## **Supporting Information**

## Facile, general allylation of unactivated alkyl halides via electrochemically enabled radical-polar crossover

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#### 1. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were HPLC grade. Anhydrous and degassed DMF used in reactions was purchased from Sigma-Aldrich in Sure/Seal<sup>TM</sup> bottle. Analytical thinlayer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed on silica gel (particle size 0.043–0.063 mm) by using Interchim PuriFlash®430 automatic purification system. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on Bruker DRX-500 and AMX-400 instruments in CDC13 and are reported relative to the solvent residual peaks. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Cyclic voltammetry (CV) was performed on BioLogic Potentiostat SP-50. Mass spectra (EI-MS, 70 eV) were conducted on an Agilent 7890 gas chromatograph equipped with 5975C EIMSD Triple-Axis Detector using DB5MS and HP5MS columns. HRMS-ESI analysis was performed using a Thermo LTQ Velos Orbitrap mass spectrometer (Thermo Scientific, Pittsburgh, PA, USA) equipped with an ESI source. HRMS-EI analysis was performed using Agilent 7890 gas chromatograph equipped with JEOL AccuTOF GCx-plus EI source. For the electrocatalyzed reactions at constant current modes, Matsusada R4K36-0.1-L (230V) was used as power supply.

#### 2. General Procedure

A dry 5-mL vial equipped with a Teflon-coated magnetic stir bar (10mm\*3mm) was charged with allylic carbonate (0.2 mmol, 1 equiv., if solid) and TBAB (0.8 mmol, 4 equiv) in glovebox. Anhydrous and degassed DMA (4.0 mL), alkyl bromide (0.4 mmol, 2 equiv., if liquid), were added via syringe. Then, it was capped with a Teflon lid equipped with iron rod (4×50 mm) as the anode and nickel foam (20×10×1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA under room temperature for 16 h. After the reaction is completed, the mixture was transferred to a 50 mL round bottom flask, electrodes were washed with ethyl acetate. Then H<sub>2</sub>O (20 mL) was added and the mixture was extracted with EtOAc (20 mL) for three times. The combined organic layer was washed with H<sub>2</sub>O (20 mL) and brine (20 mL). The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, then concentrated under vacuum. The product was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent.

## 3. Synthesis of Allylic Carbonate

Methyl chloroformate (200 mol%) was added to a solution of allylic alcohol (100 mol %) and pyridine (300 mol %) in DCM (0.4 M) at 0 °C. The reaction mixture was warmed to room temperature, and stirred overnight, at which point it was washed with brine and extracted with ethyl acetate. The combined organic layer was washed with HCl (1N), dried over MgSO<sub>4</sub>. Silica gel was added, and the solvent was removed under reduced pressure. The residue was loaded to a silica column. Flash chromatography provided the desired allylic carbonate.

## 4. Preparation of Alkyl-Br

To a 50 mL sealed tube was added the corresponding alcohol (5 mmol, 1equiv), N-bromosuccinimide (NBS, 5 mmol, 1.0 equiv), triphenylphosphine (PPh<sub>3</sub>, 5 mmol, 1.0 equiv), dry THF (40 mL) and magnetic stir bar. The tube was sealed and stirred at 60 °C for 12h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (30 mL×4). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of solvent under reduced pressure, the residue was purified by flash chromatography to afford the desired alkyl-Br.

## 5. Cyclic Voltammetry (CV) Measurements

All measurements were performed under anhydrous conditions in argon-filled glovebox. All supporting electrolytes were dried under dynamic vacuum (less than 0.1 mbar) over 24 h at 100 °C and stored inside the glovebox. The cell for the analysis was equipped with a glass vial (working volume is 10 mL) and Teflon cap, equipped with O-ring for tight sealing. Glassy carbon was used as a working electrode (circle, d=3 mm), platinum wire as a counter electrode, and saturated calomel electrode (SCE) (CHI150 from CH Instruments, Inc.) as a reference electrode. All measurements were conducted in 0.1 M solutions of  $^nBu_4NPF_6$  in DMA. All analytic concentration was 10 mM. The scan rate was 100 mV/s.

## 6. Control experiments

Entry	Fe ion	Results
1	FeBr <sub>2</sub> 10%	64%
2	FeBr <sub>2</sub> 100%	60%
3	FeBr <sub>3</sub> 10%	62%

Figure S1. Control experiments with additional iron ions. The yield was detected with GC-FID.

Entry	Electrode	Results
1	RVC//Ni foam w/ TMEDA	11%
2	RVC//RVC w/ TMEDA	13%
3	Zn//Ni foam	27%

Figure S2. Control experiments. The yield was detected with GC-FID.

## 7. Spectroscopic Data of the Products

## 1-(*Tert*-butyl)-4-(4,4-dimethylpent-1-en-2-yl)benzene (3a)

tBu tBu

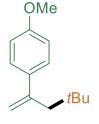
This compound was prepared according to General procedure, 30.0 mg, 65% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (s, 4H), 5.25 (d, J = 2.1 Hz, 1H), 4.98 (d, J = 2.2 Hz, 1H), 2.46 (s, 2H), 1.32 (s, 9H), 0.81 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.83, 147.19, 140.52, 126.08, 124.91, 115.55, 48.68, 34.40, 31.70, 31.35, 30.10.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{17}H_{26}^+$ ): m/z 230.20290; found: 230.20273.

## 1-(4,4-Dimethylpent-1-en-2-yl)-4-methoxybenzene (3b)



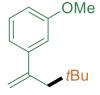
This compound was prepared according to General procedure, 29.0 mg, 71% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 5.18 (d, J = 2.1 Hz, 1H), 4.93 (d, J = 2.1 Hz, 1H), 3.81 (s, 3H), 2.43 (s, 2H), 0.80 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.71, 146.86, 136.14, 127.55, 114.87, 113.41, 55.20, 48.87, 31.69, 30.09.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{14}H_{20}O^+$ ): m/z 204.15087; found: 204.15019.

## 1-(4,4-Dimethylpent-1-en-2-yl)-3-methoxybenzene (3c)



This compound was prepared according to General procedure, 25.7 mg, 63% yield as colorless oil.

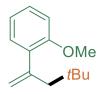
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21 (t, J = 7.9 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.92 (t, J = 2.1 Hz, 1H), 6.79 (dd, J = 8.1, 2.5 Hz, 1H), 5.25 (d, J = 2.0 Hz, 1H),

5.00 (d, J = 2.0 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 2H), 0.80 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.34, 147.42, 145.25, 129.00, 119.17, 116.37, 112.53, 112.02, 55.19, 48.93, 31.73, 30.00.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{14}H_{20}O^+$ ): m/z 204.15087; found: 204.15033.

## 1-(4,4-Dimethylpent-1-en-2-yl)-2-methoxybenzene (3d)



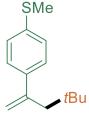
This compound was prepared according to General procedure, 19.2 mg, 47% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.20 (m, 1H), 7.17 (dd, J = 7.4, 1.7 Hz, 1H), 6.90 (t, J = 6.9 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 5.09 (d, J = 2.3 Hz, 1H), 5.07 (d, J = 2.5 Hz, 1H), 3.83 (s, 3H), 2.50 (s, 2H), 0.77 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.44, 147.29, 133.63, 130.26, 128.03, 120.49, 118.02, 110.64, 55.34, 49.88, 31.63, 29.87.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{14}H_{20}O^+$ ): m/z 204.15087; found: 204.15091.

## (4-(4,4-Dimethylpent-1-en-2-yl)phenyl)(methyl)sulfane (3e)



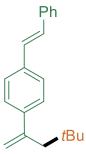
This compound was prepared according to General procedure, 33.9 mg, 77% yield as colorless oil.

<sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.31 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 5.23 (d, J = 2.0 Hz, 1H), 4.98 (s, 1H), 2.48 (s, 3H), 2.44 (s, 2H), 0.80 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.80, 140.54, 136.82, 126.94, 126.31, 115.93, 48.70, 31.73, 30.06, 15.87.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{14}H_{20}S^+$ ): m/z 220.12802; found: 220.12902.

## (2-(4-(Tert-butyl) phenyl) allyl) trimethylgermane (3f)



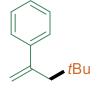
This compound was prepared according to General procedure, 24.3 mg, 44% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 – 7.45 (m, 4H), 7.40 – 7.34 (m, 4H), 7.28-7.24 (m, 1H), 7.11 (s, 2H), 5.30 (d, J = 2.0 Hz, 1H), 5.03 (d, J = 1.9 Hz, 1H), 2.48 (s, 2H), 0.82 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.08, 142.97, 137.44, 136.04, 128.70, 128.40, 128.31, 127.56, 126.85, 126.49, 126.34, 116.27, 48.71, 31.81, 30.11.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{21}H_{24}^+$ ): m/z 276.18725; found: 276.18790.

#### (4,4-Dimethylpent-1-en-2-yl)benzene (3g)



This compound was prepared according to General procedure, 17.8 mg, 51% yield as colorless oil.

<sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.37 (d, J = 7.0 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 5.24 (d, J = 2.0 Hz, 1H), 5.01 (s, 1H), 2.47 (s, 2H), 0.80 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.58, 143.69, 128.07, 126.90, 126.53, 116.27, 48.89, 31.73, 30.04.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{13}H_{18}^+$ ): m/z 174.14030; found: 174.14040.

## 1-(4,4-Dimethylpent-1-en-2-yl)naphthalene (3h)



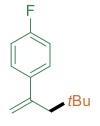
This compound was prepared according to General procedure, 25.1 mg, 56% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (dd, J = 8.2, 1.7 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.74 (d, J = 6.9 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.37 (m, 2H), 5.42 (d, J = 2.4 Hz, 1H), 5.25 (d, J = 2.4 Hz, 1H), 2.61 (s, 2H), 0.83 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.58, 142.61, 133.96, 130.99, 128.38, 126.98, 126.16, 125.56, 125.43, 125.20, 125.07, 119.51, 52.34, 32.11, 29.90.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{17}H_{20}^+$ ): m/z 224.15595; found: 224.15700.

## 1-(4,4-Dimethylpent-1-en-2-yl)-4-fluorobenzene (3i)



This compound was prepared according to General procedure, 21.2 mg, 55% yield as colorless oil.

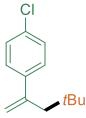
<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.33 (dd, J = 8.5, 5.6 Hz, 2H), 6.98 (t, J = 8.7 Hz, 2H), 5.20 (s, 1H), 5.00 (s, 1H), 2.43 (s, 2H), 0.79 (s, 9H).

<sup>19</sup>**F NMR (471 MHz, CDCl<sub>3</sub>)** δ -116.11.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.03 (d, J = 245.5 Hz), 146.54, 139.69 (d, J = 3.3 Hz), 128.00 (d, J = 7.9 Hz), 116.26, 114.88 (d, J = 21.2 Hz), 49.06, 31.73, 30.03.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{13}H_{17}F^+$ ): m/z 192.13088; found: 192.13135.

## 1-Chloro-4-(4,4-dimethylpent-1-en-2-yl)benzene (3j)



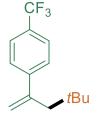
This compound was prepared according to General procedure, 21.3 mg, 51% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.29 (m, 2H), 7.29 – 7.25 (m, 2H), 5.24 (d, J = 1.9 Hz, 1H), 5.03 (s, 1H), 2.44 (s, 2H), 0.80 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.42, 142.14, 132.69, 128.24, 127.81, 116.81, 48.84, 31.76, 30.02.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{13}H_{17}C1^+$ ): m/z 208.10133; found: 208.10230.

## 1-(4,4-Dimethylpent-1-en-2-yl)-4-(trifluoromethyl)benzene (3k)



This compound was prepared according to General procedure, 20.8 mg, 43% yield as colorless oil.

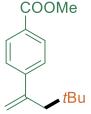
<sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.55 (d, J = 9.4 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 5.31 (s, 1H), 5.11 (s, 1H), 2.48 (s, 2H), 0.80 (s, 9H).

<sup>19</sup>F NMR (471 MHz, CDCl3)  $\delta$  -62.38.

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  147.33, 146.50, 129.01 (q, J = 32.5 Hz), 126.77, 125.11 (q, J = 3.8 Hz), 124.28 (q, J = 270.7 Hz), 118.17, 48.80, 31.82, 30.00.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{14}H_{17}F_{3}^+$ ): m/z 242.12769; found: 242.12689.

## Methyl 4-(4,4-dimethylpent-1-en-2-yl)benzoate (3l)



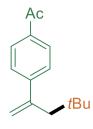
This compound was prepared according to General procedure, 28.8 mg, 62% yield as colorless oil.

<sup>1</sup>**H NMR** (**400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.97 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 5.32 (d, J = 1.8 Hz, 1H), 5.10 (s, 1H), 3.91 (s, 3H), 2.48 (s, 2H), 0.78 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.01, 148.39, 146.80, 129.51, 128.59, 126.48, 118.05, 52.02, 48.74, 31.80, 29.97.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{15}H_{20}O_2^+$ ): m/z 232.14578; found: 232.14690.

## 1-(4-(4,4-Dimethylpent-1-en-2-yl)phenyl)ethan-1-one (3m)



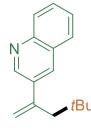
This compound was prepared according to General procedure, 16.4 mg, 38% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 5.33 (d, J = 1.7 Hz, 1H), 5.11 (d, J = 1.7 Hz, 1H), 2.59 (s, 3H), 2.48 (s, 2H), 0.79 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.71, 148.56, 146.70, 135.67, 128.35, 126.64, 118.22, 48.69, 31.81, 29.97, 26.57.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{15}H_{20}O^+$ ): m/z 216.15087; found: 216.15033.

## 3-(4,4-Dimethylpent-1-en-2-yl)quinoline (3n)



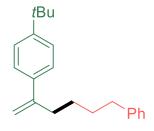
This compound was prepared according to General procedure, 15.8 mg, 35% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.99 (d, J = 2.2 Hz, 1H), 8.09 (d, J = 9.0 Hz, 2H), 7.81 (d, J = 8.2 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.54 (d, J = 15.0 Hz, 1H), 5.45 (d, J = 1.5 Hz, 1H), 5.22 (s, 1H), 2.59 (s, 2H), 0.83 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.67, 147.13, 144.32, 136.21, 132.36, 129.09, 129.02, 127.88, 127.70, 126.80, 118.65, 48.70, 31.90, 30.09.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{16}H_{19}N^+$ ): m/z 225.15120; found: 225.15211.

## 1-(Tert-butyl)-4-(6-phenylhex-1-en-2-yl)benzene (4a)



This compound was prepared according to General procedure, 33.3 mg, 57% yield as colorless oil.

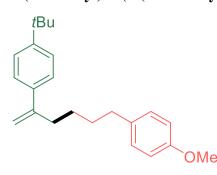
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.34 (s, 4H), 7.28 – 7.25 (m, 2H), 7.19 – 7.14 (m, 3H), 5.26 (d, J = 1.6 Hz, 1H), 5.01 (t, J = 1.4 Hz, 1H), 2.61 (t, J = 7.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 (d, J = 7.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 (d, J = 7.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 (d, J = 7.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 (d, J = 7.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 (d, J = 7.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 (d, J = 7.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 (d, J = 7.8 Hz, 2H), 2.53 (t, J = 7.8 Hz, 2H), 2.53 (t, J = 7.8 Hz, 2H), 2.54 (t, J = 7.8 Hz, 2H), 2.54 (t, J = 7.8 Hz, 2H), 2.55 (t, J = 7.8

7.7 Hz, 2H), 1.33 (s, 9H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 150.22, 148.03, 142.68, 138.28, 128.36, 128.22, 125.68, 125.58, 125.12, 111.51, 35.72, 35.03, 34.46, 31.32, 31.11, 27.93.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{22}H_{28}^+$ ): m/z 292.21855; found: 292.21773.

## 1-(*Tert*-butyl)-4-(6-(4-methoxyphenyl)hex-1-en-2-yl)benzene (4b)



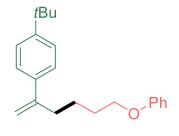
This compound was prepared according to General procedure, 31.6 mg, 49% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35 (s, 4H), 7.08 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 8.3 Hz, 2H), 5.27 (s, 1H), 5.01 (s, 1H), 3.79 (s, 3H), 2.54 (dt, J = 16.2, 7.6 Hz, 4H), 1.68 – 1.57 (m, 2H), 1.52 (p, J = 7.7, 7.3 Hz, 2H), 1.34 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.60, 150.21, 148.05, 138.29, 134.78, 129.21, 125.68, 125.11, 113.64, 111.48, 55.23, 35.03, 34.76, 34.45, 31.35, 31.32, 27.87.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{23}H_{30}O^+$ ): m/z 322.22912; found: 322.22809.

#### 1-(Tert-butyl)-4-(6-phenoxyhex-1-en-2-yl)benzene (4c)



This compound was prepared according to General procedure, 51.2 mg, 83% yield as colorless oil.

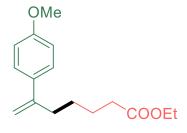
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, J = 0.8 Hz, 4H), 7.29 (dd, J = 8.7, 7.3 Hz, 2H), 6.94 (tt, J = 7.3, 1.1 Hz, 1H), 6.91 – 6.87 (m, 2H), 5.31 (d, J = 1.5 Hz, 1H), 5.07 (d, J = 1.4 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H),

2.63 – 2.55 (m, 2H), 1.89 – 1.80 (m, 2H), 1.72 – 1.62 (m, 2H), 1.35 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.01, 150.28, 147.77, 138.09, 129.37, 125.69, 125.16, 120.45, 114.44, 111.76, 67.56, 34.87, 34.45, 31.31, 28.86, 24.66.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{22}H_{28}O^+$ ): m/z 308.21347; found: 308.21215.

## Ethyl 6-(4-methoxyphenyl)hept-6-enoate (4d)



This compound was prepared according to General procedure, 22.0 mg, 42% yield as colorless oil.

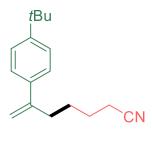
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.34 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 7.4 Hz, 2H), 5.20 (s, 1H), 4.97 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 2.49 (t, J = 7.6 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 1.66 (p, J =

7.3 Hz, 2H), 1.48 (q, J = 8.3 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 173.71, 158.98, 147.32, 133.51, 127.13, 113.60, 110.90, 60.19, 55.25, 35.00, 34.16, 27.69, 24.60, 14.21.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{16}H_{22}O_3^+$ ): m/z 362.15635; found: 362.15627.

## 6-(4-(*Tert*-butyl)phenyl)hept-6-enenitrile (4e)



This compound was prepared according to General procedure, 29.5 mg, 61% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.31 (m, 4H), 5.30 (s, 1H), 5.03 (s, 1H), 2.55 (t, J = 7.2 Hz, 2H), 2.33 (t, J = 7.0 Hz, 2H), 1.73 – 1.59 (m, 4H), 1.33 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.52, 146.99, 137.63, 125.64, 125.26, 119.67, 112.23, 34.46, 34.30, 31.27, 27.12, 24.90, 16.96.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{17}H_{23}N^+$ ): m/z 241.18250; found: 241.18353.

Tert-butyl((5-(4-(tert-butyl)phenyl)hex-5-en-1-yl)oxy)dimethylsilane (4f)

tBu OTBS

This compound was prepared according to General procedure, 42.3 mg, 61% yield as colorless oil.

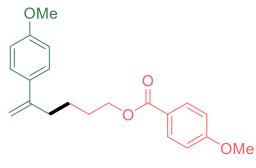
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (s, 4H), 5.27 (d, J = 1.6 Hz, 1H), 5.02 (q, J = 1.4 Hz, 1H), 3.60 (t, J = 6.2 Hz, 2H), 2.51 (t, J = 6.8 Hz, 2H), 1.53 (dtt, J = 10.7, 5.1, 2.4 Hz, 4H), 1.32 (s, 9H), 0.88 (s, 9H),

0.03 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.17, 148.09, 138.25, 125.69, 125.10, 111.44, 63.00, 34.96, 34.44, 32.47, 31.31, 25.96, 24.47, 18.33, -5.28.

**HRMS** (EI) exact mass calculated for  $[M-CH_3^+]$  ( $C_{21}H_{35}OSi^+$ ): m/z 331.24517; found: 331.24382.

## 5-(4-Methoxyphenyl)hex-5-en-1-yl 4-methoxybenzoate (4g)



This compound was prepared according to General procedure, 49.7 mg, 73% yield as colorless oil.

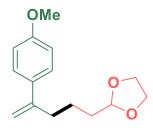
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (d, J = 8.9 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.22 (s, 1H), 5.00 (s, 1H), 4.30 – 4.25 (m, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 2.56 (t, J = 7.5 Hz,

2H), 1.82 – 1.74 (m, 2H), 1.64 – 1.57 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.36, 163.21, 158.98, 147.30, 133.38, 131.50, 127.17, 122.84, 113.61, 113.50, 111.08, 64.41, 55.36, 55.20, 34.87, 28.21, 24.49.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{21}H_{24}O_4^+$ ): m/z 340.16691; found: 340.16637.

## 2-(4-(4-Methoxyphenyl)pent-4-en-1-yl)-1,3-dioxolane (4h)



This compound was prepared according to General procedure, 26.3 mg, 53% yield as colorless oil.

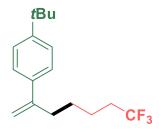
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.34 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.21 (s, 1H), 4.99 (s, 1H), 4.84 (t, J = 4.7 Hz, 1H), 3.97 – 3.92 (m, 2H), 3.82 (d, J = 8.5 Hz, 5H), 2.52 (t, J = 7.6 Hz, 2H), 1.72 – 1.66 (m,

2H), 1.59 (q, J = 6.2, 5.0 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.97, 147.36, 133.58, 127.15, 113.60, 110.96, 104.48, 64.81, 55.25, 35.14, 33.41, 22.68.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{15}H_{20}O_{3}^+$ ): m/z 248.14070; found: 248.14182.

#### 1-(*Tert*-butyl)-4-(7,7,7-trifluorohept-1-en-2-yl)benzene (4i)



This compound was prepared according to General procedure, 31.3 mg, 55% yield as colorless oil.

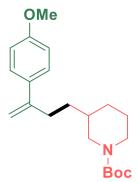
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.31 (m, 4H), 5.29 (s, 1H), 5.02 (s, 1H), 2.57 – 2.50 (m, 2H), 2.13 – 2.01 (m, 2H), 1.63 – 1.55 (m, 3H), 1.54 – 1.50 (m, 1H), 1.33 (s, 9H).

<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -66.41.

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  150.45, 147.35, 137.86, 127.18 (q, J = 278.8 Hz), 125.66, 125.23, 111.99, 34.81, 34.48, 33.57 (q, J = 28.4 Hz), 31.31, 31.30, 27.25, 21.50 (q, J = 3.1 Hz).

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{27}H_{23}F_3^+$ ): m/z 284.17464; found: 284.17443.

## *Tert*-butyl 3-(3-(4-methoxyphenyl)but-3-en-1-yl)piperidine-1-carboxylate (4j)



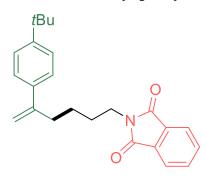
This compound was prepared according to General procedure, 31.8 mg, 46% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.20 (s, 1H), 4.98 (s, 1H), 3.89 (dt, J = 13.2, 4.2 Hz, 1H), 3.81 (s, 3H), 2.75 (t, J = 12.1 Hz, 1H), 2.51 (t, J = 7.9 Hz, 2H), 1.82 (dd, J = 13.9, 4.2 Hz, 1H), 1.63 – 1.57 (m, 1H), 1.45 (s, 15H), 1.07 (q, J = 12.7, 11.9 Hz, 1H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.99, 154.88, 147.71, 133.47, 127.11, 113.62, 110.73, 79.17, 68.98, 64.09, 55.24, 49.48, 44.49, 35.62, 32.60, 31.01, 28.46.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{21}H_{23}NO_3^+$ ): m/z 345.22985; found: 345.22891.

### 2-(5-(4-(*Tert*-butyl)phenyl)hex-5-en-1-yl)isoindoline-1,3-dione (4k)



This compound was prepared according to General procedure, 36.9 mg, 51% yield as colorless oil.

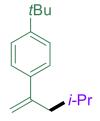
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (d, J = 7.4 Hz, 1H), 7.34 – 7.23 (m, 3H), 7.11 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 4.99 (d, J = 1.5 Hz, 1H), 4.82 (s, 1H), 4.29 – 4.19 (m, 2H), 3.93 (ddt, J = 12.0, 5.0, 1.8 Hz, 1H), 3.64 (d, J = 13.7 Hz, 1H), 3.26 (d,

J = 13.8 Hz, 1H), 3.06 - 2.96 (m, 1H), 1.82 - 1.72 (m, 1H), 1.58 (ddq, J = 13.5, 4.3, 2.0 Hz, 1H), 1.26 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.70, 149.92, 145.35, 142.62, 139.11, 131.93, 131.25, 129.21, 125.93, 124.73, 123.11, 122.34, 117.44, 90.01, 61.81, 37.02, 34.95, 34.34, 31.23, 24.77.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{24}H_{27}NO_2^+$ ): m/z 361.20363; found: 361.20367.

## 1-(*Tert*-butyl)-4-(4-methylpent-1-en-2-yl)benzene (5a)



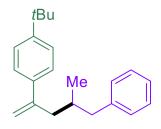
This compound was prepared according to General procedure, 20.8 mg, 48% yield as colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.34 (d, J = 1.0 Hz, 4H), 5.26 (d, J = 1.8 Hz, 1H), 4.98 (s, 1H), 2.37 (d, J = 7.2 Hz, 2H), 1.69 (dp, J = 13.6, 6.8 Hz, 1H), 1.32 (s, 9H), 0.88 (d, J = 6.6 Hz, 6H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 150.13, 147.37, 138.34, 125.84, 125.07, 112.70, 45.05, 34.44, 31.32, 26.33, 22.42.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{16}H_{24}^+$ ): m/z 216.18725; found: 216.18825.

## 1-(*Tert*-butyl)-4-(4-methyl-5-phenylpent-1-en-2-yl)benzene (5b)



This compound was prepared according to General procedure, 32.2 mg, 55% yield as colorless oil.

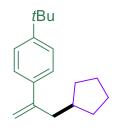
<sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.32 (dd, J = 8.4, 1.8 Hz, 2H), 7.28 – 7.25 (m, 3H), 7.18 (ddd, J = 16.3, 8.1, 3.7 Hz, 2H), 7.10 (d, J = 7.5 Hz, 2H), 5.30 (s, 1H), 5.03 (s, 1H), 2.71 – 2.59 (m, 2H), 2.40 (ddd, J = 13.4, 8.1,

1.7 Hz, 1H), 2.26 (dd, J = 14.0, 8.5 Hz, 1H), 1.91 - 1.81 (m, 1H), 1.33 (s, 9H), 0.84 (d, J = 6.7 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.21, 147.04, 141.29, 138.04, 129.21, 128.06, 125.85, 125.67, 125.10, 113.10, 43.39, 42.75, 34.46, 33.28, 31.32, 19.32.

**HRMS** (EI) exact mass calculated for  $[M-CH_3^+]$  ( $C_{21}H_{25}^+$ ): m/z 277.19508; found: 277.19455.

## 1-(*Tert*-butyl)-4-(3-cyclopentylprop-1-en-2-yl)benzene (5c)



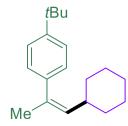
This compound was prepared according to General procedure, 28.1 mg, 58% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (s, 4H), 5.23 (d, J = 1.8 Hz, 1H), 5.00 (s, 1H), 2.49 (d, J = 7.4 Hz, 2H), 1.94 (hept, J = 7.6 Hz, 1H), 1.73 – 1.58 (m, 4H), 1.47 (dq, J = 8.6, 3.7 Hz, 2H), 1.32 (s, 9H), 1.16 (dt, J = 11.9, 7.3 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.10, 147.93, 138.48, 125.77, 125.05, 112.00, 41.87, 38.11, 34.44, 32.44, 31.32, 25.05.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{18}H_{26}^+$ ): m/z 242.20290; found: 242.20243.

## (Z)-1-(*Tert*-butyl)-4-(1-cyclohexylprop-1-en-2-yl)benzene (5d)



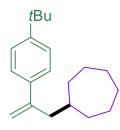
This compound was prepared according to General procedure, 28.2 mg, 55% yield as colorless oil, and the selective ratio is 1:18.

<sup>1</sup>**H NMR** (**500 MHz, CDCl**<sub>3</sub>)  $\delta$  7.33 (s, 4H), 5.62 (dd, J = 9.1, 1.6 Hz, 1H), 2.35 (tdt, J = 10.7, 8.7, 5.8 Hz, 1H), 2.04 (d, J = 1.4 Hz, 3H), 1.78 – 1.65 (m, 5H), 1.32 (s, 11H), 1.23 – 1.10 (m, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.32, 141.04, 133.97, 132.32, 125.18, 125.00, 37.71, 34.37, 33.10, 31.34, 26.12, 26.02, 15.69.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{19}H_{28}^+$ ): m/z 256.21855; found: 256.21728.

#### (2-(4-(*Tert*-butyl)phenyl)allyl)cycloheptane (5e)



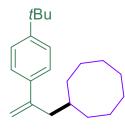
This compound was prepared according to General procedure, 20.6 mg, 38% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33 (s, 4H), 5.27 (s, 1H), 4.96 (s, 1H), 2.39 (d, J = 7.2 Hz, 2H), 1.71 (ddd, J = 13.8, 6.9, 3.2 Hz, 2H), 1.64 – 1.57 (m, 3H), 1.53 – 1.43 (m, 4H), 1.33 (d, J = 1.4 Hz, 11H), 1.22 – 1.14 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.08, 147.26, 138.38, 125.78, 125.07, 112.80, 43.87, 37.06, 34.45, 34.33, 31.33, 28.60, 26.13.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{20}H_{30}^+$ ): m/z 270.23420; found: 270.23360.

#### (2-(4-(*Tert*-butyl)phenyl)allyl)cyclooctane (5f)



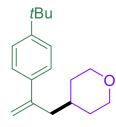
This compound was prepared according to General procedure, 22.8 mg, 40% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33 (s, 4H), 5.26 (s, 1H), 4.97 (s, 1H), 2.38 (d, J = 6.7 Hz, 2H), 1.65 - 1.62 (m, 4H), 1.53 - 1.49 (m, 2H), 1.48 - 1.40 (m, 4H), 1.34 - 1.25 (m, 14H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.08, 147.37, 138.43, 125.81, 125.07, 112.81, 43.64, 35.31, 34.45, 31.64, 31.33, 27.44, 26.07, 25.18.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{21}H_{32}^+$ ): m/z 284.24985; found: 284.25092.

## 4-(2-(4-(*Tert*-butyl)phenyl)allyl)tetrahydro-2H-pyran (5g)



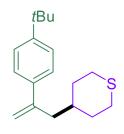
This compound was prepared according to General procedure, 31.5 mg, 61% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.31 (m, 4H), 5.30 (d, J = 1.7 Hz, 1H), 5.00 (d, J = 1.6 Hz, 1H), 3.91 (dd, J = 11.4, 4.4 Hz, 2H), 3.29 (td, J = 11.9, 2.1 Hz, 2H), 2.45 (d, J = 6.6 Hz, 2H), 1.63 – 1.57 (m, 3H), 1.33 (s, 11H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.37, 145.59, 137.86, 125.71, 125.21, 113.32, 67.96, 42.99, 34.47, 33.08, 33.02, 31.30.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{18}H_{26}O^+$ ): m/z 258.19782; found: 258.19711.

## 4-(2-(4-(*Tert*-butyl)phenyl)allyl)tetrahydro-2*H*-thiopyran (5h)



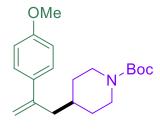
This compound was prepared according to General procedure, 36.2 mg, 66% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.29 (m, 4H), 5.30 (d, J = 1.7 Hz, 1H), 4.98 (s, 1H), 2.62 – 2.52 (m, 4H), 2.42 (d, J = 5.6 Hz, 2H), 2.01 (dt, J = 13.2, 2.9 Hz, 2H), 1.33 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.38, 145.59, 137.78, 125.71, 125.21, 113.53, 43.36, 35.08, 34.47, 34.00, 31.30, 28.60.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{18}H_{26}S^+$ ): m/z 274.17497; found: 274.17596.

## *Tert*-butyl 4-(2-(4-methoxyphenyl)allyl)piperidine-1-carboxylate (5i)



This compound was prepared according to General procedure, 34.5 mg, 52% yield as colorless oil, and the selective ratio is 1:1.

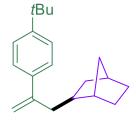
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.28 (m, 2H), 6.85 (t, J = 8.3 Hz, 2H), 5.22 (d, J = 1.7 Hz, 1H), 4.94 (s, 1H), 4.06 (dd, J = 27.7, 13.2 Hz, 2H), 3.81 (d, J = 5.3 Hz, 3H), 2.87 – 2.75 (m, 1H), 2.57 (td, J = 13.4, 12.9,

2.7 Hz, 1H), 2.41 (d, J = 7.1 Hz, 1H), 2.04 (d, J = 1.4 Hz, 1H), 1.69 - 1.58 (m, 2H), 1.45 (d, J = 11.3 Hz, 9H), 1.33 (qd, J = 12.0, 4.2 Hz, 1H), 1.08 (qd, J = 12.4, 4.3 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.02, 158.54, 154.89, 154.81, 145.50, 136.06, 133.55, 133.31, 130.60, 127.22, 126.60, 113.64, 113.50, 112.54, 79.27, 55.26, 55.22, 43.86, 43.67, 42.72, 35.85, 34.19, 32.00, 31.93, 28.45, 28.43, 15.97.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{20}H_{29}NO_3^+$ ): m/z 331.21420; found: 331.21381.

## (1*S*,2*R*,4*R*)-2-(2-(4-(*Tert*-butyl)phenyl)allyl)bicyclo[2.2.1]heptane (5j)



This compound was prepared according to General procedure, 30.6 mg, 57% yield as colorless oil.

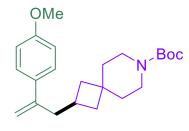
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (s, 4H), 5.26 (d, J = 1.9 Hz, 1H), 4.98 (d, J = 1.5 Hz, 1H), 2.47 (ddd, J = 14.6, 7.5, 1.3 Hz, 1H), 2.25 (ddd, J = 14.6, 7.8, 1.2 Hz, 1H), 2.19 (d, J = 4.5 Hz, 1H), 2.04 – 2.00 (m, 1H), 1.51 – 1.42

(m, 2H), 1.33 (s, 12H), 1.09 (tq, J = 6.5, 2.3 Hz, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.08, 147.01, 138.64, 125.74, 125.06, 112.23, 42.28, 40.86, 39.91, 37.79, 36.74, 35.31, 34.44, 31.32, 29.89, 28.81.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{20}H_{28}^+$ ): m/z 268.21855; found: 268.21733.

## *Tert*-butyl 2-(2-(4-methoxyphenyl)allyl)-7-azaspiro[3.5]nonane-7-carboxylate (5k)



This compound was prepared according to General procedure, 49.0 mg, 66% yield as colorless oil.

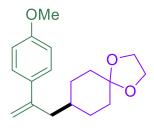
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 5.18 (s, 1H), 4.90 (s, 1H), 3.81 (s, 3H), 3.30 (t, J = 5.7 Hz, 2H), 3.25 (t, J = 5.8 Hz, 2H), 2.56 (d, J = 7.5 Hz, 2H), 2.38 (dt,

J = 16.2, 8.2 Hz, 1H), 1.94 - 1.88 (m, 2H), 1.50 (t, J = 5.7 Hz, 2H), 1.44 (d, J = 1.1 Hz, 13H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.96, 154.97, 146.07, 133.79, 127.07, 113.54, 110.90, 79.12, 55.23, 43.49, 39.67, 37.88, 36.34, 33.87, 28.44, 27.22.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{23}H_{33}NO_3^+$ ): m/z 371.24550; found: 371.24498.

## 8-(2-(4-methoxyphenyl)allyl)-1,4-dioxaspiro[4.5]decane (5l)



This compound was prepared according to General procedure, 46.7 mg, 81% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.21 (d, J = 1.7 Hz, 1H), 4.93 (d, J = 1.8 Hz, 1H), 3.92 (s, 4H), 3.81 (s, 3H), 2.41 (d, J = 7.4 Hz, 2H), 1.70 (q, J = 6.0, 5.5 Hz, 4H), 1.42

(qd, J = 13.6, 12.8, 4.4 Hz, 3H), 1.29 - 1.18 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.96, 146.25, 133.52, 127.23, 113.60, 112.14, 109.10, 64.14, 55.22, 42.42, 34.37, 34.28, 30.02.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{18}H_{24}O_3^+$ ): m/z 288.17200; found: 288.17165.

## 5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl 4-methoxybenzoate (6a)

This compound was prepared according to General procedure, 50.1 mg, 68% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, J =

8.8 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.21 (d, J = 1.9 Hz, 1H), 4.99 (d, J = 1.9 Hz, 1H), 4.30 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 2.52 (s, 2H), 1.66 (t, J = 7.3 Hz, 2H), 0.85 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.41, 163.22, 158.79, 146.12, 136.02, 131.49, 127.55, 122.91, 115.74, 113.52, 62.01, 55.39, 55.17, 47.46, 40.38, 33.65, 27.73.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{23}H_{28}O_4^+$ ): m/z 368.19821; found: 368.19979.

## 5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl thiophene-2-carboxylate (6b)

This compound was prepared according to General procedure, 48.9 mg, 71% yield as colorless oil.

<sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.76 (d, J = 3.7 Hz, 1H), 7.54 (d, J = 5.0 Hz, 1H), 7.30 (d, J = 8.8 Hz,

2H), 7.09 (t, J = 4.4 Hz, 1H), 6.83 (d, J = 8.9 Hz, 2H), 5.21 (d, J = 1.5 Hz, 1H), 4.99 (s, 1H), 4.31 (t, J = 7.2 Hz, 2H), 3.78 (s, 3H), 2.51 (s, 2H), 1.65 (t, J = 7.2 Hz, 2H), 0.85 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 162.28, 158.81, 146.09, 136.00, 134.10, 133.20, 132.16, 127.67, 127.56, 115.79, 113.53, 62.53, 55.19, 47.45, 40.27, 33.66, 27.72.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{20}H_{24}O_3S^+$ ): m/z 344.14407; found: 344.14305.

#### 5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl 2,3,4,5,6-pentafluorobenzoate (6c)

This compound was prepared according to General procedure, 34.3 mg, 40% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (d, J = 8.8

Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.21 (d, J = 2.0 Hz, 1H), 4.97 (d, J = 2.0 Hz, 1H), 4.37 (t, J = 7.5 Hz, 2H), 3.80 (s, 3H), 2.49 (s, 2H), 1.63 (t, J = 7.5 Hz, 2H), 0.84 (s, 6H).

<sup>19</sup>**F NMR** (377 MHz, CDCl<sub>3</sub>) δ -138.37 (d, J = 20.1 Hz), -148.90 (t, J = 20.8 Hz), -160.43 (t, J = 19.3 Hz).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.08, 158.86, 145.92, 135.87, 134.85, 127.53, 126.81, 115.90, 113.55, 113.36, 64.35, 55.19, 47.45, 39.84, 33.58, 27.61.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{22}H_{21}F_5O_3^+$ ): m/z 428.14054; found: 428.14233.

## 5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl methyl terephthalate (6d)

This compound was prepared according to General procedure, 52.3 mg, 66% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 –

8.04 (m, 4H), 7.30 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.21 (d, J = 2.0 Hz, 1H), 4.99 (d, J = 1.9 Hz, 1H), 4.35 (t, J = 7.3 Hz, 2H), 3.95 (s, 3H), 3.77 (s, 3H), 2.52 (s, 2H), 1.67 (t, J = 7.4 Hz, 2H), 0.86 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.32, 165.83, 158.82, 146.04, 135.96, 134.22, 133.77, 129.50, 129.47, 127.56, 126.93, 115.85, 113.53, 62.81, 55.18, 52.43, 47.46, 40.15, 33.66, 27.75.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{24}H_{28}O_5^+$ ): m/z 396.19313; found: 396.19333.

## 1-(*Tert*-butyl)-4-(4,4-dimethyl-5-phenylpent-1-en-2-yl)benzene (6e)

This compound was prepared according to General procedure, 38.6 mg, 63% yield as colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.32 (s, 4H), 7.26 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H),

5.30 (d, J = 2.6 Hz, 1H), 5.02 (s, 1H), 2.55 (s, 2H), 2.50 (s, 2H), 1.32 (s, 9H), 0.75 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.91, 146.69, 140.60, 139.27, 130.69, 127.55, 126.05, 125.71, 124.99, 116.23, 49.59, 47.84, 35.42, 34.40, 31.33, 26.87.

**HRMS** (EI) exact mass calculated for  $[M-CH_3^+]$  ( $C_{22}H_{27}^+$ ): m/z 291.21073; found: 291.21216.

## 1-(Tert-butyl)-4-(4,4-dimethyl-6-phenylhex-1-en-2-yl)benzene (6f)

This compound was prepared according to General procedure, 35.3 mg, 55% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (s, 4H), 7.20 (t, J = 7.5 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.1 Hz,

2H), 5.25 (d, J = 2.1 Hz, 1H), 5.04 (s, 1H), 2.54 (s, 2H), 2.51 - 2.45 (m, 2H), 1.43 - 1.37 (m, 2H), 1.34 (s, 9H), 0.88 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.96, 147.02, 143.37, 140.87, 128.23, 128.15, 126.27, 125.38, 125.04, 116.28, 46.32, 44.35, 34.38, 31.38, 30.78, 27.98, 21.19.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{24}H_{32}^+$ ): m/z 320.24985; found: 320.25123.

## 2-(5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl)isoindoline-1,3-dione (6g)

This compound was prepared according to General procedure, 34.2 mg, 47% yield as colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.83 (dd, J = 5.4, 3.1 Hz, 2H), 7.70 (dd, J = 5.4, 3.0 Hz, 2H), 7.31 (d, J =

8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.22 (d, J = 1.9 Hz, 1H), 5.03 (d, J = 1.9 Hz, 1H), 3.79 (s, 3H), 3.72 – 3.66 (m, 2H), 2.52 (s, 2H), 1.58 (dd, J = 11.9, 3.6 Hz, 2H), 0.84 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.29, 158.76, 145.88, 136.05, 133.79, 132.25, 127.56, 123.08, 115.82, 113.50, 55.21, 46.93, 40.48, 34.38, 33.75, 27.23.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{23}H_{25}NO_3^+$ ): m/z 363.18290; found: 363.18325.

## 1-(4,4-Dimethyl-6-phenoxyhex-1-en-2-yl)-4-methoxybenzene (6h)

This compound was prepared according to General procedure, 31.7 mg, 51% yield as colorless oil.

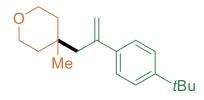
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d, J = 8.6 Hz, 2H), 7.30 – 7.26 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 6.85

(dd, J = 12.4, 8.8 Hz, 4H), 5.22 (d, J = 1.9 Hz, 1H), 4.99 (s, 1H), 3.98 (t, J = 7.2 Hz, 2H), 3.80 (s, 3H), 2.53 (s, 2H), 1.71 (t, J = 7.2 Hz, 2H), 0.86 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.96, 158.79, 146.20, 136.09, 129.36, 127.57, 120.43, 115.73, 114.47, 113.51, 64.85, 55.20, 47.68, 40.93, 33.66, 27.81.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{21}H_{26}O_2^+$ ): m/z 310.19273; found: 310.19308.

## 4-(2-(4-(*Tert*-butyl)phenyl)allyl)-4-methyltetrahydro-2*H*-pyran (6i)



This compound was prepared according to General procedure, 24.5 mg, 45% yield as colorless oil.

<sup>1</sup>**H NMR** (**500 MHz, CDCl**<sub>3</sub>)  $\delta$  7.30 (d, J = 1.7 Hz, 4H), 5.26 (d, J = 2.0 Hz, 1H), 5.00 (s, 1H), 3.65 (dt, J = 11.5, 4.6 Hz, 2H), 3.53

(ddd, J = 11.9, 9.5, 2.9 Hz, 2H), 2.54 (s, 2H), 1.46 (ddd, J = 13.3, 9.2, 3.9 Hz, 2H), 1.32 (s, 9H), 1.18 (dt, J = 14.0, 3.8 Hz, 2H), 0.86 (s, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.09, 145.93, 140.53, 126.08, 125.03, 116.45, 63.97, 47.68, 37.99, 34.43, 31.89, 31.33, 24.06.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{19}H_{28}O^+$ ): m/z 272.21347; found: 272.21235.

## 1-(2-(4-(*Tert*-butyl)phenyl)allyl)adamantane (6j)

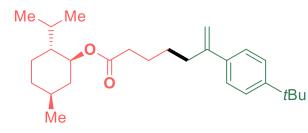
This compound was prepared according to General procedure, 24.7 mg, 40% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (q, J = 8.6 Hz, 4H), 5.27 (d, J = 2.1 Hz, 1H), 4.93 (d, J = 2.0 Hz, 1H), 2.32 (s, 2H), 1.86 (s, 3H), 1.64 – 1.60 (m, 3H), 1.54 – 1.51 (m, 2H), 1.39 (d, J = 2.9 Hz, 5H), 1.32 (s, 11H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.78, 145.45, 140.63, 125.89, 124.91, 115.37, 49.50, 42.97, 36.99, 34.41, 33.61, 31.35, 28.77.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{23}H_{31}^+$ ): m/z 307.24203; found: 308.25013.

## (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 6-(4-(tert-butyl)phenyl)hept-6-enoate (7a)



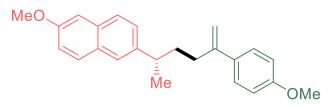
This compound was prepared according to General procedure, 32.7 mg, 41% yield as colorless oil.

<sup>1</sup>H NMR (**600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.34 (s, 4H), 5.27 (d, J = 1.6 Hz, 1H), 5.02 (d, J = 1.5 Hz, 1H), 4.67

(td, J = 10.9, 4.4 Hz, 1H), 2.51 (t, J = 7.6 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 2.01 – 1.94 (m, 1H), 1.85 (dqd, J = 13.9, 6.8, 2.1 Hz, 1H), 1.67 (tdd, J = 11.8, 6.8, 2.8 Hz, 4H), 1.50 (dq, J = 11.0, 5.8, 3.9 Hz, 3H), 1.32 (s, 10H), 1.05 (qd, J = 13.4, 12.8, 3.8 Hz, 1H), 0.98 – 0.92 (m, 1H), 0.89 (dd, J = 10.0, 6.8 Hz, 7H), 0.74 (d, J = 7.0 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 173.26, 150.26, 147.70, 138.10, 125.64, 125.15, 111.61, 47.00, 40.93, 34.88, 34.54, 34.45, 34.26, 31.36, 31.30, 27.82, 26.23, 24.86, 23.39, 22.02, 20.74, 16.25. **HRMS** (EI) exact mass calculated for [M<sup>+</sup>] ( $C_{27}H_{42}O_2^+$ ): m/z 398.31793; found: 398.31646.

## (S)-2-Methoxy-6-(5-(4-methoxyphenyl)hex-5-en-2-yl)naphthalene (7b)



This compound was prepared according to General procedure, 50.6 mg, 73% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.71 (dd, J = 8.5, 3.2 Hz, 2H), 7.55 (d, J = 1.8 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.17 – 7.13 (m, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.21 (d, J = 1.5 Hz, 1H), 4.96 (d, J = 1.5 Hz, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 2.89 (dt, J = 8.1, 6.5 Hz, 1H), 2.49 – 2.36 (m, 2H), 1.92 – 1.77 (m, 2H), 1.34 (d, J = 6.9 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.92, 157.13, 147.83, 142.39, 133.60, 133.15, 129.05, 129.00, 127.13, 126.79, 126.27, 125.14, 118.57, 113.54, 110.62, 105.60, 55.26, 55.21, 39.56, 36.86, 33.51, 22.48.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{24}H_{26}O_2^+$ ): m/z 346.19273; found: 346.19296.

# 5-(4-Methoxyphenyl)hex-5-en-1-yl 6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (7c)

This compound was prepared according to General procedure, 61.3 mg, 51% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.56 (d, J = 1.7 Hz, 1H), 8.05 –

8.00 (m, 2H), 7.97 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.79 (dd, J = 8.5, 1.8 Hz, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.55 (dd, J = 8.4, 2.3 Hz, 1H), 7.37 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 5.24 (d, J = 1.5 Hz, 1H), 5.03 (s, 1H), 4.38 (t, J = 6.5 Hz, 2H), 3.91 (s, 3H), 3.78 (s, 3H), 2.60 (t, J = 7.5 Hz, 2H), 2.19 (s, 6H), 2.11 (s, 3H), 1.90 – 1.79 (m, 8H), 1.67 (qd, J = 9.4, 8.7, 6.4 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.84, 159.02, 158.90, 147.33, 141.31, 138.99, 135.90, 133.40, 132.57, 131.22, 130.70, 129.69, 128.14, 127.20, 126.41, 125.97, 125.71, 125.59, 124.71, 113.64, 112.09, 111.15, 64.85, 55.22, 55.16, 40.60, 37.20, 37.12, 34.93, 29.10, 28.28, 24.56.

**HRMS** (ESI) exact mass calculated for  $[M+Na^+]$  ( $C_{41}H_{44}O_4Na^+$ ): m/z 623.31318; found: 623.31355.

# (4-Chlorophenyl)(5-methoxy-3-(4-(4-methoxyphenyl)pent-4-en-1-yl)-2-methyl-1H-indol-1-yl)methanone (7d)

This compound was prepared according to General procedure, 61.6 mg, 65% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 2.6 Hz, 1H), 6.63 (dd, J = 8.9,

2.5 Hz, 1H), 5.26 (d, J = 1.5 Hz, 1H), 5.03 (d, J = 1.6 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.65 (t, J = 7.8 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 2.27 (s, 3H), 1.79 (h, J = 7.5, 6.8 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.26, 159.04, 155.80, 147.25, 138.88, 134.30, 133.83, 133.40, 131.18, 131.02, 130.97, 129.01, 127.18, 119.82, 114.92, 113.63, 111.12, 111.04, 101.31, 55.65, 55.23, 35.03, 27.79, 23.38, 13.26.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{29}H_{28}ClNO_3^+$ ): m/z 473.17522; found: 473.17586.

### 1-((7-(4-(*Tert*-butyl)phenyl)-4,4-dimethyloct-7-en-1-yl)oxy)-2,4-dimethylbenzene (7e)

This compound was prepared according to General procedure, 39.3 mg, 50% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, J =

2.2 Hz, 4H), 7.02 (d, J = 7.4 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.64 (s, 1H), 5.27 (s, 1H), 5.04 (s, 1H), 3.93 (t, J = 6.4 Hz, 2H), 2.51 – 2.44 (m, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.75 (dq, J = 11.8, 6.4 Hz, 2H), 1.46 – 1.39 (m, 4H), 1.34 (s, 9H), 0.96 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.08, 150.23, 148.91, 138.34, 136.43, 130.26, 125.58, 125.16, 123.58, 120.56, 111.96, 111.07, 68.58, 40.67, 37.86, 34.46, 32.63, 31.32, 29.84, 27.18, 24.30, 21.41, 15.81.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{28}H_{40}O^+$ ): m/z 392.30737; found: 392.30781.

## (S)-4-(5-(4-(*Tert*-butyl)phenyl)hex-5-en-2-yl)-2-fluoro-1,1'-biphenyl (7f)

This compound was prepared according to General procedure, 58.8 mg, 76% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, J = 8.3 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.41 – 7.30 (m, 6H), 7.08 – 6.97 (m, 2H), 5.30 (d, J = 1.5 Hz, 1H), 5.03

(s, 1H), 2.81 (h, J = 7.0 Hz, 1H), 2.46 (h, J = 8.4, 7.9 Hz, 2H), 1.80 (dtd, J = 8.8, 6.8, 3.8 Hz, 2H), 1.35 (s, 9H), 1.30 (d, J = 6.9 Hz, 3H).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -118.48.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.98, 158.52, 150.32, 149.18 (d, J = 7.3 Hz), 147.89, 138.05, 135.89, 130.45 (d, J = 3.5 Hz), 128.92 (d, J = 2.9 Hz), 128.37, 127.37, 126.41 (d, J = 13.5 Hz), 125.64, 125.17, 123.11 (d, J = 3.1 Hz), 114.60, 114.37, 111.61, 39.25, 36.69, 34.46, 33.23, 31.30, 22.19.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{28}H_{31}F^+$ ): m/z 386.24043; found: 386.23988.

## 1-(3-(4-(*Tert*-butyl)phenyl)but-3-en-1-yl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (7g)

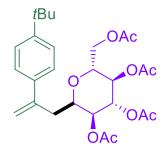
This compound was prepared according to General procedure, 55.8 mg, 63% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (s, 4H), 7.19 (d, J = 8.2 Hz, 1H), 6.99 (dd, J = 8.2, 2.0 Hz, 1H), 6.89 (s, 1H), 5.27 (d, J = 1.6 Hz, 1H), 5.02 (s, 1H),

2.92 - 2.79 (m, 3H), 2.44 - 2.37 (m, 2H), 2.29 (d, J = 12.8 Hz, 1H), 1.84 - 1.76 (m, 2H), 1.67 (dh, J = 13.3, 3.8, 2.9 Hz, 2H), 1.51 - 1.38 (m, 6H), 1.33 (s, 9H), 1.23 (d, J = 7.2 Hz, 9H), 0.95 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  150.25, 148.89, 147.70, 145.44, 138.23, 134.83, 126.80, 125.53, 125.16, 124.29, 123.80, 111.09, 47.32, 43.13, 38.65, 37.59, 37.04, 35.90, 34.47, 33.43, 31.32, 30.34, 29.04, 25.35, 23.99, 23.97, 21.00, 19.08, 18.72.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{33}H_{46}^+$ ): m/z 442.35940; found: 442.35751.

(2R,3R,4R,5S,6R)-2-(acetoxymethyl)-6-(2-(4-(tert-butyl)phenyl)allyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (7h)



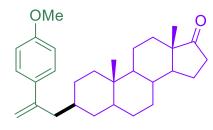
This compound was prepared according to General procedure, 57.5 mg, 57% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 6.2 Hz, 2H), 5.38 (t, J = 9.1 Hz, 1H), 5.34 (s, 1H), 5.14 (s, 1H), 5.08 (dd, J = 9.5, 5.8 Hz, 1H), 4.98 (t, J = 9.1 Hz, 1H), 4.33 (ddd, J = 10.3, 5.8, 4.4 Hz, 1H), 4.16 (dd, J = 11.9, 4.7 Hz, 1H), 3.96 – 3.88 (m, 2H), 2.92 (dd, J =

15.4, 10.4 Hz, 1H), 2.82 (dd, J = 15.4, 4.4 Hz, 1H), 2.07 (d, J = 4.4 Hz, 6H), 2.03 (d, J = 9.0 Hz, 6H), 1.32 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.63, 170.19, 169.55, 169.51, 150.79, 143.66, 137.18, 125.80, 125.38, 114.73, 71.00, 70.63, 70.25, 68.80, 68.75, 62.15, 34.49, 31.89, 31.25, 20.71, 20.68, 20.64. **HRMS** (EI) exact mass calculated for [M-C<sub>2</sub>H<sub>4</sub>O<sub>2</sub><sup>+</sup>] (C<sub>25</sub>H<sub>32</sub>O<sub>7</sub><sup>+</sup>): m/z 444.21425; found: 444.21478.

# (3S,10S,13S)-3-(2-(4-methoxyphenyl)allyl)-10,13-dimethylhexadecahydro-17*H*-cyclopenta[a]phenanthren-17-one (7i)



This compound was prepared according to General procedure, 36.2 mg, 43% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33 (dd, J = 8.8, 2.5 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.19 (t, J = 2.1 Hz, 1H), 4.93 (dd, J = 6.5, 1.8 Hz, 1H), 3.81 (d, J = 2.4 Hz, 3H), 2.56 (d, J = 7.7 Hz,

1H), 2.48 - 2.34 (m, 2H), 2.05 (ddt, J = 18.8, 15.9, 9.0 Hz, 1H), 1.92 (tdd, J = 14.6, 10.5, 5.8 Hz, 1H), 1.77 (dddd, J = 15.7, 12.6, 8.1, 3.7 Hz, 2H), 1.69 - 1.60 (m, 2H), 1.57 - 0.89 (m, 16H), 0.85 (d, J = 7.9 Hz, 3H), 0.78 (d, J = 5.5 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 221.57, 221.54, 158.91, 147.19, 146.30, 133.69, 133.63, 127.38, 127.25, 113.55, 112.02, 111.87, 55.23, 54.86, 54.70, 51.59, 51.48, 47.85, 47.80, 46.42, 43.64, 40.40, 38.42, 38.07, 36.52, 36.17, 36.09, 35.85, 35.44, 35.10, 35.07, 33.13, 32.25, 31.60, 31.57, 30.98, 30.93, 30.59, 28.75, 28.62, 24.67, 21.74, 20.24, 20.05, 13.82, 13.80, 12.29, 11.73.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{29}H_{40}O_2^+$ ): m/z 420.30228; found: 420.30039.

Methyl (4R)-4-((3S,10S,13R)-3-(2-(4-methoxyphenyl)allyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (7j)

This compound was prepared according to General procedure, 42.7 mg, 41% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (q, J = 8.6 Hz, 4H), 5.27 (d, J = 2.1 Hz, 1H), 4.93 (d, J =

2.0 Hz, 1H), 2.32 (s, 2H), 1.86 (s, 3H), 1.64 - 1.60 (m, 3H), 1.54 - 1.51 (m, 2H), 1.39 (d, J = 2.9 Hz, 5H), 1.32 (s, 11H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.78, 145.45, 140.63, 125.89, 124.91, 115.37, 49.50, 42.97, 36.99, 34.41, 33.61, 31.35, 28.77.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{35}H_{52}O_3^+$ ): m/z 520.39110; found: 520.39129.

## 1-(*Tert*-butyl)-4-(4-ethyl-4,8-dimethylnon-1-en-2-yl)benzene (7k)

This compound was prepared according to General procedure, 26.4 mg, 42% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.27 (m, 4H), 5.18 (d, J = 2.2 Hz, 1H), 4.97 (d, J = 2.2 Hz, 1H), 2.47

-2.37 (m, 2H), 1.41 (dt, J = 13.2, 6.6 Hz, 1H), 1.31 (s, 9H), 1.18 (p, J = 7.2 Hz, 2H), 1.08 (dtt, J = 11.1, 4.6, 2.4 Hz, 2H), 1.03 -0.96 (m, 2H), 0.87 (ddd, J = 13.9, 7.7, 2.1 Hz, 2H), 0.80 (d, J = 6.6 Hz, 6H), 0.74 (t, J = 7.5 Hz, 3H), 0.66 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.68, 147.36, 141.22, 126.17, 124.86, 115.98, 44.17, 39.70, 38.61, 36.63, 34.40, 31.83, 31.36, 27.91, 25.00, 22.71, 22.62, 21.28, 8.07.

**HRMS** (EI) exact mass calculated for  $[M-CH_3^+]$  ( $C_{22}H_{35}^+$ ): m/z 299.27333; found: 299.27378.

#### 5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (7l)

This compound was prepared according to General procedure, 47.2 mg, 47% yield as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz,

2H), 7.30 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.22 (d, J = 2.0 Hz, 1H), 4.99 (d, J = 1.9 Hz, 1H), 4.35 (t, J = 7.3 Hz, 2H), 3.77 (s, 3H), 3.12 – 3.06 (m, 4H), 2.52 (s, 2H), 1.67 (t, J = 7.3 Hz, 2H), 1.59 – 1.50 (m, 4H), 0.89 – 0.84 (m, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.28, 158.82, 145.99, 144.08, 135.91, 133.70, 130.11, 127.54, 126.94, 115.86, 113.53, 63.02, 55.18, 49.91, 47.46, 40.11, 33.65, 27.74, 21.92, 11.13.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{28}H_{39}NO_5S^+$ ): m/z 501.25435; found: 501.25562.

## 1-(*Tert*-butyl)-4-(3-(1-methyl-4-(propan-2-ylidene)cyclohexyl)prop-1-en-2-yl)benzene (7m)

This compound was prepared according to General procedure, 24.8 mg, 40% yield as colorless oil.

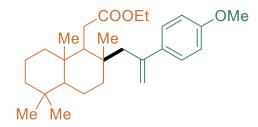
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (s, 4H), 5.22 (d, J = 2.1 Hz, 1H), 4.98 (d, J = 2.1 Hz, 1H), 2.50 (s, 2H), 2.26 – 2.18 (m, 2H), 2.03 – 1.94 (m, 2H), 1.62 (s, 6H), 1.32 (s,

9H), 1.24 (dt, J = 11.1, 5.0 Hz, 4H), 0.78 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.85, 146.83, 140.89, 131.58, 126.12, 124.94, 120.29, 115.96, 46.90, 39.12, 34.44, 34.05, 31.38, 25.59, 24.71, 19.95.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{23}H_{34}^+$ ): m/z 310.26550; found: 310.26674.

# Ethyl 2-((2*R*)-2-(2-(4-methoxyphenyl)allyl)-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)acetate (7n)



This compound was prepared according to General procedure, 42.7 mg, 50% yield as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.16 (d, J = 2.0 Hz, 1H), 4.96 (s, 1H), 4.10 (qd, J = 7.1, 2.8 Hz, 2H), 3.81 (s, 3H), 3.05 (d, J

= 13.7 Hz, 1H), 2.37 (dd, J = 16.9, 2.7 Hz, 1H), 2.03 – 1.90 (m, 2H), 1.58 – 1.27 (m, 6H), 1.24 (t, J = 7.1 Hz, 3H), 1.15 – 1.02 (m, 3H), 0.98 – 0.78 (m, 7H), 0.78 – 0.68 (m, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.94, 158.85, 147.45, 133.97, 127.45, 113.52, 112.51, 60.24, 55.23, 53.33, 53.23, 42.05, 41.90, 41.09, 39.40, 38.98, 37.47, 34.55, 33.16, 33.03, 26.89, 21.62, 18.64, 17.15, 14.34, 14.19.

M.P.:93.3-94.7 °C.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{28}H_{42}O_{3}^+$ ): m/z 426.31285; found: 426.31152.

#### 1-(*Tert*-butyl)-4-(hepta-1,6-dien-2-yl)benzene (14)

tBu tBu

This compound was prepared according to General procedure, 25.1 mg, 55% yield as colorless oil.

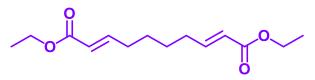
<sup>1</sup>**H NMR** (**600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.35 (s, 4H), 5.82 (ddt, J = 16.9,

10.2, 6.7 Hz, 1H), 5.28 (d, J = 1.6 Hz, 1H), 5.05 – 4.94 (m, 3H), 2.54 – 2.48 (m, 2H), 2.10 (q, J = 7.9, 7.3 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.33 (s, 9H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 150.24, 147.95, 138.69, 138.23, 125.67, 125.13, 114.62, 111.56, 34.61, 33.38, 31.31, 27.51.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{17}H_{24}^+$ ): m/z 228.18725; found: 228.18626.

## Diethyl (2E,8E)-deca-2,8-dienedioate (15a)



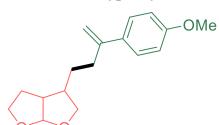
This compound was prepared according to General procedure, 22.9 mg, 45% yield as colorless oil.

<sup>1</sup>**H NMR (500 MHz, CDCl**<sub>3</sub>) δ 6.93 (dt, J = 15.7, 7.0 Hz, 1H), 5.81 (d, J = 15.6 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.24 – 2.17 (m, 2H), 1.49 (p, J = 3.5 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.67, 148.64, 121.65, 60.21, 31.88, 27.48, 14.28.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{14}H_{22}O_4^+$ ): m/z 254.15126; found: 254.15077.

## 3-(3-(4-Methoxyphenyl)but-3-en-1-yl)hexahydrofuro[2,3-b]furan (16)



This compound was prepared according to General procedure, 36.8 mg, 61% yield as colorless oil.

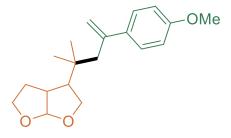
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.72 (d, J = 5.0 Hz, 1H), 5.21 (d, J = 1.5 Hz, 1H), 5.00 (s, 1H), 3.97 – 3.92 (m, 1H), 3.84 (dd, J = 7.4,

6.3 Hz, 2H), 3.82 (s, 3H), 3.40 (dd, J = 11.4, 8.4 Hz, 1H), 2.80 (ddd, J = 13.9, 8.4, 5.4 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.33 (dp, J = 11.4, 7.5 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.60 – 1.49 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.12, 147.19, 133.06, 127.11, 113.71, 111.26, 109.69, 72.39, 69.07, 55.25, 45.28, 41.70, 34.23, 26.24, 24.94.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{17}H_{22}O_3^+$ ): m/z 274.15635; found: 274.15616.

## 3-(4-(4-Methoxyphenyl)-2-methylpent-4-en-2-yl)hexahydrofuro[2,3-b]furan (17)



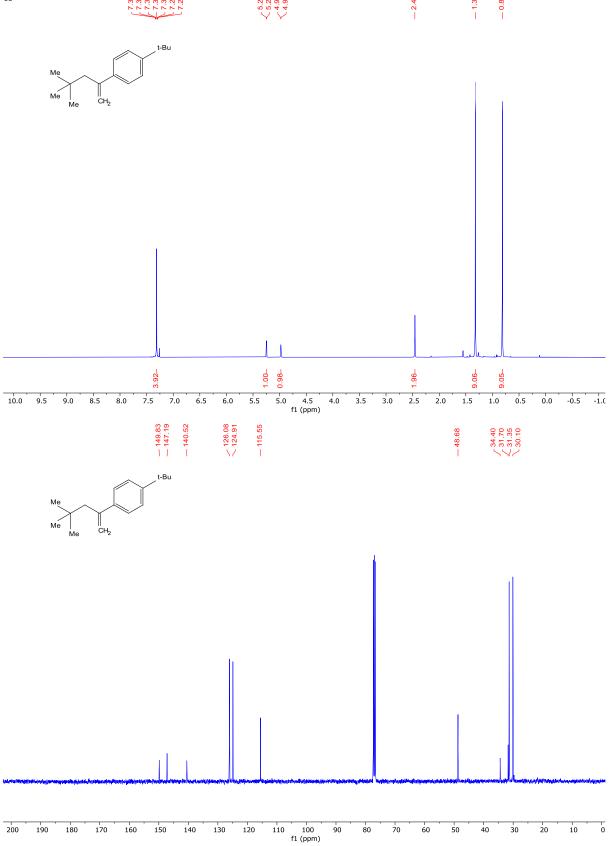
This compound was prepared according to General procedure, 18.7 mg, 31% yield as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.57 (d, J = 4.7 Hz, 1H), 5.22 (d, J = 1.9 Hz, 1H), 4.98 (s, 1H), 4.08 (td, J = 8.1, 3.7 Hz, 1H), 3.87 (t, J

= 7.5 Hz, 1H), 3.84 - 3.73 (m, 6H), 2.67 (tt, J = 9.0, 5.5 Hz, 1H), 2.53 (s, 1H), 2.25 (dt, J = 11.8, 6.6 Hz, 1H), 2.05 (dq, J = 12.4, 8.5 Hz, 1H), 1.85 (dddd, J = 12.4, 8.9, 6.2, 3.7 Hz, 1H), 0.83 (d, J = 10.9 Hz, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.90, 145.69, 136.01, 127.49, 116.32, 113.61, 109.65, 69.91, 66.99, 55.24, 51.29, 47.80, 45.19, 35.15, 27.12, 26.36, 25.84.

**HRMS** (EI) exact mass calculated for  $[M^+]$  ( $C_{19}H_{26}O_3^+$ ): m/z 302.18765; found: 302.18736.



110 100 f1 (ppm)

90

80

70

60

50

40

30

20

10

120

200

190

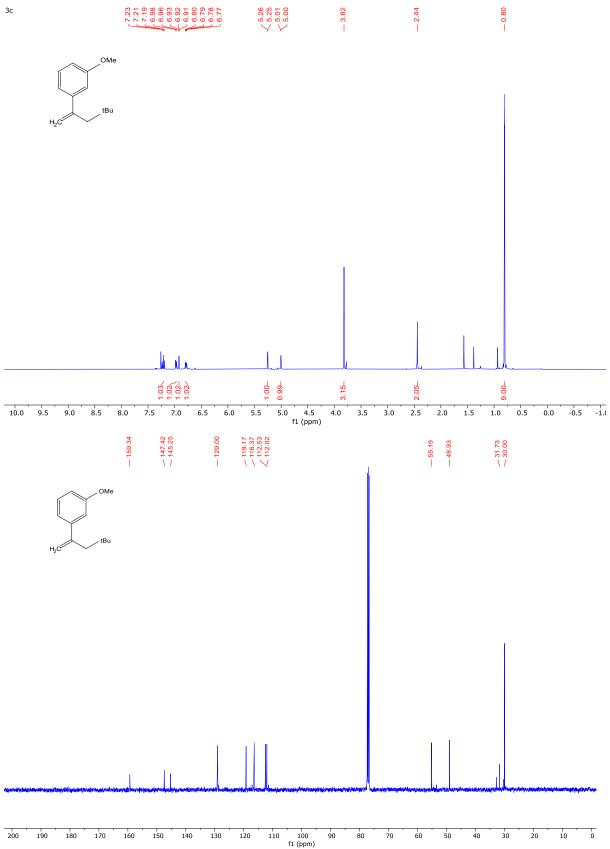
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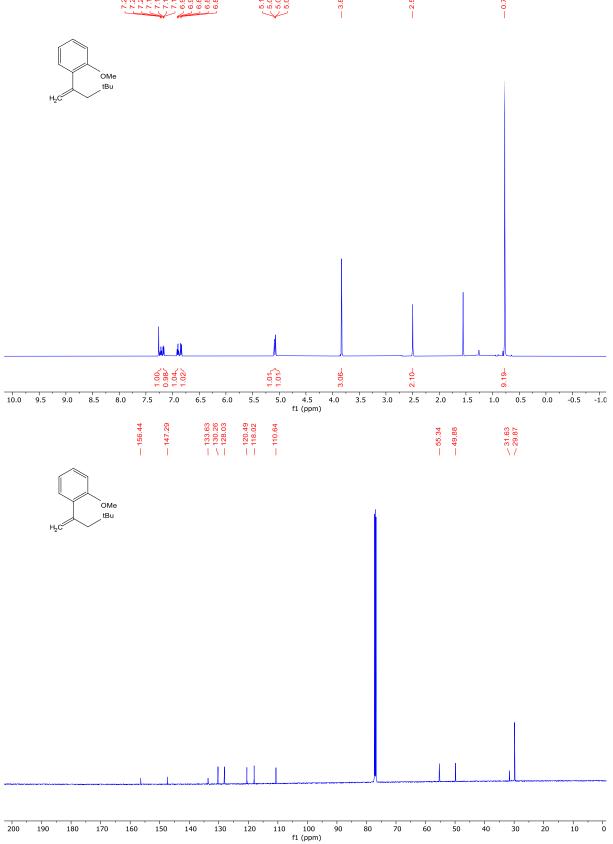
170

160

150

140 130





110 100 f1 (ppm)

90

80

70

60

50

40

30

20

10

120

200

190

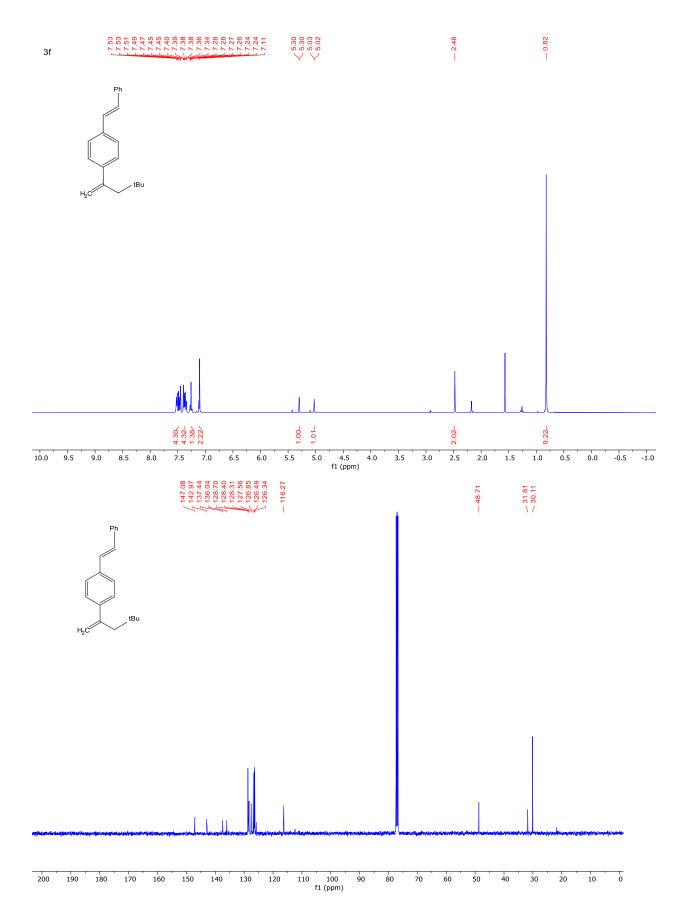
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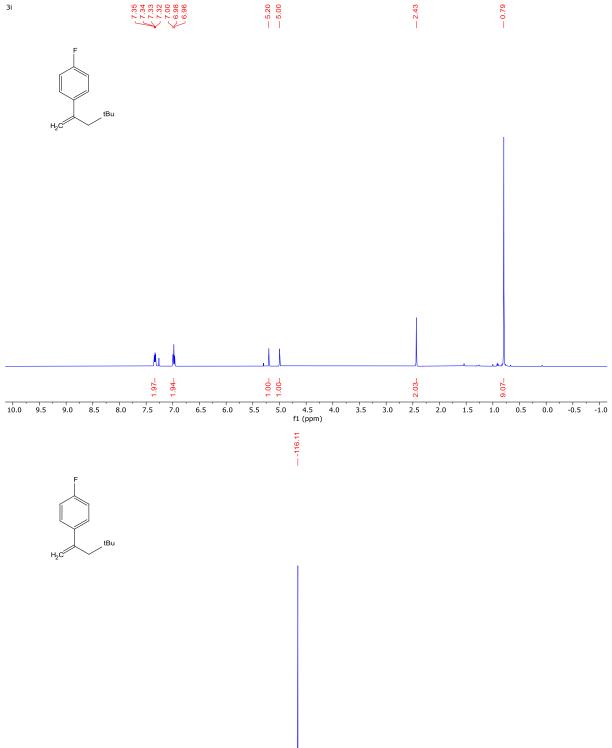
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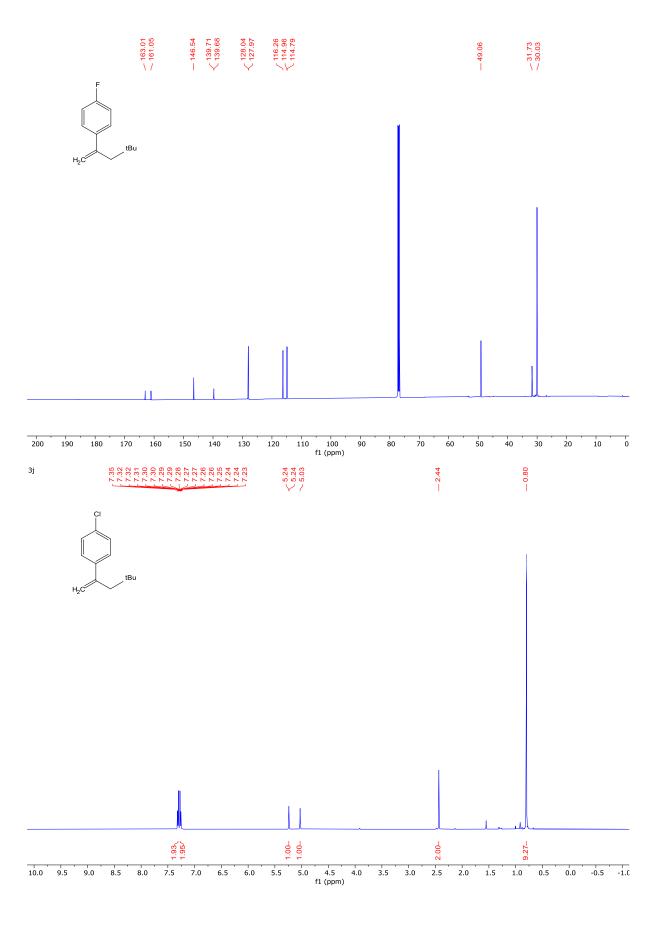
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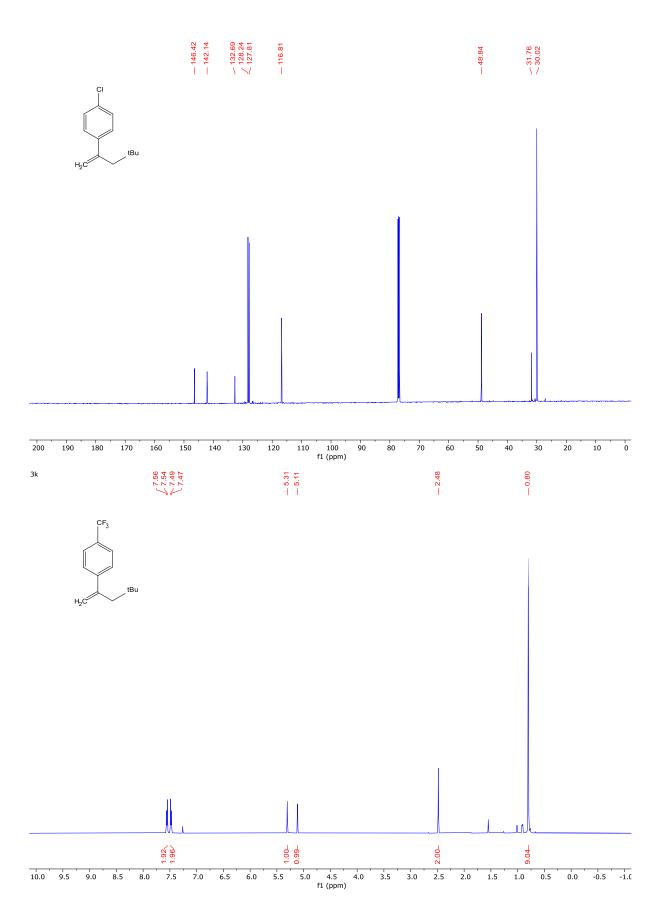
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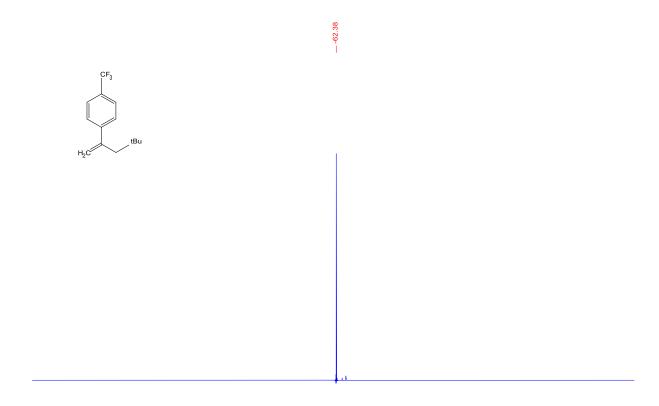
140 130

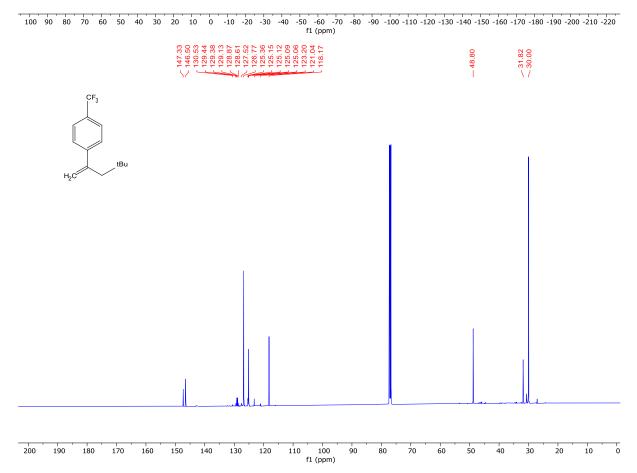












110 100 f1 (ppm)

90

80

70

60

50

40

30

20

10

200

190

180

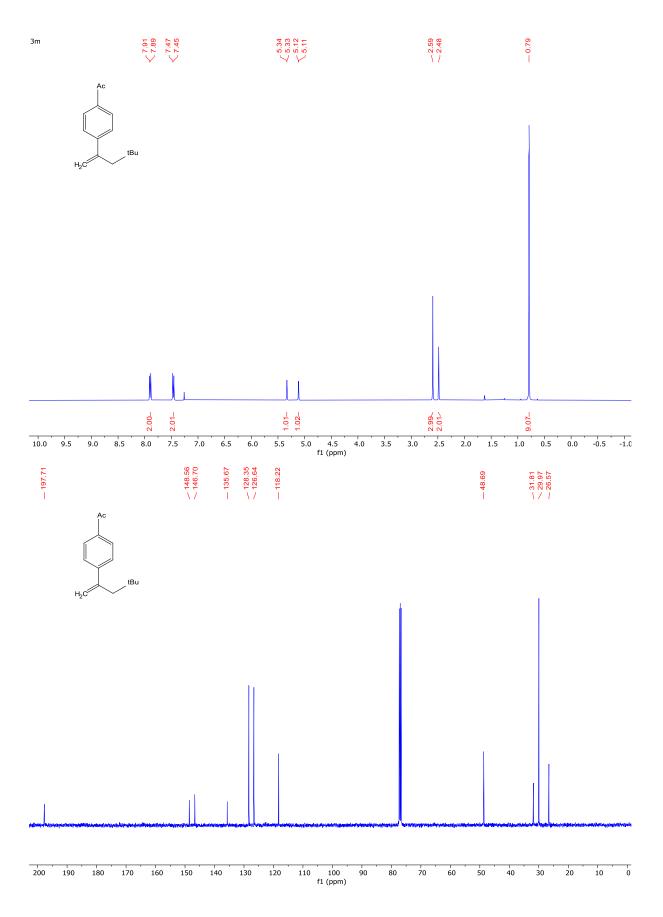
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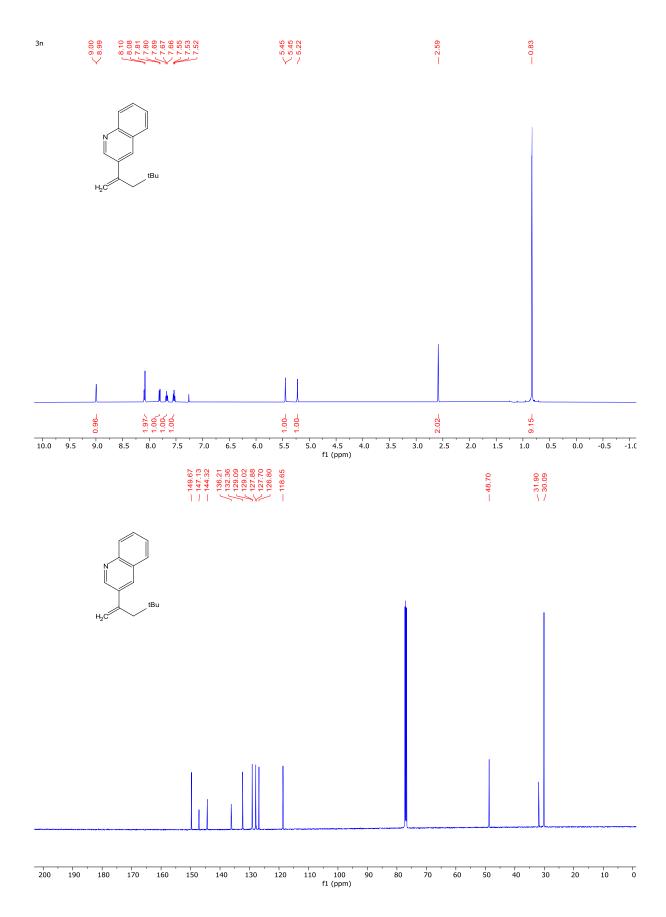
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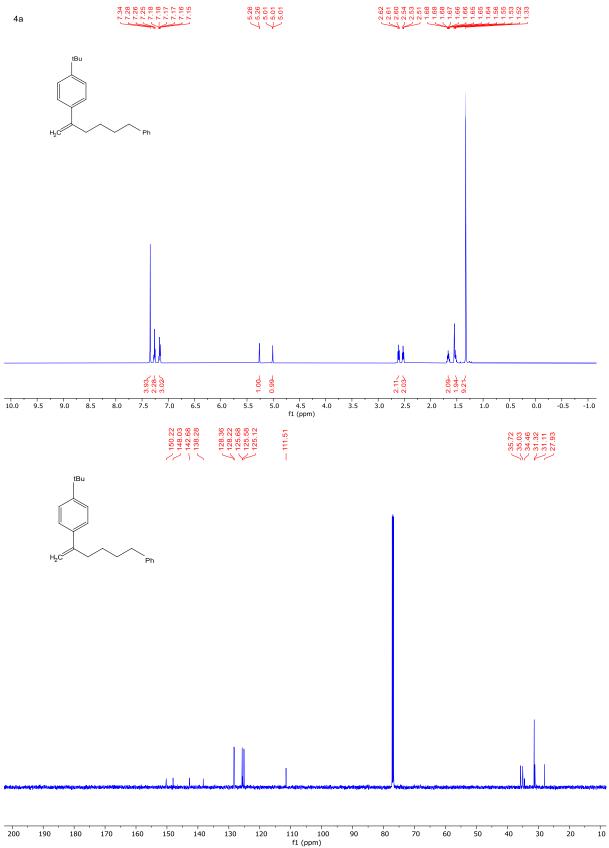
150

140

130







110 100 f1 (ppm)

90

80

70

60

50

40

30

20

200

190

170

180

140

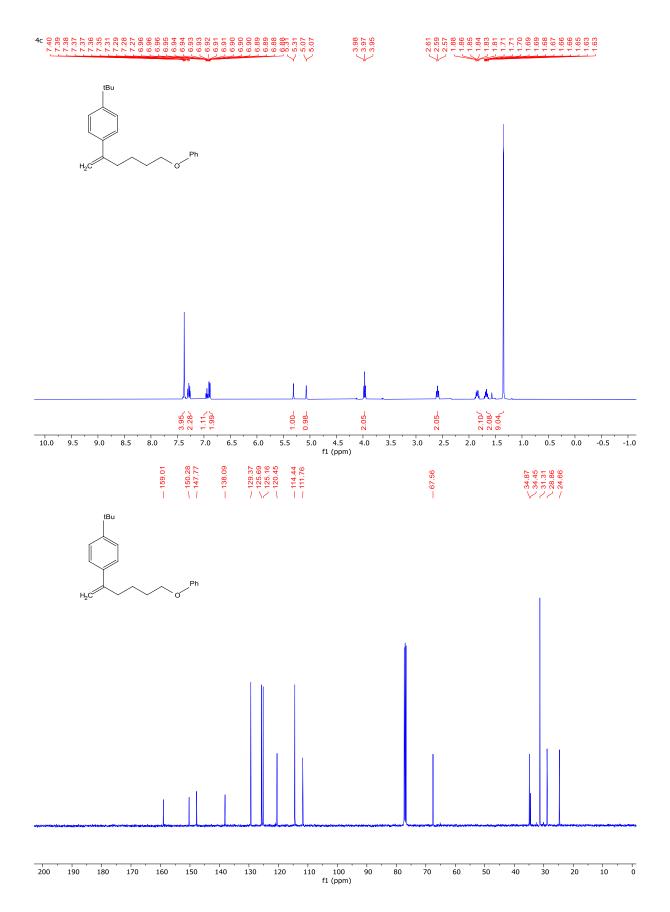
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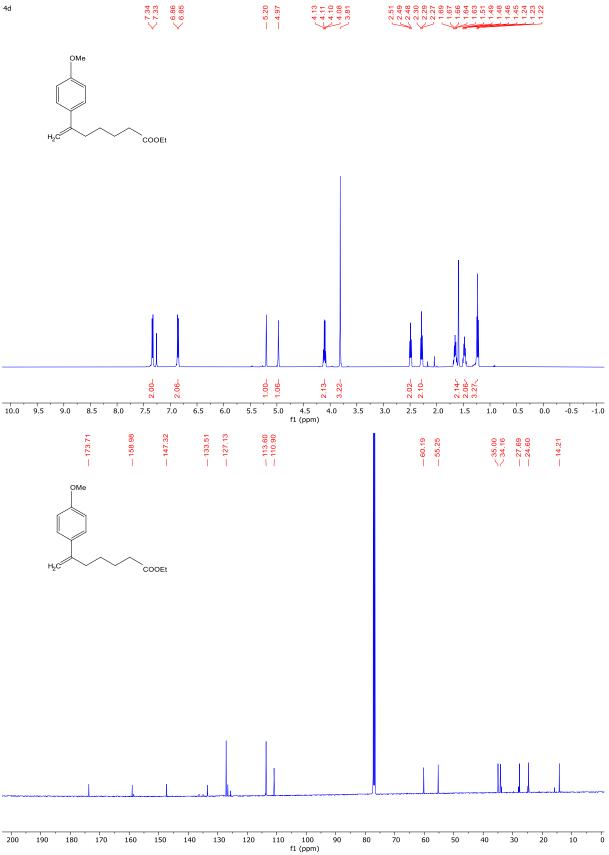
160

130

120

0





200

190

180

170

160

150

140

130

120

90

80

70

60

50

40

30

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40

30

20

10

0

-10

110

200

190

170

180

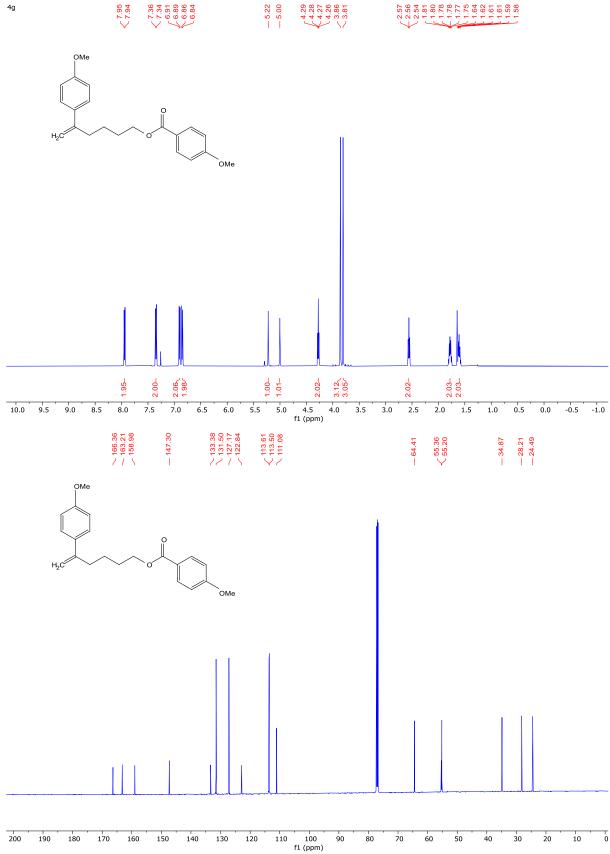
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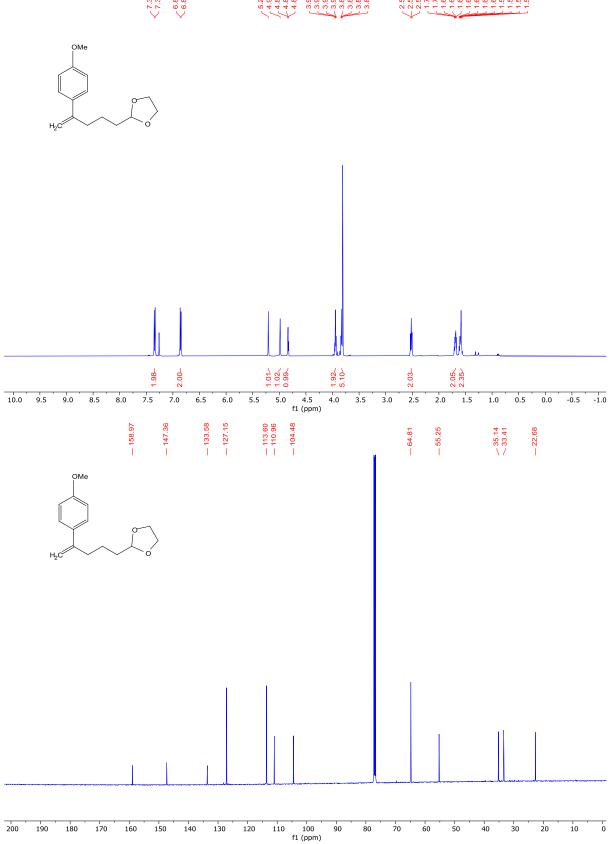
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140

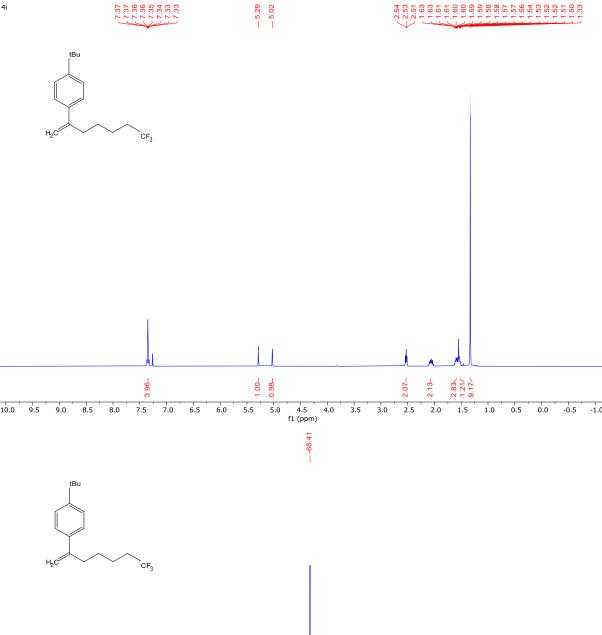
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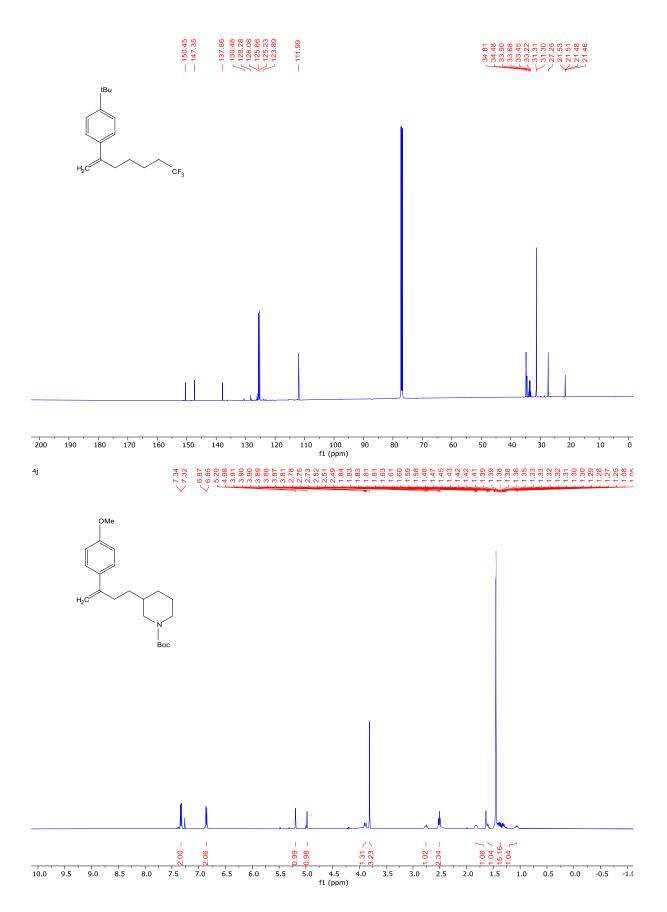


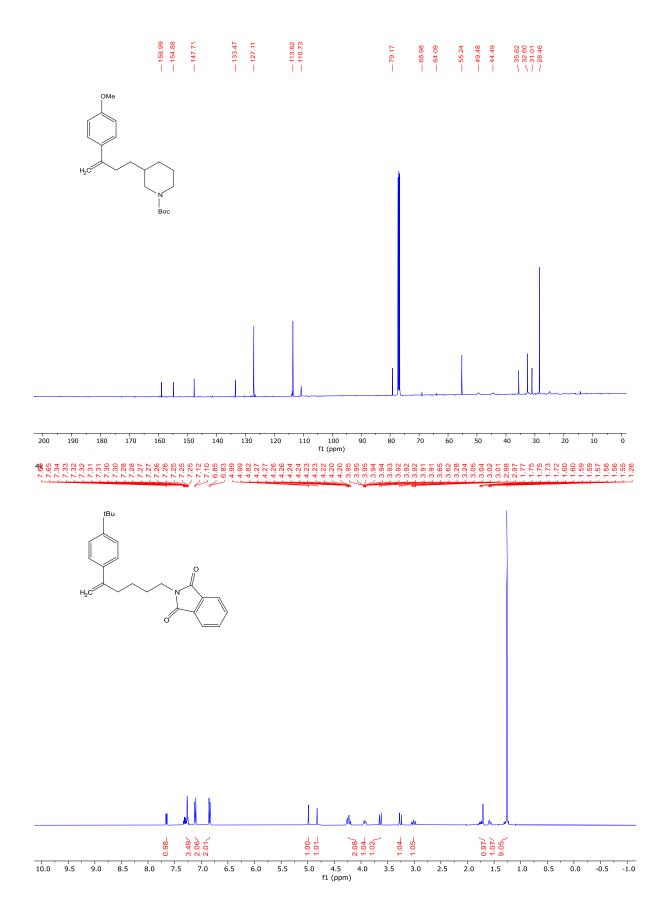


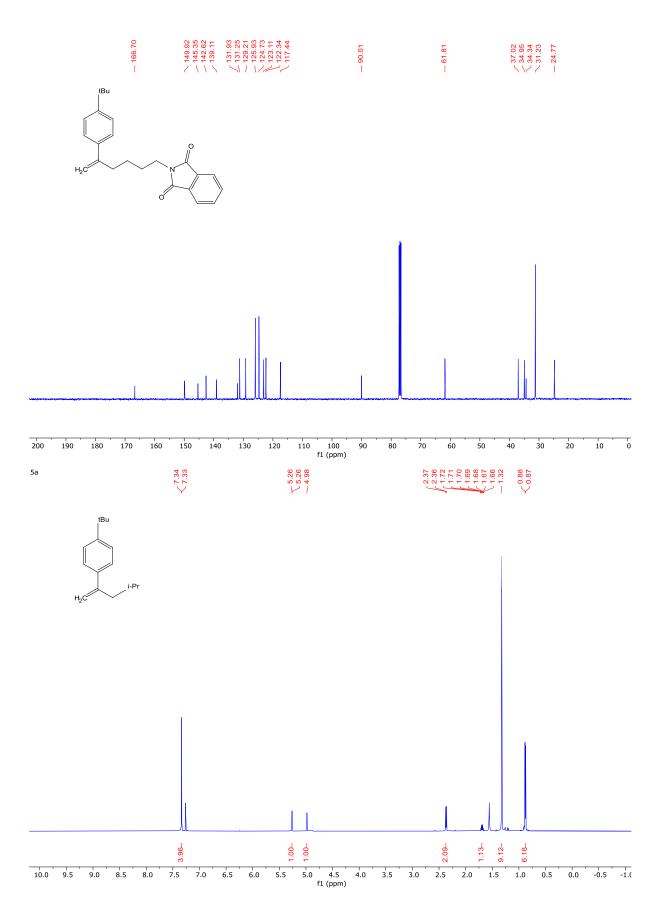


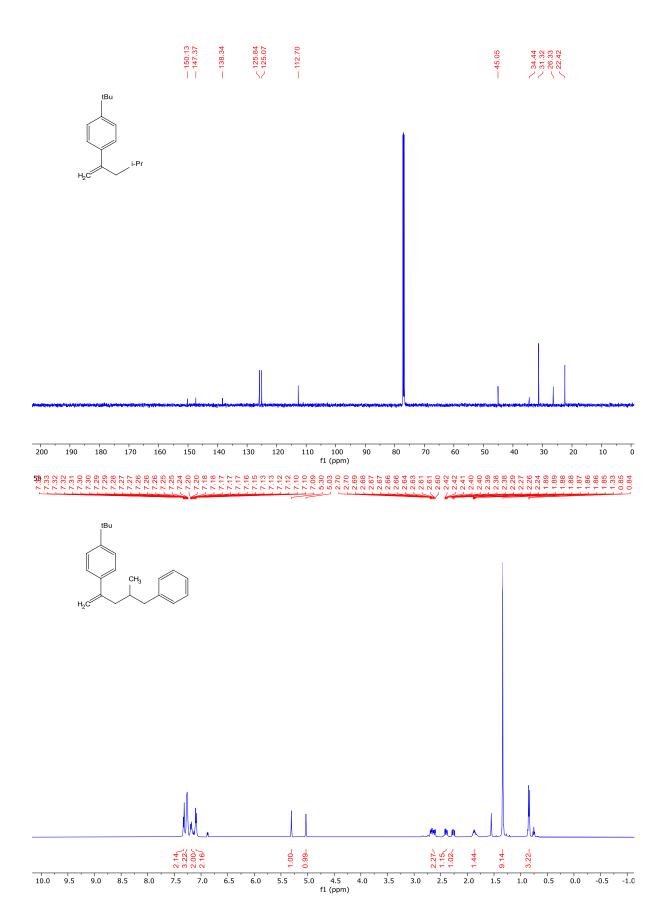




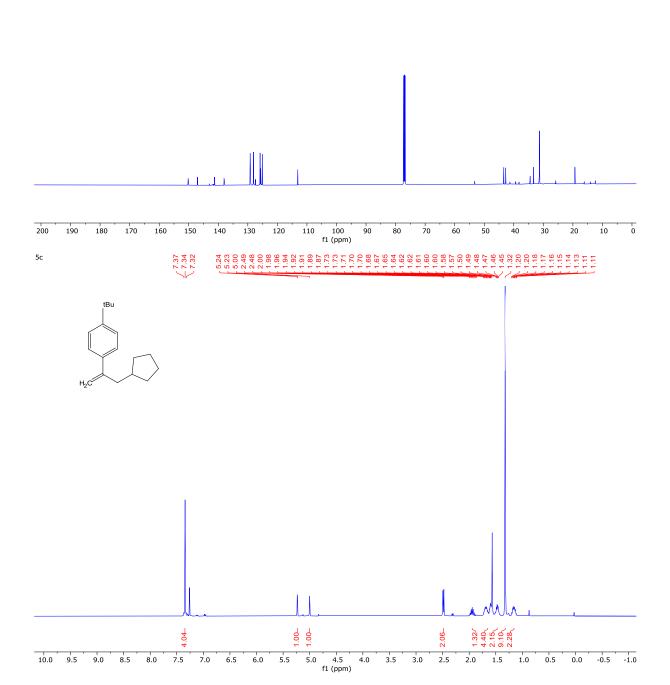


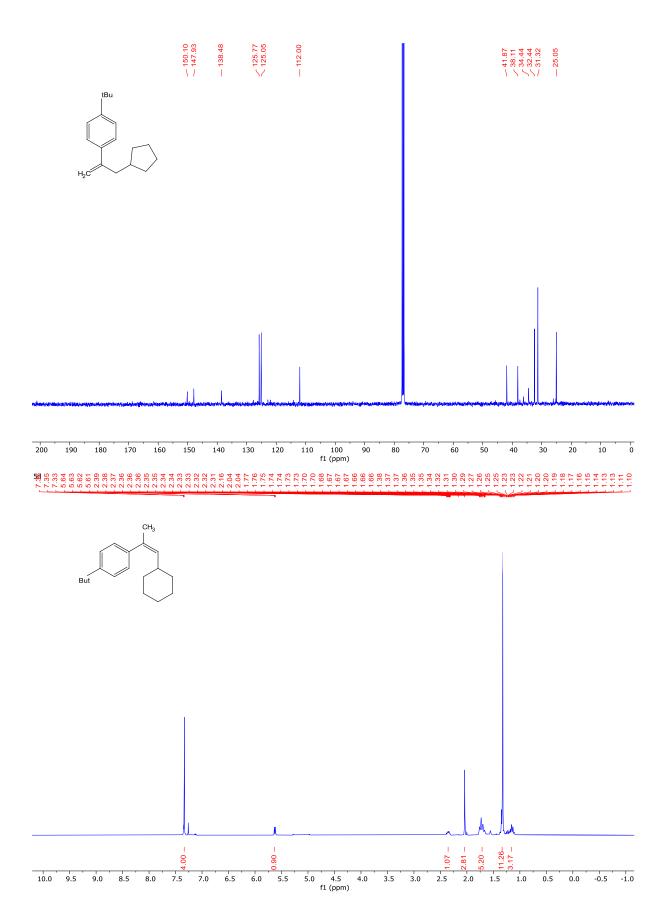


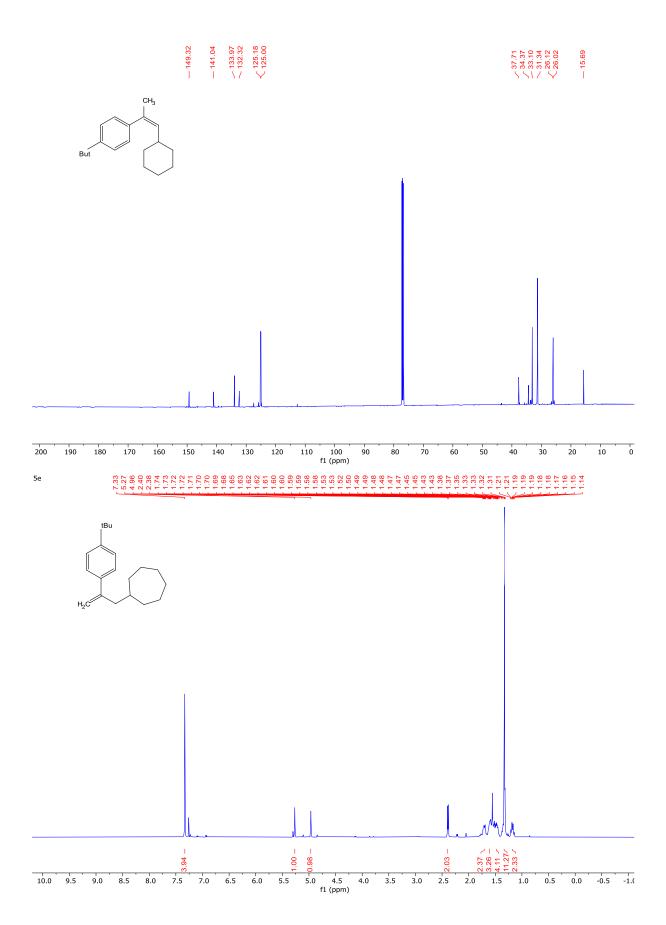


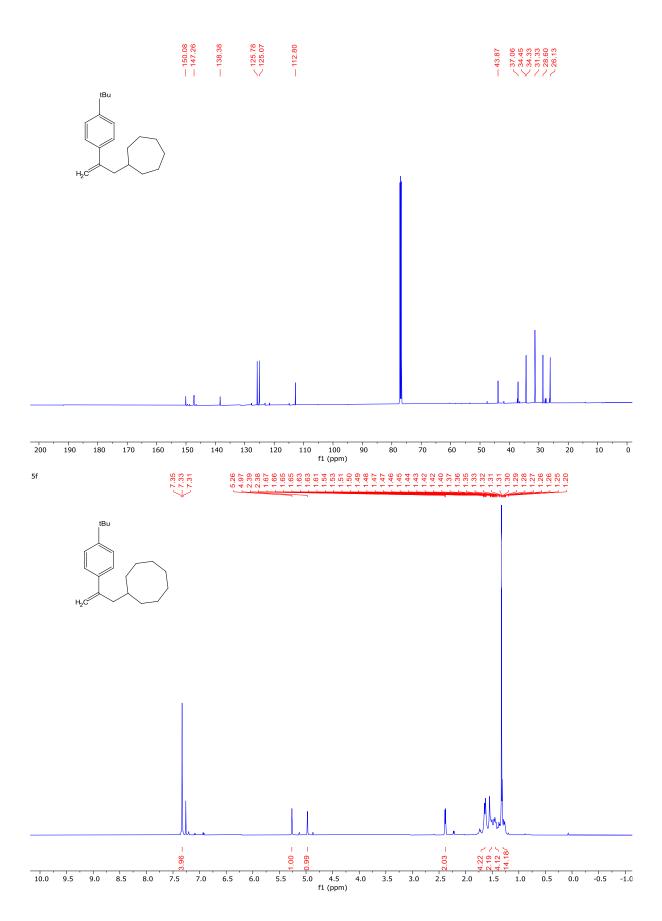


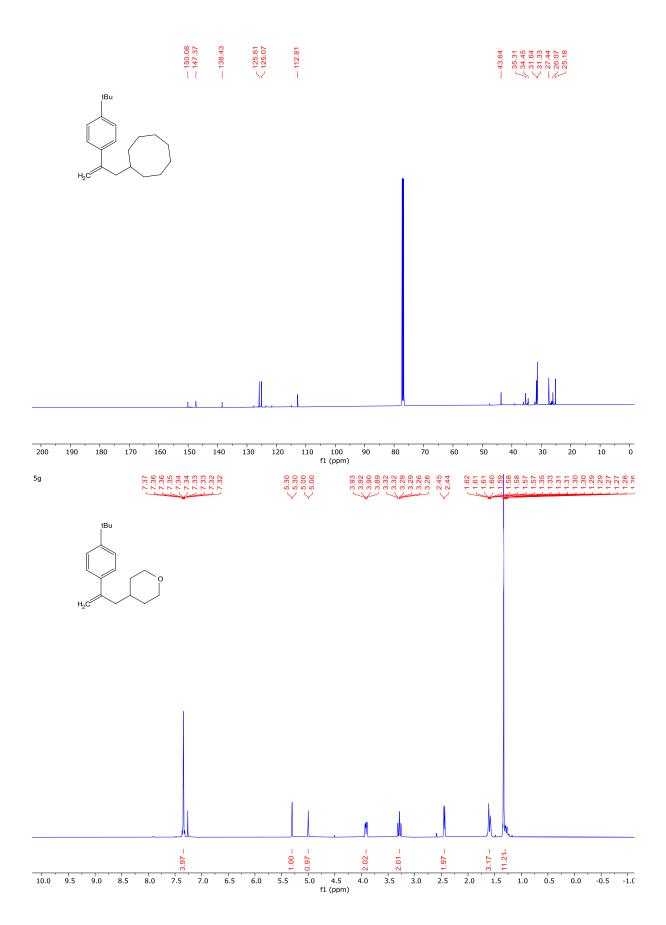


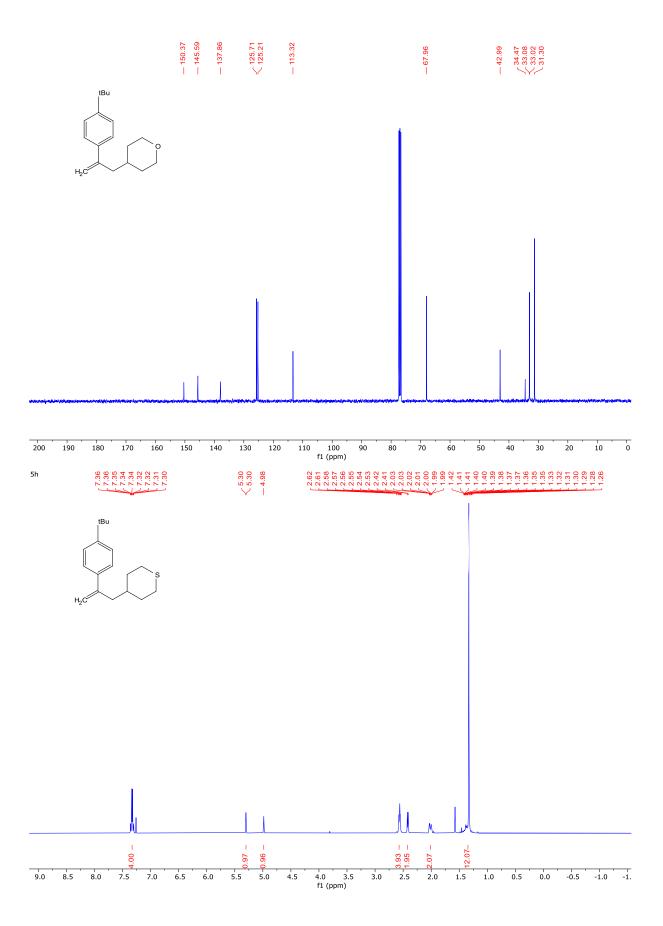


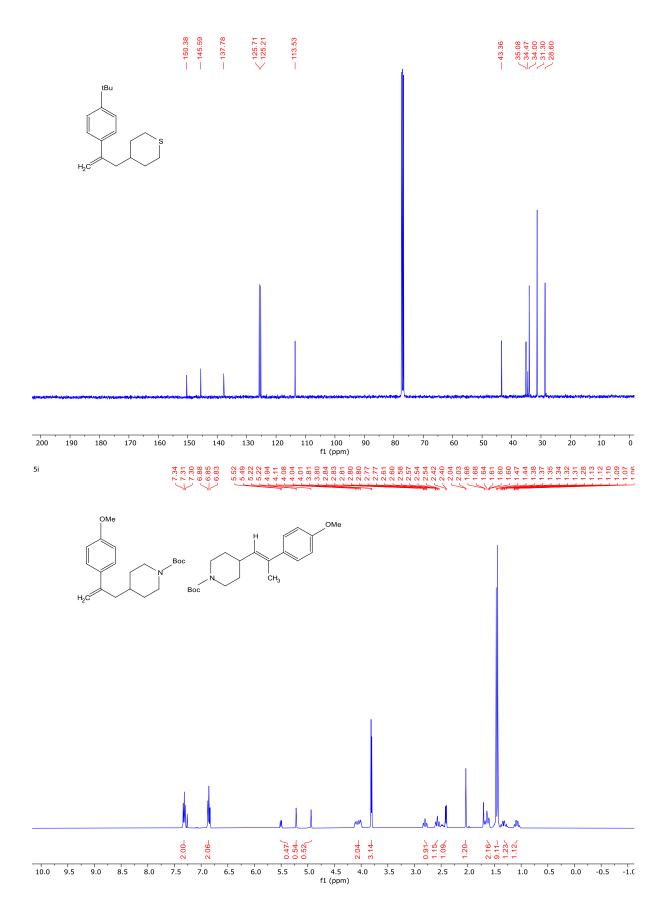


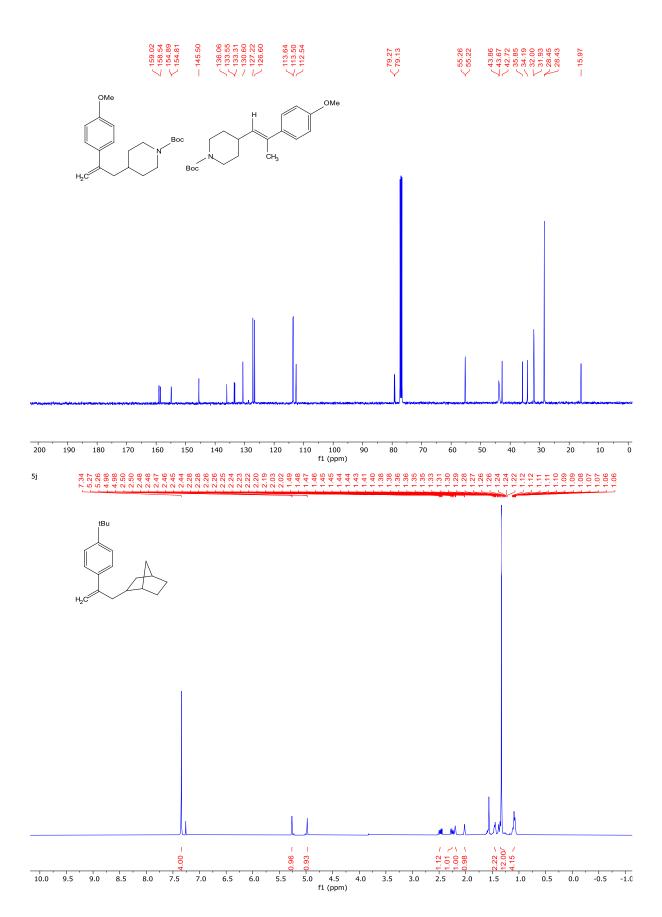


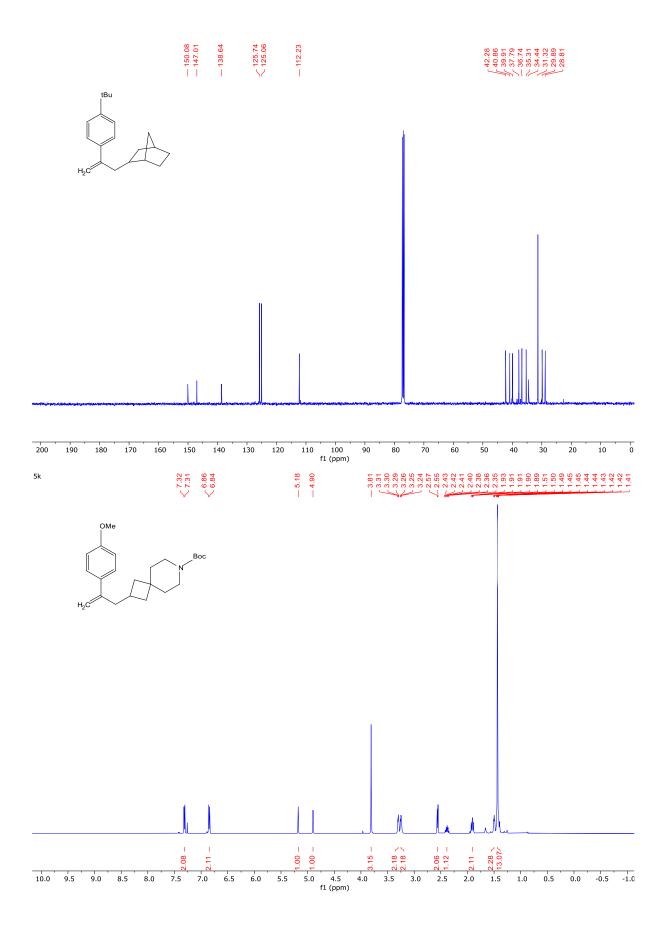


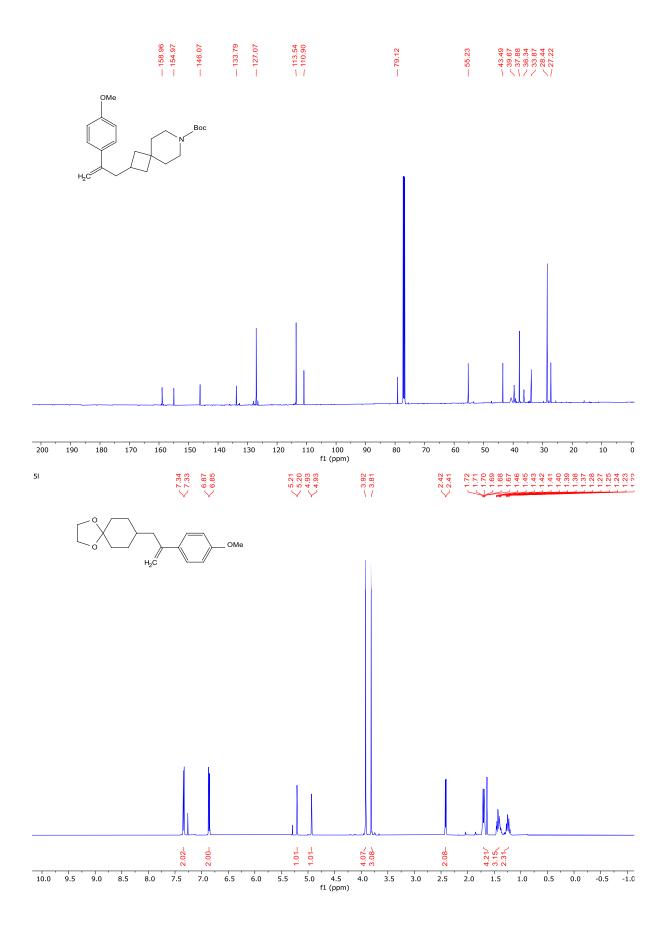


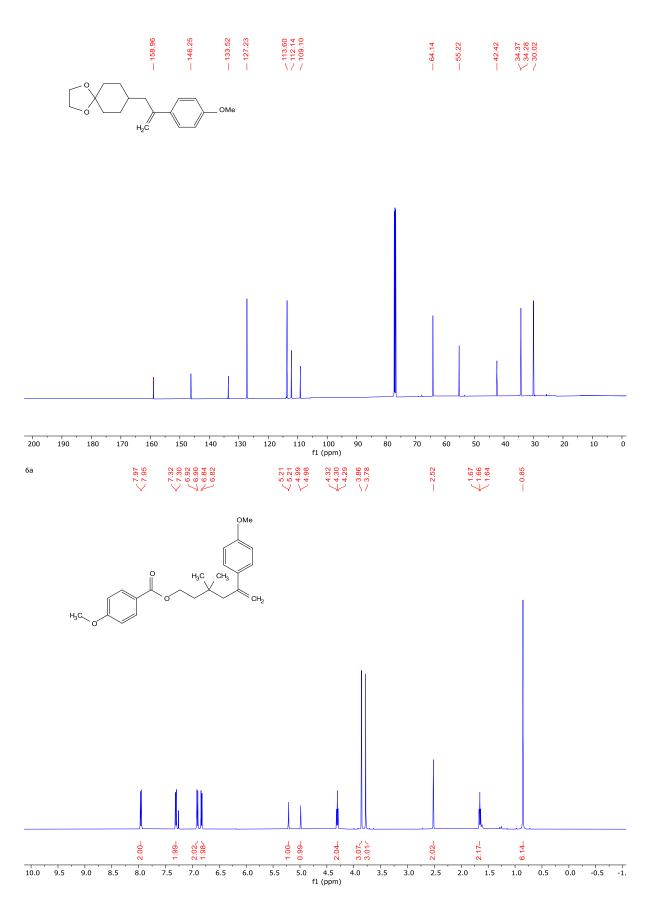


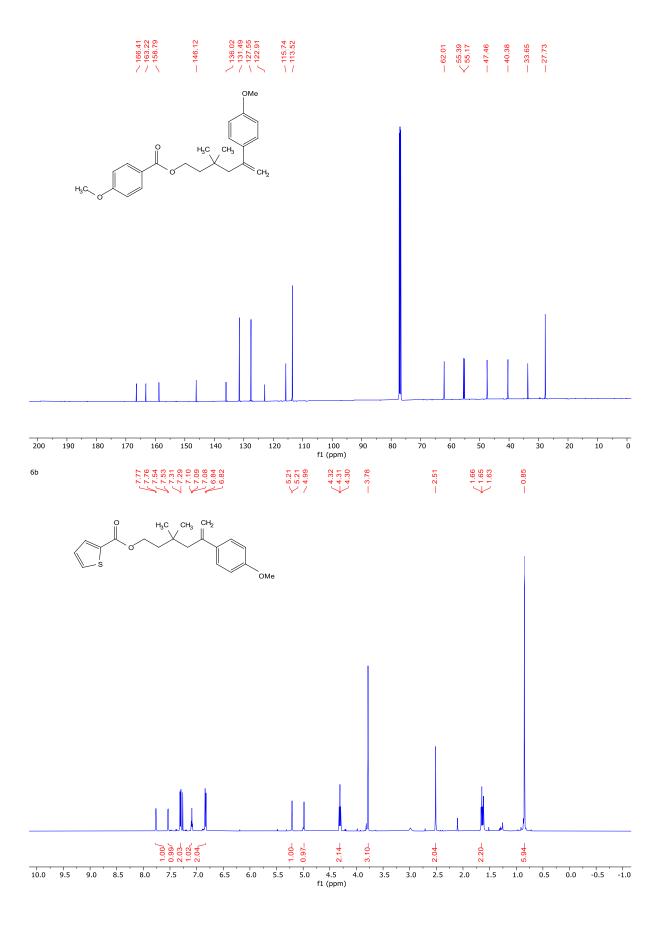


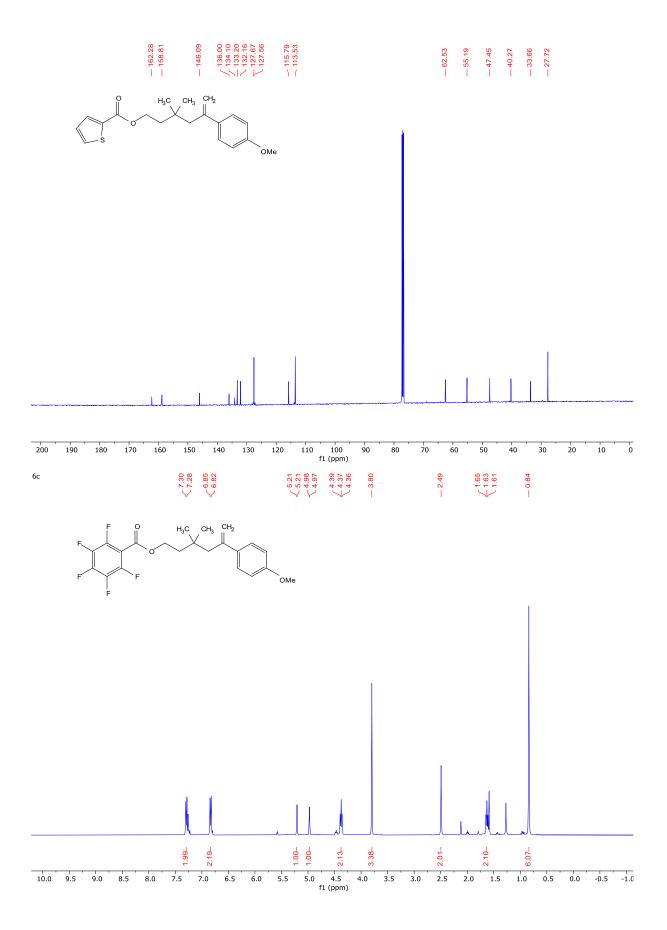


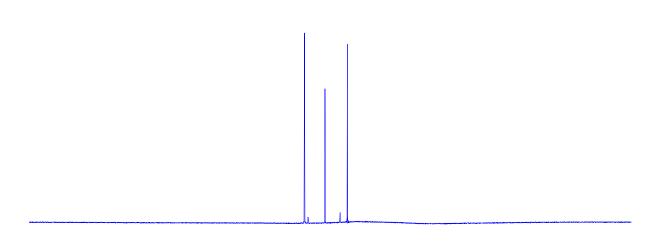


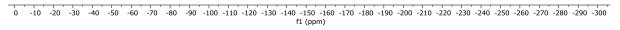


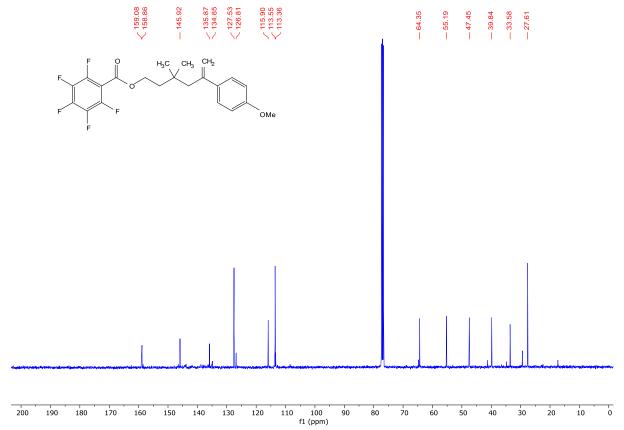












110 100 f1 (ppm)

90

80

70

60

50

40

30

20

10

130

140

150

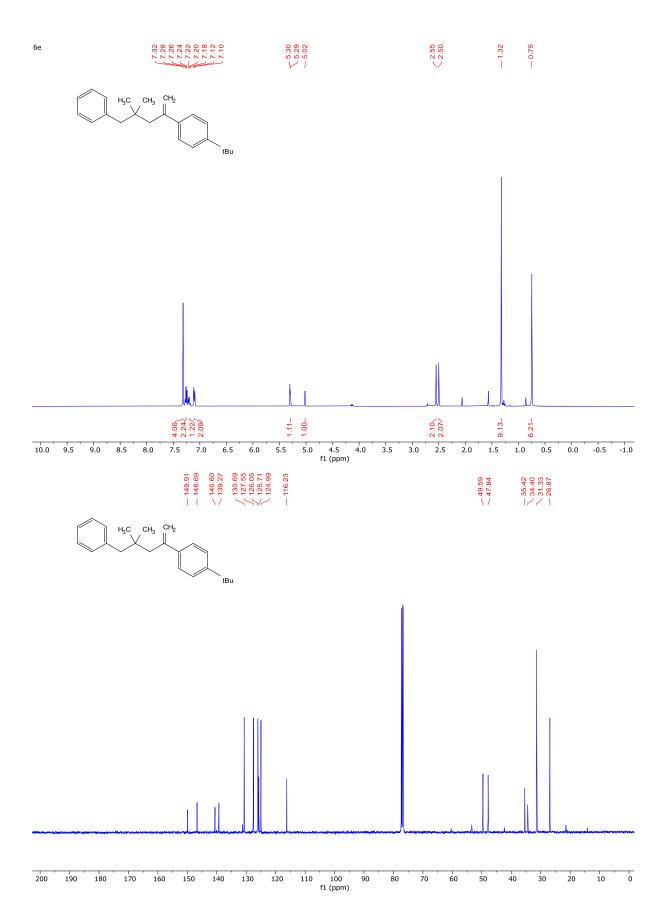
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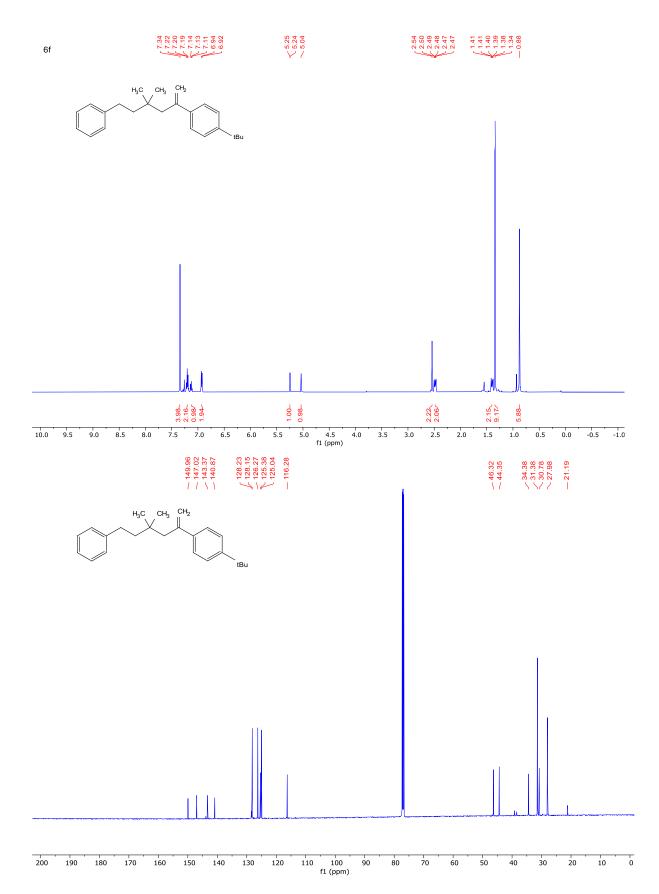
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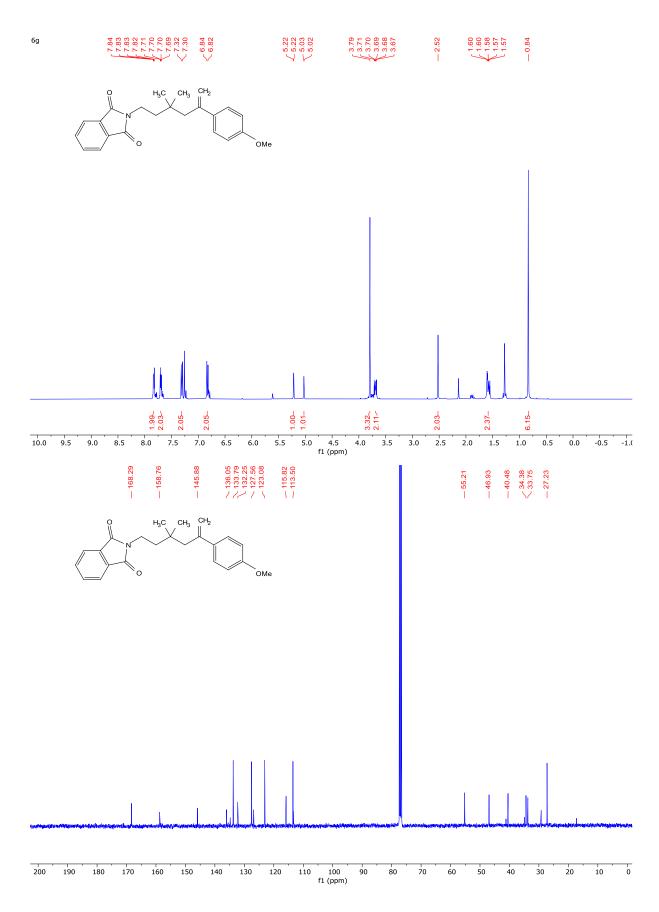
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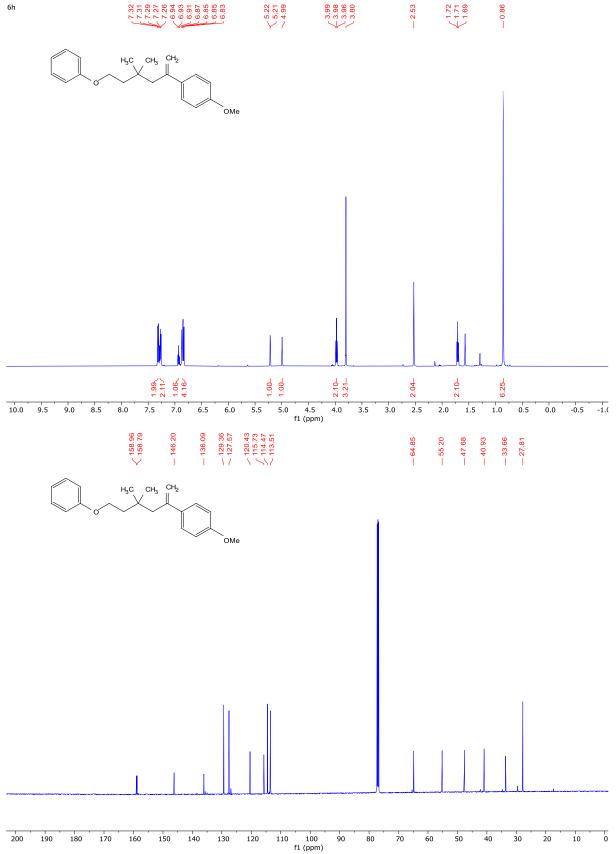
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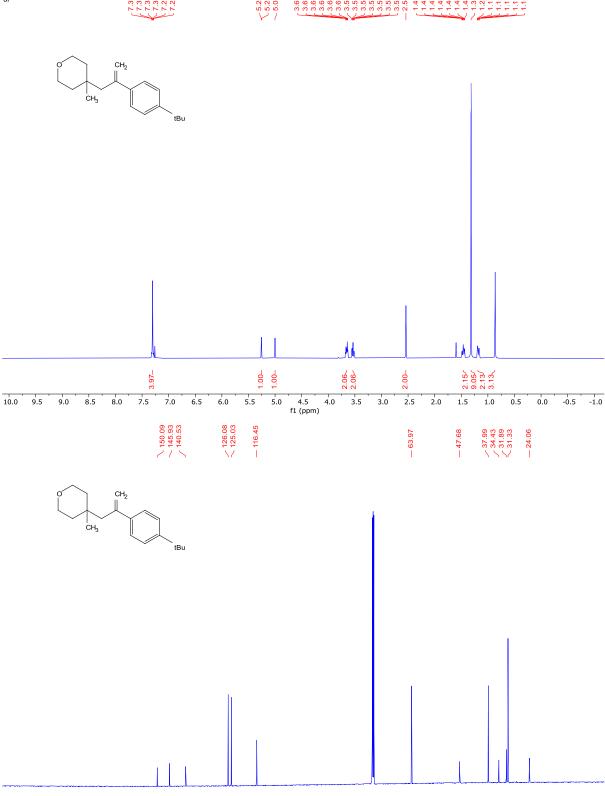
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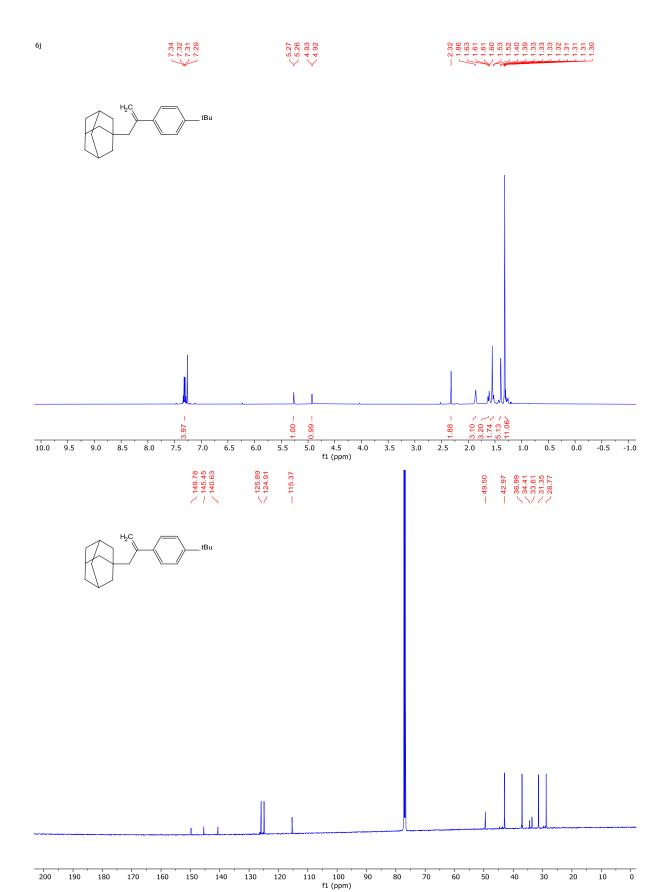


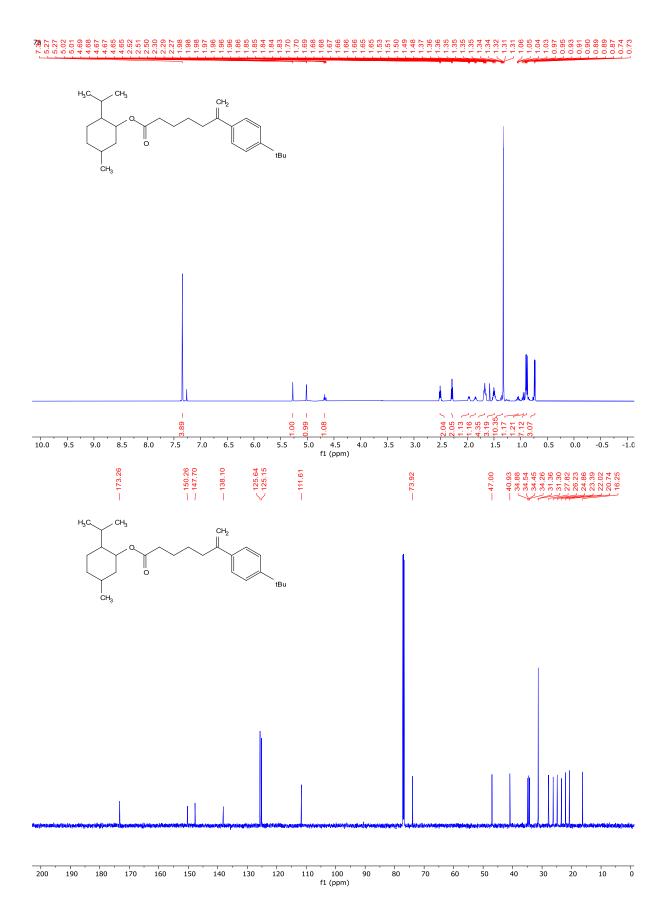






110 100 f1 (ppm)





110 100 f1 (ppm)

120

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200

190

180

170

160

150

140

130

0

100 f1 (ppm)

90

80

70

60

50

40

30

20

10

0

110

120

200

190

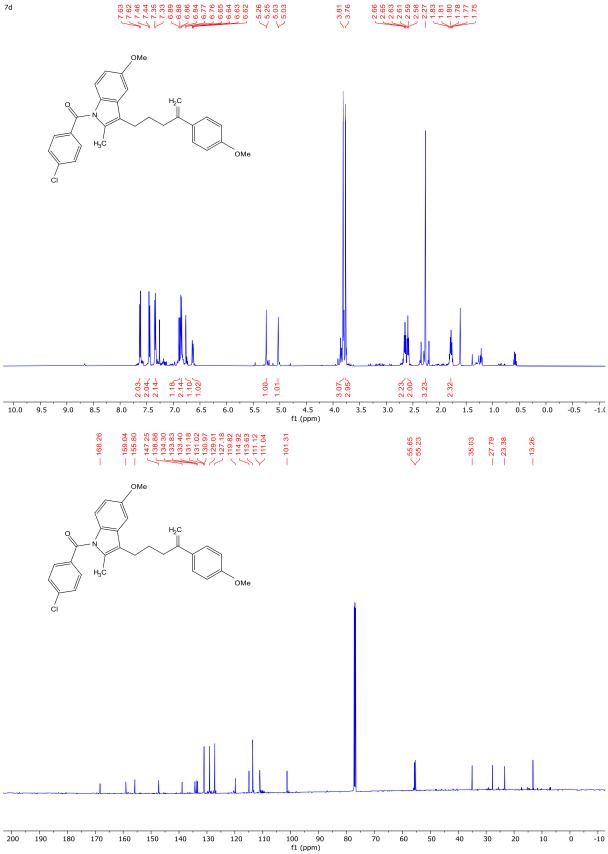
180

170

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150

140



110 100 f1 (ppm)

90

80

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200

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170

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180

140 130

0

