Supporting Information

Base and Ligand-Free Room Temperature Synthesis of N-Fused Heteroaromatic Compounds *via* the Transition Metal-Catalyzed Cycloisomerization Protocol

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General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz), instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle silica gel (43-60 μm). HRMS (EI) analysis was performed on a JEOL GCmate II instrument. All manipulations with transition metal catalysts were conducted under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous toluene, tetrahydrofuran, and dichloromethane, purchased from Aldrich, were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system. All other chemicals and solvents were purchased from Aldrich, Fisher, Acros Organics, TCI, and Alfa Aesar and used without additional purification.

Preparation of starting materials

General procedures for preparation of propargyl-containing heterocycles

A. To a flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were added terminal alkyne¹ (1.20 equiv) and anhydrous THF (0.3-0.5 M). The solution was cooled to -78 °C while stirring in a dry ice/acetone

[1] Phenylacetylene, octyne, 3-pyridylacetylene, and cyclohexenylacetylene are commercially available compounds. 1,3-Octadiyne was prepared *via* published procedure (L. Brandsma “*Preparative acetylenic chemistry*”, 2nd Ed., p.51, Amsterdam, Elsevier Science Publishers B. V., 1992).

bath and methylmagnesium bromide (1.05 equiv., 2.5 M solution in hexane) was added dropwise.² The solution was stirred at -78 °C for 1 hour, then allowed to warm up to room temperature and stirred for another hour. Heterocyclic aldehyde³ (1.00 equiv.) was added slowly dropwise and the reaction was stirred for 2 hours at room temperature. Saturated ammonium chloride solution was added and the mixture was thoroughly extracted with ethyl acetate. The organic phase was then washed once each with saturated ammonium chloride solution and brine, dried over magnesium sulfate, and concentrated. The residue was purified on short silica gel column using 1:1 ethyl acetate : hexanes as eluent.

B. *t*-Butyldimethylsilyl (TBS) protection of propargyl alcohols was done *via* typical procedure: a solution of alcohol (1.00 equiv.) in small amount of DCM was added to a stirred solution of TBSCl (1.05 equiv.) and imidazole (1.10 equiv.) in DCM. The mixture was stirred at room temperature for 1 hour. The solvent was removed under reduced pressure and the residue was purified on silica gel column using ethyl acetate/hexane mixture as eluent.

C. Acylation of propargyl alcohols was done using standard AcCl/NEt₃/DMAP protocol. In a typical procedure, to a stirred solution of propargyl alcohol (1.00 equiv.) in DCM successively were added DMAP (0.10 equiv.) and triethylamine (1.50 equiv.). The solution was cooled down to 0 °C and AcCl (1.20 equiv.) was added dropwise. The reaction was allowed to warm up to room temperature and stirred until completion as monitored by TLC and/or GC-MS. The solvent was removed under reduced pressure and the residue was purified on silica gel column using ethyl acetate/hexane mixture as eluent.

D. Phosphorylation of propargylic alcohols was done analogously to the previous procedure: to a stirred solution of propargyl alcohol (1.00 equiv.) in DCM successively were added DMAP (0.10 equiv.) and triethylamine (2.00 equiv.). The solution was cooled down to 0 °C and diethylchlorophosphate (1.10 equiv.) was added dropwise. The reaction was allowed to warm up to room temperature and stirred until completion as monitored by TLC and/or GC-MS. The solvent was removed under reduced pressure and the residue was purified on silica gel column using ethyl acetate/hexane mixture as eluent.

[2] Commercially available ethynylmagnesium bromide (0.5 M solution in THF) was employed to prepare compounds containing terminal acetylenic moiety ($R^2 = H$).

[3] Quinoxalinecarboxaldehyde was prepared *via* published procedure (Goto, Y. et al. *Heterocycles* **2003**, 60, 953); 2-pyridine-carboxaldehyde and 2-thiazole-carboxaldehyde are commercially available compounds.

Preparation of deuterium-labeled compounds

Hydroxymethylpyridine-*d*₂ (i). To a stirred solution of ethyl picolinate (0.67 ml, 5 mmol) in anhydrous methanol (10 ml), sodium tetradeuteridoborate (1.0 g, 24 mmol, 99+ %D) was added and the reaction was stirred at room temperature in argon atmosphere for 3 hours. The reaction mixture was poured into cold water and thoroughly extracted with DCM. Aqueous phase was neutralized with 1 M HCl to pH 7 and extraction with DCM was repeated. The combined organic phase was then dried over magnesium sulfate, and concentrated to give 0.542 g (98%, >99%D) of hydroxymethylpyridine-*d*₂ as yellow oil.

2-Pyridine-carboxaldehyde-*d* (ii). To a stirred solution of hydroxymethylpyridine-*d*₂ (0.45 g, 4 mmol) in chloroform (15 ml) manganese (IV) oxide (1.95 g, 22 mmol) was added and the reaction mixture was stirred at reflux overnight. The reaction was cooled down to room temperature, solid was removed by filtration, and chloroform was removed in vacuo. The residue was purified *via* silica gel column chromatography using 1:3 ethyl acetate/hexane mixture as eluent to give 0.242 g (55%, >99%D) of 2-pyridine-carboxaldehyde-*d* as yellow oil.

2-(1-(*t*-butyldimethyl)silanyloxy)-3-(hexyl)prop-2-ynylpyridine-*d* (5) was prepared *via* typical procedure for propargyl-containing heterocycles described above (61% for 2 steps, >99%D). ¹H NMR (500.13 MHz, CDCl₃) δ ppm 8.53 (1 H, d, *J*=4.95 Hz) 7.71 (1 H, dd, *J*=9.54, 7.89 Hz) 7.62 (1 H, d, *J*=7.89 Hz) 7.18 (1 H, dd, *J*=6.60, 5.32 Hz) 2.20 (2 H, t, *J*=7.34 Hz) 1.42 - 1.53 (2 H, m) 1.30 - 1.40 (2 H, m) 1.20 - 1.30 (4 H, m) 0.94 (9 H, s) 0.86 (3 H, t, *J*=6.97 Hz) 0.19 (3 H, s) 0.14 (3 H, s).

Catalyst optimization

Reactions were run in the presence of 3 mol % of catalyst in DCM (0.25 M) at room temperature until completion as monitored by TLC and/or GC-MS. Yields are based on GC-MS analysis with internal standard. 10 mol % of catalyst was used in entry 8.

no.	Catalyst	Reaction time	Yield, %
1	AgSbF ₆	30 min	52%
2	AgBF₄	30 min	>99%
3	CuCl	30 min	83%
4	AgPF₆	30 min	>99%
5	AuCl ₃	30 min	71%
6	AuI	3 h	95%
7	CuI	3 h	77%
8	AlCl ₃	48 h	64%
9	Sn(OTf) ₂	48 h	31%
10	Mg(OTf) ₂	48 h	52%
11	In(OTf) ₂	48 h	33%
12	PtCl ₂	48 h	41%
13	PdCl ₂ (PPh ₃) ₂	30 min	61%
14	Pd(OAc) ₂	30 min	74%
15	HOTf	30 min	9 %

General procedure for cycloisomerization

In a glovebox under nitrogen atmosphere, to a 5.0 mL Wheaton microreactor equipped with a spin vane and screw cap with a PTFE faced silicone septum under nitrogen atmosphere was added 3-10 mol % of AgBF₄. The microreactor was removed from the glovebox, propargyl heterocycle **1a-1l** and anhydrous toluene (0.10 M) were successively added and the mixture was stirred until completion (as monitored by TLC and/or GC/MS). The solvent was removed under reduced pressure and the residue was purified using flash-column chromatography using hexane or hexane/ethyl acetate mixture as eluent to afford pure fused pyrroloheterocycles **2a-2l**.

5-(phenyl)-7-(acetyloxy)pyrrolo[1,2]thiazole, **2i**

¹H NMR (500.13 MHz, CDCl₃) δ ppm 7.63 (1 H, d, *J*=4.22 Hz), 7.45 - 7.50 (2 H, m), 7.39 - 7.45 (2 H, m), 7.24 - 7.32 (1 H, m), 6.63 (1 H, d, *J*=4.22 Hz), 6.54 (1 H, s), 2.31 (3 H, s); ¹³C NMR (125.76 MHz, CDCl₃) δ ppm 168.1, 132.4, 128.9, 126.7, 126.2, 122.5, 119.2, 119.0, 119.0, 112.3, 105.4, 20.8. HR EI MS *m/z* 257.04997, Calcd for C₁₆H₁₁N 257.0510.

5-(hexyl)-7-(acetyloxy)pyrrolo[1,2]thiazole, **2j**

¹H NMR (500.13 MHz, CDCl₃) δ ppm 7.16 (1 H, d, *J*=4.22 Hz), 6.54 (1 H, d, *J*=4.22 Hz), 6.11 (1 H, s), 2.58 - 2.72 (2 H, m), 2.26 (3 H, s), 1.57 - 1.67 (2 H, m), 1.34 - 1.42 (2 H, m), 1.26 - 1.34 (2 H, m), 0.89 (3 H, t, *J*=6.89); ¹³C NMR (125.76 MHz, CDCl₃) δ ppm 168.2, 127.7, 121.9, 117.7, 115.3, 111.3, 103.7, 31.6, 28.9, 28.3, 26.8, 22.6, 20.8, 14.1. HR EI MS *m/z* 265.1130, Calcd for C₁₆H₁₁N 265.11365.

5-(3-pyridyl)-7-((*t*-butyldimethyl)silanyloxy)pyrrolo[1,2]thiazole, 2k

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.74 (1 H, s), 8.44 (1 H, d, $J=3.67$ Hz), 7.73 (1 H, d, $J=7.89$ Hz), 7.58 (1 H, d, $J=4.22$ Hz), 7.31 (1 H, dd, $J=7.79$, 4.86 Hz), 6.64 (1 H, d, $J=3.48$ Hz), 6.35 (1 H, s), 1.01 (9 H, s), 0.23 (6 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 146.6, 146.4, 134.2, 132.4, 129.1, 123.7, 118.8, 118.4, 118.1, 111.8, 106.6, 25.7, 18.1, -4.4.

1-(diethylphosphatoxy)indolizine, 2d

^1H NMR (500.13 MHz, CDCl_3) δ ppm 7.72 (1 H, d, $J=7.02$ Hz), 7.39 (1 H, d, $J=9.06$ Hz), 7.06 (1 H, d, $J=2.92$ Hz), 6.69 (1 H, d, $J=2.92$ Hz), 6.58 (1 H, dd, $J=9.35$, 6.43 Hz), 6.38 (1 H, dd, $J=8.45$, 2.17 Hz), 4.21 (4 H, q, $J=8.18$ Hz), 1.34 (6 H, t, $J=7.02$ Hz); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 130.8, 128.8, 124.6, 116.2, 116.0, 110.4, 108.5, 105.2, 64.5, 16.1. HR EI MS m/z 269.08157, Calcd for $\text{C}_{16}\text{H}_{11}\text{N}$ 269.08169.

1-(hexyl)-3-(acetyloxy)pyrrolo[1,2]quinoxaline, 2h

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.65 (1 H, s), 8.08 (1 H, d, $J=8.18$ Hz), 7.92 (1 H, d, $J=7.60$ Hz), 7.35 - 7.53 (2 H, m), 6.68 (1 H, s), 3.08 - 3.33 (2 H, m), 2.39 (3 H, s), 1.72 - 1.95 (2 H, m), 1.43 - 1.60 (2 H, m), 1.27 - 1.44 (4 H, m), 0.91 (3 H, t, $J=7.02$ Hz); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 168.6, 142.8, 137.5, 132.8, 131.6, 130.1, 129.4, 127.0, 124.9, 116.6, 116.1, 106.4, 31.6, 30.8, 29.1, 28.1, 22.5, 21.0, 14.0.

1-(cyclohexenyl)-3-((t-butyldimethyl)silanyloxy)pyrrolo[1,2]quinoxaline, 2g

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.63 (1 H, s), 7.97 (1 H, d, $J=4.68$ Hz), 7.82 (1 H, d, $J=4.97$ Hz), 7.28 - 7.38 (2 H, m), 6.10 (1 H, s), 5.99 - 6.08 (1 H, m), 2.17 - 2.34 (3 H, m), 1.68 - 1.90 (5 H, m), 1.03 (9 H, s), 0.25 (6 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 143.7, 139.5, 137.4, 131.9, 131.8, 130.7, 129.2, 129.1, 126.3, 124.4, 116.6, 116.1, 109.5, 105.7, 28.9, 25.6, 25.5, 22.5, 21.7, 18.2, -4.5. HR EI MS m/z 378.21249, Calcd for $\text{C}_{16}\text{H}_{11}\text{N}$ 378.2127.

1-(acetyloxy)indolizine, 2f

^1H NMR (500.13 MHz, CDCl_3) δ ppm 7.75 (1 H, d, $J=7.02$ Hz), 7.22 (1 H, d, $J=9.06$ Hz), 7.14 (1 H, d, $J=2.92$ Hz), 6.72 (1 H, d, $J=2.92$ Hz), 6.60 (1 H, dd, $J=9.06$, 6.43 Hz), 6.41 (1 H, dd, $J=7.02$, 5.55 Hz), 2.34 (3 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 169.5, 124.8, 116.4, 115.9, 115.7, 110.4, 110.1, 109.0, 106.3, 20.9. HR EI MS m/z 175.06335, Calcd for $\text{C}_{16}\text{H}_{11}\text{N}$ 175.0633.

1-(acetyloxy)-3-(phenyl)indolizine, 2a

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.18 (1 H, d, $J=7.34$ Hz), 7.56 (2 H, dd, $J=8.25$, 1.28 Hz), 7.44 - 7.50 (2 H, m), 7.32 - 7.37 (1 H, m), 7.29 (1 H, d, $J=8.99$ Hz), 6.83 (1 H, s), 6.65 (1 H, dd, $J=9.17$, 6.42 Hz), 6.44 (1 H, dd, $J=8.44$, 6.42 Hz), 2.37 (3 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 172.4, 131.8, 128.9, 128.1, 127.3, 123.0, 122.0, 121.6, 116.5, 116.3, 110.9, 109.5, 106.6, 20.9.

1-(diethylphosphatoxy)-3-(phenyl)indolizine, 2e

^1H NMR (500.13 MHz, Acetone- d_6) δ ppm 8.26 (1 H, d, $J=7.31$ Hz), 7.55 - 7.63 (2 H, m), 7.45 - 7.53 (3 H, m), 7.37 (1 H, d, $J=6.45$ Hz), 6.85 (1 H, s), 6.70 (1 H, dd, $J=8.18, 7.31$ Hz), 6.53 (1 H, dd, $J=7.02, 6.43$ Hz), 4.22 (4 H, q, $J=3.95$ Hz), 1.32 (6 H, t, $J=7.02$ Hz); ^{13}C NMR (125.76 MHz, Acetone- d_6) δ ppm 131.6, 129.0, 127.8, 127.3, 121.5, 121.4, 116.4, 116.3, 111.2, 105.4, 105.4, 64.2, 64.1, 15.6, 15.6. HR EI MS m/z 345.11313, Calcd for $\text{C}_{16}\text{H}_{11}\text{N}$ 345.11299.

1-(acetyloxy)-3-(hexyl)indolizine, 2b

^1H NMR (500.13 MHz, CDCl_3) δ ppm 7.61 (1 H, d, $J=7.02$ Hz), 7.22 (1 H, d, $J=9.06$ Hz), 6.56 (1 H, dd, $J=9.06, 6.43$ Hz), 6.53 (1 H, s), 6.45 (1 H, dd, $J=8.45, 6.99$ Hz), 2.76 (2 H, d, $J=7.60$ Hz), 2.34 (3 H, s), 1.66 - 1.79 (2 H, m), 1.37 - 1.49 (2 H, m), 1.29 - 1.37 (4 H, m), 0.90 (3 H, t, $J=5.62$); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 167.3, 121.5, 121.0, 120.9, 116.0, 114.8, 110.0, 110.0, 104.4, 31.6, 29.2, 27.1, 25.8, 22.6, 20.9, 14.1.

1-((t-butyltrimethylsilyl)ethoxy)-3-(cyclohexenyl)indolizine, 2c

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.03 (1 H, d, $J=7.89$ Hz), 7.24 (1 H, d, $J=9.06$ Hz), 6.35 (1 H, dd, $J=8.92, 6.28$ Hz), 6.27 (1 H, dd, $J=6.98, 5.72$ Hz), 6.03 (1 H, t, $J=3.80$ Hz), 2.29 - 2.38 (2 H, m), 2.20 - 2.30 (2 H, m), 1.75 - 1.85 (2 H, m), 1.65 - 1.75 (2 H, m), 1.02 (9 H, s), 0.19 (6 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 132.2, 128.9, 124.9, 122.5, 121.9, 120.8, 117.0, 112.7, 109.7, 103.3, 29.1, 25.8, 25.5, 23.0, 22.2, 18.2, -4.5.

5-(1-hexynyl)-7-((*t*-butyldimethyl)silanyloxy)pyrrolo[1,2]thiazole, 2l

^1H NMR (500.13 MHz, CDCl_3) δ ppm 7.60 (1 H, d, $J=9.87$ Hz), 7.09 (1 H, d, $J=8.07$ Hz), 6.96 (1 H, s), 2.27 (2 H, t, $J=7.52$ Hz), 1.45 - 1.54 (2 H, m), 1.36 - 1.44 (2 H, m), 0.94 (9 H, s), 0.89 (3 H, t, $J=7.49$ Hz), 0.17 (6 H, s).

As mentioned in the manuscript, **2l** was obtained in less than 10% yield, which was determined by NMR analysis of the reaction mixture. Thus, no sample suitable for ^{13}C NMR was isolated.

3-phenyl-1-(1,3-thiazol-2-yl)-2-propynyl acetate, 1i

^1H NMR (500.13 MHz, CDCl_3) δ ppm 7.84 (1 H, d, $J=3.22$ Hz), 7.47 - 7.54 (2 H, m), 7.41 (1 H, d, $J=3.51$ Hz), 7.31 - 7.36 (3 H, m), 6.97 (1 H, s), 2.19 (3 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 169.8, 165.8, 142.9, 132.7, 129.0, 123.5, 122.1, 119.9, 86.4, 84.9, 62.1, 19.8.

1-(1,3-thiazol-2-yl)-2-nonynyl acetate, 1j

^1H NMR (500.13 MHz, CDCl_3) δ ppm 7.77 (1 H, d, $J=3.12$ Hz), 7.35 (1 H, d, $J=3.12$ Hz), 6.68 (1 H, s), 2.24 (2 H, t, $J=7.15$ Hz), 2.11 (3 H, s), 1.45 - 1.57 (2 H, m), 1.31 - 1.42 (2 H, m), 1.17 - 1.31 (4 H, m), 0.85 (3 H, t, $J=6.79$ Hz); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 169.2, 166.4, 143.2, 120.5, 89.2, 75.1, 62.4, 31.2, 28.4, 28.0, 22.4, 20.8, 18.7, 14.0.

3-(3-(((tert-butyl(dimethyl)silyl)oxy)-3-(1,3-thiazol-2-yl)-1-propynyl]pyridine, 1k

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.66 (1 H, s), 8.51 (1 H, d, $J=3.80$ Hz), 7.76 (1 H, d, $J=3.22$ Hz), 7.71 (1 H, d, $J=7.89$ Hz), 7.32 (1 H, d, $J=3.22$ Hz), 7.21 (1 H, dd, $J=7.75$, 4.82 Hz), 5.97 (1 H, s), 0.96 (9 H, s), 0.24 (3 H, s), 0.20 (3 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 171.8, 152.4, 149.0, 142.8, 138.7, 122.9, 119.6, 90.8, 82.6, 63.7, 25.6, 18.2, -4.4, -5.0.

1-(2-quinoxaliny)-2-nonyl acetate, 1h

^1H NMR (500.13 MHz, CDCl_3) δ ppm 9.11 (1 H, s), 8.11 (2 H, dd, $J=6.51$, 3.39 Hz), 7.78 (2 H, dd, $J=6.42$, 3.48 Hz), 6.63 (1 H, s), 2.26 (2 H, t, $J=7.15$ Hz), 2.17 (3 H, s), 1.46 - 1.55 (2 H, m), 1.29 - 1.37 (2 H, m), 1.17 - 1.28 (4 H, m), 0.83 (3 H, t, $J=6.97$ Hz); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 169.1, 155.6, 144.9, 141.1, 140.5, 131.4, 129.0, 128.2, 127.8, 89.6, 79.3, 65.1, 31.2, 28.5, 28.3, 22.4, 20.3, 18.8, 13.9.

2-(1-(((tert-butyl(dimethyl)silyl)oxy)-3-(1-cyclohexenyl)-2-propynyl)quinoxaline, 1g

^1H NMR (500.13 MHz, CDCl_3) δ ppm 9.20 (1 H, s), 8.06 (2 H, dd, $J=17.98$, 9.79 Hz), 7.72 (2 H, dd, $J=5.41$, 4.24 Hz), 6.08 (1 H, t, $J=3.80$ Hz), 5.80 (1 H, s), 1.90 - 2.14 (6 H, m), 1.45 - 1.64 (6 H, m), 0.92 (9 H, s), 0.24 (6 H, s), 0.14 (6 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 155.3, 144.3, 142.0, 141.0, 135.7, 130.0, 129.6, 129.2, 129.2, 119.9, 89.4, 85.4, 66.7, 28.8, 25.7, 25.5, 22.1, 21.3, 18.2, -4.3, -4.8.

1-(2-pyridinyl)-2-propynyl acetate, 1f

^1H NMR (500.13 MHz, Acetone- d_6) δ ppm 8.61 (1 H, d, $J=4.01$ Hz), 7.72 (1 H, dd, $J=2.72$, 4.97 Hz), 7.54 (1 H, d, $J=5.02$), 7.28 (1 H, dd, $J=5.65$, 7.15 Hz), 6.45 (1 H, s), 2.66 (1H, s), 2.12 (3 H, s); ^{13}C NMR (125.76 MHz, Acetone- d_6) δ ppm 169.4, 155.2, 149.7, 149.7, 149.4, 137.1, 123.7, 122.2, 121.7, 120.1, 79.0, 75.8, 66.2, 20.9.

3-phenyl-1-(2-pyridinyl)-2-propynyl acetate, 1a

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.58 (1 H, d, $J=3.75$ Hz), 7.88 (1 H, dd, $J=1.12$ Hz, $J=4.02$), 7.47-7.50 (2 H, m), 7.39-7.43 (4 H, m), 6.68 (1 H, s), 2.13 (3 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 168.9, 156.3, 149.4, 137.2, 131.6, 129.0, 128.5, 123.6, 122.4, 121.9, 121.4, 120.3, 86.5, 85.4, 66.7, 19.9.

1-(2-pyridinyl)-2-nonynyl acetate, 1b

^1H NMR (500.13 MHz, Acetone- d_6) δ ppm 8.54 (1 H, d, $J=4.04$ Hz), 7.85 (1 H, dd, $J=7.89$, 5.97 Hz), 7.64 (1 H, d, $J=7.89$ Hz), 7.35 (1 H, dd, $J=7.52$, 4.77 Hz), 6.42 (1 H, s), 2.25 (2 H, t, $J=7.06$ Hz), 2.08 (3 H, s), 1.44 - 1.55 (2 H, m), 1.33 - 1.42 (2 H, m), 1.21 - 1.32 (4 H, m), 0.87 (3 H, t, $J=7.06$ Hz); ^{13}C NMR (125.76 MHz, Acetone- d_6) δ ppm 168.8, 156.9, 149.2, 149.2, 137.0, 123.4, 121.1, 87.9, 76.6, 66.6, 31.0, 28.2, 22.3, 19.9, 18.2, 13.4.

2-(1-((tert-butyl(dimethyl)silyl)oxy)-3-(1-cyclohexen-1-yl)-2-propynyl)pyridine, 1c

^1H NMR (500.13 MHz, CDCl_3) δ ppm 8.46 (1 H, d, $J=4.77$ Hz), 7.65 (1 H, dd, $J=7.89$, 3.45 Hz), 7.58 (1 H, d, $J=7.89$ Hz), 7.11 (1 H, dd, $J=6.69$, 5.59 Hz), 6.02 (1 H, t, $J=4.03$ Hz), 5.61 (1 H, s), 2.01 - 2.09 (2 H, m), 1.92 - 2.01 (2 H, m), 1.51 - 1.59 (2 H, m), 1.43 - 1.50 (2 H, m), 0.89 (9 H, s), 0.16 (6 H, s), 0.11 (6 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 161.1, 148.5, 148.5, 136.8, 134.9, 122.4, 120.2, 120.0, 87.3, 86.6, 66.9, 60.2, 28.9, 25.7, 25.5, 22.1, 21.4, 18.2, 14.1, -4.4, -5.0.

2-(1-((tert-butyl(dimethyl)silyl)oxy)-2,4-nonadiynyl)-1,3-thiazole, 1l

^1H NMR (500.13 MHz, CDCl_3) δ ppm 7.73 (1 H, d, $J=3.30$ Hz), 7.30 (1 H, d, $J=3.12$ Hz), 5.78 (1 H, s), 2.26 (2 H, t, $J=6.97$ Hz), 1.44 - 1.54 (2 H, m), 1.32 - 1.42 (2 H, m), 0.94 (9 H, s), 0.88 (3 H, t, $J=7.24$ Hz), 0.22 (3 H, s), 0.16 (3 H, s); ^{13}C NMR (125.76 MHz, CDCl_3) δ ppm 171.5, 142.7, 119.6, 82.7, 73.1, 71.3, 64.4, 63.7, 30.0, 25.6, 21.8, 18.9, 18.2, 13.4, -4.5, -5.2.

¹H spectrum of **2i** ¹³C spectrum of **2i**

¹H spectrum of **2j** ¹³C spectrum of **2j**

¹H spectrum of **2k** ¹³C spectrum of **2k**

¹H spectrum of **2h** ¹³C spectrum of **2h**

¹H spectrum of **2g** ¹³C spectrum of **2g**

¹H spectrum of **2f** ¹³C spectrum of **2f**

¹H spectrum of **2a** ¹³C spectrum of **2a**

¹H spectrum of **2e** ¹³C spectrum of **2e**

¹H spectrum of **2b** ¹³C spectrum of **2b**

¹H spectrum of **2c** ¹³C spectrum of **2c**

¹H spectrum of **11** ¹³C spectrum of **11** ¹³C DEPT spectrum of **11**

¹H spectrum of **1k** ¹³C spectrum of **1k**