Selective Hydroboration of Equilibrating Allylic Azides

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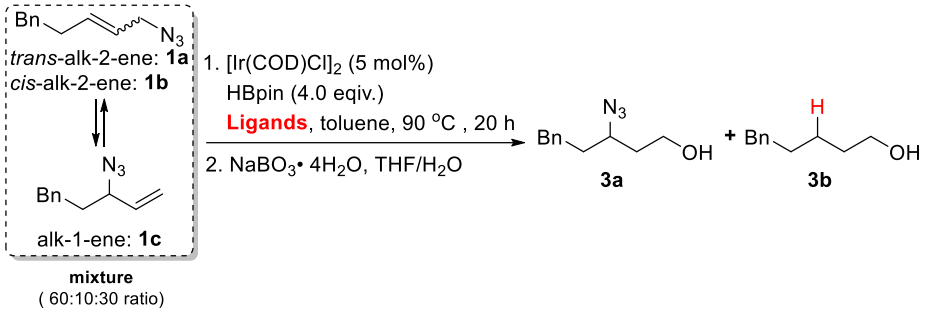
Table S1. Screening ligands for the hydroboration using $[Ir(COD)Cl]_2$ catalyst. [a]



Entry	Ligands	Ligands (mol%)	Conv. (%) [b]	Ratio [b] **3a/3b**
1	PPh_3	10	>98%	67:33
2	PPh_3	15	>98%	78:22
3	PPh_3	20	>98%	77:23
4	$P(t\text{-Bu})_3$	15	>98%	53:47
5	$P(OPh)_3$	15	>98%	67:33
6	$P(o\text{-toluene})_3$	15	>98%	74:26
7	PCy_3	20	>98%	62:38
8	S-Phos	20	>98%	57:43
9	Davephos	20	>98%	83:17
10	dppm	10	>98%	54:46
11	dppe	5	>98%	74:26
12	dppe	10	>98%	53:47
13	dppp	10	>98%	72:28
14	dppb	10	>98%	77:23
15	dppz	10	<5%	-
16	dppf	10	>98%	66:34
17	DCyPE	10	<5%	-
18	DIOP	10	>98%	65:35
19	Xantphos	10	>98%	79:21
20	DPEphos	10	>98%	80:20
21	*t*-BuPHOX	10	>98%	75:25
22	Duphos	10	>98%	53:47

23	Josiphos	10	>98%	62.5: 37.5
24	BINAP	10	>98%	64.5: 35.5
25	DTBM-SEGPHOS	10	>98%	78:22
26	*i*-PrDOX	10	>98%	50:50
27	*t*-BuBOX	10	>98%	61:39
28	*i*-PrPyBOX	10	>98%	59:41
29	*i*-PrPyOX	10	>98%	67:33
30	6,6'-Dimethyl-2,2'-bipyridyl	10	>98%	69:31
31	4,4'-Di-*tert*-butyl-2,2'-bipyridyl	10	>98%	48:52
32	$P(4\text{-}ClC_6H_4)_3$	15	>98%	78:22 [c]
33	$P(4\text{-}FC_6H_4)_3$	15	>98%	89:11 [c]
34	$P(4\text{-}CF_3C_6H_4)_3$	15	>98%	92:8 [c]
35	$P(4\text{-}CH_3C_6H_4)_3$	15	>98%	87.5:12.5 [c]
36	$P(4\text{-}OCH_3C_6H_4)_3$	15	>98%	70:30 [c]

[a] Conditions: 1. Catalyst (5 mol%), ligand, toluene (1 mL), room temperature, 10 min; then allylic azide **1** (0.2 mmol), HBpin (4.0 equiv.), toluene (2 mL), 90 °C, 20 h; 2. $NaBO_3$•$4H_2O$ (5.0 equiv.), THF/H_2O (2:1, 3 mL). [b] Determined by ^1H NMR. [c] a/b ratio determined by HPLC (Elite SinoChrom ODS-AP C18 4.6 mm × 250 mm, 5 μm column, MeOH/H_2O: 45:55, 1.0 mL/min, 40 °C, 254 nm).

Structures of ligands:

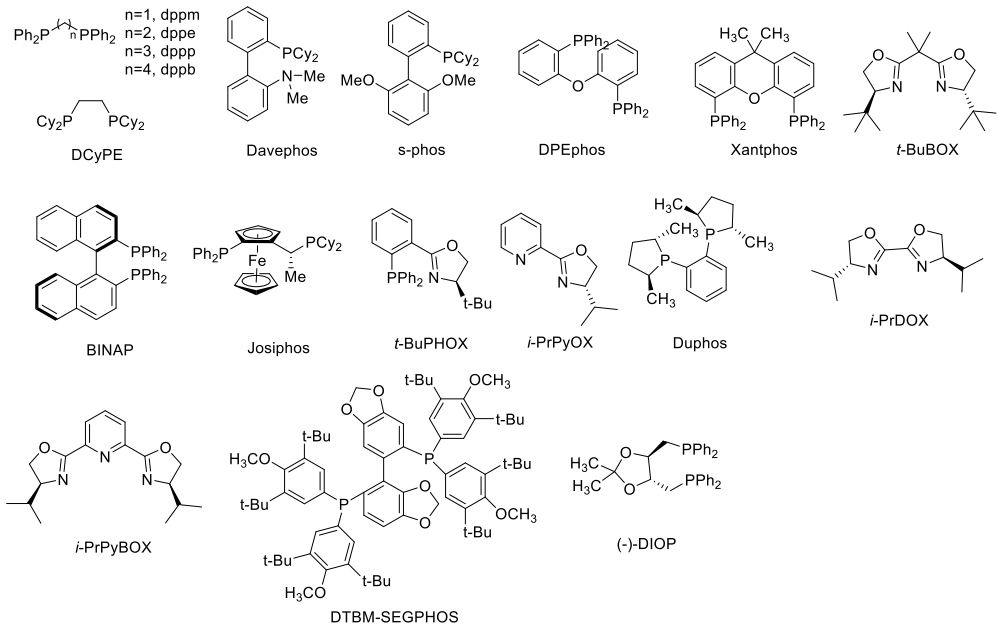
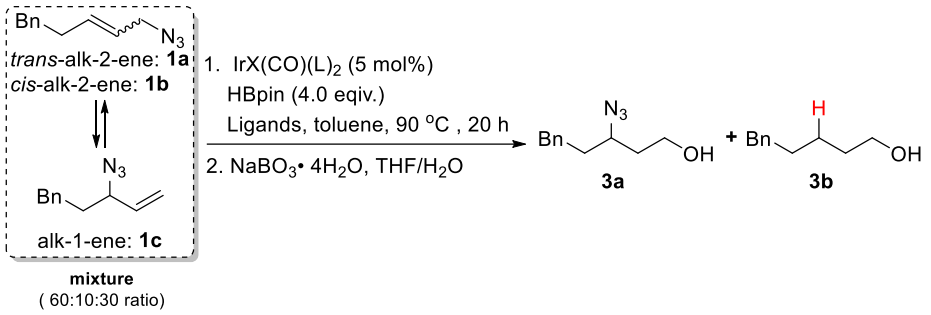


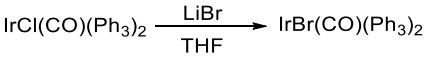
Table S2. Vaska-type catalysts screening. [a]



Entry	L of $IrX(CO)(L)_2$	X of $IrX(CO)(L)_2$	Conv. (%) [b]	Ratio [c] **3a/3b**	Isolated Yield (%)
1	PPh_3	Br	>98%	94:6	67%
2	$P(4\text{-}CH_3OC_6H_4)_3$	Cl	<5%	-	-
3	PCy_3	Cl	>98%	87:13	-
4	$P(C_6F_5)_3$	Cl	>98%	29:71	-
5	$P(4\text{-}CH_3C_6H_4)_3$	Cl	>98%	86:14	60%
6	$P(4\text{-}ClC_6H_4)_3$	Cl	>98%	94:6	44%
7	$P(4\text{-}FC_6H_4)_3$	Cl	>98%	89:11	51%
8	$P(4\text{-}CF_3C_6H_4)_3$	Cl	>98%	89:11	-
9	$P(2\text{-}CH_3C_6H_4)_3$	Cl	>98%	74:26	-
10	P(*t*-Bu)$_3$	Cl	>98%	66:34	-

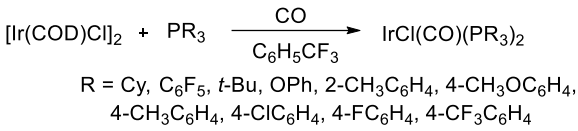
[a] Conditions: 1. Allylic azide **1** (0.2 mmol), HBpin (4.0 equiv.), catalyst (5 mol%), toluene (2 mL), 90 °C, 20 h (Sequence A in Table S4); 2. $NaBO_3$•$4H_2O$ (5.0 equiv.), THF/H_2O (2:1, 3 mL). [b] Determined by ^1H NMR. [c] a/b ratio determined by HPLC (Elite SinoChrom ODS-AP C18 4.6 mm × 250 mm, 5 μm column, MeOH/H_2O: 45:55, 1.0 mL/min, 40 °C, 254 nm).

Preparation of $IrBr(CO)(PPh_3)_2$:



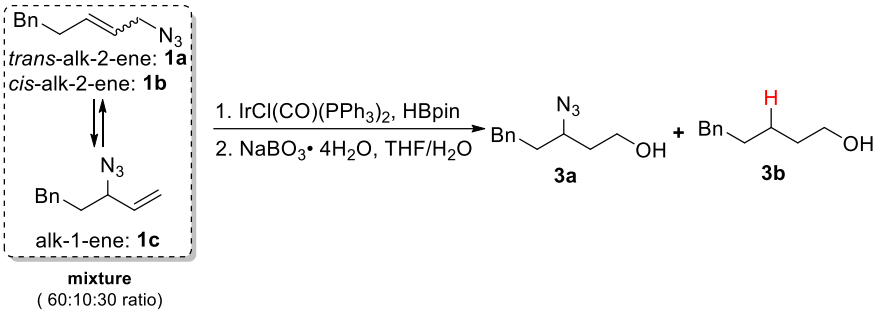
An oven-dried flask was charged with $[Ir(COD)Cl]_2$ (1.0 equiv.), LiBr (10 equiv.), and THF (50 mL/1mmol) under argon. The solution was stirred at room temperature for 1 h. The solvent was removed, and the residue was washed with H_2O (3 mL). The cake was dried, and recrystallized in toluene, and dried under vacuum to give the corresponding iridium complex as yellow solid.

Preparation of $IrCl(CO)(L)_2$:



An oven-dried flask was charged with $[Ir(COD)Cl]_2$ (1.0 equiv.), phosphane (4.0 equiv.), and $C_6H_5CF_3$(4 mL) under argon. The solution was stirred at room temperature for 15 min, and CO was added. After 2 h, the solvent was removed, the residue was washed with hexane (3 mL). After the filtration, the solid was collected and dried under vacuum to give the corresponding iridium complex. The spectral data of all the catalysts matched with the reported.[S1]

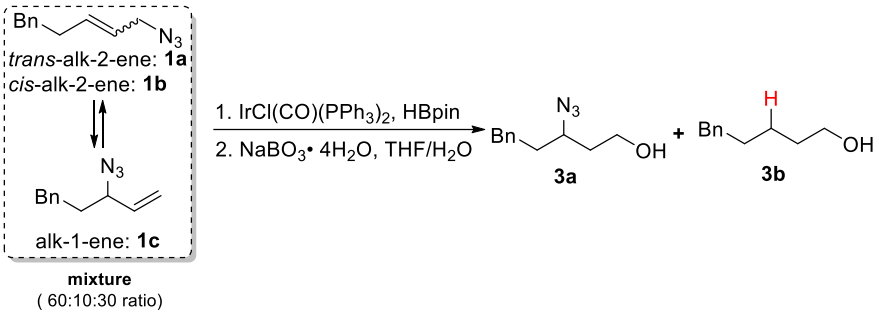
Table S3. Expanded optimization table. [a]



Entry	$IrCl(CO)(PPh_3)_3$ (mol%)	HBpin (equiv.)	Temp.(°C)	Solvent	Conv. (%) [b]	Ratio [c] **3a/3b**	Isolated Yield (%)
1	5	4.0	90	toluene	>98%	95:5	67%
2	5	4.0	90	dry THF	>98%	91:9	55%
3	5	4.0	90	DCE	>98%	91:9	69%
4	5	4.0	90	hexane	70%	91:9	48%
5	5	4.0	90	heptane	>98%	73:27	-
6	5	4.0	90	chlorobenzene	>98%	90:10	37%
7	5	4.0	90	toluene	>98%	95:5	67%
8	5	3.0	90	toluene	>98%	94:6	59%
9	5	2.0	90	toluene	>98%	95:5	60%
10	5	1.5	90	toluene	60%	97:3	-
11	5	1.1	90	toluene	45%	-	-
12	5	4.0	80	toluene	70%	97:3	-
13	5	4.0	90	toluene	>98%	95:5	59%
14	5	4.0	120	toluene	>98%	93:7	57%
15	5	4.0	90	toluene	>98%	96:4	67%
16	2.5	4.0	90	toluene	44%	-	-
17	1	4.0	90	toluene	30%	-	-
18	0.5	4.0	90	toluene	<5%	-	-

[a] Conditions: 1. $IrCl(CO)(PPh_3)_3$, allylic azide **1** (0.2 mmol), HBpin, solvent (2 mL), T, 20 h (Sequence F in Table S4); 2. $NaBO_3$•$4H_2O$ (5.0 equiv.), THF/H_2O (2:1, 3 mL). [b] Determined by ^1H NMR; [c] a/b ratio determined by HPLC (Elite SinoChrom ODS-AP C18 4.6 mm × 250 mm, 5 μm column, MeOH/H_2O: 45:55, 1.0 mL/min, 40 °C, 254 nm).

Table S4. Addition sequence optimization.



Sequence A: A solution of allylic azide **1** (0.2 mmol) in toluene (1 mL), HBpin (4.0 equiv.), toluene (1 mL), stirred for 1-3min; Catalyst (5 mol%), toluene (1 mL), heated to 90 °C for 20 h; standard oxidation. **Result**: poor reproducibility (5 runs).

Sequence B: A solution of allylic azide **1** (0.2 mmol) in toluene (1 mL), Catalyst (5 mol%), toluene (1 mL), stirred for 1-3min; HBpin (4.0 equiv.), toluene (1 mL), heated to 90 °C for 20 h; standard oxidation. **Result**: Conv. >98%, Isolated yield: 66% (86:14).

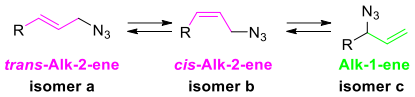
Sequence C: Catalyst (10 mol%), a solution of allylic azide **1** (0.2 mmol) in toluene (1 mL), toluene (1 mL, used to rinse the flask), stirred for 1-3min; HBpin (4.0 equiv.), toluene (1 mL), heated to 90 °C for 20 h; standard oxidation. **Result**: Conv. >98%, Isolated yield: 37% (94:6).

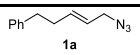
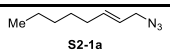
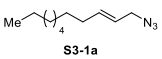
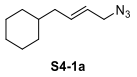
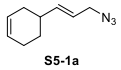
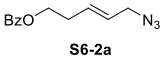
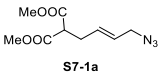
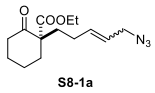
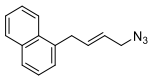
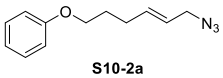
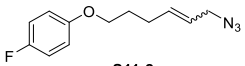
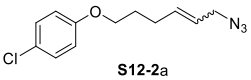
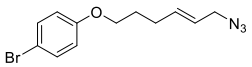
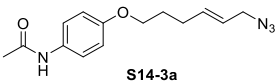
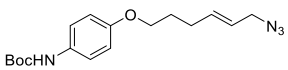
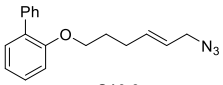
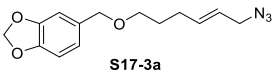
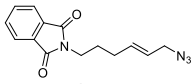
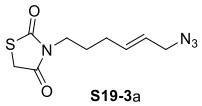
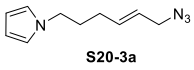
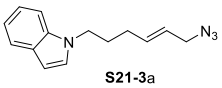
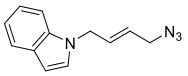
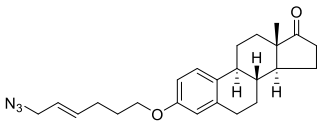
Sequence D: Catalyst (5 mol%); a solution of allylic azide **1** (0.2 mmol) in toluene (1 mL) and HBpin (4.0 equiv.), toluene (1 mL), heated to 90 °C for 20 h; standard oxidation. **Result**: poor reproducibility (5 runs).

Sequence E: Catalyst (5 mol%), HBpin (4.0 equiv.), toluene (1 mL), stirred for 0.5 h, 1h, 2 h; a solution of allylic azide **1** (0.2 mmol) in toluene (1 mL), toluene (1 mL, used to rinse the flask), heated to 90 °C for 20 h; standard oxidation. **Result**: Conv.60% (0.5h); NR (1h); NR (2h).

Sequence F: Catalyst (5 mol%), a solution of allylic azide **1** (0.2 mmol) in toluene (1 mL), toluene (1 mL, used to rinse the flask), stirred for 30 min; HBpin (4.0 equiv.), toluene (1 mL), heated to 90 °C for 20 h; standard oxidation. **Result**: Conv.>98%, Isolated yield:67% (95:5).

Table S5. Ratio of allylic azide isomers.



Entry	Isomer **a**	Ratio of isomers **a**:**b**:**c** [a]	Entry	Isomer **a**	Ratio of isomers **a**:**b**:**c** [a]
1	 **1a**	60:10:30	2	 **S2-1a**	61:7:32
3	 **S3-1a**	62:10:28	4	 **S4-1a**	67:11:22
5	 **S5-1a**	82:6:6:6 [b]	6	 **S6-2a**	54:5:41
7	 **S7-1a**	68:10:22	8	 **S8-1a**	63:7:15:15 [b]
9	 **S9-1a**	73:9:18	10	 **S10-2a**	67:6:27
11	 **S11-2a**	67:6:27	12	 **S12-2a**	67:6:27
13	 **S13-2a**	68:7:25	14	 **S14-3a**	68:7:25
15	 **S15-3a**	86:4:10	16	 **S16-3a**	54:12:34
17	 **S17-3a**	61:10:29	18	 **S18-1a**	60:9:31
19	 **S19-3a**	68:7:25	20	 **S20-3a**	69:6:25
21	 **S21-3a**	70:6:24	22	 **S22-2a**	52:16:32
23	 **S23-2a**	65:1:34			

[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Ratio of isomers ***trans*-alk-2-ene** : ***cis*-alk-2-ene** : **alk-1-ene 1** : **alk-1-ene 2**. Two internal isomers (**alk-1-enes 1** and **2**) are presented due to the additional stereocenter(s) in the molecule.

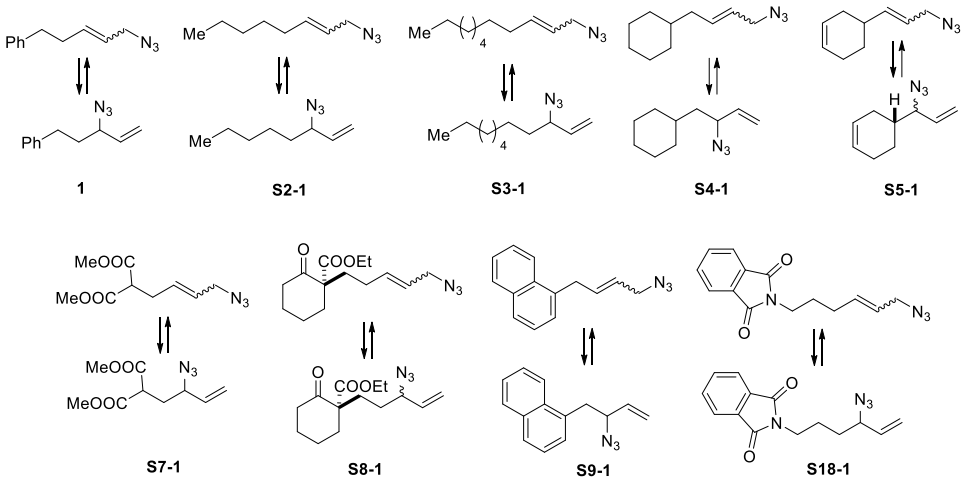
General information

NMR spectra was recorded on a Bruker Advance 600 MHz or Agilent DD2 400 MHz spectrometer in deuterated solvents (400 or 600 MHz for ^{1}H and 101 or 150 MHz for ^{13}C). Chemical shifts in ^{1}H NMR spectra are reported in ppm on the δ scale from an internal standard of TMS. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of deuterated solvents on the δ scale.

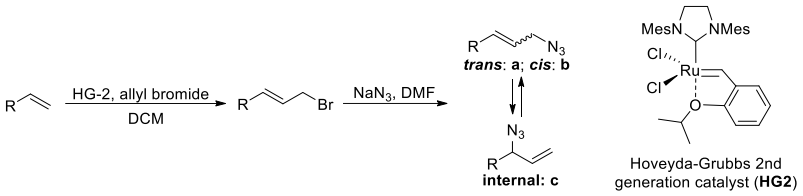
High resolution mass spectrometry (HRMS) was performed on Bruker UHR-TOF maXis and are reported as m/z. Infrared spectrometry (IR) was performed on Bruker Tensor 27 and are reported as cm^{-1}. Thin layer chromatography (TLC) was performed using TLC silica gel plates HSG F254 (Jiangyou) and visualized using UV light, or potassium permanganate. Silica gel column chromatography was carried out using 200-300 mesh silica gel (Jiangyou) on Biotage Isolera one.

Dichloromethane, DMF, THF and toluene were purified by passage through solvent purification columns. Unless otherwise noted, all other purchased reagents and solvents were used as received, without further purification.

Compounds **1**, **S2-1**, **S3-1, S4-1**, **S5-1**, **S7-1**, **S8-1**, **S9-1**, **S18-1** were prepared according to the reported procedure. [S2]

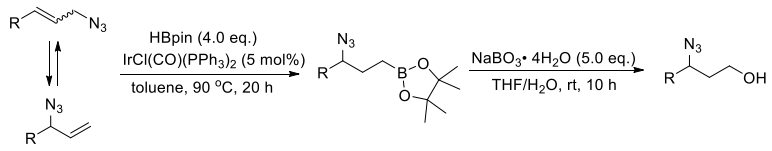


General procedure A: Preparation of allyllic azides.



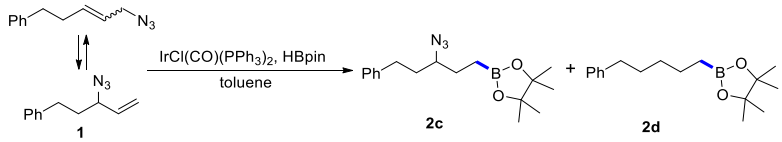
To a stirred solution of the Hoveyda-Grubbs 2nd generation catalyst (HG-2) (2 mol%) in dichloromethane (1 mL/mmol) under an argon atmosphere was added a pre-mixed solution of alkene (1.0 equiv) and allyl boromide (5.0 equiv) in dichloromethane (2 mL/mmol) at room temperature. The reaction mixture was stirred for 6 h. The crude product was purified by silica gel column chromatography to afford the corresponding allylic bromide. To a solution of the above allylic bromide in dry DMF (2 mL/mmol) was added sodium azide (1.5 equiv) portionwise. The resulting reaction mixture was stirred for 15 h. The resulting mixture was partitioned between ethyl acetate and water, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding allylic azides.

General procedure B: Selective hydroboration of allyllic azides.

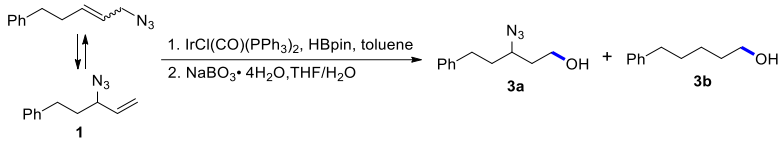


Under argon atmosphere, to an oven-dried flask was added $IrCl(CO)(PPh_3)_2$ (5 mol%), allylic azides (1.0 equiv.) and toluene (2 mL) successively. The reaction mixture was stirred for 30 min at room temperature, and then HBpin(4.0 equiv.) and toluene(1 mL) were added. The reaction mixture was heated at 90 °C for 20 h. The solvent was removed under the reduced pressure to afford the crude product. A mixture of the above crude product, $NaBO_3 \cdot 4H_2O$ (5.0 equiv.) in THF (2 mL) and H_2O (1 mL) was stirred at room temperature for 10 h. The reaction mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography to afford the desired product.

Scheme S1. Preparation of compound **3a**.

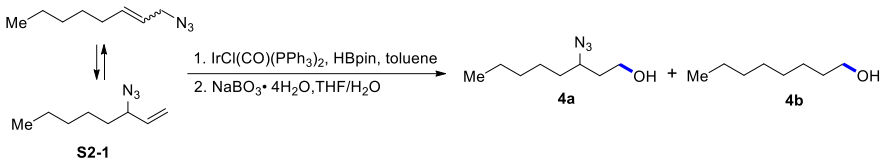


2-(3-Azido-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**) and **4,4,5,5-tetramethyl -2-(5-phenyl pentyl)-1,3,2-dioxaborolane** (**2d**). According to General procedure B, a mixture of **S1-1** (46.6 mg, 0.247 mmol), HBpin (63.2 mg, 0.494 mmol), and $IrCl(CO)(PPh_3)_2$ (9.6 mg, 5 mol%) in toluene (3 mL) afforded **2c** (24.9 mg, 34%) as a yellow oil and **2d** (1.5 mg, 2 %) as a yellow oil after column chromatography (2~5% EtOAc/PE). Azide **2c**: R_f = 0.42 (5% EtOAc/PE), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 7.21 – 7.13 (m, 3H), 3.20 (td, *J* = 7.7, 3.9 Hz, 1H), 2.77 (ddd, *J* = 14.5, 8.7, 6.1 Hz, 1H), 2.71 – 2.60 (m, 1H), 1.90 – 1.73 (m, 2H), 1.70 – 1.60 (m, 2H), 1.21 (s, 12H), 0.85 (q, *J* = 8.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.29, 128.42, 128.39, 125.94, 83.14, 63.96, 35.75, 32.35, 28.91, 24.77, 24.75. Compound **2d**: R_f = 0.45 (5% EtOAc/PE), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.3 Hz, 2H), 7.19 – 7.11 (m, 3H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.60 (p, *J* = 9.0 Hz, 2H), 1.47 – 1.37 (m, 2H), 1.38 – 1.28 (m, 2H), 1.21 (s, 12H), 0.76 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.90, 128.36, 128.13, 125.44, 82.82, 35.82, 31.96, 31.17, 24.82, 24.77, 23.82.



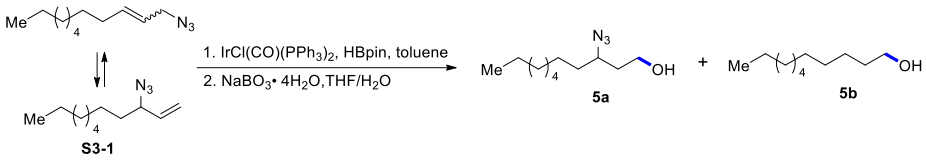
3-Azido-5-phenylpentan-1-ol (**3a**). According to General procedure B, a mixture of **1** (99.3 mg, 0.530 mmol), HBpin (136 mg, 1.06 mmol), and $IrCl(CO)(PPh_3)_2$ (20.8 mg, 5 mol%) in toluene (2 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (406 mg, 2.64 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **3a** and **3b** (69 mg, 64%, 19:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE); IR (KBr): 3329, 2937, 2100, 1257, 1050, 745, 698 cm^{-1}; HRMS (ESI) m/z calculated for $C_{11}H_{15}N_3NaO$ $(M+Na)^+$: 228.1107, Found: 228.1198. Azide **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.24 – 7.13 (m, 3H), 3.78 (td, *J* = 5.7, 1.8 Hz, 2H), 3.51 (td, *J* = 9.8, 8.4, 4.8 Hz, 1H), 2.87 – 2.75 (m, 1H), 2.76 – 2.64 (m, 1H), 1.94 – 1.70 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.00, 128.52, 128.36, 126.11, 59.68, 59.38, 36.89, 36.35, 32.32. Alcohol **3b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.6 Hz, 2H), 2.65 – 2.59 (m, 2H).

Scheme S2. Preparation of compound **4a**.



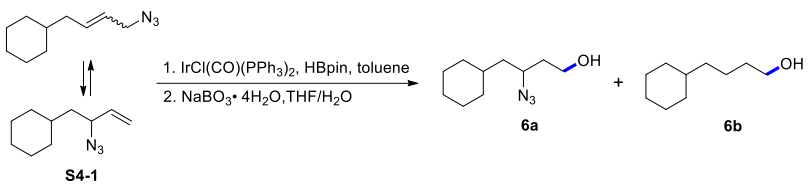
3-Azidooctan-1-ol (**4a**). According to General procedure B, a mixture of **S2-1** (34.0 mg, 0.222 mmol), HBpin (60.8 mg, 0.472 mmol), and $IrCl(CO)(PPh_3)_2$ (8.8 mg, 5 mol%) in toluene (2 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (171 mg, 1.11 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **4a** and **4b** (20.1 mg, 49%, 25:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE); IR (KBr): 3182, 2929, 2861, 2100, 1252, 1052, 806 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{13}N_3NaO_2$ $(M+Na)^+$: 254.0900, Found: 254.0898. Azide **4a**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.76 (t, *J* = 5.6 Hz, 2H), 3.54 – 3.44 (m, 1H), 1.83 – 1.73 (m, 1H), 1.72 – 1.62 (m, 1H), 1.62 – 1.50 (m, 10H), 1.50 – 1.35 (m, 2H), 1.35 – 1.22 (m, 5H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 60.17, 59.83, 36.79, 34.51, 31.55, 25.69, 22.51, 13.96. Alcohol **4b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.7 Hz, 2H).

Scheme S3. Preparation of compound **5a**.



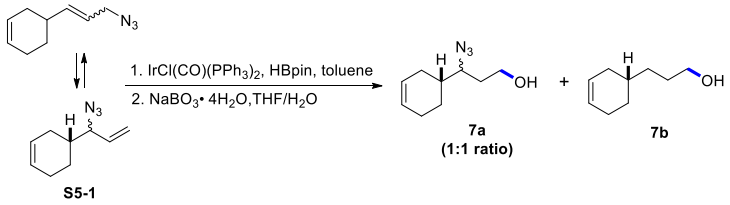
3-Azidoundecan-1-ol (**5a**). According to General procedure B, a mixture of **S3-1** (39.6 mg, 0.202 mmol), HBpin (51.9 mg, 0.406 mmol), and $IrCl(CO)(PPh_3)_2$ (8.0 mg, 5 mol%) in toluene (2 mL) afforded the borohydride product. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (155 mg, 1.01 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **5a** and **5b** (22.8 mg, 53%, 25:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE); IR (KBr): 3319, 2927, 2857, 2100, 1461, 1256, 1051 cm^{-1}; HRMS (ESI) m/z calculated for $C_8H_{17}N_3NaO$ $(M+Na)^+$: 194.1264, Found: 194.1260. Azide **5a**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.77 (t, *J* = 5.6 Hz, 2H), 3.55 – 3.41 (m, 1H), 1.85 – 1.72 (m, 1H), 1.73 – 1.52 (m, 3H), 1.48 – 1.21 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 60.17, 59.83, 36.79, 34.56, 31.82, 29.44, 29.39, 29.19, 26.02, 22.63, 14.08. Alcohol **5b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.6 Hz, 2H).

Scheme S4. Preparation of compound **6a**.



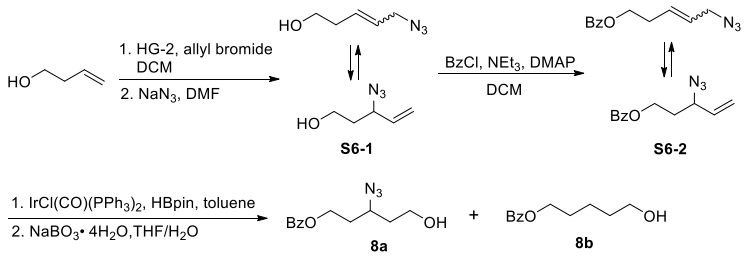
3-Azido-4-cyclohexylbutan-1-ol (**6a**). According to General procedure B, a mixture of **S4-1** (103 mg, 0.574 mmol), HBpin (150 mg, 1.17 mmol), and $IrCl(CO)(PPh_3)_2$ (22.6 mg, 5 mol%) in toluene (4 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3 \cdot 4H_2O$ (442 mg, 2.87 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **6a** and **6b** (62.1 mg, 55%, 15:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.3 (16% EtOAc/PE); IR (KBr): 3358, 2925, 2851, 2102, 1257, 1052, 659 cm^{-1}; HRMS (ESI) m/z calculated for $C_{10}H_{19}N_3NaO$ $(M+Na)^+$: 220.1420, Found: 220.1413. Azide **6a**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.76 – 3.67 (m, 2H), 3.60 – 3.49 (m, 1H), 2.41 (br, 1H), 1.85 – 1.57 (m, 7H), 1.47 – 1.38 (m, 2H), 1.37 – 1.26 (m, 1H), 1.25 – 1.08 (m, 3H), 0.97 – 0.80 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 59.66, 57.37, 42.17, 37.24, 34.45, 33.66, 32.81, 26.45, 26.22, 26.08. Alcohol **6b** (diagnostic peaks only):^{13}C NMR (151 MHz, $CDCl_3$) δ 63.04, 37.61, 33.36, 33.05, 26.71, 26.40, 22.98.

Scheme S5. Preparation of compound **7a**.



3-Azido-3-(cyclohex-3-en-1-yl)propan-1-ol (**7a**). According to General procedure B, a mixture of **S5-1** (80.0 mg, 0.490 mmol), HBpin (132 mg, 1.03 mmol), and $IrCl(CO)(PPh_3)_2$ (19.2 mg, 5 mol%) in toluene (4 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3 \cdot 4H_2O$ (378 mg, 2.46 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **7a** and **7b** (47.9 mg, 54%, > 30:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE); IR (KBr): 3346, 2923, 2099, 1257, 1050, 660 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{15}N_3NaO$ $(M+Na)^+$: 204.1107, Found: 204.1093. Azide **7a** (1:1 ratio): ^1H NMR (600 MHz, $CDCl_3$) δ 5.73 – 3.63 (m, 2H), 3.86 – 3.75 (m, 2H), 3.50 (ddd, J = 10.2, 5.4, 3.4 Hz, 0.5H), 3.39 (ddd, J = 10.1, 6.5, 3.3 Hz, 0.5H), 2.16 – 2.04 (m, 2H), 1.98 – 1.75 (m, 5H), 1.70 (dq, J = 14.7, 5.1 Hz, 1H), 1.50 – 1.42 (m, 0.5H), 1.39 – 1.31 (m, 0.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.15, 126.90, 125.74, 125.55, 64.83, 64.66, 59.90, 59.87, 38.63, 38.44, 34.19, 33.86, 28.35, 27.12, 25.87, 25.16, 25.15, 24.96.

Scheme S6. Preparation of compound **8a**.



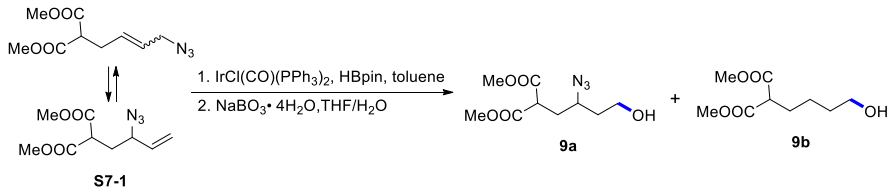
(*E*)-5-Azidopent-3-en-1-ol (**S6-1a**), **(*Z*)-5-azidopent-3-en-1-ol** (**S6-1b**), and **3-azidopent-4-en-1-ol** (**S6-1c**). According to General procedure A, but-3-en-1-ol (7.2 g, 0.10 mol), allyl bromide (26 mL, 0.30 mol), HG-2 (206 mg, 0.330 mmol), and sodium azide (26 g, 0.40 mol) afforded a mixture of azides **S6-1** (5.0 g, 40%, 75:7:18 ratio) as a colorless oil after silica gel column chromatography (5-20% EtOAc/hexanes). R_f = 0.55 (100% EtOAc/hexanes). Azide **S6-1a**: IR (neat) 3340, 2932, 2094, 1236 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}N_6O_2$ $(2M+H)^+$ 255.1569, Found: 255.1567; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73-5.83 (m, 1H), 5.60-5.69 (m, 1H), 3.75 (d, *J* = 6.4 Hz, 2H), 3.69 (q, *J* = 6.0 Hz, 2H), 2.36 (q, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.5, 52.7, 61.7, 125.7, 132.6. Azide **S6-1b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (d, *J* = 7.2 Hz, 1H). Azide **S6-1c**: IR (neat) 3342, 2931, 2094, 1236 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}N_6O_2$ $(2M+H)^+$ 255.1569, Found: 255.1552; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddd, *J* = 17.2, 10.2, 7.7 Hz, 1H), 5.34 (dt, *J* = 11.1, 1.0 Hz, 1H), 5.31 (dt, *J* = 4.1, 0.9 Hz, 1H), 4.10 (q, *J* = 7.4 Hz, 1H), 3.68-3.80 (m, 2H), 2.00 (t, *J* = 4.5 Hz, 1H), 1.75-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.7, 59.3, 62.3, 118.5, 135.3.

(*E*)-5-Azidopent-3-en-1-yl benzoate (**S6-2a**), **(*Z*)-5-azidopent-3-en-1-yl benzoate** (**S6-2b**), and **3-azidopent-4-en-1-yl benzoate** (**S6-2c**). Under argon atmosphere, to a solution of **S6-1** (119 mg, 0.933 mmol), Et_3N (280 mg, 2.75 mmol), DMAP (11.8 mg, 10 mol%) in DCM (5 mL) was added dropwise a solution of benzoyl chloride (196 mg, 1.39 mmol) in DCM (5 mL) at 0 °C. The reaction mixture was warmed to room temperature naturally and stirred for 10 h. The concentrated residue was purified by chromatography to afford **S6-2** (202 mg, 94%, 54:5:41 ratio) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 2959, 2100, 1719, 1452, 1272, 1110, 973, 710 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{13}N_3NaO_2$ $(M+Na)^+$: 254.0900, Found: 254.0898. Azide **S6-2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 5.87 – 5.74 (m, 1H), 5.73 – 5.63 (m, 1H), 4.43 – 4.32 (m, 2H), 3.72 (d, *J* = 6.6 Hz, 2H), 2.56 (q, *J* = 6.5 Hz, 1H), 2.03 – 1.93 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.45, 132.95, 131.70, 129.54, 128.39, 128.34, 125.85, 63.75, 52.56, 31.70. Azide **S6-2b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.01, 130.75, 130.01, 129.53, 128.37, 125.11, 47.10, 27.14. Azide

S6-2c (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 – 5.28 (m, 2H), 4.08 (q, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.33, 134.86, 133.04, 130.14, 128.37, 119.00, 61.97, 61.31, 33.37.

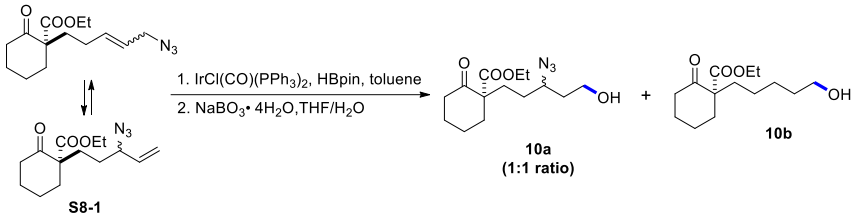
3-Azido-5-hydroxypentyl benzoate (**8a**). According to General procedure B, a mixture of **S6-3** (58.0 mg, 0.251 mmol), HBpin (134 mg, 1.05 mmol), and $IrCl(CO)(PPh_3)_2$ (9.8 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (195 mg, 1.27 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **8a** and **8b** (36.4 mg, 58%, 5:1 ratio) as a yellow oil after column chromatography (20~35% EtOAc/PE). R_f = 0.4 (25% EtOAc/PE); IR (KBr): 3728, 2944, 2102, 1719, 1275, 1068, 765 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{15}N_3NaO_3$ $(M+Na)^+$: 272.1006, Found: 272.1009. Azide **8a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.39 (m, 2H), 4.53 – 4.39 (m, 2H), 3.86 – 3.74 (m, 3H), 2.12 – 1.93 (m, 2H), 1.91 – 1.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.45, 133.09, 129.57, 128.41, 61.60, 59.37, 57.09, 36.92, 33.66. Alcohol **8b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (t, *J* = 6.6 Hz, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 1.70 – 1.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.85, 129.93, 129.51, 128.32, 64.87, 62.73, 32.31, 28.53, 22.34.

Scheme S7. Preparation of compound **9a**.



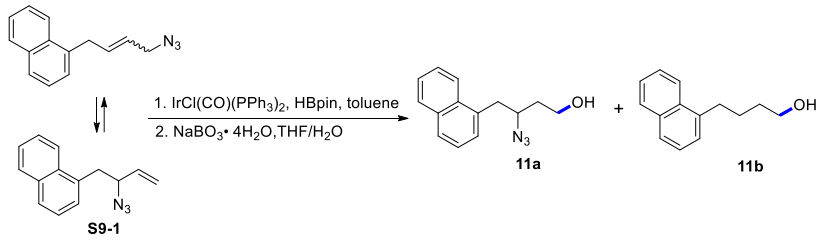
Dimethyl 2-(2-azido-4-hydroxybutyl)malonate (**9a**). According to General procedure B, a mixture of **S7-1** (38.8 mg, 0.171 mmol), HBpin (45.2 mg, 0.353 mmol), and $IrCl(CO)(PPh_3)_2$ (6.8 mg, 5 mol%) in toluene (2 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (132 mg, 0.858 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **9a** and **9b** (20.7 mg, 48%, 20:1 ratio) as a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3375, 2978, 2100, 1735, 1452, 1145, 710 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{15}N_3NaO_5$ $(M+Na)^+$: 268.0904, Found: 268.0909. Azide **9a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (t, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.62 (dd, *J* = 9.1, 5.5 Hz, 1H), 3.62 – 3.55 (m, 1H), 2.22 (m, 1H), 2.00 (m, 1H), 1.85 – 1.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.40, 169.35, 59.07, 57.79, 52.83, 52.81, 48.72, 36.94, 33.55. Alcohol **9b** (diagnostic peaks only): ^{13}C NMR (101 MHz, $CDCl_3$) δ 62.32, 61.10, 57.49, 36.27, 32.13, 28.47.

Scheme S8. Preparation of compound **10a**.



Ethyl 1-(3-azido-5-hydroxypentyl)-2-oxocyclohexane-1-carboxylate (**10a**). According to General procedure B, a mixture of **S8-1** (44.7 mg, 0.160 mmol), HBpin (82.6 mg, 0.645 mmol), and $IrCl(CO)(PPh_3)_2$ (6.3 mg, 5 mol%) in toluene (2 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (123 mg, 0.799 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **10a** and **10b** (21.4 mg, 45%, 15:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.3 (16% EtOAc/PE); IR (KBr): 2959, 2100, 1710, 1452, 1241, 1020, 730 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{23}N_3NaO_4$ $(M+Na)^+$: 320.1581, Found: 320.1592. Azide **10a** (1:1 ratio): ^1H NMR (400 MHz, $CDCl_3$) δ 4.32 – 4.12 (m, 2H), 3.77 – 3.70 (m, 2H), 3.52 – 3.42 (m, 1H), 2.52 – 2.38 (m, 1H), 2.05 – 1.82 (m, 4H), 1.82 – 1.52 (m, 7H), 1.50 – 1.32 (m, 2H), 1.27 (t, *J* = 7.9, 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.00, 207.83, 171.85(2C), 61.41, 61.38, 60.44, 60.41, 60.10, 59.97, 59.49, 59.47, 41.03(2C), 36.67, 36.52(2C), 36.20, 31.22, 30.93, 29.21, 29.03, 27.59, 27.50, 22.54, 22.50, 14.13, 14.12. Alcohol **10b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.24, 172.07, 67.63, 62.76, 61.12, 36.06, 34.57, 32.40, 29.12, 26.07, 23.95, 23.89, 21.03.

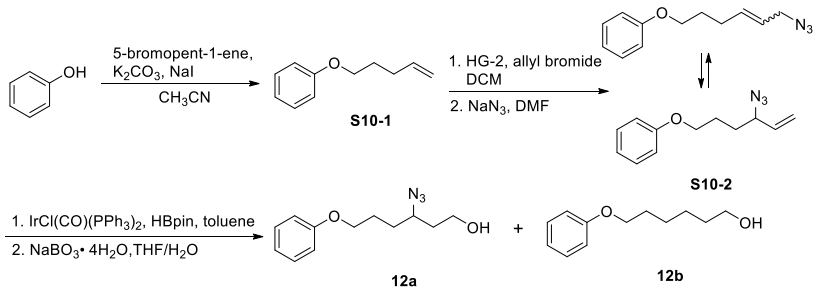
Scheme S9. Preparation of compound **11a**.



3-Azido-4-(naphthalen-1-yl)butan-1-ol (**11a**). According to General procedure B, a mixture of **S9-1** (115 mg, 0.517 mmol), HBpin (263 mg, 2.06 mmol), and $IrCl(CO)(PPh_3)_2$ (20.6 mg, 5 mol%) in toluene (4 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (398 mg, 2.59 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **11a** and **11b** (89.8 mg, 72%, 5:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.3 (16% EtOAc/PE); IR (KBr): 3741, 2932, 2099, 1260, 1046, 779 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{15}N_3NaO$ $(M+Na)^+$: 264.1107, Found: 264.1104. Azide **11a**: ^1H NMR

(400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.46 – 7.37 (m, 2H), 4.00 – 3.91 (m, 1H), 3.80 – 3.72 (m, 2H), 3.34 (dd, *J* = 7.0, 3.2 Hz, 2H), 1.98 – 1.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.94, 133.42, 131.85, 129.01, 127.89, 127.80, 126.26, 125.68, 125.47, 123.26, 60.54, 59.77, 38.35, 36.84. Alcohol **11b** (diagnostic peaks only): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 7.0, 1.3 Hz, 2H), 3.66 (t, *J* = 6.5 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.81, 128.75, 126.57, 125.94, 125.71, 125.49, 125.40, 123.77, 62.82, 32.74, 32.73, 26.88.

Scheme S10. Preparation of compound **12a**.



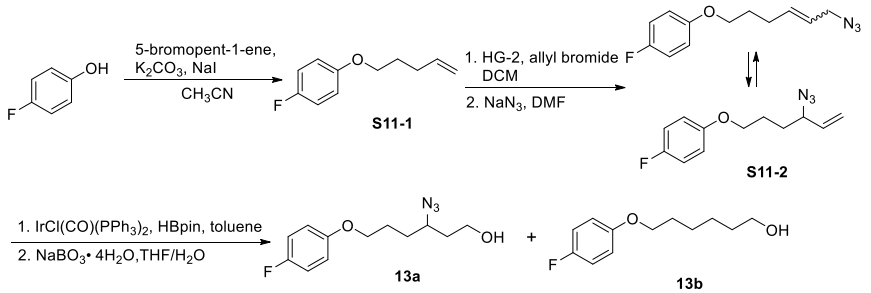
(Pent-4-en-1-yloxy)benzene (**S10-1**). Under argon atmosphere, to an oven-dried flask was added alcohol (1.00 g, 10.6 mmol), K_2CO_3 (2.20 g, 15.9 mmol), NaI (317 mg, 2.12 mmol), 5-bromopent-1-ene (3.14 g, 21.1 mmol) and acetonitrile (30 mL). The reaction mixture was heated to reflux for 12 h. After the filtration, the concentrated residue was purified by chromatography to afford target product **S10-1** (1.50 g, 87%) as a yellow oil after column chromatography (0~5% EtOAc/PE). R_f = 0.5 (5% EtOAc/PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 6.97 – 6.87 (m, 3H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.00 (dq, *J* = 10.2, 1.6 Hz, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 2.27 – 2.22 (m, 2H), 1.92 – 1.86 (m, 2H).

(*E*)-((6-Azidohex-4-en-1-yl)oxy)benzene (**S10-2a**), **(*Z*)-((6-azidohex-4-en-1-yl)oxy)benzene** (**S10-2b**), and **((4-azidohex-5-en-1-yl)oxy)benzene** (**S10-2c**). According to General procedure A, a mixture of HG-2 (145 mg, 2 mol%), **S10-1** (1.50 g, 9.25 mmol) and allyl bromide (3.33 g, 27.5 mmol) in dichloromethane (15 mL) afforded the corresponding allylic bromide (1.41 g, 60%). A mixture of the above bromide and sodium azide (536 mg, 8.26 mmol) in dry DMF (10 mL) afforded **S10-2** (1.02 g, 85%, 67:6:27 ratio) as a yellow oil after column chromatography (100% PE). R_f = 0.3 (2% EtOAc/PE); IR (KBr): 3329, 2939, 2872, 2099, 1596, 1243, 1038, 754 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{15}N_3NaO$ $(M+Na)^+$: 240.1107, Found: 240.1102. Azide **S10-2a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 6.89 – 6.84 (m, 1H), 6.84 – 6.80 (m, 2H), 5.69 – 5.60 (m, 1H), 5.48 – 5.40 (m, 1H), 3.82 (t, *J* = 6.3 Hz, 2H), 3.54 (d, *J* = 6.7 Hz, 2H), 2.19 – 2.12 (m, 2H), 1.81 – 1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

159.21, 135.78, 129.56, 123.84, 120.72, 114.63, 66.86, 52.70, 28.83, 28.81. Azide **S10-2b** (diagnostic peaks only): ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.86, 123.28, 118.27,114.60, 66.59, 47.08, 29.08, 23.97. Azide **S10-2c** (diagnostic peaks only): ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.69 – 5.62 (m, 1H), 5.22 – 5.16 (m, 2H), 3.84 – 3.78 (m, 2H), 3.75 (q, *J* = 7.1 Hz, 1H), 1.72 – 1.64 (m, 2H), 1.62 – 1.56 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.12, 135.81, 129.57, 123.28, 120.78, 114.59, 67.17, 47.08, 31.08, 25.80.

3-Azido-6-phenoxyhexan-1-ol (**12a**). According to General procedure B, a mixture of **S10-2** (66.9 mg, 0.308 mmol), HBpin (84.1 mg, 0.657 mmol), and $IrCl(CO)(PPh_3)_2$ (12.0 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (237 mg, 1.54 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **12a** and **12b** (52.2 mg, 72%, 7:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.2 (16% EtOAc/PE); IR (KBr): 3348, 2938, 2100, 1597, 1247, 1041, 753, 660 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{17}N_3NaO_2$ $(M+Na)^+$: 258.1213, Found: 258.1209. Azide **12a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.97 – 6.85 (m, 3H), 4.04 – 3.95 (m, 2H), 3.83 – 3.74 (m, 2H), 3.64 – 3.56 (m, 1H), 2.02 – 1.65 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.79, 129.45, 120.73, 114.42, 67.16, 59.82, 59.62, 36.87, 31.31, 25.90. Alcohol **12b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (d, *J* = 6.5 Hz, 2H), 3.64 (t, *J* = 6.5 Hz, 1H), 1.60 (p, *J* = 6.8 Hz, 2H), 1.54 – 1.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.39, 120.48, 114.45, 67.67, 62.88, 32.65, 29.24, 25.52.

Scheme S11. Preparation of compound **13a**.



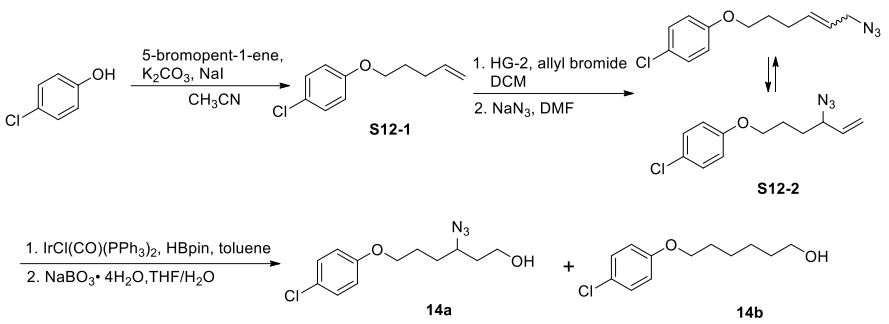
Fluoro-4-(pent-4-en-1-yloxy)benzene (**S11-1**). According to the synthetic method of compound **S10-1**, a mixture of 4-fluorophenol (2.01 g, 18.0 mmol), K_2CO_3 (3.73 g, 15.9 mmol), NaI (543 mg, 3.62 mmol), and 5-bromopent-1-ene (5.38 g, 36.1 mmol) in acetonitrile (30 mL) afforded **S11-1** (2.80 g, 88%) as a yellow oil after column chromatography (0~5% EtOAc/PE). R_f = 0.5 (5% EtOAc/PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 – 6.91 (m,

2H), 6.83 – 6.78 (m, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.02 – 4.97 (m, 1H), 3.90 (t, *J* = 6.5 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.89 – 1.81 (m, 2H).

(*E*)-1-((6-Azidohex-4-en-1-yl)oxy)-4-fluorobenzene (**S11-2a**), **(*Z*)-1-((6-azidohex-4-en-1-yl)oxy)-4-fluorobenzene** (**S11-2b**), and **1-((4-azidohex-5-en-1-yl)oxy)-4-fluorobenzene** (**S11-2c**). According to General procedure A, a mixture of HG-2 (243 mg, 2 mol%), **S11-1** (2.80 g, 15.5 mmol) and allyl bromide (5.60 g, 46.3 mmol) in dichloromethane (15 mL) afforded the corresponding allylic bromide (1.47 g, 35%). A mixture of the above bromide and sodium azide (528 mg, 8.13 mmol) in dry DMF (10 mL) afforded **S11-2** (1.16 g, 91%, 67:6:27 ratio) as a yellow oil after column chromatography (100% PE). R_f = 0.3 (2% EtOAc/PE); IR (KBr): 3731, 2942, 2100, 1399, 1210, 1037, 935, 8294 cm^{-1}; HRMS (ESI) m/z calculated for $C_{24}H_{28}F_2N_6NaO_2$ $(2M+Na)^+$: 493.2134, Found: 491.2127. Azide **S11-2a**: ^1H NMR (600 MHz, $CDCl_3$) δ 6.82 – 6.76 (m, 2H), 6.67 – 6.62 (m, 2H), 5.63 – 5.54 (m, 1H), 5.42 – 5.34 (m, 1H), 3.82 – 3.64 (m, 2H), 3.50 (d, *J* = 6.7 Hz, 2H), 2.08 (q, *J* = 7.8 Hz, 2H), 1.71 – 1.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.13 (d, *J* = 237.6 Hz), 155.23 (d, *J* = 2.2 Hz), 135.56, 123.77, 115.66 (d, *J* = 22.9 Hz), 115.40 (d, *J* = 7.9 Hz), 67.46, 52.56, 28.61, 28.59. Azide **S11-2b** (diagnostic peaks only): ^1H NMR (600 MHz, $CDCl_3$) δ 3.61 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.65, 123.17, 67.19, 46.92, 28.88, 23.75. Azide **S11-2c** (diagnostic peaks only): ^1H NMR (600 MHz, $CDCl_3$) δ 5.62 – 5.54 (m, 1H), 5.15 – 5.09 (m, 2H), 1.65 – 1.09 (m, 2H), 1.52 (q, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.16 (d, *J* = 237.8 Hz), 155.14 (d, *J* = 2.0 Hz), 135.61, 118.15, 115.68 (d, *J* = 22.9 Hz), 115.36 (d, *J* = 8.0 Hz), 67.77, 64.73, 30.88, 25.63.

3-Azido-6-(4-fluorophenoxy)hexan-1-ol (**13a**). According to General procedure B, a mixture of **S11-2** (63.2 mg, 0.269 mmol), HBpin (78.1 mg, 0.610 mmol), and $IrCl(CO)(PPh_3)_2$ (10.6 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3·4H_2O$ (208 mg, 1.35 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **13a** and **13b** (39.9 mg, 49%, > 30:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3440, 2925, 2101, 1508, 1467, 1211, 1048, 828 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{16}FN_3NaO_2$ $(M+Na)^+$: 276.1119, Found: 276.1115. ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.91 (m, 2H), 6.85 – 6.77 (m, 2H), 3.94 (td, *J* = 6.1, 2.4 Hz, 2H), 3.83 – 3.74 (m, 2H), 3.60 (tt, *J* = 8.9, 4.7 Hz, 1H), 1.97 – 1.67 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.22 (d, *J* = 238.2 Hz), 154.93, 115.76 (d, *J* = 23.0 Hz), 115.38 (d, *J* = 7.7 Hz), 67.93, 59.77, 59.60, 36.86, 31.26, 25.89.

Scheme S12. Preparation of compound **14a**.



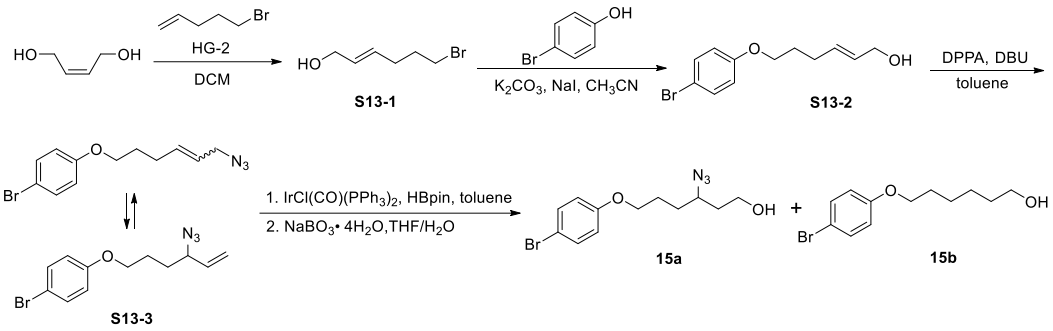
1-Chloro-4-(pent-4-en-1-yloxy)benzene (**S12-1**). According to the synthetic method of compound **S10-1**, a mixture of 4-chlorophenol (2.01 g, 15.7 mmol), K_2CO_3 (3.25 g, 23.5 mmol), NaI (468 mg, 3.12 mmol), 5-bromopent-1-ene (4.68 g, 31.4 mmol) in acetonitrile (30 mL) afforded **S12-1** (2.60 g, 84%) as a yellow oil after column chromatography (0~5% EtOAc/PE). R_f = 0.5 (5% EtOAc/PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.18 (m, 2H), 6.82 – 6.77 (m, 2H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.99 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 3.90 (t, *J* = 6.5 Hz, 2H), 2.24 – 2.18 (m, 2H), 189 – 1.81 (m, 2H).

(*E*)-1-((6-Azidohex-4-en-1-yl)oxy)-4-chlorobenzene (**S12-2a**), **(*Z*) -1-((6-azidohex-4-en-1-yl)oxy) -4-chlorobenzene** (**S12-2b**), and **1-((4-azidohex-5-en-1-yl)oxy)-4-chlorobenzene** (**S12-2c**). According to General procedure A, a mixture of HG-2 (212 mg, 2 mol%), **S12-1** (2.60 g, 13.2 mmol) and allyl bromide (4.91 g, 40.6 mmol) in dichloromethane (15 mL) afforded the corresponding allylic bromide (1.34 g, 35%). A mixture of the above bromide and sodium azide (452 mg, 6.96 mmol) in dry DMF (10 mL) afforded **S12-2** (990 mg, 85%, 68:7:25 ratio) as a yellow oil after column chromatography (100% PE). R_f = 0.3 (2% EtOAc/PE); IR (KBr): 3322, 2942, 2873, 2100, 1671, 1596, 1244, 824, 509 cm^{-1}; HRMS (ESI) m/z calculated for $C_{24}H_{28}Cl_2N_6NaO_2$ $(2M+Na)^+$: 525.1543, Found: 525.1534. Azide **S12-2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 2H), 6.73 – 6.67 (m, 2H), 5.73 – 5.61 (m, 1H), 5.52 – 5.40 (m, 1H), 3.80 (t, *J* = 6.3 Hz, 2H), 3.59 (d, *J* = 6.6 Hz, 2H), 2.20 – 2.12 (m, 2H), 1.80 – 1.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.60, 135.57, 129.25, 125.36, 123.82, 115.75, 67.22, 52.66, 28.62, 28.51. Azide **S12-2b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.66, 125.43, 123.23, 66.96, 47.01, 28.81, 23.81. Azide **S12-2c** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 – 5.16 (m, 2H), 1.63 – 1.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.51, 135.51, 129.27, 125.45, 118.40, 115.71, 67.55, 64.71, 30.90, 25.57.

3-Azido-6-(4-chlorophenoxy)hexan-1-ol (**14a**). According to General procedure B, a mixture of **S12-2** (69.3 mg, 0.275 mmol), HBpin (76.4 mg, 0.597 mmol), and $IrCl(CO)(PPh_3)_2$ (10.9 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (212 mg, 1.38 mmol) in THF (2 mL)

and H_2O (1 mL) afforded a mixture of **14a** and **14b** (43.0 mg, 58%, > 30:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3731, 2941, 2101, 1595, 1391, 1243, 1049, 824, 560 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{16}ClN_3NaO_2$ $(M+Na)^+$: 292.0823, Found: 292.0822. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 6.84 – 6.77 (m, 2H), 3.95 (td, *J* = 6.1, 2.2 Hz, 2H), 3.82 – 3.74 (m, 2H), 3.59 (tt, *J* = 9.0, 4.7 Hz, 1H), 2.00 – 1.65 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.42, 129.30, 125.56, 115.69, 67.61, 59.75, 59.59, 36.86, 31.24, 25.81.

Scheme S13. Preparation of compound **15a**.



(*E*)-6-Bromohex-2-en-1-ol (**S13-1**). According to General procedure A, a mixture of (*Z*)-but-2-ene-1,4-diol (682 mg, 7.74mmol), HG-2 (48.5 mg, 2mol%) and 5-bromopent-1-ene (577 mg, 3.87 mmol) in DCM (10 mL) afforded **S13-1** (222 mg, 32%) as a yellow oil after column chromatography (10~20% EtOAc/PE). R_f = 0.3 (16% EtOAc/PE). ^1H NMR (400 MHz, $CDCl_3$) δ 5.66 – 5.50 (m, 2H), 4.00 (d, *J* = 5.3 Hz, 2H), 3.34 (t, *J* = 6.7 Hz, 2H), 2.59 (br, 1H), 2.20 – 2. 09 (m, 2H), 1.93 – 1.81 (m, 2H).

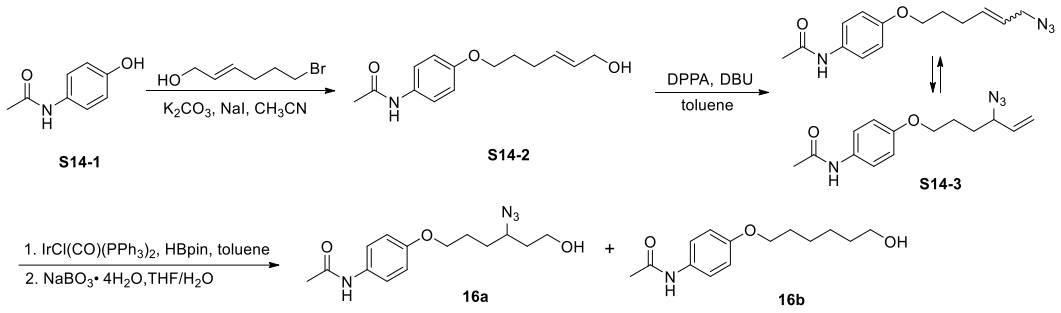
(*E*)-6-(4-Bromophenoxy)hex-2-en-1-ol (S13-2). According to the synthetic method of compound **S10-1**, a mixture of 4-bromophenol (216 mg, 1.25 mmol), K_2CO_3 (258 mg, 1.87 mmol), NaI (38.0 mg, 0.254 mmol), **S13-1** (222 mg, 1.24 mmol) in acetonitrile (5 mL) afforded **S13-2** (305 mg, 91%) as a yellow oil after column chromatography (20~40% EtOAc/PE). R_f = 0.3 (25% EtOAc/PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.71 – 5.56 (m, 2H), 4.02 (d, *J* = 4.8 Hz, 2H), 3.86 (t, *J* = 6.0 Hz, 2H), 2.18 (p, *J* = 7.4, 6.5 Hz, 2H), 1.81 (p, *J* = 6.9 Hz, 2H).

(*E*)-1-((6-Azidohex-4-en-1-yl)oxy)-4-bromobenzene (**S13-3a**), **(*Z*)-1-((6-azidohex-4-en-1-yl)oxy) -4-bromobenzene** (**S13-3b**), and **1-((4-azidohex-5-en-1-yl)oxy)-4-bromobenzene** (**S13-3c**). Under argon atmosphere, to an oven-dried flask was added **S13-2** (305 mg, 1.13 mmol), DPPA (622 mg, 2.26 mmol), DBU (421 mg, 2.76 mmol), and toluene (10 mL). The reaction mixture was heated to reflux for 12 h. The concentrated residue was purified by chromatography to afford **S13-3** (291 mg, 87%) as a yellow oil after column chromatography (2~10%

EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 3318, 2942, 2873, 2099, 1588, 1243, 1030, 822 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{14}BrN_3NaO$ $(M+Na)^+$: 318.0212, Found: 318.0218. Azide **S13-3a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 6.79 – 6.72 (m, 2H), 5.83 – 5.71 (m, 1H), 5.56 (dtt, *J* = 14.8, 6.6, 1.4 Hz, 1H), 3.97 – 3.87 (m, 2H), 3.70 (d, *J* = 6.7 Hz, 2H), 2.31 – 2.22 (m, 2H), 1.92 – 1.80 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.09, 135.55, 132.20, 123.84, 116.30, 116.26, 112.70, 67.17, 52.68, 28.63, 28.51. Azide **S13-3b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.79 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.01, 134.66, 123.25, 112.78, 66.92, 47.03, 28.80, 23.82. Azide **S13-3c** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.34 – 5.26 (m, 2H), 1.73 – 1.67 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 135.50, 132.22, 118.43, 116.26, 112.78, 67.51, 64.70, 30.90, 25.56.

3-Azido-6-(4-bromophenoxy)hexan-1-ol (**15a**). According to General procedure B, a mixture of **S13-3** (76.6 mg, 0.296 mmol), HBpin (157 mg, 1.22 mmol), and $IrCl(CO)(PPh_3)_2$ (11.5 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (228 mg, 1.48 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **15a** and **15b** (37.2 mg, 40%, > 30:1 ratio) as a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3688, 2970, 2100, 1482, 1241, 1050, 710 cm^{-1}; HRMS (ESI) m/z calculated for $C_{12}H_{16}BrN_3NaO_2$ $(M+Na)^+$: 336.0318, Found: 336.0323. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 6.79 – 6.73 (m, 2H), 3.95 (td, *J* = 6.1, 2.3 Hz, 2H), 3.83 – 3.75 (m, 2H), 3.59 (tt, *J* = 9.0, 4.7 Hz, 1H), 2.00 – 1.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.92, 132.23, 116.22, 112.86, 67.55, 59.74, 59.60, 36.86, 31.22, 25.79.

Scheme S14. Preparation of compound **16a**.



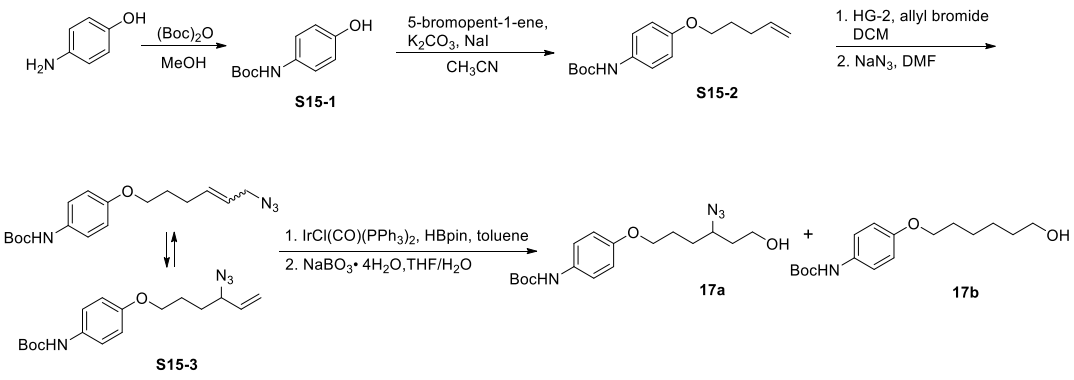
(*E*)-*N*-(4-((6-Hydroxyhex-4-en-1-yl)oxy)phenyl)acetamide (**S14-2**). According to the synthetic method of compound **S10-1**, a mixture of *N*-(4-hydroxyphenyl)acetamide (**S14-1**, 2.24 g, 14.8 mmol), K_2CO_3 (2.54 g, 18.4 mmol), NaI (457 mg, 3.05 mmol), (*E*)-6-bromohex-2-en-1-ol (**S13-1**, 1.32 g, 7.36 mmol) in acetonitrile (30 mL)

afforded **S14-2** (1.50 g, 84%) as a yellow oil after column chromatography (60~100% EtOAc/PE). R_f = 0.4 (100% EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 9.0 Hz, 2H), 7.07 (br, 1H), 6.83 (d, *J* = 9.1 Hz, 2H), 5.76 – 5.62 (m, 2H), 4.12 – 4.04 (m, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 2.22 (q, *J* = 6.8 Hz, 2H), 2.13 (s, 3H), 1.90 – 1.81 (m, 2H).

(*E*)-*N*-(4-((6-Azidohex-4-en-1-yl)oxy)phenyl)acetamide (**S14-3a**), **(*Z*)-*N*-(4-((6-azidohex-4-en-1-yl)oxy)phenyl)acetamide** (**S14-3b**), and ***N*-(4-((4-azidohex-5-en-1-yl)oxy)phenyl) acetamide** (**S14-3c**). Under argon atmosphere, to an oven-dried flask was added **S14-2** (1.50 g, 6.02 mmol), DPPA (3.31 g, 12.0 mmol), DBU (2.22 g, 14.6 mmol), and toluene (30 mL). The reaction mixture was heated to reflux for 12 h. The concentrated residue was purified by chromatography to afford **S14-3** (1.25 g, 76%, 85:4:11 ratio) as a yellow oil after column chromatography (25~60% EtOAc/PE). R_f = 0.5 (50% EtOAc/PE); IR (KBr): 3317, 2920, 2084, 1654, 1521, 1234, 964, 822, 708 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{18}N_4NaO_2$ $(M+Na)^+$: 297.1322, Found: 297.1324. Azide **S14-3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (bri, 1H), 7.35 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.82 – 5.68 (m, 1H), 5.60 – 5.50 (m, 1H), 3.91 (t, *J* = 6.3 Hz, 2H), 3.69 (d, *J* = 6.6 Hz, 2H), 2.29 – 2.21 (m, 2H), 2.10 (s, 3H), 1.96 – 1.78 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.67, 155.73, 135.73, 131.10, 123.67, 121.99, 114.67, 67.20, 52.69, 28.63, 28.58, 24.13. Azide **S14-3b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.62, 134.79, 123.08, 66.92, 47.04, 28.86, 23.83. Azide **S14-3c** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 – 5.24 (m, 2H), 1.73 – 1.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.62, 135.48, 131.18, 118.41, 114.63, 67.50, 64.73, 30.91, 25.61.

***N*-(4-((4-Azido-6-hydroxyhexyl)oxy)phenyl)acetamide** (**16a**). According to General procedure B, a mixture of **S14-2** (38.8 mg, 0.171 mmol), HBpin (45.2 mg, 0.353 mmol), and $IrCl(CO)(PPh_3)_2$ (6.8 mg, 5 mol%) in toluene (2 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (132 mg, 0.858 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **16a** and **16b** (20.7 mg, 48%, 5:1 ratio) as a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3735, 3284, 2931, 2099, 1663, 1472, 1240, 1030, 800, 539 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{21}N_4O_3$ $(M+H)^+$: 293.1608, Found: 293.1609. Azide **16a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (br, 1H), 7.34 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.97 – 3.85 (m, 2H), 3.77 – 3.71 (m, 2H), 3.56 (dt, *J* = 8.5, 4.1 Hz, 1H), 2.08 (s, 3H), 1.95 – 1.65 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.49, 155.65, 131.06, 121.98, 114.69, 67.56, 59.74, 59.47, 36.91, 31.23, 25.85, 24.24. Alcohol **16b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 121.95, 68.07, 62.80, 53.43, 32.63, 29.19, 25.51.

Scheme S15. Preparation of compound **17a**.



***tert*-Butyl (4-hydroxyphenyl)carbamate** (**S15-1**). Under argon atmosphere, a solution of 4-aminophenol (3.00 g, 27.5 mmol) and $(Boc)_2O$ (7.12 g, 32.6 mmol) in methanol (30 mL) was heated to reflux for 12 h. The concentrated residue was purified by chromatography to afford **S15-1** (5.30 g, 92%) as a white solid after column chromatography (10~25% EtOAc/PE). R_f = 0.5 (16% EtOAc/PE); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (br, 1H), 8.93 (br, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 1.42 (s, 9H).

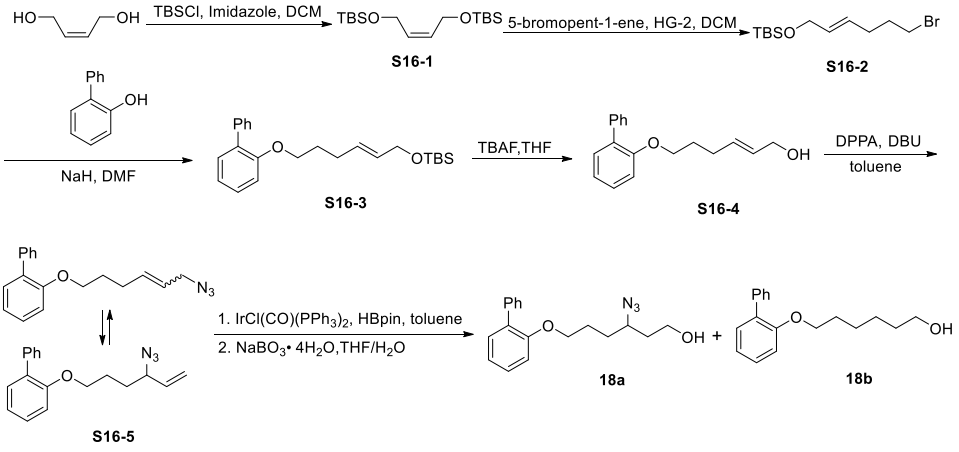
***tert*-Butyl (4-(pent-4-en-1-yloxy)phenyl)carbamate** (**S15-2**). According to the synthetic method of compound **S10-1**, a mixture of **S15-1** (2.00 g, 9.56 mmol), K_2CO_3 (1.98 g, 14.3 mmol), NaI (277 mg, 1.85 mmol), 5-bromopent-1-ene(2.89 g, 19.4 mmol) in acetonitrile (30 mL) afforded **S15-2** (2.10 g, 81%) as a yellow oil after column chromatography (5~10% EtOAc/PE). R_f = 0.4 (10% EtOAc/PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.86 – 6.82 (m, 2H), 6.32 (br, 1H), 5.84 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.02 – 4.96 (m, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 2.26 – 2.20 (m, 2H), 1.88 – 1.82 (m, 2H), 1.51 (s, 9H).

***tert*-Butyl (E)-(4-((6-azidohex-4-en-1-yl)oxy)phenyl)carbamate** (**S15-3a**), ***tert*-butyl (*Z*)-(4-((6- azidohex -4-en-1-yl)oxy)phenyl)carbamate** (**S15-3b**), and ***tert*-butyl (4-((4-azidohex-5-en-1-yl)oxy)phenyl)carbamate** (**S15-3c**). According to General procedure A, a mixture of HG-2 (119 mg, 2 mol%), S15-1 (2.10 g, 7.57 mmol) and allyl bromide (2.90 g, 23.9 mmol) in dichloromethane (15 mL) afforded the corresponding allylic bromide (1.90 g, 68%). A mixture of the above bromide and sodium azide (406 mg, 6.24 mmol) in dry DMF (10 mL) afforded S15-3 (1.35 g, 79%, 86:4:10 ratio) as a yellow oil after column chromatography (100% PE). Rf = 0.3 (2% EtOAc/PE); IR (KBr): 3366, 2940, 2872, 2090, 1696, 1517, 1240, 1161, 1048, 775, 459 cm-1; HRMS (ESI) m/z calculated for C17H24N4NaO3 (M+Na)+: 355.1441, Found: 355.1453. Azide S15-3a: 1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 2H), 6.79 (d, J = 9.0 Hz, 2H), 6.61 (br, 1H), 5.81 – 5.67 (m, 1H), 5.59 – 5.47 (m, 1H), 3.90 (t, J = 6.3 Hz, 2H), 3.67 (d, J = 6.6 Hz, 2H), 2.24 (q, J = 7.6 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.48 (s, 9H); 13C NMR (101 MHz, $CDCl_3$) δ 154.93, 153.24, 135.77, 131.53, 123.64, 120.51, 114.82, 80.07, 67.23, 52.67, 28.64, 28.60, 28.35. Azide S15-3b

(diagnostic peaks only): 1H NMR (400 MHz, $CDCl_3$) δ 3.77 (d, J = 7.3 Hz, 2H); 13C NMR (101 MHz, $CDCl_3$) δ 134.82, 123.06, 66.95, 47.01, 28.88, 23.83. Azide S15-3c (diagnostic peaks only): 1H NMR (400 MHz, $CDCl_3$) δ 5.31 – 5.23 (m, 2H), 1.72 – 1.62 (m, 2H); 13C NMR (101 MHz, $CDCl_3$) δ 154.83, 135.52, 131.60, 118.36, 114.77, 67.54, 64.73, 30.90, 28.88, 25.63.

***tert*-Butyl (4-((4-azido-6-hydroxyhexyl)oxy)phenyl)carbamate** (**17a**). According to General procedure B, a mixture of **S15-3** (80.0 mg, 0.241 mmol), HBpin (76.4 mg, 0.597 mmol), and $IrCl(CO)(PPh_3)_2$ (10.9 mg, 5 mol%), in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3 \cdot 4H_2O$ (187 mg, 1.21 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **17a** and **17b** (43.0 mg, 58%, 15:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3337, 2938, 2100, 1699, 1602, 1522, 1245, 1051, 831 cm^{-1}; HRMS (ESI) m/z calculated for $C_{17}H_{26}N_4NaO_4$ $(M+Na)^+$: 373.1846, Found: 373.1848. Azide **17a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.16 (m, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.48 (br, 1H), 3.93 (td, *J* = 6.1, 2.2 Hz, 2H), 3.77 – 3.71 (m, 2H), 3.61 – 3.52 (m, 1H), 2.07 (br, 1H), 1.97 – 1.63 (m, 6H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.89, 153.25, 131.48, 120.63, 114.82, 80.24, 67.64, 59.75, 59.44, 36.86, 31.21, 28.34, 25.86, 24.78. Alcohol **17b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.62 (t, *J* = 6.6 Hz, 2H), 2.18 (br, 1H), 1.57 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.15, 62.77, 32.59, 29.21, 25.82, 25.49.

Scheme S16. Preparation of compound **18a**.



(*Z*)-2,2,3,3,10,10,11,11-Octamethyl-4,9-dioxa-3,10-disiladodec-6-ene (**S16-1**). Under argon atmosphere, to a solution of (*Z*)-but-2-ene-1,4-diol (5.04 g, 57.3 mmol) and imidazole (11.7 g, 172 mmol) in DCM (20 mL) at 0 °C was added dropwise a solution of TBSCl (20.1 g, 133 mmol) in DCM (10 mL). The reaction mixture was warmed

and stirred for 10 h at room temperature. The solvent was removed under the reduced pressure and purified by silica gel column chromatography (100% PE) to afford **S16-1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 – 5.48 (m, 2H), 4.30 – 4.15 (m, 4H), 0.88 (s, 18H), 0.04 (s, 12H).

(*E*)-6-((*tert*-Butyldimethylsilyl)oxy)hex-2-en-1-ol (**S16-2**). To a stirred solution of the Hoveyda-Grubbs 2nd generation catalyst (HG-2) (89.0 mg, 2 mol%) in DCM (2 mL) under an argon atmosphere was added a pre-mixed solution of **S16-1** (4.51 g, 14.3 mmol) and 5-bromopent-1-ene (1.06 g, 7.12 mmol) in DCM (2 mL) at room temperature. The reaction mixture was stirred for 12 h. The concentrated residue was purified by silica gel column chromatography to afford **S16-2** (1.25 g, 60%) as a yellow oil after column chromatography (0~2% EtOAc/PE). R_f = 0.5 (2% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 – 5.65 (m, 2H), 4.13 – 4.07 (m, 2H), 3.42 – 3.34 (m, 2H), 2.17 (ddd, *J* = 5.3, 2.7, 1.3 Hz, 2H), 1.97 – 1.85 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

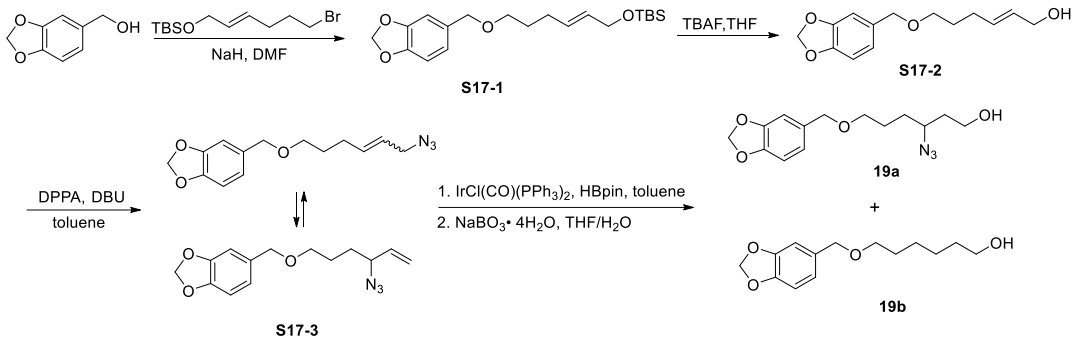
(*E*)-((6-([1,1'-Biphenyl]-2-yloxy)hex-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (**S16-3**). Under argon atmosphere, to a suspension of NaH (60% in mineral oil, 512 mg, 12.8 mmol) in DMF (20 mL) at 0 °C was added dropwise a solution of [1,1'-biphenyl]-2-ol (2.07 g, 12.2 mmol) in DMF (20 mL). The mixture was allowed of stir for 30 min and was added dropwise a solution of **S16-2** (8.94 g, 30.5 mmol) in DMF (10 mL). The reaction mixture was warmed and stirred for 10 h at room temperature. The reaction was quenched by saturated aq. NH_4Cl, and the mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography to afford **S16-2** (859 mg, 19%) as a yellow oil after column chromatography (0~2% EtOAc/PE). R_f = 0.5 (2% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.27 (m, 5H), 7.08 – 6.93 (m, 2H), 5.70 – 5.48 (m, 2H), 4.12 (q, *J* = 5.7, 4.8 Hz, 2H), 4.02 – 3.91 (m, 2H), 2.21 – 2.03 (m, 2H), 1.90 – 1.70 (m, 2H), 0.92 (s, 9H), 0.08 (s, 6H).

(*E*)-6-([1,1'-Biphenyl]-2-yloxy)hex-2-en-1-ol (**S16-4**). Under argon atmosphere, to a solution of **S16-3** (859 mg, 2.25 mmol) in tetrahydrofuran (30 mL) was added TBAF (608 mg, 2.33 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. The concentrated residue was purified by chromatography to afford **S16-4** (455 mg, 75%) as a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.03 – 6.96 (m, 1H), 6.92 (d, *J* = 9.4 Hz, 1H), 5.65 – 5.48 (m, 2H), 3.97 (d, *J* = 5.1 Hz, 2H), 3.90 (t, *J* = 6.3 Hz, 2H), 2.13 – 2.05 (m, 2H), 1.99 (br, 1H), 1.74 (p, *J* = 6.7 Hz, 2H).

(*E*)-2-((6-Azidohex-4-en-1-yl)oxy)-1,1'-biphenyl (**S16-5a**), **(*Z*)-2-((6-azidohex-4-en-1-yl)oxy) -1,1'-biphenyl** (**S16-5b**), and **2-((4-azidohex-5-en-1-yl)oxy)-1,1'-biphenyl** (**S16-5c**). Under argon atmosphere, to an oven-dried flask was added **S16-4** (455 mg, 1.69 mmol), DPPA (945 mg, 3.44 mmol), DBU (619 g, 4.07 mmol), and toluene (10 mL). The reaction mixture was heated to reflux for 12 h. The concentrated residue was purified by chromatography to afford **S16-5** (382 mg, 77%, 54:12:34 ratio) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 3321, 2934, 2750, 2099, 1595, 1479, 1389, 936, 610 cm^{-1}; HRMS (ESI) m/z calculated for $C_{18}H_{19}N_3NaO$ $(M+Na)^+$: 316.1420, Found: 316.1415. Azide **S16-5a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.5 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.37 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 5.85 – 5.73 (m, 1H), 5.63 – 5.52 (m, 1H), 4.06 (t, *J* = 6.3 Hz, 2H), 3.73 (d, *J* = 6.9 Hz, 2H), 2.28 (q, *J* = 7.1 Hz, 2H), 1.95 – 1.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.97, 138.77, 135.89, 130.99, 130.98, 129.74, 128.72, 127.96, 126.93, 123.74, 121.09, 112.77, 67.58, 52.77, 28.91, 28.74. Azide **S16-5b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.70 – 3.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.86, 134.73, 131.19, 123.27, 121.08, 112.51, 67.18, 47.05, 29.12, 24.07. Azide **S16-5c** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.38 – 5.27 (m, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 1.72 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.91, 138.69, 135.70,131.12, 130.95, 129.71, 128.00, 126.97, 121.18, 118.31, 112.74, 67.95, 64.60, 31.06, 25.61.

6-([1,1'-Biphenyl]-2-yloxy)-3-azidohexan-1-ol (**18a**). According to General procedure B, a mixture of **S16-4** (54.3 mg, 0.185 mmol), HBpin (98.1 mg, 0.766 mmol), and $IrCl(CO)(PPh_3)_2$ (7.4 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (142 mg, 0.923 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **18a** and **18b** (30.5 mg, 53%, 7:1 ratio) as a yellow oil after column chromatography (20~35% EtOAc/PE). R_f = 0.4 (25% EtOAc/PE); Azide **18a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.43 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 7.03 (td, *J* = 7.5, 1.1 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 4.06 – 3.92 (m, 2H), 3.75 – 3.63 (m, 2H), 3.46 (tt, *J* = 8.1, 5.2 Hz, 1H), 1.93 – 1.76 (m, 2H), 1.76 – 1.50 (m, 4H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.70, 138.56, 131.05, 130.88, 129.57, 128.60, 127.84, 126.80, 121.08, 112.62, 67.86, 59.57(2C), 36.65, 31.11, 25.72. Alcohol **18b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.59 (t, *J* = 6.6 Hz, 2H), 1.45 – 1.30 (m, 2H)i; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.95, 138.62, 130.83, 129.59, 129.54, 128.52, 127.76, 126.70, 120.78, 112.54, 68.30, 62.83, 32.61, 29.07, 25.90, 25.34.

Scheme S17. Preparation of compound **19a**.



(*E*)-((6-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)hex-2-en-1-yl)oxy)(*tert*-butyl)dimethyl -silane (**S17-1**). According to the synthetic method of compound **S16-3**, a mixture of NaH (60% in mineral oil, 585 mg, 14.6 mmol), benzo[d][1,3]dioxol-5-ylmethanol (2.00 g, 13.2 mmol), **S16-2** (11.5 g, 39.2 mmol) in DMF (40 mL) afforded **S17-1** (922 mg, 19%) as a yellow oil after column chromatography (0~2% EtOAc/PE). R_f = 0.5 (2% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H), 6.78 – 6.71 (m, 2H), 5.89 (s, 2H), 5.68 – 5.58 (m, 1H), 5.58 – 5.47 (m, 1H), 4.36 (s, 2H), 4.10 (d, *J* = 5.1 Hz, 2H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.11 (q, *J* = 6.5 Hz, 2H), 1.67 (dt, *J* = 13.4, 6.6 Hz, 2H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.71, 146.98, 132.48, 130.39, 129.69, 121.05, 108.32, 107.94, 100.86, 72.70, 69.43, 63.88, 29.24, 28.75, 25.97, 18.38, -5.12.

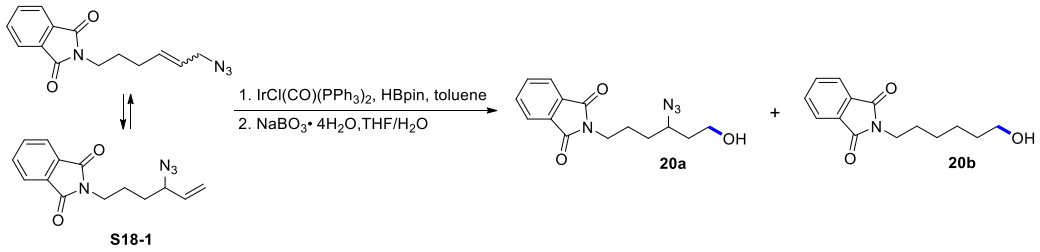
(*E*)-6-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)hex-2-en-1-ol (**S17-2**). According to the synthetic method of compound **S16-4**, a mixture of **S17-1** (922 mg, 2.53 mmol), TBAF (1.0 M in THF, 2.5 mL, 2.50 mmol) in tetrahydrofuran (30 mL) afford **S17-2** (601 mg, 95%) as a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.74 – 6.66 (m, 2H), 5.85 (s, 2H), 5.66 – 5.49 (m, 2H), 4.32 (s, 2H), 3.97 (d, *J* = 4.6 Hz, 2H), 3.38 (t, *J* = 6.5 Hz, 2H), 2.63 (br, 1H), 2.14 – 2.02 (m, 2H), 1.68 – 1.56 (m, 2H).

(*E*)-5-(((6-Azidohex-4-en-1-yl)oxy)methyl)benzo[d][1,3]dioxole (**S17-3a**), **(*Z*)-5-(((6-azidohex-4-en-1-yl)oxy) methyl)benzo[d][1,3]dioxole** (**S17-3b**), and **5-(((4-azidohex-5-en-1-yl)oxy)methyl)benzo[d][1,3]dioxole** (**S17-3c**). According to the synthetic method of compound **S16-4**, a mixture of **S17-2** (601 mg, 2.40 mmol), DPPA (1.32 g, 4.81 mmol), DBU (880 g, 5.78 mmol), in toluene (20 mL) afford **S17-3** (546 mg, 83%, 61:10:29 ratio) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 3318, 2936, 2862, 2100, 1494, 1443, 1247, 1100, 1040, 932, 809 cm^{-1}; HRMS (ESI) m/z calculated for $C_{28}H_5N_6O_6$ $(2M+H)^+$: 551.2613., Found: 551.2617. Azide **S17-3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 6.77 – 6.70 (m, 2H), 5.88 (s, 2H), 5.77 – 5.66 (m, 1H), 5.54 – 5.43 (m, 1H), 4.35 (s, 2H), 3.64 (d, *J* = 6.7 Hz, 2H), 3.41 (t, *J* = 6.4 Hz, 2H), 2.15 (q, *J* = 8.0 Hz, 2H), 1.72 – 1.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.72, 147.01, 136.16, 132.44, 123.34, 121.09, 108.32, 107.93, 100.93, 72.67, 69.04, 52.67, 29.04, 28.83. Azide **S17-3b** (diagnostic peaks only): ^{1}H NMR (400

MHz, $CDCl_3$) δ 3.76 (d, *J* = 7.4 Hz, 2H),; ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.24, 132.36, 122.69, 72.71, 68.92, 47.03, 29.42, 24.04. Azide **S17-3c** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 1H), 5.27 – 5.20 (m, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 1.63 – 1.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.74, 147.03, 135.72, 132.33, 121.07, 118.06, 108.28, 107.94, 72.65, 69.29, 64.79, 31.02, 26.01.

3-Azido-6-(benzo[*d*][1,3]dioxol-5-ylmethoxy)hexan-1-ol (**19a**). According to General procedure B, a mixture of $IrCl(CO)(PPh_3)_2$ (8.4 mg, 5 mol%), **S17-3** (57.6 mg, 0.209 mmol), and HBpin (106 mg, 0.825 mmol) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (162 mg, 1.05 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **19a** and **19b** (35.4 mg, 58%, 5:1 ratio) as a yellow oil after column chromatography (20~35% EtOAc/PE). R_f = 0.4 (25% EtOAc/PE); IR (KBr): 3424, 2936, 2866, 2101, 1495, 1444, 1248, 1096, 1040 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{19}N_3NaO_4$ $(M+Na)^+$: 316.1268, Found: 316.1278. Azide **19a**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H), 6.80 – 6.72 (m, 2H), 5.93 (s, 2H), 4.38 (s, 2H), 3.75 (t, *J* = 5.7 Hz, 2H), 3.52 (td, *J* = 8.3, 4.4 Hz, 1H), 3.48 – 3.38 (m, 2H), 1.85 – 1.52 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.72, 147.06, 132.20, 121.21, 108.37, 108.03, 100.94, 72.79, 69.40, 59.89, 59.67, 36.82, 31.33, 26.23. Alcohol **19b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 3.61 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 121.15, 108.19, 107.93, 100.90, 72.71, 70.05, 62.91, 32.66, 29.66, 25.97, 25.54.

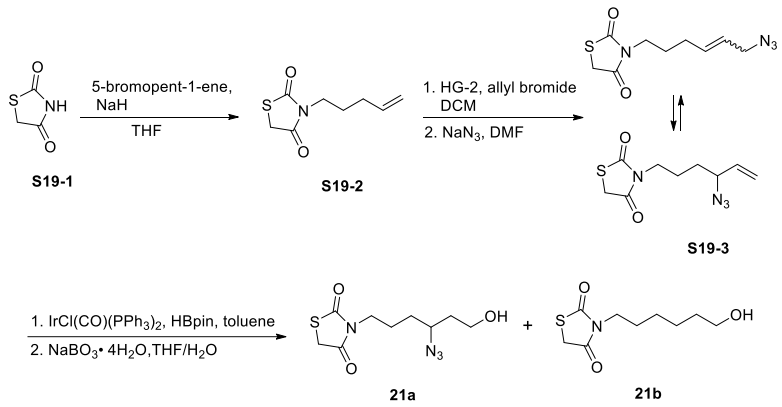
Scheme S18. Preparation of compound **20a**.



2-(4-Azido-6-hydroxyhexyl)isoindoline-1,3-dione (**20a**). According to General procedure B, a mixture of **S18-1** (72.0 mg, 0.267 mmol), HBpin (142 mg, 1.11 mmol), and $IrCl(CO)(PPh_3)_2$ (10.4 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (206 mg, 1.34 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **20a** and **20b** (63.4 mg, 82%, 6:1 ratio) as a yellow oil after column chromatography (20~40% EtOAc/PE). R_f = 0.3 (33% EtOAc/PE); IR (KBr): 2970, 2099, 1707, 1359, 1051, 718 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{23}N_3NaO_4$ $(M+Na)^+$: 311.1115, Found: 311.1122. Azide **20a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 3.80 – 3.66 (m, 4H), 3.64 – 3.54 (m, 1H), 1.93

– 1.65 (m, 4H), 1.65 – 1.53 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.41, 133.99, 132.00, 123.26, 59.50, 59.36, 37.36, 36.83, 31.63, 25.20. Alcohol **20b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 – 3.65 (m, 2H), 3.65 – 3.61 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.85, 123.15, 62.71, 37.82, 32.51, 28.50, 26.46, 25.14.

Scheme S19. Preparation of compound **21a**.



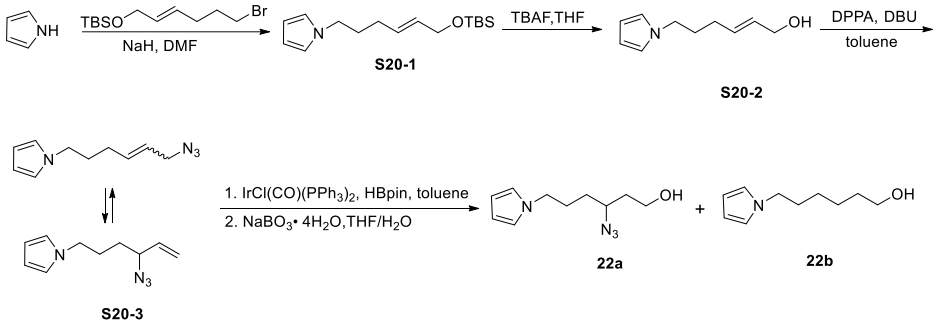
3-(Pent-4-en-1-yl)thiazolidine-2,4-dione (**S19-2**). According to the synthetic method of compound **S10-1**, a mixture of **S19-1** (2.00 g, 17.08 mmol), K_2CO_3 (3.54 g, 25.6 mmol), NaI (512 mg, 3.42 mmol), 5-bromopent-1-ene (5.09 g, 34.2 mmol) in acetonitrile (30 mL) afforded **S19-2** (2.57 g, 80%) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.4 (5% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 – 5.57 (m, 1H), 4.96 – 4.80 (m, 2H), 3.83 (s, 2H), 3.48 (dt, *J* = 7.8, 3.4 Hz, 2H), 2.00 – 1.87 (m, 2H), 1.62 – 1.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.66, 171.36, 136.96, 115.29, 41.43, 33.66, 30.65, 26.38.

(*E*)-3-(6-Azidohex-4-en-1-yl)thiazolidine-2,4-dione (**S19-3a**), **(*Z*)-3-(6-azidohex-4-en-1-yl)thiazolidine-2,4-dione** (**S19-3b**), and **3-(4-azidohex-5-en-1-yl)thiazolidine-2,4-dione** (**S19-3c**). According to General procedure A, a mixture of Hoveyda-Grubbs 2nd generation catalyst (HG-2) (150 mg, 2.5 mol%), **S19-2** (2.57 g, 13.9 mmol) and allyl bromide (5.03 g, 41.6 mmol) in dichloromethane (20 mL) afforded the allylic bromide (1.34 g, 35%). A mixture of the above bromide and sodium azide (351 mg, 5.40 mmol) in dry DMF (10 mL) afforded the title product (1.08 g, 40%, 68:7:25 ratio) as a yellow oil after column chromatography (5-15% EtOAc/PE). R_f = 0.3 (10% EtOAc/PE); IR (KBr): 3731, 3415, 2927, 2827, 2099, 1749, 1688, 1238, 896 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{12}N_4NaO_2S$ $(M+Na)^+$: 263.0573, Found: 263.0570. Azide **S19-3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 – 5.48 (m, 1H), 5.45 – 5.33 (m, 1H), 3.79 (s, 2H), 3.54 (d, *J* = 5.5 Hz, 2H), 3.47 – 3.39 (m, 2H), 1.93 (q, *J* = 6.9, 6.4 Hz, 2H), 1.52 (p, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.73, 171.39, 134.66, 123.99, 52.49, 41.28, 33.69 (2C), 29.18, 26.61. Azide **S19-3b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (q, *J* = 6.0 Hz, 2H),; ^{13}C

NMR (101 MHz, $CDCl_3$) δ 170.89, 134.06, 123.28, 46.97, 27.13, 24.59. Azide **S19-3c** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (q, *J* = 7.1 Hz, 2H), 1.38 – 1.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.37, 170.89, 135.12, 118.58, 64.27, 41.23, 31.14, 23.84.

3-(4-Azido-6-hydroxyhexyl)thiazolidine-2,4-dione (**21a**). According to General procedure B, a mixture of **S19-3** (52.4 mg, 0.218 mmol), HBpin (111 mg, 0.867 mmol), and $IrCl(CO)(PPh_3)_2$ (8.6 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (167 mg, 1.08 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **21a** and **21b** (25.0 mg, 44%, >30:1 ratio) as a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3731, 2938, 2101, 1677, 1349, 1051, 665 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{14}N_4NaO_3S$ $(M+Na)^+$: 281.0679, Found: 281.0672. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 2H), 3.80 – 3.72 (m, 2H), 3.65 (t, *J* = 7.3 Hz, 2H), 3.60 – 3.51 (m, 1H), 1.83 – 1.66 (m, 4H), 1.62 – 1.50 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.81, 171.43, 59.45, 59.29, 41.42, 36.78, 33.76, 31.48, 24.23.

Scheme S20. Preparation of compound **22a**.



(*E*)-1-(6-((*tert*-Butyldimethylsilyl)oxy)hex-4-en-1-yl)-1*H*-pyrrole (**S20-1**). According to the synthetic method of compound **S16-3**, a mixture of NaH (60% in mineral oil, 206 mg, 5.15 mmol), 1*H*-pyrrole (580 mg, 8.65 mmol), **S16-2** (1.25 g, 4.25 mmol) in DMF (30 mL) afforded **S20-1**(321 mg, 27%) as a yellow oil after column chromatography (0~2% EtOAc/PE). R_f = 0.5 (2% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (t, *J* = 2.1 Hz, 2H), 6.21 (t, *J* = 2.2 Hz, 2H), 5.75 – 5.60 (m, 2H), 4.21 (dd, *J* = 4.7, 1.1 Hz, 2H), 3.93 (t, *J* = 7.1 Hz, 2H), 2.10 (q, *J* = 6.5, 6.0 Hz, 2H), 1.97 – 1.86 (m, 1H), 1.01 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.55, 129.43, 120.46, 107.98, 63.81, 48.84, 30.98, 29.19, 26.07, 18.49, -5.03.

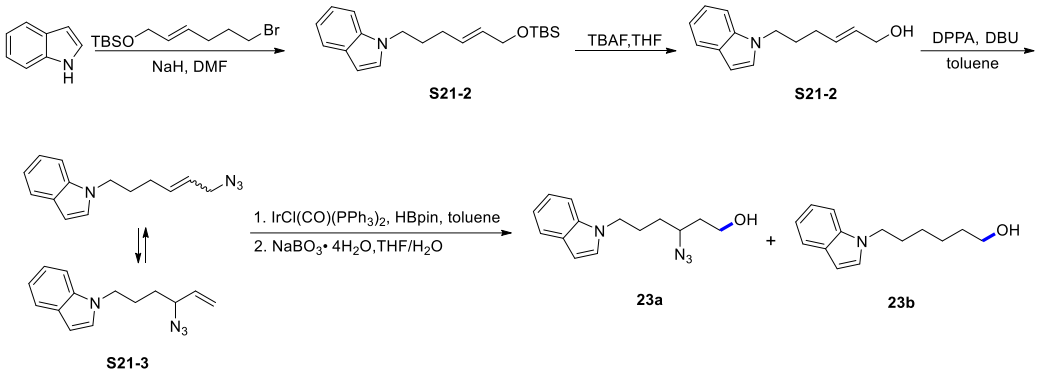
(*E*)-6-(1*H*-Pyrrol-1-yl)hex-2-en-1-ol (**S20-2**). According to the synthetic method of compound **S16-4**, a mixture of **S20-1** (321 mg, 1.15 mmol), TBAF (335 mg, 1.28 mmol) in tetrahydrofuran (10 mL) afford **S20-2** (184 mg, 97%) as

a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (t, *J* = 2.1 Hz, 2H), 6.16 (t, *J* = 2.1 Hz, 2H), 5.70 – 5.59 (m, 2H), 4.05 (dd, *J* = 3.2, 1.4 Hz, 2H), 3.89 (t, *J* = 7.0 Hz, 2H), 2.24 (br, 1H), 2.12 – 2.03 (m, 2H), 1.87 (p, *J* = 7.1 Hz, 2H).

(*E*)-1-(6-Azidohex-4-en-1-yl)-1*H*-pyrrole (**S20-3a**), **(*Z*)-1-(6-azidohex-4-en-1-yl)-1*H*-pyrrole** (**S20-3b**), and **1-(4-azidohex-5-en-1-yl)-1*H*-pyrrole** (**S20-3c**). According to the synthetic method of compound **S16-5**, a mixture of **S20-2** (512 mg, 3.11 mmol), DPPA (1.72 g, 6.31 mmol), DBU (1.37 g, 7.47 mmol) in toluene (10 mL) afford **S20-3** (470 mg, 80%, 69:6:25 ratio) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 3729, 2931, 2871, 2098, 1673, 1278, 930, 724 cm^{-1}; HRMS (ESI) m/z calculated for $C_{10}H_{14}N_4Na$ $(M+Na)^+$: 213.1103, Found: 213.1111. Azide **S20-3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (t, *J* = 2.1 Hz, 2H), 6.23 (t, *J* = 2.2 Hz, 2H), 5.84 – 5.73 (m, 1H), 5.67 – 5.57 (m, 1H), 3.97 – 3.92 (m, 2H), 3.77 (d, *J* = 6.6 Hz, 2H), 2.18 – 2.11 (m, 2H), 1.95 (p, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.37, 124.14, 120.50, 108.09, 52.72, 48.69, 30.79, 29.27. Azide **S20-3b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.50, 123.42, 120.48, 108.20, 47.12, 31.22, 24.45. Azide **S20-3c** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.30 (m, 2H), 3.84 (q, *J* = 7.4 Hz, 1H), 1.92 – 1.81 (m, 2H), 1.62 – 1.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.48, 120.45, 118.55, 108.22, 64.68, 49.15, 31.52, 27.86.

3-Azido-6-(1*H*-pyrrol-1-yl)hexan-1-ol (**22a**). According to General procedure B, a mixture of **S20-3** (543.4 mg, 0.228 mmol), HBpin (120 mg, 0.935 mmol), and $IrCl(CO)(PPh_3)_2$ (9.0 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (176 mg, 1.14 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **22a** and **22b** (24.8 mg, 52%, 3:1 ratio) as a yellow oil after column chromatography (20~35% EtOAc/PE). R_f = 0.4 (25% EtOAc/PE); IR (KBr): 3729, 2933, 2100, 1277, 1055, 725 cm^{-1}; HRMS (ESI) m/z calculated for $C_{10}H_{16}N_4NaO$ $(M+Na)^+$: 231.1216, Found: 231.1209. Azide **22a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (t, *J* = 2.2 Hz, 2H), 6.13 (t, *J* = 2.1 Hz, 2H), 3.95 – 3.85 (m, 2H), 3.78 – 3.67 (m, 2H), 3.50 – 3.42 (m, 1H), 2.00 – 1.82 (m, 2H), 1.80 – 1.64 (m, 2H), 1.63 – 1.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 120.41, 108.17, 59.54, 59.46, 49.14, 36.83, 31.68, 27.99. Alcohol **22b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (t, *J* = 2.1 Hz, 2H), 3.86 (t, *J* = 7.1 Hz, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 1.42 – 1.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 120.44, 107.79, 62.78, 49.50, 32.53, 31.48, 26.52, 25.33.

Scheme S21. Preparation of compound **23a**.



(*E*)-1-(6-((*tert*-Butyldimethylsilyl)oxy)hex-5-en-1-yl)-1*H*-indole (**S21-1**). According to the synthetic method of compound **S16-3**, a mixture of NaH (60 % in mineral oil, 795 mg, 19.0 mmol), 1*H*-indole (1.98 g, 16.9 mmol), **S16-2** (14.7 g, 50.2 mmol) in DMF (60 mL) afforded **S21-1**(2.89 g, 52%) as a yellow oil after column chromatography (0~2% EtOAc/PE). R_f = 0.5 (2% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 5.73 – 5.56 (m, 2H), 4.31 – 4.10 (m, 4H), 2.12 – 2.05 (m, 2H), 2.02 – 1.90 (m, 2H), 0.97 (s, 9H), 0.13 (s, 6H).

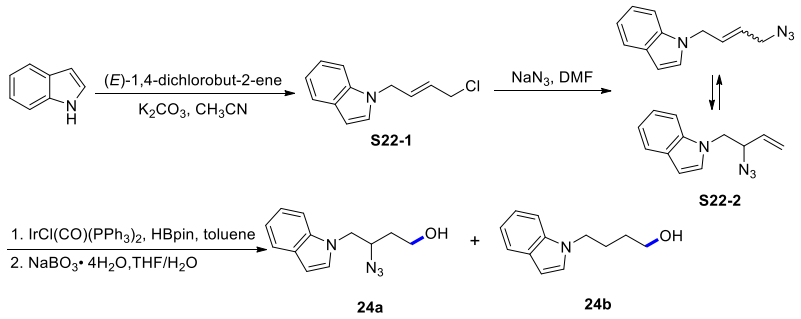
(*E*)-6-(1*H*-Indol-1-yl)hex-1-en-1-ol (**S21-2**). According to the synthetic method of compound **S16-4**, a mixture of **S21-1** (2.89 g, 8.78 mmol), TBAF (1.0 M in THF, 9 mL, 9.00 mmol) in tetrahydrofuran (20 mL) afford **S21-2** (888 mg, 47%) as a yellow oil after column chromatography (15~30% EtOAc/PE). R_f = 0.3 (20% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 1.1 Hz, 1H), 7.36 – 7.27 (m, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 3.2 Hz, 1H), 6.60 (d, *J* = 3.1 Hz, 1H), 5.65 (td, *J* = 3.3, 2.9, 1.4 Hz, 2H), 4.17 – 4.05 (m, 4H), 2.64 (br, 1H), 2.13 – 2.05 (m, 2H), 2.00 – 1.89 (m, 2H).

(*E*)-1-(6-Azidohex-4-en-1-yl)-1*H*-indole (**S21-3a**), **(*Z*)-1-(6-azidohex-4-en-1-yl)-1*H*-indole** (**S21-3b**), **and 1-(4-azidohex-5-en-1-yl)-1*H*-indole** (**S21-3c**). According to the synthetic method of compound **S16-5**, a mixture of **S21-2** (888 mg, 4.13 mmol), DPPA (2.27 g, 8.25 mmol), DBU (1.52 g, 9.98 mmol) in toluene (20 mL) afford **S21-3** (875 mg, 88%, 70:6:24 ratio) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 3318, 3051, 2934, 2872, 2098, 1576, 1313, 1240, 972, 741 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{16}N_4Na$ $(M+Na)^+$: 263.1267, Found: 263.1262. Azide **S21-3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.1 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 6.1 Hz, 1H), 7.22 (dd, *J* = 11.2, 3.1 Hz, 1H), 6.74 (d, *J* = 2.9 Hz, 1H), 5.87 – 5.74 (m, 1H), 5.69 – 5.60 (m, 1H), 4.19 (t, *J* = 6.9 Hz, 2H), 3.80 (d, *J* = 6.7 Hz, 2H), 2.19 (q, *J* = 7.1 Hz, 2H), 2.04 (p, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.22, 135.38, 128.93, 128.02, 124.22, 121.67, 121.24, 119.56, 109.68, 101.35, 52.80, 45.60, 29.56 (2C). Azide **S21-3b** (diagnostic peaks only): ^{13}C

NMR (101 MHz, $CDCl_3$) δ 134.60, 123.54, 121.71, 109.62, 47.23, 30.00, 24.73. Azide **S21-3c** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (d, *J* = 10.1 Hz, 1H), 5.37 (d, *J* = 17.1 Hz, 1H), 4.16 (t, *J* = 7.1 Hz, 2H), 3.88 – 3.80 (m, 1H), 2.00 – 1.88 (m, 2H), 1.71 – 1.56 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.17, 135.53, 127.90, 121.74, 121.28, 119.60, 118.68, 109.60, 101.46, 64.81, 45.95, 31.76, 26.69.

3-Azido-6-(1*H*-indol-1-yl)hexan-1-ol (**23a**). According to General procedure B, a mixture of **S21-3** (58.5 mg, 0.243 mmol), HBpin (124 mg, 0.967 mmol), and $IrCl(CO)(PPh_3)_2$ (9.7 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (189 mg, 1.23 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **23a** and **23b** (36.4 mg, 58%, 4:1 ratio) as a yellow oil after column chromatography (20~35% EtOAc/PE). R_f = 0.4 (25% EtOAc/PE); IR (KBr): 3326, 2934, 2106, 1708, 1462, 1264, 743 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{18}N_4NaO$ $(M+Na)^+$: 281.1373, Found: 281.1371. Azide **23a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.14 – 7.05 (m, 2H), 6.50 (d, *J* = 7.2 Hz, 1H), 4.15 (td, *J* = 7.0, 2.0 Hz, 2H), 3.73 – 3.63 (m, 2H), 3.51 – 3.40 (m, 1H), 2.10 – 1.84 (m, 2H), 1.71 – 1.62 (m, 2H), 1.59 – 1.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.87, 128.59, 127.61, 121.52, 121.04, 119.34, 109.24, 101.30, 59.56, 59.33, 45.91, 36.81, 31.89, 26.77, 24.81. Alcohol **23b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (d, *J* = 7.2 Hz, 1H), 4.11 (t, *J* = 7.1 Hz, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 1.87 – 1.80 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.89, 128.53, 127.78, 121.30, 120.93, 119.16, 109.35, 100.86, 75.08, 62.71, 46.28, 32.50, 30.19, 25.38.

Scheme S22. Preparation of compound **24a**.



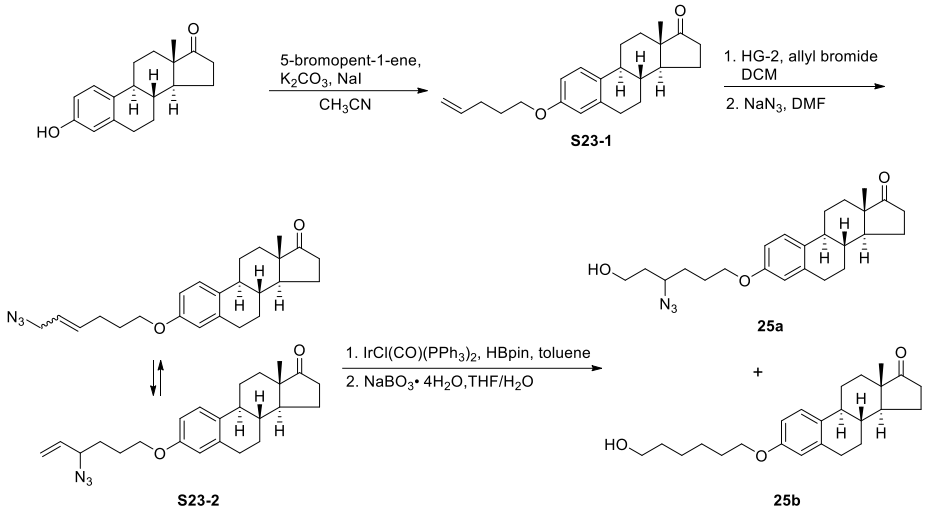
(*E*)-1-(4-Chlorobut-2-en-1-yl)-1*H*-indole (**S22-1**). According to the synthetic method of compound **S10-1**, a mixture of 1*H*-indole (2.01 g, 17.2 mmol), K_2CO_3 (2.87 g, 20.9 mmol), (*E*)-1,4-dichlorobut-2-ene (3.23 g, 25.8 mmol) in acetonitrile (30 mL) afforded **S22-1** (1.37 g, 40%) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.4 (5% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.2 Hz,

1H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 2.2 Hz, 1H), 6.54 (s, 1H), 6.01 – 5.69 (m, 2H), 4.82 (d, *J* = 6.5 Hz, 2H), 4.19 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.92, 130.02, 128.78, 128.11, 127.35, 121.73, 121.09, 119.65, 109.30, 101.82, 42.90, 38.43.

(*E*)-1-(4-Azidobut-2-en-1-yl)-1*H*-indole (**S22-2a**), **(*Z*)-1-(4-azidobut-2-en-1-yl)-1*H*-indole** (**S22-2b**), and **1-(2-azidobut-3-en-1-yl)-1*H*-indole** (**S22-2c**). According to General procedure A, a mixture of **S22-1** (793 mg, 3.86 mmol) and NaN_3 (251 mg, 3.86 mmol) in DMF (10 mL) afforded **S22-2** (508 mg, 62%, 52:16:32 ratio) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 3407, 3052, 2927, 2866, 2101, 2020, 1673, 1460, 1259, 745 cm^{-1}. Azide **S22-2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.19 – 7.04 (m, 2H), 6.54 (d, *J* = 3.7 Hz, 1H), 6.00 – 5.85 (m, 1H), 5.82 – 5.68 (m, 1H), 4.80 (d, *J* = 6.4 Hz, 2H), 3.94 (d, *J* = 7.1 Hz, 2H),. Azide **S22-2b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 – 5.47 (m, 1H), 4.76 (d, *J* = 5.2 Hz, 2H), 3.74 (d, *J* = 6.2 Hz, 2H). Azide **S22-2c** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.32 (m, 2H), 4.35 – 4.27 (m, 1H), 4.24 – 4.07 (m, 2H).

3-Azido-4-(1*H*-indol-1-yl)butan-1-ol (**24a**). According to General procedure B, a mixture of **S22-2** (102 mg, 0.480 mmol), HBpin (247 mg, 1.93 mmol), and $IrCl(CO)(PPh_3)_2$ (18.7 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (369 mg, 2.40 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **24a** and **24b** (64.1 mg, 58%, 5:1 ratio) as a yellow oil after column chromatography (20~35% EtOAc/PE). R_f = 0.4 (25% EtOAc/PE); IR (KBr): 3720, 2936, 2102, 1462, 1313, 1045, 741 cm^{-1}; HRMS (ESI) m/z calculated for $C_9H_{15}N_3NaO$ $(M+Na)^+$: 253.1060, Found: 253.1055. Azide **24a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.24 – 7.12 (m, 1H), 7.14 – 7.04 (m, 2H), 6.52 (d, *J* = 3.2 Hz, 1H), 4.26 (dd, *J* = 14.4, 4.3 Hz, 1H), 4.16 – 4.03 (m, 2H), 4.00 (dq, *J* = 10.2, 6.1, 5.1 Hz, 1H), 3.78 – 3.69 (m, 1H), 1.94 – 1.72 (m, 1H), 1.70 – 1.45 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.07, 128.75, 128.05, 121.88, 121.20, 119.72, 109.04, 102.26, 59.90, 59.17, 50.34, 34.57. Alcohol **24b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, *J* = 3.2 Hz, 1H), 3.56 (t, *J* = 6.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.90, 128.56, 127.70, 121.37, 120.95, 119.21, 109.31, 101.03, 62.37, 46.12, 30.00, 26.67.

Scheme S23. Preparation of compound **25a**.



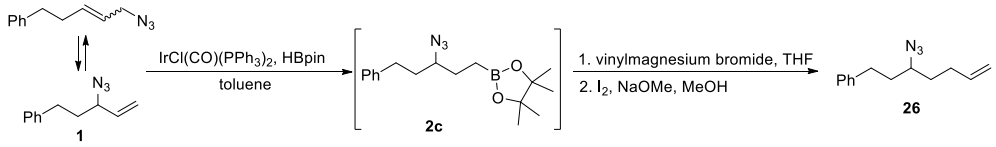
(*8R,9S,13S,14S*)-13-Methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**S23-1**). According to the synthetic method of compound **S10-1**, a mixture of estrone (2.00 g, 7.41 mmol), K_2CO_3 (1.54 g, 11.1 mmol), NaI (229 mg, 1.53 mmol), 5-bromopent-1-ene (2.21 g, 14.8 mmol) in acetonitrile (30 mL) afforded **S23-1** (2.10 g, 84%) as a white solid after column chromatography (10~20% EtOAc/PE). R_f = 0.4 (16% EtOAc/PE). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 5.85 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.06 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.99 (dd, *J* = 10.2, 1.7 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.93 – 2.86 (m, 2H), 2.50 (ddd, *J* = 19.1, 8.9, 1.0 Hz, 1H), 2.42 – 2.36 (m, 1H), 2.28 – 2.20 (m, 3H), 2.14 (dt, *J* = 19.0, 9.0 Hz, 1H), 2.07 – 2.03 (m, 1H), 2.03 – 1.98 (m, 1H), 1.97 – 1.93 (m, 1H), 1.87 – 1.83 (m, 2H), 1.66 – 1.55 (m, 2H), 1.55 – 1.46 (m, 3H), 1.48 – 1.40 (m, 1H), 0.91 (s, 3H).

(*8R,9S,13S,14S*)-3-(((*E*)-5-Azidopent-4-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12, 13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**S23-2a**), **(*8R,9S, 13S,14S*)-3-(((*Z*)-6-azidohex-4-en-1-yl)oxy) -13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one** (**S23-2b**), and **(*8R,9S,13S,14S*)-3-((4-azidohex-5-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta [*a*]phenanthren-17-one** (**S23-2c**). According to General procedure A, a mixture of HG-2 (98.1 mg, 2 mol%), **S23-1** (2.10 g, 6.20 mmol) and allyl bromide (2.27 g, 18.8 mmol) in dichloromethane (15 mL) afforded the corresponding allylic bromide (1.28 g, 40%). A mixture of the above bromide and sodium azide (232 mg, 3.71 mmol) in dry DMF (20 mL) afforded **S23-2** (559 mg, 48%, 65:1:34 ratio) as a white solid after column chromatography (5% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE); IR (KBr): 3729, 2932, 2319, 2096, 1738, 1247, 934, 754 cm^{-1}; HRMS (ESI) m/z calculated for $C_{24}H_{31}N_3NaO_2$ $(M+Na)^+$: 416.2308, Found: 416.2313. Azide **S23-2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.69 (dt, *J* = 8.6, 3.0 Hz, 1H), 6.63 (d, *J* = 2.9 Hz, 1H), 5.85 – 5.70 (m, 1H), 5.61 – 5.52

(m, 1H), 3.94 (t, *J* = 6.3 Hz, 2H), 3.70 (d, *J* = 6.6 Hz, 2H), 2.92 – 2.83 (m, 2H), 2.49 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.41 – 2.35 (m, 1H), 2.30 – 2.20 (m, 2H), 2.19 – 2.10 (m, 1H), 2.10 – 1.90 (m, 3H), 1.90 – 1.80 (m, 2H), 1.76 – 1.39 (m, 7H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.94, 156.94, 137.71, 135.84, 131.99, 126.29, 123.64, 114.52, 112.10, 66.82, 52.74, 50.39, 48.00, 43.96, 38.35, 35.86, 31.56, 29.63, 28.68, 28.67, 26.54, 25.90, 21.57, 13.84. Azide **S23-2b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (d, *J* = 7.3 Hz, 2H). Azide **S23-2c** (diagnostic peaks only)**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 – 5.25 (m, 2H), 3.89 (q, *J* = 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.87, 137.74, 135.56, 132.08, 126.31, 118.36, 114.49, 112.04, 67.15, 64.75, 30.96, 25.68.

(*8R,9S,13S,14S*)-3-((4-Azido-6-hydroxyhexyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**25a**). According to General procedure B, a mixture of **S23-2** (79.5 mg, 0.202 mmol), HBpin (103 mg, 0.807 mmol), and $IrCl(CO)(PPh_3)_2$ (8.0 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3{\cdot}4H_2O$ (187 mg, 1.21 mmol) in THF (2 mL) and H_2O (1 mL) afforded a mixture of **25a** and **25b** (54.5 mg, 67%, >30:1 ratio) as a yellow oil after column chromatography (10~25% EtOAc/PE). R_f = 0.4 (20% EtOAc/PE); IR (KBr): 3731, 2928, 2098, 1734, 1249, 1053, 573 cm^{-1}; HRMS (ESI) m/z calculated for $C_{24}H_{33}N_3NaO_3$ $(M+Na)^+$: 434.2414, Found: 434.2413. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.63 (d, *J* = 2.7 Hz, 1H), 3.97 (t, *J* = 8.4, 3.5 Hz, 2H), 3.79 (t, *J* = 2.4 Hz, 2H), 3.59 (tt, *J* = 8.98, 4.76 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.49 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.31 – 2.20 (m, 1H), 2.12 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.07 – 1.66 (m, 7H), 1.65 – 1.40 (m, 8H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.93, 156.84, 137.76, 132.13, 126.33, 114.51, 112.06, 67.23, 59.82, 59.67, 50.39, 48.00, 43.96, 38.35, 36.88, 35.86, 31.56, 31.31, 29.63, 26.53, 25.92 (2C), 21.57, 13.84.

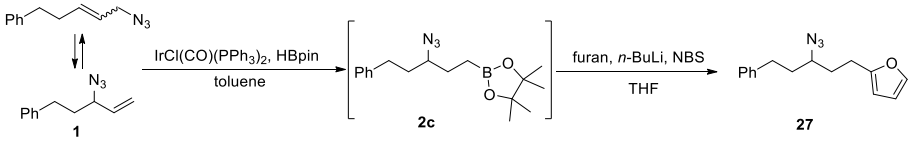
Scheme S24. Preparation of compound **26**.



(3-Azidohept-6-en-1-yl) benzene (**26**). According to the reported procedure,[S3] under argon atmosphere, to an oven-dried flask was added $IrCl(CO)(PPh_3)_2$ (17.7 mg, 5 mol%), **1** (85.0 mg, 0.454 mmol) and toluene (2 mL) successively. The reaction mixture was stirred for 30 min at room temperature, and then HBpin (232 mg, 1.82 mmol) and toluene (1 mL) were added. The reaction mixture was heated at 90 °C for 20 h. The solvent was removed under the reduced pressure to afford the crude product. To a 50-mL oven-dried flask charged with the above crude product (**2c**, 0.454 mmol), THF (2 mL), vinylmagnesium bromide (1.0 M in THF, 1.8 mL) was added dropwise. The resulted

mixture was allowed to stir as room temperature for 1 h. To the above solution at -78 ºC, a solution of iodine (466 mg, 1.82 mmol) in methanol (5 mL) was added dropwise. The reaction mixture was allowed to stir 1 h at the same temperature followed by dropwise addition of a solution of NaOMe (196 mg, 3.62 mmol) in methanol (5 mL). After warming to room temperature, the resultant mixture was allowed to stir for 10 h. The reaction was quenched by saturated aq. $Na_2S_2O_3$ (5 mL), and the mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography to afford **26** (50.8 mg, 52% yield for two steps) as a yellow oil after column chromatography (0~5% EtOAc/PE). R_f = 0.4 (2% EtOAc/PE); IR (KBr): 3731, 2928, 2318, 2100, 1339, 745, 444 cm^{-1}; HRMS (ESI) m/z calculated for $C_{24}H_{36}N_6Na$ $(2M+Na)^+$: 453.2737, Found: 453.2751. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 5.77 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 4.95 (m, 2H), 3.28 (p, *J* = 6.6 Hz, 1H), 2.i79 (dt, *J* = 14.6, 7.6 Hz, 1H), 2.66 (dt, *J* = 13.8, 8.1 Hz, 1H), 2.27 – 2.08 (m, 1H), 1.82 (td, *J* = 8.1, 6.3 Hz, 2H), 1.70 – 1.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.16, 137.32, 128.48, 128.37, 126.04, 115.48, 61.61, 36.18, 33.72, 32.35, 30.24.

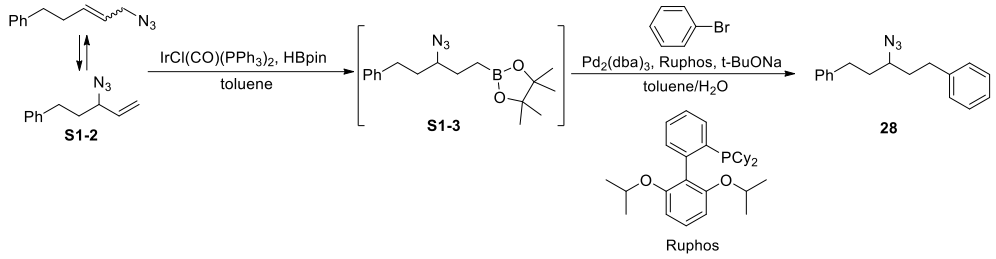
Scheme S25. Preparation of compound **27**.



2-(3-Azido-5-phenylpentyl) furan (**27**). According to the reported procedure,[S3] under argon atmosphere, to an oven-dried flask was added $IrCl(CO)(PPh_3)_2$ (11.3 mg, 5 mol%), **1** (54.3 mg, 0.290 mmol) and toluene (2 mL) successively. The reaction mixture was stirred for 30 min at room temperature, and then HBpin (148 mg, 1.16 mmol) and toluene (1 mL) were added. The reaction mixture was heated at 90 °C for 20 h. The solvent was removed under the reduced pressure to afford the crude product. To a 50-mL oven-dried flask charged with furan (194mg, 2.90 mmol) and THF (4 mL) was added *n*-BuLi (2.5 M in hexanes, 1.2 mL, 2.90 mmol) at -78 °C. The reaction was then allowed to warm to room temperature and stir at this temperature for additional 2 h. The mixture was then cooled to -78 °C again and a solution of the above crude product (**2c**, 0.290 mmol) in THF (3 mL) was added dropwise. The mixture was allowed to stir at -78 °C for 2 h. A solution of an NBS (103 mg, 0.580 mmol) in THF (2 mL) was added dropwise. After 2 h at -78 °C, the reaction was quenched by saturated aq. $Na_2S_2O_3$ (5 mL), and the mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine,

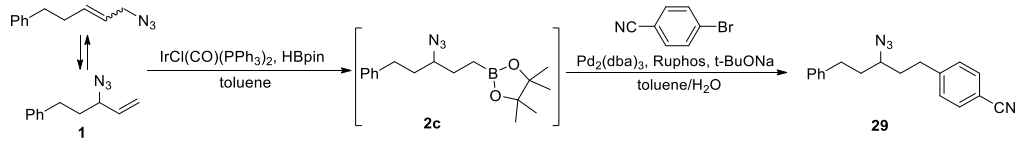
dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography to afford **27** (48.2 mg, 65% yield for two steps) as a yellow oil after column chromatography (0~5% EtOAc/PE). R_f = 0.4 (2% EtOAc/PE); IR (KBr): 3954, 3453, 2929, 2853, 2097, 1504, 1339, 1266, 921, 797, 733 cm^{-1}; HRMS (ESI) m/z calculated for $C_{30}H_{34}N_6NaO_2$ $(2M+Na)^+$: 533.2635 Found: 533.2618. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 3H), 7.23 – 7.13 (m, 3H), 6.29 – 6.24 (m, 1H), 6.01 – 5.97 (m, 1H), 3.28 (dt, *J* = 13.1, 6.8 Hz, 1H), 2.85 – 2.61 (m, 4H), 1.96 – 1.80 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.62, 141.13, 141.04, 128.49, 128.36, 126.06, 110.14, 105.38, 61.42, 36.15, 32.89, 32.29, 24.63.

Scheme S26. Preparation of compound **28**.



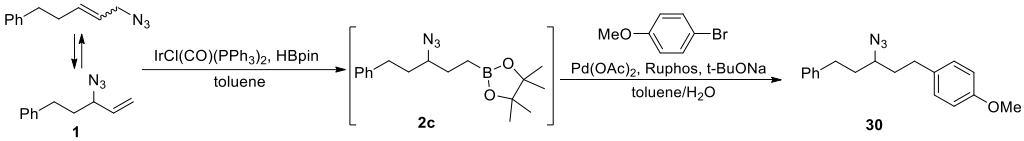
(3-Azidopentane-1,5-diyl)dibenzene (**28**). According to the reported procedure,[S4] under argon atmosphere, to an oven-dried flask was added $IrCl(CO)(PPh_3)_2$ (11.3 mg, 5 mol%), **1** (52.1 mg, 0.278 mmol) and toluene (2 mL) successively. The reaction mixture was stirred for 30 min at room temperature, and then HBpin (142 mg, 1.11 mmol) and toluene (1 mL) were added. The reaction mixture was heated at 90 °C for 20 h. The solvent was removed under the reduced pressure to afford the crude product. To a 50-mL oven-dried flask charged with the above crude product (**2c**, 0.278 mmol), $Pd_2(dba)_3$(5.2 mg, 2 mol%), Ruphos (5.4 mg, 4 mol%), bromobenzene (38.4 mg, 0.222 mmol), *t*-BuONa (82.4 mg, 0.834 mmol), toluene (4 mL) and H_2O(1 mL). The reaction mixture was heated to 100 °C for 24 h. The reaction mixture was diluted with EtOAc and water. The combined ethereal solution was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (50 : 1) as the eluent to afford target product as a yellow oil (27.6 mg, 47% yield for two steps). R_f = 0.5 (5% EtOAc/PE); IR (KBr): 3954, 3714, 2929, 2096, 1505, 1352, 1260, 1050, 767, 746 cm^{-1}; HRMS (ESI) m/z calculated for $C_{17}H_{19}N_3Na$ $(M+Na)^+$: 288.1471, Found: 288.1470. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 4H), 7.26 – 7.15 (m, 6H), 3.30 (p, *J* = 6.5 Hz, 1H), 2.81 (dt, *J* = 15.0, 7.7 Hz, 2H), 2.75 – 2.64 (m, 2H), 1.88 (q, *J* = 8.0, 7.3 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.15, 128.53, 128.41, 126.10, 61.51, 36.26, 32.37.

Scheme S27. Preparation of compound **29**.



4-(3-Azido-5-phenylpentyl)benzonitrile (**29**). According to the synthetic method of compound **28**, a mixture of **1** (prepared in situ from allylic azides **1** (88.6 mg, 0.281 mmol)), $Pd_2(dba)_3$ (5.2 mg, 2 mol%), Ruphos (5.4 mg, 4 mol%), 4-bromobenzonitrile (43.6 mg, 0.225 mmol), *t*-BuONa (83.4 mg, 0.843 mmol), toluene(4 mL) and H_2O(1 mL) afforded **29** (34.5 mg, 53% yield for two steps) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.5 (5% EtOAc/PE); IR (KBr): 3830, 3453, 2929, 2095, 1506, 1339, 1042, 797, 733 cm^{-1}; HRMS (ESI) m/z calculated for $C_{18}H_{18}N_4Na$ $(M+Na)^+$: 313.1424, Found: 313.1425. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.14 (m, 5H), 7.22 – 7.14 (m, 2H), 3.24 (p, *J* = 6.7 Hz, 1H), 2.89 – 2.64 (m, 4H), 1.95 – 1.77 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.76, 140.81, 132.33, 129.18, 128.56, 128.36, 126.19, 118.92, 110.06, 61.15, 36.12, 35.67, 32.49, 32.26.

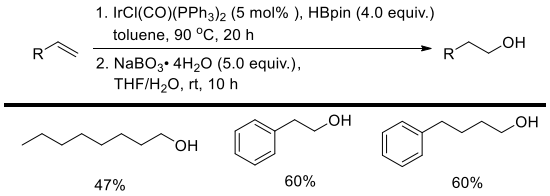
Scheme S28. Preparation of compound **30**.[S5]



1-(3-Azido-5-phenylpentyl)-4-methoxybenzene (**30**). According to the synthetic method of compound **28**, a mixture of **1** (prepared in situ from allylic azides **1** (93.6 mg, 0.297 mmol)), $Pd(OAc)_2$ (5.2 mg, 2.5 mol%), Ruphos (7.4 mg, 5 mol%), 1-bromo-4-methoxybenzene (68.2 mg, 0.356 mmol), *t*-BuONa (87.4 mg, 0.873 mmol), toluene (5 mL) and H_2O (0.5 mL) afforded **30** (45.2 mg, 43% yield for two steps) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.5 (5% EtOAc/PE); IR (KBr): 3736, 2929, 2097, 1504, 1268, 797, 733 cm^{-1}; HRMS (ESI) m/z calculated for $C_{18}H_{21}N_3NaO$ $(M+Na)^+$: 318.1577, Found: 318.1570. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.27 (p, *J* = 6.6 Hz, 1H), 2.87 – 2.55 (m, 4H), 1.92 – 1.77 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.95, 141.18, 133.15, 129.30, 128.51, 128.40, 126.07, 113.93, 61.45, 55.26, 36.46, 36.25, 32.37, 31.42.

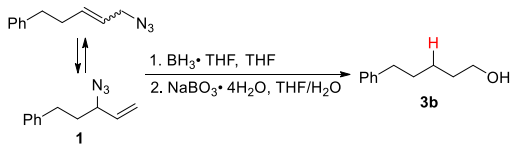
Mechanistic investigations

Scheme S29. Hydroboration of olefins using Vaska's catalyst.



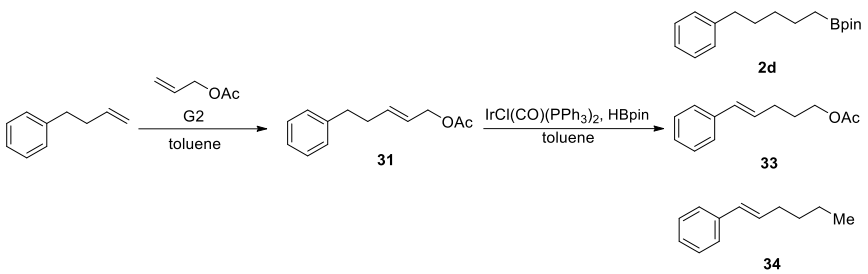
Under argon atmosphere, to an oven-dried flask was added $IrCl(CO)(PPh_3)_2$ (5 mol%), olefins (1.0 equiv.) and toluene (2 mL) successively. The reaction mixture was stirred for 30 min at room temperature, and then HBpin (4.0 equiv.) and toluene(1 mL) were added. The reaction mixture was heated at 90 °C for 20 h. The solvent was removed under the reduced pressure to afford the crude product. A mixture of the above crude product, $NaBO_3 \cdot 4H_2O$ (5.0 equiv.) in THF (2 mL) and H_2O (1 mL) was stirred at room temperature for 10 h. The reaction mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography to afford the desired product. The spectral data of all alcohols matched with the reported.[S6-S8]

Scheme S30. Hydroboration with borane.



Under argon atmosphere, to an oven-dried flask was added **1** (1.0 equiv.), $BH_3 \cdot THF$ (2.0/3.0 equiv.) and THF (3 mL). The reaction mixture was heated at 90 °C for 20 h. The solvent was removed under the reduced pressure to afford the crude product. A mixture of the above crude product, $NaBO_3 \cdot 4H_2O$ (5.0 equiv.) in THF (2 mL) and H_2O (1 mL) was stirred at room temperature for 10 h. The reaction mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography. **Result**: 2.0 equiv. $BH_3 \cdot THF$: conv. 50%; 3.0 equiv. $BH_3 \cdot THF$: **3b** (45% yield).

Scheme S31. Hydroboration of allylic acetate.

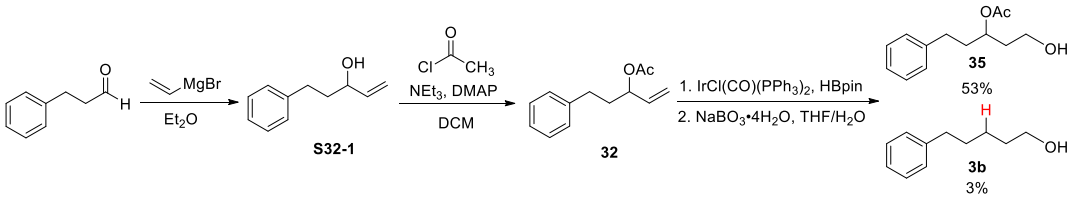


According to General procedure A, but-3-en-1-ylbenzene (243 mg, 1.83 mol), allyl acetate (733 mg, 7.32 mol), G-2 (39.2 mg, 2.5 mol%), and toluene (15 mL) afforded **31** (223 mg, 60%) as a colorless oil after silica gel column chromatography (2-10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 5.89 – 5.77 (m, 1H), 5.69 – 5.57 (m, 1H), 4.54 (d, *J* = 6.3 Hz, 2H), 2.73 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.44 – 2.36 (m, 2H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.76, 141.50, 135.36, 128.42, 128.35, 125.93, 124.50, 65.11, 35.32, 34.08, 21.01.

According to General procedure B, a mixture of **31** (36.3 mg, 0.178 mmol), HBpin (94.7 mg, 0.740 mmol), and $IrCl(CO)(PPh_3)_2$ (7.0 mg, 5 mol%) in toluene (3 mL) afforded **2d** (15.7 mg, 43%), **33** (3.4 mg, 9%) and **34** (0.8 mg, 3%) as a yellow oil after preparative TLC (5% EtOAc/PE). The spectral data of **33** and **34** matched with the reported.

S9- S10

Scheme S32. Hydroboration of allylic acetate.



Under argon atmosphere, to a 50-mL oven-dried flask charged with 3-phenylpropanal (503 mg, 3.75 mmol), Et_2O (20 mL), vinylmagnesium bromide (1.0 M in THF, 9.5 mL, 9.5 mmol) was added dropwise at 0 °C. The resulted mixture was allowed to stir at room temperature for 10 h. The reaction was quenched by saturated aq. NH_4Cl, and the mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography to afford **S32-1** (434 mg, 71%) as a yellow oil after column chromatography (10~20% EtOAc/PE). R_f = 0.3 (16% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 5.99 (ddd, *J* = 17.0, 10.4, 6.2 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.4 Hz, 1H), 4.20 (q, *J* = 6.4 Hz, 1H), 3.05 (s, 1H), 2.91 – 2.73 (m, 2H), 2.03 – 1.88 (m, 2H).

Under argon atmosphere, to a solution of **S32-1** (434 mg, 2.67 mmol), Et_3N (824 mg, 8.09 mmol), DMAP (32.8 mg, 10 mol%) in DCM (5 mL) was added dropwise a solution of acetyl chloride (343 mg, 4.37 mmol) in DCM (5 mL) at 0 °C. The reaction mixture was warmed to room temperature naturally and stirred for 10 h. The mixture was poured into water and extracted three times with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by chromatography to afford **32** (362 mg, 66%) as a yellow oil after column chromatography (2~10% EtOAc/PE). R_f = 0.3 (5% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 2H), 7.26 – 7.17 (m, 3H), 5.84 (ddd, *J* = 17.1, 10.5, 6.4 Hz, 1H), 5.35 – 5.29 (m, 1H), 5.34 – 5.25 (m, 1H), 5.24 – 5.20 (m, 1H), 2.75 – 2.62 (m, 2H), 2.07 (s, 3H), 2.04 – 1.89 (m, 2H).

According to General procedure B, a mixture of **32** (77.8 mg, 0.381 mmol), HBpin (197 mg, 1.54 mmol), and $IrCl(CO)(PPh_3)_2$ (15.0 mg, 5 mol%) in toluene (3 mL) afforded the hydroboration products. A mixture of the above products and $NaBO_3 \cdot 4H_2O$ (294 mg, 1.91 mmol) in THF (2 mL) and H_2O (1 mL) afforded **35** (45.0 mg, 53%) and **3b** (1.5 mg, 8%) as a yellow oil after preparative TLC (25% EtOAc/PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 4.36 (ddd, *J* = 11.1, 8.6, 5.0 Hz, 1H), 4.12 (dt, *J* = 11.4, 5.7 Hz, 1H), 3.73 – 3.66 (m, 1H), 2.86 – 2.74 (m, 1H), 2.73 – 2.65 (m, 1H), 2.04 (s, 3H), 1.88 – 1.71 (m, 4H).

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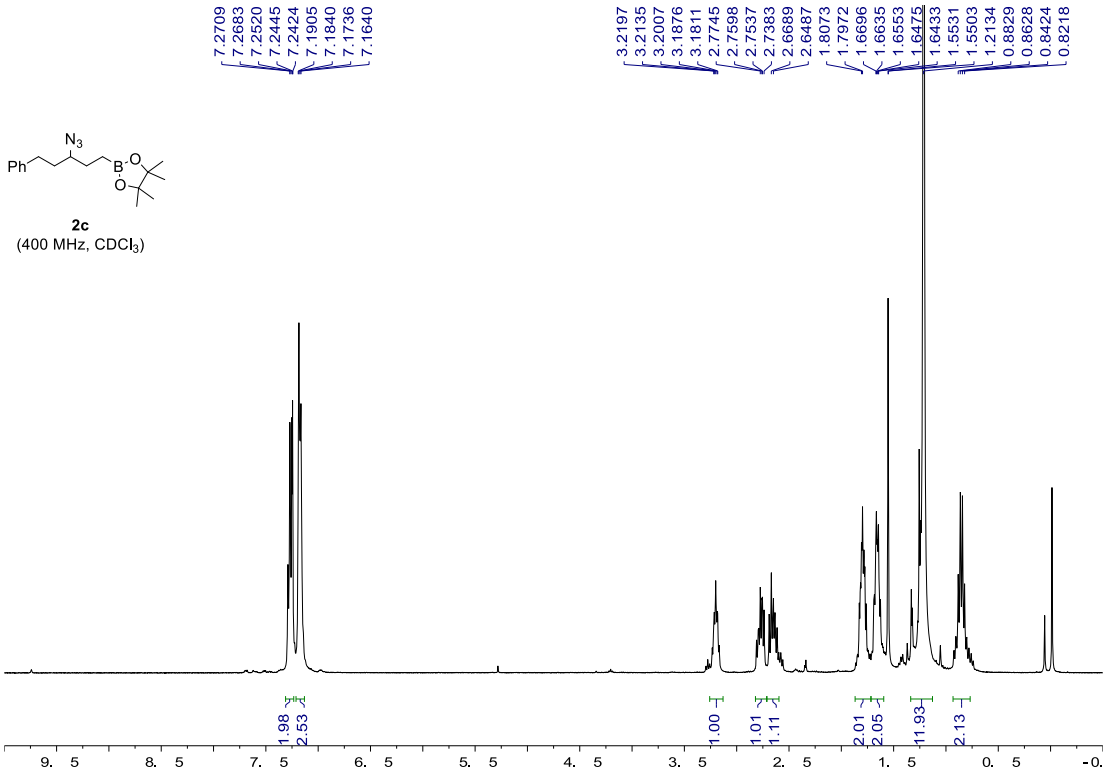
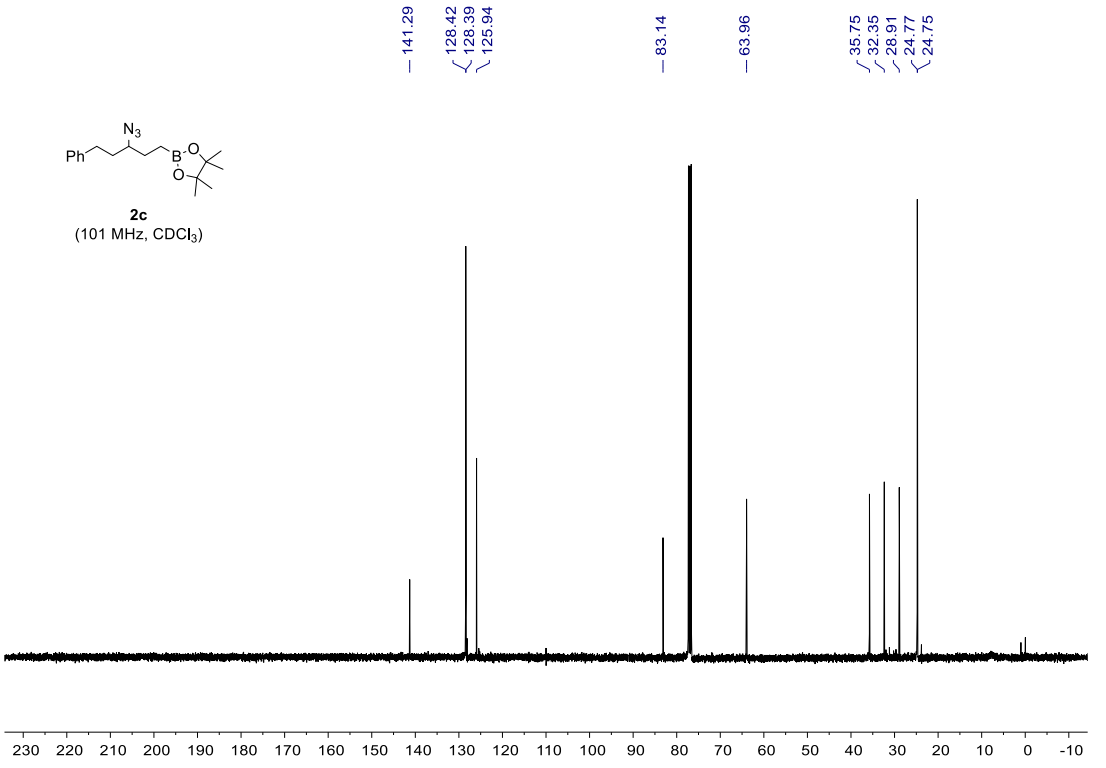
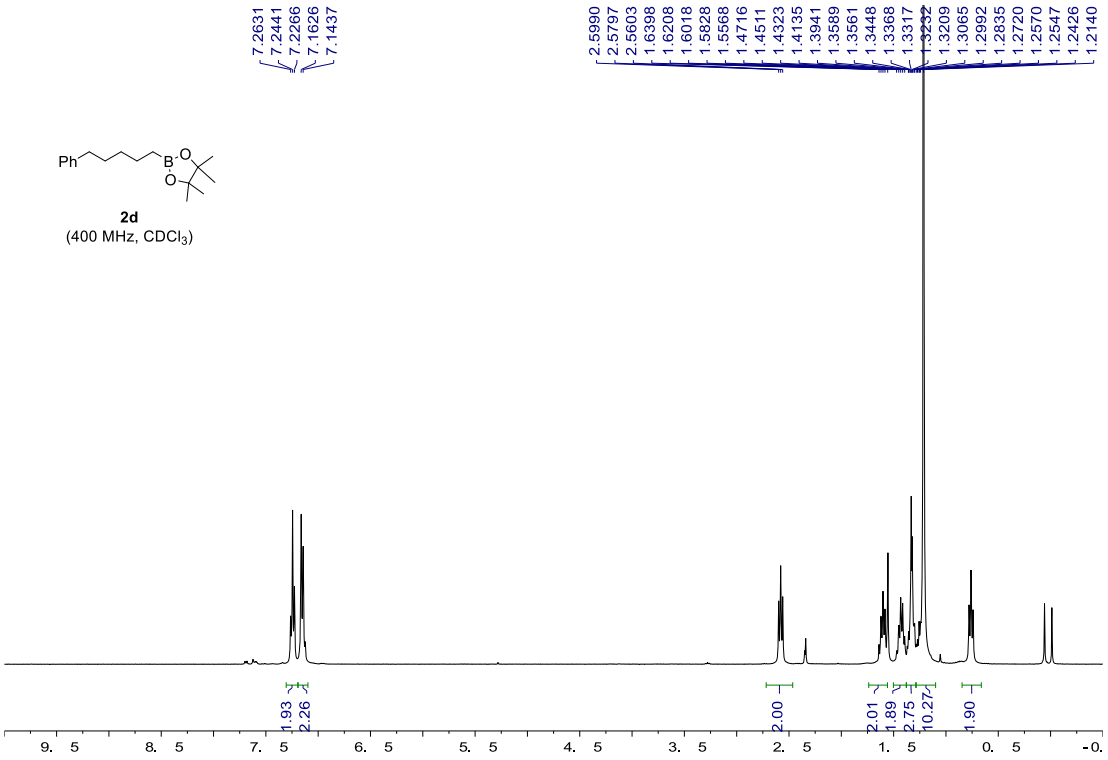
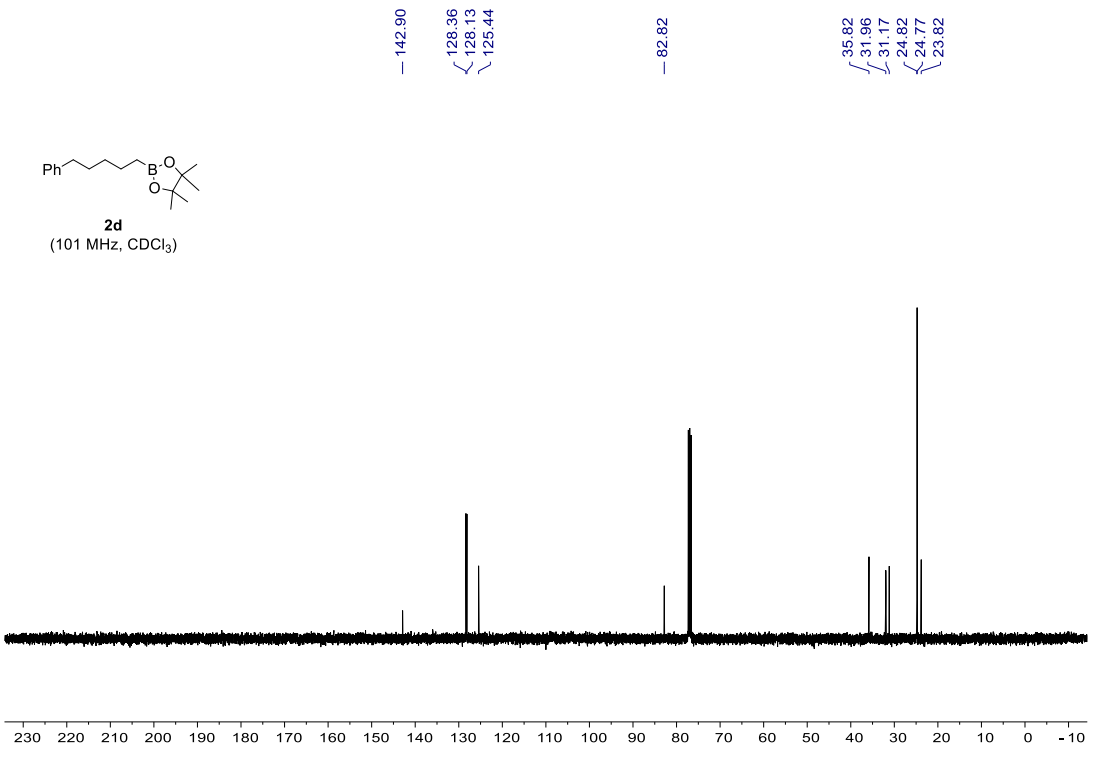
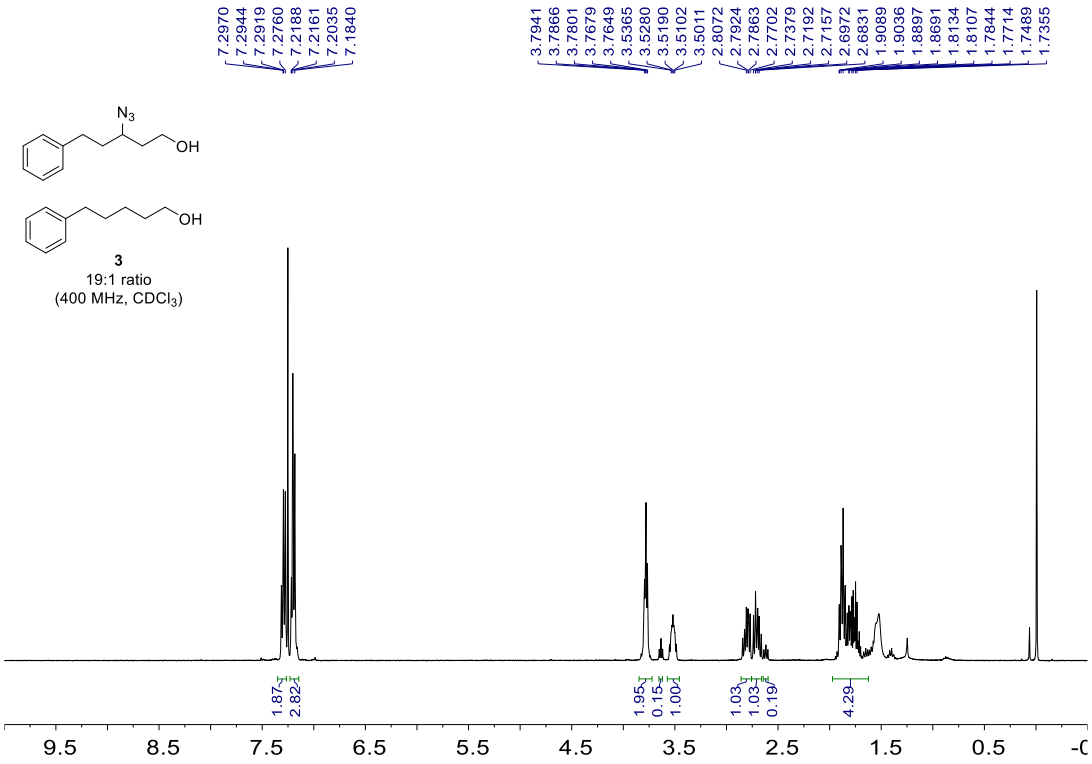
Copies of ^{1}H NMR and ^{13}C NMR

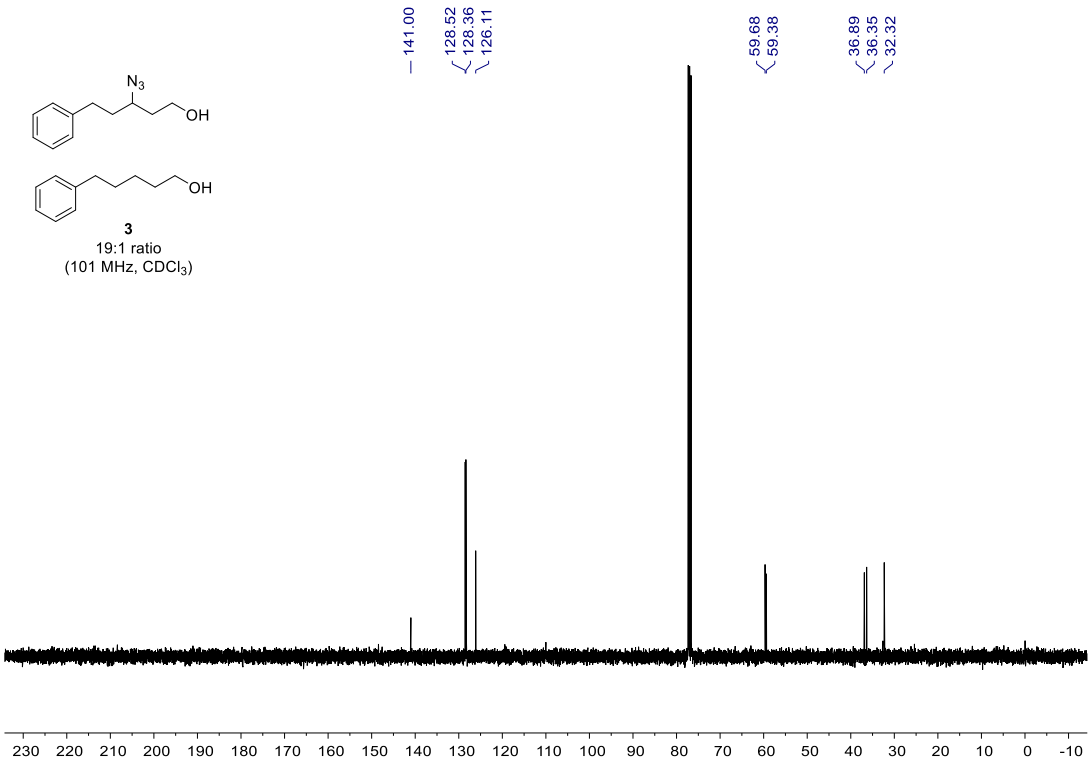


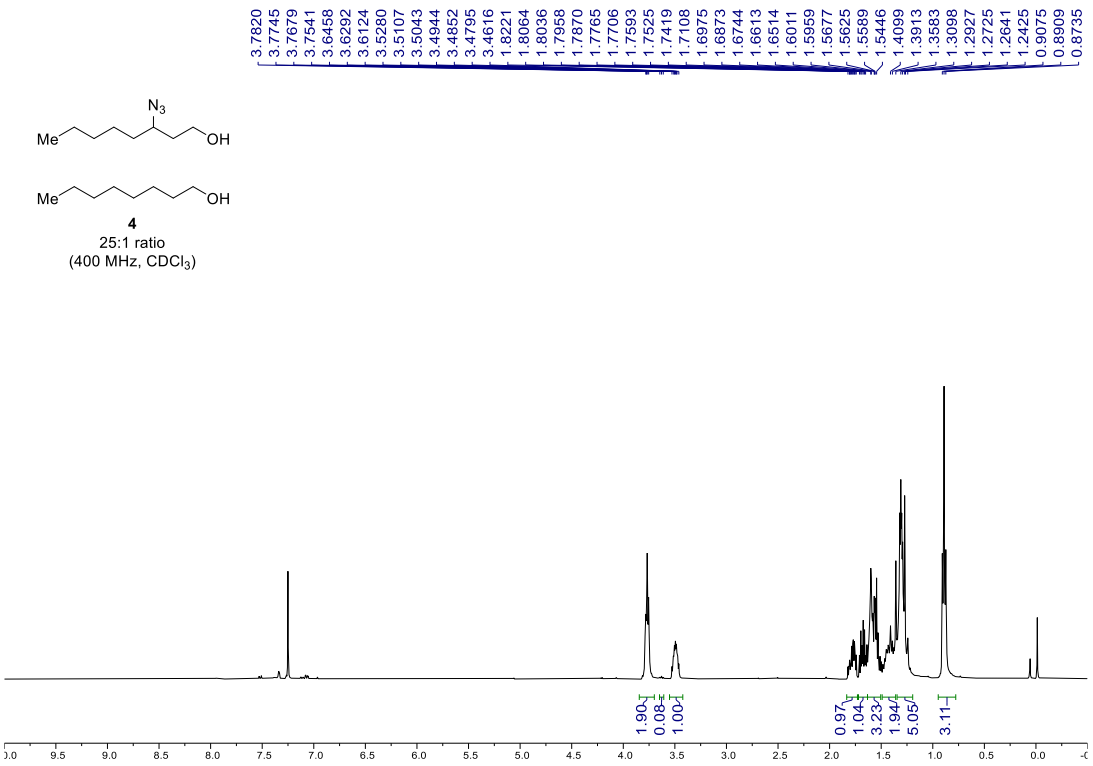


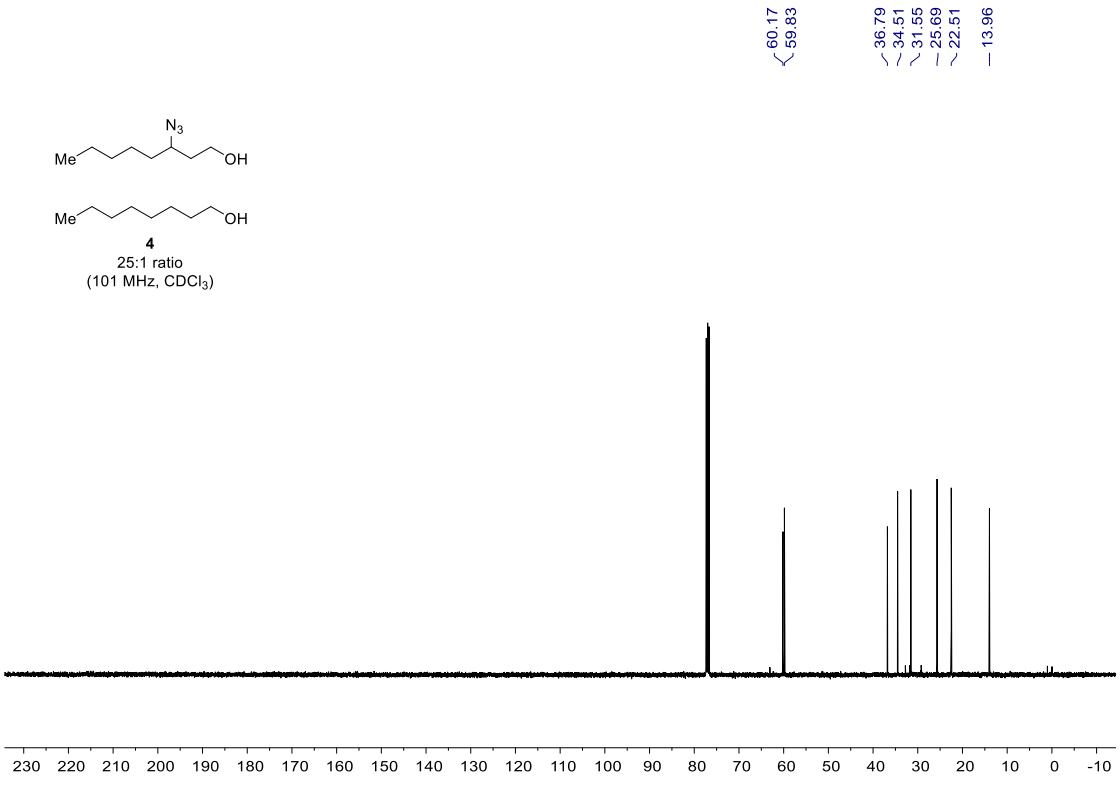

7.2631
7.2441
7.2266
7.1626
7.1437
2.5990
2.5797
2.5603
1.6398
1.6208
1.6018
1.5828
1.5568
1.4716
1.4511
1.4323
1.4135
1.3941
1.3589
1.3561
1.3448
1.3368
1.3317
1.3232
1.3209
1.3065
1.2992
1.2835
1.2720
1.2570
1.2547
1.2426
1.2140
Ph
B
O
O
2d
(400 MHz, CDCl3)
1.93
2.26
2.00
2.01
1.89
2.75
10.27
1.90
9. 5
8. 5
7. 5
6. 5
5. 5
4. 5
3. 5
2. 5
1. 5
0. 5
-0.

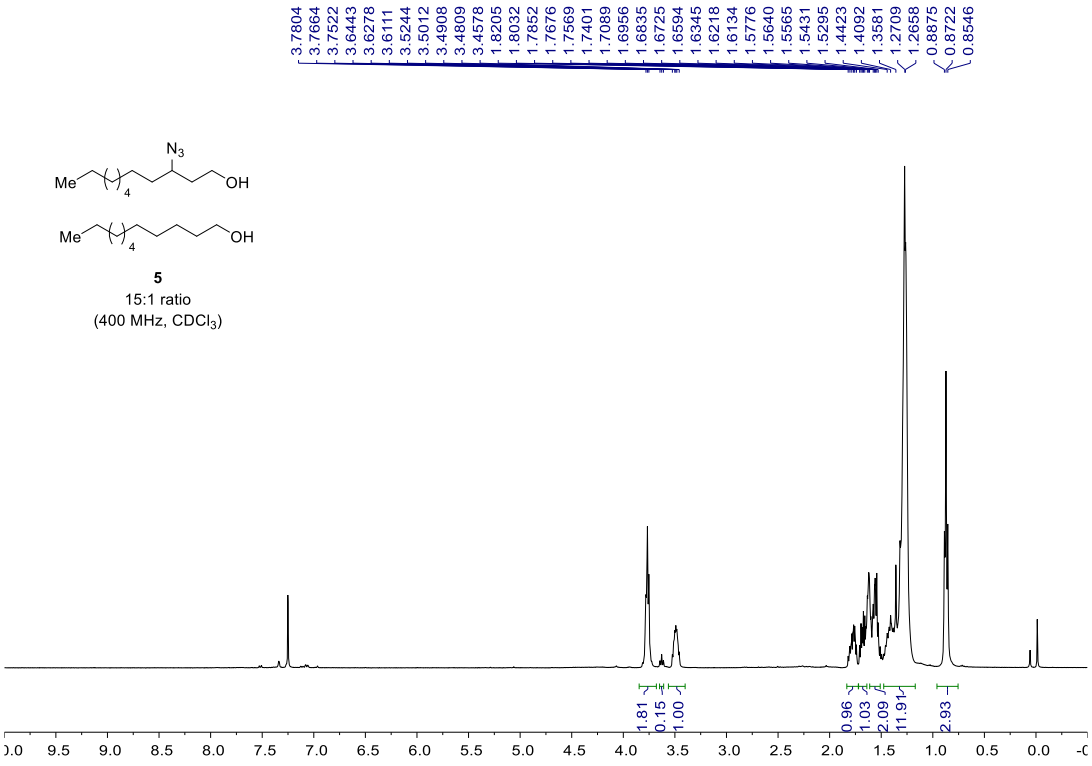

142.90
128.36
128.13
125.44
82.82
35.82
31.96
31.17
24.82
24.77
23.82
Ph
B
O
O
2d
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

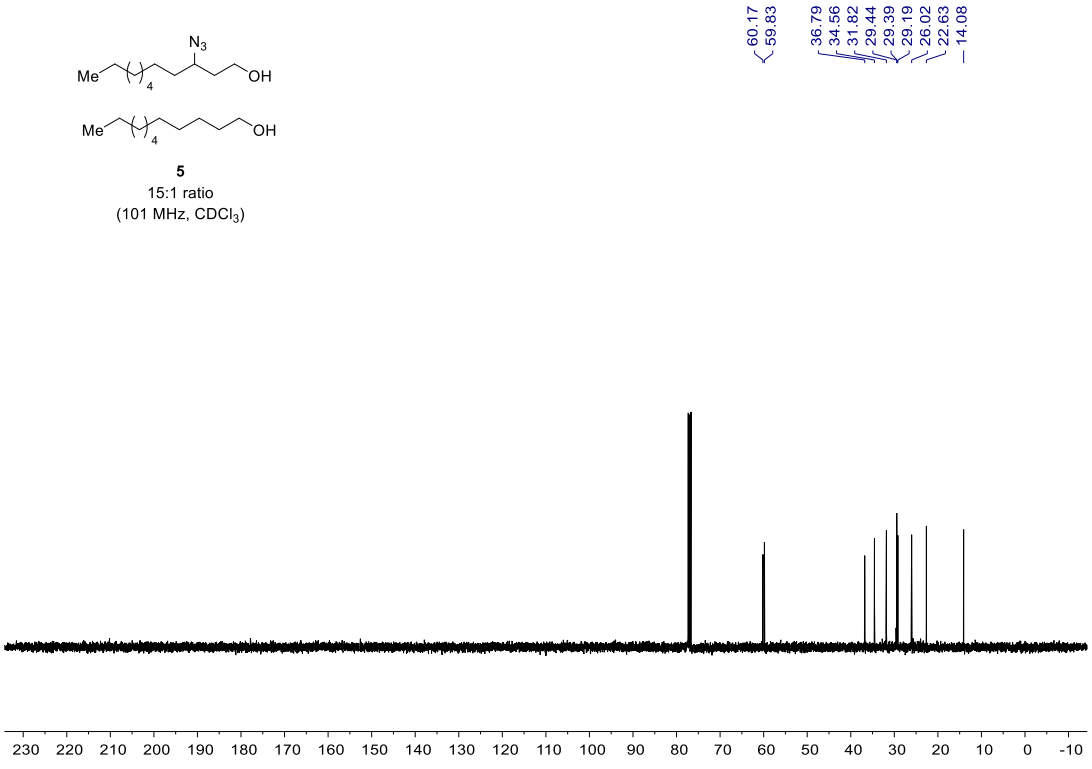

7.2970
7.2944
7.2919
7.2760
7.2188
7.2161
7.2035
7.1840
3.7941
3.7866
3.7801
3.7679
3.7649
3.5365
3.5280
3.5190
3.5102
3.5011
2.8072
2.7924
2.7863
2.7702
2.7379
2.7192
2.7157
2.6972
2.6831
1.9089
1.9036
1.8897
1.8691
1.8134
1.8107
1.7844
1.7714
1.7489
1.7355
N3
OH
OH
3
19:1 ratio
(400 MHz, CDCl3)
1.87
2.82
1.95
0.15
1.00
1.03
1.03
0.19
4.29
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

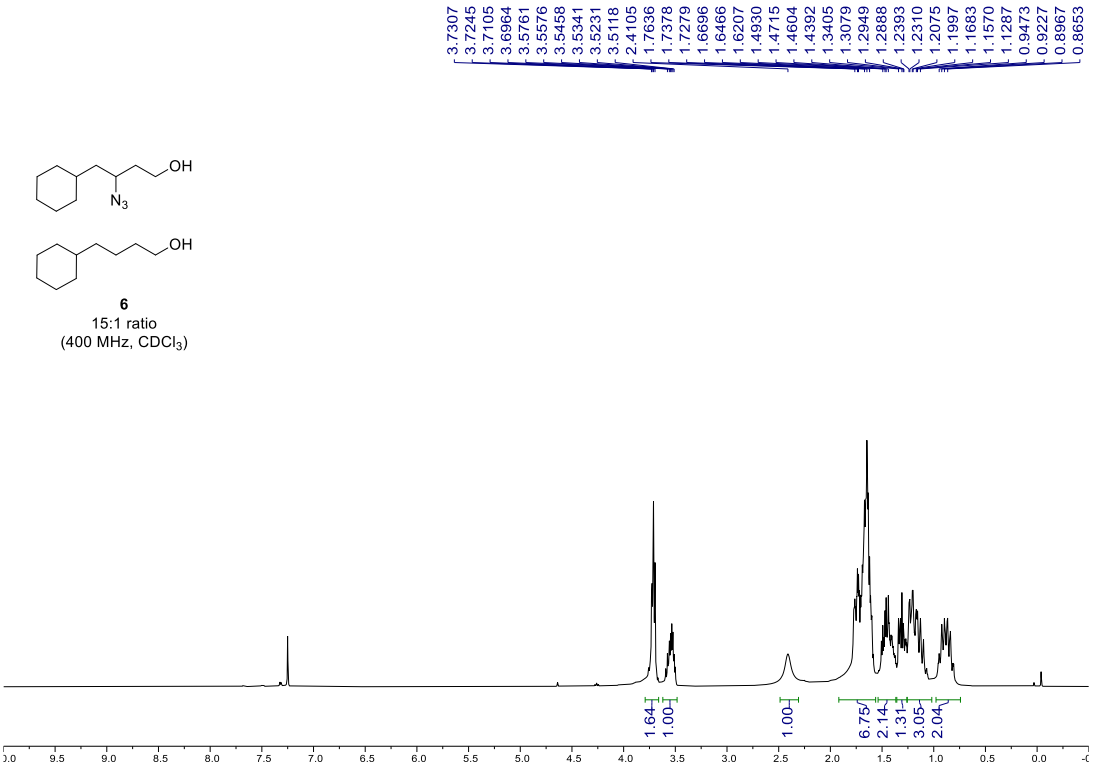

141.00
128.52
128.36
126.11
59.68
59.38
36.89
36.35
32.32
N3
OH
OH
3
19:1 ratio
(101 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

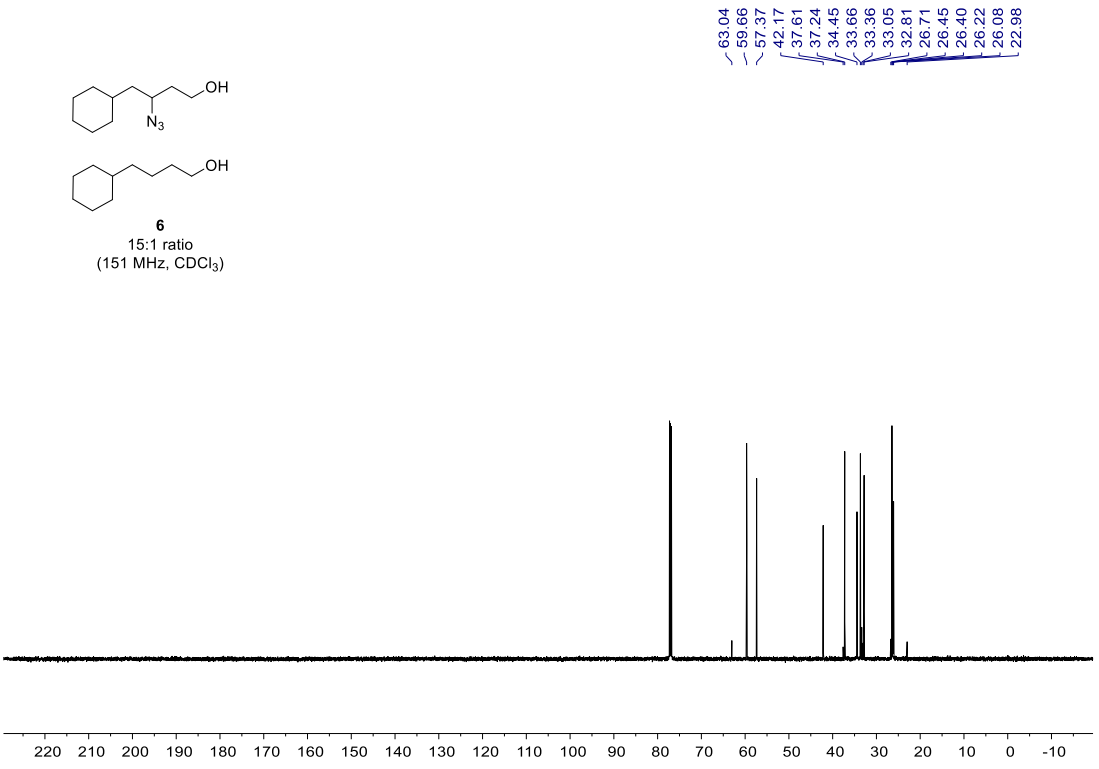

3.7820
3.7745
3.7679
3.7541
3.6458
3.6292
3.6124
3.5280
3.5107
3.5043
3.4944
3.4852
3.4795
3.4616
1.8221
1.8064
1.8036
1.7958
1.7870
1.7765
1.7706
1.7593
1.7525
1.7419
1.7108
1.6975
1.6873
1.6744
1.6613
1.6514
1.6011
1.5959
1.5677
1.5625
1.5589
1.5446
1.4099
1.3913
1.3583
1.3098
1.2927
1.2725
1.2641
1.2425
0.9075
0.8909
0.8735
N3
Me
OH
Me
OH
4
25:1 ratio
(400 MHz, CDCl3)
1.90
0.08
1.00
0.97
1.04
3.23
1.94
5.05
3.11

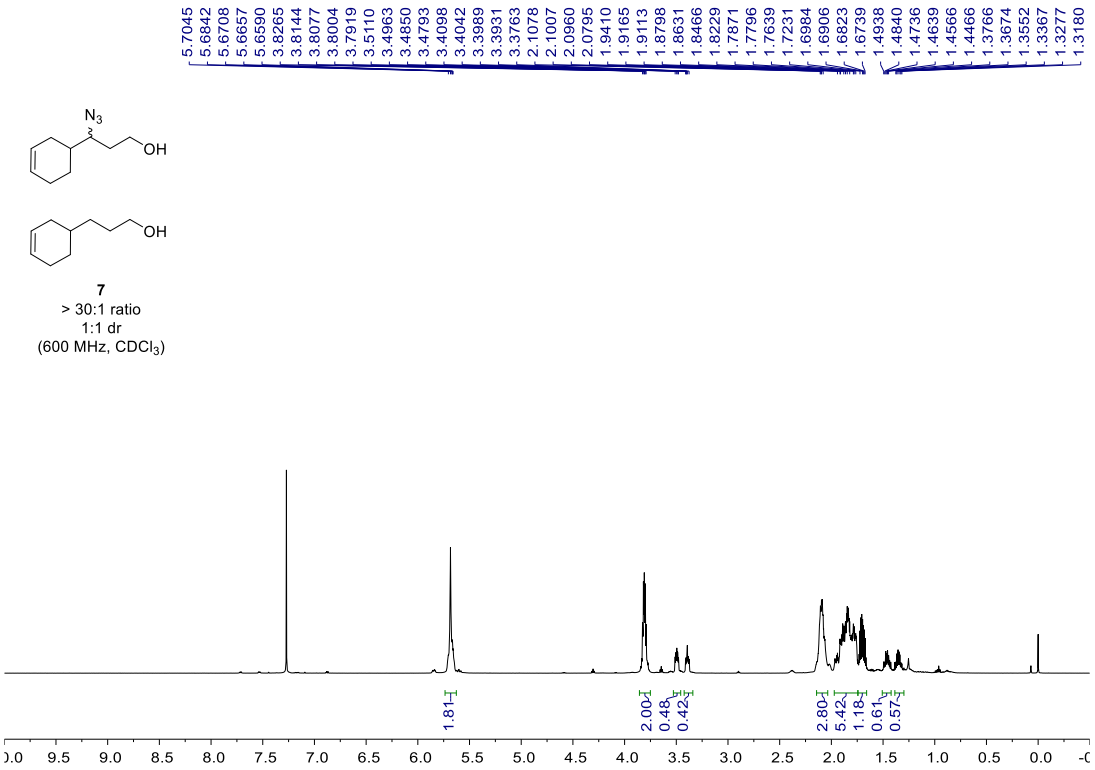

60.17
59.83
36.79
34.51
31.55
25.69
22.51
13.96
N3
Me
OH
Me
OH
4
25:1 ratio
(101 MHz, CDCl3)

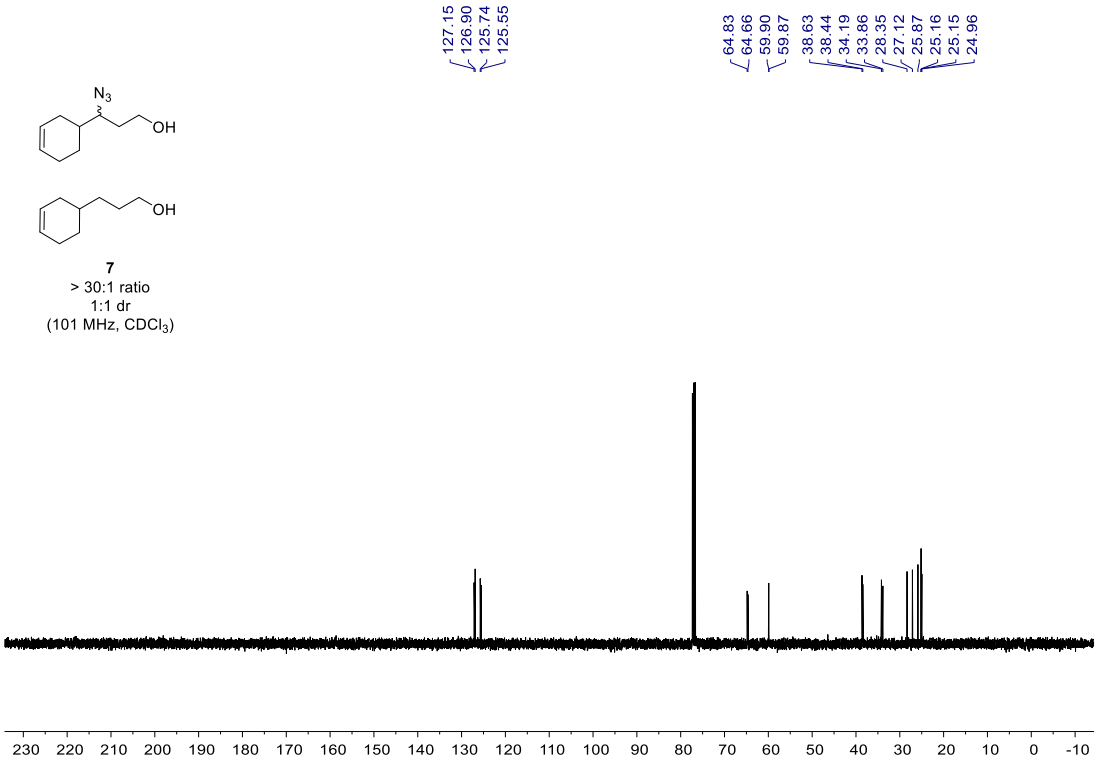

3.7804
3.7664
3.7522
3.6443
3.6278
3.6111
3.5244
3.5012
3.4908
3.4809
3.4578
1.8205
1.8032
1.7852
1.7676
1.7569
1.7401
1.7089
1.6956
1.6835
1.6725
1.6594
1.6345
1.6218
1.6134
1.5776
1.5640
1.5565
1.5431
1.5295
1.4423
1.4092
1.3581
1.2709
1.2658
0.8875
0.8722
0.8546
N3
Me
OH
Me
OH
5
15:1 ratio
(400 MHz, CDCl3)
1.81
0.15
1.00
0.96
1.03
2.09
11.91
2.93

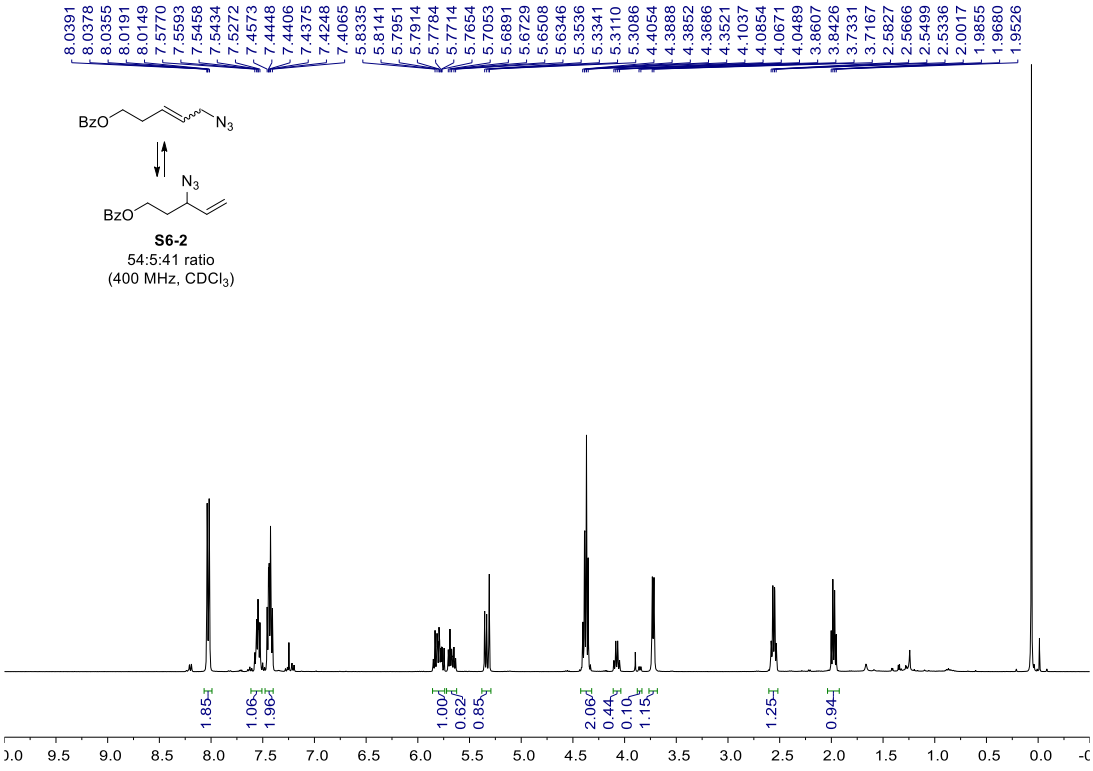

60.17
59.83
36.79
34.56
31.82
29.44
29.39
29.19
26.02
22.63
14.08
N3
Me
OH
Me
OH
5
15:1 ratio
(101 MHz, CDCl3)

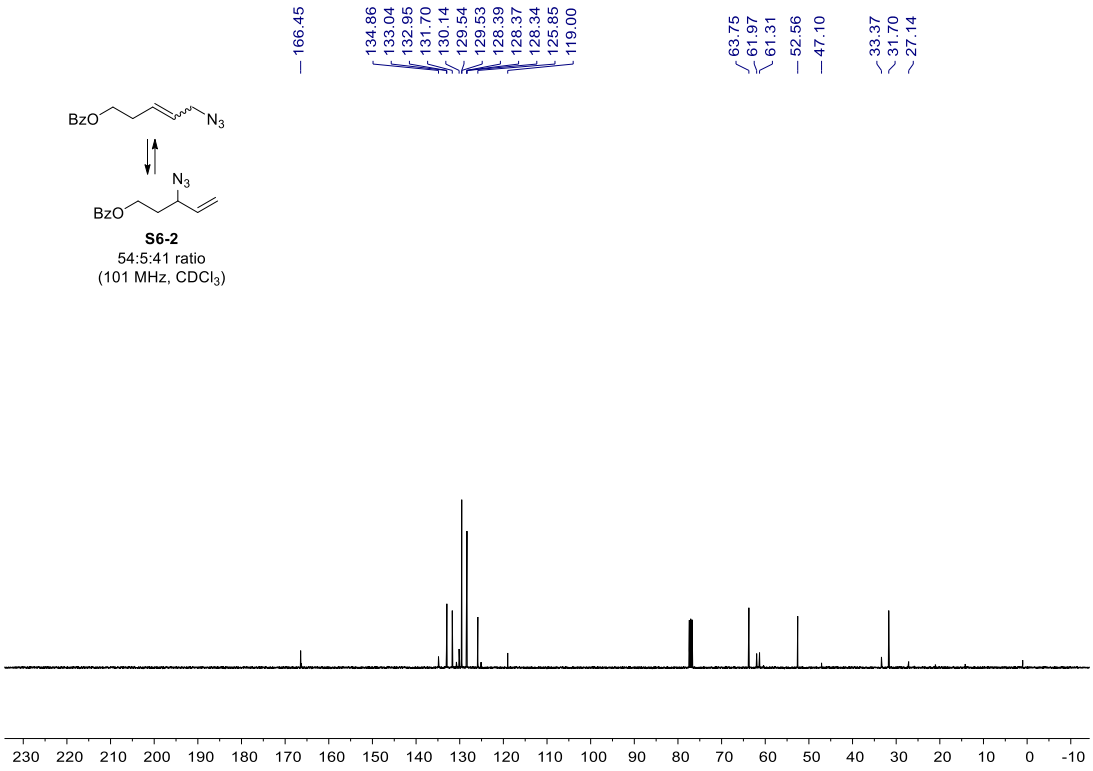

3.7307
3.7245
3.7105
3.6964
3.5761
3.5576
3.5458
3.5341
3.5231
3.5118
2.4105
1.7636
1.7378
1.7279
1.6696
1.6466
1.6207
1.4930
1.4715
1.4604
1.4392
1.3405
1.3079
1.2949
1.2888
1.2393
1.2310
1.2075
1.1997
1.1683
1.1570
1.1287
0.9473
0.9227
0.8967
0.8653
OH
N3
OH
6
15:1 ratio
(400 MHz, CDCl3)
1.64
1.00
1.00
6.75
2.14
1.31
3.05
2.04

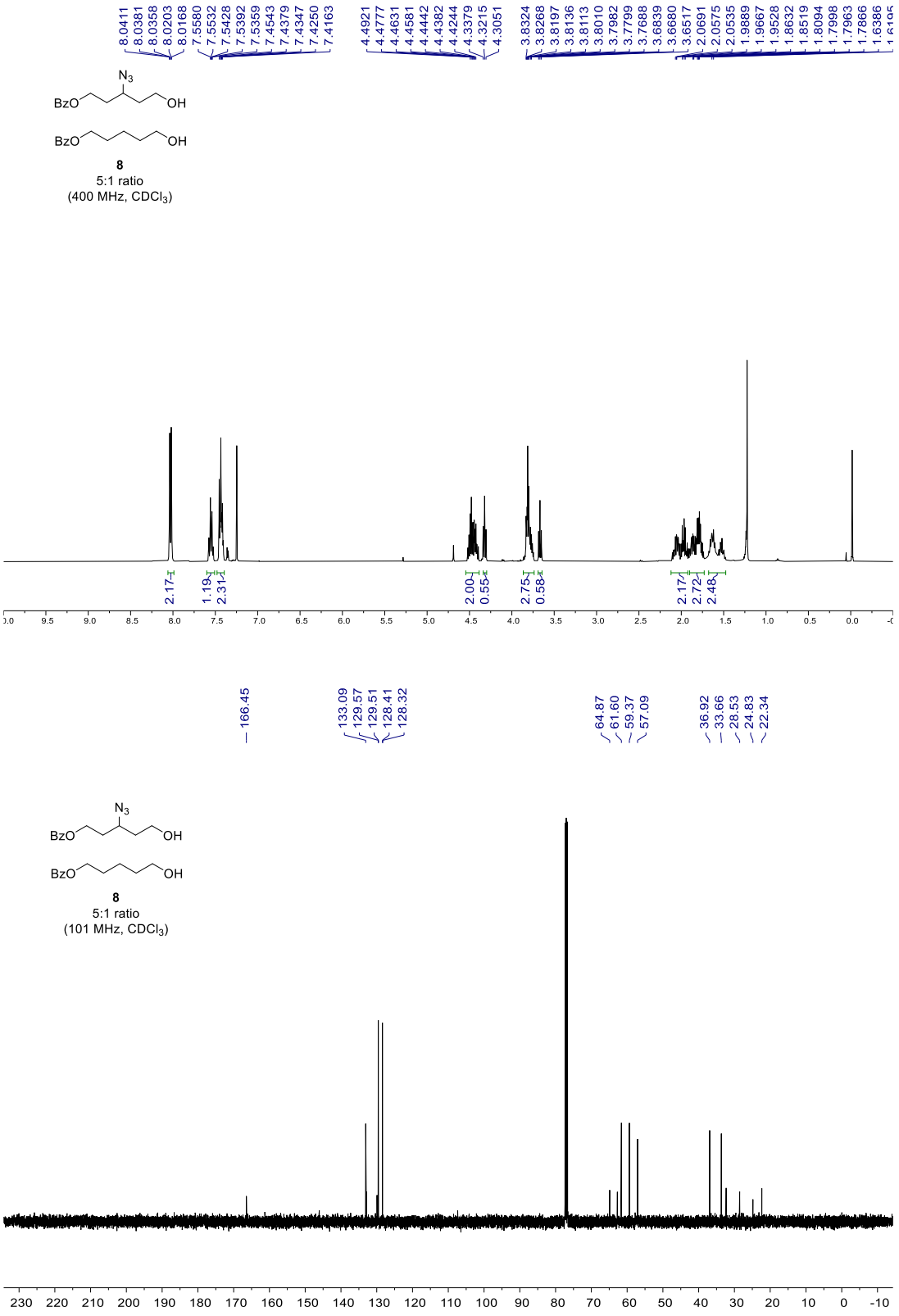

63.04
59.66
57.37
42.17
37.61
37.24
34.45
33.66
33.36
33.05
32.81
26.71
26.45
26.40
26.22
26.08
22.98
OH
N3
OH
6
15:1 ratio
(151 MHz, CDCl3)

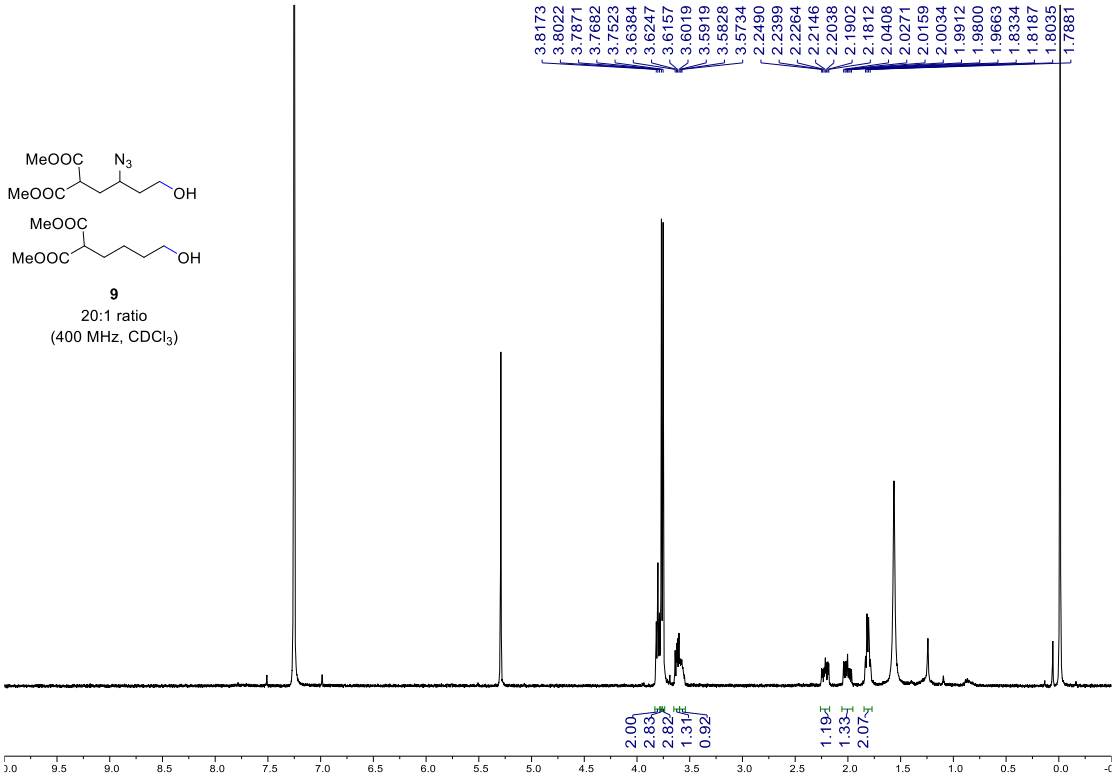

5.7045
5.6842
5.6708
5.6657
5.6590
3.8265
3.8144
3.8077
3.8004
3.7919
3.5110
3.4963
3.4850
3.4793
3.4098
3.4042
3.3989
3.3931
3.3763
2.1078
2.1007
2.0960
2.0795
1.9410
1.9165
1.9113
1.8798
1.8631
1.8466
1.8229
1.7871
1.7796
1.7639
1.7231
1.6984
1.6906
1.6823
1.6739
1.4938
1.4840
1.4736
1.4639
1.4566
1.4466
1.3766
1.3674
1.3552
1.3367
1.3277
1.3180
N3
OH
OH
7
> 30:1 ratio
1:1 dr
(600 MHz, CDCl3)
1.81
2.00
0.48
0.42
2.80
5.42
1.18
0.61
0.57


127.15
126.90
125.74
125.55
64.83
64.66
59.90
59.87
38.63
38.44
34.19
33.86
28.35
27.12
25.87
25.16
25.15
24.96
N3
OH
OH
7
> 30:1 ratio
1:1 dr
(101 MHz, CDCl3)

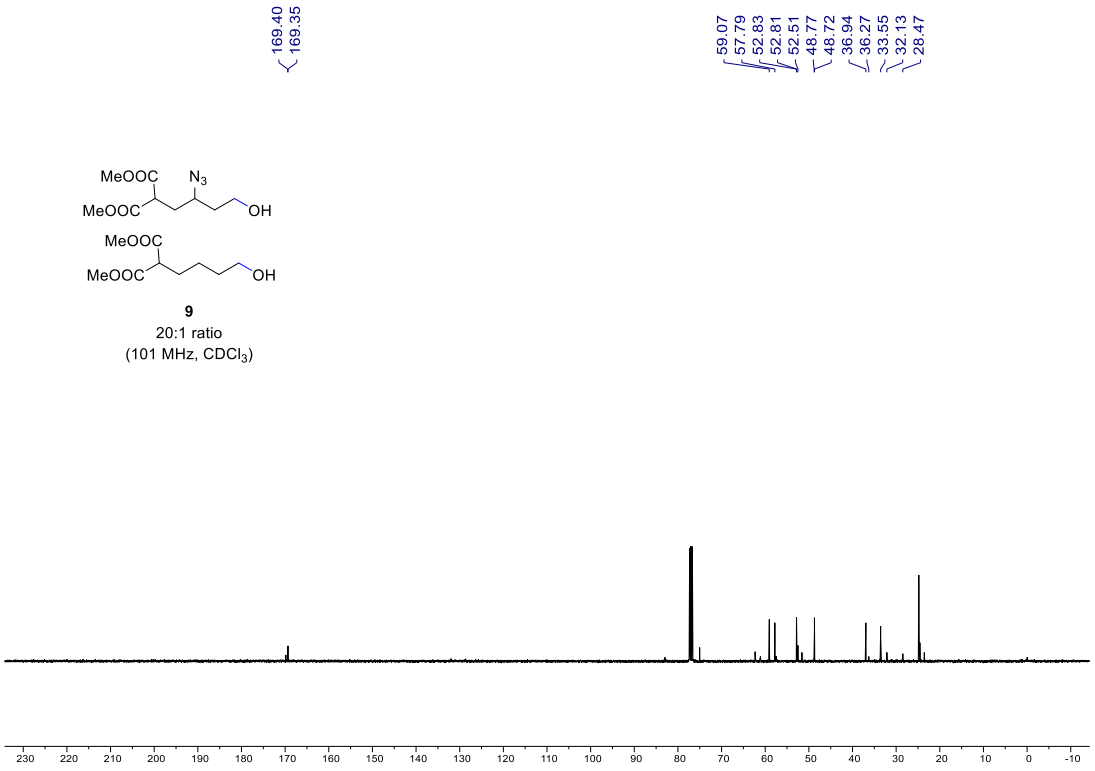

8.0391
8.0378
8.0355
8.0191
8.0149
7.5770
7.5593
7.5458
7.5434
7.5272
7.4573
7.4448
7.4406
7.4375
7.4248
7.4065
5.8335
5.8141
5.7951
5.7914
5.7784
5.7714
5.7654
5.7053
5.6891
5.6729
5.6508
5.6346
5.3536
5.3341
5.3110
5.3086
4.4054
4.3888
4.3852
4.3686
4.3521
4.1037
4.0854
4.0671
4.0489
3.8607
3.8426
3.7331
3.7167
2.5827
2.5666
2.5499
2.5336
2.0017
1.9855
1.9680
1.9526
BzO
N3
N3
BzO
S6-2
54:5:41 ratio
(400 MHz, CDCl3)
1.85
1.06
1.96
1.00
0.62
0.85
2.06
0.44
0.10
1.15
1.25
0.94


166.45
134.86
133.04
132.95
131.70
130.14
129.54
129.53
128.39
128.37
128.34
125.85
119.00
63.75
61.97
61.31
52.56
47.10
33.37
31.70
27.14
BzO
N3
N3
BzO
S6-2
54:5:41 ratio
(101 MHz, CDCl3)

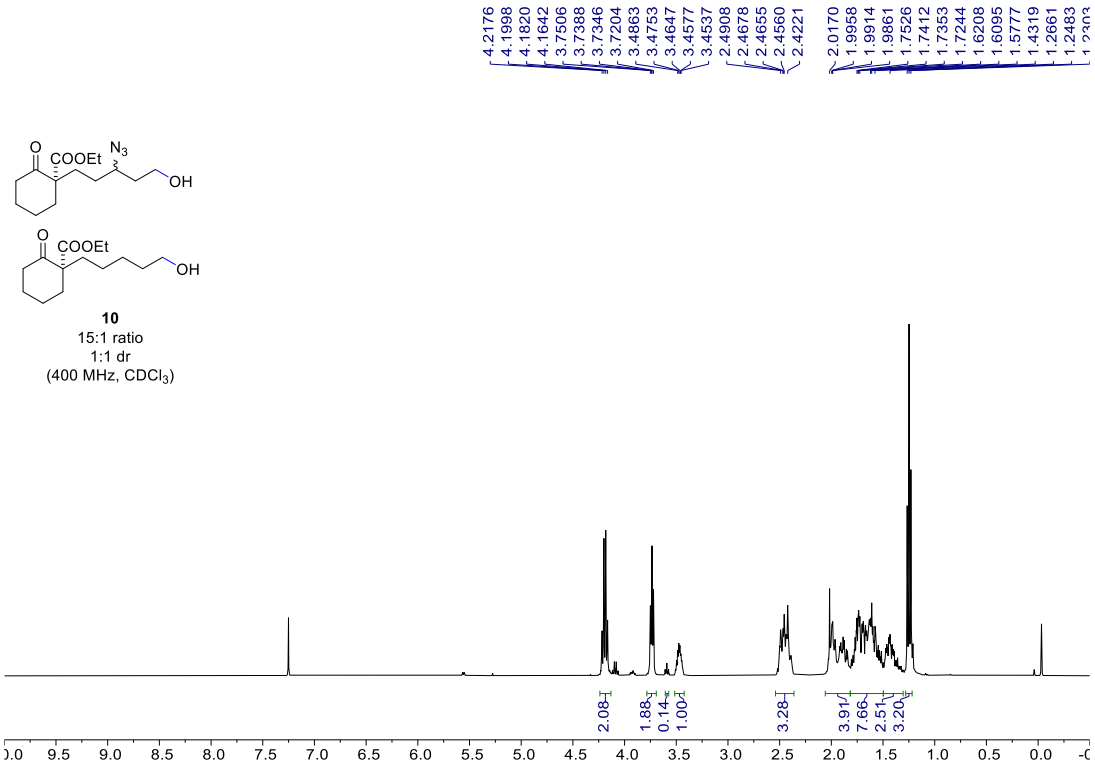

8.0411
8.0381
8.0358
8.0203
8.0168
7.5580
7.5532
7.5428
7.5392
7.5359
7.4543
7.4379
7.4347
7.4250
7.4163
4.4921
4.4777
4.4631
4.4581
4.4442
4.4382
4.4244
4.3379
4.3215
4.3051
3.8324
3.8268
3.8197
3.8136
3.8113
3.8010
3.7982
3.7799
3.7688
3.6839
3.6680
3.6517
2.0691
2.0575
2.0535
1.9889
1.9667
1.9528
1.8632
1.8519
1.8094
1.7998
1.7963
1.7866
1.6386
N3
BzO
OH
BzO
OH
8
5:1 ratio
(400 MHz, CDCl3)
2.17
1.19
2.31
2.00
0.55
2.75
0.58
2.17
2.72
2.48
166.45
133.09
129.57
129.51
128.41
128.32
64.87
61.60
59.37
57.09
36.92
33.66
28.53
24.83
22.34
N3
BzO
OH
BzO
OH
8
5:1 ratio
(101 MHz, CDCl3)

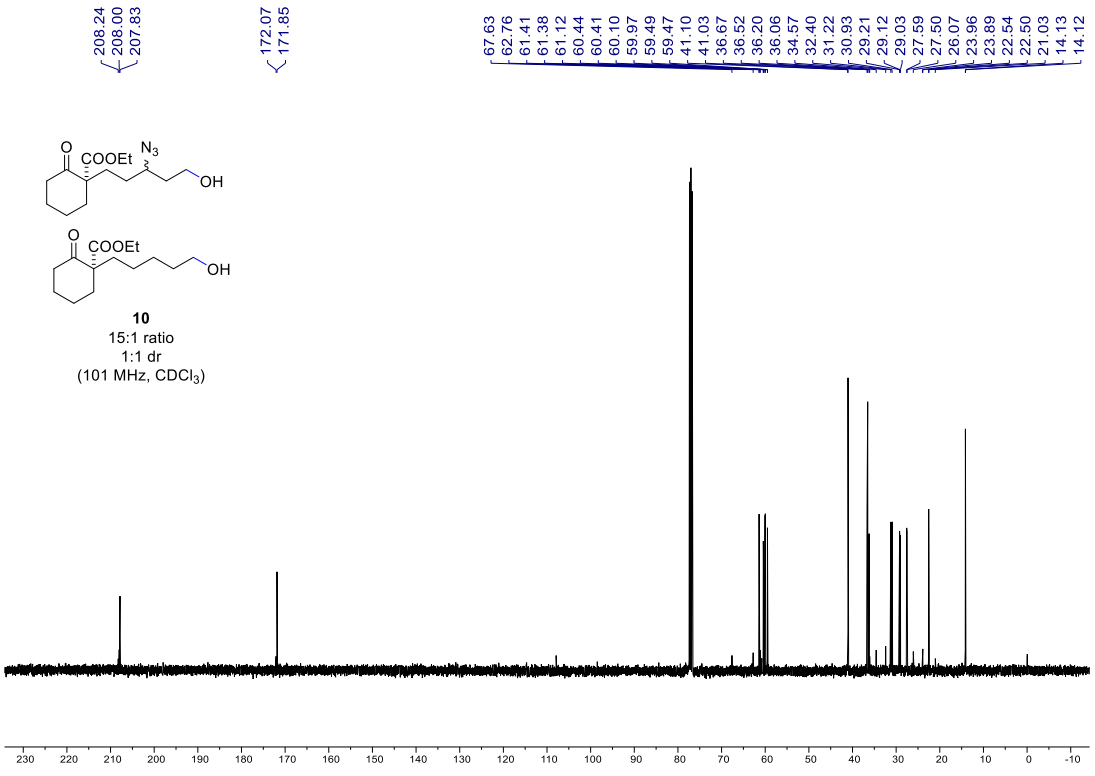


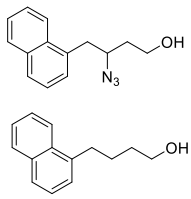
9
20:1 ratio
(400 MHz, $CDCl_3$)



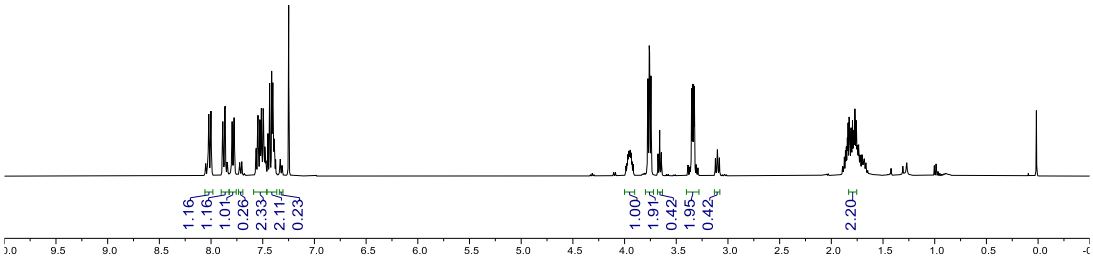
9
20:1 ratio
(101 MHz, $CDCl_3$)

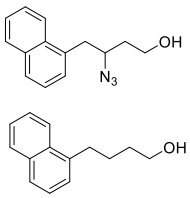

4.2176
4.1998
4.1820
4.1642
3.7506
3.7388
3.7346
3.7204
3.4863
3.4753
3.4647
3.4577
3.4537
2.4908
2.4678
2.4655
2.4560
2.4221
2.0170
1.9958
1.9914
1.9861
1.7526
1.7412
1.7353
1.7244
1.6208
1.6095
1.5777
1.4319
1.2661
1.2483
COOEt
N3
OH
10
15:1 ratio
1:1 dr
(400 MHz, CDCl3)
2.08
1.88
0.14
1.00
3.28
3.91
7.66
2.51
3.20


208.24
208.00
207.83
172.07
171.85
67.63
62.76
61.41
61.38
61.12
60.44
60.41
60.10
59.97
59.49
59.47
41.10
41.03
36.67
36.52
36.20
36.06
34.57
32.40
31.22
30.93
29.21
29.12
29.03
27.59
27.50
26.07
23.96
23.89
22.54
22.50
21.03
14.13
14.12
COOEt
N3
OH
10
15:1 ratio
1:1 dr
(101 MHz, CDCl3)

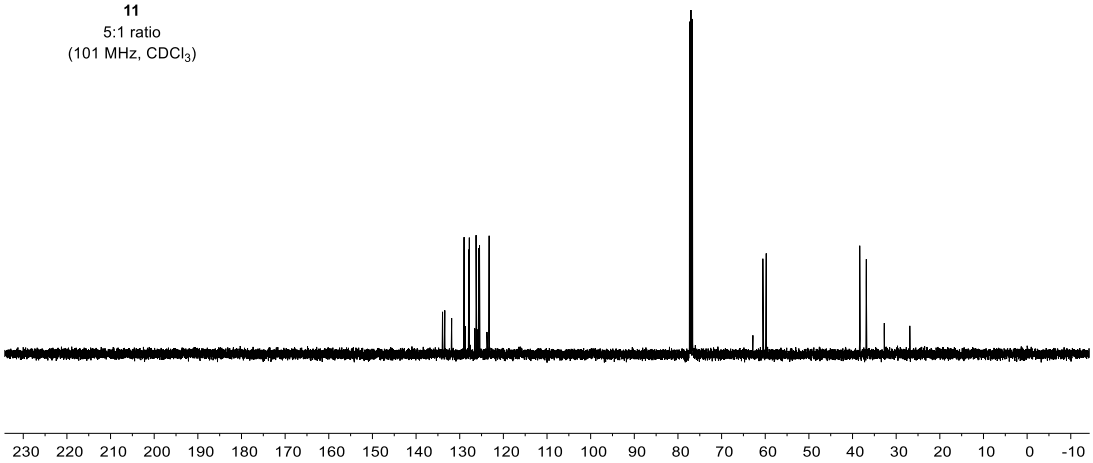


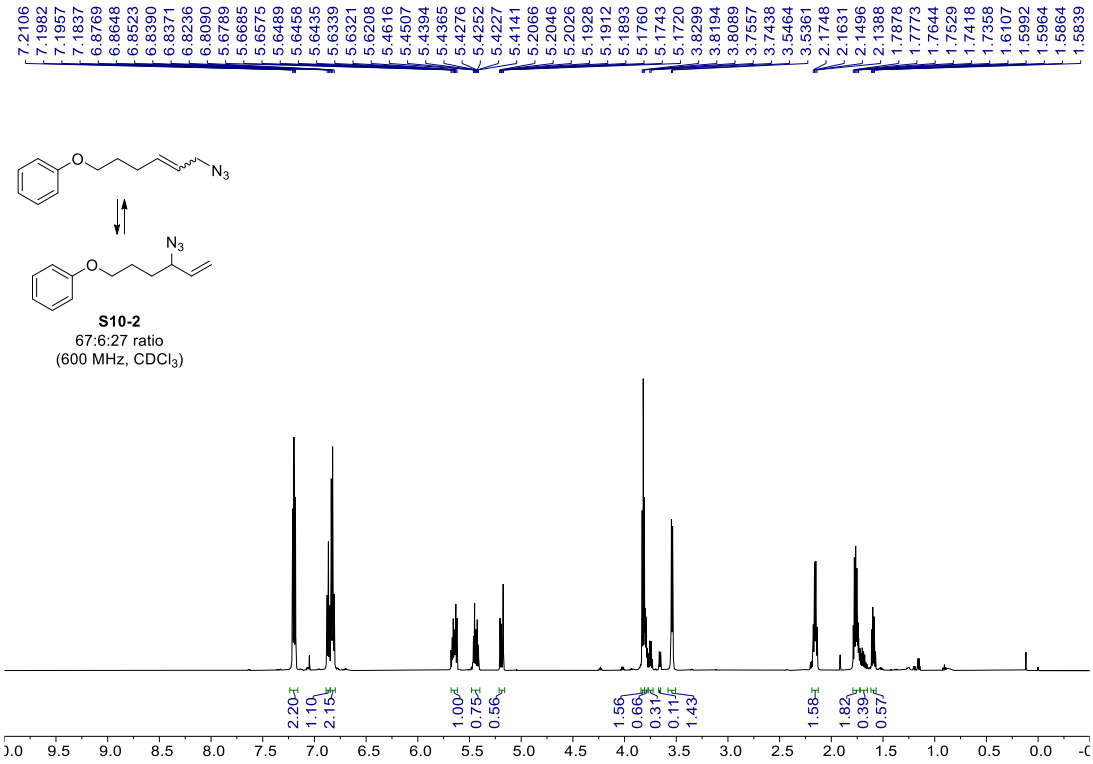
11
5:1 ratio
(400 MHz, $CDCl_3$)

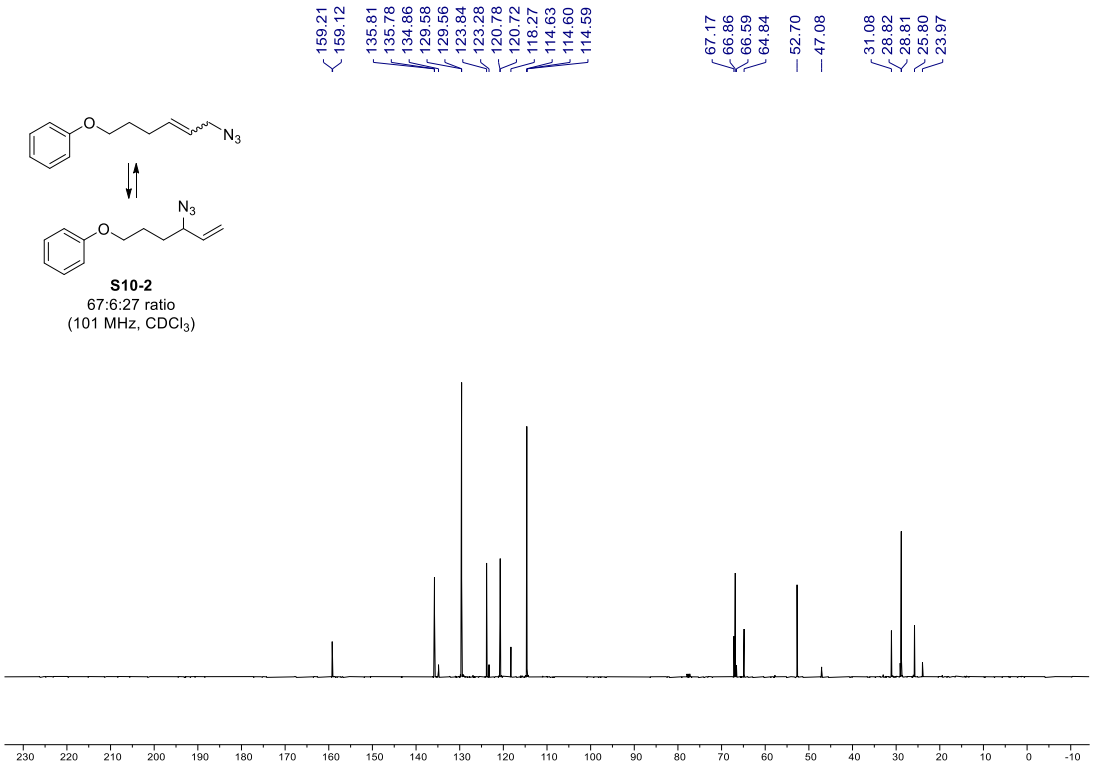


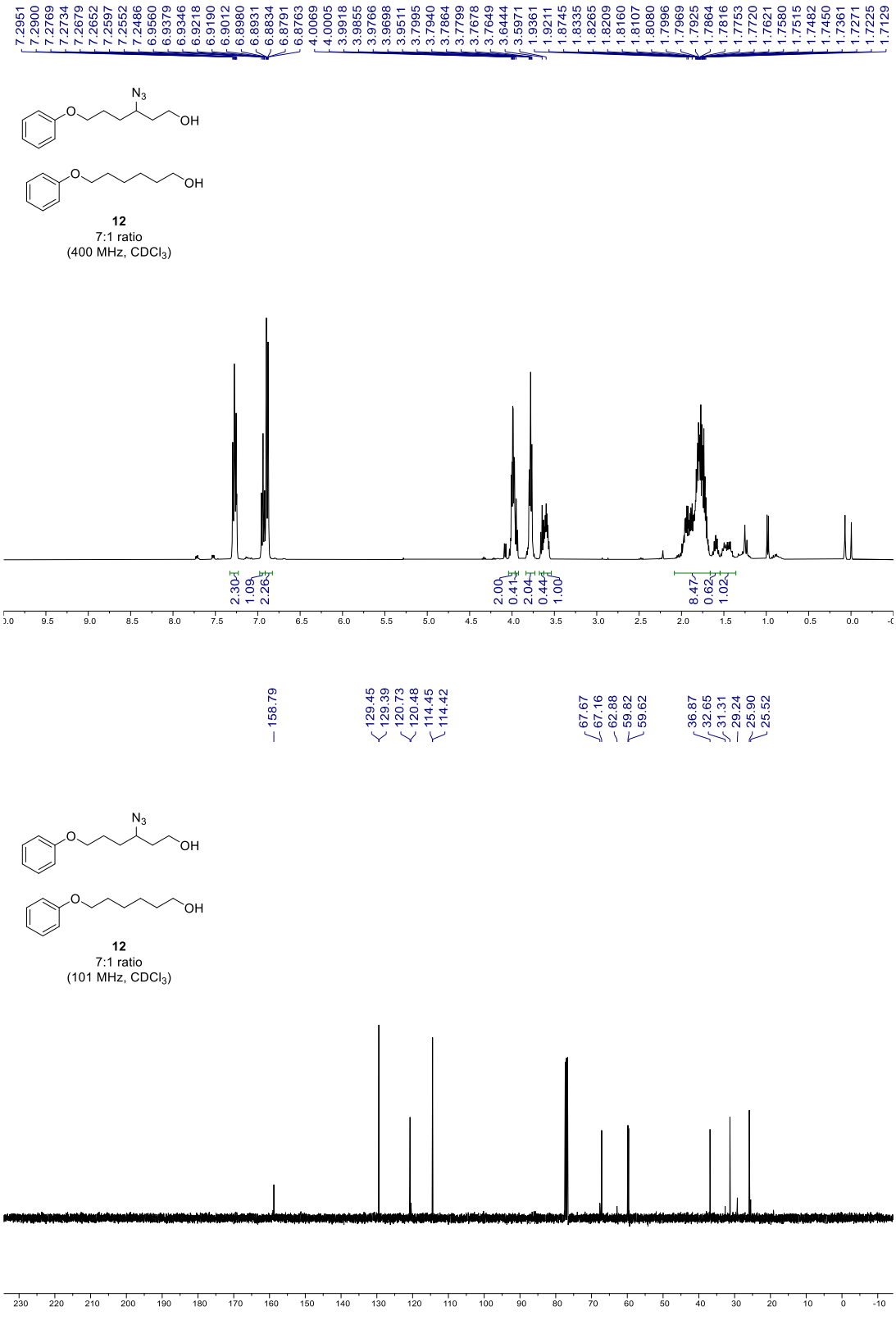


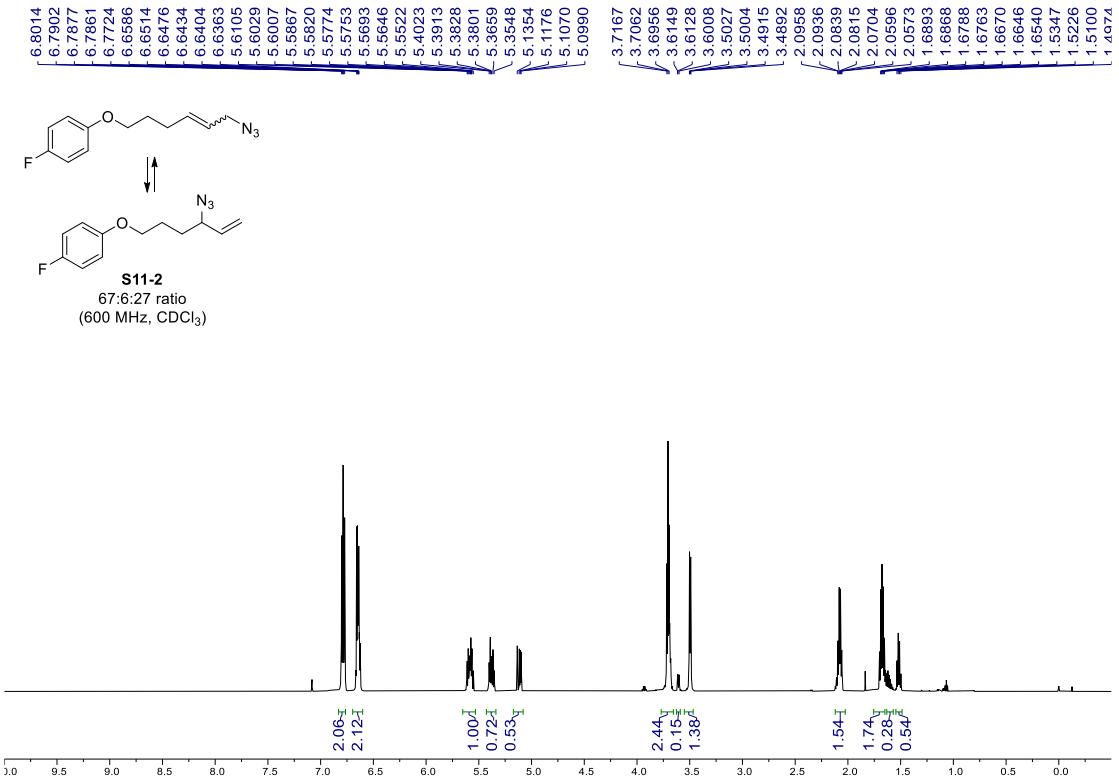
11
5:1 ratio
(101 MHz, $CDCl_3$)

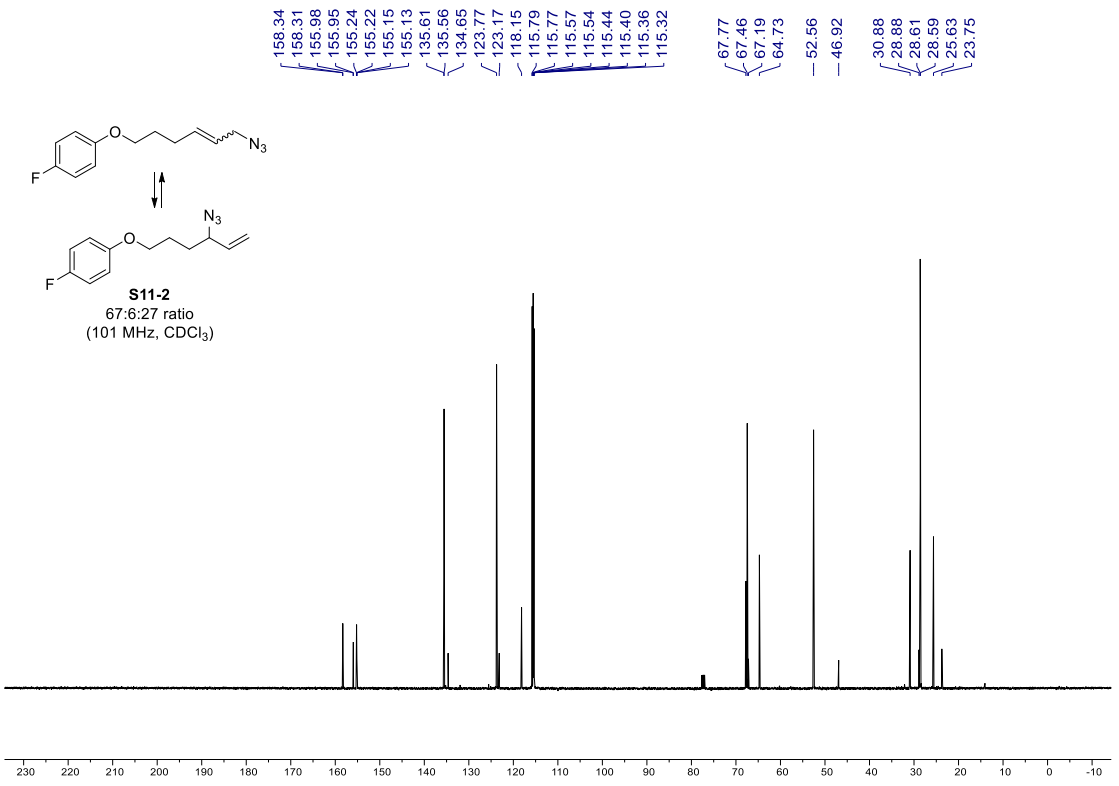


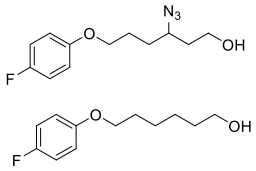

7.2106
7.1982
7.1957
7.1837
6.8769
6.8648
6.8523
6.8390
6.8371
6.8236
6.8090
5.6789
5.6685
5.6575
5.6489
5.6458
5.6435
5.6339
5.6321
5.6208
5.4616
5.4507
5.4394
5.4365
5.4276
5.4252
5.4227
5.4141
5.2066
5.2046
5.2026
5.1928
5.1912
5.1893
5.1760
5.1743
5.1720
3.8299
3.8194
3.8089
3.7557
3.7438
3.5464
3.5361
2.1748
2.1631
2.1496
2.1388
1.7878
1.7773
1.7644
1.7529
1.7418
1.7358
1.6107
1.5992
1.5964
1.5864
1.5839
N3
N3
O
O
S10-2
67:6:27 ratio
(600 MHz, CDCl3)
2.20
1.10
2.15
1.00
0.75
0.56
1.56
0.66
0.31
0.11
1.43
1.58
1.82
0.39
0.57
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


159.21
159.12
135.81
135.78
134.86
129.58
129.56
123.84
123.28
120.78
120.72
118.27
114.63
114.60
114.59
67.17
66.86
66.59
64.84
52.70
47.08
31.08
28.82
28.81
25.80
23.97
N3
N3
O
O
S10-2
67:6:27 ratio
(101 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

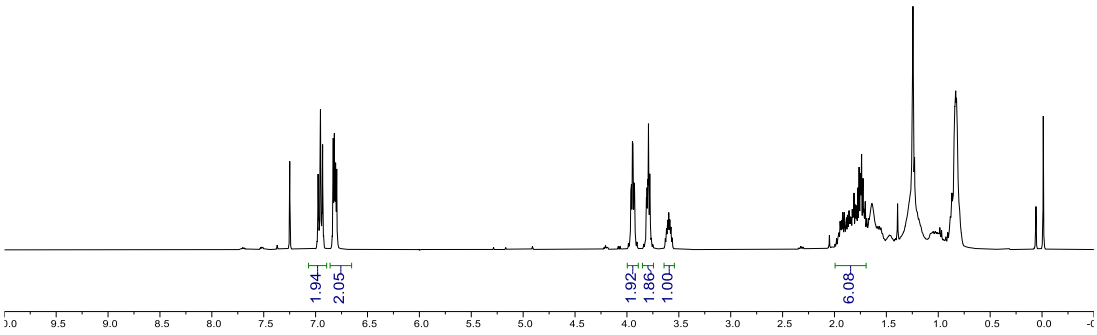

7.2951
7.2900
7.2769
7.2734
7.2679
7.2652
7.2597
7.2552
7.2486
6.9560
6.9379
6.9346
6.9218
6.9190
6.9012
6.8980
6.8931
6.8834
6.8791
6.8763
4.0069
4.0005
3.9918
3.9855
3.9766
3.9698
3.9511
3.7995
3.7940
3.7864
3.7799
3.7678
3.7649
3.6444
3.5971
1.9361
1.9211
1.8745
1.8335
1.8265
1.8209
1.8160
1.8107
1.8080
1.7996
1.7969
1.7925
1.7864
1.7816
1.7753
1.7720
1.7621
1.7580
1.7515
1.7482
1.7450
1.7361
1.7271
1.7225
1.7129
N3
OH
O
12
7:1 ratio
(400 MHz, CDCl3)
2.30
1.09
2.26
2.00
0.41
2.04
0.44
1.00
8.47
0.62
1.02
158.79
129.45
129.39
120.73
120.48
114.45
114.42
67.67
67.16
62.88
59.82
59.62
36.87
32.65
31.31
29.24
25.90
25.52
12
7:1 ratio
(101 MHz, CDCl3)

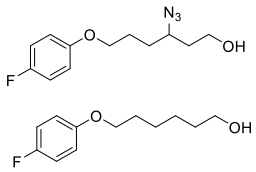

S11-2
67:6:27 ratio
(600 MHz, CDCl3)


S11-2
67:6:27 ratio
(101 MHz, CDCl3)

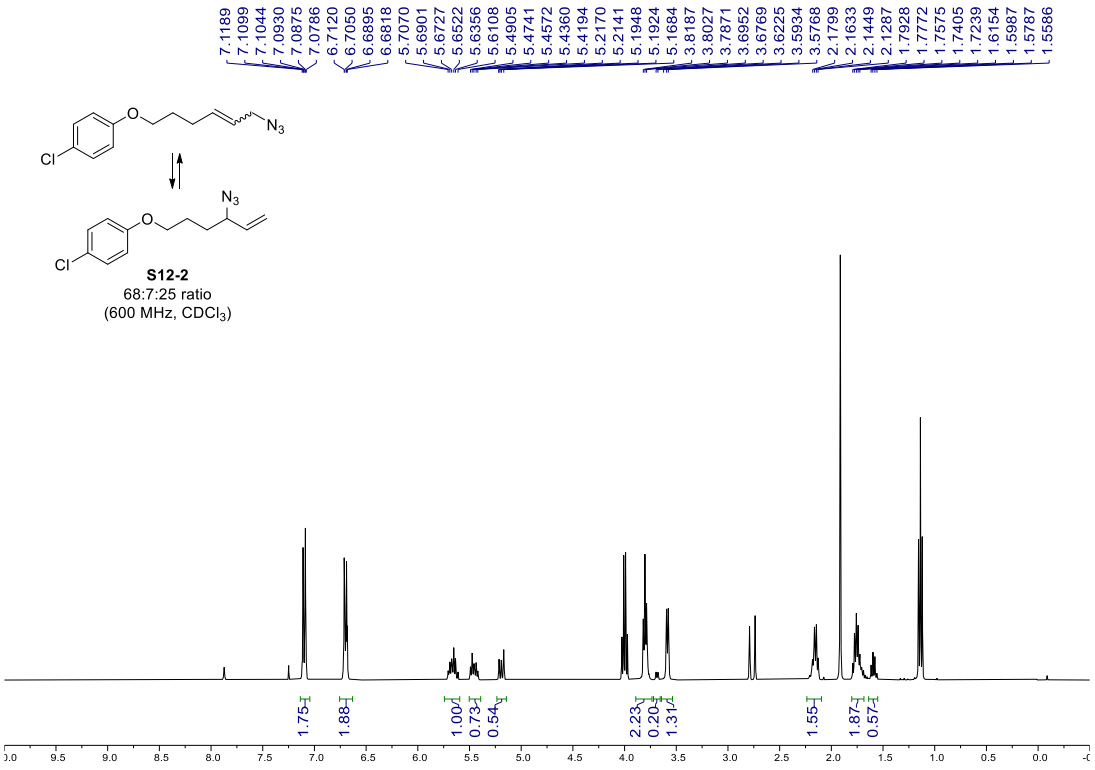


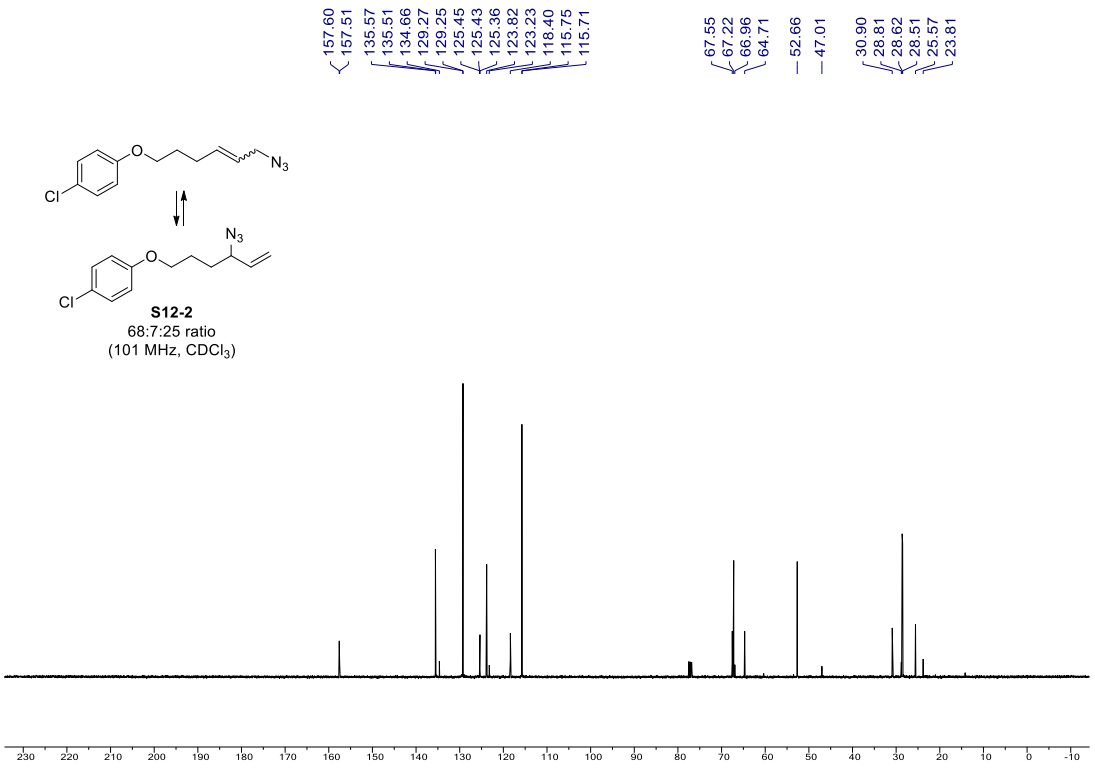
13
>30:1 ratio
(400 MHz, $CDCl_3$)

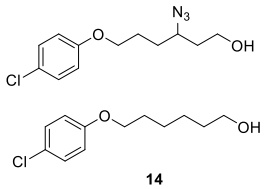




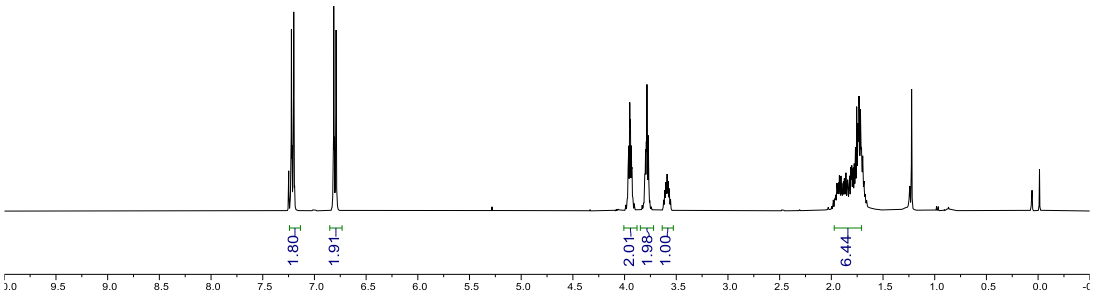
13
>30:1 ratio
(101 MHz, $CDCl_3$)

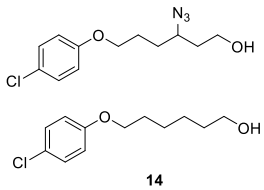

7.1189
7.1099
7.1044
7.0930
7.0875
7.0786
6.7120
6.7050
6.6895
6.6818
5.7070
5.6901
5.6727
5.6522
5.6356
5.6108
5.4905
5.4741
5.4572
5.4360
5.4194
5.2170
5.2141
5.1948
5.1924
5.1684
3.8187
3.8027
3.7871
3.6952
3.6769
3.6225
3.5934
3.5768
2.1799
2.1633
2.1449
2.1287
1.7928
1.7772
1.7575
1.7405
1.7239
1.6154
1.5987
1.5787
1.5586
Cl
O
N3
S12-2
68:7:25 ratio
(600 MHz, CDCl3)
1.75
1.88
1.00
0.73
0.54
2.23
0.20
1.31
1.55
1.87
0.57


157.60
157.51
135.57
135.51
134.66
129.27
129.25
125.45
125.43
125.36
123.82
123.23
118.40
115.75
115.71
67.55
67.22
66.96
64.71
52.66
47.01
30.90
28.81
28.62
28.51
25.57
23.81
Cl
O
N3
S12-2
68:7:25 ratio
(101 MHz, CDCl3)

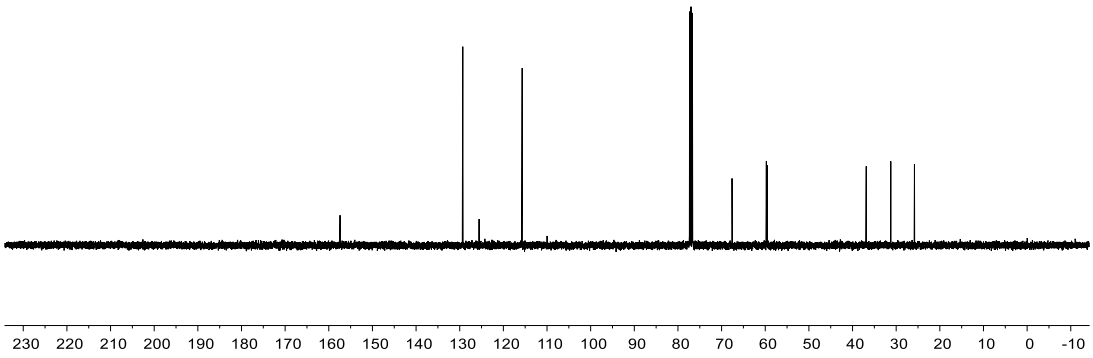


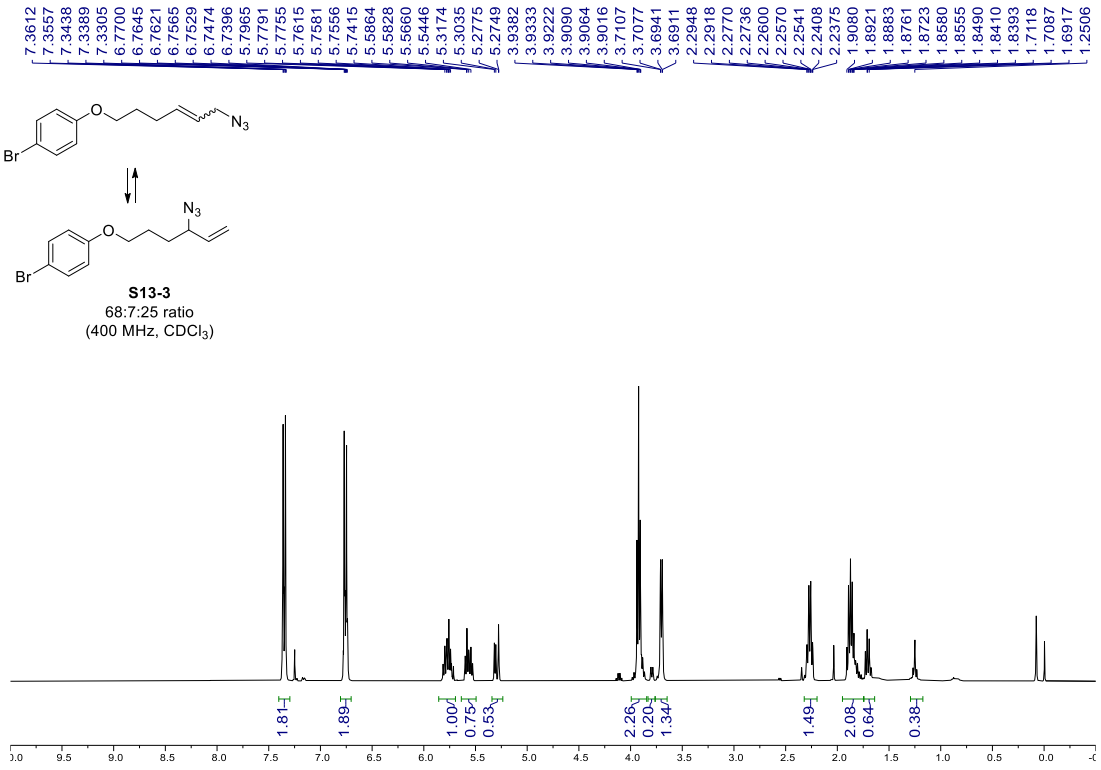
14
>30:1 ratio
(400 MHz, $CDCl_3$)

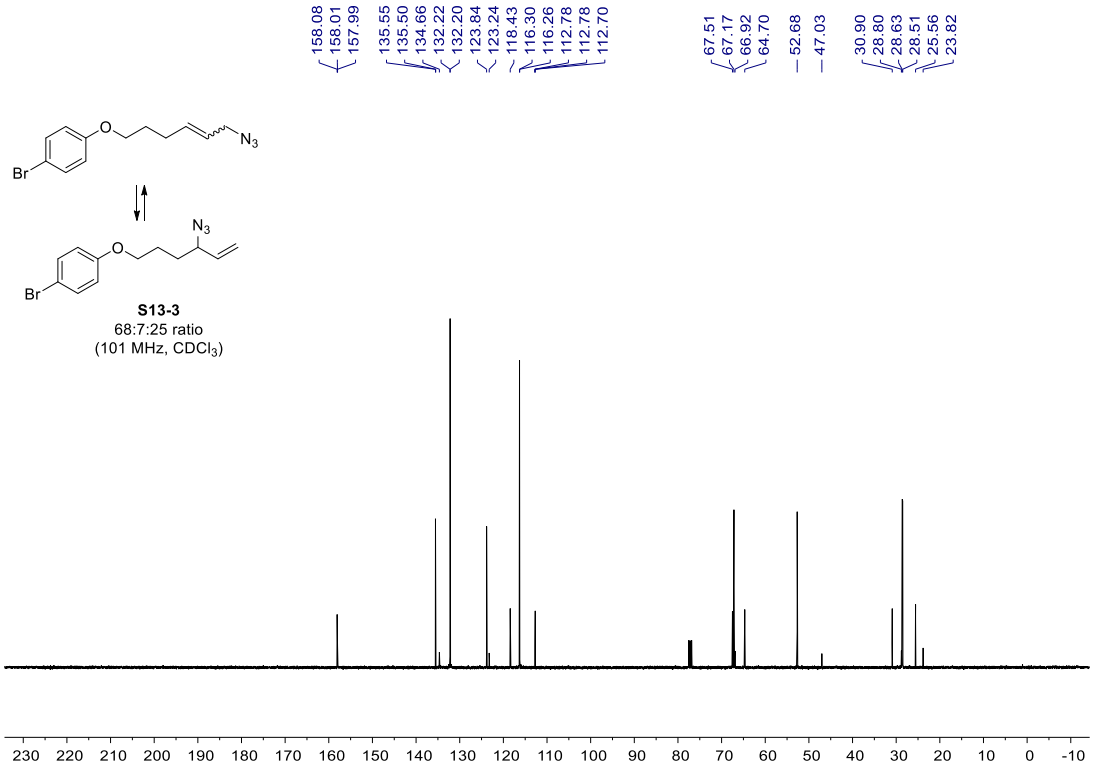


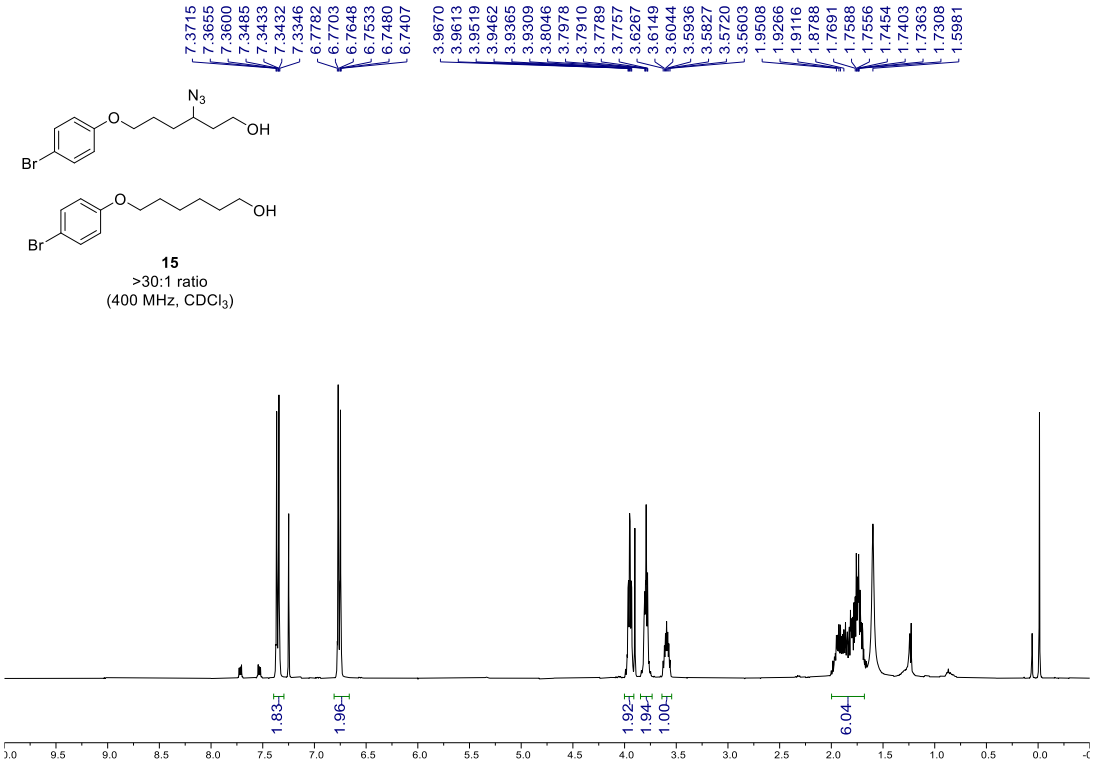


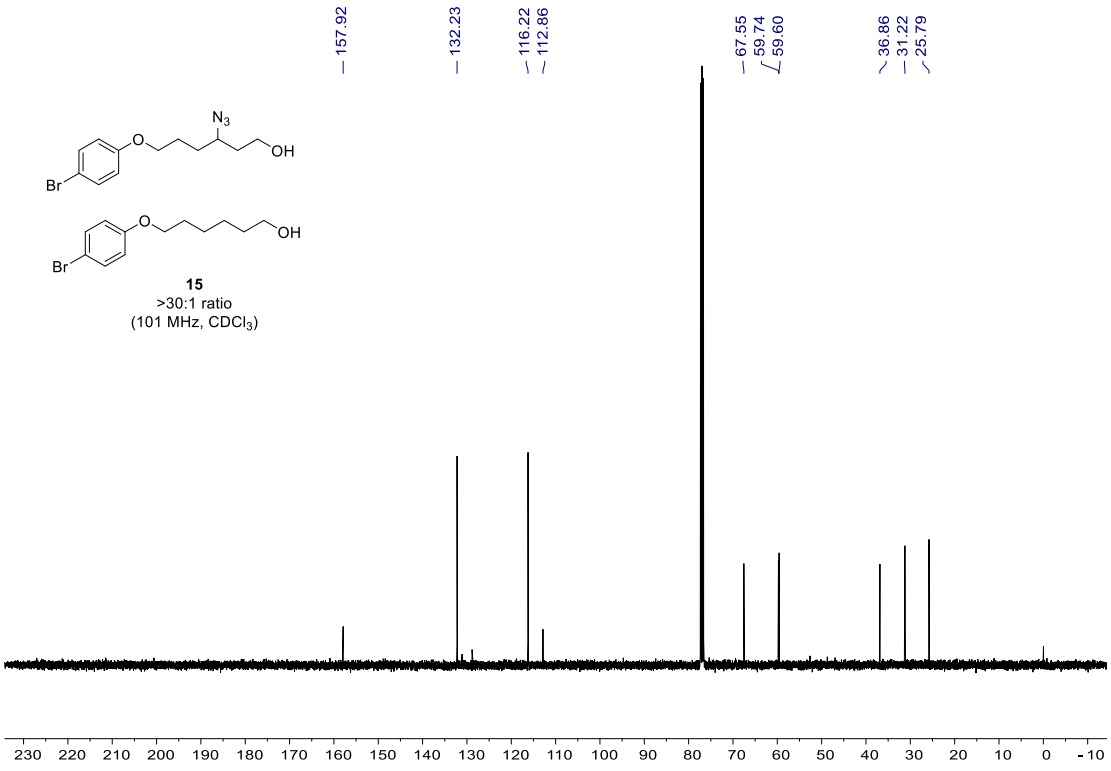
14
>30:1 ratio
(101 MHz, $CDCl_3$)

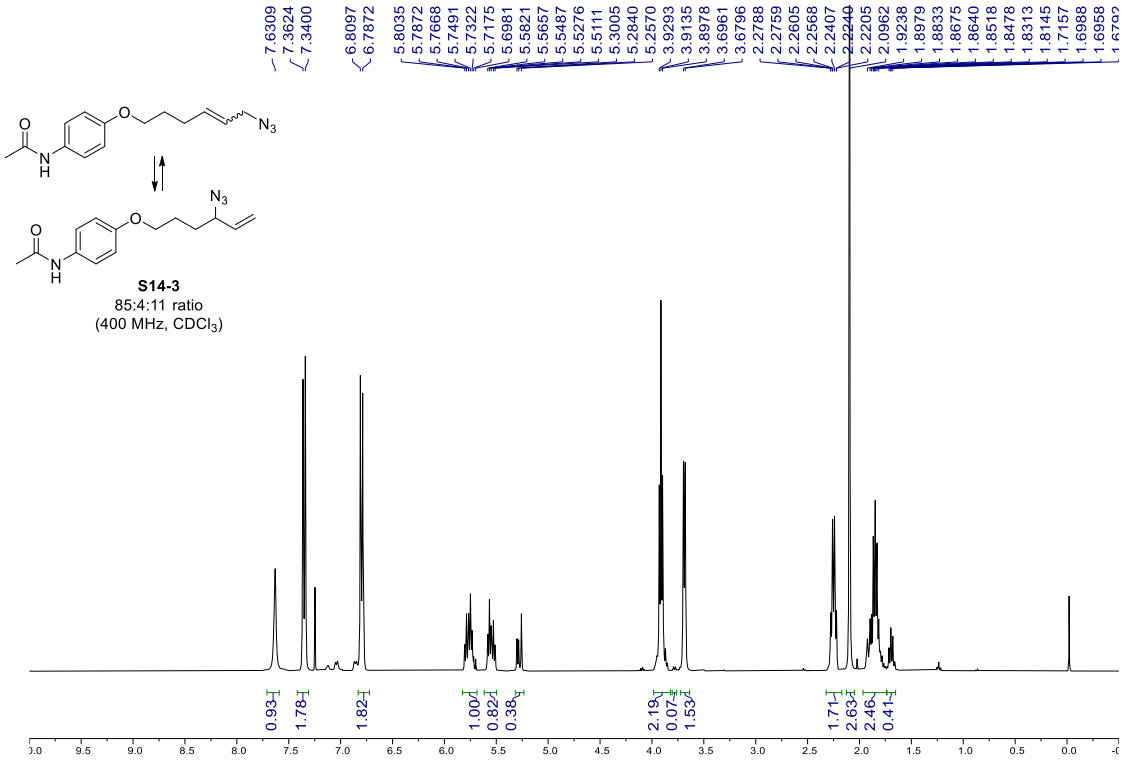


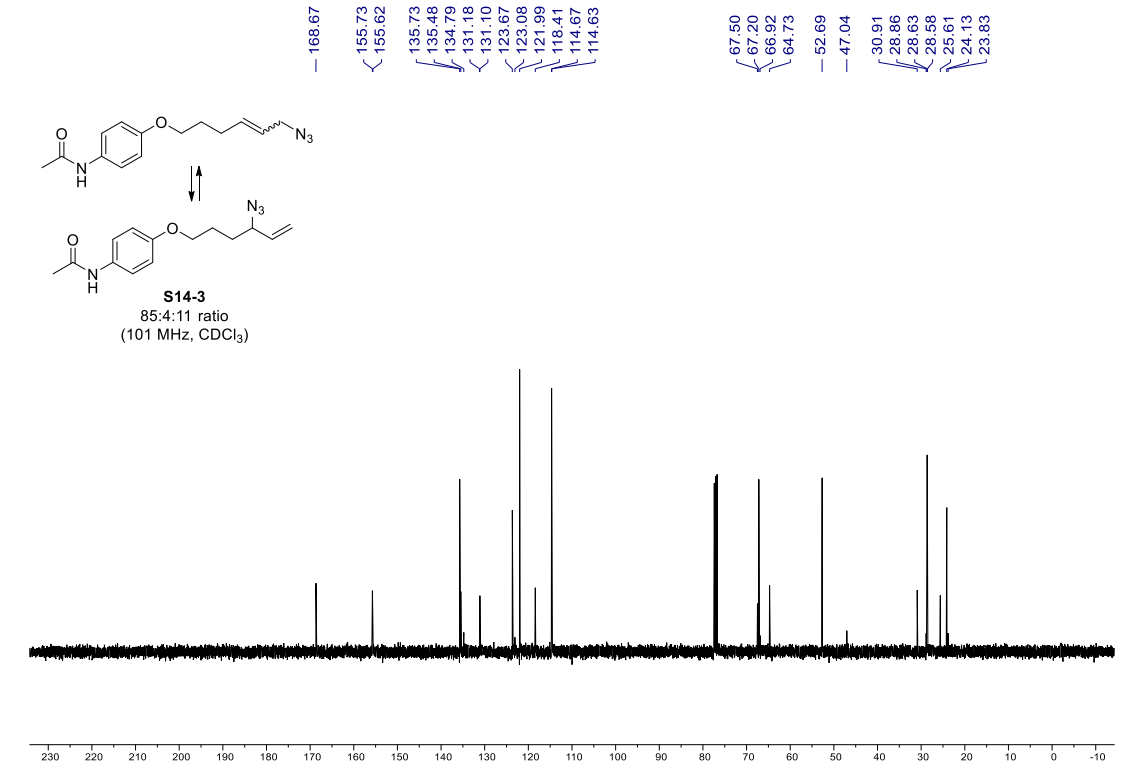

7.3612
7.3557
7.3438
7.3389
7.3305
6.7700
6.7645
6.7621
6.7565
6.7529
6.7474
6.7396
5.7965
5.7791
5.7755
5.7615
5.7581
5.7556
5.7415
5.5864
5.5828
5.5660
5.5446
5.3174
5.3035
5.2775
5.2749
3.9382
3.9333
3.9222
3.9090
3.9064
3.9016
3.7107
3.7077
3.6941
3.6911
2.2948
2.2918
2.2770
2.2736
2.2600
2.2570
2.2541
2.2408
2.2375
1.9080
1.8921
1.8883
1.8761
1.8723
1.8580
1.8555
1.8490
1.8410
1.8393
1.7118
1.7087
1.6917
1.2506
Br
O
N3
S13-3
68:7:25 ratio
(400 MHz, CDCl3)
1.81
1.89
1.00
0.75
0.53
2.26
0.20
1.34
1.49
2.08
0.64
0.38

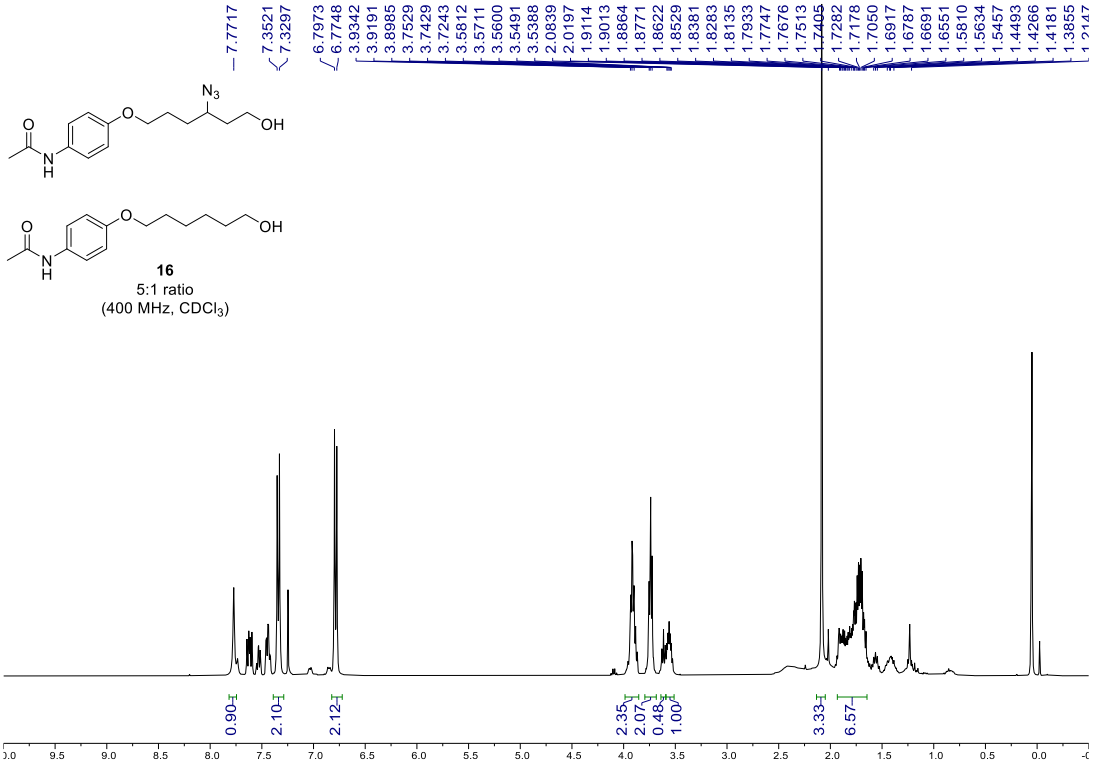

158.08
158.01
157.99
135.55
135.50
134.66
132.22
132.20
123.84
123.24
118.43
116.30
116.26
112.78
112.78
112.70
67.51
67.17
66.92
64.70
52.68
47.03
30.90
28.80
28.63
28.51
25.56
23.82
Br
O
N3
S13-3
68:7:25 ratio
(101 MHz, CDCl3)

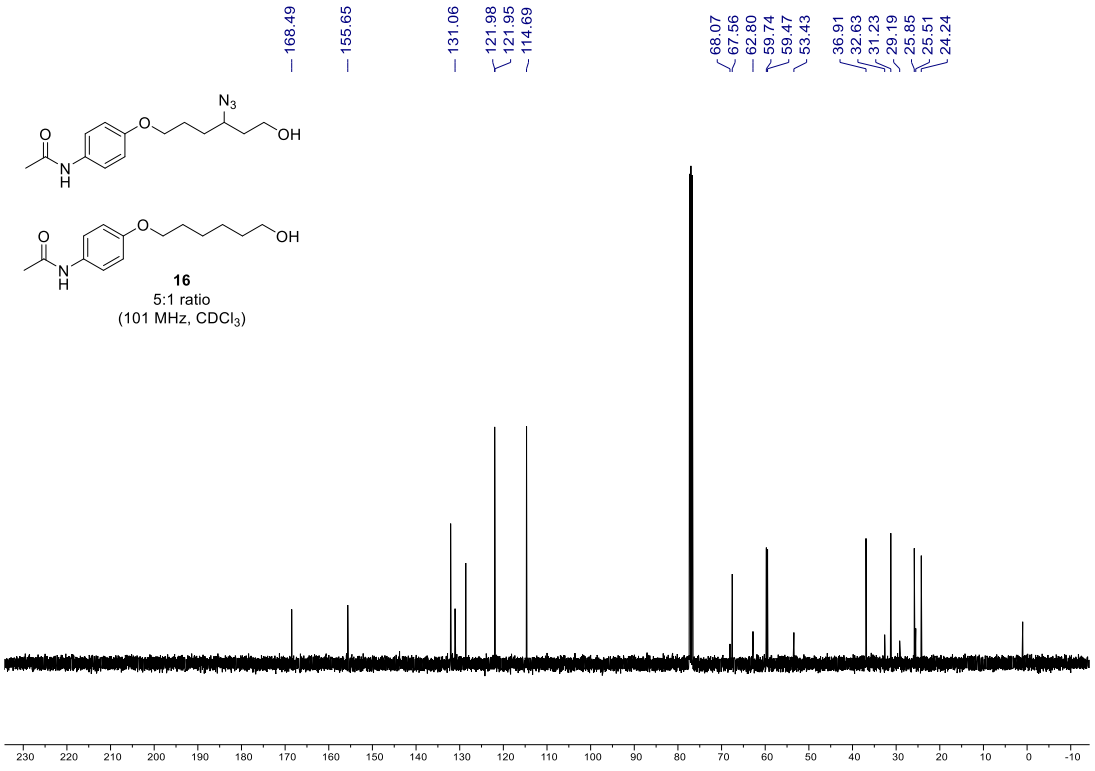

7.3715
7.3655
7.3600
7.3485
7.3433
7.3432
7.3346
6.7782
6.7703
6.7648
6.7533
6.7480
6.7407
3.9670
3.9613
3.9519
3.9462
3.9365
3.9309
3.8046
3.7978
3.7910
3.7789
3.7757
3.6267
3.6149
3.6044
3.5936
3.5827
3.5720
3.5603
1.9508
1.9266
1.9116
1.8788
1.7691
1.7588
1.7556
1.7454
1.7403
1.7363
1.7308
1.5981
N3
O
OH
Br
15
>30:1 ratio
(400 MHz, CDCl3)
1.83
1.96
1.92
1.94
1.00
6.04

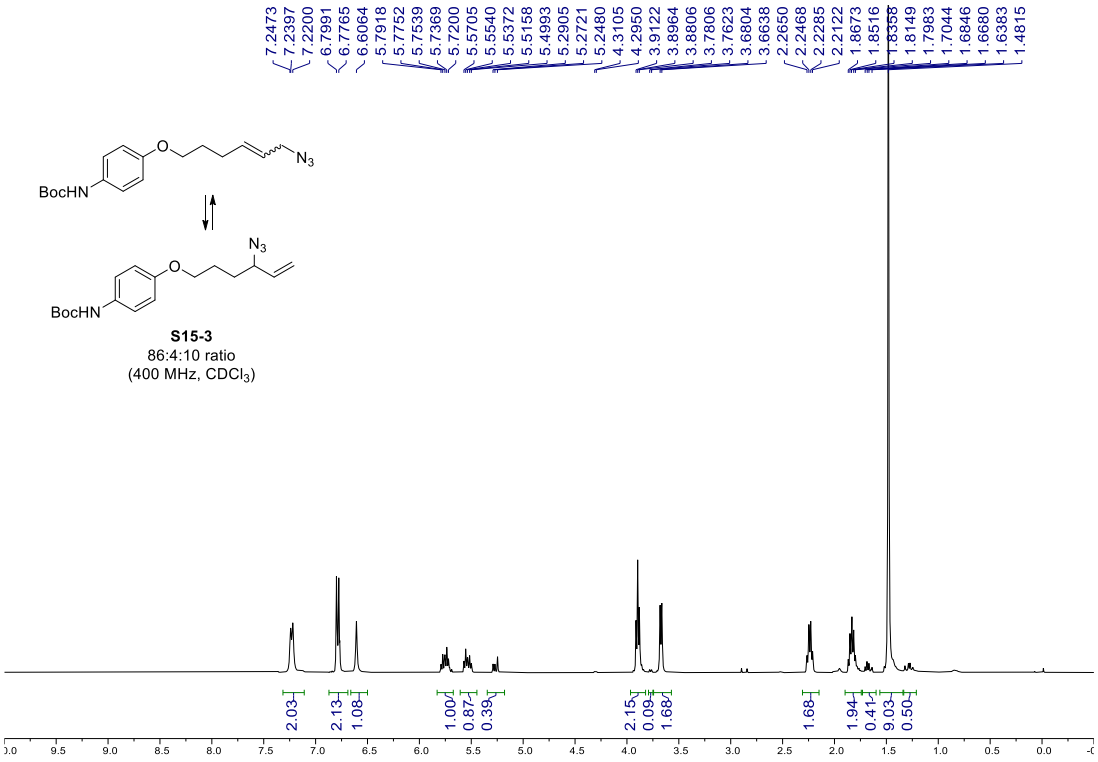

157.92
132.23
116.22
112.86
67.55
59.74
59.60
36.86
31.22
25.79
N3
O
OH
Br
15
>30:1 ratio
(101 MHz, CDCl3)

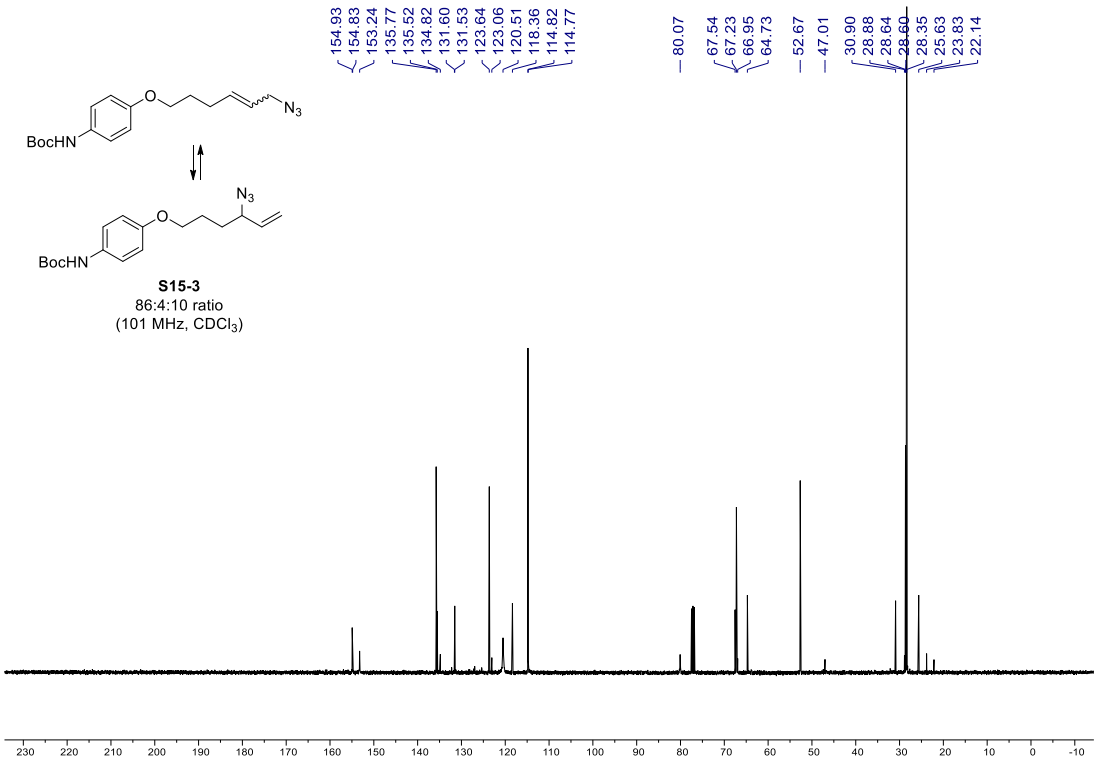

7.6309
7.3624
7.3400
6.8097
6.7872
5.8035
5.7872
5.7668
5.7491
5.7322
5.7175
5.6981
5.5821
5.5657
5.5487
5.5276
5.5111
5.3005
5.2840
5.2570
3.9293
3.9135
3.8978
3.6961
3.6796
2.2788
2.2759
2.2605
2.2568
2.2407
2.2240
2.2205
2.0962
1.9238
1.8979
1.8833
1.8675
1.8640
1.8518
1.8478
1.8313
1.8145
1.7157
1.6988
1.6958
0.93
1.78
1.82
1.00
0.82
0.38
2.19
0.07
1.53
1.71
2.63
2.46
0.41
S14-3
85:4:11 ratio
(400 MHz, CDCl3)

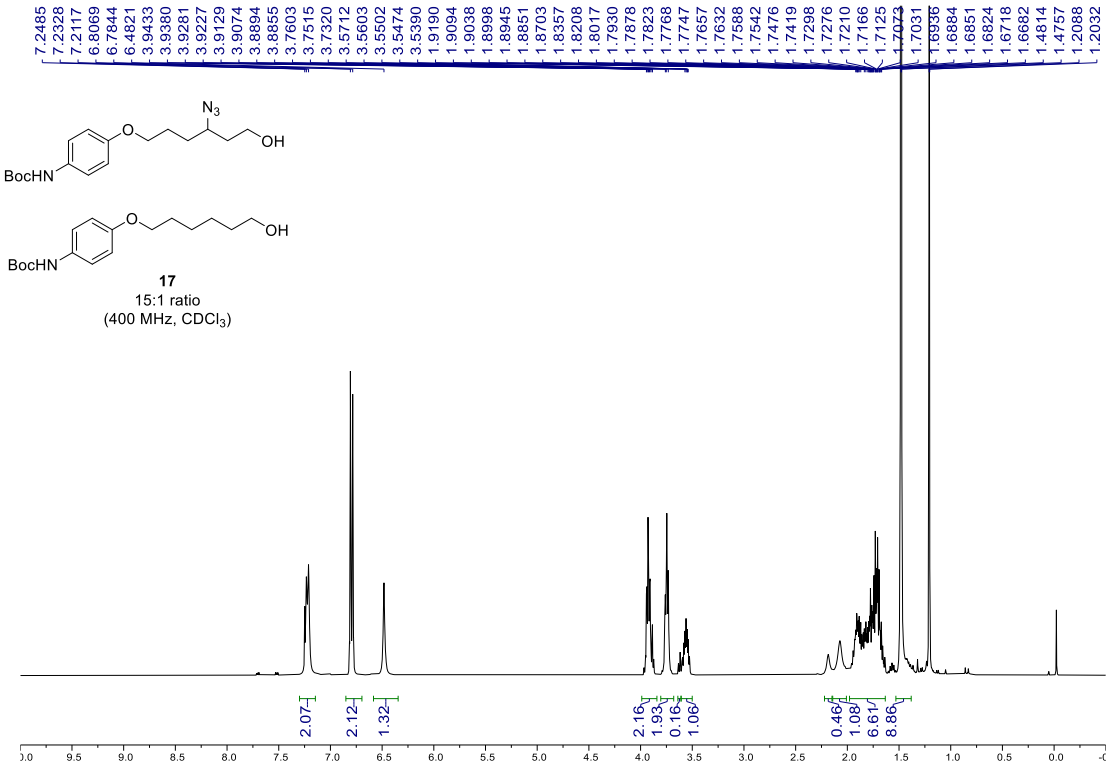

168.67
155.73
155.62
135.73
135.48
134.79
131.18
131.10
123.67
123.08
121.99
118.41
114.67
114.63
67.50
67.20
66.92
64.73
52.69
47.04
30.91
28.86
28.63
28.58
25.61
24.13
23.83
S14-3
85:4:11 ratio
(101 MHz, CDCl3)

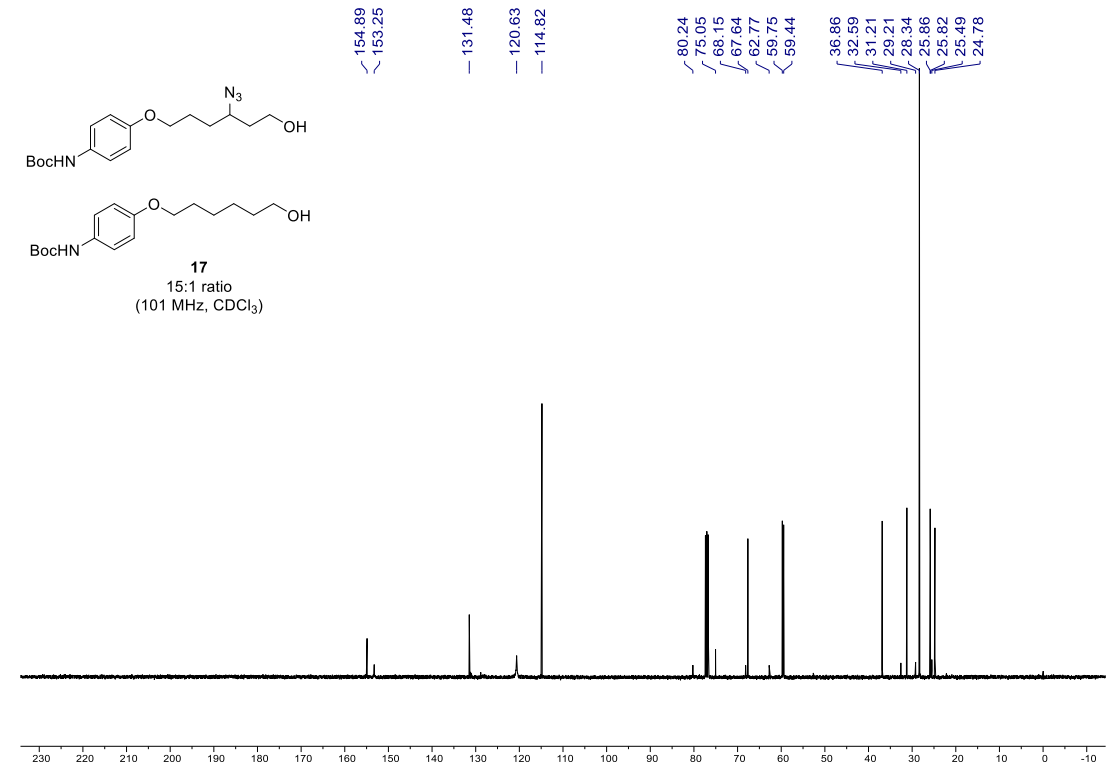

7.7717
7.3521
7.3297
6.7973
6.7748
3.9342
3.9191
3.8985
3.7529
3.7429
3.7243
3.5812
3.5711
3.5600
3.5491
3.5388
2.0839
2.0197
1.9114
1.9013
1.8864
1.8771
1.8622
1.8529
1.8381
1.8283
1.8135
1.7933
1.7747
1.7676
1.7513
1.7405
1.7282
1.7178
1.7050
1.6917
1.6787
1.6691
1.6551
1.5810
1.5634
1.5457
1.4493
1.4266
1.4181
1.3855
0.90
2.10
2.12
2.35
2.07
0.48
1.00
3.33
6.57
N3
OH
16
5:1 ratio
(400 MHz, CDCl3)

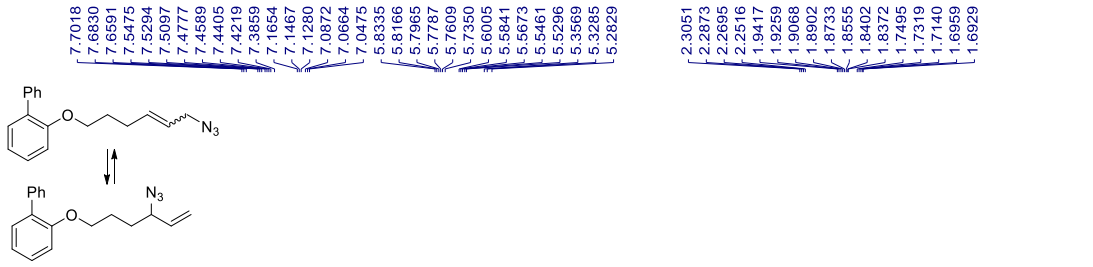

168.49
155.65
131.06
121.98
121.95
114.69
68.07
67.56
62.80
59.74
59.47
53.43
36.91
32.63
31.23
29.19
25.85
25.51
24.24
N3
OH
16
5:1 ratio
(101 MHz, CDCl3)


7.2473
7.2397
7.2200
6.7991
6.7765
6.6064
5.7918
5.7752
5.7539
5.7369
5.7200
5.5705
5.5540
5.5372
5.5158
5.4993
5.2905
5.2721
5.2480
4.3105
4.2950
3.9122
3.8964
3.8806
3.7806
3.7623
3.6804
3.6638
2.2650
2.2468
2.2285
2.2122
1.8673
1.8516
1.8358
1.8149
1.7983
1.7044
1.6846
1.6680
1.6383
1.4815
BocHN
N3
S15-3
86:4:10 ratio
(400 MHz, CDCl3)
2.03
2.13
1.08
1.00
0.87
0.39
2.15
0.09
1.68
1.68
1.94
0.41
9.03
0.50

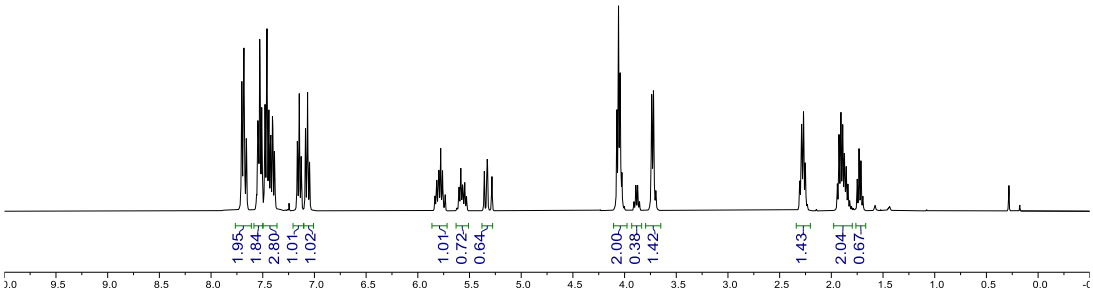

154.93
154.83
153.24
135.77
135.52
134.82
131.60
131.53
123.64
123.06
120.51
118.36
114.82
114.77
80.07
67.54
67.23
66.95
64.73
52.67
47.01
30.90
28.88
28.64
28.60
28.35
25.63
23.83
22.14
BocHN
N3
S15-3
86:4:10 ratio
(101 MHz, CDCl3)

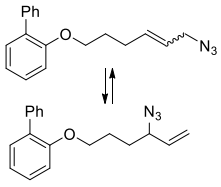

7.2485
7.2328
7.2117
6.8069
6.7844
6.4821
3.9433
3.9380
3.9281
3.9227
3.9129
3.9074
3.8894
3.8855
3.7603
3.7515
3.7320
3.5712
3.5603
3.5502
3.5474
3.5390
1.9190
1.9094
1.9038
1.8998
1.8945
1.8851
1.8703
1.8357
1.8208
1.8017
1.7930
1.7878
1.7823
1.7768
1.7747
1.7657
1.7632
1.7588
1.7542
1.7476
1.7419
1.7298
1.7276
1.7210
1.7166
1.7125
1.7073
1.7031
1.6936
1.6884
1.6851
1.6824
1.6718
1.6682
1.4814
1.4757
1.2088
1.2032
N3
O
OH
BocHN
17
15:1 ratio
(400 MHz, CDCl3)
2.07
2.12
1.32
2.16
1.93
0.16
1.06
0.46
1.08
6.61
8.86


154.89
153.25
131.48
120.63
114.82
80.24
75.05
68.15
67.64
62.77
59.75
59.44
36.86
32.59
31.21
29.21
28.34
25.86
25.82
25.49
24.78
N3
O
OH
BocHN
17
15:1 ratio
(101 MHz, CDCl3)

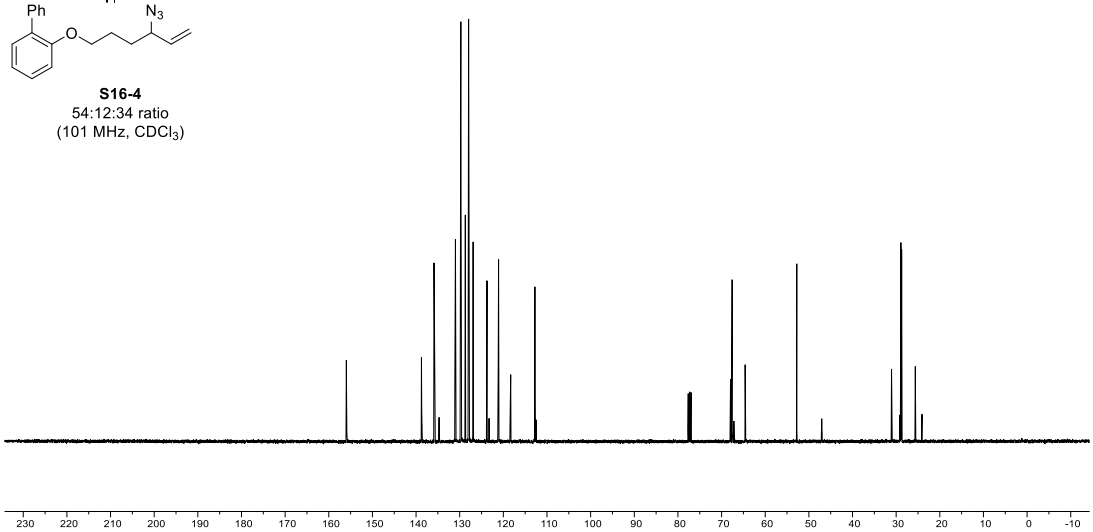


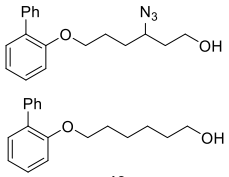
S16-4
54:12:34 ratio
(400 MHz, $CDCl_3$)



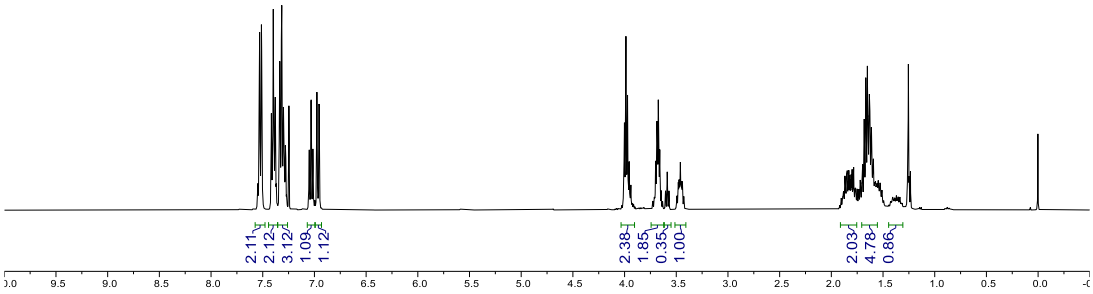


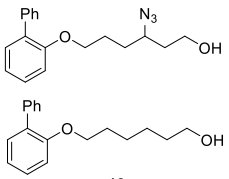
S16-4
54:12:34 ratio
(101 MHz, $CDCl_3$)



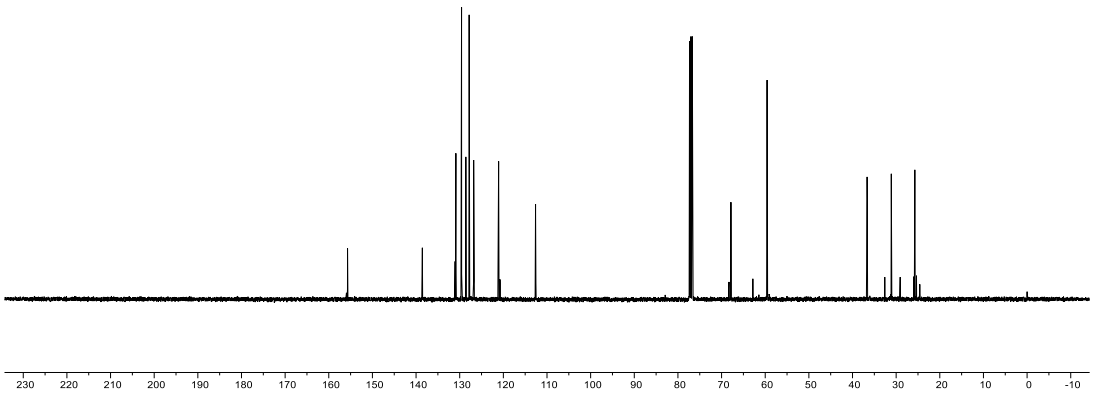


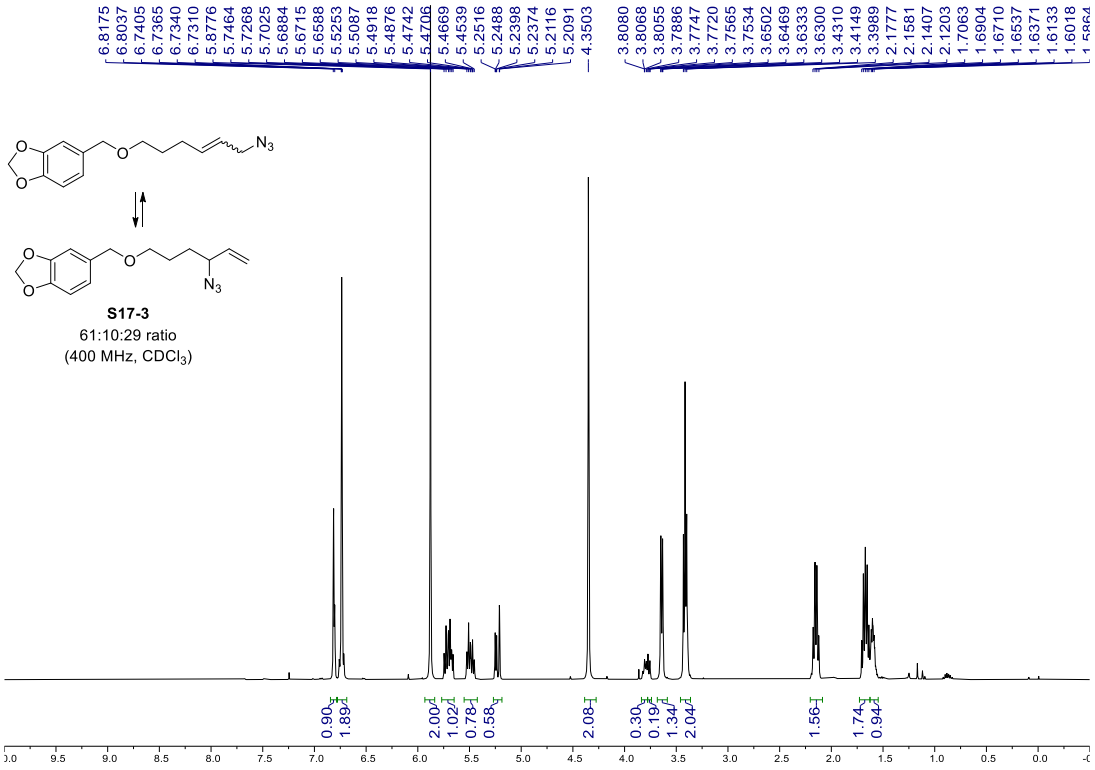
18
7:1 ratio
(400 MHz, $CDCl_3$)



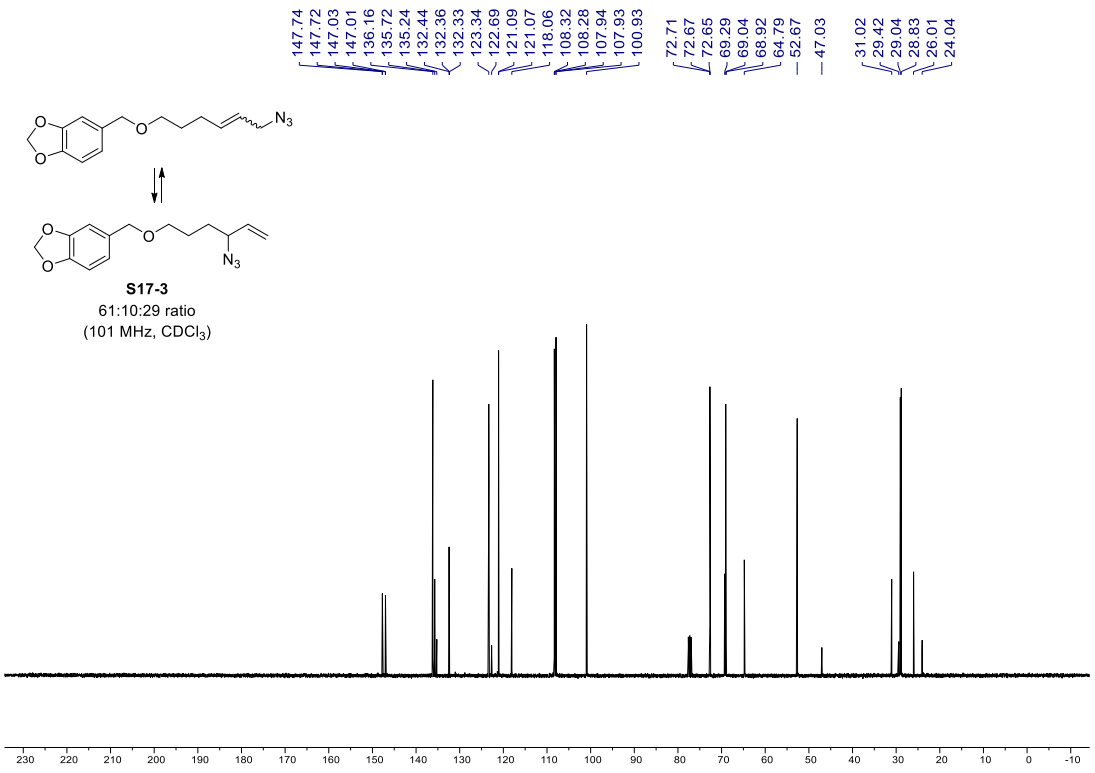


18
7:1 ratio
(101 MHz, $CDCl_3$)

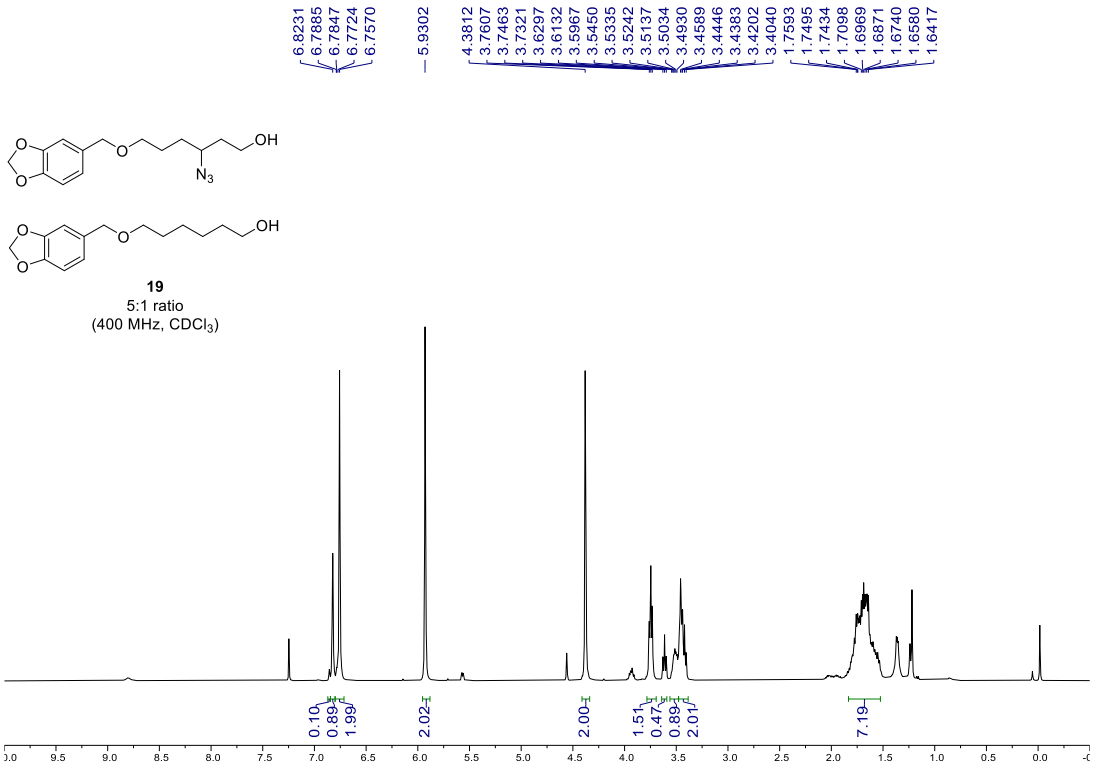


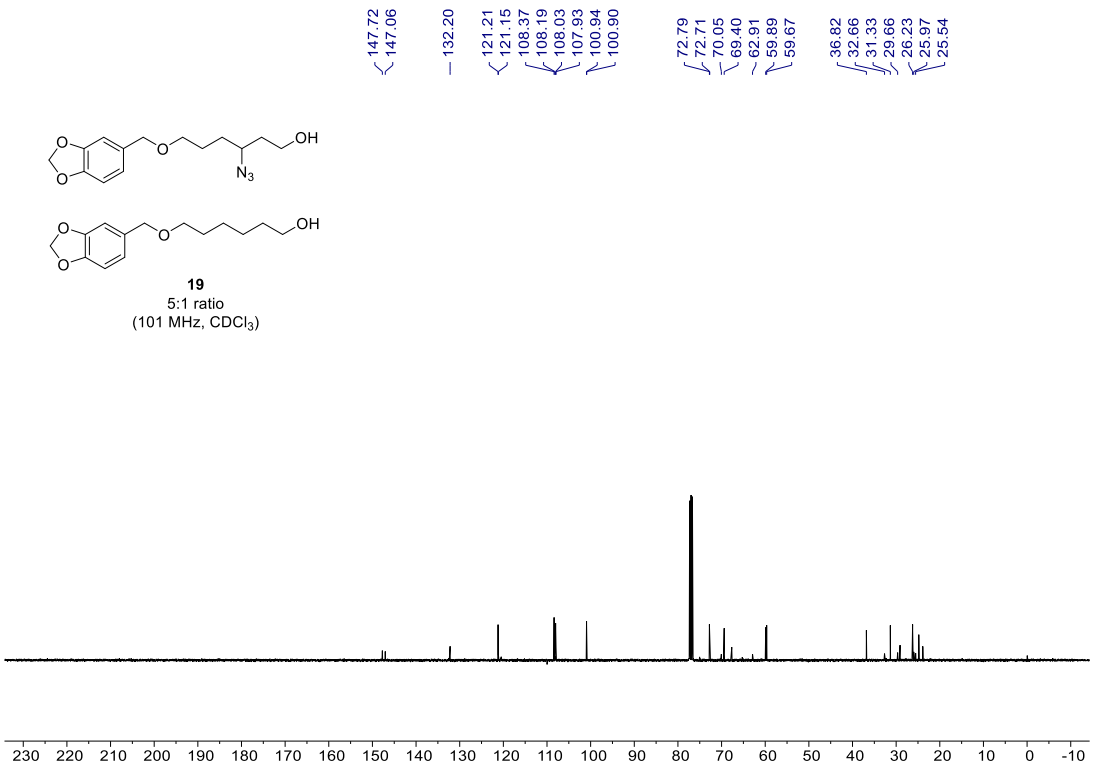


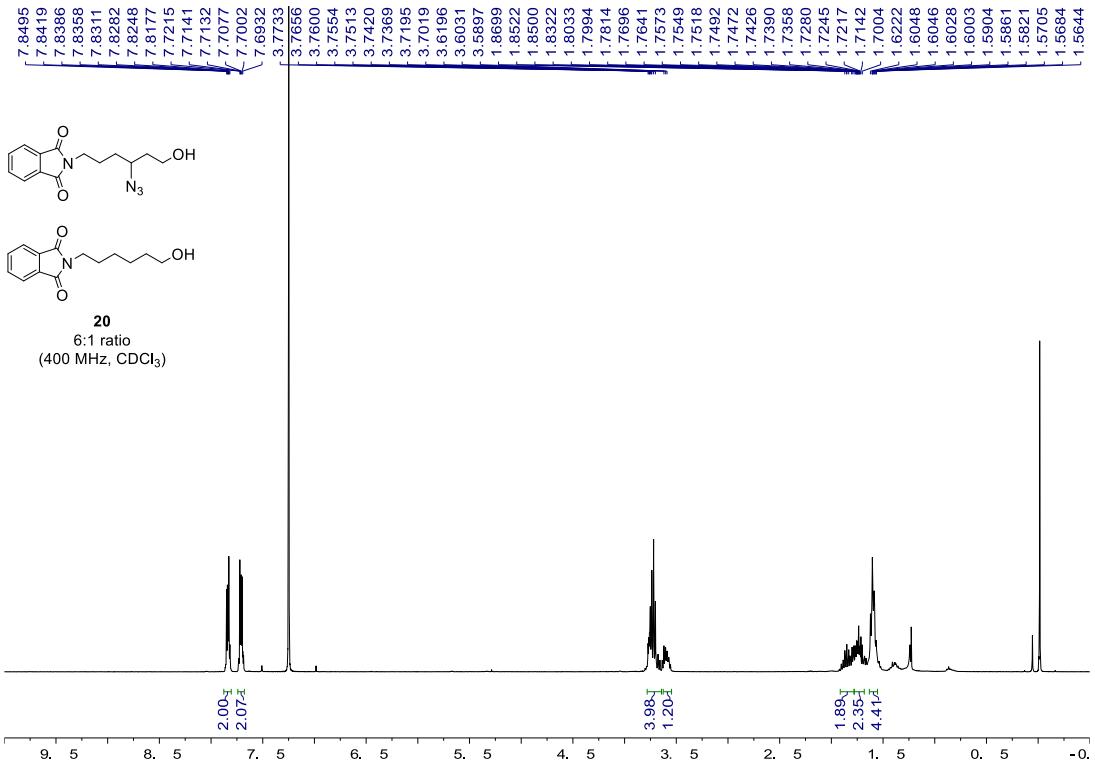
S17-3
61:10:29 ratio
(400 MHz, $CDCl_3$)

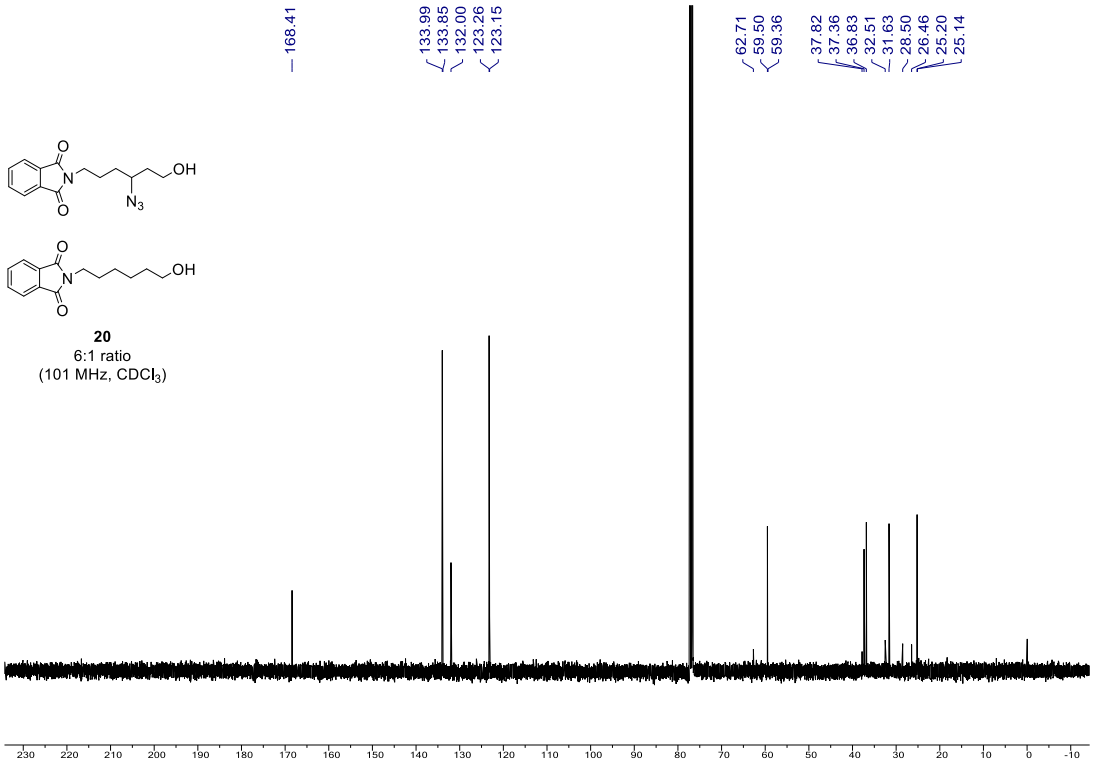


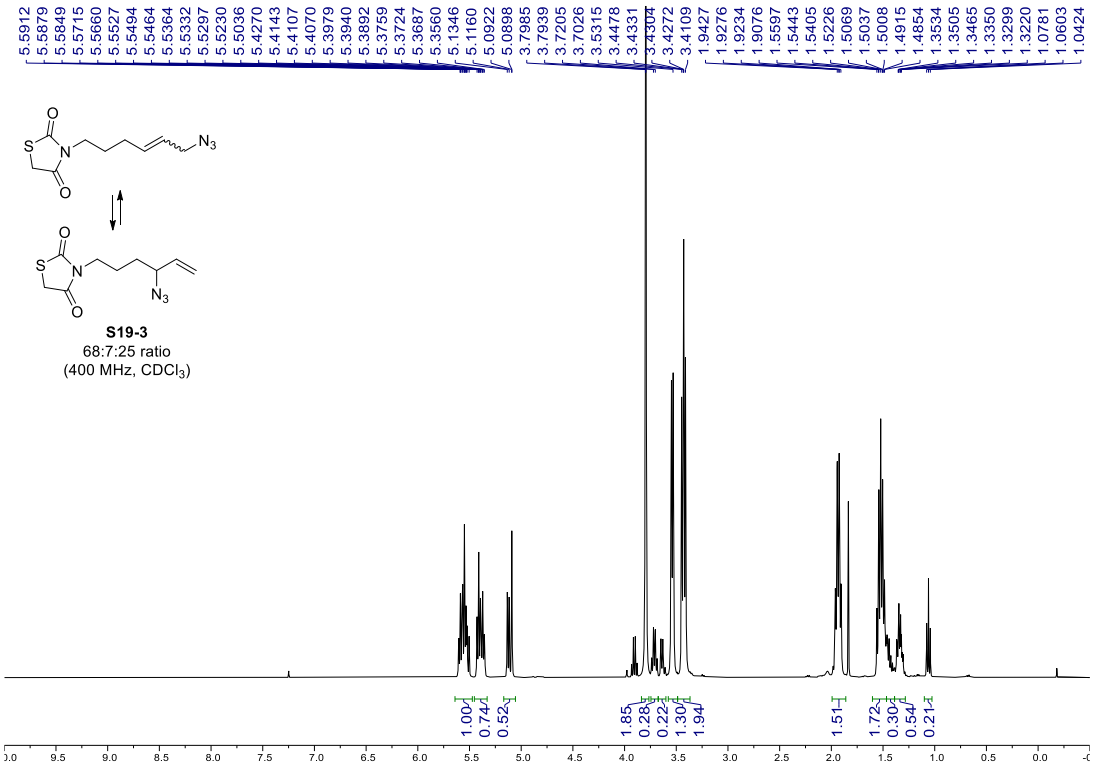
S17-3
61:10:29 ratio
(101 MHz, $CDCl_3$)


6.8231
6.7885
6.7847
6.7724
6.7570
5.9302
4.3812
3.7607
3.7463
3.7321
3.6297
3.6132
3.5967
3.5450
3.5335
3.5242
3.5137
3.5034
3.4930
3.4589
3.4446
3.4383
3.4202
3.4040
1.7593
1.7495
1.7434
1.7098
1.6969
1.6871
1.6740
1.6580
1.6417
OH
O
O
N3
OH
O
O
19
5:1 ratio
(400 MHz, CDCl3)
0.10
0.89
1.99
2.02
2.00
1.51
0.47
0.89
2.01
7.19

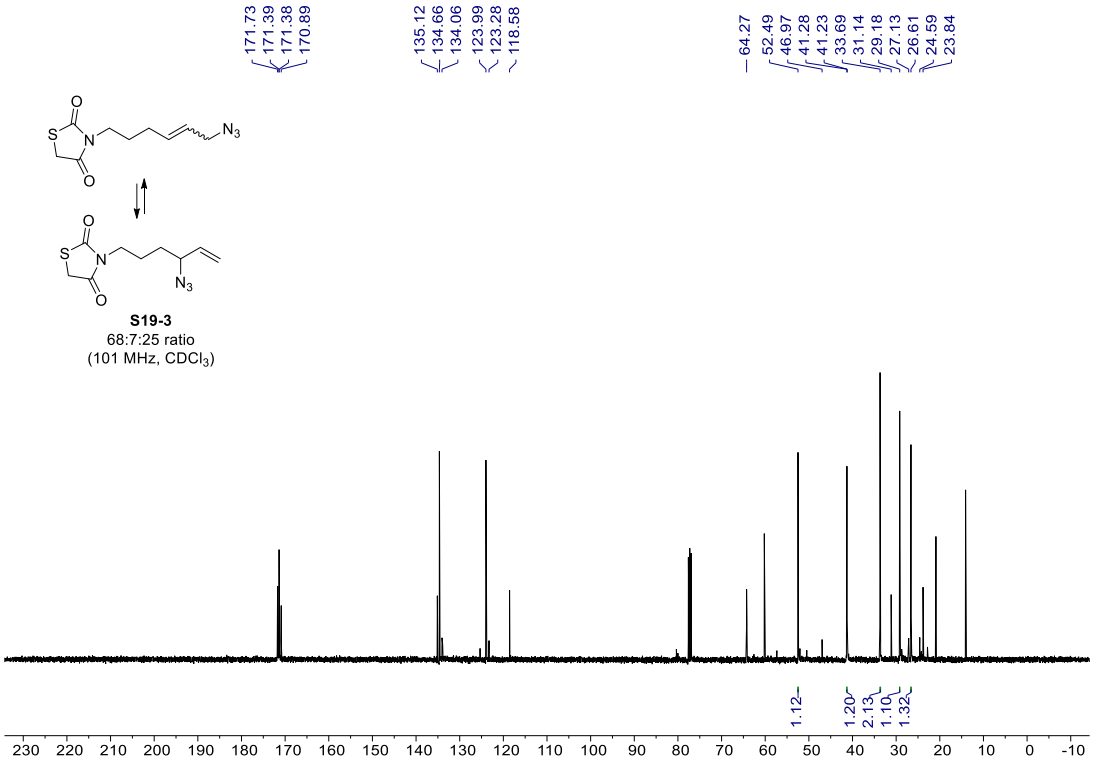

147.72
147.06
132.20
121.21
121.15
108.37
108.19
108.03
107.93
100.94
100.90
72.79
72.71
70.05
69.40
62.91
59.89
59.67
36.82
32.66
31.33
29.66
26.23
25.97
25.54
OH
O
O
N3
OH
O
O
19
5:1 ratio
(101 MHz, CDCl3)


7.8495
7.8419
7.8386
7.8358
7.8311
7.8282
7.8248
7.8177
7.7215
7.7141
7.7132
7.7077
7.7002
7.6932
3.7733
3.7656
3.7600
3.7554
3.7513
3.7420
3.7369
3.7195
3.7019
3.6196
3.6031
3.5897
1.8699
1.8522
1.8500
1.8322
1.8033
1.7994
1.7814
1.7696
1.7641
1.7573
1.7549
1.7518
1.7492
1.7472
1.7426
1.7390
1.7358
1.7280
1.7245
1.7217
1.7142
1.7004
1.6222
1.6048
1.6046
1.6028
1.6003
1.5904
1.5861
1.5821
1.5705
1.5684
1.5644
OH
N3
OH
20
6:1 ratio
(400 MHz, CDCl3)
2.00
2.07
3.98
1.20
1.89
2.35
4.41
9. 5
8. 5
7. 5
6. 5
5. 5
4. 5
3. 5
2. 5
1. 5
0. 5
-0.

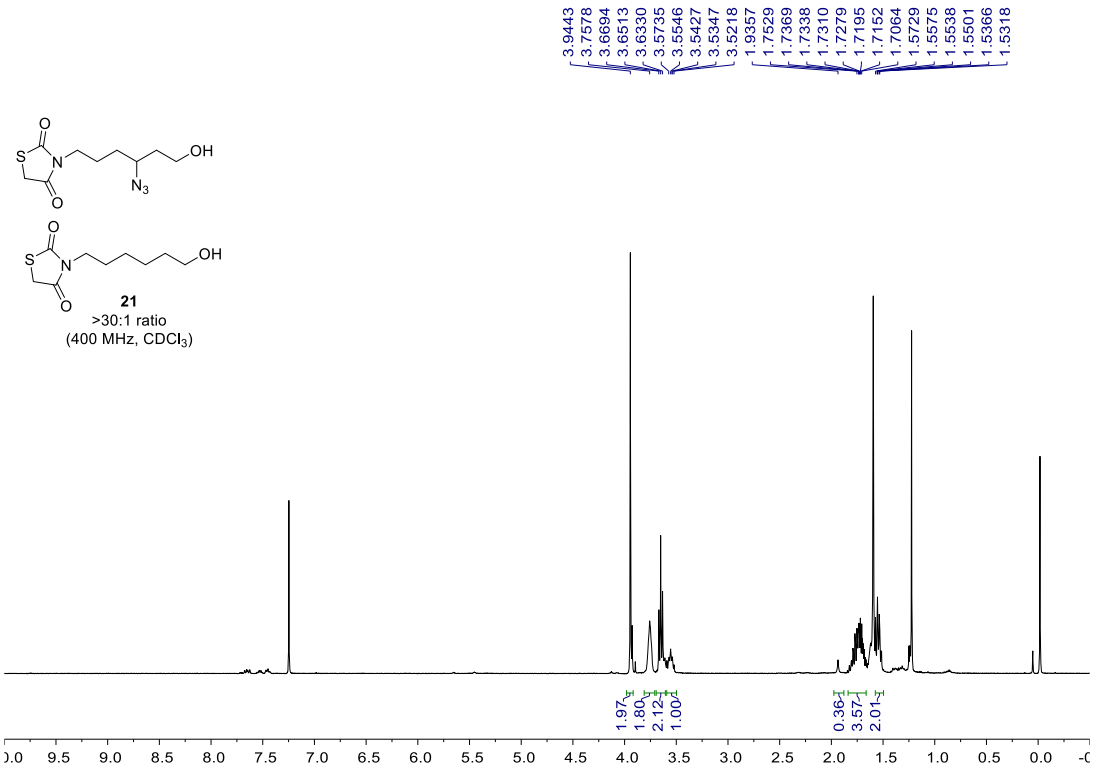

168.41
133.99
133.85
132.00
123.26
123.15
62.71
59.50
59.36
37.82
37.36
36.83
32.51
31.63
28.50
26.46
25.20
25.14
OH
N3
OH
20
6:1 ratio
(101 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

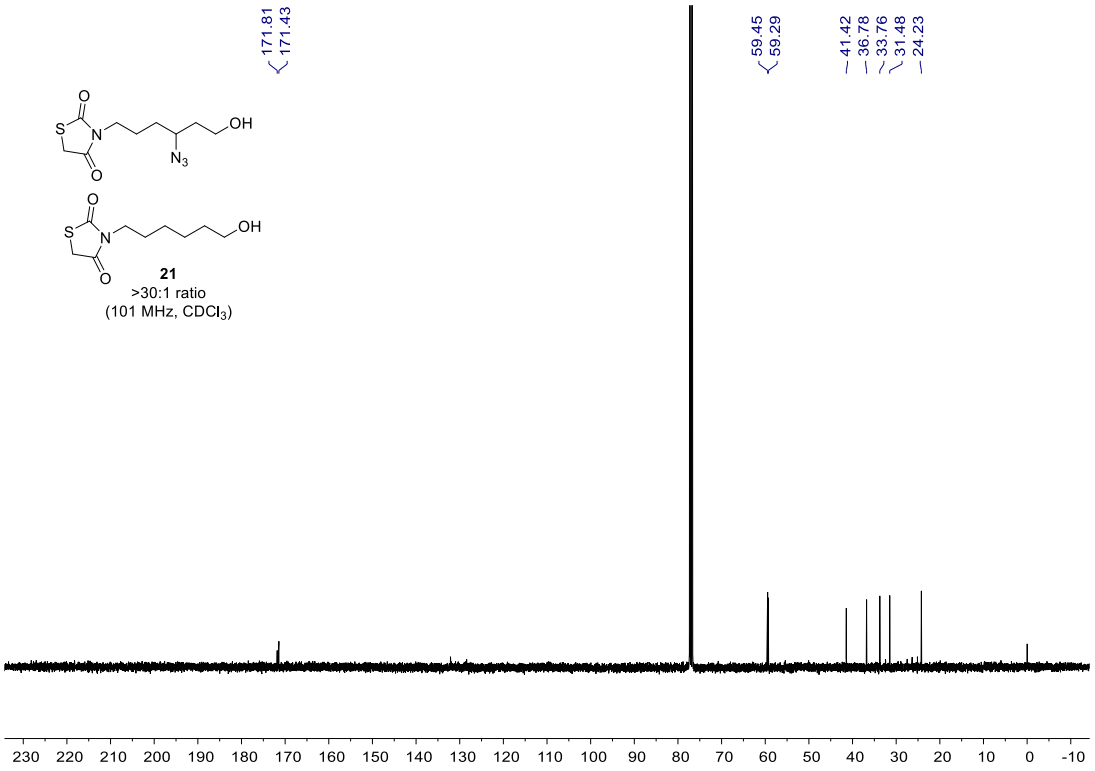


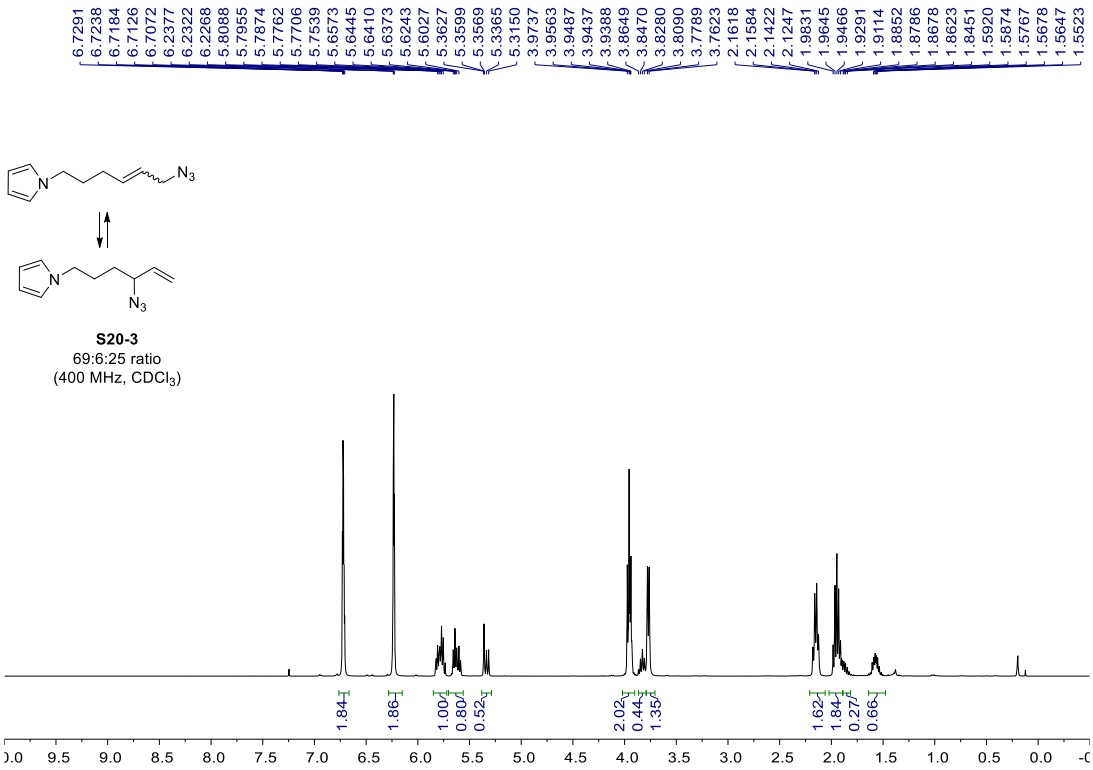
S19-3
68:7:25 ratio
(400 MHz, $CDCl_3$)

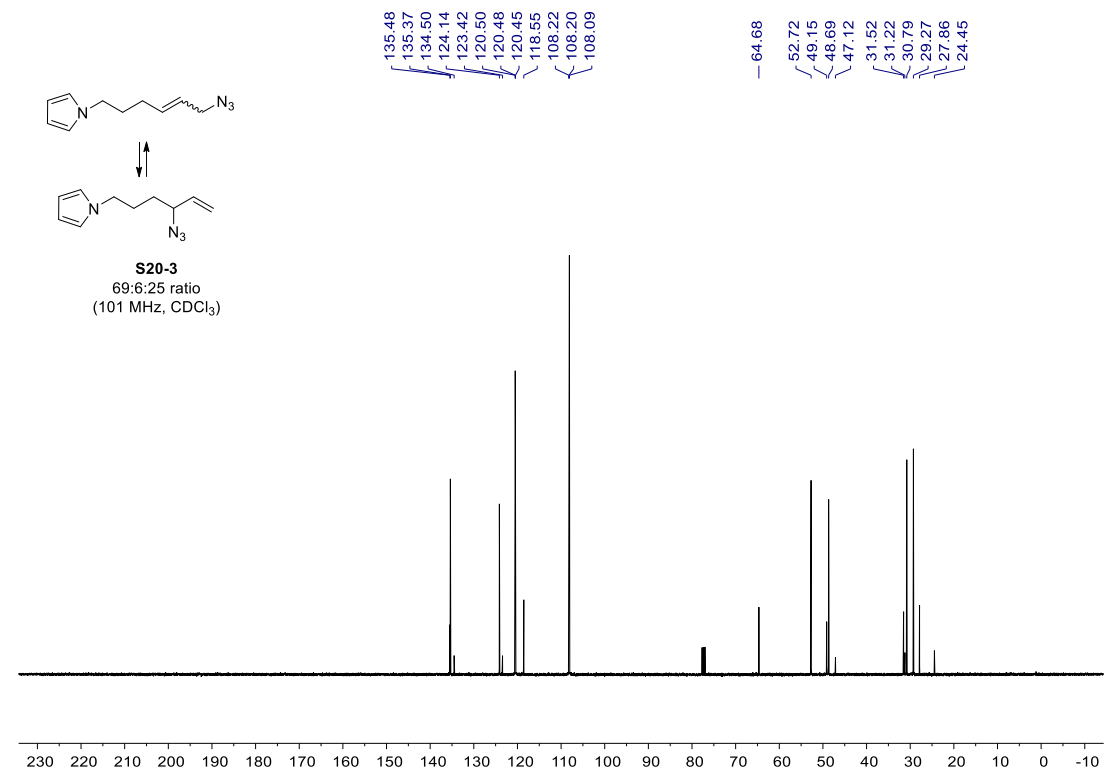


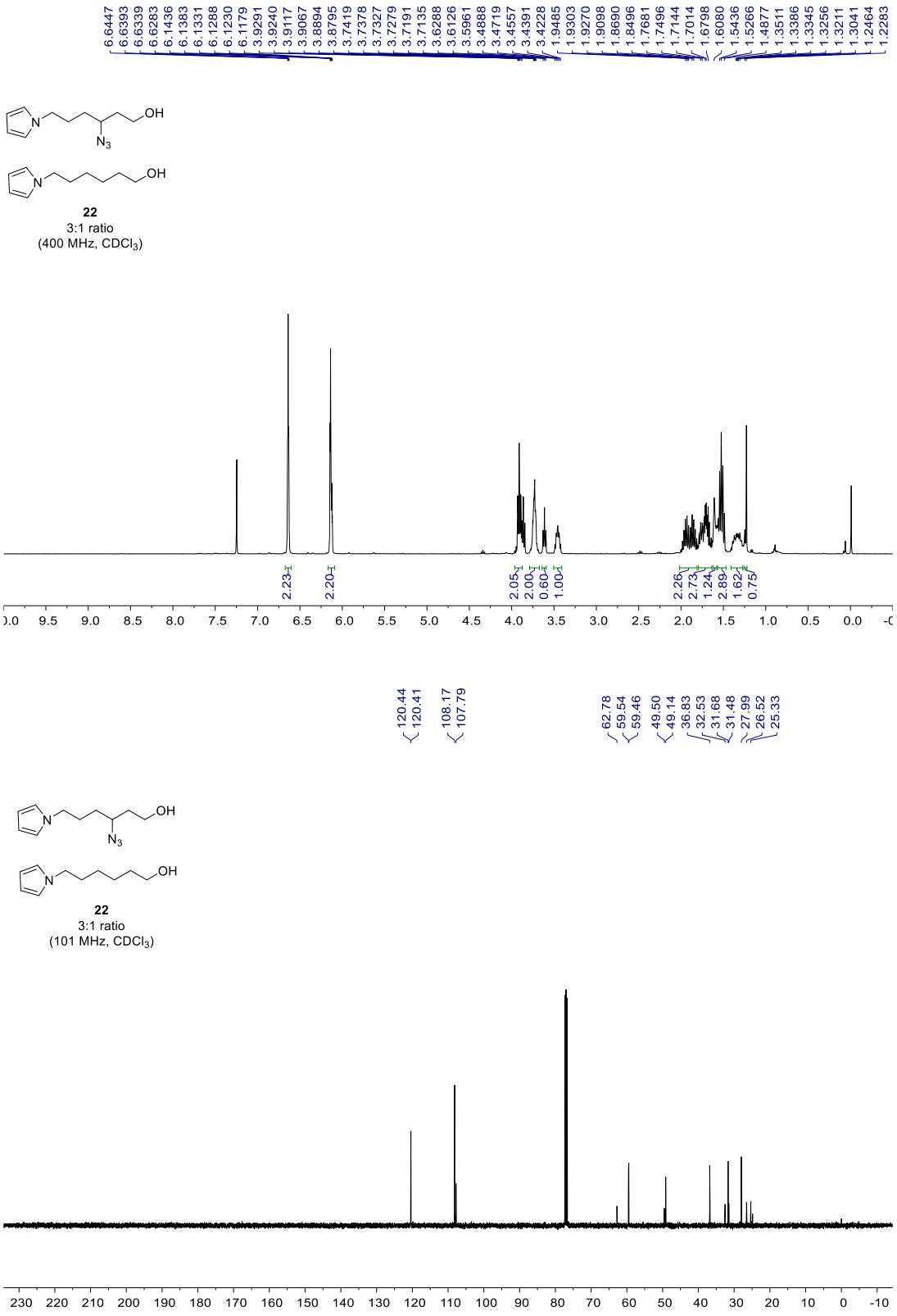
S19-3
68:7:25 ratio
(101 MHz, $CDCl_3$)

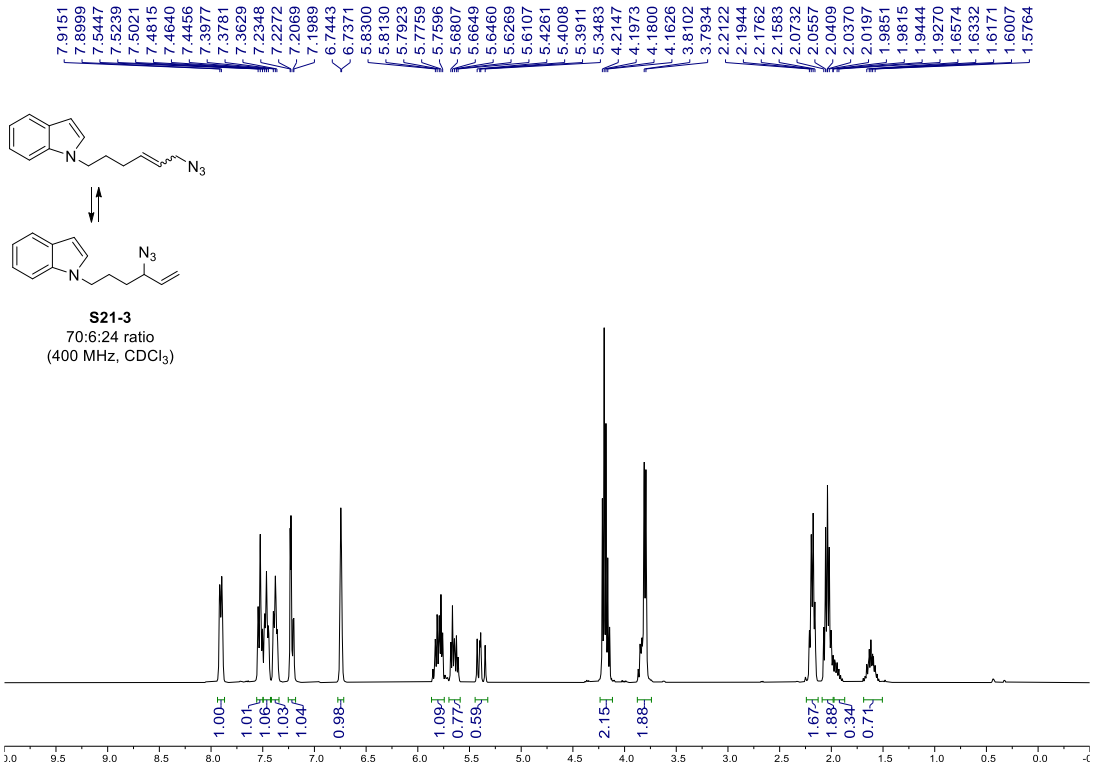

3.9443
3.7578
3.6694
3.6513
3.6330
3.5735
3.5546
3.5427
3.5347
3.5218
1.9357
1.7529
1.7369
1.7338
1.7310
1.7279
1.7195
1.7152
1.7064
1.5729
1.5575
1.5538
1.5501
1.5366
1.5318
OH
N3
21
>30:1 ratio
(400 MHz, CDCl3)
1.97
1.80
2.12
1.00
0.36
3.57
2.01

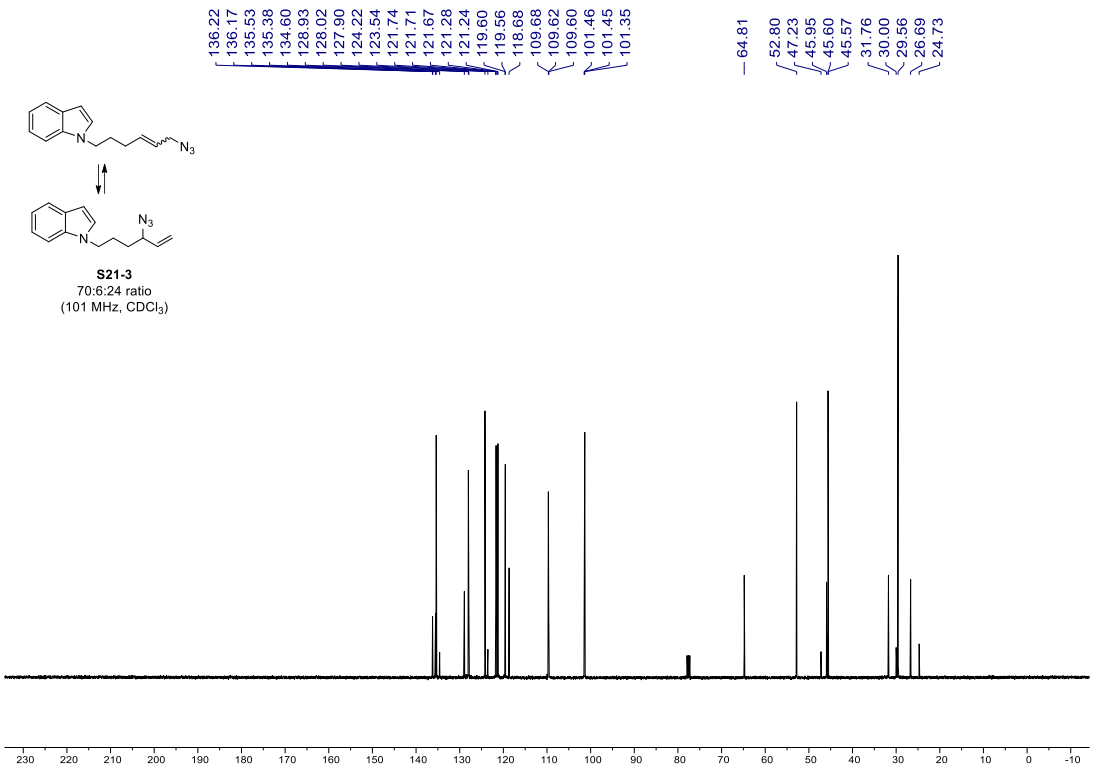

171.81
171.43
59.45
59.29
41.42
36.78
33.76
31.48
24.23
OH
N3
21
>30:1 ratio
(101 MHz, CDCl3)

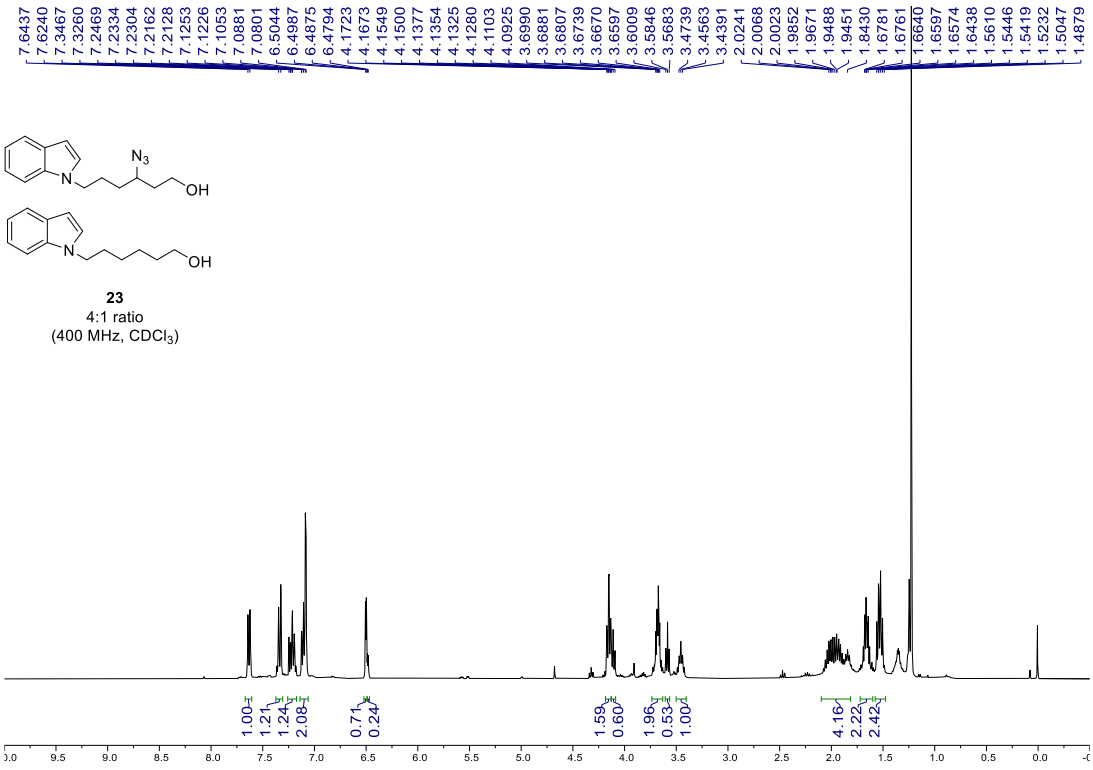

6.7291
6.7238
6.7184
6.7126
6.7072
6.2377
6.2322
6.2268
5.8088
5.7955
5.7874
5.7762
5.7706
5.7539
5.6573
5.6445
5.6410
5.6373
5.6243
5.6027
5.3627
5.3599
5.3569
5.3365
5.3150
3.9737
3.9563
3.9487
3.9437
3.9388
3.8649
3.8470
3.8280
3.8090
3.7789
3.7623
2.1618
2.1584
2.1422
2.1247
1.9831
1.9645
1.9466
1.9291
1.9114
1.8852
1.8786
1.8678
1.8623
1.8451
1.5920
1.5874
1.5767
1.5678
1.5647
1.5523
N3
N
N3
S20-3
69:6:25 ratio
(400 MHz, CDCl3)
1.84
1.86
1.00
0.80
0.52
2.02
0.44
1.35
1.62
1.84
0.27
0.66
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


135.48
135.37
134.50
124.14
123.42
120.50
120.48
120.45
118.55
108.22
108.20
108.09
64.68
52.72
49.15
48.69
47.12
31.52
31.22
30.79
29.27
27.86
24.45
N3
N
N3
S20-3
69:6:25 ratio
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

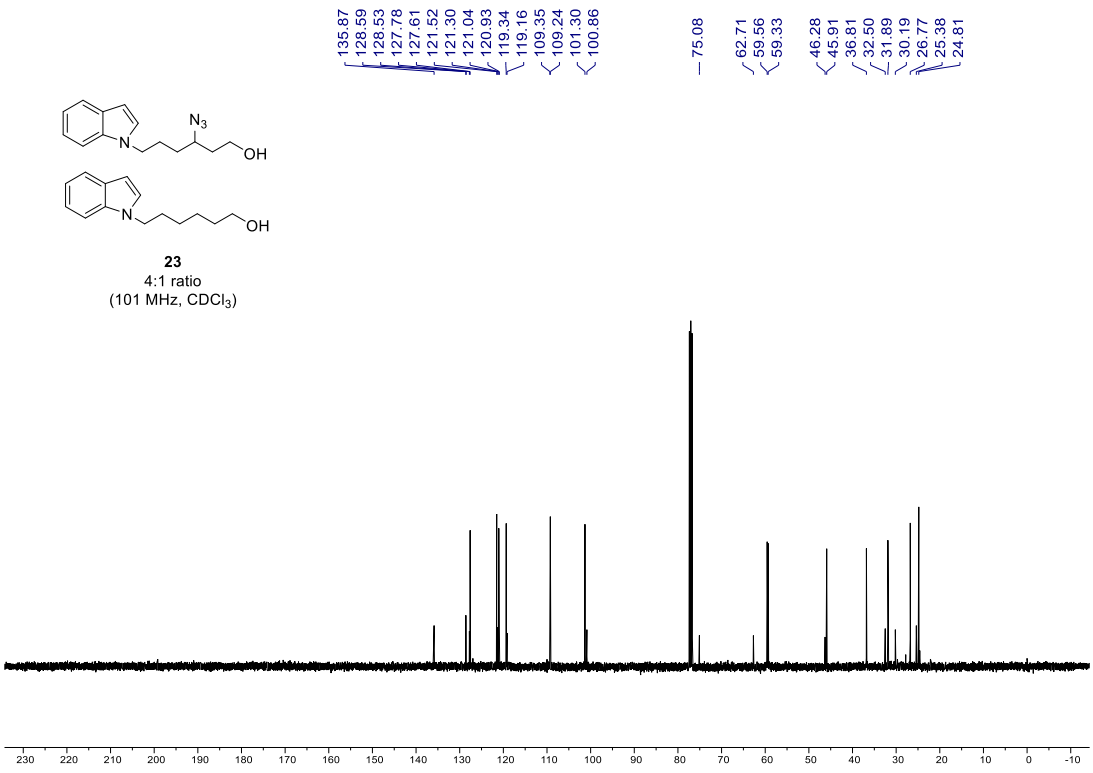

6.6447
6.6393
6.6339
6.6283
6.1436
6.1383
6.1331
6.1288
6.1230
6.1179
3.9291
3.9240
3.9117
3.9067
3.8894
3.8795
3.7419
3.7378
3.7327
3.7279
3.7191
3.7135
3.6288
3.6126
3.5961
3.4888
3.4719
3.4557
3.4391
3.4228
1.9485
1.9303
1.9270
1.9098
1.8690
1.8496
1.7681
1.7496
1.7144
1.7014
1.6798
1.6080
1.5436
1.5266
1.4877
1.3511
1.3386
1.3345
1.3256
1.3211
1.3041
1.2464
1.2283
OH
N
N3
OH
N
22
3:1 ratio
(400 MHz, CDCl3)
2.23
2.20
2.05
2.00
0.60
1.00
2.26
2.73
1.24
2.89
1.62
0.75
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
120.44
120.41
108.17
107.79
62.78
59.54
59.46
49.50
49.14
36.83
32.53
31.68
31.48
27.99
26.52
25.33
OH
N
N3
OH
N
22
3:1 ratio
(101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.9151
7.8999
7.5447
7.5239
7.5021
7.4815
7.4640
7.4456
7.3977
7.3781
7.3629
7.2348
7.2272
7.2069
7.1989
6.7443
6.7371
5.8300
5.8130
5.7923
5.7759
5.7596
5.6807
5.6649
5.6460
5.6269
5.6107
5.4261
5.4008
5.3911
5.3483
4.2147
4.1973
4.1800
4.1626
3.8102
3.7934
2.2122
2.1944
2.1762
2.1583
2.0732
2.0557
2.0409
2.0370
2.0197
1.9851
1.9815
1.9444
1.9270
1.6574
1.6332
1.6171
1.6007
1.5764
N3
N3
S21-3
70:6:24 ratio
(400 MHz, CDCl3)
1.00
1.01
1.06
1.03
1.04
0.98
1.09
0.77
0.59
2.15
1.88
1.67
1.88
0.34
0.71

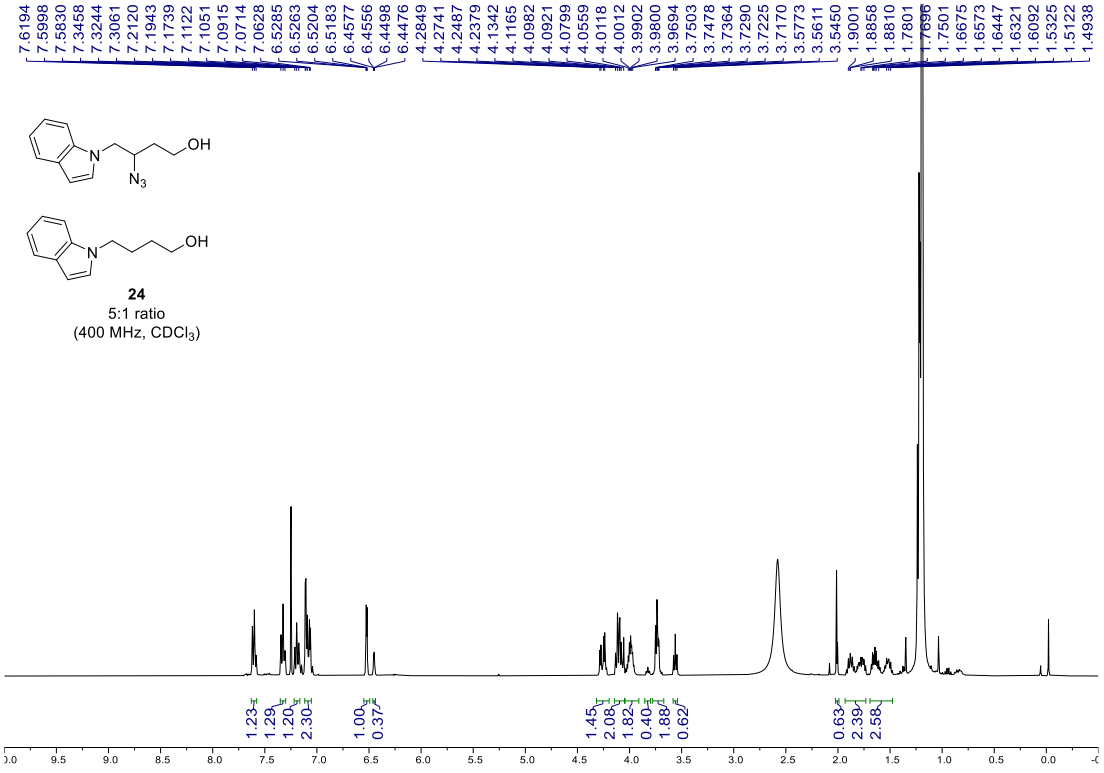

136.22
136.17
135.53
135.38
134.60
128.93
128.02
127.90
124.22
123.54
121.74
121.71
121.67
121.28
121.24
119.60
119.56
118.68
109.68
109.62
109.60
101.46
101.45
101.35
64.81
52.80
47.23
45.95
45.60
45.57
31.76
30.00
29.56
26.69
24.73
N3
N3
S21-3
70:6:24 ratio
(101 MHz, CDCl3)

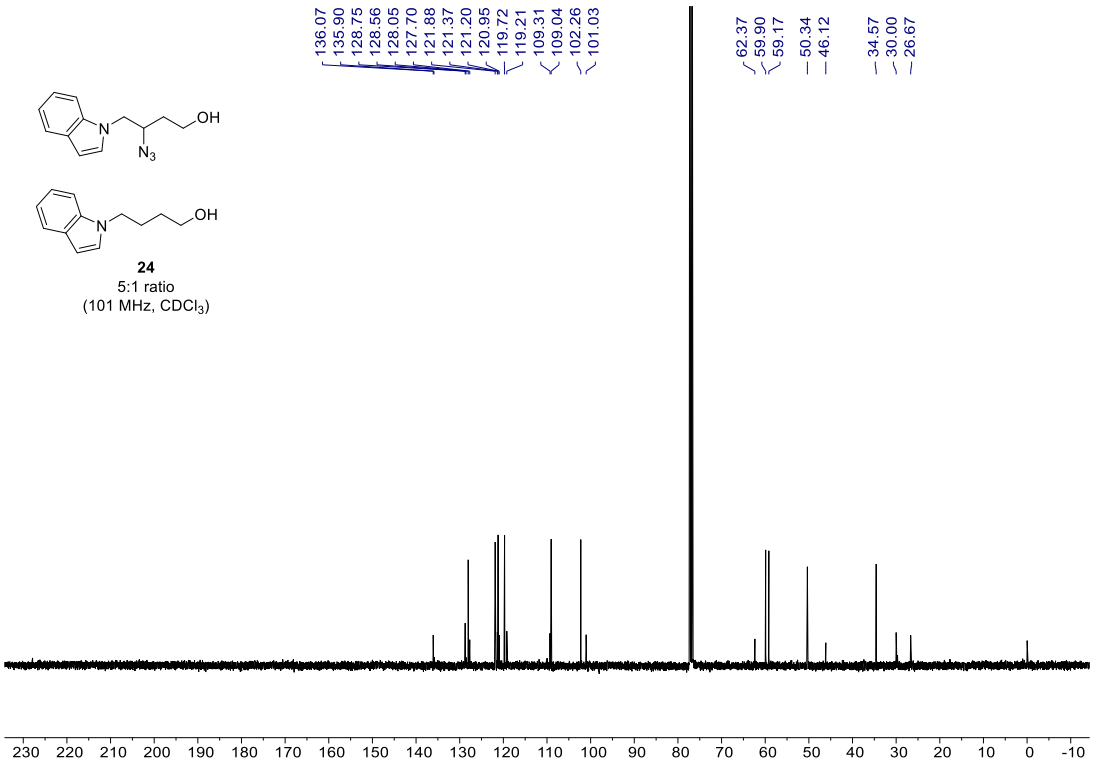


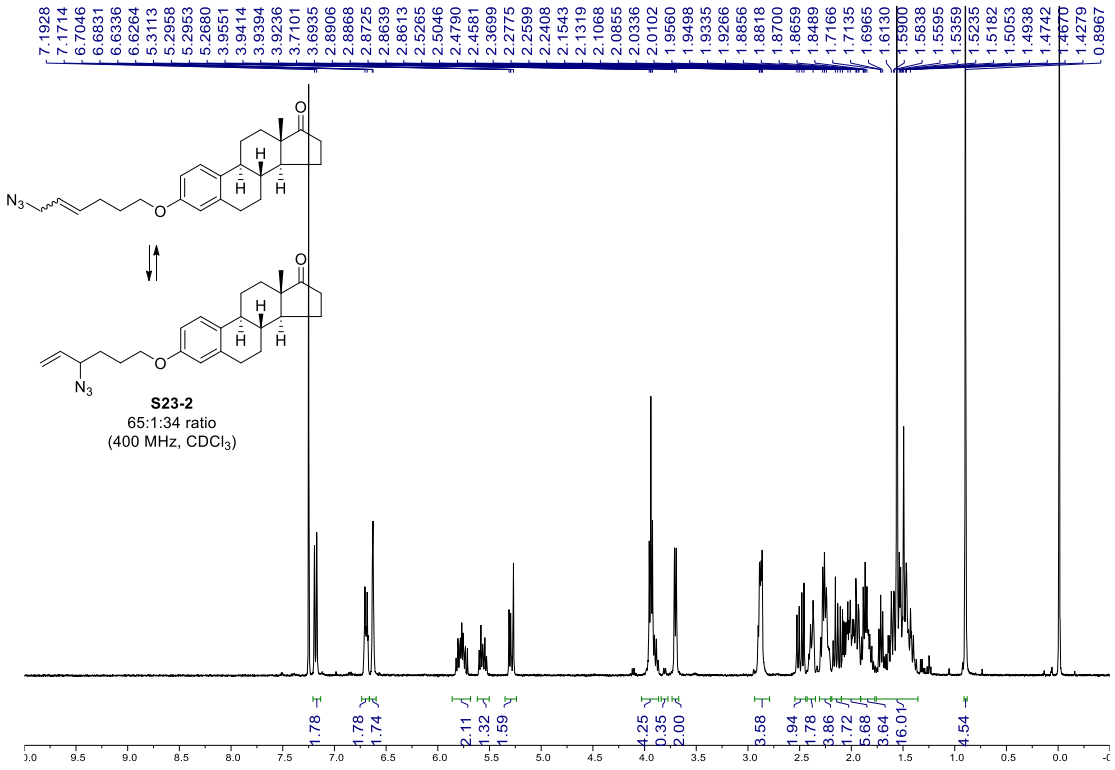
23
4:1 ratio
(400 MHz, $CDCl_3$)

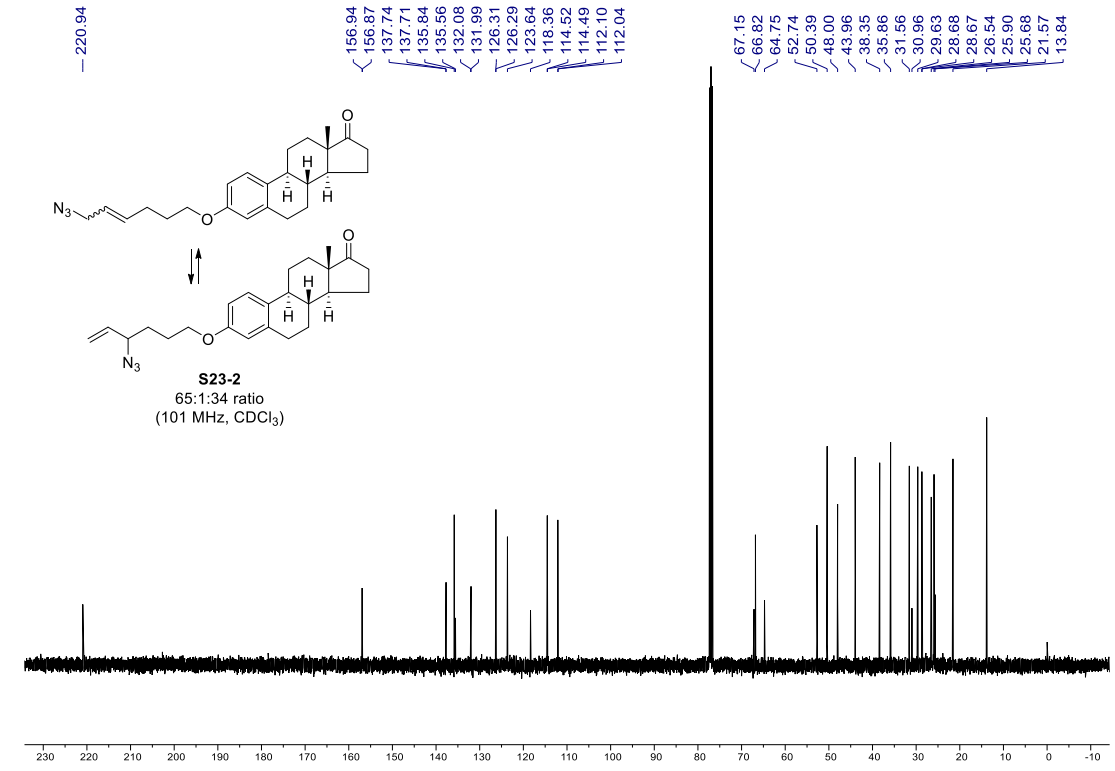


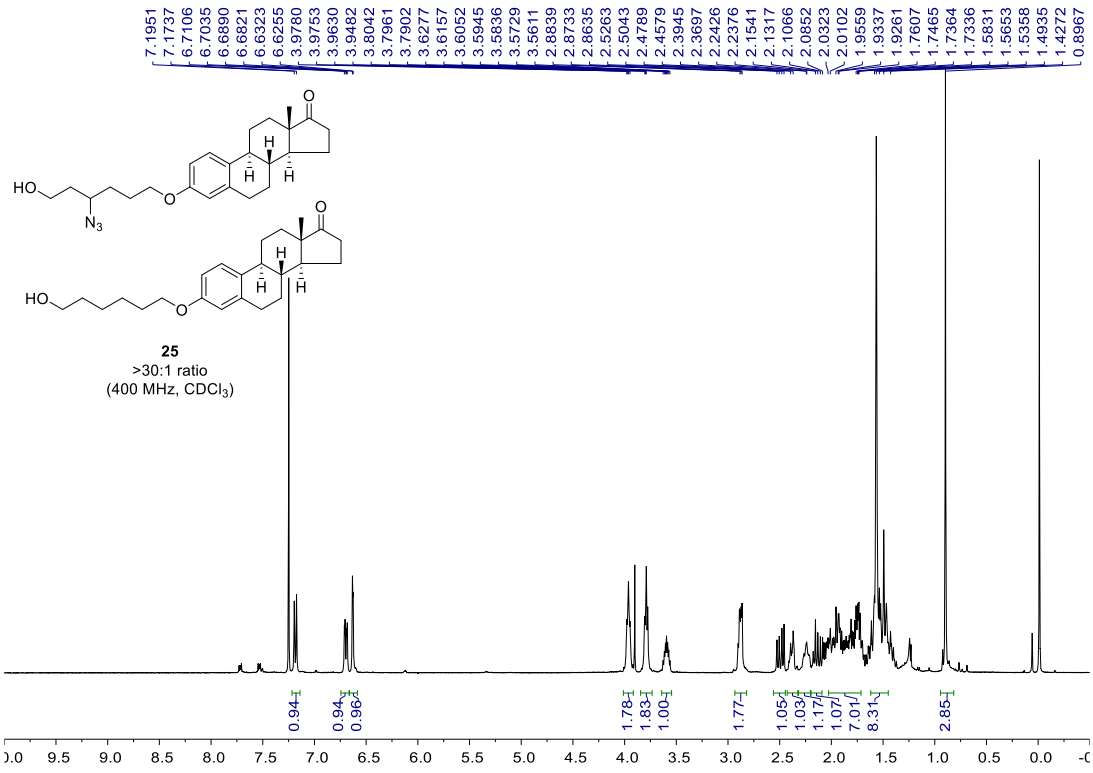
23
4:1 ratio
(101 MHz, $CDCl_3$)

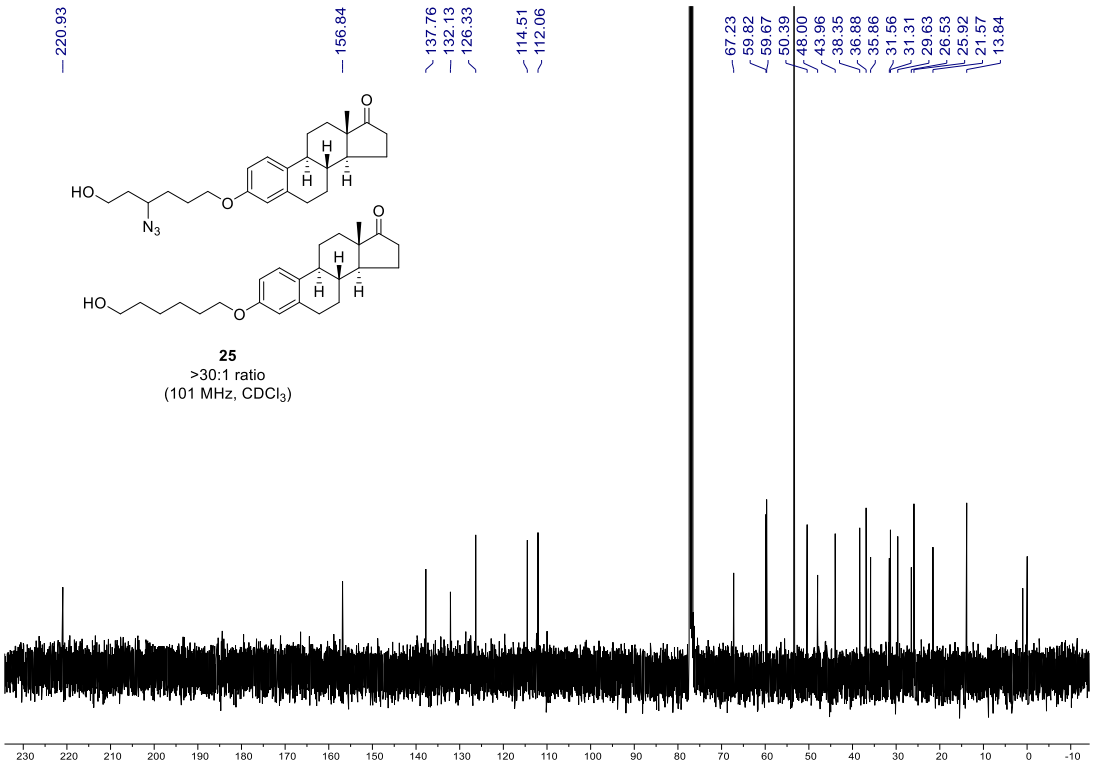

7.6194
7.5998
7.5830
7.3458
7.3244
7.3061
7.2120
7.1943
7.1739
7.1122
7.1051
7.0915
7.0714
7.0628
6.5285
6.5263
6.5204
6.5183
6.4577
6.4556
6.4498
6.4476
4.2849
4.2741
4.2487
4.2379
4.1342
4.1165
4.0982
4.0921
4.0799
4.0559
4.0118
4.0012
3.9902
3.9800
3.9694
3.7503
3.7478
3.7364
3.7290
3.7225
3.7170
3.5773
3.5611
3.5450
1.9001
1.8858
1.8810
1.7801
1.7696
1.7501
1.6675
1.6573
1.6447
1.6321
1.6092
1.5325
1.5122
1.4938
OH
N3
OH
24
5:1 ratio
(400 MHz, CDCl3)
1.23
1.29
1.20
2.30
1.00
0.37
1.45
2.08
1.82
0.40
1.88
0.62
0.63
2.39
2.58

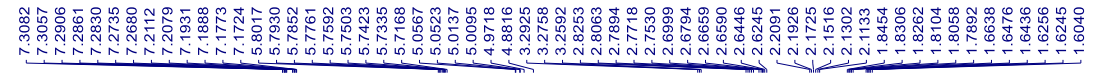

136.07
135.90
128.75
128.56
128.05
127.70
121.88
121.37
121.20
120.95
119.72
119.21
109.31
109.04
102.26
101.03
62.37
59.90
59.17
50.34
46.12
34.57
30.00
26.67
OH
N3
OH
24
5:1 ratio
(101 MHz, CDCl3)

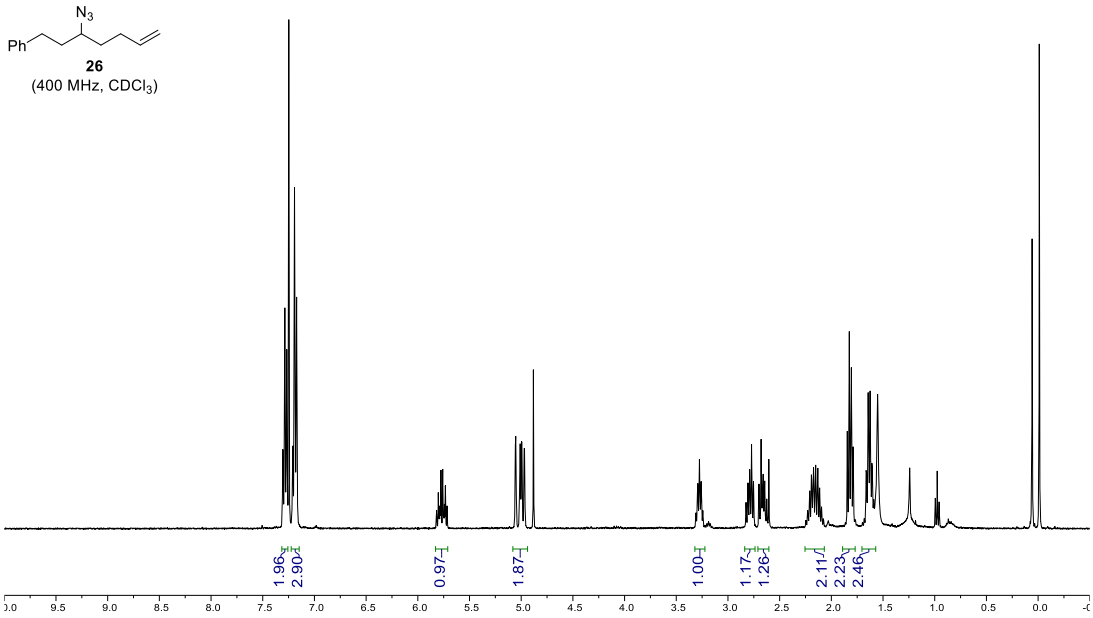

S23-2
65:1:34 ratio
(400 MHz, CDCl3)

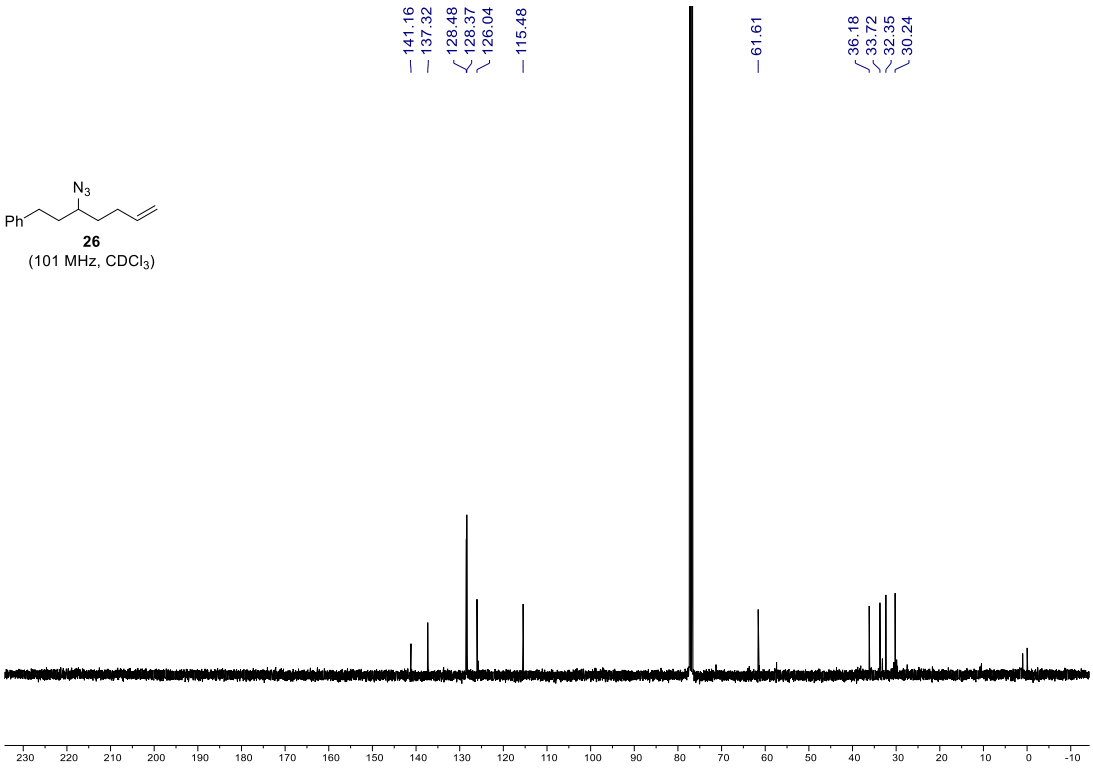

S23-2
65:1:34 ratio
(101 MHz, CDCl3)

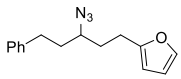

7.1951
7.1737
6.7106
6.7035
6.6890
6.6821
6.6323
6.6255
3.9780
3.9753
3.9630
3.9482
3.8042
3.7961
3.7902
3.6277
3.6157
3.6052
3.5945
3.5836
3.5729
3.5611
2.8839
2.8733
2.8635
2.5263
2.5043
2.4789
2.4579
2.3945
2.3697
2.2426
2.2376
2.1541
2.1317
2.1066
2.0852
2.0323
2.0102
1.9559
1.9337
1.9261
1.7607
1.7465
1.7364
1.7336
1.5831
1.5653
1.5358
1.4935
1.4272
0.8967
HO
N3
O
H
HO
O
25
>30:1 ratio
(400 MHz, CDCl3)
0.94
0.94
0.96
1.78
1.83
1.00
1.77
1.05
1.03
1.17
1.07
7.01
8.31
2.85
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


220.93
156.84
137.76
132.13
126.33
114.51
112.06
67.23
59.82
59.67
50.39
48.00
43.96
38.35
36.88
35.86
31.56
31.31
29.63
26.53
25.92
21.57
13.84
HO
N3
O
H
HO
O
25
>30:1 ratio
(101 MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

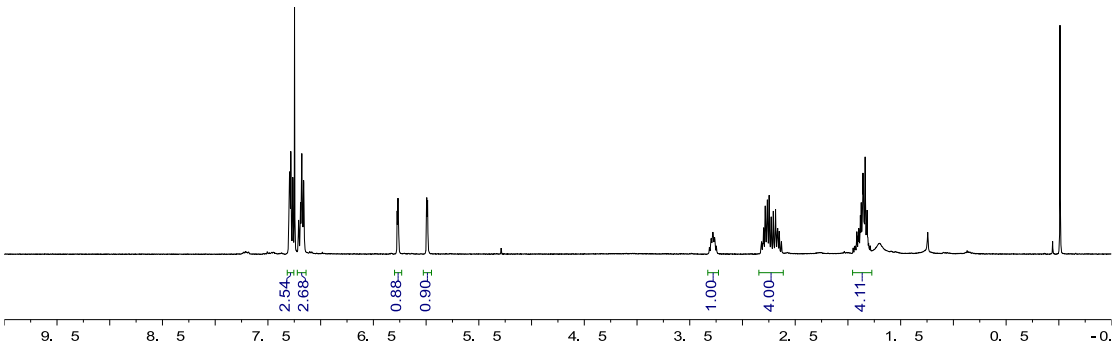

7.3082
7.3057
7.2906
7.2861
7.2830
7.2735
7.2680
7.2112
7.2079
7.1931
7.1888
7.1773
7.1724
5.8017
5.7930
5.7852
5.7761
5.7592
5.7503
5.7423
5.7335
5.7168
5.0567
5.0523
5.0137
5.0095
4.9718
4.8816
3.2925
3.2758
3.2592
2.8253
2.8063
2.7894
2.7718
2.7530
2.6999
2.6794
2.6659
2.6590
2.6446
2.6245
2.2091
2.1926
2.1725
2.1516
2.1302
2.1133
1.8454
1.8306
1.8262
1.8104
1.8058
1.7892
1.6638
1.6476
1.6436
1.6256
1.6245
1.6040

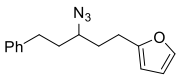

N3
Ph
26
(400 MHz, CDCl3)
1.96
2.90
0.97
1.87
1.00
1.17
1.26
2.11
2.23
2.46


141.16
137.32
128.48
128.37
126.04
115.48
61.61
36.18
33.72
32.35
30.24
N3
Ph
26
(101 MHz, CDCl3)

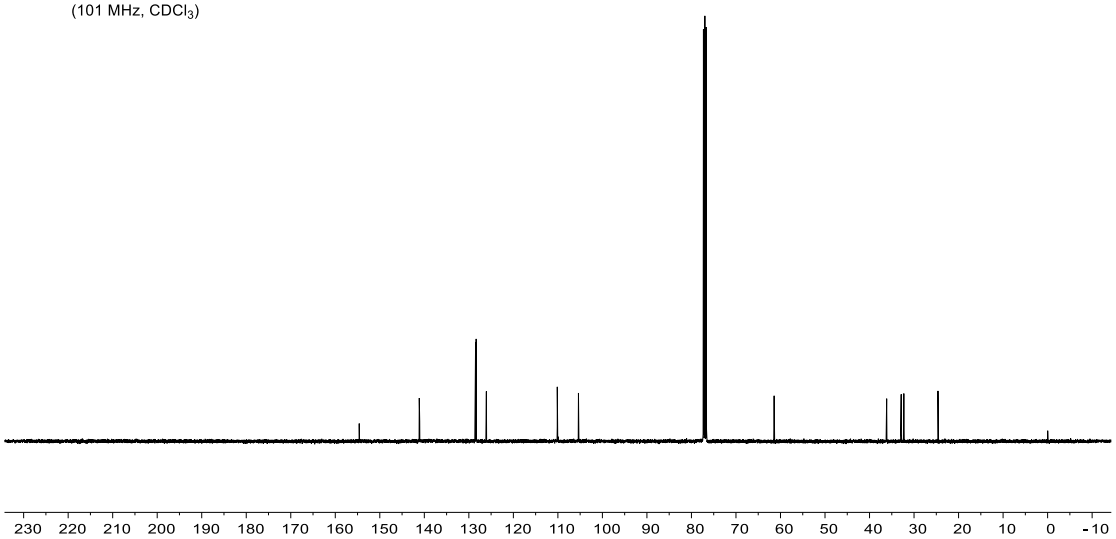


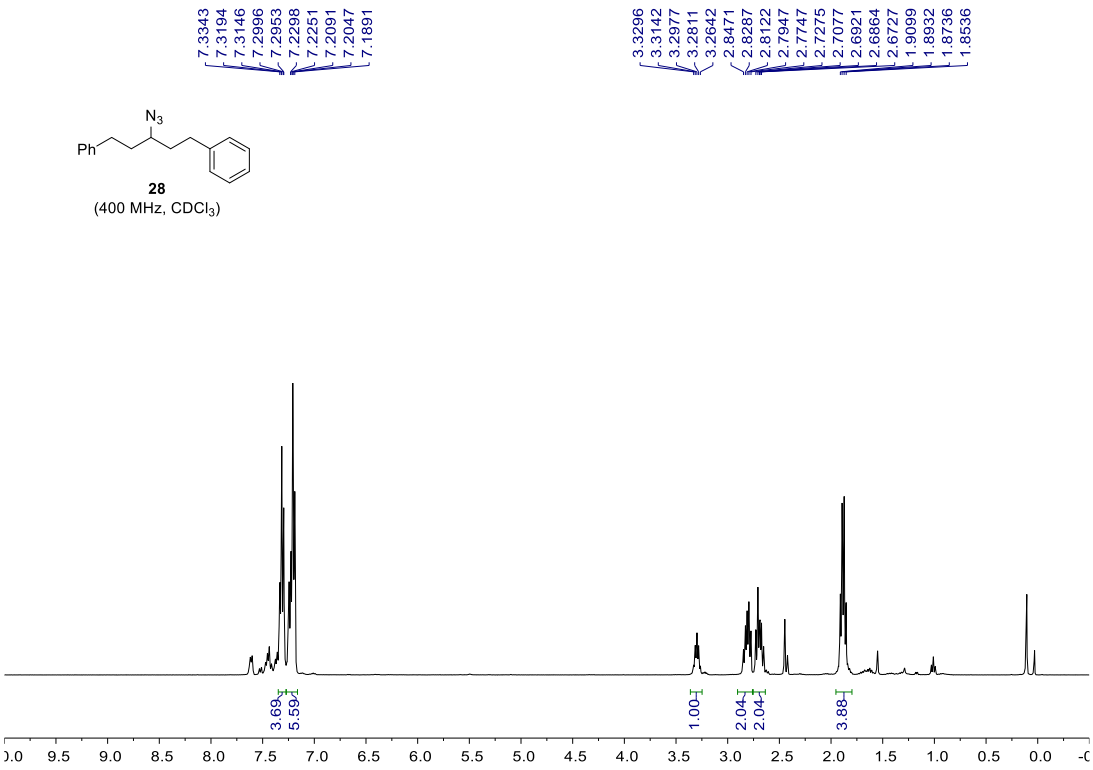
27
(400 MHz, $CDCl_3$)

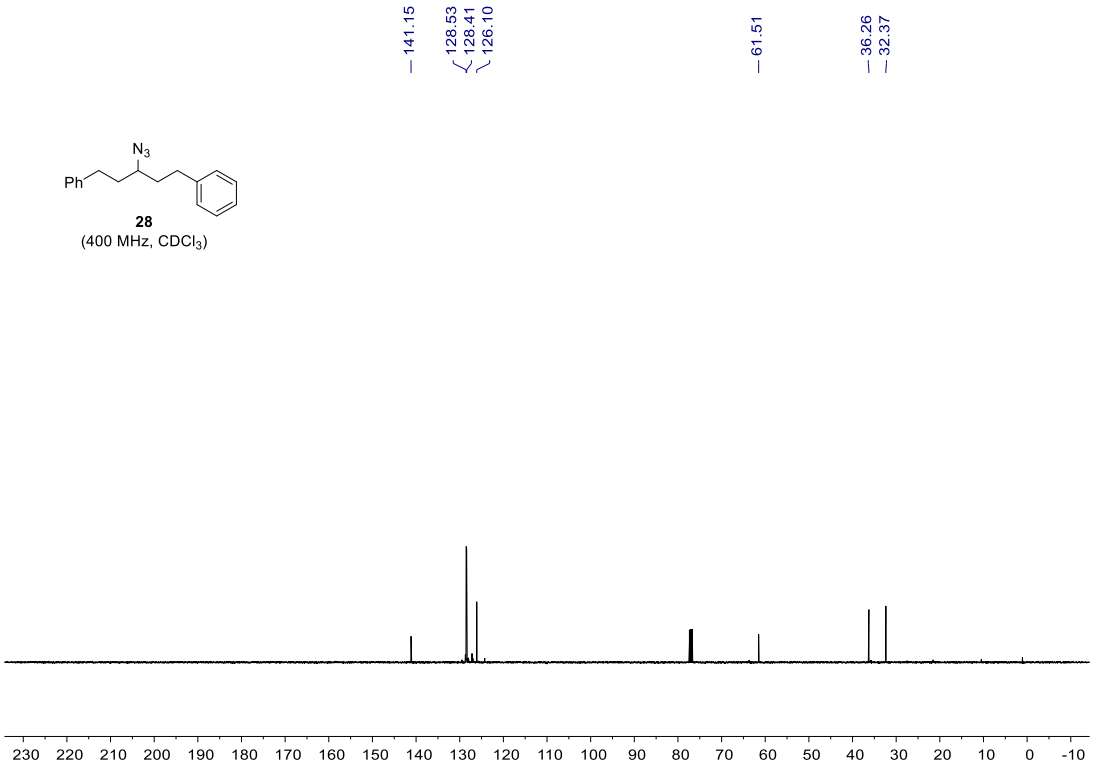


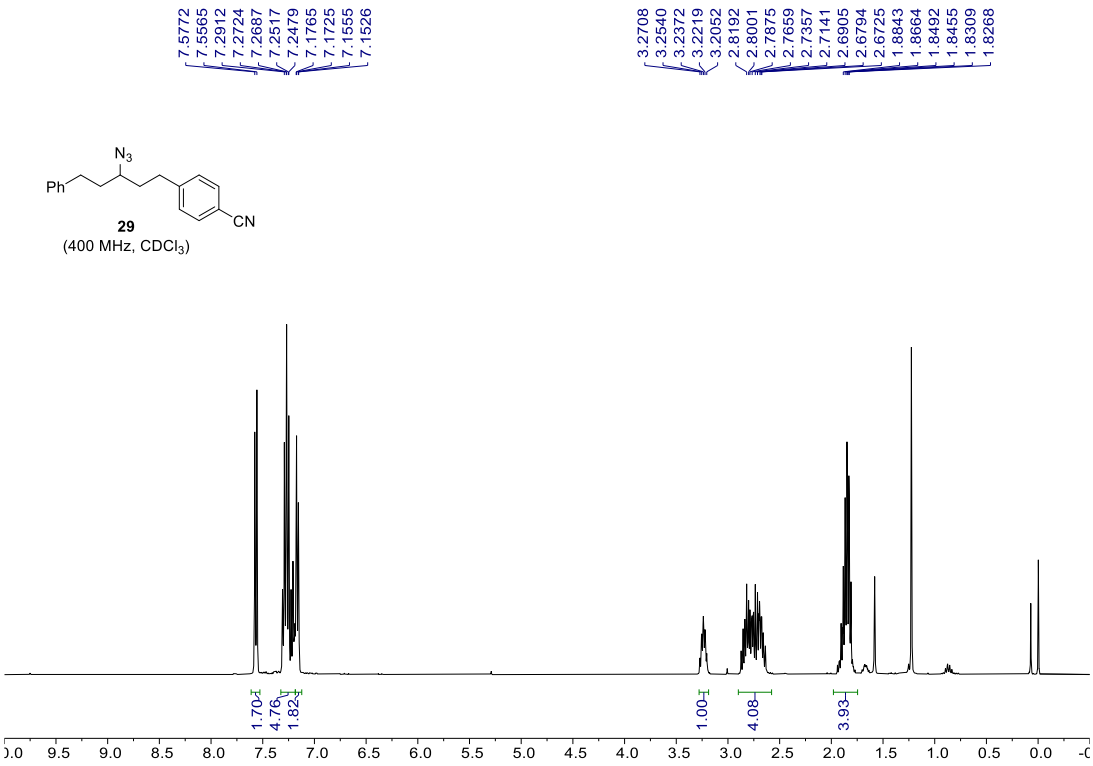


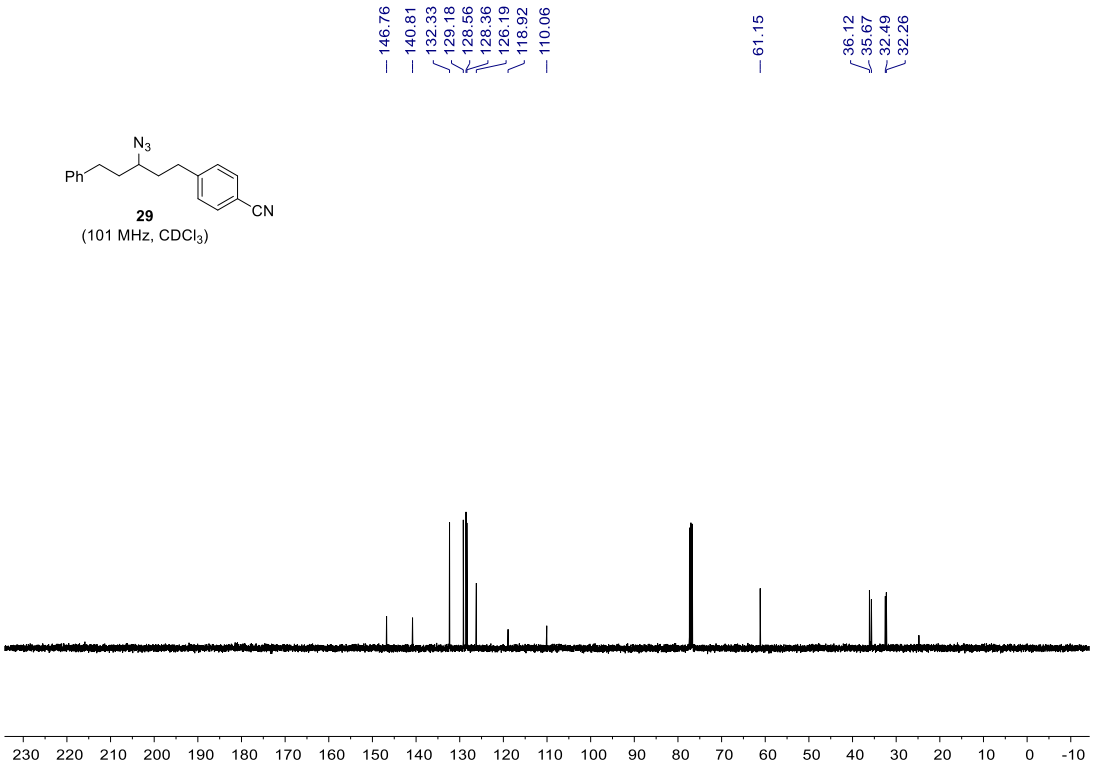
27
(101 MHz, $CDCl_3$)

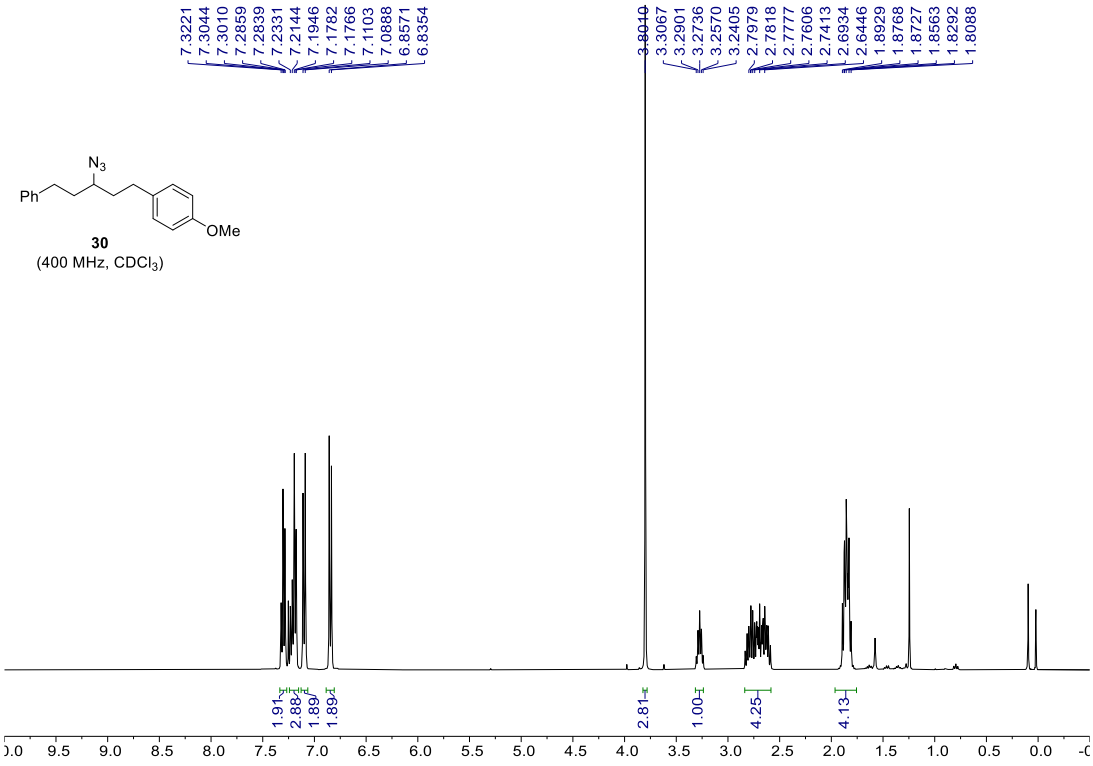


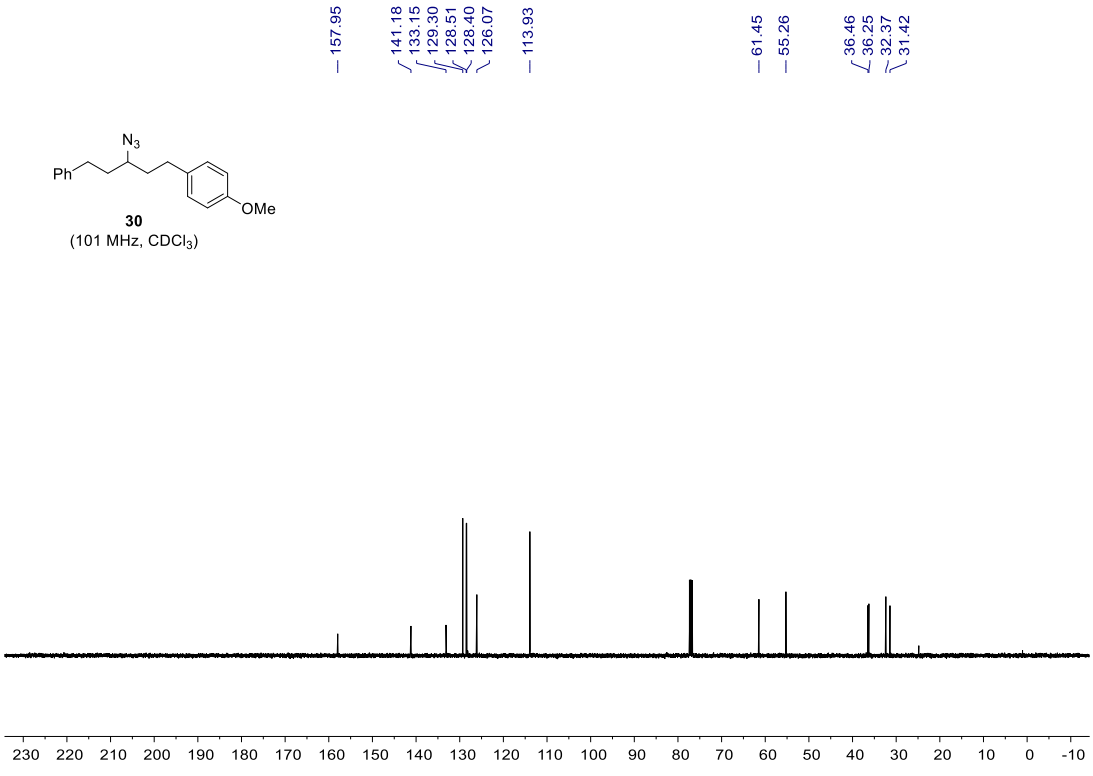

7.3343
7.3194
7.3146
7.2996
7.2953
7.2298
7.2251
7.2091
7.2047
7.1891
3.3296
3.3142
3.2977
3.2811
3.2642
2.8471
2.8287
2.8122
2.7947
2.7747
2.7275
2.7077
2.6921
2.6864
2.6727
1.9099
1.8932
1.8736
1.8536
N3
Ph
28
(400 MHz, CDCl3)
3.69
5.59
1.00
2.04
2.04
3.88


141.15
128.53
128.41
126.10
61.51
36.26
32.37
N3
Ph
28
(400 MHz, CDCl3)


7.5772
7.5565
7.2912
7.2724
7.2687
7.2517
7.2479
7.1765
7.1725
7.1555
7.1526
3.2708
3.2540
3.2372
3.2219
3.2052
2.8192
2.8001
2.7875
2.7659
2.7357
2.7141
2.6905
2.6794
2.6725
1.8843
1.8664
1.8492
1.8455
1.8309
1.8268
N3
Ph
CN
29
(400 MHz, CDCl3)
1.70
4.76
1.82
1.00
4.08
3.93


146.76
140.81
132.33
129.18
128.56
128.36
126.19
118.92
110.06
61.15
36.12
35.67
32.49
32.26
N3
Ph
CN
29
(101 MHz, CDCl3)


7.3221
7.3044
7.3010
7.2859
7.2839
7.2331
7.2144
7.1946
7.1782
7.1766
7.1103
7.0888
6.8571
6.8354
3.8010
3.3067
3.2901
3.2736
3.2570
3.2405
2.7979
2.7818
2.7777
2.7606
2.7413
2.6934
2.6446
1.8929
1.8768
1.8727
1.8563
1.8292
1.8088
N3
Ph
OMe
30
(400 MHz, CDCl3)
1.91
2.88
1.89
1.89
2.81
1.00
4.25
4.13


157.95
141.18
133.15
129.30
128.51
128.40
126.07
113.93
61.45
55.26
36.46
36.25
32.37
31.42
N3
Ph
OMe
30
(101 MHz, CDCl3)