Cobalt-Catalyzed Intramolecular [2+2+2] Cocyclotrimerization of Nitrilediynes: an Efficient Route to Tetra- and Pentacyclic Pyridine Derivatives

Hong-Tai Chang, Masilamani Jeganmohan and Chien-Hong Cheng*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

chcheng@mx.nthu.edu.tw

Supporting Information

Table of Contents

1. Procedure for the Preparation and the Spectral Data of Compounds 1a-s	S1-S16
2. General Experimental Procedure for the Intramolecular [2+2+2] Cocyclotrimerization of Nitrilediynes and Spectral Data of Compounds 2a-s	S17-S26
3. ¹ H NMR Spectra of Compounds 1a-s and ¹ H and ¹³ C NMR Spectra of Compounds 2a-s	S27-S54

Experimental Section

Procedure for the Preparation and Spectral Data of Compounds 1a-s.

Procedure for the Preparation of Compounds 1a-c.

A 50 mL round-bottomed side-arm flask containing Pd(PPh₃)₄ (0.015 mmol), CuI (0.030 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added 1,6-heptadiyne (**S1a**) (3.00 mmol), 2-(2-iodophenyl)acetonitrile (**S2a**) (6.00 mmol), diethylamine (9.00 mmol) and THF (20.0 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 6 h. Then, the reaction mixture was poured into a saturated aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure 1,7-bis(2-cyanomethylbenzene)hepta-1,6-diyne **1a** in 79% yield. Starting materials **1b-c** were synthesized according to similar procedure by using dipropargyl ether (**S1b**) for **1b** and *N*-(prop-2-ynyl)-*N*-tosylprop-2-yn-1-amine¹ (**S1c**) for **1c** as diyne reagents, respectively. Products **1b** and **1c** were prepared in 85 and 87% yields, respectively. Compounds **1a-c** was confirmed by ¹H NMR spectroscopy.

2,2'-(Hepta-1,6-diyne-1,7-diyl-di-2,1-phenylene)diacetonitrile (**1a**).

Brown solid; $R_f = 0.30$ (20% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.43 (t, $J = 7.2$ Hz, 2 H), 7.42 (t, $J = 7.6$ Hz, 2 H), 7.32 - 7.26 (m, 4 H), 3.86 (s, 4 H), 2.66 (t, $J = 6.8$ Hz, 4 H), 1.96 (quintet, $J = 7.2$ Hz, 2 H).

2,2'-[Oxybis(prop-1-yne-3,1-diyl-2,1-phenylene)]diacetonitrile (1b).

Yellow solid; $R_f = 0.35$ (20% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.49 (d, $J = 7.2$ Hz, 2 H), 7.45 (d, $J = 7.6$ Hz, 2 H), 7.38 (t, $J = 7.2$ Hz, 2 H), 7.31 (t, $J = 7.6$ Hz, 2 H), 4.59 (s, 4 H), 3.88 (s, 4 H).

***N,N*-Bis{3-[2-(cyanomethyl)phenyl]prop-2-yn-1-yl}-4-methylbenzenesulfonamide (1c).**

Pale yellow solid; $R_f = 0.30$ (25% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.78 (d, $J = 8.4$ Hz, 2 H), 7.39 (d, $J = 8.4$ Hz, 2 H), 7.34 (td, $J = 5.6, 4.0$ Hz, 2 H), 7.29 - 7.34 (m, 6 H), 4.51 (s, 4 H), 3.65 (s, 4 H), 2.33 (s, 3 H).

Procedure for the Preparation of Compounds **1d** and **1f**.

Step 1. A 50 mL round-bottomed side-arm flask containing Pd(PPh₃)₄ (0.015 mmol), CuI (0.030 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added 1,6-heptadiyne (**S1a**) (3.00 mmol), iodobenzene (**S2b**) (3.00 mmol), diethylamine (9.00 mmol) and THF (20.0 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 4 h. Then, the reaction mixture was poured into a saturated aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure 1-(hepta-1,6-diynyl)benzene (**S3a**) in 80% yield.

Step 2. A 50 mL round-bottomed side-arm flask containing Pd(PPh₃)₄ (0.010 mmol), CuI (0.020 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added 1-(hepta-1,6-diynyl)benzene (**S3a**) (2.00 mmol), 2-(2-iodophenyl)acetonitrile (**S2a**) (2.00 mmol), and diethylamine (10 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 4 h. Then, the reaction mixture poured into a saturated aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **1d** in 75% yield. Starting material **1f** was synthesized according to similar procedures by using 2-iodothiophene (**S2c**) as the

coupling partner instead of iodobenzene in step 1 giving **S3b** in 75% yield. In step 2, **S3b** was used instead of **S3a** giving **1f** in 72% yield. Compounds **1d** and **1f** were confirmed by ^1H NMR spectroscopy.

[2-(7-Phenylhepta-1,6-diyn-1-yl)phenyl]acetonitrile (1d).

Yellow oil; R_f = 0.40 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.43 (d, J = 8.0 Hz, 2 H), 7.38 (dd, J = 7.2, 3.6 Hz, 2 H), 7.31 - 7.26 (m, 5 H), 3.87 (s, 2 H), 2.65 (t, J = 7.2 Hz, 2 H), 2.59 (t, J = 7.2 Hz, 2 H), 1.92 (quintet, J = 7.2 Hz, 2 H).

2-2-[7-(2-Thienyl)-1,6-heptadiynyl]phenylacetonitrile (1f).

Brown oil; R_f = 0.45 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.43 (d, J = 8.0 Hz, 2 H), 7.31 - 7.24 (m, 2 H), 7.17 (d, J = 5.2 Hz, 1 H), 7.12 (d, J = 3.2 Hz, 1 H), 6.92 (t, J = 5.2 Hz, 1 H), 3.87 (s, 2 H), 2.63 (t, J = 7.6 Hz, 2H), 2.61 (t, J = 7.2 Hz, 2 H), 1.91 (quintet, J = 7.2 Hz, 2 H).

Procedure for the Preparation of Compounds **1e** and **1i**.

Step 1. A solution of 3-phenylprop-2-yn-1-ol (**S2d**) (10.00 mmol) in dry THF (50 mL) under a nitrogen atmosphere was treated with sodium hydride (12.0 mmol) at 0 °C and the resulting mixture was stirred at room temperature for 30 min. Then propargyl bromide (80% solution in toluene, 12.0 mmol) was added and the reaction mixture was stirred during 1.5 h at room temperature and poured into a saturated aqueous NaHCO₃ solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure 1-(3-(prop-2-ynyloxy)prop-1-ynyl)benzene (**S3c**) in 85% yield.

Step 2. A 50 mL round-bottomed side-arm flask containing Pd(PPh₃)₄ (0.010 mmol), CuI (0.020 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added 1-(3-(prop-2-ynyloxy)prop-1-ynyl)benzene (**S3c**) (2.00 mmol), 2-(2-iodophenyl)acetonitrile (**S2a**) (2.00 mmol), and diethylamine (10 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 4 h. Then, the reaction mixture was poured into a saturated aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **1e** in 88% yield. Starting material **1i** was synthesized according to similar procedure by using but-2-yn-1-ol (**S2e**) instead of **S2d** in

step 1 giving **S3d** in 80% yield. In step 2, **S3d** was used instead of **S3c** giving **1i** in 75% yield. Compounds **1e** and **1i** were confirmed by ^1H NMR spectroscopy.

(2-{3-[(3-Phenylprop-2-yn-1-yl)oxy]prop-1-yn-1-yl}phenyl)acetonitrile (1e).

Pale yellow oil; R_f = 0.40 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.48 (m, 4 H), 7.37 (t, J = 7.6 Hz, 1 H), 7.31 - 7.28 (m, 4 H), 4.58 (s, 2 H), 4.53 (s, 2 H), 3.90 (s, 2 H).

{2-[3-(But-2-yn-1-yloxy)prop-1-yn-1-yl]phenyl}acetonitrile (1i).

Brown oil; R_f = 0.40 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.49 - 7.46 (m, 2 H), 7.36 (t, J = 7.2 Hz, 1 H), 7.29 (t, J = 7.2 Hz, 1 H), 4.49 (s, 2 H), 4.26 (q, J = 2.4 Hz, 2 H), 3.89 (s, 2 H), 1.87 (t, J = 2.4 Hz, 3 H).

Procedure for the preparation of Compounds **1g and **1h**.**

Step 1. To a solution of 1,6-heptadiyne (**S1a**) (10.00 mmol) in THF (50 mL) cooled to -78 °C was added LHMDS (12.00 mmol of 1.6 M solution in THF). After stirring for 1 hr, TMS-Cl (12.00 mmol) was added and stirred for 2 hr. Saturated ammonium chloride was then added to the reaction, extracted with ether, dried over MgSO_4 , and the solvent removed in vacuo. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure (hepta-1,6-diynyl)trimethylsilane (**S3e**) in 74% yield.²

Step 2. A 50 mL round-bottomed side-arm flask containing $\text{Pd(PPh}_3)_4$ (0.010 mmol), CuI (0.020 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added (hepta-1,6-diynyl)trimethylsilane (**S3e**) (2.00 mmol), 2-(2-iodophenyl)acetonitrile (**S2a**) (2.00 mmol), and diethylamine (10 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 4 h. Then, the reaction mixture was poured into a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **1g** in 82% yield. Starting material **1h** was synthesized according to similar procedure by using dipropargyl ether (**S1b**) as a diyne reagent and TMS-Cl as the coupling partner in step 1 giving **S3f** in 85% yield. In step 2,

S3f was used instead of **S3e** giving **1h** in 80% yield. Compounds **1g** and **1h** were confirmed by ^1H NMR spectroscopy.

{2-[7-(Trimethylsilyl)hepta-1,6-diyn-1-yl]phenyl}acetonitrile (1g).

Pale yellow oil; R_f = 0.35 (5% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.47 - 7.44 (m, 2 H), 7.35 (t, J = 7.2 Hz, 1 H), 7.31 (t, J = 7.2 Hz, 1 H), 3.87 (s, 2 H), 2.62 (t, J = 7.6 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2 H), 1.90 (quintet, J = 7.2 Hz, 2 H), 0.16 (s, 9 H).

[2-(3-{[3-(Trimethylsilyl)prop-2-yn-1-yl]oxy}prop-1-yn-1-yl)phenyl]acetonitrile (1h).

Pale yellow oil; R_f = 0.30 (5% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.49 - 7.46 (m, 2 H), 7.37 (t, J = 7.2 Hz, 1 H), 7.30 (t, J = 7.2 Hz, 1 H), 4.49 (s, 2 H), 4.29 (s, 2 H), 3.89 (s, 2 H), 0.17 (s, 9 H).

Procedure for the Preparation of Compound 1j.

A 50 mL round-bottomed side-arm flask containing $\text{Pd(PPh}_3)_4$ (0.010 mmol), CuI (0.020 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added dimethyl 2,2-di(prop-2-ynyl)malonate³ (**S1d**) (2.00 mmol), 2-(2-

iodophenyl)acetonitrile (**S2a**) (2.00 mmol), and diethylamine (10.00 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 4 h. Then, the reaction mixture was poured into a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **1j** in 85% yield. Compound **1j** was confirmed by ^1H NMR spectroscopy.

Dimethyl {3-[2-(cyanomethyl)phenyl]prop-2-yn-1-yl}(prop-2-yn-1-yl)malonate (1j**).**

Pale yellow oil; $R_f = 0.30$ (35% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.42 (t, $J = 8.0$ Hz, 1 H), 7.33 (t, $J = 7.6$ Hz, 1 H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 6.4$ Hz, 1 H), 3.82 (s, 2 H), 3.87 (s, 6 H), 3.26 (s, 2 H), 3.02 (d, $J = 2.8$ Hz, 2 H), 2.06 (t, $J = 2.8$ Hz, 1 H).

Procedure for the Preparation of Compounds 1k-p.

S3a: X = CH_2 , R^3 = Ph

S3g: X = N-Ts, R^3 = SiMe_3

S3c: X = O, R^3 = Ph

S3b: X = CH_2 , R^3 = 2-thienyl

S3h: X = N-Ts, R^3 = Ph

S2f: $\text{R}^1 + \text{R}^2 = -\text{CH}_2-\text{CH}_2-$

S2g: $\text{R}^1 + \text{R}^2 = -(\text{CH}_2)_5-$

S2h: $\text{R}^1 = \text{R}^2 = \text{CH}_3$

1k: X = CH_2 , $\text{R}^1 + \text{R}^2 = -\text{CH}_2-\text{CH}_2-$, R^3 = Ph, 75%

1l: X = N-Ts, $\text{R}^1 + \text{R}^2 = -\text{CH}_2-\text{CH}_2-$, R^3 = SiMe_3 , 70%

1m: X = O, $\text{R}^1 + \text{R}^2 = -(\text{CH}_2)_5-$, R^3 = Ph, 72%

1n: X = N-Ts, $\text{R}^1 + \text{R}^2 = -(\text{CH}_2)_5-$, R^3 = SiMe_3 , 65%

1o: X = CH_2 , $\text{R}^1 + \text{R}^2 = -(\text{CH}_2)_5-$, R^3 = 2-thienyl, 70%

1p: X = N-Ts, $\text{R}^1 = \text{R}^2 = \text{CH}_3$, R^3 = Ph, 67%

A 50 mL round-bottomed side-arm flask containing $\text{Pd}(\text{PPh}_3)_4$ (0.010 mmol), CuI (0.020 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added 1-(hepta-1,6-diynyl)benzene (**S3a**) (2.00 mmol), 1-(2-

iodophenethyl)cyclopropane carbonitrile⁴ (**S2f**) (2.00 mmol), and diethylamine (10 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 6h. Then, the reaction mixture was poured into a saturated aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **1k** in 75% yield.

Starting materials **1l-p** was synthesized according to similar procedure. For compound **1l**, 3-(trimethylsilyl)-*N*-(prop-2-ynyl)-*N*-tosylprop-2-yn-1-amine (**S3g**)² as using a diyne reagent, for compound **1m**, 1-(3-(prop-2-ynyloxy)prop-1-ynyl)benzene (**S3c**) as using a diyne reagent and 1-(2-iodophenethyl)cyclohexanecarbonitrile⁴ (**S2g**) as using the coupling partner, for compound **1n**, 3-(trimethylsilyl)-*N*-(prop-2-ynyl)-*N*-tosylprop-2-yn-1-amine (**S3g**) as using a diyne reagent and 1-(2-iodophenethyl)cyclohexanecarbonitrile (**S2g**) as using the coupling partner, for compound **1o**, 2-(hepta-1,6-diynyl)thiophene (**S3b**) as using a diyne reagent and 1-(2-iodophenethyl)cyclohexanecarbonitrile (**S2g**) as using the coupling partner and for compound **1p**, 3-phenyl-*N*-(prop-2-ynyl)-*N*-tosylprop-2-yn-1-amine (**S3g**) as using a diyne reagent and 4-(2-iodophenyl)-2,2-dimethylbutanenitrile⁴ (**S2h**) as using the coupling partner. Products **1l-p** was observed in 70%, 72%, 65%, 70% and 67% yields. Compounds **1k-p** was confirmed by ¹H NMR spectroscopy.

1-[2-(7-Phenylhepta-1,6-diyn-1-yl)benzyl]cyclopropanecarbonitrile (1k).

Pale yellow oil; *R*_f = 0.30 (10% ethyl acetate in hexanes); ¹H NMR (400 MHz, CDCl₃); δ 7.45 - 7.36 (m, 3 H), 7.35 - 7.18 (m, 6 H), 3.05 (s, 2 H), 2.62 (t, *J* = 5.6 Hz, 2 H), 2.59 (t, *J* = 5.6 Hz, 2 H), 1.90 (quintet, *J* = 5.6 Hz, 2 H), 1.25 - 1.21 (m, 2 H), 1.02 - 0.99 (m, 2 H).

***N*-(3-{2-[(1-Cyanocyclopropyl)methyl]phenyl}prop-2-yn-1-yl)-4-methyl-*N*-[3-(trimethylsilyl)prop-2-yn-1-yl]benzenesulfonamide (1l).**

Yellow solid; R_f = 0.40 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.75 (d, J = 6.4 Hz, 2 H), 7.41 (d, J = 8.4 Hz, 1 H), 7.33 - 7.20 (m, 5 H), 4.37 (s, 2 H), 4.22 (s, 2 H), 2.92 (s, 2 H), 2.37 (s, 3 H), 1.27 - 1.23 (m, 2 H), 1.02 - 1.00 (m, 2 H), 0.04 (s, 9 H).

1-(2-{3-[(3-Phenylprop-2-yn-1-yl)oxy]prop-1-yn-1-yl}benzyl)cyclohexane-carbonitrile (1m).

Yellow oil; R_f = 0.20 (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.49 - 7.44 (m, 4 H), 7.33 - 7.26 (m, 4 H), 7.26 - 7.24 (m, 1 H), 4.59 (s, 2 H), 4.56 (s, 2 H), 3.09 (s, 2 H), 1.93 - 1.91 (m, 2 H), 1.72 - 1.69 (m, 4 H), 1.59 - 1.54 (m, 2 H), 1.47 - 1.40 (m, 2H).

***N*-(3-{2-[(1-Cyanocyclohexyl)methyl]phenyl}prop-2-yn-1-yl)-4-methyl-*N*-[3-(trimethylsilyl)prop-2-yn-1-yl]benzenesulfonamide (1n).**

Yellow solid; $R_f = 0.45$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.74 (d, $J = 8.4$ Hz, 2 H), 7.44 (d, $J = 8.4$ Hz, 1 H), 7.33 - 7.18 (m, 5 H), 4.37 (s, 2 H), 4.24 (s, 2 H), 2.96 (s, 2 H), 2.37 (s, 3 H), 1.88 - 1.85 (m, 2 H), 1.73-1.70 (m, 2 H), 1.42 - 1.39 (m, 2 H), 1.36 - 1.24 (m, 4 H), 0.05 (s, 9 H).

1-{2-[7-(2-Thienyl)hepta-1,6-diyn-1-yl]benzyl}cyclohexanecarbonitrile (1o).

Brown oil; $R_f = 0.35$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.39 (t, $J = 8.0$ Hz, 2 H), 7.26 (t, $J = 7.6$ Hz, 1 H), 7.20 - 7.16 (m, 2 H), 7.12 - 7.10 (m, 1 H), 6.93 (t, $J = 3.6$ Hz, 1 H), 3.07 (s, 2 H), 2.63 (t, $J = 4.0$ Hz, 2 H), 2.61 (t, $J = 3.6$ Hz, 2 H), 1.91 - 1.88 (m, 4 H), 1.71 - 1.68 (m, 4 H), 1.61 - 1.52 (m, 2 H), 1.45 - 1.39 (m, 2 H).

N-{3-[2-(2-Cyano-2-methylpropyl)phenyl]prop-2-yn-1-yl}-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1p).

Yellow solid; $R_f = 0.30$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.76 (d, $J = 8.4$ Hz, 2 H), 7.40 (d, $J = 7.6$ Hz, 2 H), 7.30 (t, $J = 7.2$ Hz, 2 H), 7.27 - 7.18 (m, 3 H), 7.15 - 7.13 (m, 4 H), 4.43 (s, 2 H), 4.42 (s, 2 H), 2.94 (s, 2 H), 2.30 (s, 3 H), 1.99 (s, 6 H).

Procedures for the Preparation of Compounds **1q** and **1r**.

A 50 mL round-bottomed side-arm flask containing $\text{Pd(PPh}_3)_4$ (0.010 mmol), CuI (0.020 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added 1-(3-(prop-2-ynyloxy)prop-1-ynyl)benzene (**S3c**) (2.00 mmol), 3-(2-iodophenyl)-2,2-dimethyl-3-oxopropanenitrile⁴ (**S2i**) (2.00 mmol), and diethylamine (10 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 6 h. Then, the reaction mixture was poured into a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **1q** in 85% yield. Starting material **1r** was synthesized according to similar procedure by using 1-(3-(prop-2-ynyloxy)prop-1-ynyl)naphthalene (**S3i**) as a diyne reagent giving **1r** in 77% yield. Compounds **1q** and **1r** were confirmed by ^1H NMR spectroscopy.

2,2-Dimethyl-3-oxo-3-(2-{3-[(3-phenylprop-2-yn-1-yl)oxy]prop-1-yn-1-yl}phenyl)propanenitrile (1q**).**

Yellow oil; $R_f = 0.35$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.56 (t, $J = 6.4$ Hz, 2 H), 7.45 - 7.41 (m, 4 H), 7.31 - 7.29 (m, 3 H), 4.52 (s, 4 H), 1.68 (s, 6 H).

2,2-Dimethyl-3-[2-(3-([3-(1-naphthyl)prop-2-yn-1-yl]oxy)prop-1-yn-1-yl)phenyl]-3-oxopropanenitrile (1r).

Yellow oil; $R_f = 0.30$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 8.30 (d, $J = 8.4$ Hz, 1 H), 7.83 - 7.82 (m, 2 H), 7.68 (d, $J = 6.8$ Hz, 1 H), 7.59 - 7.48 (m, 4 H), 7.47 - 7.39 (m, 3 H), 4.68 (s, 2 H), 4.60 (s, 2 H), 1.68 (s, 6 H).

Procedure for the Preparation of Compound 1s.

Step 1. A 50 mL round-bottomed side-arm flask containing $\text{Pd(PPh}_3)_4$ (0.020 mmol), CuI (0.040 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added octa-1,7-diyne (**S1e**) (4.00 mmol), iodobenzene (**S2b**) (4.00 mmol), diethylamine (12.00 mmol) and THF (20.0 ml) via syringes. The reaction mixture was allowed to stir at room temperature for 4 h. Then, the reaction mixture was poured into a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer

was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure 1-(octa-1,7-diynyl)benzene (**S3j**) in 74% yield.

Step 2. A 50 mL round-bottomed side-arm flask containing Pd(PPh₃)₄ (0.010 mmol), CuI (0.020 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added 1-(octa-1,7-diynyl)benzene (**S3j**) (2.00 mmol), 3-(2-iodophenyl)-2,2-dimethyl-3-oxopropanenitrile (**S2i**) (2.00 mmol),⁴ and diethylamine (10 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 6 h. Then, the reaction mixture was poured into a saturated aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **1s** in 75% yield. Compound **1s** was confirmed by ¹H NMR spectroscopy.

2,2-Dimethyl-3-oxo-3-[2-(8-phenylocta-1,7-diyn-1-yl)phenyl]propanenitrile (1s).

Yellow oil; R_f = 0.40 (10% ethyl acetate in hexanes); ¹H NMR (400 MHz, CDCl₃); δ 7.49 (d, *J* = 6.8 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.39 - 7.35 (m, 4 H), 7.33 - 7.25 (m, 3 H), 2.46 (t, *J* = 6.4 Hz, 2 H), 2.45 (t, *J* = 6.4 Hz, 2 H), 1.75-1.73 (m, 4 H), 1.65 (s, 6 H).

References:

1. Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 4763.
2. Trost, B. M.; Rudd, M. T.; Costa, M. G.; Lee, P. I.; Pomerantz, A. E. *Org. Lett.* **2004**, *6*, 4235.
3. Llerena, D.; Buisine, O.; Aubert, C.; Malacria, M. *Tetrahedron.* **1998**, *54*, 9373.
4. Pletnev, A. A.; Lorock, R. C. *J. Org. Chem.* **2002**, *67*, 9248.

General Experimental Procedure for the Intramolecular [2+2+2] Cocyclotrimerization of Nitrilediynes. A 25 mL round-bottomed side-arm flask containing $\text{CoI}_2(\text{dppe})$ (0.005 mmol), Zn (2.75 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added nitrilediyne (**1**) (1.00 mmol) and CH_3CN (3.0 mL) via syringes. The reaction mixture was allowed to stir at 80 °C for 12 h. At the end of the reaction, the reaction mixture was diluted with CH_2Cl_2 , filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **2**.

Spectral data and copy of ^1H and ^{13}C NMR spectra of all compounds are listed below.

[2-(1,2,3,6-Tetrahydrocyclopenta[*d*]indeno[2,1-*b*]pyridin-4-yl)phenyl]acetonitrile (2a).

Brown solid; $R_f = 0.20$ (25% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.77 (d, $J = 7.2$ Hz, 1 H), 7.59 (d, $J = 7.6$ Hz, 1 H), 7.57 (dd, $J = 8.0, 4.8$ Hz, 1 H), 7.44 - 7.34 (m, 5 H), 4.00 (s, 2 H), 3.81 (s, 2 H), 3.33 (t, $J = 7.6$ Hz, 2 H), 2.87 (t, $J = 7.6$ Hz, 2 H), 2.16 (quintet, $J = 7.6$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3); δ 162.1 (s), 151.1 (s), 147.8 (s), 141.8 (s), 139.6 (s), 139.5 (s), 137.7 (s), 130.9 (s), 129.6 (d), 129.3 (d), 128.7 (s), 128.7 (d), 127.9 (d), 127.3 (d), 127.1 (d), 125.2 (d), 122.5 (d), 118.0 (s), 38.7 (t), 31.7 (t), 31.1 (t), 25.0 (t), 21.8 (t); HRMS calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2$ 322.1470, found 322.1465.

[2-(3,6-Dihydro-1*H*-furo[3,4-*d*]indeno[2,1-*b*]pyridin-4-yl)phenyl]acetonitrile (2b).

Yellow solid; $R_f = 0.20$ (25% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.63 (d, $J = 7.2$ Hz, 1 H), 7.58 (d, $J = 6.8$ Hz, 1 H), 7.50 (d, $J = 6.8$ Hz, 1 H), 7.51 - 7.40 (m, 4 H), 7.37 (t, $J = 6.8$ Hz, 1 H), 5.49 (s, 2 H), 5.13 (s, 2 H), 4.07 (s, 2 H), 3.91 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3); δ 163.3 (s), 148.9 (s), 142.8 (s), 141.9 (s), 138.2 (s), 138.2 (s), 133.1 (s), 129.8 (d), 129.3 (d), 128.9 (d), 128.6 (s), 128.3 (d), 128.0 (d), 127.5 (d), 125.4 (d), 122.4 (d), 117.8 (s), 72.4 (t), 72.3 (t), 38.9 (t), 21.9 (t); HRMS calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$ 324.1263, found 324.1261.

(2-{2-[(4-Methylphenyl)sulfonyl]-1,2,3,6-tetrahydroindeno[2,1-b]pyrrolo[3,4-d]pyridin-4-yl}phenyl)acetonitrile (2c).

Pale yellow solid; $R_f = 0.15$ (25% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.77 (d, $J = 8.4$ Hz, 2 H), 7.61 (d, $J = 7.6$ Hz, 1 H), 7.57 (d, $J = 6.8$ Hz, 2 H), 7.49 - 7.39 (m, 4 H), 7.31 (d, $J = 8.0$ Hz, 2 H), 7.31 (d, $J = 8.0$ Hz, 1 H), 5.01 (s, 2 H), 4.61 (s, 2 H), 4.01 (s, 2 H), 3.76 (s, 2 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3); δ 163.7 (s), 149.9 (s), 144.1 (s), 141.8 (s), 139.5 (s), 137.7 (s), 137.5 (s), 133.7 (s), 130.3 (s), 130.0 (d), 129.9 (d), 129.6 (d), 129.6 (s), 129.0 (d), 128.8 (s), 128.5 (d), 128.3 (d),

127.6 (d), 127.5 (d), 125.5 (d), 122.5 (d), 117.7 (s), 52.7 (t), 52.3 (t), 38.8 (t), 21.9 (t), 21.5 (q); HRMS calcd for $C_{29}H_{23}N_3O_2S$ 477.1511, found 477.1513.

4-Phenyl-1,2,3,6-tetrahydrocyclopenta[*d*]indeno[2,1-*b*]pyridine (2d).

Brown solid; R_f = 0.40 (20% ethyl acetate in hexanes); 1H NMR (400 MHz, $CDCl_3$); δ 7.78 (dd, J = 8.4, 1.2 Hz, 2 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.59 (d, J = 7.6 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 2 H), 7.42 - 7.32 (m, 3 H), 4.05 (s, 2 H), 3.30 (t, J = 7.6 Hz, 2 H), 3.14 (t, J = 7.2 Hz, 2 H), 2.21 (quintet, J = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 162.5 (s), 152.0 (s), 147.6 (s), 142.0 (s), 140.6 (s), 139.9 (s), 136.3 (s), 130.2 (s), 128.5 (d), 128.3 (d), 127.9 (d), 127.0 (d), 126.9 (d), 125.2 (d), 122.4 (d), 38.9 (t), 32.3 (t), 31.6 (t), 25.6 (t); HRMS calcd for $C_{21}H_{17}N$ 283.1361, found 283.1366.

4-Phenyl-3,6-dihydro-1*H*-furo[3,4-*d*]indeno[2,1-*b*]pyridine (2e).

Yellow solid; R_f = 0.35 (20% ethyl acetate in hexanes); 1H NMR (400 MHz, $CDCl_3$); δ 7.75 (d, J = 7.2 Hz, 2 H), 7.60 (d, J = 6.8 Hz, 1 H), 7.50 - 7.46 (m, 3 H), 7.42 - 7.36 (m, 3 H), 5.42 (t, J = 1.6 Hz, 2 H), 5.35 (s, 2 H), 4.08 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 163.7 (s), 149.7 (s), 142.4 (s), 141.9 (s), 139.4 (s), 138.5 (s), 131.3 (s), 128.7 (d), 128.7 (d), 127.7 (s), 127.7 (d), 127.6 (d), 127.3 (d), 125.4 (d), 122.2 (d), 73.0 (t), 72.0 (t), 39.0 (t); HRMS calcd for $C_{20}H_{15}NO$ 285.1154, found 285.1155

4-(2-Thienyl)-1,2,3,6-tetrahydrocyclopenta[*d*]indeno[2,1-*b*]pyridine (2f).

Brown solid; $R_f = 0.40$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.72 (d, $J = 7.6$ Hz, 1 H), 7.58 (d, $J = 7.2$ Hz, 1 H), 7.53 (d, $J = 3.2$ Hz, 1 H), 7.40 (t, $J = 3.2$ Hz, 1 H), 7.39 (t, $J = 6.0$ Hz, 1 H), 7.33 (t, $J = 7.2$ Hz, 1 H), 7.14 (dd, $J = 5.2, 3.2$ Hz, 1 H), 4.03 (s, 2 H), 3.29 (t, $J = 7.6$ Hz, 2 H), 3.23 (t, $J = 7.2$ Hz, 2 H), 2.30 (quintet, $J = 7.6$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3); δ 162.3 (s), 147.9 (s), 141.9 (s), 139.9 (s), 134.2 (s), 130.1 (s), 129.9 (s), 129.0 (s), 127.8 (d), 127.0 (d), 126.9 (d), 126.8 (d), 125.9 (d), 125.2 (d), 122.2 (d), 38.7 (t), 32.6 (t), 31.4 (t), 24.8 (t); HRMS calcd for $\text{C}_{19}\text{H}_{15}\text{NS}$ 289.0925, found 289.0927.

4-(Trimethylsilyl)-1,2,3,6-tetrahydrocyclopenta[*d*]indeno[2,1-*b*]pyridine (2g).

Yellow solid; $R_f = 0.45$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.87 (d, $J = 7.2$ Hz, 1 H), 7.71 (d, $J = 8.0$ Hz, 1 H), 7.35 (td, $J = 7.6, 0.8$ Hz, 1 H), 7.22 (td, $J = 7.6, 0.8$ Hz, 1 H), 3.32 (t, $J = 7.6$ Hz, 2 H), 3.12 (t, $J = 7.6$ Hz, 2 H), 2.58 (s, 2 H), 2.24 (quintet, $J = 7.6$ Hz, 2 H), 0.40 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3); δ 156.2 (s), 152.3 (s), 143.3 (s), 140.2 (s), 138.5 (s), 132.6 (s), 125.9 (d), 124.5 (s), 122.7 (d), 121.9 (d), 120.2 (d), 31.4 (t), 31.2 (t), 25.1 (t), 22.2 (t), -1.0 (q); HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{NSi}$ 279.1443, found 279.1445.

4-(Trimethylsilyl)-3,6-dihydro-1*H*-furo[3,4-*d*]indeno[2,1-*b*]pyridine (2h).

Pale yellow solid; $R_f = 0.40$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.59 (d, $J = 6.4$ Hz, 1 H), 7.44 (d, $J = 6.4$ Hz, 1 H), 7.37 (t, $J = 5.6$ Hz, 1 H), 7.35 (t, $J = 5.2$ Hz, 1 H), 5.36 (s, 2 H), 5.25 (s, 2 H), 4.03 (s, 2 H), 0.35 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3); δ 163.0 (s), 157.5 (s), 142.0 (s), 139.5 (s), 138.8 (s), 138.8 (s), 128.2 (s), 127.7 (d), 127.2 (d), 125.3 (d), 122.4 (d), 72.7 (t), 71.6 (t), 39.0 (t), -1.3 (q); HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{NOSi}$ 281.1236, found 281.1237.

4-Methyl-3,6-dihydro-1H-furo[3,4-d]indeno[2,1-b]pyridine (2i).

Yellow solid; $R_f = 0.30$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.58 (d, $J = 7.2$ Hz, 1 H), 7.42 - 7.32 (m, 3 H), 5.41 (s, 2 H), 5.15 (s, 2 H), 3.98 (s, 2 H), 2.51 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3); δ 163.2 (s), 148.9 (s), 141.4 (s), 141.1 (s), 138.8 (s), 131.8 (s), 127.3 (d), 127.0 (s), 125.3 (d), 121.8 (d), 72.6 (t), 72.2 (t), 38.8 (t), 22.2 (q); HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{NO}$ 223.0997, found 223.0995.

Dimethyl 3,6-dihydrocyclopenta[d]indeno[2,1-b]pyridine-2,2(1H)-dicarboxylate (2j).

Brown solid; $R_f = 0.35$ (25% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 8.33 (s, 1 H), 7.86 (d, $J = 7.2$ Hz, 1 H), 7.71 (d, $J = 8.0$ Hz, 1 H), 7.36 (t, $J = 7.6$ Hz, 1 H), 7.26 (t, $J = 7.6$ Hz, 1 H), 4.05 (s, 2 H), 3.78 (s, 6 H), 3.73 (s, 2 H), 2.61 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3); δ 171.9 (s), 153.2 (s), 141.0 (s), 140.3 (d), 138.4 (s), 131.5 (s), 129.8 (s), 126.2 (d), 124.5 (s), 122.6 (d), 122.1 (d), 120.3 (d), 60.7 (s), 53.1 (q), 39.7 (t), 38.3 (t), 22.4 (t); HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_4$ 323.1158, found 323.1156.

4-Phenyl-1,2,3,7-tetrahydrospiro[benzo[*f*]cyclopenta[*c*]quinoline-6,1'-cyclopropane] (2k).

Brown solid; $R_f = 0.30$ (5% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.88 (d, $J = 7.6$ Hz, 2 H), 7.70 (d, $J = 7.6$ Hz, 1 H), 7.44 (t, $J = 7.6$ Hz, 2 H), 7.36 (t, $J = 7.2$ Hz, 1 H), 7.33 (t, $J = 7.2$ Hz, 1 H), 7.29 - 7.22 (m, 2 H), 3.29 (t, $J = 7.2$ Hz, 2 H), 3.11 (t, $J = 7.2$ Hz, 2 H), 2.89 (s, 2 H), 2.06 (quintet, $J = 6.8$ Hz, 2 H), 1.47 (dd, $J = 5.6, 3.6$ Hz, 2 H), 0.79 (dd, $J = 5.6, 3.6$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3); δ 157.5 (s), 150.8 (s), 150.6 (s), 140.3 (s), 137.2 (s), 135.7 (s), 133.6 (s), 128.6 (d), 128.1 (d), 128.0 (d), 127.9 (d), 127.3 (d), 126.9 (d), 126.4 (d), 125.9 (s), 38.8 (t), 35.1 (t), 32.9 (t), 26.9 (t), 20.9 (s), 13.8 (t); HRMS calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2$ 323.1674, found 323.1669.

2-[(4-Methylphenyl)sulfonyl]-4-(trimethylsilyl)-1,2,3,7-tetrahydrospiro[benzo[*f*]pyrrolo[3,4-*c*]quinoline-6,1'-cyclopropane] (2l).

Pale yellow solid; $R_f = 0.20$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.77 (d, $J = 8.0$ Hz, 2 H), 7.36 - 7.23 (m, 2 H), 7.31 (d, $J = 8.0$ Hz, 2 H), 7.27 (dd, $J = 6.8, 2.0$ Hz, 1 H), 7.20 (d, $J = 6.8$ Hz, 1 H), 4.89 (s, 2 H), 4.63 (s, 2 H), 2.83 (s, 2 H), 2.39 (s, 3 H), 1.34 (dd, $J = 6.0, 4.0$ Hz, 2 H), 0.74 (dd, $J = 6.0, 4.0$ Hz, 2 H), 0.28 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3); δ 158.9 (s), 158.2 (s), 144.0 (s), 138.4 (s), 137.4 (s), 136.5 (s), 133.5 (s), 132.2 (s), 129.9 (d), 128.30 (d), 128.2 (d), 127.6 (d), 126.9 (d), 126.2 (d), 124.7 (s), 54.0 (t), 52.1 (t), 38.3 (t), 21.5 (q), 20.8 (s), 14.1 (t), -1.6 (q); HRMS calcd for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_2\text{SSi}$ 474.1797, found 474.1797.

4-Phenyl-1,7-dihydro-3*H*-spiro[benzo[*f*]furo[3,4-*c*]quinoline-6,1'-cyclohexane] (2m).

Yellow oil; $R_f = 0.30$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.85 (d, $J = 7.6$ Hz, 2 H), 7.49 (t, $J = 7.6$ Hz, 2 H), 7.40 (t, $J = 7.2$ Hz, 1 H), 7.34 - 7.27 (m, 3 H), 7.24 - 7.21 (m, 1 H), 5.40 (s, 2 H), 5.33 (s, 2 H), 3.01 (s, 2 H), 2.10 (t, $J = 15.6$ Hz, 2 H), 1.69 - 1.67 (m, 3 H), 1.57 - 1.54 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3); δ 163.6 (s), 148.5 (s), 146.2 (s), 139.5 (s), 136.5 (s), 132.5 (s), 131.1 (s), 128.9 (d), 128.6 (d), 128.6 (d), 128.6 (d), 127.9 (d), 126.8 (d), 125.5 (d), 122.6 (s), 73.7 (t), 72.7 (t), 39.5 (t), 37.5 (s), 33.4 (t), 26.1 (t), 22.1 (t); HRMS calcd for $\text{C}_{26}\text{H}_{25}\text{NO}$ 367.1936, found 367.1937.

2-[(4-Methylphenyl)sulfonyl]-4-(trimethylsilyl)-1,2,3,7-tetrahydrospiro[benzo[*f*]pyrrolo[3,4-*c*]quinoline-6,1'-cyclohexane] (2n).

Pale yellow oil; $R_f = 0.20$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.78 (d, $J = 8.4$ Hz, 2 H), 7.32 - 7.30 (m, 4 H), 7.27 - 7.26 (m, 2 H), 4.86 (s, 2 H), 4.65 (s, 2 H), 2.87 (s, 2 H), 2.39 (s, 3 H), 1.91 (td, $J = 13.6, 3.2$ Hz, 2 H), 1.66 - 1.61 (m, 3 H), 1.53 - 1.32 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3); δ 162.9 (s), 158.8 (s), 143.9 (s), 138.7 (s), 136.9 (s), 136.6 (s), 133.5 (s), 132.2 (s), 129.9 (d), 128.9 (d), 128.3 (d), 127.6 (d), 126.8 (d), 125.8 (d), 123.3 (s), 54.0 (t), 52.2 (t), 39.4 (t), 38.1 (s), 33.6 (t), 26.2 (t), 22.1 (t), 21.5 (q), -1.3 (q); HRMS calcd for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_2\text{SSi}$ 516.2267, found 516.2266.

4-(2-Thienyl)-1,2,3,7-tetrahydrospiro[benzo[f]cyclopenta[c]quinoline-6,1'-cyclohexane] (2o).

Yellow oil; $R_f = 0.20$ (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.64 (d, $J = 7.6$ Hz, 1 H), 7.50 (d, $J = 3.6$ Hz, 1 H), 7.39 (d, $J = 4.4$ Hz, 1 H), 7.33 - 7.24 (m, 3 H), 7.14 (dd, $J = 4.8, 3.6$ Hz, 1 H), 3.26 (t, $J = 7.2$ Hz, 2 H), 3.18 (t, $J = 7.2$ Hz, 2 H), 2.95 (s, 2 H), 2.15 (quintet, $J = 7.6$ Hz, 2 H), 2.07 (td, $J = 14.2, 3.6$ Hz, 2 H), 1.75 - 1.67 (m, 3 H), 1.61 - 1.43 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3); δ 162.3 (s), 150.9 (s), 146.8 (s), 145.3 (s), 136.7 (s), 133.5 (s), 128.6 (d), 127.7 (d), 127.3 (d), 126.9 (d), 126.3 (d), 122.2 (d), 125.4 (d), 124.3 (s), 114.2 (s), 39.3 (t), 37.9 (s), 34.8 (t), 33.4 (t), 32.5 (t), 26.2 (t), 25.9 (t), 22.2 (t); HRMS calcd for $\text{C}_{25}\text{H}_{25}\text{NS}$ 371.1708, found 371.1715.

6,6-Dimethyl-2-[(4-methylphenyl)sulfonyl]-4-phenyl-2,3,6,7-tetrahydro-1H-benzo[f]pyrrolo[3,4-c]quinoline (2p).

Pale yellow solid; $R_f = 0.20$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 7.76 - 7.73 (m, 4 H), 7.48 (td, $J = 6.4, 1.6$ Hz, 2 H), 7.44 (t, $J = 6.8$ Hz, 1 H), 7.33 (td, $J = 6.4, 1.6$ Hz, 2 H), 7.30 - 7.25 (m, 4 H), 4.93 (s, 2 H), 4.79 (s, 2 H), 2.83 (s, 2 H), 2.39 (s, 3 H), 1.30 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3); δ 163.6 (s), 149.9 (s), 143.9 (s), 142.8 (s), 138.9 (s), 137.1 (s), 134.4 (s), 131.8 (s), 129.9 (d), 129.0 (d), 128.9 (d), 128.7 (d), 128.7 (s), 128.4 (d), 128.1 (d), 127.6 (d), 126.9 (d), 125.8 (d), 123.0 (s), 54.5 (t), 52.9 (t), 43.9 (t), 37.0 (s), 26.4 (q), 21.5 (q); HRMS calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2\text{S}$ 480.1871, found 480.1866.

6,6-Dimethyl-4-phenyl-3,6-dihydrobenzo[f]furo[3,4-c]quinolin-7(1H)-one (2q).

Yellow solid; $R_f = 0.20$ (10% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 8.17 (dd, $J = 7.6, 1.2$ Hz, 1 H), 7.84 (d, $J = 7.2$ Hz, 2 H), 7.70 (td, $J = 7.2, 1.2$ Hz, 1 H), 7.52 - 7.47 (m, 3 H), 7.44 (t, $J = 6.8$ Hz, 1 H), 7.37 (d, $J = 7.6$ Hz, 1 H), 5.50 (s, 2 H), 5.36 (s, 2 H), 1.67 (s, 6 H). ^{13}C NMR (100 MHz, CDCl_3); δ 202.9 (s), 160.4 (s), 149.9 (s), 147.0 (s), 138.7 (s), 135.2 (s), 134.2 (d), 131.9 (s), 129.8 (s), 129.2 (d), 128.7 (d), 128.4 (d), 127.9 (d), 125.9 (d), 119.7 (s), 74.3 (t), 72.6 (t), 51.1 (t), 26.0 (q); HRMS calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_2$ 341.1416, found 341.1416.

6,6-Dimethyl-4-(1-naphthyl)-3,6-dihydrobenzo[f]furo[3,4-c]quinolin-7(1H)-one (2r).

Yellow solid; $R_f = 0.30$ (15% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 8.21 (d, $J = 6.8$ Hz, 1 H), 7.94 (d, $J = 6.8$ Hz, 2 H), 7.93 (t, $J = 6.8$ Hz, 1 H), 7.74 (t, $J = 7.2$ Hz, 1 H), 7.58 - 7.49 (m, 5 H), 7.44 (t, $J = 8.4$ Hz, 1 H), 5.58 (s, 2 H), 5.01 (s, 2 H), 1.65 (s, 6 H). ^{13}C NMR (100 MHz, CDCl_3); δ 202.8 (s), 160.5 (s), 151.4 (s), 146.5 (s), 136.5 (s), 135.2 (s), 134.2 (d), 134.2 (d), 134.0 (s), 130.8 (s), 129.8 (s), 129.4 (d), 128.8 (d), 128.5 (d), 128.5 (s), 126.6 (d), 126.5 (d), 126.1 (d), 126.0 (d), 125.7 (d), 125.2 (d), 119.9 (s), 74.9 (t), 72.2 (t), 51.1 (s), 25.9 (q); HRMS calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_2$ 391.1572, found 391.1571.

7,7-Dimethyl-5-phenyl-2,3,4,7-tetrahydrobenzo[*a*]phenanthridin-8(1*H*)-one (2s).

Pale yellow solid; $R_f = 0.25$ (2% ethyl acetate in hexanes); ^1H NMR (400 MHz, CDCl_3); δ 8.15 (d, $J = 8.4$ Hz, 1 H), 7.97 (d, $J = 7.6$ Hz, 1 H), 7.81 (d, $J = 8.0$ Hz, 1 H), 7.62 (dd, $J = 8.0, 7.6$ Hz, 1 H), 7.55 (d, $J = 8.0$ Hz, 2 H), 7.51 - 7.39 (m, 3 H), 3.11 (t, $J = 6.4$ Hz, 2 H), 2.79 (t, $J = 6.4$ Hz, 2 H), 1.76 (quintet, $J = 6.8$ Hz, 2 H), 1.66 (quintet, $J = 6.8$ Hz, 2 H), 1.52 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3); δ 204.7 (s), 157.2 (s), 156.1 (s), 144.9 (s), 140.9 (s), 135.6 (s), 133.8 (s), 132.3 (d), 132.0 (s), 129.4 (d), 128.9 (d), 128.7 (d), 128.1 (d), 127.9 (d), 127.3 (d), 123.8 (s), 51.1 (s), 30.3 (t), 26.6 (t), 24.7 (q), 22.3 (t), 21.9 (t); HRMS calcd for $\text{C}_{25}\text{H}_{23}\text{NO}$ 353.1780 found 353.1787.

¹H NMR Spectrum of Starting Material 1a.

¹H NMR Spectrum of Starting Material 1b.

¹H NMR Spectrum of Starting Material 1c.

¹H NMR Spectrum of Starting Material 1d.

¹H NMR Spectrum of Starting Material 1e.

¹H NMR Spectrum of Starting Material 1f.

¹H NMR Spectrum of Starting Material 1h.

¹H NMR Spectrum of Starting Material 1i.

¹H NMR Spectrum of Starting Material 1j.

¹H NMR Spectrum of Starting Material 1k.

¹H NMR Spectrum of Starting Material 1l.

¹H NMR Spectrum of Starting Material 1m.

¹H NMR Spectrum of Starting Material 1n.

¹H NMR Spectrum of Starting Material 1o.

¹H NMR Spectrum of Starting Material 1n

¹H NMR Spectrum of Starting Material 1q.

¹H NMR Spectrum of Starting Material 1r.

¹H NMR Spectrum of Starting Material 1s.

¹H and ¹³C NMR Spectra of Compound 2a.

¹H and ¹³C NMR Spectra of Compound 2b.

¹H and ¹³C NMR Spectra of Compound 2c.

¹H and ¹³C NMR Spectra of Compound 2d.

¹H and ¹³C NMR Spectra of Compound 2e.

¹H and ¹³C NMR Spectra of Compound 2f.

¹H and ¹³C NMR Spectra of Compound 2g.

¹H and ¹³C NMR Spectra of Compound 2h.

¹H and ¹³C NMR Spectra of Compound 2i.

¹H and ¹³C NMR Spectra of Compound 2j.

¹H and ¹³C NMR Spectra of Compound 2k.

¹H and ¹³C NMR Spectra of Compound 21.

¹H and ¹³C NMR Spectra of Compound 2m.

¹H and ¹³C NMR Spectra of Compound 2n.

¹H and ¹³C NMR Spectra of Compound 2o.

¹H and ¹³C NMR Spectra of Compound 2p.

¹H and ¹³C NMR Spectra of Compound 2q.

¹H and ¹³C NMR Spectra of Compound 2r.

¹H and ¹³C NMR Spectra of Compound 2s.