Supplementary data

Spectra and Experimental Procedures

One-Carbon Extrusion from a Tetraazafulvalene.

Isolation of Aldehydes and a Study of Their Origin

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| Compound                                                                 | Identification Tag | Page  |
|-------------------------------------------------------------------------|--------------------|-------|
| 1-(5-iodopentyl)benzene                                                 | 16                 | S4-S5 |
| 6-phenylhexanal                                                         | 17                 | S6-S7 |
| 1-(6-bromohexyloxy)benzene                                             | 18                 | S8-S9 |
| 7-phenoxyheptanal                                                       | 19                 | S10-S11 |
| 1,3-Dimethyl-2-(3-phenylpropyl)-1H-imidazolium iodide                  | 33                 | S12-S13 |
| 4-Phenylbutyric acid                                                    | 35                 | S14   |
| 1-(3-(3-methylbut-3-enyloxy)propyl)benzene                              | A                  | S15-S16 |
| 1-((4-(3-phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy)methyl)benzene     | 45a                | S17-S18 |
| 1-(4-(4-(3-phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy)butyl)benzene   | 45b                | S19-S20 |
| 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propyl)benzene                   | 45c                | S21-S22 |
| 1-(3-(4-bromo-3-methoxy-3-methylbutoxy)propyl)benzene                   | 45d                | S23-S24 |
| 1-(4-bromobutyl)benzene                                                 | B                  | S25-S26 |
| 1-(4-(3-methylbut-3-enyloxy)butyl)benzene                               | C                  | S27-S28 |
| 1-(4-(4-iodo-3-methoxy-3-methylbutoxy)butyl)benzene                    | 45e                | S29-S30 |
| 1-(3-bromopropoxy)benzene                                               | D                  | S31-S32 |
| 1-(3-(3-methylbut-3-enyloxy)propoxy)benzene                             | E                  | S33-S34 |
| 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)benzene                   | 45f                | S35-S36 |
| 3-(4-methoxyphenoxy)propan-1-ol                                         | F                  | S37-S38 |
| 1-(3-bromopropoxy)-4-methoxybenzene                                     | G                  | S39-S40 |
| 1-(3-(3-methylbut-3-enyloxy)propoxy)-4-methoxybenzene                   | H                  | S41-S42 |
| 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methoxybenzene         | 45g                | S43-S44 |
| 4-(3-phenylpropoxy)butan-1-ol                                            | I                  | S45-S46 |
| 1-(3-(4-bromobutoxy)propyl)benzene                                      | J                  | S47-S48 |
1-(3-(4-(3-methylbut-3-enyloxy)butoxy)propyl)benzene  
1-(3-(4-(4-iodo-3-methoxy-3-methylbutoxy)butoxy)propyl)benzene  
3-phenylpropan-1-ol  
4-phenylbutan-1-ol  
3-phenoxypropan-1-ol  
Mixture L+O isolated from reaction of 45a with 2  
Mixture L+M isolated from reaction of 45b with 2  
N-((E)-But-2-enyl)-N-phenyl-methanesulfonamide  
3-(2-propanal)-1-methanesulfonyl-2,3-dihydro-1H-indole  
1-(2-iodophenyl)but-3-en-1-ol  
1-(3-(1-(2-iodophenyl)but-3-enyloxy)propyl)benzene  
1-(3-(1-phenylbut-3-enyloxy)propyl)benzene  
2-(1-(4-phenylbutoxy)-2,3-dihydro-1H-inden-3-yl)propanal  
(Z)-4-(3-phenylpropoxy)but-2-en-1-ol  
N-((Z)-4-(3-phenylpropoxy)but-2-enyl)-N-(2-iodophenyl)-methanesulfonamide  
N-((Z)-4-(3-phenylpropoxy)but-2-enyl)-N-phenyl-methanesulfonamide  
3-(2-(3-phenylpropoxy)ethyl)-1-methanesulfonyl-2,3-dihydro-1H-indole  
Experimental Procedures  
Cartesian coordinates for computational results on compounds 24 and 25  
References
### Current Data Parameters

**NAME**: A08374  
**EXPNO**: 1  
**PROCNO**: 1

**F2 - Acquisition Parameters**

- **Date**: 20090128  
- **Time**: 8:13  
- **INSTRUM**: DRX500  
- **PROBHD**: 5 mm DUL 13C-1  
- **PULPROG**: zg30  
- **TD**: 65536  
- **SOLVENT**: DMSON  
- **DS**: 2  
- **SWH**: 10288.065 Hz  
- **FIDRES**: 0.156983 Hz  
- **AQ**: 3.185996 sec  
- **RG**: 143.9  
- **NW**: 48.600 usec  
- **DE**: 6.000 usec  
- **TE**: 300.1 K  
- **TD0**: 1  

**========= CHANNEL f1 =========**

- **NUC**: 1H  
- **P1**: 12.00 usec  
- **PL1**: -2.70 dB  
- **SP01**: 500.1330885 MHz

**F2 - Processing parameters**

- **SI**: 32768  
- **SF**: 500.1300084 MHz  
- **WDW**: EM  
- **SSB**: 0  
- **LB**: 0.30 Hz  
- **GB**: 0  
- **FC**: 1.00
Current Data Parameters
NAME             A08658EXPNO                 1PROCNO                1
F2 - Acquisition Parameters
Date_          20090210
Time              18:56
INSTRUM          DRX500
PROBHD   5 mm DUL 13C-1PULPROG            zg30
TD                65536
SOLVENT           CDCl3NS                   16
DS                    2
SWH           10288.065 Hz
FIDRES         0.156983 Hz
AQ            3.1850996 sec
RG                724.1
DW                  48.600 usec
TE                300.0 K
D1                   1.00000000 sec
TDO                   1
-------- CHANNEL f1 --------
NUC1                 1H
F1                 12.00 usec
PL1               -2.70 dB
SF01        500.1330885 MHz
F2 - Processing parameters
SI                32768
SF          500.1300084 MHz
NDW                   EM
SSR                    0
LB                0.30 Hz
GR                    0
PC                   1.00

person 1-10
NJF398 aft col 18
Current Data Parameters
NAME = D93308
EXPNO = 1
PROCNO = 1

F2 - Acquisition Parameters
Date_ = 20061128
Time = 11.43
INSTRUM = dpx_400PROBHD
FIDRES = 0.125483 Hz
AQ = 3.9846387 sec
RG = 256
WM = 8223.685 Hz
NS = 16
DS = 2
SFO = 0.125483 Hz
DSW = 3.9846387 sec
 RG = 256
DW = 60.800 usec
TE = 300.0 K
DI = 0.10000000 sec

---------- CHANNEL f1 ----------
NOC1 = 1Hz
P1 = 7.50 usec
FF1 = -3.00 dB
SFO1 = 400.1332010 MHz

F2 - Processing parameters
SI = 32768
SF = 400.1299951 MHz
WDW = EM
LB = 0 Hz
PC = 4.00

Person 1-10
NJF027_aft_col
Current Data Parameters
NAME             D93387
EXPO            1
PROCNO           1

F2 - Acquisition Parameters
Date_          20061129
Time            20.23
INSTRUM        dpx_400PROBHD     5 mm QNP  1H
F2 - Processing parameters
SI                65536
SF          100.6127483 MHz
WDW                  EMSSB                   0
LB                 1.00 Hz
PC                 2.00

Person 1-10
NJF027
Current Data Parameters
NAME     B03838
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_          20070604
Time              17.17
INSTRUM           AV400PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD            32768
SOLVENT        CDC13
NS                16
DS                2
SNH            8278.146 Hz
FIDRES         0.252629 Hz
AQ            1.9792372 sec
RG                181
DN              60.400 usec
HE                6.00 usec
TE               300.2 K
DI            2.00000000 sec
TDO                1

D = 60.400 usec
E = 6.00 usec

---------- CHANNEL f1 ----------
NUC1              1H
P1                12.00 usec
PL1              -2.50 dB
SFO1        400.0324703 MHz

F2 - Processing parameters
SI           32768
SF        400.0300028 MHz

NJF119_aft_col

9.5  9.0  8.5  8.0  7.5  7.0  6.5  6.0  5.5  5.0  4.5  4.0  3.5  3.0  2.5  2.0  1.5  1.0  0.5 ppm
Current Data Parameters
NAME     B03959
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_          20070606
Time              20.07
INSTRUM           AV400
PROBHD 5 mm PABBO BB-
PULPROG           zg30
TD            32768
SOLVENT        CDCl3
NS             16
DS             2
SNH    8278.146 Hz
FIDRES 0.252629 Hz
AQ    1.9792372 sec
RG            181
DN    60.400 usec
DE             6.00 usec
TE         300.2 K
DI   2.000000000 sec
TDO         1

--- CHANNEL f1 ---
NUC1         1H
P1     12.00 usec
PL1    -2.50 dB
SF01 400.0324703 MHz

F2 - Processing parameters
SI            32768
SF  400.0300028 MHz
MOW      BM
SSB            0
LB             0.30 Hz
GB            0
PC             1.00

NJF122_aft_col
Current Data Parameters
NAME  B03959
EXPN0  2
PROCNO  1

F2 - Acquisition Parameters
Date_  20070606
Time  20.47
INSTRUM  AV400
PULPROG  jmod
TD  16384
SOLVENT  CDCl3
NS  512
DS  4
SNR  23980.814 Hz
FIDRES  1.463673 Hz
AQ  0.3416564 sec
RG  16384
DM  20.850 usec
DE  20.00 usec
TE  300.0 K

DUST1  1.0000000
DUST2  145.0000000
D1  4.00000000 sec
d20  0.00689655 sec
DELTA  0.0001019 sec
TD0  1

======== CHANNEL f1 ========
NUC1  13C
P1  8.00 usec
P2  16.00 usec
PL1  -2.80 dB
SF01  100.5976818 MHz

======== CHANNEL f2 ========
CPDPRG2  waltz16
NUC2  1H
PCFD2  90.00 usec
PL12  14.30 dB
PL2  -3.20 dB
SF02  400.0316001 MHz

F2 - Processing parameters
SI  32768
SP  100.5876580 MHz
MCW  EM
SSB  0
LB  1.00 Hz
GB  0
FC  1.40

NJF122_aft_col
Current Data Parameters
NAME: D93927
EXPN: 1
PROCNO: 1

F2 - Acquisition Parameters
Date: 20061208
Time: 3.21
INSTRUM: dpx_400PROBHD
SOLVENT: CDCl3
NS: 16
DS: 2
DD: 8223.685 Hz
AQ: 3.9846387 sec
RG: 228.1
DE: 60.800 usec
TE: 360.0 kHz
D1: 0.10000000 sec

F1 - Acquisition Parameters
NCH1: 1H
PL1: -3.00 dB
SFO1: 400.1332010 MHz

F2 - Processing parameters
SI: 32768
SF: 400.1299940 MHz
WDW: EMSSB
LB: 0.30 Hz
PC: 4.00

Person 1-10
NJF034B
Current Data Parameters
NAME                D93927
EXPMO               2
PROCNO              1

F2 - Acquisition Parameters
Date_          20061208
Time               3.40
INSTRUM         dpx_400PROBHD     5 mm QNP  1H
PULPROG          zgdc30
TD                16384
SOLVENT         CDCl3NS                 1024
DS                    2
SWH           24154.590 Hz
FIDRES         1.474279 Hz
AQ               0.3391988 sec
RG               2896.3
DM               20.700 usec
DE                5.14 usec
TE                300.0 K
D1              0.6999999 sec
D11            0.830000000 sec

----------- CHANNEL f1 -----------
NUC1                13C
PL1               -3.00 dB
SF01        100.6237964 MHz

----------- CHANNEL f2 -----------
CPDPRG2          waltz16
NUC2                 1H
PCPD2           150.00 usec
PL2               -3.00 dB
PL12            10.00 dB
SF02        400.331808 MHz

F2 - Processing parameters
SI                65536
SF              100.62748 MHz
WDE               EM
SSB              0
LB                1.00 Hz
GR                0
PC                2.00

Person 1-10
NJF034B
Current Data Parameters
NAME  B03892
EXPNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20070605
Time  16.35
INSTRUM  AV400
PROBHD  5 mm PABBO BB-
PULPROG  zg30
TD  32768
SOLVENT  CDCl3
NS  16
DS  2
SNH  8278.146 Hz
FIDRES  0.252629 Hz
AQ  1.9792372 sec
RG  228.1
DN  60.400 usec
DE  6.00 usec
TE  300.2 K
DI  2.00000000 sec
TD0  1

D = CHANNEL f1
NUC1  1H
P1  12.00 usec
PL1  -2.50 dB
SF01  400.0324703 MHz

F2 - Processing parameters
SI  32768
SF  400.0300028 MHz
WDW  BM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00

NJf121_aft_col

45d

9.5  9.0  8.5  8.0  7.5  7.0  6.5  6.0  5.5  5.0  4.5  4.0  3.5  3.0  2.5  2.0  1.5  1.0  0.5 ppm
Current Data Parameters
NAME             B03897
EXPNO             1
PROCNO             1

F2 - Acquisition Parameters
Date_          20070606
Time               3.37
INSTRUM           AV400PROBHD   5 mm PABBO BB-
PULPROG            jmod
TD                16384
SOLVENT           CDCl3NS                  512
DS                    4
SNR                 23980.814 Hz
FIDRES            1.463673 Hz
AQ            0.3416564 sec
RG                 16384
DM                20.850 usec
DE                20.00 usec
TE                300.2 K
CNST11        1.0000000
CNST2       145.0000000
d1           4.00000000 sec
d20          0.00689655 sec
DELTA        0.00001019 sec
TD0                  1

====== CHANNEL f1 ======
NUC1                13C
P1                8.00 usec
P2                16.00 usec
PL1               -2.80 dB
SFO1    100.5976818 MHz

====== CHANNEL f2 ======
CPDPRG2         waltz16
NUC2                 1H
PCPD2              90.00 usec
PL12              14.30 dB
PL2               -3.20 dB
SFO2        400.0316001 MHz

F2 - Processing parameters
SI                32768
SP          100.5876240 MHz
MDW               EM
SSB             0
LB                1.00 Hz
GB             0
FC                1.40

NJF121
Current Data Parameters
NAME                D98738
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date               20070420
Time               4.18
INSTRUM            spect
PROBHD             5 mm QNP 1H/13
PULPROG            zgpp30
TD                 16384
SOLVENT            CDCl3
NS                 1024
DS                2
SWH               23980.814 Hz
FIDRES            1.463673 Hz
AQ                0.3416564 sec
RG                3649.1
DW                 20.850 usec
DE                  6.00 usec
TE               297.2 K
D1            0.69999999 sec
D11           0.03000000 sec
DELTA          0.59999996 sec
TD0             1

------ CHANNEL f1 ------
NUC1              13C
P1                8.00 usec
PL1             -2.60 dB
SF01            100.6228298 MHz

------ CHANNEL f2 ------
CPDPRG2         waltz16
NUC2              1H
PCPD2           80.00 usec
PL2                0.00 dB
PLL2              17.00 dB
PLL13            18.00 dB
SF02            400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW             EM
SSB                0
LB             1.00 Hz
GB                0
PC             1.40

NJF093
Current Data Parameters
NAME             D98893
EXPNO                1
PROCNO                1
F2 - Acquisition Parameters
Date_          20070424
Time               0.53
INSTRUM           spectPROBHD   5 mm QNP 1H/13
PULPROG            jmod
TD                16384
SOLVENT           CDCl3NS                  512
DS                    4
SNR            23980.814 Hz
FIDRES          1.463673 Hz
AQ                 0.3416564 sec
RG                 16384
DM                 0.0000 usec
DE                 6.00 usec
TE                297.2 K
CST2        145.0000000
CST11        1.0000000
D1           4.00000000 sec
d20            0.06489655 sec
DETA             0.00001019 sec
TD0                1

==== CHANNEL f1 ====
NUC1                13C
P1                 8.00 usec
P2                16.00 usec
PL1                -2.60 dB
SFO1        100.6228298 MHz

==== CHANNEL f2 ====
CPDPRG2         waltz16
NUC2                 1H
CPD2             80.00 usec
PL2             0.00 dB
PL12            17.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SP             100.6127690 MHz
MDW        EM
SSB            0
LB                1.00 Hz
GB             0
PC                1.40

NJF096
Current Data Parameters
NAME            B03095
EXPNO            2
PROCNO           1

F2 - Acquisition Parameters
Date_           20070426
Time              19.09
INSTRUM           AV400
PULPROG          jmod
TD              16384
SOLVENT           CDCl3NS
NS          512
DS             4
SNR           23980.814 Hz
FIDRES          1.463673 Hz
AQ            0.3416564 sec
RG              16384
DM            20.850 usec
DE              20.00 usec
TE            300.0 K
CNST2       145.0000000
CNST11       1.0000000
D1           4.00000000 sec
d20         0.00688655 sec
DELTA       0.00001019 sec
TD0             1

====== CHANNEL f1 ======
NUC1     13C
P1             8.00 usec
PL1            -2.80 dB
SFO1    100.5976818 MHz

====== CHANNEL f2 ======
CPDPGR2         waltz16
NUC2     1H
PCPD2         90.00 usec
PL2            -3.20 dB
PL12          14.30 dB
SFO2  400.0316001 MHz

F2 - Processing parameters
SI              32768
SP          100.5876240 MHz
MDW             EM
SSB              0
LB            1.00 Hz
GB             0
PC             1.40

NJF100
Current Data Parameters
NAME            D98528
EXPNO           1
PROCNO          1

F2 - Acquisition Parameters
Date_          20070416
Time              22.13
INSTRUM           spectPROBHD   5 mm QNP 1H/13PULPROG            zg30TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SNR                8278.146 Hz
FIDRES         0.252629 Hz
AQ            1.9792372 sec
RG                287.4
DN                60.400 usec
DE                6.00 usec
TE                300.2 K
DI                2.00000000 sec
TD0                   1

---------- CHANNEL f1 ----------
NUC1                 1H
P1                12.00 usec
PLL               1.10 dB
SF01           400.1324710 MHz

F2 - Processing parameters
SI                32768
SP           400.1300000 MHz
WDW                  EMSSB                   0
LB                 0.30 Hz
GB                0
PC                4.00

NJF090_aft_col
Current Data Parameters
NAME             D98536
EXPNO             1
PROCNO             1

F2 - Acquisition Parameters
Date           20070417
Time            0.20
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD            16384
SOLVENT          CDCl3
NS             1024
DS             2
SWH         23980.814 Hz
FIDRES     1.463673 Hz
AQ             0.3416564 sec
RG         18390.4
DW            20.850 usec
DE             6.00 usec
TE            300.2 K
D1        0.69999999 sec
d11         0.03000000 sec
DELTA       0.59999996 sec
TD0                    1

======= CHANNEL f1 ========
NUC1          13C
P1             8.00 usec
PL1        -2.60 dB
SFO1     100.6228298 MHz

======= CHANNEL f2 ========
CPDPRG2        waltz16
NUC2          1H
CPD2         80.00 usec
PL2           0.00 dB
PL22         17.00 dB
PLL3         18.00 dB
SFO2    400.1316005 MHz

F2 - Processing parameters
SI            32768
SF     100.6127690 MHz
WDW             EM
SB              0
LB          1.00 Hz
GB            0
PC             1.40

NJF090
Current Data Parameters
NAME D98794
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date  20070420
Time  18.59
INSTRUM spectPROBHD 5 mm QNP 1H/13PUL
PROG zg30TD 32768
SOLVENT CDCl3
NS 16
DS 2
SNR 8278.146 Hz
FIDRES 0.252629 Hz
AQ 1.9792372 sec
RG 287.4
DN 60.400 usec
HE 6.00 usec
TE 296.2 K
DI 2.00000000 sec
TDO 1

------ CHANNEL f1 ------
NUC1 1H
P1 12.00 usec
PLL 1.10 dB
SF01 400.1324710 MHz

F2 - Processing parameters
SF 32768
SF 400.1300000 MHz

NJF095b
Current Data Parameters
NAME             D98807
EXPNO             1
PROCNO             1

F2 - Acquisition Parameters
Date_          20070423
Time              19.02
INSTRUM           spect
PROBHD       5 mm QNP 1H/13
PULPROG            jmod
TD                16384
SOLVENT          CDCl3NS
NS                512
DS                4
SNH               23900.814 Hz
FIDRES          1.443673 Hz
AQ             0.3416564 sec
RG                4096
DN              20.850 usec
DE                6.00 usec
TE                 297.2 K
CNST2       145.0000000
CNST11        1.0000000
D1                4.00000000 sec
d20             0.00689655 sec
DELTA            0.00001019 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
p1                8.00 usec
p2               16.00 usec
pL1              -2.60 dB
SF01          100.6228298 MHz

======== CHANNEL f2 ========
CPDPDG2         waltz16
NUC2                1H
CPFD2              80.00 usec
FL2                 0.00 dB
FL12              17.00 dB
SF02          400.1316005 MHz

F2 - Processing parameters
SI                32768
SP            100.612769 MHz
MDW            140
GGB             0
LB               1.00 Hz
GB                0
PC                1.40

NJF095b
Current Data Parameters
NAME D98968
EXPNO 1
PROCHNO 1

F2 - Acquisition Parameters
Date_ 20070425
Time 17.41
INSTRUM spectPROBHD
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SNH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 1.9792372 sec
RG 362
DN 60.400 usec
DE 6.00 usec
TE 296.2 K
D1 2.00000000 sec
TDO 1

---------- CHANNEL f1 ----------
NUC1 1H
P1 12.00 usec
PL1 1.10 dB
SF01 400.1324710 MHz

F2 - Processing parameters
SI 32768
SP 400.1300000 MHz
WMW BM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

NJF098b

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MeO
O
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45f
F

Current Data Parameters
NAME          D99750
EXPNO         2
PROCNO        1

F2 - Acquisition Parameters
Date    20070516
Time    3.57
INSTRUM  spect
PROBHD   5 mm QNP 1H/13
PULPROG  zgpg30
TD       16384
SOLVENT   CDCl3
NS       1024
DS        2
SWH     23980.814 Hz
FIDRES   1.463673 Hz
AQ       0.3416564 sec
RG      5160.6
DW       20.850 usec
DE       6.00 usec
TE       296.2 K
D1     0.69999999 sec
d11    0.03000000 sec
DELTA  0.5999996 sec
TD0    1

====== CHANNEL f1 ======
NUC1         13C
Pl1         -2.60 dB
SF01        100.6228298 MHz

====== CHANNEL f2 ======
CPDPRG2      waltz16
NUC2         1H
PCPD2        80.00 usec
PL2          0.00 dB
PL12         17.00 dB
PL13         18.00 dB
SF02        400.1316005 MHz

F2 - Processing parameters
SI         32768
SP        100.6127690 MHz
WDW        EM
S2B         0
LB          1.00 Hz
GB          0
PC          1.40

NJF108
Current Data Parameters
NAME             D99953
EXPNO            1
PROCNO           1

F2 - Acquisition Parameters
Date_          20070521
Time              20.56
INSTRUM           spect
PROBHD      5 mm QNP 1H/13P
PROG            zg30
TD                32768
SOLVENT        CDCl3
NS             16
DS             2
SNR           3278.146 Hz
FIDRES          0.252629 Hz
AQ            1.9792372 sec
RG                322.5
DW            60.4000 usec
DE             6.00 usec
TE                296.2 K
DI            2.00000000 sec
TDO           1

------ CHANNEL f1 ------
NUC1                 1H
P1                12.00 usec
PLL               1.10 dB
SF01        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300053 MHz
WDW              EMSSB
LB           0.30 Hz
GB             0
PC             4.00

NJF112_aft_col
### Current Data Parameters

| NAME            | D100133EXPNO | 1 |
|-----------------|--------------|---|
| PROCNO          | 1            |   |

### F2 - Acquisition Parameters

- **Date**: 20070524
- **Time**: 1.58
- **INSTRUM**: spect
- **PROBHD**: 5 mm QNP 1H/13
- **PULPROG**: zg30
- **TD**: 32768
- **SOLVENT**: CDCl3
- **NS**: 16
- **DS**: 2
- **SNH**: 8278.146 Hz
- **FIDRES**: 0.252629 Hz
- **AQ**: 1.9792372 sec
- **RG**: 256
- **DN**: 60.400 usec
- **HE**: 6.00 usec
- **TE**: 296.2 K
- **DI**: 2.00000000 sec
- **TD0**: 1

### CHANNEL f1

- **NUC1**: 1H
- **P1**: 12.00 usec
- **PL1**: 1.10 dB
- **SF01**: 400.1324710 MHz

### F2 - Processing parameters

- **SI**: 32768
- **SF**: 400.1300053 MHz
- **WCD**: BM
- **SSB**: 0
- **LB**: 0.30 Hz
- **GB**: 0
- **PC**: 4.00

---

NJF115_aft_col

---

**S-41**
Current Data Parameters
NAME           B03662
EXPNO         1
PROCNO         1

F2 - Acquisition Parameters
Date_        20070531
Time         8.32
INSTRUM       AV400
PROPHD       5 mm PABBO BB-
PULPROG       zg30
TD          32768
SOLVENT       CDCl3
NS           16
DS           2
SNR         8278.146 Hz
FIDRES       0.252629 Hz
AQ           1.9792372 sec
RG          228.1
DW         60.400 usec
DE           6.00 usec
TE           300.2 K
DI    2.00000000 sec
TDO         1

----------- CHANNEL f1 -----------
NUC1            1H
P1         12.00 usec
PL1         2.50 dB
SF01       400.0324703 MHz

F2 - Processing parameters
SI          32768
SP       400.0300028 MHz
MDW        BM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00

NJF117_aft_col
Current Data Parameters
NAME     B03664
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date     20070531
Time     20.44
INSTRUM  AV400
PROBHD   5 mm PABBO BB-
PULPROG  jmod
TD       16384
SOLVENT  CDCl3
NS       512
DS       4
SNH      23980.814 Hz
FIDRES   1.463673 Hz
AQ       0.3416564 sec
RG       16384
DN       20.850 usec
DE       20.00 usec
TE       300.2 K
CNST11   1.0000000
CNST2    145.0000000
D1       4.00000000 sec
d20      0.00689655 sec
DELTA    0.00001019 sec
TD0      1

--- CHANNEL f1 ---
NUC1     13C
P1       8.00 usec
P2       16.00 usec
PL1      -2.80 dB
SFO1     100.5976818 MHz

--- CHANNEL f2 ---
CPDPRG2  waltz16
NUC2     1H
PCPD2    90.00 usec
PL12     14.30 dB
PL2      -3.20 dB
SFO2     400.0316001 MHz

F2 - Processing parameters
SI       32768
SP       100.5876240 MHz
MDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40

NJF117
Current Data Parameters
NAME D98448
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070413
Time 20:14
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 1.9792372 sec
RG 228.1
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
TD0 1

-------- CHANNEL f1 --------
NUC1 1H
P1 12.00 usec
PL1 1.10 dB
SF01 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

NJF085_2
Current Data Parameters
NAME             D98626
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20070418
Time              20.21
INSTRUM           spectPROBHD   5 mm QNP 1H/13
PROBP>>            zg30
TD                  32768
SOLVENT           CDCl3
NS                   16
DS                    2
SNR             8278.146 Hz
FIDRES         0.252629 Hz
AQ            1.9792372 sec
RG                 228.1
DW               60.4000 usec
DE                 6.00 usec
TE                296.2 K
DI               2.00000000 sec
TD0                   1

----- CHANNEL f1 -------
NUC1                 1H
P1                12.00 usec
PL1                1.10 dB
SF01         400.1324710 MHz

F2 - Processing parameters
SI                32768
SP                     400.1300000 MHz
WDW                  BM
SSB                  0
LB                0.30 Hz
GB                  0
PC                  4.00

NJJ092_aft_col
Current Data Parameters
NAME                D98632
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Data               20070419
Time               7.45
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            jmod
TD                16384
SOLVENT           CDCl3
NS                512
DS                4
SWH           23980.814 Hz
FIDRES         1.463673 Hz
AQ            0.3416564 sec
RG                4096
DN               20.850 usec
DR                6.00 usec
TE                297.2 K
CNST1        145.0000000
CNST11        1.00000000 sec
d20            0.00689655 sec
DELTA        0.00001019 sec
TD0                1

------- CHANNEL f1 -------
NUC1                13C
p1                8.00 usec
p2                16.00 usec
PL1                2.60 dB
SP01              100.628298 MHz

------- CHANNEL f2 -------
CPDPDG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              17.00 dB
SP02            400.1316005 MHz

F2 - Processing parameters
S1                32768
SF                 100.6127690 MHz
WDM                EM
SSB                0
LB                1.00 Hz
GR                0
PC                1.40

NJF092
Current Data Parameters
NAME          D99237
EXPNO            1
PROCNO           1

F2 - Acquisition Parameters
Date_          20070502
Time              21.33
INSTRUM         spectPROBHD
PROBHD           5 mm QNP 1H/13
PULPROG         zg30
TD                32768
SOLVENT         CDC13
NS                16
DS                 2
SNR           8278.146 Hz
FIDRES       0.252629 Hz
AQ                1.9792372 sec
RG                362
DN            60.4000 usec
DE                6.00 usec
TE            299.2 K
DI      2.00000000 sec
TD0                 1

------------- CHANNEL f1 -------------
NUC1            1H
P1                12.00 usec
PL1              1.10 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                32768
SF            400.1300000 MHz
WCM                 BM
SSB               0
LB                0.30 Hz
GB                0
PC                4.00

NJF102_aft_col
Current Data Parameters

NAME             D99268
EXPNO                1
PROCNO                1

F2 - Acquisition Parameters
Date_          20070503
Time               2.22
INSTRUM           spectPROBHD   5 mm QNP 1H/13
PULPROG            jmod
TD                16384
SOLVENT           CDCl3NS                  512
DS                    4
SNR               23980.814 Hz
FIDRES            1.443673 Hz
AQ            0.3416564 sec
RG                16384
DM                20.850 usec
DE                6.00 usec
TE                299.2 K
CNST2       145.0000000
CNST11        1.0000000
D1           4.00000000 sec
d20          0.00689655 sec
DELTA        0.00001019 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
p2                16.00 usec
PL1               -2.60 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              17.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SP             100.6127690 MHz
MDW                EM
SSB                0
LE                1.00 Hz
GB                0
FC                1.40

NJF102
Current Data Parameters
NAME              D99554
EXPNO             1
PROCNO            1

F2 - Acquisition Parameters
Date_          20070511
Time              14.21
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG            jmod
TD                16384
SOLVENT           CDCl3NS                  512
DS                    4
SWH           23980.814 Hz
AQ            0.3416564 sec
RG                16384
DM              20,850 usec
DE                6.00 usec
TD0 296.2 K
C1ST2        145.0000000
C1ST11       1.0000000
D1           4.00000000 sec
d20          0.00689655 sec
DELTA        0.00001019 sec

====== CHANNEL f1 ======
NUC1                13C
P1                 8.00 usec
p2              16.00 usec
PFL1             -2.60 dB
SFO1       100.6228298 MHz

====== CHANNEL f2 ======
CPDPRG2        waltz16
NUC2                 1H
CPFD2            80.00 usec
FL2                0.00 dB
PL12             17.00 dB
SFO2      400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EMSSB                   0
LB                1.00 Hz
GB                   0
PC                1.40

NJJ105
From reaction of NJF034 with the doubly-bridged donor

\[
\text{HO-} \quad \begin{array}{c}
  \text{L} \\
\end{array} \quad \text{Ph}
\]
From the reaction of NJF034 with the doubly-bridged donor

\[
\text{HO} - \text{L} - \text{Ar}
\]
From the reaction of NJF100 with the doubly-bridged donor.
From the reaction of NJF100 with the doubly-bridged donor
Current Data Parameters
NAME          D98090
EXPNO             1
PROCNO            1

F2 - Acquisition Parameters
Date_          20070403
Time              20.55
INSTRUM           spect
PROBHD         5 mm QNP 1H/13C
PULPROG      zg30
TD              32768
SOLVENT         CDCl3
NS              16
DS               2
SWH            8278.146 Hz
FIDRES        0.252629 Hz
AQ              1.9792372 sec
RG              322.5
DW             60.400 usec
DE               6.00 usec
TE            300.2 K
DI        2.00000000 sec
TD0          1

-------- CHANNEL f1 --------
NUC1            1H
P1              12.00 usec
PL1            1.10 dB
FO1         400.1324710 MHz

F2 - Processing parameters
SI              32768
SF           400.1300000 MHz
WDW            EM
SSB             0
LB              0.30 Hz
GB              0
PC              4.00

NJJF086_aft_col
is isolated from reaction of 45a with 2
isolated from reaction of 45b with 2

Current Data Parameters
NAME C100498
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070618
Time_ 20.36
INSTRUM spect
PROBHD 5 mm QNP 1H/13PUL
PROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 1.9792372 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 296.2 K
D1 2.00000000 sec
TDO 1

--- CHANNEL f1 ---
NUC1 1H
P1 12.00 usec
PL1 1.10 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

NJJF128_aft_col
NAME              D86452
EXPNOS            2
FREQNO             1
Date_              20060608
Time               22.23
INSTRUM            dpx-400
PROCNO             1
PROBHD              5 mm QNP 1H
PULPROG           jmod
TD                4536
SOLVENT            CDCl3
NS               600
DS               1
MHz               24514.590 Hz
FIDRES           0.368570 Hz
AQ               1.3566452 sec
AQ              1.3566452 sec
DW               20.700 usec
DE               2.14 usec
TE                300.0 K
D1            0.00000000 sec
D13              0.00000000 sec
D13              0.00000000 sec
DELTA            0.00000980 sec

-------------- CHANNEL f1 --------------
CH1               13C
P1                7.70 usec
P2               15.40 usec
Pll               0.00 dB
SV1              100.127598 MHz
-------------- CHANNEL f2 --------------
CPDPRG2        waltz16
CH2               1H
PCPD2              90.00 usec
PCPD2              90.00 usec
P12               18.90 dB
SF               400.1318006 MHz
SI                65536
WDW             EM
SSB                0
PC                 4.00

C-18  210  200  190  180  170  160  150  140  130  120  110  100  90  80  70  60  50  40  30  20  10  0  ppm
S-62
| ppm  | 145.665 | 139.546 | 134.471 | 128.723 | 124.711 | 118.985 | 97.692 | 77.642 | 62.505 |
|------|---------|---------|---------|---------|---------|---------|-------|-------|-------|

**NAME** | D558D8  
**EXPNO** | 2  
**PROCNO** | 1  
**Date** | 20050813  
**Time** | 18.12  
**INSTRUM** | dpx_400  
**PROBHD** | 5 mm QNP 1H  
**PULPROG** | jmod  
**TD** | 65536  
**SOLVENT** | CDCl3  
**NS** | 400  
**SWH** | 24154.590 Hz  
**FIDRES** | 0.368570 Hz  
**AQ** | 1.3565482 sec  
**RG** | 9195.2  
**DW** | 20.700 usec  
**DE** | 7.14 usec  
**TE** | 305.0 K  
**CL** | 4.00000000 sec  
**SU** | 0.00000000 sec  
**DELTA** | 0.00000000 sec  

--- **CHANNEL f1** ---

**NUC1** | 13C  
**P1** | 7.70 usec  
**P2** | 15.40 usec  
**PL1** | -3.00 dB  
**SFO1** | 100.6237964 MHz  
**SFO2** | 400.1311606 MHz  
**WDW** | no  
**SSB** | 0  
**LB** | 0.00 Hz  
**PC** | 4.00  

--- **CHANNEL f2** ---

**NUC2** | 1H  
**PL2** | 9.30 usec  
**CL2** | -3.00 dB  
**SFO2** | 400.1311606 MHz  
**SF** | 100.612768 MHz  
**NWM** | no  
**SHI** | 0  
**IA** | 0.00 Hz  
**IB** | 0  
**IC** | 4.00
**Experimental**

$^1$H NMR spectra were recorded at 400.13 MHz on a Bruker DPX400 or AV400 spectrometer. $^{13}$C NMR spectra were recorded at 100.6 MHz using a broadband decoupled mode on the Bruker DPX400 or AV400 spectrometer. JMOD spectra were used to determine the multiplicities of the carbon resonances. Experiments were carried out using deuterochloroform (CDCl$_3$) unless otherwise stated and chemical shifts are reported in parts per million (ppm). Coupling constants $J$ are reported in Hertz (Hz). The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet; p d, pair of doublets; b, broad; td, triplet of doublets; ddd, doublet of doublet of doublets.

Infrared spectra were recorded on a Perkin Elmer “spectrum One FT-IR” spectrometer. Melting points were recorded using a Gallenkamp 2C 7065 melting point apparatus.

Column chromatography was performed using Prolabo 35-75 μm particle sized silica gel 60 (200-400 mesh). Reactions were followed using thin layer chromatography (TLC) carried out on Merck silica gel 60 F$_{254}$ precoated aluminium plates. Visualisation was achieved under UVP mineralight UVG-11 lamp or by developing plates with methanolic vanillin.

All reagents were obtained from commercial suppliers. Tetrahydrofuran, dichloromethane, hexane, diethyl ether and toluene were dried and deoxygenated with a Pure-Solv 400 solvent purification system (by Innovative Technology Inc., USA). Sodium hydride was supplied as a 60% suspension in mineral oil and was washed with hexane to remove the oil prior to use. Dimethylformamide was obtained from commercial suppliers as anhydrous (99.98%) and used directly.

**Preparation and Reactions of Substrates 16 and 18**

**General Procedure to generate 2 in situ**

Imidazole salt $^{15}$ was heated at 110°C for 1h under vacuum in a centrifuge tube, then cooled to room temperature and sodium hydride (60% suspension with mineral oil, 10 x salt equivalents) was added under argon atmosphere. This mixture was then washed with hexane (2 x 20 ml) and subsequently dried under argon. Dry DMF (15 ml) was deoxygenated with argon for 20 min [alternatively DMA (15 ml) was dried by vacuum distillation and purged with argon for 1 h prior to use] and then added dropwise to
the salt/ sodium hydride residue. This mixture was stirred for 4h at room temperature under argon and then centrifuged. The resulting supernatant liquid was transferred via cannula to the particular substrate [dried beforehand under vacuum at room temperature for 3 h]. The reaction mixture was stirred at room temperature for 18 h [alternatively heated at 110°C for 18 h] under argon atmosphere [see experiment for exact conditions]. Work-up was then carried out.

**Work-up procedures**

Where ‘neutral work-up’ is stated in the experiment, the following procedure was carried out: The reaction mixture was poured into water (20 ml). The aqueous layer was extracted with diethyl ether (3 x 20 ml) and the combined organic layer was then washed with water (4 x 20 ml) and brine (20 ml), dried over sodium sulfate, filtered and removed in vacuo.

Where ‘acidic work-up’ is stated in the experimental procedure, the following was applied: 2 N hydrochloric acid (20 ml) was added and the aqueous layer was extracted with diethyl ether (3 x 20 ml). The combined organic layer was then washed with 2N hydrochloric acid (4 x 20 ml), followed by brine/ hydrochloric acid (20 ml + 10 ml), was subsequently dried over sodium sulfate, filtered and evaporated.

5-Iodopentylbenzene 16.

![5-Iodopentylbenzene](image)

Triphenylphosphine (2.69 g, 0.01025 mol, 1.0 equiv.) was dissolved in dichloromethane (60 ml) at 0°C under an argon atmosphere. To this was added imidazole (0.698 g, 0.1025 mol, 1.0 equiv.) followed by dropwise addition of 5-phenylpentanol (2.59 ml, 15.38 mmol, 1.5 equiv.). The resulting mixture was stirred at 0°C for 30 min, after which iodine (3.9 g, 0.01538 mol, 1.5 equiv.) was added and reaction mixture was stirred at room temperature for 3 h. Diethyl ether (150 ml) was then added and the organic layer was washed with sodium thiosulfate solution (2 x 150 ml), brine (150 ml), was then dried over sodium sulfate, filtered and concentrated in vacuo. The residue was filtered through silica gel (petroleum ether) to afford 5-iodopentylbenzene 16 as a colorless liquid (3.66 g, 87 %);
(Found: $M^+$ 274.0211. $C_{11}H_{15}I$ requires $M^+$, 274.0213); $\nu_{\text{max}}$ (NaCl)/cm$^{-1}$ 3061 (Ar-H), 3025 (Ar-H), 2931 (C-H), 2855 (C-H), 1603 (Ar), 1453 (C-H), 1426 (C-H); $\delta_{\text{H}}$ (CDCl$_3$) 1.42-1.50 (2H, m, CH$_2$), 1.66 (2H, quintet, $J$ 7.7, CH$_2$), 1.87 (2H, quintet, $J$ 7.3, CH$_2$), 2.64 (2H, t, $J$ 7.7, ArCH$_2$), 3.20 (2H, t, $J$ 7.0, CH$_2$I), 7.18-7.21 (3H, m, ArH), 7.27-7.31 (2H, m, ArH); $\delta_{\text{C}}$ (CDCl$_3$) 7.1 (CH$_2$), 30.4 (CH$_2$), 30.6 (CH$_2$), 33.7 (CH$_2$), 35.9 (CH$_2$), 126.0 (CH), 128.5 (CH), 128.6 (CH), 142.2 (C); $m/z$ (El) 274 ($M^+$, 8 %), 183 (3), 147 (19), 105 (18), 91 (100), 65 (21).

**Reaction of 2 with 5-iodopentylbenzene 16.**

(i)

The experiment was carried out according to the general procedure.

*Conditions and reagents:* Room temperature, 18 h, DMF (15 ml), salt 15 (212 mg, 0.45 mmol, 1.5 equiv.), 5-iodopentylbenzene 16 (82 mg, 0.3 mmol, 1.0 equiv.). *Neutral* work-up was carried out and $^1$H-NMR spectroscopic analysis of the crude mixture showed the characteristic aldehyde peak at $\delta$ 9.85 of 17 in trace amount; for data see below.

(ii)

The experiment was carried out according to the general procedure.
Conditions and reagents: Room temperature, 18 h, DMF (15 ml), salt 15 (204 mg, 0.432 mmol, 1.5 equiv.), 5-iodopentylbenzene 16 (79 mg, 0.288 mmol, 1.0 equiv.). The purification of the crude mixture after acidic work-up was carried out by column chromatography on silica gel (20:80 ethyl acetate/ petroleum ether) to afford 6-phenylhexanal 17 as a colorless liquid (9.7 mg, 19 %); ν_{max} (NaCl)/cm^{-1} 2944 (C-H), 2863 (C-H), 2726 (CO-H), 1723 (C=O), 1605 (Ar), 1482 (C-H); δ_{H} (CDCl3) 1.43-1.51 (2H, m, CH₂CH₂CH₂), 1.70-1.79 (4H, m, CH₂CH₂CH₂), 2.51 (2H, td, J 7.3, 1.8, CH₂COH), 2.71 (2H, t, J 7.7, CH₂Ph), 7.25-7.29 (3H, m, ArH), 7.35-7.39 (2H, m, ArH), 9.85 (1H, t, J 1.8, COH); δ_{C} (CDCl3) 22.1 (CH₂), 29.0 (CH₂), 31.4 (CH₂), 35.9 (CH₂), 44.0 (CH₂), 125.9 (CH), 128.5 (CH), 128.6 (CH), 142.6 (C), 202.9 (COH); m/z (EI) 176 (M^+, 17 %), 158 (13), 143 (18), 130 (31), 98 (40), 91 (100), 65 (22).

(iii)

![Chemical structure](image)

The experiment was carried out according to the general procedure with acidic work-up.

Conditions and reagents: Room temperature, 18 h, DMA (15 ml), salt 15 (425 mg, 0.9 mmol, 3.0 equiv.), 5-iodopentylbenzene 16 (80.0 mg, 0.292 mmol, 1.0 equiv.). The purification of the crude mixture after acidic work-up was carried out by column chromatography on silica gel (20:80 ethyl acetate/ petroleum ether) to afford 6-phenylhexanal 17 as a colorless liquid (16.5 mg, 32 %); for data, see experiment (ii) above.

6-Bromohexyloxybenzene 18.
6-Bromohexan-1-ol (0.38 ml, 2.93 mmol, 1.0 equiv.), phenol (275 mg, 2.93 mmol, 1.0 equiv.) and triphenylphosphine (767 mg, 2.93 mmol, 1.0 equiv.) were dissolved in tetrahydrofuran (5 ml) under argon and cooled to 0°C. Diisopropyl azodicarboxylate (0.62 ml, 3.22 mmol, 1.1 equiv.) was then added dropwise and the reaction mixture was stirred at room temperature overnight. The mixture was then concentrated under reduced pressure, loaded onto silica and purified by column chromatography (2:98, then 5:95 ethyl acetate/petroleum ether) to afford 6-bromohexyloxybenzene 18 as a colorless liquid (660 mg, 88%); (Found: M⁺ 256.0455. C₁₂H₁₇BrO requires M⁺, 256.0457; νmax (NaCl)/cm⁻¹ 3039 (Ar-H), 2938 (C-H), 2861 (C-H), 1600 (Ar), 1497 (C-H); δH (CDCl₃) 1.51-1.54 (4H, m, CH₂C₆H₄CH₂), 1.80-1.83 (2H, m, CH₂C₆H₄CH₂), 1.88-1.93 (2H, m, CH₂C₆H₄CH₂), 3.44 (2H, t, J 6.8, C₆H₂Br), 3.97 (2H, t, J 6.4, C₆H₂OPh), 6.89-6.96 (3H, m, ArH), 7.28-7.31 (2H, m, ArH); δC (CDCl₃) 25.4 (CH₂), 28.0 (CH₂), 29.2 (CH₂), 32.8 (CH₂), 33.8 (CH₂), 67.6 (CH₂), 114.5 (CH), 120.6 (CH), 129.5 (CH), 159.1 (C); m/z (EI) 258 (M⁺, 4 % ⁸¹Br), 256 (M⁺, 4 % ⁷⁹Br), 107 (5), 94 (100), 77 (18), 65 (22), 55 (24).

**Test reactions with 6-bromohexyloxybenzene 18**

![Test reaction diagram]

The experiment was carried out according to the general procedure, using an acidic work-up.

**Conditions and reagents:** Room temperature, 18 h, DMF (15 ml), salt 15 (708 mg, 1.5 mmol, 5.0 equiv.), 6-bromohexyloxybenzene 18 (74.3 mg, 0.289 mmol, 1.0 equiv.). The purification of the crude mixture was carried out by column chromatography on silica gel (10:90 ethyl acetate/petroleum ether) to afford 7-phenoxyheptanal 19 as a colorless liquid (30.4 mg, 61%); (Found: M⁺ 206.1299. C₁₃H₁₈O₂ requires M⁺, 206.1301; νmax (NaCl)/cm⁻¹ 2938 (C-H), 2861 (C-H), 2722 (CO-H), 1724 (C=O), 1601 (Ar), 1497 (C-H); δH (CDCl₃) 1.39-1.44 (2H, m, CH₂C₆H₄CH₂), 1.46-1.55 (2H, m, CH₂C₆H₄CH₂), 1.65-1.72 (2H, m, CH₂C₆H₄CH₂), 1.77-1.84 (2H, m, CH₂C₆H₄CH₂), 2.46 (2H, td, J 7.3, 1.8, CH₂COH), 3.97 (2H, t, J 6.4, CH₂O), 6.89-6.97 (3H, m, ArH), 7.26-7.32 (2H, m, ArH), 9.79
(1H, t, J 1.8, COH); δ\textsubscript{H} (CDCl₃) 22.2 (CH₂), 26.1 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 44.0 (CH₂), 67.9 (CH₂), 114.7 (CH), 120.8 (CH), 129.6 (CH), 159.3 (C), 202.9 (CH); m/z (EI) 206 (M⁺, 8 %), 94 (100), 77 (13), 55 (22), 41 (37).

1,3-Dimethyl-2-(3-phenylpropyl)-1H-imidazolium iodide 33

1-Methylimidazole (1.035 g, 1.0 ml, 12.61 mmol, 1.0 equiv.) was dissolved in dry tetrahydrofuran (15 ml) and cooled to –50 °C. Once cool, n-butyllithium (2.4 M in hexane, 5.25 ml, 12.61 mmol, 1.0 equiv.) was added dropwise, to control the temperature below –43 °C. The reaction mixture was stirred for 20 min at low temperature then a solution of 3-phenyl-1-iodopropane (3.41 g, 13.87 mmol, 1.1 equiv.) in tetrahydrofuran (5 ml) was added dropwise. The resulting light yellow solution was stirred under argon for 19 h while slowly warming to room temperature. After this time, the reaction mixture was diluted with diethyl ether (30 ml) and 2M HCl (30 ml) added. The solution was stirred for 10 min, and then the aqueous layer separated. The organic layer was extracted with further 2M HCl (2 x 15 ml) and the combined acidic aqueous layers basified with 2M NaOH until pH 12. The now basic aqueous layer was extracted with chloroform (4 x 40 ml), and the organic layers combined and dried with sodium sulfate, filtered and concentrated \textit{in vacuo} to a clear oil. The oil was dried under vacuum at 120 °C to afford 1-methyl-2-(3-phenylpropyl)-1H-imidazole as a light yellow, clear oil (2.289 g, 91%); (Found: [M+H]⁺ 201.1385. C\textsubscript{13}H\textsubscript{16}N\textsubscript{2} requires [M+H]⁺, 201.1386; \(\nu\)\textsubscript{max} (neat) 3374, 3026, 2943, 2859, 1603, 1497, 1455, 1282, 1123, 1081; δ\textsubscript{H} (CDCl₃, 400 MHz) 2.11 (2H, quintet, J 7.6, CH₂), 2.67 (2H, t, J 7.6, CH₂), 2.74 (2H, t, J 7.4, CH₂), 3.50 (3H, s, CH₃), 6.77 (1H, s, ArH), 6.94 (1H, s, ArH), 7.17-7.21 (3H, m, ArH), 7.27-7.31 (2H, m, ArH); δ\textsubscript{C} (CDCl₃, 125 MHz) 26.0 (CH₂), 29.1 (CH₂), 32.5 (CH₃), 35.3 (CH₂), 120.3 (CH), 125.9 (CH), 127.1 (CH), 128.4 (CH), 128.5 (CH), 141.7 (C), 148.1 (C); m/z (ESI) 201 ([M+H]⁺, 100%), 223 ([M+Na]⁺, 5).
A solution of 1-methyl-2-(3-phenylpropyl)-1H-imidazole (2.0 g, 9.99 mmol, 1.0 equiv.) in acetonitrile (20 ml) was stirred at room temperature and iodomethane (3.11 ml, 49.93 mmol, 5.0 equiv.) was added. The reaction mixture was heated to reflux and stirred under argon for 24 h then slowly cooled to room temperature. Diethyl ether (50 ml) was added resulting in a light yellow solid precipitating. The solid was filtered and washed with further diethyl ether (2 x 50 ml) and dried under vacuum for 18 h to afford 1,3-dimethyl-2-(3-phenylpropyl)-1H-imidazolium iodide as light yellow crystals (2.81 g, 82%); m.p. 136-139 °C; (Found: [M-I]+ 215.1544. C14H19N2I requires [M-I]+, 215.1543; υmax (KBr/cm⁻¹); 3073, 2923, 1633, 1445; δH (DMSO, 500 MHz) 1.90 (2H, quintet, J 8.0, CH₂), 2.70 (2H, t, J 8.0, CH₂), 3.02 (2H, t, J 8.0, CH₂), 3.77 (6H, s, 2 x CH₃), 7.17-7.20 (1H, m, ArH), 7.25-7.31 (4H, m, ArH), 7.60 (2H, s, ArH); δC (DMSO, 125 MHz) 22.6 (CH₂), 27.5 (CH₂), 34.7 (CH₂), 39.5 (CH₃), 122.8 (CH), 126.5 (CH), 128.7 (CH), 128.8 (CH), 141.2 (C), 147.1 (C); m/z (ES+) 215 ([M-I]+, 100%), 365 (6).

Reaction of 1,3-Dimethyl-2-(3-phenylpropyl)-1H-imidazolium iodide 33 with doubly bridged imidazole donor 2

The doubly-bridged imidazole donor diiodide salt (850 mg, 1.8 mmol, 3.0 equiv.) was dried under vacuum for 1 h at 100 °C then cooled to room temperature and purged with argon. Sodium hydride (60 % in oil, 762 mg, 18.0 mmol, 30.0 equiv.) was added and the mixture washed with hexane (2 x 20 ml) and dried under an argon stream. Once dry, degassed, anhydrous N,N-dimethylformamide (20 ml) was added and the resulting yellow mixture stirred under argon at room temperature for 4 h. After this time, the mixture was centrifuged at 2000 rpm for 10 min and the resulting orange liquid added to 1,3-dimethyl-2-(3-phenylpropyl)-1H-imidazolium iodide (205 mg, 0.6 mmol, 1.0 equiv.) via cannula, causing a colour change to dark red. The reaction mixture was stirred under argon for 18 h then exposed to air and 2M HCl (20 ml) added and stirring continued for 30 min. The orange aqueous solution was extracted with
diethyl ether (3 x 30 ml) and the organic layers combined and washed with 2M HCl (4 x 20 ml) and brine/2M HCl (20 ml + 10 ml),
then dried with sodium sulfate, filtered and concentrated to a green waxy residue (20 mg). Purification on silica gel eluting with 20-
80% ethyl acetate/dichloromethane afforded 4-phenylbutyric acid as a white solid (2 mg, 2%); m.p. 46-48 °C (lit.7 49-51 °C); $\nu_{\text{max}}$
(neat) 3400-2400 (b), 3027, 2918, 2849, 1708, 1497, 1454, 1412; $\delta_{\text{H}}$ (CDCl$_3$, 500 MHz) 1.99 (2H, quintet, $J$ 7.5, CH$_2$), 2.39 (2H, t, $J$
7.5, CH$_2$), 2.69 (2H, t, $J$ 7.5, CH$_2$), 7.19-7.22 (3H, m, ArH), 7.27-7.31 (2H, m, ArH); m/z (ESI) 165 ([M+H]$^+$, 41%), 197 (100), 187
(M+Na, 53), 149 (20).

**Preparation of Substrates 45**

**Preparation of 45a**

$1\text {-[3-(3-Methylbut-3-enyloxy)propyl]benzene A.}$

Sodium hydride (60% in mineral oil, 1.12 g, 27.86 mmol, 1.2 equiv.) was washed with dry hexane and dried and then suspended in
DMF (20 ml). 3-Methyl-3-butenol (2.36 ml, 23.22 mmol, 1.0 equiv.) was added and the resultant orange suspension stirred under
argon at r.t. for 1 h. The reaction mixture was cooled to 0 °C and 1-bromo-3-phenylpropane (3.53 ml, 23.22 mmol, 1.0 equiv.) was
added and the resultant reaction mixture warmed to r.t. and stirred under argon for 18 h. Water (5 ml) was added to quench the
reaction mixture, and the organic residues extracted with diethyl ether (3 x 75 ml). The combined organic layers were washed with
water (4 x 75 ml) and brine (75 ml), then dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 5%
diethyl ether in petroleum ether afforded $1\text {-[3-(3-methylbut-3-enyloxy)propyl]benzene A}$ as a colorless oil (2.43 g, 51%); (found:
[M+NH$_4$]$^+$ 222.1852. C$_{14}$H$_{20}$O requires [M+NH$_4$]$^+$ 222.1856); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3064, 3027, 2938, 2860, 1650, 1603, 1497, 1454, 888;
$\delta_{\text{H}}$ (CDCl$_3$) 1.79 (3H, s, CH$_3$), 1.91-1.95 (2H, m, CH$_2$), 2.34 (2H, t, $J$ 6.9, CH$_2$C), 2.72 (2H, t, $J$ 7.0, CH$_2$O), 3.47 (2H, t, $J$
6.4, CH$_2$O), 3.56 (2H, t, $J$ 7.0, CH$_2$O), 4.77 (1H, m, HCH=C), 4.81 (1H, m, HCH=C), 7.21-7.23 (3H, m, ArH), 7.28-7.32 (2H, m, ArH).$\delta_{\text{C}}$ (CDCl$_3$)
1-\{[4-(3-Phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy]methyl\}benzene 45a.

\[
\begin{aligned}
&23.0 \text{ (CH}_3), 31.5 \text{ (CH}_2), 32.6 \text{ (CH}_2), 38.1 \text{ (CH}_2), 69.6 \text{ (CH}_2), 70.2 \text{ (CH}_2), 111.6 \text{ (CH)}, 126.0 \text{ (CH)}, 128.5 \text{ (CH)}, 128.7 \text{ (CH)}, 142.5 \text{ (C)}, 143.3 \text{ (C)}; m/z \text{ (CI)} 222 ([M+NH}_4]^+, 80\%), 205 (100).
\end{aligned}
\]

1-\{[4-(3-Phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy]methyl\}benzene 45a.

\[
\begin{aligned}
&1-\{3-(3-Methylbut-3-enyloxy)propyl\}benzene A \ (1.0 \text{ g}, 4.89 \text{ mmol}, 1.0 \text{ equiv.}) \text{ was dissolved in dry DCM (15 ml) and anhydrous benzyl alcohol (2.02 ml, 19.56 \text{ mmol}, 4.0 \text{ equiv.}) was added and cooled to } -78 \degree \text{ C. } \text{N-Iodosuccinimide (1.65 g, 7.34 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at } -78 \degree \text{ C for 1 h, then warmed to r.t and stirred under argon for 18 h. Sodium thiosulfate (30 ml) was added, causing a color change from dark purple to colorless. The reaction mixture was extracted with DCM (3 x 50 ml) and the combined organic layers then washed with water (3 x 50 ml) and brine (70 ml), dried and concentrated } in \text{ vacuo to give a yellow oil. Purification by silica gel chromatography, eluting with 0-10\% diethyl ether in PE, afforded 1-\{[4-(3-phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy]methyl\}benzene 45a as a colorless oil (1.46 g, 72\%); (found: [M+NH}_4]^+ 456.1400. C\text{\textsubscript{21}}H\text{\textsubscript{27}}IO\textsubscript{2} \text{requires} [M+NH}_4]^+ 456.1394); \nu_{max} (\text{neat})/\text{cm}^{-1} \ 3062, 3026, 2938, 2864, 1602, 1496, 1453; \delta_{\text{H}} (\text{CDCl}_3) 1.41 \ (3\text{H}, s, \text{CH}_3), 1.87-1.94 \ (2\text{H}, m, \text{CH}_2), 2.01-2.16 \ (2\text{H}, m, \text{CH}_2\text{C}), 2.70 \ (2\text{H}, t, J 7.7, \text{CH}_2\text{Ar}), 3.38-3.46 \ (4\text{H}, m, \text{CH}_2\text{I, CH}_2\text{O}), 3.56 \ (2\text{H}, t, J 6.8, \text{CH}_2\text{O}), 4.49 \ (2\text{H}, s, \text{OCH}_2\text{Ar}), 7.18-7.21 \ (3\text{H}, m, \text{ArH}), 7.26-7.31 \ (3\text{H}, m, \text{ArH}), 7.32-7.39 \ (4\text{H}, m, \text{ArH}); \delta_{\text{C}} (\text{CDCl}_3) 16.6 \ (\text{CH}_2), 23.6 \ (\text{CH}_3), 31.3 \ (\text{CH}_2), 32.4 \ (\text{CH}_2), 37.2 \ (\text{CH}_2), 63.9 \ (\text{CH}_2), 66.7 \ (\text{CH}_2), 70.2 \ (\text{CH}_2), 74.4 \ (\text{C}), 125.7 \ (\text{CH}), 127.5 \ (\text{CH}), 128.3 \ (\text{CH}), 128.5 \ (\text{CH}), 138.7 \ (\text{C}), 141.9 \ (\text{C}); m/z \text{ (CI)} 456 ([M+NH}_4]^+, 75\%), 311 (100).
\end{aligned}
\]

1-\{[4-(3-Phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy]butyl\}benzene 45b.
1-[3-(3-Methylbut-3-enyloxy)propyl]benzene A (500 mg, 2.45 mmol, 1.0 equiv.) was dissolved in dry DCM (8 ml) and 4-phenylbutanol (0.755 ml, 4.90 mmol, 2.0 equiv.) added and cooled to -78 °C. N-Iodosuccinimide (828 mg, 3.68 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at -78 °C for 1 h, then warmed to r.t and stirred under argon for 18 h. Sodium thiosulfate (15 ml) was added, causing a color change from dark purple to colorless. The reaction mixture was extracted with DCM (3 x 50 ml) and then the combined organic layers were washed with water (3 x 50 ml) and brine (50 ml), dried and concentrated in vacuo to give a yellow oil. Purification by silica gel chromatography, eluting with 0-10% diethyl ether in PE, afforded 1-{4-[4-(3-phenylpropoxy)-1-iodo-2-methylbutan-2- yloxy]butyl}benzene 45b as a colorless oil (717 mg, 61%); (found: [M+NH4]+ 498.1860. C24H33IO2 requires [M+NH4]+ 498.1861); v_max (neat)/cm⁻¹ 3060, 3025, 2936, 2861, 1602, 1495, 1453; δ_H (CDCl3) 1.33 (3H, s, CH₃), 1.56-1.64 (2H, m, CH₂), 1.69-1.76 (2H, m, CH₂), 1.86-2.04 (4H, m, CH₂C, CH₂), 2.63-2.71 (4H, m, CH₂Ar x 2), 3.32-3.36 (4H, m, CH₂I, CH₂O), 3.42 (2H, t, J 6.4, CH₂O), 3.50 (2H, t, J 6.9, OCH₂Ar), 7.15-7.21 (6H, m, ArH), 7.27-7.31 (4H, m, ArH); δ_C (CDCl3) 16.9 (CH₂), 23.4 (CH₃), 28.1 (CH₂), 29.9 (CH₂), 31.3 (CH₂), 32.4 (CH₂), 35.8 (CH₂), 37.1 (CH₂), 61.2 (CH₂), 66.7 (CH₂), 70.2 (CH₂), 73.5 (C), 125.7 (CH), 125.8, 128.2 (CH), (CH), 128.3 (CH), 128.4 (CH), 142.0 (C), 142.5 (C); m/z (Cl) 498 ([M+NH₄]⁺, 36%), 481 (52), 355 (100)

1-[3-(4-Iodo-3-methoxy-3-methylbutoxy)propyl]benzene 45c.

1-[3-(3-Methylbut-3-enyloxy)propyl]benzene A (1.4g, 6.85 mmol, 1.0 equiv.) was dissolved in dry DCM (30 ml) and anhydrous methanol (0.55 ml, 13.70 mmol, 2.0 equiv.) added and cooled to -78 °C. N-Iodosuccinimide (2.31 g, 10.28 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at -78 °C for 1 h, and then warmed to r.t and stirred under argon for 18 h.
Sodium thiosulfate (20 ml) was added, causing a color change from dark purple to clear. The reaction mixture was extracted with DCM (3 x 60 ml) and the combined organic layers washed with brine (3 x 50 ml), dried and concentrated in vacuo to give a red oil. Purification by silica gel chromatography eluting with 0-15% diethyl ether in PE afforded 1-[3-(4-iodo-3-methoxy-3-methylbutoxy)propyl]benzene 45c as a light brown oil (1.75 g, 71%); (found: [M+H]^+ 363.0815. C_{15}H_{23}I_{2}O requires [M+H]^+ 363.0862); v_{max} (neat)/cm^{-1} 3061, 3025, 2939, 2863, 1602, 1496, 1454, 1374; \delta_1 (CDCl_3) 1.40 (3H, s, CH_3), 1.93-2.08 (4H, m, CH_2C, CH_2), 2.76 (2H, t, J 7.9, CH_2Ar), 3.28 (3H, s, CH_2O), 3.38 (1H, d, J 10.8, CH(HI)), 3.43 (1H, d, J 10.8, CH(HI)), 3.49 (2H, t, J 6.4, CH_2O), 3.56 (2H, t, J 6.8, CH_2O), 7.24-7.27 (3H, m, ArH), 7.33-7.37 (2H, m, ArH); \delta_C (CDCl_3) 16.4 (CH_2), 23.0 (CH_3), 31.5 (CH_2), 32.6 (CH_2), 36.8 (CH_2), 49.7 (CH_3), 66.9 (CH_2), 70.4 (CH_2), 74.1 (C), 125.9 (CH), 128.5 (CH), 128.7 (CH), 142.2 (C); m/z (Cl) 363 ([M+H]^+, 20%), 91 (100), 222 (65).

1-[3-(4-Bromo-3-methoxy-3-methylbutoxy)propyl]benzene 45d

1-[3-(3-Methylbut-3-enyloxy)propyl]benzene A (500 mg, 2.45 mmol, 1.0 equiv.) was dissolved in dry DCM (8 ml) and anhydrous methanol (0.4 ml, 9.80 mmol, 4.0 equiv.) added and cooled to -78 °C. N-Bromosuccinimide (655 mg, 3.68 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at -78 °C for 1 h, then warmed to r.t and stirred under argon for 18 h. Sodium thiosulfate (20 ml) was added, causing a color change from dark purple to colorless. The reaction mixture was extracted with DCM (2 x 50 ml) and then washed with water (3 x 50 ml) and brine (50 ml), dried and concentrated in vacuo to give a yellow oil. Purification by silica gel chromatography eluting with 0-10% diethyl ether in PE afforded 1-[3-(4-bromo-3-methoxy-3-methylbutoxy)propyl]benzene 45d as a colorless oil (360 mg, 47%); (found: [M+NH_4]^+ 332.1220. C_{15}H_{23}BrO_2 requires [M+NH_4]^+ 322.1220); v_{max} (neat)/cm^{-1} 3062, 3026, 2940, 2864, 1602, 1496, 1455; \delta_1 (CDCl_3) 1.32 (3H, s, CH_3), 1.88-2.01 (4H, m, CH_2, CH_2C), 2.70 (2H, t, J 7.7, CH_2Ar), 3.23 (3H, s, OCH_3), 3.39-3.51 (6H, m, CH_2Br, CH_2OCH_2), 7.17-7.21 (3H, m, ArH), 7.24-7.31 (2H, m,
ArH); δC (CDCl3) 21.9 (CH3), 31.3 (CH2), 32.4 (CH2), 35.9 (CH2), 39.6 (CH2), 49.5 (CH3), 66.4 (CH2), 70.2 (CH2), 74.8 (C), 125.8 (CH), 128.3 (CH), 128.5 (CH), 142.0 (C); m/z (Cl) 317 ([MH]+ 81Br, 21%), 315 ([MH]+ 79Br, 22), 205 (100).

**Preparation of 45e**

**1-Bromo-4-phenylbutane B**

![](image1)

4-Phenyl-1-butanol (3.076 ml, 19.97 mmol, 1.0 equiv.) was dissolved in dry diethyl ether (20 ml) and cooled to -5 °C where phosphorus tribromide (0.939 ml, 9.99 mmol, 0.5 equiv.) was added (temperature maintained below 0 °C for duration of addition). The clear solution was stirred under argon for 18 h and the color changed from colorless to orange during the reaction time. The orange solution was quenched by slowly pouring into water and the organic residue extracted with diethyl ether (100 ml), then washed with water (3 x 50 ml) and brine (50 ml), then dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 0-5% EtOAc in petroleum ether afforded 1-bromo-4-phenylbutane B as a colorless oil (2.55 g, 60%); δ (CDCl3) 1.79-1.83 (2H, m, CH2), 1.91-1.95 (2H, t, J 7.6, CH2Ar), 2.68 (2H, t, J 7.6, CH2Ar), 3.45 (2H, t, J 6.7, CH2Br), 7.20-7.24 (3H, m, ArH), 7.28-7.34 (2H, m, ArH); δC (CDCl3) 29.8 (CH2), 32.3 (CH2), 33.7 (CH2), 34.9 (CH2), 125.9 (CH), 128.3 (CH), 128.5 (CH), 141.8 (C); m/z (EI) 214 ([M]+, 81Br, 100%), 212 (79Br, 95), 205 (79Br, 95), 133 (73), 132 (61).

**1-[4-(3-Methylbut-3-enyloxy)butyl]benzene C**

Sodium hydride (60% in mineral oil, 497 mg, 12.39 mmol, 1.2 equiv.) was washed with dry hexane and dried, then suspended in DMF (7 ml). 3-Methyl-3-butenol (1.05 ml, 10.32 mmol, 1.0 equiv.) was added and the resultant orange suspension stirred under argon at r.t.
for 1 h. The reaction mixture was cooled to 0 °C and 1-bromo-4-phenylbutane B (2.2 g, 10.32 mmol, 1.0 equiv.) was added and the resultant reaction mixture warmed to r.t. and stirred under argon for 18 h. Water (5 ml) was added to quench the reaction mixture, and the reaction mixture was extracted with diethyl ether (3 x 50 ml). The combined organic layers were washed with water (4 x 50 ml) and brine (50 ml), then dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 3-5% diethyl ether in petroleum ether afforded 1-[4-(3-methylbut-3-enyloxy)butyl]benzene C as a colorless oil (822 mg, 37%); (found: [M+NH₄]+ 236.2010. C₁₂H₂₂O requires [M+NH₄]+ 236.2009); νmax (neat)/cm⁻¹ 3064, 3027, 2937, 2859, 1650, 1604, 1496, 1453, 888; δH (CDCl₃) 1.60-1.73 (4H, m, CH₂CH₂), 1.78 (3H, s, CH₃), 2.32 (2H, t, J 7.0, CH₂C), 2.66 (2H, t, J 7.7, CH₂Ar) 3.47 (2H, t, J 6.9, CH₂O), 3.54 (2H, t, J 6.2, CH₂O), 4.75 (1H, m, HCH=C), 4.80 (1H, m, HCH=C), 7.18-7.21 (3H, m, ArH), 7.28-7.32 (2H, m, ArH); δC (CDCl₃) 22.8 (CH₃), 28.1 (CH₂), 29.4 (CH₂), 35.7 (CH₂), 37.8 (CH₂), 69.4 (CH₂), 70.8 (CH₂), 111.3 (CH₂), 125.7 (CH), 128.3 (CH), 128.5 (CH), 142.5 (C), 143.0 (C); m/z (Cl) 236 ([M+NH₄]+, 100%), 219 (94), 91 (40).

1-[4-(3-Methylbut-3-enyloxy)butyl]benzene 45e

1-[4-(3-Methylbut-3-enyloxy)butyl]benzene C (750 mg, 3.44 mmol, 1.0 equiv.) was dissolved in dry DCM (10 ml) and anhydrous methanol (0.56 ml, 13.76 mmol, 4.0 equiv.) added and cooled to -78 °C. N-Iodosuccinimide (1.16 g, 5.16 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at -78 °C for 1 h, then warmed to r.t and stirred under argon for 18 h. Sodium thiosulfate (20 ml) was added, causing a color change from dark purple to colorless. The reaction mixture was extracted into DCM (3 x 60 ml) and the combined organic layers then washed with brine (3 x 50 ml), dried and concentrated in vacuo to give a pale pink oil. Purification by silica gel chromatography eluting with 10% diethyl ether in PE afforded 1-[4-(4-iodo-3-methoxy-3-methylbutoxy)butyl]benzene 45e as a pale red oil (977 g, 75%); (found: [M+H]+ 377.0974. C₁₆H₂₃IO₂ requires [M+H]+ 377.0972); νmax (neat)/cm⁻¹ 3061, 3025, 2938, 2861, 1603, 1496, 1454, 1374; δH (CDCl₃) 1.33 (3H, s, CH₃), 1.59-1.74 (4H, m, CH₂CH₂), 1.89-2.03 (2H, m, CH₂C), 2.65 (2H, t, J 7.7, CH₂Ar), 3.22 (3H, s, CH₃O), 3.32 (1H, d, J 10.8, CHH), 3.36 (1H, d, J 10.8, CHH), 3.43 (2H, t, J 6.8, CH₂O), 3.49 (2H, t, J 6.8, CH₂O), 7.19-7.24 (3H, m, ArH), 7.27-7.32 (2H, m, ArH); δC (CDCl₃) 16.2 (CH₂), 22.9 (CH₃),
Preparation of 45f.

1-(3-Bromopropoxy)benzene D.

3-Phenoxypropan-1-ol C (3.0 g, 19.71 mmol, 1.0 equiv.) was dissolved in dry diethyl ether (20 ml) and cooled to -5 °C where phosphorus tribromide (0.649 ml, 6.90 mmol, 0.35 equiv.) was added (temperature maintained below 0 °C for duration of addition). The clear solution was stirred under argon for 18 h. A color change of colorless to orange was noted during the reaction time. The orange solution was quenched by slowly pouring into water and the organic residue extracted with diethyl ether (100 ml), then washed with water (3 x 50 ml) and brine (50 ml), dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 0-5% EtOAc in petroleum ether afforded 1-(3-bromopropoxy)benzene D as a colorless oil (2.69 g, 64%); \( \text{C}_{9} \text{H}_{11} \text{BrO} \) requires \([M]^+ 213.9988\); \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 3039, 2928, 1498, 1387; \( \delta_{\text{H}} \) (400.133 MHz, CDCl\(_3\)) 2.35 (2H, quintet, \( J = 6.2 \)) \( \text{CH}_2 \), 3.64 (2H, t, \( J = 6.4 \)) \( \text{CH}_2\text{Br} \), 4.14 (2H, t, \( J = 5.8 \)) \( \text{CH}_2\text{O} \), 6.92-7.00 (3H, m, ArH), 7.28-7.34 (2H, m, ArH); \( \delta_{\text{C}} \) (100.61 MHz, CDCl\(_3\)) 30.0 (CH\(_2\)), 32.4 (CH\(_2\)), 65.2 (CH\(_2\)), 114.5 (CH), 120.9 (CH), 129.5 (CH), 158.7 (C); \( m/z \) (EI) 216 ([M]+, 81Br, 12%), 214 ([M]+, 79Br, 12%), 94 (100).

1-[3-(3-Methylbut-3-enyloxy)propoxy]benzene E
Sodium hydride (60% in mineral oil, 447 mg, 11.16 mmol, 1.2 equiv.) was washed with dry hexane and dried as usual, then suspended in DMF (10 ml). 3-Methyl-3-butenol (0.95 ml, 9.30 mmol, 1.0 equiv.) was added and the resultant orange suspension stirred under argon at r.t. for 1 h. The reaction mixture was cooled to 0 °C where 1-(3-bromopropoxy)benzene (2.0 g, 9.30 mmol, 1.0 equiv.) was added and the resultant reaction mixture warmed to r.t. and stirred under argon for 18 h. Water (5 ml) was added to quench the reaction mixture, and the reaction mixture extracted with diethyl ether (3 x 50 ml). The combined organic layers were washed with water (4 x 50 ml) and brine (50 ml), then dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 5% diethyl ether in petroleum ether afforded 1-[3-[(3-methylbut-3-enyloxy)propoxy]benzene as a colorless oil (303 mg, 15%); (found: [M+NH₄]⁺ 238.1800. C₁₄H₂₀O₂ requires [M+NH₄]⁺ 238.1802; νmax (neat)/cm⁻¹ 3065, 3029, 2934, 2858, 1650, 1601, 1497, 1470, 888; δH (CDCl₃) 1.76 (3H, s, CH₃), 2.07 (2H, quintet, J 6.2, CH₂), 2.32 (2H, t, J 6.9, CH₂C), 3.58 (2H, t, J 6.9, CH₂O), 3.64 (2H, t, J 6.2, CH₂O), 4.08 (2H, t, J 6.2, CH₂OAr), 4.74 (1H, m, HCH=C), 4.79 (1H, m, HCH=C), 6.92-6.98 (3H, m, ArH), 7.28-7.32 (2H, m, ArH); δC (CDCl₃) 22.7 (CH₃), 29.7 (CH₂), 37.8 (CH₂), 64.7 (CH₂), 67.3 (CH₂), 69.5 (CH₂), 111.4 (CH₂), 114.5 (CH), 120.6 (CH), 129.4 (CH), 142.9 (C), 159.0 (C); m/z (CI) 238 ([M+NH₄]⁺, 93%), 221 (64), 133 (100).

1-[3-(4-Iodo-3-methoxy-3-methylbutoxy)propoxy]benzene 45f

1-[3-(3-Methylbut-3-enyloxy)propoxy]benzene (250 mg, 1.13 mmol, 1.0 equiv.) was dissolved in dry DCM (5 ml) and anhydrous methanol (0.18 ml, 4.54 mmol, 4.0 equiv.) added and cooled to -78 °C. N-Iodosuccinimide (383 mg, 1.70 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at -78 °C for 1 h, then warmed to r.t and stirred under argon for 18 h. Sodium thiosulfate (10 ml) was added, causing a color change from dark purple to colorless. The reaction mixture was extracted with DCM (3 x 30 ml) and the organic layers combined then washed with brine (3 x 30 ml), dried and concentrated in vacuo to give a yellow oil. Purification by silica gel chromatography eluting with 5-10% diethyl ether in PE afforded 1-[3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy]benzene 45f as a colorless oil (271 mg, 63%); (found: [M+NH₄]⁺ 396.1028. C₁₅H₂₃O₃I requires [M+NH₄]⁺ 396.1030; νmax (neat)/cm⁻¹ 3062, 3039, 2935, 2872, 1600, 1587, 1497, 1470; δH (CDCl₃) 1.33 (3H, s, CH₃), 1.93-2.08 (4H, m,
CH₂CH₂C), 3.21 (3H, s, OCH₃), 3.31 (1H, d, J 10.8, CHH₁), 3.35 (1H, d, J 10.8, CHH₁), 3.54 (2H, t, J 6.8, CH₂O), 3.61 (2H, t, J 6.2, CH₂O), 4.08 (2H, t, J 6.3, CH₂OAr) 6.91-6.98 (3H, m, ArH), 7.28-7.32 (2H, m, ArH); δC (CDCl₃) 16.2 (CH₂), 22.8 (CH₃), 29.7 (CH₂), 36.5 (CH₂), 49.5 (CH₃), 64.7 (CH₂), 66.9 (CH₂), 67.5 (CH₂), 73.8 (C), 114.5 (CH), 120.6 (CH), 129.4 (CH), 159.0 (C); m/z (EI) 378 ([M]⁺, 100%), 379 (17), 251 (58).

**Preparation of 45g**

3-(4-Methoxyphenoxy)propan-1-ol F

![Image](https://via.placeholder.com/150)

4-Methoxyphenol (3.0 g, 24.17 mmol, 1.0 equiv.), 3-bromopropanol (2.11 ml, 24.17 mmol, 1.0 equiv.) and potassium carbonate (16.7 g, 120.8 mmol, 5.0 equiv.) were stirred together in DMF (30 ml) under argon for 64 h at r.t. Water (20 ml) was added and the reaction mixture was extracted with diethyl ether (3 x 50 ml). The combined organics were washed with water (5 x 50 ml) and brine (50 ml), then dried and concentrated *in vacuo*. Purification by silica gel chromatography eluting with 25-50% EtOAc in petroleum ether afforded 3-(4-methoxyphenoxy)propan-1-ol F as a white solid (3.66 g, 83%); (found: [M+NH₄]⁺ 200.1282. C₁₀H₁₄O₃ requires [M+NH₄]⁺ 200.1281); m.p. 54-56 °C; νmax (neat)/cm⁻¹ 3348, 3089, 2970, 2832; δH (CDCl₃) 2.04 (2H, quintet, J 5.9, CH₂), 3.78 (3H, s, CH₃O), 3.88 (2H, t, J 5.9, CH₂OH), 4.09 (2H, t, J 5.9, CH₂OAr), 6.82-6.88 (4H, m, ArH); δC (CDCl₃) 32.0 (CH₂), 55.7 (CH₃), 60.8 (CH₂), 66.7 (CH₂), 114.6 (CH), 115.4 (CH), 152.9 (C), 153.9 (C); m/z (CI) 200 ([M+NH₄]⁺, 100%), 183 (38), 124 (20).

1-(3-Bromopropoxy)-4-methoxybenzene G

![Image](https://via.placeholder.com/150)

3-(4-Methoxyphenoxy)propan-1-ol F (3.0 g, 16.46 mmol, 1.0 equiv.) was dissolved in dry diethyl ether (25 ml) and cooled to -5 °C where phosphorus tribromide (0.78 ml, 8.23 mmol, 0.5 equiv.) was added (temperature maintained below 0 °C for duration of
addition). The clear solution was stirred under argon for 20 h. A color change of colorless to orange was noted during the reaction time. The orange solution was quenched by slowly pouring into water (50 ml) and the reaction mixture extracted with diethyl ether (3 x 50 ml), then washed with water (2 x 50 ml) and brine (50 ml), dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 5% EtOAc in PE afforded 1-(3-bromopropoxy)-4-methoxybenzene G as a colorless oil (1.97 g, 49%); ν_{max} (neat)/cm^{-1} 3044, 2998, 2951, 1592, 1508, 1441; δ_{H} (CDCl_{3}) 2.31 (2H, m, CH_{2}), 3.62 (2H, t, J 6.5, CH_{2}Br), 3.78 (3H, s, OCH_{3}), 4.07 (2H, t, J 5.8, CH_{2}OAr), 6.82-6.88 (4H, m, ArH); δ_{C} (CDCl_{3}) 30.2 (CH_{2}), 32.5 (CH_{2}), 55.7 (CH_{3}), 66.0 (CH_{2}), 114.7 (CH), 115.5 (CH), 152.8 (C), 154.0 (C); m/z (CI) 264 ([M+NH_{4}]^{+}, 81Br, 12%), 262 ([M+NH_{4}]^{+}, 79Br, 12), 244 (53), 124 (100).

1-[3-(3-Methylbut-3-enyloxy)propoxy]-4-methoxybenzene H

Sodium hydride (60% in mineral oil, 333 mg, 8.32 mmol, 1.2 equiv.) was washed with dry hexane and dried, then suspended in DMF (10 ml). 3-Methyl-3-butenol (0.70 ml, 6.94 mmol, 1.0 equiv.) was added and the resultant orange suspension stirred under argon at r.t. for 1 h. The reaction mixture was cooled to 0 °C where 1-(3-bromopropoxy)-4-methoxybenzene G (1.70 g, 6.94 mmol, 1.0 equiv.), as a solution in DMF (5 ml), was added and the resultant reaction mixture warmed to r.t. and stirred under argon for 18 h. Water (5 ml) was added to quench the reaction mixture, and the reaction mixture was then extracted with diethyl ether (3 x 40 ml). The combined organic layers were washed with water (4 x 40 ml) and brine (40 ml), then dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 0-3% diethyl ether in petroleum ether afforded 1-[3-(3-methylbut-3-enyloxy)propoxy]-4-methoxybenzene H as a colorless oil (343 mg, 20%); (found: [M+NH_{4}]^{+} 268.1910.  C_{15}H_{22}O_{3} requires [M+NH_{4}]^{+} 268.1907); ν_{max} (neat)/cm^{-1} 3074, 2935, 1649, 1598, 1467, 1442, 890; δ_{H} (CDCl_{3}) 1.75 (3H, s, CH_{3}), 2.02-2.05 (2H, m, CH_{2}), 2.31 (2H, t, J 6.9, CH_{2}C), 3.56 (2H, t, J 6.9, CH_{2}O), 3.62 (2H, t, J 6.2, CH_{2}O), 3.78 (3H, s, OCH_{3}), 4.02 (2H, t, J 6.2, CH_{2}OAr), 4.73 (1H, m, HCH=C), 4.78 (1H, m, HCH=C), 6.81-6.87 (4H, m, ArH); δ_{C} (CDCl_{3}) 22.8 (CH_{3}), 29.8 (CH_{2}), 37.8 (CH_{2}), 55.7 (CH_{3}), 65.5 (CH_{2}), 67.4 (CH_{2}), 69.4 (CH_{2}), 111.4 (CH_{2}), 114.6 (CH), 115.6 (CH), 142.9 (C), 153.2 (C), 153.7 (C); m/z (CI) 268 ([M+NH_{4}]^{+}, 40%), 251 (60), 200 (100).
1-[3-(4-Iodo-3-methoxy-3-methylbutoxy)propoxy]-4-methoxybenzene 45g

1-[3-(3-Methylbut-3-enyloxy)propoxy]-4-methoxybenzene H (250 mg, 1.00 mmol, 1.0 equiv.) was dissolved in dry DCM (5 ml) and anhydrous methanol (0.16 ml, 4.00 mmol, 4.0 equiv.) added and cooled to -78 °C. N-Iodosuccinimide (337 mg, 1.50 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at -78 °C for 1 h, then warmed to r.t and stirred under argon for 18 h. Sodium thiosulfate (10 ml) was added, causing a color change from dark purple to colorless. The reaction mixture was extracted with DCM (2 x 50 ml) and then washed with water (3 x 30 ml) and brine (30 ml), dried and concentrated in vacuo to give a yellow oil. Purification by silica gel chromatography eluting with 0-20% diethyl ether in PE afforded 1-[3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy]-4-methoxybenzene 37g as a colorless oil (314 mg, 77%); (found: [M+NH4]+ 426.1135. C_{16}H_{25}O_{4}I requires [M+NH4]+ 426.1136); ν_{max}/cm^{-1} 3044, 2934, 2831, 1591, 1495, 1464; δ_{H} (CDCl_{3}) 1.32 (3H, s, CH_{3}), 1.88-2.05 (4H, m, CH_{2}, CH_{2}C), 3.19 (3H, s, CH_{3}O), 3.29 (1H, d, J 10.8, HCH), 3.34 (1H, d, J 10.8, HCHI), 3.52 (2H, t, J 6.7, CH_{2}O), 3.59 (2H, t, J 6.2, CH_{2}O), 3.77 (3H, s, CH_{3}O), 4.01 (2H, t, J 6.2, CH_{2}OAr), 6.81-6.87 (4H, m, ArH); δ_{C} (CDCl_{3}) 16.1 (CH_{2}), 22.8 (CH_{3}), 29.8 (CH_{2}), 36.5 (CH_{2}), 49.5 (CH_{3}), 55.7 (CH_{3}), 65.6 (CH_{2}), 66.8 (CH_{2}), 67.6 (CH_{2}), 73.8 (C), 114.6 (CH), 115.4 (CH), 153.2 (C), 153.8 (C); m/z (Cl) 426 ([M+NH_{4}]^{+}, 80%), 408 (65), 394 (100).

Preparation of 45h

4-(3-Phenylpropoxy)butan-1-ol I

Sodium hydride (60% in mineral oil, 8.10 g, 200.9 mmol, 4.0 equiv.) was washed with dry hexane and dried, and then suspended in DMF (100 ml) and cooled to 0 °C whereupon 1,4-butanediol (17.8 ml, 200.09 mmol, 4.0 equiv.) was added. The resultant orange
suspension was warmed to r.t. and stirred under argon for 1 h, then cooled to 0 °C. 1-Bromo-3-phenylpropane (7.64 ml, 50.22 mmol, 1.0 equiv.) was added dropwise and the resultant suspension stirred under argon at r.t. for 4 days. After this time, due to slow rate of reaction, the reaction mixture was then heated at 75 °C for 7 days. After this time, the reaction mixture was cooled to r.t. and quenched with water (25 ml). Solvent reduced in volume in vacuo, then the reaction mixture was extracted with diethyl ether (3 x 100 ml) and the combined organic layers washed with water (4 x 150 ml) and brine (150 ml), dried and concentrated in vacuo. Purification by silica gel column chromatography, eluting with 15-30% EtOAc in petroleum ether, afforded 4-(3-phenylpropoxy)butan-1-ol I as a colorless oil (6.88 g, 67%); (found: [M+H]⁺ 209.1538. C₁₃H₂₀O₂ requires [M+H]⁺ 209.1536); νmax (neat)/cm⁻¹ 3390, 3026, 2939, 2861, 1603, 1496, 1454; δH (CDCl₃) 1.69-1.74 (4H, m, C₆H₄C₂H₂), 1.91-1.95 (2H, m, C₂H₂), 2.71 (2H, t, J 7.9, CH₂Ar), 3.46-3.50 (4H, m, CH₂OCH₂), 3.67-3.70 (2H, m, CH₂OH), 7.20-7.22 (3H, m, ArH), 7.28-7.32 (2H, m, ArH); δC (CDCl₃) 26.9 (CH₂), 30.4 (CH₂), 31.2 (CH₂), 32.3 (CH₂), 62.8 (CH₂), 70.1 (CH₂), 70.9 (CH₂), 125.8 (CH), 128.3 (CH), 128.4 (CH), 141.9 (C); m/z (CI) 209 ([M+H]⁺, 100%), 91 (13), 118 (33).

1-[3-(4-Bromobutoxy)propyl]benzene J

4-(3-Phenylpropoxy)butan-1-ol I (3.0 g, 14.40 mmol, 1.0 equiv.) was dissolved in dry diethyl ether (20 ml) and cooled to -5 °C where phosphorus tribromide (0.677 ml, 7.20 mmol, 0.5 equiv.) was added (temperature maintained below 0 °C for duration of addition). The clear solution was stirred under argon for 18 h at r.t. A color change from colorless to orange was noted during the reaction time. The orange solution was quenched by slowly pouring into water and the organic residue extracted with diethyl ether (100 ml), then washed with water (3 x 50 ml) and brine (50 ml), dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 0-5% EtOAc in petroleum ether afforded 1-[3-(4-bromobutoxy)propyl]benzene J as a colorless oil (2.15 g, 56%); (found: [M+NH₄]⁺ 288.0956. C₁₃H₁₉O₇Br requires [M+NH₄]⁺ 288.0956); νmax (neat)/cm⁻¹ 3026, 2937, 2859, 1602, 1496, 1454; δH (400.133 MHz, CDCl₃) 1.73-1.79 (2H, m, CH₂), 1.90-2.01 (4H, m, CH₂CH₂), 2.71 (2H, t, J 7.9, CH₂Ar), 3.42-3.50 (6H, m, CH₂OCH₂, CH₂Br),
7.21-7.22 (3H, m, ArH), 7.28-7.33 (2H, m, ArH); δ_C (100.61 MHz, CDCl_3) 28.4 (CH_2), 29.8 (CH_2), 31.3 (CH_2), 32.4 (CH_2), 33.8 (CH_2), 69.8 (CH_2), 70.0 (CH_2), 125.8 (CH), 128.3 (CH), 128.5 (CH), 142.0 (C); m/z (CI) 290 ([M+NH_4]^+, 81Br, 100%), 288 ([M+NH_4]^+, 79Br, 100), 273 (10), 271 (10).

1-{3-[4-(3-Methylbut-3-enyloxy)butoxy]propyl}benzene K

Sodium hydride (60% in mineral oil, 177 mg, 4.43 mmol, 1.2 equiv.) was washed with dry hexane and dried, and then suspended in DMF (7 ml). 3-Methyl-3-butenol 2.5 (0.38 ml, 3.69 mmol, 1.0 equiv.) was added and the resultant orange suspension stirred under argon at r.t. for 1 h. The reaction mixture was cooled to 0 °C where 1-[3-(4-bromobutoxy)propyl]benzene J (1.0 g, 3.69 mmol, 1.0 equiv.) was added and the resultant reaction mixture warmed to r.t. and stirred under argon for 18 h. Water (10 ml) was added to quench the reaction mixture, and the reaction mixture then extracted with diethyl ether (3 x 50 ml). The combined organic layers were washed with water (4 x 50 ml) and brine (50 ml), then dried and concentrated in vacuo. Purification by silica gel chromatography, eluting with 0-5% diethyl ether in PE, afforded 1-{3-[4-(3-methylbut-3-enyloxy)butoxy]propyl}benzene K as a colorless oil (334 mg, 33%); (found: [M+H]^+ 277.2164. C_{18}H_{28}O_2 requires [M+H]^+ 277.2162); ν_{max} (neat)/cm\(^{-1}\) 3075, 3027, 2940, 2859, 1649, 1603, 1496, 1454, 888; δ_H (CDCl_3) 1.66-1.68 (4H, m, CH_2CH_2), 1.77 (3H, s, CH_3), 1.89-1.93 (2H, m, CH_2) 2.32 (2H, t, J 6.9, CH_2C), 2.71 (2H, t, J 7.9, CH_2Ar) 3.42-3.49 (6H, m, CH_2O x 3), 3.55 (2H, t, J 7.0, CH_2O), 4.75 (1H, m, HCH=C), 4.79 (1H, m, HCH=C), 7.18-7.21 (3H, m, ArH), 7.28-7.32 (2H, m, ArH); δ_C (CDCl_3) 22.8 (CH_3), 26.5 (CH_2 x 2), 31.3 (CH_2), 32.4 (CH_2), 37.8 (CH_2), 69.3 (CH_2), 69.9 (CH_2), 70.6 (CH_2), 70.7 (CH_2), 111.3 (CH_2), 125.7 (CH), 128.3 (CH), 128.5 (CH), 142.0 (C), 143.0 (C); m/z (CI) 277 ([M+H]^+, 100%), 294 (15), 191 (11), 91 (21).

1-{3-[4-(4-Iodo-3-methoxy-3-methylbutoxy)butoxy]propyl}benzene 45h
1-\{3-[4-(3-Methylbut-3-enyloxy)butoxy]propyl\}benzene K (250 mg, 0.91 mmol, 1.0 equiv.) was dissolved in dry DCM (5 ml) and anhydrous methanol (0.18 ml, 4.52 mmol, 5.0 equiv.) added and cooled to -78 °C. N-Iodosuccinimide (306 mg, 1.36 mmol, 1.5 equiv.) was added in one portion and the resultant suspension stirred at -78 °C for 1 h, and then warmed to r.t and stirred under argon for 18 h. Sodium thiosulfate (10 ml) was added, causing a color change from dark purple to colorless. The reaction mixture was extracted with DCM (3 x 30 ml) and combined then washed with water (2 x 30 ml) and brine (2 x 30 ml), dried and concentrated in vacuo to give a green oil. Purification by silica gel chromatography eluting with 10% diethyl ether in PE afforded 1-\{3-[4-(4-iodo-3-methoxy-3-methylbutoxy)butoxy]propyl\}benzene 45h as a clear oil (332 mg, 84%); (found: [M+NH₄]⁺ 452.1658. C₁₉H₃₁O₃I requires [M+NH₄]⁺ 452.1656); ν max (neat)/cm⁻¹ 3061, 3025, 2860, 2799, 1496, 1454, 1374; δ H (400.133 MHz, CDCl₃) 1.34 (3H, s, CH₃), 1.65-1.68 (4H, m, CH₂CH₂), 1.89-2.00 (4H, m, CH₂, CH₂C), 2.71 (2H, t, J 7.9, CH₂Ar), 3.22 (3H, s, CH₃O), 3.32 (1H, d, J 10.8, CHI), 3.36 (1H, d, J 10.8, CH/HI), 3.42-3.46 (6H, m, CH₂OCH₂, CH₂O), 3.51 (2H, t, J 7.0, CH₂O), 7.20-7.22 (3H, m, ArH), 7.28-7.32 (2H, m, ArH); δ C (100.61 MHz, CDCl₃) 16.3 (CH₂), 22.9 (CH₃), 26.5 (CH₂), 31.3 (CH₂), 32.4 (CH₂), 36.5 (CH₂), 49.5 (CH₃), 66.7 (CH₂), 69.9 (CH₂), 70.6 (CH₂), 70.9 (CH₂), 73.9 (C), 125.8 (CH), 128.3 (CH), 128.5 (CH), 142.1 (C); m/z (Cl) 435 ([M+H]⁺, 100%), 403 (55).

**General procedure for the reaction of aliphatic halides 45 with 2.**

Salt 15 (319 mg, 0.68 mmol, 1.5 equiv.) was dried under vacuum at 100 °C for 1 h then cooled and sodium hydride (271 mg, 6.75 mmol, 15.0 equiv.) added. The solid mixture was washed with hexane (x 2) and dried, then DMF was added causing a yellow
suspension to form which was stirred under argon at r.t. for 4 h. After this time, the yellow donor suspension was centrifuged at 2000 r.p.m. for 10 min to afford a yellow/orange solution and this solution was added via cannula to the aliphatic halide 45 (0.45 mmol, 1.0 equiv.). Generally a color change to dark red was observed after less than 15 min, and the solution was stirred under argon at r.t. for 18 h. The dark solution was then extracted with diethyl ether (3 x 50 ml) and the combined organic layers were washed with water (4 x 50 ml) and brine (50 ml), then dried and concentrated in vacuo. Purification by silica gel chromatography eluting with 0-25% diethyl ether in PE afforded the corresponding alcohol R"OH.

**Reaction of 2 with 45a**

Using the above general procedure, 1-{[4-(3-phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy]methyl}benzene 45a (197 mg, 0.45 mmol, 1.0 equiv.) afforded a mixture of 3-phenylpropan-1-ol L and benzyl alcohol as a colorless oil (48 mg); \(^1\)H NMR showed a mixture of 3-phenylpropanol L and benzyl alcohol in a 1.5:1 ratio. (Spectrum is reproduced in the supplementary data)
Using the above general procedure, 1-{4-[4-(3-Phenylpropoxy)-1-iodo-2-methylbutan-2-yloxy]butyl}benzene 45b (216 mg, 0.45 mmol, 1.0 equiv.) afforded a mixture of 3-phenylpropan-1-ol L and 4-phenylbutan-1-ol M as a colorless oil (93 mg); $^1$H NMR showed a mixture of 3-phenylpropanol L and 4-phenylbutan-1-ol M in a 1:1 ratio. (Spectrum is reproduced in the supplementary data)

1-[3-(4-Iodo-3-methoxy-3-methylbutoxy)propyl]benzene 45c (163 mg, 0.45 mmol, 1.0 equiv.) was reacted with donor 2 to afford 3-phenylpropanol L as a colorless oil (42 mg, 70%); $^7$ (found: [M]$^+$ 136.0883. C$_9$H$_{12}$O requires [M]$^+$ 136.0883); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3349, 3085, 3027, 2939, 2863, 1667, 1603, 1496, 1454; $\delta_1$ (CDCl$_3$) 1.89-2.02 (2H, m C$_2$H$_2$), 2.74 (2H, m J 7.9, CH$_2$Ar), 3.70 (2H, m J 6.5, CH$_2$OH), 7.21-7.25 (3H, m, ArH), 7.28-7.34 (2H, m, ArH); $\delta_2$ (CDCl$_3$) 125.9 (CH), 128.3 (CH), 128.5 (CH), 141.8 (C); m/z (EI) 136 ([M]$^+$, 14%), 117 (55), 91 (100), 77 (42).

1-[3-(4-Bromo-3-methoxy-3-methylbutoxy)propyl]benzene 45d (142 mg, 0.45 mmol, 1.0 equiv.) was reacted with donor 2 to afford 3-phenylpropanol L as a colorless oil (42 mg, 69%); $^7$. The spectroscopic data agreed with those described above for this compound.

1-[4-(4-Iodo-3-methoxy-3-methylbutoxy)butyl]benzene 45e (169 mg, 0.45 mmol, 1.0 equiv.) was reacted with donor 2 to afford 4-phenylbutan-1-ol M as a colorless oil (45 mg, 67%); $^7$ (found: [M+NH$_4$]$^+$ 168.1383. C$_{10}$H$_{13}$O requires [M+NH$_4$]$^+$ 168.1383); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3369, 3062, 3027, 2926, 2856, 1666, 1496, 1453; $\delta_1$ (CDCl$_3$) 1.62-1.75 (2H, m C$_2$H$_2$C$_2$), 2.68 (2H, m J 7.7, CH$_2$Ar), 3.69 (2H, m J 6.4, CH$_2$OH), 7.20-7.22 (3H, m, ArH), 7.28-7.34 (2H, m, ArH); $\delta_2$ (CDCl$_3$) 27.5 (CH$_2$), 32.3 (CH$_2$), 35.7 (CH$_2$), 62.9 (CH$_2$), 125.8 (CH), 128.3 (CH), 128.4 (CH), 142.3 (C); m/z (CI) 168 ([M+NH$_4$]$^+$, 100%), 104 (30), 91 (18).
1-[3-(4-Iodo-3-methoxy-3-methylbutoxy)propoxy]benzene 45f (170 mg, 0.45 mmol, 1.0 equiv.) was reacted with donor 2 to afford 3-phenoxypropan-1-ol N as a colorless oil (53 mg, 77%); $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3349, 3040, 2950, 1665, 1599, 1496; $\delta_{\text{H}}$ (CDCl$_3$) 2.07 (2H, quintet, $J$ 5.9, CH$_2$), 3.88 (2H, t, $J$ 5.9, CH$_2$OH), 4.14 (2H, t, $J$ 6.0, CH$_2$OAr), 6.93-7.00 (3H, m, ArH), 7.28-7.33 (2H, m, ArH). $\delta_{\text{C}}$ (CDCl$_3$) 32.0 (CH$_2$), 60.5 (CH$_2$), 65.7 (CH$_2$), 114.5 (CH), 120.9 (CH), 129.5 (CH), 158.7 (C); m/z (CI) 170 ([M+NH$_4$]$^+$, 100%) 153 (20), 152 (15).

1-[3-(4-Iodo-3-methoxy-3-methylbutoxy)propoxy]-4-methoxybenzene 45g (184 mg, 0.45 mmol, 1.0 equiv.) was reacted with donor 2 to afford 3-(4-methoxyphenoxy)propan-1-ol F as a white solid (53 mg, 63%); m.p. 53-55 °C; $^7$ The spectroscopic data agreed with those described above for this compound.

1-{3-[4-(4-Iodo-3-methoxy-3-methylbutoxy)butoxy]propyl}benzene 45h (195 mg, 0.45 mmol, 1.0 equiv.) was reacted with donor 2 to afford 4-(3-phenylpropoxy)butan-1-ol I as a clear oil (66 mg, 70%); data were consistent I, reported above.

Reduction of $N$-but-2-enyl-$N$-(2-iodophenyl)methanesulfonamide 47 with donor 2
(i) The experiment was carried out according to the ‘general NaH-method’ procedure. **Conditions and reagents:** Room temperature, 18 h, DMF (15 ml), salt 15 (348 mg, 0.74 mmol, 2.4 equiv.), N-but-2-enyl-N-(2-iodophenyl)methanesulfonamide 47 (108 mg, 0.308 mmol, 1.0 equiv.)\(^1\). The residue after *acidic* work-up was purified by column chromatography on silica gel (10:90 ethyl acetate/petroleum ether) to afford *N*-but-2-enyl-*N*-phenylmethanesulfonamide 48 (29 mg, 42 %) as a colourless oil; (Found: [M+NH\(_4\)]\(^+\) 243.1161. C\(_{11}\)H\(_{15}\)NO\(_2\)S requires [M+NH\(_4\)]\(^+\) 243.1162); \(\nu\)\(_{\text{max}}\) (NaCl)/cm\(^{-1}\) 3016 (C-H), 2928 (Ar-H), 2852 (Ar-H), 1598 (C-H), 1495 (C-H), 1335 and 1153 (SO\(_2\)); \(\delta\)\(_H\) (CDCl\(_3\)) 1.56 (3H, d, \(J\) 6.9, CH\(_3\)), 2.91 (3H, s, SO\(_2\)CH\(_3\)), 4.22 (2H, d, \(J\) 6.4, CH\(_2\)), 5.45-5.53 (1H, m, CH=CH), 5.56-5.64 (1H, m, CH=CH), 7.23-7.33 (3H, m, ArH), 7.35-7.42 (2H, m, ArH); \(\delta\)\(_C\) (CDCl\(_3\)) 18.1 (CH\(_3\)), 38.7 (CH\(_3\)), 53.6 (CH\(_2\)), 125.8 (CH), 128.1 (CH), 128.8 (CH), 129.5 (CH), 129.6 (CH), 130.9 (CH) and 139.7 (C). m/z (EI) 225 (M\(^+\), 15 %), 171 (80), 104 (60), 92 (100), 77 (80), 55 (75).

2-(1-Methanesulfonyl-2,3-dihydro-1H-indol-3-yl)propionaldehyde 49 was also isolated as a colorless oil (14 mg, 13 %) (mixture of diastereoisomers); (Found: [M+NH\(_4\)]\(^+\) 271.1107. C\(_{12}\)H\(_{15}\)NO\(_3\)S requires [M+NH\(_4\)]\(^+\) 271.1111); \(\nu\)\(_{\text{max}}\) (NaCl)/cm\(^{-1}\) 2972, 2934, 2726, 1723, 1601, 1481, 1461, 1347, 1159, 966, 772, 548; \(\delta\)\(_H\) (CDCl\(_3\)) 1.16 and 1.17 (3H, 2 x d, \(J\) 7.4, CH\(_3\)), 2.70-2.79 (4H, m, SO\(_2\)CH\(_3\) and CHCH\(_3\)), 3.74-3.84 (2H, m, NCH\(_2\)H\(_2\)), 4.05-4.07 (1H, m, NCH\(_2\)C\(_H\)), 7.02-7.08 (1H, m, ArH), 7.17 (1H, d, \(J\) 7.4, ArH), 7.23-7.27 (1H, m, ArH), 7.42 (1H, d, \(J\) 8.1, ArH), 9.72 and 9.78 (1H, 2 x s, COH); m/z (CI) 271 ([M + NH\(_4\)]\(^+\), 100 %), 243 (12), 176 (10), 118 (3). \(\delta\)\(_C\) (CDCl\(_3\)) 8.88, 10.65 (CH\(_3\)), 34.45, 34.60 (CH), 39.06, 39.90 (CH\(_3\)), 49.90, 50.15 (CH), 52.31, 54.31 (CH\(_2\)), 113.26, 113.36 (CH), 123.55, 123.78 (CH), 124.79, 125.77 (CH), 128.89, 128.92 (CH), 131.07, 142.39 (C), 142.26, 142.39 (C) and 202.82, 202.99 (CH). m/z (EI) 225 (M\(^+\), 15 %), 171 (80), 104 (60), 92 (100), 77 (80), 55 (75).
(ii) The experiment was repeated, but using deuterated DMF (DMF-d7) as solvent. This afforded products 48 (42%) and 49 (5%) – the 1H NMR and mass spectra for 49 were examined and were identical with those above – i.e. there was no indication of incorporation of deuterium.

1-Iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene, 50.

A suspension of washed sodium hydride (350 mg, 8.76 mmol, 1.2 equiv.) in N,N-dimethylformamide (15 ml) under argon was cooled to 0 °C. A solution of 1-(2-iodophenyl)but-3-en-1-ol P9 (2.0 g, 7.30 mmol, 1.0 equiv.) in N,N-dimethylformamide (5 ml) under argon was added dropwise and the reaction mixture was stirred at 0 °C for 1 h. 1-Bromo-3-phenylpropane (1.33 ml, 8.76 mmol, 1.2 equiv.) was added and then sodium iodide (218 mg, 1.46 mmol, 0.2 equiv.) and the reaction mixture was warmed to room temperature and stirred for 18 h. The reaction mixture was poured into diethyl ether (50 ml) and water (50 ml). The organic phase was washed with water (2 x 50 ml) and then saturated brine solution. The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (100 : 0, 98 : 2 petroleum ether - ethyl acetate) to afford 1-iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene 50 as a colorless oil (1.908 g, 67%);10. [Found: (ESI) [M+NH₄]⁺, 410.0971. C₁₉H₂₁IO requires [M+NH₄]⁺, 410.0975]; νmax (NaCl)/cm⁻¹ 3061 (Ar-H), 3025 (Ar-H), 2938 (C-H), 2862 (C-H), 1640 (C=C), 1562 (Ar), 1496 (Ar) and 1455 (C-H); δH (CDCl₃) 1.86-1.93 (2H, m, CH₂C₆H₄CH₂), 2.36-2.50 (2H, m, CHCH₂CH=), 2.65-2.78 (2H, m, CH₂Ph), 3.29-3.41 (2H, m, OCH₂), 4.57 (1H, dd, J 8.1, 4.4, OCH), 5.07-5.16 (2H, m, =CH₂), 5.90-6.01 (1H, m, =CH), 6.98 (1H, ddd, J 9.1, 7.7, 1.8, ArH), 7.17-7.21 (3H, m, ArH), 7.21-7.30 (2H, m, ArH), 7.38 (1H, ddd, J 9.1, 7.9, 1.1, ArH), 7.45 (1H, dd, J 7.7, 1.1, ArH) and 7.81 (1H, ddd, J 7.9, 1.8, ArH); δC (CDCl₃) 31.7 (CH₂), 32.6 (CH₂), 41.6 (CH₂), 68.6 (CH₂), 84.8 (CH), 98.9 (C), 117.2 (CH₂), 125.9 (CH), 127.7
(CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.3 (CH), 135.0 (CH), 142.3 (C) and 144.5 (C); m/z (Cl) 410 (M+NH4+, 45%), 284 (15), 274 (20), 257 (50) 154 (85), 152 (100), 148 (75) and 131 (90).

**Reaction between tetraazafulvalene 2 and 1-iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene 50 (i).**

![Reaction scheme]

The experiment was carried out according to the ‘general NaH-method’ procedure. **Conditions and reagents:** Room temperature, 18 h, DMF (15 ml), salt 15 (212 mg, 0.45 mmol, 1.5 equiv.), 1-iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene 50 (118 mg, 0.3 mmol, 1.0 equiv.). The residue after acidic work-up was purified by column chromatography on silica gel (10:90 ethyl acetate/petroleum ether) to afford [1-(3-phenylpropoxy)but-3-enyl]benzene 51 as a colorless oil (35 mg, 44%). (Found: (ESI) [M+NH4]+, 284.2009. C19H22O requires [M+NH4]+, 284.2009); νmax (NaCl)/cm⁻¹ 3063 (Ar-H), 3027 (Ar-H), 2929 (C-H), 2859 (C-H), 1640 (Ar), 1603 (Ar), 1496 (C-H) and 1454 (C-H); δH (CDCl3) 1.84-1.91 (2H, m, CH2CH2CH2), 2.37-2.44 (1H, m, CHCH=CH=), 2.56-2.75 (3H, m, CHCHHCH= and CH2Ph), 3.27-3.31 (1H, m, OCH), 3.34-3.39 (1H, m, OCH2), 4.24 (1H, dd, J 7.6, 5.8, OCH), 7.15-7.19 (3H, m, 3 x ArH) and 7.25-7.37 (7H, m, 7 x ArH); δC (CDCl3) 31.7 (CH2), 32.6 (CH2), 42.9 (CH2), 68.2 (CH2), 82.3 (CH), 117.0 (CH2), 125.9 (CH), 126.9 (CH), 127.6 (CH), 127.7 (CH), 128.5 (CH), 128.7 (CH), 135.3 (CH), 142.4 (C) and 142.6 (C); m/z (Cl) 284 (M+NH4+, 40%), 148 (30), 131 (100) and 52 (50).

The reaction also afforded [3-(3-phenylpropoxy)indan-1-yl]acetaldehyde 52 as a yellow oil (4 mg, 5%); (Found: (EI) [M]+, 294.1612. C20H22O2 requires [M]+, 294.1614); νmax (NaCl)/cm⁻¹ 3063 (Ar-H), 3026 (Ar-H), 2919 (C-H), 2858 (C-H), 2721 (OC-H), 1723 (C=O), 1603 (Ar), 1496 (C-H) and 1477 (C-H); δH (CDCl3) 1.69-1.74 and 1.89-1.97 (4 H, 2 x m, CH2CH2CH2 and CHCH2CH), 2.59-2.75 and 2.80-3.01 (2H, 2 x m, CH2C=O), 2.79-2.82 (2H, m, CH2Ph), 3.50-3.64 (3H, m, OCH2 and CH2CHCH2), 4.84-4.89 (1H, m, OCH), 7.16-7.24 (4H, m, 4 x ArH), 7.26-7.37 (4H, m, 4 x ArH), 7.39-7.42 (1H, m, ArH) and 9.89 (1H, m, O=CH); δC (CDCl3) 31.7 (CH2),
31.8 (CH₂), 32.5 (CH₂), 32.6 (CH₂), 36.6 (CH), 37.0 (CH), 39.8 (CH₂), 39.9 (CH₂), 49.7 (CH₂), 50.9 (CH₂), 68.0 (CH₂), 68.5 (CH₂), 81.9 (CH), 82.2 (CH), 123.9 (CH), 124.0 (CH), 125.3 (CH), 125.8 (CH), 125.9 (CH), 126.0 (CH), 127.3 (CH), 127.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 141.2 (C), 141.8 (C), 142.4 (C), 146.1 (C) and 201.9 (CH); m/z (EI) 294 (M⁺, 10%), 250 (35), 131 (50), 118 (70), 117 (100) and 91 (95).

**Reaction between tetraazafulvalene 2 and 1-iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene 50 (ii).**

![Reaction diagram]

A solution of 1,1':3,3'-bis(trimethylene)bis(imidazolium) diiodide 15 (212 mg, 0.45 mmol, 1.5 equiv.) in N,N-dimethyl formamide (10 ml) was purged with argon. This solution was added to washed sodium hydride (144 mg, 3.60 mmol, 12.0 equiv.) under argon and stirred for 1 h. The suspension obtained was centrifuged and the supernatant solution only added to a purged solution of 1-iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene 50 (118 mg, 0.3 mmol, 1.0 equiv.) in N,N-dimethylformamide (5 ml) and the reaction mixture was stirred at room temperature for 1 h. 0.5 M hydrochloric acid (3 ml) was added and the reaction mixture stirred for 15 min and then poured into diethyl ether (30 ml) and 0.5M hydrochloric acid (30 ml). The aqueous phase was extracted with further diethyl ether (2 x 30 ml) and the combined organic phases were washed with water (2 x 75 ml) and finally saturated brine solution (75 ml). The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (98 : 2, 95 : 5, 90 : 10 petroleum ether - ethyl acetate) to afford [1-(3-phenylpropoxy)but-3-enyl]benzene¹¹ 51 as a colorless oil (32 mg, 40%), the data agreed with those given in page 226.

The reaction also afforded [3-(3-phenylpropoxy)indan-1-yl]acetaldehyde 52 as a yellow oil (4mg, 5%), the data agreed with those given above.
Reaction between tetraazafulvalene 2 and 1-iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene 50 (iii).

A solution of 1,1':3,3'-bis(trimethylene)bis(imidazolium) diiodide 15 (212 mg, 0.45 mmol, 1.5 equiv.) in \(N,N\)-dimethylformamide (10 ml) was purged with argon. This solution was added to washed sodium hydride (144 mg, 3.60 mmol, 12.0 equiv.) under argon and stirred for 1 h. The suspension obtained was centrifuged and the supernatant solution only was transferred to a different round-bottomed flask under argon and heated at 80 °C. A purged solution of 1-iodo-2-[1-(3-phenylpropoxy)but-3-enyl]benzene 50 (118 mg, 0.3 mmol, 1.0 equiv.) in \(N,N\)-dimethylformamide (5 ml) was also heated at 80 °C and then added to the electron donor solution once both solution were at the required temperature. The reaction mixture was then heated at 80 °C for 18 h. The reaction mixture was then cooled and 0.5 M hydrochloric acid (3 ml) was added and the reaction mixture stirred for 15 min and then poured into diethyl ether (30 ml) and 0.5 M hydrochloric acid (30 ml). The aqueous phase was extracted with further diethyl ether (2 x 30 ml) and the combined organic phases were washed with water (3 x 75 ml) and then finally saturated brine solution (75 ml). The organic phase was then dried over sodium sulfate, filtered and evaporated. The residue was purified by column chromatography (98 : 2, 95 : 5, 90 : 10 petroleum ether - ethyl acetate) to afford [1-(3-phenylpropoxy)but-3-enyl]benzene 51 as a colorless oil (27 mg, 34%), the data agreed with those given above.

The reaction also afforded [3-(3-phenylpropoxy)inden-1-yl]acetaldehyde 52 as a yellow oil (7 mg, 8%), the data agreed with those given above.

Preparation of substrate 53

\((Z)\)-4-(3-Phenylpropoxy)-but-2-en-1-ol (Q)
(Z)-But-2-ene-1,4-diol (16.5 ml, 17.6 g, 200 mmol, 10 eq.) was added dropwise to a stirred suspension of sodium hydride (528 mg, 22 mmol, 1.1 eq.) in dry DMF (10 ml) at 0°C and under inert atmosphere. Once the solution cleared up, 1-bromo-3-phenylpropane (3.04 ml, 3.98 g, 20 mmol, 1 eq.) was added dropwise and the reaction left to stir at 0°C for 1 h, at r.t. for 16 h and at 90°C for 24 h until no more starting material was observed. The mixture was then poured in water (125 ml), and extracted with diethyl ether (125 and 2 x 100 ml). The combined organic phases were washed with water (2 x 125 ml), brine (125 ml) and dried over magnesium sulfate. Purification by column chromatography provided (Z)-4-(3-Phenylpropoxy)-but-2-en-1-ol Q (1.55 g, 38%) as a pale-yellow oil; [Found: (ESI⁺) (M+NH₄)⁺ 224.1642. C₁₃H₁₈O₂ requires M+NH₄, 224.1645]; νₑₓₐ₅ (film)/cm⁻¹ 13391, 3026, 2933, 2862, 1603, 1497, 1455, 1104, 1030, 747, 700;  δ₁ (CDCl₃) 1.89 – 1.96 (2H, m, PhCH₂CH₂), 1.98 (1H, broad s, OH), 2.71 (2H, t, J 7.3, PhCH₂CH₂), 3.47 (2H, t, J 6.4, PhCH₂CH₂CH₂), 4.06 (2H, d, J 6.0, =CHCH₂O), 4.22 (2H, t, J 5.9, CH₂OH), 5.70 – 5.76 (1H, m, HOCH₂CH=CH), 5.80 – 5.86 (1H, m, HOCH₂CH=CH), 7.18 – 7.21 (3H, m, ArH), 7.28 – 7.31 (2H, m, ArH); δ C(CDCl₃) 31.5 (CH₂), 32.2 (CH₂), 59.0 (CH₂), 66.7 (CH₂), 70.1 (CH₂), 126.0 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 132.3 (CH), 142.0 (C); m/z (Cl⁺) 224 [(M+NH₄)⁺, 100%], 207 (95), 189 (50), 118 (30).

N-(2-Iodophenyl)-N-[(Z)-4-(3-phenylpropoxy)-but-2-enyl]methanesulfonamide 53

To a stirred solution of (Z)-4-(3-Phenylpropoxy)-but-2-en-1-ol Q (621 mg, 3 mmol, 1 eq.), N-(2-Iodophenyl)methanesulfonamide¹² (1.07 g, 3.6 mmol, 1.2 eq.) and triphenylphosphine (1.18 g, 4.5 mmol, 1.5 eq.) in THF (12 ml) at 0°C was added dropwise diisopropyl
azodicarboxylate (0.886 ml, 910 mg, 4.5 mmol, 1.5 eq.) and the mixture was allowed to warm up to room temperature overnight. After evaporation of the solvent under reduced pressure, the remaining solid was dissolved in dichloromethane (100 ml). The solution was then sequentially washed with 2N NaOH (3 x 75 ml), 2N hydrochloric acid (75 ml), sat. aqueous NaHCO₃ (75 ml) and brine (75 ml). After being dried on magnesium sulphate, the organic layer was evaporated under reduced pressure, and the crude mixture remaining was purified by column chromatography providing N-(2-Iodophenyl)-N-[(Z)-4-(3-phenylpropoxy)but-2-enyl]methanesulfonamide 53 (1.40 g, 96%) as a colorless oil; [Found: (ESI⁺) (M+NH₄)⁺ 503.0852. C₂₀H₂₄INO₃S requires M+NH₄, 503.0860]; νmax (film)/cm⁻¹ 3060, 3025, 2931, 2860, 1602, 1577, 1496, 1467, 1342, 1152, 1101, 1070, 1020, 959; δH (CDCl₃) 1.79 – 1.85 (2H, m, PhCH₂CH₂), 2.64 (2H, t, J 7.7 PhCH₂CH₂), 3.11 (3H, s, SO₂CH₃), 3.23 (2H, t, J 6.4, PhCH₂CH₂CH₂), 3.77 (1H, dd, J 12.4, 5.4, NCH₂), 3.86 (1H, dd, J 12.6, 5.4, NCH₂), 4.20 (1H, dd, J 15.3, 6.9, OCHHCH=CH), 4.44 (1H, dd, J 15.3, 5.9, OCHHCH=CH), 5.69 – 5.79 (2H, m, OCH₂CH=CH), 7.05 (1H, ddd, J 7.1, 1.9, 0.03, ArH), 7.16 – 7.22 (3H, m, ArH), 7.28 – 7.31 (2H, m, ArH), 7.34 – 7.42 (2H, m, ArH), 7.91 (1H, dd, J 8.0, 1.4, ArH); δH (CDCl₃) 31.4 (CH₂), 32.5 (CH₃), 41.7 (CH₂), 48.1 (CH₂), 66.1 (CH₂), 69.7 (CH₂), 101.7 (C), 126.0 (CH), 126.6 (CH), 128.5 (CH), 128.6 (CH), 129.4 (CH), 130.4 (CH), 131.9 (CH), 132.8 (CH), 140.5 (CH), 141.1 (C), 142.0 (C); m/z (CI+) 503 [(M+NH₄)⁺, 100%], 486 (13), 408 (10), 377 (97), 360 (15), 349 (12), 280 (34), 241 (92), 189 (65).

Reduction of substrate 53
Under inert atmosphere, a solution of donor 2 (328 mg, 1.5 mmol, 1.5 eq.) in DMF (7 ml) was added to a stirred solution of N-(2-Iodophenyl)-N-[(Z)-4-(3-phenylpropoxy)-but-2-enyl]methanesulfonamide 53 (486 mg, 1 mmol, 1 eq.) in DMF (5 ml). After 18h stirring at room temperature, aqueous hydrochloric acid (2N, 10 ml) was added and the reaction mixture stirred for an hour and poured 2N hydrochloric acid (40 ml). Extraction using diethyl ether (3 x 50 ml) followed by washing of the combined organic phase (2 x 2N hydrochloric acid (50 ml) and drying over magnesium sulfate provided a crude mixture, which upon purification by chromatography columns provided N-phenyl-N-[(Z)-4-(3-phenylpropoxybut-2-enyl]methanesulfonamide 54 (97 mg, 27%), 1-methanesulfonyl-3-[2-(3-phenyl propoxy)ethyl]-2,3-dihydro-1H-indole 55 (27 mg, 7.5%) and 3-phenyl-1-propanol 56 (48 mg, 35%).

N-Phenyl-N-[(Z)-4-(3-phenylpropoxy)but-2-enyl]methanesulfonamide 54 was obtained as a colorless oil; [Found: (ESI\(^+\)) (M+NH\(_4\))\(^+\) 377.1894. C\(_{20}\)H\(_{25}\)NO\(_3\)S requires M+NH\(_4\), 377.1893]; \(\nu\) max (film)/cm\(^{-1}\) 3061, 3026, 2932, 2861, 1596, 1493, 1454, 1341, 1154, 1102, 1067, 956, 868; \(\delta\)\(_H\) (CDCl\(_3\)) 1.81 – 1.89 (2H, m, PhCH\(_2\)C\(_H\)\(_2\)); 2.66 (2H, t, \(J = 7.7\) Hz, PhCH\(_2\)CH\(_2\)); 2.93 (3H, s, SO\(_2\)CH\(_3\)); 3.03 (2H, t, \(J = 6.5\) Hz, PhCH\(_2\)O); 5.60 – 5.72 (2H, m, NCH\(_2\)C\(_H\)=C\(_H\)); 7.17 – 7.22 (3H, m, ArH), 7.28 – 7.41 (7H, m, ArH); \(\delta\)\(_C\) (CDCl\(_3\)) 31.4 (CH\(_2\)), 32.4 (CH\(_2\)), 38.4 (CH\(_3\)), 48.2 (CH\(_2\)), 66.3 (CH\(_2\)), 69.8 (CH\(_2\)), 126.0 (CH), 127.2 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.7 (CH), 131.1 (CH), 139.5 (C), 142.0 (C); \(m/z\) (\(\text{CI}^+\)) 377 [(M+NH\(_4\))^+, 78%], 360 (40), 282 (45), 189 (100).
1-Methanesulfonyl-3-[2-(3-phenylpropoxy)ethyl]-2,3-dihydro-1H-indole 55 was obtained as a pale yellow oil: [Found: (ESI\(^{+}\)) (M+NH\(_4\))\(^{+}\) 377.1891. \(C_{20}H_{25}NO_3S\) requires M+NH\(_4\), 377.1893]; \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 3025, 2933, 2862, 1714, 1604, 1479, 1458, 1350, 1162, 1111; \(\delta_1\) (CDCl\(_3\)) \(\delta\) 1.78 – 1.87 (1H, m, CHCH\(_2\)H\(_2\)O), 1.90 – 1.97 (2H, m, PhCH\(_2\)CH\(_2\)), 2.05 - 2.13 (1H, m, CHCH\(_2\)H\(_2\)O), 2.72 (2H, t, \(J\) 7.7, PhCH\(_2\)CH\(_2\)), 2.88 (3H, s, SO\(_2\)CH\(_3\)), 3.46 (2H, td, \(J\) 6.5, 2.0, CHCH\(_2\)CH\(_2\)O), 3.53 (2H, t, \(J\) 6.1 PhCH\(_2\)CH\(_2\)CH\(_2\)O), 3.51 – 3.55 (1H, broad m, NCH\(_2\)CH\(_3\)), 3.72 (1H, dd, \(J\) 9.12, 10.3, NCH\(_2\)); 4.10 (1H, dd, \(J\) 6.5, 10.3, NCH\(_2\)H), 7.04 – 7.08 (1H, m, ArH), 7.18 – 7.31 (7H, m, ArH), 7.41 (1H, d, \(J\) 8.0, ArH); \(^{13}\)C-NMR \(\delta\) C (CDCl\(_3\)) \(\delta\) 31.4 (CH\(_2\)), 32.6 (CH\(_2\)), 34.5 (CH\(_2\)), 34.9 (CH\(_2\)), 37.8 (CH\(_3\)), 56.7 (CH\(_3\)), 68.5 (CH\(_2\)), 70.5 (CH\(_2\)), 113.7 (CH), 123.8 (CH), 124.9 (CH), 126.0 (CH), 128.49 (CH), 128.55 (CH), 128.63 (CH), 135.0 (C), 141.9 (C), 142.0 (C); \(m/z\) (CI\(^{+}\)) 377 [(M+NH\(_4\))\(^{+}\), 100%], 360 (55), 282 (45) 144 (58), 118 (33).

3-Phenyl-1-propanol 56 (= compound \(L\)) was obtained as a colorless oil; \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 3340, 3062, 2940, 1603, 1496, 1454, 1059, 1031, 745, 699; \(\delta_1\) (CDCl\(_3\)) 1.62 (1H, s, OH), 1.88 – 1.95 (2H, m, PhCH\(_2\)CH\(_2\)), 2.73 (2H, t, \(J\) 7.8, PhCH\(_2\)CH\(_2\)), 3.67 – 3.72 (2H, m, PhCH\(_2\)CH\(_2\)CH\(_2\)O), 7.17 – 7.25 (3H, m, ArH) 7.28 – 7.32 (2H, m, ArH); \(\delta_1\) (CDCl\(_3\)) 32.3 (CH\(_2\)), 34.4 (CH\(_2\)), 62.5 (CH\(_2\)), 126.1 (CH), 128.6 (CH), 142.0 (C). \(^1\)H-NMR, \(^{13}\)C-NMR and IR were matched to the corresponding analyses of the commercial compound.

**Cartesian coordinates for structures 24 and 25 (R=Me) [calculated at B3LYP/6-31G(d)]\(^{13}\)**

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| 24   |            |            |            |
| C    | 0.67772300 | 2.98201400 | 0.02721400 |
| C    | -0.67629300| 2.98231600 | 0.02697400 |
| C    | 0.00020000 | 0.85477700 | 0.22199000 |
| N    | 1.08696600 | 1.66495600 | 0.15389200 |
| C    | -0.66878900| -1.51260900| -1.83968100|
| C    | 0.66881100 | -1.51285400| -1.83947200|
| C    | 2.51578200 | 1.33504800 | 0.38936300 |
| C    | 3.09352300 | 0.23696000 | -0.49352600|
| C    | 2.51240800 | -1.14736200| -0.18381400|
| C    | -2.51511500| 1.33609900 | 0.38942700 |
| C    | -2.51281200| -1.14606900| -0.18466800|
| C    | -3.09307800| 0.23866000 | -0.49411000|
| N    | -1.08615500| 1.66551000 | 0.15420000 |
| N    | -1.11200200| -1.29387600| -0.51362100|
| N    | 1.11165100 | -1.29430100| -0.51331200|
C  -0.00018200  -0.77551600   0.25973200  
C  -0.00060200  -1.18856600   1.74584500  
C  -0.00159600  -2.70263700   1.97031300  
H   1.38323800   3.79423700  -0.05231500  
H  -1.38143100   3.79484800  -0.05270200  
H  -1.36775700  -1.73279500  -2.63219600  
H   4.17621500   0.22505600  -0.31781000  
H   3.05908900  -0.73055400   2.23200300  
H  -0.00190000  -2.92020400   3.04280500  
H  -0.88353600  -3.17244900   1.52489000  
H   0.87099500  -0.73169100   2.23212100  
S-114

Zero-point correction=  0.345476 (Hartree/Particle)
Thermal correction to Energy=  0.361016
Thermal correction to Enthalpy=  0.361960
Thermal correction to Gibbs Free Energy=  0.304090

Sum of electronic and zero-point Energies=  -764.549595
Sum of electronic and thermal Energies=  -764.534055
Sum of electronic and thermal Enthalpies=  -764.533110
Sum of electronic and thermal Free Energies=  -764.590980
|   |   |   |   |
|---|---|---|---|
| C | -1.01170500 | -2.50413300 | 0.29561600 |
| C | 0.44206700 | -3.01364300 | 0.26601800 |
| N | 1.78384500 | -1.03702600 | -0.57885100 |
| N | -1.13892100 | -1.10638700 | 0.74830400 |
| N | -1.17417000 | 1.06820400 | 0.74818800 |
| C | -1.37176200 | -0.02260500 | -0.02832400 |
| C | -2.01124200 | -0.03281600 | -1.38259900 |
| C | -3.55120900 | -0.05634600 | -1.30395000 |
| H | 3.55931500 | 1.44002300 | 0.59004400 |
| H | 3.60447900 | -1.32344100 | 0.58973700 |
| H | -0.52622700 | -1.39059800 | 2.80261900 |
| H | -0.57099600 | 1.37233300 | 2.80246400 |
| H | 0.83520800 | 2.49732600 | -1.79057200 |
| H | 2.18829800 | 3.11105600 | -0.84213200 |
| H | 0.24452100 | 4.10371900 | 0.08512300 |
| H | 0.79979600 | 2.92571700 | 1.25917400 |
| H | -1.70300200 | 3.06586400 | 0.98000900 |
| H | -1.55655700 | 2.53191500 | -0.68984500 |
| H | 2.28815000 | -3.03809600 | -0.84364700 |
| H | 0.91547600 | -2.46761700 | -1.79110200 |
| H | -1.60161400 | -3.12026000 | 0.98079600 |
| H | -1.47407000 | -2.58222600 | -0.68927200 |
| H | 0.89528300 | -2.89892700 | 1.25829800 |
| H | 0.37814600 | -4.09376600 | 0.08389900 |
| H | -1.63295300 | -0.88955500 | -1.94236200 |
| H | -1.65914200 | 0.83479000 | -1.94274700 |
| H | -3.94349400 | 0.82290600 | -0.78196600 |
| H | -3.96904800 | -0.06297100 | -2.31433800 |
| H | -3.91636700 | -0.94697100 | -0.78158200 |

Zero-point correction= 0.345946 (Hartree/Particle)
Thermal correction to Energy= 0.361710
Thermal correction to Enthalpy= 0.362654
Thermal correction to Gibbs Free Energy= 0.303729
Sum of electronic and zero-point Energies= -764.552850
Sum of electronic and thermal Energies= -764.537086
Sum of electronic and thermal Enthalpies= -764.536142
Sum of electronic and thermal Free Energies= -764.595067

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