Supporting Information for

Access to functionalized alkynylcyclopropanes via reductive radical-polar
crossover-based reactions of 1,3-enynes with alkyl radicals

Beibei Zhang, Junfei Luo and Yewen Fang
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1 General Information

1.1 Solvents, Reagents, and Starting Materials

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Photocatalysts \( \text{Ir}[(dF(CF_3)ppy)]_2(dtbbpy)PF_6^{[1a]} \) and \( 4\text{CzIPN}^{[1b]} \) were prepared according to published procedures. 1,3-Enynes were synthesized with reported procedures. Alkyl silicates and 2-(1-alkynyl)-2-2-alken-1-ones were reported in our previous literatures.\(^2\) All redox-active NHP esters are known compounds and prepared according to the literatures.\(^3\) Dried solvents were obtained from commercial sources and used without further purification unless otherwise noted.

1.2 Instruments

NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz) (500 MHz for \( ^1\text{H} \) NMR, 126 MHz for \( ^13\text{C} \) NMR, and 471 MHz for \( ^19\text{F} \) NMR). Chemical shifts were reported in ppm downfield from tetramethylsilane and calibrated using residue undeuterated solvent (Chloroform-\( d \) at 7.26 ppm \( ^1\text{H} \) NMR; 77.0 ppm \( ^13\text{C} \) NMR). Spectra were reported as follows: chemical shift (\( \delta \) ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Coupling constants are reported in Hertz where available. High resolution mass spectra (HRMS) were recorded on Waters Premier GC-TOF MS, Waters G2-Xs QTOF MS, and JEOL-AccuTOF-GCv4G-GCT MS. Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or KMnO\(_4\) staining solutions. Flash column chromatography was performed using silica gel (300-400 mesh) with solvents to use.
1.3 Picture of a Typical Reaction Setup

2 Synthesis of 1,3-Enynes

2.1 General Procedure for the Preparation of Alkyl Bromide-Tethered 1,3-Enynes 1

To a solution of NaI (15.0 g, 100 mmol) in MeCN (20 mL) at room temperature was added TMSCl (12.7 mL, 100 mmol) followed by H₂O (0.9 mL) and the cloudy solution was stirred for 10 minutes. But-3-yn-1-ol (3.76 mL, 50 mmol) in MeCN (10
mL) was then added dropwise and the solution stirred for an additional hour. The reaction was then quenched with H₂O (25 mL) and extracted with Et₂O (3 x 20 mL). The organic layers were pooled and washed with 5% aqueous NaOH (20 mL), brine (20 mL), dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. The product was then purified by silica gel chromatography to give the 3-iodo-3-buten-1-ol.

In an oven dried round bottom flask containing a solution Pd(PPh₃)₂Cl₂ (280.8 mg, 0.4 mmol) and CuI (266.6 mg, 1.4 mmol) in THF (15 mL) at room temperature, under an argon atmosphere was added 3-iodo-3-buten-1-ol (4.0 g, 20 mmol). Et₃N (13.9 mL, 100 mmol), was then added followed by phenyl acetylene (2.8 mL, 25 mmol), and the solution was stirred at room temperature for 3 h. Saturated aqueous NH₄Cl (10 mL) was then added and the solution extracted with ethyl acetate (3 x 10 mL), the organic fractions pooled, and washed with brine (20 mL), dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. The product was then purified by silica gel chromatography to give the 3-methylene-5-phenyl-4-pentyn-1-ol.[4a]

A round-bottom flask containing 3-methylene-5-phenyl-4-pentyn-1-ol (2.1 g, 12.0 mmol) in dichloromethane (15 mL) was immersed into an ice bath. Carbon tetrabromide (4.8 g, 14.4 mmol) and triphenylphosphine (3.8 g, 14.4 mmol) were added and the resultant mixture was stirred at room temperature for 12 h. Dichloromethane was removed under reduced pressure and the residue was purified through a thin plug of silica gel column eluted with petroleum ether to give alkyl bromide-tethered 1a as a light brown liquid.[4b]

![1a](image1)

(5-Bromo-3-methylenepent-1-yn-1-yl)benzene (1a). Flash column chromatography to afford product 1a as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.46-7.44 (m, 2H), 7.34-7.32 (m, 3H), 5.56 (s, 1H), 5.41 (s, 1H), 3.63 (t, J = 5Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 131.6, 128.4, 128.3(2), 128.2(6), 123.7, 122.8, 90.2, 88.0, 40.4, 30.6; HRMS (ESI) [M+H]⁺: calculated for C₁₂H₁₂Br: 235.0122, found:235.0115.

![1b](image2)

1-(5-Bromo-3-methylenepent-1-yn-1-yl)-4-fluorobenzene (1b). Flash column chromatography to afford product 1b as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.44-7.41 (m, 2H), 7.04-7.00 (m, 2H), 5.59-5.51 (m, 1H), 5.45-5.37 (m, 1H), 3.60 (t,
$J = 5 \text{ Hz}, 2\text{H}$, 2.80-2.77 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 162.5 (d, $J = 252$ Hz), 133.5 (d, $J = 8.2$ Hz), 128.1, 123.8, 118.9 (d, $J = 3.7$ Hz), 115.6 (d, $J = 22.2$ Hz), 89.1, 87.7, 40.3, 30.5; $^{19}$F NMR (471 MHz, CDCl$_3$) δ -110.5; HRMS (ESI) [M+H]$^+$: calculated for C$_{12}$H$_{11}$BrF: 253.0028, found 253.0024.

(5-Bromo-3-methylenepent-1-yn-1-yl)-4-(tert-butyl)benzene (1c). Flash column chromatography to afford product 1c as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39-7.33 (m, 4H), 5.54-5.53 (m, 1H), 5.39-5.38 (m, 1H), 3.61 (t, $J = 5$ Hz, 2H), 2.81-2.77 (m, 2H), 1.31 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 151.8, 131.4, 128.4, 125.4, 123.3, 119.8, 90.4, 87.4, 40.5, 34.8, 31.2, 30.7; HRMS (ESI) [M+H]$^+$: calculated for C$_{16}$H$_{20}$Br: 291.0748, found 291.0746.

2.2 General Procedure for the Preparation of Tosylate-Tethered 1,3-Enynes 10 and 13.

To a flask containing DCM (10 mL) was added homoallylic alcohol (2 mmol), Et$_3$N (0.33 mL, 2.4 mmol). The resulting mixture was cooled to 0 °C where after 4-toluenesulfonyl chloride (420 mg, 2.2 mmol) was added. The reaction mixture was then stirred at room temperature overnight. The mixture was extracted with ethyl acetate (3 x 10 mL), washed with water and brine, then dried over MgSO$_4$ and concentrated. The residue was purified by flash chromatography to afford the product tosylate-tethered 1,3-enyne.

3-Methylene-5-phenylpent-4-yn-1-yl 4-methylbenzenesulfonate (10). Flash column chromatography to afford product 10 as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.80-7.78 (m, 2H), 7.34-7.29 (m, 4H), 7.27-7.26 (m, 3H), 5.48-5.47 (m, 1H), 5.36-5.35 (m, 1H), 4.26 (t, $J = 5.0$ Hz, 2H), 2.60-2.57 (m, 2H), 2.35 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 144.7, 132.9, 131.5, 129.7, 128.4, 128.3, 127.9, 125.9, 124.3,
122.7, 90.2, 87.9, 68.1, 36.6, 21.5. These data are consistent with the published literature.[5]

But-3-en-1-yl 4-methylbenzenesulfonate (13a). Flash column chromatography to afford product 13a as a pale yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80-7.78 (m, 2H), 7.34 (d, $J = 5$ Hz, 2H), 5.71-5.63 (m, 1H), 5.10-5.05 (m, 2H), 4.06 (t, $J = 7.5$ Hz, 2H), 2.45 (s, 3H), 2.42-2.38 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.7, 133.1, 132.4, 129.8, 127.9, 118.2, 69.4, 33.1, 21.6. These data are consistent with the published literature.[4b]

Methylbut-3-en-1-yl 4-methylbenzenesulfonate (13b). Flash column chromatography to afford product 13b as a pale yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80-7.78 (m, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.79 (s, 1H), 4.67 (s, 1H), 4.13 (t, $J = 6.9$ Hz, 2H), 2.45 (s, 3H), 2.37-2.34 (m, 2H), 1.66 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.7, 140.1, 133.1, 129.8, 127.9, 113.1, 68.5, 36.7, 22.3, 21.6. These data are consistent with the published literature.[4b]

2.3 General Procedure for the Preparation of Oximes 8

In a three necked flask, (E)-3-benzylidene-5-phenylpent-4-yn-2-one (492 mg, 2.0 mmol) was dissolved in 10 mL absolute ethyl alcohol under nitrogen. Potassium carbonate (552 mg, 4.0 mmol) and methoxylamine hydrochloride (334 mg, 4.0 mmol) was added to the solution. The resulting mixture was stirred for 12 h. Then the mixture was quenched by HCl (1.0 M) and the aqueous layer was extracted by ethyl acetate (3×10 mL). The combined organic layer was washed with brine (20 mL), dried by anhydrous sodium sulfate. After filtration and concentration in vacuo, the residue was purified by column chromatography on silica gel to afford the corresponding oxime product 8a.[6]
3-(Benzyldiene)-5-phenylpent-4-yn-2-one O-methyl oxime (8a). Flash column chromatography to afford product 8a as a red brown oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99-7.97 (m, 2H), 7.52-7.50 (m, 2H), 7.41-7.31 (m, 6H), 7.21 (s, 1H), 4.02 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.3, 136.3, 135.9, 131.5, 129.6, 128.9, 128.5, 128.4, 128.2, 123.2, 118.6, 97.3, 86.6, 62.0, 12.6; These data are consistent with the published literature.[6]

2-(Phenylethynyl)cyclohex-2-en-1-one O-methyl oxime (8b). Flash column chromatography to afford product 8b as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51-7.49 (m, 2H), 7.31-7.29 (m, 3H), 6.69 (t, $J = 7.5$ Hz, 1H), 3.98 (s, 3H), 2.63-2.60 (m, 2H), 2.32-2.28 (m, 2H), 1.79-1.74 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 153.8, 142.8, 131.7, 128.1, 128.0, 123.5, 119.3, 90.4, 85.5, 62.0, 25.7, 22.8, 20.4. These data are consistent with the published literature.[6]

## 3 General Procedure of Cyclopropanation Reactions

### 3.1 General Procedure for Cyclopropanation of Alkyl Bromide-Tethered 1,3-Enynes with Alkyl Silicates

To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $\text{Ir[}dF(CF}_3\text{ppy)}_2(\text{dtbbpy})\text{PF}_6$ (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-crown-6] bis(catecholato)-alkylsilicate 2 (0.40 mmol, 2.0 equiv), the arylethynyl-substituted homoallylic bromide 1 (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After the
reaction was complete, the reaction solution was diluted with saturated organic layer was washed with brine, dried over MgSO$_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product 4.

\[
\text{Ph} \quad \equiv \quad \text{4a}
\]

((1-Heptylcyclopropyl)ethynyl)benzene (4a). Flash column chromatography to afford product 4a as a colorless oil (31.2 mg, 65% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39-7.38 (m, 2H), 7.27-7.25 (m, 3H), 1.63-1.61 (m, 2H), 1.44-1.40 (m, 2H), 1.36-1.29 (m, 8H), 1.00-0.97 (m, 2H), 0.91-0.89 (m, 3H), 0.68-0.66 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 131.6, 128.1, 127.3, 124.1, 95.4, 76.7, 38.3, 31.9, 29.5, 29.4, 27.9, 22.7, 15.7, 14.1, 12.5; HRMS (ESI) [M+H]$^+$: calculated for C$_{18}$H$_{25}$: 241.1953, found 241.1956.

\[
\text{Ph} \quad \equiv \quad \text{4b}
\]

((1-Propylcyclopropyl)ethynyl)benzene (4b). Flash column chromatography to afford product 4b as a colorless oil (18.4 mg, 54% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38-7.36 (m, 2H), 7.28-7.24 (m, 3H), 1.67-1.63 (m, 2H), 1.41-1.37 (m, 2H), 0.99-0.96 (m, 5H), 0.68-0.65 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 131.6, 128.1, 127.3, 124.1, 95.3, 76.7, 40.4, 21.1, 15.6, 14.0, 12.3; HRMS (ESI) [M+H]$^+$: calculated for C$_{13}$H$_{15}$: 171.1174, found 171.1174.

\[
\text{Ph} \quad \equiv \quad \text{4c}
\]

((1-Hexylcyclopropyl)ethynyl)benzene (4c). Flash column chromatography to afford product 4c as a pale yellow oil (30.7 mg, 68 %yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39-7.37 (m, 2H), 7.28-7.24 (m, 3H), 1.65-1.58 (m, 2H), 1.38-1.26 (m, 8H), 0.99-0.97 (m, 2H), 0.91-0.88 (m, 3H), 0.67-0.65 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 131.6, 128.1, 127.3, 124.1, 95.3, 76.7, 38.3, 31.9, 29.1, 27.9, 22.7, 15.6, 14.1, 12.5. These data are consistent with the published literature.$^7$

\[
\text{Ph} \quad \equiv \quad \text{4d}
\]

((1-Isopentylcyclopropyl)ethynyl)benzene (4d). Flash column chromatography to afford product 4d as a colorless oil (22.0 mg, 52% yield). $^1$H NMR (500 MHz, CDCl$_3$)
δ 7.42-7.40 (m, 2H), 7.31-7.27 (m, 3H), 1.67-1.61 (m, 1H), 1.58-1.52 (m, 2H), 1.46-1.41 (m, 2H), 1.02-1.00 (m, 2H), 0.94 (d, J = 10 Hz, 6H), 0.70-0.68 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 131.6, 128.1, 127.3, 124.1, 95.3, 76.7, 37.0, 36.1, 27.8, 22.7, 15.6, 12.6; HRMS (ESI) [M+H]+: calculated for C16H21: 213.1643, found 213.1638.

4-(1-(Phenylethynyl)cyclopropyl)butanenitrile (4e). Flash column chromatography to afford product 4e as a pale yellow oil (25.1 mg, 60% yield). 1H NMR (500 MHz, CDCl3) δ 7.37-7.35 (m, 2H), 7.28-7.26 (m, 3H), 2.50 (t, J = 7.5 Hz, 2H), 2.05-1.99 (m, 2H), 1.61-1.57 (m, 2H), 1.06-1.03 (m, 2H), 0.74-0.72 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 131.6, 128.2, 127.7, 123.5, 119.7, 93.5, 77.7, 36.6, 24.0, 16.7, 15.6, 11.5; HRMS (ESI) [M+H]+: calculated for C15H16N: 210.1283, found 210.1280.

((1-(4-Chlorobutyl)cyclopropyl)ethynyl)benzene (4f). Flash column chromatography to afford product 4f as a colorless oil (25.5 mg, 55% yield). 1H NMR (500 MHz, CDCl3) δ 7.38-7.36 (m, 2H), 7.28-7.25 (m, 3H), 3.57 (t, J = 7.5 Hz 2H), 1.90-1.84 (m, 2H), 1.81-1.75 (m, 2H), 1.47-1.44 (m, 2H), 1.01-0.99 (m, 2H), 0.69-0.67 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 131.6, 128.2, 127.5, 123.9, 94.7, 77.3, 45.1, 37.5, 32.4, 25.4, 15.7, 12.3; HRMS (ESI) [M+H]+: calculated for C15H16Cl: 233.1092, found 223.1097.

((1-(4,4,4-Trifluorobutyl)cyclopropyl)ethynyl)benzene (4g). Flash column chromatography to afford product 4g as a colorless oil (35.3 mg, 70% yield). 1H NMR (500 MHz, CDCl3) δ 7.39-7.36 (m, 2H), 7.30-7.25 (m, 3H), 2.24-2.15 (m, 2H), 1.95-1.89 (m, 2H), 1.50 (t, J = 7.5 Hz 2H), 1.04-1.02 (m, 2H), 0.70-0.68 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 131.6, 128.2, 127.6, 127.2 (q, J = 277.2 Hz), 123.7, 93.9, 77.45, 37.0, 33.3 (q, J = 13.9 Hz), 20.5 (q, J = 1.3 Hz), 15.7, 12.0; 19F NMR (471 MHz, CDCl3) δ -66.3; HRMS (ESI) [M+H]+: calculated for C15H16F3: 253.1204, found 253.1196.
N-(2-(1-(phenylethynyl)cyclopropyl)ethyl)aniline (4h). Flash column chromatography to afford product 4h as a brown oil (33.9 mg, 65% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.40-7.38 (m, 2H), 7.30-7.27 (m, 3H), 7.20-7.17 (m, 2H), 6.70 (t, $J$ = 5 Hz, 1H), 6.66-6.64 (m, 2H), 3.99 (br, 1H), 3.48 (t, $J$ = 7.5 Hz, 2H), 1.75 (t, $J$ = 5 Hz, 2H), 1.07-1.04 (m, 2H), 0.75-0.73 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 148.2, 131.6, 129.3, 128.2, 127.6, 123.6, 117.3, 112.9, 94.2, 77.6, 42.7, 37.3, 15.6, 10.6; HRMS (ESI) [M+H]$^+$: calculated for C$_{19}$H$_{20}$N: 262.1596, found 262.1602.

((1-(2-Methoxyethyl)cyclopropyl)ethynyl)benzene (4i). Flash column chromatography to afford product 4i as a colorless oil (34.0 mg, 74% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38-7.36 (m, 2H), 7.28-7.25 (m, 3H), 3.68 (t, $J$ = 7.5 Hz, 2H), 3.38 (s, 3H), 1.72 (t, $J$ = 7.5 Hz, 2H), 1.07-1.00 (m, 2H), 0.75-0.73 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 131.6, 131.6, 128.1, 127.5, 123.8, 94.3, 71.4, 58.8, 37.8, 15.4, 9.7; HRMS (ESI) [M+Na]$^+$: calculated for C$_{14}$H$_{16}$ONa: 223.1096, found 223.1099.

1-(1-(Phenylethynyl)cyclopropyl)ethyl acetate (4j). Flash column chromatography to afford product 4j as a pale yellow oil (32.8 mg, 72% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39-7.37 (m, 2H), 7.29-7.26 (m, 3H), 4.38 (t, $J$ = 7.5 Hz, 2H), 2.07 (s, 3H), 1.79 (t, $J$ = 7.5 Hz, 2H), 1.06-1.04 (m, 2H), 0.78-0.75 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.1, 131.6, 128.2, 127.6, 123.6, 93.6, 77.4, 63.3, 36.9, 21.1, 15.3, 9.7; HRMS (ESI) [M+H]$^+$: calculated for C$_{15}$H$_{17}$O$_2$: 229.1229, found 229.1210.

((1-Phenethylcyclopropyl)ethynyl)benzene (4k). Flash column chromatography to afford product 4k as a pale yellow oil (24.6 mg, 50% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.33-7.30 (m, 2H), 7.21-7.14 (m, 7H), 7.11-7.08 (m, 1H), 2.88-2.85 (m, 2H), 1.66-1.62 (m, 2H), 0.91-0.89 (m, 2H), 0.55-0.53 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.2, 131.7, 128.6, 128.3, 128.2, 127.5, 125.8, 124.0, 94.7, 77.4, 40.4, 34.3, 15.7, 12.4; HRMS (ESI) [M+H]$^+$: calculated for C$_{19}$H$_{19}$: 247.1481, found 247.1485.
((1-(Cyclohexylmethyl)cyclopropyl)ethynyl)benzene (4l). Flash column chromatography to afford product 4l as a colorless oil (37.6 mg, 79% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.39-7.37 (m, 2H), 7.29-7.25 (m, 3H), 1.97-1.93 (m, 2H), 1.83-1.66 (m, 4H), 1.35-1.27 (m, 4H), 1.21-1.13 (m, 1H), 1.04-0.90 (m, 4H), 0.67 (q, $J$ = 5 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 131.5, 128.1, 127.2, 124.2, 95.5, 76.6, 45.5, 37.2, 33.5, 26.7, 26.4, 16.0, 10.7; HRMS (ESI) [M+H]$^+$: calculated for C$_{18}$H$_{23}$: 239.1800, found 239.1791.

1-Fluoro-4-((1-(2-methoxyethyl)cyclopropyl)ethynyl)benzene (4m). Flash column chromatography to afford product 4m as a colorless oil (29.6 mg, 68% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35-7.32 (m, 2H), 6.97-6.94 (m, 2H), 3.66 (t, $J$ = 7.5 Hz, 2H), 3.38 (s, 3H), 1.71 (t, $J$ = 7.5 Hz, 2H), 1.00-0.98 (m, 2H), 0.75-0.73 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 162.0 (d, $J$ = 248.6 Hz), 133.3 (d, $J$ = 8.2 Hz), 119.9 (d, $J$ = 3.5 Hz), 115.3 (d, $J$ = 21.9 Hz), 93.9, 75.9, 71.4, 58.7, 37.8, 15.3, 9.6; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -112.3; HRMS (ESI) [M+H]$^+$: calculated for C$_{14}$H$_{16}$FO: 219.1185, found 219.1180.

1-(Tert-butyl)-4-((1-(2-methoxyethyl)cyclopropyl)ethynyl)benzene 4n. Flash column chromatography to afford product 4n as a colorless oil (30.7 mg, 60% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32-7.26 (m, 4H), 3.68 (t, $J$ = 7.5 Hz, 2H), 3.38 (s, 3H), 1.72 (t, $J$ = 7.5 Hz, 2H), 1.30 (s, 9H), 1.01-0.98 (m, 2H), 0.74-0.72 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.6, 131.3, 125.1, 120.8, 93.4, 77.0, 71.5, 58.7, 37.9, 34.6, 31.2, 15.4, 9.7; HRMS (ESI) [M+H]$^+$: calculated for C$_{18}$H$_{25}$O: 257.1905, found 257.1901.

3.2 General Procedure for the Cyclopropanation of 2-(1-Alkynyl)-2-2-Alken-1-Ones and Oximes
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-crown-6] bis(catecholato)chloromethylsilicate 6 (238.6 mg, 0.4 mmol, 2.0 equiv), the (5-bromo-3-methylenepent-1-yn-1-yl)benzene 5 (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated organic layer was washed with brine, dried over MgSO₄, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product (+/-)-7.

(1R*,6S*)-1-(Phenylethynyl)bicyclo[4.1.0]heptan-2-one (7a). Flash column chromatography to afford product 7a as a pale yellow oil (31.1 mg, 74% yield). ^1H NMR (500 MHz, CDCl₃) δ 7.44-7.41 (m, 2H), 7.28-7.25 (m, 3H), 2.43-2.37 (m, 1H), 2.22-2.17 (m, 2H), 2.12-1.99 (m, 2H), 1.81-1.75 (m, 2H), 1.71-1.62 (m, 2H); ^13C NMR (126 MHz, CDCl₃) δ 203.8, 131.8, 128.0, 127.8, 123.1, 89.2, 79.7, 36.3, 29.4, 27.0, 21.3, 21.2, 18.2. These data are consistent with the published literature.[8]

(1R*,6S*)-1-((4-Ethylphenyl)ethynyl)bicyclo[4.1.0]heptan-2-one (7b). Flash column chromatography to afford product 7b as a pale yellow oil (35.7 mg, 75% yield). ^1H NMR (500 MHz, CDCl₃) δ 7.34-7.33 (m, 2H), 7.10-7.08 (m, 2H), 2.61 (q, J = 7.5 Hz, 2H), 2.41-2.35 (m, 1H), 2.22-2.15 (m, 2H), 2.11-1.98 (m, 2H), 1.76-1.73 (m, 2H), 1.68-1.60 (m, 2H), 1.20 (t, J = 7.5 Hz, 3H); ^13C NMR (126 MHz, CDCl₃) δ 203.9, 144.2, 131.8, 127.6, 120.3, 88.4, 79.8, 36.3, 29.4, 28.7, 27.0, 21.3, 21.2, 18.3, 15.3; HRMS (ESI) [M+H]^+; calculated for C₁₇H₁₉O: 239.1436, found 239.1439.
(1R\textsuperscript{\textastripedright},6S\textsuperscript{\textastripedright})-1-((4-Fluorophenyl)ethynyl)bicyclo[4.1.0]heptan-2-one (7c). Flash column chromatography to afford product 7c as a pale yellow oil (36.5 mg, 80% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.41-7.37 (m, 2H), 6.98-6.93 (m, 2H), 2.42-2.36 (m, 1H), 2.23-2.16 (m, 2H), 2.11-1.98 (m, 2H), 1.79-1.74 (m, 2H), 1.70-1.60 (m, 3H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 203.8, 162.2 (d, \textit{J} = 249.2 Hz), 133.7 (d, \textit{J} = 8.4 Hz), 119.2 (d, \textit{J} = 3.5 Hz), 115.3 (d, \textit{J} = 21.9 Hz), 88.8, 78.7, 36.3, 29.4, 26.9, 21.3, 21.2, 18.3; \textsuperscript{19}F NMR (471 MHz, CDCl\textsubscript{3}) δ -111.61; HRMS (ESI) [M+H]\textsuperscript{+}: calculated for C\textsubscript{15}H\textsubscript{14}FO: 229.1029, found 229.1029.

(1R\textsuperscript{\textastripedright},6S\textsuperscript{\textastripedright})-1-((Trimethylsilyl)ethynyl)bicyclo[4.1.0]heptan-2-one (7d). Flash column chromatography to afford product 7d as a colorless oil (30.5 mg, 74% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 2.35-2.30 (m, 1H), 2.17-2.10 (m, 2H), 2.07-1.93 (m, 2H), 1.75-1.71 (m, 1H), 1.66-1.63 (m, 2H), 1.54-1.51 (m, 1H), 0.15 (s, 9H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 203.4, 105.5, 84.0, 36.3, 29.4, 27.1, 21.3, 21.2, 18.2, 0.1. These data are consistent with the published literature.\textsuperscript{[8]}

(1R\textsuperscript{\textastripedright},6S\textsuperscript{\textastripedright})-1-(3,3-Dimethylbut-1-yn-1-yl)bicyclo[4.1.0]heptan-2-one (7e). Flash column chromatography to afford product 7e as a pale yellow oil (24.7 mg, 65% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 2.33-2.28 (m, 1H), 2.15-2.08 (m, 1H), 2.05-1.89 (m, 3H), 1.73-1.67 (m, 2H), 1.63-1.56 (m, 1H), 1.42-1.39 (m, 1H), 1.19 (s, 9H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 204.5, 88.3, 78.0, 36.3, 31.2, 29.1, 27.3, 26.5, 21.2, 21.1, 18.3; HRMS (ESI) [M+H]\textsuperscript{+}: calculated for C\textsubscript{13}H\textsubscript{19}O: 191.1436, found 191.1428.
(1R*,6S*)-1-(Hex-1-yn-1-yl)bicyclo[4.1.0]heptan-2-one (7f). Flash column chromatography to afford product 7f as a pale yellow oil (27.8 mg, 73% yield).  \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.35-2.30 (m, 1H), 2.19 (t, \(J = 7.5\) Hz, 2H), 2.17-2.09 (m, 1H), 2.06-1.90 (m, 3H), 1.74-1.67 (m, 1H), 1.65-1.56 (m, 2H), 1.49-1.42 (m, 3H), 1.41-1.32 (m, 2H), 0.88 (t, \(J = 7.5\) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 204.9, 80.3, 79.4, 36.2, 31.0, 29.1, 26.8, 22.0, 21.2, 21.0, 18.6, 18.4, 13.7. These data are consistent with the published literature.\(^8\)

![7g](image)

(1R*,6S*)-1-(Cyclopropylethynyl)bicyclo[4.1.0]heptan-2-one (7g). Flash column chromatography to afford product 7g as a pale yellow oil (27.8 mg, 72% yield).  \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.34-2.28 (m, 1H), 2.15-2.08 (m, 1H), 2.02-1.90 (m, 2H), 1.73-1.68 (m, 1H), 1.63-1.55 (m, 2H), 1.43-1.41 (m, 1H), 1.26-1.21 (m, 1H), 0.72-0.67 (m, 2H), 0.66-0.62 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 204.7, 83.2, 74.8, 36.2, 29.0, 26.6, 21.2, 20.9, 18.3, 8.3, 8.2. These data are consistent with the published literature.\(^8\)

![7h](image)

(1R*,6R*)-1-(3,3-Dimethylbut-1-yn-1-yl)-5,5-dimethylbicyclo[4.1.0]heptan-2-one (7h). Flash column chromatography to afford product 7h as a colorless oil (33.5 mg, 77% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.26-2.23 (m, 2H), 1.78-1.74 (m, 1H), 1.62-1.59 (m, 1H), 1.52-1.45 (m, 1H), 1.40-1.36 (m, 2H), 1.19 (s, 9H), 1.16 (s, 3H), 1.09 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 204.6, 88.5, 77.8, 41.3, 32.8, 31.2, 31.0, 29.6, 29.2, 27.4, 27.3, 26.9, 21.2; HRMS (ESI) [M+H]\(^+\): calculated for C\(_{15}\)H\(_{23}\)O: 219.1749, found 219.1752.

![7i](image)

(1R*,5S*)-1-(Phenylethynyl)bicyclo[3.1.0]hexan-2-one (7i). Flash column chromatography to afford product 7i as a pale yellow oil (20.8 mg, 53% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.42 (m, 2H), 7.29-7.26 (m, 3H), 2.57-2.53 (m, 1H), 2.29-2.23 (m, 1H), 2.22-2.19 (m, 2H), 2.05-2.00 (m, 1H), 1.75-1.72 (m, 1H), 1.52-1.50 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 209.4, 131.9, 128.1, 128.1, 123.0, 85.3,
82.0, 32.4, 31.4, 29.0, 23.7, 21.6; HRMS (ESI) [M+H]+: calculated for C_{14}H_{13}O: 197.0966, found 197.0970.

1-(2-Phenyl-1-(phenylethynyl)cyclopropyl)ethan-1-one O-methyl oxime (9a).
Flash column chromatography to afford product 9a as a pale yellow oil (46.2 mg, 80% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.32 (m, 4H), 7.29-7.26 (m, 1H), 7.22-7.17 (m, 3H), 7.11-7.08 (m, 2H), 3.88 (s, 3H), 2.71-2.67 (m, 1H), 2.18-2.15 (m, 1H), 2.14 (s, 3H), 1.69-1.67 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 155.9, 137.2, 131.4, 128.5, 128.0, 127.8, 127.6, 126.6, 123.3, 88.6, 82.2, 61.6, 34.3, 26.5, 20.9, 13.9. These data are consistent with the published literature.[8]

(1R*,6S*)-1-(Phenylethynyl)bicyclo[4.1.0]heptan-2-one O-methyl oxime (9b).
Flash column chromatography to afford product 9b as a pale yellow oil (40.6 mg, 85% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.42 (m, 2H), 7.28-7.25 (m, 3H), 3.92 (s, 3H), 2.64-2.59 (m, 1H), 2.15-2.08 (m, 1H), 1.95-1.89 (m, 3H), 1.62-1.58 (m, 1H), 1.46-1.43 (m, 1H), 1.34-1.26 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 156.6, 131.8, 128.0, 127.5, 123.8, 92.3, 77.9, 61.6, 25.5, 22.1, 21.3, 19.3, 16.4, 16.1. These data are consistent with the published literature.[8]

3.3 General Procedure for the Cyclopropanation Enabled by Nickel Catalysis

To an oven-dried Schlenk tube was charged with 3-methylene-5-phenylpent-4-yn-1-yl 4-methylbenzenesulphonate 10 (64 mg, 0.2 mmol), NHP ester 11 (0.5 mmol, 2.5 equiv), Ni(BF\(_4\))\(_2\)-6H\(_2\)O (3.4 mg, 5 mol%), Zn (26 mg, 0.4 mmol, 2.0 equiv) in DMSO (4 mL). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times. The reaction mixture was allowed to stir at room temperature for 24 h, 3 mL of H\(_2\)O and 3 mL saturate NH\(_4\)Cl solution was added to quench the reaction and
the mixture was extracted by ethyl acetate. The combined organic layer was dried over MgSO₄. After filtration and concentration, the residue was purified by column chromatography on silica gel to give product 12.

**(1-Neopentylcyclopropyl)ethynyl)benzene (12a).** Flash column chromatography to afford product 12a as a pale yellow oil (33.1 mg, 78% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.35 (m, 2H), 7.29-7.25 (m, 3H), 1.41 (s, 2H), 1.12 (s, 9H), 1.04-1.01 (m, 2H), 0.74-0.72 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 131.2, 128.1, 127.2, 124.3, 96.9, 76.4, 51.1, 32.7, 30.4, 16.9, 9.7; HRMS (ESI) [M+H]⁺: calculated for C₁₆H₂₁: 213.1643, found 213.1637.

**(1-(2,2-Dimethylbutyl)cyclopropyl)ethynyl)benzene (12b).** Flash column chromatography to afford product 12b as a pale yellow oil (31.2 mg, 69% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.35 (m, 2H), 7.29-7.25 (m, 3H), 1.47 (q, J = 7.5 Hz, 2H), 1.40 (s, 2H), 1.07 (s, 6H), 1.02 (q, J = 5 Hz, 2H), 0.89 (t, J = 7.5 Hz, 3H), 0.74-0.72 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 131.2, 128.1, 127.2, 124.3, 97.0, 76.2, 48.6, 35.1, 35.1, 27.3, 17.1, 9.4, 8.5; HRMS (ESI) [M+H]⁺: calculated for C₁₇H₂₃: 227.1800, found 227.1794.

**(1-(3-Methoxy-2,2-dimethylpropyl)cyclopropyl)ethynyl)benzene (12c).** Flash column chromatography to afford product 12c as a pale yellow oil (31.9 mg, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.35 (m, 2H), 7.29-7.25 (m, 3H), 3.35 (s, 3H), 3.27 (s, 2H), 1.48 (s, 2H), 1.12 (s, 6H), 1.01 (q, J = 5 Hz, 2H), 0.76 (q, J = 5 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 131.3, 128.1, 127.2, 124.3, 97.0, 81.7, 76.2, 59.0, 46.0, 36.5, 25.5, 16.9, 9.1; HRMS (ESI) [M+Na]⁺: calculated for C₁₆H₂₀ONa: 251.1412, found 251.1409.
2,2-Dimethyl-3-(1-(phenylethynyl)cyclopropyl)propyl acetate (12d). Flash column chromatography to afford product 12d as a pale yellow oil (28.1 mg, 52% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.35-7.33 (m, 2H), 7.28-7.23 (m, 3H), 4.03 (s, 2H), 2.06 (s, 3H), 1.13 (s, 6H), 1.03 (q, \(J = 5\) Hz, 2H), 0.72 (q, \(J = 5\) Hz, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 171.2, 131.3, 128.1, 127.4, 123.9, 96.0, 76.6, 72.4, 46.2, 35.7, 25.2, 21.0, 16.9, 9.0; HRMS (ESI) [M+Na]^+: calculated for C\(_{18}\)H\(_{22}\)O\(_2\)Na: 293.1517, found 293.1514.

(2,2-Dimethyl-3-(1-(phenylethynyl)cyclopropyl)propyl)benzene (12e). Flash column chromatography to afford product 12e as a pale yellow oil (31.8 mg, 58% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.36-7.34 (m, 2H), 7.29-7.20 (m, 8H), 2.76 (s, 2H), 1.44 (s, 2H), 1.09 (s, 6H), 1.05-1.03 (m, 2H), 0.73-0.71 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 139.4, 131.2, 130.9, 128.2, 127.6, 127.3, 125.7, 124.2, 96.9, 76.8, 49.2, 49.1, 36.3, 27.5, 17.3, 9.4; HRMS (ESI) [M+Na]^+: calculated for C\(_{21}\)H\(_{22}\)Na: 297.1619, found 297.1625.

1-((1-(Pheny lethynyl)cyclopropyl)methyl)adamantane (12f). Flash column chromatography to afford product 12f as a pale yellow oil (29 mg, 55% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.35-7.33 (m, 2H), 7.28-7.23 (m, 3H), 1.98-1.96 (m, 3H), 1.77 (d, \(J = 3\) Hz, 6H), 1.73-1.69 (m, 6H), 1.26 (s, 2H), 0.98 (q, \(J = 5\) Hz, 2H), 0.70-0.68 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 131.2, 128.1, 127.2, 124.4, 97.4, 76.2, 52.3, 43.2, 37.2, 34.7, 28.8, 16.9, 8.5; HRMS (ESI) [M+H]^+: calculated for C\(_{22}\)H\(_{27}\): 291.2113, found 291.2115.

4 Further Transformation

To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Cu(O Tf)\(_2\) (7.5 mg, 10 mol%), to a solution of the (1R\(^*\), 6S\(^*\))-1-(phenylethynyl)bicyclo[4.1.0]heptan-2-one (42.2 mg, 0.2 mmol) in dry CH\(_2\)Cl\(_2\) (5 mL) was added sodium MeOH (40 \(\mu\)L, 0.4 mmol, 2.0 equiv) was added. The resulting mixture was stirred for 20 h. After concentration in vacuo, the residue was purified by column chromatography on silica gel to afford the furan product 15.[8]
5-Methoxy-2-phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan (15). Flash column chromatography to afford product 15 as pale yellow oil (41.4 mg, 85% yield). 

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61-7.59 (m, 2H), 7.36-7.33 (m, 2H), 7.22-7.19 (m, 1H), 6.46 (s, 1H), 3.40 (s, 3H), 3.36-3.31 (m, 1H), 2.90-2.85 (m, 2H), 2.78-2.71 (m, 1H), 2.62-2.57 (m, 1H), 2.23-2.18 (m, 1H), 2.01-1.96 (m, 1H), 1.78-1.58 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 153.1, 150.2, 131.0, 128.5, 126.6, 123.1, 116.6, 108.9, 79.7, 56.1, 35.7, 31.1, 28.3, 22.7. These data are consistent with the published literature.\cite{8}
5 References


6. M. Zhang and J. Zhang, Gold(I)-Catalyzed Cyclization of 2-(1-Alkynyl)-alk-2-en-1-one Oximes: A Facile Access to Highly Substituted N-Alkoxypyrroles,


6 NMR Spectra of New Compounds