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# Electronic Supplementary Information

# Fe-catalyzed radical-type difunctionalization of styrenes with aliphatic aldehydes and trimethylsilyl azide via decarbonylative alkylation-azidation cascade

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#### I. General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Dry solvents (toluene, ethyl acetate, dichloromethane, acetonitrile, chlorobenzene, fluorobenzene) were used as commercially available.

Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for <sup>1</sup>H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform:  $\delta$  7.26 ppm). Chemical shifts for <sup>13</sup>C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl<sub>3</sub>:  $\delta$  77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

#### **II.** General experimental procedures

A general experimental procedure is described as following:

An oven-dried microwave reaction vessel was charged with  $Fe(acac)_3$  (0.0005 mmol, 0.25 mol%) in fluorobenzene (1.0 mL, pre-prepared solution), alkene (**1a**, 0.2 mmol, 1.0 equiv), TMSN<sub>3</sub> (0.4 mmol, 2.0 equiv), isobutyraldehyde (**2a**, 0.6 mmol, 3.0 equiv) and DTBP (0.6 mmol, 3.0 equiv) under argon atmosphere. The vessel was sealed and heated was stirred at 110 °C (oil bath temperature) for 12 h. Afterwards the resulting mixture was cooled to room temperature, The solvent was removed in vacuo, The residue was purified by column chromatography on silica gel with a mixture of dichloromethane/petroleum ether as eluent to give products **3a**.

#### **III.** Condition optimization

#### Table S1. Optimization of the reactants ratio<sup>*a*</sup>

TMSN <sub>3</sub> + Ph +	Сно	DTBP (2.0 equiv) Fe(acac) <sub>3</sub> (10 mol%) DCM,110 °C, 12 h	Ph Ph	
1a	<u>2</u> a		за	
entry	ratio		yield [%]	
TMSN <sub>3</sub> :1a:2a				
1		2:1:2	32	
2	:	2:1:3	59	
3	í	3:1:2	38	
4		3:1:3	61	

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (equiv), TMSN<sub>3</sub> (equiv), DTBP (0.4 mmol 2.0 equiv), Fe(acac)<sub>3</sub> (0.02 mmol, 10 mol %), DCM (1.0 mL), stirred at 110 °C for 12 h under air. <sup>*b*</sup> Isolated yields.

# Table S2. Optimization of the oxidants <sup>a</sup>

TMSN <sub>3</sub> + Ph + 1a	CHO 2a [C Fe(acac) <sub>3</sub> DCM, 110	<sup>1</sup> ] (10 mol%) 0 °C, 12 h <b>Ph</b> <b>3a</b>
entry	[O] (equiv)	yield [%] <sup>b</sup>
1	DTBP	59
2	<b>TBHP</b> in decane	31
3	PhI(AcO) <sub>2</sub>	<2
4	$K_2S_2O_8$	<2
5	<b>DTBP</b> (2.5)	66
6	<b>DTBP (3.0)</b>	74

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), TMSN<sub>3</sub> (0.4 mmol, 2.0 equiv), [O] (2.0 equiv), Fe(acac)<sub>3</sub> (0.02 mmol, 10 mol %), DCM (1.0 mL), stirred at 110 °C for 12 h under air. <sup>*b*</sup> Isolated yields.

TMSN <sub>3</sub> + Ph +	СНО	DTBP (3.0 eq Cat. (10 mo DCM, 110 °C,	<sup>uiv</sup> ) <mark>%) →</mark> Ph <sup>-</sup> 12 h	N <sub>3</sub>
1a	<u>2</u> a			за
entry	Cat.	(mol%)	yield [%	b] <sup>b</sup>
1	FeCl <sub>2</sub>		57	
2	FeCl <sub>3</sub>		55	
3	Fe(acac) <sub>3</sub>		74	
4	Fe(AcO) <sub>2</sub> ·4H <sub>2</sub> O		38	
5	Co	(acac) <sub>3</sub>	<2	
6	Mn(AcO) <sub>2</sub>		<2	
7	Cu	$(AcO)_2$	51	
8	0	CuCl	49	
9	A	gNO <sub>3</sub>	17	

#### Table S3. Optimization of the catalyst<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), TMSN<sub>3</sub> (0.4 mmol, 2.0 equiv), DTBP (0.6 mmol, 3.0 equiv), Cat. (0.02 mmol, 10 mol %), DCM (1.0 mL), stirred at 110 °C for 12 h under air. <sup>*b*</sup> Isolated yields.



1	100	67
2	110	74
3	120	68

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), TMSN<sub>3</sub> (0.4 mmol, 2.0 equiv), DTBP (0.6 mmol, 3.0 equiv), Fe(acac)<sub>3</sub> (0.02 mmol, 10 mol %), DCM (1.0 mL) for 12 h under air. <sup>*b*</sup> Isolated yields.

TMSN3 + Ph 🔨 +	Сно	DTBP (3.0 equiv) Fe(acac) <sub>3</sub> (X mol%) DCM, 110 °C, 12 h	Ph Ph
1a	<u>2</u> a		3a
entry	Fe(acac)	)3 (X mol%)	yield [%] <sup>b</sup>
1		10	74
2		5	75
3		1	77
4		0.5	79
5		0.25	80
6		0.1	65
7			11
<b>8</b> <sup>c</sup>		0.25	81

# Table S5. Optimization of the amounts of catalyst <sup>a</sup>

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), TMSN<sub>3</sub> (0.4 mmol, 2.0 equiv), DTBP (0.6 mmol, 3.0 equiv), Fe(acac)<sub>3</sub> (X mol %), DCM (1.0 mL), stirred at 110 °C for 12 h under air. For precise weighting, a solution of Fe(acac)<sub>3</sub> in organic solvent was prepared and used. <sup>*b*</sup> Isolated yields. <sup>*c*</sup> Argon atmosphere.

## Table S6. Optimization of the solvent <sup>*a*</sup>

TMSN <sub>3</sub> + Ph +	CHO DTBP (3.0 Fe(acac) <sub>3</sub> (0.1 Sol., 110 °	equiv) <u>25 mol%)</u> C, 12 h Ph
1a	2a	3a
entry	Sol.	yield $[\%]^b$
1	DCM	81
2	PhCl	71
3	o-PhCl <sub>2</sub>	67
4	DCE	<2
5	EA	33
6	PhMe	75
7	CH <sub>3</sub> CN	68
8	PhF	84

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), TMSN<sub>3</sub> (0.4 mmol, 2.0 equiv), DTBP (0.6 mmol, 3.0 equiv), Fe(acac)<sub>3</sub> (0.0005 mmol, 0.25 mol %), Sol. (1.0 mL), stirred at 110 °C for 12 h under Ar. For precise weighting, a solution of Fe(acac)<sub>3</sub> in organic solvent was prepared and used. <sup>*b*</sup> Isolated yields.

#### **IV. Mechanistic experiments**

To further understand this Fe-catalyzed alkylative azidation of styrenes with aliphatic aldehydes and trimethylsilyl azide, several mechanistic experiments were carried out in the presence of various radical scavengers.

We found that: (a) in the presence of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, 2.0 equiv), this reaction was completely inhibited and the 1-isopropoxy-2,2,6,6-tetramethylpiperidine was detected by GC-MS, which supported our speculation that the reaction proceeded via a radical pathway and confirmed the generation of alkyl radical; (b) in the presence of BHT (2,6-di-tert-butyl-4-methylphenol, 2.0 equiv), the product **3a** was detected in an 9% yield, which further confirmed that this cascade reaction was realized via radical pathway.



The detected GC-MS spectrum of 1-isopropoxy-2,2,6,6-tetramethylpiperidine:



#### V. Synthetic transformations of alkylation-azidation product



An oven-dried sealed tube containing **3a** (0.2 mmol, 1.0 equiv), PPh<sub>3</sub> (0.24 mmol, 1.2 equiv), was evacuated and purged with argon gas three times. Then, THF/H<sub>2</sub>O (3:1, 2.0 mL) was added via syringe. The reaction mixture was stirred at room temperature for 16 h. The reaction was quenched with NH<sub>4</sub>Cl (aq.), extracted with CH<sub>2</sub>Cl<sub>2</sub> (10×3.0 mL), dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 40:1) to give the colorless oil **4** (24.8 mg, 76%).

To an oven-dried glass tube, **3a** (0.2 mmol, 1.0 equiv) was dissolved in THF (1.0 mL), then phenylacetylene (0.6 mmol, 3.0 equiv) and CuI (0.02 mmol, 0.1 equiv) were added. The reaction was performed at 60 °C for 10 h, and the resulting solution was concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent of petroleum ether and ethyl acetate (5:1) to afford the white solid **5** (47.7 mg, 82%).

#### VI. Spectra data of products

#### (3a) (1-azido-3-methylbutyl)benzene<sup>1</sup>



The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with  $TMSN_3$  and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (31.7 mg, 84%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.29 (m, 5H), 4.47 (dd, J = 8.4, 6.4 Hz, 1H), 1.76 (ddd, J = 14.4, 8.4, 6.0 Hz, 1H), 1.70 – 1.53 (m, 2H), 0.94 (s, 3H), 0.93 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.15, 128.93, 128.34, 127.05, 64.65, 45.19, 25.13, 22.76, 22.34. IR (cm<sup>-1</sup>): 2959, 2870, 2097, 1245, 699.

### (3b) 1-(1-azido-3-methylbutyl)-4-methoxybenzene<sup>2</sup>

Yoshikawa, K. Sato, M. Narita, S. Ohuchida, H. Naka and M. Toda, Bioorganic and Medicinal Chemistry., 2010, 18, 1641.

<sup>&</sup>lt;sup>1</sup> M. Asada, M. Iwahashi, T. Obitsu, A. Kinoshita, Y. Naka, T. Onoda, T. Nagase, M. Tanaka, Y. Yamaura, H. Takizawa, K.

 <sup>&</sup>lt;sup>2</sup> G. V. M. Sharma, K. S. Kumar, B. S. Kumar, S. V. Reddy, R. S. Prakasham and H. Hugel, *Synthetic Communications.*, 2014, 44, 3156.



The title compound was prepared according to the general procedure described above by the reaction between 4-methoxystyrene (**1b**) with TMSN<sub>3</sub> and isobutyraldehyde (**2a**), and purified by flash column chromatography as colorless oil (29.8 mg, 68%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.22 (m, 2H), 6.93 – 6.88 (m, 2H), 4.42 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.82 (s, 3H), 1.74 (ddd, *J* = 14.0, 8.0, 6.0 Hz, 1H), 1.67 – 1.52 (m, 2H), 0.93 (s, 3H), 0.92 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.54, 132.04, 128.32, 114.21, 64.16, 55.42, 44.96, 25.11, 22.66, 22.41. IR(cm<sup>-1</sup>): 2958, 2870, 2096, 1250, 833.

#### (3c) 1-(1-azido-3-methylbutyl)-4-(tert-butyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between 4-tert-butylstyrene (1c) with TMSN<sub>3</sub> and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (37.3 mg, 75%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.37 (m, 2H), 7.25 – 7.21 (m, 2H), 4.43 (dd, J = 8.4, 6.4 Hz, 1H), 1.76 (ddd, J = 14.8, 8.4, 6.0 Hz, 1H), 1.71 – 1.52 (m, 2H), 1.32 (s, 9H), 0.95 (d, J = 1.2 Hz, 3H), 0.93 (d, J = 1.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.24, 137.13, 126.69, 125.80, 64.36, 45.09, 34.72, 31.46, 25.15, 22.81, 22.32, 0.15. IR (cm<sup>-1</sup>): 2960, 2870, 2097, 1248, 699. HRMS: calcd. for C<sub>15</sub>H<sub>24</sub>N (M + H<sup>+</sup> – N<sub>2</sub>): 218.1909, Found: 218.1899.

#### (3d) 1-(1-azido-3-methylbutyl)-4-methylbenzene



The title compound was prepared according to the general procedure described above by the reaction between 4-methylphenylene (1d) with  $TMSN_3$  and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (32.3 mg, 78%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.29 (m, 4H), 4.47 (dd, J = 8.4, 6.4 Hz, 1H), 1.76 (ddd, J = 14.4, 8.4, 6.0 Hz, 1H), 1.70 – 1.53 (m, 2H), 0.94 (s, 3H), 0.93 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.15, 128.93, 128.34, 127.05, 64.65, 45.19, 25.13, 22.76, 22.34. IR (cm<sup>-1</sup>): 2958, 2927, 2069, 1248, 699. HRMS: calcd. for C<sub>12</sub>H<sub>18</sub>N (M + H<sup>+</sup> - N<sub>2</sub>): 176.1439, Found: 176.1433.

#### (3e) 1-(1-azido-3-methylbutyl)-4-(chloromethyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between 1-(chloromethyl)-4-ethenyl-benzene (1e) with  $TMSN_3$  and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (33.5 mg, 71%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.60 (s, 2H), 4.48 (dd, J = 8.8, 6.4 Hz, 1H), 1.76 (ddd, J = 14.4, 8.4, 6.0 Hz, 1H), 1.70 – 1.69 (m, 1H), 1.59 – 1.51 (m, 1H), 0.95 (d, J = 1.2 Hz, 3H), 0.93 (d, J = 1.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.50, 137.52, 129.17, 127.42, 64.25, 45.93, 45.21, 25.10, 22.74, 22.32. IR (cm<sup>-1</sup>): 2958, 2870, 2097, 1267, 669. HRMS: calcd. for C<sub>12</sub>H<sub>17</sub>NCl (M + H<sup>+</sup> – N<sub>2</sub>): 210.1050, Found: 210.1043.

#### (3f) 1-(1-azido-3-methylbutyl)-4-(trifluoromethyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between 4-vinylbenzotrifluoride (**1f**) with  $\text{TMSN}_3$  and isobutyraldehyde (**2a**), and purified by flash column chromatography as colorless oil (31.3 mg, 61%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 4.54 (dd, J = 8.5, 6.3 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.70 – 1.61 (m, 1H), 1.59 – 1.50 (m, 1H), 0.96 (d, J = 2.2 Hz, 2H), 0.94 (d, J = 2.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.36, 130.50 (q, J = 32.5 Hz), 127.34, 125.95 (q, J = 3.8 Hz), 124.11 (q, J = 272.0 Hz), 64.08, 45.39, 25.09, 22.74, 22.22. IR (cm<sup>-1</sup>): 2959, 2873, 2099, 1270, 669. HRMS: calcd. for C<sub>12</sub>H<sub>15</sub>NF<sub>3</sub> (M + H<sup>+</sup> – N<sub>2</sub>): 230.1157, Found: 230.1151.

#### (3g) 1-(1-azido-3-methylbutyl)-4-fluorobenzene



The title compound was prepared according to the general procedure described above by the reaction between 4-fluorostyrene (**1g**) with TMSN<sub>3</sub> and isobutyraldehyde (**2a**), and purified by flash column chromatography as colorless oil (34.4 mg, 83%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.26 (m, 2H), 7.11 – 7.04 (m, 2H), 4.46 (dd, *J* = 8.4, 6.6 Hz, 1H), 1.74 (ddd, *J* = 14.8, 8.4, 6.4 Hz, 1H), 1.68 – 1.59 (m, 1H), 1.58 – 1.50 (m, 1H), 0.94 (s, 3H), 0.93 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.61 (d, *J* = 245.5 Hz), 135.97 (d, *J* = 3.0 Hz), 128.73 (d, *J* = 8.1 Hz), 115.95 (d, *J* = 21.3 Hz), 63.93, 45.25, 25.10, 22.70, 22.33. IR (cm<sup>-1</sup>): 2960, 2872, 2098, 1280, 836. HRMS: calcd. for C<sub>11</sub>H<sub>15</sub>NF (M + H<sup>+</sup> – N<sub>2</sub>): 180.1189, Found: 180.1182.

#### (3h) 1-(1-azido-3-methylbutyl)-4-chlorobenzene<sup>1</sup>



The title compound was prepared according to the general procedure described above by the reaction between 4-chlorostyrene (**1h**) with  $\text{TMSN}_3$  and isobutyraldehyde (**2a**), and purified by flash column chromatography as colorless oil (32.2 mg, 71%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 – 7.39 (m, 2H), 7.32 – 7.29 (m, 2H), 4.60 (s, 2H), 4.48 (dd, *J* = 8.8, 6.4 Hz, 1H), 1.76 (ddd, *J* = 14.4, 8.4, 6.0 Hz, 1H), 1.70 – 1.69 (m, 1H), 1.59 – 1.51 (m, 1H), 0.95 (d, *J* = 1.2 Hz, 3H), 0.93 (d, *J* = 1.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.72, 134.10, 129.14, 128.40, 63.96, 45.21, 25.09, 22.71, 22.32. IR (cm<sup>-1</sup>): 2959, 2871, 2098, 1246, 699.

#### (3i) 1-(1-azido-3-methylbutyl)-4-bromobenzene



The title compound was prepared according to the general procedure described above by the reaction between 4-bromostyrene (1i) with  $TMSN_3$  and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (34.7 mg, 67%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 – 7.42 (m, 2H), 7.26 – 7.23 (m, 2H), 4.43 (dd, *J* = 8.4, 6.4 Hz, 1H), 1.77 – 1.61 (m, 2H), 1.57 – 1.48 (m, 1H), 0.95 (d, *J* = 1.2 Hz, 3H), 0.93 (d, *J* = 1.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.26, 132.09, 128.72, 122.21, 64.02, 45.20, 25.09, 22.71, 22.31. IR (cm<sup>-1</sup>): 2958, 2869, 2097, 1246, 783. HRMS: calcd. for C<sub>11</sub>H<sub>15</sub>NBr (M + H<sup>+</sup> – N<sub>2</sub>): 240.0388, Found: 240.0381.

#### (3j) 1-(1-azido-3-methylbutyl)-2-chlorobenzene



The title compound was prepared according to the general procedure described above by the reaction between 2-chlorostyrene (1j) with TMSN<sub>3</sub> and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (34.8 mg, 78%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (dd, J = 7.6, 0.8 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.23 (dd, J = 7.6, 1.2 Hz, 1H), 5.07 (dd, J = 9.2, 5.4 Hz, 1H), 1.77 (tt, J = 13.6, 6.8 Hz, 1H), 1.67 (ddd, J = 14.0, 9.2, 5.2 Hz, 1H), 1.60 – 1.50 (m, 2H), 1.01 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.29, 132.90, 129.89, 129.16, 127.72, 127.54, 60.67, 44.76, 25.37, 23.22, 21.81. IR (cm<sup>-1</sup>): 2959, 2870, 2106, 1248, 784. HRMS: calcd. for C<sub>11</sub>H<sub>15</sub>NCl (M + H<sup>+</sup> – N<sub>2</sub>): 196.0893, Found: 196.0887.

#### (3k) 1-(1-azido-3-methylbutyl)-3-chlorobenzene<sup>1</sup>



The title compound was prepared according to the general procedure described above by the reaction between 3-chlorostyrene (1k) with  $TMSN_3$  and isobutyraldehyde (2a), and purified by

flash column chromatography as colorless oil (33.9 mg, 76%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.29 (m, 3H), 7.20 – 7.17 (m, 1H), 4.44 (dd, J = 8.5, 6.3 Hz, 1H), 1.77 – 1.62 (m, 2H), 1.56 – 1.48 (m, 1H), 0.95 (d, J = 0.8 Hz, 1H), 0.93 (d, J = 0.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.66, 131.41, 130.50, 130.08, 125.61, 122.98, 64.01, 45.30, 25.08, 22.78, 22.22. IR (cm<sup>-1</sup>): 2958, 2870, 2102, 1247, 754.

#### (3l) 1-(1-azido-3-methylbutyl)-3-bromobenzene



The title compound was prepared according to the general procedure described above by the reaction between 3-bromostyrene (11) with  $TMSN_3$  and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (40.0 mg, 75%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 – 7.44 (m, 2H), 7.26 – 7.22 (m, 2H), 4.44 (dd, *J* = 8.4, 6.4 Hz, 1H), 1.79 – 1.61 (m, 2H), 1.59 – 1.51 (m, 1H), 0.95 (s, 3H), 0.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.65, 131.42, 130.51, 130.07, 125.61, 122.98, 64.00, 45.30, 25.07, 22.79, 22.23. IR (cm<sup>-1</sup>): 2958, 2869, 2102, 1244, 818. HRMS: calcd. for C<sub>11</sub>H<sub>15</sub>NBr (M + H<sup>+</sup> – N<sub>2</sub>): 240.0388, Found: 240.0382.

#### (3m) (2-azido-4-methylpentan-2-yl)benzene



The title compound was prepared according to the general procedure described above by the reaction between alpha-methylstyrene (1m) with TMSN<sub>3</sub> and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (31.0 mg, 71%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.33 (m, 4H), 7.29 – 7.24 (m, 1H), 1.79 (d, *J* = 2.0 Hz, 1H), 1.78 (d, *J* = 2.0 Hz, 1H), 1.68 (d, *J* = 2.0 Hz, 3H), 1.57 – 1.50 (m, 1H), 0.85 (dd, *J* = 6.8, 2.0 Hz, 3H), 0.75 (dd, *J* = 6.8, 2.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.92, 128.52, 127.22, 125.67, 67.09, 50.46, 26.95, 24.74, 24.35, 23.85. IR (cm<sup>-1</sup>): 2957, 2870, 2107, 1260, 699. HRMS: calcd. for C<sub>12</sub>H<sub>18</sub>N (M+H<sup>+</sup> – N<sub>2</sub>): 176.1439. Found: 176.1434.

#### (3n) (1-azido-3-methylbutane-1, 1-diyl)dibenzene



The title compound was prepared according to the general procedure described above by the reaction between 1,1-diphenylethylene (1n) with TMSN<sub>3</sub> and isobutyraldehyde (2a), and purified by flash column chromatography as colorless oil (41.1 mg, 81%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.29 (m, 8H), 7.28 – 7.23 (m, 2H), 2.34 (s, 1H), 2.33 (s, 1H), 1.56 – 1.48 (m, 1H), 0.85 (s, 3H), 0.83 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.70, 128.36,

127.44, 127.15, 72.52, 46.56, 24.46, 24.16. IR (cm<sup>-1</sup>): 2956, 2869, 2106, 1259, 298. HRMS: calcd. for  $C_{17}H_{20}N$  (M + H<sup>+</sup> – N<sub>2</sub>): 238.1596, Found: 238.1590.

#### (30) (1-azido-3, 3-dimethylbutyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with  $\text{TMSN}_3$  and pivaldehyde (2b), and purified by flash column chromatography as colorless oil (34.1 mg, 84%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.29 (m, 5H), 4.45 (dd, J = 8.0, 4.8 Hz, 1H), 1.82 (dd, J = 14.4, 8.4 Hz, 1H), 1.66 (dd, J = 14.4, 4.8 Hz, 1H), 0.97 (d, J = 6.7 Hz, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.40, 128.95, 128.23, 127.00, 63.72, 49.24, 30.65, 29.99. IR (cm<sup>-1</sup>): 2959, 2868, 2104, 1243, 700. HRMS: calcd. for C<sub>12</sub>H<sub>18</sub>N (M + H<sup>+</sup> – N<sub>2</sub>): 176.1439, Found: 176.1434.

#### (3p) (1-azido-3-methylpentyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with  $TMSN_3$  and 2-methylbutanal (2c), and purified by flash column chromatography as colorless oil (31.7 mg, 78%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 3H), 4.52 – 4.45 (m, 1H), 1.87 (ddd, *J* = 14.0, 9.6, 4.8 Hz, 0.63×1H), 1.80 – 1.61 (m, 0.86×1H), 1.56 – 1.49 (m, 0.75×1H), 1.48 – 1.30 (m, 2H), 1.26 – 1.30 (m, 1H), 0.95 – 0.82 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.56, 139.92, 128.93, 128.38, 128.28, 127.15, 126.95, 64.63, 64.49, 43.40, 42.81, 31.43, 31.28, 29.75, 29.22, 19.22, 18.90, 11.28, 11.11. IR (cm<sup>-1</sup>): 2962, 2929, 2095, 1242, 699. HRMS: calcd. for C<sub>12</sub>H<sub>18</sub>N (M + H<sup>+</sup> – N<sub>2</sub>): 176.1439, Found: 176.1434.

#### (3q) (1-azido-3-ethylpentyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**) with TMSN<sub>3</sub> and 2-ethylbutanal (**2e**), and purified by flash column chromatography as colorless oil (29.5 mg, 68%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.29 (m, 5H), 4.47 (dd, J = 8.4, 6.8 Hz, 1H), 1.78 (ddd, J = 13.6, 8.4, 4.8 Hz, 1H), 1.66 – 1.59 (m, 1H), 1.43 – 1.25 (m, 5H), 0.89 – 0.79 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.32, 128.92, 128.31, 127.03, 64.58, 39.76, 36.97, 25.35, 24.92, 10.67,

10.48. IR (cm<sup>-1</sup>): 2962, 2932, 2093, 1245, 699. HRMS: calcd. for  $C_{13}H_{20}N$  (M + H<sup>+</sup> – N<sub>2</sub>): 190.1596, Found: 190.1590.

#### (3r) (1-azido-3- methylhexyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**) with  $\text{TMSN}_3$  and 2-methylpentanal (**2d**), and purified by flash column chromatography as colorless oil (31.7 mg, 73%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.28 (m, 5H), 4.48 (t, *J* = 7.6 Hz, 1H), 1.86 (ddd, *J* = 14.0, 9.6, 4.8 Hz, 0.32×1H), 1.80 – 1.60 (m, 2H), 1.47 – 1.37 (m, 0.78×1H), 1.36 – 1.22 (m, 3H), 1.16 – 1.07 (m, 1H), 0.93 – 0.83 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.87, 128.92, 128.37, 127.15, 126.94, 64.56, 64.43, 43.80, 43.19, 39.51, 39.04, 29.54, 20.00, 19.92, 19.76, 19.35, 14.41. IR (cm<sup>-1</sup>): 2959, 2928, 2094, 1243, 699. HRMS: calcd. for C<sub>13</sub>H<sub>20</sub>N (M + H<sup>+</sup> – N<sub>2</sub>): 190.1596, Found: 190.1590.

#### (4s) (1-azido-3-ethylheptyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (**1a**) with TMSN<sub>3</sub> and 2-ethylhexanal (**2f**), and purified by flash column chromatography as colorless oil (32.8 mg, 67%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.29 (m, 5H), 4.47 (t, *J* = 7.4 Hz, 1H), 1.82 – 1.73 (m, 1H), 1.66 – 1.58 (m, 1H), 1.38 – 1.20 (m, 9H), 0.91 – 0.81 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.39, 140.33, 128.91, 128.31, 127.06, 127.04, 64.63, 40.23, 35.69, 35.60, 32.77, 32.44, 28.69, 28.58, 25.95, 25.46, 23.17, 14.25, 10.63, 10.45. IR (cm<sup>-1</sup>): 2930, 2928, 2094, 1244, 699. HRMS: calcd. for C<sub>15</sub>H<sub>24</sub>N (M + H<sup>+</sup> – N<sub>2</sub>): 218.1909, Found: 218.1903.

#### (3t) (1-azido-2-cyclohexylethyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with  $TMSN_3$  and cyclohexanecarboxaldehyde (2g), and purified by flash column chromatography as colorless oil (29.3 mg, 64%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.28 (m, 5H), 4.51 (dd, *J* = 8.4, 6.4 Hz, 1H), 1.80 – 1.53 (m, 7H), 1.39 – 1.31 (m, 1H), 1.26 – 1.12 (m, 3H), 0.99 – 0.87 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 140.29, 128.92, 128.30, 127.02, 63.94, 43.85, 34.47, 33.57, 32.97, 26.60, 26.26, 26.17. IR (cm<sup>-1</sup>): 2957, 2929, 2106, 1261, 699. HRMS: calcd. for  $C_{14}H_{20}N$  (M+H<sup>+</sup> – N<sub>2</sub>): 202.1596, Found: 202.1590

#### (3u) (1-azido-2-cyclopentylethyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with  $TMSN_3$  and cyclopentanecarbaldehyde (2h), and purified by flash column chromatography as colorless oil (28.0 mg, 65%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.30 (m, 5H), 4.43 (t, J = 7.0 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.84 – 1.71 (m, 4H), 1.67 – 1.57 (m, 2H), 1.56 – 1.46 (m, 2H), 1.19 – 1.07 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.13, 128.88, 128.31, 127.06, 65.89, 42.55, 36.99, 32.66, 25.20, 25.11. IR (cm<sup>-1</sup>): 2949, 2867, 2560, 2094, 1246, 700. HRMS: calcd. for C<sub>13</sub>H<sub>18</sub>N (M+H<sup>+</sup> – N<sub>2</sub>): 188.1439, Found: 188.1434.

#### (3v) (1-azido-2-(cyclohex-3-en-1-yl)ethyl)benzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with  $TMSN_3$  and 1-cyclohexene-3-carboxaldehyde (2i), and purified by flash column chromatography as colorless oil (34.0 mg, 75%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.30 (m, 5H), 5.65 (d, *J* = 3.2 Hz, 2H), 4.53 (t, *J* = 7.4 Hz, 1H), 2.13 (d, *J* = 13.6 Hz, 1H), 2.03 (d, *J* = 3.2 Hz, 1H), 1.87 – 1.61 (m, 5H), 1.34 – 1.23 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.16, 139.93, 128.95, 128.39, 128.37, 127.25, 127.14, 127.07, 126.98, 126.10, 125.98, 64.08, 64.04, 43.03, 42.81, 31.84, 31.45, 30.44, 30.37, 28.98, 28.47, 25.02, 24.91. IR (cm<sup>-1</sup>): 3025, 2915, 2837, 2094, 1244, 700. HRMS: calcd. for C<sub>14</sub>H<sub>18</sub>N (M + H<sup>+</sup> – N<sub>2</sub>): 200.1439, Found: 200.1434.

#### (3w) (1-azidopropane-1, 3-diyl)dibenzene



The title compound was prepared according to the general procedure described above by the reaction between styrene (1a) with  $TMSN_3$  and phenylacetaldehyde (2j), and purified by flash column chromatography as colorless oil (26.1 mg, 55%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.15 (m, 10H), 4.40 (t, *J* = 7.2 Hz, 1H), 2.75 – 2.60 (m, 2H), 2.21 – 2.11 (m, 1H), 2.10 – 2.00 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.01, 139.60, 128.97, 128.64, 128.58, 128.46, 127.09, 126.25, 65.56, 37.80, 32.47. IR (cm<sup>-1</sup>): 2926, 2861, 2095, 1244, 697. HRMS: calcd. for C<sub>15</sub>H<sub>16</sub>N (M + H<sup>+</sup> – N<sub>2</sub>): 210.1283, Found: 210.1278.

#### (4) 3-methyl-1-phenylbutan-1-amine<sup>3</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.20 (m, 5H), 3.95 (s, 1H), 1.62 – 1.47 (m, 5H), 0.94 – 0.83 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.18, 128.62, 127.00, 126.42, 54.21, 49.08, 25.24, 22.97, 22.67. IR (cm<sup>-1</sup>): 2440, 2955, 1463, 699.

(5) 1-(3-methyl-1-phenylbutyl)-4-phenyl-1H-1,2,3-triazole

Melting point: 128.5 - 130 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (s, 1H), 7.80 (s,1H), 7.70 (s, 1H), 7.42 – 7.20 (m, 8H), 5.76 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.13 (dt, *J* = 14.4, 7.2 Hz, 1H), 1.48 (dp, *J* = 13.4, 6.6 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.82, 139.27, 130.78, 129.14, 128.89, 128.65, 128.19, 127.09, 125.77, 118.53, 63.46, 44.11, 24.95, 22.64, 22.27. IR (cm<sup>-1</sup>): 2958, 2870, 1459, 1074, 694. HRMS: calcd. for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub> (M + H<sup>+</sup>): 292.1814, Found: 292.1803.

<sup>&</sup>lt;sup>3</sup> Y. Mori , Y. Ogawa, A. Mochizuki, Y. Nakamura, T. Fujimoto, C. Sugita, S. Miyazaki, K. Tamaki, T. Nagayama, Y. Nagai, S. Inoue, K. Chiba and T. Nishi, *Bioorganic and Medicinal Chemistry.*, **2013**, *18*. 5907.

# VII. Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of products







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