Electronic Supplementary Information

Electrochemical Multicomponent Reaction toward C–H Tetrazolation of Alkyl Arenes and Vicinal Azidotetrazolation of Alkenes

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1 General information

All reactions were performed under an atmosphere of nitrogen using standard undivided three-necked glassware, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance ($^1$H NMR) spectra, carbon nuclear magnetic resonance ($^{13}$C NMR) spectra and fluorine nuclear magnetic resonance ($^{19}$F NMR) were recorded on Bruker AV-400 (400 MHz), JEOL-500 (500 MHz), and JEOL ECZ600S (600 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl$_3$ = $\delta$ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR. HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer and Aglient 1290-6545xt with the use of quadrupole analyzer. All chemicals were purchased from TCI Shanghai or Energy Chemical and used as received.

Electrolysis experiments were performed using MESTEK DC power supply, graphite rod (ϕ 6 mm, >99.99%), electrode clips (PT-1 or PT-3) and platinum plate (99.99%, 15*15*1 mm) was purchased from Gaoss Union. The graphite plate (>99.99%) was cut into 15 x 15 x 0.3 mm pieces before use, and was clamped between electrode clips.

CAUTION: Organic azides are known to be potentially explosive compounds. While we did not encounter any issues during their synthesis, proper precautions were taken. All azidation reactions and subsequent workups should be performed behind a blast shield. Once isolated, organic azides should be stored below room temperature and away from sources of heat, light, pressure and shock.
Figure S1. Electrolysis setup

[Description of the electrolysis setup with labels for PT-3, PT-1, platinum plate, graphite plate, graphite rod, and connections 24#, 19#, 19#.]
2. General procedures

General procedure for the electrochemical C–H tetrazolation

![Chemical reaction diagram]

**Method A:** In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, $^n$Bu$_4$NClO$_4$ (0.3 mmol) was added. The glassware was equipped with a graphite rod (φ 6 mm, about 20±1 mm immersion depth in solution) as the anode and a platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N$_2$, alkyl arenes (0.3 mmol), TMSN$_3$ (1.7 equiv.), CH$_3$CN (10 mL), and HFIP (1 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 75 mA at room temperature for 20 minutes. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

**Method B:** In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, LiClO$_4$ (0.3 mmol) was added. The glassware was equipped with a graphite rod (φ 6 mm, about 20±1 mm immersion depth in solution) as the anode and a platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N$_2$, alkyl arenes (0.3 mmol), TMSN$_3$ (1.7 equiv.), CH$_3$CN (10 mL), and HFIP (1 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 75 mA at room temperature for 23 minutes. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

**Method C:** General procedure for the electrochemical synthesis of vicinal azidotetrazoles (constant cell-potential electrolysis)
In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, \( \text{Bu}_4\text{NCIO}_4 \) (0.3 mmol) was added. The glassware was equipped with a graphite plate (15 mm × 15 mm × 1 mm) as the anode and a platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N\(_2\), olefin substrates (0.3 mmol), TMSN\(_3\) (2.5 equiv.), CH\(_3\)CN (10 mL), and HFIP (0.8 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant cell potential of 2.8 V at room temperature for 4 h. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.
3. Optimization of reaction conditions

**Table S1.** Screening of electrode materials

| Entry | (+) \(\text{C}_{\text{rod}}\) | (-) \(\text{Pt}\) | Yield \(^{a}\) / % |
|-------|-----------------|----------------|------------------|
| 1     | \(\text{C}_{\text{rod}}\) | \(\text{Pt}\)   | 57/61\(^{b}\)    |
| 2     | \(\text{C}_{\text{felt}}\) | \(\text{Pt}\)   | 11               |
| 3     | \(\text{C}_{\text{block}}\) | \(\text{Pt}\)   | 47/54\(^{b}\)    |
| 4     | \(\text{C}_{\text{rod}}\) | \(\text{Ni}\)   | 52               |
| 5     | \(\text{C}_{\text{rod}}\) | \(\text{Fe}\)   | 34               |
| 6     | \(\text{C}_{\text{rod}}\) | \(\text{C}_{\text{block}}\) | 43               |

\(^{a}\) Yield was determined by \(^1\)H NMR with 1,3,5-trimethoxybenzene as the internal standard; \(^{b}\) isolated yield.

**Table S2.** Screening of current

| Entry | \(\text{mA}, \text{t / min}\) | Yield \(^{a}\) / % |
|-------|-------------------------------|------------------|
| 1     | 20, 70                        | 62               |
| 2     | 25, 60                        | 62               |
| 3     | 50, 30                        | 62/68\(^{b}\)    |
| 4     | 75, 20                        | 62/68\(^{b}\)    |
| 5     | 150, 10                       | 48               |

\(^{a}\) Yield was determined by \(^1\)H NMR with 1,3,5-trimethoxybenzene as the internal standard; \(^{b}\) isolated yield.
Table S3. Screening of the amount of TMSN₃

| Entry | TMSN₃ (X equiv.) | 4, Yield⁹ | 25, Yield⁹ |
|-------|-----------------|-----------|------------|
| 1     | 1.3             | 49        | --         |
| 2     | 1.5             | 57        | --         |
| 3     | 1.7             | 63        | --         |
| 4     | 2               | 57        | 60         |
| 5     | 2.2             | 55        | 64         |
| 6     | 2.5             | --        | 68         |
| 7     | 2.7             | --        | 56         |
| 8     | 3.5             | --        | 46         |

⁹ Yield was determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard.

Table S4. Screening of the amount of H₂O

| Entry | H₂O (X equiv.) | Yield (%)⁹ |
|-------|----------------|------------|
| 1     | 0              | 63b        |
| 2     | 0              | 33         |
| 3     | 3              | 18         |
| 4     | 10             | 2          |

⁹ Yield was determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard, undehydrated acetonitrile; b dry acetonitrile.
4. Procedure for control experiments using chemical oxidants

In an oven-dried schlenk (10 mL) equipped with a stirring bar, "Bu₄NClO₄ (0.1 mmol) was added. Under the protection of N₂, 4-ethylfluorobenzene or 4-tert-butylstyrene (0.1 mmol), TMSN₃ (1.7 or 2.5 equiv.), oxidant (1 equiv.), CH₃CN/HFIP (1:0.1) were injected respectively into the glassware via syringes. The reaction mixture was stirred at room temperature for 4 h. Following concentration in vacuo, the yield and conversion were determined by NMR of the crude reaction mixture with PhOCF₃ or CH₂Br₂ as the internal standard.

| Entry | Oxidant     | 4, yield (Conv, %)ᵃ | 26, yield (Conv, %)ᵃ |
|-------|-------------|---------------------|----------------------|
| 1     | anode       | 68 (>95)            | 70 (>95)             |
| 2     | NFSI        | n.d. (11)           | n.d. (51)            |
| 3     | TBHP        | n.d. (20)           | n.d. (73)            |
| 4     | CAN         | n.d. (36)           | n.d. (35)            |
| 5     | m-CPBA      | n.d. (14)           | n.d. (22)            |
| 6     | DDQ         | n.d. (15)           | n.d. (91)            |
| 7     | Phl(OAc)₂   | n.d. (30)           | n.d. (>95)           |
| 8     | Mn(OAc)₃    | n.d. (69)           | n.d. (>95)           |
| 9     | AgNO₃       | n.d. (>95)          | n.d. (>95)           |

ᵃ Yield and conversion were determined by NMR of the crude reaction mixture with PhOCF₃ or CH₂Br₂ as the internal standard; n.d. = not detected.
5 Characterization of products

5-Methyl-1-(1-phenylethyl)-1H-tetrazole (3)

Followed Method A, $F = 3.11$ F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 38.4 mg (68% yield) of 3 as a yellow oil.

IR (neat, cm$^{-1}$): 3055(w), 1733(w), 1402(w), 1264(m), 731(s), 704(s). $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.43 – 7.29 (m, 3H), 7.25 – 7.13 (m, 2H), 5.56 (q, $J = 7.1$ Hz, 1H), 2.38 (s, 3H), 2.05 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 151.2, 138.9, 129.2, 128.7, 126.0, 58.2, 21.8, 9.2. HRMS (ESI) calculated for C$_{10}$H$_{12}$N$_4$Na$^+$ [M+Na]$^+$: 211.0954; found: 211.0952.

1-(1-(4-Fluorophenyl)ethyl)-5-methyl-1H-tetrazole (4)

Followed Method A, $F = 3.11$ F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 33.3 mg (54% yield) of 4 as a white solid.

IR (neat, cm$^{-1}$): 3055(w), 1513(w), 1422(w), 1264(m), 896(s), 731(s). $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.26 – 7.19 (m, 2H), 7.12 – 6.90 (m, 2H), 5.56 (q, $J = 7.1$ Hz, 1H), 2.41 (s, 3H), 2.04 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$162.6 (d, $J = 248.3$ Hz), 151.1, 134.7 (d, $J = 3.4$ Hz), 127.9 (d, $J = 8.4$ Hz), 116.2 (d, $J = 21.8$ Hz), 57.5, 21.9, 9.2. $^{19}$F NMR (471 MHz, Chloroform-d) $\delta$ -112.5 (td, $J = 8.5, 8.1, 4.5$ Hz). HRMS (ESI) calculated for C$_{10}$H$_{11}$FN$_4$Na$^+$ [M+Na]$^+$: 229.0860; found: 229.0862.
1-(1-(4-Chlorophenyl)ethyl)-5-methyl-1H-tetrazole (5)

Followed Method A, \( F = 3.11 \text{ F/mol} \), the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 41.6 mg (62% yield) of 5 as a white solid.

IR (neat, cm\(^{-1}\)): 3055(w), 1493(w), 1264(m), 1091(w), 733(s), 543(w). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \( \delta \) 7.37 – 7.32 (m, 2H), 7.19 – 7.13 (m, 2H), 5.55 (q, \( J = 7.0 \text{ Hz} \), 1H), 2.41 (s, 3H), 2.03 (d, \( J = 7.1 \text{ Hz} \), 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \( \delta \) 151.2, 137.3, 134.7, 129.4, 127.7, 57.5, 21.8, 9.2. HRMS (ESI) calculated for \( \text{C}_{10}\text{H}_{11}\text{ClN}_4\text{Na}^+ \) [M+Na]+: 245.0564; found: 245.0566.

1-(1-(4-Bromophenyl)ethyl)-5-methyl-1H-tetrazole (6)

Followed Method A, \( F = 3.11 \text{ F/mol} \), the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 45.1 mg (57% yield) of 6 as a white solid.

IR (neat, cm\(^{-1}\)): 3054(w), 1405(w), 1264(m), 1074(w), 731(s), 706(m). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \( \delta \) 7.53 – 7.44 (m, 2H), 7.14 – 7.05 (m, 2H), 5.54 (q, \( J = 7.0 \text{ Hz} \), 1H), 2.41 (s, 3H), 2.03 (d, \( J = 7.1 \text{ Hz} \), 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \( \delta \) 151.2, 137.9, 132.3, 127.9, 122.7, 57.5, 21.7, 9.1. HRMS (ESI) calculated for \( \text{C}_{10}\text{H}_{11}\text{BrN}_4\text{Na}^+ \) [M+Na]+: 289.0059; found: 289.0057.

1-Benzyl-5-methyl-1H-tetrazole (7)
Followed **Method A**, \( F = 3.11 \) \( \text{F/mol} \), the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give \( 23.7 \text{mg} \) (45% yield) of 7 as a yellow oil.

IR (neat, \( \text{cm}^{-1} \)): 2930(w), 1528 (m), 1408(m), 1246(w), 726(s), 698(s), 580(w). \( ^1{\text{H}} \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 7.41 – 7.32 (m, 3H), 7.23 – 7.16 (m, 2H), 5.51 (s, 2H), 2.45 (s, 3H). \( ^{13}{\text{C}} \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 151.6, 133.0, 129.2, 128.9, 127.4, 50.8, 9.0. HRMS (ESI) calculated for \( \text{C}_9\text{H}_{11}\text{N}_4^+ \) [M+H]\(^+\): 175.0978; found: 175.0988.

![Image of 5-Methyl-1-(2-methyl-1-phenylpropyl)-1H-tetrazole (8)]

**5-Methyl-1-(2-methyl-1-phenylpropyl)-1H-tetrazole (8)**

Followed **Method A**, \( F = 3.11 \) \( \text{F/mol} \), the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give \( 46.7 \text{mg} \) (72% yield) of 8 as a yellow oil.

IR (neat, \( \text{cm}^{-1} \)): 3055(w), 1422(w), 1264(m), 896(w), 731(s), 524(w). \( ^1{\text{H}} \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 7.45 – 7.36 (m, 2H), 7.38 – 7.31 (m, 3H), 4.75 (d, \( J = 10.5 \text{ Hz} \), 1H), 2.99 (ddt, \( J = 13.2, 10.7, 6.6 \text{ Hz} \), 1H), 2.51 (s, 3H), 0.90 (dd, \( J = 9.1, 6.6 \text{ Hz} \), 6H). \( ^{13}{\text{C}} \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 151.5, 136.8, 129.0, 128.7, 127.6, 70.0, 33.2, 20.1, 20.0, 9.1. HRMS (ESI) calculated for \( \text{C}_{12}\text{H}_{16}\text{N}_4\text{Na}^+ \) [M+Na]\(^+\): 239.1267; found: 239.1272.

![Image of 5-Methyl-1-(1-phenylpentyl)-1H-tetrazole (9)]

**5-Methyl-1-(1-phenylpentyl)-1H-tetrazole (9)**

Followed **Method A**, \( F = 3.11 \) \( \text{F/mol} \), the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give \( 47.1 \text{mg} \) (68% yield) of 9 as a yellow oil.
IR (neat, cm⁻¹): 3055(w), 1423(w), 1264(m), 896(w), 731(s), 706(m). ¹H NMR (500 MHz, Chloroform-⁶d) δ 7.38 – 7.29 (m, 3H), 7.32 – 7.23 (m, 2H), 5.26 (dd, J = 8.7, 6.7 Hz, 1H), 2.58 (dq, J = 15.5, 8.3 Hz, 1H), 2.44 (s, 3H), 2.32 (dq, J = 14.3, 7.4 Hz, 1H), 1.37 (dq, J = 14.6, 7.0 Hz, 2H), 1.25 (h, J = 6.7 Hz, 2H), 0.88 (t, J = 7.3 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-⁶d) δ 151.4, 137.9, 129.0, 128.6, 126.6, 63.0, 35.2, 28.5, 22.1, 13.7, 9.1. HRMS (ESI) calculated for C₁₃H₁₈N₄Na⁺ [M+Na]⁺: 253.1424; found: 253.1423.

1-(4-(1-(5-Methyl-1H-tetrazol-1-yl)ethyl)phenyl)ethan-1-one (10)

Followed Method B, F = 3.58 F/mol the desired pure product was purified using silica gel chromatography (EA) to give 43.7 mg (63% yield) of 10 as a yellow oil.

IR (neat, cm⁻¹): 2991(w), 1683(s), 1406(m), 1267(s), 1077(m), 840(m). ¹H NMR (500 MHz, Methanol-⁶d₁) δ 6.46 – 6.40 (m, 2H), 5.87 – 5.81 (m, 2H), 4.39 (q, J = 7.0 Hz, 1H), 1.03 (s, 3H), 0.91 (s, 3H), 0.46 (d, J = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Methanol-⁶d₁) δ 197.0, 150.7, 143.0, 135.3, 127.4, 124.8, 55.9, 23.9, 19.0, 6.0. HRMS (ESI) calculated for C₁₂H₁₄N₄NaO⁺ [M+Na]⁺: 253.1060; found: 253.1064.

4-(1-(5-Methyl-1H-tetrazol-1-yl)ethyl)-N-(phenylsulfonyl)benzamide (11)

Followed Method B, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (DCM : CH₃OH = 20:1) to give 58.1 mg (53% yield) of 11 as a yellow oil.

IR (neat, cm⁻¹): 3318(m), 2942(w), 2831(w), 1495(w), 1021(s), 625(w). ¹H NMR (600 MHz, Methanol-⁶d₄) δ 8.05 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.63 (t, J =
7.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.87 (q, J = 7.0 Hz, 1H), 2.41 (s, 3H), 1.98 (d, J = 7.0 Hz, 3H). \(^{13}\)C NMR (126 MHz, Methanol-\(d_4\)) \(\delta\) 172.3, 151.5, 143.5, 141.3, 137.6, 130.1, 128.6, 127.2, 126.2, 124.7, 57.1, 20.0, 6.8.

HRMS (ESI) calculated for C\(_{17}\)H\(_{17}\)N\(_5\)NaO\(_3\)S\(^+\) [M+Na\(^+\): 394.0944; found: 394.0947.

2,2,2-Trifluoro-N-(4-(5-methyl-1H-tetrazol-1-yl)-4-phenylbutyl)acetamide (12)

Followed Method A, 20 mA, 90 min, F = 3.73 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1.5) to give 50.5 mg (52% yield) of 12 as a yellow oil.

IR (neat, cm\(^{-1}\)): 3056(w), 1716(w), 1556(w), 1264(m), 1210(w), 731(s), 706(s).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.43 (t, J = 4.7 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.26 – 7.21 (m, 2H), 5.38 (dd, J = 8.7, 6.6 Hz, 1H), 3.50 – 3.39 (m, 2H), 2.68 – 2.58 (m, 1H), 2.43 (s, 3H), 2.36 (ddt, J = 14.1, 9.9, 6.1 Hz, 1H), 1.71 – 1.51 (m, 2H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 157.7 (q, J = 37.0 Hz), 151.9, 137.2, 129.3, 129.0, 126.5, 115.8 (q, J = 287.7 Hz), 62.3, 38.9, 32.4, 25.7, 9.0. HRMS (ESI) calculated for C\(_{14}\)H\(_{16}\)F\(_3\)N\(_5\)NaO\(^+\) [M+Na\(^+\): 350.1199; found: 350.1202.

1-(4-(5-Methyl-1H-tetrazol-1-yl)-4-phenylbutyl)pyrroloidine-2,5-dione (13)

Followed Method A, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 52.7 mg (56% yield) of 13 as a yellow oil.

IR (neat, cm\(^{-1}\)): 3055(w), 1704(w), 1420(w), 1264(m), 897(w), 731(s), 706(s). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.41 – 7.27 (m, 3H), 7.29 – 7.25 (m, 2H), 5.41 (dd, J = 8.5, 6.9 Hz, 1H), 3.56 (t, J = 6.9 Hz, 2H), 2.72 (s, 4H), 2.60 – 2.49 (m, 1H), 2.46 (s, 3H), 2.38 – 2.21 (m, 1H), 1.65 – 1.49 (m, 2H). \(^{13}\)C NMR (126 MHz,
Chloroform-$d$ δ 177.3, 151.6, 137.3, 129.2, 128.8, 126.6, 61.7, 37.2, 32.2, 28.1, 24.2, 9.0. HRMS (ESI) calculated for $C_{16}H_{19}N_5O_2^+$ [M]$^+$: 313.1539; found: 313.1547.

1-(4-Chloro-1-phenylbutyl)-5-methyl-1H-tetrazole (14)
Followed Method A, $F = 3.11$ F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 41.0 mg (55% yield) of 14 as a yellow oil.
IR (neat, cm$^{-1}$): 3055(w), 1443(w), 1264(m), 895(w), 731(s), 704(m). $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.40 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 5.36 (dd, $J = 8.7, 6.7$ Hz, 1H), 3.57 (dtd, $J = 7.0, 3.8, 1.5$ Hz, 2H), 2.79 – 2.65 (m, 1H), 2.60 – 2.49 (m, 1H), 2.44 (s, 3H), 1.87 – 1.69 (m, 2H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 151.6, 137.3, 129.2, 128.9, 126.5, 62.3, 44.0, 32.9, 29.1, 9.1. HRMS (ESI) calculated for $C_{12}H_{15}ClN_4^+$ [M]$^+$: 250.0983; found: 250.0985.

3-(5-Methyl-1H-tetrazol-1-yl)-3-phenylpropyl acetate (15)
Followed Method A, $F = 3.11$ F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 35.9 mg (46% yield) of 15 as a yellow oil.
IR (neat, cm$^{-1}$): 3056(w), 1738(m), 1524(w), 1399(w), 1261(m), 1040(w), 731(s), 704(s). $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.40 – 7.32 (m, 3H), 7.27 (dt, $J = 7.5, 1.7$ Hz, 2H), 5.45 (dd, $J = 8.7, 6.5$ Hz, 1H), 4.10 (ddd, $J = 11.6, 6.7, 4.9$ Hz, 1H), 4.03 (ddd, $J = 11.8, 7.4, 4.6$ Hz, 1H), 2.97 (dddd, $J = 15.4, 8.7, 6.8, 4.6$ Hz, 1H), 2.69 – 2.61 (m, 1H), 2.45 (s, 3H), 2.05 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 170.6,
151.7, 136.9, 129.3, 129.1, 126.6, 60.5, 59.6, 34.6, 20.7, 9.0. HRMS (ESI) calculated for C\textsubscript{13}H\textsubscript{12}N\textsubscript{4}O\textsubscript{2}\textsuperscript{+} [M+H]: 261.1346; found: 261.1353.

Followed Method A, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 60.6 mg (52% yield) of 16 as a colourless oil.

IR (neat, cm\textsuperscript{-1}): 2958(w), 1555(m), 1174(s), 1096(w), 927(m), 734(s), 702(m), 555(s). \textsuperscript{1}H NMR (500 MHz, Chloroform-\textit{d}) \(\delta\) 7.79 – 7.72 (m, 2H), 7.38 – 7.31 (m, 5H), 7.25 – 7.19 (m, 2H), 5.34 (dd, \(J = 8.9, 6.5\) Hz, 1H), 4.05 (t, \(J = 6.0\) Hz, 2H), 2.67 – 2.56 (m, 1H), 2.45 (s, 3H), 2.44 – 2.35 (m, 4H), 1.67 (dt, \(J = 8.1, 6.2\) Hz, 2H). \textsuperscript{13}C NMR (126 MHz, Chloroform-\textit{d}) \(\delta\) 151.7, 145.1, 137.2, 132.5, 129.9, 129.2, 128.9, 127.8, 126.5, 69.6, 62.0, 31.9, 25.6, 21.6, 9.0. HRMS (ESI) calculated for C\textsubscript{19}H\textsubscript{22}N\textsubscript{4}O\textsubscript{3}Na\textsuperscript{+} [M+Na]: 409.1305; found: 409.1307.

Followed Method B, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 37.9 mg (56% yield) of 17 as a white solid.

IR (neat, cm\textsuperscript{-1}): 3055(w), 1693(w), 1422(w), 1264(m), 895(w), 731(s). \textsuperscript{1}H NMR (500 MHz, Chloroform-\textit{d}) \(\delta\) 8.19 – 8.15 (m, 1H), 7.58 – 7.48 (m, 2H), 6.63 (dt, \(J = 6.1, 1.2\) Hz, 1H), 5.99 (dd, \(J = 9.5, 4.5\) Hz, 1H), 3.03 (ddd, \(J = 16.1, 5.8, 3.5\) Hz, 1H), 2.87 – 2.71 (m, 2H), 2.68 – 2.61 (m, 1H), 2.55 (s, 3H). \textsuperscript{13}C NMR (126 MHz, Chloroform-\textit{d}) \(\delta\) 194.8, 151.5, 138.5, 134.4, 132.0, 129.5, 128.1, 126.1, 56.5, 36.0, 29.5, 9.6. HRMS (ESI) calculated for C\textsubscript{12}H\textsubscript{12}NaNaO\textsuperscript{+} [M+Na]\textsuperscript{+}: 251.0903; found: 251.0903.
9-(5-Methyl-1H-tetrazol-1-yl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (18)

Followed Method B, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (PE : EA = 1:2) to give 28.7 mg (40% yield) of 18 as a white solid.

IR (neat, cm\(^{-1}\)): 3055(w), 2158(w), 1683(w), 1422(w), 1264(m), 860(w), 731(s).

\(^1\)H NMR (500 MHz, Chloroform-\(d_2\)) \(\delta\) 7.75 – 7.69 (m, 1H), 7.49 – 7.38 (m, 2H), 6.29 – 6.21 (m, 1H), 5.75 (dd, \(J = 11.7, 5.3\) Hz, 1H), 3.03 – 2.89 (m, 2H), 2.77 (ddd, \(J = 18.3, 12.7, 2.9\) Hz, 1H), 2.55 – 2.43 (m, 1H), 2.35 (s, 3H), 2.19 (ddd, \(J = 18.5, 6.4, 3.9\) Hz, 1H), 1.94 – 1.81 (m, 1H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d_2\)) \(\delta\) 204.8, 152.0, 137.0, 135.6, 133.0, 129.1, 129.0, 123.9, 58.8, 40.3, 30.6, 19.0, 9.1. HRMS (ESI) calculated for C\(_{13}\)H\(_{14}\)N\(_4\)NaO\(_2\)\([\text{M+Na}]^+\): 265.1060; found: 265.1065.

5-((5-Methyl-1H-tetrazol-1-yl)methyl)-N-(phenylsulfonyl)thiophene-2-carboxamide (19)

Followed Method B, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (DCM : CH\(_3\)OH = 10:1) to give 57.7 mg (53% yield) of 19 as a white solid.

IR (neat, cm\(^{-1}\)): 3336(m), 2944(w), 2832(w), 1450(w), 1267(m), 1024(s), 734(s). \(^1\)H NMR (500 MHz, Methanol-\(d_4\)) \(\delta\) 7.98 – 7.90 (m, 2H), 7.51 – 7.39 (m, 4H), 7.02 (d, \(J = 3.8\) Hz, 1H), 5.77 (s, 2H), 2.54 (s, 3H). \(^{13}\)C NMR (126 MHz, Methanol-\(d_4\)) \(\delta\) 167.2, 151.6, 144.5, 143.3, 139.0, 130.2, 129.0, 127.2, 127.2, 126.2, 44.7, 6.7. HRMS (ESI) calculated for C\(_{14}\)H\(_{14}\)N\(_3\)NaO\(_2\)S\(_2\)\([\text{M+Na}]^+\): 386.0352; found:386.0357.
1,1,1,2,2-Pentafluoro-7-(5-methyl-1H-tetrazol-1-yl)-7-phenylheptan-3-one (20)

Followed Method A, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 37.5 mg (35% yield) of 20 as a white solid.

IR (neat, cm\(^{-1}\)): 3056(w), 1754(w), 1401(w), 1264(w), 1201(w), 733(s) 703(s). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.40 – 7.31 (m, 3H), 7.26 – 7.21 (m, 2H), 5.34 – 5.21 (m, 1H), 2.84 (q, \(J = 6.8\) Hz, 2H), 2.71 – 2.52 (m, 1H), 2.43 (s, 3H), 2.41 – 2.33 (m, 1H), 1.67 (dt, \(J = 15.3, 7.0\) Hz, 2H). \(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 193.7 (t, \(J = 26.7\) Hz), 151.6, 137.2, 129.3, 129.1, 126.5, 117.7 (dt, \(J = 286.6, 34.0\) Hz), 106.7 (tq, \(J = 266.8, 37.9\) Hz), 62.9, 36.7, 34.4, 19.3, 9.1. \(^19\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) -81.8, -123.2. HRMS (ESI) calculated for C\(_{15}\)H\(_{15}\)F\(_5\)N\(_4\)O\(_2\)Na\(^+\) [M+Na]\(^+\): 385.1058; found: 385.1057.

Methyl 2-(4-(2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)phenyl)propanoate (21)

Followed Method A, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 50.0 mg (55% yield) of 21 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2972(w), 1734(s), 1519(w), 1209(w), 1167(m), 1073(m), 794(w). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 2H), 4.74 (d, \(J = 10.5\) Hz, 1H), 3.71 (q, \(J = 7.1\) Hz, 1H), 3.65 (d, \(J = 0.9\) Hz, 3H), 3.03 – 2.90 (m, 1H), 2.52 (d, \(J = 0.6\) Hz, 3H), 1.47 (dd, \(J = 7.2, 1.4\) Hz, 3H), 0.89 (dd, \(J = 6.6, 1.7\) Hz, 6H). \(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 174.5, 151.5, 141.1, 135.7, 128.1, 127.9,
69.6, 52.0, 44.9, 33.2, 20.0, 18.4, 9.1. HRMS (ESI) calculated for C\textsubscript{16}H\textsubscript{23}N\textsubscript{4}O\textsubscript{2} [M+H]\textsuperscript{+}: 303.1816; found: 303.1815.

\[ \text{1-(6-(Tert-butyl)-1,1-dimethyl-3-(5-methyl-1H-tetrazol-1-yl)-2,3-dihydro-1H-inden-4-yl)ethan-1-one (22)} \]

Followed Method B, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (PE : EA = 1:1) to give 34.7 mg (36% yield) of 22 as a yellow oil.

IR (neat, cm\textsuperscript{-1}): 2959(s), 2869(w), 1680(s), 1361(m), 1237(s), 734(s), 657(m). \textsuperscript{1}H NMR (500 MHz, Chloroform-d) \textdelta 7.75 (d, J = 1.7 Hz, 1H), 7.50 (d, J = 1.7 Hz, 1H), 6.32 (dd, J = 8.9, 4.6 Hz, 1H), 2.79 (s, 3H), 2.59 (dd, J = 13.7, 8.9 Hz, 1H), 2.39 (s, 3H), 2.12 (dd, J = 13.7, 4.6 Hz, 1H), 1.46 (s, 3H), 1.40 (s, 9H), 1.36 (s, 3H). \textsuperscript{13}C NMR (126 MHz, Chloroform-d) \textdelta 199.4, 154.7, 153.8, 152.0, 133.9, 133.3, 126.5, 123.9, 59.8, 48.5, 42.9, 35.0, 31.3, 30.4, 29.7, 27.4, 9.1. HRMS (ESI) calculated for C\textsubscript{19}H\textsubscript{26}N\textsubscript{4}O\textsubscript{Na}\textsuperscript{+} [M+Na]\textsuperscript{+}: 349.1999; found: 349.2008.

\[ \text{Methyl -4'-(1-(5-methyl-1H-tetrazol-1-yl)hexyl)-[1,1'-biphenyl]-4-carboxylate (23)} \]

Followed Method A, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 46.5 mg (41% yield) of 23 as a yellow oil.
IR (neat, cm⁻¹): 3055(w), 1720(w), 1264(m), 1112(w), 732(s), 706(m). ¹H NMR (500 MHz, Chloroform-d) δ 8.14 – 8.04 (m, 2H), 7.67 – 7.55 (m, 4H), 7.42 – 7.33 (m, 2H), 5.31 (dd, J = 8.6, 6.6 Hz, 1H), 3.94 (s, 3H), 2.61 (dt, J = 14.9, 7.3 Hz, 1H), 2.48 (s, 3H), 2.36 (dt, J = 14.8, 7.0 Hz, 1H), 1.41 – 1.21 (m, 6H), 0.87 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 166.8, 151.5, 144.4, 140.4, 137.8, 130.1, 129.3, 127.9, 127.3, 126.9, 62.7, 52.1, 35.5, 31.1, 26.1, 22.3, 13.9, 9.2. HRMS (ESI) calculated for C₂₂H₂₇N₄O₂⁺ [M+H]^+: 379.2129; found: 379.2119.

1-(2-Azido-1-phenylethyl)-5-methyl-1H-tetrazole (25)
Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 46.7 mg (68% yield) of 25 as a yellow solid.
IR (neat, cm⁻¹): 2934(w), 2103(s), 1402(m), 1272(w), 732(w), 701(m). ¹H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.34 (m, 3H), 7.33 – 7.26 (m, 2H), 5.50 (dd, J = 9.6, 5.1 Hz, 1H), 4.47 (dd, J = 12.9, 9.6 Hz, 1H), 4.02 (dd, J = 12.9, 5.1 Hz, 1H), 2.48 (s, 3H).
¹³C NMR (101 MHz, Chloroform-d) δ 152.1, 134.2, 129.4, 129.2, 126.7, 61.8, 54.2, 8.7. HRMS (ESI) calculated for C₁₀H₁₂N₇⁺ [M+H]^+: 230.1149; found: 230.1147.

1-(2-Azido-1-(4-(tert-butyl)phenyl)ethyl)-5-methyl-1H-tetrazole (27)
Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 60 mg (70% yield) of 27 as a yellow solid.
IR (neat, cm⁻¹): 3693(m), 2104(s), 1525(m), 1401(m), 1270(m), 835(m), 568(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.42 – 7.36 (m, 2H), 7.24 – 7.19 (m, 2H), 5.38 (dd, J = 9.8, 4.9 Hz, 1H), 4.49 (dd, J = 12.9, 9.8 Hz, 1H), 3.98 (dd, J = 12.9, 4.9 Hz, 1H), 2.49 (s, 3H), 1.30 (s, 9H). ¹³C NMR (126 MHz, Chloroform-d) δ 152.9, 152.0, 131.3,
126.5, 126.3, 61.8, 54.5, 34.6, 31.1, 9.0. HRMS (ESI) calculated for C_{14}H_{19}N_{7}Na^{+} [M+Na]^+: 308.1594; found: 308.1596.

Methyl 4-(2-azido-1-(5-methyl-1H-tetrazol-1-yl)ethyl)benzoate (28)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 38.8 mg (45% yield) of 28 as a yellow oil.

IR (neat, cm⁻¹): 2953(w), 2106(s), 1722(s), 1436(m), 1281(s), 1113(m), 707(m). \(^1\)H NMR (500 MHz, Chloroform-d) δ 8.11 – 8.01 (m, 2H), 7.42 – 7.33 (m, 2H), 5.45 (dd, J = 9.4, 5.2 Hz, 1H), 4.50 (dd, J = 12.9, 9.4 Hz, 1H), 4.04 (dd, J = 12.9, 5.2 Hz, 1H), 3.93 (s, 3H), 2.49 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-d) δ 166.0, 152.1, 138.9, 131.5, 130.7, 127.0, 61.7, 54.3, 52.4, 8.9. HRMS (ESI) calculated for C_{12}H_{14}N_{7}O_{2}^{+} [M+H]^+: 288.1203; found: 288.1201.

1-(2-Azido-1-(3-fluorophenyl)ethyl)-5-methyl-1H-tetrazole (29)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 32.6 mg (44% yield) of 29 as a yellow oil.

IR (neat, cm⁻¹): 2939(w), 2105(s), 1594(m), 1491(m), 1267(m), 701(s), 522(m). \(^1\)H NMR (400 MHz, Chloroform-d) δ 7.40 (q, J = 7.1 Hz, 1H), 7.15-7.06 (m, 3H), 5.39 (dd, J = 9.0, 5.3 Hz, 1H), 4.53 – 4.41 (m, 1H), 4.02 (dd, J = 12.6, 4.7 Hz, 1H), 2.50 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-d) δ 163.0 (d, J = 249.1 Hz), 152.1, 136.6 (d, J = 7.0 Hz), 131.3 (d, J = 8.3 Hz), 122.6 (d, J = 3.2 Hz), 116.8 (d, J = 21.1 Hz), 114.1 (d, J = 23.0 Hz), 61.4, 54.4, 9.0. HRMS (ESI) calculated for C_{10}H_{11}FN_{7}^{+} [M+H]^+: 248.1054; found: 248.1052.
1-(2-Azido-1-(o-tolyl)ethyl)-5-methyl-1H-tetrazole (30)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 40.9 mg (56% yield) of 30 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2935(w), 2103(s), 1525(m), 1402(m), 1270(m), 735(s), 544(m). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.29 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 7.08 (d, \(J = 7.8\) Hz, 1H), 6.44 (dd, \(J = 9.5, 4.8\) Hz, 1H), 4.32 (dd, \(J = 13.0, 9.5\) Hz, 1H), 3.93 (dd, \(J = 13.0, 4.8\) Hz, 1H), 2.49 (s, 3H), 2.46 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 151.9, 134.8, 132.6, 131.1, 129.4, 127.4, 126.4, 58.3, 53.9, 19.2, 8.9. HRMS (ESI) calculated for \(\text{C}_{11}\text{H}_{13}\text{N}_{7}\text{Na}^+ [\text{M+Na}]^+\): 266.1125; found: 266.1124.

1-(1-Azido-2-phenylpropan-2-yl)-5-methyl-1H-tetrazole (31)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 45.9 mg (58% yield) of 31 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2941(w), 2103(s), 1525(m), 1401(m), 1273(m), 1038(m), 747(m). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.47 (dd, \(J = 7.5, 1.2\) Hz, 1H), 7.38 – 7.32 (m, 1H), 7.32 – 7.28 (m, 2H), 5.98 (dd, \(J = 9.9, 4.5\) Hz, 1H), 4.44 (dd, \(J = 12.9, 9.9\) Hz, 1H), 4.00 (dd, \(J = 12.9, 4.5\) Hz, 1H), 2.53 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 152.3, 132.6, 131.9, 130.9, 130.1, 128.3, 128.1, 57.8, 53.5, 8.8. HRMS (ESI) calculated for \(\text{C}_{10}\text{H}_{10}\text{ClN}_{7}\text{Na}^+ [\text{M+Na}]^+\): 286.0578; found: 286.0586.

1-(1-Azido-2-phenylpropan-2-yl)-5-methyl-1H-tetrazole (32)
Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 54.7 mg (75% yield) of 32 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2996(w), 2105(s), 1515(m), 1449(m), 1380(m), 1093(m), 699(s).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.37 (m, 3H), 7.12 – 7.07 (m, 2H), 4.38 (d, \(J = 12.7\) Hz, 1H), 4.09 (d, \(J = 12.7\) Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H).

\(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 151.8, 138.7, 129.3, 129.2, 125.6, 66.4, 60.2, 23.8, 10.9.

HRMS (ESI) calculated for \(\text{C}_{11}\text{H}_{13}\text{N}_{7}\text{Na}^+\) [M+Na]^+: 266.1125; found: 266.1132.

\[
\begin{align*}
\text{N–N} & \quad \text{N–Me} \\
\text{N} & \quad \text{N}
\end{align*}
\]

1-(2-Azido-1-cyclopentyl-1-phenylethyl)-5-methyl-1H-tetrazole (33)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 48.2 mg (54% yield) of 33 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2958(w), 2102(s), 1512(m), 1448(m), 1288(m), 734(m), 703(s).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.49 – 7.40 (m, 3H), 7.18 – 7.07 (m, 2H), 4.36 (d, \(J = 12.7\) Hz, 1H), 4.17 (d, \(J = 12.8\) Hz, 1H), 3.32 (p, \(J = 8.1, 7.7\) Hz, 1H), 1.99 (d, \(J = 9.1\) Hz, 1H), 1.96 (s, 3H), 1.91 – 1.77 (m, 1H), 1.59 (dq, \(J = 13.2, 8.0\) Hz, 2H), 1.53 – 1.32 (m, 3H), 1.19 – 1.02 (m, 1H).

\(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 152.7, 136.3, 129.0, 128.8, 127.2, 71.8, 57.9, 45.3, 27.8, 27.6, 24.4, 24.2, 12.9. HRMS (ESI) calculated for \(\text{C}_{15}\text{H}_{19}\text{N}_{7}\text{Na}^+\) [M+Na]^+: 320.1594; found: 320.1599.

\[
\begin{align*}
\text{N–N} & \quad \text{N–Me} \\
\text{N} & \quad \text{N}
\end{align*}
\]

1-(2-Azido-1-cyclohexyl-1-phenylethyl)-5-methyl-1H-tetrazole (34)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 59.8 mg (64% yield) of 34 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2934(m), 2856(w), 2102(s), 1447(m), 1372(m), 734(m), 703(s).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.44 (d, \(J = 4.9\) Hz, 3H), 7.11 (d, \(J = 4.9\) Hz, 2H), 7.05 (d, \(J = 4.9\) Hz, 1H), 6.83 (d, \(J = 4.9\) Hz, 1H), 4.39 (d, \(J = 12.7\) Hz, 1H), 4.05 (d, \(J = 12.7\) Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H).

\(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 153.9, 137.4, 130.8, 128.9, 128.8, 127.2, 71.8, 57.9, 45.3, 27.8, 27.6, 24.4, 24.2, 12.1. HRMS (ESI) calculated for \(\text{C}_{16}\text{H}_{20}\text{N}_{7}\text{Na}^+\) [M+Na]^+: 320.1607; found: 320.1607.
4.40 (d, $J = 12.9$ Hz, 1H), 4.14 (d, $J = 12.9$ Hz, 1H), 2.87 (t, $J = 11.9$ Hz, 1H), 2.00–1.98 (m, 1H), 1.97 (s, 3H), 1.89 – 1.63 (m, 4H), 1.43 – 1.43 (m, 2H), 1.05 – 0.95 (m, 1H), 0.88 – 0.72 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 152.9, 135.6, 128.9, 128.7, 127.2, 72.8, 56.9, 42.8, 28.2, 28.1, 26.5, 26.2, 25.9, 12.4. HRMS (ESI) calculated for C$_{16}$H$_{21}$N$_7$K$^+$ [M+K]$^+$: 350.1490; found: 350.1498.

1-(1-Azido-2-phenylpentan-2-yl)-5-methyl-1H-tetrazole (35)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 61.1 mg (75% yield) of 35 as a yellow oil.

IR (neat, cm$^{-1}$): 2964(m), 2875(w), 2105(s), 1515(m), 1449(m), 1282(m), 700(s). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.45 – 7.38 (m, 3H), 7.12 (dt, $J = 6.6$, 1.7 Hz, 2H), 4.39 (d, $J = 12.7$ Hz, 1H), 4.23 (d, $J = 12.6$ Hz, 1H), 2.61 (td, $J = 13.6$, 4.7 Hz, 1H), 2.36 (td, $J = 14.0$, 13.4, 4.5 Hz, 1H), 1.99 (s, 3H), 1.43 – 1.19 (m, 1H), 0.95 (t, $J = 7.2$ Hz, 3H), 0.85 – 0.60 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 151.9, 138.7, 129.3, 129.2, 126.1, 68.7, 57.2, 36.8, 16.4, 14.0, 10.9. HRMS (ESI) calculated for C$_{13}$H$_{17}$N$_7$Na$^+$ [M+Na]$^+$: 294.1438; found: 294.1437.

1-(1-Azido-2,3-diphenylpropan-2-yl)-5-methyl-1H-tetrazole (36)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 59.4 mg (62% yield) of 36 as a yellow oil.

IR (neat, cm$^{-1}$): 3031(w), 2106(s), 1497(m), 1449(m), 1289(m), 735(m), 699(s). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.48 – 7.36 (m, 3H), 7.25 – 7.15 (m, 3H), 7.15 – 7.09 (m, 2H), 6.62 (d, $J = 7.5$ Hz, 2H), 4.21 (d, $J = 12.5$ Hz, 1H), 4.09 (d, $J = 12.5$ Hz, 1H), 3.87 (d, $J = 13.7$ Hz, 1H), 3.76 (d, $J = 13.7$ Hz, 1H), 2.07 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 152.0, 138.0, 133.0, 129.9, 129.4, 129.3, 128.5, 127.7, 126.4,
HRMS (ESI) calculated for C\text{17}H\text{18}N\text{7} [M+H]^+: 320.1618; found: 320.1598.

1-(1-Azido-2-phenyldecan-2-yl)-5-methyl-1H-tetrazole (37)
Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 79.8 mg (72% yield) of 37 as a yellow oil.
IR (neat, cm\(^{-1}\)): 2924(s), 2853(m), 2105(s), 1449(m), 1379(m), 1283(m), 700(s). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.48 – 7.36 (m, 3H), 7.17 – 7.07 (m, 2H), 4.39 (d, \(J = 12.5\) Hz, 1H), 4.23 (d, \(J = 12.6\) Hz, 1H), 2.62 (t, \(J = 13.3\) Hz, 1H), 2.38 (t, \(J = 12.5\) Hz, 1H), 1.99 (s, 3H), 1.31 – 1.23 (m, 15H), 0.87 (t, \(J = 6.1\) Hz, 3H), 0.70 (d, \(J = 7.4\) Hz, 1H). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 151.9, 138.7, 129.2, 129.1, 126.1, 68.7, 56.1, 40.6, 11.2. HRMS (ESI) calculated for C\text{20}H\text{31}N\text{7}Na\text{+} [M+Na]\text{+}: 392.2533; found: 392.2539.

1-(2-Azido-1-phenylpropyl)-5-methyl-1H-tetrazole (38)
Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 57.7 mg (79%, dr = 1.5:1) of 38 as a yellow oil.
diastereoisomer 1:
IR (neat, cm\(^{-1}\)): 2983(w), 2112(s), 1524(m), 1261(m), 749(m), 701(s), 519(w). \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 7.45 – 7.42 (m, 2H), 7.42 – 7.36 (m, 3H), 4.94 (d, \(J = 10.0\) Hz, 1H), 4.77 (dq, \(J = 10.0, 6.6\) Hz, 1H), 2.53 (s, 3H), 1.23 (d, \(J = 6.6\) Hz, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-d) \(\delta\) 151.9, 134.0, 129.7, 129.4, 127.8, 67.4, 60.4, 17.6, 9.0. HRMS (ESI) calculated for C\text{11}H\text{13}N\text{7}Na\text{+} [M+Na]\text{+}: 266.1125; found: 266.1143.
diastereoisomer 2:
IR (neat, cm\(^{-1}\)): 2936(w), 2105(s), 1523(m), 1267(m), 750(m), 702(s), 523(w). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.38 (m, 5H), 5.03 (d, \(J = 9.0\) Hz, 1H), 4.66 (dq, \(J = 8.9, 6.4\) Hz, 1H), 2.50 (s, 3H), 1.29 (d, \(J = 6.4\) Hz, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 151.9, 134.5, 129.6, 129.3, 127.8, 66.6, 60.4, 17.5, 9.1. HRMS (ESI) calculated for C\(_{11}\)H\(_{13}\)N\(_3\)Na\(^+\) [M+Na]\(^+\): 266.1125; found: 266.1126

1-(2-Azido-3-chloro-1-phenylpropyl)-5-methyl-1H-tetrazole (39)
Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 53.2 mg (64%, dr= 1:1) of 39 as a yellow oil.
IR (neat, cm\(^{-1}\)): 2953(w), 2127(s), 1605(m), 1525(m), 1001(m), 700(s), 547(m). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 4.52 – 4.47 (m, 4H), 4.45 – 4.41 (m, 6H), 5.52 (d, \(J = 9.1\) Hz, 1H), 5.33 (d, \(J = 10.2\) Hz, 1H), 4.99 (ddd, \(J = 10.2, 4.6, 3.0\) Hz, 1H), 4.91 (dt, \(J = 9.1, 3.6\) Hz, 1H), 3.81 (dd, \(J = 12.3, 3.1\) Hz, 1H), 3.75 (dd, \(J = 12.1, 3.0\) Hz, 1H), 3.51 (dd, \(J = 12.3, 3.9\) Hz, 1H), 3.39 (dd, \(J = 12.2, 4.6\) Hz, 1H), 2.55 (s, 3H), 2.54 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 152.1, 133.4, 132.7, 130.2, 130.0, 129.7, 129.5, 128.0, 127.7, 64.5, 64.0, 63.6, 61.6, 44.7, 44.4, 8.9. HRMS (ESI) calculated for C\(_{11}\)H\(_{13}\)ClN\(_7\)\(^-\) [M+H\(^-\)]\(^\ddagger\): 278.0915; found: 278.0913

1-(2-Azido-2-methyl-1-phenylpropyl)-5-methyl-1H-tetrazole (40)
Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 57.1 mg (74% yield) of 40 as a yellow oil.
IR (neat, cm\(^{-1}\)): 2981(w), 2107(s), 1584(m), 1373(m), 1108(m), 707(s), 538(m). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.60 – 7.54 (m, 2H), 7.42 – 7.36 (m, 3H), 5.17 (s, 1H), 2.56 (s, 3H), 1.50 (s, 3H), 1.46 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\)
152.6, 132.9, 129.3, 128.7, 69.6, 64.2, 24.4, 23.0, 9.4. HRMS (ESI) calculated for C_{12}H_{15}N_{7}Na^{+} [M+Na]^{+}: 280.1281; found: 280.1285.

1-(2-Azido-1-phenylcyclohexyl)-5-methyl-1H-tetrazole (41)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 58.9 mg (69%, dr = 1.1:1) of 41 as a yellow oil.

diastereoisomer 1:

$^1$H NMR (500 MHz, Chloroform-$d$) δ 7.43 – 7.32 (m, 3H), 7.19 – 7.10 (m, 2H), 4.90 – 4.81 (m, 1H), 2.73 (ddd, $J = 15.1, 12.0, 3.2$ Hz, 1H), 2.64 – 2.47 (m, 2H), 2.13 – 2.04 (m, 4H), 1.80 – 1.53 (m, 4H), 1.25 – 0.75 (m, 1H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 152.1, 139.5, 129.1, 128.9, 126.4, 68.6, 65.6, 29.3, 27.7, 20.6, 20.2, 11.3.

diastereoisomer 2:

$^1$H NMR (500 MHz, Chloroform-$d$) δ 7.45 – 7.33 (m, 3H), 7.23 – 7.15 (m, 2H), 4.43 (dd, $J = 9.0, 3.9$ Hz, 1H), 2.76 (ddt, $J = 14.4, 3.8, 2.5$ Hz, 1H), 2.41 (ddd, $J = 14.0, 9.9, 3.7$ Hz, 1H), 2.25 – 2.09 (m, 3H), 2.09 (s, 3H), 2.00 – 1.77 (m, 2H), 1.65 – 1.53 (m, 2H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 152.5, 139.3, 129.1, 128.8, 126.2, 68.9, 64.0, 36.0, 26.9, 22.6, 21.5, 11.7.

IR (neat, cm$^{-1}$): 2931(w), 2108(s), 1513(w), 1448(w), 1376(w), 759(m), 703(m).

HRMS (ESI) calculated for C_{14}H_{17}N_{7}Na^{+} [M+Na]^{+}: 306.1438; found: 306.1443.

1-(3-Azido-2,3-dimethylbutan-2-yl)-5-methyl-1H-tetrazole (42)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 47.1 mg (75% yield) of 42 as a colorless solid.
IR (neat, cm⁻¹): 2998(w), 2110(s), 2085(m), 1509(m), 1376(m), 1267(m), 1137(m).

¹H NMR (400 MHz, Chloroform-d) δ 2.81 (s, 3H), 1.82 (s, 6H), 1.35 (s, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 152.9, 68.2, 67.6, 24.4, 22.2, 13.0. HRMS (ESI) calculated for C₈H₁₆N₇⁺ [M+H]⁺: 210.1462; found: 210.1460.

1-(4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)-1H-indol-1-yl)ethan-1-one (43)

Followed Method C, 2.5 V, 4.5 h. The desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 27.4 mg (27%) of 43 as a black oil.

IR (neat, cm⁻¹): 2926(w), 2108(s), 1710(s), 1430(s), 1325(s), 1271(m), 764(m).

¹H NMR (600 MHz, Chloroform-d) δ 8.51 (d, J = 8.3 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 3.9 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 3.9 Hz, 1H), 5.65 (s, 1H), 2.67 (s, 3H), 2.48 (s, 3H), 1.60 (s, 3H), 1.51 (s, 3H). ¹³C NMR (151 MHz, Chloroform-d) δ 168.6, 152.6, 135.5, 129.9, 126.6, 125.4, 124.9, 124.7, 117.5, 105.9, 66.0, 64.7, 24.6, 23.9, 23.5, 9.4. HRMS (ESI) calculated for C₁₆H₁₆N₈NaO⁺ [M+Na]⁺: 361.1496; found: 361.1498.

1-(2-Azido-1-(dibenzo[b,d]thiophen-3-yl)-2-methylpropyl)-5-methyl-1H-tetrazole (44)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 43.2 mg (40%) of 44 as a yellow oil.
IR (neat, cm\(^{-1}\)): 3055(w), 2111(m), 1398(w), 1264(m), 731(s), 705(w). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.20 – 8.13 (m, 2H), 8.05 (d, \(J = 8.2\) Hz, 1H), 7.93 – 7.84 (m, 1H), 7.58 – 7.47 (m, 3H), 5.57 (s, 1H), 2.63 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 152.8, 140.2, 137.9, 136.3, 135.7, 128.1, 128.0, 127.5, 125.3, 125.2, 122.7, 122.5, 122.0, 67.5, 65.0, 24.8, 23.1, 9.5. HRMS (ESI) calculated for C\(_{12}\)H\(_{17}\)N\(_7\)Na\(^+\) [M+Na\(^+\)]: 386.1164; found: 386.1161.

1-(2-Azido-1-phenylpropyl)-5-isopropyl-1H-tetrazole (45)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 56.2 mg (69%, dr = 1.2:1) of 45 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2977(w), 2931(w), 2109(s), 1456(m), 1261(m), 1100(m), 748(m), 699(s). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.50 – 7.44 (m, 4H), 7.43 – 7.35 (m, 6H), 5.10 (d, \(J = 9.1\) Hz, 1H), 4.98 (d, \(J = 10.0\) Hz, 1H), 4.78 (p, \(J = 6.6\) Hz, 1H), 4.65 (p, \(J = 6.7\) Hz, 1H), 3.19 – 3.10 (m, 2H), 1.49 – 1.44 (m, 6H), 1.25 – 1.18 (m, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 159.8, 159.7, 135.1, 134.4, 129.6, 129.4, 129.3, 129.2, 127.9, 127.8, 67.2, 66.2, 60.8, 60.7, 24.10, 24.09, 21.1, 21.02, 20.96, 20.93, 17.6, 17.4. HRMS (ESI) calculated for C\(_{13}\)H\(_{17}\)N\(_7\)Na\(^+\) [M+Na\(^+\)]: 294.1438; found: 294.1437.

1-(2-Azido-1-phenylpropyl)-5-propyl-1H-tetrazole (46)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 68.4 mg (84%, dr = 1.5:1) of 46 as a yellow oil.
IR (neat, cm⁻¹): 2967(w), 2935(w), 2110(s), 1512(m), 1457(m), 1262(m), 749(m), 701(s). ¹H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.37 (m, 10H), 5.03 (d, J = 9.5 Hz, 1H), 4.92 (d, J = 10.0 Hz, 1H), 4.84 – 4.71 (m, 1H), 4.65 (p, J = 7.3 Hz, 1H), 2.68 – 2.88 (m, 4H), 1.85 – 1.71 (m, 4H), 1.27 – 1.21 (m, 6H), 1.00 – 0.93 (m, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 155.2, 155.1, 134.8, 134.2, 129.5, 129.4, 129.3, 129.1, 127.8, 127.7, 67.2, 66.2, 60.54, 60.49, 25.0, 20.4, 20.3, 17.5, 17.3, 13.49, 13.46. HRMS (ESI) calculated for C₁₃H₁₈N₇⁺ [M+H]⁺: 272.1618; found: 272.1614.

4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)benzyl

4-(N,N-dipropylsulfamoyl)benzoate (47)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 114.3 mg (69%) of 47 as a yellow oil.

IR (neat, cm⁻¹): 2972(w), 2111(w), 1724(w), 1265(m), 1105(w), 731(s). ¹H NMR (500 MHz, Chloroform-d) δ 8.22 – 8.12 (m, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 5.39 (s, 2H), 5.20 (d, J = 1.7 Hz, 1H), 3.14 – 3.05 (m, 4H), 2.57 (s, 3H), 1.55 (q, J = 7.4 Hz, 4H), 1.49 (s, 3H), 1.47 (s, 3H), 0.87 (td, J = 7.3, 1.1 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-d) δ 164.9, 152.6, 144.4, 136.7, 133.2, 133.0, 130.3, 129.8, 128.4, 127.0, 69.2, 66.3, 64.2, 49.8, 24.2, 23.1, 21.8, 11.0, 9.3. HRMS (ESI) calculated for C₂₆H₃₄N₈NaO₄S⁺ [M+Na]⁺: 577.2321; found: 577.2323.

4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)benzyl

2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (48)
Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 79.9 mg (45%) of 48 as a white solid.

IR (neat, cm\(^{-1}\)): 2987(w), 2110(m), 1739(w), 1596(m), 1263(m), 1135(w), 732(s). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.69 (ddt, \(J = 11.7, 9.6, 2.5\) Hz, 4H), 7.54 (d, \(J = 8.3\) Hz, 2H), 7.48 – 7.43 (m, 2H), 7.25 (d, \(J = 8.3\) Hz, 2H), 6.87 – 6.76 (m, 2H), 5.19 (d, \(J = 2.7\) Hz, 2H), 5.14 (s, 1H), 2.55 (s, 3H), 1.68 (d, \(J = 3.3\) Hz, 6H), 1.44 (s, 3H), 1.42 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 194.1, 173.4, 159.4, 138.4, 136.4, 136.2, 133.1, 131.9, 131.1, 130.4, 129.7, 128.5, 128.2, 117.2, 79.3, 69.2, 66.4, 64.2, 25.5, 25.2, 24.2, 23.1, 9.4. HRMS (ESI) calculated for \(\text{C}_{30}\text{H}_{30}\text{ClN}_7\text{NaO}_4^+\) [M+Na]^+: 610.1945; found: 610.1946.

![4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)benzyl](image)

4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)benzyl

2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (49)

Followed Method C, MeCN/DCM (7:3, 10mL) as co-solvent. The desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 63.5 mg (36%) of 49 as a white solid.

IR (neat, cm\(^{-1}\)): 2966(w), 2109(m), 1711(w), 1375(w), 1261(s), 1088(w), 732(s). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.17 (d, \(J = 2.2\) Hz, 1H), 8.08 (dd, \(J = 8.8, 2.3\) Hz, 1H), 7.62 (d, \(J = 8.2\) Hz, 2H), 7.46 (d, \(J = 8.2\) Hz, 2H), 7.02 (d, \(J = 8.9\) Hz, 1H), 5.33 (s, 2H), 5.18 (s, 1H), 3.90 (d, \(J = 6.5\) Hz, 2H), 2.76 (s, 3H), 2.57 (s, 3H), 2.20 (dp, \(J = 13.3, 6.6\) Hz, 1H), 1.49 (d, \(J = 6.5\) Hz, 6H), 1.10 (s, 3H), 1.08 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 167.5, 162.5, 161.8, 161.6, 152.6, 136.9, 133.0, 132.5, 132.0, 129.8, 128.2, 125.7, 121.0, 115.3, 112.6, 102.9, 75.6, 69.2, 65.9, 64.2, 28.1, 24.3, 23.1, 19.0, 17.5, 9.4. HRMS (ESI) calculated for \(\text{C}_{29}\text{H}_{32}\text{N}_9\text{NaO}_4\text{S}^+\) [M+H]^+: 586.2343; found: 586.2334.
6. Derivatization of products

The mixture solution of 1-(2-azido-1-phenylethyl)-5-methyl-1H-tetrazole (25, 41 mg, 0.18 mmol, 1.0 equiv.), phenylacetylene (3 equiv.) and CuI (30 mol%) in THF (2 mL) was stirred at temperature for 4 h. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (PE/EA=1:2) to give product 5-methyl-1-(1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-tetrazole (50, 55.5 mg, 93% yield) as a white solid.

5-Methyl-1-(1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-tetrazole (50).

IR (neat, cm⁻¹): 2925(w), 1524(w), 1458(w), 1265(w), 1077(w), 765(s), 696(s). ¹H NMR (500 MHz, Chloroform-d) δ 7.71 (dd, J = 8.3, 1.2 Hz, 2H), 7.62 (s, 1H), 7.46 – 7.35 (m, 7H), 7.35 – 7.28 (m, 1H), 6.10 (dd, J = 10.0, 4.9 Hz, 1H), 5.51 (dd, J = 14.2, 10.0 Hz, 1H), 5.13 (dd, J = 14.2, 4.9 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 152.3, 147.7, 133.7, 130.0, 129.8, 129.7, 128.8, 128.4, 126.8, 125.7, 121.2, 62.0, 53.5, 8.7. HRMS (ESI) calculated for C₁₈H₁₈N₇⁺ [M+H]⁺: 332.1618; found: 332.1611.

The mixture solution of 1-(2-Azido-1-phenylethyl)-5-methyl-1H-tetrazole (25, 23 mg, 0.1 mmol, 1.0 equiv.), alkyne (1.1 equiv.), CuI (2 equiv.) and DIPEA (3 equiv.) in MeCN (2 mL) was stirred at temperature for 4 h. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column
chromatography on silica gel (DCM/CH$_3$OH=10:1) to give product 5-methyl-1-(1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-tetrazole (51, 36.1mg, 73% yield) as a white solid.

1-((3R,4S,5R)-4-Hydroxy-5-(hydroxymethyl)tetrahydrofuran-3-yl)-5-(1-(2-(5-methyl-1H-tetrazol-1-yl)-2-phenylethyl)-1H-1,2,3-triazol-5-yl)pyrimidine-2,4(1H,3H)-dione (51).

IR (neat, cm$^{-1}$): 3385 (s), 2490 (s), 2071 (m), 1686 (m), 1120 (m), 972 (s).

$^{1}$H NMR (500 MHz, Methanol-$d_4$) $\delta$ 8.57 (s, 1H), 8.31 (s, 1H), 7.57 – 7.45 (m, 2H), 7.43 (q, $J = 5.7$ Hz, 3H), 6.43 – 6.35 (m, 1H), 6.32 (t, $J = 6.7$ Hz, 1H), 5.59 (dd, $J = 14.2$, 9.6 Hz, 1H), 5.29 (dd, $J = 14.2$, 5.7 Hz, 1H), 4.42 (dq, $J = 6.4$, 3.2 Hz, 1H), 3.95 (q, $J = 3.2$ Hz, 1H), 3.82 (dt, $J = 12.0$, 5.9, 3.0 Hz, 1H), 3.75 (dd, $J = 12.0$, 4.1 Hz, 1H), 2.40 (s, 3H), 2.33 (ddt, $J = 12.0$, 5.9, 3.0 Hz, 1H), 2.26 (ddt, $J = 13.6$, 6.8, 4.0 Hz, 1H), 1.90 (s, 1H), 1.36 (d, $J = 6.6$ Hz, 1H). $^{13}$C NMR (126 MHz, Methanol-$d_4$) $\delta$ 163.0, 154.1, 151.5, 140.8, 138.0, 135.6, 130.8, 128.6, 124.8, 106.4, 89.1, 86.9, 72.3, 62.9, 62.5, 54.2, 41.5, 8.6. HRMS (ESI) calculated for C$_{21}$H$_{26}$N$_9$O$_5$ $^+$ [M+H]$^+$: 484.2051; found: 484.2050.

The mixture solution of 25 (0.2 mmol, 1.0 equiv), P(OMe)$_3$ (1.5 equiv) in toluene (1.2 mL) was stirred at 80 °C for 3 h. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (DCM/CH$_3$OH=10:1) to give the desired products (52, 52.1 mg, 84% yield).

Dimethyl (2-(5-methyl-1H-tetrazol-1-yl)-2-phenylethyl)phosphoramidate (52).

IR (neat, cm$^{-1}$): 3216(w), 2952(w), 1455(w), 1240(w), 1034(s), 834(m), 525(w). $^{1}$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.41 – 7.32 (m, 3H), 7.24 (dd, $J = 7.3$, 1.9 Hz, 2H), 5.57 (dd, $J = 9.7$, 4.7 Hz, 1H), 4.02 (dddd, $J = 16.9$, 14.7, 9.7, 6.9 Hz, 1H), 3.76 – 3.69 (m, 1H), 3.67 (d, $J = 11.2$ Hz, 3H), 3.60 (d, $J = 11.2$ Hz, 2H), 2.45 (s, 3H). $^{13}$C
NMR (126 MHz, Chloroform-\textit{d}) $\delta$ 152.5, 135.1, 129.23, 129.16, 126.7, 53.2 (d, $J = 5.8$ Hz), 53.3 (d, $J = 6.0$ Hz), 53.2 (d, $J = 5.8$ Hz), 45.8, 8.9. $^{31}$P NMR (162 MHz, Chloroform-\textit{d}) $\delta$ 10.7 (m). HRMS (ESI) calculated for C$_{12}$H$_{19}$N$_{5}$O$_{3}$P$^+$ [M+H$^+$]: 312.1220; found: 312.1216.

The mixture solution of 1-(2-azido-1-phenylethyl)-5-methyl-1H-tetrazole (25, 23 mg, 0.1 mmol, 1.0 equiv.), $^t$BuOK (2 equiv.) in THF (1 mL) was stirred at temperature for 1 min. The mixture was then filtered and washed with DCM, and the organic solvent evaporates under reduced pressure to give the pure compound 53 as colorless oil (18.6 mg, 99% yield).

5-Methyl-1-(1-phenylvinyl)-1H-tetrazole (53)

IR (neat, cm$^{-1}$): 3924 (w), 1518 (m), 1407 (m), 1266 (m), 918 (w), 775 (m), 732 (s), 701 (s).

$^1$H NMR (500 MHz, Chloroform-\textit{d}) $\delta$ 7.51 – 7.34 (m, 3H), 7.21 – 7.12 (m, 2H), 6.00 (d, $J = 1.5$ Hz, 1H), 5.61 (d, $J = 1.5$ Hz, 1H), 2.36 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-\textit{d}) $\delta$ 152.1, 140.2, 133.4, 130.3, 129.2, 125.7, 115.0, 9.4. HRMS (ESI) calculated for C$_{10}$H$_{11}$N$_{4}$ $^+$ [M+H$^+$]: 187.0978; found: 187.0977.
7. Unsuccessful substrates

Unsuccessful substrates of C‒H tetrazolation are shown in Table S5. For S1-S5, S13-S15, these reaction systems were clean but the yields were generally low. For S7, the desired tetrazole cannot be separated from the C-H acetylation byproduct. For S8-S12, S20-S22, these reactions only afforded complex reaction mixtures. For S6, S16-S18, low conversions were obtained as there were a lot of raw materials recovered. For S19, the desired C-H tetrazolization reaction did not occur at all. For S23 and S24, no formation of C-H tetrazolization products was detected.

Table S5. Unsuccessful substrates of C‒H tetrazolation.

| Unsuccessful Substrates of C‒H Tetrazolation | Unsuccessful Substrates of Vicinal Azidotetrazolation |
|---------------------------------------------|------------------------------------------------------|

Unsuccessful substrates of vicinal azidotetrazolation are shown in Table S6. F6-F8, F10-F16, F31-F36 these reactions only afforded complex reaction mixtures. For F9, F42-F44, the yields of these reactions were generally low and the desired products were difficult to purify. For F21-F26, F29, F37-F39, F40 and F41, low conversions were obtained as there were a lot of raw materials recovered. For F1-F5, F17-F20, F27, F28, F30, F45-F47, these reaction systems were clean but the yields were generally low.

Table S6. Unsuccessful substrates of vicinal azidotetrazolation.
8. Mechanistic experiments

8.1 Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode and submerged in saturated aqueous KCl solution Ag/AgCl reference electrode. Current was reported in mA, while all potentials were reported in V.

![Cyclic voltammogram with tBuNCIO₄ (10 mM) as electrolyte. Scan rate: 0.1 V/s.](image1)

**Figure S2.** Cyclic voltammogram with tBuNCIO₄ (10 mM) as electrolyte. Scan rate: 0.1 V/s.

![Cyclic voltammogram with tBuNCIO₄ (10 mM) as electrolyte. Scan rate: 0.1 V/s.](image2)

**Figure S3.** Cyclic voltammogram with tBuNCIO₄ (10 mM) as electrolyte. Scan rate: 0.1 V/s.

8.2 Hammett plot experiment

To a solution of ethylbenzene (0.3 mmol, 1.0 equiv.), p-substituted ethylbenzene (0.3 mmol, 1.0 equiv.), TMSN₃ (0.4 mmol, 3.4 equiv.), in MeCN/HFIP (10/1, ml) reacted at 75 mA for 8 min. The crude mixture was monitored by ¹H NMR (figure S5-S8). As
shown in figure S3, the electronic effect on the aromatic ring of ethylbenzene is significant, and a much negative ρ value (-2.97) in Hammett plot was given in below.

\[
\begin{align*}
\sigma_p^+ & \quad \text{H} & \quad \text{Ph} & \quad \text{F} & \quad \text{Cl} & \quad \text{CN} \\
\log(K_X/K_H) & \quad 0 & \quad -0.18 & \quad -0.07 & \quad 0.11 & \quad 0.66 \\
\end{align*}
\]

**Figure S4.** Hammett plot of tetrazolation of ethylbenzene
Figure S5. $^1$H NMR Spectrum of ethylbenzene and $p$-Ph ethylbenzene reaction mixture

Figure S6. $^1$H NMR Spectrum of ethylbenzene and $p$-F ethylbenzene reaction mixture
**Figure S7.** $^1$H NMR Spectrum of ethylbenzene and $p$-Cl ethylbenzene reaction mixture

**Figure S8.** $^1$H NMR Spectrum of ethylbenzene and $p$-CN ethylbenzene reaction mixture
8.3 Radical clock experiment

Following the standard procedure for the synthesis of vicinal azidotetrazoles and azidoacetamides using 1- (2-phenylcyclopropyl)vinylbenzene (0.3 mmol) as the starting material. After work-up, the crude mixture was purified using column chromatography to afford 55.

1-(4-Azido-1,4-diphenylbut-3-en-1-yl)-5-methyl-1H-tetrazole (55)

Followed Method C, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 22.1 mg (21%, dr = 7.5:1) of 55 as a yellow oil.

IR (neat, cm\(^{-1}\)): 2926(w), 2099(s), 1523(m), 1402(m), 1247(m), 702(s).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.27 (m, 9H), 7.24 (s, 1H), 5.86 (t, \(J = 7.6\) Hz, 1H), 5.38 (dd, \(J = 8.6, 6.7\) Hz, 1H), 4.28 (d, \(J = 13.7\) Hz, 1H), 4.12 (d, \(J = 13.7\) Hz, 1H), 3.60 (dt, \(J = 14.5, 6.9\) Hz, 1H), 3.28 (dt, \(J = 16.4, 8.3\) Hz, 1H). 13C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 151.7, 140.0, 138.0, 129.4, 129.2, 128.6, 128.0, 127.4, 126.6, 126.1, 63.0, 49.2, 35.3, 9.1.

HRMS (ESI) calculated for C\(_{19}\)H\(_{20}\)N\(_{7}\)\([\text{M+H}]^+\) : 346.1775; found: 346.1769.

8.4 Trapping the carbocation intermediate

N-(1-phenylethyl)acetamide (57).\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.37 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 5.76 (brs, 1H), 5.13 (p, \(J = 7.0\) Hz, 1H), 1.98 (s, 3H), 1.49 (d, \(J = 6.9\) Hz, 2H). 13C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 169.2, 143.1, 128.7, 127.4, 126.2, 48.8, 23.5, 21.7.
8.5 Probing arene radical cations

The procedure is the same as Method A

\[
\text{Ph} \text{~TMS} \xrightarrow{\text{graphite (\(\pm\)) | (-) Pt}} \text{Bu}_4\text{NCIO}_4 (0.3 \text{ mmol}) \xrightarrow{\text{MeCN/HFIP}} \text{ND} + \text{Ph} \text{~TMS} \text{~Me} \quad 7, 34\%
\]

8.6 \(\text{H}_2\) detection experiment

We have carried out the headspace GC analysis of the reaction mixture and confirmed the formation of \(\text{H}_2\) both in the tetrazolation and azidotetrazolation.
9. TG-DSC experiments

The TG-DSC curves of compound 25, 27, 42 were measured at N₂ flow rate of 20 mL min⁻¹, heating rate of 10.0 °C min⁻¹ and temperature range of RT to 400 °C. Crucible with aluminum lid was used as the sample tank.

Compound 25 (6.78 mg was used, ΔH = −1270 J g⁻¹)

Compound 27 (5.48 mg was used, ΔH = −1330 J g⁻¹)

Compound 42 (6.5 mg was used, ΔH = −1330 J g⁻¹)

Table S7. Onset Temperatures and Decomposition Enthalpies Calculated from DSC.
| Compound | $T_{\text{onset}}$ (°C) | $T_{m}^{a}$ (°C) | $TD_{24}^{b}$ (°C) | $\Delta H$ (J g$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) |
|----------|------------------|----------------|------------------|----------------|----------------|
| 25       | 233              | 246            | 117.1            | -1270          | -291           |
| 27       | 229              | 253            | 114.3            | -1330          | -379           |
| 42       | 215              | 246            | 104.5            | -1330          | -278           |

$^{a}$ Temperature of maximum in the DSC curve. $^{b}$ Temperature in which the time of maximum rate is 24 h.

10 Reference

1. Y. Chen, X. Yi, Y. Cheng, A. Huang, Z. Yang, X. Zhao, F. Ling and W. Zhong, *J. Org. Chem.*, 2022, 87, 7864-7874.
11. Spectral data (\( ^1\text{H}, ^{13}\text{C}, ^{19}\text{F} \)) of products

3. \( ^1\text{H} \) (500 MHz, CDCl\(_3\))

3. \( ^{13}\text{C} \) (126 MHz, CDCl\(_3\))
4. $^1$H (500 MHz, CDCl$_3$)

4. $^{13}$C (500 MHz, CDCl$_3$)
5. $^1$H (500 MHz, CDCl$_3$)

5. $^{13}$C (126 MHz, CDCl$_3$)
6, $^1$H (500 MHz, CDCl$_3$)

6, $^{13}$C (126 MHz, CDCl$_3$)
7. $^1$H (500 MHz, CDCl$_3$)

7. $^{13}$C (126 MHz, CDCl$_3$)
8. $^1$H (500 MHz, CDCl$_3$)

8. $^{13}$C (126 MHz, CDCl$_3$)
9. $^1$H (500 MHz, CDCl$_3$)

9. $^{13}$C (126 MHz, CDCl$_3$)
10, $^1$H (500 MHz, CH$_3$OD)

10, $^{13}$C (126 MHz, CH$_3$OD)
$^{1}H$ (600 MHz, COD$_4$)

$^{13}C$ (126 MHz, COD$_4$)
12, $^1$H (500 MHz, CDCl₃)

12, $^{13}$C (126 MHz, CDCl₃)
13, $^1$H (500 MHz, CDCl$_3$)

13, $^{13}$C (126 MHz, CDCl$_3$)
14. $^1$H (500 MHz, CDCl$_3$)

14. $^{13}$C (126 MHz, CDCl$_3$)
15, $^1$H (500 MHz, CDCl$_3$)

15, $^{13}$C (126 MHz, CDCl$_3$)
16, $^1$H (500 MHz, CDCl$_3$)

16, $^{13}$C (126 MHz, CDCl$_3$)
$^{13}$C (126 MHz, CDCl$_3$)

$^1$H (500 MHz, CDCl$_3$)
18, $^1$H (600 MHz, CDCl$_3$)

18, $^{13}$C (151 MHz, CDCl$_3$)
19, $^1$H (500 MHz, CD$_3$OD)

19, $^{13}$C (126 MHz, CD$_3$OD)
20, $^1$H (500 MHz, CDCl$_3$)

20, $^{13}$C (126 MHz, CDCl$_3$)
20, $^{19}$F (471 MHz, CDCl$_3$)
$21, ^1H$ (500 MHz, CDCl$_3$)

$21, ^{13}C$ (126 MHz, CDCl$_3$)
22, $^1$H (500 MHz, CDCl$_3$)

22, $^{13}$C (126 MHz, CDCl$_3$)
23. $^1{\text{H}}$ (500 MHz, CDCl$_3$)

23. $^{13}{\text{C}}$ (126 MHz, CDCl$_3$)
25, $^1$H (400 MHz, CDCl$_3$)

25, $^{13}$C (101 MHz, CDCl$_3$)
27, $^1$H (500 MHz, CDCl$_3$)

27, $^{13}$C (126 MHz, CDCl$_3$)
28, $^1$H (500 MHz, CDCl$_3$)

28, $^{13}$C (126 MHz, CDCl$_3$)
$^{29}$, $^1$H (500 MHz, CDCl$_3$)

$^{29}$, $^{13}$C (101 MHz, CDCl$_3$)
\[ 30, {^1}\text{H} (500 \text{ MHz, CDCl}_3) \]

\[ 30, {^{13}}\text{C} (126 \text{ MHz, CDCl}_3) \]
31, $^1$H (500 MHz, CDCl$_3$)

31, $^{13}$C (126 MHz, CDCl$_3$)
32, $^1$H (500 MHz, CDCl$_3$)

32, $^{13}$C (126 MHz, CDCl$_3$)
33, $^1$H (400 MHz, CDCl$_3$)

33, $^{13}$C (101 MHz, CDCl$_3$)
35, $^1$H (400 MHz, CDCl$_3$)

35, $^{13}$C (101 MHz, CDCl$_3$)
$\text{36, } {^1}\text{H} \ (400 \text{ MHz, CDCl}_3)$

$\text{36, } {^{13}}\text{C} \ (101 \text{ MHz, CDCl}_3)$
37, \( ^1H \) (400 MHz, CDCl\(_3\))

37, \( ^{13}C \) (101 MHz, CDCl\(_3\))
38, \textsuperscript{1}H (500 MHz, CDCl\textsubscript{3})

diastereoisomer 1

38, \textsuperscript{13}C (126 MHz, CDCl\textsubscript{3})

diastereoisomer 1
diastereoisomer 2

\[ \begin{align*}
  &\text{N}^\text{N} \quad \text{N}^\text{N} \\
  &\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
39, $^1$H (500 MHz, CDCl$_3$), $dr = 1:1$

39, $^{13}$C (126 MHz, CDCl$_3$), $dr = 1:1$
40, $^1$H (500 MHz, CDCl$_3$)

40, $^{13}$C (126 MHz, CDCl$_3$)
diastereoisomer 1:

41, $^1$H (500 MHz, CDCl$_3$)

41, $^{13}$C (126 MHz, CDCl$_3$)
diastereoisomer 2:

41, $^1$H (500 MHz, CDCl$_3$)

41, $^{13}$C (126 MHz, CDCl$_3$)
42, $^1$H (400 MHz, CDCl$_3$)

42, $^{13}$C (101 MHz, CDCl$_3$)
43, $^1$H (600 MHz, CDCl$_3$)

43, $^{13}$C (151 MHz, CDCl$_3$)
44, $^1$H (500 MHz, CDCl$_3$)

44, $^{13}$C (126 MHz, CDCl$_3$)
45, $^1$H (400 MHz, CDCl$_3$), dr = 1.2:1

45, $^{13}$C (101 MHz, CDCl$_3$), dr = 1.2:1
46, $^1$H (400 MHz, CDCl$_3$), dr = 1.5:1

46, $^{13}$C (101 MHz, CDCl$_3$), dr = 1.5:1
47, $^1$H (500 MHz, CDCl$_3$)

47, $^{13}$C (126 MHz, CDCl$_3$)
48, $^1$H (500 MHz, CDCl$_3$)

48, $^{13}$C (128 MHz, CDCl$_3$)
49, $^1$H (500 MHz, CDCl$_3$)

49, $^{13}$C (126 MHz, CDCl$_3$)
50, $^1$H (500 MHz, CDCl$_3$)

50, $^{13}$C (126 MHz, CDCl$_3$)
51, $^1$H (500 MHz, CH$_3$OD)

51, $^{13}$C (126 MHz, CH$_3$OD)
52, $^1$H (500 MHz, CDCl$_3$)

52, $^{13}$C (126 MHz, CDCl$_3$)
52, $^{31}$P (162 MHz, CDCl$_3$)
53, $^1$H (500 MHz, CDCl$_3$)

53, $^{13}$C (126 MHz, CDCl$_3$)
55, $^1$H (400 MHz, CDCl$_3$), dr = 7.5:1

55, $^{13}$C (101 MHz, CDCl$_3$), dr = 7.5:1
57, $^1$H (500 MHz, CDCl$_3$)

57, $^{13}$C (126 MHz, CDCl$_3$)