Supporting Information

Rhodium-catalyzed olefination of aryl tetrazoles via direct C-H bond activation

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1 General experimental details

Chemicals were used as received without special purification unless stated otherwise. $^1$H and $^{13}$C NMR were recorded at ambient temperature on a 300 or 500 MHz NMR spectrometer (125 MHz for $^{13}$C NMR). NMR experiments are reported in $\delta$ units, parts per million (ppm), and were referenced to CDCl$_3$ ($\delta$ 7.26 or 77.0 ppm) as the internal standard. The coupling constants $J$ are given in Hz. Melting points (m.p.) are determined with a MPA 100 apparatus and are not corrected. High-resolution mass spectrometry (HRMS) was performed on a TOF MS instrument with an ESI source.

**General procedure for the 5-aryl-1H-tetrazoles:**

![ Chemical Reaction Diagram ](image)

5-aryl-1H-tetrazoles were prepared according to the literature$^{[1]}$. To a 250 mL round-bottomed flask was added the nitrile (20 mmol), sodium azide (1.43 g, 22 mmol), zinc bromide (4.50 g, 20 mmol) and 40 mL of water. The reaction mixture was refluxed for 24 h; vigorous stirring is essential. HCl (3 N, 30 mL) and ethyl acetate (100 mL) were added, and vigorous stirring was continued until no solid was present and the aqueous layer had a pH of 1. If necessary, additional ethyl acetate was added. The organic layer was isolated and the aqueous layer extracted with $2 \times 100$ mL of ethyl acetate. The combined organic layers were evaporated, 200 mL of 0.25 N NaOH was added, and the mixture was stirred for 30 min., until the original precipitate was dissolved and a suspension of zinc hydroxide was formed. The suspension was filtered, and the solid washed with 20 mL of 1 N NaOH. To the filtrate was added 40 mL of 3 N HCl with vigorous stirring causing the tetrazole to precipitate. The tetrazole was filtered and washed with HCl (3 N, $2 \times 20$ mL) and dried in a drying oven to furnish the tetrazole as a white or slightly colored powder.
General procedure for N-methylation of 5-aryl-1H-tetrazoles:

\[
\begin{align*}
R & \quad N \quad N \\
\text{N-methylation of 5-aryl-1H-tetrazoles were prepared as follows:}^{[2]} & \\
& \text{In a flame-dried 100-mL Schlenk flask, a solution of the corresponding 5-aryl-1H-tetrazoles (10.0 mmol, 1.00 equiv) in dry DMF (20 mL) is added slowly via syringe to a suspension of oil-free sodium hydride (0.288 g, 12.0 mmol, 1.20 equiv) in dry DMF (40 mL) at 0°C. After complete addition, the reaction mixture is maintained at 0°C for an additional hour, followed by dropwise addition of methyl iodide (0.810 mL, 1.85 g, 13.0 mmol, 1.30 equiv). The reaction mixture is stirred at room temperature for 1-3 h until complete consumption of the starting materials (TLC). The reaction is carefully quenched with saturated aqueous NH}_4\text{Cl solution (25 mL), and the aqueous layer is extracted with tert-butyl methyl ether (25 mL} \times 3). The combined organic phases are washed with brine (5 mL) and dried over anhydrous Na}_2\text{SO}_4. After evaporation of the solvents under reduced pressure, the resulting residue is purified by flash column chromatography on silica gel using cyclohexane/tert-butyl methyl ether mixtures, affording the 2-methyl-5-aryl-2H-tetrazoles (1a–1m) in analytically pure form.}
\end{align*}
\]

Synthesis of d5-2-methyl-5-phenyl-2H-tetrazole:

The d5-benzonitrile was prepared as follows:thur[3] To a solution of d8-toluene (10 mmol, 1.00 g, 99.5% of D) in dry CCl4 (10 mL) were added DBDMH (5.5 mmol, 1.57 g) and benzoyl peroxide (1 mmol, 0.32 g) at room temperature, and the mixture was stirred for 3 hours at 80 °C. Then, the mixture was cooled to r.t., followed by
slow addition of aq. NH₃ (concentration: 28.0~30.0 %, 30 mL) and I₂ (25 mmol, 6.35 g), and then stirred for 12 hours at 60 °C. The reaction mixture was quenched by the addition of saturated aq. Na₂SO₃ (30 mL) and extracted with CHCl₃ (20 mL×3). The organic layer was dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue (without purification) reacted with NaN₃, followed by N-methylation with CH₃I to provide the d₅-2-methyl-5-phenyl-2H-tetrazole (1a’) in 51% yield.

**General procedure for C–H olefination:**

A sealed tube was charged with 2-methyl-5-aryl-2H-tetrazoles (0.1 mmol, 1 equiv), olefin (0.2 mmol, 2 equiv), Cu(OAc)₂ (0.2 mmol, 2 equiv), RhCp*(CH₃CN)₅(SbF₆)₂ (0.005 mmol, 5 mol%) and dioxane (1.5 mL). The mixture was kept stirring under air at 110 °C for 12 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature, concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate-dichloromethane as eluent to give the desired product.

**2 KIE experiment of 2-methyl-5-phenyl-2H-tetrazole:**

In a sealed tube, the mixture of 1a (0.1 mmol) and 1 a’ (0.1 mmol) was treated by standard procedures and heated for 5 min.. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate-dichloromethane as eluent to give product 4aa and 4aa’. The mixture was analyzed using ¹H NMR spectrometer. As shown in Figure S1, the ratio of 4aa and 4aa’ is 2.85:1.
Scheme S1 KIE experiment of 1a and 1a’

Figure S1 The $^1$H NMR spectrum of the KIE results
3 Characterization data for the products

(2E,2'E)-dimethyl 3,3’-(2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)diacrylate (3aa):

```
O
N
N
N
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Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (30.2 mg, 92% yield) as a white solid. mp: 146.1-148.4 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.75 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 1H), 7.48 (d, J = 15.9 Hz, 2H), 6.38 (d, J = 15.9 Hz, 2H), 4.49 (s, 3H), 3.74 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ 166.6, 161.9, 141.8, 135.8, 130.5, 128.1, 127.5, 121.0, 51.7, 39.9. HRMS (ESI): Calcd. for C₁₆H₁₆N₄O₄Na (M+Na)⁺ 351.1064, found 351.1060.

(2E,2'E)-dimethyl 3,3’-(5-methyl-2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)diacrylate (3ba):

```
N
N
N
N
```

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (32.2 mg, 94% yield) as a white solid. mp: 168.1-169.4 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.55 (s, 2H), 7.46 (d, J = 15.9 Hz, 2H), 6.36 (d, J = 15.9 Hz, 2H), 4.46 (s, 3H), 3.72 (s, 6H), 2.44 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 166.7, 161.9, 142.0, 140.5, 135.7, 128.9, 124.9, 120.7, 51.7, 39.8, 21.4. HRMS (ESI): Calcd. for C₁₇H₁₈N₄O₄Na (M+Na)⁺ 365.1220, found 365.1217.

(2E,2'E)-dimethyl 3,3’-(5-methoxy-2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)diacrylate (3ca):

```
N
N
N
N
```

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1)
give the product (34.0 mg, 95% yield) as a white solid. mp: 141.9-144.6 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.47 (d, \(J = 15.8\) Hz, 2H), 7.23 (s, 2H), 6.35 (d, \(J = 16.4\) Hz, 2H), 4.46 (s, 3H), 3.89 (s, 3H), 3.72 (s, 6H); \(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 166.6, 161.8, 160.5, 141.9, 137.2, 121.1, 120.3, 113.5, 55.5, 51.7, 39.8. HRMS (ESI): Calcd. for C\(_{17}\)H\(_{18}\)N\(_4\)O\(_5\)Na (M+Na)\(^+\) 381.1169, found 381.1165.

\((2E,2'E)-\text{dimethyl \ } 3,3'-(5\text{-bromo-2-(2-methyl-2H-tetrazol-5-yl)}-1,3\text{-phenylene})\text{diacrylate (3da):}\)

\[
\text{MeO}_2C\begin{array}{c}||\end{array}\begin{array}{c}||\end{array}\text{Br}
\]

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane, 10:1:1) give the product (36.1 mg, 89% yield) as a white solid. mp: 178.3-180.1 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.86 (s, 2H), 7.43 (d, \(J = 15.8\) Hz, 2H), 6.38 (d, \(J = 15.8\) Hz, 2H), 4.48 (s, 3H), 3.74 (s, 6H).

\(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 166.3, 161.2, 140.5, 137.6, 130.8, 126.2, 124.9, 122.2, 51.9, 39.9. HRMS (ESI): Calcd. for C\(_{16}\)H\(_{15}\)BrN\(_4\)O\(_4\)Na (M+Na)\(^+\) 429.0169, found 429.0164.

\((2E,2'E)-\text{dimethyl \ } 3,3'-(5\text{-fluoro-2-(2-methyl-2H-tetrazol-5-yl)}-1,3\text{-phenylene})\text{diacrylate (3ea):}\)

\[
\text{MeO}_2C\begin{array}{c}||\end{array}\begin{array}{c}||\end{array}\text{F}
\]

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (32.2 mg, 93% yield) as a white solid. mp: 164.4-166.0 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.45 (s, 1H), 7.44 (d, \(J = 15.8\) Hz, 2H), 7.42 (s, 1H), 6.37 (d, \(J = 15.9\) Hz, 2H), 4.49 (s, 3H), 3.75 (s, 6H); \(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 166.3, 163.3 (d, \(J_{C,F} = 251.1\) Hz), 161.2, 140.7 (d, \(J_{C,F} = 1.7\) Hz), 138.4 (d, \(J_{C,F} = 8.4\) Hz), 123.8 (d, \(J_{C,F} = 3.0\) Hz), 122.1, 114.8 (d, \(J_{C,F} = 23.0\) Hz), 51.9, 39.9. HRMS (ESI): Calcd. for C\(_{16}\)H\(_{16}\)FN\(_4\)O\(_4\) (M+H)\(^+\) 347.1150, found 347.1152.

\((2E,2'E)-\text{dimethyl \ } 3,3'-(2-(2-methyl-2H-tetrazol-5-yl)-5-(trifluoromethyl)}-1,3\text{-phenylene})\text{diacrylate (3fa):}\)
Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (36.4 mg, 92% yield) as a white solid. mp: 159.9-162.0 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.94 (s, 2H), 7.49 (d, $J = 15.9$ Hz, 2H), 6.45 (d, $J = 15.9$ Hz, 2H), 4.50 (s, 3H), 3.75 (s, 6H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 166.2, 160.9, 140.5, 137.0, 132.8 (d, $J = 33.2$ Hz), 130.4, 124.5 (q, $J = 3.6$ Hz), 123.1 (q, $J = 271.6$ Hz), 122.7, 51.9, 40.0. HRMS (ESI): Calcd. for C$_{17}$H$_{15}$F$_3$N$_4$O$_4$Na (M+Na)$^+$ 419.0938, found 419.0935.

(2E,2'E)-dimethyl 3,3'-(5-cyano-2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)diacrylate (3ga):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (20.5 mg, 58% yield) as a white solid. mp: 210.3-211.5 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.97 (s, 2H), 7.48 (d, $J = 15.9$ Hz, 2H), 6.42 (d, $J = 15.9$ Hz, 2H), 4.51 (s, 3H), 3.77 (s, 6H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 166.0, 160.6, 139.8, 137.5, 131.0, 130.8, 123.3, 117.1, 115.0, 52.0, 40.0. HRMS (ESI): Calcd. for C$_{17}$H$_{15}$N$_5$O$_4$Na (M+Na)$^+$ 376.1016, found 376.1025.

(E)-methyl 3-(5-cyano-2-(2-methyl-2H-tetrazol-5-yl)phenyl)acrylate (4ga):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (8.3 mg, 31% yield) as a white solid. mp: 161.1-164.5 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.44 (d, $J = 15.9$ Hz, 1H), 8.24 (d, $J = 8.1$ Hz, 1H), 7.98 (s, 1H), 7.77 (d, $J = 9.7$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 4.47 (s, 3H), 3.83 (s, 3H). $^{13}$C
NMR (CDCl$_3$, 125 MHz): $\delta$ 166.6, 163.1, 141.3, 135.0, 132.5, 131.3, 130.7, 130.5, 122.6, 117.7, 114.3, 52.0, 39.8. HRMS (ESI): Calcd. for C$_{13}$H$_{12}$N$_5$O$_2$ (M+H)$^+$ 270.0986, found 270.0972.

$(2E,2'E)$-dimethyl 3,3'-(4-methyl-2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)diacrylate (3ha):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (17.4 mg, 51% yield) as a white solid. mp: 108.2-109.0 $^\circ$C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.58 (d, $J$ = 8.0 Hz, 1H), 7.51 (d, $J$ = 16.3 Hz, 1H), 7.34 (d, $J$ = 8.2 Hz, 1H), 7.29 (d, $J$ = 15.8 Hz, 1H), 6.31 (d, $J$ = 15.8 Hz, 1H), 5.67 (d, $J$ = 17.0 Hz, 1H), 4.40 (s, 3H), 3.66 (s, 6H), 2.36 (s, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 166.8, 166.2, 162.6, 142.1, 141.6, 138.9, 136.3, 133.3, 132.5, 127.1, 126.4, 125.1, 120.0, 51.7 (51.67, 51.66), 39.7, 21.0. HRMS (ESI): Calcd. for C$_{17}$H$_{18}$N$_4$O$_4$Na (M+Na)$^+$ 365.1220, found 365.1216.

$(E)$-methyl 3-(4-methyl-2-(2-methyl-2H-tetrazol-5-yl)phenyl)acrylate (4ha):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (5.2 mg, 20% yield) as a white solid. mp: 117.2-118.0 $^\circ$C. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.39 (d, $J$ = 15.9 Hz, 1H), 7.84 (s, 1H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.30 (d, $J$ = 7.9 Hz, 1H), 6.43 (d, $J$ = 15.9 Hz, 1H), 4.43 (s, 3H), 3.78 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 167.3, 164.5, 143.1, 140.4, 131.1, 130.9, 130.6, 127.2, 126.8, 119.2, 51.6, 39.6, 21.2. HRMS (ESI): Calcd. for C$_{13}$H$_{15}$N$_4$O$_2$ (M+H)$^+$ 259.1190, found 259.1177.

$(2E,2'E)$-dimethyl 3,3'-(2-(2-methyl-2H-tetrazol-5-yl)-4-nitro-1,3-phenylene)diacrylate (3ia):

S9
Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (8.2 mg, 22% yield) as a white solid. mp: 135.9-137.2 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.14 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 16.3 Hz, 1H), 7.35 (d, J = 15.9 Hz, 1H), 6.46 (d, J = 15.9 Hz, 1H), 5.65 (d, J = 16.3 Hz, 1H), 4.44 (s, 3H), 3.75 (s, 3H), 3.70 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 165.9, 165.2, 160.9, 148.8, 140.4, 139.6, 139.0, 133.0, 129.0, 127.4, 126.0, 125.4, 124.2, 52.0, 51.9, 39.9. HRMS (ESI): Calcd. for C₁₆H₁₅N₅O₆Na (M+Na)⁺ 396.0915, found 396.0911.

(E)-methyl 3-(2-(2-methyl-2H-tetrazol-5-yl)-4-nitrophenyl)acrylate (4ia):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (5.8 mg, 20% yield) as a white solid. mp: 124.7-127.4 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.94 (d, J = 2.4 Hz, 1H), 8.49 (d, J = 15.9 Hz, 1H), 8.32 (dd, J = 8.7, 2.3 Hz, 1H), 7.87 (d, J = 8.7 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 4.49 (s, 3H), 3.83 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 166.3, 162.9, 148.3, 141.2, 139.6, 128.8, 128.0, 125.1, 124.6, 123.8, 52.0, 39.9. HRMS (ESI): Calcd. for C₁₂H₁₁N₅O₄Na (M+Na)⁺ 312.0703, found 312.0693.

(E)-methyl 3-(3-methyl-2-(2-methyl-2H-tetrazol-5-yl)phenyl)acrylate (3ja):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (24.5 mg, 95% yield) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz): δ 7.57 (d, J = 7.6 Hz, 1H), 7.43-7.32 (m, 2H), 7.42 (d, J = 15.8 Hz, 1H), 6.35 (d, J = 15.9 Hz, 1H), 4.46 (s, 3H), 3.72 (s, 3H), 2.20 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 166.9, 162.9, 142.5, 139.0, 135.0, 131.8, 129.9, 127.5, 124.1, 119.9, 51.5, 39.6, 20.3. HRMS (ESI): Calcd. for C₁₃H₁₄N₄O₂Na (M+Na)⁺ 281.1009, found 281.0997.

(E)-methyl 3-(3-chloro-2-(2-methyl-2H-tetrazol-5-yl)phenyl)acrylate (3ka):
Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (25.0 mg, 90% yield) as a white solid. mp: 102.9-104.8 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.71-7.68 (m, 1H), 7.59-7.57 (m, 2H), 7.08 (d, J = 15.9 Hz, 1H), 6.34 (d, J = 15.9 Hz, 1H), 4.41 (s, 3H), 3.65 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 166.4, 161.1, 140.9, 137.2, 135.6, 131.3, 131.0, 127.2, 124.9, 121.5, 51.7, 39.8. HRMS (ESI): Calcd. for C₁₂H₁₁ClN₄O₂Na (M+Na)⁺ 301.0463, found 301.0458.

(2E,2'E)-dimethyl 3,3'-(5-(2-methyl-2H-tetrazol-5-yl)benzo[d][1,3]dioxole-4,6-diyl)diacrylate (3la):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (34.2 mg, 92% yield) as a white solid. mp: 201.3-202.6 °C. ¹H NMR (CDCl₃, 300 MHz): δ 7.42 (d, J = 15.9 Hz, 1H), 7.41 (d, J = 17.3 Hz, 1H), 7.32 (s, 1H), 6.89 (d, J = 16.1 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.32 (s, 2H), 4.61 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 167.2, 166.8, 161.6, 149.5, 148.4, 141.5, 136.4, 130.3, 123.7, 122.6, 119.2, 117.7, 106.6, 102.5, 51.7 (51.71, 51.67), 39.9. HRMS (ESI): Calcd. for C₁₇H₁₆N₄O₆Na (M+Na)⁺ 395.0962, found 395.0964.

(2E,2'E)-dimethyl 3,3'-(2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)bis(but-2-enoate) (3ab):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (8.9 mg, 25% yield) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz): δ 7.49 (d, J = 8.2 Hz, 2H), 7.47-7.35 (m, 3H), 4.39 (s, 3H), 3.73 (s, 6H), 1.95 (s, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 168.4, 162.7, 137.4, 137.0, 130.0, 129.2, 126.7, 125.4, 52.0, 39.6, 14.0. HRMS (ESI): Calcd. for C₁₈H₂₀N₄O₄Na (M+Na)⁺ 379.1377, found 379.1369.
(E)-methyl 3-(2-(2-methyl-2H-tetrazol-5-yl)phenyl)but-2-enoate (4ab):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (7.2 mg, 28% yield) as a colorless oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta \) 8.09 (dd, \(J = 7.3, 1.7 \text{ Hz}, 1\)H), 8.03 (s, 1H), 7.53-7.35 (m, 3H), 4.39 (s, 3H), 3.81 (s, 3H), 1.98 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta \) 168.8, 164.7, 138.9, 134.9, 130.1, 129.6, 129.4, 128.7, 128.3, 126.4, 51.9, 39.5, 14.0. HRMS (ESI): Calcd. for C\(_{13}\)H\(_{14}\)N\(_4\)O\(_2\)Na (M+Na)\(^+\) 281.1009, found 281.0997.

(2E,2'E)-diethyl 3,3'-(2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)diacrylate (3ac):

Flash column chromatography on a silica gel (PE/EtOAc/dichloromethane = 10:1:1) give the product (31.7 mg, 89% yield) as a white solid. mp: 134.9-136.7 \(^\circ\)C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta \) 7.74 (d, \(J = 7.8 \text{ Hz}, 2\)H), 7.53 (d, \(J = 7.9 \text{ Hz}, 1\)H), 7.46 (d, \(J = 15.9 \text{ Hz}, 2\)H), 6.36 (d, \(J = 15.8 \text{ Hz}, 2\)H), 4.47 (s, 3H), 4.17 (q, \(J = 7.1 \text{ Hz}, 4\)H), 1.25 (t, \(J = 7.1 \text{ Hz}, 6\)H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta \) 166.2, 161.8, 141.5, 135.9, 130.4, 128.0, 127.6, 121.5, 60.6, 39.8, 14.2. HRMS (ESI): Calcd. for C\(_{18}\)H\(_{20}\)N\(_4\)O\(_4\)Na (M+Na)\(^+\) 379.1377, found 379.1370.

(2E,2'E)-di-tert-butyl 3,3'-(2-(2-methyl-2H-tetrazol-5-yl)-1,3-phenylene)diacrylate (3ad):

Flash column chromatography on a silica gel (PE/EtOAc = 10:1) give the product (25.6 mg, 62% yield) as a white solid. mp: 171.8-174.2 \(^\circ\)C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta \) 7.75 (d, \(J = 7.9 \text{ Hz}, 2\)H), 7.51 (t, \(J = 7.9 \text{ Hz}, 1\)H), 7.36 (d, \(J = 15.8 \text{ Hz}, 2\)H), 6.32 (d, \(J = 15.8 \text{ Hz}, 2\)H), 4.48 (s, 3H), 1.47 (s, 18H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta \) 165.5, 161.9, 140.4, 136.0, 130.3, 127.6, 123.1, 121.1, 80.6, 39.7, 28.1. HRMS (ESI): Calcd. for C\(_{22}\)H\(_{28}\)N\(_4\)O\(_4\)Na (M+Na)\(^+\) 435.2003, found 435.1995.
5-(2,6-di((E)-styryl)phenyl)-2-methyl-2H-tetrazole (3ae):

Flash column chromatography on a silica gel (PE/EtOAc = 10:1) give the product (33.5 mg, 92% yield) as a white solid. mp:164.7-165.9 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta 7.70 (d, J = 7.8 \text{ Hz}, 2H), 7.55-7.44 (m, 1H), 7.37-7.16 (m, 10H), 7.02 (d, J = 16.1 \text{ Hz}, 2H), 6.85 (d, J = 16.1 \text{ Hz}, 2H), 4.45 (s, 3H).\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta 138.5, 137.1, 131.4, 130.2, 128.6, 127.8, 126.8, 126.7, 126.7, 126.3, 125.0, 39.7.\) HRMS (ESI): Calcd. for C\(_{24}\)H\(_{20}\)N\(_4\)Na (M+Na)^+ 387.1580, found 387.1573.
4 Copies of $^1$H NMR and $^{13}$C NMR spectra
$^{1}H$ NMR

$^{13}C$ NMR
3ad, $^1$H NMR

3ad, $^{13}$C NMR
5 Reference

