Electronic Supplementary Material (ESI) for ChemComm.

Fe-Catalyzed Dicarbofunctionalization of Electron-Rich Alkenes with Grignard Reagents and (Fluoro)Alkyl Halides

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Supporting Information

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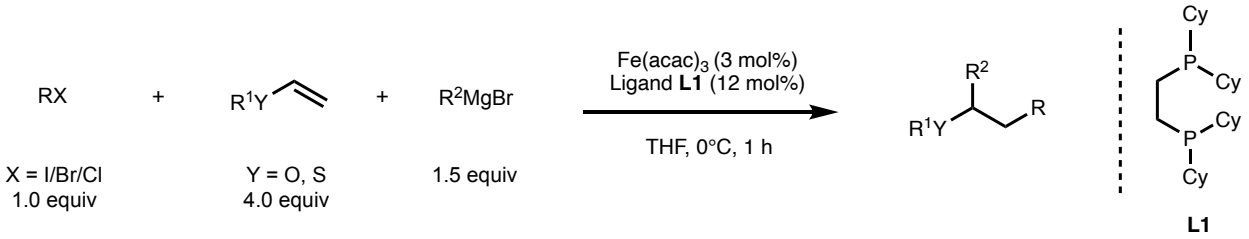
1. General Considerations

All non-aqueous reactions were carried out under a nitrogen atmosphere in oven- (120 °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 reagent grade solvents were purchased from VWR, Sigma-Aldrich, or Fisher and Organometallic reagents were purchased from Sigma-Aldrich. Analytical thin layer chromatography (TLC) was performed on Silicycle 250 μm silica-gel F-254 plates. Silica gel (230-400 mesh) was used for column chromatography. NMR (^{1}H, ^{13}C and ^{19}F) spectra were recorded on Bruker AV III HD NanoBay (400 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 all ^{1}H and δ 77.16 ($CDCl_3$) and δ 0.00 (TMS) for all ^{13}C. Other data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd= doublet of doublets), coupling constants (*J*) are reported in Hertz (Hz), and number of protons. High Resolution Mass (HRMS) spectra using DART mode were recorded on JEOL AccuTOF-CS. Agilent 7820A GC system and 5977B MSD was used to measure GC-MS. IR spectra were recorded on a Thermo Nicolet NEXUS 670 FTIR and are reported in wavenumbers (cm^{-1}). Enantiomeric ratio (er) values were determined by HPLC with the Daicel Chiralcel OJ-H column (Hexane/*i*-PrOH 99.5:0.5, 0.7 mL/min, 214 nm). Melting points were obtained and are uncorrected.

2. General Procedure for Iron-Catalyzed Multicomponent Cross-Coupling Reaction

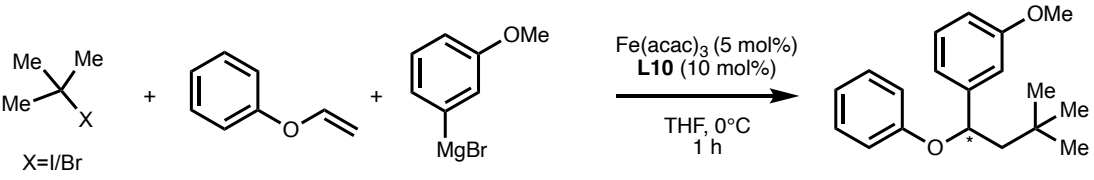
Procedure 1: Iron-Catalyzed Cross-Coupling Reaction



Standard-scale: A flame-dried 5 mL microwave vial with a stir bar was transferred 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 (0.8 mmol, 4.0 equiv.) (using oven-dried glass pipette to transfer alkyl halide and alkene

to the vial). The vial was sealed with a Teflon cap and brought out of the glovebox without solvent. THF (0.2 mL) was then added into the reaction mixture. The resulting red solution was stirred at room temperature for 5 min. The reaction mixture was then cooled to 0 °C and a R^2MgBr 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 or yellow, brown, grass green or orange color (depending on R^2MgBr and substrate). The resulting reaction mixture was then stirred at 0 °C for an additional 10 min. After completion, reaction mixture was quenched with a 1.0 M aqueous solution of hydrochloric acid (0.5 mL) and water (0.5 mL) and then extracted with ethyl acetate (3 x 2 mL). The combined organic solution was filtered through a short pad of silica and evaporation of solvent gave a residue that was purified on silica gel column chromatography with hexane/CH_2Cl_2 to obtain product.

Procedure 2: Iron-Catalyzed Enantioselective Cross-Coupling Reaction



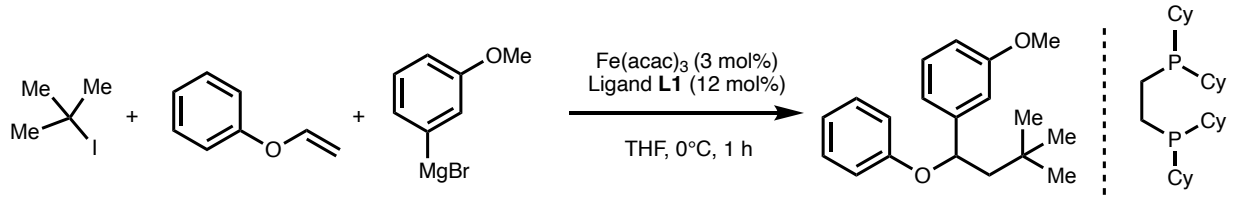
A flame-dried 5 mL microwave vial with a stir bar was transferred into an argon-filled glovebox and the vial was charged with $Fe(acac)_3$ (3.5 mg, 5 mol %), 1,2-bis(*tert*-butyl(methyl)phosphanyl)benzene **L10** (5.6 mg, 10 mol %), alkyl halide (0.2 mmol, 1.0 equiv.) and alkene (0.8 mmol, 4.0 equiv.) (using oven-dried glass pipette to transfer alkyl halide and alkene to the vial). The vial was sealed with a Teflon cap and brought out of the glovebox without solvent. THF (0.2 mL) was then added into the reaction mixture. The resulting red solution was stirred at room temperature for 5 min. The reaction mixture was then cooled to 0 °C and a 3-methoxyphenyl Grignard solution (1.0 M solution in THF, 1.5 equiv.) was added slowly for 1 h using a syringe pump. The resulting reaction mixture was then stirred at 0 °C for an additional 10 min. After completion, reaction mixture was quenched with a 1.0 M aqueous solution of hydrochloric acid (0.5 mL) and water (0.5 mL) and then extracted with ethyl acetate (3 x 2 mL). The combined organic solution was filtered through a short pad of silica and evaporation of solvent gave a residue that was purified on silica gel column chromatography with hexane/CH_2Cl_2 to obtain product.

3. Synthesis of 1-Chloro-4-(vinyloxy)benzene: In an oven dried round bottom flask, 2-bromoethyl 4-chlorophenyl ether (8.5 mmol, 2.0 g) and potassium *tert*-butoxide (12.1 mmol, 1.36 g) were stirred in dimethyl sulfoxide (29 mL) at room temperature for 2 h under nitrogen atmosphere. After completion of the reaction, the reaction mixture was then diluted with water (10 mL) and extracted with diethyl ether (25 x 2 mL). The organic solution was successively washed with brine (1 x 15 mL) and water (1 x 15 mL). The resulting organic solution was dried over sodium sulfate and then solvent was evaporated by rotary evaporator. The crude residue was then purified on silica gel column chromatography using hexane and dichloromethane (99:1) as an eluent to obtain product (831 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 9.2 Hz, 2H), 6.58 (dd, J = 13.6, 6.4 Hz, 1H), 4.76 (dd, J = 13.6, 2.0 Hz, 1H), 4.46 (dd, J = 6.0, 2.0 Hz 1H). Spectral data matched with the previously reported compound.[1]

4. Screening of Reaction Conditions

Table S1. Screening of alkene loading

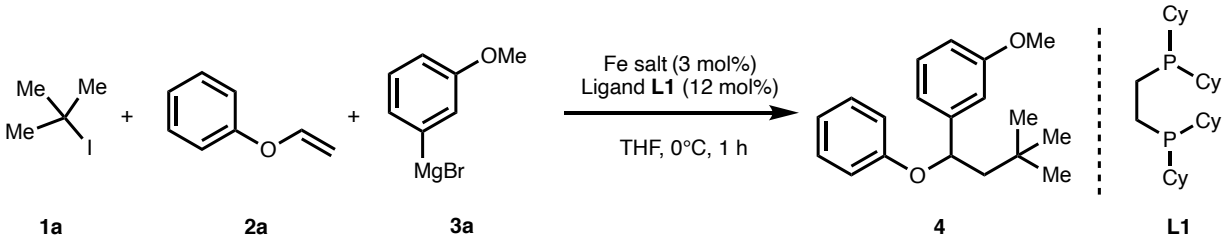


1a **2a** **3a** **4** **L1**

Entry	1a (equiv.)	2a (equiv.)	3a (equiv.)	Yield (%)	Recovered 2a (equiv.)
1	1	14	1.5	89	12.4
2	1	8	1.5	81	5.1
3	1	4	1.5	75	2.4
4	1	3	1.5	44	1.94
5	1	2	1.5	44	0.68
6	2	1	1.5	33	0.48

Reactions were performed with a 0.10 mmol scale, THF (0.1 mL) and Grignard addition for 1 h at 0 ºC. Reactions were then stirred additional 10 min after Grignard addition. Yield and recovered **2a** were determined by crude ^{1}H NMR with CH_2Br_2 as internal standard.

Table S2. Screening of iron salts

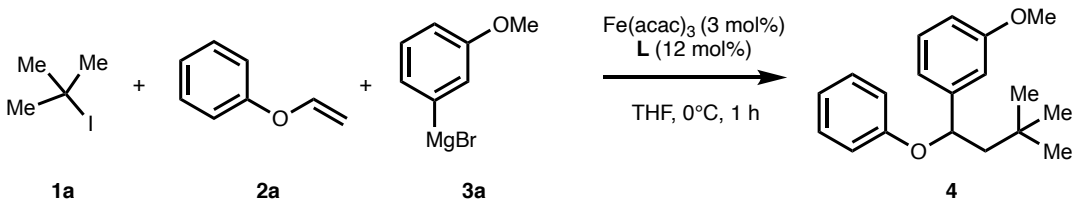


1a **2a** **3a** **4** **L1**

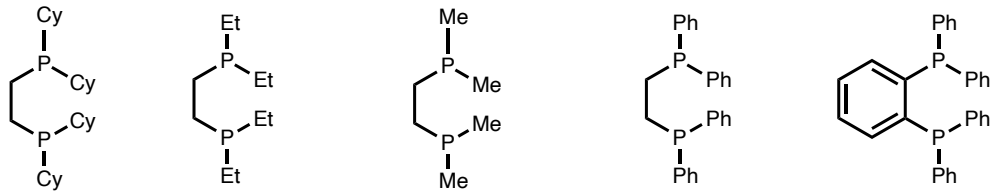
Entry	1a (equiv.)	2a (equiv.)	3a (equiv.)	Fe salt	Yield (%)	Recovered 2a (equiv.)
1	1	4	1.5	$Fe(acac)_3$	75	2.40
2	1	4	1.5	$FeCl_2$	69	2.36
3	1	4	1.5	$FeBr_2$	63	2.20
4	1	4	1.5	$FeCl_3$	60	2.80
5	1	4	1.5	$Fe(OTf)_2$	63	0.28

Reactions were performed with a 0.10 mmol scale, THF (0.1 mL) and Grignard addition for 1 h at 0 ºC. Reactions were then stirred additional 10 min after Grignard addition. Yield and recovered **2a** were determined by crude ^1H NMR with CH_2Br_2 as internal standard.

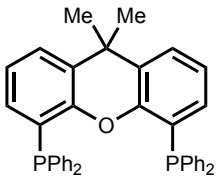
Table S3. Screening of ligands



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



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



L6

L7

L8

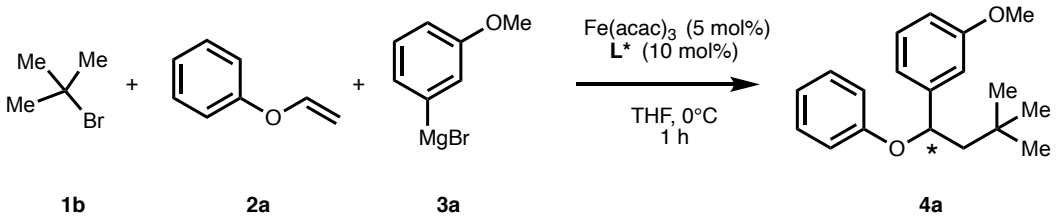
L9

Entry	Ligand (L)	Yield (%)	Recovered 2a (equiv.)
1	**L1**	75	2.4
2	**L2**	0	--
3	**L3**	0	--
4	**L4**	45	3.1
5	**L5**	0	--
6	**L6**	0	--
7	**L7**	0	--
8	**L8**	0	--
9	**L9**	0	--

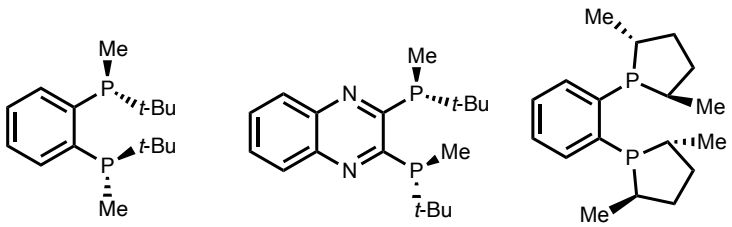
10	No **L**	0	--
11	No Fe, No **L**	0	--
12	neat	67	2.7

Reactions were performed with a 0.10 mmol scale of *tert*-butyl iodide, 4 equiv. of alkene, 1.5 equiv. of Grignard reagent, THF (0.1 mL) and Grignard addition for 1 h at 0 ºC. Reactions were then stirred additional 10 min after Grignard addition. Yield and recovered **2a** were determined by crude ^{1}H NMR with CH_2Br_2 as internal standard.

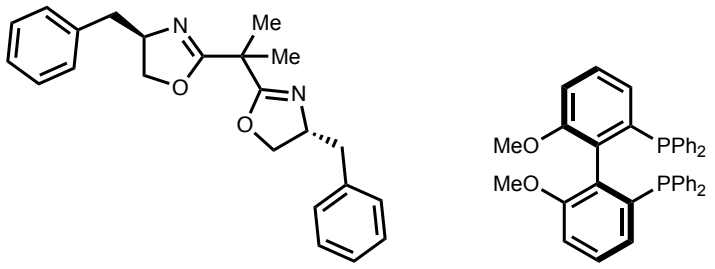
Table S4. Screening of chiral ligands



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



L10 **L11** **L12**

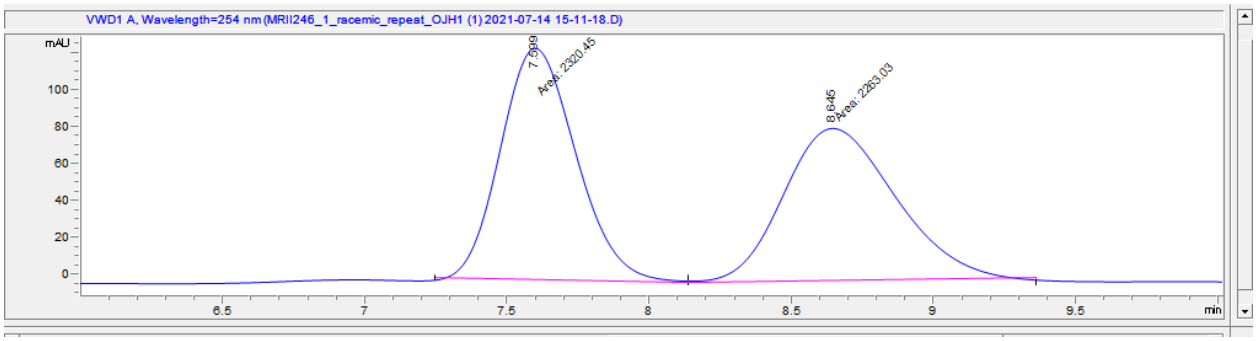


L13 **L14**

Entry	Ligand (L)	Yield (%)	Enantiomeric Ratio (er)
1	**L10**	58	75:25
2	**L11**	22	28:72
3	**L12**	18	73:27
4	**L13**	0	--
5	**L14**	0	--

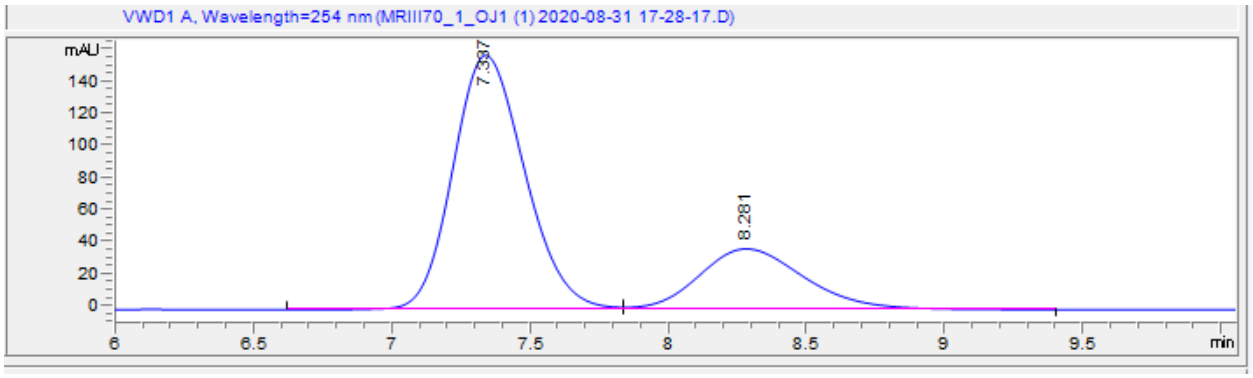
Reactions were performed with a 0.20 mmol scale of *tert*-butyl bromide, 4 equiv. of alkene, 1.5 equiv. of Grignard reagent, THF (0.2 mL) and Grignard addition for 1 h at 0 ºC. Reactions were then stirred additional 10 min after Grignard addition. Yield determined by crude ^{1}H NMR with CH_2Br_2 as internal standard for all entries except entry 1 (isolated yield as an average of 4 trials). Enantiomeric ratio determined by chiral HPLC. Enantiomeric ratio of entry 2 determined as an average of 4 trials. Enantiomeric ratio of entries 3 and 4 determined as an average of 2 trials. Enantiomeric ratio (er) values were determined by HPLC with the Daicel Chiralcel OJ-H column (Hexane/*i*-PrOH 99.5:0.5, 0.7 mL/min, 214 nm).

HPLC Trace 1 (racemic)



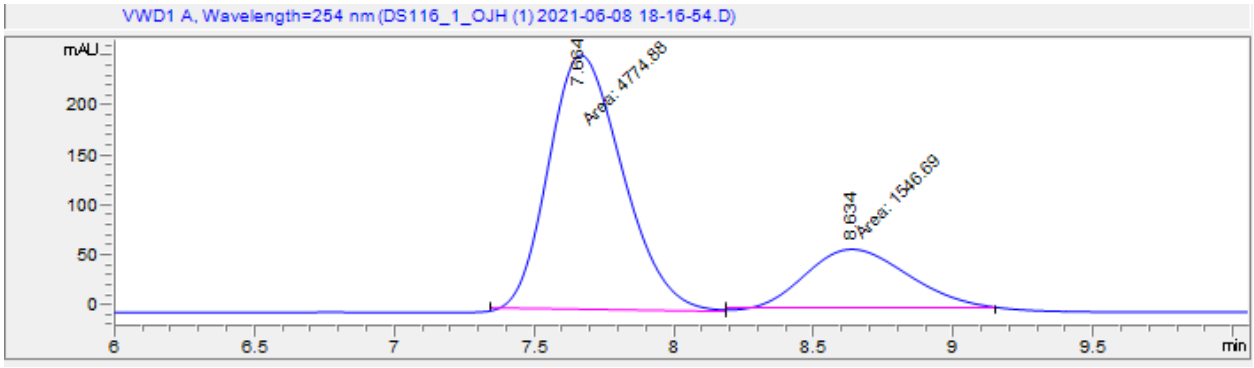
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.599	MM	2320.4	125.5	0.3083	50.626	0.825
2	8.645	MM	2263	82.6	0.4567	49.374	0.781

HPLC Trace 2 (entry 1, **L10**, run 1)



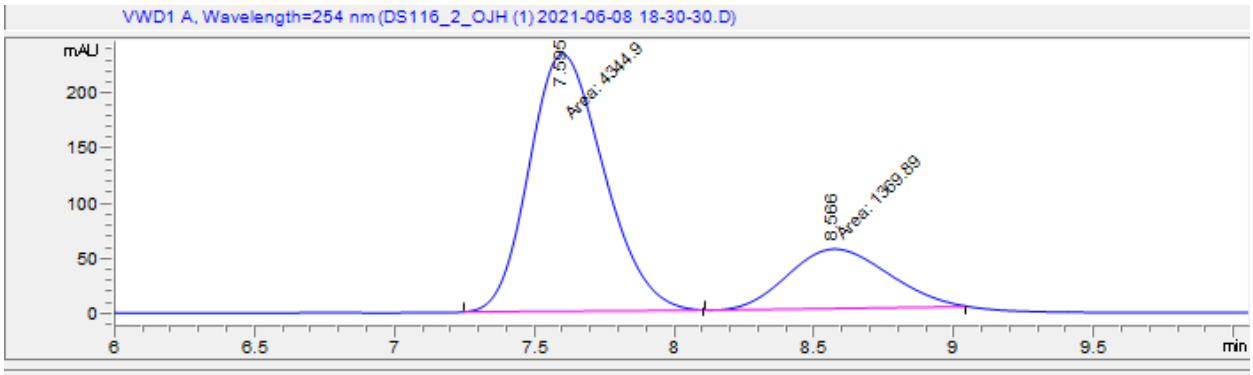
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.337	MM	2875.6	159.3	0.3008	74.118	0.821
2	8.281	MM	1004.2	38	0.4409	25.882	0.803

HPLC Trace 3 (entry 1, **L10**, run 2)



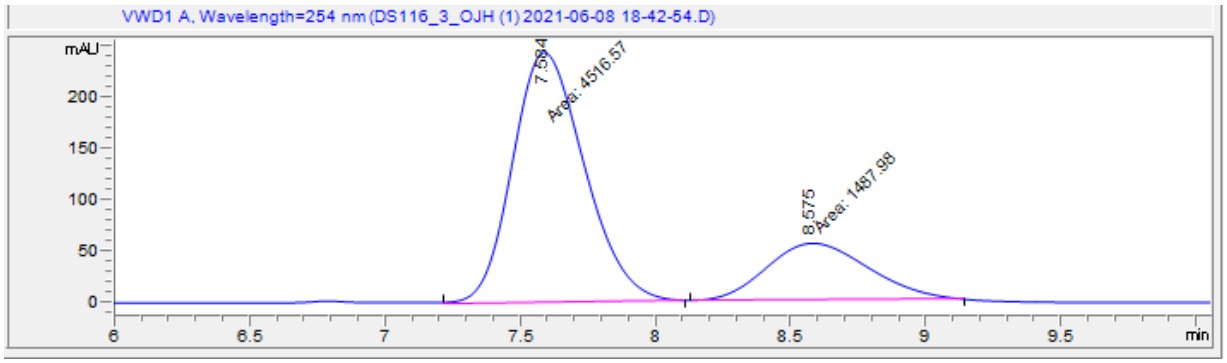
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.664	MM	4774.9	257.6	0.3089	75.533	0.757
2	8.634	MM	1546.7	60.2	0.4284	24.467	0.801

HPLC Trace 4 (entry 1, **L10**, run 3)



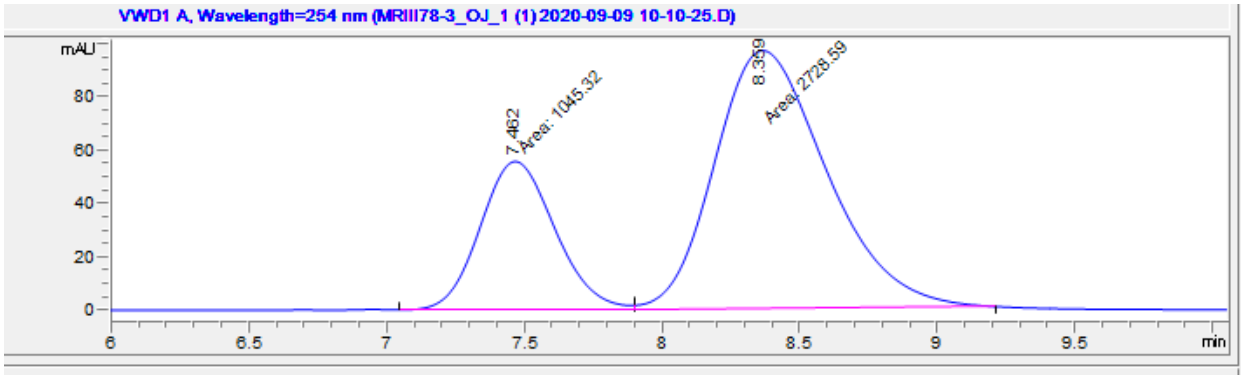
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.595	MM	4344.9	233.9	0.3097	76.029	0.777
2	8.566	MM	1369.9	54.3	0.4201	23.971	0.859

HPLC Trace 5 (entry 1, **L10**, run 4)



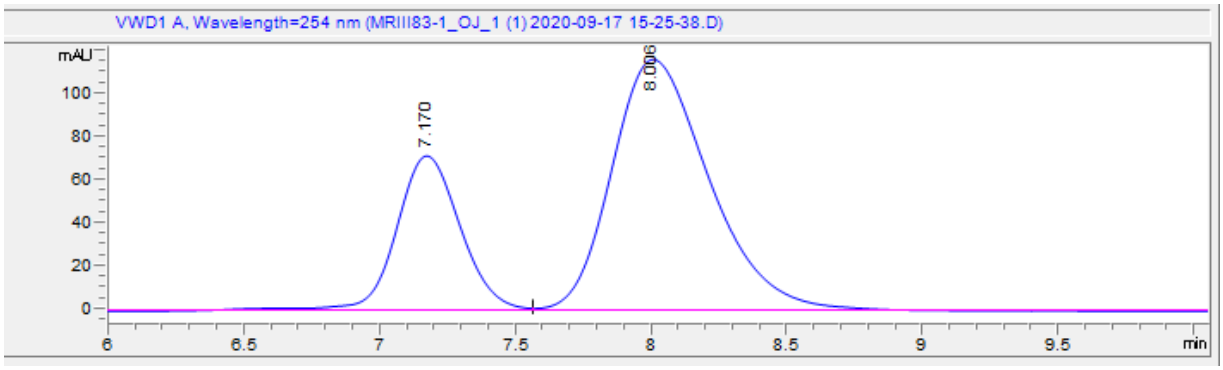
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.584	MM	4516.6	243.9	0.3087	75.219	0.778
2	8.575	MM	1488	55.9	0.4439	24.781	0.808

HPLC Trace 6 (entry 2, **L11**, run 1)



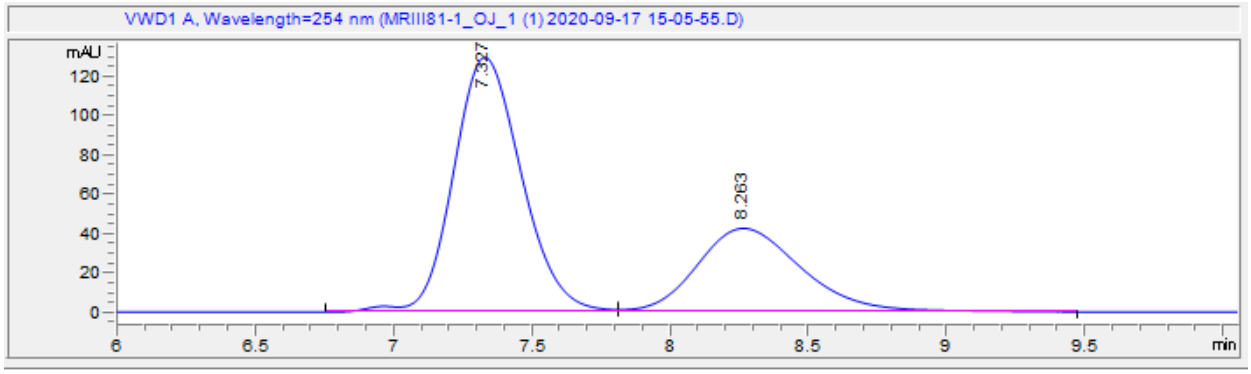
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.462	MM	1045.3	55.3	0.3152	27.699	0.86
2	8.359	MM	2728.6	96.2	0.4727	72.301	0.735

HPLC Trace 7 (entry 2, **L11**, run 2)



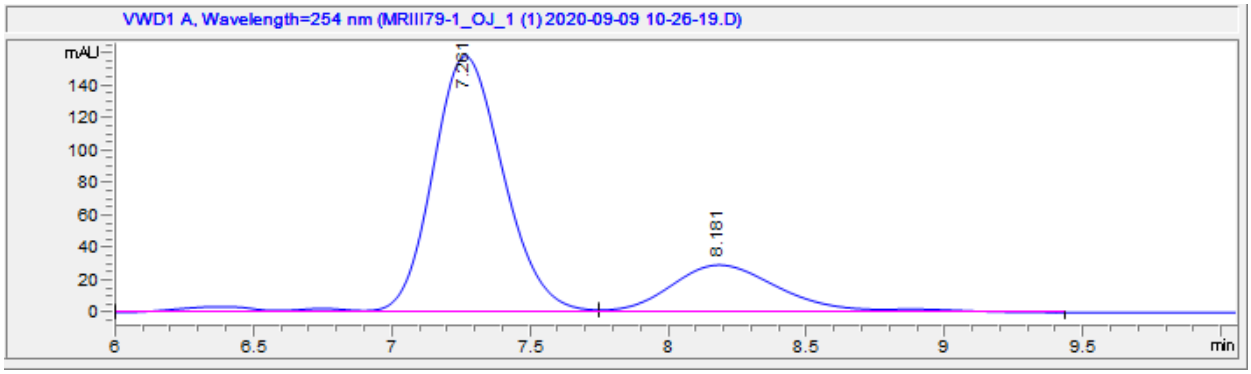
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.17	BV	1217.7	72.2	0.2606	29.202	0.943
2	8.006	VB	2952.3	117.1	0.3882	70.798	0.697

HPLC Trace 8 (entry 3, **L12**, run 1)



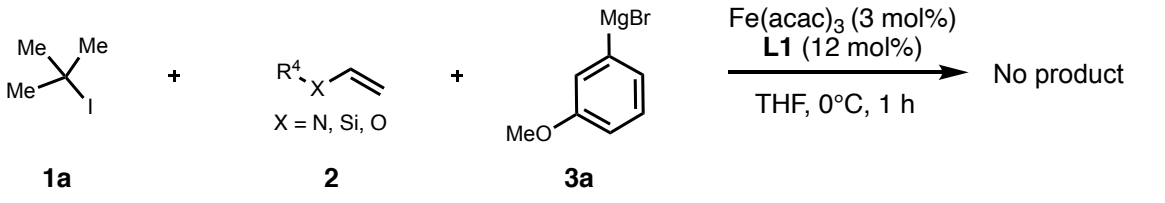
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.327	VV R	2231.2	130	0.2644	66.425	0.851
2	8.263	VB	1127.8	42.6	0.4085	33.575	0.759

HPLC Trace 9 (entry 3, **L12**, run 2)

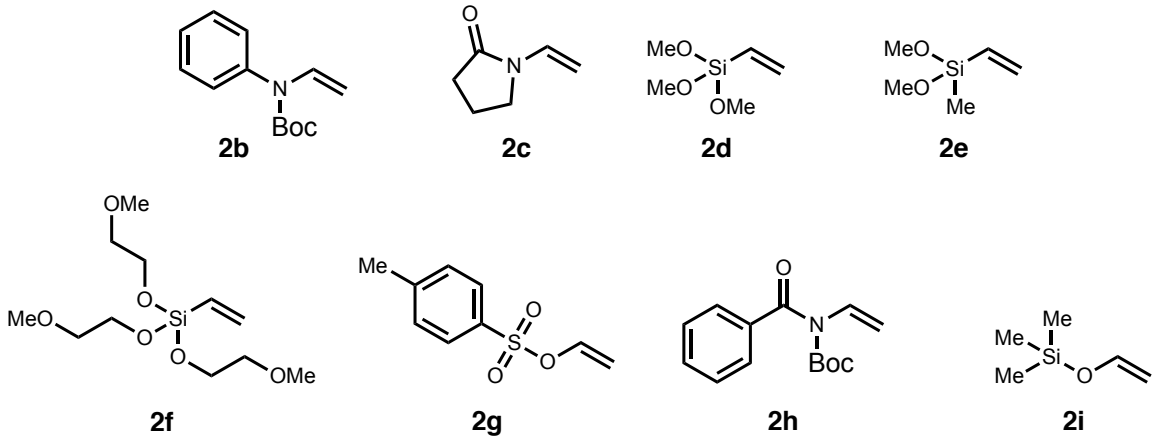


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.261	MM	2699.1	155.8	0.2887	78.868	0.825
2	8.181	MM	723.2	28	0.4303	21.132	0.789

5. Substrate Limitations



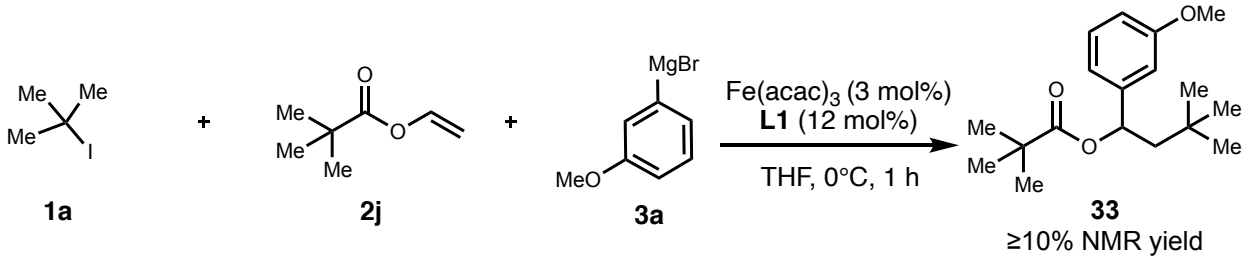
1a 2 3a



2b 2c 2d 2e

2f 2g 2h 2i

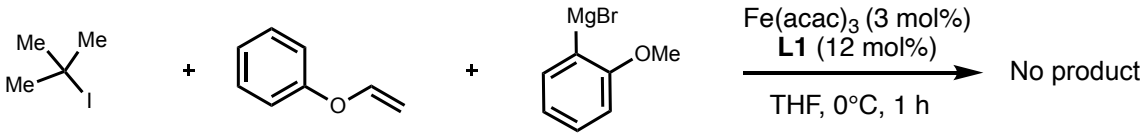
Figure S1. Unsuccessful electron-rich alkenes. All reactions were performed under the optimized conditions (Table 1, entry 1) using 0.2 mmol of alkyl halide and yielded none of the desired product.



1a 2j 3a 33

≥10% NMR yield

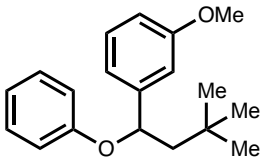
Figure S2. Dicarbofunctionalization of vinyl acetate **2j** (4.0 equiv., 0.4 mmol) with *tert*-butyl iodide **1a** (1.0 equiv., 0.1 mmol) and 3-methoxyphenyl magnesium bromide **3a** (1.5 equiv., 0.15 mmol) to give product **33** (≥ 10% NMR yield.) The reaction was performed under the optimized conditions (Table 1, entry 1) using 0.1 mmol of alkyl halide.



1a 2a 3a'

Figure S3. Unsuccessful reaction of phenyl vinyl ether **2a** (14.0 equiv., 1.4 mmol) with *tert*-butyl iodide **1a** (1.0 equiv., 0.1 mmol) and *ortho*-methoxyphenyl magnesium bromide **3a'** (1.5 equiv., 0.15 mmol).

6. Product Characterization Data



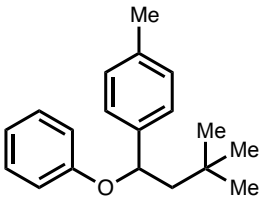
1-(3,3-Dimethyl-1-phenoxybutyl)-3-methoxybenzene (4): Compound **4** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **4** was obtained as a colorless liquid (40 mg, 71% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (9:1) to hexane/CH_2Cl_2 (22:3)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.18 (m, 3H), 6.95-6.84 (m, 5H), 6.78 (dd, J = 8.0, 2.4 Hz, 1H), 5.19 (dd, J = 9.6, 2.0 Hz, 1H), 3.80 (s, 3H), 2.06 (dd, J = 14.8, 9.6 Hz, 1H), 1.61 (dd, J = 14.8, 2.0 Hz, 1H), 1.05 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.0, 158.2, 145.7, 129.8, 129.4 (2C), 120.6, 118.1, 115.9 (2C), 112.5, 111.4, 78.0, 53.3, 52.9, 30.9, 30.3 (3C);

IR (film) 2953, 2835, 1598, 1585, 1491, 1364, 1234, 1064, 750, 690 cm^{-1};

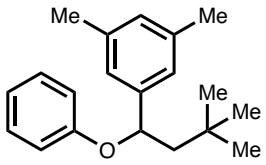
HRMS (DART) calcd for $C_{19}H_{24}O_2$ $[M+NH_4]^+$ m/z = 302.2120; found: 302.2125.



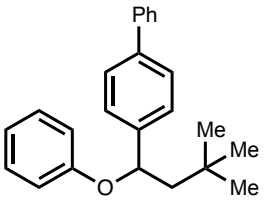
1-(3,3-Dimethyl-1-phenoxybutyl)-4-methylbenzene (5): Compound **5** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and *p*-tolylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **5** was obtained as a white solid (37 mg, 70% yield) after purification by column chromatography on silica gel with hexane to hexane/CH_2Cl_2 (99:1).

mp: 55-56 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23-7.11 (m, 6H), 6.86-6.81 (m, 3H), 5.18 (dd, J = 9.6, 2.0 Hz, 1H), 2.31 (s, 3H), 2.03 (dd, J = 14.8, 9.6 Hz, 1H), 1.57 (dd, J = 14.8, 2.4 Hz, 1H), 1.02 (s, 9H);
^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 140.9, 136.9, 129.4, 129.4 (2C), 125.7 (2C), 120.5, 115.9 (2C), 77.9, 53.0, 30.9 (2C), 30.3 (3C), 21.3;
IR (film) 2954, 2866, 1598, 1494, 1237, 1052, 815, 751, 690 cm^{-1};
HRMS (DART) calcd for $C_{19}H_{24}O$ $[M+NH_4]^+$ m/z = 286.2171; found: 286.2175.



1-(3,3-Dimethyl-1-phenoxybutyl)-3,5-dimethylbenzene (6): Compound **6** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and (3,5-dimethylphenyl) magnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **6** was obtained as a colorless liquid (32 mg, 57% yield) after purification by column chromatography on silica gel with hexane to hexane/CH_2Cl_2 (99:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21-7.17 (m, 2H), 6.95 (s, 2H), 6.88-6.83 (m, 4H), 5.13 (dd, J = 9.6, 1.6 Hz, 1H), 2.30 (s, 6H), 2.03 (dd, J = 14.8, 10 Hz, 1H), 1.56 (dd, J = 14.8, 2.0 Hz, 1H), 1.03 (s, 9H);
^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.4, 143.9, 138.2 (2C), 129.4 (2C), 129.0, 123.4 (2C), 120.5, 115.9 (2C), 78.3, 53.1, 31.0, 30.3 (3C), 21.5 (2C);
IR (film) 2952, 2866, 1597, 1586, 1493, 1237, 1057, 847, 751, 689 cm^{-1};
HRMS (DART) calcd for $C_{20}H_{26}O$ $[M+NH_4]^+$ m/z =300.2327; found: 300.2319.



4-(3,3-Dimethyl-1-phenoxybutyl)-1,1'-biphenyl (7): Compound **7** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **7** was obtained as a white solid (37 mg, 56% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (49:1) to hexane/CH_2Cl_2(24:1).

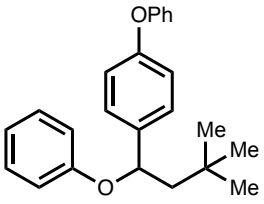
mp: 140-141 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.54 (m, 4H), 7.45-7.40 (m, 4H), 7.35-7.32 (m, 1H), 7.22-7.18 (m, 2H), 6.90-6.86 (m, 3H), 5.27 (dd, J = 9.6, 2.0 Hz, 1H), 2.10 (dd, J = 14.8, 9.6 Hz, 1H), 1.64 (dd, J = 14.8, 2.0 Hz, 1H), 1.06 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 142.9, 141.0, 140.2, 129.5 (2C), 128.9 (2C), 127.5 (2C), 127.3, 127.2 (2C), 126.2 (2C), 120.6, 115.9 (2C), 77.9, 53.0, 31.0, 30.3 (3C);

IR (film) 3028, 2953, 1597, 1492, 1364, 1236, 1172, 1053, 751, 691 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{26}O$ $[M+NH_4]^+$ m/z = 348.2327; found: 348.2330.



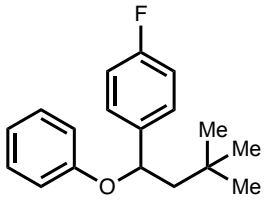
1-(3,3-Dimethyl-1-phenoxybutyl)-4-phenoxybenzene (8): Compound **8** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and (4-phenoxyphenyl) magnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **8** was obtained as a colorless liquid (42 mg, 61% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (43:7) to hexane/CH_2Cl_2 (21:4).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.28 (m, 4H), 7.21-7.17 (m, 2H), 7.11-7.07 (m, 1H), 7.00-6.94 (m, 4H), 6.89-6.82 (m, 3H), 5.20 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.05 (dd, *J* = 14.8, 9.6 Hz, 1H), 1.59 (dd, *J* = 14.4, 2.4 Hz, 1H), 1.03 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 157.3, 156.5, 138.6, 129.9 (2C), 129.4 (2C), 127.2 (2C), 123.4, 120.6, 119.1 (2C), 119.0 (2C), 116.0 (2C), 77.6, 52.9, 30.9, 30.3 (3C);

IR (film) 2953, 2866, 1587, 1504, 1487, 1230, 1165, 1052, 871, 750, 689 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{26}O_2$ $[M-H]^-$ m/z = 345.1845; found: 345.1858.



1-(3,3-Dimethyl-1-phenoxybutyl)-4-fluorobenzene (9): Compound **9** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-fluorophenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **9** was obtained as a colorless liquid (25 mg, 46% yield) after purification by column chromatography on silica gel with hexane to hexane/CH_2Cl_2 (99:1).

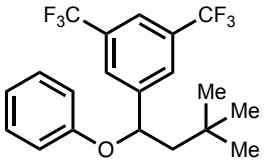
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31-7.27 (m, 2H), 7.19-7.15 (m, 2H), 7.01-6.97 (m, 2H), 6.88-6.84 (m, 1H), 6.79 (dd, *J* = 8.8, 1.2 Hz, 2H), 5.19 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.02 (dd, *J* = 14.8, 9.6 Hz, 1H), 1.55 (dd, *J* = 14.8, 2.0 Hz, 1H), 1.02 (s, 9H);.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2 ($J_{C\text{-}F}$ = 243.6 Hz), 157.9, 139.55($J_{C\text{-}F}$ = 3.2 Hz), 129.5 (2C), 127.4 ($J_{C\text{-}F}$ = 8.0 Hz, 2C), 120.8, 115.9 (2C), 115.7 ($J_{C\text{-}F}$ = 21.3 Hz, 2C), 77.4, 52.9, 30.9, 30.3 (3C);

^{19}F NMR (376 MHz, $CDCl_3$) δ = -115.530;

IR (film) 2954, 2868, 1598, 1509, 1494, 1365, 1223, 1155, 1053, 834, 752, 690 cm^{-1};

HRMS (DART) calcd for $C_{18}H_{21}FO$ $[M+NH_4]^+$ m/z = 290.1920; found: 290.1919.



1-(3,3-Dimethyl-1-phenoxybutyl)-3,5-bis(trifluoromethyl)benzene (10): Compound **10** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 3,5-Bis(trifluoromethyl)phenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **10** was obtained as a white solid (22 mg, 28% yield) after purification by column chromatography on silica gel with hexane to hexane/CH_2Cl_2 (99:1).

mp: 54-55 °C;

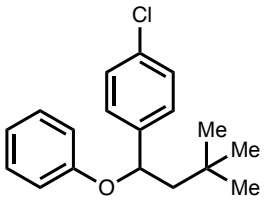
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (s, 2H), 7.76 (s, 1H), 7.23-7.19 (m, 2H), 6.94-6.90 (m, 1H), 6.80-6.77 (m, 2H), 5.32 (dd, J = 10, 2.0 Hz, 1H), 2.05 (dd, J = 14.8, 10 Hz, 1H), 1.54 (dd, J = 14.8, 2.0 Hz, 1H), 1.05 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.4, 146.7, 132.2 (q, $J_{C\text{-}F}$ = 33.1Hz, 2C), 129.7 (4C), 126.0 (2C), 121.5 (2C), 115.8 (2C), 77.2, 52.8, 31.1, 30.3 (3C);

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.67, -105.82;

IR (film) 2958, 1590, 1494, 1348, 1276, 1234, 1168, 1130, 895, 752, 682 cm^{-1};

HRMS (DART) calcd for $C_{20}H_{20}F_6O$ $[M+NH_4]^+$ m/z = 408.1762; found: 408.1769.



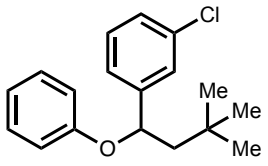
1-Chloro-4-(3,3-dimethyl-1-phenoxybutyl)benzene (11): Compound **11** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and (4-chlorophenyl)magnesium bromide (0.3 mL, 1.0 M solution in diethyl ether, 0.3 mmol). The product **11** was obtained as a colorless liquid (38 mg, 66% yield) after purification by column chromatography on silica gel with hexane to hexane/CH_2Cl_2 (99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.27 (m, 4H), 7.20-7.16 (m, 2H), 6.89-6.85 (m, 1H), 6.80-6.78 (m, 2H), 5.18 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.02 (dd, *J* = 14.8, 9.6 Hz, 1H), 1.55 (dd, *J* = 14.8, 2.4 Hz, 1H), 1.02 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ =157.9, 142.4, 133.0, 129.5 (2C), 128.9 (2C), 127.2 (2C), 120.8, 115.9 (2C), 77.4, 52.8, 30.9, 30.3 (3C);

IR (film) 2954, 2866, 1598, 1587, 1491, 1235, 1172, 1087, 1053, 883, 822, 751, 690 cm^{-1};

HRMS (DART) calcd for $C_{18}H_{21}ClO$ $[M+NH_4]^+$ m/z =306.1624; found: 306.1613.



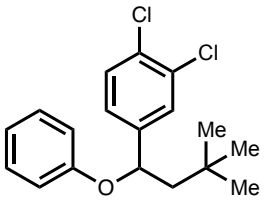
1-Chloro-3-(3,3-dimethyl-1-phenoxybutyl)benzene (12): Compound **12** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and (3-chlorophenyl)magnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **12** was obtained as a colorless liquid (36 mg, 62% yield) after purification by column chromatography on silica gel with hexane to hexane/CH_2Cl_2 (99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.34 (s, 1H), 7.24-7.18 (m, 5H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.18 (dd, *J* = 9.6, 2.0 Hz, 1H), 2.03 (dd, *J* = 14.8, 10.0 Hz, 1H), 1.57 (dd, *J* = 14.4, 2.4 Hz, 1H), 1.04 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ =157.8, 146.1, 134.7, 130.1, 129.5 (2C), 127.5, 125.9, 123.9, 120.9, 115.8 (2C), 77.5, 52.8, 31.0, 30.3 (3C);

IR (film) 2954, 2867, 1596, 1586, 1492, 1475, 1234, 1077, 1053, 885, 785, 751, 689 cm^{-1};

HRMS (DART) calcd for $C_{18}H_{21}ClO$ $[M+NH_4]^+$ m/z =306.1624; found: 306.1627.



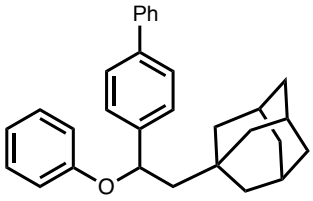
1,2-Dichloro-4-(3,3-dimethyl-1-phenoxybutyl)benzene (13): Compound **13** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and (3,4-dichlorophenyl)magnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **13** was obtained as a colorless liquid (22 mg, 34% yield) after purification by column chromatography on silica gel with hexane to hexane/CH_2Cl_2 (99:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, J = 2.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.22-7.16 (m, 3H), 6.91-6.87 (m, 1H), 6.79-6.77 (m, 2H), 5.14 (dd, J = 10.0, 2.0 Hz, 1H), 2.00 (dd, J = 14.8, 9.6 Hz, 1H), 1.52 (dd, J = 14.8, 2.4 Hz, 1H), 1.02 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ =157.6, 144.3, 132.9, 131.3, 130.8, 129.6 (2C), 127.8, 125.2, 121.1, 115.8 (2C), 77.0, 52.7, 31.0, 30.2 (3C);

IR (film) 2954, 2868, 1598, 1587, 1493, 1472, 1234, 1152, 1055, 1029, 887, 751, 689;

HRMS (DART) calcd for $C_{18}H_{20}Cl_2O$ $[M+NH_4]^+$ m/z =340.1234; found: 340.1232.



1-(2-([1,1'-Biphenyl]-4-yl)-2-phenoxyethyl)adamantine (14): Compound **14** was synthesized following the general procedure 1 (standard-scale), using iodoadamantane (52.4 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **14** was obtained as a white solid (40 mg, 49% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (23:2) to hexane/CH_2Cl_2 (9:1).

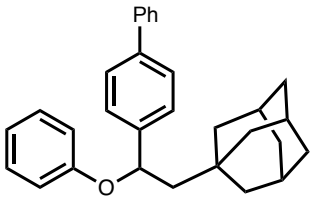
mp: 143-144 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.54 (m, 4H), 7.44-7.38 (m, 4H), 7.35-7.31 (m, 1H), 7.23-7.19 (m, 2H), 6.90-6.86 (m, 3H), 5.32 (dd, *J* = 9.6, 1.6 Hz, 1H), 2.02-1.96 (m, 4H), 1.74-1.64 (m, 12H), 1.49 (dd, *J* = 15.2, 2.0 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 143.1, 141.0, 140.1, 129.4 (2C), 128.6 (2C), 127.5 (2C), 127.3, 127.2 (2C), 126.2 (2C), 120.6, 116.0 (2C), 76.3, 54.0, 43.1 (3C), 37.2 (3C), 33.0, 28.9 (3C);

IR (film) 3027, 2898, 2845, 1598, 1586, 1492, 1448, 1234, 1171, 1007, 751, 691 cm^{-1};

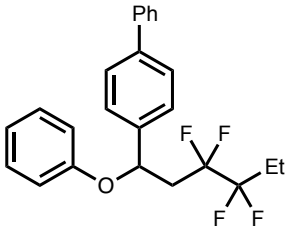
HRMS (DART) calcd for $C_{30}H_{32}O$ $[M-H]^-$ m/z =407.2374; found: 407.2382.



1-(2-([1,1'-Biphenyl]-4-yl)-2-phenoxyethyl)adamantine (15): Compound **15** was synthesized following the general procedure 1 (standard-scale), using bromoadamantane (43 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **15** was obtained as a white solid (30 mg, 37% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (23:2) to hexane/CH_2Cl_2 (9:1).

mp: 143-144 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57-7.52 (m, 4H), 7.43-7.37 (m, 4H), 7.34-7.30 (m, 1H), 7.22-7.17 (m, 2H), 6.88-6.84 (m, 3H), 5.30 (dd, *J* = 9.6, 2.0 Hz, 1H), 2.00-1.94 (m, 4H), 1.72-1.62 (m, 12H), 1.47 (dd, *J* = 14.8, 2.0 Hz, 1H); Spectral data matched compound **14**.



4-(3,3,4,4-Tetrafluoro-1-phenoxyhexyl)-1,1'-biphenyl (16): Compound **16** was synthesized following the general procedure 1 (standard-scale), using 1-bromo-1,1,2,2-tetrafluorobutane (41.7 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **16** was obtained as a white solid (70 mg, 87%

yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (24:1) to hexane/CH_2Cl_2 (47:3).

mp: 88-89 °C;

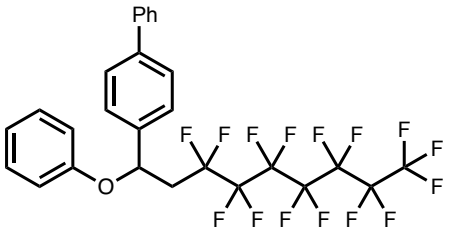
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60-7.56 (m, 4H), 7.49-7.41 (m, 4H), 7.36-7.33 (m, 1H), 7.23-7.20 (m, 2H), 6.93-6.89 (m, 3H), 5.61 (dd, *J* = 8.8, 3.6 Hz, 1H), 2.94-2.79 (m, 1H), 2.60-2.46 (m, 1H), 2.14-1.99 (m, 2H), 1.11 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 141.2, 140.7, 140.2, 129.5 (2C), 128.9 (2C), 127.7 (2C), 127.6, 127.2 (2C), 126.5 (2C), 122.2-115.3 (2C), 121.4, 116.3 (2C), 74.1, 39.2 (t, *J*= 21.5 Hz), 23.4 (t, *J* = 23.4 Hz), 5.0 (t, *J* = 5.2 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.84 to -113.58 (m, 1F), -113.96 to -114.70 (m, 1F), -117.33 to -117.36 (m, 2F);

IR (film) 3030, 2991, 2950, 1598, 1492, 1289, 1235, 1172, 1101, 1084, 1003, 851, 752, 689 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{22}F_4O$ $[M+NH_4]^+$ m/z = 420.1951; found: 420.1954.

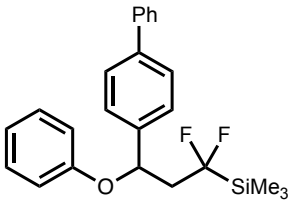


4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-phenoxynonyl)-1,1'-biphenyl (17): Compound **17** was synthesized following the general procedure 1 (standard-scale), using 1-bromo-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoroheptane (89.7 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **17** was obtained as a white solid (82 mg, 64% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (9:1) to hexane/CH_2Cl_2 (22:3).

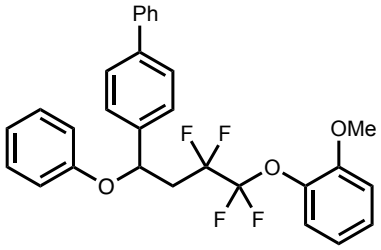
mp: 95-96 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.56 (m, 4H), 7.49-7.42 (m, 4H), 7.37-7.33 (m, 1H), 7.24-7.20 (m, 2H), 6.95-6.88 (m, 3H), 5.61 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.02-2.87 (m, 1H), 2.62-2.49 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.5, 141.5, 140.6, 139.3, 129.6 (2C), 129.0 (2C), 127.9 (2C), 127.7, 127.2 (2C), 126.4 (2C), 121.7 , 120.0-108.4 (7C) 116.3 (2C), 73.6, 40.0 (t, J = 20.7 Hz);
^{19}F NMR (376 MHz, $CDCl_3$) δ = -111.86 to -113.61 (m, 2F), -121.46 to -123.46 (m, 10F), -126.05 to -126.14 (m, 3F);
IR (film) 3016, 2926, 2862, 2604, 2359, 2337, 2186, 2032, 1215, 771, 667 cm^{-1};
HRMS (DART) calcd for $C_{27}H_{17}F_{15}O$ $[M+NH_4]^+$ m/z = 660.1383; found: 660.1364.



(3-([1,1'-Biphenyl]-4-yl)-1,1-difluoro-3-phenoxypropyl)trimethylsilane (18): Compound **18** was synthesized following the general procedure 1 (standard-scale), using (bromodifluoromethyl)trimethylsilane (40.6 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **18** was obtained as a colorless liquid (52 mg, 65% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (23:2) to hexane/CH_2Cl_2 (9:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.56 (m, 4H), 7.47-7.41 (m, 4H), 7.36-7.32 (m, 1H), 7.23-7.19 (m, 2H), 6.91-6.88 (m, 3H), 5.59 (dd, J = 8.8, 2.8 Hz, 1H), 2.78-2.61 (m, 1H), 2.39-2.24 (m, 1H), 0.22 (s, 9H);
^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.4, 140.8, 140.8 (2C), 129.5 (2C), 128.9 (2C), 127.6 (2C), 127.5, 127.2 (2C), 126.5 (2C), 121.1 (2C), 116.2 (2C), 74.0 (dd, J = 10.4, 4.2 Hz), 45.8 (t, J = 20.4 Hz), - 4.2 (3C);
^{19}F NMR (376 MHz, $CDCl_3$) δ = -107.82 to -108.69 (m, 1F), -113.16 to -114.02 (m, 1F);
IR (film) 3030, 2959, 1598, 1489, 1232, 1172, 1082, 1063, 1007, 956, 844, 752, 690 cm^{-1};
HRMS (DART) calcd for $C_{24}H_{26}F_2OSi$ $[M+NH_4]^+$ m/z = 414.2064; found: 414.2059.



4-(3,3,4,4-Tetrafluoro-4-(2-methoxyphenoxy)-1-phenoxybutyl)-1,1'-biphenyl (19): Compound **19** was synthesized following the general procedure 1 (standard-scale), using 1-(2-bromo-1,1,2,2-tetrafluoroethoxy)-2-methoxybenzene (60.6 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **19** was obtained as a colorless liquid (91 mg, 92% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (43:7) to hexane/CH_2Cl_2 (21:4).

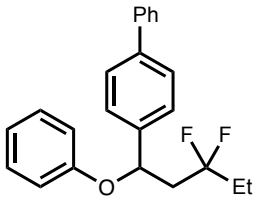
^{1}H NMR (400 MHz, $CDCl_3$) δ =7.61-7.51 (m, 6H), 7.45-7.41 (m, 2H), 7.36-7.33 (m, 1H), 7.25-7.19 (m, 4H), 6.98-6.89 (m, 5H), 5.73 (dd, J = 8.8, 3.6 Hz, 1H), 3.81 (s, 3H), 3.12-2.97 (m, 1H), 2.81-2.67 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 152.5, 141.2, 140.7, 140.1, 137.9, 129.5 (2C), 128.9 (2C), 127.7 (2C), 127.6, 127.6, 127.2 (2C), 126.6 (2C), 124.0, 121.4, 120.7, 120.2-113.6 (2C), 116.4 (2C), 112.9, 74.1, 56.1, 40.3 (t, J = 20.9 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.29 to -115.01 (m, 2F), -116.04 to -116.74 (m, 2F);

IR (film) 3030, 2925, 2841, 1598, 1501, 1493, 1456, 1261, 1237, 1189, 1170, 1105, 1025, 1007, 750, 692 cm^{-1};

HRMS (DART) calcd for $C_{29}H_{24}F_4O_3$ $[M+NH_4]^+$ m/z = 514.2005; found: 514.1995.



4-(3,3-Difluoro-1-phenoxypentyl)-1,1'-biphenyl (20): Compound **20** was synthesized following the general procedure 1 (standard-scale), using 1-bromo-1,1-difluoropropane (31.7 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **20** was obtained as a colorless liquid (37 mg, 52% yield)

after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (22:3) to hexane/CH_2Cl_2 (43:7).

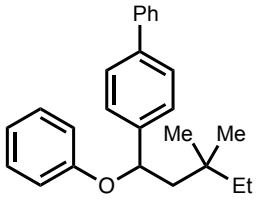
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.56 (m, 4H), 7.46-7.41 (m, 4H), 7.36-7.32 (m, 1H), 7.23-7.19 (m, 2H), 6.93-6.87 (m, 3H), 5.46 (dd, *J* = 9.2, 2.8 Hz, 1H), 2.76-2.61 (m, 1H), 2.39-2.27 (m, 1H), 2.06-1.92 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.6, 141.0, 140.7, 140.4, 129.6 (2C), 128.9 (2C), 127.7 (2C), 127.5, 127.2 (2C), 126.4 (2C), 124.5, 121.3, 116.4 (2C), 75.1 (dd, *J* = 8.5, 3.3 Hz), 45.0 (t, *J* = 26 Hz), 30.2 (t, *J* = 25.4 Hz), 6.8 (dd, *J* = 6.8, 4.8 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ = -95.07 (d, *J* = 64.8 Hz, 1F), -97.98 (d, *J* = 64.8 Hz, 1F);

IR (film) 3030, 2941, 2853, 1598, 1492, 1377, 1235, 1007, 965, 887, 754, 691 cm^{-1};

HRMS (DART) calcd for $C_{23}H_{22}F_2O$ $[M+NH_4]^+$ m/z = 370.1982; found: 370.1996.



4-(3,3-Dimethyl-1-phenoxypentyl)-1,1'-biphenyl (21): Compound **21** was synthesized following the general procedure 1 (standard-scale), using 2-bromo-2-methylbutane (30.2 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **21** was obtained as a white solid (35 mg, 51% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (24:1) to hexane/CH_2Cl_2 (47:3).

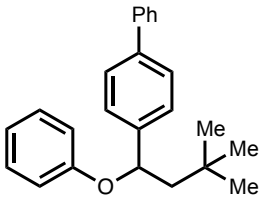
mp: 81-82 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.54 (m, 4H), 7.44-7.39 (m, 4H), 7.35-7.31 (m, 1H), 7.22-7.18 (m, 2H), 6.87-6.84 (m, 3H), 5.25 (dd, *J* = 9.6, 2.0 Hz, 1H), 2.09 (dd, *J* = 15.2, 9.6 Hz, 1H), 1.60 (dd, *J* = 15.2, 2.0 Hz, 1H), 1.46-1.31 (m, 2H), 1.01 (d, *J* = 3.2 Hz, 6H), 0.90 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 143.0, 141.0, 140.2, 129.4 (2C), 128.9 (2C), 127.5 (2C), 127.3, 127.2 (2C), 126.1 (2C), 120.6, 115.9 (2C), 77.6, 50.5, 35.1, 33.5, 27.5, 27.5, 8.7;

IR (film) 3028, 2969, 1597, 1492, 1300, 1236, 1171, 1077, 1006, 765, 752, 690 cm^{-1};

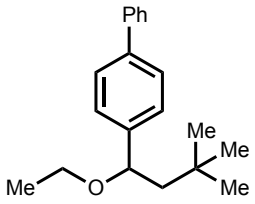
HRMS (DART) calcd for $C_{25}H_{28}O$ $[M+NH_4]^+$ m/z =362.2483; found: 362.2484.



4-(3,3-Dimethyl-1-phenoxybutyl)-1,1'-biphenyl (22): Compound **22** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl chloride (18.5 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **22** was obtained as a white solid (26 mg, 39% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (49:1) to hexane/CH_2Cl_2 (24:1).

mp: 140-141 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60-7.56 (m, 4H), 7.46-7.42 (m, 4H), 7.37-7.33 (m, 1H), 7.24-7.20 (m, 2H), 6.91-6.87 (m, 3H), 5.28 (dd, *J* = 10.0, 2.0 Hz, 1H), 2.11 (dd, *J* = 14.8, 9.6 Hz, 1H), 1.66 (dd, *J* = 14.8, 2.4 Hz, 1H), 1.08 (s, 9H); Spectral data matched compound **7**.



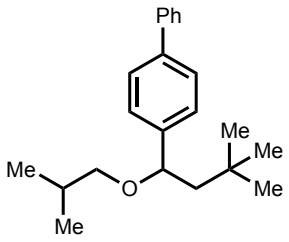
4-(1-Ethoxy-3,3-dimethylbutyl)-1,1'-biphenyl (23): Compound **23** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), ethyl vinyl ether (57.6 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **23** was obtained as a colorless liquid (20 mg, 36% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (23:2) to hexane/CH_2Cl_2 (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60-7.55 (m, 4H), 7.45-7.41 (m, 2H), 7.36-7.31 (m, 3H), 4.36 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.40-3.29 (m, 2H), 1.83 (dd, *J* = 14.4, 9.2 Hz, 1H), 1.46 (dd, *J* = 14.4, 3.2 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.99 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.9, 141.2, 140.2, 128.9 (2C), 127.3, 127.2 (2C), 127.2 (2C), 126.9 (2C), 79.9, 64.1, 52.3, 30.8, 30.4 (3C), 15.6;

IR (film) 2917, 2849, 1486, 1364, 1215, 1091, 838, 751, 697, 668 cm^{-1};

HRMS (DART) calcd for $C_{20}H_{26}O$ $[M+ NH_4]^+$ m/z = 300.2327; found: 300.2331.



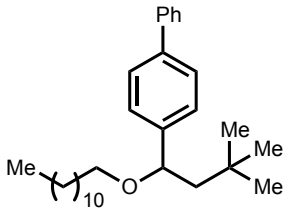
4-(1-Isobutoxy-3,3-dimethylbutyl)-1,1'-biphenyl (24): Compound **24** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), isobutyl vinyl ether (80.1 mg, 0.4 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **24** was obtained as a colorless liquid (20 mg, 33% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (24:1) to hexane/CH_2Cl_2 (47:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.54 (m, 4H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 3H), 4.32 (dd, J = 9.2, 2.8 Hz, 1H), 3.09 (dd, J = 8.8, 6.0 Hz, 1H), 2.98 (dd, J = 8.8, 6.8 Hz, 1H), 1.87-1.79 (m, 2H), 1.44 (dd, J = 14.8, 2.4 Hz, 1H), 1.00 (s, 9H), 0.90 (dd, J = 14.0, 6.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.1, 141.2, 140.1, 128.9 (2C), 127.3, 127.2 (4C), 126.9 (2C), 80.2, 75.9, 52.6, 30.8, 30.4 (3C), 28.9, 19.9, 19.8;

IR (film) 2954, 2917, 2849, 1486, 1472, 1364, 1215, 1099, 838, 754, 697 cm^{-1};

HRMS (DART) calcd for $C_{22}H_{30}O$ $[M+ NH_4]^+$ m/z = 328.2640; found: 328.2632.



4-(1-(Dodecyloxy)-3,3-dimethylbutyl)-1,1'-biphenyl (25): Compound **25** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol),

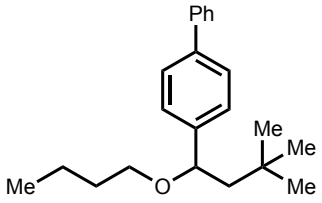
1-(vinyloxy)dodecane (169.6 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **25** was obtained as a colorless liquid (25 mg, 29% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (23:2) to hexane/CH_2Cl_2 (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.55 (m, 4H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 3H), 4.34 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.33-3.19 (m, 2H), 1.83 (dd, *J* = 14.4, 9.2 Hz, 1H), 1.58-1.52 (m, 2H), 1.46 (dd, *J* = 14.8, 2.8 Hz, 1H), 1.30-1.25 (m, 18H), 1.00 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 141.2, 140.1, 128.9 (2C), 127.3, 127.2 (2C), 127.2 (2C), 126.9 (2C), 80.1, 69.0, 52.5, 32.1, 30.8, 30.4 (3C), 30.2, 29.8, 29.8, 29.8, 29.8, 29.6, 29.5, 26.5, 22.9, 14.3;

IR (film) 3028, 2923, 2853, 1486, 1465, 1363, 1101, 1008, 838, 753, 696 cm^{-1};

HRMS (DART) calcd for $C_{30}H_{46}O$ $[M+NH_4]^+$ m/z = 440.3892; found: 440.3886.



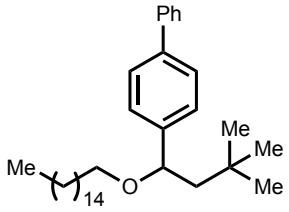
4-(1-Butoxy-3,3-dimethylbutyl)-1,1'-biphenyl (26): Compound **26** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1-(vinyloxy)butane (80.1 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **26** was obtained as a colorless liquid (26 mg, 42% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (22:3) to hexane/CH_2Cl_2 (43:7).

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.61-7.55 (m, 4H), 7.45-7.41 (m, 2H), 7.36-7.31 (m, 3H), 4.34 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.33-3.20 (m, 2H), 1.82 (dd, *J* = 14.8, 8.8 Hz, 1H), 1.57-1.50 (m, 2H), 1.45 (dd, *J* = 14.4, 2.8 Hz, 1H), 1.40-1.34 (m, 2H), 1.00 (s, 9H), 0.89 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 141.2, 140.1, 128.9 (2C), 127.3, 127.2 (2C), 127.2 (2C), 126.9 (2C), 80.1, 68.7, 52.5, 32.4, 30.8, 30.4 (3C), 19.7, 14.1;

IR (film) 3028, 2954, 2929, 2865, 1600, 1486, 1464, 1363, 1098, 1008, 837, 769, 753, 696 cm^{-1};

HRMS (DART) calcd for $C_{22}H_{30}O$ $[M+NH_4]^+$ m/z = 328.2640; found: 328.2638.



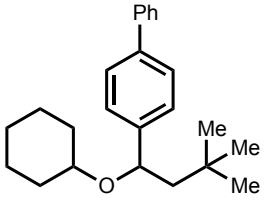
4-(1-(Hexadecyloxy)-3,3-dimethylbutyl)-1,1'-biphenyl (27): Compound **27** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1-(vinyloxy)hexadecane (214.7 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **27** was obtained as a colorless liquid (28 mg, 29% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (9:1) to hexane/CH_2Cl_2 (22:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.55 (m, 4H), 7.45-7.41 (m, 2H), 7.36-7.31 (m, 3H), 4.33 (dd, J = 9.2, 2.8 Hz, 1H), 3.32-3.19 (m, 2H), 1.82 (dd, J = 14.4, 8.8 Hz, 1H), 1.59 -1.51 (m, 2H), 1.45 (dd, J = 14.4, 2.8 Hz, 1H), 1.28-1.25 (m, 26H), 1.00 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 141.2, 140.1, 128.9 (2C), 127.3, 127.2 (4C), 126.9 (2C), 80.1, 69.0, 52.4, 32.1, 30.8, 30.4 (3C), 30.2, 29.9 (4C), 29.8 (2C), 29.8, 29.8, 29.6, 29.5, 26.5, 22.9, 14.3;

IR (film) 3028, 2922, 2852, 1600, 1486, 1465, 1363, 1100, 1008, 838, 753, 696 cm^{-1};

HRMS (DART) calcd for $C_{34}H_{54}O$ $[M+NH_4]^+$ m/z = 496.4518; found: 496.4529.



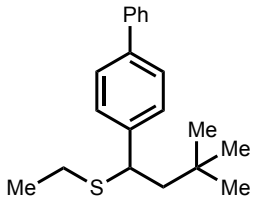
4-(1-(Cyclohexyloxy)-3,3-dimethylbutyl)-1,1'-biphenyl (28): Compound **28** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), (vinyloxy)cyclohexane (100.9 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **28** was obtained as a colorless liquid (28 mg, 41% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (21:4) to hexane/CH_2Cl_2 (41:9).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.54 (m, 4H), 7.45-7.41 (m, 2H), 7.37-7.31 (m, 3H), 4.60 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.17-3.10 (m, 1H), 2.05-2.02 (m, 1H), 1.83-1.62 (m, 4H), 1.42 (dd, *J* = 14.4, 2.8 Hz, 1H), 1.37-1.27 (m, 2H), 1.22-1.07 (m, 4H), 1.00 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.9, 141.2, 139.9, 128.9 (2C), 127.2, 127.2 (2C), 127.1 (2C), 127.0 (2C), 76.5, 75.1, 52.9, 34.1, 31.8, 30.9, 30.4 (3C), 26.0, 24.6, 24.5;

IR (film) 3027, 2929, 2855, 1600, 1486, 1449, 1362, 1258, 1087, 1064, 838, 754, 696 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{32}O$ $[M+NH_4]^+$ m/z = 354.2796; found: 354.2796.



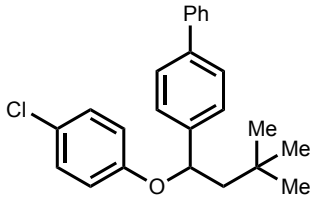
(1-([1,1'-Biphenyl]-4-yl)-3,3-dimethylbutyl)(ethyl)sulfane (29): Compound **29** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), ethyl vinyl sulfide (70.5 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **29** was obtained as a colorless liquid (18 mg, 31% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (49:1) to hexane/CH_2Cl_2 (24:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.52 (m, 4H), 7.45-7.41 (m, 2H), 7.38-7.30 (m, 3H), 3.94 (dd, *J* = 8.4, 4.4 Hz, 1H), 2.30-2.17 (m, 2H), 1.98 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.81 (dd, *J* = 14.0, 4.4 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.7, 140.9, 139.6, 128.9 (2C), 128.5 (2C), 127.3, 127.1 (2C), 127.1 (2C), 50.1, 45.6, 31.8, 30.2 (3C), 25.4, 14.5;

IR (film) 3027, 2955, 2926, 2865, 1601, 1486, 1364, 1265, 1007, 843, 762, 696 cm^{-1};

HRMS (DART) calcd for $C_{20}H_{26}S$ $[M+NH_4]^+$ m/z = 316.2099; found: 316.2092.



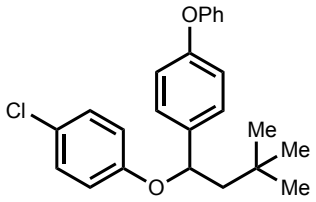
4-(1-(4-Chlorophenoxy)-3,3-dimethylbutyl)-1,1'-biphenyl (30): Compound **30** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1-chloro-4-(vinyloxy)benzene (123.2 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **30** was obtained as a colorless liquid (52 mg, 71% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (24:1) to hexane/CH_2Cl_2 (47:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.55 (m, 4H), 7.45-7.32 (m, 5H), 7.16 (d, J = 9.2 Hz, 2H), 6.80 (d, J = 8.8Hz, 2H), 5.20 (dd, J = 9.6, 2.0 Hz, 1H), 2.08 (dd, J = 15.2, 9.6 Hz, 1H), 1.64 (dd, J = 14.8, 2.0 Hz, 1H), 1.05 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.7, 142.3, 140.9, 140.5, 129.4 (2C), 128.9 (2C), 127.6 (2C), 127.4, 127.2 (2C), 126.1 (2C), 125.6, 117.2 (2C), 78.4, 52.8, 31.0, 30.3 (3C);

IR (film) 3028, 2953, 2866, 1596, 1487, 1364, 1235, 1168, 1052, 1006, 990, 821, 752, 696, 665 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{25}ClO$ $[M+NH_4]^+$ m/z = 382.1937; found: 382.1935.



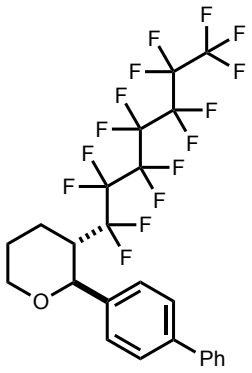
1-Chloro-4-(3,3-dimethyl-1-(4-phenoxyphenyl)butoxy)benzene (31): Compound **31** was synthesized following the general procedure 1 (standard-scale), using *tert*-butyl iodide (36.8 mg, 0.2 mmol), 1-chloro-4-(vinyloxy)benzene (123.2 mg, 0.8 mmol) and 4-Phenoxyphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **31** was obtained as a colorless liquid (50 mg, 66% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (24:1) to hexane/CH_2Cl_2 (47:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.30 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.15-7.08 (m, 3H), 7.01-6.94 (m, 4H), 6.76 (d, J = 8.8 Hz, 2H), 5.14 (dd, J = 9.6, 2.0 Hz, 1H), 2.03 (dd, J = 14.8, 9.2 Hz, 1H), 1.59 (dd, J = 14.8, 2.0 Hz, 1H), 1.02 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 156.7, 137.9, 129.9 (2C), 129.3 (2C), 127.1 (2C), 125.5, 123.5 (2C), 119.2 (2C), 119.0 (2C), 117.2 (2C), 78.2, 52.8, 30.9, 30.3 (3C);

IR (film) 3038, 2953, 2866, 1589, 1486, 1231, 1165, 1051, 989, 821, 752, 691, 665 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{25}ClO_2$ $[M-H]^-$ m/z = 379.1464; found: 379.1480.



***trans*-2-([1,1'-Biphenyl]-4-yl)-3-(perfluoroheptyl)tetrahydro-2H-pyran (32):** Compound **32** was synthesized following the general procedure 1 (standard-scale), using 1-bromo-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoroheptane (89.7 mg, 0.2 mmol), 3,4-dihydro-2H-pyran (67.2 mg, 0.8 mmol) and 4-biphenylmagnesium bromide (0.6 mL, 0.5 M solution in THF, 0.3 mmol). The product **32** was obtained as a brown solid (38 mg, 31% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (24:1) to hexane/CH_2Cl_2 (47:3).

mp: 84-85 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.58 (m, 4H), 7.45-7.41 (m, 4H), 7.36-7.32 (m, 1H), 4.55 (d, J = 9.6 Hz, 1H), 4.13-4.09 (m, 1H), 3.63-3.57 (m, 1H), 2.78-2.71 (m, 1H), 2.29-2.26 (m, 1H), 1.87-1.79 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.3, 141.0, 139.7 (d, J = 1.5 Hz), 128.9 (3C), 127.8 (d, J = 1.8 Hz), 127.4, 127.3 (4C), 121.6-107.7 (7C), 79.5, 68.5, 45.0 (t, J = 18.6 Hz), 24.8, 23.7;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.64 to -105.53 (m, 1F), -116.41 to -123.85 (m, 14F);

IR (film) 3062, 2959, 2860, 1990, 1971, 1684, 1558, 1456, 1219, 772, 684, 659 cm^{-1};

HRMS (DART) calcd for $C_{24}H_{17}F_{15}O$ $[M+NH_4]^+$ m/z = 624.1383; found: 624.1398.

The stereochemistry of compound **32** was studied by 2D NOESY Spectrum (spectral data, compound 32). The absence of ^{1}H-^{1}H interaction between CH proton "a" and CH proton "b" indicates that both vicinal protons are in the *trans* diastereomer.

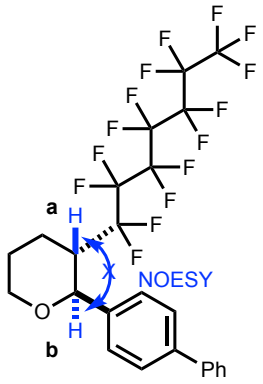
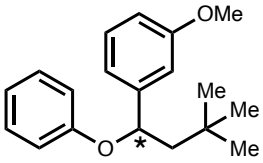
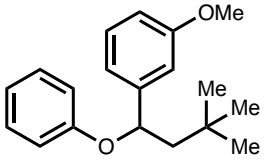


Figure S4: Confirmed the structure of **32** as *trans* based on NOESY NMR.



1-(3,3-Dimethyl-1-phenoxybutyl)-3-methoxybenzene (4a): Compound **4a** was synthesized following the general procedure 2, using *tert*-butyl bromide (27.4 mg, 0.2 mmol), phenyl vinyl ether (96.1 mg, 0.8 mmol) and 3-methoxyphenylmagnesium bromide (0.3 mL, 1.0 M solution in THF, 0.3 mmol). The product **4a** was obtained as a colorless liquid (33 mg, 58% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (9:1) to hexane/CH_2Cl_2 (22:3)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.18 (m, 3H), 6.95-6.84 (m, 5H), 6.78 (dd, J = 8.0, 2.4 Hz, 1H), 5.19 (dd, J = 9.6, 2.0 Hz, 1H), 3.80 (s, 3H), 2.06 (dd, J = 14.8, 9.6 Hz, 1H), 1.61 (dd, J = 14.8, 2.0 Hz, 1H), 1.05 (s, 9H); Spectral data matched compound **4**.



1-(3,3-Dimethyl-1-phenoxybutyl)-3-methoxybenzene (4)-gram-scale: Compound **4** was synthesized following the general procedure 1, using *tert*-butyl iodide (1.0 g, 5.4 mmol), phenyl vinyl ether (2.6 g, 21.7 mmol) and 3-methoxyphenylmagnesium bromide (8.1 mL, 1.0 M solution in THF, 8.1 mmol). The product **4** was obtained as a colorless liquid (1.02 g, 66% yield) after purification by column chromatography on silica gel with hexane/CH_2Cl_2 (9:1) to hexane/CH_2Cl_2 (22:3)

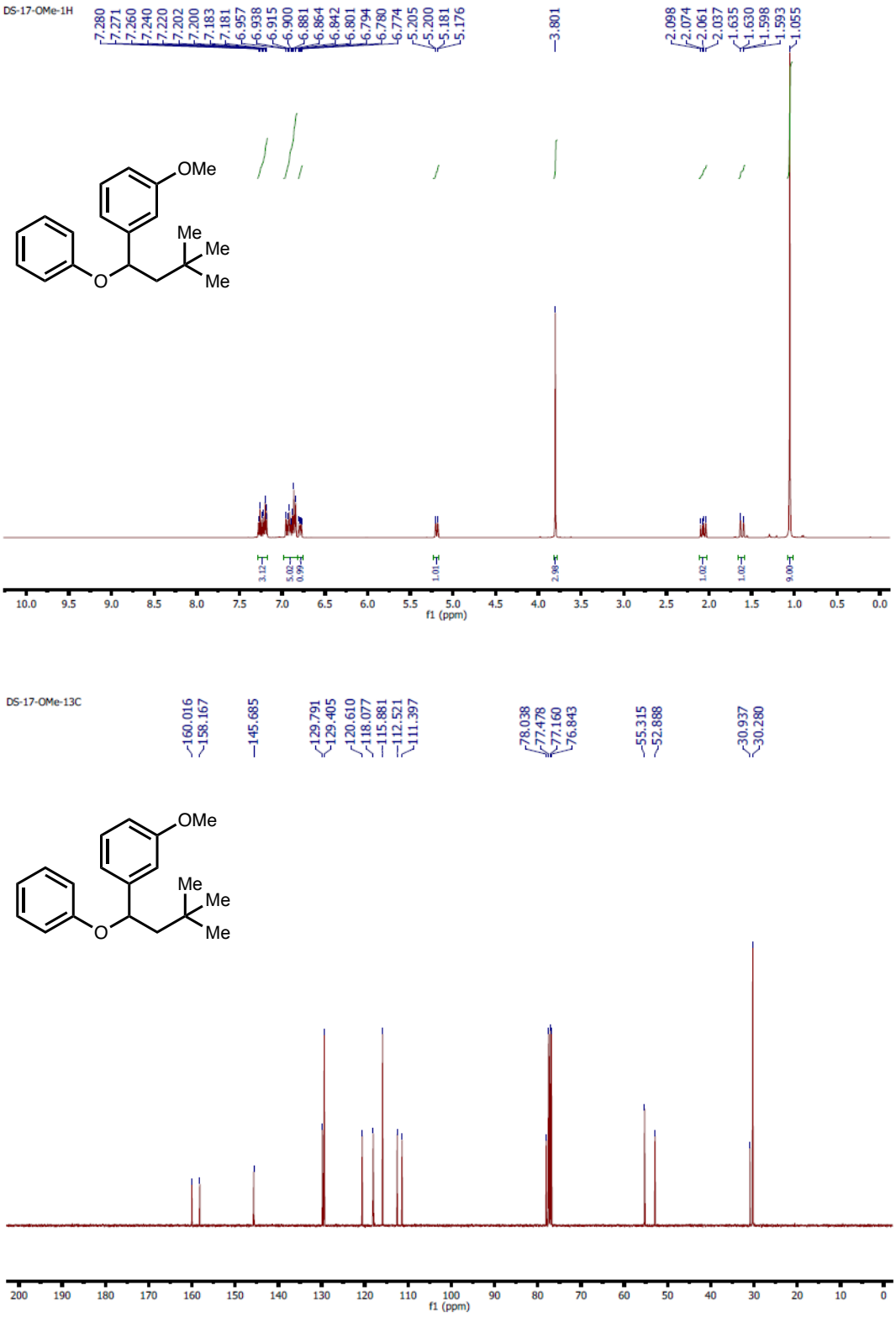
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.17 (m, 3H), 6.95-6.83 (m, 5H), 6.77 (dd, J = 8.4, 2.4 Hz, 1H), 5.18 (dd, J = 9.6, 2.0 Hz, 1H), 3.79 (s, 3H), 2.06 (dd, J = 14.8, 9.6 Hz, 1H), 1.60 (dd, J = 14.4, 2.4 Hz, 1H), 1.04 (s, 9H); Spectral data matched compound **4**.

7. References

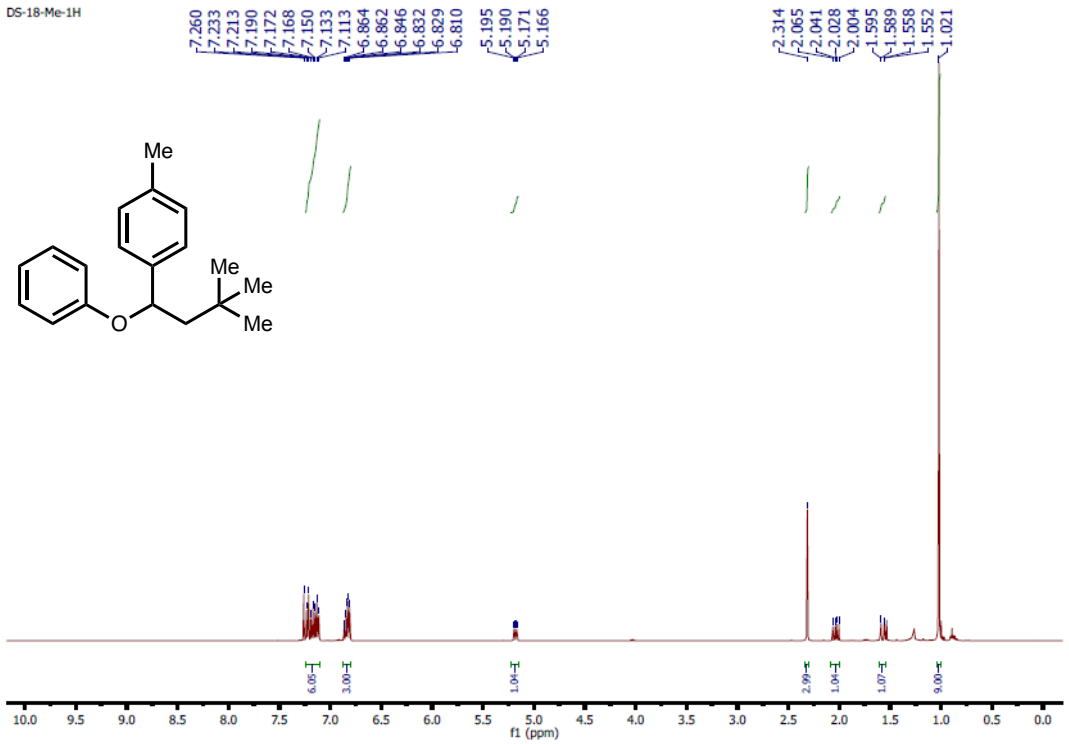
1. T. Asakawa, A. Kanazawa, and S. Aoshima. *Macromolecules*, **2020,** *53***,** 6887-6897**.**

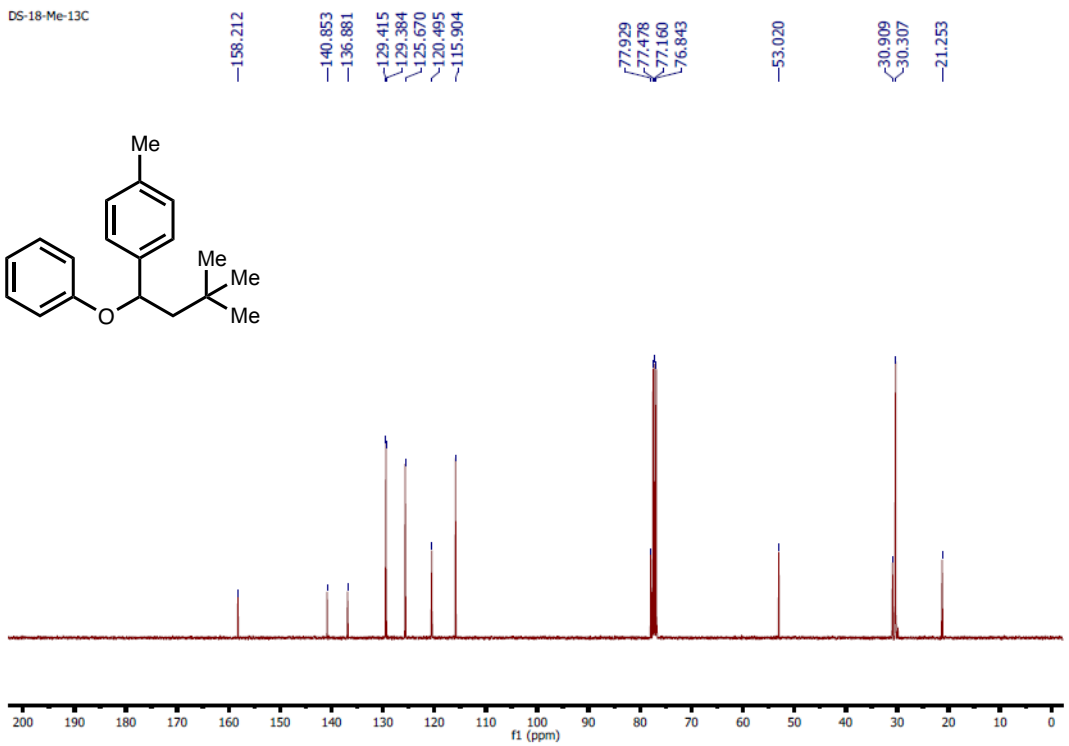
8. Spectral data

Compound 4. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

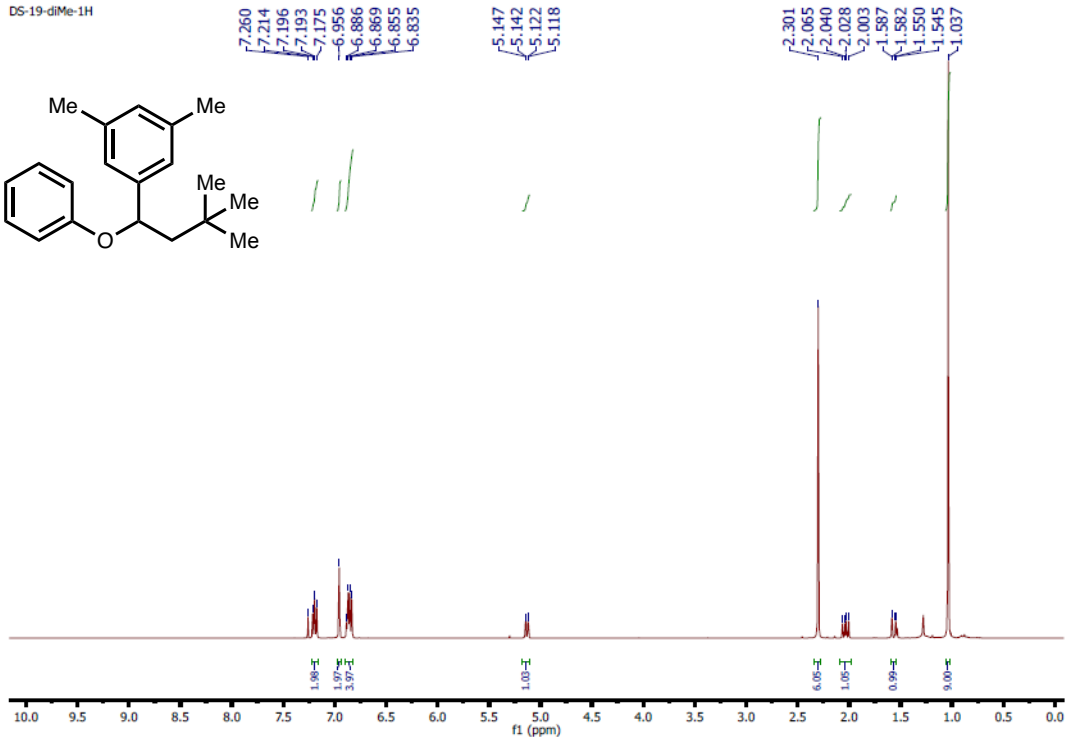


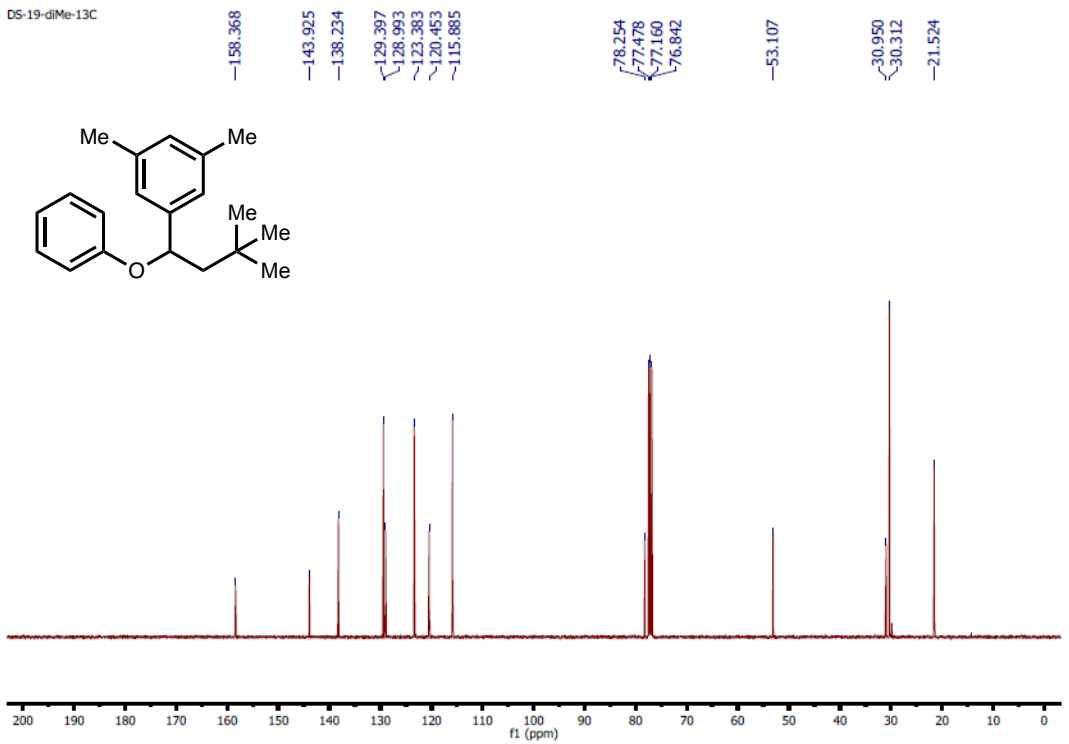
Compound 5. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



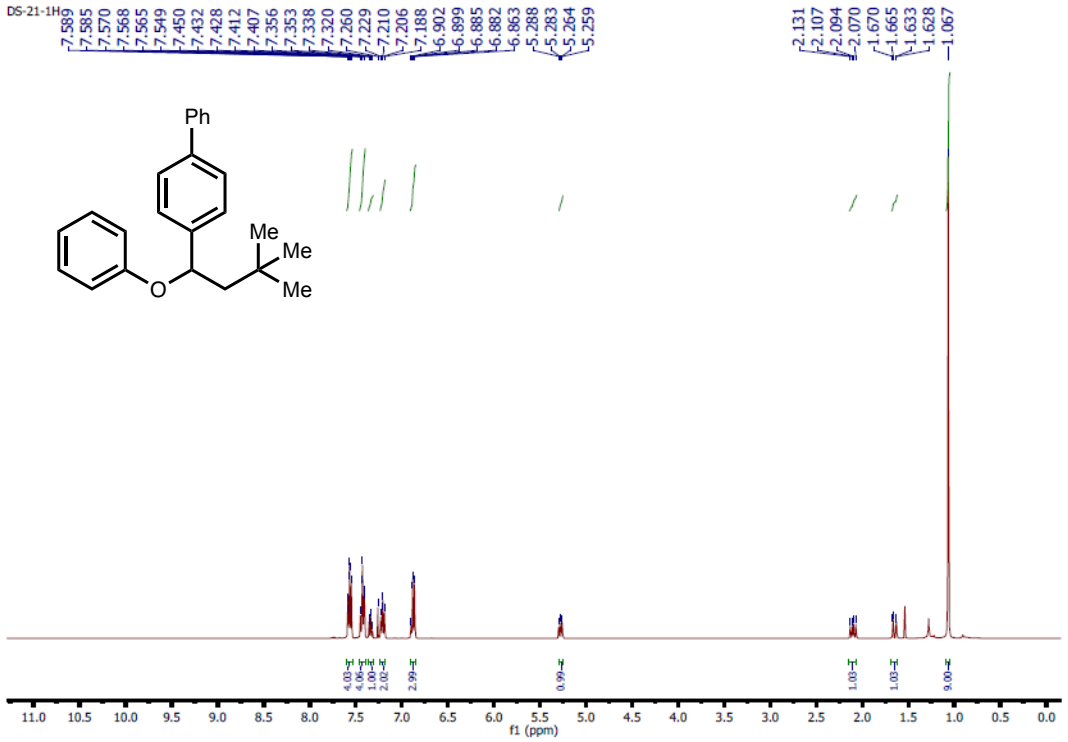


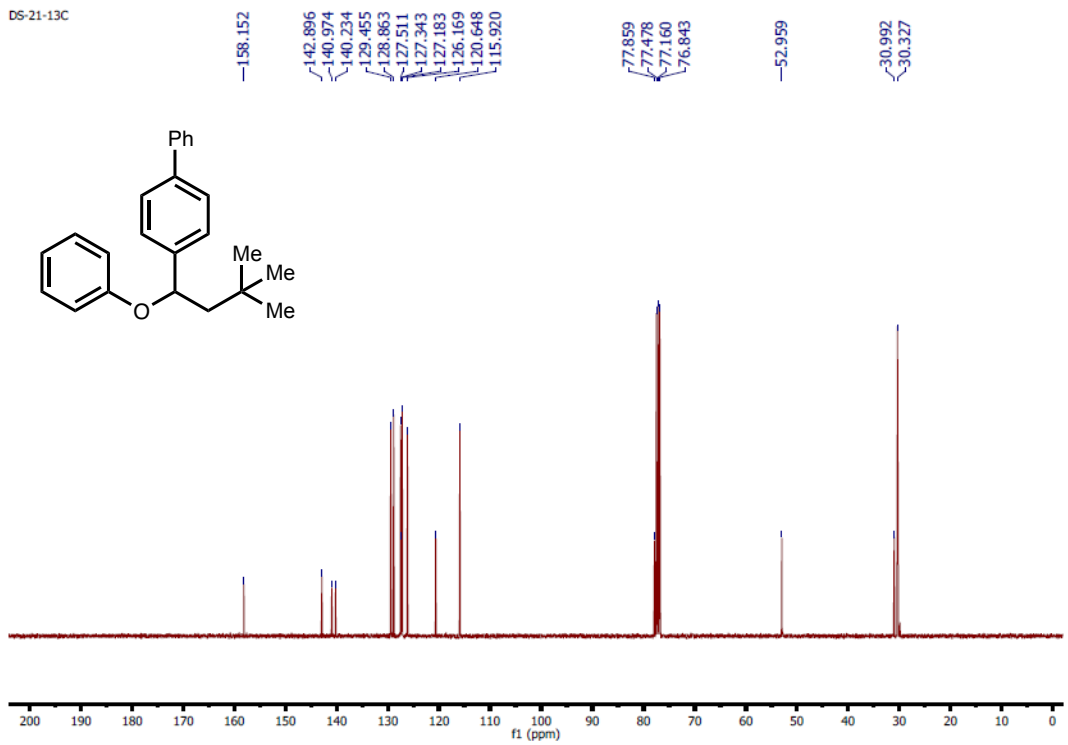
Compound 6. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



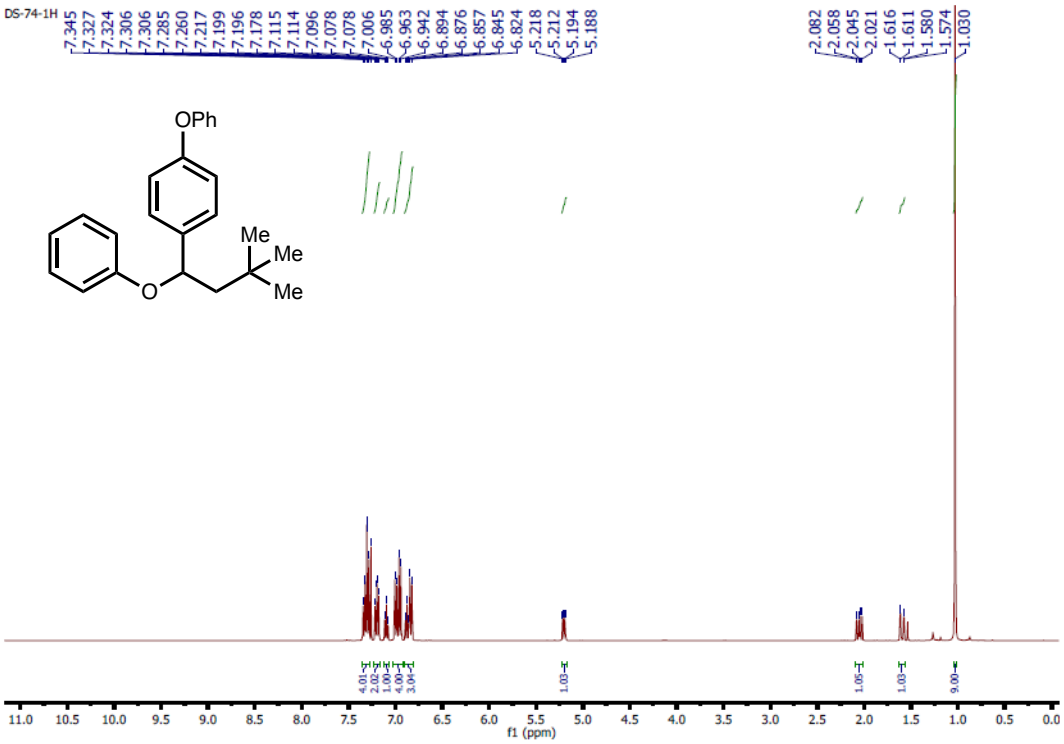


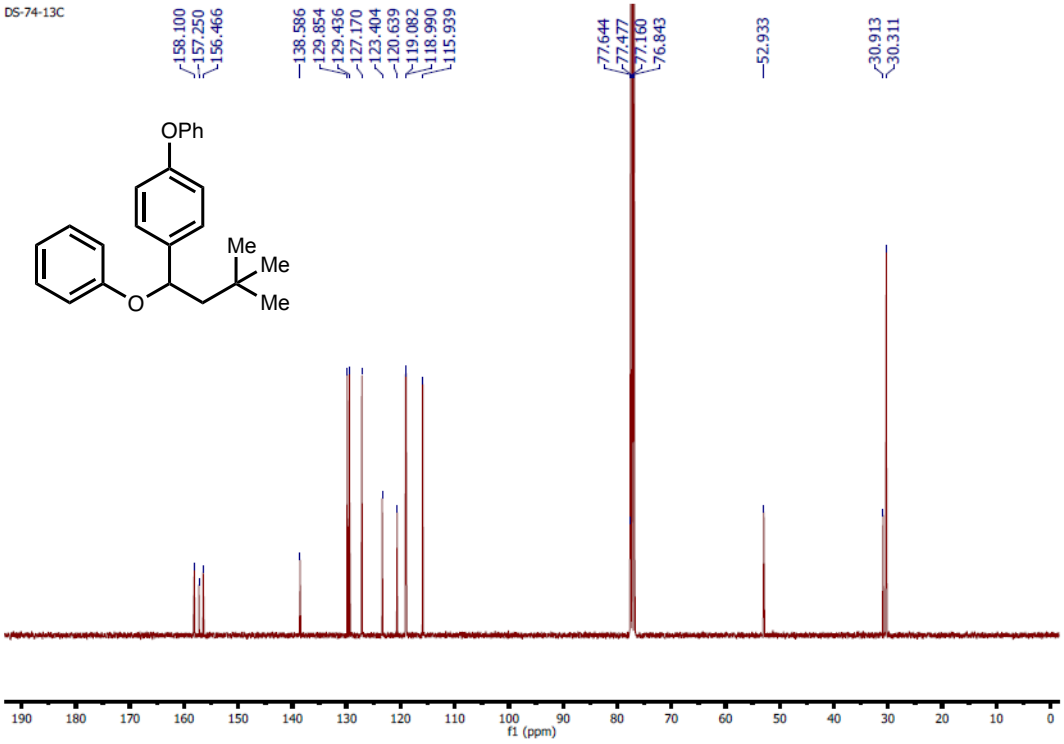
Compound 7. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



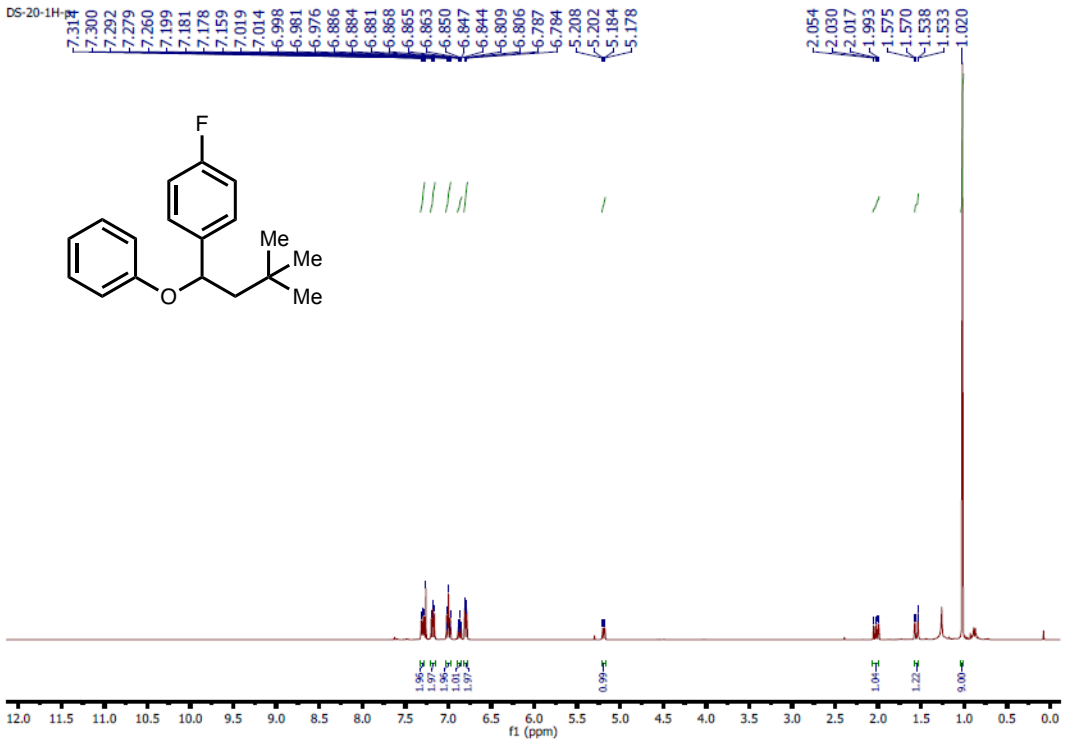


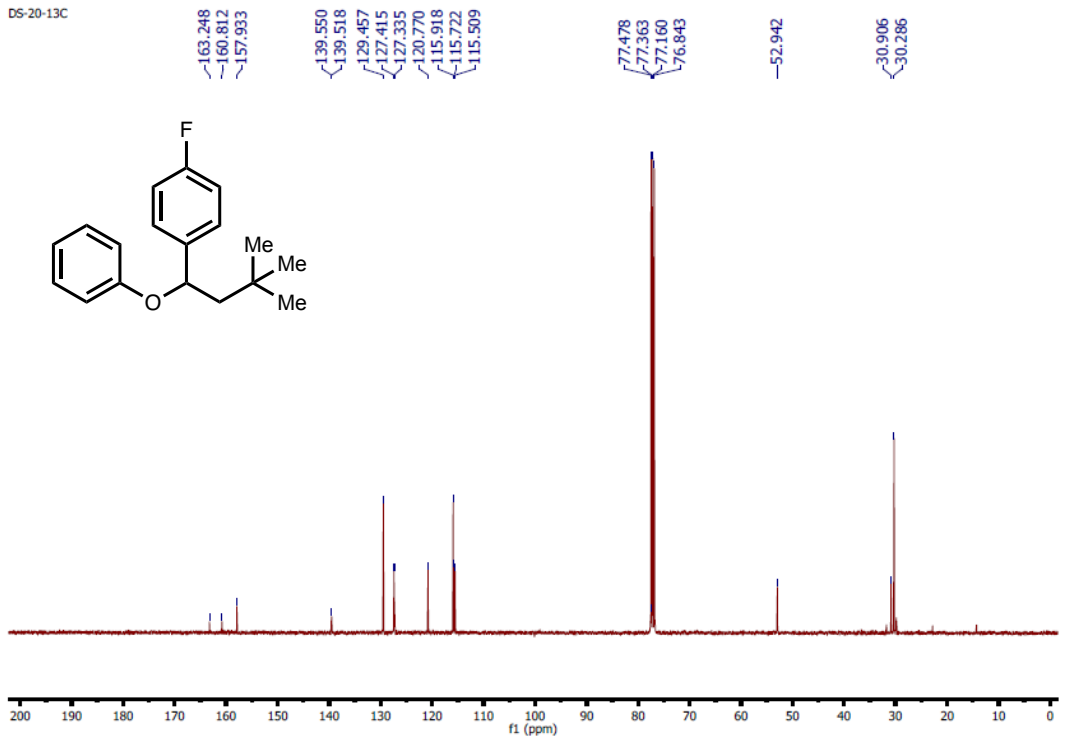
Compound 8. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



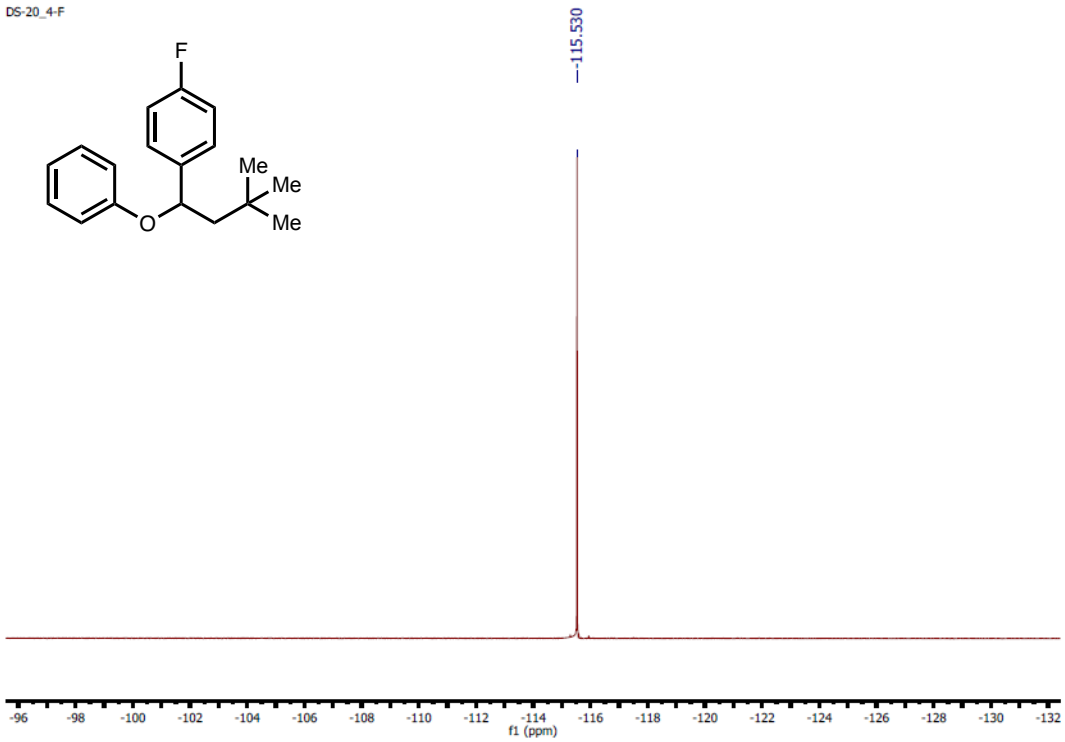


Compound 9. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

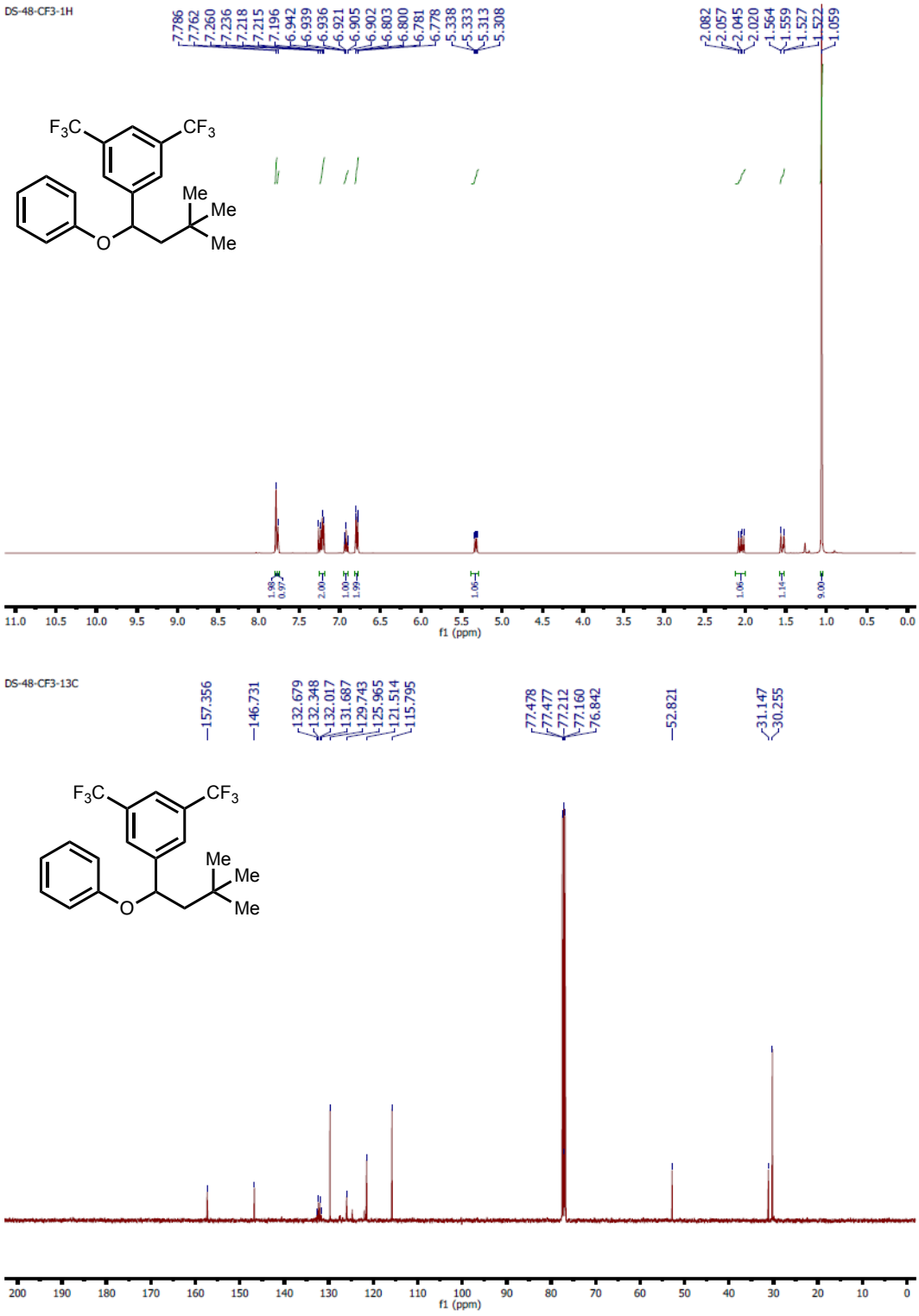




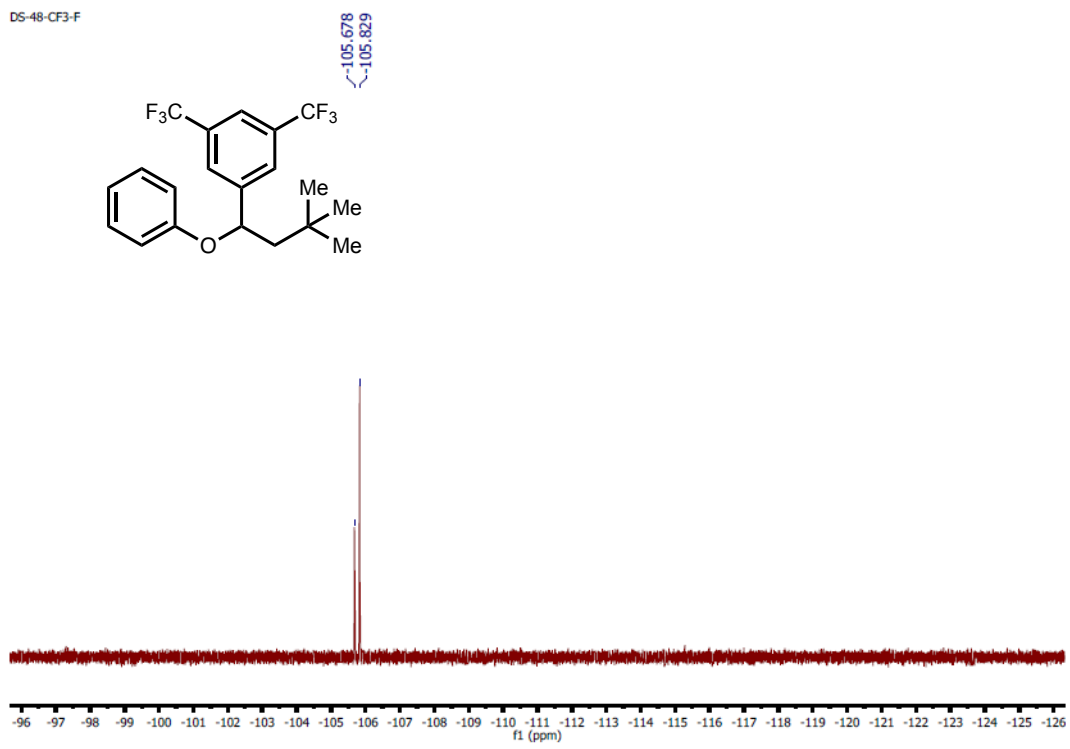
Compound 9. ^{19}F NMR ($CDCl_3$, 376 MHz)



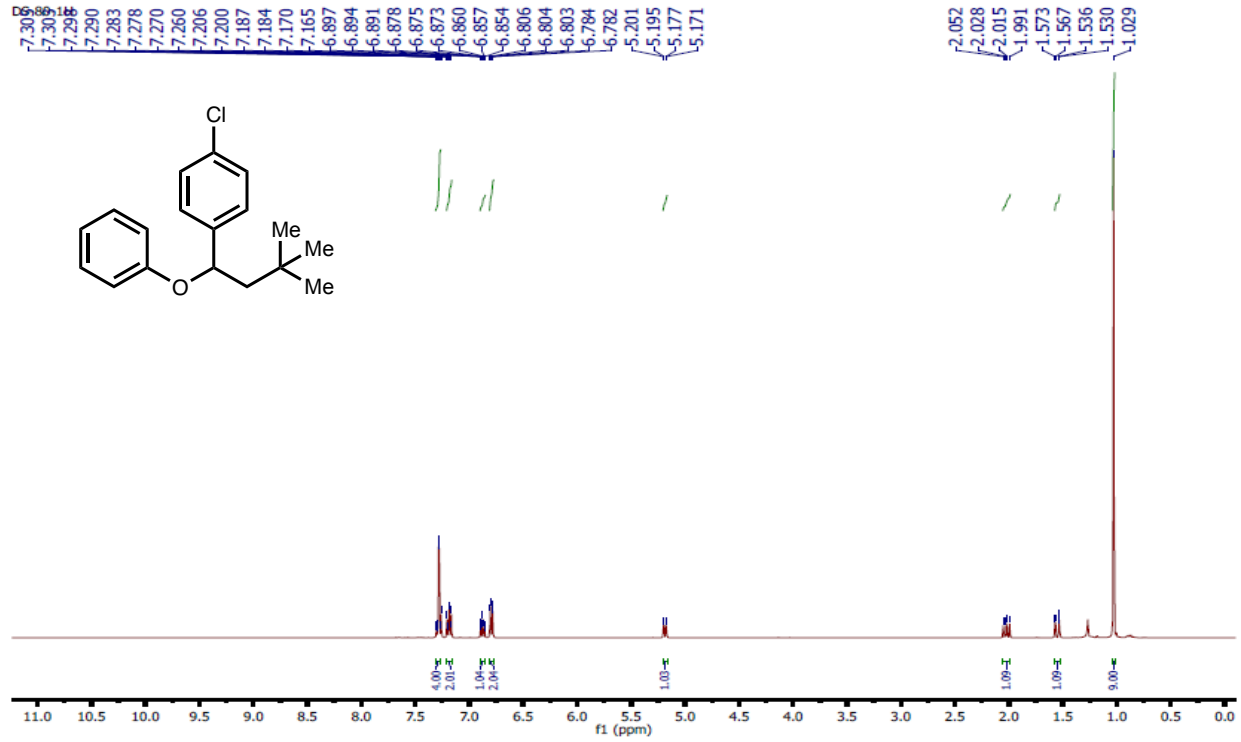
Compound 10. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

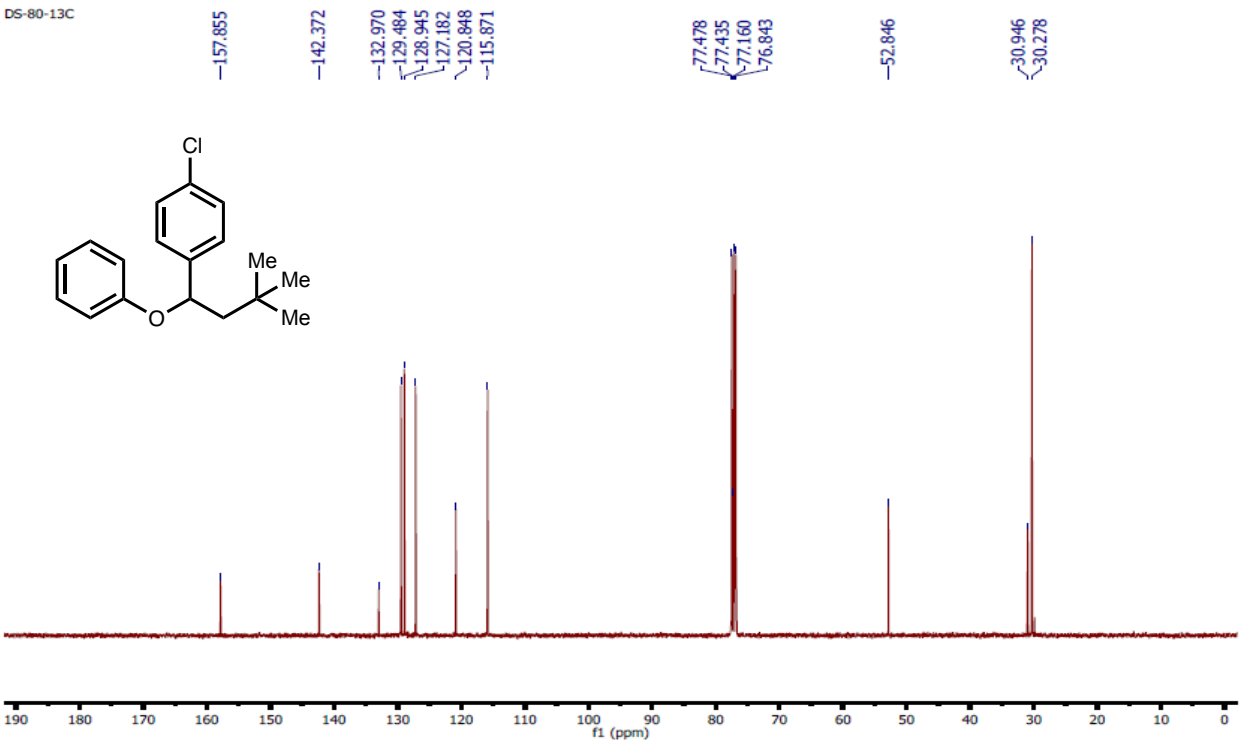


Compound 10. ^{19}F NMR ($CDCl_3$, 376 MHz)

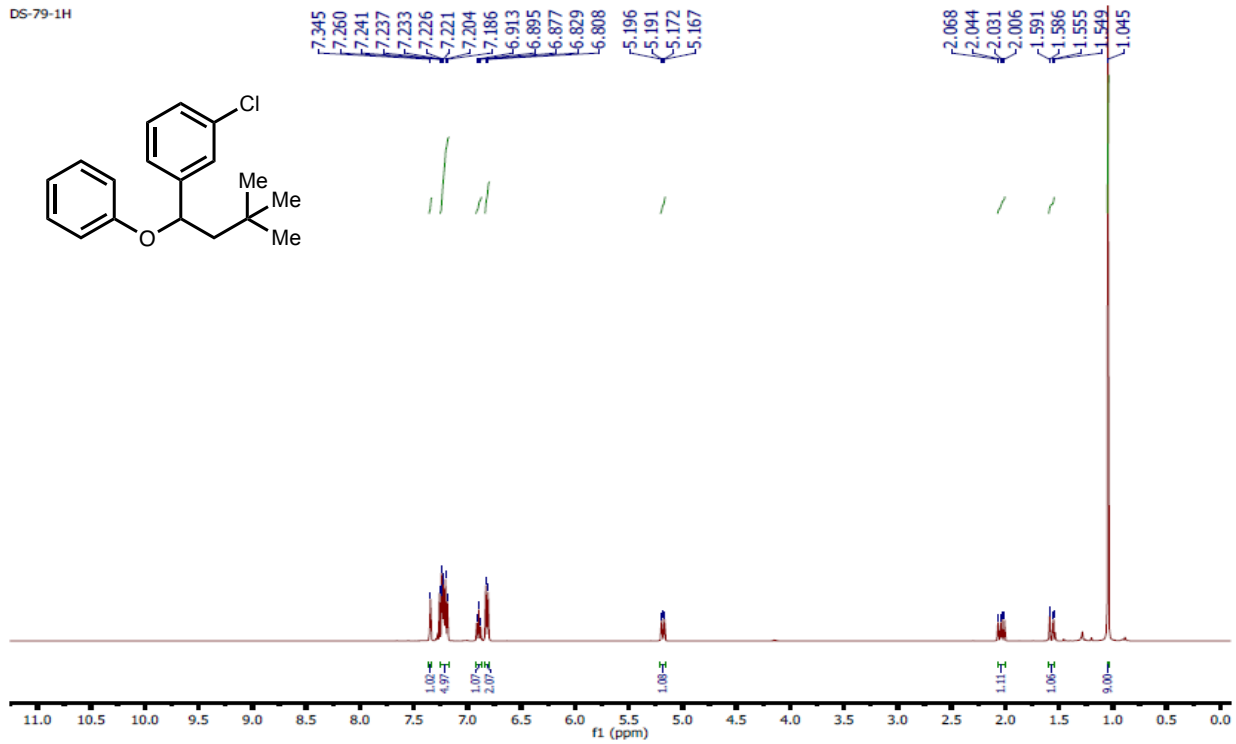


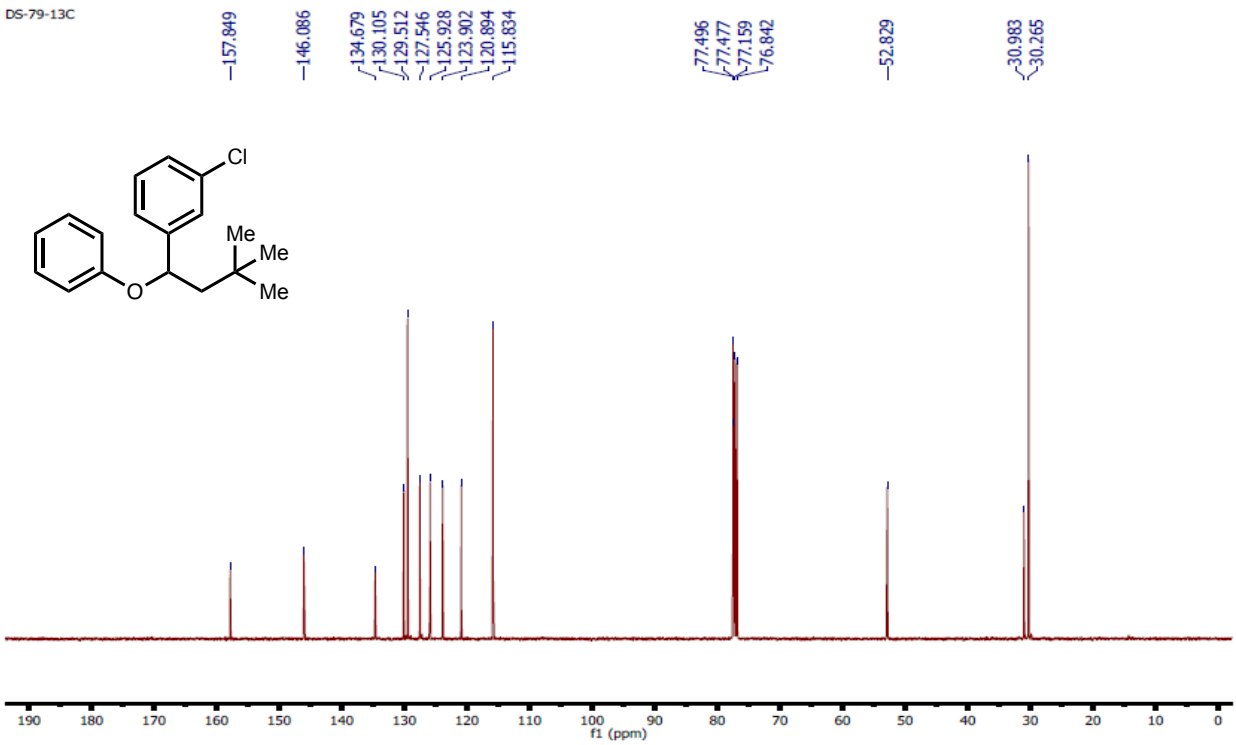
Compound 11. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



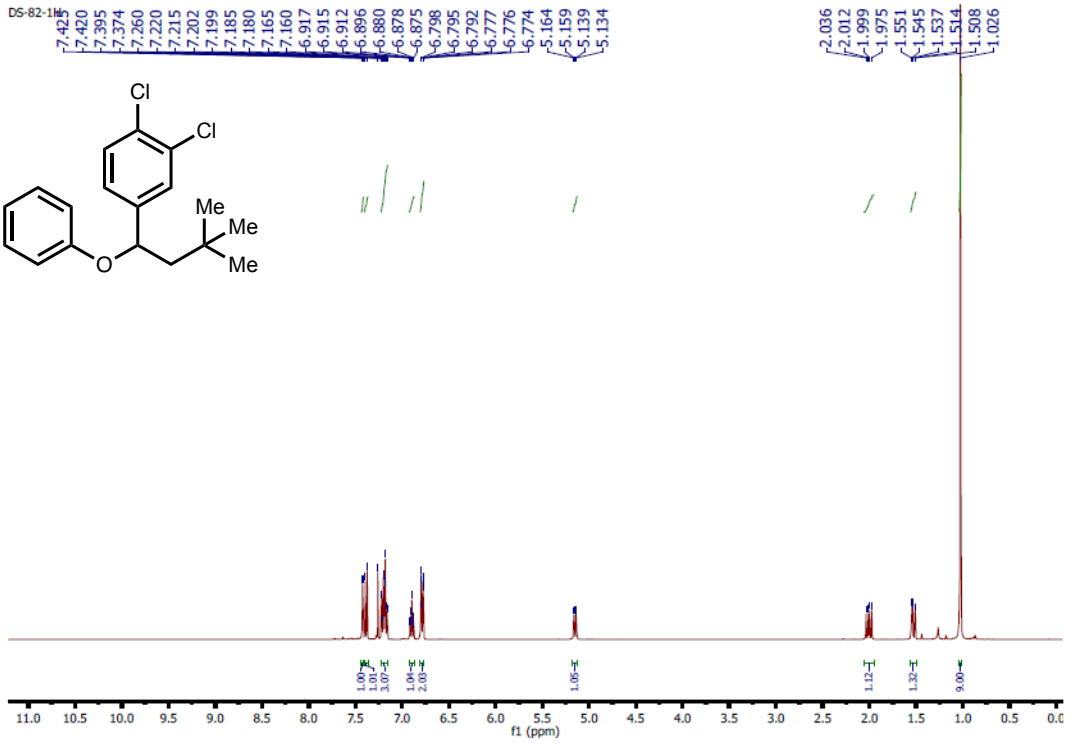


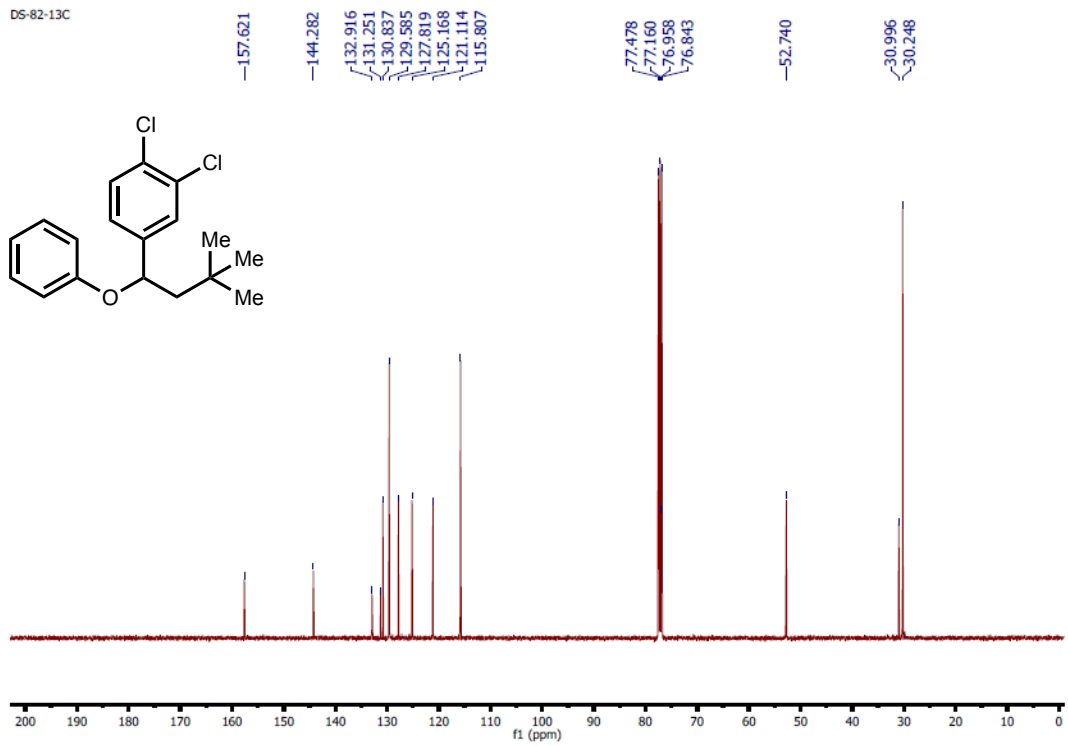
Compound 12. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



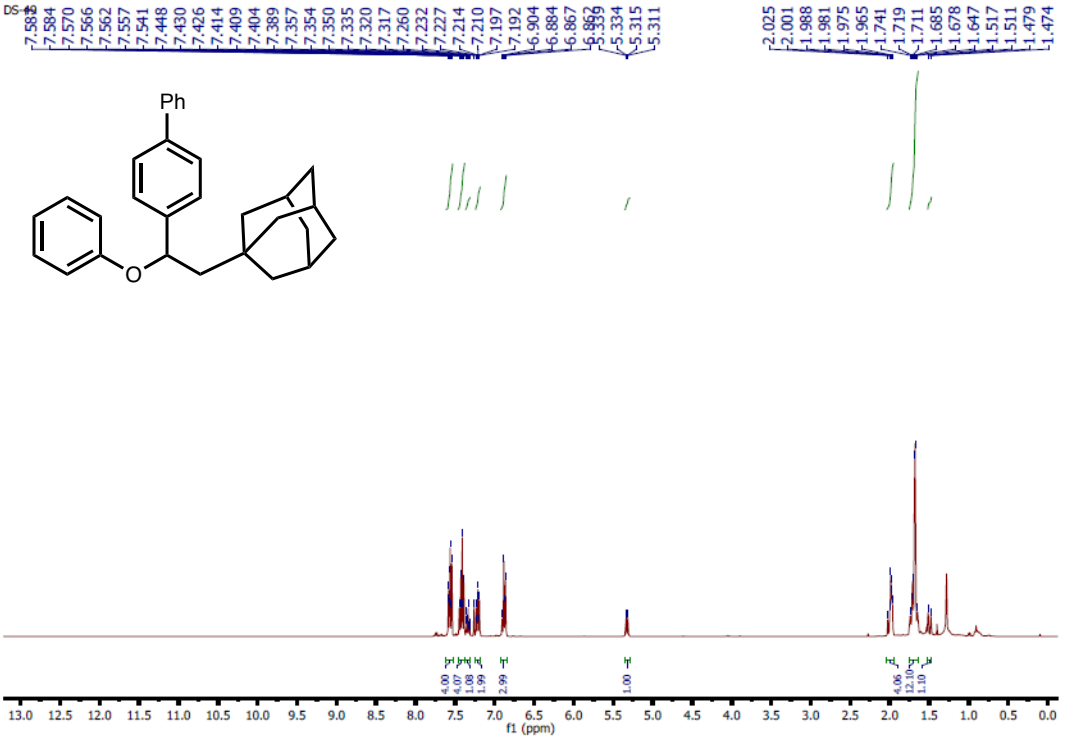


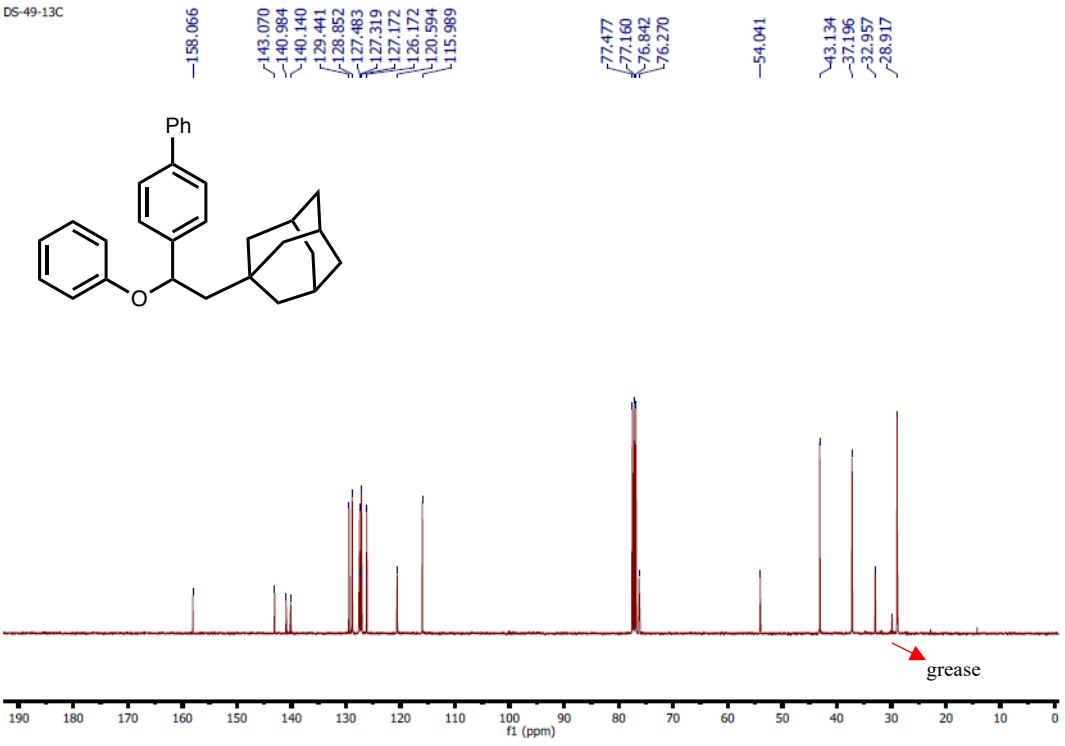
Compound 13. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



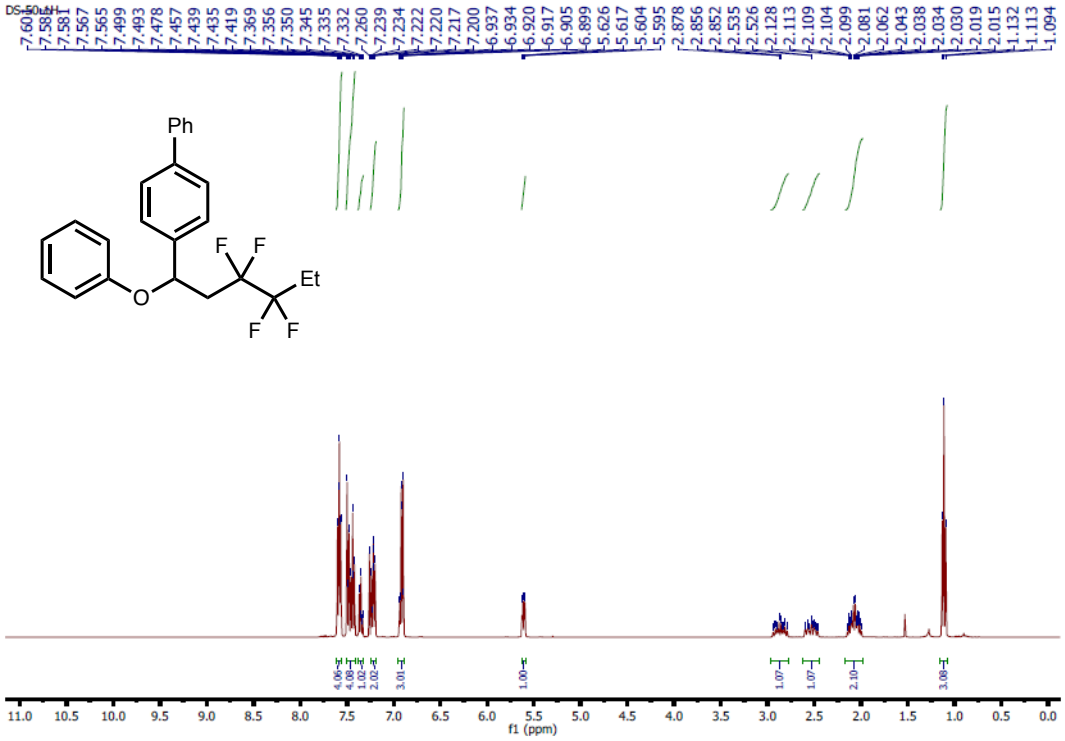


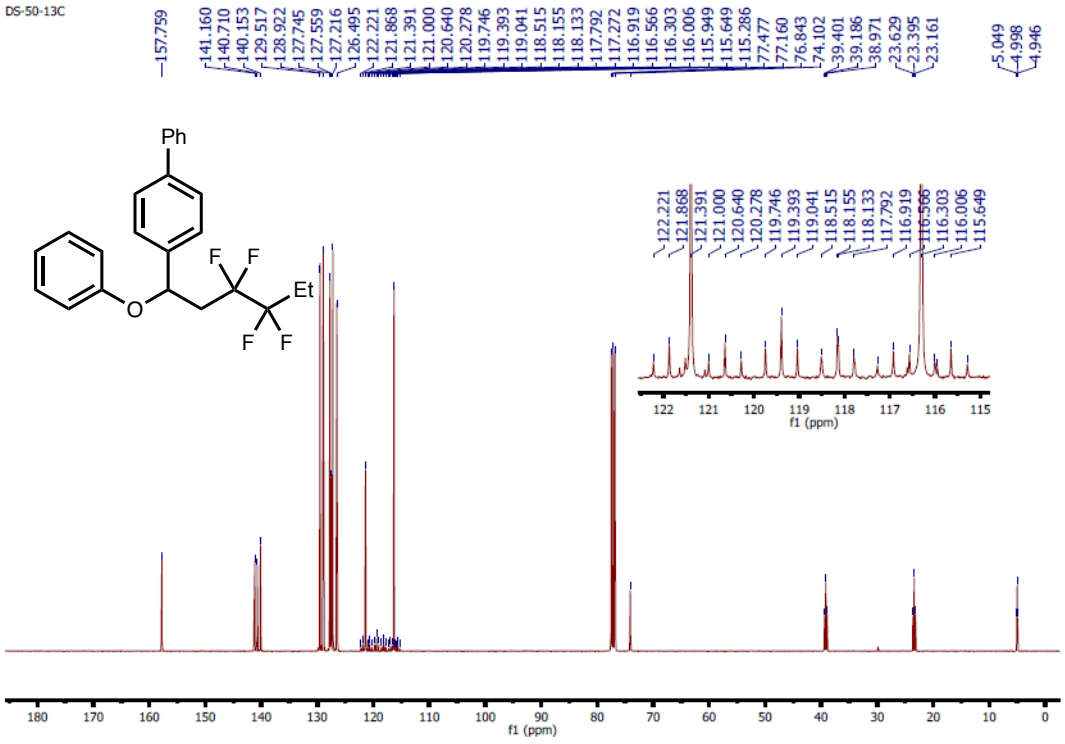
Compound 14. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



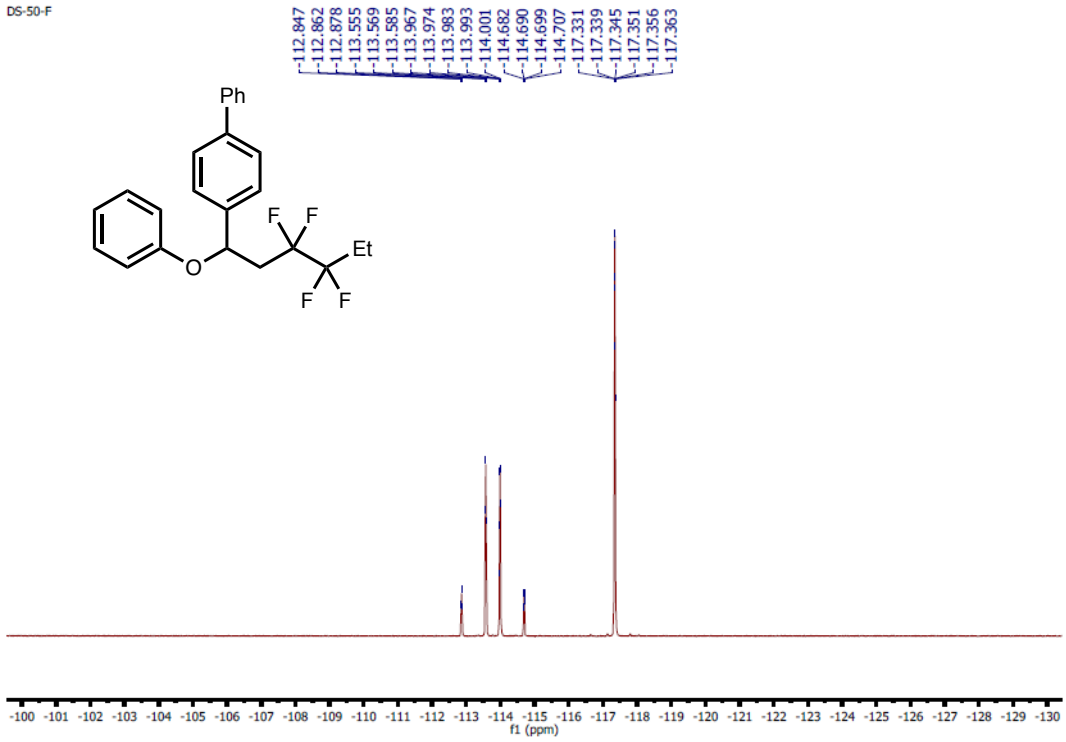


Compound 16. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

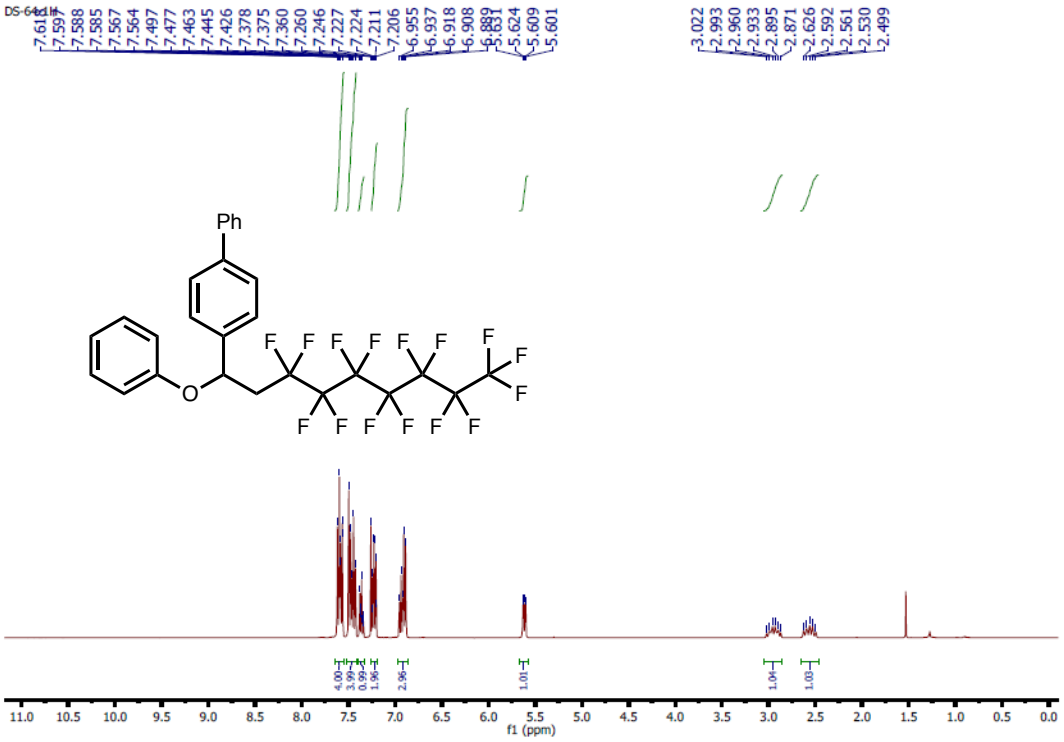


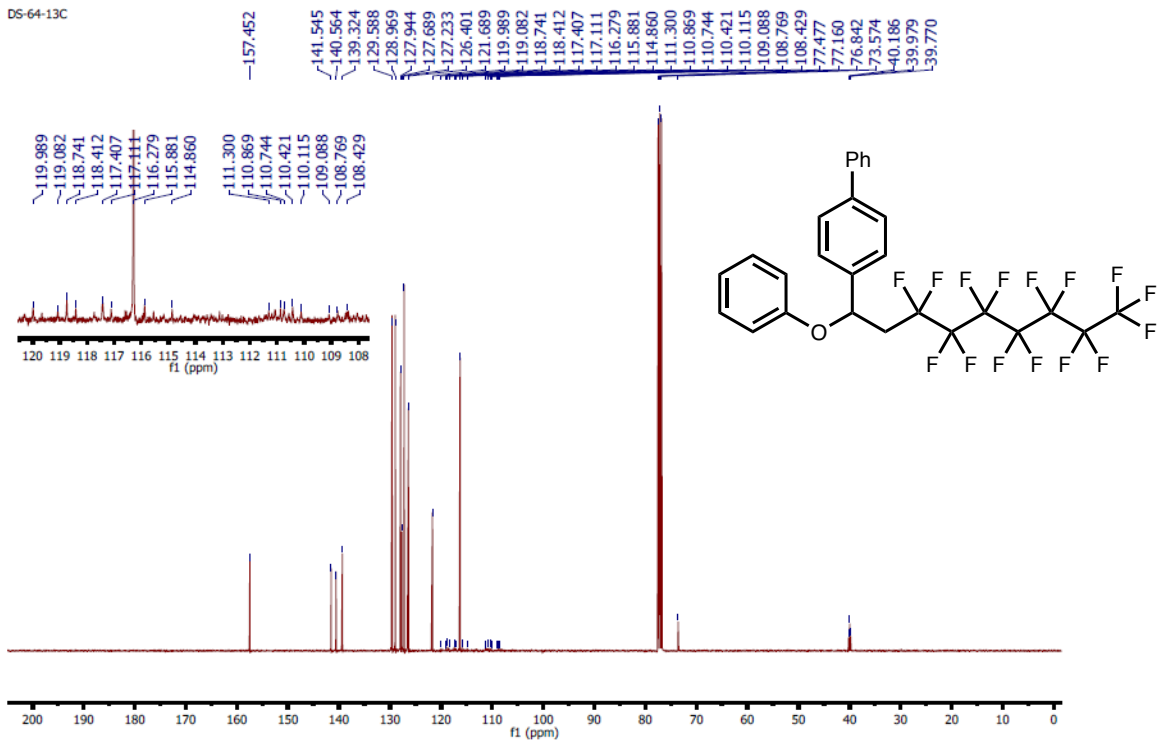


Compound 16. ^{19}F NMR ($CDCl_3$, 376 MHz)

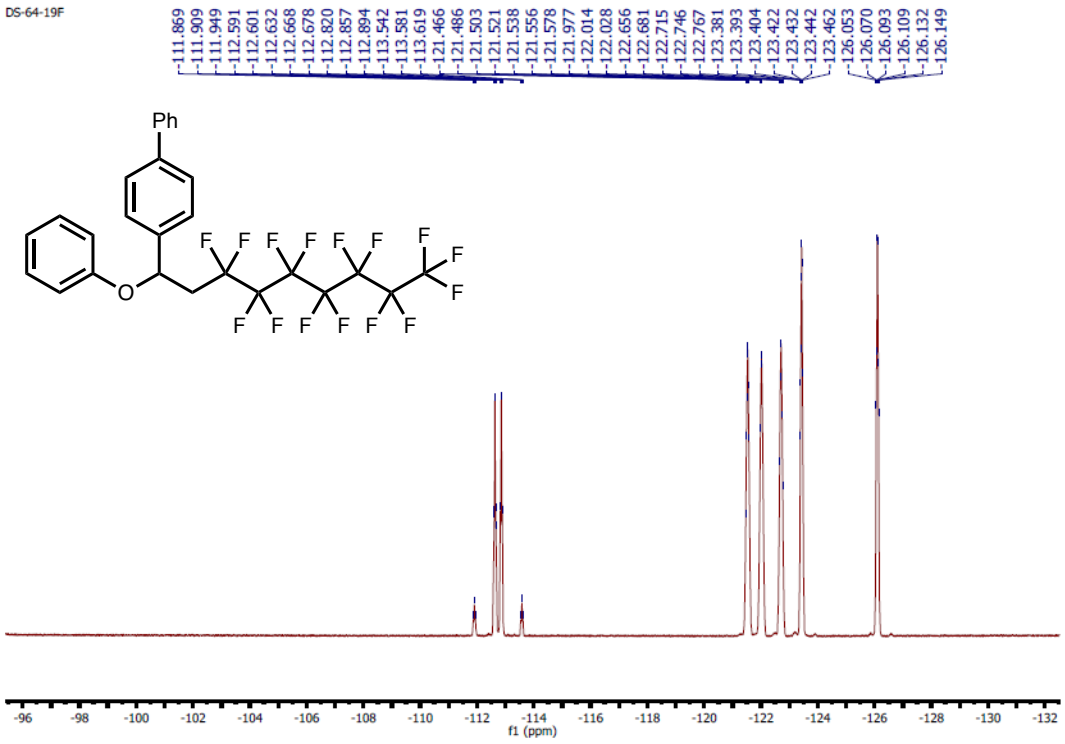


Compound 17. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

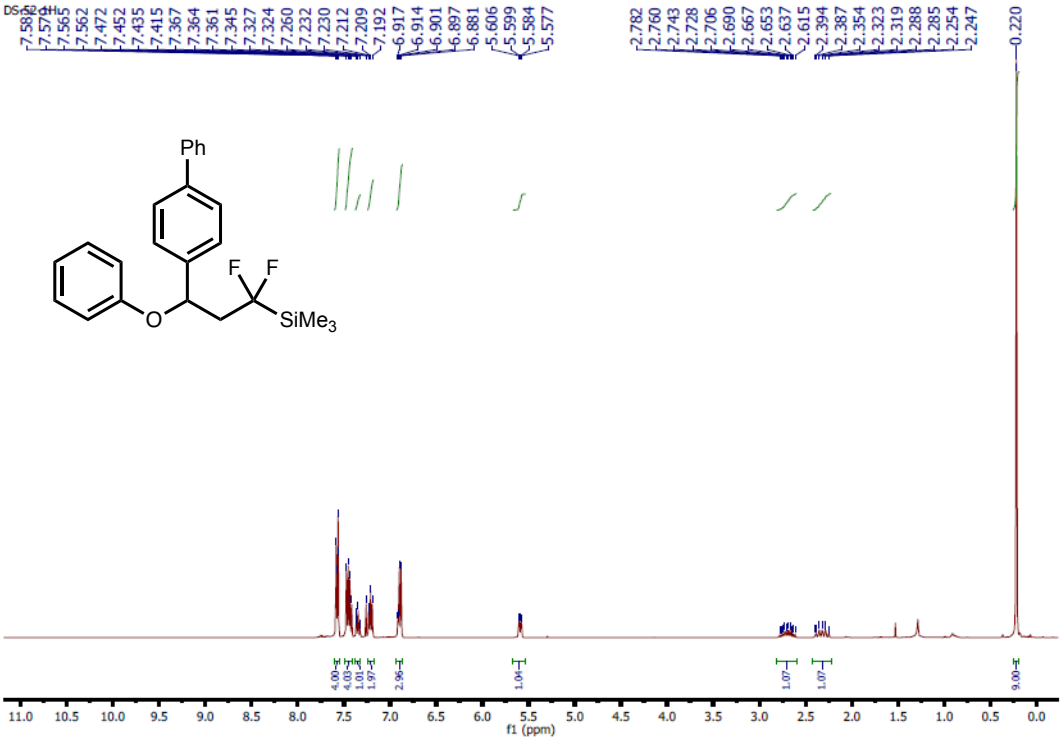


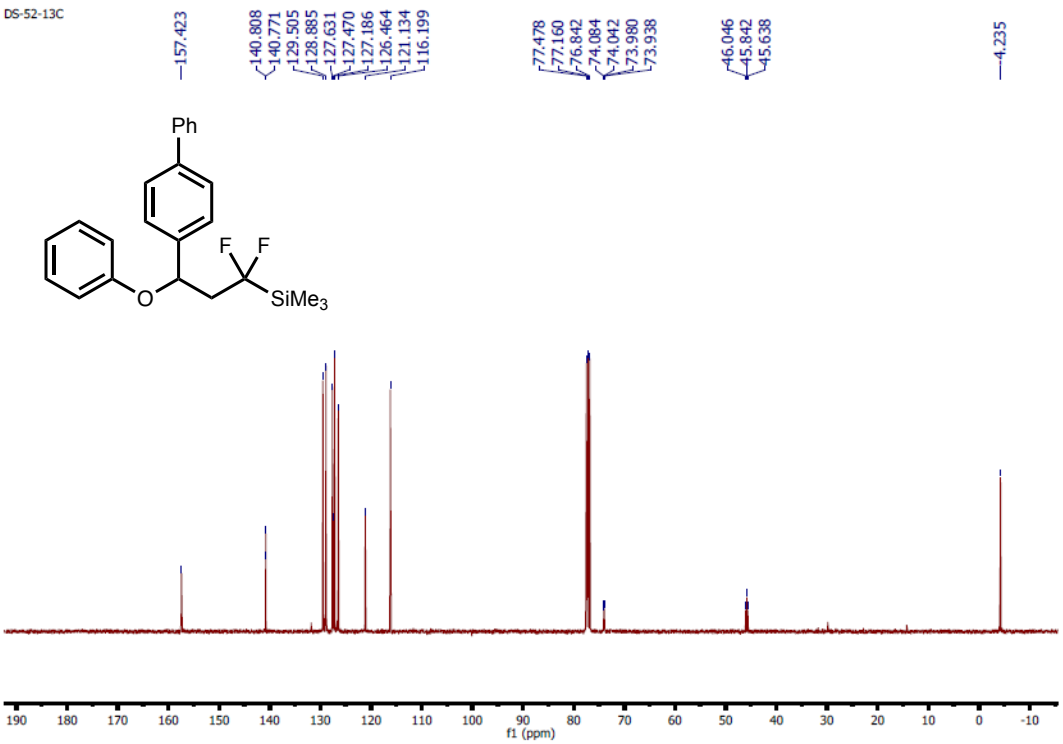


Compound 17. ^{19}F NMR ($CDCl_3$, 376 MHz)

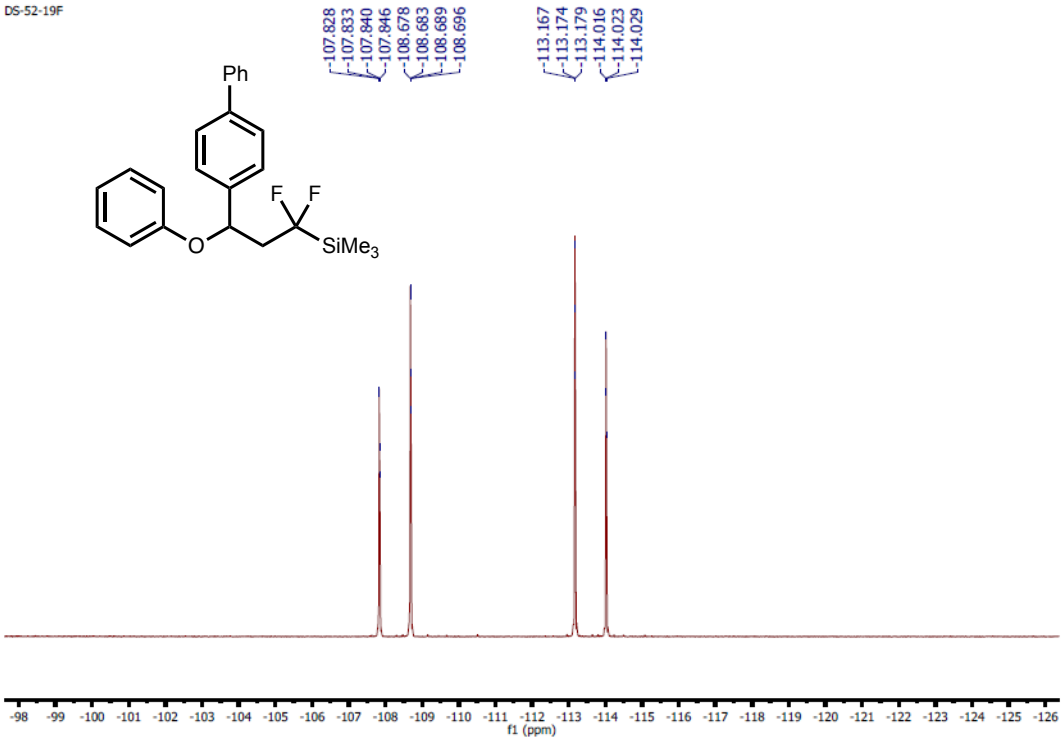


Compound 18. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

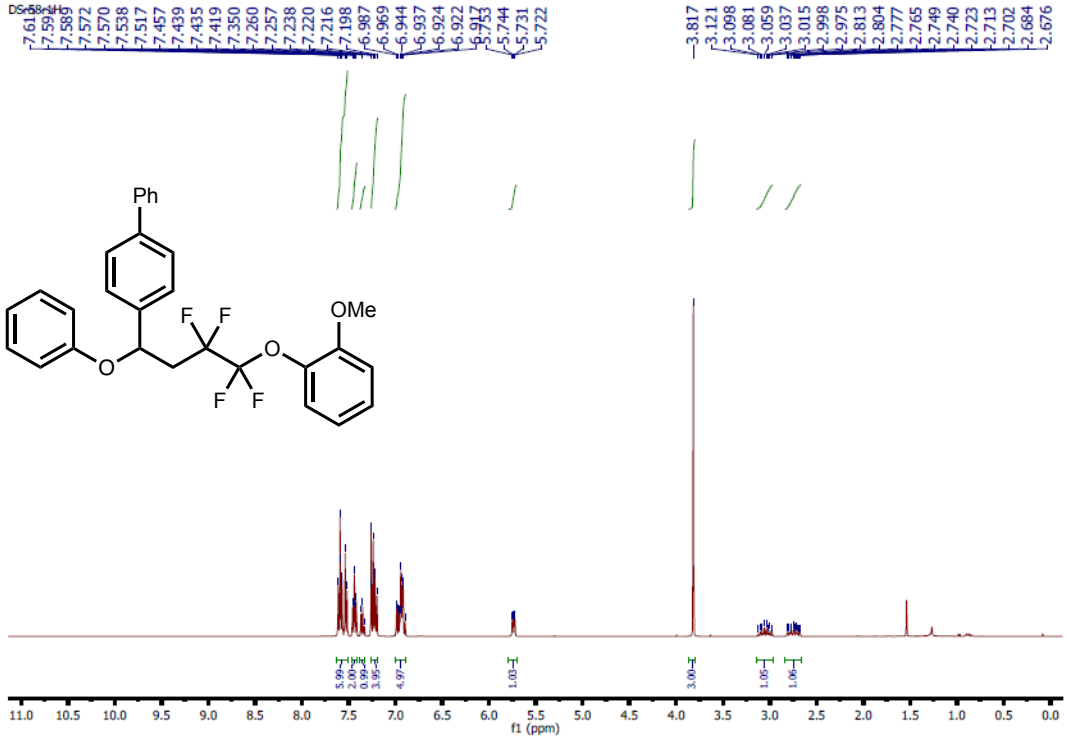


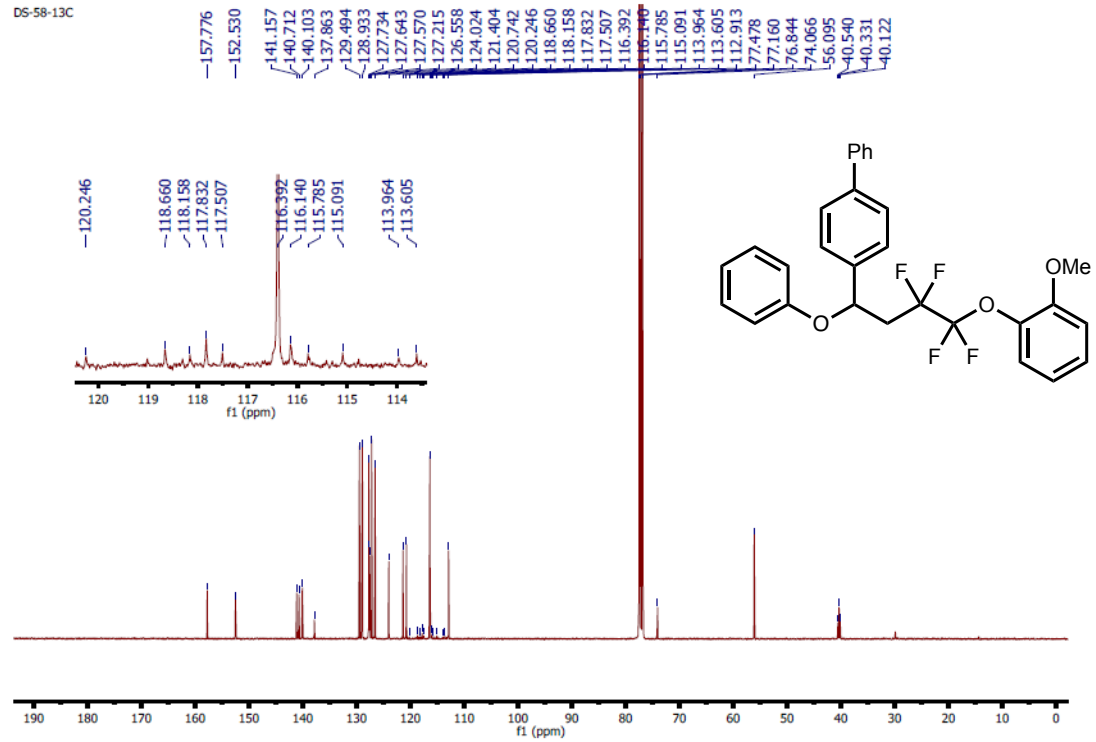


Compound 18. ^{19}F NMR ($CDCl_3$, 376 MHz)

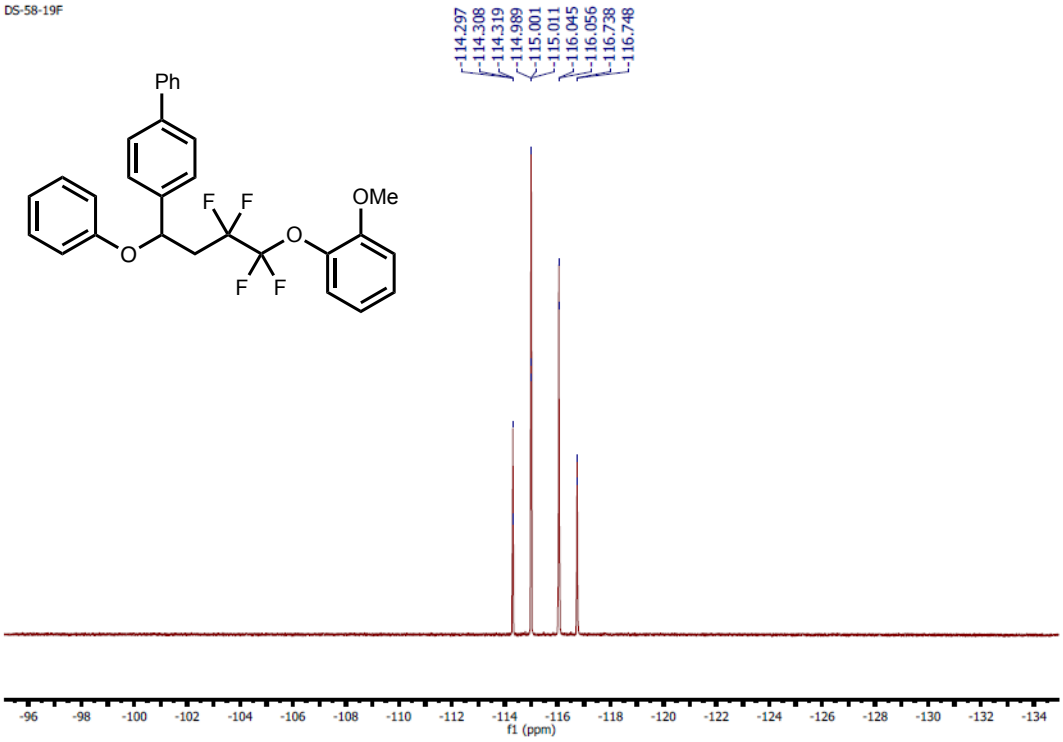


Compound 19. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

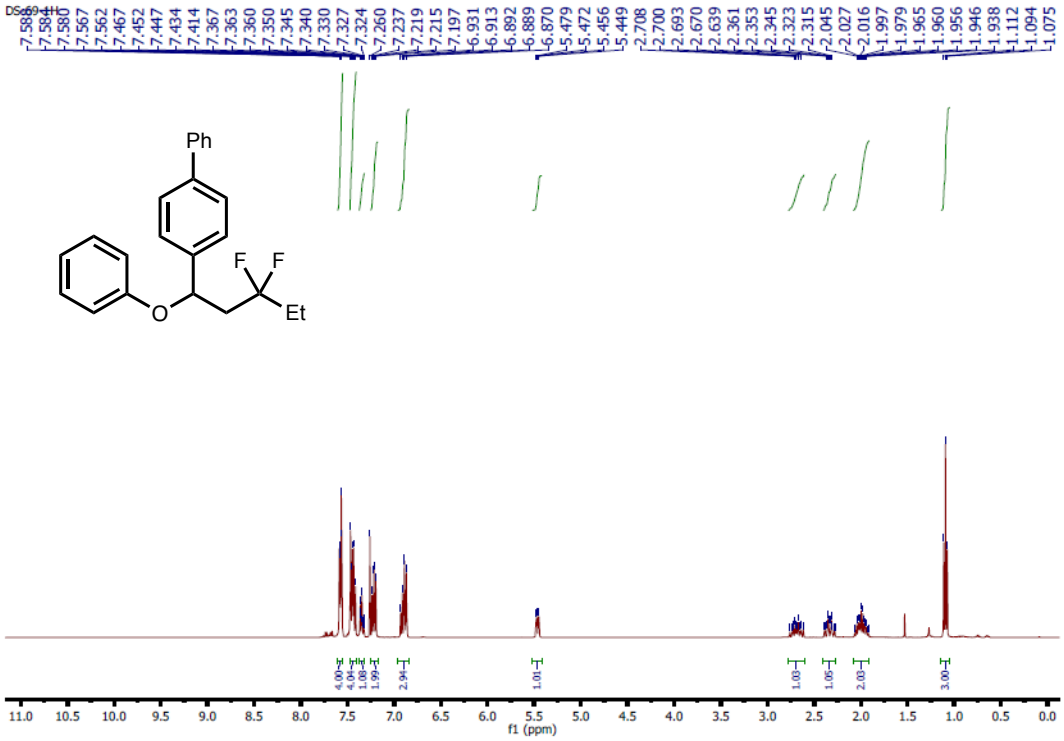


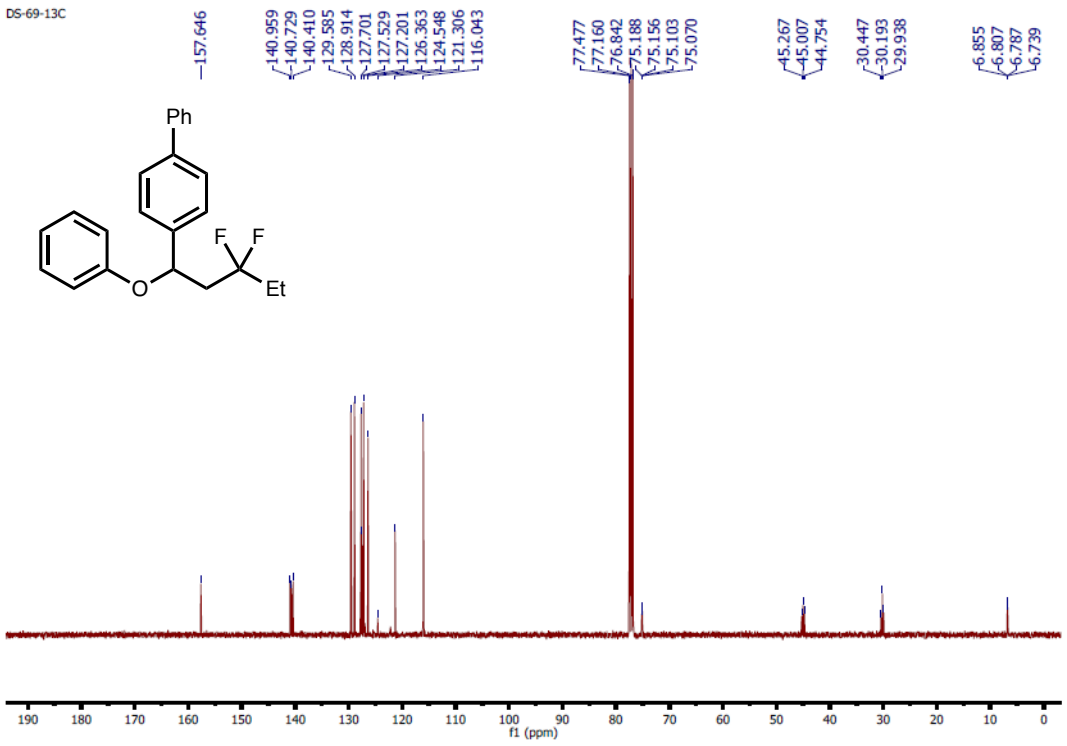


Compound 19. ^{19}F NMR ($CDCl_3$, 376 MHz)

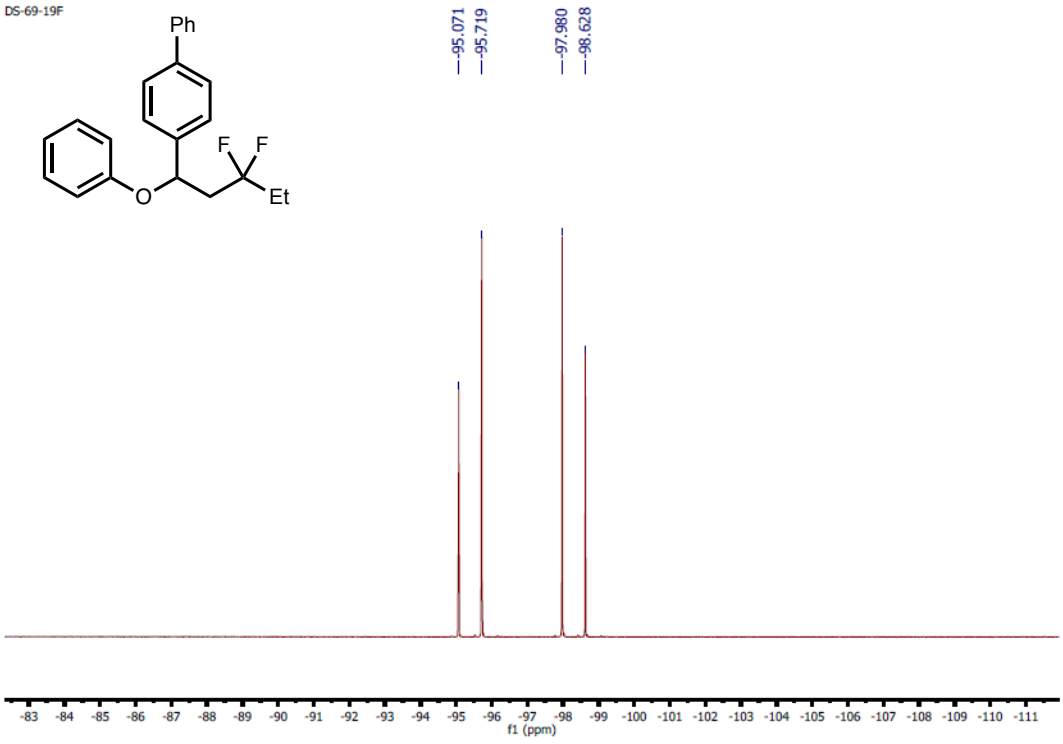


Compound 20. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

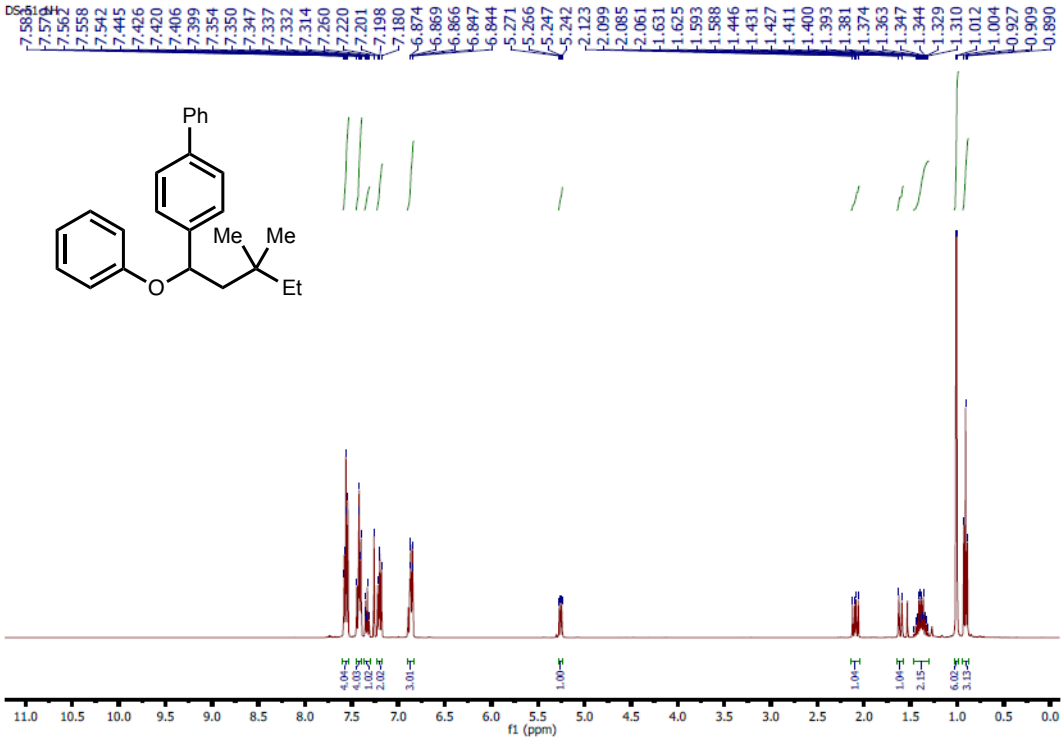


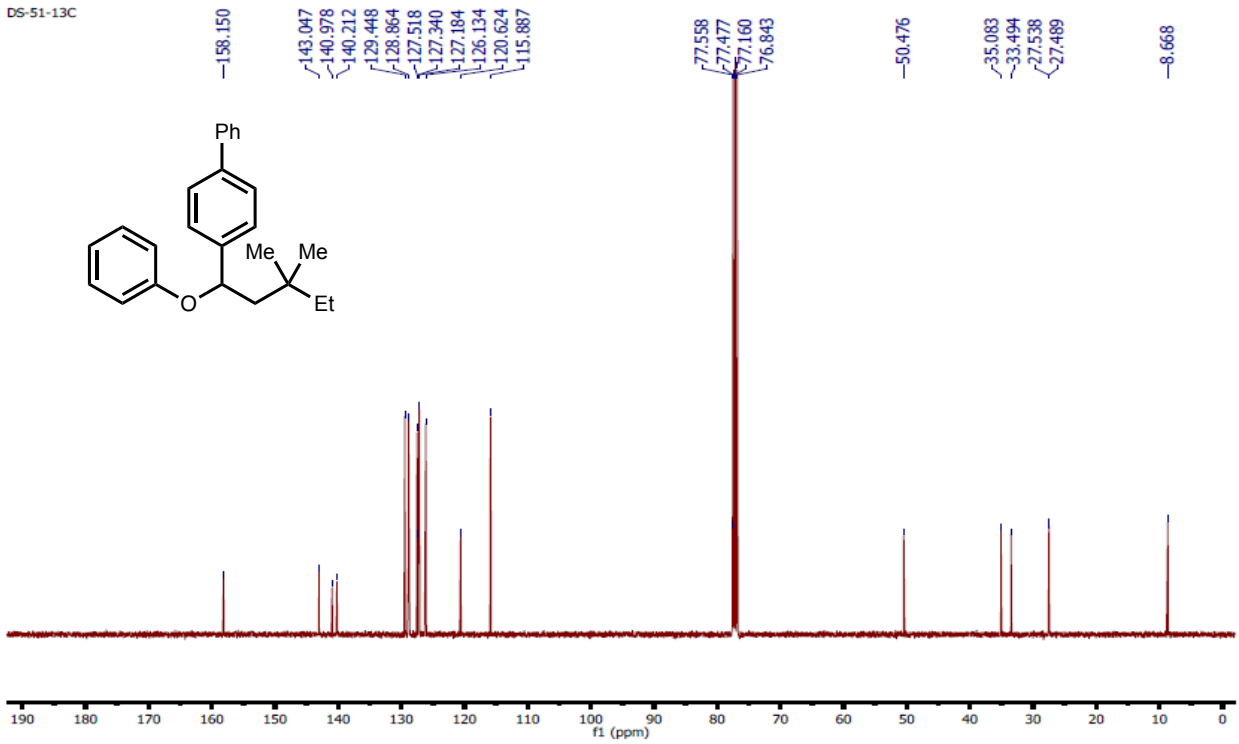


Compound 20. ^{19}F NMR ($CDCl_3$, 376 MHz)

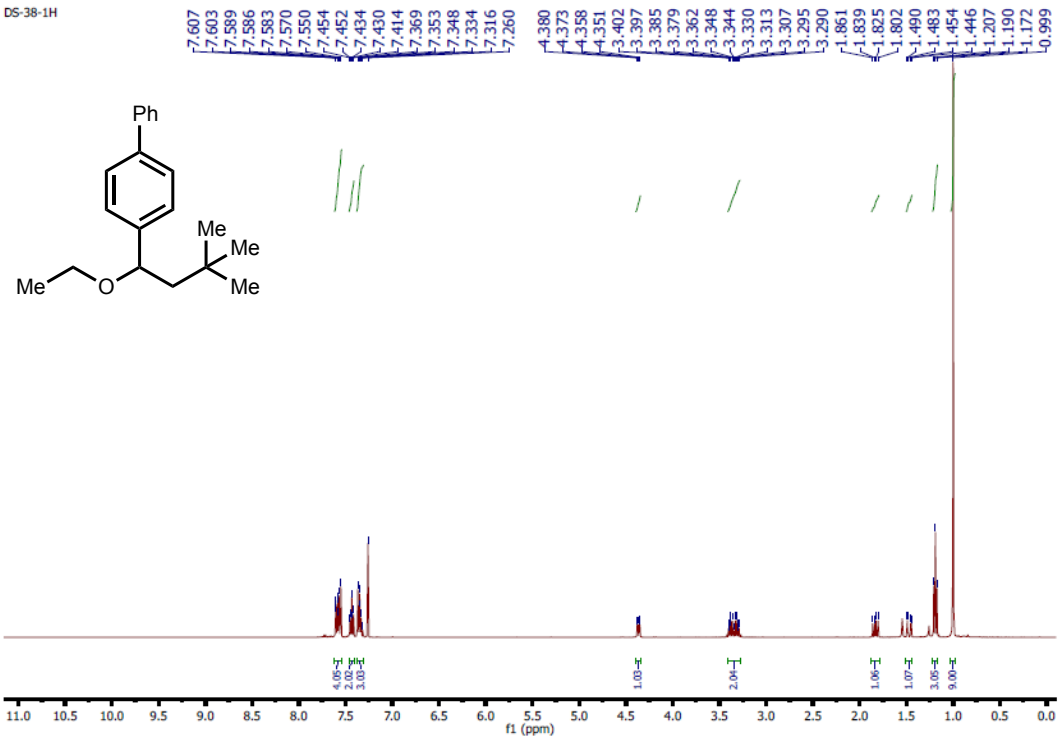


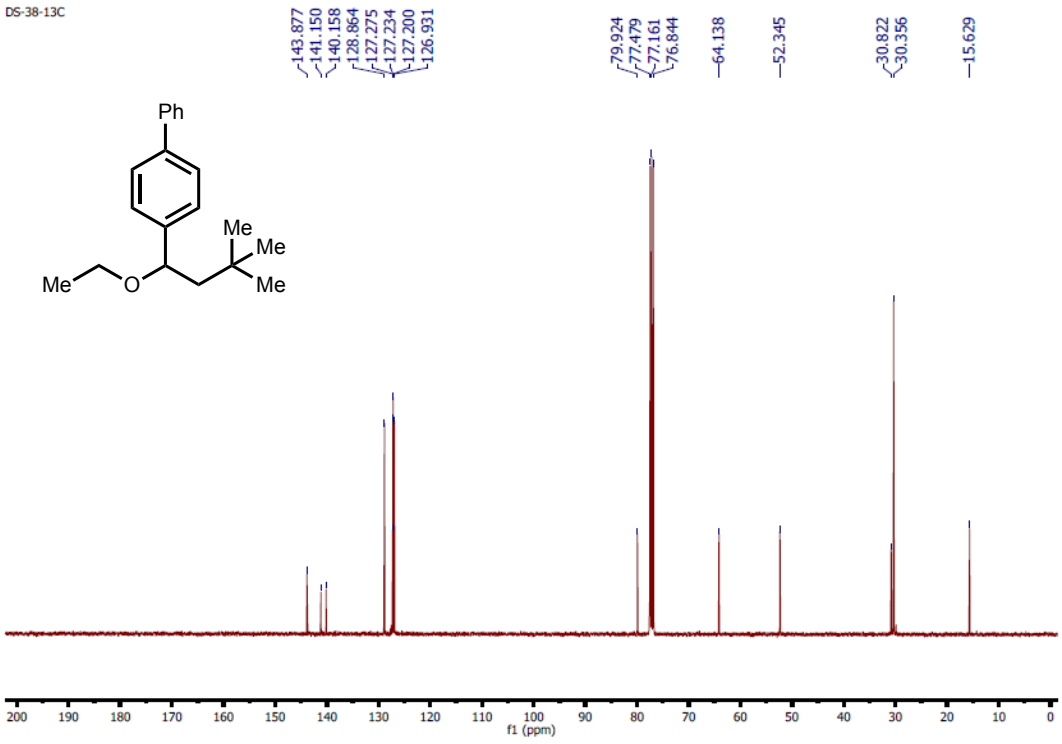
Compound 21. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



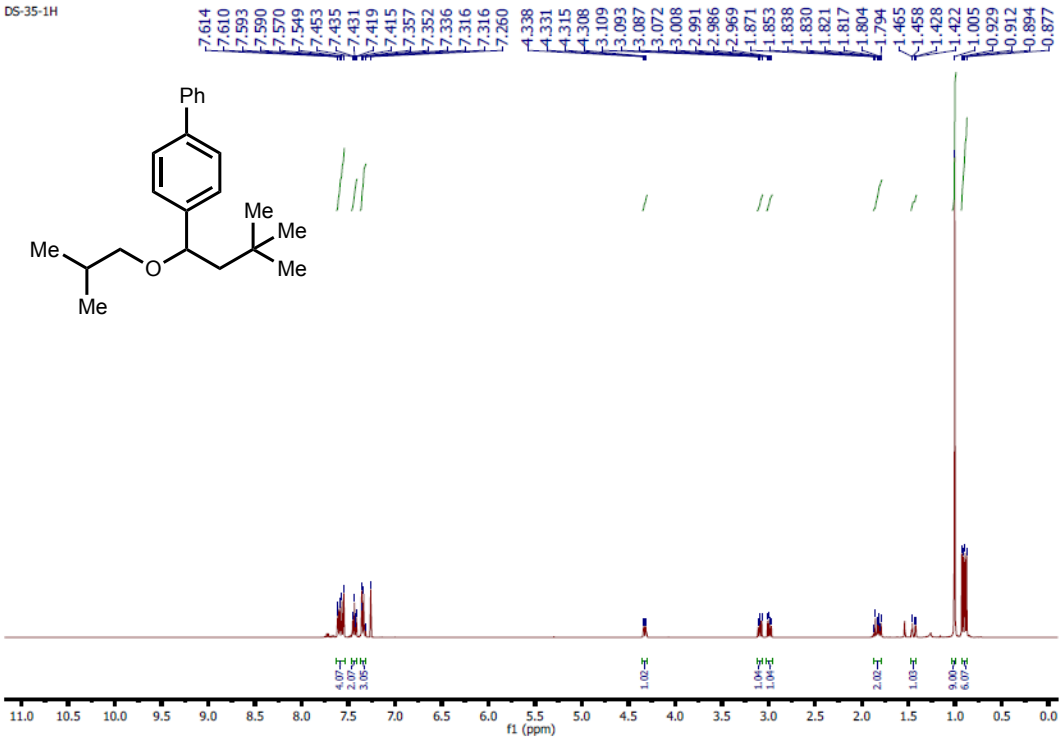


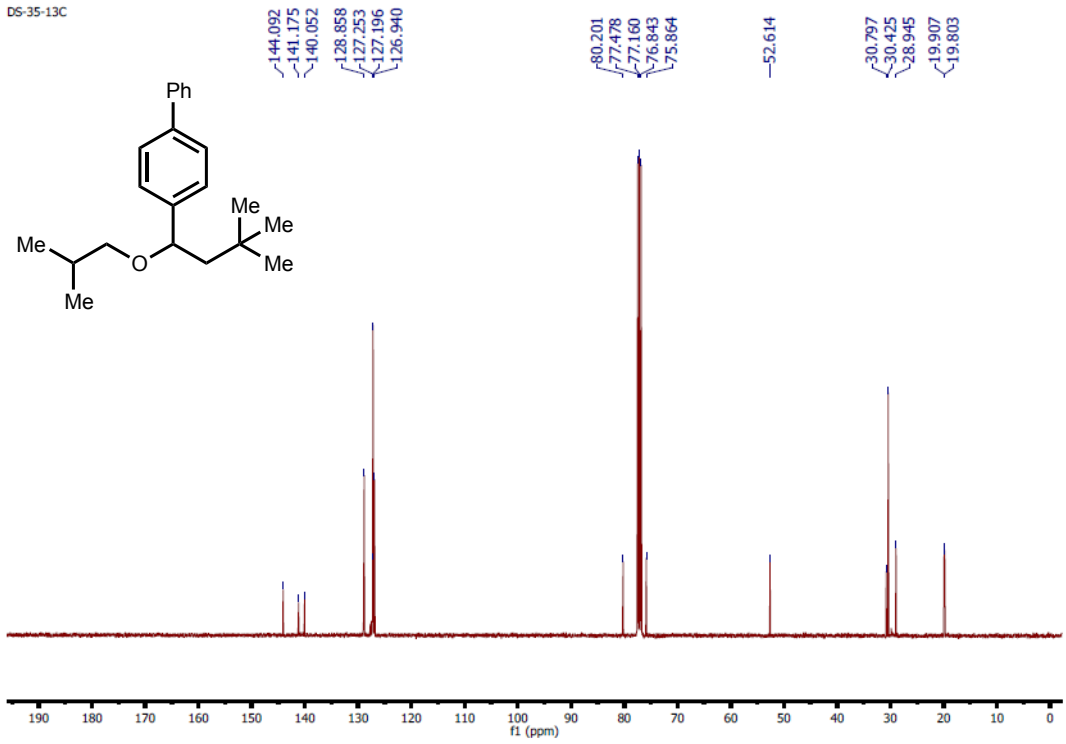
Compound 23. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



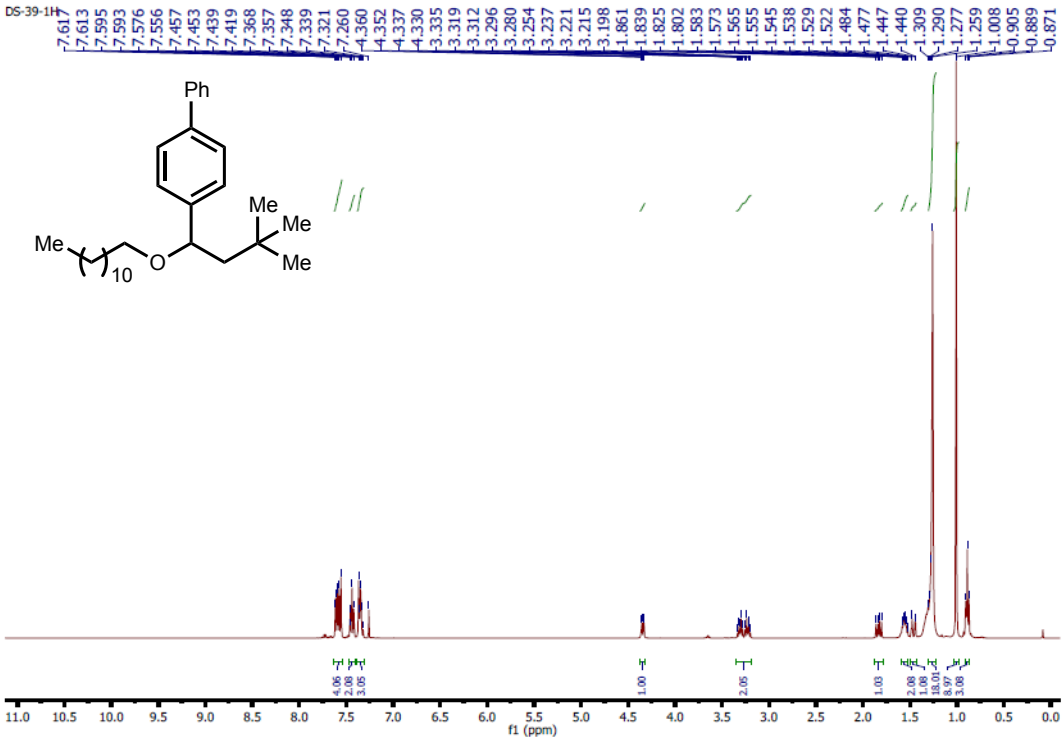


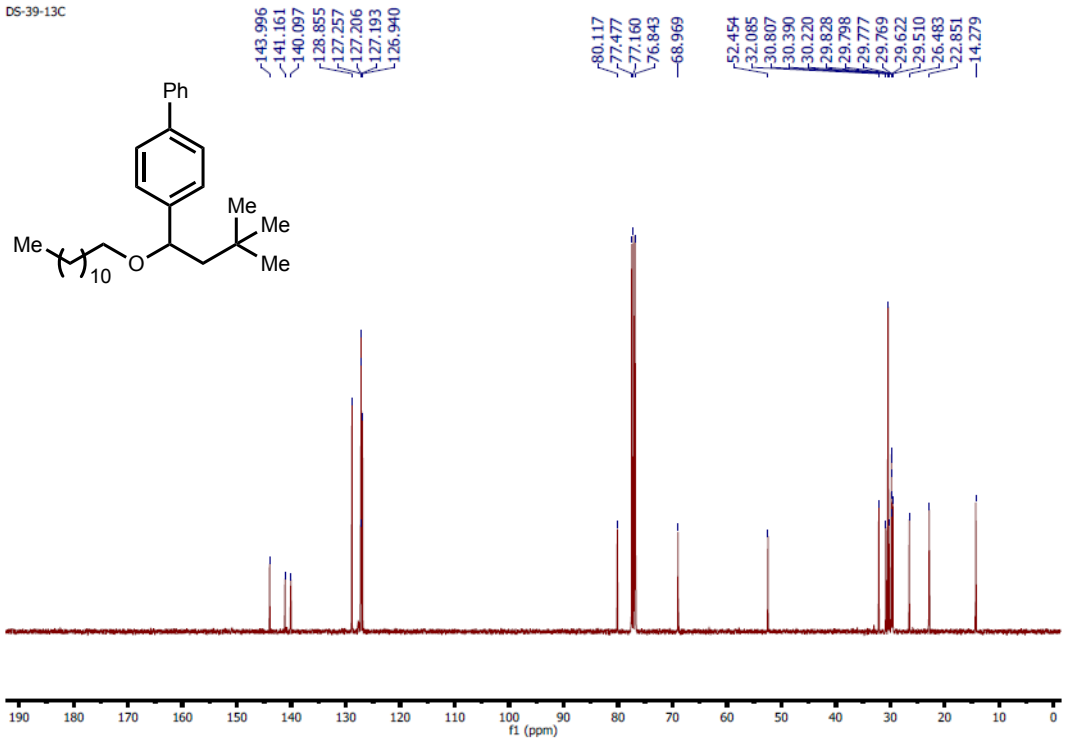
Compound 24. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



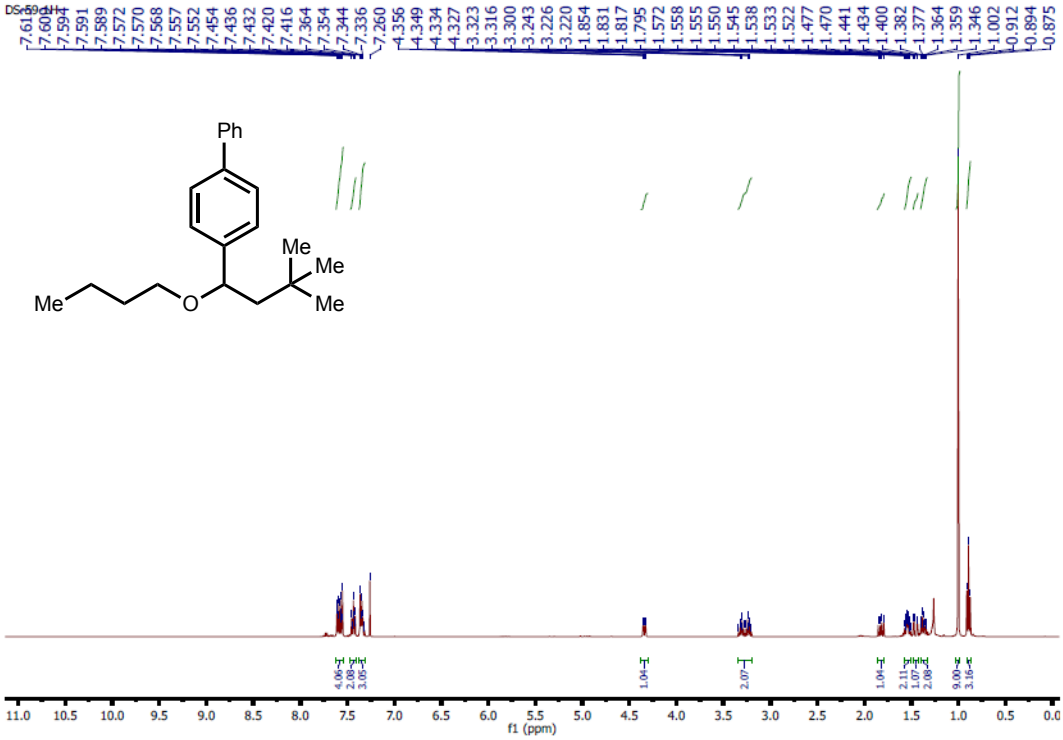


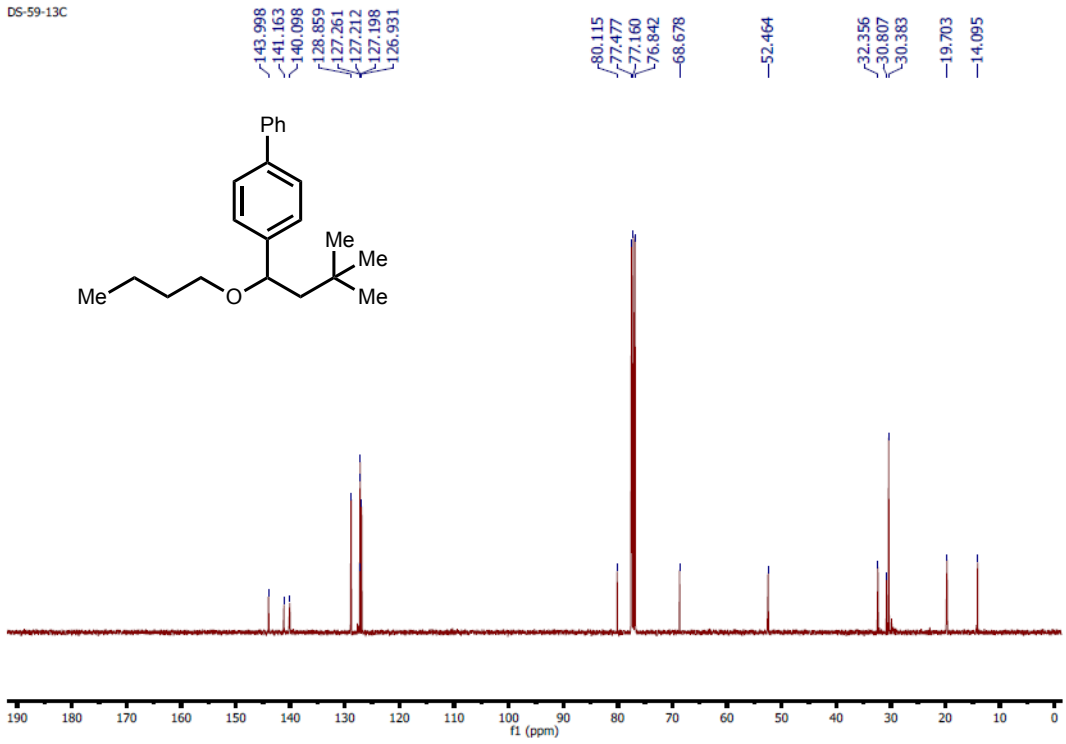
Compound 25. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



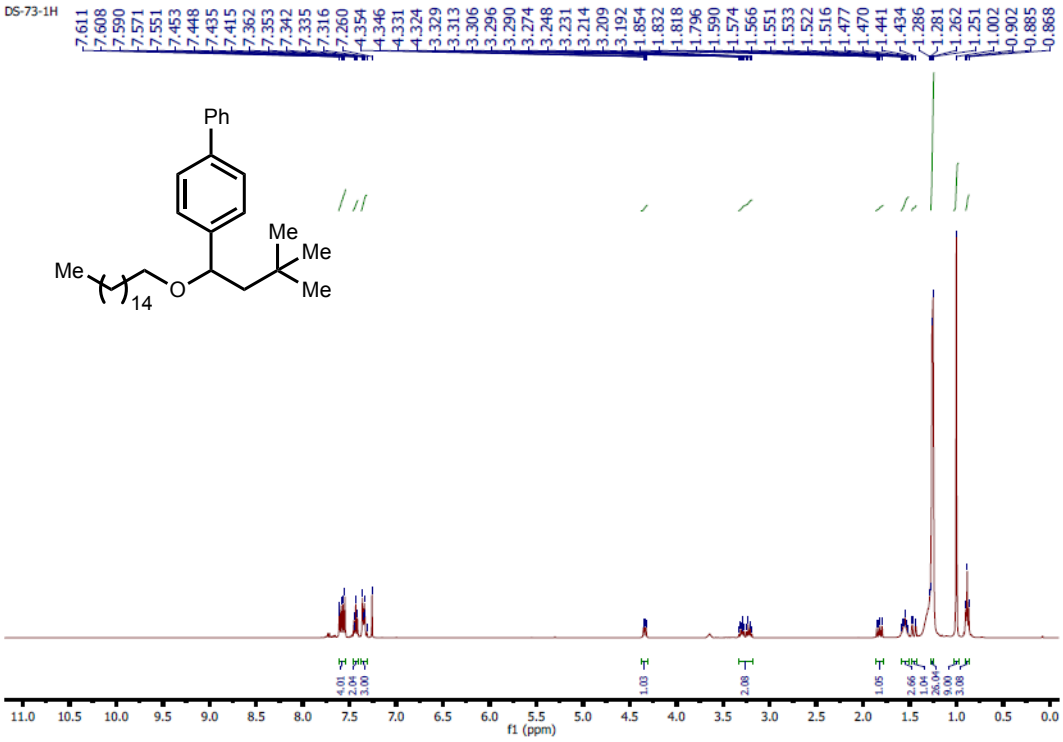


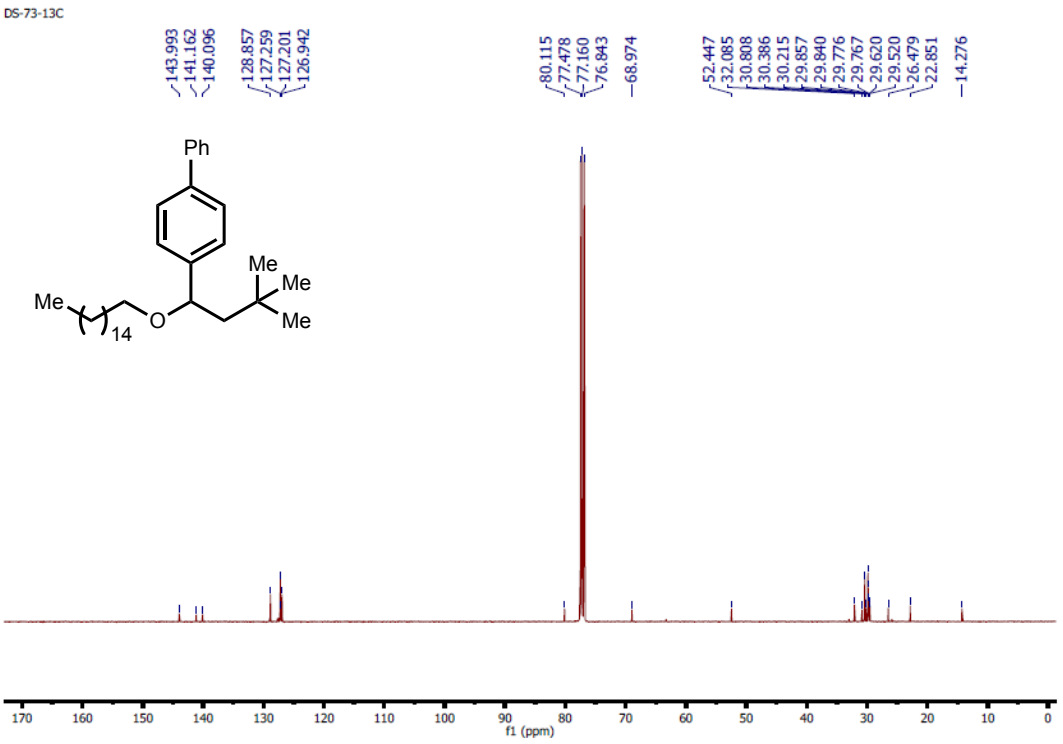
Compound 26. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



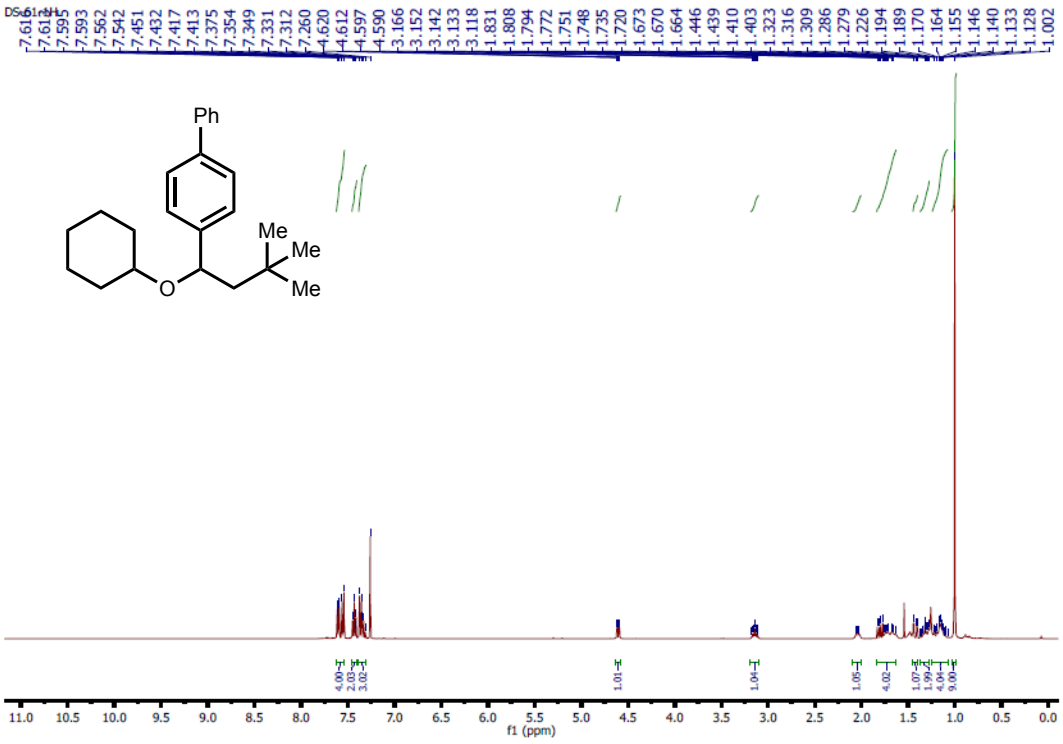


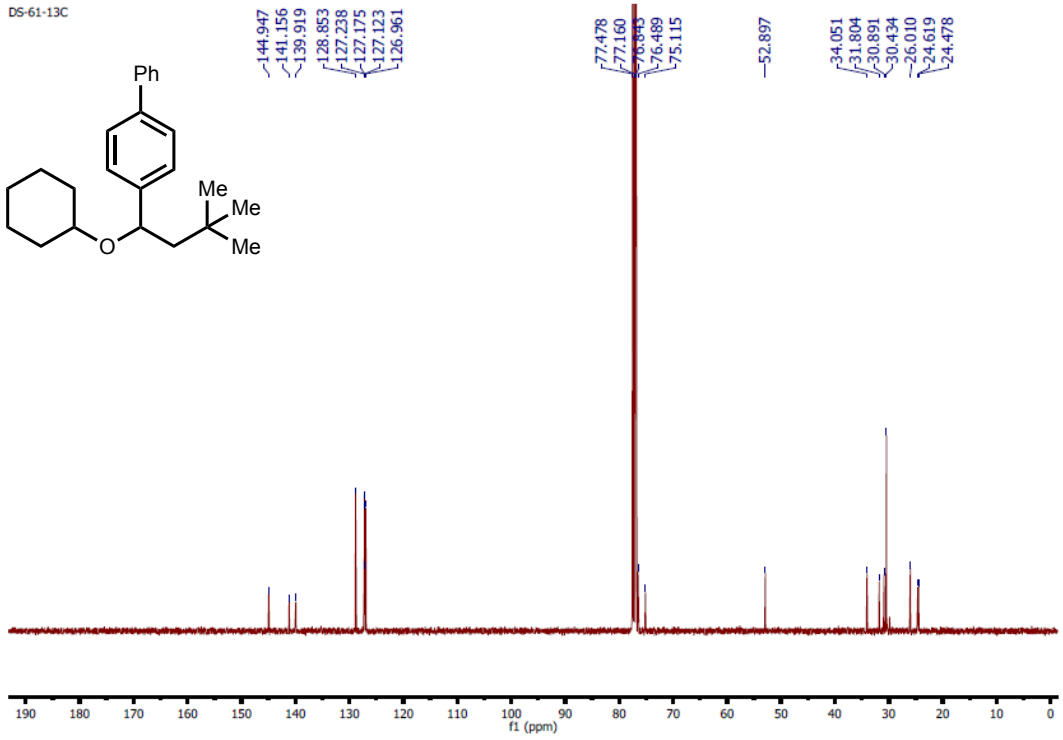
Compound 27. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



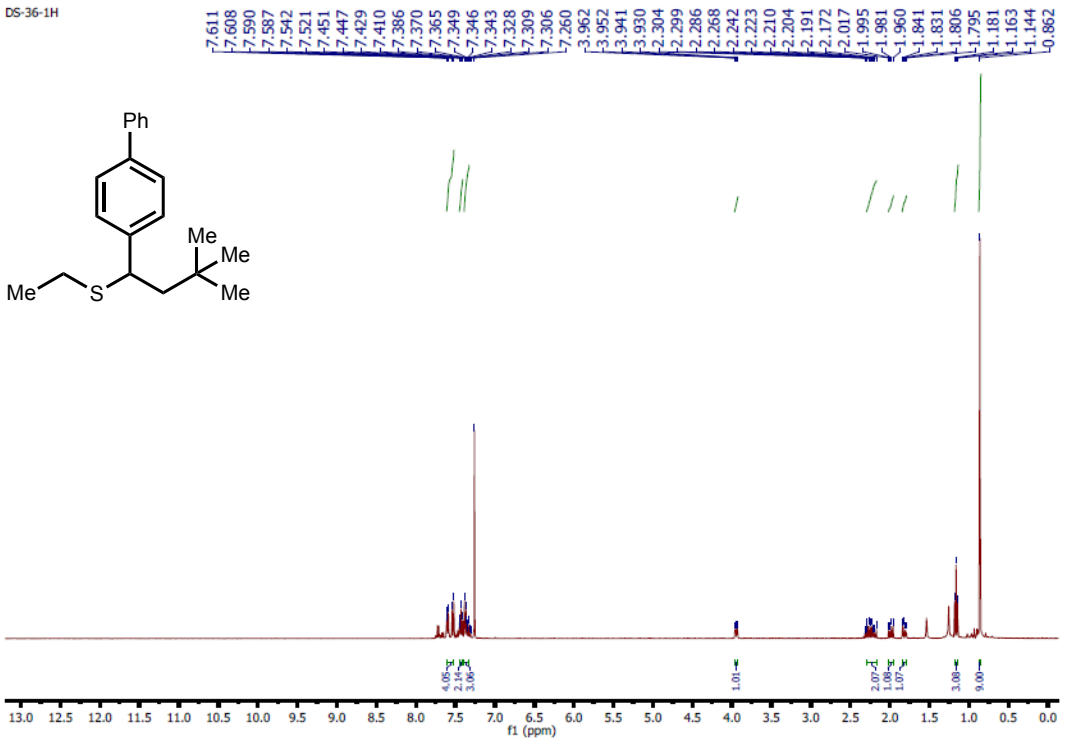


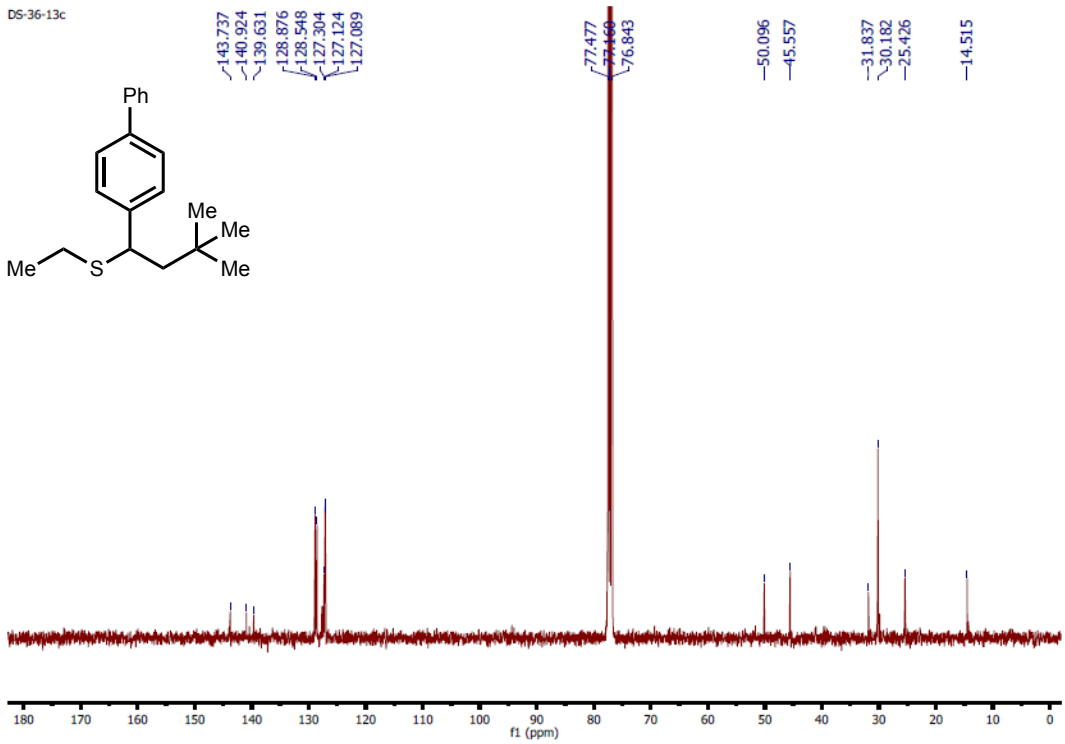
Compound 28. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



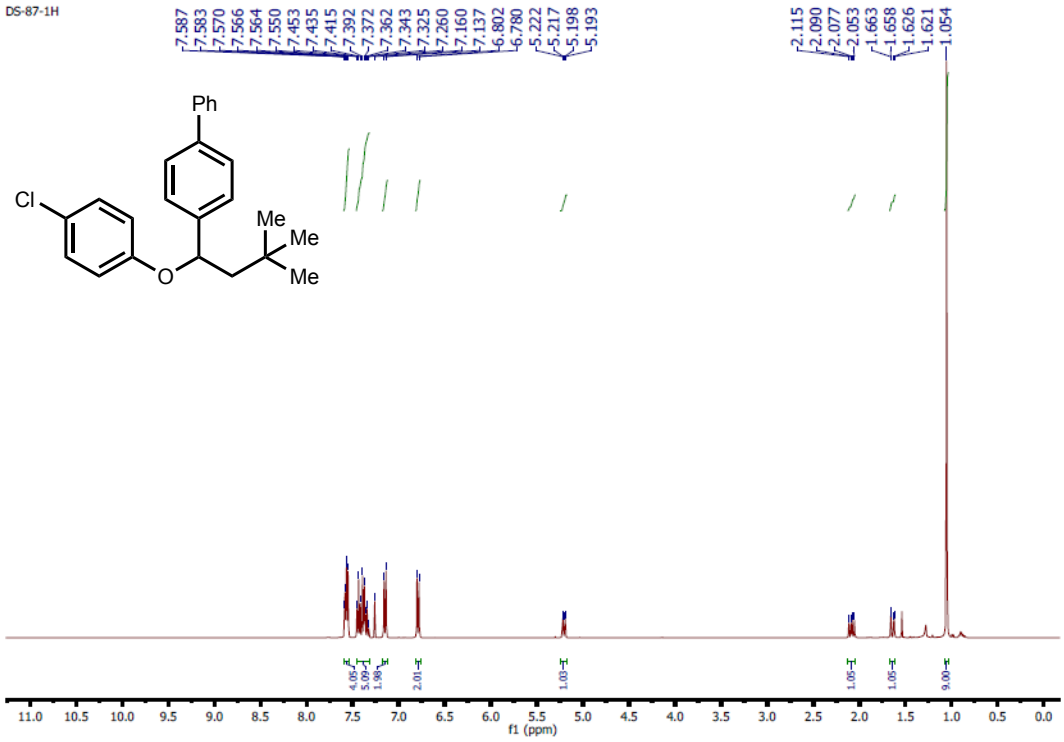


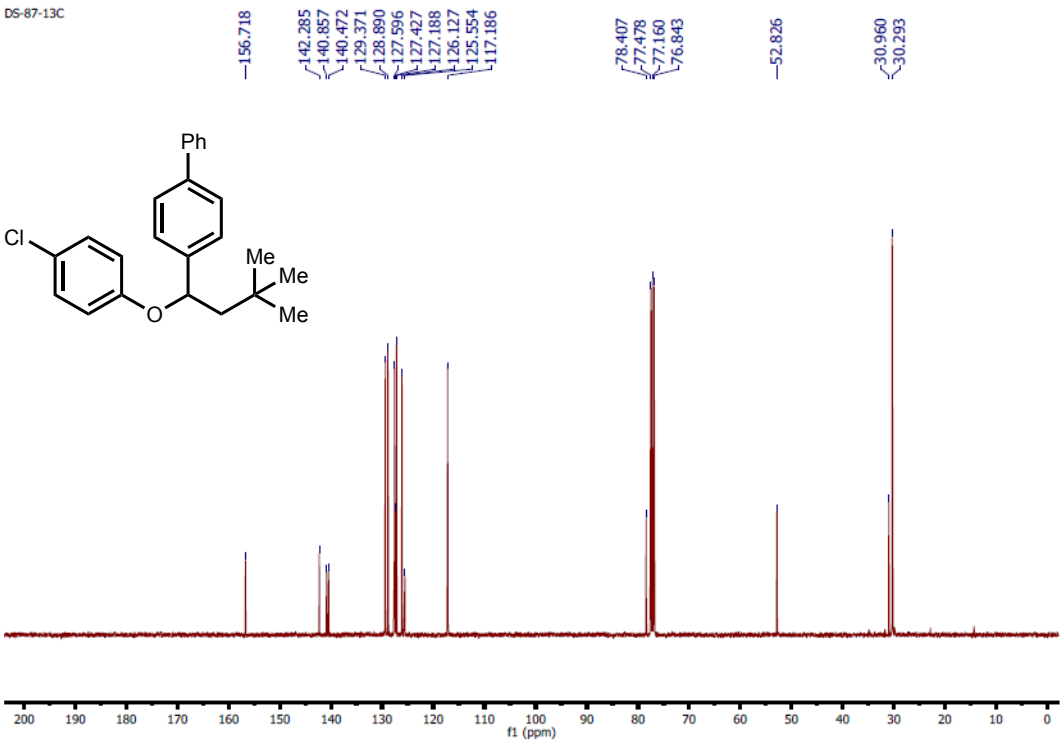
Compound 29. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



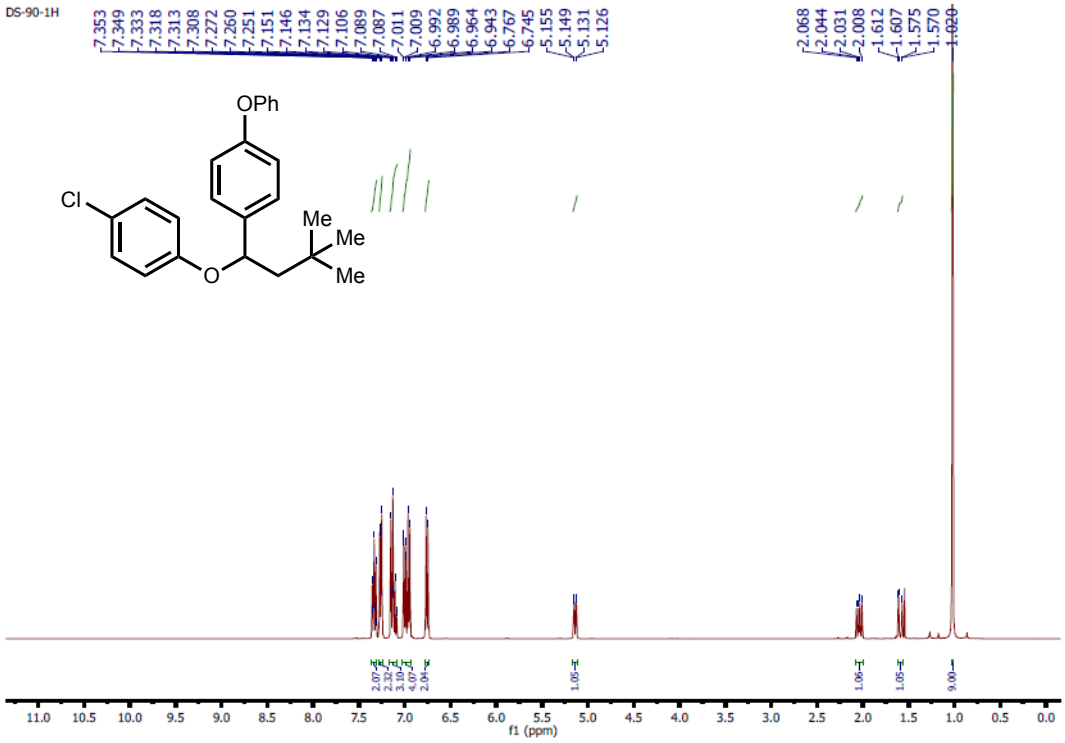


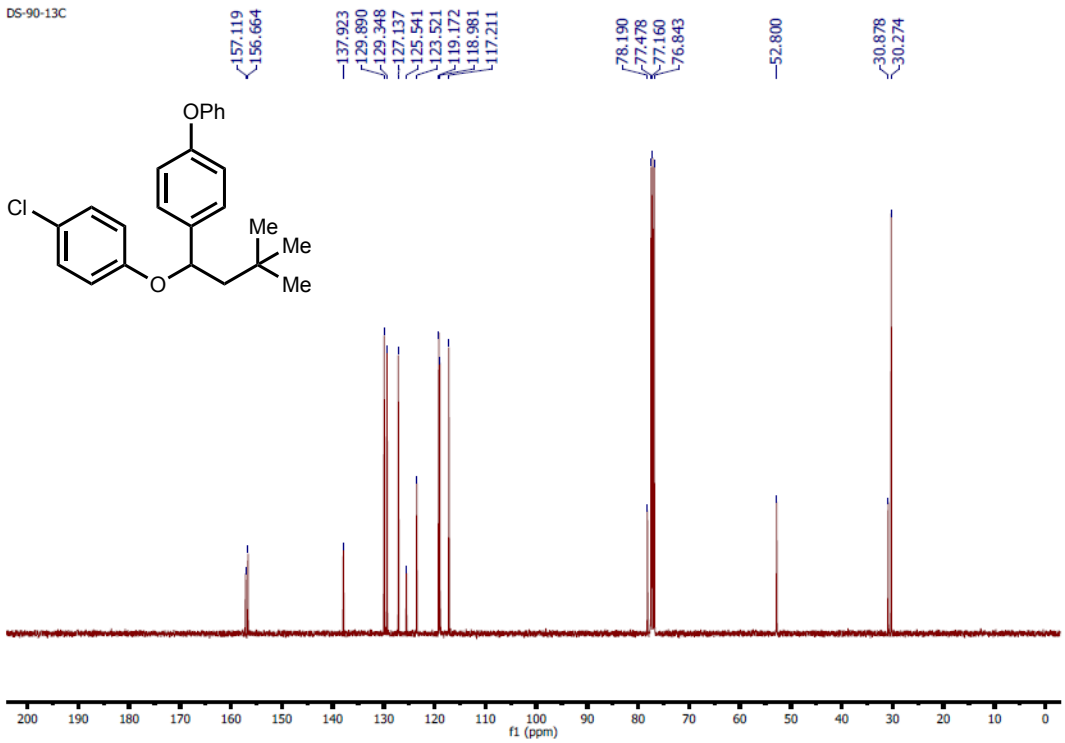
Compound 30. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



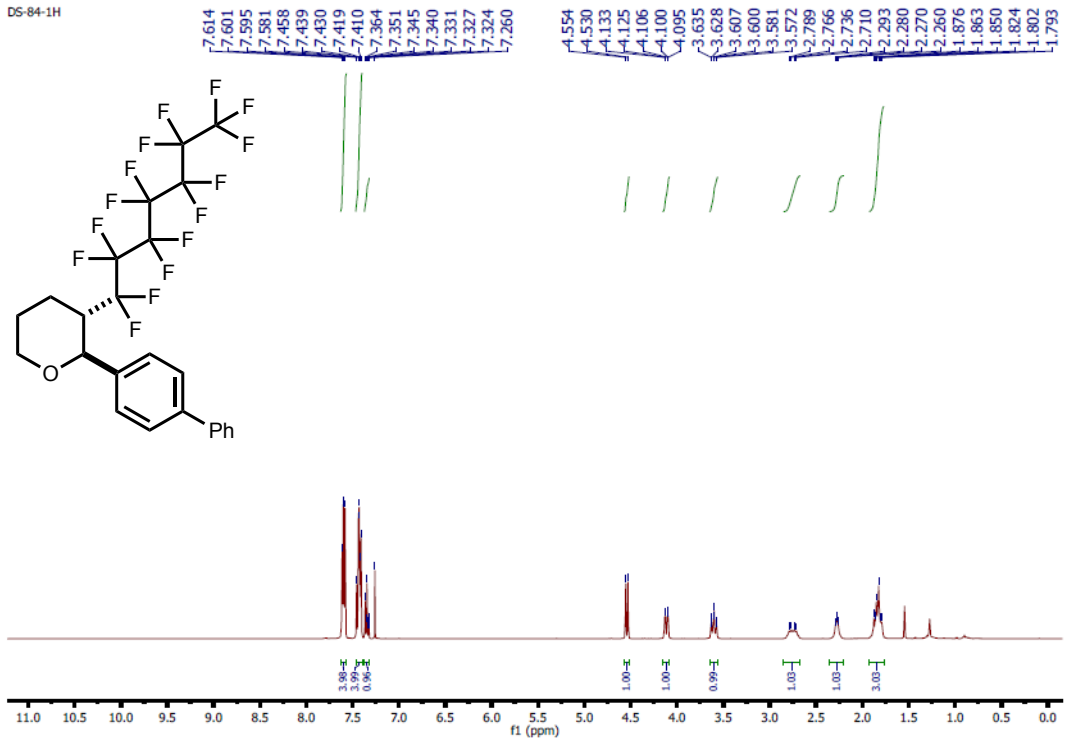


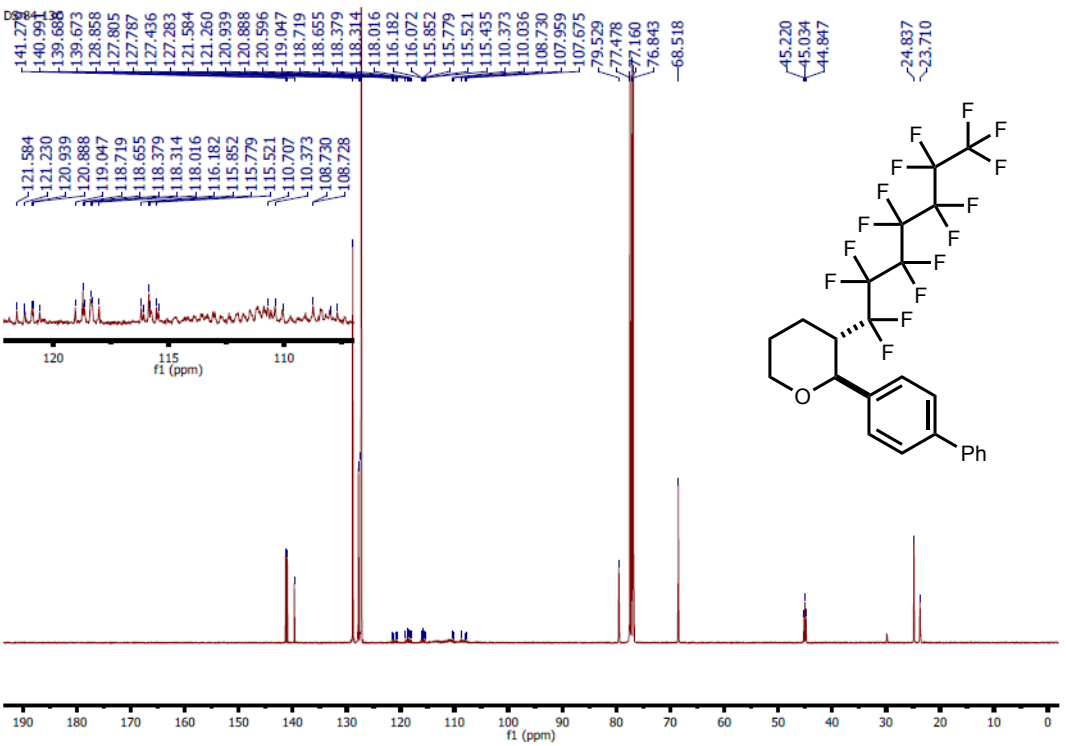
Compound 31. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)





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





Compound 32. Top: ^{19}F NMR ($CDCl_3$, 376 MHz). Bottom: NOESY ($CDCl_3$, 600 MHz)