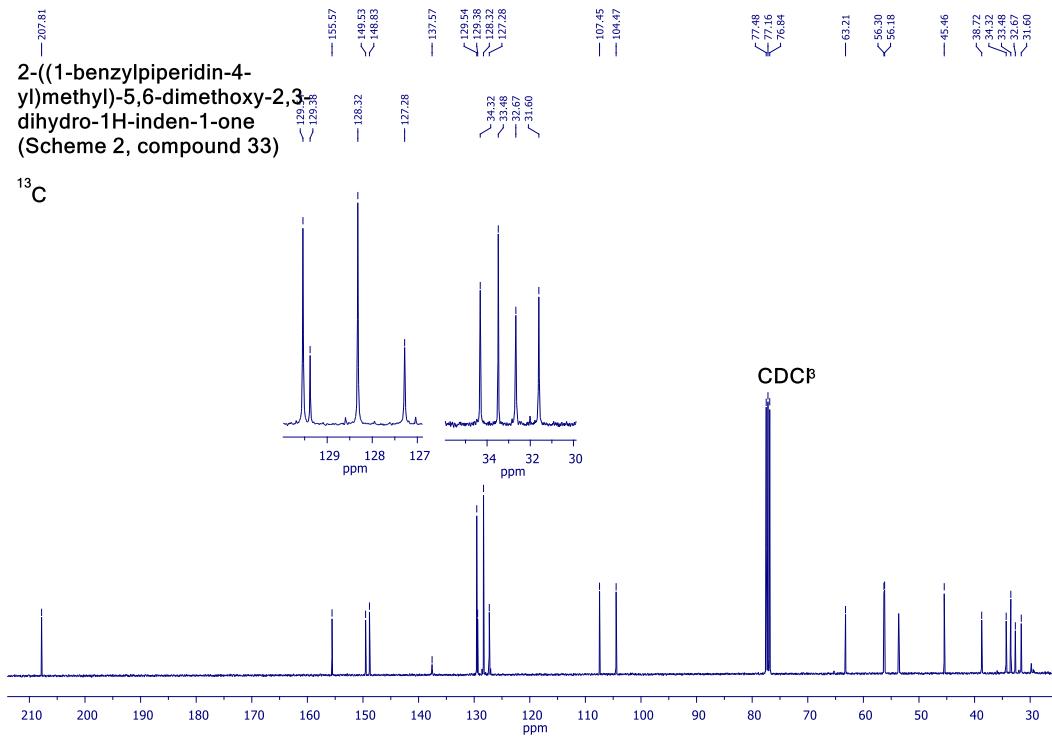


Figure S56. ¹³C NMR of 2-((1-benzylpiperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (Scheme 2, compound 33).