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Methods

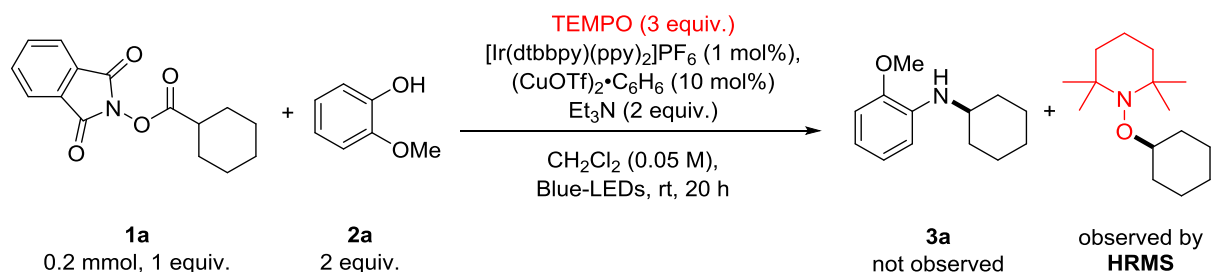
General Analytical Information

Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature. All ^1H NMR spectra were measured in part per million (ppm) relative to the signals of tetramethylsilane (TMS, 0.00 ppm) added into the deuterated chloroform (CDCl_3 , 7.26 ppm) unless otherwise stated.¹ Data for ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, and br = broad signal), coupling constants, and integration. All ^{13}C NMR spectra were reported in ppm relative to CDCl_3 (77.16 ppm) unless otherwise stated, and were obtained with complete ^1H decoupling. All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All GC-MS analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. High-resolution mass spectra (HRMS) by electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI) method were performed at the EPFL ISIC Mass Spectroscopy Service.

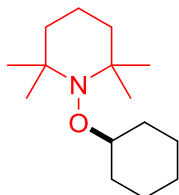
General Manipulation Considerations

All manipulations for the decarboxylative $\text{C}(\text{sp}^3)\text{-O}$ cross coupling via synergetic photoredox and copper catalyzed reactions were set up in a 15 mL Teflon-screw capped test tubes (unless otherwise noted) under an inert nitrogen (N_2) atmosphere using glove-box techniques. The test tubes were then sealed with airtight electrical tapes and the reaction mixtures were stirred under the irradiation of blue LEDs with a fan cooling down the temperature (approximately room temperature). Blue LEDs were purchased from Kessil Co., Ltd. (40 W max., product No. A160WE). Table fan was purchased from Galaxus Co., Ltd. (35 W max.). Flash column chromatography was performed using silica gel (Silicycle, ultra-pure grade). Preparative Thin Layer Chromatography (PTLC) was performed using glass plates from Merck KGaA, Darmstadt, Germany. The eluents for column chromatography and PTLC were presented as ratios of solvent volumes. Yields reported in the publication are of isolated materials unless otherwise noted.

TEMPO trapping experiment



A reaction under the optimized reaction conditions (Table 1, entry 13) was conducted in the presence of 3.0 equivalents of TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) as a radical scavenger. Under such conditions, the corresponding product **3a** was not observed. This experiment suggest a radical pathway. Moreover, the corresponding TEMPO-adduct formed by the trapping of the photogenerated alkyl radical by TEMPO was characterized by HR-MS (ESI).



HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₅H₃₀NO⁺ 240.2322; Found 240.2328.

Fluorescence quenching experiment

All solutions were prepared inside the glovebox before analyzing. The solutions were irradiated at 410 nm and the luminescence was measured at 581 nm.

Fluorescence quenching studies were carried out using a 1.0×10^{-6} M solution of [Ir(dtbbpy)(ppy)₂]PF₆ in CH₂Cl₂, upon addition of a 1.0×10^{-3} M solution of guaiacol, Et₃N, Cu(MeCN)₄PF₆, NHPI ester (**1a**), mixture of Cu(MeCN)₄PF₆ and NHPI ester (**1a**), or mixture of Cu(MeCN)₄PF₆ and guaiacol. Under these conditions, no obvious fluorescence quenching were detected (Figure S1).

When Fluorescence quenching studies were carried out using a 1.0×10^{-6} M solution of [Ir(dtbbpy)(ppy)₂]PF₆ in CH₂Cl₂, upon addition of variable concentration of the mixture of Cu(MeCN)₄PF₆ and Et₃N. Under these conditions, obvious fluorescence quenching were detected, depending on the concentration of the solution (Figure S2).

Stern-Volmer kinetic analysis

All solutions were prepared inside the glovebox before analyzing. The solutions were irradiated at 410 nm and the luminescence was measured at 581 nm.

Stern-Volmer constants were determined using Stern–Volmer kinetics (eq 1).

$$I_0/I = 1 + K_{sv}[\text{Quencher}] \quad (1)$$

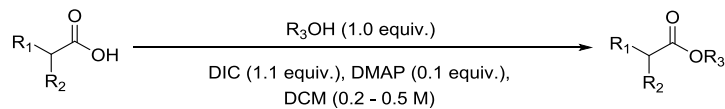
$$K_{sv} = k_q\tau_0 \quad (2)$$

As shown in equation (1), I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher, K_{sv} is the Stern-Volmer constant.

As shown in equation (2), the actual bimolecular rate of quenching (k_q) can be calculated from K_{sv} using the lifetime (τ_0) of [Ir(dtbbpy)(ppy)₂]PF₆.

Under these conditions, the mixture of Cu(MeCN)₄PF₆ and Et₃N (1:1, concentration) was the only species that quenched the photoexcited catalyst with the Stern-Volmer constant of 1173 M⁻¹S⁻¹ (Figure S3).

General Procedure for the synthesis of NHPI esters (General Procedure A)

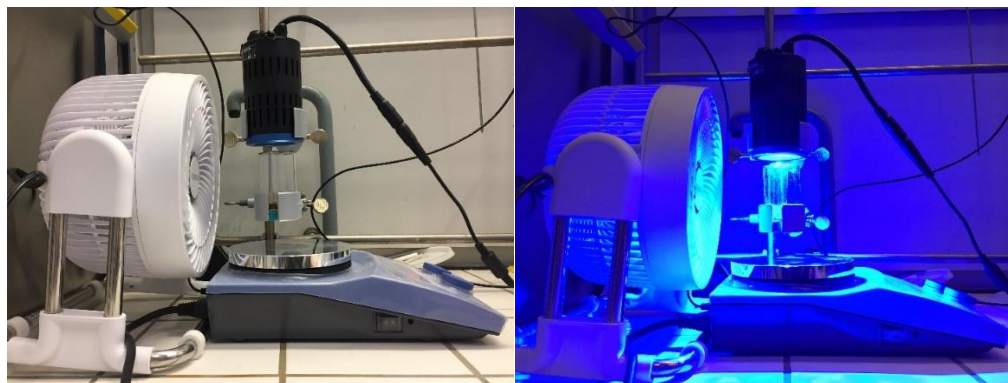


A round-bottom flask or culture tube was charged with carboxylic acid (if solid, 1.0 equiv), nucleophile (*N*-hydroxyphthalimide, 1.0 equiv) and DMAP (0.1 equiv.). dichloromethane (DCM) was added (0.2 M-0.5 M) and the mixture was stirred vigorously. Carboxylic acid (if liquid, 1.0 equiv.) was added via syringe. DIC (1.1 equiv.) was then added dropwise via syringe and the mixture was allowed to stir until the carboxylic acid or the *N*-hydroxyphthalimide was fully consumed (determined by TLC). Typical reaction times were between 0.5 h and 12 h. Afterwards, the mixture was filtered over Celite and rinsed with additional CH₂Cl₂. The solvent was removed under reduced pressure, and purified by column chromatography to give the corresponding NHPI esters. Most NHPI esters are solid, which could be recrystallized (ethyl acetate and hexanes system) after column chromatography. Unless otherwise stated, NHPI esters were prepared following the General Procedure A.

The preparation and spectral data of all NHPI esters used have been reported before.²⁻⁷

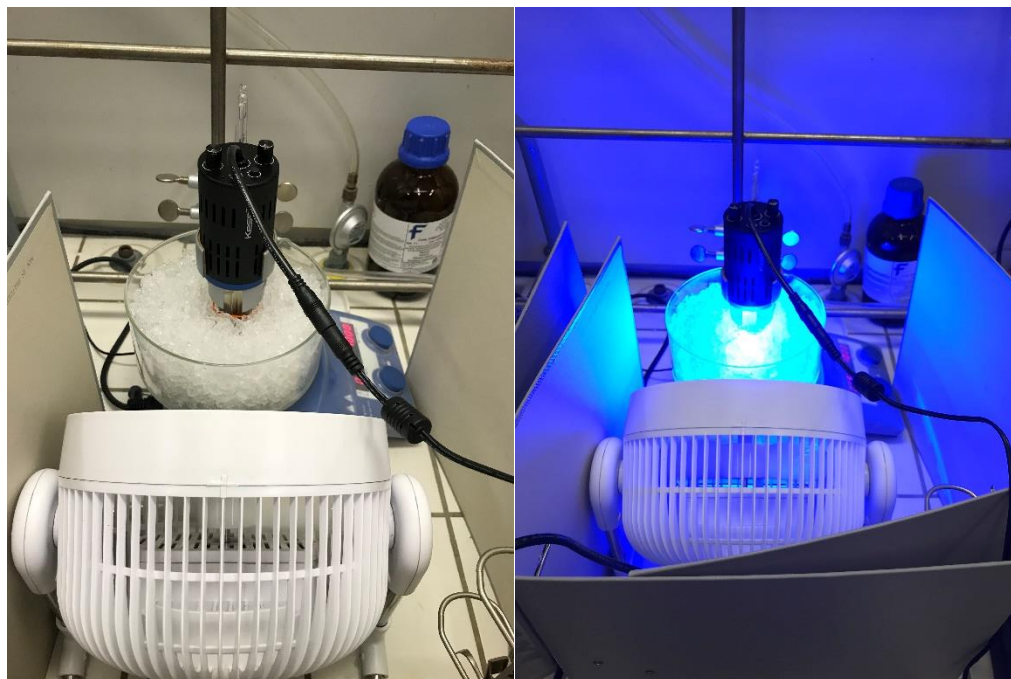
General procedure for visible-light-mediated decarboxylative etherification of phenols with secondary or tertiary NHPI esters (General Procedure B)

An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with a secondary or tertiary NHPI ester (1 equiv.), phenol (2 equiv), [Ir(dtbbpy)(ppy)₂](PF₆) (1 mol%), (CuOTf)₂•C₆H₆ (10 mol%), CH₂Cl₂ (0.05 M), Et₃N (2 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After which time the vial was removed from the light source. The crude reaction mixture was then diluted with EtOAc or diethyl ether (20 mL), washed with brine (2 x 10 mL), and separated. The aqueous layer was subsequently extracted with EtOAc or diethyl ether (2 x 10 mL), and separated. The organic fractions were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product residue was purified by preparative TLC using a solvent mixture (EtOAc, hexanes) as an eluent to afford the purified product.

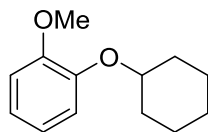


General procedure for visible-light-mediated decarboxylative etherification of phenols with primary NHPI esters (General Procedure C)

An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with a primary NHPI ester (2 equiv.), phenol (1 equiv.), [Ir(dtbbpy)(ppy)₂](PF₆) (1 mol%), Cu(MeCN)₄OTf (40 mol%), CH₂Cl₂ (0.05 M), *N*-isopropyl-*N*-methyl-*tert*-butylamine (1 equiv.) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated at 0-RT (ice bath and fan cooling) for 20 h. After which time the vial was removed from the light source. The crude reaction mixture was then diluted with EtOAc or diethyl ether (20 mL), washed with brine (2 x 10 mL), and separated. The aqueous layer was subsequently extracted with EtOAc or diethyl ether (2 x 10 mL), and separated. The organic fractions were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product residue was purified by preparative TLC using a solvent mixture (EtOAc, hexanes) as an eluent to afford the purified product.



1-(cyclohexyloxy)-2-methoxybenzene (3a)



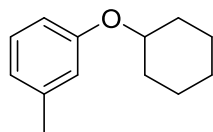
Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **3a** (58 mg) in 94%.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.07 – 6.70 (m, 4H), 4.18 (tt, $J = 9.5, 3.9$ Hz, 1H), 3.85 (s, 3H), 2.12 – 1.93 (m, 2H), 1.93 – 1.72 (m, 2H), 1.70 – 1.47 (m, 3H), 1.44 – 1.19 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 150.83, 147.36, 121.51, 120.87, 116.80, 112.45, 77.45, 56.12, 32.19, 25.79, 24.28.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.⁸

1-(cyclohexyloxy)-3-methylbenzene (3b)



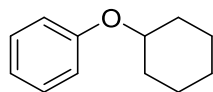
Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **3b** (38 mg) in 67%.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.15 (t, $J = 8.0$, 1H), 6.74 (d, $J = 6.3$ Hz, 3H), 4.23 (tt, $J = 8.8, 4.2$ Hz, 1H), 2.33 (d, $J = 3.1$ Hz, 3H), 2.11 – 1.89 (m, 2H), 1.89 – 1.72 (m, 2H), 1.63 – 1.47 (m, 3H), 1.42 – 1.27 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 157.93, 139.56, 129.26, 121.45, 117.13, 112.98, 75.40, 32.06, 25.82, 23.98, 21.67.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.⁹

Cyclohexyl phenyl ether (3c)



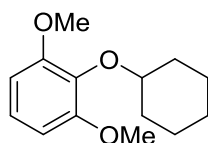
Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **3c** (48 mg) in 90%.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.29 – 7.24 (m, 2H), 6.96 – 6.86 (m, 3H), 4.24 (tt, $J = 9.0$, 3.8 Hz, 1H), 2.06 – 1.93 (m, 2H), 1.87 – 1.74 (m, 2H), 1.62 – 1.48 (m, 3H), 1.42 – 1.27 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 157.92, 129.55, 120.60, 116.22, 75.50, 32.02, 25.81, 23.97.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.¹⁰

2-(cyclohexyloxy)-1,3-dimethoxybenzene (**3d**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3d** (57 mg) in 81%.

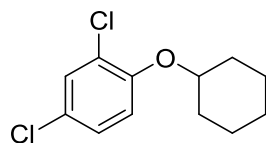
¹H NMR (400 MHz, Chloroform-*d*): δ 6.96 (t, $J = 8.3$ Hz, 1H), 6.64 – 6.49 (m, 2H), 4.04 – 3.92 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.02 – 1.93 (m, 2H), 1.84 – 1.76 (m, 2H), 1.62 – 1.51 (m, 3H), 1.29 – 1.19 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 154.29, 136.43, 123.27, 105.54, 81.07, 56.26, 32.74, 25.85, 24.52.

Physical State: white solid.

HRMS (APPI/LTQ-Orbitrap) m/z : $[M + H]^+$ Calcd for C₁₄H₂₁O₃⁺ 237.1485; Found 237.1487.

2,4-dichloro-1-(cyclohexyloxy)benzene (**3e**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3e** (59 mg) in 81%.

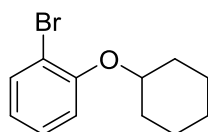
¹H NMR (400 MHz, Chloroform-*d*): δ 7.35 (d, *J* = 2.6 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.25 (tt, *J* = 8.3, 3.6 Hz, 1H), 2.02 – 1.87 (m, 2H), 1.88 – 1.75 (m, 2H), 1.67 – 1.50 (m, 3H), 1.41 – 1.26 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 152.47, 130.23, 127.52, 125.82, 125.37, 117.06, 77.63, 31.65, 25.68, 23.56.

Physical State: white solid.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₅Cl₂O⁺ 245.0494; Found 245.0499.

1-bromo-2-(cyclohexyloxy)benzene (3f)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3f** (56 mg) in 73%.

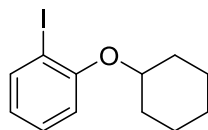
¹H NMR (400 MHz, Chloroform-*d*): δ 7.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.22 (td, *J* = 7.8, 1.7 Hz, 1H), 6.92 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.80 (td, *J* = 7.6, 1.5 Hz, 1H), 4.32 (tt, *J* = 8.1, 3.6 Hz, 1H), 2.00 – 1.88 (m, 2H), 1.89 – 1.80 (m, 2H), 1.73 – 1.60 (m, 2H), 1.58 – 1.49 (m, 1H), 1.42 – 1.32 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 154.51, 133.63, 128.31, 121.96, 116.02, 114.01, 77.01, 31.69, 25.78, 23.53.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M]⁺ Calcd for C₁₂H₁₅BrO⁺ 254.0301; Found 254.2479.

1-(cyclohexyloxy)-2-iodobenzene (3g)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3g** (59 mg) in 65%.

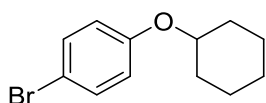
¹H NMR (400 MHz, Chloroform-*d*): δ 7.77 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.26 (td, $J = 8.1, 7.5, 1.7$ Hz, 1H), 6.83 (dd, $J = 8.3, 1.4$ Hz, 1H), 6.68 (td, $J = 7.6, 1.4$ Hz, 1H), 4.36 (tt, $J = 7.8, 3.2$ Hz, 1H), 1.94 – 1.81 (m, 4H), 1.76 – 1.64 (m, 2H), 1.57 – 1.50 (m, 1H), 1.47 – 1.35 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 156.65, 139.70, 129.31, 122.48, 114.39, 88.65, 76.65, 31.56, 25.80, 23.36.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) m/z : $[M]^+$ Calcd for C₁₂H₁₅IO⁺ 302.0162; Found 302.0165.

1-bromo-4-(cyclohexyloxy)benzene (3h)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3h** (57 mg) in 75%.

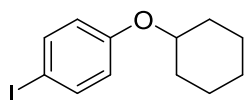
¹H NMR (400 MHz, Chloroform-*d*): δ 7.41 – 7.29 (m, 2H), 7.15 – 6.86 (m, 2H), 2.57 (tt, $J = 11.2, 3.6$ Hz, 1H), 2.12 – 1.96 (m, 2H), 1.90 – 1.76 (m, 2H), 1.77 – 1.66 (m, 1H), 1.64 – 1.55 (m, 2H), 1.45 – 1.25 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 157.03, 132.36, 118.01, 112.64, 75.89, 31.80, 25.71, 23.83.

Physical State: pale brown oil.

HRMS (APPI/LTQ-Orbitrap) m/z : $[M]^+$ Calcd for C₁₂H₁₅BrO⁺ 254.0301; Found 254.0304.

1-(cyclohexyloxy)-4-iodobenzene (3i)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3i** (53 mg) in 59%.

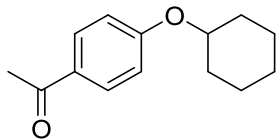
¹H NMR (400 MHz, Chloroform-*d*): δ 7.53 (dd, $J = 8.9, 2.0$ Hz, 2H), 6.68 (dd, $J = 8.7, 2.0$ Hz, 2H), 4.26 – 4.09 (m, 1H), 2.00 – 1.91 (m, 2H), 1.84 – 1.70 (m, 2H), 1.60 – 1.47 (m, 3H), 1.39 – 1.27 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 157.81, 138.33, 118.57, 82.46, 75.71, 31.78, 25.71, 23.82.

Physical State: brown oil.

The ^1H NMR and ^{13}C NMR spectra were consistent with the spectrum reported in the literature.¹¹

1-(4-(cyclohexyloxy)phenyl)ethan-1-one (3j)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **3j** (33 mg) in 51%.

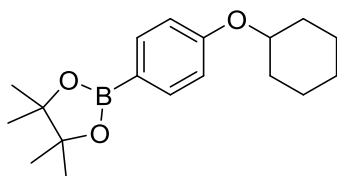
^1H NMR (400 MHz, Chloroform-*d*): δ 7.98 – 7.83 (m, 2H), 6.95 – 6.81 (m, 2H), 4.35 (tt, J = 9.0, 4.2 Hz, 1H), 2.54 (s, 3H), 2.04 – 1.91 (m, 2H), 1.85 – 1.77 (m, 2H), 1.62 – 1.48 (m, 3H), 1.46 – 1.31 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 196.86, 162.08, 130.73, 130.03, 115.30, 75.58, 31.74, 26.44, 25.64, 23.77.

Physical State: white solid.

HRMS (APPI/LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2^+$ 219.1380; Found 219.1382.

2-(4-(cyclohexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3k** (59 mg) in 65%.

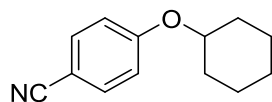
^1H NMR (400 MHz, Chloroform-*d*): δ 7.83 – 7.60 (m, 2H), 6.97 – 6.73 (m, 2H), 4.31 (tt, J = 8.8, 3.8 Hz, 1H), 2.09 – 1.88 (m, 2H), 1.84 – 1.70 (m, 2H), 1.61 – 1.48 (m, 3H), 1.45 – 1.23 (m, 15H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.62, 136.63, 115.30, 83.63, 75.09, 31.87, 25.77, 25.01, 23.86.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{28}\text{BO}_3^+$ 303.2126; Found 303.2125.

4-(cyclohexyloxy)benzonitrile (**3l**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3l** (30 mg) in 49%.

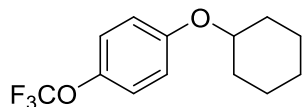
¹H NMR (400 MHz, Chloroform-*d*): δ 7.63 – 7.43 (m, 2H), 7.03 – 6.81 (m, 2H), 4.32 (tt, *J* = 8.5, 3.7 Hz, 1H), 2.01 – 1.91 (m, 2H), 1.80 (m, 2H), 1.59 – 1.52 (m, 3H), 1.41 – 1.30 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 161.44, 134.11, 119.54, 116.30, 103.45, 75.85, 31.62, 25.57, 23.71.

Physical State: pale yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₆NO⁺ 202.1226; Found 202.1228.

1-(cyclohexyloxy)-4-(trifluoromethoxy)benzene (**3m**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3m** (42 mg) in 54%.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.98 – 6.73 (m, 2H), 4.20 (tt, *J* = 8.3, 3.9 Hz, 1H), 2.04 – 1.91 (m, 2H), 1.87 – 1.72 (m, 2H), 1.62 – 1.46 (m, 3H), 1.39 – 1.32 (m, 2H), 0.93 – 0.74 (m, 1H).

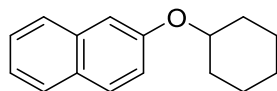
¹³C NMR (101 MHz, Chloroform-*d*): δ 156.47, 142.62, 122.50, 120.74 (q, *J* = 255.8 Hz), 116.86, 76.13, 31.85, 25.72, 23.85.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -58.38.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₆F₃O₂⁺ 261.1097; Found 261.1095.

2-(cyclohexyloxy)naphthalene (**3n**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **3n** (58 mg) in 86%.

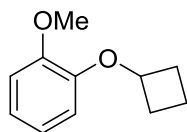
¹H NMR (400 MHz, Chloroform-*d*): δ 7.93 – 7.71 (m, 3H), 7.52 (td, *J* = 7.4, 6.7, 1.3 Hz, 1H), 7.41 (td, *J* = 7.5, 6.8, 1.3 Hz, 1H), 7.30 – 7.19 (m, 4H), 4.51 (tt, *J* = 8.6, 3.8 Hz, 1H), 2.23 – 2.10 (m, 2H), 2.03 – 1.87 (m, 2H), 1.76 – 1.61 (m, 3H), 1.60 – 1.38 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 155.75, 134.76, 129.50, 128.99, 127.73, 126.77, 126.34, 123.57, 119.97, 108.80, 75.53, 31.91, 25.84, 23.97.

Physical State: yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [*M*]⁺ Calcd for C₁₆H₁₈O⁺ 226.1352; Found 226.1357.

1-cyclobutoxy-2-methoxybenzene (**4a**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **4a** (42 mg) in 78%.

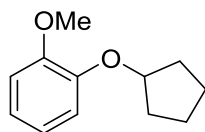
¹H NMR (400 MHz, Chloroform-*d*): δ 6.98 – 6.79 (m, 3H), 6.79 – 6.65 (m, 1H), 4.66 (p, *J* = 7.3 Hz, 1H), 3.87 (s, 3H), 2.54 – 2.39 (m, 2H), 2.37 – 2.18 (m, 2H), 1.91 – 1.78 (m, 1H), 1.77 – 1.59 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 149.31, 147.17, 120.93, 120.87, 113.50, 111.72, 72.21, 55.99, 30.95, 13.31.

Physical State: pale yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [*M*]⁺ Calcd for C₁₁H₁₄O₂⁺ 178.0988; Found 178.0991.

1-(cyclopentyloxy)-2-methoxybenzene (**4b**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **4b** (29 mg) in 50%.

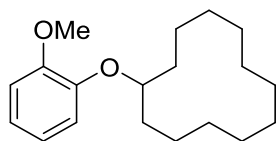
¹H NMR (400 MHz, Chloroform-*d*): δ 6.91 (s, 4H), 4.86 – 4.73 (m, 1H), 3.87 (s, 3H), 1.99 – 1.79 (m, 6H), 1.66 – 1.58 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 150.23, 147.92, 120.94, 120.92, 115.29, 112.31, 80.54, 56.18, 33.00, 24.23.

Physical State: pale yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₇O₂⁺ 193.1223; Found 193.1227.

(2-methoxyphenoxy)cyclododecane (**4c**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **4c** (68 mg) in 78%.

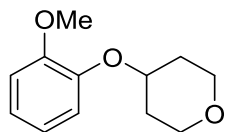
¹H NMR (400 MHz, Chloroform-*d*): δ 6.99 – 6.81 (m, 4H), 4.42 (tt, *J* = 7.4, 4.3 Hz, 1H), 3.84 (s, 3H), 1.88 – 1.74 (m, 2H), 1.75 – 1.60 (m, 2H), 1.50 – 1.28 (m, 18H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 150.73, 147.99, 121.22, 120.98, 116.25, 112.59, 76.95, 56.19, 29.13, 24.58, 24.20, 23.45, 23.39, 21.11.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₉H₃₁O₂⁺ 291.2319; Found 291.2324.

4-(2-methoxyphenoxy)tetrahydro-2H-pyran (**4d**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **4d** (43 mg) in 69%.

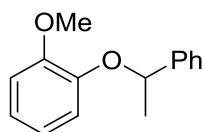
¹H NMR (400 MHz, Chloroform-*d*): δ 7.06 – 6.79 (m, 4H), 4.41 (tt, *J* = 8.3, 4.0 Hz, 1H), 4.02 (dt, *J* = 11.8, 4.6 Hz, 2H), 3.86 (s, 3H), 3.53 (ddd, *J* = 11.8, 9.0, 3.0 Hz, 2H), 2.10 – 1.90 (m, 2H), 1.92 – 1.76 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 151.21, 146.61, 122.47, 120.93, 117.98, 112.60, 74.04, 65.59, 56.08, 32.32.

Physical State: yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₇O₃⁺ 209.1172; Found 209.1172.

1-methoxy-2-(1-phenylethoxy)benzene (4e)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **4e** (54 mg) in 79%.

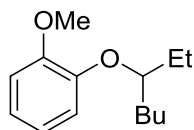
¹H NMR (400 MHz, Chloroform-*d*): δ 7.41 (d, *J* = 6.9 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 6.88 (dd, *J* = 4.4, 3.0 Hz, 2H), 6.75 (dd, *J* = 4.1, 2.0 Hz, 2H), 5.32 (q, *J* = 6.5 Hz, 1H), 3.90 (s, 3H), 1.70 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 150.29, 147.61, 143.37, 128.62, 127.52, 125.82, 121.53, 120.82, 116.51, 112.27, 77.43, 56.16, 24.43.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₆NaO₂⁺ 251.1043; Found 251.1045

1-(heptan-3-yloxy)-2-methoxybenzene (4f)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **4f** (43 mg) in 65%.

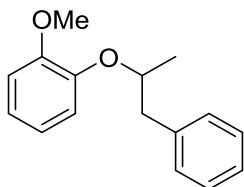
¹H NMR (400 MHz, Chloroform-*d*): δ 6.89 (m, 4H), 4.14 (p, *J* = 5.9 Hz, 1H), 3.85 (s, 3H), 1.75 – 1.57 (m, 4H), 1.43 – 1.27 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 150.73, 148.46, 121.17, 120.94, 116.25, 112.51, 81.13, 56.15, 33.44, 27.83, 26.86, 22.97, 14.23, 9.85.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₄H₂₃O₂⁺ 223.1693; Found 223.1692.

1-methoxy-2-((1-phenylpropan-2-yl)oxy)benzene (**4g**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **4g** (33 mg) in 46%.

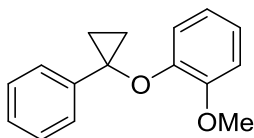
¹H NMR (400 MHz, Chloroform-*d*): δ 7.32 – 7.20 (m, 5H), 7.04 – 6.74 (m, 4H), 4.62 – 4.45 (m, 1H), 3.85 (s, 3H), 3.21 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.83 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.32 (dd, *J* = 6.1, 1.3 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 150.84, 147.53, 138.58, 129.68, 128.45, 126.42, 121.77, 120.99, 116.72, 112.55, 56.14, 42.96, 19.62.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M]⁺ Calcd for C₁₆H₁₈O₂⁺ 242.1301; Found 242.1306.

1-methoxy-2-(1-phenylcyclopropoxy)benzene (**5a**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **5a** (61 mg) in 85%.

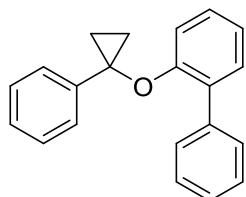
¹H NMR (400 MHz, Chloroform-*d*): δ 7.39 – 7.18 (m, 5H), 6.97 – 6.82 (m, 3H), 6.78 – 6.68 (m, 1H), 3.91 (s, 3H), 1.57 – 1.47 (m, 2H), 1.41 – 1.30 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.25, 146.70, 141.41, 128.52, 126.36, 124.19, 121.04, 120.54, 116.07, 111.80, 60.96, 56.09, 18.33.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{NaO}_2^+$ 263.1043; Found 263.1041.

2-(1-phenylcyclopropoxy)-1,1'-biphenyl (**5b**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **5b** (59 mg) in 69%.

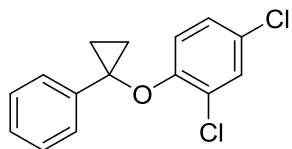
^1H NMR (400 MHz, Chloroform-*d*): δ 7.62 – 7.55 (m, 2H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.37 – 7.28 (m, 4H), 7.23 – 7.18 (m, 3H), 7.16 – 7.11 (m, 1H), 6.99 (t, $J = 7.1$ Hz, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.28 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.21, 141.73, 138.78, 131.02, 130.96, 129.71, 128.57, 128.15, 128.05, 126.93, 126.36, 124.17, 121.05, 115.93, 60.85, 18.40.

Physical State: colorless oil.

HRMS (APCI/QTOF) *m/z*: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{19}\text{O}^+$ 287.1430; Found 287.1431.

2,4-dichloro-1-(1-phenylcyclopropoxy)benzene (**5c**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **5c** (54 mg) in 65%.

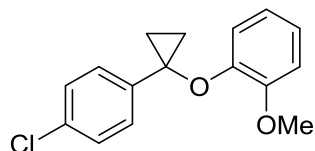
^1H NMR (400 MHz, Chloroform-*d*): δ 7.35 (d, $J = 2.5$ Hz, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 6.99 (dd, $J = 8.9, 2.5$ Hz, 1H), 6.86 (d, $J = 8.9$ Hz, 1H), 1.51 – 1.44 (m, 2H), 1.40 – 1.32 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 151.99, 140.27, 130.01, 128.77, 127.27, 126.88, 125.99, 124.20, 123.58, 117.28, 62.04, 17.76.

Physical State: colorless oil.

HRMS (APCI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃Cl₂O⁺ 279.0338; Found 279.0330.

1-(1-(4-chlorophenyl)cyclopropoxy)-2-methoxybenzene (5d)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **5d** (62 mg) in 75%.

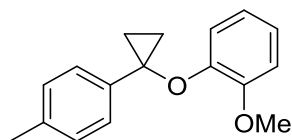
¹H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.22 (m, 2H), 7.21 – 7.10 (m, 2H), 7.01 – 6.81 (m, 3H), 6.76 (ddd, *J* = 8.1, 6.1, 2.8 Hz, 1H), 3.93 (s, 3H), 1.60 – 1.48 (m, 2H), 1.41 – 1.29 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 149.25, 146.37, 140.10, 132.18, 128.68, 125.69, 121.32, 120.51, 115.91, 111.83, 60.62, 56.04, 18.36.

Physical State: white solid.

HRMS (APCI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆ClO₂⁺ 275.0833; Found 275.0829.

1-methoxy-2-(1-(*p*-tolyl)cyclopropoxy)benzene (5e)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **5e** (62 mg) in 82%.

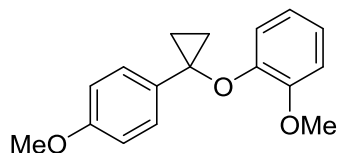
¹H NMR (400 MHz, Chloroform-*d*): δ 7.14 – 7.07 (m, 4H), 6.93 – 6.83 (m, 3H), 6.73 (ddd, *J* = 8.0, 7.1, 2.1 Hz, 1H), 3.91 (s, 3H), 2.30 (s, 3H), 1.53 – 1.45 (m, 2H), 1.35 – 1.29 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 149.24, 146.78, 138.32, 135.97, 129.24, 124.24, 120.96, 120.54, 116.08, 111.77, 60.95, 56.08, 21.09, 18.01.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₈NaO₂⁺ 277.1199; Found 277.1200.

1-methoxy-2-(1-(4-methoxyphenyl)cyclopropoxy)benzene (5f)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **5f** (64 mg) in 79%.

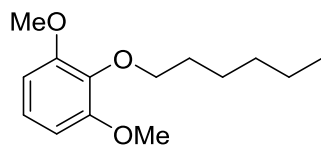
¹H NMR (400 MHz, Chloroform-*d*): δ 7.22 – 7.10 (m, 2H), 6.95 – 6.80 (m, 5H), 6.73 (ddd, J = 8.0, 6.8, 2.3 Hz, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 1.50 – 1.41 (m, 2H), 1.30 – 1.25 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 158.33, 149.30, 146.75, 133.18, 125.81, 120.99, 120.52, 116.15, 113.97, 111.77, 60.92, 56.07, 55.36, 17.41.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z : $[M + Na]^+$ Calcd for $C_{17}H_{18}NaO_3^+$ 293.1148; Found 293.1153

2-(hexyloxy)-1,3-dimethoxybenzene (6a)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6a** (53 mg) in 74%.

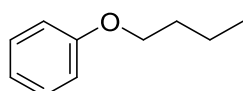
¹H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, J = 8.4 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 3.96 (t, J = 6.9 Hz, 2H), 3.84 (s, 6H), 1.76 (p, J = 7.0 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.36 – 1.26 (m, 5H), 0.91 – 0.84 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.93, 137.72, 123.46, 105.55, 73.64, 56.26, 31.83, 30.22, 25.70, 22.82, 14.23.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) m/z : $[M + Na]^+$ Calcd for $C_{14}H_{22}NaO_3^+$ 261.1461; Found 261.1463.

butoxybenzene (6b)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **6b** (25 mg) in 56%.

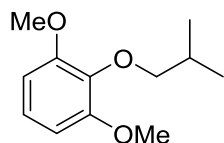
¹H NMR (400 MHz, Chloroform-*d*): δ 7.29 (t, J = 7.8 Hz, 2H), 7.08 – 6.84 (m, 3H), 3.98 (t, J = 6.5 Hz, 2H), 1.85 – 1.71 (m, 2H), 1.51 (h, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.29, 129.53, 120.58, 114.64, 67.70, 31.52, 19.42, 14.01.

Physical State: colorless oil.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.¹²

2-isobutoxy-1,3-dimethoxybenzene (**6c**)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6c** (44 mg) in 70%.

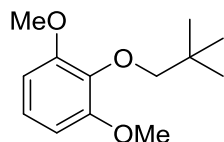
¹H NMR (400 MHz, Chloroform-*d*): δ 6.96 (t, J = 8.4 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 3.84 (s, 6H), 3.73 (d, J = 6.7 Hz, 2H), 2.07 (dp, J = 13.4, 6.7 Hz, 1H), 1.02 (d, J = 6.7 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.87, 138.16, 123.36, 105.78, 80.27, 56.34, 29.20, 19.45.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) m/z: [M + Na]⁺ Calcd for C₁₂H₁₈NaO₃⁺ 233.1148; Found 233.1149.

1,3-dimethoxy-2-(neopentyloxy)benzene (**6d**)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6d** (33 mg) in 49%.

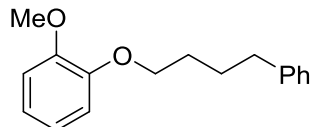
¹H NMR (400 MHz, Chloroform-*d*): δ 6.95 (t, J = 8.3 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 3.83 (s, 6H), 3.62 (s, 2H), 1.06 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.90, 138.79, 123.25, 106.16, 83.59, 56.49, 32.59, 26.71.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}NaO_3^+$ 247.1305; Found 247.1304.

1-methoxy-2-(4-phenylbutoxy)benzene (6e)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6e** (61 mg) in 79%.

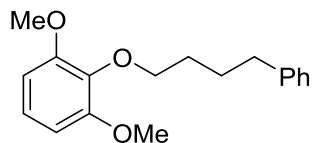
1H NMR (400 MHz, Chloroform-*d*): δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 6.90 (td, $J = 5.9$, 3.1 Hz, 4H), 4.05 (t, $J = 6.5$ Hz, 2H), 3.87 (s, 3H), 2.71 (t, $J = 7.4$ Hz, 2H), 1.98 – 1.75 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 149.63, 148.69, 142.35, 128.56, 128.41, 125.87, 121.05, 120.95, 113.36, 112.00, 68.95, 56.06, 35.72, 28.94, 27.92.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}NaO_2^+$ 279.1356; Found 279.1352.

1,3-dimethoxy-2-(4-phenylbutoxy)benzene (6f)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6f** (75 mg) in 87%.

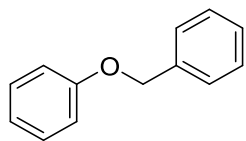
1H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 6.98 (t, $J = 8.4$ Hz, 1H), 6.58 (d, $J = 8.4$ Hz, 2H), 4.04 – 3.96 (m, 2H), 3.83 (s, 6H), 2.72 – 2.65 (m, 2H), 1.86 – 1.78 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 153.92, 142.80, 137.61, 128.60, 128.36, 125.75, 123.55, 105.51, 73.22, 56.24, 35.80, 29.91, 27.90.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_3^+$ 287.1642; Found 287.1643.

(benzyloxy)benzene (6g)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6g** (33 mg) in 60%.

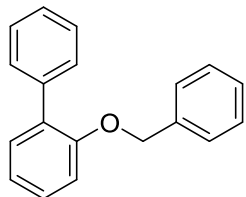
¹H NMR (400 MHz, Chloroform-*d*): δ 7.50 – 7.37 (m, 4H), 7.37 – 7.27 (m, 3H), 7.04 – 6.93 (m, 3H), 5.08 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 158.93, 137.23, 129.62, 128.71, 128.07, 127.61, 121.08, 115.00, 70.06.

Physical State: colorless solid.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.¹³

2-(benzyloxy)-1,1'-biphenyl (6h)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6h** (56 mg) in 72%.

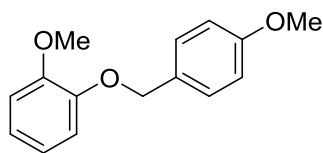
¹H NMR (400 MHz, Chloroform-*d*): δ 7.72 – 7.54 (m, 2H), 7.51 – 7.27 (m, 10H), 7.14 – 7.00 (m, 2H), 5.12 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 155.72, 138.65, 137.38, 131.54, 131.13, 129.78, 128.69, 128.53, 128.03, 127.69, 127.02, 126.95, 121.48, 113.55, 70.58.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₉H₁₇O⁺ 261.1274; Found 261.1278.

1-methoxy-2-((4-methoxybenzyl)oxy)benzene (6i)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **6i** (53 mg) in 72%.

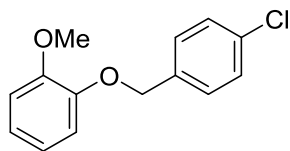
¹H NMR (400 MHz, Chloroform-*d*): δ 7.37 (d, *J* = 8.3 Hz, 2H), 6.96 – 6.84 (m, 6H), 5.08 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.45, 149.93, 148.37, 129.44, 129.13, 121.52, 120.90, 114.53, 114.05, 112.07, 77.36, 70.97, 56.07, 55.40.

Physical State: white solid.

HRMS (APCI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₆NaO₃⁺ 267.0992; Found 267.0987.

1-((4-chlorobenzyl)oxy)-2-methoxybenzene (6j)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **6j** (51 mg) in 68%.

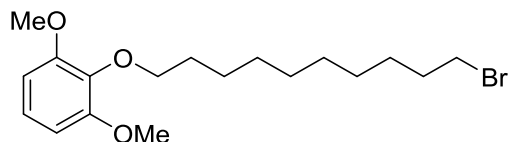
¹H NMR (400 MHz, Chloroform-*d*): δ 7.43 – 7.30 (m, 4H), 7.00 – 6.82 (m, 4H), 5.12 (s, 2H), 3.89 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 149.87, 147.99, 135.87, 133.64, 128.77, 128.72, 121.85, 120.87, 114.47, 112.08, 70.40, 55.99.

Physical State: yellow oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₄H₁₃ClNaO₂⁺ 271.0496; Found 271.0497.

2-((10-bromodecyl)oxy)-1,3-dimethoxybenzene (6k)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **6k** (95 mg) in 85%.

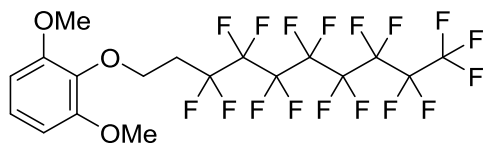
¹H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 1.85 (p, *J* = 7.0 Hz, 2H), 1.75 (p, *J* = 7.0 Hz, 2H), 1.49 – 1.27 (m, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.90, 137.67, 123.46, 105.52, 73.58, 56.25, 34.17, 32.97, 30.22, 29.63, 29.52, 28.90, 28.31, 25.98.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₈H₂₉BrNaO₃⁺ 395.1192; Found 395.1196.

2-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)oxy)-1,3-dimethoxybenzene (**6l**)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **6l** (119 mg) in 66%.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.15 (t, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 6H), 3.02 – 2.84 (m, 2H), 2.61 (tt, *J* = 18.1, 8.0 Hz, 2H).

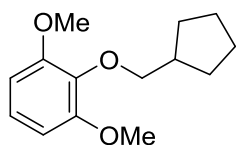
¹³C NMR (101 MHz, Chloroform-*d*): δ 169.23, 152.36, 128.62, 126.68, 104.97, 56.23, 26.90 (t, *J* = 22.2 Hz), 25.35 (t, *J* = 4.1 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -80.81 (t, *J* = 10.0 Hz), -114.66 (t, *J* = 14.1 Hz), -121.68, -121.91, -122.72, -123.45, -126.12.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₈H₁₄F₁₇O₃⁺ 601.0666; Found 601.0661.

2-(cyclopentylmethoxy)-1,3-dimethoxybenzene (**6m**)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **6m** (28 mg) in 40%.

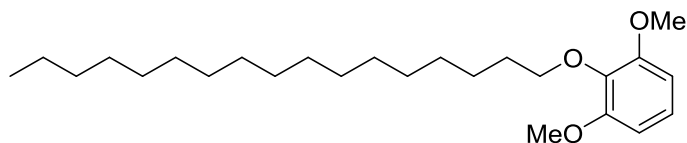
¹H NMR (400 MHz, Chloroform-*d*): δ 6.96 (t, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.88 – 3.78 (m, 8H), 2.37 (hept, *J* = 7.6 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.63 – 1.54 (m, 4H), 1.45 – 1.35 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.92, 137.99, 123.41, 105.71, 77.92, 56.33, 39.99, 29.57, 25.68.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₄H₂₀NaO₃⁺ 259.1305; Found 259.1307.

2-(heptadecyloxy)-1,3-dimethoxybenzene (**7a**)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **7a** (91 mg) in 77%.

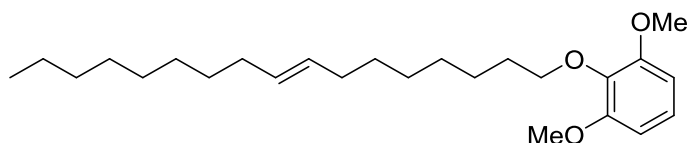
¹H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.84 (s, 6H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.26 (m, 30H), 0.87 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.92, 137.70, 123.45, 105.53, 73.63, 56.24, 32.07, 30.25, 29.84, 29.80, 29.61, 29.51, 26.02, 22.83, 14.25.

Physical State: white solid.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₅H₄₄NaO₃⁺ 415.3183; Found 415.3180.

(*E*)-2-(heptadec-8-en-1-yloxy)-1,3-dimethoxybenzene (**7b**)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **7b** (88 mg) in 75%.

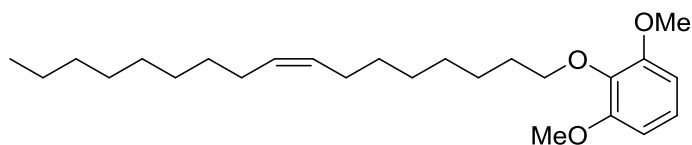
¹H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.39 (td, *J* = 3.8, 1.9 Hz, 2H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 6H), 1.96 (dt, *J* = 8.0, 4.2 Hz, 4H), 1.75 (p, *J* = 7.0 Hz, 2H), 1.51 – 1.22 (m, 20H), 0.88 (t, *J* = 6.5 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.93, 137.71, 130.53, 130.45, 123.46, 105.54, 73.61, 56.26, 32.76, 32.05, 30.25, 29.81, 29.78, 29.64, 29.47, 29.34, 29.30, 25.99, 22.83, 14.26.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₅H₄₂NaO₃⁺ 413.3026; Found 413.3028.

(Z)-2-(heptadec-8-en-1-yloxy)-1,3-dimethoxybenzene (7c)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **7c** (82 mg) in 70%.

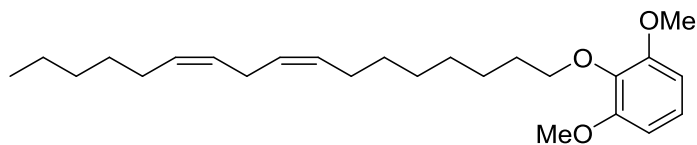
¹H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.42 – 5.27 (m, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.84 (s, 6H), 2.06 – 1.94 (m, 4H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.48 – 1.19 (m, 20H), 0.88 (t, *J* = 6.5 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.92, 137.70, 130.07, 129.98, 123.46, 105.53, 73.60, 56.25, 32.05, 30.23, 29.92, 29.90, 29.85, 29.67, 29.50, 29.47, 29.45, 27.37, 25.99, 22.82, 14.25.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₅H₄₂NaO₃⁺ 413.3026; Found 413.3028.

2-(((8Z,11Z)-heptadeca-8,11-dien-1-yl)oxy)-1,3-dimethoxybenzene (7d)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **7d** (83 mg) in 71%.

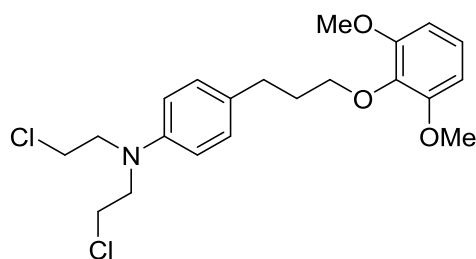
¹H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.35 (tq, *J* = 10.9, 6.8, 5.4 Hz, 4H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 6H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.09 – 2.00 (m, 4H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.51 – 1.24 (m, 13H), 0.89 (t, *J* = 6.7 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.91, 137.69, 130.33, 130.27, 128.11, 128.07, 123.46, 105.53, 73.58, 56.24, 31.66, 30.23, 29.79, 29.49, 29.44, 27.39, 27.34, 25.98, 25.77, 22.71, 14.20.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₅H₄₀NaO₃⁺ 411.2870; Found 411.2879.

***N,N*-bis(2-chloroethyl)-4-(3-(2,6-dimethoxyphenoxy)propyl)aniline (7e)**



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7e** (60 mg) in 49%.

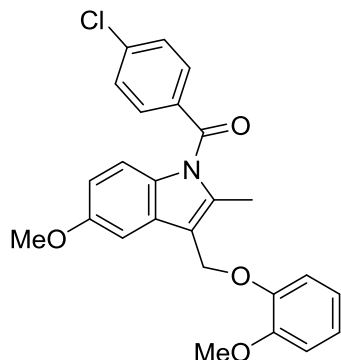
¹H NMR (400 MHz, Chloroform-*d*): δ 7.18 – 7.07 (m, 2H), 6.98 (t, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 18.0, 8.5 Hz, 4H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 6H), 3.74 – 3.66 (m, 4H), 3.62 (m, 4H), 2.80 – 2.68 (m, 2H), 2.08 – 1.95 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 153.90, 144.27, 137.57, 131.74, 129.88, 123.57, 112.32, 105.54, 72.85, 56.26, 53.81, 40.71, 32.24, 31.24.

Physical State: light brown oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₁H₂₇Cl₂NNaO₃⁺ 434.1260; Found 434.1264

(4-chlorophenyl)(5-methoxy-3-((2-methoxyphenoxy)methyl)-2-methyl-1*H*-indol-1-yl)methanone (7f)



Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7f** (86 mg) in 66%.

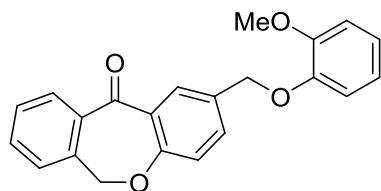
¹H NMR (400 MHz, Chloroform-*d*): δ 7.68 – 7.61 (m, 2H), 7.50 – 7.44 (m, 2H), 7.17 (d, J = 2.6 Hz, 1H), 7.05 – 6.96 (m, 2H), 6.96 – 6.88 (m, 2H), 6.83 (d, J = 9.0 Hz, 1H), 6.67 (dd, J = 9.0, 2.6 Hz, 1H), 5.22 (s, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 2.42 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 168.56, 156.20, 150.66, 148.18, 139.52, 137.17, 133.90, 131.40, 131.12, 130.58, 129.26, 122.37, 120.96, 116.05, 115.39, 114.93, 112.27, 112.15, 101.85, 63.11, 56.03, 55.82, 13.41.

Physical State: bright yellow oil.

HRMS (APPI/LTQ-Orbitrap) m/z : $[M + H]^+$ Calcd for C₂₅H₂₃ClNO₄⁺ 436.1310; Found 436.1300.

2-((2-methoxyphenoxy)methyl)dibenzo[b,e]oxepin-11(6*H*)-one (7g)



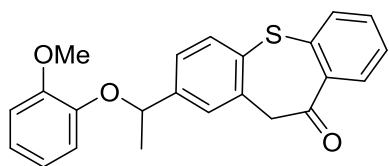
Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7g** (76 mg) in 73%.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.29 (d, *J* = 2.3 Hz, 1H), 7.90 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.63 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.56 (td, *J* = 7.4, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.3 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.96 – 6.84 (m, 4H), 5.19 (s, 2H), 5.14 (s, 2H), 3.89 (s, 3H).
¹³C NMR (101 MHz, Chloroform-*d*): δ 190.95, 161.16, 150.00, 148.15, 140.59, 135.67, 134.94, 132.90, 131.20, 129.61, 129.41, 127.94, 125.20, 121.86, 121.30, 120.94, 114.74, 112.12, 73.78, 70.60, 56.07.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₂H₁₈NaO₄⁺ 369.1097; Found 369.1095.

2-(1-(2-methoxyphenoxy)ethyl)dibenzo[b,f]thiepin-10(11*H*)-one (7h)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7h** (78 mg) in 69%.

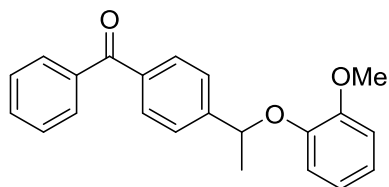
¹H NMR (400 MHz, Chloroform-*d*): δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 – 7.56 (m, 2H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.44 (td, *J* = 7.6, 1.7 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.00 – 6.82 (m, 2H), 6.82 – 6.61 (m, 2H), 5.33 (q, *J* = 6.5 Hz, 1H), 4.39 (s, 2H), 3.91 (s, 3H), 1.66 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 191.49, 150.36, 147.23, 145.77, 140.37, 137.93, 136.30, 133.50, 132.61, 131.64, 131.58, 130.97, 126.94, 126.89, 124.67, 121.97, 120.82, 116.69, 112.28, 76.93, 56.09, 51.27, 24.28.

Physical State: pale yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₀NaO₃S⁺ 399.1025; Found 399.1037.

(4-(1-(2-methoxyphenoxy)ethyl)phenyl)(phenyl)methanone (7i)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7i** (75 mg) in 75%.

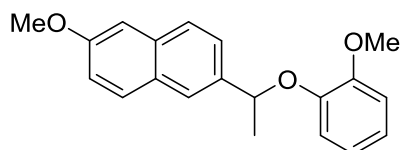
¹H NMR (400 MHz, Chloroform-*d*): δ 7.82 (s, 1H), 7.77 – 7.63 (m, 4H), 7.62 – 7.54 (m, 1H), 7.45 (td, J = 7.6, 3.6 Hz, 3H), 6.94 – 6.82 (m, 2H), 6.82 – 6.69 (m, 2H), 5.40 (q, J = 6.5 Hz, 1H), 3.84 (s, 3H), 1.71 (d, J = 6.5 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 196.72, 150.45, 147.21, 143.62, 137.87, 137.69, 132.52, 130.21, 129.96, 129.40, 128.74, 128.40, 127.68, 121.99, 120.82, 116.92, 112.36, 77.06, 56.07, 24.20.

Physical State: white solid.

HRMS (APPI/LTQ-Orbitrap) m/z : $[M + H]^+$ Calcd for C₂₂H₂₁O₃⁺ 333.1485; Found 333.1485.

2-methoxy-6-(1-(2-methoxyphenoxy)ethyl)naphthalene (**7j**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7j** (73 mg) in 79%.

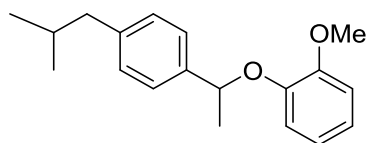
¹H NMR (400 MHz, Chloroform-*d*): δ 7.77 (d, J = 1.7 Hz, 1H), 7.72 (t, J = 8.5 Hz, 2H), 7.54 (dd, J = 8.4, 1.8 Hz, 1H), 7.18 – 7.10 (m, 2H), 6.93 – 6.83 (m, 2H), 6.81 (dd, J = 8.0, 1.5 Hz, 1H), 6.72 (ddd, J = 8.2, 6.9, 2.1 Hz, 1H), 5.45 (q, J = 6.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 1.77 (d, J = 6.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 157.75, 150.33, 147.66, 138.57, 134.15, 129.53, 128.89, 127.32, 124.56, 124.51, 121.55, 120.82, 118.97, 116.69, 112.24, 105.81, 77.68, 56.16, 55.42, 24.46.

Physical State: white solid.

HRMS (ESI/QTOF) m/z : $[M + Na]^+$ Calcd for C₂₀H₂₀NaO₃⁺ 331.1305; Found 331.1311.

1-(1-(4-isobutylphenyl)ethoxy)-2-methoxybenzene (**7k**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7k** (68 mg) in 80%.

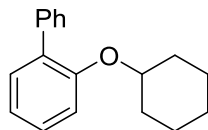
¹H NMR (400 MHz, Chloroform-*d*): δ 7.35 – 7.27 (m, 2H), 7.15 – 7.07 (m, 2H), 6.93 – 6.82 (m, 2H), 6.81 – 6.72 (m, 2H), 5.29 (q, *J* = 6.4 Hz, 1H), 3.89 (s, 3H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.68 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 3H), 0.88 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 150.34, 147.74, 140.95, 140.58, 129.33, 125.62, 121.44, 120.82, 116.60, 112.27, 77.41, 56.18, 45.28, 30.31, 24.31, 22.54, 22.53.

Physical State: yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [*M*]⁺ Calcd for C₁₉H₂₄O₂⁺ 284.1771; Found 284.1774.

2-(cyclohexyloxy)-1,1'-biphenyl (**7l**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 30/1 (v/v) as an eluent, to yield the title compound **7l** (64 mg) in 85%.

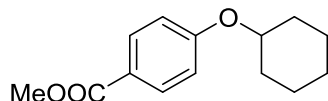
¹H NMR (400 MHz, Chloroform-*d*): δ 7.60 – 7.52 (m, 2H), 7.41 – 7.25 (m, 6H), 7.01 (t, *J* = 7.5 Hz, 2H), 4.20 (tt, *J* = 8.1, 3.7 Hz, 1H), 1.91 – 1.77 (m, 2H), 1.70 – 1.60 (m, 2H), 1.53 – 1.44 (m, 3H), 1.33 – 1.23 (m, 4H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 154.89, 139.06, 132.23, 131.19, 129.78, 128.46, 127.85, 126.75, 121.00, 115.19, 76.14, 31.75, 25.77, 23.57.

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [*M* + H]⁺ Calcd for C₁₈H₂₁O⁺ 253.1587; Found 253.1589.

methyl 4-(cyclohexyloxy)benzoate (**7m**)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **7m** (43 mg) in 61%.

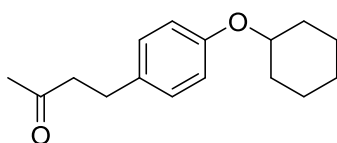
¹H NMR (400 MHz, Chloroform-*d*): δ 7.96 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.33 (tt, *J* = 8.7, 3.8 Hz, 1H), 3.87 (s, 3H), 2.06 – 1.90 (m, 2H), 1.87 – 1.74 (m, 2H), 1.54 (td, *J* = 12.6, 11.3, 7.8 Hz, 3H), 1.43 – 1.27 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 167.06, 161.90, 131.71, 122.21, 115.27, 75.54, 51.94, 31.76, 25.66, 23.80.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₉O₃⁺ 235.1329; Found 235.1327.

4-(4-(cyclohexyloxy)phenyl)butan-2-one (7n)



Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 20/1 (v/v) as an eluent, to yield the title compound **7n** (52 mg) in 71%.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.06 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.18 (tt, *J* = 8.8, 3.8 Hz, 1H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.13 (s, 3H), 2.05 – 1.89 (m, 2H), 1.89 – 1.70 (m, 2H), 1.59 – 1.41 (m, 3H), 1.39 – 1.25 (m, 3H).

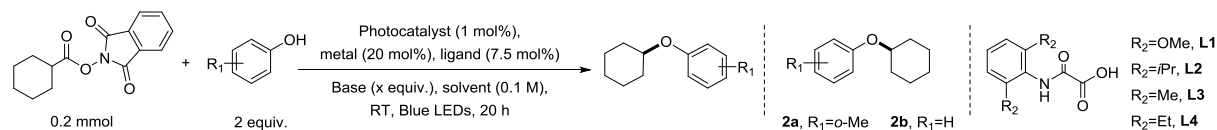
¹³C NMR (101 MHz, Chloroform-*d*): δ 156.27, 132.99, 129.30, 116.31, 75.69, 45.61, 32.02, 30.24, 29.07, 25.78, 23.95.

Physical State: white solid.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₆H₂₂NaO₂⁺ 269.1512; Found 269.1512.

Tables

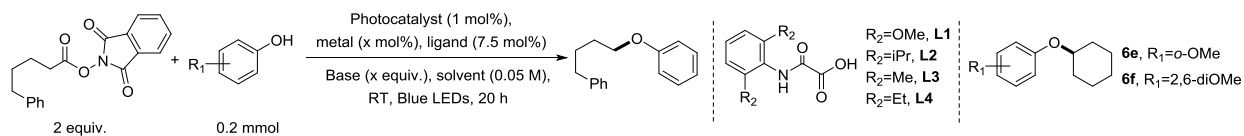
Table S1. Optimization of reaction parameters for secondary NHPI ester



Entry	Nucleophile	Photocatalyst	Metal	Ligand	Base	Solvent	GC yield ^a
1	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	L1	Et ₃ N (5 equiv.)	MeCN	16%
2	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	L2	Et ₃ N (5 equiv.)	MeCN	14%
3	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	L3	Et ₃ N (5 equiv.)	MeCN	9%
4	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	L4	Et ₃ N (5 equiv.)	MeCN	12%
5	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	PCy ₃	Et ₃ N (5 equiv.)	MeCN	trace
6	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	dtbbpy	Et ₃ N (5 equiv.)	MeCN	trace
7	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	w/o ligand	Et ₃ N (5 equiv.)	MeCN	19%
8	2a	Ru(bpy) ₃ (PF ₆) ₂	CuTc	w/o ligand	Et ₃ N (5 equiv.)	MeCN	16%
9	2a	Ru(bpy) ₃ (PF ₆) ₂	CuOAc	w/o ligand	Et ₃ N (5 equiv.)	MeCN	17%
10	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	Et ₃ N (5 equiv.)	MeCN	22%
11	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl (40 mol%)	w/o ligand	Et ₃ N (5 equiv.)	MeCN	31%
12	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu (100 mol%)	w/o ligand	Et ₃ N (5 equiv.)	MeCN	9%
13	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl ₂	w/o ligand	Et ₃ N (5 equiv.)	MeCN	11%
14	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	Cs ₂ CO ₃ (2 equiv.)	MeCN	trace
15	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	K ₂ CO ₃ (2 equiv.)	MeCN	trace
16	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	DBU (2 equiv.)	MeCN	trace
17	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	DIPEA (2 equiv.)	MeCN	trace
18	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	quinuclidine (2 equiv.)	MeCN	trace
19	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	Et ₃ N (5 equiv.)	DMF	trace
20	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	Et ₃ N (5 equiv.)	THF	trace
21	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	Et ₃ N (5 equiv.)	DCM	32%
22	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	Et ₃ N (3 equiv.)	DCM	40%
23	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	w/o ligand	Et ₃ N (2 equiv.)	DCM	44%
24	2a	Ir(ppy) ₃	CuCl	w/o ligand	Et ₃ N (2 equiv.)	DCM	39%
25	2a	[Ir(dFCF ₃ ppy) ₂ (dtbbpy)]PF ₆	CuCl	w/o ligand	Et ₃ N (2 equiv.)	DCM	21%
26	2a	Ir[(ppy) ₂ (dtbbpy)]PF ₆	CuCl	w/o ligand	Et ₃ N (2 equiv.)	DCM	62%
27	2a	Ir[(ppy) ₂ (dtbbpy)]PF ₆	CuCl (40 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM	71%
28	2a	Ir[(ppy) ₂ (dtbbpy)]PF ₆	CuOAc	w/o ligand	Et ₃ N (2 equiv.)	DCM	65%
29	2a	Ir[(ppy) ₂ (dtbbpy)]PF ₆	(CuOTf) ₂ ·C ₆ H ₆ (10 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM	82%
30	2a	Ir[(ppy) ₂ (dtbbpy)]PF ₆	(CuOTf) ₂ ·C ₆ H ₆ (10 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM (0.05 M)	94%
31	2b	Ir[(ppy) ₂ (dtbbpy)]PF ₆	(CuOTf) ₂ ·C ₆ H ₆ (10 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM (0.05 M)	90%

^aCorrected GC yield, *n*-dodecane as an internal standard. ^b1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).

Table S2. Optimization of reaction parameters for primary NHPI ester



Entry	Nu	Photocatalyst	Metal	Ligand	Base	Solvent	GC yield ^a
1	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl (20 mol%)	w/o ligand	Et ₃ N (3 equiv.)	MeCN	9%
2	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (10 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM	16%
3	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (10 mol%)	w/o ligand	w/o base	DCM	trace
4	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(PPh ₃)Br (20 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM	trace
5	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (20 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM	20%
6	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (10 mol%)	L1	Et ₃ N (2 equiv.)	DCM	trace
7	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (10 mol%)	L2	Et ₃ N (2 equiv.)	DCM	trace
8	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (10 mol%)	L3	Et ₃ N (2 equiv.)	DCM	trace
9	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (10 mol%)	PCy ₃	Et ₃ N (2 equiv.)	DCM	trace
10	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	(Cu(OTf) ₂ ·C ₆ H ₆) (10 mol%)	dtbbpy	Et ₃ N (2 equiv.)	DCM	trace
11	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ PF ₆ (20 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM	21%
12	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	Et ₃ N (2 equiv.)	DCM	25%
13	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	Cs ₂ CO ₃ (1 equiv.)	DMA	trace ^b
14	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	DABCO (1 equiv.)	DCM	9%
15	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	DIPEA (1 equiv.)	DCM	26%
16	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	Piperidine (1 equiv.)	DCM	trace
17	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	DBU (1 equiv.) ^b	DCM	trace
18	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	BTMG (1 equiv.) ^c	DCM	trace
19	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	Diisopropylamine (1 equiv.)	DCM	35%
20	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	Dicyclohexylamine (1 equiv.)	DCM	21%
21	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	Di- <i>sec</i> -butylamine (1 equiv.)	DCM	28%
22	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	<i>N</i> -Isopropyl- <i>tert</i> -butylamine (1 equiv.)	DCM	32%
23	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (20 mol%)	w/o ligand	<i>N</i> -Isopropyl- <i>N</i> -Methyl- <i>tert</i> -butylamine (1 equiv.)	DCM	43%
24	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (40 mol%)	w/o ligand	<i>N</i> -Isopropyl- <i>N</i> -Methyl- <i>tert</i> -butylamine (1 equiv.)	DCM	65%
25 ^d	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (40 mol%)	w/o ligand	<i>N</i> -Isopropyl- <i>N</i> -Methyl- <i>tert</i> -butylamine (1 equiv.)	DCM	79%
26 ^d	2b	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ OTf (40 mol%)	w/o ligand	<i>N</i> -Isopropyl- <i>N</i> -Methyl- <i>tert</i> -butylamine (1 equiv.)	DCM	87%

^aCorrected GC yield, *n*-dodecane as an internal standard. ^b1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). ^c2-*tert*-Butyl-1,1,3,3-tetramethylguanidine (BTMG). ^d0-RT

Figures

Figure S1. Fluorescence quenching experiments I

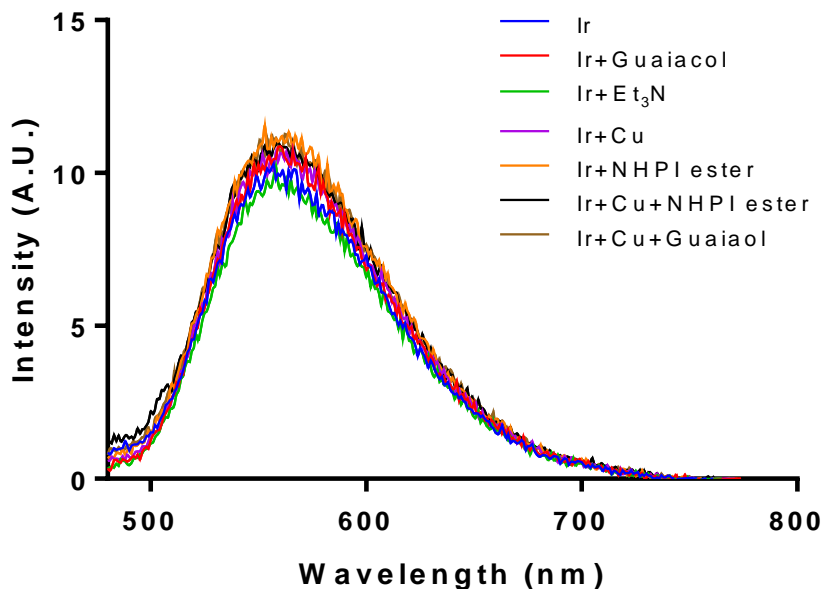


Figure S2. Fluorescence quenching experiments II; quenching is done with a mixture (1:1 molar ratio) of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ and Et_3N .

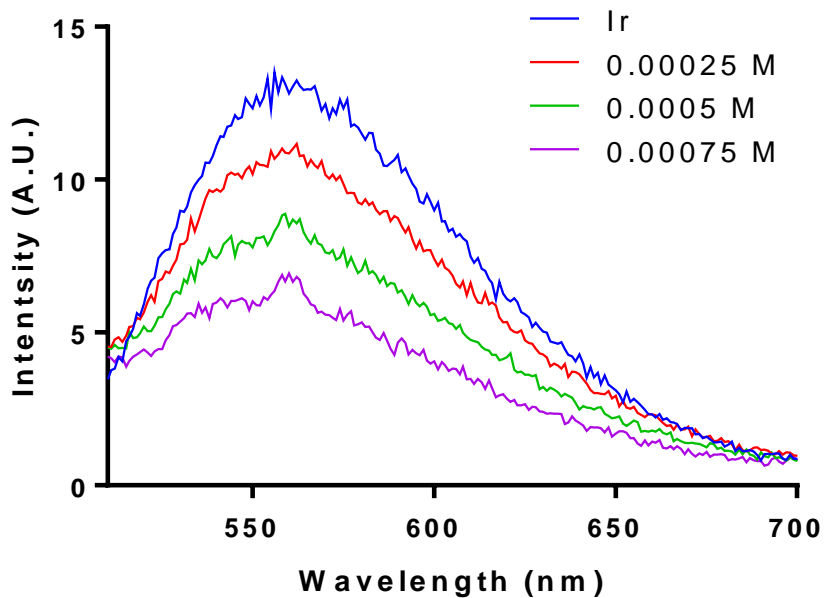


Figure S3. Stern-Volmer kinetic analysis

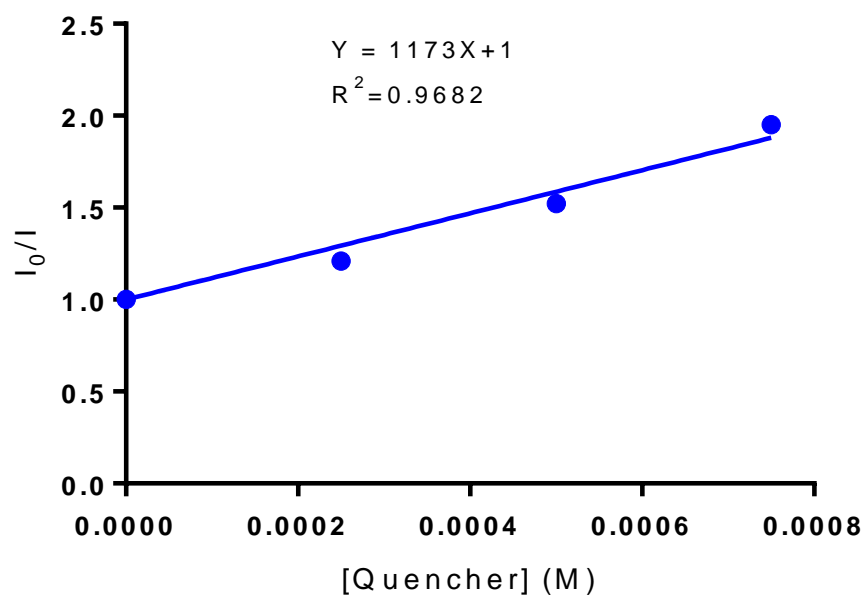


Figure S4. NMR spectra of 3a

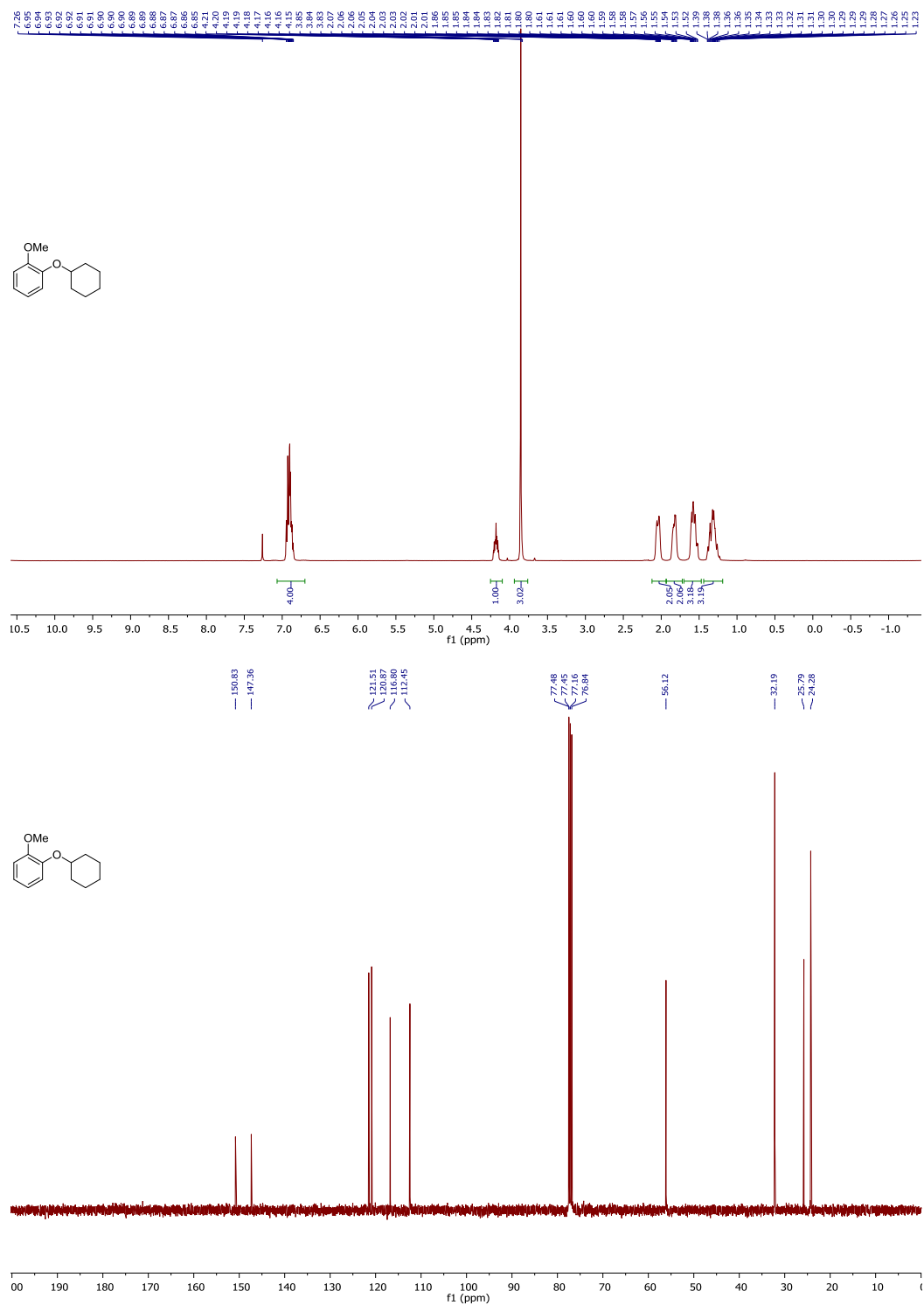


Figure S5. NMR spectra of 3b

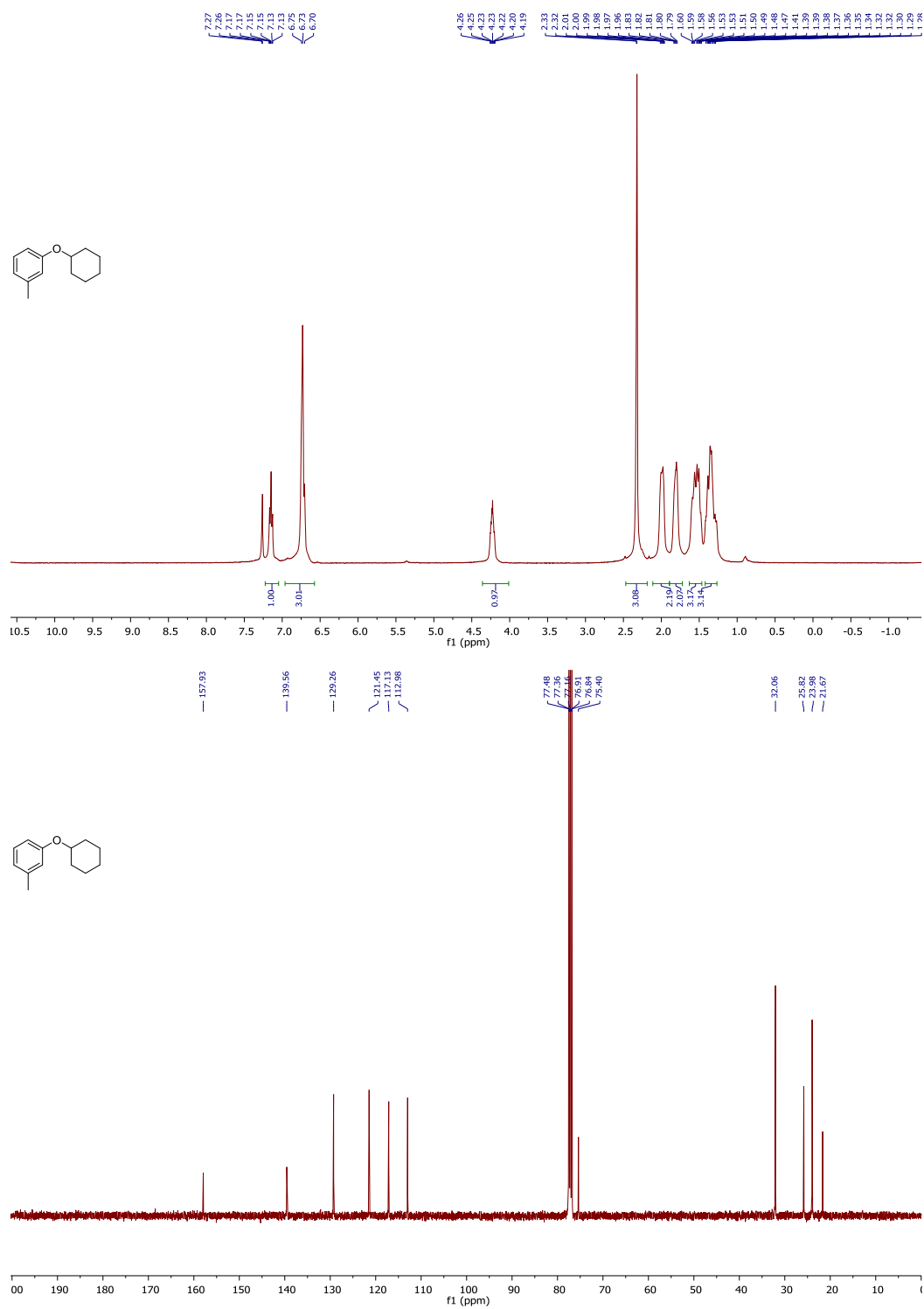


Figure S6. NMR spectra of 3c

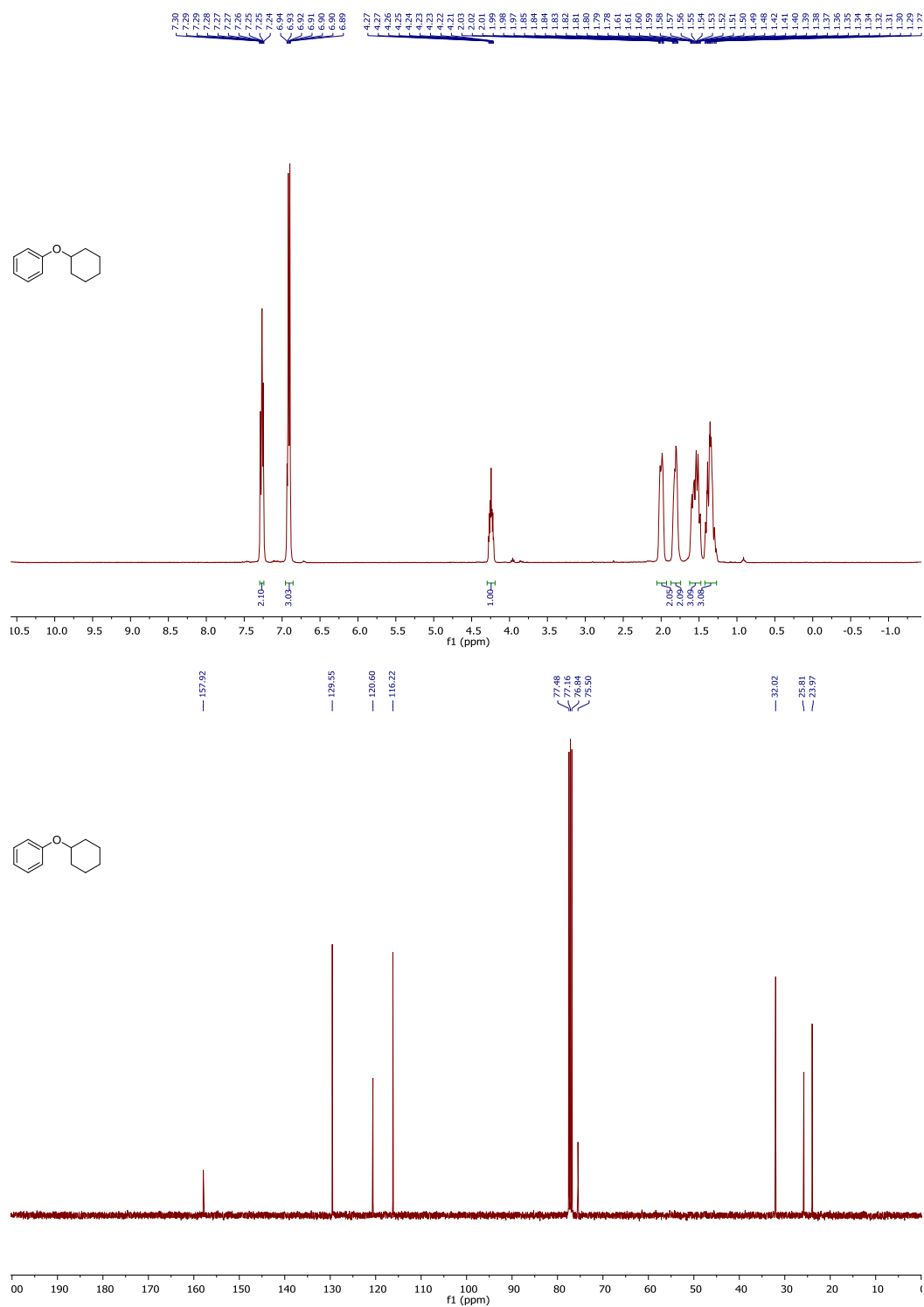


Figure S7. NMR spectra of 3d

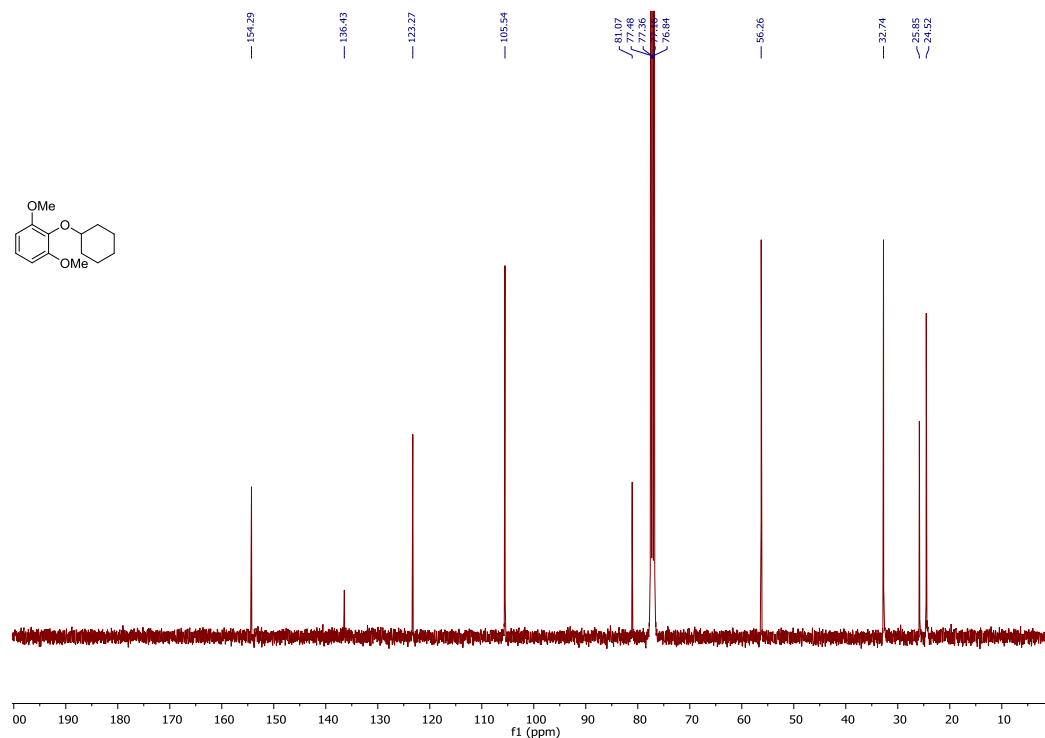
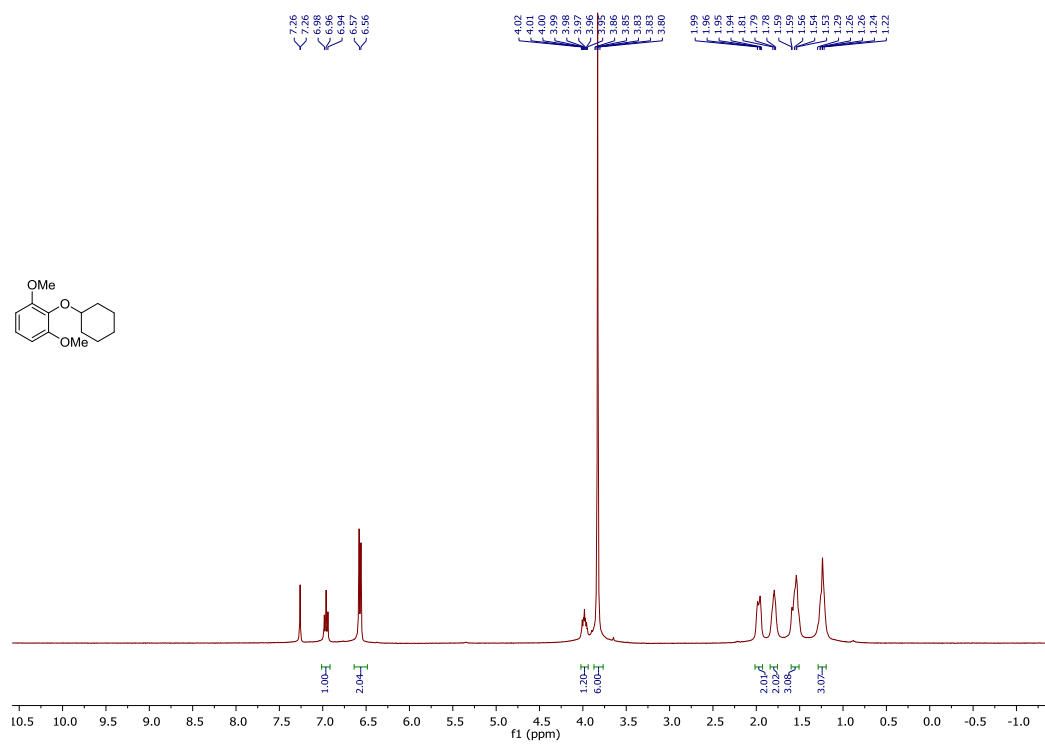


Figure S8. NMR spectra of 3e

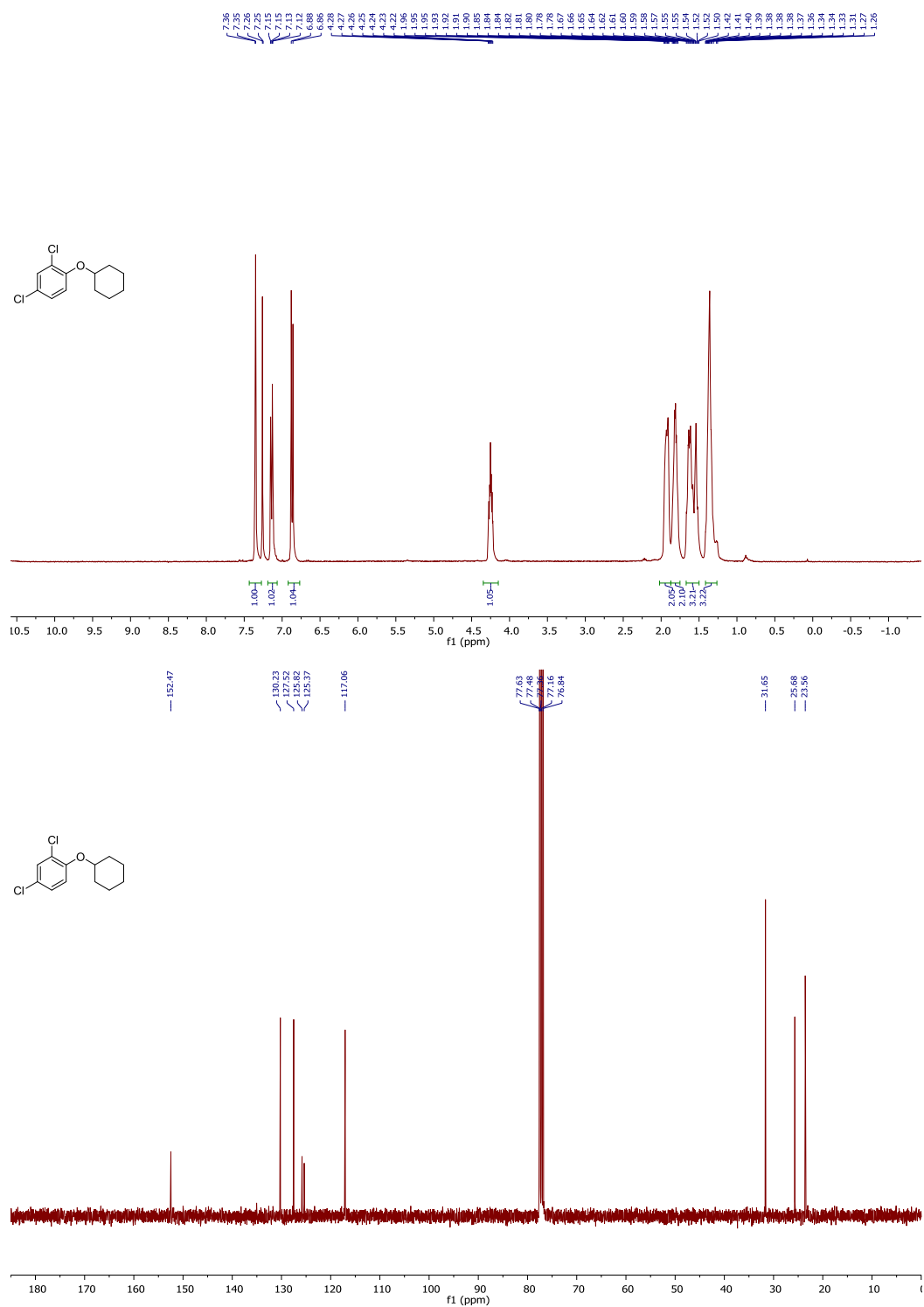


Figure S9. NMR spectra of 3f

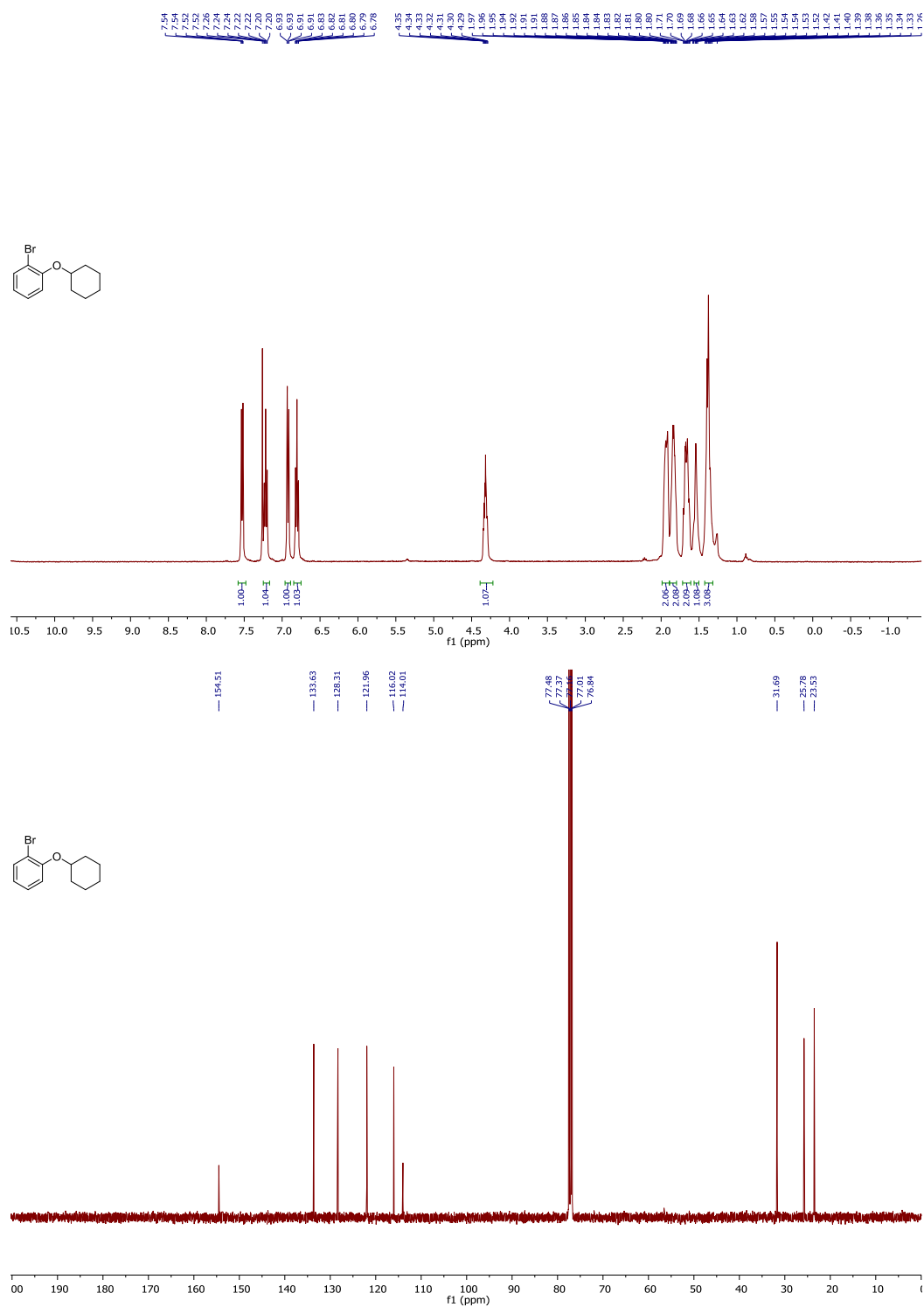


Figure S10. NMR spectra of 3g

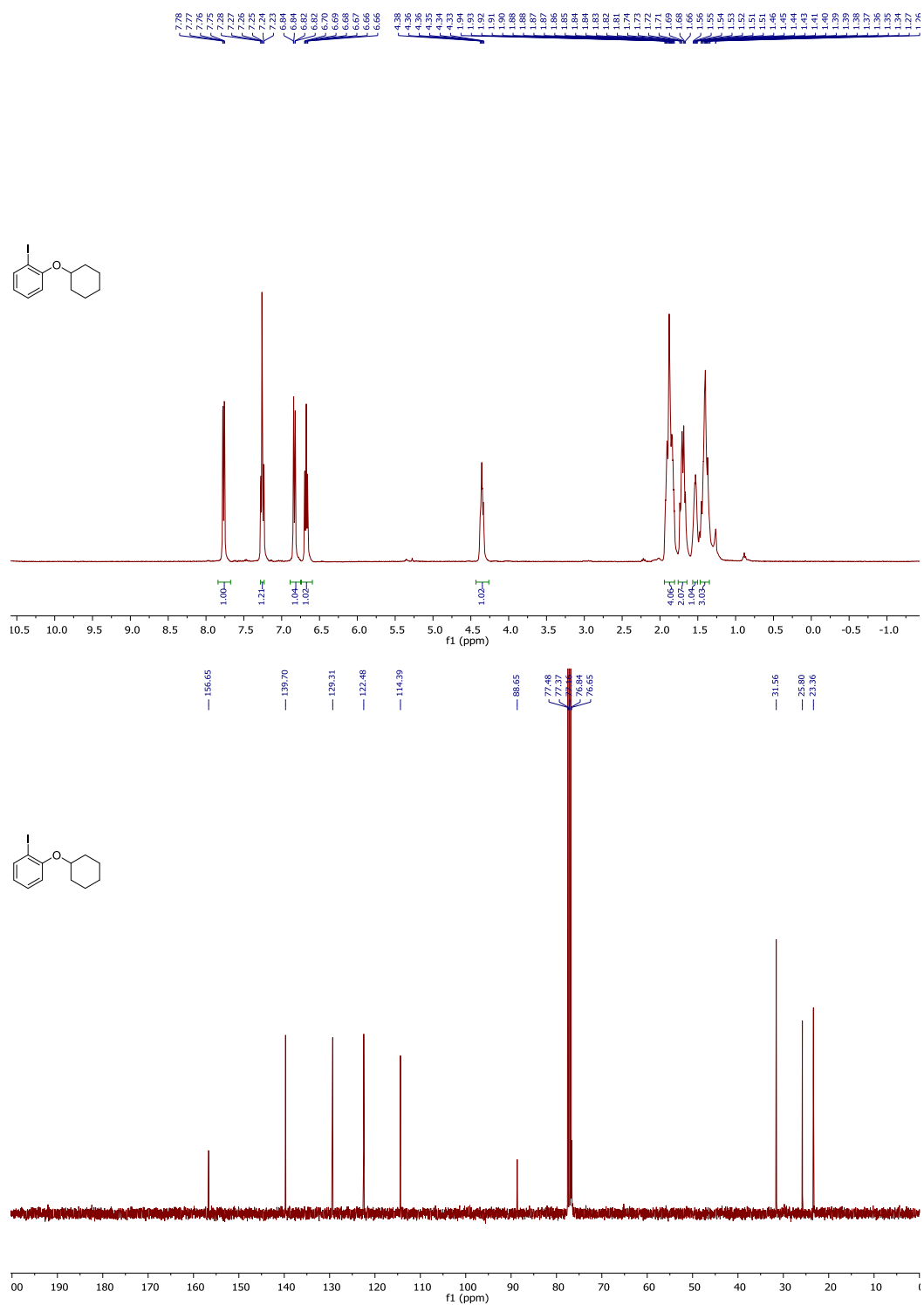


Figure S11. NMR spectra of 3h

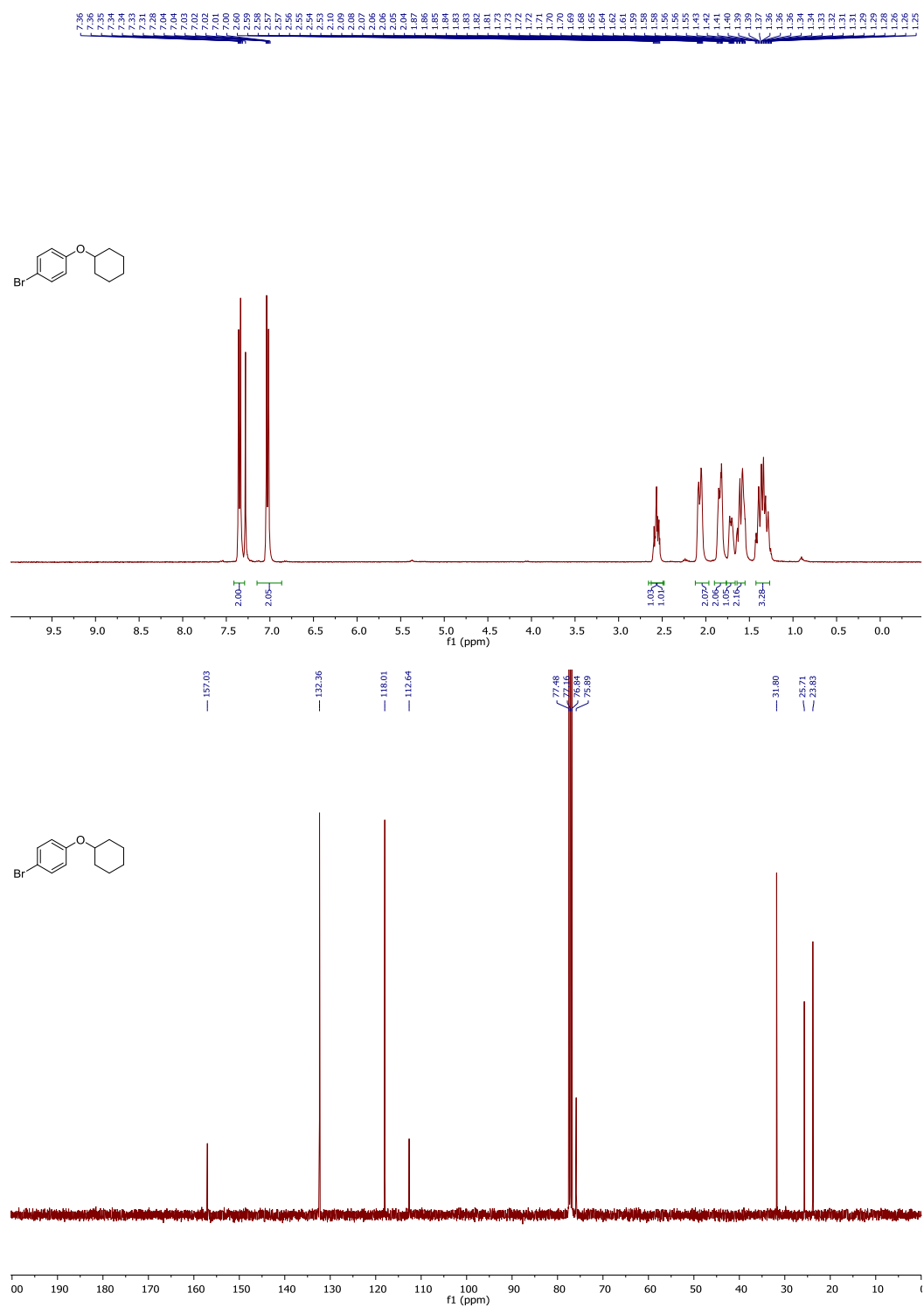


Figure S12. NMR spectra of 3i

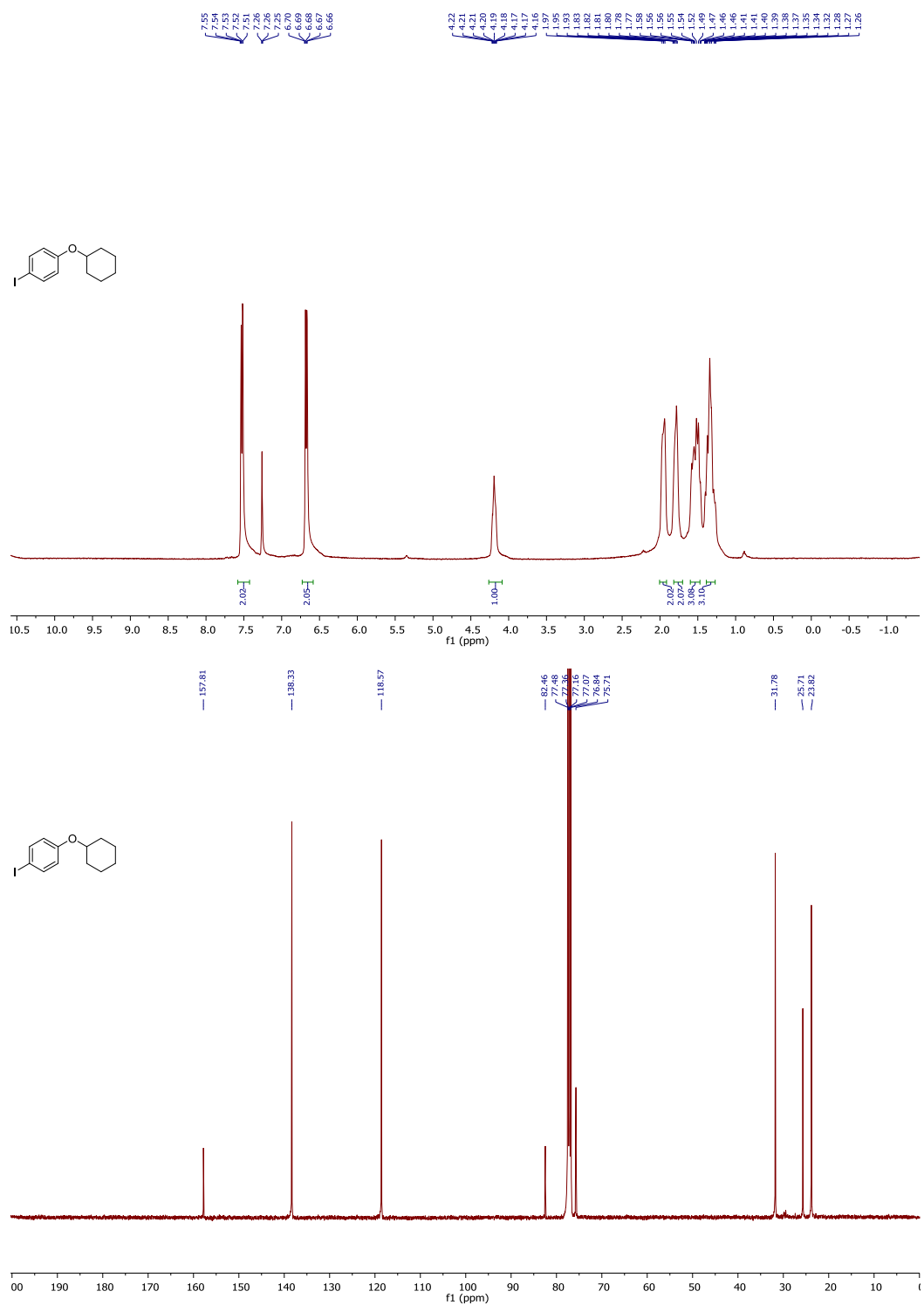


Figure S13. NMR spectra of 3j

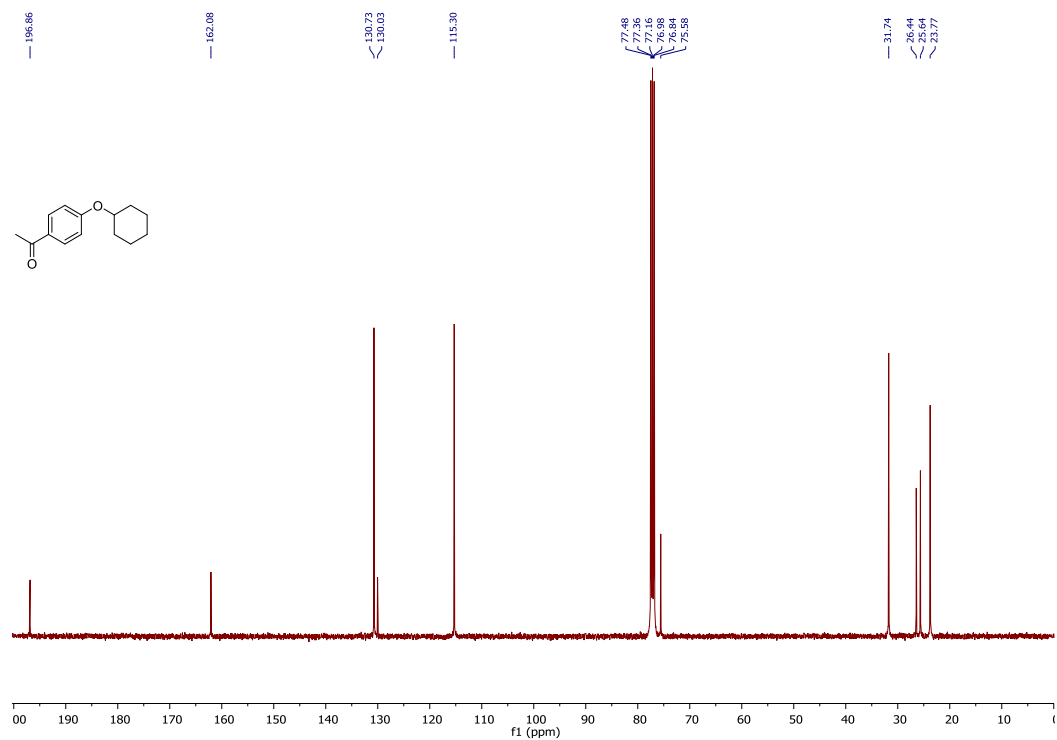
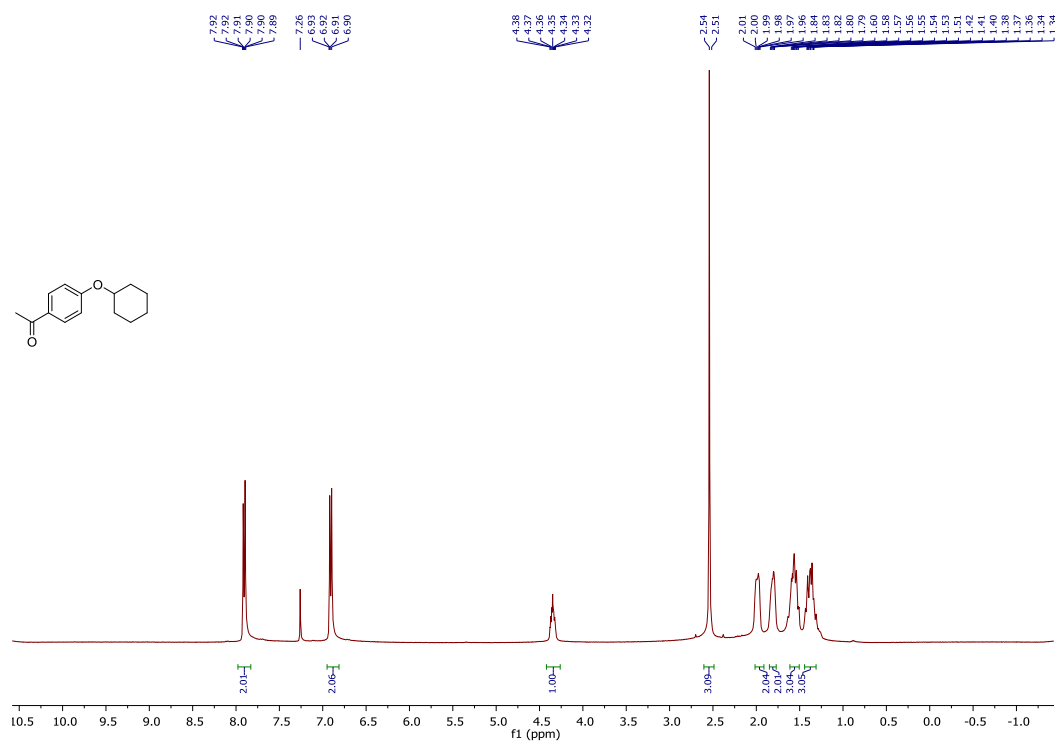


Figure S14. NMR spectra of 3k

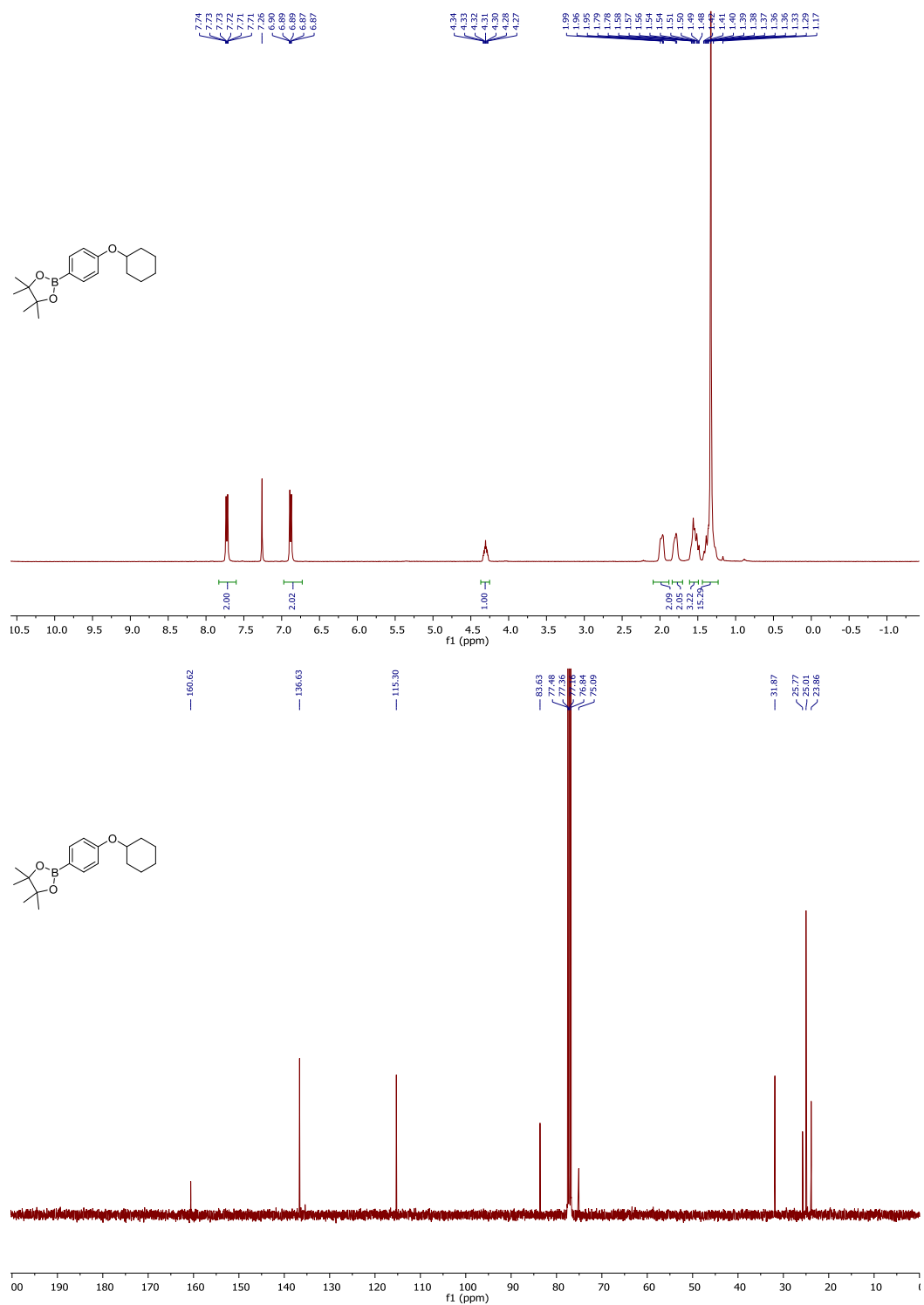


Figure S15. NMR spectra of 31

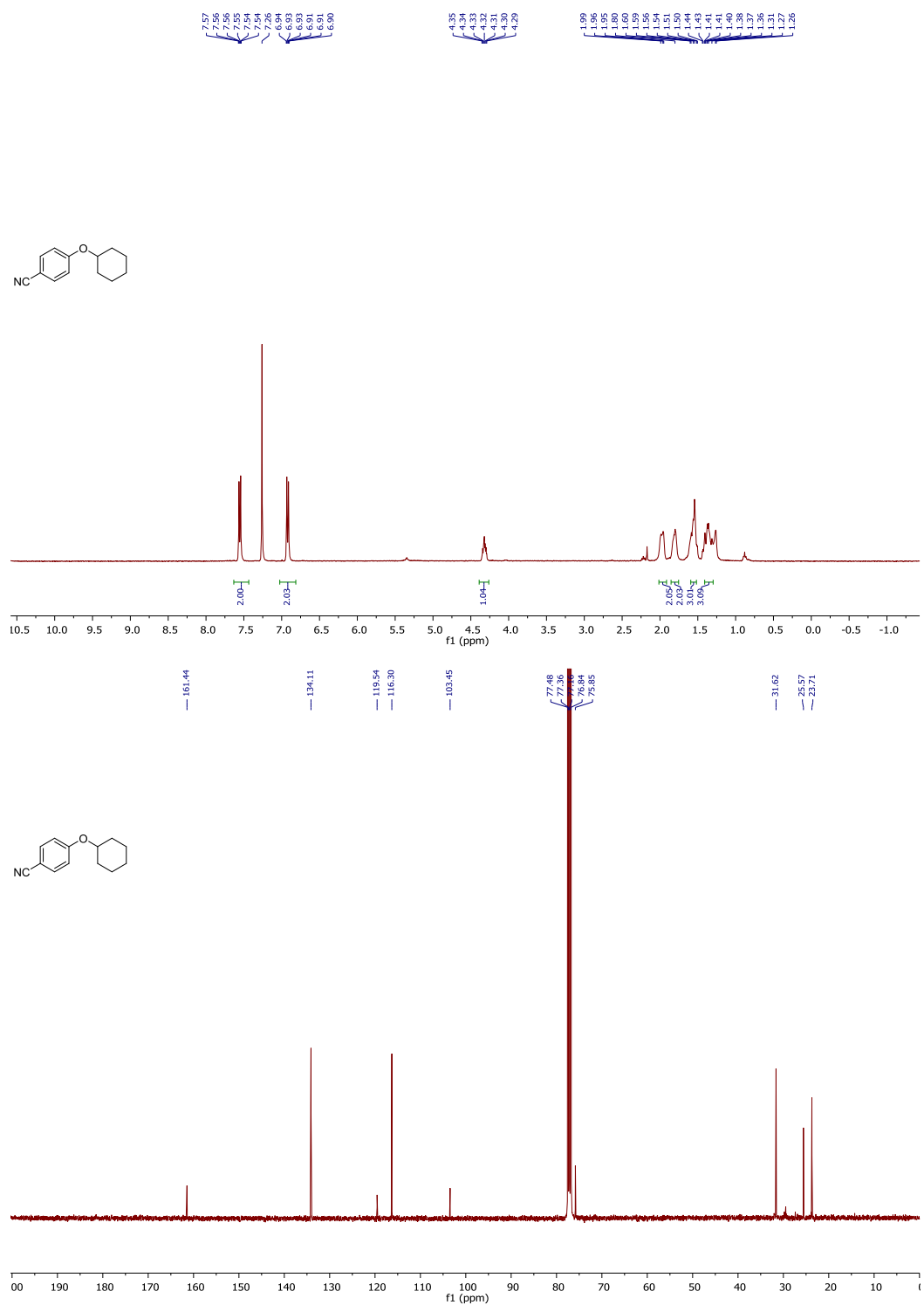
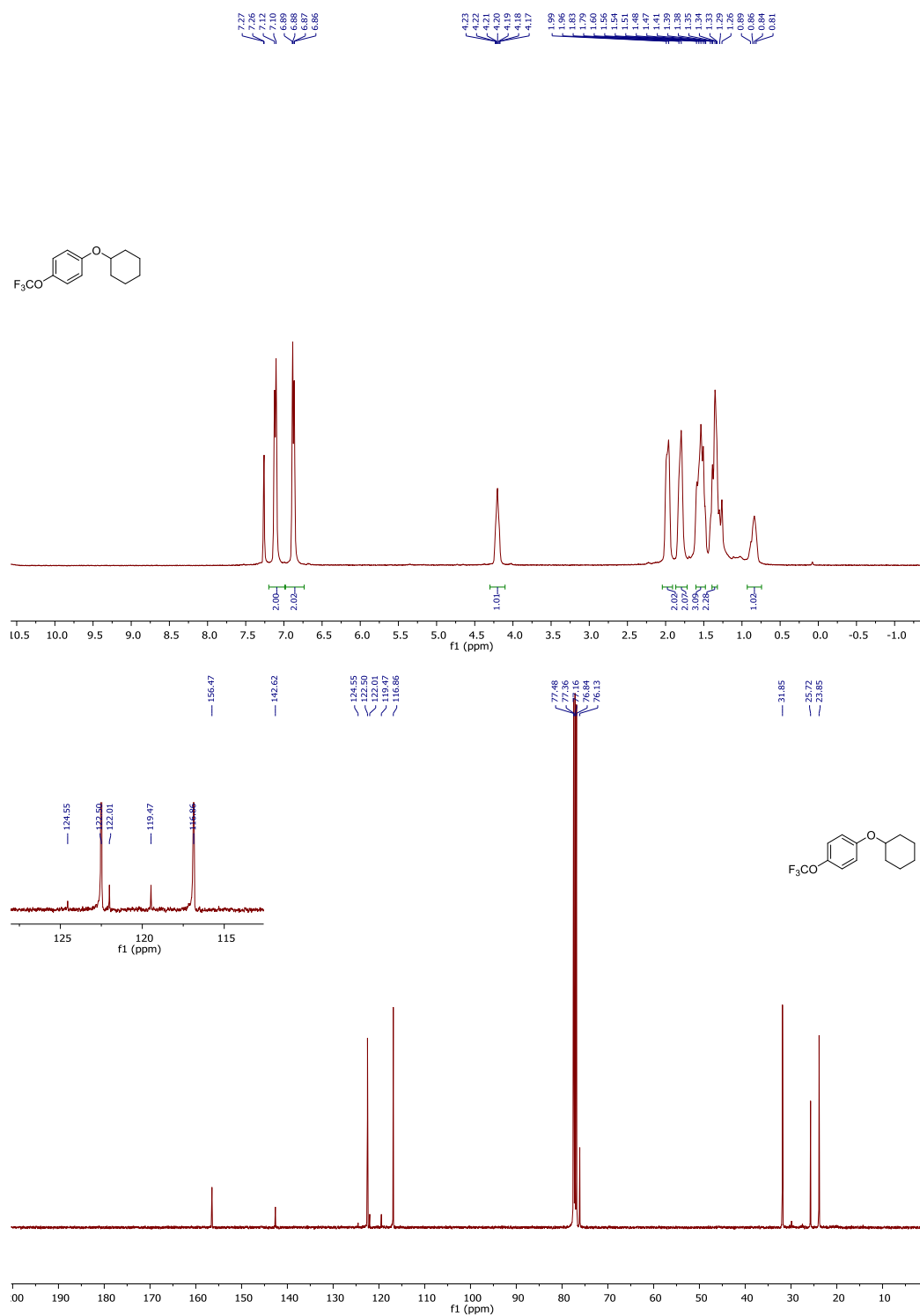


Figure S16. NMR spectra of 3m



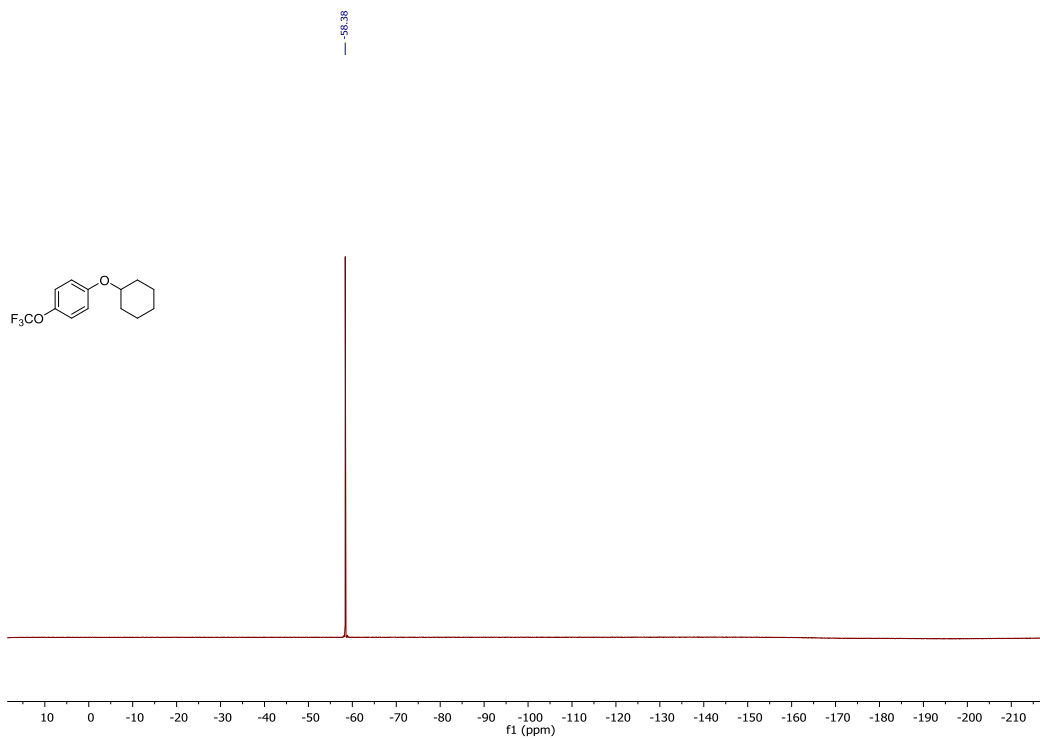
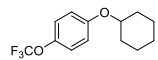


Figure S17. NMR spectra of 3n

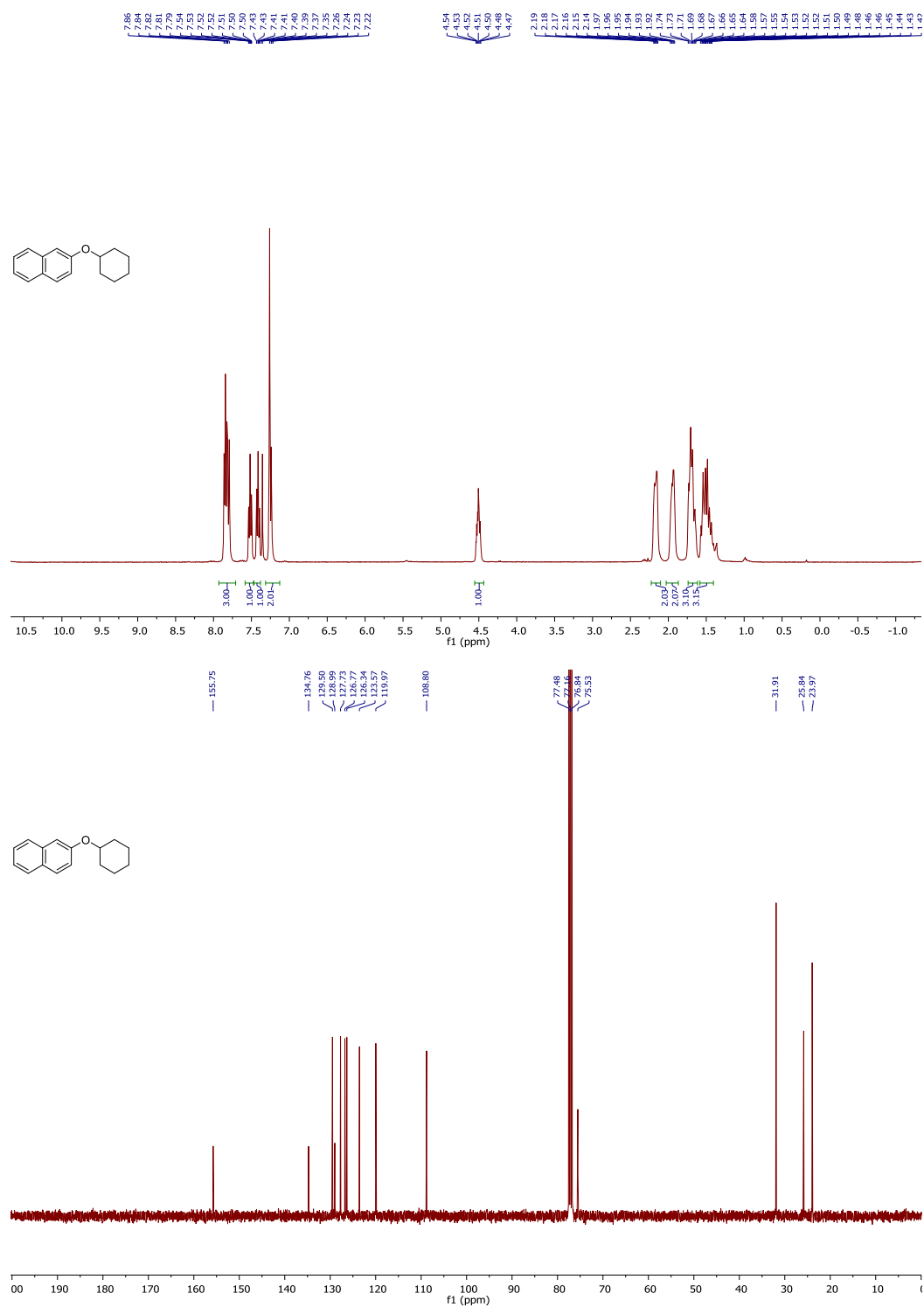


Figure S18. NMR spectra of 4a

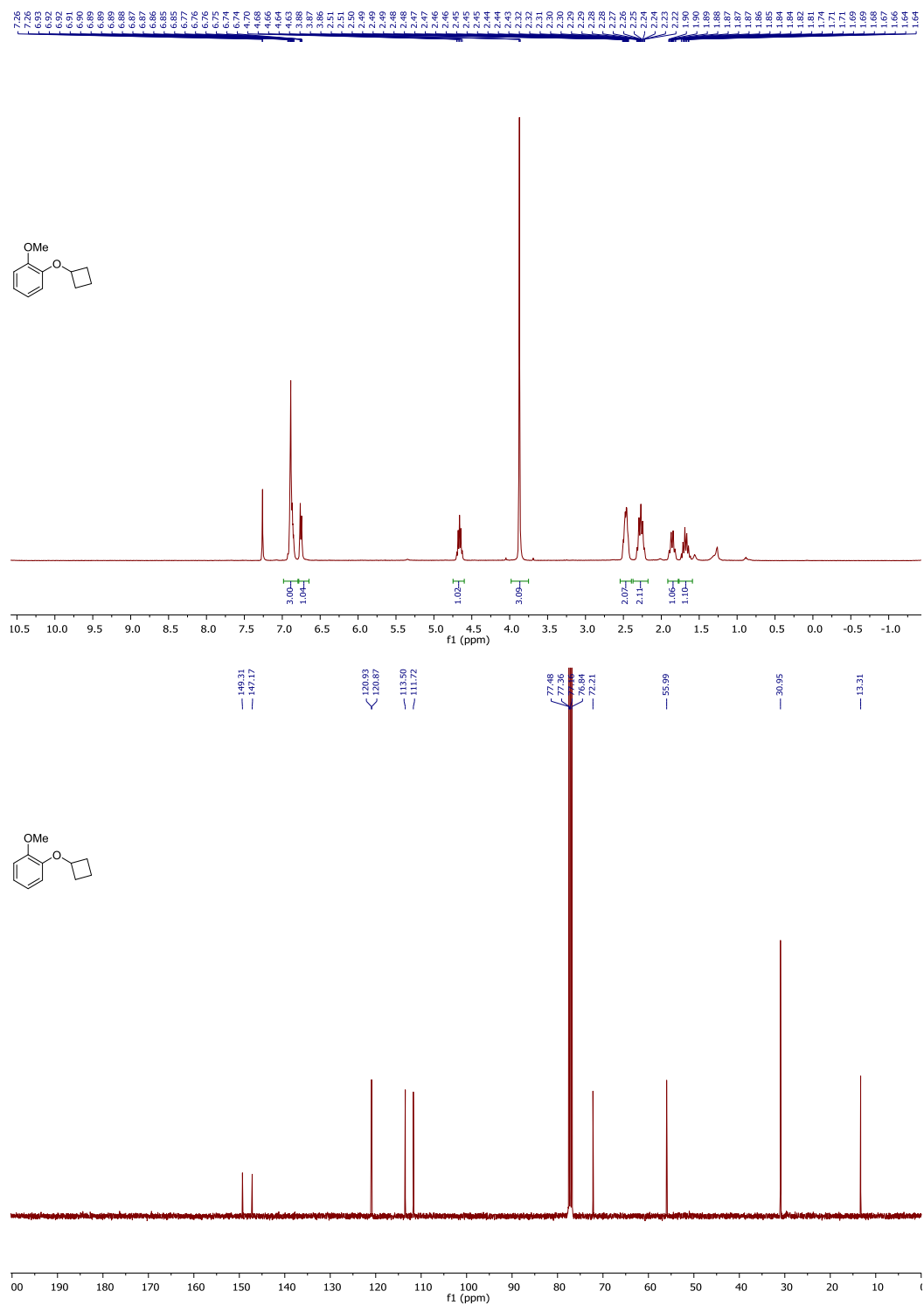


Figure S19. NMR spectra of 4b

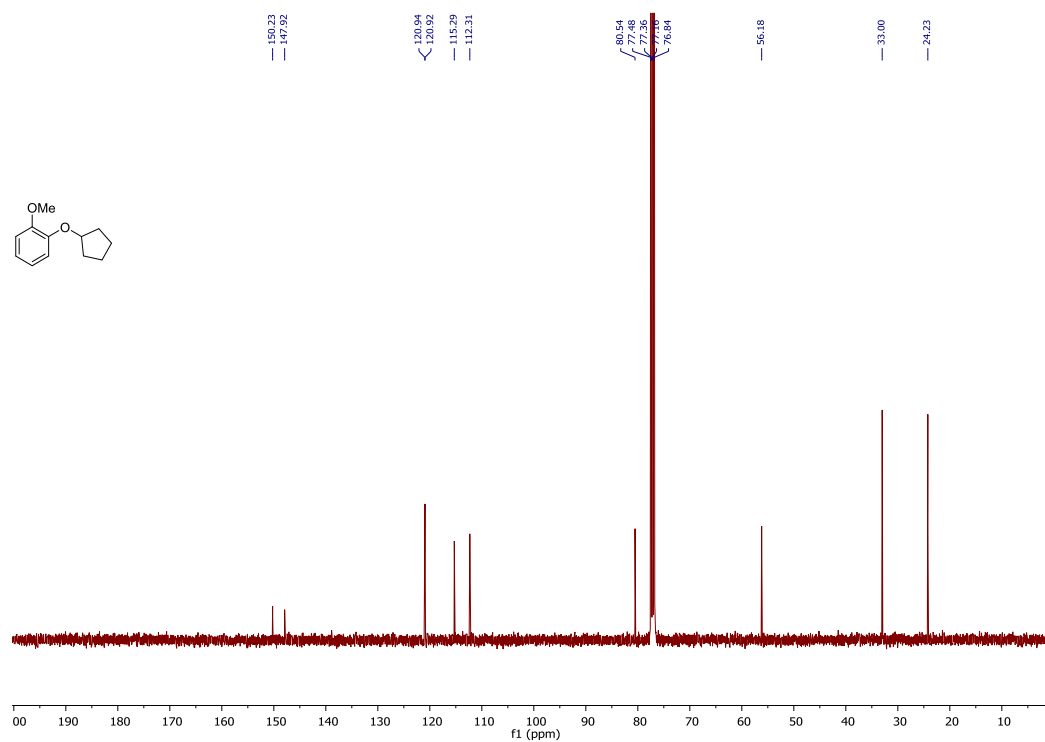
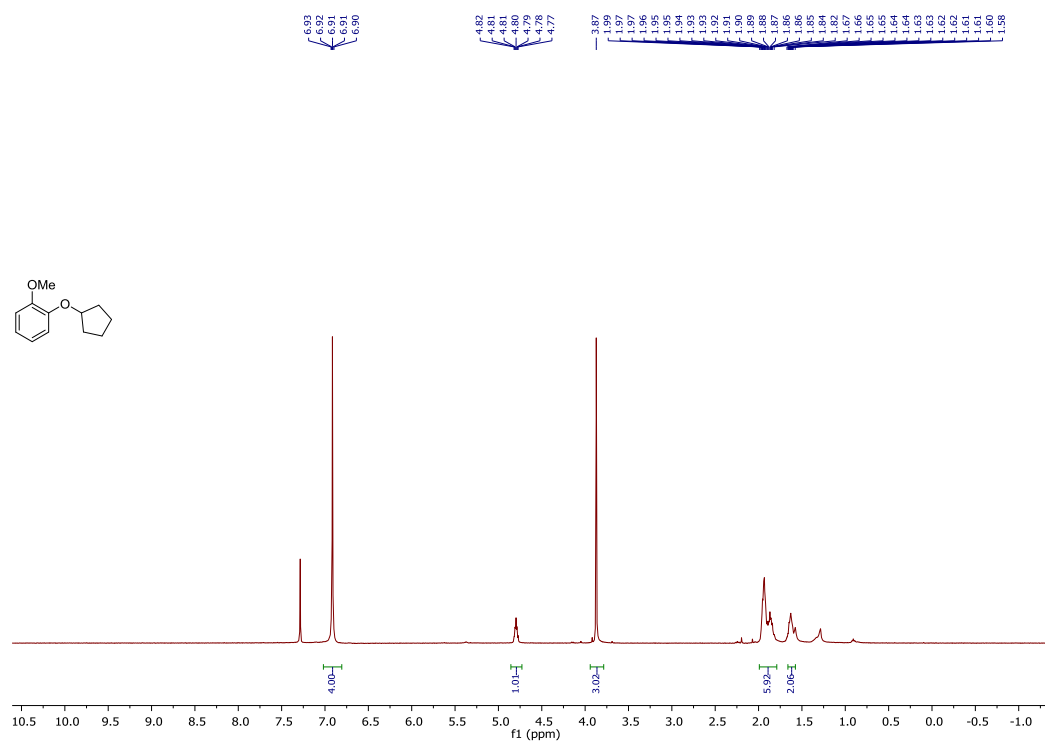


Figure S20. NMR spectra of 4c

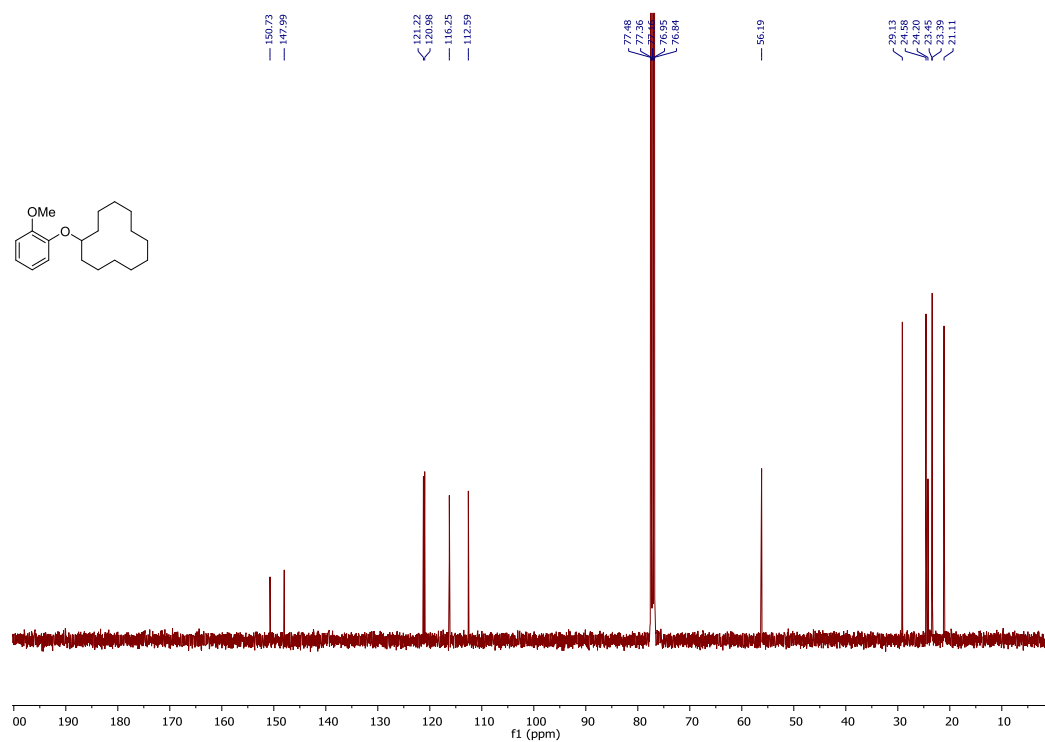
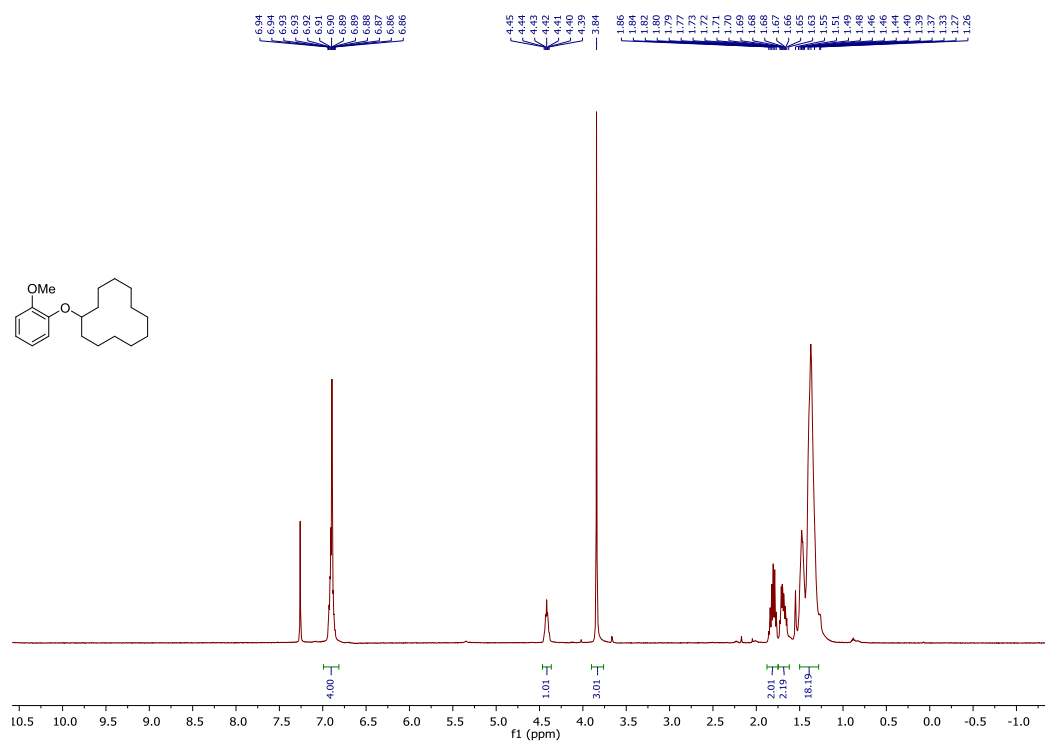


Figure S21. NMR spectra of 4d

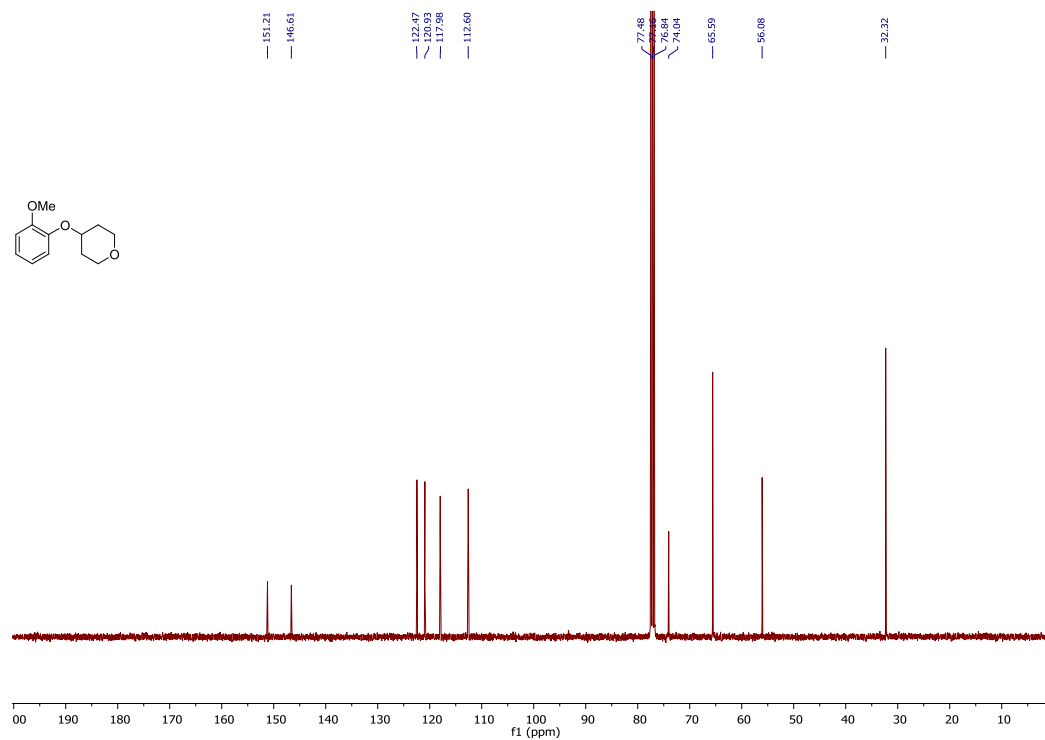
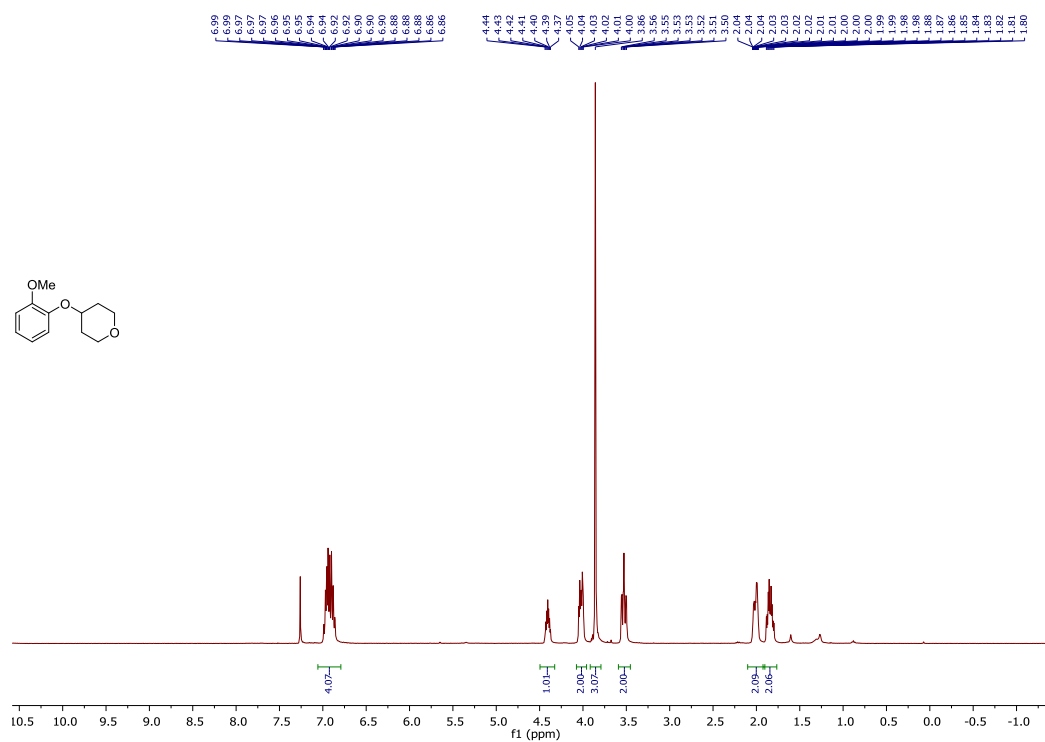


Figure S22. NMR spectra of 4e

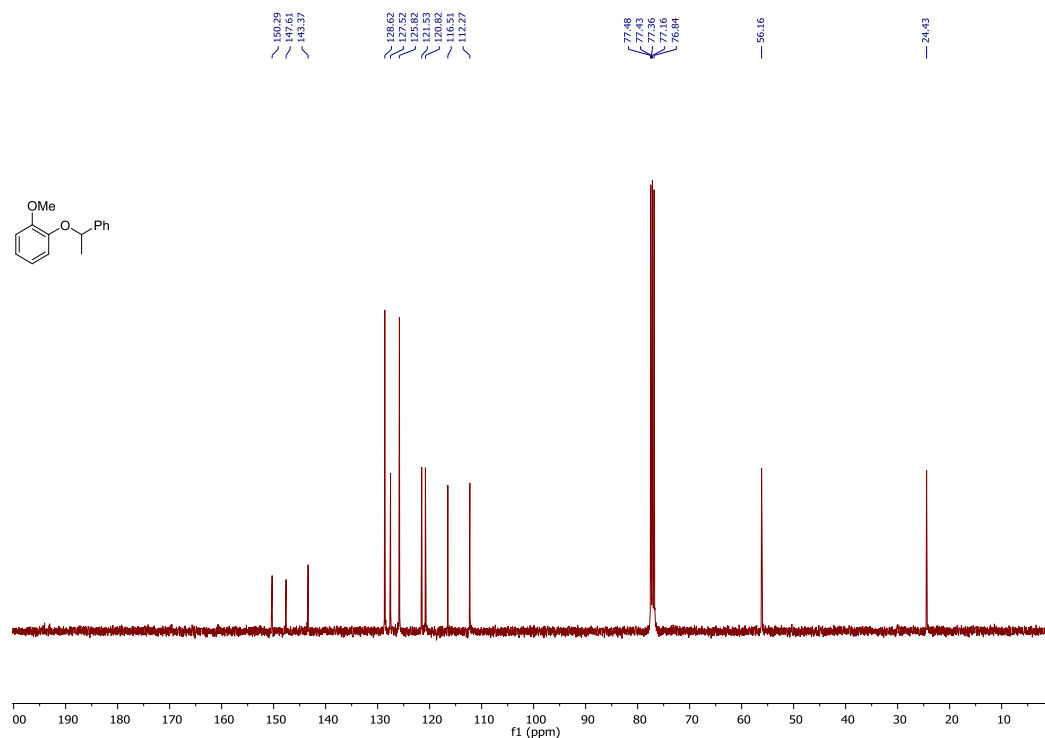
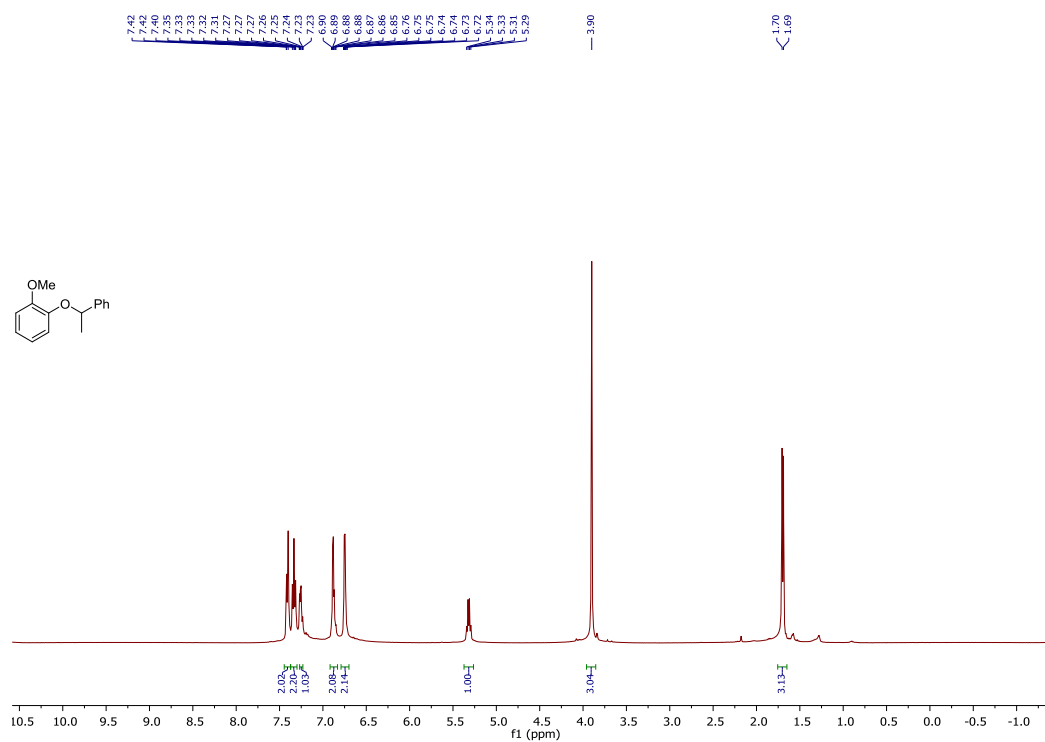


Figure S23. NMR spectra of 4f

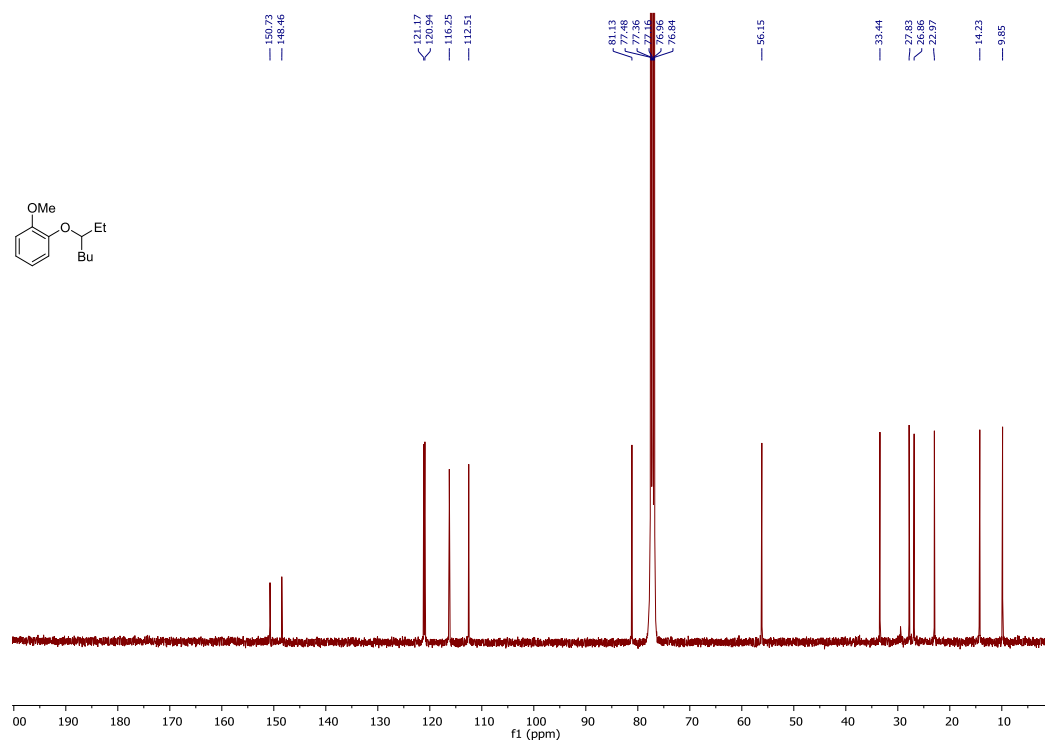
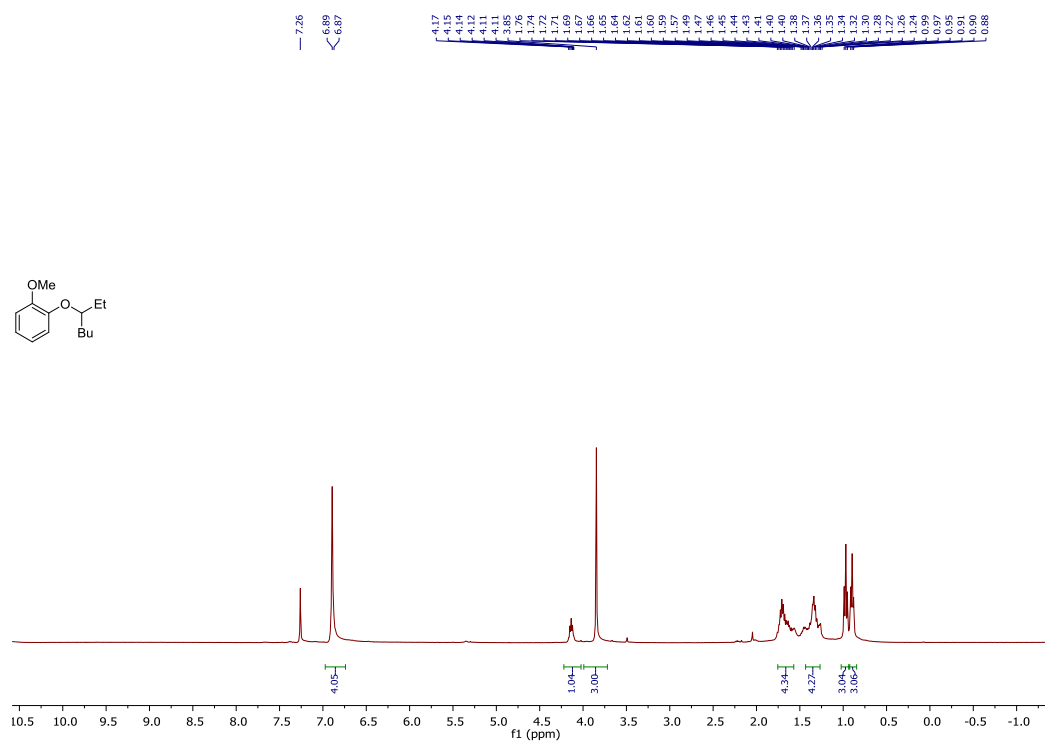


Figure S24. NMR spectra of 4g

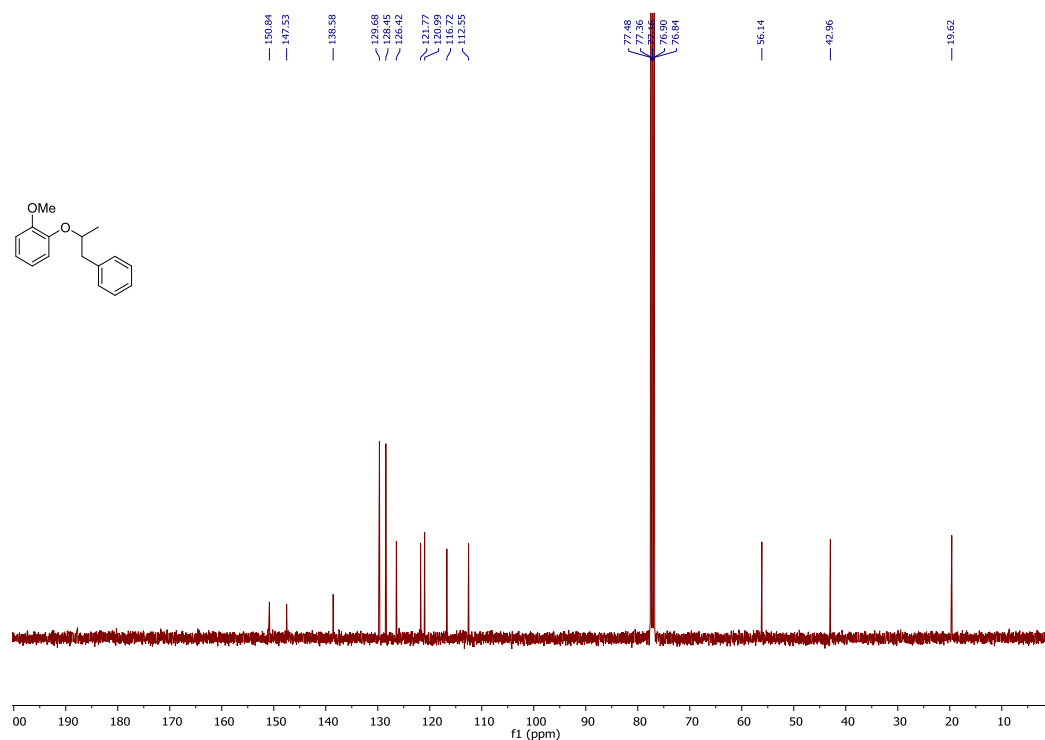
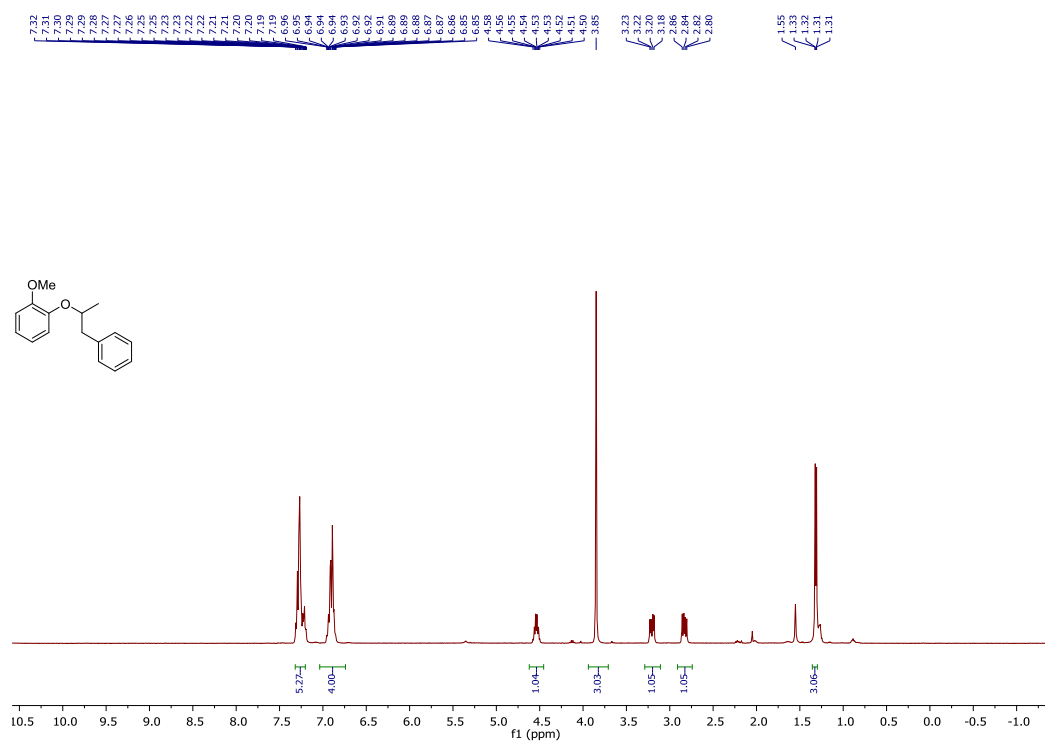


Figure S25. NMR spectra of 5a

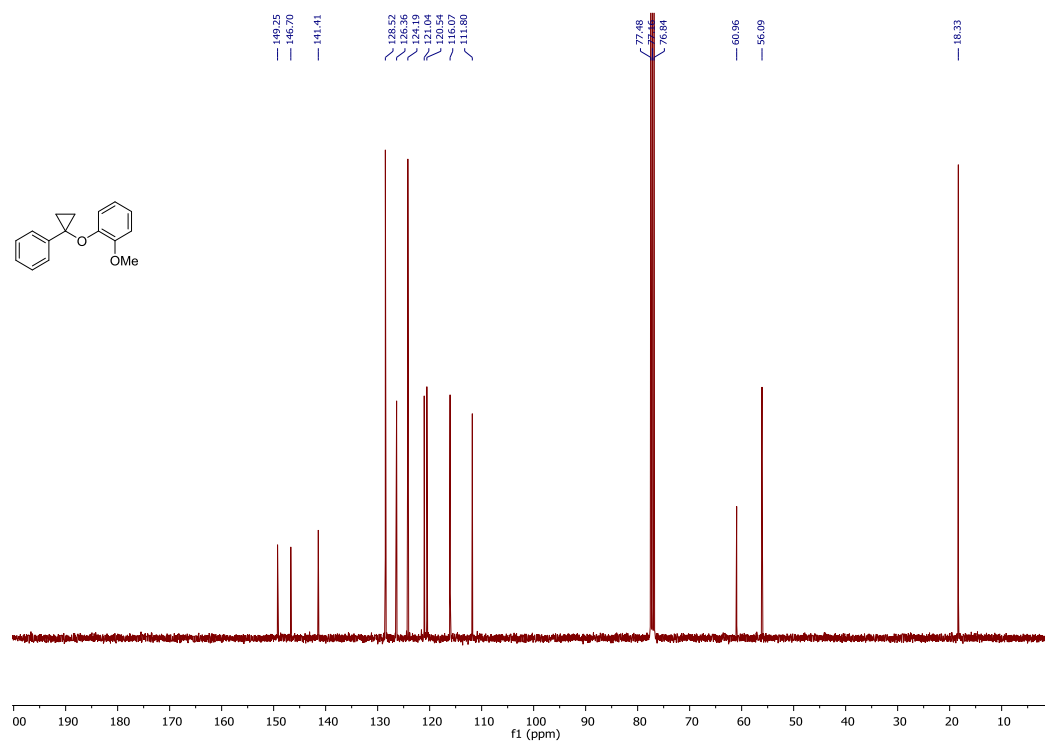
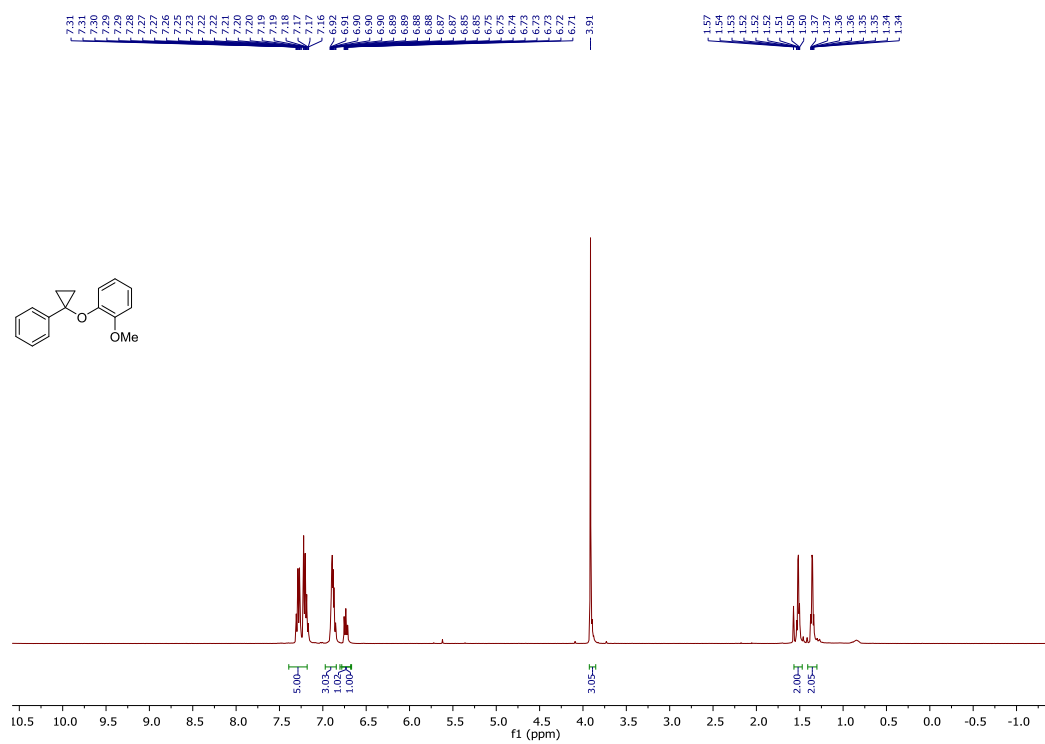


Figure S26. NMR spectra of 5b

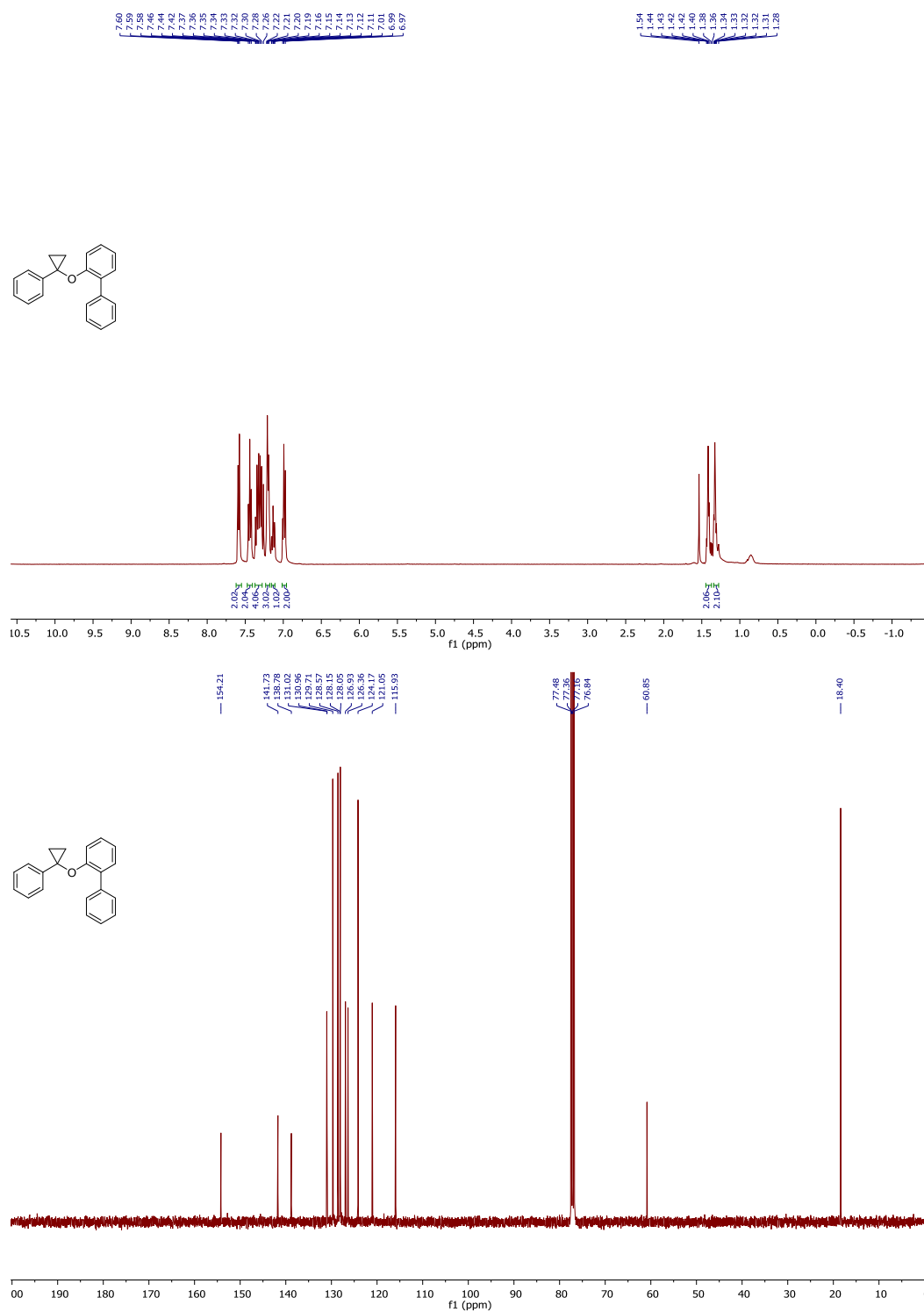


Figure S27. NMR spectra of 5c

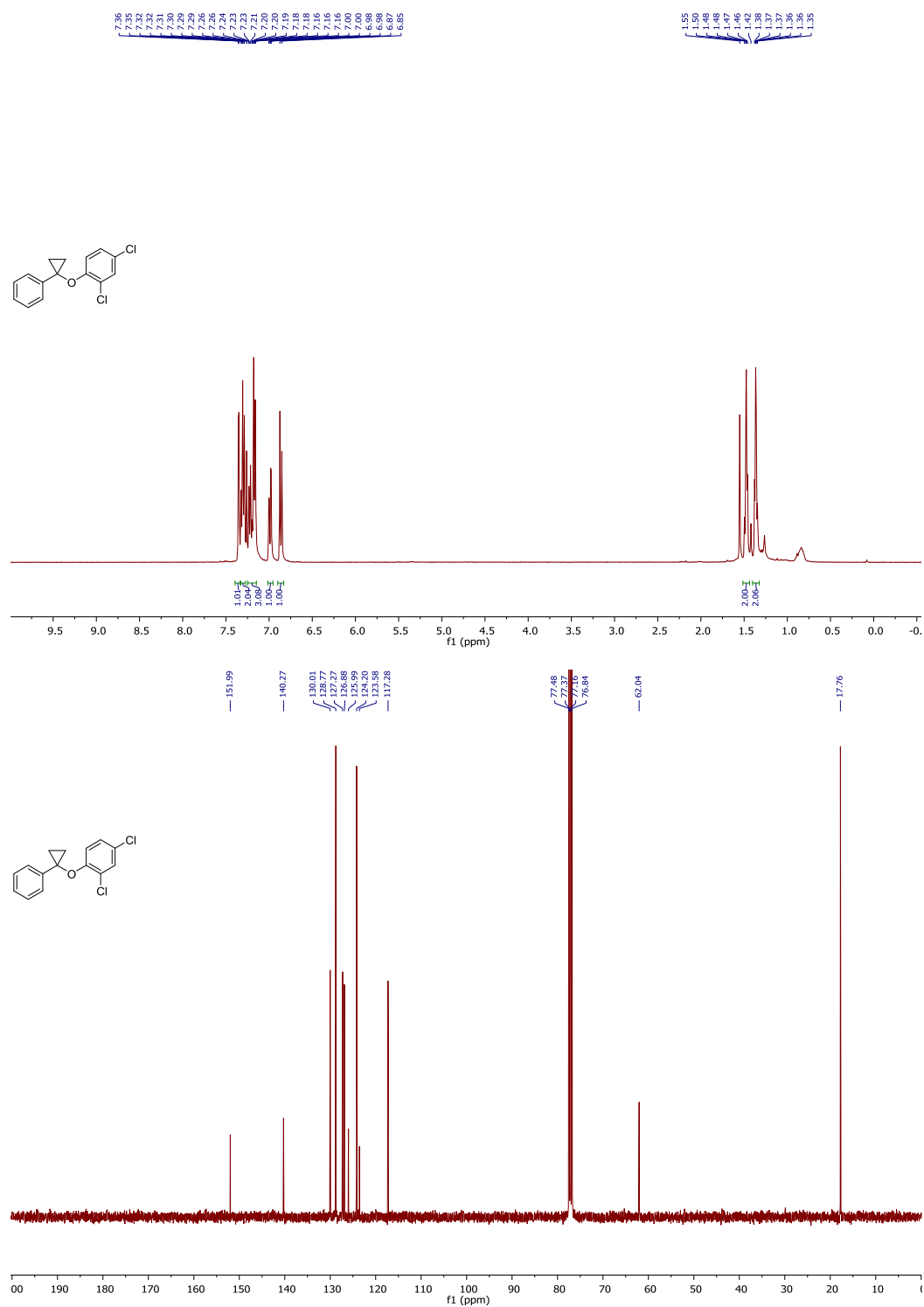


Figure S28. NMR spectra of 5d

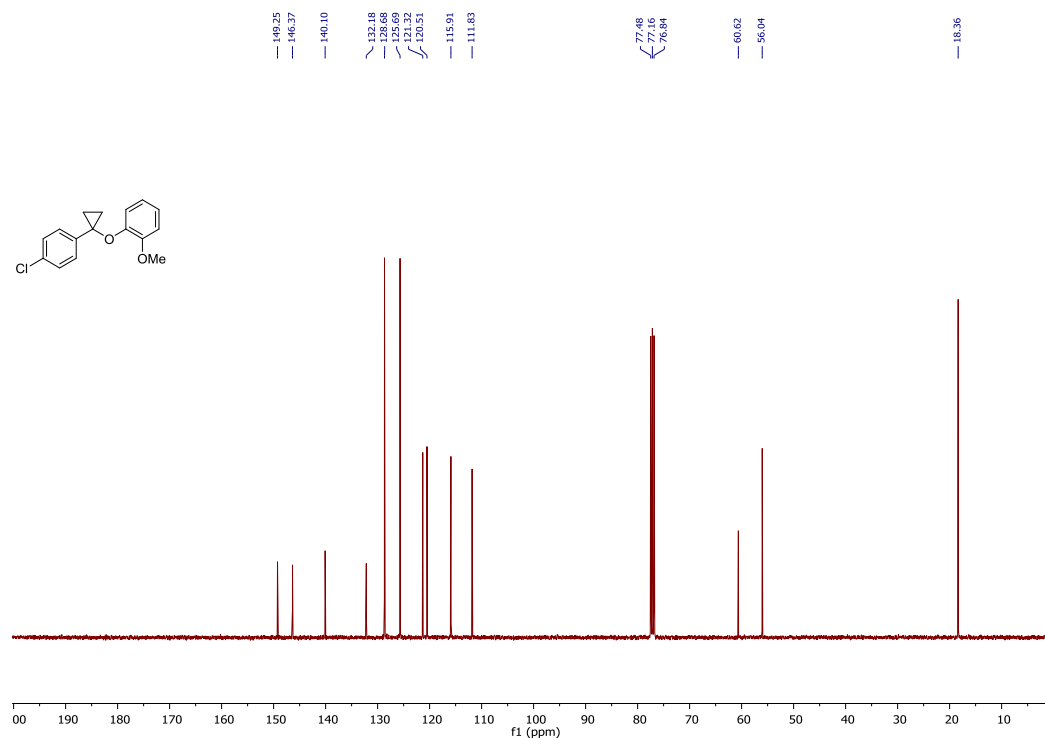
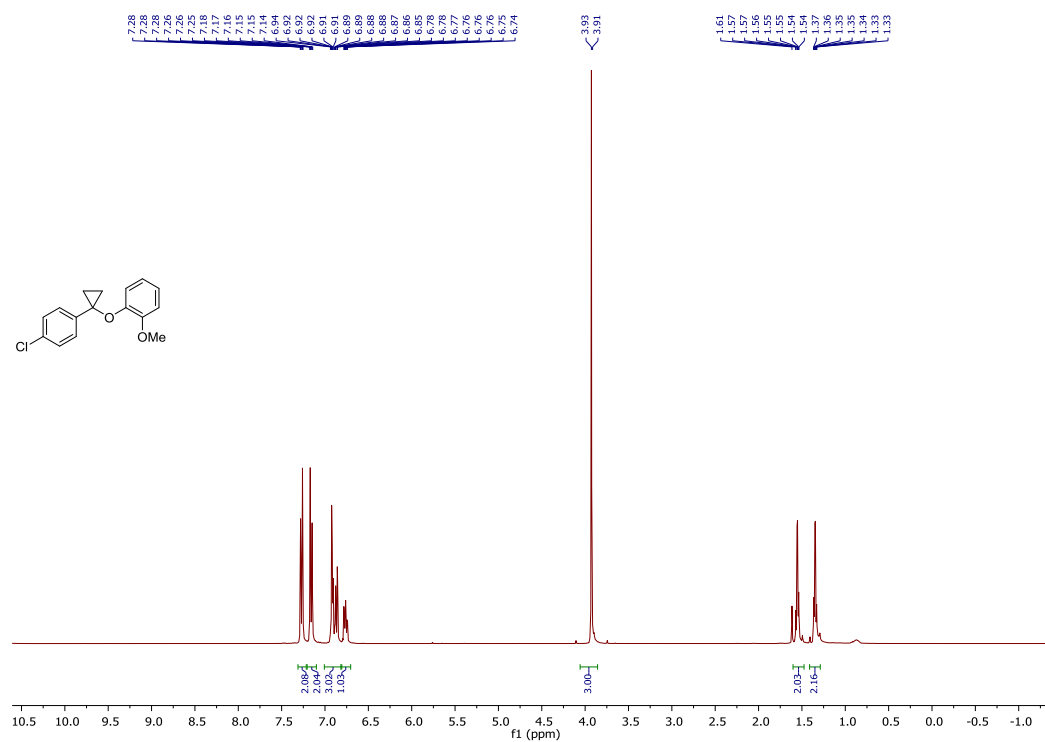


Figure S29. NMR spectra of 5e

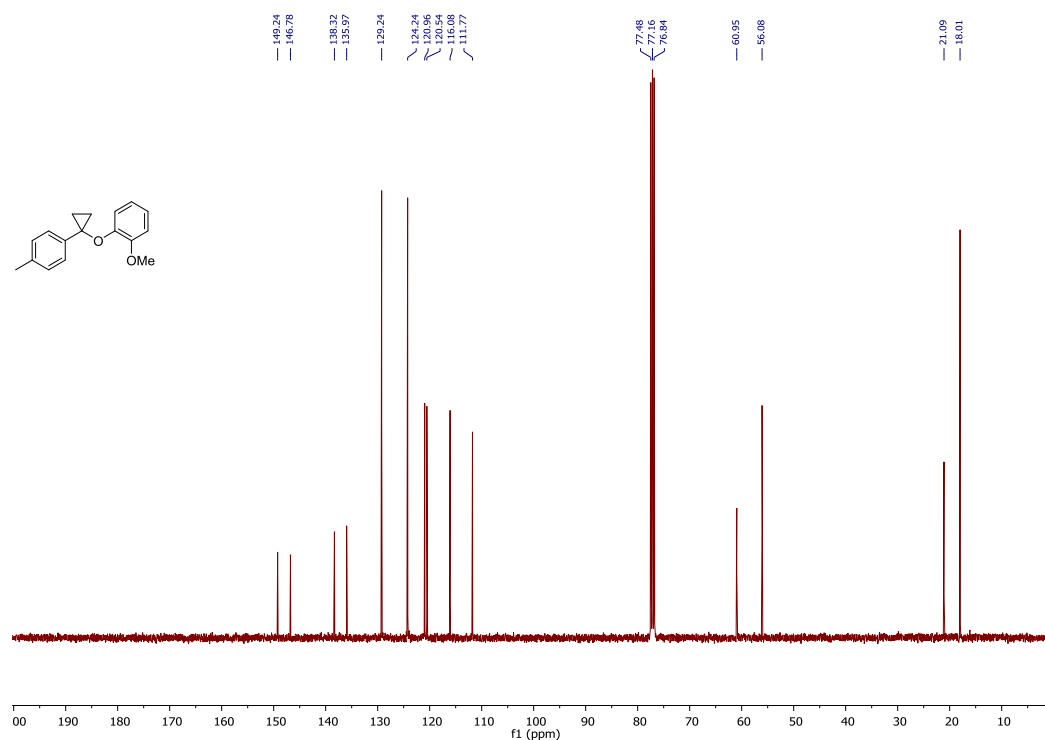
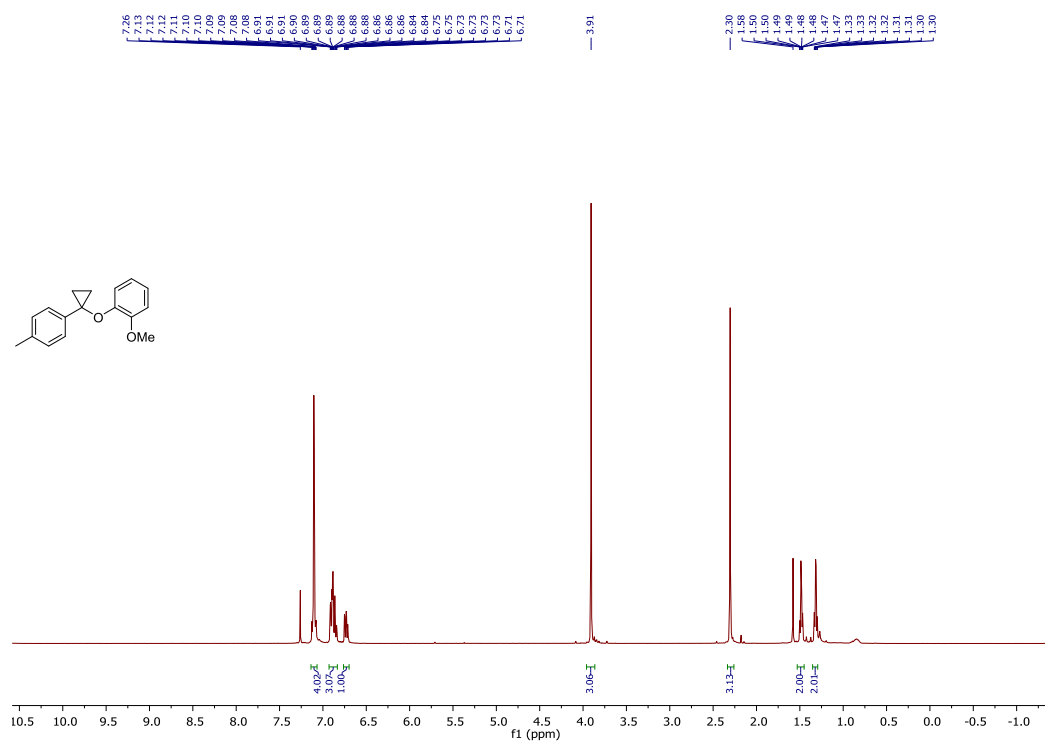


Figure S30. NMR spectra of 5f

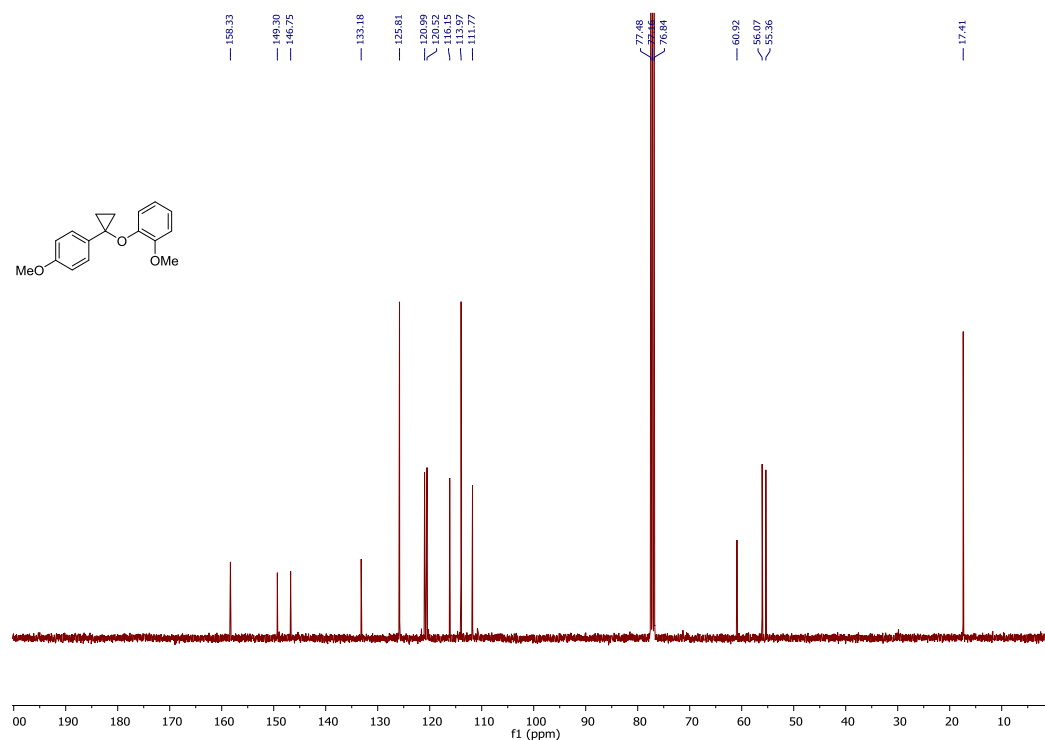
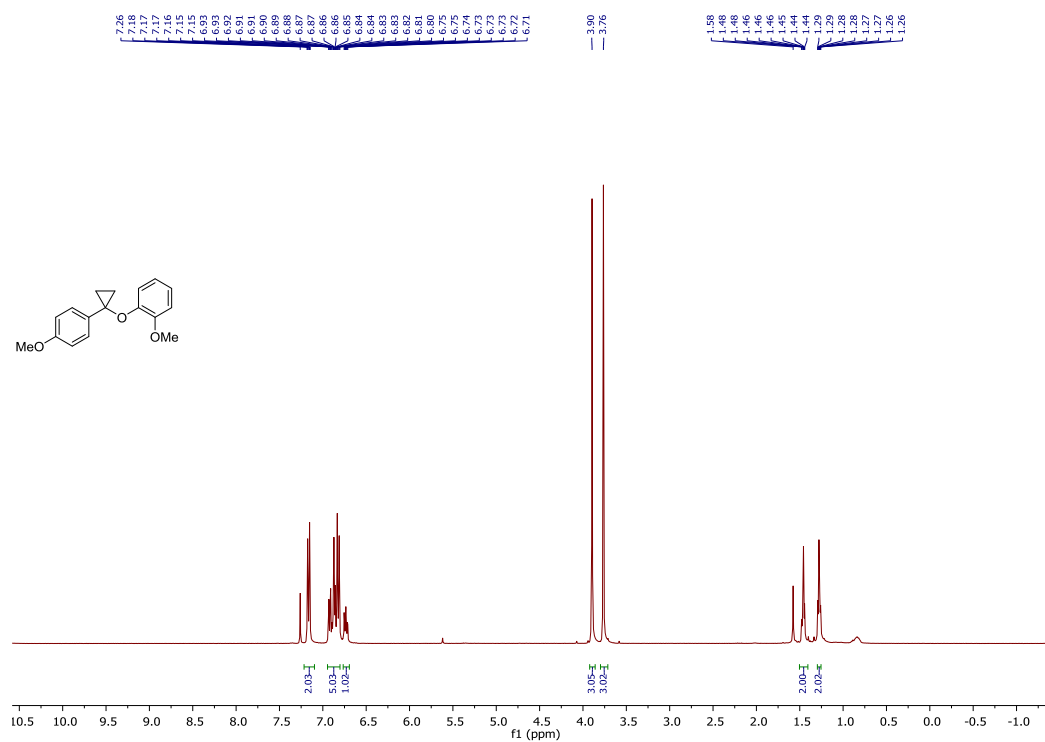


Figure S31. NMR spectra of 6a

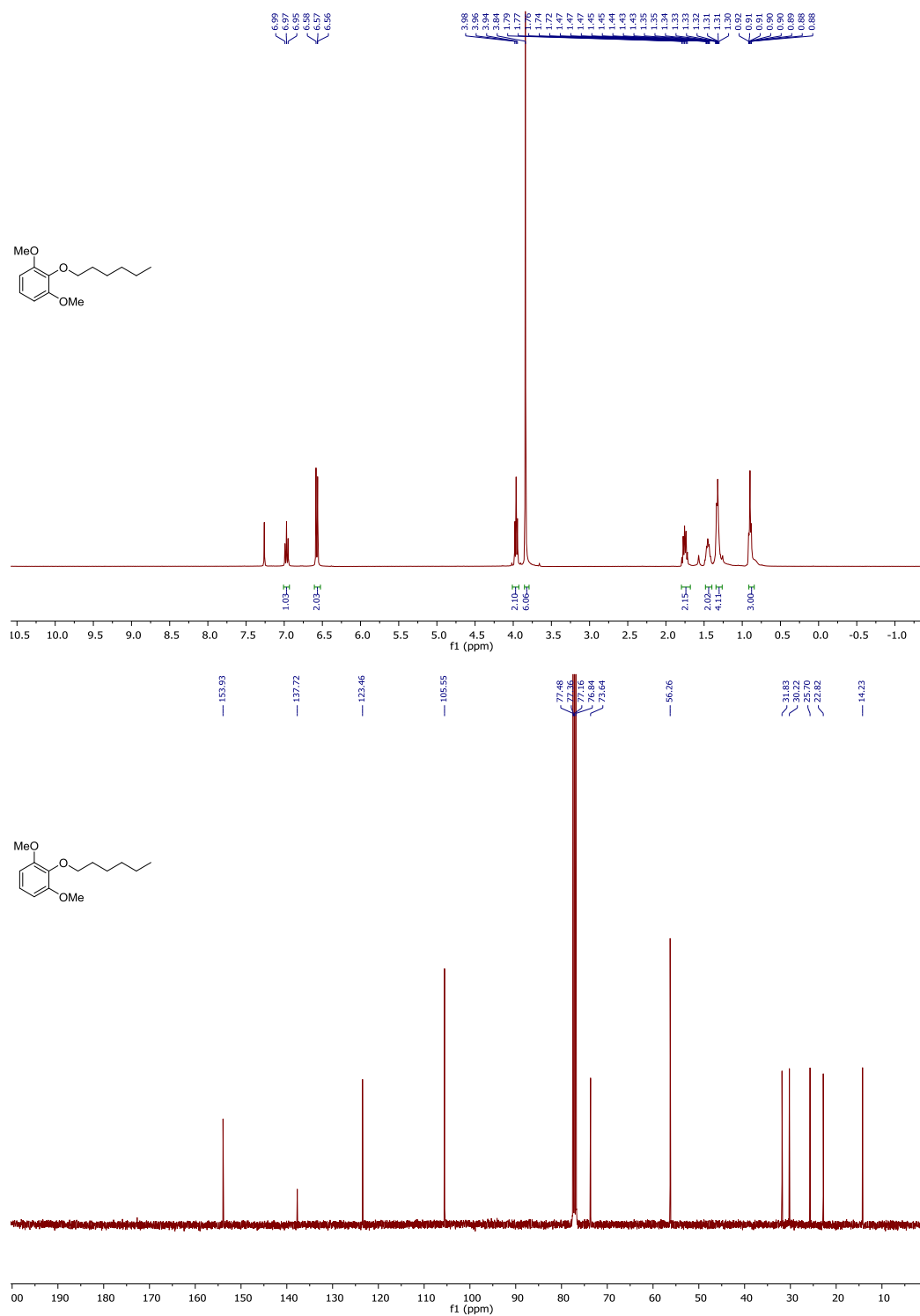


Figure S32. NMR spectra of 6b

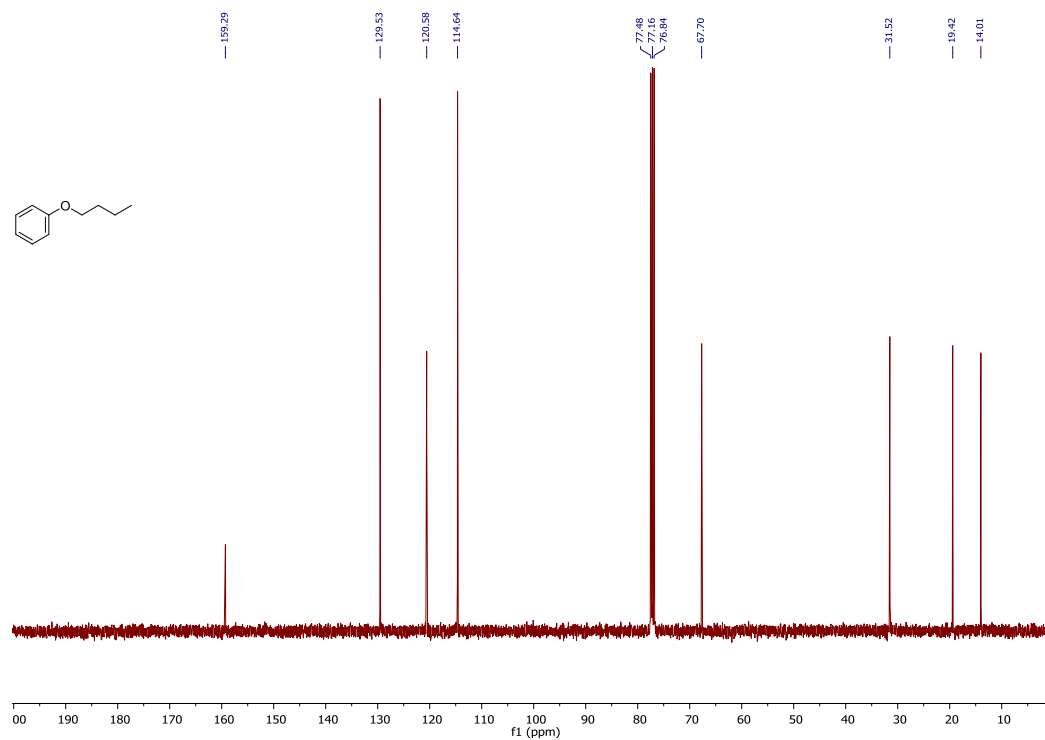
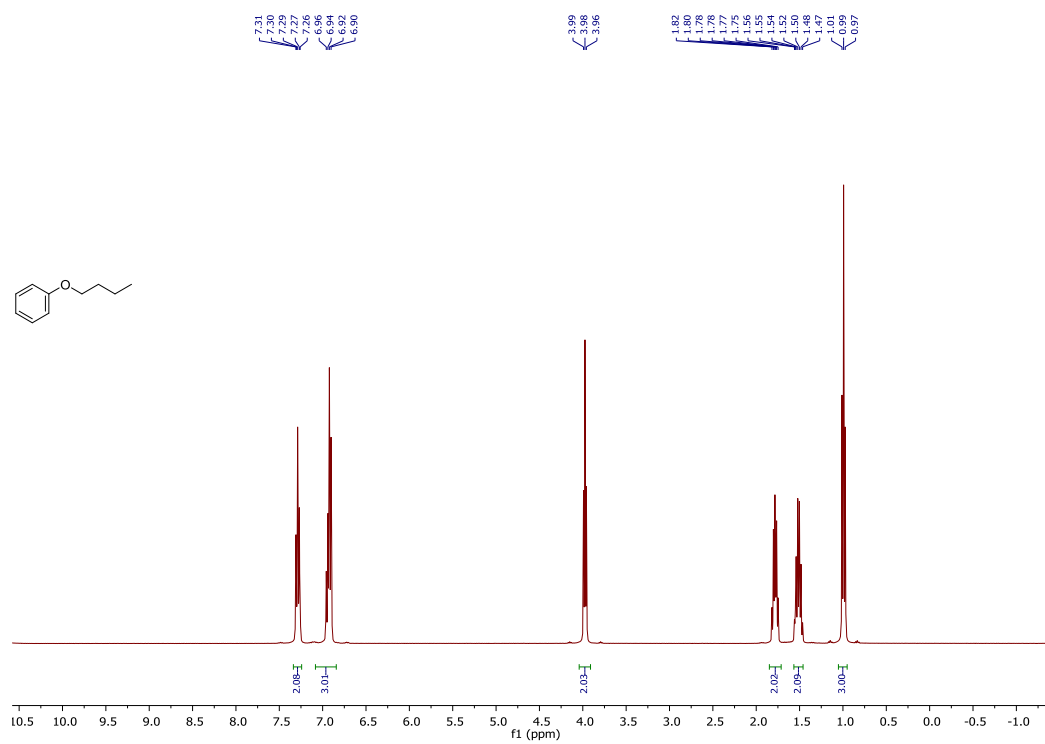


Figure S33. NMR spectra of 6c

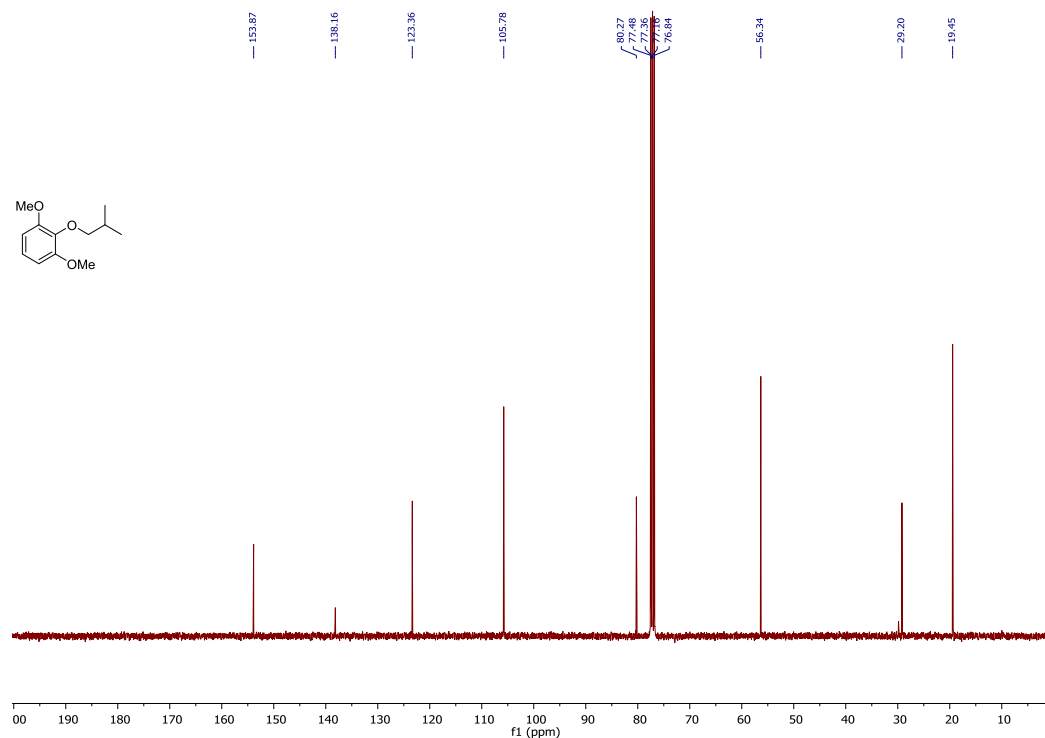
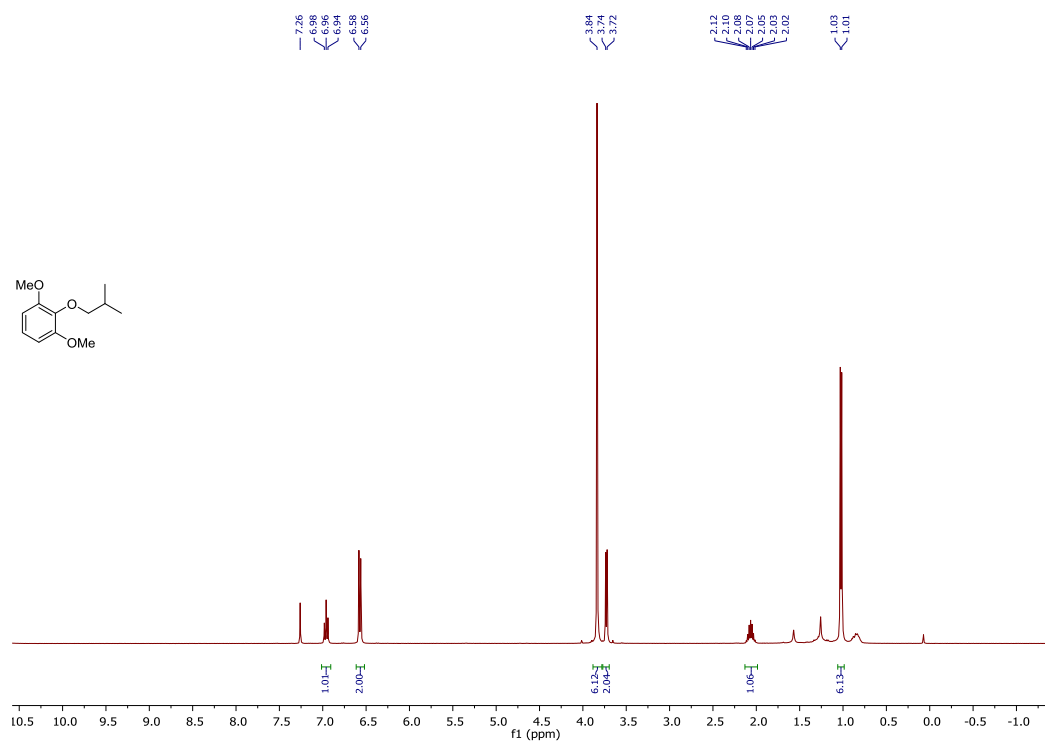


Figure S34. NMR spectra of 6d

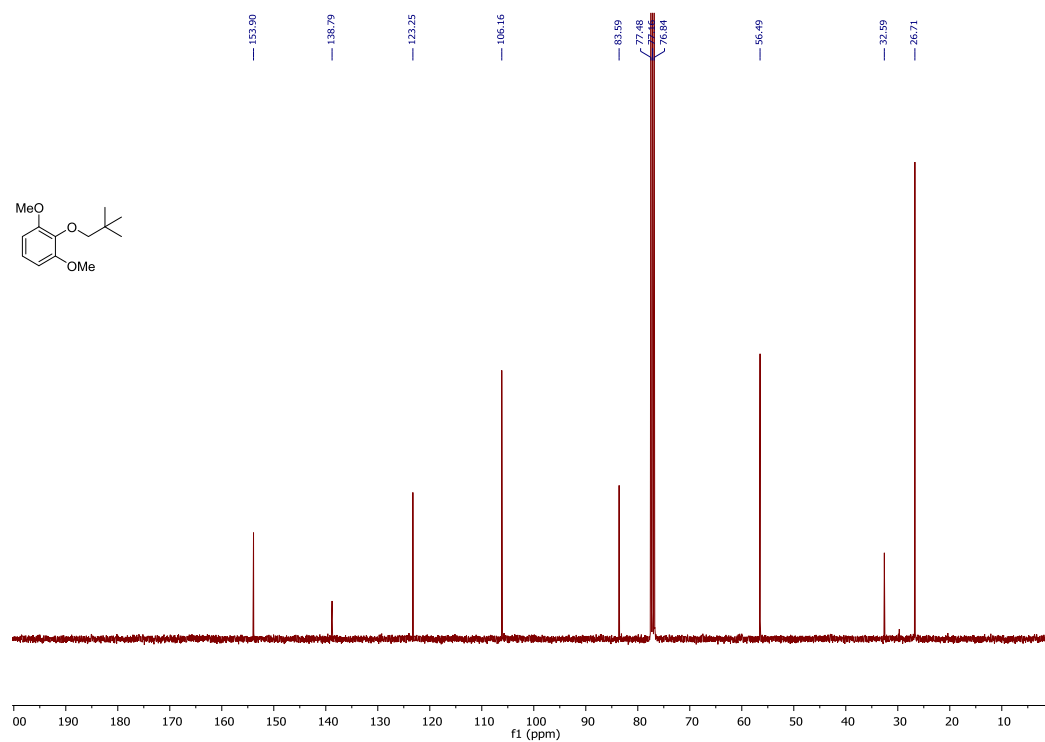
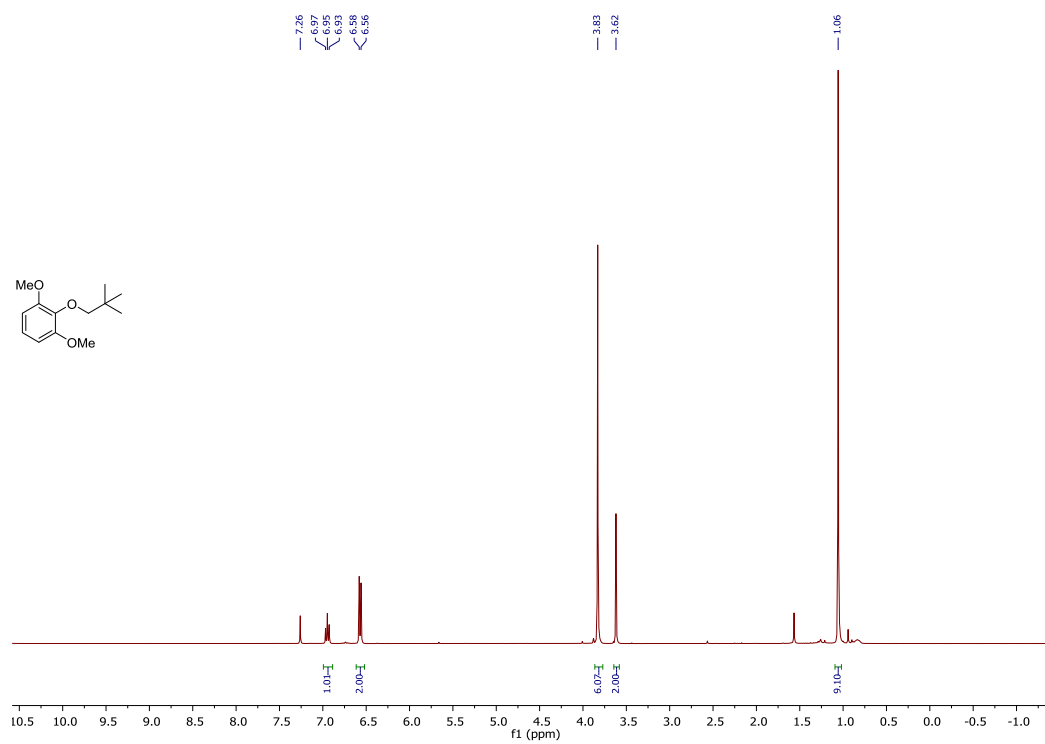


Figure S35. NMR spectra of 6e

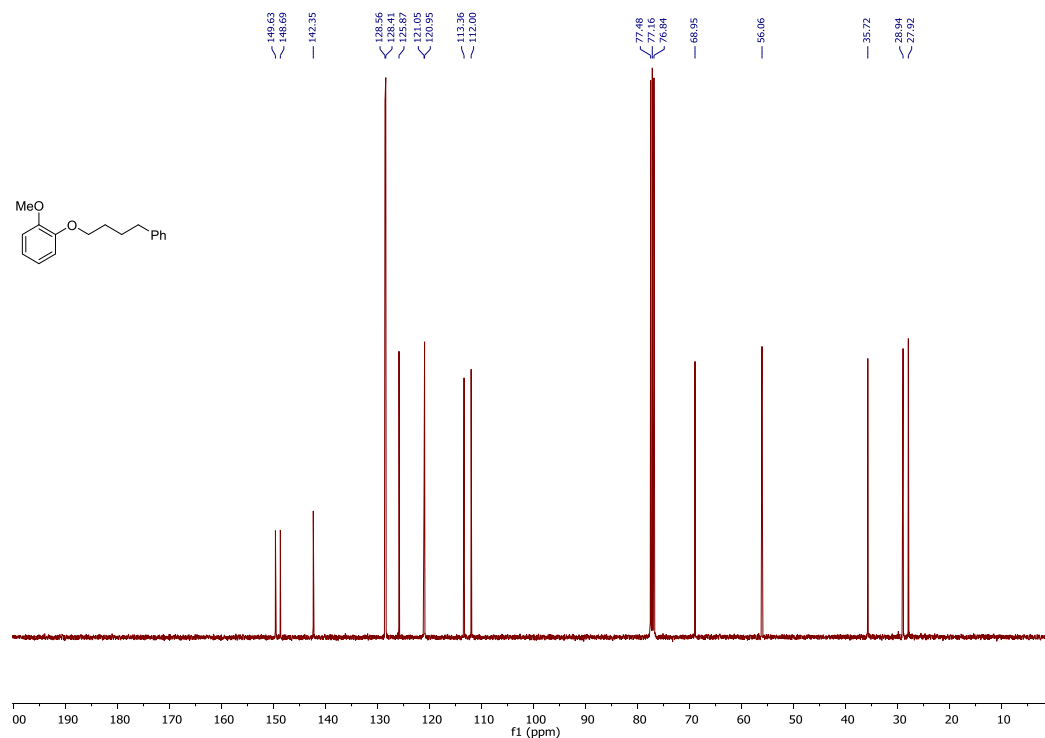
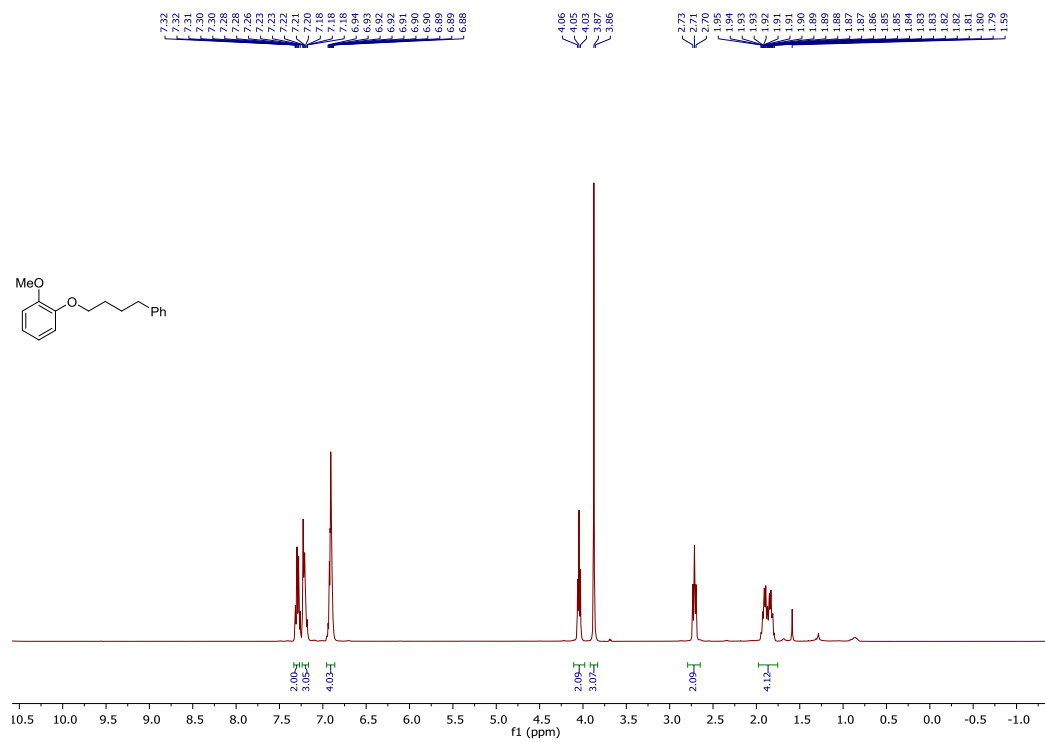


Figure S36. NMR spectra of 6f

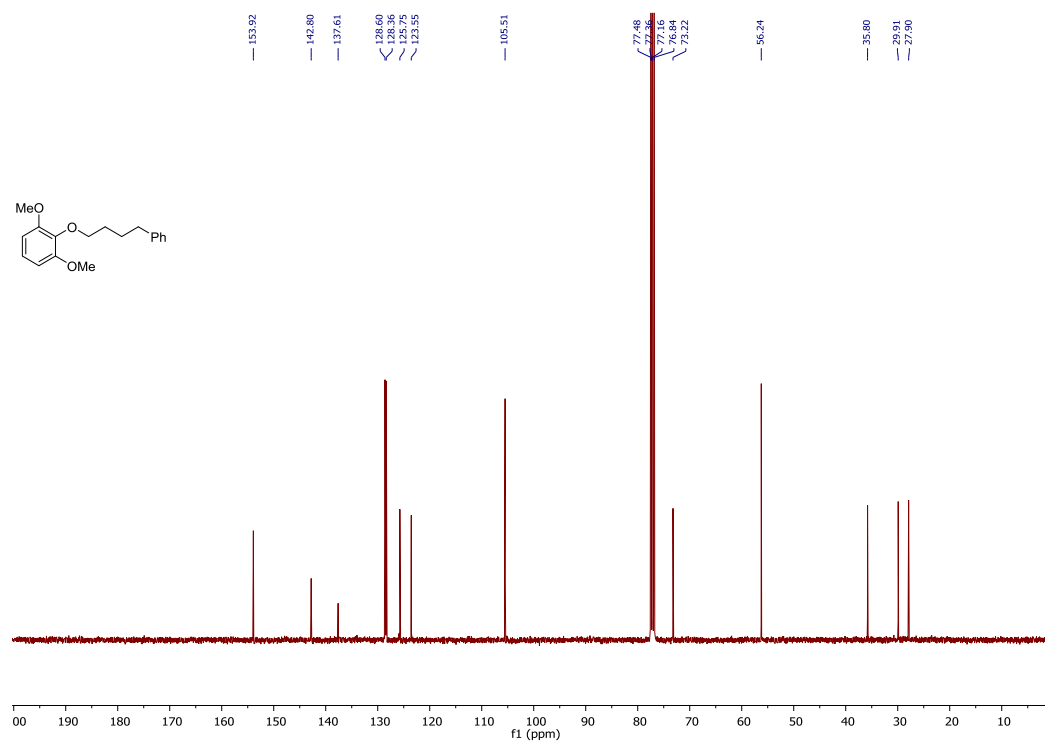
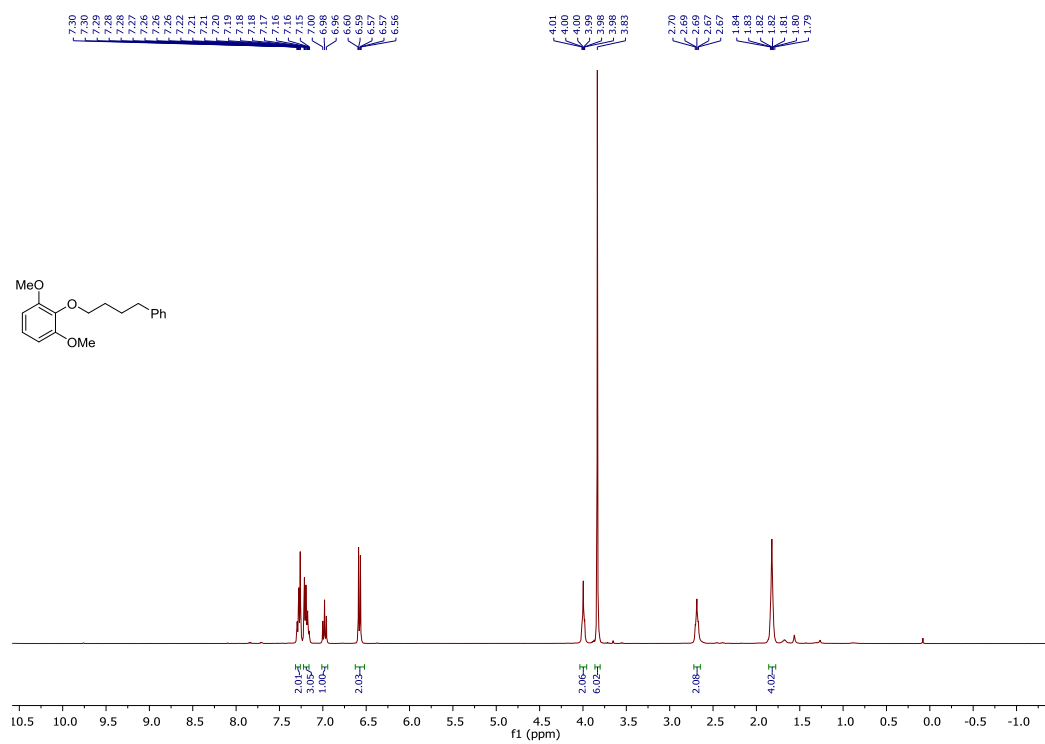


Figure S37. NMR spectra of 6g

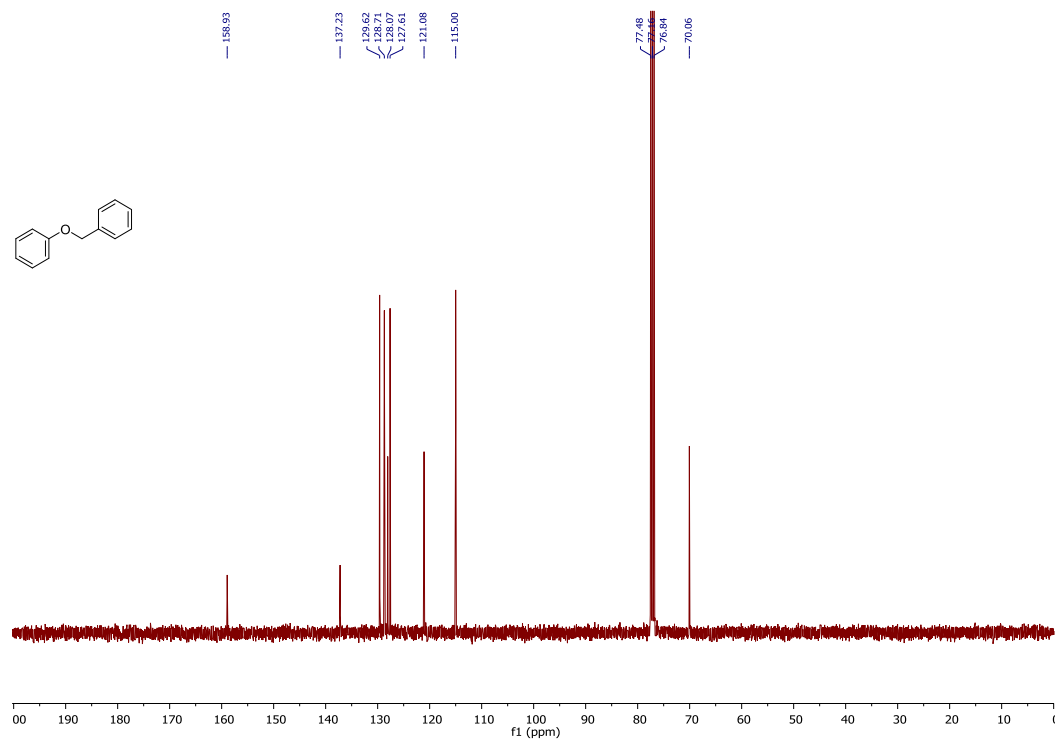
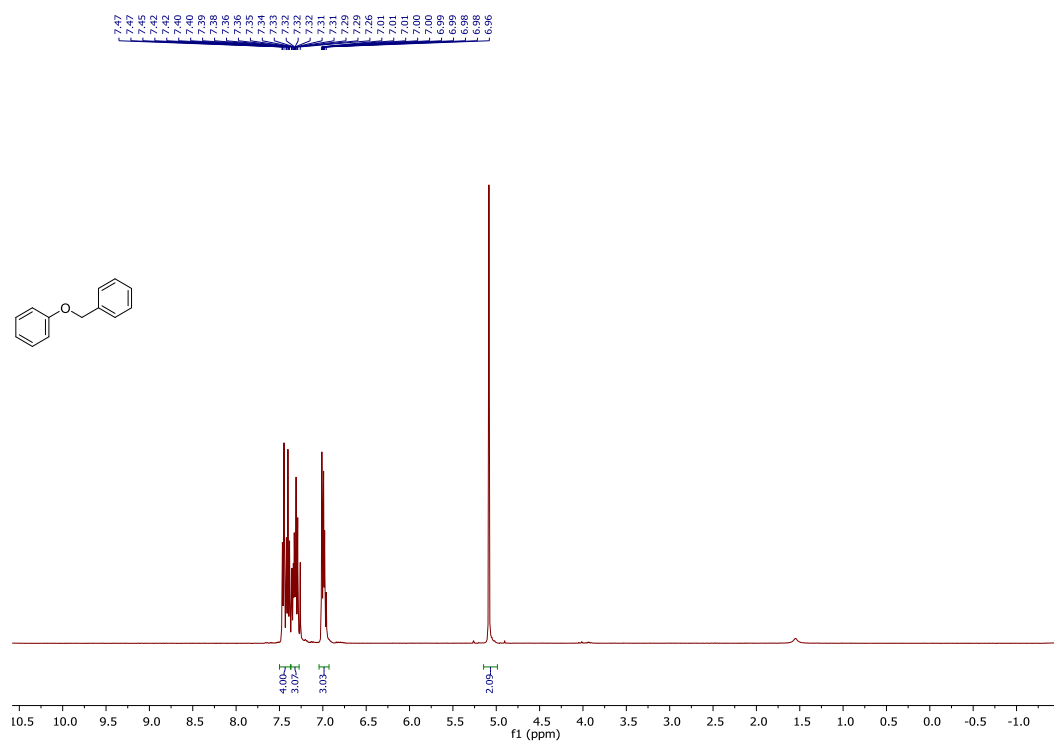


Figure S38. NMR spectra of 6h

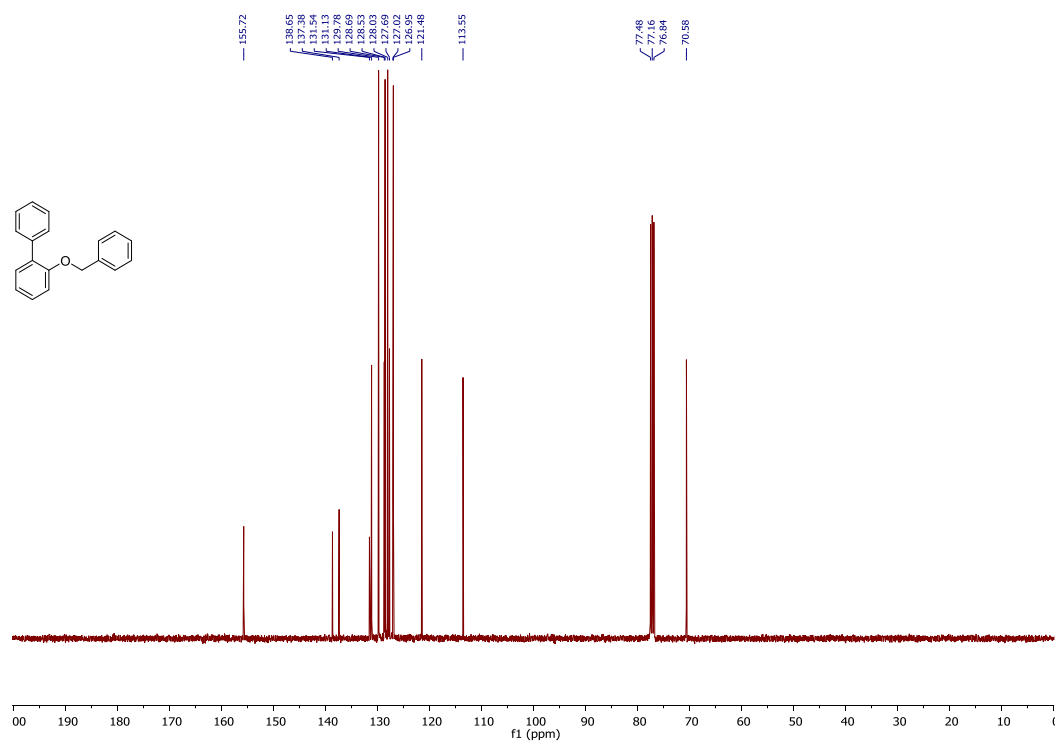
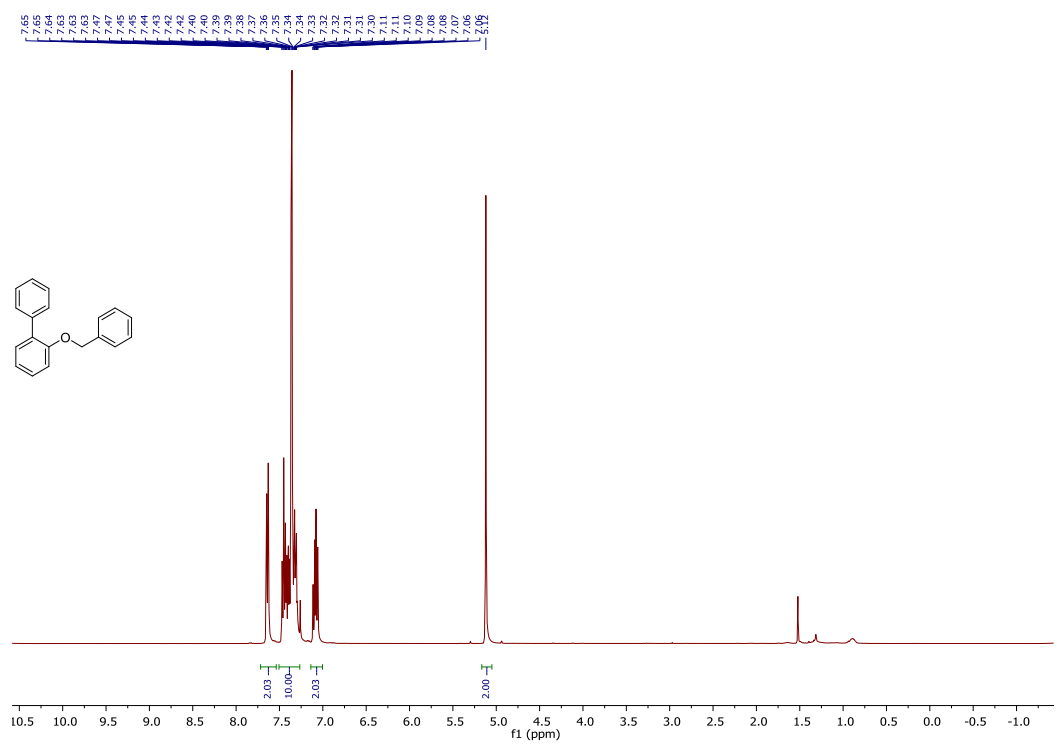


Figure S39. NMR spectra of 6i

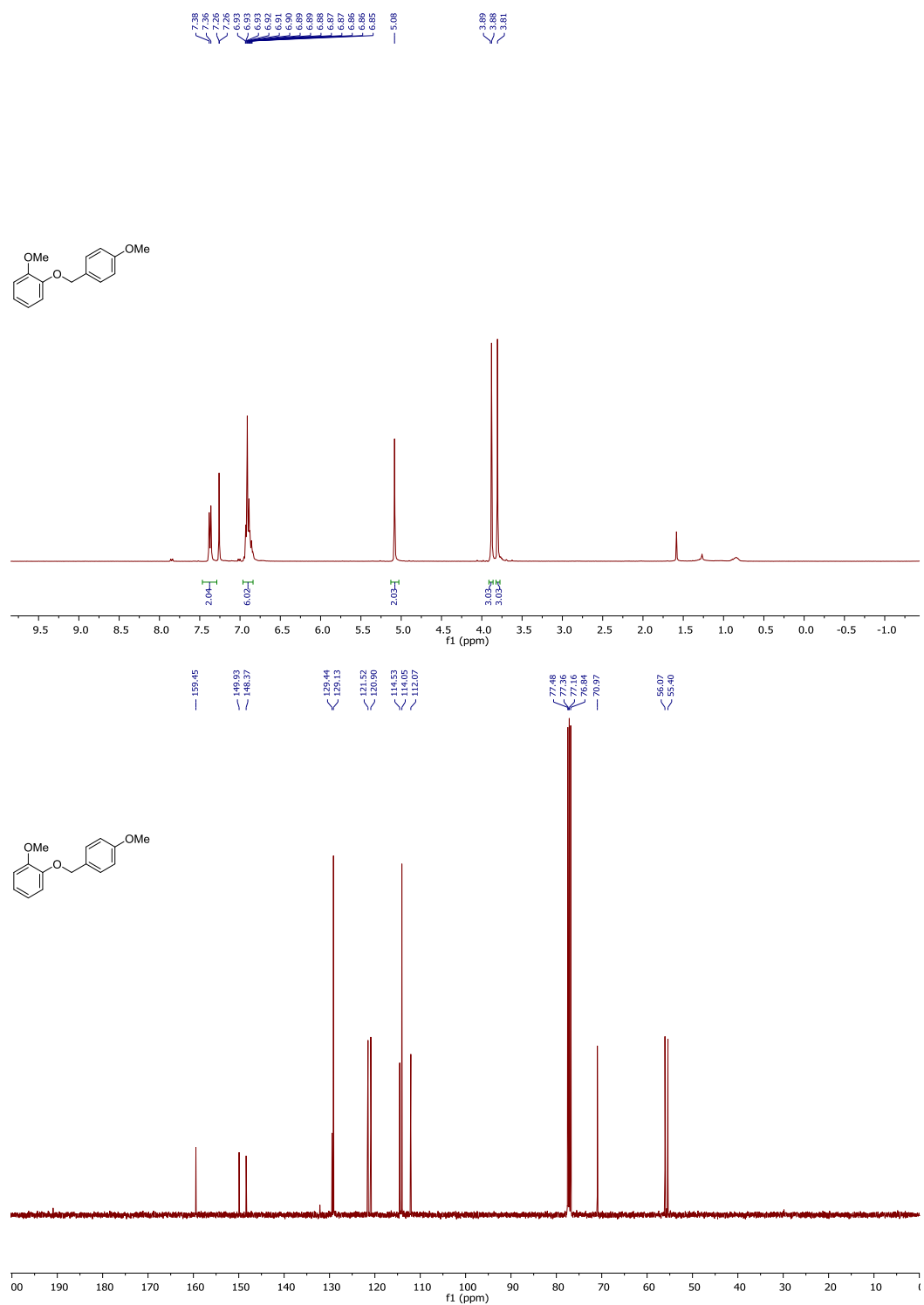


Figure S40. NMR spectra of 6j

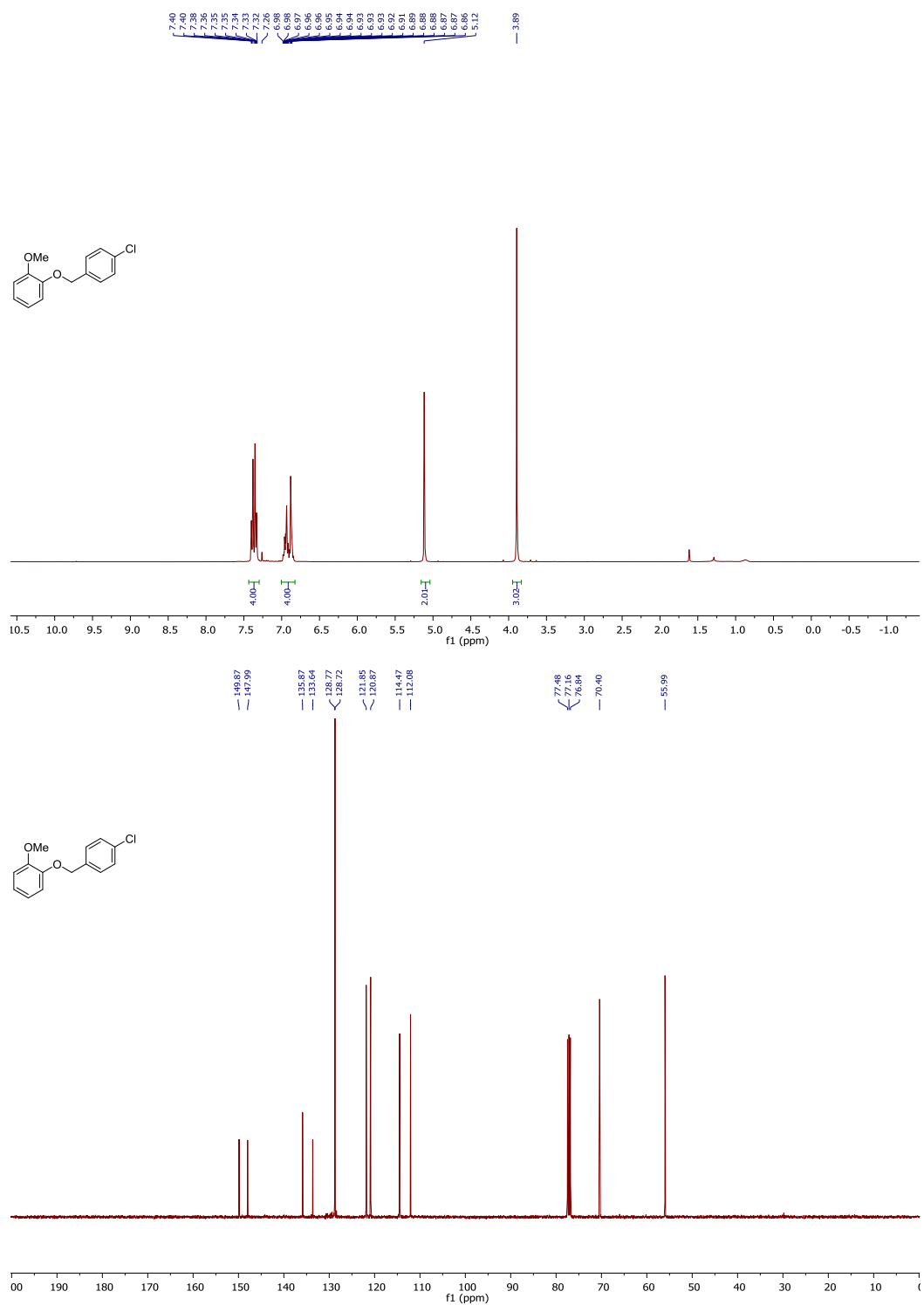


Figure S41. NMR spectra of 6k

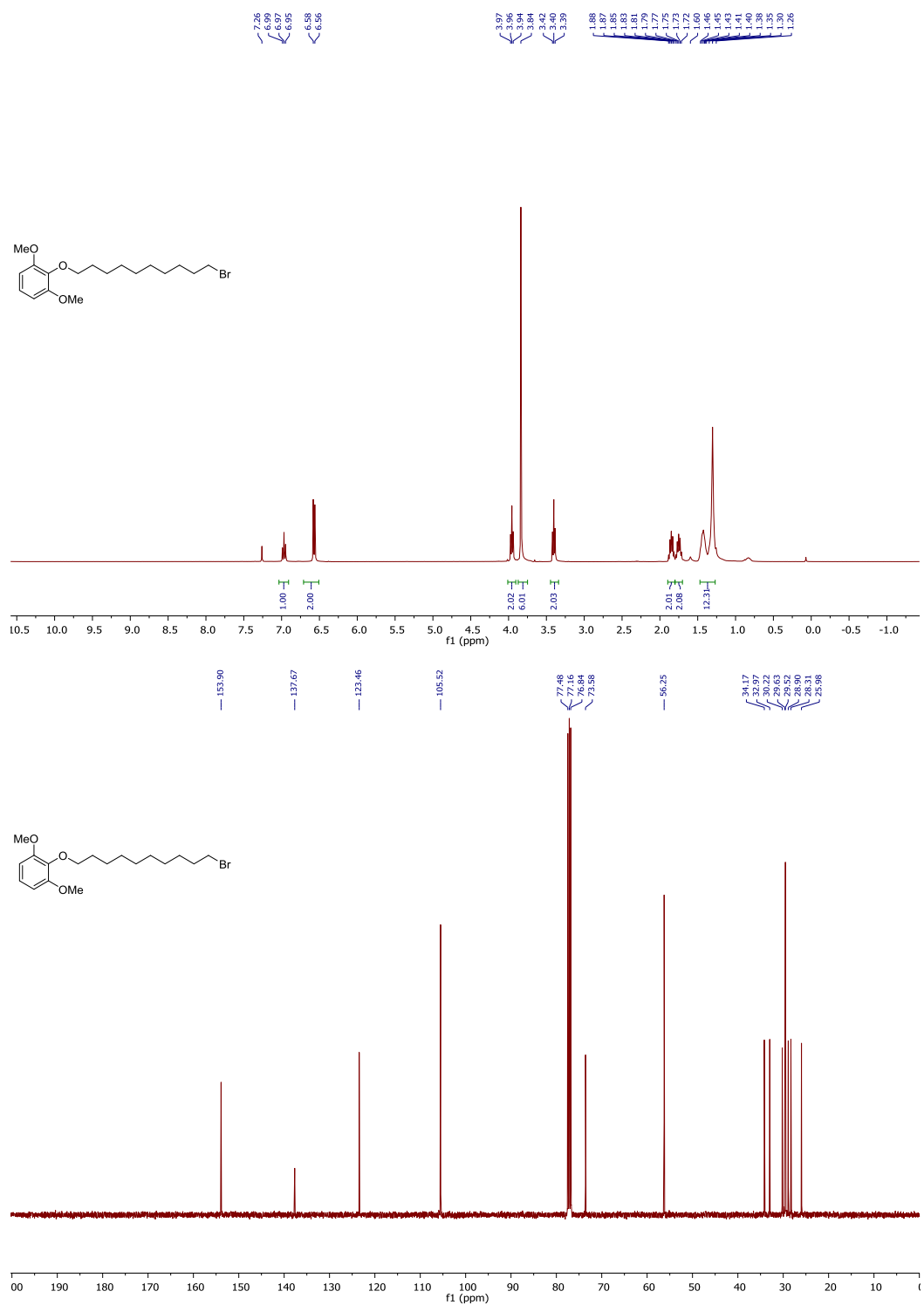
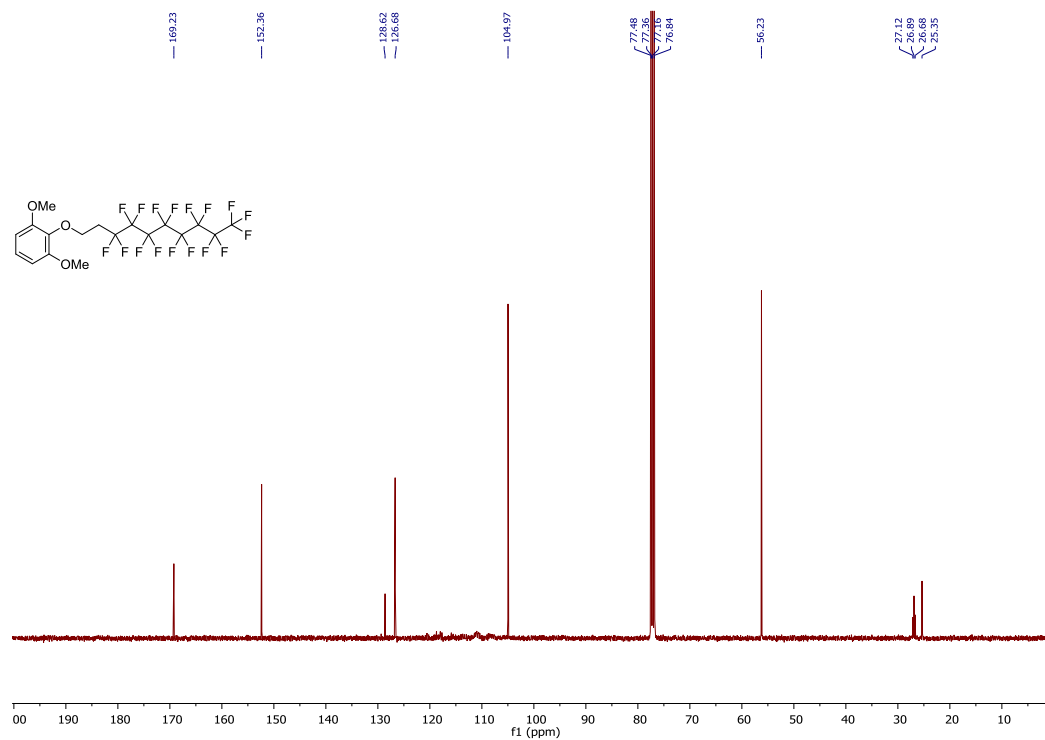
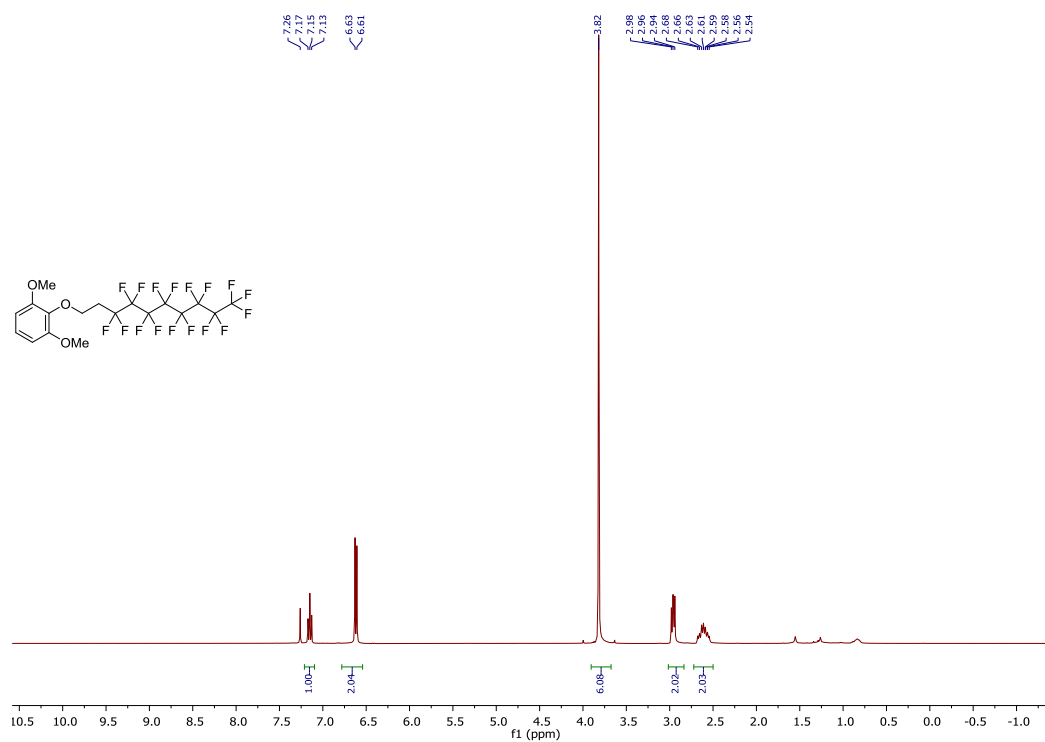


Figure S42. NMR spectra of 6l



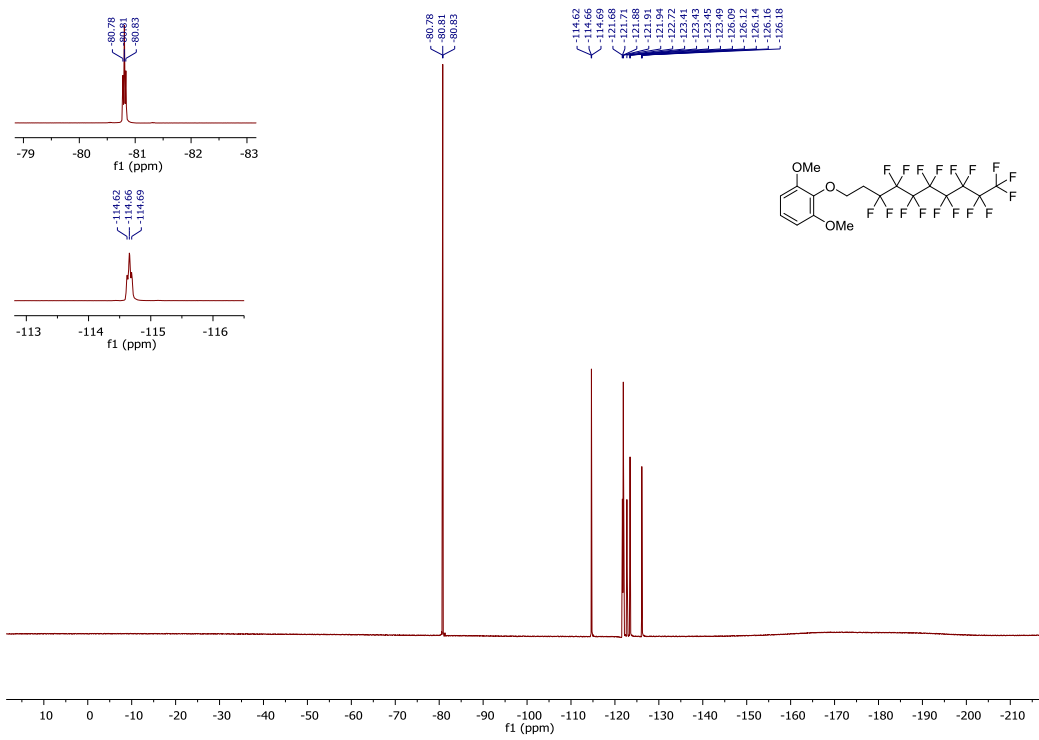


Figure S43. NMR spectra of 6m

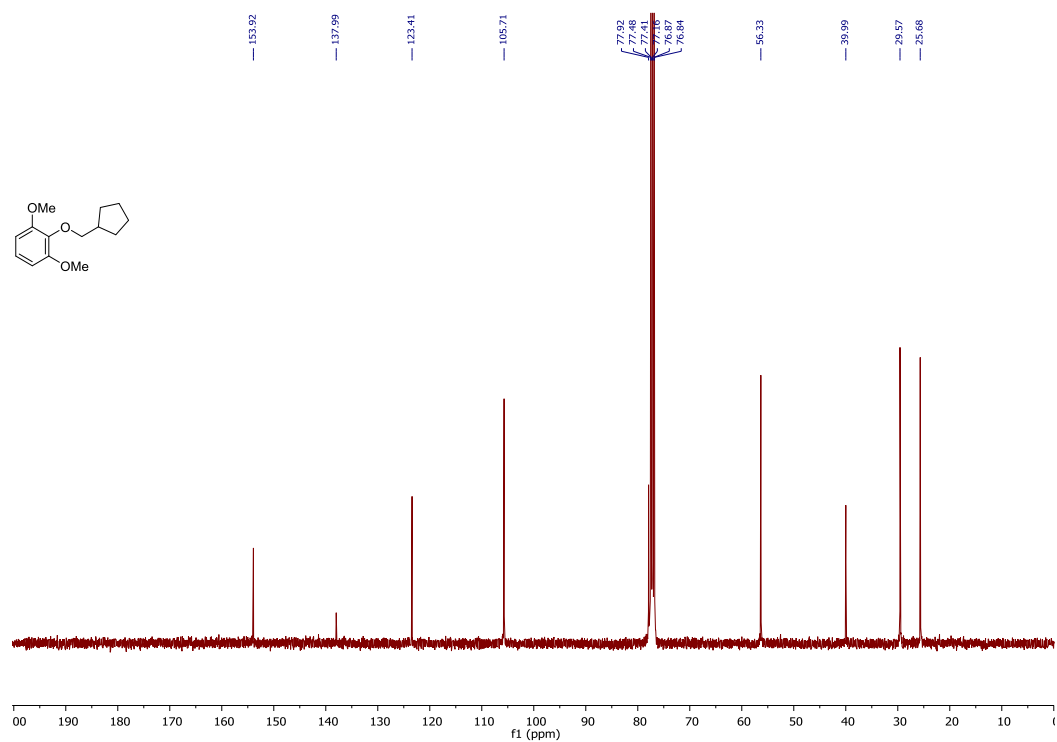
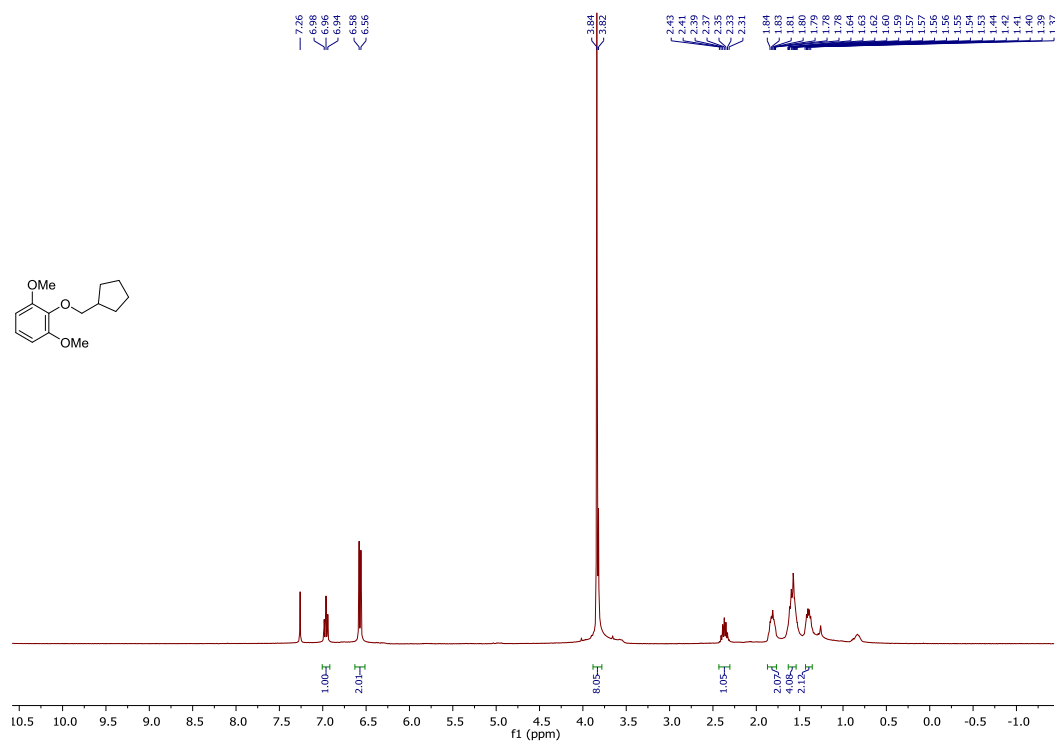


Figure S44. NMR spectra of 7a

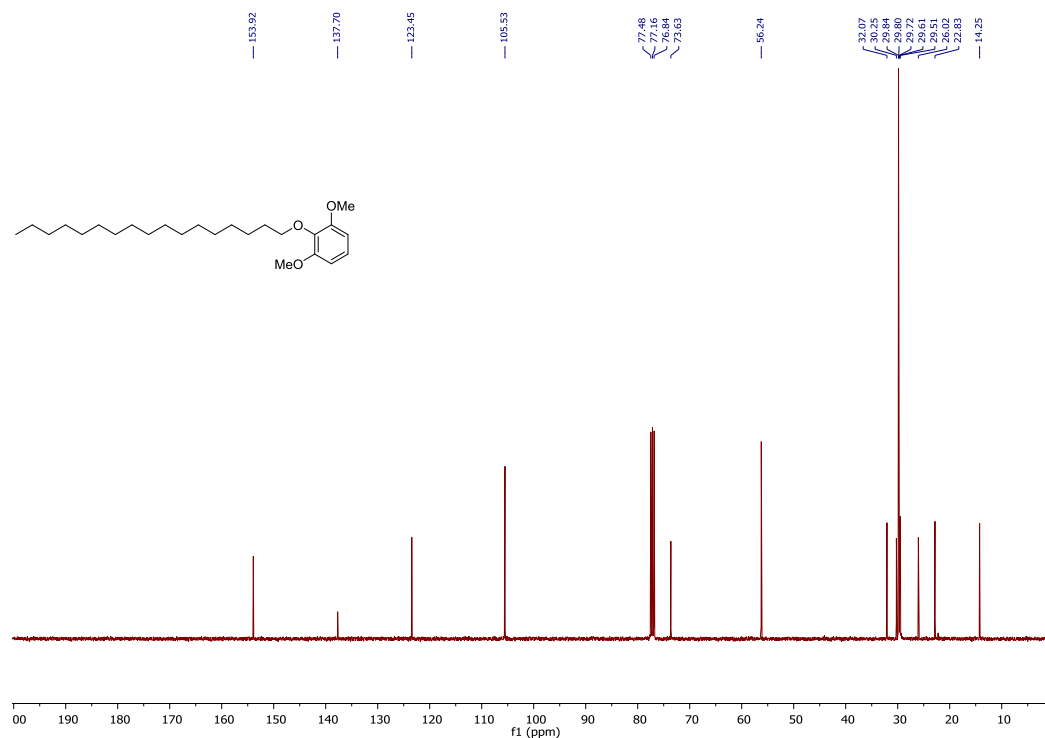
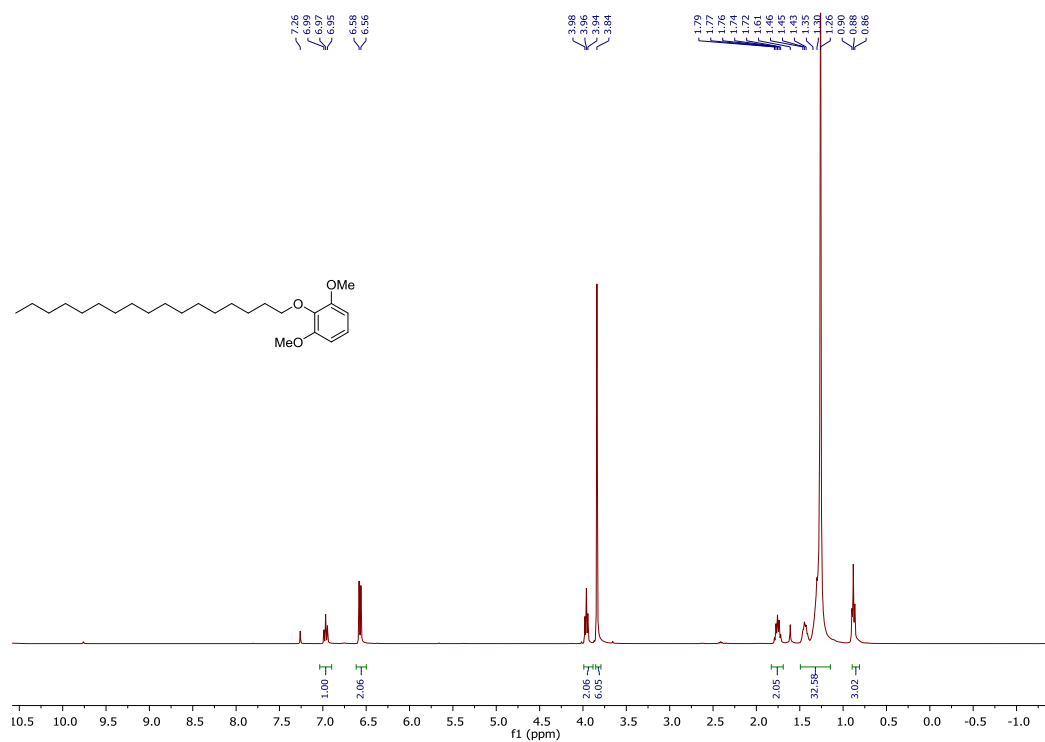


Figure S45. NMR spectra of 7b

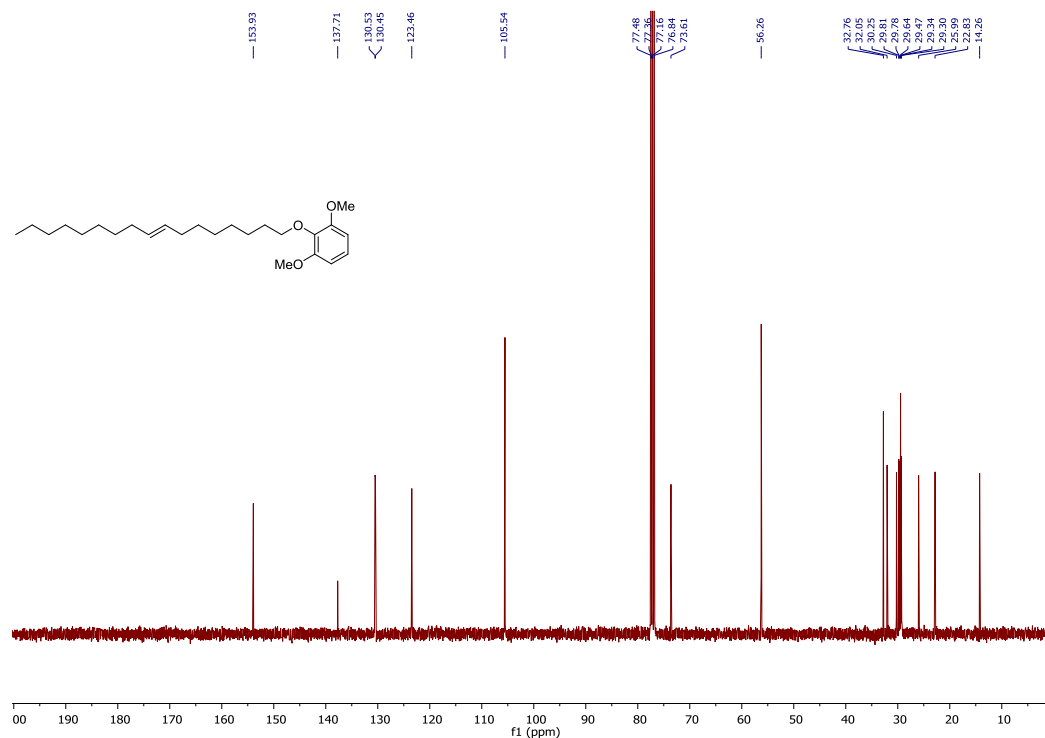
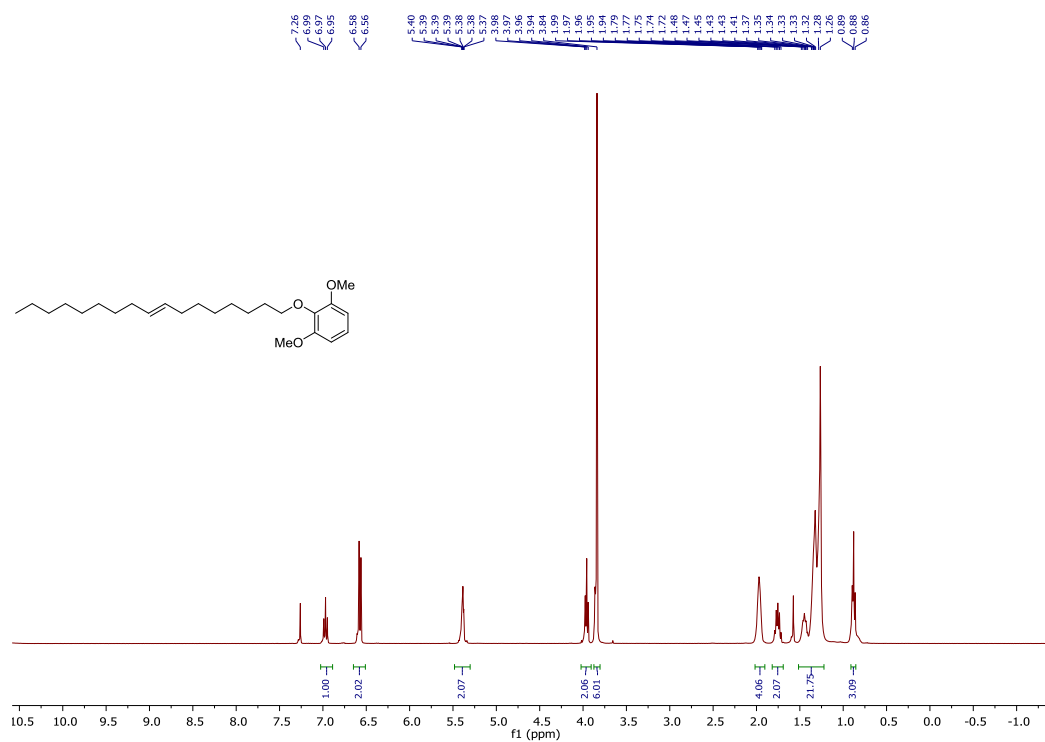


Figure S46. NMR spectra of 7c

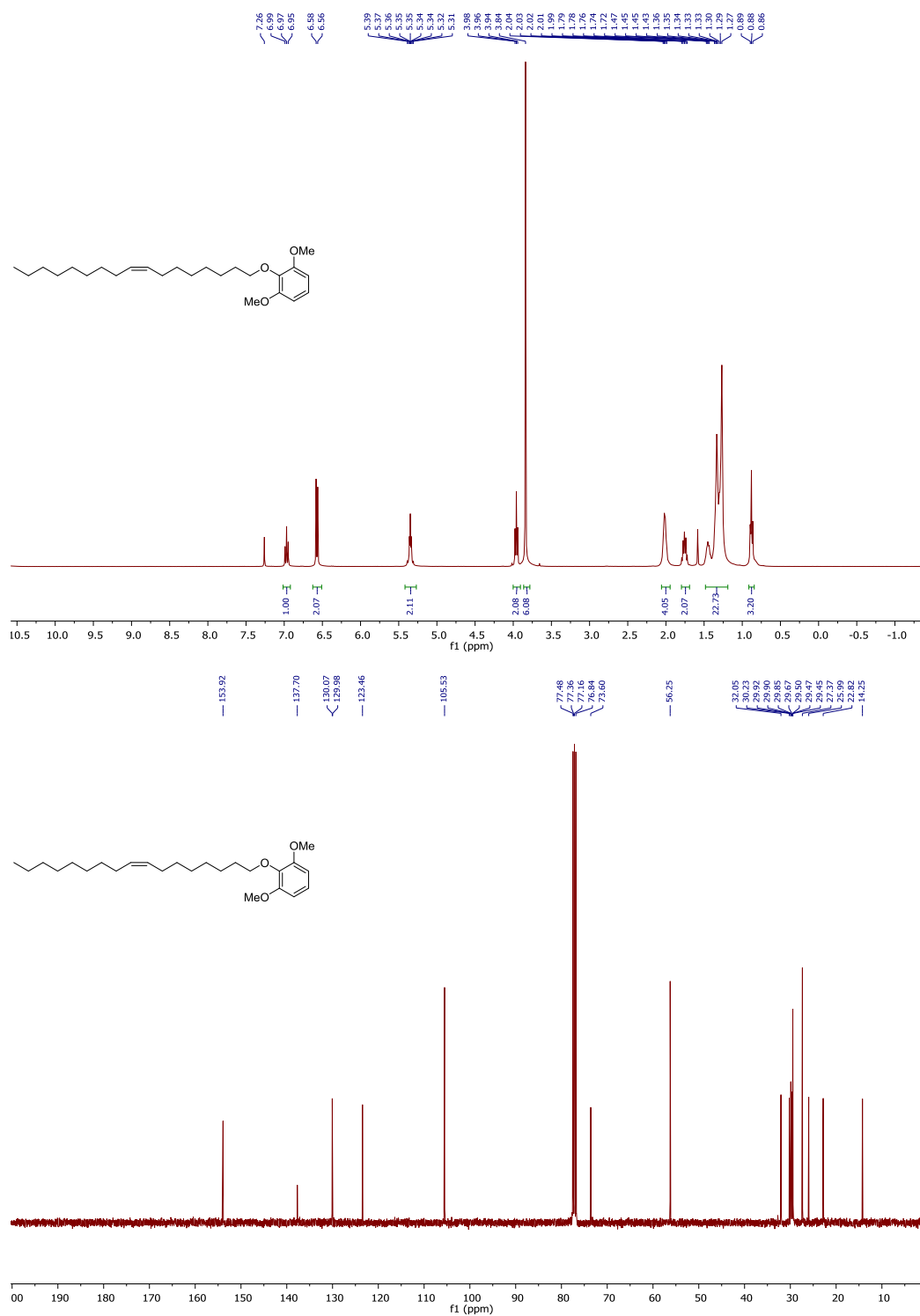


Figure S47. NMR spectra of 7d

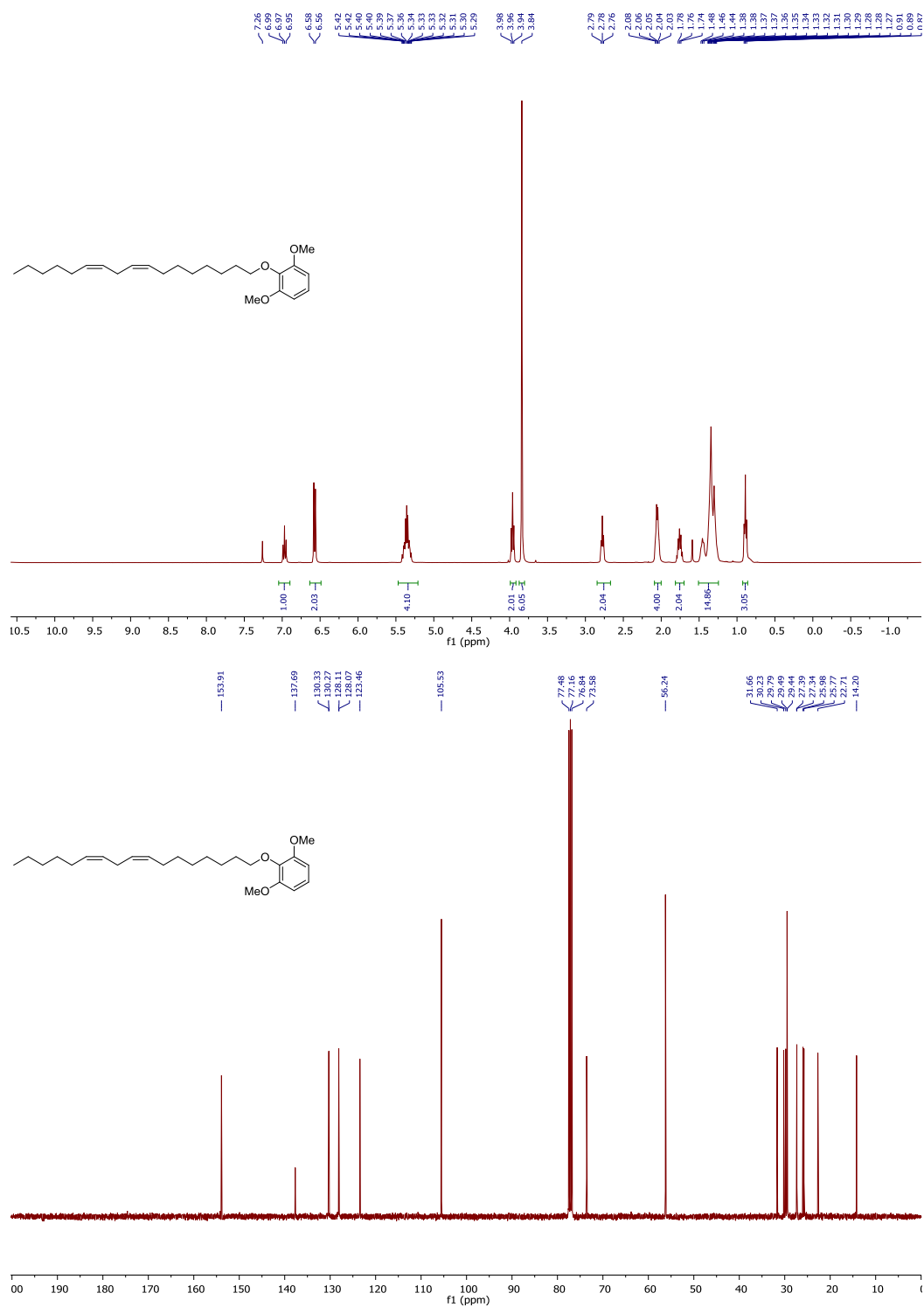


Figure S48. NMR spectra of 7e

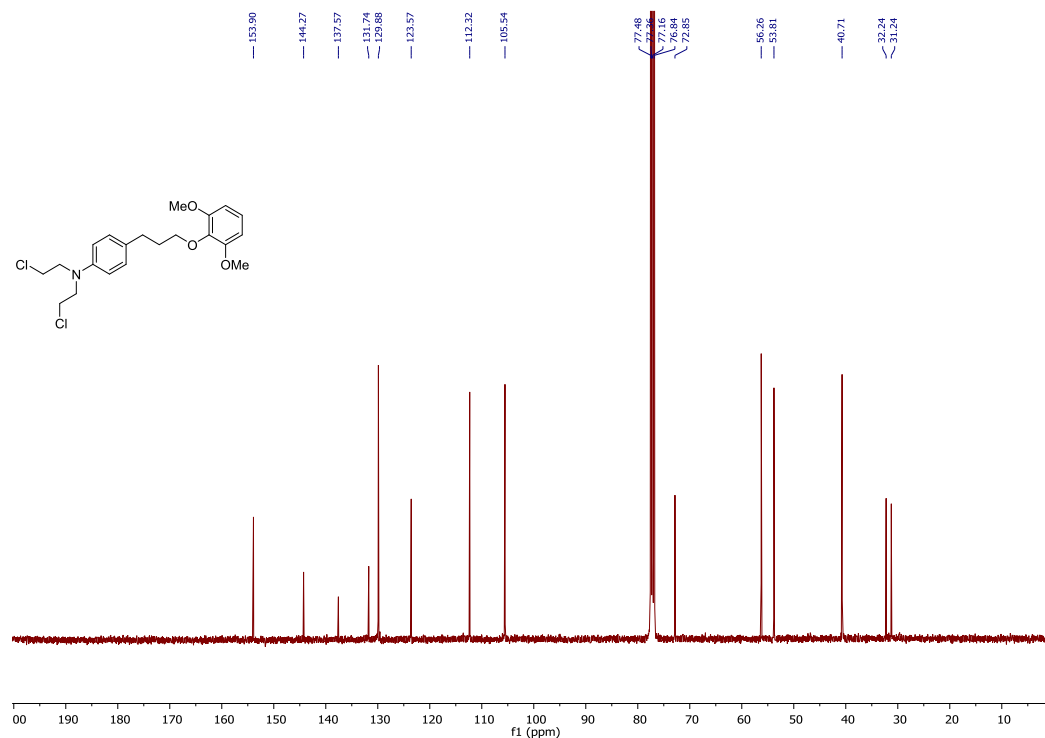
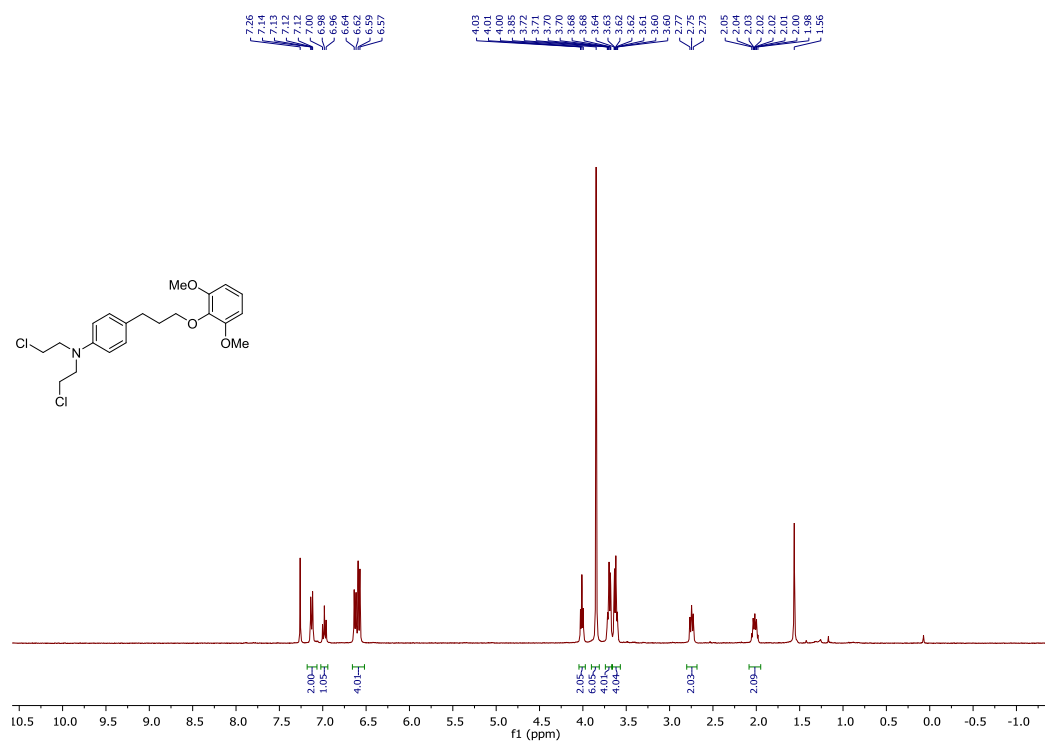


Figure S49. NMR spectra of 7f

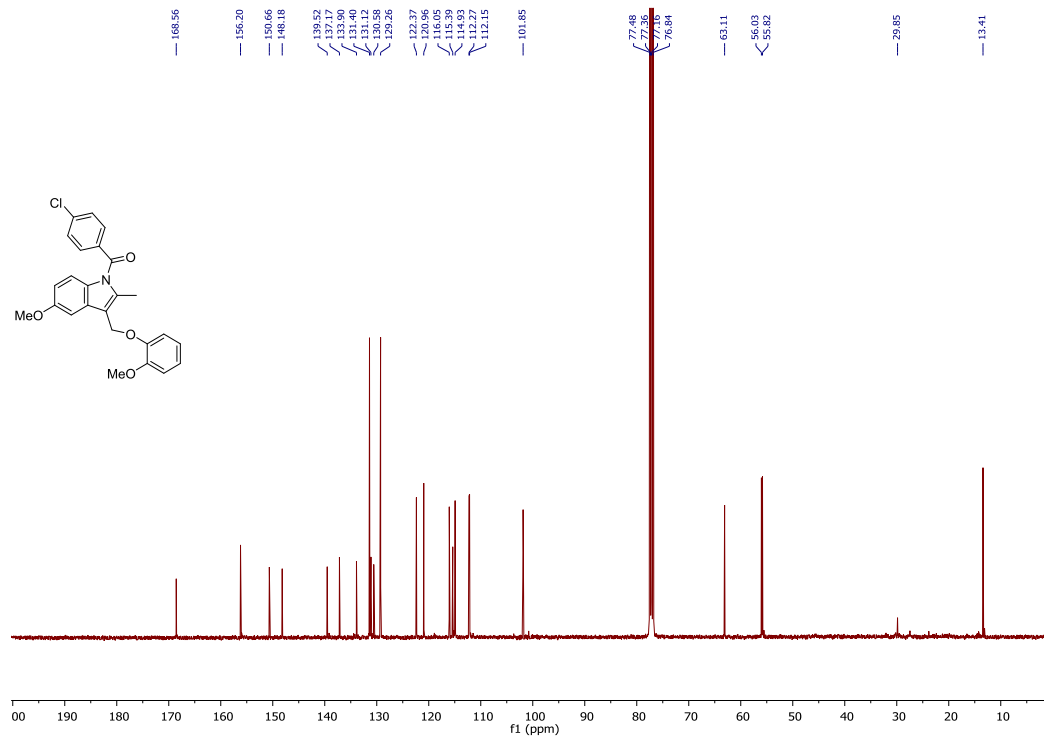
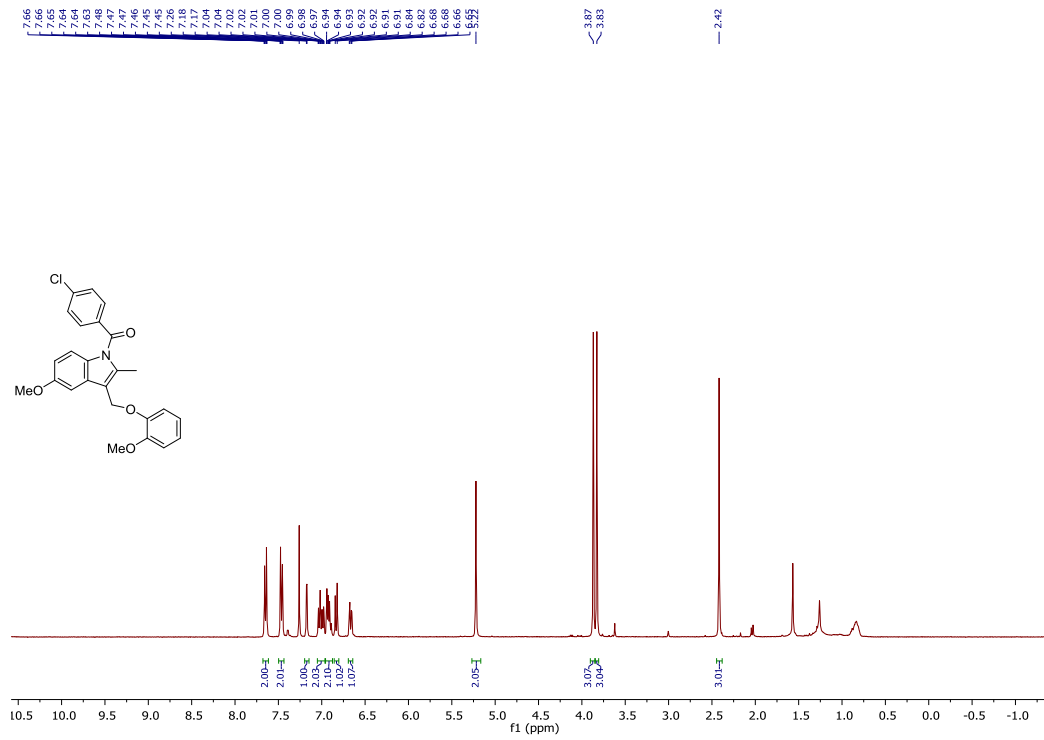


Figure S50. NMR spectra of 7g

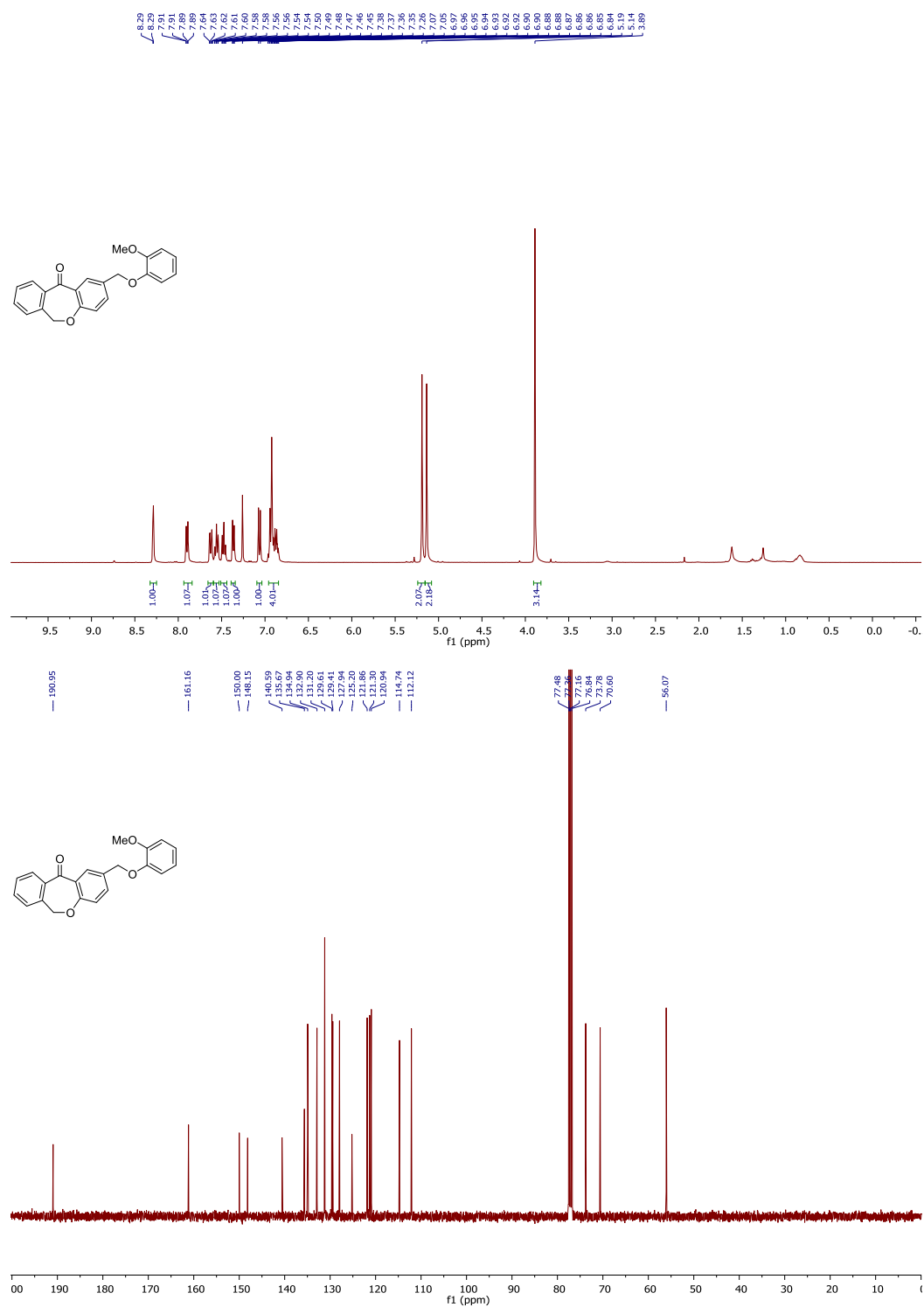


Figure S51. NMR spectra of 7h

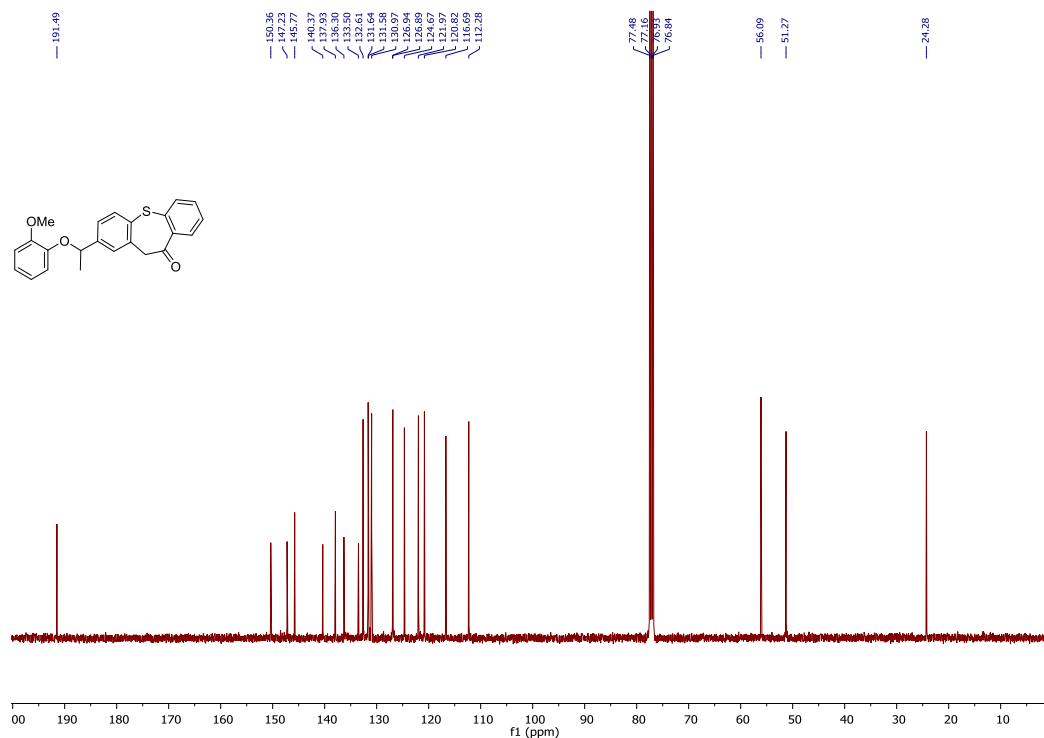
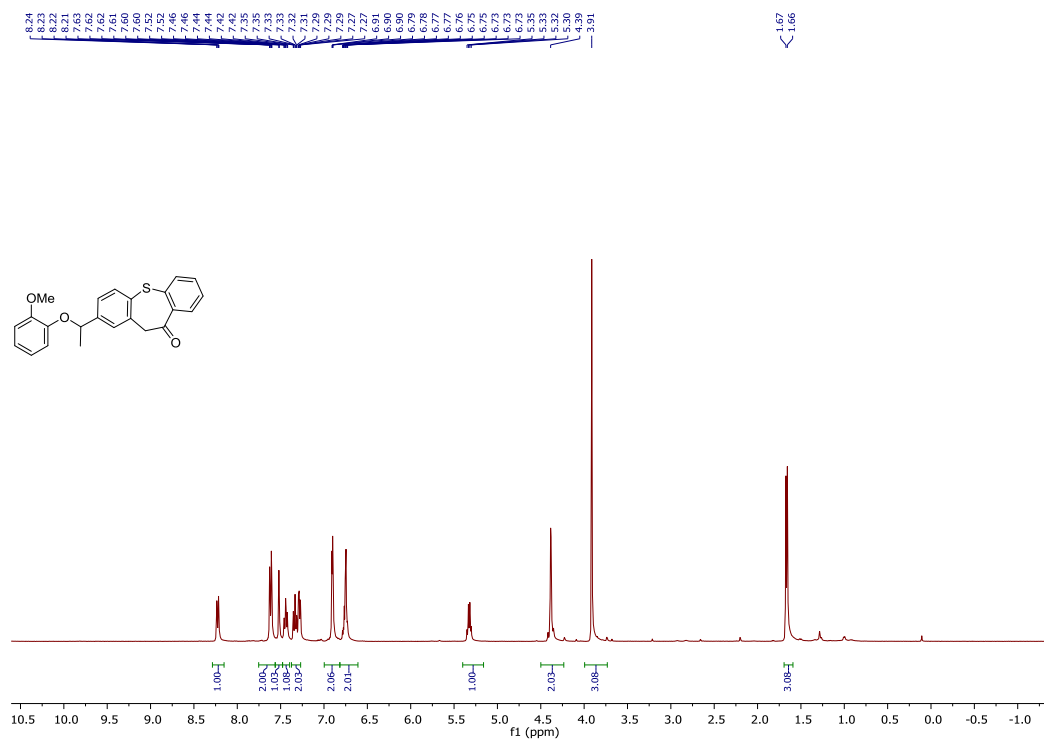


Figure S52. NMR spectra of 7i

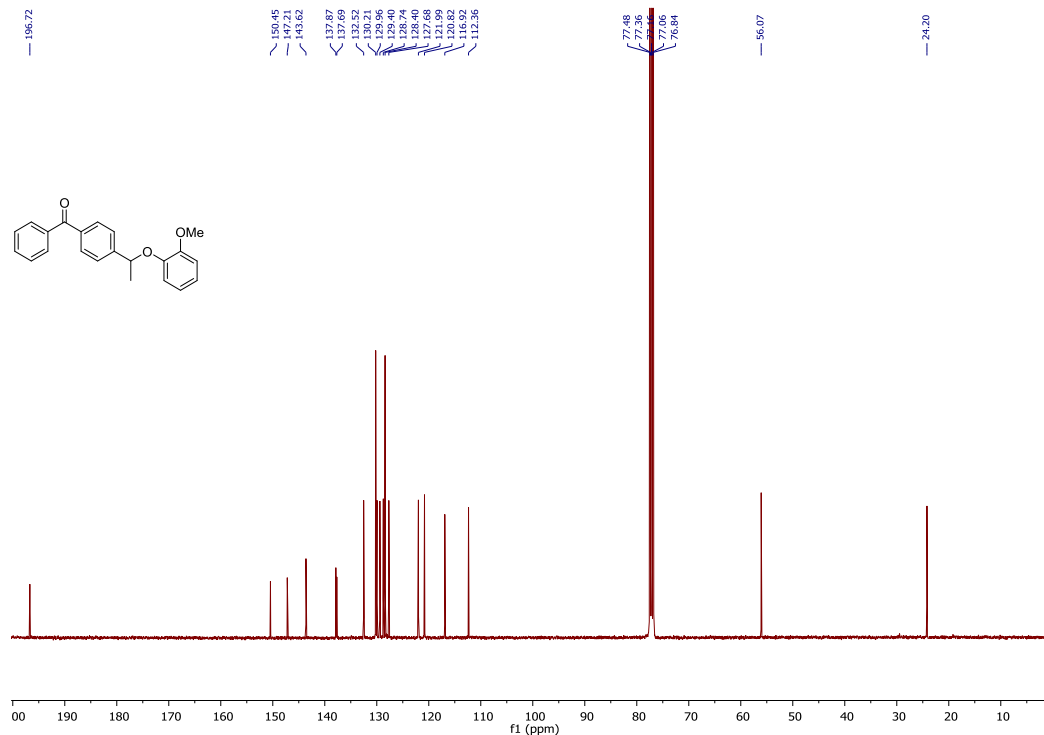
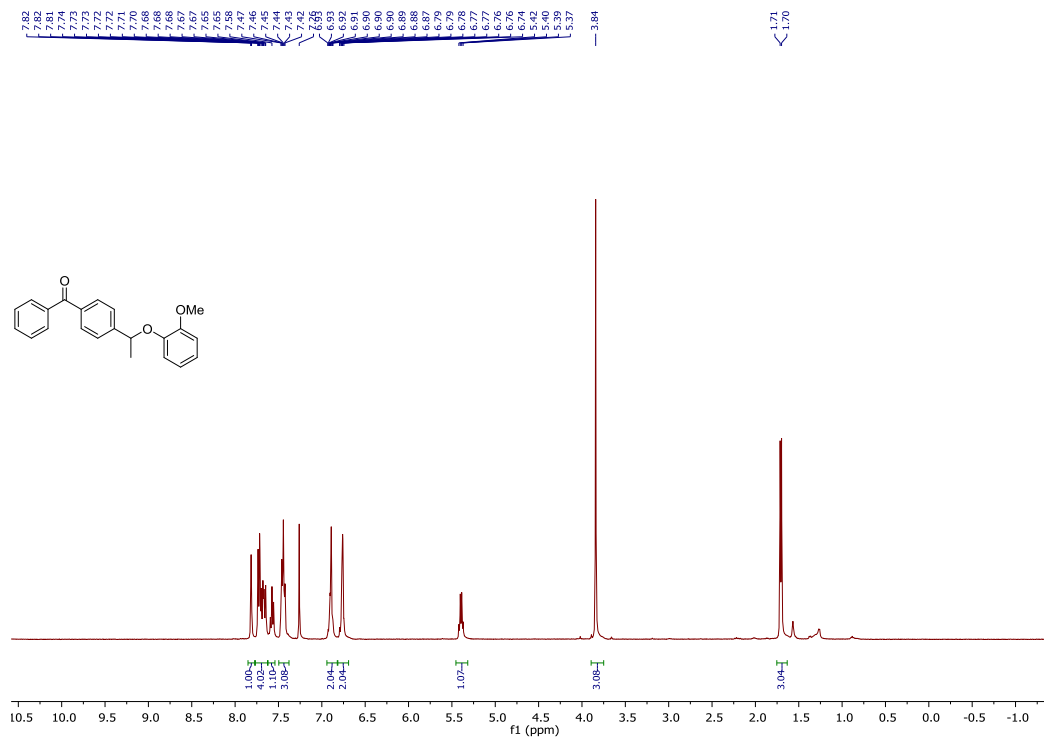


Figure S53. NMR spectra of 7j

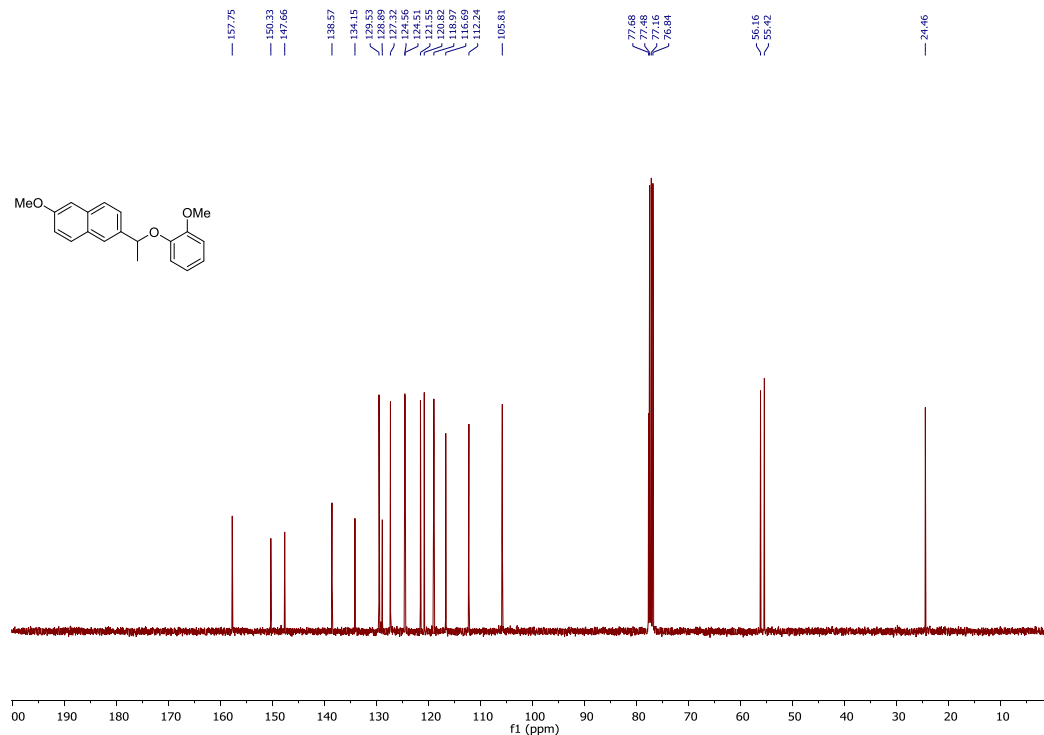
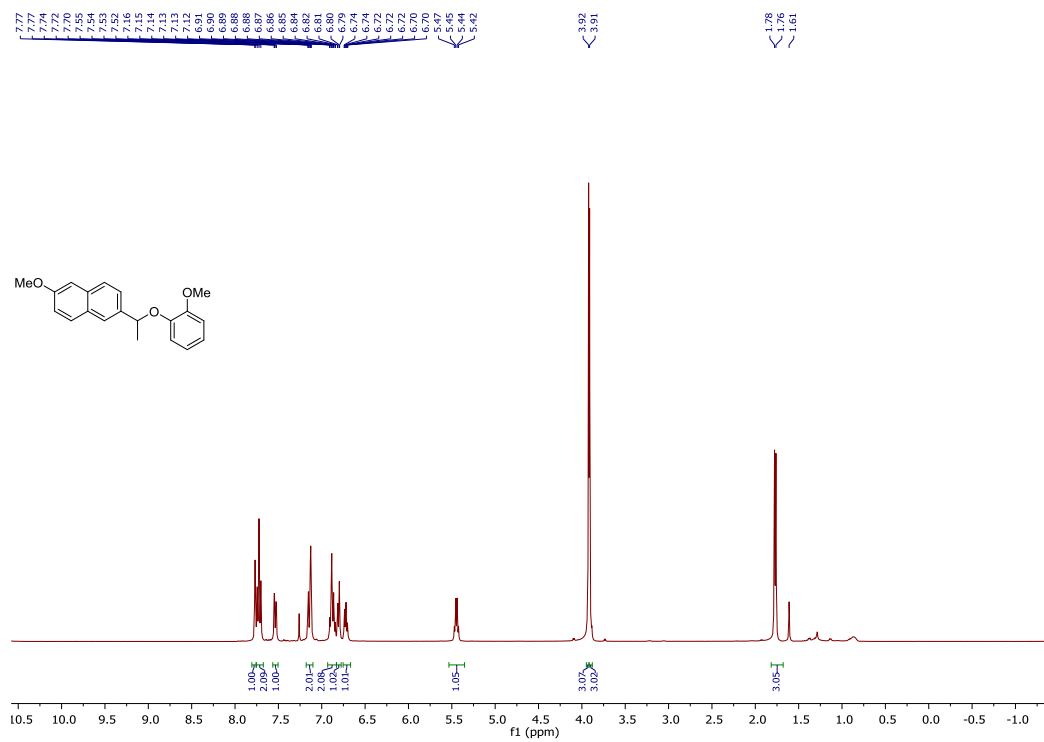


Figure S54. NMR spectra of 7k

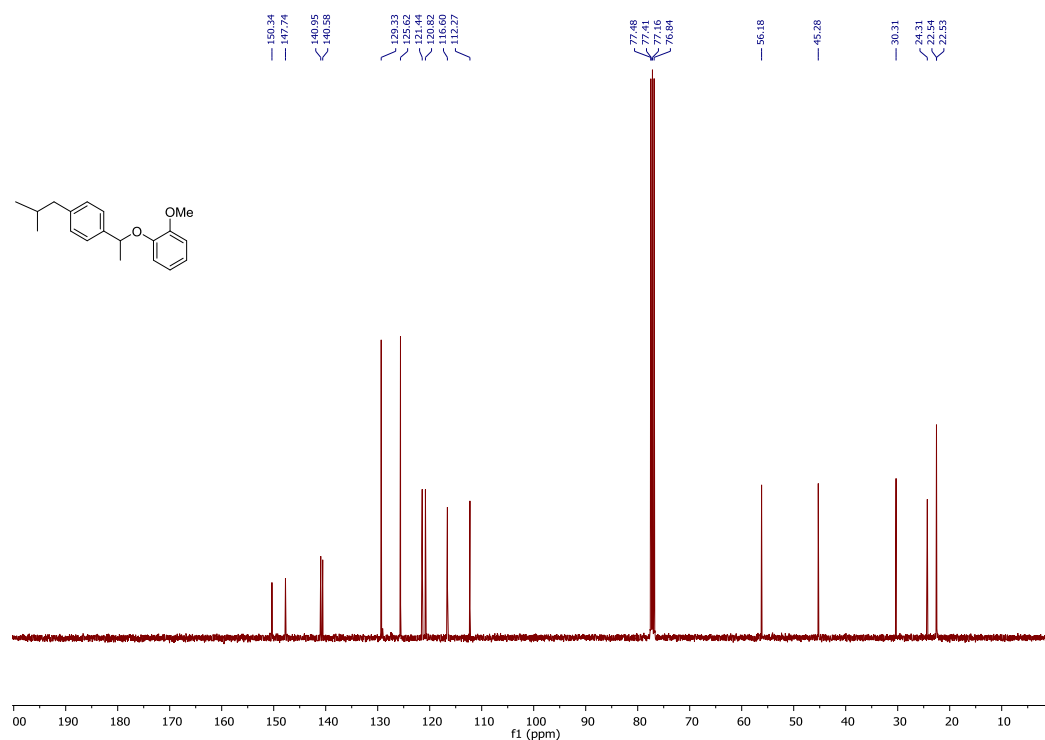
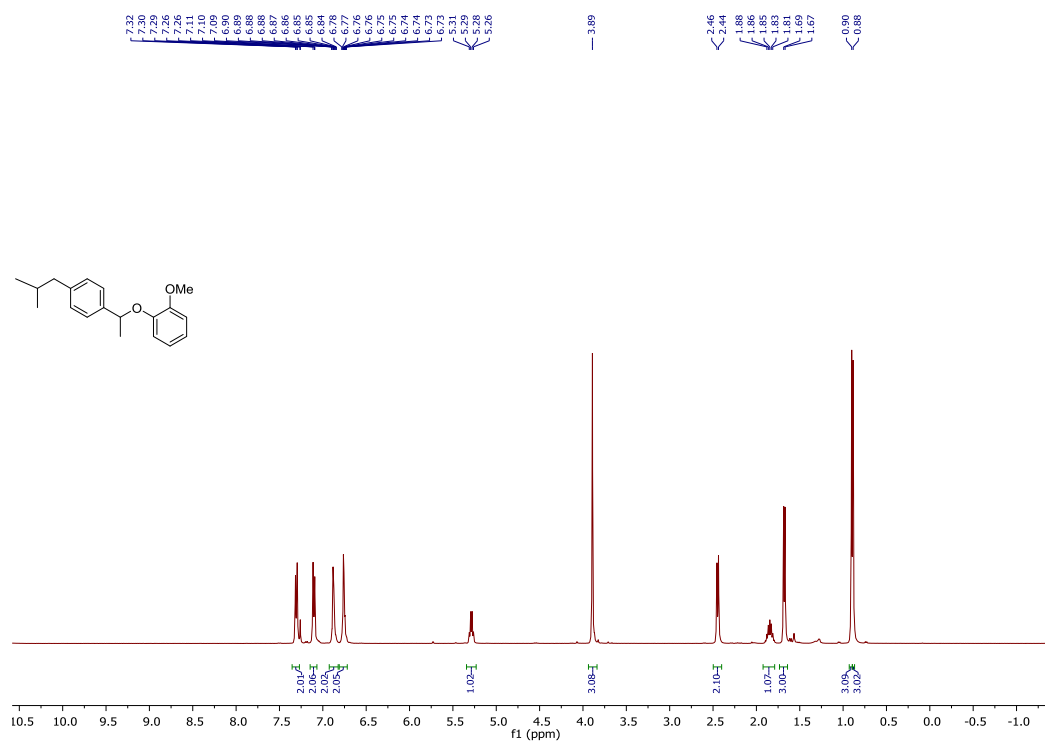


Figure S55. NMR spectra of 7l

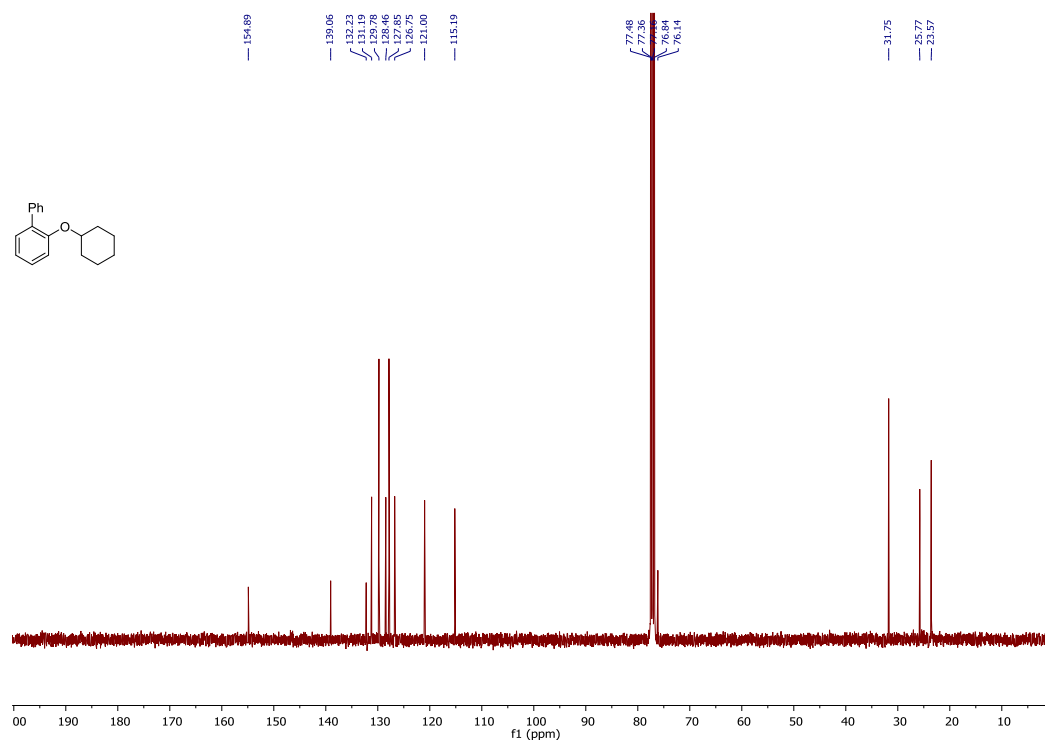
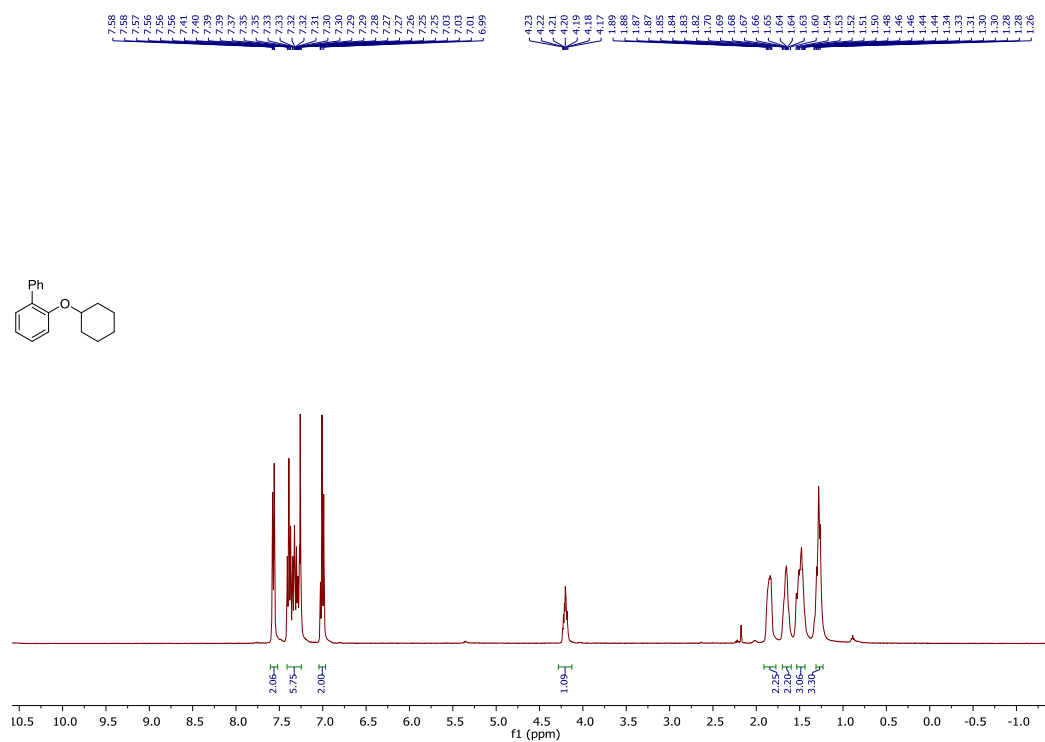


Figure S56. NMR spectra of 7m

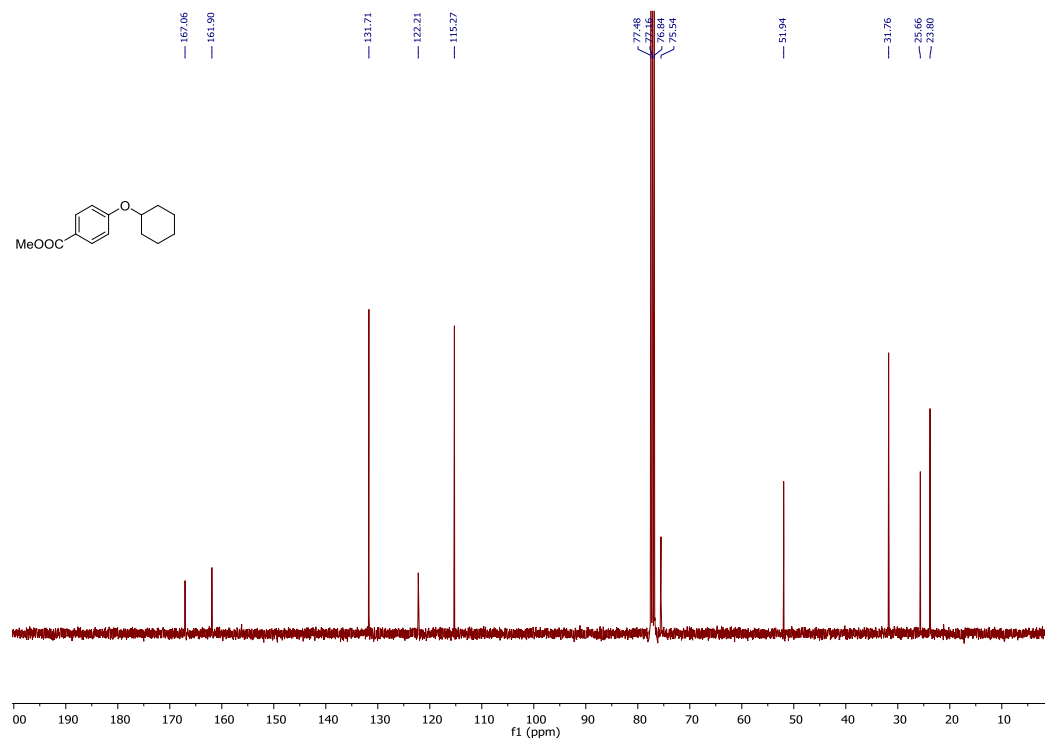
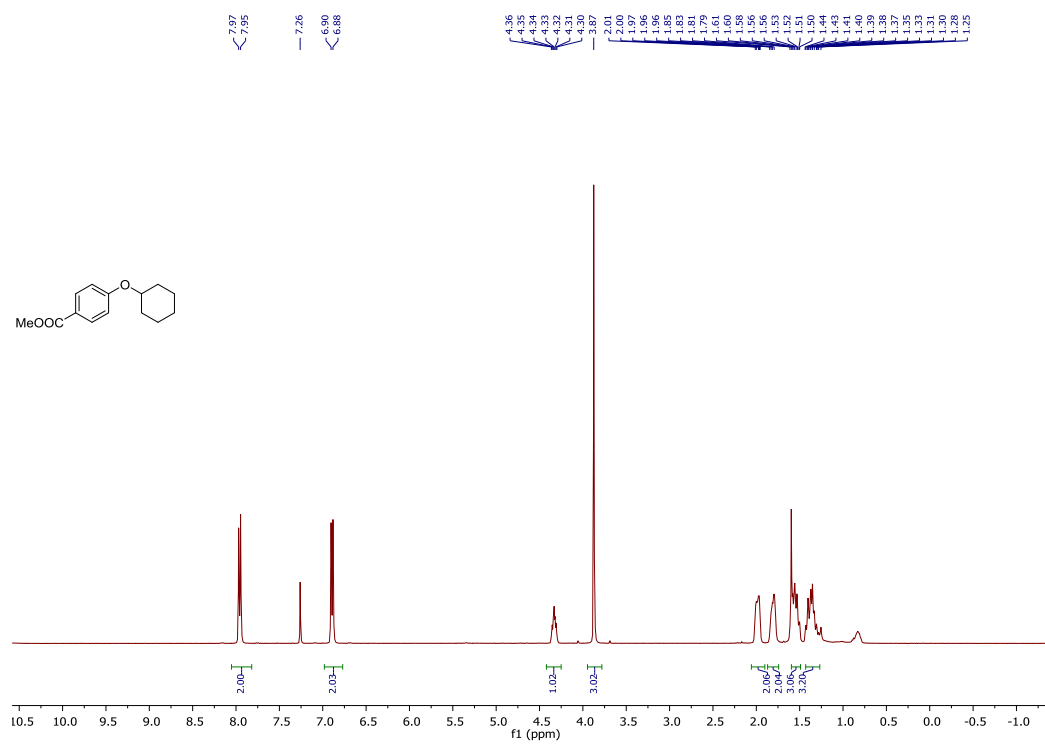
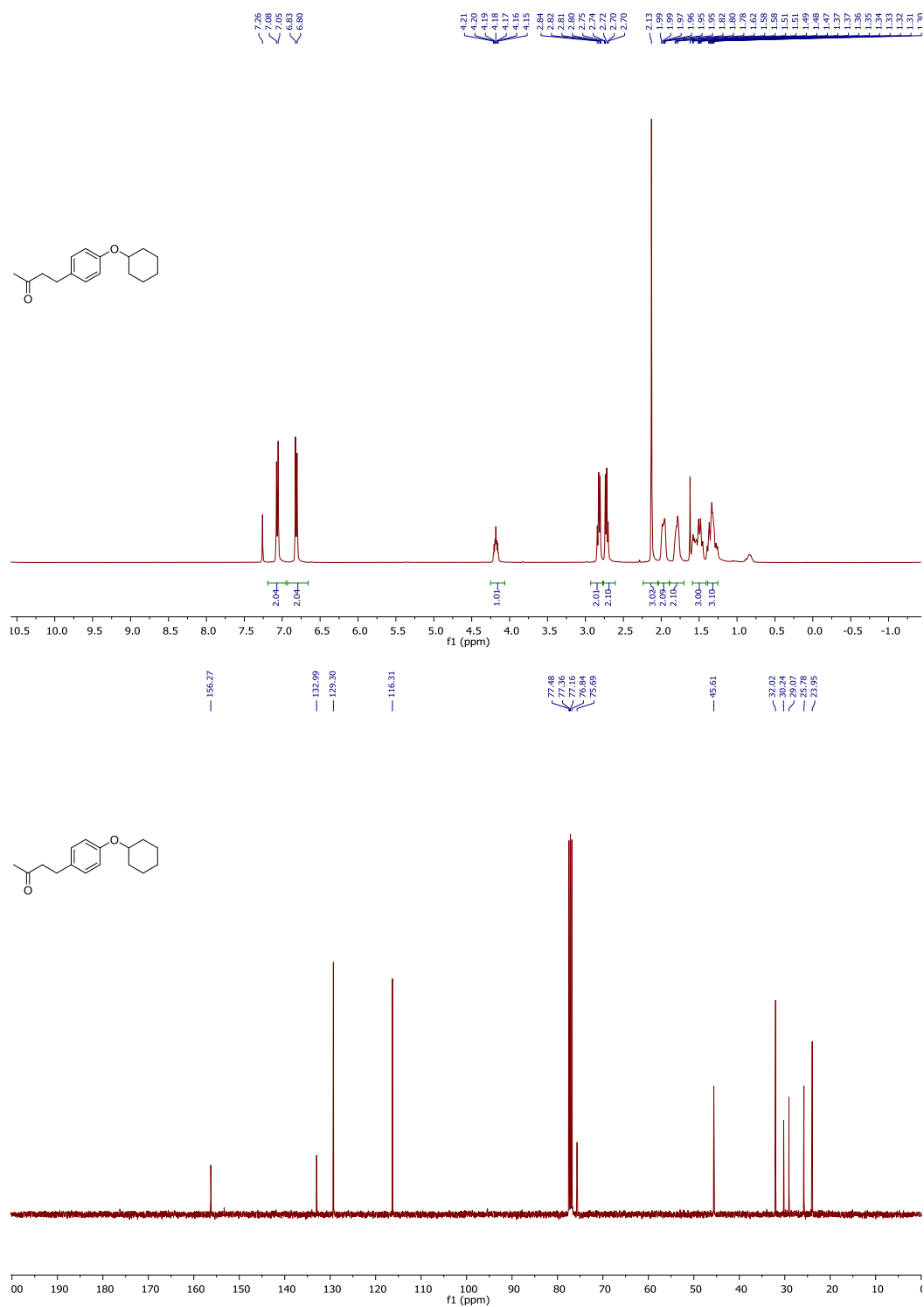


Figure S57. NMR spectra of 7n



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