Convergent Synthesis of Bis-1,2,4-triazinyl-2,2'-bipyridines (BTBPs) and Related Congeners via a Pd-catalyzed Ullman-type Reaction

Supporting Information

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Figure S1. $^1$H NMR Spectrum of Compound 10 (CDCl₃)
Figure S2. $^{13}$C NMR of Compound 10 (CDCl$_3$)
Figure S3. $^1$H NMR spectrum of 11 [(CD$_3$)$_2$SO]
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Figure S5. $^1$H NMR spectrum of compound 12 (CDCl$_3$)
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[Schematic diagram of the compound with ppm values]
Figure S7. $^1$H NMR spectrum of compound 13 (CDCl$_3$)
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Figure 11. $^1$H NMR spectrum of compound 15 (CDCl$_3$)
Figure S12. $^{13}$C NMR spectrum of compound 15 (CDCl$_3$)
**Figure S13.**
Sample: GDW-B-243-1

4x Column: 4
RediSep Column: Silica 4g
Flow Rate: 18 ml/min
Equilibration Volume: 33.6 ml
Initial Waste: 0.0 ml
Air Purge: 0.5 min
Solvent: A1 hexane
Solvent: B1 ethyl acetate

Run Notes: 6,6'-bis-[5,6-bis(4-methylphenyl)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (10)

Peak Tube Volume: 15 ml
Non-Peak Tube Volume: 15 ml
Loading Type: Solid
Wavelength 1 (red): 254nm
Peak Width: 30 sec
Threshold: 0.20 AU
Wavelength 2 (purple): 280nm

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### Rack A

| Peak # | Start Tube | End Tube |
|--------|------------|----------|
| 1      | A:3        | A:3      |
| 2      | A:4        | A:4      |
| 3      | A:11       | A:13     |
| 4      | A:20       | A:20     |

| Duration | % B | Solvent A | Solvent B |
|----------|-----|-----------|-----------|
| 0.0      | 0.0 | A1 hexane | B1 ethyl acetate |
| 3.0      | 0.0 | A1 hexane | B1 ethyl acetate |
| 9.0      | 100.0| A1 hexane | B1 ethyl acetate |
| 2.0      | 100.0| A1 hexane | B1 ethyl acetate |
| 5.0      | 100.0| A1 hexane | B1 ethyl acetate |
| 0.0      | 0.0 | A1 hexane | B1 ethyl acetate |
| 1.0      | 0.0 | A1 hexane | B1 ethyl acetate |

18 mm x 150 mm Tubes
Figure S14.
Sample: GDW-C-51-1

RediSep Column: Silica 4g
Flow Rate: 18 ml/min
Equilibration Volume: 33.6 ml
Initial Waste: 0.0 ml
Air Purge: 0.5 min
Solvent: A1 hexane
Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
Non-Peak Tube Volume: Max.
Loading Type: Solid
Wavelength 1 (red): 254 nm
Peak Width: 30 sec
Threshold: 0.20 AU
Wavelength 2 (purple): 280 nm

Run Notes: 6,6′-bis-[5,6-bis(4-fluoro)-[1,2,4]triazin-3-yl]-2,2′-bipyridine (11)

| Peak # | Start Tube | End Tube |
|--------|------------|----------|
| 1      | A:12       | A:12     |
| 2      | A:18       | A:18     |
| 3      | A:20       | A:20     |

| Duration | % B  | Solvent A     | Solvent B       |
|----------|------|---------------|-----------------|
| 0.0      | 0.0  | A1 hexane     | B1 ethyl acetate|
| 4.0      | 0.0  | A1 hexane     | B1 ethyl acetate|
| 11.0     | 100.0| A1 hexane     | B1 ethyl acetate|
| 0.3      | 100.0| A1 hexane     | B1 ethyl acetate|
| 2.7      | 100.0| A1 hexane     | B1 ethyl acetate|

18 mm x 150 mm Tubes
Figure S15.
Sample: GDW-C-129-1

RediSep Column: Silica 4g
Flow Rate: 18 ml/min
Equilibration Volume: 33.6 ml
Initial Waste: 0.0 ml
Air Purge: 0.5 min
Solvent: A2 dichloromethane
Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
Non-Peak Tube Volume: Max.
Loading Type: Solid
Wavelength 1 (red): 254nm
Peak Width: 30 sec
Threshold: 0.20 AU
Wavelength 2 (purple): 280nm

Run Notes: 6,6’-bis-[5,6-bis(4-methoxy)-1,2,4-triazin-3-yl]-2,2’-bipyridine (12)

![Graph showing absorbance and run length](image-url)

| Rack A | Peak # | Start Tube | End Tube |
|--------|--------|------------|----------|
| 71 72 73 74 75 | 1 | A:3 | A:4 |

| Duration | % B | Solvent A | Solvent B |
|----------|-----|-----------|-----------|
| 0.0 | 0.0 | A2 dichloromethane | B1 ethyl acetate |
| 4.0 | 0.0 | A2 dichloromethane | B1 ethyl acetate |
| 3.4 | 28.7 | A2 dichloromethane | B1 ethyl acetate |
| 5.3 | 28.7 | A2 dichloromethane | B1 ethyl acetate |
| 0.0 | 28.7 | A2 dichloromethane | B1 ethyl acetate |
| 8.6 | 100.0 | A2 dichloromethane | B1 ethyl acetate |
| 1.2 | 100.0 | A2 dichloromethane | B1 ethyl acetate |
| 3.6 | 100.0 | A2 dichloromethane | B1 ethyl acetate |
| 6.4 | 100.0 | A2 dichloromethane | B1 ethyl acetate |
| 0.0 | 100.0 | A2 dichloromethane | B1 ethyl acetate |
Figure S16.
Sample: GDW-C-229-1

RediSep Column: Silica 4g
Flow Rate: 18 ml/min
Equilibration Volume: 33.6 ml
Initial Waste: 0.0 ml
Air Purge: 0.5 min
Solvent: A2 dichloromethane
Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
Non-Peak Tube Volume: Max.
Loading Type: Solid
Wavelength 1 (red): 254nm
Peak Width: 30 sec
Threshold: 0.20 AU
Wavelength 2 (purple): 280nm

Run Notes: 6,6'-bis-[5,6-bis(4-butyphenyl)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (13)
Figure S17.
Sample: GDW-C-139-1

RediSep Column: Silica 4g
Flow Rate: 18 ml/min
Equilibration Volume: 33.6 ml
Initial Waste: 0.0 ml
Air Purge: 0.5 min
Solvent: A2 dichloromethane
Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
Non-Peak Tube Volume: Max.
Loading Type: Solid
Wavelength 1 (red): 254nm
Peak Width: 30 sec
Threshold: 0.20 AU
Wavelength 2 (purple): 280nm

Run Notes: 6,6'-bis-[5,6-bis(4-(3-methylbutyl)phenyl) [1,2,4]triazin-3-yl]-2,2'-bipyridine (14)

Absorbance

| Peak # | Start Tube | End Tube |
|--------|-------------|----------|
| 1      | A:32        | A:32     |
| 2      | A:54        | A:54     |

Duration | % B | Solvent A | Solvent B
---------|-----|-----------|-----------
0.0       | 0.0 | A2 dichloromethane | B1 ethyl acetate
4.0       | 0.0 | A2 dichloromethane | B1 ethyl acetate
0.2       | 2.5 | A2 dichloromethane | B1 ethyl acetate
2.7       | 2.5 | A2 dichloromethane | B1 ethyl acetate
0.0       | 2.5 | A2 dichloromethane | B1 ethyl acetate
0.7       | 10.2 | A2 dichloromethane | B1 ethyl acetate
1.9       | 10.2 | A2 dichloromethane | B1 ethyl acetate
0.0       | 10.1 | A2 dichloromethane | B1 ethyl acetate
5.4       | 100.0 | A2 dichloromethane | B1 ethyl acetate
1.5       | 100.0 | A2 dichloromethane | B1 ethyl acetate
...       | ...  | ...       | ...       |

Rack A

16 mm x 100 mm Tubes
Figure S18.
Sample: GDW-B-197-1

4x Column: 3
RediSep Column: Silica 4g
Flow Rate: 18 ml/min
Equilibration Volume: 33.6 ml
Initial Waste: 0.0 ml
Air Purge: 0.5 min
Solvent: A1 hexane
Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
Non-Peak Tube Volume: Max.
Loading Type: Solid
Wavelength 1 (red): 254nm
Peak Width: 30 sec
Threshold: 0.20 AU
Wavelength 2 (purple): 280nm
Peak Width: 30 sec
Threshold: 0.20 AU
All Wavelength (orange): 200-300nm

Run Notes: 6,6'bis-[5,6-bis(3-methoxy)-[1,2,4]triazin-3-yl]-2,2'-bipyridine (15)

Rack A

Peak #  Start Tube  End Tube
1  A:3  A:3
2  A:4  A:4
3  A:5  A:5

Duration  % B  Solvent A  Solvent B
0.0  0.0  A1 hexane  B1 ethyl acetate
4.0  0.0  A1 hexane  B1 ethyl acetate
5.0  75.0  A1 hexane  B1 ethyl acetate
4.0  75.0  A1 hexane  B1 ethyl acetate
6.0  100.0  A1 hexane  B1 ethyl acetate
4.0  100.0  A1 hexane  B1 ethyl acetate
0.0  0.0  A1 hexane  B1 ethyl acetate
1.0  0.0  A1 hexane  B1 ethyl acetate

16 mm x 100 mm Tubes

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