Gold-Catalyzed Intermolecular Formal (3+2) Cycloaddition of
Stabilized Vinyldiazo Derivatives and Electronically Unbiased Allenes

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1. General Considerations

All reactions were carried out under nitrogen using standard Schlenck techniques. Dichloromethane and 1,2-dichloroethane were distilled from CaH₂. The solvents used in column chromatography, hexane and ethyl acetate, were obtained from commercial suppliers and used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F₂₅₄ indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). H NMR (300, 400 MHz) and C NMR (75.5 and 100 MHz) spectra were recorded at room temperature in CDCl₃ on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts are given in ppm relative to TMS (H, 0.0 ppm) or CDCl₃ (C, 77.0 ppm). 2D NMR experiments were recorded on a Bruker AVANCE-400 MHz. High-resolution mass spectra were determined on a VG Autospec M mass spectrometer. This study was carried out using vinyldiazoacetates 1a-g¹ and allenes 2a-k² (Figure S1), which were prepared according to well-known procedures previously described in the literature. Allene [D]-2k was prepared following the procedure developed by Moreau and Gaudemar.³ [Au(IPr)(CH₂CN)]SbF₆ was prepared according to a literature procedure.⁴ All other reagents used in this work were of the best commercial grade available and used without further purification.

Figure S1. Starting materials used in this work
2. Summary of the Catalyst Screening

Table S1. Summary of the Catalyst Screening for the Reaction of Diazocompound 1a and 3-methylpropa-1,2-diene (2a)

| entry | catalyst           | solvent | T (ºC) | 3a (%)a |
|-------|--------------------|---------|--------|---------|
| 1     | CuBr               | CH₂Cl₂  | RT     | -       |
| 2     | CuBr               | THF     | RT     | -       |
| 3     | [Cu(MeCN)₄][BF₄]   | CH₂Cl₂  | RT     | -       |
| 4     | Cu(OTf)₂           | CH₂Cl₂  | RT     | -       |
| 5     | Rh₂(OAc)₄          | CH₂Cl₂  | RT     | -       |
| 6     | AgSbF₆             | CH₂Cl₂  | RT     | 17      |
| 7     | AuCl₃              | CH₂Cl₂  | RT     | -       |
| 8     | AuCl               | CH₂Cl₂  | RT     | -       |
| 9     | (Ph₃P)AuNTf₂       | CH₂Cl₂  | RT     | -       |
| 10    | (JohnPhos)AuNTf₂   | CH₂Cl₂  | RT     | 49      |
| 11    | (IPr)AuNTf₂        | CH₂Cl₂  | RT     | 36      |
| 12    | [IPrAu(MeCN)][SbF₆] | CH₂Cl₂  | RT     | 75      |
| 13    | [IPrAu(MeCN)][SbF₆] | DCE     | 50     | 23      |
| 14    | [IPrAu(MeCN)][SbF₆] | DMF     | RT     | 5       |

a Yield of isolated product after column chromatography.
3. General Procedure for the Synthesis of Compounds 3

![Chemical structure](image)

[Au(IPr)(CH₃CN)]SbF₆ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of vinyldiazo compound 1 (0.5 mmol) and the corresponding allene 2 (2 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4-12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate mixtures) to afford the (3+2) cycloadducts as colorless oils.

The reaction of diethyl (E)-4-diazopent-2-enedioate (1f) and 3-methylbuta-1,2-diene (2a) was performed at 50ºC in dichloroethane.
4. Characterization Data of Compounds 3

\[ \text{Ethyl 4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3a)} \]

The general procedure was followed using ethyl 2-diazo-3-enoate (1a, 70 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (2a, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound 3a (68 mg, 75%) as a colorless oil.

\(^1H\text{-NMR:} \ 1.30 (t, J = 7.2 \text{ Hz}, 3H), \ 1.63 (s, 3H), \ 1.66 (s, 3H), \ 3.16 (s, 2H), \ 3.22 (s, 2H), \ 4.21 (q, J = 7.2 \text{ Hz}, 2H), \ 6.79-6.81 (m, 1H); \ ^{13}C\text{-NMR:} \ 14.3, \ 20.7, \ 20.9, \ 36.2, \ 38.0, \ 60.1, \ 124.4, \ 129.8, \ 135.7, \ 142.2, \ 165.1; \ HRMS \ (EI) \text{ calculated for } [\text{C}_{11}\text{H}_{16}\text{O}_{2}]^+ (M^+) : 180.1150, \text{ found } 180.1153.

\[ \text{Benzyl 4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3b)} \]

The general procedure was followed using benzyl 2-diazo-3-enoate (1b, 101 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (2a, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound 3b (102 mg, 84%) as a colorless oil.

\(^1H\text{-NMR:} \ 1.66 (s, 3H), \ 1.68 (s, 3H), \ 3.19 (s, 2H), \ 3.28 (s, 2H), \ 5.24 (s, 2H), \ 6.88-6.91 (m, 1H), \ 7.37-7.41 (m, 5H); \ ^{13}C\text{-NMR:} \ 20.8, \ 21.0, \ 36.2, \ 38.1, \ 65.9, \ 124.5, \ 128.1, \ 128.5, \ 129.6, \ 135.4, \ 136.3, \ 143.0, \ 164.8; \ HRMS \ (EI) \text{ calculated for } [\text{C}_{16}\text{H}_{18}\text{O}_{2}]^+ (M^+) : 242.1307, \text{ found } 242.1303.

\[ \text{tert-butyl 4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3c)} \]

The general procedure was followed using tert-butyl 2-diazo-3-enoate (1c, 84 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (2a, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound 3c (68 mg, 65%) as a colorless oil.
$^1$H-NMR: 1.51 (s, 9H), 1.64 (s, 3H), 1.66 (s, 3H), 3.15 (s, 2H), 3.19 (s, 2H), 6.71-6.72 (m, 1H); $^{13}$C-NMR: 20.7, 20.9, 28.2, 36.2, 37.9, 80.1, 124.1, 130.1, 137.3, 141.1, 164.6; HRMS (EI) calculated for [C$_{13}$H$_{20}$O$_2$]$^+$ (M$^+$): 208.1463, found 208.1467.

![3d](image)

**Ethyl 4-cyclohexyldenecyclopent-1-ene-1-carboxylate (3d).** The general procedure was followed using ethyl 2-diazobut-3-enoate (1a, 70 mg, 0.5 mmol) and vinyldinycyclohexane (2b, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3d (78 mg, 71%) as a colorless oil.

$^1$H-NMR: 1.32 (t, $J = 7.2$ Hz, 3H), 1.51-1.57 (m, 6H), 2.07-2.11 (m, 4H), 3.20 (s, 2H), 3.26 (s, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 6.83 (m, 1H); $^{13}$C-NMR: 14.3, 26.5, 27.4, 31.3, 31.5, 35.5, 37.3, 60.1, 126.3, 132.5, 135.6, 142.2, 165.2; HRMS (EI) calculated for [C$_{14}$H$_{20}$O$_2$]$^+$ (M$^+$): 220.1463, found 220.1459.

![3e](image)

**Benzyl 4-cyclohexyldenecyclopent-1-ene-1-carboxylate (3e).** The general procedure was followed using benzyl 2-diazobut-3-enoate (1b, 101 mg, 0.5 mmol) and vinyldinycyclohexane (2b, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3e (97 mg, 69%) as a colorless oil.

$^1$H-NMR: 1.50-1.55 (m, 6H), 2.06-2.11 (m, 4H), 3.22 (s, 2H), 3.30 (s, 2H), 5.23 (s, 2H), 6.89-6.90 (m, 1H), 7.34-7.41 (m, 5H); $^{13}$C-NMR: 26.6, 27.39, 27.42, 31.3, 31.5, 35.5, 37.4, 65.9, 126.1, 128.0, 128.1, 128.5, 132.6, 135.3, 136.3, 143.0, 164.9; HRMS (EI) calculated for [C$_{19}$H$_{22}$O$_2$]$^+$ (M$^+$): 282.1620, found 282.1616.

![3f](image)

**3f**
**tert-Butyl 4-cyclohexylicenecyclopent-1-ene-1-carboxylate (3f).** The general procedure was followed using tert-butyl 2-diazo-3-enoate (1c, 84 mg, 0.5 mmol) and vinylidene-cyclohexane (2b, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3f (79 mg, 64%) as a colorless oil.

\[ \text{H-NMR:} \ 1.50-1.54 (m + s, 15H), 2.06-2.11 (m, 4H), 3.18 (s, 2H), 3.21 (s, 2H), 6.71-6.73 (m, 1H); \text{C-NMR:} \ 26.6, 27.4, 28.2, 31.3, 31.5, 35.5, 37.2, 80.0, 126.6, 132.3, 137.2, 141.1, 164.6; \text{HRMS (EI)} \text{ calculated for } [C_{16}H_{24}O_{2}]^{+} (M^+) : 248.1776, \text{found} 248.1779. \]

![3g]

**Benzyl 4-(4-(tert-butyl)cyclohexylicene) cyclopent-1-ene-1-carboxylate (3g).** The general procedure was followed using benzyl 2-diazo-3-enoate (1b, 101 mg, 0.5 mmol) and 1-(tert-butyl)-4-vinylidene-cyclohexane (2c, 329 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3g (115 mg, 68%) as a colorless oil.

\[ \text{H-NMR:} \ 0.87 (s, 9H), 0.94-1.19 (m, 3H), 1.77-1.86 (m, 4H), 2.38-2.49 (m, 2H), 3.12-3.38 (m, 4H), 5.22 (s, 2H), 6.88-6.91 (m, 1H), 7.34-7.41 (m, 5H); \text{C-NMR:} \ 27.6, 28.0, 31.2, 31.4, 32.5, 35.6, 37.4, 48.1, 65.9, 125.8, 128.0, 128.5, 132.5, 135.3, 136.3, 143.0, 164.9; \text{HRMS (EI)} \text{ calculated for } [C_{23}H_{30}O_{2}]^{+} (M^+) : 338.2246, \text{found} 338.2244. \]

![3h]

**Benzyl 4-(1,3-diphenylpropan-2-ylidene)cyclopent-1-ene-1-carboxylate (3h).** The general procedure was followed using benzyl 2-diazo-3-enoate (1b, 101 mg, 0.5 mmol) and 1,1-dibenzylpropan-1,2-diene (2d, 440 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3h (118 mg, 60%) as a colorless oil.

\[ \text{H-NMR:} \ 3.32 (s, 2H), 3.36 (s, 2H), 3.45 (br s, 2H), 3.57 (br s, 2H), 5.27 (s, 2H), 6.96-6.97 (m, 1H), 7.13-7.37 (m, 15H); \text{C-NMR:} \ 36.6, 37.9, 38.3, 38.4, 66.1, 126.1, 128.2, 128.5, 128.6, 128.7, 131.1, 134.3, 135.2, 136.2, 139.5, 139.6, 142.6, 164.7; \text{HRMS (EI)} \text{ calculated for } [C_{28}H_{26}O_{2}]^{+} (M^+) : 394.1933, \text{found} 394.1938. \]
Ethyl 4-(diphenylmethylene)cyclopent-1-ene-1-carboxylate (3i). The general procedure was followed using ethyl 2-diazobut-3-enolate (1a, 70 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (2e, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3i (134 mg, 88%) as a colorless oil.

$^1$H-NMR: 1.30 (t, $J = 7.2$ Hz, 3H), 3.37 (d, $J = 2.7$ Hz, 2H), 3.46 (d, $J = 1.8$ Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 6.81-6.83 (m, 1H), 7.22-7.37 (m, 10H); $^{13}$C-NMR: 14.7, 38.2, 40.2, 60.7, 127.0, 128.8, 129.1, 135.8, 136.7, 137.4, 141.7, 142.7, 142.8, 165.2; HRMS (EI) calculated for [C$_{21}$H$_{20}$O$_2$]$^+$ (M$^+$): 304.1463, found 304.1466.

Benzyl 4-(diphenylmethylene)cyclopent-1-ene-1-carboxylate (3j). The general procedure was followed using benzyl 2-diazobut-3-enolate (1b, 101 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (2e, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3j (128 mg, 70%) as a colorless oil.

$^1$H-NMR: 3.38 (d, $J = 2.4$ Hz, 2H), 3.50 (d, $J = 2.1$ Hz, 2H), 5.23 (s, 2H), 6.87-6.89 (m, 1H), 7.23-7.40 (m, 15H); $^{13}$C-NMR: 37.8, 39.8, 66.0, 126.6, 128.2, 128.4, 128.5, 128.6, 128.7, 135.0, 136.2, 136.5, 136.8, 142.1, 142.4, 164.5; HRMS (EI) calculated for [C$_{26}$H$_{22}$O$_2$]$^+$ (M$^+$): 366.1620, found 366.1620.

tert-Butyl 4-(diphenylmethylene)cyclopent-1-ene-1-carboxylate (3k). The general procedure was followed using tert-butyl 2-diazobut-3-enolate (1c, 84 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (2e, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3k (115 mg, 69%) as a colorless oil.
**H-NMR**: 1.51 (s, 9H), 3.35 (d, J = 2.7 Hz, 2H), 3.44 (d, J = 2.1 Hz, 2H), 6.71-6.72 (m, 1H), 7.22-7.28 (m, 6H), 7.32-7.36 (m, 4H); **13C-NMR**: 28.2, 37.9, 39.7, 80.3, 126.5, 128.3, 128.4, 128.7, 128.8, 136.2, 136.9, 137.3, 140.2, 142.3, 142.5, 164.3; **HRMS** (EI) calculated for [C_{23}H_{24}O_{2}]^+ (M^+): 332.1776, found 332.1779.

### tert-Butyl 4-(bis(4-methoxyphenyl)methylene)cyclopent-1-ene-1-carboxylate (3l)

The general procedure was followed using tert-butyl 2-diazobut-3-enoate (1c, 84 mg, 0.5 mmol) and 1,1-di(4-methoxyphenyl)propa-1,2-diene (2f, 504 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3l (98 mg, 50%) as a colorless oil.

**H-NMR**: 1.49 (s, 9H), 3.32 (d, J = 2.4 Hz, 2H), 3.40 (d, J = 1.8 Hz, 2H), 3.82 (s, 6H), 6.70 (t, J = 2.1 Hz, 1H), 6.84-6.88 (m, 4H), 7.11-7.17 (m, 4H); **13C-NMR**: 28.6, 38.3, 40.2, 55.6, 80.7, 114.0, 114.05, 130.2, 130.3, 135.5, 135.7, 136.4, 137.3, 140.7, 158.4, 164.8; **HRMS** (EI) calculated for [C_{25}H_{28}O_{4}]^+ (M^+): 392.1988, found 392.1985.

### Ethyl (Z)-4-(1-phenylethylidene)cyclopent-1-ene-1-carboxylate (3m)

The general procedure was followed using ethyl 2-diazobut-3-enoate (1a, 70 mg, 0.5 mmol) and 3-phenylbuta-1,2-diene (2g, 260 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3m (84 mg, 69%) as a 15:1 Z/E mixture as a colorless oil.

**H-NMR**: 1.28 (t, J = 7.2 Hz, 3H), 2.01 (s, 3H), 3.27 (s, 2H), 3.36 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 6.85-6.88 (m, 1H), 7.24-7.27 (m, 3H), 7.33-7.38 (m, 2H); **13C-NMR**: 14.7, 21.4, 37.4, 39.4, 60.6, 126.7, 127.8, 128.6, 130.2, 134.1, 136.5, 141.5, 144.2, 165.3; **HRMS** (EI) calculated for [C_{16}H_{18}O_{2}]^+ (M^+): 242.1307, found 242.1305.
Ethyl 4-(1-(trimethylsilyl)ethylidene)cyclopent-1-ene-1-carboxylate (3n). The general procedure was followed using ethyl 2-diazobut-3-enoate (1a, 70 mg, 0.5 mmol) and 3-trimethylsilylbuta-1,2-diene (2h, 252 mg, 2.0 mmol). $^1$H-NMR analysis of the crude reaction mixture revealed that two isomers were formed in about 4:1 ratio. Chromatographic work-up (silica gel; hexanes) allowed the isolation of the major isomer in pure form (3n, 55 mg, 46%) as a colorless oil. The configuration of this isomer could not be unambiguously assigned due to overlapping of key signals in the $^1$H-NMR spectrum.

$^1$H-NMR (CD$_2$Cl$_2$): 0.23 (s, 9H), 1.32 (t, $J = 7.2$ Hz, 3H), 2.01 (s, 2H), 2.07 (s, 5H, accidental equivalence of methyl and methylene groups), 4.21 (q, $J = 7.2$ Hz, 2H), 6.89 (br s, 1H); $^{13}$C-NMR (CD$_2$Cl$_2$): -0.2, 14.0, 20.2, 22.8, 25.7, 60.2, 134.1, 134.3, 137.6, 138.0, 167.3; HRMS (El) calculated for [C$_{13}$H$_{22}$O$_2$Si]$^+$ (M$^+$): 238.1389, found 238.1386.

Ethyl 2-methyl-4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3o). The general procedure was followed using ethyl 2-diazoo-3-methylbut-3-enoate (1d, 77 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (2a, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 100:1) afforded compound 3o (54 mg, 56%) as a colorless oil. An unknown byproduct with identical mass (GC-MS analysis) was observed in the $^1$H NMR spectrum. On the basis of similar results with other allene derivatives, this byproduct is supposed to be ethyl 3,6-dimethyl-5-methylenehepta-2,6-dienoate.

$^1$H-NMR: 1.32 (t, $J = 7.2$ Hz, 3H), 1.64 (s, 3H), 1.66 (s, 3H), 2.17 (s, 3H), 3.16 br s, 2H), 3.27 (br s, 2H), 4.24 (q, $J = 7.2$ Hz, 2H); $^{13}$C-NMR: 14.4, 16.3, 20.6, 20.7, 38.3, 45.1, 59.7, 123.4, 126.5, 128.4, 154.1, 166.1; HRMS (El) calculated for [C$_{12}$H$_{18}$O$_2$]$^+$ (M$^+$): 194.1307, found 194.1305.
Ethyl 4-(diphenylmethylene)-2-methylcyclopent-1-ene-1-carboxylate (3p). The general procedure was followed using ethyl 2-diazo-3-methylbut-3-enoate (1d, 77 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (2e, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3p (48 mg, 30%) and 3p´ (24 mg, 15%) as colorless oils.

\textbf{1H-NMR:} 1.30 (t, \(J = 7.2\) Hz, 3H), 2.14 (s, 3H), 3.36 (s, 2H), 3.51 (s, 2H), 4.21 (q, \(J = 7.2\) Hz, 2H), 7.23-7.38 (m, 10H); \textbf{13C-NMR:} 14.4, 16.1, 39.8, 46.7, 59.8, 126.2, 126.5, 128.4, 128.8, 135.4, 135.7, 142.2, 142.6, 153.4, 165.8; \textbf{HRMS (EI)} calculated for [C_{22}H_{22}O_{2}]^+ (M^+): 318.1620, found 318.1620.

Ethyl (Z)-3-methyl-4-(3-phenyl-1H-inden-2-yl)but-2-enoate (3p´). \textbf{1H-NMR:} 1.33 (t, \(J = 7.2\) Hz, 3H), 1.71 (s, 3H), 3.46 (s, 2H), 3.97 (s, 2H), 4.21 (q, \(J = 7.2\) Hz, 2H), 5.76 (s, 1H), 7.19-7.45 (m, 9H); \textbf{13C-NMR:} 14.3, 24.6, 32.3, 40.4, 59.7, 117.2, 119.7, 123.5, 124.4, 126.2, 127.3, 128.4, 128.5, 129.2, 135.2, 140.8, 141.3, 142.7, 157.5, 166.4; \textbf{HRMS (EI)} calculated for [C_{22}H_{22}O_{2}]^+ (M^+): 318.1620, found 318.1621. The Z configuration of 3p´ was determined by NOE experiments.

Ethyl 4-cyclohexylidene-2-methylcyclopent-1-ene-1-carboxylate (3q). The general procedure was followed using ethyl 2-diazo-3-methylbut-3-enoate (1d, 77 mg, 0.5 mmol) and
vinylidenecyclohexane (2b, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 100:1) afforded compound 3q (33 mg, 28%) and 3q' (27 mg, 23%) as colorless oils.

^1H-NMR: 1.32 (t, J = 7.2 Hz, 3H), 1.46-1.55 (m, 6H), 2.01-2.15 (m + s, 7H), 3.20 (br s, 2H), 3.30 (br s, 2H), 4.22 (q, J = 7.2 Hz, 2H); ^13C-NMR: 14.4, 16.3, 26.6, 27.4, 31.1, 31.3, 37.6, 44.4, 59.6, 124.8, 126.4, 131.6, 154.1, 166.1; HRMS (EI) calculated for [C_{15}H_{22}O_{2}]^+ (M^+): 234.1620, found 234.1622.

Ethyl (Z)-5-(cyclohex-1-en-yl)-3-methylhexa-2,5-dienoate (3q'). ^1H-NMR: 1.29 (t, J = 7.2 Hz, 3H), 1.54-1.72 (m, 2H), 1.82 (s, 3H), 2.10-2.26 (m, 4H), 3.39 (s, 2H), 4.17 (q, J = 7.2 Hz, 2H), 4.79 (s, 1H), 5.08 (s, 1H), 5.80 (br s, 1H), 5.93 (t, J = 3.9 Hz, 3H); ^13C-NMR: 14.3, 22.1, 22.9, 24.6, 25.9, 26.0, 37.4, 59.5, 110.3, 117.1, 125.0, 135.8, 145.0, 158.8, 166.4; HRMS (EI) calculated for [C_{15}H_{22}O_{2}]^+ (M^+): 234.1620, found 234.1620. The Z configuration of 3q' was determined by NOE experiments.

Ethyl 2-(tert-butyl dimethylsilyloxy)-4-(diphenylmethylenec)cyclopent-1-ene-1-carboxylate (3r). The general procedure was followed using ethyl 3-((tert-butyl dimethylsilyloxy)-2-diazo-5-but-3-enoate (1e, 135 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (2e, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound 3r (55 mg, 25%) as a colorless oil.

^1H-NMR: 0.19 (s, 6H), 0.97 (s, 9H), 1.28 (t, J = 7.2 Hz, 3H), 3.32 (s, 2H), 3.40 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 7.19-7.33 (m, 10H); ^13C-NMR: -3.7, 14.8, 18.4, 25.7, 36.5, 42.3, 59.6, 107.7, 126.8, 128.5, 128.6, 128.8, 129.0, 132.4, 136.6, 141.8, 142.5, 162.1, 165.0; HRMS (EI) calculated for [C_{27}H_{34}O_{3}Si]^+ (M^+): 434.2277, found 434.2271.
Diethyl 4-(propan-2-ylidene)cyclopent-1-ene-1,3-dicarboxylate (3s). The general procedure was followed using diethyl (E)-4-diazopent-2-enedioate (1f, 106 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (2a, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound 3s (53 mg, 42%) as a colorless oil.

\[ ^1 \text{H-NMR: } 1.29 \text{ (t, } J = 7.2 \text{ Hz, 3H)}, 1.32 \text{ (t, } J = 7.2 \text{ Hz, 3H)}, 1.68 \text{ (s, 3H)}, 1.72 \text{ (s, 3H)}, 3.22-3.40 \text{ (m, 2H)}, 4.16 \text{ (q, } J = 7.2 \text{ Hz, 2H)}, 4.23 \text{ (t, } J = 7.2 \text{ Hz, 2H)}, 4.27-4.30 \text{ (m, 1H)}, 6.68-6.71 \text{ (m, 1H)}; ^{13} \text{C-NMR: } 14.2, 14.3, 20.9, 21.4, 36.4, 55.1, 60.5, 61.1, 128.5, 128.9, 138.6, 138.9, 164.6, 171.4; \text{HRMS (EI) calculated for [C}_{14}H_{20}O_4]^+ (M^+): 252.1362, found 252.1361. \]

1-[4-(diphenylmethylene)-2-methylcyclopent-1-en-1-yl]ethan-1-one (3t). The general procedure was followed using 3-diazo-4-methylpent-4-en-2-one (1g, 62 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (2e, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound 3t (58 mg, 40%) as a colorless oil.

\[ ^1 \text{H-NMR: } 2.12 \text{ (s, 3H)}, 2.26 \text{ (s, 3H)}, 3.39 \text{ (s, 2H)}, 3.54 \text{ (s, 2H)}, 7.21-7.37 \text{ (m, 10H)}; ^{13} \text{C-NMR: } 16.7, 30.4, 40.4, 47.2, 126.6, 128.4, 128.7, 134.6, 135.4, 135.6, 142.2, 142.4, 151.8, 197.6; \text{HRMS (EI) calculated for [C}_{21}H_{28}O]^+ (M^+): 288.1514, found 288.1512. \]
5. Reaction with phenyl-1,2-propadiene (2i)

Ethyl 4-benzylidencyclopent-1-ene-1-carboxylate (3u) and ethyl 4-methylene-5-phenylcyclopent-1-ene-1-carboxylate (3u'). The general procedure was followed using ethyl 2-diazobut-3-enoate (1a, 70 mg, 0.5 mmol) and phenylallene (2i, 232 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 100:1) afforded an inseparable 4:1 mixture of 3u and 3u' (69 mg, 60%).

![Diagram of 3u and 3u']

$^1$H-NMR (major isomer 3u): 1.33 (t, $J = 7.2$ Hz, 3H), 3.50-3.61 (m, 4H), 4.25 (t, $J = 7.2$ Hz, 2H), 6.44-6.46 (m, 1H), 6.87-6.89 (m, 1H), 7.17-7.38 (m, 5H); (minor isomer 3u', only clearly assignable signals are listed): 1.14 (t, $J = 7.2$ Hz, 3H), 3.36-3.41 (m, 2H), 4.00-4.13 (m, 2H), 4.62 (br s, 1H), 4.89 (br s, 1H), 5.08-5.10 (m, 1H), 7.02 (br s, 1H);

$^{13}$C-NMR (major isomer 3u): 14.3, 37.1, 42.2, 60.4, 123.9, 126.4, 127.5, 128.0, 128.4, 135.7, 137.5, 139.9, 141.2, 141.5, 142.3, 164.7; (minor isomer 3u', only clearly assignable signals are listed): 14.0, 39.1, 55.2, 60.1, 110.5, 142.3, 143.8, 152.0, 164.2; HRMS (EI) calculated for [C$_{15}$H$_{16}$O$_2$]$^+$ (M$^+$): 228.1150, found 228.1148.
6. General procedure for the synthesis of triene derivatives 4a-c from vinylidrazo compounds 1a-c and tetramethyallene (2j)

\[
\text{Diazo compound} + \text{Tetramethyallene} \xrightarrow{\text{[Au(1Pr)(CH}_3\text{CN)]SbF}_6 (5 \text{ mol\%})} \text{Triene Derivative}
\]

\[
\begin{align*}
1a \ (R = \text{Et}) \\
1b \ (R = \text{Bn}) \\
1c \ (R = \text{Bu})
\end{align*}
\]

\[
\begin{align*}
2i \\
4a \ (R = \text{Et}) \\
4b \ (R = \text{Bn}) \\
4c \ (R = \text{Bu})
\end{align*}
\]

[Au(1Pr)(CH\text{3CN)]SbF}_6 (21.6 mg, 0.025 mmol, 5 mol\%) was added to a solution of vinylidazo compound 1 (0.5 mmol) and 2,4-dimethylpenta-2,3-diene (2j, 192 mg, 2 mmol) in CH\text{2Cl}_2 (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4-12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 20:1) to afford triene derivatives 4a-c.
7. Characterization Data of Compounds 4

**Ethyl (E)-6-methyl-5-(prop-1-en-2-yl)hepta-2,5-dienoate (4a).** The general procedure was followed using ethyl 2-diazobut-3-enoate (1a, 70 mg, 0.5 mmol). Final chromatographic purification afforded compound 4a (86 mg, 83%) as a colorless oil.

\[
{^1}H-NMR: 1.29 (t, J = 7.2 Hz, 3H), 1.68 (s, 3H), 1.72 (s, 3H), 1.76 (s, 3H), 2.99 (d, J = 6.6 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 4.61 (br s 1H), 4.94 (br s, 1H), 5.79 (dt, J = 15.6 and 1.5 Hz, 1H), 6.90 (dt, J = 15.6 and 6.6 Hz, 1H); \]

\[
{^{13}}C-NMR: 14.6, 20.2, 22.1, 22.9, 35.0, 60.5, 114.3, 121.6, 128.9, 132.3, 146.3, 147.2, 167.2; HRMS (EI) calculated for [C_{13}H_{20}O_2]^+ (M^+): 208.1463, found 208.1467.
\]

**Benzyl (E)-6-methyl-5-(prop-1-en-2-yl)hepta-2,5-dienoate (4b).** The general procedure was followed using benzyl 2-diazobut-3-enoate (1b, 101 mg, 0.5 mmol). Final chromatographic purification afforded compound 4b (78 mg, 58%) as a colorless oil.

\[
{^1}H-NMR: 1.69 (s, 3H), 1.73 (s, 3H), 1.78 (s, 3H), 3.01 (d, J = 6.6 Hz, 2H), 4.63 (br s 1H), 4.96 (br s, 1H), 5.20 (s, 2H), 5.87 (dt, J = 15.6 and 1.6 Hz, 1H), 6.98 (dt, J = 15.6 and 6.6 Hz, 1H), 7.36-7.41 (m, 5H); \]

\[
{^{13}}C-NMR: 19.9, 21.8, 22.6, 34.6, 66.0, 114.0, 120.9, 128.2, 128.6, 131.8, 136.2, 145.8, 147.6, 166.6; HRMS (EI) calculated for [C_{18}H_{22}O_2]^+ (M^+): 270.1620, found 270.1617.
\]
**tert-Butyl (E)-6-methyl-5-(prop-1-en-2-yl)hepta-2,5-dienoate (4c).** The general procedure was followed using tert-butyl 2-diazobut-3-enoate (1c, 84 mg, 0.5 mmol). Final chromatographic purification afforded compound 4c (71 mg, 60%) as a colorless oil.

**H-NMR:** 1.49 (s, 9H), 1.68 (s, 3H), 1.72 (s, 3H), 1.76 (s, 3H), 2.96 (d, $J = 6.6$ Hz, 2H), 4.61-4.62 (m, 1H), 4.94-4.95 (m, 1H), 5.71 (dt, $J = 15.6$ and 1.6 Hz, 1H), 6.80 (dt, $J = 15.6$ and 6.6 Hz, 1H);

**C-NMR:** 19.8, 21.8, 22.6, 28.2, 34.4, 80.0, 113.8, 122.9, 128.3, 132.1, 145.6, 145.9, 166.3;

**HRMS (El) calculated** for $[C_{15}H_{24}O_2]^+$ ($M^+$): 236.1776, found 236.1778.
8. Reaction with cyclohexyl-1,2-propadiene (2k)

\[
\begin{align*}
\text{COOEt} & \quad + \quad \text{Cy} \quad \text{(Au(Pr)(MeCN))SbF}_6 \quad (5 \text{ mol\%}) \\
\text{CH}_2\text{Cl}_2 \quad \text{rt} \\
\text{5/5'} = 4:1
\end{align*}
\]

[Au(Pr)(MeCN)]SbF$_6$ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of ethyl 2-diazobut-3-enate (1a, 70 mg, 0.5 mmol) and cyclohexylpropa-1,2-diene (2k, 244 mg, 2 mmol) in CH$_2$Cl$_2$ (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 8 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 40:1) to afford a 4:1 mixture (GC/MS) of 5 and 5' (41 mg, 35%).

Ethyl (E)-7-cyclohexylhept-2-en-6-ynoate (5). $^1$H-NMR: 1.22-1.50 (m + t, 9H), 1.60-1.79 (m, 4H), 2.31-2.44 (m, 5H), 4.21 (q, $J$ = 7.2 Hz, 2H), 5.89 (d, $J$ = 15.0 Hz, 1H), 7.00 (dt, $J$ = 15.0 and 2.0 Hz, 1H); $^{13}$C-NMR: 14.3, 17.8, 24.8, 25.9, 29.0, 31.9, 33.0, 60.2, 78.3, 86.0, 122.2, 147.2, 166.5; HRMS (El) calculated for [C$_{15}$H$_{22}$O$_2$]$^+$ (M$^+$): 234.1620, found 234.1624. NMR spectroscopic data of compound 5 macht those reported in the literature (G. A. Molander, W. H. Retsch, J. Org. Chem. 1998, 63, 5507).

An experiment performed with the deuteriated allene [D]-2k afforded the following result:
9. Computational study

Preliminary Density-functional theory calculations on the reaction mechanism of the gold-catalyzed reaction of unbiased allenes and vinyl diazo derivatives, using the hybrid B3LYP functional, have been carried out. The 6-31G(d) basis set was employed for all elements, with the exception of gold which has been described with the LANL2DZ basis set and pseudopotential. The stationary points located were fully optimized and characterized to be a minimum or a first-order saddle point (transition structure) by computing the harmonic vibrational frequencies. The connection of either, the reactants or products, with the corresponding transition structure was established by computation of the intrinsic reaction coordinate (IRC). All the calculations described in this work were carried out with Gaussian09 package.

The geometries of ethyl 2-diazo-3-butenoate (1a) and dimethyl (2a)- or cyclohexylallene (2k) as reactants and the gold (I)-NHC-carbene complex (A), as catalyst are shown in Figure S2.

![Figure S2. Selected bond lengths (Å) for reactants and gold (I) catalyst.](image)

First, the coordination of allenes and the gold catalyst was studied. The complexes between the catalyst A and the allenes 2a and 2k were characterized, and in both cases, the complexation to the external or the internal double bond was considered (Figure S3).
Figure S3. Selected bond lengths (Å) for the complexes formed between the NHC-gold carbene (A) and allenes 2a and 2k.

The coordination of the allenes to the catalyst is predicted to happen without activation barrier, and the complexation free-energies, ΔG are collected in Table S2.

Table S2.

| Complex     | ΔG (kcal mol⁻¹)* |
|-------------|-----------------|
| 2a-A-ext    | -23.5           |
| 2a-A-int    | -21.3           |
| 2k-A-ext    | -22.4           |
| 2k-A-int    | -20.1           |

* Relative to the free reactants.
The data shown in Table S2 indicates that the coordination of gold catalyst to the external double bond of the allene is favoured, which can be understood on steric grounds, the internal position being more sterically crowded than the external one. The most salient geometrical features of these complexes are the increase (relative to the free cumulene) of the length of the double bond complexed to gold, and the slight bending of the C-C-C moiety in the case of the complexes involving the internal double bond.

On the other hand, the reaction of diazoester derivative 1a with the gold (I)-NHC-carbene complex, A, involves a barrierless coordination of gold to the diazo-carbon atom leading to the intermediate I (Figure S4). The diazo-carbon atom in I is slightly pyramidalized and its distance to the nitrogen of the diazo group has increased, as compared with the diazoester 1a.

![Figure S4](image_url)

**Figure S4.** Stationary points located for the reaction of diazoester 1a with NHC-gold carbene A. Selected bond lengths (Å), bond angles (degrees) and relative Gibbs free-energies (kcal mol⁻¹) are shown.
A transition state (TS), corresponding to the loss of dinitrogen from intermediate I, was found, and leads to the NHC-gold(I) carbene intermediate II. As could be expected, the normal mode associated with the imaginary frequency of TS, corresponds to the stretching of the bond between the diazo carbon atom and one of the nitrogen atoms. The gold-carbene intermediate II shows a length of 2.009 Å between the gold atom and the carbon atom coming from the reactant 1a. In addition, the C-C-C angle in intermediate II is very close to the value corresponding to the sp³ hybridization.

The dinitrogen molecule is almost fully formed in the transition structure, and the loss of the very stable N₂ molecule can be seen as the driving force of the reaction, with a predicted value for the reaction free-energy of 32.7 kcal mol⁻¹.

According to these data, the key step in the catalytic cycle is the activation of the diazocompound derivative 1a by the NHC-gold complex A: this process is very favoured thermodynamically, and leads to the formation of the gold carbene derivative II, an electrophilic intermediate which could easily react with the allene component.
### Cartesian Coordinates and Gibbs free-Energies (au) of the Stationary Points.

| 1a                  | 2a                  | 2a-A-ext             |
|---------------------|---------------------|----------------------|
| C -0.9457 1.7103 0.0001 | C 0.8729 -0.0000 0.0001 | C -1.7550 2.9043 0.4808 |
| C -1.9176 0.7875 0.0002 | C -0.4388 -0.0001 0.0001 | C -1.1020 2.4238 -0.5497 |
| C -1.7844 -0.6696 0.0002 | C -1.7469 -0.0001 0.0001 | C -0.0690 -3.9759 0.3932 |
| N -2.9096 -1.3638 0.0003 | C 1.6688 -1.2889 0.0000 | C -0.4643 2.1363 -1.7031 |
| C -0.5980 -1.5461 0.0002 | C 1.6685 1.2891 0.0001 | C -2.0996 2.1269 1.7281 |
| H -2.9531 1.1252 0.0001 | H -2.3213 0.0001 -0.9257 | H 0.5813 2.4146 -1.8446 |
| H -1.2108 2.7626 0.0001 | H 1.0177 -2.1669 -0.0006 | C 1.2529 -3.6881 0.4411 |
| H 0.1057 1.4557 0.0001 | H 2.3206 -1.3417 0.8829 | C -2.2061 4.3545 0.4318 |
| N -3.8760 -1.9617 0.0001 | H 2.3215 -1.3411 -0.8822 | H -1.7601 1.0894 1.6832 |
| O -0.6551 -2.7626 0.0000 | H 2.3207 1.3418 -0.8824 | H -3.1856 2.1328 1.8800 |
| O 0.5517 -0.8406 0.0003 | H 2.3207 1.3419 0.8826 | N -0.7404 -2.8121 0.0434 |
| C 1.7643 -1.6332 0.0003 | H 1.0171 2.1669 0.0000 | H -1.6467 2.6081 2.6035 |
| C 2.9364 -0.6707 0.0001 | H -2.3215 -0.0002 0.9257 | H -1.7697 4.9053 1.2736 |
| H 1.7602 -2.2792 -0.8830 | H -3.2968 4.4051 0.5328 | G=-195.210490 |
| H 1.7604 -2.2790 0.8837 | G=-493.240241 | N 1.3637 -2.3207 0.1262 |
| H 2.9193 -0.0309 0.8884 | H -1.9177 4.8508 -0.4973 | H -1.9177 4.8508 -0.4973 |
| H 2.9192 -0.0312 -0.8884 | H -1.0292 1.8902 -2.6035 | H -1.0292 1.8902 -2.6035 |
| H 3.8760 -1.2337 0.0001 | Au -0.2742 0.1319 -0.6585 | Au -0.2742 0.1319 -0.6585 |
| C 2.6165 -1.6094 0.0711 | C 0.1380 -1.7882 -0.1205 | C 0.1380 -1.7882 -0.1205 |
| C -0.5907 -4.9053 0.5584 | C -2.1699 -2.7296 -0.1215 | C -2.1699 -2.7296 -0.1215 |
| H 2.1162 -4.2690 0.6797 | H 2.1162 -4.2690 0.6797 | H 2.1162 -4.2690 0.6797 |
| H 2.1622 -3.0115 0.9702 | H 2.1622 -3.0115 0.9702 | H 2.1622 -3.0115 0.9702 |
| H 4.3794 -2.9561 0.8076 | H 4.3794 -2.9561 0.8076 | H 4.3794 -2.9561 0.8076 |
| H 4.9272 -2.6183 -0.4318 | H 4.9272 -2.6183 -0.4318 | H 4.9272 -2.6183 -0.4318 |
| H -4.0919 -2.3413 -1.5166 | H -4.0919 -2.3413 -1.5166 | H -4.0919 -2.3413 -1.5166 |
| C -2.7053 -2.4023 -1.3692 | C -2.7053 -2.4023 -1.3692 | C -2.7053 -2.4023 -1.3692 |
|   | 1.1897 | -0.002 | -1.6084 |   | 2.4670 | -0.108 | 0.0381 |   | 2.558 | -3.2599 | 1.9326 |
|---|--------|--------|---------|---|--------|--------|--------|---|--------|---------|---------|
| H | 0.9230 | 1.2683 | 0.1502  | C | 0.0000 | -2.4377 | -0.3227 |   | -5.0262 | -3.1735 | 1.6513  |
| C | 2.3076 | 1.2669 | -0.5169 | H | 1.3927 | 2.4377  | 0.3666  |   | -6.0053 | -2.5775 | 0.5359  |
| C | 3.1022 | 0.0000 | -0.1680 | H | -1.3926 | 2.4377  | 0.3666  |   | -4.5174 | -2.0929 | 2.4841  |
| C | 2.3077 | -1.2669 | -0.5170 | C | 2.9729 | -0.9361 | 1.0427  |   | -2.0462 | -2.2201 | -2.2123 |
| C | 0.9231 | -1.2684 | 0.1502  | C | 4.3108 | -1.3296 | 0.9808  |   | 3.5829  | -2.0150 | -0.8514 |
| H | -0.0768 | -0.0001 | -1.2790 | C | 5.1255 | -0.8874 | -0.0642 |   | 4.8059  | -1.3442 | -0.8915 |
| H | 1.0453 | 1.3241 | 1.2429  | C | 4.6064 | -0.0504 | -1.0553 |   | 5.0521  | -0.2797 | -0.0210 |
| H | 0.3552 | 2.1631 | -0.1452 | C | 3.2688 | 0.3441  | -1.0113 |   | 4.0771  | 0.1146  | 0.8984  |
| H | 2.8672 | 2.1631 | -0.2195 | H | 2.3387 | -1.2454 | 1.8675  |   | 2.8530  | -0.5538 | 0.9542  |
| H | 2.1827 | 1.3261 | -1.6083 | H | 4.7172 | -1.9695 | 1.7575  |   | 3.3750  | -2.8342 | -1.5333 |
| H | 3.3292 | -0.0000 | 0.9086  | H | 6.1669 | -1.1915 | -0.1040 |   | 5.625   | -1.6516 | -1.6067 |
| H | 4.0674 | 0.0000 | -0.6905 | H | 5.2392 | 0.2926  | -1.8678 |   | 6.0053  | 0.2389  | -0.0558 |
| H | 2.8673 | -2.1631 | -0.2196 | H | 2.8505 | 0.9816  | -1.7845 |   | 4.2725  | 0.9333  | 1.5842  |
| H | 2.1828 | -1.3261 | -1.6084 | C | -3.2687 | 0.3440  | -1.0113 |   | 2.0982  | -0.2763 | 1.6832  |
| H | 0.3553 | -2.1594 | -0.1452 | C | -4.6064 | -0.0505 | -1.0554 |   | G=1018.617312 |
| H | 1.0454 | -1.3242 | 1.2428  | C | -5.1255 | -0.8874 | -0.0642 |   | G=351.167050 |
| C | -4.3108 | -1.3295 | 0.9808  | C | -2.9730 | -0.9360 | 1.0428  |   | G=823.369308 |
| H | -2.8504 | 0.9815  | -1.7846 | H | -5.2392 | 0.2924  | -1.8679 |   | H | -6.1669 | -1.1915 | -0.041 |
| H | -4.7173 | -1.9693 | 1.7579  | H | -2.3387 | -1.2453 | 1.8679  |   | G=823.369308 |
| 2a-A-int | 2k-A-ext | 2k-A-int |
|---------|---------|---------|
| C -0.0002 2.9689 -0.7781 | C -1.3231 -0.5395 0.7978 | C -0.6678 -2.3506 -0.4458 |
| C -0.0001 2.6452 0.5397 | C -0.5109 -0.6037 1.8203 | C -0.2739 -2.3030 0.8452 |
| C -0.6791 -3.5773 -0.7673 | C 0.1634 -0.6827 2.9861 | C -0.0854 -2.4949 2.1289 |
| C -0.0002 2.7619 1.8493 | C 5.6013 -0.8892 -0.4837 | C 4.1044 2.0466 -1.0351 |
| C -1.2918 3.2955 -1.5055 | H 0.2836 0.1979 3.6176 | H 0.5635 -1.8693 2.7331 |
| C 1.2915 3.2956 -1.5055 | H 0.3580 -1.6500 3.4504 | H -0.5886 -3.3220 2.6279 |
| C 0.6792 -3.5772 -0.7673 | C -2.8354 -0.6180 0.9245 | C -1.9856 -1.8248 -1.0009 |
| H -0.0003 3.7532 2.3013 | H -0.9206 -0.4277 -0.2084 | H -0.1082 -3.0157 -1.1089 |
| H -2.1725 2.9789 -0.9435 | C 5.5040 0.4655 -0.4741 | C 3.0860 2.9414 -0.9500 |
| H -1.3140 2.8422 -2.5018 | C -3.4888 0.6674 0.3674 | C -2.9034 -3.0418 -1.2939 |
| N -1.0814 -2.2505 -0.7042 | C -5.0229 0.5842 0.4305 | C -4.2391 -2.5878 -1.9058 |
| H -1.3381 4.3846 -1.6415 | C -5.5530 -0.6634 -0.2912 | C -4.9492 -1.5571 -1.0165 |
| H 1.3378 4.3847 -1.6414 | N 4.4559 -1.3791 0.1284 | N 3.5549 0.7904 -0.8200 |
| H 1.3136 2.8423 -2.5018 | C -4.9018 -1.9428 0.2544 | C -4.0364 -0.3600 -0.7116 |
| N 1.0815 -2.2505 -0.7042 | C -3.3675 -1.8700 0.1896 | C -2.7000 -0.8069 -0.0973 |
| H 2.1722 2.9789 -0.9435 | H -3.0918 -0.7055 1.9888 | H -1.7635 -1.3455 -1.9657 |
| H -0.0003 1.9102 2.5213 | H -3.1718 0.8043 -0.6773 | H -3.0899 -3.5788 -0.3532 |
| H -0.0001 0.5936 -0.4034 | H -3.1278 1.5403 0.9249 | H -2.3965 -3.7451 -1.9668 |
| Au 0.0000 -1.4285 -0.6554 | N 4.3032 0.7778 0.1481 | N 1.9344 2.2152 -0.6792 |
| C -2.4592 -1.8296 -0.6752 | H -5.4557 1.4928 -0.0045 | H -4.8796 -3.4627 -2.0668 |
| C 2.4592 -1.8295 -0.6752 | H -5.3399 0.5604 1.4830 | H -4.0510 -2.1503 -2.8968 |
| H -1.3911 -4.3847 -0.8338 | H -5.4873 -0.4935 1.4850 | Au 0.9204 -0.6361 -0.2263 |
| H 1.3913 -4.3846 -0.8338 | H -5.3425 -0.5786 -1.3673 | H -5.2490 -2.0355 -0.0730 |
| C -3.2778 -2.2635 0.3693 | C 3.6525 -0.3555 0.5201 | C 2.2178 0.8884 -0.5990 |
| C -4.6185 -1.8770 0.3861 | H -6.6430 -0.7227 -0.1905 | H -5.8718 -1.2152 -1.4997 |
| C -5.1281 -1.0638 -0.6291 | C 4.1801 2.7822 0.3108 | C 4.3165 -0.4339 -0.8374 |
| C -4.2988 -0.6387 -1.6696 | H -5.2494 -2.8193 -0.3052 | H -4.5373 0.3385 -0.0310 |
| C -2.9580 -1.0253 -1.7021 | C 3.8392 2.1251 0.3680 | C 0.6326 2.8091 -0.5062 |
| H -2.8680 -2.8830 1.1616 | H -5.2123 -2.0955 1.2979 | H -3.8400 0.1956 -1.6402 |
| H -5.2614 -2.2082 1.1956 | H 6.3615 -1.5462 -0.8759 | H 5.1551 2.1801 -1.2391 |
| H -6.1722 -0.7665 -0.6122 | H -2.9209 -2.7735 0.6226 | H -2.0536 0.0642 0.0751 |
| Au 0.1905 1.3673 0.6773 | Au 1.3455 0.6773 0.1896 | Au 3.4504 0.6773 0.1896 |

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|   | H     |  -4.6976  |  -0.0193  |  -2.4672  |   | H     |  6.1733  |  1.2307  |  -0.8345  |   | H     |  -2.8829  |  -1.2639  |  0.8851  |
|---|-------|-----------|-----------|-----------|---|-------|---------|---------|-----------|---|-------|---------|---------|---------|
|   | H     |  -2.3107  |  -0.7277  |  -2.5212  |   | H     |  -3.0471  |  -1.8290  |  -0.8623  |   | C     |  5.3205  |  -0.6191  |  0.1147  |
|   | C     |  2.9580   |  -1.0253  |  -1.7022  |   | C     |  5.0500   |  -3.5460  |  1.0911   |   | C     |  6.0726   |  -1.7943  |  0.0872  |
|   | C     |  4.2988   |  -0.6386  |  -1.6697  |   | C     |  4.7988   |  -4.9095  |  1.2498   |   | C     |  5.8173   |  -2.7691  |  -0.8804 |
|   | C     |  5.1281   |  -1.0636  |  -0.6291  |   | C     |  3.6883   |  -5.4953  |  0.6372   |   | C     |  4.8117   |  -2.5695  |  -1.8292 |
|   | C     |  4.6185   |  -1.8767  |  0.3862   |   | C     |  2.8271   |  -4.7198  |  -0.1426  |   | C     |  4.0577   |  -1.3950  |  -1.8169 |
|   | C     |  3.2778   |  -2.2632  |  0.3694   |   | C     |  3.0723   |  -3.3567  |  -0.3161  |   | H     |  5.5013   |  0.1395   |  0.8705  |
|   | H     |  2.3108   |  -0.7278  |  -2.5213  |   | H     |  5.9017   |  -3.0773  |  1.5750   |   | H     |  6.8539   |  -1.9481  |  0.8250  |
|   | H     |  4.6976   |  -0.0193  |  -2.4673  |   | H     |  5.4688   |  -5.5107  |  1.8566   |   | H     |  6.4053   |  -3.6816  |  -0.8980 |
|   | H     |  6.1722   |  -0.7662  |  -0.6121  |   | H     |  3.4972   |  -6.5565  |  0.7635   |   | H     |  4.6213   |  -3.3208  |  -2.5895 |
|   | H     |  5.2614   |  -2.2078  |  1.1958   |   | H     |  1.9713   |  -5.1767  |  -0.6300  |   | H     |  3.2918   |  -1.2148  |  -2.5648 |
|   | H     |  2.8680   |  -2.8826  |  1.1617   |   | H     |  2.4278   |  -2.7488  |  -0.9431  |   | C     |  0.0602   |  3.5067   |  -1.5716 |
|   | C     |  3.5668   |  2.9353   |  -0.7357  |   | C     |  3.1422   |  4.2478   |  -0.5252  |   | C     |  3.1891   |  4.1040   |  -1.3984 |
|   | C     |  3.1422   |  4.2478   |  -0.5252  |   | C     |  3.1891   |  4.1040   |  -1.3984  |   | C     |  3.1422   |  4.2478   |  -0.5252  |
|   | C     |  2.9903   |  4.7369   |  0.7745   |   | C     |  2.9903   |  4.7369   |  0.7745   |   | C     |  2.9903   |  4.7369   |  0.7745   |
|   | C     |  3.2684   |  3.9161   |  1.8700   |   | C     |  2.9903   |  4.7369   |  0.7745   |   | C     |  2.9903   |  4.7369   |  0.7745   |
|   | C     |  3.7016   |  2.6040   |  1.6726   |   | C     |  3.7016   |  2.6040   |  1.6726   |   | C     |  3.7016   |  2.6040   |  1.6726   |
|   | H     |  3.6763   |  2.5402   |  -1.7414  |   | H     |  2.9268   |  4.8848   |  -1.3775  |   | H     |  2.8255   |  4.4667   |  -0.0442 |
|   | H     |  2.6605   |  5.7591   |  0.9334   |   | H     |  1.7787   |  3.2303   |  1.8405   |   | H     |  1.7787   |  3.2303   |  1.8405   |
|   | H     |  3.1633   |  4.2995   |  2.8804   |   | H     |  0.4618   |  2.1843   |  1.5493   |   | H     |  0.4618   |  2.1843   |  1.5493   |
|   | H     |  3.9494   |  1.9654   |  2.5148   |   |   |         |         |         |   |   |         |         |         |

G = -1018.613782

G = -1174.572117

G = -1174.568440
| I          | TS          | II + N₂       |
|------------|-------------|---------------|
| C -1.0604  | -3.2012     | 2.3523        |
| C 1.2964   | 3.6450      | 0.0731        |
| C -0.3469  | -3.0709     | 1.2323        |
| C 2.5293   | 3.0854      | 0.1659        |
| C -0.7945  | -2.4044     | -0.0470       |
| N 0.3911   | 2.6012      | -0.0769       |
| N -0.2748  | -3.1032     | -1.1446       |
| N 2.3555   | 1.7100      | 0.0712        |
| C 1.0389   | 1.4064      | -0.0680       |
| C -2.2576  | -2.1166     | -0.4001       |
| H 0.6789   | -3.4323     | 1.1998        |
| C -1.0315  | 2.7827      | -0.2064       |
| H -0.6076  | -3.6744     | 3.2177        |
| C 3.4346   | 0.7577      | 0.1298        |
| Au 0.1911  | -0.4375     | -0.1216       |
| H -2.0743  | -2.8364     | 2.4534        |
| N 0.1691   | -3.6418     | -2.0156       |
| H 0.9807   | 4.6762      | 0.0696        |
| O -2.7064  | -2.3039     | -1.5083       |
| H 3.5077   | 3.5291      | 0.2606        |
| O -2.9066  | -1.6017     | 0.6398        |
| C -1.6855  | 2.3281      | -1.3538       |
| C -4.3001  | -1.2174     | 0.3951        |
| C -3.0621  | 2.5269      | -1.4742       |
| C -4.8377  | -0.6199     | 1.6785        |
| C -3.7688  | 3.1836      | -0.4635       |
| H -4.8461  | -2.1120     | 0.0849        |
| C -3.1008  | 3.6405      | 0.6757        |
| H -4.3060  | -0.5036     | -0.4327       |
| C -1.7265  | 3.4395      | 0.8113        |
| H -4.2686  | 0.2693      | 1.9671        |

S-27
| H    | -1.1215  | 1.8461  | -2.1459 | H    | -1.0826  | 2.2994  | -2.2574 | H    | 0.7213   | 1.8657  | 1.4762  |
|------|----------|---------|---------|------|----------|---------|---------|------|----------|---------|---------|
| H    | -4.8039  | -1.3428 | 2.4994  | H    | -4.4722  | -2.1413 | 3.2474  | H    | 5.0987   | -2.4829 | -3.2555 |
| H    | -3.5753  | 2.1860  | -2.3684 | H    | -3.4119  | 3.0079  | -2.6064 | H    | 3.0521   | 2.6863  | 1.7310  |
| H    | -5.8820  | -0.3266 | 1.5282  | H    | -5.6794  | -0.8508 | 3.0679  | H    | 6.2598   | -1.2680 | -2.6884 |
| H    | -4.8370  | 3.3486  | -0.5677 | H    | -4.6133  | 4.3300  | -0.8579 | H    | 4.0339   | 4.2000  | 0.0199  |
| H    | -3.6473  | 4.1529  | 1.4615  | H    | -3.4338  | 4.9230  | 1.2486  | H    | 2.6903   | 4.8699  | -1.9616 |
| H    | -1.2003  | 3.7773  | 1.6991  | H    | -1.0932  | 4.1709  | 1.6172  | H    | 0.3758   | 4.0091  | -2.2428 |
| C    | 4.2316   | 0.7061  | 1.2749  | C    | 3.8226   | 0.2644  | 1.3711  | C    | -4.3546  | -0.1575 | -1.9234 |
| C    | 5.2940   | -0.1975 | 1.3223  | C    | 4.7427   | -0.7836 | 1.4185  | C    | -5.2147  | -1.2548 | -1.9793 |
| C    | 5.5495   | -1.0393 | 0.2371  | C    | 4.9554   | -1.5836 | 0.2931  | C    | -5.2542  | -2.1715 | -0.9259 |
| C    | 4.7454   | -0.9764 | -0.9036 | C    | 4.2507   | -1.3342 | -0.8870 | C    | -4.4360  | -1.9897 | 0.1916  |
| C    | 3.6847   | -0.0712 | -0.9662 | C    | 3.3336   | -0.2837 | -0.9489 | C    | -3.5777  | -0.8913 | 0.2630  |
| H    | 4.0149   | 1.3546  | 2.1186  | H    | 3.6388   | 0.8829  | 2.2446  | H    | -4.3034  | 0.5503  | -2.7454 |
| H    | 5.9179   | -0.2450 | 2.2095  | H    | 5.2891   | -0.9758 | 2.3367  | H    | -5.8490  | -1.3943 | -2.8492 |
| H    | 6.3788   | -1.7390 | 0.2777  | H    | 5.6745   | -2.3961 | 0.3340  | H    | -5.9370  | -3.0225 | -0.9731 |
| H    | 4.9527   | -1.6190 | -1.7539 | H    | 4.4265   | -1.9449 | -1.7674 | H    | -4.4773  | -2.6917 | 1.0190  |
| H    | 3.0707   | 0.0095  | -1.8577 | H    | 2.8027   | -0.0585 | -1.8685 | H    | -2.9608  | -0.7215 | 1.1396  |

G = -1316.628004  
\( v = 340.48 \text{ cm}^{-1} \)  
G = -1316.621563  
G = -1316.661061
10. References

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11. \(^{1}H\)- and \(^{13}C\)-NMR spectra for new compounds

![NMR Spectra](image)

3a
3e
\[ \text{3g} \]
NOESY experiment (400 MHz, CDCl₃) for compound 3m
3p
NOESY experiment (400 MHz, CDCl₃) for compound 3p⁻
