Supporting Information for
SYNTHESIS OF ISOOQUINOLINIUM VIA RHODIUM(III)-CATALYZED OXIDITIVE ANNULATION BETWEEN ALDIMINES AND ALKYNES
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Table of Contents

1. General methods ........................................... 2
2. General procedure for synthesis of isoquinolinium salts derived fused compounds and Characterization data .......................... 2-7
3. Substrate scope of unsymmetrically disubstituted alkynes .......................................................... 7
4. NMR spectra of isoquinolinium salts derived fused compounds and structure determination ......................... 7-33
1. General Methods

NMR data were obtained for ¹H at 400 MHz or 600 MHz, and for ¹³C at 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl₃ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with dichloromethane and methanol. All aldehydes and anilines were commercially available. Substituted isoquinoliniums were prepared according to the literature procedures.

2. General procedure for synthesis of isoquinolinium salts derived fused compounds and Characterization data

**General procedure:** (E)-N-benzylideneaniline 1a (19.7 mg, 0.10 mmol), diphenylacetylene 2a (26.7 mg, 0.15 mmol), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), additive (1 equiv) and acid (1 equiv) were stirred in solvent (1 mL) at Ar atmosphere at 90 °C for 1 h. After completion, the reaction mixture was purified by flash chromatography eluting with dichloromethane and methanol to give the desired product.

**Procedure for synthesis of 2,3,4-Triphenylisoquinolinium trifluoromethanesulfonate (3aa-CF₃SO₃):** (E)-N-benzylideneaniline 1a (19.7 mg, 0.10 mmol), diphenylacetylene 2a (26.7 mg, 0.15 mmol), [Cp*RhCl₂]₂ (3.1 mg, 5 mol%), Cu(OAc)₂.H₂O (20 mg, 1 equiv) and trifluoromethanesulfonic acid (15 mg, 1 equiv) were stirred in methanol (1 mL) at Ar atmosphere at 90 °C for 1 h. After completion, the reaction mixture was purified by flash chromatography eluting with dichloromethane and methanol (10:1) to give the desired product 3aa-CF₃SO₃ as a grey solid (42.6 mg, 82%).

IR (KBr) 3565, 3499, 3062, 1625 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.93 (s, 1H), 8.68 (d, J = 8.0 Hz, 1H), 8.08 (t, J = 8.0 Hz, 1H), 7.98 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.37-7.32 (m, 6H), 7.28-7.27 (m, 2H), 7.08-7.03 (m, 5H). ¹³C NMR (151 MHz, CDCl₃): δ 150.5, 142.1, 139.3, 138.8, 137.8, 133.1, 131.9, 131.3, 131.2, 131.0, 130.4, 130.3, 129.5, 129.1, 128.7, 128.4, 127.9, 126.9, 126.8, 126.5, 120.6, 119.4, 112.4. ESI HRMS: calcd. For C₂₇H₂₀N⁺ 358.1590, found 358.1586.

KI was added into isolated product 3aa-CF₃SO₃ (26 mg, 0.05 mmol) in methanol (0.5 mL), and then vigorously stirred overnight at room temperature. The reaction mixture was purified by flash chromatography eluting with dichloromethane and methanol (10:1) to give the desired product 2,3,4-Triphenylisoquinolinium iodide (3aa-I). 99% yield; IR (KBr) 3422, 3062, 1622 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 10.09 (s, 1H), 8.74 (d, J = 8.0 Hz, 1H), 8.05 (t, J = 8.0 Hz, 1H), 7.94 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.37-7.32 (m, 6H), 7.28-7.27 (m, 2H), 7.08-7.03 (m, 5H). ¹³C NMR (151 MHz, CDCl₃): δ 149.3, 142.1, 139.3, 138.8, 137.8, 133.1, 131.9, 131.3, 131.2, 131.0, 130.4, 130.3, 129.5, 129.1, 128.7, 128.4, 127.9, 126.9, 126.8, 126.5, 120.6, 119.4, 112.4. ESI HRMS: calcd. For C₂₇H₂₀N⁺ 358.1590, found 358.1586.

2,3,4-Triphenylisoquinolinium acetate (3aa-OAc), (see Table 1, entry 5). 42% yield; IR (KBr) 3453, 2960, 2926, 1713, 1625 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 11.09 (s, 1H), 9.29 (d, J = 8.0 Hz, 1H), 8.08 (t, J = 8.0 Hz, 1H), 8.01 (t, J = 8.0 Hz, 1H), 7.94 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.37-7.32 (m, 6H), 7.28-7.27 (m, 2H), 7.08-7.03 (m, 5H). ¹³C NMR (151 MHz, CDCl₃): δ 150.5, 142.1, 139.3, 138.8, 137.8, 133.1, 131.9, 131.3, 131.2, 131.0, 130.4, 130.3, 129.5, 129.1, 128.7, 128.4, 127.9, 126.9, 126.8, 126.5, 120.6, 119.4, 112.4. ESI HRMS: calcd. For C₂₇H₂₀N⁺ 358.1590, found 358.1586.
7.75 (t, J = 8.0 Hz, 1H), 7.66-7.65 (m, 2H), 7.39-7.34 (m, 5H), 7.27-7.26 (m, 3H), 7.09-7.04 (m, 5H), 2.04 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 152.6, 138.8, 138.4, 137.8, 133.5, 133.2, 131.2, 131.2, 130.3, 129.5, 128.7, 128.5, 128.0, 127.2, 126.9, 126.1.

2,3,4-Triphenylisoquinolinium methanesulfonate (3aa-CH$_3$SO$_3$) (see Table 1, entry 8). 30% yield; IR (KBr) 3493, 3434, 3057, 1626 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.58 (s, 1H), 9.07 (s, 1H), 8.10-8.03 (m, 2H), 7.76 (t, J = 8.0 Hz, 1H), 7.62 (m, 2H), 7.38-7.34 (m, 6H), 7.27-7.26 (m, 2H), 7.05 (m, 5H), 2.04 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.7, 143.9, 142.1, 138.9, 138.6, 137.8, 133.3, 133.2, 131.3, 131.2, 130.4, 129.5, 129.2, 128.6, 128.0, 127.2, 126.3, 39.4.

2,3,4-Triphenylisoquinolinium benzenesulfonate (3aa-PhSO$_3$) (see Table 1, entry 10). 33% yield; IR (KBr) 3427, 3054, 1627 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.48 (s, 1H), 8.94 (d, J = 8.0 Hz, 1H), 8.02 (t, J = 8.4 Hz, 1H), 7.92 (t, J = 6.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 7.2 Hz, 2H) 7.59 (d, J = 7.2 Hz, 2H), 7.31-7.27 (m, 6H), 7.22-7.18 (m, 5H), 7.06-7.00 (m, 5H).

2,3,4-Triphenylisoquinolinium 4-methylbenzenesulfonate (3aa-TsO&OAc) (see Table 1, entry 11). 29% yield of acetate salt, 43% yield of tosylate salt; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.50 (s, 1H), 8.93 (d, J = 8.0 Hz, 1H), 7.95 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 6.8 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.26-7.19 (m, 6H), 7.15-7.13 (m, 2H), 7.00-6.93 (m, 7H), 2.23 (s, 3H), 1.90 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.1, 144.1, 143.9, 142.1, 138.8, 138.5, 138.4, 137.6, 133.3, 133.2, 131.3, 131.3, 130.4, 130.2, 129.4, 129.1, 128.7, 128.5, 128.3, 127.9, 127.2, 127.1, 127.0, 126.1, 125.9, 21.3.

3,4-Diphenyl-2-o-tolylisoquinolinium trifluoromethanesulfonate (3ba). 85% yield; IR (KBr) 3436, 3057, 1627 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.93 (s, 1H), 8.69 (d, J = 8.0 Hz, 1H), 7.95 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 6.8 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.26-7.17 (m, 5H), 7.05 (m, 5H), 2.29 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 150.0, 149.9, 143.4, 141.0, 139.2, 138.3, 137.7, 136.8, 132.2, 131.0, 131.0, 130.3, 130.2, 129.3, 128.2, 128.1, 127.7, 127.5, 126.9, 126.3, 126.0, 125.5, 122.7, 119.6 (q, J = 319 Hz), 21.2. ESI HRMS: calcd. For C$_{28}$H$_{22}$N$^+$ 372.1747, found 372.1747.

3,4-Diphenyl-2-m-tolylisoquinolinium trifluoromethanesulfonate (3ca). 80% yield; IR (KBr) 3440, 3069, 1622 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.93 (s, 1H), 8.78 (d, J = 8.0 Hz, 1H), 8.11 (t, J = 8.0 Hz, 1H), 8.02 (t, J = 8.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.37-7.23 (m, 8H), 7.18-7.16 (m, 1H), 7.08-7.07 (m, 2H), 7.01-7.00 (m, 1H), 6.93-6.91 (m, 1H), 2.09 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 151.2, 144.5, 141.1, 139.6, 138.8, 138.0, 133.0, 132.3, 132.0, 131.4, 131.2, 130.9, 130.6, 130.5, 129.4, 129.3, 128.9, 128.8, 128.2, 127.9, 127.6, 127.3, 127.2, 126.5, 120.5 (q, J = 318 Hz), 17.6. For C$_{28}$H$_{22}$N$^+$ 372.1747, found 372.1748.
3,4-Diphenyl-2-p-tolylisoquinolinium trifluoromethanesulfonate (3da).

79% yield; IR (KBr) 3482, 3060, 1626 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.93 (s, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.06 (t, J = 8.0 Hz, 1H), 7.97 (t, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.37-7.26 (m, 4H), 7.26-7.17 (m, 5H), 7.05 (m, 5H), 7.03 (m, 5H), 2.30 (s, 3H). ^13C NMR (100 MHz, CDCl₃): δ 151.1, 144.5, 140.8, 139.8, 139.3, 138.7, 137.8, 133.2, 132.0, 131.3, 131.2, 130.3, 130.1, 129.2, 128.7, 128.5, 128.0, 127.0, 126.5, 126.5, 120.6 (q, J = 319 Hz), 21.2. ESI HRMS: calcd. For C₂₇H₂₂N⁺ 372.1747, found 372.1752.

2-(3-Chlorophenyl)-3,4-diphenylisoquinolinium-trifluoromethanesulfonate (3ea). 77% yield; IR (KBr) 3468, 3240, 1624 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.88 (s, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.07 (t, J = 8.0 Hz, 1H), 7.95 (t, J = 7.2 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.52 (s, 1H), 7.32-7.31 (m, 5H), 7.28-7.26 (m, 2H), 7.11-7.08 (m, 5H). ^13C NMR (100 MHz, CDCl₃): δ 150.9, 144.3, 142.7, 139.5, 139.0, 135.0, 133.1, 132.0, 131.4, 131.2, 130.9, 130.7, 130.3, 129.4, 128.8, 128.5, 128.1, 127.1, 127.0, 125.6, 120.4 (q, J = 319 Hz). ESI HRMS: calcd. for C₂₇H₁₉ClN⁺ 392.1201, found 392.1119, 394.1229.

2-Cyclohexyl-3,4-diphenylisoquinolinium trifluoromethanesulfonate (3fa). 85% yield; IR (KBr) 3440, 3065, 3019, 1625 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 10.40 (s, 1H), 8.95 (d, J = 7.2 Hz, 1H), 8.00 (t, J = 8.0 Hz, 1H), 7.97 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.39 (m, 3H), 7.29-7.27 (m, 3H), 7.23 (m, 2H), 7.12 (m, 2H), 4.34 (m, 1H), 2.39-2.36 (m, 2H), 2.13 (m, 1H), 1.93-1.90 (m, 2H), 1.58-1.48 (m, 2H), 1.07-1.04 (m, 2H). ^13C NMR (100 MHz, CDCl₃): δ 148.2, 143.9, 139.4, 137.6, 137.4, 133.4, 133.3, 132.1, 131.2, 131.0, 130.3, 129.8, 129.0, 128.7, 128.5, 128.0, 120.8 (q, J = 319 Hz), 68.5, 33.6, 25.8, 23.9. ESI HRMS: calcd. for C₂₇H₂₆N⁺ 364.2060, found 364.2058.

2-Benzyl-3,4-diphenylisoquinolinium trifluoromethanesulfonate (3ga). 52% yield; IR (KBr) 3431, 3052, 1630 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 10.33 (s, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.02 (t, J = 8.0 Hz, 1H), 7.96 (t, J = 8.0 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.09-7.07 (m, 4H), 6.92 (d, J = 7.2 Hz, 2H), 5.89 (s, 2H). ^13C NMR (100 MHz, CDCl₃): δ 151.3, 144.3, 142.5, 142.2, 140.3, 139.1, 137.1, 133.3, 131.3, 131.2, 130.4, 130.3, 129.6, 129.2, 128.7, 128.6, 128.4, 128.3, 127.3, 63.3. ESI HRMS: calcd. for C₂₈H₂₂N⁺ 372.1747, found 372.1755.

5-Methyl-2,3,4-triphenylisoquinolinium trifluoromethanesulfonate (3ha). 78% yield; IR (KBr) 3455, 3066, 1634 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 1H), 8.46 (s, 1H), 7.90 (t, J = 8.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.52-7.51 (m, 2H), 7.34-7.32 (m, 6H), 7.24 (m, 2H), 7.04 (m, 5H), 2.66 (s, 3H). ^13C NMR (100 MHz, CDCl₃): δ 150.0, 143.7, 142.5, 142.2, 140.3, 139.1, 137.1, 133.3, 131.3, 131.2, 130.4, 130.3, 129.6, 129.2, 128.7, 128.5, 128.0, 127.3, 126.8, 126.3, 120.6 (q, J = 319 Hz), 21.8. ESI HRMS: calcd. For C₂₉H₂₂N⁺ 372.1747, found 372.1746.
6-Methyl-2,3,4-triphenylisoquinolinium trifluoromethanesulfonate. (3ia) 93% yield; IR (KBr) 3476, 3245, 3061, 1626 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.83 (s, 1H), 8.55 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.51-7.49 (m, 3H), 7.34-7.31 (m, 6H), 7.26-7.23 (m, 2H), 7.03-6.99 (m, 5H), 2.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 150.1, 144.4, 142.1, 139.0, 138.3, 133.7, 133.3, 131.7, 131.2, 130.4, 130.3, 129.5, 129.1, 128.7, 128.5, 127.9, 126.9, 125.5, 125.4, 120.6 (q, J = 319 Hz), 23.3. ESI HRMS: calcd. for C₃₈H₃₂N⁺ 372.1747, found 372.1748.

8-Methoxy-2,3,4-triphenylisoquinolinium trifluoromethanesulfonate (3ja). 81% yield. IR (KBr) 3488, 3245, 3060, 1622 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.74 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.37-7.35 (m, 3H), 7.29-7.26 (m, 7H), 7.14-7.13 (m, 2H), 7.04-7.00 (m, 3H), 4.15 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 157.7, 144.5, 144.0, 141.6, 138.8, 138.7, 137.8, 132.5, 130.2, 130.2, 129.4, 129.3, 128.5, 128.1, 127.6, 127.4, 126.8, 125.9, 119.6 (q, J = 319 Hz), 118.6, 117.4, 108.2, 55.9. ESI HRMS: calcd. for C₃₈H₃₂NO⁺ 388.1696, found 389.1693.

5,8-Dimethoxy-2,3,4-triphenylisoquinolinium trifluoromethanesulfonate (3ka). 75% yield; IR (KBr) 3062, 2920, 1650 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.69 (s, 1H), 9.51-9.49 (s, 2H), 7.44 (d, J = 8.4 Hz, 1H), 7.34-7.33 (m, 3H), 7.27-7.25 (m, 1H), 7.17-7.16 (m, 2H), 7.12-7.11 (m, 3H), 7.06-7.04 (m, 2H), 6.96-6.94 (m, 3H), 4.07 (s, 3H), 3.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 152.3, 149.9, 145.6, 145.1, 142.6, 137.7, 137.1, 131.5, 131.2, 129.8, 129.5, 128.8, 127.5, 127.1, 126.9, 126.8, 120.9, 120.7 (q, J = 319 Hz), 120.1, 110.3, 57.1, 56.8. ESI HRMS: calcd. For C₃₉H₃₄NO₂⁺ 418.1802, found 418.1807.

6,7,8-Triphenyl-[1,3]dioxolo[4,5-g]isoquinolinium trifluoromethanesulfonate (3la). 6,7,8-Triphenyl-[1,3]dioxolo[4,5-g]isoquinolinium trifluoromethanesulfonate (3la'); (3la:3la' = 10:1). 74% yield; IR (KBr) 3470, 3062, 1630 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.74 (s, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.34 (m, 3H), 7.21 (m, 5H), 7.00 (m, 5H), 6.05 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 155.4, 151.4, 143.8, 142.1, 141.9, 131.3, 130.3, 129.5, 129.1, 128.3, 127.8, 127.6, 126.8, 122.7, 122.6, 120.6 (q, J = 319 Hz), 116.0, 103.9. ESI HRMS: calcd. For C₃₈H₃₄NO₂⁺ 402.1489, found 402.1493.

1,2,3-Triphenylbenzo[f]isoquinolinium trifluoromethanesulfonate (3ma). 80% yield; IR (KBr) 3463, 3062, 1613 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 10.12 (s, 1H), 8.85 (d, J = 7.6 Hz, 1H), 8.25 (t, J = 9.2 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.62-7.57 (m, 3H), 7.37-7.36 (m, 3H), 7.32 (m, 5H), 7.15-7.13 (m, 2H), 7.06-7.00 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 147.3, 143.5, 142.6, 140.7, 139.7, 139.3, 133.5, 132.4, 131.1, 130.5, 129.7, 129.6, 129.3, 128.8, 128.6, 127.9, 127.1, 123.5, 122.8, 120.5 (q, J = 319 Hz). ESI HRMS: calcd. For C₃₁H₂₂N⁺ 408.1747, found 408.1749.
2-Phenyl-3,4-dip-tolylisoquinolinium trifluoromethanesulfonate (3ab). 72 % yield; IR (KBr) 3564, 3492, 3066, 1625, 1491 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.96 (s, 1H), 8.70 (d, \(J = 8.0\) Hz, 1H), 8.05 (t, \(J = 8.0\) Hz, 1H), 7.97 (t, \(J = 8.0\) Hz, 1H), 7.70 (d, \(J = 8.0\) Hz, 1H), 7.50-7.48 (m, 2H), 7.37 (m, 3H), 7.15-7.09 (m, 4H), 6.91-6.89 (m, 2H), 6.84-6.82 (s, 2H), 2.34(s, 3H), 2.15 (s, 3H). 13C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.9, 144.6, 142.3, 139.5, 139.3, 139.0, 138.6, 137.7, 132.0, 131.2, 131.0, 130.4, 130.2, 129.5, 129.3, 128.7, 128.2, 126.9, 126.8, 126.6, 120.6 (q, \(J = 319\) Hz), 21.32, 21.27. ESI HRMS: calcld. For C\(_{29}\)H\(_{24}\)N\(^+\) 386.1903, found 386.1898.

3,4-Bis(4-methoxyphenyl)-2-phenylisoquinolinium trifluoromethanesulfonate (3ac). 75% yield; IR (KBr) 3561, 3500, 3066, 1611 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.83 (s, 1H), 8.61 (d, \(J = 8.0\) Hz, 1H), 8.04 (t, \(J = 8.0\) Hz, 1H), 7.93 (t, \(J = 7.6\) Hz, 1H), 7.79 (d, \(J = 8.4\) Hz, 1H), 7.50-7.48 (m, 2H), 7.37-7.35 (m, 3H), 7.15 (d, \(J = 8.4\) Hz, 2H), 6.95 (d, \(J = 8.4\) Hz, 2H), 6.85 (d, \(J = 7.6\) Hz, 2H), 3.79 (s, 3H), 3.64 (s, 3H). 13C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 159.7, 159.6, 150.6, 144.7, 142.4, 139.5, 139.2, 137.6, 132.7, 131.9, 131.7, 131.1, 130.4, 129.6, 126.9, 126.7, 126.6, 125.3, 123.3, 120.6 (d, \(J = 319\) Hz), 114.1, 113.5, 55.3, 55.1. ESI HRMS: calcld. For C\(_{29}\)H\(_{24}\)NO\(_2\)\(^+\) 418.1802, found 418.1798.

3,4-Bis(4-chlorophenyl)-2-phenylisoquinolinium trifluoromethanesulfonate (3ad). 65% yield; IR (KBr) 3564, 3242, 3066, 2924, 1626 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.75 (s, 1H), 8.55 (d, \(J = 8.0\) Hz, 1H), 8.09 (t, \(J = 8.0\) Hz, 1H), 7.96 (t, \(J = 7.6\) Hz, 1H), 7.72 (d, \(J = 8.0\) Hz, 1H), 7.56-7.55 (m, 2H), 7.42-7.35 (m, 5H), 7.27-7.25 (m, 2H), 7.11-7.09 (m, 2H), 7.05-7.03 (m, 2H). \(^1\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 150.9, 144.6, 142.3, 139.5, 139.0, 138.6, 137.7, 132.0, 131.2, 131.0, 130.4, 130.2, 129.5, 129.3, 128.7, 128.2, 126.9, 126.8, 126.6, 120.6 (q, \(J = 319\) Hz). ESI HRMS: calcld. For C\(_{27}\)H\(_{18}\)Cl\(_2\)N\(^+\) 426.0811, found 426.0824, 426.0841, 430.0847.

3,4-Bis(2-chlorophenyl)-2-phenylisoquinolinium trifluoromethanesulfonate (3ae). 64% yield; IR (KBr) 3564, 3242, 3064, 2924, 1626 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.80 (s, 1H), 8.58 (d, \(J = 8.4\) Hz, 1H), 8.10 (t, \(J = 7.6\) Hz, 1H), 7.96 (t, \(J = 7.6\) Hz, 1H), 7.72 (d, \(J = 8.0\) Hz, 1H), 7.56-7.55 (m, 2H), 7.42-7.35 (m, 5H), 7.27-7.25 (m, 2H), 7.11-7.09 (m, 2H), 7.05-7.03 (m, 2H). \(^1\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 151.3, 142.9, 141.8, 138.5, 138.1, 137.9, 134.7, 134.5, 133.9, 132.5, 131.9, 131.5, 130.7, 130.0, 129.6, 129.4, 129.2, 127.0, 126.8, 126.4, 120.4, 119.1 (q, \(J = 259\) Hz). ESI HRMS: calcld. For C\(_{27}\)H\(_{18}\)Cl\(_2\)N\(^+\) 426.0811, found 426.0815, 428.0798, 430.0801.

3,4-Dibutyl-2-phenylisoquinolinium trifluoromethanesulfonate (3af). 49 % yield; IR (KBr) 3446, 3066, 1631 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.73 (s, 1H), 8.59 (d, \(J = 8.0\) Hz, 1H), 8.22-8.16 (m, 2H), 7.92 (t, \(J = 7.2\) Hz, 1H), 7.86-7.78 (m, 2H), 7.70 (d, \(J = 8.0\) Hz, 1H), 7.50-7.48 (m, 2H), 7.37-7.35 (m, 3H), 7.15-7.12 (m, 4H), 6.92-6.89 (m, 2H), 6.84-6.82 (s, 2H), 2.34(s, 3H), 2.15 (s, 3H). 13C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.9, 144.6, 142.3, 139.5, 139.0, 138.6, 137.7, 132.0, 131.2, 131.0, 130.4, 130.2, 129.5, 129.3, 128.7, 128.2, 126.9, 126.8, 126.6, 120.6 (q, \(J = 319\) Hz), 21.32, 21.27. ESI HRMS: calcld. For C\(_{30}\)H\(_{24}\)N\(^+\) 386.1903, found 386.1898.
Hz, 1H), 7.69-7.68 (m, 3H), 7.63 (m, 2H), 3.20 (t, \(J = 8.0\) Hz, 2H), 2.86 (t, \(J = 8.0\) Hz, 2H), 1.75-1.71 (m, 2H), 1.65-1.59 (m, 2H), 1.48 (t, \(J = 8.0\) Hz, 2H), 1.24-1.18 (m, 2H), 1.05 (t, \(J = 7.2\) Hz, 3H), 0.73 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.2, 144.2, 140.1, 137.2, 136.7, 136.3, 131.6, 130.5, 129.6, 129.3, 125.1, 125.0, 122.6, 119.6 (q, \(J = 3.3.\) Hz, 3H), 0.73 (t, \(J = 1.75-1.71\) Hz, 1H), 7.69-7.68 (m, 3H), 7.63 (m, 2H), 3.20 (t, \(J = 1.75-1.71\) Hz, 2H), 1.65-1.59 (m, 2H), 1.48 (t, \(J = 8.0\) Hz, 1H), 7.45-7.42 (m, 5H), 7.38-7.36 (m, 8H), 7.31-7.29 (m, 4H), 7.25-7.24 (m, 2H), 7.17 (d, \(J = 8.4\) Hz, 2H), 4.05 (s, 3H), 4.03 (s, 4H), 4.00 (s, 3H), 3.38 (s, 4H), 2.75 (s, 2H), 2.18 (s, 5H).

3. Substrate scope of unsymmetrically disubstituted alkynes

Unfortunately, asymmetric disubstituted alkynes as coupling partners can be employed in the reaction but giving the two isomers which were very hard to separate and confirm the structure. Only the structure of 3kg and 3kg' can be confirmed in 82% yield but albeit with poor regioselectivity.

4. NMR spectra of isoquinolinium salts derived fused compounds and structure determination
Internal standard

$\text{CH}_3\text{SO}_3^-$
3da
3ga
3ia
The single peaks indicate the other isomer is 3la'.

Noe of Hc

Noe of Ha

irradiation of Hb at 8.42ppm
3ma
irradiation of Ha at 10.19ppm

noe of Hb

Noe of Hc
3ad

3ad
3ae
noe of Hₐ at 7.715 ppm
noe of H₈ at 7.347 ppm
irradiation of Hc at 2.173 ppm