Electronic Supplementary Material (ESI) for ChemComm.

From insertion to multicomponent coupling: temperature dependent reactions of arynes with aliphatic alcohols

Manikandan Thangaraj,[a] Sachin Suresh Bhojgude,[a] Manoj V. Mane[b] and Akkattu T. Biju*[,a]

[a]*Organic Chemistry Division,* [b]*Physical/Materials Chemistry Division,*
CSIR-National Chemical Laboratory (CSIR-NCL),
Dr. Homi Bhabha Road, Pune - 411008, India
at.biju@ncl.res.in

Supporting Information

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel 30 °C corresponds to the room temperature of the lab, when the experiments were carried out. THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. 18-Crown-6 was recrystallized from dry CH_3CN and KF was dried by heating at 110 °C for 12 h and left to cool under argon and stored in glove box. The 2(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.[1] The alcohols are used in this work are either commercially available or prepared from the corresponding aldehydes by standard $NaBH_4$ reduction. The alcohol **1c**, **1d** and **1s** are prepared following the known procedure.[2]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with solvents as indicated.

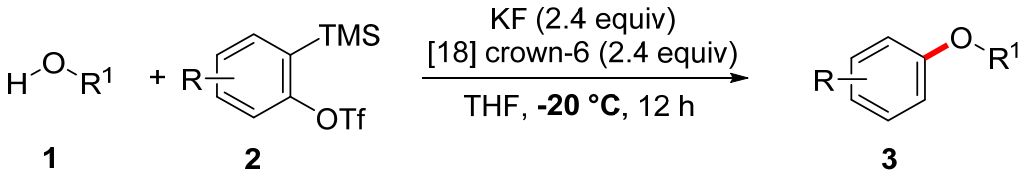
All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). Gas Chromatography was recorded on Agilent 7890 B GC. GCMS data were recorded on Agilent 7890 B GC and 5977 A MSD mass analyser. Infrared spectra were recorded on a Bruker Alpha-E Infrared Spectrophotometer. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump.

---

[1] (*a*) Y. Sato, T. Tamura, A. Kinbara, M. Morib, *Adv. Synth. Catal.,* 2007, **349**, 647; (*b*) D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis,* 2002, 1454.

[2] (*a*) W. S. Cho, S. H. Kim, D. J. Kim, S. Mun, R. Kim, M, J. Go, M. H. Park, M. Kim, J. Lee and Y. Kim, *Polyhedron,* 2014**, 67**, 205; (*b*) K. Kashinath, S. Dhara and D. S. Reddy, *Org. Lett.*, 2015, **17**, 2090.

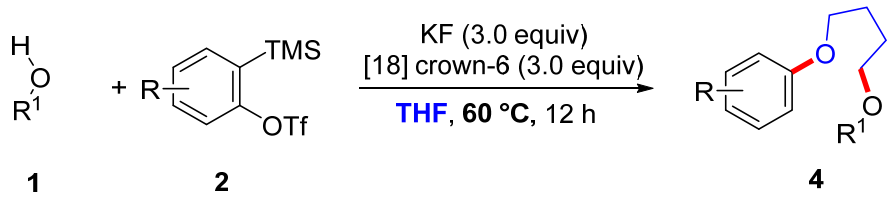
2. General Procedure for the Insertion (Arylation) of Aliphatic Alcohols with Arynes



1 **2** **3**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.317 g, 1.2 mmol), KF (0.070 g, 1.2 mmol) inside the glove box. The mixture was dissolved in 3.0 mL of THF outside the glove box under argon. To the stirring solution was added corresponding alcohol **1** (0.5 mmol). The resultant reaction mixture was cooled to -20 °C and kept stirring for 5 min. To the stirring solution was added aryne precursor **2** (0.60 mmol) and kept stirring at -20 °C for 12 h. When TLC control showed the completion of the reaction (typically after 12 h), the reaction was quenched and the solvent was evaporated. Subsequently the crude residue was purified by flash column chromatography on silica gel to afford the corresponding alkyl aryl ether derivatives **3** in moderate to good yields. Selectivity ratio was determined by GC analysis of crude reaction mixture.

3. General Procedure for the MCR Involving Aliphatic Alcohols, THF and Aryne



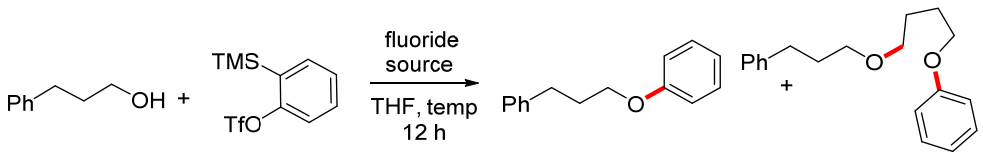
1 **2** **4**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.396 g, 1.5 mmol), KF (0.087 g, 1.5 mmol) inside the glove box. The mixture was dissolved in 4.0 mL of THF outside the glove box under argon. To the stirring solution was added corresponding alcohol **1** (0.5 mmol) and the resultant reaction mixture kept stirring at 30 °C for 5 min. To the stirring solution was added aryne precursor **2** (0.75 mmol). Then the reaction mixture was placed in a preheated oil bath at 60 °C. When TLC

control showed the completion of the reaction (typically after 12 h), the reaction mixture cooled to room temperature and the solvent was evaporated. Subsequently, the crude residue was purified by flash column chromatography on silica gel to afford the corresponding (4-(alkoxy)butoxy)arenes **4** in moderate to good yields. Selectivity ratio was determined by GC analysis of crude reaction mixture.

4. Optimization Studies

The present optimization study commenced with treating 3-phenyl propanol **1a** with aryne generated from 2-(trimethylsilyl)aryl triflate **2a**. When the reaction was performed using KF as the fluoride source (using [18] crown-6 as additive) at 30 °C, the *O*-arylated product **3a** was isolated in 12% yield and the MCC product **4a** was isolated in 44% yield with a selectivity of 20:80 (table, entry 1). When the reaction was carried out using tetrabutyl ammonium fluoride (TBAF), better selectivity for **3a** was observed while CsF returned almost similar results (entries 2, 3). Interestingly, using KF at 0 °C, **3a** was formed in 59% yield with 82:18 selectivity (entry 4). Moreover, when the temperature was further reduced to -20 °C, **3a** was isolated in 75% yield and excellent selectivity of 95:5 (entry 5). Under similar conditions, TBAF and CsF furnished inferior results (entries 6, 7). Gratifyingly, performing the reaction at 60 °C using KF, the selectivity was switched to MCC product **4a** (**3a: 4a** 13:87; 56% yield; entry 8). Using slight excess of **2a** and under dilution conditions, the selectivity for **4a** was improved to 9:91 and **4a** was isolated in 61% yield (entry 9).



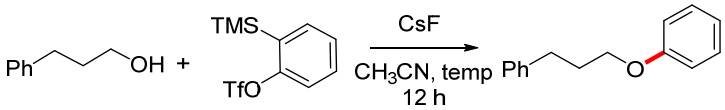
1a **2a** **3a** **4a**

entry	fluoride source	temp (°C)	yield of **3a**[b]	yield of **4a**[b]	**3a:4a**[c]
1	KF/[18] crown-6	30	12	44	20:80
2	TBAF	30	25	<5	>95:5
3[d]	CsF	30	11	43	19:81
4	KF/[18] crown-6	0	59	12	82:18

5	*KF/[18] crown-6*	*-20*	*75*	*<5*	*95:5*
6	TBAF	-20	41	<5	>95:5
7[d]	CsF	-20	<5	11	27:73
8	KF/[18] crown-6	60	9	56	13:87
9[e]	*KF/[18] crown-6*	*60*	*<5*	*61*	*9:91*

[a] General conditions: **1a** (0.25 mmol), **2a** (0.30 mmol), KF (2.4 equiv), [18] crown-6 (2.4 equiv), THF (1.5 mL), for the indicated temperature and 12 h. [b] The yields of the isolated products are given. [c] Selectivity was determined using GC analysis of the crude reaction mixture. [d] Reaction performed using 1:1 CH_3CN:THF. [e] Using 1.5 equiv of **2a**, 3.0 equiv of KF and [18]-crown-6 and 2.0 mL of THF.

Reactions performed using CsF in CH_3CN



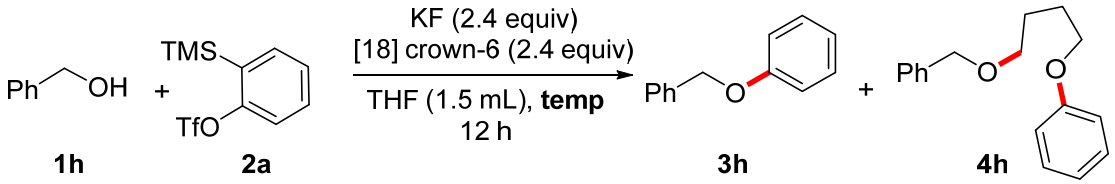
1a **2a** **3a**

entry	temp (°C)	Yield of **3a**(%)
1	-20	<5
2	-10	9
3	0	21
4	10	36
5	20	40
6	30	42
6	60	32

All the reactions are performed in 0.25 mmol scale of **1a**, 1.2 equiv of aryne precursor **2a** and 2.4 equiv of CsF in 1.5 mL CH_3CN. Given are isolated yield of **3a**.

5. Variation of Temperature on Aryne Reactions with Benzyl Alcohol

We have carried out a series of experiments with benzyl alcohol **1h** and aryne generated from **2a** under varying temperature from -20 °C to 60 °C.



1h **2a** **3h** **4h**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.158 g, 0.6 mmol), KF (0.035 g, 0.6 mmol) inside the glove box. The mixture was dissolved in 1.5 mL of THF outside the glove box under argon. To the stirring solution was added benzyl alcohol **1h** (0.027 g, 0.25 mmol). Then the resultant reaction mixture was cooled to -20 °C and kept stirring for 5 min. To the stirring solution was added aryne precursor **2a** (0.089 g, 73µL, 0.30 mmol) and kept stirring at -20°C for 12 h. After 12 h, the reaction was quenched and subsequently purified by flash column chromatography on silica gel to afford the corresponding ether derivatives **3h** and **4h.** Selectivity ratio was determined by GC analysis of crude reaction mixture.

The same procedure was followed for other reactions carried out at different temperature (-20 °C to 60 °C), and the results are summarized in the following table.

entry	temp (°C)	Yield of **3h**(%)[b]	Yield of **4h** (%)[b]	selectivity **3h:4h**[c]
1	-20 °C	86	<5	96:04
2	-10 °C	80	<5	94:06
3	0 °C	73	8	91:09
4	10 °C	63	14	83:17
5	20 °C	57	19	70:30
6	30 °C	22	49	32:68
7	40 °C	20	53	31:69
8	50 °C	13	55	14:86

9	60 °C	11	58	14:86

[a] General conditions: **1h** (0.25 mmol), **2a** (0.30 mmol), KF (2.4 equiv), [18] crown-6 (2.4 equiv), THF (1.5 mL), for the indicated temperature and 12 h. [b] The yields of the isolated products are given. [c] Selectivity was determined using GC analysis of the crude reaction mixture.

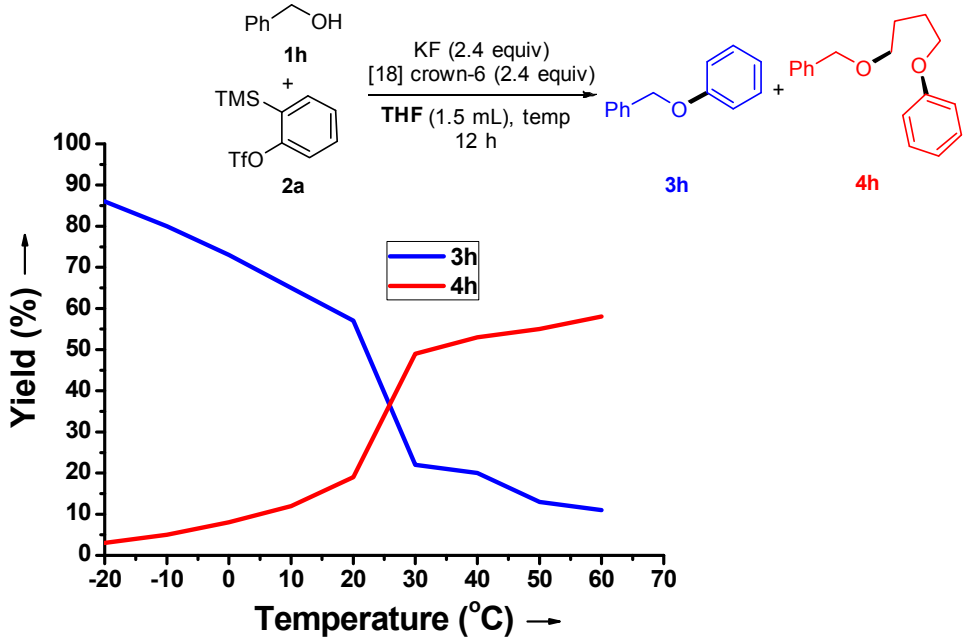
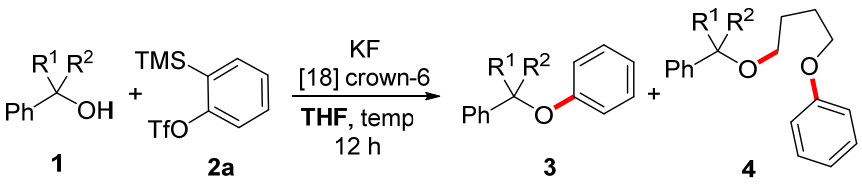


Figure 1. Variation of temperature of aryne reactions with alcohols

6. Comparative Study of Primary, Secondary and Tertiary Alcohols



$R^1 = R^2 = H$, **1h**
$R^1 = H$, $R^2 = Ph$, **1ad**
$R^1 = R^2 = Ph$, **1ae**

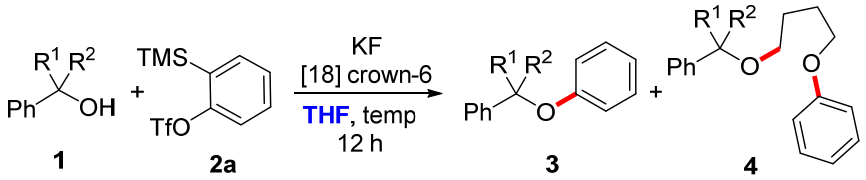
Procedure for the Comparative Experiments of Primary, Secondary and Tertiary Alcohols at -20 °C

Three reactions were carried out in parallel. To each of the flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.317 g, 1.2 mmol), KF

(0.070 g, 1.2 mmol) inside the glove box. The mixture was dissolved in 3.0 mL of THF outside the glove box under argon. To the stirring solution was added corresponding alcohol **1** (0.5 mmol). The resultant reaction mixture was cooled to -20 °C and kept stirring for 5 min. To the stirring solution was added aryne precursor **2** (0.60 mmol) and kept stirring at -20 °C for another 12 h. The reaction was quenched and the solvent was evaporated. Subsequently, the crude residue was purified by flash column chromatography on silica gel to afford the corresponding ether derivatives **3** and **4**. Selectivity ratio was determined by GC analysis of crude reaction mixture.

Procedure for the Comparative Experiment of Primary, Secondary and Tertiary Alcohols at 60 °C

Three reactions were carried out in parallel. To each of the flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.396 g, 1.5 mmol), KF (0.087 g, 1.5 mmol) inside the glove box. The mixture was dissolved in 4.0 mL of THF outside the glove box under argon. To the stirring solution was added corresponding alcohol **1** (0.5 mmol). The resultant reaction mixture was kept stirring at 30 °C for 5 min. To the stirring solution was added aryne precursor **2** (0.750 mmol). Then the reaction mixture was placed in preheated oil bath at 60 ° C. After 12 h, the reaction was quenched and the solvent was evaporated. Subsequently, the crude residue was purified by flash column chromatography on silica gel to afford the corresponding ether derivatives **3** and **4**. Selectivity ratio was determined by GC analysis of crude reaction mixture. the results are summarized below.



1 **2a** **3** **4**

$R^1 = R^2 = H$, **1h**
$R^1 = H$, $R^2 = Ph$, **1ad**
$R^1 = R^2 = Ph$, **1ae**

entry	R^1	R^2	temp (°C)	yield of **3** (%)[c]	yield of **4** (%)[c]	**3:4**[d]
1[a]	H	H	-20	86	<5	96:4

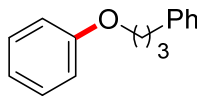
2[b]	H	H	60	<5	71	6:94
3[a]	Ph	H	-20	18	17	50:50
4[b]	Ph	H	60	<5	65	1:99
5[a]	Ph	Ph	-20	<5	32	1:99
6[b]	Ph	Ph	60	<5	64	1:99

[a] Conditions: **1** (0.50 mmol), **2a** (0.60 mmol), KF (2.4 equiv), [18] crown-6 (2.4 equiv), THF (3.0 mL), 12 h. [b] Conditions: **1** (0.50 mmol), **2a** (0.75 mmol), KF (3.0 equiv), [18] crown-6 (3.0 equiv), THF (4 mL), 12 h. [c] Isolated yields. [d] Selectivity was determined using GC analysis of the crude reaction mixture.

These studies indicate that the ability of arynes to insert into O-H bond of alcohols are in the order primary>secondary>tertiary with arynes do not undergoing insertion to tertiary alcohols even at -20 °C.

7. Synthesis and Characterization of Alkyl Aryl Ethers

(3-Phenoxypropyl)benzene (3a)[3]



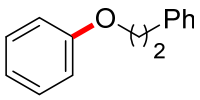
3a

Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (3-phenoxypropyl)benzene as a colourless oil **3a** (0.079 g, 75% yield, selectivity determined by GC analysis of crude reaction mixture is 95:05).

***R*f** (Pet. ether /EtOAc = 95/05): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.38-7.33 (m, 4H), 7.30-7.25 (m, 3H), 7.01-6.96 (m, 3H), 4.03 (t, *J* = 6.3 Hz, 2H), 2.89 (t, *J* = 7.8 Hz, 2H), 2.21-2.15 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.13, 141.67, 129.55, 128.65, 128.54, 126.05, 120.70, 114.63, 66.85, 32.29, 30.99. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{15}H_{16}ONa$: 235.1093, found: 235.1082. **FTIR (cm^{-1})** 3021, 2943, 2871, 1596, 1489, 1391, 1295, 1222, 1170, 1037, 761, 698.

[3] J. A. Murphy, J. Garnier, S. R. Park, F. Schoenebeck, S-Z. Zhou and A. T. Turner, *Org. Lett*., 2008, **10**, 1227.

Phenethoxybenzene (3b)[4]

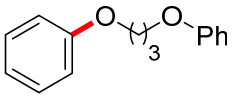


3b

Following the general procedure, treatment of 2-phenylethan-1-ol **1b** (0.061 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded phenethoxybenzene as a colourless oil **3b** (0.080 g, 81% yield, selectivity determined by GC analysis of crude reaction mixture is 96:04).

***R*f** (Pet. ether /EtOAc = 95/05): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40-7.28 (m, 7H), 6.98-6.96 (m, 3H), 4.23 (t, *J* = 7.2 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.90, 138.39, 129.58, 129.14, 128.62, 126.62, 120.84, 114.67, 77.48, 77.16, 76.84, 68.67, 35.93. **GCMS (EI)** calculated $[M]^+$ for $C_{14}H_{14}O$: 198.1, found: 198.1. **FTIR (cm^{-1})** 3022, 2938, 2875, 1595, 1489, 1387, 1297, 1232, 1170, 762.

1,3-Diphenoxypropane (3c)



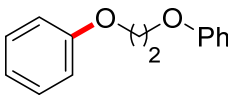
3c

Following the general procedure, treatment of 3-phenylpropan-1-ol **1c** (0.076 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded 1,3-diphenoxypropane as a colourless oil **3c** (0.088 g, 77% yield, selectivity determined by GC analysis of crude reaction mixture is 97:03).

***R*f** (Pet. ether /EtOAc = 95/05): 0.38; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.34-7.28 (m, 4H), 7.0-6.94 (m, 6H), 4.20 (t, *J* = 6.1 Hz, 4H), 2.30 (p, *J* = 6.0 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.99, 129.60, 120.86, 114.64, 64.47, 29.49. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{15}H_{16}O_2Na$: 251.1043, found: 251.1046. **FTIR (cm^{-1})** 3369, 3023, 2941, 1944, 1848, 1648, 1594, 1390, 1097, 1029, 991.

[4] W.-B. Wu and J.-M. Huang, *J. Org. Chem.*, 2014, **79**, 10189.

1,2-Diphenoxyethane (3d)[5]

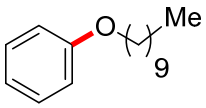


3d

Following the general procedure, treatment of 2-phenoxyethan-1-ol **1d** (0.069 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded 1,2-diphenoxyethane as a colourless oil **3d** (0.085 g, 79% yield, selectivity determined by GC analysis of crude reaction mixture is 96:04).

***R*f** (Pet. ether /EtOAc = 95/05): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.36-7.33 (m, 4H), 7.04-7.0 (m, 6H), 4.37 (s, 4H), **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.78, 129.63, 121.23, 114.84, 66.58. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{14}H_{14}O_2Na$: 237.0886, found: 237.0884. **FTIR (cm^{-1})** 3018, 2932, 2880, 1599, 1497, 1218, 772.

(Decyloxy)benzene (3e) [6]



3e

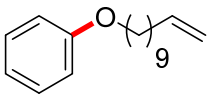
Following the general procedure, treatment of decan-1-ol **1e** (0.079 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.298 g, 242 µL, 1.0 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (decyloxy)benzene as a colourless oil **3e** (0.086 g, 74% yield, selectivity determined by GC analysis of crude reaction mixture is 94:06).

***R*f** (Pet. ether /EtOAc = 95/05): 0.61; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30-7.25 (m, 2H), 6.95-6.90 (m, 3H), 3.96 (t, *J* = 6.6 Hz, 2H), 1.79 (quin, *J* = 6.6 Hz, 2H), 1.50-1.43 (m, 2H), 1.36-1.30 (m, 12H), 0.90 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.29, 129.52, 120.57, 114.63, 68.01, 32.06, 29.74, 29.72, 29.57, 29.47, 29.46, 26.22, 22.83, 14.26. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{27}O$: 235.2056, found: 235.2061. **FTIR (cm^{-1})** 3020, 1595, 1487, 1387, 1296, 1171, 1038, 931, 882, 767.

[5] D. W. Manley and J. C. Walton, *Org. Lett.*, 2014, **16**, 5394.

[6] K. Swapna, S. N. Murthy, M. T. Jyothi and Y. V. D. Nageswar, *Org. Biomol. Chem.*, 2011, **9**, 5978

(Undec-10-en-1-yloxy)benzene (3f)[7]

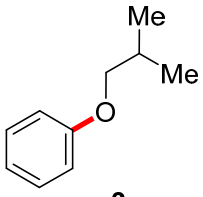


3f

Following the general procedure, treatment of undec-10-en-1-ol **1f** (0.085 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.298 g, 242 µL, 1.0 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (undec-10-en-1-yloxy)benzene as a colourless oil **3f** (0.089 g, 72% yield, selectivity determined by GC analysis of crude reaction mixture is 96:04).

***R*f** (Pet. ether /EtOAc = 95/05): 0.29; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.31-7.29 (m, 2H), 6.98-6.92 (m, 3H), 5.91-5.81 (m, 1H), 5.06-4.96 (m, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 2.08 (q, *J* = 6.9 Hz, 2H), 1.82 (quin, *J* = 6.7 Hz, 2H), 1.50-1.34 (m, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.26, 139.32, 129.51, 120.56, 114.61, 114.27, 67.96, 33.95, 29.66, 29.56, 29.53, 29.44, 29.26, 29.06, 26.20. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{27}O$: 247.2056, found: 247.2045. **FTIR (cm^{-1})** 3020, 1639, 1595, 1488, 1295, 1171, 1036, 769, 677.

Isobutoxybenzene (3g)[8]



3g

Following the general procedure, treatment of 3-phenylpropan-1-ol **1g** (0.037 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.298 g, 242 µL, 1.0 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.529 g, 2.0 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded isobutoxybenzene as a colourless oil **3g** (0.041 g, 55% yield, selectivity determined by GC analysis of crude reaction mixture is 93:07).

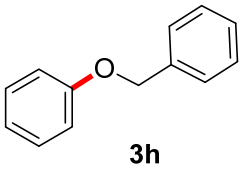
***R*f** (Pet. ether /EtOAc = 95/05): 0.65; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.35-7.31 (m, 2H), 7.0-6.95 (m, 3H), 3.78 (d, *J* = 6.6 Hz, 2H), 2.14 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.40, 129.52, 120.55, 114.66, 74.45, 28.43, 19.42. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{10}H_{15}O$: 151.1117, found: 151.1120. **FTIR (cm^{-1})** 3021, 2963, 2874, 1594, 1487, 1398, 1293, 1219, 1171, 1075, 926, 847.

---

[7] S. Maisch, F. Buckel and F. Effenberger, *J. Am. Chem. Soc.*, 2005, **127**, 17315.

[8] M. Sutter, R. Lafon, Y. Raoul, E. Metay and M. Lemaire, *Eur. J. Org. Chem.*, 2013, **26**, 5902.

(Benzyloxy)benzene (3h) [9]

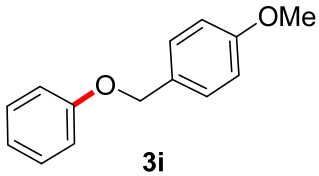


3h

Following the general procedure, treatment of phenylmethanol **1h** (0.054 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (benzyloxy)benzene as a colourless oil **3h** (0.079 g, 86% yield, selectivity determined by GC analysis of crude reaction mixture is 96:04).

***R*f** (Pet. ether /EtOAc = 95/05): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.41-7.39 (m, 2H), 7.36-7.32 (m, 2H), 7.27-7.23 (m, 3H), 6.95-6.92 (m, 3H), 5.02 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.90, 137.18, 129.61, 128.71, 128.06, 127.61, 121.06, 114.95, 70.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{13}H_{13}O$: 185.0961, found: 185.0961. **FTIR (cm^{-1})** 3035, 2922, 2870, 1593, 1493, 1459, 1379, 1168, 1113, 1079, 761.

1-Methoxy-4-(phenoxymethyl)benzene (3i)[9]



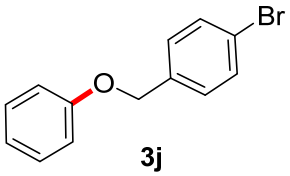
3i

Following the general procedure, treatment of (4-methoxy phenyl)methanol **1i** (0.069 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-methoxy-4-(phenoxymethyl)benzene as a white solid **3i** (0.090 g, 84% yield, selectivity determined by GC analysis of crude reaction mixture is 95:05).

***R*f** (Pet. ether /EtOAc = 95/05): 0.56; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40 (d, *J* = 8.5 Hz, 2H), 7.35-7.31 (m, 2H), 7.03-6.95 (m, 5H), 5.02 (s, 2H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.54, 158.94, 129.57, 129.35, 129.18, 120.95, 114.94, 114.09, 69.77, 55.38. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{14}H_{14}O_2Na$: 237.0886, found: 237.0886. **FTIR (cm^{-1})** 3019, 1600, 1506, 1378, 1224, 1033, 930, 818.

[9] R. Kuwano and H. Kusano, *Org. Lett.*, 2008, **10**, 1979.

1-Bromo-4-(phenoxymethyl)benzene (3j)[10]

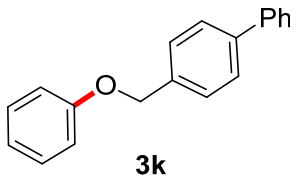


3j

Following the general procedure, treatment of (4-bromophenyl) methanol **1j** (0.094 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-bromo-4-(phenoxymethyl)benzene as a white solid **3j** (0.106 g, 80% yield, selectivity determined by GC analysis of crude reaction mixture is 97:03).

***R*f** (Pet. ether /EtOAc = 95/05): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.54 (d, *J* = 8.3 Hz, 2H), 7.34-7.31 (m, 4H), 7.03-6.98 (m, 3H), 5.03 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.59, 136.21, 131.80, 129.65, 129.17, 121.93, 121.27, 114.92, 69.20. **GCMS (EI)** calculated $[M]^+$ for $C_{13}H_{11}BrO$: 261.9, found: 262.0. **FTIR (cm^{-1})** 3021, 1595, 1411, 1298, 1172, 1021, 866, 765.

4-(Phenoxymethyl)-1,1'-biphenyl (3k)[11]



3k

Following the general procedure, treatment of [1,1'-biphenyl]-4-ylmethanol **1k** (0.092 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 4-(phenoxymethyl)-1,1'-biphenyl as a colourless oil **3k** (0.101 g, 78% yield, selectivity determined by GC analysis of crude reaction mixture is 94:06).

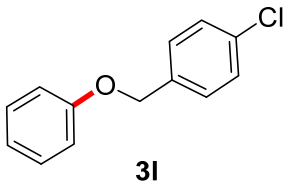
***R*f** (Pet. ether /EtOAc = 95/05): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.69-7.65 (m, 4H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.52-7.49 (m, 2H), 7.43-7.35 (m, 3H), 7.09-7.02 (m, 3H), 5.16 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.90, 141.03, 140.90, 136.18, 129.63, 128.91, 128.10, 127.46, 127.24, 121.10, 114.97, 69.76. **HRMS (ESI)** calculated $[M+H]^+$ for

[10] H. Wang , Y. Ma, H. Tian, A. Yu, J. Chang and Y. Wu, *Tetrahedron,* 2014, **70**, 2669.

[11] P. A. Champagne, J. Pomarole, M. E. Therien, Y. Benhassine, S. Beaulieu, C. Y. Legault and J. F. Paquin, *Org. Lett*., 2013, **15**, 2210.

$C_{19}H_{17}O$: 261.1274, found: 261.1274. **FTIR (cm^{-1})** 3021, 1595, 1526, 1379, 1220, 1115, 927, 768.

1-Chloro-4-(phenoxymethyl)benzene (3l)[9]

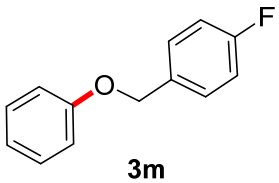


3l

Following the general procedure, treatment of (4-chlorophenyl) methanol **1l** (0.071 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-chloro-4-(phenoxymethyl)benzene as a white solid **3l** (0.092 g, 84% yield, selectivity determined by GC analysis of crude reaction mixture is 97:03).

***R*f** (Pet. ether /EtOAc = 95/05): 0.59; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40-7.35 (m, 4H), 7.33-7.29 (m, 2H), 7.01-6.96 (m, 3H), 5.04 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.64, 135.71, 133.84, 129.67, 128.90, 128.89, 121.28, 114.95, 69.23. **GCMS (EI)** calculated $[M]^+$ for $C_{13}H_{11}ClO$: 218.0, found: 218.1. **FTIR (cm^{-1})** 3021, 1595, 1494, 1413, 1376, 1220, 1028, 868, 675.

1-Fluoro-4-(phenoxymethyl)benzene (3m)[12]



3m

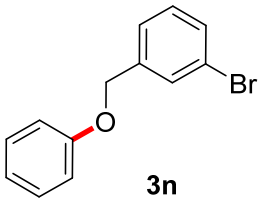
Following the general procedure, treatment of (4-fluorophenyl) methanol **1m** (0.063 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-fluoro-4-(phenoxymethyl)benzene as a colourless oil **3m** (0.078 g, 77% yield, selectivity determined by GC analysis of crude reaction mixture is 97:03).

***R*f** (Pet. ether /EtOAc = 95/05): 0.51; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.45-7.41 (m, 2H), 7.34-7.30 (m, 2H), 7.12-7.07 (m, 2H), 7.02-6.98 (m, 3H), 5.04 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.62 (d, $J_{C\text{-}F}$ = 246.2 Hz), 158.73, 132.94 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.66, 129.46 (d, $J_{C\text{-}F}$ = 8.2 Hz), 121.21, 115.61 (d, $J_{C\text{-}F}$ = 21.5 Hz), 114.94, 69.34. **GCMS (EI)**

[12] J. H. Penn and Z. Lin, *J.Org. Chem.,* 1990, **55**, 1554.

calculated $[M]^+$ for $C_{13}H_{11}FO$: 202.2, found: 202.1. **FTIR (cm^{-1})** 3021, 1598, 1505, 1423, 1378, 1298, 1163, 929, 821, 764.

1-Bromo-3-(phenoxymethyl)benzene (3n)[13]

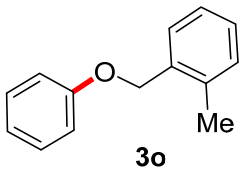


3n

Following the general procedure, treatment of (3-bromophenyl)methanol **1n** (0.094 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded 1-bromo-3-(phenoxymethyl)benzene as a pale yellow oil **3n** (0.097 g, 73% yield, selectivity determined by GC analysis of crude reaction mixture is 96:04).

***R*f** (Pet. ether /EtOAc = 95/05): 0.58; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.64 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.40-7.28 (m, 4H), 7.04-6.99 (m, 3H), 5.07 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.58, 139.56, 131.12, 130.46, 130.27, 129.69, 125.97, 122.81, 121.35, 114.94, 69.11. **GCMS (EI)** calculated $[M]^+$ for $C_{13}H_{11}OBr$: 261.9, found: 262.0. **FTIR (cm^{-1})** 3020, 1590, 1490, 1375, 1297, 1036, 926, 882, 766.

1-Methyl-2-(phenoxymethyl)benzene (3o)[9]



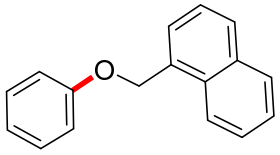
3o

Following the general procedure, treatment of *o*-tolylmethanol **1o** (0.061 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-methyl-2-(phenoxymethyl)benzene as a colourless oil **3o** (0.075 g, 76% yield, selectivity determined by GC analysis of crude reaction mixture is 95:05).

[13] P. B. Huleatt, M. L. Khoo, Y. Y. chua, T. W. Tan, R. S. Liew, B. Balogh, R. Deme, F. Goloncser, K. Magyar, D. P. Sheela, H. K. Ho, B. Sperlagh, P. Matyus and C. L. L. Chai, *J. Med. Chem.*, 2015, **58**, 1400.

***R*f** (Pet. ether /EtOAc = 95/05): 0.54; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.52-7.50 (m, 1H), 7.42-7.38 (m, 2H), 7.35-7.28 (m, 3H), 7.11-7.05 (m, 3H), 5.12 (s, 2H), 2.47 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.03, 136.81, 134.97, 130.51, 129.60, 128.75, 128.37, 126.15, 121.04, 114.88, 68.59, 19.00. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{15}O$: 199.1117, found: 199.1118. **FTIR (cm^{-1})** 3062, 1594, 1492, 1379, 1227, 1118, 939, 763.

1-(Phenoxymethyl)naphthalene (3p)[8]

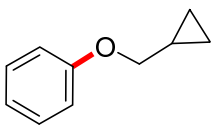


3p

Following the general procedure, treatment of naphthalen-1-ylmethanol **1p** (0.079 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-(phenoxymethyl)naphthalene as a colourless oil **3p** (0.094 g, 80% yield, selectivity determined by GC analysis of crude reaction mixture is 97:03).

***R*f** (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.18-8.16 (m, 1H), 8.01-7.99 (m, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 6.9 Hz, 1H), 7.67-7.60 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47-7.43 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.57 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.95, 133.86, 132.42, 131.62, 129.64, 129.08, 128.78, 126.68, 126.53, 125.99, 125.42, 123.82, 121.16, 114.98, 68.59. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{17}H_{14}ONa$: 257.0937, found: 257.0936. **FTIR (cm^{-1})** 3020, 1594, 1494, 1295, 1070, 1021, 923, 766, 675.

(Cyclopropylmethoxy)benzene (3q)[14]



3q

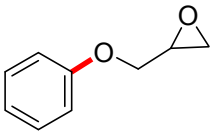
Following the general procedure, treatment of 3-phenylpropan-1-ol **1q** (0.036 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.298 g, 242 µL, 1.0 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.529 g, 2.0 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (cyclopropylmethoxy)benzene as a

[14] J. C. Lorenz, J. Long, Z. Yang, S. Xue, Y. Xie and Y. Shi, *J. Org. Chem.*, 2004, **69**, 327.

colourless oil **3q** (0.047 g, 64% yield, selectivity determined by GC analysis of crude reaction mixture is 93:07).

***R*f** (Pet. ether /EtOAc = 95/05): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.33-7.28 (m, 2H), 6.99-6.93 (m, 3H), 3.84 (d, *J* = 7.0 Hz, 2H), 1.34-1.28 (m, 1H), 0.70-0.66 (m, 2H), 0.40-0.37 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.10, 129.55, 120.71, 114.67, 72.76, 10.42, 3.31. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{10}H_{13}O$: 149.0961, found: 149.0959. **FTIR (cm^{-1})** 3075, 3020, 2924, 2871, 1591, 1485, 1404, 1367, 1024, 924.

2-(Phenoxymethyl)oxirane (3r)[15]

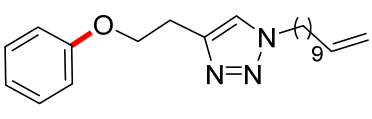


3r

Following the general procedure, treatment of oxiran-2-ylmethanol **1r** (0.037 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.298 g, 242 µL, 1.0 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.529 g, 2.0 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded 2-(phenoxymethyl)oxirane as a colourless oil **3r** (0.033 g, 44% yield, selectivity determined by GC analysis of crude reaction mixture is 90:10).

***R*f** (Pet. ether /EtOAc = 95/05): 0.27; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.34-7.28 (m, 2H), 7.02-6.95 (m, 3H), 4.25 (dd, J_1 = 3.2 Hz, J_2 = 11.0 Hz, 1H), 4.0 (dd, J_1 = 5.6 Hz, J_2 = 11.1 Hz, 1H), 3.41-3.37 (m, 1H), 2.93 (t, *J* = 4.6 Hz, 1H), 2.80-2.78 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.57, 129.62, 121.33, 114.72, 68.76, 50.26, 44.84. **GCMS (EI)** calculated $[M]^+$ for $C_9H_{10}O_2$: 150.0, found: 150.1. **FTIR (cm^{-1})** 3058, 3011, 2926, 2876, 1595, 1493, 1347, 1295, 1169, 1142, 915.

4-(2-Phenoxyethyl)-1-(undec-10-en-1-yl)-1*H*-1,2,3-triazole (3s)



3s

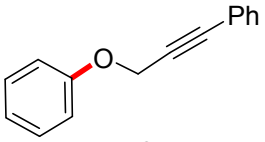
Following the general procedure, treatment of 2-(1-(undec-10-en-1-yl)-1*H*-1,2,3-triazol-4-yl)ethan-1-ol **1s** (0.066 g, 0.25 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.298 g, 121 µL, 0.5 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.5 mL) at -20 °C for 12 h. After 12 h the reaction was quenched with H_2O (5ml) and the reaction mixture was

[15] C. Tacon, E. M. Guantai, P. J. Smith and K. Chibale, *Bioorg. Med. Chem.,* 2012, **20**, 893.

extracted with EtOAc (3 x 5mL). The combined organic layers were dried over anhydrous Na2SO4, concentrated under reduced pressure to get the crude product which was purified by silica gel column chromatography (silica gel 100-200 mesh, DCM) to afford the compound 4-(2-phenoxyethyl)-1-(undec-10-en-1-yl)-1*H*-1,2,3-triazole as a brown colour oil **3s** (0.043 g, 51% yield).

***R*f** (Pet. ether /EtOAc = 50/50): 0.4; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.42 (s, 1H), 7.29-7.25 (m, 2H), 6.96-6.89 (m, 3H), 5.85-5.75 (m, 1H), 5.00-4.91 (m, 2H), 4.30 (t, *J* = 7.2 Hz, 2H), 4.24 (t, *J* = 6.4 Hz, 2H), 3.21 (t, *J* = 6.4 Hz, 2H), 2.05-2.00 (m, 2H), 1.89-1.85 (m, 2H), 1.37-1.34 (m, 2H), 1.30-1.26 (m, 10H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.72, 139.23, 129.59, 120.98, 114.60, 114.26, 66.81, 50.35, 33.86, 30.41, 29.41, 29.12, 29.06, 28.95, 26.58, 26.29. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{32}ON_3$: 342.2540, found: 342.2531. **FTIR (cm^{-1})** 3016, 1638, 1595, 1381, 1297, 1043, 915, 768, 674.

(3-Phenoxyprop-1-yn-1-yl)benzene (3t)[16]



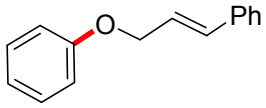
3t

Following the general procedure, treatment of 3-phenylprop-2-yn-1-ol **1t** (0.066 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (3-phenoxyprop-1-yn-1-yl)benzene as a pale yellow oil **3t** (0.090 g, 87% yield, selectivity determined by GC analysis of crude reaction mixture is 96:04).

***R*f** (Pet. ether /EtOAc = 95/05): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.49-7.46 (m, 2H), 7.37-7.32 (m, 5H), 7.09-7.02 (m, 3H), 4.94 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.92, 131.93, 129.59, 128.77, 128.40, 122.41, 121.54, 115.09, 87.24, 84.09, 56.71. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{13}O$: 209.0961, found: 209.0958. **FTIR (cm^{-1})** 3021, 2920, 2867, 1594, 1491, 1451, 1297, 1220, 922, 882.

[16] X.-F. Wu, H. Neumann and M. Beller, *Chem. Commun.,* 2010, **46**, 3131.

(Cinnamyloxy)benzene (3u)[17]

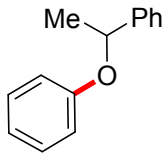


3u

Following the general procedure, treatment of (E)-3-phenylprop-2-en-1-ol **1u** (0.067 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (cinnamyloxy)benzene as a pale yellow oil **3u** (0.087 g, 83% yield, selectivity determined by GC analysis of crude reaction mixture is 95:05).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.47-7.45 (m, 2H), 7.39-7.28 (m, 5H), 7.03-7.01 (m, 3H), 6.81-6.77 (d, *J* = 16.1 Hz, 1H), 6.51-6.44 (m, 1H), 4.76 (d, *J* = 5.9 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.75, 136.58, 133.09, 129.63, 128.72, 128.02, 126.71, 124.64, 121.03, 114.90, 68.67. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{15}H_{14}ONa$: 233.0937, found: 233.0938. **FTIR (cm^{-1})** 3021, 2926, 1593, 1492, 1379, 1297, 1220, 1076, 1023, 972.

(1-Phenoxyethyl)benzene (3v)[7]



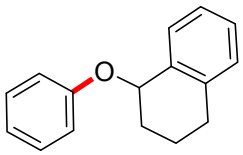
3v

Following the general procedure, treatment of 1-phenylethan-1-ol **1v** (0.061 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (1-phenoxyethyl)benzene as a colourless oil **3v** (0.037 g, 37% yield, 52% yield based on starting material recovery, selectivity determined by GC analysis of crude reaction mixture is 68:32).

***R*f** (Pet. ether /EtOAc = 95/05): 0.55; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.44-7.23 (m, 7H), 6.94-6.91 (m, 3H), 5.37 (q, *J* = 6.4 Hz, 1H), 1.70 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.11, 143.40, 129.44, 128.73, 127.53, 125.67, 120.76, 116.05, 75.99, 24.62. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{14}ONa$: 221.0937, found: 221.0941. **FTIR (cm^{-1})** 3391, 3021, 1594, 1491, 1370, 1220, 1075, 926, 767, 683.

[17] X. Shang, Y. Xiong, Y. Zhang, L. Zhang, and Z. Liu, *Synlett*, 2012, **23**, 259.

1-Phenoxy-1,2,3,4-tetrahydronaphthalene (3w)

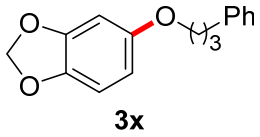


3w

Following the general procedure, treatment of 1,2,3,4-tetrahydronaphthalen-1-ol **1w** (0.074 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded 1-phenoxy-1,2,3,4-tetrahydronaphthalene as a colourless oil **3w** (0.035 g, 31% yield, 69% yield based on starting material recovery, selectivity determined by GC analysis of crude reaction mixture is 75:25).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.44 (d, *J* = 7.4 Hz, 1H), 7.38-7.34 (m, 2H), 7.30-7.19 (m, 3H), 7.09-7.07 (m, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 5.42 (t, *J* = 5.1 Hz, 1H), 2.98-2.78 (m, 2H), 2.23-1.83 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.38, 137.84, 135.87, 129.70, 129.57, 129.17, 128.05, 126.19, 121.11, 116.51, 74.04, 29.28, 28.14, 18.96. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{16}H_{16}ONa$: 247.1093, found: 247.1089. **FTIR (cm^{-1})** 3020, 2939, 2873, 1592, 1488,1359, 1286, 1228, 1163, 1032, 961, 879.

5-(3-Phenylpropoxy)benzo[*d*][1,3]dioxole (3x)[18]



3x

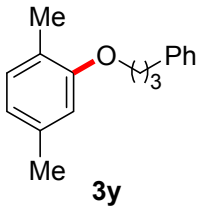
Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 6-(trimethylsilyl)benzo[*d*][1,3] dioxol-5-yl trifluoromethanesulfonate **2b** (0.205 g, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 5-(3-phenylpropoxy)benzo[*d*][1,3]dioxole as a colourless oil **3x** (0.102 g, 80% yield, selectivity determined by GC analysis of crude reaction mixture is 90:10).

***R*f** (Pet. ether /EtOAc = 95/05): 0.32; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.36 -7.32 (m, 2H), 7.28-7.23 (m, 3H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.37 (dd, J_1 = 8.5, J_2 = 2.5 Hz, 1H), 5.95 (s, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.15-2.08 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.67, 148.34, 141.64, 128.63, 128.53, 126.04,

[18] I. Engelbrecht, J. P. Petzer and A. Petzer, *Bioorg. Med. Chem. Lett.*, 2015**, 25**, 1896.

108.05, 105.82, 101.19, 98.20, 67.94, 32.26, 30.98. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{17}O_3$: 257.1172, found: 257.1166. **FTIR (cm^{-1})** 3020, 1739, 1622, 1488, 1348, 1187, 1097, 933, 831, 766.

1,4-Dimethyl-2-(3-phenylpropoxy)benzene (3y)

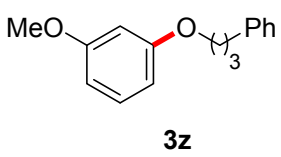


3y

Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 3,6-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2c** (0.196 g, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded 1,4-dimethyl-2-(3-phenylpropoxy)benzene as a colourless oil **3y** (0.094 g, 78% yield, selectivity determined by GC analysis of crude reaction mixture is 92:08).

***R*f** (Pet. ether /EtOAc = 95/05): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.36-7.33 (m, 2H), 7.28-7.23 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 4.00 (t, *J* = 6.2 Hz, 2H), 2.89 (t, *J* = 7.9 Hz, 2H), 2.36 (s, 3H), 2.28 (s, 3H), 2.21 – 2.14 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.08, 141.83, 136.59, 130.43, 128.66, 128.53, 126.01, 123.73, 120.81, 112.09, 66.76, 32.40, 31.18, 21.53, 15.95. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{21}O$: 241.1587, found: 241.1583. **FTIR (cm^{-1})** 3019, 1598, 1507, 1422, 1262, 1162, 1039, 925, 849, 767.

1-Methoxy-3-(3-phenylpropoxy)benzene (3z)

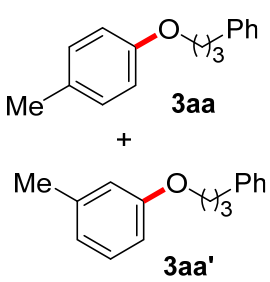


3z

Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.034 g, 0.25 mmol) with 2-methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (0.099 g, 0.3 mmol) in the presence of KF (0.035 g, 0.6 mmol) and 18-crown-6 (0.159 g, 0.6 mmol) in THF (1.5 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-methoxy-4-(3-phenylpropoxy)benzene and 1-methoxy-3-(3-phenylpropoxy)benzene as a colourless oil **3z** (0.041 g, 67% yield, selectivity determined by GC analysis of crude reaction mixture is 92:08).

***R*f** (Pet. ether /EtOAc = 95/05): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.35-7.31 (m, 2H), 7.26-7.19 (m, 4H), 6.55-6.50 (m, 3H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.17-2.10 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.95, 160.42, 141.65, 129.98, 128.66, 128.55, 126.06, 106.86, 106.32, 101.10, 67.01, 55.38, 32.29, 30.95. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{19}O_2$: 243.1380, found: 243.1373. **FTIR (cm^{-1})** 3018, 1598, 1484, 1458, 1277, 1209, 1043, 966, 841.

1-Methyl-4-(3-phenylpropoxy)benzene[19] (3aa) and 1-Methyl-3-(3-phenylpropoxy)benzene[20] (3aa')



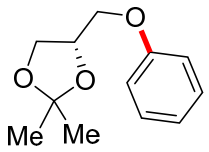
Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2e** (0.187 g, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded 1-Methyl-4-(3-phenylpropoxy)benzene **3aa** and 1-Methyl-3-(3-phenylpropoxy)benzene **3aa'** as a colourless oil (0.074 g, 65% yield, selectivity and regioisomeric ratio determined by GC analysis of crude reaction mixture is 89:11 and 1.5:1).

***R*f** (Pet. ether /EtOAc = 95/05): 0.64; **^{1}H NMR (400 MHz, $CDCl_3$) of major isomer δ** 7.38-7.14 (m, 6H), 6.89-6.77 (m, 3H), 4.04-3.99 (m, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 2.19-2.15 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) of major isomer** δ 159.15, 147.71, 129.99, 128.66, 126.02, 114.51, 111.49, 66.79, 32.29, 21.65. **^{1}H NMR (400 MHz, $CDCl_3$) of minor isomer δ** 4.04-3.99 (m, 2H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) of minor isomer** δ 157.01, 139.55, 129.28, 128.52, 121.54, 115.51, 67.03, 31.02, 20.59. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{16}H_{18}ONa$: 249.1250, found: 249.1239. **FTIR (cm^{-1})** 3020, 1598, 1502, 1390, 1252, 1164, 1041, 948, 815, 762.

[19] D. Gartner, A. Welther, B. R. Rad, R. Wolf and A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.*, 2014, **53**, 3722.

[20] M.-O. Simon, S. A. Girard and C.-J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 7537.

(*S*)-2,2-Dimethyl-4-(phenoxymethyl)-1,3-dioxolane (3ab)

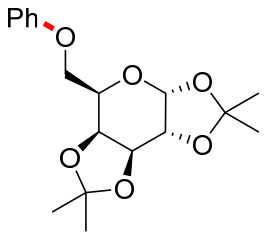


3ab

Following the general procedure, treatment of (S)-2,2-dimethyl-4-(phenoxymethyl)-1,3-dioxolane **1ab** (0.066 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 96/04) of the crude reaction mixture using silica gel afforded (*S*)-2,2-dimethyl-4-(phenoxymethyl)-1,3-dioxolane as a colourless oil **3ab** (0.084 g, 81% yield, selectivity determined by GC analysis of crude reaction mixture is 96:04).

***R*f** (Pet. ether /EtOAc = 90/10): 0.5; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.33-7.29 (m, 2H), 7.01-6.94 (m, 3H), 4.54-4.46 (m, 1H), 4.22-4.18 (m, 1H), 4.11-4.07 (m, 1H), 3.98-3.92 (m, 2H), 1.50 (s, 3H), 1.44 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.63, 129.57, 121.20, 114.60, 109.82, 74.12, 68.78, 66.97, 26.89, 25.47. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{12}H_{16}O_3Na$: 231.0992, found: 231.0993. **FTIR (cm^{-1})** 3061, 1596, 1493, 1463, 1375, 1243, 1158, 1052, 985, 846, 750.

(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyl-5-(phenoxymethyl)tetrahydro-5*H*-bis([1,3]dioxolo) [4,5-b:4',5'-d]pyran (3ac)



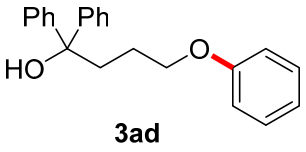
3ac

Following the general procedure, treatment of galactose **1ac** (0.130 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-(phenoxymethyl)tetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran as a white solid **3ac** (0.088 g, 52% yield, selectivity determined by GC analysis of crude reaction mixture is 88:12).

***R*f** (Pet. ether /EtOAc = 90/10): 0.46; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.32-7.28 (m, 2H), 6.98-6.95 (m, 3H), 5.61 (d, J = 5.0 Hz, 1H), 4.68 (dd, J_1 = 2.3 Hz, J_2 = 8.0 Hz, 1H), 4.41-4.36 (m, 2H), 4.23-4.12 (m, 3H), 1.54 (s, 3H), 1.49 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.68, 129.51, 121.05, 114.94, 109.56, 108.87, 96.51, 71.08,

70.76, 66.56, 66.26, 26.15, 26.12, 25.08, 24.58. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{24}O_6Na$: 359.1465, found: 359.1460. **FTIR (cm^{-1})** 3015, 1596, 1493, 1465, 1380, 1249, 1216, 1169, 1006, 762.

4-Phenoxy-1,1-diphenylbutan-1-ol (3ad)

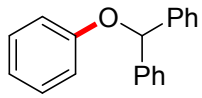


3ad

Following the general procedure, treatment of 1,1-diphenylbutane-1,4-diol **1ad** (0.121 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 94/06) of the crude reaction mixture using silica gel afforded 4-phenoxy-1,1-diphenylbutan-1-ol as a colourless oil **3ad** (0.112 g, 70% yield).

***R*f** (Pet. ether /EtOAc = 90/10): 0.3; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.49-7.47 (m, 4H), 7.37-7.24 (m, 8H), 6.98-6.89 (m, 3H), 4.0 (t, *J* = 6.1 Hz, 2H), 2.55-2.50 (m, 3H, the tertiary O-H signal exchangeable with D_2O), 1.88-1.81 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.95, 147.07, 129.56, 128.34, 127.01, 126.20, 120.83, 114.62, 78.14, 68.10, 38.75, 24.16. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{22}H_{22}O_2Na$: 341.1512, found: 341.1515. **FTIR (cm^{-1})** 3435, 3066, 1597, 1487, 1385, 1297, 1241, 1167, 1093, 1040, 909, 736.

(Phenoxymethylene)dibenzene (3ah)[9]



3ah

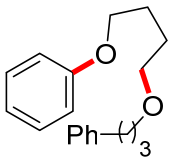
Following the general procedure, treatment of diphenylmethanol **1ah** (0.092 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -20 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (phenoxymethylene)dibenzene as a white solid **3ah** (0.024 g, 18% yield, selectivity determined by GC analysis of crude reaction mixture is 50:50).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.47-7.45 (m, 4H), 7.39-7.36 (m, 4H), 7.32-7.23 (m, 4H), 7.0-6.94 (m, 3H), 6.25 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.23, 141.41, 129.49, 128.73, 127.86, 127.03, 121.10, 116.22, 81.79. **GCMS**

(EI) calculated $[M]^+$ for $C_{19}H_{16}O$: 260.1, found: 260.1. **FTIR (cm^{-1})** 3021, 1721, 1592, 1487, 1462, 1365, 1222, 1114, 1072, 1024, 924.

8. Synthesis and Characterization of (4-(Alkoxy)butoxy)arenes

(3-(4-Phenoxybutoxy)propyl)benzene (4a)

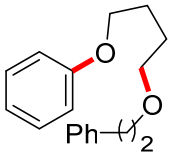


4a

Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (3-(4-phenoxybutoxy)propyl)benzene as a colourless oil **4a** (0.087 g, 61% yield, selectivity determined by GC analysis of crude reaction mixture is 91:09).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34-7.30 (m, 4H), 7.24-7.21 (m, 3H), 6.99-6.93 (m, 3H), 4.03 (t, *J* = 6.0 Hz, 2H), 3.54 -3.46 (m, 4H), 2.74 (t, *J* = 7.4 Hz, 2H), 1.98-1.89 (m, 4H), 1.84-1.78 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.15, 142.12, 129.52, 128.58, 128.42, 125.85, 120.62, 114.58, 70.54, 70.06, 67.64, 32.49, 31.44, 26.50, 26.31. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{19}H_{24}O_2Na$: 307.1669, found: 307.1669. **FTIR (cm^{-1})** 3018, 2942, 2866, 1596, 1489, 1379, 1295, 1219, 1171, 1112, 1043, 763, 701, 682.

(4-Phenethoxybutoxy)benzene (4b)



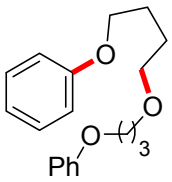
4b

Following the general procedure, treatment of 2-phenylethan-1-ol **1b** (0.061 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (4-phenethoxybutoxy)benzene as a colourless oil **4b** (0.089 g, 66% yield, selectivity determined by GC analysis of crude reaction mixture is 89:11).

***R*f** (Pet. ether /EtOAc = 95/05): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35-7.25 (m, 7H), 6.98-6.92 (m, 3H), 4.0 (t, *J* = 6.1 Hz, 2H), 3.69 (t, *J* = 7.2 Hz, 2H), 3.55 (t, *J* = 6.2 Hz, 2H),

2.94 (t, *J* = 7.1 Hz, 2H), 1.91-1.87 (m, 2H), 1.82-1.78 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.15, 139.18, 129.53, 129.03, 128.45, 126.28, 120.63, 114.60, 71.95, 70.65, 67.60, 36.51, 26.43, 26.25. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{22}O_2Na$: 293.1512, found: 293.1510. **FTIR (cm^{-1})** 3018, 2942, 2865, 2797, 1595, 1488, 1373, 1296, 1111, 762.

(3-(4-Phenoxybutoxy)propoxy)benzene (4c)

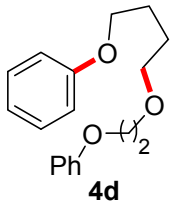


4c

Following the general procedure, treatment of 3-phenoxypropan-1-ol **1c** (0.076 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (3-(4-phenoxybutoxy)propoxy)benzene as a colourless oil **4c** (0.104 g, 69% yield, selectivity determined by GC analysis of crude reaction mixture is 91:09).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33-7.29 (m, 4H), 6.97-6.91 (m, 6H), 4.10 (t, *J* = 6.1 Hz, 2H), 4.0 (t, *J* = 6.0 Hz, 2H), 3.65 (t, *J* = 6.1 Hz, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 2.11-2.07 (m, 2H), 1.91-1.87 (m, 2H), 1.81-1.78 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.14, 129.54, 120.70, 120.64, 114.63, 114.60, 70.72, 67.60, 67.42, 64.87, 29.90, 26.46, 26.26. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{19}H_{24}O_3Na$: 323.1618, found: 323.1618. **FTIR (cm^{-1})** 3013, 2950, 2871, 1587, 1497, 1472, 1301, 1218, 1118, 770.

(2-(4-Phenoxybutoxy)ethoxy)benzene (4d)



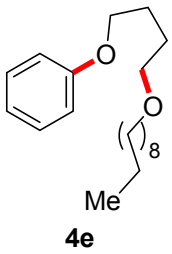
4d

Following the general procedure, treatment of 2-phenoxyethan-1-ol **1d** (0.069 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (2-(4-phenoxybutoxy)ethoxy)benzene as a colourless oil **4d** (0.088 g, 62% yield, selectivity determined by GC analysis of crude reaction mixture is 91:09).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33-7.28 (m, 4H), 6.98-6.92 (m, 6H), 4.15 (t, *J* = 4.7 Hz, 2H), 4.02 (t, *J* = 6.3 Hz, 2H), 3.83 (t, *J* = 4.8 Hz,

2H), 3.64 (t, *J* = 6.3 Hz, 2H) 1.95-1.88 (m, 2H), 1.87-1.82 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.11, 158.91, 129.51, 120.93, 120.61, 114.74, 114.57, 71.20, 69.34, 67.55, 67.41, 26.37, 26.17. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{22}O_3Na$: 309.1461, found: 309.1459. **FTIR (cm^{-1})** 3041, 2937, 2869, 1595, 1489, 1382, 1295, 1242, 1166, 1125, 921.

(4-(Decyloxy)butoxy)benzene (4e)

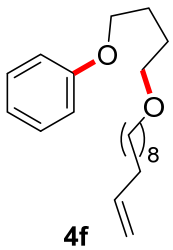


4e

Following the general procedure, treatment of decan-1-ol **1e** (0.079 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (4-(decyloxy)butoxy)benzene as a colourless oil **4e** (0.101 g, 66% yield, selectivity determined by GC analysis of crude reaction mixture is 84:16).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30-7.25 (m, 2H), 6.96-6.89 (m, 3H), 3.99 (t, *J* = 6.4 Hz, 2H), 3.48 (t, *J* = 6.3 Hz, 2H), 3.42 (t, *J* = 6.7 Hz, 2H), 1.91-1.84 (m, 2H), 1.80-1.73 (m, 2H), 1.63-1.55 (m, 2H), 1.32-1.28 (m, 14H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.17, 129.49, 120.59, 114.57, 71.14, 70.50, 67.64, 32.03, 29.91, 29.75, 29.71, 29.64, 29.46, 26.49, 26.35, 26.32, 22.81, 14.24. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{20}H_{34}O_2Na$: 329.2451, found: 329.2455. **FTIR (cm^{-1})** 3019, 1721, 1595, 1487, 1381, 1295, 1109, 929, 882, 768.

(4-(Undec-10-en-1-yloxy)butoxy)benzene (4f)

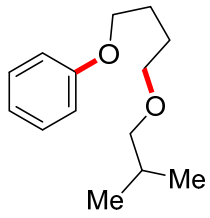


4f

Following the general procedure, treatment of undec-10-en-1-ol **1f** (0.085 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99.5/0.5) of the crude reaction mixture using silica gel afforded (4-(undec-10-en-1-yloxy)butoxy)benzene as a colourless oil **4f** (0.092 g, 58% yield, selectivity determined by GC analysis of crude reaction mixture is 85:15).

***R*f** (Pet. ether /EtOAc = 95/05): 0.66; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30-7.28 (m, 2H), 6.97-6.91 (m, 3H), 5.89-5.79 (m, 1H), 5.04-4.94 (m, 2H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.50 (t, *J* = 6.2 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 2.09-2.04 (m, 2H), 1.93-1.86 (m, 2H), 1.81-1.75 (m, 2H), 1.63-1.56 (m, 2H), 1.40-1.31 (m, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.18, 139.39, 129.54, 120.63, 114.62, 114.24, 71.17, 70.54, 67.69, 33.95, 29.92, 29.69, 29.63, 29.58, 29.27, 29.07, 26.51, 26.35, 26.34. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{21}H_{34}O_2Na$: 341.2451, found: 341.2442. **FTIR (cm^{-1})** 3016, 1639, 1595, 1488, 1381, 1220, 1110, 1042, 916, 765, 677.

(4-Isobutoxybutoxy)benzene (4g)

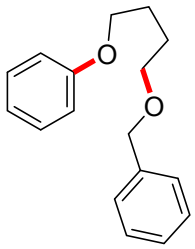


4g

Following the general procedure, treatment of 2-methylpropan-1-ol **1g** (0.037 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (4-isobutoxybutoxy)benzene as a colourless oil **4g** (0.080 g, 72% yield, selectivity determined by GC analysis of crude reaction mixture is 92:08).

***R*f** (Pet. ether /EtOAc = 95/05): 0.51; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.28 (m, 2H), 6.98-6.92 (m, 3H), 4.02 (t, *J* = 6.3 Hz, 2H), 3.50 (t, *J* = 6.3 Hz, 2H), 3.32 (d, *J* = 6.8 Hz, 2H), 1.94-1.86 (m, 3H), 1.82-1.76 (m, 2H), 0.95 (d, *J* =6.7 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.20, 129.54, 120.62, 114.62, 78.02, 70.66, 67.72, 28.61, 26.50, 26.34, 19.56. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{14}H_{22}O_2Na$: 245.1512, found: 245.1516. **FTIR (cm^{-1})** 3017, 2957, 2868, 1595, 1487, 1382, 1296, 1219, 1169, 1106.

(4-(Benzyloxy)butoxy)benzene (4h)



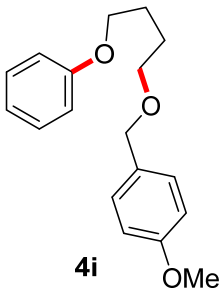
4h

Following the general procedure, treatment of phenylmethanol **1h** (0.054 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (4-

(benzyloxy)butoxy)benzene as a colourless oil **4h** (0.091 g, 71% yield, selectivity determined by GC analysis of crude reaction mixture is 94:06).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39-7.38 (m, 4H), 7.33-7.29 (m, 3H), 6.97-6.91 (m, 3H), 4.55 (s, 2H), 4.01 (t, *J* = 5.9 Hz, 2H), 3.58 (t, *J* = 6.3 Hz, 2H), 1.95-1.91 (m, 2H), 1.86-1.82 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.13, 138.66, 129.52, 128.49, 127.75, 127.65, 120.62, 114.59, 73.02, 70.05, 67.59, 26.49, 26.27. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{17}H_{20}O_2Na$: 279.1356, found: 279.1354. **FTIR (cm^{-1})** 3018, 2943, 2864, 1595, 1488, 1368, 1296, 1231, 1104, 764.

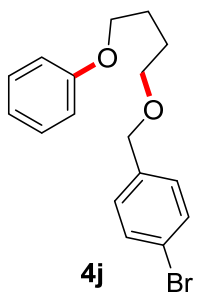
1-Methoxy-4-((4-phenoxybutoxy)methyl)benzene (4i)



Following the general procedure, treatment of (4-methoxyphenyl) methanol **1i** (0.069 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-methoxy-4-((4-phenoxybutoxy)methyl)benzene as a colourless oil **4i** (0.099 g, 69% yield, selectivity determined by GC analysis of crude reaction mixture is 90:10).

***R*f** (Pet. ether /EtOAc = 95/05): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.28 (m, 4H), 6.98-6.90 (m, 5H), 4.48 (s, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 3.82 (s, 3H), 3.55 (t, *J* = 6.3 Hz, 2H), 1.95-1.88 (m, 2H), 1.85-1.79 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.22, 159.11, 130.71, 129.48, 129.34, 120.58, 114.56, 113.84, 72.63, 69.69, 67.56, 55.32, 26.44, 26.24. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{22}O_3Na$: 309.1461, found: 309.1473. **FTIR (cm^{-1})** 3017, 1600, 1506, 1298, 1220, 1099, 1039, 767.

1-Bromo-4-((4-phenoxybutoxy)methyl)benzene (4j)

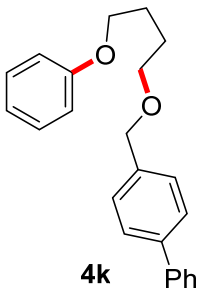


Following the general procedure, treatment of (4-bromophenyl) methanol **1j** (0.094 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc

= 99/01) of the crude reaction mixture using silica gel afforded 1-bromo-4-((4-phenoxy butoxy)methyl)benzene as a colourless oil **4j** (0.115 g, 68% yield, selectivity determined by GC analysis of crude reaction mixture is 87:13).

***R*f** (Pet. ether /EtOAc = 95/05): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.32-7.28 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.48 (s, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 3.56 (t, *J* = 6.3 Hz, 2H), 1.94-1.88 (m, 2H), 1.86-1.79 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.08, 137.70, 131.56, 129.52, 129.33, 121.45, 120.65, 114.56, 72.21, 70.18, 67.53, 26.46, 26.23. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{17}H_{19}O_2BrNa$: 357.0461, found: 357.0478. **FTIR (cm^{-1})** 3016, 1595, 1488, 1394, 1294, 1168, 1018, 765.

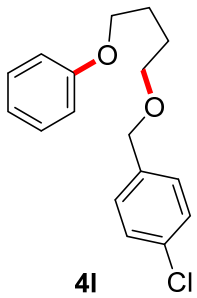
4-((4-Phenoxybutoxy)methyl)-1,1'-biphenyl (4k)



Following the general procedure, treatment of [1,1'-biphenyl]-4-yl methanol **1k** (0.092 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 4-((4-phenoxy butoxy)methyl)-1,1'-biphenyl as a colourless oil **4k** (0.113 g, 68% yield, selectivity determined by GC analysis of crude reaction mixture is 91:09).

***R*f** (Pet. ether /EtOAc = 95/05): 0.31; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68-7.65 (m, 4H), 7.53-7.48 (m, 4H), 7.44-7.40 (m, 1H), 7.37-7.33 (m, 2H), 7.03-6.97 (m, 3H), 4.63 (s, 2H), 4.06 (t, *J* = 6.3 Hz, 2H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.02-1.96 (m, 2H), 1.93-1.87 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.11, 141.00, 140.57, 137.69, 129.50, 128.85, 128.19, 127.33, 127.22, 127.17, 120.60, 114.56, 72.70, 70.07, 67.55, 26.48, 26.25. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{23}H_{24}O_2Na$: 355.1669, found: 355.1681. **FTIR (cm^{-1})** 3019, 1596, 1488, 1397, 1296, 1172, 1046, 766.

1-Chloro-4-((4-phenoxybutoxy)methyl)benzene (4l)

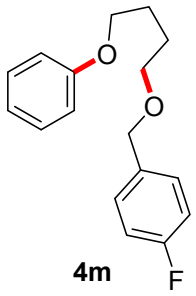


4l

Following the general procedure, treatment of (4-chlorophenyl)methanol **1l** (0.071 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-chloro-4-((4-phenoxybutoxy)methyl)benzene as a yellow oil **4l** (0.102 g, 70% yield, selectivity determined by GC analysis of crude reaction mixture is 92:08).

***R*f** (Pet. ether /EtOAc = 95/05): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.36-7.30 (m, 6H), 6.98-6.92 (m, 3H), 4.52 (s, 2H), 4.02 (t, *J* = 6.3 Hz, 2H), 3.58 (t, *J* = 6.1 Hz, 2H), 1.95-1.90 (m, 2H), 1.88-1.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.11, 137.19, 133.35, 129.54, 129.03, 128.63, 120.67, 114.59, 72.21, 70.19, 67.56, 26.48, 26.26. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{17}H_{19}O_2ClNa$: 313.0966, found: 313.0966. **FTIR (cm^{-1})** 3013, 2947, 2866, 1495, 1472, 1360, 1301, 1245, 1059, 808.

1-Fluoro-4-((4-phenoxybutoxy)methyl)benzene (4m)

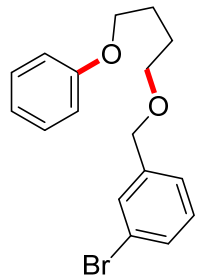


4m

Following the general procedure, treatment of (4-fluorophenyl) methanol **1m** (0.063 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-fluoro-4-((4-phenoxy butoxy)methyl)benzene as a colourless oil **4m** (0.082 g, 60% yield, selectivity determined by GC analysis of crude reaction mixture is 92:08).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35-7.28 (m, 4H), 7.07-7.03 (m, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.93-6.91 (m, 2H), 4.50 (s, 2H), 4.01 (t, *J* = 6.2 Hz, 2H), 3.57 (t, *J* = 6.2 Hz, 2H), 1.95-1.88 (m, 2H), 1.86-1.79 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.38 (d, J_{C-F} = 245.4 Hz), 159.10, 134.40 (d, J_{C-F} = 2.8 Hz), 129.52, 129.46 (d, J_{C-F} = 8.5 Hz), 120.64, 115.30 (d, J_{C-F} = 21.3 Hz), 114.57, 72.28, 70.07, 67.54, 26.46, 26.25. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{17}H_{19}O_2FNa$: 297.1261, found: 297.1273. **FTIR (cm^{-1})** 3017, 1598, 1503, 1362, 1224, 1094, 825, 766.

1-Bromo-3-((4-phenoxybutoxy)methyl)benzene (4n)

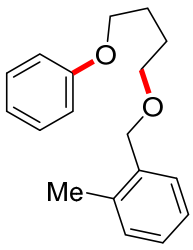


4n

Following the general procedure, treatment of (3-bromophenyl)methanol **1n** (0.094 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-bromo-3-((4-phenoxybutoxy)methyl)benzeneas a yellow oil **4n** (0.111 g, 66% yield, selectivity determined by GC analysis of crude reaction mixture is 89:11).

***R*f** (Pet. ether /EtOAc = 95/05): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.33-7.24 (m, 4H), 6.99-6.92 (m, 3H), 4.51 (s, 2H), 4.02 (t, *J* = 6.1 Hz, 2H), 3.58 (t, *J* = 6.3 Hz, 2H), 1.97-1.90 (m, 2H), 1.88-1.81 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.11, 141.08, 130.69, 130.61, 130.08, 129.55, 126.12, 122.64, 120.67, 114.59, 72.16, 70.35, 67.56, 26.48, 26.26. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{20}O_2Br$: 335.0641, found: 335.0627. **FTIR (cm^{-1})** 3017, 1590, 1486, 1393, 1293, 1098, 880, 772.

1-Methyl-2-((4-phenoxybutoxy)methyl)benzene (4o)



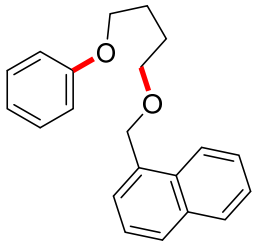
4o

Following the general procedure, treatment of *o*-tolylmethanol **1o** (0.061 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-methyl-2-((4-phenoxybutoxy)methyl) benzene as a colourless oil **4o** (0.094 g, 70% yield, selectivity determined by GC analysis of crude reaction mixture is 89:11).

***R*f** (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.47-7.43 (m, 2H), 7.40-7.33 (m, 3H), 7.12-7.05 (m, 3H), 4.68 (s, 2H), 4.14 (t, *J* = 6.3 Hz, 2H), 3.74 (t, *J* = 6.3 Hz, 2H), 2.52 (s, 3H), 2.10-2.04 (m, 2H), 2.02-1.95 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.12, 136.67, 136.48, 130.29, 129.49, 128.56, 127.82, 125.85, 120.59, 114.57, 71.42, 70.14, 67.56, 26.51, 26.30, 18.88. **HRMS (ESI)** calculated

[M+Na] $^{+}$ for $C_{18}H_{22}O_2Na$: 293.1512, found: 293.1510. **FTIR (cm^{-1})** 3018, 1728, 1595, 1371, 1294, 1220, 1089, 1046, 881.

1-((4-Phenoxybutoxy)methyl)naphthalene (4p)

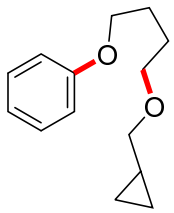


4p

Following the general procedure, treatment of naphthalen-1-ylmethanol **1p** (0.079 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-((4-Phenoxybutoxy) methyl)naphthalene as a colourless oil **4p** (0.105 g, 68% yield, selectivity determined by GC analysis of crude reaction mixture is 91:09).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.54; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.63-7.55 (m, 3H), 7.52-7.48 (m, 1H), 7.36-7.32 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.95-6.93 (m, 2H), 5.03 (s, 2H), 4.00 (t, *J* = 6.1 Hz, 2H), 3.69 (t, *J* = 6.1 Hz, 2H), 1.95-1.90 (m, 4H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 159.10, 134.05, 133.84, 131.82, 129.47, 128.60, 126.40, 126.22, 125.83, 125.29, 124.13, 120.57, 114.55, 71.52, 70.06, 67.50, 26.49, 26.25. **HRMS (ESI)** calculated [M+Na] $^{+}$ for $C_{21}H_{22}O_2Na$: 329.1512, found: 329.1514. **FTIR (cm^{-1})** 3018, 1595, 1494, 1293, 1169, 1095, 1045, 765.

(4-(Cyclopropylmethoxy)butoxy)benzene (4q)

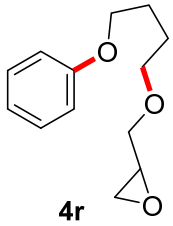


4q

Following the general procedure, treatment of cyclopropylmethanol **1q** (0.036 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (4-(cyclopropylmethoxy)butoxy)benzene as a colourless oil **4q** (0.059 g, 54% yield, selectivity determined by GC analysis of crude reaction mixture is 88:12).

***R*f** (Pet. ether /EtOAc = 95/05): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.28 (m, 2H), 6.97-6.91 (m, 3H), 4.02 (t, *J* = 6.1 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 3.31 (d, *J* = 7.0 Hz, 2H), 1.92-1.88 (m, 2H), 1.82-1.78 (m, 2H), 1.11-1.07 (m, 1H), 0.58-0.54 (m, 2H), 0.25-0.21 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.15, 129.52, 120.62, 114.60, 75.70, 70.33, 67.65, 26.49, 26.28, 10.78, 3.09. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{14}H_{20}O_2Na$: 243.1356, found: 243.1351. **FTIR (cm^{-1})** 3020, 1596, 1488, 1430, 1217, 1108, 1044, 925, 769, 673.

2-((4-Phenoxybutoxy)methyl)oxirane (4r)

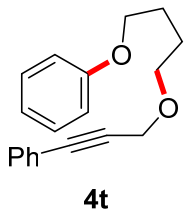


4r

Following the general procedure, treatment of oxiran-2-ylmethanol **1r** (0.033 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 2-((4-phenoxybutoxy)methyl)oxirane as a colourless oil **4r** (0.044 g, 40% yield, selectivity determined by GC analysis of crude reaction mixture is 85:15).

***R*f** (Pet. ether /EtOAc = 95/05): 0.15; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.28 (m, 2H), 6.97-6.91 (m, 3H), 4.01 (t, *J* = 6.2 Hz, 2H), 3.77 (dd, J_1 = 2.8 Hz, J_2 = 11.1 Hz, 1H), 3.63 - 3.56 (m, 2H), 3.42 (dd, J_1 = 5.8 Hz, J_2 = 11.5 Hz, 1H) 3.19-3.16 (m, 1H) 2.82 (t, *J* = 4.7 Hz, 1H), 2.65-2.63 (m, 1H), 1.93-1.86 (m, 2H), 1.84-1.77 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.12, 129.54, 120.66, 114.59, 71.59, 71.26, 67.57, 51.0, 44.41, 26.45, 26.16. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{13}H_{18}O_3Na$: 245.1148, found: 245.1145. **FTIR (cm^{-1})** 3019, 2945, 2868, 1656, 1595, 1488, 1462, 1295, 1221, 1088, 923.

(3-(4-Phenoxybutoxy)prop-1-yn-1-yl)benzene (4t)



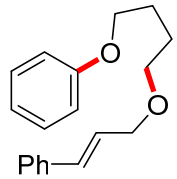
4t

Following the general procedure, treatment of 3-phenylprop-2-yn-1-ol **1t** (0.066 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (3-(4-phenoxybutoxy)prop-

1-yn-1-yl)benzene as a yellow oil **4t** (0.061 g, 44% yield, selectivity determined by GC analysis of crude reaction mixture is 87:13).

***R*f** (Pet. ether /EtOAc = 95/05): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.48 (m, 2H), 7.36-7.31 (m, 5H), 6.99-6.93 (m, 3H), 4.42 (s, 2H), 4.05 (t, *J* = 6.2 Hz, 2H), 3.71 (t, *J* = 6.5 Hz, 2H), 1.97-1.92 (m, 2H), 1.90-1.86 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.12, 131.87, 129.52, 128.51, 128.39, 122.79, 120.63, 114.60, 86.17, 85.45, 69.78, 67.49, 58.93, 26.33, 26.18. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{19}H_{20}O_2Na$: 303.1356, found: 303.1348. **FTIR (cm^{-1})** 3020, 2946, 2872, 1596, 1489, 1437, 1358, 1091, 928, 767.

(4-(Cinnamyloxy)butoxy)benzene (4u)

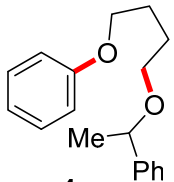


4u

Following the general procedure, treatment of (E)-3-phenylprop-2-en-1-ol **1u** (0.067 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (4-(cinnamyloxy)butoxy)benzene as a yellow oil **4u** (0.075 g, 53% yield, selectivity determined by GC analysis of crude reaction mixture is 91:09).

***R*f** (Pet. ether /EtOAc = 95/05): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.42 (m, 2H), 7.38-7.26 (m, 6H), 6.99-6.93 (m, 2H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.38-6.31 (m, 1H), 4.20 (d, *J* = 5.9 Hz, 2H), 4.04 (t, *J* = 6.2 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 1.98-1.91 (m, 2H), 1.89-1.82 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.15, 136.86, 132.33, 129.54, 128.66, 127.75, 126.60, 126.41, 120.64, 114.61, 71.56, 70.09, 67.62, 26.53, 26.30. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{19}H_{22}O_2Na$: 305.1512, found: 305.1516. **FTIR (cm^{-1})** 3018, 2943, 2864, 1723, 1595, 1488, 1365, 1295, 1229, 971.

(1-(4-Phenoxybutoxy)ethyl)benzene (4v)



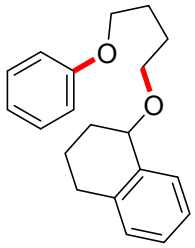
4v

Following the general procedure, treatment of 1-phenylethan-1-ol **1v** (0.061 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude

reaction mixture using silica gel afforded (1-(4-phenoxybutoxy)ethyl)benzene as a colourless oil **4v** (0.099 g, 73% yield, selectivity determined by GC analysis of crude reaction mixture is 98:02).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.32 (m, 7H), 7.01-6.93 (m, 3H), 4.48 (q, *J* = 6.4 Hz, 1H), 4.02 (t, *J* = 6.3 Hz, 2H), 3.44 (t, *J* = 6.3 Hz, 2H), 1.97-1.90 (m, 2H), 1.88-1.76 (m, 2H), 1.53 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.13, 144.23, 129.49, 128.50, 127.45, 126.23, 120.58, 114.57, 78.09, 68.27, 67.61, 26.61, 26.28, 24.27. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{22}O_2Na$: 293.1512, found: 293.1516. **FTIR (cm^{-1})** 3018, 2941, 2871, 1595, 1487, 1218, 1105, 764.

1-(4-Phenoxybutoxy)-1,2,3,4-tetrahydronaphthalene (4w)



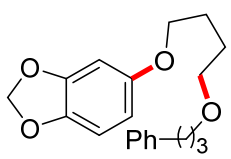
4w

Following the general procedure, treatment of 1,2,3,4-tetrahydronaphthalen-1-ol **1w** (0.074 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-(4-phenoxybutoxy)-1,2,3,4-tetrahydronaphthalene as a colourless oil **4w** (0.047 g, 32% yield, 69% yield based on starting material recovery, selectivity determined by GC analysis of crude reaction mixture is 75:25).

***R*f** (Pet. ether /EtOAc = 95/05): 0.38; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41-7.39 (m, 1H), 7.32-7.28 (m, 2H), 7.22-7.19 (m, 2H), 7.13-7.11 (m, 1H), 6.98-6.92 (m, 3H), 4.45 (t, *J* = 4.5 Hz, 1H), 4.02 (t, *J* = 6.2 Hz, 2H), 3.77-3.72 (m, 1H), 3.63 -3.57 (m, 1H), 2.90-2.83 (m, 1H), 2.78-2.70 (m, 1H), 2.06-1.77 (m, 8H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.17, 137.57, 137.15, 129.52, 129.31, 129.03, 127.50, 125.83, 120.61, 114.61, 75.60, 68.27, 67.73, 29.28, 28.18, 26.95, 26.43, 19.06.

HRMS (ESI) calculated $[M+Na]^+$ for $C_{20}H_{24}O_2Na$: 319.1669, found: 319.1664. **FTIR (cm^{-1})** 3061, 3020, 2939, 2866, 1595, 1487, 1390, 1240, 1086, 882.

5-(4-(3-Phenylpropoxy)butoxy)benzo[*d*][1,3]dioxole (4x)



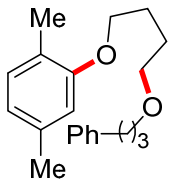
4x

Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 6-(trimethylsilyl)benzo[*d*][1,3] dioxol-5-yl

trifluoromethanesulfonate **2b** (0.257 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 96/04) of the crude reaction mixture using silica gel afforded 5-(4-(3-phenylpropoxy)butoxy) benzo[*d*][1,3]dioxole as a colourless oil **4x** (0.088 g, 54% yield, selectivity determined by GC analysis of crude reaction mixture is 78:22).

***R*f** (Pet. ether /EtOAc = 95/05): 0.26; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.31-7.27 (m, 2H), 7.21-7.17 (m, 3H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.33 (dd, J_1 = 8.5, J_2 = 2.4 Hz, 1H), 5.90 (s, 2H), 3.92 (t, *J* = 6.3 Hz, 2H), 3.49-3.42 (m, 4H), 2.72-2.68 (m, 2H), 1.94-1.82 (m, 4H), 1.78-1.72 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 154.71, 148.33, 142.13, 128.58, 128.42, 125.86, 108.04, 105.76, 101.17, 98.17, 70.54, 70.08, 68.74, 32.49, 31.44, 26.47, 26.33. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{20}H_{24}O_4Na$: 351.1567, found: 351.1562. **FTIR (cm^{-1})** 3019, 1620, 1489, 1327, 1216, 1107, 1039, 935, 768.

1,4-Dimethyl-2-(4-(3-phenylpropoxy)butoxy)benzene (4y)

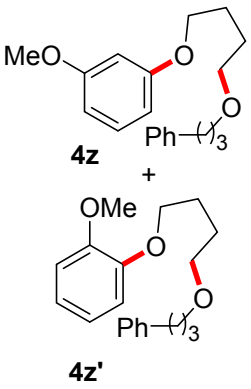


4y

Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 3,6-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2c** (0.245 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1,4-dimethyl-2-(4-(3-phenylpropoxy)butoxy)benzene as a colourless oil **4y** (0.096 g, 62% yield, selectivity determined by GC analysis of crude reaction mixture is 89:11).

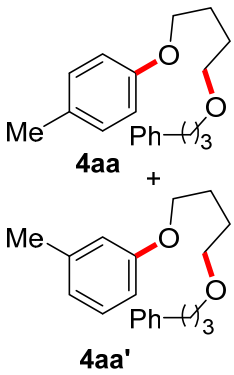
***R*f** (Pet. ether /EtOAc = 95/05): 0.63; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.32-7.28 (m, 2H), 7.23-7.19 (m, 3H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.70-6.66 (m, 2H), 4.00 (t, *J* = 6.2 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 1.97-1.88 (m, 4H), 1.85-1.78 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 157.15, 142.16, 136.58, 130.41, 128.60, 128.43, 125.87, 123.73, 120.75, 112.07, 70.64, 70.09, 67.65, 32.52, 31.47, 26.63, 26.44, 21.54, 15.95. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{21}H_{28}O_2Na$: 335.1982, found: 335.1964. **FTIR (cm^{-1})** 3017, 1877, 1722, 1599, 1455, 1380, 1259, 1117, 1040, 928, 848, 766.

1-Methoxy-3-(4-(3-phenylpropoxy)butoxy)benzene (4z) and 1-Methoxy-2-(4-(3-phenyl propoxy)butoxy)benzene (4z')



Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.034 g, 0.25 mmol) with 2-methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (0.123 g, 0.375 mmol) in the presence of KF (0.044 g, 0.75 mmol) and 18-crown-6 (0.198 g, 0.75 mmol) in THF (2.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/02) of the crude reaction mixture using silica gel afforded region isomeric mixture of 1-methoxy-3-(4-(3-phenylpropoxy)butoxy)benzene **4z** and 1-methoxy-2-(4-(3-phenylpropoxy) butoxy)benzene **4z'** oil (0.040 g, 51% yield, selectivity and regioisomeric ratio determined by GC analysis of crude reaction mixture is 56:44 and 4.5:1). ***R*f** (Pet. ether /EtOAc = 95/05): 0.47; **^{1}H NMR (400 MHz, $CDCl_3$) of major isomer** δ 7.33-7.28 (m, 2H), 7.23-7.18 (m, 4H), 6.54-6.49 (m, 3H), 4.02-3.99 (m, 2H), 3.81 (s, 3H), 3.52-3.45 (m, 4H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.96-1.87 (m, 4H), 1.82-1.77 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) of major isomer** δ 160.95, 142.16, 129.97, 128.44, 106.82, 106.28, 70.56, 70.12, 67.80, 55.39, 31.47, 26.51, 26.14. **^{1}H NMR (400 MHz, $CDCl_3$) of minor isomer** δ 4.05-4.03 (m), 2.01-1.98 (m). **^{13}C NMR (100 MHz, $CDCl_3$) of minor isomer** δ 160.46, 128.61, 125.88, 106.38, 101.08, 67.57, 32.52, 26.30. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{20}H_{26}O_3Na$: 337.1774, found: 337.1760. **FTIR (cm^{-1})** 3021, 1599, 1525, 1485, 1214, 1156, 1044, 926, 775.

1-Methyl-4-(4-(3-phenylpropoxy)butoxy)benzene (4aa) and 1-Methyl-3-(4-(3-phenyl propoxy)butoxy)benzene (4aa')

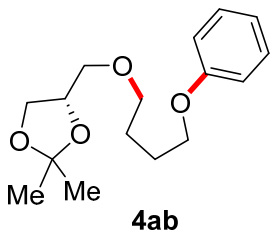


Following the general procedure, treatment of 3-phenylpropan-1-ol **1a** (0.068 g, 0.5 mmol) with 4-methyl-2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2e** (0.234 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded 1-methyl-4-(4-(3-phenylpropoxy)butoxy) benzene **4aa** and 1-methyl-3-(4-(3-phenyl propoxy)butoxy) benzene **4aa'** as a colourless oil

(0.078 g, 52% yield, selectivity and regioisomeric ratio determined by GC analysis of crude reaction mixture is 91:9 and 1.2:1).

***R*f** (Pet. ether /EtOAc = 95/05): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$) OF major isomer** δ 7.37-7.33 (m, 2H), 7.28-7.21 (m, 4H), 7.15-7.13 (m, 1H), 6.88-6.77 (m, 2H), 4.06-4.01 (m, 2H), 3.56-3.49 (m, 4H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.99-1.92 (m, 4H), 1.86-1.80 (m, 2H). **^{1}H NMR (400 MHz, $CDCl_3$) OF minor isomer** δ 4.06-4.01 (m, 2H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) of major isomer** δ 159.17, 142.12, 129.95, 128.58, 125.85, 115.45, 111.45, 70.55, 67.80, 67.58, 32.48, 31.44, 26.33, 21.63.). **^{13}C NMR (100 MHz, $CDCl_3$) of minor isomer** δ 157.03, 139.50, 129.78, 129.26, 128.41, 121.46, 114.45, 70.05, 26.49, 20.56. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{20}H_{26}O_2Na$: 321.1825, found: 321.1808. **FTIR (cm^{-1})** 3016, 1597, 1379, 1221, 1164, 1047, 923, 816, 767.

(S)-2,2-Dimethyl-4-((4-phenoxybutoxy)methyl)-1,3-dioxolane (4ab)

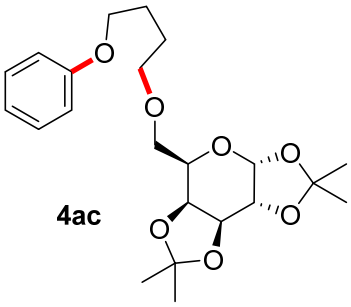


4ab

Following the general procedure, treatment of (S)-(2,2-dimethyl-1,3-dioxolan-4-yl)methanol **1ab** (0.066 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 94/06) of the crude reaction mixture using silica gel afforded (S)-2,2-dimethyl-4-((4-phenoxybutoxy)methyl)-1,3-dioxolane as a colourless oil **4ab** (0.075 g, 54% yield, selectivity determined by GC analysis of crude reaction mixture is 93:07).

***R*f** (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.28 (m, 2H), 6.97-6.90 (m, 3H), 4.32-4.26 (m, 1H), 4.09-4.06 (m, 1H), 4.0 (t, *J* = 6.1 Hz, 2H), 3.77-3.73 (m, 1H), 3.62-3.52 (m, 3H), 3.49-3.45 (m, 1H), 1.92-1.85 (m, 2H), 1.83-1.76 (m, 2H), 1.45 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.05, 129.47, 120.59, 114.51, 109.44, 74.80, 71.91, 71.36, 67.49, 66.89, 26.84, 26.27, 26.10, 25.49. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{16}H_{24}O_4Na$: 303.1567, found: 303.1568. **FTIR (cm^{-1})** 3055, 1597, 1487, 1380, 1261, 1085, 911, 843, 741.

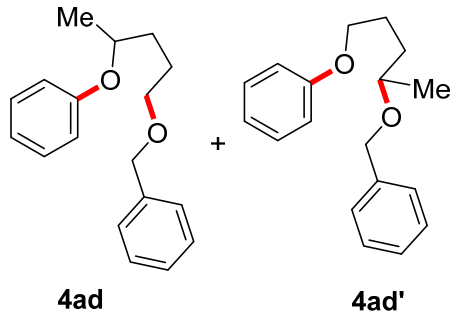
(3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyl-5-((4-phenoxybutoxy)methyl)tetrahydro-5H- bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (4ac)



Following the general procedure, treatment of galactose **1ac** (0.130 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-((4-phenoxybutoxy)methyl)tetrahydro-5*H*- bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran as a colourless oil **4ac** (0.105 g, 51% yield, selectivity determined by GC analysis of crude reaction mixture is 93:07).

***R*f** (Pet. ether /EtOAc = 90/10): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29-7.26 (m, 2H), 6.95-6.89 (m, 3H), 5.56 (d, J = 5.1 Hz, 1H), 4.62 (dd, J_1 = 2.2 Hz, J_2 = 7.8 Hz, 1H), 4.33-4.24 (m, 2H), 4.01-3.96 (m, 3H), 3.65-3.54 (m, 4H), 1.89-1.76 (m, 4H), 1.54 (s, 3H), 1.46 (s, 3H), 1.34 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.17, 129.51, 120.59, 114.61, 109.35, 108.66, 96.50, 71.35, 71.15, 70.77, 70.71, 69.57, 67.64, 66.89, 26.33, 26.20, 26.11, 25.06, 24.56. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{22}H_{32}O_7Na$: 431.2040, found: 431.2038. **FTIR (cm^{-1})** 2997, 1595, 1488, 1380, 1298, 1247, 1217, 1169, 891, 680.

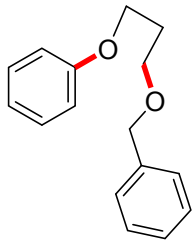
((5-(Benzyloxy)pentan-2-yl)oxy)benzene (4ad) and ((4-(Benzyloxy)pentyl)oxy)benzene (4ad')



Following the general procedure, treatment of phenylmethanol **1h** (0.054 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in 2-methyltetrahydrofuran (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded ((5-(benzyloxy)pentan-2-yl)oxy)benzene **4ad** and ((4-(benzyloxy)pentyl)oxy)benzene **4ad'** as a colourless oil (0.086 g, 64% yield, selectivity and regio isomeric ratio determined by GC analysis of crude reaction mixture is 92:08 and 2.5:1).

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR of major isomer (400 MHz, $CDCl_3$)** δ 7.41-7.37 (m, 5H), 7.35-7.29 (m, 2H), 7.0-6.92 (m, 3H), 4.55 (s, 2H), 4.66-4.40 (m, 1H), 3.56 (t, *J* = 5.8 Hz, 2H), 1.85-1.75 (m, 4H), 1.36 (d, *J* = 6.0Hz, 3H). **^{1}H NMR of minor isomer (400 MHz, $CDCl_3$) δ** 4.04-3.96 (m), 3.67-3.63 (m), 1.99-1.95 (m), 1.30 (d, *J* = 6.0Hz). **^{13}C NMR of major isomer (100 MHz, $CDCl_3$)** δ 158.29, 138.71, 129.57, 127.79, 127.64, 120.62, 116.0, 74.60, 73.01, 70.30, 33.30, 25.94, 19.89. **^{13}C NMR of minor isomer (100 MHz, $CDCl_3$)** δ 159.20, 139.12, 128.48, 127.76, 127.55, 116.05, 114.65, 73.60, 70.49, 67.93, 33.25, 25.53, 19.76. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{22}O_2Na$: 293.1512, found: 293.1511. **FTIR (cm^{-1})** 3022, 1643, 1524, 1427, 1216, 1039, 928, 774, 673.

(3-(Benzyloxy)propoxy)benzene (4ae)

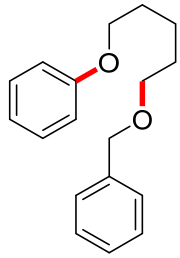


4ae

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.149 g, 121 µL, 0.5 mmol) with Oxetane and benzyl alcohol (1.0 mL, 0.5 mL each) in presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (3-(benzyloxy)propoxy)benzene as a colourless oil **4ae** (0.029 g, 24% yield, NMR yield 29% determined by ^{1}H NMR analysis of crude products using CH_2Br_2 as the internal standard.

***R*f** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.36-7.28 (m, 7H), 6.99-6.92 (m, 3H), 4.56 (s, 2H), 4.12 (t, *J* = 6.1 Hz, 2H), 3.70 (t, *J* = 6.2 Hz, 2H), 2.13 (p, *J* = 6.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.10, 138.53, 129.55, 128.52, 127.77, 127.72, 120.72, 114.65, 73.19, 67.01, 64.84, 29.90. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{16}H_{18}O_2Na$: 265.1199, found: 265.1199. **FTIR (cm^{-1})** 3022, 1817, 1717, 1595, 1491, 1460, 1376, 1171, 922.

((5-(Benzyloxy)pentyl)oxy)benzene (4af)



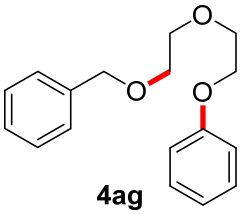
4af

Following the general procedure, treatment of phenylmethanol **1h** (0.054 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in tetrahydro-2*H*-pyran (4.0 mL) at 80

°C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded ((5-(benzyloxy)pentyl)oxy) benzene as a colourless oil **4af** (0.062 g, 46% yield, NMR yield 48% determined by ^{1}H NMR analysis of crude reaction mixture using CH_2Br_2 as the internal standard, selectivity determined by GC analysis of crude reaction mixture is 83:17).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39-7.29 (m, 7H), 6.98-6.92 (m, 3H), 4.55 (s, 2H), 3.99 (t, *J* = 6.3 Hz, 2H), 3.54 (t, *J* = 6.3 Hz, 2H), 1.86-1.81 (m, 2H), 1.75-1.72 (m, 2H), 1.62-1.60 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.14, 138.68, 129.51, 128.47, 127.74, 127.62, 120.58, 114.55, 73.03, 70.33, 67.74, 29.63, 29.21, 22.91. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{22}O_2Na$: 293.1512, found: 293.1508. **FTIR (cm^{-1})** 3018, 2940, 2864, 1595, 1487, 1222, 1095, 1037, 769.

(2-(2-(Benzyloxy)ethoxy)ethoxy)benzene (4ag)

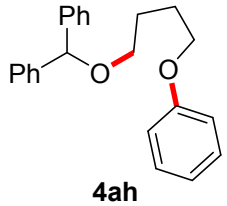


4ag

Following the general procedure, treatment of phenylmethanol **1h** (0.054 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in 1,4-dioxane (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded (2-(2-(benzyloxy)ethoxy)ethoxy)benzene as a colourless oil **5** (0.050 g, 37% yield, selectivity determined by GC analysis of crude reaction mixture is 70:30).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.13; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.41-7.30 (m, 7H), 6.99-6.95 (m, 3H), 4.62 (s, 2H), 4.18 (t, *J* = 4.5 Hz, 2H), 3.91 (t, *J* = 5.1 Hz, 2H), 3.81-3.78 (m, 2H), 3.72-3.69 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.86, 138.31, 129.51, 128.47, 127.87, 127.71, 120.94, 114.73, 73.39, 70.98, 69.89, 69.56, 67.41. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{17}H_{20}O_3Na$: 295.1305, found: 295.1313. **FTIR (cm^{-1})** 3017, 2925, 2873, 1595, 1491, 1458, 1359, 1294, 1220, 928.

((4-Phenoxybutoxy)methylene)dibenzene (4ah)



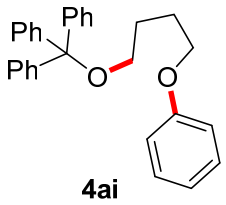
4ah

Following the general procedure, treatment of diphenylmethanol **1ah** (0.092 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane

sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded ((4-phenoxybutoxy)methylene)dibenzene as a white crystalline solid **4ah** (0.108 g, 65% yield, selectivity determined by GC analysis of crude reaction mixture is 99:01).

***R*f** (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40-7.28 (m, 12H), 6.98-6.90 (m, 3H), 5.39 (s, 1H), 4.01 (t, *J* = 6.3 Hz, 2H), 3.56 (t, *J* = 6.3 Hz, 2H), 2.0-1.93 (m, 2H), 1.90-1.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.15, 142.62, 129.53, 128.50, 127.50, 127.06, 120.63, 114.61, 83.78, 68.78, 67.67, 26.60, 26.41. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{23}H_{24}O_2Na$: 355.1669, found: 355.1651. **FTIR (cm^{-1})** 3019, 2945, 2868, 1656, 1595, 1488, 1462, 1295, 1221, 1088, 923.

((4-Phenoxybutoxy)methanetriyl)tribenzene (4ai)



4ai

Following the general procedure, treatment of triphenylmethanol **1ai** (0.130 g, 0.5 mmol) with 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 60 °C for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 99/01) of the crude reaction mixture using silica gel afforded ((4-phenoxybutoxy)methanetriyl)tribenzene as a white crystalline solid **4ai** (0.131 g, 64% yield, selectivity determined by GC analysis of crude reaction mixture is 99:01).

***R*f** (Pet. ether /EtOAc = 95/05): 0.46; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.49 (m, 6H), 7.35-7.25 (m, 11H), 6.99-6.90 (m, 3H), 3.98 (t, *J* = 6.6 Hz, 2H), 3.19 (t, *J* = 6.3 Hz, 2H), 1.98-1.91 (m, 2H), 1.87-1.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.16, 144.52, 129.52, 128.82, 127.87, 127.0, 120.62, 114.64, 86.54, 67.75, 63.27, 26.74, 26.45. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{29}H_{29}O_2$: 409.2162, found: 409.2162. **FTIR (cm^{-1})** 3020, 2935, 1596, 1487, 1217, 1041, 761, 667.

9. Computational Studies

The geometry optimizations were conducted employing density functional theory (DFT) with the Turbomole 6.4 suite of programs.[21] The Perdew, Burke, and Ernzerhof (PBE)[22] functional was used for the geometry optimization calculations. The triple-ζ basis set augmented by a polarization function (Turbomole basis set TZVP) was used for all the atoms. The resolution of identity (RI)[23] along with the multipole accelerated resolution of identity (marij)[24] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term. Solvent effects were accounted for as follows: we have done full geometry optimizations of all intermediates and transition states calculations using the COSMO model. The solvent used in this study is THF (ε =7.52). To improve the calculation of the energy values, a further correction was made through single-point B3-LYP calculations[25,26] for the DFT (PBE)-optimized structures. The contributions of internal energy and entropy were obtained from frequency calculations done on the DFT structures: thus, the energies reported in the figures are the ΔG values. With regard to the transition states obtained during the investigation process, care was taken to ensure that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode.

To gain insight into the mechanism, we performed quantum chemical calculations by using density functional theory (DFT), employing the TZVP/PBE/B3LYP approach with Turbomole 6.4.[1] Herein we proposed two different reaction pathways based on the temperature effect. In the first pathway, at -20 °C direct attack of alcohol (**1b**) on aryne followed by intramolecular proton transfer resulted in the formation of phenethoxybenzene and in the second pathway, at 60 °C, the THF attacked the aryne resulting in the formation of 1,4 dipolar intermediate, the dipolar intermediate abstracted the hydrogen of alcohol (**1b**) to afford the oxonium ion and alkoxyanion. When oxonium cation was finally attacked by alkoxyanion, the corresponding (4-phenethoxybutoxy)benzene were formed. In both the

[21] R. Ahlrichs, M. Bar, M. Haser, H. Horn and C. Kolmel, *Chem. Phy. Lett.* 1989, **162**, 165.
[22] J. P. Perdew, K. Burke and M. Ernzerhof, *Phy. Rev. Lett.* 1996, 77, 3865.
[23] K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phy. Lett.* 1995, **240**, 283.
[24] M. Sierka, A. Hogekamp and R. Ahlrichs, R. *J. Chem. Phys.* 2003, **118**, 9136.
[25] A. D. Becke, *J. Chem. Phy.* 1993, **98**, 5648.
[26] C. Lee, W. Yang and R. G. Parr, *Phy. Rev. B* 1988, **37**, 785.

pathways, first step is the formation common aryne through **int.1**. The results are summarized in terms of a free energy diagram as depicted in Figure 1 and Figure 2.

In the lower temperature (-20 °C) mechanism, the generation of aryne through the intermediate (**int.1**=0.4 kcal/mol) from aryne precursor and potassium fluoride. The addition of alcohol in presence of THF to the aryne to form the unstable intermediate **int.1a**, followed by transfer of hydrogen via transition state (**TS1a**) to form the exergonic aryl ether product **3b** (ΔG= -75.7) having transition state barrier 14.6 kcal/mol.

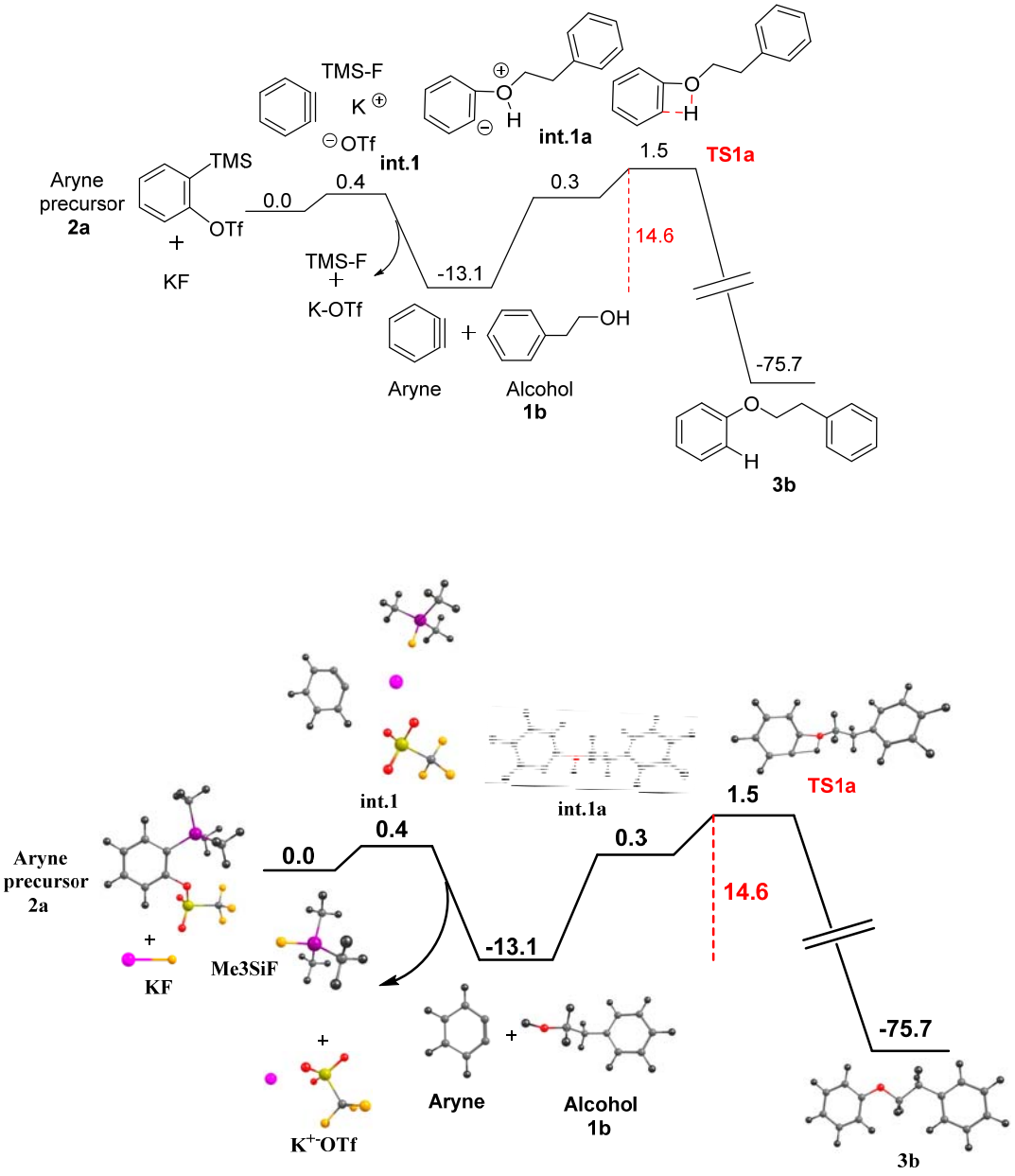


Figure 1

The proposed mechanism at higher temperature (60 °C), after formation of the aryne, the THF attacks on the aryne to form the 1,4 dipolar species (**int.2b**, ΔG= -1.8). Then the attack of **1b** on the **int.2b** to form the **int.3b** through the **TS2b**, the transition state barrier was found to be 19.6 kcal/mol. This is followed to formation of less exergonic product **4b** (ΔG= -68.3) comparison to lower temperature product **3b**. The experimental yields found to be 81% and 66% at low and high temperature respectively. Our proposed mechanism gives the thermodynamic products -75.7 kcal/mol and -68.3 kcal/mol, which are agreement with experimental work.

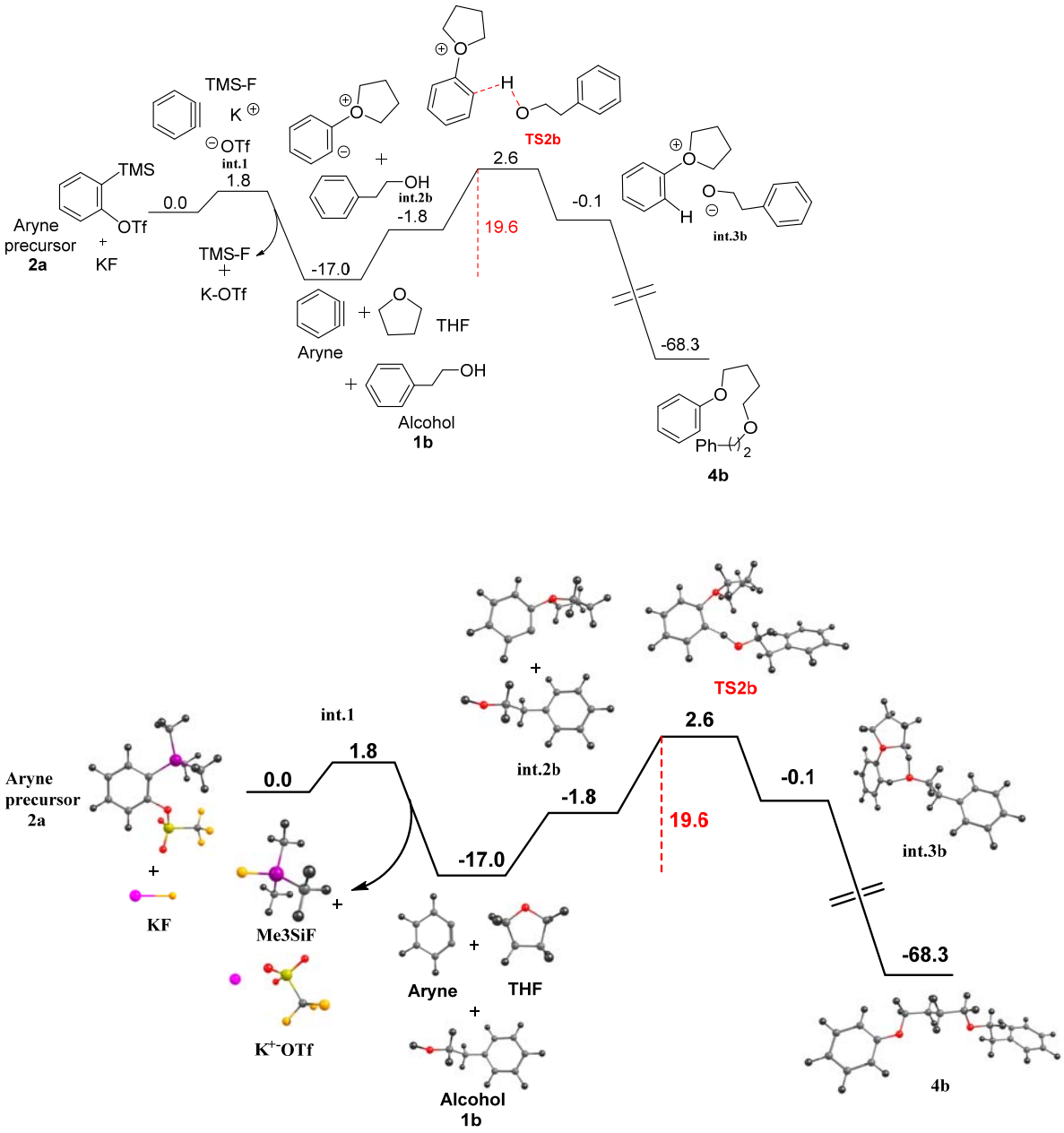


Figure 2

*The formation of **int.1a** and **int.2b** was found to 13.4 kcal/mol and 15.2 kcal/mol higher in energy at low and high temperature mechanisms respectively. This is an indication that at low temperature arylation will be prefered and at high temperature, the formation of MCR products will be preferred.*

II. The optimized geometries of the structures reported in the manuscript (the atomic symbol followed by the three Cartesian coordinates, in Å).

K-OTf
9

C	3.204	0.064	2.469
F	3.690	-1.153	2.790
S	1.372	0.220	2.997
O	1.400	0.020	4.478
O	0.683	-0.861	2.196
F	3.322	0.230	1.130
F	3.957	1.001	3.081
K	-0.815	0.829	0.473
O	0.988	1.603	2.523

KF
2

K	0.000	0.000	-0.060
F	0.000	0.000	2.382

TMS-F
14

Si	0.044	-0.076	0.031
C	-0.009	0.018	1.909
C	1.796	0.018	-0.646
C	-0.914	-1.547	-0.646
F	-0.749	1.294	-0.527
H	-0.923	-1.536	-1.746
H	-0.449	-2.489	-0.318
H	-1.954	-1.537	-0.289
H	1.794	0.031	-1.746
H	2.308	0.923	-0.289
H	2.379	-0.855	-0.317
H	-1.048	0.032	2.272
H	0.493	-0.855	2.350
H	0.497	0.924	2.272

Aryne

precursor
2a
31

C	2.158	0.137	0.046
C	0.949	0.005	-0.665
C	-0.203	-0.118	0.120
C	-0.194	-0.137	1.514
C	1.025	0.018	2.178
C	2.204	0.156	1.443
Si	0.961	-0.009	-2.589
C	0.138	1.571	-3.239
O	-1.421	-0.313	-0.603
S	-2.848	0.321	-0.013
O	-3.460	-0.606	0.959
C	2.771	-0.038	-3.153
C	0.093	-1.566	-3.241
C	-3.798	0.109	-1.684
F	-3.654	-1.134	-2.144
F	-5.085	0.356	-1.422
F	-3.337	0.988	-2.577
H	-1.112	-0.279	2.087
H	1.044	0.017	3.269
H	3.160	0.275	1.957
H	3.093	0.233	-0.510
H	0.147	1.571	-4.340
H	-0.904	1.663	-2.908
H	0.687	2.459	-2.892
H	0.154	-1.591	-4.340
H	0.580	-2.473	-2.852
H	-0.966	-1.599	-2.954
H	2.800	-0.072	-4.254
H	3.320	0.859	-2.833
H	3.303	-0.925	-2.777
O	-2.710	1.763	0.274

Int.1
33

C	3.009	-0.059	0.697
C	1.888	-0.186	-0.094
C	0.667	-0.113	0.196
C	0.178	0.143	1.478
C	1.240	0.299	2.400
C	2.592	0.204	2.029
K	-1.768	-0.778	-1.818
F	-0.879	-0.253	-4.283
Si	-0.249	-0.060	-5.846
C	-0.973	1.552	-6.481
C	1.615	-0.003	-5.627
C	-0.835	-1.562	-6.811
O	-4.066	-1.965	-0.610
S	-4.168	-1.057	0.594
O	-3.058	-0.032	0.634
C	-5.718	-0.002	0.217
F	-6.824	-0.774	0.178
F	-5.890	0.945	1.162
F	-5.583	0.611	-0.982
H	-0.872	0.210	1.761
H	0.991	0.502	3.444
H	3.367	0.337	2.789
H	4.056	-0.133	0.407
H	-0.621	1.747	-7.506
H	-2.072	1.508	-6.500
H	-0.667	2.398	-5.848
H	-0.457	-1.518	-7.844
H	-0.469	-2.493	-6.354
H	-1.934	-1.600	-6.853
H	2.107	0.111	-6.605
H	1.911	0.845	-4.994
H	1.985	-0.930	-5.165
O	-4.486	-1.727	1.892

Alcohol
1b
19

C	1.024	0.295	-0.715
C	-0.174	-0.231	-0.203
C	-0.154	-0.816	1.073

C	1.029	-0.882	1.815
C	2.216	-0.358	1.292
C	2.209	0.231	0.023
C	-1.459	-0.122	-0.989
C	-2.170	1.218	-0.743
O	-3.364	1.366	-1.527
H	-3.998	0.691	-1.227
H	-1.514	2.049	-1.040
H	-2.391	1.331	0.333
H	-2.141	-0.941	-0.707
H	-1.256	-0.213	-2.068
H	-1.076	-1.234	1.486
H	1.025	-1.348	2.803
H	3.143	-0.413	1.867
H	3.132	0.639	-0.395
H	1.028	0.752	-1.708

Aryne

10

C	0.108	0.000	0.045
C	-0.068	0.000	1.418
C	1.191	0.000	2.069
C	2.409	-0.000	1.367
C	2.475	-0.000	-0.049
C	1.196	-0.000	-0.582
H	-1.011	-0.000	1.965
H	1.209	-0.000	3.162
H	3.347	0.000	1.928
H	3.420	0.000	-0.592

Int.1a

29

C	1.028	0.299	-0.714
C	-0.131	-0.208	-0.213
C	0.060	-0.764	1.075
C	1.316	-0.773	1.706
C	2.438	-0.212	1.079
C	2.309	0.366	-0.192
H	-0.785	-1.210	1.612
H	1.426	-1.219	2.698
H	3.410	-0.211	1.576
H	3.159	0.828	-0.698
O	0.774	0.949	-2.096
H	-0.217	0.750	-2.086
C	1.429	0.299	-3.277
C	1.010	1.028	-4.543
H	2.502	0.393	-3.080
H	1.135	-0.759	-3.271
C	1.718	0.429	-5.742
H	-0.079	0.947	-4.672
H	1.262	2.094	-4.445
C	1.117	-0.591	-6.494
C	1.783	-1.160	-7.585
C	3.063	-0.716	-7.935
C	3.672	0.299	-7.190
C	3.004	0.866	-6.101
H	0.115	-0.937	-6.230
H	1.299	-1.949	-8.164
H	3.582	-1.158	-8.788
H	4.668	0.654	-7.461
H	3.482	1.665	-5.528

TS1a

29

C	3.089	0.909	-6.003
C	1.793	0.503	-5.643
C	1.171	-0.509	-6.391
C	1.827	-1.101	-7.475
C	3.117	-0.689	-7.825
C	3.746	0.318	-7.087
C	1.095	1.121	-4.449
C	1.401	0.318	-3.195
O	0.723	0.961	-2.031
C	0.803	0.225	-0.721
C	-0.485	-0.152	-0.435
C	-0.598	-0.819	0.802
C	0.533	-1.054	1.605
C	1.807	-0.623	1.208
C	1.977	0.059	-0.008
H	-1.571	-1.174	1.159
H	0.425	-1.583	2.557
H	2.674	-0.807	1.845
H	2.954	0.418	-0.335
H	-0.340	0.732	-1.976
H	2.469	0.327	-2.948
H	1.037	-0.717	-3.254
H	0.007	1.138	-4.615
H	1.432	2.158	-4.305
H	0.160	-0.830	-6.126
H	1.326	-1.882	-8.050
H	3.628	-1.148	-8.674
H	4.751	0.650	-7.358
H	3.583	1.701	-5.435

3b

29

C	0.894	0.001	-0.729
C	-0.284	-0.006	0.030
C	-0.169	-0.006	1.433
C	1.079	0.001	2.055
C	2.248	0.009	1.284
C	2.150	0.009	-0.108
C	-1.668	-0.013	-0.585
C	-1.710	-0.013	-2.104
O	-3.101	-0.014	-2.475
C	-3.413	-0.014	-3.810
C	-4.787	-0.022	-4.112
C	-5.210	-0.024	-5.439
C	-4.275	-0.019	-6.484
C	-2.912	-0.010	-6.179
C	-2.470	-0.008	-4.849
H	-6.279	-0.030	-5.660
H	-4.608	-0.021	-7.523
H	-2.171	-0.006	-6.982
H	-1.400	-0.002	-4.639
H	-1.214	-0.909	-2.518
H	-1.215	0.882	-2.517
H	-2.227	0.864	-0.222
H	-2.219	-0.896	-0.221
H	-1.077	-0.013	2.043
H	1.142	0.001	3.145
H	3.227	0.016	1.768
H	3.053	0.015	-0.722
H	0.849	0.001	-1.820
H	-5.507	-0.026	-3.290

THF

13

O	1.460	-1.433	-0.871
C	2.764	-2.073	-0.899
C	3.374	-1.919	0.507
C	2.164	-1.529	1.372
C	1.332	-0.726	0.378
H	2.608	-3.128	-1.175
H	4.121	-1.111	0.518
H	2.444	-0.947	2.261
H	0.262	-0.672	0.622
H	3.390	-1.600	-1.674
H	3.865	-2.839	0.850
H	1.608	-2.421	1.698
H	1.726	0.304	0.281

Int.2b

23

C	-0.108	-0.834	-2.683
O	1.239	-0.496	-2.098
C	1.827	0.610	-2.909
C	1.278	0.338	-4.291
C	-0.178	-0.064	-3.998
C	1.210	-0.154	-0.524
C	0.294	0.744	-0.109
C	0.390	0.960	1.289
C	1.333	0.299	2.095
C	2.233	-0.618	1.533
C	2.182	-0.873	0.153
H	-0.289	1.666	1.783
H	1.371	0.497	3.170

H	2.964	-1.137	2.155
H	2.859	-1.582	-0.327
H	-0.091	-1.924	-2.793
H	-0.801	0.832	-3.877
H	1.347	1.229	-4.928
H	2.912	0.521	-2.793
H	-0.844	-0.508	-1.937
H	-0.608	-0.679	-4.799
H	1.829	-0.481	-4.774
H	1.455	1.550	-2.476

TS2b

42

C	0.830	0.495	-2.812
O	1.201	-0.599	-1.857
C	0.430	-1.849	-2.236
C	-0.094	-1.560	-3.640
C	0.629	-0.273	-4.095
C	1.212	-0.221	-0.392
C	0.017	0.034	0.233
C	0.184	0.383	1.594
C	1.440	0.458	2.210
C	2.604	0.175	1.483
C	2.498	-0.176	0.133
O	-2.536	-0.331	-0.129
C	-3.052	-0.233	-1.418
C	-4.175	0.832	-1.542
C	-4.856	0.779	-2.884
C	-4.356	1.490	-3.989
C	-4.947	1.373	-5.251
C	-6.055	0.538	-5.436
C	-6.566	-0.175	-4.346
C	-5.970	-0.055	-3.087
H	-0.707	0.604	2.190
H	1.517	0.731	3.266
H	3.586	0.225	1.957
H	3.378	-0.406	-0.471
H	1.175	-2.649	-2.177
H	0.108	-2.397	-4.318
H	1.597	-0.504	-4.560
H	-0.083	0.964	-2.423
H	-1.349	-0.145	-0.102
H	-2.266	0.034	-2.164
H	-3.480	-1.201	-1.766
H	-4.903	0.638	-0.738
H	-3.735	1.826	-1.362
H	-6.378	-0.613	-2.239
H	-7.435	-0.825	-4.476
H	-6.519	0.447	-6.420
H	-4.545	1.939	-6.095
H	-3.495	2.151	-3.854
H	1.672	1.195	-2.796
H	0.029	0.303	-4.811
H	-1.179	-1.396	-3.607
H	-0.349	-1.973	-1.477

Int.3b

42

C	-6.309	0.976	-2.100
C	-5.859	0.206	-1.011
C	-6.815	-0.544	-0.300
C	-8.168	-0.519	-0.654
C	-8.597	0.255	-1.738
C	-7.661	1.004	-2.461
C	-4.397	0.097	-0.691
C	-3.685	-1.039	-1.509
O	-2.364	-1.204	-1.201
C	-0.041	-0.347	0.437
C	1.002	0.024	-0.402
C	2.183	0.613	0.039
C	2.327	0.826	1.415
C	1.304	0.467	2.297
C	0.127	-0.108	1.806
O	0.799	-0.223	-1.808
C	-0.380	0.435	-2.541
C	-0.122	-0.023	-3.954
C	1.413	-0.032	-4.088
C	1.906	-0.596	-2.769
H	-0.675	-0.384	2.493
H	1.423	0.641	3.368
H	3.245	1.282	1.789
H	2.977	0.909	-0.645
H	-1.284	-0.016	-2.046
H	-0.538	-1.029	-4.104
H	1.754	-0.655	-4.923
H	2.836	-0.156	-2.402
H	-0.978	-0.767	0.018
H	-3.866	-0.781	-2.590
H	-4.303	-1.962	-1.334
H	-4.247	-0.126	0.377
H	-3.876	1.042	-0.914
H	-6.488	-1.151	0.547
H	-8.890	-1.107	-0.082
H	-9.653	0.277	-2.017
H	-7.986	1.617	-3.305
H	-5.587	1.572	-2.665
H	1.946	-1.690	-2.731
H	1.791	0.988	-4.232
H	-0.589	0.661	-4.673
H	-0.242	1.514	-2.389

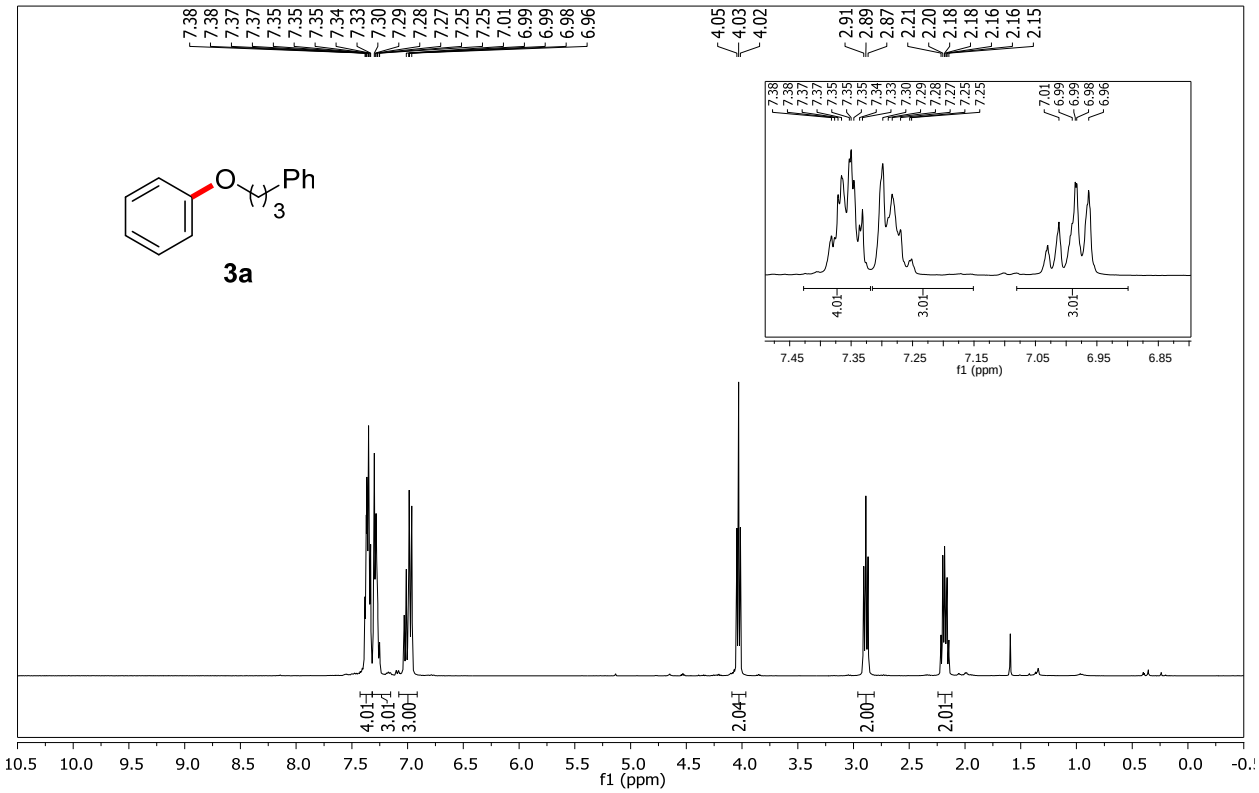
4b

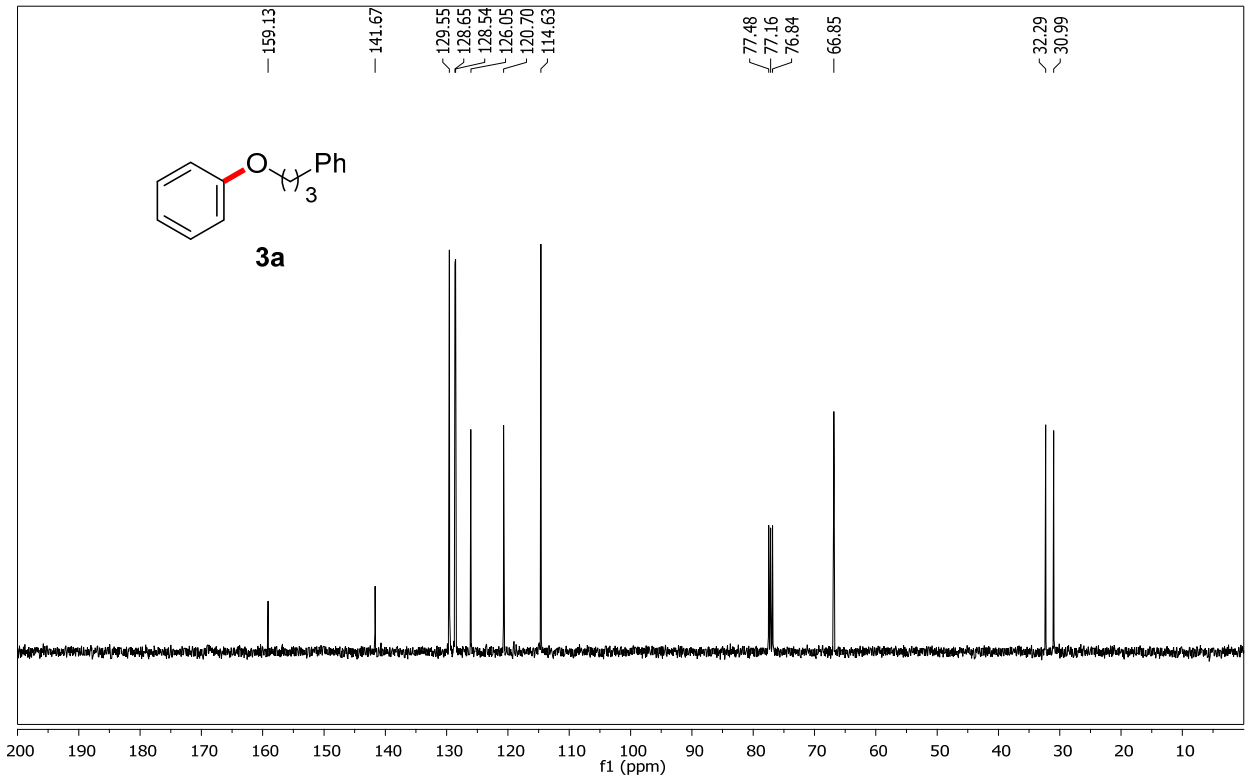
42

C	4.589	-0.221	0.980
C	3.573	0.137	0.085
C	2.341	-0.536	0.131
C	2.143	-1.563	1.073
C	3.165	-1.908	1.956
C	4.398	-1.239	1.916
O	1.278	-0.268	-0.689
C	1.427	0.772	-1.678
C	0.132	0.866	-2.466
C	-0.185	-0.386	-3.288
C	-1.448	-0.259	-4.127
H	2.998	-2.706	2.681
H	5.196	-1.511	2.609
H	5.543	0.308	0.936
H	3.749	0.935	-0.635
H	-1.575	-1.155	-4.765
H	0.650	-0.598	-3.976
H	-0.696	1.086	-1.775
H	2.274	0.528	-2.344
H	-1.378	0.621	-4.798
H	-0.281	-1.259	-2.625
H	0.224	1.736	-3.139
H	1.645	1.729	-1.174
O	-2.581	-0.117	-3.263
H	1.180	-2.077	1.096
C	-3.798	0.033	-3.993
C	-4.949	0.189	-2.999
H	-3.739	0.923	-4.652
H	-3.968	-0.848	-4.641
C	-6.274	0.375	-3.702
H	-4.983	-0.703	-2.357
H	-4.737	1.056	-2.354
C	-6.686	1.647	-4.133
C	-7.895	1.820	-4.813
C	-8.717	0.718	-5.074
C	-8.321	-0.553	-4.649
C	-7.109	-0.721	-3.970
H	-6.053	2.514	-3.926
H	-8.199	2.818	-5.135
H	-9.664	0.851	-5.601
H	-8.958	-1.419	-4.843
H	-6.809	-1.718	-3.636

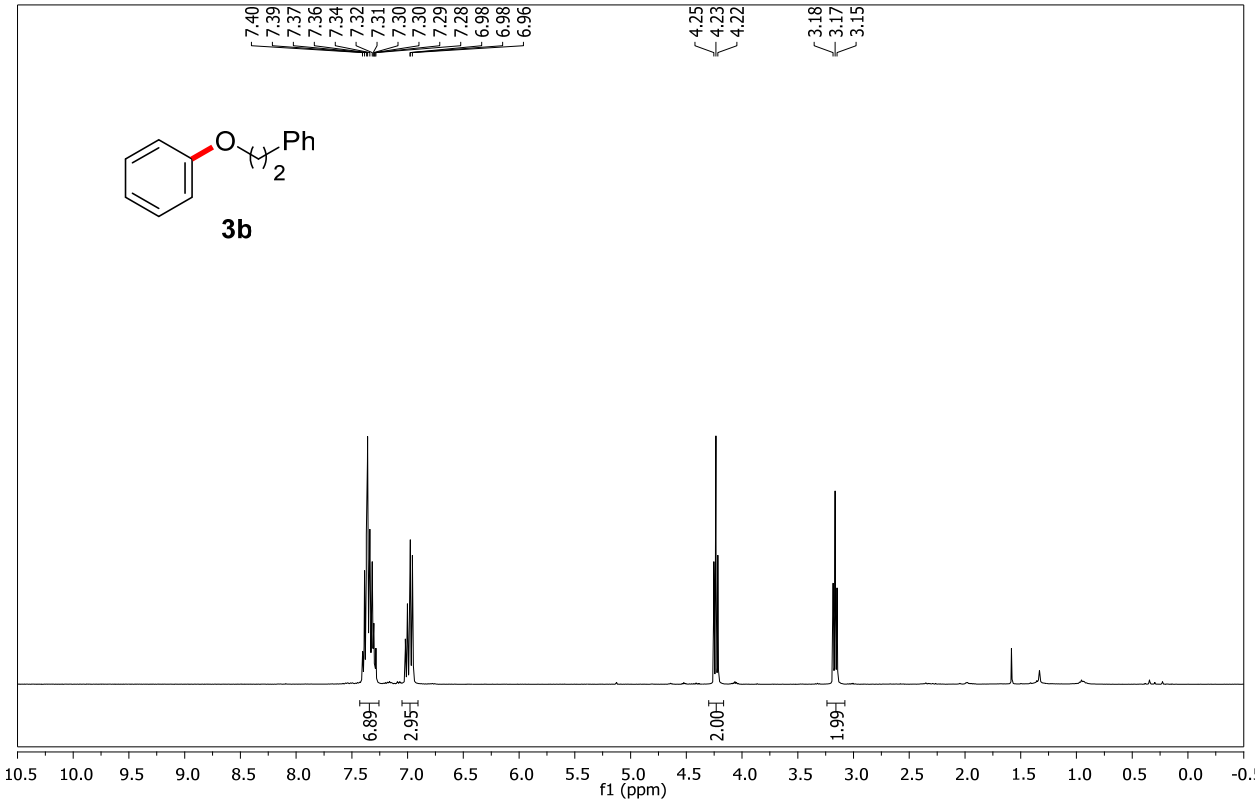
10.^{1}H and ^{13}C NMR Spectra of Alkyl Aryl Ethers

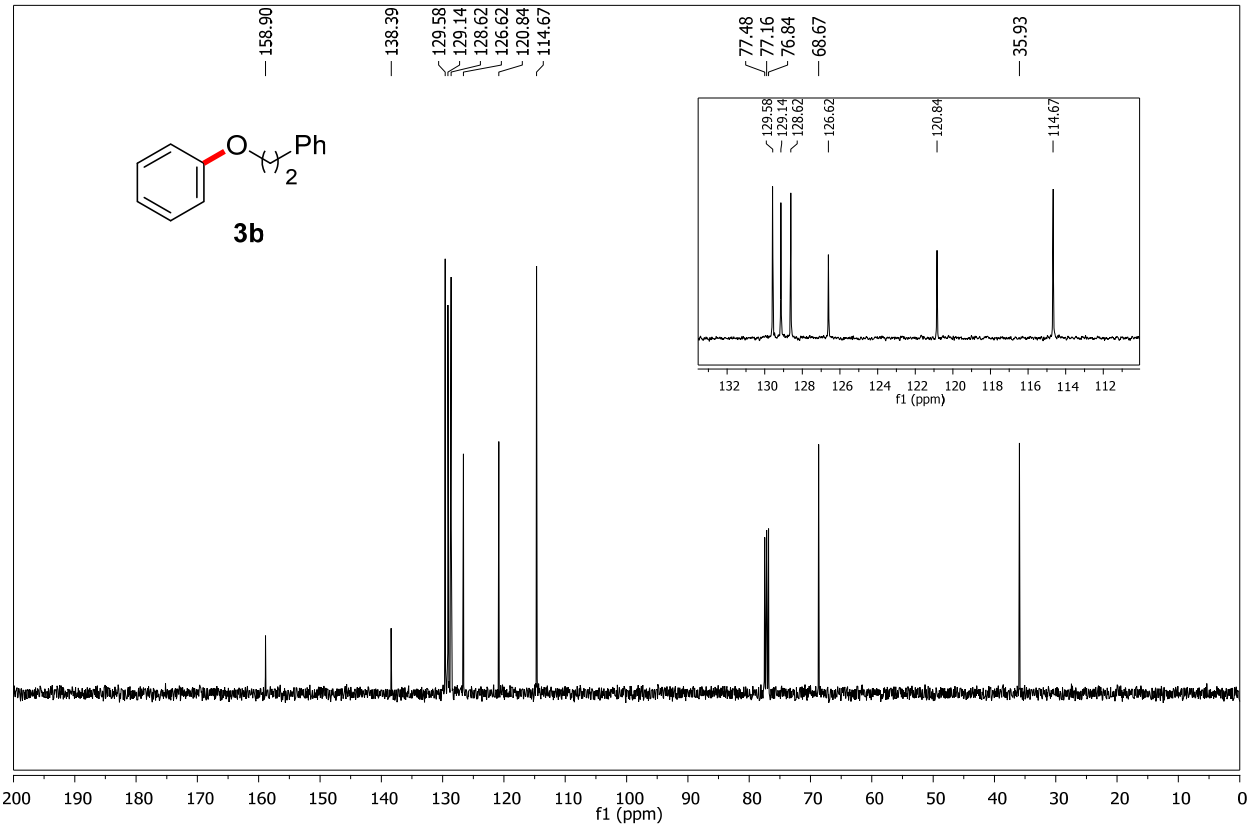
(3-Phenoxypropyl)benzene (3a)



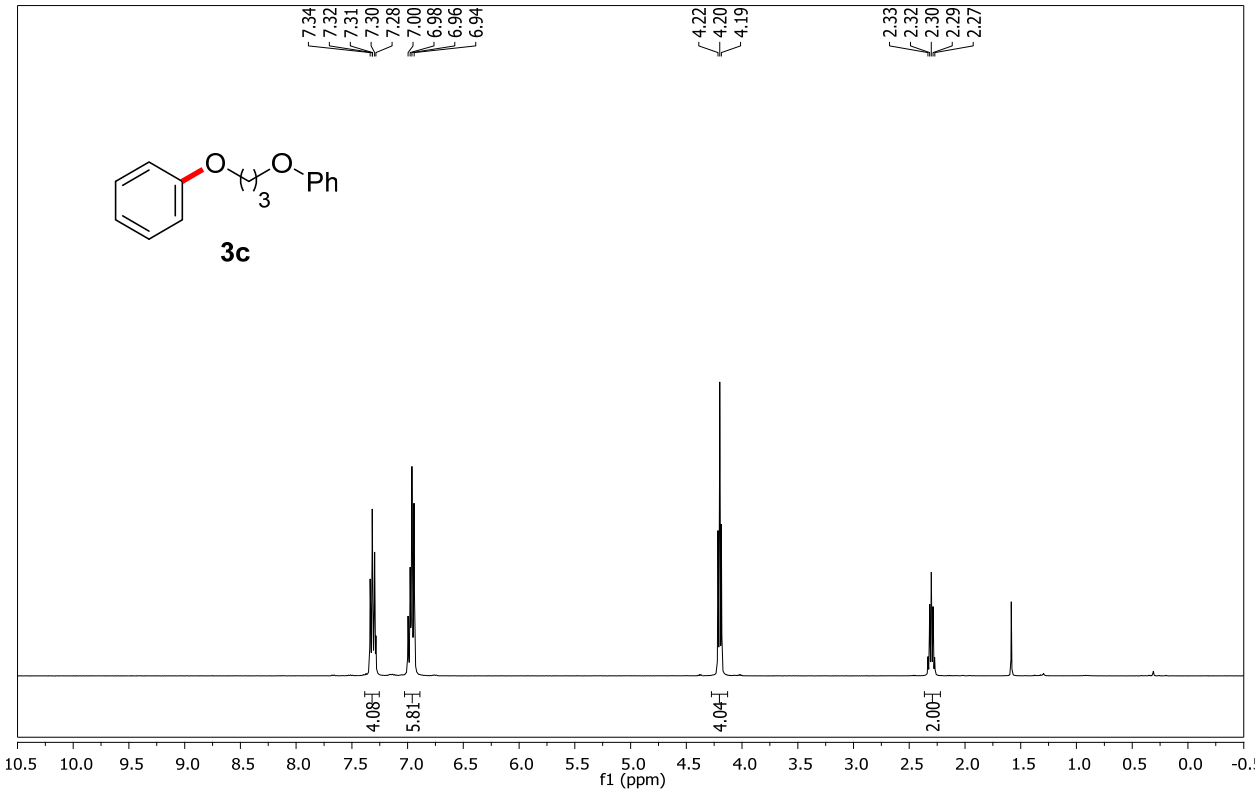


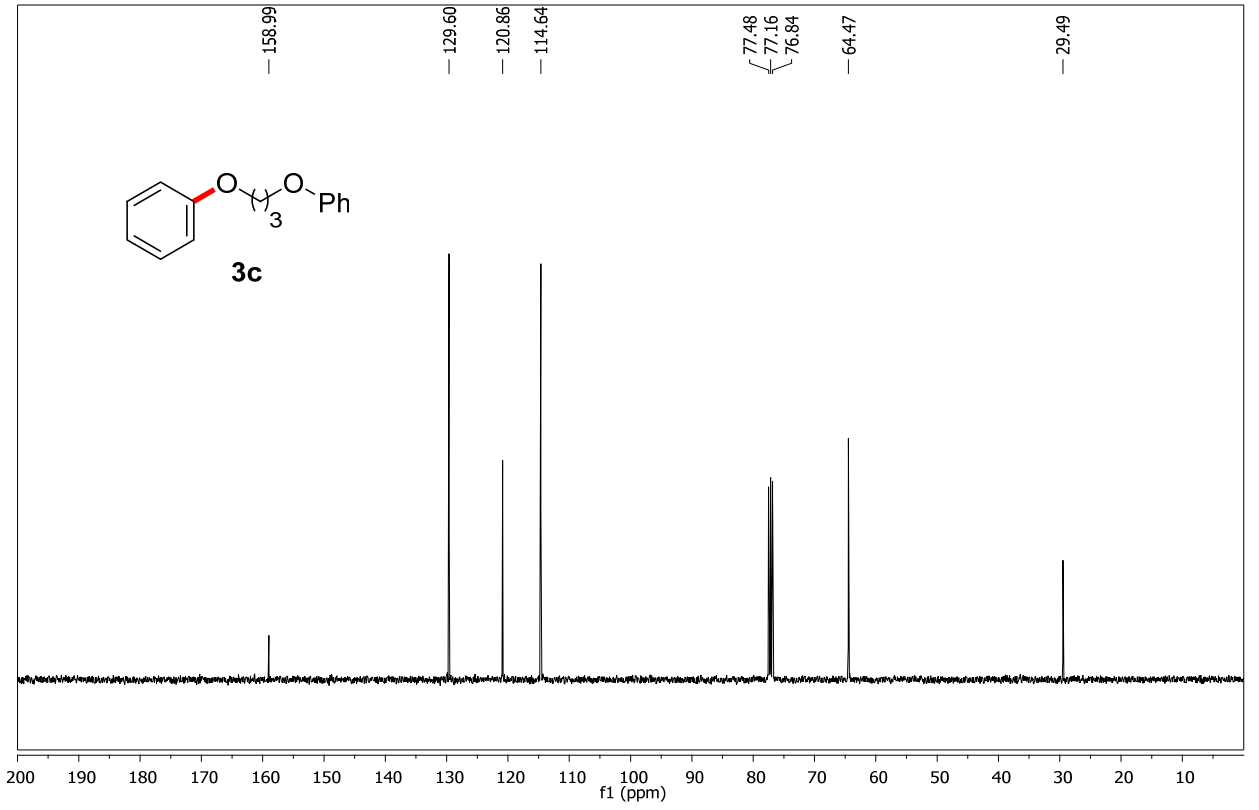
Phenethoxybenzene (3b)



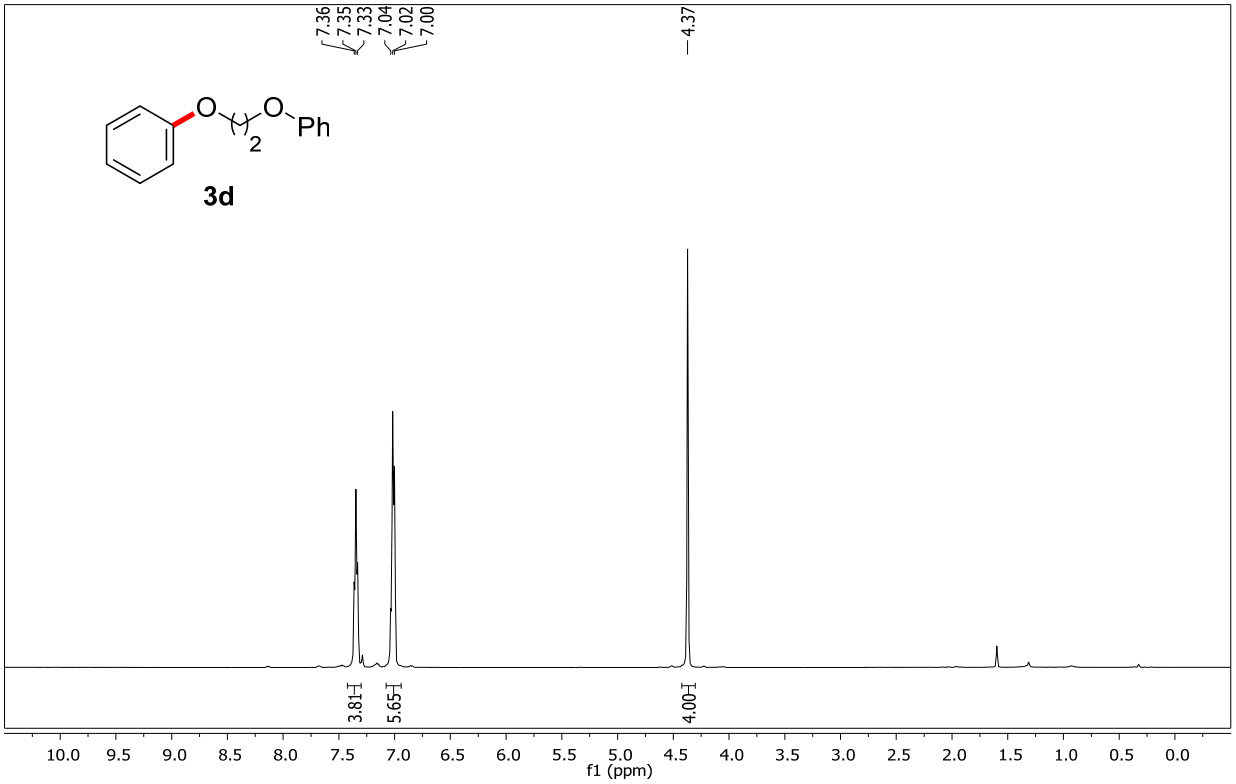


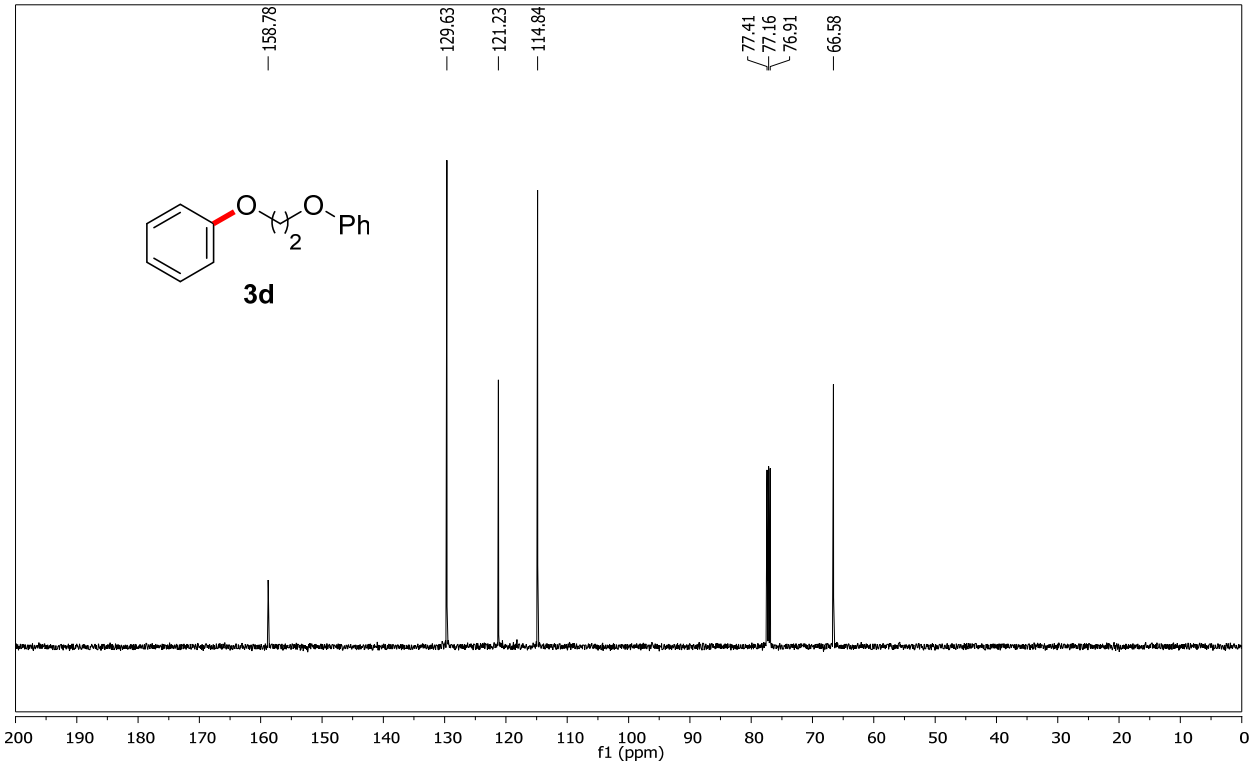
1,3-Diphenoxypropane (3c)



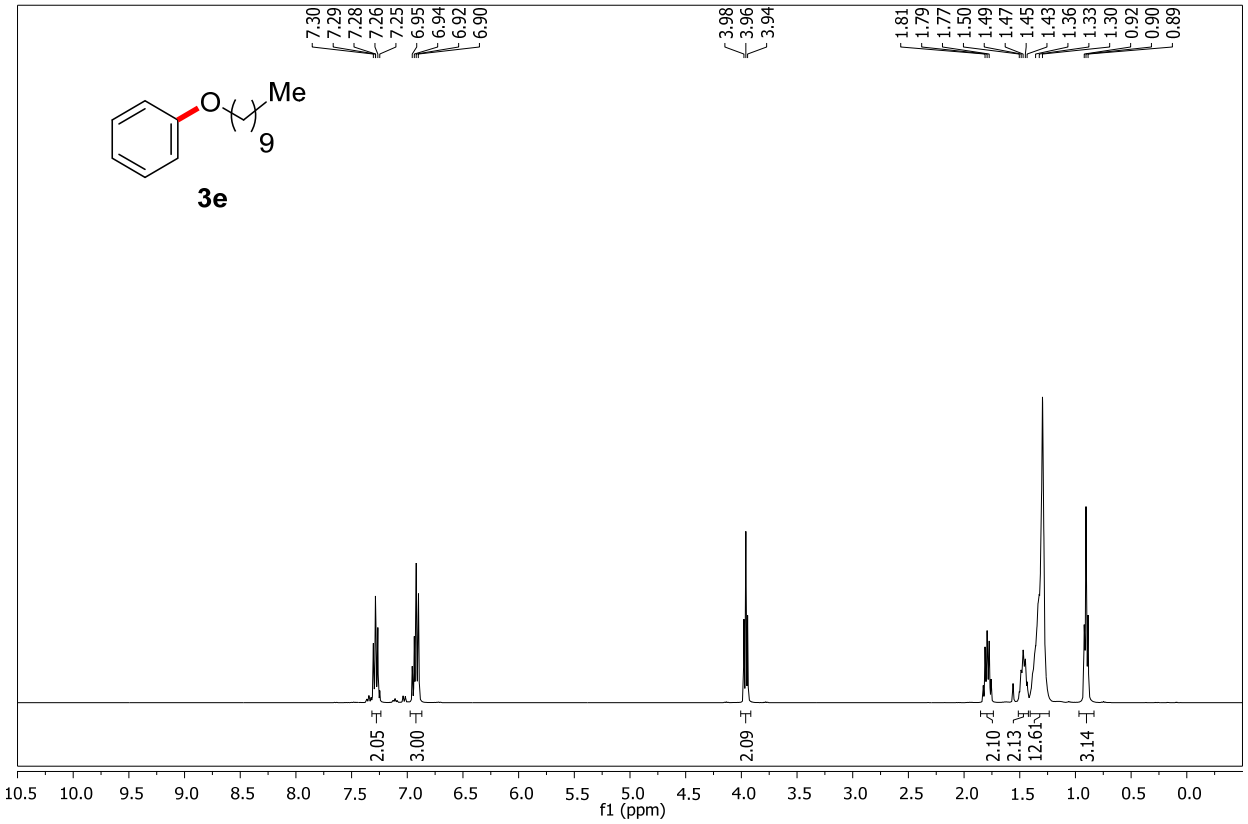


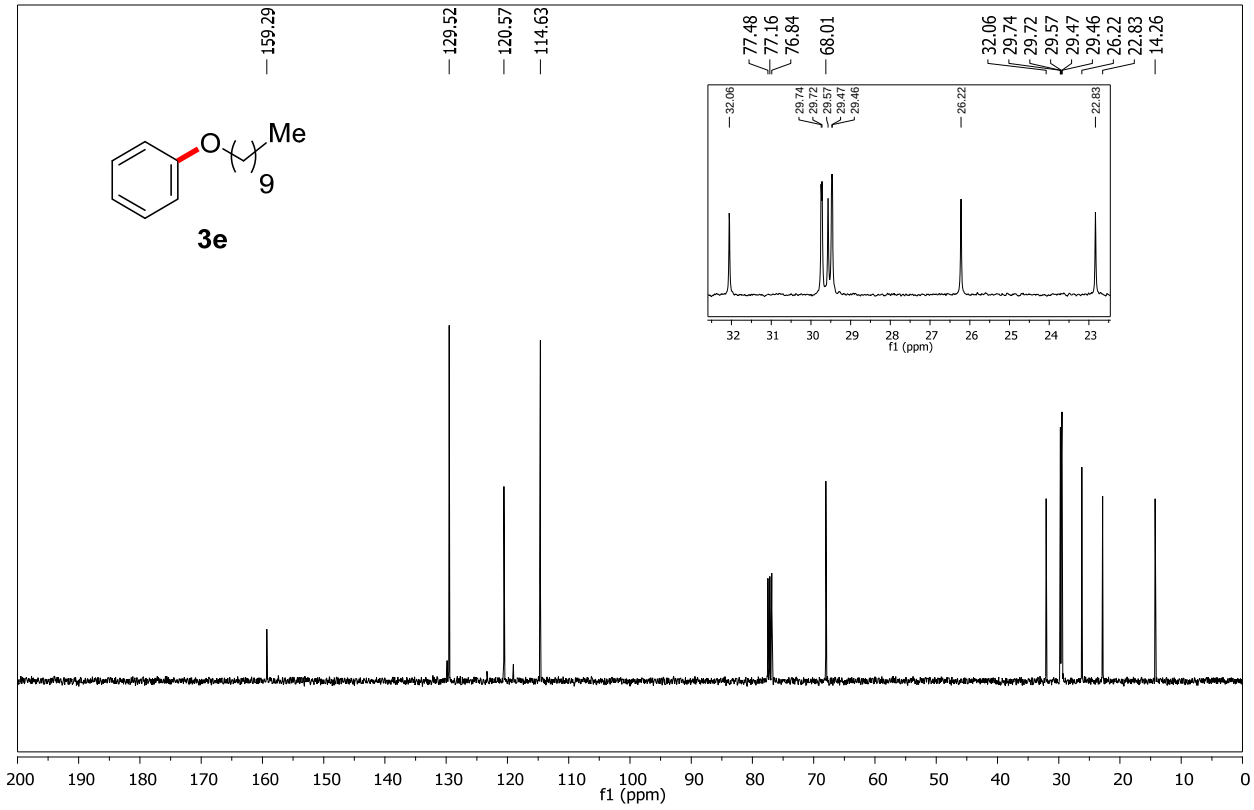
1,2-Diphenoxyethane (3d)



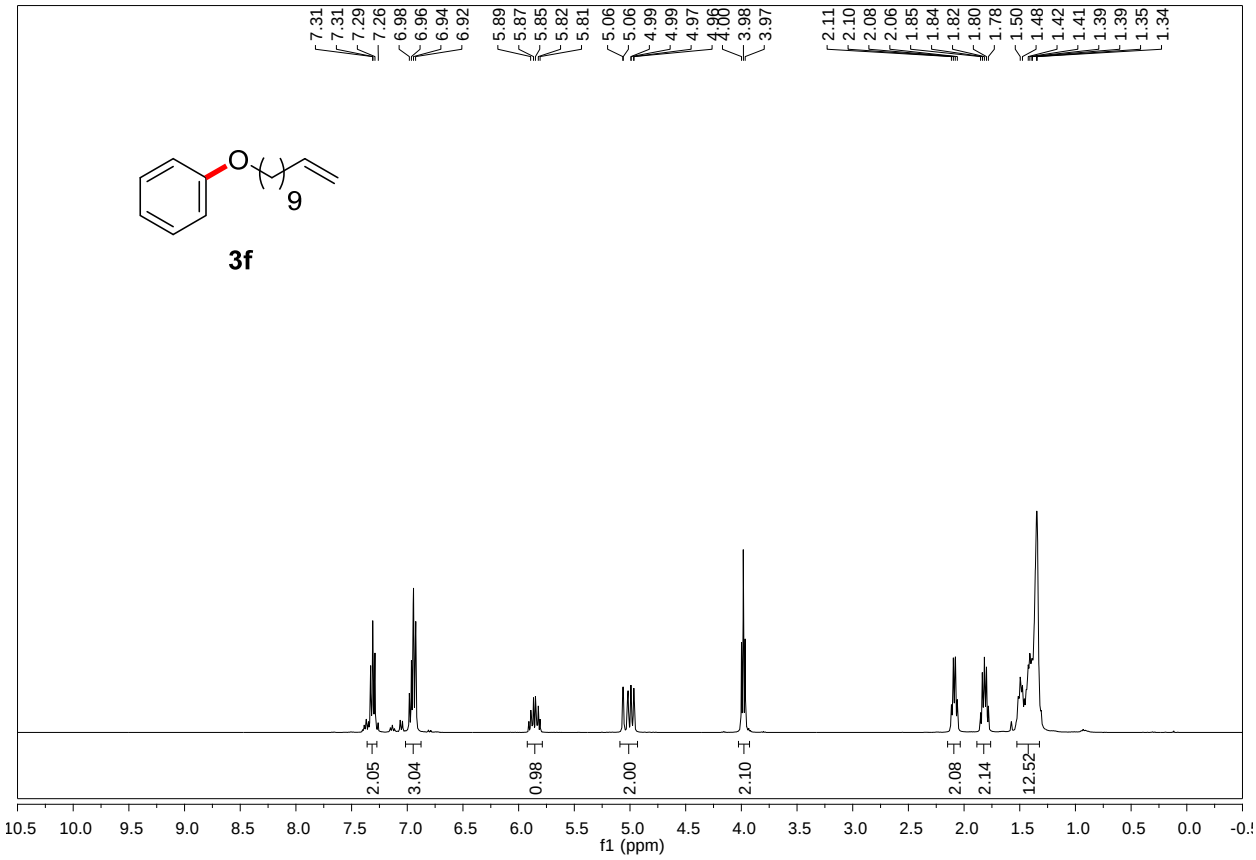


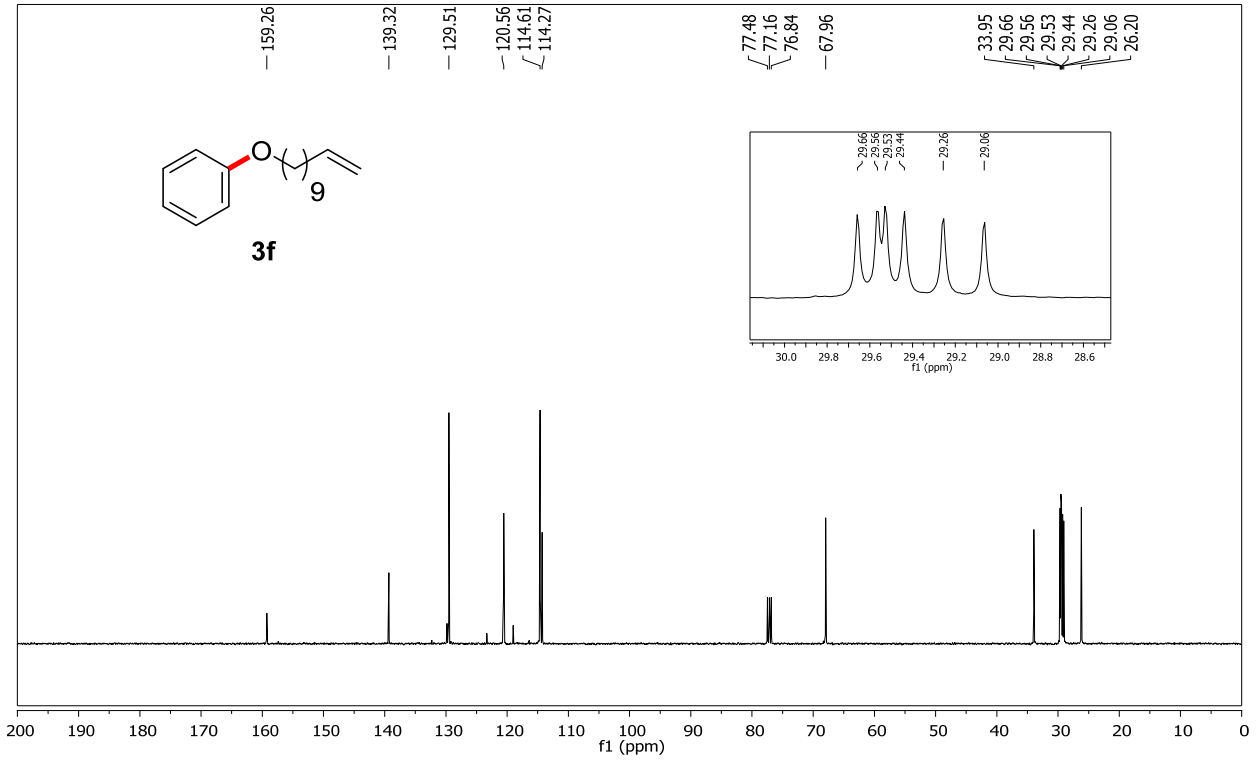
(Decyloxy)benzene (3e)



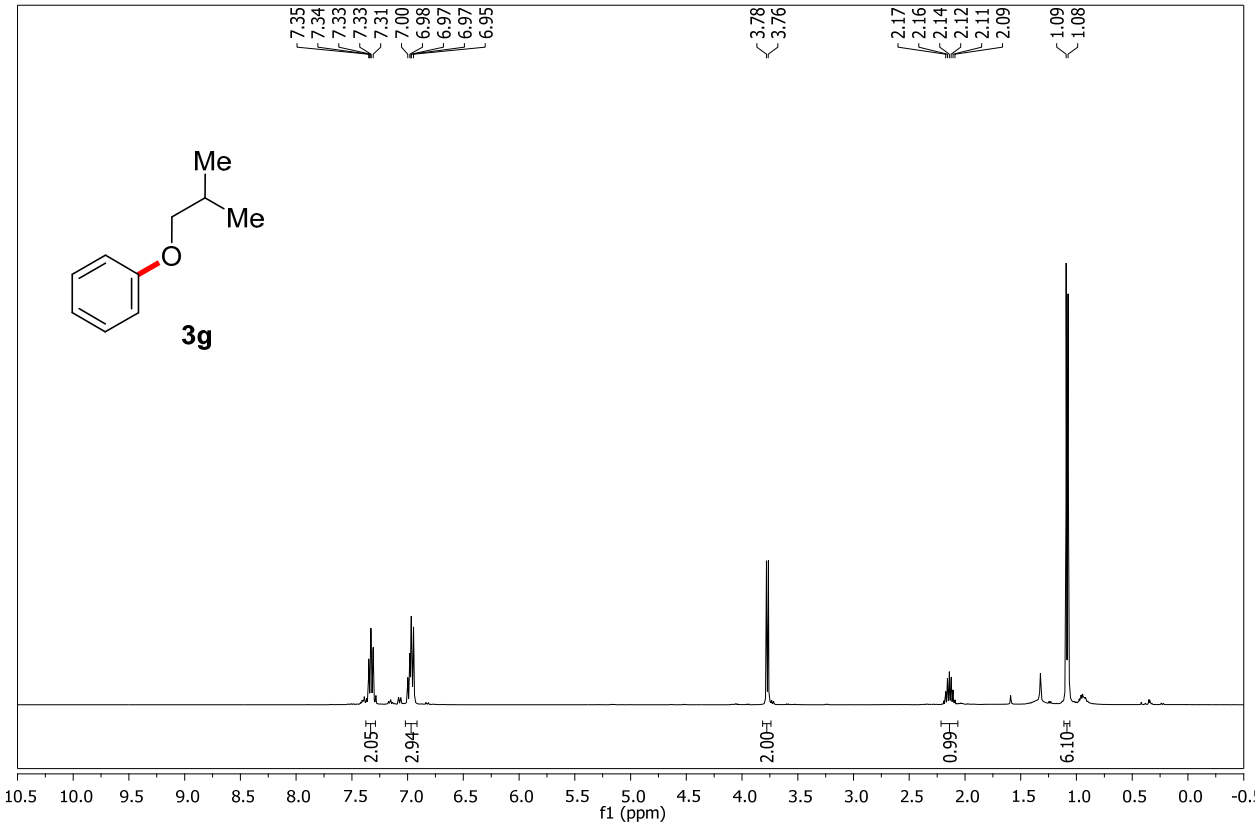


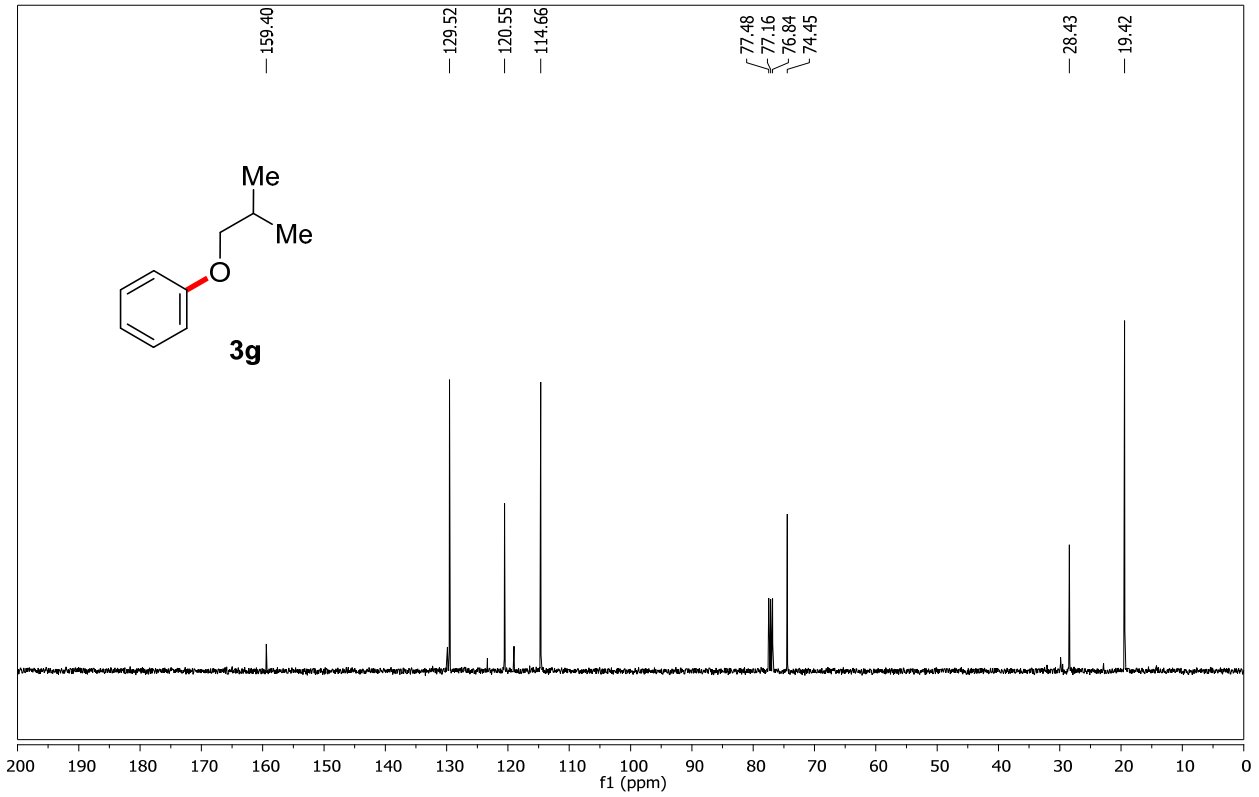
(Undec-10-en-1-yloxy)benzene (3f)



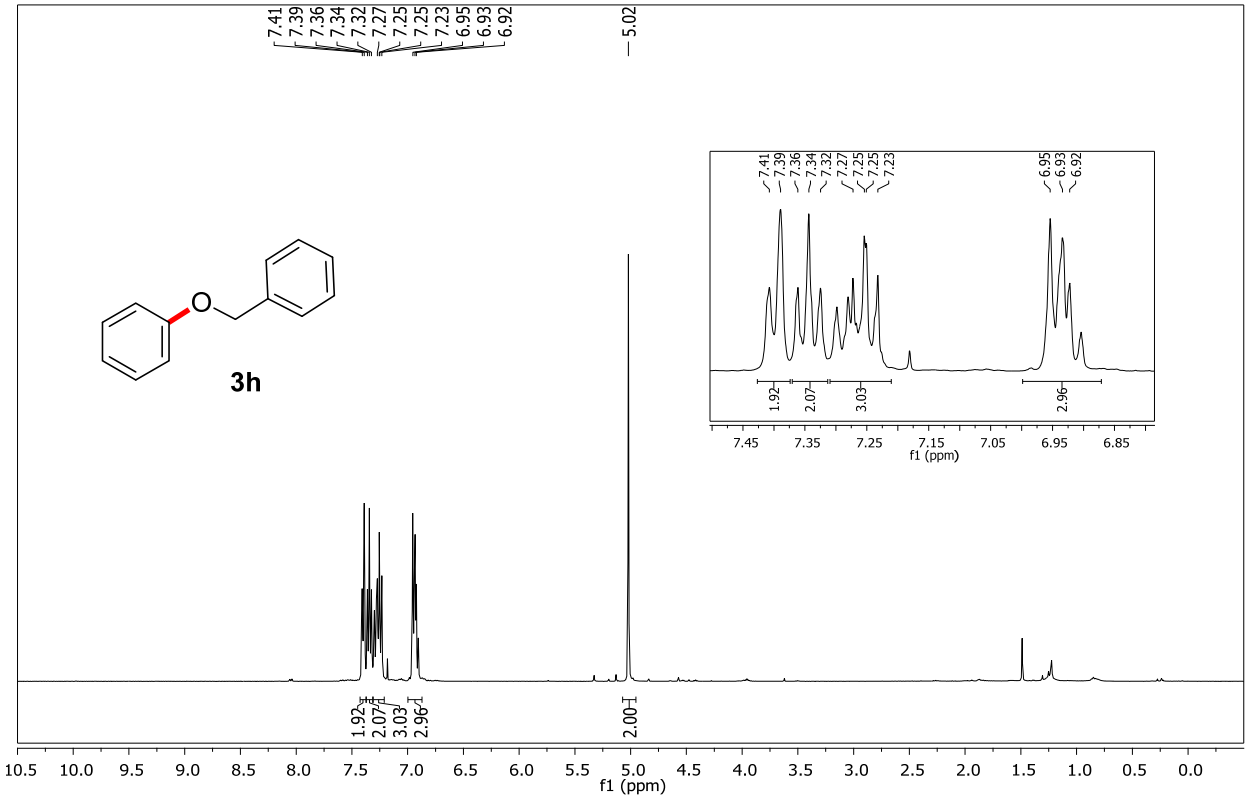


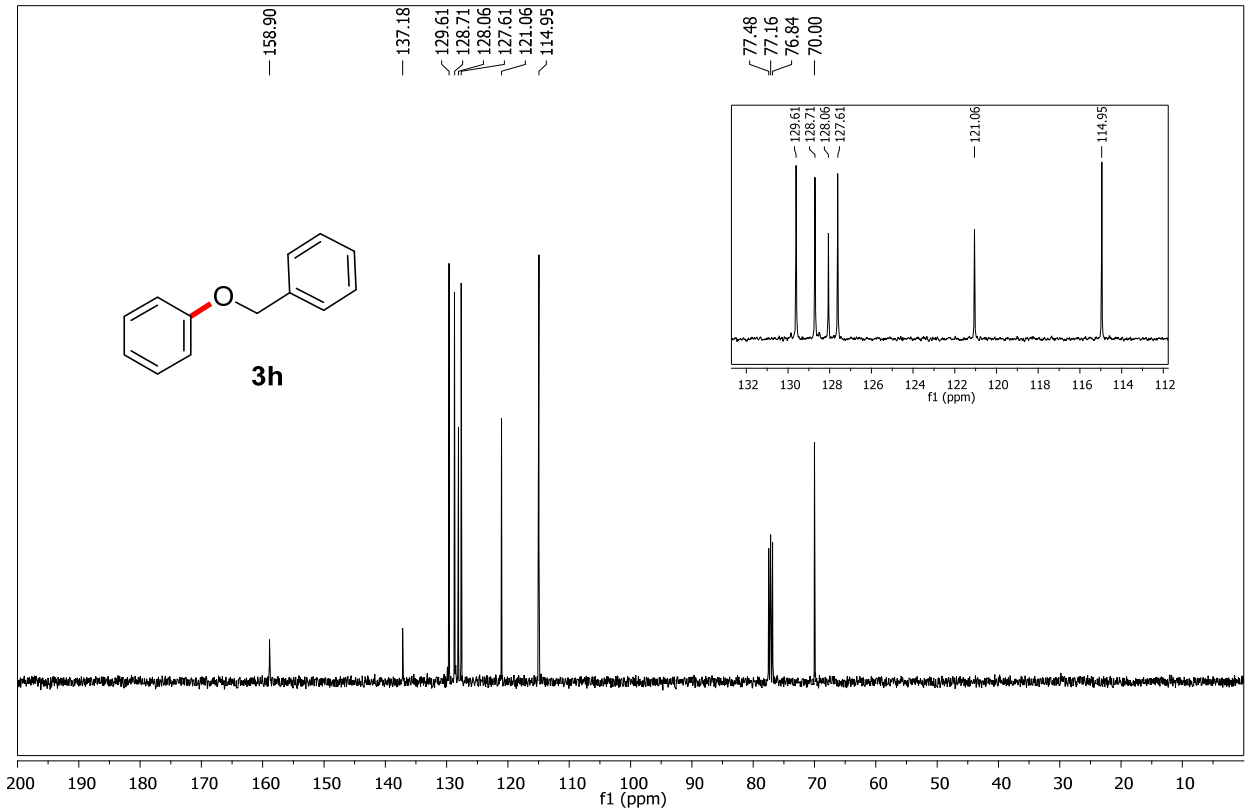
Isobutoxybenzene (3g)



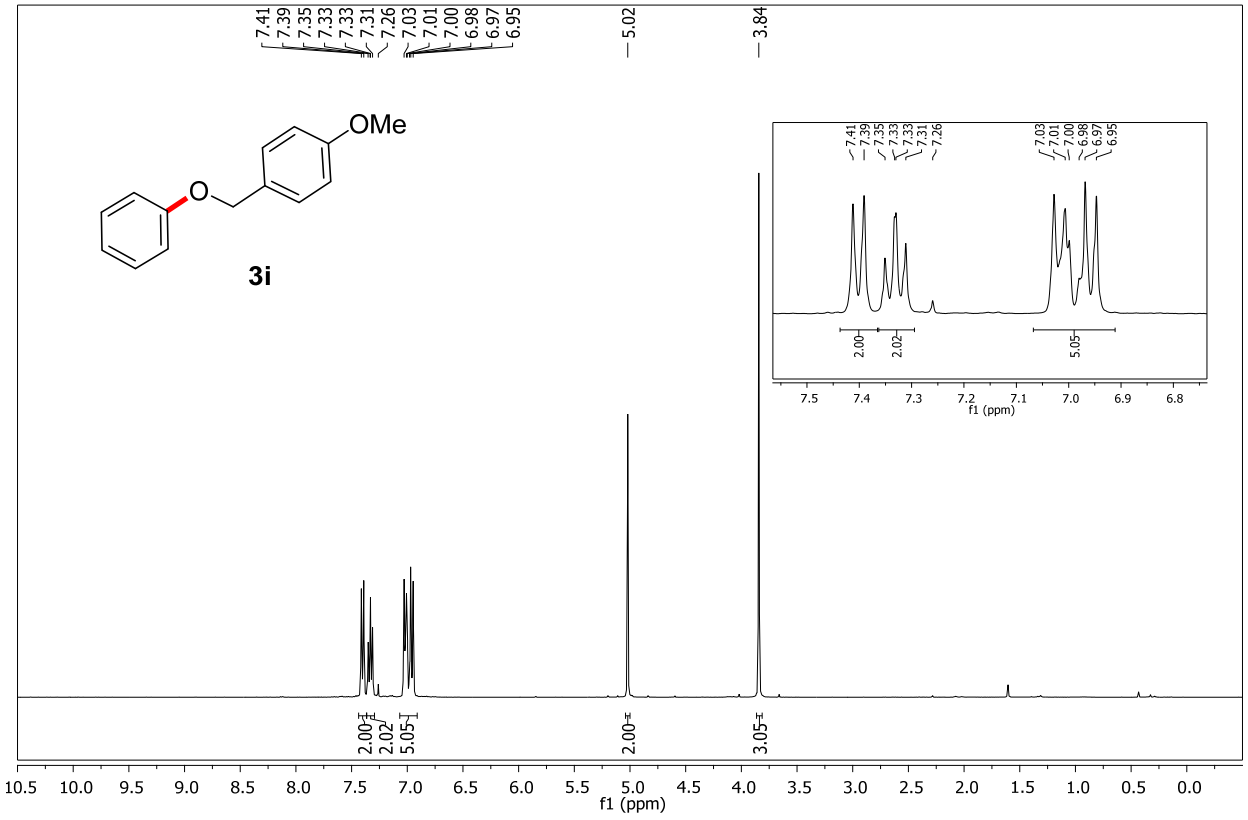


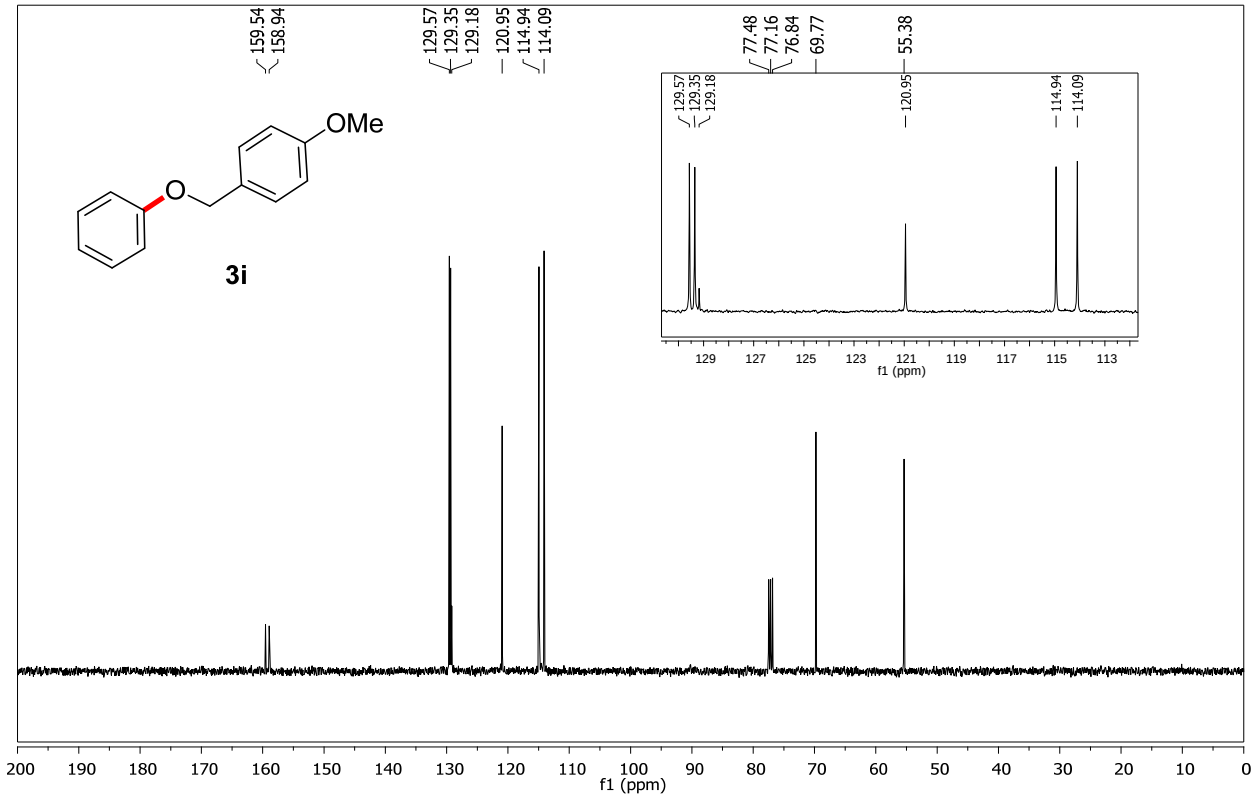
(Benzyloxy)benzene (3h)



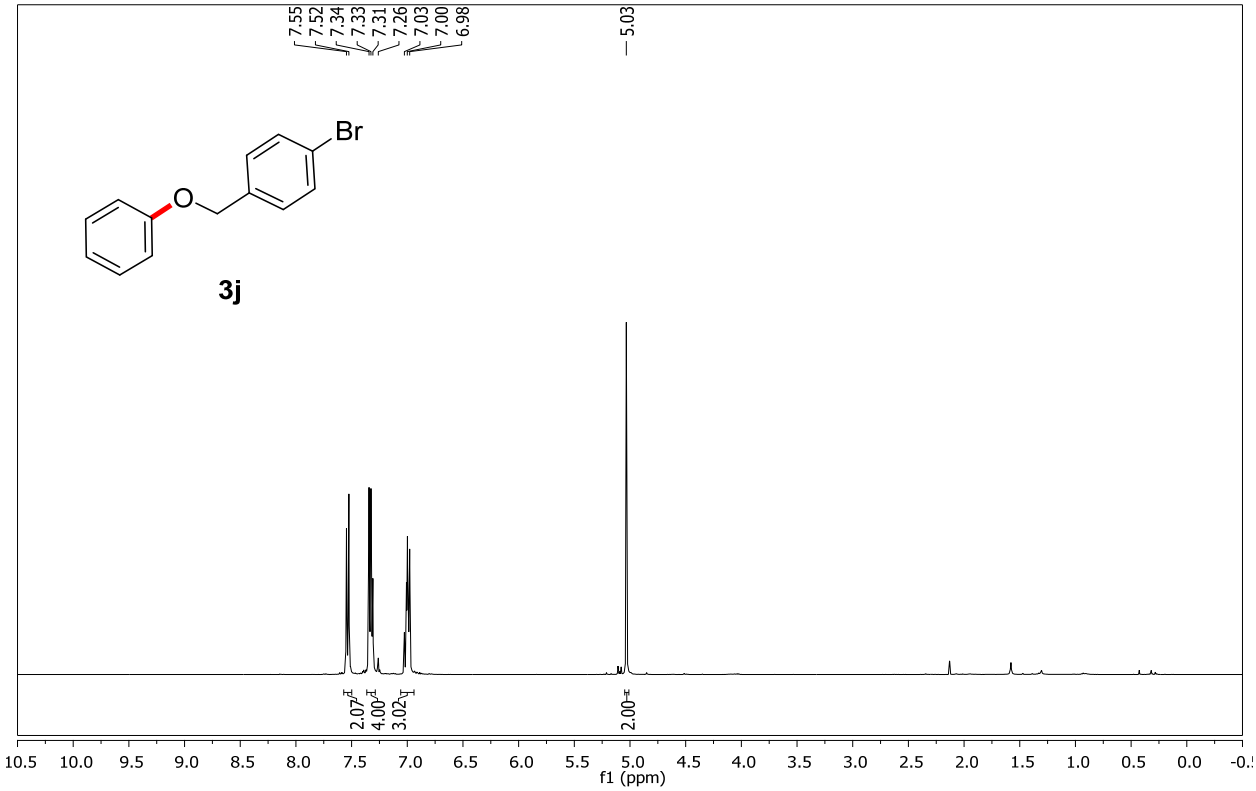


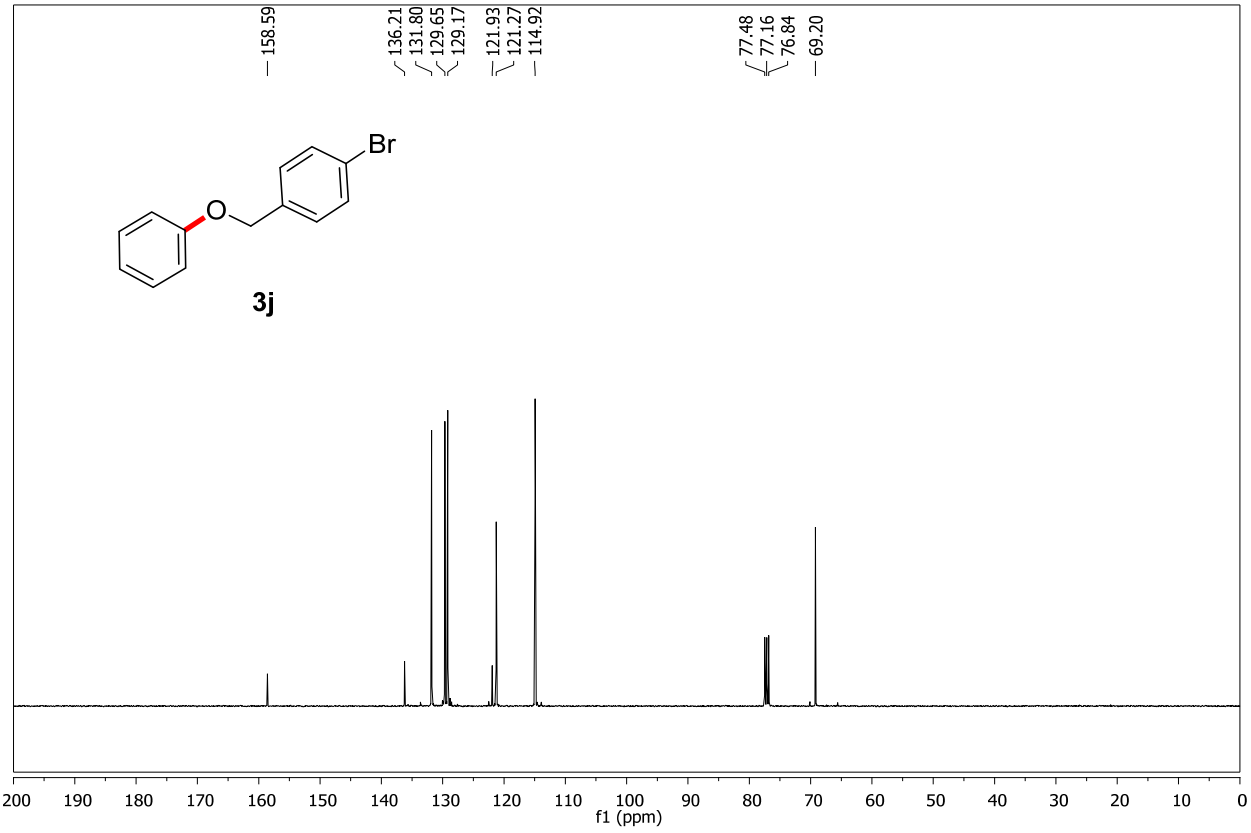
1-Methoxy-4-(phenoxymethyl)benzene (3i)



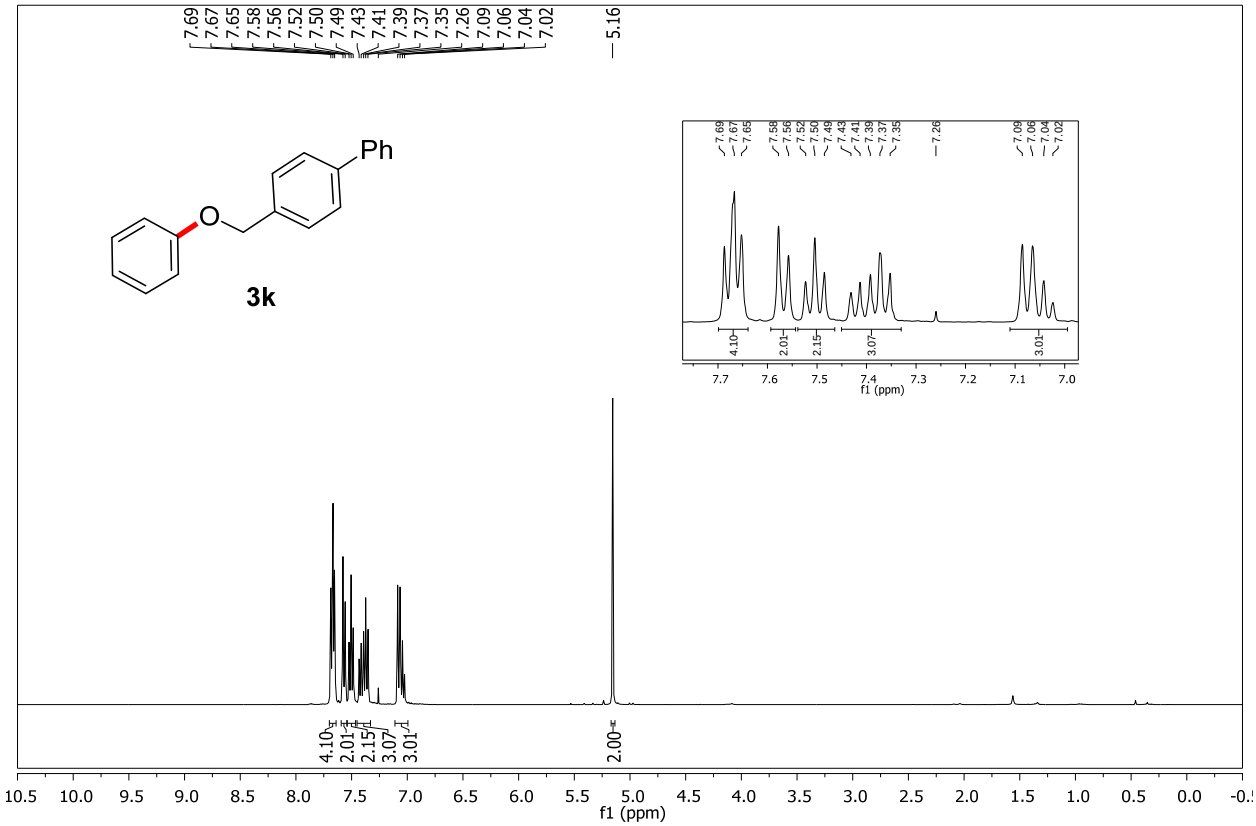


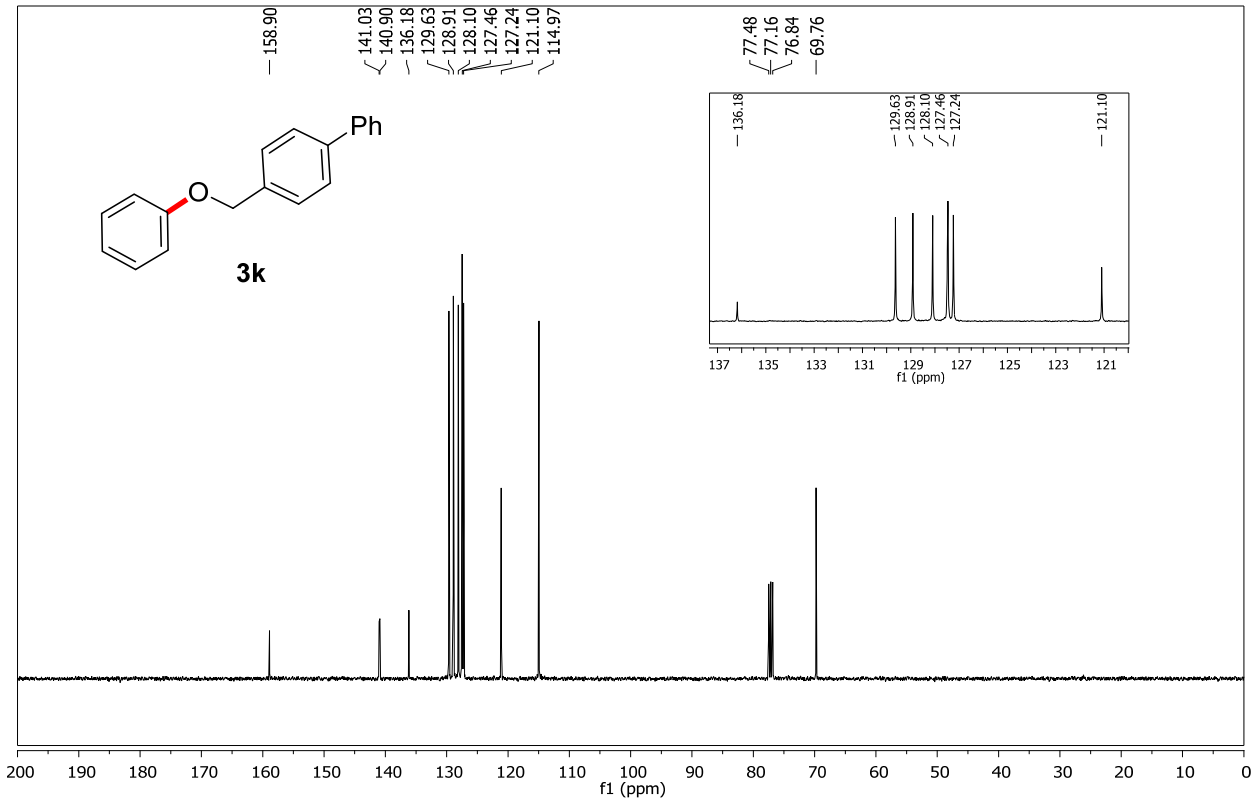
1-Bromo-4-(phenoxymethyl)benzene (3j)



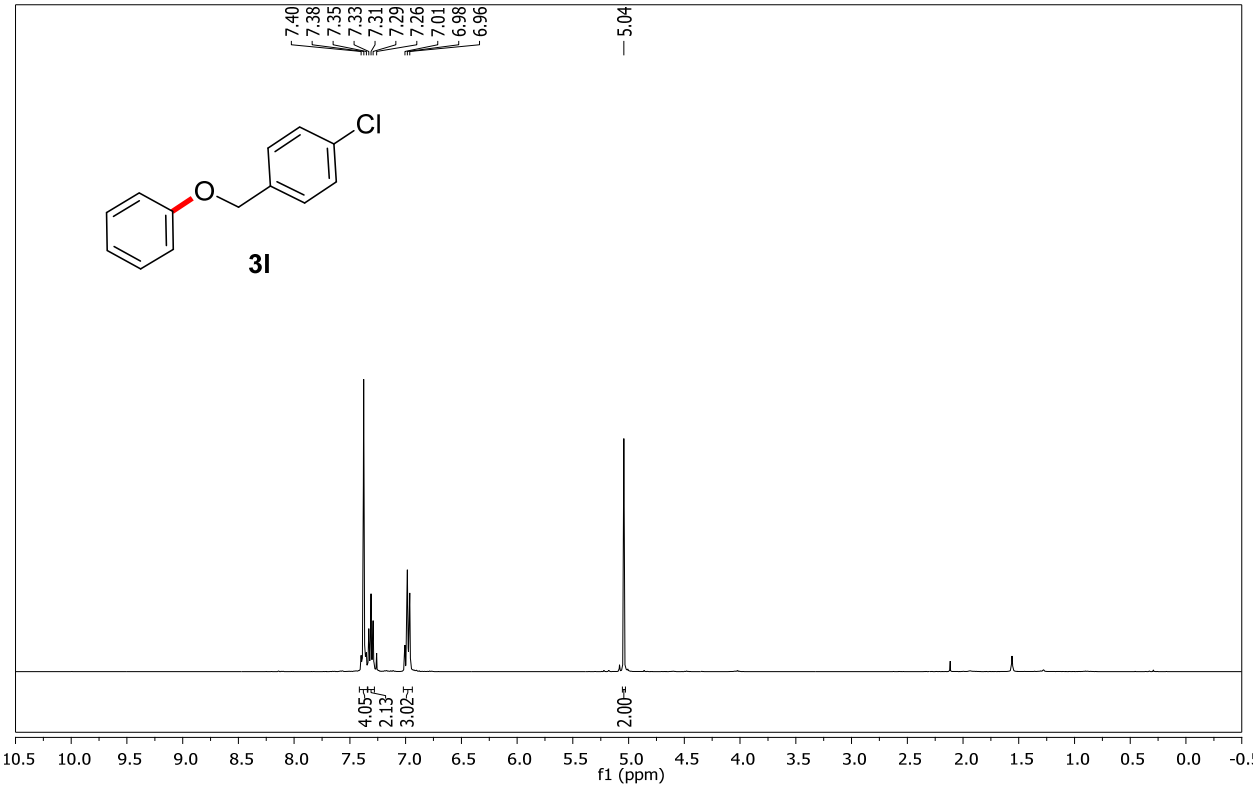


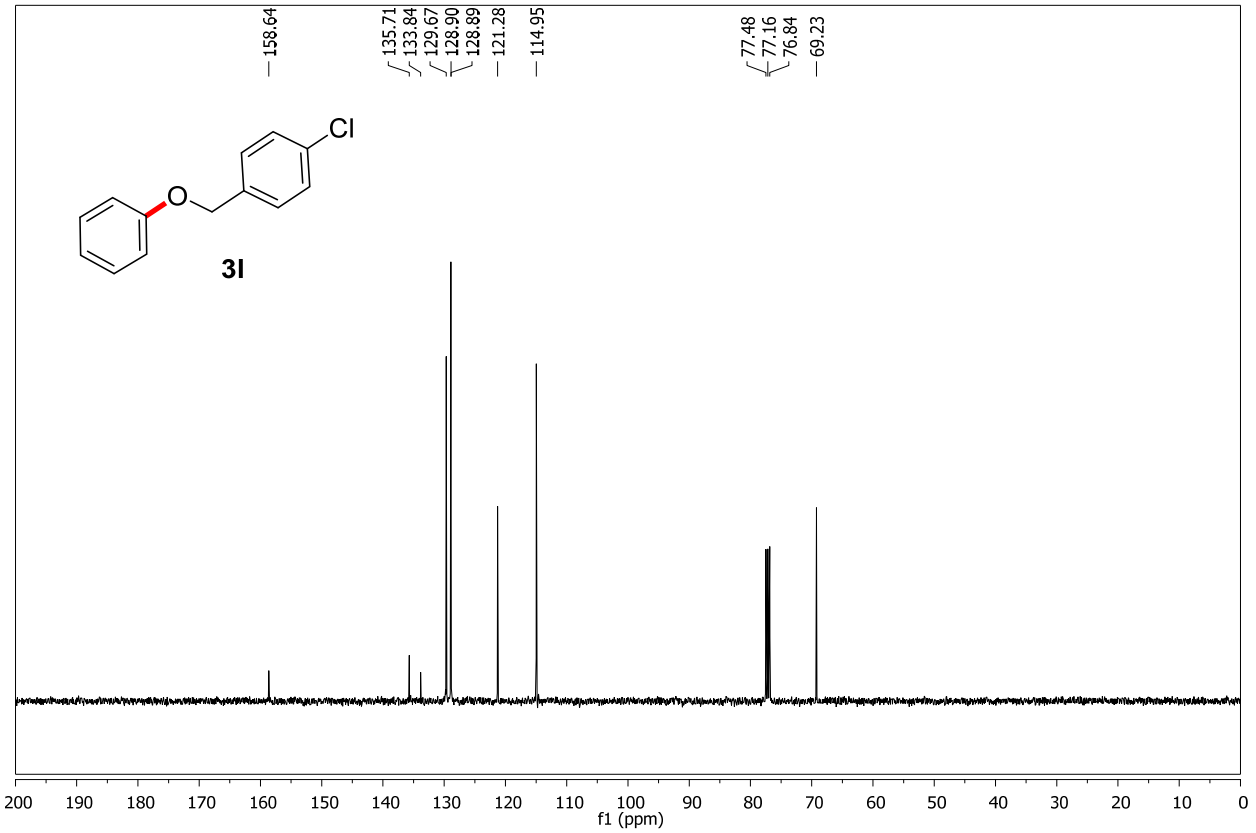
4-(Phenoxymethyl)-1,1'-biphenyl (3k)



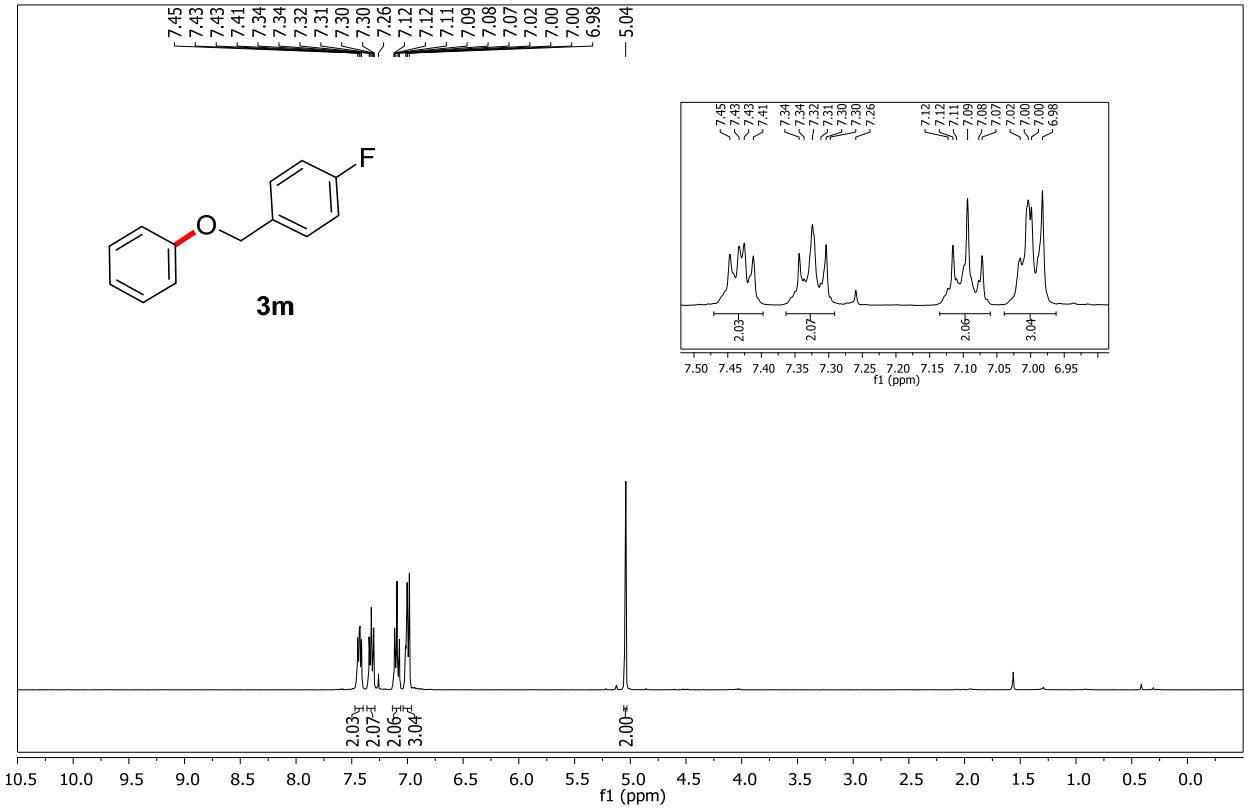


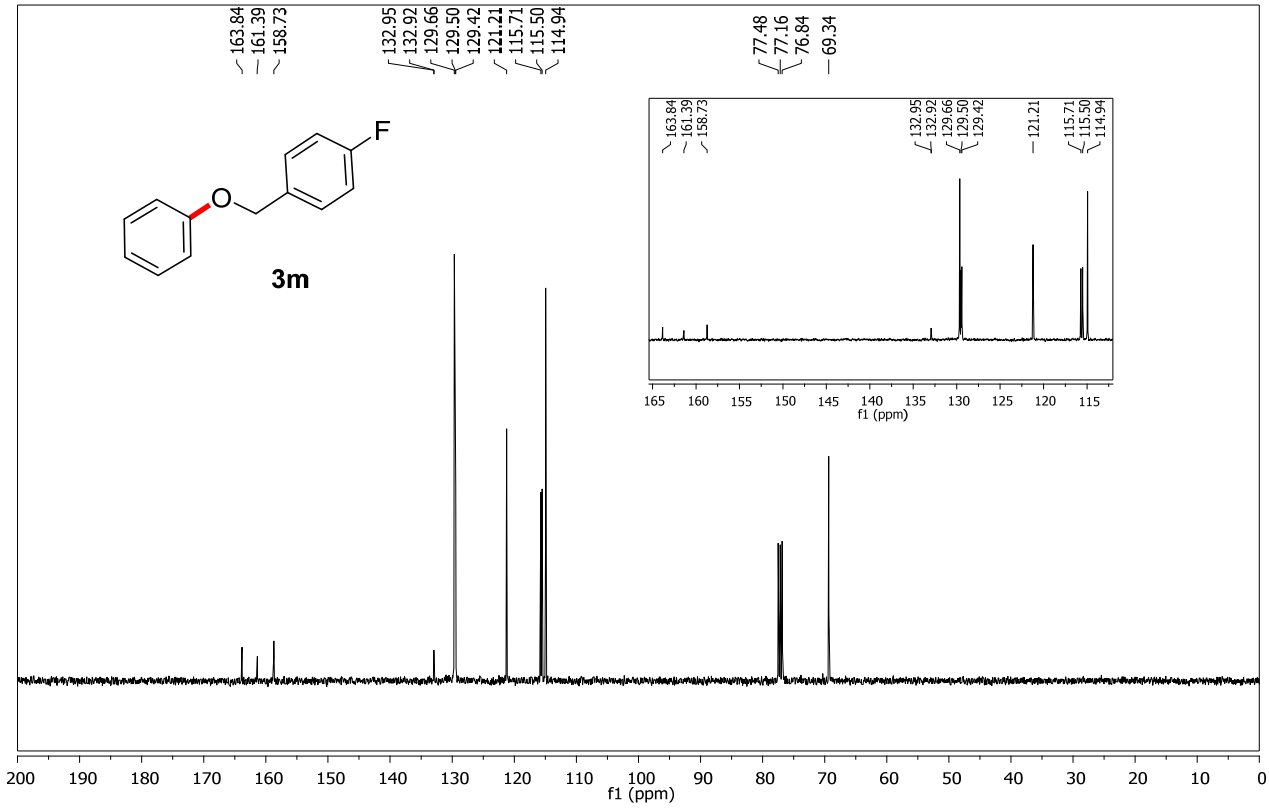
1-Chloro-4-(phenoxymethyl)benzene (3l)



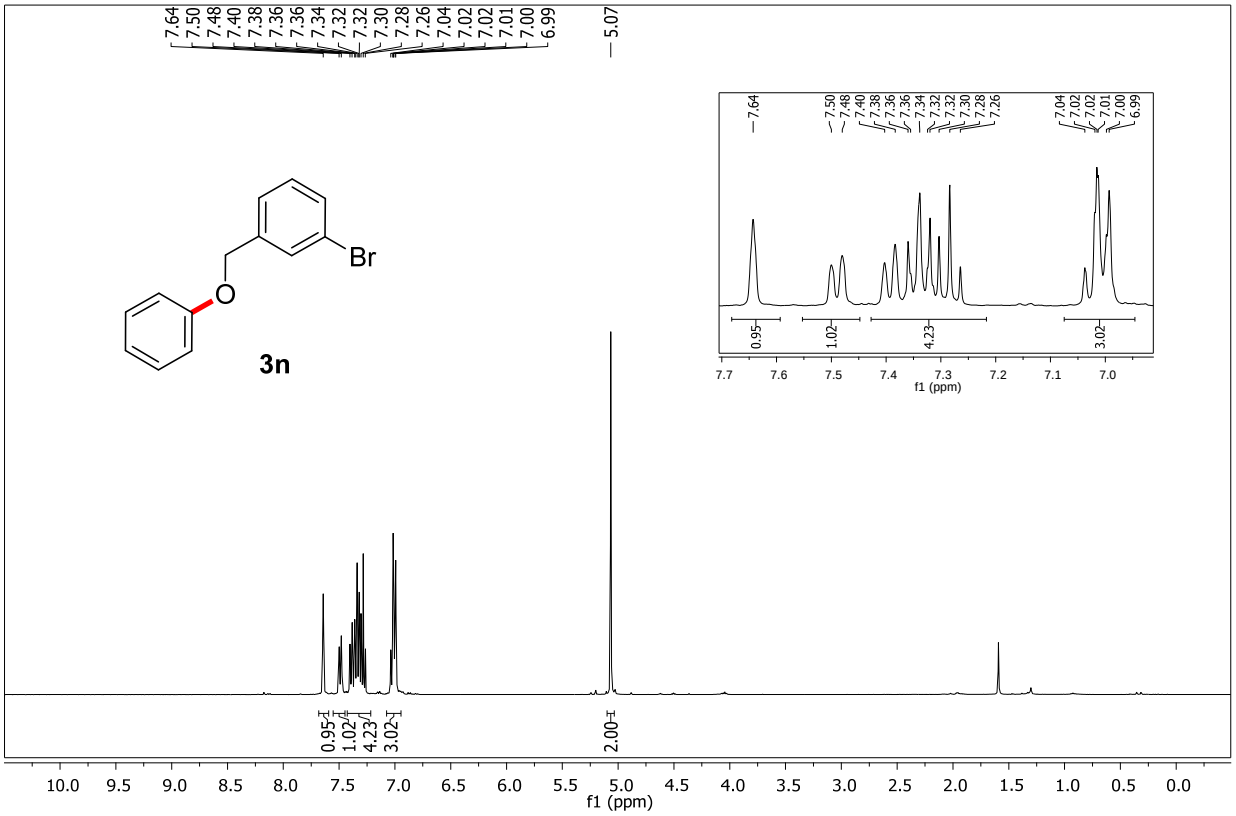


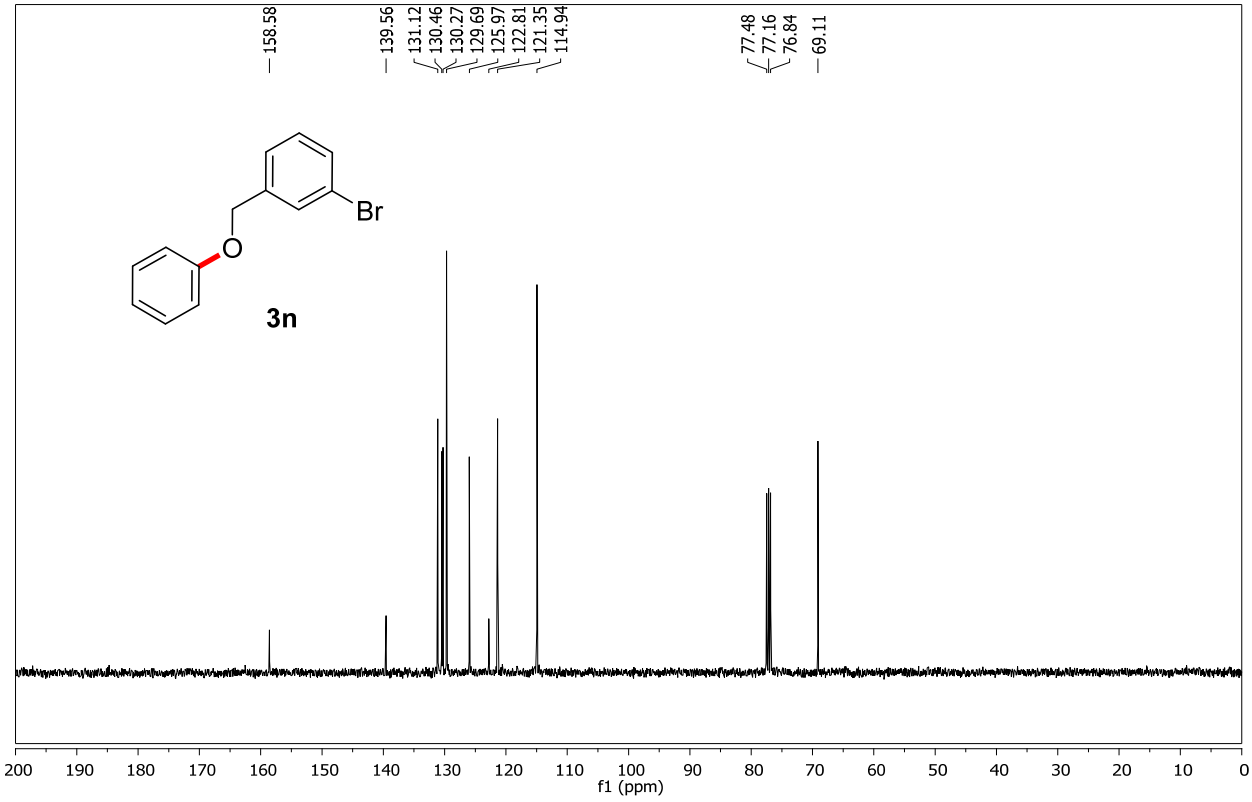
1-Fluoro-4-(phenoxymethyl)benzene (3m)



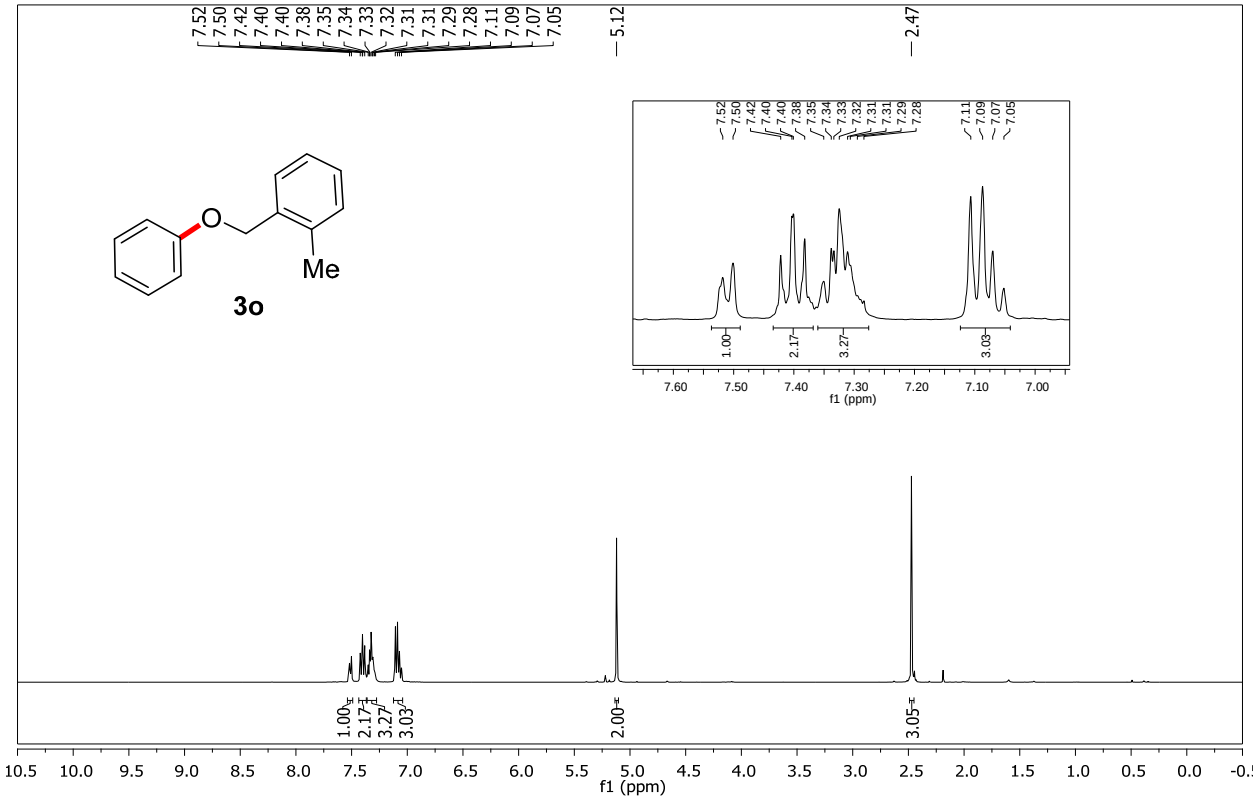


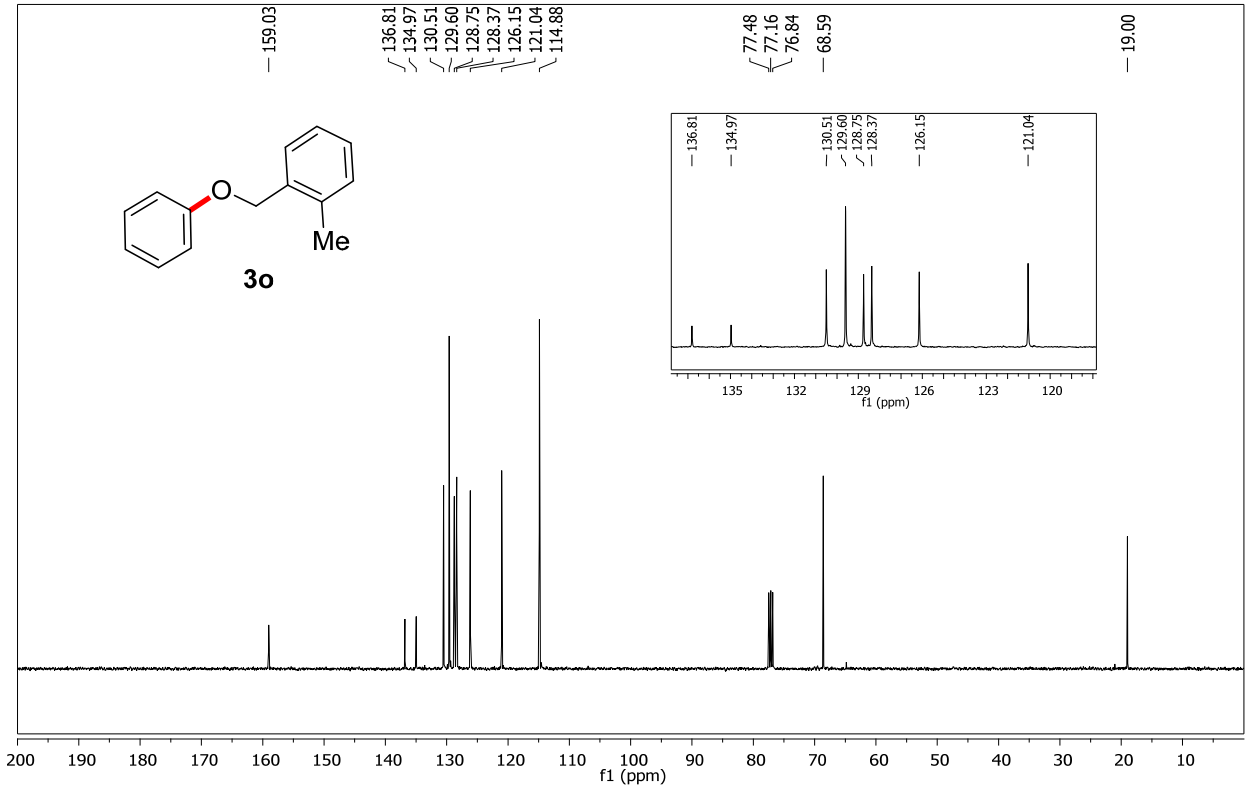
1-Bromo-3-(phenoxymethyl)benzene (3n)



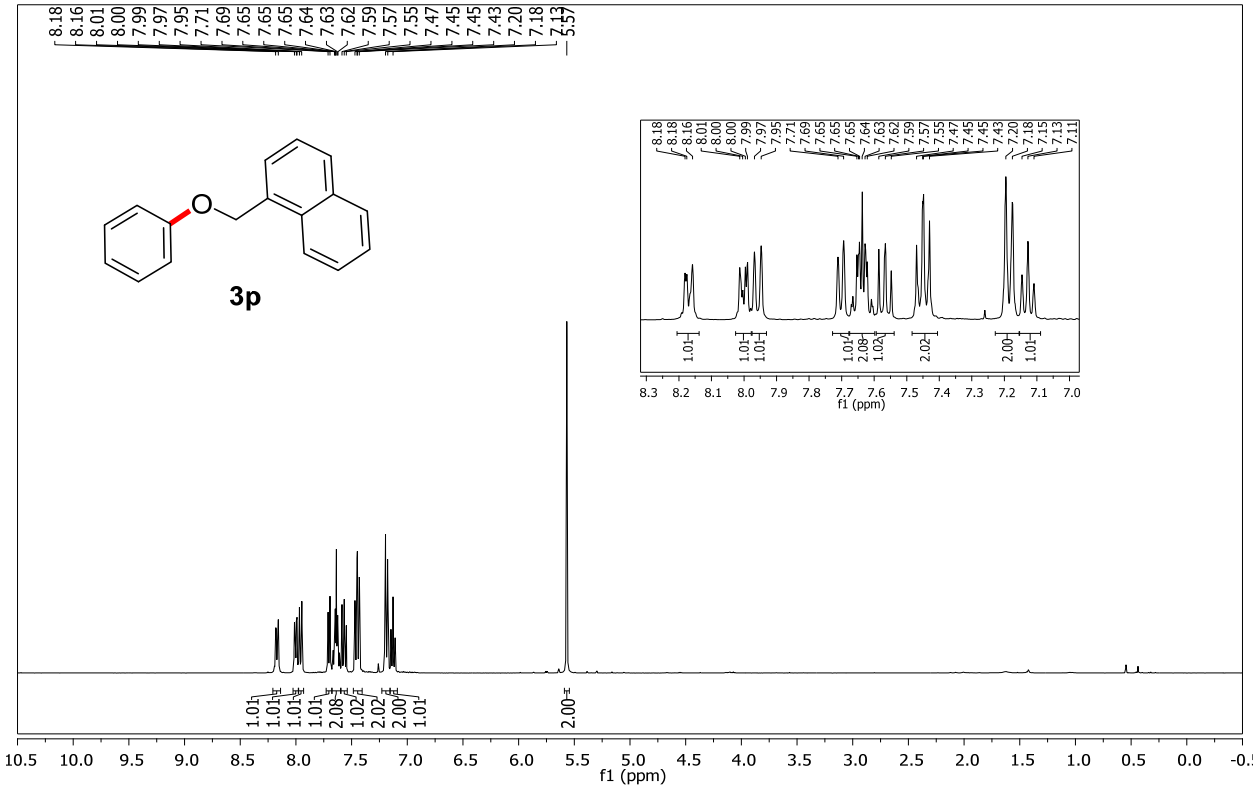


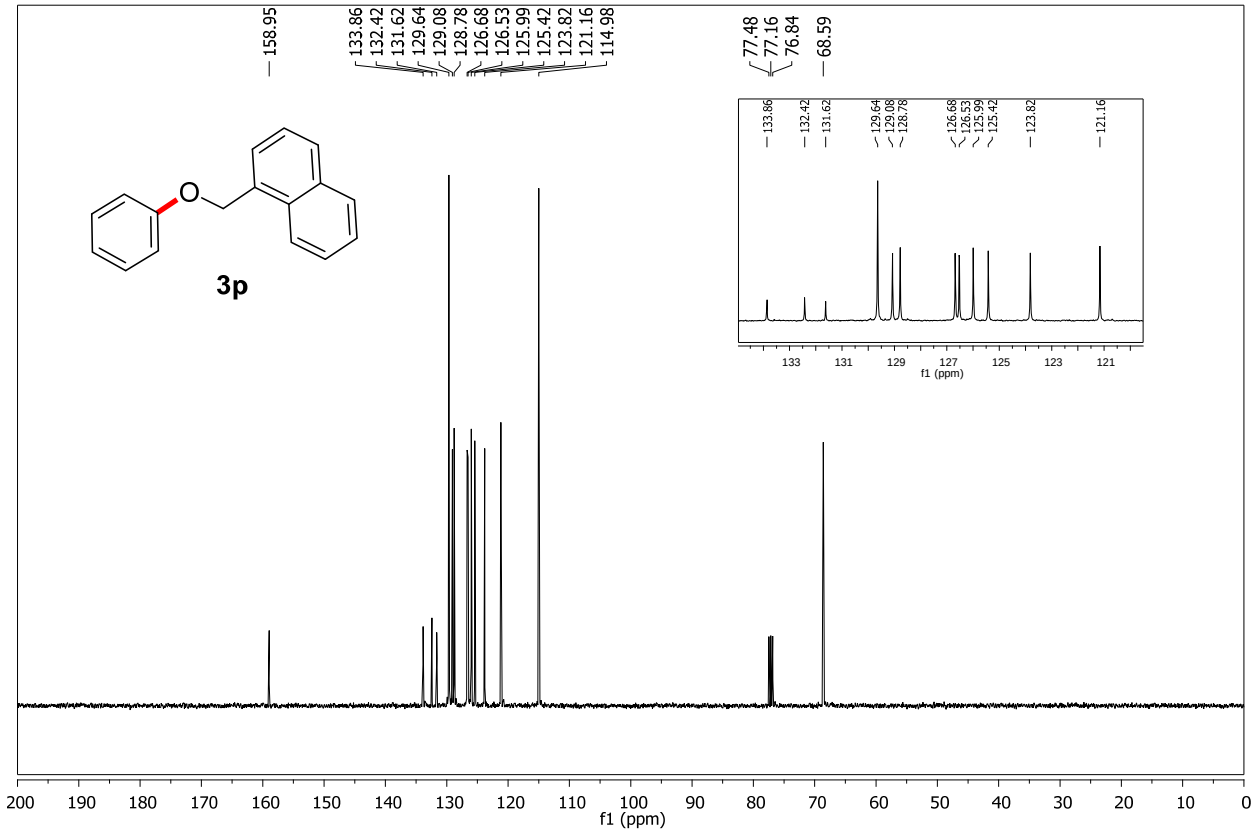
1-Methyl-2-(phenoxymethyl)benzene (3o)



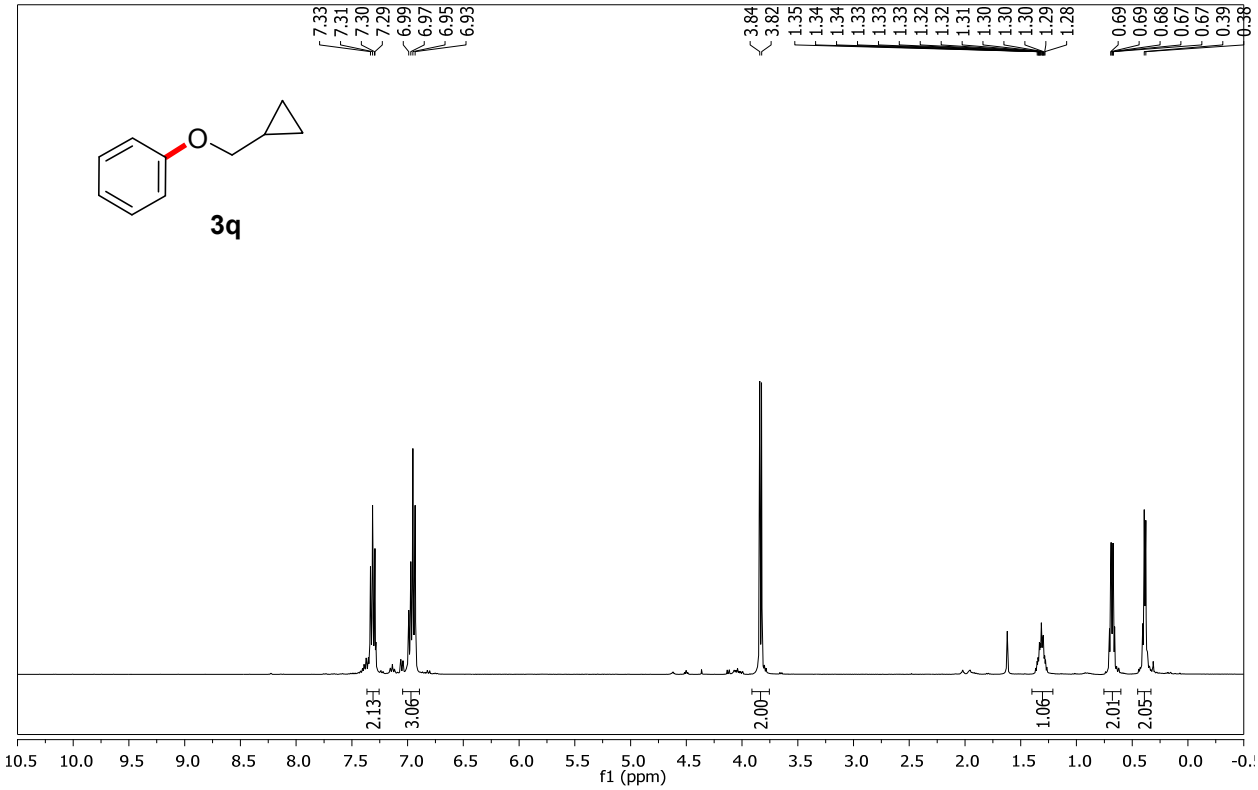


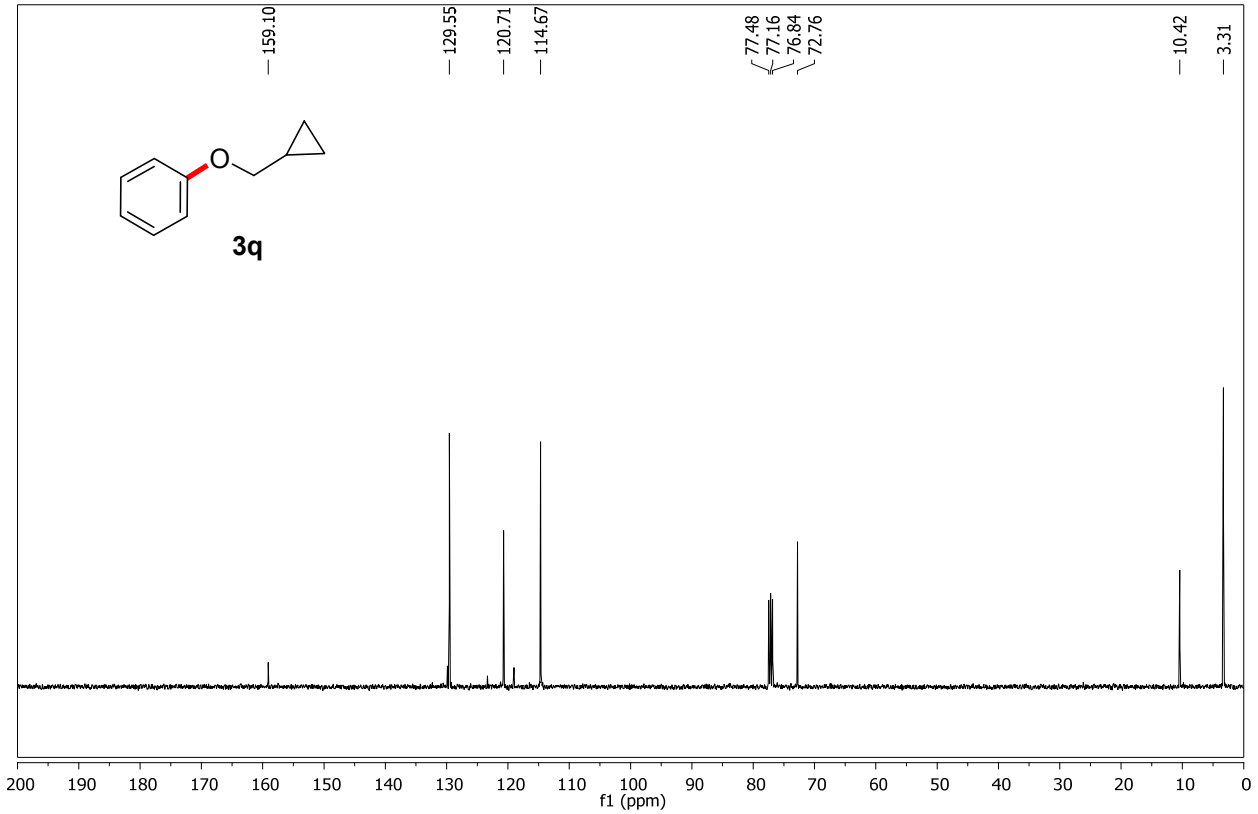
1-(Phenoxymethyl)naphthalene (3p)



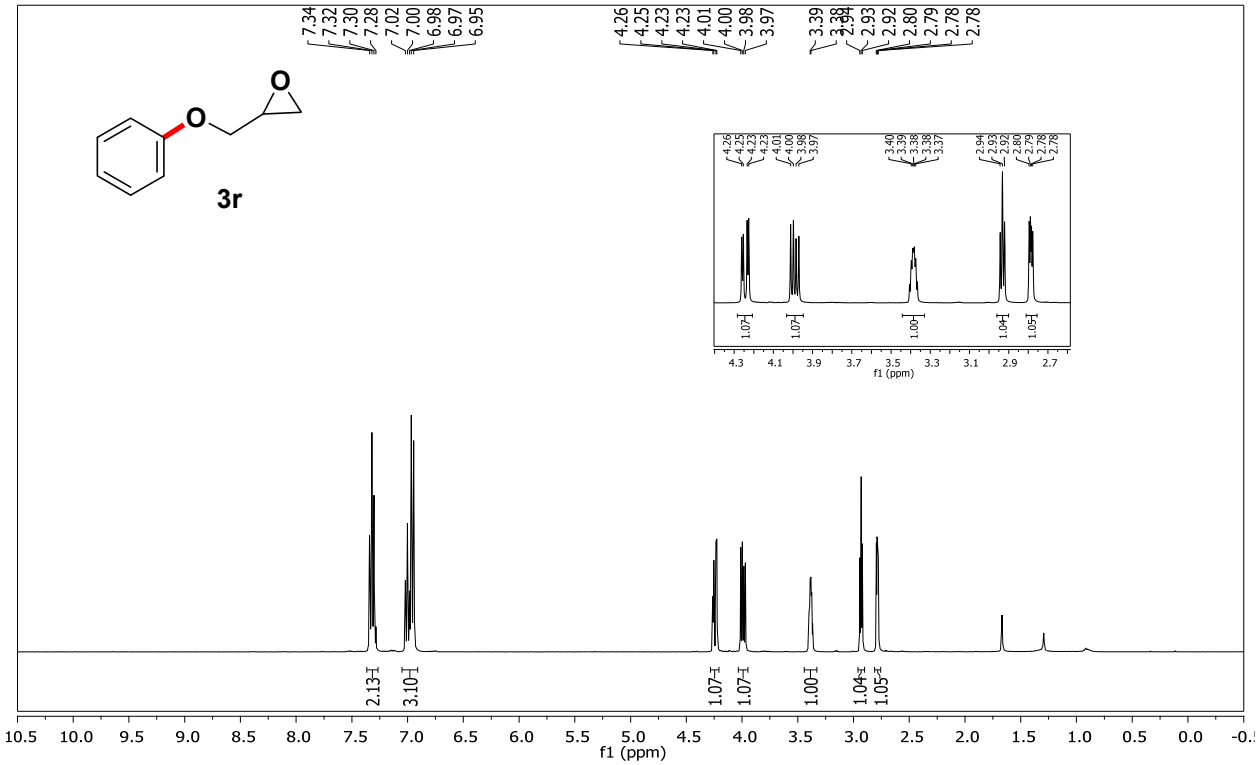


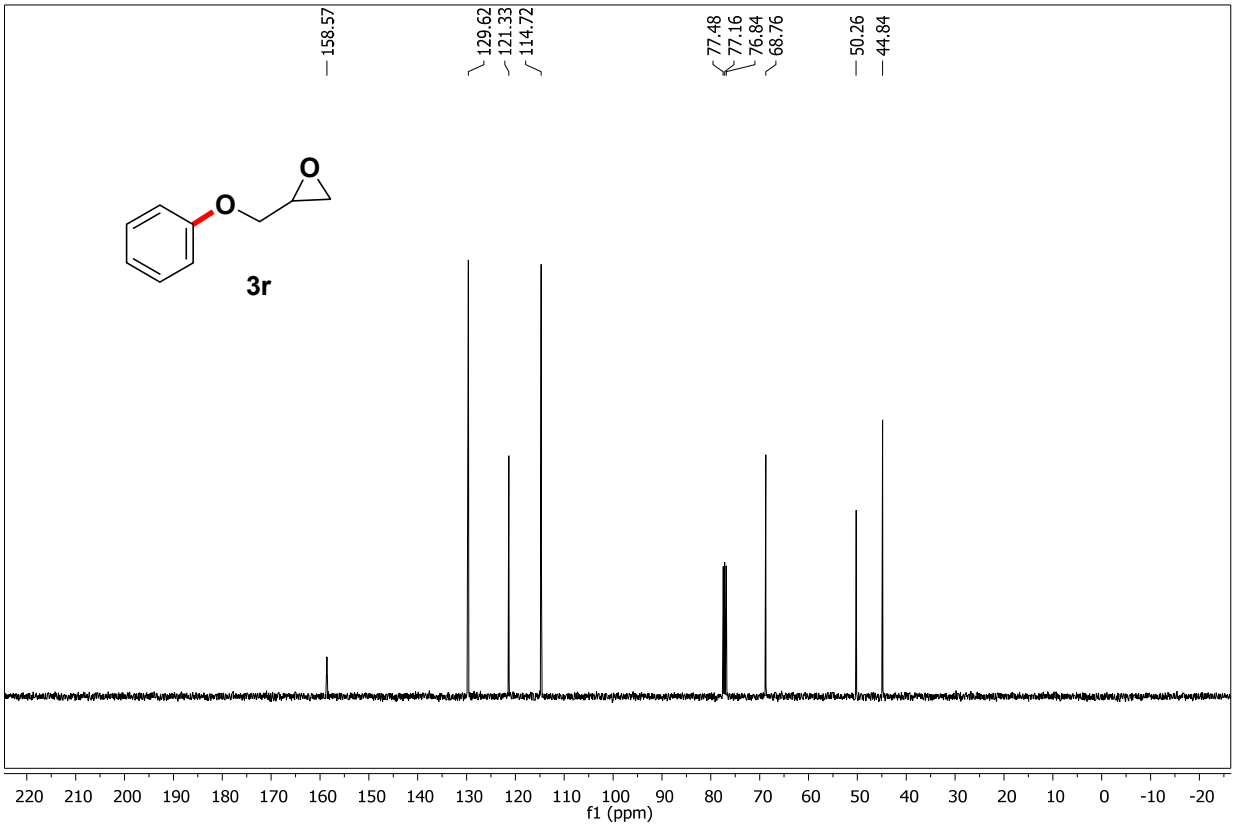
(Cyclopropylmethoxy)benzene (3q)



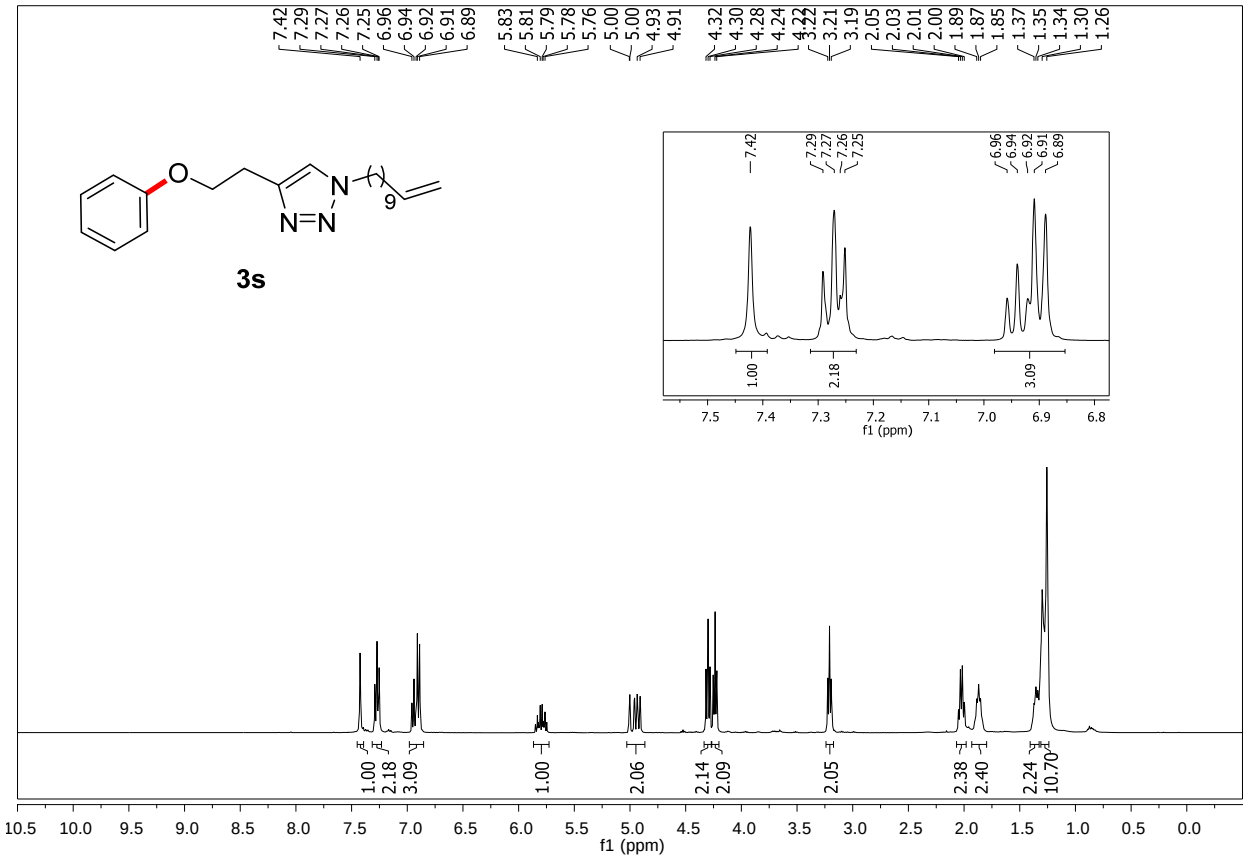


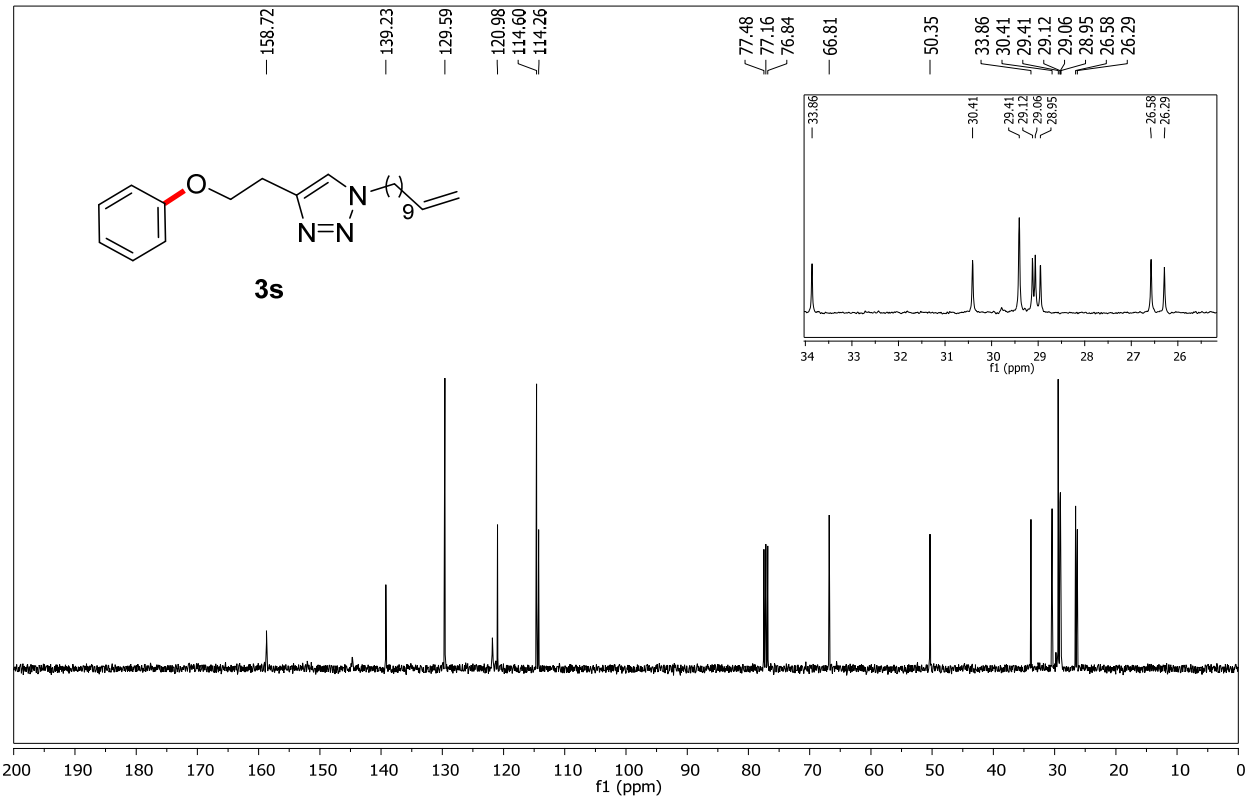
2-(Phenoxymethyl)oxirane (3r)



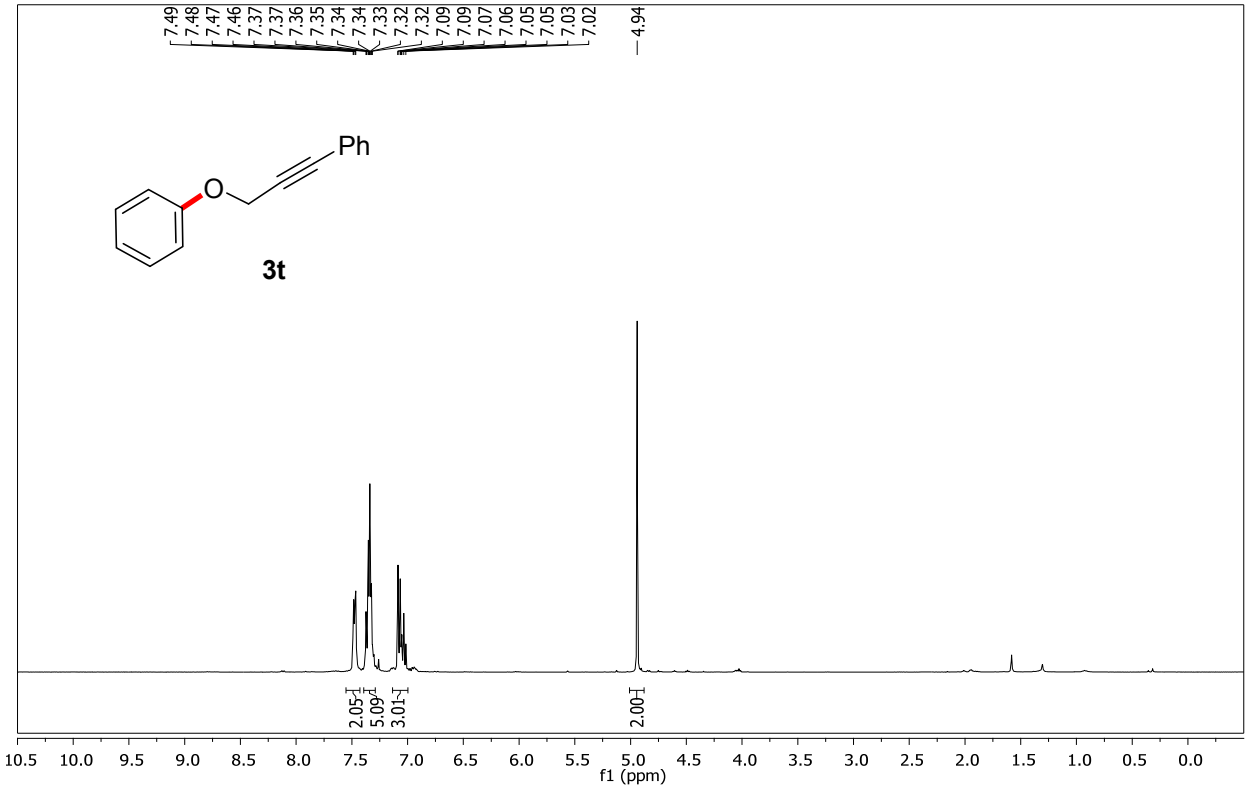


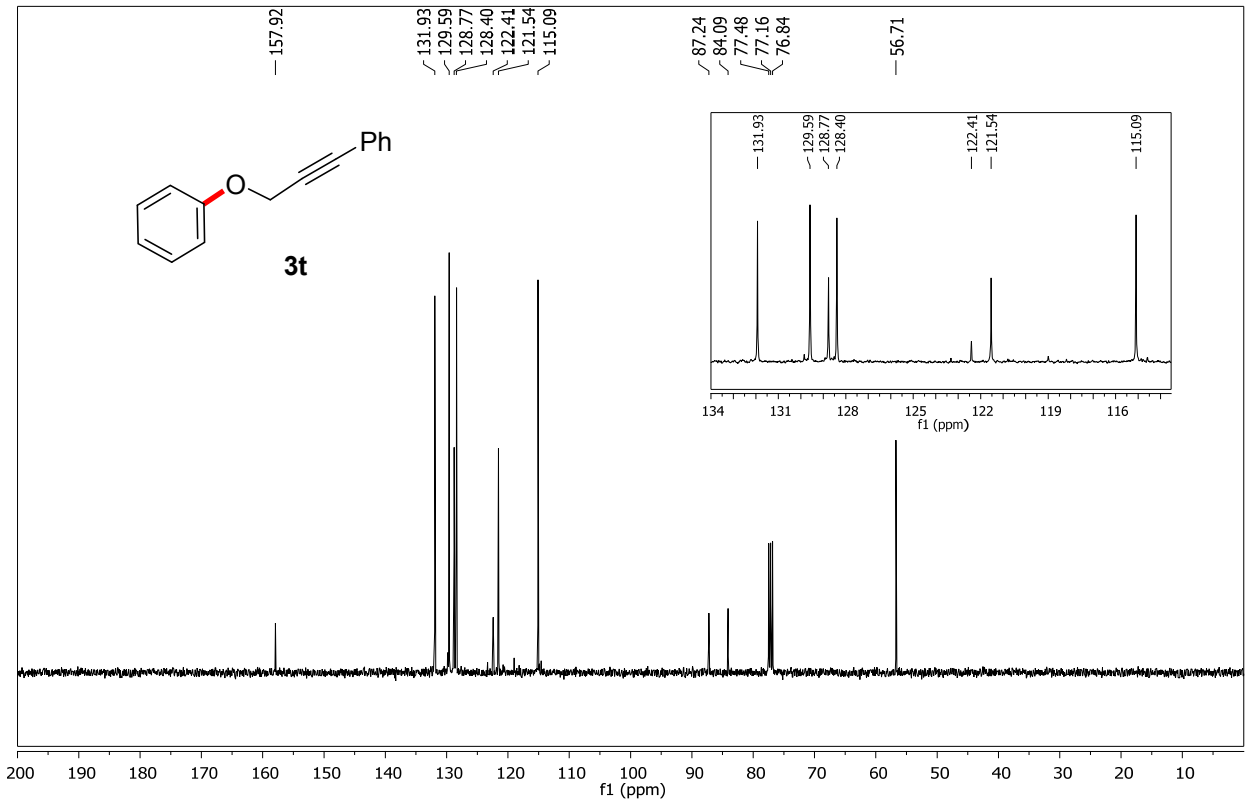
4-(2-Phenoxyethyl)-1-(undec-10-en-1-yl)-1*H*-1,2,3-triazole (3s)



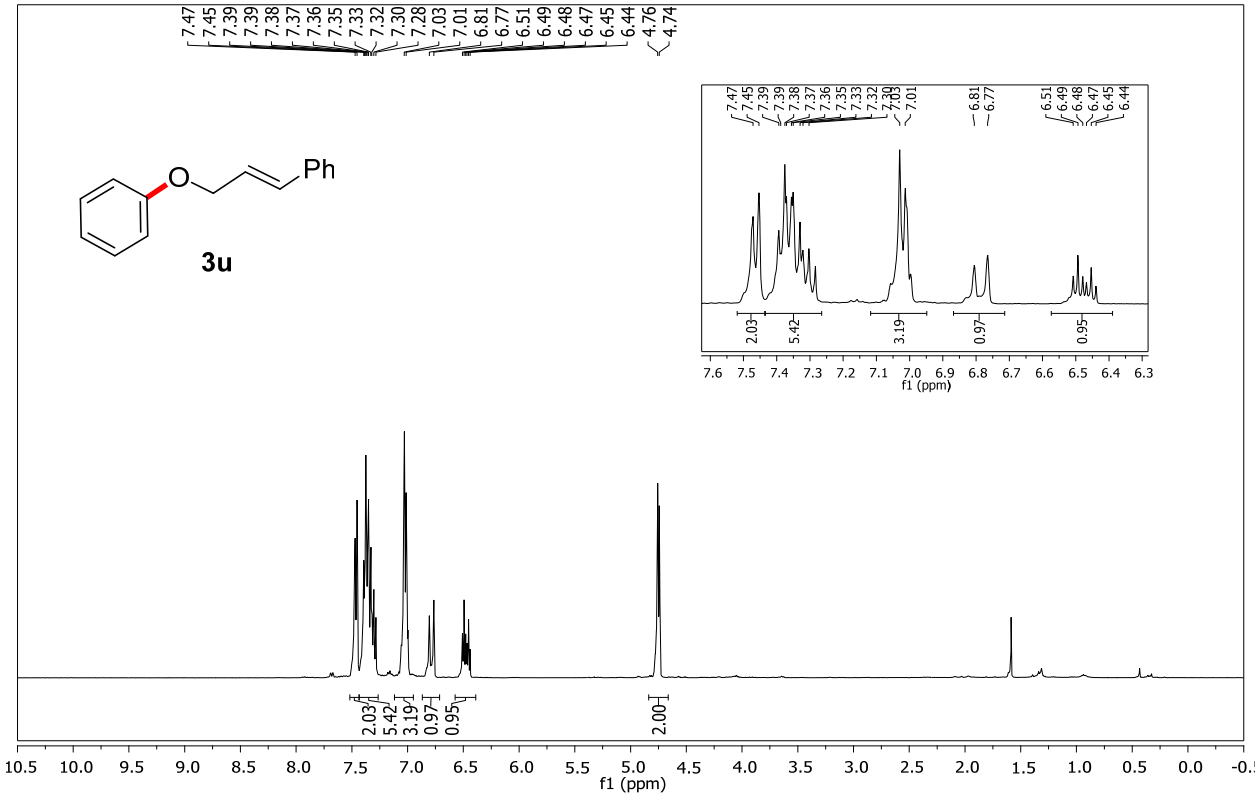


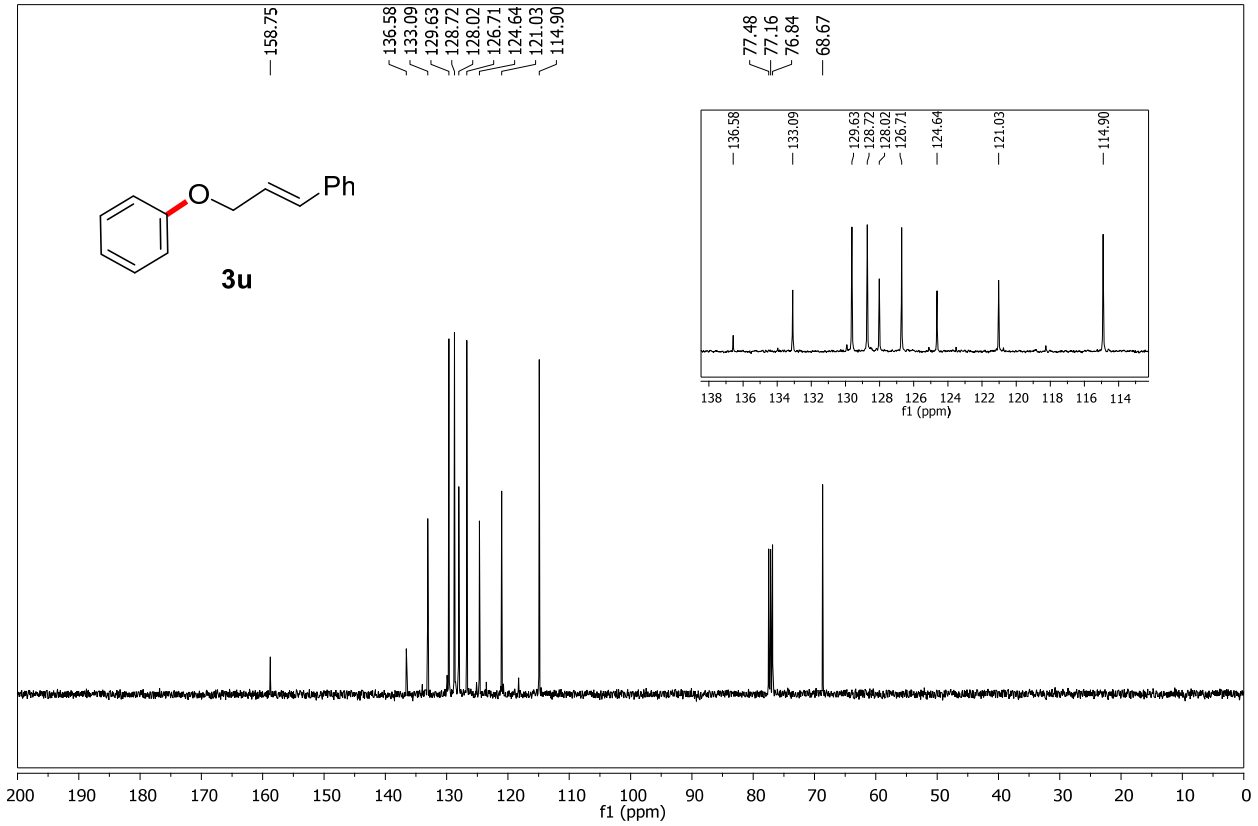
(3-Phenoxyprop-1-yn-1-yl)benzene (3t)



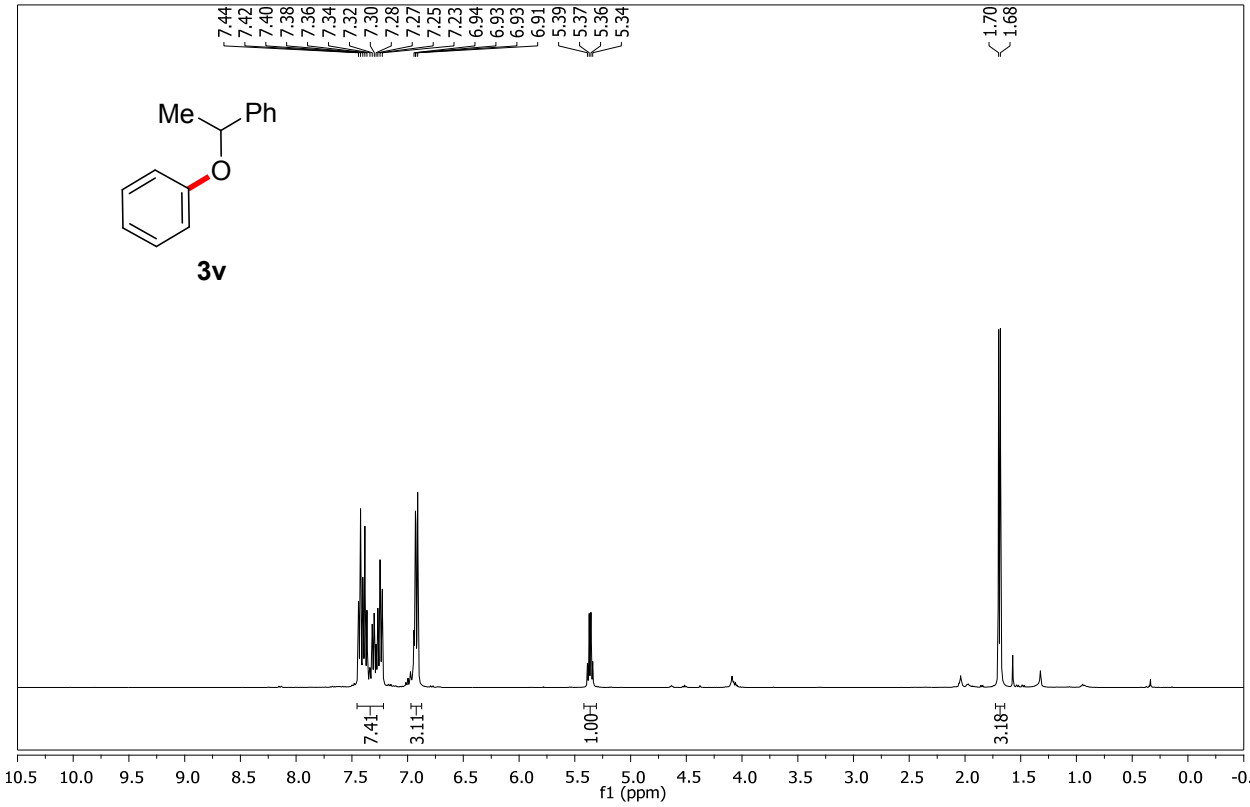


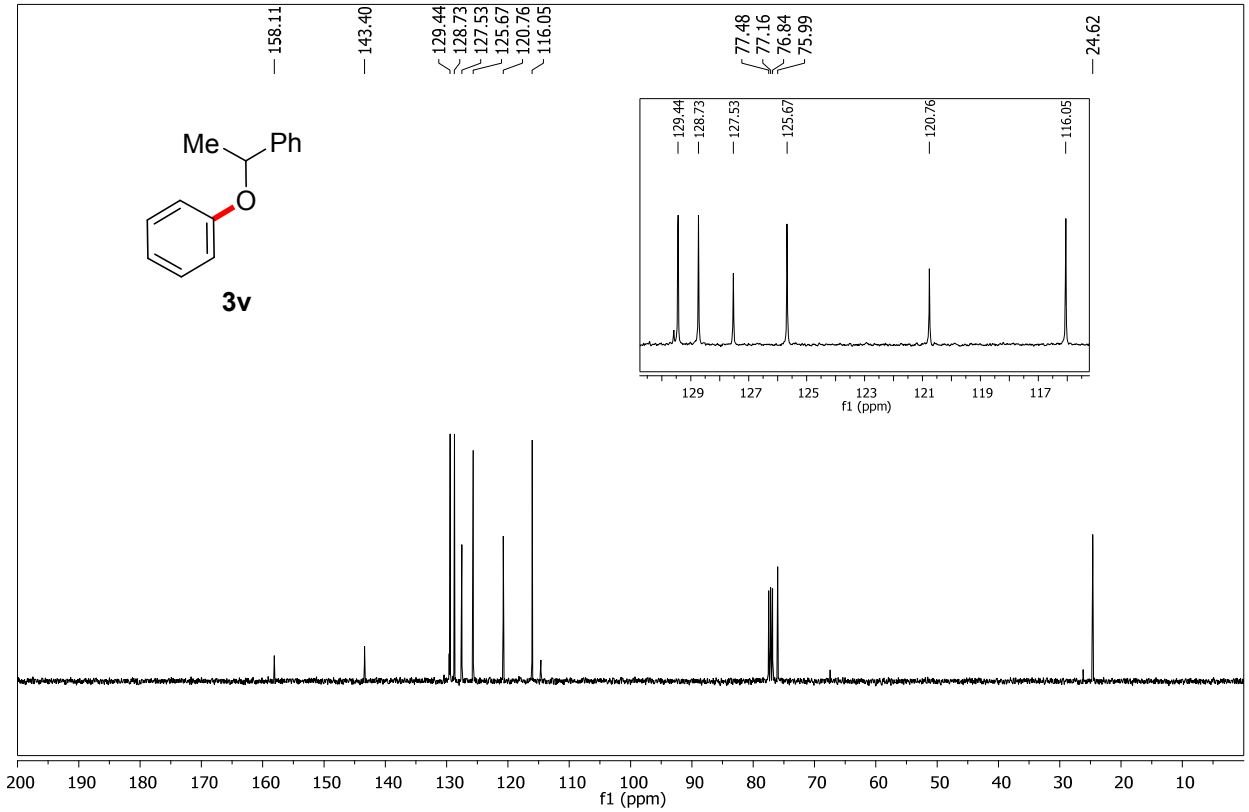
(Cinnamyloxy)benzene (3u)



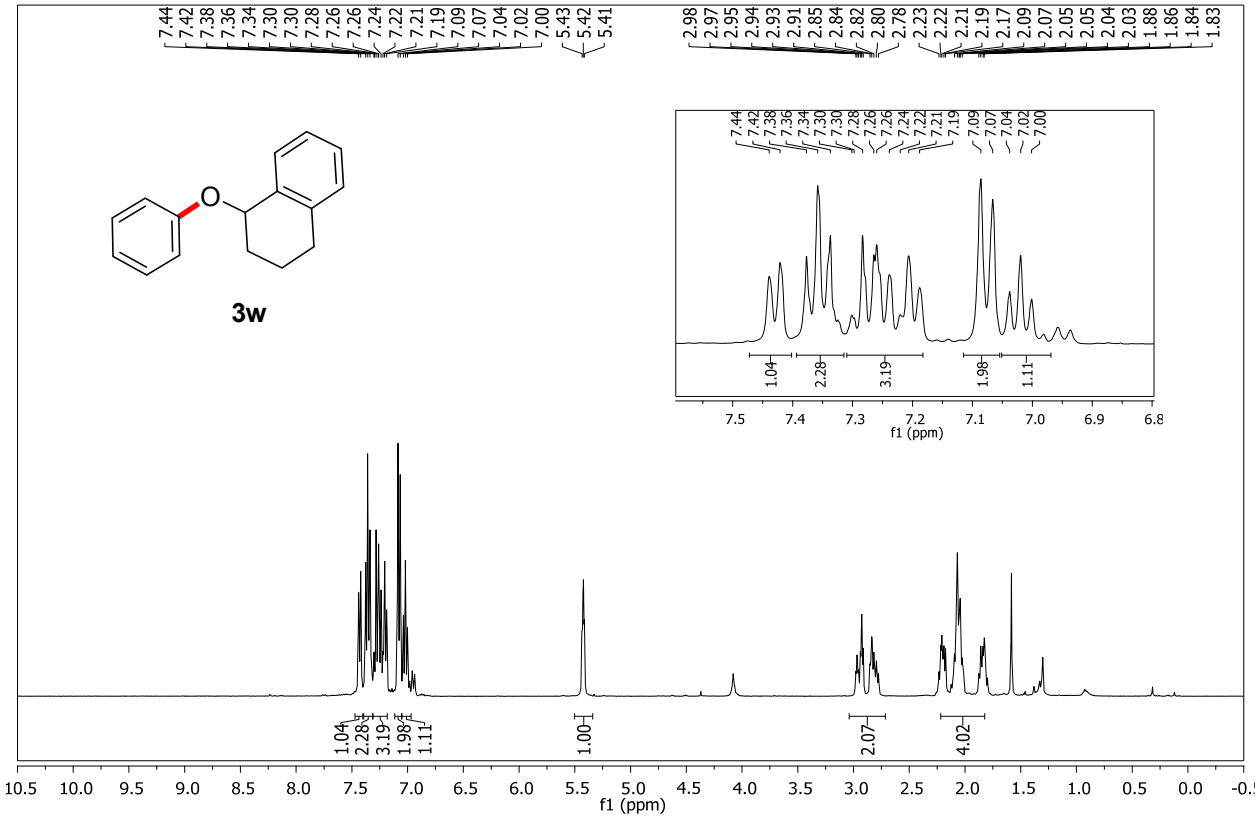


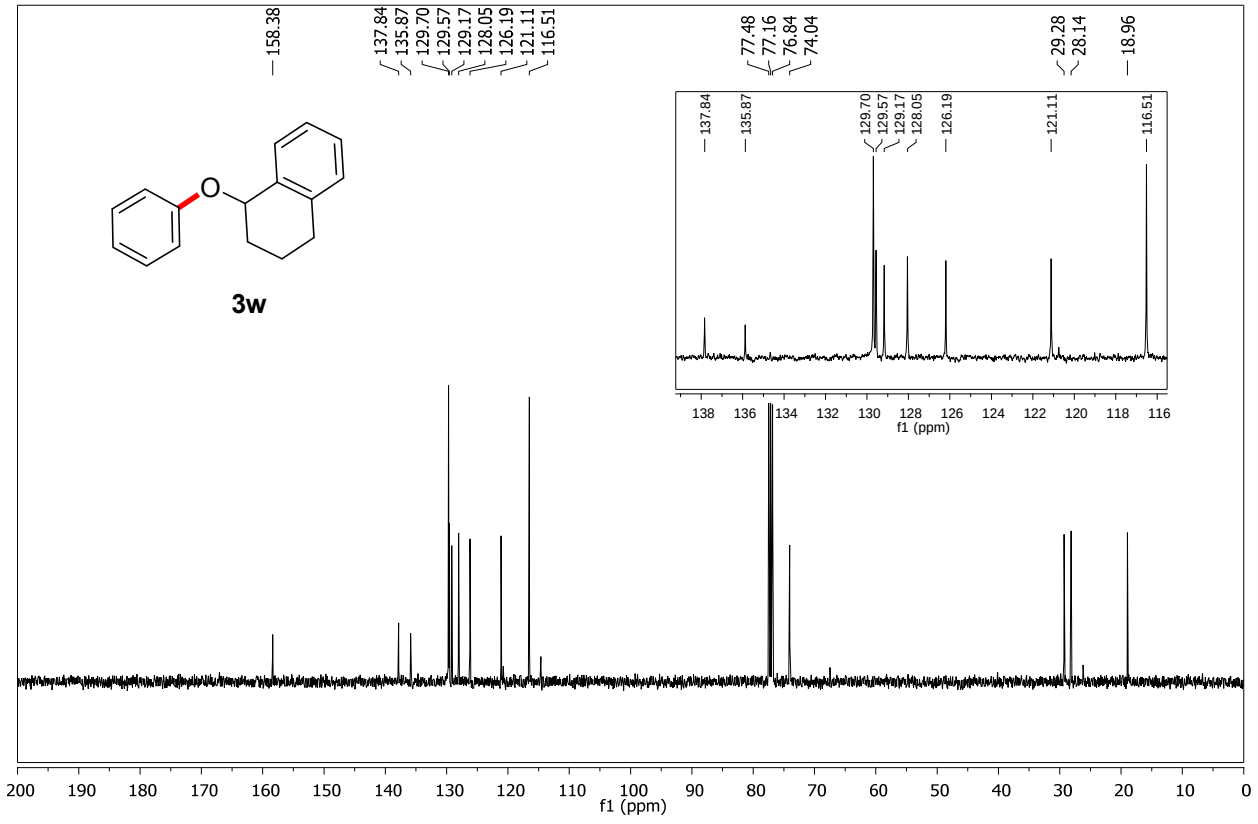
(1-Phenoxyethyl)benzene (3v)



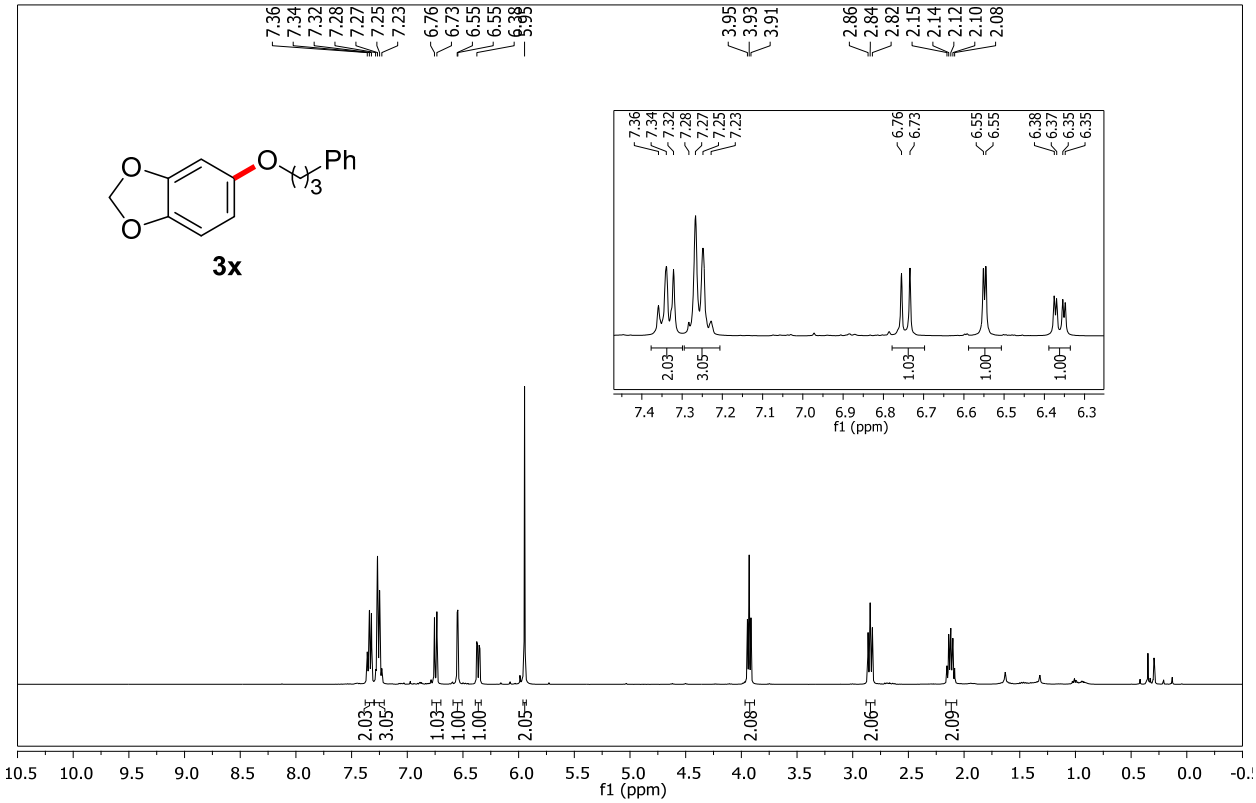


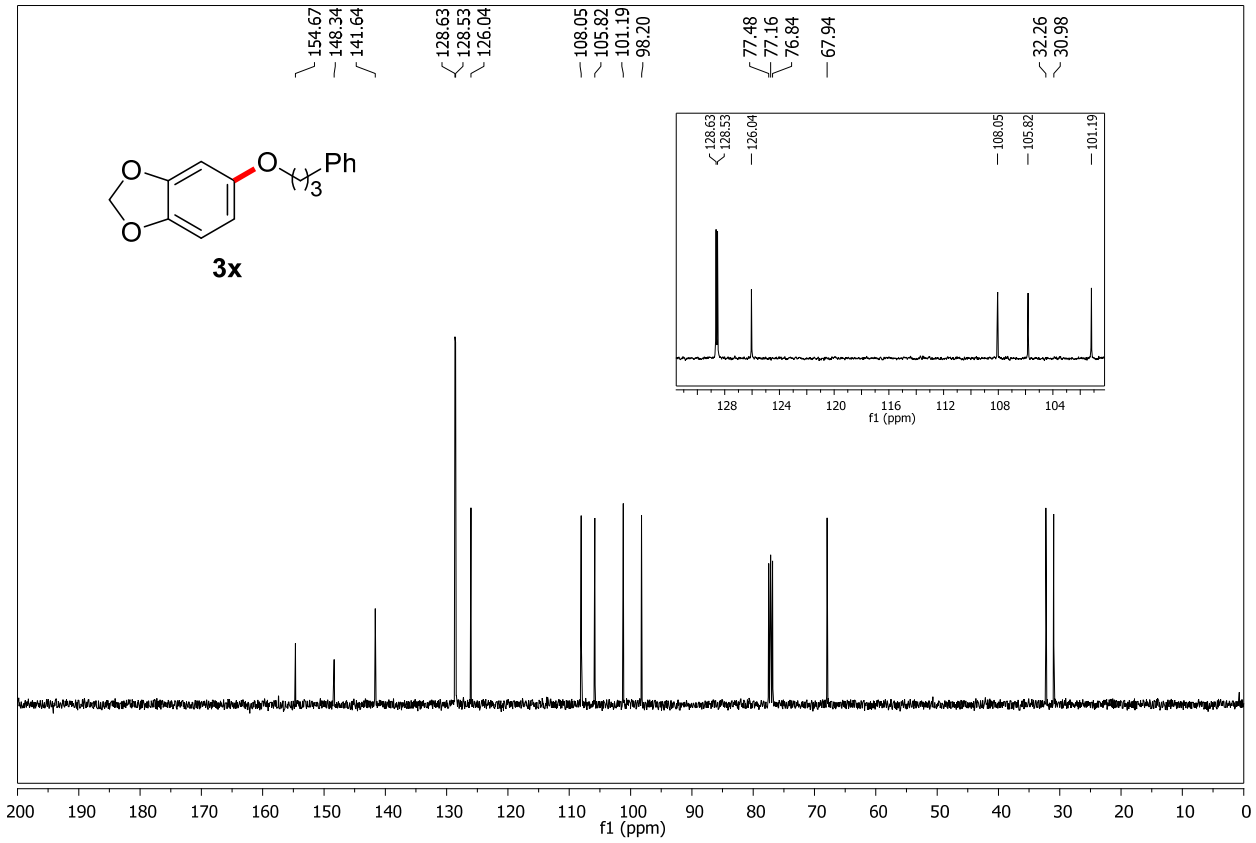
1-Phenoxy-1,2,3,4-tetrahydronaphthalene (3w)



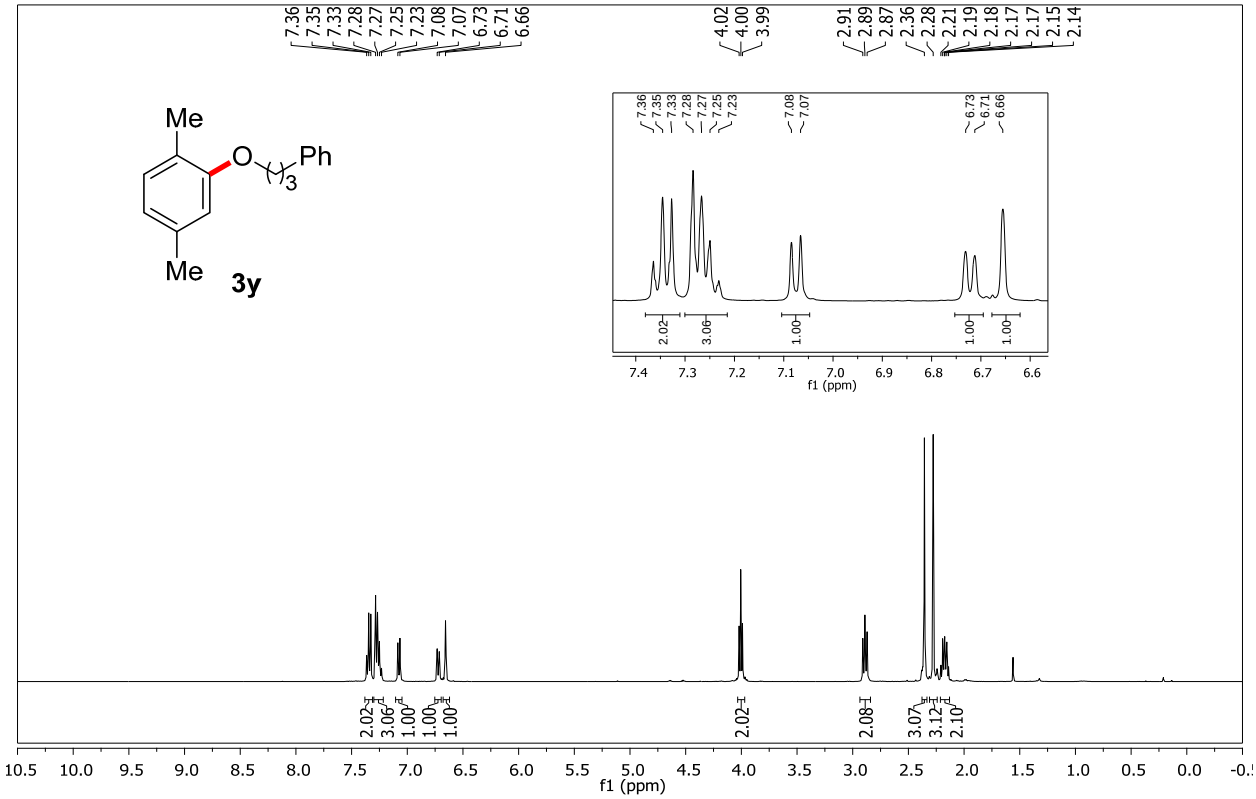


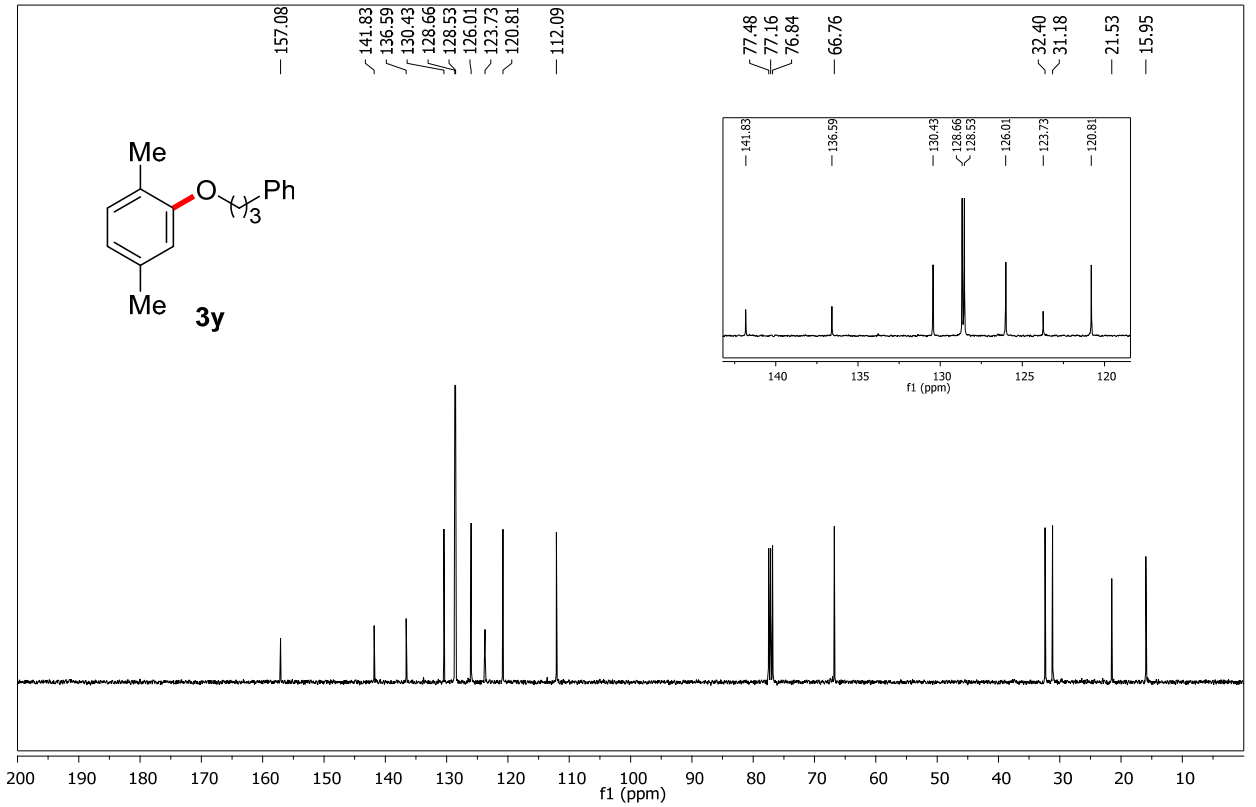
5-(3-Phenylpropoxy)benzo[*d*][1,3]dioxole (3x)



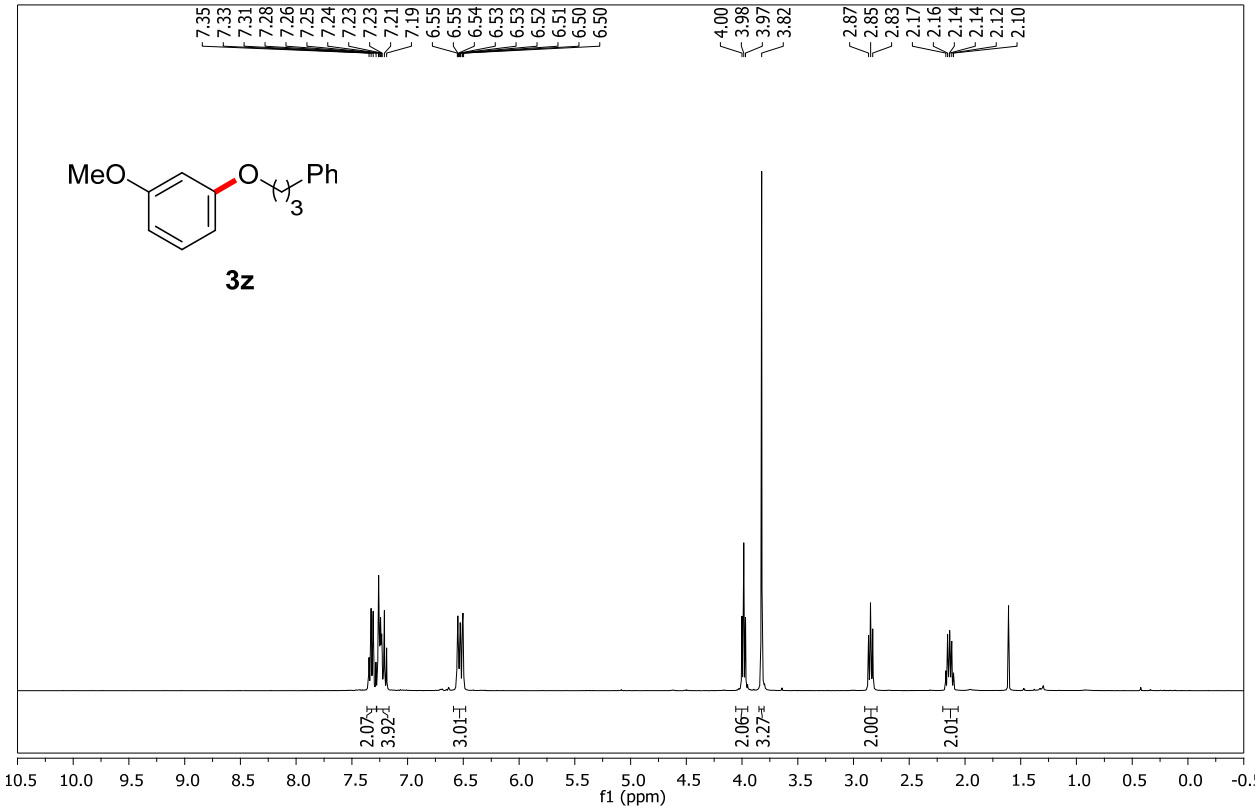


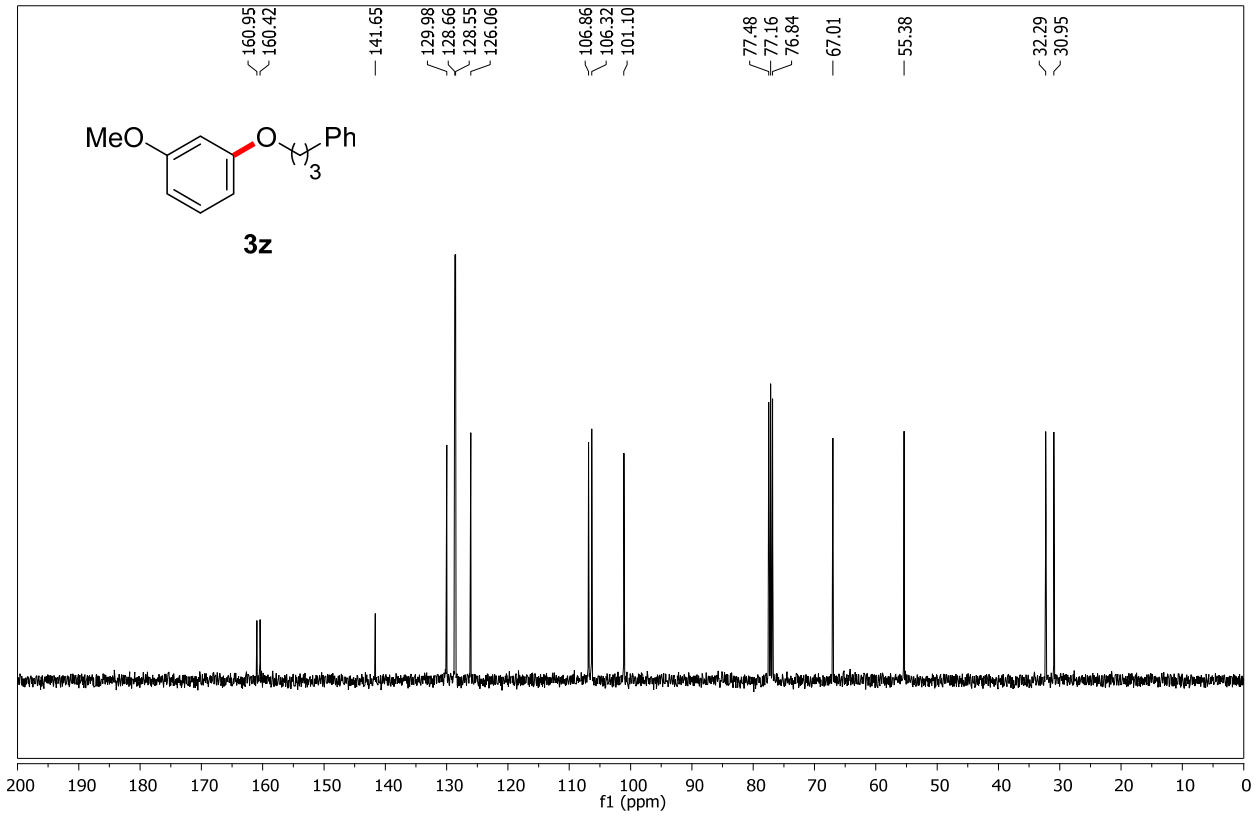
1,4-Dimethyl-2-(3-phenylpropoxy)benzene (3y)



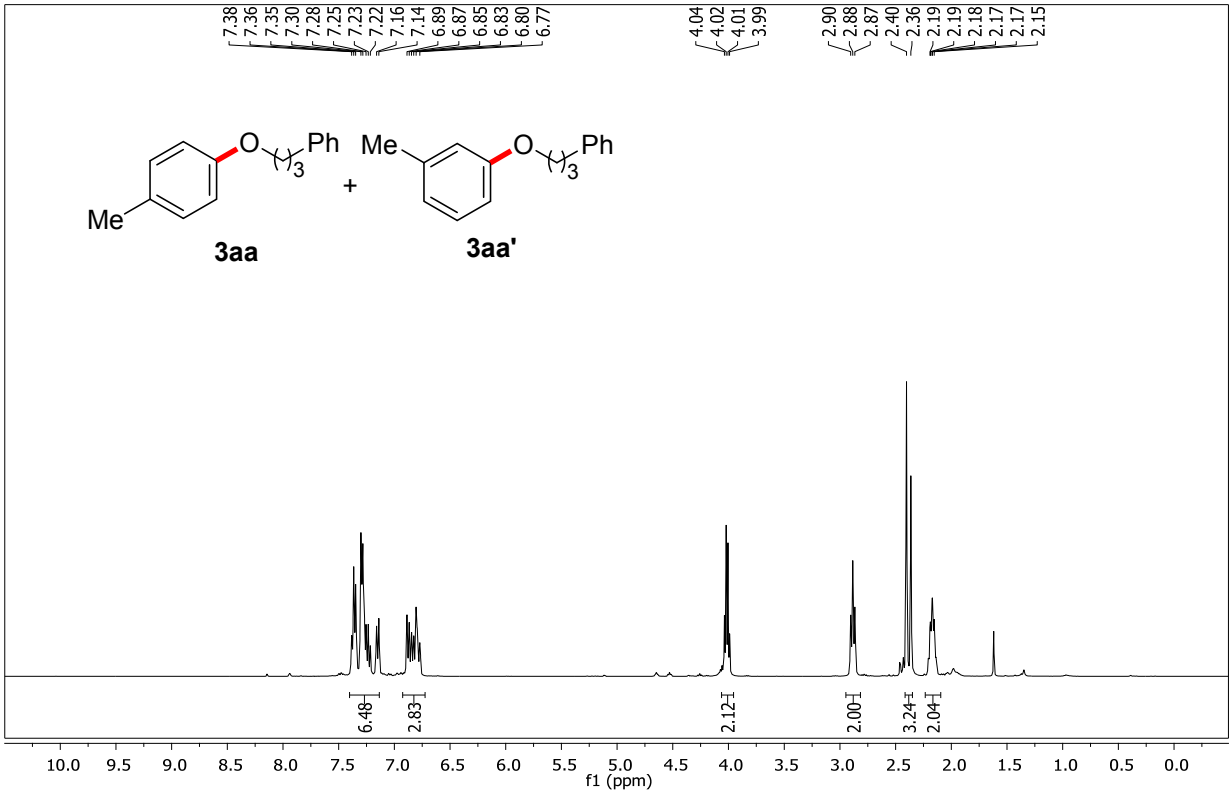


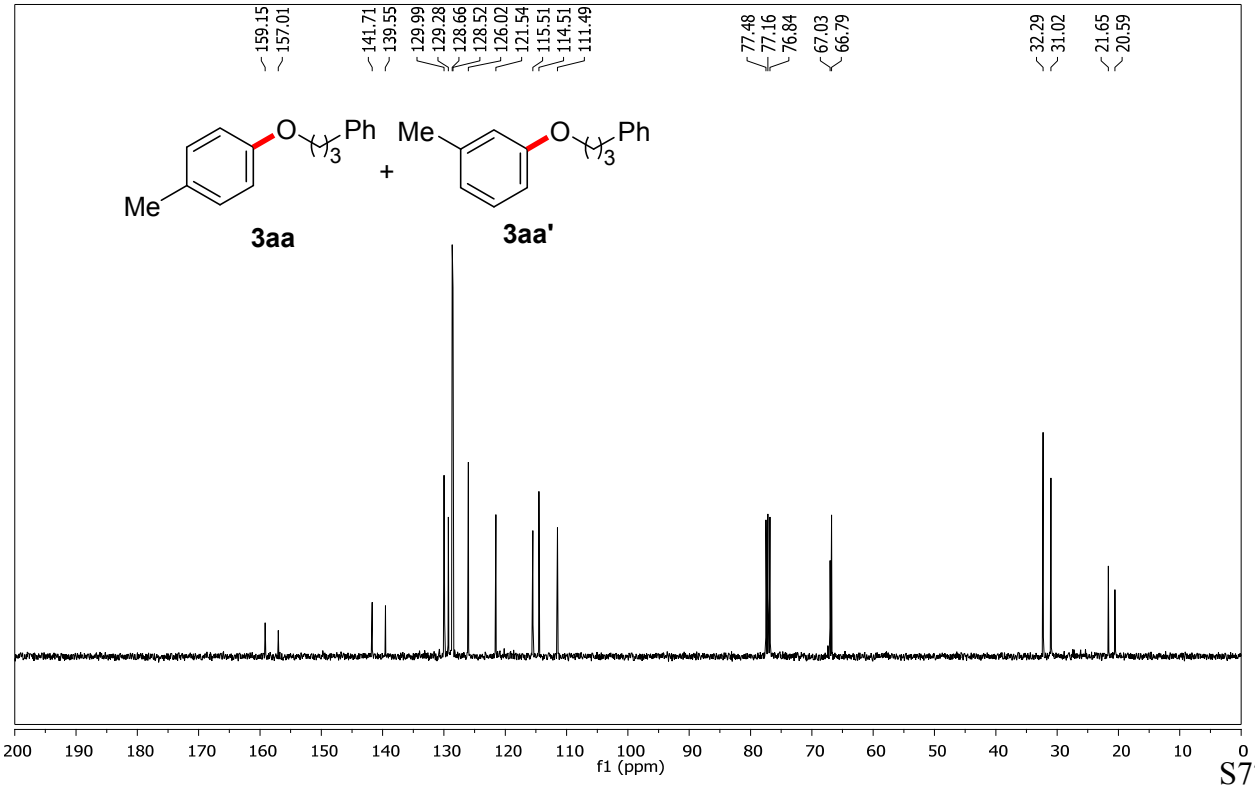
1-Methoxy-3-(3-phenylpropoxy)benzene (3z)



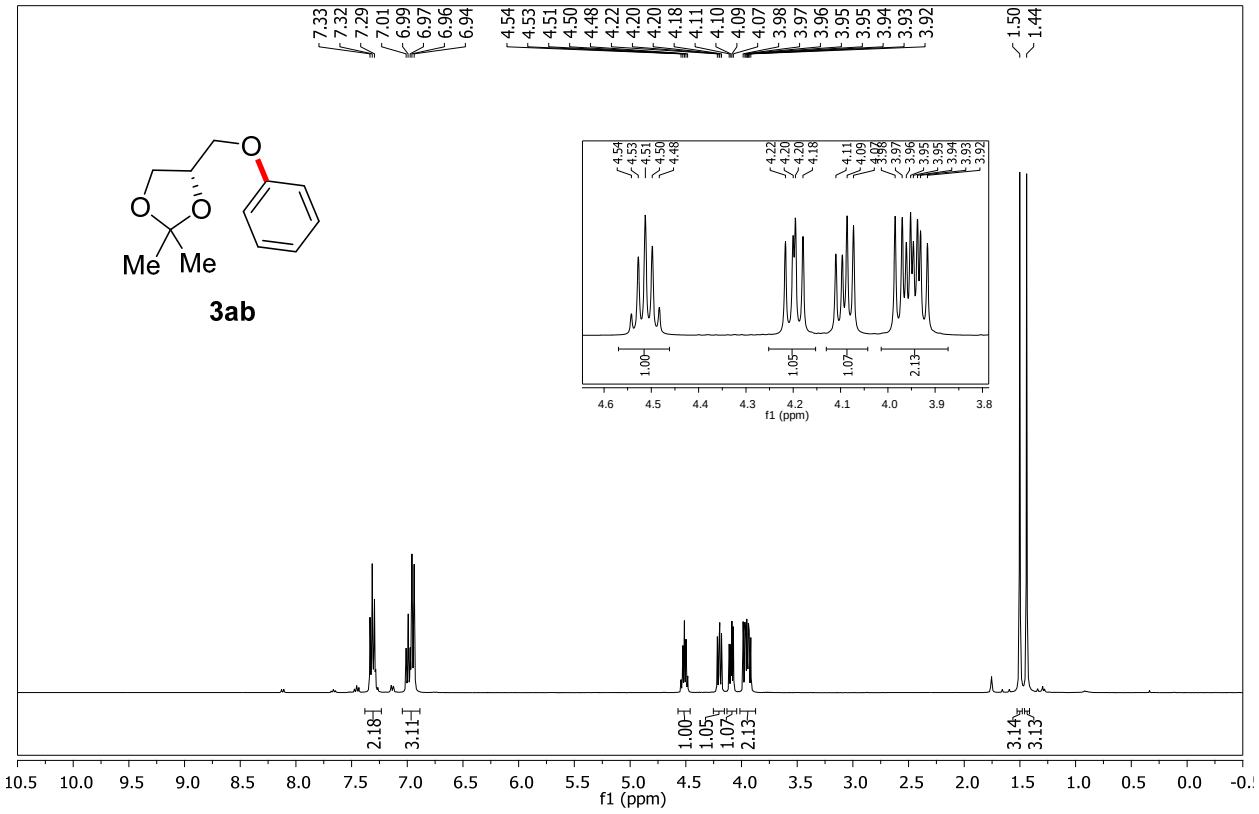


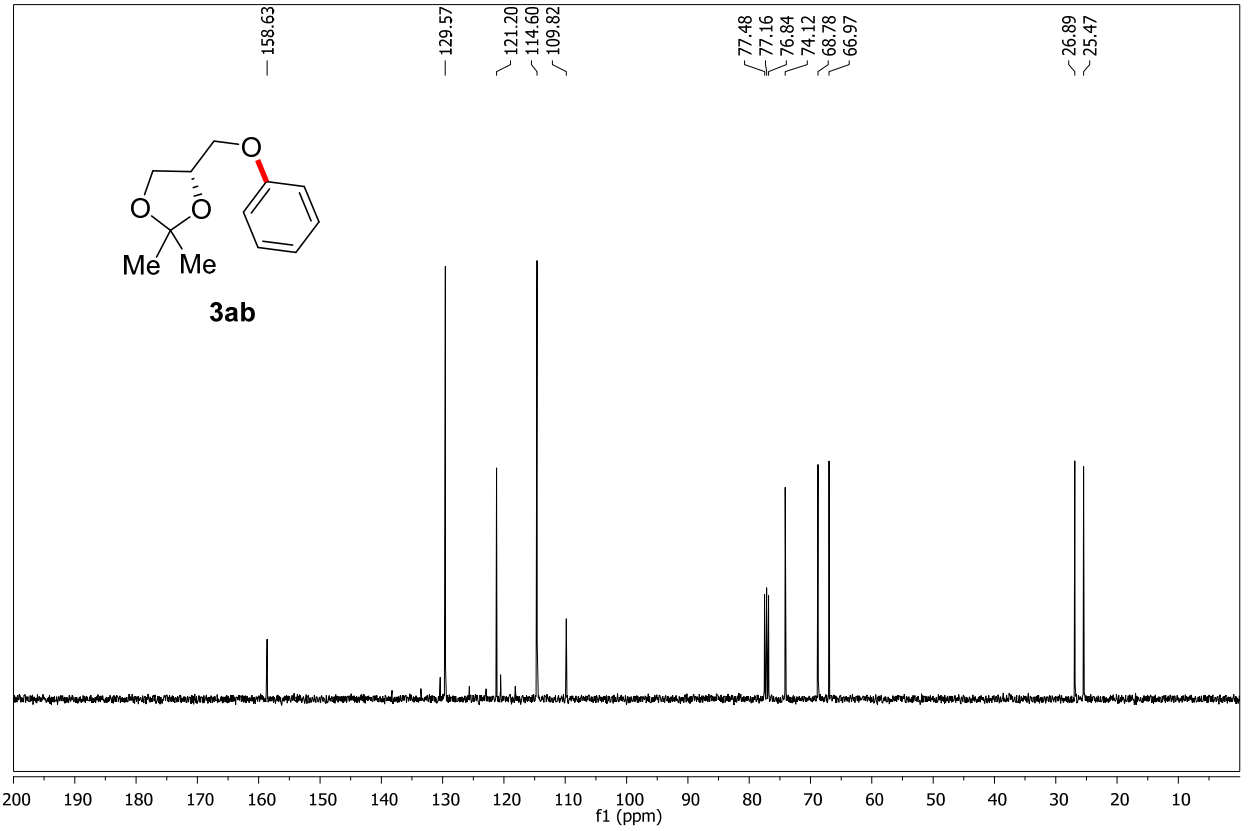
1-Methyl-4-(3-phenylpropoxy)benzene (3aa) and 1-Methyl-3-(3-phenylpropoxy)benzene (3aa')



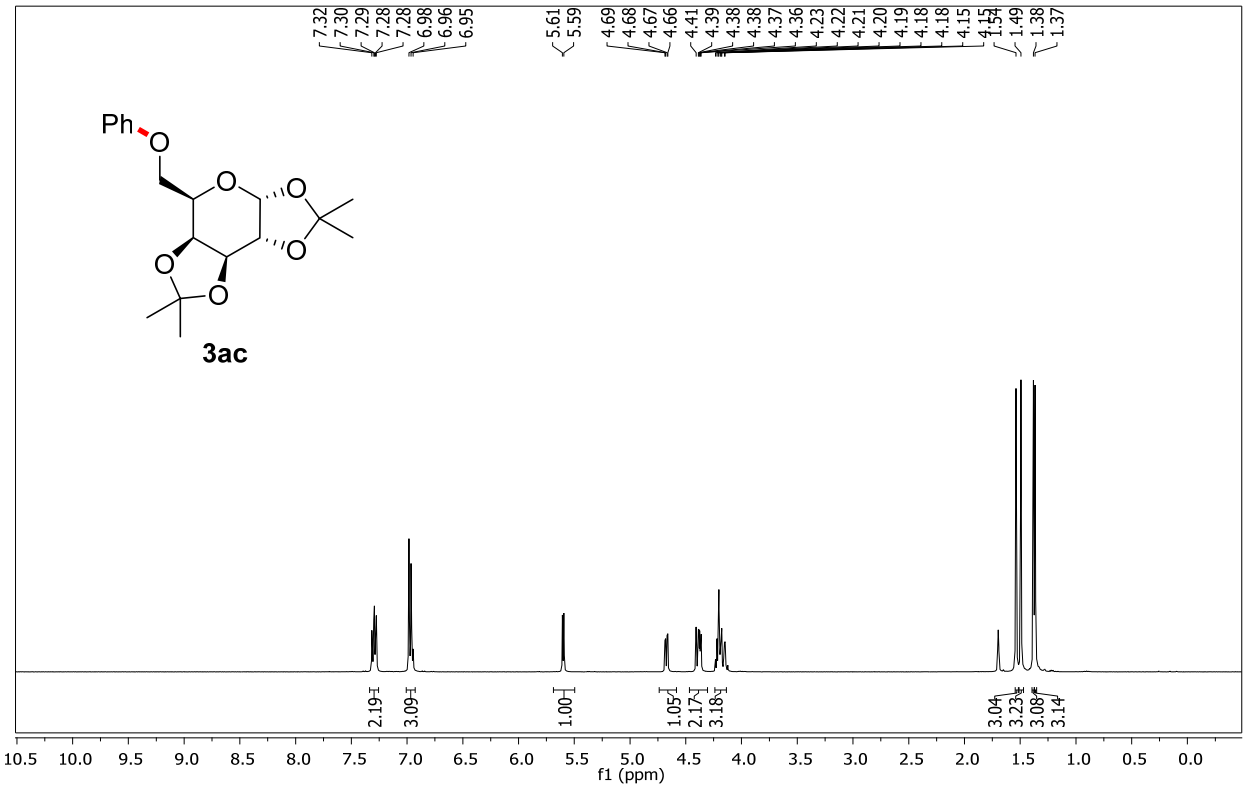


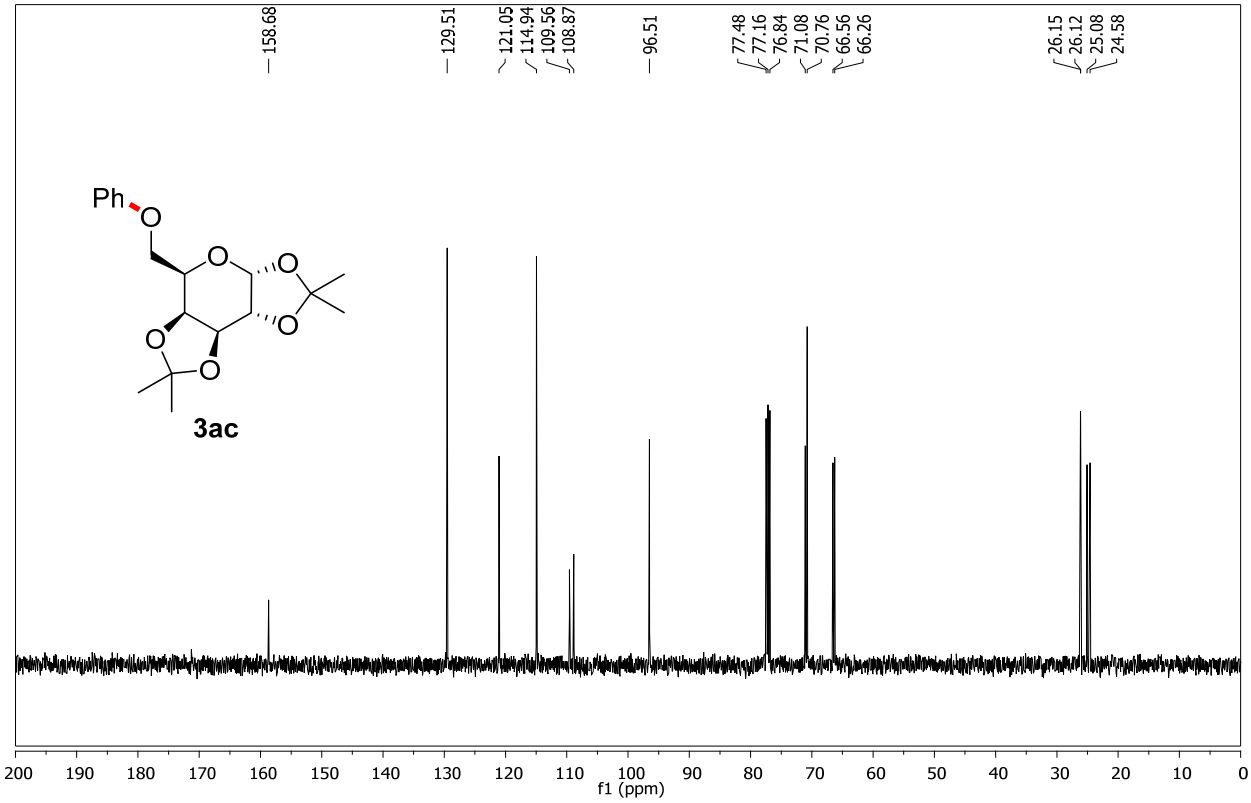
(S)-2,2-Dimethyl-4-(phenoxymethyl)-1,3-dioxolane (3ab)



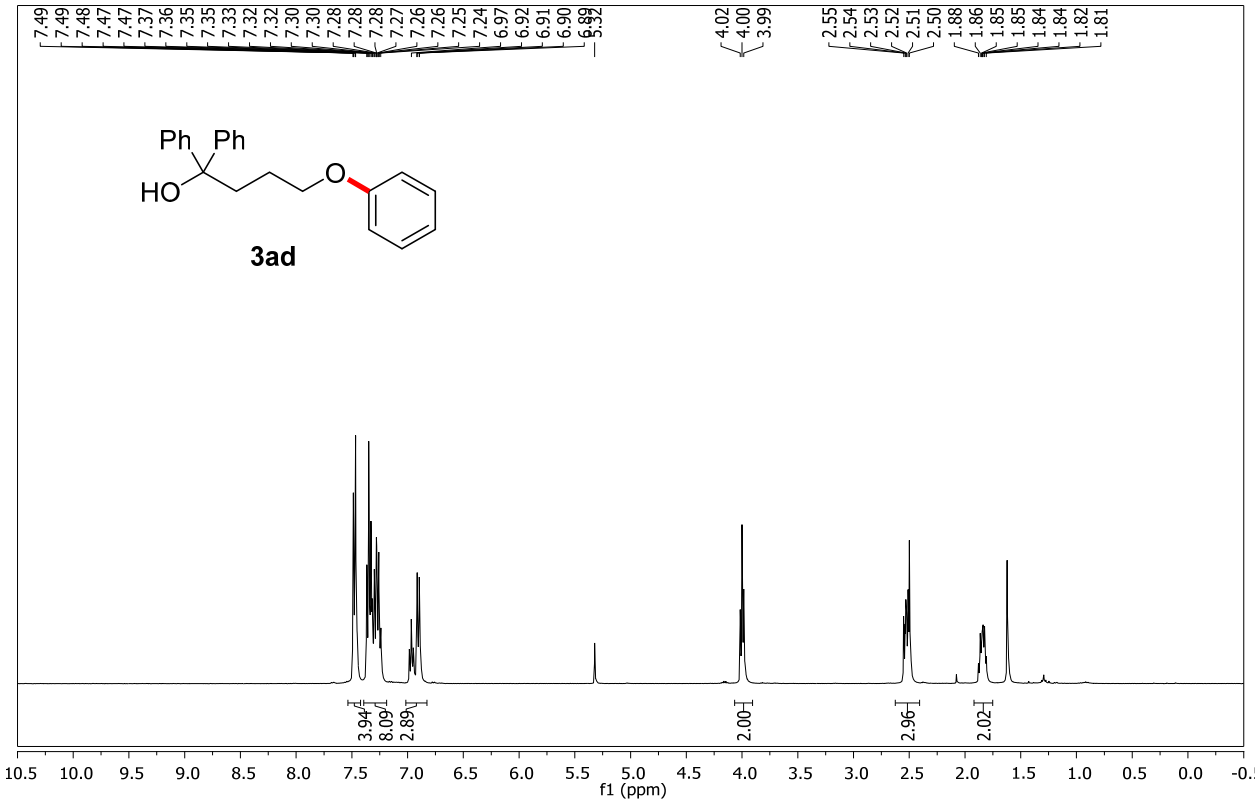


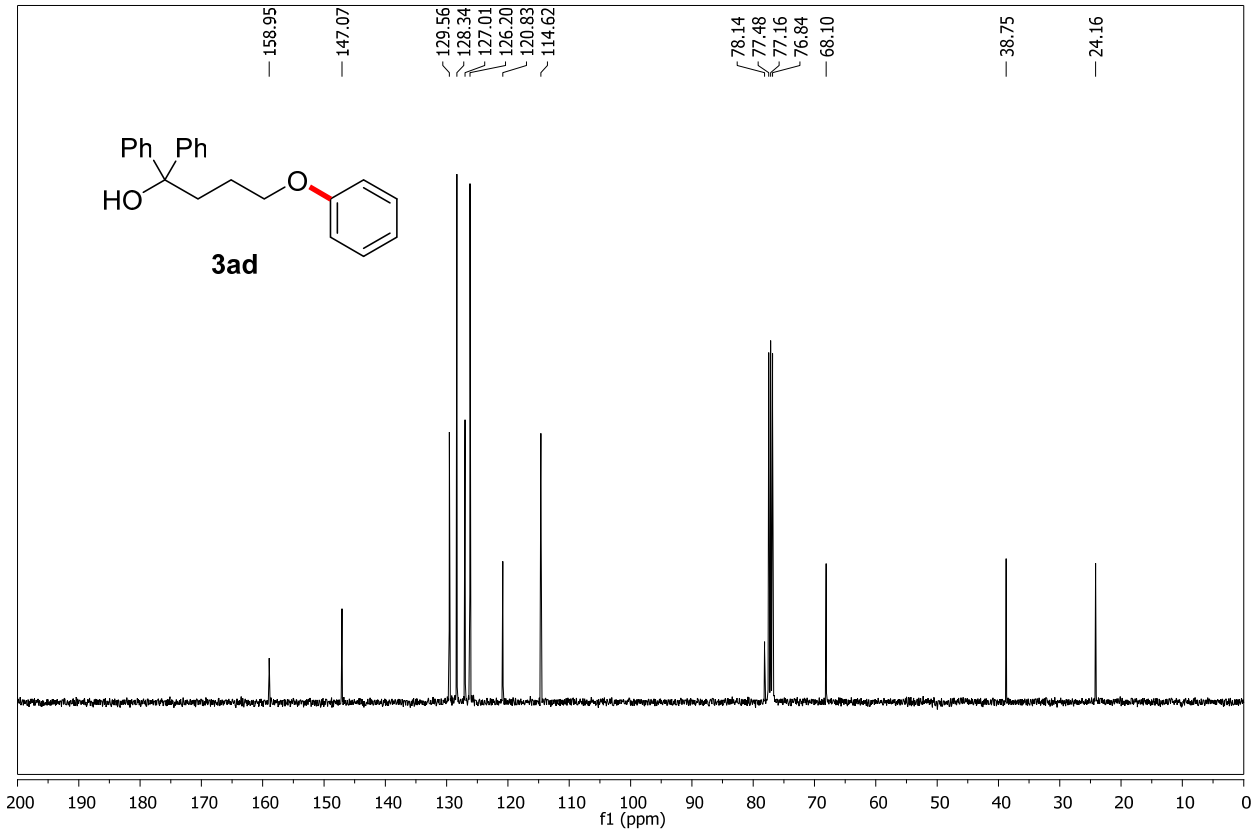
(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyl-5-(phenoxymethyl)tetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3ac)



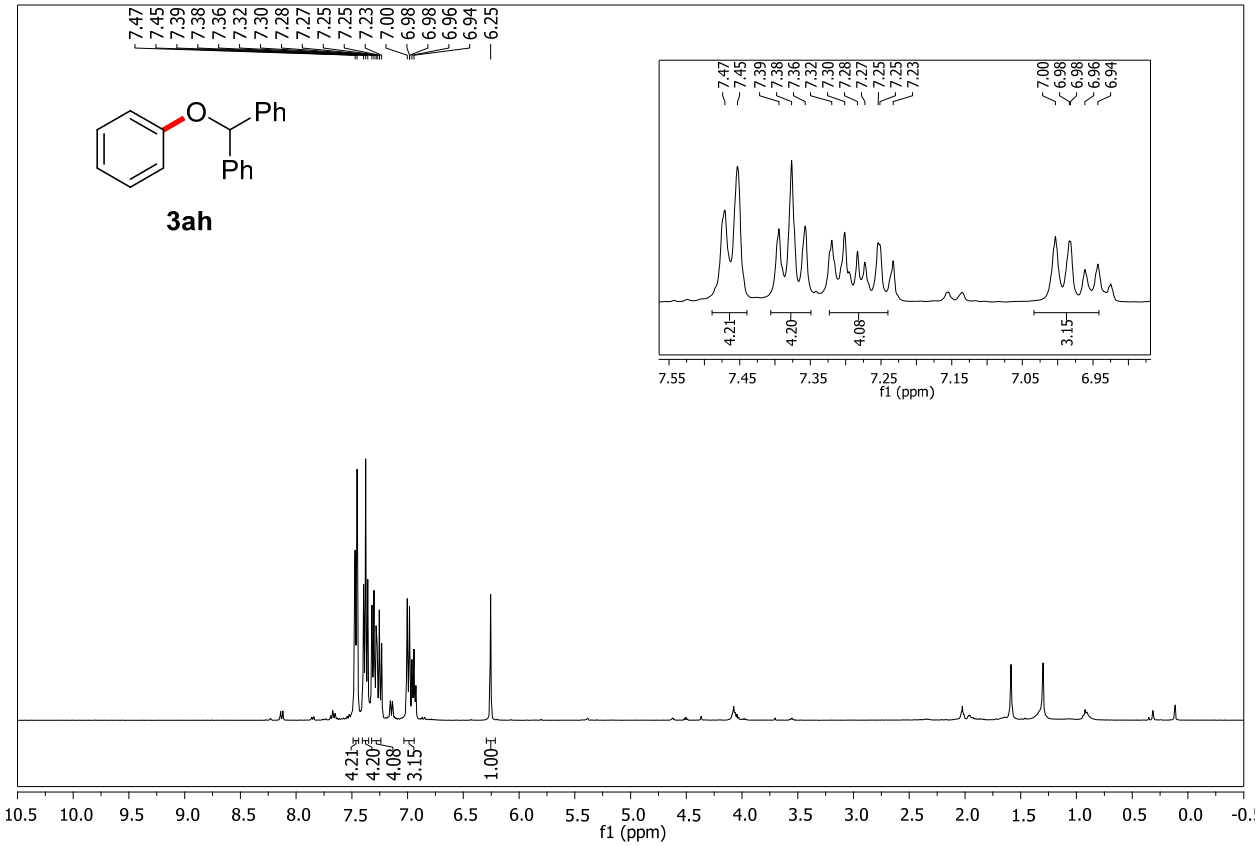


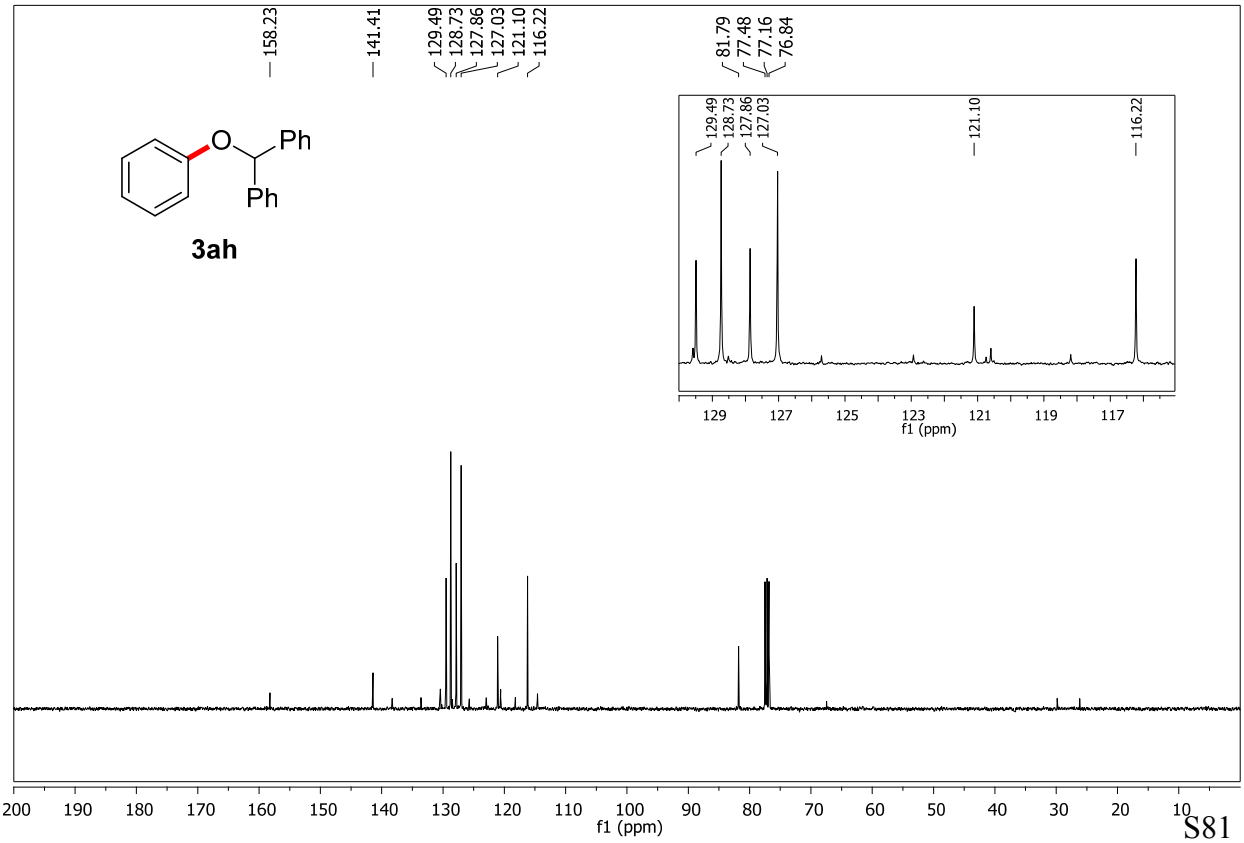
4-Phenoxy-1,1-diphenylbutan-1-ol (3ad)





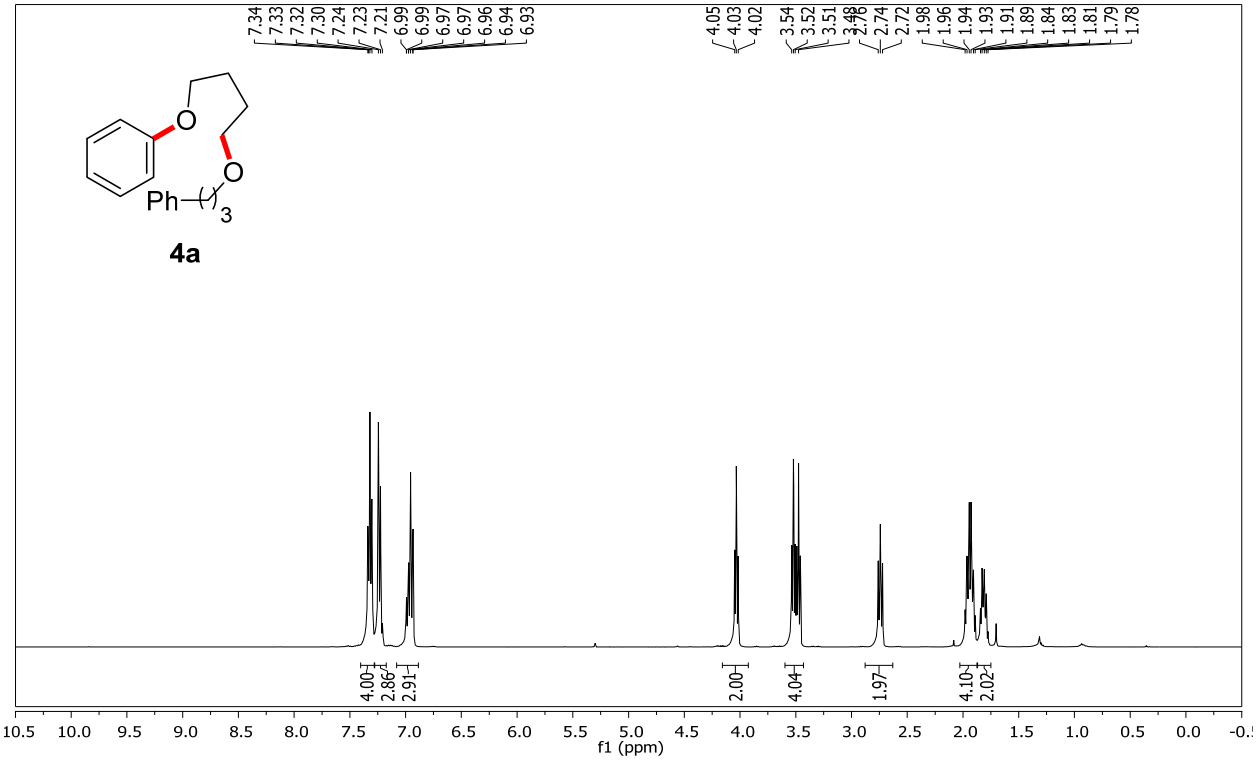
(Phenoxymethylene)dibenzene (3ah)

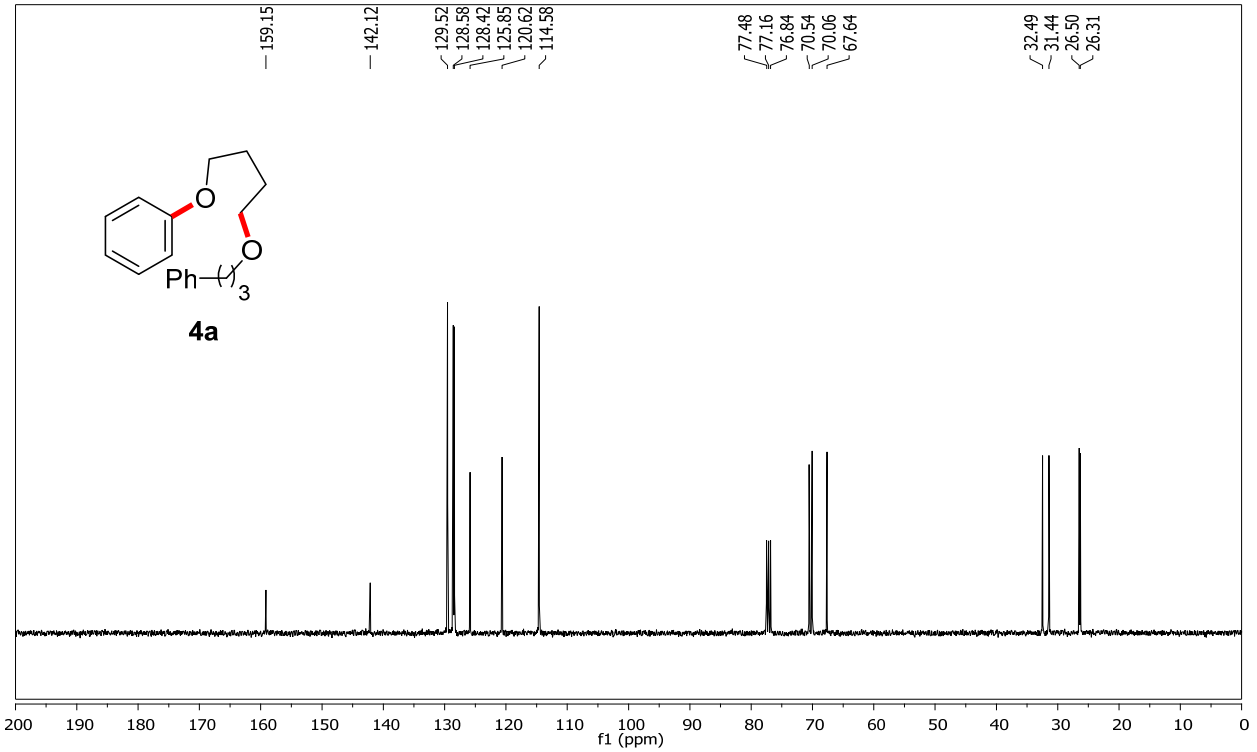




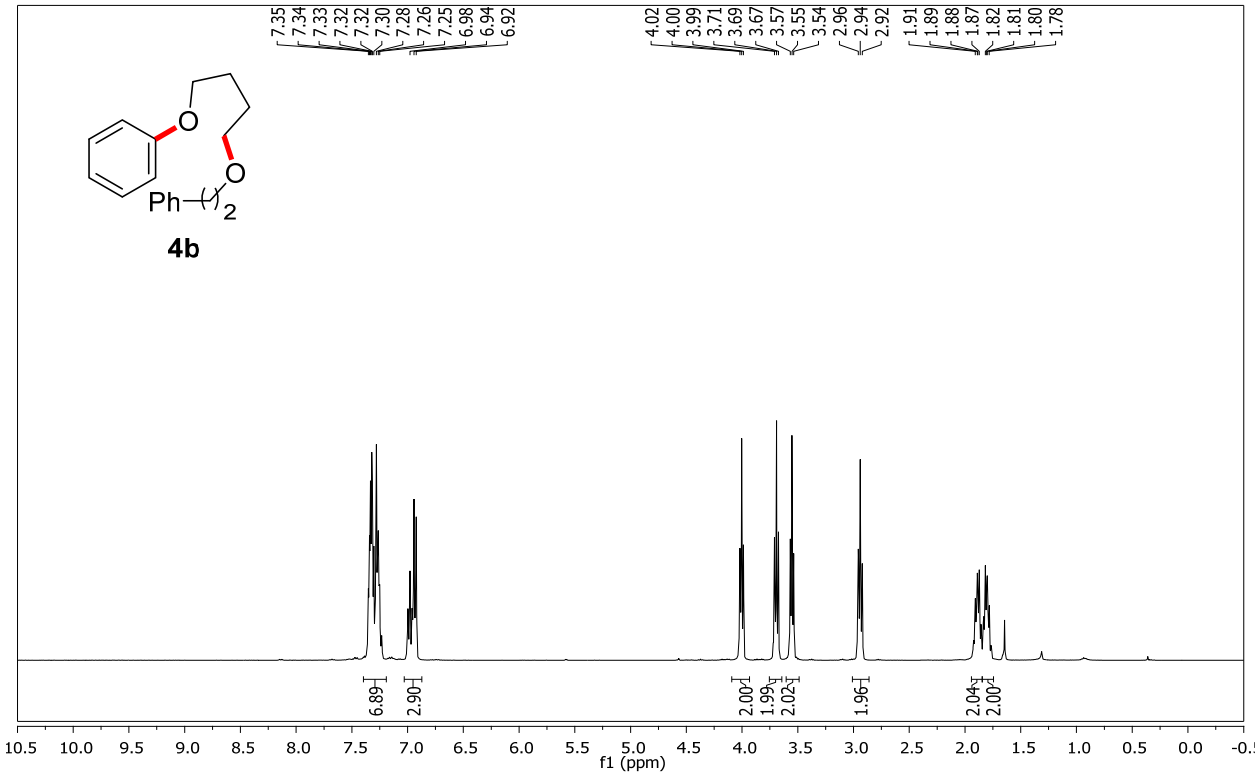
11. ^{1}H and ^{13}C NMR Spectra of 4-(Alkoxy)butoxy)arenes

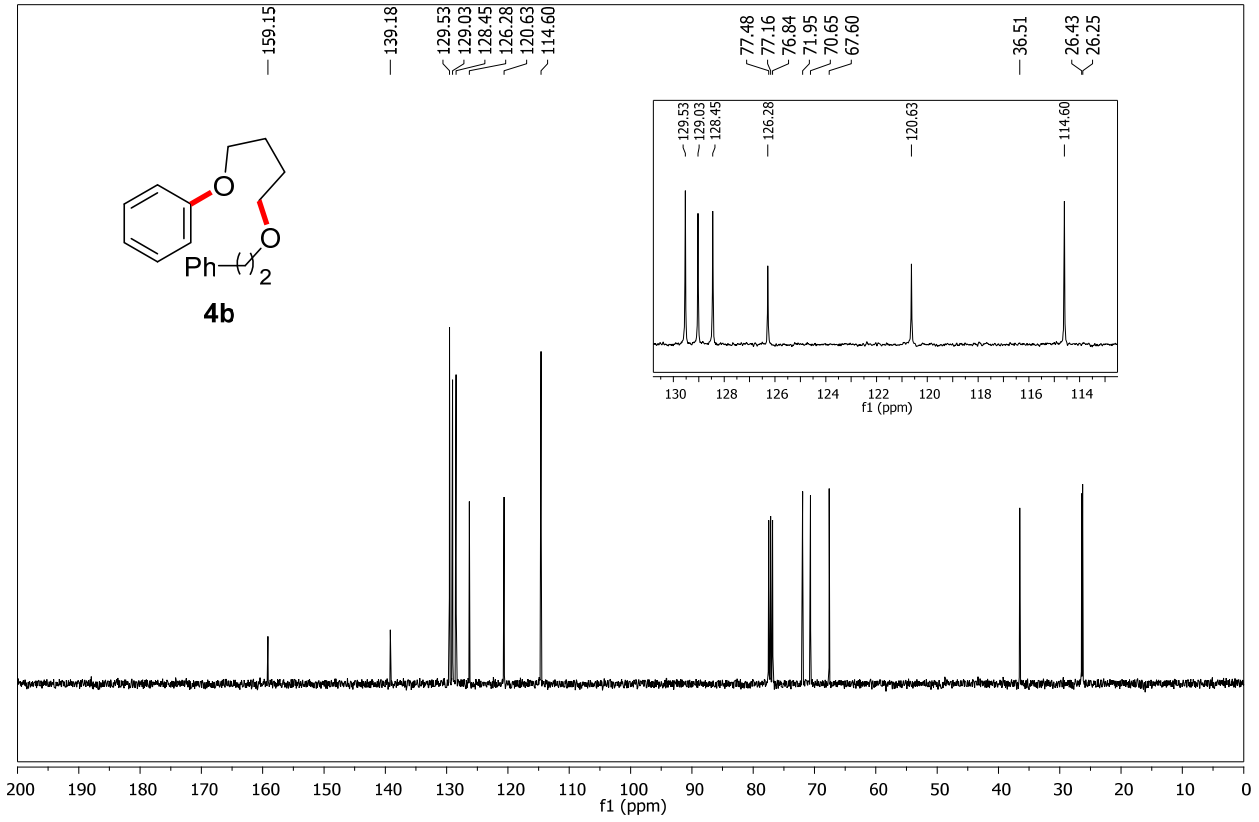
(3-(4-Phenoxybutoxy)propyl)benzene (4a)



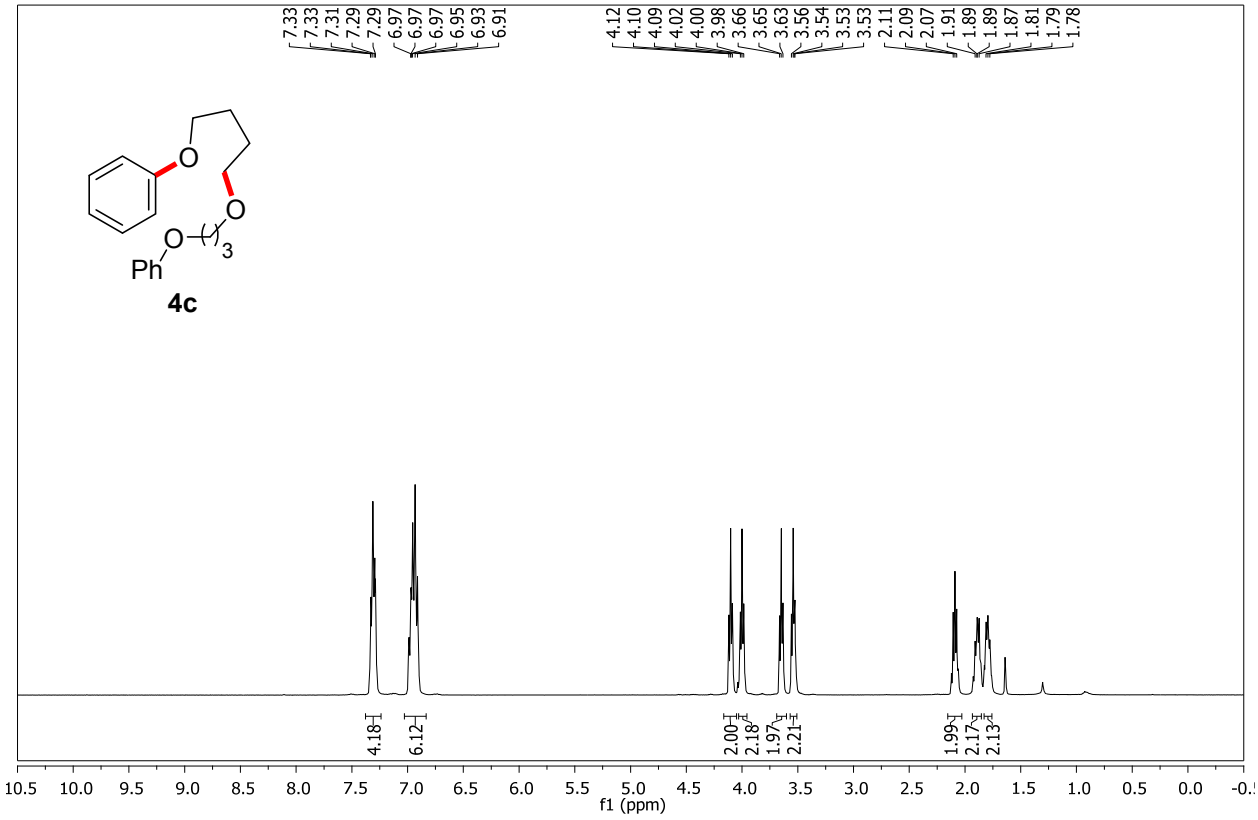


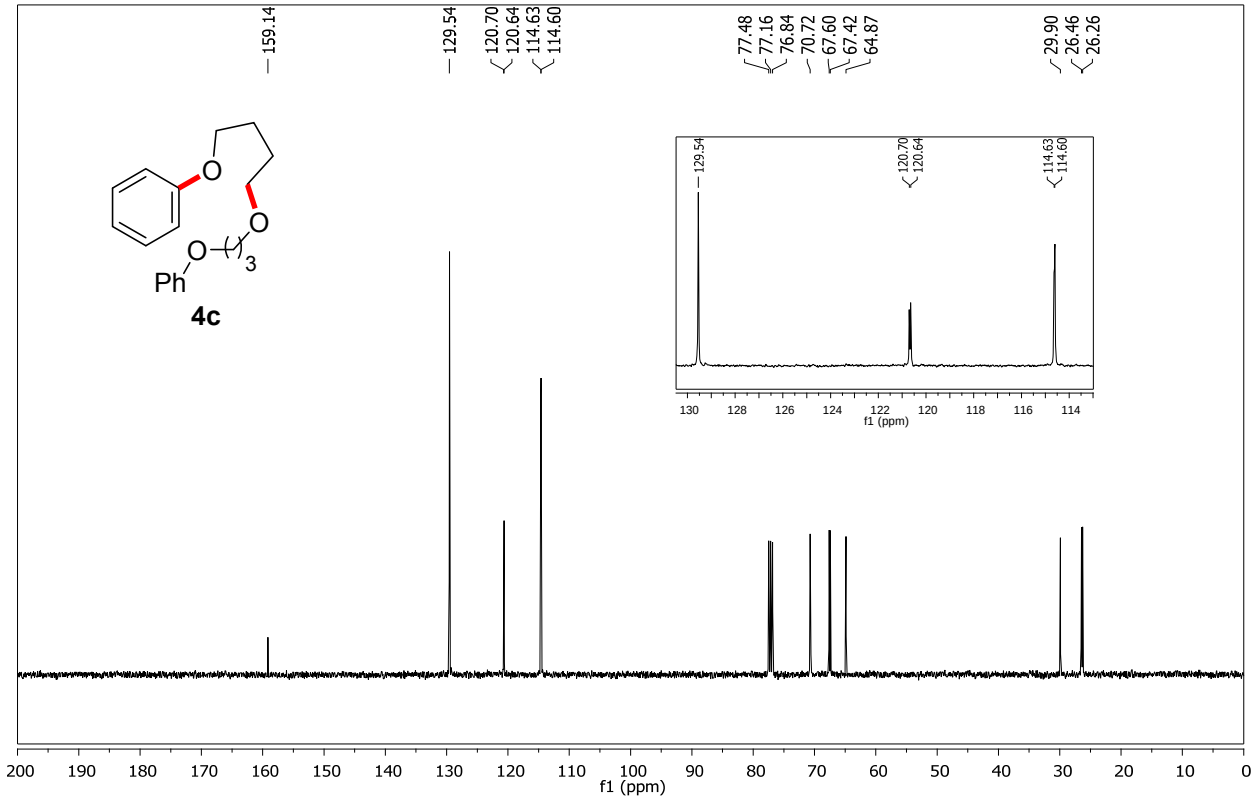
(4-Phenethoxybutoxy)benzene (4b)



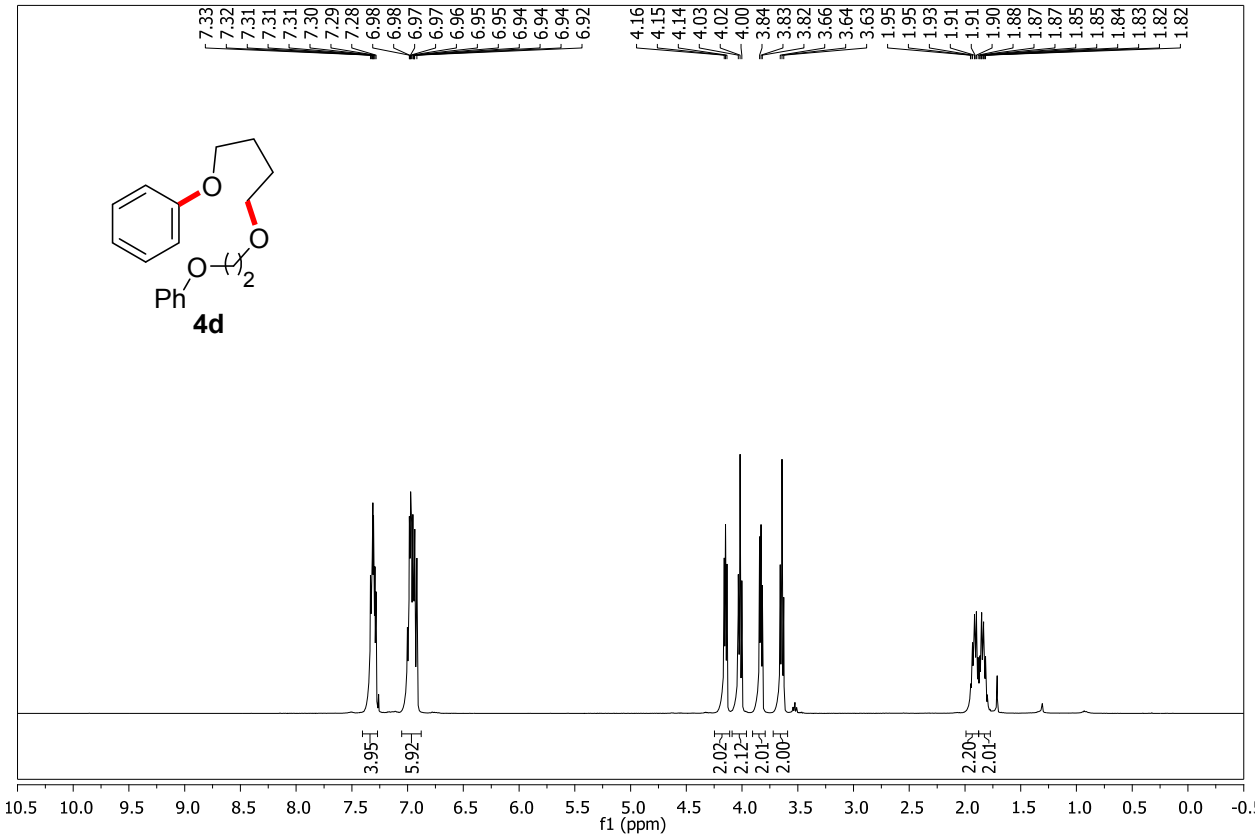


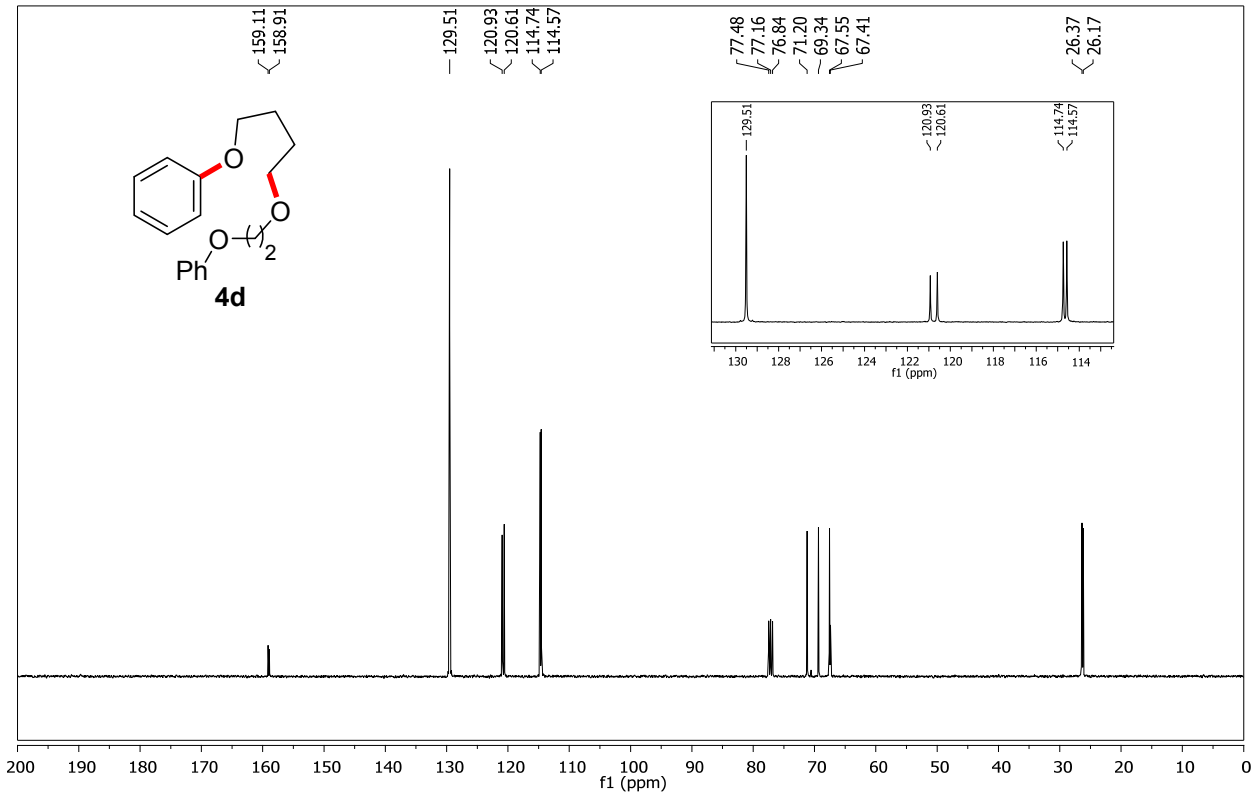
(3-(4-Phenoxybutoxy)propoxy)benzene (4c)



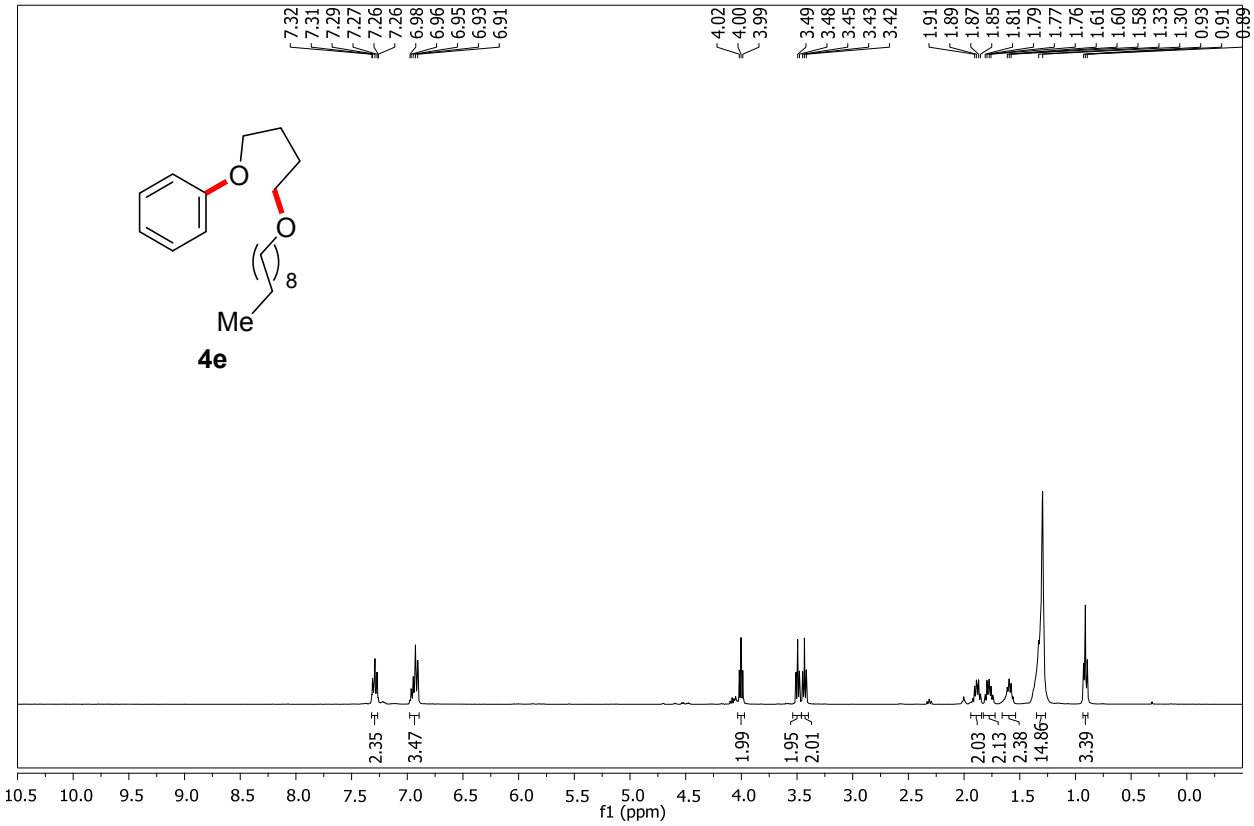


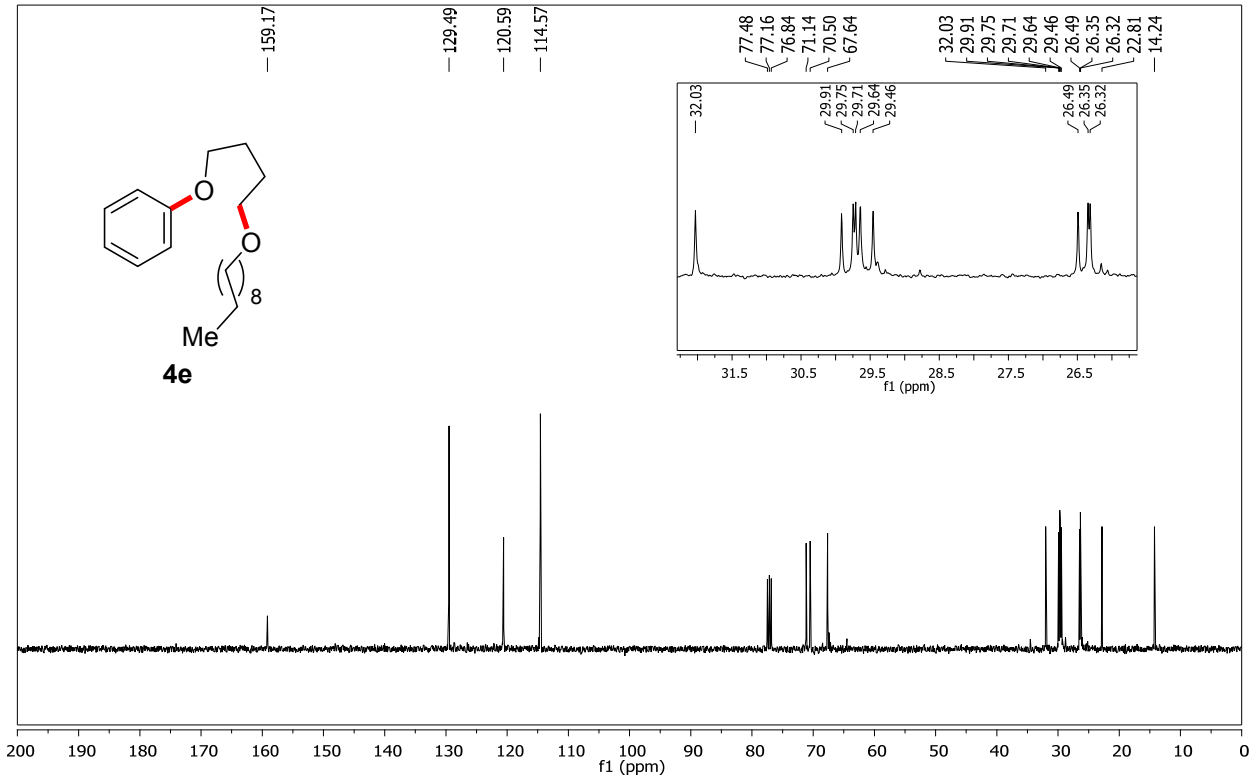
(2-(4-Phenoxybutoxy)ethoxy)benzene (4d)



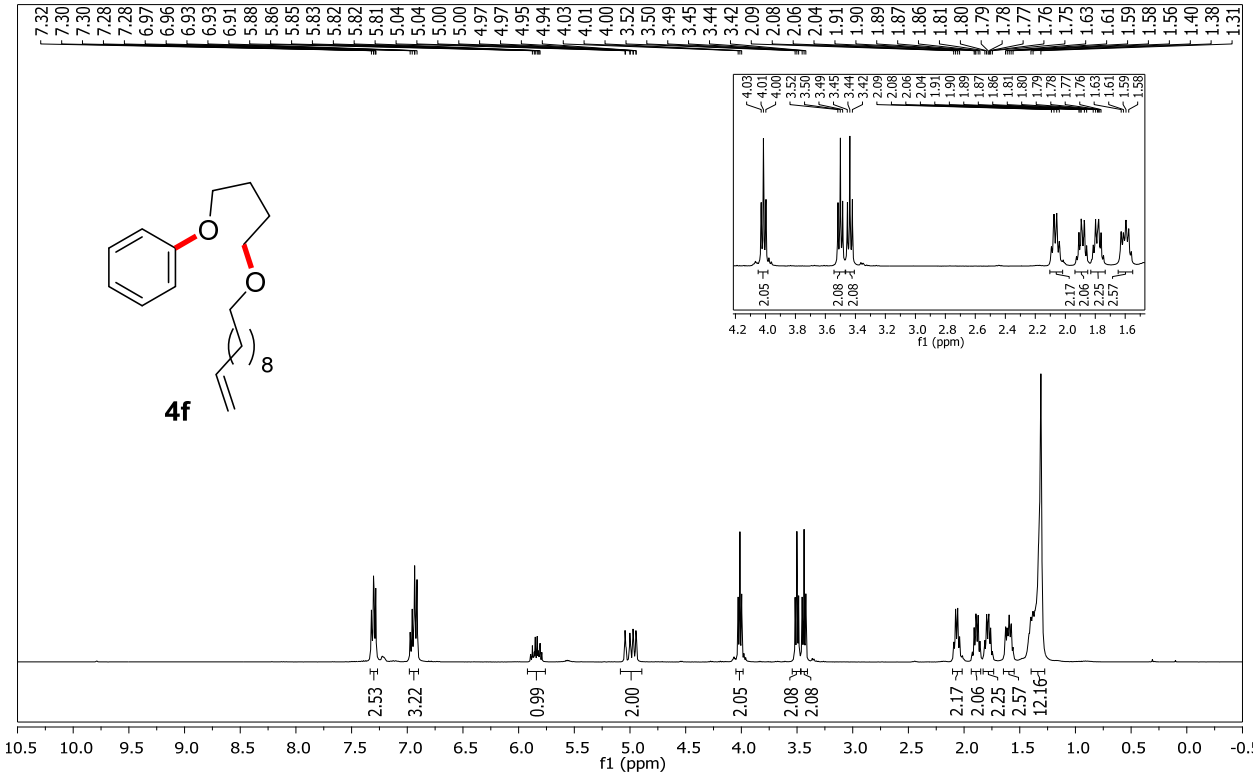


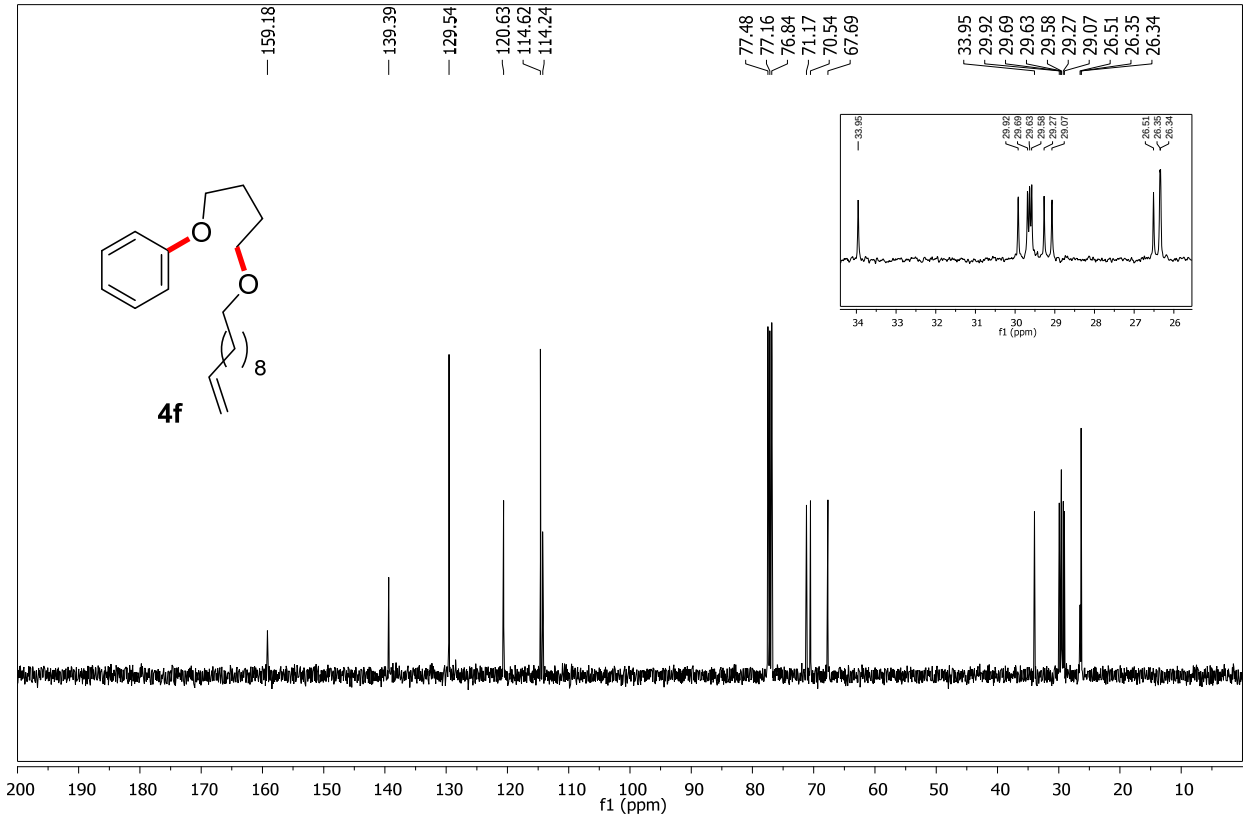
(4-(Decyloxy)butoxy)benzene (4e)



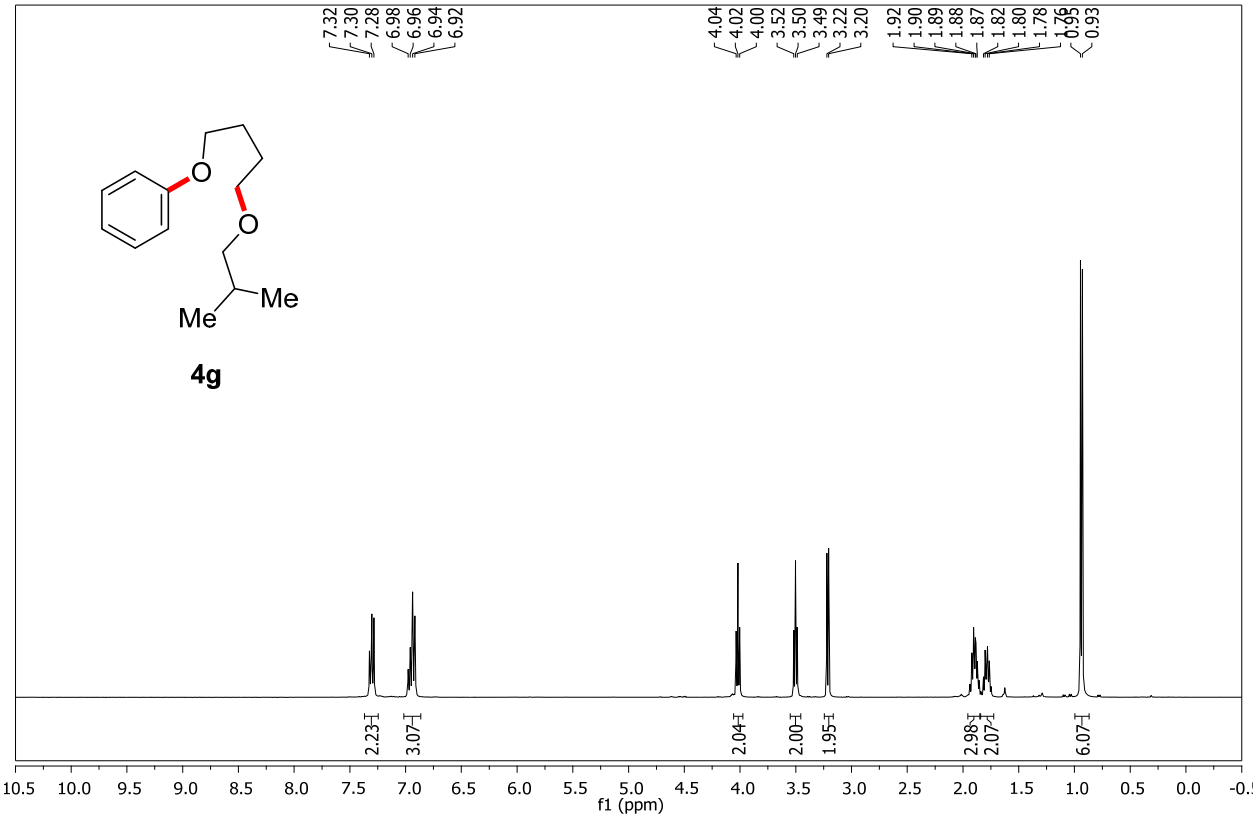


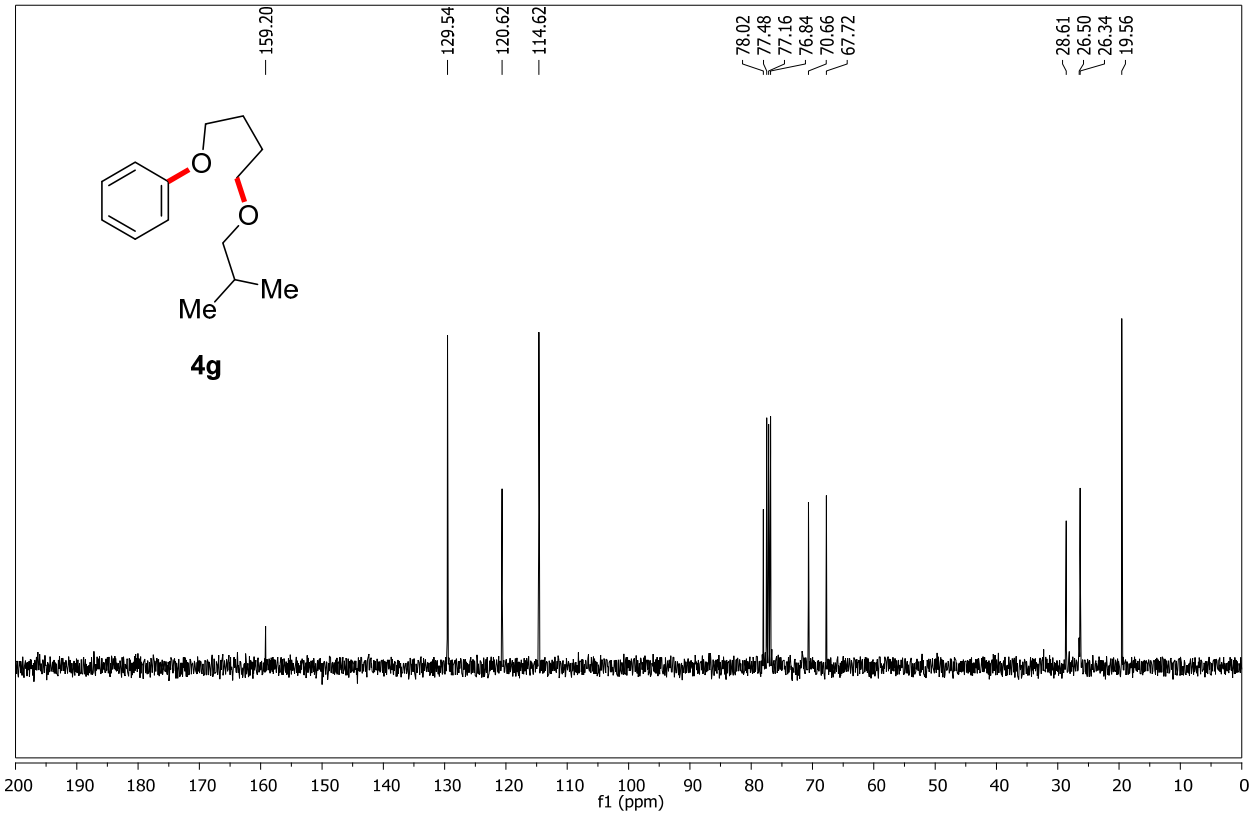
(4-(Undec-10-en-1-yloxy)butoxy)benzene (4f)



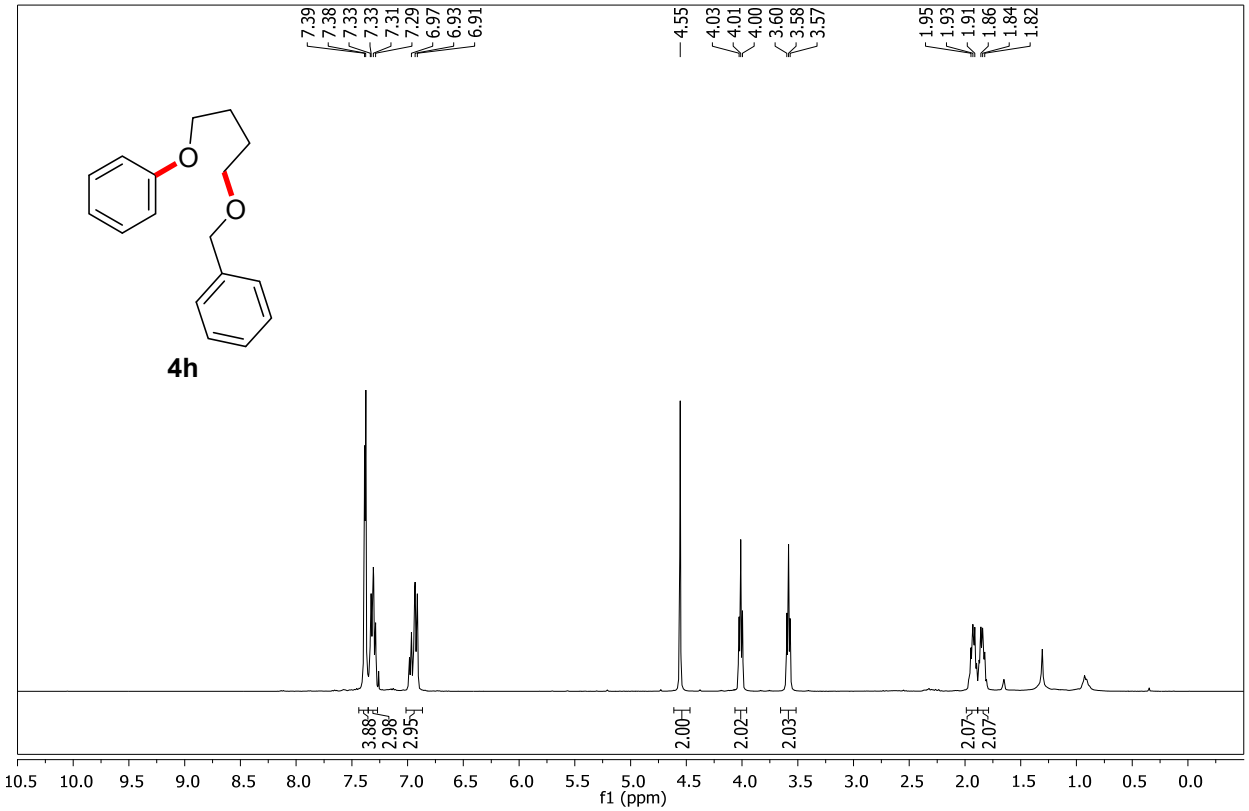


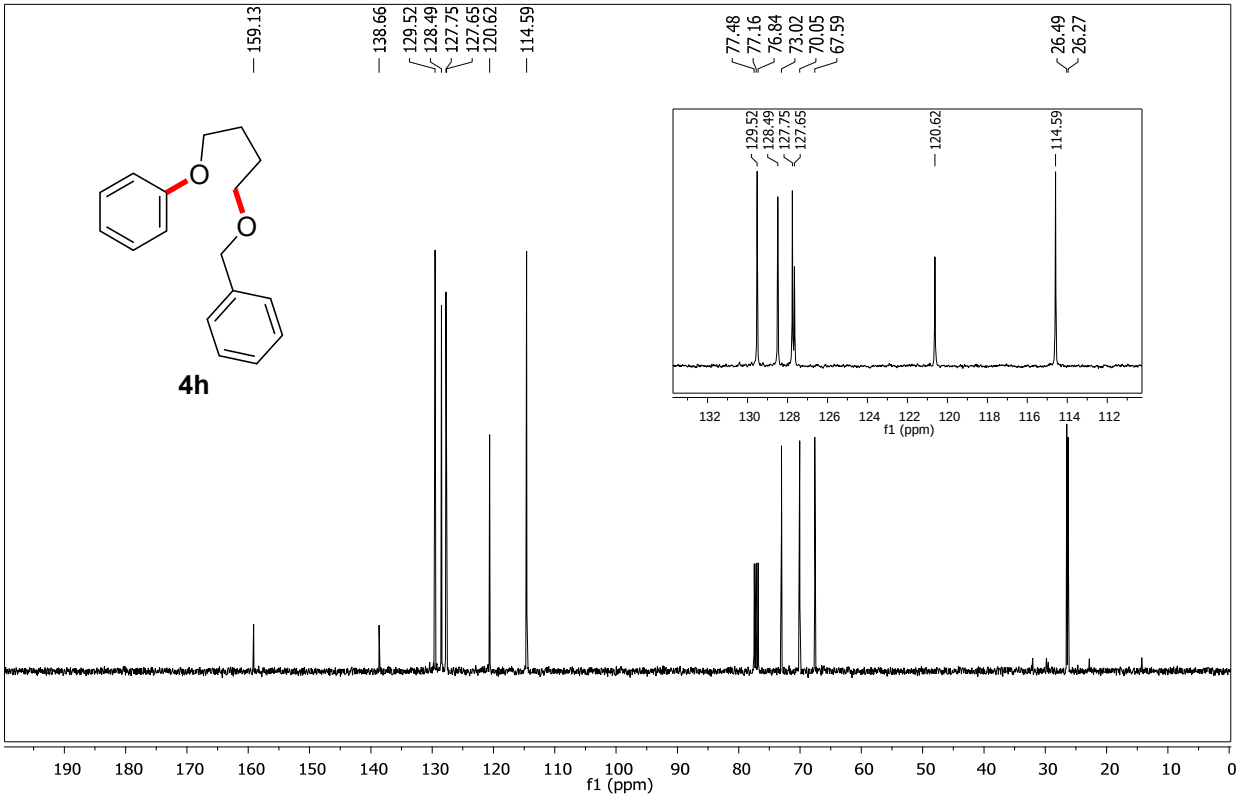
(4-Isobutoxybutoxy)benzene (4g)



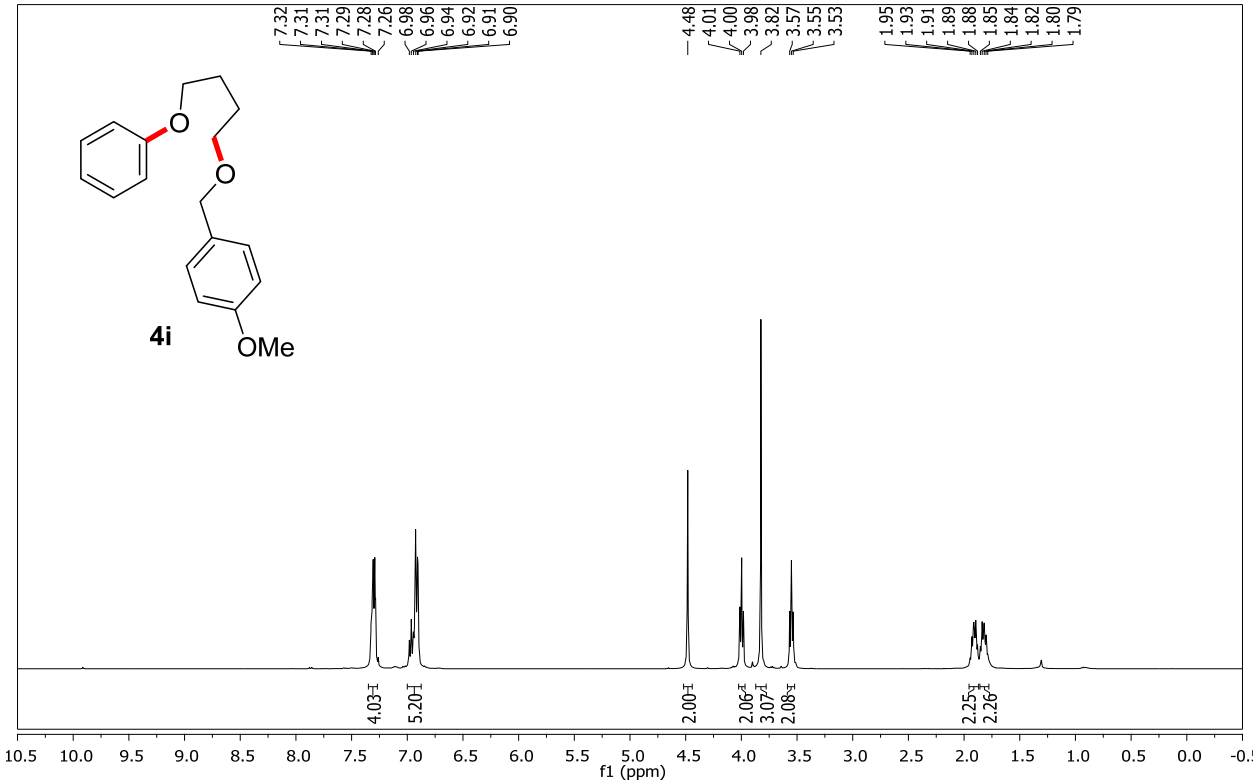


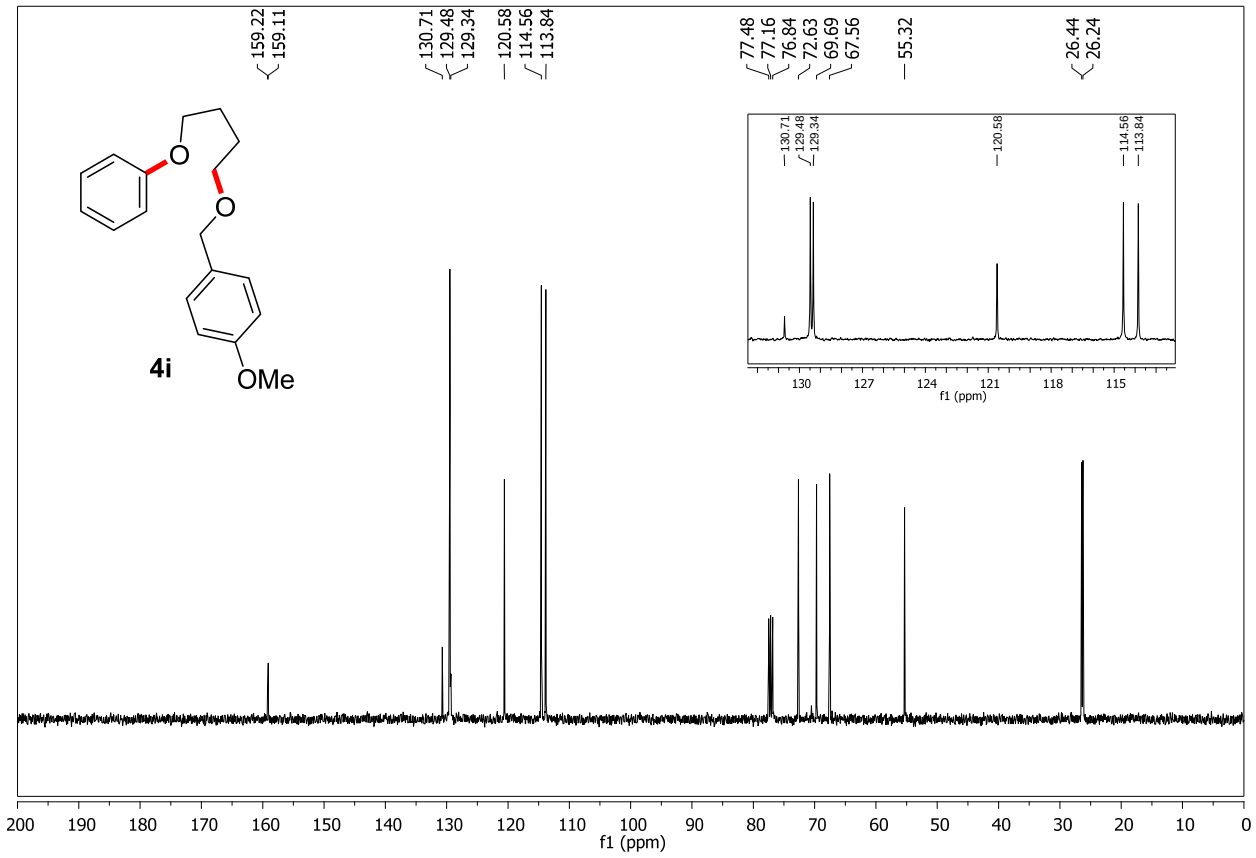
(4-(Benzyloxy)butoxy)benzene (4h)



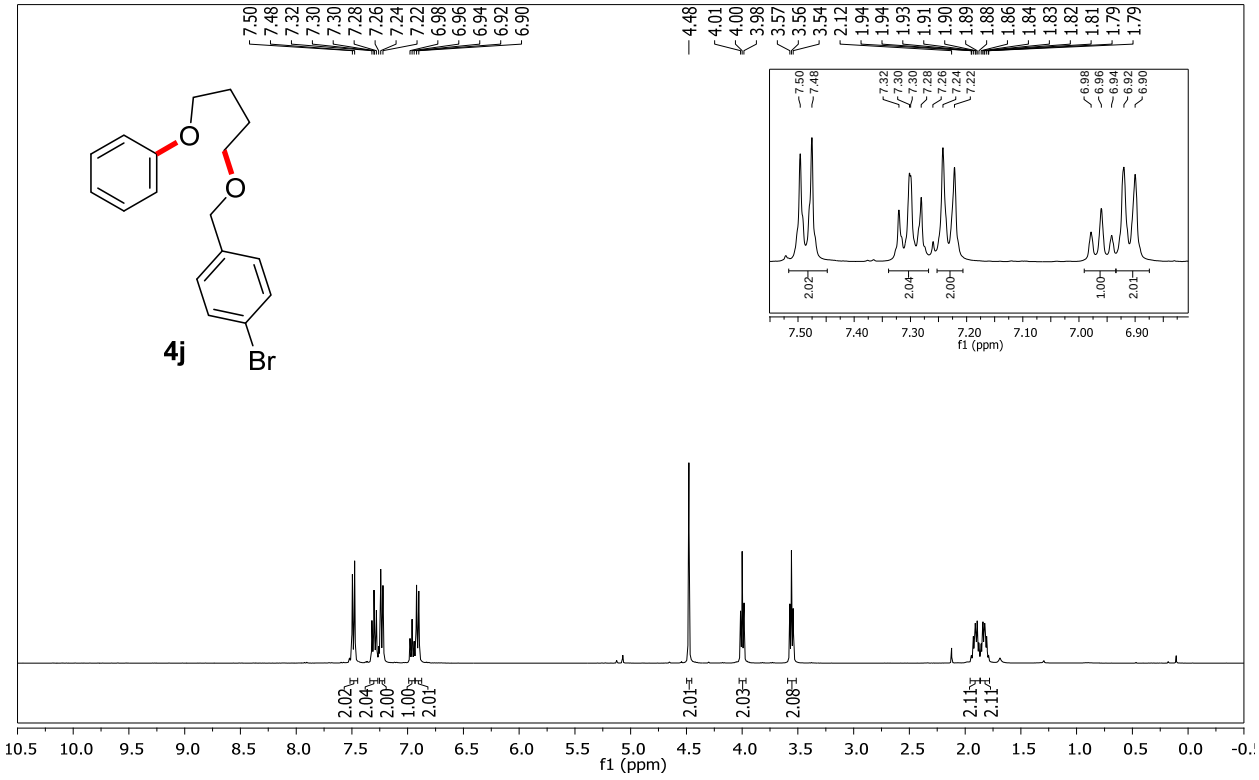


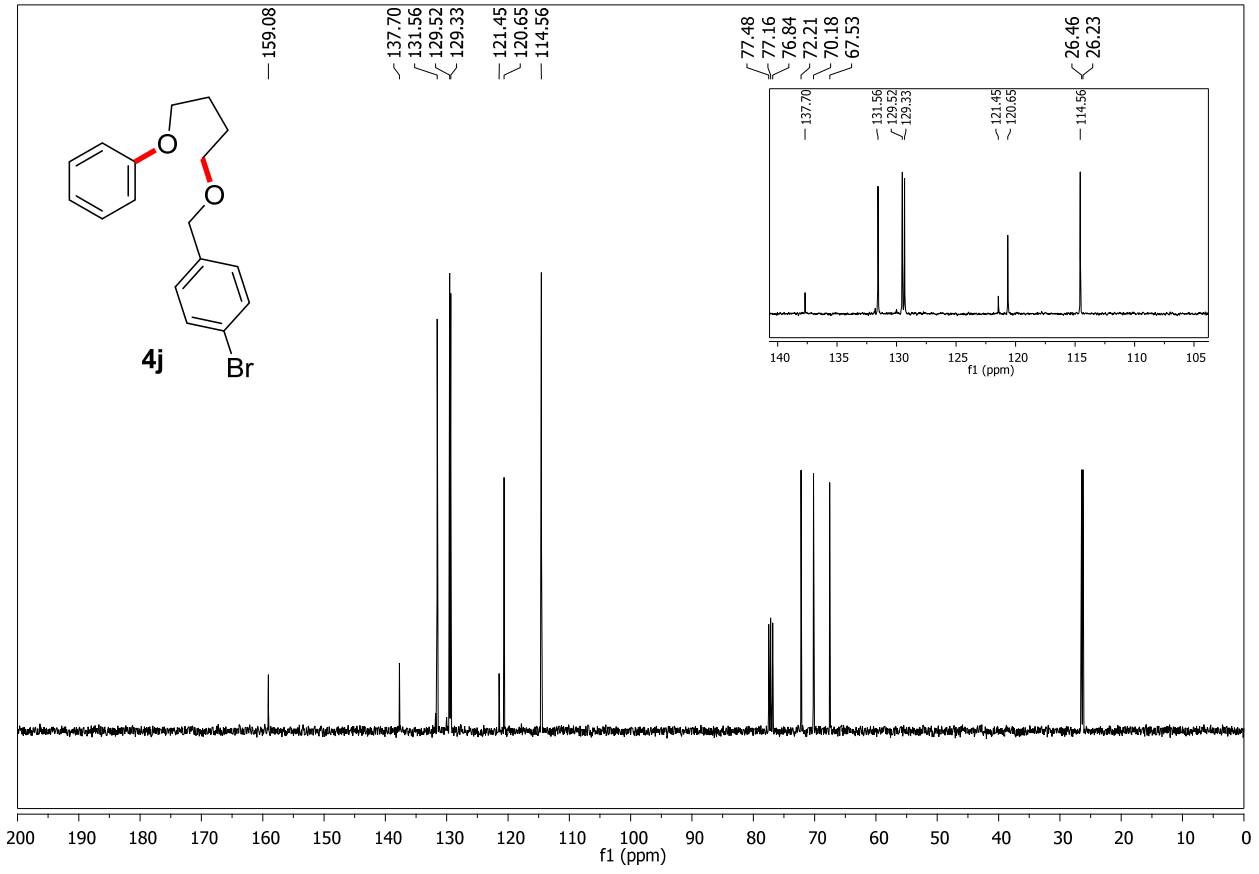
1-Methoxy-4-((4-phenoxybutoxy)methyl)benzene (4i)



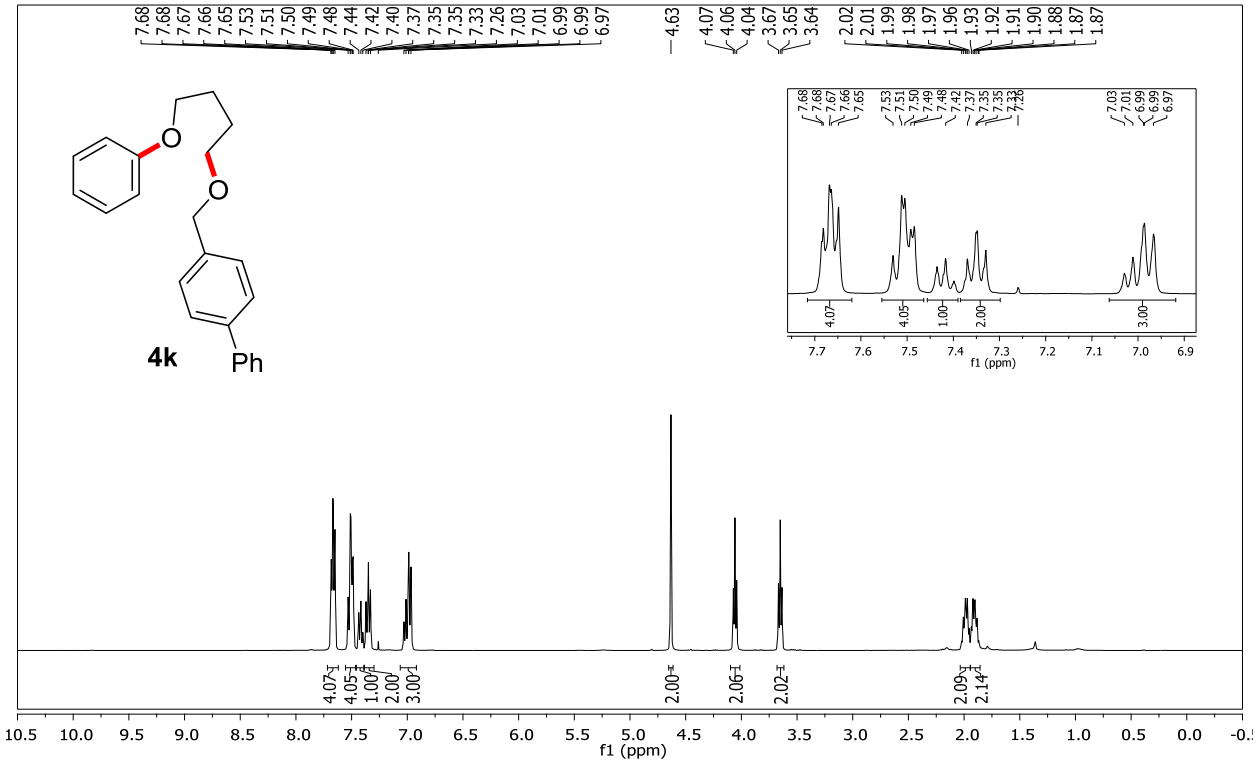


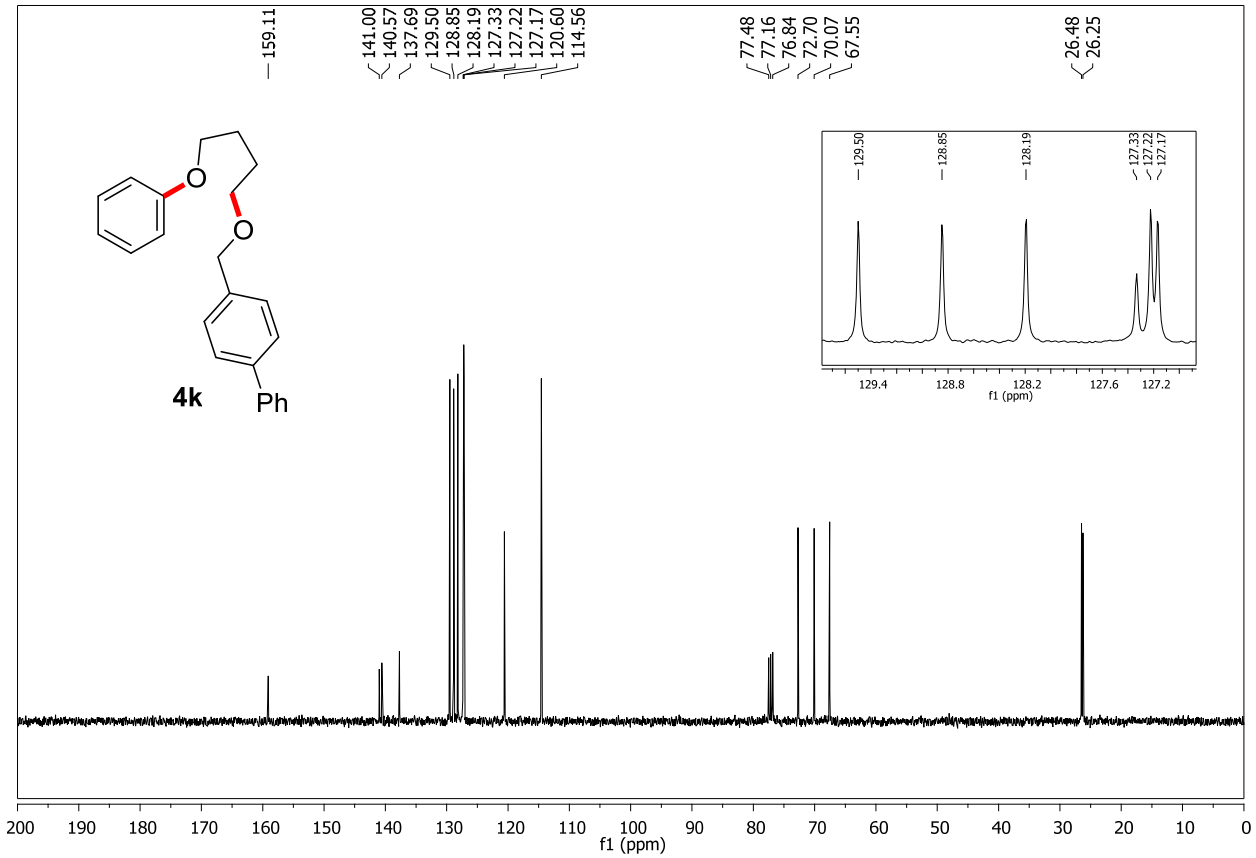
1-Bromo-4-((4-phenoxybutoxy)methyl)benzene (4j)



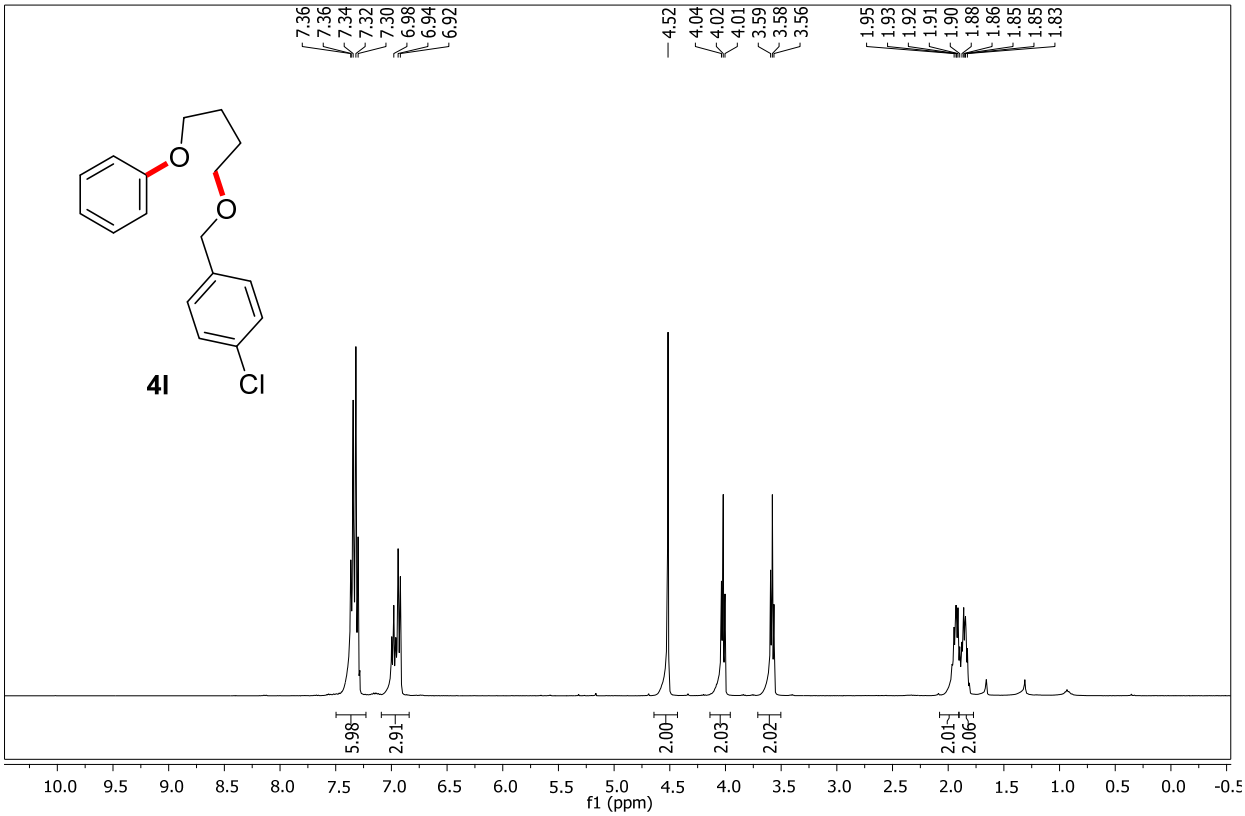


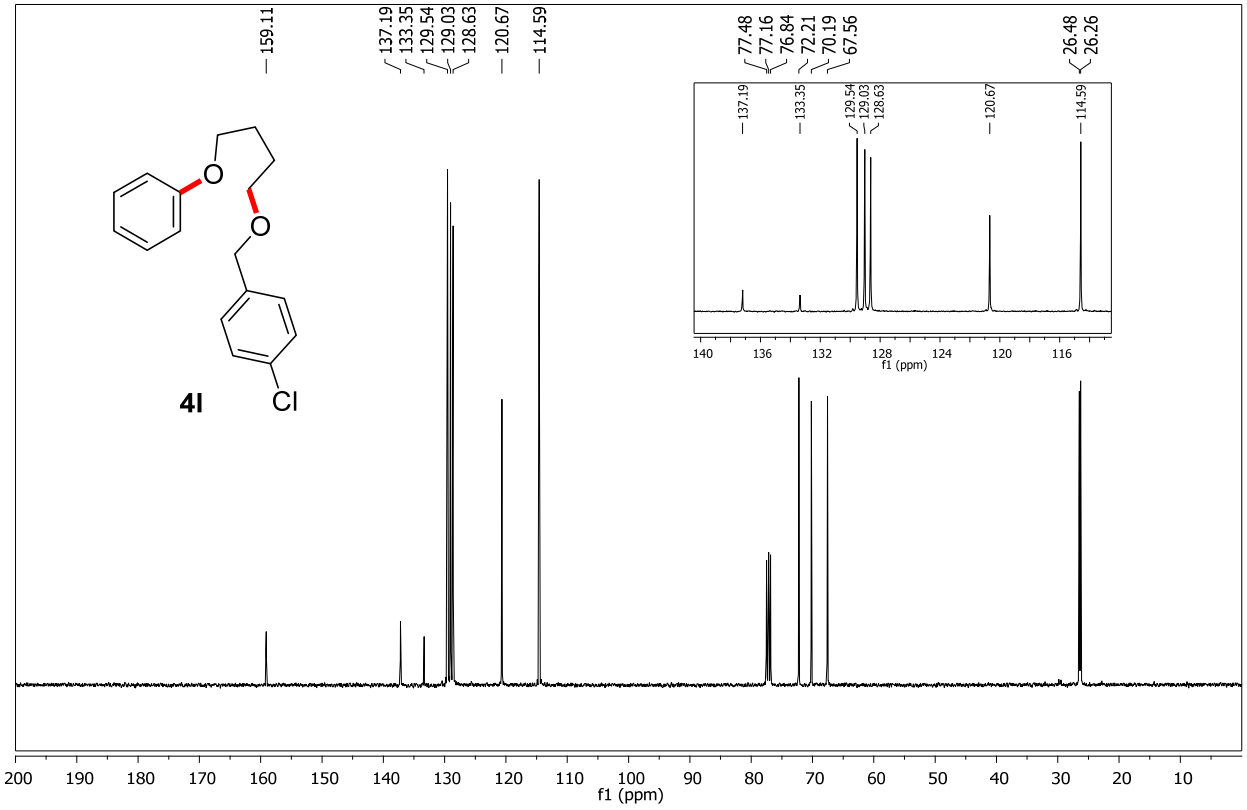
4-((4-Phenoxybutoxy)methyl)-1,1'-biphenyl (4k)



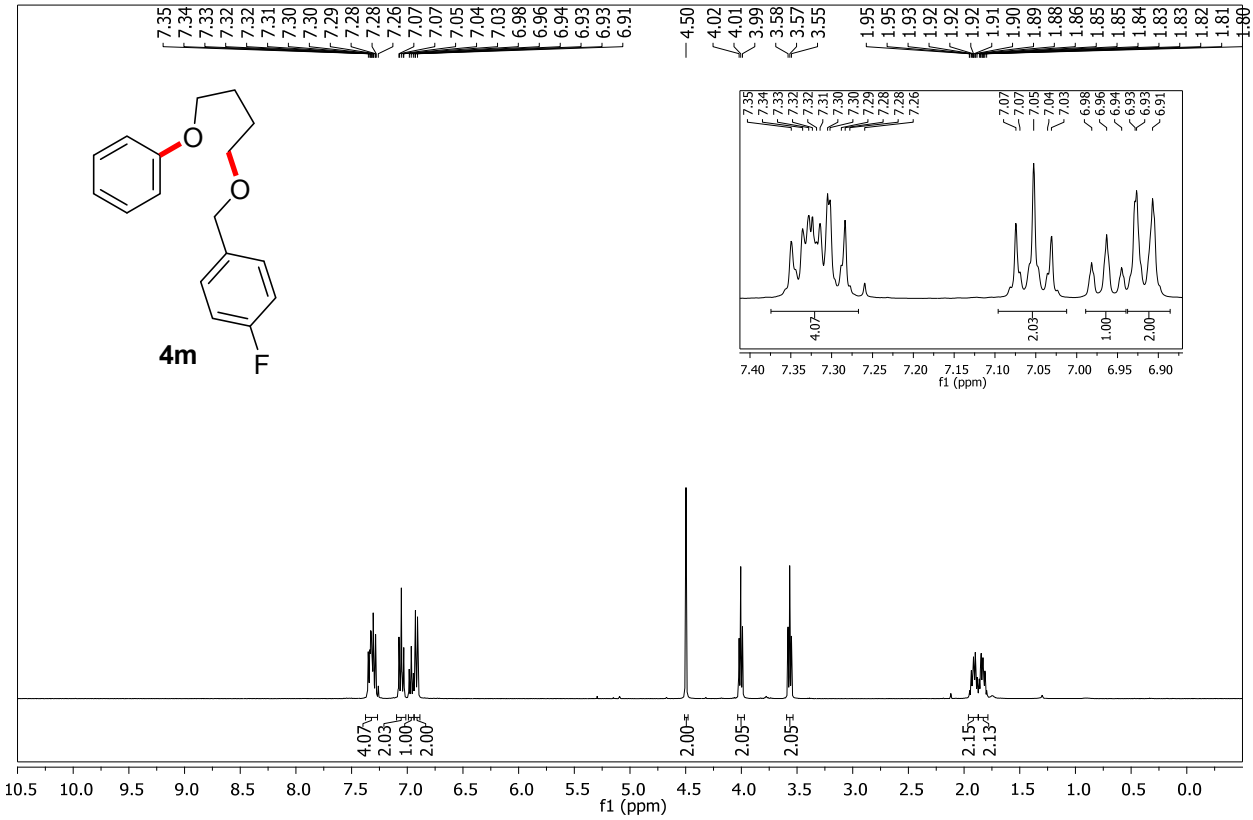


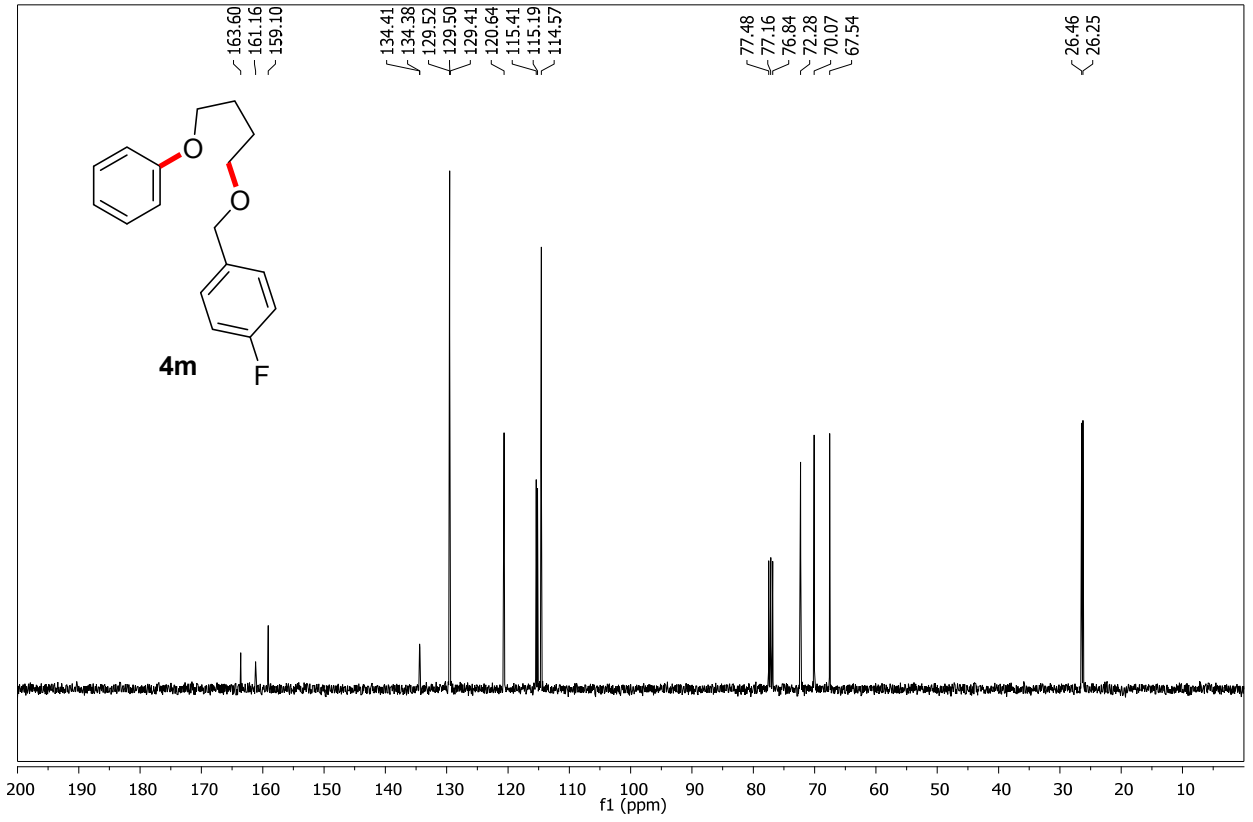
1-Chloro-4-((4-phenoxybutoxy)methyl)benzene (4l)



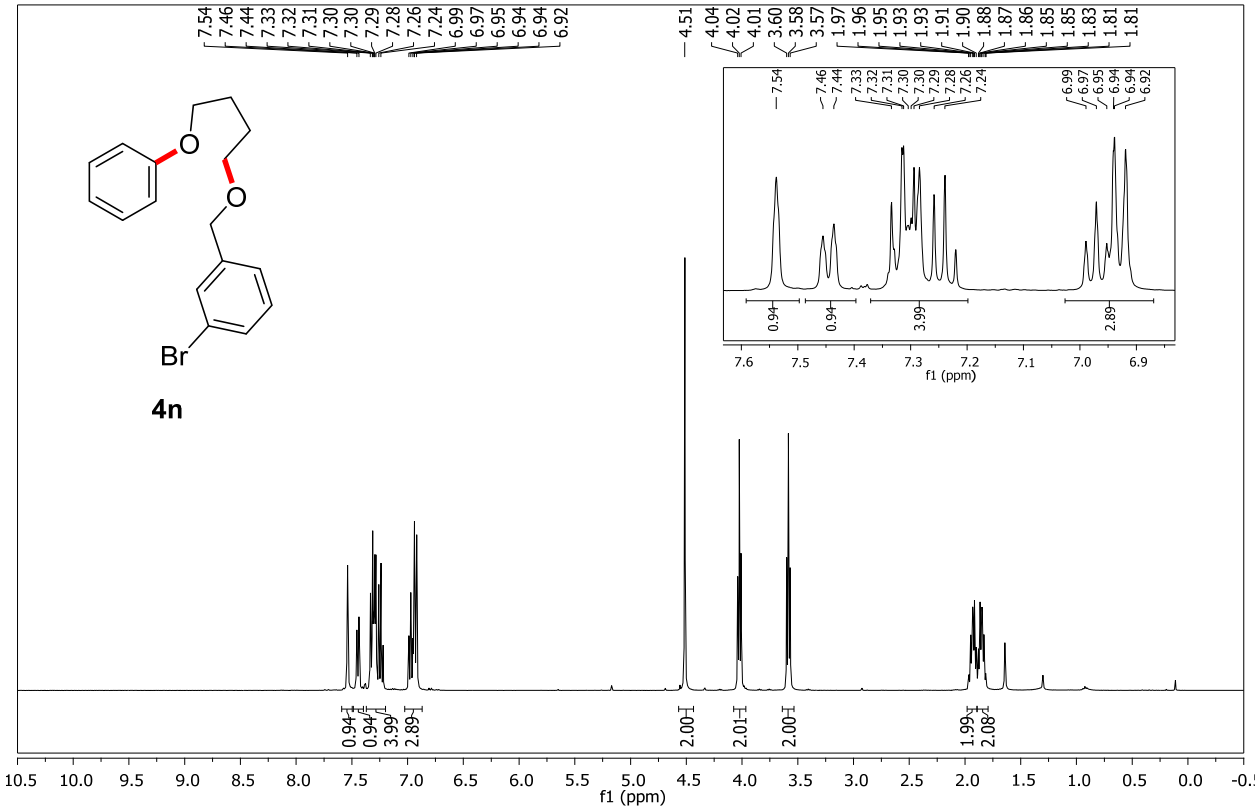


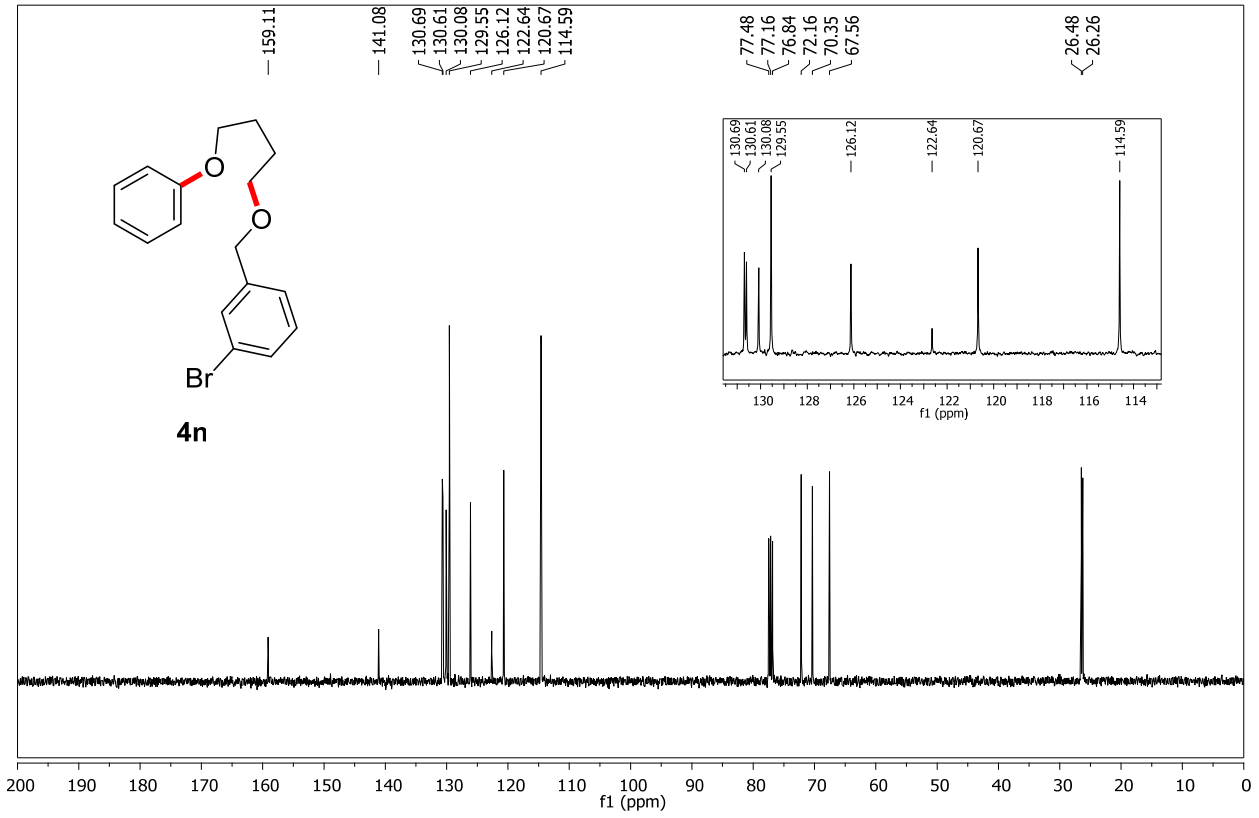
1-Fluoro-4-((4-phenoxybutoxy)methyl)benzene (4m)



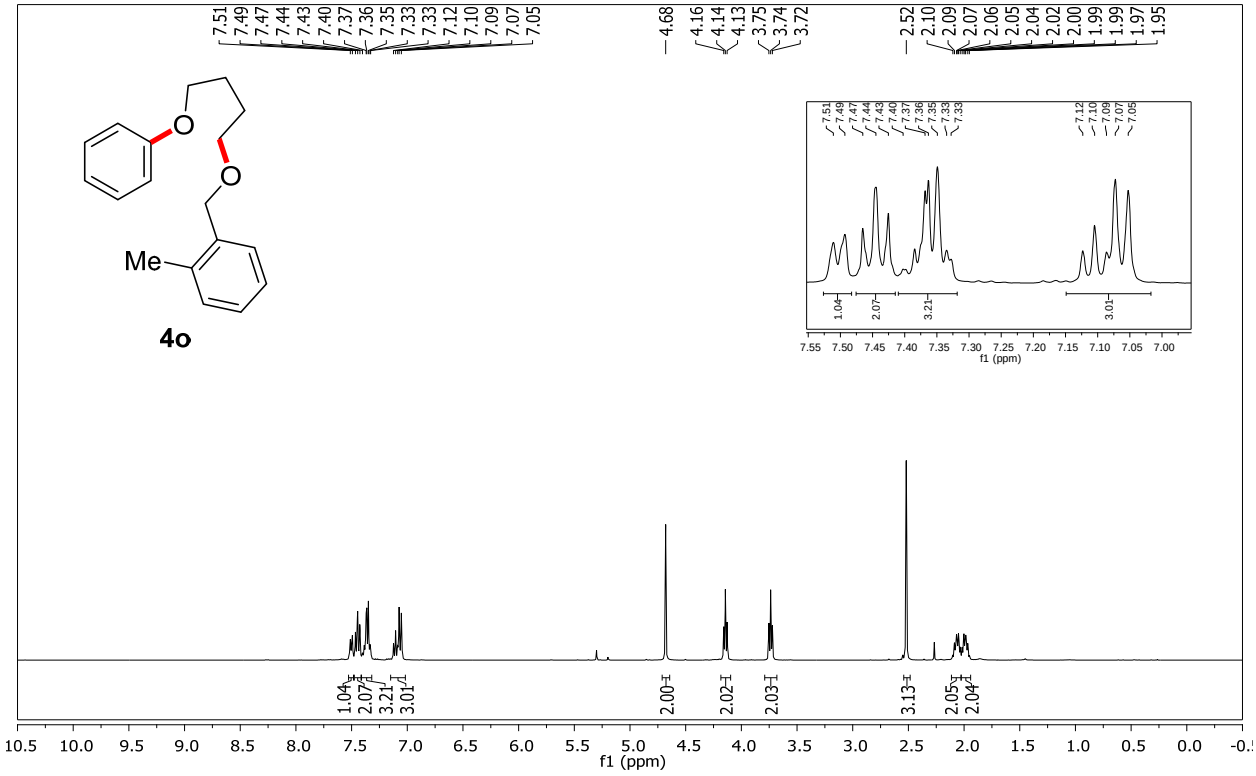


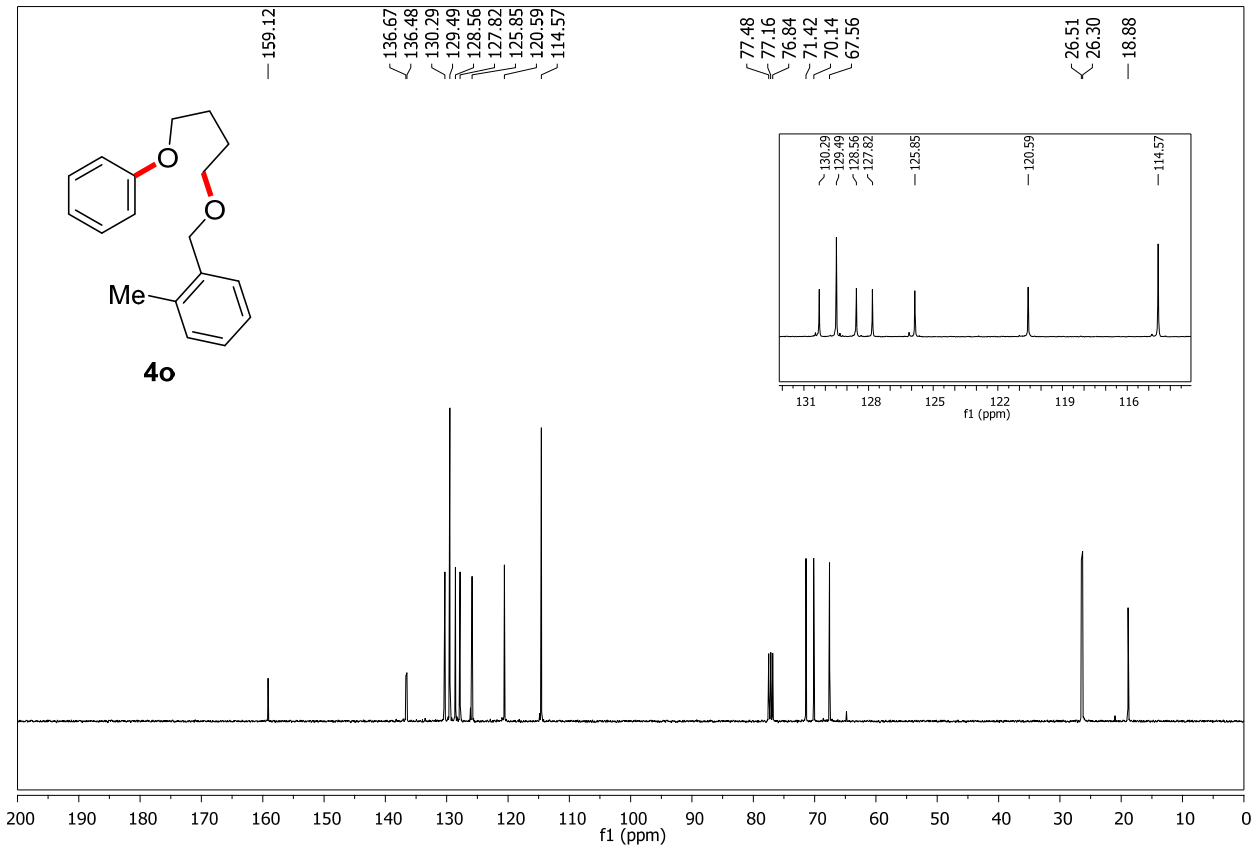
1-Bromo-3-((4-phenoxybutoxy)methyl)benzene (4n)



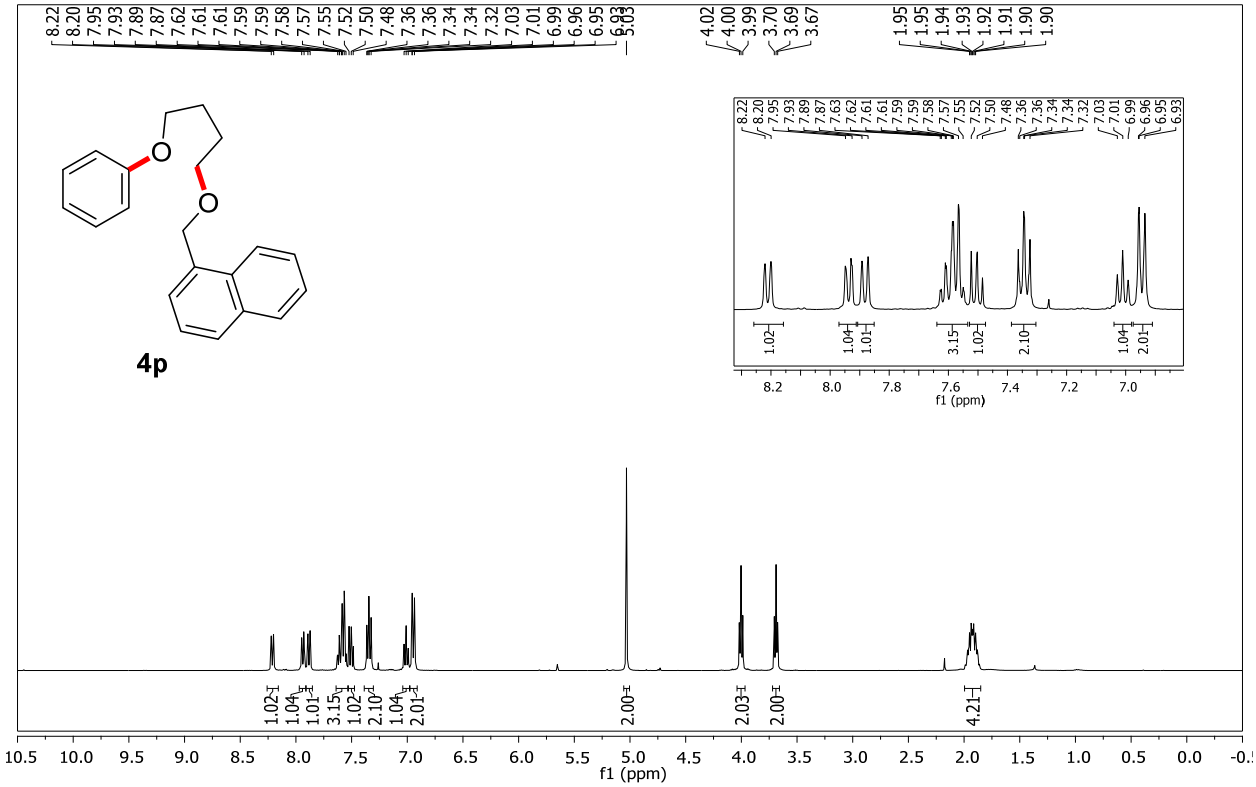


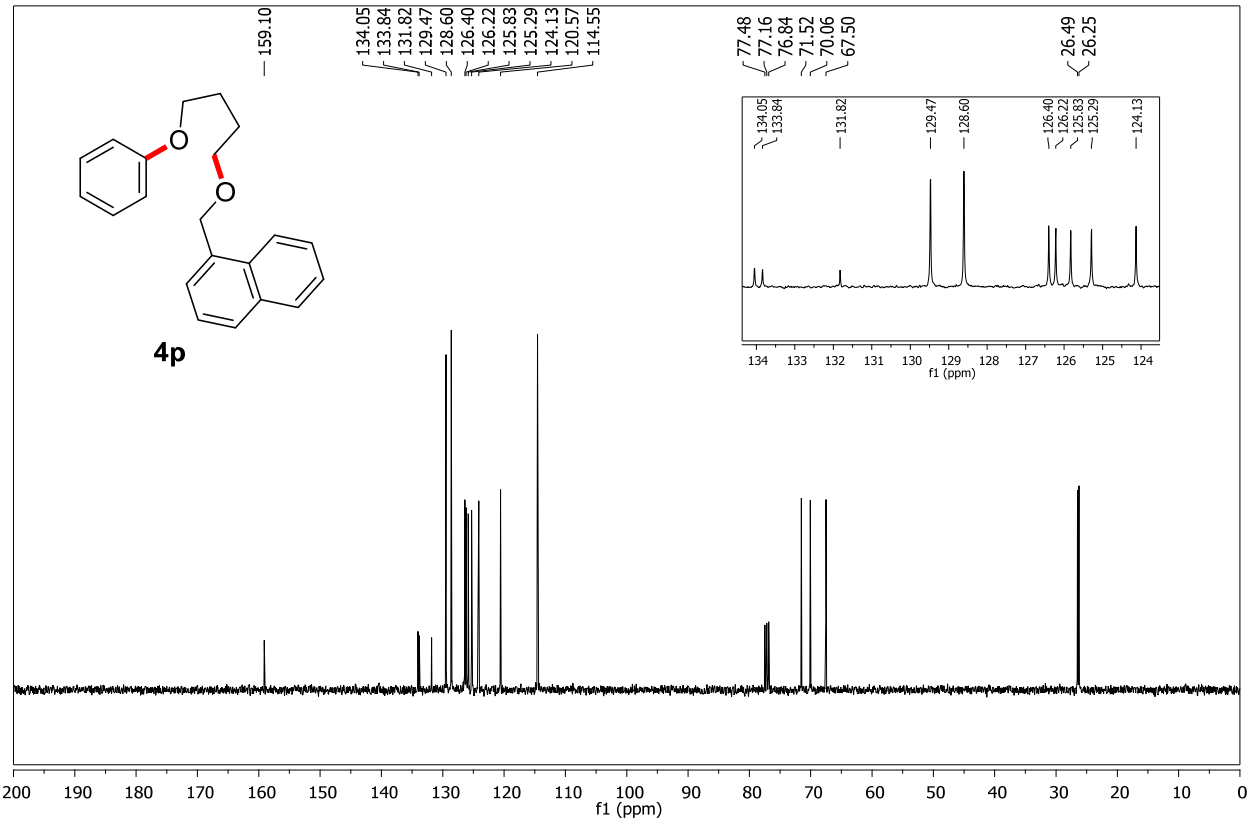
1-Methyl-2-((4-phenoxybutoxy)methyl)benzene (4o)



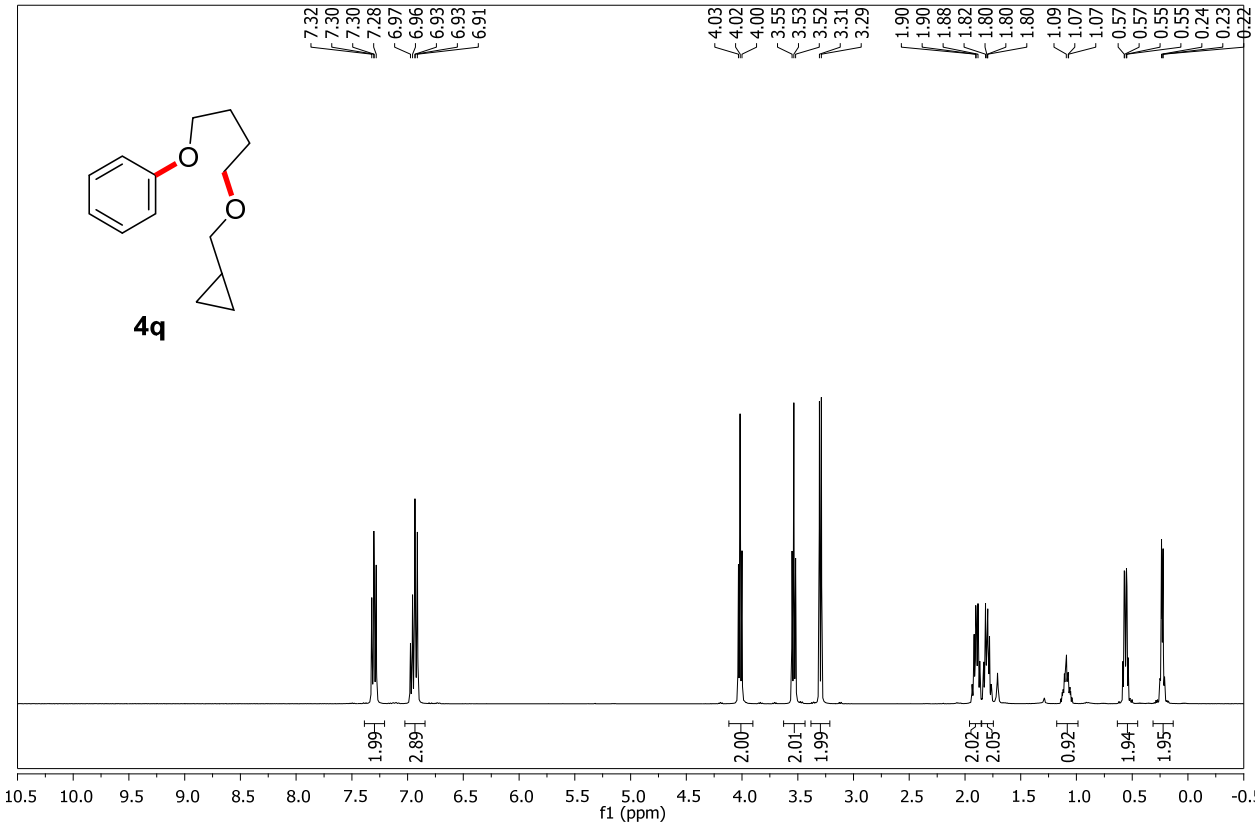


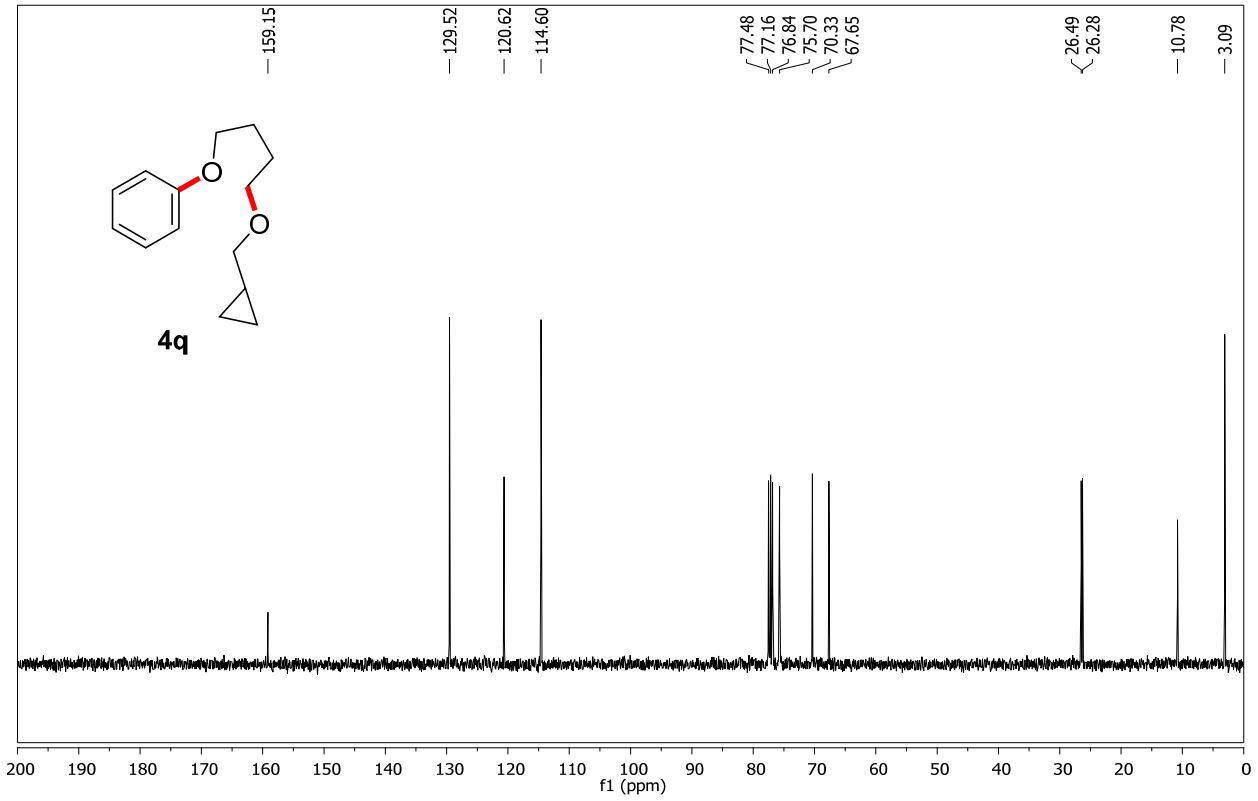
1-((4-Phenoxybutoxy)methyl)naphthalene (4p)



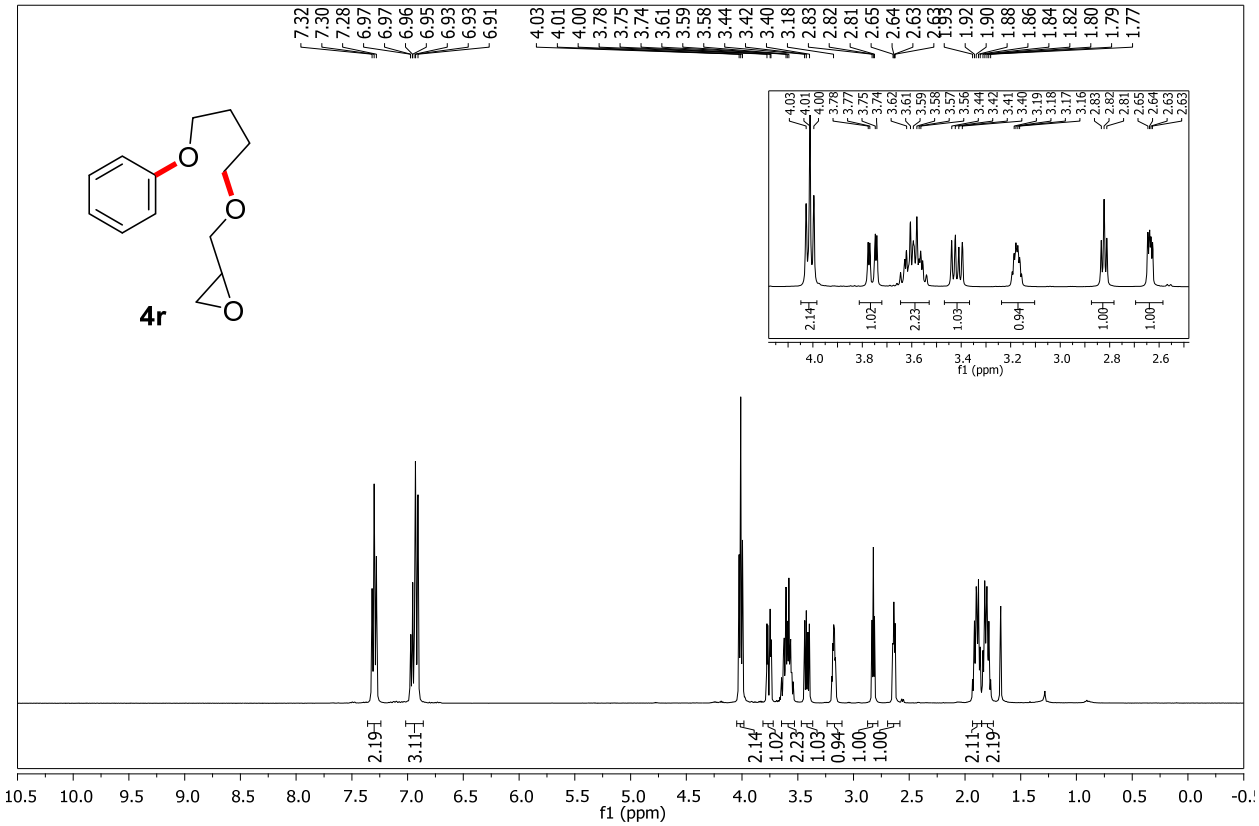


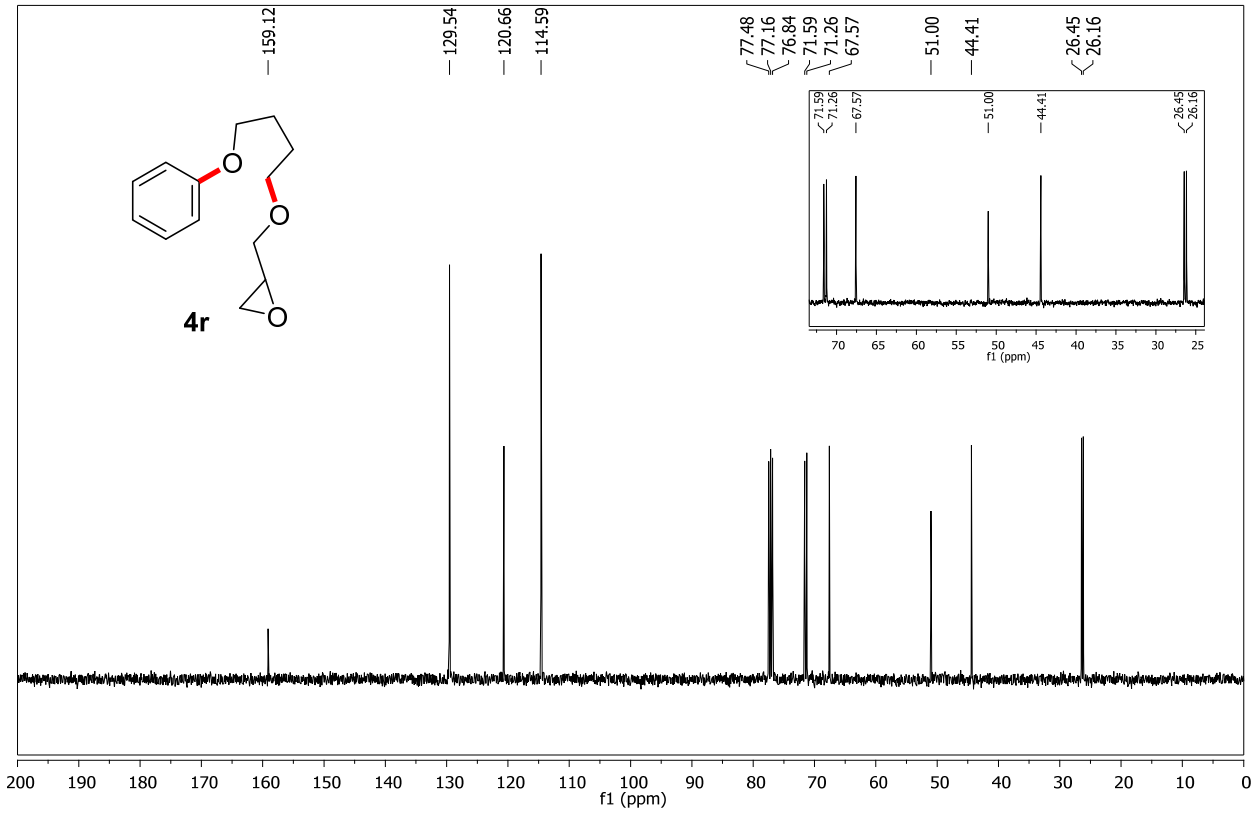
(4-(Cyclopropylmethoxy)butoxy)benzene (4q)



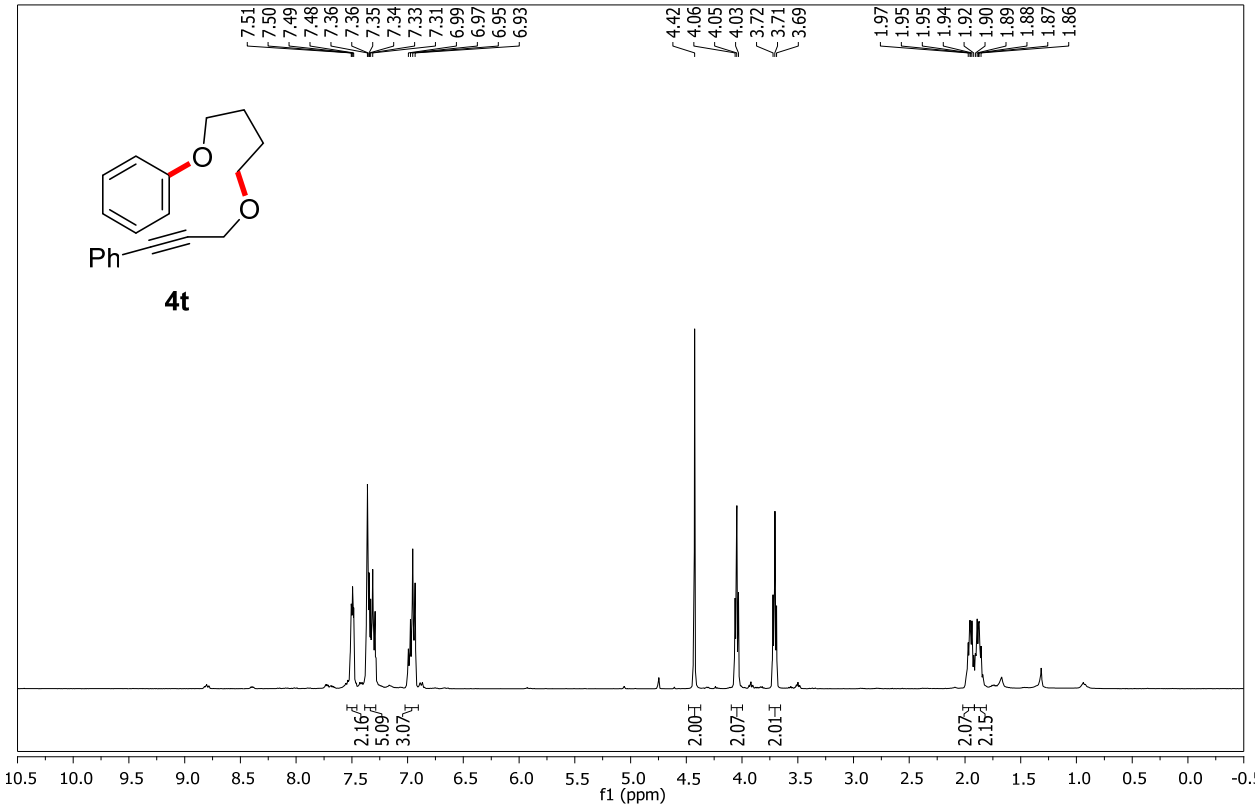


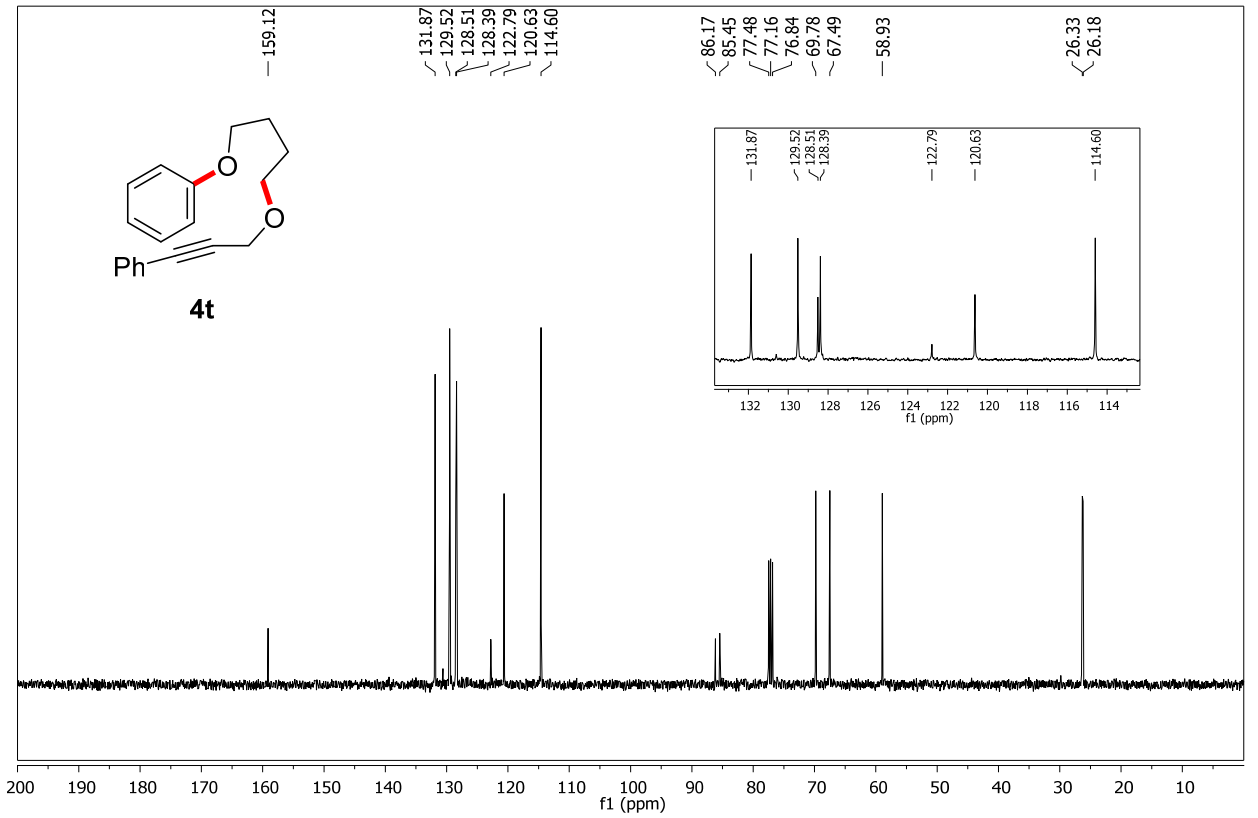
2-((4-Phenoxybutoxy)methyl)oxirane (4r)



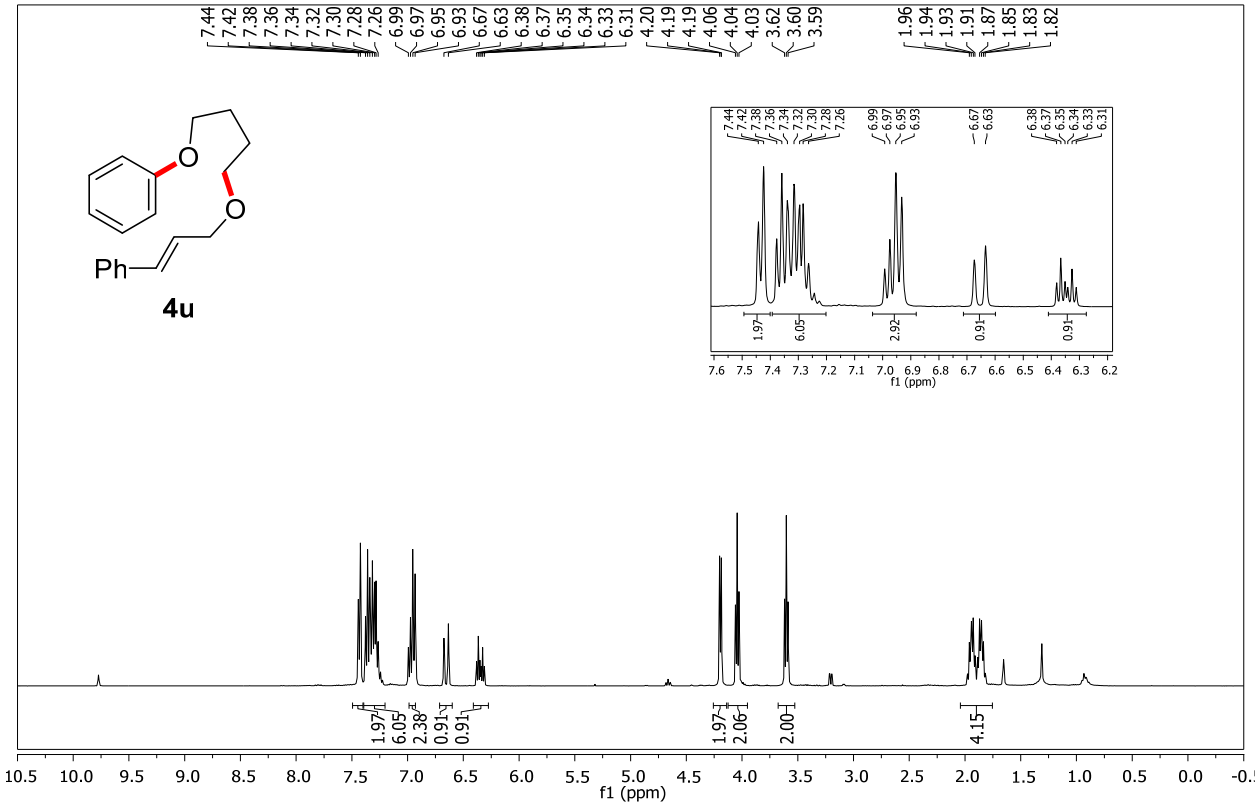


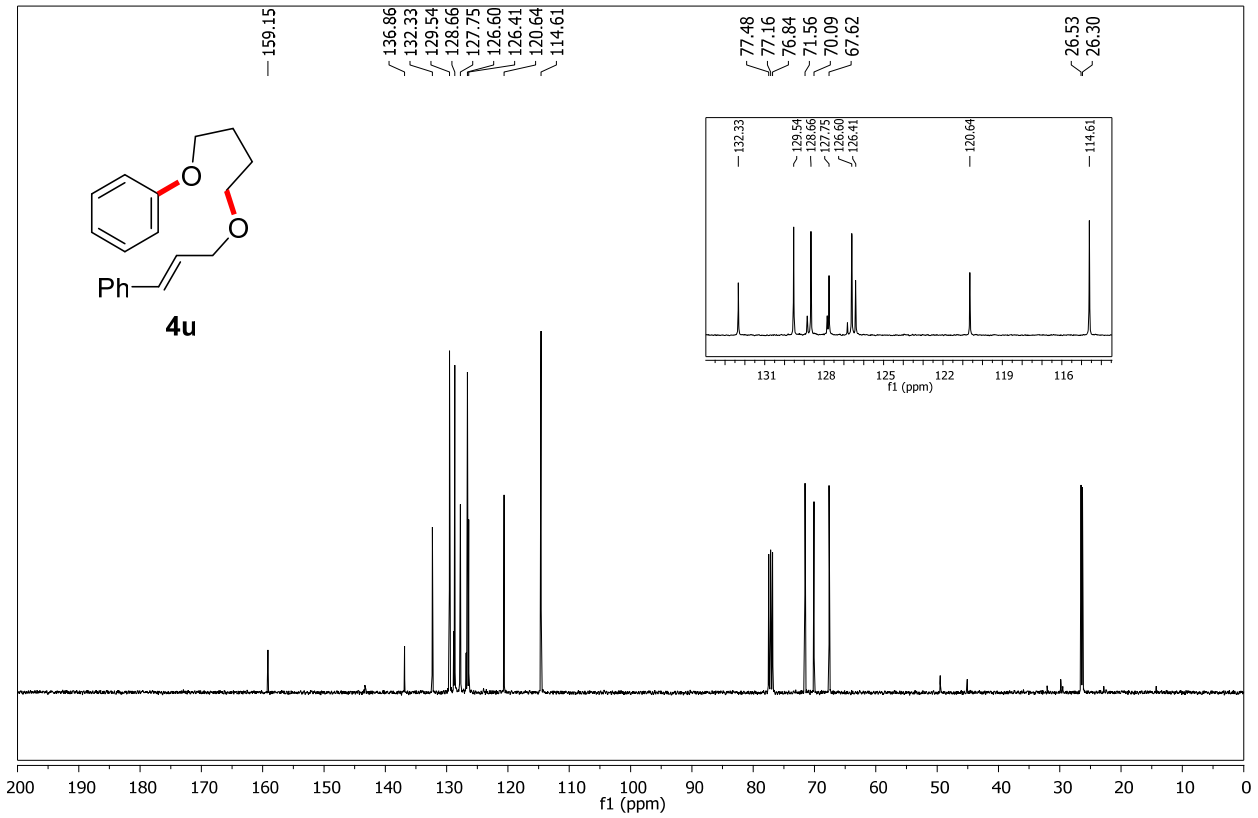
(3-(4-Phenoxybutoxy)prop-1-yn-1-yl)benzene (4t)



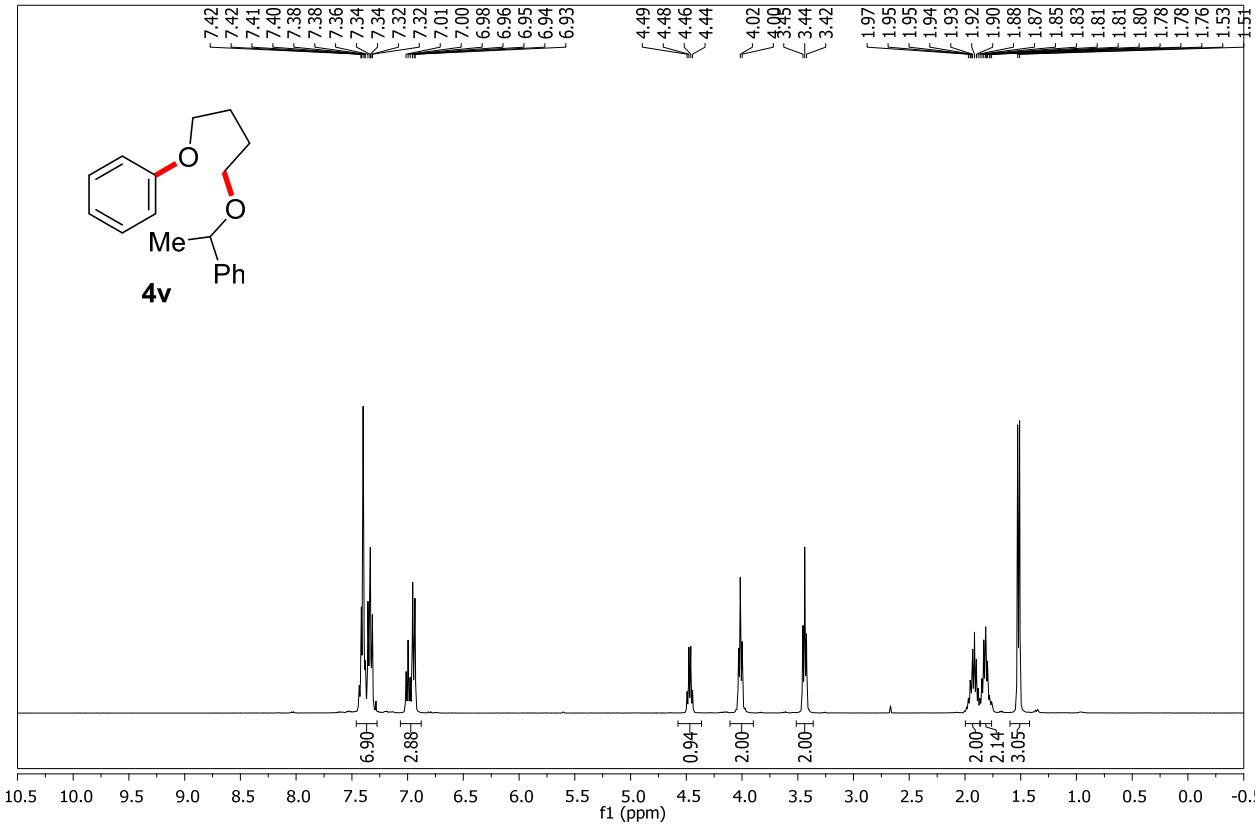


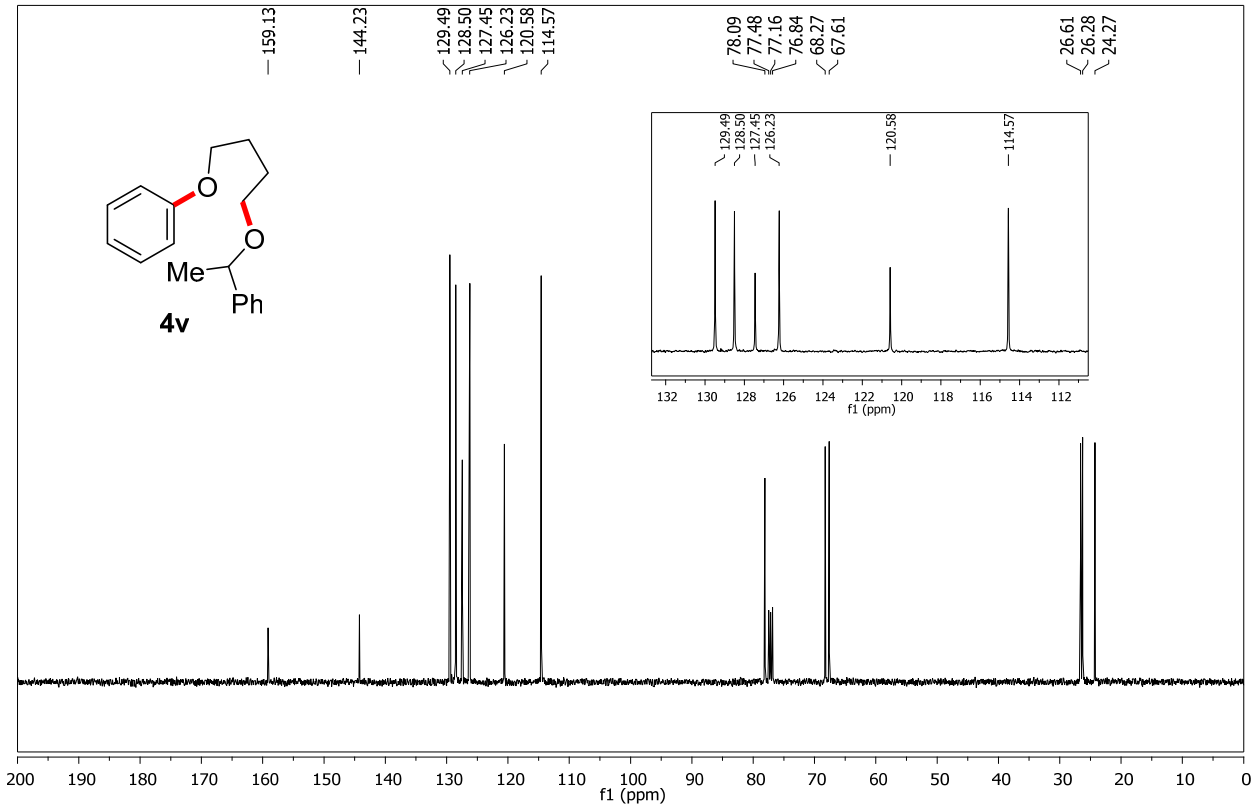
(4-(Cinnamyloxy)butoxy)benzene (4u)



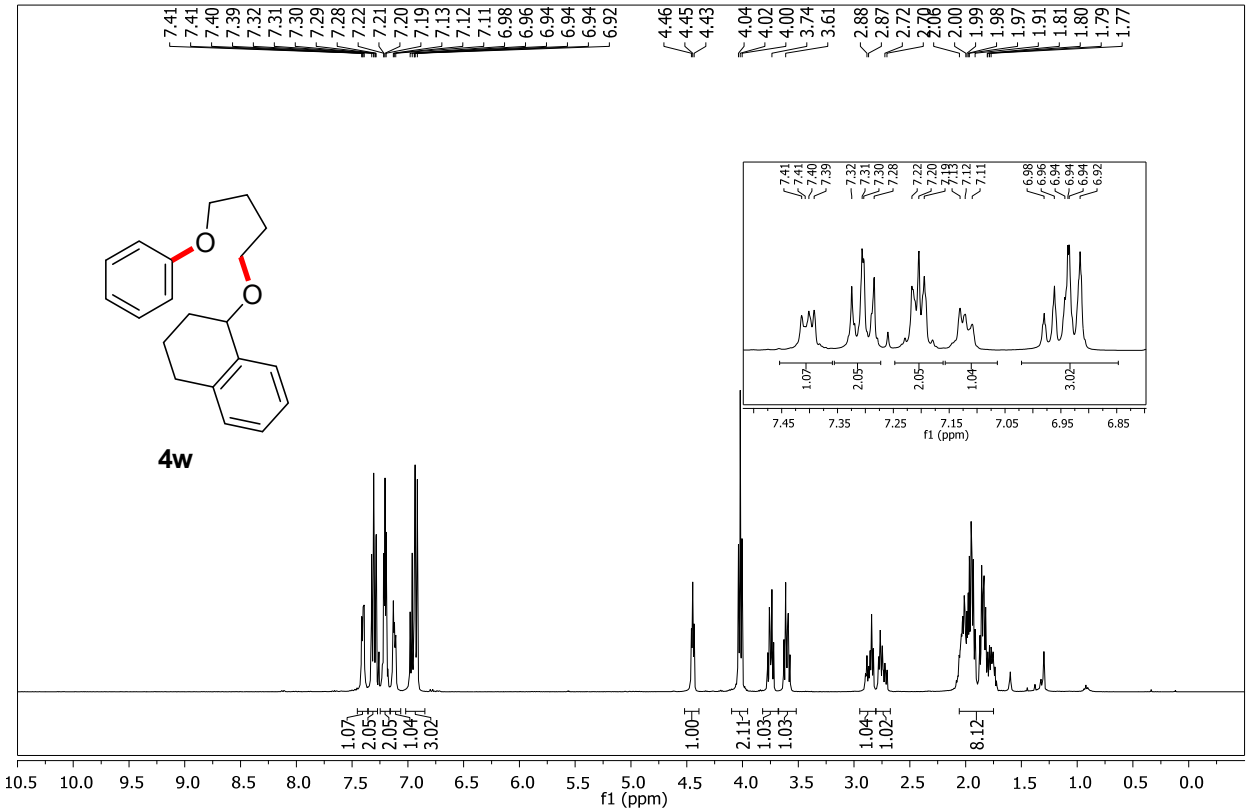


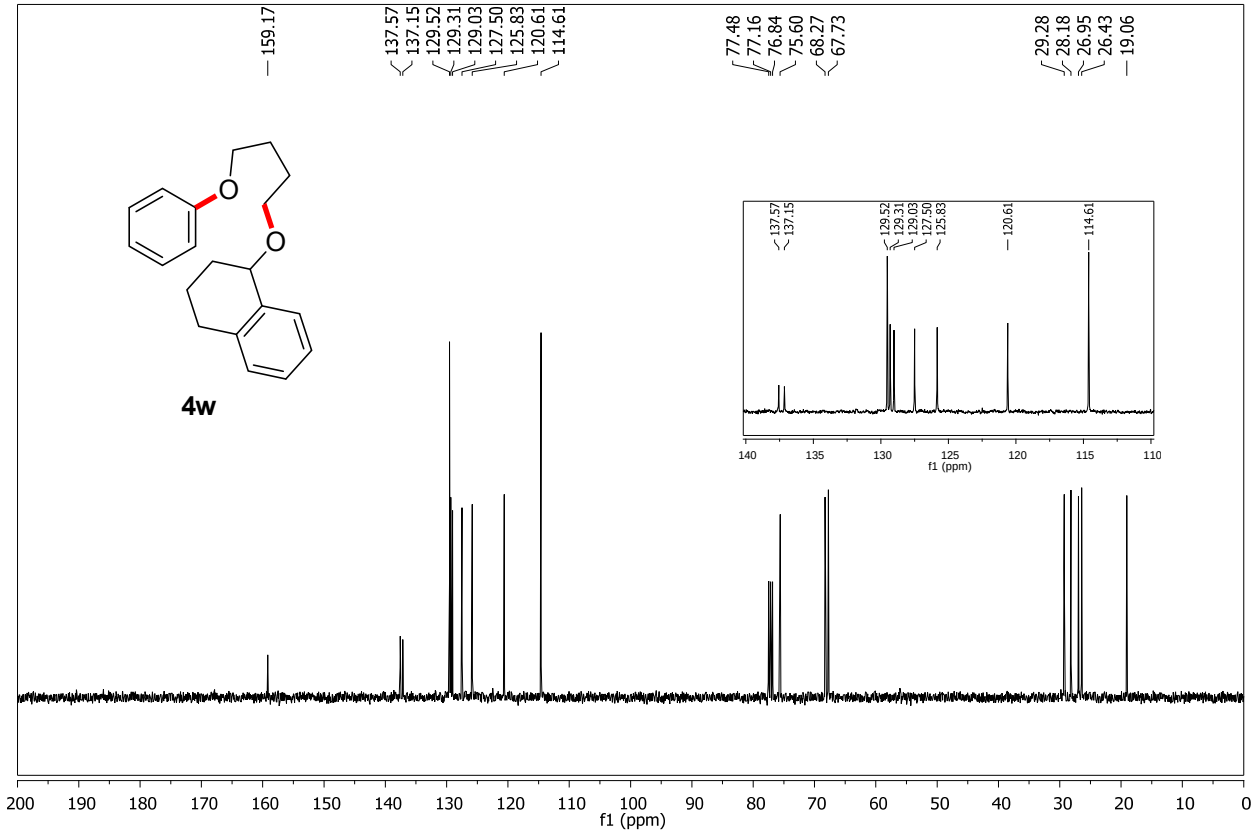
(1-(4-Phenoxybutoxy)ethyl)benzene (4v)



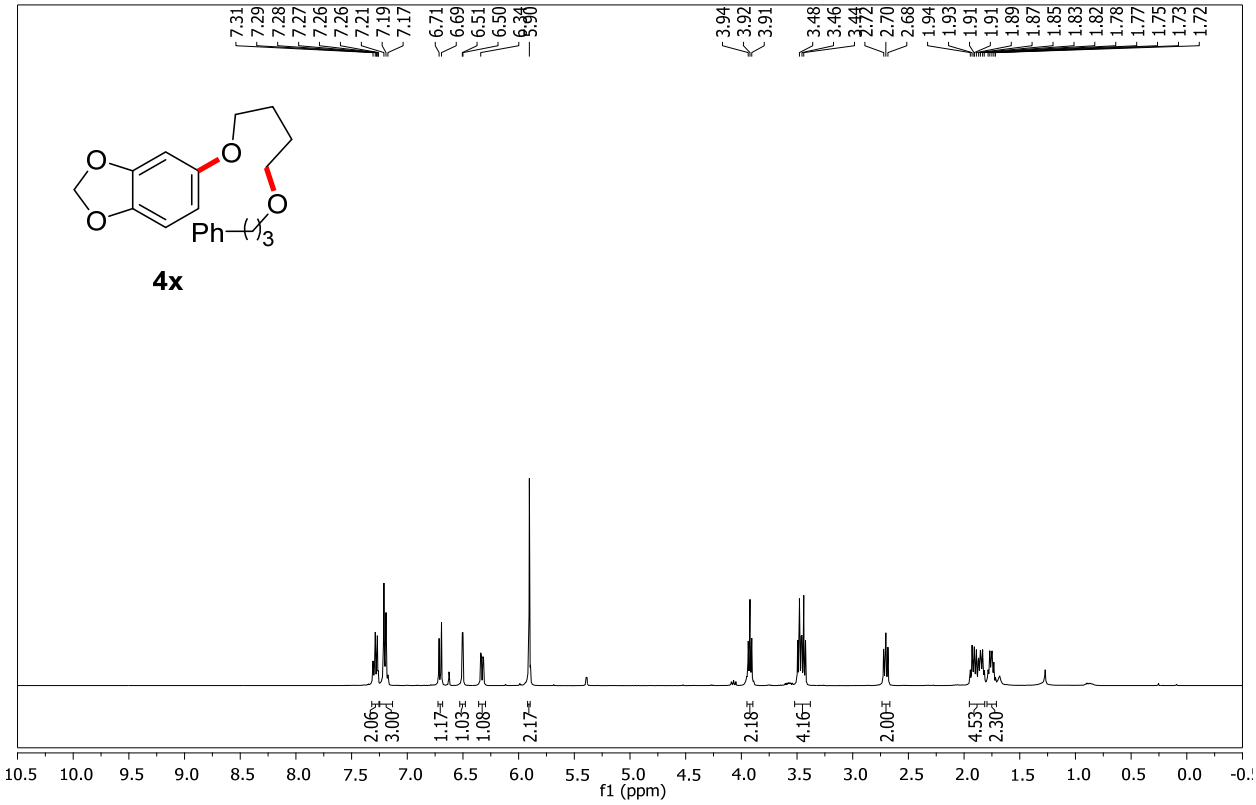


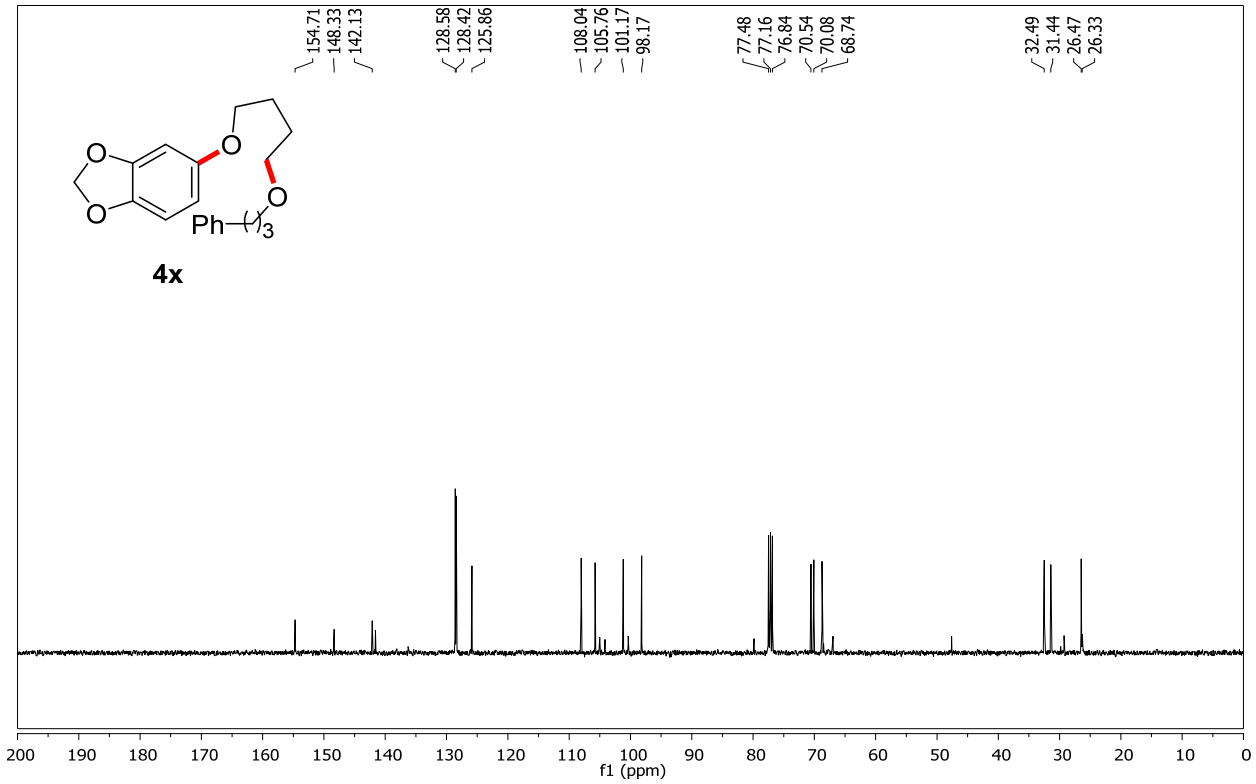
1-(4-phenoxybutoxy)-1,2,3,4-tetrahydronaphthalene (4w)



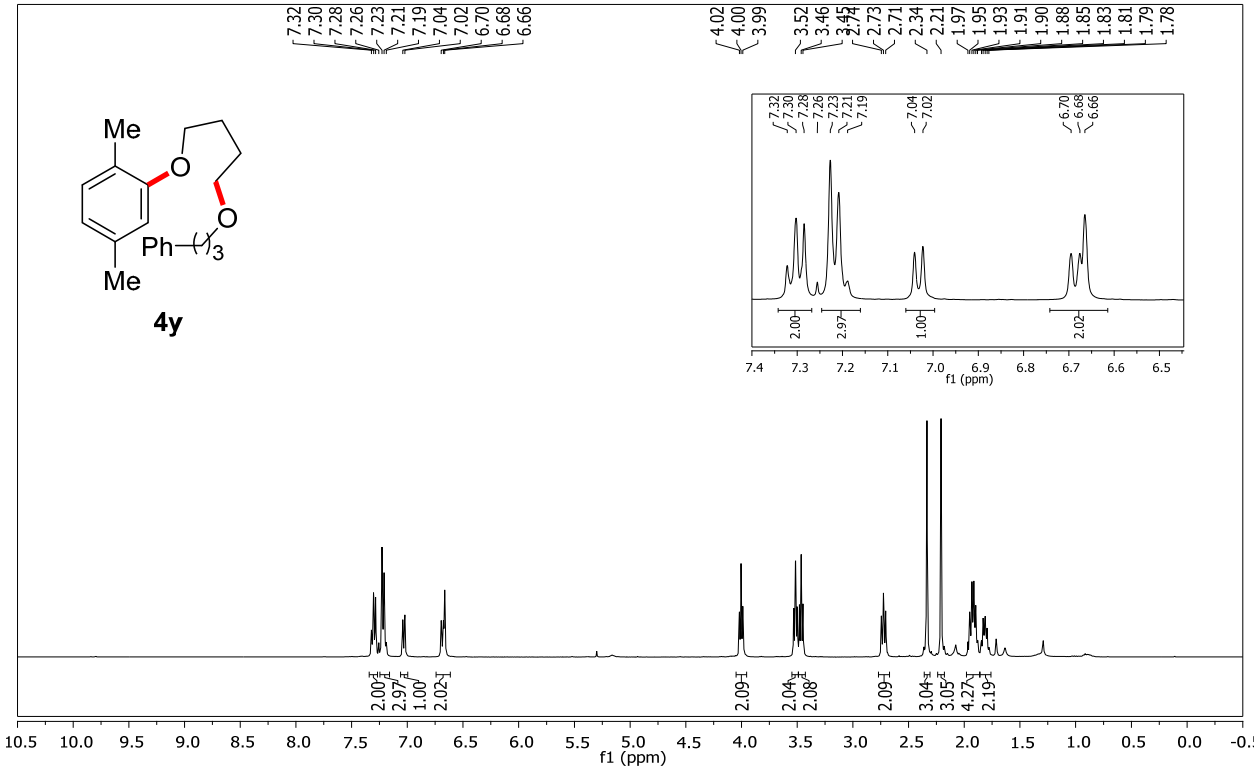


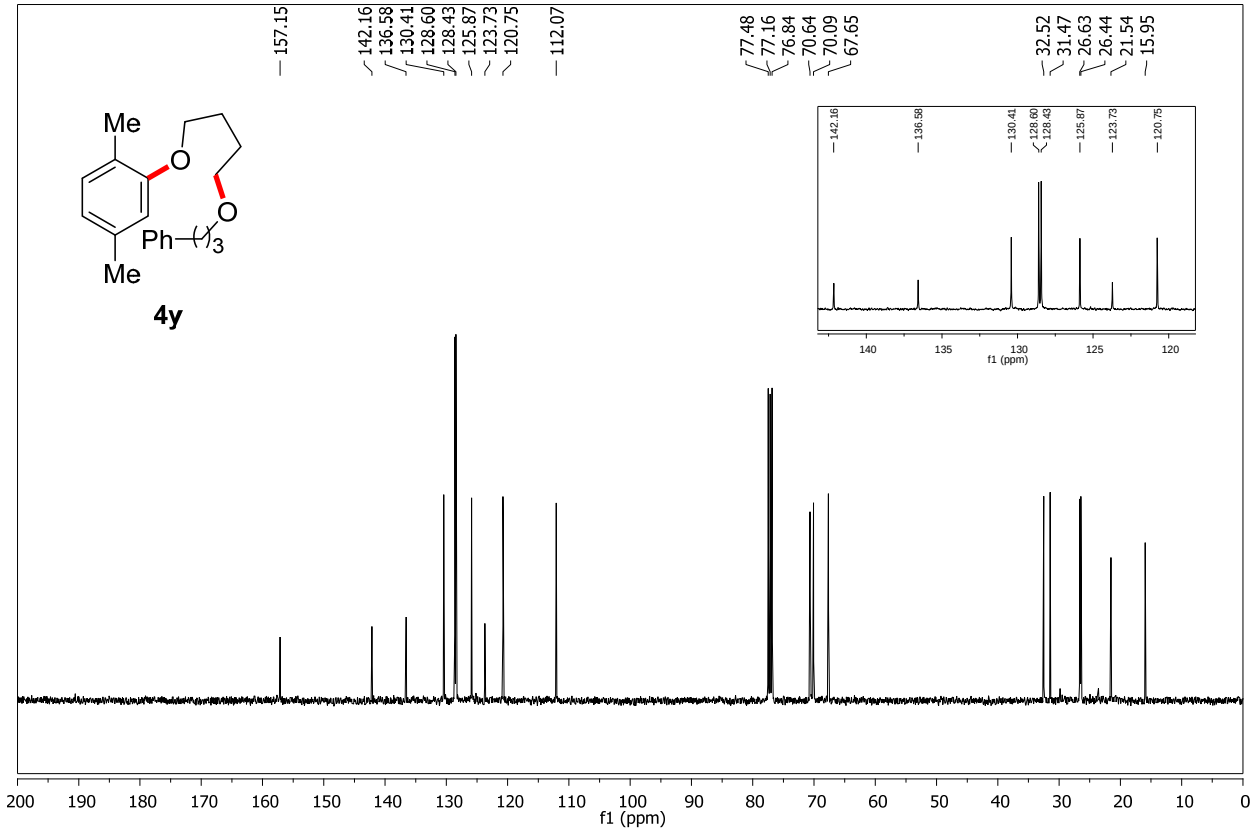
5-(4-(3-Phenylpropoxy)butoxy)benzo[*d*][1,3]dioxole (4x)



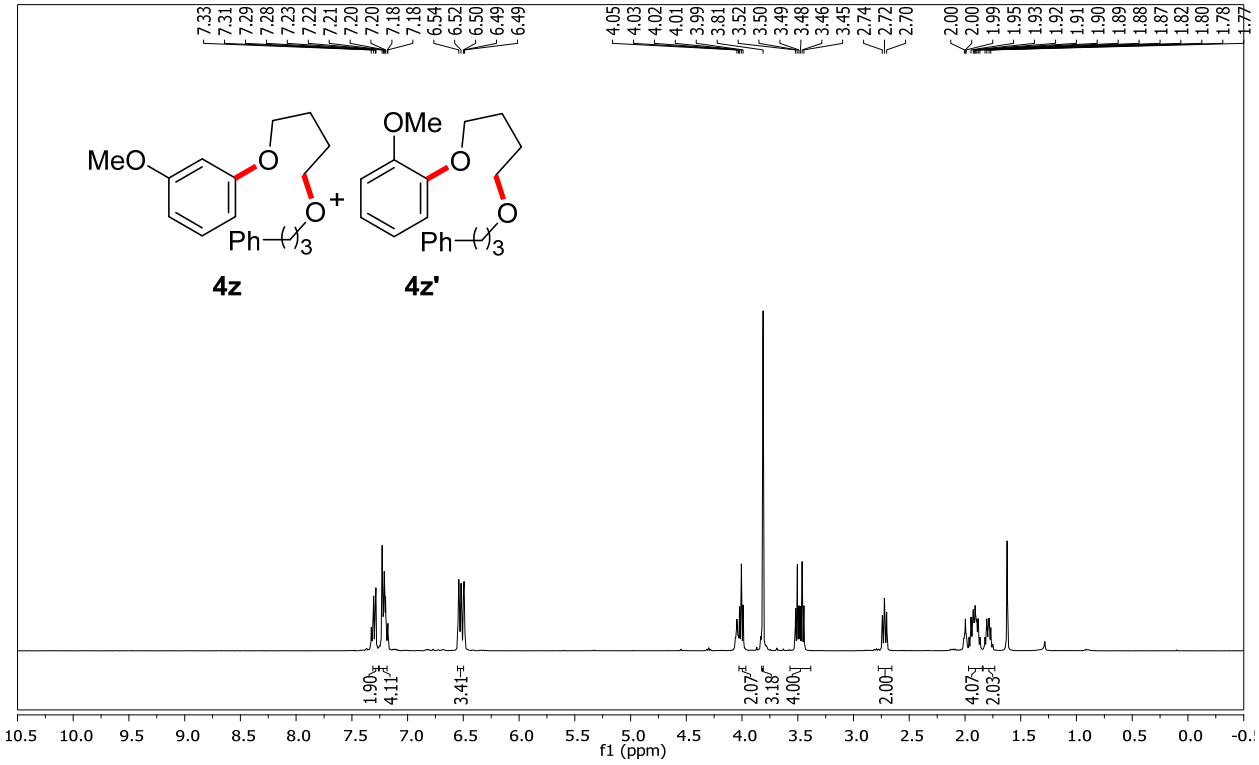


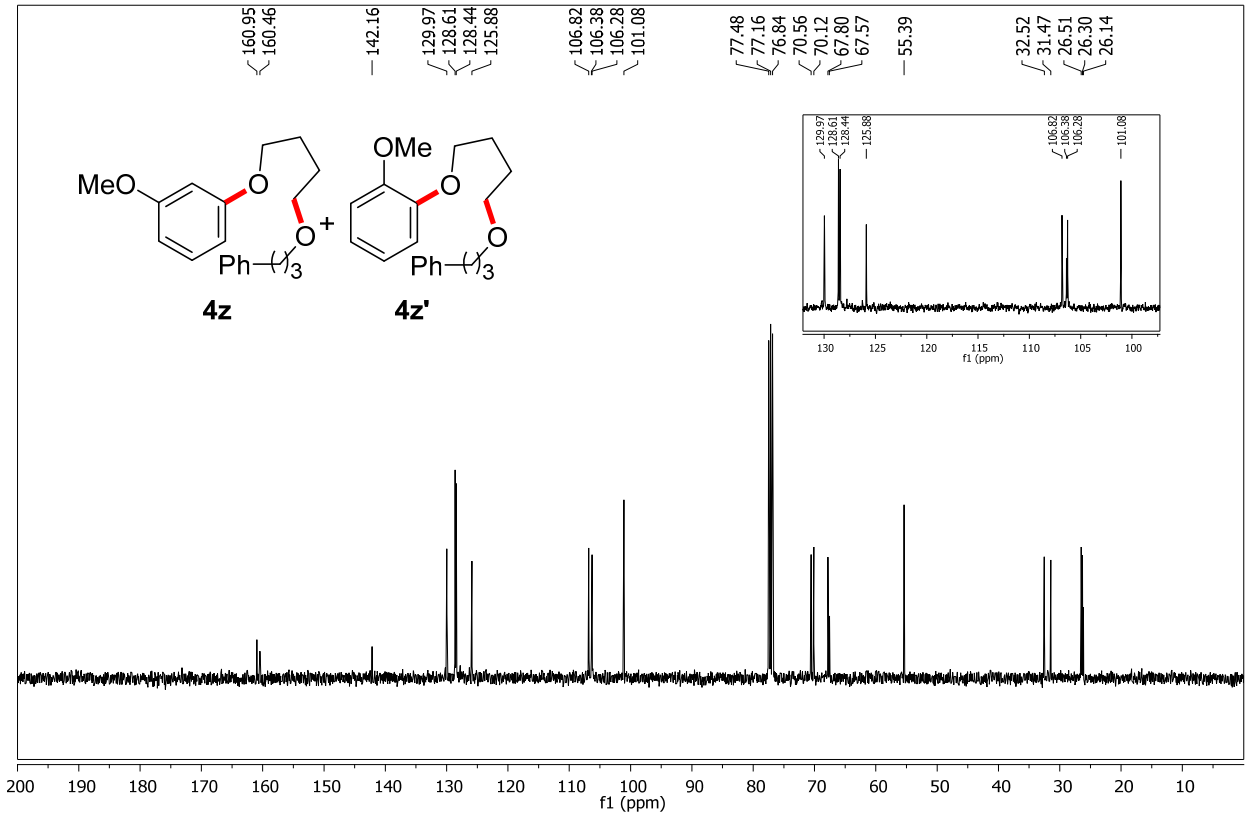
1,4-Dimethyl-2-(4-(3-phenylpropoxy)butoxy)benzene (4y)



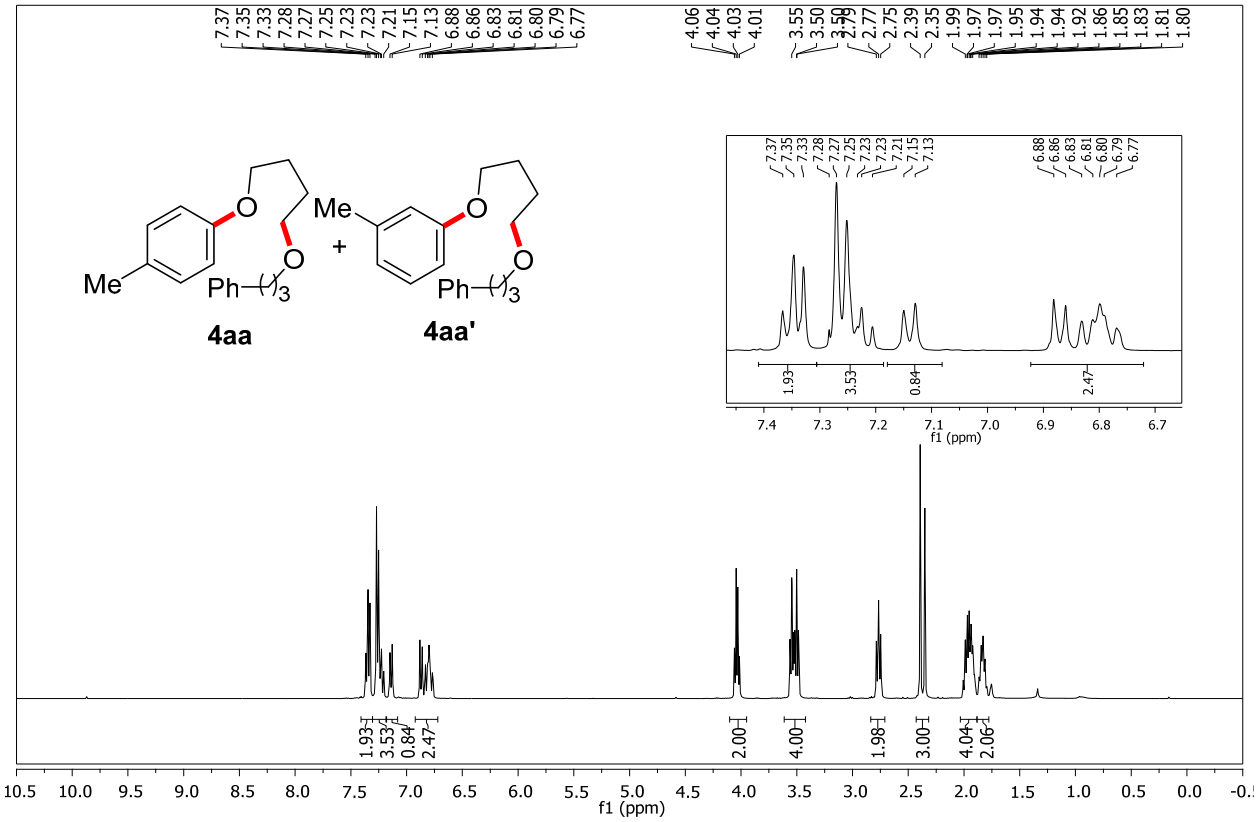


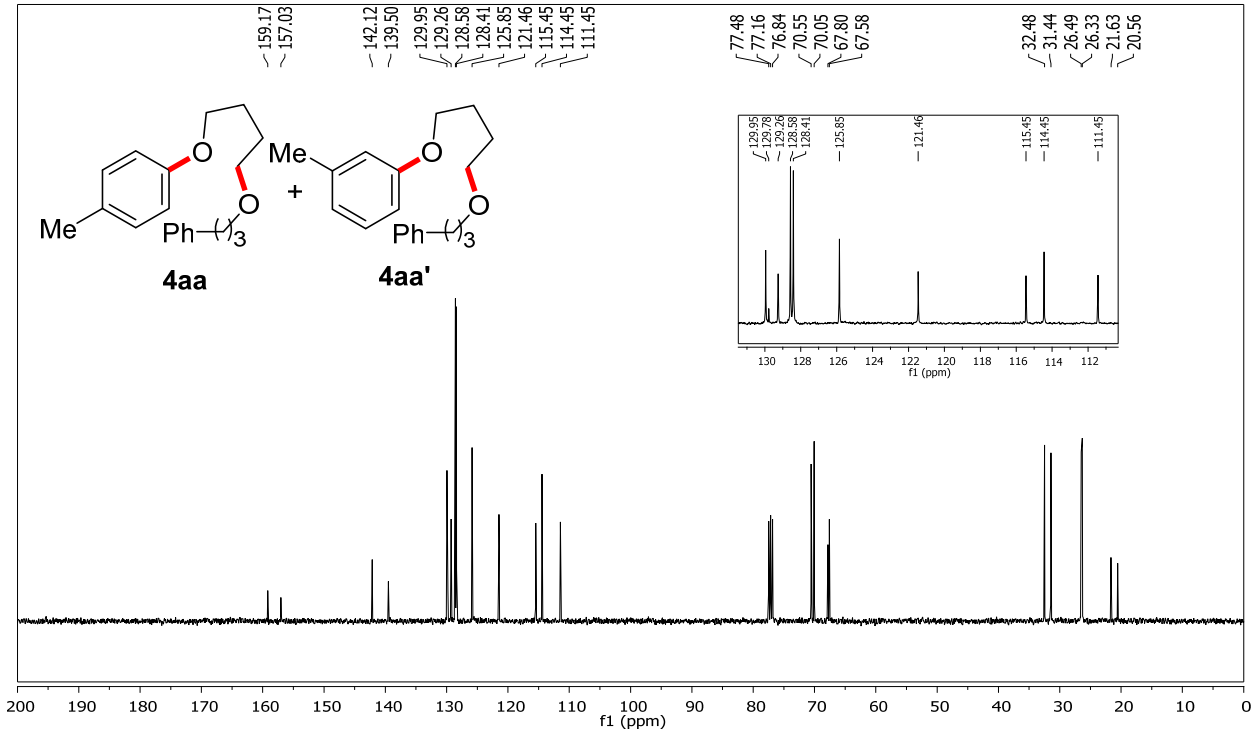
1-Methoxy-3-(4-(3-phenylpropoxy)butoxy)benzene (4z) and 1-Methoxy-2-(4-(3-phenylpropoxy) butoxy)benzene (4z')



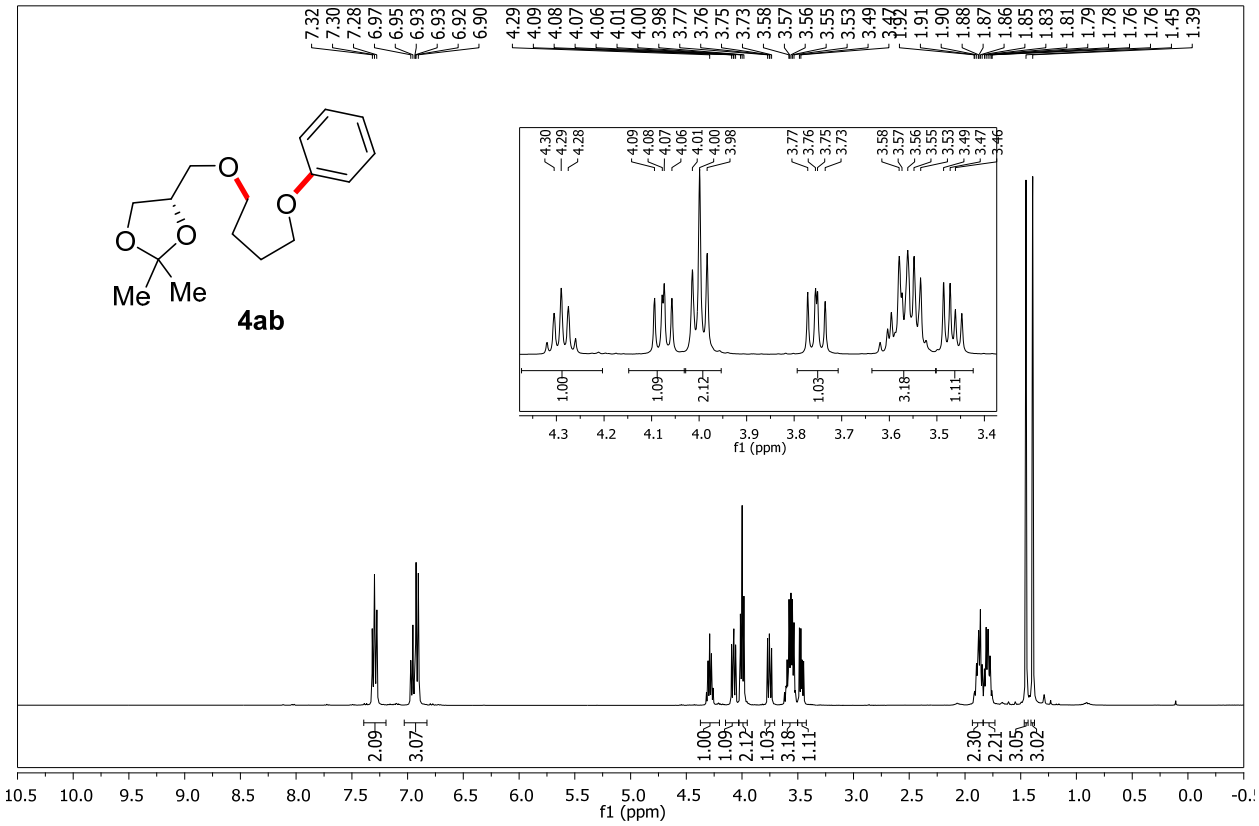


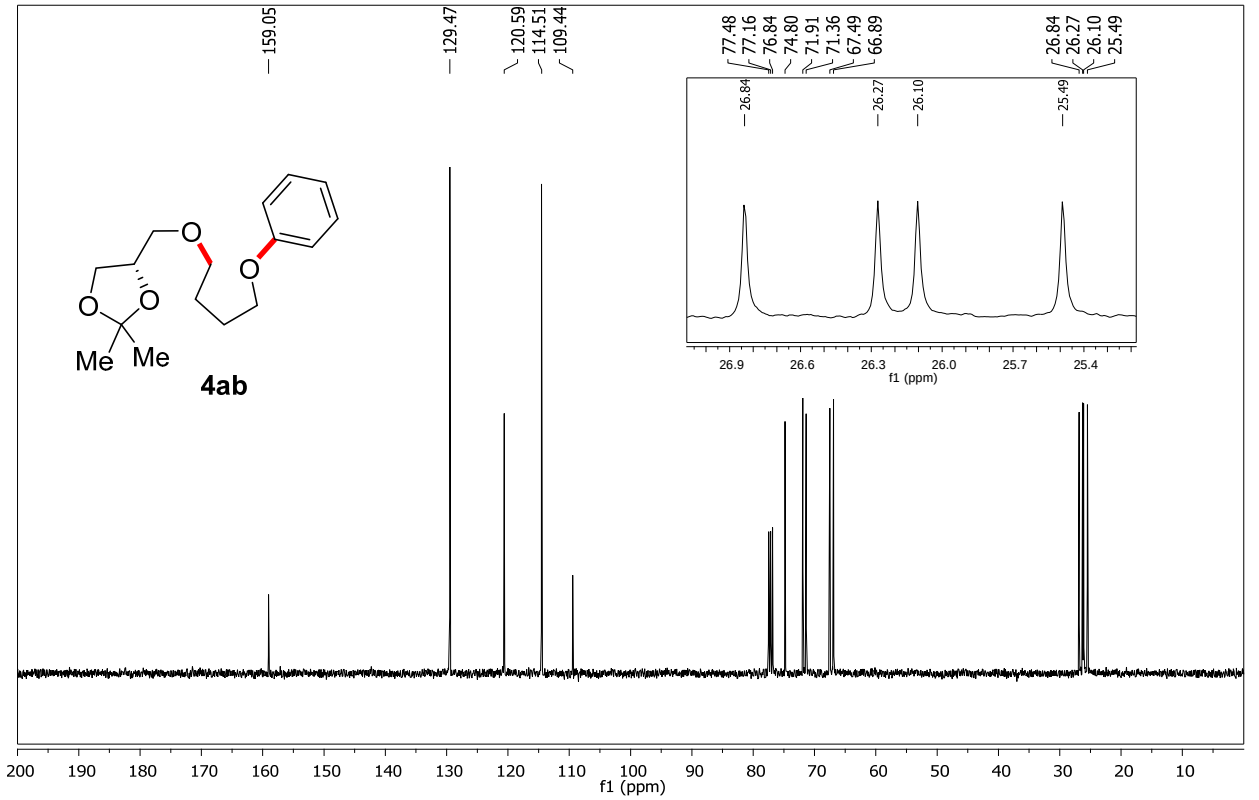
1-Methyl-4-(4-(3-phenylpropoxy)butoxy)benzene (4aa) and 1-Methyl-3-(4-(3-phenyl propoxy)butoxy)benzene (4aa')



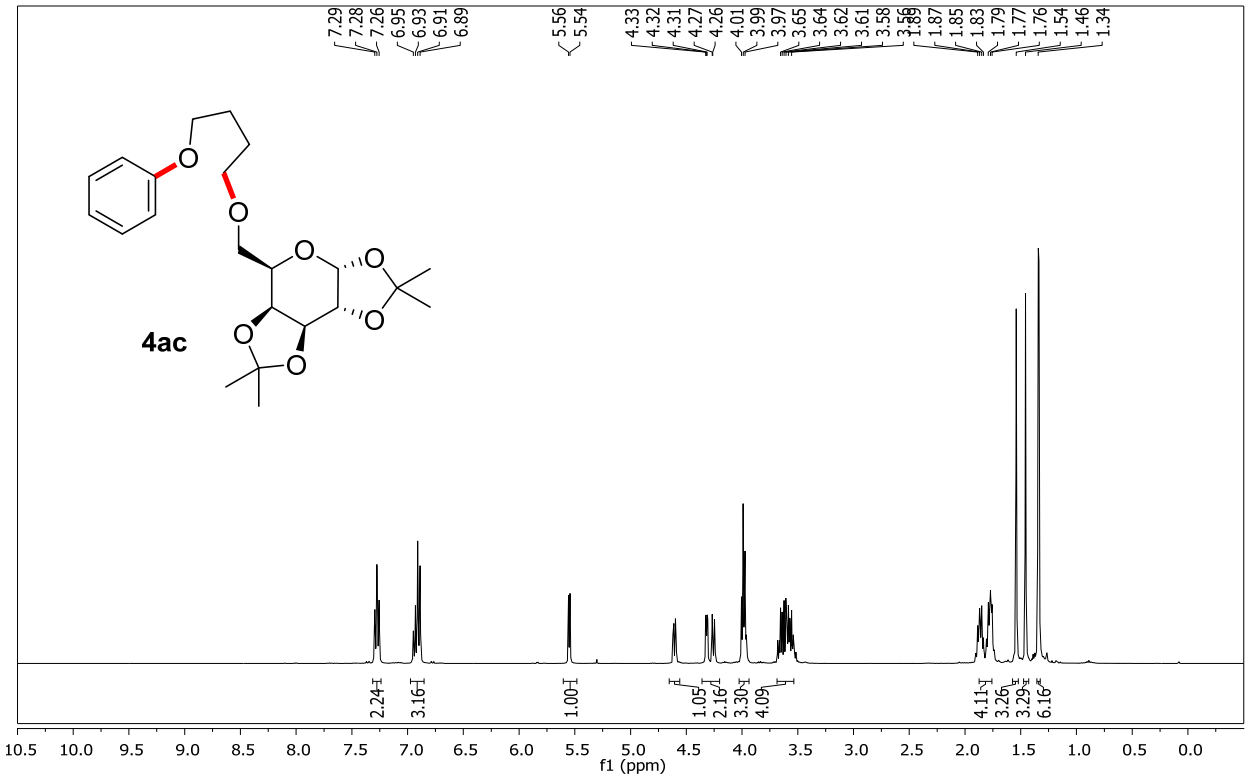


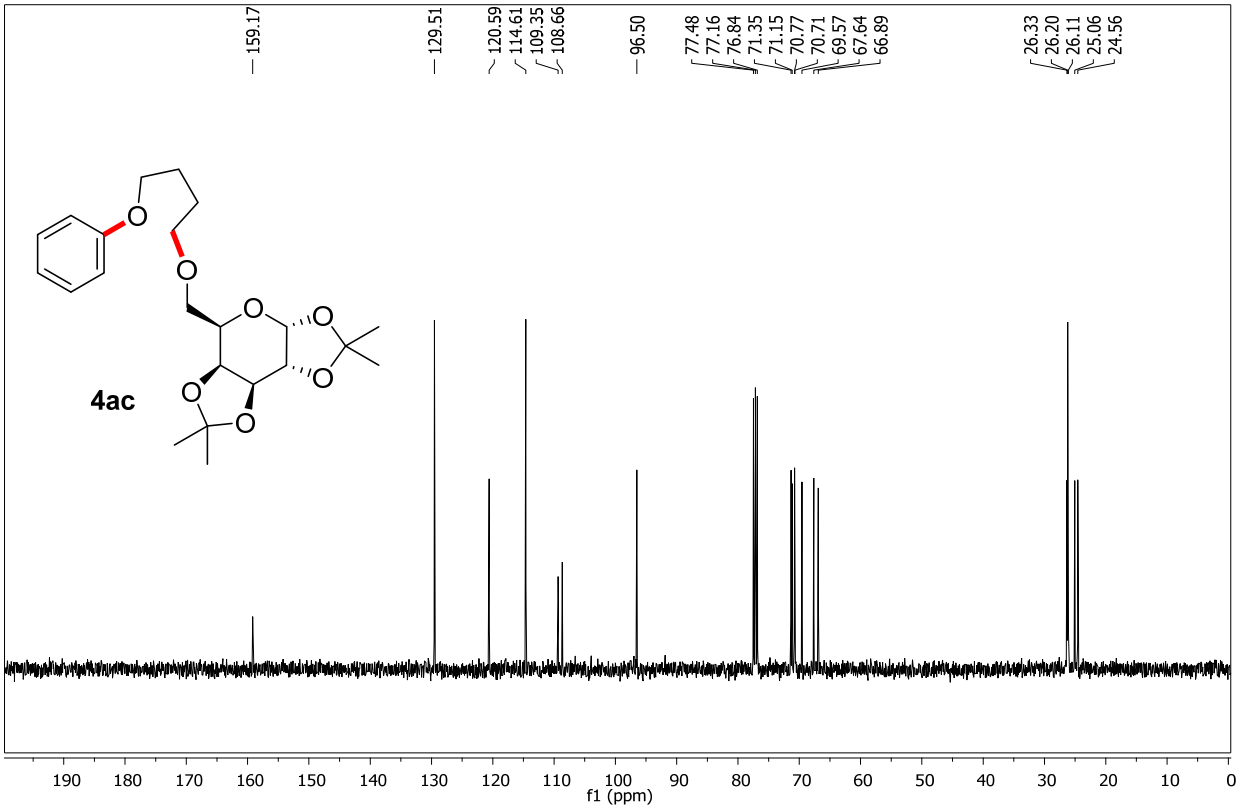
(S)-2,2-Dimethyl-4-((4-phenoxybutoxy)methyl)-1,3-dioxolane (4ab)



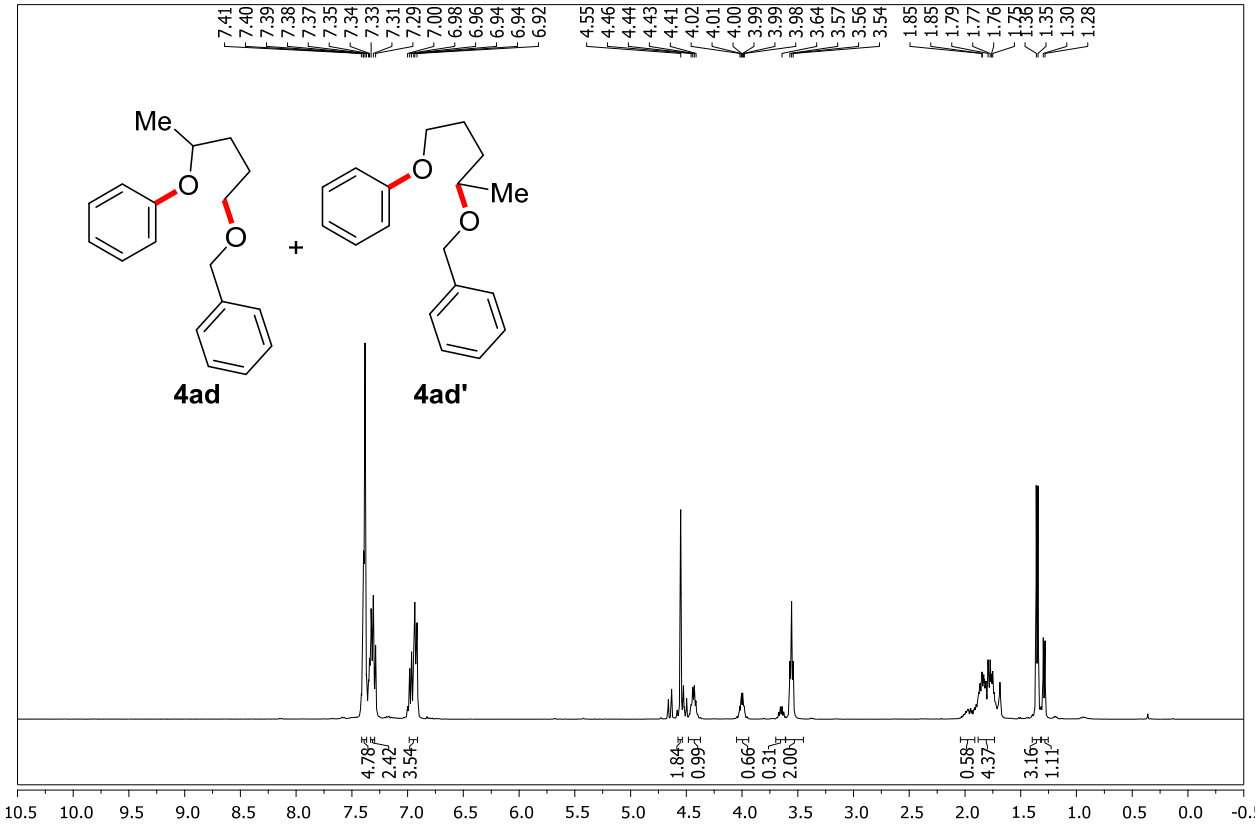


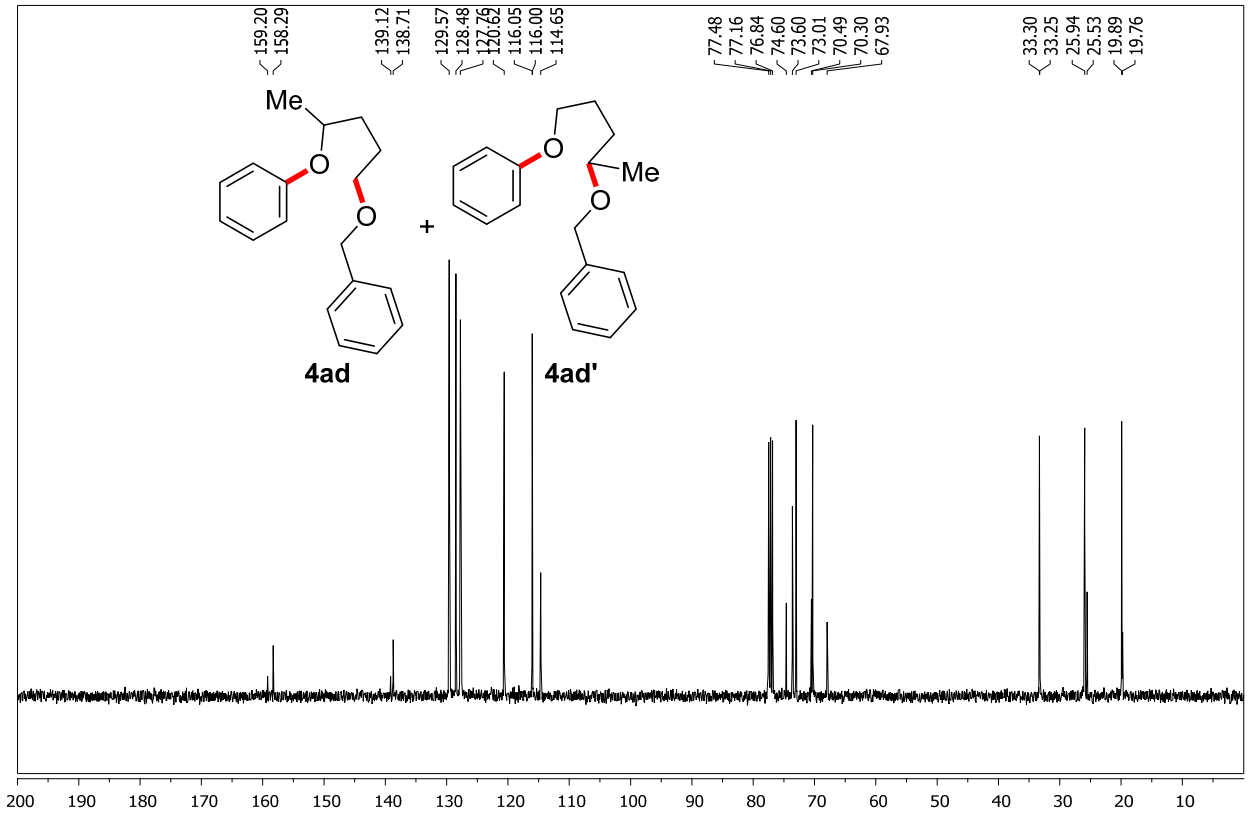
(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyl-5-((4-phenoxybutoxy)methyl)tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (4ac)



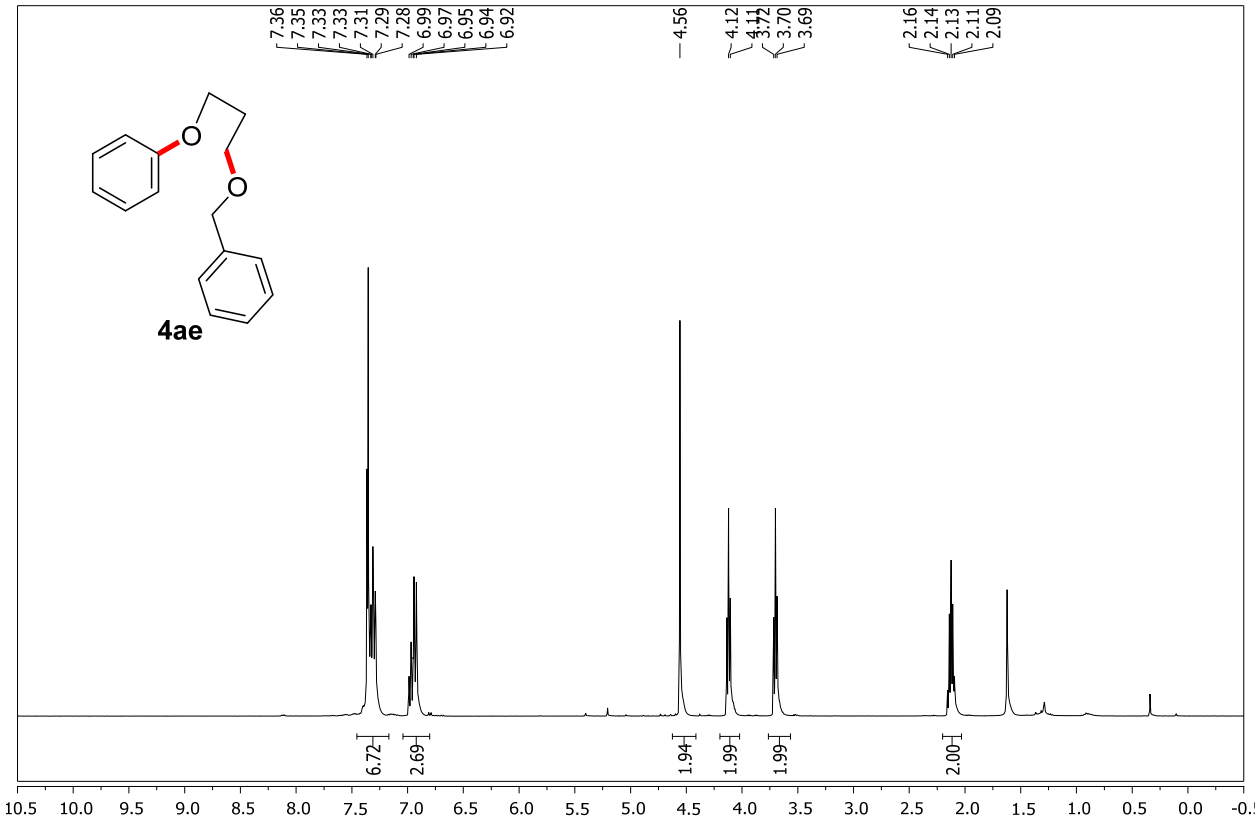


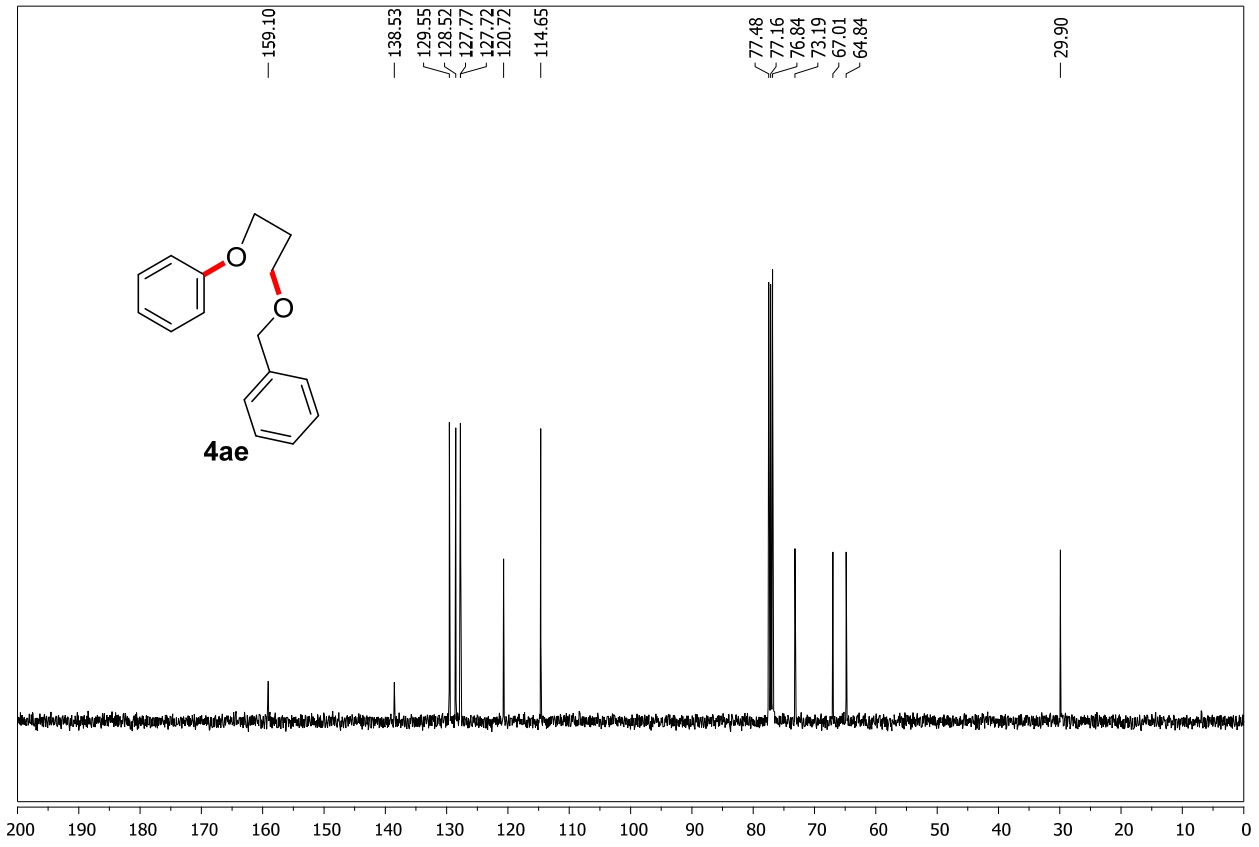
((5-(Benzyloxy)pentan-2-yl)oxy)benzene (4ad) and ((4-(Benzyloxy)pentyl)oxy)benzene (4ad')



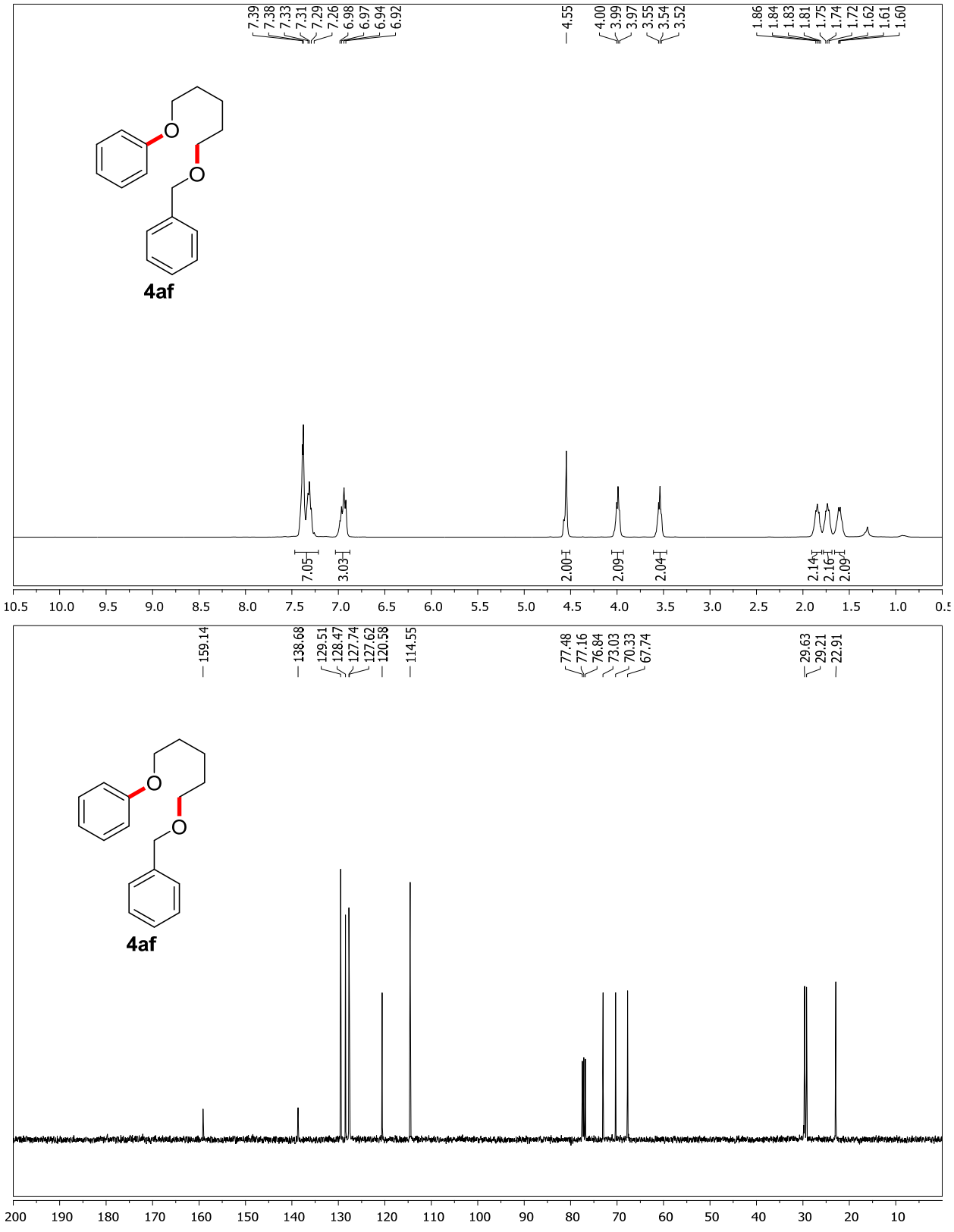


(3-(Benzyloxy)propoxy)benzene (4ae)

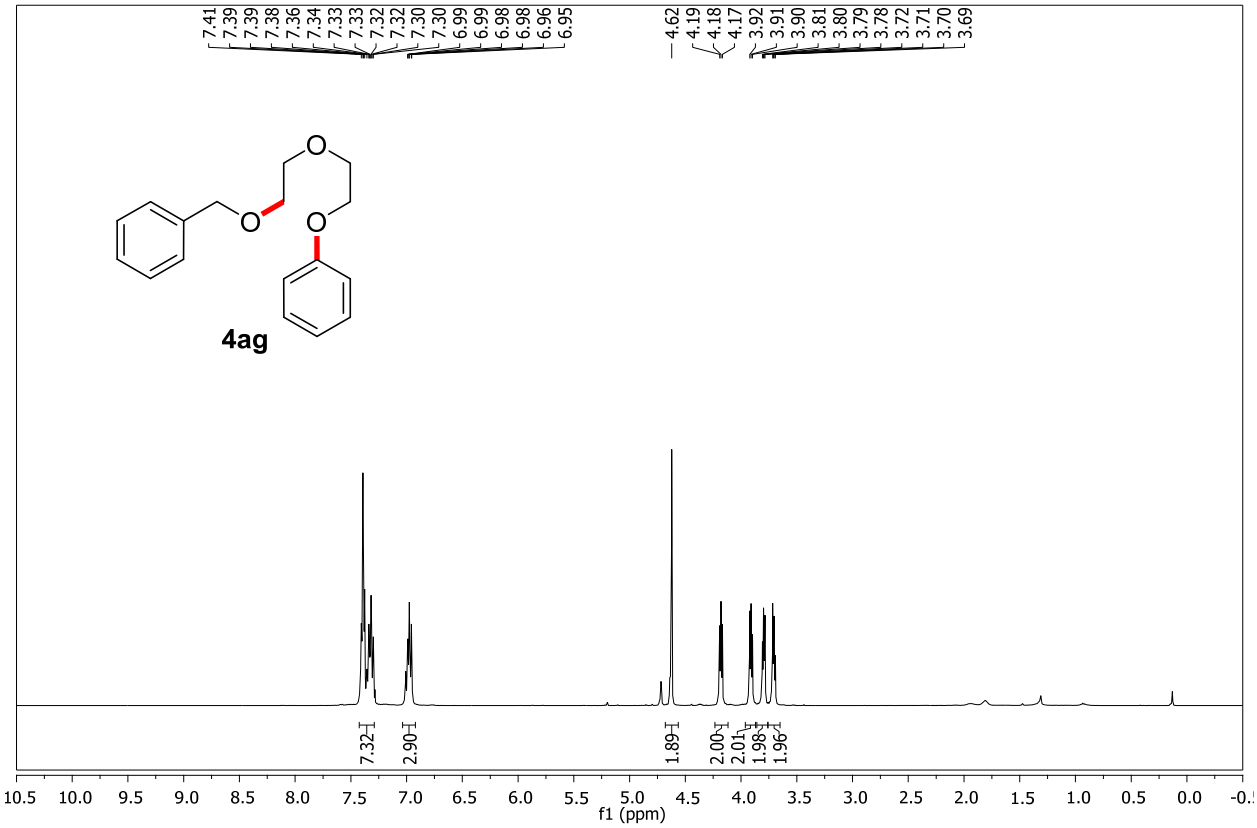


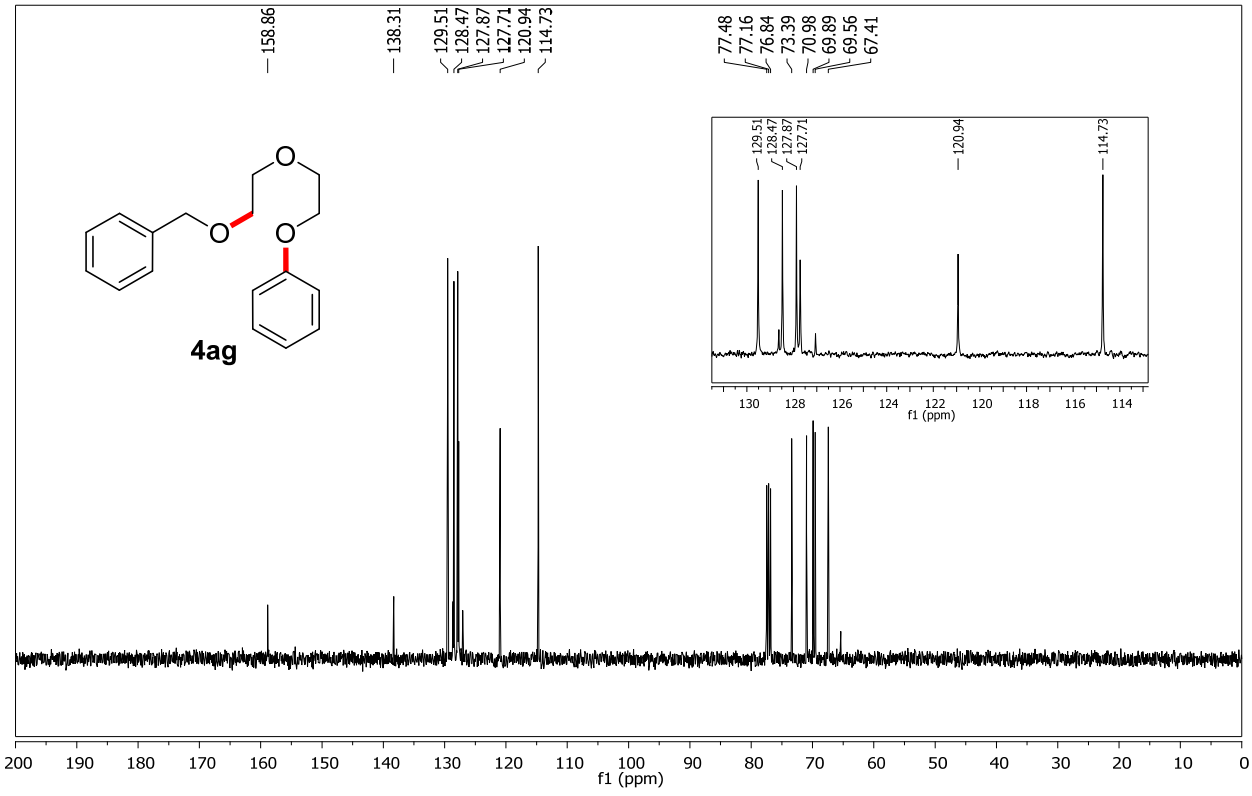


((5-(Benzyloxy)pentyl)oxy)benzene (4af)

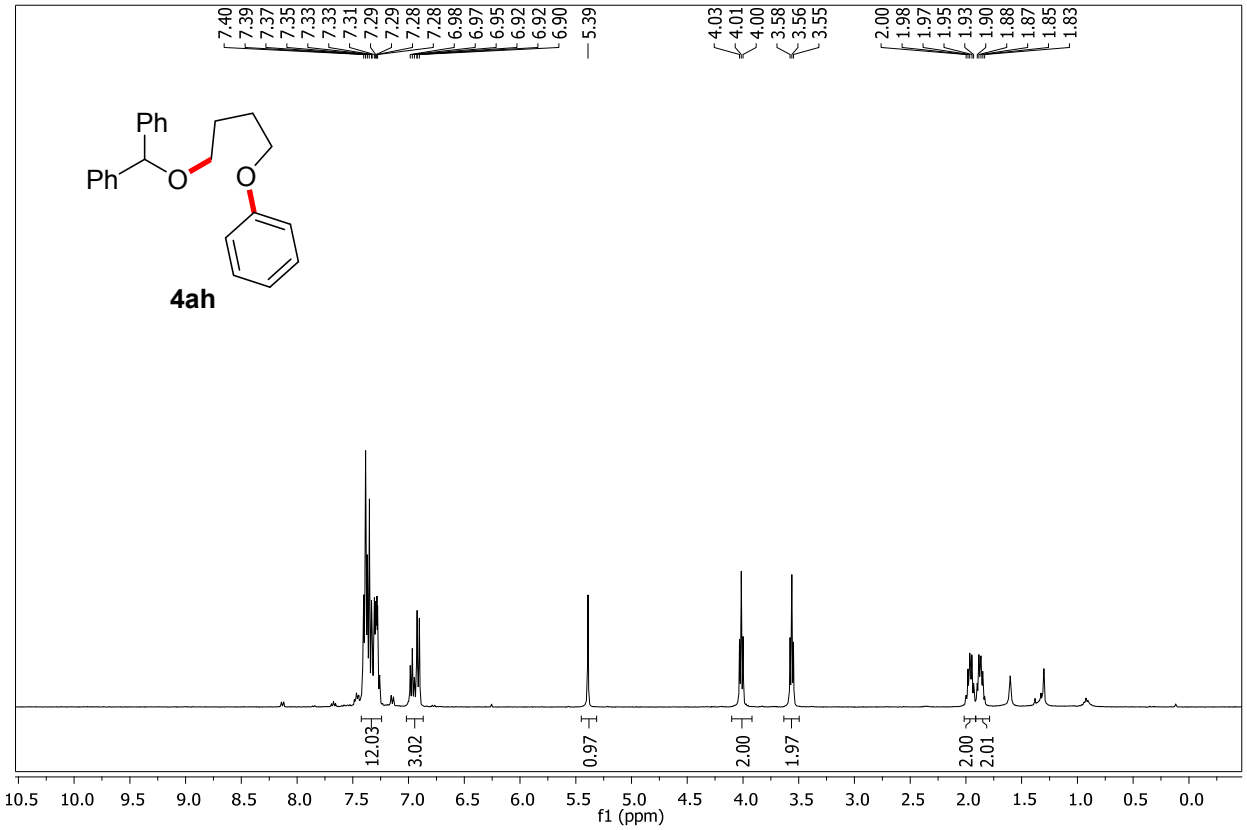


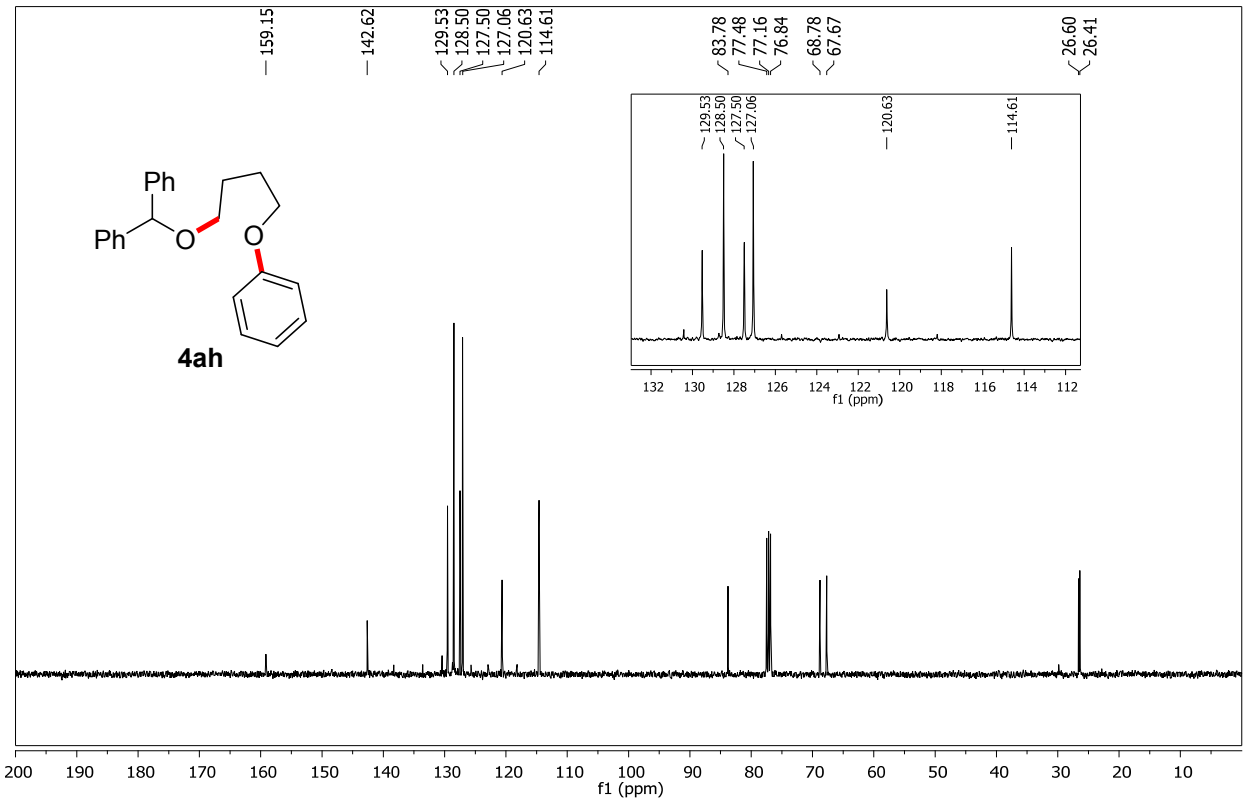
(2-(2-(Benzyloxy)ethoxy)ethoxy)benzene (4ag)





((4-Phenoxybutoxy)methylene)dibenzene (4ah)





((4-Phenoxybutoxy)methanetriyl)tribenzene (4ai)