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I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker Avance NEO-600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.00 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on Agilent 6320 TOF MS/Agilent 1200 HPLC spectrometer and an Agilent 7890 GC-MS QTOF 7200 and 6540 LC/QTOF spectrometer in the mass-spec facility in the University of South Florida.

II. General Procedures

2.1 General procedure for the synthesis of Me-Dalpos-AuCl



In glove box, to a 25 mL round bottom flask with Me-Dalpos (843.2 mg, 2 mmol) was added Me_2SAuCl (589.1 mg, 2 mmol) and DCM (10 mL). The reaction mixture was stirred in the dark at rt for 2 h. The reaction mixture was then taken out of glove box, filtered with celite and washed with DCM. The filtrate was evaporated under reduced pressure in a rt water bath to get the crude product. Then the crude product was recrystallized with DCM and hexane to get the desired product as a white solid (1.23 g, 94%). The product was stored in glove box at 0 °C for future usage.

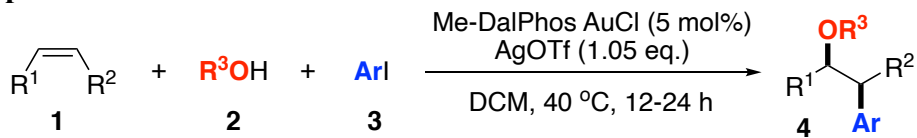
NMR data for Me-DalposAuCl

^1H NMR (600 MHz, Chloroform-*d*) δ 7.74 (ddd, J = 8.0, 6.6, 1.5 Hz, 1H), 7.62 – 7.48 (m, 2H), 7.31 – 7.27 (m, 1H), 2.60 (s, 6H), 2.21 (ddt, J = 11.8, 5.5, 3.0 Hz, 6H), 2.08 (ddt, J = 12.5, 6.3, 3.0 Hz, 6H), 2.00 – 1.95 (m, 6H), 1.67 (d, J = 3.3 Hz, 12H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.67 (d, J = 7.7 Hz), 134.84, 132.54, 126.38 (d, J = 3.3 Hz), 124.63 (d, J = 6.7 Hz), 122.67 (d, J = 47.7 Hz), 46.96, 42.06 (d, J = 3.1 Hz), 41.49 (d, J = 23.3 Hz), 36.32, 28.55 (d, J = 9.9 Hz).

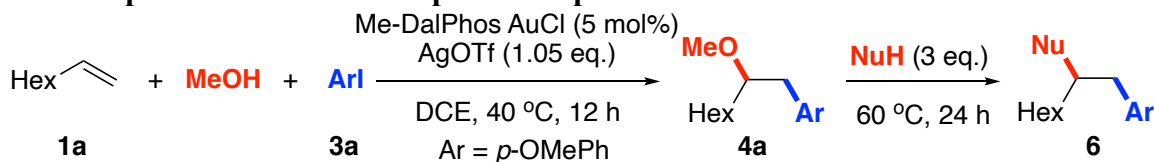
^{31}P NMR (243 MHz, Chloroform-*d*) δ 56.41.

2.2 General procedure for the alkene difunctionalization reaction



To a 5 mL vial with a stir bar was added DCM (2 mL or 0.4 mL), **1** (0.4 mmol), **2** (0.6 mmol), **3** (0.2 mmol), Me-DalPhosAuCl (6.5 mg, 0.01 mmol) and AgOTf (54.0 mg, 0.21 mmol) sequentially. The vial was flushed with N₂ and capped tight. Then the reaction system was stirred at 40 °C for 12-24 h. After **3** was fully consumed (determined by TLC and GC-MS), the reaction system was filtered and washed with DCM. The filtrate was evaporated under reduced pressure and purified by column chromatography to give the desired product (**4a-4s**, **5a-5q**, **6a-6j**).

2.3 General procedure for the one-pot nucleophile transformation reaction



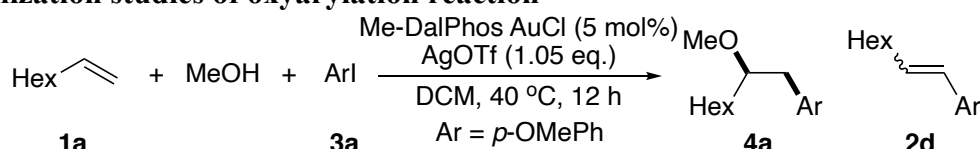
To a 5 mL vial with a stir bar was added DCE (2 mL), **1a** (44.9 mg, 62.8 μL, 0.4 mmol), MeOH (19.2 mg, 24 μL, 0.6 mmol), **3a** (46.8 mg, 0.2 mmol), Me-DalPhos-AuCl (6.5 mg, 0.01 mmol) and AgOTf (54.0 mg, 0.21 mmol) sequentially. The vial was flushed with N₂ and capped tight. Then the reaction system was stirred at 40 °C for 12 h. After **3a** was fully consumed (determined by TLC), the corresponding NuH (0.6 mmol) was added to the reaction system and stir at 60 °C for 24 h. Then the reaction system was filtered and washed with DCM. The filtrate was evaporated under reduced pressure and purified by column chromatography to give the desired product (**2a**, **6k-6m**).

2.4 Gram-scale synthesis of **4a**

To a 100 mL round bottom flask with a stir bar was added DCM (40 mL), **1a** (897.7 mg, 1.26 mL, 8 mmol), MeOH (384 mg, 0.48 mL, 12 mmol), **3a** (936.1 mg, 4 mmol), Me-DalPhos-AuCl (130.8 mg, 0.2 mmol) and AgOTf (1.08 g, 4.2 mmol) sequentially. The flask was flushed with N₂ and capped with a rubber plug. Then the reaction system was stirred at 40 °C for 12 h. After **3a** was fully consumed (determined by TLC), the reaction system was filtered and washed with DCM. The filtrate was evaporated under reduced pressure and purified by column chromatography (50:1 Hexane/EtOAc) to give the desired product **4a** as a colorless oil (953.1 mg, 95%)

III. Condition Optimization and Nucleophile Screening

3.1 Optimization studies of oxyarylation reaction^{[a][b]}



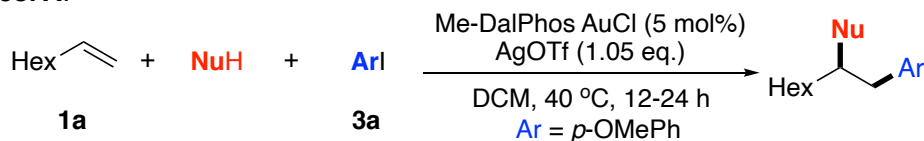
| Entry | Variation from “standard conditions” | conv. (3a) | 4a | 2d |
|-------|--|----------------------------|-----------|-----------|
| 1 | none | 100% | 95% (93%) | <5% |
| 2 | AgSbF ₆ | 100% | 73% | 25% |
| 3 | AgNTf ₂ | 100% | 61% | 10% |
| 4 | AgBF ₄ | 100% | 90% | 10% |
| 5 | AgPF ₆ | <5% | 0% | 0% |
| 6 | AgF | <5% | 0% | 0% |
| 7 | Add 1 eq K ₂ CO ₃ | 100% | 82% | 15% |
| 8 | Add 1 eq K ₃ PO ₄ | 100% | 87% | 10% |
| 9 | Add 1 eq KOAc | <5% | 0% | 0% |
| 9 | Add 1 eq 2,6-dimethylpyridine | <5% | 0% | 0% |
| 10 | Add 1 eq 2,6-di- <i>tert</i> -butyl-4-methylpyridine | 100% | 87% | 10% |
| 11 | DCE as solvent | 100% | 92% | <5% |
| 12 | DCB as solvent | 100% | 89% | 10% |
| 13 | Toluene as solvent | 70% | 56% | 10% |
| 14 | MeOH as solvent | 50% | 45% | <5% |
| 15 | rt | 20% | 15% | <5% |
| 16 | 60 °C | 100% | 65% | 30% |
| 17 | 80 °C, 2 h | 100% | 32% | 65% |
| 18 | AgSbF ₆ , add 1 eq K ₃ PO ₄ | 100% | 80% | 15% |
| 19 | Mor-DalphosAuCl 5% | 20% | 15% | <5% |
| 20 | No [Au] | <5% | 0% | 0% |
| 21 | No [Ag] | <5% | 0% | 0% |
| 22 | No [ArI] | No conversion on 1a | | |

[a] Conditions: **1a** (0.4 mmol), MeOH (0.6 mmol), **3a** (0.2 mmol), Au cat. (0.01 mmol), AgOTf (0.21 mmol), DCM (2 mL), 40 °C, 12 h. [b] ¹H NMR yields using 1,3,5-tribromobenzene as an internal standard (isolated yields).

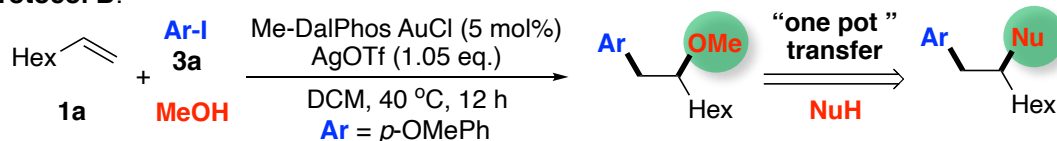
3.2 Direct nucleophilic attack VS “one-pot” nucleophile transfer

We tested different nucleophiles, and the comparison between the two protocols is listed below.

Protocol A:



Protocol B:



| | | | | | | |
|-------------------|--------------------------|----------------|-----------------|------------------|--------------------|-----------------|
| TsNH ₂ | Ph-C(=O)-NH ₂ | | | | | |
| A: <10% B: 76% | A: 0% B: 0% | A: 0% B: 0% | A: 75% B: 0% | A: 48% B: 82% | A: trace B: 84% | A: 0% B: 73% |

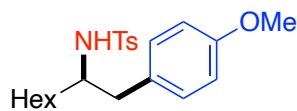
For N nucleophiles, aryl amine with electron-deficient substituents worked in a direct nucleophilic addition pathway. In contrast, aryl amine with electron-rich group failed to give the desired product using both protocols. Sulfonamide gave a trace amount of product using protocol A, and the good yield was obtained using protocol B. Also, as shown in **Figure 1B**, the aryl amidation product (Ar-NHTs) is the major byproducts even in the presence of alkene. These results suggest a stronger binding ability of N than alkene towards Au(III) intermediate. The detailed competitive coordination studies are currently undergoing in our lab.

For electron rich arenes, direct nucleophilic addition pathway (Protocol A) provided lower yield due to the cross-coupling as major byproduct (aryl-aryl coupling).

For sulfur nucleophiles, no reaction is observed, mainly due to the strong binding between silver salt and S nucleophiles. The formation of Ag-S complex completely quenched the catalytic cycle. We can obtain the desired product in good to excellent yield using protocol B.

Therefore, the development of “one-pot” transformation protocol, which is the “in-situ” formation of C-OMe intermediate and sequentially transferred into other C-Nus, is the only plausible solution for the intermolecular alkene difunctionalization, which is the highlight of this work.

IV. Compound Characterization



2a

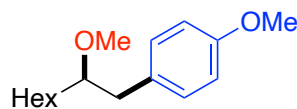
N-(1-(4-methoxyphenyl)octan-2-yl)-4-methylbenzenesulfonamide

2a was prepared following the General Procedure 2.3 and purified by column chromatography (8:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 4.40 (d, J = 8.1 Hz, 1H), 3.78 (s, 3H), 3.40 – 3.32 (m, 1H), 2.62 (qd, J = 13.8, 6.2 Hz, 2H), 2.41 (s, 3H), 1.41 (ddt, J = 14.8, 10.1, 4.9 Hz, 1H), 1.29 (qt, J = 6.1, 3.2 Hz, 1H), 1.20 (q, J = 6.9 Hz, 3H), 1.10 (tt, J = 10.6, 7.4, 6.4 Hz, 5H), 0.84 (t, J = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 158.29, 143.05, 137.91, 130.47, 129.53, 129.17, 127.02, 113.83, 55.22, 55.12, 40.38, 34.35, 31.69, 28.94, 25.34, 22.54, 21.52, 14.09.

HRMS m/z (ESI) calcd. for C₂₂H₃₂O₃NS⁺ (M+H)⁺ 390.2097, found 390.2098.



4a

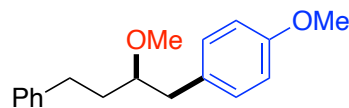
1-methoxy-4-(2-methoxyoctyl)benzene

4a was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.11 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 3.25 – 3.35 (m, 4H), 2.70 (ddd, J = 73.2, 13.8, 6.2 Hz, 2H), 1.41 (h, J = 6.9, 6.4 Hz, 3H), 1.35 – 1.18 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 157.84, 131.17, 130.26, 113.57, 82.45, 56.93, 55.15, 39.08, 33.40, 31.82, 29.40, 25.27, 22.59, 14.06.

HRMS m/z (ESI) calcd. for C₁₆H₂₆O₂Na⁺ (M+Na)⁺ 273.1825, found 273.1828.



4b

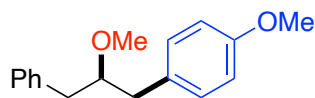
1-methoxy-4-(2-methoxy-4-phenylbutyl)benzene

4b was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.26 (t, J = 7.4 Hz, 2H), 7.16 (dd, J = 15.6, 7.4 Hz, 3H), 7.10 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 3.35 (s, 4H), 2.82 (dd, J = 13.9, 5.8 Hz, 1H), 2.77 (ddd, J = 13.7, 10.0, 5.8 Hz, 1H), 2.69 (dd, J = 13.9, 6.4 Hz, 1H), 2.60 (ddd, J = 13.7, 10.0, 6.6 Hz, 1H), 1.74 (dt, J = 15.6, 7.3, 2.7 Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.93, 142.28, 130.72, 130.30, 128.38, 128.28, 125.67, 113.65, 81.57, 56.97, 55.19, 38.91, 35.23, 31.58.

HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 293.1512, found 293.1528.



4c

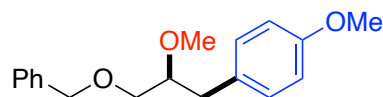
1-methoxy-4-(2-methoxy-3-phenylpropyl)benzene

4c was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform- d) δ 7.28 (t, $J = 7.5$ Hz, 2H), 7.23 – 7.17 (m, 3H), 7.11 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.56 (p, $J = 6.7, 6.1$ Hz, 1H), 3.24 (s, 3H), 2.74 (dq, $J = 24.7, 14.0, 6.2$ Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.92, 139.07, 130.96, 130.31, 129.39, 128.20, 126.03, 113.61, 83.72, 57.48, 55.18, 40.06, 39.15.

HRMS m/z (ESI) calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 279.1356, found 279.1358.



4d

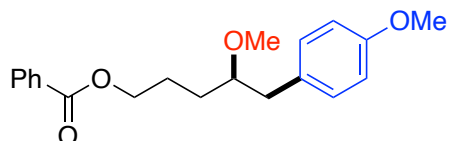
1-(3-(benzyloxy)-2-methoxypropyl)-4-methoxybenzene

4d was prepared following the General Procedure 2.2 and purified by column chromatography (10:1) as colorless oil.

^1H NMR (600 MHz, Chloroform- d) δ 7.42 – 7.26 (m, 5H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 4.53 (d, $J = 4.3$ Hz, 2H), 3.78 (s, 3H), 3.56 – 3.45 (m, 2H), 3.43 – 3.38 (m, 4H), 2.80 (d, $J = 6.4$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.95, 138.23, 130.46, 130.32, 128.32, 127.70, 127.55, 113.63, 81.44, 73.32, 70.75, 57.65, 55.18, 36.51.

HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 309.1461, found 309.1465.



4e

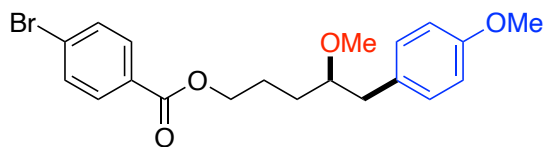
4-methoxy-5-(4-methoxyphenyl)pentyl benzoate

4e was prepared following the General Procedure 2.2 and purified by column chromatography (8:1) as colorless oil.

^1H NMR (600 MHz, Chloroform- d) δ 7.99 (d, $J = 6.9$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 4.34 – 4.21 (m, 2H), 3.78 (s, 3H), 3.39 (qd, $J = 6.8, 4.5$ Hz, 1H), 3.36 (s, 3H), 2.85 (dd, $J = 13.8, 5.8$ Hz, 1H), 2.65 (dd, $J = 13.8, 6.7$ Hz, 1H), 1.93 (dddd, $J = 17.1, 13.7, 6.7, 5.2$ Hz, 1H), 1.83 – 1.71 (m, 1H), 1.67 – 1.58 (m, 1H), 1.53 (dddd, $J = 13.8, 10.3, 7.3, 5.1$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 166.65, 158.01, 132.86, 130.67, 130.40, 130.33, 129.55, 128.33, 113.75, 81.89, 64.96, 57.08, 55.23, 38.95, 29.66, 24.60.

HRMS m/z (ESI) calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 351.1567, found 351.1568.



4f

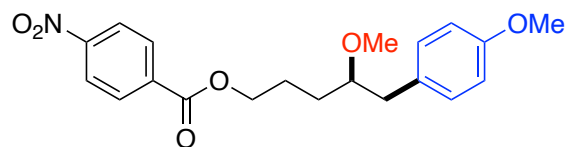
4-methoxy-5-(4-methoxyphenyl)pentyl 4-bromobenzoate

4f was prepared following the General Procedure 2.2 and purified by column chromatography (8:1) as colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.28 (td, J = 6.6, 1.8 Hz, 2H), 3.78 (s, 3H), 3.36 (s, 4H), 2.86 (dd, J = 13.8, 5.6 Hz, 1H), 2.64 (dd, J = 13.8, 6.9 Hz, 1H), 1.92 (dddd, J = 17.2, 13.8, 6.8, 5.2 Hz, 1H), 1.84 – 1.73 (m, 1H), 1.68 – 1.56 (m, 1H), 1.51 (dddd, J = 14.0, 10.3, 7.5, 5.1 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 165.83, 157.97, 131.62, 131.04, 130.54, 130.27, 129.22, 127.90, 113.69, 81.79, 65.13, 57.02, 55.17, 38.84, 29.54, 24.50.

HRMS m/z (ESI) calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_4\text{BrNa}^+$ ($\text{M}+\text{Na}$) $^+$ 429.0672, found 429.0678.



4g

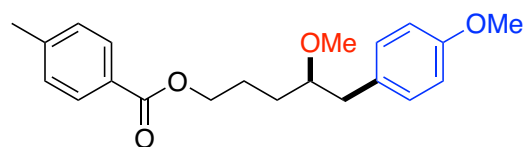
4-methoxy-5-(4-methoxyphenyl)pentyl 4-nitrobenzoate

4g was prepared following the General Procedure 2.2 and purified by column chromatography (5:1) as yellow oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 8.27 (d, J = 8.8 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.34 (td, J = 6.6, 2.6 Hz, 2H), 3.78 (s, 3H), 3.38 (s, 4H), 2.89 (dd, J = 13.8, 5.5 Hz, 1H), 2.64 (dd, J = 13.8, 7.1 Hz, 1H), 1.96 (dddd, J = 17.1, 13.8, 6.8, 5.2 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.72 – 1.57 (m, 1H), 1.57 – 1.47 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 164.63, 157.99, 150.42, 135.68, 130.60, 130.45, 130.27, 123.46, 113.70, 81.74, 65.78, 57.03, 55.15, 38.78, 29.49, 24.48.

HRMS m/z (ESI) calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_6\text{NNa}^+$ ($\text{M}+\text{Na}$) $^+$ 396.1418, found 396.1428.



4h

4-methoxy-5-(4-methoxyphenyl)pentyl 4-methylbenzoate

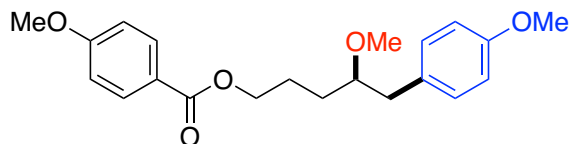
4h was prepared following the General Procedure 2.2 and purified by column chromatography (8:1) as colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.28 (t, J = 6.6 Hz, 2H), 3.78 (s, 3H), 3.39 (qd, J = 6.7,

4.5 Hz, 1H), 3.35 (s, 3H), 2.85 (dd, $J = 13.8, 5.8$ Hz, 1H), 2.65 (dd, $J = 13.8, 6.7$ Hz, 1H), 2.41 (s, 3H), 2.00 – 1.86 (m, 1H), 1.82 – 1.72 (m, 1H), 1.61 (ddd, $J = 14.5, 6.9, 4.3$ Hz, 1H), 1.53 (dddd, $J = 13.9, 10.4, 7.3, 5.1$ Hz, 1H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.68, 157.94, 143.43, 130.64, 130.27, 129.53, 128.99, 127.60, 113.68, 81.84, 64.72, 57.01, 55.15, 38.90, 29.61, 24.55, 21.64.

HRMS m/z (ESI) calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_4\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 365.1723, found 365.1725.



4i

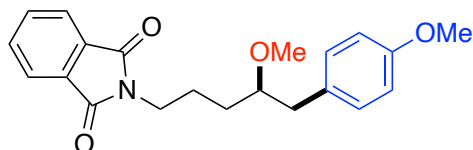
4-methoxy-5-(4-methoxyphenyl)pentyl 4-methoxybenzoate

4i was prepared following the General Procedure 2.2 and purified by column chromatography (7:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.93 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 4.26 (td, $J = 6.6, 1.4$ Hz, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 3.39 (qd, $J = 6.7, 4.5$ Hz, 1H), 3.35 (s, 3H), 2.85 (dd, $J = 13.8, 5.8$ Hz, 1H), 2.65 (dd, $J = 13.8, 6.7$ Hz, 1H), 1.91 (dddd, $J = 17.1, 13.6, 6.8, 5.2$ Hz, 1H), 1.82 – 1.72 (m, 1H), 1.66 – 1.58 (m, 1H), 1.57 – 1.48 (m, 1H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.35, 163.21, 157.93, 131.50, 130.65, 130.27, 122.76, 113.68, 113.49, 81.83, 64.57, 57.00, 55.37, 55.16, 38.89, 29.60, 24.57.

HRMS m/z (ESI) calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 381.1672, found 381.1676.



4j

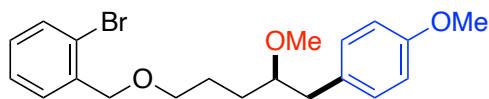
2-(4-methoxy-5-(4-methoxyphenyl)pentyl)isoindoline-1,3-dione

4j was prepared following the General Procedure 2.2 and purified by column chromatography (4:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 7.83 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.71 (dd, $J = 5.5, 3.0$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 2H), 6.78 (d, $J = 8.6$ Hz, 2H), 3.76 (s, 3H), 3.66 (td, $J = 7.6, 2.2$ Hz, 2H), 3.34 (qd, $J = 6.4, 4.4$ Hz, 1H), 3.31 (s, 3H), 2.78 (dd, $J = 13.8, 6.0$ Hz, 1H), 2.62 (dd, $J = 13.8, 6.4$ Hz, 1H), 1.84 (ddtd, $J = 13.0, 10.8, 7.6, 5.3$ Hz, 1H), 1.76 – 1.64 (m, 1H), 1.56 – 1.36 (m, 2H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 168.36, 157.88, 133.81, 132.06, 130.62, 130.24, 123.10, 113.62, 81.75, 57.11, 55.14, 38.95, 37.87, 30.44, 24.43.

HRMS m/z (ESI) calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_4\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 354.1700, found 354.1698.



4k

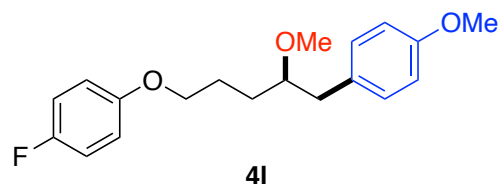
1-bromo-2-(((4-methoxy-5-(4-methoxyphenyl)pentyl)oxy)methyl)benzene

4k was prepared following the General Procedure 2.2 and purified by column chromatography (10:1) as pale yellow oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.57 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.43 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.32 (td, $J = 7.5, 1.3$ Hz, 1H), 7.20 (td, $J = 7.7, 1.7$ Hz, 1H), 7.10 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 5.24 (s, 2H), 4.16 (td, $J = 6.7, 2.6$ Hz, 2H), 3.78 (s, 3H), 3.40 – 3.28 (m, 4H), 2.80 (dd, $J = 13.8, 5.9$ Hz, 1H), 2.63 (dd, $J = 13.8, 6.5$ Hz, 1H), 1.89 – 1.80 (m, 1H), 1.77 – 1.67 (m, 1H), 1.60 – 1.52 (m, 1H), 1.50 – 1.40 (m, 1H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 157.92, 154.90, 134.64, 132.76, 130.52, 130.24, 129.84, 129.72, 127.49, 123.19, 113.65, 81.75, 68.72, 68.40, 57.01, 55.14, 38.90, 29.45, 24.57.

HRMS m/z (ESI) calcd. for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{Br}^+$ ($\text{M}+\text{H}$) $^+$ 395.1039, found 395.1129.



1-fluoro-4-((4-methoxy-5-(4-methoxyphenyl)pentyl)oxy)benzene

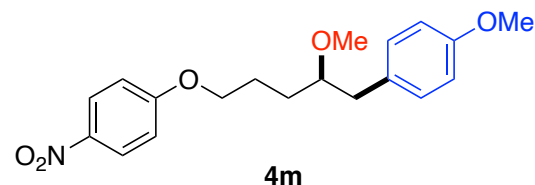
4l was prepared following the General Procedure 2.2 and purified by column chromatography (10:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.12 (d, $J = 8.5$ Hz, 2H), 6.95 (t, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.79 (dd, $J = 9.1, 4.3$ Hz, 2H), 3.89 (td, $J = 6.5, 3.3$ Hz, 2H), 3.79 (s, 3H), 3.38 (dq, $J = 11.6, 6.5, 5.4$ Hz, 1H), 3.35 (s, 3H), 2.83 (dd, $J = 13.8, 5.9$ Hz, 1H), 2.67 (dd, $J = 13.9, 6.5$ Hz, 1H), 1.98 – 1.87 (m, 1H), 1.83 – 1.74 (m, 1H), 1.68 – 1.61 (m, 1H), 1.53 (dddd, $J = 13.9, 10.3, 7.5, 5.2$ Hz, 1H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 157.96, 157.08 (d, $J = 237.7$ Hz), 155.08, 130.72, 130.31, 115.68 (d, $J = 22.9$ Hz), 115.34 (d, $J = 8.0$ Hz), 113.68, 82.04, 68.50, 57.02, 55.20, 38.99, 29.79, 25.18.

$^{19}\text{F NMR}$ (564 MHz, Chloroform-*d*) δ -124.38 (tt, $J = 8.2, 4.2$ Hz).

HRMS m/z (EI) calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{F}$ (M) $^+$ 318.1631, found 318.1631.



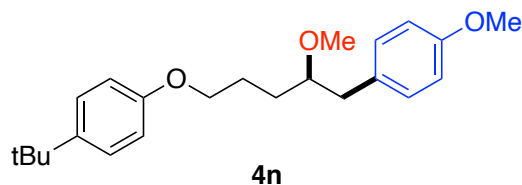
1-methoxy-4-(2-methoxy-5-(4-nitrophenoxy)pentyl)benzene

4m was prepared following the General Procedure 2.2 and purified by column chromatography (5:1) as yellow oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.18 (d, $J = 9.2$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 9.2$ Hz, 2H), 6.83 (d, $J = 8.5$ Hz, 2H), 4.03 (td, $J = 6.5, 1.9$ Hz, 2H), 3.79 (s, 3H), 3.36 (s, 4H), 2.86 (dd, $J = 13.9, 5.7$ Hz, 1H), 2.66 (dd, $J = 13.9, 6.7$ Hz, 1H), 2.03 – 1.92 (m, 1H), 1.90 – 1.78 (m, 1H), 1.70 – 1.62 (m, 1H), 1.57 – 1.49 (m, 1H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 164.07, 158.01, 141.27, 130.49, 130.28, 125.87, 114.35, 113.70, 81.94, 68.79, 57.03, 55.19, 38.88, 29.65, 24.95.

HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_5\text{NNa}^+$ ($\text{M}+\text{Na}$) $^+$ 368.1468, found 368.1460.



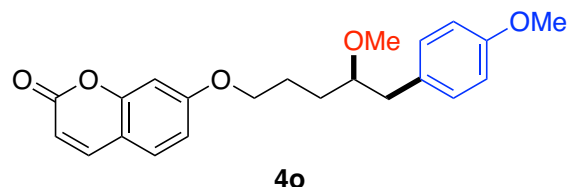
1-(tert-butyl)-4-((4-methoxy-5-(4-methoxyphenyl)pentyl)oxy)benzene

4n was prepared following the General Procedure 2.2 and purified by column chromatography (10:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.28 (d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 8.5$ Hz, 2H), 6.82 (dd, $J = 14.2, 8.7$ Hz, 4H), 3.96 – 3.87 (m, 2H), 3.79 (s, 3H), 3.39 (dq, $J = 11.3, 6.3, 5.3$ Hz, 1H), 3.34 (s, 3H), 2.81 (dd, $J = 13.9, 5.9$ Hz, 1H), 2.68 (dd, $J = 13.9, 6.4$ Hz, 1H), 1.99 – 1.86 (m, 1H), 1.79 (tdd, $J = 13.3, 11.2, 6.2$ Hz, 1H), 1.68 – 1.61 (m, 1H), 1.53 (dddd, $J = 13.9, 10.4, 7.4, 5.2$ Hz, 1H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 157.99, 156.75, 143.17, 130.85, 130.37, 126.19, 113.90, 113.72, 82.11, 67.86, 57.09, 55.25, 39.09, 34.06, 31.55, 29.96, 25.30.

HRMS m/z (ESI) calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 379.2244, found 379.2248



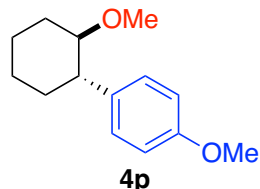
7-((4-methoxy-5-(4-methoxyphenyl)pentyl)oxy)-2H-chromen-2-one

4o was prepared following the General Procedure 2.2 and purified by column chromatography (4:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.63 (d, $J = 9.5$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.12 (d, $J = 8.5$ Hz, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 6.80 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.77 (d, $J = 2.4$ Hz, 1H), 6.24 (d, $J = 9.5$ Hz, 1H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.79 (s, 3H), 3.43 – 3.37 (m, 1H), 3.36 (s, 3H), 2.85 (dd, $J = 13.8, 5.7$ Hz, 1H), 2.67 (dd, $J = 13.9, 6.6$ Hz, 1H), 2.01 – 1.92 (m, 1H), 1.88 – 1.77 (m, 1H), 1.72 – 1.62 (m, 1H), 1.59 – 1.49 (m, 1H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 162.20, 161.24, 157.94, 155.78, 143.42, 130.51, 130.24, 128.63, 113.65, 112.85, 112.82, 112.31, 101.23, 81.90, 68.50, 56.97, 55.14, 38.86, 29.63, 24.87.

HRMS m/z (ESI) calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 391.1516, found 391.1521.



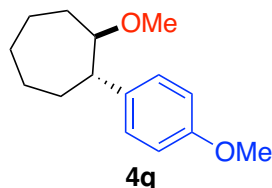
1-methoxy-4-(2-methoxycyclohexyl)benzene

4p was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.15 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.20 (td, $J = 10.4, 4.2$ Hz, 1H), 3.11 (s, 3H), 2.46 (ddd, $J = 12.2, 10.1, 3.8$ Hz, 1H), 2.30 – 2.21 (m, 1H), 1.84 (ddt, $J = 19.0, 13.2, 2.8$ Hz, 2H), 1.72 (dd, $J = 10.7, 3.0$ Hz, 1H), 1.44 (qd, $J = 12.7, 3.6$ Hz, 1H), 1.39 – 1.20 (m, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.77, 137.01, 128.31, 113.59, 83.33, 56.69, 55.15, 50.16, 34.55, 31.45, 26.11, 25.00.

HRMS m/z (ESI) calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 243.1356, found 243.1358.



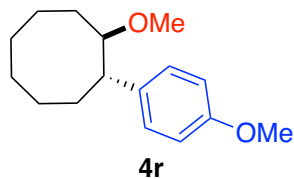
1-methoxy-2-(4-methoxyphenyl)cycloheptane

4q was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.13 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.78 (s, 3H), 3.30 (ddd, $J = 8.8, 6.0, 4.0$ Hz, 1H), 3.07 (s, 3H), 2.63 (td, $J = 9.3, 3.3$ Hz, 1H), 1.90 – 1.78 (m, 3H), 1.77 – 1.62 (m, 4H), 1.57 – 1.41 (m, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.49, 139.91, 128.09, 113.44, 87.21, 56.80, 55.10, 52.27, 32.88, 30.75, 28.95, 27.70, 22.15.

HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 257.1512, found 257.1520.



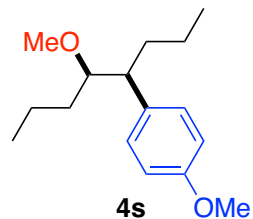
1-methoxy-2-(4-methoxyphenyl)cyclooctane

4r was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.11 (d, $J = 8.7$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 3.77 (s, 3H), 3.36 (qd, $J = 6.6, 3.8$ Hz, 1H), 3.32 (s, 3H), 2.65 (ddt, $J = 11.0, 8.0, 3.8$ Hz, 1H), 1.97 (dddd, $J = 14.7, 9.6, 6.8, 2.3$ Hz, 1H), 1.93 – 1.67 (m, 9H), 1.54 (qd, $J = 9.0, 5.4$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.53, 141.75, 127.75, 113.65, 80.69, 55.91, 55.25, 44.39, 33.27, 30.03, 29.90, 29.71, 25.89, 22.81.

HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 271.1669, found 271.1673.



1-methoxy-4-(5-methoxyoctan-4-yl)benzene

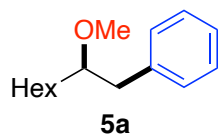
4s was prepared following the General Procedure 2.2 (cis-4-octene as **1**) and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.13 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.32 (s, 3H), 3.19 (dt, $J = 7.5, 4.5$ Hz, 1H), 2.70 (dt, $J = 9.9, 4.7$ Hz, 1H), 1.74 – 1.61 (m,

2H), 1.44 – 1.32 (m, 2H), 1.31 – 1.23 (m, 2H), 1.16 (dddt, $J = 27.4, 13.6, 9.5, 7.2$ Hz, 2H), 0.86 (td, $J = 7.2, 2.1$ Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.77, 134.29, 129.82, 113.32, 85.43, 58.38, 55.13, 47.91, 33.55, 33.19, 20.85, 19.14, 14.24, 14.18.

HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 273.1825, found 273.1828.



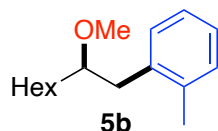
5a (2-methoxyoctyl)benzene

5a was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform- d) δ 7.29 – 7.24 (m, 2H), 7.19 (d, $J = 8.2$ Hz, 3H), 3.34 (p, $J = 5.9$ Hz, 1H), 3.30 (s, 3H), 2.82 (dd, $J = 13.7, 6.3$ Hz, 1H), 2.69 (dd, $J = 13.7, 6.2$ Hz, 1H), 1.43 (p, $J = 7.2, 6.2$ Hz, 3H), 1.33 – 1.20 (m, 7H), 0.87 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.27, 129.48, 128.27, 126.04, 82.44, 57.02, 40.23, 33.62, 31.94, 29.51, 25.37, 22.71, 14.17.

HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{ONa}^+$ ($\text{M}+\text{Na}$) $^+$ 243.1719, found 243.1718.



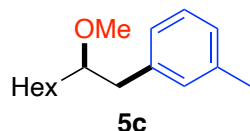
5b 1-(2-methoxyoctyl)-2-methylbenzene

5b was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform- d) δ 7.13 (dt, $J = 14.5, 6.0, 2.4$ Hz, 4H), 3.34 (p, $J = 5.3, 4.4$ Hz, 1H), 3.29 (s, 3H), 2.90 (dd, $J = 13.8, 6.6$ Hz, 1H), 2.65 (dd, $J = 13.8, 6.5$ Hz, 1H), 2.34 (s, 3H), 1.51 – 1.41 (m, 3H), 1.32 – 1.21 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 137.55, 136.29, 130.20, 130.12, 126.09, 125.74, 81.70, 57.17, 37.80, 33.97, 31.85, 29.44, 25.41, 22.60, 19.70, 14.07.

HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{26}\text{ONa}^+$ ($\text{M}+\text{Na}$) $^+$ 257.1876, found 257.1878.



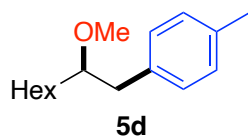
5c 1-(2-methoxyoctyl)-3-methylbenzene

5c was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform- d) δ 7.17 (t, $J = 7.7$ Hz, 1H), 7.03 – 6.98 (m, 3H), 3.32 (s, 4H), 2.81 (dd, $J = 13.7, 6.2$ Hz, 1H), 2.65 (dd, $J = 13.7, 6.3$ Hz, 1H), 2.33 (s, 3H), 1.47 – 1.38 (m, 3H), 1.33 – 1.21 (m, 7H), 0.87 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.08, 137.67, 130.17, 128.06, 126.67, 126.37, 82.36, 56.90, 40.02, 33.48, 31.83, 29.39, 25.24, 22.59, 21.38, 14.06.

HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{26}\text{ONa}^+$ ($\text{M}+\text{Na}$) $^+$ 257.1876, found 257.1879.



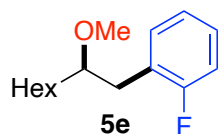
1-(2-methoxyoctyl)-4-methylbenzene

5d was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.09 (s, 4H), 3.32 (s, 4H), 2.80 (dd, $J = 13.7, 6.1$ Hz, 1H), 2.65 (dd, $J = 13.8, 6.3$ Hz, 1H), 2.32 (s, 3H), 1.42 (qt, $J = 6.0, 3.7$ Hz, 3H), 1.34 – 1.17 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 136.03, 135.36, 129.24, 128.88, 82.41, 56.90, 39.60, 33.44, 31.83, 29.41, 25.27, 22.59, 21.00, 14.06.

HRMS m/z (ESI) calcd. for C₁₆H₂₆ONa⁺ (M+Na)⁺ 257.1876, found 257.1877.



1-fluoro-2-(2-methoxyoctyl)benzene

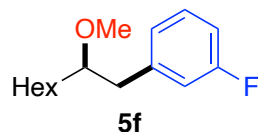
5e was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as pale yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.19 (m, 1H), 7.17 (ddt, $J = 7.4, 5.2, 2.0$ Hz, 1H), 7.05 (td, $J = 7.4, 1.2$ Hz, 1H), 7.00 (ddd, $J = 9.7, 8.2, 1.2$ Hz, 1H), 3.43 – 3.36 (m, 1H), 3.32 (s, 3H), 2.91 – 2.84 (m, 1H), 2.78 – 2.70 (m, 1H), 1.44 (q, $J = 4.2, 3.4$ Hz, 3H), 1.33 – 1.20 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 161.25 (d, $J = 244.6$ Hz), 131.87 (d, $J = 5.0$ Hz), 127.74 (d, $J = 8.0$ Hz), 126.02 (d, $J = 15.8$ Hz), 123.77 (d, $J = 3.6$ Hz), 115.07 (d, $J = 22.4$ Hz), 81.13, 57.04, 33.75, 33.34, 31.81, 29.37, 25.27, 22.58, 14.05.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -118.05 (q, $J = 7.5$ Hz).

HRMS m/z (ESI) calcd. for C₁₅H₂₃FONa⁺ (M+Na)⁺ 261.1625, found 261.1625.



1-fluoro-3-(2-methoxyoctyl)benzene

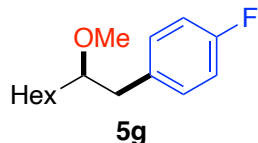
5f was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as pale yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.23 (td, $J = 7.9, 6.0$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.94 – 6.86 (m, 2H), 3.34 (p, $J = 5.8$ Hz, 1H), 3.31 (s, 3H), 2.80 (dd, $J = 13.8, 6.5$ Hz, 1H), 2.71 (dd, $J = 13.9, 5.7$ Hz, 1H), 1.43 (hept, $J = 6.4$ Hz, 3H), 1.34 – 1.21 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 162.73 (d, $J = 245.0$ Hz), 141.75 (d, $J = 7.3$ Hz), 129.49 (d, $J = 8.3$ Hz), 125.04 (d, $J = 2.7$ Hz), 116.16 (d, $J = 20.8$ Hz), 112.83 (d, $J = 20.8$ Hz), 81.97, 56.97, 39.82, 33.49, 31.80, 29.36, 25.23, 22.58, 14.04.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -113.96 (q, $J = 8.7$ Hz).

HRMS m/z (ESI) calcd. for $C_{15}H_{23}FONa^+$ ($M+Na$) $^+$ 261.1625, found 261.1623.



1-fluoro-4-(2-methoxyoctyl)benzene

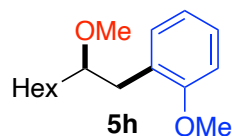
5g was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as pale yellow oil.

1H NMR (600 MHz, Chloroform-*d*) δ 7.19 – 7.12 (m, 2H), 6.96 (t, J = 8.7 Hz, 2H), 3.30 (s, 4H), 2.77 (dd, J = 13.9, 6.4 Hz, 1H), 2.69 (dd, J = 13.9, 5.8 Hz, 1H), 1.46 – 1.37 (m, J = 6.8 Hz, 3H), 1.27 (dt, J = 18.7, 5.4 Hz, 7H), 0.87 (t, J = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.39 (d, J = 243.5 Hz), 134.77 (d, J = 3.3 Hz), 130.71 (d, J = 7.7 Hz), 114.91 (d, J = 21.0 Hz), 82.23, 77.21, 77.00, 76.79, 57.00, 39.20, 33.42, 31.81, 29.39, 25.26, 22.59, 14.06.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -117.54 (dd, J = 9.2, 4.7 Hz).

HRMS m/z (ESI) calcd. for $C_{15}H_{23}FONa^+$ ($M+Na$) $^+$ 261.1625, found 261.1628.



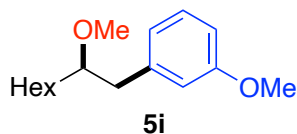
1-methoxy-2-(2-methoxyoctyl)benzene

5h was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

1H NMR (600 MHz, Chloroform-*d*) δ 7.18 (td, J = 7.8, 1.8 Hz, 1H), 7.15 (dd, J = 7.4, 1.8 Hz, 1H), 6.88 (td, J = 7.4, 1.1 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 3.81 (s, 3H), 3.40 (q, J = 6.6 Hz, 1H), 3.31 (s, 3H), 2.91 (dd, J = 13.4, 6.0 Hz, 1H), 2.66 (dd, J = 13.4, 6.7 Hz, 1H), 1.48 – 1.38 (m, 3H), 1.32 – 1.20 (m, 7H), 0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.49, 131.20, 127.61, 127.22, 120.24, 110.07, 80.89, 56.83, 55.13, 34.78, 33.84, 31.85, 29.41, 25.30, 22.59, 14.06.

HRMS m/z (ESI) calcd. for $C_{16}H_{26}O_2Na^+$ ($M+Na$) $^+$ 273.1825, found 273.1827.



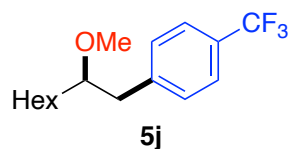
1-methoxy-3-(2-methoxyoctyl)benzene

5i was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

1H NMR (600 MHz, Chloroform-*d*) δ 7.20 (t, J = 7.7 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 6.77 – 6.73 (m, 2H), 3.79 (s, 3H), 3.35 (p, J = 5.9 Hz, 1H), 3.32 (s, 3H), 2.81 (dd, J = 13.7, 6.3 Hz, 1H), 2.66 (dd, J = 13.7, 6.2 Hz, 1H), 1.44 (qd, J = 6.2, 4.0, 2.8 Hz, 3H), 1.33 – 1.22 (m, 7H), 0.87 (t, J = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.42, 140.81, 129.09, 121.77, 115.13, 111.16, 82.25, 56.95, 55.06, 40.19, 33.54, 31.81, 29.38, 25.24, 22.58, 14.05.

HRMS m/z (ESI) calcd. for $C_{16}H_{26}O_2Na^+$ ($M+Na$) $^+$ 273.1825, found 273.1825.



1-(2-methoxyoctyl)-4-(trifluoromethyl)benzene

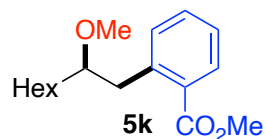
5j was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as pale yellow oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.53 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 7.9$ Hz, 1H), 3.40 – 3.34 (m, 1H), 3.30 (s, 1H), 2.84 (dd, $J = 13.8, 6.6$ Hz, 1H), 2.79 (dd, $J = 13.8, 5.5$ Hz, 1H), 1.43 (tdd, $J = 15.0, 7.9, 3.8$ Hz, 1H), 1.34 – 1.21 (m, 4H), 0.87 (t, $J = 6.9$ Hz, 2H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 143.38, 128.32 (q, $J = 32.2$ Hz), 125.06 (q, $J = 4.0$ Hz), 124.36 (q, $J = 271.7$ Hz), 81.88, 77.21, 77.00, 76.79, 57.03, 39.93, 33.51, 31.81, 29.37, 25.24, 22.58, 14.05.

$^{19}\text{F NMR}$ (564 MHz, Chloroform-*d*) δ -62.31.

HRMS m/z (EI) calcd. for $\text{C}_{16}\text{H}_{23}\text{OF}_3$ (M) $^+$ 288.1701, found 288.1666.



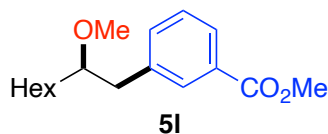
methyl 2-(2-methoxyoctyl)benzoate

5k was prepared following the General Procedure 2.2 and purified by column chromatography (20:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.87 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.41 (td, $J = 7.5, 1.5$ Hz, 1H), 7.31 – 7.24 (m, 2H), 3.89 (s, 3H), 3.40 – 3.32 (m, 1H), 3.21 (s, 3H), 3.18 (dd, $J = 13.1, 7.2$ Hz, 1H), 3.09 (dd, $J = 13.1, 5.4$ Hz, 1H), 1.50 – 1.40 (m, 3H), 1.34 – 1.19 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 168.22, 140.88, 132.46, 131.53, 130.43, 129.93, 126.05, 82.09, 57.36, 51.86, 39.04, 34.23, 31.81, 29.43, 25.26, 22.58, 14.05.

HRMS m/z (ESI) calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 301.1774, found 301.1781.



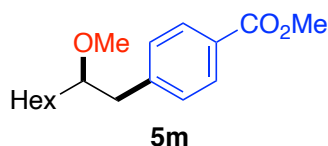
methyl 3-(2-methoxyoctyl)benzoate

5l was prepared following the General Procedure 2.2 and purified by column chromatography (20:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.89 (dt, $J = 4.9, 1.4$ Hz, 2H), 7.41 (dt, $J = 7.6, 1.6$ Hz, 1H), 7.36 (t, $J = 7.9$ Hz, 1H), 3.91 (s, 3H), 3.37 (p, $J = 5.8$ Hz, 1H), 3.31 (s, 3H), 2.86 (dd, $J = 13.8, 6.5$ Hz, 1H), 2.77 (dd, $J = 13.8, 5.8$ Hz, 1H), 1.49 – 1.38 (m, 3H), 1.34 – 1.22 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.21, 139.52, 134.11, 130.37, 129.99, 128.19, 127.28, 82.03, 57.01, 52.01, 39.86, 33.47, 31.76, 29.33, 25.21, 22.54, 14.02.

HRMS m/z (ESI) calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 301.1774, found 301.1776.



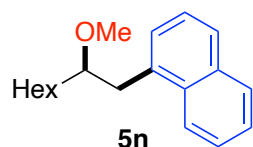
methyl 4-(2-methoxyoctyl)benzoate

5m was prepared following the General Procedure 2.2 and purified by column chromatography (20:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 3.90 (s, 3H), 3.44 – 3.31 (m, 1H), 3.29 (s, 3H), 2.86 (dd, $J = 13.7, 6.6$ Hz, 1H), 2.77 (dd, $J = 13.7, 5.7$ Hz, 1H), 1.48 – 1.36 (m, 3H), 1.34 – 1.19 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.18, 144.87, 129.55, 129.47, 127.99, 82.03, 57.11, 52.00, 40.25, 33.64, 31.83, 29.40, 25.27, 22.62, 14.09.

HRMS m/z (ESI) calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 301.1774, found 301.1777.



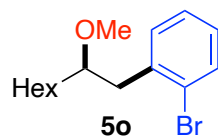
1-(2-methoxyoctyl)naphthalene

5n was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.84 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.51 (ddd, $J = 8.3, 6.7, 1.5$ Hz, 1H), 7.46 (ddd, $J = 8.0, 6.7, 1.2$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.36 (dd, $J = 7.1, 1.4$ Hz, 1H), 3.58 – 3.51 (m, 1H), 3.35 (dd, $J = 13.9, 6.6$ Hz, 1H), 3.28 (s, 3H), 3.09 (dd, $J = 14.0, 6.4$ Hz, 1H), 1.50 (hept, $J = 6.2$ Hz, 3H), 1.33 – 1.20 (m, 7H), 0.86 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 135.36, 133.82, 132.17, 128.75, 127.63, 126.84, 125.70, 125.44, 125.34, 123.81, 81.65, 57.25, 37.80, 34.17, 31.82, 29.43, 25.27, 22.58, 14.06.

HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{26}\text{ONa}^+$ ($\text{M}+\text{Na}$) $^+$ 293.1876, found 293.1879.



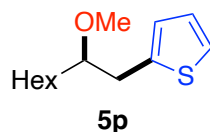
1-bromo-2-(2-methoxyoctyl)benzene

5o was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.53 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.26 (dd, $J = 7.5, 2.0$ Hz, 1H), 7.22 (td, $J = 7.4, 1.3$ Hz, 1H), 7.07 (td, $J = 7.6, 1.9$ Hz, 1H), 3.49 – 3.43 (m, 1H), 3.29 (s, 3H), 2.98 (dd, $J = 13.6, 6.9$ Hz, 1H), 2.83 (dd, $J = 13.6, 5.9$ Hz, 1H), 1.52 – 1.43 (m, 3H), 1.34 – 1.22 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 138.63, 132.66, 132.01, 127.78, 127.16, 124.65, 80.55, 57.27, 40.76, 33.93, 31.82, 29.41, 25.31, 22.60, 14.08.

HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{23}\text{OBrNa}^+$ ($\text{M}+\text{Na}$) $^+$ 321.0824, found 321.0827.



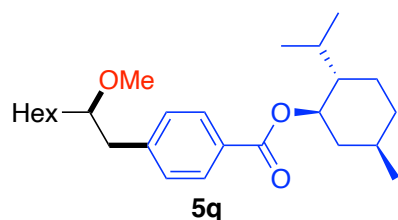
2-(2-methoxyoctyl)thiophene

5p was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as pale yellow oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.15 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.93 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.84 – 6.81 (m, 1H), 3.37 (s, 4H), 2.99 (d, $J = 5.8$ Hz, 2H), 1.52 – 1.44 (m, 2H), 1.45 – 1.35 (m, 1H), 1.37 – 1.22 (m, 7H), 0.88 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.11, 126.51, 125.50, 123.80, 81.78, 56.95, 33.96, 33.29, 31.81, 29.38, 25.23, 22.60, 14.08.

HRMS m/z (ESI) calcd. for $\text{C}_{13}\text{H}_{22}\text{OSNa}^+$ ($\text{M}+\text{Na}$) $^+$ 249.1284, found 249.1285.



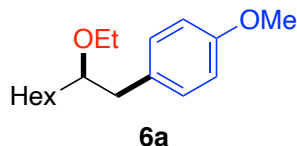
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(2-methoxyoctyl)benzoate

5q was prepared following the General Procedure 2.2 and purified by column chromatography (20:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.97 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 4.92 (td, $J = 10.9, 4.4$ Hz, 1H), 3.37 (p, $J = 5.7$ Hz, 1H), 3.30 (s, 3H), 2.86 (dt, $J = 13.4, 6.6$ Hz, 1H), 2.77 (ddd, $J = 13.6, 7.7, 5.7$ Hz, 1H), 2.12 (d, $J = 12.1$ Hz, 1H), 1.97 (pd, $J = 6.9, 2.6$ Hz, 1H), 1.73 (dt, $J = 11.8, 3.0$ Hz, 2H), 1.55 (ddd, $J = 14.8, 8.5, 3.2$ Hz, 2H), 1.49 – 1.38 (m, 3H), 1.34 – 1.22 (m, 7H), 1.17 – 1.05 (m, 2H), 0.92 (dd, $J = 6.9, 3.7$ Hz, 7H), 0.87 (t, $J = 6.9$ Hz, 3H), 0.79 (d, $J = 7.0$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 166.15, 144.61, 144.58, 129.53, 129.42, 129.40, 128.70, 82.05, 82.03, 74.60, 57.08, 57.06, 47.28, 41.01, 40.22, 40.19, 34.35, 33.62, 33.59, 31.85, 31.45, 29.41, 26.45, 25.31, 25.27, 23.60, 22.63, 22.08, 20.82, 16.51, 14.10.

HRMS m/z (ESI) calcd. for $\text{C}_{26}\text{H}_{42}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 425.3026, found 425.3027.



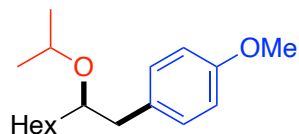
1-(2-ethoxyoctyl)-4-methoxybenzene

6a was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.12 (d, $J = 8.2$ Hz, 2H), 6.82 (d, $J = 8.3$ Hz, 2H), 3.79 (s, 3H), 3.43 (q, $J = 7.0$ Hz, 2H), 3.36 (t, $J = 6.0$ Hz, 1H), 2.75 (dd, $J = 13.8, 6.3$ Hz, 1H), 2.64 (dd, $J = 13.8, 6.0$ Hz, 1H), 1.41 (dq, $J = 11.7, 4.2, 2.9$ Hz, 3H), 1.26 (d, $J = 12.4$ Hz, 7H), 1.14 (t, $J = 7.0$ Hz, 3H), 0.87 (t, $J = 6.9$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 157.86, 131.46, 130.37, 113.57, 80.96, 64.80, 55.24, 39.98, 34.18, 31.90, 29.45, 25.58, 22.66, 15.59, 14.13.

HRMS m/z (ESI) calcd. for $C_{17}H_{28}O_2Na^+$ ($M+Na$) $^+$ 287.1982, found 287.1983.



6b

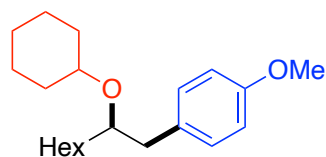
1-(2-isopropoxyoctyl)-4-methoxybenzene

6b was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

1H NMR (600 MHz, Chloroform- d) δ 7.11 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.50 (p, $J = 6.1$ Hz, 1H), 3.41 (dq, $J = 10.4, 6.1$ Hz, 1H), 2.70 (dd, $J = 13.7, 6.3$ Hz, 1H), 2.63 (dd, $J = 13.7, 6.1$ Hz, 1H), 1.47 – 1.32 (m, 3H), 1.26 (dd, $J = 16.7, 5.9$ Hz, 7H), 1.10 (d, $J = 6.1$ Hz, 3H), 1.01 (d, $J = 6.1$ Hz, 3H), 0.87 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.86, 131.59, 130.47, 113.51, 78.67, 70.09, 55.24, 40.93, 34.90, 31.92, 29.50, 25.74, 22.94, 22.66, 22.57, 14.13.

HRMS m/z (ESI) calcd. for $C_{18}H_{30}O_2Na^+$ ($M+Na$) $^+$ 301.2138, found 301.2138.



6c

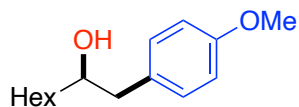
1-(2-(cyclohexyloxy)octyl)-4-methoxybenzene

6c was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

1H NMR (600 MHz, Chloroform- d) δ 7.11 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.49 – 3.40 (m, 1H), 3.15 (td, $J = 9.1, 4.0$ Hz, 1H), 2.72 (dd, $J = 13.6, 6.1$ Hz, 1H), 2.63 (dd, $J = 13.6, 6.3$ Hz, 1H), 1.87 (dd, $J = 10.7, 4.8$ Hz, 1H), 1.76 – 1.68 (m, 2H), 1.65 (q, $J = 6.0$ Hz, 1H), 1.50 (dt, $J = 9.0, 4.5$ Hz, 1H), 1.45 – 1.34 (m, 3H), 1.24 (h, $J = 11.1, 10.3$ Hz, 9H), 1.19 – 1.11 (m, 3H), 0.87 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.80, 131.56, 130.43, 113.45, 78.33, 76.26, 55.21, 40.90, 34.77, 33.21, 32.90, 31.88, 29.46, 25.76, 25.73, 24.47, 24.44, 22.62, 14.09.

HRMS m/z (ESI) calcd. for $C_{21}H_{34}O_2Na^+$ ($M+Na$) $^+$ 341.2451, found 341.2451.



6d

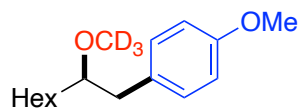
1-(4-methoxyphenyl)octan-2-ol

6d was prepared following the General Procedure 2.2 and purified by column chromatography (20:1) as white solid.

1H NMR (600 MHz, Chloroform- d) δ 7.13 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 3.80 (s, 3H), 3.76 (dt, $J = 7.7, 4.1$ Hz, 1H), 2.78 (dd, $J = 13.7, 4.2$ Hz, 1H), 2.58 (dd, $J = 13.7, 8.5$ Hz, 1H), 1.49 (tdd, $J = 13.0, 6.4, 4.2$ Hz, 4H), 1.38 – 1.22 (m, 7H), 0.88 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.20, 130.52, 130.34, 113.93, 72.75, 55.23, 43.05, 36.72, 31.81, 29.32, 25.72, 22.60, 14.08.

HRMS m/z (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 259.1669, found 259.1674.



6e

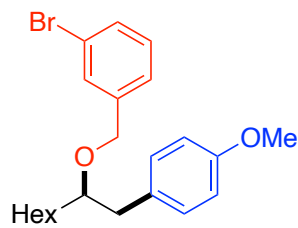
1-methoxy-4-(2-(methoxy-d3)octyl)benzene

6e was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.12 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.33 – 3.27 (m, 1H), 2.76 (dd, $J = 13.9, 6.2$ Hz, 1H), 2.64 (dd, $J = 13.9, 6.2$ Hz, 1H), 1.46 – 1.37 (m, 3H), 1.33 – 1.21 (m, 7H), 0.87 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.84, 131.21, 130.28, 130.17, 113.63, 113.59, 82.35, 55.19, 39.12, 33.43, 31.83, 29.42, 25.28, 22.60, 14.08.

HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{23}\text{D}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 276.2013, found 276.2016.



6f

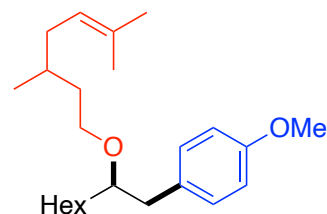
1-bromo-3-(((1-(4-methoxyphenyl)octan-2-yl)oxy)methyl)benzene

6f was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.37 (dd, $J = 6.0, 1.8$ Hz, 2H), 7.19 – 7.07 (m, 4H), 6.84 (d, $J = 8.6$ Hz, 2H), 4.46 – 4.34 (m, 2H), 3.80 (s, 3H), 3.51 (h, $J = 5.6$ Hz, 1H), 2.79 (dd, $J = 13.9, 6.9$ Hz, 1H), 2.72 (dd, $J = 13.9, 5.6$ Hz, 1H), 1.47 (dddd, $J = 33.0, 12.9, 9.8, 5.8$ Hz, 3H), 1.35 – 1.21 (m, 7H), 0.88 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.01, 141.24, 131.15, 130.73, 130.44, 130.40, 129.81, 126.15, 122.42, 113.69, 80.98, 70.59, 55.27, 39.92, 33.98, 31.86, 29.43, 25.42, 22.65, 14.13.

HRMS m/z (ESI) calcd. for $\text{C}_{22}\text{H}_{29}\text{BrO}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 427.1243, found 427.1242.



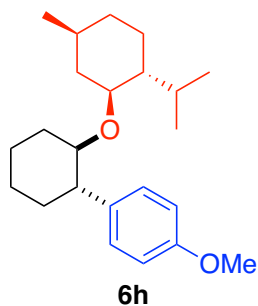
6g

1-(2-(((3,6-dimethylhept-5-en-1-yl)oxy)octyl)-4-methoxybenzene

6g was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as pale yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 5.08 (d, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.38 (ddt, *J* = 28.8, 12.3, 6.7 Hz, 3H), 2.75 (dt, *J* = 12.7, 5.5 Hz, 1H), 2.63 (dd, *J* = 13.9, 6.0 Hz, 1H), 1.95 (dp, *J* = 23.5, 7.8 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.52 (tt, *J* = 12.9, 5.7 Hz, 2H), 1.41 (s, 3H), 1.37 – 1.21 (m, 7H), 1.16 – 1.06 (m, 1H), 0.85 (dt, *J* = 20.9, 6.5 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 157.86, 131.51, 131.09, 130.37, 124.92, 113.57, 81.15, 67.68, 55.24, 39.90, 37.26, 37.17, 34.07, 34.03, 31.90, 29.47, 29.44, 29.40, 25.76, 25.57, 25.53, 25.49, 22.66, 19.54, 19.48, 17.66, 14.13.



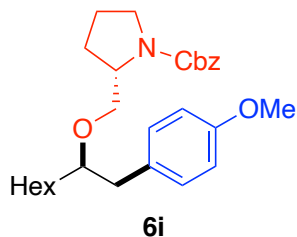
1-(2-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)cyclohexyl)-4-methoxybenzene

6h was prepared following the General Procedure 2.2 and purified by column chromatography (50:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.81 (dd, *J* = 8.6, 4.5 Hz, 2H), 3.78 (d, *J* = 4.8 Hz, 3H), 3.28 (dtd, *J* = 44.5, 9.9, 4.1 Hz, 1H), 2.83 (dtd, *J* = 49.6, 10.4, 4.3 Hz, 1H), 2.44 (dddd, *J* = 25.8, 13.3, 10.1, 3.8 Hz, 1H), 2.21 (pd, *J* = 7.0, 2.3 Hz, 0.5H), 2.13 (ddd, *J* = 15.6, 7.9, 3.3 Hz, 1H), 2.01 (ddt, *J* = 14.2, 5.9, 2.7 Hz, 0.5H), 1.88 – 1.76 (m, 2H), 1.75 – 1.67 (m, 1H), 1.56 – 1.21 (m, 8H), 1.03 (qq, *J* = 9.6, 3.3 Hz, 1H), 0.86 (dd, *J* = 13.6, 6.8 Hz, 4H), 0.72 (d, *J* = 6.8 Hz, 2H), 0.66 (d, *J* = 6.6 Hz, 2H), 0.65 – 0.57 (m, 1H), 0.54 (d, *J* = 7.1 Hz, 1H), 0.09 (d, *J* = 6.9 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 157.91, 157.81, 137.54, 129.03, 128.70, 113.49, 113.10, 81.74, 79.66, 78.92, 76.47, 55.27, 50.73, 50.26, 49.06, 48.09, 43.67, 40.30, 35.47, 34.57, 34.34, 34.23, 33.77, 32.98, 31.61, 31.34, 26.07, 25.97, 25.24, 24.85, 23.87, 22.94, 22.68, 22.45, 22.15, 21.37, 21.31, 15.98, 15.50.

HRMS *m/z* (ESI) calcd. for C₂₃H₃₆O₂Na⁺ (*M*+Na)⁺ 367.2608, found 367.2608.



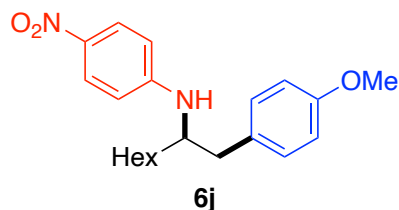
benzyl (*S*)-2-(((1-(4-methoxyphenyl)octan-2-yl)oxy)methyl)pyrrolidine-1-carboxylate

6i was prepared following the General Procedure 2.2 and purified by column chromatography (10:1) as pale yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 5H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.02 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.79 (td, *J* = 12.3, 11.8, 8.0 Hz, 2H), 5.17 – 5.07 (m, 2H), 4.01 – 3.72 (m, 4H), 3.65 – 3.11 (m, 5H), 2.83 – 2.52 (m, 2H), 1.96 – 1.72 (m, 4H), 1.38 (dq, *J* = 20.1, 8.5, 6.6 Hz, 3H), 1.32 – 1.15 (m, 7H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.81, 154.83, 137.01, 136.83, 131.22, 130.35, 130.28, 128.41, 127.92, 127.83, 127.72, 113.93, 113.51, 113.47, 81.43, 81.34, 81.29, 81.21, 69.95, 69.88, 69.00, 66.69, 66.46, 57.38, 56.66, 55.19, 46.89, 46.73, 46.61, 39.82, 39.59, 34.01, 33.93, 33.84, 33.71, 31.82, 29.68, 29.39, 28.80, 28.71, 27.97, 25.41, 25.30, 23.75, 23.67, 22.72, 22.60, 14.08.

HRMS m/z (ESI) calcd. for $\text{C}_{28}\text{H}_{40}\text{O}_4\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 454.2952, found 454.2954.



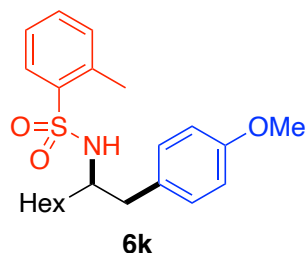
N-(1-(4-methoxyphenyl)octan-2-yl)-4-nitroaniline

6j was prepared following the General Procedure 2.2 and purified by column chromatography (10:1) as yellow oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 8.06 (d, $J = 9.2$ Hz, 2H), 7.04 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.5$ Hz, 2H), 6.49 (d, $J = 9.2$ Hz, 2H), 4.30 (d, $J = 8.8$ Hz, 1H), 3.78 (s, 3H), 3.68 (dp, $J = 11.4, 5.8$ Hz, 1H), 2.84 (dd, $J = 13.9, 6.1$ Hz, 1H), 2.75 (dd, $J = 13.9, 5.4$ Hz, 1H), 1.45 – 1.31 (m, 3H), 1.31 – 1.20 (m, 7H), 0.86 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.31, 152.94, 137.53, 130.40, 129.28, 126.57, 113.86, 111.16, 55.22, 53.81, 39.22, 34.05, 31.69, 29.14, 26.04, 22.53, 14.01.

HRMS m/z (ESI) calcd. for $\text{C}_{21}\text{H}_{28}\text{O}_3\text{N}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 379.1992, found 379.1996.



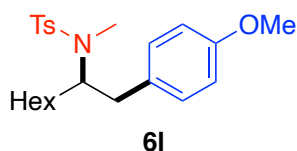
N-(1-(4-methoxyphenyl)octan-2-yl)-2-methylbenzenesulfonamide

6k was prepared following the General Procedure 2.3 and purified by column chromatography (8:1) as pale yellow oil.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.96 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.42 (td, $J = 7.5, 1.4$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 2H), 6.74 (d, $J = 8.5$ Hz, 2H), 4.31 (d, $J = 8.3$ Hz, 1H), 3.78 (s, 3H), 3.35 (q, $J = 6.8$ Hz, 1H), 2.70 (dd, $J = 13.8, 6.6$ Hz, 1H), 2.61 (dd, $J = 13.8, 6.0$ Hz, 1H), 2.48 (s, 3H), 1.42 (tt, $J = 10.2, 5.2$ Hz, 1H), 1.34 (qt, $J = 6.9, 3.7$ Hz, 1H), 1.25 – 1.00 (m, 8H), 0.83 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.29, 138.41, 136.94, 132.56, 132.48, 130.37, 129.45, 129.07, 126.03, 113.89, 55.24, 55.14, 40.40, 34.37, 31.66, 28.89, 25.25, 22.52, 20.40, 14.07.

HRMS m/z (ESI) calcd. for $\text{C}_{22}\text{H}_{32}\text{O}_3\text{NS}^+$ ($\text{M}+\text{H}$) $^+$ 390.2097, found 390.2098.



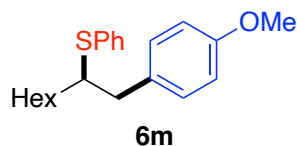
N-(1-(4-methoxyphenyl)octan-2-yl)-N,4-dimethylbenzenesulfonamide

6l was prepared following the General Procedure 2.3 and purified by column chromatography (10:1) as pale yellow oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.52 (d, $J = 8.3$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.04 – 6.98 (m, 2H), 6.82 – 6.74 (m, 2H), 4.08 (tt, $J = 8.4, 5.9$ Hz, 1H), 3.79 (s, 3H), 2.70 (s, 3H), 2.50 (qd, $J = 13.7, 7.3$ Hz, 2H), 2.38 (s, 3H), 1.34 (td, $J = 9.1, 4.5$ Hz, 3H), 1.24 – 1.09 (m, 7H), 0.84 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.20, 142.74, 137.40, 130.52, 130.09, 129.44, 127.10, 113.86, 59.15, 55.23, 38.36, 31.71, 31.22, 29.02, 27.74, 26.35, 22.57, 21.48, 14.11.

HRMS m/z (ESI) calcd. for $\text{C}_{23}\text{H}_{34}\text{O}_3\text{NS}^+$ ($\text{M}+\text{H}$) $^+$ 404.2254, found 404.2259.



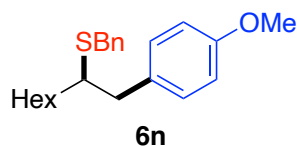
1-(4-methoxyphenyl)octan-2-yl(phenyl)sulfane

6m was prepared following the General Procedure 2.3 and purified by column chromatography (50:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.38 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.22 – 7.19 (m, 1H), 7.07 (d, $J = 8.5$ Hz, 1H), 6.81 (d, $J = 8.5$ Hz, 1H), 3.78 (s, 2H), 3.28 (tt, $J = 7.8, 5.3$ Hz, 1H), 2.88 (dd, $J = 14.0, 5.9$ Hz, 1H), 2.73 (dd, $J = 14.1, 8.1$ Hz, 1H), 1.65 – 1.51 (m, 1H), 1.45 (dddd, $J = 24.7, 14.9, 7.9, 4.3$ Hz, 1H), 1.33 – 1.14 (m, 4H), 0.85 (t, $J = 7.1$ Hz, 2H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.10, 135.67, 131.88, 131.50, 130.22, 128.84, 126.64, 113.67, 55.25, 50.74, 40.52, 33.38, 31.73, 29.15, 26.70, 22.64, 14.13.

HRMS m/z (EI) calcd. for $\text{C}_{21}\text{H}_{28}\text{OS}^+$ (M) $^+$ 328.1861, found 328.1870.



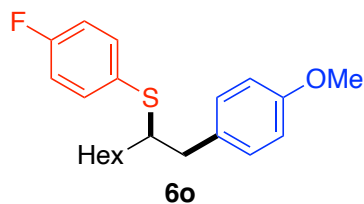
benzyl(1-(4-methoxyphenyl)octan-2-yl)sulfane

6n was prepared following the General Procedure 2.3 and purified by column chromatography (50:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.35 – 7.16 (m, 5H), 7.04 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 3.79 (s, 3H), 3.65 – 3.50 (m, 2H), 2.82 (dd, $J = 13.8, 6.8$ Hz, 1H), 2.73 (dd, $J = 13.8, 7.4$ Hz, 1H), 2.65 (qd, $J = 7.2, 4.8$ Hz, 1H), 1.54 – 1.47 (m, 1H), 1.41 (tt, $J = 12.5, 7.7, 7.3, 4.3$ Hz, 2H), 1.32 – 1.08 (m, 7H), 0.85 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.04, 138.69, 131.81, 130.26, 128.97, 128.39, 126.85, 113.61, 55.26, 46.68, 41.15, 35.49, 33.88, 31.75, 29.11, 26.50, 22.63, 14.12.

HRMS m/z (ESI) calcd. for $\text{C}_{22}\text{H}_{31}\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 343.2090, found 343.2094.



(4-fluorophenyl)(1-(4-methoxyphenyl)octan-2-yl)sulfane

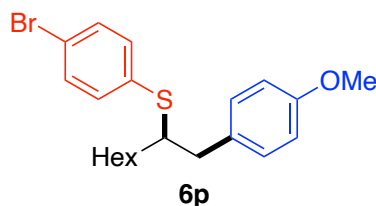
6o was prepared following the General Procedure 2.3 and purified by column chromatography (50:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 2H), 7.05 (d, $J = 8.5$ Hz, 2H), 6.98 (t, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 3.78 (s, 4H), 3.20 – 3.11 (m, 1H), 2.83 (dd, $J = 14.0, 6.2$ Hz, 1H), 2.71 (dd, $J = 14.0, 7.9$ Hz, 1H), 1.59 – 1.51 (m, 3H), 1.43 (ddd, $J = 16.8, 12.6, 8.8$ Hz, 3H), 1.32 – 1.15 (m, 9H), 0.86 (t, $J = 7.1$ Hz, 4H).

$^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 162.19 (d, $J = 246.9$ Hz), 158.12, 134.96 (d, $J = 8.2$ Hz), 131.42, 130.32 (d, $J = 3.0$ Hz), 130.18, 115.89 (d, $J = 21.7$ Hz), 113.68, 55.24, 51.99, 40.58, 33.44, 31.72, 29.11, 26.66, 22.63, 14.11.

$^{19}\text{F NMR}$ (564 MHz, Chloroform-*d*) δ -114.74.

HRMS m/z (EI) calcd. for $\text{C}_{21}\text{H}_{27}\text{OF}^+$ (M) $^+$ 346.1767, found 346.1771.



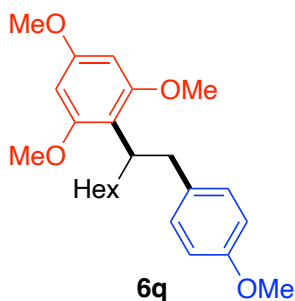
(4-bromophenyl)(1-(4-methoxyphenyl)octan-2-yl)sulfane

6p was prepared following the General Procedure 2.3 and purified by column chromatography (100:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.38 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.24 (qd, $J = 7.1, 5.2$ Hz, 1H), 2.84 (dd, $J = 14.1, 6.3$ Hz, 1H), 2.75 (dd, $J = 14.1, 7.7$ Hz, 1H), 1.69 – 1.36 (m, 5H), 1.34 – 1.17 (m, 5H), 0.86 (t, $J = 7.0$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.16, 134.95, 133.36, 131.86, 131.19, 130.20, 120.60, 113.69, 55.26, 51.15, 40.51, 33.49, 31.70, 29.11, 26.68, 22.61, 14.10.

HRMS m/z (ESI) calcd. for $\text{C}_{21}\text{H}_{28}\text{OSBrNa}^+$ ($\text{M}+\text{Na}$) $^+$ 431.0838, found 431.0841.



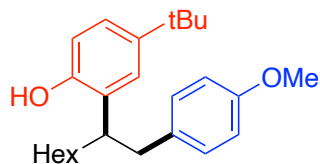
1,3,5-trimethoxy-2-(1-(4-methoxyphenyl)octan-2-yl)benzene

6q was prepared following the General Procedure 2.3 and purified by column chromatography (20:1) as colorless oil.

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 6.97 (d, $J = 8.5$ Hz, 2H), 6.70 (d, $J = 8.6$ Hz, 2H), 6.14 – 5.95 (m, 2H), 3.75 (d, $J = 18.8$ Hz, 9H), 3.69 – 3.52 (m, 3H), 3.46 (dtd, $J = 10.0, 7.7, 5.4$ Hz, 1H), 2.92 (dd, $J = 13.4, 8.3$ Hz, 1H), 2.85 (dd, $J = 13.4, 7.2$ Hz, 1H), 1.91 – 1.81 (m, 1H), 1.57 – 1.48 (m, 1H), 1.25 – 1.02 (m, 8H), 0.82 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 161.48, 160.00, 159.09, 158.84, 157.18, 134.79, 129.81, 113.71, 113.01, 92.82, 91.23, 90.92, 56.13, 55.27, 55.12, 55.08, 39.30, 37.04, 32.82, 31.84, 29.43, 28.15, 22.65, 14.08.

HRMS m/z (ESI) calcd. for $C_{24}H_{34}O_4Na^+$ ($M+Na$) $^+$ 409.2349, found 409.2350.



6r

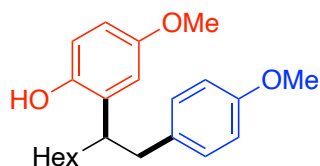
4-(tert-butyl)-2-(1-(4-methoxyphenyl)octan-2-yl)phenol

6r was prepared following the General Procedure 2.3 and purified by column chromatography (10:1) as colorless oil.

1H NMR (600 MHz, Chloroform- d) δ 7.06 (d, J = 2.4 Hz, 1H), 7.03 (dd, J = 8.3, 2.5 Hz, 1H), 6.94 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 6.60 (d, J = 8.3 Hz, 1H), 4.45 (s, 1H), 3.75 (s, 3H), 3.14 (p, J = 7.2 Hz, 1H), 2.81 (d, J = 6.8 Hz, 2H), 1.66 (q, J = 7.4 Hz, 2H), 1.33 – 1.14 (m, 8H), 1.24 (s, 9H), 0.83 (t, J = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.60, 151.06, 143.24, 133.03, 130.27, 130.04, 125.03, 123.13, 114.80, 113.40, 55.15, 41.50, 33.92, 31.70, 31.53, 29.35, 27.43, 22.58, 14.05.

HRMS m/z (ESI) calcd. for $C_{25}H_{36}O_2Na^+$ ($M+Na$) $^+$ 391.2608, found 391.2616.



6s

(2-methoxyphenyl)(1-(4-methoxyphenyl)octan-2-yl)sulfane

6s was prepared following the General Procedure 2.3 and purified by column chromatography (10:1) as colorless oil.

1H NMR (600 MHz, Chloroform- d) δ 6.96 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 2.9 Hz, 1H), 6.63 (d, J = 8.6 Hz, 1H), 6.59 (dd, J = 8.7, 2.9 Hz, 1H), 4.03 (s, 1H), 3.76 (d, J = 2.8 Hz, 6H), 3.13 (ddd, J = 12.2, 8.5, 6.1 Hz, 1H), 2.83 (dd, J = 13.5, 6.6 Hz, 1H), 2.74 (dd, J = 13.5, 8.0 Hz, 1H), 1.65 (ddt, J = 13.7, 10.0, 6.2 Hz, 2H), 1.21 (qt, J = 14.2, 4.1 Hz, 8H), 0.83 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.78, 153.94, 147.51, 132.86, 132.79, 129.97, 116.38, 113.63, 113.55, 111.16, 55.68, 55.20, 41.92, 34.48, 31.79, 29.43, 27.53, 22.66, 14.10.

HRMS m/z (EI) calcd. for $C_{22}H_{30}O_3^+$ (M) $^+$ 342.2195, found 342.2196.

IV. NMR Spectra Data

