Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for Chemical Communications

Cobalt/Rhodium Heterobimetallic Nanoparticle-catalyzed Carbonylative [2+2+1] Cycloaddition of Allenes and Bisallenes to Pauson-Khand-Type Reaction Products

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Ⅰ. General Informaiton

Workup procedures were done in air. Toluene was freshly distilled from sodium prior to use. Liquid was transferred via a syringe or a cannula. Unless otherwise noted, all commercial materials were used without purification. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and acidic *p*-anisaldehyde and heat as a developing procedure. Flash chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^{1}H and ^{13}C NMR spectra were recorded with Bruker (300 MHz) spectrometer. ^{1}H NMR spectra were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.23 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. Single crystal data for **1b** and **1c** were collected on an Enraf-Nonius CCD single crystal X-ray diffractometer at room temperature using graphite-monochromated Mo Kα radiation (λ= 0.71073Å). Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97. Compounds **1a**,[1] **2a**,[2] **3a**,[3] **4a**,[4] **5a**,[5] **6a**,[6] **7a**,[7] **8a**,[8] **9a**,[9] **13a**,[10] **14a**, and **14b**[11] were known.

Ⅱ. General procedure for Co_2Rh_2-Catalyzed Carbonylative [2+2+1] Cycloaddition of Allenes and Bisallenes

1. Intermolecular Carbonylative [2+2+1] Cycloaddition of Allenes

Phenylallene **1a** (1.0 mmol, 116 mg), 5 mol % Co_2Rh_2 (45 mg of the immobilized Co_2Rh_2), and toluene (5 mL) were placed in a 100 mL stainless steel autoclave equipped with a stirring bar. The reactor was charged with 2 atm of CO and heated at 130^{o}C for 6 h. After the reactor was cooled to room temperature, the solution was filtered and concentrated, and the product was isolated by chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 4 : 1).

2. Intramolecular Carbonylative [2+2+1] Cycloaddition of BisAllenes

Bisallene **9a** (0.3 mmol, 83 mg), 5 mol % Co_2Rh_2 (27 mg of the immobilized Co_2Rh_2), and toluene (3 mL) were placed in a 100 mL stainless steel autoclave equipped with a stirring bar. The reactor was charged with 2 atm of CO and heated at 100^{o}C for 4 h. After the reactor was cooled to room temperature, the solution was filtered and concentrated, and the product was isolated by chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 1 : 2).

-**10b**, **11b**, and **12b**

For **10b**, **11b**, and **12b**, two regioisomers could be formed depending upon the direction of double bond shift within the proposed mechanism. However, only one regioisomer was formed. The two possible regioisomers could be easily discriminated by the ^{1}H NMR peaks of the vinyl protons. In the case of **10b**, the vinyl proton on the seven-membered ring appears as doublet. It means that there exists only one proton next to this vinyl proton. Thus, one of the two double bonds in **10b** is located close to the carbon with the methyl group. In the cases of **11b** and **12b**, the number of vinyl proton can be one or two depending on the regioisomer formed. According to the ^{1}H NMR spectra of **11b** and **12b**, there is only one vinyl proton. It means that one of the double bonds is located at the carbon with a substituent. Thus, we can easily establish the structure of the regioisomer.

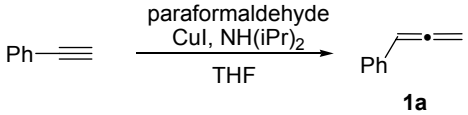
III. Synthesis and Immobilization of Metal Nanoparticles on Charcoal

To a two-neck flask were added *o*-dichlorobenzene (24 mL), oleic acid (0.2 mL), and trioctylphosphine oxide (0.4 g). While the solution was heated at 180^{o}C, a solution of metal carbonyl, $Co_2Rh_2(CO)_{12}$ (1.0 g), in 6 mL *o*-dichlorobenzene was injected into the flask. The resulting solution was heated to 180^{o}C for 2 h and then concentrated to a volume of 5 mL. The concentrated solution was cooled to room temperature. To the cooled solution was added 25 mL of THF. After the solution was well stirred for 10 min, flame-dried charcoal (2.0 g) was added to the solution. After the resulting solution was refluxed for 12 h, the precipitates were filtered and washed with diethyl ether (20 mL), dichloromethane (20 mL), acetone (20 mL), and methanol (20 mL). Vacuum drying gave a black solid.

IV. Preparation of allenes and bisallenes

1. Allene

Compounds **1a** and **8a:** Allenes **1a** and **8a** were prepared from the corresponding alkynes by using a Crabbe reaction.[1]



1a

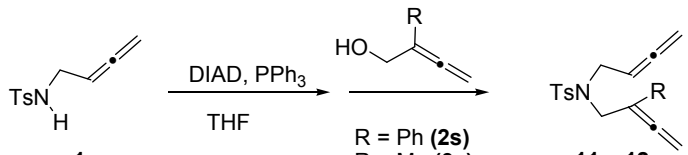
To a flame-dried 100 mL Schlenk flask capped with a rubber septum, 50 mL THF was injected via syringe under N_2 flow. Phenyl acetylene (40 mmol, 4.48 mL), paraformaldehyde (100 mmol, 3.0 g), diisopropylamine (80 mmol, 11.21 mL), and cuprous iodide (20 mmol, 3.81 g) were added to the flask in the dark. The reaction mixture was heated at reflux for 12 h and cooled to room temperature. The reaction mixture was diluted with water and acidified with HCl to pH 2, and extracted with diethyl ether three times. The ether extracts were washed with water until the pH of the extract reached 6.7. The combined organic phase was dried over $MgSO_4$. The solvent was removed by rotary evaporation and the residue was purified by silica gel flash chromatography with *n*-haxane to give phenylallene (**1a**) (12 mmol, 30%).

For compounds **2a**, **3a**, **4a**, **5a**, **6a**, and **7a**, allenes were synthesized by the literature method.[4]

2. Bisallene

For compounds **9a**, **10a**, and **13a**, bisallenes were prepared from the cooresponding diynes by using a Crabbe reaction.[1]

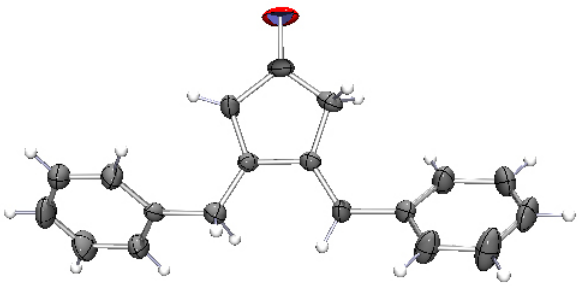
For compounds **11a** and **12a:** To a flame-dried 100 mL Schlenk flask capped with a rubber septum, 15 mL THF was injected via syringe under N_2 flow. Diisopropyl azodicarboxylate (DIAD) (3.9 mmol, 0.75 mL) and PPh_3 (3.9 mmol, 1.02 g) were added to the flask. After the solution was stirred for 10 min, **1s** (0.67 g, 3.0 mmol) and allene alcohol **2s** (or **3s**) (3.0 mmol) were added under N_2. After the reactant had been consumed, the solvent was evaporated under reduced pressure. The mixture was purified by flash chromatography on a silica gel column eluting with *n*-hexane /EtOAc (v/v = 10:2) to afford **11a** and **12a**.



1s **11a, 12a**

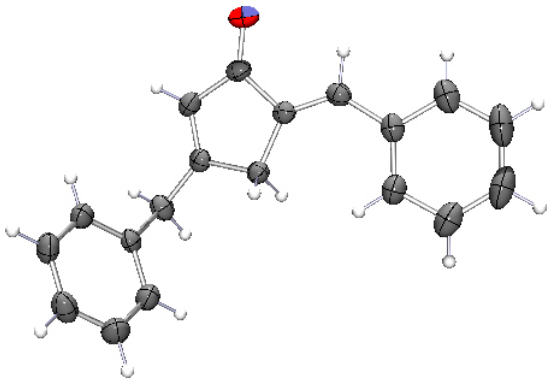
V. X-ray analysis

Diffraction data were collected by a Bruker-Nonius CCD single-crystal X-ray diffractometer at room temperature by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO. The structure was solved by direct methods using SHELXS-97, and refined by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were treated as idealized contributions.
Crystal data for **1b**: $C_{19}H_{16}O$ (293K). M = 260.32, monoclinic, space group Cc, a = 27.151(3) Å, b = 7.5779(4) Å, c = 7.2416(8) Å, β = 101.694(3)°, V = 1459.0(2) $Å^3$, Z = 4, $\rho_{calc.}$ = 1.185 g/cm^{-3}, absorption coefficient = 0.072 mm^{-1}, total reflections collected 2833, unique 2830 (R_{int} = 0.0130), GOF = 1.037, R_1 = 0.0496, R_w = 0.1230 (I>2σ(I)).



An ORTEP drawing of **1b** with 30% probability of thermal ellipsoids.

Crystal data for **1c**: $C_{19}H_{16}O$ (293K). M = 260.32, monoclinic, space group $P2_1/c$, a = 11.6112(5) Å, b = 6.3622(3) Å, c = 19.4174(6) Å, β = 91.098(2)°, V = 1434.15(10) $Å^3$, Z = 4, $\rho_{calc.}$ = 1.206 g/cm^{-3}, absorption coefficient = 0.073 mm^{-1}, total reflections collected 5891, unique 3231 (R_{int} = 0.0199), GOF = 1.033, R_1 = 0.0442, R_w = 0.1019 (I>2σ(I)).



An ORTEP drawing of **1c** with 30% probability of thermal ellipsoids.

VI. Reference

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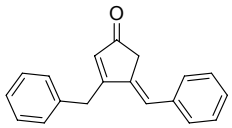
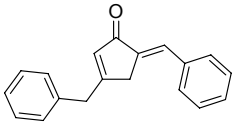
(11) P. Lu and S. Ma, *Org. Lett.* 2007, **9**, 2095-2097.

VII. Characterization of new compounds



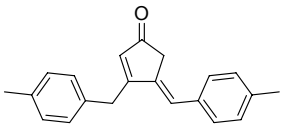
(*E*)-3-benzyl-4-benzylidenecyclopent-2-enone (**1b**)

IR (ν_{CO}): 1685 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 3.32 (s, 2 H), 3.94 (s, 2 H), 5.93 (s, 1 H), 6.78 (s, 1H), 7.23-7.44 (m, 10 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 35.0, 40.6, 125.5, 127.1, 128.4, 128.9, 129.0, 129.1, 129.4, 132.3, 136.2, 137.1, 137.2, 174.1, 204.6 ppm. **HRMS (EI)** calc. for $[C_{19}H_{16}O]^+$ 260.1201, found 260.1204.



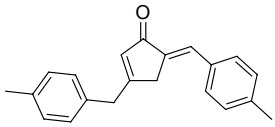
(*E*)-3-benzyl-5-benzylidenecyclopent-2-enone (**1c**)

IR (ν_{CO}): 1692 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 3.43 (s, 2 H), 3.81 (s, 2 H), 6.17 (s, 1 H), 7.21-7.52 (m, 11 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 36.6, 39.9, 127.2, 128.9, 129.0, 129.2, 129.5, 130.4, 130.9, 131.9, 133.9, 135.3, 136.8, 173.8, 197.4 ppm. **HRMS (EI)** calc. for $[C_{19}H_{16}O]^+$ 260.1201, found 260.1201.



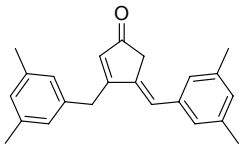
(*E*)-3-(4-methylbenzyl)-4-(4-methylbenzylidene)cyclopent-2-enone (**2b**)

IR (ν_{CO}): 1684 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 2.33 (s, 3 H), 2.36 (s, 3 H), 3.35 (m, 2 H), 3.90 (s, 2 H), 5.92 (s, 1 H), 6.76 (s, 1 H), 7.13 (s, 4 H), 7.19 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.2, 21.5, 34.6, 40.8, 125.4, 129.0, 129.5, 129.7, 129.8, 132.0, 133.6, 134.3, 136.4, 136.7, 138.6, 174.6, 204.8 ppm. **HRMS (EI)** calc. for $[C_{21}H_{20}O]^+$ 288.1514, found 288.1515.



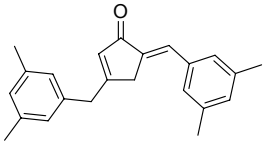
(*E*)-3-(4-methylbenzyl)-5-(4-methylbenzylidene)cyclopent-2-enone (**2c**)

IR (ν_{CO}): 1679 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 2.35 (s, 3 H), 2.37 (s, 3 H), 3.41 (s, 2 H), 3.78 (s, 2 H), 6.18 (s, 1 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 7.8 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.31 (s, 1 H), 7.41 (d, J = 8.0 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.3, 21.7, 36.7, 39.6, 129.1, 129.7, 129.8, 130.5, 131.0, 131.8, 132.7, 133.1, 133.8, 136.9, 139.9, 173.8, 197.6 ppm. **HRMS (EI)** calc. for $[C_{21}H_{20}O]^+$ 288.1514, found 288.1515.



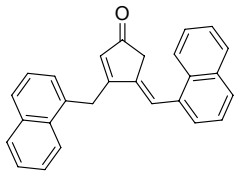
(*E*)-3-(3,5-dimethylbenzyl)-4-(3,5-dimethylbenzylidene)cyclopent-2-enone (**3b**)

IR (ν_{CO}): 1684 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 2.30 (s, 6 H), 2.33 (s, 6 H), 3.34 (s, 2 H), 3.85 (s, 2 H), 5.94 (s, 1 H), 6.73 (s, 1 H), 6.84 (s, 2 H), 6.90 (s, 1 H), 6.95 (s, 1 H), 7.05 (s, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.4, 21.5, 34.8, 40.9, 125.7, 127.0, 127.4(2), 127.4(3), 128.7, 130.3, 132.1, 136.3, 137.0, 137.2, 138.5, 174.6, 205.0 ppm. **HRMS (EI)** calc. for $[C_{23}H_{24}O]^+$ 316.1827, found 316.1822.

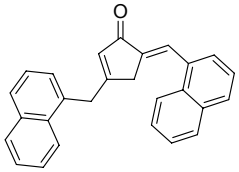


(*E*)-3-(3,5-dimethylbenzyl)-5-(3,5-dimethylbenzylidene)cyclopent-2-enone (**3c**)

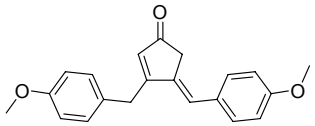
IR (ν_{CO}): 1681 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 2.31 (s, 6 H), 2.34 (s, 6 H), 3.44 (s, 2 H), 3.75 (s, 2 H), 6.17 (s, 1 H), 6.84 (s, 2 H), 6.91 (s, 1 H), 6.99 (s, 1 H), 7.13 (s, 2 H), 7.29 (s, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.4, 21.5, 36.9, 39.8, 127.0, 127.4, 128.4, 128.9, 131.4, 132.0, 133.8, 135.5, 136.8, 138.5, 138.6, 173.9, 197.6 ppm. **HRMS (EI)** calc. for $[C_{23}H_{24}O]^+$ 316.1827, found 316.1824.



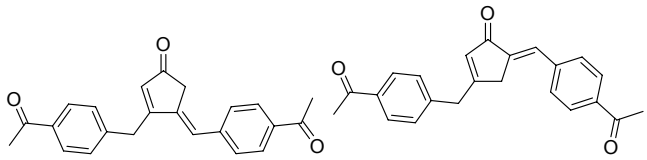
(*E*)-3-(naphthalen-1-ylmethyl)-4-(naphthalen-1-ylmethylene)cyclopent-2-enone (**4b**)
IR (ν_{CO}): 1682 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 3.26 (s, 2 H), 4.51 (s, 2 H), 5.80 (s, 1 H), 7.47-7.55 (m, 9 H), 7.82-7.97 (m, 6 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 32.7, 40.2, 122.7, 123.9, 124.1, 125.6, 125.8, 126.2, 126.4, 126.5, 126.7, 126.8, 127.6, 128.3, 128.9, 129.0, 129.2, 132.0, 132.1, 133.3, 133.5, 133.7, 133.9, 134.3, 139.7, 172.8, 204.6 ppm. **HRMS (EI)** calc. for $[C_{27}H_{20}O]^+$ 360.1514, found 360.1517.



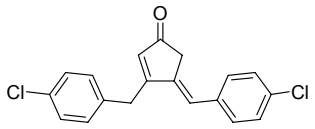
(*E*)-3-(naphthalen-1-ylmethyl)-5-(naphthalen-1-ylmethylene)cyclopent-2-enone (**4c**)
IR (ν_{CO}): 1688 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 3.40 (s, 2 H), 4.19 (s, 2 H), 6.12 (s, 1 H), 7.30-7.54 (m, 8 H), 7.80-7.87 (m, 5 H), 8.11 (m, 2 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 36.6, 37.5, 123.8, 124.3, 125.2, 125.4, 125.7, 126.1, 126.4, 126.6, 126.7, 126.9, 127.7, 128.1, 128.2, 128.8, 129.1, 129.7, 132.0, 132.4, 132.5, 133.0, 133.8, 134.2, 136.3, 174.5, 196.6 ppm. **HRMS (EI)** calc. for $[C_{27}H_{20}O]^+$ 360.1514, found 360.1511.



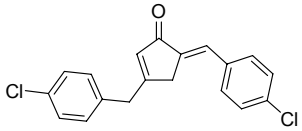
(*E*)-3-(4-methoxybenzyl)-4-(4-methoxybenzylidene)cyclopent-2-enone (**5b**)
IR (ν_{CO}): 1675 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 3.30 (s, 2 H), 3.80 (s, 3 H), 3.84 (s, 3 H), 3.88 (s, 2 H), 5.89 (s, 1 H), 6.73 (s, 1 H), 6.87 (d, *J* = 8.5 Hz , 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.8 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 34.2, 40.8, 55.5, 55.7, 113.9, 114.1, 114.4, 114.6, 125.1, 130.1, 130.2, 130.3, 131.0, 131.4, 135.0, 175.0, 204.9 ppm. **HRMS (EI)** calc. for $[C_{21}H_{20}O_3]^+$ 320.1412, found 320.1414.



(*E*)-1,1'-(4,4'-(4-oxocyclopent-2-ene-2-yl-1-ylidene)bis(methylene)bis(4,1-phenylene))diethanone (**6b**)
(*E*)-1,1'-(4,4'-(5-oxocyclopent-3-ene-3-yl-1-ylidene)bis(methylene)bis(4,1-phenylene))diethanone (**6c**)
IR (ν_{CO}): 1712, 1682 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 2.61 (s, 25.2 H), 3.35 (s, 6.4 H, 6b), 3.47 (s, 2 H, 6c), 3.91 (s, 2 H, 6c), 4.04 (s, 6.4 H, 6b), 5.99 (s, 3.2 H, 6b), 6.19 (s, 1 H, 6c), 6.80 (s, 3.2 H, 6b), 7.34 (s, 1 H, 6c), 7.36 (d, *J* = 8.2 Hz, 8.4 H), 7.50 (d, *J* = 8.2 Hz, 6.4 H, 6b), 7.58 (d, *J* = 8.2 Hz, 2 H, 6c), 7.94 (d, *J* = 7.8 Hz, 8.4 H), 7.97 (d, *J* = 8.2 Hz, 8.4 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 26.7(6), 26.7(8), 26.7(9), 34.9, 36.6, 39.8, 40.5, 124.4, 128.9, 129.0, 129.2, 129.4, 129.5, 129.8, 130.4, 131.1, 132.3, 133.5, 135.7, 136.4, 136.5, 137.3, 139.8, 140.5, 142.0, 142.5, 172.3, 172.6, 196.5, 197.4(1), 197.4(3), 197.6, 203.6 ppm. **HRMS (EI)** calc. for $[C_{23}H_{20}O_3]^+$ 344.1412, found 344.1412.

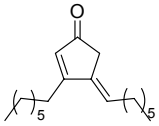


(*E*)-3-(4-chlorobenzyl)-4-(4-chlorobenzylidene)cyclopent-2-enone (**7b**)
IR (ν_{CO}): 1684 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 3.29 (s, 2 H), 3.91 (s, 2 H), 5.93 (s, 1 H), 6.69 (s, 1 H), 7.17 (d, *J* = 8.3 Hz, 2 H), 7.30-7.38 (m, 6 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 34.3, 40.5, 124.2, 129.2, 129.3, 130.5, 130.6, 132.7, 133.1, 134.5, 134.6, 135.5, 137.6, 173.1, 203.9 ppm. **HRMS (EI)** calc. for $[C_{19}H_{14}Cl_2O]^+$ 328.0422, found 328.0424.



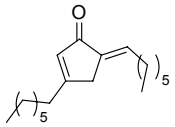
(*E*)-3-(4-chlorobenzyl)-5-(4-chlorobenzylidene)cyclopent-2-enone (**7c**)

IR (ν_{CO}): 1685 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 3.38 (s, 2 H), 3.79 (s, 2 H), 6.16 (s, 1 H), 7.16 (m, 2 H), 7.33 (m, 5 H), 7.42 (m, 2 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 36.5, 39.2, 129.2, 129.3, 129.8, 130.5, 131.5, 132.1, 133.3, 133.8, 134.1, 135.1, 135.6, 172.9, 196.8 ppm. **HRMS (EI)** calc. for $[C_{19}H_{14}Cl_2O]^+$ 328.0422, found 328.0424.



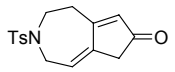
(*E*)-3-heptyl-4-heptylidenecyclopent-2-enone (**8b**)

IR (ν_{CO}): 1681 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 0.89 (t, *J* = 6.7 Hz, 6 H), 1.30 (m, 14 H), 1.45 (m, 2 H), 1.59 (m, 2 H), 2.15 (dd, *J* = 7.4 Hz, 14.7 Hz, 2 H), 2.47 (t, *J* = 7.6 Hz, 2 H), 2.91 (s, 2 H), 5.82 (t, *J* = 7.6 Hz, 1 H), 6.03 (s, 1 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 14.3, 22.7, 22.8, 22.9, 28.1, 28.2, 29.3, 29.7, 30.3, 31.8, 31.9, 38.5, 127.3, 130.6, 137.6, 174.9, 205.3 ppm. **HRMS (EI)** calc. for $[C_{19}H_{32}O]^+$ 276.2453, found 276.2451.



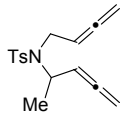
(*E*)-3-heptyl-5-heptylidenecyclopent-2-enone (**8c**)

IR (ν_{CO}): 1688 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 0.89 (m, 6 H), 1.31 (m, 14 H), 1.47 (m, 2 H), 1.60 (m, 2 H) , 2.18 (dd, *J* = 7.3 Hz, 14.7 Hz, 2 H), 2.44 (t, *J* = 7.6 Hz, 2 H), 3.08 (s, 2 H), 6.11 (t, *J* = 1.4 Hz, 1 H), 6.53 (tt, *J* = 1.8 Hz, 7.6 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 14.3, 22.7, 22.8, 27.3, 28.7, 29.3, 29.5, 29.8, 31.8, 31.9, 33.5, 35.0, 131.4, 134.3, 135.6, 175.5, 196.9 ppm. **HRMS (EI)** calc. for $[C_{19}H_{32}O]^+$ 276.2453, found 276.2453.



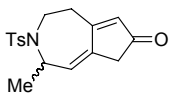
3-tosyl-1,2,3,4-tetrahydrocyclopenta[d]azepin-7(6H)-one (**9b**)

IR (ν_{CO}): 1680 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 2.43 (s, 3 H), 3.03 (s, 2 H), 3.07 (t, *J* = 5.3 Hz, 2 H), 3.42 (t, *J* = 5.3 Hz, 2 H), 4.08 (d, *J* = 3.9 Hz, 2 H), 5.75 (t, *J* = 4.0 Hz, 1 H), 6.13 (s, 1 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.69 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 21.7, 33.8, 42.8, 46.0, 50.0, 124.2, 127.2, 130.1, 135.0, 135.7, 136.9, 144.0, 169.8, 204.2 ppm. **HRMS (EI)** calc. for $[C_{16}H_{17}NO_3S]^+$ 303.0929, found 303.0926.



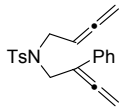
N-(buta-2,3-dienyl)-4-methyl-N-(penta-3,4-dien-2-yl)benzenesulfonamide (**10a**)

IR (ν_{allene}): 1953 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 1.22 (d, *J* = 6.8 Hz, 3 H), 2.41 (s, 3 H), 3.74 (tdd, *J* = 2.1 Hz, 7.2 Hz, 15.7 Hz, 1 H), 3.89 (m, 1 H), 4.63 (m, 1 H), 4.75 (m, 4 H), 4.95 (dd, *J* = 6.4 Hz, 11.9 Hz, 1 H), 5.20 (m, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 18.7, 21.5, 42.7, 51.7, 76.3, 77.7, 89.4, 91.7, 127.2, 129.7, 138.1, 143.2, 208.6, 208.7 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1139.



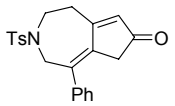
4-methyl-3-tosyl-1,2,3,4-tetrahydrocyclopenta[d]azepin-7(6H)-one (**10b**)

IR (ν_{CO}): 1681 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$)** δ 1.13 (d, *J* = 6.9 Hz, 3 H), 2.42 (s, 3 H), 3.01 (s, 2 H), 2.94-3.13 (m, 2 H), 3.23 (m, 1 H), 3.90 (tdd, *J* = 1.0 Hz, 3.3 Hz, 14.9 Hz, 1 H), 4.94 (m, 1 H), 5.67 (d, *J* = 5.1 Hz, 1 H), 6.10 (s, 1 H), 7.28 (m, *J* = 8.3 Hz, 2 H), 7.72 (d, *J* = 8.4 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 18.2, 21.7, 34.3, 39.8, 43.2, 54.3, 127.2, 130.0, 130.7, 134.7, 135.2, 138.4, 143.7, 170.2, 204.2 ppm. **HRMS (EI)** calc. for $[C_{17}H_{19}NO_3S]^+$ 317.1086, found 317.1089.



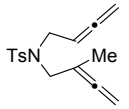
N-(buta-2,3-dienyl)-4-methyl-N-(2-phenylbuta-2,3-dienyl)benzenesulfonamide (**11a**)

IR (ν_{allene}): 1946 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 2.41 (s, 3 H), 3.85 (td, *J* = 2.5 Hz, 7.0 Hz, 2 H), 4.33 (t, *J* = 2.4 Hz, 2 H), 4.62 (td, *J* = 2.5 Hz, 6.6 Hz, 2 H), 4.84 (m, 1 H), 5.04 (t, *J* = 2.4 Hz, 2 H), 7.26 (m, 5 H), 7.46 (d, *J* = 7.3 Hz, 2 H), 7.69 (d, *J* = 8.3 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.6, 45.8, 47.2, 76.1, 79.1, 85.3, 100.8, 126.6, 127.4, 127.5, 128.6, 129.8, 133.8, 137.3, 143.5, 209.6, 210.0 ppm. **HRMS (EI)** calc. for $[C_{21}H_{21}NO_2S]^+$ 351.1293, found 351.1291.



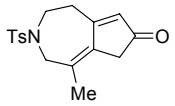
5-phenyl-3-tosyl-1,2,3,4-tetrahydrocyclopenta[d]azepin-7(6H)-one (**11b**)

IR (ν_{CO}): 1680 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 2.38 (s, 3 H), 2.77 (s, 2 H), 3.06 (t, *J* = 6.2 Hz, 2 H), 3.64 (t, *J* = 6.2 Hz, 2 H), 4.41 (s, 2 H), 5.98 (s, 1 H) , 7.21 (d, *J* = 8.0 Hz, 2 H), 7.34-7.41 (m, 5 H), 7.62 (d, *J* = 8.0 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.7, 32.1, 42.8, 46.0, 52.2, 127.3, 128.4, 128.6, 129.1, 129.9, 133.6(2), 133.6(3), 136.3, 138.6, 140.2, 144.0, 169.9, 204.3 ppm. **HRMS (EI)** calc. for $[C_{22}H_{21}NO_3S]^+$ 379.1242, found 379.1244.



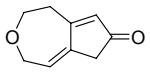
N-(buta-2,3-dienyl)-4-methyl-N-(2-methylbuta-2,3-dienyl)benzenesulfonamide (**12a**)

IR (ν_{allene}): 1956 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.67 (t, *J* = 3.0 Hz, 3 H), 2.41 (s, 3 H), 3.81 (t, *J* = 2.2 Hz, 2 H), 3.86 (td, *J* = 2.3 Hz, 7.1 Hz, 2 H), 4.61 (td, *J* = 2.9 Hz, 5.5 Hz, 2 H), 4.66 (m, 2 H), 4.85 (m, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.3 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 16.0, 21.6, 45.8, 50.3, 75.1, 76.0, 85.3, 94.1, 127.3, 129.7, 137.8, 143.3, 207.8, 209.8 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1140.



5-methyl-3-tosyl-1,2,3,4-tetrahydrocyclopenta[d]azepin-7(6H)-one (**12b**)

IR (ν_{CO}): 1679 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.82 (s, 3 H), 2.42 (s, 3 H), 2.86 (s, 2 H), 3.00 (t, *J* = 5.8 Hz, 2 H), 3.49 (t, *J* = 5.8 Hz, 2 H), 4.03 (s, 2 H), 5.98 (s, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.65 (d, *J* = 8.3 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.3, 21.7, 32.9, 41.6, 45.8, 52.7, 127.2, 130.0, 133.0, 133.7, 134.1, 136.4, 143.9, 170.4, 203.9 ppm. **HRMS (EI)** calc. for $[C_{17}H_{19}NO_3S]^+$ 317.1086, found 317.1082.



4,5-dihydro-2H-cyclopenta[d]oxepin-7(8H)-one (**13b**)

IR (ν_{CO}): 1673 cm^{-1}. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 3.04 (t, *J* = 5.1 Hz, 2 H), 3.07 (d, *J* = 0.8 Hz, 2 H), 3.88 (t, *J* = 5.1 Hz, 2 H), 4.45 (dd, *J* = 1.0 Hz, 3.2 Hz, 2 H), 5.77 (dt, *J* = 1.6 Hz, 3.1 Hz, 1 H), 6.13 (s, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 35.1, 42.7, 67.9, 71.7, 128.2, 134.2, 135.7, 171.2, 204.9 ppm. **HRMS (EI)** calc. for $[C_9H_{10}O_2]^+$ 150.0681, found 150.0678.