Supporting Information

1,5-Cyclooctadienyl alcohols and ketones generate a new class of COD Pt complexes

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1 General

All reactions containing air- and moisture-sensitive compounds were executed under an argon atmosphere using oven-dried glassware. The starting materials, solvents, and reagents were purchased from Acros, ABCR, Alfa Aesar, or Sigma-Aldrich and used without further purification. THF and diethyl ether were distilled from sodium under argon prior to use. ^{1}H NMR spectra were recorded on a Bruker AM 400 (400 MHz), a Bruker DRX 500 (500 MHz) or a Bruker AM 600 (600 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM 400 (100 MHz), a Bruker DRX 500 (125 MHz) or a Bruker AM 600 (150 MHz) spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to tetramethylsilane as the internal standard (δ = 0 ppm) by using the signals of the residual protons of $CHCl_3$ (7.26 ppm (^{1}H) or 77.0 ppm (^{13}C)) in $CDCl_3$. The signal structure was analysed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal), and C_q = quaternary C-atom (no signal).

EI-MS (electron ionization mass spectrometry) was performed by using a *Finnigan* MAT 90 spectrometer (70 eV). The molecular fragments are quoted as the relation between mass and charge (*m/z*), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation [M^+] refers to the molecule ion.

^{195}Pt NMR spectra were recorded at 300 K on a 600 MHz spectrometer using either an inversely detected double-resonance 1H-BB probe head or an inversely detected triple-resonance ^{1}H-^{13}C, BB probe head. Platinum frequencies were determined by 1D ^{195}Pt spectra or an ultra-broad-band version of a gradient-selected ^{1}H,^{195}Pt-HMBC. Due to the very large chemical shift range of platinum complexes (15000 ppm, 1.94 MHz @ 14.1 T), it is not possible to cover this range in one conventional experiment. Conventional experiments area acquired with hard pulses that can excite a bandwidth of about 50 kHz. Therefore, to cover the complete chemical shift range, nearly 40 experiments would be needed. With new ultra-broad-band versions of conventional experiments that can acquire a bandwidth of 500 kHz, the number of needed spectra is decreased by a factor of 10. Although Pt(II) complexes only have a chemical shift range of 4000 ppm, three experiments would still be needed to determine the chemical shift of a complex reliably.

IR (infrared spectroscopy) data were recorded on FT-IR *Bruker* IFS 88 spectrometer and are reported as follows: frequency of absorption (cm^{-1}), intensity of absorption (vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad).

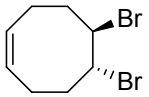
Reactions were monitored by silica gel coated aluminium plates (*Merck*, silica gel 60, F_{254}). Detection was performed by examination under UV light (254 nm) or by staining with "Seebach staining solution" (mixture of molybdato phosphoric acid, cerium (IV)-sulphate tetrahydrate, sulfuric acid and water).[1, 2]

2 Experimental Section

2.1 General Procedures

Selective bromination:

(*Z*)-5,6-*trans*-Dibromocyclooct-1-ene (1a):



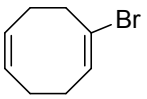
Bromine (10.5 mL, 32.6 g, 204 mmol, 1.00 equiv.) was added dropwise to 1,4-dioxane (17.5 mL, 18.0 g, 204 mmol, 1.00 equiv.). The newly formed light sensitive solid was immediately dissolved in 170 mL diethyl ether and added to a solution of 1,5-cyclooctadiene (28.4 mL, 25.0 g, 231 mmol, 1.19 equiv.) dissolved in 170 mL diethyl ether. The mixture was cooled to –20 °C and vigorously stirred avoiding that a temperature of 15 °C was passed. The reaction mixture was washed with saturated aqueous solution of $Na_2S_2O_3$ (3 × 250 mL), $NaHCO_3$ (2 × 250 mL) and brine (1 × 300 mL). The organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was purified by column chromatography (CH) and dibromide **1a** was obtained as colourless oil (25.5 g, 94.7 mmol, 42%).

R_f = 0.46 (CH). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.65 (t, ^3J = 4.1 Hz, 2 H, C*H*), 4.66 (t, ^3J = 2.3 Hz, 2 H, C*H*Br), 2.92–2.54 (m, 4 H, CH_2), 2.36–2.00 (m, 4 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 128.7 (+, 2 × *C*H), 59.3 (+, 2 × *C*HBr), 35.3 (–, 2 × *C*H_2), 24.9 (–, 2 × *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3442 (vw), 3014 (vw), 2935 (w), 1655 (vw), 1480 (vw), 1466 (vw), 1427 (w), 1348 (vw), 1294 (vw), 1225 (vw), 1202 (vw), 1180 (vw), 1148 (w), 1055 (vw), 1007 (vw), 977 (vw), 964 (vw), 919 (vw), 885 (vw), 834 (vw), 800 (vw), 762 (vw), 719 (vw), 677 (w), 636 (vw), 546 (vw), 521 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 299/297/295 (4/10/5) [M^+], 199/197 (3/5) [$(M–Br)^+$], 107 (100) [$C_8H_{11}^+$], 91 (27), 79 (92), 77 (44), 67 (25), 65 (18), 53 (26), 51 (17), 41 (52), 39 (30). – **HRMS** ($C_8H_{12}{}^{78}Br_2$): calc. 265.9305; found 265.9304.

Chemical analysis accords to reference.[2]

Elimination:

(1*Z*,5*Z*)-1-Bromocycloocta-1,5-diene (1)



A solution of dibromide **1a** (25.5 g, 95.9 mmol, 1.00 equiv.) dissolved in 90 mL diethyl ether was cooled to –10 °C. KO*t*Bu (16.1 g, 144 mmol, 1.50 equiv.) dissolved in 80 mL THF was slowly added to the cold solution maintaining the temperature. The reaction was allowed to warm to room temperature. After stirring for another 2 h at room temperature, the reaction was quenched with water (170 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (CH) to obtain the desired product **1a** as bright yellow oil (11.5 g, 61.8 mmol, 65%).

R_f = 0.43 (CH). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.08–6.00 (m, 1 H, C*H*), 5.65–5.50 (m, 2 H, C*H*), 2.84 (t, ^3J = 6.6 Hz, 2 H, CH_2), 2.47–2.39 (m, 2 H, CH_2), 2.39–2.30 (m, 4 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 130.3 (+, *C*H), 128.3 (+, *C*H), 127.9 (+, *C*H), 125.0 (C_q, *C*Br), 38.9 (–, *C*H_2), 28.3 (–, *C*H_2), 27.4 (–, *C*H_2), 27.2 (–, *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3454 (vw), 3010 (vw), 2942 (vw), 2920 (vw), 2891 (w), 2831 (vw), 1648 (w), 1484 (w), 1425 (w), 1342 (vw), 1301 (vw), 1214 (vw), 1159 (vw), 1079 (w), 1024 (vw), 995 (w), 919 (vw), 837 (w), 788 (vw), 731 (w), 693 (w), 657 (vw), 558 (vw), 496 (vw) cm^{-1}. – **MS** (GC-MS), *m/z* (%): 188/186 (20/21) [M^+], 107 (78) [$C_8H_{11}^+$], 91 (17), 79 (100).

Chemical analysis accords to reference.[2]

General procedure 1 (GP 1): Addition of aldehydes to COD-Li

To a solution of the bromide (1.10 equiv.) in anhydrous diethyl ether, *t*BuLi (2.20 equiv.) *[Caution: this material is pyrophoric]* was added dropwise at –78 °C under argon atmosphere. After 30 min of stirring at –78 °C, the reaction mixture was warmed to 0 °C. Temperature was maintained at 0 °C for 30 min. The reaction mixture was cooled then back to −78°C followed by dropwise addition of aldehyde (1.00 equiv.) dissolved in anhydrous diethyl ether. The reaction mixture was then warmed to room temperature and left to stir for 2 h. NH_4Cl solution was added to quench the reaction. After the separation of phases, the aqueous layer was extracted with diethyl ether. The organic layers were collected and washed with water and brine. Next, the combined organic layers were dried with sodium sulphate, filtered and the solvent was removed under reduced pressure. The crude residue was purified via flash column chromatography.

General procedure 2 (GP 2): Oxidation from the alcohol to the ketone

To a solution of the alcohol (1.00 equiv.) in dry dichloromethane, manganese dioxide (25.0 equiv.) was added in a few little portions at room temperature. Upon consumption of the starting material, the reaction was stirred for up to 24 h under an argon atmosphere. The reaction mixture was filtered and the solvent of the filtrate was removed under reduced pressure. The crude residue was purified via flash column chromatography.

General procedure 3 (GP 3): Addition of carboxylic acids to COD-Li

To a solution of the bromide (2.50 equiv.) in anhydrous diethyl ether, *t*BuLi (5.00 equiv.) *[Caution: this material is pyrophoric]* was added dropwise at –78 °C under argon atmosphere. After 30 min of stirring at –78 °C, the reaction mixture was warmed to 0 °C. Temperature was maintained at 0 °C for 30 min. Lithiated COD was then added to a solution of the carboxylic acid (1.00 equiv.) dissolved in anhydrous diethyl ether at −78°C. The reaction mixture was then warmed to room temperature and left to stir for 2 h. NH_4Cl solution was added to quench the reaction. After the separation of phases, the aqueous layer was extracted with diethyl ether. The organic layers were collected and washed with water and brine. Next, the combined organic layers were dried with sodium sulphate, filtered and the solvent was removed under reduced pressure. The crude residue was purified via flash column chromatography.

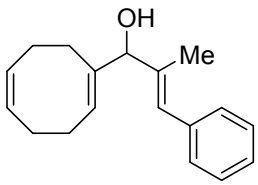
General procedure 4 (GP 4): Synthesis of monometallic platinum(II) complexes

Potassium tetrachloroplatinate(II) (1.00 equiv.) was dissolved in water and a solution of the cyclooctadiene derivative (6.90 equiv.) dissolved in *n*-propanol was added (solvent ratio: water 1.0/ *n*-propanol 0.7). At the end tin(II) chloride (3.00 mol%) was added and the mixture was stirred, at room temperature until the solution was decolorized. The newly formed colourless solid was filtered off, washed with water and ethanol and dried under high vacuum.

2.2 Syntheses

2.2.1 Syntheses of racemic alcohol derivatives

(*rac*)-(*E*)-1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2-methyl-3-phenylprop-2-en-1-ol (2a)

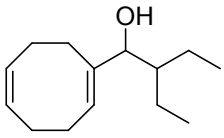


This compound was synthesized following **GP 1** from **1** (500 mg, 2.69 mmol, 1.10 equiv.) and the corresponding aldehyde (0.194 mL, 203 mg, 2.42 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 10/1) and the desired product **2a** was obtained as a bright-yellow oil (327 mg, 1.28 mmol, 53%).

R_f = 0.22 (CH/EE: 9/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35−7.10 (m, 5 H, CH_{Ar}), 6.62 (s, 1 H, C*H*OH), 5.74 (t, ^3J = 6.2 Hz, 1 H, CH_{COD}), 5.55−5.47 (m, 2 H, 2 × CH_{COD}), 4.47 (s, 1 H, C*H*), 2.43−2.27 (m, 8 H, CH_2), 1.71 (s, 3 H, CH_3) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 138.9 (C_q), 138.4 (C_q), 137.9 (C_q), 128.9 (+, 2 × CH_{Ar}), 128.7 (+, *C*H), 128.6 (+, *C*H), 128.0 (+, 2 × CH_{Ar}), 126.5 (+, *C*H), 126.2 (+, CH_{Ar}), 124.97 (+, *C*H), 82.5 (+, *C*HOH), 27.9 (−, *C*H_2), 27.7 (−, *C*H_2), 27.6 (−, *C*H_2), 26.6 (−, *C*H_2), 14.6 (+, *C*H_3) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3365 (vw), 2936 (w), 2878 (w), 1653 (vw), 1598 (vw), 1486 (w), 1443 (w), 1426 (w), 1353 (w), 1291 (w), 1212 (w), 1163 (vw), 1129 (vw), 1097 (vw), 1041 (w), 1009 (w), 916 (w), 844 (w), 748 (w), 698 (m), 516 (w), 389 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 254 (9) [M^+], 147 (100) [$C_{10}H_{11}O^+$], 129 (43) [$C_{18}H_{20}^+$], 113 (29), 91 (40). – **HRMS** ($C_{18}H_{22}O$): calc. 254.1665; found 254.1664.

Chemical analysis accords to reference.[3]

(*rac*)-1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2-ethylbutan-1-ol (2b)

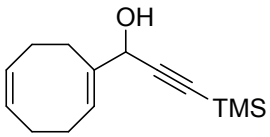


This compound was synthesized following **GP 1** from **1** (500 mg, 2.69 mmol, 1.10 equiv.) and the corresponding aldehyde (0.299 mL, 174 mg, 2.42 mmol, 1.00 equiv.). The crude product was purified by column chromatography

(CH/EE: 20/1) and the desired product **2b** was obtained as a yellow oil (474 mg, 2.28 mmol, 94%).

***R*$_f$** = 0.27 (CH/EE: 10/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.59–5.48 (m, 3 H, CH_{COD}), 3.81 (d, ^3J = 6.9 Hz, 1 H, C*H*OH), 2.49–2.22 (m, 8 H, CH_2), 1.63–1.51 (m, 1 H, C$H(CH_3)_2$), 1.40–1.25 (m, 4 H, CH_2), 0.86–0.80 (m, 6 H, CH_3) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 140.7 (C_q), 128.9 (+, *C*H), 128.5 (+, *C*H), 125.8 (+, *C*H), 80.2 (+, *C*HOH), 42.9 (+, *C*H$(CH_3)_2$), 28.1 (–, *C*H_2), 27.8 (–, *C*H_2), 27.3 (–, *C*H_2), 26.6 (–, *C*H_2), 21.5 (–, *C*H_2), 20.1 (–, *C*H_2), 10.8 (+, *C*H_3), 10.4 (+, *C*H_3) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3404 (vw), 2957 (m), 2935 (w), 1655 (vw), 1485 (vw), 1460 (w), 1427 (w), 1377 (m), 1275 (w), 1215 (w), 1143 (vw), 1144 (vw), 998 (w), 910 (w), 841 (w), 750 (vw), 718 (w), 655 (w), 542 (vw), 396 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 208 (6) [M^+], 137 (100) [$C_9H_{13}O^+$], 57 (33). – **HRMS** ($C_{14}H_{24}O$): calc. 208.1822; found 208.1820.

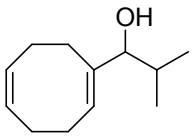
(*rac*)-1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-3-(trimethylsilyl)prop-2-yn-1-ol (2c)



This compound was synthesized following **GP 1** from **1** (2.00 g, 10.8 mmol, 1.10 equiv.) and the corresponding aldehyde (1.43 mL, 1.22 g, 9.68 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 10/1) and the desired product **2c** was obtained as a yellow oil (342 mg, 1.46 mmol, 15%).

***R*$_f$** = 0.21 (CH/EE: 10/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.84–5.77 (m, 1 H, CH_{COD}), 5.61–5.50 (m, 2 H, CH_{COD}), 4.73 (s, 1 H, C*H*OH), 2.59–2.36 (m, 8 H, CH_2), 0.17 (s, 9 H, Si(CH_3)$_3$) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 138.0 (C_q), 128.9 (+, *C*H), 128.4 (+, *C*H), 127.5 (+, *C*H), 105.1 (C_q), 90.6 (C_q), 69.3 (+, *C*HOH), 28.4 (–, *C*H_2), 27.9 (–, *C*H_2), 27.1 (–, *C*H_2), 27.0 (–, *C*H_2), –0.1 (+, Si(*C*H_3)$_3$) ppm. – **MS** (3NBA, FAB), *m/z* (%): 233 (51) [M^+–H], 231 (31), 217 (36), 155 (53), 147 (77), 137 (50), 125 (97), 115 (48), 107 (62), 97 (100) [$C_5H_9Si^+$], 95 (63).

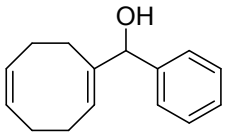
(*rac*)-1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2-methylpropan-1-ol (2d)



This compound was synthesized following **GP 1** from **1** (500 mg, 2.69 mmol, 1.10 equiv.) and the corresponding aldehyde (0.220 mL, 174 mg, 2.42 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 10/1) and the desired product **2d** was obtained as a yellow oil (342 mg, 1.90 mmol, 78%).

R_f = 0.27 (CH/EE: 9/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.59−5.44 (m, 3 H, CH_{COD}), 3.52 (d, ^3J = 8.3 Hz, 1 H, C*H*OH), 2.47−2.22 (m, 8 H, CH_2), 1.76−1.63 (m, 1 H, C$H(CH_3)_2$), 0.95 (d, ^3J = 6.6 Hz, 3 H, CH_3), 0.77 (d, ^3J = 6.8 Hz, 3 H, CH_3) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 140.6 (C_q), 128.9 (+, *C*H), 128.6 (+, *C*H), 126.1 (+, *C*H), 85.1 (+, *C*HOH), 31.3 (+, *C*$H(CH_3)_2$), 28.1 (−, *C*H_2), 27.7 (−, *C*H_2), 27.3 (−, *C*H_2), 26.3 (−, *C*H_2), 19.5 (+, *C*H_3), 18.8 (+, *C*H_3) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3394 (vw), 2952 (w), 2877 (w), 2832 (w), 1655 (vw), 1486 (w), 1468 (w), 1427 (w), 1380 (w), 1364 (w), 1294 (w), 1245 (vw), 1168 (vw), 1149 (vw), 1112 (vw), 1057 (vw), 1001 (m), 956 (vw), 929 (vw), 894 (vw), 831 (w), 720 (w), 655 (w), 525 (w), 492 (vw), 410 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 180 (10) [M^+], 137 (100) [$C_9H_{13}O^+$], 119 (31), 91 (35), 67 (39), 55 (34). – **HRMS** ($C_{12}H_{20}O$): calc. 180.1509; found 180.1511.

(*rac*)-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(phenyl)methanol (2e)

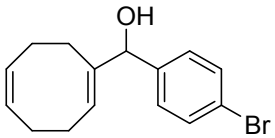


This compound was synthesized following **GP 1** from **1** (2.00 g, 10.8 mmol, 1.10 equiv.) and the corresponding aldehyde (0.201 mL, 232 mg, 2.42 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **2e** was obtained as a colourless oil (1.35 g, 6.32 mmol, 65%).

R_f = 0.28 (CH/EE: 10/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.30−7.09 (m, 5 H, CH_{Ar}), 5.74 (t, ^3J = 6.3 Hz, 1 H, CH_{COD}), 5.49−5.37 (m, 1 H, CH_{COD}), 5.37−5.26 (m, 1 H, CH_{COD}), 5.02 (s, 1 H, C*H*OH), 2.37−1.96 (m, 8 H, CH_2), 1.81 (s, 1 H, CHO*H*) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 142.4 (C_q), 140.8 (C_q), 128.8 (+, *C*H), 128.5 (+, *C*H), 128.0 (+, 2 × *C*H_{Ar}), 127.1 (+, *C*H), 126.3 (+, 2 × *C*H_{Ar}), 126.1 (+, *C*H_{Ar}), 79.9 (+, *C*HOH), 27.8 (−, *C*H_2), 27.7 (−, *C*H_2), 27.6 (−, *C*H_2), 26.8 (−, *C*H_2) ppm. – **IR (ATR)**:

$\tilde{\nu}$ = 3354 (w), 3059 (vw), 3006 (w), 2937 (w), 2879 (w), 2830 (w), 1654 (vw), 1600 (vw), 1514 (vw), 1487 (w), 1448 (m), 1426 (w), 1321 (vw), 1187 (w), 1097 (vw), 1079 (vw), 1051 (w), 1002 (m), 913 (w), 822 (w), 795 (w), 766 (w), 698 (m), 658 (w), 550 (w), 503 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 214 (5) [M^+], 108 (33), 107 (100) [$C_7H_7O^+$], 95 (39), 79 (32). – **HRMS** ($C_{15}H_{18}O$): calc. 214.1352; found 214.1350.

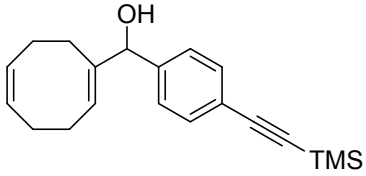
(*rac*)-(4-Bromophenyl)((1*Z*,5*Z*)-cycloocta-1,5-dien-1-yl)methanol (2f)



This compound was synthesized following **GP 1** from **1** (300 mg, 1.61 mmol, 1.10 equiv.) and the corresponding aldehyde (267 mg, 1.45 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **2f** was obtained as a colourless oil (294 mg, 1.01 mmol, 69%).

R_f = 0.41 (CH/EE: 20/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.43 (d, ^3J = 8.5 Hz, 2 H, CH_{Ar}), 7.24 (d, ^3J = 8.0 Hz, 2 H, CH_{Ar}), 5.82 (t, ^3J = 6.5 Hz, 1 H, CH_{COD}), 5.60−5.47 (m, 1 H, CH_{COD}), 5.48−5.35 (m, 1 H, CH_{COD}), 5.06 (s, 1 H, C*H*OH), 2.45−2.12 (m, 8 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 141.4 (C_q), 140.6 (C_q), 131.0 (+, 2 × CH_{Ar}), 128.7 (+, *C*H), 128.5 (+, *C*H), 128.0 (+, 2 × CH_{Ar}), 126.8 (+, *C*H), 120.9 (C_q), 79.4 (+, *C*HOH), 27.6 (−, CH_2), 27.6 (−, CH_2), 27.5 (−, CH_2), 26.5 (−, CH_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3363 (w), 3005 (w), 2879 (w), 2830 (w), 1590 (w), 1483 (m), 1425 (w), 1396 (w), 1168 (w), 1068 (m), 1008 (m), 833 (w), 729 (w), 702 (w), 510 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 292 (10) [M^+], 187 (68), 185 (100) [$C_7H_6BrO^+$], 107 (44), 105 (49), 79 (48), 77 (55). – **HRMS** ($C_{15}H_{17}{}^{79}BrO$): calc. 292.0457; found 292.0458.

(*rac*)-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(4-((trimethylsilyl)ethynyl)phenyl)methanol (2g)

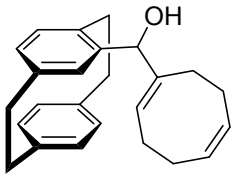


This compound was synthesized following **GP 1** from **1** (2.00 g, 10.7 mmol, 1.10 equiv.) and the corresponding aldehyde (1.96 g, 9.68 mmol, 1.00 equiv.). The crude product was purified by

column chromatography (CH/EE: 20/1) and the desired product **2g** was obtained as a colourless oil (1.88 g, 6.05 mmol, 63%).

R_f = 0.31 (CH/EE: 20/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.42 (d, ^3J = 8.3 Hz, 2 H, CH_{Ar}), 7.30 (d, ^3J = 7.8 Hz, 2 H, CH_{Ar}), 5.52 (t, ^3J = 6.2 Hz, 1 H, CH_{COD}), 5.52 (dt, ^2J = 11.9, ^3J = 5.9 Hz, 1 H, CH_{COD}), 5.39 (dt, ^2J = 11.4, ^3J = 6.0 Hz, 1 H, CH_{COD}), 5.13 (s, 1 H, C*H*OH), 2.21–1.98 (m, 8 H, CH_2), 0.24 (s, 9 H, Si(CH_3)$_3$) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 142.9 (C_q), 140.6 (C_q), 131.7 (+, 2 × CH_{Ar}), 128.7 (+, *C*H), 128.5 (+, *C*H), 127.0 (+, *C*H), 126.1 (+, 2 × CH_{Ar}), 121.7 (C_q), 105.1 (C_q), 79.8 (+, *C*HOH), 27.7 (–, *C*H_2), 27.6 (–, *C*H_2), 26.9 (–, *C*H_2), 26.5 (–, *C*H_2), 0.0 (+, Si(*C*H_3)$_3$) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3474 (w), 3397 (w), 2957 (w), 2877 (w), 2155 (w), 1502 (w), 1403 (w), 1247 (m), 1190 (w), 1169 (w), 1094 (vw), 1064 (w), 1016 (w), 841 (m), 791 (w), 759 (m), 701 (w), 661 (w), 638 (m), 599 (w), 566 (w), 532 (w), 532 (w), 440 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 310 (4) [M$^+$], 203 (100) [$C_{12}H_{15}OSi^+$]. – **HRMS** ($C_{20}H_{26}O^{28}Si$): calc. 310.1753; found 310.1754.

(*rac*)-[2,2]-Paracyclophanyl((1*Z*,5*Z*)-cycloocta-1,5-dien-1-yl)methanol (2h)

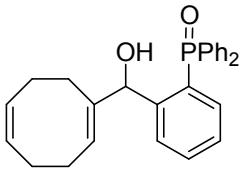


This compound was synthesized following **GP 1** from **1** (435 mg, 2.34 mmol, 1.10 equiv.) and the corresponding aldehyde (497 mg, 2.11 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 50/1) and the desired product **2h** was obtained as a colourless oil (289 mg, 0.842 mmol, 40%). There was just one diastereomer found in the NMR.

R_f = 0.17 (CH/EE: 50/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.71 (dd, ^3J = 7.1, ^4J = 1.7 Hz, 1 H, CH_{Ar}), 6.66–6.62 (m, 1H, CH_{Ar}), 6.48 (ddd, ^3J = 13.0, 5.6, ^4J = 1.8 Hz, 4 H, CH_{Ar}), 6.37 (d, ^3J = 7.7 Hz, 1 H, CH_{Ar}), 5.75 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 5.52–5.43 (m, 1 H, CH_{COD}), 5.40–5.32 (m, 1 H, CH_{COD}), 5.06 (s, 1 H, C*H*OH), 3.37 (ddd, ^3J = 13.6, 9.9, ^4J = 2.0 Hz, 1 H, CH_2), 3.16–3.01 (m, 6 H, CH_2), 2.73 (ddd, ^3J = 13.7, 10.7, 6.5 Hz, 1 H, CH_2), 2.40–1.80 (m, 8 H, CH_2), 1.60 (s, 1 H, CHO*H*) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 141.1 (C_q), 140.8 (C_q), 139.7 (C_q), 139.5 (C_q), 139.3 (C_q), 136.4 (C_q), 134.8 (+, CH_{Ar}), 133.4 (+, CH_{Ar}), 132.9 (+, CH_{Ar}), 132.4 (+, CH_{Ar}), 131.4 (+, CH_{Ar}), 130.0 (+, CH_{Ar}), 129.7 (+, *C*H), 128.9 (+, *C*H), 128.2 (+, *C*H), 127.1 (+, CH_{Ar}), 78.5 (+, *C*HOH), 35.3 (–, *C*H_2), 35.2 (–, *C*H_2), 34.1 (–, *C*H_2), 33.6 (–, *C*H_2), 27.9 (–, *C*H_2), 27.6 (–, *C*H_2), 27.4 (–, *C*H_2), 26.6 (–, *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ =

3437 (vw), 3006 (w), 2922 (m), 2885 (w), 2849 (w), 1654 (vw), 1592 (w), 1483 (w), 1412 (w), 1300 (vw), 1210 (w), 1137 (w), 1104 (w), 1058 (vw), 1000 (w), 932 (vw), 902 (w), 854 (w), 796 (w), 737 (w), 716 (m), 635 (m), 514 (w), 500 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 344 (17) [M^+], 315 (47), 239 (100) [$C_{17}H_{19}O^+$], 221 (64), 119 (34), 105/104 (78/95). – **HRMS** ($C_{25}H_{28}O$): calc. 344.2135; found 344.2135.

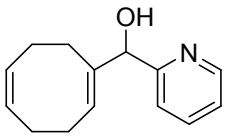
(*rac*)- (2-(((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(hydroxy)methyl)phenyl)diphenylphosphine-oxide (2i)



This compound was synthesized following **GP 1** from **1** (1.50 g, 8.06 mmol, 1.10 equiv.) and the corresponding aldehyde (2.11 g, 7.26 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH → CH/EE: 20/1) and the desired product **2i** was obtained as a yellow oil (1.14 g, 2.76 mmol, 33%).

R_f = 0.36 (CH/EE: 20/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.50–7.21 (m, 12 H, CH_{Ar}), 7.13 (ddd, ^3J = 7.6, ^3J = 3.7, ^4J = 1.3 Hz, 1 H, CH_{Ar}), 7.08 (s, 1 H, CH_{Ar}), 5.84 (t, ^3J = 5.7 Hz, 1 H, CH_{COD}), 5.33 (dt, ^3J = 10.7, ^3J = 5.1 Hz, 1 H, CH_{COD}), 5.28–5.20 (m, 1 H, CH_{COD}), 2.45 (t, ^3J = 6.7 Hz, 2 H, CH_2), 2.13 (dq, ^2J = 13.6, ^3J = 7.0, ^3J = 6.4 Hz, 4 H, CH_2), 1.93–1.85 (m, 2 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 149.0 (C_q), 136.9 (C_q), 133.1 (C_q), 131.0 (C_q), 132.7 (+, *C*H_{Ar}), 132.3 (+, *C*H_{Ar}), 132.2 (+, 2 × *C*H_{Ar}), 131.7 (+, *C*H_{Ar}), 131.7 (+, *C*H_{Ar}), 128.9 (+, *C*H), 128.7 (+, 4 × *C*H_{Ar}), 128.5 (+, 4 × *C*H_{Ar}), 128.4 (+, *C*H), 124.3 (+, *C*H), 73.6 (+, *C*HOH), 60.4 (C_q), 29.5 (–, *C*H_2), 28.0 (–, *C*H_2), 27.4 (–, 2 × *C*H-$_2$) ppm. – **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 34.91 ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3366 (w), 3051 (w), 2878 (w), 1735 (w), 1585 (w), 1435 (w), 1290 (w), 1229 (w), 1199 (w), 1116 (w), 1101 (w), 998 (vw), 864 (vw), 830 (vw), 776 (w), 747 (w), 719 (m), 695 (m), 643 (w), 540 (m), 460 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 414 (3) [M^+], 398 (34), 381 (40), 348 (44), 333 (62), 290/291 (46/80), 186 (43), 183 (100), 165 (45), 108 (39). – **HRMS** ($C_{27}H_{27}O_2P$): calc. 414.1743; found 414.1744.

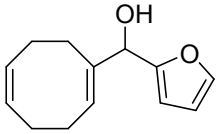
(*rac*)-((1*E*,5*Z*)-Cycloocta-1,5-dien-1-yl)(pyridin-2-yl)methanol (2j)



This compound was synthesized following **GP 1** from **1** (500 mg, 2.69 mmol, 1.10 equiv.) and the corresponding aldehyde (0.23 mL, 259 mg, 2.42 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **2j** was obtained as a dark green oil (288 mg, 1.34 mmol, 55%).

R_f = 0.18 (CH/EE: 10/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.52 (d, ^3J = 4.9 Hz, 1 H, C$H_{pyridine}$), 7.64 (td, ^3J = 7.7, ^4J = 1.8 Hz, 1 H, C$H_{pyridine}$), 7.28 (d, ^3J = 7.9 Hz, 1 H, C$H_{pyridine}$), 7.23−7.15 (m, 1 H, C$H_{pyridine}$), 5.87 (t, ^3J = 6.2 Hz, 1 H, CH_{COD}), 5.59−5.48 (m, 1 H, CH_{COD}), 5.39−5.30 (m, 1 H, CH_{COD}), 5.15 (s, 1 H, CHO*H*), 5.10 (s, 1 H, C*H*OH), 2.57−2.26 (m, 6 H, CH_2), 2.09−1.96 (m, 1 H, CH_2), 1.85−1.71 (m, 1 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 160.2 (C_q), 147.3 (+, *C*H$_{pyridine}$), 140.1 (C_q), 136.4 (+, *C*H$_{pyridine}$), 128.9 (+, *C*H), 128.8 (+, *C*H), 128.4 (+, *C*H), 122.2 (+, *C*H$_{pyridine}$), 121.2 (+, *C*H$_{pyridine}$), 79.3 (+, *C*HOH), 27.9 (−, *C*H_2), 27.8 (−, *C*H_2), 27.5 (−, *C*H_2), 25.4 (−, *C*H_2) ppm. − **IR (ATR)**: $\tilde{\nu}$ = 3379 (w), 3007 (w), 2879 (w), 2830 (w), 1654 (vw), 1592 (w), 1569 (w), 1471 (w), 1432 (m), 1394 (w), 1306 (w), 1203 (w), 1146 (w), 1101 (w), 1065 (w), 999 (w), 901 (vw), 842 (w), 749 (m), 711 (w), 665 (w), 623 (w), 496 (w), 405 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 215 (6) [M^+], 109 (82), 108 (100) [$C_6H_6NO^+$]. – **HRMS** ($C_{14}H_{17}O_1N_1$): calc. 215.1305; found 215.1303.

(*rac*)-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(furan-2-yl)methanol (2k)

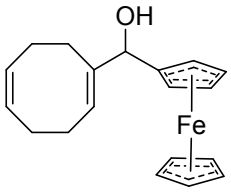


This compound was synthesized following **GP 1** from **1** (500 mg, 2.69 mmol, 1.10 equiv.) and the corresponding aldehyde (0.201 mL, 232 mg, 2.42 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **2k** was obtained as a yellow oil (222 mg, 1.08 mmol, 45%).

R_f = 0.30 (CH/EE: 5/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.39−7.35 (m, 1 H, CH_{furan}), 6.33 (dd, ^3J = 3.2, ^4J = 1.8 Hz, 1 H, CH_{furan}), 6.25 (dd, ^3J = 3.3, ^4J = 0.8 Hz, 1 H, CH_{furan}), 5.82 (t, ^3J = 6.2 Hz, 1 H, CH_{COD}), 5.62−5.45 (m, 2 H, CH_{COD}), 5.10 (s, 1 H, C*H*OH), 2.48−2.15 (m, 8 H, CH_2), 2.01 (s, 1 H, CHO*H*)

ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 155.6 (C_q), 141.9 (+, CH_{furan}), 138.5 (C_q), 128.7 (+, *C*H), 128.5 (+, *C*H), 126.7 (+, *C*H), 110.2 (+, CH_{furan}), 106.6 (+, CH_{furan}), 74.0 (+, *C*HOH), 27.8 (–, CH_2), 27.7 (–, CH_2), 27.5 (–, CH_2), 27.2 (–, CH_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3389 (vw), 3006 (vw), 2880 (w), 1654 (vw), 1485 (w), 1426 (w), 1218 (w), 1141 (w), 1061 (w), 1000 (m), 937 (w), 884 (w), 844 (w), 811 (w), 731 (m), 660 (w), 598 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 204 (34) [M^+], 186 (31), 145 (32), 97 (100) [$C_5H_5O_2^+$], 95 (39), 79 (32). – **HRMS** ($C_{13}H_{16}O_2$): calc. 204.1145; found 204.1146.

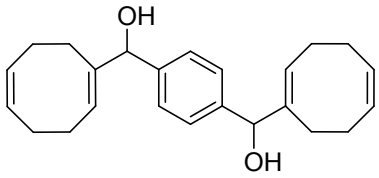
(*rac*)-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(ferrocenyl)methanol (2l)



This compound was synthesized following **GP 1** from **1** (1.50 g, 8.06 mmol, 1.10 equiv.) and the corresponding aldehyde (1.55 g, 7.26 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 5/1) and the desired product **2l** was obtained as a red oil (1.21 g, 3.76 mmol, 52%).

R_f = 0.38 (CH/EE: 3/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.67 (t, ^3J = 6.1 Hz, 1 H, CH_{COD}), 5.56–5.40 (m, 2 H, CH_{COD}), 4.80 (s, 1 H, C*H*OH), 4.33–4.08 (m, 9 H, CH_{Cp}), 2.47–2.10 (m, 8 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 140.6 (C_q), 128.9 (+, *C*H), 128.4 (+, *C*H), 125.5 (+, *C*H), 93.1 (C_q), 76.4 (+, *C*HOH), 68.4 (+, 5 × CH_{Cp}), 67.9 (+, CH_{Cp}), 67.7 (+, CH_{Cp}), 67.5 (+, CH_{Cp}), 65.5 (+, CH_{Cp}), 28.1 (–, CH_2), 27.7 (–, CH_2), 27.5 (–, CH_2), 26.5 (–, CH_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3436 (vw), 3092 (vw), 3007 (w), 2879 (w), 1655 (vw), 1484 (w), 1426 (w), 1345 (w), 1215 (w), 1105 (w), 1040 (w), 1000 (m), 815 (m), 717 (w), 660 (w), 484 (m) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 322 (10) [M^+], 272 (34), 215 (30), 75 (100). – **HRMS** ($C_{19}H_{22}O^{56}Fe$): calc. 322.1015; found 322.1014.

(*meso*/*rac*)-1,4-Phenylenebis(((1*E*,5*Z*)-cycloocta-1,5-dien-1-yl)methanol) (2m)



This compound was synthesized following **GP 1** from **1** (2.00 g, 10.8 mmol, 2.20 equiv.) and the corresponding aldehyde (0.451 mL, 649 mg, 4.84 mmol, 1.00 equiv.). The crude product was

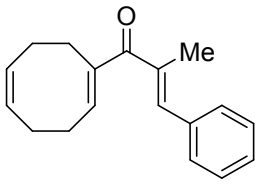
purified by column chromatography (CH/EE: 20/1) and the desired product **2m** was obtained as a colorless oil (725 mg, 2.07 mmol, 43%).

There was just one diastereomer found in the NMR.

R_f = 0.27 (CH/EE: 20/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31 (s, 4 H, 4 × CH_{Ar}), 5.84 (t, ^3J = 6.2 Hz, 2 H, 2 × CH_{COD}), 5.59−5.34 (m, 4 H, 4 × CH_{COD}), 5.13 (s, 2 H, 2 × C*H*OH), 2.47−2.06 (m, 16 H, 2 × CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 141.4 (2 × C_q), 140.9 (2 × C_q), 128.8 (+, 2 × *C*H), 128.5 (+, 2 × *C*H), 126.1 (+, 2 × *C*H, 4 × *C*H_{Ar}), 79.8 (+, 2 × *C*HOH), 27.8 (−, 2 × *C*H_2), 27.7 (−, 2 × *C*H_2), 27.6 (−,2 × *C*H_2), 26.7 (−,2 × *C*H_2) ppm. − **IR (ATR)**: $\tilde{\nu}$ = 3371 (w), 3006 (w), 2937 (w), 2879 (m), 2830 (w), 1655 (vw), 1508 (vw), 1484 (w), 1425 (w), 1195 (w), 1138 (vw), 1060 (w), 1002 (m), 902 (vw), 843 (w), 808 (w), 713 (w), 659 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 350 (51) [M^+], 243 (63), 241 (84), 213 (64), 181 (60), 131 (60), 79 (64), 69 (100). – **HRMS** ($C_{24}H_{30}O_2$): calc. 350.2240; found 350.2241.

2.2.2 Syntheses of ketone derivatives

(*E*)-1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2-methyl-3-phenylprop-2-en-1-one (3a)

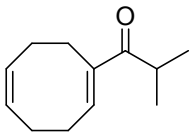


This compound was synthesized following **GP 2** from the alcohol **2a** (275 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1→10/1) and the desired product **3a** was obtained as a yellow oil (184 mg, 730 µmol, 67%).

R_f = 0.51 (CH/EE: 10/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.30−7.23 (m, 4 H, CH_{Ar}), 7.21−7.11 (m, 1 H, CH_{Ar}), 7.00−6.90 (m, 1 H, C=C*H*), 6.31 (t, ^3J = 5.9 Hz, 1 H, CH_{COD}), 5.55−5.42 (m, 2 H, 2 × CH_{COD}), 4.47 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.46−2.39 (m, 2 H, CH_2), 2.39−2.29 (m, 4 H, CH_2), 1.99 (d, ^4J = 1.5 Hz, 3 H, CH_3) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 202.4 (C_q), 140.8 (+, *C*H), 140.0 (C_q), 138.4 (C=*C*H), 137.4 (C_q), 136.1 (C_q), 129.5 (+, 2 × *C*H_{Ar}), 129.2 (+, *C*H_{Ar}), 128.3 (+, 2 × *C*H_{Ar}), 128.0 (+, *C*H), 127.9 (+, *C*H), 29.0 (−, *C*H_2), 28.3 (−, *C*H_2), 26.7 (−, *C*H_2), 26.6 (−, *C*H_2), 14.8 (+, *C*H_3) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3356 (vw), 3010 (w), 2883 (w), 1719 (vw), 1627 (m), 1488 (w), 1444 (w), 1377 (w), 1263 (w), 1209 (w), 1126 (w), 1061 (vw), 1027 (w), 1000 (w), 925 (w), 860 (vw), 748 (w), 694 (m), 617 (w), 516 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 252 (23) [M^+], 230 (31), 145 (100) [$C_{10}H_9O^+$], 117 (62) 115 (33), 108 (47), 105 (37), 91 (44) 79 (39). – **HRMS** ($C_{18}H_{20}O$): calc. 252.1509; found 252.1509.

Chemical analysis accords to reference.[3]

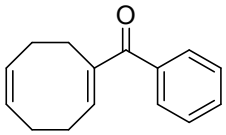
1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2-methylpropan-1-one (3d)



This compound was synthesized following **GP 2** from the alcohol **2d** (268 mg, 1.49 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **3d** was obtained as a yellow oil (23.5 mg, 132 µmol, 9%).

R_f = 0.20 (CH/EE: 10/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.80 (t, ^3J = 6.2 Hz, 1 H, CH_{COD}), 5.51–5.38 (m, 2 H, CH_{COD}), 3.42–3.20 (m, 1 H, $CH(CH_3)_2$), 2.69 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.60–2.51 (m, 2 H, CH_2), 2.50–2.43 (m, 2 H, CH_2), 2.35–2.30 (m, 2 H, CH_2), 1.05 (d, ^3J = 6.8 Hz, 6 H, CH_3) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.5 (C_q), 140.2 (+, *C*H), 140.0 (C_q), 129.6 (+, *C*H), 127.4 (+, *C*H) 33.8 (+, *C*H$(CH_3)_2$), 29.2 (–, *C*H_2), 28.5 (–, *C*H_2), 26.5 (–, *C*H_2), 24.9 (–, *C*H_2), 19.7 (+, 2 × *C*H_3) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3365 (vw), 2936 (w), 2878 (w), 1653 (vw), 1598 (vw), 1486 (w), 1443 (w), 1426 (w), 1353 (w), 1291 (w), 1212 (w), 1163 (vw), 1129 (vw), 1097 (vw), 1041 (w), 1009 (w), 916 (w), 844 (w), 748 (w), 698 (m), 516 (w), 389 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 177 (16) [M^+–H], 150/149 (45/56), 121 (30), 105 (39), 79 (36), 71 (100) [$C_4H_7O^+$]. – **HRMS** ($C_{12}H_{18}O$): calc. 178.1352; found 178.1352.

((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(phenyl)methanone (3e)



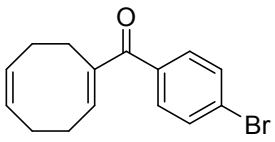
Method A: This compound was synthesized following **GP 2** from the alcohol **2e** (210 mg, 0.719 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **3e** was obtained as a colourless oil (341 mg, 1.61 mmol, 76%).

Method B: This compound was also synthesized following a one-step procedure (**GP 3**) based on **1** (500 mg, 2.69 mmol, 2.50 equiv.) and the corresponding carboxylic acid (131 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 50/1) and the desired product **3e** was obtained as a colourless oil (125 mg, 589 µmol, 55%).

R_f = 0.22 (CH/EE: 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.61–7.53 (m, 2 H, CH_{Ar}), 7.49–7.39 (m, 1 H, CH_{Ar}), 7.39–7.29 (m, 2 H, CH_{Ar}), 6.39 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 5.66–5.48 (m, 2 H, CH_{COD}), 2.83 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.57–2.39 (m, 6 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.8 (C_q), 145.2 (*C*H), 145.0 (*C*H_{Ar}), 140.4 (C_q), 139.2 (C_q), 131.2 (+, *C*H), 129.4 (+, *C*H), 129.3 (+, 2 × *C*H_{Ar}), 127.9 (+, 2 × *C*H_{Ar}), 127.8 (+, *C*H), 29.4 (–, *C*H_2), 28.5 (–, *C*H_2), 26.5 (–, *C*H_2), 26.1 (–, *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3010 (vw), 2882 (vw), 1642 (m), 1596 (w), 1576 (w), 1483 (vw), 1444 (w), 1427 (w), 1379 (w), 1313 (w), 1275 (vw), 1226 (m), 1176 (w), 1126 (w), 1053 (w), 1013 (w), 983 (w), 927 (vw), 854 (w), 769 (w), 748 (w), 718 (m), 698 (m), 654 (w), 410 (vw) cm^{-1}. – **MS**

(70 eV, EI), *m/z* (%): 212 (5) [M^+], 184 (63), 107 (100) [$C_8H_{11}^+$], 105 (78), 79 (31), 77 (39). – **HRMS** ($C_{15}H_{16}O_1$): calc. 212.1196; found 212.1195.

(4-Bromophenyl)((1*Z*,5*Z*)-cycloocta-1,5-dien-1-yl)methanone (3f)

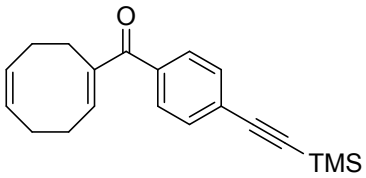


Method A: This compound was synthesized following **GP 2** from the alcohol **2f** (210 mg, 0.719 mmol, 1.00 equiv.). The crude product was purified by recrystallization (pentane) and the desired product **3f** was obtained as a colourless solid (143 mg, 493 µmol, 69%).

Method B: This compound was also synthesized following a one-step procedure (**GP 3**) based on **1** (500 mg, 2.69 mmol, 2.50 equiv.) and the corresponding carboxylic acid (215 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **3f** was obtained as a colourless solid (104 mg, 263 µmol, 24%).

R_f = 0.43 (CH/EE: 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.54 (d, ^3J = 8.5 Hz, 2 H, CH_{Ar}), 7.49 (d, ^3J = 8.6 Hz, 2 H, CH_{Ar}), 6.41 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 5.79–5.51 (m, 2 H, CH_{COD}), 2.85 (t, ^3J = 6.9 Hz, 2 H, CH_2), 2.62–2.40 (m, 6 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 198.6 (C_q), 145.2 (*C*H), 140.3 (C_q), 137.9 (C_q), 131.2 (+, 2 × *C*H_{Ar}), 130.9 (+, 2 × *C*H_{Ar}), 129.4 (+, *C*H), 127.8 (+, *C*H), 126.1 (C_q), 29.4 (–, *C*H_2), 28.4 (–, *C*H_2), 26.4 (–, *C*H_2), 26.1 (–, *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3014 (vw), 2875 (vw), 1626 (w), 1582 (w), 1483 (w), 1443 (vw), 1392 (w), 1286 (w), 1228 (w), 1176 (w), 1127 (vw), 1065 (w), 1007 (w), 985 (w), 962 (w), 870 (w), 844 (w), 826 (w), 793 (w), 741 (w), 710 (w), 653 (w), 625 (vw), 596 (vw), 514 (w), 460 (w), 429 (vw), 415 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 290 (3) [M^+], 264 (87), 262 (91), 185 (87), 183 (100) [$C_7H_4BrO^+$], 157 (40), 155 (33), 105 (40). – **HRMS** ($C_{15}H_{15}{}^{79}BrO$): calc. 290.0301; found 290.0299.

((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(4-((trimethylsilyl)ethynyl)phenyl)methanone (3g)



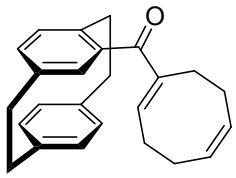
Method A: This compound was synthesized following **GP 2** from the alcohol **2g** (300 mg, 0.967 mmol, 1.00 equiv.). After the filtration step there was just one spot on the TLC, no purification

was needed. The desired product **3g** was obtained as a colourless oil which solidifies upon standing (255 mg, 827 µmol, 85%).

Method B: This compound was also synthesized following a one-step procedure (**GP 3**) based on **1** (500 mg, 2.69 mmol, 2.50 equiv.) and the corresponding carboxylic acid (131 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **3g** was obtained as a colorless oil (35 mg, 113 µmol, 12%).

R_f = 0.60 (CH/EE: 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.54 (d, ^3J = 8.5 Hz, 2 H, CH_{Ar}), 7.46 (d, ^3J = 8.5 Hz, 2 H, CH_{Ar}), 6.38 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 2.84 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.57−2.42 (m, 6 H, CH_2), 0.25 (s, 9 H, Si(CH_3)$_3$) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 198.9 (C_q), 145.1 (*C*H), 145.0 (*C*H), 104.2 (C_q), 96.8 (C_q), 131.2 (+, *C*H), 131.4 (+, 2 × *C*H$_{Ar}$), 129.3 (+, *C*H), 129.1 (+, 2 × *C*H$_{Ar}$), 127.8 (+, *C*H), 126.0 (C_q), 104.2 (C_q), 96.80 (C_q), 29.4 (−, *C*H$_2$), 28.4 (−, *C*H$_2$), 26.4 (−, *C*H$_2$), 26.0 (−, *C*H$_2$), −0.17 (+, Si(*C*H$_3$)$_3$) ppm. − **IR (ATR)**: $\tilde{\nu}$ = 2956 (w), 2158 (w), 1646 (m), 1599 (m), 1484 (w), 1402 (w), 1305 (w), 1270 (m), 1249 (m), 1219 (m), 1176 (w), 1126 (w), 1012 (w), 984 (w), 840 (s), 758 (m), 700 (w), 656 (m), 534 (w) cm^{-1}. − **MS** (70 eV, EI), *m/z* (%): 308 (5) [M$^+$], 280 (46), 271 (31), 203 (58), 201 (100) [$C_{12}H_{13}Si^+$]. − **HRMS** ($C_{15}H_{16}O_1$): calc. 208.1596; found 308.1595.

[2,2]-Paracylophanyl((1*Z*,5*Z*)-cycloocta-1,5-dien-1-yl)methanone (3h)

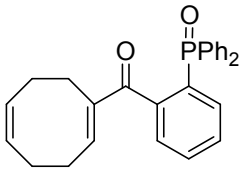


This compound was synthesized following **GP 3** based on **1** (200 mg. 1.08 mmol, 2.50 equiv.) and the corresponding carboxylic acid (108 mg, 0.430 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 50/1) and the desired product **3h** was obtained as a colourless solid (13 mg, 38.0 µmol, 9%).

R_f = 0.17 (CH/EE: 50/1). − **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.75 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 1 H, CH_{Ar}), 6.60−6.53 (m, 4 H, CH_{Ar}), 6.48 (d, ^3J = 7.7 Hz, 1 H, CH_{Ar}), 6.34 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 1 H, CH_{Ar}), 6.15 (t, ^3J = 5.6 Hz, 1 H, CH_{COD}), 5.67−5.48 (m, 2 H, CH_{COD}), 3.29 (ddd, ^3J = 12.8, 10.2, ^4J = 2.6 Hz, 1 H, CH_2), 3.20−2.77 (m, 9 H, CH_2), 2.54−2.32 (m, 6 H, CH_2) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$):

δ = 199.5 (C_q), 145.4 (+, *C*H), 142.1 (C_q), 140.4 (C_q), 139.6 (C_q), 139.2 (C_q), 139.1 (C_q), 137.2 (C_q), 135.0 (+, 2 × CH_{Ar}), 133.3 (+, CH_{Ar}), 132.6 (+, CH_{Ar}), 132.5 (+, CH_{Ar}), 132.1 (+, CH_{Ar}), 131.3 (+, CH_{Ar}), 129.4 (+, *C*H), 127.8 (+, *C*H), 35.5 (−, CH_2), 35.2 (−, CH_2), 35.1 (−, CH_2), 34.8 (−, CH_2), 29.3 (−, CH_2), 28.6 (−, CH_2), 26.4 (−, CH_2), 25.4 (−, CH_2) ppm. − **IR (ATR)**: $\tilde{\nu}$ = 2924 (w), 1628 (m), 1555 (w), 1480 (w), 1434 (w), 1414 (w), 1321 (vw), 1287 (w), 1233 (w), 1175 (w), 1159 (w), 1107 (w), 991 (w), 900 (w), 864 (w), 844 (w), 799 (w), 744 (w), 703 (m), 672 (w), 637 (m), 531 (w), 508 (m), 456 (vw), 408 (w) cm^{-1}. − **MS** (70 eV, EI), *m/z* (%): 342 (15) [M^+], 292 (37), 263 (100), 188 (30), 131 (349), 104 (46). − **HRMS** ($C_{25}H_{28}O_1$): calc. 342.1984; found 342.1984.

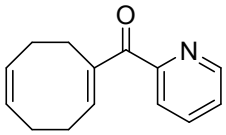
((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(2-(diphenylphosphoryl)phenyl)methanone (3i)



This compound was synthesized following **GP 2** from the alcohol **2i** (111 mg, 0.380 mmol, 1.00 equiv.). The crude product was purified by recrystallization (pentane) and the desired product **3i** was obtained as a colourless solid (12.5 mg, 30.3 µmol, 8%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50−7.21 (m, 12 H, CH_{Ar}), 7.13 (ddd, ^3J = 7.6, ^3J = 3.7, ^4J = 1.3 Hz, 1 H, CH_{Ar}), 7.08 (s, 1 H, CH_{Ar}), 5.84 (t, ^3J = 5.7 Hz, 1 H, CH_{COD}), 5.33 (dt, ^3J = 10.7, ^3J = 5.1 Hz, 1 H, CH_{COD}), 5.28−5.20 (m, 1 H, CH_{COD}), 2.45 (t, ^3J = 6.7 Hz, 2 H, CH_2), 2.13 (dq, ^2J = 13.6, ^3J = 7.0, ^3J = 6.4 Hz, 4 H, CH_2), 1.93−1.85 (m, 2 H, CH_2) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.3 (C_q), 148.2 (+, *C*H), 145.4 (C_q), 141.9 (C_q), 132.4 (C_q), 132.2 (+, 4 × CH_{Ar}), 131.7 (+, 2 × CH_{Ar}), 131.2 (+, C_q, 2 × CH_{Ar}), 130.2 (C_q), 129.9 (+, *C*H), 129.0 (+, CH_{Ar}), 128.6 (+, CH_{Ar}), 128.3 (+, 4 × CH_{Ar}), 127.2 (+, *C*H), 29.7 (−, CH_2), 28.5 (−, CH_2), 25.7 (−, CH_2), 24.4 (−, CH_2) ppm. − **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.32 ppm. **IR (ATR)**: $\tilde{\nu}$ = 2881 (vw), 1659 (w), 1626 (w), 1588 (vw), 1482 (vw), 1435 (w), 1290 (w), 1229 (w), 1199 (w), 1116 (w), 1101 (w), 998 (vw), 864 (vw), 830 (vw), 776 (w), 747 (w), 719 (m), 695 (m), 643 (w), 540 (m), 460 (w) cm^{-1}. − **MS** (70 eV, EI), *m/z* (%): 412 (100) [M^+], 305 (94), 277 (41), 202 (32), 69 (35). − **HRMS** ($C_{27}H_{25}O_2P$): calc. 412.1587; found 412.1586.

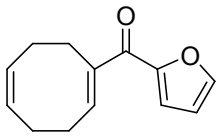
((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(pyridin-2-yl)methanone (3j)



This compound was synthesized following **GP 2** from the alcohol **2j** (258 mg, 1.20 mmol, 1.00 equiv.). After the filtration step there was just one spot on the TLC, no purification was needed. The desired product **3j** was obtained as a black oil (205 mg, 0.96 mmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (dt, ^3J = 4.9, ^4J = 1.2 Hz, 1 H, C$H_{pyridine}$), 7.76 (td, ^3J = 7.7, ^4J = 1.7 Hz, 1 H, C$H_{pyridine}$), 7.62 (dd, ^3J = 7.8 Hz, 1 H, C$H_{pyridine}$), 7.34 (ddd, ^3J = 7.7, 4.8, ^4J = 1.3 Hz, 1 H, C$H_{pyridine}$), 6.72 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 5.69−5.41 (m, 2 H, CH_{COD}), 2.87 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.58 (q, ^3J = 6.2 Hz, 2 H, CH_2), 2.47 (quin, ^3J = 6.6 Hz, 4 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 196.8 (C_q), 156.9 (C_q), 148.7 (+, *C*H), 148.3 (+, *C*H$_{pyridine}$), 139.4 (C_q), 136.6 (+, *C*H$_{pyridine}$), 129.5 (+, *C*H), 127.6 (+, *C*H), 128.8 (+, *C*H$_{pyridine}$), 123.8 (+, *C*H$_{pyridine}$), 30.1 (−, *C*H$_2$), 28.6 (−, *C*H$_2$), 26.1 (−, *C*H$_2$), 25.6 (−, *C*H$_2$) ppm. − **IR (ATR)**: $\tilde{\nu}$ = 2922 (w), 1627 (m), 1582 (w), 1563 (w), 1380 (m), 1299 (m), 1230 (m), 1184 (w), 1136 (m), 1018 (w), 994 (w), 864 (vw), 801 (vw), 748 (w), 720 (m), 698 (ww), 662 (w), 617 (w), 404 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 213 (27) [M$^+$], 185 (39), 137 (50), 130 (32), 109/108 (82/100). − **HRMS** ($C_{14}H_{15}ON$): calc. 213.1154; found 213.1153.

((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(furan-2-yl)methanone (3k)

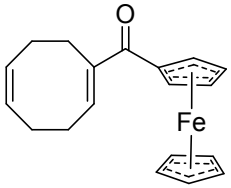


This compound was synthesized following **GP 2** from the alcohol **2k** (217 mg, 0.70 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **3k** was obtained as a colourless solid (72 mg, 35.6 µmol, 51%).

***R*$_f$** = 0.46 (CH/EE: 10/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.61−7.59 (m, 1 H, CH_{furan}), 7.00 (d, ^3J = 3.4 Hz, 1 H, CH_{furan}), 6.75 (t, ^3J = 6.0 Hz, 1 H, CH_{COD}), 6.48 (dd, ^3J = 3.5, ^4J = 1.7 Hz, 1 H, CH_{furan}) 5.69−5.41 (m, 2 H, CH_{COD}), 2.81 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.59 (q, ^3J = 6.4 Hz, 2 H, CH_2), 2.54−2.41 (m, 4 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 185.8 (C_q), 152.3 (C_q), 146.4 (+, *C*H$_{furan}$), 141.6 (+, *C*H$_{furan}$), 140.1 (C_q), 129.3 (+, *C*H), 127.8 (+, *C*H), 119.2 (+, *C*H), 111.5 (+, *C*H$_{furan}$), 29.2 (−, *C*H$_2$), 28.5 (−, *C*H$_2$), 26.6 (−, *C*H$_2$), 26.5 (−, *C*H$_2$) ppm. **– IR (ATR)**: $\tilde{\nu}$ = 3131 (vw), 2885 (w), 1710 (w), 1629

(m), 1559 (w), 1463 (m), 1389 (m), 1292 (m), 1163 (m), 1130 (w), 1082 (w), 1014 (m), 918 (w), 884 (w), 826 (w), 726 (m), 685 (w), 594 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 202 (7) [M^+], 174 (100) [$C_{11}H_{10}O_2^+$], 95 (86). – **HRMS** ($C_{13}H_{14}O_2$): calc. 202.0994; found 202.0993.

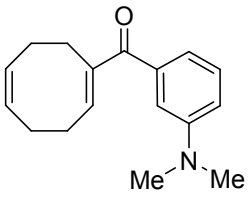
((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(ferrocenyl)methanone (3l)



This compound was synthesized following **GP 2** from the alcohol **2l** (460 mg, 1.43 mmol, 1.00 equiv.). After the filtration step there was just one spot on the TLC, no purification was needed. The desired product **3l** was obtained as a red solid (409 mg, 1.28 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.56 (t, ^3J = 5.9 Hz, 1 H, CH_{COD}), 5.63 (q, 2 H, CH_{COD}), 4.76 (t, ^3J = 2.0 Hz, 2 H, CH_{Cp}), 4.46–4.44 (m, 2 H, CH_{Cp}), 4.15 (s, 5 H, CH_{Cp}), 2.80 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.56–2.42 (m, 6 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 201.7 (C_q), 141.2 (C_q), 137.4 (+, *C*H), 129.2 (+, *C*H), 128.0 (+, *C*H), 79.0 (C_q), 71.6 (+, 2 × *C*H_{Cp}), 71.2 (+, 2 × *C*H_{Cp}), 69.9 (+, 5 × *C*H_{Cp}), 28.7 (–, *C*H_2), 28.6 (–, *C*H_2), 27.1 (–, *C*H_2), 26.9 (–, *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3093 (vw), 2881 (w), 1623 (m), 1484 (w), 1440 (m), 1376 (w), 1280 (m), 1235 (m), 1138 (w), 1106 (w), 1066 (w), 1027 (m), 1002 (m), 819 (m), 736 (m), 665 (w), 482 (m) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 320 (76) [M^+], 272 (94), 266 (33), 215 (89), 187/186 (51/87), 181 (34), 131 (32), 121 (47), 75/69 (100/57). – **HRMS** ($C_{19}H_{20}OFe$): calc. 320.0864; found 320.0865.

((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(3-(dimethylamino)phenyl)methanone (3n)

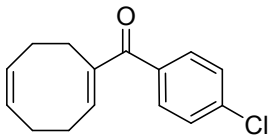


This compound was synthesized following **GP 3** based on **1** (500 mg. 2.69 mmol, 2.50 equiv.) and the corresponding carboxylic acid (177 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **3n** was obtained as a yellow oil (275 mg, 1.66 mmol, 46%).

R_f = 0.38 (CH/EE: 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.27–7.19 (m, 1 H, CH_{Ar}), 7.00 (s, 1 H, C*H*-$_{Ar}$) 6.93 (d, ^3J = 7.4 Hz, 1 H, CH_{Ar}), 6.85 (d, ^3J = 8.1 Hz, 1 H, CH_{Ar}), 6.46 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 5.68–5.55 (m, 2 H, CH_{COD}), 2.97 (s, 6 H, N(CH_3)$_2$) 2.86 (t, ^3J = 6.9 Hz, 2 H, CH_2), 2.60–2.43 (m, 6 H,

CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.6 (C_q), 144.3 (+, *C*H), 140.4 (2 × C_q), 140.0 (C_q), 129.5 (+, *C*H), 128.4 (+, *C*H_{Ar}), 127.8 (+, *C*H), 117.9 (+, *C*H_{Ar}), 115.4 (+, *C*H_{Ar}), 113.1 (+, *C*H_{Ar}), 40.6 (+, N(*C*H_3)$_2$), 29.2 (–, *C*H_2), 28.5 (–, *C*H_2), 26.6 (–, *C*H_2), 26.3 (–, *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 2881 (w), 1640 (m), 1596 (m), 1572 (m), 1493 (m), 1493 (m), 1431 (m), 1350 (m), 1269 (m), 1223 (m), 1124 (w), 1061 (w), 1024 (w), 987 (m), 955 (w), 861 (w), 772 (w), 733 (m), 695 (w), 657 (w), 493 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 255 (51) [M^+], 148 (38), 120 (32), 104 (100). – **HRMS** ($C_{17}H_{21}ON$): calc. 255.1623; found 255.1622.

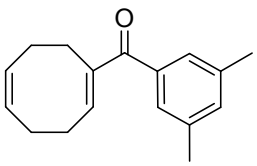
(4-Chlorophenyl)((1*Z*,5*Z*)-cycloocta-1,5-dien-1-yl)methanone (3o)



This compound was synthesized following **GP 3** based on **1** (500 mg. 2.69 mmol, 2.50 equiv.) and the corresponding carboxylic acid (168 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 50/1→20/1) and the desired product **3o** was obtained as a yellow oil (144 mg, 584 µmol, 54%).

***R*$_f$** = 0.39 (CH/EE: 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.56 (d, ^3J = 8.5 Hz, 2 H, CH_{Ar}), 7.37 (d, ^3J = 8.5 Hz, 2 H, CH_{Ar}), 6.40 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 5.66–5.56 (m, 2 H, CH_{COD}), 2.85 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.60–2.50 (m, 6 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 198.5 (C_q), 145.1 (+, *C*H), 140.3 (C_q), 137.6 (C_q), 137.4 (C_q), 130.8 (+, 2 × *C*H_{Ar}), 129.4 (+, *C*H), 128.3 (+, 2 × *C*H_{Ar}), 127.8 (+, *C*H), 28.7 (–, *C*H_2), 28.6 (–, *C*H_2), 27.1 (–, *C*H_2), 26.9 (–, *C*H_2) ppm. – **IR (ATR)**: $\tilde{\nu}$ = 2948 (w), 1644 (m), 1587 (m), 1485 (w), 1398 (w), 1270 (m), 1226 (m), 1173 (w), 1089 (m), 1012 (m), 840 (m), 757 (m), 474 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 246 (13) [M^+], 139 (100) [$C_7H_4ClO^+$], – **HRMS** ($C_{15}H_{15}O^{35}Cl$): calc. 246.0811; found 246.0813.

((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)(3,5-dimethylphenyl)methanone (3p)

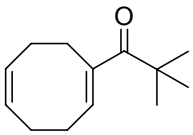


This compound was synthesized following **GP 3** based on **1** (500 mg. 2.69 mmol, 2.50 equiv.) and the corresponding carboxylic acid (162 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column

chromatography (CH/EE: 20/1) and the desired product **3p** was obtained as a colourless oil (117 mg, 487 µmol, 45%).

R_f = 0.59 (CH/EE: 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.20 (d, ^4J = 1.5 Hz, 2 H, CH_{Ar}), 7.11 (s, 1 H, CH_{Ar}), 6.44 (t, ^3J = 5.8 Hz, 1 H, CH_{COD}), 5.68−5.54 (m, 2 H, CH_{COD}), 2.85 (t, ^3J = 6.8 Hz, 2 H, CH_2), 2.61−2.43 (m, 6 H, CH_2), 2.26 (s, 6 H, CH_3) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.3 (C_q), 144.8 (+, *C*H), 140.5 (C_q), 139.3 (C_q), 137.4 (2 × C_q), 132.8 (+, 2 × *C*H_{Ar}), 129.5 (+, *C*H), 127.8 (+, *C*H), 127.0 (+, *C*H_{Ar}), 29.4 (−, *C*H_2), 28.6 (−, *C*H_2), 26.5 (−, *C*H_2), 26.1 (−, *C*H_2), 21.2 (+, 2 × CH_3) ppm. − **IR (ATR)**: $\tilde{\nu}$ = 3399 (vw), 2918 (w), 1716 (w), 1641 (m), 1601 (m), 1443 (w), 1381 (w), 1306 (m), 1189 (m), 1038 (w), 946 (w), 861 (w), 753 (w), 730 (w), 679 (w), 544 (vw), 497 (vw), 464 (vw) cm^{-1}. − **MS** (70 eV, EI), *m/z* (%): 240 (5) [M^+], 212 (91), 150 (30), 133 (100) [$C_9H_9O^+$], 105 (71). − **HRMS** ($C_{17}H_{20}O$): calc. 240.1514; found 240.1512.

1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2,2-dimethylpropan-1-one (3q)

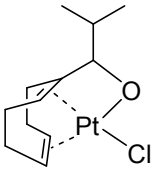


This compound was synthesized following **GP 3** based on **1** (500 mg. 2.69 mmol, 2.50 equiv.) and the corresponding carboxylic acid (110 mg, 1.08 mmol, 1.00 equiv.). The crude product was purified by column chromatography (CH/EE: 20/1) and the desired product **3q** was obtained as a colourless oil (49 mg, 255 µmol, 24%).

R_f = 0.59 (CH/EE: 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.15 (t, ^3J = 6.3 Hz, 1 H, CH_{COD}), 5.62−5.51 (m, 2 H, CH_{COD}), 2.58−2.53 (m, 2 H, CH_2), 2.51−2.45 (m, 2 H, CH_2), 2.44−2.35 (m, 4 H, CH_2), 1.22 (s, 9 H, CCH_3) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.3 (C_q), 140.3 (C_q), 132.7 (+, *C*H), 128.9 (+, *C*H), 128.1 (+, *C*H), 44.1 (C_q), 28.4 (+, C(*C*H_3)$_3$), 28.3 (−, *C*H_2), 28.2 (−, 2 × *C*H_2), 27.3 (−, *C*H_2) ppm. − **IR (ATR)**: $\tilde{\nu}$ = 3399 (w), 2965 (w), 1692 (m), 1479 (w), 1462 (w), 1396 (w), 1366 (w), 1151 (m), 1064 (w), 510 (vw), 417 (vw) cm^{-1}. − **MS** (70 eV, EI), *m/z* (%): 192 (3) [M^+], 164 (32), 135 (65), 79 (68), 57 (100) [$C_4H_9^+$]. − **HRMS** ($C_{13}H_{20}O$): calc. 192.1514; found 192.1514.

2.2.3 Syntheses of monometallic platinum(II) complexes

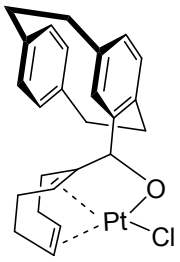
(1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2-methylpropoxy)platinum(II) chloride (4d)



This complex was synthesized following **GP 4** from the alcohol **2d** (596 mg, 3.31 mmol, 6.90 equiv.). The crude product was recrystallized from methanol to obtain the desired product **4d** as a colourless solid (147 mg, 359 µmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81−5.55 (m, 2 H, C*H*$_{COD}$), 5.38 (dd, ^{3}J = 7.1, ^{4}J = 3.1 Hz, 1 H, C*H*$_{COD}$), 3.80 (dd, ^{3}J = 9.7, ^{4}J = 4.4 Hz, 1 H, C*H*OPt), 2.93−2.59 (m, 5 H, C*H*$(CH_3)_2$, 2 × C*H*$_2$), 2.44−2.25 (m, 1 H, C*H*$_2$), 2.13 (dq, ^{3}J = 13.6, 7.4 Hz, 1 H, C*H*$_2$),), 1.91 (dt, ^{3}J = 14.6, 7.6 Hz, 1 H, C*H*$_2$), 1.85−1.74 (m, 1 H, C*H*$_2$), 1.02 (d, ^{3}J = 6.4 Hz, 3 H, CHC*H*$_3$), 0.56 (d, ^{3}J = 6.8 Hz, 3 H, CHC*H*$_3$) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 127.4 (*C*$_q$), 101.1 (+, *C*H), 100.0 (+, *C*H), 95.9 (+, *C*H), 82.2 (*C*HOPt), 31.9 (+, *C*H$(CH_3)_2$), 31.3 (−, *C*H$_2$), 30.9 (−, *C*H$_2$), 30.3 (−, *C*H$_2$), 29.5 (−, *C*H$_2$), 20.2 (+, CH_3), 19.1 (+, *C*H$_3$) ppm. − **^{195}Pt-NMR** (129 MHz, $CDCl_3$): δ = −3333 ppm. − **IR (ATR)**: $\tilde{\nu}$ = 3504 (vw), 2956 (w), 1459 (vw), 1421 (vw), 1384 (vw), 1364 (w), 1338 (vw), 1315 (w), 1238 (vw), 1168 (vw), 1117 (vw), 1051 (vw), 1024 (w), 952 (vw), 905 (vw), 885 (w), 866 (w), 866 (w), 827 (w), 804 (vw), 769 (vw), 732 (vw), 691 (vw), 636 (w), 571 (vw), 529 (vw), 479 (w), 463 (w), 416 (m) cm^{-1}. − **MS** (70 eV, EI), *m/z* (%): 409 (20) [M^+], 374/373/372 (82/99/100) [$C_{12}H_{19}OPt^+$]. − **HRMS** ($C_{12}H_{19}OClPt$): calc. 409.0767; found 409.0765.

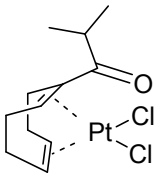
[2,2]Paracyclophanyl(((1*Z*,5*Z*)-cycloocta-1,5-dien-1-yl)methoxy)-platinum(II) chloride (4h)



This complex was synthesized following **GP 4** from the alcohol **2h** (285 mg, 0.827 mmol, 6.90 equiv.). The ligand was not soluble in *n*-propanol thus methanol was used instead. The crude product was recrystallized from dichloromethane to obtain the desired product **4h** as a colorless solid (36 mg, 62.8 µmol, 53%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.86 (s, 1 H, CH_{Ar}), 6.51−6.43 (m, 5 H, CH_{Ar}), 6.38 (s, 1 H, CH_{Ar}), 5.50−5.43 (m, 1 H, CH_{COD}), 5.38−5.33 (m, 1 H, CH_{COD}), 5.06 (s, 1 H, C*H*OPt), 3.39−3.15 (m, 8 H, CH_2), 2.58−1.88 (m, 8 H, CH_2) ppm. – **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 141.1 (C_q), 140.8 (C_q), 139.7 (C_q), 139.5 (C_q), 139.3 (C_q), 136.4 (C_q), 134.8 (+, *C*H$_{Ar}$), 133.4 (+, *C*H$_{Ar}$), 132.9 (+, *C*H$_{Ar}$), 132.4 (+, *C*H$_{Ar}$), 131.4 (+, *C*H$_{Ar}$), 130.0 (+, *C*H$_{Ar}$), 129.7 (+, *C*H), 128.9 (+, *C*H), 128.2 (+, *C*H), 127.1 (+, *C*H$_{Ar}$), 78.5 (+, *C*HOH), 35.3 (−, *C*H$_2$), 35.2 (−, *C*H$_2$), 34.1 (−, *C*H$_2$), 33.6 (−, *C*H$_2$), 27.9 (−, *C*H$_2$), 27.6 (−, *C*H$_2$), 27.4 (−, *C*H$_2$), 26.6 (−, *C*H$_2$) ppm. – **^{195}Pt-NMR** (129 MHz, $CDCl_3$): δ = −3312 ppm. – **IR (ATR)**: $\tilde{\nu}$ = 3413 (vw), 3008 (vw), 2922 (w), 2849 (vw), 1591 (vw), 1498 (vw), 1480 (vw), 1431 (w), 1412 (vw), 1298 (vw), 1260 (w), 1087 (w), 1011 (w), 870 (vw), 795 (w), 716 (w), 655 (vw), 636 (vw), 598 (vw), 513 (vw), 392 (vw) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 577/575/573/ (6) [M$^+$], 328/327/326 (15/45/20) [$C_{25}H_{27}^+$], 239 (32), 221(37), 155/154 (38/74), 136 (93), 105 (66), 91 (100). – **HRMS** ($C_{25}H_{27}O_1{}^{35}Cl^{195}Pt$): calc. 573.1393; found 573.1398.

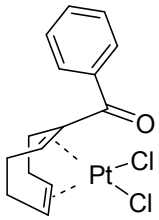
(1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)-2-methylpropanon)platinum(II) chloride (5d)



This complex was synthesized following **GP 4** from the ketone **3d** (144 mg, 0.513 mmol, 6.90 equiv.). The crude product was recrystallized from methanol to obtain the desired product **5d** as a beige solid (20 mg, 44.4 µmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.16 (d, ^3J = 7.8 Hz, 1 H, CH_{COD}), 5.87 (t, ^3J = 7.3 Hz, 1 H, CH_{COD}), 5.68 (q, ^3J = 7.7 Hz, 1 H, CH_{COD}), 3.26−2.99 (m, 3 H, C*H*(CH$_3$)$_2$, CH_2), 2.74−2.43 (m, 4 H, CH_2), 2.15−1.92 (m, 2 H, CH_2), 1.13 (d, ^3J = 6.3 Hz, 3 H, CHCH_3), 1.03 (d, ^3J = 7.3 Hz, 3 H, CHCH_3) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.4 (C_q), 106.7 (C_q), 102.7 (+, *C*H), 101.6 (+, *C*H), 96.9 (+, *C*H), 39.7 (+, *C*H(CH$_3$)$_2$), 34.1 (−, *C*H$_2$), 32.9 (−, *C*H$_2$), 32.0 (−, *C*H$_2$), 28.4 (−, *C*H$_2$) ppm. – **^{195}Pt-NMR** (129 MHz, $CDCl_3$): δ = −3185 ppm. – **IR (ATR)**: $\tilde{\nu}$ = 2919 (m), 2850 (m), 1697 (w), 1463 (w), 1422 (w), 1379 (w), 1261 (w), 1141 (w), 1092 (m), 1030 (m), 951 (w), 882 (w), 795 (m), 720 (w), 614 (vw), 560 (vw), 446 (m) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 409 (10) [M$^+$], 150 (70), 135 (73), 107 (40), 79 (100), 71 (50), 69 (63), 57 (51). – **HRMS** ($C_{12}H_{18}O^{35}Cl^{195}Pt$): calc. 408.0694; found 408.0692.

(1-((1*Z*,5*Z*)-Cycloocta-1,5-dien-1-yl)((phenyl)methanone)platinum(II) chloride (5e)



This complex was synthesized following **GP 4** from the ketone **3e** (144 mg, 0.513 mmol, 6.90 equiv.). The crude product was recrystallized from methanol to obtain the desired product **5e** as a beige solid (20 mg, 44.4 µmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15−8.09 (m, 2 H, CH_{Ar}), 7.54 (t, ^{3}J = 7.4 Hz, 1 H, CH_{Ar}), 7.46 (t, ^{3}J = 7.5 Hz, 2 H, CH_{Ar}), 6.25 (d, ^{3}J = 6.7 Hz, 1 H, CH_{COD}), 6.05 (t, ^{3}J = 7.4 Hz, 1 H, CH_{COD}), 5.75 (q, ^{3}J = 7.5 Hz, 1 H, CH_{COD}), 3.13−3.01 (m, 2 H, CH_2), 2.60−2.42 (m, 4 H, 2 × CH_2), 2.11−1.97 (m, 2 H, CH_2) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 192.7 (C_q), 139.2 (C_q), 139.1 (C_q), 133.2 (+, 2 × CH$_{Ar}$), 130.3 (+, CH$_{Ar}$), 128.7 (+, 2 × CH$_{Ar}$), 106.1 (+, CH), 103.8 (+, CH), 78.1 (+, CH), 33.9 (−, CH$_2$), 31.8 (−, CH$_2$), 29.7 (−, CH$_2$), 27.8 (−, CH$_2$) ppm. – **^{195}Pt-NMR** (129 MHz, $CDCl_3$): δ = −3331 ppm. – **IR (ATR)**: $\tilde{\nu}$ = 2961 (w), 1674 (m), 1559 (vw), 1467 (w), 1445 (vw), 1423 (w), 1339 (w), 1312 (vw), 1258 (m), 1229 (w), 1174 (w), 1014 (m), 960 (m), 796 (s), 707 (m), 692 (m), 670 (m), 645 (w), 553 (w), 503 (w), 470 (w), 394 (w) cm^{-1}. – **MS** (70 eV, EI), *m/z* (%): 442/441 (35/30) [M$^+$], 1874 (35), 105 (100) [$C_7H_5O^+$]. – **HRMS** ($C_{15}H_{16}O^{35}Cl^{195}Pt$): calc. 442.0532; found 442.0532.

3 Crystal Structure Determinations of 3f and 5d

The single-crystal X-ray diffraction study were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-Ka radiation (*l* = 1.54178 Å) for **3f** or Mo-Ka radiation (*l* = 0.71073 Å) for **5e**. Direct Methods (**3f**) or Patterson Methods (**5e**) (SHELXS-97)[4] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).[5] Hydrogen atoms were localized by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. For **5e** an extinction correction was applied.

3f: colourless crystals, $C_{15}H_{15}BrO$, M_r = 291.18, crystal size 0.16 × 0.08 × 0.03 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 7.2898(3) Å, b = 11.2179(5) Å, c = 15.9281(6) Å, β = 100.977(2)°, V = 1278.71(9) Å^3, Z = 4, ρ = 1.513 Mg/m^{-3}, μ(Cu-K$_\alpha$) = 4.211 mm^{-1}, F(000) = 592, $2\theta_{max}$ = 144.4°, 9167 reflections, of which 2497 were independent (R_{int} = 0.036), 154 parameters, R_1 = 0.033 (for 2237 I > 2σ(I)), wR_2 = 0.089 (all data), S = 1.05, largest diff. peak / hole = 0.532 / -0.340 e Å^{-3}.

5d: colourless crystals, $C_{12}H_{18}Cl_2OPt$, M_r = 444.25, crystal size 0.22 × 0.18 × 0.10 mm, monoclinic, space group $C2/c$ (No. 15), a = 15.9169(10) Å, b = 12.7655(9) Å, c = 13.2994(10) Å, β = 99.665(2)°, V = 2663.9(3) Å^3, Z = 8, ρ = 2.215 Mg/m^{-3}, μ(Mo-K$_\alpha$) = 10.913 mm^{-1}, F(000) = 1680, $2\theta_{max}$ = 55.0°, 54670 reflections, of which 3073 were independent (R_{int} = 0.049), 146 parameters, R_1 = 0.015 (for 2975 I > 2σ(I)), wR_2 = 0.034 (all data), S = 1.14, largest diff. peak / hole = 1.928 / -0.850 e Å^{-3}.

CCDC 1812128 (**3f**), and 1812129 (**5d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

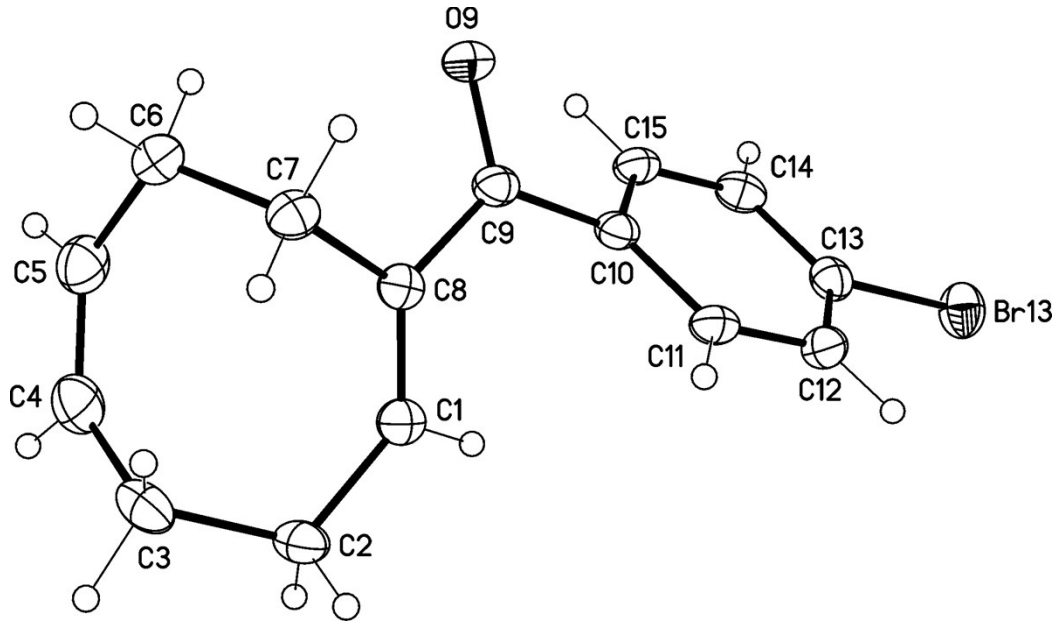


Fig. 1. Molecular structure of **3f** (displacement parameters are drawn at 50 % probability level).

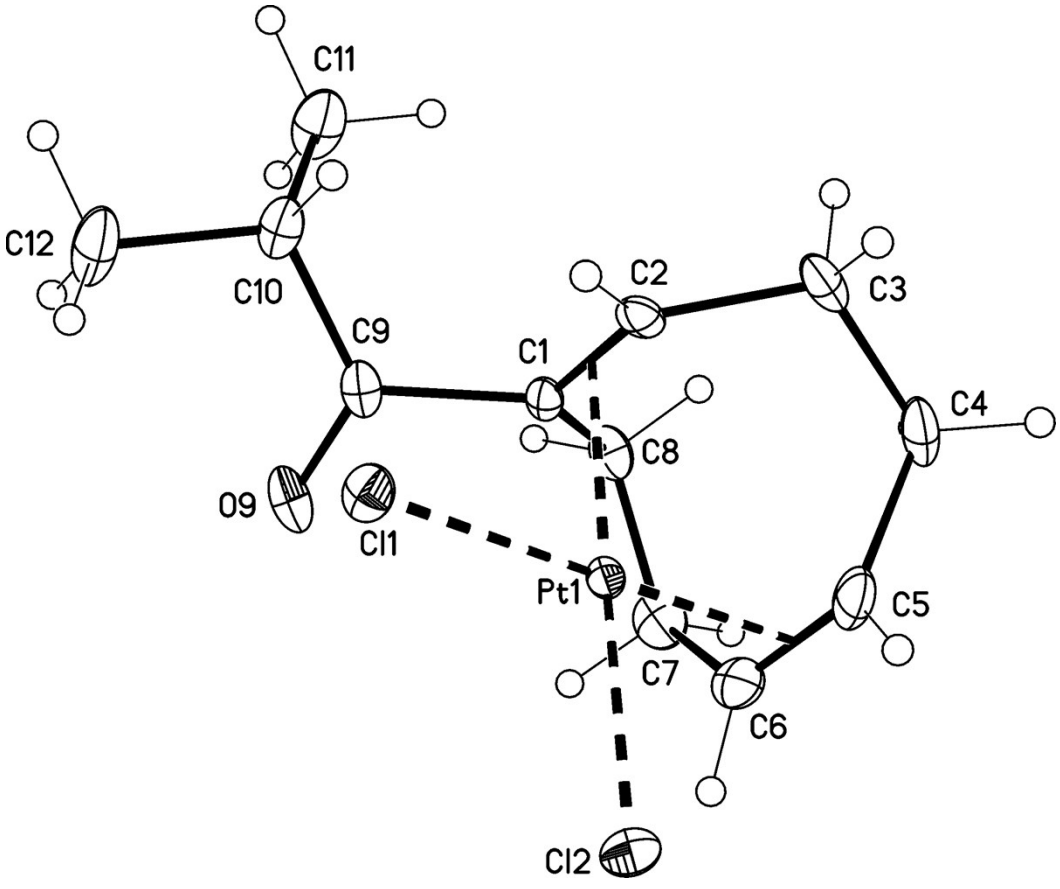


Fig. 2. Molecular structure of **5d** (displacement parameters are drawn at 50 % probability level)

4 References

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