

Electronic Supplementary Information

Electrochemical synthesis of vicinal azidoacetamides

Yi Yu, Yaofeng Yuan and Ke-Yin Ye*

Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province University), College of Chemistry,
Fuzhou University, Fuzhou 350108

E-mail: kyye@fzu.edu.cn (K.-Y. Ye)

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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 (^1H 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) and JEOL-500 (500 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 ($\text{CHCl}_3 = \delta$ 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 Agilent 1290-6545xt with the use of a 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 and DJS-292B. Electrode clips (PT-1 or PT-3) and graphite plate (99.99%, 15*15*0.3 mm) was purchased from Gaoss Union. The graphite plate (>99.99%) was cut into 15 x 15 x 1 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.

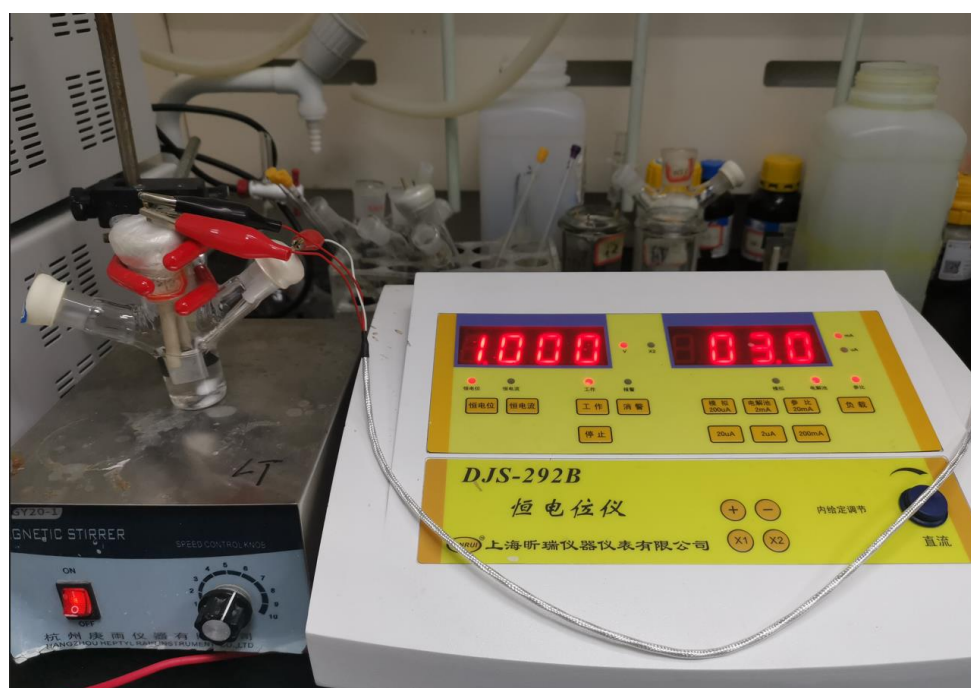


Figure S1. Electrolysis device and constant-potential electrolysis

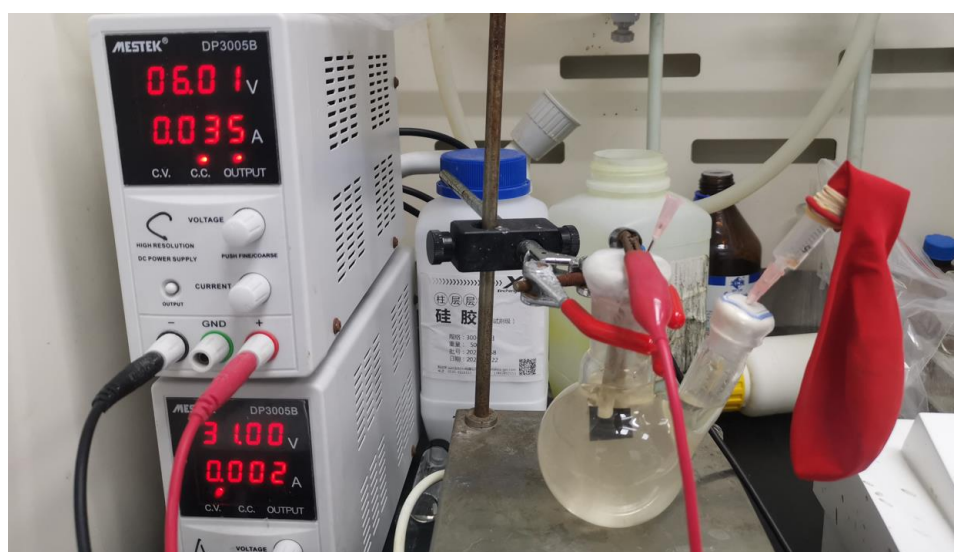
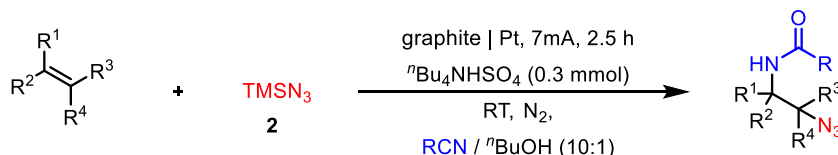


Figure S2. Scaled electrolysis

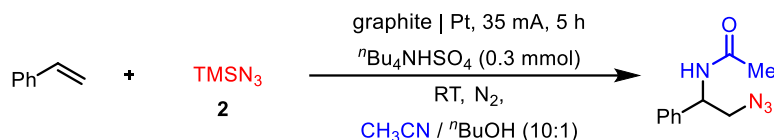
2. General Procedures

Method A: General procedure for the electrochemical synthesis of vicinal azidoacetamides (constant-current electrolysis)



In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, nBu_4NHSO_4 (0.3 mmol) was added. The glassware was equipped with a graphite plate (15 mm \times 15 mm \times 1 mm) as the anode and a platinum plate (15 mm \times 15 mm \times 0.3 mm) as the cathode. Under the protection of N_2 , olefin substrates (0.3 mmol), $TMSN_3$ (1.7 equiv.), RCN (10 mL), and nBuOH (1 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA at room temperature for 2.5 h. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

Method B: Scale-up synthesis



In an oven-dried undivided three-necked glassware (100 mL) equipped with a stirring bar, nBu_4NHSO_4 (0.3 mmol) was added. The glassware was equipped with a graphite plate (15 mm \times 15 mm \times 1 mm) as the anode and a platinum plate (15 mm \times 15 mm \times 0.3 mm) as the cathode. Under the protection of N_2 , olefin substrates (3 mmol), $TMSN_3$ (1.7 equiv.), CH_3CN (100 mL), and nBuOH (10 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 35 mA at room temperature for 5 h. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

3. Optimization of the Reaction Conditions

Table S1. Screening of solvents

Entry	CH ₃ CN / co-solvent (10:1)	Yield/% ^a
1	MeCN/EtOH	45
2	MeCN/CF ₂ CH ₂ OH	33
3	MeCN/CCl ₃ CH ₂ OH	36
4	MeCN/CF ₃ CF ₃ CH ₂ OH	15
5	MeCN/ ⁿ BuOH	57/56 ^b
6	MeCN/ ⁿ PrOH	33
7	MeCN/EG	10
8	MeCN/H ₂ O	26
9	MeCN/HOAc	6

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

Table S2. Screening of the ratio of solvents

Entry	MeCN / ⁿ BuOH (X:Y)	Yield/% ^a
1	16.6:1	36
2	12.5:1	45
3	12:1	50

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

Table S3. Screening of the current

Entry	I / mA, t / h	Yield/% ^a
1	1 mA, 17.5 h	37 ^b
2	2 mA, 8.75 h	55 ^b
3	3 mA, 5.8 h	46/52 ^b
4	9 mA, 1.94 h	41
5	12 mA, 1.48 h	38

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

Table S4. Screening of the voltage

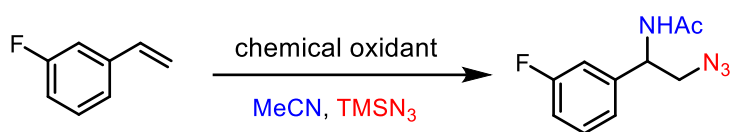
Entry	U / V, t / h	Yield/% ^a
1	$E_{cell} = 1$ V, 4 h	ND
2	$E_{cell} = 1.5$ V, 4 h	6
3	$E_{cell} = 2$ V, 4 h	15
4 ^b	$E_{anode} = 1$ V, 4 h	trace
5 ^b	$E_{anode} = 1$ V, 8 h	trace
6 ^b	$E_{anode} = 1.5$ V, 4 h	19
7 ^b	$E_{anode} = 2$ V, 4 h	trace

^a Yield was determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard;

^b Ag/AgCl as the reference electrode.

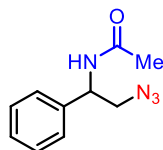
4. Control Experiments with Chemical Oxidants

In an oven-dried schlenk (10 mL) equipped with a stirring bar, $t\text{Bu}_4\text{NHSO}_4$ (0.3 mmol) was added. Under the protection of N_2 , 3-fluorostyrene (0.3 mmol), TMSN_3 (1.7 equiv.), oxidant (1 equiv.), $\text{CH}_3\text{CN}/t\text{BuOH}$ (10:1) 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 ^{19}F NMR of the crude reaction mixture with PhOCF_3 as the internal standard.



Entry	Oxidant	Conversion (%)	10 , Yield (%)
1	Anode	>95	56
2	NFSI	<5	n.d.
3	TBHP	<1	n.d.
4	CAN	79	n.d.
5	<i>m</i> -CPBA	10	n.d.
6	DDQ	10	n.d.
7	$\text{PhI}(\text{OAc})_2$	>95	n.d.
8	AgNO_3	10	n.d.

5. Characterization of Products

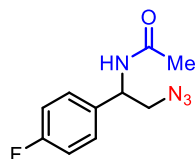


N-(2-azido-1-phenylethyl)acetamide (**3**)¹

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 33.9 mg (56% yield) of **3** as a yellow oil.

Followed **Method B**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 287 mg (47% yield) of **3**.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 6.15 (br s, 1H), 5.21 (dt, J = 8.0, 5.4 Hz, 1H), 3.71 – 3.60 (m, 2H), 2.04 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 169.7, 138.6, 128.9, 128.2, 126.7, 55.0, 52.6, 23.3.

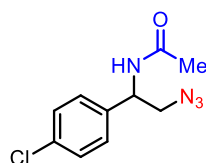


N-(2-azido-1-(4-fluorophenyl)ethyl)acetamide (**4**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 26.2 mg (39% yield) of **4** as a yellow oil.

IR (neat, cm⁻¹): 3276(m), 3070(w), 2096(s), 1649(s), 1509(s), 1224(s), 833(s), 532(s).

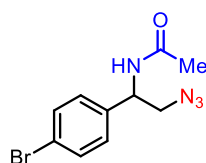
¹H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.09 – 7.00 (m, 2H), 6.20 (br s, 1H), 5.18 (dt, J = 7.9, 5.3 Hz, 1H), 3.69 – 3.60 (m, 2H), 2.03 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 169.7, 162.4 (d, J = 247.4 Hz), 134.6 (d, J = 3.3 Hz), 128.4 (d, J = 8.1 Hz), 115.8 (d, J = 21.3 Hz), 55.0, 51.9, 23.2. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -113.7 (td, J = 8.9, 4.6 Hz). HRMS (ESI) calculated for C₁₀H₁₂FN₄O⁺ [M+H]⁺: 223.0990; found: 223.0988.



N-(2-azido-1-(4-chlorophenyl)ethyl)acetamide (**5**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 37.5 mg (52% yield) of **5** as a yellow oil.

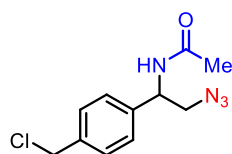
IR (neat, cm^{-1}): 3276(m), 2927(w), 2101(s), 1653(s), 1544(m), 1494(m), 1092(m), 826(w). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 2H), 7.26 – 7.22 (m, 2H), 6.18 (br s, 1H), 5.17 (dt, $J = 8.0, 5.2$ Hz, 1H), 3.70 – 3.59 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 137.3, 134.0, 129.0, 128.1, 54.9, 51.9, 23.2. HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{ClN}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 239.0694; found: 239.0692.



N-(2-azido-1-(4-bromophenyl)ethyl)acetamide (6)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 43.9 mg (51% yield) of **6** as a yellow oil.

IR (neat, cm^{-1}): 3275(m), 2926(w), 2099(s), 1651(s), 1543(m), 1296(m), 1011(m), 821(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.46 (m, 2H), 7.21 – 7.16 (m, 2H), 6.21 (br s, 1H), 5.15 (dt, $J = 8.0, 5.2$ Hz, 1H), 3.72 – 3.58 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 137.8, 132.0, 128.4, 122.1, 54.8, 52.0, 23.2. HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{BrN}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 283.0189; found: 283.0187.

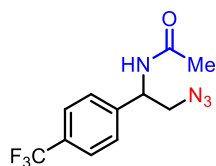


N-(2-azido-1-(4-(chloromethyl)phenyl)ethyl)acetamide (7)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 37.3 mg (49% yield) of **7** as a yellow oil.

IR (neat, cm^{-1}): 3272(m), 2926(m), 2101(s), 1652(s), 1546(m), 1267(m), 680(w). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.37 (m, 2H), 7.32 – 7.29 (m, 2H), 6.24 (br s, 1H), 5.20 (dt, $J = 8.0, 5.4$ Hz, 1H), 4.57 (s, 2H), 3.77 – 3.55 (m, 2H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 139.0, 137.4, 129.1, 127.1, 54.9, 52.2,

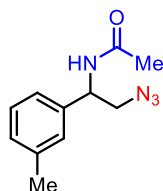
45.6, 23.2. HRMS (ESI) calculated for $C_{11}H_{14}ClN_4O^+$ $[M+H]^+$: 253.0851; found: 253.0847.



N-(2-azido-1-(4-(trifluoromethyl)phenyl)ethyl)acetamide (8)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 28.5 mg (35% yield) of **8** as a yellow oil.

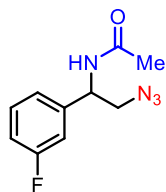
IR (neat, cm^{-1}): 3273(w), 2927(w), 2104(s), 1654(s), 1546(m), 1326(s), 1068(s), 840(m). 1H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, $J = 8.1$ Hz, 2H), 7.51 – 7.41 (m, 2H), 6.30 (br s, 1H), 5.28 – 5.22 (m, 1H), 3.70 (qd, $J = 12.5, 5.2$ Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.8, 142.8, 130.3 (q, $J = 32.7$ Hz), 127.1, 125.8 (q, $J = 3.8$ Hz), 123.9 (q, $J = 216.3$ Hz), 54.8, 52.1, 23.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.6. HRMS (ESI) calculated for $C_{11}H_{12}F_3N_4O^+$ $[M+H]^+$: 273.0958; found: 273.0953.



N-(2-azido-1-(m-tolyl)ethyl)acetamide (9)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 31.9 mg (49% yield) of **9** as a yellow oil.

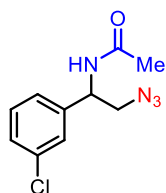
IR (neat, cm^{-1}): 3272(m), 2924(w), 2095(s), 1648(s), 1543(m), 1294(m), 704(m), 450(m). 1H NMR (500 MHz, Chloroform-*d*) δ 7.25 (t, $J = 7.8$ Hz, 1H), 7.15 – 7.07 (m, 3H), 6.15 (br s, 1H), 5.16 (dt, $J = 8.0, 5.5$ Hz, 1H), 3.69 – 3.60 (m, 2H), 2.36 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 138.6, 138.6, 128.9, 128.8, 127.5, 123.6, 55.0, 52.6, 23.3, 21.4. HRMS (ESI) calculated for $C_{11}H_{15}N_4O^+$ $[M+H]^+$: 219.1240; found: 219.1239.



N-(2-azido-1-(3-fluorophenyl)ethyl)acetamide (**10**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 37.6 mg (56% yield) of **10** as a yellow oil.

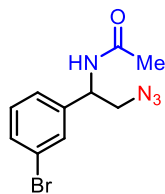
IR (neat, cm^{-1}): 3285(m), 2925(w), 2104(s), 1652(s), 1547(m), 1265(m), 788(w), 699(w). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.33 (td, $J = 8.0, 5.9$ Hz, 1H), 7.11 – 7.08 (m, 1H), 7.07 – 6.97 (m, 2H), 6.34 (br s, 1H), 5.20 (dt, $J = 8.0, 5.3$ Hz, 1H), 3.74 – 3.54 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.8, 163.0 (d, $J = 247.2$ Hz), 141.3 (d, $J = 6.9$ Hz), 130.4 (d, $J = 8.1$ Hz), 122.4, 115.0 (d, $J = 21.2$ Hz), 113.7 (d, $J = 22.3$ Hz), 54.9, 52.1, 23.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -111.9 (m). HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{FN}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 223.0990; found: 223.0988.



N-(2-azido-1-(3-chlorophenyl)ethyl)acetamide (**11**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 38.6 mg (54% yield) of **11** as a yellow oil.

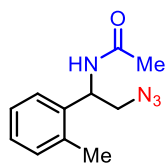
IR (neat, cm^{-1}): 3275(m), 3064(w), 2098(s), 1649(s), 1542(s), 1293(m), 786(m), 696(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 3H), 7.21 – 7.18 (m, 1H), 6.31 (br s, 1H), 5.17 (dt, $J = 8.1, 5.3$ Hz, 1H), 3.70 – 3.60 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.8, 140.8, 134.7, 130.1, 128.3, 126.8, 125.0, 54.9, 52.1, 23.2. HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{ClN}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 239.0694; found: 239.0692.



N-(2-azido-1-(3-bromophenyl)ethyl)acetamide (**12**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 39.9 mg (47% yield) of **12** as a yellow oil.

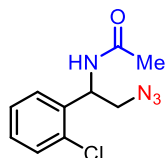
IR (neat, cm^{-1}): 3276(m), 2926(w), 2102(s), 1651(s), 1545(m), 1265(m), 732(m), 702(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.38 (m, 2H), 7.28 – 7.20 (m, 2H), 6.26 (br s, 1H), 5.17 (dt, $J = 8.1, 5.2$ Hz, 1H), 3.72 – 3.58 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 141.1, 131.2, 130.4, 129.7, 125.5, 122.9, 54.9, 52.0, 23.2. HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{BrN}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 283.0189; found: 283.0187.



N-(2-azido-1-(o-tolyl)ethyl)acetamide (**13**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 33.7 mg (51% yield) of **13** as a yellow oil.

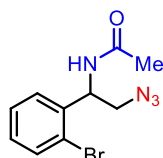
IR (neat, cm^{-1}): 3275(m), 3066(w), 2100(s), 1649(s), 1546(m), 1297(m), 759(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 1H), 7.24 – 7.16 (m, 3H), 6.16 (br s, 1H), 5.42 (dt, $J = 7.9, 5.9$ Hz, 1H), 3.61 (h, $J = 6.2$ Hz, 2H), 2.39 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.6, 136.8, 136.1, 131.0, 128.1, 126.4, 125.4, 54.1, 48.8, 23.1, 19.3. HRMS (ESI) calculated for $\text{C}_{11}\text{H}_{15}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 219.1240; found: 219.1238.



N-(2-azido-1-(2-chlorophenyl)ethyl)acetamide (**14**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 45.2 mg (63% yield) of **14** as a yellow oil.

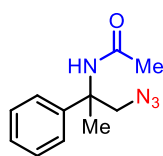
IR (neat, cm^{-1}): 3278(m), 3068(w), 2102(s), 1653(s), 1547(m), 1294(m), 756(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 1H), 7.36 – 7.33 (m, 1H), 7.30 – 7.21 (m, 2H), 6.58 (br s, 1H), 5.57 (dt, $J = 8.0, 5.4$ Hz, 1H), 3.72 – 3.59 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 136.0, 132.8, 130.1, 129.3, 128.0, 127.1, 53.6, 50.4, 23.2. HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{ClN}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 239.0694; found: 239.0692.



N-(2-azido-1-(2-bromophenyl)ethyl)acetamide (**15**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 49.0 mg (58% yield) of **15** as a yellow oil.

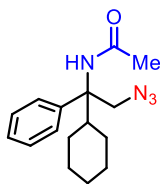
IR (neat, cm^{-1}): 3274(m), 3064(w), 2099(s), 1651(s), 1545(m), 1294(m), 755(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 1H), 7.36 – 7.28 (m, 2H), 7.17 (ddd, $J = 8.0, 6.5, 2.5$ Hz, 1H), 6.48 (br s, 1H), 5.53 (dt, $J = 7.8, 5.3$ Hz, 1H), 3.67 (qd, $J = 12.6, 5.3$ Hz, 2H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.6, 137.6, 133.4, 129.6, 128.0, 127.7, 123.0, 53.6, 52.4, 23.2. HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{12}\text{BrN}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 283.0189; found: 283.0187.



N-(1-azido-2-phenylpropan-2-yl)acetamide (**16**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 27.4 mg (42% yield) of **16** as a yellow oil.

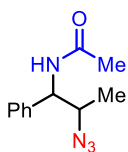
IR (neat, cm^{-1}): 3291(m), 2927(w), 2100(s), 1655(s), 1547(m), 1299(m), 699(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 4H), 7.30 – 7.26 (m, 1H), 5.82 (br s, 1H), 4.03 (d, $J = 12.2$ Hz, 1H), 3.76 (d, $J = 12.2$ Hz, 1H), 2.05 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 142.8, 128.7, 127.5, 125.1, 59.3, 58.0, 25.2, 24.2. HRMS (ESI) calculated for $\text{C}_{11}\text{H}_{15}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 219.1240; found: 219.1238.



N-(2-azido-1-cyclohexyl-1-phenylethyl)acetamide (**17**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 40.5 mg (47% yield) of **17** as a yellow oil.

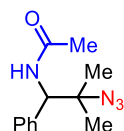
IR (neat, cm^{-1}): 3300(w), 2931(m), 2855(m), 2097(s), 1655(s), 1538(m), 1292(m), 703 (m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 7.20 – 7.13 (m, 2H), 5.74 (br s, 1H), 4.39 (d, $J = 12.5$ Hz, 1H), 4.15 (d, $J = 12.5$ Hz, 1H), 2.07 (s, 3H), 2.03 (tt, $J = 12.0, 2.8$ Hz, 1H), 1.81 – 1.70 (m, 3H), 1.61 (dd, $J = 35.1, 14.2$ Hz, 2H), 1.32 – 1.12 (m, 2H), 0.99 – 0.81 (m, 1H), 0.67 (pd, $J = 12.9, 3.5$ Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.0, 138.7, 127.9, 127.1, 126.1, 65.3, 52.0, 43.7, 27.4, 27.1, 26.34, 26.31, 26.0, 24.2. HRMS (ESI) calculated for $\text{C}_{16}\text{H}_{23}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 287.1866; found: 287.1862.



N-(2-azido-1-phenylpropyl)acetamide (**18**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 26.0 mg (40%, dr = 2:1) of **18** as a yellow oil.

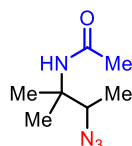
IR (neat, cm^{-1}): 3285(m), 2930(w), 2108(s), 1650(s), 1545(m), 1374(m), 1262(m), 701(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 4H), 7.33 – 7.27 (m, 6H), 6.19 (br s, 1H, minor), 6.10 (br s, 1H, major), 5.07 (dd, $J = 9.1, 3.9$ Hz, 1H, major), 4.98 (dd, $J = 8.4, 4.5$ Hz, 1H, minor), 4.01 (qd, $J = 6.7, 4.5$ Hz, 1H, minor), 3.93 (qd, $J = 6.6, 3.9$ Hz, 1H, major), 2.08 (s, 3H, major), 2.02 (s, 3H, minor), 1.34 (d, $J = 6.6$ Hz, 3H, major), 1.15 (d, $J = 6.7$ Hz, 3H, minor). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.8, 169.3, 139.6, 137.0, 128.7, 128.6, 128.2, 128.0, 127.8, 126.6, 61.8, 60.0, 56.9, 56.4, 23.4, 23.3, 17.4, 16.1. HRMS (ESI) calculated for $\text{C}_{11}\text{H}_{15}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 219.1240; found: 219.1237.



N-(2-azido-2-methyl-1-phenylpropyl)acetamide (**19**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 37.6 mg (54% yield) of **19** as a yellow oil.

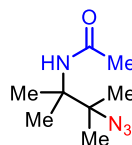
IR (neat, cm^{-1}): 3297(m), 2976(w), 2103(s), 1648(s), 1538(m), 1371(m), 1262(m), 701(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 5H), 6.33 (br s, 1H), 4.90 (d, $J = 9.5$ Hz, 1H), 2.01 (s, 3H), 1.44 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 138.5, 128.3, 128.2, 127.9, 64.1, 59.9, 25.3, 24.0, 23.4. HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{17}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 233.1397; found: 233.1395.



N-(3-azido-2-methylbutan-2-yl)acetamide (**20**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 25.7 mg (50% yield) of **20** as a yellow oil.

IR (neat, cm^{-1}): 3298(m), 2979(w), 2089(s), 1653(s), 1550(m), 1298(m), 626(w). ^1H NMR (500 MHz, Chloroform-*d*) δ 5.41 (br s, 1H), 4.30 (q, $J = 6.8$ Hz, 1H), 1.95 (s, 3H), 1.34 (s, 3H), 1.27 (s, 3H), 1.21 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.9, 62.0, 56.9, 24.4, 23.6, 22.5, 14.4. HRMS (ESI) calculated for $\text{C}_7\text{H}_{15}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 171.1240; found: 171.1235.

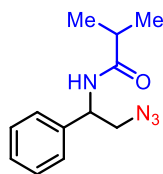


N-(3-azido-2,3-dimethylbutan-2-yl)acetamide (**21**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 26.1 mg (47% yield) of **21** as a yellow oil.

IR (neat, cm^{-1}): 3311(w), 2983(w), 2104(s), 1661(m), 1551(m), 1372(m), 1129(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 5.63 (br s, 1H), 1.95 (s, 3H), 1.42 (s, 6H), 1.35 (s,

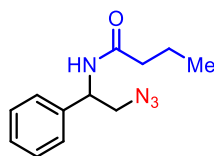
6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.9, 67.9, 59.4, 25.0, 22.0, 21.5. HRMS (ESI) calculated for $\text{C}_8\text{H}_{17}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 185.1397; found: 185.1395.



N-(2-azido-1-phenylethyl)isobutyramide (22)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 40.8 mg (59% yield) of **22** as a yellow oil.

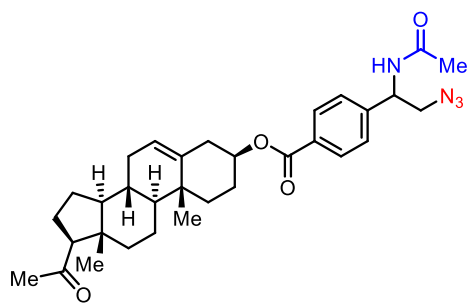
IR (neat, cm^{-1}): 3290(w), 2970(w), 2928(w), 2100(s), 1649(m), 1537(m), 1246(m), 700(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 5.94 (br s, 1H), 5.22 (dt, $J = 7.9, 5.2$ Hz, 1H), 3.79 – 3.62 (m, 2H), 2.42 (p, $J = 6.9$ Hz, 1H), 1.20 (d, $J = 6.9$ Hz, 3H), 1.18 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.5, 138.8, 128.9, 128.1, 126.6, 55.0, 52.3, 35.7, 19.5. HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{17}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 233.1397; found: 233.1393.



N-(2-azido-1-phenylethyl)butyramide (23)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 30.6 mg (40% yield) of **23** as a yellow oil.

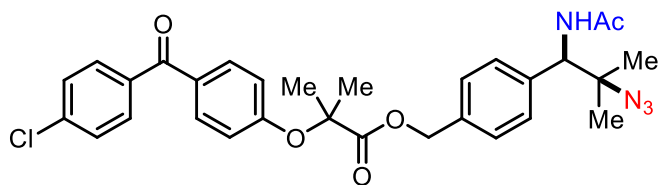
IR (neat, cm^{-1}): 3283(w), 2964(w), 2930(w), 2098(s), 1646(m), 1542(m), 1282(m), 700(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.33 (m, 2H), 7.32 (td, $J = 6.5, 1.4$ Hz, 3H), 5.95 (br s, 1H), 5.23 (dt, $J = 8.0, 5.2$ Hz, 1H), 3.76 – 3.62 (m, 2H), 2.23 (td, $J = 7.3, 1.4$ Hz, 2H), 1.69 (q, $J = 7.5$ Hz, 2H), 0.96 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 138.8, 128.9, 128.2, 126.7, 55.1, 52.3, 38.6, 19.0, 13.7. HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{17}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 233.1397; found: 233.1394.



(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1-acetamido-2-azidoethyl)benzoate (24)

Followed **Method A**, CCE = 7 mA, 5 h. The desired pure product was purified using silica gel chromatography (PE:EA = 1:2) to give 38.7 mg (24% yield) of **24** as a yellow oil.

IR (neat, cm^{-1}): 3286(w), 2925(s), 2854(m), 2101(s), 1709(s), 1661(m), 1274(s), 1115(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.03 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 6.05 (br s, 1H), 5.45 – 5.37 (m, 1H), 5.25 (dt, $J = 8.0, 5.1$ Hz, 1H), 4.84 (ddt, $J = 16.3, 8.2, 4.5$ Hz, 1H), 3.77 – 3.63 (m, 2H), 2.54 (t, $J = 9.0$ Hz, 1H), 2.45 (d, $J = 7.8$ Hz, 2H), 2.22 – 2.14 (m, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 2.06 – 1.87 (m, 4H), 1.81 – 1.64 (m, 4H), 1.56 – 1.38 (m, 4H), 1.23 – 1.10 (m, 3H), 1.06 (s, 3H), 1.05 – 0.99 (m, 1H), 0.63 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.6, 169.6, 165.4, 143.6, 139.6, 130.6, 130.1, 126.6, 122.5, 74.6, 63.7, 56.8, 55.0, 52.2, 49.9, 44.0, 38.8, 38.1, 37.0, 36.6, 31.81, 31.77, 31.6, 27.8, 24.5, 23.3, 22.8, 21.0, 19.4, 13.2. HRMS (ESI) calculated for $\text{C}_{32}\text{H}_{43}\text{N}_4\text{O}_4^+$ $[\text{M}+\text{H}]^+$: 547.3279; found: 547.3277.

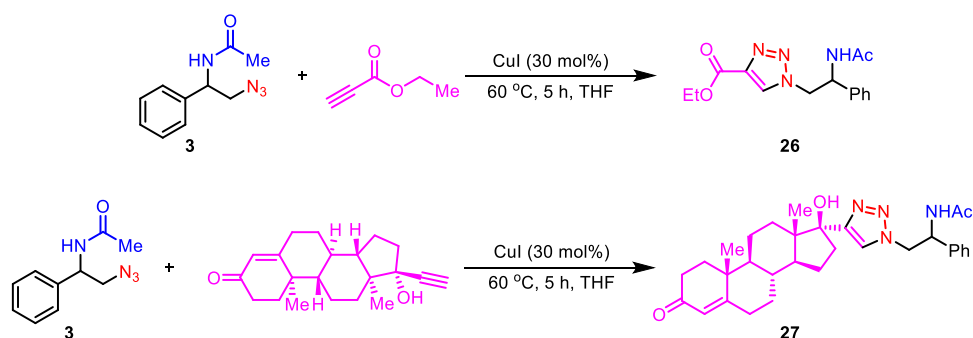


4-(1-Acetamido-2-azido-2-methylpropyl)benzyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (25)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 43.6 mg (26% yield) of **25** as a yellow oil.

IR (neat, cm^{-1}): 3286(w), 2987(w), 2095(s), 1709(s), 1661(m), 1274(s), 1263(m), 1135(w), 732(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.67 (m, 2H), 7.51 – 7.40 (m, 2H), 7.51 – 7.40 (m, 2H), 7.34 – 7.23 (m, 2H), 7.20 – 7.08 (m, 2H), 6.85 – 6.74 (m, 2H), 6.54 (d, $J = 9.3$ Hz, 1H), 5.17 (m, 2H), 4.89 (d, $J = 9.4$ Hz, 1H), 2.01 (s, 3H), 1.68 (d, $J = 5.3$ Hz, 6H), 1.44 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 194.3, 173.4, 169.4, 159.6, 138.9, 138.5, 136.2, 134.6, 132.0, 131.2, 128.5, 128.5, 128.3, 117.2, 79.4, 66.9, 64.0, 59.7, 29.7, 25.9, 25.2, 25.0, 24.1, 23.2. HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{32}\text{ClN}_4\text{O}_5^+$ $[\text{M}+\text{H}]^+$: 563.2056; found: 563.2057.

6. Derivatizations of the Product



The mixture solution of N-(2-azido-1-phenylethyl)acetamide (**3**, 40.8 mg, 0.2 mmol, 1.0 equiv.), alkyne (3 equiv) and CuI (30 mol%) in THF (2 mL) was stirred at 60 °C for 5 h. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (DCM/CH₃OH=10:1) to give the desired products (**26**, 50.1 mg, 83% yield and **27**, 98.1 mg, 95% yield, dr = 1:1).

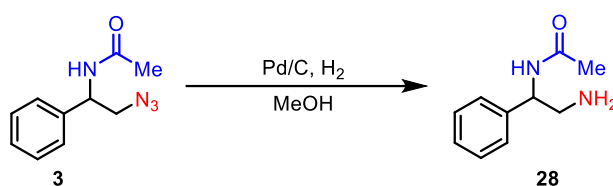
Ethyl 1-(2-acetamido-2-phenylethyl)-1H-1,2,3-triazole-4-carboxylate (**26**)

IR (neat, cm⁻¹): 3282(w), 2924(w), 1725(s), 1656(s), 1544(s), 1376(m), 1209(s), 701(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.31 – 7.27 (m, 1H), 7.27 – 7.24 (m, 1H), 7.23 – 7.13 (m, 3H), 5.54 – 5.36 (m, 1H), 4.83 – 4.67 (m, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.91 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 170.2, 160.5, 139.9, 137.4, 129.0, 128.5, 128.4, 126.5, 61.3, 54.4, 53.3, 23.0, 14.2. HRMS (ESI) calculated for C₁₅H₁₉N₄O₃⁺ [M+H]⁺: 303.1452; found: 303.1446.

N-(2-(4-((8R,9S,10R,13S,14S,17S)-17-hydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-1H-1,2,3-triazol-1-yl)-1-phenylethyl)acetamide (**27**)

IR (neat, cm⁻¹): 3322(w), 2927(m), 2855(w), 1655(s), 1536(w), 1376(w), 1057(w), 702(m). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.53 – 8.48 (m, 1H), 7.71 (d, *J* = 37.4 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.30 – 7.20 (m, 1H), 5.61 (s, 1H), 5.43 – 5.23 (m, 1H), 5.03 (d, *J* = 5.2 Hz, 1H), 4.68 – 4.47 (m, 2H), 2.45 – 2.04 (m, 5H),

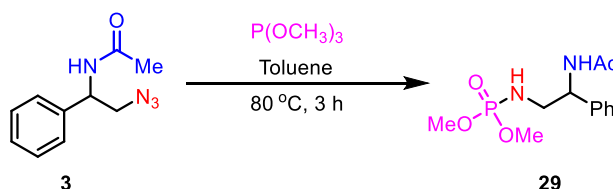
1.97 – 1.78 (m, 3H), 1.75 (d, $J = 8.9$ Hz, 3H), 1.73 – 1.64 (m, 1H), 1.61 – 1.42 (m, 2H), 1.41 – 1.24 (m, 4H), 1.12 (s, 3H), 0.91 (d, $J = 12.1$ Hz, 3H), 0.90 – 0.77 (m, 2H), 0.59 – 0.41 (m, 1H), 0.32 – 0.02 (m, 1H). ^{13}C NMR (126 MHz, DMSO- D_6) δ 198.51, 198.49, 171.6, 169.12, 169.07, 154.0, 153.9, 140.0, 139.9, 128.89, 128.85, 128.00, 127.99, 127.5, 127.4, 81.3, 53.70, 53.66, 53.6, 53.4, 53.3, 53.2, 48.5, 48.4, 46.7, 46.6, 38.7, 38.6, 37.5, 37.4, 36.10, 36.08, 35.6, 34.11, 34.08, 32.7, 32.6, 32.5, 32.1, 32.0, 24.3, 24.2, 23.1, 23.0, 20.8, 17.5, 17.4, 14.81, 14.79. HRMS (ESI) calculated for $\text{C}_{31}\text{H}_{41}\text{N}_4\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 517.3173; found: 517.3166.



The mixture solution of **3** (0.1 mmol, 1.0 equiv), 10% Pd/C (0.1 mmol) in MeOH (1 mL) under an atmosphere of H_2 was stirred at room temperature overnight. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (DCM/ CH_3OH =8:1) to give the desired product (**28**, 10.3 mg, 58% yield).

N-(2-amino-1-phenylethyl)acetamide (**28**)

IR (neat, cm^{-1}): 3271(m), 2927(w), 1649(m), 1265(m), 907(m), 728(s). ^1H NMR (500 MHz, Chloroform- d) δ 7.37 – 7.27 (m, 5H), 6.89 (br s, 1H), 5.19 – 4.99 (m, 1H), 3.23 – 2.87 (m, 2H), 2.74 (brs, 2H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, Chloroform- d) δ 169.8, 140.0, 128.8, 127.5, 126.5, 55.2, 46.8, 23.3. HRMS (ESI) calculated for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 179.1179; found: 179.1177.



The mixture solution of **3** (0.2 mmol, 1.0 equiv), $\text{P}(\text{OMe})_3$ (1.5 equiv) in toluene (1.2 mL) was stirred at 80 °C for 3 h. The organic solvent was then evaporated under

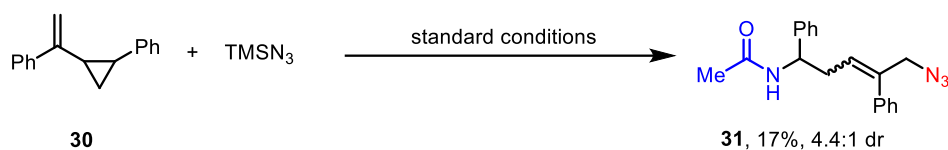
reduced pressure and the residue was purified by flash column chromatography on silica gel (DCM/CH₃OH=10:1) to give the desired product (**29**, 47.4 mg, 83% yield).

Dimethyl (2-acetamido-2-phenylethyl)phosphoramidate (29).

IR (neat, cm⁻¹): 3269(m), 2953(w), 1656(m), 1233(m), 1032(s), 832(m), 702(w). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.22 – 7.14 (m, 2H), 5.01 (td, *J* = 7.3, 4.5 Hz, 1H), 3.70 (dt, *J* = 11.5, 3.7 Hz, 1H), 3.61 (d, *J* = 11.2 Hz, 3H), 3.44 (d, *J* = 11.2 Hz, 3H), 3.25 – 3.08 (m, 2H), 1.94 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 170.5, 139.7, 128.7, 127.6, 126.7, 54.2 (d, *J* = 4.9 Hz), 53.2 (d, *J* = 5.7 Hz), 53.0 (d, *J* = 5.6 Hz), 46.5, 23.2. ³¹P NMR (162 MHz, Chloroform-*d*) δ 11.9 (m). HRMS (ESI) calculated for C₁₂H₂₀N₂O₄P⁺ [M+H]⁺: 287.1155; found: 287.1151.

7. Mechanistic Experiments

Radical clock experiments



Following the standard procedure for the synthesis of vicinal azidoacetamides using 1-(2-phenylcyclopropyl)vinylbenzene (0.3 mmol) as the starting material. After the work-up, the crude mixture was purified using column chromatography to afford **31**.

N-(4-azido-1,4-diphenylbut-3-en-1-yl)acetamide (**31**)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 16.3 mg (17%, dr = 4.4:1) of **31** as a yellow oil.

IR (neat, cm⁻¹): 3278(w), 2926(w), 2098(s), 1647(s), 1546(m), 1285(m), 700(s). ¹H NMR (400 MHz, Chloroform-*d*, major diastereoisomer) δ 7.48 – 7.00 (m, 10H), 5.94 (t, *J* = 7.6 Hz, 1H), 5.16 (q, *J* = 7.3 Hz, 1H), 4.20 (d, *J* = 2.6 Hz, 1H), 2.99 – 2.69 (m, 2H), 2.00 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*, major diastereoisomer) δ 169.5, 141.0, 140.4, 136.3, 129.6, 128.9, 128.6, 127.7, 127.7, 126.5, 126.1, 53.3, 49.2, 35.4, 23.4. HRMS (ESI) calculated for C₁₉H₂₁N₄O⁺ [M+H]⁺: 321.1710; found: 321.1706.

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. The current was reported in mA, while all potentials were reported in V.

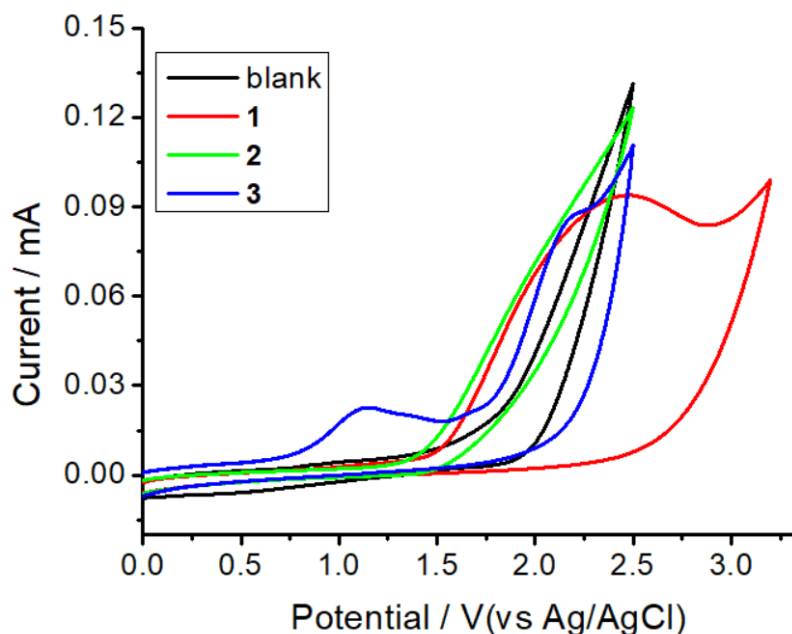


Figure S1. Cyclic voltammogram with $n\text{Bu}_4\text{NHSO}_4$ (10 mM) as electrolyte, MeCN/ $n\text{BuOH}$ (10:1) as solvent. Scan rate: 0.1 V/s.

In addition, we also measured the oxidation potentials of some electron-deficient olefins. For example, 4-fluorostyrene (**S1**), 4-(trifluoromethyl)styrene (**S2**), methyl-4-vinylbenzoate (**S3**), 4-vinylpyridine (**S4**). Among them, the oxidation potential of **S1** is $E_{p/2} = 1.65$ V vs. Ag/AgCl and that of **S2** is $E_{p/2} = 1.96$ V vs. Ag/AgCl. However, no obvious oxidation peaks of **S3** or **S4** can be observed. Consistent with this observation, the anticipated vicinal azidoacetamidation reaction did not proceed with those highly electron-deficient olefins (**S3** and **S4**) under the standard conditions.

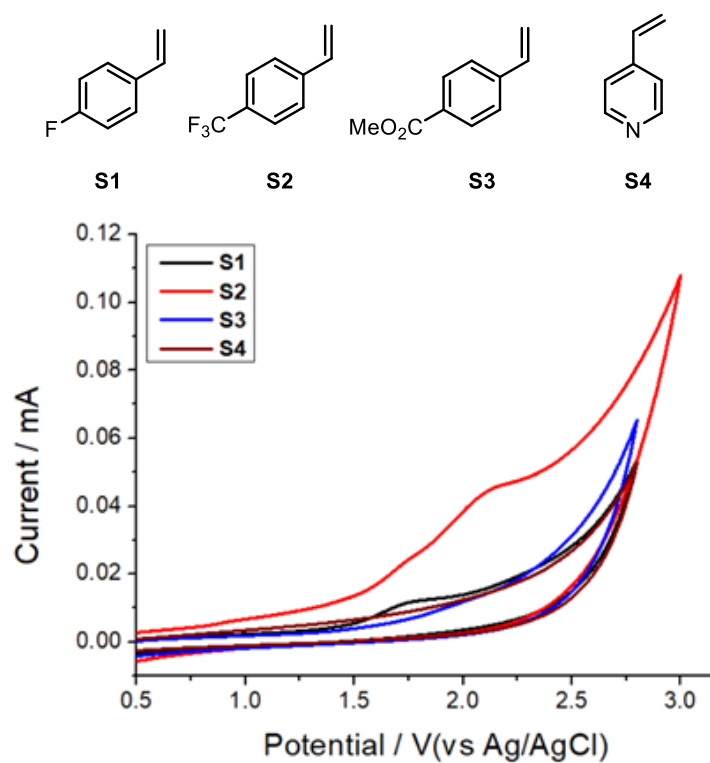


Figure S2. Cyclic voltammogram with $n\text{Bu}_4\text{NHSO}_4$ (10 mM) as the electrolyte, MeCN/ $n\text{BuOH}$ (10:1) as solvent. Scan rate: 0.1 V/s.

8. Reference

1. Gutmann, B., Roduit, J.-P., Roberge, D., Kappe, C. O. A two-step continuous-flow synthesis of N-(2-aminoethyl)acylamides through ring-opening/hydrogenation of oxazolines. *Chem. Eur. J.* **17**, 13146-13150 (2011).

9. Spectral Data (^1H , ^{13}C , ^{19}F) of Products

