

A Microwave-Assisted Intramolecular [2+2] Allenic Cycloaddition Reaction for the Rapid Assembly of Bicyclo[4.2.0]octa-1,6-dienes and Bicyclo[5.2.0]nona-1,7-dienes

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Supporting Information

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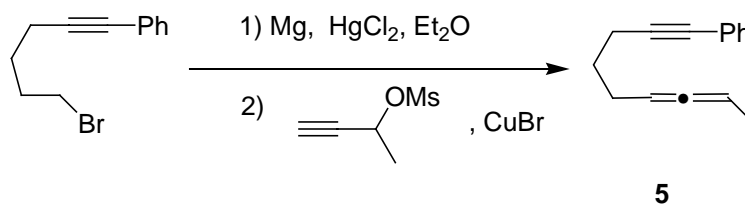
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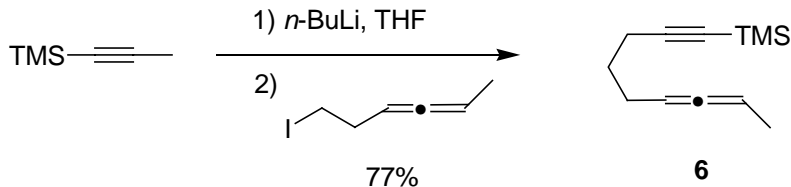
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General methods

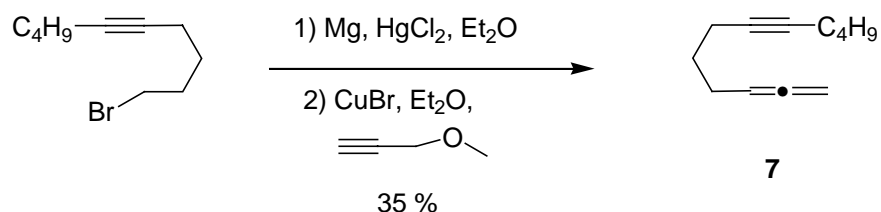
Unless otherwise noted, all reactions were performed under nitrogen atmosphere. All commercially available compounds were purchased from Aldrich Chemical Co., Strem Chemicals and Acros and used as received, unless otherwise specified. Tetrahydrofuran (THF), diethyl ether (Et₂O) and dichloromethane (CH₂Cl₂) were purified with alumina using the Sol-Tek ST-002 solvent purification system. Toluene and diisopropylamine were freshly distilled from CaH₂ prior to use. Purification of the compounds by flash chromatography was performed by using silica gel (32-63 μ m particle size, 60 Å pore size). TLC analyses were performed on silica gel 60 F₂₅₄ plates (250 μ m thickness). All ¹H and ¹³C NMR spectra were obtained on a 300 MHz instrument unless otherwise specified, and chemical shifts (δ) reported relative to residual solvent peak CHCl₃ or C₆H₆. All NMR spectra were obtained at room temperature unless otherwise specified. IR spectra were obtained using a 360 FT-IR. EI mass spectrometry was performed on a Micromass Autospec high resolution mass spectrometer. Microwave assisted reactions were performed on a CEM discoverTM reactor. In some cases, mixtures of diastereomers were obtained and were not separated for characterization purposes. Consequently, the spectroscopic data has been reported as a mixture of diastereomers. Where possible, the diastereomeric ratios were measured by integration of the resonances in the ¹H NMR. All known compounds **4**,¹ **8-11**,² **12-13**,³ **14-15**, **19**⁴ were prepared according to reported methods.



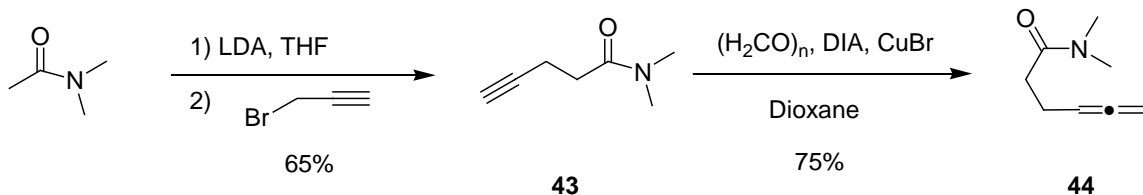
1-(Nona-6,7-dien-1-ynyl)benzene (5): To a flame dried 25 mL round bottomed flask, 1-(6-bromohex-1-ynyl)benzene⁵ (450 mg, 2.0 mmol), magnesium turnings (98 mg, 4.0 mmol) and HgCl₂ (1 mg) were added followed by Et₂O (10 mL). The mixture was vigorously stirred for 2 h before being cannulated into a suspension of CuBr (290 mg, 2.0 mmol) and but-3-yn-2-yl methanesulfonate⁶ (440 mg, 3.0 mmol) in Et₂O at −5 °C. The resulting gray-yellow mixture was allowed to stir at −5 °C for 2 h before being poured into a mixture of ice-cold Et₂O/HCl (1 N). The layers were separated and the aqueous phase was extracted with Et₂O (2 x 10 mL). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated under vacuum. Purification of the yellow oil by flash chromatography (hexanes) afforded the title compound (**5**, 92 mg, 23%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.37 (m, 2H), 7.32- 7.24 (m, 3H), 5.12-5.05 (m, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 2.19-2.12 (m, 2H), 1.78-1.65 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 205.1, 131.8, 128.4, 127.7, 124.2, 90.2, 89.6, 86.1, 81.0, 28.3, 28.2, 18.9, 14.8; IR (thin film) ν 2941, 2856, 2227, 1975, 1598 1489 cm^{−1}; MS *m/z* (%) 196 (6), 181 (7), 167 (15), 115 (18), 73 (100); EI-HRMS calcd for C₁₅H₁₆ *m/z* [*M*⁺] 196.1252; found 196.1228.



Trimethyl(nona-6,7-dien-1-ynyl)silane (6): To a flame dried 25 mL round bottomed flask, trimethyl(prop-1-ynyl)silane (0.30 mL, 2.0 mmol) was added followed by THF (10 mL). The reaction flask was cooled to $-78\text{ }^{\circ}\text{C}$ and *n*-BuLi (1.25 mL, 1.6 M solution in hexanes, 2.0 mmol) was added dropwise. Following the addition, the solution became light yellow and was held at $-78\text{ }^{\circ}\text{C}$ for 30 min before 6-iodohexa-2,3-diene⁷ (500 mg, 2.4 mmol) was added slowly. The yellow solution was allowed to warm to room temperature over 8 h and quenched by adding sat. NH_4Cl (10 mL) and Et_2O (10 mL). The layers were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated under reduced pressure to afford a yellow oil. Flash chromatography (hexanes) afforded the title compound (**6**, 290 mg, 77%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 5.07-5.00 (m, 2H), 2.56 (t, $J = 7.2\text{ Hz}$, 2H), 2.05 (dq, $J = 3.3, 7.2\text{ Hz}$, 2H), 1.66-1.59 (m, 6H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.2, 107.4, 89.5, 85.9, 84.7, 28.2, 28.1, 19.3, 14.7, 0.37; IR (thin film) ν 2957, 2853, 2175, 1966, 1440 cm^{-1} ; MS m/z (%) 192 (7), 191 (8), 177 (23), 149 (25), 118 (42), 73 (100); EI-HRMS calcd for $\text{C}_{11}\text{H}_{17}\text{Si}$ m/z [M^+] 177.1099; found 177.1098.



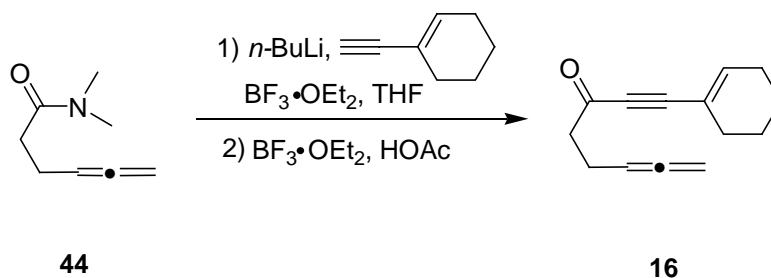
Dodeca-1,2-dien-7-yne (7): To a flame dried 25 mL round bottomed flask, 1-bromodec-5-yne (406 mg, 2.0 mmol), magnesium turnings (98 mg, 4.0 mmol) and HgCl_2 (1 mg) were added followed by Et_2O (10 mL). The mixture was vigorously stirred for 2 h before being cannulated into a suspension of CuBr (290 mg, 2.0 mmol) and methyl propargyl ether (0.25 mL, 3.0 mmol) in Et_2O at -5°C . The resulting gray-yellow mixture was allowed to stir at -5°C for 2 h before being poured into a mixture of ice-cold $\text{Et}_2\text{O}/\text{HCl}$ (1 N). The layers were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated under reduced pressure. Purification of the yellow oil by flash chromatography (hexanes) afforded the title compound (**7**, 112 mg, 35%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 5.15-5.00 (p, $J = 3.0$ Hz, 1H), 4.70- 4.66 (dt, $J = 3.0$ and 6.6 Hz, 2H), 2.20-2.01 (m, 6H), 1.66-1.59 (m, 2H), 1.45-1.34 (m, 4H), 0.93 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 208.8, 89.5, 80.8, 79.8, 75.1, 31.4, 28.7, 27.5, 22.1, 18.6, 18.4, 13.9; IR (thin film) ν 2932, 2861, 1956, 1434 cm^{-1} ; MS m/z (%) 162 (2), 147 (9), 193 (38), 119 (70), 105 (60), 91 (100); EI-HRMS calcd for $\text{C}_{12}\text{H}_{18}$ m/z [M^+] 162.1409; found 162.1403.



***N,N*-dimethylpent-4-ynamide⁸ (43):** A flame dried 100 mL flask was charged with a solution of *N,N*-dimethylacetamide (870 mg, 10.0 mmol) in THF (30 mL) and cooled to -78°C . To this stirring solution was slowly added LDA (2.0 M in hexane, 11.0 mmol). The mixture was allowed to stir at that temperature for 30 min, then propargyl bromide (80% in toluene, 20.0 mmol) was added via syringe. The resulting mixture was allowed to warm up to room temperature overnight before being poured into brine (50 mL). The layers were separated and the aqueous phase was extracted with Et₂O (2 x 30 mL). The combined organic phases was dried over MgSO₄ and concentrated under reduced pressure. Purification of the obtained yellow oil by flash chromatography (hexanes-EtOAc, 1:1, v/v) afforded the title compound (**43**, 820 mg, 65%) as a yellow powder. ¹H NMR (300 MHz, CDCl₃) δ 3.02 (s, 3H), 2.97 (s, 3H), 2.58-2.55 (m, 4H), 1.98 (t, $J = 1.9$ Hz, 1H).

***N,N*-dimethylhexa-4,5-dienamide (44):** To a suspension of *N,N*-dimethylpent-4-ynamide (**43**, 250 mg, 2.0 mmol), paraformaldehyde (230 mg, 77.0 mmol), and CuBr (95 mg, 0.66 mmol) in dioxane (10 mL) was added *i*-Pr₂NH (0.56mL, 40.0 mmol). The brown mixture was heated at gentle reflux for 18 h then cooled to room temperature and filtered. The solid was washed with Et₂O, and the combined filtrates were concentrated under reduced pressure. Purification of the brown gel by flash chromatography (hexanes-EtOAc, 1:1, v/v) afforded the title compound (**44**, 210 mg, 75%) as a light yellow oil. ¹H

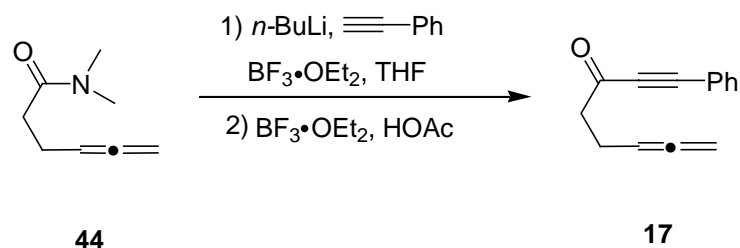
NMR (300 MHz, CDCl₃) δ 5.23 (p, J = 6.5 Hz, 1H), 4.70 (dt, J = 3.5 and 6.5 Hz, 2H), 3.01 (s, 3H), 2.96 (s, 3H), 2.47-2.42 (m, 2H), 2.37-2.33 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 208.5, 172.4, 89.7, 75.8, 37.4, 35.6, 32.5, 23.6; IR (thin film) ν 2928, 1954, 1647, 1496, 1397 cm⁻¹; MS m/z (%) 139 (65), 124 (18), 110 (30), 87 (27), 72 (100); EI-HRMS calcd for C₁₃H₁₄NO m/z [M⁺] 139.0997; found 139.0992.



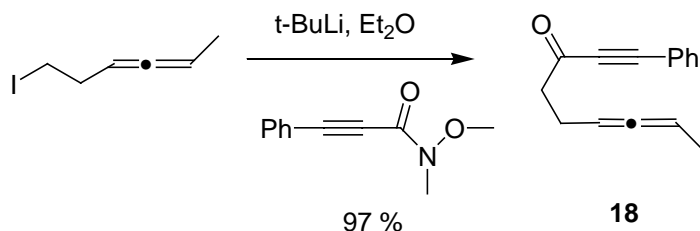
General procedure for the preparation of allenyl alkynone:⁴

1-Cyclohexenylocta-6,7-dien-1-yn-3-one (16): To a flame dried 10 mL round bottomed flask, 1-ethynylcyclohex-1-ene (0.21 mL, 1.8 mmol) was added followed by THF (4 mL). The reaction flask was cooled to -78 °C and *n*-BuLi (1.0 mL, 1.6 M solution in hexanes, 1.6 mmol) was added dropwise. After 5 min of stirring, BF₃·OEt₂ (0.21 mL, 1.7 mmol) was added and the light yellow solution was held at -78 °C for 15 min. A solution of *N,N*-dimethylhexa-4,5-dienamide (**44**, 140 mg, 1.0 mmol) in THF (4 mL) was added via cannula. The reaction was allowed to stir at -78 °C for 2 h when another portion of BF₃·OEt₂ (0.21 mL, 1.7 mmol), then HOAc (0.1 mL, 1.7 mmol) were immediately added. The yellow solution was then allowed to warm to -20 °C and quenched by adding sat. NH₄Cl (10 mL). The mixture was partitioned into Et₂O (5 mL) and H₂O (5 mL). The layers were separated and the aqueous phase was extracted with Et₂O (2 x 5 mL). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated

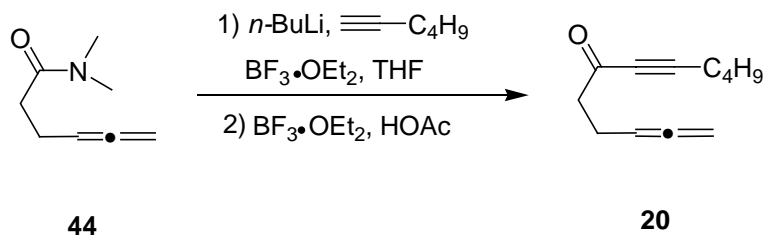
under reduced pressure. Purification of the yellow oil by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**16**, 190 mg, 95%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 6.42 (t, $J = 1.9$ Hz, 1H), 5.14 (p, $J = 6.5$ Hz, 1H), 4.69 (dt, $J = 3.4$ and 3.5 Hz, 2H), 2.67 (t, $J = 7.1$ Hz, 2H), 2.36-2.31 (m, 2H), 2.16-2.12 (m, 4H), 1.63-1.55 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 208.5, 187.2, 142.4, 119.1, 93.5, 88.7, 86.2, 76.2, 44.3, 28.4, 26.2, 22.5, 22.0, 21.2; IR (thin film) ν 2932, 2860, 2185, 1956, 1669, 1622, 1453 cm^{-1} ; MS m/z (%) 200 (42), 158 (70), 129 (100), 115 (75); EI-HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}$ m/z [M^+] 200.1201; found 200.1190.



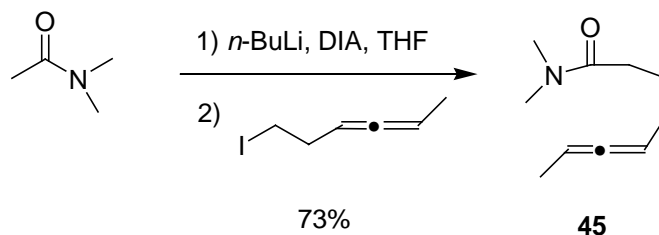
1-Phenylocta-6,7-dien-1-yn-3-one (17): Following the general procedure for the preparation of allenyl alkynone. From 1-ethynylbenzene (0.20 mL, 1.8 mmol) and *N,N*-dimethylhexa-4,5-dienamide (**44**, 140 mg, 1.0 mmol), The title compound (**17**, 180 mg, 92%) was obtained as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.57 (m, 2H), 7.47-7.36 (m, 3H), 5.22 (p, $J = 6.6$ Hz, 1H), 4.76 (dt, $J = 3.5$ and 6.6 Hz, 2H), 2.82 (t, $J = 6.9$ Hz, 2H), 2.48-2.39 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 208.4, 187.0, 133.0, 130.7, 128.6, 119.9, 90.9, 88.5, 87.7, 76.4, 44.2, 22.3; MS m/z (%) 196 (21), 181 (8), 167 (33), 154 (66), 129 (100); EI-HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{O}$ m/z [M^+] 196.0888; found 196.0884.



1-Phenylnona-6,7-dien-1-yn-3-one (18): To a flame dried 25 mL round bottomed flask, 6-iodohexa-2,3-diene (300 mg, 1.4 mmol) was added followed by Et₂O (10 mL) under N₂ atmosphere. The reaction flask was cooled to −78 °C and *t*-BuLi (1.1 mL, 1.7 M solution in pentane, 1.9 mmol) was added dropwise. The light yellow solution was held at that temperature for 1 h before a solution of *N*-methoxy-*N*-methyl-3-phenylpropionamide⁹ (230 mg, 1.2 mmol) in Et₂O (2 mL) was added via cannula. The yellow solution was allowed to stir at −78 °C for another hour and then quenched by adding sat. NH₄Cl (10 mL) and Et₂O (10 mL). The layers were separated and the aqueous phase was extracted with Et₂O (2 x 10 mL). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. Purification of the yellow oil by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**18**, 200 mg, 97%) as a light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.56-7.53 (m, 2H), 7.45-7.27 (m, 3H), 5.17-5.08 (m, 2H), 2.77 (t, *J* = 6.9 Hz, 2H), 2.44-2.36 (m, 2H), 1.62 (dd, *J* = 5.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 204.8, 187.2, 133.0, 130.7, 128.7, 120.0, 90.6, 88.8, 87.8, 87.5, 44.2, 23.1, 14.5; IR (thin film) ν 2923, 2202, 1964, 1670, 1489, 1443, 1357, 1269, 1093, 1041 cm^{−1}; MS *m/z* (%) 210 (20), 209 (18), 168 (50), 167 (65), 129 (100); EI-HRMS calcd for C₁₅H₁₄O *m/z* [*M*⁺] 210.1045; found 210.1050.

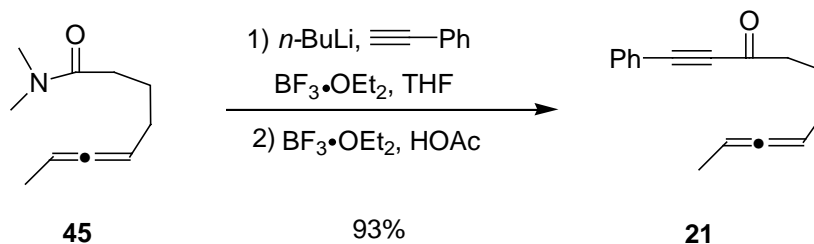


Dodeca-1,2-dien-7-yn-6-one (20) : Following the general procedure for the preparation of allenyl alkynone. Hex-1-yne (0.41 mL, 3.6 mmol) and *N,N*-dimethylhexa-4,5-dienamide (**44**, 280 mg, 2.0 mmol), the title compound (**20**, 180 mg, 68%) was obtained as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 5.13 (p, $J = 6.6$ Hz, 1H), 4.69 (dt, $J = 3.5$ and 6.6 Hz, 2H), 2.64 (t, $J = 7.2$ Hz, 2H), 2.37-2.27 (m, 4H), 1.59-1.52 (m, 2H), 1.47-1.35 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 208.5, 187.3, 94.7, 88.7, 80.9, 76.2, 44.3, 29.8, 22.4, 22.1, 18.7, 13.6; IR (thin film) ν 2959, 2213, 1957, 1674 cm^{-1} ; MS m/z (%) 176 (17), 161 (23), 147 (18), 133 (47), 105 (70), 91 (100).



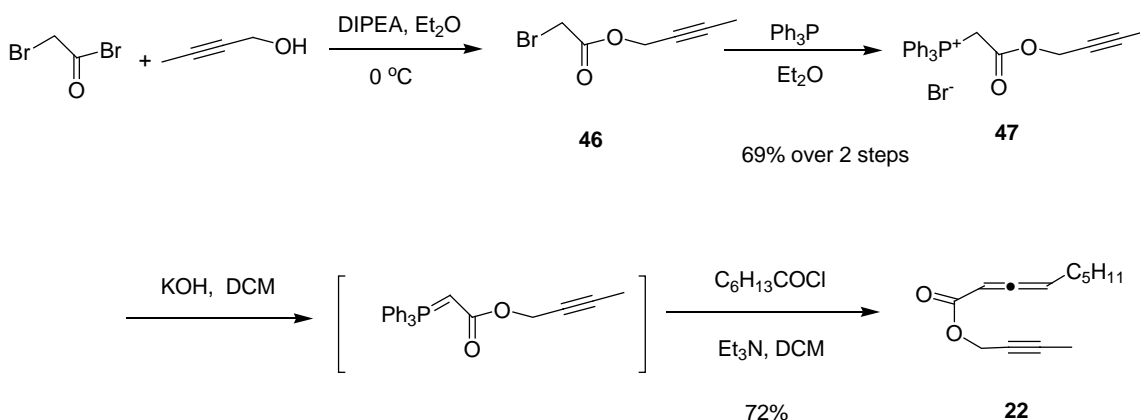
***N,N*-dimethylocta-5,6-dienamide (45)**: To a flame dried 100 mL round bottomed flask, *i*-Pr₂NH (1.5 mL, 11.0 mmol) was added, followed by THF (40 mL) under N₂ atmosphere. The reaction flask was cooled to -78 °C and *n*-BuLi (6.9 mL, 1.6 M solution in hexanes, 11.0 mmol) was added dropwise. The colorless solution was stirred at -78 °C for 30 min, then *N,N*-dimethylacetamide (0.93 mL, 10.0 mmol) was added via syringe. The light yellow solution was allowed to stir at -78 °C for 2 h then 6-iodohexa-2,3-diene (2.3 g, 11.0 mmol) was added slowly. The yellow solution was allowed to warm to room

temperature over 4 h and quenched by adding sat. NH_4Cl (30 mL) and Et_2O (50 mL). The layers were separated and the aqueous phase was extracted with Et_2O (2 x 30 mL). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated under reduced pressure. Purification of the yellow oil by flash chromatography (hexanes- EtOAc , 1:1, v/v) afforded the title compound (**45**, 1.2 g, 73%) as a light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 5.09-5.03 (m, 2H), 3.01 (s, 3H), 2.96 (s, 3H), 2.36 (t, $J = 7.3$ Hz, 2H), 2.09-2.00 (m, 2H), 1.74 (p, $J = 7.2$ Hz, 2H), 1.65 (dd, $J = 6.2, 4.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.0, 173.1, 89.8, 85.9, 37.4, 35.5, 32.7, 28.6, 24.6, 14.7; IR (thin film) ν 2928, 1964, 1647, 1457, 1396, 1265, 1137, 1058 cm^{-1} ; MS m/z (%) 167 (32), 152 (15), 111 (58), 87 (49), 72 (100); EI-HRMS calcd for $\text{C}_{10}\text{H}_{17}\text{NO}$, m/z [M^+] 167.1310; found 167.1311.



1-Phenyldeca-7,8-dien-1-yn-3-one (21): Following the general procedure for the preparation of allenyl alkynone. From 1-ethynylbenzene (0.40 mL, 3.6 mmol) and *N,N*-dimethylocta-5,6-dienamide (330 mg, 2.0 mmol), the title compound (**21**, 420 mg, 93%) was obtained as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.60-7.57 (m, 2H), 7.47-7.36 (m, 3H), 5.12-5.03 (m, 2H), 2.73 (t, $J = 3.3$ Hz, 2H), 2.11-2.03 (m, 2H), 1.92-1.82 (m, 2H), 1.65 (dd, $J = 6.7, 3.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.0, 187.8, 133.0, 130.7, 128.7, 120.0, 90.6, 89.3, 87.9, 86.1, 44.7, 28.0, 23.4, 14.6; IR (thin film) ν 2926, 2856, 2201, 1964, 1670, 1489, 1443, 1404, 1369, 1282, 1097 cm^{-1} ; MS m/z (%) 224 (27),

209 (6), 168 (59), 129 (100); EI-HRMS calcd for C₁₆H₁₇O, m/z [M⁺] 225.1279; found 225.1255.



Preparation of But-2-ynyl nona-2,3-dienoate (22):

But-2-ynyl 2-bromoacetate (46): A modification of the method of Jorgensen was employed.¹⁰ To a flame dried 50 mL round bottomed flask, but-2-yn-1-ol (1.5 mL, 20.0 mmol) and DIPEA (2 mL) were added followed by Et₂O (20 mL). The reaction flask was cooled to 0 °C and 2-bromoacetyl bromide (1.7 mL, 20.0 mmol) was added dropwise. The mixture was stirred at 0 °C for 90 min and then allowed to warm to room temperature for 30 min before being poured into a mixture of Et₂O (20 mL) and H₂O (20 mL). The layers were separated and the organic phase was washed sequentially with HCl (1N, 20 mL), H₂O (20 mL) and brine. The combined organic layers were dried over MgSO₄ and concentrated under vacuum afforded the title compound (**46**) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 4.74 (q, J = 2.4, 2H), 3.87 (s, 2H), 0.93 (t, J = 2.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 166.8, 84.4, 72.4, 54.8, 25.7, 3.8.

But-2-ynyl 2-(Triphenylphosphonium) acetate bromide(47) : The yellow oil (**46**) was taken up into Et₂O (20 mL) and PPh₃ (5.3 g, 20.0 mmol) was slowly added. Vigorous stirring was maintained for 24 h and then the solution was allowed to stand for additional

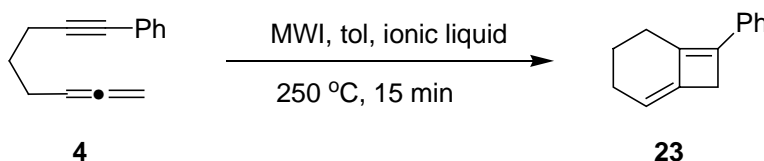
12h. The white precipitate was collected by filtration and washed with Et₂O to afford the phosphonium salt (**47**, 6.3 g, 69% for 2 steps) as a fine white powder. ¹H NMR (300 MHz, CDCl₃) δ 7.89-7.63 (m, 15H), 5.56 (d, ²J_{HP} = 13.8 Hz, 2H), 4.50 (q, *J* = 2.4 Hz, 2H), 1.71 (t, *J* = 2.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 163.5 (C=O, ²J_{HP} = 3.6 Hz), 135.0 (C₄', ⁴J_{CP} = 2.8 Hz), 133.6 (C₃', C₅', ³J_{CP} = 10.8 Hz), 130.0 (C₂', C₆', ²J_{CP} = 13.1 Hz), 117.2 (C₁', ¹J_{CP} = 88.5 Hz), 83.9, 71.3, 54.3, 32.2 (CH₂, ¹J_{CP} = 55.3 Hz), 3.3.

But-2-ynyl nona-2,3-dienoate (22): A modification of the method of Marshall was employed.¹¹ The phosphonium salt (**47**, 1.4 g, 3.8 mmol) was dissolved in CH₂Cl₂ (20 mL) and the solution was shaken gently with KOH (1N, 20 mL) in a separatory funnel for 5 min. The layers were separated and the organic phase was dried over MgSO₄ and concentrated under reduced pressure. The yellow oily residue was briefly dried under vacuum and taken up into CH₂Cl₂ (20 mL). To the solution was added Et₃N (0.58 mL, 4.2 mmol), followed by heptanoyl chloride (0.54 mL, 3.5 mmol). The yellow solution was kept stirring at room temperature for 12 h before being concentrated under reduced pressure. The brown gel was taken into hexane (50 mL) and the mixture was passed through a short pack of silica gel eluted with hexanes-EtOAc (9:1, v/v). The combined filtrates were concentrated under reduced pressure and purification of the yellow oil by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**22**, 520 mg, 72%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 5.66-5.61 (m, 2H), 4.70 (q, *J* = 2.4 Hz, 2H), 2.23-2.10 (m, 2H), 1.87 (t, *J* = 2.4 Hz, 3H), 1.54-1.45 (m, 2H), 1.39-1.29 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 212.9, 165.8, 95.9, 87.8, 83.3, 73.3, 53.2, 31.3, 28.5, 27.6, 22.5, 14.2, 3.8; IR (thin film) ν 2930, 2859, 2241, 1959, 1722, 1436 cm⁻¹; MS *m/z* (%) 207 (31), 137 (16), 81 (32), 53 (100).

General procedure for the microwave assisted [2+2] cycloaddition reaction

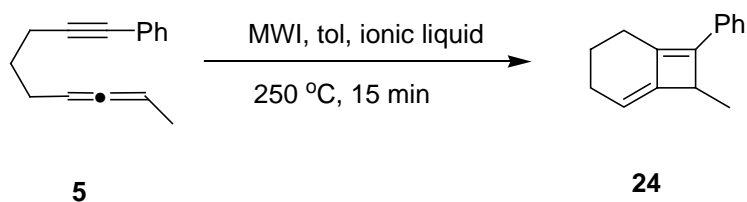
To a flame dried 10 mL microwave reactor vial* equipped with a magnetic stirring bar was added the ionic liquid 1-ethyl-3-methylimidazolium hexafluorophosphate (3 equivalent). The vial was sealed with a septum and N₂ was allowed to flow through the vial for 5 min before a 0.1 M solution of alkynyl allene in toluene was added. Then the septum was removed and replaced by a reusable cap*, and the vial was placed into the microwave reactor. The reaction was carried out with the following parameters temperature: 250 °C; max. pressure: 250 psi; max. power: 300 W; ramp time: 5 min; reaction time: 15 min. After a brief cool down period, the solution was directly applied to silica gel column. Gradient elution (hexanes-EtOAc) afforded the desired cycloadducts.

* Purchased from CEM, vial part # 908035; Reusable cap part # 908140.



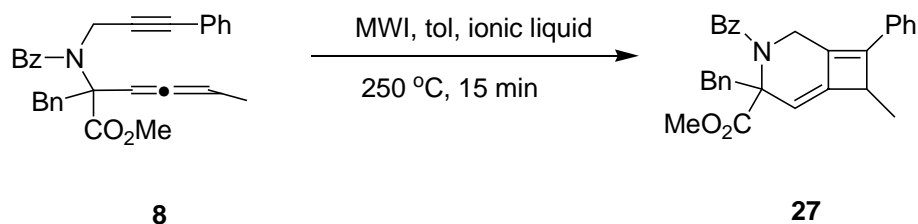
2-Phenylbicyclo-[4.2.0]-octa-1,4-diene (23). Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: 1-(octa-6,7-dien-1-ynyl)benzene (**4**, 18 mg, 0.1 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash Chromatography (hexanes) afforded the title compound (**23**, 13 mg, 74%) as pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.21 (m, 5H), 5.35 (t, *J* = 3.9 Hz, 1H), 3.26 (t, *J* = 2.7 Hz, 2H), 2.57-2.53 (m, 2H), 2.27-2.20

(m, 2H), 1.91-1.83 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.1, 138.6, 137.1, 135.9, 128.6, 126.9, 126.0, 110.5, 35.8, 24.8, 23.6, 23.4; IR (thin film) ν 2932, 1682, 1446 cm^{-1} ; MS m/z (%) 182 (100), 167 (62), 115 (53), 104 (39), 77 (50).



2-Phenyl-3-methylbicyclo-[4.2.0]-octa-1,4-diene (24): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: 1-(nona-6,7-dien-1-ynyl)benzene (**5**, 20 mg, 0.1 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash chromatography (hexanes) afforded the title compound (**24**, 14 mg, 70%) as a light yellow oil that was isolated as a 9:1 mixture of **24** and triene. ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.18 (m, 5H), 5.32 (t, J = 3.9 Hz, 1H), 3.66 (m, 1H), 2.56-2.52 (m, 2H), 2.22-2.17 (m, 2H), 1.87-1.78 (m, 2H), 1.36 (d, J = 6.8 Hz, 3H); ^{13}C NMR* (75 MHz, CDCl_3) δ 145.5, 142.4, 140.9, 135.5, 128.7, 126.7, 126.3, 108.5, 44.1, 24.6, 23.6, 23.4, 16.9; MS m/z (%) 196 (16), 181 (28), 155 (32), 141 (78), 105 (100).

* Decomposition was observed when spectrum was taken over a period of 12 h.

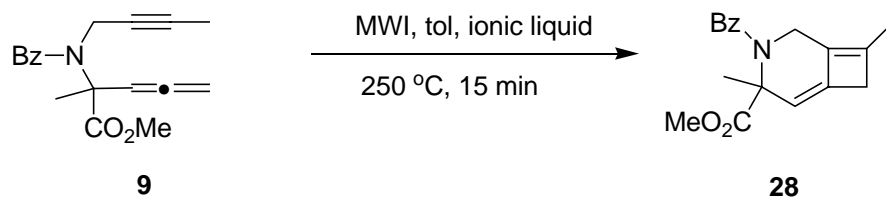


N-benzoyl-2-phenyl-3-methyl-6-benzyl-6-carbomethoxy-7-aza-bicyclo[4.2.0]-octa-

1,4-diene (27): Followed the general procedure for the microwave assisted [2+2] cycloaddition reaction: methyl 2-(*N*-(3-phenylprop-2-ynyl)benzamido)-2-benzylhexa-3,4-dienoate (**8**, 22 mg, 0.05 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (40 mg, 0.15 mmol), toluene (0.5 mL). Purification by flash chromatography (hexanes-EtOAc, 4:1, v/v) afforded the title compound (**27**, 13 mg, 60%) as a light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.45-6.92 (m, 15H), 5.27 (s, 0.5H)^a, 5.26 (s, 0.5H)^a, 4.23 (d, J = 16.2 Hz, 0.5H)^a, 4.15 (d, J = 13.6 Hz, 0.5H)^a, 3.81 (s, 3H), 3.82-3.76 (m, 1H)^a, 3.33 (dd, J = 13.4, 7.4 Hz, 0.5H)^a, 2.96 (dd, J = 17.1, 4.1 Hz, 0.5H)^a 1.41 (d, J = 6.8 Hz, 3H)^b.

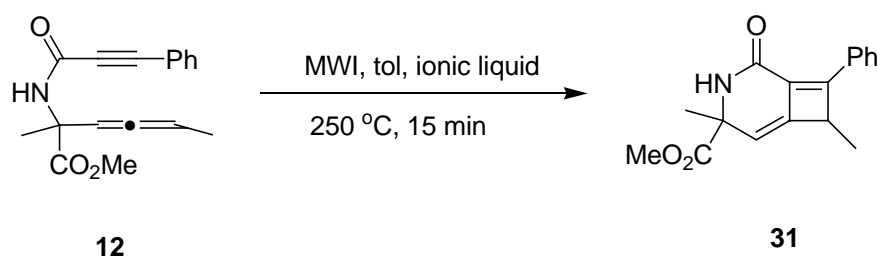
^a spin set of diastereomera is resolved. ^b spin set of diastereomeras is not resolved.

Spectra were recorded as a mixture of diastereomers.



N-benzoyl-2-methyl-6-methyl-6-carbomethoxy-7-aza-bicyclo[4.2.0]-octa-1,4-diene

(28): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: methyl 2-(*N*-(but-2-ynyl)benzamido)-2-methylpenta-3,4-dienoate (**9**, 18 mg, 0.06 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (50 mg, 0.19 mmol), toluene (0.6 mL). Purification by flash chromatography (hexanes-EtOAc, 4:1, v/v) afforded the title compound (**27**, 15 mg, 81%) as a light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.19 (m, 5H), 4.99 (s, 1H), 4.25 (d, *J* = 16.6 Hz, 1H), 3.86 (d, *J* = 18.7 Hz, 1H), 3.74 (s, 3H), 3.03 (s, 2H), 1.83 (s, 3H) 1.73 (dd, *J* = 4.1, 2.2 Hz, 3H).



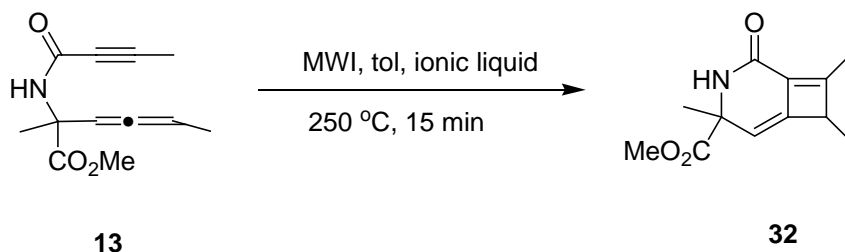
2-Phenyl-3-methyl-6-methyl-6-carbomethoxy-7-aza-8-oxo-bicyclo[4.2.0]-octa-1,4-

diene (31): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: methyl 2-(but-2-ynamido)-2-methylhexa-3,4-dienoate (**12**, 19 mg, 0.07 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (60 mg, 0.22 mmol),

toluene (0.7 mL). Purification by flash chromatography (hexanes-EtOAc, 1:1, v/v) afforded the title compound (**31**, 11 mg, 60%) as a light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.03-7.98 (m, 2H), 7.48-7.36 (m, 3H), 6.08 (br s, 0.5H)^a, 6.04 (br s, 0.5H)^a, 5.46 (s, 0.5H)^a, 5.45 (s, 0.5H)^a, 3.94-3.88 (m, 1H)^b, 3.80 (s, 1.5H)^a, 3.78 (s, 1.5H)^a, 1.65 (s, 1.5H)^a, 1.63 (s, 1.5H)^a, 1.50 (d, $J = 7.1$ Hz, 1.5H)^a, 1.48 (d, $J = 7.1$ Hz, 1.5H)^a; ^{13}C NMR (75 MHz, CDCl_3) δ 173.2, 158.4, 156.0, 143.3, 132.2, 130.5, 129.4, 128.9, 126.9, 106.6, 65.8, 53.3, 45.4, 30.0, 16.1; IR (thin film) ν 3214, 3058, 2958, 1736, 1665, 1631, 1493, 1448 cm^{-1} ; MS m/z (%) 283 (22), 268 (15), 254 (10), 225 (30), 224 (100); EI-HRMS calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ m/z [M^+] 283.1208; found 283.1208.

^a spin set of diastereomera is resolved. ^b spin set of diastereomeras is not resolved.

Spectra were recorded as a mixture of diastereomers.



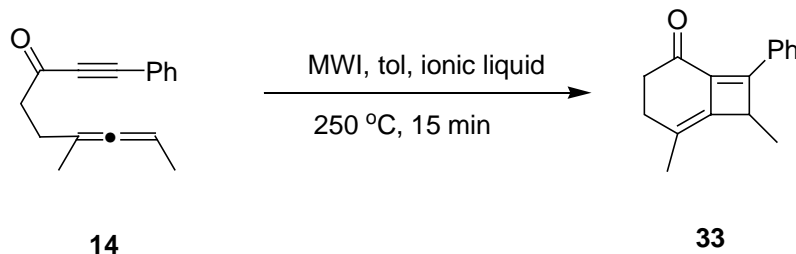
2,3-Dimethyl-6-methyl-6-carbomethoxy-7-aza-8-oxo-bicyclo[4.2.0]-octa-1,4-diene

(**32**): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: methyl 2-(but-2-ynamido)-2-methylhexa-3,4-dienoate (**13**, 20 mg, 0.09 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (72 mg, 0.27 mmol), toluene (0.9 mL). Purification by flash chromatography (hexanes-EtOAc, 1:1, v/v) afforded the title compound (**32**, 4.5 mg, 21%) as light yellow oil as a 1:1 mixture of diastereomers. ^1H NMR (300 MHz, C_6D_6) δ 6.14 (br s, 1H), 5.08 (s, 0.5H)^a, 5.06 (s, 0.5H)^a, 3.19 (s, 1.5H)^a,

3.16 (s, 1.5H)^a, 3.01-2.87 (m, 1H)^b, 1.76 (s, 1.5H)^a, 1.75 (s, 1.5H)^a, 1.26 (s, 1.5H)^a, 1.25 (s, 1.5H)^a, 0.87 (d, $J = 5.8$ Hz, 1.5H)^a, 0.85 (d, $J = 5.8$ Hz, 1.5H)^a.

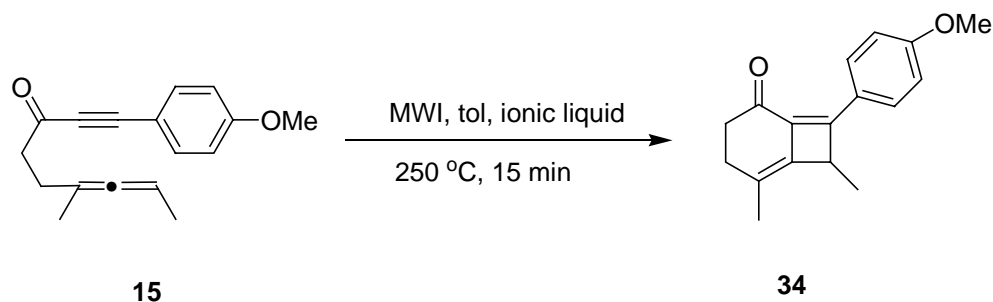
^a spin set of diastereomera is resolved. ^b spin set of diastereomeras is not resolved.

Spectra were recorded as a mixture of diastereomers.



2-Phenyl-3-methyl-5-methyl-8-oxo-bicyclo[4.2.0]-octa-1,4-diene (33): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: 6-methyl-1-phenylnona-6,7-dien-1-yn-3-one (**14**, 20 mg, 0.09 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**33**, 16 mg, 79%) as a light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.93-7.90 (m, 2H), 7.44-7.35(m, 3H), 3.87 (q, $J = 7.1$ Hz, 1H), 2.70-2.64 (m, 2H), 2.60-2.53 (m, 2H), 1.82 (s, 3H), 1.50 (d, $J = 7.1$ Hz, 3H); ¹³C NMR* (75 MHz, CDCl₃) δ 194.2, 152.0, 138.7, 133.1, 133.0, 130.1, 128.9, 128.5, 117.8, 44.9, 41.2, 32.5, 17.0, 16.4.

* Decomposition was observed when spectrum was taken over a period of 10 h.

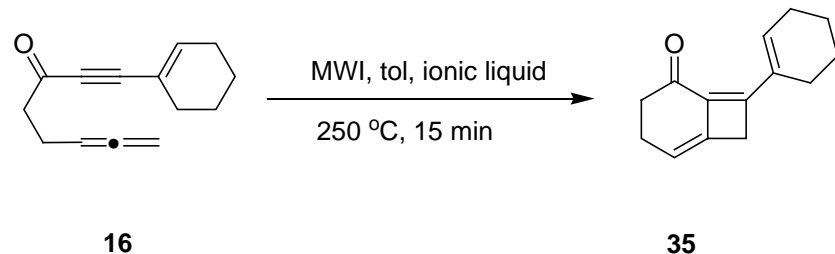


8-(4-Methoxyphenyl)-5,7-dimethylbicyclo[4.2.0]octa-1(8),5-dien-2-one (34**):**

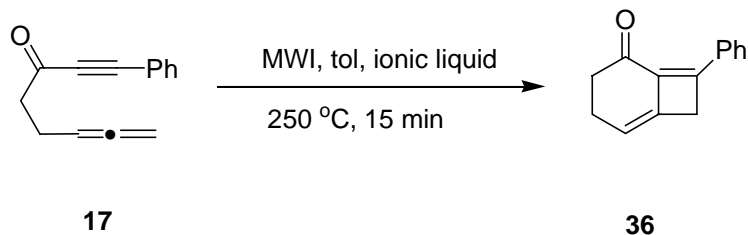
Following the general procedure for the microwave assisted [2+2] cycloaddition reaction:

1-(4-methoxyphenyl)-6-methylnona-6,7-dien-1-yn-3-one (**15**, 13 mg, 0.05 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (40 mg, 0.31 mmol), toluene (0.5 mL).

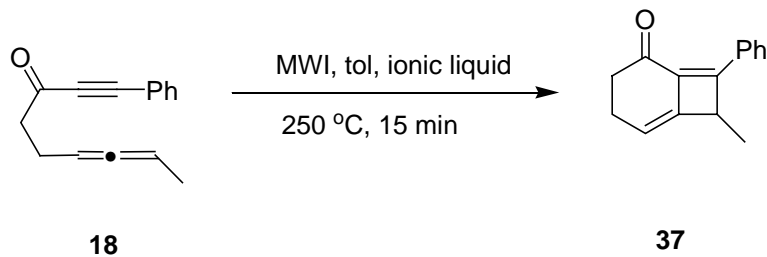
Purification by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**34**, 8.9 mg, 70%) as a light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.90 (d, $J = 8.9$ Hz, 2H), 6.92 (d, $J = 8.9$ Hz, 2H), 3.85 (s, 3H), 3.87-3.83 (m, 1H), 2.65-2.61 (m, 2H), 2.57-2.51 (m, 2H), 1.80 (s, 3H), 1.48 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 194.0, 161.3, 153.2, 138.5, 131.4, 130.5, 126.3, 116.0, 114.4, 55.6, 44.9, 40.9, 32.4, 16.9, 16.5; IR (thin film) ν 2937, 1673, 1599, 1510 cm^{-1} ; MS m/z (%) 254 (100), 239 (50), 211 (40); EI-HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$ m/z [M^+] 254.1307; found 254.1306.



8-Cyclohexenylbicyclo[4.2.0]octa-1(8),5-dien-2-one (35): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: 1-cyclohexenylocta-6,7-dien-1-yn-3-one (**16**, 20 mg, 0.1 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**35**, 15 mg, 77%) as a light yellow oil. ^1H NMR (600 MHz, C_6D_6) δ 5.99 (t, $J = 4.3$ Hz, 1H), 5.08 (t, $J = 3.8$ Hz, 1H), 2.96 (s, 2H), 2.65-2.62 (m, 2H), 2.34 (t, $J = 6.4$ Hz, 2H), 2.20 (dt, $J = 6.4, 10.3$ Hz, 2H), 1.88-1.86 (m, 2H), 1.49-1.45 (m, 2H), 1.35-1.31 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 191.8, 151.5, 138.7, 134.8, 134.6, 134.2, 108.3, 40.8, 36.5, 27.1, 26.7, 26.5, 22.4, 21.9; IR (thin film) ν 2930, 2857, 1682, 1564; MS m/z (%) 200 (100), 157 (20), 129 (40); EI-HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}$ m/z [M^+] 200.1201; found 200.1210; Ana. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C, 83.96; H, 8.05. Found: C, 60.69; H, 5.91.

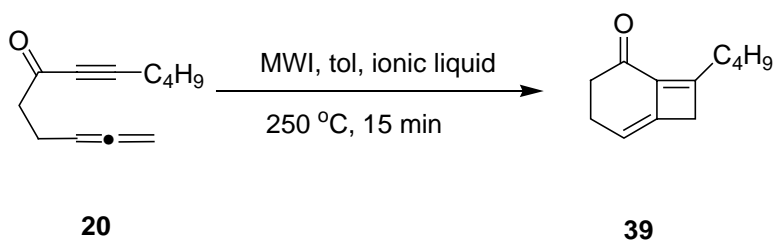


2-Phenyl-8-oxo-bicyclo[4.2.0]-octa-1,4-diene (36): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: 1-Phenylocta-6,7-dien-1-yn-3-one (**17**, 20 mg, 0.1 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**36**, 13 mg, 68%) as a light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.95-7.92 (m, 2H), 7.46-7.37(m, 3H), 5.46 (t, $J = 3.5$ Hz, 1H), 3.49 (s, 2H), 2.71-2.62 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.7, 150.8, 138.3, 135.4, 133.3, 130.8, 128.9, 128.7, 109.7, 40.6, 37.3, 27.1; IR (thin film) ν 2924, 1674, 1596, 1449, 1147 cm^{-1} ; MS m/z (%) 196 (10), 167 (20), 154 (55), 129 (100); EI-HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{O}$ m/z [M^+] 196.0888; found 196.0885.



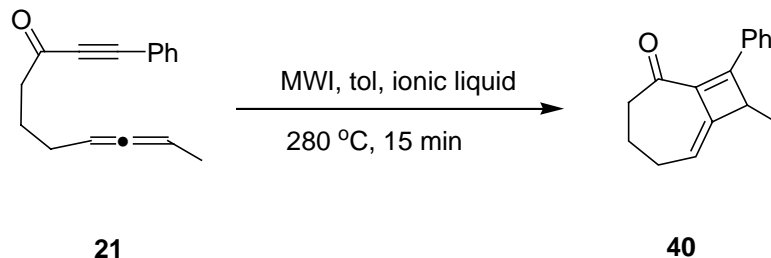
2-Phenyl-3-methyl-8-oxo-bicyclo[4.2.0]-octa-1,4-diene (37): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: 1-phenylnona-6,7-dien-1-yn-3-one (**18**, 21 mg, 0.1 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash

chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**37**, 14 mg, 66%) as a light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.96-7.93 (m, 2H), 7.48-7.38(m, 3H), 5.43 (t, J = 3.3 Hz, 1H), 3.88 (q, J = 7.1 Hz, 1H), 2.72-2.61 (m, 4H), 1.48 (d, J = 7.1, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 194.2, 155.6, 145.2, 132.8, 130.6, 129.7, 129.0, 128.9, 107.8, 45.6, 40.9, 27.0, 16.2; IR (thin film) ν 2934, 1680, 1597, 1448, 1237 cm^{-1} ; MS m/z (%) 209 (41), 194 (10), 165 (28), 129 (100).

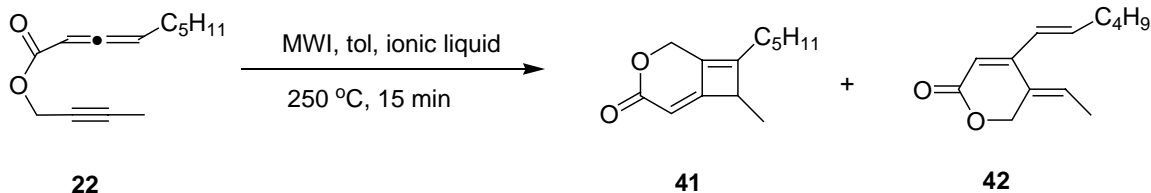


8-Butylbicyclo[4.2.0]octa-1(8),5-dien-2-one (39) : Following the general procedure for the microwave assisted [2+2] cycloaddition reaction: dodeca-1,2-dien-7-yn-6-one (**20**, 18 mg, 0.1 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash Chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**39**, 6 mg, 33%). ^1H NMR* (300 MHz, CDCl_3) δ 5.20 (t, J = 3.5 Hz, 1H), 3.10 (s, 3H), 2.60-2.57 (m, 2H), 2.52-2.50 (m, 2H), 1.65-1.59 (m, 6H), 0.93 (t, J = 7.2 Hz, 3H).

* Spectrum was taken as an inseparable mixture of product and starting material. Attempts to push this reaction to completion by heating for longer time gave the similar result. Raising the reaction temperature led to decomposition.



2-Phenyl-3-methyl-9-oxo-bicyclo[5.2.0]-nona-1,4-diene (40): Following the general procedure for the microwave assisted [2+2] cycloaddition reaction except the reaction temperature was increased to 280 °C: 1-phenyldeca-7,8-dien-1-yn-3-one (**21**, 22 mg, 0.1 mmol), 1-ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash chromatography (hexanes-EtOAc, 9:1, v/v) afforded the title compound (**40**, 18 mg, 83%) as a light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 8.14-8.12 (m, 2H), 7.47-7.40 (m, 3H), 5.42 (t, *J* = 4.3 Hz, 1H), 3.56 (q, *J* = 7.0 Hz, 1H), 2.71-2.67 (m, 2H), 2.47-2.42 (m, 2H), 1.99-1.92 (m, 2H), 1.38 (d, *J* = 7.0, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 197.3, 160.7, 140.5, 135.2, 132.5, 130.8, 129.7, 128.6, 114.3, 45.5, 42.3, 30.7, 21.8, 16.2; IR (thin film) ν 2929, 2199, 1665, 1595, 1490, 1447 cm⁻¹; MS *m/z* (%) 224 (28), 167 (22), 153 (22), 129 (43), 95 (48), 53 (100).



7-Methyl-8-pentyl-3-oxa-bicyclo[4.2.0]octa-1(8),5-dien-4-one (41) and 5-ethylidene-4-(hex-1-enyl)-5,6-dihydropyran-2-one (42): Following the general procedure for the [2+2] cycloaddition reaction: but-2-ynyl nona-2,3-dienoate (**22**, 21 mg, 0.1 mmol), 1-

ethyl-3-methylimidazolium hexafluorophosphate (80 mg, 0.31 mmol), toluene (1 mL). Purification by flash Chromatography (hexanes-EtOAc, 4:1 to 1:1, v/v) afforded two products. The title compound (**41**, 10 mg, 47%) as a light yellow oil. ^1H NMR (600 MHz, C_6D_6) δ 5.43 (s, 1H), 4.18-4.39 (m, 2H), 2.82 (q, J = 2.2 Hz, 1H), 1.28-1.25 (m, 2H), 1.24-1.72 (m, 4H), 1.13-1.09 (m, 5H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 162.0, 159.7, 148.6, 134.1, 99.7, 65.0, 52.3, 32.1, 30.3, 27.7, 22.8, 14.2, 13.5; IR (thin film) ν 2929, 2859, 1722; MS m/z (%) 206 (44), 191 (8), 177 (20), 133 (35), 119 (100); EI-HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ m/z [M^+] 206.1306; found 206.1307. The other product was identified as the cross-conjugated triene (**42**, 6 mg, 28%) as a light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 6.31 (t, J = 6.8 Hz, 0.3H)^a, 6.26 (t, J = 6.8 Hz, 0.7H)^a, 6.19-5.90 (m, 2H)^b, 5.86 (s, 0.7H)^a, 5.74 (s, 0.3H)^a, 5.02 (s, 0.6H)^a, 4.97 (s, 1.4H)^a, 2.25-2.14 (m, 2H)^b, 1.86 (d, J = 7.2 Hz, 0.9H)^a, 1.86 (d, J = 7.3 Hz, 2.1H)^a, 1.49-1.29 (m, 4H)^b; 0.93 (t, J = 7.2 Hz, 2.1H)^a, 0.87 (t, J = 6.8 Hz, 0.9H)^a; ^{13}C NMR (75 MHz, CDCl_3) δ 165.6, 152.0, 141.1, 139.8, 130.1, 129.8, 128.7, 124.4, 111.3, 66.0, 33.1, 31.0, 29.0, 22.4, 14.1; IR (thin film) ν 2928, 2858, 1712, 1644 cm^{-1} ; MS m/z (%) 206 (32), 177 (18), 149 (90), 121 (90), 105 (95), 91 (100); EI-HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}$, m/z [M^+] 206.1304; found 206.1307.

^a spin set of E/Z isomers is resolved. ^b spin set of E/Z isomers is not resolved. Spectra were recorded as a mixture of E/Z isomers.

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