Supporting Information

Solvent-Tuned Chemoselective Carboazidation and Diazidation of Alkenes via iron catalysis

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1. General Information.

Commercial reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. $^1$H and $^{13}$C NMR spectra were recorded on Bruker 400 (400 and 100 MHz) and Bruker 600 (600 and 150 MHz), and are internally referenced to residual solvent signals (for CDCl$_3$, δ 7.26 and 77.0 ppm). Data for $^1$H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). $^{13}$C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. All alkenes were used from commercial suppliers or prepared using standard literature procedures or the preparation procedures described in this supporting information.
2. General procedures

**General procedure for the carboazidation reaction:** Fe(OTf)$_2$ (0.02 mmol, 10 mol%) were placed in a flame-dried 25 mL sealed tube in glovebox, After DCM (6 mL) was added via a syringe, followed by the addition of DTBP (73.6 ul, 0.4 mmol, 2.0 equiv.) , TMSN$_3$(34.0 ul, 0.26 mmol, 1.3 equiv.) and olefin (0.2 mmol, 1.0 equiv.) under N$_2$ atmosphere. Sealed tube was sealed and the mixture was stirred at 110 °C (oil bath temperature). After 24 h the reaction mixture was cooled down to room temperature, after evaporation in vacuo, purification by column chromatography on silica gel to afford the product.

**General procedure for the diazidation reaction:** Fe(OTf)$_2$ (0.01 mmol, 5 mol%) were placed in a flame-dried 25 mL sealed tube in glovebox, After DCM: tBuOH =5:1(1 ml:0.2ml) was added via a syringe, followed by the addition of DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.) , TMSN$_3$(91.8 ul, 0.7mmol, 3.5 equiv.) and olefin (0.2 mmol,1.0 eq). under N$_2$ atmosphere. Sealed tube was sealed and the mixture was stirred at 80 °C (oil bath temperature). After 24 h the reaction mixture was cooled down to room temperature, after evaporation in vacuo, purification by column chromatography on silica gel to afford the product.
3. Characterizations of products

![Chemical Structure](image)

**(1-Azido-3,3-dichloropropyl)benzene:** According to the general procedure, styrene (23.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (33.4 mg, 73%);¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.40 (m, 2H), 7.39 (dt, J = 9.7, 4.4 Hz, 1H), 7.34 (dd, J = 5.3, 3.3 Hz, 2H), 5.74 (dd, J = 8.4, 4.9 Hz, 1H), 4.75 (dd, J = 9.5, 5.1 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.51 – 2.46 (m, 1H).¹³C NMR (150 MHz, CDCl₃) δ 137.46, 129.21, 129.04, 126.93, 70.03, 63.15, 49.70. HRMS (EI): calcd for C₉H₉Cl₂N₃ 229.0174, found 229.0180.

![Chemical Structure](image)

**1-(1-Azido-3,3-dichloropropyl)-4-methylbenzene:** According to the general procedure, 1-methyl-4-vinylbenzene (25.1 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (36.1 mg, 74%);¹H NMR (600 MHz, CDCl₃) δ 7.22 (s, 4H), 5.71 (dd, J = 8.3, 5.1 Hz, 1H), 4.71 (dd, J = 9.4, 5.3 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.49 – 2.45 (m, 1H), 2.37 (s, 3H).¹³C NMR (150 MHz, CDCl₃) δ 138.97, 134.33, 129.85, 126.89, 70.11, 62.93, 49.63, 21.17. HRMS (EI): calcd for C₁₀H₁₁Cl₂N₃ 243.0330, found 243.0339.
1-(1-Azido-3,3-dichloropropyl)-3-methylbenzene: According to the general procedure, 1-methyl-3-vinylbenzene (26.2 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (32.6 mg, 67%);$^1$H NMR (600 MHz, CDCl$_3$) δ 7.30 (t, $J = 7.9$ Hz, 1H), 7.19 (d, $J = 7.8$ Hz, 1H), 7.13 (d, $J = 7.8$ Hz, 2H), 5.73 (dd, $J = 8.4$, 4.8 Hz, 1H), 4.70 (dd, $J = 9.5$, 5.2 Hz, 1H), 2.66 – 2.61 (m, 1H), 2.49 – 2.45 (m, 1H), 2.39 (s, 3H).$^{13}$C NMR (150 MHz, CDCl$_3$) δ 139.00, 137.36, 129.78, 129.04, 127.56, 123.96, 70.10, 63.15, 49.68, 21.43. HRMS (EI): calcd for C$_{10}$H$_{11}$Cl$_2$N$_3$ 243.0330, found 243.0336.

1-(1-Azido-3,3-dichloropropyl)-4-(tert-butyl)benzene: According to the general procedure, 1-(tert-butyl)-4-vinylbenzene (37.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (43.9 mg, 77%);$^1$H NMR (600 MHz, CDCl$_3$) δ 7.43 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 8.3$ Hz, 2H), 5.73 (dd, $J = 8.4$, 5.0 Hz, 1H), 4.72 (dd, $J = 9.4$, 5.2 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.50 – 2.45 (m, 1H), 1.33 (s, 9H).$^{13}$C NMR (150 MHz, CDCl$_3$) δ 152.05, 134.37, 126.61, 126.06, 70.16, 62.86, 49.64, 34.65, 31.24. HRMS (EI): calcd for C$_{13}$H$_{17}$Cl$_2$N$_3$ 285.0800, found 285.0525.
1-(1-Azido-3,3-dichloropropyl)-2-methylbenzene: According to the general procedure, 1-methyl-2-vinyl-benzene (25.9 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (37.1 mg, 76%).¹H NMR (600 MHz, CDCl₃) δ 7.36 (d, J = 7.5 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.23 (d, J = 7.0 Hz, 1H), 5.84 (dd, J = 9.1, 4.1 Hz, 1H), 5.04 (dd, J = 10.0, 4.1 Hz, 1H), 2.60 – 2.56 (m, 1H), 2.47 – 2.43 (m, 1H), 2.41 (s, 3H).¹³C NMR (150 MHz, CDCl₃) δ 135.72, 135.46, 131.14, 128.60, 126.88, 126.15, 70.29, 59.47, 49.15, 19.14. HRMS (EI): calcd for C₁₀H₁₁Cl₂N₃ 243.0330, found 243.0332.

1-(1-Azido-3,3-dichloropropyl)-4-methoxybenzene: According to the general procedure, 1-methoxy-4-vinylbenzene (26.8 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (38.4 mg, 74%);¹H NMR (600 MHz, CDCl₃) δ 7.26 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 5.71 (dd, J = 8.2, 5.1 Hz, 1H), 4.70 (dd, J = 9.3, 5.4 Hz, 1H), 3.83 (s, 3H), 2.67 – 2.62 (m, 1H), 2.48 – 2.44 (m, 1H).¹³C NMR (150 MHz, CDCl₃) δ 160.03, 129.27, 128.27, 114.50, 70.11, 62.66, 55.31, 49.59. HRMS (EI): calcd for C₁₀H₁₁Cl₂N₃O 259.0279, found 259.0222.
4-(1-Azido-3,3-dichloropropyl)phenyl acetate: According to the general procedure, 4-vinylphenyl acetate (30.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.9 mg, 73%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.38 – 7.34 (m, 2H), 7.18 – 7.14 (m, 2H), 5.75 (dd, $J = 8.5$, 4.8 Hz, 1H), 4.76 (dd, $J = 9.6$, 5.0 Hz, 1H), 2.62 (m, 1H), 2.50 – 2.41 (m, 1H), 2.31 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 169.19, 150.98, 135.09, 128.01, 122.38, 69.89, 62.60, 49.76, 21.11. HRMS (EI): calcld for C$_{11}$H$_{11}$Cl$_2$N$_3$O$_2$ 287.0228, found 287.0234.

6-(1-Azido-3,3-dichloropropyl)-2,3-dihydrobenzo[b][1,4]dioxine: According to the general procedure, 6-vinyl-2,3-dihydrobenzo[b][1,4]dioxine (32.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.6 mg, 72%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.89 (d, $J = 8.3$ Hz, 1H), 6.85 (d, $J = 2.1$ Hz, 1H), 6.80 (dd, $J = 8.3$, 2.1 Hz, 1H), 5.69 (dd, $J = 8.1$, 5.2 Hz, 1H), 4.63 (dd, $J = 9.2$, 5.5 Hz, 1H), 4.27 (s, 4H), 2.63 – 2.58 (m, 1H), 2.46 – 2.42 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 144.10 , 143.91 , 130.46 , 120.02 , 117.86 , 115.87 , 70.06 , 64.31 , 62.64 , 49.57 . HRMS (EI): calcld for C$_{11}$H$_{11}$Cl$_2$N$_3$O$_2$ 287.0228, found 287.0226.
4-(1-Azido-3,3-dichloropropyl)phenyl 4-methylbenzenesulfonate: According to the general procedure, toluene-4-sulfonic acid 4-vinyl-phenyl ester (54.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=10:1) as a colorless oil liquid (62.6 mg, 78%); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.71 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.6$ Hz, 2H), 7.08 – 7.03 (m, 2H), 5.73 (dd, $J = 8.7$, 4.6 Hz, 1H), 4.73 (dd, $J = 9.7$, 4.8 Hz, 1H), 2.60 – 2.55 (m, 1H), 2.45 (d, $J = 5.5$ Hz, 3H), 2.45 – 2.38 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 149.84, 145.62, 136.55, 132.21, 129.56, 128.35, 128.24, 123.25, 69.76, 62.43, 49.67, 21.75. HRMS (EI): calcd for C$_{16}$H$_{15}$Cl$_2$N$_3$O$_3$S 399.0211, found 399.0216.

N-(4-(1-Azido-3,3-dichloropropyl)phenyl)benzamide: According to the general procedure, N-(4-vinyl-phenyl)-benzamide (44.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=10:1) as a white solid (49.6 mg, 71%); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.95 (s, 1H), 7.87 (d, $J = 7.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 5.73 (dd, $J = 8.3$, 5.0 Hz, 1H), 4.75 (dd, $J = 9.4$, 5.2 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.49 – 2.45 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 165.86, 138.60, 134.64, 133.41, 132.13, 128.90, 127.86, 127.05, 120.74, 70.01, 62.72, 49.60. HRMS (EI): calcd for C$_{16}$H$_{15}$Cl$_2$N$_4$O 348.0545, found 348.0539.
Methyl 4-(1-azido-3,3-dichloropropyl)benzoate: According to the general procedure, 4-vinyl-benzoic acid methyl ester (32.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=5:1) as a colorless oil liquid (40.4 mg, 70%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 8.3$ Hz, 2H), 7.43 (d, $J = 8.3$ Hz, 2H), 5.76 (dd, $J = 8.7$, 4.6 Hz, 1H), 4.82 (dd, $J = 9.7$, 4.8 Hz, 1H), 3.94 (s, 3H), 2.65 – 2.60 (m, 1H), 2.49 – 2.45 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 166.34, 142.46, 130.82, 130.49, 126.91, 69.72, 62.79, 52.29, 49.59. HRMS (EI): calcd for C$_{11}$H$_{11}$Cl$_2$N$_3$O$_2$ 287.0228, found 287.0231.

4-(1-Azido-3,3-dichloropropyl)-1,1'-biphenyl: According to the general procedure, 4-vinyl-1,1'-biphenyl (36.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (47.5 mg, 78%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.67 – 7.57 (m, 4H), 7.50 – 7.32 (m, 5H), 5.77 (dd, $J = 8.4$, 4.9 Hz, 1H), 4.80 (dd, $J = 9.5$, 5.2 Hz, 1H), 2.70 – 2.65 (m, 1H), 2.54 – 2.49 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 142.00, 140.21, 136.36, 128.87, 127.90, 127.68, 127.37, 127.10, 70.03, 62.91, 49.68. HRMS (EI): calcd for C$_{15}$H$_{13}$Cl$_2$N$_3$ 305.0487, found 305.0490.
4-(1-Azido-3,3-dichloropropyl)benzonitrile: According to the general procedure, 4-vinylbenzonitrile (16.3 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (30.8 mg, 61%); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 8.2$ Hz, 2H), 5.78 (dd, $J = 8.8$, 4.4 Hz, 1H), 4.84 (dd, $J = 9.9$, 4.6 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.47 – 2.42 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 169.19, 150.98, 135.09, 128.01, 122.38, 69.89, 62.60, 49.76, 21.11. HRMS (EI): calcd for C$_{10}$H$_8$Cl$_2$N$_4$ 254.0126, found 254.0129.

1-(1-Azido-3,3-dichloropropyl)-4-(trifluoromethyl)benzene: According to the general procedure, 1-(trifluoromethyl)-4-vinylbenzene (29.4 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (24.7 mg, 42%); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.70 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 8.2$ Hz, 2H), 5.77 (dd, $J = 8.7$, 4.6 Hz, 1H), 4.84 (dd, $J = 9.7$, 4.8 Hz, 1H), 2.65 – 2.60 (m, 1H), 2.49 – 2.44 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 141.69 (s), 131.28 (q, $J = 32.7$ Hz), 127.31 (s), 126.28 (q, $J = 3.7$ Hz), 123.75 (q, $J = 272.3$ Hz), 69.64, 62.68, 49.72. HRMS (EI): calcd for C$_{10}$H$_8$F$_3$Cl$_2$N$_3$ 297.0047, found 296.9949.
1-(1-Azido-3,3-dichloropropyl)-4-fluorobenzene: According to the general procedure, 1-fluoro-4-vinylbenzene (23.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (30.8 mg, 62%);¹H NMR (600 MHz, CDCl₃) δ 7.33 (dd, J = 8.5, 5.3 Hz, 2H), 7.12 (t, J = 8.5 Hz, 2H), 5.73 (dd, J = 8.5, 4.8 Hz, 1H), 4.75 (dd, J = 9.5, 5.1 Hz, 1H), 2.65 – 2.60 (m, 1H), 2.47 – 2.43 (m, 1H).¹³C NMR (150 MHz, CDCl₃) δ 162.88 (d, J = 248.5 Hz), 133.35 (d, J = 3.3 Hz), 128.73 (d, J = 8.3 Hz), 116.23 (d, J = 21.7 Hz), 69.85, 62.46, 49.74. HRMS (EI): calcd for C₉H₈Cl₂F₃N₂ 247.0079, found 247.0081.

4-(1-Azido-3,3-dichloropropyl)-2-fluoro-1-methoxybenzene: According to the general procedure, 2-fluoro-1-methoxy-4-vinyl-benzene (30.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.3 mg, 74%);¹H NMR (600 MHz, CDCl₃) δ 7.08 (dd, J = 17.3, 5.6 Hz, 2H), 6.99 (t, J = 8.3 Hz, 1H), 5.71 (dd, J = 8.4, 5.0 Hz, 1H), 4.69 (dd, J = 9.4, 5.2 Hz, 1H), 3.91 (d, J = 9.2 Hz, 3H), 2.62 – 2.58 (m, 1H), 2.46 – 2.41 (m, 1H).¹³C NMR (150 MHz, CDCl₃) δ 152.50 (d, J = 248.1 Hz), 148.16 (d, J = 10.6 Hz), 130.16 (d, J = 5.6 Hz), 123.08 (d, J = 3.5 Hz), 114.61 (d, J = 19.2 Hz), 113.58 (d, J = 2.0 Hz), 69.83, 62.30, 56.26, 49.53. HRMS (EI): calcd for C₁₀H₁₀Cl₂F₃N₉O 277.0185, found 277.0178.
4-(1-Azido-3,3-dichloropropyl)-1-bromo-2-methylbenzene: According to the general procedure, 1-bromo-2-methyl-4-vinyl-benzene (39.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (43.9 mg, 68%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 8.2$ Hz, 1H), 7.20 (d, $J = 1.9$ Hz, 1H), 7.03 (dd, $J = 8.2$, 2.1 Hz, 1H), 5.73 (dd, $J = 8.5$, 4.9 Hz, 1H), 4.69 (dd, $J = 9.5$, 5.1 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.46 – 2.41 (m, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 139.05, 136.79, 133.17, 129.27, 125.76, 125.50, 69.85, 62.61, 49.63, 23.05. HRMS (EI): calcd for C$_{10}$H$_9$BrCl$_2$N$_3$ 320.9435, found [M-N$_2$]$^+$ 292.9387.

1-(1-Azido-3,3-dichloropropyl)-4-chlorobenzene: According to the general procedure, 1-chloro-4-vinylbenzene (24.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (31.2 mg, 59%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 5.73 (dd, $J = 8.5$, 4.8 Hz, 1H), 4.74 (dd, $J = 9.6$, 5.0 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.46 – 2.42 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 136.05, 134.97, 129.48, 128.30, 69.79, 62.61, 49.67. HRMS (EI): calcd for C$_9$H$_8$Cl$_2$N$_3$ 262.9784, found 262.9787.
1-(1-Azido-3,3-dichloropropyl)-4-bromobenzene: According to the general procedure, 1- bromo -4-vinylbenzene (26.2 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (31.9 mg, 52%);$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.3$ Hz, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 5.73 (dd, $J = 8.5$, 4.8 Hz, 1H), 4.73 (dd, $J = 9.6$, 5.0 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.46 – 2.41 (m, 1H).$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 136.61, 132.44, 128.59, 123.09, 69.76, 62.59, 49.63. HRMS (EI): calcd for C$_9$H$_8$BrClN$_3$ 306.9279, found 306.9282.

2-(1-Azido-3,3-dichloropropyl)naphthalene: According to the general procedure, 2-vinyl-naphthalene (30.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (26.0 mg, 47%);$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 8.5$ Hz, 1H), 7.86 (dd, $J = 5.4$, 2.8 Hz, 2H), 7.80 (s, 1H), 7.53 (dd, $J = 6.3$, 3.0 Hz, 2H), 7.43 (dd, $J = 8.5$, 1.6 Hz, 1H), 5.76 (dd, $J = 8.3$, 5.0 Hz, 1H), 4.92 (dd, $J = 9.4$, 5.3 Hz, 1H), 2.76 – 2.71 (m, 1H), 2.59 – 2.54 (m, 1H).$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 134.77 , 133.47 , 133.18 , 129.44 , 128.09 , 127.83 , 126.82 , 126.79 , 126.60 , 123.94 , 70.08 , 63.43 , 49.65. HRMS (EI): calcd for C$_{13}$H$_{11}$Cl$_2$N$_3$ 279.0330, found 279.0333.
5-(1-Azido-3,3-dichloropropyl)benzofuran: According to the general procedure, 5-vinyl-benzofuran (26.5 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=5:1) as a colorless oil liquid (35.2 mg, 65%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J$ = 2.1 Hz, 1H), 7.59 (d, $J$ = 1.5 Hz, 1H), 7.56 (d, $J$ = 8.5 Hz, 1H), 7.27 (dd, $J$ = 8.5, 1.7 Hz, 1H), 6.79 (t, $J$ = 7.6 Hz, 1H), 5.72 (dd, $J$ = 8.2, 5.2 Hz, 1H), 4.86 (dd, $J$ = 9.3, 5.4 Hz, 1H), 2.73 – 2.68 (m, 1H), 2.54 – 2.50 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 155.00 , 146.15 , 132.07 , 128.06 , 123.10 , 119.98 , 112.24 , 106.66 , 70.11 , 63.33 , 50.08 . HRMS (EI): calcd for C$_{11}$H$_9$Cl$_2$N$_3$O 269.0123, found 269.0125.

5-(1-Azido-3,3-dichloropropyl)-4-methylthiazole: According to the general procedure, 4-methyl-5-vinylthiazole (22.9 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=5:1) as a colorless oil liquid (25.4 mg, 51%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.77 (s, 1H), 5.75 (dd, $J$ = 8.4, 4.9 Hz, 1H), 5.15 (dd, $J$ = 9.3, 5.2 Hz, 1H), 2.69 – 2.64 (m, 1H), 2.53 (s, 3H), 2.51 – 2.44 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 152.28 , 151.63 , 128.52 , 69.29 , 55.74 , 50.15 , 15.48 . HRMS (EI): calcd for C$_7$H$_9$Cl$_2$N$_4$S 250.9925, found 250.9920.
(2-Azido-4,4-dichlorobutan-2-yl)benzene: According to the general procedure, prop-1-en-2-ylbenzene (26.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (37.3 mg, 77%); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J$ = 4.1 Hz, 4H), 7.33 (dt, $J$ = 8.7, 4.2 Hz, 1H), 5.55 (t, $J$ = 5.7 Hz, 1H), 2.84 – 2.74 (m, 2H), 1.82 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 141.53, 128.95 , 128.08 , 68.84 , 65.33 , 55.25 , 25.71 . HRMS (EI): calcd for C$_{10}$H$_{11}$Cl$_2$N$_3$ 243.0330, found 243.0272.

(1-Azido-3,3-dichloro-2-methylpropyl)benzene: According to the general procedure, (Z)-prop-1-en-1-ylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (32.8 mg, 67%), dr = 1.25:1 (determined by crude $^1$H NMR). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.48 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 6.37 (d, $J$ = 2.3 Hz, 0.54H), 5.39 (d, $J$ = 3.8 Hz, 0.43H), 4.52 (d, $J$ = 8.6 Hz, 0.44H), 4.34 (d, $J$ = 10.6 Hz, 0.55H), 2.48 – 2.37 (m, 1H), 1.34 (d, $J$ = 6.5 Hz, 1.43H), 0.92 (d, $J$ = 6.7 Hz, 1.72H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 136.83 (137.02), 129.25 (129.025), 129.11 (129.080), 127.84 (127.31), 75.86 (75.58), 68.65 (68.46), 48.37 (49.59), 10.28 (10.79). HRMS (EI): calcd for C$_{10}$H$_{11}$Cl$_2$N$_3$ 243.0330, found 243.0336.
(1-Azido-3,3-dichloro-2-methylpropyl)benzene: According to the general procedure, (E)-prop-1-en-1-ylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (34.7 mg, 71%), dr = 1.16:1 (determined by crude $^1$H NMR). $^1$H NMR (600 MHz, CDCl$_3$) δ 7.46 – 7.37 (m, 3H), 7.35 – 7.28 (m, 2H), 6.37 (d, $J$ = 2.3 Hz, 0.51H), 5.39 (d, $J$ = 3.8 Hz, 0.44H), 4.52 (d, $J$ = 8.6 Hz, 0.44H), 4.34 (d, $J$ = 10.6 Hz, 0.52H), 2.43 – 2.42 (m , 1H), 1.34 (d, $J$ = 6.5 Hz, 1.51H), 0.92 (d, $J$ = 6.7 Hz, 1.64H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 136.83 (137.02), 129.25 (129.03), 129.11 (129.08), 127.84 (127.31), 75.87 (75.58), 68.65 (68.46), 48.37 (49.59), 10.28 (10.79).HRMS (EI): calcd for C$_{10}$H$_{11}$Cl$_2$N$_3$ 243.0330, found 243.0334.

1-(1-Azido-3,3-dichloro-2-methylpropyl)-4-methoxybenzene: According to the general procedure, (E)-1-methoxy-4-(prop-1-en-1-yl)benzene (29.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 20 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (48.3 mg, 89%), dr = 1.32:1 (determined by crude $^1$H NMR). $^1$H NMR (600 MHz, CDCl$_3$) δ 7.25 – 7.19 (m, 2H), 6.94 (m, 2H), 6.35 (d, $J$ = 2.3 Hz, 0.5H), 5.37 (d, $J$ = 3.4 Hz, 0.38H), 4.41 (d, $J$ = 9.1 Hz, 0.39H), 4.29 (d, $J$ = 10.6 Hz, 0.52H), 3.84 (s, 1.13H), 3.83 (s, 1.48H), 2.39 (m, 1H), 1.35 (d, $J$ = 6.5 Hz, 1.29H), 0.92 (d, $J$ = 6.6 Hz, 1.64H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 160.02 (160.00), 129.04 (128.61), 128.79(128.76), 114.60 (114.42), 75.95 (75.64), 68.17 (68.22), 55.32 (55.35), 48.46 (49.48), 29.10,
Azido-2-(dichloromethyl)-2,3-dihydro-1H-indene: According to the general procedure, 1H-indene (23.3 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.5 mg, 86%);¹H NMR (600 MHz, CDCl₃) δ 7.40 (d, J = 7.0 Hz, 1H), 7.32 (dd, J = 7.2, 5.9 Hz, 2H), 7.27 (s, 1H), 6.03 (d, J = 4.1 Hz, 1H), 4.94 (d, J = 6.0 Hz, 1H), 3.32 (dd, J = 14.3, 6.6 Hz, 1H), 3.19 – 3.07 (m, 2H).¹³C NMR (150 MHz, CDCl₃) δ 140.37, 139.25, 129.29, 127.56, 125.06, 124.54, 73.96, 67.79, 57.02, 33.20. HRMS (EI): calcd for C₁₀H₉Cl₂N₃ 241.0174, found [M-N₂]+ 213.0118

5-Azido-7,7-dichloroheptyl benzoate: According to the general procedure, benzoic acid hex-5-enyl ester (40.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN₃ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)₂ (14.0 mg, 0.04 mmol, 10 mol%) in CH₂Cl₂ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (30.4 mg, 46%);¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 5.88 – 5.77 (m, 1H), 5.04 (d, J = 17.1 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.33 (t, J = 6.5 Hz, 2H), 2.14 (d, J = 7.0 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.63 – 1.51 (m, 3H).¹³C NMR (150 MHz, CDCl₃) δ 166.64, 132.85, 130.40, 129.51, 128.33, 73.52, 64.83, 43.46,
28.54, 28.20, 25.83, 25.79. HRMS (EI): calcd for C\textsubscript{14}H\textsubscript{17}Cl\textsubscript{2}N\textsubscript{3}O\textsubscript{2} 329.0698, found 329.0692.

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\text{N}_3\text{HCCl}_2
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(E)-Buta-1,3-dien-1-ylbenzene was prepared through a known procedure\textsuperscript{1}

\textbf{(E)-(3-azido-5,5-dichloropent-1-en-1-yl)benzene: } According to the general procedure, (E)-buta-1,3-dien-1-ylbenzene (28.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN\textsubscript{3} (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)\textsubscript{2} (14.0 mg, 0.04 mmol, 10 mol\%) in CH\textsubscript{2}Cl\textsubscript{2} (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (27.4 mg, 54%);\textsuperscript{1}\textsuperscript{H} NMR (600 MHz, CDCl\textsubscript{3}) δ 7.42 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.31 (dd, J = 8.4, 6.1 Hz, 1H), 6.73 (d, J = 15.8 Hz, 1H), 6.09 (dd, J = 15.8, 8.4 Hz, 1H), 5.82 (dd, J = 8.3, 5.0 Hz, 1H), 4.35 (td, J = 8.7, 5.3 Hz, 1H), 2.48 – 2.45 (m, 1H), 2.43 – 2.37 (m, 1H).\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) δ 135.24, 135.20, 128.75, 128.66, 126.80, 124.31, 69.84, 61.90, 48.07.. HRMS (EI): calcd for C\textsubscript{11}H\textsubscript{11}Cl\textsubscript{3}N\textsubscript{3} 255.0330, found 255.0323.

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\text{Cl}_2\text{HC}_{\text{Cl}}\text{N}_3\text{OTBS}
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\textbf{(2-Azido-2,4,4-trichlorobutoxy)(tert-butyl)dimethylsilane: } According to the general procedure, tert-Butyl-(2-chloro-allyloxy)-dimethyl-silane (38.9 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN\textsubscript{3} (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)\textsubscript{2} (14.0 mg, 0.04 mmol, 10 mol\%) in CH\textsubscript{2}Cl\textsubscript{2} (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (29.1 mg, 44%);\textsuperscript{1}\textsuperscript{H} NMR (600 MHz, CDCl\textsubscript{3}) δ 6.07 (t, J = 5.6 Hz, 1H), 4.00 (s, 2H), 3.22 (d, J = 5.6 Hz, 2H), 0.94 – 0.91 (m, 9H), 0.12 (s, 6H).\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3})
$\delta$ 87.93, 72.00, 68.17, 55.18, 25.70, 18.27, -5.35. HRMS (EI): calcd for C$_{10}$H$_{20}$Cl$_3$N$_3$OSi 331.0441, found 331.0446.

1-(1-Azido-3,3,3-trichloropropyl)-4-(tert-butyl)benzene: According to the general procedure, 1-(tert-butyl)-4-vinylbenzene (37.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CHCl$_3$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (45.0 mg, 46%);$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.3 Hz, 2H), 4.92 (dd, $J$ = 7.6, 3.5 Hz, 1H), 3.22 (dd, $J$ = 15.2, 7.6 Hz, 1H), 3.11 (dd, $J$ = 15.2, 3.5 Hz, 1H), 1.34 (s, 9H).$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 151.92, 135.70, 126.51, 126.08, 63.15, 60.11, 34.68, 31.29. HRMS (EI): calcd for C$_{13}$H$_{16}$Cl$_3$N$_3$ 319.0410, found 319.0413.

3-(1-Azido-3,3-dichloropropyl)-13-methyl 6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one: According to the general procedure, 13-Methyl-3-vinyl 6,7,8,9,11,12,13,14,15,16-decahydro-cyclopenta[a]phenanthren-17-one (56.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=10:1) as a colorless oil liquid (45.4 mg, 56%);$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J$ = 8.0 Hz, 1H), 7.11 (d, $J$ = 8.0 Hz, 1H), 7.05 (s, 1H), 5.73 (dd, $J$ = 8.3, 5.0 Hz, 1H), 4.92 (dd, $J$ = 7.6, 3.5 Hz, 1H), 3.22 (dd, $J$ = 15.2, 7.6 Hz, 1H), 3.11 (dd, $J$ = 15.2, 3.5 Hz, 1H), 1.34 (s, 9H). HRMS (EI): calcd for C$_{13}$H$_{16}$Cl$_3$N$_3$ 319.0410, found 319.0413.
Hz, 1H), 4.68 (dd, J = 9.4, 5.2 Hz, 1H), 2.97 – 2.90 (m, 2H), 2.65 – 2.61 (m, 1H), 2.58 – 2.39 (m, 3H), 2.31 (td, J = 10.9, 3.7 Hz, 1H), 2.16 (dt, J = 18.6, 9.1 Hz, 1H), 2.10 – 2.04 (m, 2H), 1.98 (dd, J = 12.5, 3.3 Hz, 1H), 1.69 – 1.61 (m, 2H), 1.58 – 1.42 (m, 4H), 0.92 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 220.67, 140.74, 137.49, 134.83, 127.53, 126.18, 124.29, 70.14, 62.90, 50.48, 49.64, 47.93, 44.36, 37.96, 35.82, 31.55, 29.39, 26.34, 25.64, 21.57, 13.83. HRMS (ESI): calcd for C$_{21}$H$_{25}$Cl$_2$N$_3$O 405.1375, found [M+H] 406.1447.

1-(tert-Butyl)-4-(1,2-diazidoethyl)benzene: According to the general procedure, 1-(tert-butyl)-4-vinylbenzene (37.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN$_3$ (91.8 ul, 0.7 mmol, 3.5 equiv.) and Fe(OTf)$_2$ (0.01 mmol, 5 mol%) in DCM:BuOH = 5:1 (1 ml:0.2 ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (38.0 mg, 78%); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 4.65 (dd, J = 8.6, 4.7 Hz, 1H), 3.50 (dd, J = 12.8, 8.6 Hz, 1H), 3.43 (dd, J = 12.8, 4.7 Hz, 1H), 1.32 (s, 9H).

1-(1,2-Diazidoethyl)-4-methoxybenzene: According to the general procedure, 1-methoxy-4-vinylbenzene (20.8 ul, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN$_3$ (91.8 ul, 0.7 mmol, 3.5 equiv.) and Fe(OTf)$_2$ (0.01 mmol, 5 mol%) in DCM:BuOH = 5:1 (1 ml:0.2 ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (33.1 mg, 76%); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.26 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 4.62 (dd, J =
8.3, 5.0 Hz, 1H), 3.82 (s, 3H), 3.49 (dd, J = 12.7, 8.4 Hz, 1H), 3.41 (dd, J = 12.7, 5.0 Hz, 1H).

1-(1,2-Diazidoethyl)-3-methylbenzene: 

According to the general procedure, 1-methyl-3-vinylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN$_3$ (91.8 ul, 0.7 mmol, 3.5 eq.) and Fe(OTf)$_2$ (0.01 mmol, 5 mol%) in DCM:tBuOH = 5:1 (1 ml:0.2 ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (28.3 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 7.7 Hz, 2H), 4.63 (dd, J = 8.4, 4.9 Hz, 1H), 3.46 (dd, J = 17.6, 12.7, 6.7 Hz, 2H), 2.39 (s, 3H).

1-(1,2-Diazidoethyl)-2-methylbenzene: 

According to the general procedure, 1-methyl-2-vinylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN$_3$ (91.8 ul, 0.7 mmol, 3.5 eq.) and Fe(OTf)$_2$ (0.01 mmol, 5 mol%) in DCM:tBuOH = 5:1 (1 ml:0.2 ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (33.9 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.34 (m, 1H), 7.27 (dd, J = 6.1, 3.2 Hz, 2H), 7.24 – 7.20 (m, 1H), 4.93 (dd, J = 8.7, 4.5 Hz, 1H), 3.50 (dd, J = 12.8, 8.7 Hz, 1H), 3.41 (dd, J = 12.8, 4.5 Hz, 1H), 2.39 (s, 3H).
1-Chloro-4-(1,2-diazidoethyl)benzene: ² According to the general procedure, 1-chloro-4-vinylbenzene (24.0 µl, 0.2 mmol, 1.0 equiv.), DTBP (55.0 µl, 0.3 mmol, 1.5 equiv.), TMSN₃ (91.8 µl, 0.7 mmol, 3.5 eq.) and Fe(OTf)₂ (0.01 mmol, 5 mol%) in DCM:tBuOH = 5:1 (1 ml:0.2 ml) were used. After 24 h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (30.2 mg, 68%); ¹H NMR (600 MHz, CDCl₃) δ 7.39 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.65 (dd, J = 8.1, 5.0 Hz, 1H), 3.48 (dd, J = 12.8, 8.1 Hz, 1H), 3.43 (dd, J = 12.8, 5.0 Hz, 1H).

![1-Chloro-4-(1,2-diazidoethyl)benzene](image)

1-(1,2-Diazidoethyl)-4-fluorobenzene: ² According to the general procedure, 1-fluoro-4-vinylbenzene (23.8 µl, 0.2 mmol, 1.0 equiv.), DTBP (55.0 µl, 0.3 mmol, 1.5 equiv.), TMSN₃ (91.8 µl, 0.7 mmol, 3.5 eq.) and Fe(OTf)₂ (0.01 mmol, 5 mol%) in DCM:tBuOH = 5:1 (1 ml:0.2 ml) were used. After 24 h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (35.4 mg, 86%); ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.30 (m, 2H), 7.11 (dd, J = 11.7, 5.2 Hz, 2H), 4.66 (dd, J = 8.0, 5.1 Hz, 1H), 3.49 (dd, J = 12.7, 8.2 Hz, 1H), 3.43 (dd, J = 12.7, 5.0 Hz, 1H).

![1-(1,2-Diazidoethyl)-4-fluorobenzene](image)

2-(1,2-Diazidoethyl)naphthalene: ² According to the general procedure, 2-vinyl naphthalene (30.8 µg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 µl, 0.3 mmol, 1.5 equiv.), TMSN₃ (91.8 µl, 0.7 mmol, 3.5 eq.) and Fe(OTf)₂ (0.01 mmol, 5 mol%) in DCM:tBuOH = 5:1 (1 ml:0.2 ml) were used. After 24 h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (20.2 mg, 48%); ¹H NMR (600 MHz, CDCl₃) δ 7.93 – 7.73 (m, 4H), 7.56 – 7.51 (m, 2H), 7.40 (d, J = 8.5 Hz, 1H) 4.85 (dd, J = 8.4, 4.9 Hz, 1H), 3.60 (dd, J = 12.8, 8.5 Hz, 1H), 3.53 (dd, J = 12.8, 4.8 Hz, 1H).
1-azido-1-(azidomethyl)-2,3-dihydro-1H-indene: According to the general procedure, 1-methylene-2,3-dihydro-1H-indene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN\(_3\) (91.8 ul, 0.7 mmol, 3.5 eq.) and Fe(OTf)\(_2\) (0.01 mmol, 5 mol\%) in DCM:\(^{t} \text{BuOH} = 5:1\) (1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (27.1 mg, 63%);\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.31 (m, 4H), 4.16 (t, \(J = 6.8\) Hz, 2H), 3.33 – 3.31 (m, 2H), 2.92 – 2.88 (m, 2H).\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 142.55, 138.05, 129.27, 127.83, 125.22, 122.99, 73.42, 70.11, 35.46, 19.78. HRMS (EI): calcd for C\(_{10}\)H\(_{10}\)N\(_6\) 214.0967, found 214.0970.

1-Azido-1-(azidomethyl)-1,2,3,4-tetrahydronaphthalene: According to the general procedure, 1-methylene-1,2,3,4-tetrahydronaphthalene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN\(_3\) (91.8 ul, 0.7 mmol, 3.5 eq.) and Fe(OTf)\(_2\) (0.01 mmol, 5 mol\%) in DCM:\(^{t} \text{BuOH} = 5:1\) (1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (29.8 mg, 65%);\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.48 – 7.42 (m, 1H), 7.16 (dt, \(J = 3.2\), 2.1 Hz, 2H), 7.16 (dd, \(J = 5.6\), 3.2 Hz, 1H), 3.56 (d, \(J = 12.8\) Hz, 1H), 3.46 (d, \(J = 12.8\) Hz, 1H), 2.88 – 2.81 (m, 1H), 2.81 (dt, \(J = 16.9\), 5.9 Hz, 1H), 2.31 – 2.23 (m, 1H), 2.05 (m, \(J = 12.2\), 7.7, 2.7 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.88 – 1.79 (m, 1H).\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 137.79, 134.38, 129.65, 128.51, 126.96, 126.65, 65.50, 59.02, 31.23, 29.38, 19.56. HRMS (EI): calcd for C\(_{11}\)H\(_{12}\)N\(_6\) 228.1123, found 228.1126.
(1,2-Diazidopropyl)benzene: According to the general procedure, (E)-prop-1-en-1-ylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN₃ (91.8 ul, 0.7 mmol, 3.5 equiv.) and Fe(OTf)₂ (0.01 mmol, 5 mol%) in DCM: tBuOH =5:1 (1 ml:0.2 ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (28.5 mg, 71%), dr = 1:1.09 (determined by crude ¹H NMR); ¹H NMR (600 MHz, CDCl₃) δ 7.44 – 7.35 (m, 3H), 7.32 (dd, J = 18.9, 7.6 Hz, 2H), 4.53 (d, J = 5.8 Hz, 0.49H), 4.37 (d, J = 7.7 Hz, 0.51H), 3.74 – 3.63 (m, 1H), 1.26 (d, J = 6.6 Hz, 1.47H), 1.11 (d, J = 6.7 Hz, 1.59H).

1,2-diazido-2,3-dihydro-1H-indene: According to the general procedure, 1H-indene (23.2 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN₃ (91.8 ul, 0.7 mmol, 3.5 equiv.) and Fe(OTf)₂ (0.01 mmol, 5 mol%) in DCM: tBuOH =5:1 (1 ml:0.2 ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (25.9 mg, 65%); ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.23 (m, 4H), 4.77 (d, J = 5.6 Hz, 1H), 4.17 (d, J = 12.7, 6.2 Hz, 1H), 3.35 (dd, J = 15.9, 7.3 Hz, 1H), 2.95 (dd, J = 15.9, 6.5 Hz, 1H).

(E)-(3,4-Diazidobut-1-en-1-yl)benzene: According to the general procedure, (E)-Buta-1,3-dien-1-ylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol,
1.5 equiv.), TMSN₃ (91.8 ul, 0.7 mmol, 3.5 eq.) and Fe(OTf)₂ (0.01 mmol, 5 mol%) in DCM: 'BuOH = 5:1 (1 ml: 0.2 ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (28.5 mg, 71%); ¹H NMR (600 MHz, CDCl₃) δ 7.44 – 7.40 (m, 2H), 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 6.74 (d, J = 15.8 Hz, 1H), 6.13 (dd, J = 15.8, 8.0 Hz, 1H), 4.30 – 4.23 (m, 1H), 3.40 (m, 2H).
4. Synthetic transformations of products

To a mixture of (1-azido-3,3-dichloropropyl)benzene (22.9 mg, 0.1 mmol, 1.0 equiv.), phenyl acetylene (11 µl, 0.11 mmol, 1.1 equiv.) in H₂O/tBuOH (1 mL/1 mL) was added CuSO₄ · 5H₂O (10 mg, 0.4 equiv.) and sodium ascorbate (16 mg, 0.8 equiv.). The resulting mixture was stirred at room temperature for 17 h before diluted with ethyl acetate (5 mL) and water (5 mL). The aqueous layer was extracted with ethyl acetate (5 mL ×3). The combined organic layers were dried over Na₂SO₄, filtered through a short silica gel plug, and concentrated in vacuo to afford 1-(3,3-dichloro-1-phenylpropyl)-4-phenyl-1H-1,2,3-triazole as white solid (32.3 mg, 98% yield).

1-(3,3-Dichloro-1-phenylpropyl)-4-phenyl-1H-1,2,3-triazole: ¹H NMR (600 MHz, CDCl₃) δ 7.86 – 7.76 (m, 2H), 7.69 (s, 1H), 7.43 – 7.38 (m, 5H), 7.38 – 7.35 (m, 2H), 7.33 (ddd, J = 6.9, 2.3, 1.2 Hz, 1H), 5.82 (dd, J = 9.2, 5.7 Hz, 1H), 5.66 (dd, J = 8.1, 5.3 Hz, 1H), 3.64 – 3.6 (m, 1H), 3.11 – 3.07 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 148.05, 137.29, 130.14, 129.42, 129.29, 128.83, 128.36, 126.81, 125.68, 119.85, 69.75, 62.54, 48.48. HRMS (EI): calcd for C₁₇H₁₅Cl₂N₃ 331.0643, found 331.0646.
To an oven-dried three neck round bottom flask (10 mL) was added Pd/C (10.0 mg, 5 wt%). After the flask was evacuated and back filled with H₂. A solution of the (1-azido-3,3-dichloropropyl) benzene (45.8 mg, 0.2 mmol, 1.0 equiv.) and Boc₂O (52.0 mg, 0.2 mmol, 1.0 equiv.) in ethyl acetate (3.0 mL) was added to the flask via syringe. Then, the reaction mixture was vigorously stirred under H₂ (1 atm, hydrogen-filled balloon) at room temperature until the reduction completed. After that, the balloon was removed and the reaction mixture was further stirred for 10 h. The mixture was then concentrated in vacuo and the residue was subsequently purified through a silica gel column to afford tert-butyl (3,3-dichloro-1-phenylpropyl) carbamate as white solid (52.1 mg, 86% yield).

**tert-Butyl (3,3-dichloro-1-phenylpropyl)carbamate:** ^1^H NMR (600 MHz, CDCl₃) δ 7.37 (t, J = 7.4 Hz, 2H), 7.30 (dd, J = 15.4, 7.7 Hz, 3H), 5.52 (s, 1H), 4.94 (s, 1H), 2.79 (dd, J = 13.9, 7.1 Hz, 1H), 2.59 (s, 1H), 1.42 (s, 9H). ^1^C NMR (150 MHz, CDCl₃) δ 154.90, 140.21, 129.05, 128.07, 126.35, 70.25, 52.63, 50.20, 28.29. HRMS (EI): calcd for C₁₄H₁₉Cl₂NO₂ 303.0793, found 303.0796.

According to the general procedure, Fe(OTf)_2 (0.02 mmol, 10 mol%) were placed in a flame-dried 25 mL sealed tube in glovebox. After DCM (6 mL) was added via a syringe, followed by the addition of DTBP (73.6 ul, 0.4 mmol, 2.0 equiv.), TMSN_3(34.0 ul, 0.26mmol, 1.3 eq.) and (1-cyclopropylvinyl)benzene (0.2 mmol, 1.0 eq). and the mixture was stirred 24h at 110 °C. After 24 h the reaction mixture was cooled down to room temperature, after evaporation in vacuo, purification by column chromatography on silica gel to afford the product.

4-(2,2-Dichloroethyl)-1,2-dihyronaphthalene: \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.22 (m, \(J = 7.6, 5.7, 3.3\) Hz, 1H), 7.19 – 7.16 (m, 2H), 7.14 (d, \(J = 7.6\) Hz, 1H), 6.06 (t, \(J = 4.6\) Hz, 1H), 5.85 (t, \(J = 6.6\) Hz, 1H), 3.34 (dd, \(J = 6.6, 1.0\) Hz, 2H), 2.81 – 2.73 (m, 2H), 2.34 – 2.26 (m, 2H). \(^13C\) NMR (150 MHz, CDCl\(_3\)) \(\delta\) 136.84, 133.26 , 131.02 , 130.61 , 128.08 , 127.28 , 126.60 , 121.87 , 71.63 , 47.42 , 27.99 , 23.09 . HRMS (EI): calcd for C\(_{12}\)H\(_{12}\)Cl\(_2\) 226.0316, found 226.0319.

(Z)-(6-Azido-1,1-dichloro-3-en-3-y1)benzene: \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.35 (m, 2H), 7.33 (d, \(J = 6.9\) Hz, 3H), 5.87 (t, \(J = 7.2\) Hz, 1H), 5.57 (t, \(J = 6.8\) Hz, 1H), 3.67 (t, \(J = 6.8\) Hz, 2H), 3.47 (d, \(J = 6.8\) Hz, 2H), 2.80 (q, \(J = 7.1\) Hz, 2H). \(^13C\)
NMR (150 MHz, CDCl₃) δ 140.48, 137.21, 129.17, 128.74 , 127.83, 126.66, 71.29, 44.29, 43.79, 32.09 . HRMS (EI): calcd for C₁₁H₁₃Cl₂N₃ 269.0487, found 269.0490.

6 References

7. Spectral Data.
\[
\text{N}_3\text{CHCl}_2\text{Me} \quad \text{dr 1.18:1}
\]
dr = 1.3:1