

Gold(I)-Catalysed Dehydrative Formation of Ethers From Benzylic Alcohols and Phenols

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
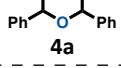
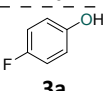
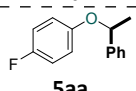
2. General experimental section

Reactions were monitored using gas chromatography (GC) on a Agilent instrument: 90 °C to 300 °C at 45°C /min, 1 µl injection volume, flow 6.5 µl/min, flame ionisation detector at 5 Hz, resolution of 0.04 min. Deuterated solvent (CDCl₃) was filtered through basic alumina in order to remove traces of HCl. Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 300 MHz, 400 MHz and 500 MHz spectrometers. Chemical shifts are expressed in δ values (ppm) referenced internally to residual solvent resonances (¹H, 7.26 ppm (CDCl₃); ¹³C, 77.16 ppm (CDCl₃)). Assignment was accomplished using 2D NMR techniques: ¹H-¹H COSY, ¹H-¹³C HSQC and ¹H-¹³C HMBC. Peaks are assigned as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or br (broad). Peaks of aromatic nuclei are assigned *i* (*ipso*), *o* (*ortho*), *m* (*meta*) or *p* (*para*), and benzyl or phenol (in subscript), referring to their origin in the starting alcohols. High resolution mass spectrometry (HRMS) was performed by the EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea University, Singleton Park, Swansea, SA2 8PP, UK.

3. Initial alcohol reactivity screening

The reactivity of various combinations of alcohols in the presence of $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{CH}_3\text{CN})][\text{BF}_4]$ (**1c**, 0.6 mol%, Figure 1) at 80 °C under neat conditions was evaluated (Table S1). In contrast to other reports using gold(I),¹ or gold(III)² catalysts, no ethers were formed from *n*-BuOH, *i*-PrOH or BnOH (or mixtures of those alcohols) using the gold(I) catalyst **1c** (Table S1, entry 1). The formation of symmetrical ethers from secondary benzylic alcohols is not only known to proceed in the presence of gold(I) complexes,³ but also as by-products in reactions with arenes,⁴ malonates,⁵ or styrene⁶ in the presence of other Lewis-acidic catalysts. Indeed, the formation of symmetrical ether **4a** from **2a** was observed under our test conditions (Table S1, entries 2-3). We were delighted to observe the formation of unsymmetrical ether **5aa** from the reaction of a secondary benzylic alcohol (**2a**) with a phenol (**3a**) (Table S1, entry 4).⁷ Finally, no reaction occurred in the reaction of only phenol **3a** (Table S1, entry 5).

Table S1 Evaluation of reactivity of combinations of alcohols.^a

Entry	R ¹ -OH	+	R ² -OH	$\xrightarrow[\text{neat, 80 } ^\circ\text{C}]{\text{1c (0.6 mol\%)}}$	R ¹ -O-R ²
1 ^b	R-OH		R-OH		n.r.
2 ^b	R-OH				
3	2a		2a		4a
4	2a				
5	3a		3a		n.r.

^a Reaction condition: R¹-OH (0.25 mmol), R¹-OH (0.25 mmol), neat, in air. ^b R = *n*-Bu, *i*-Pr, Bn. N.r. = no reaction.

4. Solvent screening

Compared to the reaction between 1-phenylethanol (**2a**) and 4-fluorophenol (**3a**) under neat conditions (Table 1, entry 4), the use of CH₃CN as the reaction solvent shifted the product distribution towards symmetrical ether **4a** (Table S2, entry 1). In contrast to the report by Hashmi and co-workers, the formation of amides was not observed under these conditions.^{3a} No reaction took place in dioxane (Table S2, entry 2). The reactions in DCE or toluene were much slower compared to the reaction under neat conditions, whilst the product distributions were only affected moderately (Table S2, entries 3-4), obtaining better conversion towards the desired product when toluene was used as solvent. This outcome suggested that toluene could be used to modulate the selectivity of the transformation.

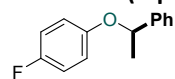
Table S2 Solvent screening.^a

Entry	Solvent	t (h)	Conversion (%) (4a / 5aa) ^b
1	CH ₃ CN	0.25	>95 (67/33)
2	dioxane	3	0
3	1,2-DCE	3	61 (45/55)
4	PhCH ₃	3	81 (31/69)

^a Reaction conditions: **2a** (0.25 mmol), **3a** (0.25 mmol), solvent (2.5 M), in air. ^b Determined by GC analysis, with respect to **2a**.

5. Characterisation data

1-fluoro-4-(1-phenylethoxy)benzene (5aa)



According to the general procedure, a crude product, which was prepared from 1-phenylethanol (**2a**) (30.5 mg, 0.25 mmol), 4-fluorophenol (**3a**) (140.1 mg, 1.25 mmol) and [Au(IPr^{Cl})(MeCN)][BF₄] (**1c**) (2.0 mg, 2.5 μmol, 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5aa** (44.2 mg, 82%) as a colourless liquid.

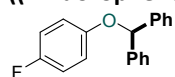
¹H-NMR (500 MHz, CDCl₃): 7.37-7.31 (m, 4H; Ph_{benzyl}H), 7.30-7.25 (m, 2H; Ph_{benzyl}H), 6.89-6.85 (m, 2H; *m*-Ph_{phenol}H), 6.81-6.77 (m, 2H; *o*-Ph_{phenol}H), 5.22 (q, ³J_{HH} = 6.5 Hz, 1H; CH), 1.62 (d, ³J_{HH} = 6.5 Hz, 1H; CH₃).

¹³C{¹H}-NMR (126 MHz, CDCl₃): 158.2 (1C; *i*-Ph_{phenol}C), 157.3 (d, ¹J_{CF} = 238.0 Hz, 1C; *p*-Ph_{phenol}C), 143.1 (1C; *i*-Ph_{benzyl}C), 128.8 (2C; Ph_{benzyl}C), 127.7 (1C; *p*-Ph_{benzyl}C), 125.7 (2C; Ph_{benzyl}C), 117.2 (d, ³J_{CF} = 8.0 Hz, 2C; *o*-Ph_{phenol}C), 115.8 (d, ²J_{CF} = 22.9 Hz, 2C; *m*-Ph_{phenol}C), 76.9 (1C; CH), 24.6 (1C; CH₃).

¹⁹F-NMR (282 MHz, CDCl₃): -124.8.

HRMS (APCI) calcd for C₁₄H₁₇ONF [(M+NH₄)⁺] 234.1289, found 234.1287.

((4-fluorophenoxy)methylene)dibenzene (5ab)



According to the general procedure, a crude product, which was prepared from benzhydrol (**2b**) (46.1 mg, 0.25 mmol), 4-fluorophenol (**3a**) (140.1 mg, 1.25 mmol) and [Au(IPr^{Cl})(MeCN)][BF₄] (**1c**) (2.0 mg, 2.5 μmol, 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5ab** (59.8 mg, %) as a pale yellow liquid.

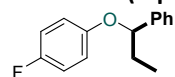
¹H-NMR (500 MHz, CDCl₃): 7.42-7.40 (m, 4H; Ph_{benzyl}H), 7.36-7.33 (m, 4H; Ph_{benzyl}H), 7.29-7.28 (m, 2H; *p*-Ph_{phenol}H), 6.92-6.88 (m, 2H; Ph_{phenol}H), 6.13 (s, 1H; CH).

¹³C{¹H}-NMR (126 MHz, CDCl₃): 157.5 (d, ¹J_{CF} = 238.7 Hz, 1C; *p*-Ph_{phenol}C), 154.3 (1C; *i*-Ph_{phenol}C), 141.2 (2C; *i*-Ph_{benzyl}C), 128.8 (4C; *m*-Ph_{benzyl}C), 128.0 (2C; *p*-Ph_{benzyl}C), 127.0 (4C; *o*-Ph_{benzyl}C), 117.4 (d, ³J_{CF} = 7.9 Hz, 2C; *o*-Ph_{phenol}C), 115.9 (d, ⁴J_{CF} = 23.0 Hz, 2C; *m*-Ph_{phenol}C), 82.7 (1C; CH).

¹⁹F-NMR (470 MHz, CDCl₃): -123.4.

HRMS (ASAP) calcd for C₁₉H₁₅FO [(M)⁺] 278.1101, found 278.1101.

1-fluoro-4-(1-phenylpropoxy)benzene (5ac)



According to the general procedure, a crude product, which was prepared from 1-phenyl-1-propanol (**2c**) (34.0 mg, 0.25 mmol), 4-fluorophenol (**3a**) (140.1 mg, 1.25 mmol) and [Au(IPr^{Cl})(MeCN)][BF₄] (**1c**) (2.0 mg, 2.5 μmol, 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5ac** (94.4 mg, 71%) as a colourless liquid.

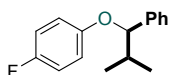
¹H-NMR (500 MHz, CDCl₃): 7.35-7.31 (m, 4H; Ph_{benzyl}H), 7.27-7.23 (m, 4H; *p*-Ph_{benzyl}H), 6.88-6.84 (m, 2H; *m*-Ph_{phenol}H), 6.79-6.76 (m, 2H; *m*-Ph_{phenol}H), 4.93 (t, ³J_{HH} = 6.4 Hz, 1H; CH), 2.04-1.96 (m, 1H; CH), 1.91-1.82 (m, 1H; CH), 1.00 (t, ³J_{HH} = 7.4 Hz, 3H; CH₃).

¹³C{¹H}-NMR (126 MHz, CDCl₃): 157.22 (d, ¹J_{CF} = 238.0 Hz, 1C; *p*-Ph_{phenol}C), 154.6 (1C; *i*-Ph_{phenol}C), 141.8 (1C; *i*-Ph_{benzyl}C), 128.6 (2C; *m*-Ph_{benzyl}C), 127.7 (1C; *p*-Ph_{benzyl}C), 126.2 (2C; *o*-Ph_{benzyl}C), 117.1 (d, ³J_{CF} = 7.8 Hz, 2C; *o*-Ph_{phenol}C), 115.7 (d, ²J_{CF} = 22.9 Hz, 2C; *m*-Ph_{phenol}C), 82.5 (1C; CH), 31.7 (2C; CH₂), 10.3 (1C; CH₃).

¹⁹F-NMR (470 MHz, CDCl₃): -124.1.

HRMS (EI) calcd for C₁₅H₁₅FO [(M)⁺] 230.1107, found 230.1105.

1-fluoro-4-(2-methyl-1-phenylpropoxy)benzene (5ad)



According to the general procedure, a crude product, which was prepared from 2-methyl-1-phenyl-1-propanol (**2d**) (37.6 mg, 0.25 mmol), 4-fluorophenol (**3a**) (140.1 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5ad** (48.0 mg, 79%) as a colourless liquid.

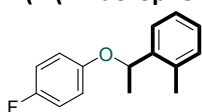
$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.32-7.29 (m, 4H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.26-7.23 (m, 4H; $p\text{-Ph}_{\text{benzyl}}\text{H}$), 6.86-6.82 (m, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.76-6.74 (m, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 4.70 (d, $^3J_{\text{HH}} = 6.3$ Hz, 1H; CH), 2.15-2.08 (m, 1H; CH), 1.05 (d, $^3J_{\text{HH}} = 6.6$ Hz, 3H; CH_3), 0.90 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 157.2 (d, $^1J_{\text{CF}} = 238.2$ Hz, 1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 154.9 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 140.5 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 128.4 (2C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 127.6 (1C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 127.0 (2C; $m\text{-Ph}_{\text{benzyl}}\text{C}$), 117.1 (d, $^3J_{\text{CF}} = 7.9$ Hz, 2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 115.7 (d, $^2J_{\text{CF}} = 23.0$ Hz, 2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 86.3 (1C; CH), 35.4 (1C; CH), 19.1 (1C; CH_3), 18.4 (1C; CH_3).

$^{19}\text{F-NMR}$ (470 MHz, CDCl_3): -124.3.

HRMS (EI) calcd for $\text{C}_{16}\text{H}_{17}\text{FO}$ [(M)+] 244.1263, found 244.1266.

1-(1-(4-fluorophenoxy)ethyl)-2-methylbenzene (5ae)



According to the general procedure, a crude product, which was prepared from 1-(2-methylphenyl)ethanol (**2e**) (34.0 mg, 0.25 mmol), 4-fluorophenol (**3a**) (140.1 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 80 °C for 1 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5ae** (50.8 mg, 88%) as a colourless liquid.

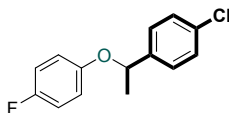
$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.41-7.40 (m, 1H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.19-7.15 (m, 4H; $\text{Ph}_{\text{benzyl}}\text{H}$), 6.88-6.84 (m, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.72-6.69 (m, 2H; $o\text{-Ph}_{\text{phenol}}\text{H}$), 5.39 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH), 2.40 (s, 3H; CH_3), 1.59 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 157.19 (d, $^1J_{\text{CF}} = 238.0$ Hz, 1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 154.1 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 141.0 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 133.9 (1C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 130.7 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 127.4 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 126.9 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 125.2 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 116.74 (d, $^3J_{\text{CF}} = 8.0$ Hz, 2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 115.8 (d, $^2J_{\text{CF}} = 23.1$ Hz, 2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 73.7 (1C; CH), 22.9 (1C; CH_3), 19.1 (1C; CH_3).

$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): -124.7.

HRMS (APCI) calcd for $\text{C}_{15}\text{H}_{19}\text{ONF}$ [(M+ NH_4) $^+$] 248.1445, found 248.1443.

1-chloro-4-(1-(4-fluorophenoxy)ethyl)benzene (5ah)



According to the general procedure, a crude product, which was prepared from 1-(4-chlorophenyl)ethanol (**2h**) (39.2 mg, 0.25 mmol), 4-fluorophenol (**3a**) (140.1 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5ah** (36.2 mg, 58%) as a pale yellow liquid.

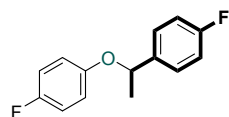
$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.34-7.27 (m, 4H; $\text{Ph}_{\text{benzyl}}\text{H}$), 6.91-6.86 (m, 2H; $\text{Ph}_{\text{phenol}}\text{H}$), 6.78-6.75 (m, 2H; $\text{Ph}_{\text{phenol}}\text{H}$), 5.19 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH), 1.60 (d, $^3J_{\text{HH}} = 6.5$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 157.4 (d, $^1J_{\text{CF}} = 238.8$ Hz, 1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 153.9 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 141.6 (1C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 133.4 (1C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 129.0 (2C; $m\text{-Ph}_{\text{benzyl}}\text{C}$), 127.1 (2C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 117.2 (d, $^3J_{\text{CF}} = 8.0$ Hz, 2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 115.9 (d, $^2J_{\text{CF}} = 22.9$ Hz, 2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 76.3 (1C; CH), 24.5 (1C; CH_3).

$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): -123.5.

HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{ClFO}$ [(M) $^+$] 250.0561, found 250.0551.

1-fluoro-4-(1-(4-fluorophenoxy)ethyl)benzene (**5ai**)



According to the general procedure, a crude product, which was prepared from 1-(4-fluorophenyl)ethanol (**2i**) (35.0 mg, 0.25 mmol), 4-fluorophenol (**3a**) (140.1 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5ai** (45.9 mg, 78%) as a pale yellow liquid.

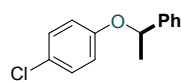
$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.33-7.30 (m, 2H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.04-7.00 (m, 2H; $\text{Ph}_{\text{benzyl}}\text{H}$), 6.90-6.85 (m, 2H; $\text{Ph}_{\text{phenol}}\text{H}$), 6.79-6.75 (m, 2H; $\text{Ph}_{\text{phenol}}\text{H}$), 5.20 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH), 1.60 (d, $^3J_{\text{HH}} = 6.5$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 162.24 (d, $^1J_{\text{CF}} = 245.9$ Hz, 1C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 157.4 (d, $^1J_{\text{CF}} = 238.4$ Hz, 1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 154.0 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 138.8 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 127.4 (d, $^3J_{\text{CF}} = 8.1$ Hz, 2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 117.3 (d, $^3J_{\text{CF}} = 8.0$ Hz, 2C; $m\text{-Ph}_{\text{benzyl}}\text{C}$), 115.9 (d, $^2J_{\text{CF}} = 23.1$ Hz, 2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 115.7 (d, $^2J_{\text{CF}} = 21.4$ Hz, 2C; $m\text{-Ph}_{\text{benzyl}}\text{C}$), 76.3 (1C; CH), 24.6 (1C; CH_3).

$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): -114.9, -123.6.

HRMS (EI) calcd for $\text{C}_{16}\text{H}_{17}\text{FO}$ [(M) $^+$] 234.0856, found 234.0852.

1-chloro-4-(1-phenylethoxy)benzene (**5ba**)



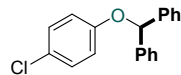
According to the general procedure, a crude product, which was prepared from 1-phenylethanol (**2a**) (30.5 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) in 50 μL toluene at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5ba** (33.7 mg, 58%) as a pale yellow solid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.34-7.33 (m, 4H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.29-7.27 (m, 1H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.13 (dt, $^3J_{\text{HH}} = 9.9$ Hz, $^5J_{\text{HH}} = 2.9$ Hz, 2H; $\text{Ph}_{\text{phenol}}\text{H}$), 6.77 (dt, $^3J_{\text{HH}} = 9.9$ Hz, $^5J_{\text{HH}} = 2.9$ Hz, 2H; $\text{Ph}_{\text{phenol}}\text{H}$), 5.25 (q, $^3J_{\text{HH}} = 6.5$ Hz, 1H; CH), 1.63 (d, $^3J_{\text{HH}} = 6.5$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 156.7 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 142.9 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 129.3 (2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 128.8 (2C; $\text{Ph}_{\text{benzyl}}\text{C}$), 127.7 (1C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 125.6 (3C; $\text{Ph}_{\text{benzyl}}\text{C} + p\text{-Ph}_{\text{phenol}}\text{C}$), 117.3 (2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 76.5 (1C; CH), 24.6 (1C; CH_3).

HRMS (EI) calcd for $\text{C}_{14}\text{H}_{13}\text{ClO}$ [(M) $^+$] 232.0655, found 232.0648.

((4-chlorophenoxy)methylene)dibenzene (**5bb**)



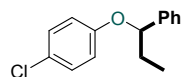
According to the general procedure, a crude product, which was prepared from benzhydrol (**2b**) (46.1 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) in 100 μL at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5bb** (59.0 mg, 80%) as a pale yellow solid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.41-7.40 (m, 4H; $o\text{-Ph}_{\text{benzyl}}\text{H}$), 7.36-7.32 (m, 4H; $m\text{-Ph}_{\text{benzyl}}\text{H}$), 7.30-7.25 (m, 2H; $p\text{-Ph}_{\text{benzyl}}\text{H}$), 7.16 (dd, $^3J_{\text{HH}} = 9.8$ Hz, $^5J_{\text{HH}} = 2.8$ Hz, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.87 (dd, $^3J_{\text{HH}} = 9.8$ Hz, $^5J_{\text{HH}} = 2.8$ Hz, 2H; $o\text{-Ph}_{\text{phenol}}\text{H}$), 6.16 (s, 1H; CH).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 156.8 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 140.9 (2C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 129.4 (2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 128.8 (4C; $m\text{-Ph}_{\text{benzyl}}\text{C}$), 128.0 (2C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 127.0 (4C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 126.0 (1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 117.6 (2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 82.2 (1C; CH).

HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{ClO}$ [(M) $^+$] 294.0811, found 294.0805.

1-chloro-4-(1-phenylpropoxy)benzene (**5bc**)



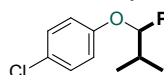
According to the general procedure, a crude product, which was prepared from 1-phenyl-1-propanol (**2c**) (34.0 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5bc** (36.4 mg, 59%) as a colourless liquid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.35-7.30 (m, 4H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.27-7.24 (m, 1H; $p\text{-Ph}_{\text{benzyl}}\text{H}$), 7.13-7.10 (m, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.78-6.75 (m, 2H; $o\text{-Ph}_{\text{phenol}}\text{H}$), 4.98-4.95 (m, 1H; CH), 2.05-1.96 (m, 1H; CH_2), 1.91-1.83 (m, 1H; CH_2), 1.00 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 157.1 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 141.6 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 129.3 (2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 128.7 (2C; $\text{Ph}_{\text{benzyl}}\text{C}$), 127.7 (2C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 126.2 (2C; $\text{Ph}_{\text{benzyl}}\text{C}$), 125.5 (1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 117.3 (2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 82.0 (1C; CH), 31.7 (1C; CH_2), 10.3 (1C; CH_3).

HRMS (EI) calcd for $\text{C}_{15}\text{H}_{15}\text{ClO}$ [(M) $^+$] 246.0811, found 246.0799.

1-chloro-4-(2-methyl-1-phenylpropoxy)benzene (5bd)



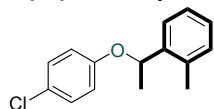
According to the general procedure, a crude product, which was prepared from 2-methyl-1-phenyl-1-propanol (**2d**) (37.6 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5bd** (58.4 mg, 93%) as a colourless liquid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.33-7.23 (m, 5H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.10 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^4J_{\text{HH}} = 2.8$ Hz, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.75 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^4J_{\text{HH}} = 2.8$ Hz, 2H; $o\text{-Ph}_{\text{phenol}}\text{H}$), 4.74 (d, $^1J_{\text{HH}} = 6.3$ Hz, 1H; CH), 2.15-2.09 (m, 1H; CH), 1.05 (d, $^3J_{\text{HH}} = 6.7$ Hz, 3H; CH_3), 0.90 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 157.3 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 140.2 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 129.2 (2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 128.4 (2C; $\text{Ph}_{\text{benzyl}}\text{C}$), 127.7 (1C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 126.9 (2C; $\text{Ph}_{\text{benzyl}}\text{C}$), 125.4 (1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 117.3 (2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 85.8 (1C; CH), 35.3 (1C; CH), 19.1 (1C; CH_3), 18.3 (1C; CH_3).

HRMS (EI) calcd for $\text{C}_{16}\text{H}_{17}\text{ClO}$ [(M) $^+$] 260.0968, found 260.0965.

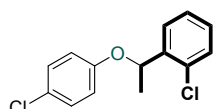
1-(1-(4-chlorophenoxy)ethyl)-2-methylbenzene (5be)



According to the general procedure, a crude product, which was prepared from 1-(2-methylphenyl)ethanol (**2e**) (34.0 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5be** (55.1 mg, 89%) as a colourless liquid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.39-7.37 (m, 1H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.18-7.16 (m, 3H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.15-7.12 (m, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.72-6.69 (m, 2H; $o\text{-Ph}_{\text{phenol}}\text{H}$), 5.41 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH), 2.41 (s, 3H; CH_3), 1.61 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 156.6 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 140.8 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 133.9 (1C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 130.7 (2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 129.3 (2C; $\text{Ph}_{\text{benzyl}}\text{C}$), 127.5 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 126.8 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 125.5 (1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 125.1 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 117.0 (2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 73.4 (1C; CH), 22.9 (1C; CH_3), 19.1 (1C; CH_3).



HRMS (EI) calcd for $\text{C}_{15}\text{H}_{15}\text{ClO}$ [(M) $^+$] 246.0811, found 246.0806.

1-chloro-4-(1-(4-chlorophenoxy)ethyl)benzene (5bf)

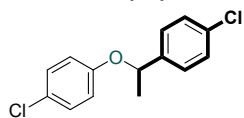
According to the general procedure, a crude product, which was prepared from 1-(2-chlorophenyl)ethanol (**2f**) (39.2 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 80 °C for 1 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5bf** (42.9 mg, 64%) as a yellow liquid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.43 (dd, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 2.1$ Hz, 1H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.36 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, 1H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.23-7.17 (m, 2H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.14 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^2J_{\text{HH}} = 2.8$ Hz, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.72 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^2J_{\text{HH}} = 2.8$ Hz, 2H; $o\text{-Ph}_{\text{phenol}}\text{H}$), 5.64 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH), 1.62 (d, $^3J_{\text{HH}} = 6.3$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 156.4 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 141.4 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 133.4 (1C; $p\text{-Ph}_{\text{benzyl}}\text{C}$), 129.4 (2C; $m\text{-Ph}_{\text{phenol}}\text{C}$), 129.0 (2C; $m\text{-Ph}_{\text{benzyl}}\text{C}$), 127.1 (2C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 117.3 (2C; $o\text{-Ph}_{\text{phenol}}\text{C}$), 75.9 (1C; CH), 24.5 (1C; CH_3).

HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{O}$ [(M) $^+$] 266.0265, found 266.0267.

1-chloro-2-(1-(4-chlorophenoxy)ethyl)benzene (5bh)

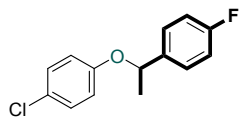


According to the general procedure, a crude product, which was prepared from 1-(4-chlorophenyl)ethanol (**2h**) (39.2 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) at 50 °C for 15 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5bh** (48.9 mg, 73%) as a colourless liquid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.32-7.26 (m, 4H; $\text{Ph}_{\text{benzyl}}\text{H}$), 7.14 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^4J_{\text{HH}} = 2.8$ Hz, 2H; $m\text{-Ph}_{\text{phenol}}\text{H}$), 6.75 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^4J_{\text{HH}} = 2.8$ Hz, 2H; $o\text{-Ph}_{\text{phenol}}\text{H}$), 5.23 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH), 1.60 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (126 MHz, CDCl_3): 156.2 (1C; $i\text{-Ph}_{\text{phenol}}\text{C}$), 140.2 (1C; $i\text{-Ph}_{\text{benzyl}}\text{C}$), 131.7 (1C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 129.6 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 129.4 (2C; $m\text{-Ph}_{\text{benzyl}}\text{C}$), 128.9 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 127.7 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 126.8 (1C; $\text{Ph}_{\text{benzyl}}\text{C}$), 125.7 (1C; $p\text{-Ph}_{\text{phenol}}\text{C}$), 116.9 (2C; $o\text{-Ph}_{\text{benzyl}}\text{C}$), 72.7 (1C; CH), 22.7 (1C; CH_3). HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{O}$ [(M) $^+$] 266.0265, found 266.0273.

1-chloro-4-(1-(4-fluorophenyl)ethoxy)benzene (**5bi**)



According to the general procedure, a crude product, which was prepared from 1-(4-fluorophenyl)ethanol (**2i**) (35.0 mg, 0.25 mmol), 4-chlorophenol (**3b**) (160.7 mg, 1.25 mmol) and $[\text{Au}(\text{IPr}^{\text{Cl}})(\text{MeCN})][\text{BF}_4]$ (**1c**) (2.0 mg, 2.5 μmol , 1.0 mol%) in 50 μL toluene at 80 $^\circ\text{C}$ for 1 h, was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 9/1) to give **5bi** (51.5 mg, 82%) as a colourless liquid.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.32-7.29 (m, 2H; *m*- $\text{Ph}_{\text{benzyl}}\text{H}$), 7.14 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^4J_{\text{HH}} = 2.8$ Hz, 2H; *m*- $\text{Ph}_{\text{phenol}}\text{H}$), 7.04-6.70 (m, 2H; *o*- $\text{Ph}_{\text{benzyl}}\text{H}$), 6.76 (dt, $^3J_{\text{HH}} = 9.8$ Hz, $^4J_{\text{HH}} = 2.8$ Hz, 2H; *o*- $\text{Ph}_{\text{phenol}}\text{H}$), 5.24 (q, $^3J_{\text{HH}} = 6.4$ Hz, 1H; CH), 1.61 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H; CH_3).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz, CDCl_3): 157.5 (d, $^1J_{\text{CF}} = 237.9$ Hz, *p*- $\text{Ph}_{\text{benzyl}}\text{C}$), 156.4 (1C; *i*- $\text{Ph}_{\text{phenol}}\text{C}$), 138.6 (1C; *i*- $\text{Ph}_{\text{benzyl}}\text{C}$), 129.4 (2C; *m*- $\text{Ph}_{\text{phenol}}\text{C}$), 127.3 (d, $^3J_{\text{CF}} = 8.1$ Hz, *o*- $\text{Ph}_{\text{benzyl}}\text{C}$), 117.4 (2C; *o*- $\text{Ph}_{\text{phenol}}\text{C}$), 115.74 (d, $^2J_{\text{HH}} = 21.5$ Hz, 2C; *m*- $\text{Ph}_{\text{benzyl}}\text{C}$), 75.9 (1C; CH), 24.6 (1C; CH_3).

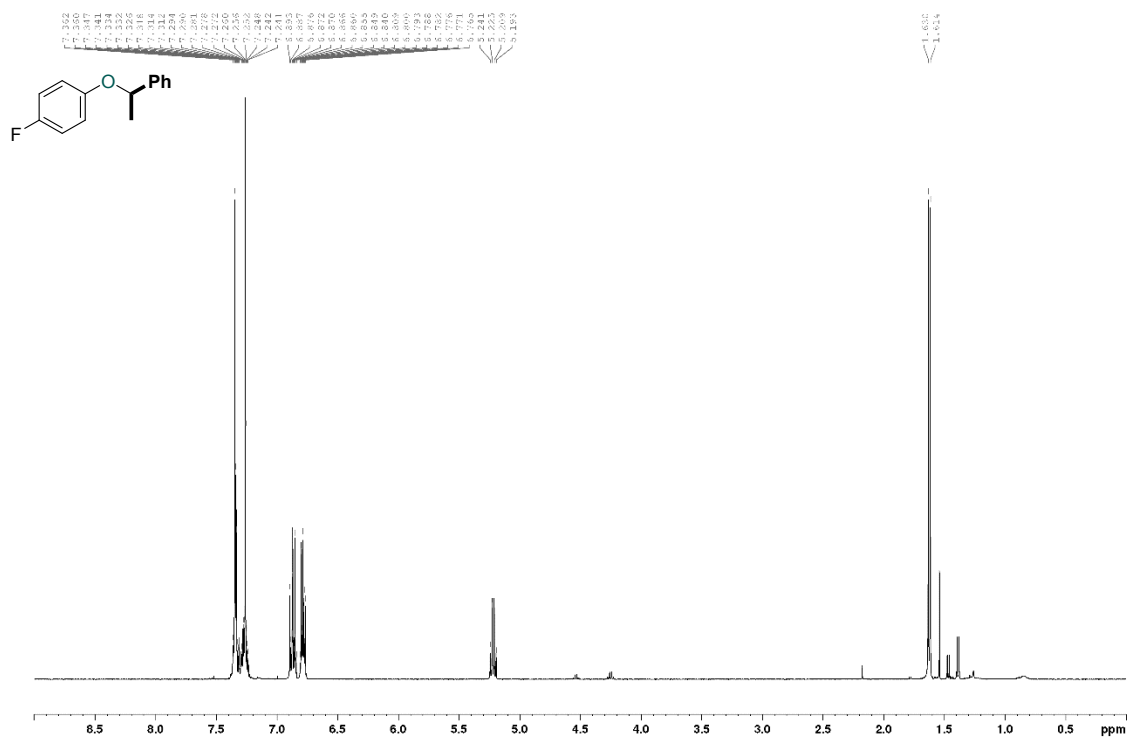
$^{19}\text{F-NMR}$ (470 MHz, CDCl_3): -114.8.

HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{ClFO}$ [(M) $^+$] 250.0561, found 250.0557.

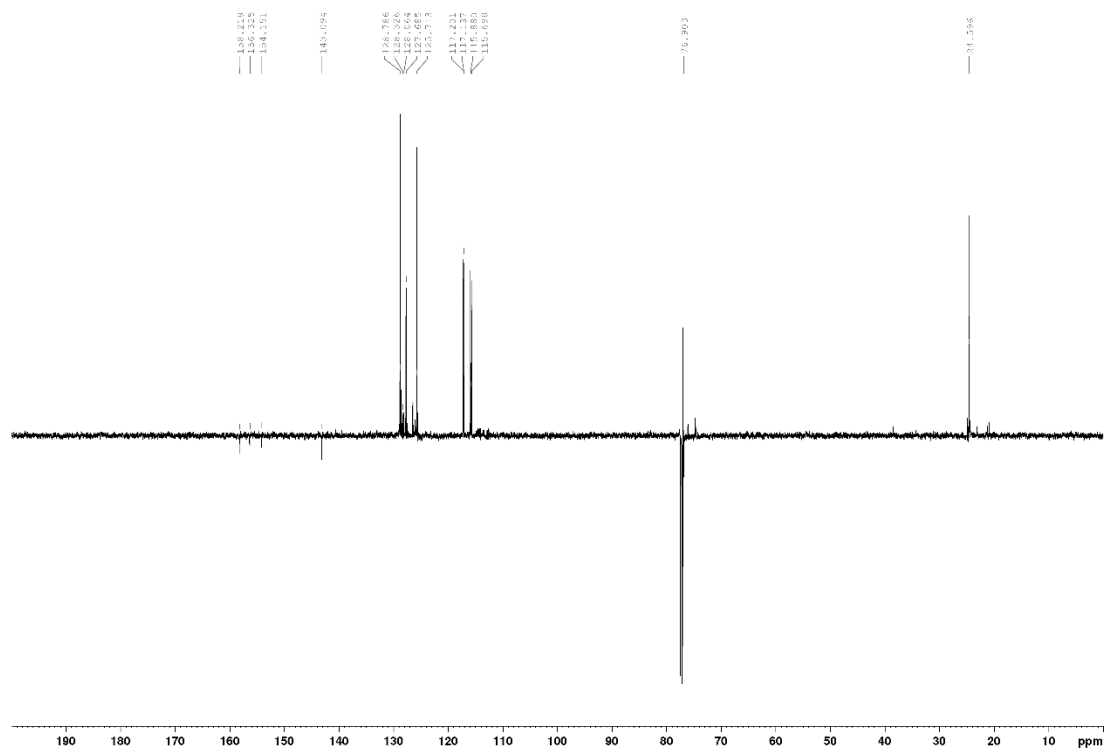
6. NMR Spectra

1-fluoro-4-(1-phenylethoxy)benzene (5aa)

^1H

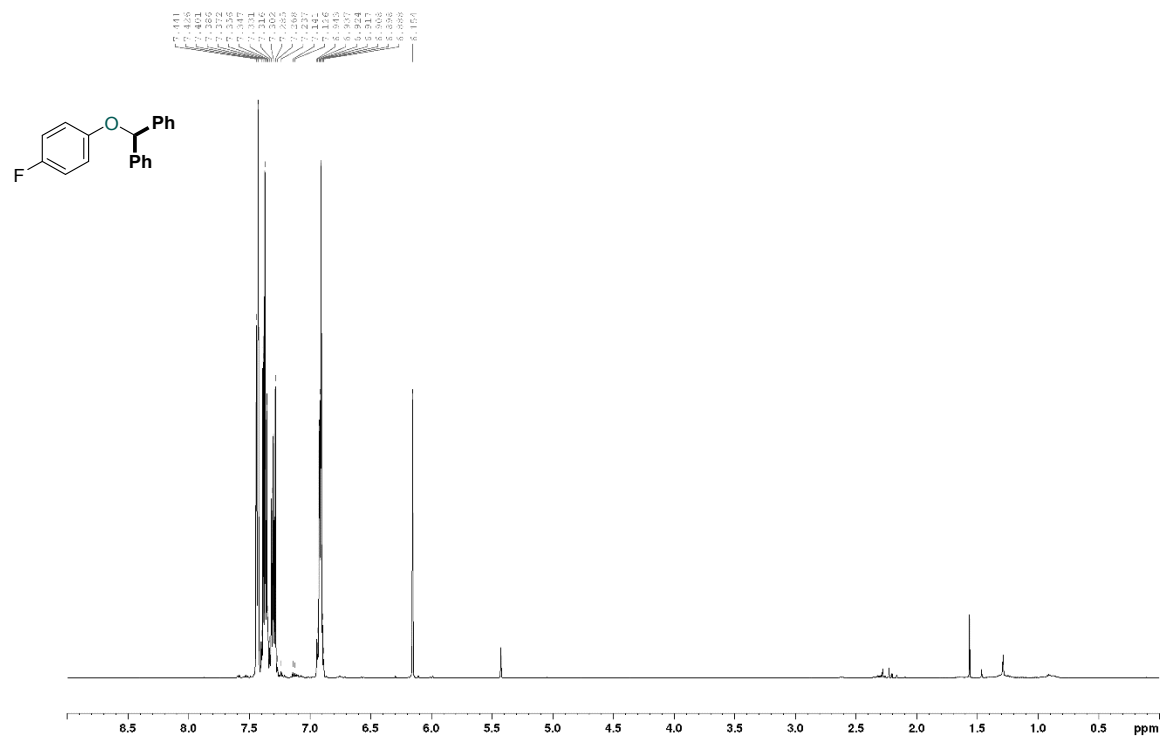


$^{13}\text{C}\{^1\text{H}\}$

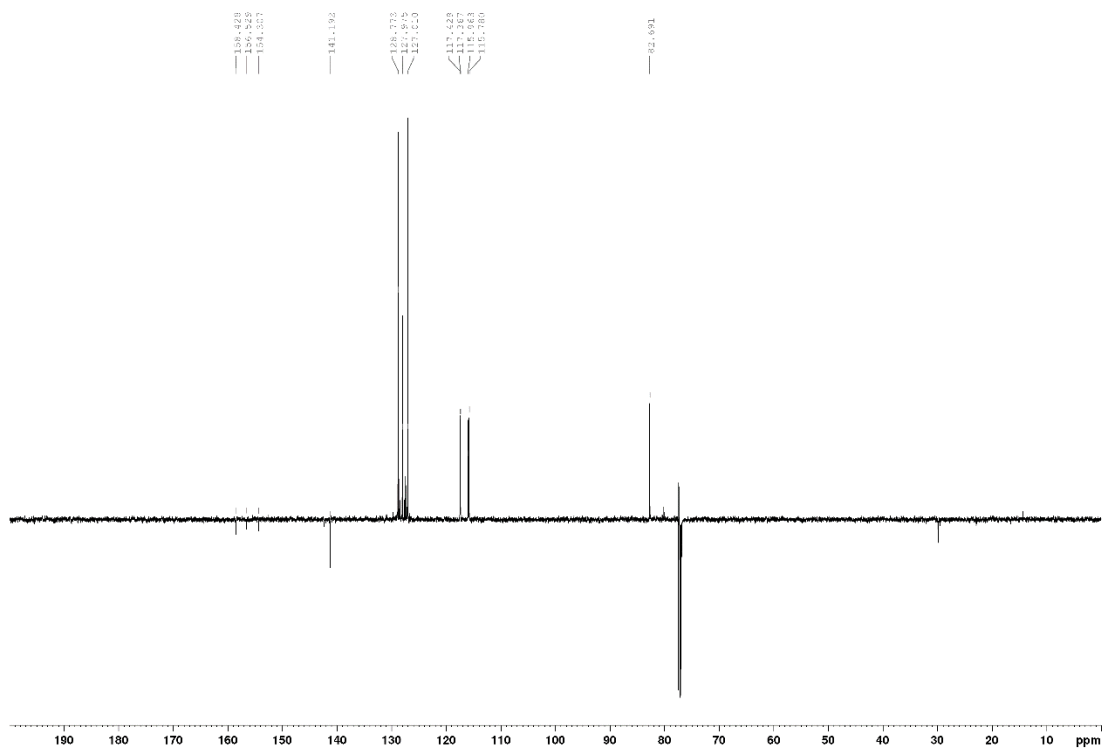


((4-fluorophenoxy)methylene)dibenzene (5ab)

¹H

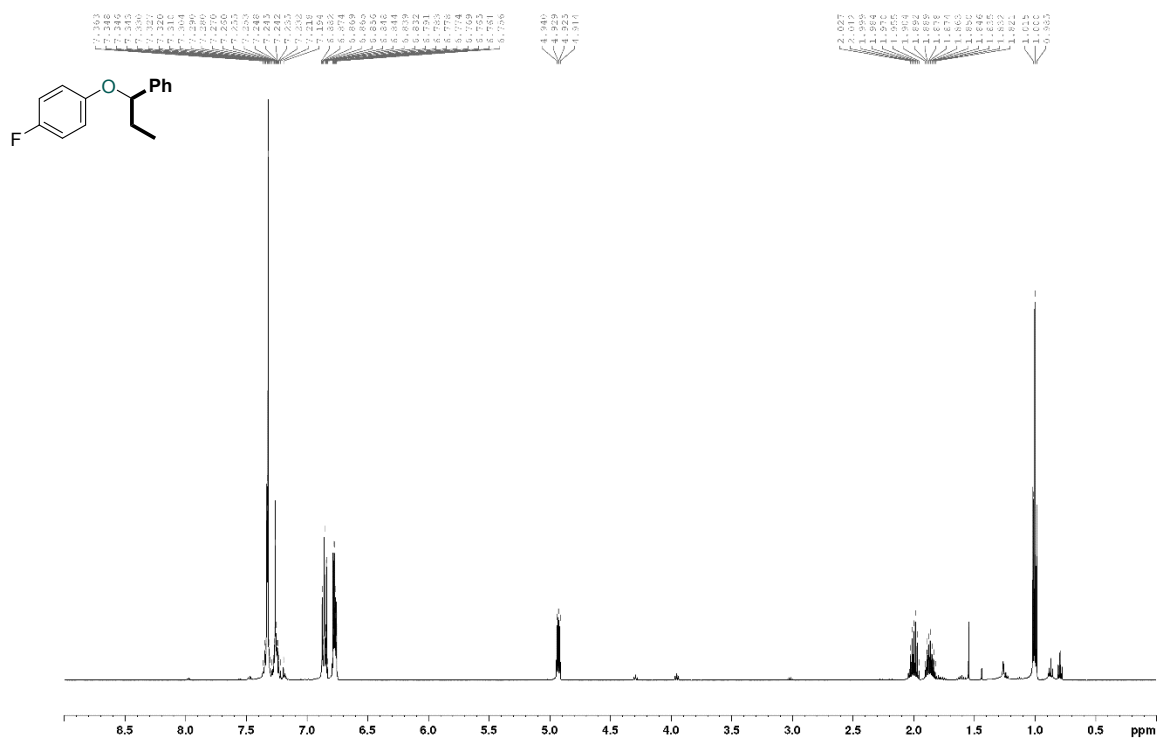


¹³C{¹H}

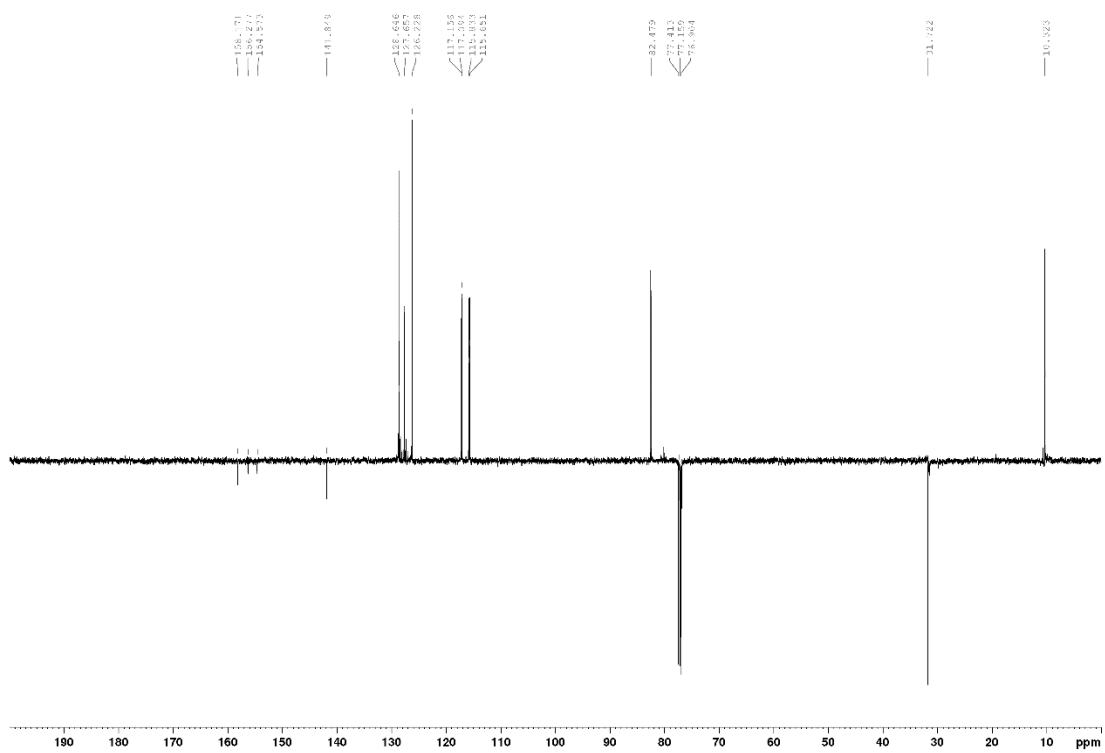


1-fluoro-4-(1-phenylpropoxy)benzene (5ac)

^1H

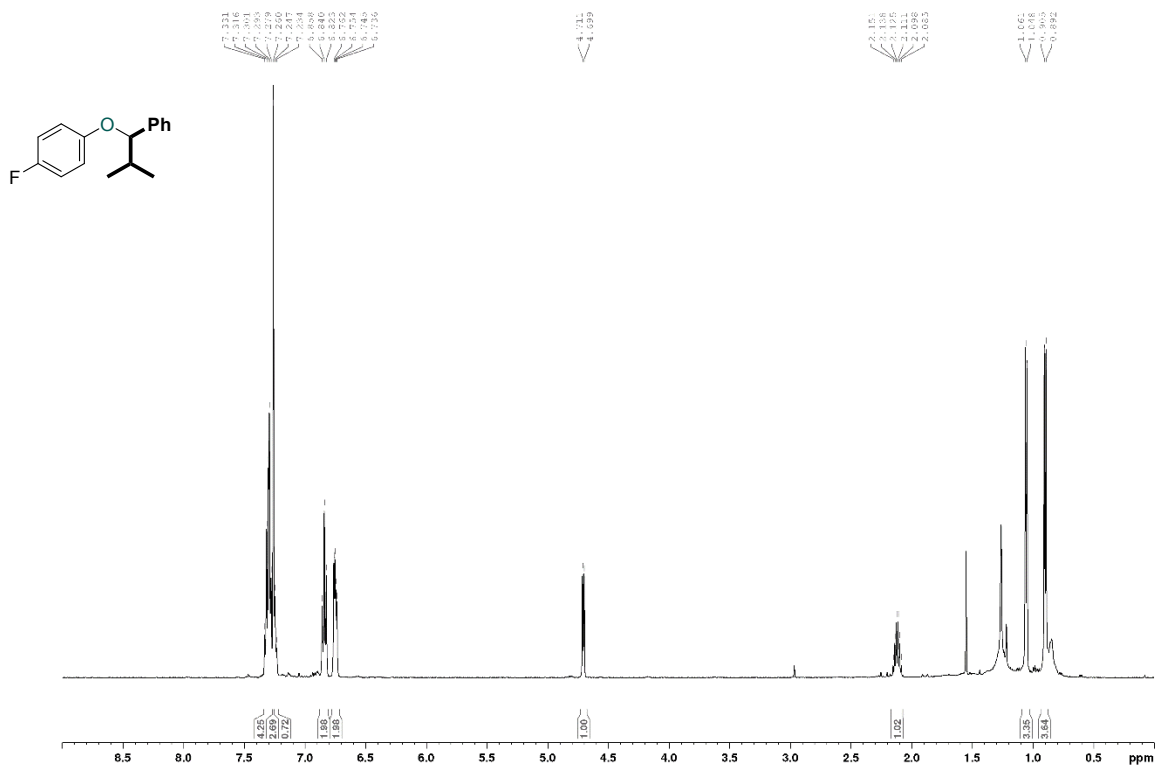


$^{13}\text{C}\{^1\text{H}\}$

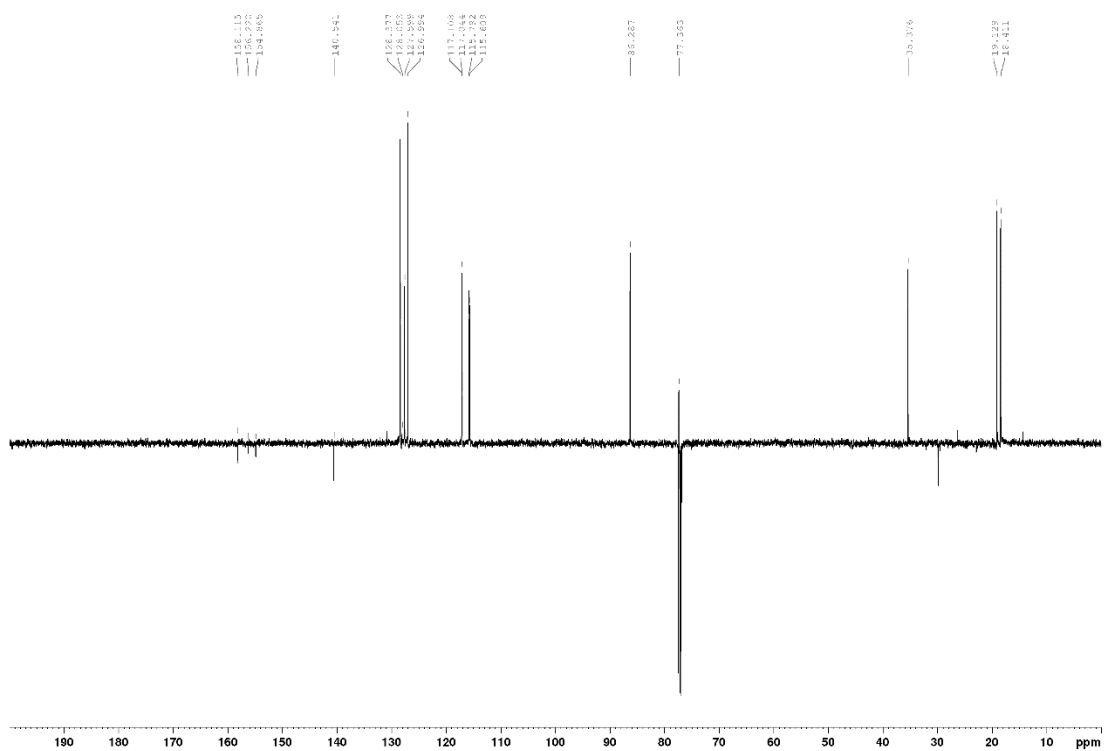


1-fluoro-4-(2-methyl-1-phenylpropoxy)benzene (5ad)

^1H

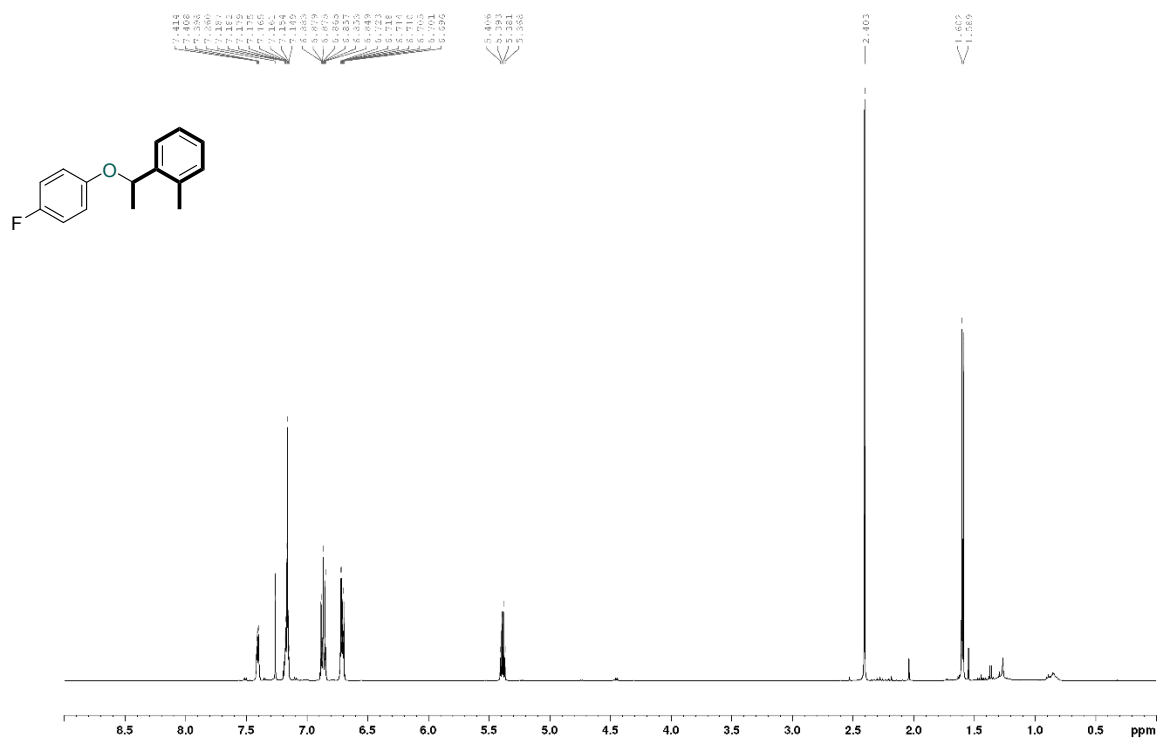


$^{13}\text{C}\{^1\text{H}\}$

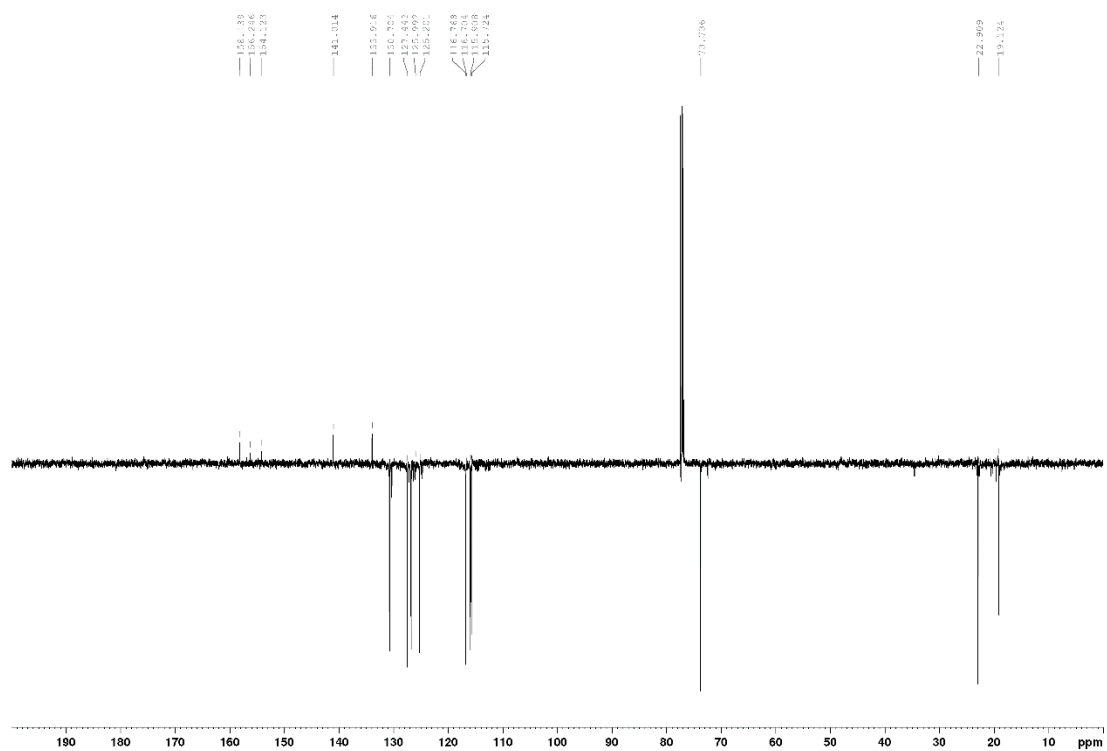


1-(1-(4-fluorophenoxy)ethyl)-2-methylbenzene (5ae)

^1H

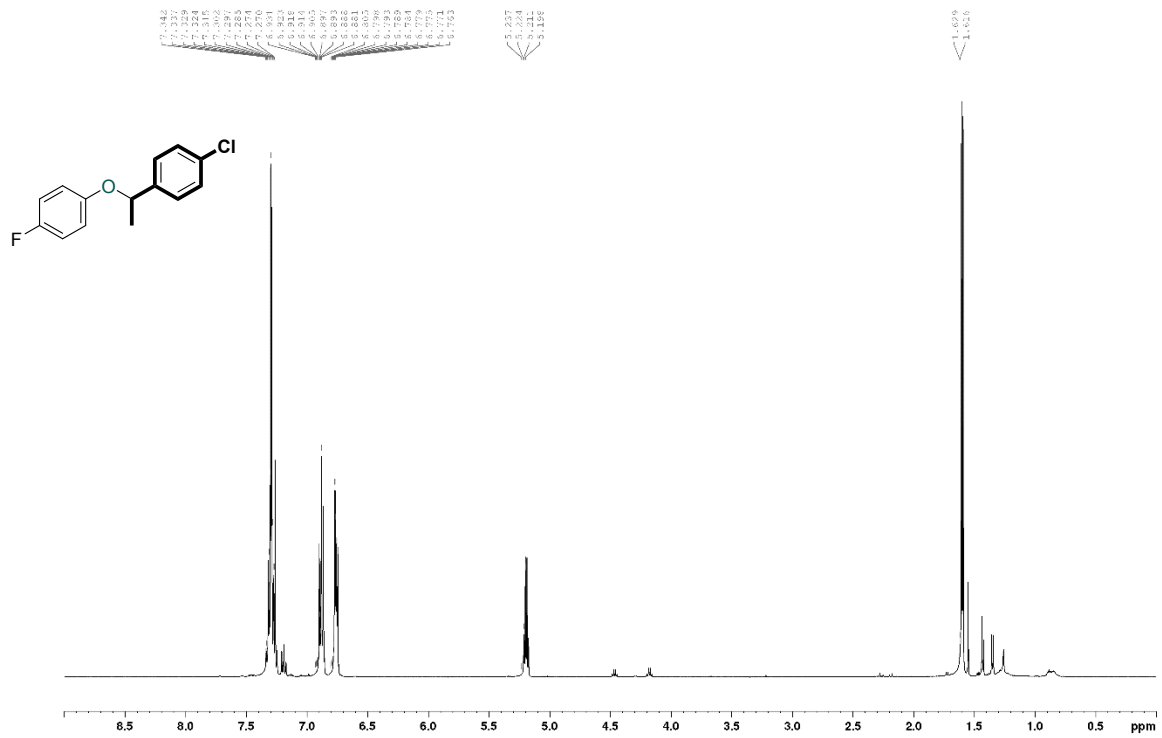


$^{13}\text{C}\{^1\text{H}\}$

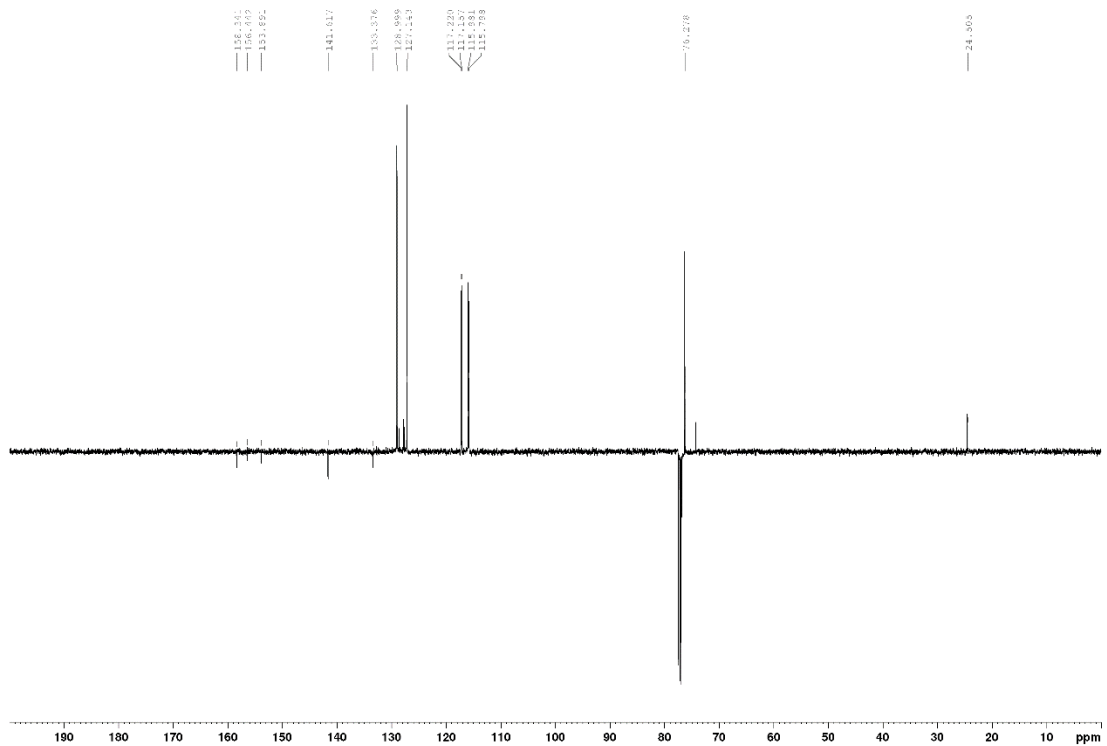


1-chloro-4-(1-(4-fluorophenoxy)ethyl)benzene (5ah)

^1H

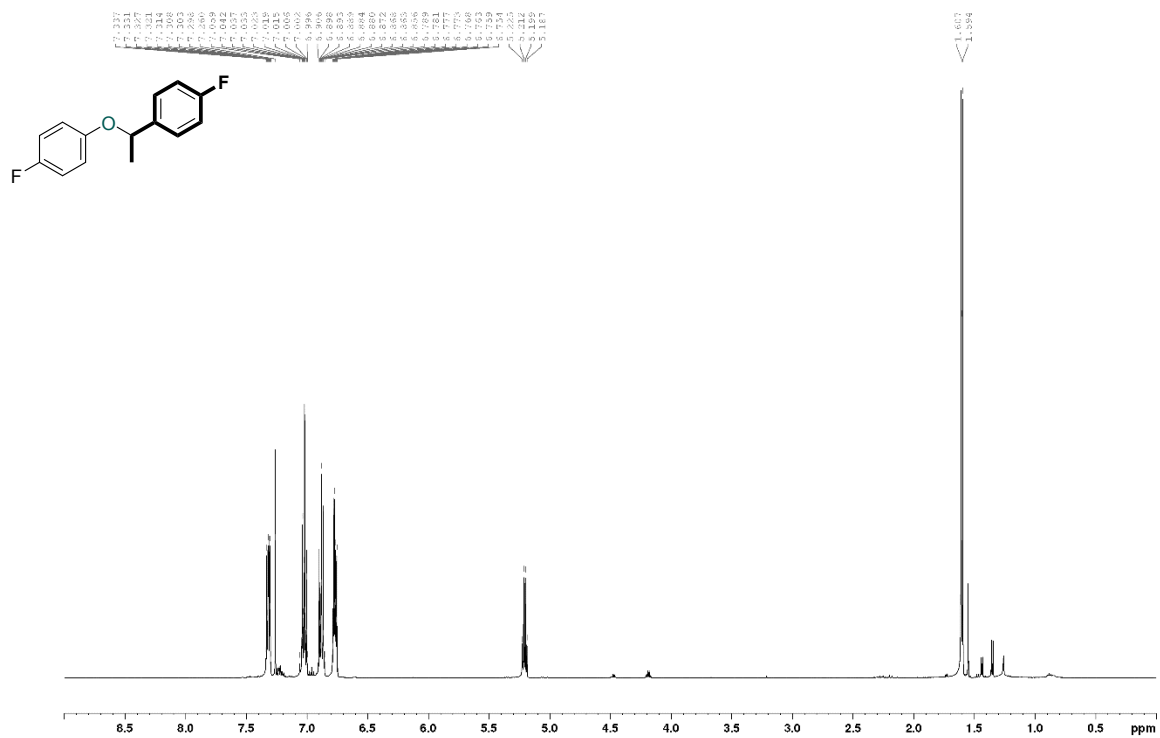


$^{13}\text{C}\{^1\text{H}\}$

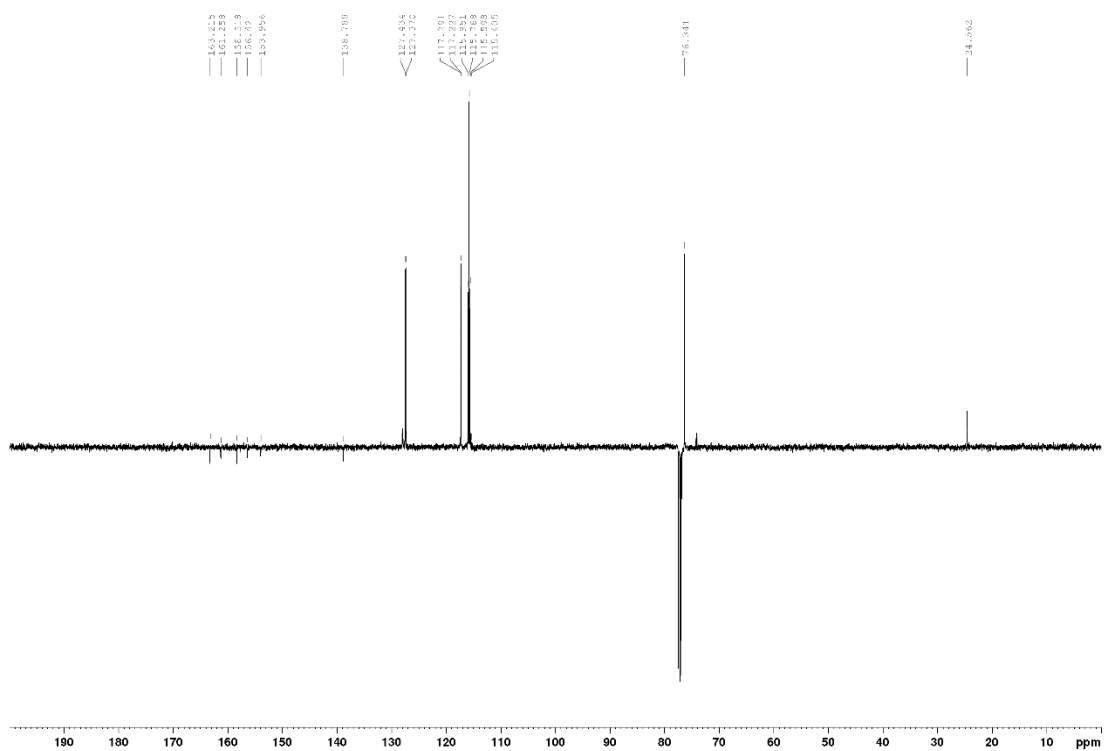


1-fluoro-4-(1-(4-fluorophenoxy)ethyl)benzene (5ai)

^1H

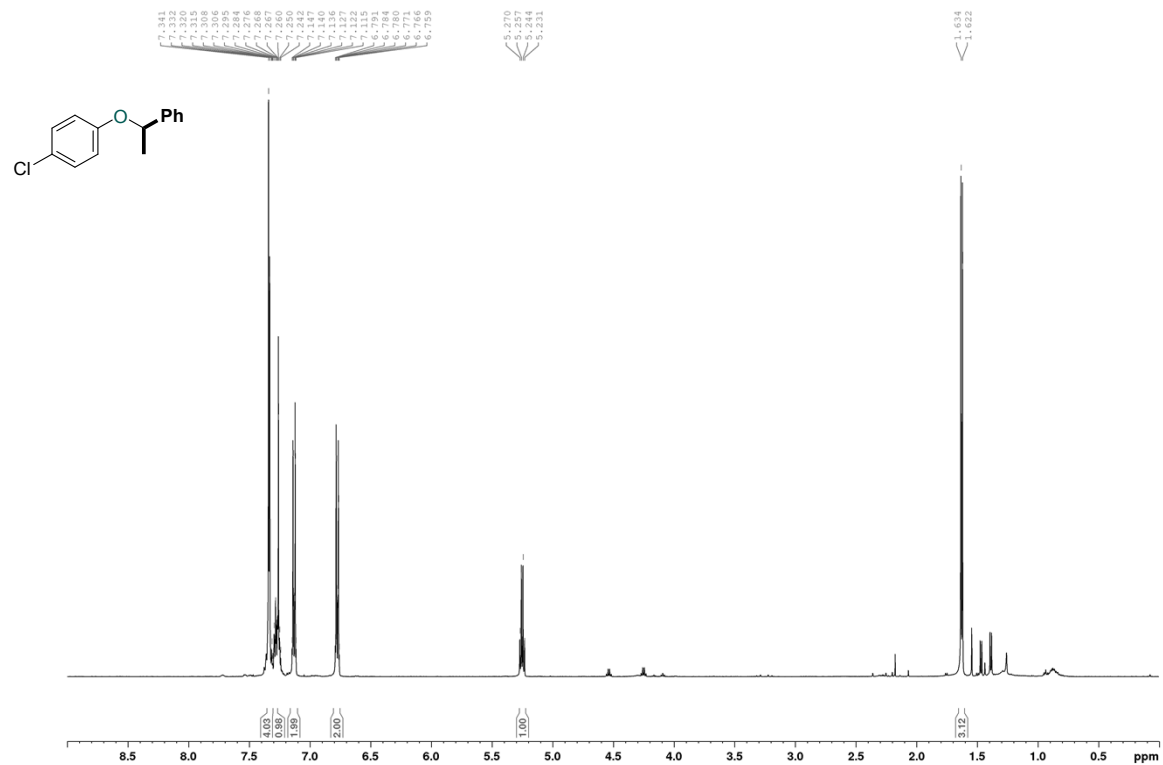


$^{13}\text{C}\{^1\text{H}\}$

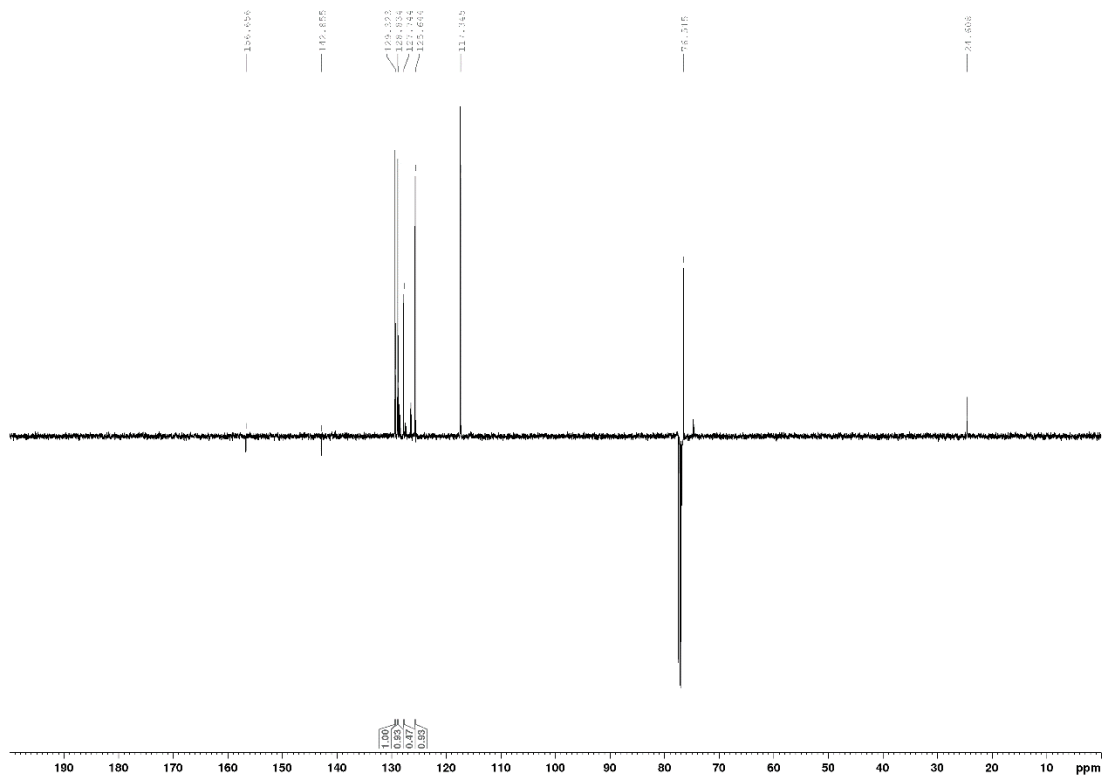


1-chloro-4-(1-phenylethoxy)benzene (5ba)

¹H

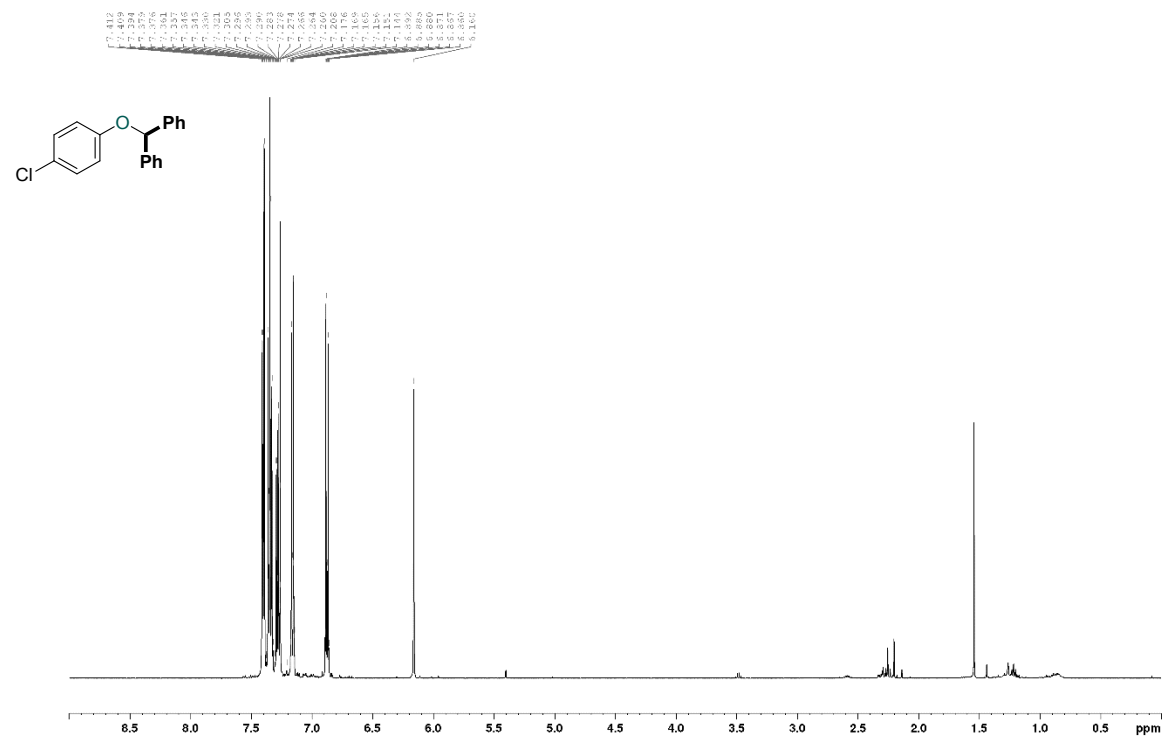


¹³C{¹H}

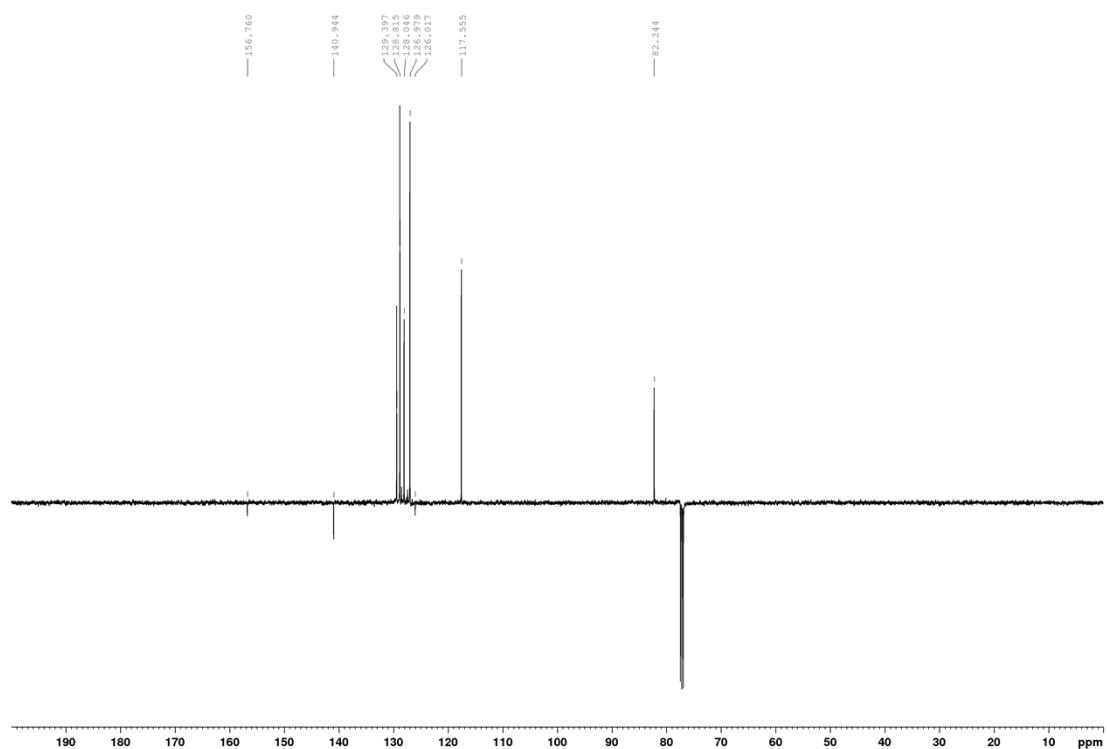


((4-chlorophenoxy)methylene)dibenzene (5b)

¹H

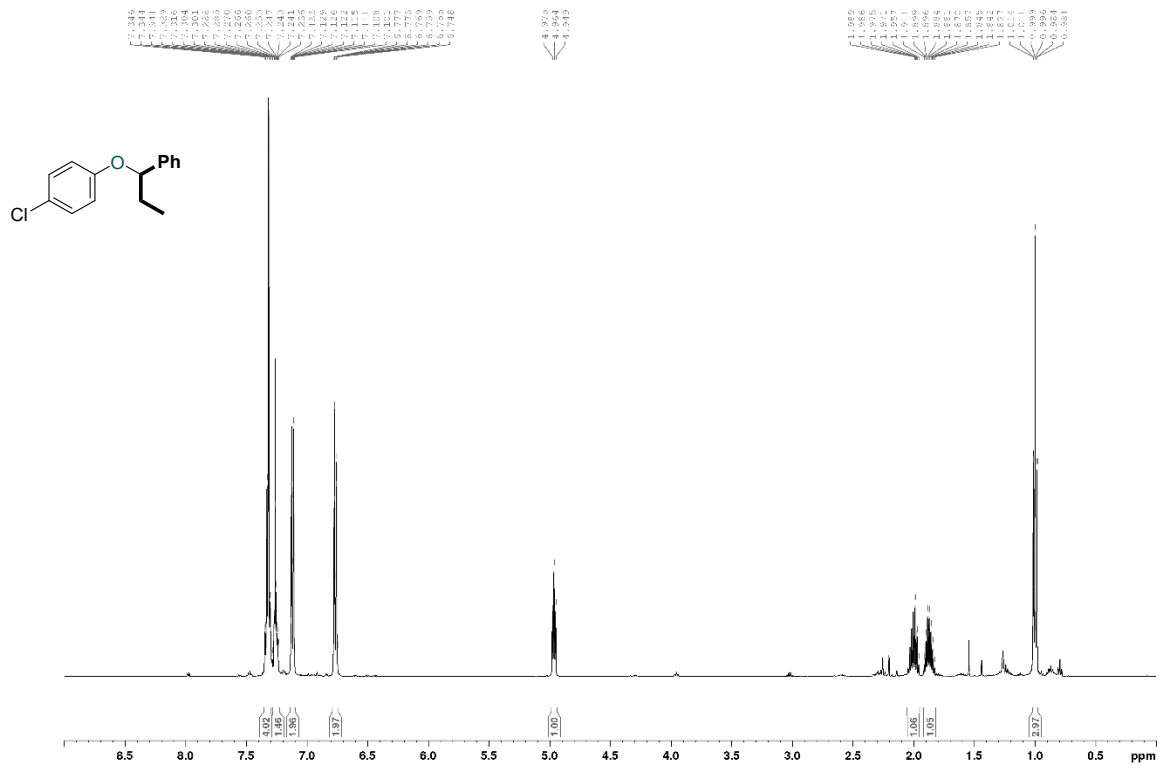


¹³C{¹H}

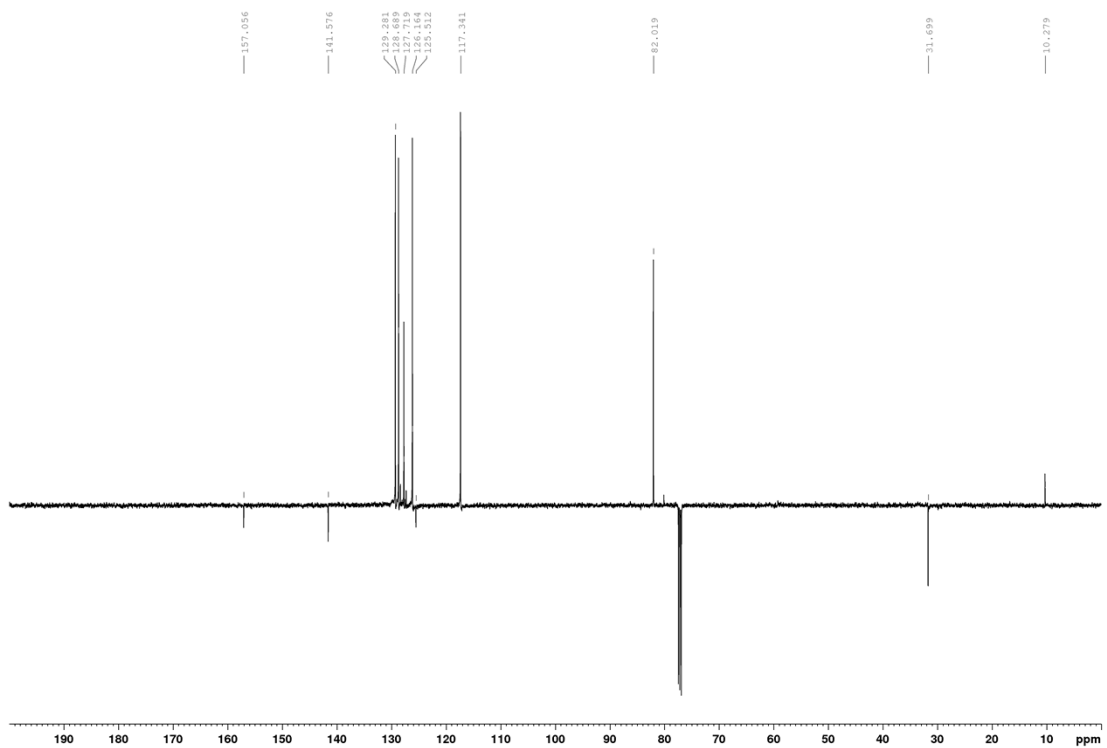


1-chloro-4-(1-phenylpropoxy)benzene (5bc)

¹H

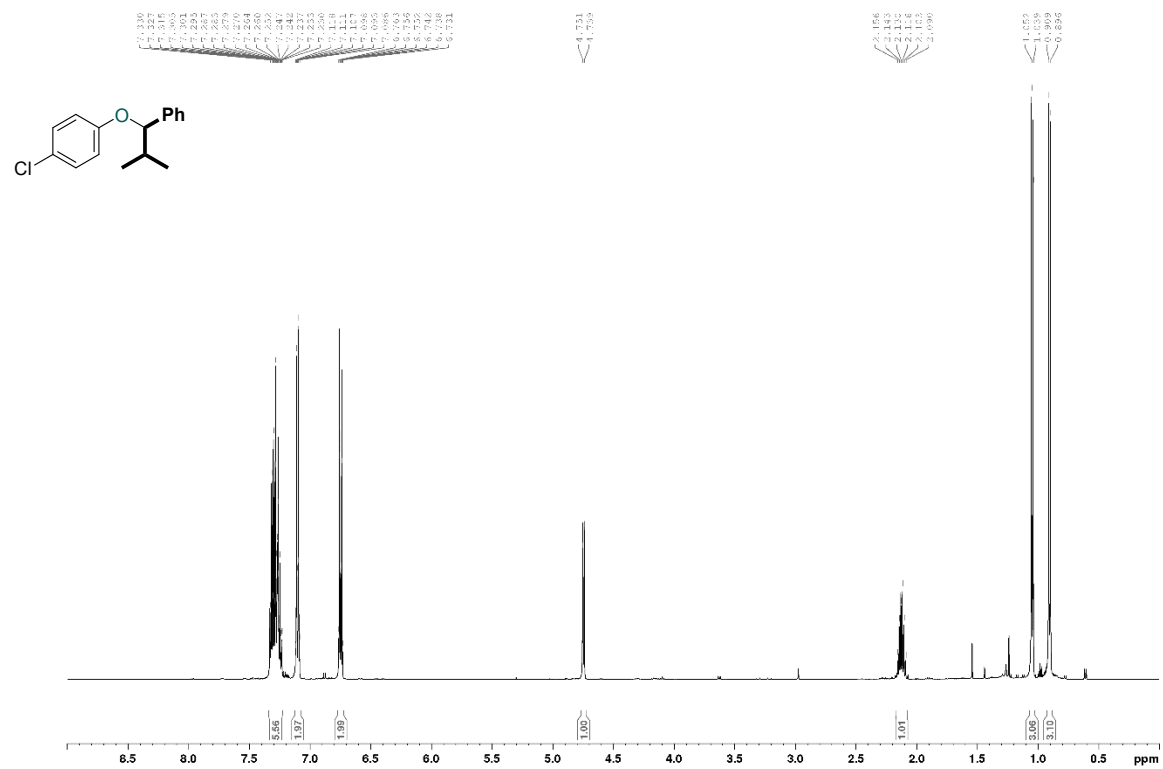


¹³C{¹H}

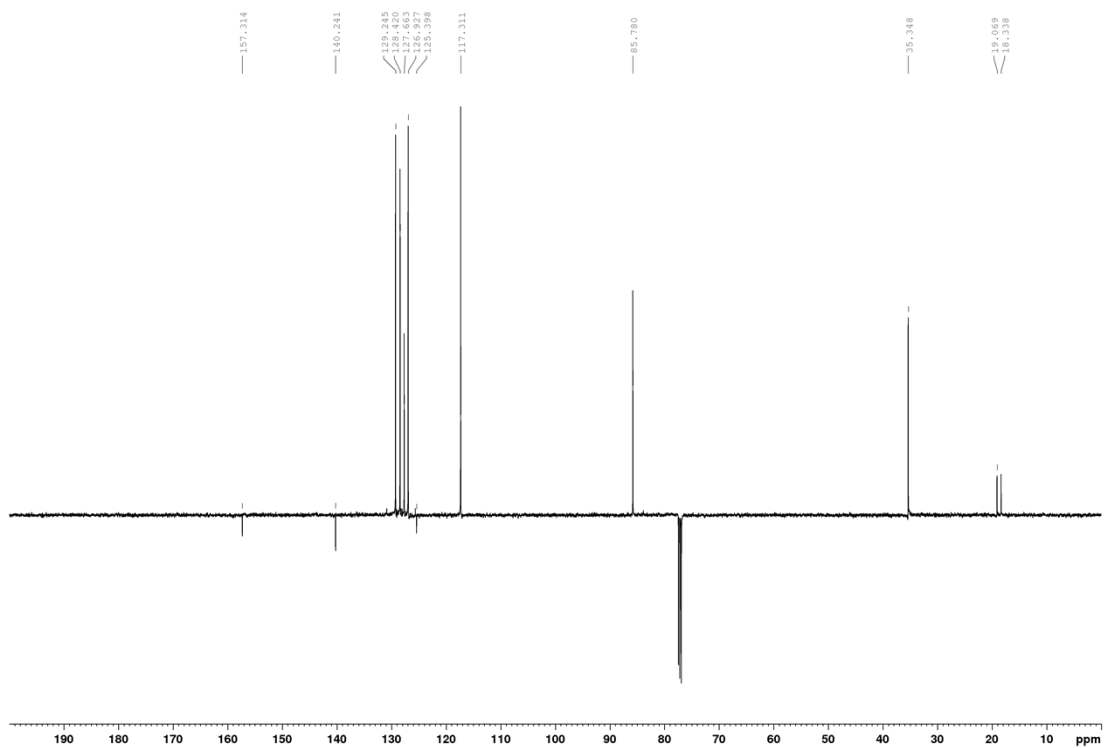


1-chloro-4-(2-methyl-1-phenylpropoxy)benzene (5bd)

^1H

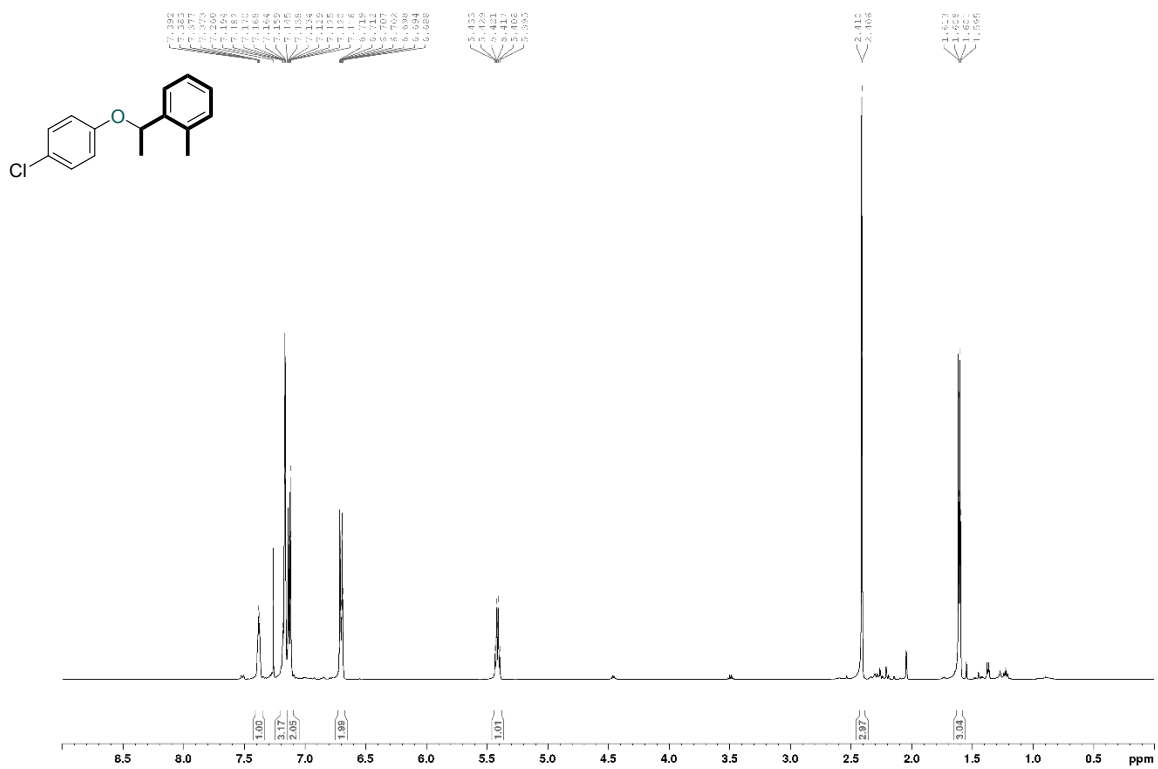


$^{13}\text{C}\{^1\text{H}\}$

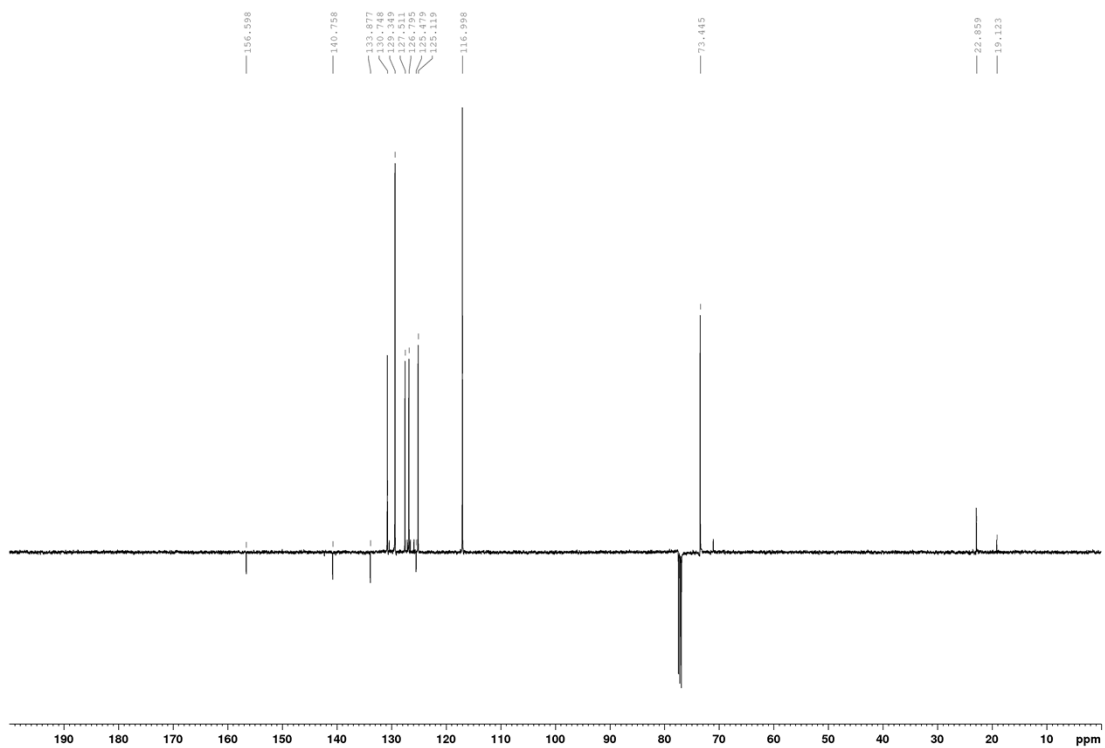


1-(1-(4-chlorophenoxy)ethyl)-2-methylbenzene (5be)

^1H

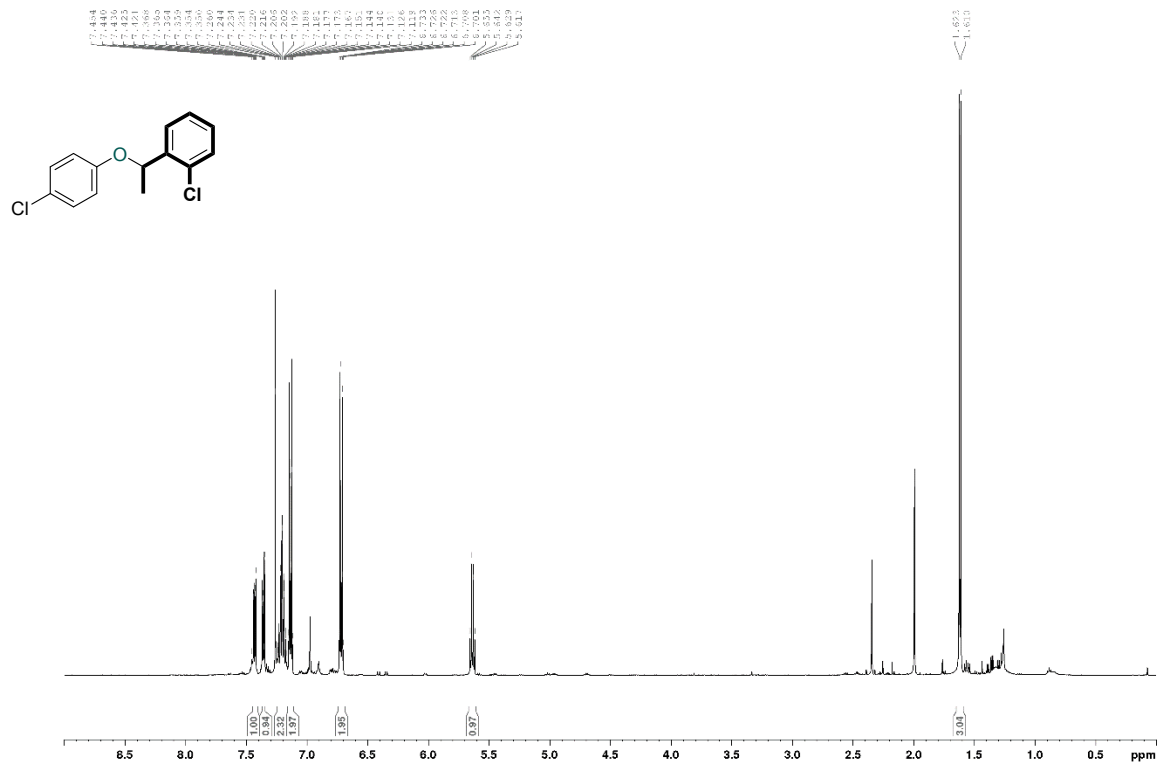


$^{13}\text{C}\{^1\text{H}\}$

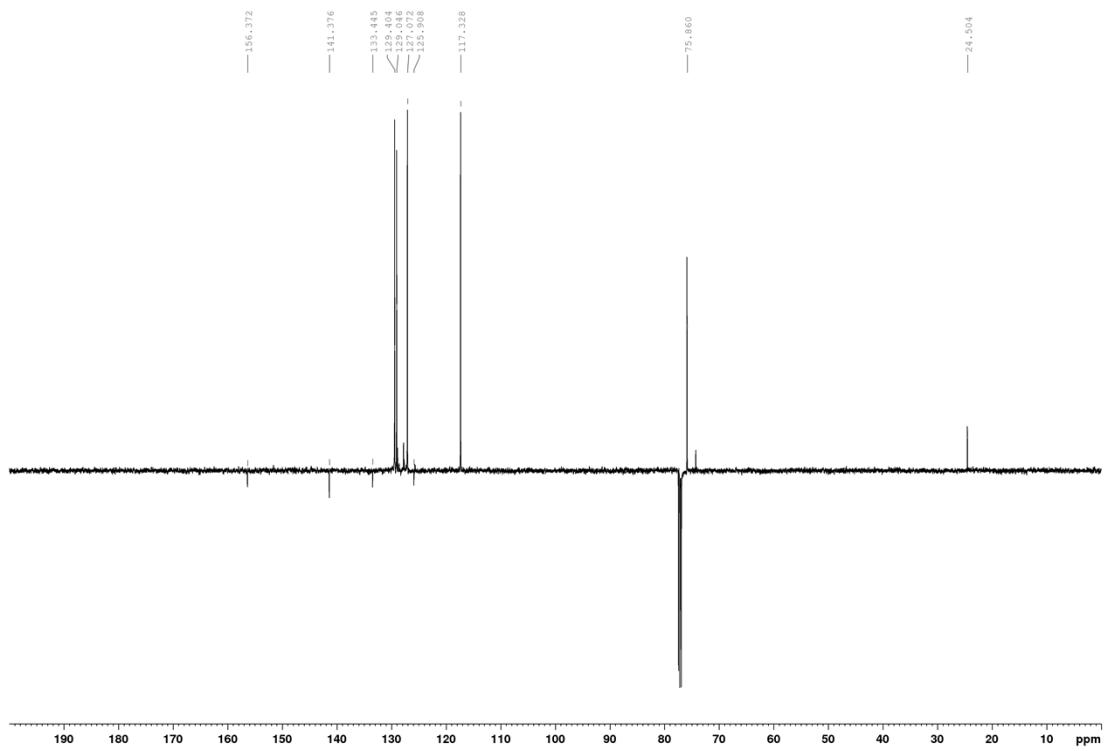


1-chloro-4-(1-(4-chlorophenoxy)ethyl)benzene (5bf)

¹H

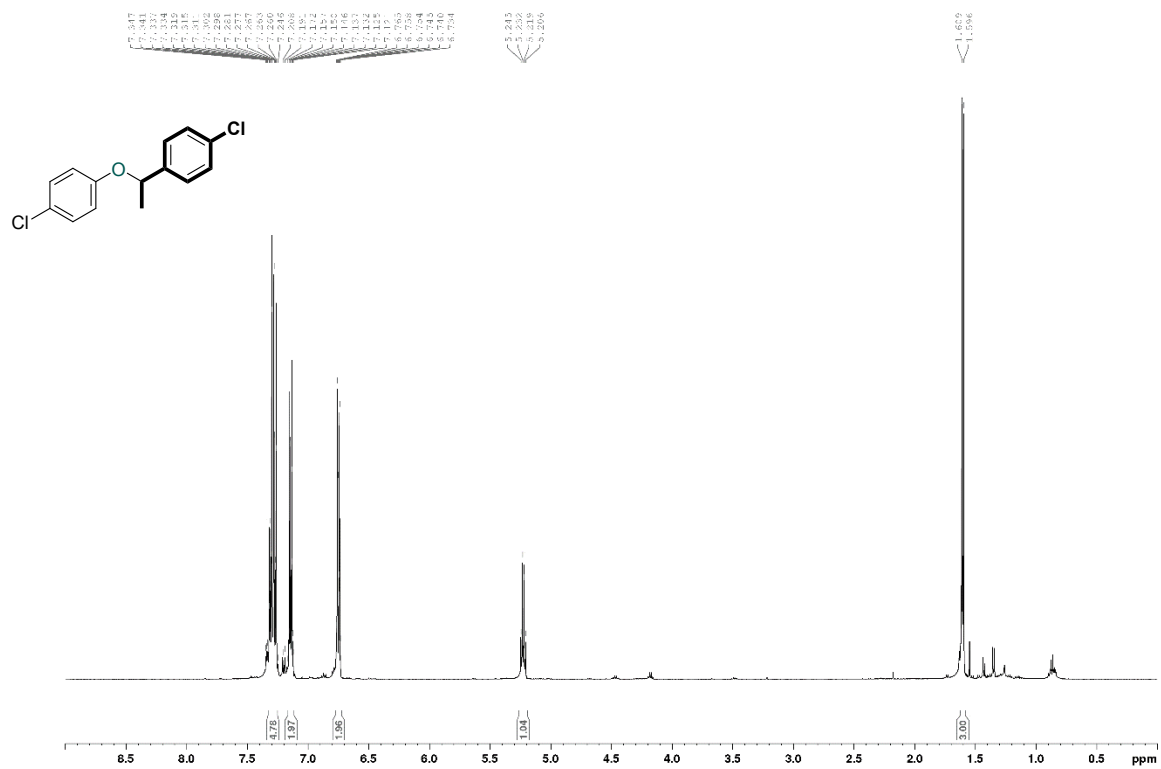


¹³C{¹H}

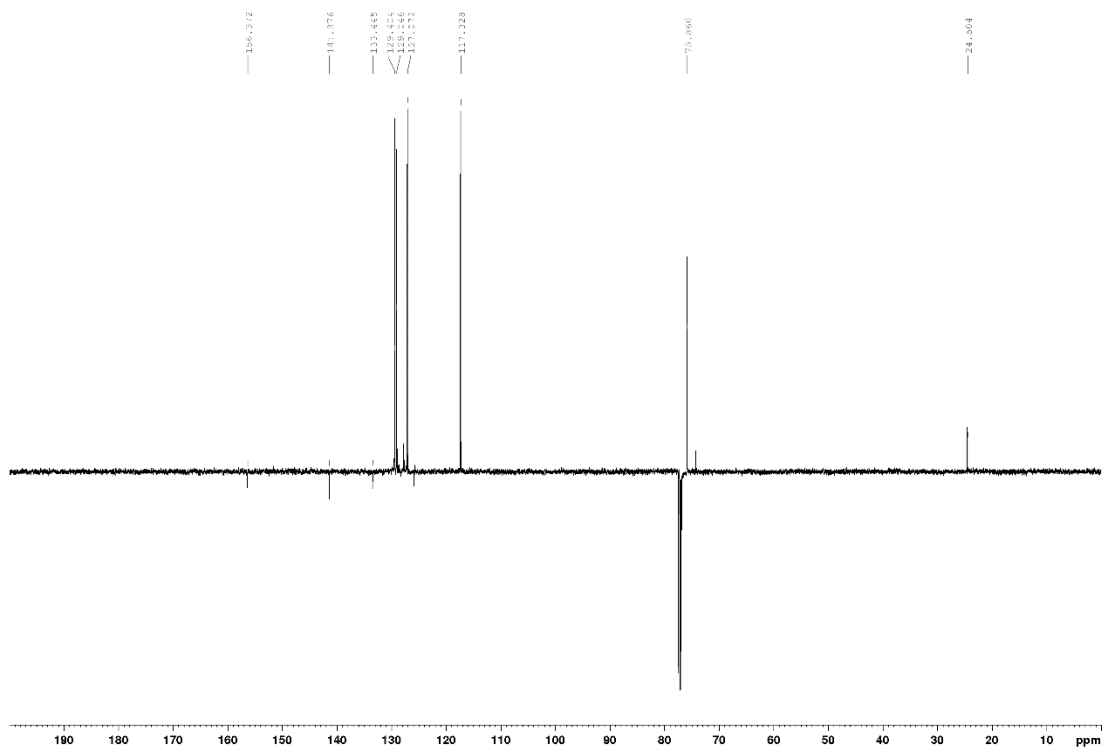


1-chloro-2-(1-(4-chlorophenoxy)ethyl)benzene (5bh)

^1H

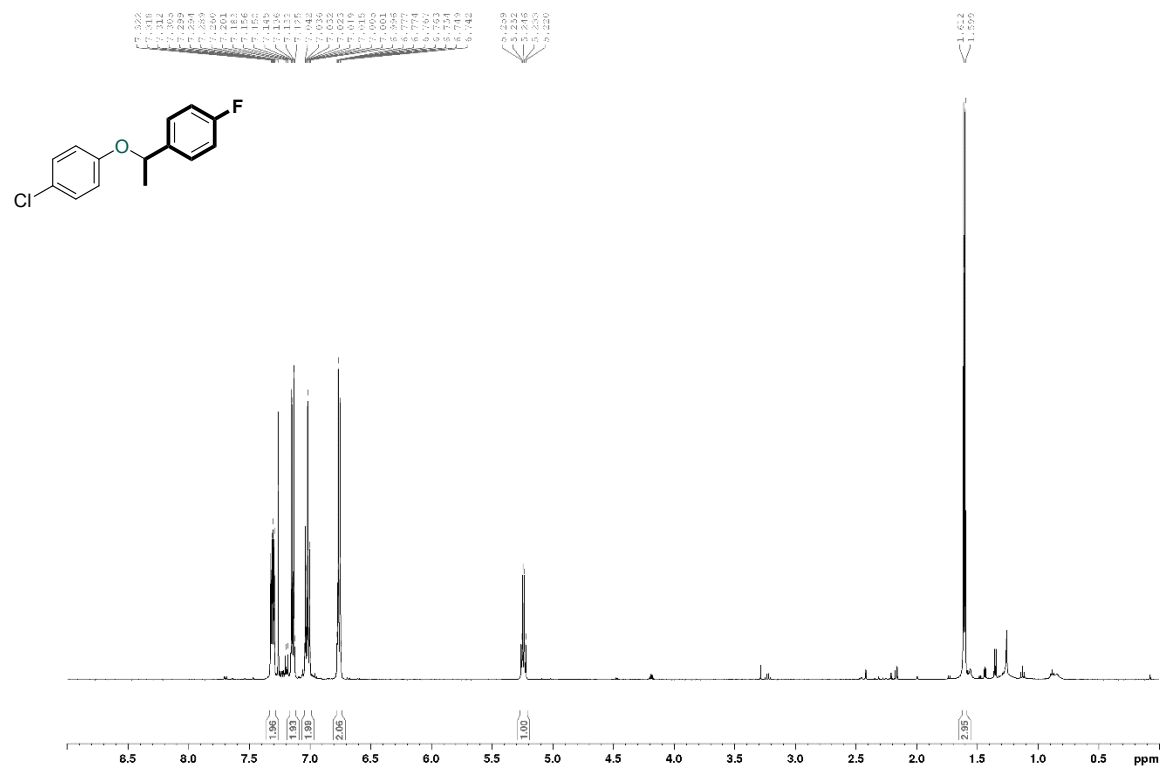


$^{13}\text{C}\{^1\text{H}\}$

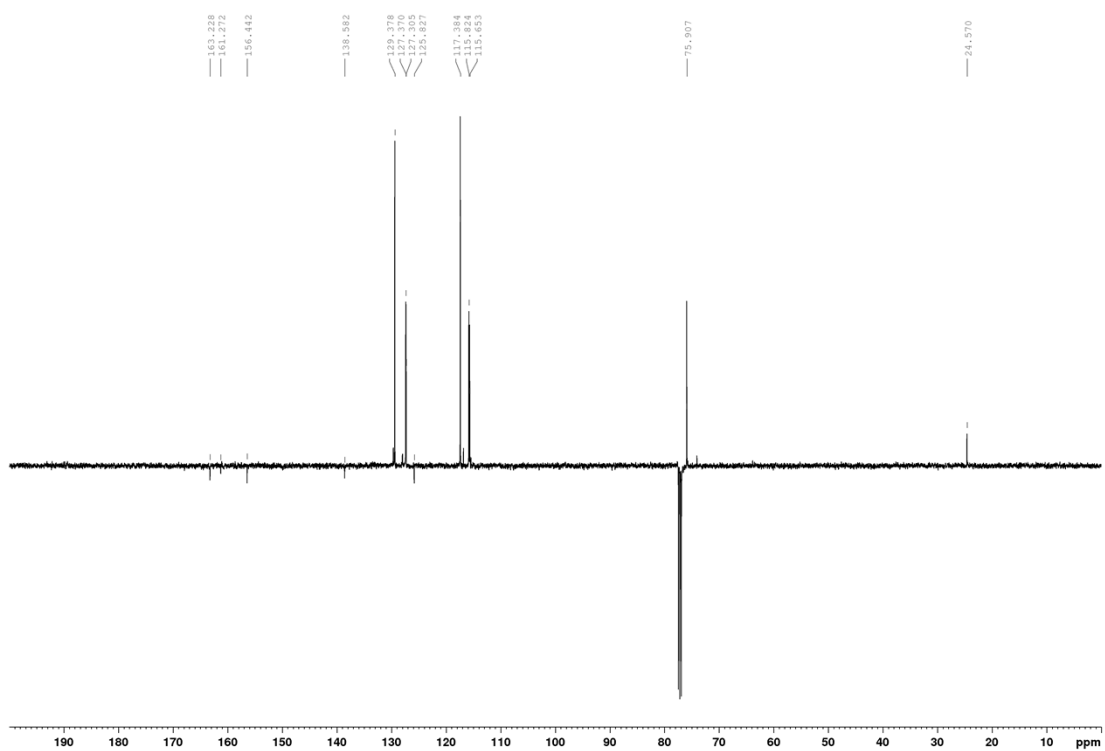


1-chloro-4-(1-(4-fluorophenyl)ethoxy)benzene (5bi)

^1H



$^{13}\text{C}\{^1\text{H}\}$



7. References

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7. Phenol 3a was chosen because its fluorine substituent presents a diagnostic aid for NMR analysis.