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

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Ⅰ. General Information

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). 1H and 13C NMR spectra were recorded with Bruker (300 MHz) spectrometer. 1H 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 13C NMR spectra were measured relative to CDCl3 (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, 2a, 3a, 4a, 5a, 6a, 7a, 8a, 9a, 13a, 14a, and 14b were known.

Ⅱ. General procedure for Co2Rh2-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 % Co2Rh2 (45 mg of the immobilized Co2Rh2), 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°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 % Co2Rh2 (27 mg of the immobilized Co2Rh2), 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°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).

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 1H 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 1H 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°C, a solution of metal carbonyl, Co2Rh2(CO)12 (1.0 g), in 6 mL o-dichlorobenzene was injected into the flask. The resulting solution was heated to 180°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

\[
\begin{align*}
\text{Ph} \quad & \xrightarrow{\text{paraformaldehyde, CuI, NH(iPr)}_2} \quad \text{Ph} \\
\text{1a} \\
\end{align*}
\]

To a flame-dried 100 mL Schlenk flask capped with a rubber septum, 50 mL THF was injected via syringe under N₂ 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 MgSO₄. The solvent was removed by rotary evaporation and the residue was purified by silica gel flash chromatography with n-hexane 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 corresponding diynes by using a Crabbe reaction.1

\[
\begin{align*}
\text{TsN} \quad & \xrightarrow{\text{DIAD, PPh}_3} \quad \text{TsN} \\
\text{1s} \\
\text{R = Ph (2s)} \\
\text{R = Me (3s)} \\
\text{11a, 12a} \\
\end{align*}
\]

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: C₁₉H₁₆O (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) Å³, Z = 4, \( \rho_{\text{calc}} = 1.185 \) g/cm³, absorption coefficient = 0.072 mm⁻¹, total reflections collected 2833, unique 2830 \( (R_{\text{int}} = 0.0130), \text{GOF} = 1.037, R_1 = 0.0496, wR_2 = 0.1230 \) (I>2σ(I)).
An ORTEP drawing of 1b with 30% probability of thermal ellipsoids.

Crystal data for 1c: C₁₉H₁₆O (293K). M = 260.32, monoclinic, space group P2₁/c, a = 11.6112(5) Å, b = 6.3622(3) Å, c = 19.4174(6) Å, β = 91.098(2)°, V = 1434.15(10) Å³, Z = 4, ρcalc = 1.206 g/cm³, absorption coefficient = 0.073 mm⁻¹, total reflections collected 5891, unique 3231 (Rint = 0.0199), GOF = 1.033, R₁ = 0.0442, Rw = 0.1019 (I>2σ(I)).

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

VI. Reference

VII. Characterization of new compounds

(E)-3-benzyl-4-benzylidencyclopent-2-enone (1b)
IR (ν_CO): 1685 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 3.32 (s, 2 H), 3.94 (s, 2 H), 5.93 (s, 1 H), 6.78 (s, 1 H), 7.23-7.44 (m, 10 H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 35.0, 40.6, 125.5, 127.1, 128.4, 128.9, 129.0, 129.4, 132.3, 136.2, 137.1, 137.2, 204.6 ppm. HRMS (EI) calc. for [C₁₉H₁₆O]⁺ 260.1201, found 260.1204.

(E)-3-benzyl-5-benzylidene-cyclopent-2-enone (1c)
IR (ν_CO): 1692 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 3.43 (s, 2 H), 3.81 (s, 2 H), 6.17 (s, 1 H), 7.21-7.52 (m, 11 H) ppm. ¹³C NMR (75 MHz, CDCl₃) 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 [C₁₉H₁₆O]⁺ 260.1201, found 260.1201.

(E)-3-(4-methylbenzyl)-4-(4-methylbenzylidene)cyclopent-2-enone (2b)
IR (ν_CO): 1684 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) 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 [C₂₁H₂₀O]⁺ 288.1514, found 288.1515.

(E)-3-(4-methylbenzyl)-5-(4-methylbenzylidene)cyclopent-2-enone (2c)
IR (ν_CO): 1679 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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), 6.76 (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), 7.32 (d, J = 8.2 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃) 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 [C₂₁H₂₀O]⁺ 288.1514, found 288.1515.

(E)-3-(3,5-dimethylbenzyl)-4-(3,5-dimethylbenzylidene)cyclopent-2-enone (3b)
IR (ν_CO): 1684 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 2.30 (s, 6 H), 2.33 (s, 6 H), 3.34 (s, 2 H), 3.85 (s, 2 H), 6.17 (s, 1 H), 6.84 (s, 2 H), 6.90 (s, 1 H), 6.95 (s, 1 H), 7.05 (s, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃) 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 [C₂₃H₂₄O]⁺ 316.1827, found 316.1822.

(E)-3-(3,5-dimethylbenzyl)-5-(3,5-dimethylbenzylidene)cyclopent-2-enone (3c)
IR (ν_CO): 1681 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) δ 21.4, 21.5, 34.8, 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 [C₂₃H₂₄O]⁺ 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 32.7, 40.2, 122.7, 123.9, 124.1, 125.6, 125.8, 126.2, 126.4, 126.5, 126.7, 126.8, 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 \([\text{C}_{27}\text{H}_{20}\text{O}]^+\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 36.6, 37.5, 123.8, 124.3, 125.2, 125.4, 125.7, 126.1, 126.4, 126.6, 126.7, 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 \([\text{C}_{27}\text{H}_{20}\text{O}]^+\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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 \([\text{C}_{21}\text{H}_{20}\text{O}_3]^+\) 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)

IR (ν_{CO}): 1712, 1682 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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, 131.1, 131.2, 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 \([\text{C}_{23}\text{H}_{20}\text{O}_3]^+\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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 \([\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{O}_3]^+\) 328.0422, found 328.0424.
(E)-3-(4-chlorobenzyl)-5-(4-chlorobenzylidene)cyclopent-2-enone (7c)

IR (νCO): 1685 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) 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 [C₁₉H₁₄Cl₂O]+ 328.0422, found 328.0424.

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

IR (νCO): 1681 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) 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 [C₁₉H₃₂O]+ 276.2453, found 276.2451.

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

IR (νCO): 1688 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) 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 [C₁₉H₃₂O]+ 276.2453, found 276.2453.

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

IR (νCO): 1680 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) 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 [C₁₆H₁₇NO₃S]+ 303.0929, found 303.0926.

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

IR (νallene): 1953 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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), 5.79 (d, J = 8.1 Hz, 2 H), 7.29 (d, J = 8.2 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 18.7, 21.5, 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 [C₁₆H₁₉NO₂S]+ 289.1136, found 289.1139.

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

IR (νCO): 1681 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) 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. ¹³C NMR (75 MHz, CDCl₃) δ 18.2, 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 [C₁₆H₁₉NO₂S]+ 317.1086, found 317.1089.
\[ \text{TsN} \text{Ph} \]

\[ N-(\text{buta-2,3-dienyl})-4\text{-methyl-N-(2-phenylbuta-2,3-dienyl)}\text{benzenesulfonylamine} ~ (11a) \]

**IR (\text{\nu} \text{allene})**: 1946 cm\(^{-1}\).

**\(^{1}H\) NMR (300 MHz, CDCl\(_3\))**: \(\delta 2.41 (s, 3 \text{ H}), 3.85 (td, J = 2.5 \text{ Hz}, 7.0 \text{ Hz}, 2 \text{ H}), 4.33 (t, J = 2.4 \text{ Hz}, 2 \text{ H}), 4.62 (td, J = 2.5 \text{ Hz}, 6.6 \text{ Hz}, 2 \text{ H}), 4.84 (m, 1 \text{ H}), 5.04 (t, J = 2.4 \text{ Hz}, 2 \text{ H}), 7.26 (m, 5 \text{ H}), 7.46 (d, J = 7.3 \text{ Hz}, 2 \text{ H}), 7.69 (d, J = 8.3 \text{ Hz}, 2 \text{ H}) \text{ ppm.} \)

**\(^{13}C\) NMR (75 MHz, CDCl\(_3\))**: \(\delta 21.6, 45.8, 47.2, 76.1, 79.1, 85.3, 100.8, 126.6, 127.4, 127.5, 128.6, 129.8, 133.8, 137.3, 143.5, 209.6, 210.0 \text{ ppm.} \)

**HRMS (EI)** calc. for \([C_{21}H_{21}NO_2S]+\) 351.1293, found 351.1291.

\[ \text{TsN} \text{OPh} \]

\[ 5\text{-phenyl-3-tosyl-1,2,3,4-tetrahydrocyclopenta}\[d\]azepin-7(6H)-one ~ (11b) \]

**IR (\text{\nu} \text{CO})**: 1680 cm\(^{-1}\).

**\(^{1}H\) NMR (300 MHz, CDCl\(_3\))**: \(\delta 2.38 (s, 3 \text{ H}), 2.77 (s, 2 \text{ H}), 3.06 (t, J = 6.2 \text{ Hz}, 2 \text{ H}), 3.64 (t, J = 6.2 \text{ Hz}, 2 \text{ H}), 4.41 (s, 2 \text{ H}), 5.98 (s, 1 \text{ H}), 7.21 (d, J = 8.0 \text{ Hz}, 2 \text{ H}), 7.34-7.41 (m, 5 \text{ H}), 7.62 (d, J = 8.0 \text{ Hz}, 2 \text{ H}) \text{ ppm.} \)

**\(^{13}C\) NMR (75 MHz, CDCl\(_3\))**: \(\delta 21.7, 32.1, 42.8, 46.0, 52.2, 127.3, 128.4, 128.6, 129.1, 129.9, 133.6(2), 133.6(3), 136.3, 138.6, 140.2, 144.0, 169.9, 204.3 \text{ ppm.} \)

**HRMS (EI)** calc. for \([C_{22}H_{21}NO_3S]+\) 379.1242, found 379.1244.

\[ \text{TsN} \text{OMe} \]

\[ N-(\text{buta-2,3-dienyl})-4\text{-methyl-N-(2-methylbuta-2,3-dienyl)}\text{benzenesulfonylamine} ~ (12a) \]

**IR (\text{\nu} \text{allene})**: 1956 cm\(^{-1}\).

**\(^{1}H\) NMR (300 MHz, CDCl\(_3\))**: \(\delta 1.67 (t, J = 3.0 \text{ Hz}, 3 \text{ H}), 2.41 (s, 3 \text{ H}), 3.81 (t, J = 2.2 \text{ Hz}, 2 \text{ H}), 3.86 (td, J = 2.3 \text{ Hz}, 7.1 \text{ Hz}, 2 \text{ H}), 4.61 (td, J = 2.9 \text{ Hz}, 5.5 \text{ Hz}, 2 \text{ H}), 4.85 (m, 1 \text{ H}), 7.29 (d, J = 8.2 \text{ Hz}, 2 \text{ H}), 7.70 (d, J = 8.3 \text{ Hz}, 2 \text{ H}) \text{ ppm.} \)

**\(^{13}C\) NMR (75 MHz, CDCl\(_3\))**: \(\delta 16.0, 21.6, 45.8, 50.3, 75.1, 76.0, 85.3, 94.1, 127.3, 129.7, 137.8, 143.3, 207.8, 209.8 \text{ ppm.} \)

**HRMS (EI)** calc. for \([C_{16}H_{19}NO_2S]+\) 289.1136, found 289.1140.

\[ \text{TsN} \text{OMe} \]

\[ 5\text{-methyl-3-tosyl-1,2,3,4-tetrahydrocyclopenta}\[d\]azepin-7(6H)-one ~ (12b) \]

**IR (\text{\nu} \text{CO})**: 1679 cm\(^{-1}\).

**\(^{1}H\) NMR (300 MHz, CDCl\(_3\))**: \(\delta 1.82 (s, 3 \text{ H}), 2.42 (s, 3 \text{ H}), 2.86 (s, 2 \text{ H}), 3.00 (t, J = 5.8 \text{ Hz}, 2 \text{ H}), 3.49 (t, J = 5.8 \text{ Hz}, 2 \text{ H}), 4.03 (s, 2 \text{ H}), 5.98 (s, 1 \text{ H}), 7.29 (d, J = 8.2 \text{ Hz}, 2 \text{ H}), 7.65 (d, J = 8.3 \text{ Hz}, 2 \text{ H}) \text{ ppm.} \)

**\(^{13}C\) NMR (75 MHz, CDCl\(_3\))**: \(\delta 16.8, 21.3, 21.7, 32.9, 41.6, 45.8, 52.7, 127.2, 130.0, 133.0, 133.7, 134.1, 136.4, 143.9, 170.4, 203.9 \text{ ppm.} \)

**HRMS (EI)** calc. for \([C_{17}H_{19}NO_3S]+\) 317.1086, found 317.1082.

\[ \text{O} \]

\[ \text{4,5-dihydro-2H-cyclopenta}\[d\]oxepin-7(8H)-one ~ (13b) \]

**IR (\text{\nu} \text{CO})**: 1673 cm\(^{-1}\).

**\(^{1}H\) NMR (300 MHz, CDCl\(_3\))**: \(\delta 3.04 (t, J = 5.1 \text{ Hz}, 2 \text{ H}), 3.07 (d, J = 0.8 \text{ Hz}, 2 \text{ H}), 3.00 (t, J = 5.1 \text{ Hz}, 2 \text{ H}), 4.45 (dd, J = 1.0 \text{ Hz}, 3.2 \text{ Hz}, 2 \text{ H}), 5.77 (dt, J = 1.6 \text{ Hz}, 3.1 \text{ Hz}, 1 \text{ H}), 6.13 (s, 1 \text{ H}) \text{ ppm.} \)

**\(^{13}C\) NMR (75 MHz, CDCl\(_3\))**: \(\delta 35.1, 42.7, 67.9, 71.7, 128.2, 134.2, 135.7, 171.2, 204.9 \text{ ppm.} \)

**HRMS (EI)** calc. for \([C_{9}H_{10}O_2]+\) 150.0681, found 150.0678.