Fe-Catalyzed Three-component Dicarbofunctionalization of Unactivated Alkenes with Alkyl Halides and Grignard Reagents

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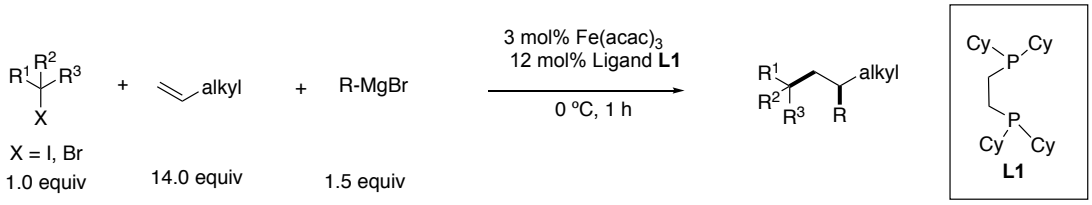
Supporting Information

Table of Contents

1. General Considerations

Unless otherwise stated, all non-aqueous reactions were carried out under an atmosphere of dry nitrogen in oven- (150 °C) or flame-dried glassware. When necessary, solvents and reagents were dried prior to use. Tetrahydrofuran (THF) was dried by passage through activated alumina in Inert's PureSolv PS-MD-3 solvent purification system. All work-up and purification procedures used reagent grade solvents purchased from VWR, Sigma-Aldrich, or Fisher. Organometallic reagents were purchased from Sigma-Aldrich. Analytical thin layer chromatography (TLC) was performed on Silicycle 250 μm silica-gel F-254 plates. Isolera™ Flash Systems silica gel chromatography was performed on prepacked silica-gel cartridges (SNAP Ultra; Biotage). Purification via flash column chromatography was performed on silica gel 60 (230-400 mesh ASTM). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV III HD NanoBay (400 MHz) and Bruker AV-III (600 MHz) NMR spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to the internal residual solvent resonance peak δ 7.26 ($CDCl_3$) and δ 0.00 (TMS) for ^{1}H and δ 77.16 ($CDCl_3$) and δ 0.00 (TMS) for ^{13}C. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, b = broad singlet, m = multiplet, dd= doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, qd = quartet of doublets, pd = quintet of doublets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, dtt = doublet of triplet of triplets, tdd = triplet of doublet of doublets, qdd = quartet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, dddt = doublet of doublet of doublet of triplets), coupling constants (*J)* are reported in Hertz (Hz), and number of protons. High Resolution Mass (HRMS) spectra using DART modes was obtained using a JEOL AccuTOF-CS. GC-MS was measured on an Agilent 7820A GC system and 5977B MSD. IR spectra were recorded on a Thermo Nicolet NEXUS 670 FTIR and are reported in wavenumbers (cm^{-1}). Melting points were obtained and are uncorrected.

2. General Procedure of Iron-catalyzed Difunctionalization



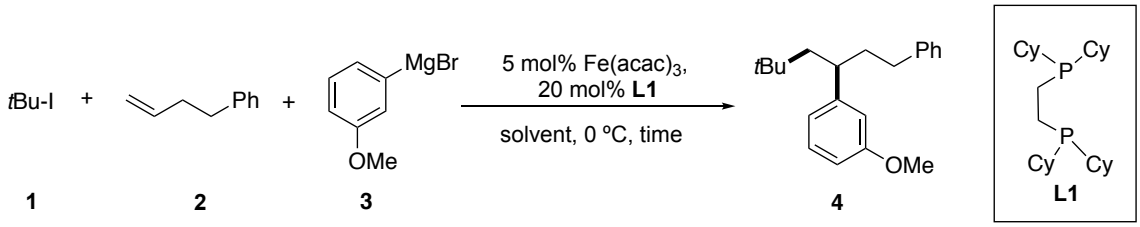
Standard-scale: A flame-dried 5 mL microwave vial with a stir bar was brought into an argon-filled glovebox and the vial was charged with $Fe(acac)_3$ (2.1 mg, 3 mol%), 1,2-bis(dicyclohexylphosphanyl)ethane **L1** (10.1 mg, 12 mol%), alkyl halide (0.2 mmol, 1.0 equiv) and alkene (2.8 mmol, 14.0 equiv) (using oven-dried glass pipet to transfer alkyl halide and alkene to the vial which was on the balance). The vial was sealed with a Teflon cap and was brought out of the glovebox without solvent (0.2 mL of THF was added if need). The red solution was stirred at room temperature for 5 min. The reaction mixture was then cooled to 0 °C and a ArMgBr solution (0.5–1.0 M solution in THF, 1.5 equiv) was added slowly for 1 h using a syringe pump, over which time the heterogeneous solution turned from red to colorless to yellow, brown, grass green or orange color (depending on ArMgBr and substrate). After the addition was complete, the reaction mixture was maintained at 0 °C for an additional 20 min. Then the resulting mixture was quenched with a 1.0 M aqueous solution (0.5 mL) of hydrochloric acid and water (0.5 mL), or saturated aqueous NH_4Cl (1 mL) (depending on product properties), then extracted with ethyl acetate or diethyl ether (3 x 2 mL) depending on recovered alkene boiling point. The combined organic layer was filtered through a plug of silica and concentrated in *vacuo* (the low boiling point recovered alkene was obtained by vigreux column vacuum distillation). The resulting residue was purified by flash column chromatography on silica gel with hexane/CH_2Cl_2 or Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution of hexane/Et_2O (hexane/EtOAc, or hexane/CH_2Cl_2) to obtain products and recovered alkene.

Gram-scale: A flame-dried 100 mL round-bottom flask with a stir bar was brought into an argon-filled glovebox and the flask was charged with $Fe(acac)_3$ (63.6 mg, 3 mol%), 1,2-

bis(dicyclohexylphosphanyl)ethane **L1** (304.3 mg, 12 mol%), alkyl halide (6.0 mmol, 1.0 equiv) and alkene (84 mmol, 14.0 equiv) (using oven-dried glass pipet to transfer alkyl halide and alkene to the flask which was on the balance). The flask was sealed with a Teflon cap and was brought out of the glovebox without solvent (10 mL of THF was added if need). The red solution was stirred at room temperature for 5 min. The reaction mixture was then cooled to 0 °C and maintained 10 min then a ArMgBr solution (9.0 mmol, 0.5–1.0 M solution in THF, 1.5 equiv) was added slowly for 1 h using a syringe pump, over which time the heterogeneous solution turned from red to colorless to yellow, brown, grass green or orange color (depending on ArMgBr and substrates). After the addition was complete, the reaction mixture was maintained at 0 °C for an additional 20 min. The resulting mixture was quenched with a 1.0 M aqueous solution (15 mL) of hydrochloric acid and water (15 mL) at 0 °C, then extracted with ethyl acetate or diethyl ether (3 x 20 mL) depending on recovered alkene boiling point. The combined organic layer was dried over Na_2SO_4. After filtration, the recovered alkene was obtained by vigreux column vacuum distillation. The resulting residue was purified by flash column chromatography on silica gel with hexane/CH_2Cl_2 to get difunctionalization products.

3. Screening of Reaction Condition for Iron-Catalyzed 1,2-Difunctionalization [1,2]

Table S1. Screening of substrates with Grigand equiv, solvent and reaction time for iron-catalyzed 1,2-difunctionalization

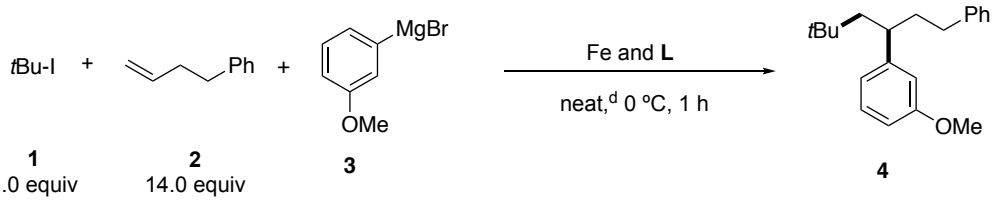


1 **2** **3** **4**

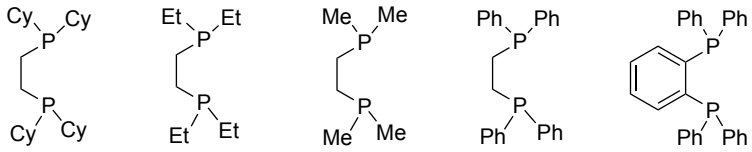
entry	**1** (eq)	**2** (eq)	Grignard (eq)	solvent	time (mins)[b]	yield (%)[a]	recovered **2** (eq.)[a]
1	2.0	1.0	2.6	THF	10	32	0.67
2[c]	5.5	1.0	8.0	THF	10	54	0.44
3	1.0	6.0	1.5	THF	180	65	5.2
4	1.0	6.0	2.0	THF	180	64	5.2
5	1.0	6.0	2.5	THF	180	66	5.2
6	1.0	6.0	1.5	THF	20	65	5.2
7[d]	1.0	6.0	1.5	THF	20	60	5.1
8	1.0	8.0	1.5	THF	20	70	6.9
9	1.0	10.0	1.5	THF	20	74	8.8
10	1.0	12.0	1.5	THF	20	80	10.8
11	1.0	14.0	1.5	THF	20	83	12.9
12	1.0	14.0	1.5	neat[g]	20	86	12.5
13	1.0	16.0	1.5	neat	20	86	14.7
14	1.0	18.0	1.5	neat	20	84	16.9
15	1.0	12.0	1.5	neat	20	80	10.5
16	1.0	10.0	1.5	neat	20	74	8.9
17[e]	1.0	14.0	1.5	neat	20	<5%	13.2
18[f]	1.0	14.0	1.5	neat	20	NA	13.3
19	**1.0**	**14.0**	**1.4**	**neat**	**20**	**86**	**12.5**
20	1.0	14.0	1.3	neat	20	81	12.8

Reactions were carry out on a 0.10 mmol scale, THF (0.1 mL) and Grignard addtion for 1 h at 0 ºC. [a] Determined by crude ^{1}H NMR with CH_2Br_2 as internal standard. [b] Stirred addtional time after Grignard addtion. [c] Grignard addtion for 4 h. [d] 4-FPhMgBr. [e] Only $Fe(acac)_3$. [f] Without $Fe(acac)_3$ and **L1**. [g] Neat means no addtional THF.

Table S2. Screening of ligands, iron salt and catalyst loading for iron-catalyzed 1,2-difunctionalization



1 1.0 equiv | **2** 14.0 equiv | **3** | **4**



L1 **L2** **L3** **L4** **L5**

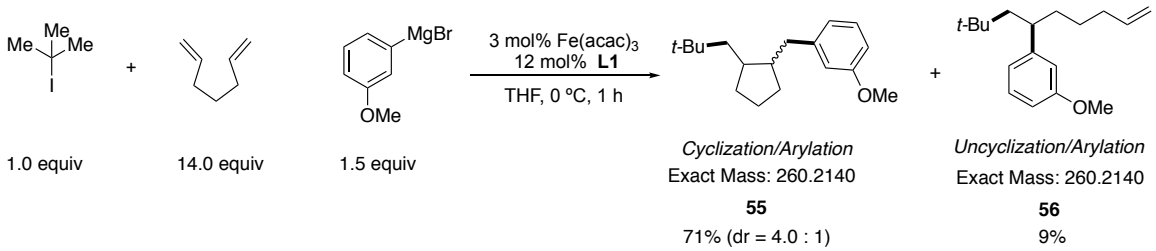
entry	Fe	L	Fe/**L** (mol%)	Grignard (eq)	yield (%)[a]	recovered **2** (eq)[a]
1	$Fe(acac)_3$	**L1**	5/15	1.4	81	12.6
2	$Fe(acac)_3$	**L1**	5/10	1.4	82	12.7
3	$Fe(acac)_3$	**L1**	5/20	1.4	86	12.5
4	$Fe(acac)_3$	**L2**	5/20	1.4	NA	13.1
5	$Fe(acac)_3$	**L3**	5/20	1.4	NA	13.2
6	$Fe(acac)_3$	**L4**	5/20	1.4	< 2	13.2
7	$Fe(acac)_3$	**L5**	5/20	1.4	14	13.0
8	$Fe(OAc)_2$	**L1**	5/20	1.4	< 5	13.3
9	$FeBr_2$	**L1**	5/20	1.4	80	12.7
10	$Fe(OTf)_2$	**L1**	5/20	1.4	41	13.2
11	$FeCl_3$	**L1**	5/20	1.4	78	12.7
12	$Fe(acac)_3$	**L1**	3/12	1.4	83	13.1
13[b]	$Fe(acac)_3$	**L1**	5/20	1.4	71	12.5
14[c]	$Fe(acac)_3$	**L1**	5/20	1.5	90	12.9
15[c]	**$Fe(acac)_3$**	**L1**	**3/12**	**1.5**	**90**	**13.0**
16[c]	$Fe(acac)_3$	**L1**	5/20	1.4	89	13.0

Reactions were carry out on a 0.10 mmol scale, *tert*-butyl iodide **1** (0.1 mmol, 1.0 equiv), 4-phenyl-1-butene **2** (14.0 equiv), neat, Grignard addtion for 1 h and stirred addtional for 20 min at 0 ºC. [a] Determined by crude ^1H NMR with CH_2Br_2 as internal standard. [b] room temp. [c] 0.20 mmol scale of *tert*-butyl iodide **1**. [d] Neat means no addtional THF.

4. Radical Cascade Cyclization/Arylation

Part A. Experimental study of radical cascade cyclization/arylation reactions

Scheme S1: Radical cascade cyclization/arylation of 1,6-diene with ArMgBr

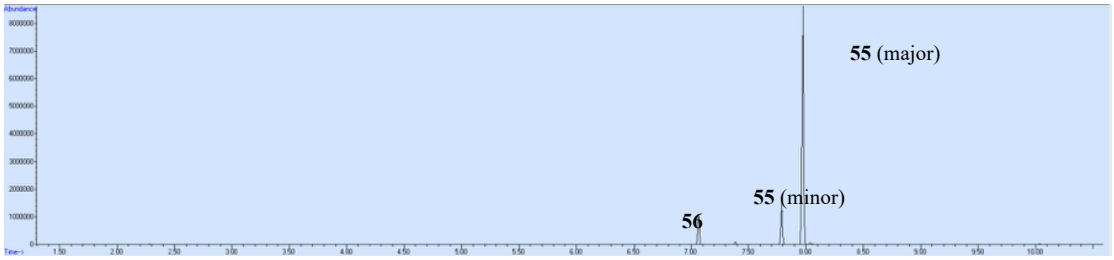


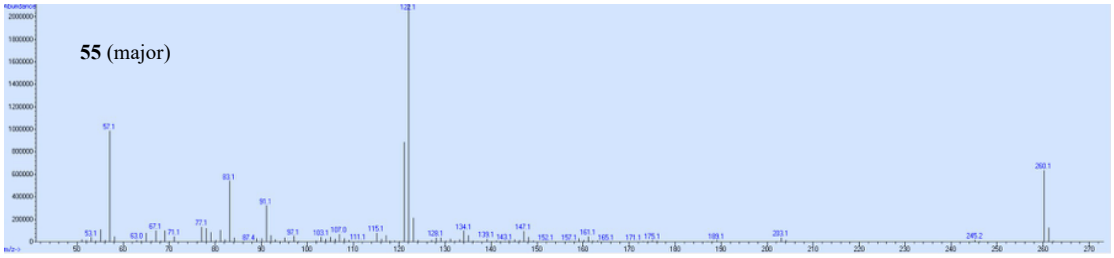
1.0 equiv | 14.0 equiv | 1.5 equiv

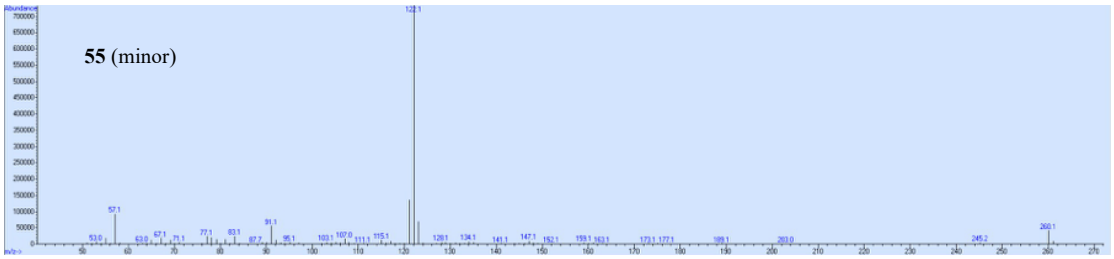
Cyclization/Arylation
Exact Mass: 260.2140
55
71% (dr = 4.0 : 1)

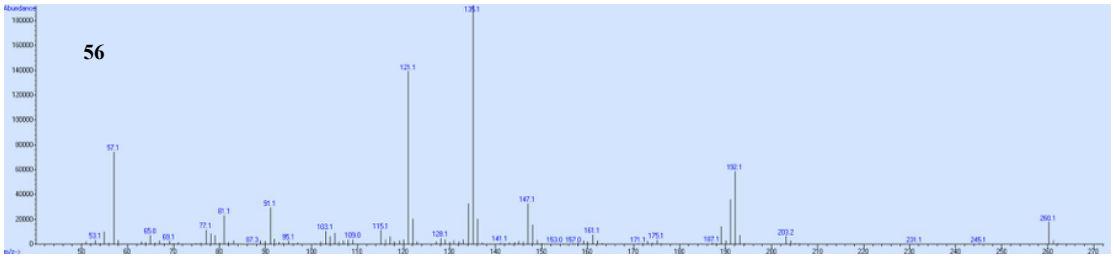
Uncyclization/Arylation
Exact Mass: 260.2140
56
9%

GC-MS result after flash chromatography:

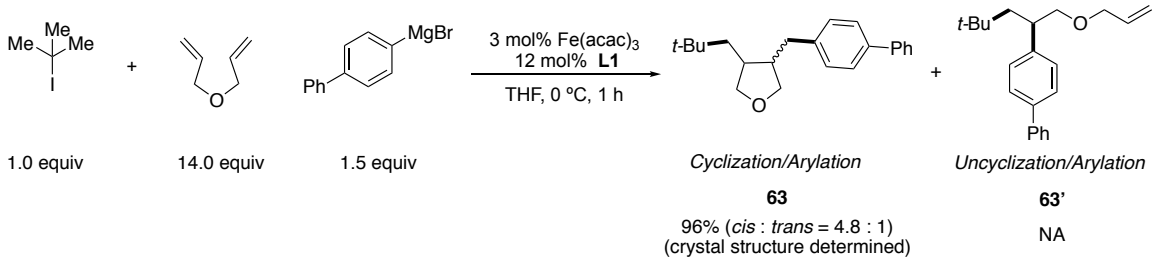




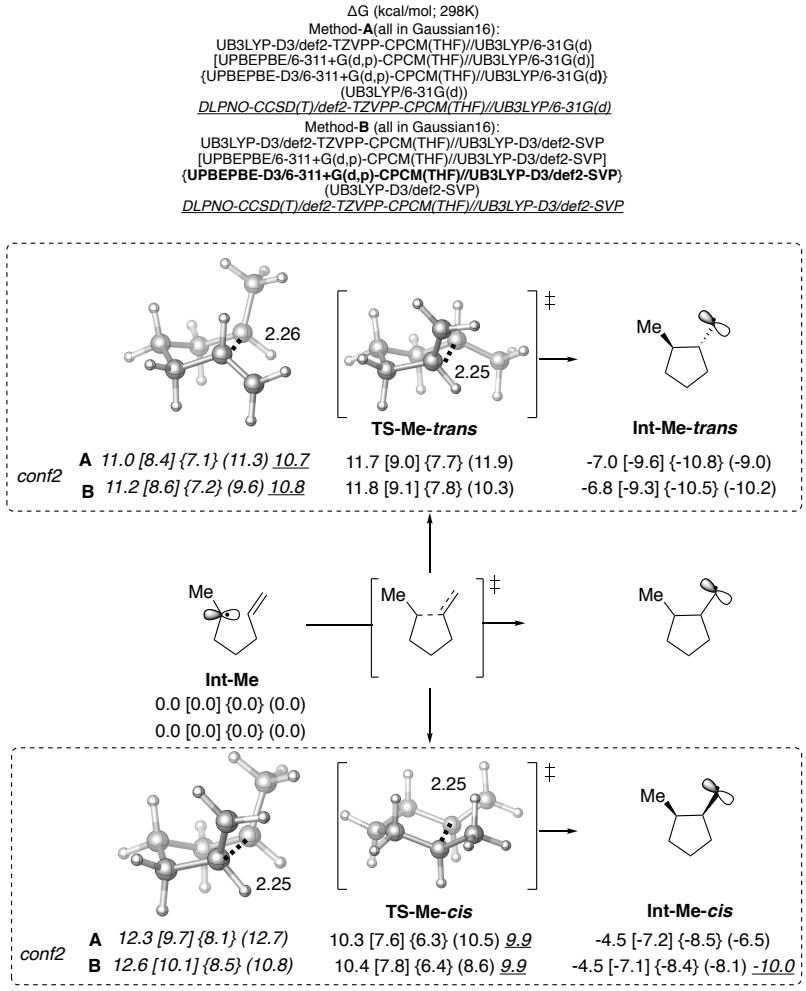




Scheme S2: Radical cascade cyclization/arylation of allyl ether with ArMgBr



Part B. Computational study of radical cascade cyclization/arylation reactions



Ref:
Ingold, K. U. et al. J. *Org. Chem.* **1987**, *52*, 3509-3514.
k^{298K}(cis) = 1*10^5 s^{-1}, E_a^*(cis) = ~**6.50** kcal/mol, logA = ~9.79 s^{-1};
k^{298K}(trans) = 2.9*10^4 s^{-1}, E_a^*(trans) = ~**7.44** kcal/mol, logA = ~9.92 s^{-1}.
*calculated from corresponding Arrenhius parameters instead of Eyring equation

Figure S1. Benchmark on 5-*exo*-trig cyclization of 1-methyl-5-hexenyl radical.

Based on the benchmark results on 5-exo-trig cyclization of 1-methyl-5-hexenyl radical, UPBEPBE-D3/6-311+G(d,p)-CPCM(THF)//UB3LYP/6-31G(d) provides results that are most consistent with the experimental measurement. Specifically, computational method predicts barrier of 7.1 kcal/mol and 6.3 kcal/mol for trans- and cis-cyclization, respectively, which are similar to the barrier of 7.44 kcal/mol and 6.50 kcal/mol calculated in experiment. Thus, **UPBEPBE-D3/6-311+G(d,p)-CPCM(THF)//UB3LYP/6-31G(d)** will be used for following calculations and discussions.

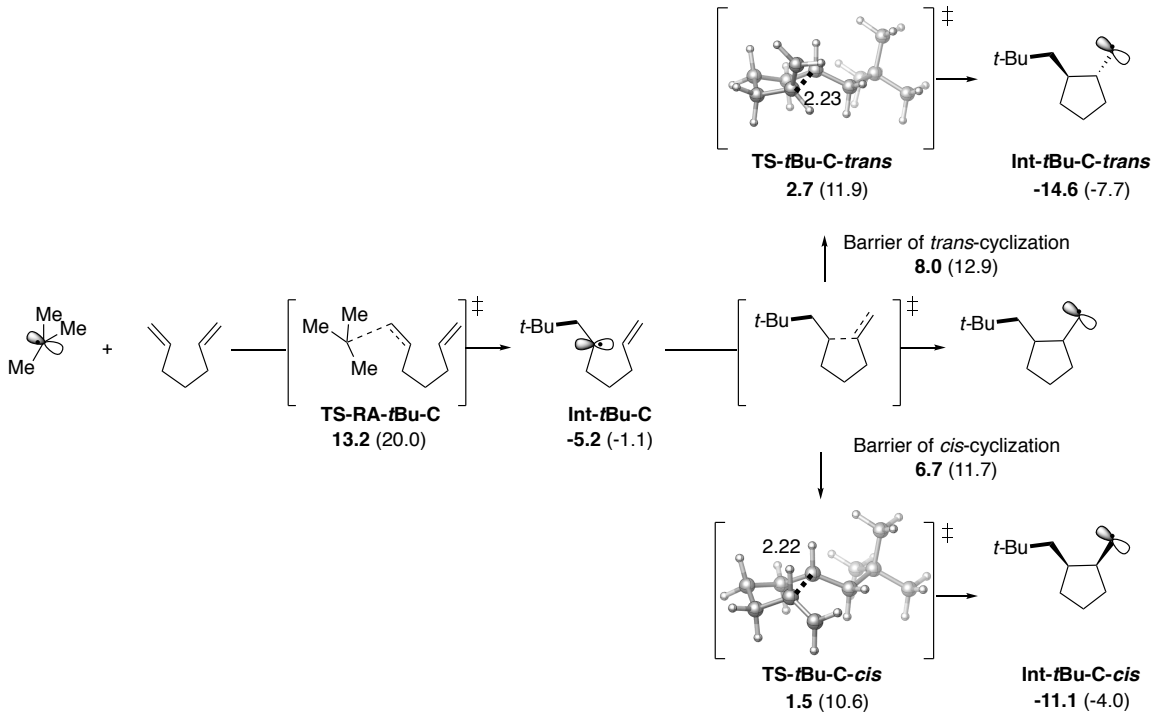


Figure S2. Δ*G* (kcal/mol; 298 K). Calculation of radical addition and cyclization steps of 1,6-heptadiene with UPBEPBE-D3/6-311+G(d,p)-CPCM(THF)//UB3LYP/6-31G(d) and UB3LYP/6-31G(d) (in parenthesis) levels of theory.

Calculations on the Giese addition and the 5-exo-trig cyclization steps showed that the cyclization process is reversible, where cis-cyclization is only 5.9 kcal/mol downhill in energy with barrier of 6.7 kcal/mol with respect to the intermediate after Giese addition (**Int-*t*Bu-C**), and that of trans-cyclization is 9.4 kcal/mol downhill in energy with barrier of 8.0 kcal/mol. This suggests that both **Int-*t*Bu-C** and **Int-*t*Bu-C-*cis*/*trans*** are applicable to subsequent cross-coupling steps, which is consistent with the experimental observations

where both uncyclized and cyclized product were obtained for this substrate. Moreover, the slight difference in barrier of cis-cyclization and trans-cyclization (only 1.3 kcal/mol) is consistent with the experimental results where both cis and products were observed.

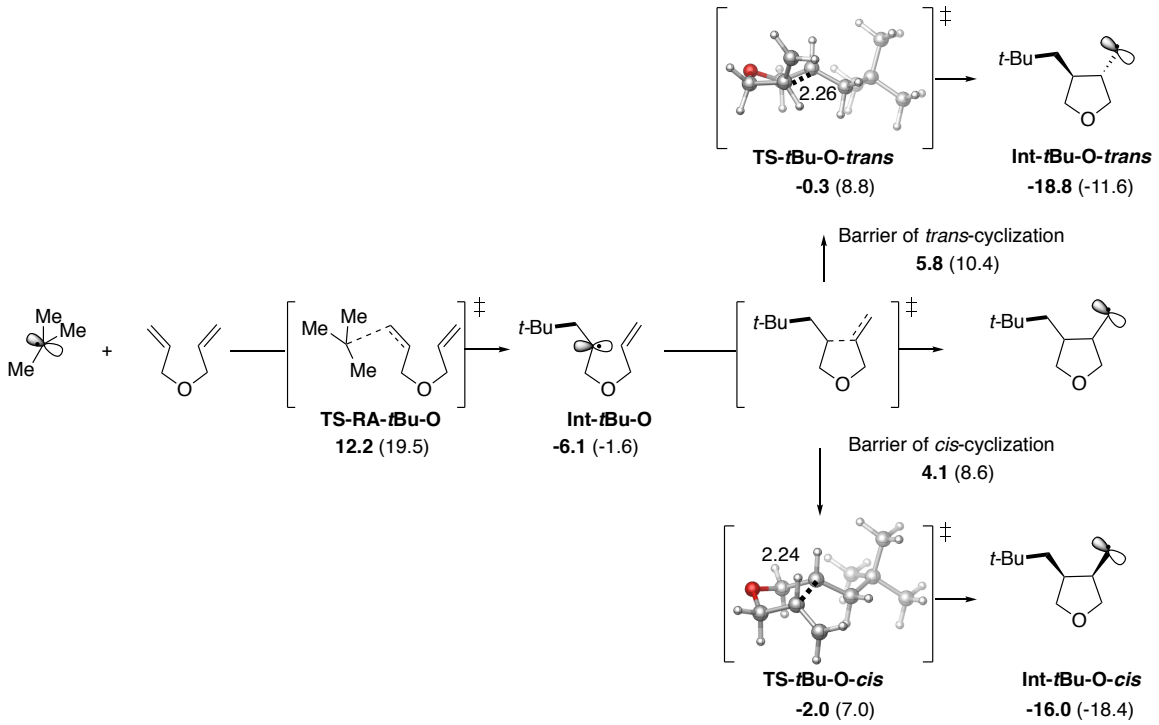


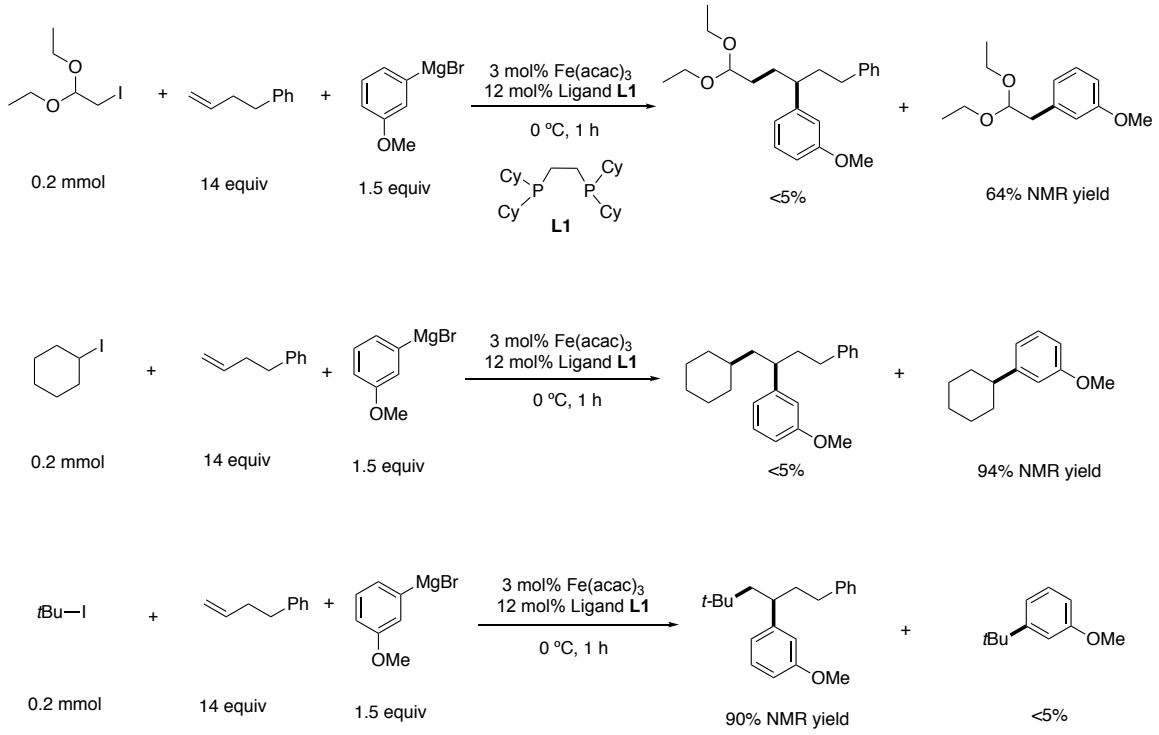
Figure S3. Δ*G* (kcal/mol; 298 K). Calculation of radical addition and cyclization steps of 1-propenyl ether with UPBEPBE-D3/6-311+G(d,p)-CPCM(THF)//UB3LYP/6-31G(d) and UB3LYP/6-31G(d) (in parenthesis) levels of theory.

We also explored the Giese addition and the 5-exo-trig cyclization steps with 1-propenyl ether. Although the barrier of Giese addition of this substrate is similar to that of 1,6-heptadiene (12.2 kcal/mol versus 13.2 kcal/mol), the following cyclization step shows great difference between these two substrates. Specifically, the barrier of both cis-cyclization and trans-cyclization are lower than those forming the all-carbon 5-membered ring for 2~3 kcal/mol, thus this substrate is easier to undergo 5-exo-trig cyclization. Moreover, the cis-cyclization and trans-cyclization in this case have thermodynamic drive of 9.9 and 12.7 kcal/mol, respectively, implying that the 5-exo-trig cyclization is less reversible than the previous case. Therefore, cross-coupling is more likely to occur on the cyclized intermediate **Int-*t*Bu-O-*cis*/*trans*** rather than the acyclized **Int-*t*Bu-O**, which can explain

the fact that only cyclized cross-coupling product was observed for 1-propenyl ether in experiment.

5. Comparison of 1,2-Alkylarylation and Direct Arylation

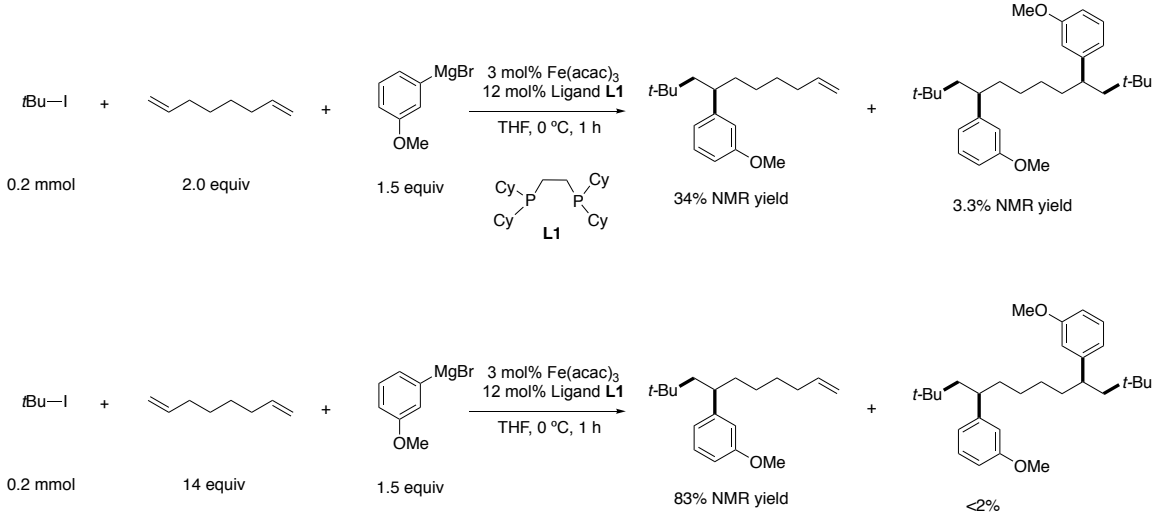
Scheme S3: Primary, Secondary and Tertiary Alkyl Radical on 1,2-dicarbofunctionalization reaction.



We performed the tertiary radical on 3-component 1,2-dicarbofunctionalization in high yield of desired product (90% NMR yield, **Scheme S3**). We also explored the primary and secondary alkyl radical on 1,2-alkylarylation reaction. However, they are not compatible radical precursors in this transformation to form 1,2-alkyaryl products due to the competing direct cross-coupling formation (64% and 94% NMR yield of direct arylation products, respectively).

6. Preliminary Study of the Selectivity for monofunctionalization of Diene

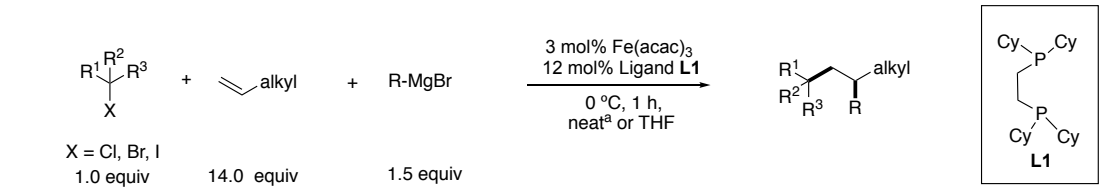
Scheme S4:

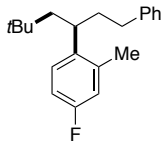


Overall, at lower concentration of alkene (2 equiv) we find that the monofunctionalized diene is the major product (34% yield). Notably, at this concentration, we also observe competitive (~3 % yield) formation of the difunctionalized diene. Overall, these results are consistent with selective monofunctionalization of the diene even at lower concentrations. However, we do note that the selectivity for the monofunctionalized product is increased due to the higher concentration of the alkene as both the yield and product ratios are affected.

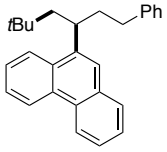
7. Current Limitation and Solvent Effect

Scheme S5: Current limitations or low yields of Fe-catalyzed difunctionalization.

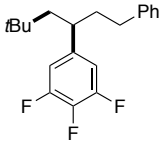




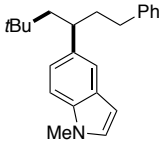
S1
X = I, < 5% (neat)



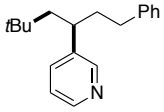
S2
X = I, 14% (neat)
X = Br, 10% (neat)



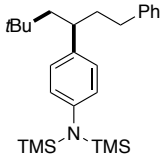
S3
X = I, 14% (neat)



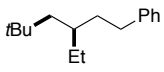
S4
X = I, 29% (neat)



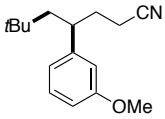
S5
X = I, < 2% (neat)



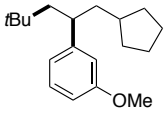
S6
X = I, < 5% (neat)



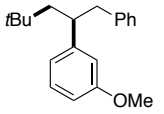
S7
X = I, < 5% (neat)



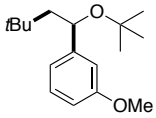
S8
X = I, NA (THF)



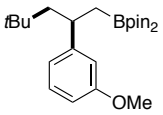
S9
X = I, < 5% (neat)



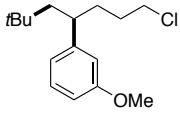
S10
X = I, < 5% (neat)



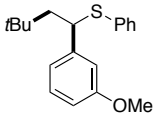
S11
X = I, < 2% (THF)



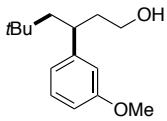
S12
X = Br, < 5% (neat)
X= I, < 2% (neat)



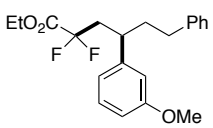
S13
X = I, 19% (THF)



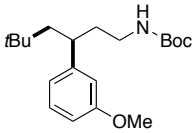
S14
X = I, < 2% (THF)



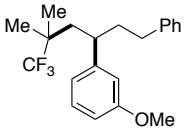
S15
X = I, NA (THF)



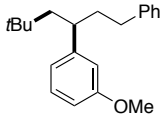
S16
X = I, < 5% (neat)



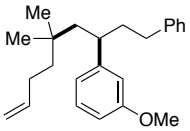
S17
X = I, < 2% (THF)



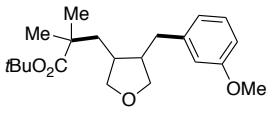
S18
X = Br, 26% (neat)



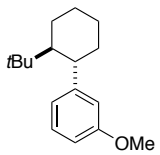
S19
X = Cl, 7% (neat)



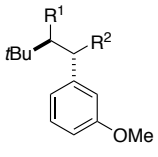
S20
X = Br, < 5% (neat)



S21
X = Br, 19% (dr = 3.8: 1) (THF)



S22
<5% (THF)



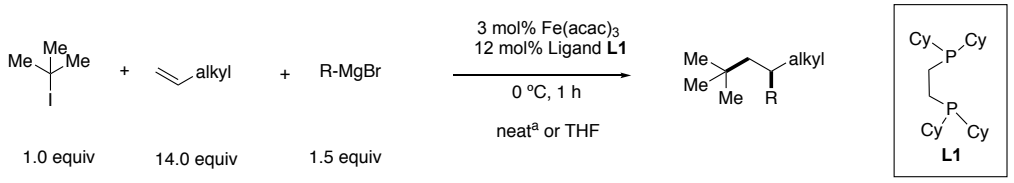
S23 R^1, R^2 = $-CH_3$ or $-(CH_2)_4CH_3$
<5% (THF)

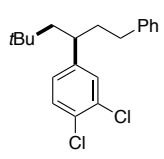
Reactions were carry out on a 0.20 mmol scale under the optimized conditions, neat or THF (0.2 mL). Yield were determined by crude ^1H NMR with CH_2Br_2 as internal standard. [a] Neat means no addtional THF.

Here are some limitation results of 3-component 1,2-dicarbofunctionalization (**Scheme S5**). We found that the method is not compatible the sterically hindered nucleophile (e.g., **S1**, **S2**) and unactivated alkenes (e.g., **S9**, **S11**) in this transformation presuemly due to the high energy to undergo inner-sphere reductive elimination. Alkenes bearing O- and S-heteroatoms were not compatible with this transformation (**S11**, **S14**). The unprotected alcohol (**S15**) and amine (**S17**), halide alkene (**S13**) and alkene (**S8**) did not work using this method because they were easily attacked by Grignard reagents. So far, this ligand (**L1**) is not compatible alkyl Grignard reagents on forming 1,2-alkylalkyl products (**S7**, sp^3-sp^3 cross-coupling) and *tert*-butyl chloride on generating the alkyl radical (**S19**). We also explored the internal unactivated alkenes on 1,2-dicarbofunctionalization. However, the tertiary alkyl radical without perfluororated were not compatible in this transformation to form desired products (**S22**, **S23**).

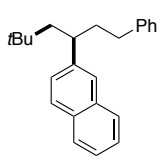
From the Scheme S6 results, a large amount of solvent is not likely necessary in this 3-component 1,2-dicarbofunctionalization reactions. The additional solvent played a supporting role for the unactivated alkenes on reaction solvability.

Scheme S6: Neat (no additional solvent) vs THF of iron-catalyzed 1,2-difunctionalization

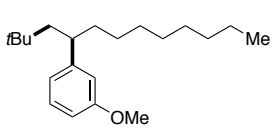




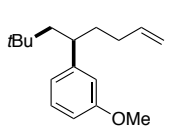
S22
45% (neat)
41% (THF)



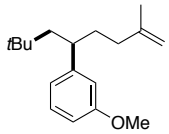
S23
56% (neat)
56% (THF)



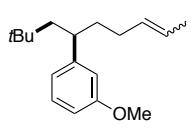
S24
44% (neat)
53% (THF)



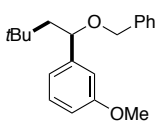
S25
65% (neat)
79% (THF)



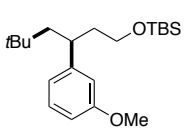
S26
41% (neat)
49% (THF)



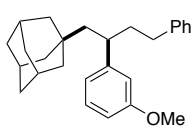
S27
48% (neat)
64% (THF)



S28
39% (neat)
43% (THF)



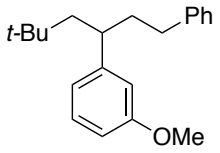
S29
55% (neat)
72% (THF)



S30
38% (neat)
31% (THF)

Reactions were carry out on a 0.20 mmol scale under the optimized conditions, neat or THF (0.2 mL). Yield were determined by crude ^{1}H NMR with CH_2Br_2 as internal standard. [a] Neat means no addtional THF.

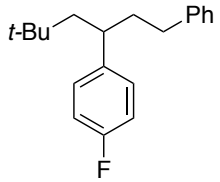
8. Product Characterization Data



1-(5,5-dimethyl-1-phenylhexan-3-yl)-3-methoxybenzene (4): Compound **4** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **4** was obtained as a colorless liquid (50.4 mg, 85% yield) and recovered 4-phenyl-1-butene (339 mg, 2.56 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1) to hexane/CH_2Cl_2 (10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30–7.20 (m, 3H), 7.20–7.15 (m, 1H), 7.15–7.07 (m, 2H), 6.82 (dt, *J* = 7.5, 1.3 Hz, 1H), 6.78–6.71 (m, 2H), 3.83 (s, 3H), 2.76–2.55 (m, 1H), 2.54–2.30 (m, 2H), 2.00–1.81 (m, 2H), 1.73 (dd, *J* = 14.0, 8.5 Hz, 1H), 1.57 (dd, *J* = 14.1, 3.7 Hz, 1H), 0.80 (s, 9H);

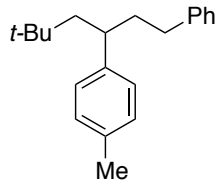
^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.73, 149.39, 142.72, 129.31, 128.50 (2C), 128.34 (2C), 125.71, 120.66, 114.08, 110.75, 55.27, 50.89, 42.52, 41.52, 34.11, 31.51, 30.24 (3C);
IR (film) 3026, 2949, 2861, 1684, 1486, 1453, 1363, 1263, 1149, 1045, 697 cm^{-1};
HRMS (DART) calcd for $C_{21}H_{29}O$ $[M+H]^+$ *m/z* = 297.2218; found 297.2216.



1-(5,5-dimethyl-1-phenylhexan-3-yl)-4-fluorobenzene (5): Compound **5** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 4-fluorophenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **5** was obtained as a colorless liquid (43.8 mg, 77% yield) and recovered 4-phenyl-1-butene (341 mg, 2.58 mmol) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked

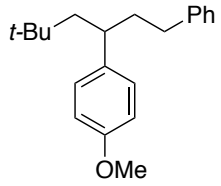
silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31–7.24 (m, 2H), 7.22–7.14 (m, 3H), 7.13–7.10 (m, 2H), 7.05–6.99 (m, 2H), 2.74–2.63 (m, 1H), 2.51–2.32 (m, 2H), 2.00–1.88 (m, 1H), 1.88–1.75 (m, 1H), 1.70 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.61 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.78 (s, 9H). Spectral data matched those reported previously.[3]



1-(5,5-dimethyl-1-phenylhexan-3-yl)-4-methylbenzene (6): Compound **6** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and *p*-tolylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product product **6** was obtained as a colorless liquid (43.3 mg, 79% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30–7.23 (m, 2H), 7.20–7.16 (m, 1H), 7.15–7.08 (m, 6H), 2.70–2.57 (m, 1H), 2.47–2.35 (m, 2H), 2.35 (s, 3H), 1.97–1.77 (m, 2H), 1.73 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.59 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.79 (s, 9H). Spectral data matched those reported previously.[3]



1-(5,5-dimethyl-1-phenylhexan-3-yl)-4-methoxybenzene (7): Compound **7** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 4-methoxyphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **7** was obtained as a colorless liquid (43.2 mg, 73% yield) and recovered 4-phenyl-1-butene (343 mg, 2.59

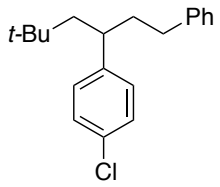
mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1) to hexane/CH_2Cl_2 (10:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33–7.21 (m, 2H), 7.19–7.13 (m, 1H), 7.14–7.02 (m, 4H), 6.92–6.77 (m, 2H), 3.82 (s, 3H), 2.71–2.54 (m, 1H), 2.49–2.31 (m, 2H), 1.91 (dddd, *J* = 13.4, 10.0, 6.7, 5.0 Hz, 1H), 1.81 (dtd, *J* = 13.4, 9.9, 5.5 Hz, 1H), 1.69 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.56 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.78 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.79, 142.82, 139.60, 128.84 (2C), 128.50 (2C), 128.33 (2C), 125.67, 113.79 (2C), 55.33, 51.10, 41.78, 41.58, 34.09, 31.46, 30.29 (3C);

IR (film) 3026, 2949, 2862, 1610, 1510, 1494, 1363, 1301, 1243, 1176, 1035, 828, 698 cm^{-1};

HRMS (DART) calcd for $C_{21}H_{29}O$ $[M+H]^+$ *m/z* = 297.2218; found 297.2220.



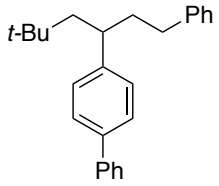
1-chloro-4-(5,5-dimethyl-1-phenylhexan-3-yl)benzene (8): Compound **8** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 4-chlorophenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **8** was obtained as a colorless liquid (42.7 mg, 71% yield) and recovered 4-phenyl-1-butene (335 mg, 2.53 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (100:1) to hexane/CH_2Cl_2 (50:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29–7.21 (m, 4H), 7.18–7.14 (m, 1H), 7.14–7.10 (m, 2H), 7.10–7.05 (m, 2H), 2.69–2.58 (m, 1H), 2.49–2.28 (m, 2H), 1.91 (dddd, *J* = 13.5, 10.1, 6.6, 5.1 Hz, 1H), 1.79 (dtd, *J* = 13.5, 9.9, 5.4 Hz, 1H), 1.68 (dd, *J* = 14.1, 8.7 Hz, 1H), 1.56 (dd, *J* = 14.1, 3.5 Hz, 1H), 0.76 (s, 8H);

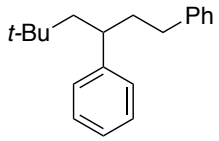
^{13}C NMR (150 MHz, $CDCl_3$) δ = 146.11, 142.38, 131.46, 129.39 (2C), 128.58 (2C), 128.46 (2C), 128.41 (2C), 125.83, 50.94, 41.88, 41.53, 33.97, 31.51, 30.27 (3C);

IR (film) 3026, 2951, 2859, 1493, 1364, 1092, 1013, 827, 698 cm^{-1};

HRMS (DART) calcd for $C_{20}H_{26}Cl$ $[M+H]^+$ *m/z* = 301.1723; found 301.1718.

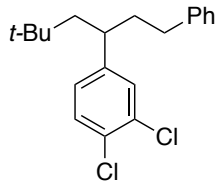


4-(5,5-dimethyl-1-phenylhexan-3-yl)-1,1'-biphenyl (9): Compound **9** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **9** was obtained as a colorless liquid (59.6 mg, 87% yield) and recovered 4-phenyl-1-butene (337 mg, 2.55 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (50:1) to hexane/CH_2Cl_2 (20:1).
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.74–7.62 (m, 2H), 7.62–7.54 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40–7.34 (m, 1H), 7.34–7.27 (m, 4H), 7.24–7.18 (m, 1H), 7.18–7.10 (m, 2H), 2.86–2.63 (m, 1H), 2.58–2.36 (m, 2H), 2.07–1.88 (m, 2H), 1.81 (dd, *J* = 14.0, 8.5 Hz, 1H), 1.65 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.85 (s, 9H);
^{13}C NMR (150 MHz, $CDCl_3$) δ = 146.82, 142.69, 141.21, 138.68, 128.83 (2C), 128.52 (2C), 128.46 (2C), 128.36 (2C), 127.08 (2C), 127.06 (2C), 125.74 (2C), 50.97, 42.11, 41.59, 34.13, 31.56, 30.32 (3C);
IR (film) 3025, 2949, 2861, 1486, 1363, 837, 763, 696 cm^{-1};
HRMS (DART) calcd for $C_{26}H_{31}$ $[M+H]^+$ *m/z* = 343.2426; found 343.2433.



(5,5-dimethylhexane-1,3-diyl)dibenzene (10): Compound **10** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and phenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **10** was obtained as a colorless liquid (43.2 mg, 81% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.05 (m, 8H), 7.04–7.00 (m, 2H), 2.62–2.51 (m,

1H), 2.40–2.23 (m, 2H), 1.89–1.69 (m, 2H), 1.65 (dd, *J* = 14.0, 8.5 Hz, 1H), 1.49 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.69 (s, 9H). Spectral data matched those reported previously.[3]



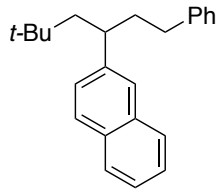
1,2-dichloro-4-(5,5-dimethyl-1-phenylhexan-3-yl)benzene (11): Compound **11** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3,4-dichlorophenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **11** was obtained as a colorless liquid (27.5 mg, 41% yield) and recovered 4-phenyl-1-butene (345 mg, 2.61 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (50:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.2 Hz, 1H), 7.29–7.19 (m, 3H), 7.20–7.14 (m, 1H), 7.11–7.05 (m, 2H), 7.02 (dd, *J* = 8.2, 2.1 Hz, 1H), 2.72–2.52 (m, 1H), 2.45–2.31 (m, 2H), 1.91 (dddd, *J* = 13.7, 10.0, 6.7, 5.1 Hz, 1H), 1.78 (dtd, *J* = 13.7, 9.7, 5.5 Hz, 1H), 1.65 (dd, *J* = 14.1, 8.6 Hz, 1H), 1.57 (dd, *J* = 15.1, 4.5 Hz, 1H), 0.77 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 148.13, 142.02, 132.37, 130.41, 129.94, 129.68, 128.47 (2C), 128.44 (2C), 127.52, 125.95, 50.76, 41.78, 41.29, 33.91, 31.54, 30.26 (3C);

IR (film) 3026, 2953, 2862, 1470, 1364, 1029, 698 cm^{-1};

HRMS (DART) calcd for $C_{20}H_{25}Cl_2$ $[M+H]^+$ *m/z* = 335.1333; found 335.1341.



2-(5,5-dimethyl-1-phenylhexan-3-yl)naphthalene (12): Compound **12** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 2-naphthylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **12** was obtained as a colorless liquid (32.3 mg, 51% yield) and recovered 4-phenyl-1-butene (352 mg, 2.66 mmol) after purified

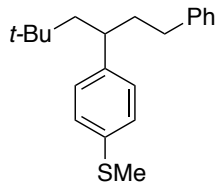
by flash chromatography on silica gel with hexane/CH_2Cl_2 (50:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.92–7.74 (m, 3H), 7.70–7.60 (m, 1H), 7.49 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.29–7.25 (m, 2H), 7.20–7.16 (m, 1H), 7.13–7.09 (m, 2H), 2.93–2.73 (m, 1H), 2.48 (ddd, *J* = 13.9, 10.2, 6.5 Hz, 1H), 2.40 (ddd, *J* = 13.9, 10.1, 5.4 Hz, 1H), 2.08–1.92 (m, 2H), 1.87 (dd, *J* = 14.1, 8.6 Hz, 1H), 1.67 (dd, *J* = 14.1, 3.5 Hz, 1H), 0.82 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 145.05, 142.65, 133.75, 132.35, 128.50 (2C), 128.35 (2C), 128.16, 127.76, 127.65, 126.68, 126.36, 125.93, 125.73, 125.18, 50.90, 42.61, 41.50, 34.14, 31.61, 30.32 (3C);

IR (film) 3025, 2949, 2861, 1600, 1459, 1363, 853, 817, 698 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{29}$ $[M+H]^+$ *m/z* = 317.2269; found 317.2273.



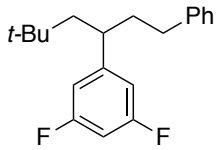
(4-(5,5-dimethyl-1-phenylhexan-3-yl)phenyl)(methyl)sulfane (13): Compound **13** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 4-(methylsulfanyl)phenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **13** was obtained as a colorless liquid (45 mg, 72% yield) and recovered 4-phenyl-1-butene (342 mg, 2.59 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29–7.25 (m, 2H), 7.25–7.20 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.15–7.13 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 2.71–2.58 (m, 1H), 2.50 (s, 3H), 2.47–2.32 (m, 2H), 2.01–1.88 (m, 1H), 1.89–1.78 (m, 1H), 1.75–1.67 (m, 1H), 1.58 (dd, *J* = 14.1, 3.4 Hz, 1H), 0.79 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.74, 142.59, 135.16, 128.59 (2C), 128.47 (2C), 128.34 (2C), 127.11 (2C), 125.72, 50.92, 41.92, 41.57, 34.03, 31.49, 30.28 (3C), 16.35;

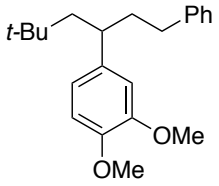
IR (film) 3025, 2949, 2861, 1494, 1363, 1095, 817, 698 cm^{-1};

HRMS (DART) calcd for $C_{21}H_{29}S$ $[M+H]^+$ *m/z* = 313.1990; found 313.1996.



1-(5,5-dimethyl-1-phenylhexan-3-yl)-3,5-difluorobenzene (14): Compound **14** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3,5-difluorophenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **14** was obtained as a colorless liquid (41.7 mg, 69% yield) and recovered 4-phenyl-1-butene (346 mg, 2.62 mmol) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22–7.14 (m, 2H), 7.13–7.06 (m, 1H), 7.04–6.98 (m, 2H), 6.67–6.61 (m, 2H), 6.59–6.51 (m, 1H), 2.62–2.52 (m, 1H), 2.40–2.23 (m, 2H), 1.87–1.65 (m, 2H), 1.58 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.47 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.69 (s, 9H). Spectral data matched those reported previously.[3]



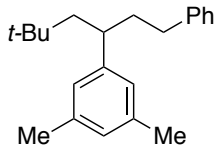
4-(5,5-dimethyl-1-phenylhexan-3-yl)-1,2-dimethoxybenzene (15): Compound **15** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3,4-dimethoxyphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **15** was obtained as a colorless liquid (30.7 mg, 47% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1) to hexane/CH_2Cl_2 (10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30–7.21 (m, 2H), 7.20–7.13 (m, 1H), 7.12–7.03 (m, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.73 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.70 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.68–2.55 (m, 1H), 2.47–2.32 (m, 2H), 1.90 (dddd, *J* = 13.2, 9.9, 6.9, 5.0 Hz, 1H), 1.80 (dtd, *J* = 13.4, 9.7, 5.6 Hz, 1H), 1.68 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.54 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.78 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 148.95, 147.20, 142.74, 140.12, 128.49 (2C), 128.33 (2C), 125.70, 120.13, 111.13, 111.05, 56.03, 55.96, 51.05, 42.06, 41.66, 34.07, 31.46, 30.25 (3C);

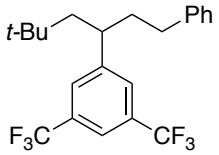
IR (film) 2949, 2860, 1516, 1464, 1259, 1235, 1139, 1030, 699 cm^{-1};

HRMS (DART) calcd for $C_{22}H_{31}O_2$ $[M+H]^+$ *m/z* = 327.2324; found 327.2328.



1-(5,5-dimethyl-1-phenylhexan-3-yl)-3,5-dimethylbenzene (16): Compound **16** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3,5-dimethylphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **16** was obtained as a colorless liquid (46.5 mg, 79% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).

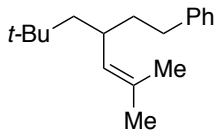
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33–7.24 (m, 2H), 7.23–7.11 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03–6.93 (m, 2H), 2.67–2.59 (m, 1H), 2.53–2.36 (m, 2H), 2.31 (s, 3H), 2.30 (s, 3H), 1.99–1.79 (m, 2H), 1.75 (dd, *J* = 14.0, 8.2 Hz, 1H), 1.60 (dd, *J* = 14.0, 3.8 Hz, 1H), 0.83 (s, 9H). Spectral data matched those reported previously.[3]



1-(5,5-dimethyl-1-phenylhexan-3-yl)-3,5-bis(trifluoromethyl)benzene (17): Compound **17** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3,5-bis(trifluoromethyl)phenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **17** was obtained as a colorless liquid (53.9 mg, 67% yield) and recovered 4-phenyl-1-butene (339 mg, 2.56 mmol) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient

elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (s, 1H), 7.53 (s, 2H), 7.22–7.14 (m, 2H), 7.13–7.06 (m, 1H), 7.02–6.95 (m, 2H), 2.78–2.67 (m, 1H), 2.39–2.26 (m, 2H), 1.99–1.86 (m, 1H), 1.84–1.71 (m, 1H), 1.67–1.55 (m, 2H), 0.69 (s, 9H). Spectral data matched those reported previously.[3]



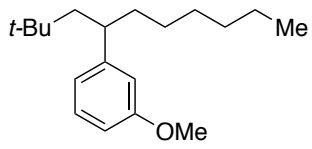
(5-methyl-3-neopentylhex-4-en-1-yl)benzene (18): Compound **18** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 2-methyl-1-propenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **18** was obtained as a colorless liquid (20 mg, 41% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/Et_2O (99: 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30–7.22 (m, 2H), 7.21–7.12 (m, 3H), 4.91 (dp, *J* = 9.9, 1.4 Hz, 1H), 2.59 (ddd, *J* = 13.7, 10.9, 5.4 Hz, 1H), 2.48 (ddd, *J* = 13.8, 10.8, 5.8 Hz, 1H), 2.34 (dtdd, *J* = 9.8, 8.6, 4.8, 3.3 Hz, 1H), 1.70 (d, *J* = 1.5 Hz, 3H), 1.68–1.61 (m, 1H), 1.59 (d, *J* = 1.4 Hz, 3H), 1.43 (dddd, *J* = 13.2, 10.9, 8.9, 5.4 Hz, 1H), 1.30 (dd, *J* = 13.8, 3.3 Hz, 1H), 1.23 (dd, *J* = 13.8, 8.7 Hz, 1H), 0.86 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.35, 132.24, 129.19, 128.51 (2C), 128.32 (2C), 125.59, 50.40, 40.28, 34.91, 33.73, 31.14, 30.39 (3C), 26.00, 18.50;

IR (film) 3027, 2951, 2862, 1495, 1453, 1363, 697 cm^{-1};

HRMS (DART) calcd for $C_{18}H_{29}$ $[M+H]^+$ *m/z* = 245.2269; found 245.2274.



1-(2,2-dimethyldecan-4-yl)-3-methoxybenzene (19): Compound **19** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2

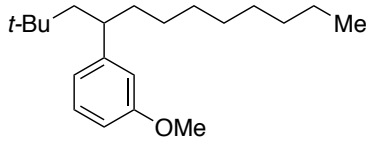
mmol), 1-octene (314.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **19** was obtained as a colorless liquid (31.5 mg, 57% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.72 (t, *J* = 2.1 Hz, 1H), 6.70 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.80 (s, 3H)， 2.56 (tdd, *J* = 8.9, 5.6, 3.4 Hz, 1H), 1.68 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.55–1.43 (m, 3H), 1.27–1.15 (m, 6H), 1.16–1.09 (m, 1H), 1.07–0.98 (m, 1H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.78 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.61, 150.09, 129.10, 120.64, 114.00, 110.46, 55.25, 50.81, 42.83, 40.02, 31.95, 31.47, 30.28 (3C), 29.51, 27.80, 22.80, 14.23;

IR (film) 2952, 2925, 2855, 1584, 1363, 1261, 1150, 1049, 701 cm^{-1};

HRMS (DART) calcd for $C_{19}H_{33}O$ $[M+H]^+$ *m/z* = 277.2531; found 277.2533.



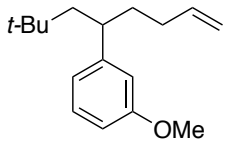
1-(2,2-dimethyldodecan-4-yl)-3-methoxybenzene (20): Compound **20** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1-dectene (392.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **20** was obtained as a colorless liquid (34.1 mg, 56% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.72 (t, *J* = 2.1 Hz, 1H), 6.70 (ddd, *J* = 8.0, 2.7, 0.9 Hz, 1H), 3.80 (s, 3H), 2.56 (tdd, *J* = 8.9, 5.6, 3.4 Hz, 1H), 1.68 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.60–1.41 (m, 3H), 1.33–1.16 (m, 10H), 1.15–1.08 (m, 1H), 1.07–0.96 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.78 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.61, 150.09, 129.10, 120.64, 114.01, 110.45, 55.24, 50.82, 42.83, 40.01, 32.03, 31.47, 30.28 (3C), 29.84, 29.67, 29.47, 27.82, 22.81, 14.24;

IR (film) 2923, 2853, 1584, 1465, 1363, 1262, 1149, 1049, 701 cm^{-1};

HRMS (DART) calcd for $C_{21}H_{37}O$ $[M+H]^+$ *m/z* = 305.2844; found 305.2842.



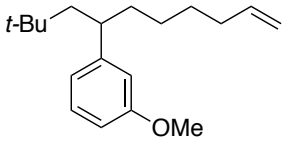
1-(2,2-dimethyloct-7-en-4-yl)-3-methoxybenzene (21): Compound **21** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1,5-hexadiene (300 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **21** was obtained as a colorless liquid (37.9 mg, 77% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (40:1) to hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.73–6.68 (m, 2H), 5.76 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.02–4.82 (m, 2H), 3.80 (s, 3H), 2.61 (tdd, *J* = 9.0, 5.4, 3.4 Hz, 1H), 1.93–1.78 (m, 2H), 1.70 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.68–1.56 (m, 2H), 1.52 (dd, *J* = 14.0, 3.4 Hz, 1H), 0.78 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.67, 149.45, 139.00, 129.21, 120.67, 114.51, 114.08, 110.64, 55.26, 50.76, 42.16, 38.98, 31.95, 31.52, 30.26 (3C);

IR (film) 2926, 2863, 1584, 1486, 1364, 1259, 1149, 1048, 909, 702 cm^{-1};

HRMS (DART) calcd for $C_{17}H_{27}O$ $[M+H]^+$ *m/z* = 247.2062; found 247.2060.



1-(2,2-dimethyldec-9-en-4-yl)-3-methoxybenzene (22): Compound **22** was synthesized following the general procedure (gram-scale**)**, using *tert*-butyl iodide (1.1 g, 6.0 mmol), 1,7-octadiene (9.26 g, 84 mmol) and 3-methoxyphenylmagnesium bromide (9 mL, 1.0 M solution in THF, 9.0 mmol). Recovered 1,7-octadiene (8.38 g, 76 mmol) was obtained by vigreux column vacuum distillation and the product **22** was obtained as a colorless liquid (1.38 g, 83% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (50:1) to hexane/CH_2Cl_2 (20:1)

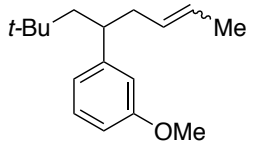
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.19 (t, *J* = 7.8 Hz, 1H), 6.78 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.74 (t, *J* = 2.1 Hz, 1H), 6.72 (ddd, *J* = 8.0, 2.6, 0.9 Hz, 1H), 5.78 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.13–4.73 (m, 2H), 3.81 (s, 3H), 2.59 (tdd, *J* = 8.9, 5.6, 3.4 Hz, 1H), 1.99 (dtdd,

J = 7.8, 6.3, 2.7, 1.3 Hz, 2H), 1.70 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.62–1.48 (m, 3H), 1.39–1.27 (m, 2H), 1.25–1.14 (m, 1H), 1.13–1.03 (m, 1H), 0.81 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.63, 149.90, 139.21, 129.13, 120.59, 114.25, 113.98, 110.49, 55.22, 50.82, 42.77, 39.80, 33.83, 31.46, 30.27 (3C), 29.13, 27.31;

IR (film) 2928, 2856, 1584, 1486, 1363, 1261, 1150, 1048, 909, 701 cm^{-1};

HRMS (DART) calcd for $C_{19}H_{31}O$ $[M+H]^+$ *m/z* = 275.2375; found 275.2370.



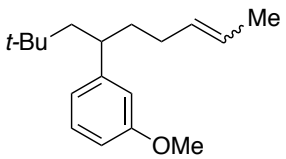
1-(2,2-dimethyloct-6-en-4-yl)-3-methoxybenzene (23): Compound **23** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1,4-hexadiene, mixture of *cis* and *trans* (230 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **23** was obtained as a colorless liquid (15.8 mg, 32% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

23 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.74–6.67 (m, 2H), 5.44–5.31 (m, 1H), 5.30–5.18 (m, 1H), 3.80 (s, 3H), 2.62 (dtd, *J* = 8.6, 7.2, 3.4 Hz, 1H), 2.19 (ddt, *J* = 7.3, 6.1, 1.3 Hz, 2H), 1.65 (dd, *J* = 14.0, 8.8 Hz, 1H), 1.61–1.52 (m, 4H), 0.78 (s, 9H);

23 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.59, 149.60, 129.83, 129.12, 126.38, 120.62, 114.00, 110.64, 55.27, 49.35, 43.27, 43.01, 31.43, 30.28 (3C), 18.05;

IR (film) 2951, 1584, 1486, 1363, 1260, 1148, 1049, 966, 701 cm^{-1};

HRMS (DART) calcd for $C_{17}H_{27}O$ $[M+H]^+$ *m/z* = 247.2062; found 247.2060.



1-(2,2-dimethylnon-7-en-4-yl)-3-methoxybenzene (24): Compound **24** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1,5-heptadiene, mixture of *cis* and *trans* (269.3 mg, 2.8 mmol) and 3-

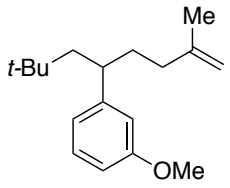
methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **24** was obtained as a colorless liquid (31.8 mg, 61% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.25–7.10 (m, 1H, major + minor), 6.84–6.74 (m, 1H, major + minor), 6.74–6.63 (m, 2H, major + minor), 5.44–5.28 (m, 2H, major + minor), 3.81–3.80 (m, 3H, major + minor), 2.70–2.49 (m, 1H, major + minor), 1.97–1.71 (m, 2H, major + minor), 1.71–1.64 (m, 1H, major + minor), 1.64–1.45 (m, 6H, major + minor), 0.79–0.78 (m, 9H, major + minor);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.65 (major + minor), 149.66 (major), 149.58 (minor), 131.42 (major), 130.64 (minor), 129.18 (minor), 129.16 (major), 124.94 (major), 124.00 (minor), 120.69 (major + minor), 114.08 (major), 114.07 (minor), 110.66 (minor), 110.58 (major), 55.26 (major, minor), 50.82 (minor), 50.73 (major), 42.31 (minor), 42.23 (major), 39.70 (major), 39.63 (minor), 31.51 (major), 30.76 (major + minor), 30.27 (3C major + 3C minor), 25.11 (minor) , 18.07 (major), 12.94 (minor);

IR (film) 2951, 2864, 1584, 1486, 1363, 1263, 1148, 1049, 965, 701 cm^{-1};

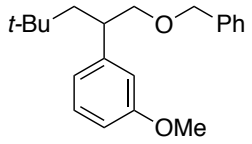
HRMS (DART) calcd for $C_{18}H_{29}O$ $[M+H]^+$ *m/z* = 261.2218; found 261.2214.



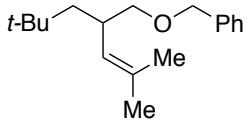
1-methoxy-3-(2,2,7-trimethyloct-7-en-4-yl)benzene (25): Compound **25** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 2-methyl-1,5-hexadiene (269.3 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **25** was obtained as a colorless liquid (22.9 mg, 44% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.72 (t, *J* = 2.1 Hz, 1H), 6.70 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 4.68–4.60 (m, 2H), 3.80 (s, 3H), 2.58 (tdd, *J* = 8.8, 5.2, 3.4 Hz, 1H), 1.86 (ddd, *J* = 14.9, 10.0, 5.7 Hz, 1H), 1.79–1.67 (m, 3H), 1.66 (s, 3H), 1.67–1.59 (m, 1H), 1.55–1.50 (m, 1H), 0.78 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.66, 149.61, 146.13, 129.20, 120.67, 114.08, 110.64, 109.80, 55.27, 50.83, 42.40, 37.70, 35.92, 31.50, 30.27 (3C), 22.70;
IR (film) 2950, 1584, 1486, 1364, 1262, 1148, 1047, 884, 701 cm^{-1};
HRMS (DART) calcd for $C_{18}H_{29}O$ $[M+H]^+$ *m/z* = 261.2218; found 261.2211.



1-(1-(benzyloxy)-4,4-dimethylpentan-2-yl)-3-methoxybenzene (26): Compound **26** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl benzyl ether (415 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **26** was obtained as a colorless liquid (51.2 mg, 82% yield) and recovered allyl benzyl ether (382 mg, 2.58 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (3:1) to hexane/CH_2Cl_2 (3:2).
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.37–7.31 (m, 2H), 7.30–7.24 (m, 3H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.86 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.81 (t, *J* = 2.1 Hz, 1H), 6.77 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 4.55–4.43 (m, 2H), 3.81 (s, 3H), 3.50 (qd, *J* = 9.3, 7.0 Hz, 2H), 3.01 (dtd, *J* = 8.4, 7.0, 3.4 Hz, 1H), 1.72 (dd, *J* = 14.0, 3.4 Hz, 1H), 1.67 (dd, *J* = 14.0, 8.6 Hz, 1H), 0.84 (s, 9H);
^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.67, 146.95, 138.74, 129.27, 128.37 (2C), 127.56 (2C), 127.49, 120.84, 114.22, 111.28, 76.51, 72.96, 55.24, 46.07, 43.11, 31.31, 30.23 (3C);
IR (film) 2951, 2862, 1712, 1599, 1453, 1363, 1261, 1103, 1047, 778, 734, 699 cm^{-1};
HRMS (DART) calcd for $C_{21}H_{29}O_2$ $[M+H]^+$ *m/z* = 313.2168; found 313.2166.



(((4-methyl-2-neopentylpent-3-en-1-yl)oxy)methyl)benzene (27): Compound **27** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl benzyl ether (415 mg, 2.8 mmol) and 2-methyl-1-propenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **27** was obtained as a

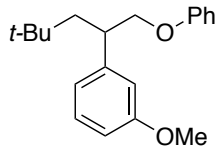
colorless liquid (20.3 mg, 39% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/Et_2O (97: 3).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.38–7.30 (m, 4H), 7.29–7.24 (m, 1H), 5.00–4.83 (m, 1H), 4.55–4.43 (m, 2H), 3.22 (d, *J* = 6.8 Hz, 2H), 2.67 (ttd, *J* = 9.5, 6.8, 2.8 Hz, 1H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.65 (d, *J* = 1.4 Hz, 3H), 1.51 (dd, *J* = 13.7, 2.8 Hz, 1H), 1.14 (dd, *J* = 13.7, 9.1 Hz, 1H), 0.88 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 139.07, 130.92, 129.16, 128.39 (2C), 127.54 (2C), 127.45, 75.41, 72.83, 46.15, 35.59, 30.94, 30.36 (3C), 26.03, 18.33;

IR (film) 2953, 2862, 1453, 1363, 1101, 733, 696 cm^{-1};

HRMS (DART) calcd for $C_{18}H_{29}O$ $[M+H]^+$ *m/z* = 261.2218; found 261.2217.



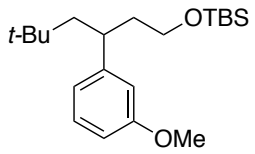
1-(4,4-dimethyl-1-phenoxypentan-2-yl)-3-methoxybenzene (28): Compound **28** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl phenyl ether (375.7 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **28** was obtained as a colorless liquid (22.1 mg, 37% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (5:1) to hexane/CH_2Cl_2 (2:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28–7.25 (m, 2H), 7.25–7.22 (m, 1H), 6.93 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.90 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.88–6.80 (m, 3H), 6.77 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 4.02–3.90 (m, 2H), 3.82 (s, 3H), 3.22–3.08 (m, 1H), 1.85 (dd, *J* = 14.0, 3.2 Hz, 1H), 1.78 (dd, *J* = 14.0, 8.8 Hz, 1H), 0.86 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.76, 159.08, 146.17, 129.50 (2C), 129.46, 120.82, 120.74, 114.83 (2C), 114.44, 111.46, 73.63, 55.30, 45.99, 42.66, 31.35, 30.23 (3C);

IR (film) 2952, 2864, 1713, 1598, 1496, 1465, 1241, 1152, 1034, 753, 701 cm^{-1};

HRMS (DART) calcd for $C_{20}H_{27}O_2$ $[M+H]^+$ *m/z* = 299.2011; found 299.2014.



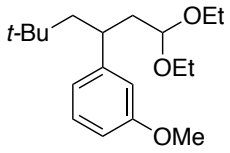
***tert*-butyl((3-(3-methoxyphenyl)-5,5-dimethylhexyl)oxy)dimethylsilane (29):** Compound **29** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), (but-3-en-1-yloxy)-*tert*-butyldimethylsilane (521.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **29** was obtained as a colorless liquid (47 mg, 67% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (3:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 7.8 Hz, 1H), 6.78 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.73 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.70 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 3.80 (s, 3H), 3.41 (ddd, *J* = 10.2, 6.9, 4.8 Hz, 1H), 3.33 (ddd, *J* = 10.2, 7.9, 6.3 Hz, 1H), 2.83 (tt, *J* = 8.8, 4.3 Hz, 1H), 1.82 (dddd, *J* = 13.0, 7.8, 6.9, 4.9 Hz, 1H), 1.73–1.64 (m, 2H), 1.52 (dd, *J* = 14.0, 3.7 Hz, 1H), 0.89 (s, 9H), 0.80 (s, 9H), -0.01 (d, *J* = 2.4 Hz, 6H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.66, 149.35, 129.19, 120.68, 113.99, 110.81, 61.08, 55.25, 50.70, 42.67, 38.72, 31.57, 30.24 (3C), 26.09 (3C), 18.37, -5.18 (2C);

IR (film) 2952, 2858, 1599, 1471, 1254, 1102, 835, 774, 701 cm^{-1};

HRMS (DART) calcd for $C_{21}H_{39}O_2Si$ $[M+H]^+$ *m/z* = 351.2719; found 351.2716.



1-(1,1-diethoxy-5,5-dimethylhexan-3-yl)-3-methoxybenzene (30): Compound **30** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 3-butenal diethyl acetal (403.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **30** was obtained as a colorless liquid (19.7 mg, 32% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:2).

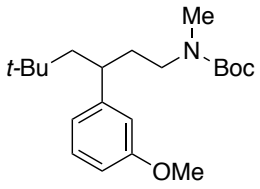
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 7.8 Hz, 1H), 6.79 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.74 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.70 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 4.08 (dd, *J* = 8.1, 3.7 Hz, 1H), 3.79 (s, 3H), 3.61 (dq, *J* = 9.4, 7.0 Hz, 1H), 3.49 (dq, *J* = 9.4, 7.0 Hz, 1H), 3.37

(ddq, J = 16.3, 9.4, 7.1 Hz, 2H), 2.81 (dddd, J = 10.2, 8.7, 5.0, 3.6 Hz, 1H), 1.91 (ddd, J = 13.4, 8.2, 5.0 Hz, 1H), 1.77 (ddd, J = 13.9, 10.3, 3.7 Hz, 1H), 1.68 (dd, J = 14.0, 8.9 Hz, 1H), 1.51 (dd, J = 14.0, 3.6 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H), 0.78 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.73, 148.85, 129.32, 120.66, 113.97, 110.94, 101.51, 61.44, 60.94, 55.26, 50.74, 43.34, 38.69, 31.52, 30.26 (3C), 15.57, 15.53;

IR (film) 2950, 2904, 1599, 1487, 1364, 1260, 1128, 1053, 703 cm^{-1};

HRMS (DART) calcd for $C_{19}H_{36}O_3N$ $[M+NH_4]^+$ *m/z* = 326.2695; found 326.2699.



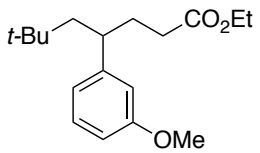
***tert*-butyl (3-(3-methoxyphenyl)-5,5-dimethylhexyl)(methyl)carbamate (31):** Compound **31** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), *tert*-butyl N-(but-3-en-1-yl)-N-methylcarbamate (518.7 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **31** was obtained as a colorless liquid (48.2 mg, 69% yield) and recovered *tert*-butyl N-(but-3-en-1-yl)-N-methylcarbamate (473 mg, 2.55 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:1) to pentane/Et_2O (10: 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (t, J = 7.8 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.73–6.64 (m, 2H), 3.78 (s, 3H), 3.31 (d, J = 96.9 Hz, 1H), 2.94 (bs, 1H), 2.74 (s, 3H), 2.56 (bs, 1H), 1.86–1.62 (m, 3H), 1.56–1.49 (m, 1H), 1.40 (s, 9H), 0.78 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.72, 155.79, 148.82, 129.39, 120.32, 113.90, 110.78, 79.16, 55.21, 50.93, 47.84, 40.55, 37.40, 34.29, 31.44, 30.18 (3C), 28.56 (3C);

IR (film) 2950, 1693, 1600, 1485, 1392, 1364, 1261, 1156, 1047, 878, 774, 702 cm^{-1};

HRMS (DART) calcd for $C_{21}H_{36}O_3N$ $[M+H]^+$ *m/z* = 350.2695; found 350.2691.



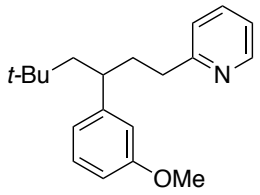
ethyl 4-(3-methoxyphenyl)-6,6-dimethylheptanoate (32): Compound **32** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), ethyl 4-pentenoate (358.9 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **32** was obtained as a colorless liquid (42.7 mg, 73% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22–7.10 (m, 1H), 6.75 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.73–6.67 (m, 2H), 4.07 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.79 (s, 3H), 2.71–2.51 (m, 1H), 2.17–1.99 (m, 2H), 1.99–1.87 (m, 1H), 1.84–1.74 (m, 1H), 1.72 (dd, *J* = 13.9, 8.4 Hz, 1H), 1.52 (dd, *J* = 14.0, 3.6 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.79 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.82, 159.75, 148.36, 129.40, 120.58, 113.99, 110.99, 60.27, 55.25, 50.67, 42.16, 34.54, 32.66, 31.46, 30.18 (3C), 14.37;

IR (film) 2951, 1732, 1608, 1486, 1365, 1256, 1159, 1043, 779, 702 cm^{-1};

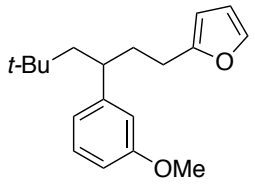
HRMS (DART) calcd for $C_{18}H_{29}O_3$ $[M+H]^+$ *m/z* = 293.2117; found 293.2121.



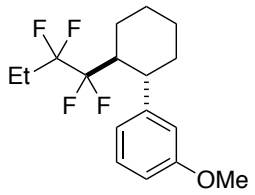
2-(3-(3-methoxyphenyl)-5,5-dimethylhexyl)pyridine (33): Compound **33** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 2-(but-3-en-1-yl)pyridine (372.9 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **33** was obtained as a colorless liquid (39.2 mg, 66% yield) after purified by flash chromatography on silica gel with CH_2Cl_2/EtOAc (20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.52 (td, *J* = 7.7, 1.9 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.05 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.00 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.80 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.75 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.71 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.80 (s, 3H), 2.72–2.57 (m, 2H), 2.52 (ddd, *J* = 13.9, 10.3, 5.4 Hz, 1H), 2.13–1.98 (m, 1H), 1.97–1.84 (m, 1H), 1.74 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.58 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.77 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.38, 159.70, 149.31, 149.17, 136.21, 129.31, 122.87, 120.92, 120.66, 114.07, 110.79, 55.24, 50.71, 42.72, 39.66, 36.72, 31.46, 30.21 (3C);
IR (film) 2950, 1586, 1474, 1433, 1363, 1255, 1149, 1047, 777, 702 cm^{-1};
HRMS (DART) calcd for $C_{20}H_{28}ON$ $[M+H]^+$ *m/z* = 298.2171; found 298.2164.



2-(3-(3-methoxyphenyl)-5,5-dimethylhexyl)furan (34): Compound **34** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 2-(but-3-en-1-yl)furan[4] (342.1 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **34** was obtained as a colorless liquid (24.6 mg, 43% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.20 (td, *J* = 7.6, 1.0 Hz, 1H), 6.78 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.75–6.67 (m, 2H), 6.25 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.98–5.84 (m, 1H), 3.81 (s, 3H), 2.62 (dddd, *J* = 9.8, 8.5, 5.0, 3.6 Hz, 1H), 2.51–2.28 (m, 2H), 2.01–1.90 (m, 1H), 1.88–1.76 (m, 1H), 1.73 (dd, *J* = 14.0, 8.5 Hz, 1H), 1.54 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.78 (s, 9H);
^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.73, 156.38, 148.97, 140.78, 129.34, 120.65, 114.09, 110.82, 110.14, 104.81, 55.28, 50.74, 42.17, 37.76, 31.47, 30.20 (3C), 26.30;
IR (film) 2951, 1608, 1486, 1364, 1260, 1148, 1047, 779, 701 cm^{-1};
HRMS (DART) calcd for $C_{19}H_{27}O_2$ $[M+H]^+$ *m/z* = 287.2011; found 287.2015.



(*trans*)-1-methoxy-3-(2-(1,1,2,2-tetrafluorobutyl)cyclohexyl)benzene (35): Compound **35** was synthesized following the general procedure (standard-scale**)**, using 1-bromo-1,1,2,2-tetrafluorobutane (41.8 mg, 0.2 mmol), cyclohexene (230 mg, 2.8 mmol) and 3-

methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). GC-MS analysis of the reaction mixture after 1h confirms formation of a single diastereoisomer. The product **35** was obtained as a colorless liquid (33.7 mg, 53% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.20 (t, *J* = 7.8 Hz, 1H), 6.80 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.76–6.74 (m, 1H), 6.73 (ddd, *J* = 8.0, 2.6, 0.9 Hz, 1H), 3.80 (s, 3H), 2.79 (td, *J* = 11.6, 3.8 Hz, 1H), 2.64–2.41 (m, 1H), 2.29 – 2.13 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.96–1.82 (m, 4H), 1.80–1.75 (m, 1H), 1.57–1.42 (m, 2H), 1.42–1.31 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.52, 148.53 (d, *J* = 2.0 Hz, 1C), 129.05, 122.69–117.78 (m, 2C), 119.79 (d, *J* = 2.4 Hz, 1C), 113.44 (d, *J* = 2.5 Hz, 1C), 110.82, 55.23, 45.03 (t, *J* = 19.2 Hz, 1C), 44.21, 37.19, 26.33, 26.16, 25.61, 24.40 (t, *J* = 23.9 Hz, 1C), 4.96 (t, *J* = 5.5 Hz, 1C);

^{19}F NMR (565 MHz, $CDCl_3$) δ = -102.51 (ddd, *J* = 273.8, 18.4, 2.7 Hz, 1F), -112.85 – -115.73 (m, 2F), -119.03 (ddd, *J* = 273.9, 19.8, 9.7 Hz, 1F);

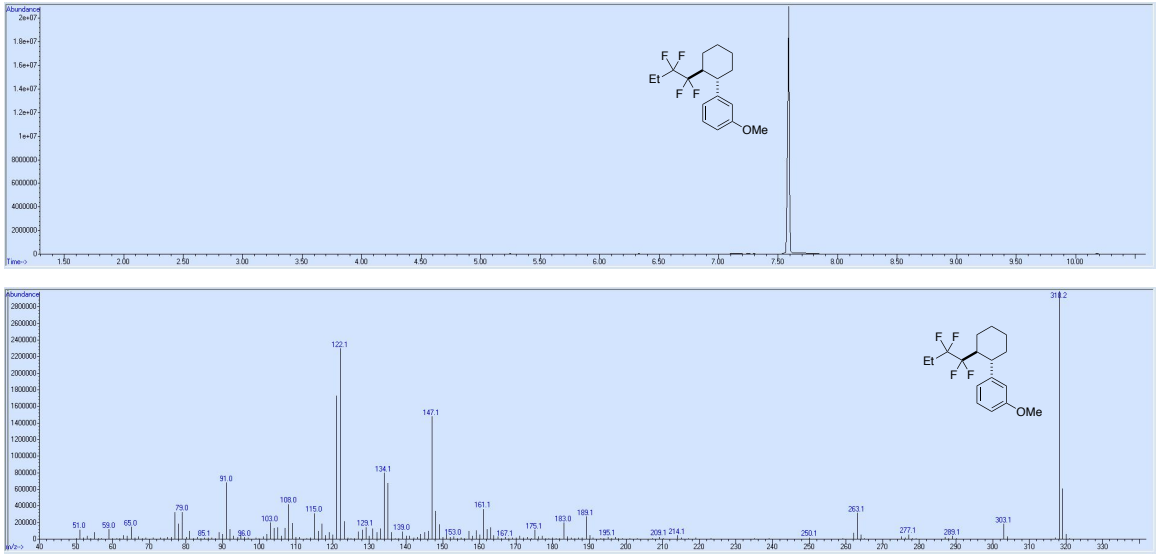
IR (film) 2933, 2857, 1585, 1452, 1260, 1152, 1047, 1003, 776, 698 cm^{-1};

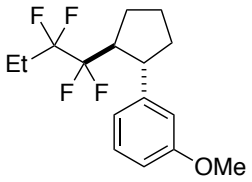
GC-MS (EI) calcd for $C_{17}H_{22}F_4O$ $[M]^+$ *m/z* = 318.16; found 318.2;

HRMS (DART) calcd for $C_{17}H_{23}F_4O$ $[M+H]^+$ *m/z* = 319.1685; found 319.1681.

This diastereomer has two methine protons which are both coupled to vicinal protons with *J* values of 3.8 and 11.6 Hz. It is consistent with the expectation for a pair of diaxial protons in the *trans* diastereomer.

GC-MS (EI):





(*trans*)-1-methoxy-3-(2-(1,1,2,2-tetrafluorobutyl)cyclopentyl)benzene (36): Compound **36** was synthesized following the general procedure (standard-scale**)**, using 1-bromo-1,1,2,2-tetrafluorobutane (41.8 mg, 0.2 mmol), cyclopentene (190.7 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). GC-MS analysis of the reaction mixture after 1h confirms formation of a single diastereoisomer. The product **36** was obtained as a colorless liquid (45 mg, 74% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.22 (t, *J* = 7.9 Hz, 1H), 6.85 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.80 (t, *J* = 2.1 Hz, 1H), 6.75 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.81 (s, 3H), 3.34 (q, *J* = 8.2 Hz, 1H), 2.84 (dp, *J* = 24.8, 8.3 Hz, 1H), 2.20–2.10 (m, 1H), 2.10–2.03 (m, 1H), 2.00–1.90 (m, 3H), 1.89–1.82 (m, 1H), 1.82–1.74 (m, 1H), 1.74–1.66 (m, 1H), 1.03 (t, *J* = 7.5 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.75, 147.82, 129.46, 122.13–118.032 (m, 2C), 119.73, 113.55, 111.15, 55.26, 48.11–47.83 (m, 1C), 45.91–45.87 (m, 1C), 36.80, 27.72–27.65 (m, 1C), 26.27, 24.15 (t, *J* = 23.8 Hz, 1C), 5.00 (t, *J* = 5.3 Hz, 1C);

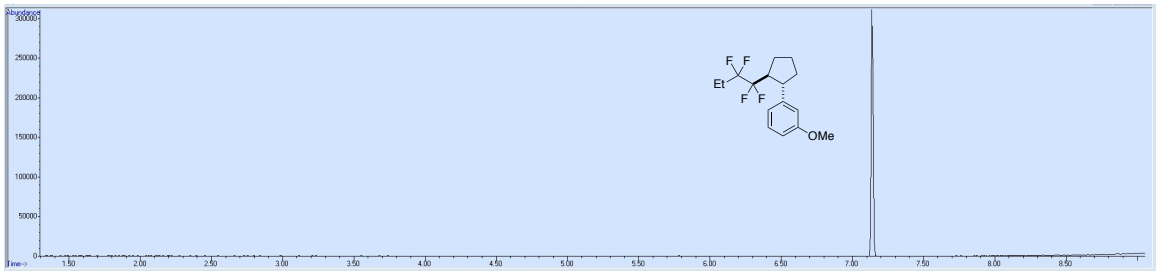
^{19}F NMR (565 MHz, $CDCl_3$) δ = -111.83 – -112.32 (m, 1F), -115.32 – -115.33 (m, 2F), -121.85 – -122.35 (m, 1F);

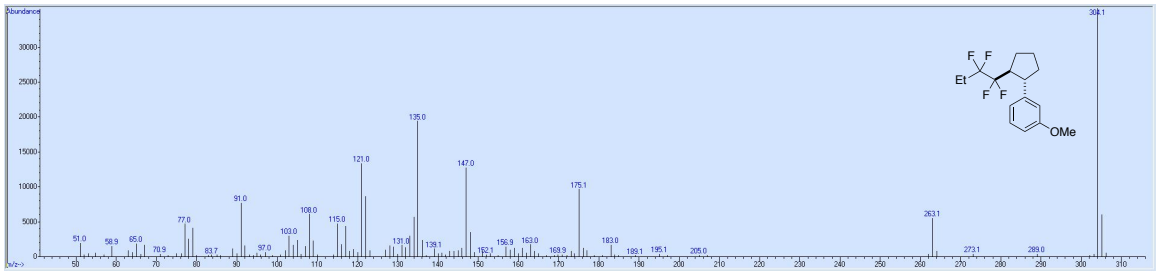
IR (film) 2954, 1585, 1454, 1264, 1156, 1049, 1003, 776, 699 cm^{-1};

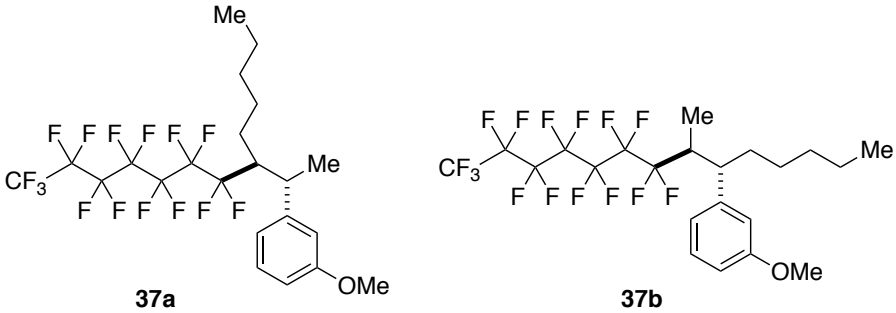
GC-MS (EI) calcd for $C_{16}H_{20}F_4O$ $[M]^+$ *m/z* = 304.14; found 304.1;

HRMS (DART) calcd for $C_{16}H_{21}F_4O$ $[M+H]^+$ *m/z* = 305.1528; found 305.1529.

GC-MS (EI):







(*trans*)-1-methoxy-3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-pentyldecan-2-yl)benzene (37a) and (*trans*)-1-methoxy-3-(8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentadecafluoro-7-methyltetradecan-6-yl)benzene (37b) (37): Mixture **37** was synthesized following the general procedure (standard-scale), using 1-bromoperfluoroheptane (89.8 mg, 0.2 mmol), (*E*)-oct-2-ene (314.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). GC-MS analysis of the reaction mixture after 1h confirms formation of a mixture diastereomers (**37a** and **37b**). The mixture **37** was obtained as a colorless liquid (54.1 mg, 46% yield, **37a**: **37b** = 1: 1.2) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27–7.23 (m, 2H), 6.85–6.83 (m, 1H), 6.82–6.80 (m, 1H), 6.80–6.75 (m, 4H), 3.82 (s, 3H), 3.81 (s, 3H), 3.44 (qd, *J* = 7.1, 2.8 Hz, 1H), 3.21 (dt, *J* = 12.2, 2.9 Hz, 1H), 2.56–2.38 (m, 2H), 1.81 (dddd, *J* = 14.0, 12.0, 10.0, 4.4 Hz, 1H), 1.69 (dddd, *J* = 13.1, 9.1, 5.9, 2.8 Hz, 1H), 1.61 (ddt, *J* = 16.0, 11.0, 5.6 Hz, 1H), 1.43 (ddt, *J* = 15.1, 10.3, 5.0 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 3H), 1.29–1.05 (m, 9H), 1.09 (d, *J* = 7.3 Hz, 3H), 1.03–0.96 (m, 2H), 0.87–0.80 (m, 3H), 0.80–0.69 (m, 4H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.92, 159.86, 145.93, 144.41, 129.61, 129.48, 120.85, 120.23, 120.02–108.50 (m, 14C), 114.80, 114.12, 111.51 (2C), 55.35, 55.32, 47.20 (t, *J* =

19.0 Hz, 1C), 42.91, 42.39 (t, J = 19.8 Hz, 1C), 36.38, 32.01, 31.70, 29.03, 27.50, 27.34, 22.72, 22.63, 22.21, 14.13, 13.94, 13.59, 7.60;

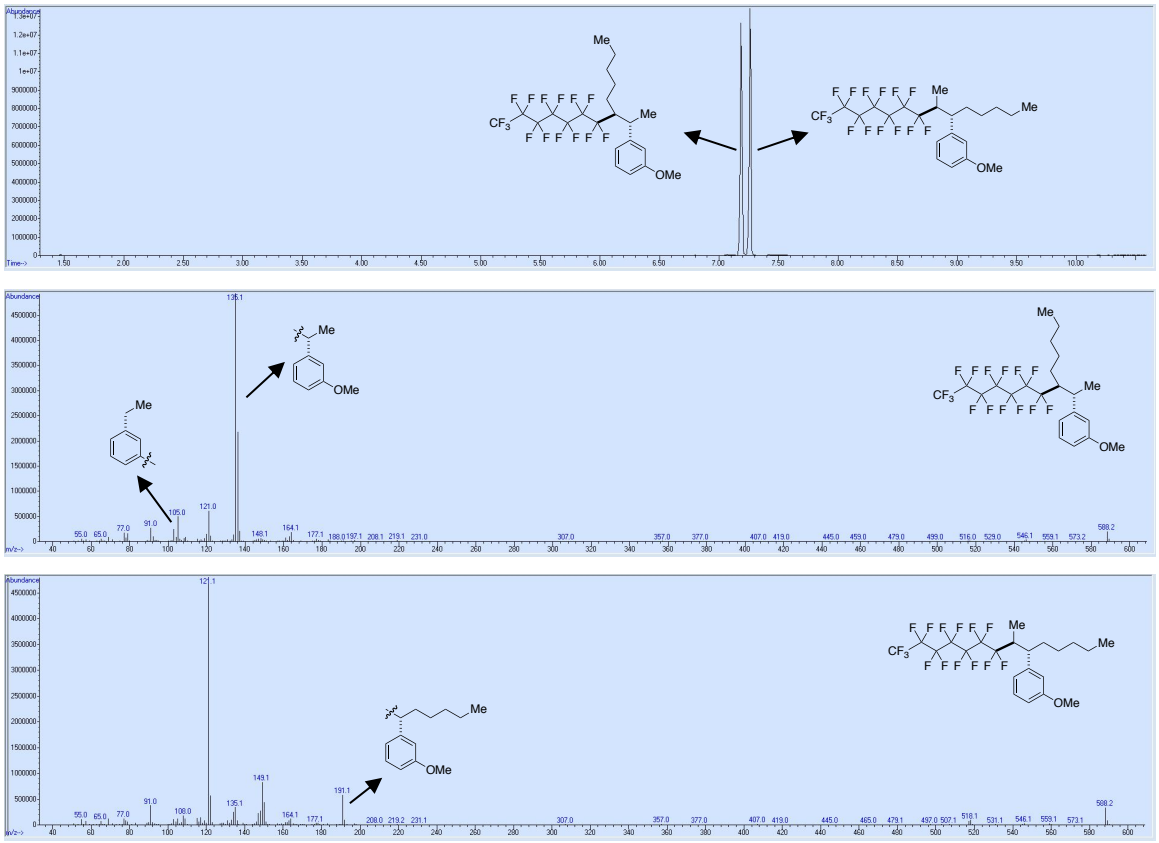
^{19}F NMR (565 MHz, $CDCl_3$) δ = -79.20 – -83.13 (m, 6F), -108.18 – -116.21 (m, 4F), -118.99 – -123.70 (m, 16F), -125.15 – -126.99 (m, 4F);

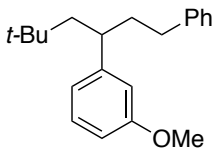
IR (film) 2959, 1586, 1491, 1467, 1238, 1201, 1147, 1051, 1051, 777, 697 cm^{-1};

GC-MS (EI) calcd for $C_{22}H_{23}F_{15}O$ $[M]^+$ m/z = 588.15; found 588.2;

HRMS (DART) calcd for $C_{22}H_{24}F_{15}O$ $[M+H]^+$ m/z = 589.1588; found 589.1579.

GC-MS (EI):

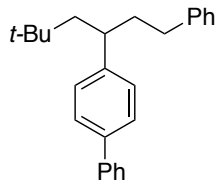




1-(5,5-dimethyl-1-phenylhexan-3-yl)-3-methoxybenzene (38): Compound **38** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The

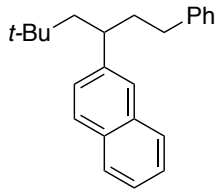
product **38** was obtained as a colorless liquid (48.6 mg, 82% yield) recovered 4-phenyl-1-butene (332 mg, 2.51 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1) to hexane/CH_2Cl_2 (10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31–7.20 (m, 3H), 7.20–7.15 (m, 1H), 7.15–7.06 (m, 2H), 6.82 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.78–6.71 (m, 2H), 3.83 (s, 3H), 2.77–2.55 (m, 1H), 2.54–2.30 (m, 2H), 2.00–1.80 (m, 2H), 1.73 (dd, *J* = 14.0, 8.5 Hz, 1H), 1.57 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.80 (s, 9H). Spectral data matched compound **4** (*vide supra*).



4-(5,5-dimethyl-1-phenylhexan-3-yl)-1,1'-biphenyl (39): Compound **39** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **39** was obtained as a colorless liquid (58.2 mg, 85% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (50:1) to hexane/CH_2Cl_2 (20:1).

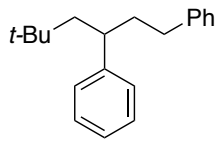
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.74–7.63 (m, 2H), 7.63–7.54 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40–7.33 (m, 1H), 7.33–7.27 (m, 4H), 7.24–7.18 (m, 1H), 7.18–7.10 (m, 2H), 2.87–2.63 (m, 1H), 2.58–2.36 (m, 2H), 2.06–1.87 (m, 2H), 1.81 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.65 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.86 (s, 9H). Spectral data matched compound **9** (*vide supra*).



2-(5,5-dimethyl-1-phenylhexan-3-yl)naphthalene (40): Compound **40** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 2-naphthylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **40** was obtained as a colorless liquid

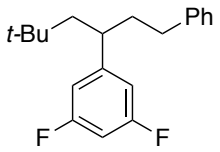
(38.6 mg, 61% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (50:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.92–7.74 (m, 3H), 7.71–7.61 (m, 1H), 7.49 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.30–7.25 (m, 2H), 7.20–7.16 (m, 1H), 7.14–7.09 (m, 2H), 2.92–2.73 (m, 1H), 2.48 (ddd, *J* = 13.9, 10.2, 6.5 Hz, 1H), 2.40 (ddd, *J* = 13.9, 10.2, 5.5 Hz, 1H), 2.08–1.92 (m, 2H), 1.87 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.66 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.82 (s, 9H). Spectral data matched compound **12** (*vide supra*).



(5,5-dimethylhexane-1,3-diyl)dibenzene (41): Compound **41** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and phenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **41** was obtained as a colorless liquid (42.1 mg, 79% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).

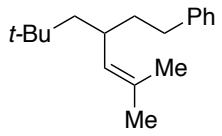
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.13 (m, 4H), 7.13–7.05 (m, 4H), 7.05–7.00 (m, 2H), 2.62–2.51 (m, 1H), 2.41–2.23 (m, 2H), 1.90–1.70 (m, 2H), 1.65 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.49 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.69 (s, 9H). Spectral data matched compound **10** (*vide supra*).



1-(5,5-dimethyl-1-phenylhexan-3-yl)-3,5-difluorobenzene (42): Compound **42** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3,5-difluorophenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The

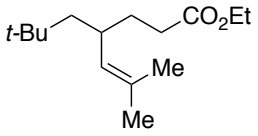
product **42** was obtained as a colorless liquid (37.5 mg, 62% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/CH_2Cl_2 (95: 5).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22–7.14 (m, 2H), 7.13–7.05 (m, 1H), 7.04–6.99 (m, 2H), 6.67–6.61 (m, 2H), 6.59–6.51 (m, 1H), 2.63–2.52 (m, 1H), 2.40–2.23 (m, 2H), 1.88–1.65 (m, 2H), 1.58 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.48 (dd, *J* = 14.0, 3.7 Hz, 1H), 0.68 (s, 9H). Spectral data matched compound **14** (*vide supra*).



(5-methyl-3-neopentylhex-4-en-1-yl)benzene (43): Compound **43** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 2-methyl-1-propenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **43** was obtained as a colorless liquid (17.6 mg, 36% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/Et_2O (99: 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30–7.23 (m, 2H), 7.21–7.12 (m, 3H), 4.91 (dp, *J* = 9.9, 1.3 Hz, 1H), 2.59 (ddd, *J* = 13.8, 10.9, 5.4 Hz, 1H), 2.48 (ddd, *J* = 13.8, 10.9, 5.7 Hz, 1H), 2.34 (dtdd, *J* = 9.8, 8.6, 4.8, 3.3 Hz, 1H), 1.70 (d, *J* = 1.5 Hz, 3H), 1.69–1.61 (m, 1H), 1.59 (d, *J* = 1.4 Hz, 3H), 1.44 (dddd, *J* = 13.3, 10.9, 8.9, 5.4 Hz, 1H), 1.30 (dd, *J* = 13.8, 3.4 Hz, 1H), 1.23 (dd, *J* = 13.8, 8.6 Hz, 1H), 0.87 (s, 9H). Spectral data matched compound **18** (*vide supra*).



ethyl 6-methyl-4-neopentylhept-5-enoate (44): Compound **44** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), ethyl 4-pentenoate (358.9 mg, 2.8 mmol) and 2-methyl-1-propenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **44** was obtained as a colorless liquid (16.8

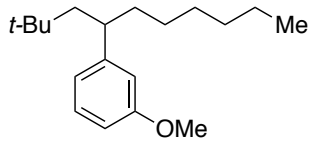
mg, 35% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100% Hexene to Hexene/Et_2O (96: 4).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.87–4.73 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.39–2.12 (m, 3H), 1.74–1.60 (m, 1H), 1.67 (d, *J* = 1.5 Hz, 3H), 1.59 (d, *J* = 1.3 Hz, 3H), 1.48–1.34 (m, 1H), 1.28–1.19 (m, 5H), 0.86 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.33, 131.29, 130.09, 60.27, 50.35, 34.49, 33.13, 32.29, 31.10, 30.31 (3C), 25.95, 18.36, 14.43;

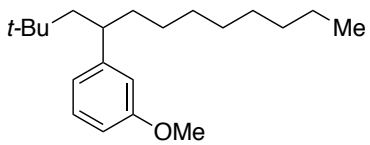
IR (film) 2953, 2865, 1737, 1446, 1364, 1155 cm^{-1};

HRMS (DART) calcd for $C_{15}H_{29}O_2$ $[M+H]^+$ *m/z* = 241.2168; found 241.2169.



1-(2,2-dimethyldecan-4-yl)-3-methoxybenzene (45): Compound **45** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 1-octene (314.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **45** was obtained as a colorless liquid (31.5 mg, 57% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

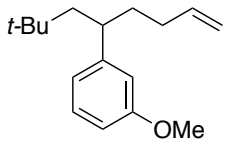
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.77(dt, *J* = 7.5, 1.2 Hz, 1H), 6.70 (t, *J* = 2.1 Hz, 1H), 6.72 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.81 (s, 3H), 2.57 (tdd, *J* = 8.9, 5.6, 3.4 Hz, 1H), 1.68 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.62–1.43 (m, 3H), 1.28–1.15 (m, 6H), 1.17–1.09 (m, 1H), 1.08–0.98 (m, 1H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.79 (s, 9H). Spectral data matched compound **19** (*vide supra*).



1-(2,2-dimethyldodecan-4-yl)-3-methoxybenzene (46): Compound **46** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2

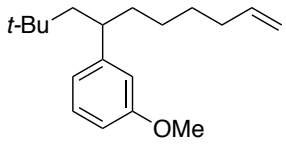
mmol), 1-dectene (392.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **46** was obtained as a colorless liquid (35.3 mg, 58% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.72 (t, *J* = 2.1 Hz, 1H), 6.70 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.80 (s, 3H), 2.56 (tdd, *J* = 8.9, 5.5, 3.3 Hz, 1H), 1.68 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.58–1.44 (m, 3H), 1.28–1.16 (m, 10H), 1.16–1.09 (m, 1H), 1.09–0.98 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.79 (s, 9H). Spectral data matched compound **20** (*vide supra*).



1-(2,2-dimethyloct-7-en-4-yl)-3-methoxybenzene (47): Compound **47** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 1,5-hexadiene (300 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **47** was obtained as a colorless liquid (37.8 mg, 77% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (40:1) to hexane/CH_2Cl_2 (20:1).

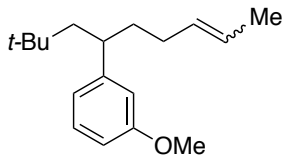
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.75–6.67 (m, 2H), 5.76 (ddt, *J* = 17.0, 10.1, 6.5 Hz, 1H), 5.04–4.82 (m, 2H), 3.80 (s, 3H), 2.61 (tdd, *J* = 9.0, 5.5, 3.4 Hz, 1H), 1.93–1.77 (m, 2H), 1.70 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.67–1.56 (m, 2H), 1.52 (dd, *J* = 14.0, 3.5 Hz, 1H), 0.78 (s, 9H). Spectral data matched compound **21** (*vide supra*).



1-(2,2-dimethyldec-9-en-4-yl)-3-methoxybenzene (48): Compound **48** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 1,7-octadiene (308.6 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide

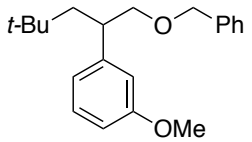
(0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **48** was obtained as a colorless liquid (44.4 mg, 81% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (50:1) to hexane/CH_2Cl_2 (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.74 (t, *J* = 2.1 Hz, 1H), 6.72 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 5.79 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.15–4.73 (m, 2H), 3.80 (s, 3H), 2.58 (tdd, *J* = 8.9, 5.6, 3.4 Hz, 1H), 1.98 (dtdd, *J* = 7.8, 6.4, 2.7, 1.3 Hz, 2H), 1.70 (dd, *J* = 14.0, 8.7 Hz, 1H), 1.65–1.47 (m, 3H), 1.41–1.27 (m, 2H), 1.25–1.15 (m, 1H), 1.13–1.02 (m, 1H), 0.81 (s, 9H). Spectral data matched compound **22** (*vide supra*).



1-(2,2-dimethylnon-7-en-4-yl)-3-methoxybenzene (49): Compound **49** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), 1,5-heptadiene, mixture of *cis* and *trans* (269.3 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **49** was obtained as a colorless liquid (29.7 mg, 57% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

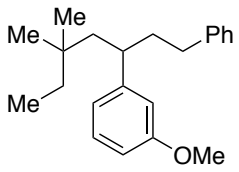
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.24–7.08 (m, 1H, major + minor), 6.86–6.74 (m, 1H, major + minor), 6.73–6.64 (m, 2H, major + minor), 5.47–5.29 (m, 2H, major + minor), 3.81–3.80 (m, 3H, major + minor), 2.72–2.49 (m, 1H, major + minor), 1.99–1.70 (m, 2H, major + minor), 1.70–1.65 (m, 1H, major + minor), 1.64–1.43 (m, 6H, major + minor), 0.79–0.78 (m, 9H, major + minor). Spectral data matched compound **24** (*vide supra*).



1-(1-(benzyloxy)-4,4-dimethylpentan-2-yl)-3-methoxybenzene (50): Compound **50** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), allyl benzyl ether (415 mg, 2.8 mmol) and 3-

methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **50** was obtained as a colorless liquid (31.8 mg, 51% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (3:1) to hexane/CH_2Cl_2 (3:2).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.35–7.30 (m, 2H), 7.30–7.24 (m, 3H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.86 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.81 (t, *J* = 2.1 Hz, 1H), 6.77 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 4.53–4.45 (m, 2H), 3.81 (s, 3H), 3.50 (qd, *J* = 9.2, 7.0 Hz, 2H), 3.01 (dtd, *J* = 8.4, 7.1, 3.5 Hz, 1H), 1.72 (dd, *J* = 14.0, 3.5 Hz, 1H), 1.68 (dd, *J* = 14.0, 8.6 Hz, 1H), 0.84 (s, 9H). Spectral data matched compound **26** (*vide supra*).



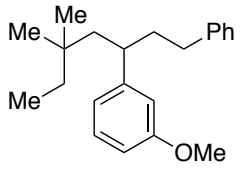
1-(5,5-dimethyl-1-phenylheptan-3-yl)-3-methoxybenzene (51): Compound **51** was synthesized following the general procedure (standard-scale**)**, using 2-iodo-2-methylbutane (39.6 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **51** was obtained as a colorless liquid (39.1 mg, 63% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (4:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30–7.25 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.19–7.15 (m, 1H), 7.15–7.10 (m, 2H), 6.82 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.77 (t, *J* = 2.0 Hz, 1H), 6.75 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.83 (s, 3H), 2.64 (tdd, *J* = 8.7, 5.0, 3.5 Hz, 1H), 2.49–2.34 (m, 2H), 1.98–1.81 (m, 2H), 1.72 (dd, *J* = 14.1, 8.4 Hz, 1H), 1.55 (dd, *J* = 14.1, 3.5 Hz, 1H), 1.25–1.10 (m, 2H), 0.76–0.73 (m, 6H), 0.72 (s, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.73, 149.50, 142.73, 129.28, 128.50 (2C), 128.33 (2C), 125.70, 120.68, 114.10, 110.77, 55.28, 48.48, 42.03, 41.62, 34.93, 34.14, 33.97, 27.41, 27.29, 8.52;

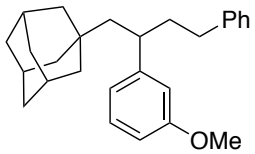
IR (film) 2958, 1599, 1486, 1453, 1262, 1158, 1048, 777, 749, 699 cm^{-1};

HRMS (DART) calcd for $C_{22}H_{31}O$ $[M+H]^+$ *m/z* = 311.2375; found 311.2385.



1-(5,5-dimethyl-1-phenylheptan-3-yl)-3-methoxybenzene (52): Compound **52** was synthesized following the general procedure (standard-scale**)**, using 2-bromo-2-methylbutane (30.2 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **52** was obtained as a colorless liquid (37.9 mg, 61% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (4:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29–7.26 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.19–7.16 (m, 1H), 7.15–7.11(m, 2H), 6.82 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.77 (t, *J* = 2.0 Hz, 1H), 6.75 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.82 (s, 3H), 2.64 (tdd, *J* = 8.7, 5.0, 3.4 Hz, 1H), 2.47–2.34 (m, 2H), 1.96–1.82 (m, 2H), 1.71 (dd, *J* = 14.0, 8.4 Hz, 1H), 1.55 (dd, *J* = 14.0, 3.5 Hz, 1H), 1.23–1.11 (m, 2H), 0.77–0.73 (m, 6H), 0.72 (s, 3H). Spectral data matched compound **51** (*vide supra*).



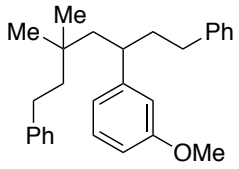
1-(2-(3-methoxyphenyl)-4-phenylbutyl)adamantine (53): Compound **53** was synthesized following the general procedure (standard-scale**)**, using 1-iodoadamantane (52.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **53** was obtained as a colorless liquid (23.2 mg, 31% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27–7.23 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.18–7.13 (m, 1H), 7.13–7.06 (m, 2H), 6.81 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.76 (t, *J* = 2.0 Hz, 1H), 6.73 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.82 (s, 3H), 2.76–2.64 (m, 1H), 2.52–2.29 (m, 2H), 1.99–1.73 (m, 5H), 1.70–1.49 (m, 7H), 1.44–1.30 (m, 7H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.69, 149.82, 142.78, 129.27, 128.51 (2C), 128.33 (2C), 125.69, 120.62, 114.00, 110.67, 55.30, 51.82, 43.13 (3C), 41.71, 40.47, 37.24 (3C), 34.14, 33.52, 28.86 (3C);

IR (film) 3025, 2899, 2845, 1600, 1486, 1451, 1254, 1047, 699 cm^{-1};

HRMS (DART) calcd for $C_{27}H_{35}O$ $[M+H]^+$ *m/z* = 375.2688; found 375.2684.



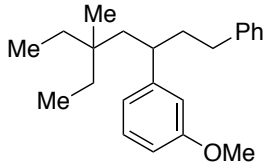
(5-(3-methoxyphenyl)-3,3-dimethylheptane-1,7-diyl)dibenzene (54): Compound **54** was synthesized following the general procedure (standard-scale), using (3-bromo-3-methylbutyl)benzene (45.4 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **54** was obtained as a colorless liquid (33.2 mg, 43% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (6.5:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27–7.23 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.18–7.13 (m, 1H), 7.13–7.06 (m, 2H), 6.81 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.76 (t, *J* = 2.0 Hz, 1H), 6.73 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.82 (s, 3H), 2.76–2.64 (m, 1H), 2.52–2.29 (m, 2H), 1.99–1.73 (m, 5H), 1.70–1.49 (m, 7H), 1.44–1.30 (m, 7H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.82, 149.23, 143.54, 142.61, 129.43, 128.53 (2C), 128.42 (2C), 128.37 (2C), 128.35 (2C), 125.75, 125.58, 120.74, 114.21, 110.89, 55.30, 48.51, 44.75, 41.98, 41.64, 34.18, 34.06, 30.82, 28.20, 28.06;

IR (film) 3025, 2930, 2859, 1601, 1487, 1453, 1261, 1156, 1050, 738, 698 cm^{-1};

HRMS (DART) calcd for $C_{28}H_{35}O$ $[M+H]^+$ *m/z* = 387.2688; found 387.2682.



1-(5-ethyl-5-methyl-1-phenylheptan-3-yl)-3-methoxybenzene (55): Compound **55** was synthesized following the general procedure (standard-scale), using 3-bromo-3-

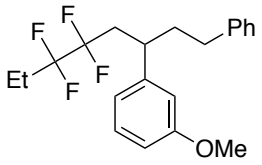
methylpentane (33 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **55** was obtained as a colorless liquid (24 mg, 37% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (4:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29–7.23 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.18–7.14 (m, 1H), 7.13–7.08 (m, 2H), 6.81 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.76 (t, *J* = 2.1 Hz, 1H), 6.73 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.82 (s, 3H), 2.60 (dddd, *J* = 9.7, 8.4, 5.0, 3.4 Hz, 1H), 2.46–2.28 (m, 2H), 1.97–1.79 (m, 2H), 1.70 (dd, *J* = 14.3, 8.3 Hz, 1H), 1.51 (dd, *J* = 14.3, 3.4 Hz, 1H), 1.22–1.05 (m, 4H), 0.67 (dt, *J* = 14.9, 7.5 Hz, 6H), 0.64 (s, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.69, 149.53, 142.74, 129.25, 128.49 (2C), 128.33 (2C), 125.70, 120.73, 114.10, 110.78, 55.30, 45.76, 41.68, 41.61, 36.30, 34.16, 31.51, 31.32, 24.66, 8.07 (2C);

IR (film) 3025, 2961, 2924, 1600, 1486, 1453, 1259, 1158, 1050, 777, 748, 699 cm^{-1};

HRMS (DART) calcd for $C_{23}H_{33}O$ $[M+H]^+$ *m/z* = 325.2531; found 325.2528.

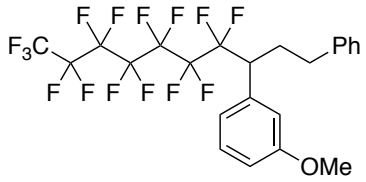


1-methoxy-3-(5,5,6,6-tetrafluoro-1-phenyloctan-3-yl)benzene (56): Compound **56** was synthesized following the general procedure (standard-scale**)**, using 1-bromo-1,1,2,2-tetrafluorobutane (41.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **56** was obtained as a colorless liquid (64.1 mg, 87% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (4:1).

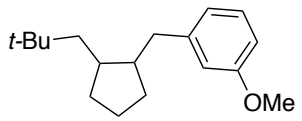
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.34–7.27 (m, 3H), 7.23–7.18 (m, 1H), 7.17–7.11 (m, 2H), 6.89–6.84 (m, 1H), 6.84–6.78 (m, 2H), 3.85 (s, 3H), 3.22–2.95 (m, 1H), 2.48 (dd, *J* = 9.2, 6.6 Hz, 2H), 2.44–2.29 (m, 2H), 2.23–2.11 (m, 1H), 2.09–1.87 (m, 3H), 1.09 (td, *J* = 7.5, 1.8 Hz, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.91, 146.22, 142.00, 129.67, 128.48 (2C), 128.44 (2C), 125.93, 121.23–117.37 (m, 2C), 120.01, 113.78, 111.62, 55.28, 38.73, 38.61, 38.59, 36.69 (t, *J* = 21.7 Hz, 1C), 33.66, 23.40 (t, *J* = 23.7 Hz, 1C), 4.98 (t, *J* = 5.2 Hz, 1C);

^{19}F NMR (565 MHz, $CDCl_3$) δ = -113.62 – -113.69 (m, 2F), -117.05 – -118.03 (m, 2F);
IR (film) 3002, 2949, 1712, 1601, 1488, 1437, 1360, 1220, 1172, 1089, 1046, 1002, 919, 734, 700 cm^{-1};
HRMS (DART) calcd for $C_{21}H_{25}OF_4$ $[M+H]^+$ *m/z* = 369.1842; found 369.1841.



1-methoxy-3-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-1-phenyldecan-3-yl)benzene (57): Compound **57** was synthesized following the general procedure (standard-scale**)**, using 1-bromoperfluoroheptane (89.8 mg, 0.2 mmol), 4-phenyl-1-butene (370.2 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **57** was obtained as a colorless liquid (91.5 mg, 77% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (4:1).
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.38–7.27 (m, 3H), 7.24–7.19 (m, 1H), 7.17–7.10 (m, 2H), 6.85 (dd, *J* = 8.2, 2.8 Hz, 2H), 6.80 (t, *J* = 2.1 Hz, 1H), 3.85 (s, 3H), 3.18–3.02 (m, 1H), 2.69–2.30 (m, 4H), 2.23–2.11 (m, 1H), 2.03 (dtd, *J* = 13.5, 9.7, 5.7 Hz, 1H);
^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.11, 145.23, 141.66, 129.93, 128.54 (2C), 128.49 (2C), 126.10, 120.45–108.50 (m, 7C), 119.88, 113.81, 111.93, 55.29, 38.63, 38.36, 37.55 (t, *J* = 21.0 Hz, 1C), 33.58;
^{19}F NMR (565 MHz, $CDCl_3$) δ = -80.84 (td, *J* = 10.0, 5.0 Hz, 3F), -109.44 – -115.34 (m, 2F), -121.65 (ddt, *J* = 22.9, 15.1, 7.6 Hz, 2F), -121.93 – -122.52 (m, 2F), -122.53 – -123.01 (m, 2F), -123.57 (tt, *J* = 13.5, 5.3 Hz, 2F), -126.17 (ddd, *J* = 21.9, 10.9, 5.2 Hz, 2F);
IR (film) 2942, 1715, 1602, 1489, 1362, 1208, 1146, 1047, 699 cm^{-1};
HRMS (DART) calcd for $C_{24}H_{20}OF_{15}$ $[M+H]^+$ *m/z* = 609.1275; found 609.1257.



1-methoxy-3-((2-neopentylcyclopentyl)methyl)benzene (58): Compound **58** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8

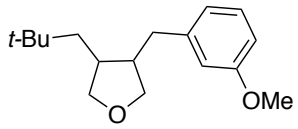
mg, 0.2 mmol), 1,6-heptadiene (269.3 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The mixture products of **58** (71% yield, dr = 4: 1, 37 mg) and **59** (acyclic/arylation, 9% yield, 4.7 mg) were obtained as a colorless liquid (determined by ^{1}H NMR and GC-MS) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (10:1). The purity product **58** was obtained as a colorless liquid after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100 % hexene to hexene/Et_2O (98:2).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.21–7.14 (m, 1H, major + minor), 6.79–6.73 (m, 1H, major + minor), 6.73–6.68 (m, 2H, major + minor), 3.80 (s, 3H, major + minor), 2.88–2.72 (m, 1H, major + minor), 2.28–1.92 (m, 3H, major + minor), 1.84–1.54 (m, 3H, major + minor), 1.54–1.33 (m, 4H, major + minor), 1.18–1.12 (m, 1H, major + minor), 0.93–0.90 (m, 9H, major + minor);

58 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.67, 144.38, 129.17, 121.68, 115.03, 110.79, 55.28, 45.79, 44.25, 39.88, 34.97, 32.31, 31.14, 30.37 (3C), 29.57, 22.15;

IR (film) 2949, 2867, 1601, 1489, 1363, 1260, 1152, 1049, 772, 696 cm^{-1};

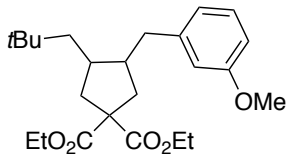
HRMS (DART) calcd for $C_{18}H_{29}O$ $[M+H]^+$ *m/z* = 261.2218; found 261.2214.



3-(3-methoxybenzyl)-4-neopentyltetrahydrofuran (60): Compound **60** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **60** was obtained as a colorless liquid (49.8 mg, dr = 4.7: 1, 95% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:1) to hexane/EtOAc (8:1).

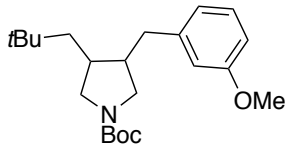
(*cis*)-60 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.20 (t, *J* = 7.8 Hz, 1H), 6.78–6.72 (m, 3H), 4.02 (t, *J* = 7.8 Hz, 1H), 3.79 (s, 3H), 3.63 (ddd, *J* = 8.5, 5.0, 1.0 Hz, 1H), 3.59 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.50 (t, *J* = 8.3 Hz, 1H), 2.81 (dd, *J* = 13.1, 3.4 Hz, 1H), 2.44–2.33 (m, 3H), 1.61 (dd, *J* = 14.0, 3.7 Hz, 1H), 1.27 (dd, *J* = 13.9, 8.3 Hz, 1H), 0.94 (s, 9H);

(*trans*)-60 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.19 (t, *J* = 7.9 Hz, 1H), 6.78–6.70 (m, 3H), 4.13 (t, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.77 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.44 (dd, *J* = 8.5, 7.8 Hz, 1H), 3.37 (t, *J* = 8.3 Hz, 1H), 2.86 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.48 (dd, *J* = 13.7, 9.8 Hz, 1H), 2.11–2.00 (m, 1H), 1.89 (dqd, *J* = 10.4, 8.1, 2.5 Hz, 1H), 1.52 (dd, *J* = 13.9, 2.4 Hz, 1H), 1.24 (dd, *J* = 14.0, 9.0 Hz, 1H), 0.88 (s, 9H);
(*cis*)-60 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.81, 142.79, 129.45, 121.52, 114.89, 111.34, 73.45, 71.60, 55.24, 44.93, 41.74, 39.00, 33.31, 30.87, 30.07 (3C);
(*trans*)-60 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.79, 142.32, 129.48, 121.17, 114.63, 111.40, 75.60, 72.55, 48.49, 47.72, 42.22, 38.74, 33.29, 30.79, 30.01 (3C);
IR (film) 2863, 1601, 1488, 1364, 1260, 1152, 1047, 906, 776, 696 cm^{-1};
HRMS (DART) calcd for $C_{17}H_{27}O_2$ $[M+H]^+$ *m/z* = 263.2011; found 263.2003.



diethyl 3-(3-methoxybenzyl)-4-neopentylcyclopentane-1,1-dicarboxylate (62): Compound **62** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), diethyl diallylmalonate (672.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **62** was obtained as a colorless liquid (41.2 mg, dr = 18: 1, 51% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution hexene/Et_2O (99:1) to hexene/Et_2O (85:15);
(*cis*)-62 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.18 (t, *J* = 7.8 Hz, 1H), 6.78 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.75 (t, *J* = 2.0 Hz, 1H), 6.72 (ddd, *J* = 8.1, 2.7, 0.9 Hz, 1H), 4.27–4.08 (m, 4H), 3.80 (s, 3H), 2.74 (dd, *J* = 12.4, 3.0 Hz, 1H), 2.47 (dd, *J* = 12.9, 6.1 Hz, 1H), 2.37–1.98 (m, 6H), 1.53 (dd, *J* = 14.0, 3.9 Hz, 1H), 1.27–1.18 (m, 7H), 0.94 (s, 9H);
(*cis*)-62 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 173.30, 173.24, 159.71, 143.22, 129.28, 121.77, 115.15, 111.10, 61.49, 61.44, 58.85, 55.27, 45.50, 43.40, 40.81, 39.53, 37.60, 34.56, 31.07, 30.27 (3C), 14.22, 14.18;
(*cis*)-62 (major): **IR (film)** 2951, 1728, 1601, 1489, 1364, 1255, 1153, 1106, 1052 cm^{-1};
(*cis*)-62 (major): **HRMS (DART)** calcd for $C_{24}H_{37}O_5$ $[M+H]^+$ *m/z* = 405.2641; found

405.2645.



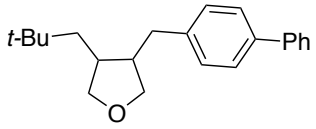
***tert*-butyl 3-(3-methoxybenzyl)-4-neopentylpyrrolidine-1-carboxylate (64):** Compound **64** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), *tert*-butyl N,N-diallylcarbamate (552.4 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **64** was obtained as a colorless liquid (41.2 mg, dr = 1.6: 1, 57% yield) and recovered *tert*-butyl N,N-diallylcarbamate (497 mg, 2.52 mmol) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (2:1) to hexane/EtOAc (20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.23–7.11 (m, 1H), 6.82–6.58 (m, 3H), 3.86–3.43 (m, 4H), 3.44–2.71 (m, 4H), 2.45–2.16 (m, 2H), 2.06–1.75 (m, 1H), 1.65–1.51 (m, 1H), 1.49–1.35 (m, 9H), 1.32–1.15 (m, 1H), 1.02–0.84 (m, 9H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.85, 155.12, 154.96, 154.54, 154.46, 142.57, 142.34, 142.08, 141.90, 129.53, 129.49, 121.59, 121.18, 115.03, 114.94, 114.62, 111.57, 111.45, 111.44, 111.39, 79.12, 79.09, 55.30, 55.27, 54.00, 53.60, 51.83, 51.18, 50.85, 50.67, 49.59, 49.40, 47.12, 46.50, 44.59, 43.81, 42.52, 42.06, 40.98, 40.17, 38.41, 38.37, 38.32, 37.76, 33.52, 33.31, 30.92, 30.81, 30.10, 28.71, 28.67;

IR (film) 2951, 2866, 1693, 1601, 1453, 1403, 1364, 1261, 1168, 1125, 1048, 773 cm^{-1};

HRMS (DART) calcd for $C_{22}H_{36}O_3N$ $[M+H]^+$ *m/z* = 362.2695; found 362.2683.



3-([1,1'-biphenyl]-4-ylmethyl)-4-neopentyltetrahydrofuran (66): Compound **66** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **66** was obtained as a white solid (59.2 mg, dr = 4.8: 1, 96% yield) after purified by flash chromatography on silica gel with

hexane/CH_2Cl_2 (1:1) to hexane/EtOAc (6:1).

mp: 72-73 °C;

(*cis*)-66 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.64–7.58 (m, 2H), 7.57–7.53 (m, 2H), 7.48–7.42 (m, 2H), 7.37–7.33 (m, 1H), 7.29–7.26 (m, 2H), 4.06 (t, *J* = 7.8 Hz, 1H), 3.71–3.64 (m, 2H), 3.55 (t, *J* = 8.4 Hz, 1H), 2.93–2.84 (m, 1H), 2.52–2.36 (m, 3H), 1.67 (dd, *J* = 14.0, 3.7 Hz, 1H), 1.32 (dd, *J* = 14.0, 8.3 Hz, 1H), 0.98 (s, 9H);

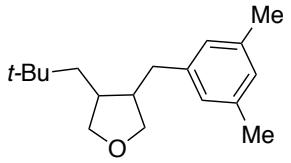
(*trans*)-66 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.63–7.58 (m, 2H), 7.55–7.51 (m, 2H), 7.48–7.42 (m, 2H), 7.37–7.32 (m, 1H), 7.26–7.22 (m, 2H), 4.18 (dd, *J* = 8.4, 7.7 Hz, 1H), 3.83 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.51 (dd, *J* = 8.5, 7.7 Hz, 1H), 3.41 (t, *J* = 8.3 Hz, 1H), 2.95 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.58 (dd, *J* = 13.8, 9.7 Hz, 1H), 2.11 (dqd, *J* = 9.7, 7.7, 5.0 Hz, 1H), 1.95 (dqd, *J* = 10.3, 8.0, 2.5 Hz, 1H), 1.57 (dd, *J* = 13.9, 2.5 Hz, 1H), 1.29 (dd, *J* = 13.9, 9.7 Hz, 1H), 0.91 (s, 9H);

(*cis*)-66 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 141.07, 140.27, 139.01, 129.53 (2C), 128.84 (2C), 127.24 (2C), 127.18, 127.08 (2C), 73.49, 71.61, 45.04, 41.79, 39.04, 32.89, 30.90, 30.10 (3C);

(*trans*)-66 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 141.07, 139.79, 139.17, 129.20 (2C), 128.84 (2C), 127.24 (2C), 127.20, 127.08 (2C), 75.63, 72.56, 48.58, 47.76, 42.23, 38.32, 30.82, 30.03 (3C);

IR (film) 3029, 2953, 2862, 1488, 1362, 1057, 757, 692 cm^{-1};

HRMS (DART) calcd for $C_{22}H_{29}O$ $[M+H]^+$ *m/z* = 309.2218; found 309.2214.



3-(3,5-dimethylbenzyl)-4-neopentyltetrahydrofuran (67): Compound **67** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 3,5-dimethylphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **67** was obtained as a colorless liquid (47.4 mg, dr = 4.7: 1, 91% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (5:1) to hexane/EtOAc (30:1).

(*cis*)-67 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 6.87–6.79 (m, 3H), 4.02 (t, *J* = 7.7 Hz, 1H), 3.67–3.56 (m, 2H), 3.51 (t, *J* = 8.2 Hz, 1H), 2.77 (dd, *J* = 13.2, 3.3 Hz, 1H), 2.40–2.34 (m, 2H), 2.33–2.23 (m, 1H), 2.30 (s, 6H), 1.63 (dd, *J* = 13.9, 3.4 Hz, 1H), 1.27 (dd, *J* = 14.0, 8.0 Hz, 1H), 0.96 (s, 9H);

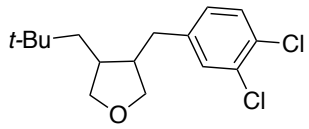
(*trans*)-67 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 6.84 (s, 1H), 6.78 (s, 2H), 4.14 (t, *J* = 8.0 Hz, 1H), 3.78 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.45 (t, *J* = 8.2 Hz, 1H), 3.37 (t, *J* = 8.3 Hz, 1H), 2.83 (dd, *J* = 13.7, 4.8 Hz, 1H), 2.44 (dd, *J* = 13.7, 9.8 Hz, 1H), 2.30 (s, 6H), 2.04 (dqd, *J* = 9.8, 7.8, 4.8 Hz, 1H), 1.89 (dqd, *J* = 10.4, 8.1, 2.4 Hz, 1H), 1.54 (dd, *J* = 13.9, 2.4 Hz, 1H), 1.25 (dd, *J* = 13.8, 9.7 Hz, 1H), 0.89 (s, 9H);

(*cis*)-67 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 141.06, 137.95, 127.66 (2C), 127.02 (2C), 73.48, 71.61, 45.10, 41.76, 39.05, 33.00, 30.89, 30.10 (3C), 21.38 (2C);

(*trans*)-67 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 140.59, 137.95, 127.78 (2C), 126.65 (2C), 75.64, 72.60, 48.56, 47.71, 42.20, 38.44, 30.83, 30.04 (3C), 21.38 (2C);

IR (film) 3013, 2950, 2862, 1606, 1467, 1363, 1058, 909, 855 cm^{-1};

HRMS (DART) calcd for $C_{18}H_{29}O$ $[M+H]^+$ *m/z* = 261.2218; found 261.2218.



3-(3,4-dichlorobenzyl)-4-neopentyltetrahydrofuran (68): Compound **68** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 3,4-dichlorophenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **68** was obtained as a colorless liquid (56.6 mg, dr = 5.0: 1, 94% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (5:1) to hexane/EtOAc (10:1).

(*cis*)-68 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.01 (t, *J* = 7.8 Hz, 1H), 3.65–3.58 (m, 1H), 3.51 (dd, *J* = 8.6, 2.0 Hz, 1H), 3.47 (t, *J* = 8.4 Hz, 1H), 2.80–2.72 (m, 1H), 2.42–2.27 (m, 3H), 1.56 (dd, *J* = 14.0, 3.6 Hz, 1H), 1.25 (dd, *J* = 13.9, 8.5 Hz, 1H), 0.93 (s, 9H);

(*trans*)-68 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.34 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 6.98 (dd, *J* = 10.2, 2.1 Hz, 1H), 4.12 (dd, *J* = 8.5, 7.6 Hz, 1H), 3.74 (dd, *J* =

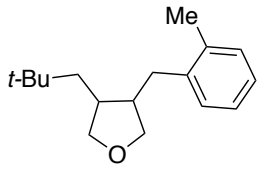
8.6, 7.3 Hz, 1H), 3.39 (dd, *J* = 8.6, 7.6 Hz, 1H), 3.36 (t, *J* = 8.3 Hz, 1H), 2.83 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.46 (dd, *J* = 13.9, 9.8 Hz, 1H), 2.00 (dqd, *J* = 9.7, 7.6, 5.0 Hz, 1H), 1.86 (dqd, *J* = 10.3, 8.0, 2.5 Hz, 1H), 1.48 (dd, *J* = 13.9, 2.5 Hz, 1H), 1.25 (dd, *J* = 13.9, 8.5 Hz, 7H), 0.86 (s, 9H);

(*cis*)-68 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 141.45, 132.47, 130.97, 130.44, 130.11, 128.57, 73.35, 71.23, 44.85, 41.90, 38.94, 32.43, 30.88, 30.06 (3C);

(*trans*)-68 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 140.96, 132.47, 130.68, 130.46, 130.25, 128.19, 75.56, 72.20, 48.35, 47.74, 42.15, 37.83, 30.82, 29.99 (3C);

IR (film) 2952, 2863, 1471, 1394, 1364, 1131, 1057, 1031, 909, 807 cm^{-1};

HRMS (DART) calcd for $C_{16}H_{23}OCl_2$ $[M+H]^+$ *m/z* = 301.1126; found 301.1126.



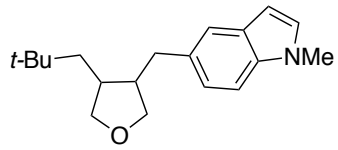
3-(2-methylbenzyl)-4-neopentyltetrahydrofuran (69): Compound **69** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 2-methylphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **69** was obtained as a colorless liquid (25.1 mg, dr = 6.7: 1, 51% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (5:1) to hexane/Et_2O (30:1) to hexane/Et_2O (10:1).

(*cis*)-69 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.17–7.08 (m, 4H), 4.05 (t, *J* = 7.8 Hz, 1H), 3.62–3.57 (m, 2H), 3.57–3.53 (m, 1H), 2.78 (dd, *J* = 13.0, 2.9 Hz, 1H), 2.49–2.38 (m, 3H), 2.33 (s, 3H), 1.65 (dd, *J* = 14.0, 3.6 Hz, 1H), 1.32 (dd, *J* = 13.9, 8.4 Hz, 1H), 0.96 (s, 9H);

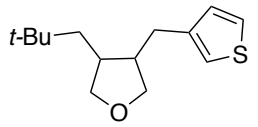
(*trans*)-69 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.20–7.06 (m, 4H), 4.16 (t, *J* = 8.0 Hz, 1H), 3.77 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.46 (dd, *J* = 8.5, 7.6 Hz, 1H), 3.38 (t, *J* = 8.3 Hz, 1H), 2.89 (dd, *J* = 14.0, 4.9 Hz, 1H), 2.52 (dd, *J* = 14.0, 9.9 Hz, 1H), 2.33 (s, 3H), 2.07 (dtd, *J* = 9.8, 4.9, 2.1 Hz, 1H), 1.97–1.90 (m, 1H), 1.52 (dd, *J* = 13.9, 2.5 Hz, 1H), 1.25 (dd, *J* = 13.9, 9.7 Hz, 2H), 0.88 (s, 9H);

(*cis*)-69 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 139.22, 136.41, 130.46, 129.80, 126.20, 126.02, 73.38, 71.37, 43.71, 42.00, 39.21, 30.87, 30.12, 30.10 (3C), 19.67;

(*trans*)-69 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 138.94, 135.94, 130.46, 129.30, 126.35, 126.07, 75.62, 72.68, 47.79, 47.10, 42.48, 36.02, 30.82, 30.04 (3C), 19.61;
IR (film) 3016, 2952, 2863, 1480, 1466, 1364, 1058, 909, 742 cm^{-1};
HRMS (DART) calcd for $C_{17}H_{27}O$ $[M+H]^+$ *m/z* = 247.2062; found 247.2068.



1-methyl-5-((4-neopentyltetrahydrofuran-3-yl)methyl)-1*H*-indole (70): Compound **70** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and N-methylindole-5-magnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **70** was obtained as a colorless liquid (27.4 mg, dr = 4.6: 1, 48% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:1) to hexane/EtOAc (8:1).
(*cis*)-70 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.43 (d, *J* = 1.6 Hz, 1H), 7.30–7.25 (m, 1H), 7.07–6.99 (m, 2H), 6.45–6.35 (m, 1H), 4.04 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.67 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.61 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.57–3.52 (m, 1H), 3.00–2.93 (m, 1H), 2.50–2.43 (m, 2H), 2.42–2.36 (m, 1H), 1.70 (dd, *J* = 14.0, 3.9 Hz, 1H), 1.32 (dd, *J* = 14.0, 8.3 Hz, 1H), 0.98 (s, 9H);
(*trans*)-70 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.40 (d, *J* = 1.6 Hz, 1H), 7.26–7.22 (m, 1H), 7.08–7.01 (m, 2H), 6.46–6.38 (m, 1H), 4.16 (t, *J* = 8.1 Hz, 1H), 3.78–3.74 (m, 4H), 3.51 (t, *J* = 8.2 Hz, 1H), 3.39 (t, *J* = 8.4 Hz, 1H), 3.04 (dd, *J* = 13.8, 4.5 Hz, 1H), 2.58 (dd, *J* = 13.8, 10.1 Hz, 1H), 2.15–2.08 (m, 1H), 2.00–1.90 (m, 1H), 1.62 (dd, *J* = 13.9, 2.5 Hz, 1H), 1.27 (dd, *J* = 14.1, 9.7 Hz, 1H), 0.91 (s, 9H);
(*cis*)-70 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 135.54, 131.85, 129.08, 128.83, 123.09, 120.88, 109.18, 100.59, 73.55, 71.70, 45.70, 41.75, 39.14, 33.22, 32.95, 30.93, 30.14 (3C);
(*trans*)-70 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 135.60, 131.55, 129.08, 128.79, 122.72, 120.46, 109.15, 100.62, 75.70, 72.71, 49.26, 47.69, 42.29, 38.65, 33.22, 30.93, 30.08 (3C);
IR (film) 2948, 2862, 1492, 1363, 1244, 1056, 907, 790, 718 cm^{-1};
HRMS (DART) calcd for $C_{19}H_{28}ON$ $[M+H]^+$ *m/z* = 286.2171; found 286.2171.



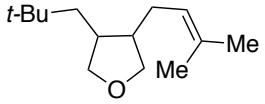
3-neopentyl-4-(thiophen-3-ylmethyl)tetrahydrofuran (71): Compound **71** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and thiophen-3-ylmagnesium bromide[5] (0.67 mL, 0.45 M solution in THF, 0.3 mmol). The product **71** was obtained as a colorless liquid (31.9 mg, dr = 5.4: 1, 67% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (3:1) to hexane/EtOAc (40:1).

(*cis*)-71 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.27–7.24 (m, 1H), 6.96–6.94 (m, 1H), 6.92 (dd, *J* = 4.9, 1.4 Hz, 1H), 4.01 (t, *J* = 7.8 Hz, 1H), 3.69 (ddd, *J* = 8.5, 5.3, 1.1 Hz, 1H), 3.58 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.47 (t, *J* = 8.4 Hz, 1H), 2.78 (dd, *J* = 13.9, 3.9 Hz, 1H), 2.49 (dd, *J* = 13.9, 11.4 Hz, 1H), 2.46–2.33 (m, 2H), 1.58 (dd, *J* = 14.0, 3.8 Hz, 1H), 1.24 (dd, *J* = 14.0, 8.5 Hz, 1H), 0.92 (s, 9H);

(*cis*)-71 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 141.33, 128.39, 125.66, 121.02, 73.46, 71.97, 44.31, 41.66, 38.87, 30.86, 30.07 (3C), 27.95;

(*cis*)-71 (major): **IR (film)** 2951, 2862, 1467, 1363, 1056, 908, 768 cm^{-1};

(*cis*)-71 (major): **HRMS (DART)** calcd for $C_{14}H_{23}OS$ $[M+H]^+$ *m/z* = 239.1470; found 239.1471.



3-(3-methylbut-2-en-1-yl)-4-neopentyltetrahydrofuran (72): Compound **72** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 2-methyl-1-propenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **72** was obtained as a colorless liquid (21.8 mg, dr = 5.2: 1, 52% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100 % hexene to hexene/EtOAc (95:5).

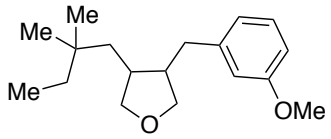
(*cis*)-72 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 5.06 (ddq, *J* = 7.6, 4.5, 1.4 Hz, 1H), 3.95 (t, *J* = 7.8 Hz, 1H), 3.74 (ddd, *J* = 8.3, 5.6, 1.1 Hz, 1H), 3.57 (dd, *J* = 8.2, 3.4 Hz, 1H),

3.42 (t, *J* = 8.4 Hz, 1H), 2.31–2.23 (m, 1H), 2.13–2.00 (m, 2H), 1.95–1.87 (m, 1H), 1.70 (s, 3H), 1.62 (s, 3H), 1.49 (dd, *J* = 14.0, 3.8 Hz, 1H), 1.16 (dd, *J* = 14.0, 8.6 Hz, 1H), 0.90 (s, 9H);

(*cis*)-72 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 132.79, 123.14, 73.62, 72.22, 43.79, 41.48, 38.77, 30.83, 30.07 (3C), 25.95, 25.83, 18.07;

(*cis*)-72 (major): **IR (film)** 2954, 2860, 1467, 1364, 1060, 910 cm^{-1};

(*cis*)-72 (major): **HRMS (DART)** calcd for $C_{14}H_{27}O$ $[M+H]^+$ *m/z* = 211.2062; found 211.2057.



3-(2,2-dimethylbutyl)-4-(3-methoxybenzyl)tetrahydrofuran (73): Compound **73** was synthesized following the general procedure (standard-scale**)**, using 2-iodo-2-methylbutane (39.6 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **73** was obtained as a colorless liquid (48.6 mg, dr = 4.5: 1, 88% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:1) to hexane/EtOAc (8:1).

(*cis*)-73 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.20 (t, *J* = 7.8 Hz, 1H), 6.79–6.72 (m, 3H), 4.01 (t, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 3.66–3.57 (m, 2H), 3.49 (t, *J* = 8.4 Hz, 1H), 2.82 (dd, *J* = 12.8, 3.0 Hz, 1H), 2.43–2.30 (m, 3H), 1.60 (dd, *J* = 14.1, 3.6 Hz, 1H), 1.28 (q, *J* = 7.5 Hz, 2H), 1.25 (dd, *J* = 14.1, 8.2 Hz, 1H), 0.88 (d, *J* = 1.5 Hz, 6H), 0.85 (t, *J* = 7.5 Hz, 3H);

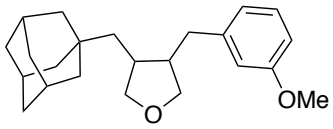
(*trans*)-73 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.19 (t, *J* = 7.9 Hz, 1H), 6.76–6.69 (m, 3H), 4.13 (t, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.77 (dd, *J* = 8.6, 7.3 Hz, 1H), 3.44 (dd, *J* = 8.5, 7.7 Hz, 1H), 3.36 (t, *J* = 8.4 Hz, 1H), 2.88 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.47 (dd, *J* = 13.7, 9.9 Hz, 1H), 2.10–2.01 (m, 1H), 1.93–1.84 (m, 1H), 1.53 (dd, *J* = 14.0, 2.4 Hz, 1H), 1.25–1.18 (m, 3H), 0.81 (d, *J* = 1.1 Hz, 6H), 0.80 (t, *J* = 7.5 Hz, 3H);

(*cis*)-73 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.80, 142.79, 129.45, 121.52, 114.89, 111.33, 73.39, 71.57, 55.23, 45.01, 39.31, 38.56, 34.99, 33.32, 33.25, 27.10, 27.01, 8.59;

(*trans*)-73 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.80, 142.34, 129.48, 121.13, 114.60, 111.39, 75.61, 72.53, 48.57, 45.26, 41.82, 38.80, 34.89, 33.32, 33.18, 27.05, 27.03, 8.52;

IR (film) 2959, 2853, 1601, 1489, 1260, 1153, 1046, 906, 777, 696 cm^{-1};

HRMS (DART) calcd for $C_{18}H_{29}O_2$ $[M+H]^+$ *m/z* = 277.2168; found 277.2171.



3-((-adamantan-1-yl)methyl)-4-(3-methoxybenzyl)tetrahydrofuran (74): Compound **74** was synthesized following the general procedure (standard-scale**)**, using 1-iodoadamantane (52.4 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **74** was obtained as a colorless liquid (38.8 mg, dr = 3.6: 1, 57% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:1) to hexane/EtOAc (8:1).

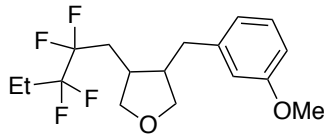
(*cis*)-74 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.20 (t, *J* = 7.8 Hz, 1H), 6.79–6.71 (m, 3H), 3.99 (t, *J* = 7.8 Hz, 1H), 3.80 (s, 3H), 3.66–3.60 (m, 1H), 3.58 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.46 (t, *J* = 8.3 Hz, 1H), 2.81 (dd, *J* = 12.8, 3.0 Hz, 1H), 2.44–2.30 (m, 3H), 1.99–1.93 (m, 3H), 1.75–1.70 (m, 3H), 1.66–1.62 (m, 3H), 1.57–1.52 (m, 3H), 1.50–1.44 (m, 4H), 1.12 (dd, *J* = 14.1, 8.0 Hz, 1H);

(*trans*)-74 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.19 (t, *J* = 7.9 Hz, 1H), 6.75–6.68 (m, 3H), 4.11 (t, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.77 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.42 (t, *J* = 8.1 Hz, 1H), 3.32 (t, *J* = 8.3 Hz, 1H), 2.86 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.46 (dd, *J* = 13.7, 9.7 Hz, 1H), 2.06–2.00 (m, 1H), 2.00–1.90 (m, 4H), 1.72–1.68 (m, 3H), 1.63–1.59 (m, 3H), 1.50–1.44 (m, 4H), 1.40–1.35 (m, 3H), 1.11 (dd, *J* = 14.1, 8.9 Hz, 1H);

(*cis*)-74 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.79, 142.88, 129.45, 121.53, 114.90, 111.31, 73.67, 71.61, 55.26, 45.01, 43.05 (3C), 42.58, 37.19 (3C), 37.09, 33.35, 32.73, 28.83 (3C);

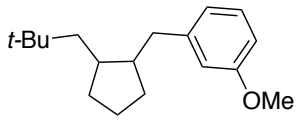
(*trans*)-74 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.79, 142.38, 129.47, 121.19, 114.65, 111.38, 75.78, 72.52, 48.62, 48.54, 43.02, 43.00 (3C), 40.30, 38.70, 37.16 (3C), 32.65, 28.78 (3C);

IR (film) 2898, 2844, 1600, 1489, 1451, 1261, 1152, 1047, 696 cm^{-1};
HRMS (DART) calcd for $C_{23}H_{33}O_2$ $[M+H]^+$ *m/z* = 341.2481; found 341.2475.

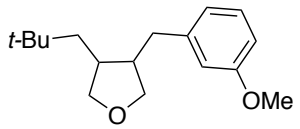


3-(3-methoxybenzyl)-4-(2,2,3,3-tetrafluoropentyl)tetrahydrofuran (75): Compound **75** was synthesized following the general procedure (standard-scale**)**, using 1-bromo-1,1,2,2-tetrafluorobutane (41.8 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **75** was obtained as a colorless liquid (51.5 mg, dr = 4.5: 1, 77% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (1:1) to hexane/EtOAc (5:1).
(*cis*)-75 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.21 (t, *J* = 7.9 Hz, 1H), 6.80–6.74 (m, 2H), 6.73 (t, *J* = 2.0 Hz, 1H), 4.05 (ddd, *J* = 8.9, 7.5, 1.6 Hz, 1H), 3.80 (s, 3H), 3.72 (ddd, *J* = 8.7, 5.8, 0.8 Hz, 1H), 3.66–3.58 (m, 2H), 2.78 (dd, *J* = 13.3, 4.5 Hz, 1H), 2.76–2.69 (m, 1H), 2.60–2.54 (m, 1H), 2.40 (dd, *J* = 13.3, 11.4 Hz, 1H), 2.37–2.25 (m, 1H), 2.22–1.86 (m, 3H), 1.11 (t, *J* = 7.5 Hz, 3H);
(*trans*)-75 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.19 (t, *J* = 7.9 Hz, 1H), 6.75–6.68 (m, 3H), 4.11 (t, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.77 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.42 (t, *J* = 8.1 Hz, 1H), 3.32 (t, *J* = 8.3 Hz, 1H), 2.86 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.46 (dd, *J* = 13.7, 9.7 Hz, 1H), 2.06–2.00 (m, 1H), 2.00–1.90 (m, 4H), 1.72–1.68 (m, 3H), 1.63–1.59 (m, 3H), 1.50–1.44 (m, 4H), 1.40–1.35 (m, 3H), 1.11 (dd, *J* = 14.1, 8.9 Hz, 1H);
(*cis*)-75 (major): **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 159.88, 141.83, 129.62, 122.64–116.40 (m, 2C), 121.38, 114.75, 111.64, 72.17 (d, *J* = 3.7 Hz, 1C), 71.71, 55.24, 43.54, 35.36, 33.51, 28.03 (t, *J* = 22.5 Hz, 1C), 23.41 (t, *J* = 23.7 Hz, 1C), 4.96 (t, *J* = 5.0 Hz, 1C);
(*trans*)-75 (minor): **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 159.90, 141.54, 129.65, 122.64–116.40 (m, 2C), 121.13, 114.56, 111.72, 74.04 (d, *J* = 4.2 Hz, 1C), 72.67, 55.24, 47.17, 38.80, 38.56, 32.93 (t, *J* = 22.6 Hz, 1C), 23.41 (t, *J* = 23.7 Hz, 1C), 4.96 (t, *J* = 5.0 Hz, 1C);
(*cis*)-75 (major): **^{19}F NMR (565 MHz, $CDCl_3$)** δ = -113.30 (dd, *J* = 263.9, 9.3 Hz, 1F), -115.47 (dd, *J* = 264.2, 8.7 Hz, 1F), -117.28 (t, *J* = 9.5 Hz, 2F);

(*trans*)-75 (minor): **^{19}F NMR (565 MHz, $CDCl_3$)** δ = -113.13 (dd, *J* = 264.2, 11.2 Hz, 1F), -114.94 (dd, *J* = 264.2, 11.0 Hz, 1F), -117.41 (dd, *J* = 41.7, 11.1 Hz, 2F);
IR (film) 2945, 2860, 1601, 1489, 1261, 1170, 1045, 1003, 929, 773, 696 cm^{-1};
HRMS (DART) calcd for $C_{17}H_{23}O_2F_4$ $[M+H]^+$ *m/z* = 335.1634; found 335.1625.



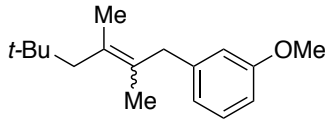
1-methoxy-3-((2-neopentylcyclopentyl)methyl)benzene (76): Compound **76** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1,6-heptadiene (269.3 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The mixture products of **76** (76% yield, dr = 3.8: 1, 39.6 mg) and **76'** (acyclic/arylation, 9% yield, 4.7 mg) were obtained as a colorless liquid (determined by ^{1}H NMR and GC-MS) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (10:1). The purity product **76** was obtained as a colorless liquid after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100 % hexene to hexene/Et_2O (98:2);
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.22–7.14 (m, 1H, major + minor), 6.81–6.73 (m, 1H, major + minor), 6.73–6.68 (m, 2H, major + minor), 3.81–3.80 (m, 3H, major + minor), 2.87–2.73 (m, 1H, major + minor), 2.28–1.91 (m, 3H, major + minor), 1.84–1.53 (m, 3H, major + minor), 1.53–1.33 (m, 4H, major + minor), 1.21–1.13 (m, 1H, major + minor), 0.94–0.89 (m, 9H, major + minor). Spectral data matched compound **58** (*vide supra*).



3-(3-methoxybenzyl)-4-neopentyltetrahydrofuran (77): Compound **77** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), allyl ether (274.8 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **77** was obtained as a colorless liquid (26.7 mg, dr = 4.2: 1, 51% yield) after purified by flash chromatography on silica gel with

hexane/CH_2Cl_2 (1:1) to hexane/EtOAc (8:1).

(*cis*)-77 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.20 (t, *J* = 7.8 Hz, 1H), 6.77–6.72 (m, 3H), 4.02 (t, *J* = 7.8 Hz, 1H), 3.80 (s, 3H), 3.63 (ddd, *J* = 8.7, 5.0, 1.0 Hz, 1H), 3.59 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.51 (t, *J* = 8.4 Hz, 1H), 2.81 (dd, *J* = 13.1, 3.4 Hz, 1H), 2.46–2.32 (m, 3H), 1.61 (dd, *J* = 14.0, 3.7 Hz, 1H), 1.27 (dd, *J* = 13.9, 8.3 Hz, 1H), 0.93 (s, 9H). Spectral data matched compound **60** (*vide supra*).



1-methoxy-3-(2,3,5,5-tetramethylhex-2-en-1-yl)benzene (78): Compound **78** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 2,3-dimethyl-1,3-butadiene (230 mg, 2.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **78** was obtained as a colorless liquid (21.2 mg, dr = 7.6: 1, 43% yield) after purified by flash chromatography on silica gel with hexane/CH_2Cl_2 (20:1).

(*E*)-78 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.19 (dd, *J* = 9.0, 7.5 Hz, 1H), 6.82–6.76 (m, 1H), 6.75–6.70 (m, 2H), 3.79 (s, 3H), 3.41 (s, 2H), 2.10 (s, 2H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.61 (d, *J* = 1.5 Hz, 3H), 0.96 (s, 9H);

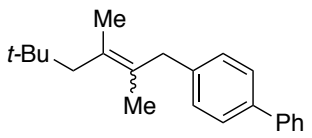
(*Z*)-78 (minor): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.22–7.15 (m, 1H), 6.73–6.67 (m, 3H), 3.79 (s, 3H), 3.41 (s, 2H), 2.16 (s, 2H), 1.76 (q, *J* = 1.0 Hz, 3H), 1.56 (q, *J* = 0.9 Hz, 3H), 0.95 (s, 9H);

(*E*)-78 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.85, 142.76, 129.96, 129.29, 129.11, 121.07, 114.03, 111.20, 55.26, 48.22, 40.76, 33.81, 30.78 (3C), 22.09, 19.85;

(*Z*)-78 (minor): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 159.76, 142.92, 129.33, 129.22, 128.90, 121.29, 114.68, 110.83, 55.25, 48.07, 40.80, 33.32, 30.70 (3C), 22.03, 18.65;

IR (film) 2950, 2864, 1599, 1487, 1259, 1156, 1052, 692 cm^{-1};

HRMS (DART) calcd for $C_{17}H_{27}O$ $[M+H]^+$ *m/z* = 247.2062; found 247.2065.



4-(2,3,5,5-tetramethylhex-2-en-1-yl)-1,1'-biphenyl (79): Compound **79** was synthesized following the general procedure (standard-scale**)**, using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 2,3-dimethyl-1,3-butadiene (230 mg, 2.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **79** was obtained as a colorless liquid (35 mg, dr = 11: 1, 60% yield) after purified by Isolera™ Flash Systems silica gel chromatography with prepacked silica-gel cartridges (SNAP Ultra; Biotage) and a gradient elution 100 % hexene to hexene/Et_2O (98:2);

(*E*)-79 (major): **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.62–7.56 (m, 2H), 7.55–7.48 (m, 2H), 7.44–7.40 (m, 2H), 7.36–7.30 (m, 1H), 7.26–7.23 (m, 2H), 3.47 (s, 2H), 2.12 (s, 2H), 1.85 (d, *J* = 1.5 Hz, 3H), 1.64 (d, *J* = 1.5 Hz, 3H), 0.97 (s, 9H);

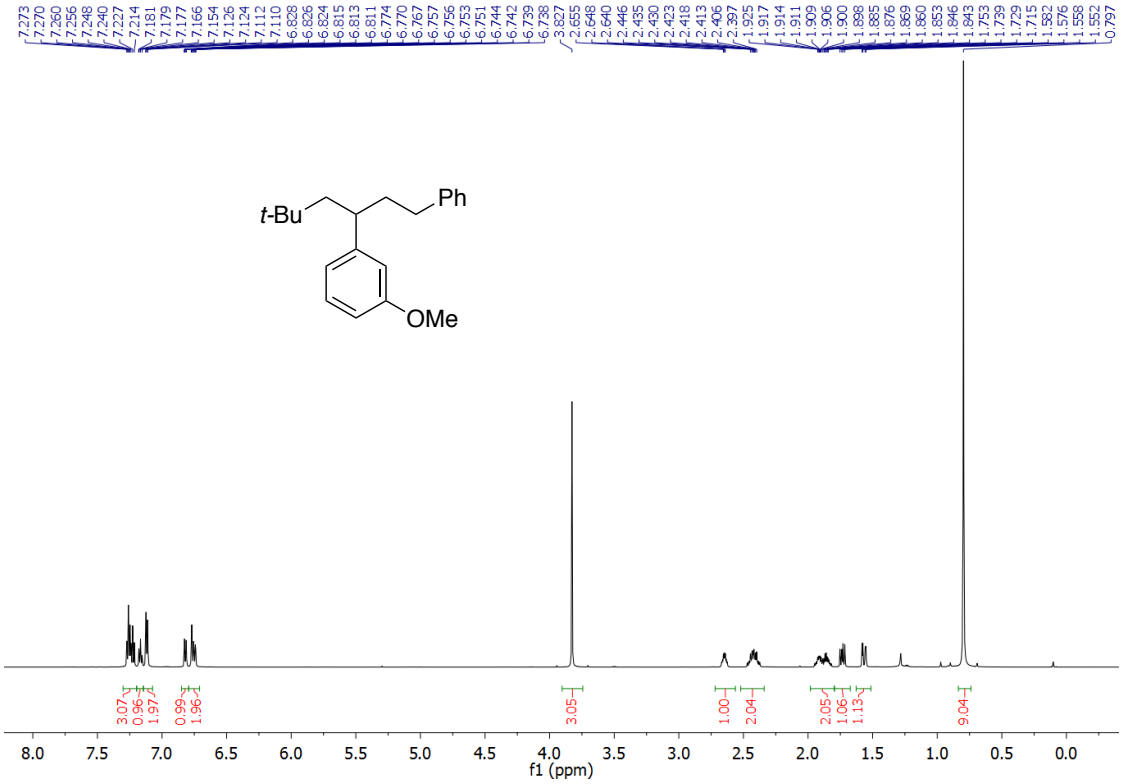
(*E*)-79 (major): **^{13}C NMR (150 MHz, $CDCl_3$)** δ = 141.32, 140.23, 138.76, 129.98, 129.11, 128.92 (2C), 128.83 (2C), 127.16 (2C), 127.12 (2C), 127.08, 48.26, 40.42, 33.83, 30.80 (3C), 22.15, 19.90;

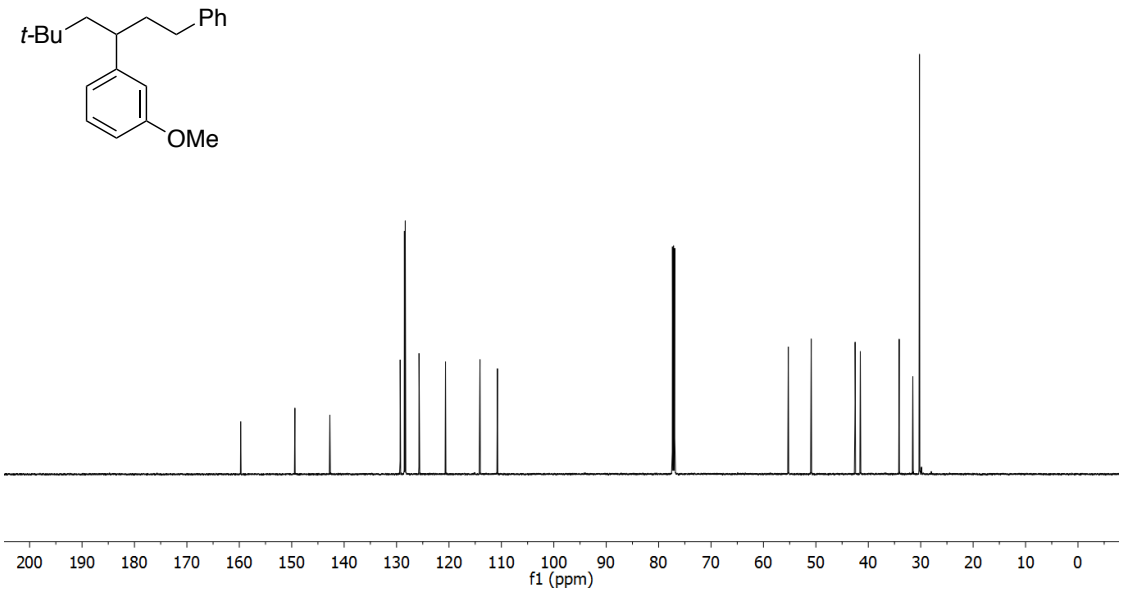
(*E*)-79 (major): **IR (film)** 2951, 2864, 1715, 1486, 1361, 1219, 750, 697 cm^{-1};

(*E*)-79 (major): **HRMS (DART)** calcd for $C_{22}H_{29}$ $[M+H]^+$ *m/z* = 293.2269; found 293.2269.

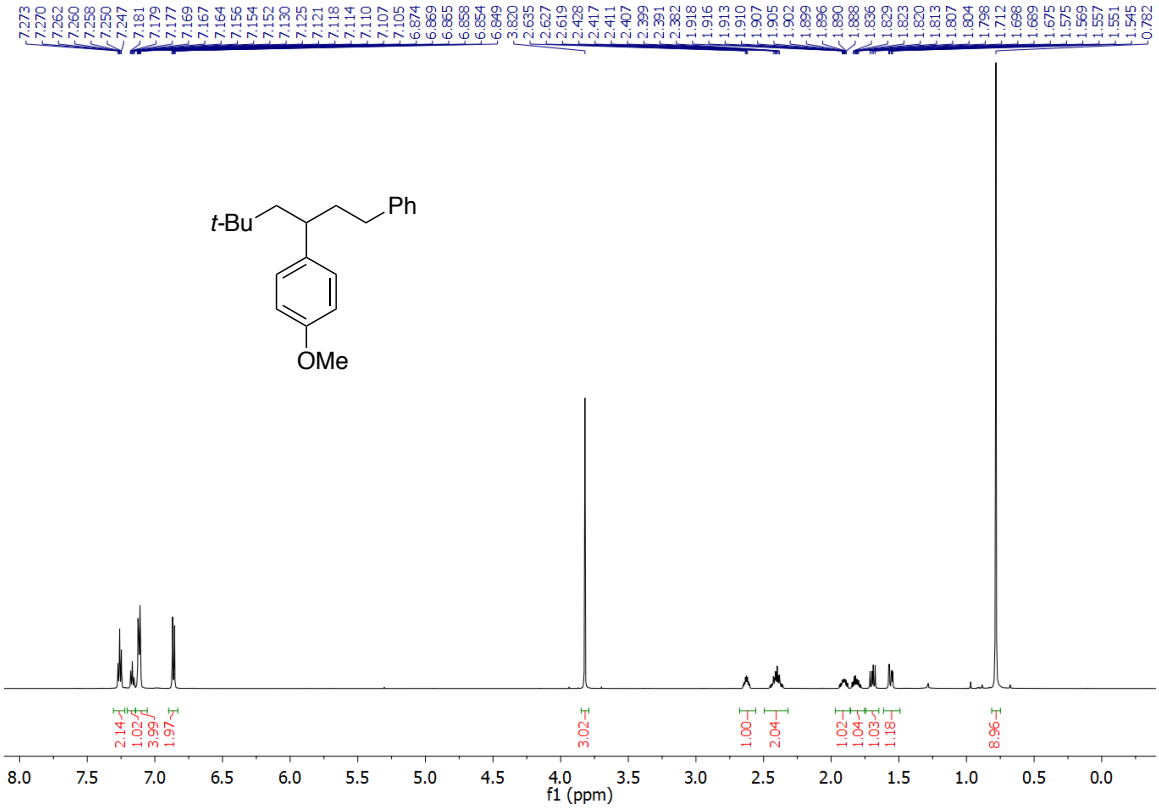
9. Spectral Data

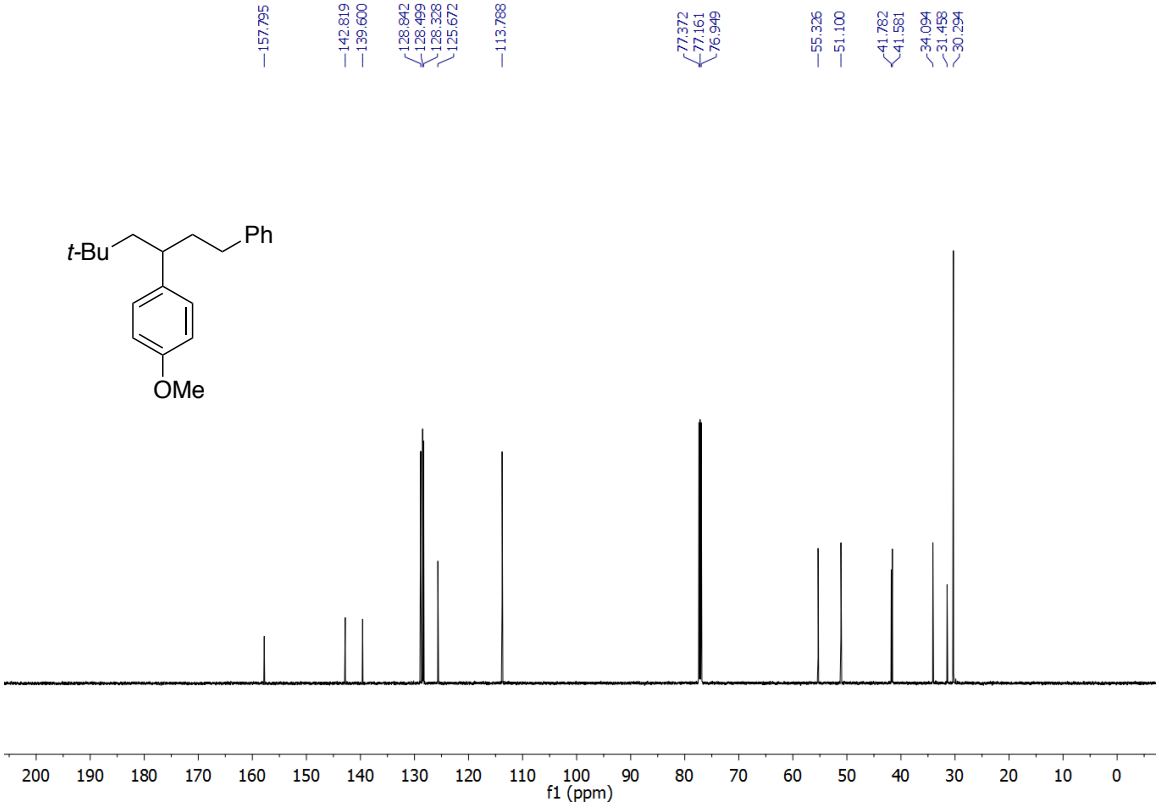
Compound 4. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



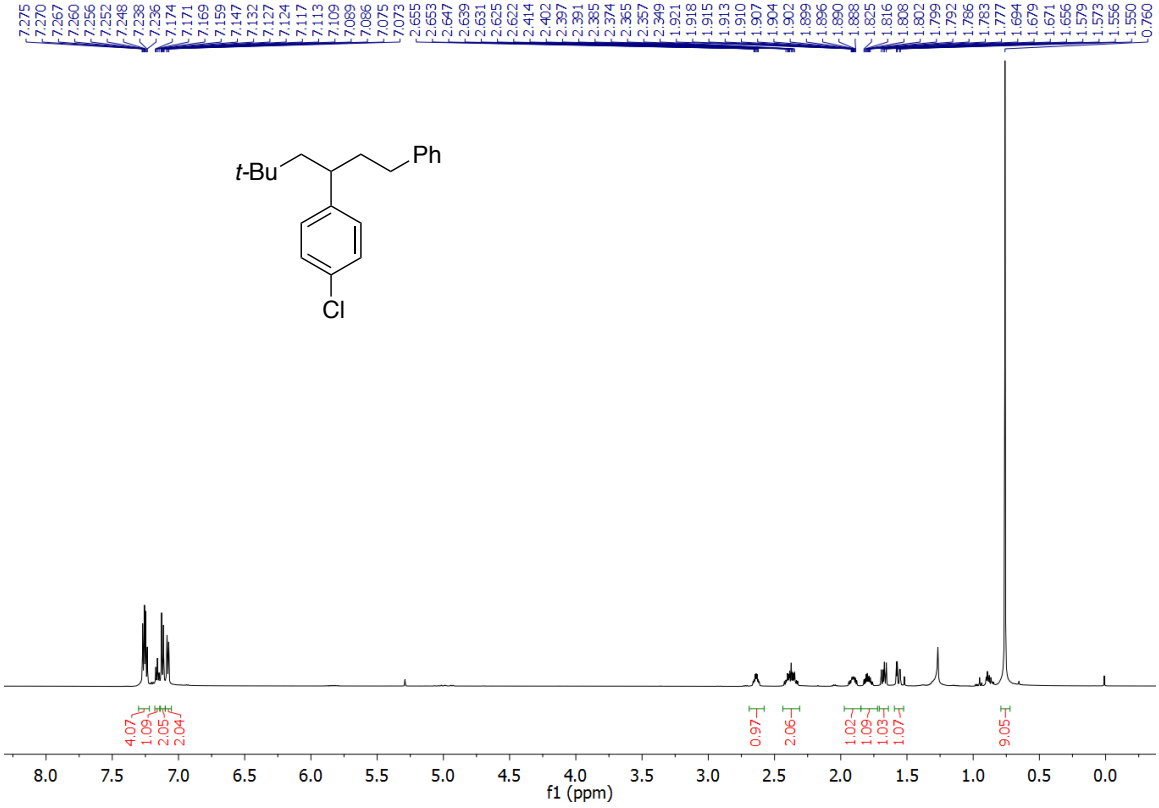


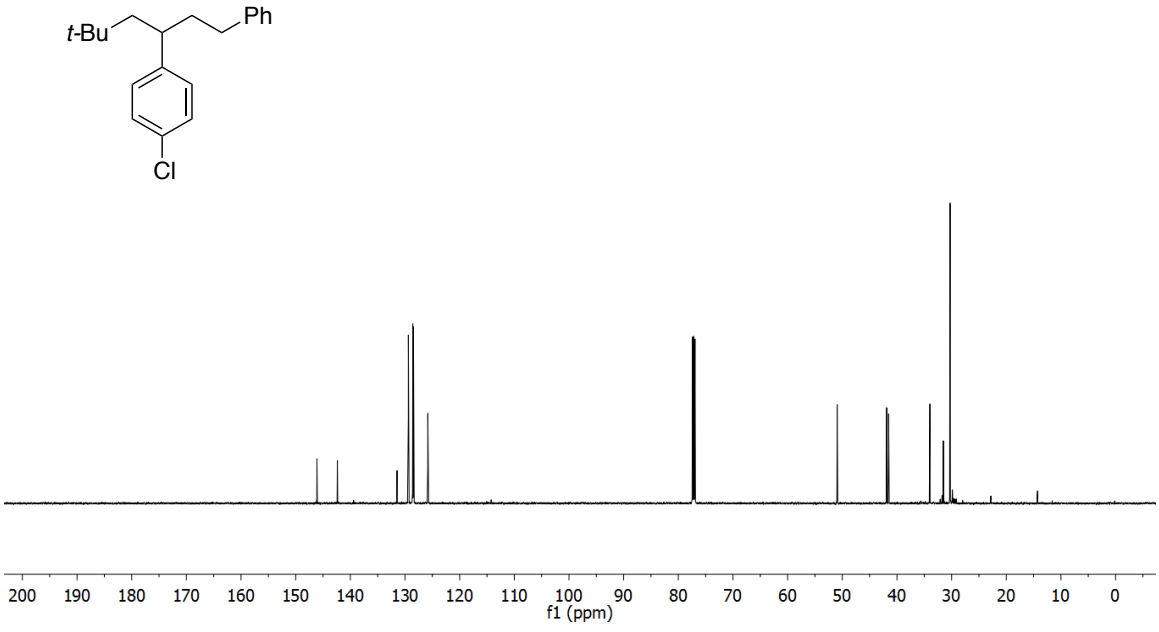
Compound 7. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



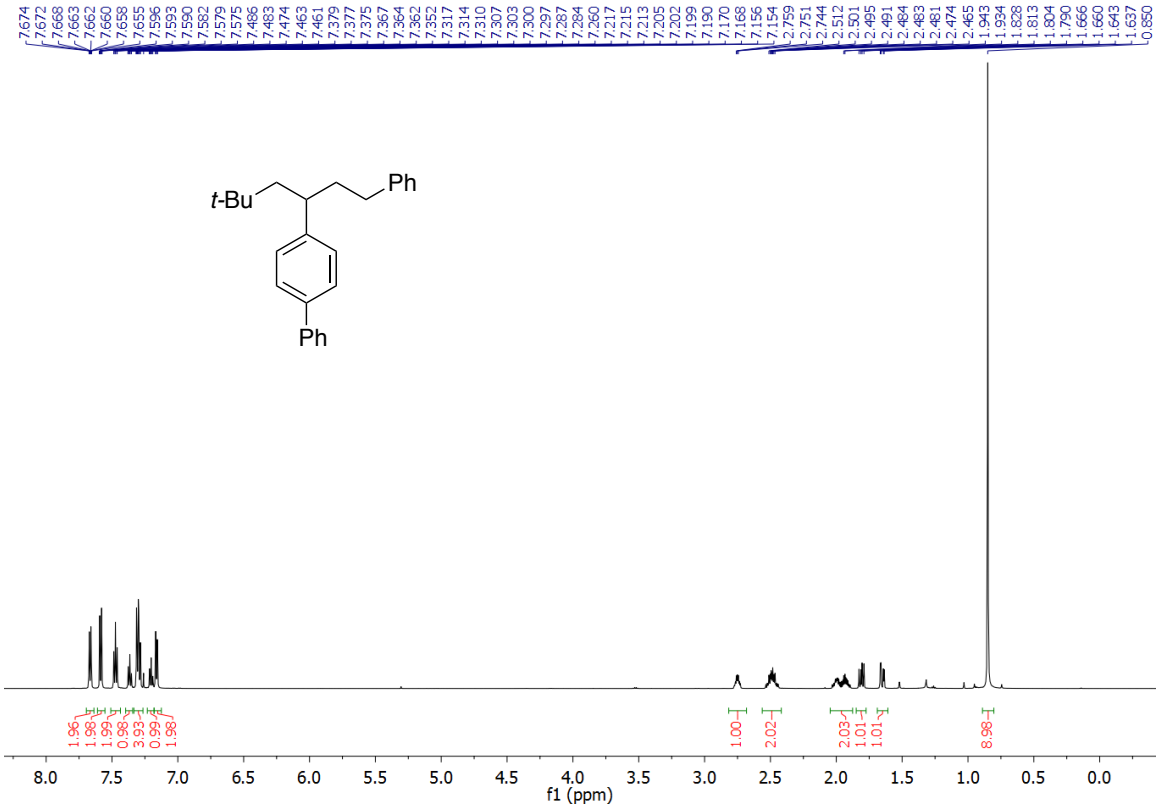


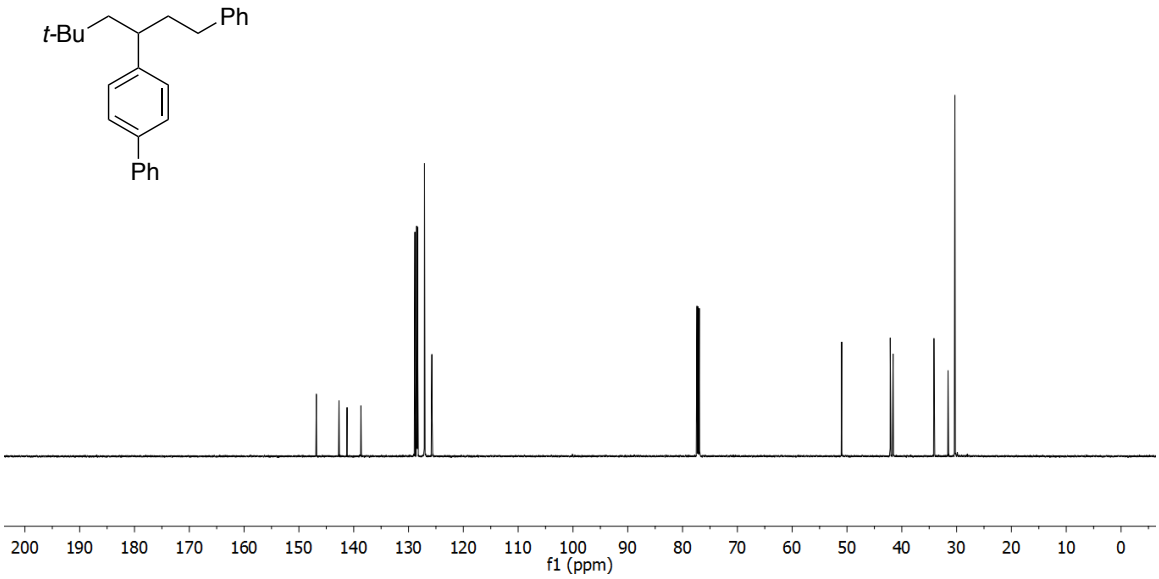
Compound 8. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



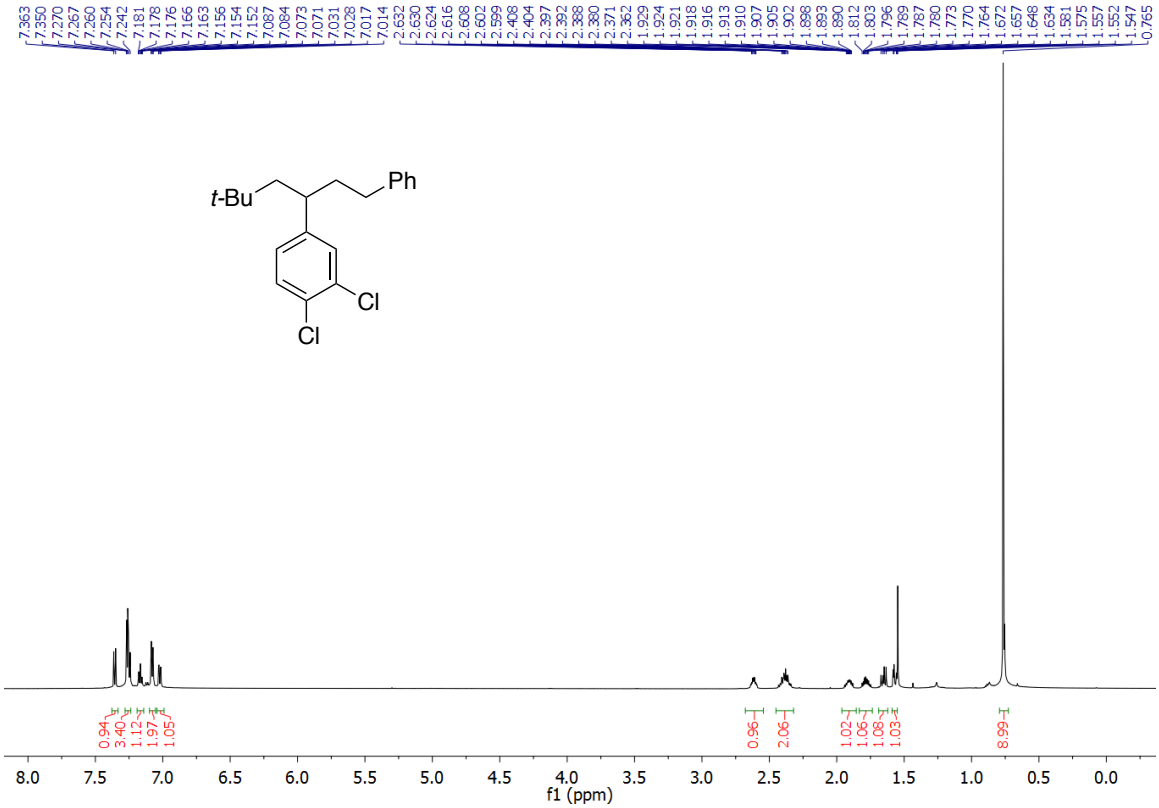


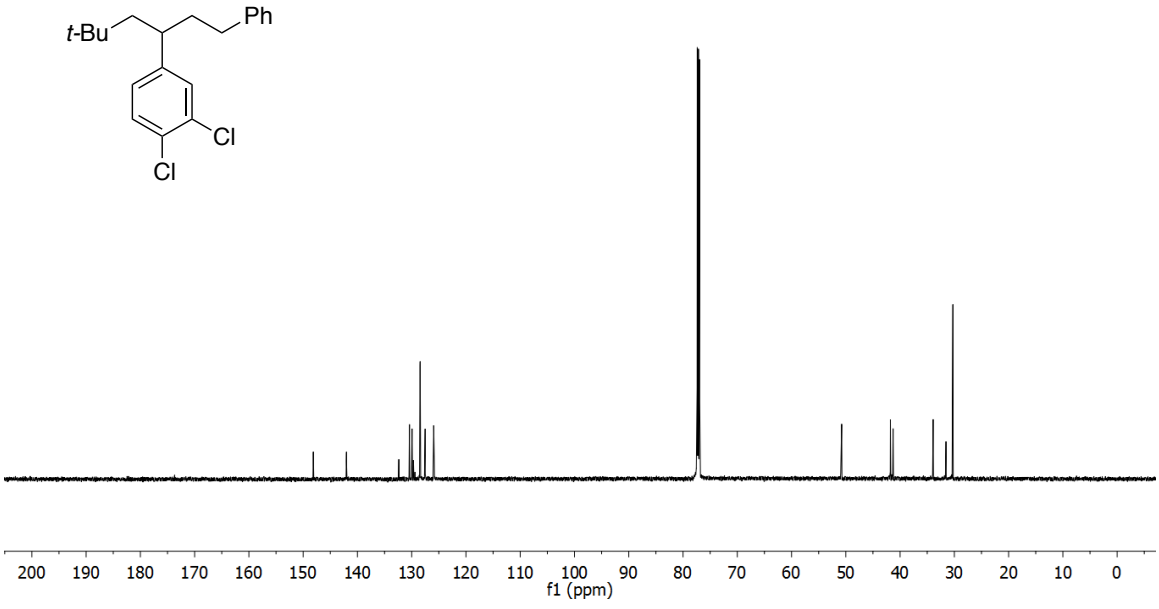
Compound 9. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



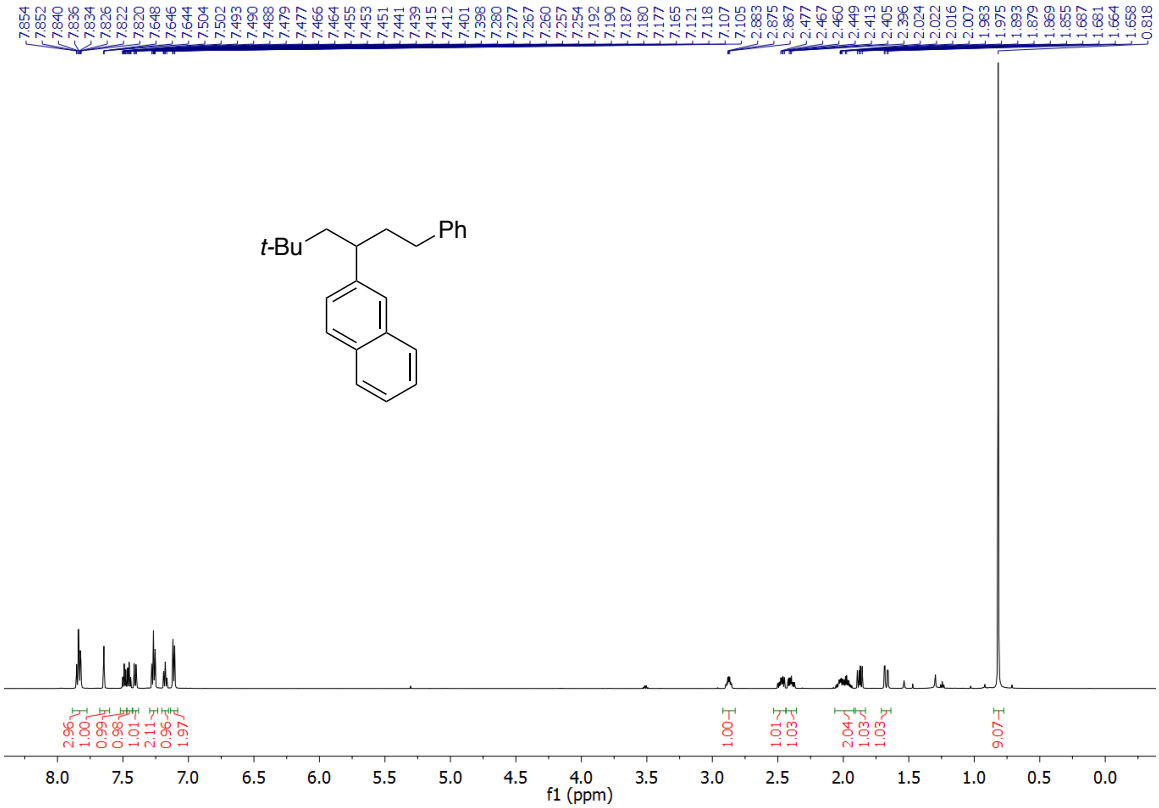


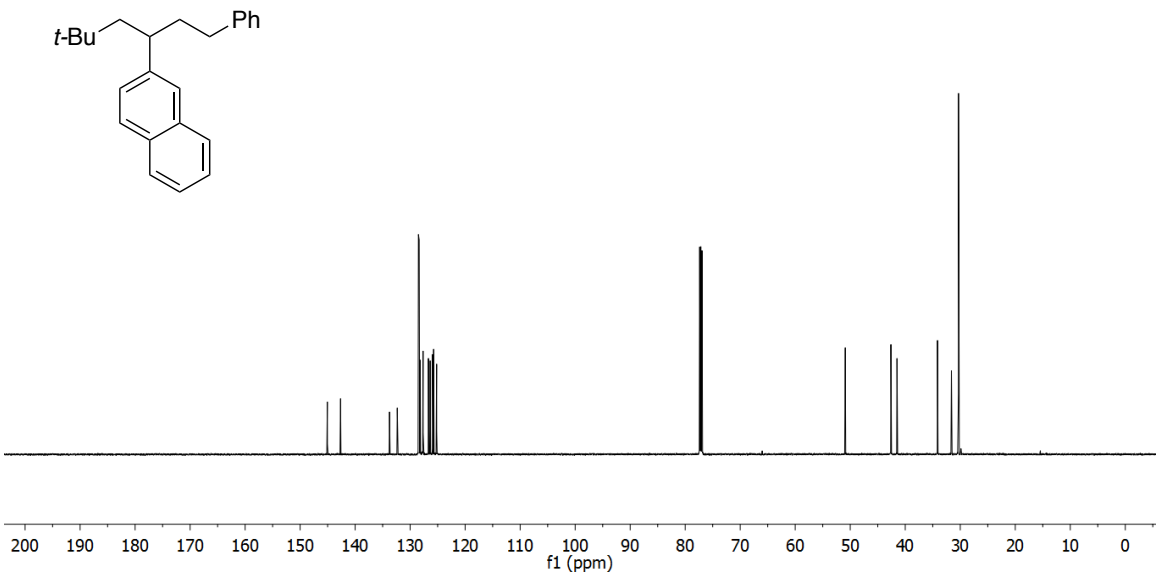
Compound 11. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



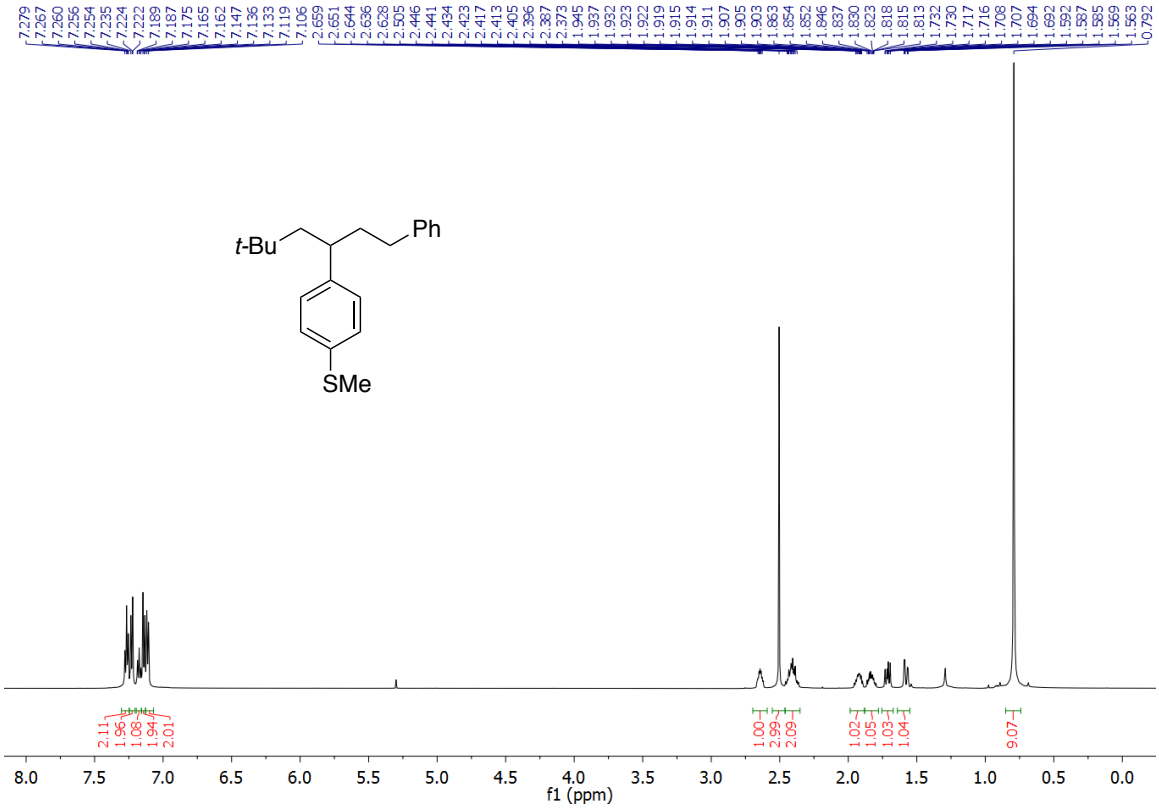


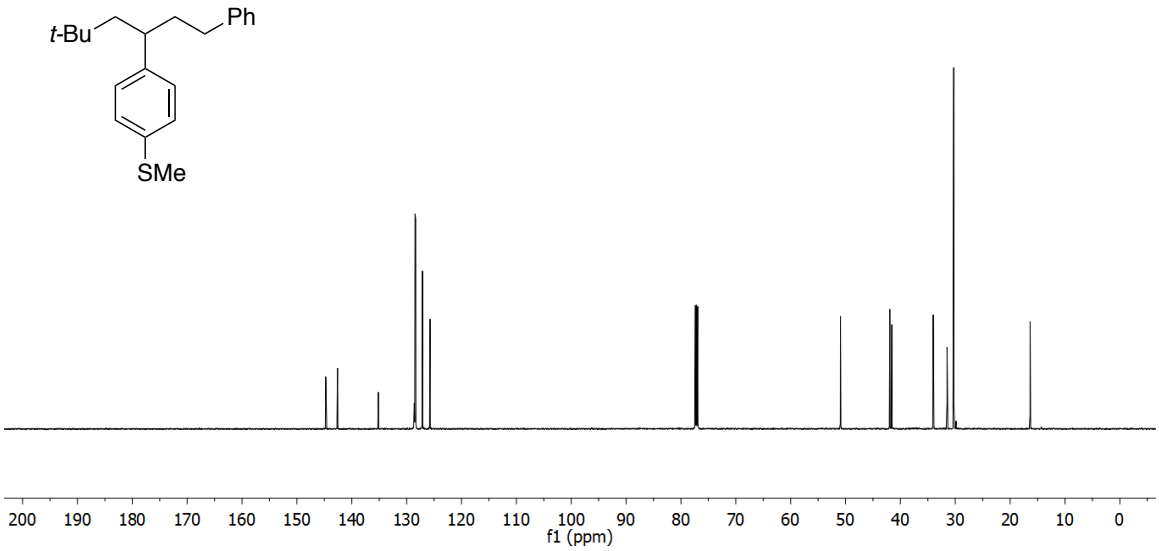
Compound 12. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



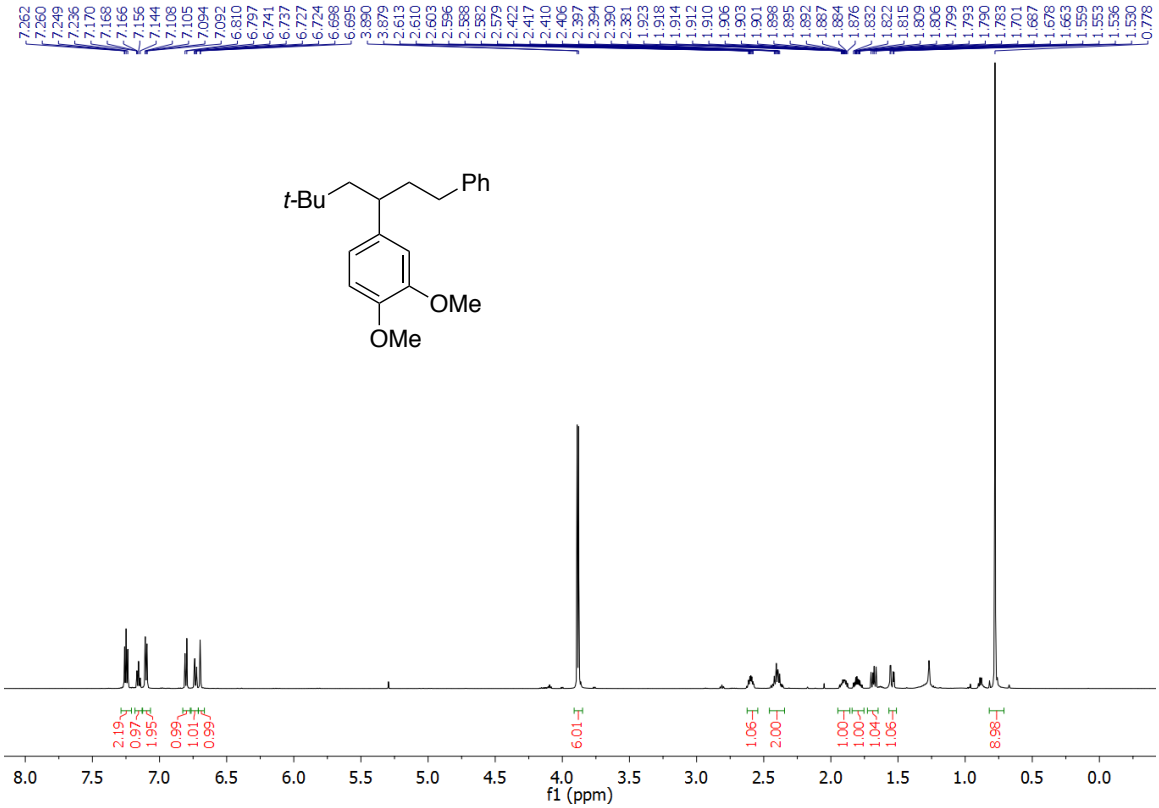


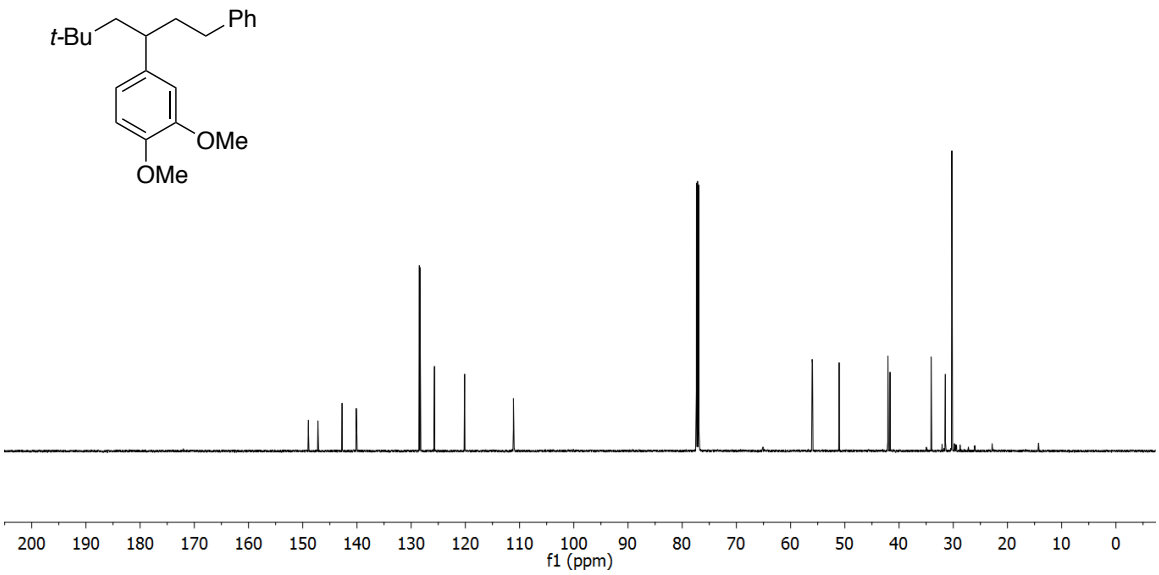
Compound 13. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



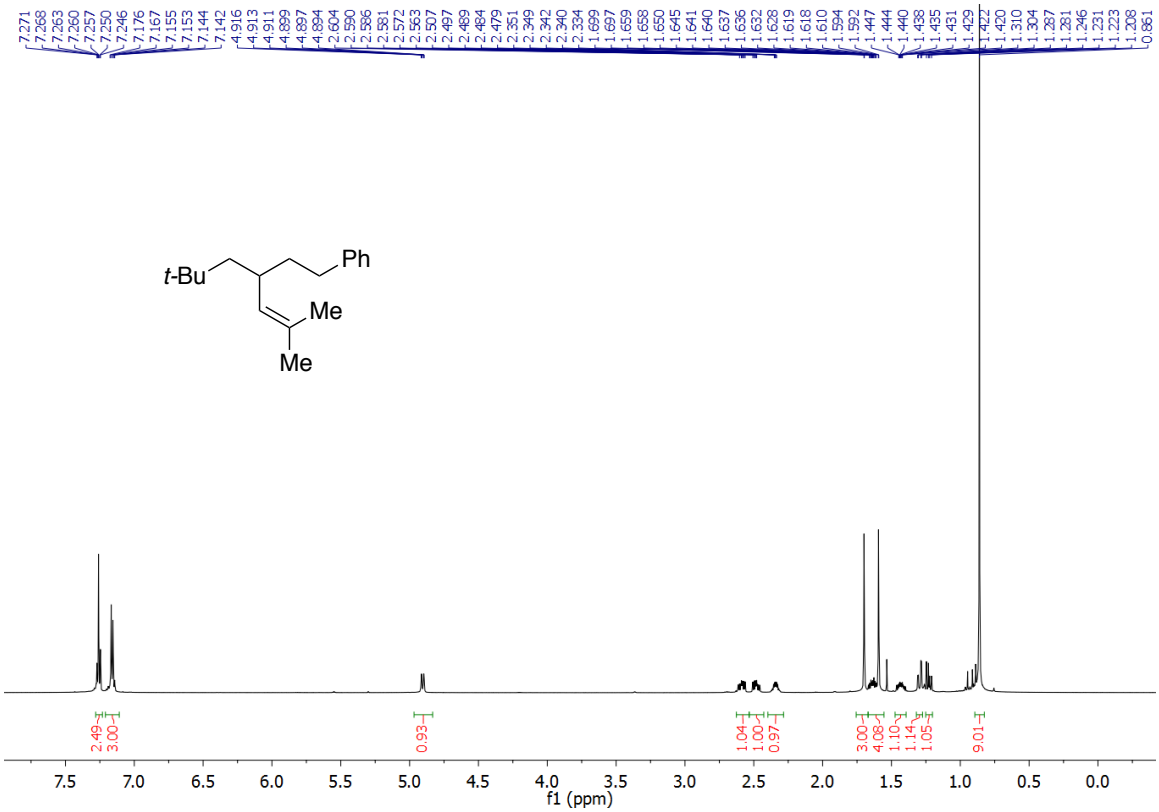


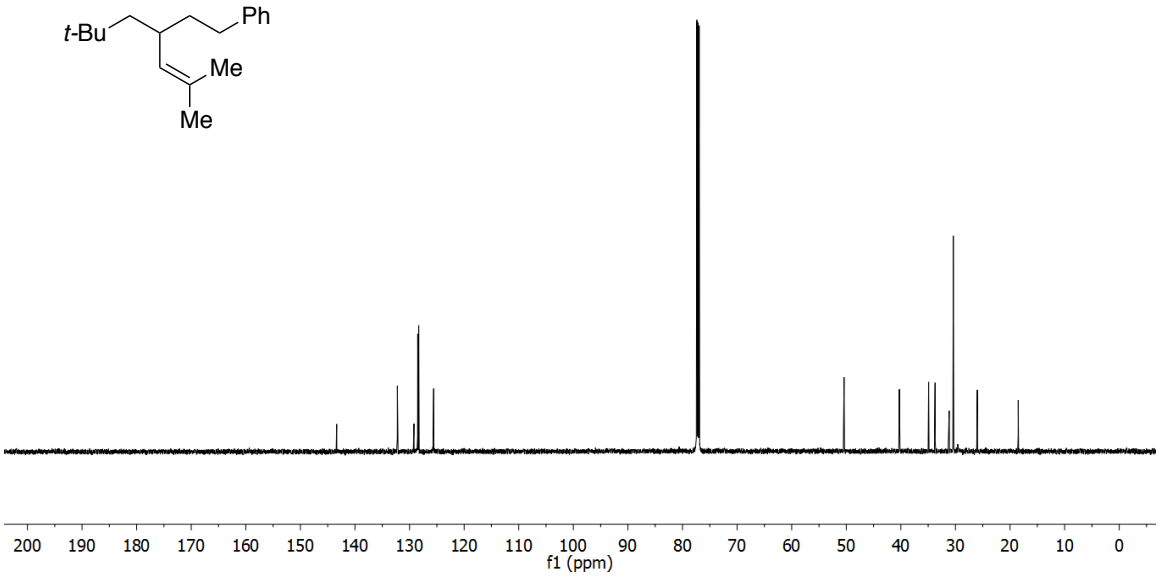
Compound 15. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



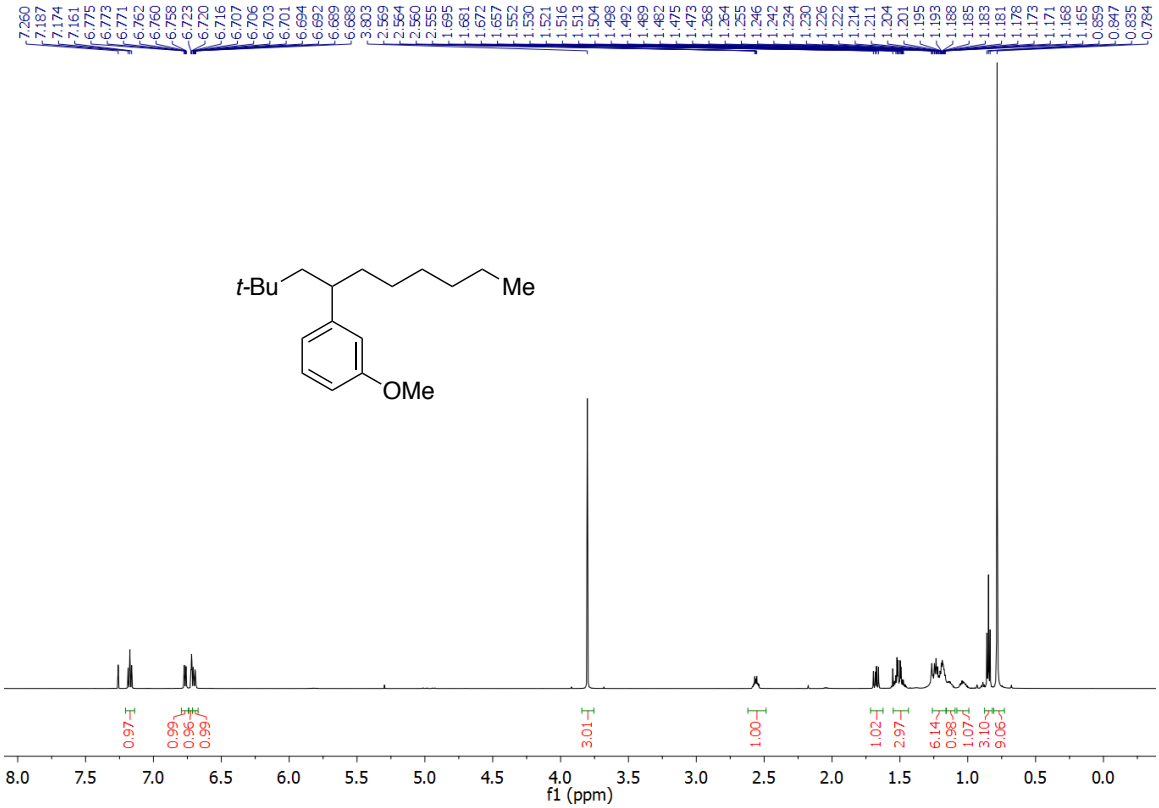


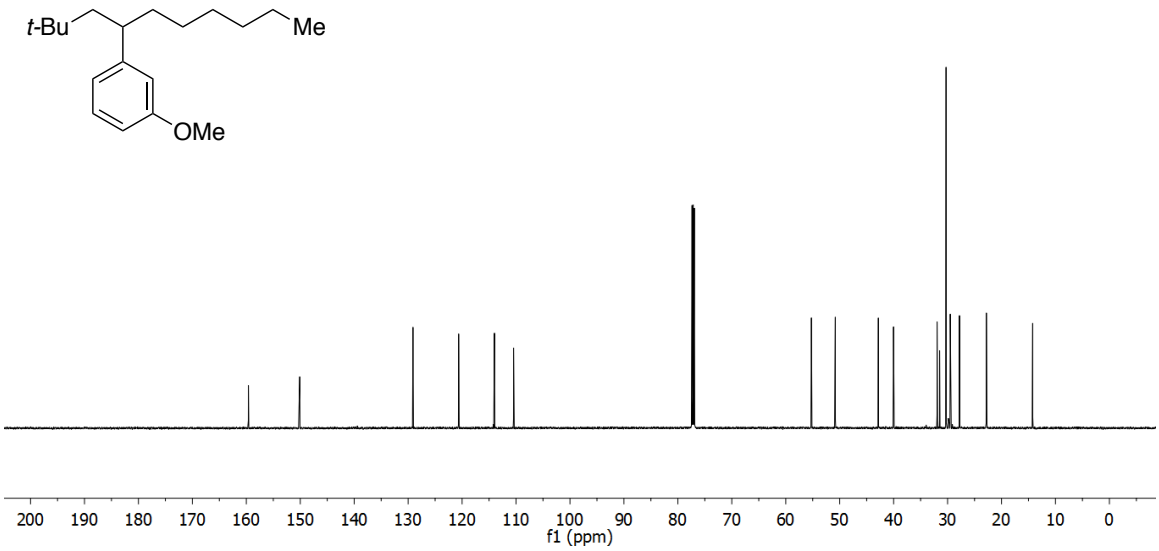
Compound 18. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



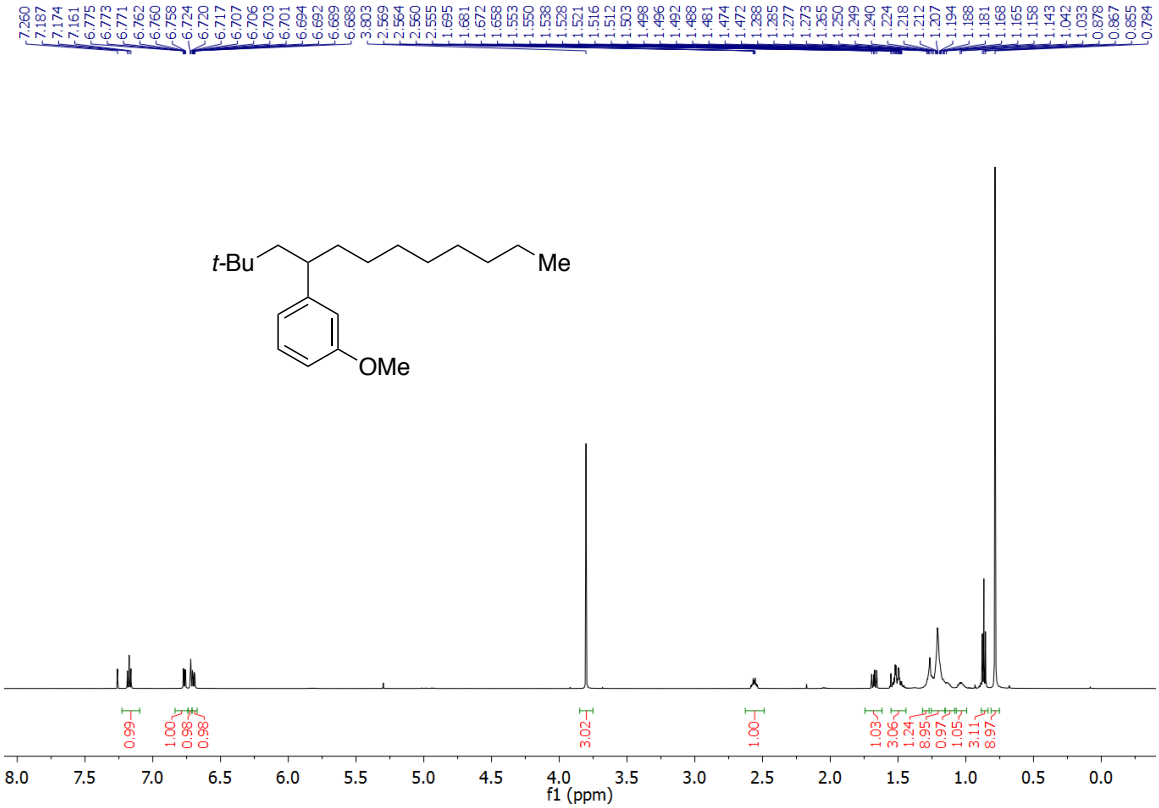


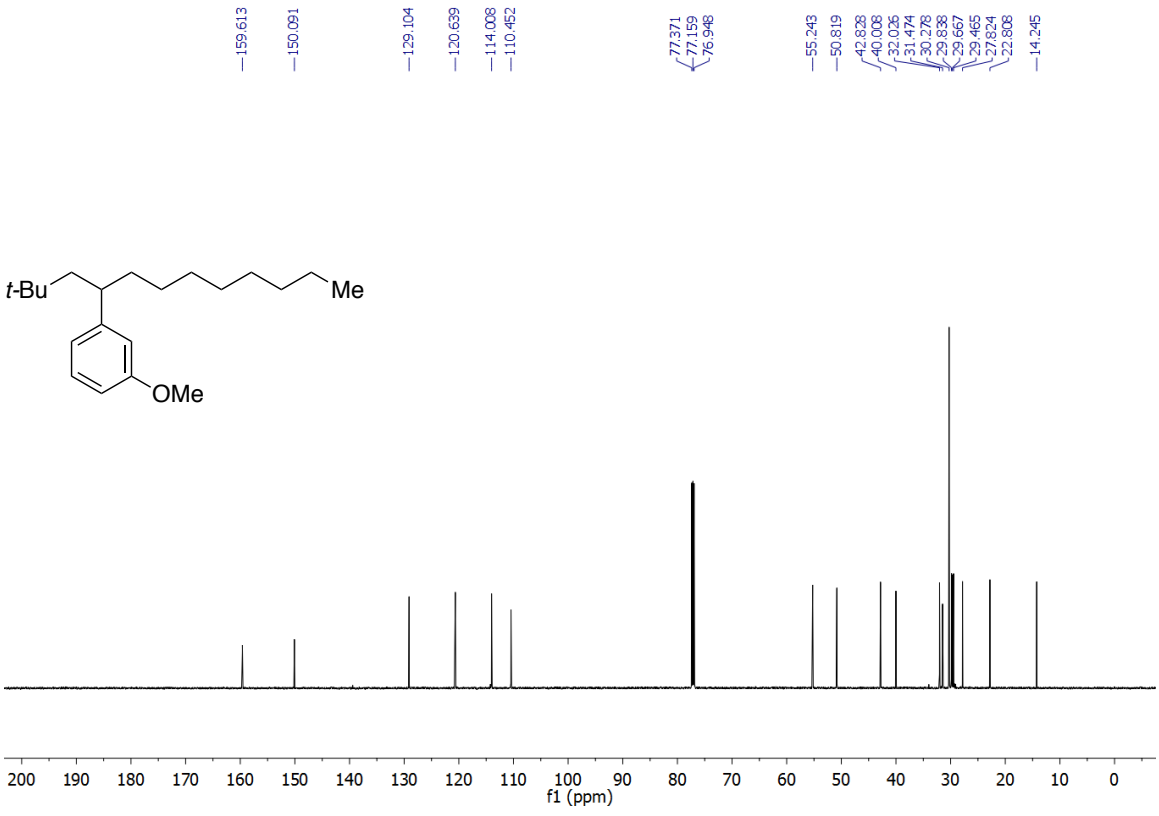
Compound 19. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



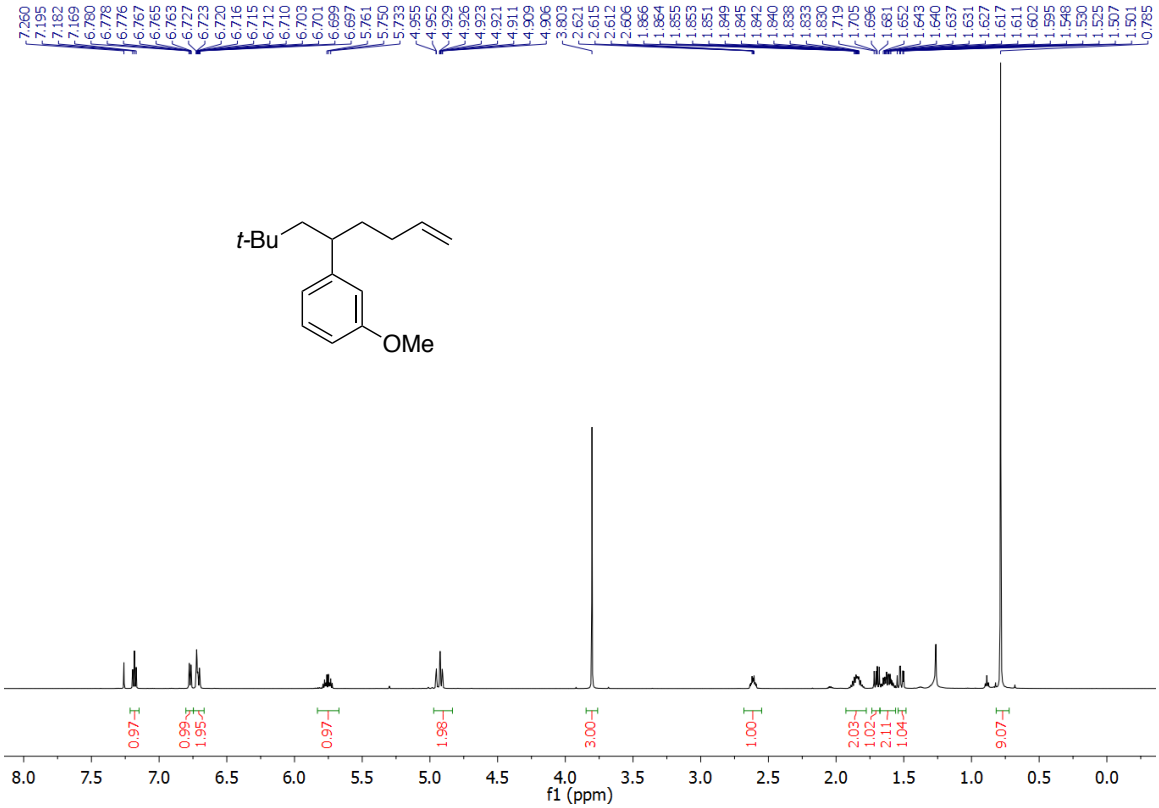


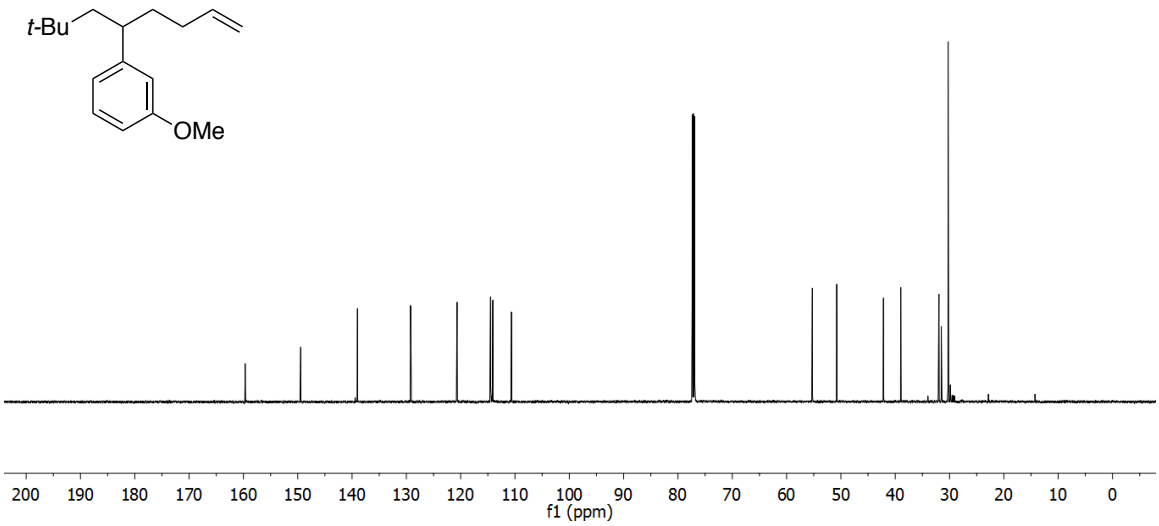
Compound 20. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



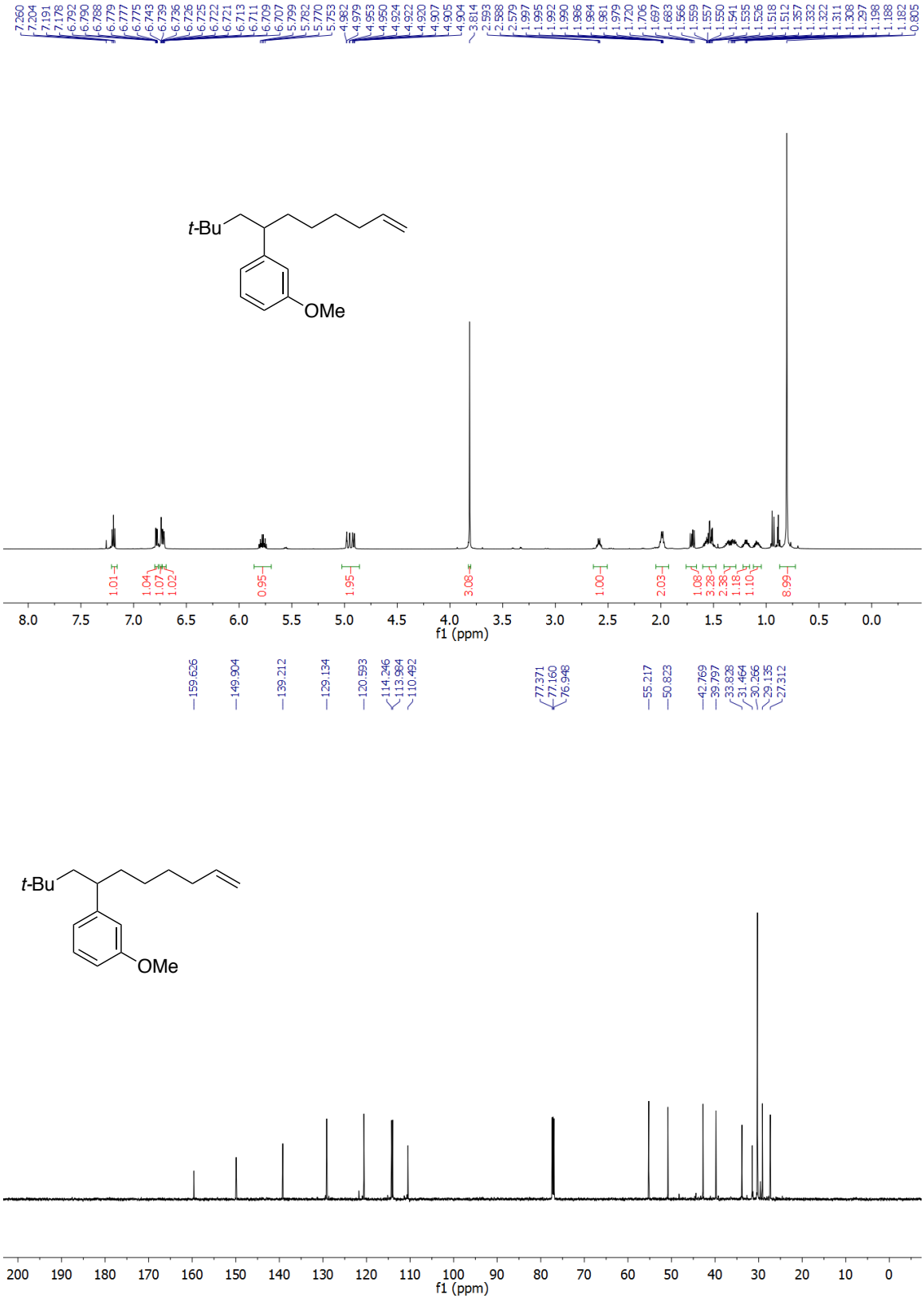


Compound 21. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

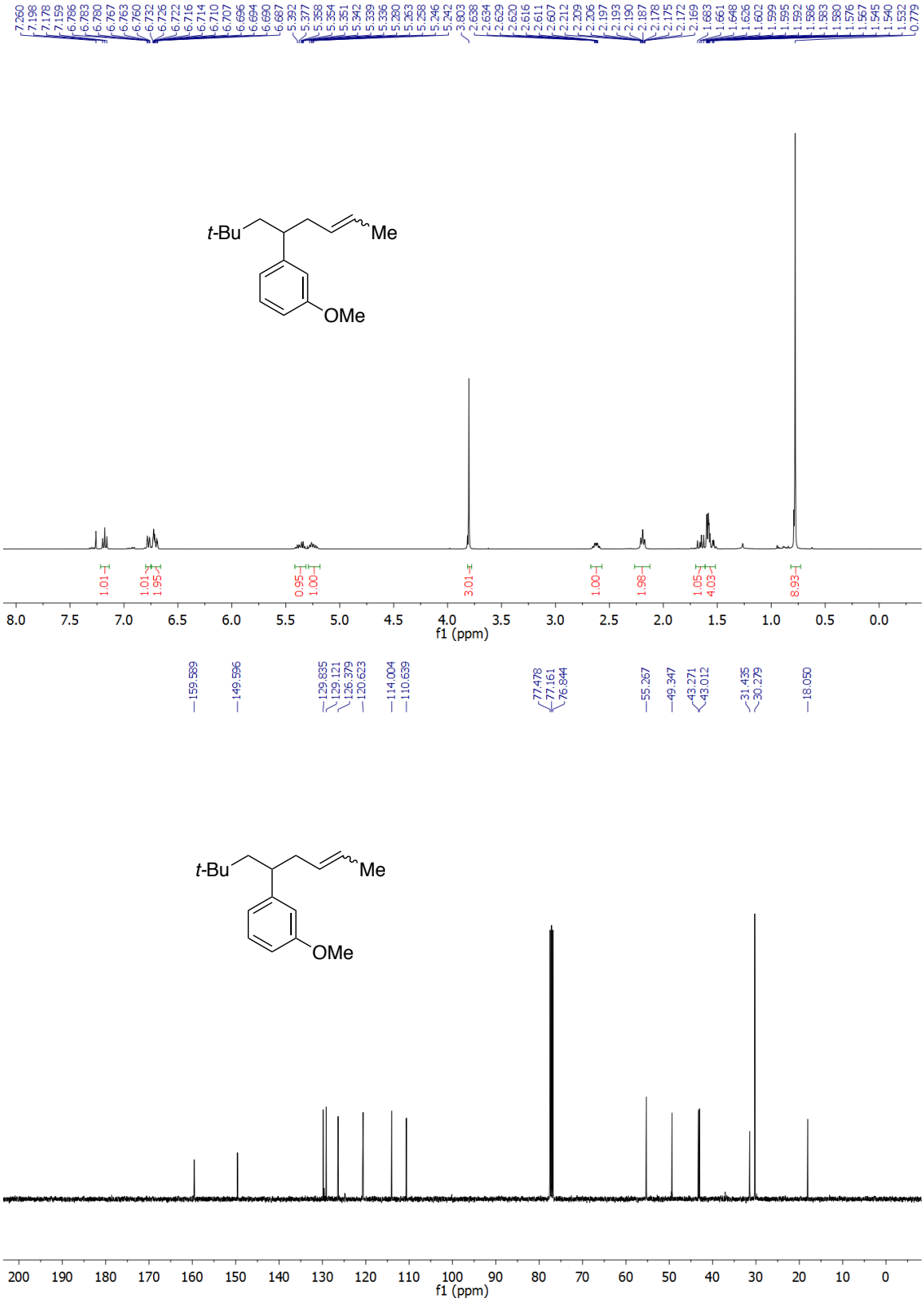




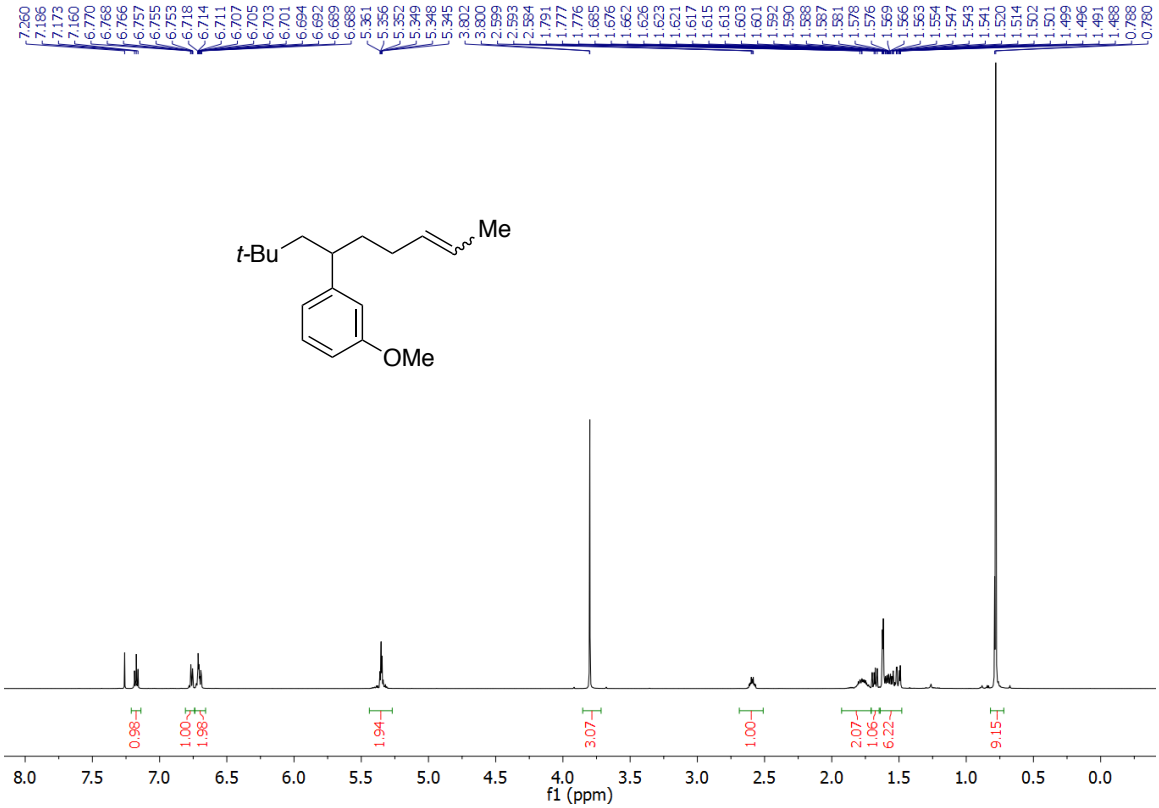
Compound 22. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

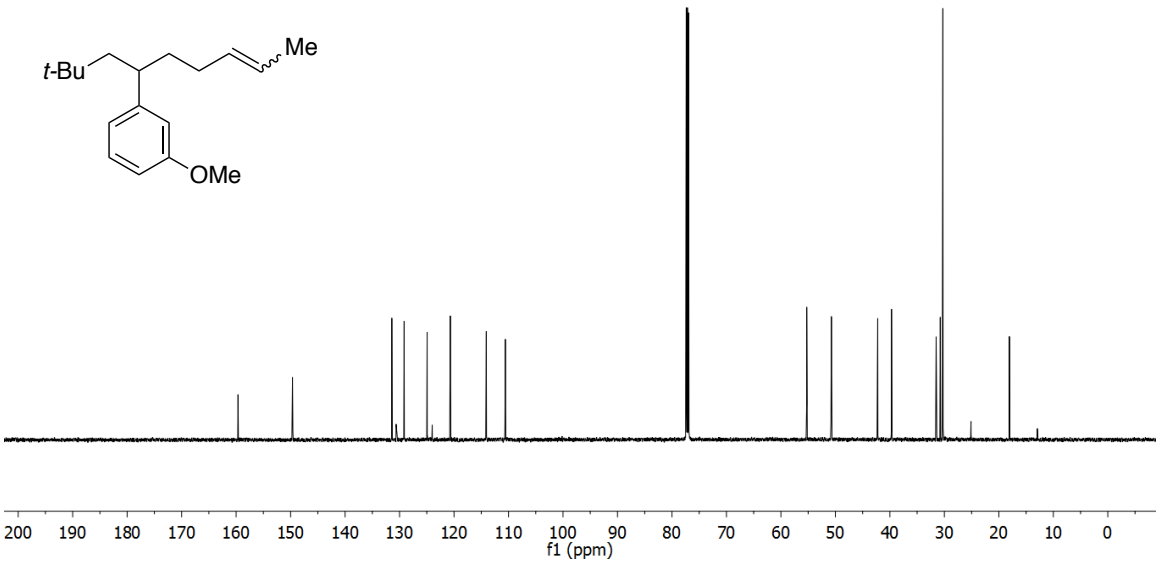


Compound 23. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

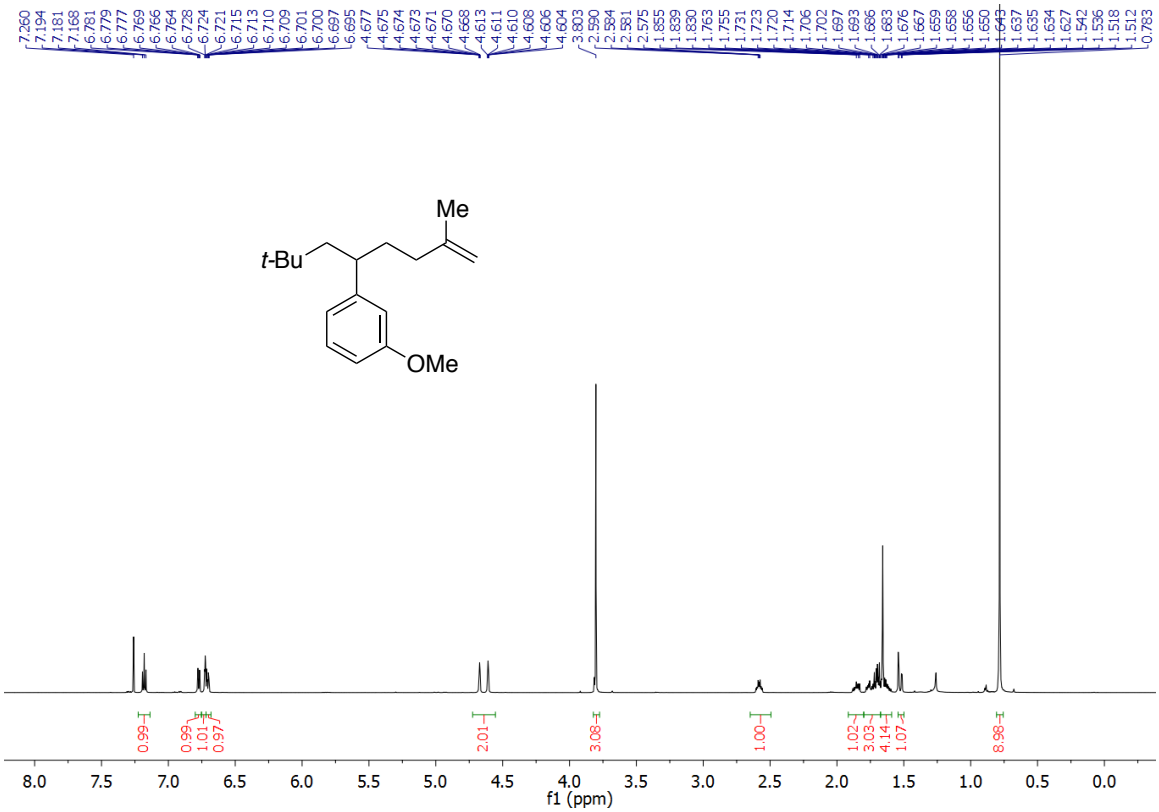


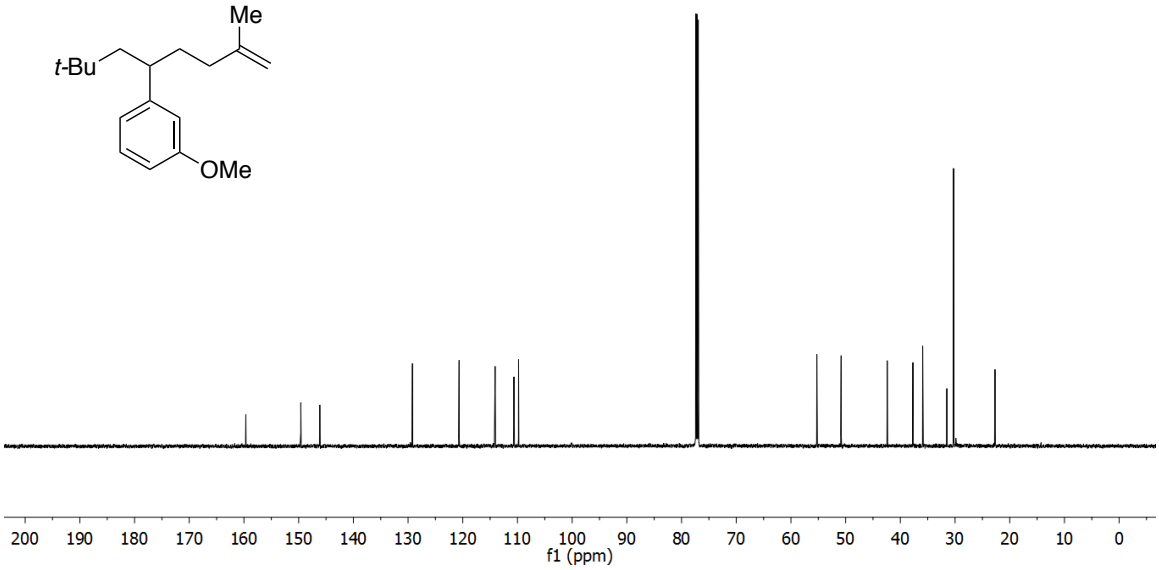
Compound 24. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



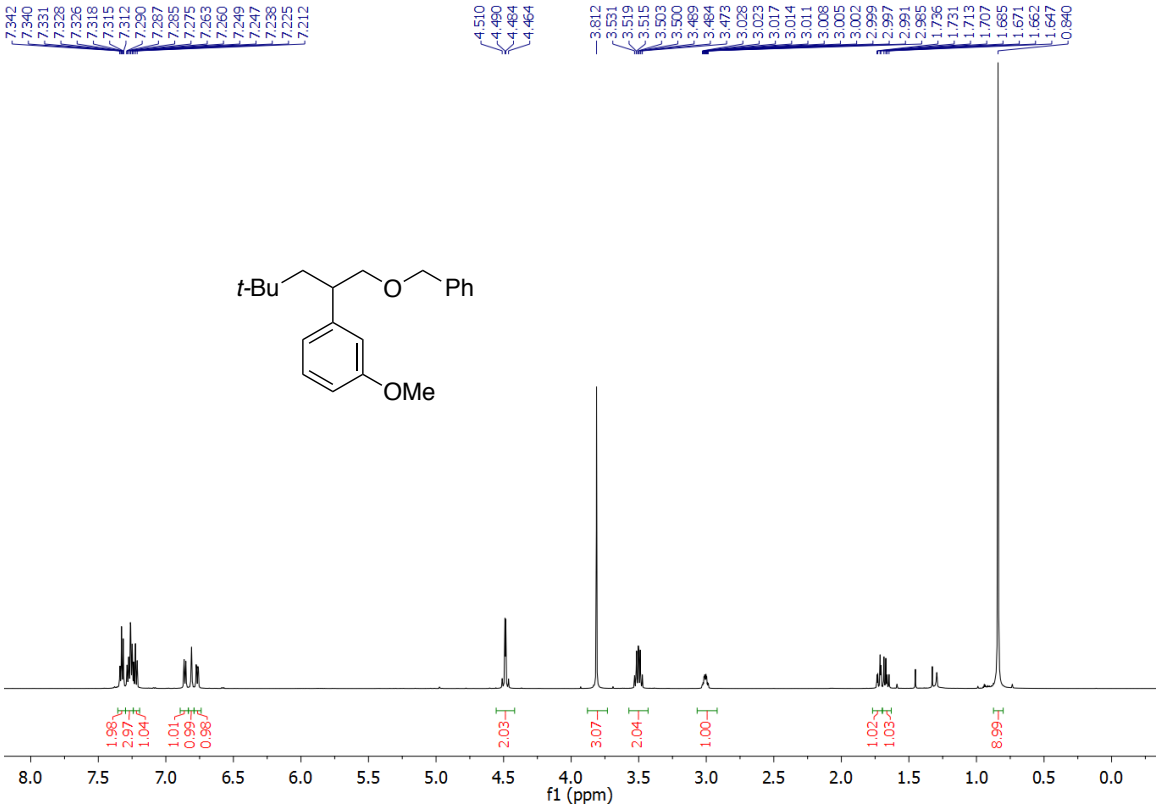


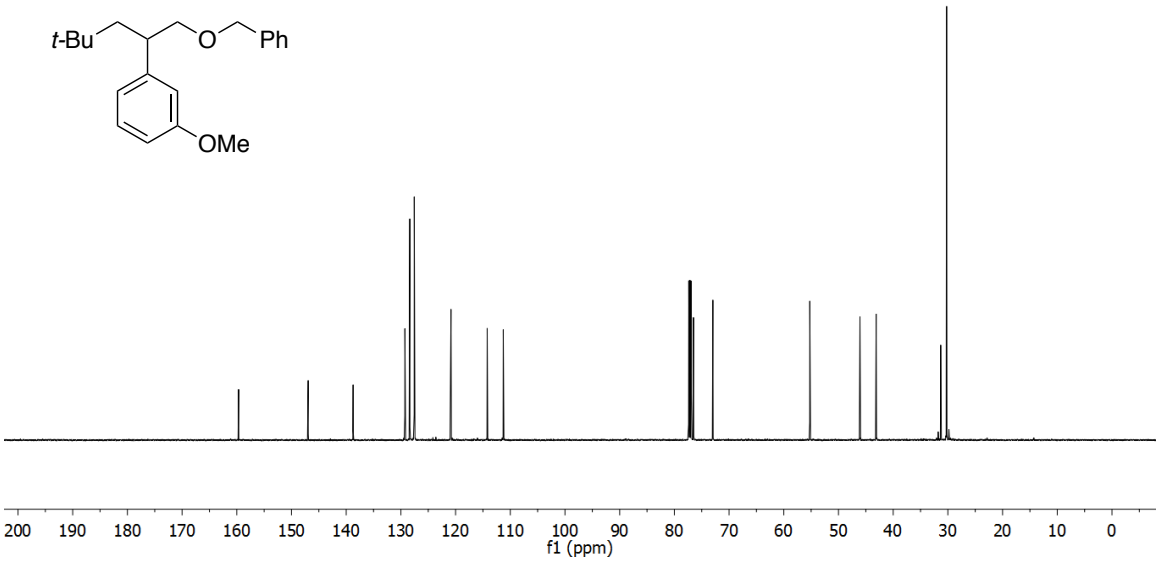
Compound 25. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



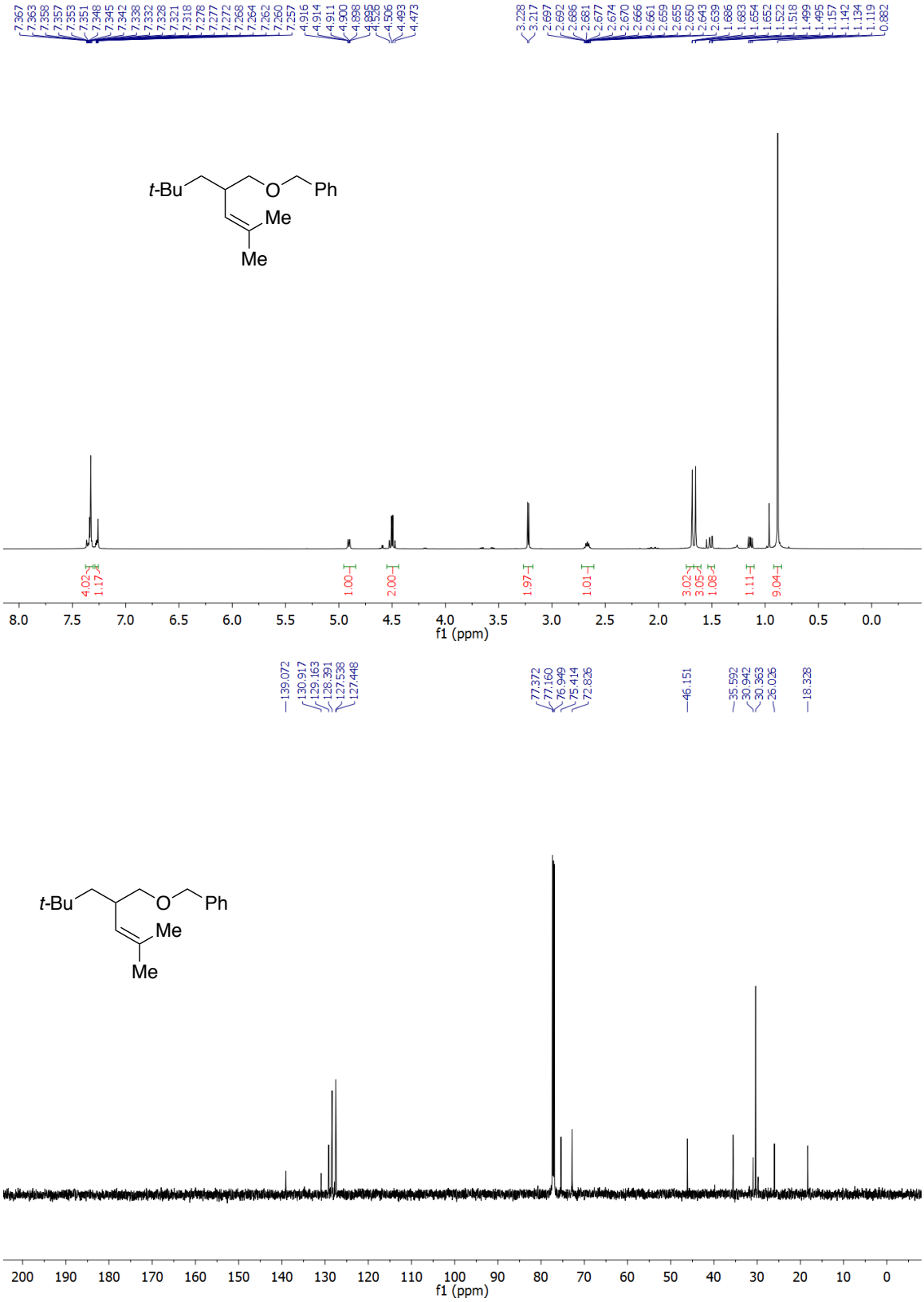


Compound 26. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

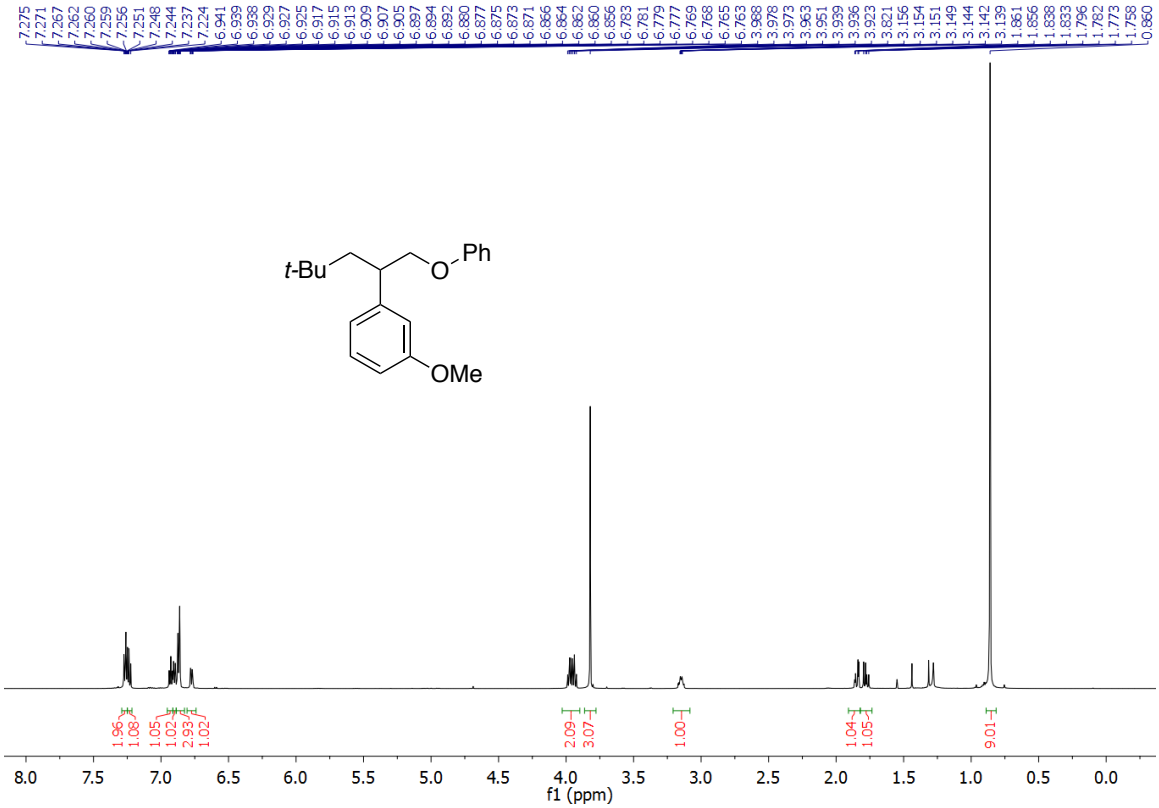


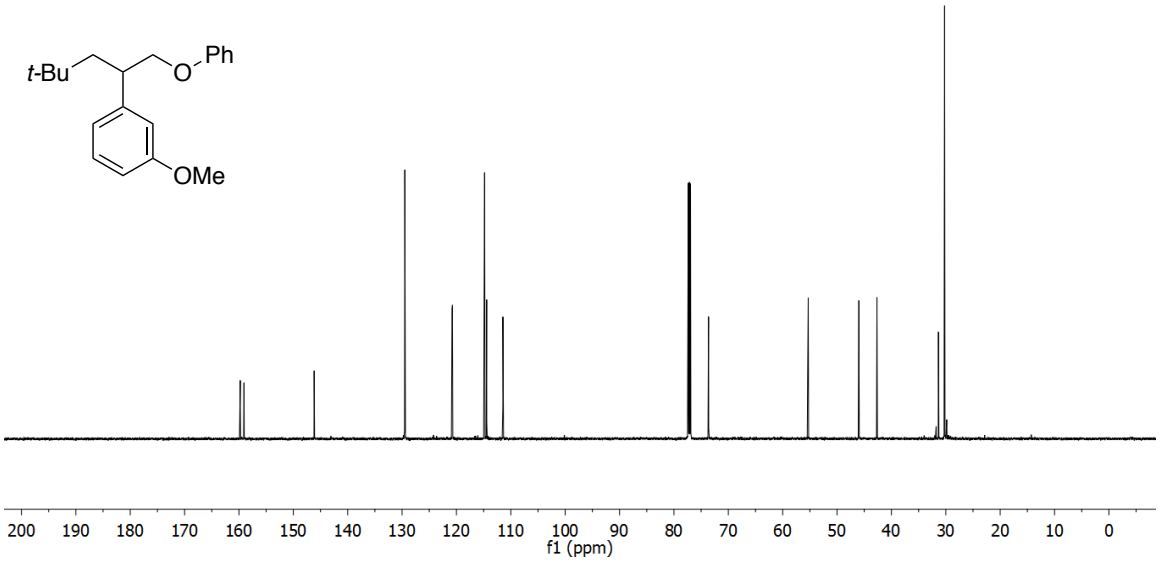


Compound 27. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

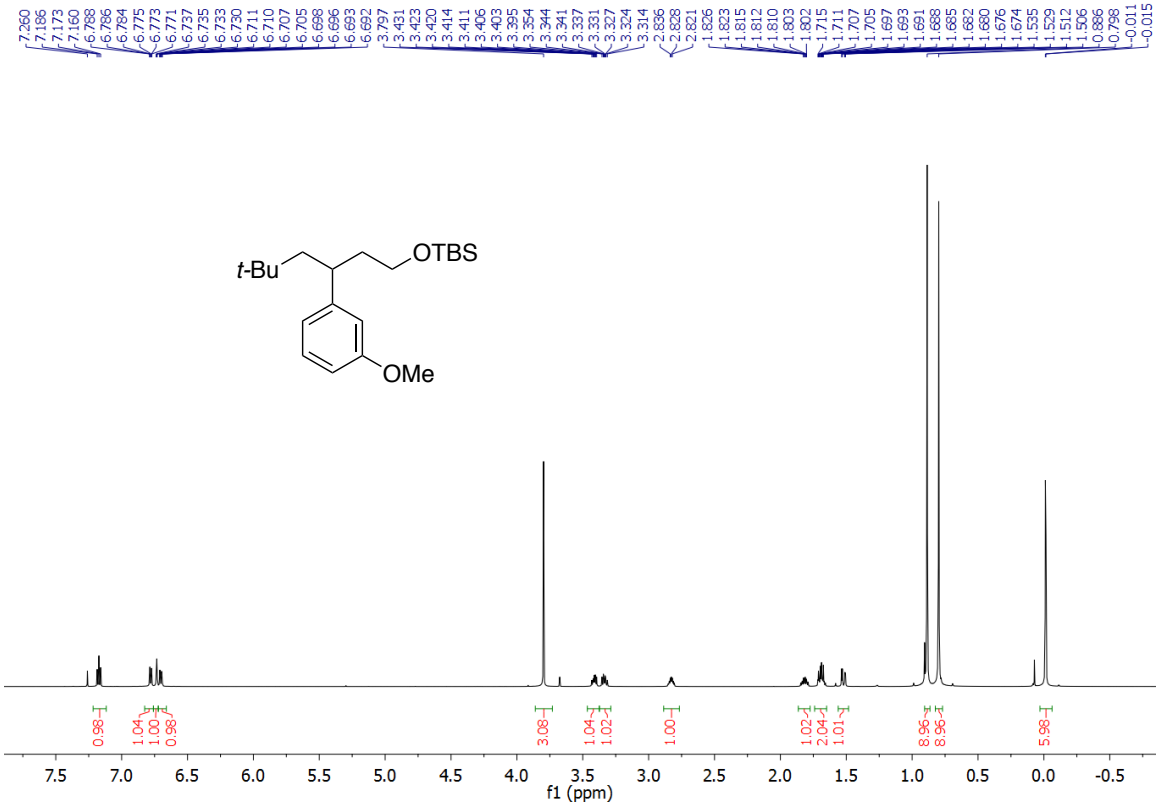


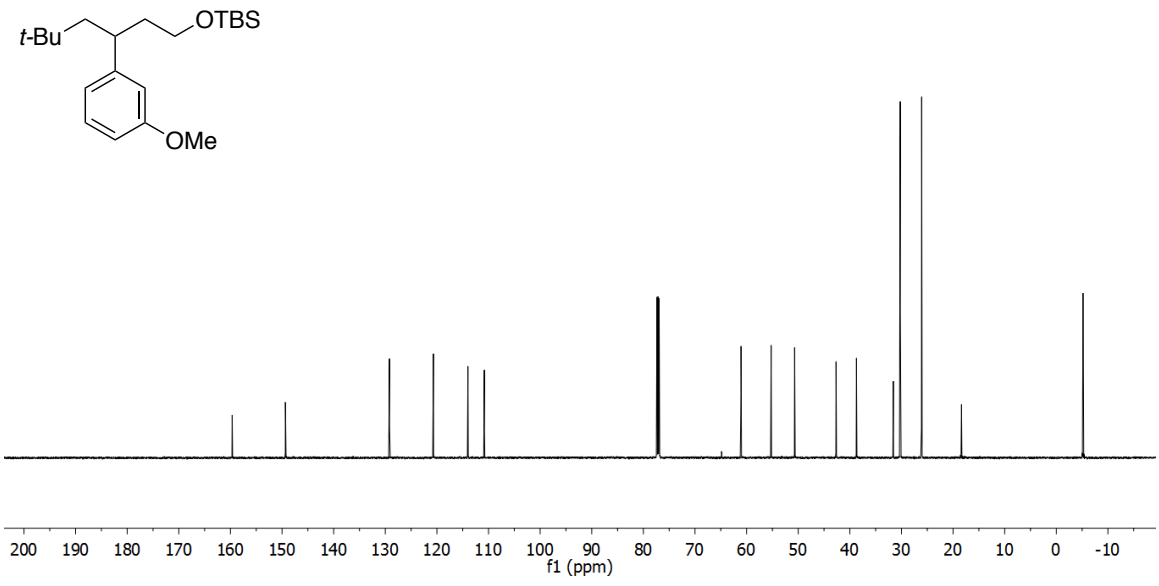
Compound 28. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



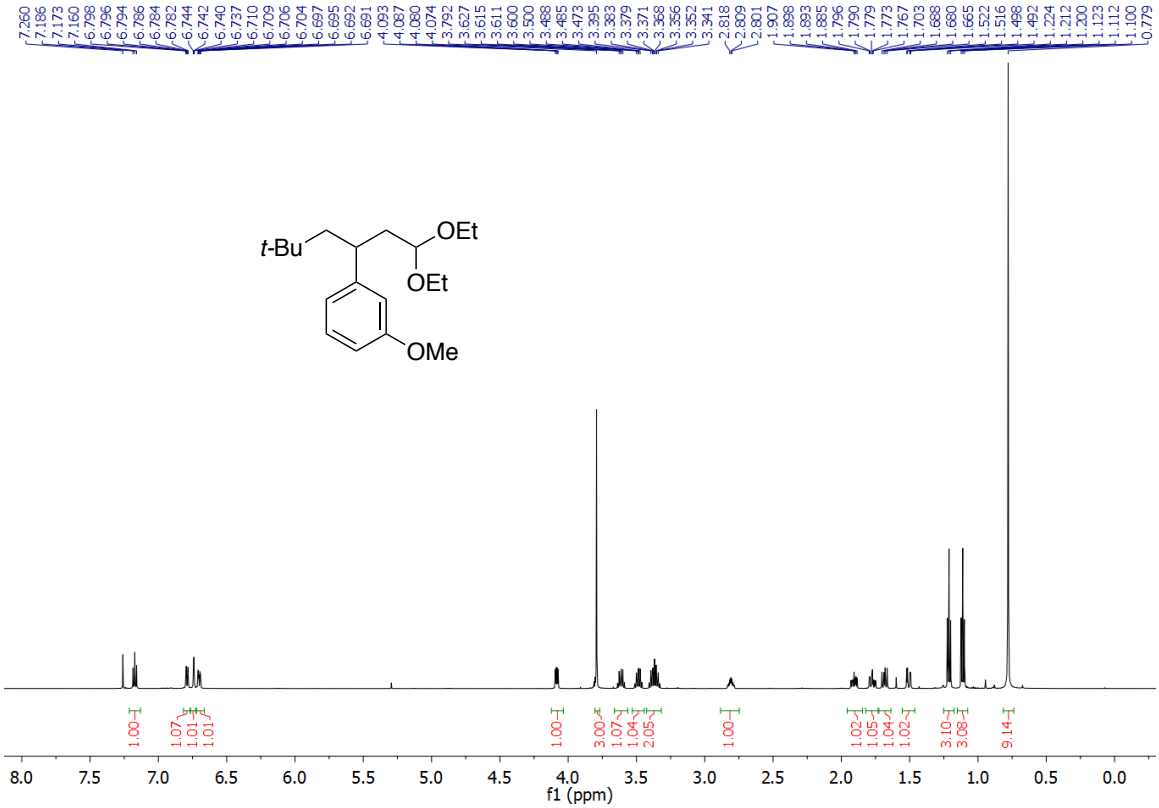


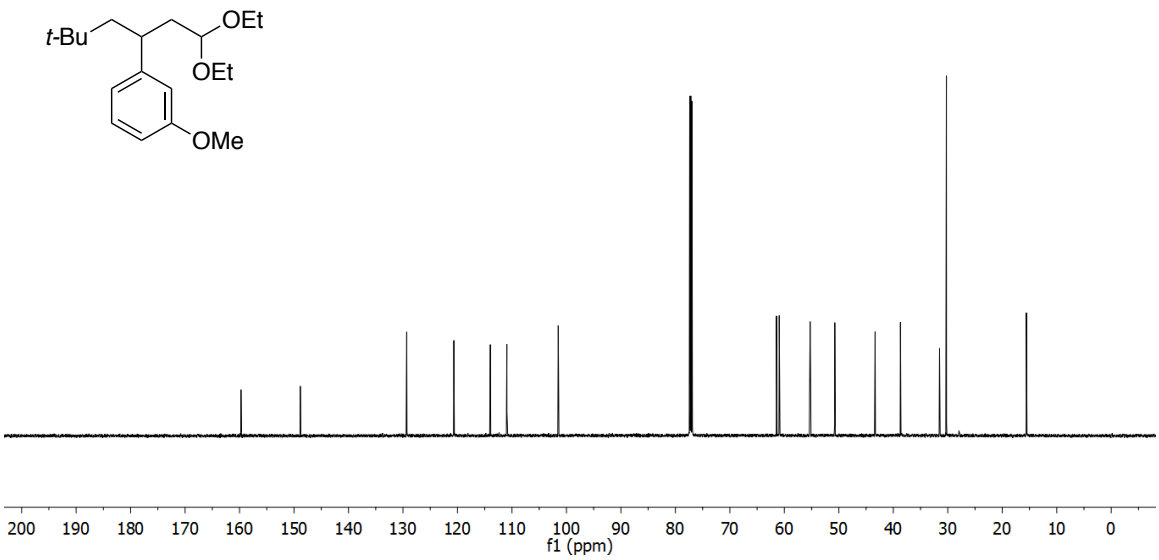
Compound 29. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



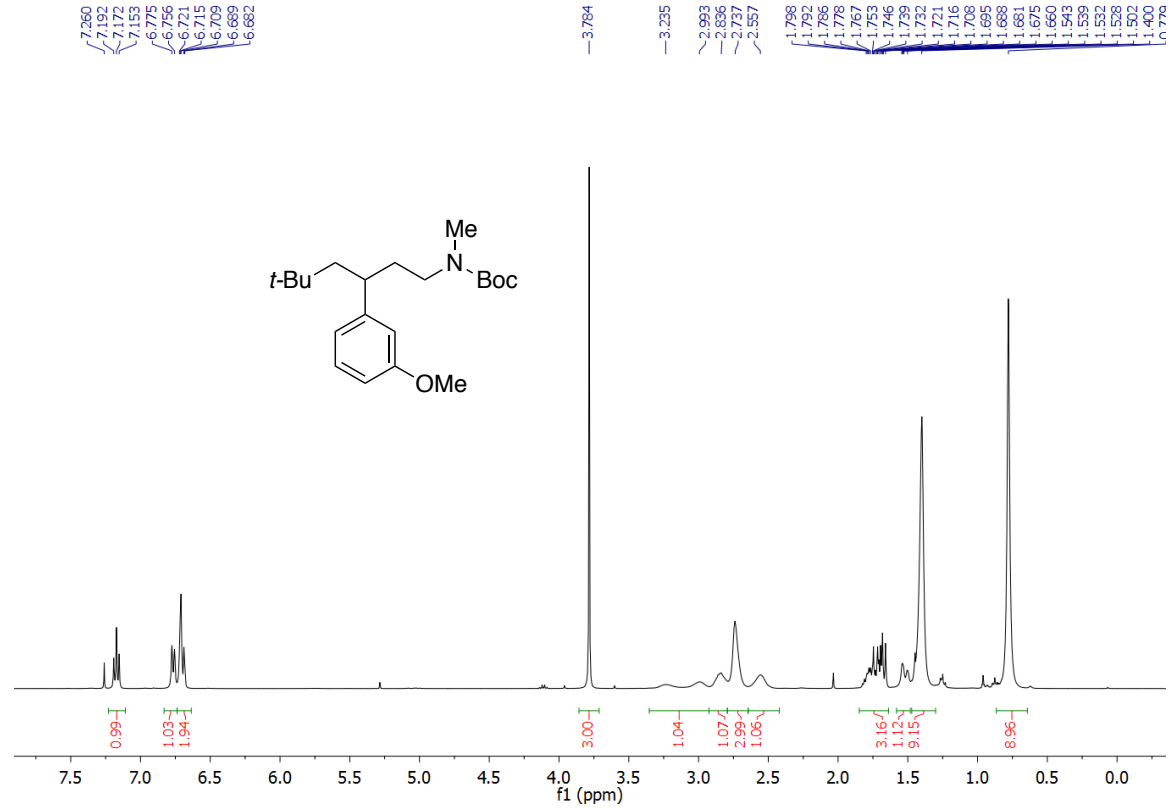


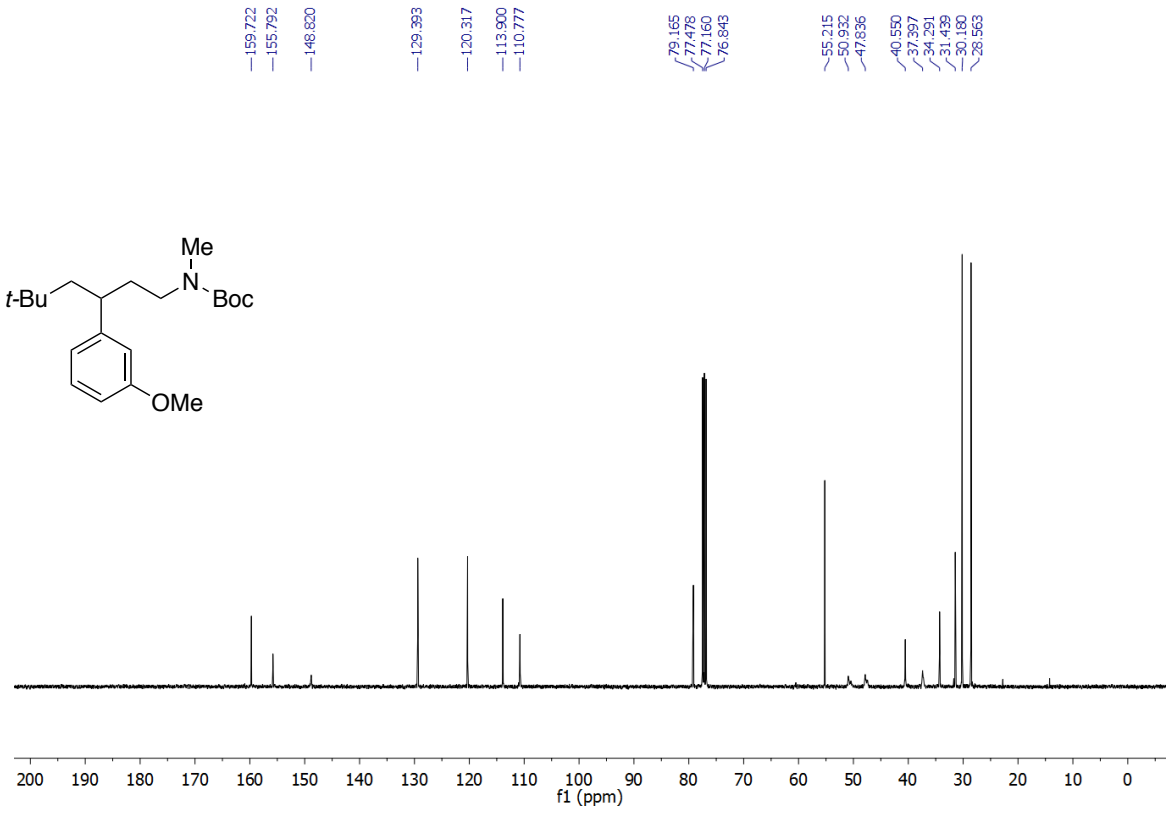
Compound 30. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



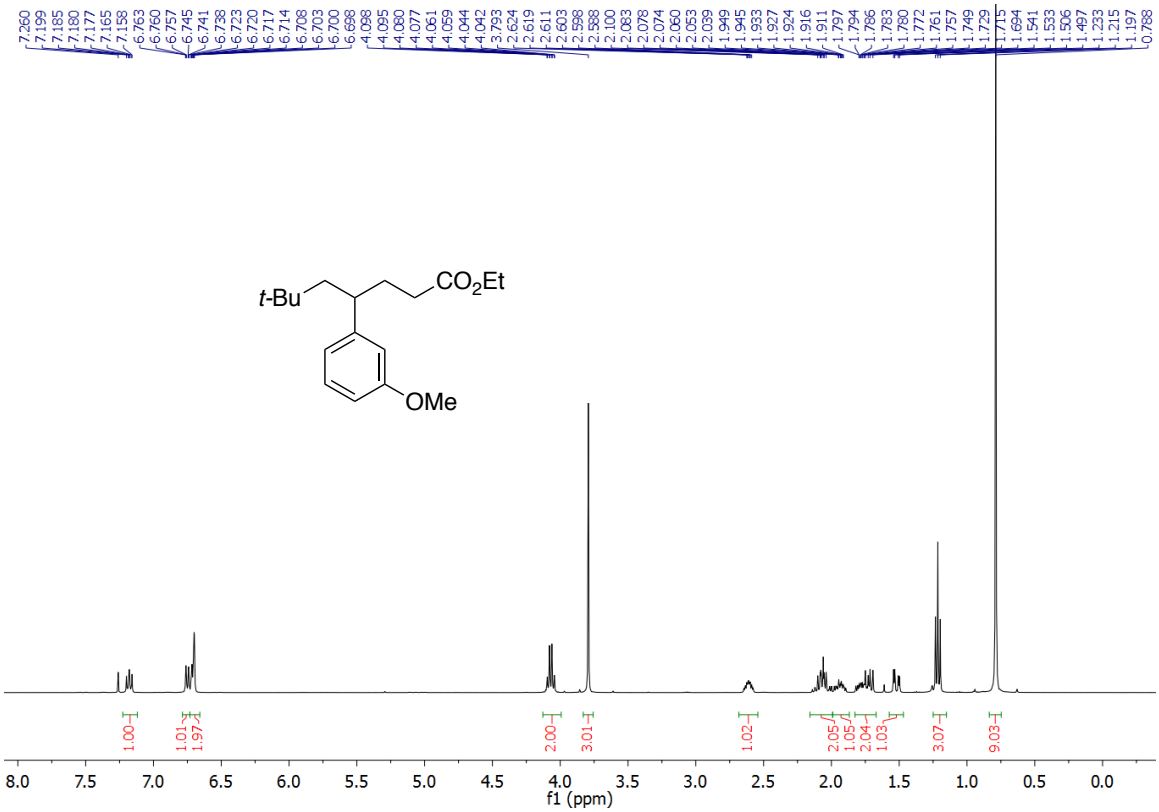


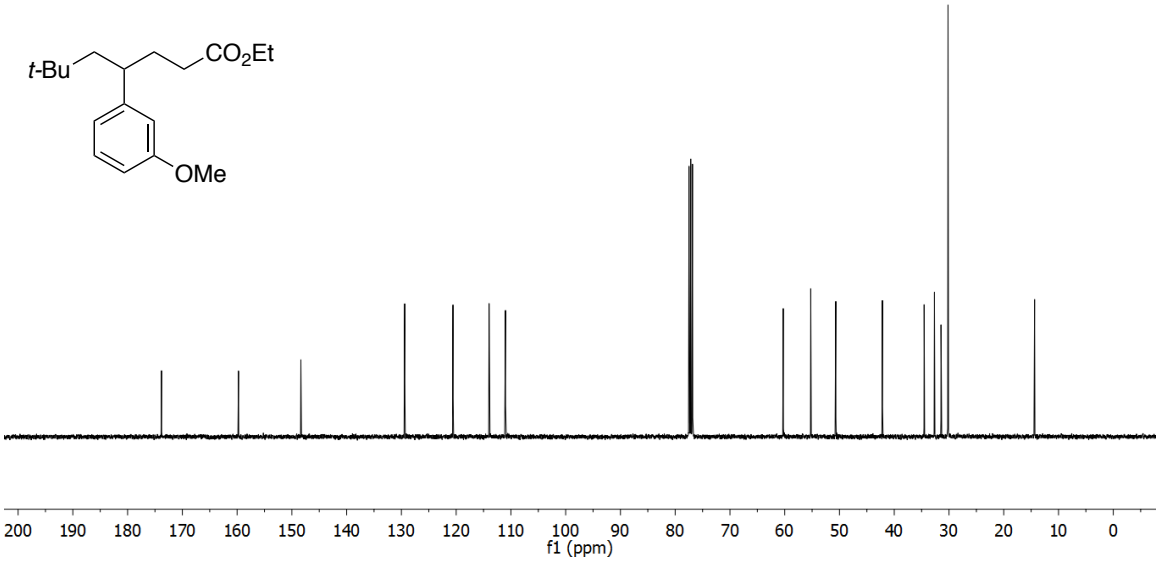
Compound 31. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



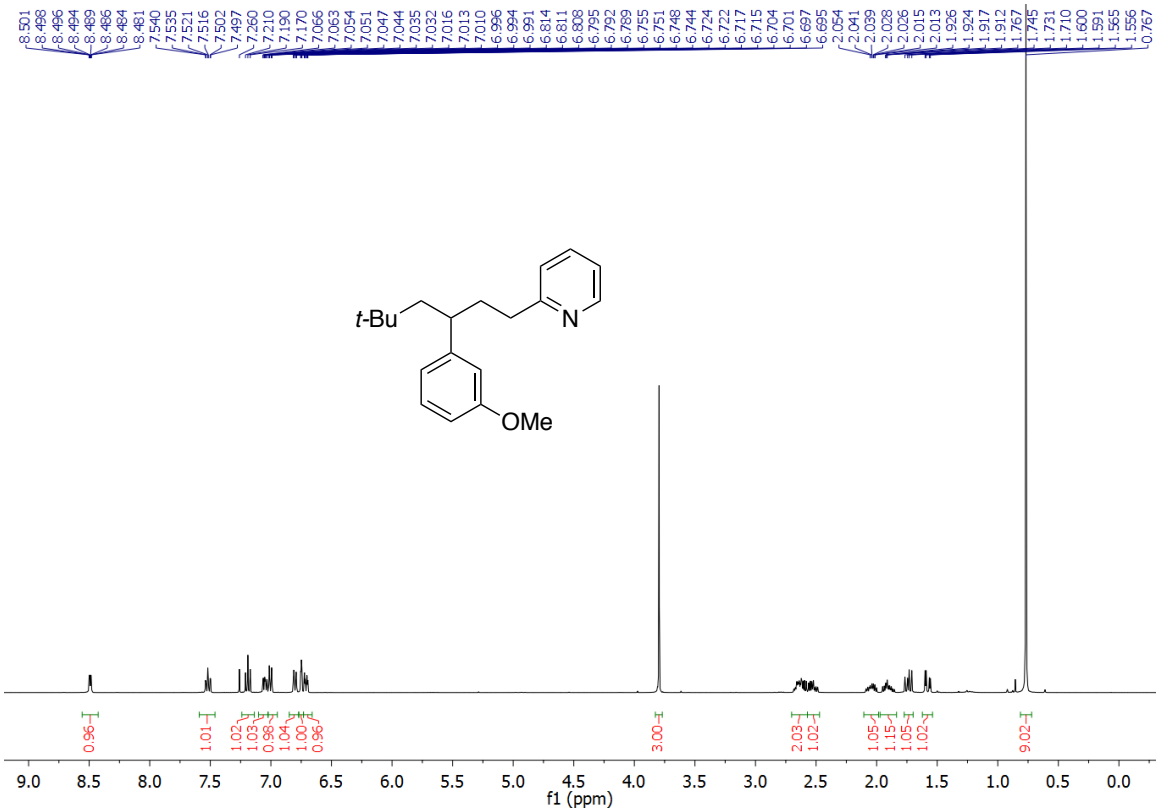


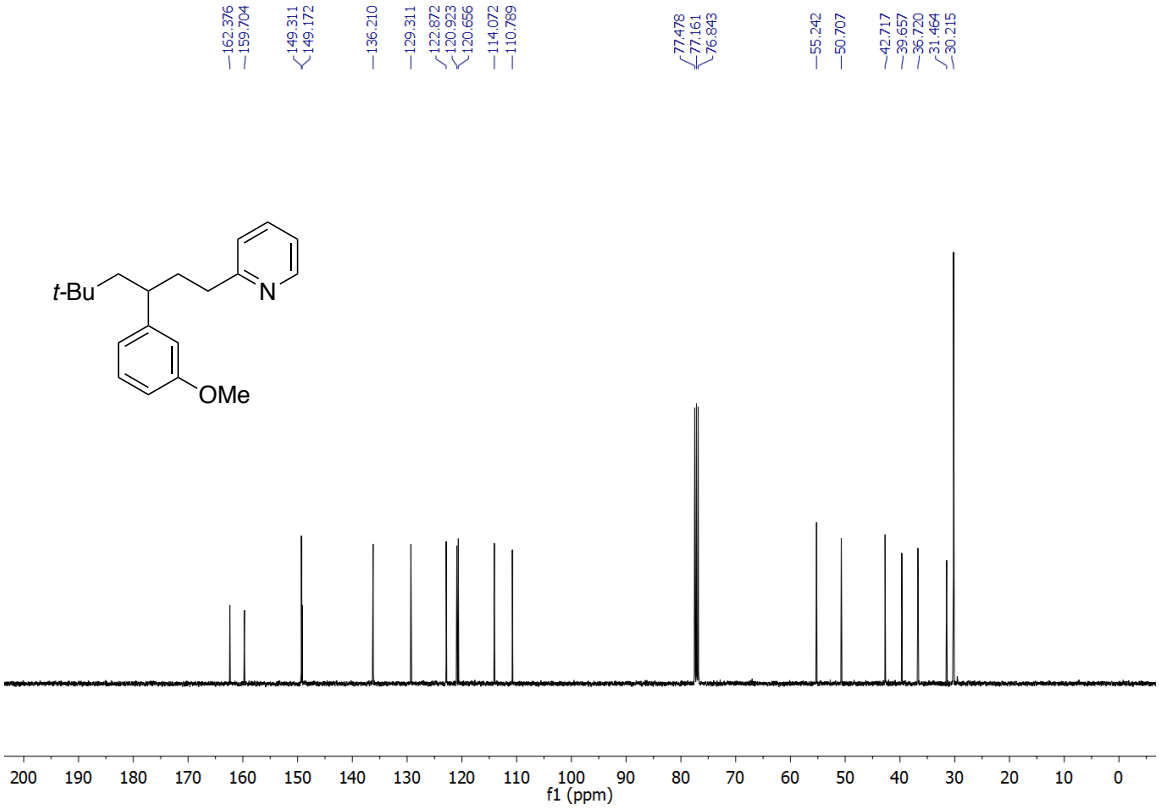
Compound 32. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



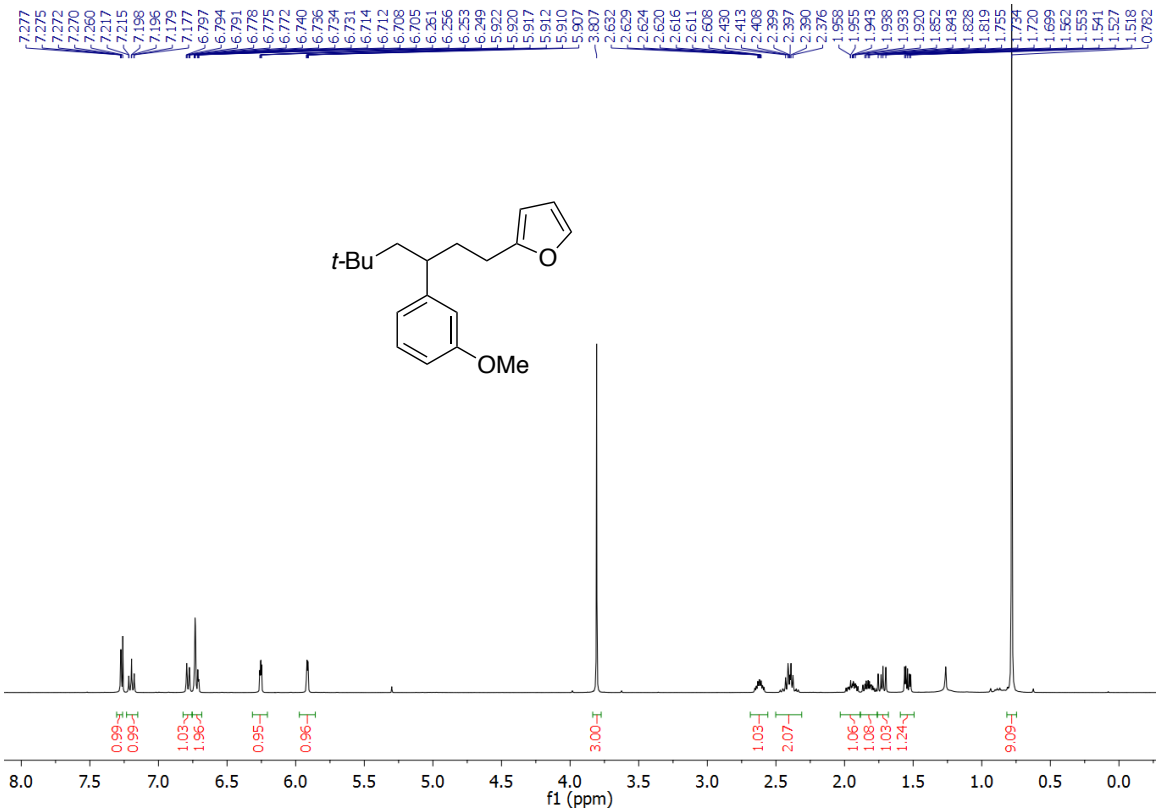


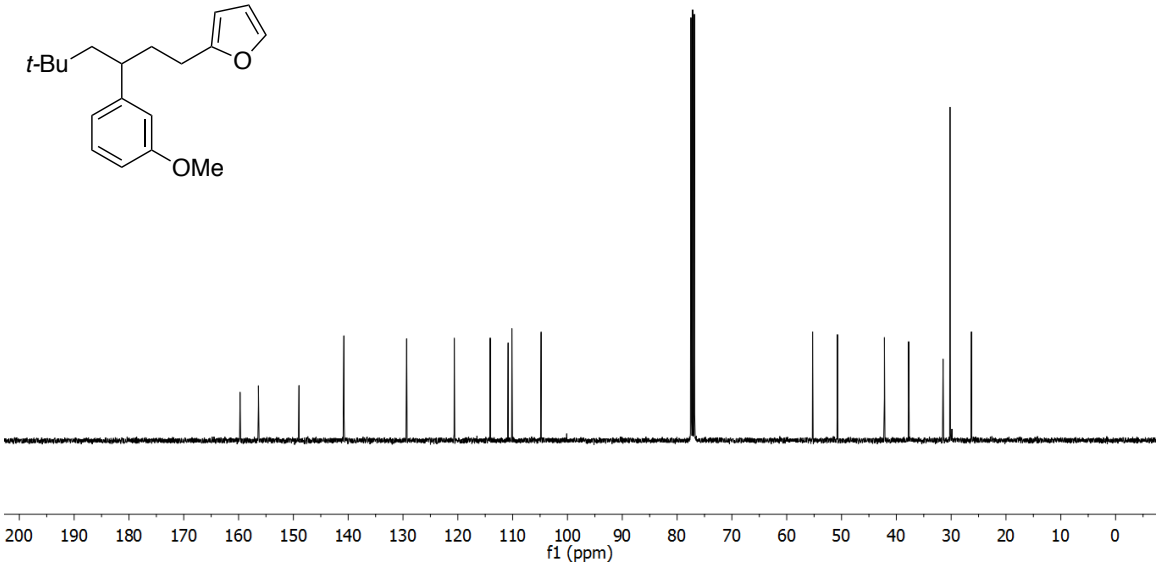
Compound 33. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



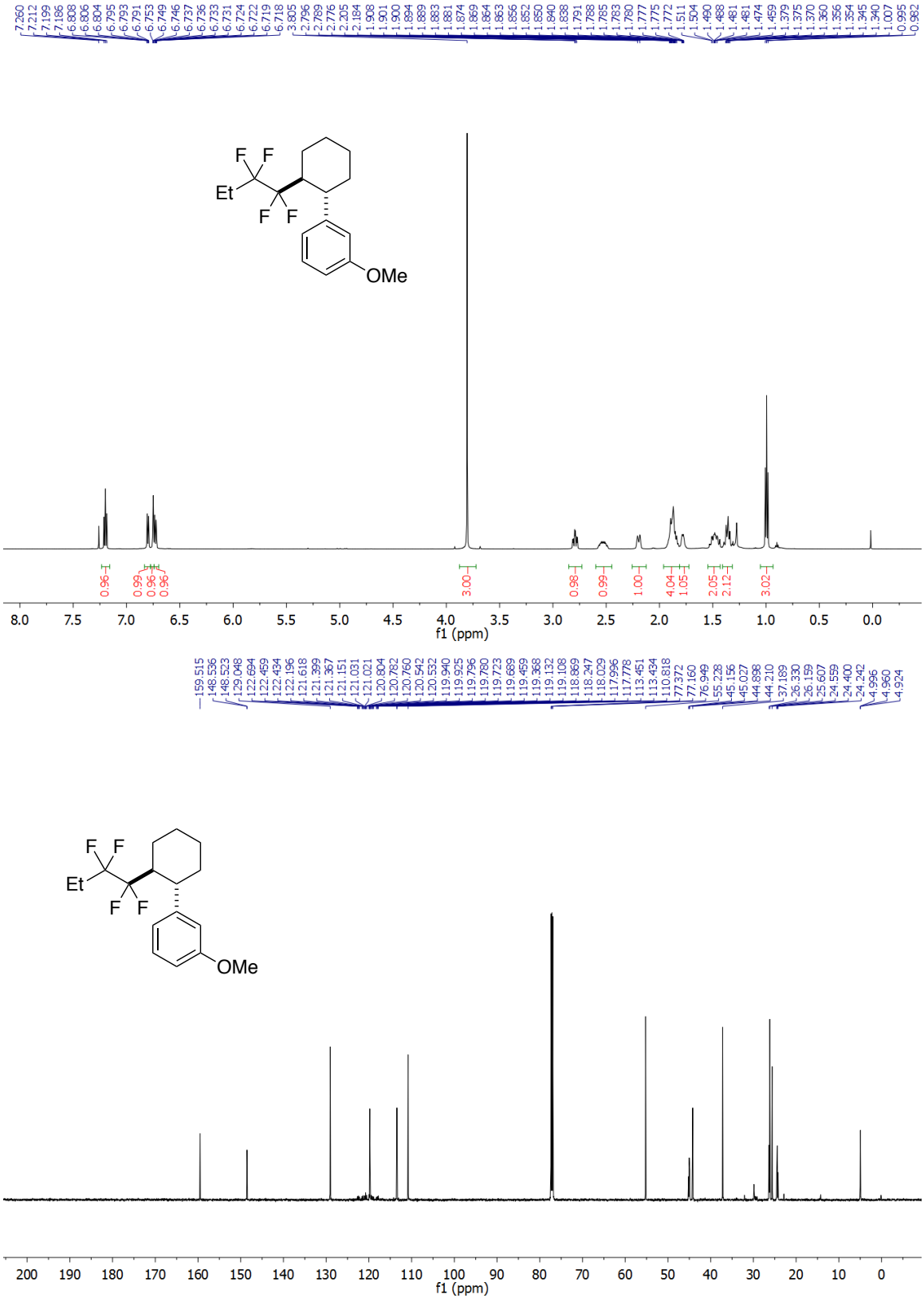


Compound 34. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

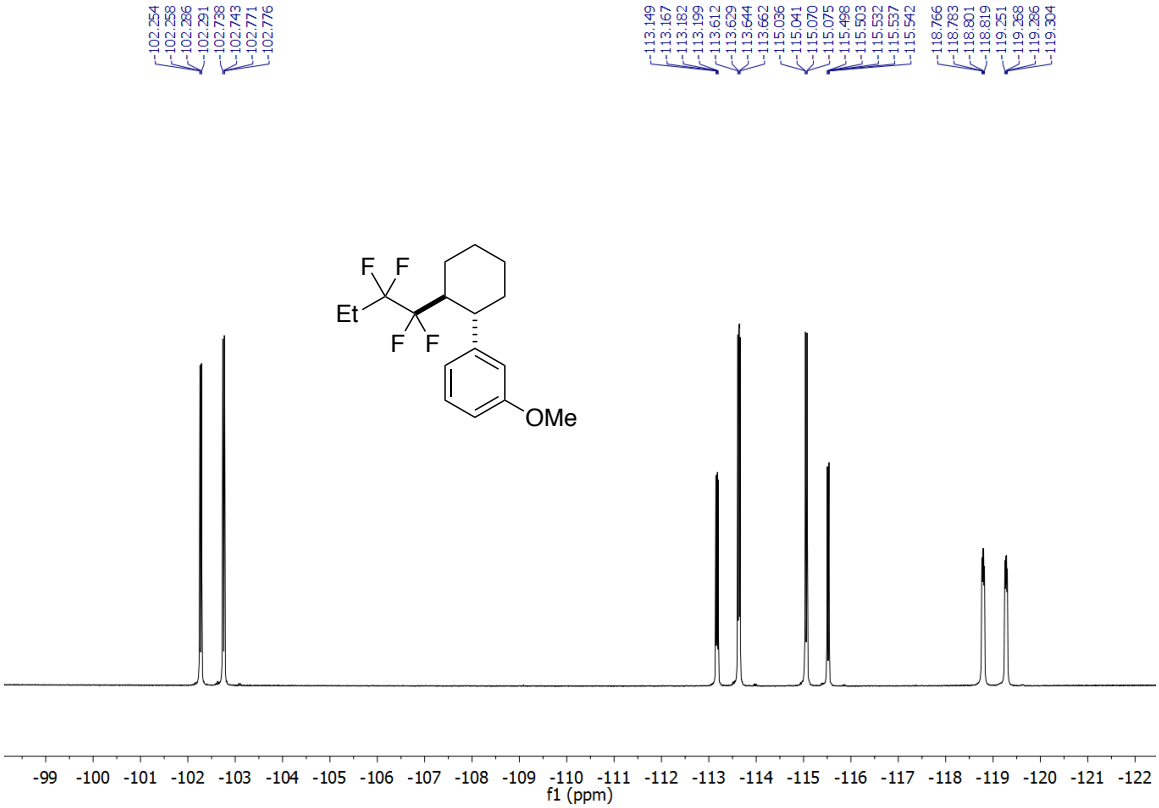




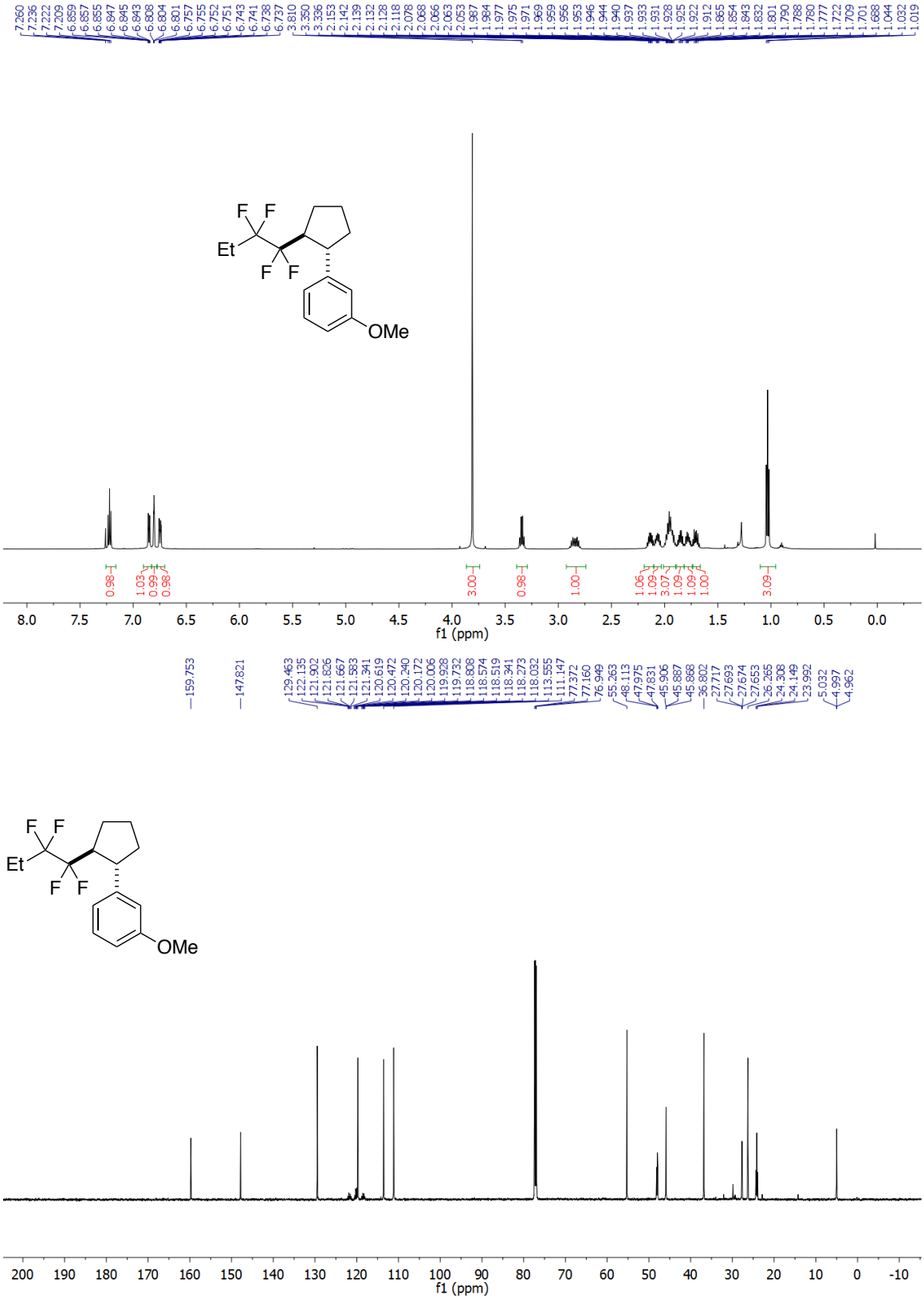
Compound 35. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



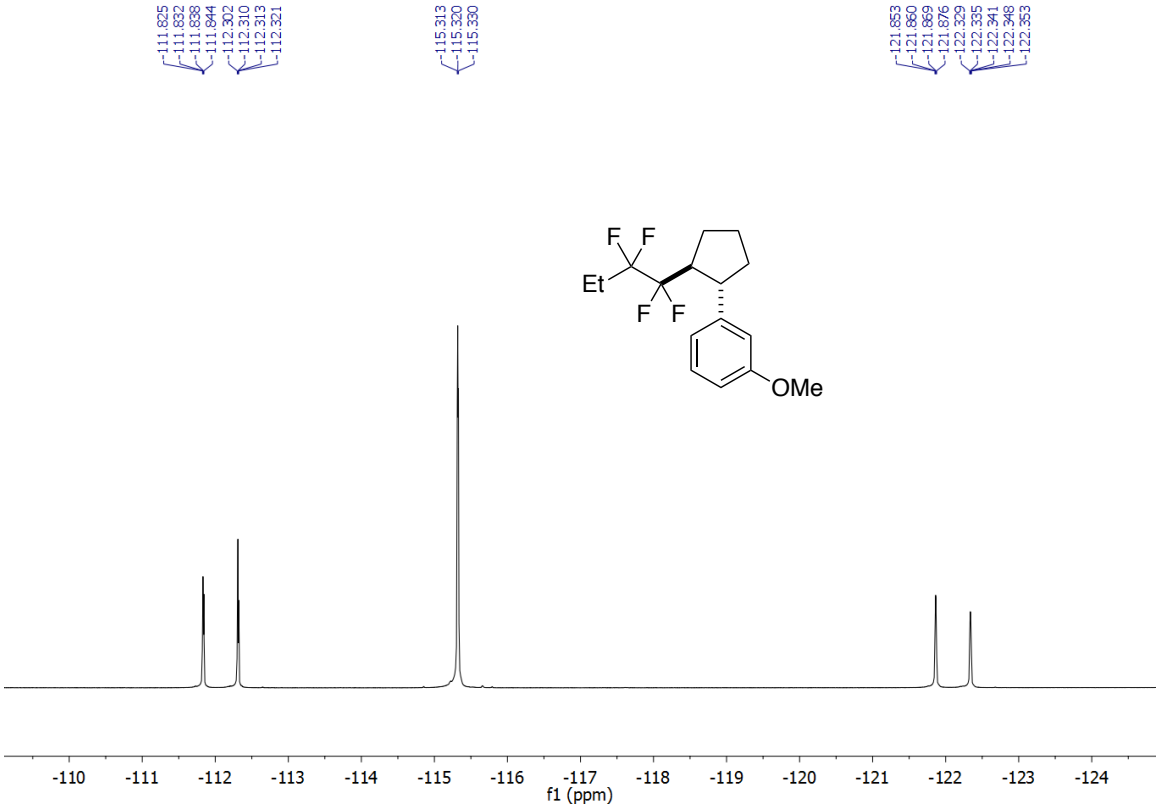
Compound 35. ^{19}F NMR ($CDCl_3$, 565 MHz).



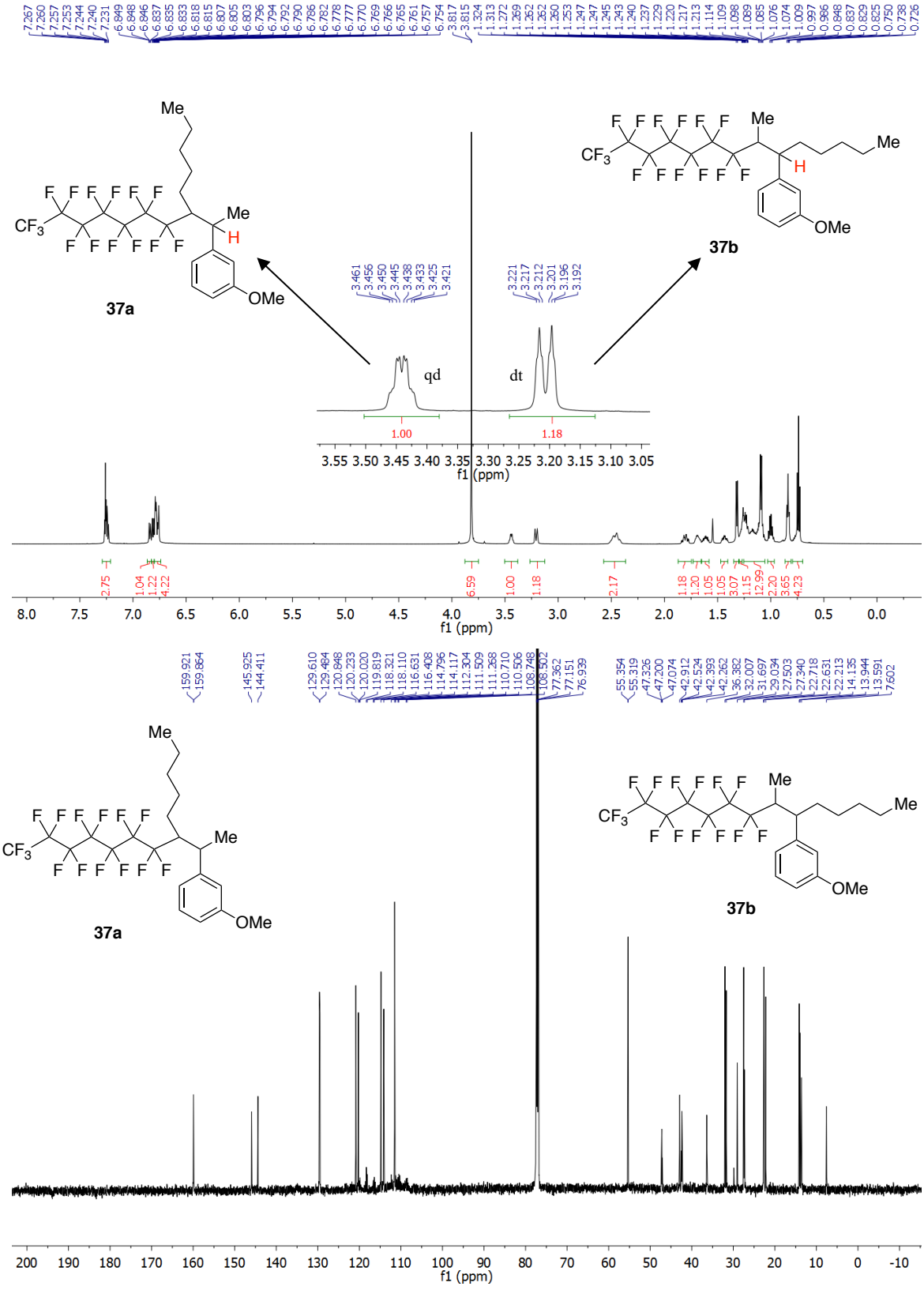
Compound 36. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



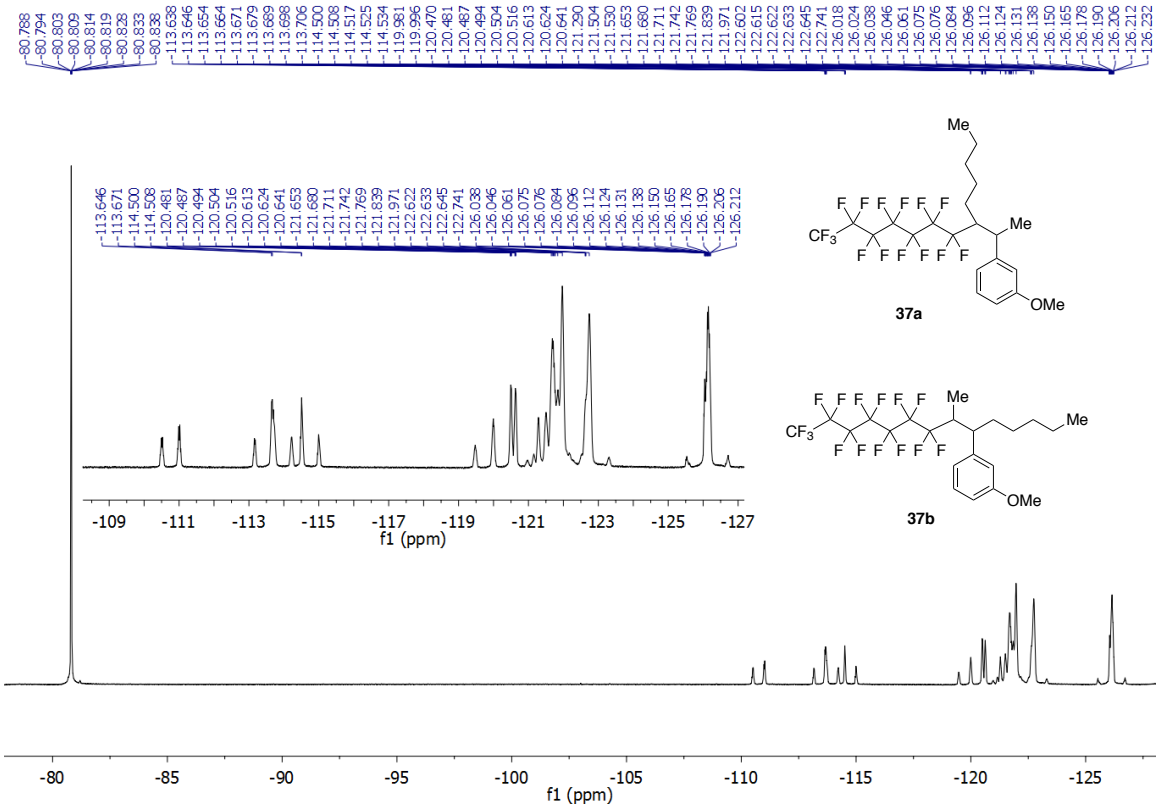
Compound 36. ^{19}F NMR ($CDCl_3$, 565 MHz).



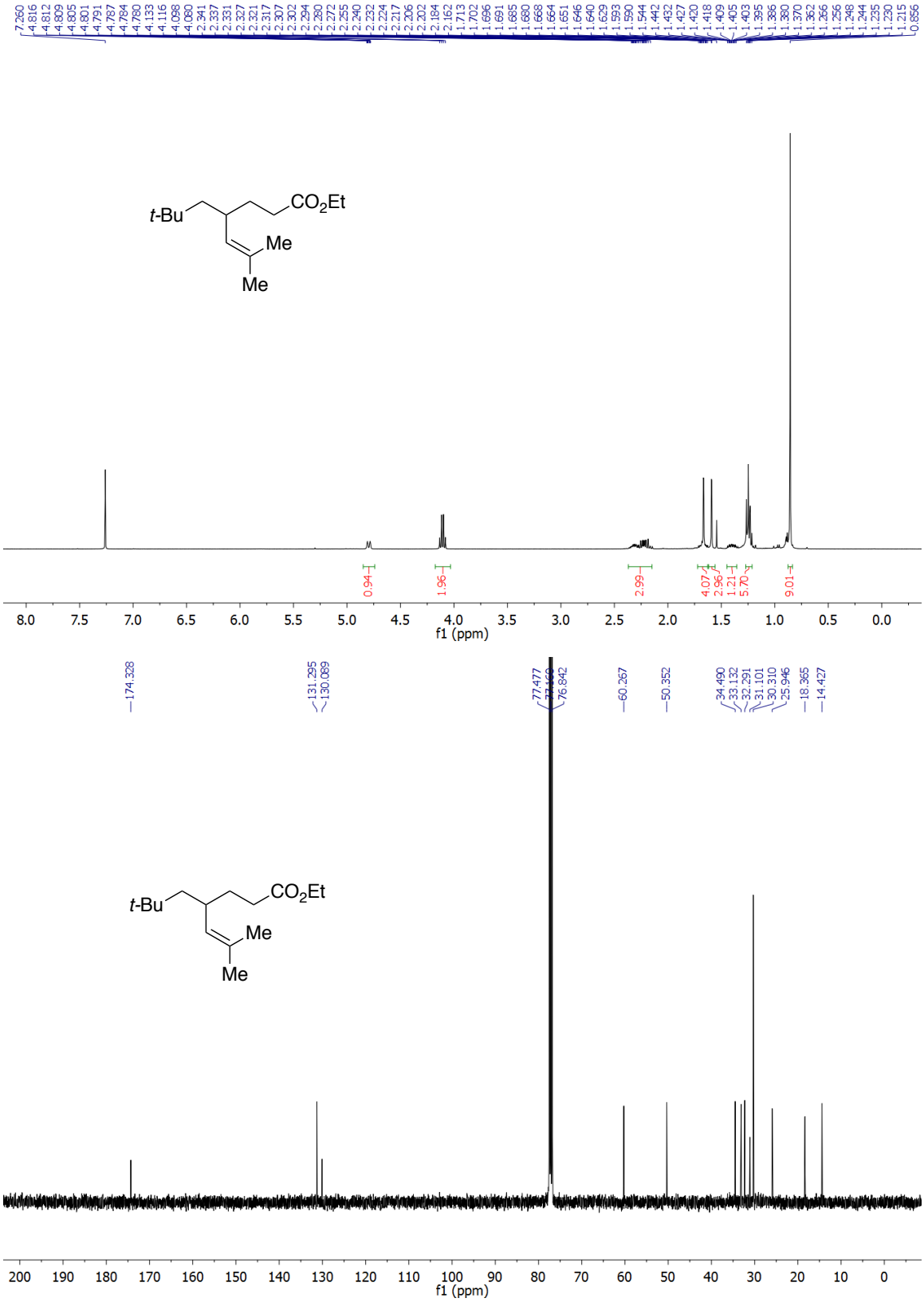
Mixture 37. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



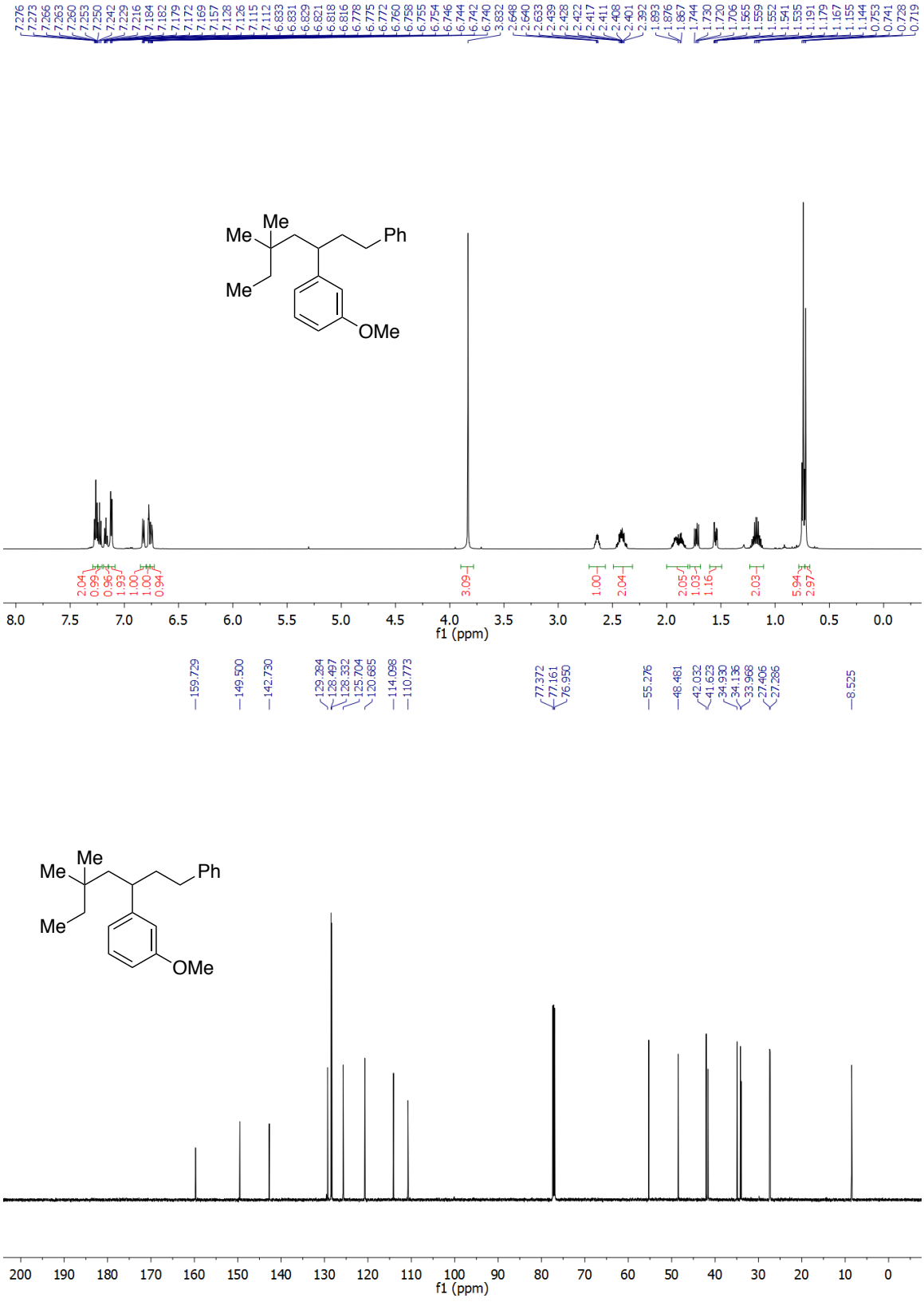
Mixture 37. ^{19}F NMR ($CDCl_3$, 565 MHz).



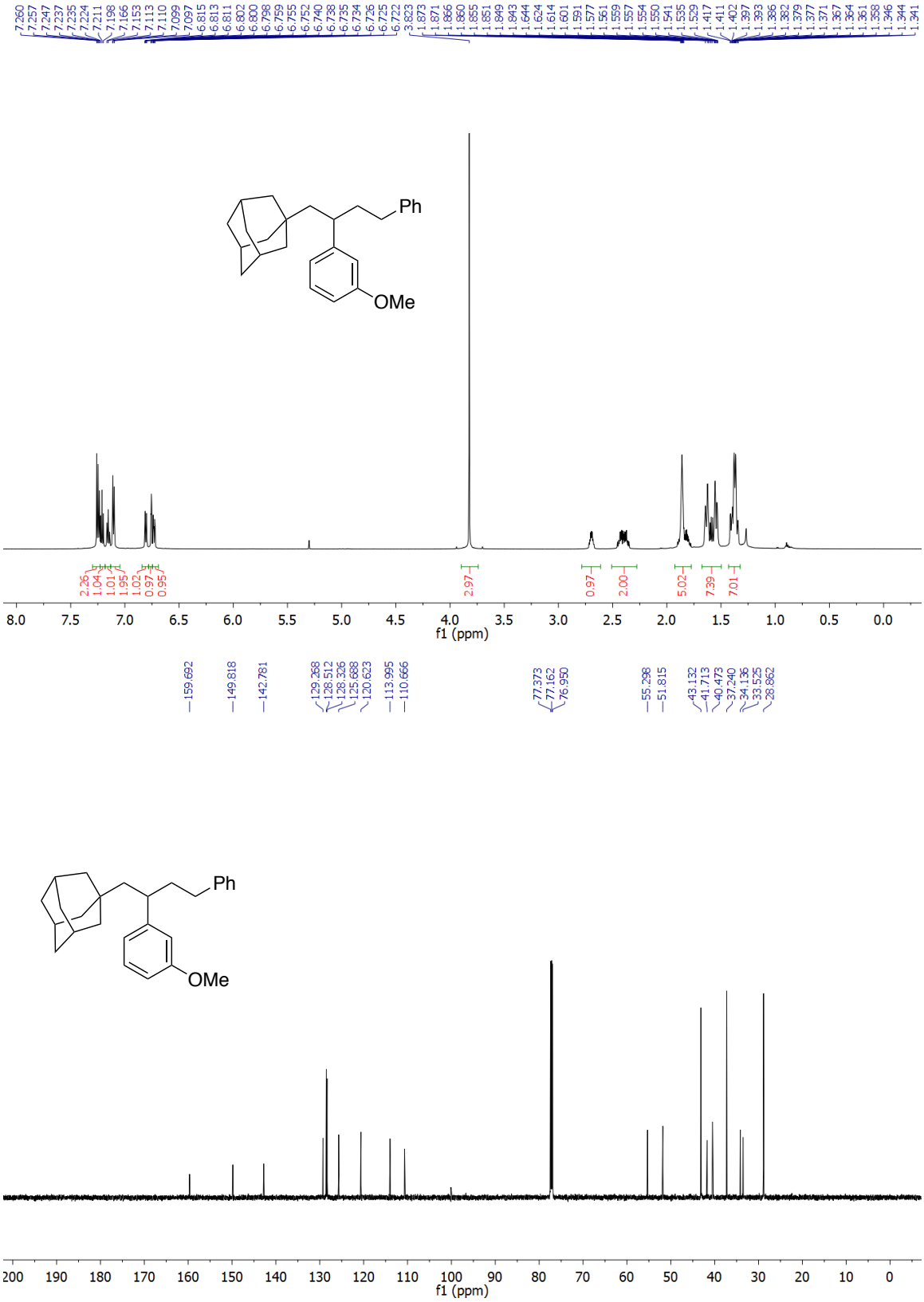
Compound 44. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



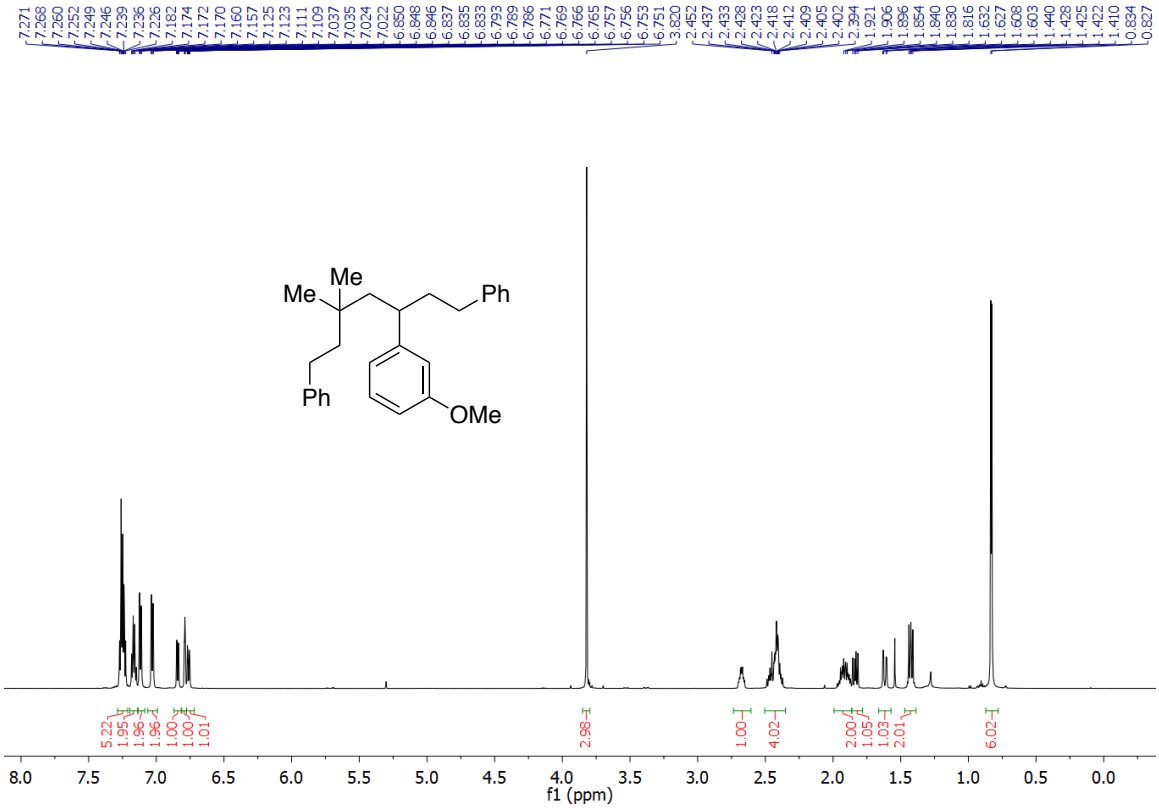
Compound 51. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

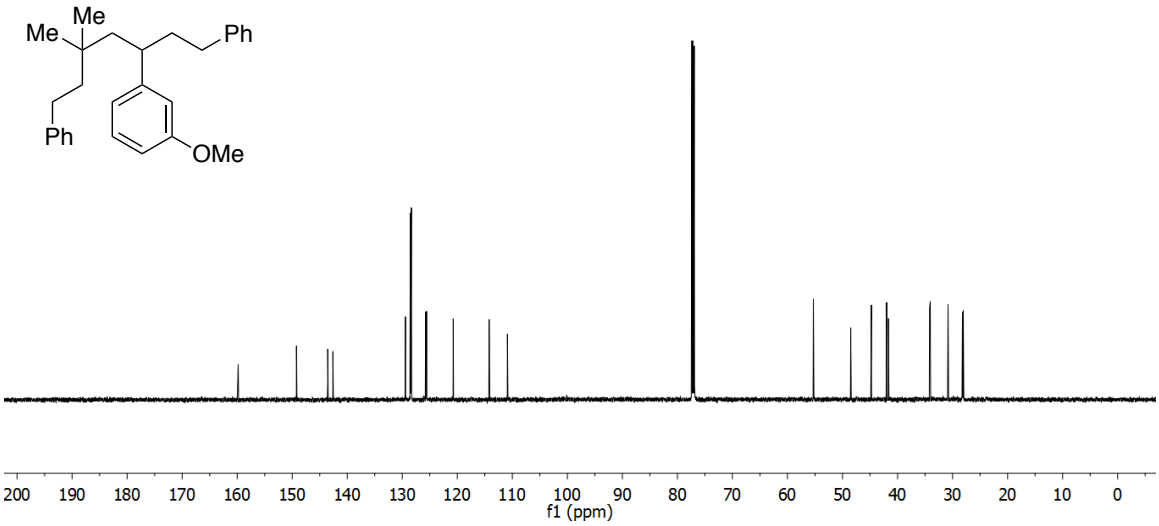


Compound 53. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

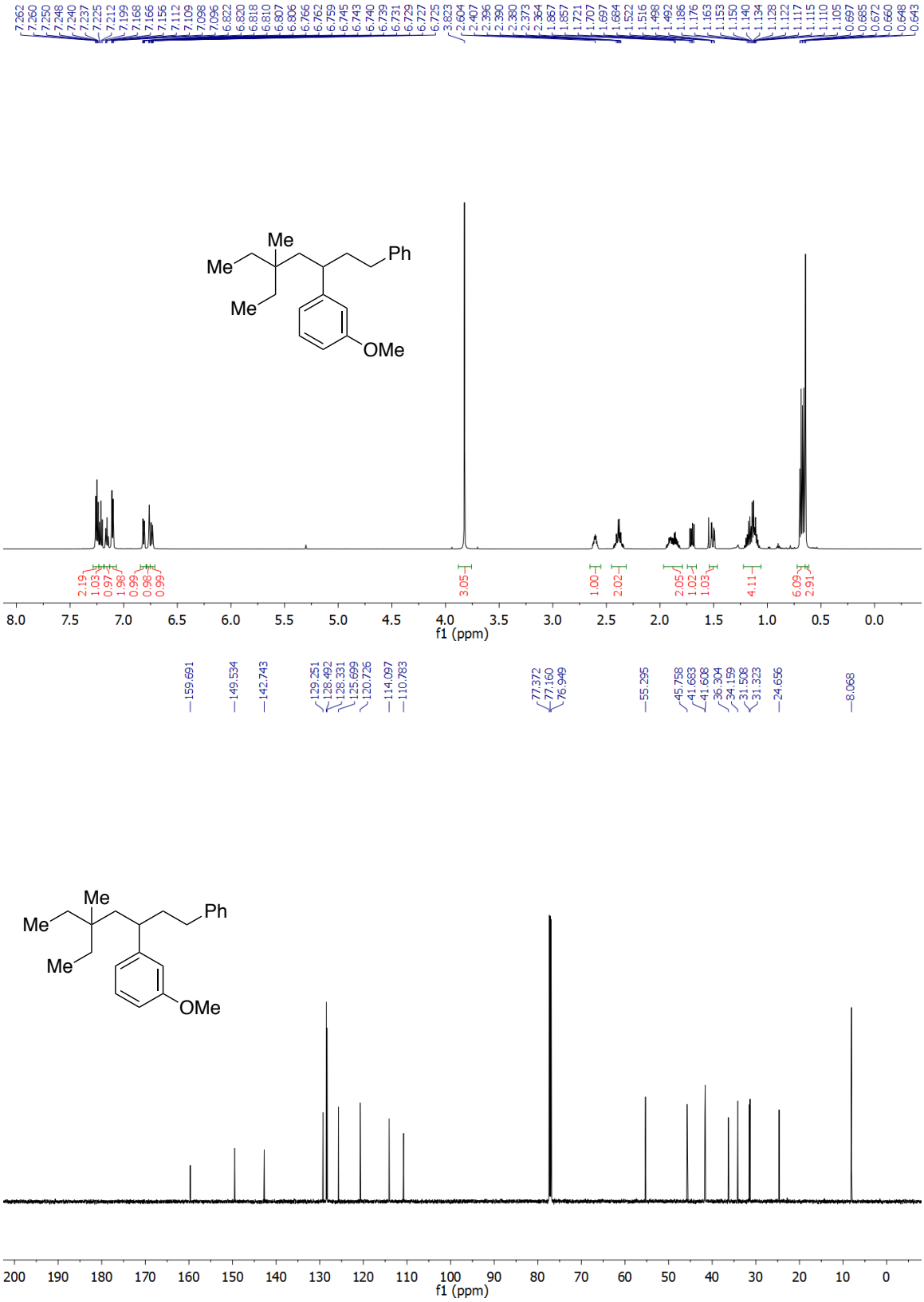


Compound 54. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

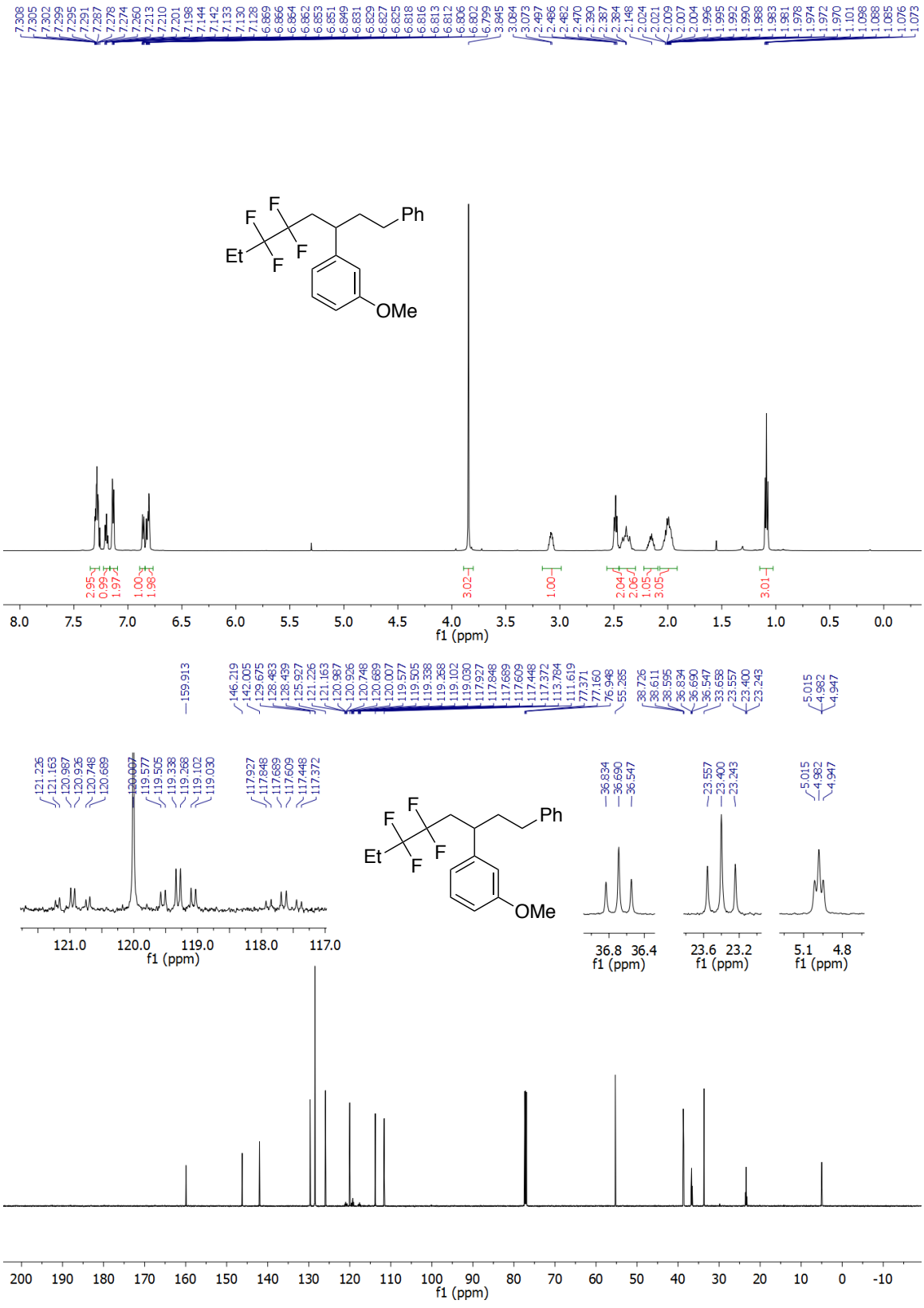




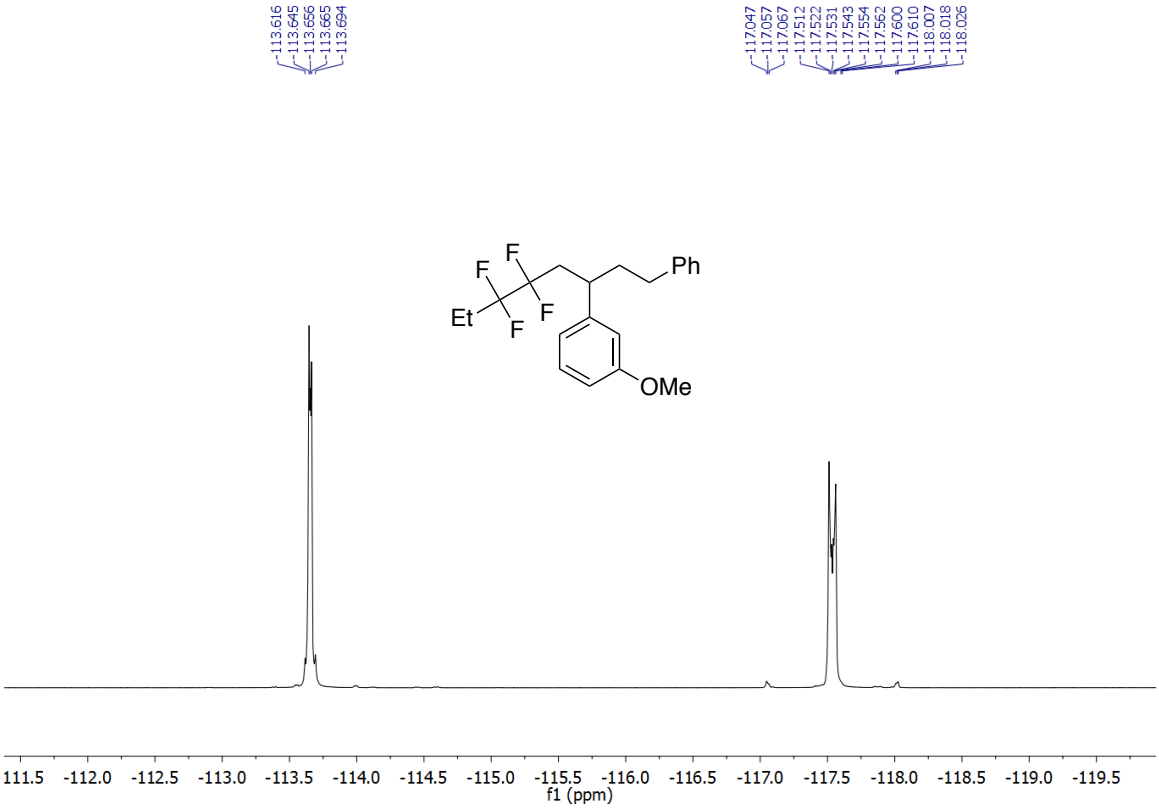
Compound 55. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



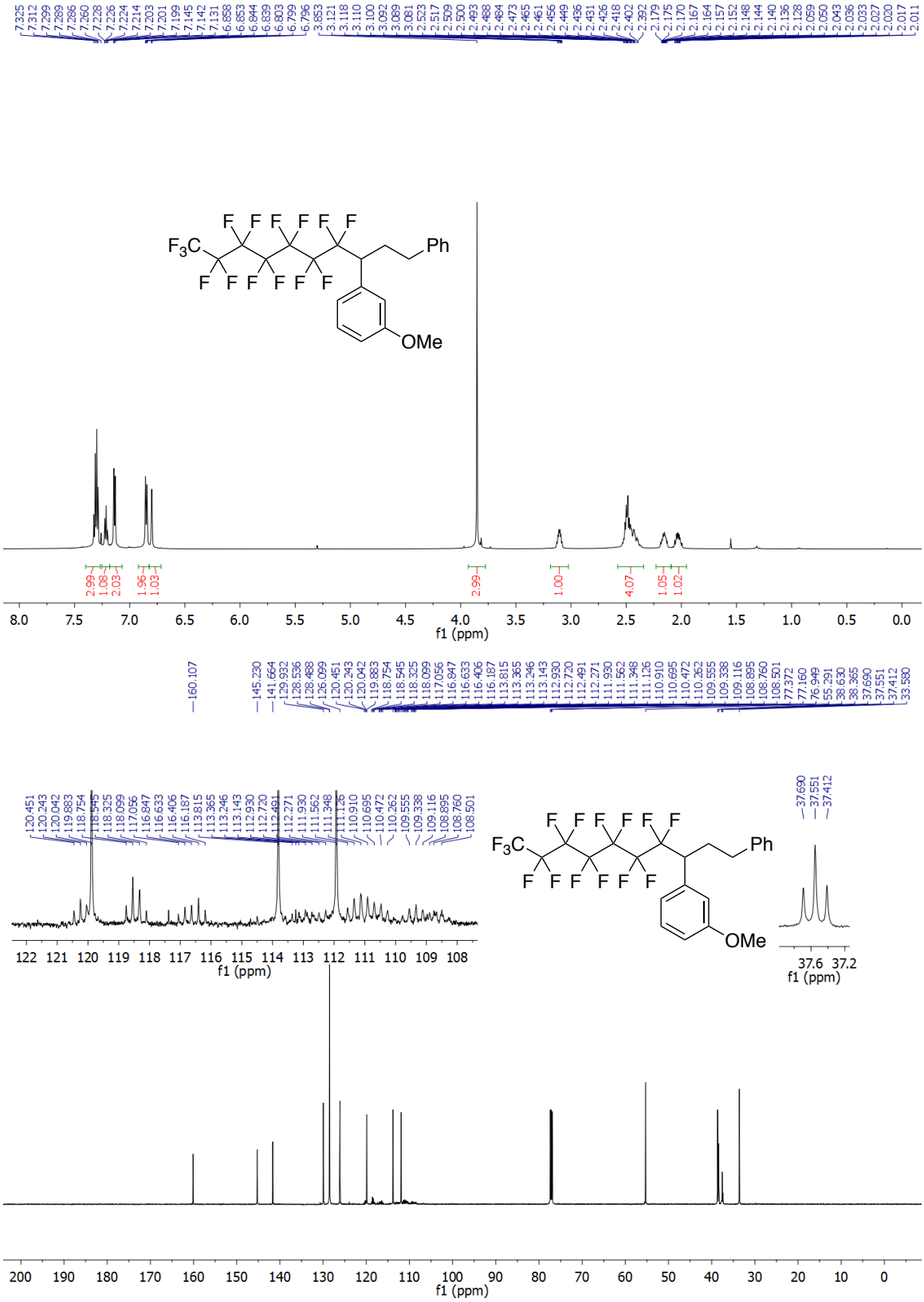
Compound 56. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



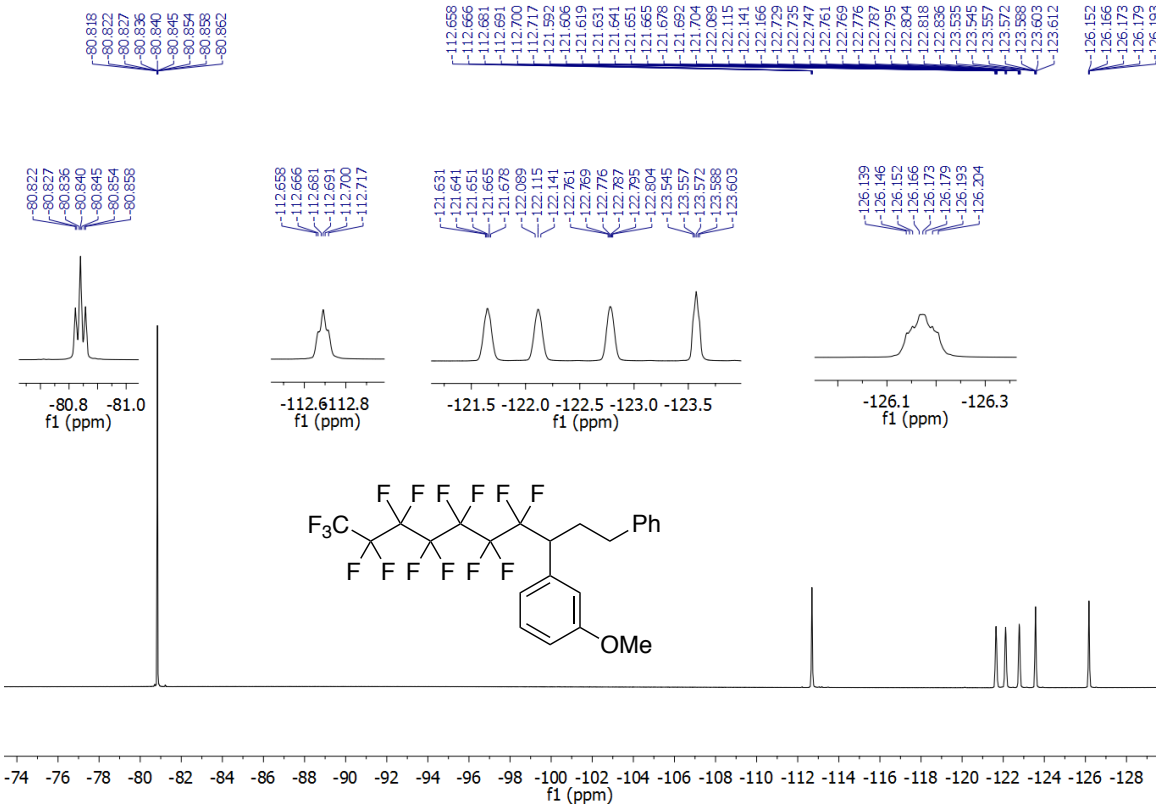
Compound 56. ^{19}F NMR ($CDCl_3$, 565 MHz).



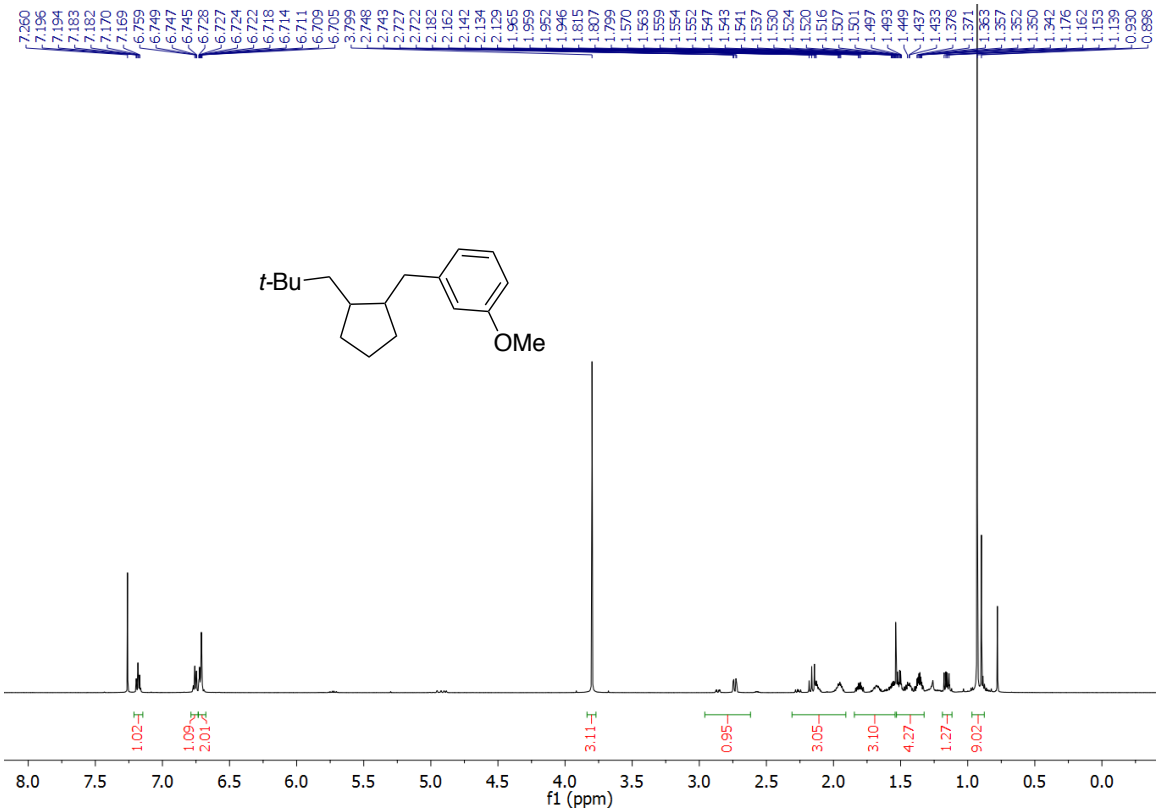
Compound 57. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

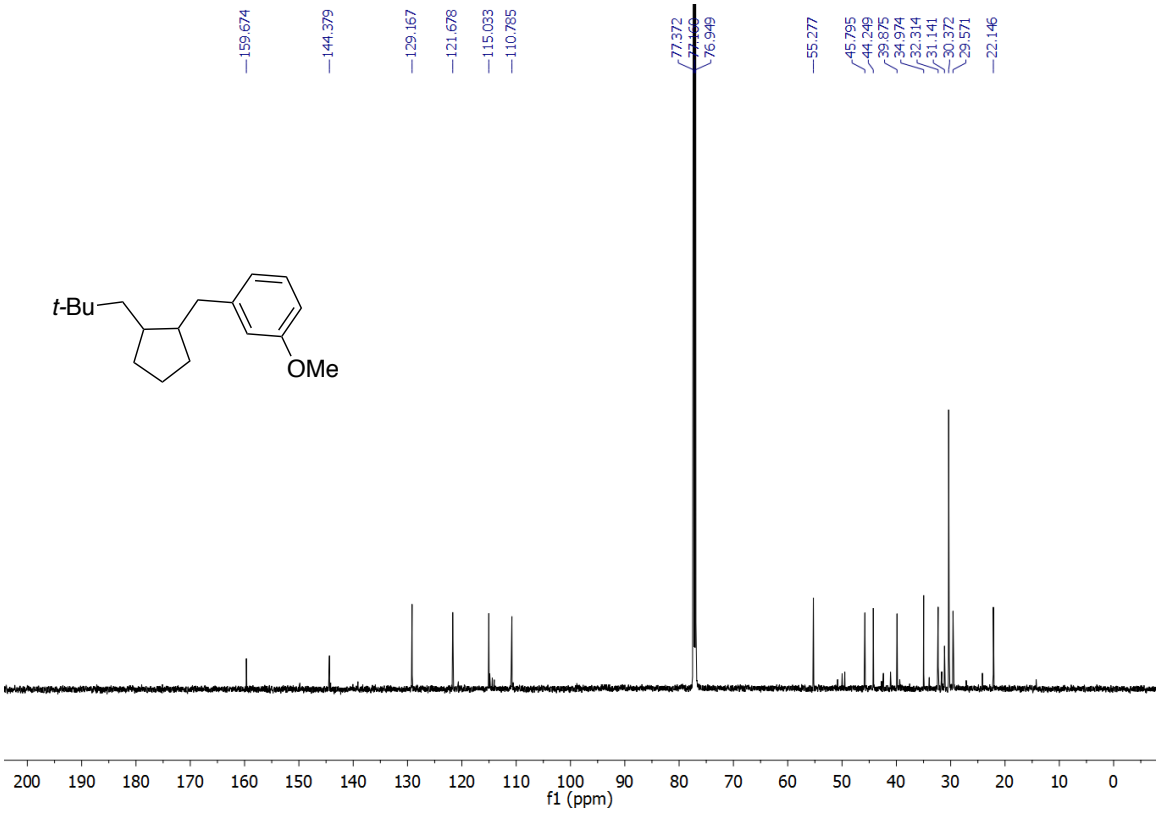


Compound 57. ^{19}F NMR ($CDCl_3$, 565 MHz).

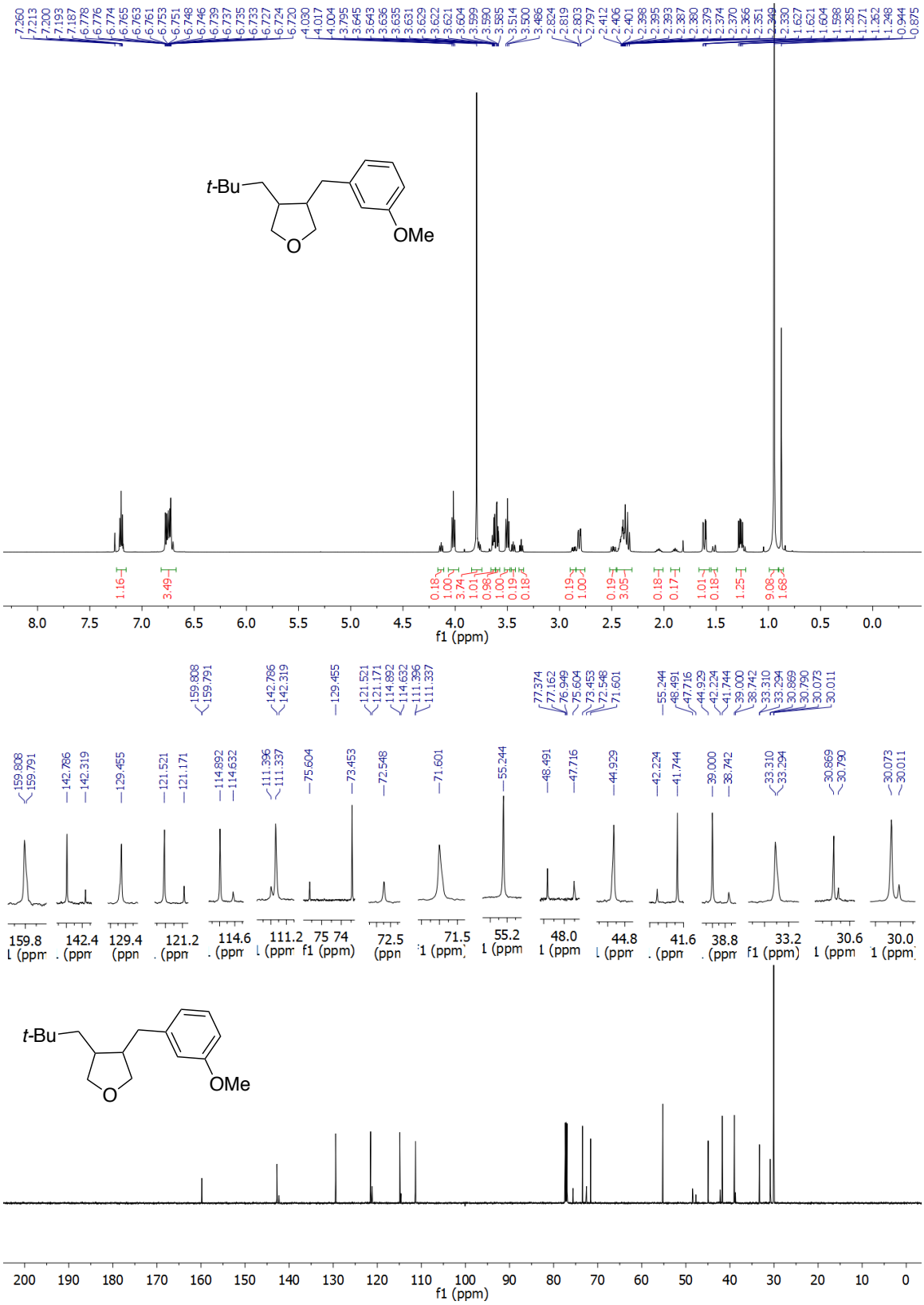


Compound 58. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

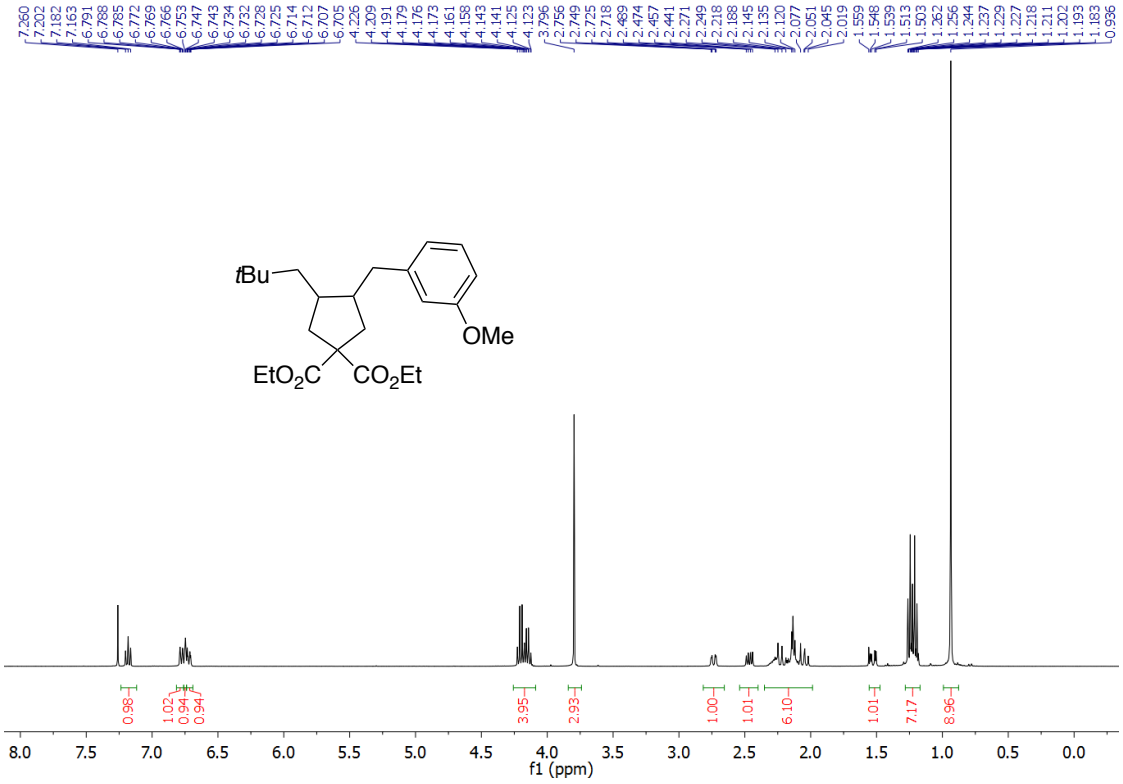


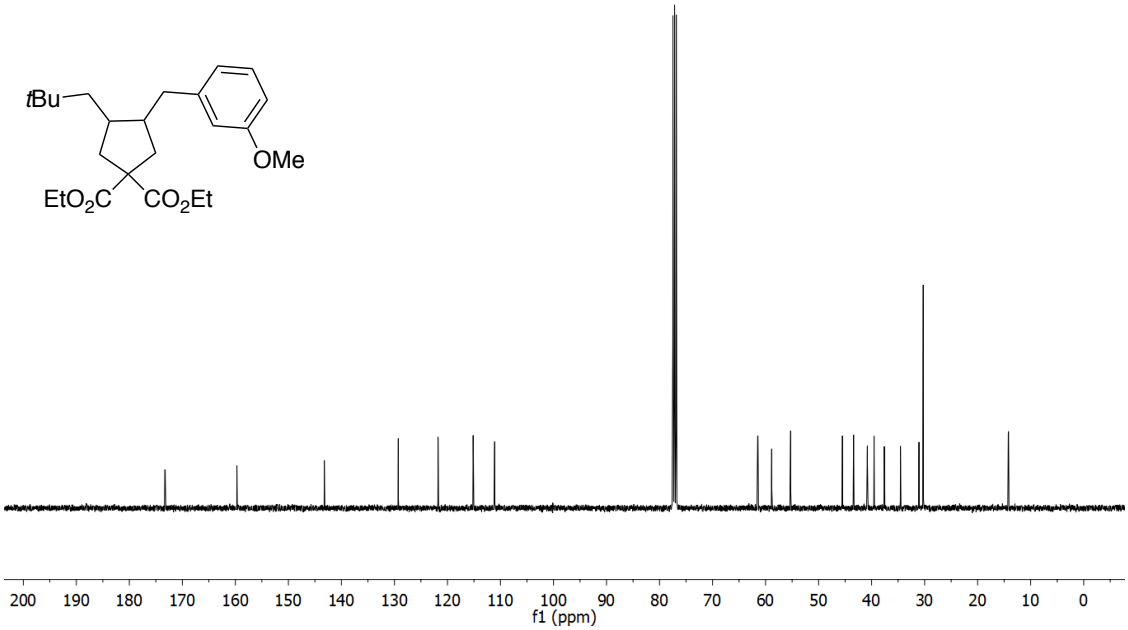


Compound 60. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

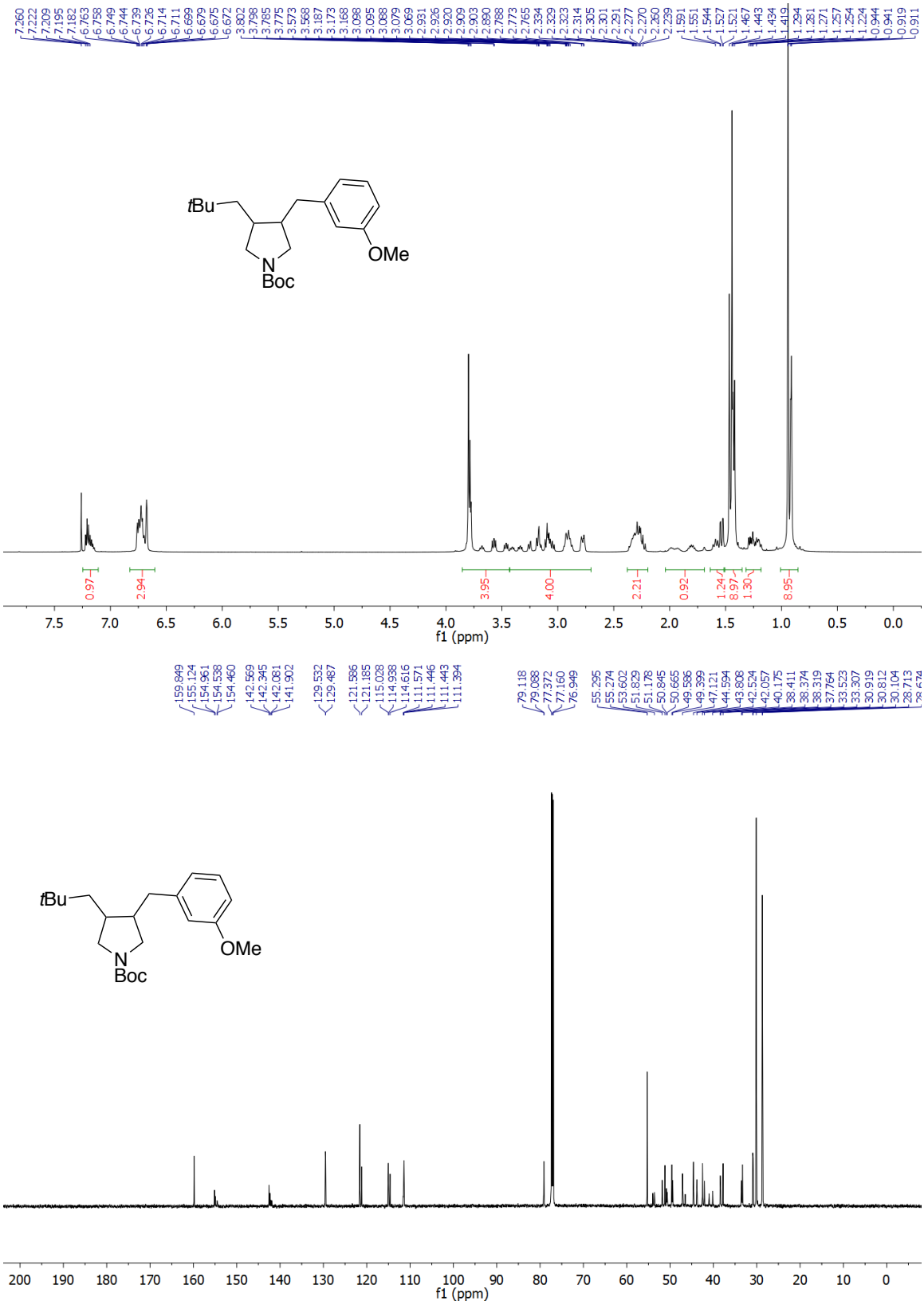


Compound 62 (major). Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

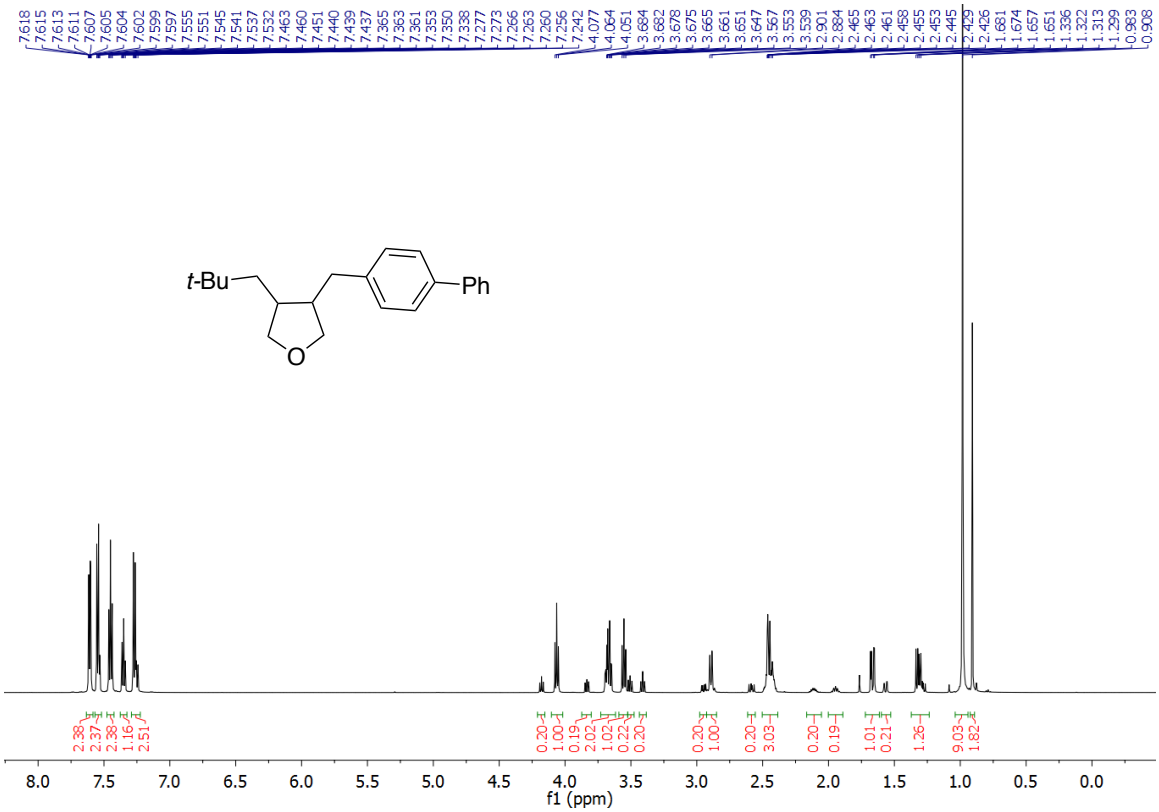


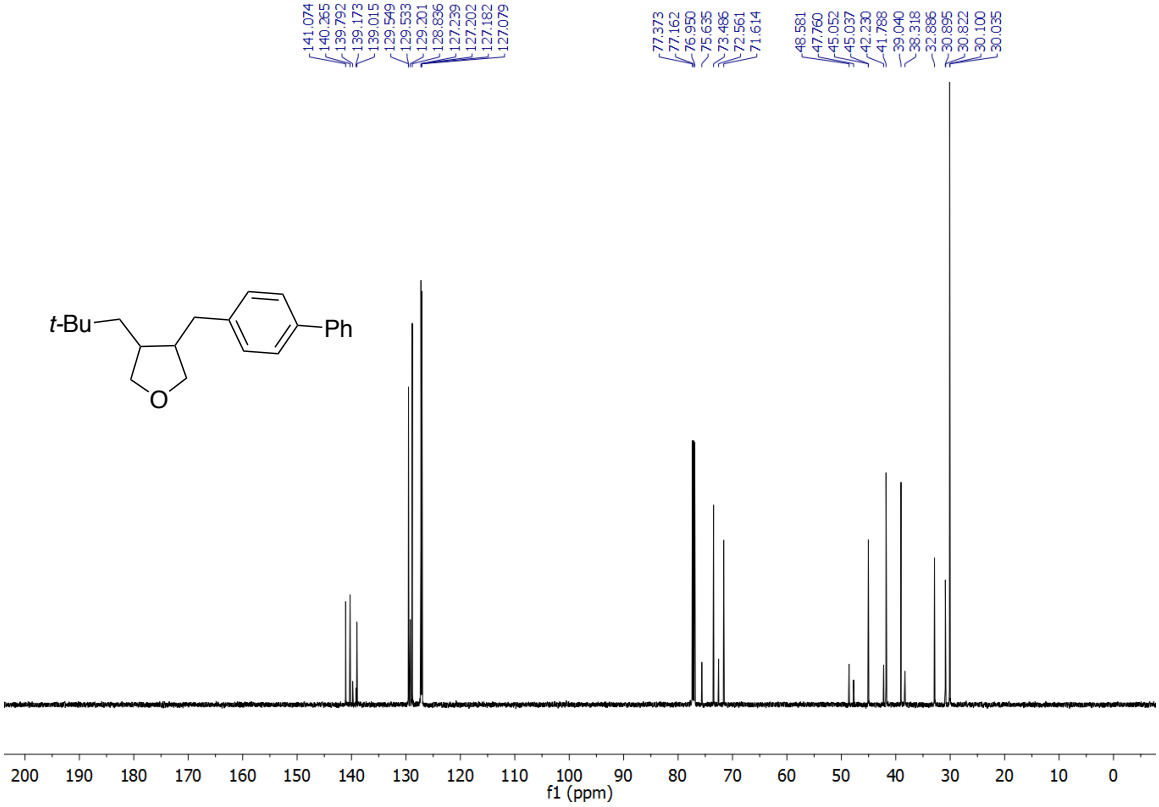


Compound 64. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

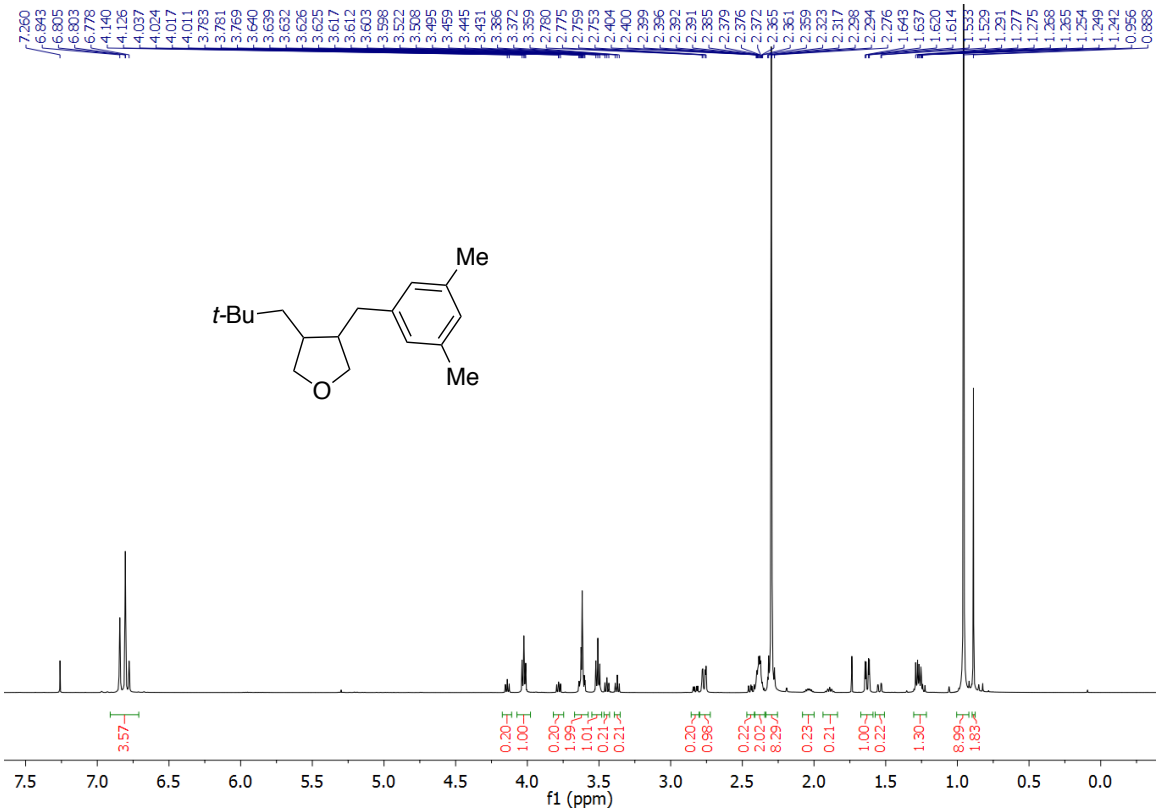


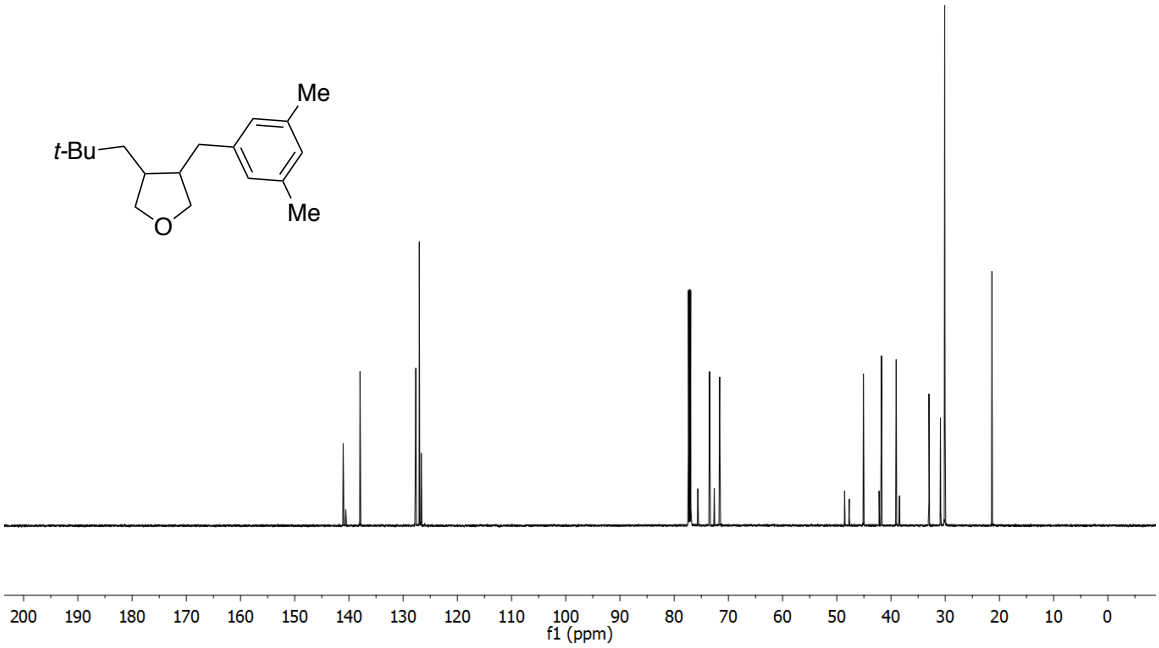
Compound 66. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



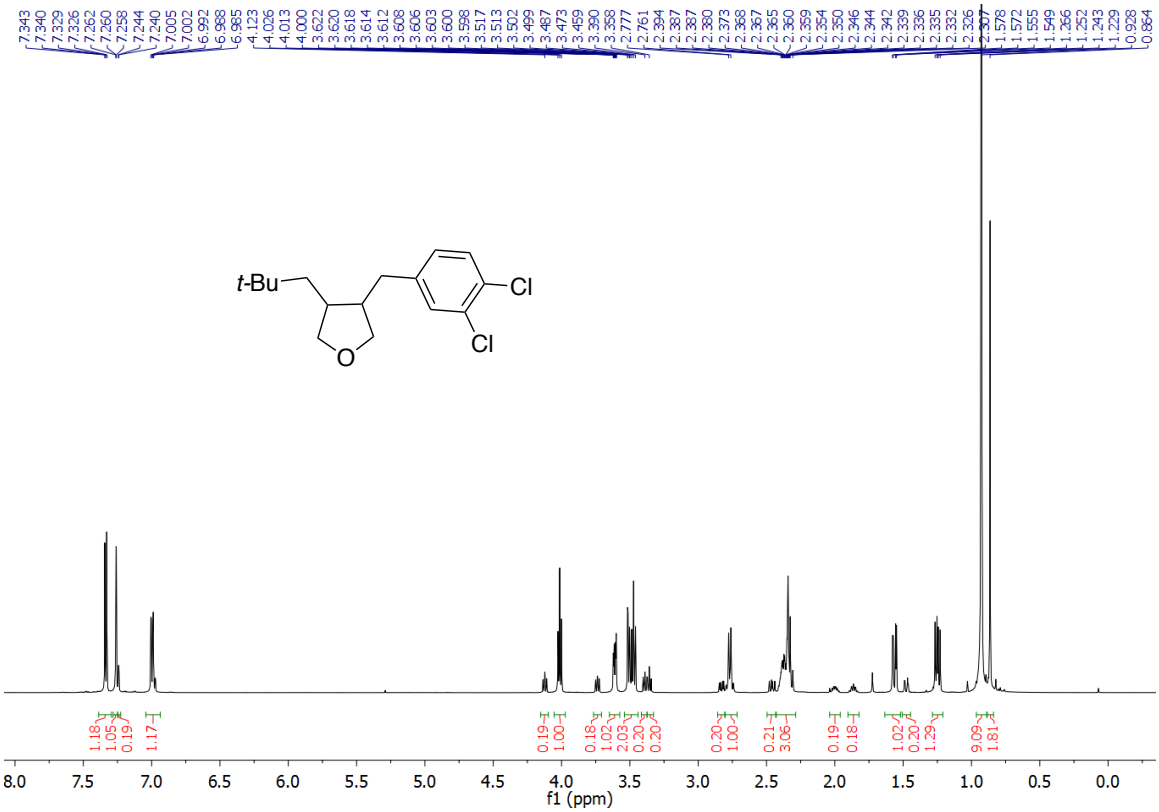


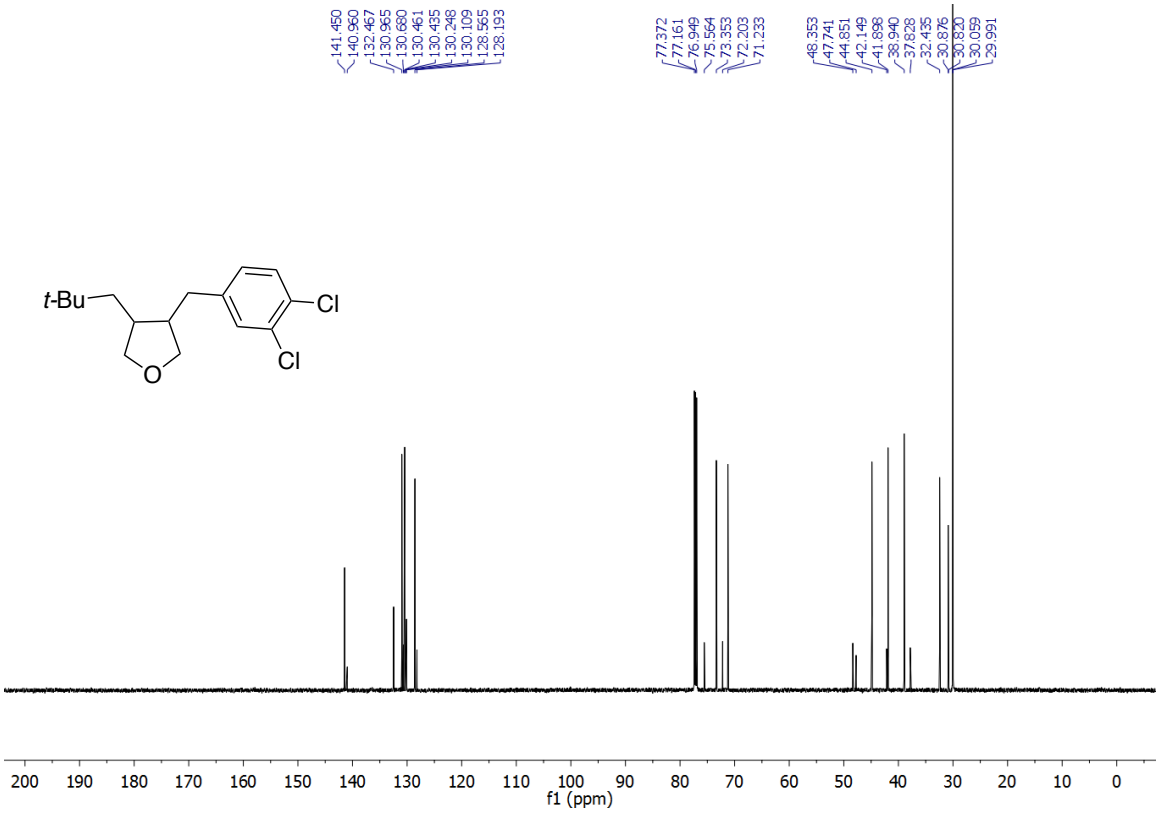
Compound 67. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



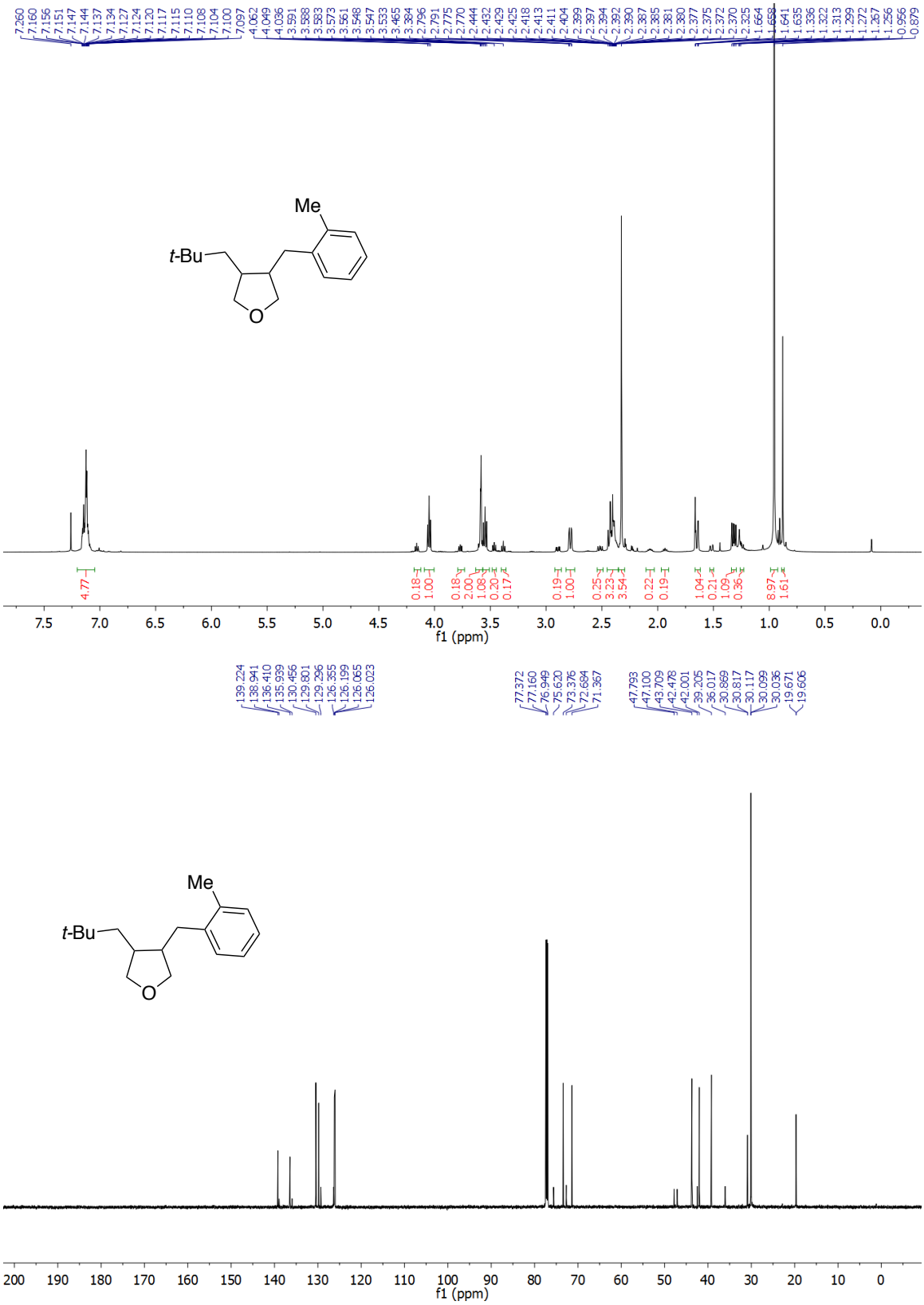


Compound 68. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

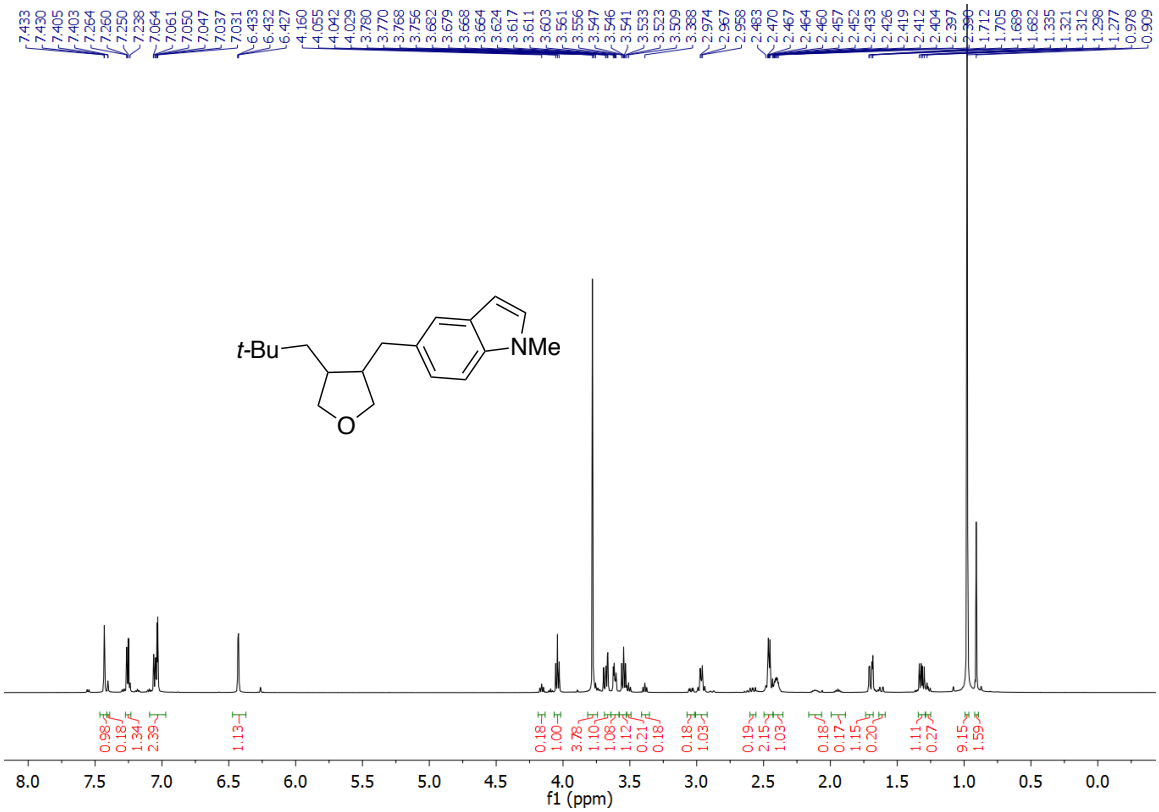


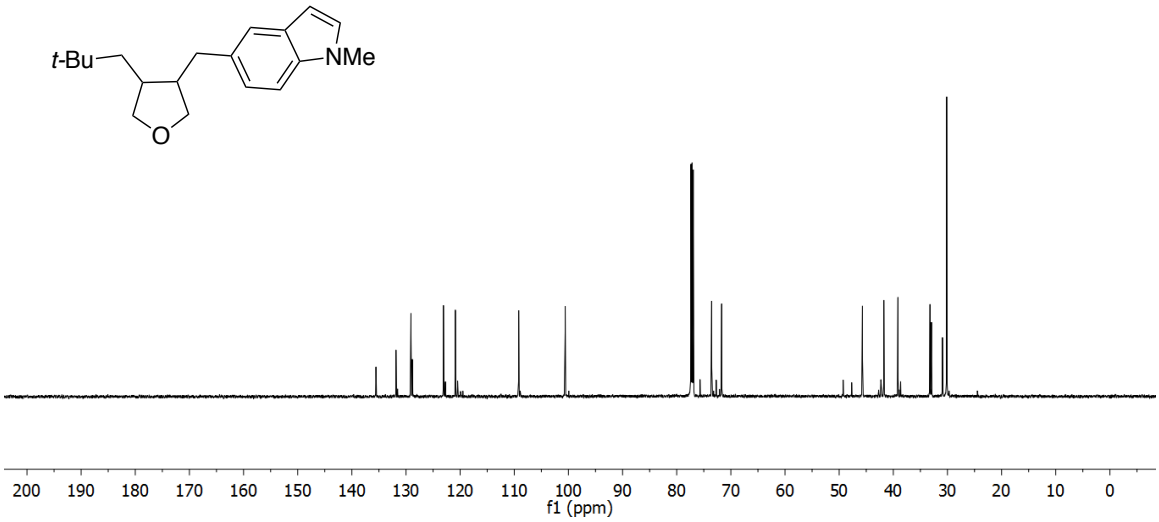


Compound 69. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

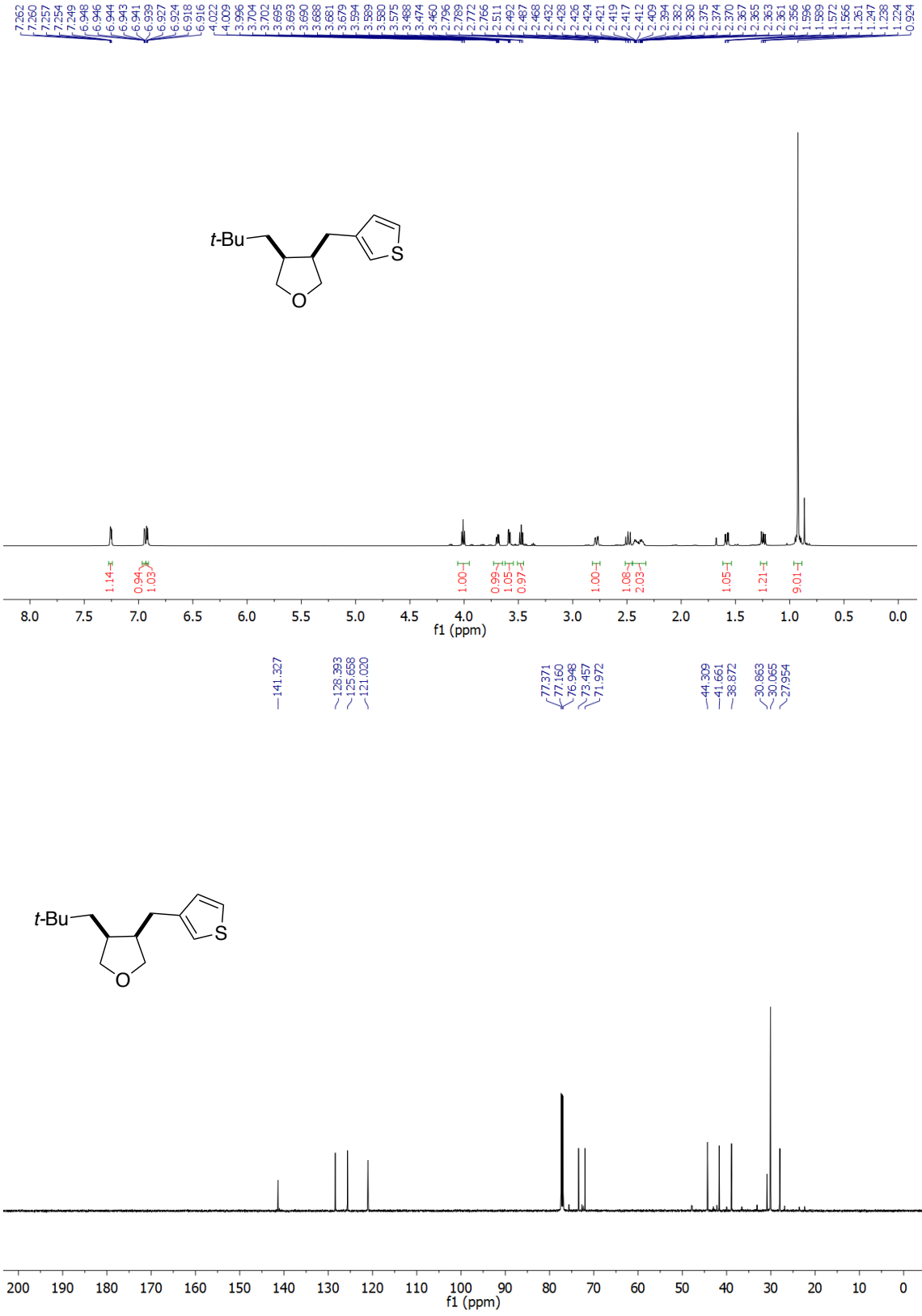


Compound 70. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

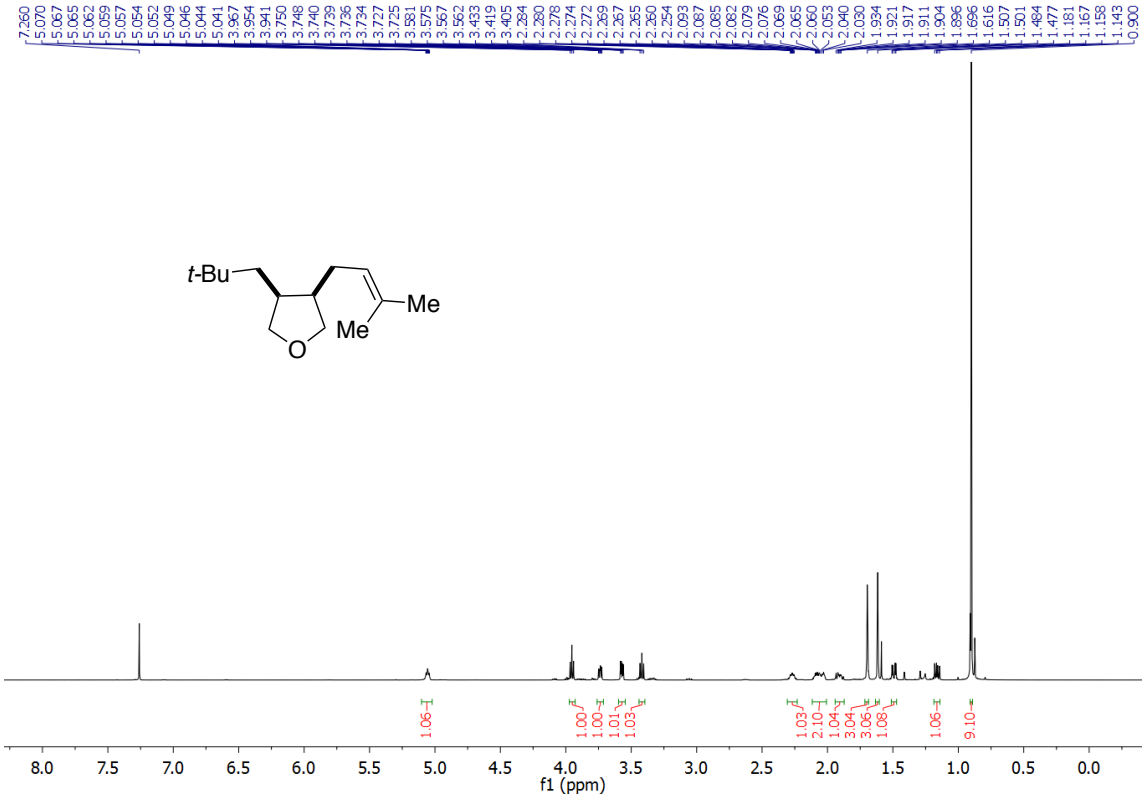


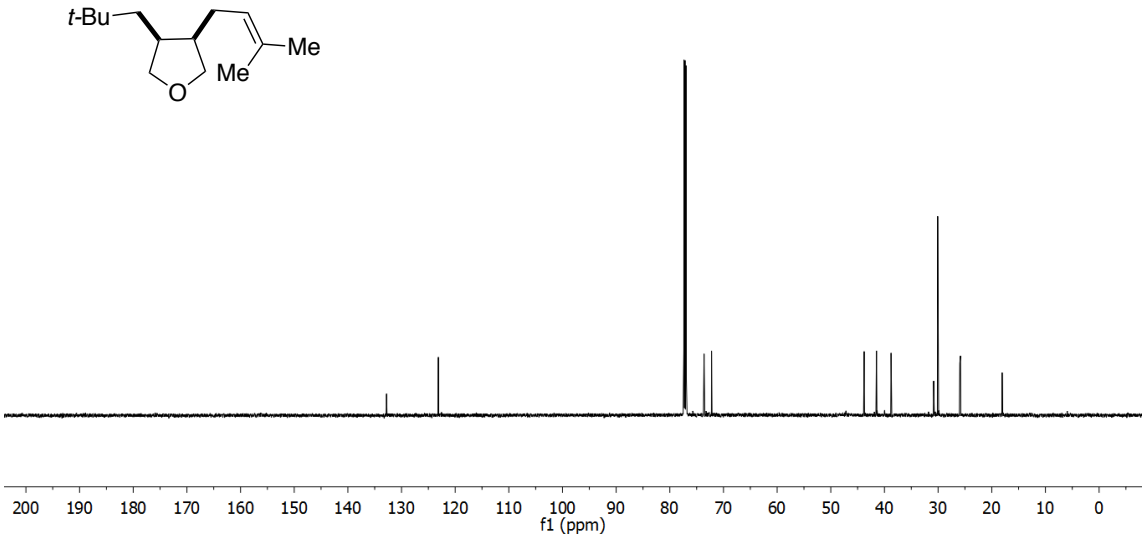


Compound (*cis*)-71 (major). Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

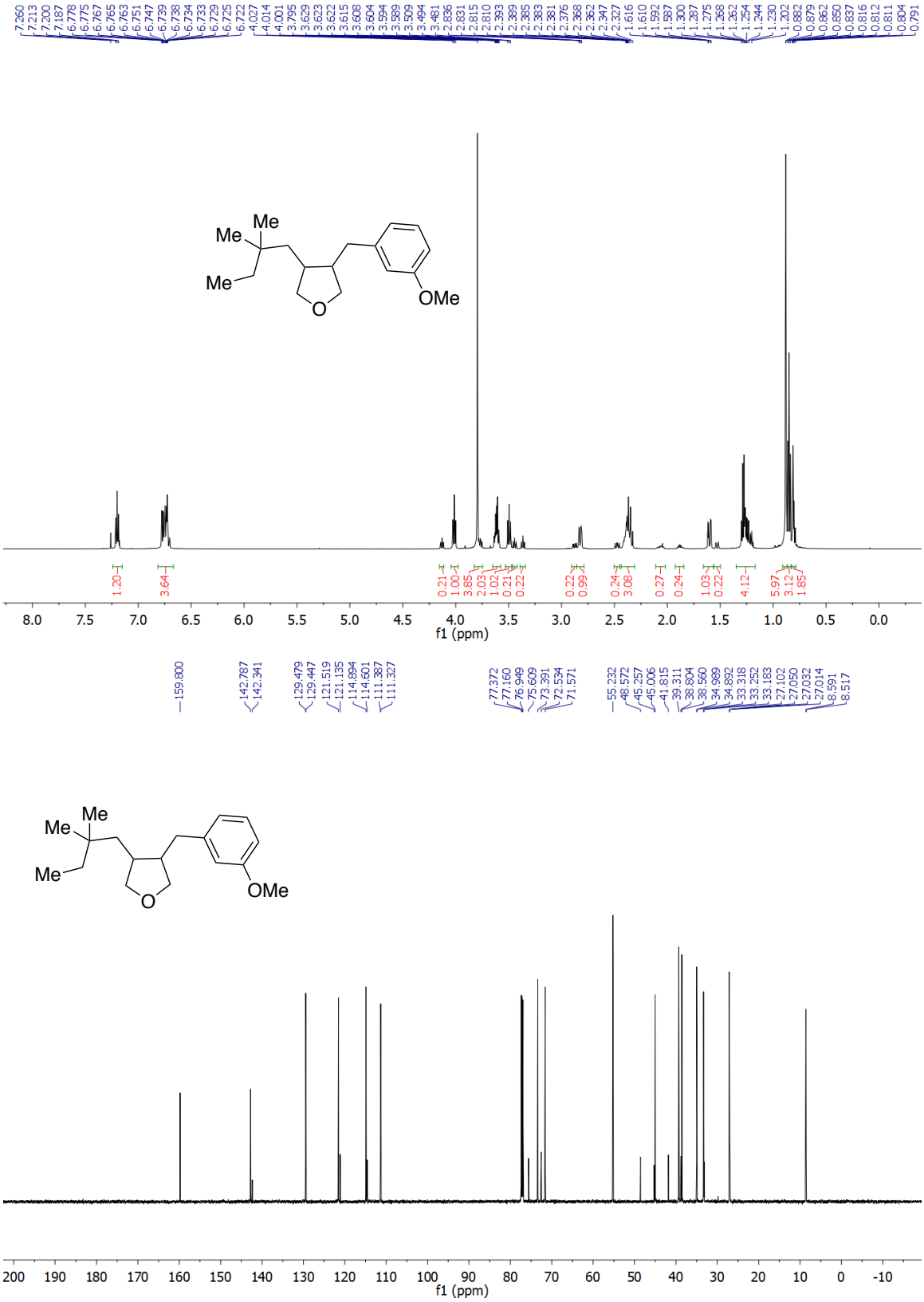


Compound (*cis*)-72 (major). Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

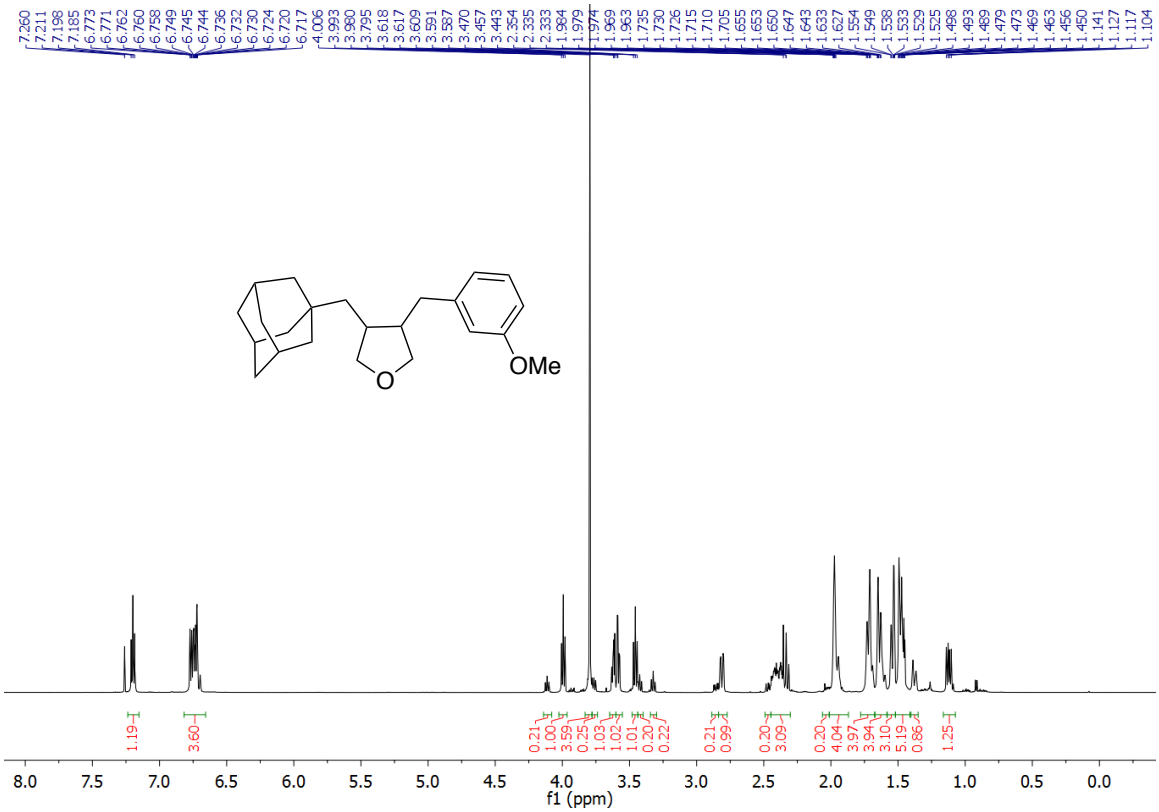


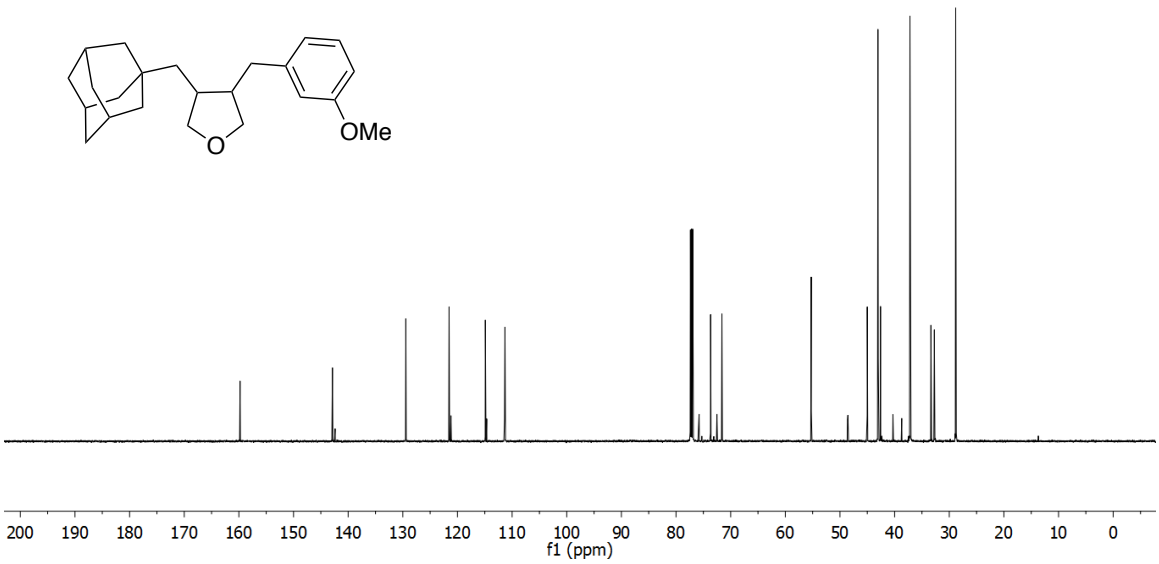


Compound 73. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

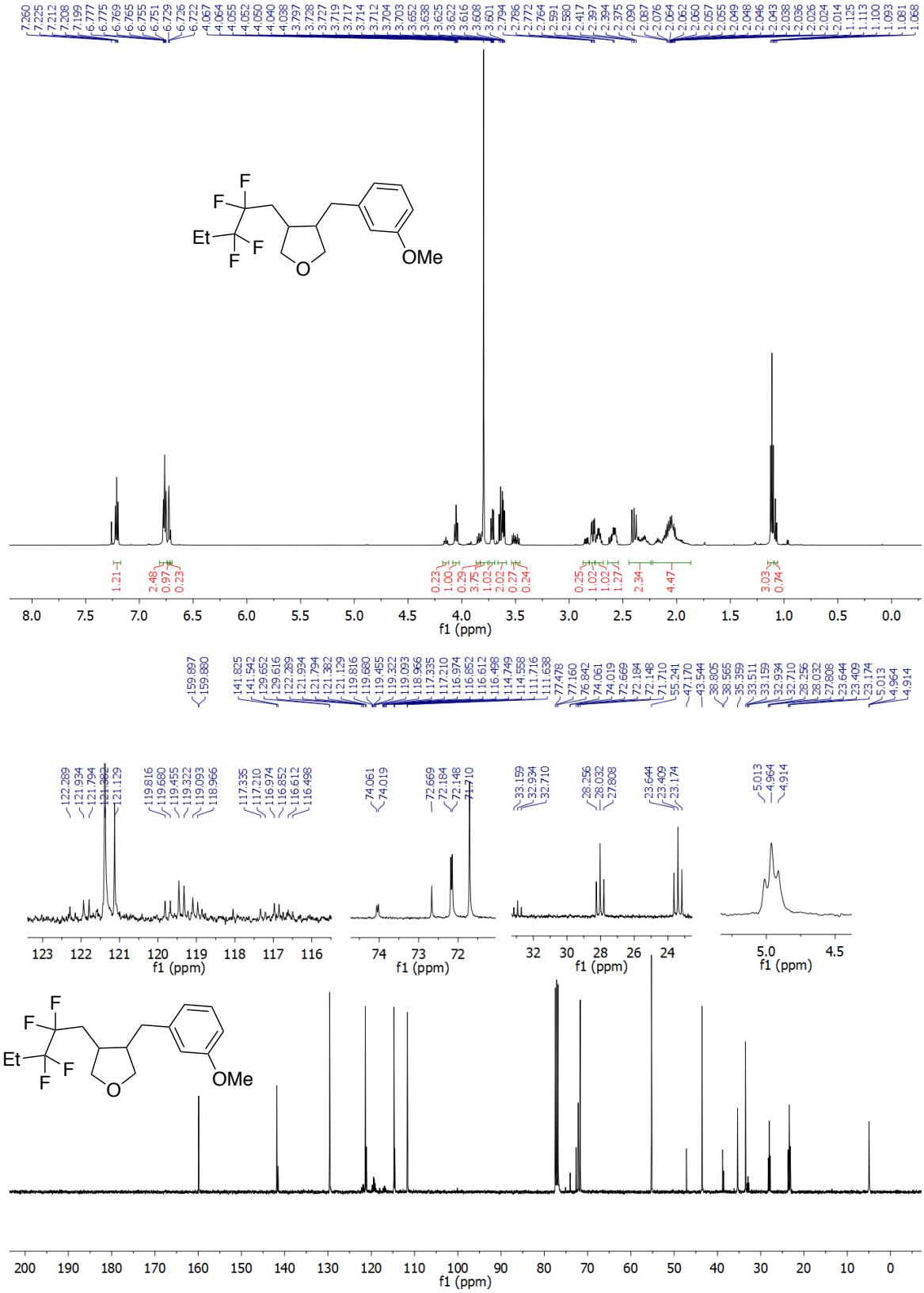


Compound 74. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)

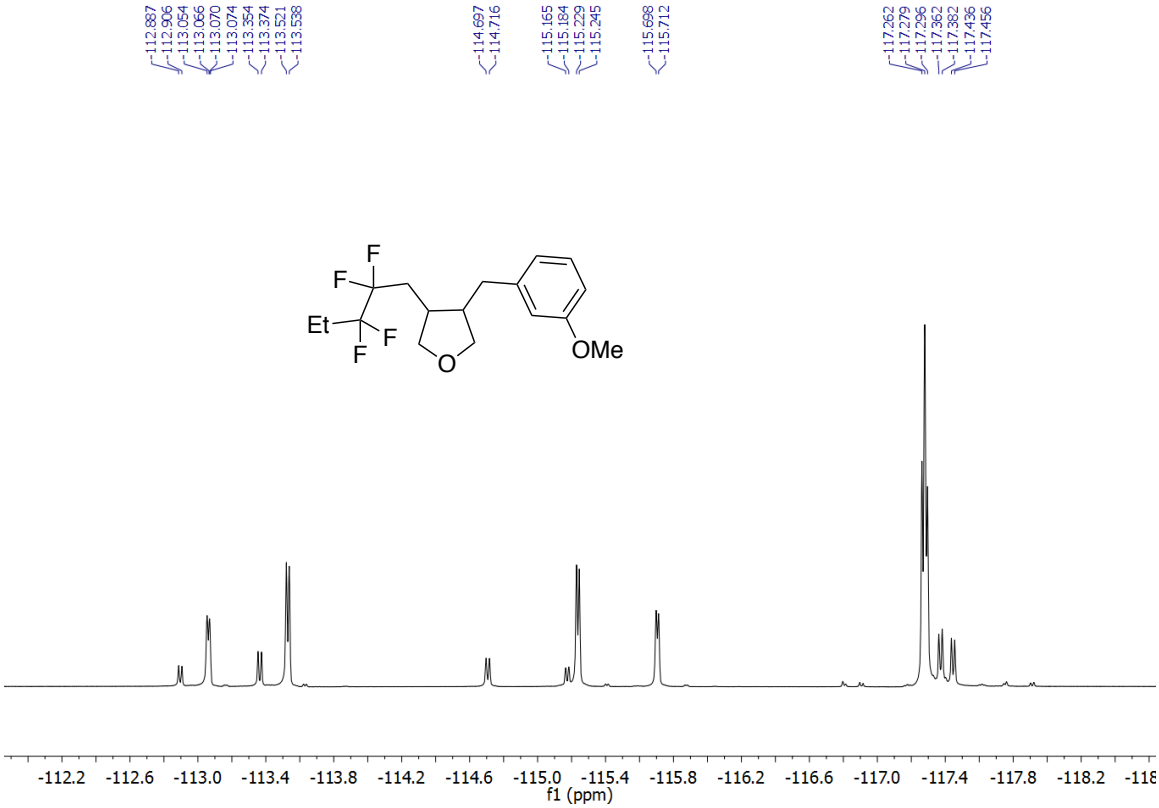




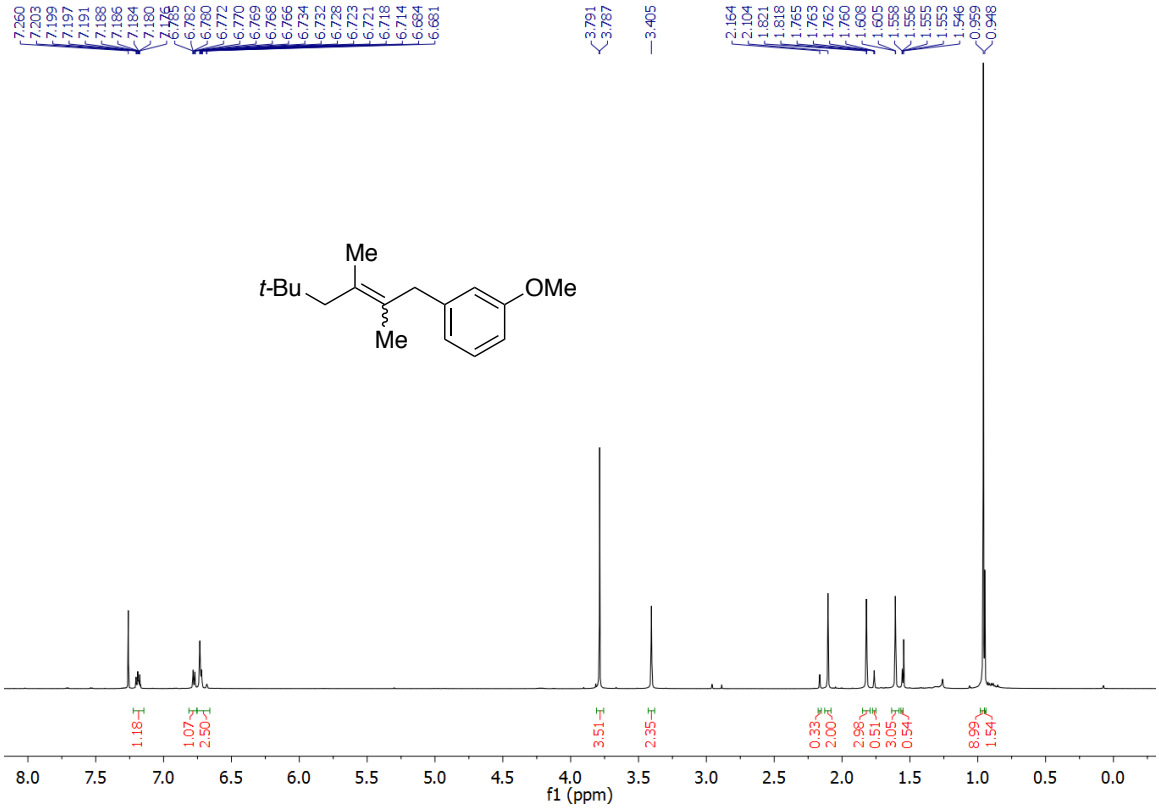
Compound 75. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

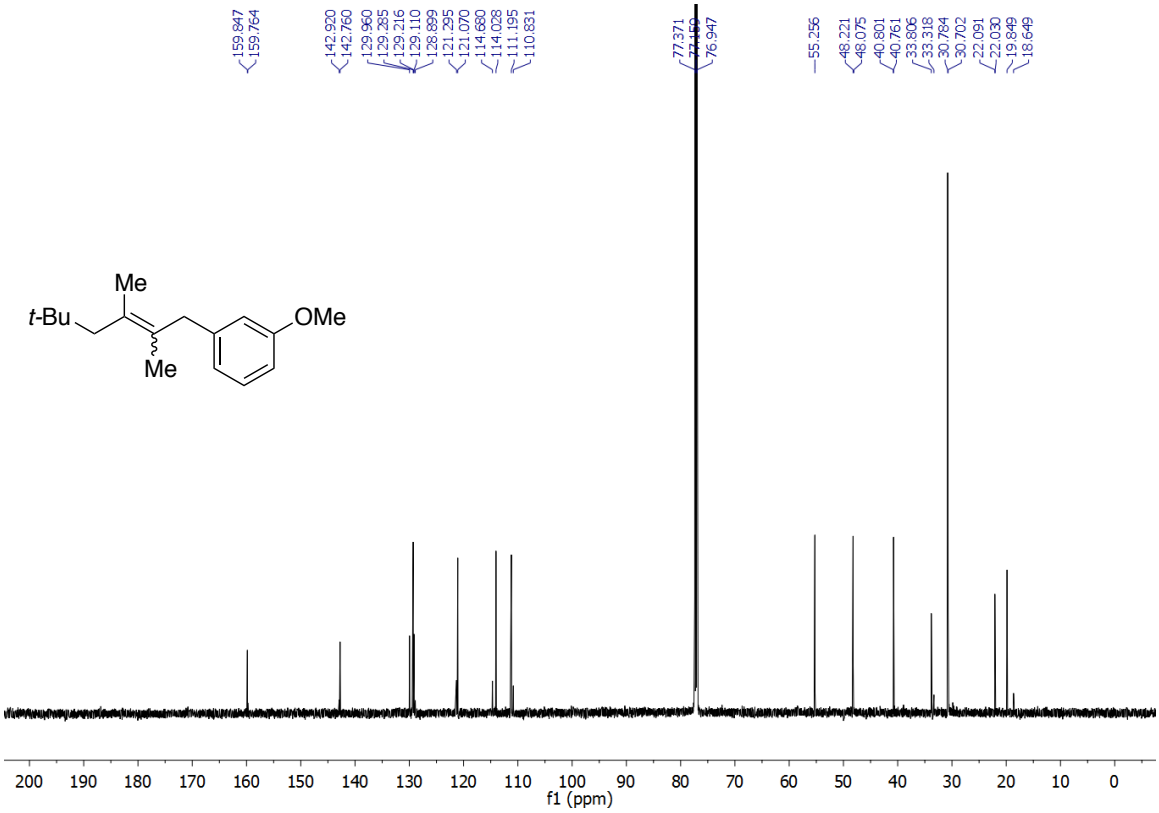


Compound 75. ^{19}F NMR ($CDCl_3$, 565 MHz).

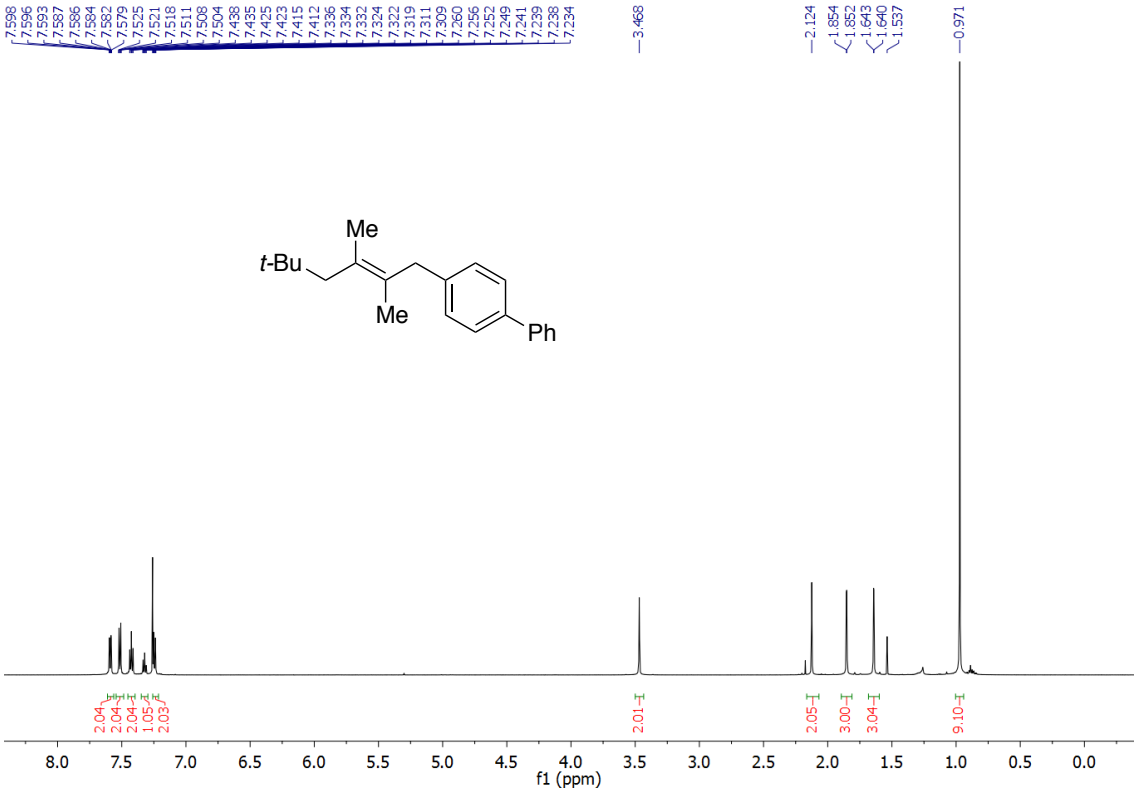


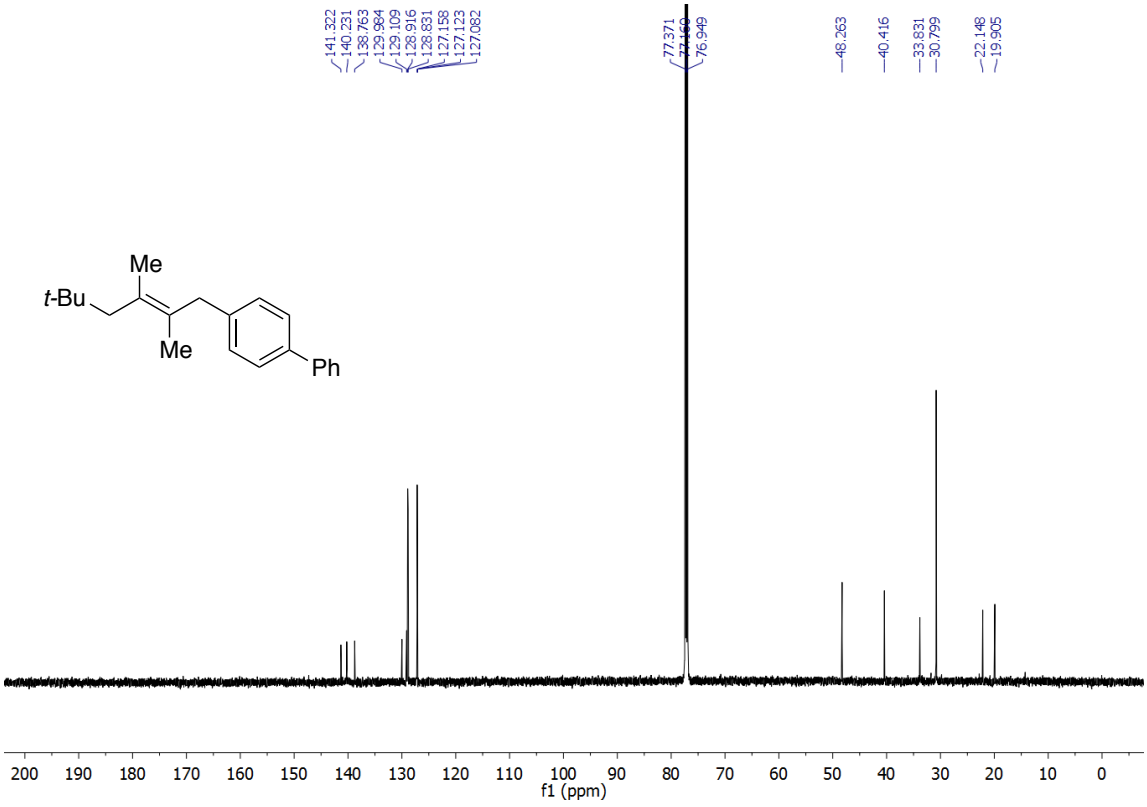
Compound 78. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)





Compound (*E*)-79 (major). Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



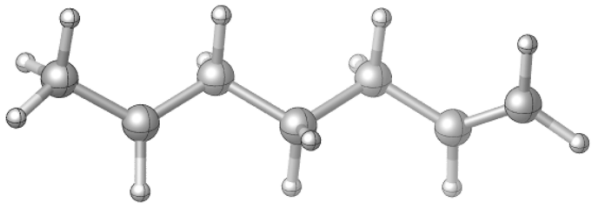


10. Computational Methods, Energies, and Coordinates

Computational Methods

All optimizations were carried out without constraints at the (U)B3LYP/6-31G(d)[11] [also (U)B3LYP-D3/def2-SVP[12] in benchmark] level of theory with the "guess=mix" keyword as implemented in Gaussian16[13]. To refine energetics, we performed single point energy calculations using (U)PBEPBE[14]-D3/6-311+G(d,p)-CPCM(THF) in a polarizable continuum solvent (THF) with CPCM as the conductor calculation model[15] to account for the condensed phase effects with Grimme's empirical dispersion using the original D3 damping function[16] to take into consideration the effect of dispersion in this system. Benchmark on the 5-*exo*-trig cyclization of 1-methyl-5-hexenyl radical was performed and shown in Figure S1, with variance in functionals in single point energy calculation. DLPNO-CCSD(T)[17] calculations were also performed in the benchmark process with def2-TZVPP basis set[12] and auxiliary basis set def2-TZVPP/C[18] as implemented in ORCA program in version 4.1.1.[19] Vibrational frequencies were computed at the same level of optimization method to obtain thermal corrections (at 298 K; enthalpic and free energy) and to identify the stationary points as transition states (one and only one imaginary frequency) or minima (zero imaginary frequencies). Extensive conformational searches were carried out for all intermediates to obtain the lowest energy profile, and intrinsic reaction coordinate (IRCs) calculations were conducted for selected transition state structures to ensure that they connected the corresponding intermediates as illustrated. All structural figures were generated using CLYview.[20]

Coordinates and Energies
Figure S1
Int-Me



(U)B3LYP/6-31G(d)
Zero-point correction= 0.179599 (Hartree/Particle)
Thermal correction to Energy= 0.189305
Thermal correction to Enthalpy= 0.190249
Thermal correction to Gibbs Free Energy= 0.143558
Sum of electronic and zero-point Energies= -274.316546
Sum of electronic and thermal Energies= -274.306841
Sum of electronic and thermal Enthalpies= -274.305897
Sum of electronic and thermal Free Energies= -274.352588
HF=-274.4961458 (U)B3LYP/6-31G(d)
HF=-274.6225802 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1727277 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1796734 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-273.974616396310 (U)DLPNO-CCSD(T)/def2-TZVPP//(U)B3LYP-D3/def2-SVP

C	-0.06532100	0.81570000	1.08611800
C	-2.68252700	-2.08622200	1.20931100
C	1.20350800	1.06211900	0.33485900
C	-2.04166100	-0.76302900	1.52779700
C	-0.75278200	-0.51051400	0.72371200
H	0.12593900	0.82395500	2.17840500
H	-0.76301600	1.65178400	0.91769000
H	-2.75841900	0.04834700	1.34308800
H	-1.79655900	-0.72523500	2.60101600
H	-0.04978600	-1.33888700	0.89396100
H	-0.98593400	-0.52156000	-0.34871500
C	-3.90790600	-2.25030800	0.70946700
H	-2.06770900	-2.96806700	1.40119000
H	-4.55715800	-1.40227400	0.49922700
H	1.81208200	0.20032300	0.06448900
H	-4.31271200	-3.23561800	0.49364700
C	1.81813800	2.42004700	0.25425600
H	2.31515900	2.71221000	1.19809100
H	2.57906500	2.47760500	-0.53252200
H	1.06383100	3.19407700	0.05480700

(U)B3LYP-D3/def2-SVP
Zero-point correction= 0.177868 (Hartree/Particle)

Thermal correction to Energy= 0.187562
Thermal correction to Enthalpy= 0.188506
Thermal correction to Gibbs Free Energy= 0.141935
Sum of electronic and zero-point Energies= -274.134176
Sum of electronic and thermal Energies= -274.124483
Sum of electronic and thermal Enthalpies= -274.123539
Sum of electronic and thermal Free Energies= -274.170110

HF=-274.3120446 (U)B3LYP-D3/def2-SVP

HF=-274.621889 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP-D3/def2-SVP

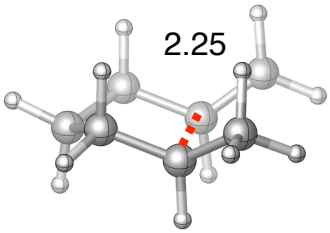
HF=-274.173041 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-274.180003 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-273.973985386757 (U)DLPNO-CCSD(T)/def2-TZVPP//(U)B3LYP-D3/def2-SVP

C	-0.07465400	0.82035200	1.05019000
C	-2.68065000	-2.08264800	1.22678800
C	1.18335100	1.07329300	0.28745600
C	-2.04325400	-0.75408300	1.52120600
C	-0.75498600	-0.51255500	0.71936000
H	0.13145500	0.85333500	2.14551000
H	-0.78588400	1.65425800	0.88247100
H	-2.76260700	0.06001700	1.32362200
H	-1.79984800	-0.69945400	2.59989700
H	-0.04494900	-1.33874200	0.90782100
H	-0.98468300	-0.55020800	-0.35962800
C	-3.90454700	-2.26404100	0.72259100
H	-2.05884800	-2.96362000	1.43854500
H	-4.55826900	-1.41573900	0.49106700
H	1.75251800	0.20882400	-0.07374300
H	-4.30227300	-3.26352300	0.52443100
C	1.83313400	2.41450500	0.29035400
H	2.31792000	2.63952100	1.26583500
H	2.61549400	2.50112500	-0.48021900
H	1.09781500	3.22383500	0.12634000

TS-Me-*cis*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.180648 (Hartree/Particle)
Thermal correction to Energy= 0.188506
Thermal correction to Enthalpy= 0.189450
Thermal correction to Gibbs Free Energy= 0.148209
Sum of electronic and zero-point Energies= -274.303441
Sum of electronic and thermal Energies= -274.295583
Sum of electronic and thermal Enthalpies= -274.294639
Sum of electronic and thermal Free Energies= -274.335880
HF=-274.4840894 (U)B3LYP/6-31G(d)
HF=-274.6108202 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1652178 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1743476 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-273.964059285217 (U)DLPNO-CCSD(T)/def2-TZVPP//(U)B3LYP-D3/def2-SVP

C	-0.16766400	0.86776000	1.00486200
C	0.99671300	-0.17809700	-1.33275200
C	1.26444700	0.99818200	0.56337900
C	-0.45310400	-0.50966000	-1.03149600
C	-0.73601400	-0.45796100	0.47603300
H	-0.25994600	0.91783200	2.10249600
H	-0.75763000	1.70400400	0.60325200
H	-1.10051400	0.20903400	-1.55247700
H	-0.69833300	-1.50230900	-1.43474900
H	-1.80735700	-0.55898100	0.68926700
H	-0.23110000	-1.29677800	0.97639600
C	1.36403500	0.57709000	-2.41989900
H	1.72398400	-0.90186800	-0.96372500
H	0.64459200	1.20166800	-2.94462800
H	1.95075900	0.29605400	1.04127100
H	2.39964500	0.65205400	-2.73925100
C	1.84744500	2.34810600	0.26797200
H	1.98141300	2.94169500	1.18781700
H	2.82996000	2.26683300	-0.21070900
H	1.19778200	2.92684000	-0.39948000

(U)B3LYP-D3/def2-SVP
Zero-point correction= 0.179110 (Hartree/Particle)
Thermal correction to Energy= 0.186903
Thermal correction to Enthalpy= 0.187847

Thermal correction to Gibbs Free Energy= 0.146815
Sum of electronic and zero-point Energies= -274.124031
Sum of electronic and thermal Energies= -274.116238
Sum of electronic and thermal Enthalpies= -274.115294
Sum of electronic and thermal Free Energies= -274.156326

HF=-274.3031408 (U)B3LYP-D3/def2-SVP

HF=-274.6101573 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP-D3/def2-SVP

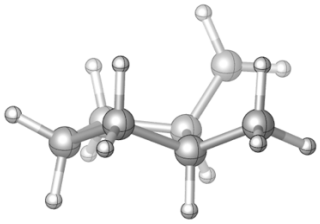
HF=-274.1655238 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-274.1747295 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-273.963634377005 (U)DLPNO-CCSD(T)/def2-TZVPP//(U)B3LYP-D3/def2-SVP

C	-0.16836900	0.86243100	1.00535200
C	0.99385600	-0.17948000	-1.32509500
C	1.26269400	0.99220700	0.56655300
C	-0.45700400	-0.50314800	-1.02785300
C	-0.73426900	-0.46239600	0.47857300
H	-0.26041400	0.91797100	2.10827800
H	-0.76104900	1.70146400	0.59810400
H	-1.10397800	0.22929800	-1.54204700
H	-0.70964200	-1.49443900	-1.44442000
H	-1.80881500	-0.57234000	0.70016200
H	-0.21802700	-1.30455200	0.97482700
C	1.37589300	0.59951000	-2.39327800
H	1.71807000	-0.91923600	-0.96302400
H	0.65853500	1.24743200	-2.90715900
H	1.95327200	0.28955700	1.05143200
H	2.42244700	0.67399100	-2.70015300
C	1.84085200	2.33319500	0.23996900
H	1.96817700	2.95379800	1.14964400
H	2.82978600	2.24348000	-0.23691400
H	1.18709500	2.89275600	-0.44937300

Int-Me-*cis*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.182884 (Hartree/Particle)
Thermal correction to Energy= 0.190944
Thermal correction to Enthalpy= 0.191889
Thermal correction to Gibbs Free Energy= 0.149560
Sum of electronic and zero-point Energies= -274.329689
Sum of electronic and thermal Energies= -274.321629
Sum of electronic and thermal Enthalpies= -274.320684
Sum of electronic and thermal Free Energies= -274.363013
HF=-274.5125731 (U)B3LYP/6-31G(d)
HF=-274.635703 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1901884 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1991761 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.21429000	0.94453400	0.83865300
C	1.06316500	0.03981000	-1.06494900
C	1.22407500	0.82352300	0.30928700
C	-0.31119000	-0.69727300	-0.93329300
C	-0.83307600	-0.41552800	0.49147300
H	-0.25073400	1.18088800	1.90891200
H	-0.74291400	1.74945100	0.30701200
H	-1.01335000	-0.28976600	-1.67103200
H	-0.22380400	-1.76801800	-1.14613300
H	-1.92715400	-0.42658900	0.54958300
H	-0.46420200	-1.17548600	1.19334600
C	1.13605300	0.88763800	-2.28916700
H	1.88260400	-0.69038800	-1.11473000
H	0.24920600	1.37037700	-2.69142600
H	1.76097900	0.14543800	0.98937700
H	2.09176600	1.16641800	-2.72354100
C	2.00106000	2.13773000	0.24281600
H	2.08404200	2.58832700	1.23945900
H	3.01842400	1.98694800	-0.13779000
H	1.50574900	2.86176600	-0.41427900

(U)B3LYP-D3/def2-SVP
Zero-point correction= 0.181325 (Hartree/Particle)
Thermal correction to Energy= 0.189336
Thermal correction to Enthalpy= 0.190280
Thermal correction to Gibbs Free Energy= 0.147929

Sum of electronic and zero-point Energies= -274.149610
Sum of electronic and thermal Energies= -274.141600
Sum of electronic and thermal Enthalpies= -274.140656
Sum of electronic and thermal Free Energies= -274.183006

HF=-274.3309356 (U)B3LYP-D3/def2-SVP

HF=-274.6350684 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP-D3/def2-SVP

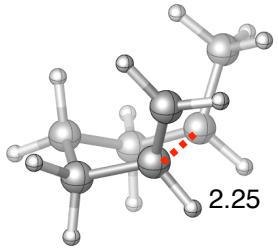
HF=-274.1904158 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-274.1994342 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-273.996889908565 (U)DLPNO-CCSD(T)/def2-TZVPP//(U)B3LYP-D3/def2-SVP

C	-0.20686000	0.94297500	0.83596100
C	1.04950900	0.04065500	-1.07370900
C	1.22634100	0.81200000	0.30293500
C	-0.32465200	-0.69061200	-0.93311800
C	-0.82893900	-0.41446700	0.49680000
H	-0.24089300	1.19200300	1.90928900
H	-0.73340100	1.75060100	0.29393800
H	-1.03717900	-0.27290600	-1.66349000
H	-0.24609900	-1.76582200	-1.15577000
H	-1.92761900	-0.43032000	0.57316000
H	-0.44446300	-1.17733800	1.19611300
C	1.12333800	0.90816700	-2.28339900
H	1.87166800	-0.69404900	-1.13700900
H	0.23019000	1.40170100	-2.67912300
H	1.76016100	0.11963600	0.97944600
H	2.08931800	1.21074300	-2.69658400
C	2.01511300	2.11563300	0.24020800
H	2.12207100	2.55539400	1.24542500
H	3.02741600	1.95880300	-0.16647800
H	1.51139100	2.85700300	-0.40101900

TS-Me-*cis-conf2*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.180654 (Hartree/Particle)
Thermal correction to Energy= 0.188590
Thermal correction to Enthalpy= 0.189534
Thermal correction to Gibbs Free Energy= 0.147814
Sum of electronic and zero-point Energies= -274.299448
Sum of electronic and thermal Energies= -274.291512
Sum of electronic and thermal Enthalpies= -274.290568
Sum of electronic and thermal Free Energies= -274.332288
HF=-274.4801022 (U)B3LYP/6-31G(d)
HF=-274.6073112 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1615438 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1709578 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.24657500	1.04687400	0.99142600
C	1.08073200	-0.10783300	-1.19799800
C	1.20152200	1.22241800	0.60656800
C	-0.35879300	-0.53415900	-0.92017100
C	-0.72214300	-0.35137300	0.56197000
H	-0.38974400	1.18058000	2.07602000
H	-0.86584300	1.80501900	0.49411300
H	-1.03917900	0.07093800	-1.53393600
H	-0.50719100	-1.57774100	-1.22298200
H	-1.79772700	-0.48555100	0.73457500
H	-0.20523000	-1.11377200	1.16010600
C	2.11565700	-1.01213400	-1.19342100
H	1.20827600	0.78084300	-1.81403900
H	2.00251100	-2.00418400	-0.76128600
H	1.45972300	2.15968300	0.11323200
H	3.11029500	-0.74235100	-1.53705100
C	2.26638100	0.68598500	1.52053600
H	3.23769100	0.62731700	1.01704600
H	2.39224400	1.33321000	2.40426000
H	2.02392000	-0.31845500	1.88668400

(U)B3LYP-D3/def2-SVP
Zero-point correction= 0.179191 (Hartree/Particle)
Thermal correction to Energy= 0.187000
Thermal correction to Enthalpy= 0.187944

Thermal correction to Gibbs Free Energy= 0.146784
Sum of electronic and zero-point Energies= -274.120421
Sum of electronic and thermal Energies= -274.112612
Sum of electronic and thermal Enthalpies= -274.111668
Sum of electronic and thermal Free Energies= -274.152828

HF=-274.2996121 (U)B3LYP-D3/def2-SVP

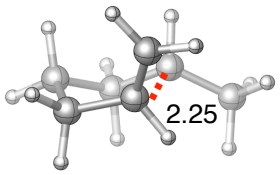
HF=-274.6066553 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-274.1617958 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-274.1713161 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

C	-0.24746200	1.02177900	1.00452100
C	1.08469400	-0.10964400	-1.19949100
C	1.18737500	1.23371400	0.59405700
C	-0.36760000	-0.49718000	-0.94134100
C	-0.71031200	-0.37027900	0.54811000
H	-0.36643000	1.12697300	2.10080200
H	-0.89435300	1.78448400	0.53848400
H	-1.03206200	0.16716800	-1.51963900
H	-0.55807400	-1.52314800	-1.29754100
H	-1.78549700	-0.52830700	0.73781200
H	-0.16780800	-1.14636300	1.11650500
C	2.10299200	-1.03276300	-1.11507600
H	1.25325700	0.75615400	-1.84864700
H	1.95018700	-2.00499800	-0.63480000
H	1.41868100	2.18202500	0.09465100
H	3.12051100	-0.79167200	-1.43337900
C	2.27601100	0.70373200	1.47827900
H	3.24985000	0.69388500	0.96451400
H	2.38547000	1.32623900	2.38840200
H	2.06709500	-0.32648600	1.80942900

TS-Me-*trans*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.180557 (Hartree/Particle)
Thermal correction to Energy= 0.188520
Thermal correction to Enthalpy= 0.189464
Thermal correction to Gibbs Free Energy= 0.147636
Sum of electronic and zero-point Energies= -274.300719
Sum of electronic and thermal Energies= -274.292755
Sum of electronic and thermal Enthalpies= -274.291811
Sum of electronic and thermal Free Energies= -274.333639
HF=-274.4812754 (U)B3LYP/6-31G(d)
HF=-274.6079746 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.162464 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1714941 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

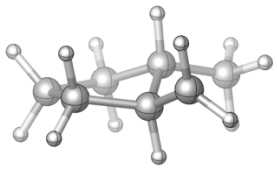
C	-0.20047700	0.92608100	0.96360600
C	1.02970200	-0.16000400	-1.30040000
C	1.26169000	0.99040300	0.62190600
C	-0.40556700	-0.58652100	-1.00379000
C	-0.75641200	-0.42236600	0.48708300
H	-0.37050600	1.04928800	2.04664400
H	-0.73947700	1.74709900	0.46867200
H	-1.09144500	0.02623400	-1.60363600
H	-0.56037100	-1.62603200	-1.31650800
H	-1.83750500	-0.50466600	0.65643100
H	-0.27980800	-1.22845300	1.06186000
C	2.04883000	-1.07041400	-1.42502600
H	1.14960000	0.79034300	-1.81923200
H	1.93545900	-2.09908000	-1.08927600
H	1.88483800	0.27403300	1.15769700
H	3.03514800	-0.77784100	-1.77431300
C	1.92401600	2.30078200	0.31283400
H	2.05739300	2.91707000	1.21840000
H	2.92074300	2.15494300	-0.12097300
H	1.33089900	2.89890200	-0.39140100

(U)B3LYP-D3/def2-SVP
Zero-point correction= 0.179002 (Hartree/Particle)
Thermal correction to Energy= 0.186904
Thermal correction to Enthalpy= 0.187848
Thermal correction to Gibbs Free Energy= 0.146223
Sum of electronic and zero-point Energies= -274.120897

Sum of electronic and thermal Energies= -274.112995
Sum of electronic and thermal Enthalpies= -274.112051
Sum of electronic and thermal Free Energies= -274.153676
HF=-274.2998991 (U)B3LYP-D3/def2-SVP
HF=-274.6073059 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP-D3/def2-SVP
HF=-274.1627942 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP
HF=-274.1718806 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

C	-0.19294800	0.90775900	0.97400400
C	1.03552700	-0.15681100	-1.30205100
C	1.26280000	0.99235600	0.61777000
C	-0.40908500	-0.55356100	-1.01713100
C	-0.74235800	-0.43411000	0.47896400
H	-0.35008500	1.01288800	2.06651800
H	-0.74796100	1.73618100	0.49682700
H	-1.08352600	0.10790700	-1.58715400
H	-0.59928600	-1.57949600	-1.37261000
H	-1.82516100	-0.53374400	0.66407700
H	-0.24535500	-1.25304800	1.02928700
C	2.04617500	-1.08525900	-1.38373700
H	1.18418000	0.78903000	-1.83485000
H	1.90493200	-2.11085700	-1.02647200
H	1.90305000	0.27466400	1.14470200
H	3.04972800	-0.80784200	-1.71759100
C	1.90564200	2.30405400	0.29166600
H	2.04638000	2.92926900	1.19716000
H	2.90253200	2.16558000	-0.15872900
H	1.29157000	2.89484200	-0.41007400

Int-Me-*trans*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.182570 (Hartree/Particle)
Thermal correction to Energy= 0.190916
Thermal correction to Enthalpy= 0.191860
Thermal correction to Gibbs Free Energy= 0.149182
Sum of electronic and zero-point Energies= -274.333591
Sum of electronic and thermal Energies= -274.325245
Sum of electronic and thermal Enthalpies= -274.324301
Sum of electronic and thermal Free Energies= -274.366979
HF=-274.5161612 (U)B3LYP/6-31G(d)
HF=-274.6393466 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1935998 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.2024373 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.21690000	0.96628600	0.92766900
C	0.93053900	0.08809400	-1.01812800
C	1.20358600	0.72548200	0.38160800
C	-0.23270300	-0.89127300	-0.71002400
C	-1.07731900	-0.21497700	0.40451900
H	-0.23288200	1.05378700	2.02007500
H	-0.59565400	1.91739000	0.52915400
H	-0.81513200	-1.12849800	-1.60636000
H	0.18854600	-1.83821700	-0.34822500
H	-2.03932300	0.14048200	0.01985800
H	-1.30701000	-0.92778000	1.20400800
C	2.10851500	-0.54493000	-1.66782200
H	0.55023900	0.89418800	-1.66473900
H	2.53239000	-1.45779300	-1.25585300
H	1.69229500	-0.04549000	0.99773200
H	2.62645000	-0.08454200	-2.50256600
C	2.09288500	1.96685800	0.35318700
H	2.23729200	2.37707000	1.36002700
H	3.08165400	1.73792300	-0.06061700
H	1.64408300	2.75554000	-0.26512500

(U)B3LYP-D3/def2-SVP
Zero-point correction= 0.181096 (Hartree/Particle)
Thermal correction to Energy= 0.189343
Thermal correction to Enthalpy= 0.190287
Thermal correction to Gibbs Free Energy= 0.147945
Sum of electronic and zero-point Energies= -274.153171
Sum of electronic and thermal Energies= -274.144924

Sum of electronic and thermal Enthalpies= -274.143980
Sum of electronic and thermal Free Energies= -274.186322
HF=-274.3342666 (U)B3LYP-D3/def2-SVP
HF=-274.6386959 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP-D3/def2-SVP
HF=-274.1938415 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP
HF=-274.2027048 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

C	-0.21438400	0.96784300	0.92535600
C	0.91931200	0.08993800	-1.01997900
C	1.20191700	0.71796000	0.38009800
C	-0.23514700	-0.89072400	-0.70334100
C	-1.08005100	-0.20782300	0.40391500
H	-0.22888300	1.06314500	2.02282500
H	-0.58522600	1.92518300	0.51908000
H	-0.81778100	-1.14719000	-1.60129100
H	0.19917200	-1.83309600	-0.32783000
H	-2.04335900	0.15427100	0.01214400
H	-1.32073800	-0.92034500	1.20834900
C	2.09546700	-0.52818600	-1.68540000
H	0.52839400	0.90734000	-1.65632000
H	2.50618100	-1.46722200	-1.29971200
H	1.68343100	-0.06868500	0.99280200
H	2.64532900	-0.02002600	-2.48088300
C	2.10492500	1.94535000	0.35813900
H	2.25242300	2.35363100	1.37137600
H	3.09637500	1.70415400	-0.05752300
H	1.66419300	2.74408500	-0.26342900

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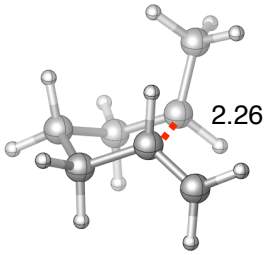


(U)B3LYP/6-31G(d)
Zero-point correction= 0.180704 (Hartree/Particle)
Thermal correction to Energy= 0.188538
Thermal correction to Enthalpy= 0.189482
Thermal correction to Gibbs Free Energy= 0.148354
Sum of electronic and zero-point Energies= -274.302198
Sum of electronic and thermal Energies= -274.294364
Sum of electronic and thermal Enthalpies= -274.293420
Sum of electronic and thermal Free Energies= -274.334548
HF=-274.4829022 (U)B3LYP/6-31G(d)
HF=-274.6098598 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1640674 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-274.1732095 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)
HF=-273.962894887981 (U)DLPNO-CCSD(T)/def2-TZVPP//(U)B3LYP-D3/def2-SVP

C	-0.29880500	0.82520900	1.05450400
C	1.04766600	-0.08783100	-1.25429400
C	1.12561600	1.11622800	0.65178900
C	-0.39115900	-0.51207200	-1.03063600
C	-0.73695000	-0.52833100	0.46291600
H	-0.41336800	0.81657100	2.15076100
H	-0.96335300	1.61113600	0.67316700
H	-1.05837200	0.18198500	-1.56001200
H	-0.55608200	-1.50519100	-1.47239900
H	-1.80463100	-0.71748900	0.63033900
H	-0.19034800	-1.34279900	0.95855800
C	1.42956000	0.69342200	-2.31606300
H	1.79815400	-0.75943100	-0.83520800
H	0.70375100	1.27341100	-2.88167400
H	1.32413100	2.11040500	0.25660400
H	2.47567700	0.83790100	-2.57085400
C	2.24944400	0.52276500	1.45527300
H	2.07458000	-0.53435300	1.69282900
H	3.20695900	0.59356800	0.92519600
H	2.37555200	1.04708200	2.41784900

(U)B3LYP-D3/def2-SVP
Zero-point correction= 0.179207 (Hartree/Particle)
Thermal correction to Energy= 0.186956

Thermal correction to Enthalpy= 0.187900
Thermal correction to Gibbs Free Energy= 0.147043
Sum of electronic and zero-point Energies= -274.122571
Sum of electronic and thermal Energies= -274.114822
Sum of electronic and thermal Enthalpies= -274.113878
Sum of electronic and thermal Free Energies= -274.154735

HF=-274.3017778 (U)B3LYP-D3/def2-SVP

HF=-274.6091978 (U)B3LYP-D3/def2-TZVPP-CPCM(THF)//(U)B3LYP-D3/def2-SVP

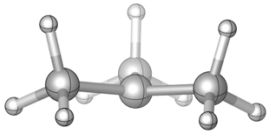
HF=-274.164434 (U)PBEPBE/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-274.1736124 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP-D3/def2-SVP

HF=-273.962399137473 (U)DLPNO-CCSD(T)/def2-TZVPP//(U)B3LYP-D3/def2-SVP

C	-0.30056600	0.82803500	1.04835600
C	1.04551200	-0.08867500	-1.24888900
C	1.12207500	1.11976700	0.64708500
C	-0.39185200	-0.51181200	-1.02466500
C	-0.73062600	-0.53027000	0.46786700
H	-0.41583400	0.83106900	2.15041700
H	-0.97101800	1.61105900	0.65594800
H	-1.06444200	0.18739700	-1.55217400
H	-0.55707900	-1.50804200	-1.47279900
H	-1.80016200	-0.73251000	0.64442100
H	-0.16952000	-1.34186000	0.96515800
C	1.43542400	0.69976900	-2.30576400
H	1.79790500	-0.76626500	-0.82657100
H	0.70604300	1.28661900	-2.87350100
H	1.32382700	2.11714900	0.24337200
H	2.49107800	0.84232200	-2.55184100
C	2.24212000	0.51773000	1.44297100
H	2.05738000	-0.54391400	1.67983600
H	3.20406300	0.58242300	0.90817000
H	2.37369500	1.04219500	2.41124900

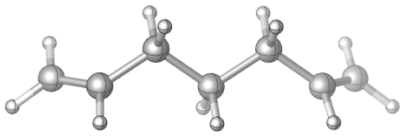
Figure S2
***t*Bu radical**



(U)B3LYP/6-31G(d)
Zero-point correction= 0.117262 (Hartree/Particle)
Thermal correction to Energy= 0.123644
Thermal correction to Enthalpy= 0.124588
Thermal correction to Gibbs Free Energy= 0.087750
Sum of electronic and zero-point Energies= -157.681055
Sum of electronic and thermal Energies= -157.674674
Sum of electronic and thermal Enthalpies= -157.673730
Sum of electronic and thermal Free Energies= -157.710568
HF=-157.7983175 (U)B3LYP/6-31G(d)
HF=-157.60776 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-5.37808700	4.84904000	-2.26998200
H	-4.31060600	5.09368200	-2.19728100
H	-5.54578500	4.33293200	-3.22400700
H	-5.91500600	5.81456000	-2.33946900
C	-7.11264900	3.24818100	-1.22953300
H	-7.21583400	2.79264400	-2.22275000
H	-7.17495600	2.44930600	-0.47948000
H	-8.00752200	3.88316600	-1.08346300
C	-5.83974300	4.02756100	-1.10591100
C	-5.31959800	4.35202500	0.26053900
H	-4.25445400	4.61585400	0.23822700
H	-5.84483800	5.21453700	0.71389800
H	-5.44868700	3.51193200	0.95497300

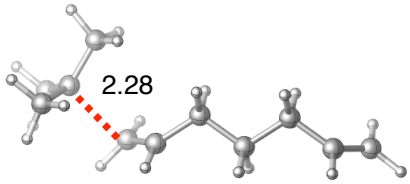
C-olefin



(U)B3LYP/6-31G(d)
Zero-point correction= 0.171110 (Hartree/Particle)
Thermal correction to Energy= 0.179776
Thermal correction to Enthalpy= 0.180721
Thermal correction to Gibbs Free Energy= 0.137255
Sum of electronic and zero-point Energies= -273.754436
Sum of electronic and thermal Energies= -273.745770
Sum of electronic and thermal Enthalpies= -273.744826
Sum of electronic and thermal Free Energies= -273.788291
HF=-273.9255467 (U)B3LYP/6-31G(d)
HF=-273.6149472 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-4.36655200	2.06336000	-1.50932100
H	-4.89331100	1.76162000	-0.60782300
H	-4.94354400	2.06103500	-2.43231200
C	-3.08232600	2.42187100	-1.48792400
H	-2.54467100	2.40582500	-0.53765000
C	-2.27604100	2.84227500	-2.68641300
H	-1.90269800	3.86730100	-2.53468800
H	-2.92194900	2.87356400	-3.57399000
C	-1.07242600	1.91856000	-2.95290200
H	-1.42923500	0.89596600	-3.12917600
H	-0.44168000	1.87354700	-2.05323100
C	-0.21991600	2.37737300	-4.15117700
H	0.11072100	3.41200000	-3.96861600
H	-0.83938900	2.40307100	-5.05758600
C	0.98179500	1.50276300	-4.38375100
H	1.69323900	1.44632200	-3.55730800
C	1.22219500	0.80082000	-5.49177200
H	0.54155100	0.82312100	-6.34092600
H	2.10785800	0.17971700	-5.59688700

TS-RA-*t*Bu-C

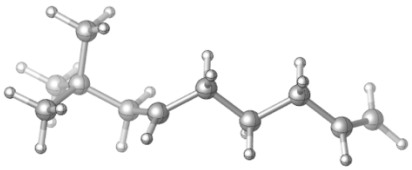


(U)B3LYP/6-31G(d)
Zero-point correction= 0.290274 (Hartree/Particle)
Thermal correction to Energy= 0.305476
Thermal correction to Enthalpy= 0.306420
Thermal correction to Gibbs Free Energy= 0.245929
Sum of electronic and zero-point Energies= -431.422656
Sum of electronic and thermal Energies= -431.407453
Sum of electronic and thermal Enthalpies= -431.406509
Sum of electronic and thermal Free Energies= -431.467001
HF=-431.7129297 (U)B3LYP/6-31G(d)
HF=-431.222546 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-5.40860700	4.84316700	-2.26050200
H	-4.35093400	5.12953600	-2.24050500
H	-5.62388500	4.39692800	-3.23914000
H	-5.99806200	5.77491600	-2.19601200
C	-7.10583200	3.25672300	-1.20454300
H	-7.29140200	2.81065000	-2.18958400
H	-7.22455300	2.47224000	-0.44692900
H	-7.91079600	3.99257200	-1.03085600
C	-5.74920300	3.90788000	-1.13056700
C	-4.40241300	2.11390600	-1.51783800
H	-4.86041900	1.62267700	-0.66340500
H	-4.89892700	1.95235600	-2.47284700
C	-3.07123900	2.42559200	-1.49028600
C	-5.30538700	4.35347800	0.23764800
H	-4.24066000	4.61473000	0.24722700
H	-5.86353000	5.24763000	0.56633000
H	-5.47242200	3.57632300	0.99360300
H	-2.54634500	2.40923600	-0.53395100
C	-2.26100500	2.84889800	-2.68253900
H	-1.87419000	3.87188300	-2.53984800
H	-2.90272400	2.88442900	-3.57346000
C	-1.06088600	1.91823400	-2.95284900
H	-1.42375000	0.89864800	-3.13413900
H	-0.43337600	1.86531200	-2.05141700
C	-0.20214000	2.37739000	-4.14675500
H	0.13389200	3.40928600	-3.95826400
H	-0.81877900	2.41123700	-5.05493600
C	0.99511200	1.49729400	-4.38031500
H	1.70359100	1.43262700	-3.55187400

C	1.23512500	0.79860900	-5.49062000
H	0.55736600	0.82863100	-6.34187200
H	2.11733000	0.17251300	-5.59554700

Int-*t*Bu-C

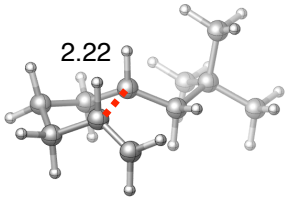


(U)B3LYP/6-31G(d)
Zero-point correction= 0.293760 (Hartree/Particle)
Thermal correction to Energy= 0.308427
Thermal correction to Enthalpy= 0.309371
Thermal correction to Gibbs Free Energy= 0.249589
Sum of electronic and zero-point Energies= -431.456417
Sum of electronic and thermal Energies= -431.441750
Sum of electronic and thermal Enthalpies= -431.440806
Sum of electronic and thermal Free Energies= -431.500588
HF=-431.7501771 (U)B3LYP/6-31G(d)
HF=-431.2556316 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-5.49293900	4.83542500	-2.15662000
H	-4.54639300	5.38122300	-2.06991800
H	-5.61103500	4.53092200	-3.20434800
H	-6.30683000	5.53162200	-1.91883000
C	-6.85729500	2.87273900	-1.38015500
H	-6.99475300	2.52368600	-2.41128600
H	-6.90859300	1.99713700	-0.72090700
H	-7.70351100	3.52596800	-1.13369800
C	-5.51952200	3.61696400	-1.21680800
C	-4.36115800	2.62956000	-1.58693600
H	-4.47156400	1.74881000	-0.93163800
H	-4.53852300	2.27421800	-2.61250400
C	-2.96994300	3.16927700	-1.48265400
C	-5.37304400	4.08539800	0.24233300
H	-4.44077000	4.64119100	0.39261600
H	-6.20303500	4.74490600	0.52451900
H	-5.37423200	3.23392900	0.93485600
H	-2.54484700	3.31439100	-0.49057200
C	-2.06363000	3.34866500	-2.65888500
H	-1.43674500	4.24370200	-2.52299600
H	-2.65801800	3.51903000	-3.56826300
C	-1.12286100	2.14180700	-2.90749500

H	-1.72247900	1.23681800	-3.06893300
H	-0.52558100	1.95955300	-2.00333500
C	-0.18521700	2.35456200	-4.11183800
H	0.39113000	3.27830000	-3.94602400
H	-0.78103500	2.51688900	-5.02001800
C	0.76134300	1.20535700	-4.32516000
H	1.44371300	0.99461100	-3.49915900
C	0.81045800	0.43783600	-5.41479600
H	0.14945300	0.60726400	-6.26288800
H	1.51330700	-0.38622600	-5.50534800

TS-*t*Bu-C-*cis*

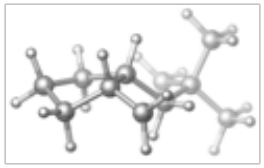


(U)B3LYP/6-31G(d)
Zero-point correction= 0.294359 (Hartree/Particle)
Thermal correction to Energy= 0.307367
Thermal correction to Enthalpy= 0.308311
Thermal correction to Gibbs Free Energy= 0.254513
Sum of electronic and zero-point Energies= -431.442128
Sum of electronic and thermal Energies= -431.429120
Sum of electronic and thermal Enthalpies= -431.428176
Sum of electronic and thermal Free Energies= -431.481974
HF=-431.736487 (U)B3LYP/6-31G(d)
HF=-431.2498538 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.25949200	0.92453100	0.93280600
C	1.08223800	-0.22032900	-1.24285900
C	1.20352300	1.03314700	0.58609400
C	-0.39834800	-0.50595300	-1.07847300
C	-0.81159900	-0.40453900	0.39440700
H	-0.42987500	0.99159800	2.01898200
H	-0.81086300	1.75973700	0.47865300
H	-0.97315000	0.21543700	-1.67542300
H	-0.63266100	-1.50264600	-1.47791900
H	-1.89931200	-0.47478600	0.51800300
H	-0.37204500	-1.23913700	0.95934900
C	1.57861400	0.45399500	-2.33699200
H	1.74423300	-0.95280600	-0.77931400
H	0.93627700	1.07186900	-2.96035300
H	1.84542300	0.33989600	1.13275700
H	2.64117800	0.47342500	-2.56186900
C	1.84096000	2.35420800	0.24538100
H	1.12264100	2.96026200	-0.32529100
H	2.68487600	2.17014600	-0.43519600
C	2.38570900	3.22802700	1.42161900
C	2.99582600	4.50434300	0.80866100
H	2.24248800	5.07695400	0.25333600
H	3.40478000	5.15869900	1.58857700
H	3.80988200	4.26198400	0.11434500
C	3.48263600	2.47213200	2.19481500
H	3.09020900	1.57118200	2.67994300
H	4.29883900	2.16652500	1.52799900
H	3.91330600	3.10735700	2.97875600
C	1.25828800	3.63085300	2.38994500

H	1.63705700	4.30837600	3.16549800
H	0.44753100	4.14929400	1.86295800
H	0.82716400	2.75984900	2.89505000

Int-*t*Bu-C-*cis*

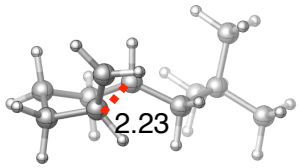


(U)B3LYP/6-31G(d)
Zero-point correction= 0.296519 (Hartree/Particle)
Thermal correction to Energy= 0.309741
Thermal correction to Enthalpy= 0.310685
Thermal correction to Gibbs Free Energy= 0.256315
Sum of electronic and zero-point Energies= -431.465014
Sum of electronic and thermal Energies= -431.451793
Sum of electronic and thermal Enthalpies= -431.450849
Sum of electronic and thermal Free Energies= -431.505219
HF=-431.7615336 (U)B3LYP/6-31G(d)
HF=-431.2716865 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.16319600	0.81623900	1.08964700
C	1.14423600	-0.05676200	-0.85154400
C	1.25912000	0.87323800	0.45035200
C	-0.37556500	-0.19281900	-1.08732800
C	-0.95158300	-0.26707000	0.32961800
H	-0.13254100	0.62498900	2.16772400
H	-0.66278200	1.78359300	0.95609900
H	-0.75419500	0.70068500	-1.60482700
H	-0.62263700	-1.05982300	-1.70996600
H	-2.03508800	-0.10812300	0.37059200
H	-0.75307300	-1.25945500	0.75689300
C	1.91365400	0.35200900	-2.05629100
H	1.51122500	-1.04446000	-0.53632500
H	1.51604300	1.08940500	-2.74849200
H	1.98184500	0.38900000	1.11658600
H	2.93045500	0.01029100	-2.22480800
C	1.76442600	2.29902300	0.14860600
H	0.96444500	2.86043900	-0.35787100
H	2.57939200	2.21948200	-0.58369300
C	2.30614700	3.16860300	1.31973800
C	2.77069700	4.51012400	0.71373700
H	1.93815700	5.03586500	0.22969300

H	3.17794900	5.17159000	1.48837700
H	3.55250200	4.35706300	-0.04044200
C	3.51739600	2.48903000	1.98905600
H	3.24008600	1.55406100	2.48887800
H	4.29893300	2.25811800	1.25425600
H	3.95813000	3.14639000	2.74873600
C	1.23640300	3.46515700	2.38867100
H	1.63303900	4.15519000	3.14414600
H	0.34840200	3.93369600	1.94679900
H	0.91391200	2.55845600	2.91002600

TS-*t*Bu-C-*trans*

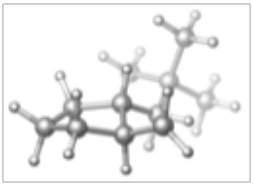


(U)B3LYP/6-31G(d)
Zero-point correction= 0.294269 (Hartree/Particle)
Thermal correction to Energy= 0.307408
Thermal correction to Enthalpy= 0.308352
Thermal correction to Gibbs Free Energy= 0.254010
Sum of electronic and zero-point Energies= -431.439704
Sum of electronic and thermal Energies= -431.426565
Sum of electronic and thermal Enthalpies= -431.425621
Sum of electronic and thermal Free Energies= -431.479964
HF=-431.7339731 (U)B3LYP/6-31G(d)
HF=-431.2473367 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.26266100	0.92471500	0.94031000
C	1.04847500	-0.14793700	-1.26682700
C	1.20756700	1.01406800	0.63040300
C	-0.38717200	-0.60271900	-1.02014300
C	-0.78559100	-0.43527300	0.45714600
H	-0.46510600	1.04048900	2.01746100
H	-0.80521600	1.73536400	0.43300900
H	-1.06408200	-0.00609000	-1.64566000
H	-0.51143300	-1.64671100	-1.33142200
H	-1.86983500	-0.53129600	0.59671600
H	-0.31456700	-1.23039600	1.05153600
C	2.09077200	-1.04164400	-1.34592000
H	1.16489000	0.78995400	-1.80841100
H	1.98865200	-2.06543800	-0.99219200
H	1.82602400	0.30623000	1.18211700
H	3.08172900	-0.73401100	-1.66813900
C	1.88438200	2.30815200	0.26511700
H	1.20533500	2.90662200	-0.36104600
H	2.75968700	2.07808000	-0.36194400
C	2.39614300	3.22517700	1.42528400
C	3.06975000	4.45511200	0.78528600
H	2.36101200	5.01885400	0.16575100
H	3.45605400	5.13601200	1.55384000
H	3.91146300	4.16019100	0.14643300
C	3.43114600	2.47761300	2.28625900
H	2.98919300	1.60950100	2.78805300
H	4.27122600	2.12125300	1.67682300
H	3.83872100	3.13664200	3.06281200
C	1.23186200	3.69944800	2.31400200
H	1.58872500	4.40299900	3.07656300

H	0.46290500	4.21233300	1.72275800
H	0.75309600	2.86342600	2.83481400

Int-*t*Bu-C-*trans*

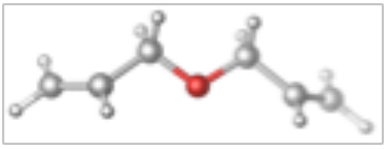


(U)B3LYP/6-31G(d)
Zero-point correction= 0.296069 (Hartree/Particle)
Thermal correction to Energy= 0.309694
Thermal correction to Enthalpy= 0.310638
Thermal correction to Gibbs Free Energy= 0.254748
Sum of electronic and zero-point Energies= -431.469873
Sum of electronic and thermal Energies= -431.456248
Sum of electronic and thermal Enthalpies= -431.455304
Sum of electronic and thermal Free Energies= -431.511194
HF=-431.7659422 (U)B3LYP/6-31G(d)
HF=-431.2757388 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.36379100	1.07569400	1.03599200
C	1.04321500	0.01357500	-0.68293800
C	1.11558900	0.94405300	0.57355200
C	-0.07763800	-0.98125500	-0.28994100
C	-1.14598100	-0.09942900	0.38255700
H	-0.44266000	1.04842700	2.12768700
H	-0.77971900	2.03925300	0.71921400
H	-0.45822000	-1.54536300	-1.14818500
H	0.32756900	-1.71048500	0.42489300
H	-1.84175100	0.28361300	-0.37354200
H	-1.74737500	-0.65812100	1.10782800
C	2.33320700	-0.62518500	-1.05622900
H	0.67878100	0.61808800	-1.52756800
H	2.85720200	-1.25015200	-0.33660300
H	1.67250500	0.38237400	1.33688300
H	2.76493200	-0.53235000	-2.04695800
C	1.86107200	2.25648500	0.27208500
H	1.21280000	2.88398600	-0.35927800
H	2.73176400	2.00157300	-0.34943600
C	2.38737000	3.12573700	1.44808700
C	3.13046600	4.33025000	0.83264500
H	2.45993300	4.93187600	0.20626500
H	3.53372900	4.98523900	1.61482000
H	3.96877600	4.00257500	0.20549300
C	3.37970300	2.32793500	2.31681000

H	2.89386700	1.48977700	2.82908000
H	4.19913100	1.92116800	1.71104700
H	3.82184900	2.97042700	3.08832100
C	1.24677100	3.65990100	2.33588900
H	1.64141800	4.34559500	3.09625700
H	0.50602300	4.21204300	1.74429500
H	0.72408500	2.85402900	2.86075700

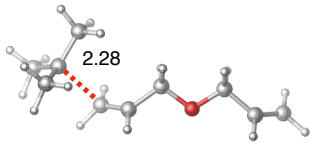
O-olefin



(U)B3LYP/6-31G(d)
Zero-point correction= 0.146796 (Hartree/Particle)
Thermal correction to Energy= 0.155246
Thermal correction to Enthalpy= 0.156191
Thermal correction to Gibbs Free Energy= 0.113095
Sum of electronic and zero-point Energies= -309.664862
Sum of electronic and thermal Energies= -309.656411
Sum of electronic and thermal Enthalpies= -309.655467
Sum of electronic and thermal Free Energies= -309.698563
HF=-309.8116579 (U)B3LYP/6-31G(d)
HF=-309.5017672 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-4.36371600	2.05320900	-1.56883300
H	-4.83654500	1.78101700	-0.62918700
H	-5.00746000	2.08142900	-2.44578100
C	-3.06530200	2.34154000	-1.64327100
H	-2.43784800	2.29597500	-0.75378800
C	-2.36221400	2.76673500	-2.89793400
H	-2.06922800	3.83143200	-2.82560200
H	-3.03325200	2.67504400	-3.76858600
C	-0.41392600	2.37005900	-4.17639500
H	-0.15952000	3.44257000	-4.07810000
H	-0.97506700	2.25654400	-5.11925700
C	0.83884500	1.54607600	-4.20597700
H	1.39437500	1.51450000	-3.26931400
C	1.29070000	0.90177600	-5.28080700
H	0.74735700	0.91028300	-6.22364700
H	2.22254400	0.34324500	-5.26356700
O	-1.20080100	1.96752600	-3.06531100

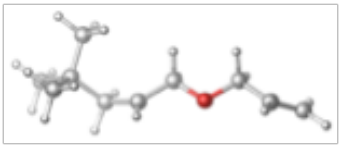
TS-RA-*t*Bu-O



(U)B3LYP/6-31G(d)
Zero-point correction= 0.266007 (Hartree/Particle)
Thermal correction to Energy= 0.280975
Thermal correction to Enthalpy= 0.281919
Thermal correction to Gibbs Free Energy= 0.221812
Sum of electronic and zero-point Energies= -467.333796
Sum of electronic and thermal Energies= -467.318828
Sum of electronic and thermal Enthalpies= -467.317884
Sum of electronic and thermal Free Energies= -467.377991
HF=-467.5998028 (U)B3LYP/6-31G(d)
HF=-467.1110399 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-5.38141900	4.82286500	-2.30654200
H	-4.32023900	5.09417600	-2.34847400
H	-5.65661000	4.36195600	-3.26302600
H	-5.95234200	5.76464300	-2.22802000
C	-7.04388000	3.28778600	-1.12559000
H	-7.29534300	2.83139100	-2.09091000
H	-7.13162200	2.51730300	-0.34987100
H	-7.82290700	4.04174700	-0.91632000
C	-5.67464100	3.91574500	-1.14114300
C	-4.38629000	2.08519000	-1.57468100
H	-4.79467600	1.62822300	-0.67772900
H	-4.94889400	1.91109600	-2.48954200
C	-3.05328000	2.37414800	-1.64225800
C	-5.14142400	4.37300500	0.19064600
H	-4.07312800	4.61204100	0.13362300
H	-5.66168500	5.28388100	0.53454800
H	-5.27993800	3.61228100	0.96847600
H	-2.44579300	2.36927800	-0.73865100
C	-2.34666800	2.78889600	-2.89374400
H	-2.02872000	3.84889600	-2.84042100
H	-3.01807900	2.70126100	-3.76521500
C	-0.39974500	2.37117100	-4.17211100
H	-0.13123800	3.44009400	-4.06863100
H	-0.95975300	2.27068100	-5.11754300
C	0.84300400	1.53212900	-4.20496800
H	1.39430300	1.48566900	-3.26636000
C	1.29141100	0.89060600	-5.28302400
H	0.75198600	0.91326200	-6.22792000
H	2.21606900	0.32013500	-5.26653500
O	-1.19233800	1.97221200	-3.06511600

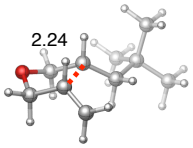
Int-*t*Bu-O



(U)B3LYP/6-31G(d)
Zero-point correction= 0.269223 (Hartree/Particle)
Thermal correction to Energy= 0.283688
Thermal correction to Enthalpy= 0.284632
Thermal correction to Gibbs Free Energy= 0.225659
Sum of electronic and zero-point Energies= -467.368122
Sum of electronic and thermal Energies= -467.353657
Sum of electronic and thermal Enthalpies= -467.352713
Sum of electronic and thermal Free Energies= -467.411686
HF=-467.6373454 (U)B3LYP/6-31G(d)
HF=-467.1440517 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-5.27163900	4.86464300	-2.15217500
H	-4.21605600	5.15081200	-2.22530900
H	-5.62032700	4.59978900	-3.15854100
H	-5.83431400	5.74866900	-1.82775900
C	-6.96635100	3.34923000	-1.08285300
H	-7.36434800	3.05886000	-2.06324300
H	-7.14196800	2.51659000	-0.39043400
H	-7.54928000	4.20771000	-0.72715500
C	-5.46897600	3.69745900	-1.16879700
C	-4.70350900	2.42727100	-1.67755900
H	-4.92800800	1.61446400	-0.96795600
H	-5.14850400	2.13096200	-2.63860200
C	-3.22316700	2.54711200	-1.83052800
C	-4.95901200	4.10233200	0.22596100
H	-3.89775800	4.37415200	0.20169200
H	-5.51571900	4.96687700	0.60799300
H	-5.08067700	3.28325600	0.94603400
H	-2.58724900	2.57306400	-0.94920200
C	-2.54159800	2.72393800	-3.14184700
H	-2.39981300	3.79936600	-3.38849400
H	-3.15809500	2.30630500	-3.95958200
C	-0.50598600	2.31304600	-4.27561200
H	-0.41857400	3.40074800	-4.46066700
H	-1.00349300	1.87544800	-5.15779400
C	0.85622200	1.71422500	-4.08820200
H	1.36964500	2.01020800	-3.17395700
C	1.44536900	0.89470300	-4.95770900
H	0.94786300	0.57677200	-5.87187000
H	2.44877500	0.51141600	-4.79364800
O	-1.26853200	2.09253700	-3.09943600

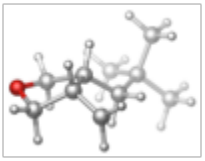
TS-*t*Bu-O-*cis*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.270494 (Hartree/Particle)
Thermal correction to Energy= 0.283255
Thermal correction to Enthalpy= 0.284199
Thermal correction to Gibbs Free Energy= 0.230901
Sum of electronic and zero-point Energies= -467.358328
Sum of electronic and thermal Energies= -467.345567
Sum of electronic and thermal Enthalpies= -467.344623
Sum of electronic and thermal Free Energies= -467.397921
HF=-467.6288221 (U)B3LYP/6-31G(d)
HF=-467.1428262 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.16648100	0.81405500	0.89365600
C	1.14709300	-0.27244400	-1.25153900
C	1.29509500	0.98887100	0.59018700
C	-0.31986500	-0.52954500	-0.98355600
H	-0.37736600	0.78941600	1.97108900
H	-0.74575100	1.64649500	0.45654700
H	-0.92967600	0.17606300	-1.57500400
H	-0.59713700	-1.54731500	-1.28069100
C	1.56532000	0.40164200	-2.37158900
H	1.83038300	-0.99647200	-0.80973000
H	0.88171200	1.02119700	-2.94765100
H	1.95192100	0.29915200	1.11974400
H	2.60544900	0.40246100	-2.68365100
C	1.87822600	2.32980900	0.24454300
H	1.13662100	2.90567300	-0.32749400
H	2.73103600	2.17842100	-0.43321600
C	2.37976900	3.22206300	1.42628200
C	2.92248300	4.53274100	0.82380200
H	2.14032900	5.07117800	0.27427700
H	3.29832600	5.19988200	1.60926100
H	3.74732100	4.33841900	0.12718100
C	3.51303000	2.51575800	2.19380200
H	3.16737400	1.59066600	2.66892500
H	4.34530500	2.26039500	1.52583200
H	3.90831500	3.16442500	2.98511100
C	1.22949200	3.55364300	2.39459800
H	1.56938200	4.23778300	3.18187400
H	0.39539600	4.03795500	1.87152900
H	0.84241700	2.65411900	2.88652900
O	-0.64212000	-0.43361600	0.39534500

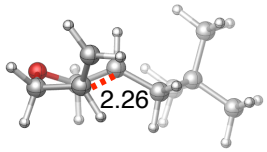
Int-*t*Bu-O-*cis*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.272704 (Hartree/Particle)
Thermal correction to Energy= 0.285703
Thermal correction to Enthalpy= 0.286647
Thermal correction to Gibbs Free Energy= 0.232726
Sum of electronic and zero-point Energies= -467.382837
Sum of electronic and thermal Energies= -467.369839
Sum of electronic and thermal Enthalpies= -467.368895
Sum of electronic and thermal Free Energies= -467.422816
HF=-467.6555418 (U)B3LYP/6-31G(d)
HF=-467.1669802 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.14432800	0.81001200	0.97436700
C	1.20562100	-0.07148100	-0.87470000
C	1.30456400	0.86992300	0.41546700
C	-0.31651800	-0.30621700	-0.98190800
H	-0.19796700	0.64610400	2.05402700
H	-0.67821400	1.74668200	0.74093500
H	-0.78490900	0.49552600	-1.58132800
H	-0.57882500	-1.26985300	-1.42678100
C	1.82213900	0.41274300	-2.13573700
H	1.67062000	-1.02446500	-0.59665200
H	1.33753000	1.17834500	-2.73554000
H	1.98378600	0.37365000	1.11588000
H	2.80409400	0.07835400	-2.45352100
C	1.82812700	2.28992400	0.13254500
H	1.05065500	2.85495900	-0.40343500
H	2.66995400	2.20766400	-0.56767500
C	2.32004100	3.15043500	1.33101500
C	2.78439500	4.50685100	0.76017200
H	1.95994700	5.03004900	0.25998100
H	3.16013900	5.16043100	1.55685900
H	3.59020700	4.37547400	0.02754400
C	3.51695500	2.47751100	2.03198000
H	3.23847800	1.52797000	2.50300500
H	4.32940700	2.27526100	1.32283300
H	3.91705300	3.12657700	2.82050500
C	1.20625200	3.41137400	2.36342000
H	1.55983900	4.09678300	3.14362000
H	0.32557300	3.86865200	1.89609900
H	0.88504900	2.49094300	2.86258500
O	-0.79746300	-0.28849300	0.35002500

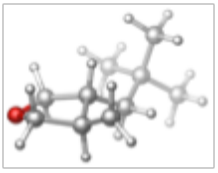
TS-*t*Bu-O-*trans*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.270244 (Hartree/Particle)
Thermal correction to Energy= 0.283197
Thermal correction to Enthalpy= 0.284141
Thermal correction to Gibbs Free Energy= 0.229984
Sum of electronic and zero-point Energies= -467.354843
Sum of electronic and thermal Energies= -467.341890
Sum of electronic and thermal Enthalpies= -467.340946
Sum of electronic and thermal Free Energies= -467.395103
HF=-467.6250868 (U)B3LYP/6-31G(d)
HF=-467.1391477 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.21911600	0.86179400	0.87147100
C	1.06609300	-0.21934200	-1.24572100
C	1.25964700	0.98113000	0.65611400
C	-0.30401400	-0.73922000	-0.83317100
H	-0.50728100	0.97650100	1.92596800
H	-0.75594400	1.63836700	0.29625600
H	-1.06209900	-0.32071500	-1.51668000
H	-0.34292100	-1.82971100	-0.91460900
C	2.13148500	-1.06065900	-1.41957500
H	1.07734800	0.72295300	-1.79236300
H	2.11866400	-2.07672600	-1.03186500
H	1.85461800	0.26338700	1.21780600
H	3.05729900	-0.72316600	-1.87717400
C	1.92811900	2.27250300	0.28275100
H	1.25392500	2.85649200	-0.36188700
H	2.81756200	2.04458500	-0.32468900
C	2.40262800	3.20408300	1.44749100
C	3.05230900	4.45001800	0.81490600
H	2.33693000	4.99679300	0.18795300
H	3.41333700	5.13933200	1.58799000
H	3.90810800	4.17609700	0.18555800
C	3.44368600	2.48248300	2.32308900
H	3.01786700	1.60176200	2.81675400
H	4.30260300	2.15082500	1.72622600
H	3.82079000	3.15078700	3.10685300
C	1.21096900	3.64425200	2.31697800
H	1.53447600	4.35422200	3.08802400
H	0.43848100	4.13816700	1.71420300
H	0.74739300	2.79311800	2.82813900
O	-0.66246000	-0.43981900	0.51489800

Int-*t*Bu-O-*trans*



(U)B3LYP/6-31G(d)
Zero-point correction= 0.272262 (Hartree/Particle)
Thermal correction to Energy= 0.285545
Thermal correction to Enthalpy= 0.286489
Thermal correction to Gibbs Free Energy= 0.231904
Sum of electronic and zero-point Energies= -467.387265
Sum of electronic and thermal Energies= -467.373982
Sum of electronic and thermal Enthalpies= -467.373038
Sum of electronic and thermal Free Energies= -467.427624
HF=-467.6595273 (U)B3LYP/6-31G(d)
HF=-467.1705119 (U)PBEPBE-D3/6-311+G(d,p)-CPCM(THF)//(U)B3LYP/6-31G(d)

C	-0.34623900	1.05940400	0.78710700
C	1.03584700	0.10034000	-0.95293700
C	1.13638200	0.94832300	0.35592400
C	-0.17653200	-0.78885000	-0.60835400
H	-0.47329700	0.90910500	1.86790200
H	-0.77416300	2.03743100	0.53122700
H	-0.68409300	-1.19217500	-1.48999300
H	0.14095700	-1.63449900	0.02607600
C	2.27070700	-0.63793000	-1.31868800
H	0.73916700	0.76868100	-1.77274600
H	2.71554700	-1.33919300	-0.61711500
H	1.67574500	0.33560200	1.09027400
H	2.73920800	-0.53288000	-2.29075200
C	1.88964000	2.27131800	0.13958400
H	1.25941500	2.92924800	-0.47801500
H	2.77769700	2.04514700	-0.46752000
C	2.37478800	3.07382400	1.37834300
C	3.11648200	4.32212900	0.85640000
H	2.45383400	4.95360400	0.25159200
H	3.49192300	4.93177800	1.68724700
H	3.97422000	4.04330600	0.23198000
C	3.35399600	2.23609900	2.22408500
H	2.86714900	1.36174100	2.67085100
H	4.19613600	1.87866800	1.61843700
H	3.76474700	2.83549000	3.04570300
C	1.20049400	3.53538000	2.26269300
H	1.56160800	4.17274200	3.07923700
H	0.47088300	4.11770900	1.68658000
H	0.67394500	2.69023900	2.71901200
O	-1.08569100	0.05851100	0.07756000

11. Crystallographic Data of 66

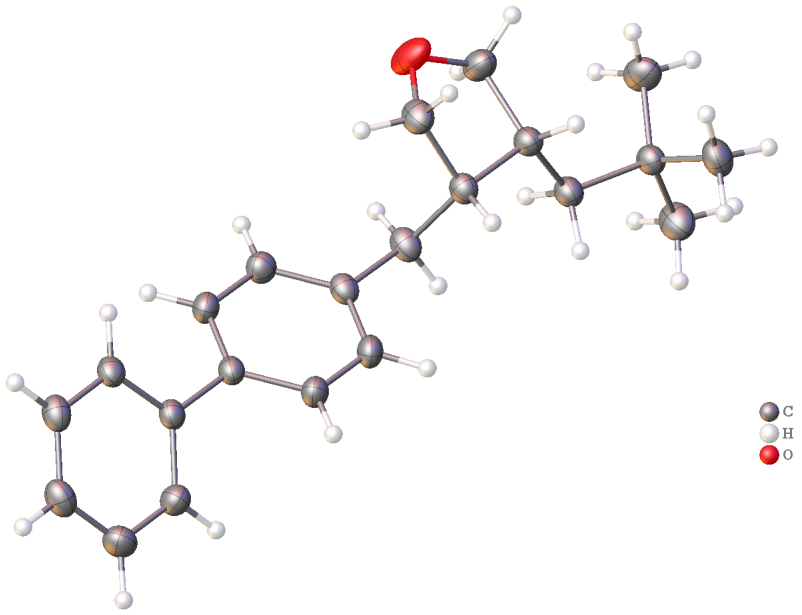


Table S3. Crystal data and structure refinement for **66**.

Identification code	**66**
Empirical formula	$C_{22}H_{28}O$
Formula weight	308.44
Temperature/K	149(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.1587(5)
b/Å	9.3173(8)
c/Å	15.9930(13)
α/°	96.1247(13)
β/°	90.4111(13)
γ/°	99.2413(14)
Volume/Å^3	900.36(13)
Z	2

ρ_{calc}g/cm^3	1.138
μ/mm^{-1}	0.067
F(000)	336.0
Crystal size/mm^3	0.44 × 0.27 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.456 to 62.486
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -22 ≤ l ≤ 23
Reflections collected	16141
Independent reflections	5721 [R_{int} = 0.0145, R_{sigma} = 0.0181]
Data/restraints/parameters	5721/0/320
Goodness-of-fit on F^2	1.000
Final R indexes [I>=2σ (I)]	R_1 = 0.0487, wR_2 = 0.0938
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.0963
Largest diff. peak/hole / e Å^{-3}	0.55/-0.24

Table S4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for **66**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	0.90557(18)	0.30670(12)	0.40180(8)	0.0309(2)
C2	0.9239(2)	0.19593(13)	0.45189(8)	0.0356(3)
C3	0.7576(2)	0.15282(13)	0.50630(8)	0.0344(2)
C4	0.5720(2)	0.21983(12)	0.51016(7)	0.0311(2)
C5	0.55184(18)	0.32929(11)	0.45924(7)	0.0267(2)
C6	0.71947(17)	0.37532(10)	0.40466(6)	0.02432(19)

C7	0.70076(16)	0.49314(10)	0.35059(6)	0.02387(19)
C8	0.50485(17)	0.49796(11)	0.30752(7)	0.0274(2)
C9	0.48860(18)	0.60703(12)	0.25576(7)	0.0286(2)
C10	0.66799(18)	0.71526(11)	0.24551(7)	0.0262(2)
C11	0.86389(18)	0.71085(12)	0.28881(7)	0.0293(2)
C12	0.88104(18)	0.60196(11)	0.34038(7)	0.0279(2)
C13	0.6516(2)	0.83642(12)	0.19089(7)	0.0298(2)
C14	0.65342(18)	0.98502(11)	0.24311(7)	0.0259(2)
C15	0.4477(2)	0.98622(13)	0.29471(8)	0.0340(2)
O16	0.28179(15)	1.01528(12)	0.23833(7)	0.0516(3)
C17	0.38802(19)	1.10093(15)	0.17699(9)	0.0359(3)
C18	0.63748(17)	1.11407(11)	0.19093(7)	0.0266(2)
C19	0.77595(19)	1.11699(12)	0.11221(7)	0.0281(2)
C20	0.82833(18)	1.26323(11)	0.07353(7)	0.0270(2)
C21	0.6197(2)	1.31716(16)	0.04621(9)	0.0398(3)
C22	0.9626(2)	1.38142(13)	0.13476(9)	0.0374(3)
C23	0.9667(3)	1.23430(15)	-0.00444(9)	0.0408(3)

Table S5 Anisotropic Displacement Parameters ($Å^2$) for **66**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
C1	0.0266(5)	0.0299(5)	0.0368(6)	0.0072(4)	0.0040(4)	0.0041(4)
C2	0.0326(6)	0.0321(6)	0.0442(7)	0.0083(5)	-0.0014(5)	0.0091(5)
C3	0.0434(6)	0.0265(5)	0.0336(6)	0.0078(4)	-0.0035(5)	0.0039(5)
C4	0.0385(6)	0.0255(5)	0.0278(5)	0.0039(4)	0.0048(4)	0.0000(4)
C5	0.0300(5)	0.0212(4)	0.0279(5)	0.0006(4)	0.0046(4)	0.0028(4)

C6	0.0263(5)	0.0194(4)	0.0262(5)	0.0015(3)	0.0012(4)	0.0011(3)
C7	0.0253(4)	0.0200(4)	0.0260(5)	0.0023(3)	0.0044(4)	0.0025(3)
C8	0.0246(5)	0.0241(5)	0.0323(5)	0.0038(4)	0.0026(4)	-0.0001(4)
C9	0.0278(5)	0.0274(5)	0.0301(5)	0.0030(4)	-0.0014(4)	0.0029(4)
C10	0.0324(5)	0.0222(4)	0.0240(5)	0.0021(4)	0.0043(4)	0.0044(4)
C11	0.0277(5)	0.0231(5)	0.0359(6)	0.0054(4)	0.0043(4)	-0.0010(4)
C12	0.0245(5)	0.0241(5)	0.0342(6)	0.0043(4)	0.0002(4)	0.0007(4)
C13	0.0400(6)	0.0258(5)	0.0241(5)	0.0046(4)	0.0039(4)	0.0055(4)
C14	0.0292(5)	0.0243(5)	0.0248(5)	0.0055(4)	0.0021(4)	0.0038(4)
C15	0.0392(6)	0.0316(6)	0.0324(6)	0.0077(5)	0.0114(5)	0.0061(5)
O16	0.0287(4)	0.0661(7)	0.0671(7)	0.0360(6)	0.0148(4)	0.0096(4)
C17	0.0269(5)	0.0390(6)	0.0448(7)	0.0158(5)	0.0038(5)	0.0071(5)
C18	0.0269(5)	0.0250(5)	0.0290(5)	0.0058(4)	0.0031(4)	0.0055(4)
C19	0.0306(5)	0.0240(5)	0.0302(5)	0.0048(4)	0.0042(4)	0.0051(4)
C20	0.0288(5)	0.0245(5)	0.0294(5)	0.0082(4)	0.0029(4)	0.0054(4)
C21	0.0358(6)	0.0448(7)	0.0440(7)	0.0202(6)	0.0002(5)	0.0119(5)
C22	0.0424(7)	0.0259(5)	0.0429(7)	0.0048(5)	-0.0019(5)	0.0017(5)
C23	0.0485(7)	0.0380(6)	0.0375(7)	0.0087(5)	0.0133(6)	0.0081(6)

Table S6. Bond Lengths for **66**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
C1	C2	1.3901(16)	C11	C12	1.3901(15)
C1	C6	1.3980(15)	C13	C14	1.5371(15)
C2	C3	1.3869(18)	C14	C15	1.5177(15)
C3	C4	1.3864(17)	C14	C18	1.5499(14)
C4	C5	1.3911(15)	C15	O16	1.4347(16)

C5	C6	1.4008(14)	O16	C17	1.4268(15)
C6	C7	1.4859(14)	C17	C18	1.5342(16)
C7	C8	1.3944(15)	C18	C19	1.5260(15)
C7	C12	1.4014(14)	C19	C20	1.5443(14)
C8	C9	1.3924(15)	C20	C22	1.5235(17)
C9	C10	1.3944(15)	C20	C21	1.5298(16)
C10	C11	1.3953(15)	C20	C23	1.5397(17)
C10	C13	1.5144(15)			

Table S7. Bond Angles for **66**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C2	C1	C6	120.88(11)	C10	C13	C14	112.26(9)
C3	C2	C1	120.16(11)	C15	C14	C13	111.55(9)
C4	C3	C2	119.79(11)	C15	C14	C18	100.23(9)
C3	C4	C5	120.15(11)	C13	C14	C18	114.90(9)
C4	C5	C6	120.78(10)	O16	C15	C14	105.60(9)
C1	C6	C5	118.22(10)	C17	O16	C15	108.12(9)
C1	C6	C7	120.52(9)	O16	C17	C18	108.04(10)
C5	C6	C7	121.26(9)	C19	C18	C17	116.31(10)
C8	C7	C12	117.88(9)	C19	C18	C14	115.10(9)
C8	C7	C6	121.24(9)	C17	C18	C14	101.96(9)
C12	C7	C6	120.88(9)	C18	C19	C20	117.67(9)
C9	C8	C7	121.18(10)	C22	C20	C21	109.19(10)
C8	C9	C10	120.97(10)	C22	C20	C23	108.71(10)
C9	C10	C11	117.90(10)	C21	C20	C23	108.93(10)
C9	C10	C13	121.61(10)	C22	C20	C19	111.31(9)

C11	C10	C13	120.47(10)	C21	C20	C19	112.07(9)
C12	C11	C10	121.33(10)	C23	C20	C19	106.53(9)
C11	C12	C7	120.74(10)				

Table S8 Torsion Angles for **66**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C6	C1	C2	C3	-0.63(19)	C6	C7	C12	C11	179.08(10)
C1	C2	C3	C4	0.47(19)	C9	C10	C13	C14	108.15(12)
C2	C3	C4	C5	0.44(18)	C11	C10	C13	C14	-70.45(13)
C3	C4	C5	C6	-1.20(17)	C10	C13	C14	C15	-66.89(12)
C2	C1	C6	C5	-0.12(17)	C10	C13	C14	C18	179.90(9)
C2	C1	C6	C7	-179.70(11)	C13	C14	C15	O16	-82.28(11)
C4	C5	C6	C1	1.03(16)	C18	C14	C15	O16	39.82(11)
C4	C5	C6	C7	-179.39(10)	C14	C15	O16	C17	-29.15(13)
C1	C6	C7	C8	136.43(11)	C15	O16	C17	C18	5.58(14)
C5	C6	C7	C8	-43.14(15)	O16	C17	C18	C19	145.30(11)
C1	C6	C7	C12	-42.66(15)	O16	C17	C18	C14	19.25(13)
C5	C6	C7	C12	137.77(11)	C15	C14	C18	C19	-161.56(10)
C12	C7	C8	C9	0.20(16)	C13	C14	C18	C19	-41.87(13)
C6	C7	C8	C9	-178.92(10)	C15	C14	C18	C17	-34.73(11)
C7	C8	C9	C10	-0.14(17)	C13	C14	C18	C17	84.97(11)
C8	C9	C10	C11	-0.08(16)	C17	C18	C19	C20	80.09(13)
C8	C9	C10	C13	-178.71(10)	C14	C18	C19	C20	-160.77(9)
C9	C10	C11	C12	0.25(16)	C18	C19	C20	C22	62.07(13)
C13	C10	C11	C12	178.89(10)	C18	C19	C20	C21	-60.53(14)
C10	C11	C12	C7	-0.19(17)	C18	C19	C20	C23	-179.57(10)

C8 C7 C12 C11 -0.03(16)

Table S9. Hydrogen Atom Coordinates and Isotropic Displacement Parameters (Å^2) for **66**.

Atom	*x*	*y*	*z*	U(eq)
H1	1.020(2)	0.3360(15)	0.3635(9)	0.036(4)
H2	1.053(2)	0.1510(16)	0.4482(9)	0.044(4)
H3	0.772(2)	0.0775(16)	0.5415(9)	0.041(4)
H4	0.455(2)	0.1899(15)	0.5484(9)	0.037(4)
H5	0.423(2)	0.3752(14)	0.4614(8)	0.030(3)
H8	0.379(2)	0.4222(15)	0.3123(8)	0.033(3)
H9	0.351(2)	0.6066(15)	0.2256(9)	0.037(4)
H11	0.992(2)	0.7838(15)	0.2823(8)	0.034(4)
H12	1.015(2)	0.6007(14)	0.3701(8)	0.033(3)
H13A	0.515(2)	0.8114(16)	0.1550(9)	0.040(4)
H13B	0.776(2)	0.8434(15)	0.1532(9)	0.038(4)
H14	0.790(2)	1.0076(14)	0.2795(8)	0.032(3)
H15A	0.392(2)	0.8921(15)	0.3154(9)	0.035(4)
H15B	0.473(2)	1.0654(17)	0.3444(10)	0.045(4)
H17A	0.338(3)	1.1951(18)	0.1817(10)	0.050(4)
H17B	0.340(3)	1.0504(17)	0.1208(10)	0.051(4)
H18	0.697(2)	1.2102(15)	0.2283(8)	0.032(3)
H19A	0.694(2)	1.0377(16)	0.0673(9)	0.039(4)
H19B	0.928(2)	1.0879(15)	0.1276(9)	0.039(4)
H21A	0.657(3)	1.3998(18)	0.0129(10)	0.050(4)
H21B	0.535(3)	1.3484(16)	0.0943(10)	0.045(4)

H21C	0.520(3)	1.2391(18)	0.0098(10)	0.051(4)
H22A	1.012(2)	1.4627(16)	0.1056(9)	0.040(4)
H22B	1.101(3)	1.3488(18)	0.1542(11)	0.059(5)
H22C	0.875(3)	1.4120(18)	0.1862(11)	0.058(5)
H23A	1.105(3)	1.1905(18)	0.0120(10)	0.057(5)
H23B	1.017(3)	1.3297(19)	-0.0319(11)	0.061(5)
H23C	0.878(3)	1.1614(19)	-0.0447(11)	0.057(5)

Experimental:

A suitable single crystals of $C_{22}H_{28}O$ (**66**) was selected and measured on a Bruker Smart Apex II CCD diffractometer [6]. The crystal was kept at 149(2) K during data collection. The integral intensity were correct for absorption using SADABS software [7] using multi-scan method. Resulting minimum and maximum transmission are 0.924 and 0.991 respectively. The structure was solved with the ShelXT (Sheldrick, 2015a) [8] program and refined with the ShelXL (Sheldrick, 2015c) [9] program and least-square minimisation using ShelX software package [9]. Number of restraints used = 0.

Crystal structure determination:

Crystal Data for $C_{22}H_{28}O$ (M =308.44 g/mol): triclinic, space group P-1 (no. 2), a = 6.1587(5) Å, b = 9.3173(8) Å, c = 15.9930(13) Å, α = 96.1247(13)°, β = 90.4111(13)°, γ = 99.2413(14)°, V = 900.36(13) Å^3, Z = 2, T = 149(2) K, μ(MoKα) = 0.067 mm^{-1}, *Dcalc* = 1.138 g/cm^3, 16141 reflections measured (4.456° ≤ 2Θ ≤ 62.486°), 5721 unique (R_{int} = 0.0145, R_{sig} = 0.0181) which were used in all calculations. The final R_1 was 0.0487 (I > 2σ(I)) and wR_2 was 0.0963 (all data).

Refinement details:

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This report has been created with Olex2 [10], compiled on 2018.05.29 svn.r3508 for OlexSy

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