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Methods

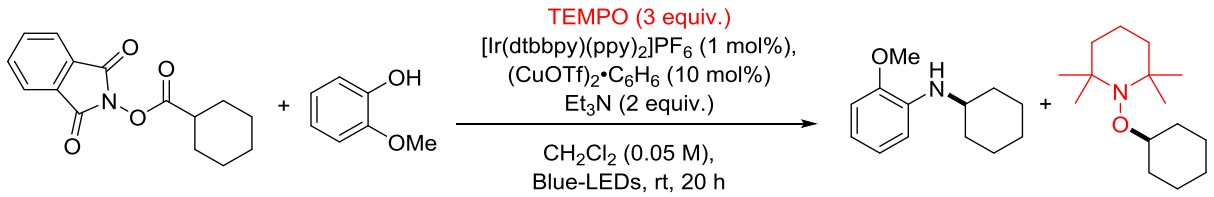
General Analytical Information

Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature. All ^{1}H 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 ^{1}H 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 ^{1}H 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

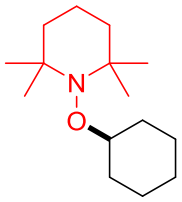
All manipulations for the decarboxylative C(sp^3)-O cross coupling via synergetic photoredox and copper catalyzed reactions were set up in a 15 mL Teflon-screw capped test tubes (unless otherwise noted) under an inert nitrogen (N_2) atmosphere using glove-box techniques. The test tubes were then sealed 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



1a 0.2 mmol, 1 equiv. + **2a** 2 equiv. → **3a** not observed + observed by **HRMS**

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 $C_{15}H_{30}NO^+$ 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 $[Ir(dtbbpy)(ppy)_2]PF_6$ in CH_2Cl_2, upon addition of a 1.0×10^{-3} M solution of guaiacol, Et_3N, $Cu(MeCN)_4PF_6$, NHPI ester (**1a**), mixture of $Cu(MeCN)_4PF_6$ and NHPI ester (**1a**), or mixture of $Cu(MeCN)_4PF_6$ 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 $[Ir(dtbbpy)(ppy)_2]PF_6$ in CH_2Cl_2, upon addition of variable concentration of the mixture of $Cu(MeCN)_4PF_6$ and Et_3N. 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).

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

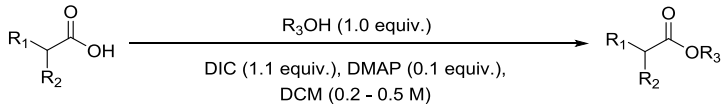
$$K_{sv} = k_q \tau_0 \qquad (2)$$

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 $[Ir(dtbbpy)(ppy)_2]PF_6$.

Under these conditions, the mixture of $Cu(MeCN)_4PF_6$ and Et_3N (1:1, concentration) was the only species that quenched the photoexcited catalyst with the Stern-Volmer constant of 1173 $M^{-1}S^{-1}$ (Figure S3).

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

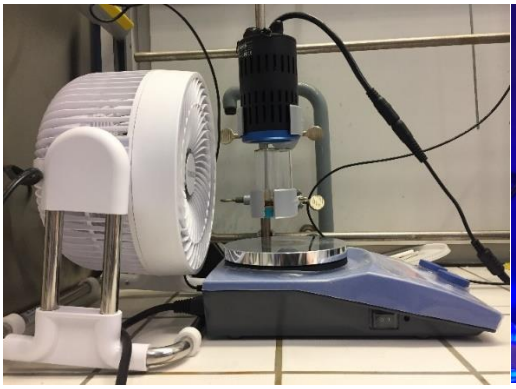
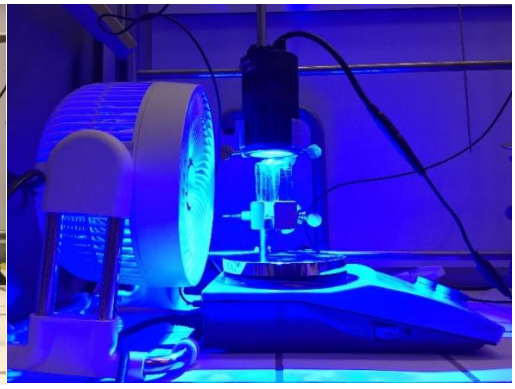


A round-bottom flask or culture tube was charged with carboxylic acid (if solid, 1.0 equiv), nucleophile (*N*-hydroxyphthalimide, 1.0 equiv) and DMAP (0.1 equiv.). dichloromethane (DCM) was added (0.2 M-0.5 M) and the mixture was stirred vigorously. Carboxylic acid (if liquid, 1.0 equiv.) was added via 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 and12 h. Afterwards, the mixture was filtered over Celite and rinsed with additional CH_2Cl_2. 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]

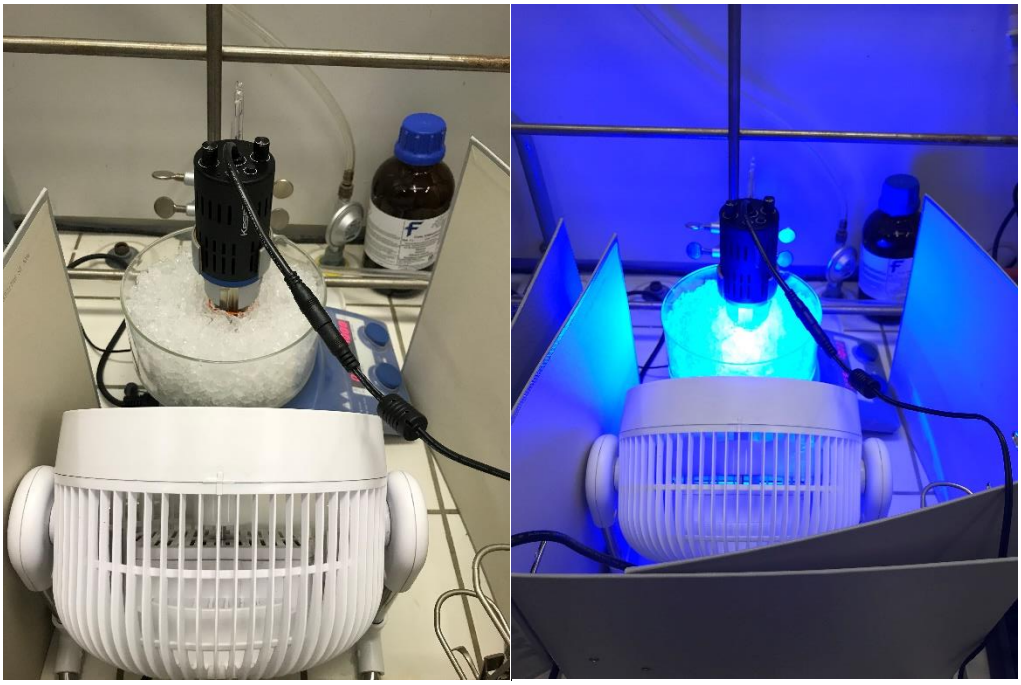
General procedure for visible-light-mediated decarboxylative etherification of phenols with secondary or tertiary NHPI esters (General Procedure B)

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), $[Ir(dtbbpy)(ppy)_2]PF_6$ (1 mol%), $(CuOTf)_2 \bullet C_6H_6$ (10 mol%), CH_2Cl_2 (0.05 M), Et_3N (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 Na_2SO_4, 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.

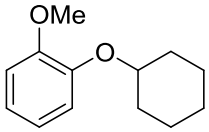



General procedure for visible-light-mediated decarboxylative etherification of phenols with primary NHPI esters (General Procedure C)

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), $[Ir(dtbbpy)(ppy)_2]PF_6$ (1 mol%), $Cu(MeCN)_4OTf$ (40 mol%), CH_2Cl_2 (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 Na_2SO_4, 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)



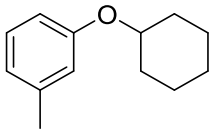
Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **3a** (58 mg) in 94%.

^{1}H 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).

^{13}C 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 ^{1}H NMR and ^{13}C NMR spectra were consistent with the spectrum reported in the literature.[8]

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



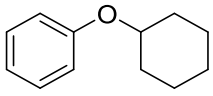
Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **3b** (38 mg) in 67%.

^{1}H 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).

^{13}C 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 ^{1}H NMR and ^{13}C NMR spectra were consistent with the spectrum reported in the literature.[9]

Cyclohexyl phenyl ether (3c)



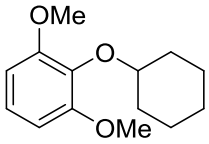
Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 40/1 (v/v) as an eluent, to yield the title compound **3c** (48 mg) in 90%.

^{1}H 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).

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

The ^{1}H NMR and ^{13}C 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%.

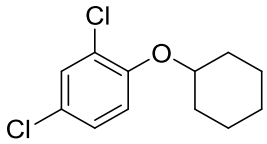
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.96 (t, *J* = 8.3 Hz, 1H), 6.64 – 6.49 (m, 2H), 4.04 – 3.92 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.02 – 1.93 (m, 2H), 1.84 – 1.76 (m, 2H), 1.62 – 1.51 (m, 3H), 1.29 – 1.19 (m, 3H).

^{13}C 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 $C_{14}H_{21}O_3^+$ 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%.

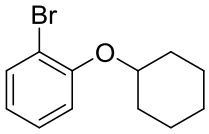
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.35 (d, *J* = 2.6 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.25 (tt, *J* = 8.3, 3.6 Hz, 1H), 2.02 – 1.87 (m, 2H), 1.88 – 1.75 (m, 2H), 1.67 – 1.50 (m, 3H), 1.41 – 1.26 (m, 3H).

^{13}C 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 $C_{12}H_{15}Cl_2O^+$ 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%.

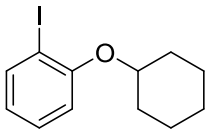
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.22 (td, *J* = 7.8, 1.7 Hz, 1H), 6.92 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.80 (td, *J* = 7.6, 1.5 Hz, 1H), 4.32 (tt, *J* = 8.1, 3.6 Hz, 1H), 2.00 – 1.88 (m, 2H), 1.89 – 1.80 (m, 2H), 1.73 – 1.60 (m, 2H), 1.58 – 1.49 (m, 1H), 1.42 – 1.32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

^{13}C 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 $C_{12}H_{15}BrO^+$ 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%.

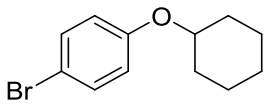
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.26 (td, *J* = 8.1, 7.5, 1.7 Hz, 1H), 6.83 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.68 (td, *J* = 7.6, 1.4 Hz, 1H), 4.36 (tt, *J* = 7.8, 3.2 Hz, 1H), 1.94 – 1.81 (m, 4H), 1.76 – 1.64 (m, 2H), 1.57 – 1.50 (m, 1H), 1.47 – 1.35 (m, 3H).

^{13}C 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 $C_{12}H_{15}IO^+$ 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%.

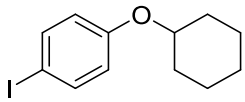
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.41 – 7.29 (m, 2H), 7.15 – 6.86 (m, 2H), 2.57 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.12 – 1.96 (m, 2H), 1.90 – 1.76 (m, 2H), 1.77 – 1.66 (m, 1H), 1.64 – 1.55 (m, 2H), 1.45 – 1.25 (m, 3H).

^{13}C 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 $C_{12}H_{15}BrO^+$ 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%.

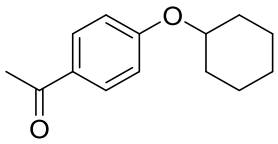
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.53 (dd, *J* = 8.9, 2.0 Hz, 2H), 6.68 (dd, *J* = 8.7, 2.0 Hz, 2H), 4.26 – 4.09 (m, 1H), 2.00 – 1.91 (m, 2H), 1.84 – 1.70 (m, 2H), 1.60 – 1.47 (m, 3H), 1.39 – 1.27 (m, 3H).

^{13}C 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 ^{1}H 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%.

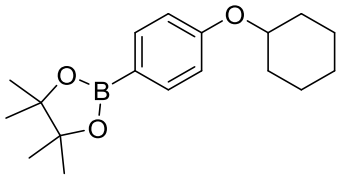
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.98 – 7.83 (m, 2H), 6.95 – 6.81 (m, 2H), 4.35 (tt, *J* = 9.0, 4.2 Hz, 1H), 2.54 (s, 3H), 2.04 – 1.91 (m, 2H), 1.85 – 1.77 (m, 2H), 1.62 – 1.48 (m, 3H), 1.46 – 1.31 (m, 3H).

^{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: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2^+$ 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%.

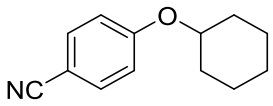
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.83 – 7.60 (m, 2H), 6.97 – 6.73 (m, 2H), 4.31 (tt, *J* = 8.8, 3.8 Hz, 1H), 2.09 – 1.88 (m, 2H), 1.84 – 1.70 (m, 2H), 1.61 – 1.48 (m, 3H), 1.45 – 1.23 (m, 15H).

^{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: $[M + H]^+$ Calcd for $C_{18}H_{28}BO_3^+$ 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%.

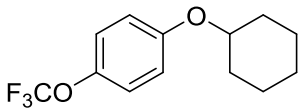
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.63 – 7.43 (m, 2H), 7.03 – 6.81 (m, 2H), 4.32 (tt, *J* = 8.5, 3.7 Hz, 1H), 2.01 – 1.91 (m, 2H), 1.80 (m, 2H), 1.59 – 1.52 (m, 3H), 1.41 – 1.30 (m, 3H).

^{13}C 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 $C_{13}H_{16}NO^+$ 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%.

^{1}H 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).

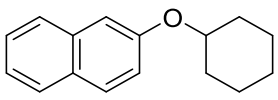
^{13}C NMR (101 MHz, Chloroform-*d*): δ 156.47, 142.62, 122.50, 120.74 (q, *J* = 255.8 Hz), 116.86, 76.13, 31.85, 25.72, 23.85.

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

Physical State: colorless oil.

HRMS (APPI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}F_3O_2^+$ 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%.

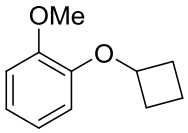
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.93 – 7.71 (m, 3H), 7.52 (td, *J* = 7.4, 6.7, 1.3 Hz, 1H), 7.41 (td, *J* = 7.5, 6.8, 1.3 Hz, 1H), 7.30 – 7.19 (m, 4H), 4.51 (tt, *J* = 8.6, 3.8 Hz, 1H), 2.23 – 2.10 (m, 2H), 2.03 – 1.87 (m, 2H), 1.76 – 1.61 (m, 3H), 1.60 – 1.38 (m, 3H).

^{13}C 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 $C_{16}H_{18}O^+$ 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%.

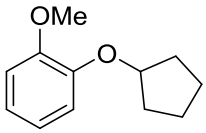
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.98 – 6.79 (m, 3H), 6.79 – 6.65 (m, 1H), 4.66 (p, *J* = 7.3 Hz, 1H), 3.87 (s, 3H), 2.54 – 2.39 (m, 2H), 2.37 – 2.18 (m, 2H), 1.91 – 1.78 (m, 1H), 1.77 – 1.59 (m, 1H).

^{13}C 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 $C_{11}H_{14}O_2^+$ 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%.

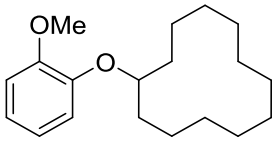
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.91 (s, 4H), 4.86 – 4.73 (m, 1H), 3.87 (s, 3H), 1.99 – 1.79 (m, 6H), 1.66 – 1.58 (m, 2H).

^{13}C 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 $C_{12}H_{17}O_2^+$ 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%.

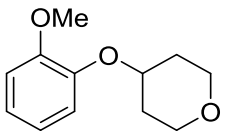
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.99 – 6.81 (m, 4H), 4.42 (tt, *J* = 7.4, 4.3 Hz, 1H), 3.84 (s, 3H), 1.88 – 1.74 (m, 2H), 1.75 – 1.60 (m, 2H), 1.50 – 1.28 (m, 18H).

^{13}C 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 $C_{19}H_{31}O_2^+$ 291.2319; Found 291.2324.

4-(2-methoxyphenoxy)tetrahydro-2*H*-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%.

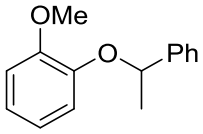
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.06 – 6.79 (m, 4H), 4.41 (tt, *J* = 8.3, 4.0 Hz, 1H), 4.02 (dt, *J* = 11.8, 4.6 Hz, 2H), 3.86 (s, 3H), 3.53 (ddd, *J* = 11.8, 9.0, 3.0 Hz, 2H), 2.10 – 1.90 (m, 2H), 1.92 – 1.76 (m, 2H).

^{13}C 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 $C_{12}H_{17}O_3^+$ 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%.

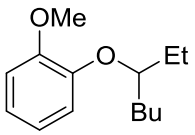
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.41 (d, *J* = 6.9 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 6.88 (dd, *J* = 4.4, 3.0 Hz, 2H), 6.75 (dd, *J* = 4.1, 2.0 Hz, 2H), 5.32 (q, *J* = 6.5 Hz, 1H), 3.90 (s, 3H), 1.70 (d, *J* = 6.4 Hz, 3H).

^{13}C 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 $C_{15}H_{16}NaO_2^+$ 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%.

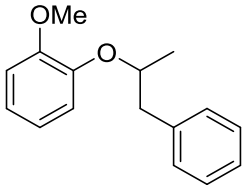
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.89 (m, 4H), 4.14 (p, *J* = 5.9 Hz, 1H), 3.85 (s, 3H), 1.75 – 1.57 (m, 4H), 1.43 – 1.27 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H).

^{13}C 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 $C_{14}H_{23}O_2^+$ 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%.

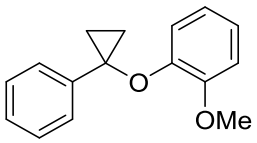
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.32 – 7.20 (m, 5H), 7.04 – 6.74 (m, 4H), 4.62 – 4.45 (m, 1H), 3.85 (s, 3H), 3.21 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.83 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.32 (dd, *J* = 6.1, 1.3 Hz, 3H).

^{13}C 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 $C_{16}H_{18}O_2^+$ 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%.

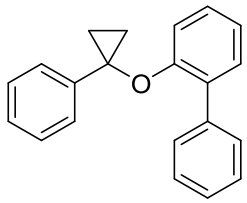
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.39 – 7.18 (m, 5H), 6.97 – 6.82 (m, 3H), 6.78 – 6.68 (m, 1H), 3.91 (s, 3H), 1.57 – 1.47 (m, 2H), 1.41 – 1.30 (m, 2H).

^{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: $[M + Na]^+$ Calcd for $C_{16}H_{16}NaO_2^+$ 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%.

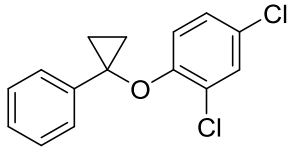
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.62 – 7.55 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.23 – 7.18 (m, 3H), 7.16 – 7.11 (m, 1H), 6.99 (t, *J* = 7.1 Hz, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.28 (m, 2H).

^{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: $[M + H]^+$ Calcd for $C_{21}H_{19}O^+$ 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%.

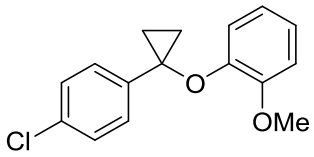
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.35 (d, *J* = 2.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 6.99 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 1H), 1.51 – 1.44 (m, 2H), 1.40 – 1.32 (m, 2H).

^{13}C 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 $C_{15}H_{13}Cl_2O^+$ 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%.

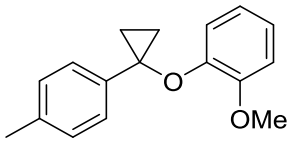
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.22 (m, 2H), 7.21 – 7.10 (m, 2H), 7.01 – 6.81 (m, 3H), 6.76 (ddd, *J* = 8.1, 6.1, 2.8 Hz, 1H), 3.93 (s, 3H), 1.60 – 1.48 (m, 2H), 1.41 – 1.29 (m, 2H).

^{13}C 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 $C_{16}H_{16}ClO_2^+$ 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%.

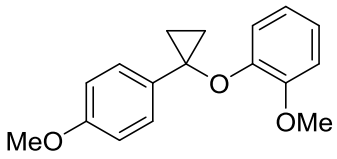
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.14 – 7.07 (m, 4H), 6.93 – 6.83 (m, 3H), 6.73 (ddd, *J* = 8.0, 7.1, 2.1 Hz, 1H), 3.91 (s, 3H), 2.30 (s, 3H), 1.53 – 1.45 (m, 2H), 1.35 – 1.29 (m, 2H).

^{13}C 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 $C_{17}H_{18}NaO_2^+$ 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%.

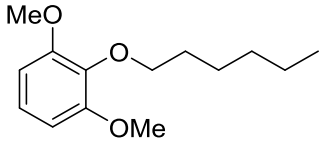
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.22 – 7.10 (m, 2H), 6.95 – 6.80 (m, 5H), 6.73 (ddd, *J* = 8.0, 6.8, 2.3 Hz, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 1.50 – 1.41 (m, 2H), 1.30 – 1.25 (m, 2H).

^{13}C 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%.

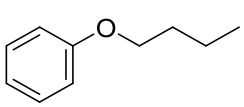
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.84 (s, 6H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.36 – 1.26 (m, 5H), 0.91 – 0.84 (m, 3H).

^{13}C 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%.

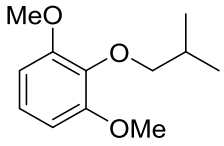
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.29 (t, *J* = 7.8 Hz, 2H), 7.08 – 6.84 (m, 3H), 3.98 (t, *J* = 6.5 Hz, 2H), 1.85 – 1.71 (m, 2H), 1.51 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C 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 ^{1}H NMR and ^{13}C 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%.

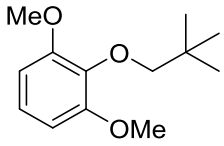
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.96 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 6H), 3.73 (d, *J* = 6.7 Hz, 2H), 2.07 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 6H).

^{13}C 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 $C_{12}H_{18}NaO_3^+$ 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%.

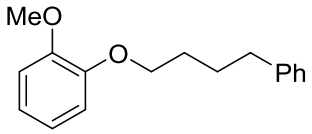
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.95 (t, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 6H), 3.62 (s, 2H), 1.06 (s, 9H).

^{13}C 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%.

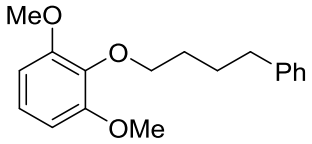
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 6.90 (td, *J* = 5.9, 3.1 Hz, 4H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 2.71 (t, *J* = 7.4 Hz, 2H), 1.98 – 1.75 (m, 4H).

^{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%.

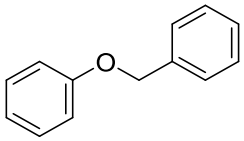
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 6.98 (t, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.04 – 3.96 (m, 2H), 3.83 (s, 6H), 2.72 – 2.65 (m, 2H), 1.86 – 1.78 (m, 4H).

^{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%.

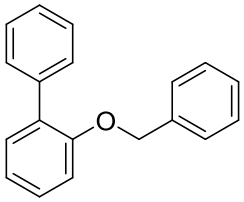
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50 – 7.37 (m, 4H), 7.37 – 7.27 (m, 3H), 7.04 – 6.93 (m, 3H), 5.08 (s, 2H).

^{13}C 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 ^{1}H NMR and ^{13}C 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%.

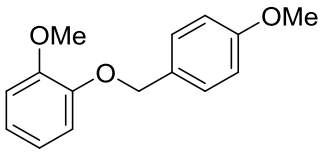
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.72 – 7.54 (m, 2H), 7.51 – 7.27 (m, 10H), 7.14 – 7.00 (m, 2H), 5.12 (s, 2H).

^{13}C 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 $C_{19}H_{17}O^+$ 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%.

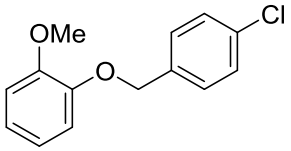
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.37 (d, *J* = 8.3 Hz, 2H), 6.96 – 6.84 (m, 6H), 5.08 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H).

^{13}C 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 $C_{15}H_{16}NaO_3^+$ 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%.

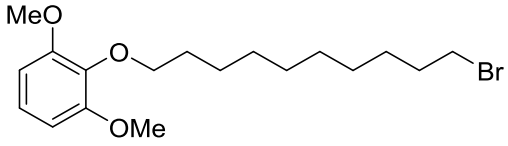
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.43 – 7.30 (m, 4H), 7.00 – 6.82 (m, 4H), 5.12 (s, 2H), 3.89 (s, 3H).

^{13}C 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 $C_{14}H_{13}ClNaO_2^+$ 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%.

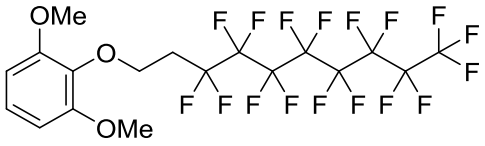
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 6H), 3.40 (t, *J* = 6.9 Hz, 2H), 1.85 (p, *J* = 7.0 Hz, 2H), 1.75 (p, *J* = 7.0 Hz, 2H), 1.49 – 1.27 (m, 12H).

^{13}C 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 $C_{18}H_{29}BrNaO_3^+$ 395.1192; Found 395.1196.

2-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)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%.

^{1}H 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).

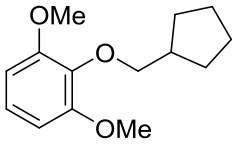
^{13}C NMR (101 MHz, Chloroform-*d*): δ 169.23, 152.36, 128.62, 126.68, 104.97, 56.23, 26.90 (t, *J* = 22.2 Hz), 25.35 (t, *J* = 4.1 Hz).

^{19}F 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 $C_{18}H_{14}F_{17}O_3^+$ 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%.

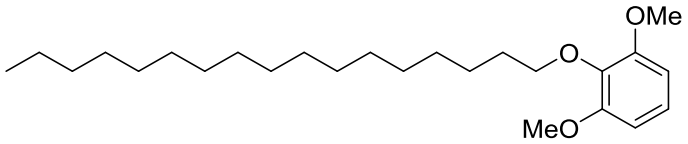
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.96 (t, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.88 – 3.78 (m, 8H), 2.37 (hept, *J* = 7.6 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.63 – 1.54 (m, 4H), 1.45 – 1.35 (m, 2H).

^{13}C 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 $C_{14}H_{20}NaO_3^+$ 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%.

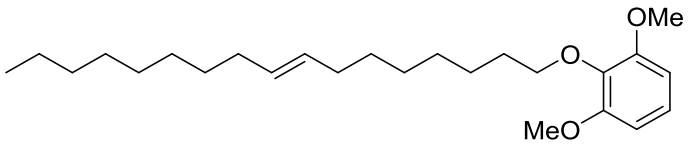
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.84 (s, 6H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.26 (m, 30H), 0.87 (d, *J* = 7.0 Hz, 3H).

^{13}C 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 $C_{25}H_{44}NaO_3^+$ 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%.

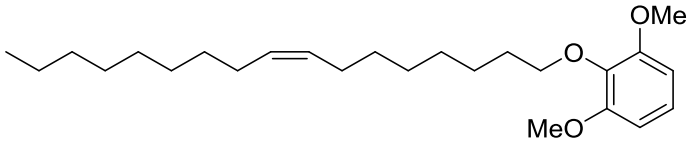
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.39 (td, *J* = 3.8, 1.9 Hz, 2H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 6H), 1.96 (dt, *J* = 8.0, 4.2 Hz, 4H), 1.75 (p, *J* = 7.0 Hz, 2H), 1.51 – 1.22 (m, 20H), 0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C 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 $C_{25}H_{42}NaO_3^+$ 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%.

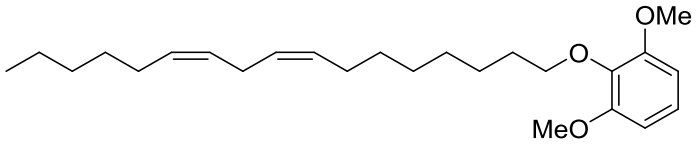
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.42 – 5.27 (m, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.84 (s, 6H), 2.06 – 1.94 (m, 4H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.48 – 1.19 (m, 20H), 0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C 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 $C_{25}H_{42}NaO_3^+$ 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%.

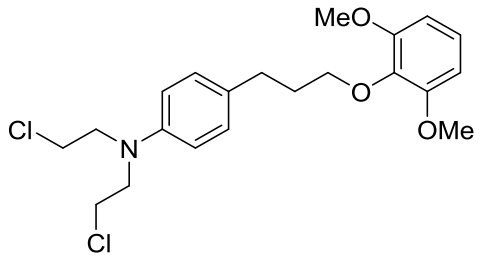
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.35 (tq, *J* = 10.9, 6.8, 5.4 Hz, 4H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 6H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.09 – 2.00 (m, 4H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.51 – 1.24 (m, 13H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C 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 $C_{25}H_{40}NaO_3^+$ 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%.

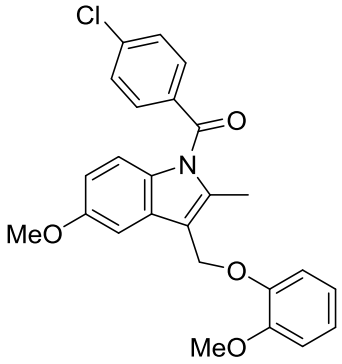
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.18 – 7.07 (m, 2H), 6.98 (t, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 18.0, 8.5 Hz, 4H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 6H), 3.74 – 3.66 (m, 4H), 3.62 (m, 4H), 2.80 – 2.68 (m, 2H), 2.08 – 1.95 (m, 2H).

^{13}C 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 $C_{21}H_{27}Cl_2NNaO_3^+$ 434.1260; Found 434.1264

(4-chlorophenyl)(5-methoxy-3-((2-methoxyphenoxy)methyl)-2-methyl-*1H*-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%.

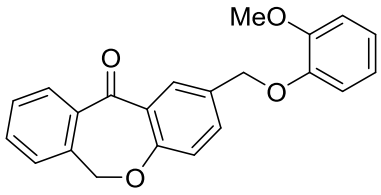
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.68 – 7.61 (m, 2H), 7.50 – 7.44 (m, 2H), 7.17 (d, *J* = 2.6 Hz, 1H), 7.05 – 6.96 (m, 2H), 6.96 – 6.88 (m, 2H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.22 (s, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 2.42 (s, 3H).

^{13}C 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 $C_{25}H_{23}ClNO_4^+$ 436.1310; Found 436.1300.

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



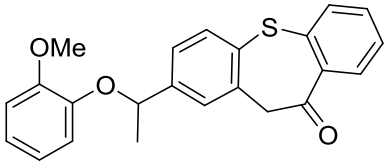
Following the General Procedure C with the corresponding phenol (0.3 mmol) and NHPI ester (2 equiv.). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7g** (76 mg) in 73%.

^{1}H 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).
^{13}C 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 $C_{22}H_{18}NaO_4^+$ 369.1097; Found 369.1095.

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



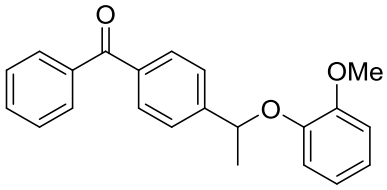
Following the General Procedure B with the corresponding phenol (2 equiv.) and NHPI ester (0.3 mmol). The crude product was purified by preparative TLC, using hexanes/EA = 10/1 (v/v) as an eluent, to yield the title compound **7h** (78 mg) in 69%.

^{1}H 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).
^{13}C 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 $C_{23}H_{20}NaO_3S^+$ 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%.

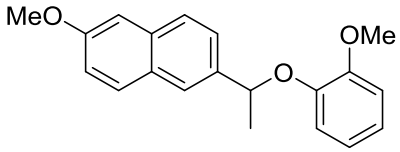
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.82 (s, 1H), 7.77 – 7.63 (m, 4H), 7.62 – 7.54 (m, 1H), 7.45 (td, *J* = 7.6, 3.6 Hz, 3H), 6.94 – 6.82 (m, 2H), 6.82 – 6.69 (m, 2H), 5.40 (q, *J* = 6.5 Hz, 1H), 3.84 (s, 3H), 1.71 (d, *J* = 6.5 Hz, 3H).

^{13}C 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 $C_{22}H_{21}O_3^+$ 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%.

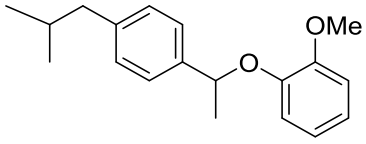
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.77 (d, *J* = 1.7 Hz, 1H), 7.72 (t, *J* = 8.5 Hz, 2H), 7.54 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.18 – 7.10 (m, 2H), 6.93 – 6.83 (m, 2H), 6.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.72 (ddd, *J* = 8.2, 6.9, 2.1 Hz, 1H), 5.45 (q, *J* = 6.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H),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

^{13}C 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 $C_{20}H_{20}NaO_3^+$ 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%.

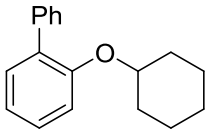
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.35 – 7.27 (m, 2H), 7.15 – 7.07 (m, 2H), 6.93 – 6.82 (m, 2H), 6.81 – 6.72 (m, 2H), 5.29 (q, *J* = 6.4 Hz, 1H), 3.89 (s, 3H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.68 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 3H), 0.88 (s, 3H).

^{13}C 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 $C_{19}H_{24}O_2^+$ 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%.

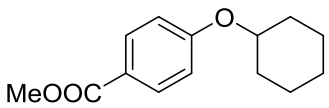
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.60 – 7.52 (m, 2H), 7.41 – 7.25 (m, 6H), 7.01 (t, *J* = 7.5 Hz, 2H), 4.20 (tt, *J* = 8.1, 3.7 Hz, 1H), 1.91 – 1.77 (m, 2H), 1.70 – 1.60 (m, 2H), 1.53 – 1.44 (m, 3H), 1.33 – 1.23 (m, 4H).

^{13}C 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 $C_{18}H_{21}O^+$ 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%.

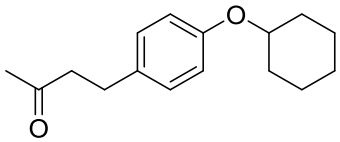
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.96 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.33 (tt, *J* = 8.7, 3.8 Hz, 1H), 3.87 (s, 3H), 2.06 – 1.90 (m, 2H), 1.87 – 1.74 (m, 2H), 1.54 (td, *J* = 12.6, 11.3, 7.8 Hz, 3H), 1.43 – 1.27 (m, 3H).

^{13}C 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 $C_{14}H_{19}O_3^+$ 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%.

^{1}H 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).

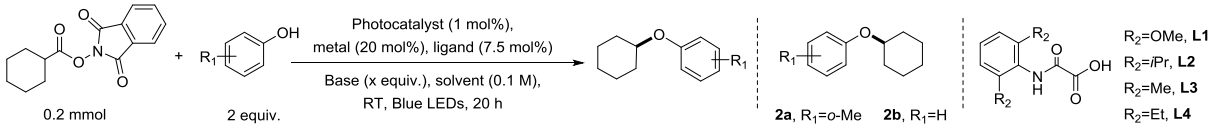
^{13}C NMR (101 MHz, Chloroform-*d*): δ 156.27, 132.99, 129.30, 116.31, 75.69, 45.61, 32.02, 30.24, 29.07, 25.78, 23.95.

Physical State: white solid.

HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{22}NaO_2^+$ 269.1512; Found 269.1512.

Tables

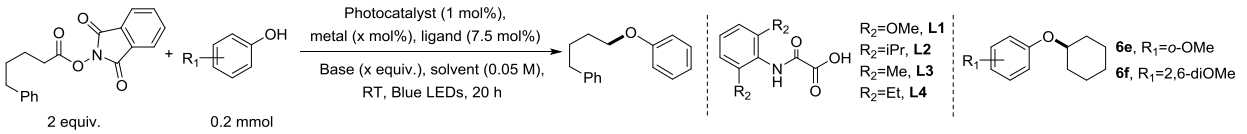
Table S1. Optimization of reaction parameters for secondary NHPI ester



Entry	Nucleophile	Photocatalyst	Metal	Ligand	Base	Solvent	GC yield[a]
1	**2a**	$Ru(bpy)_3(PF_6)_2$	CuBr	**L1**	Et_3N (5 equiv.)	MeCN	16%
2	**2a**	$Ru(bpy)_3(PF_6)_2$	CuBr	**L2**	Et_3N (5 equiv.)	MeCN	14%
3	**2a**	$Ru(bpy)_3(PF_6)_2$	CuBr	**L3**	Et_3N (5 equiv.)	MeCN	9%
4	**2a**	$Ru(bpy)_3(PF_6)_2$	CuBr	**L4**	Et_3N (5 equiv.)	MeCN	12%
5	**2a**	$Ru(bpy)_3(PF_6)_2$	CuBr	PCy_3	Et_3N (5 equiv.)	MeCN	trace
6	**2a**	$Ru(bpy)_3(PF_6)_2$	CuBr	dtbbpy	Et_3N (5 equiv.)	MeCN	trace
7	**2a**	$Ru(bpy)_3(PF_6)_2$	CuBr	w/o ligand	Et_3N (5 equiv.)	MeCN	19%
8	**2a**	$Ru(bpy)_3(PF_6)_2$	CuTc	w/o ligand	Et_3N (5 equiv.)	MeCN	16%
9	**2a**	$Ru(bpy)_3(PF_6)_2$	CuOAc	w/o ligand	Et_3N (5 equiv.)	MeCN	17%
10	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl	w/o ligand	Et_3N (5 equiv.)	MeCN	22%
11	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl (40 mol%)	w/o ligand	Et_3N (5 equiv.)	MeCN	31%
12	**2a**	$Ru(bpy)_3(PF_6)_2$	Cu (100 mol%)	w/o ligand	Et_3N (5 equiv.)	MeCN	9%
13	**2a**	$Ru(bpy)_3(PF_6)_2$	$CuCl_2$	w/o ligand	Et_3N (5 equiv.)	MeCN	11%
14	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl	w/o ligand	Cs_2CO_3 (2 equiv.)	MeCN	trace
15	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl	w/o ligand	K_2CO_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_3N (5 equiv.)	DMF	trace
20	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl	w/o ligand	Et_3N (5 equiv.)	THF	trace
21	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl	w/o ligand	Et_3N (5 equiv.)	DCM	32%
22	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl	w/o ligand	Et_3N (3 equiv.)	DCM	40%
23	**2a**	$Ru(bpy)_3(PF_6)_2$	CuCl	w/o ligand	Et_3N (2 equiv.)	DCM	44%
24	**2a**	$Ir(ppy)_3$	CuCl	w/o ligand	Et_3N (2 equiv.)	DCM	39%
25	**2a**	$[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$	CuCl	w/o ligand	Et_3N (2 equiv.)	DCM	21%
26	**2a**	$Ir[(ppy)_2(dtbbpy)]PF_6$	CuCl	w/o ligand	Et_3N (2 equiv.)	DCM	62%
27	**2a**	$Ir[(ppy)_2(dtbbpy)]PF_6$	CuCl (40 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM	71%
28	**2a**	$Ir[(ppy)_2(dtbbpy)]PF_6$	CuOAc	w/o ligand	Et_3N (2 equiv.)	DCM	65%
29	**2a**	$Ir[(ppy)_2(dtbbpy)]PF_6$	$(CuOTf)_2{\bullet}C_6H_6$ (10 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM	82%
30	**2a**	$Ir[(ppy)_2(dtbbpy)]PF_6$	$(CuOTf)_2{\bullet}C_6H_6$ (10 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM (0.05 M)	94%
31	**2b**	$Ir[(ppy)_2(dtbbpy)]PF_6$	$(CuOTf)_2{\bullet}C_6H_6$ (10 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM (0.05 M)	90%

[a]Corrected GC yield, *n*-dodecane as an internal standard. [b]1,8-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_3N (3 equiv.)	MeCN	9%
2	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (10 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM	16%
3	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (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_3N (2 equiv.)	DCM	trace
5	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (20 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM	20%
6	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (10 mol%)	**L1**	Et_3N (2 equiv.)	DCM	trace
7	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (10 mol%)	**L2**	Et_3N (2 equiv.)	DCM	trace
8	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (10 mol%)	**L3**	Et_3N (2 equiv.)	DCM	trace
9	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (10 mol%)	PCy_3	Et_3N (2 equiv.)	DCM	trace
10	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$(Cu(OTf)_2{\bullet}C_6H_6$ (10 mol%)	dtbbpy	Et_3N (2 equiv.)	DCM	trace
11	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4PF_6$ (20 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM	21%
12	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	Et_3N (2 equiv.)	DCM	25%
13	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	Cs_2CO_3 (1 equiv.)	DMA	trace¨
14	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	DABCO (1 equiv.)	DCM	9%
15	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	DIPEA (1 equiv.)	DCM	26%
16	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	Piperidine (1 equiv.)	DCM	trace
17	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	DBU (1 equiv.)[b]	DCM	trace
18	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	BTMG (1 equiv.)[c]	DCM	trace
19	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	Diisopropylamine (1 equiv.)	DCM	35%
20	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	Dicyclohexylamine (1 equiv.)	DCM	21%
21	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	Di-*sec*-butylamine (1 equiv.)	DCM	28%
22	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	*N*-Isopropyl-*tert*-butylamine (1 equiv.)	DCM	32%
23	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (20 mol%)	w/o ligand	*N*-Isopropyl-*N*-Methyl-*tert*-butylamine (1 equiv.)	DCM	43%
24	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (40 mol%)	w/o ligand	*N*-Isopropyl-*N*-Methyl-*tert*-butylamine (1 equiv.)	DCM	65%
25[d]	**2a**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (40 mol%)	w/o ligand	*N*-Isopropyl-*N*-Methyl-*tert*-butylamine (1 equiv.)	DCM	79%
26[d]	**2b**	$Ir[(ppy)_2(dtbbpy)](PF_6)$	$Cu(MeCN)_4OTf$ (40 mol%)	w/o ligand	*N*-Isopropyl-*N*-Methyl-*tert*-butylamine (1 equiv.)	DCM	87%

[a]Corrected GC yield, *n*-dodecane as an internal standard. [b]1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). [c]2-*tert*-Butyl-1,1,3,3-tetramethylguanidine (BTMG). [d]0-RT

Figures

Figure S1. Fluorescence quenching experiments I

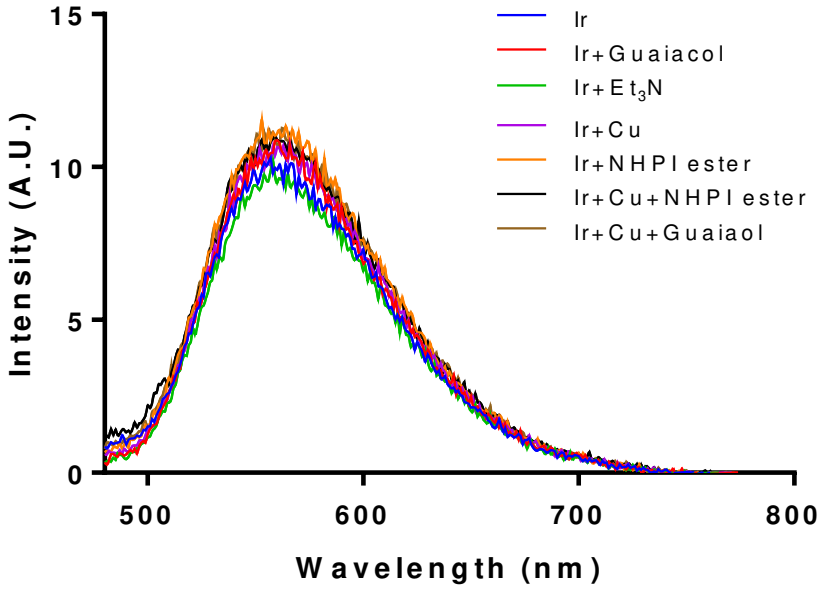


Figure S2. Fluorescence quenching experiments II; quenching is done with a mixture (1:1 molar ratio) of $Cu(MeCN)_4PF_6$ and Et_3N.

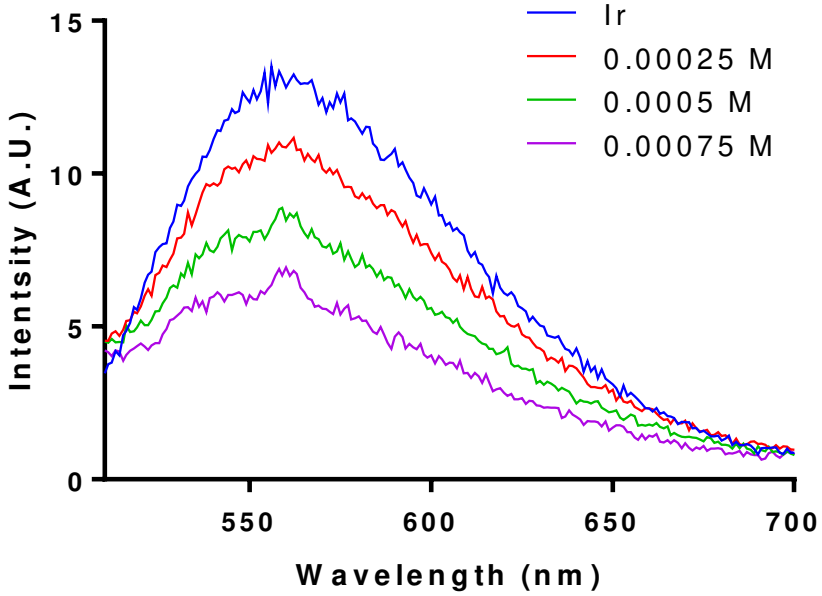


Figure S3. Stern-Volmer kinetic analysis

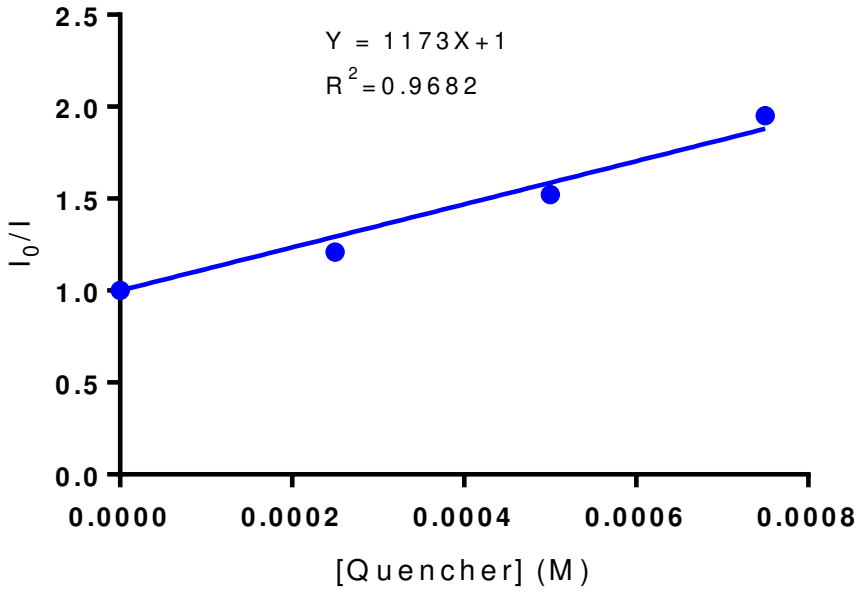


Figure S4. NMR spectra of 3a

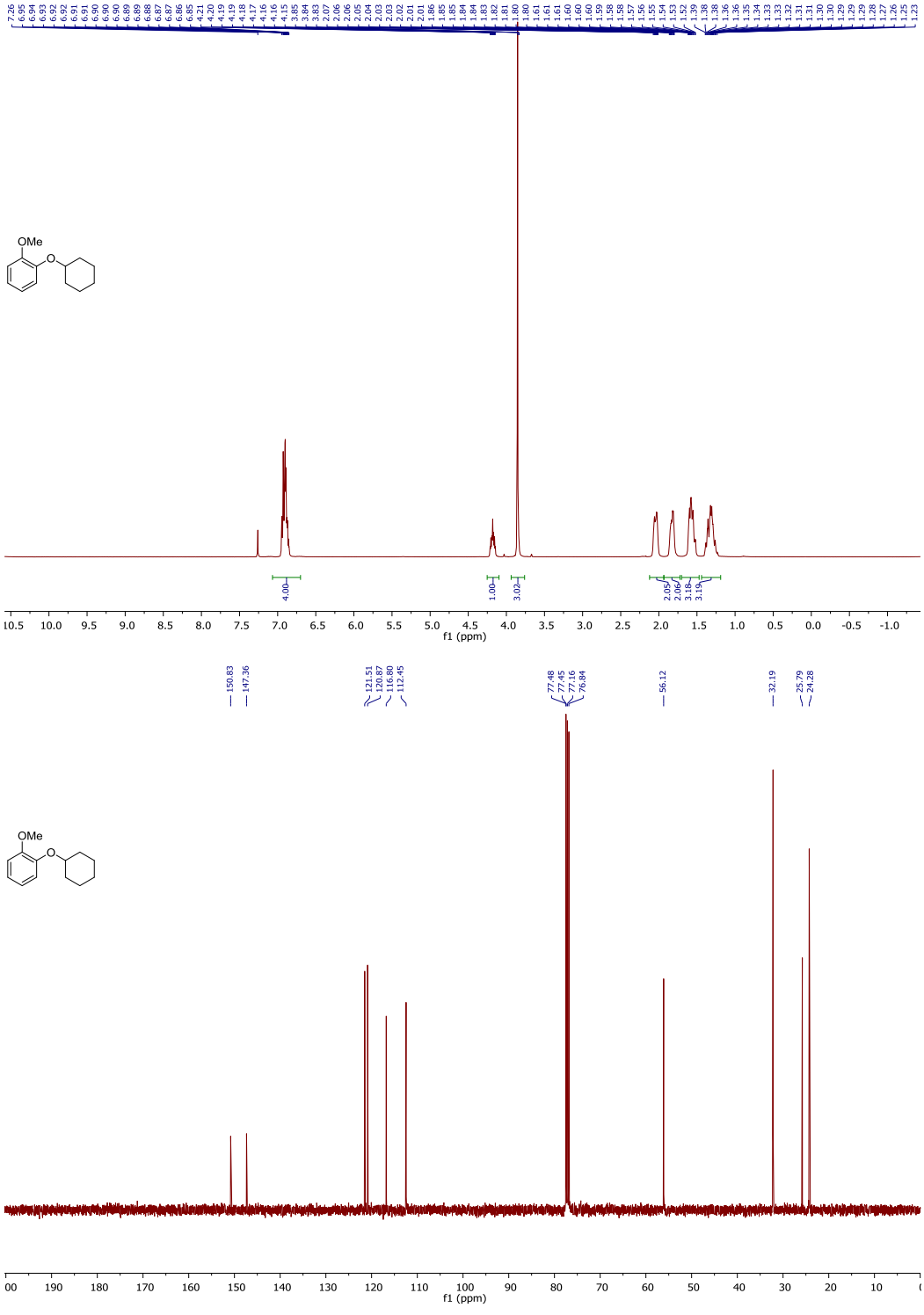


Figure S5. NMR spectra of 3b

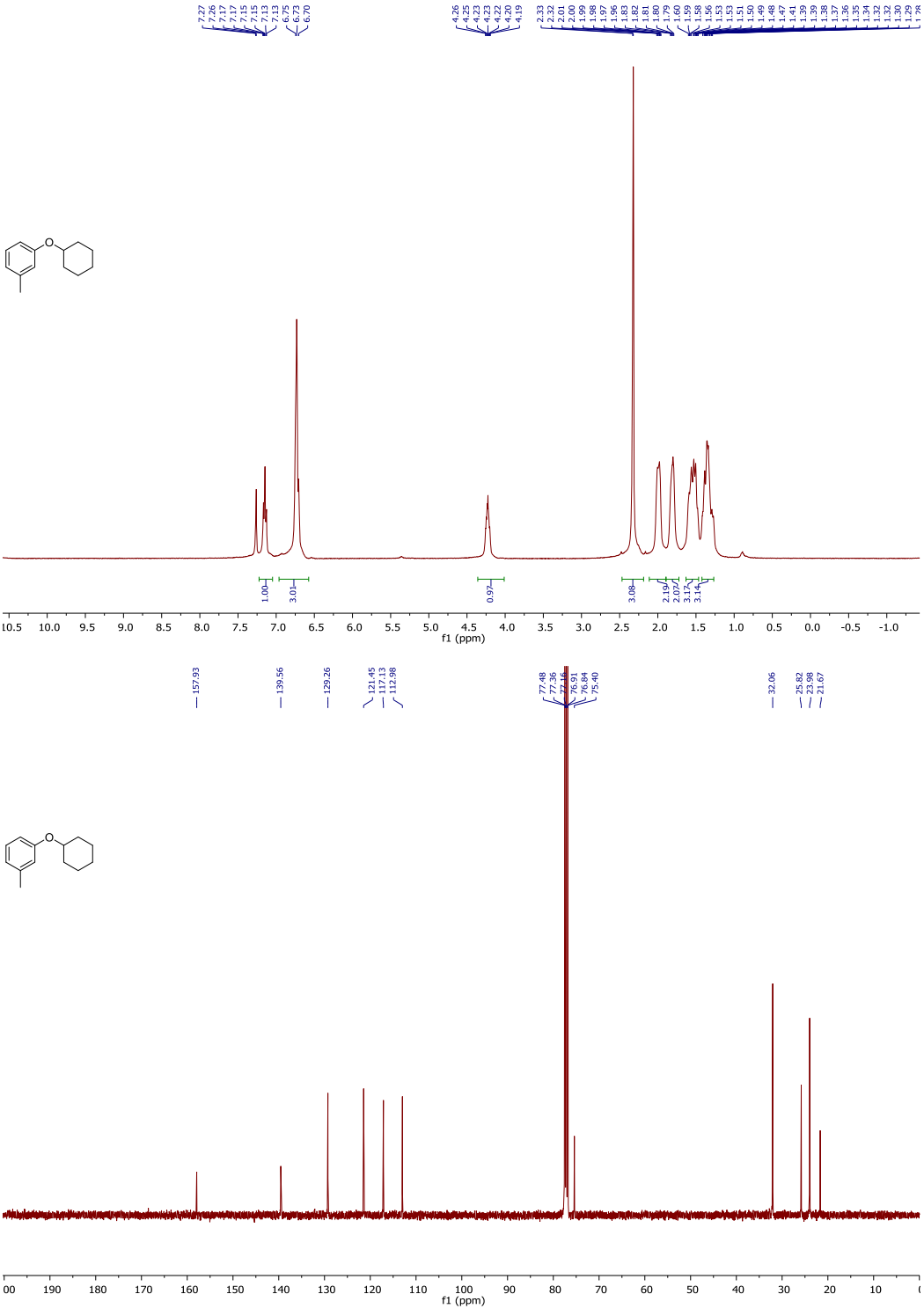


Figure S6. NMR spectra of 3c

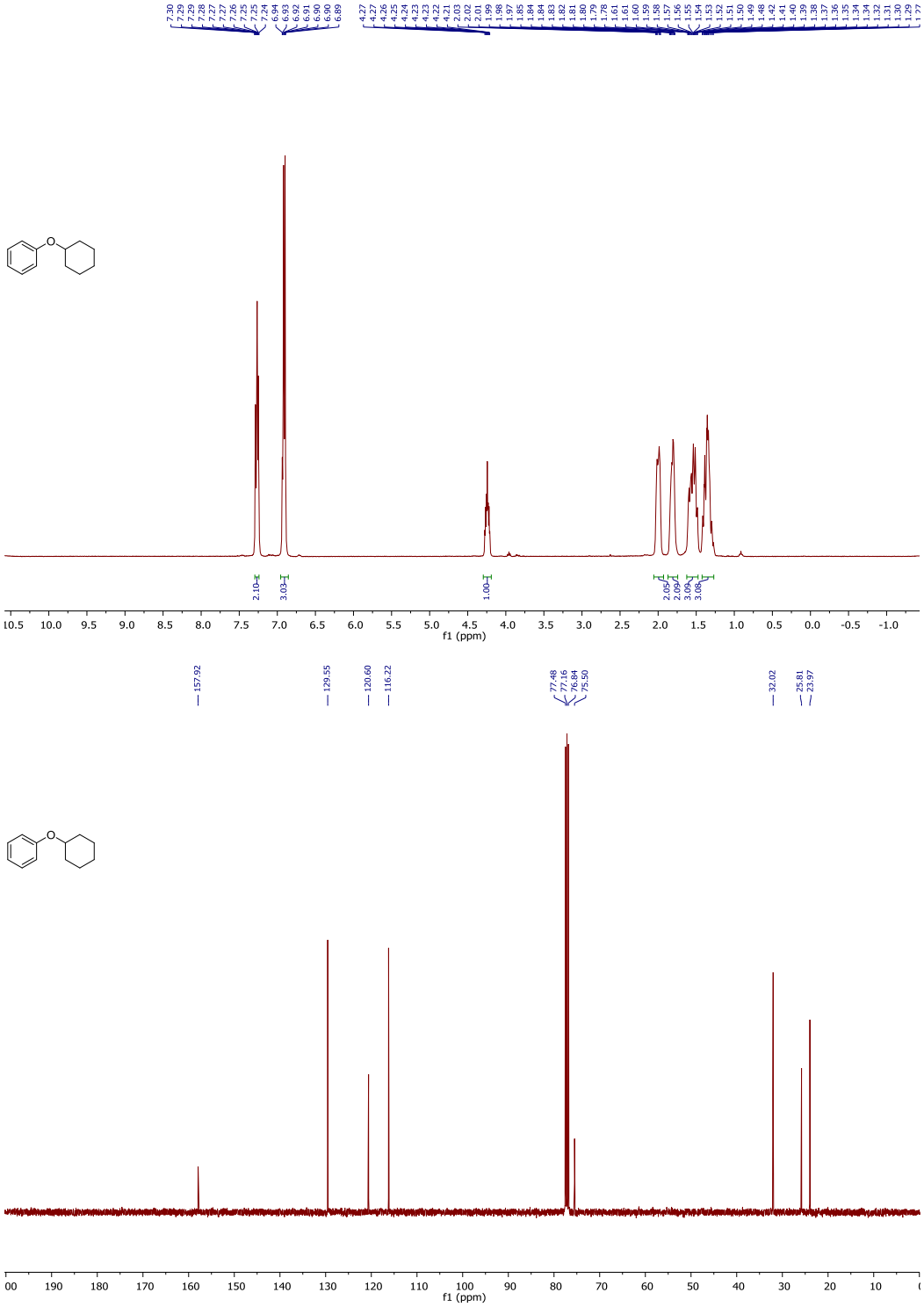


Figure S7. NMR spectra of 3d

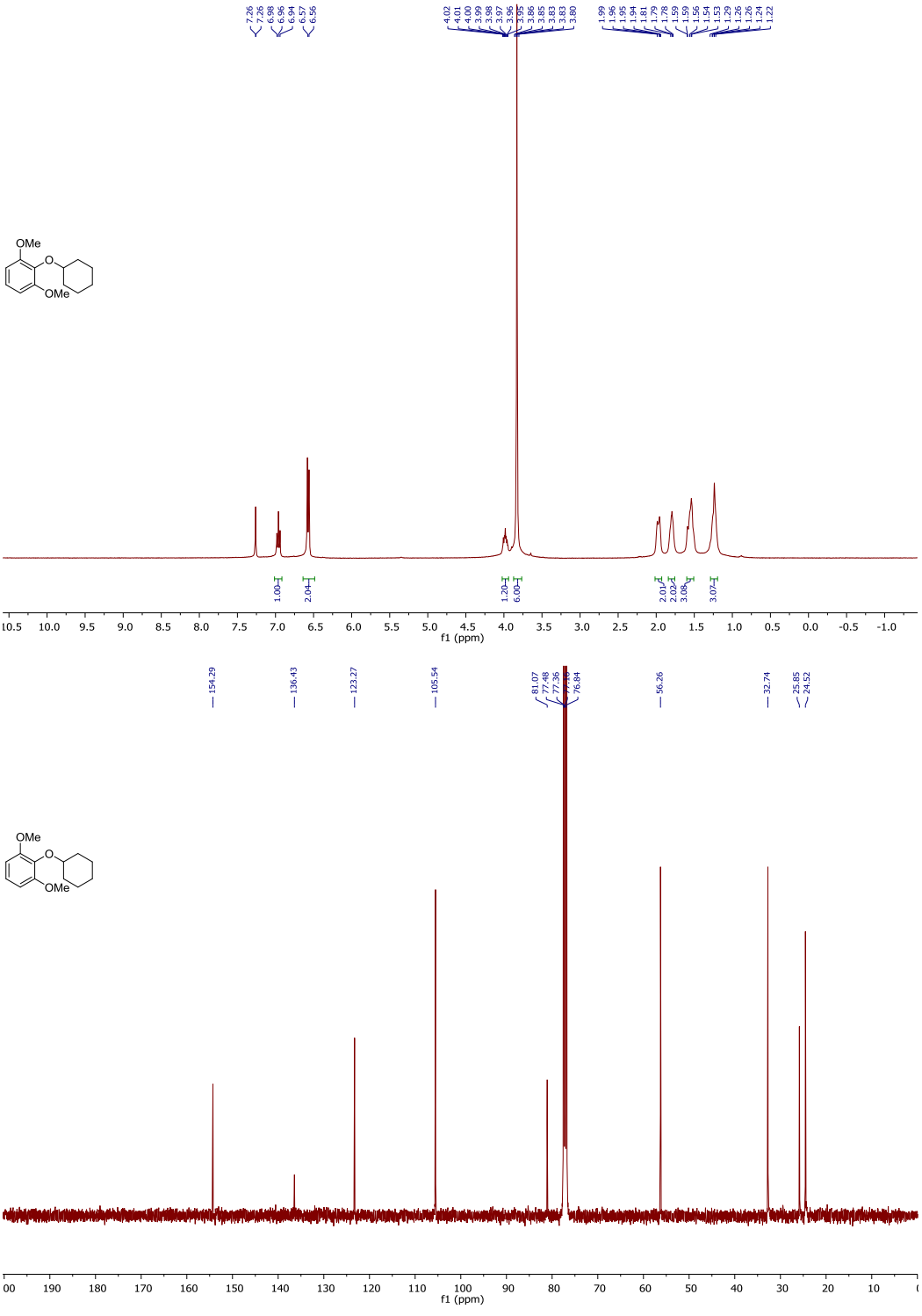


Figure S8. NMR spectra of 3e

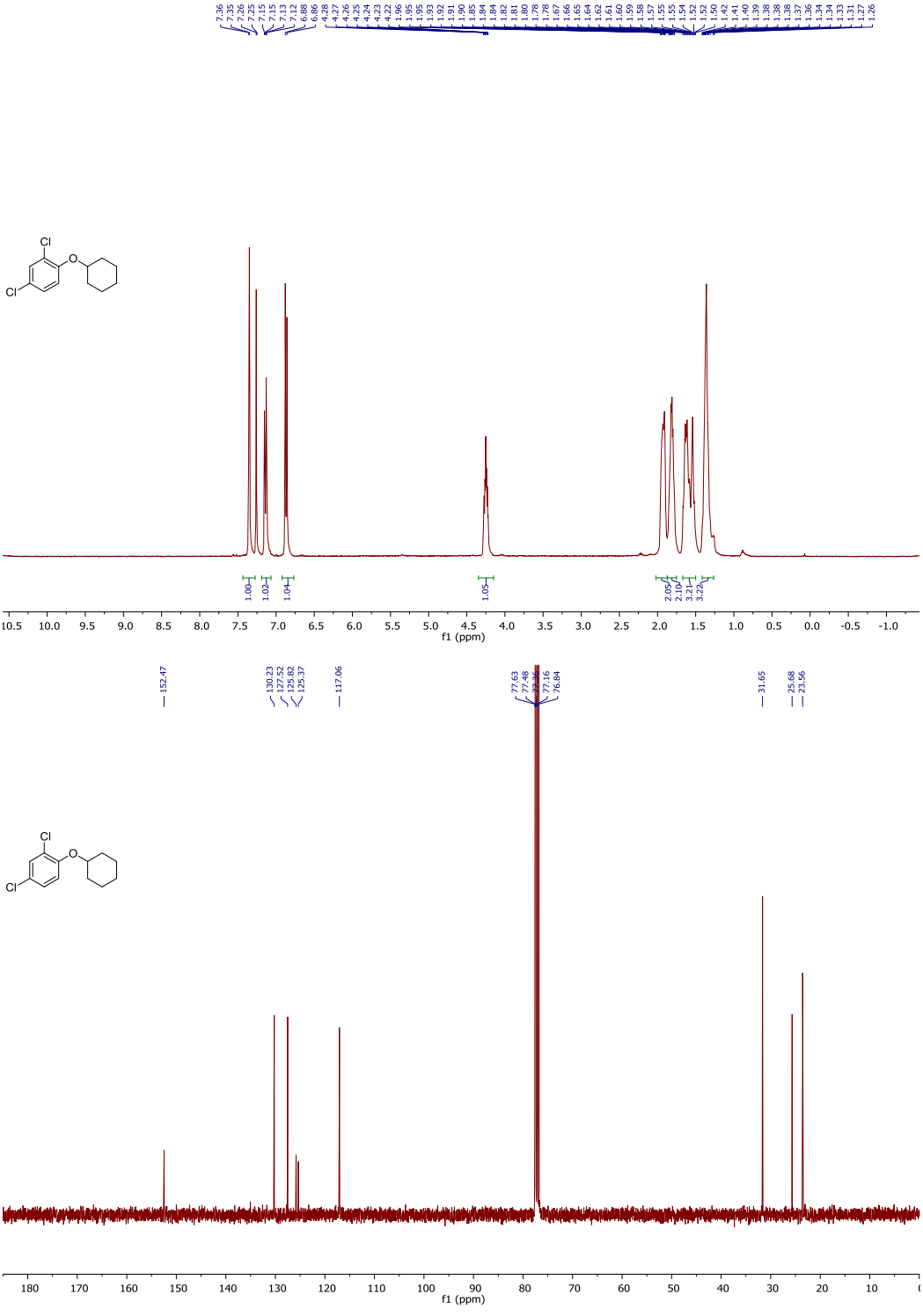


Figure S9. NMR spectra of 3f

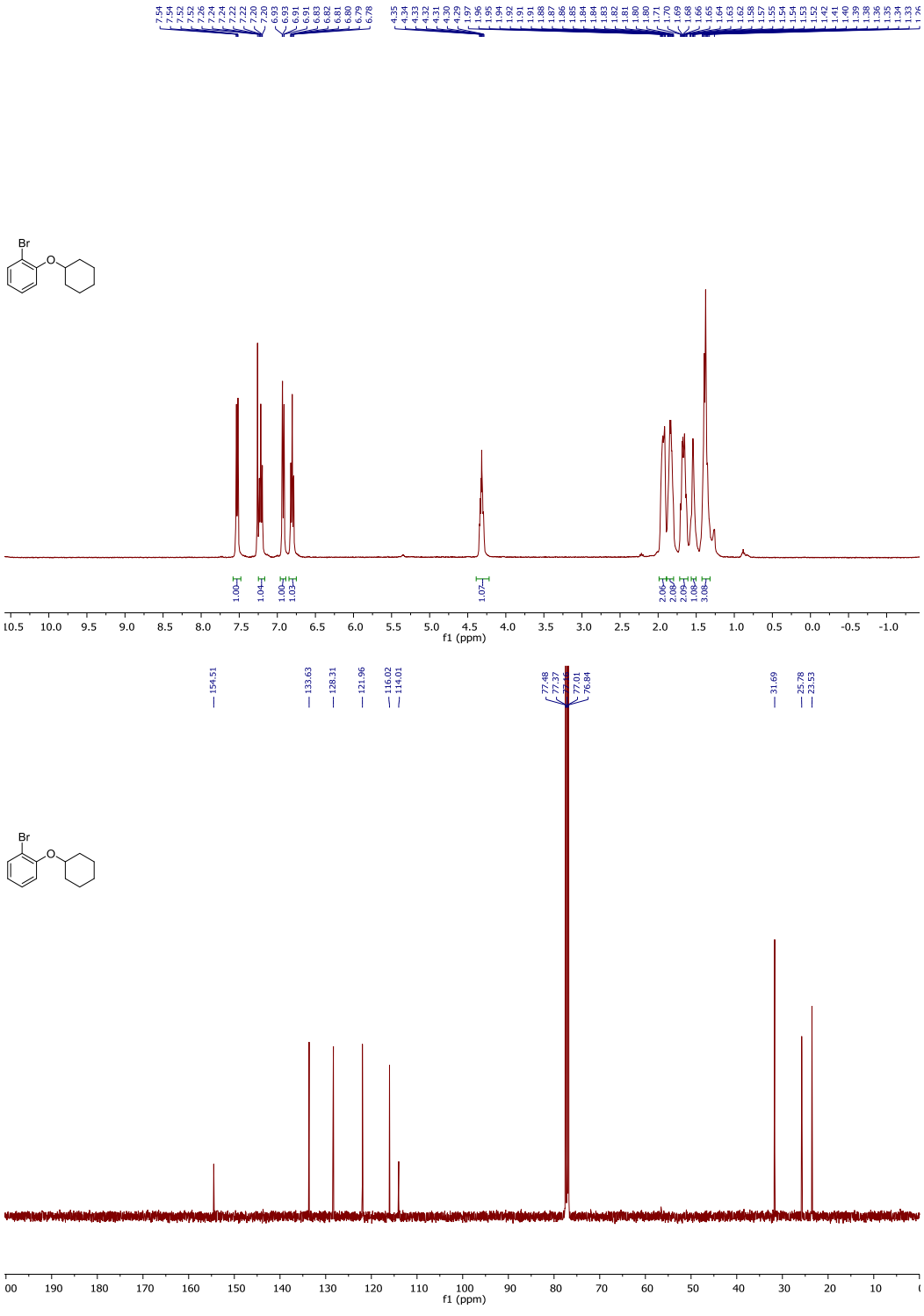


Figure S10. NMR spectra of 3g

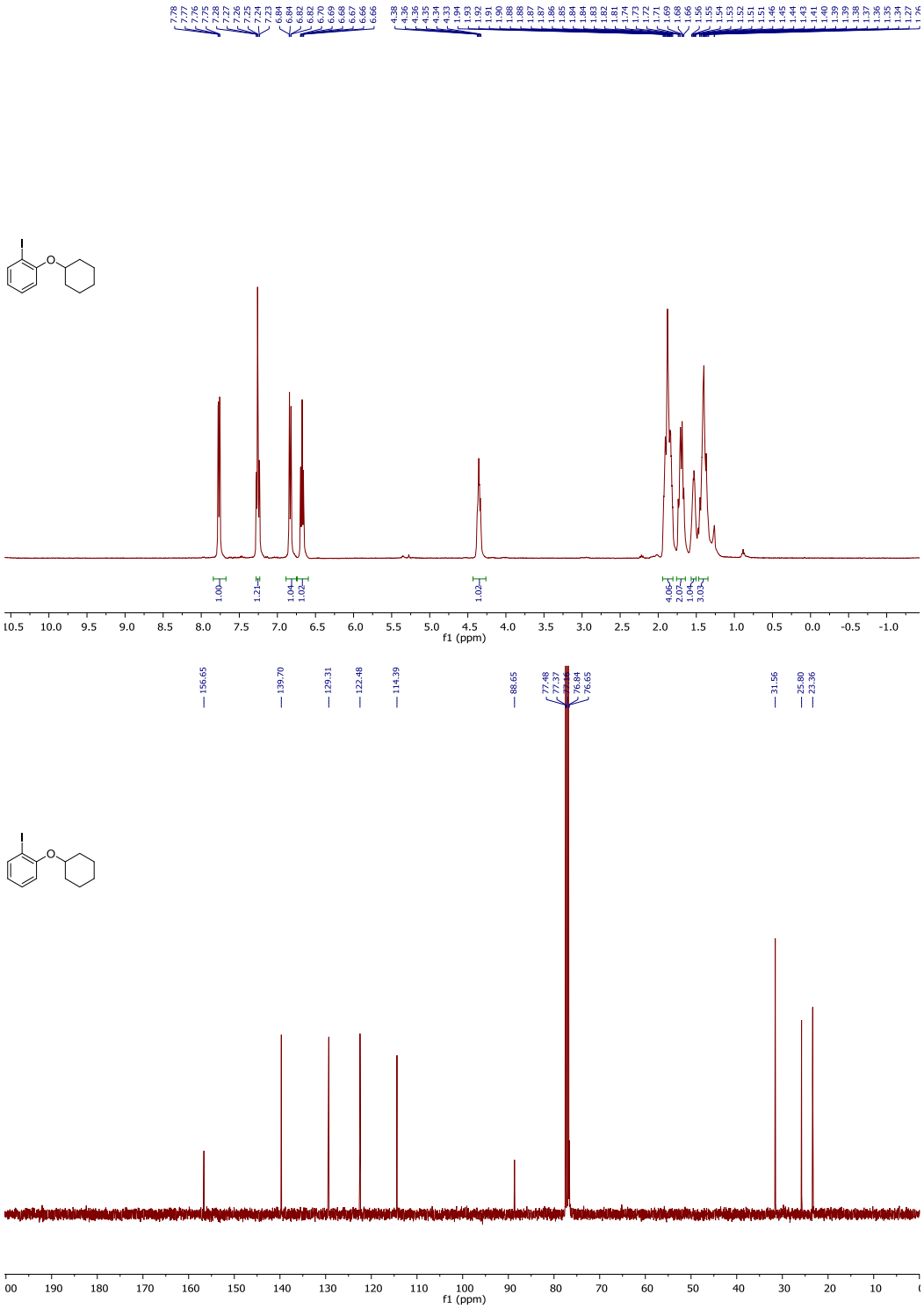


Figure S11. NMR spectra of 3h

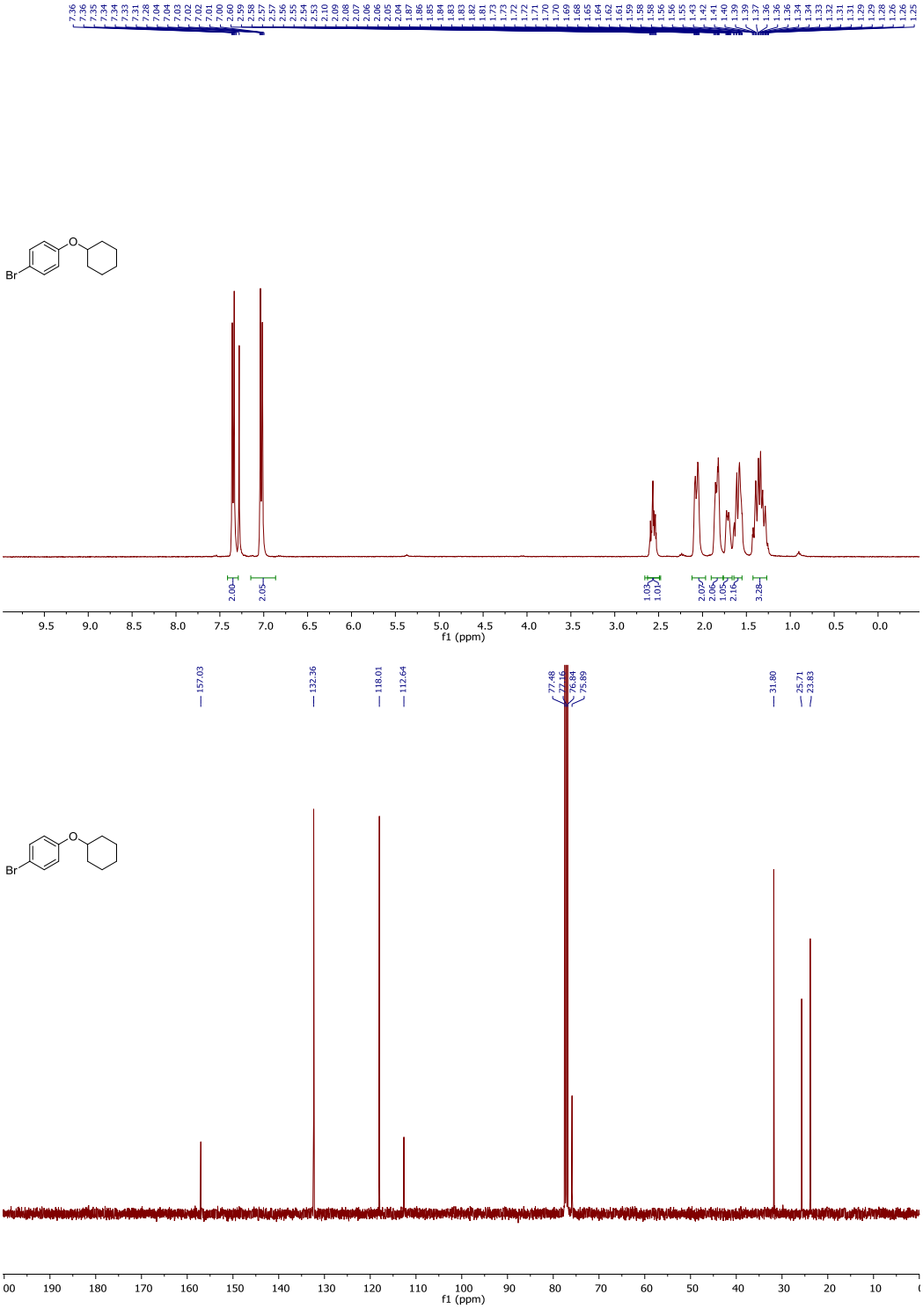


Figure S12. NMR spectra of 3i

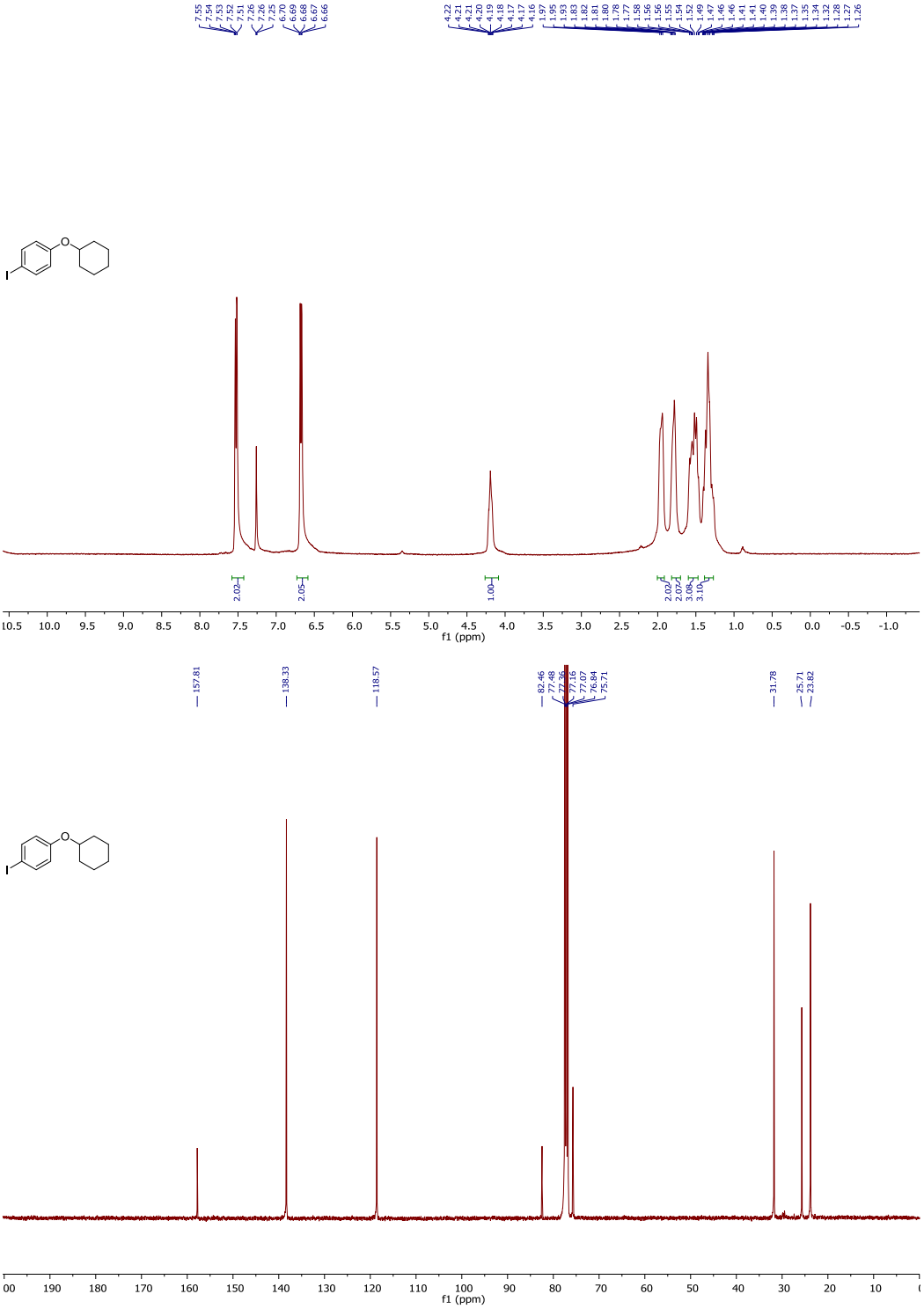


Figure S13. NMR spectra of 3j

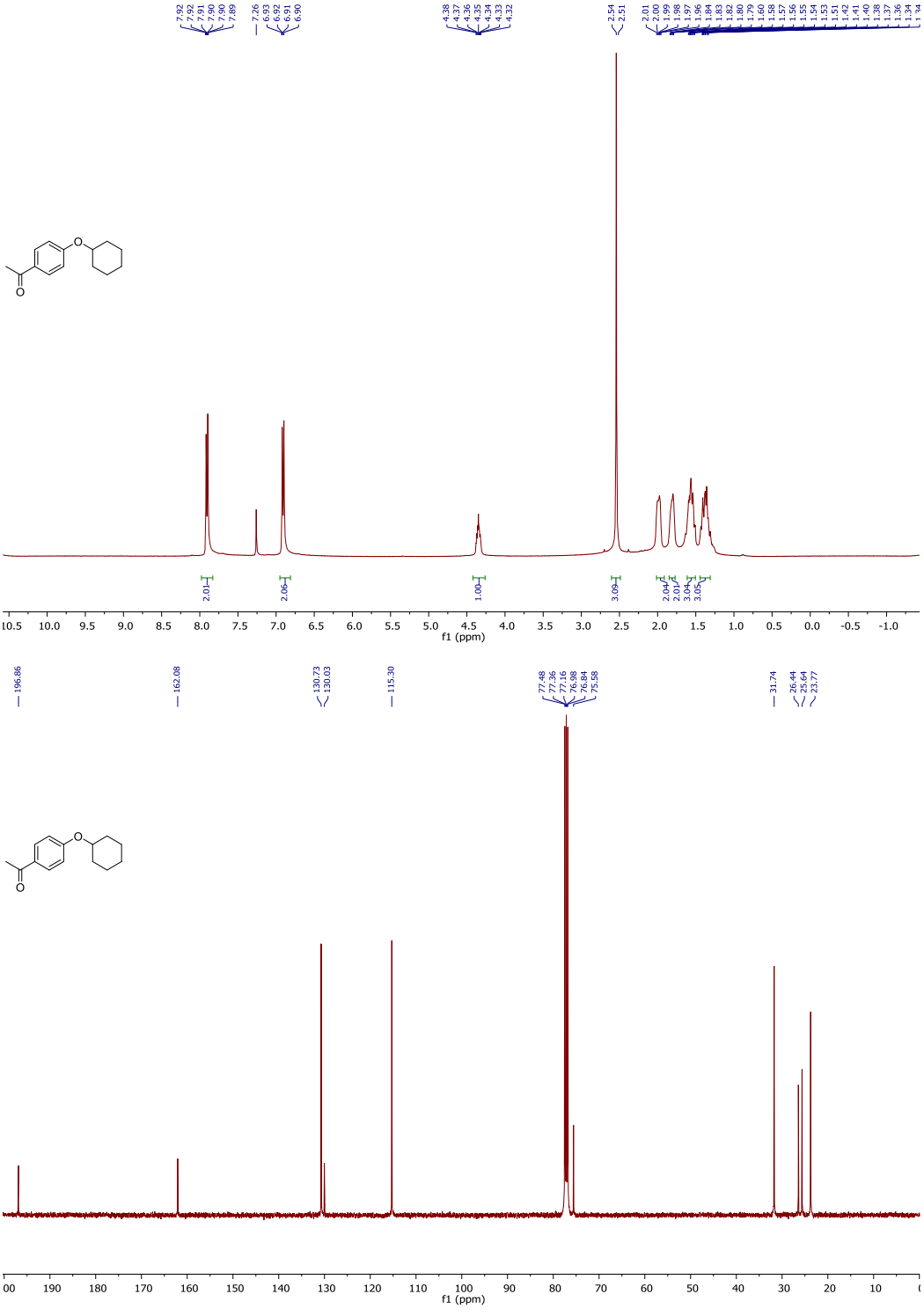


Figure S14. NMR spectra of 3k

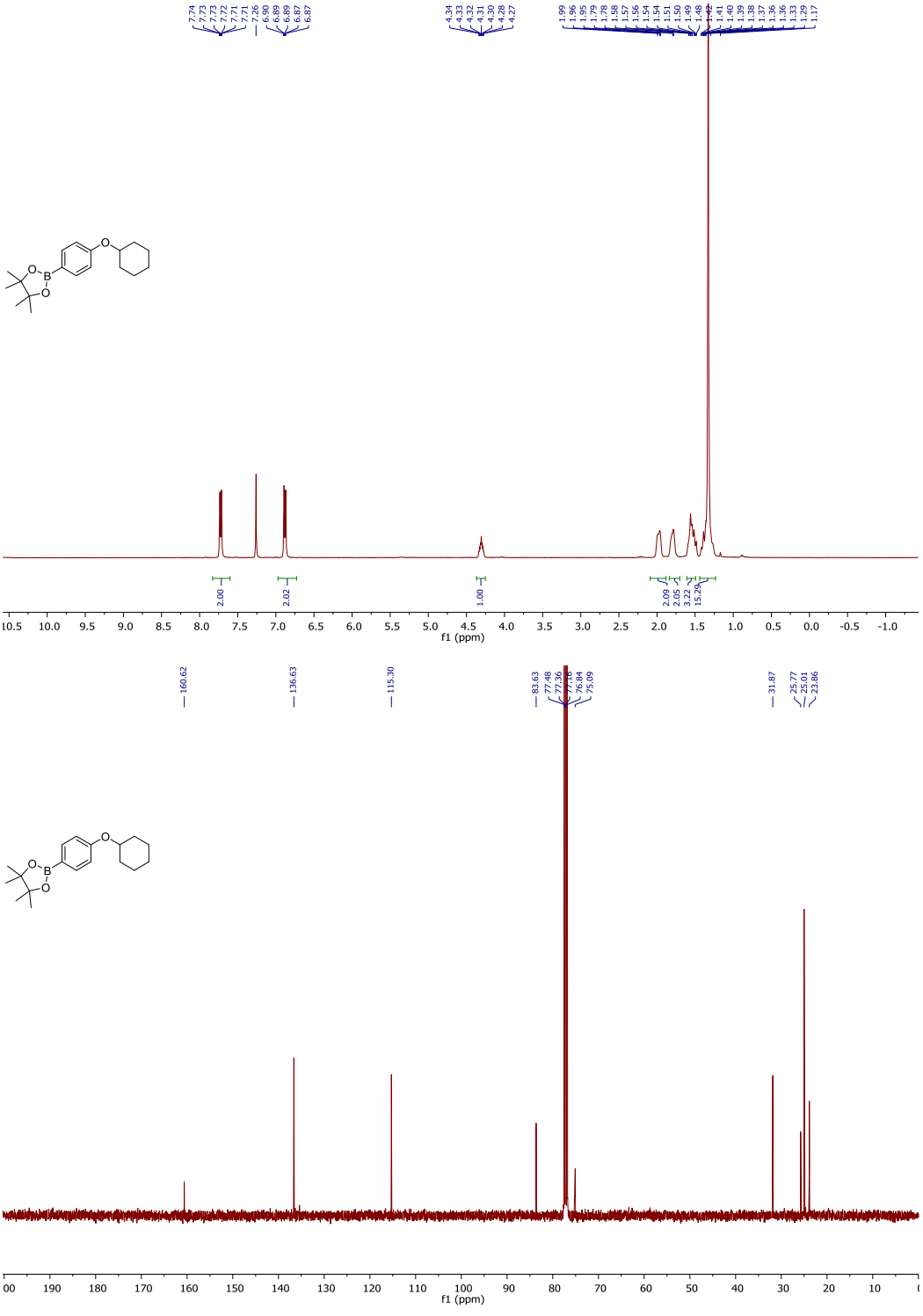


Figure S15. NMR spectra of 3l

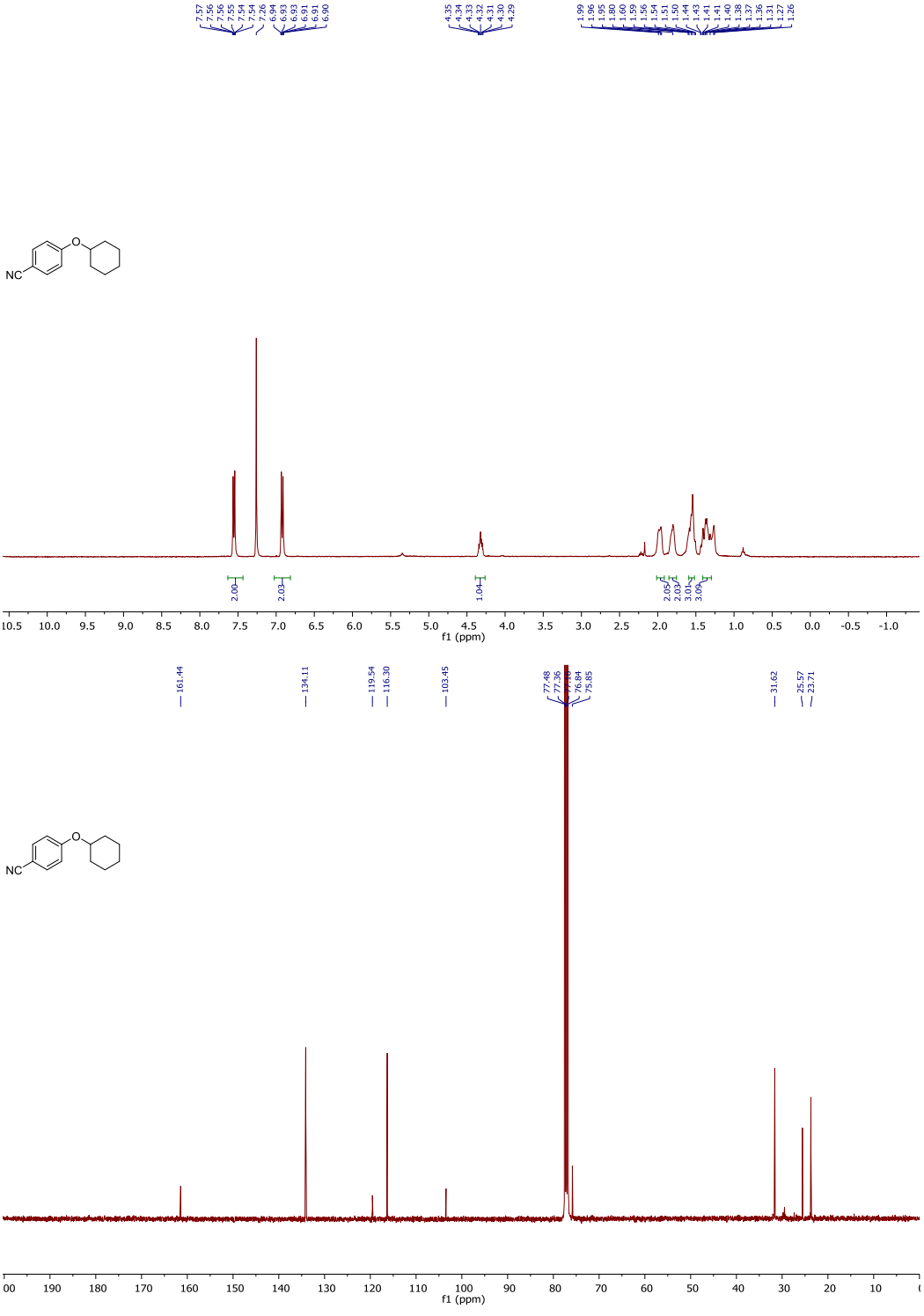
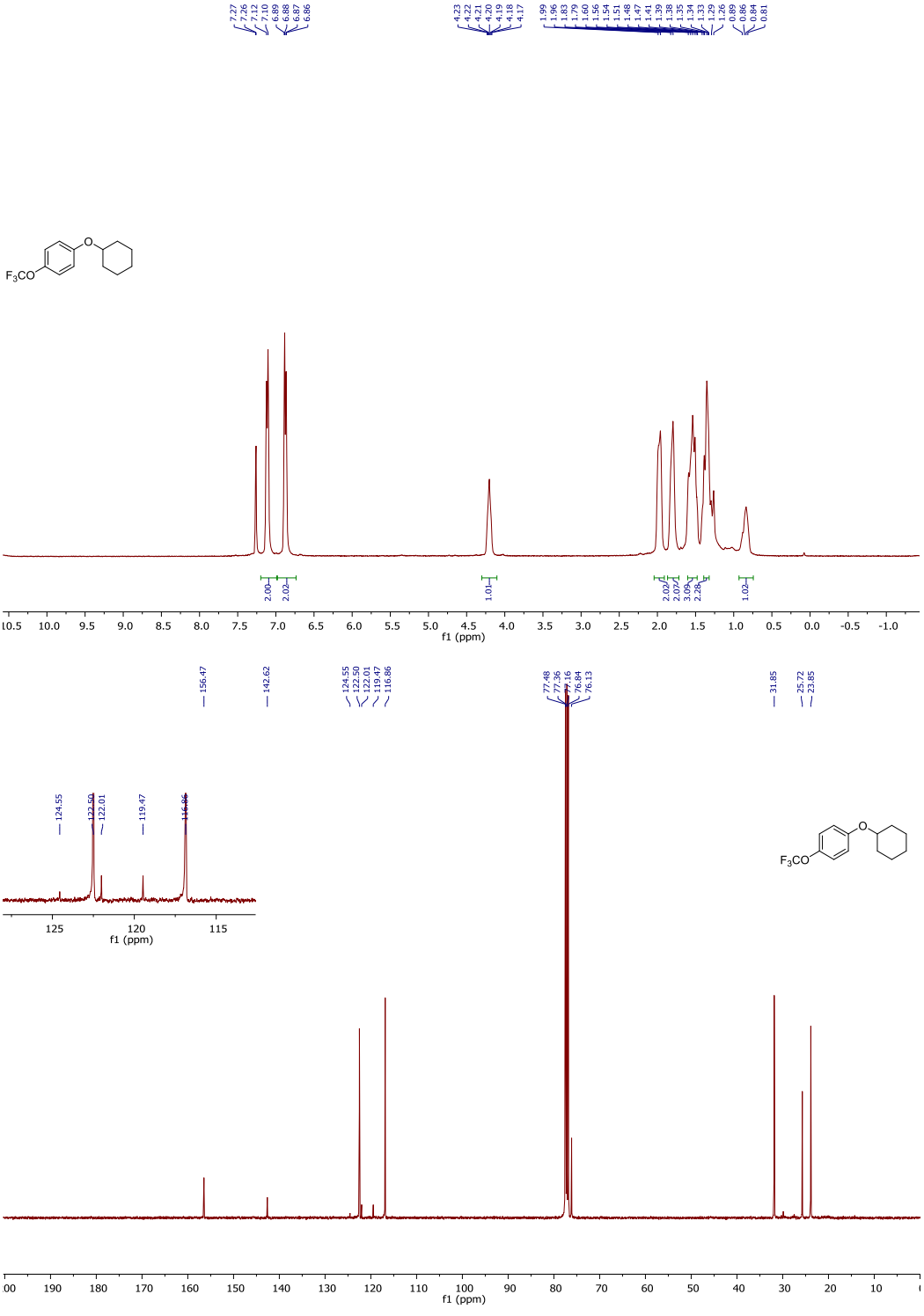


Figure S16. NMR spectra of 3m



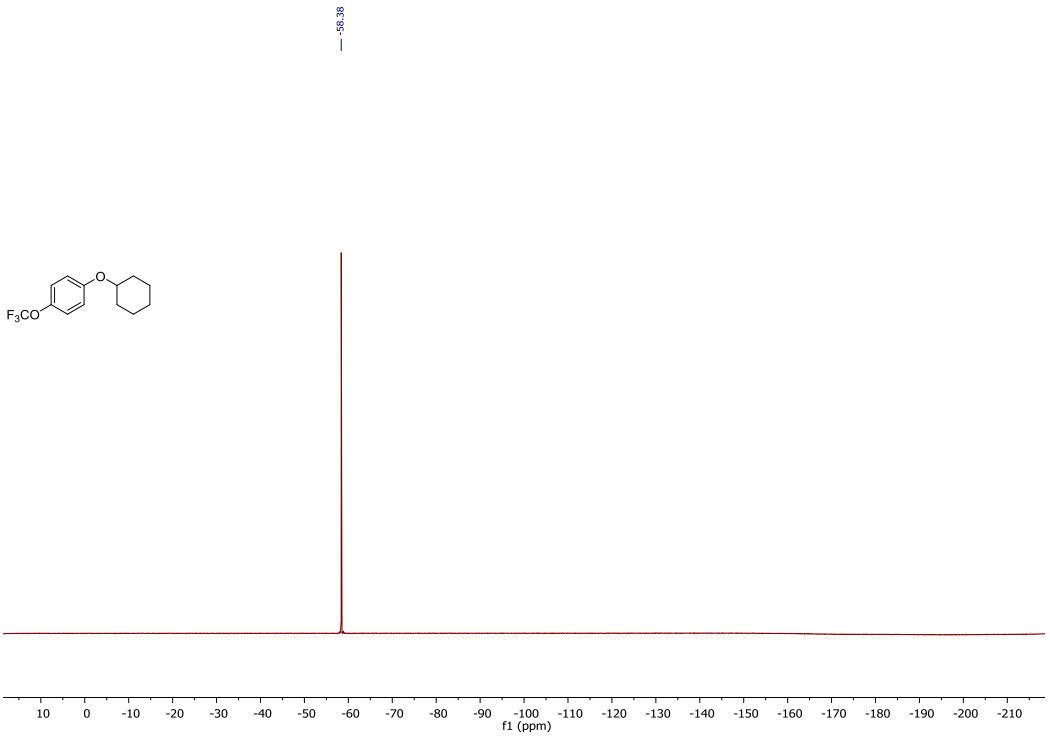

-58.38
O
F3CO
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Figure S17. NMR spectra of 3n

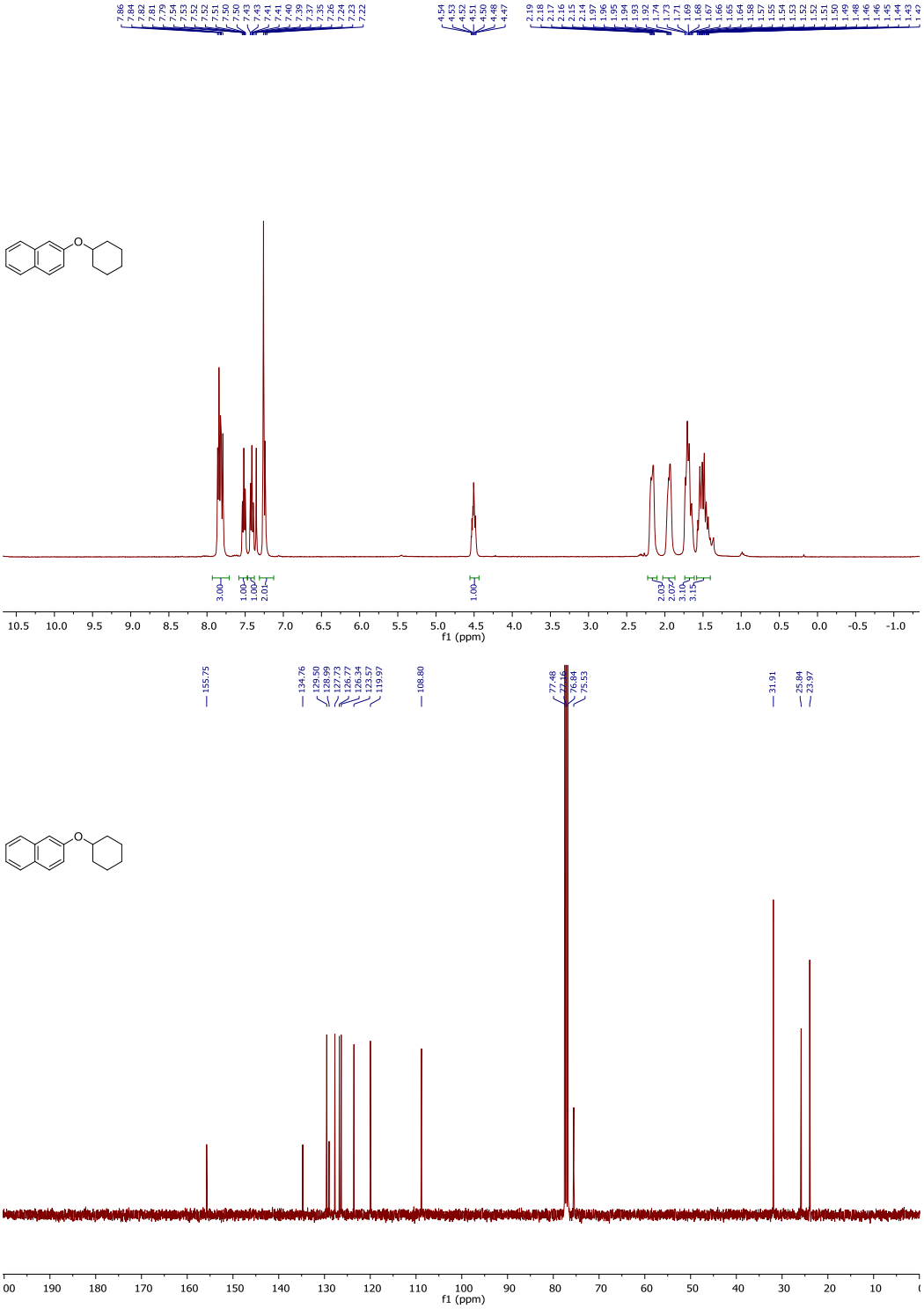


Figure S18. NMR spectra of 4a

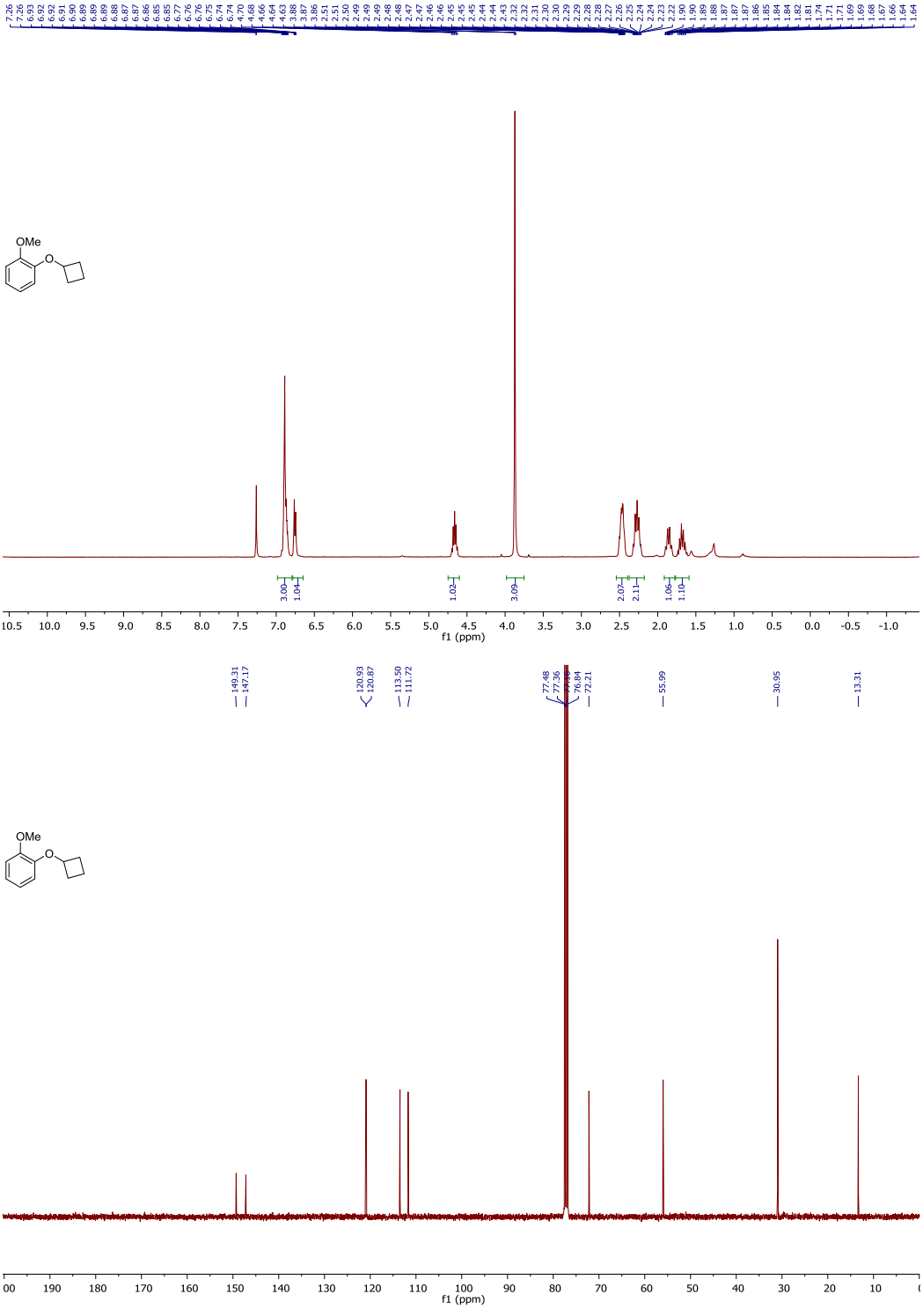


Figure S19. NMR spectra of 4b

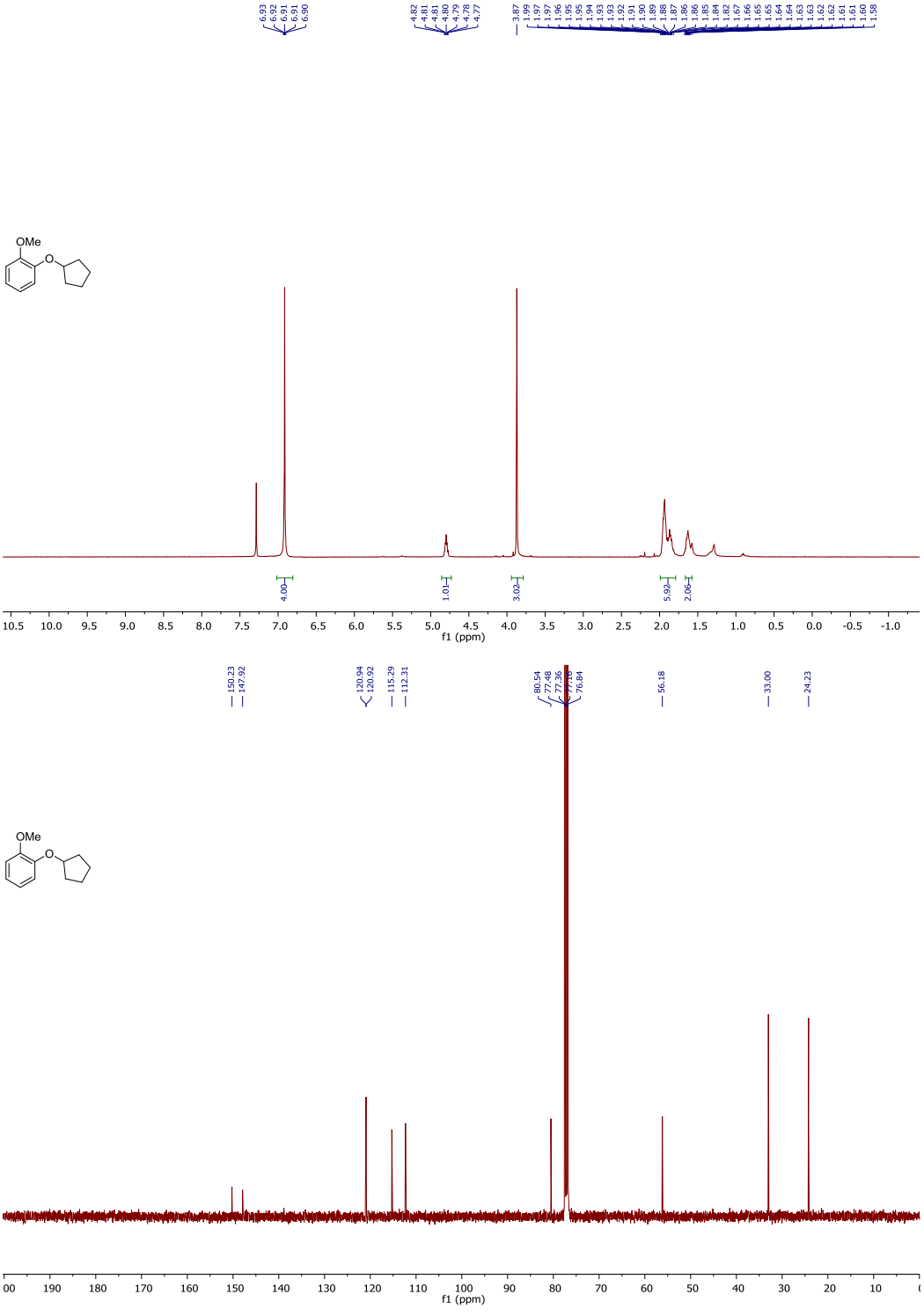


Figure S20. NMR spectra of 4c

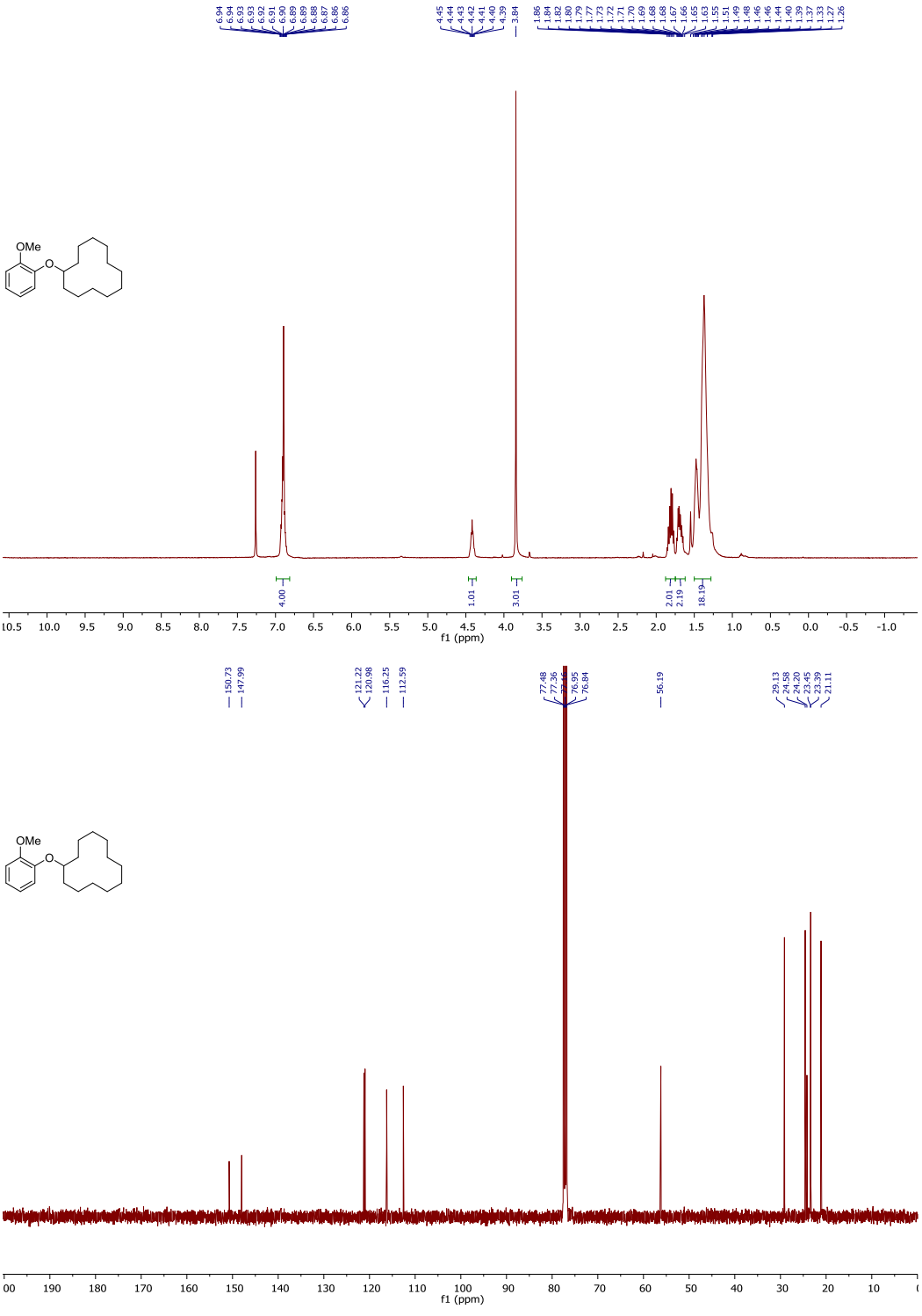


Figure S21. NMR spectra of 4d

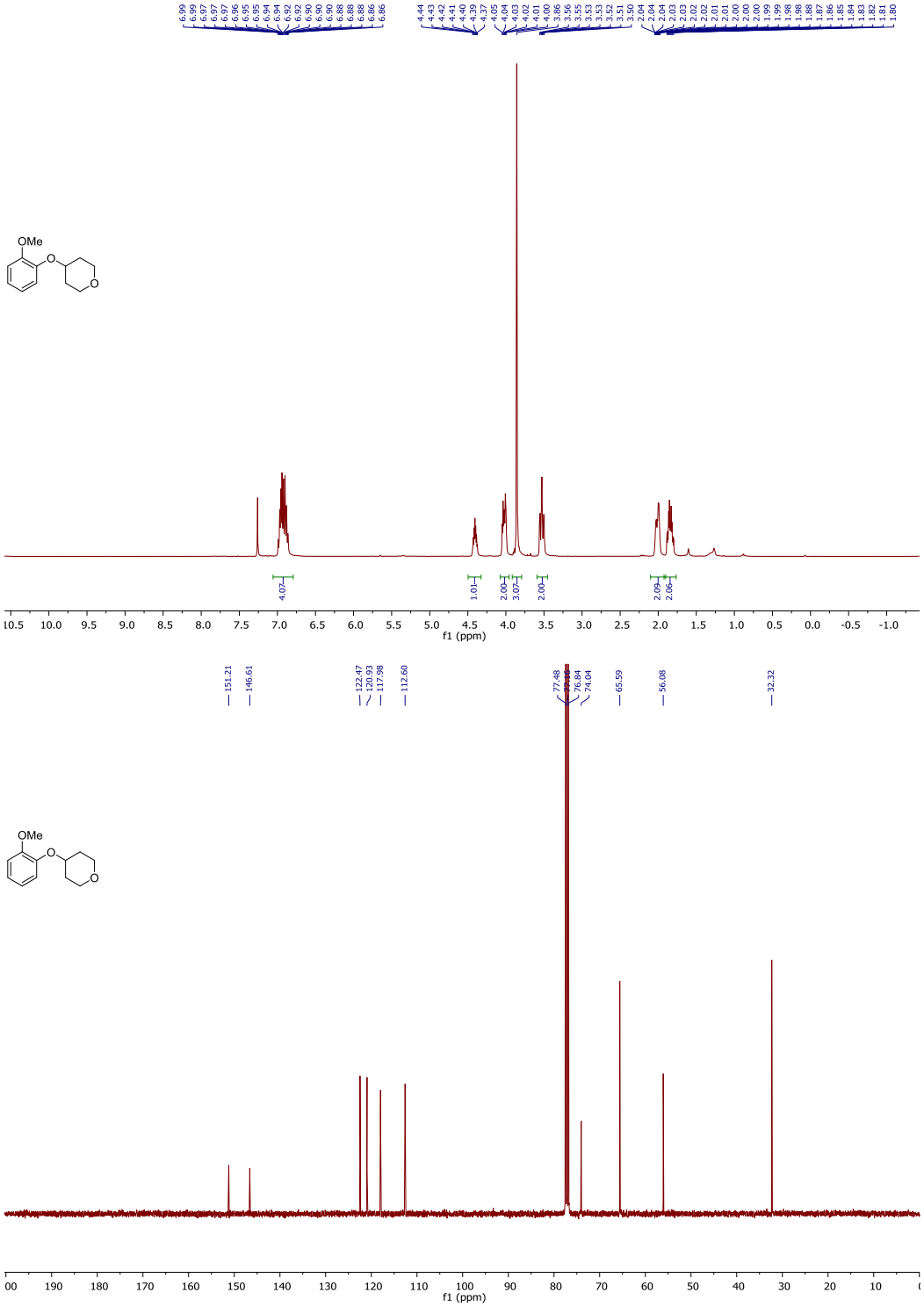


Figure S22. NMR spectra of 4e

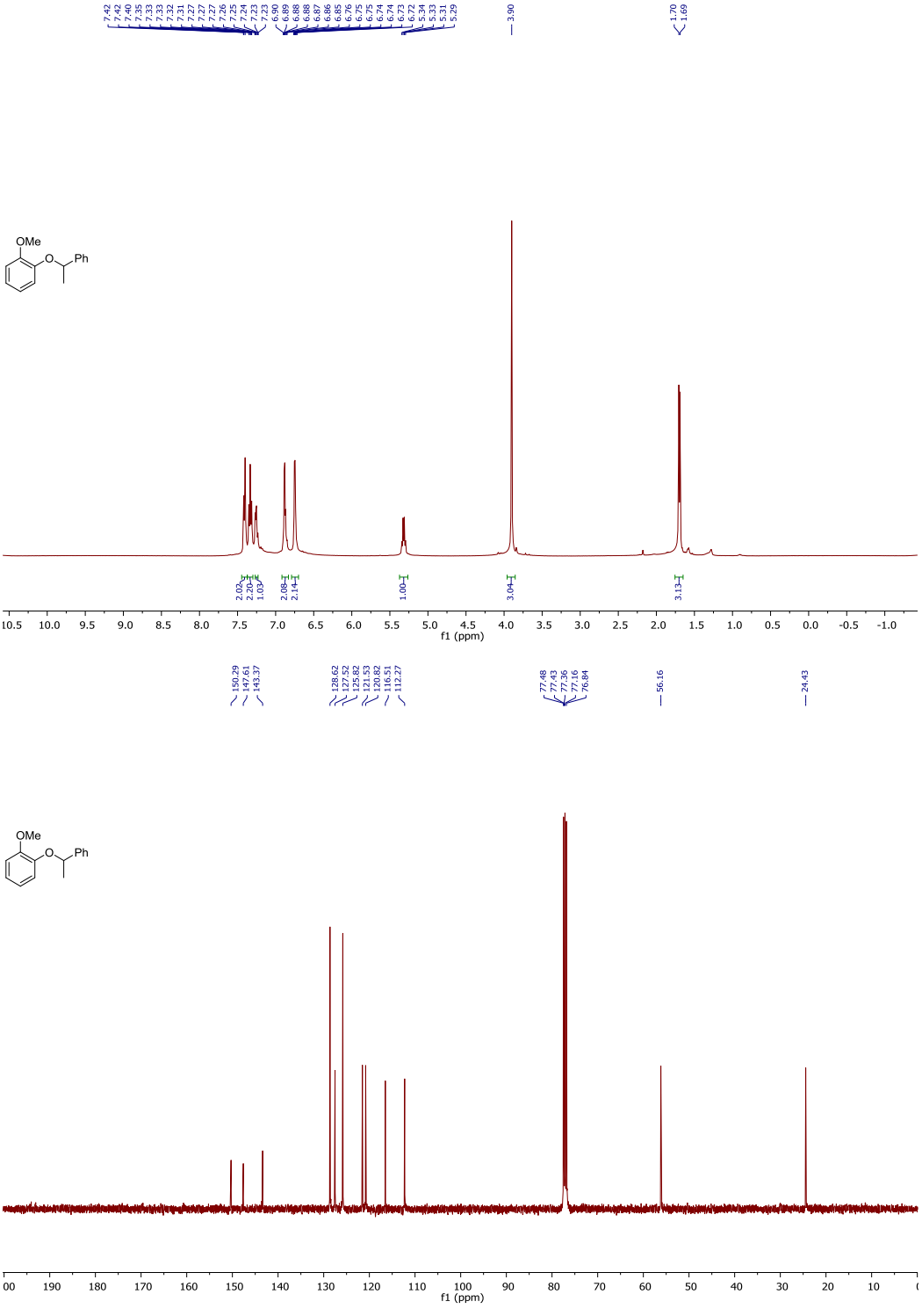


Figure S23. NMR spectra of 4f

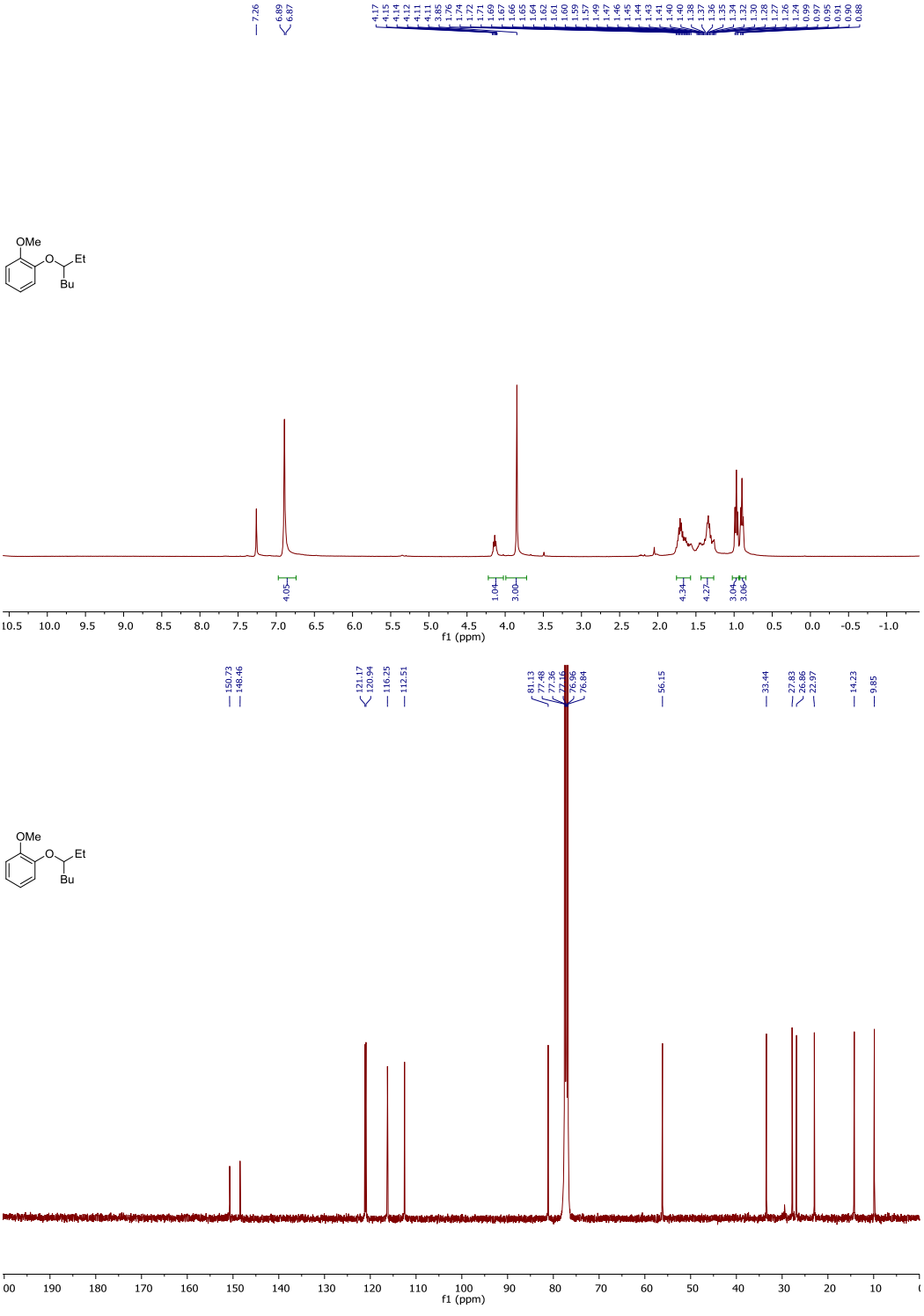


Figure S24. NMR spectra of 4g

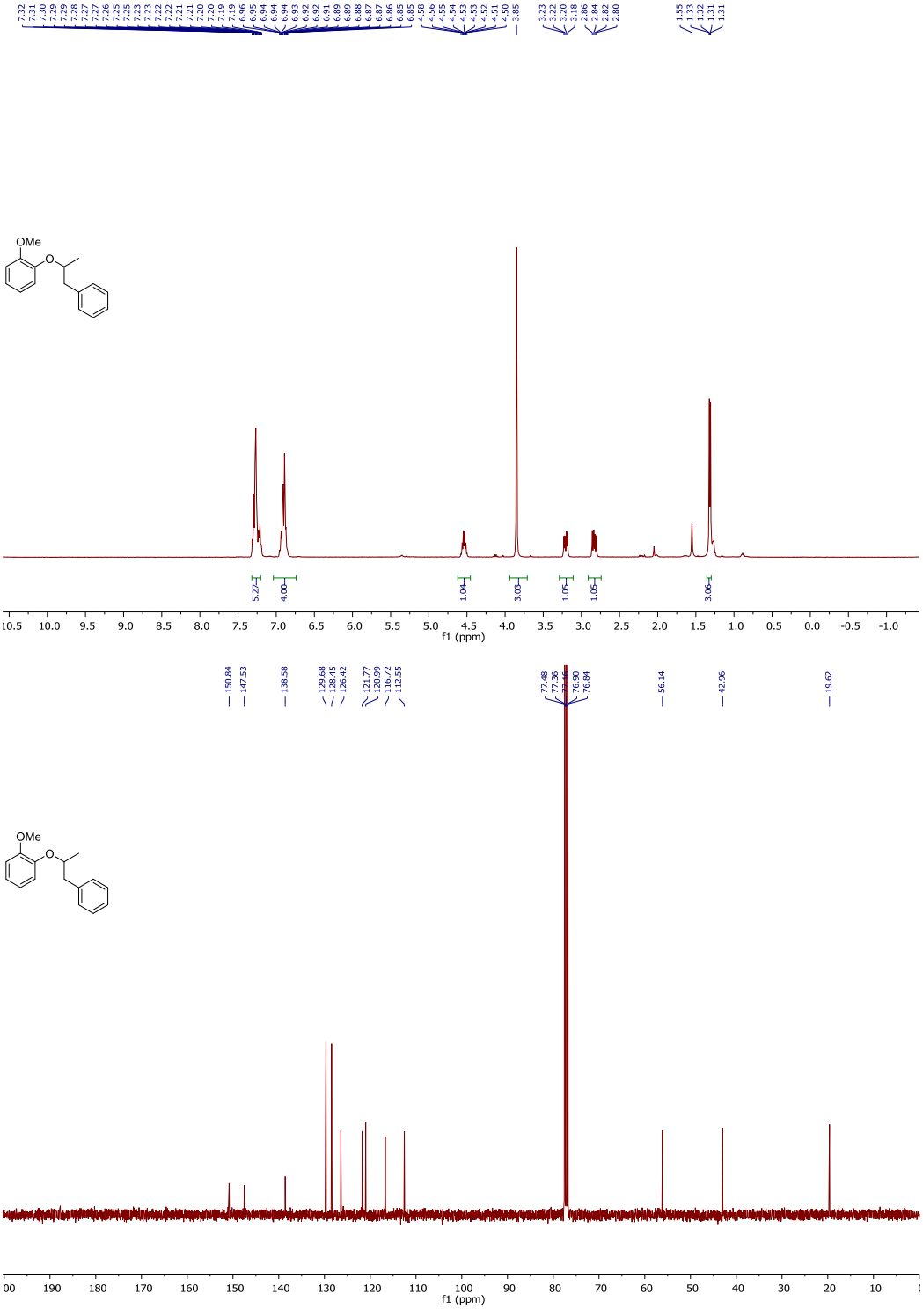


Figure S25. NMR spectra of 5a

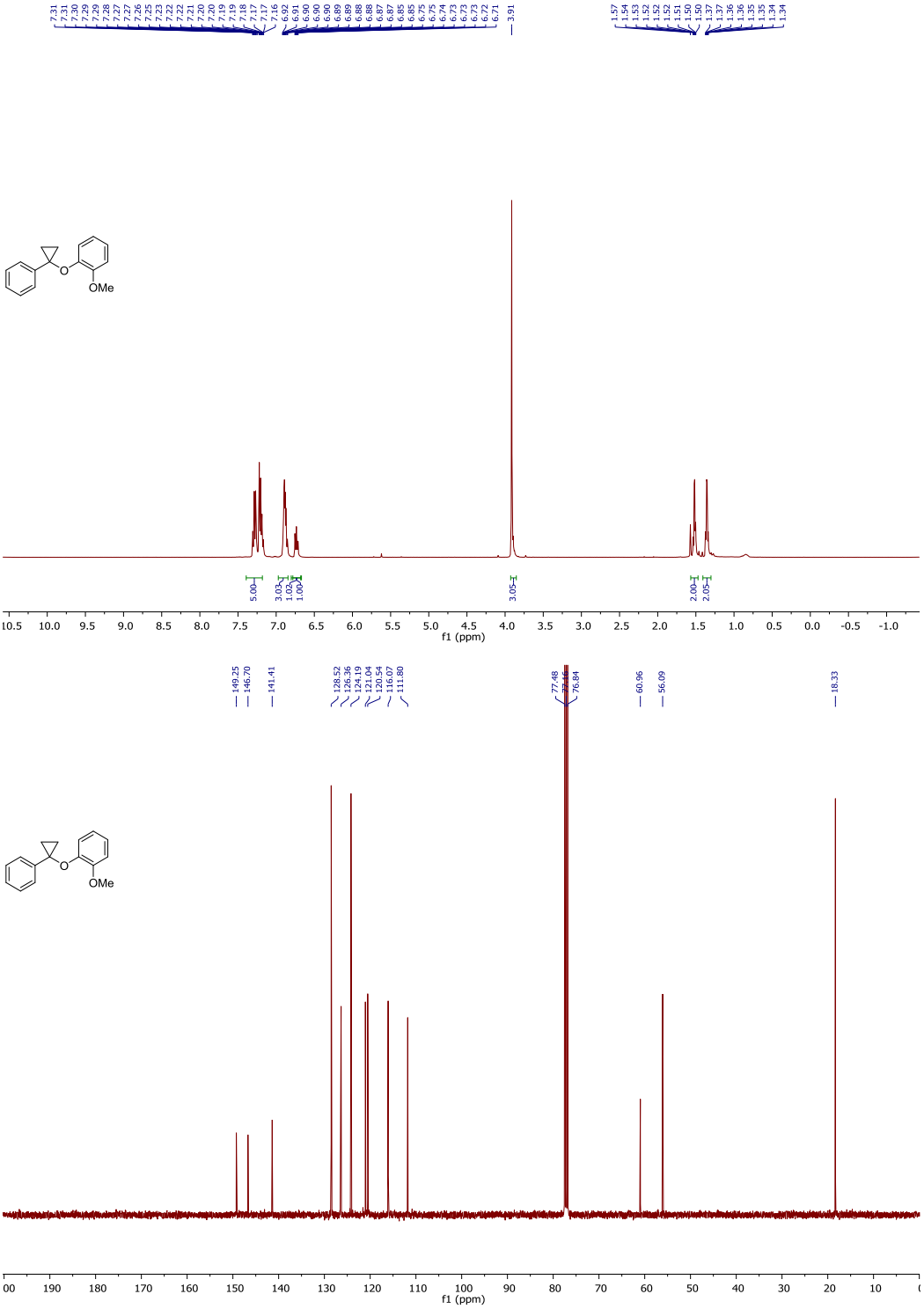


Figure S26. NMR spectra of 5b

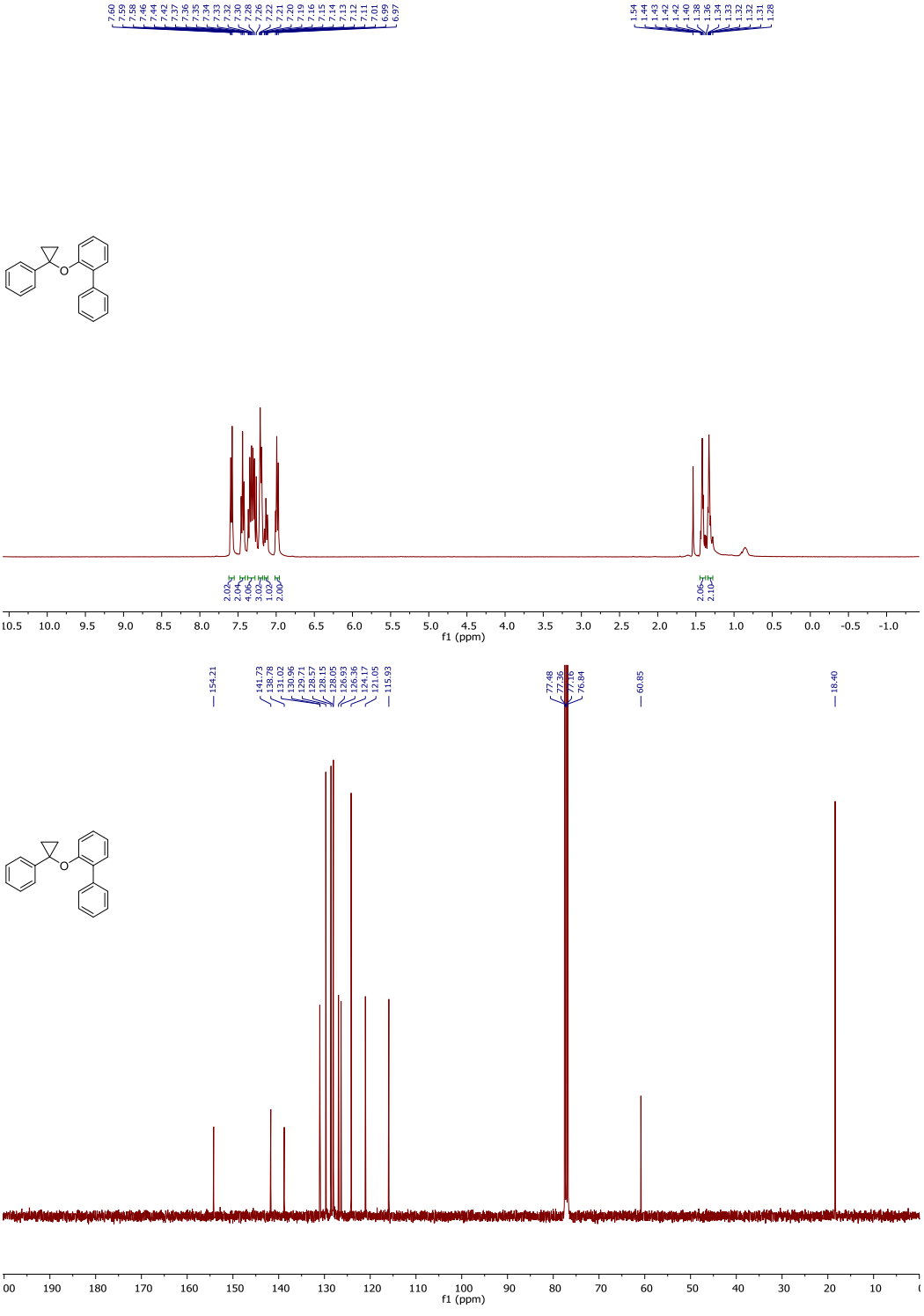


Figure S27. NMR spectra of 5c

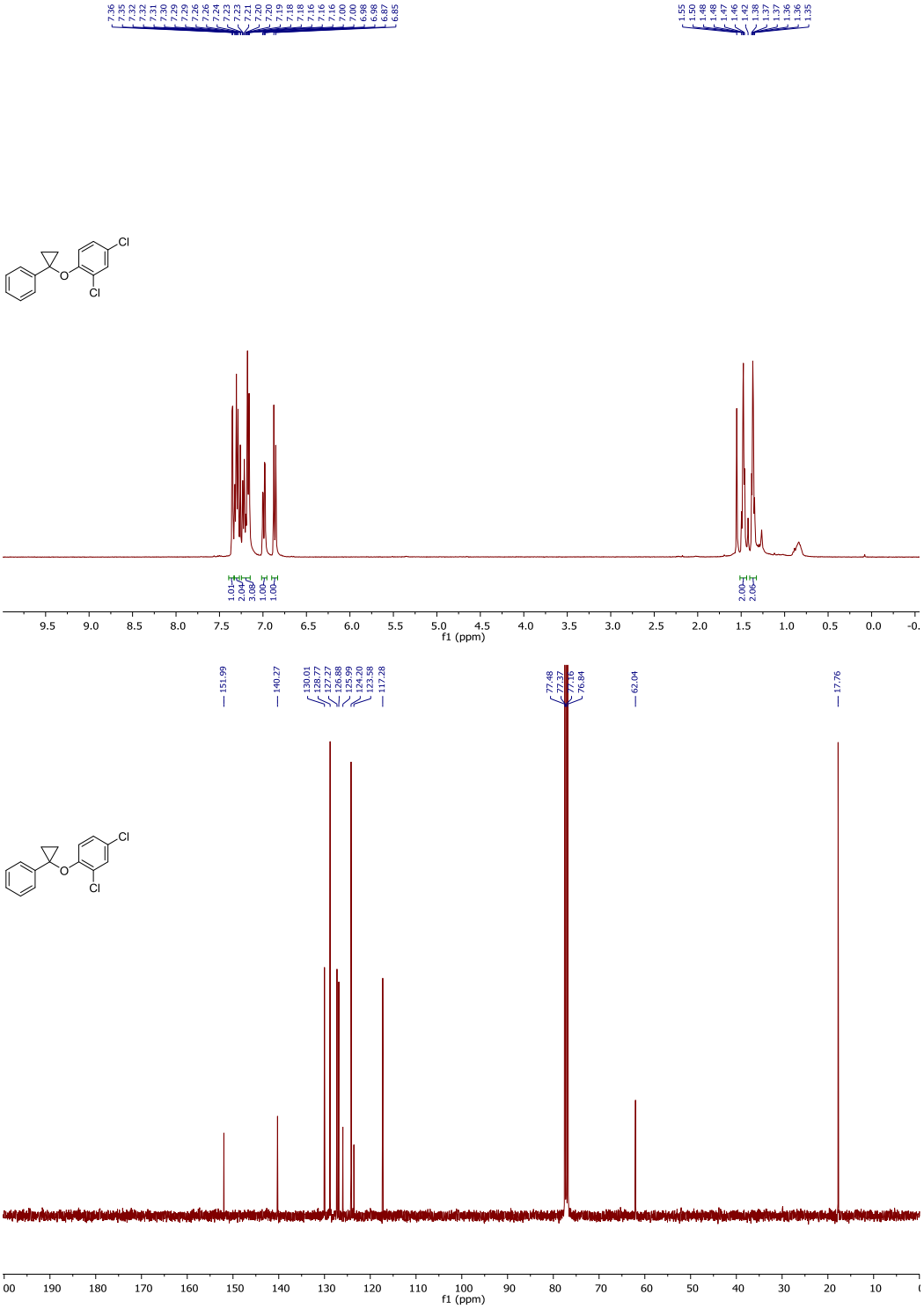


Figure S28. NMR spectra of 5d

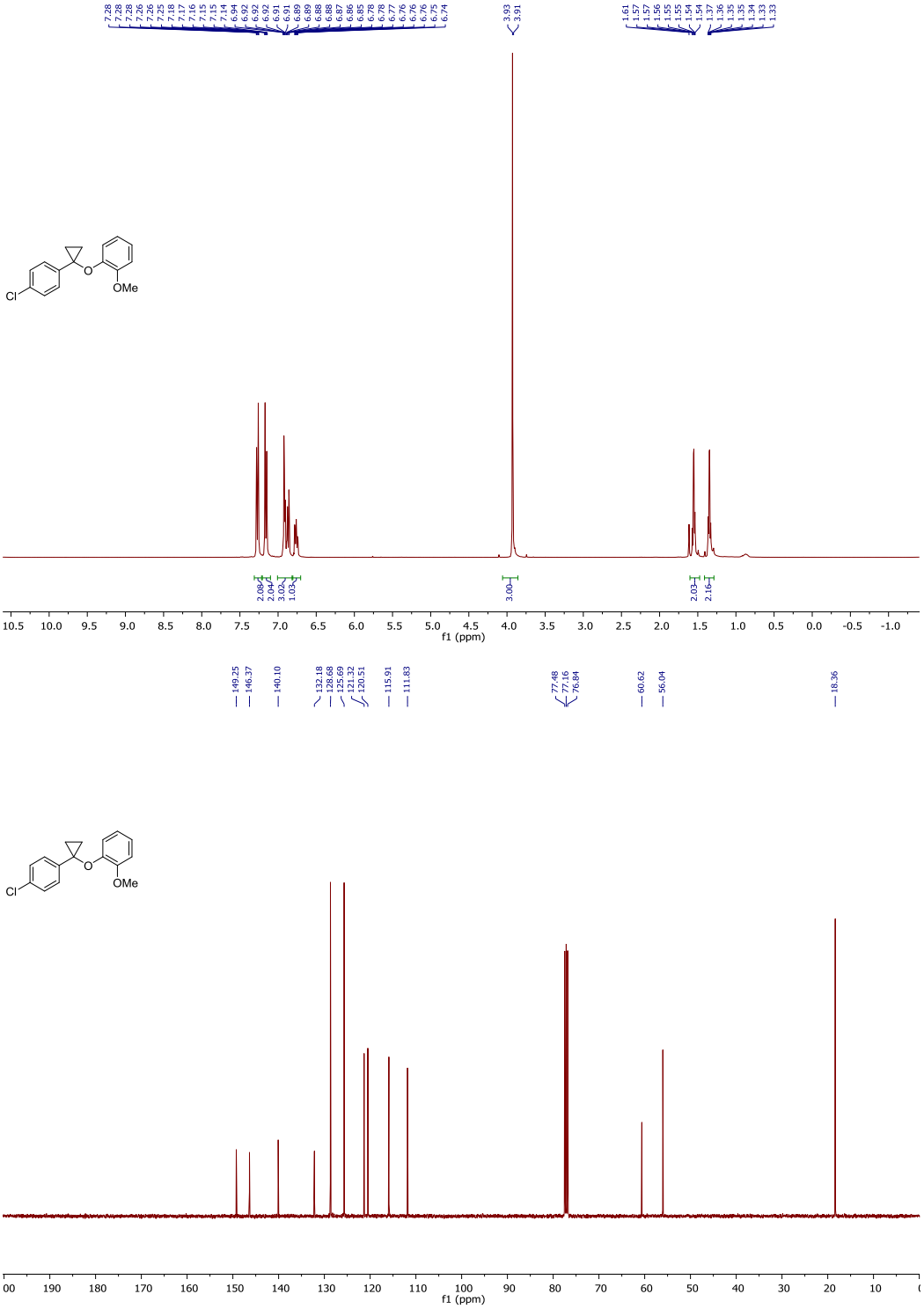


Figure S29. NMR spectra of 5e

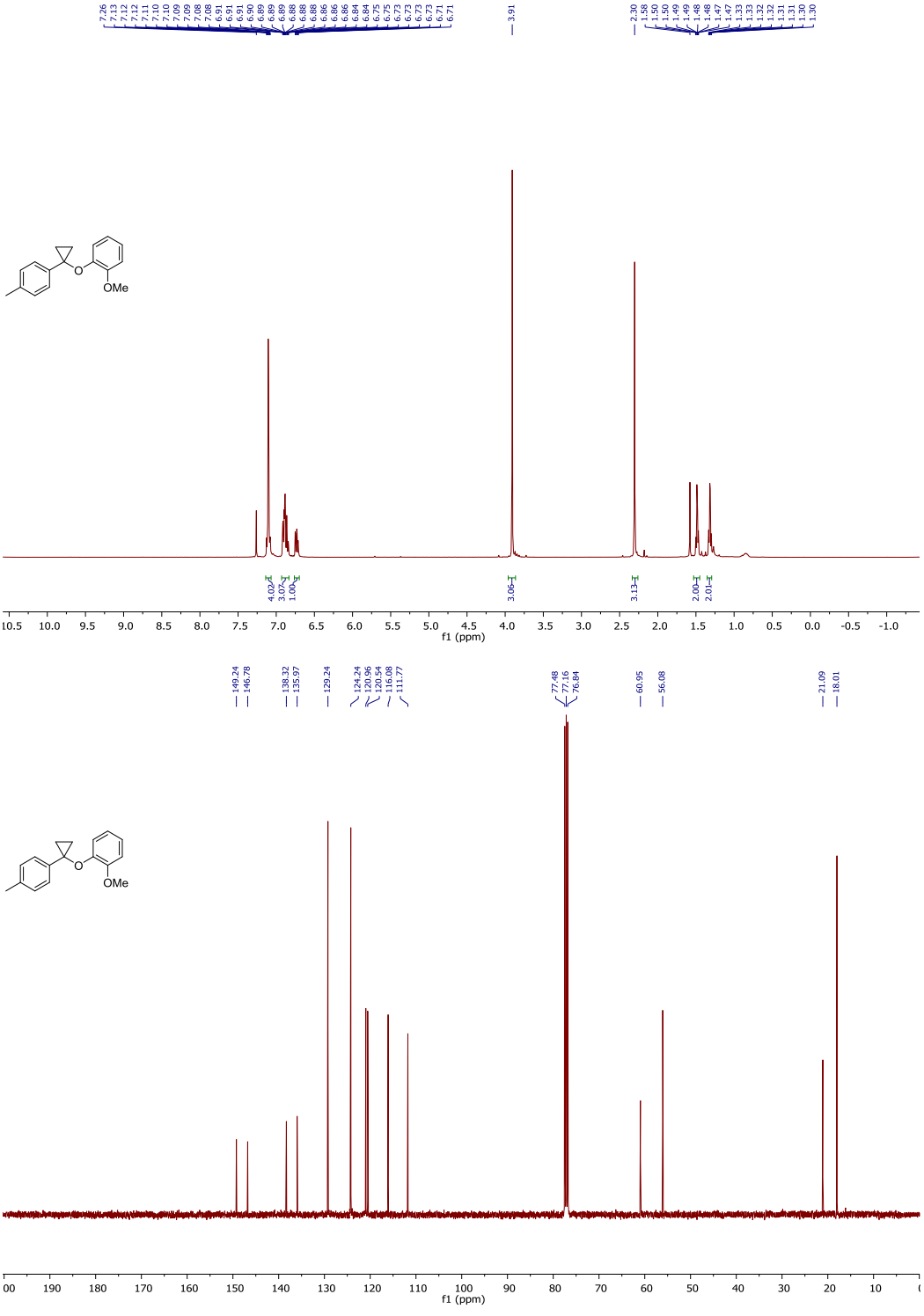


Figure S30. NMR spectra of 5f

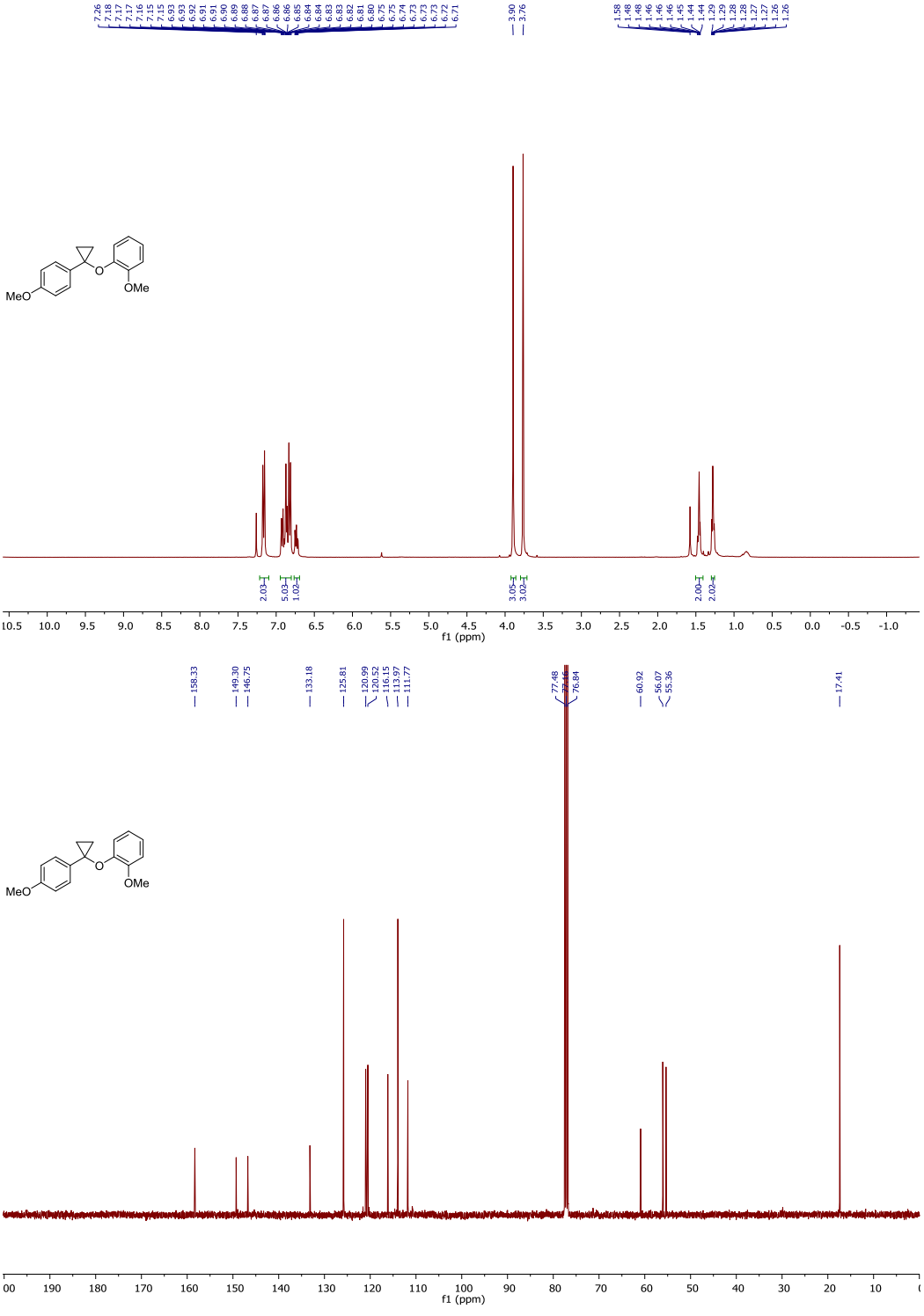


Figure S31. NMR spectra of 6a

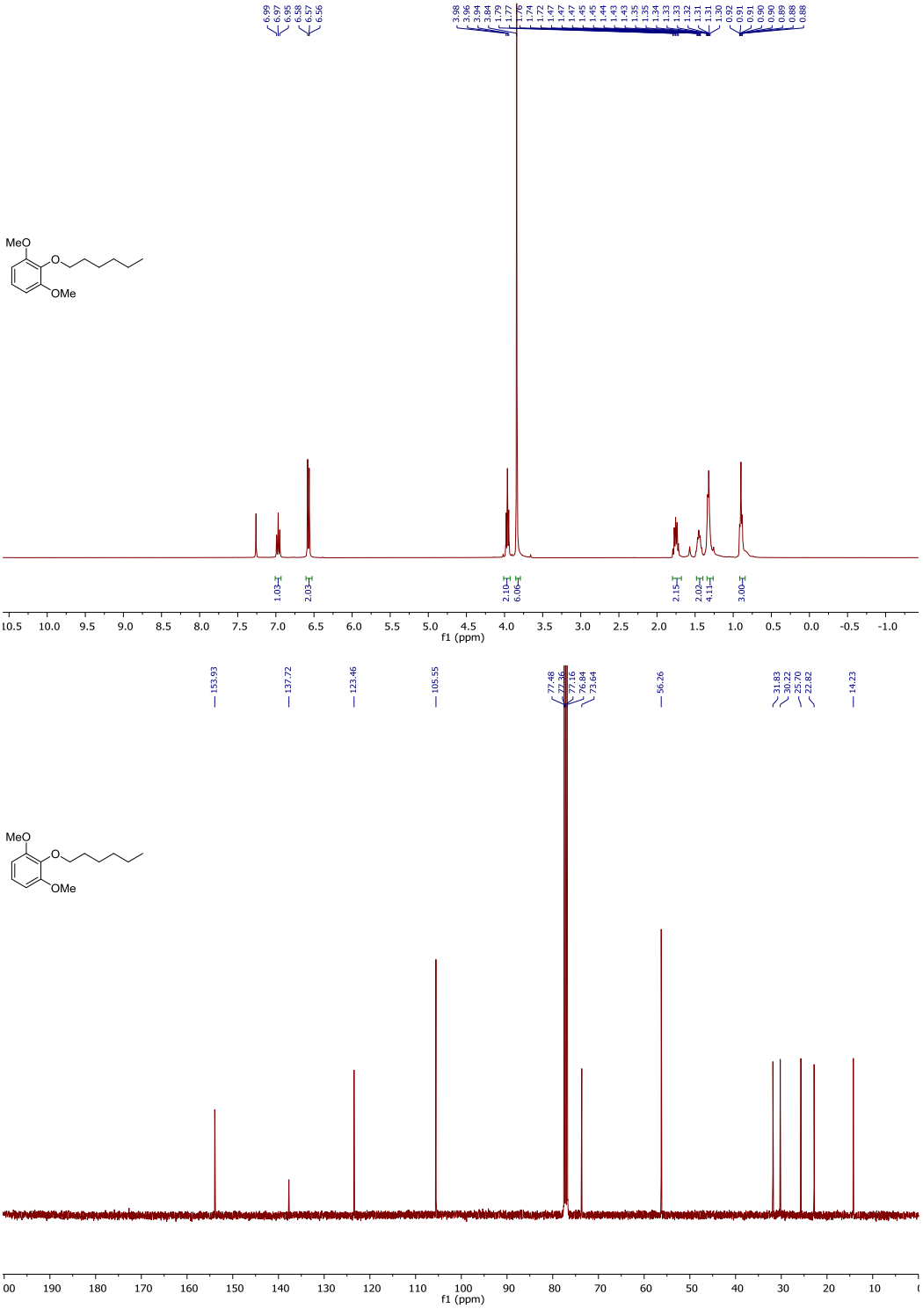


Figure S32. NMR spectra of 6b

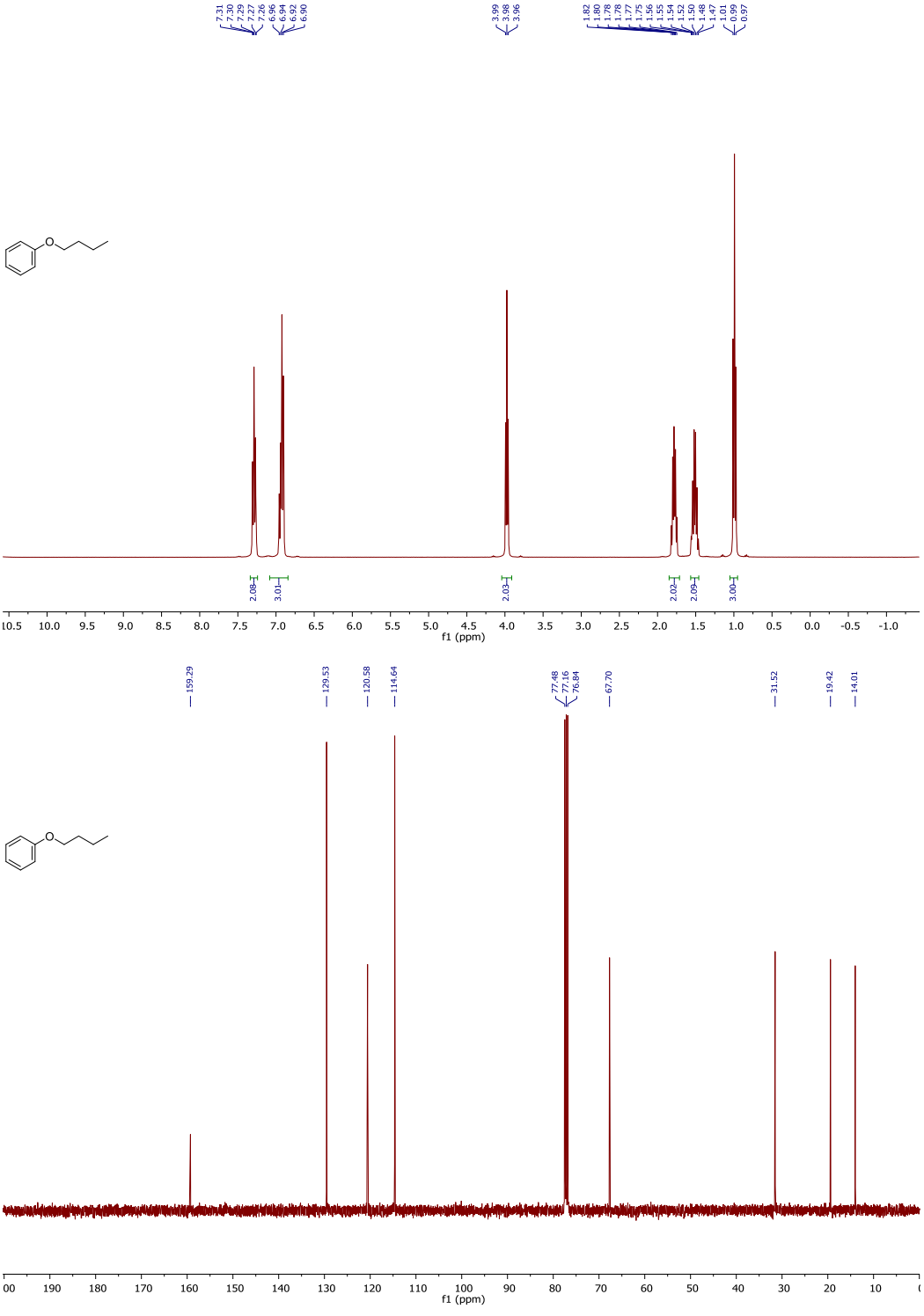


Figure S33. NMR spectra of 6c

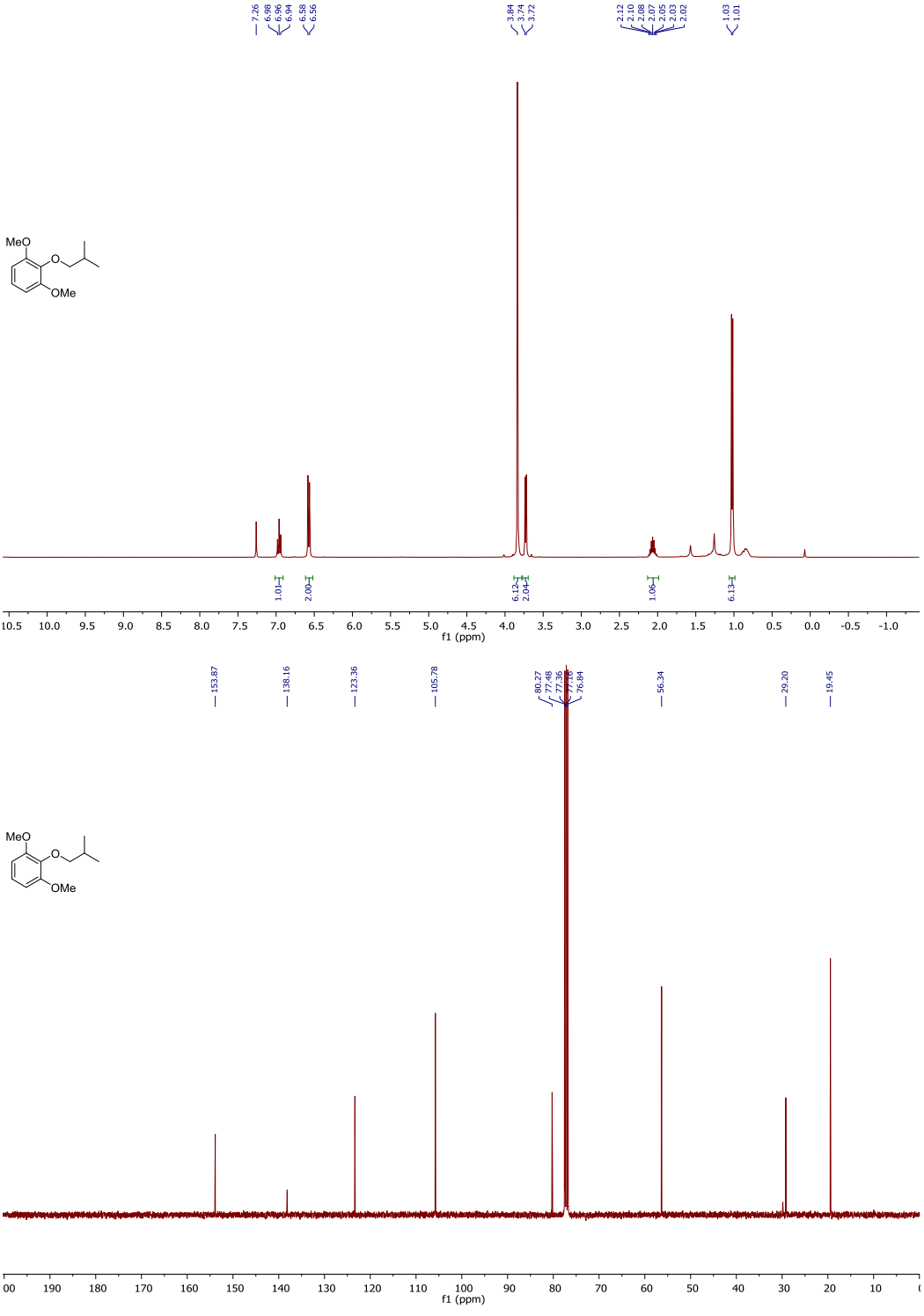


Figure S34. NMR spectra of 6d

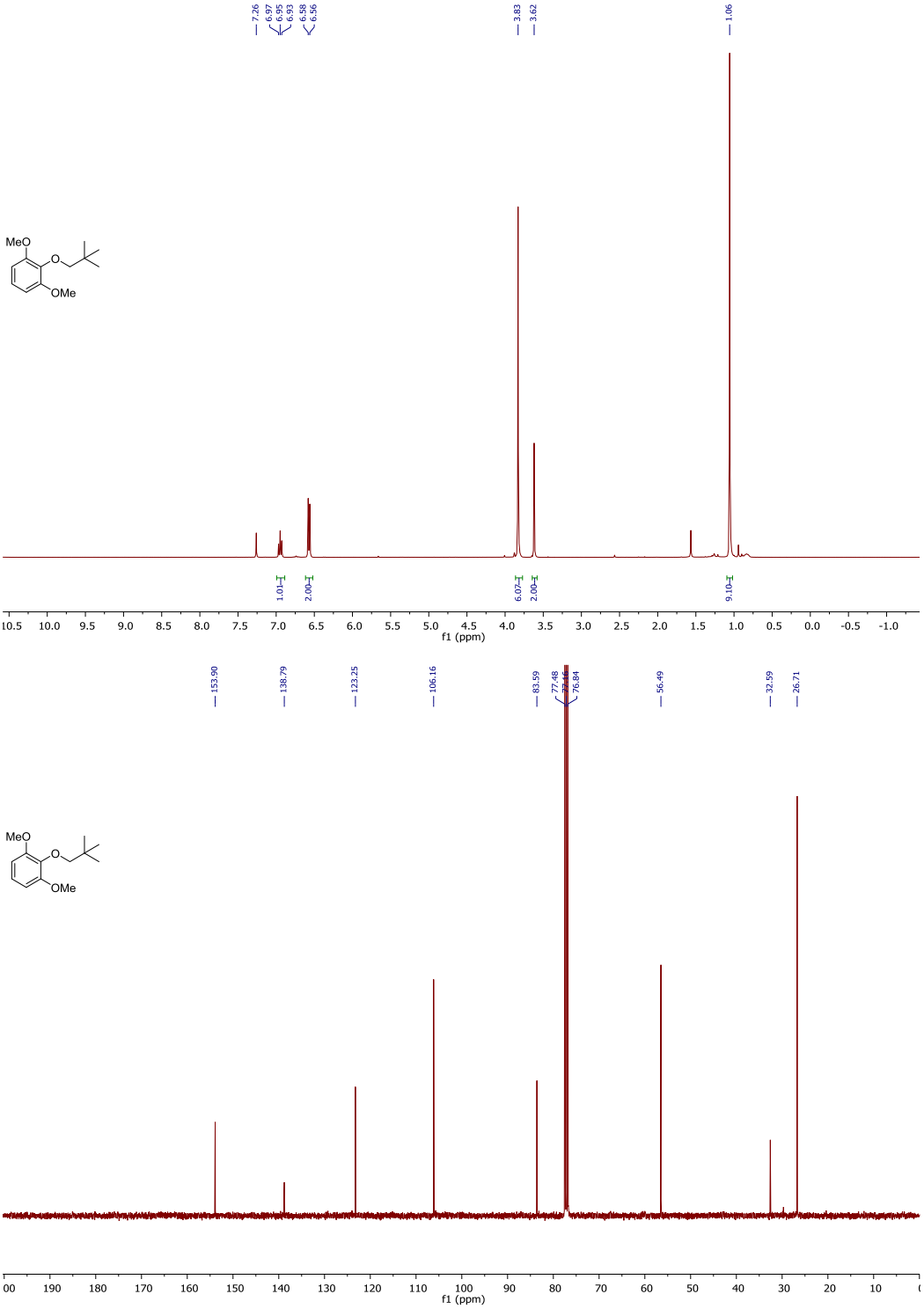


Figure S35. NMR spectra of 6e

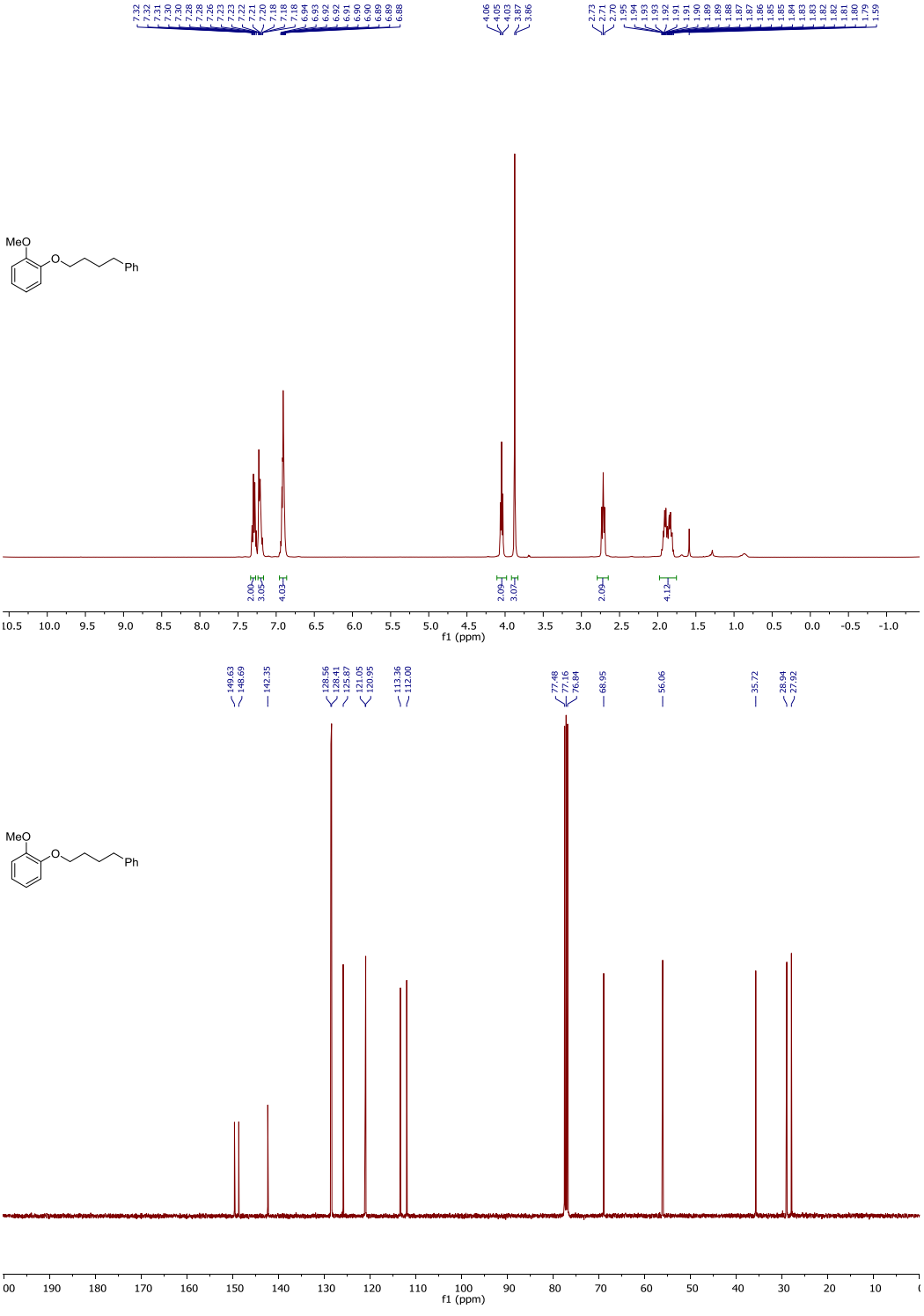


Figure S36. NMR spectra of 6f

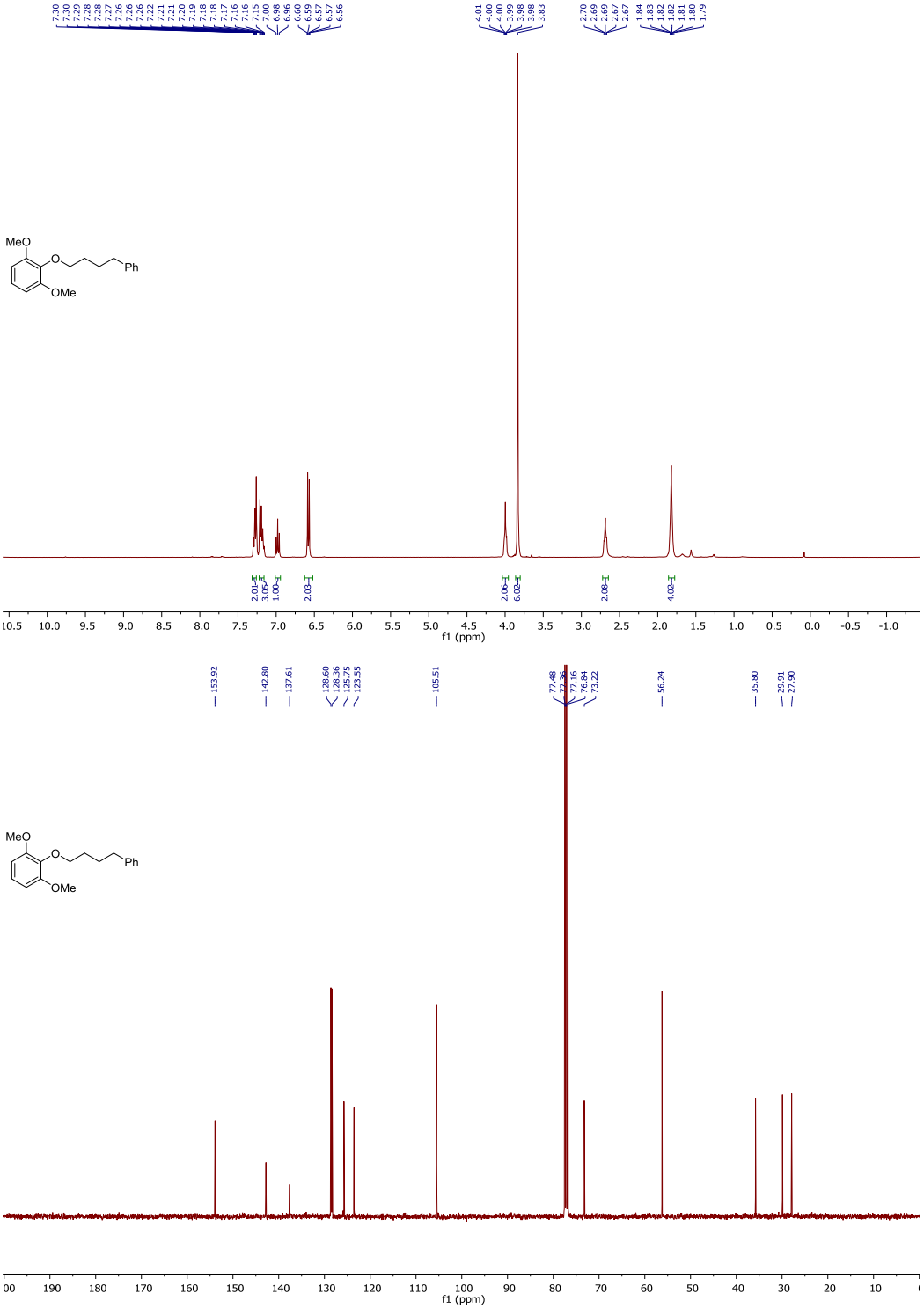


Figure S37. NMR spectra of 6g

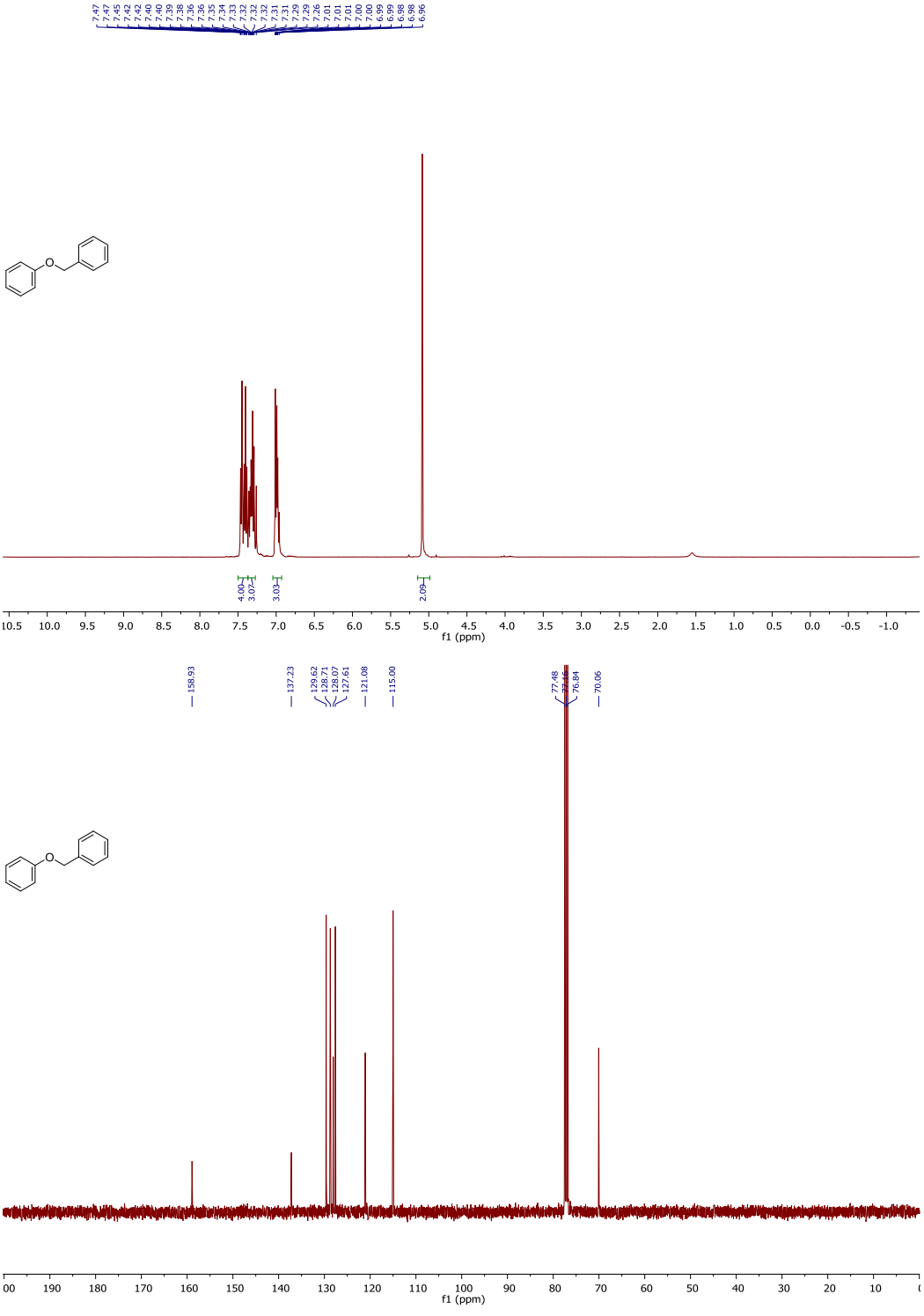


Figure S38. NMR spectra of 6h

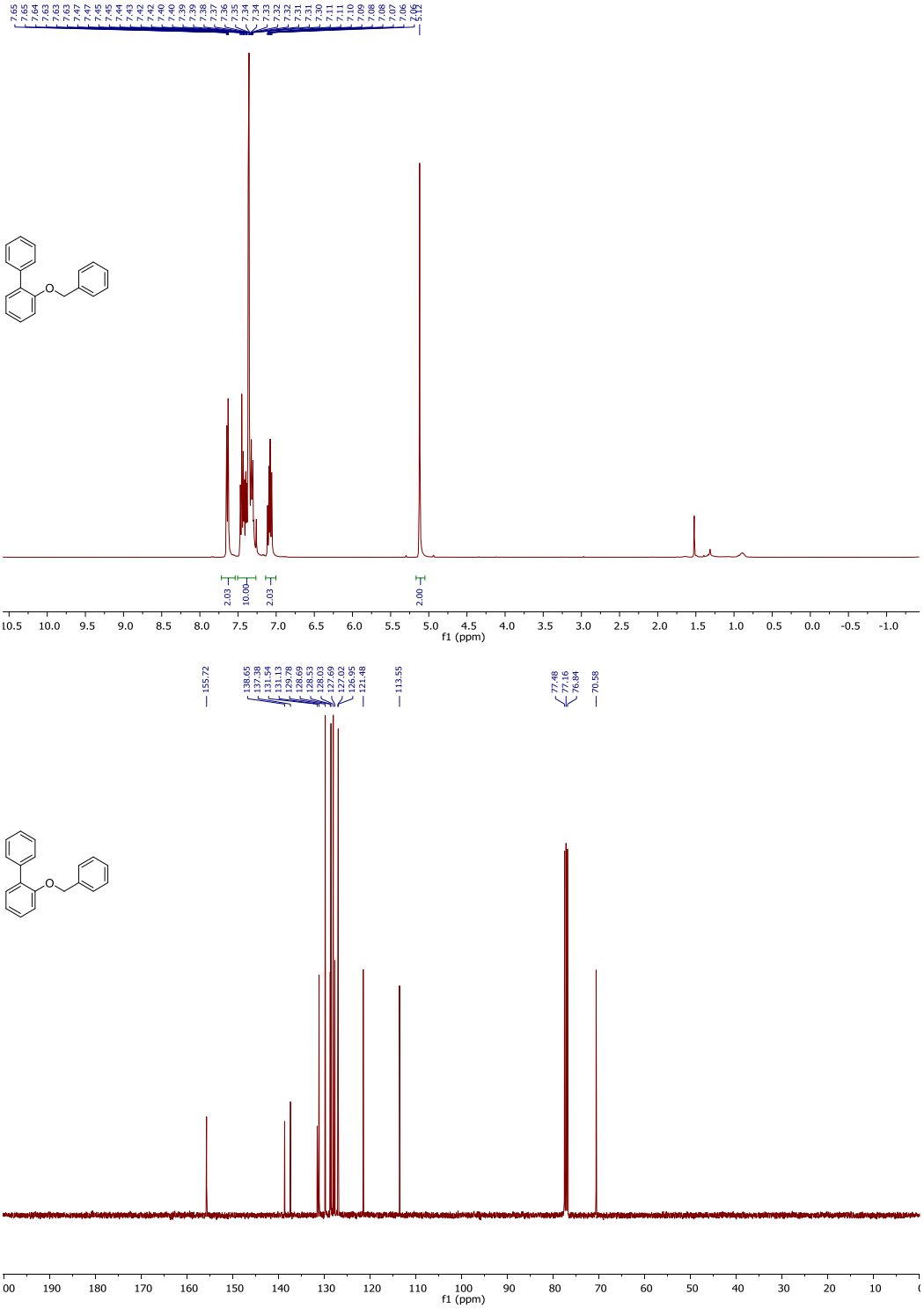


Figure S39. NMR spectra of 6i

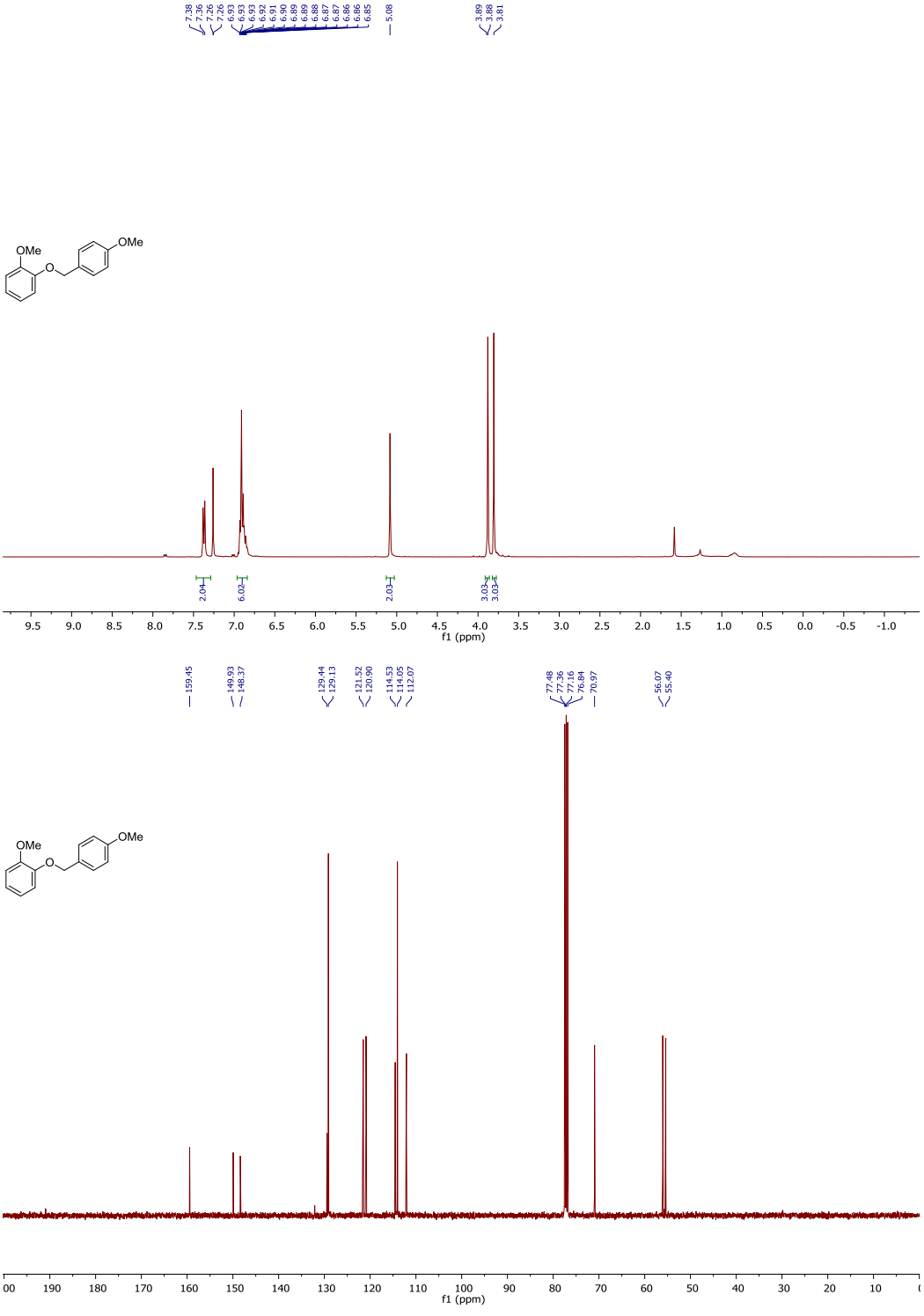


Figure S40. NMR spectra of 6j

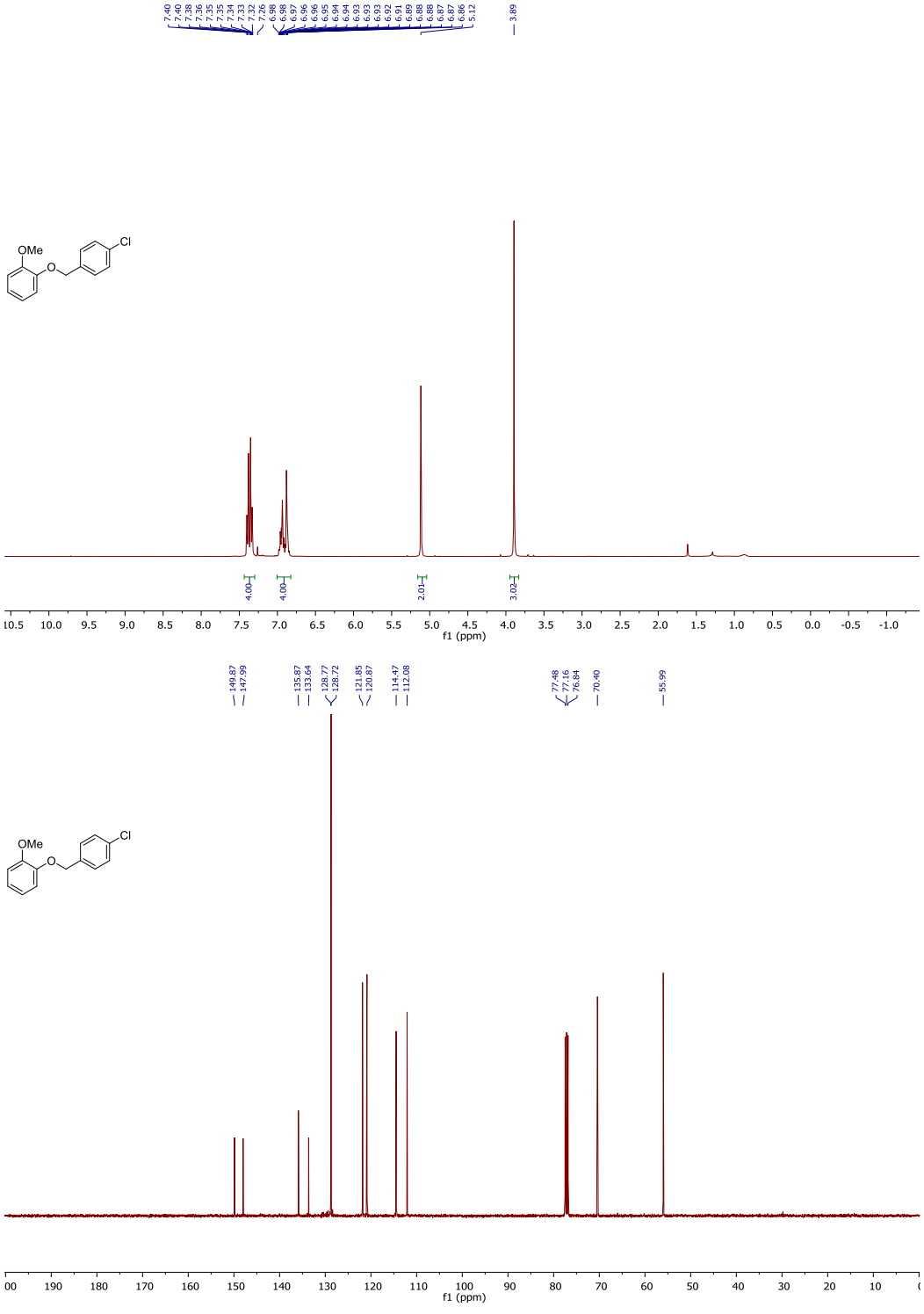


Figure S41. NMR spectra of 6k

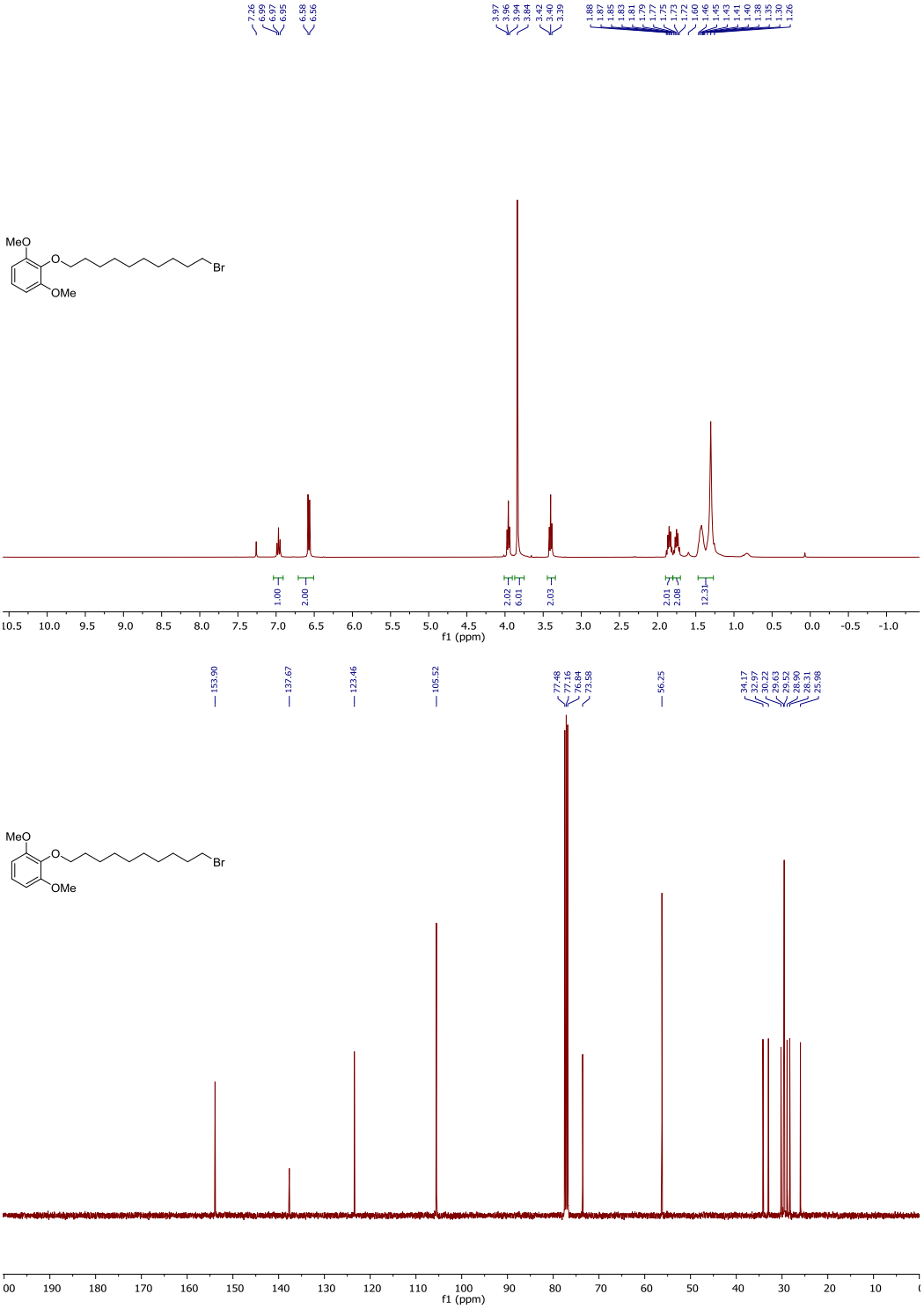
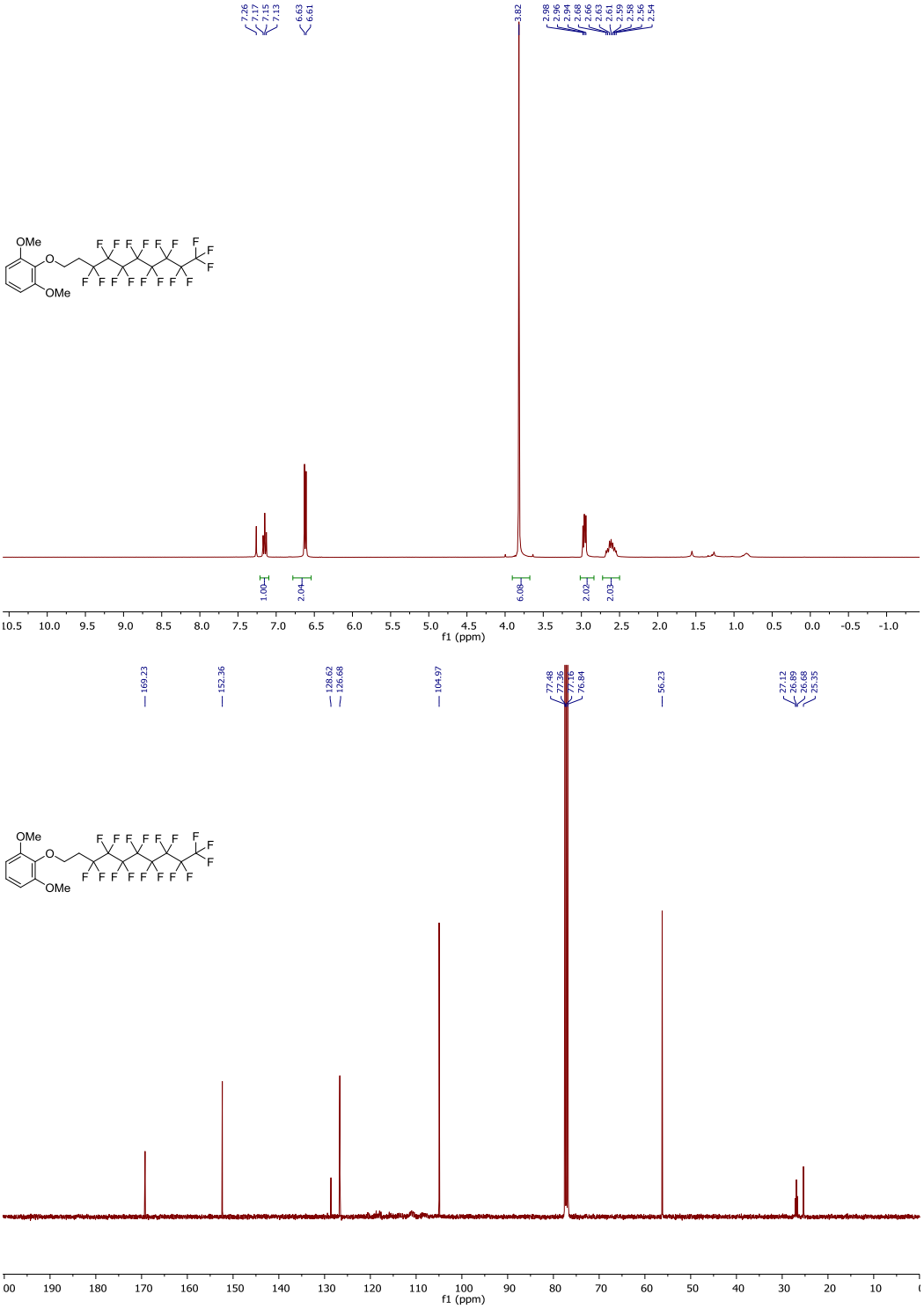
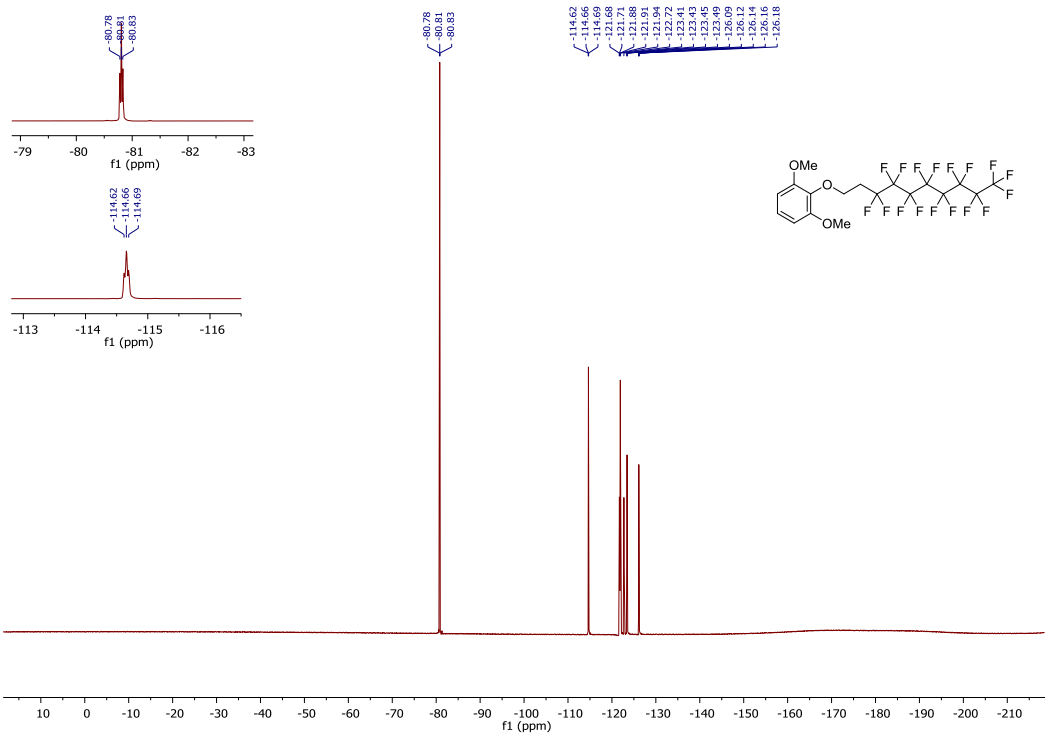


Figure S42. NMR spectra of 6l

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-114.66
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-121.94
-122.72
-123.41
-123.45
-123.49
-126.09
-126.12
-126.14
-126.16
-126.18
OMe
OMe
f1 (ppm)

Figure S43. NMR spectra of 6m

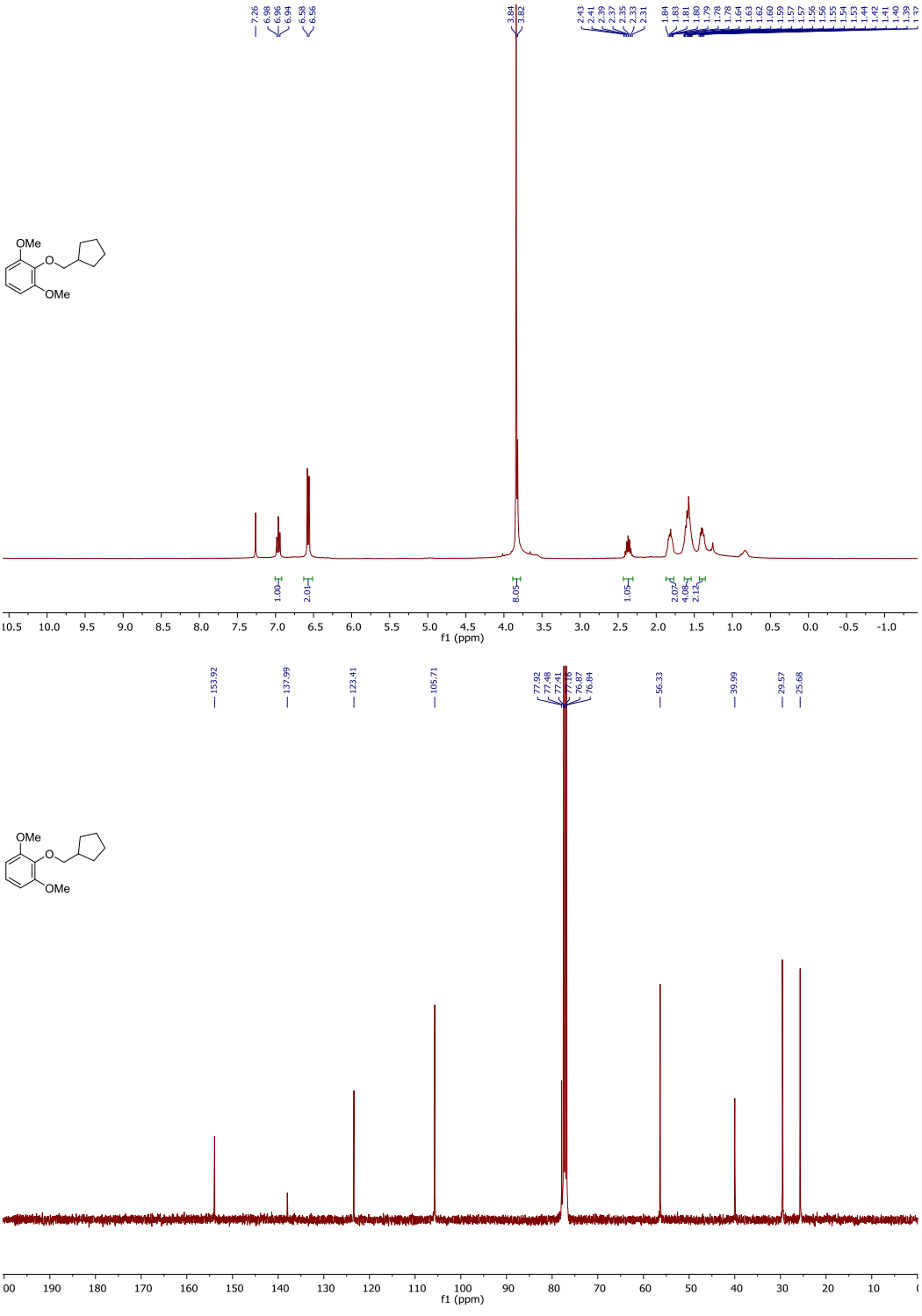


Figure S44. NMR spectra of 7a

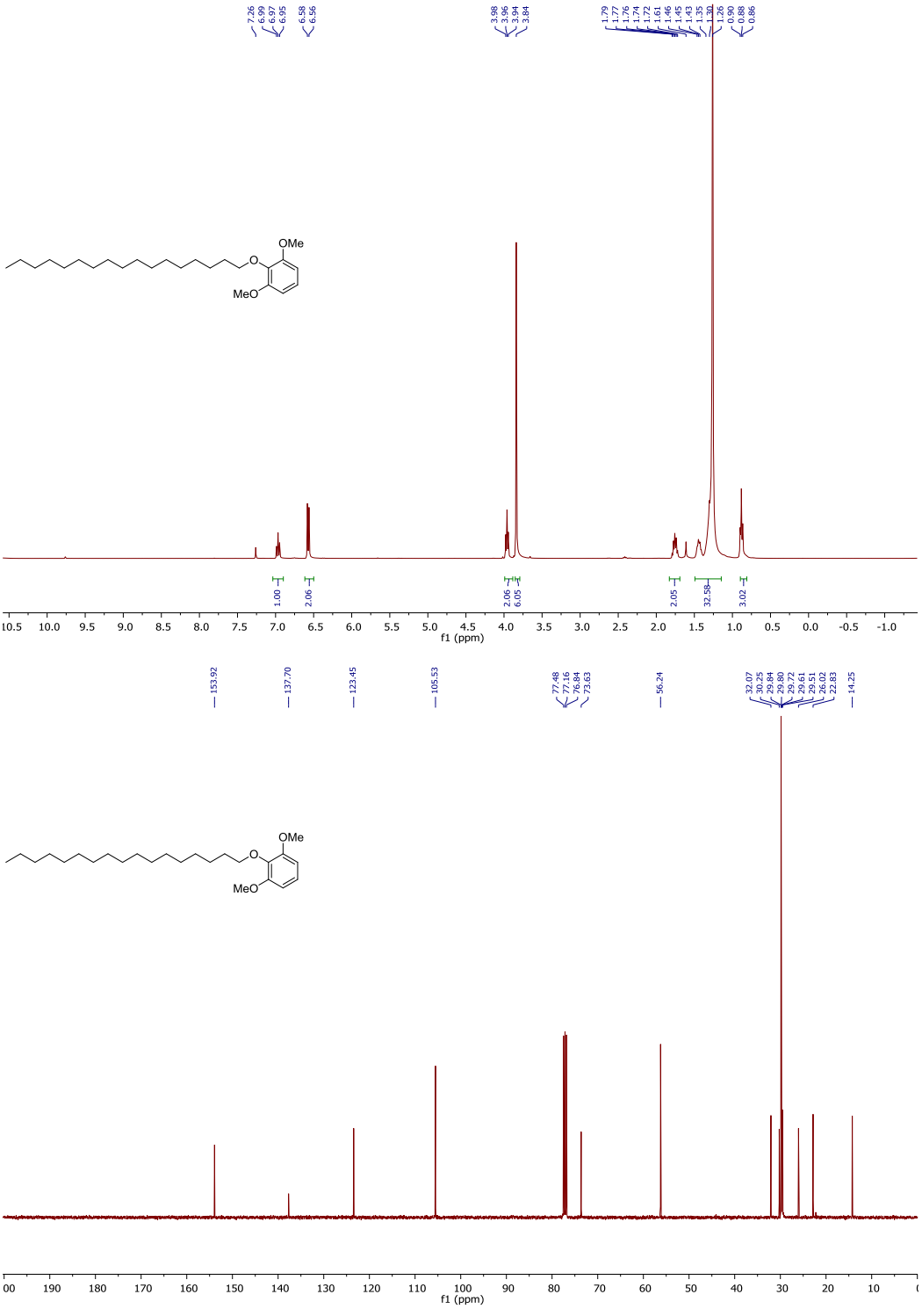


Figure S45. NMR spectra of 7b

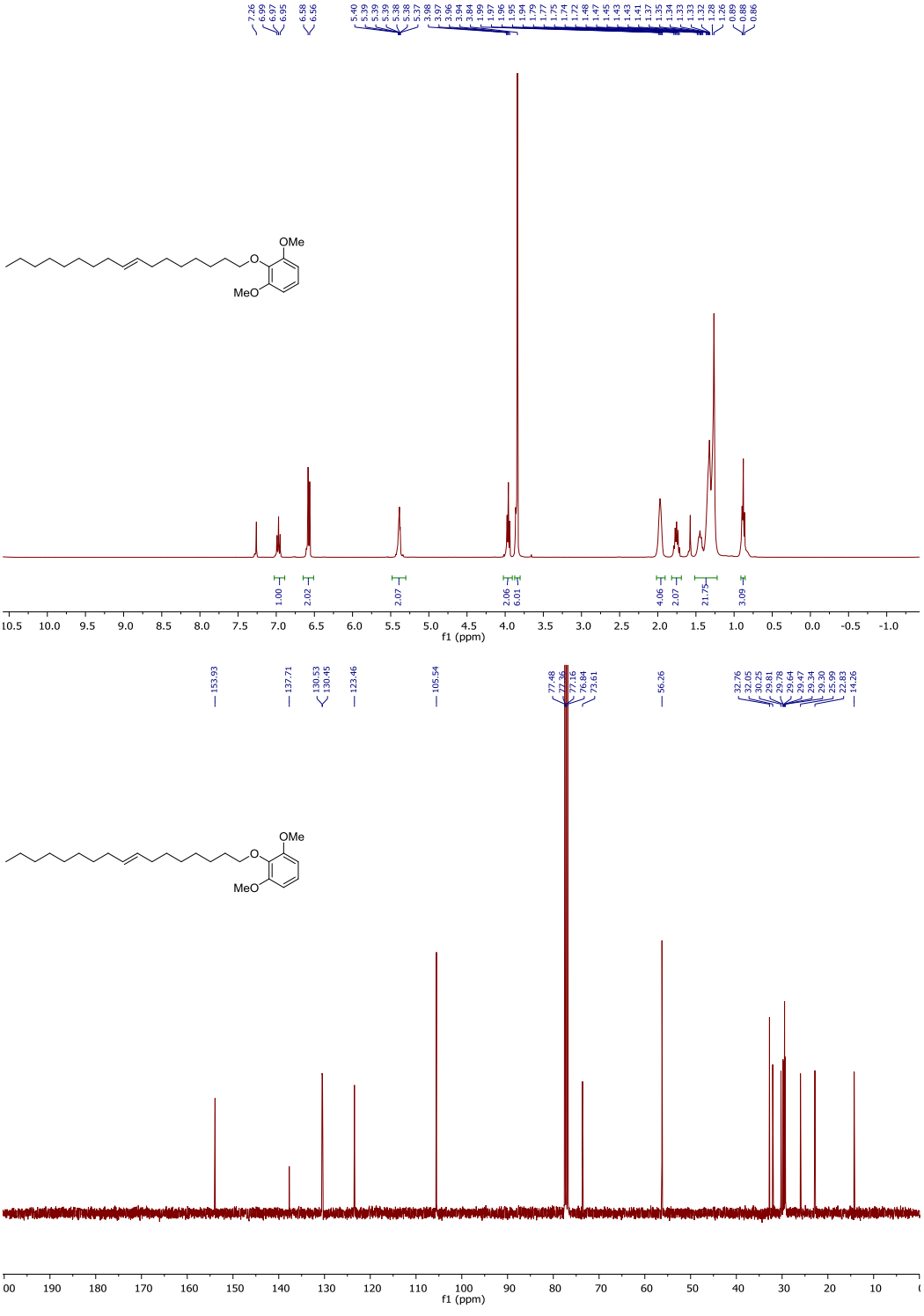


Figure S46. NMR spectra of 7c

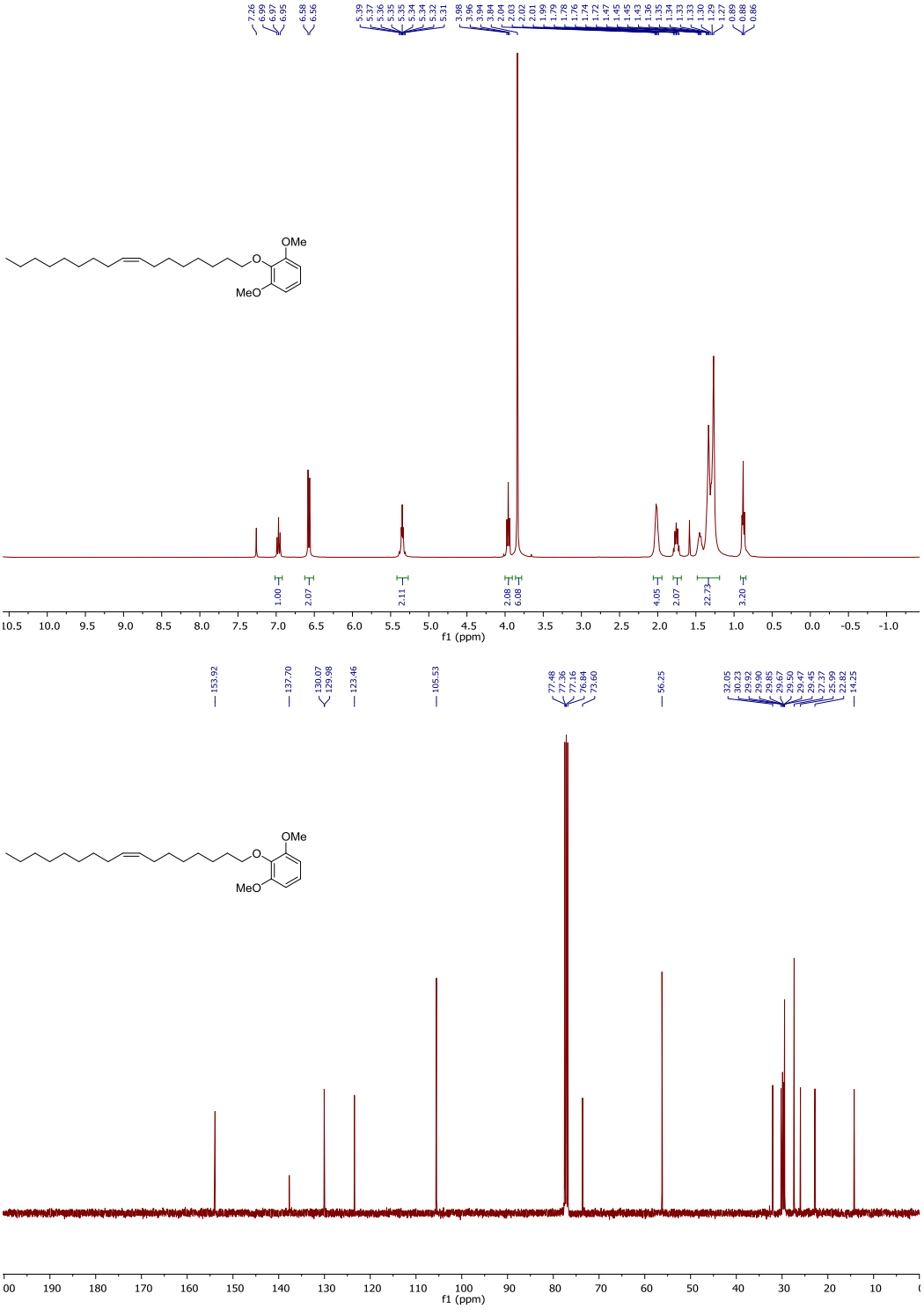


Figure S47. NMR spectra of 7d

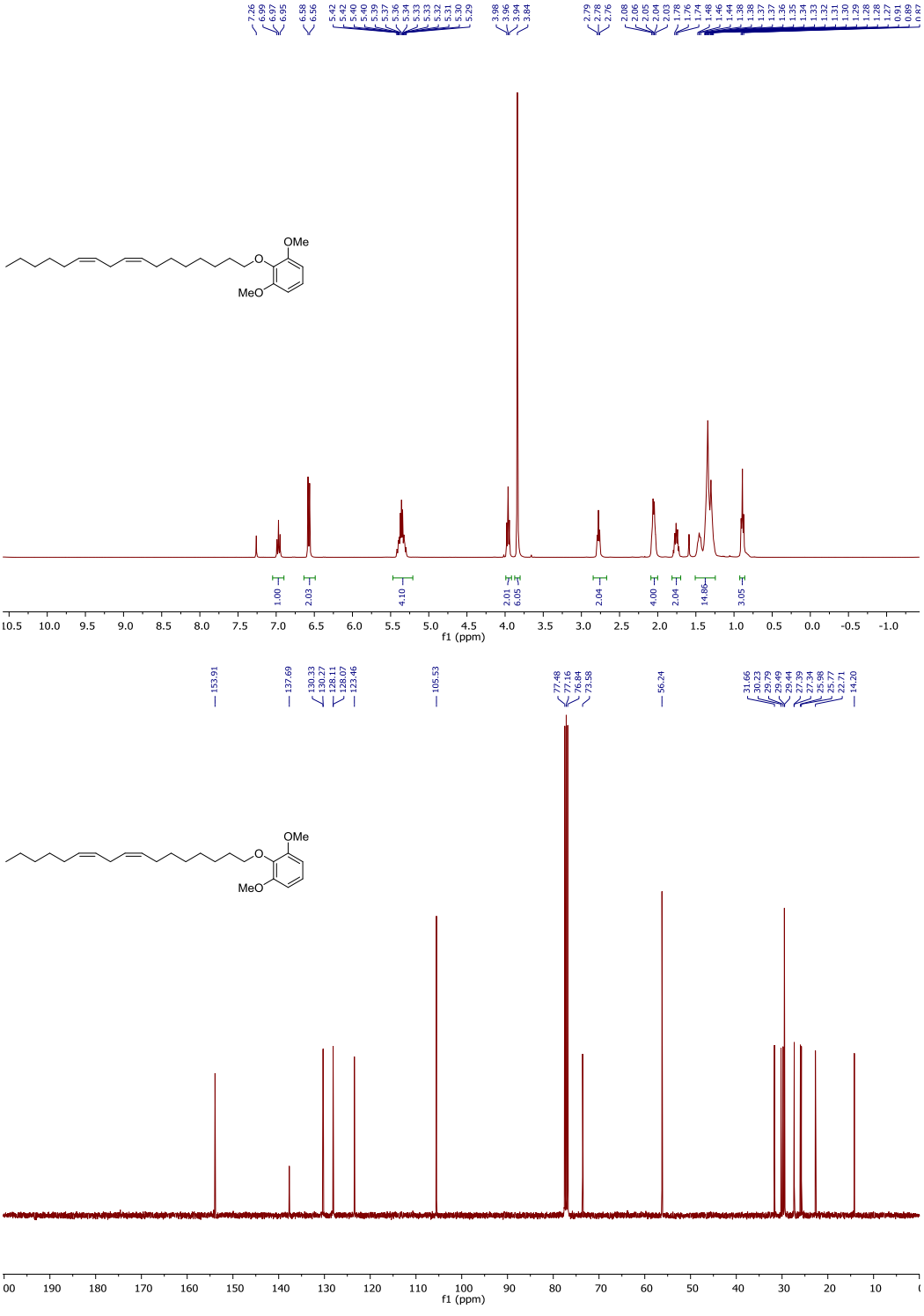


Figure S48. NMR spectra of 7e

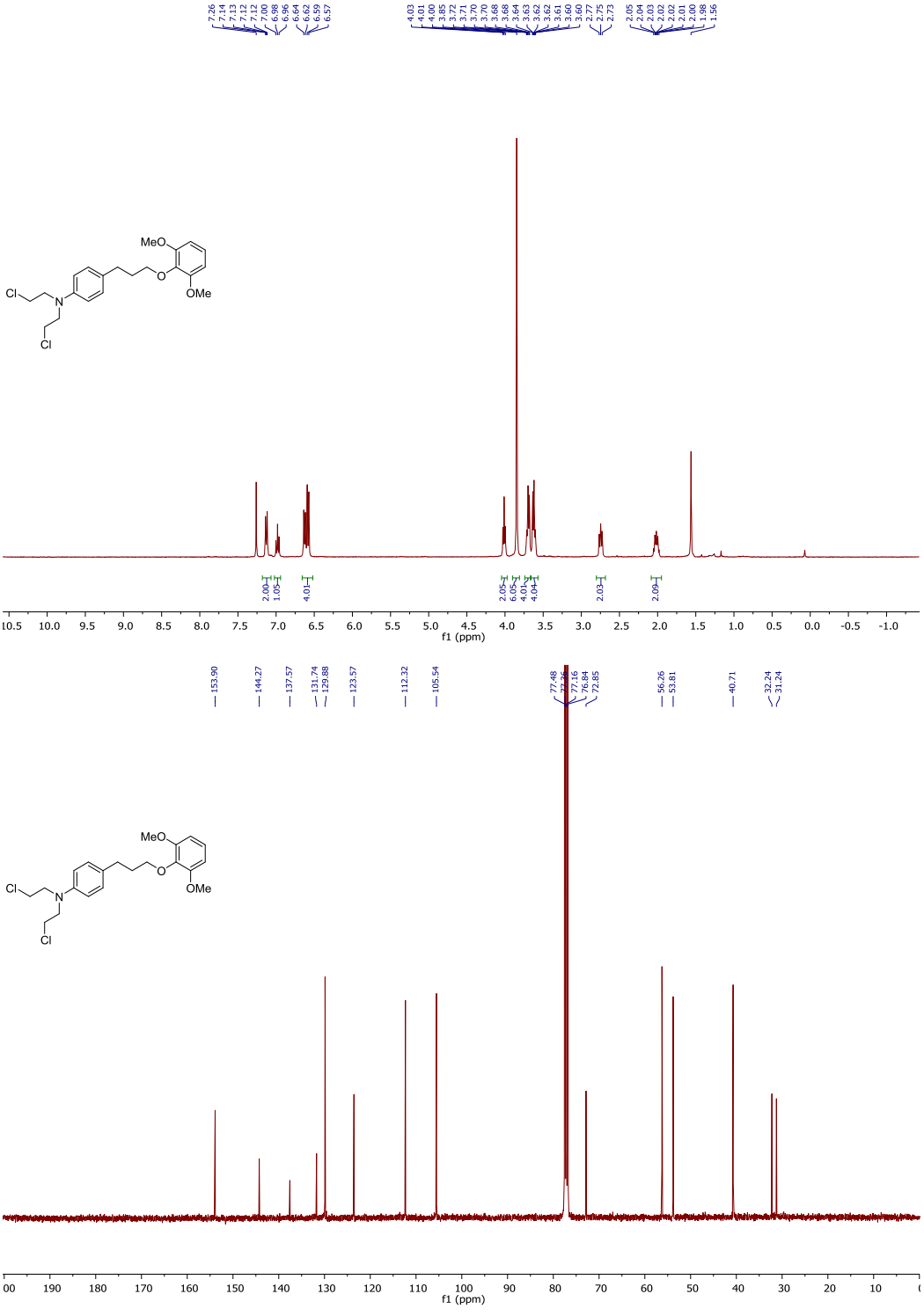


Figure S49. NMR spectra of 7f

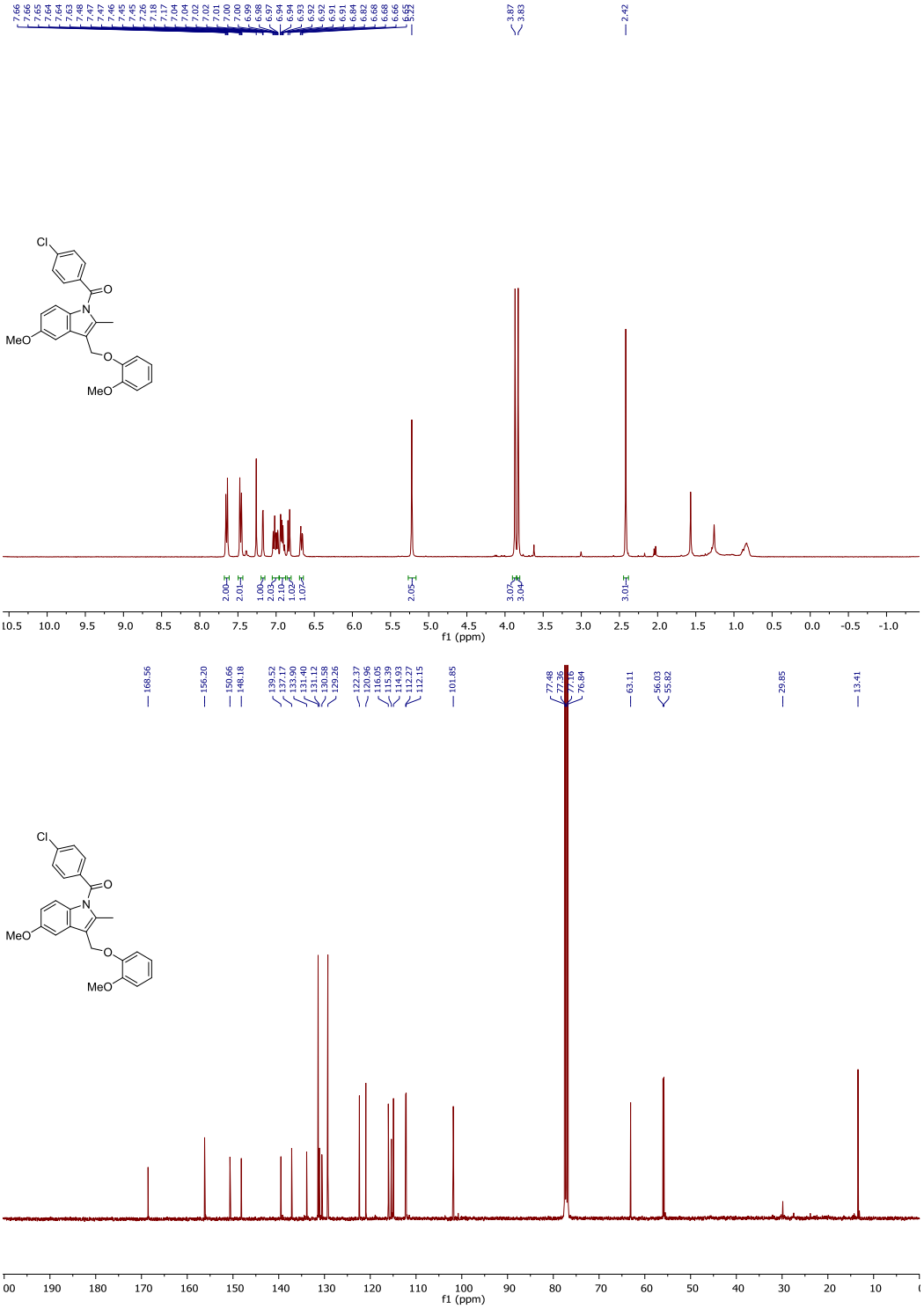


Figure S50. NMR spectra of 7g

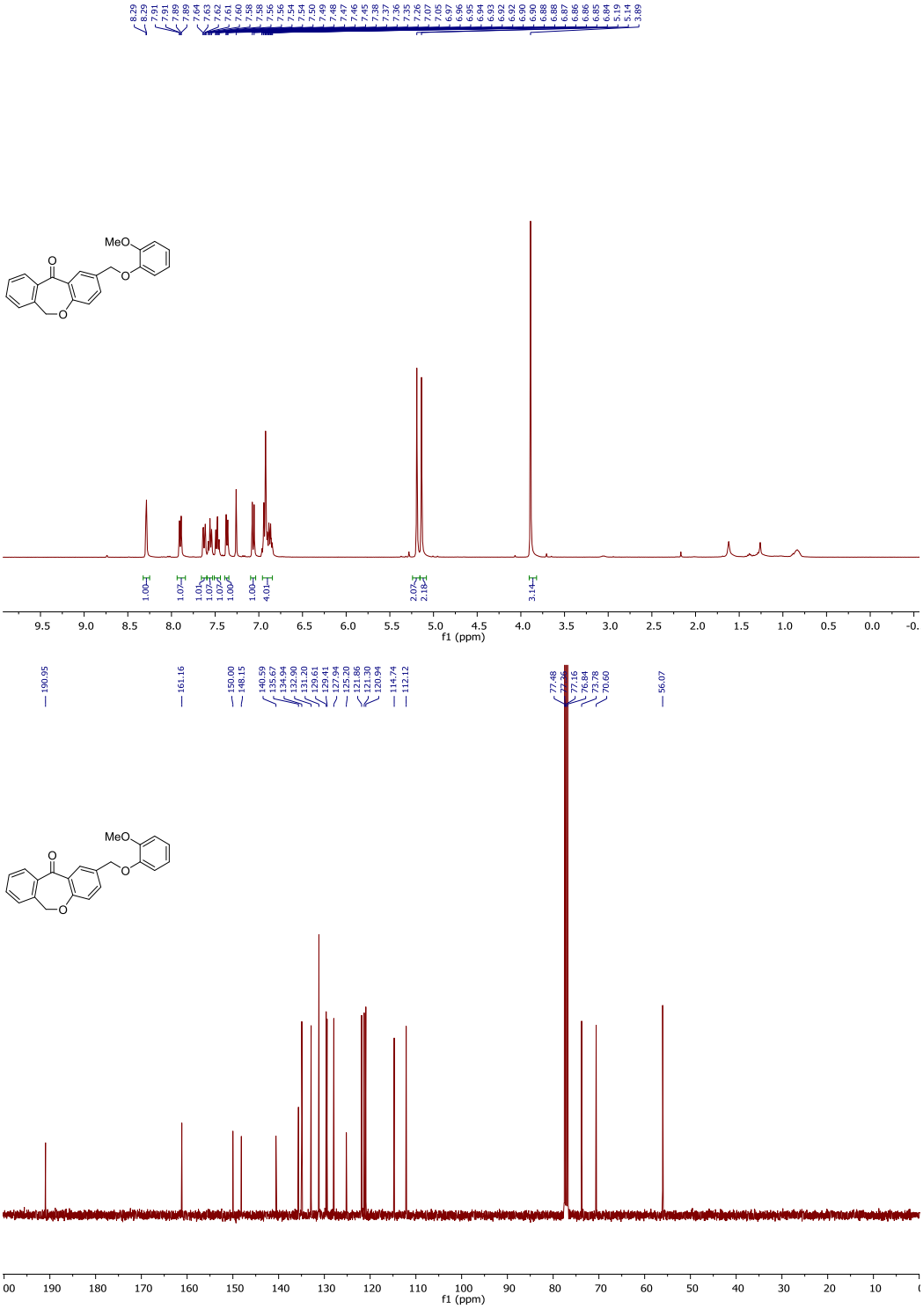


Figure S51. NMR spectra of 7h

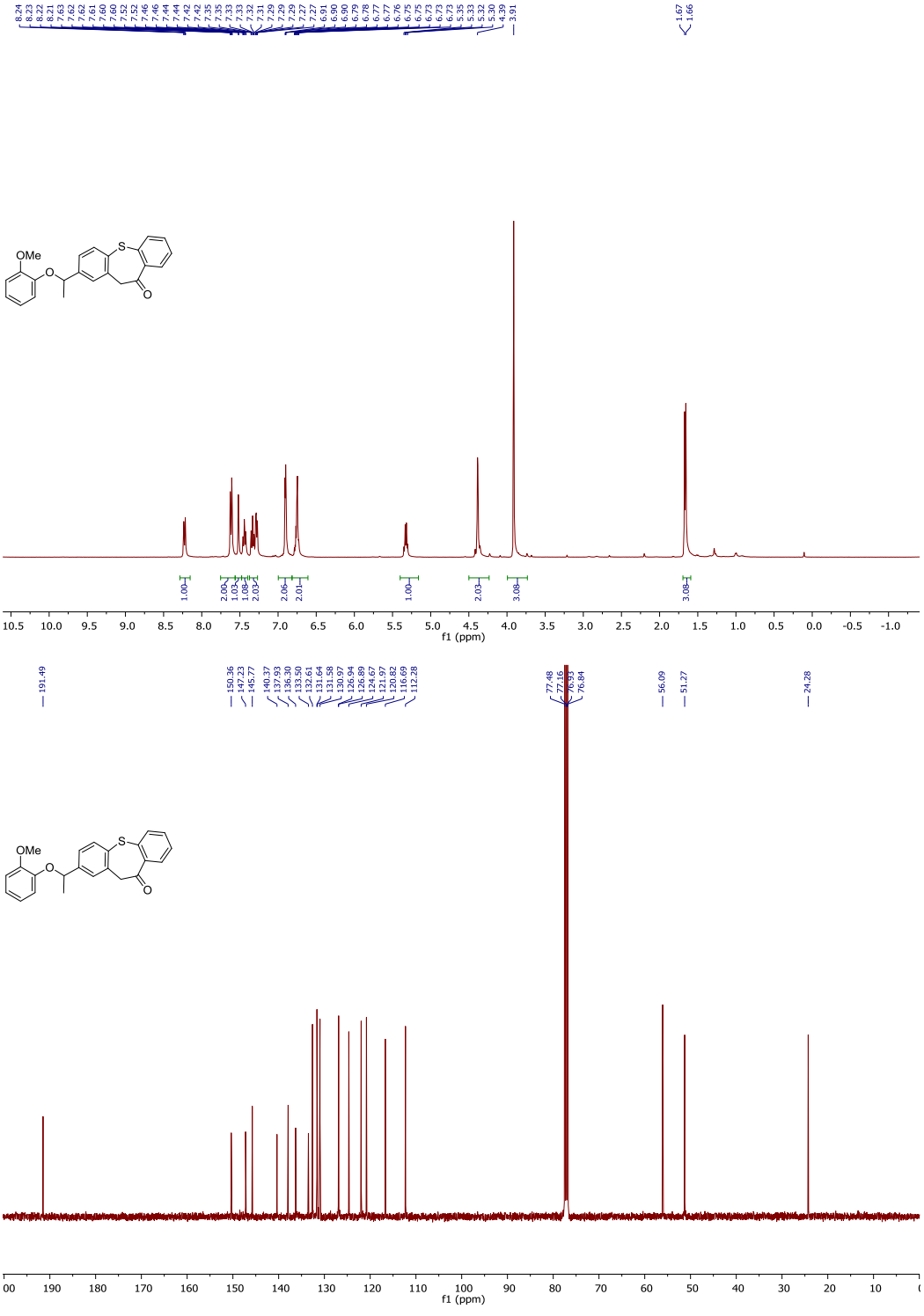


Figure S52. NMR spectra of 7i

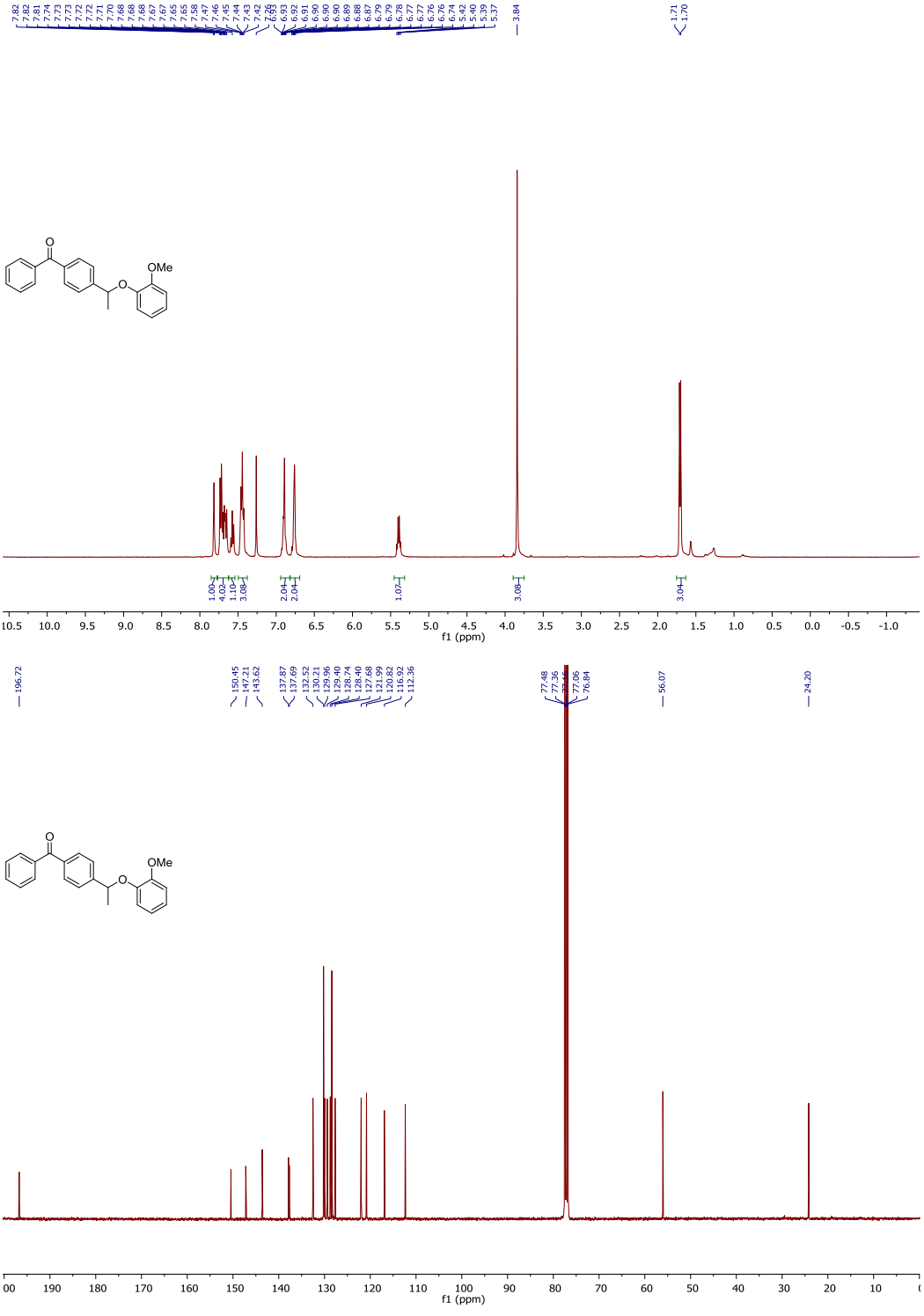


Figure S53. NMR spectra of 7j

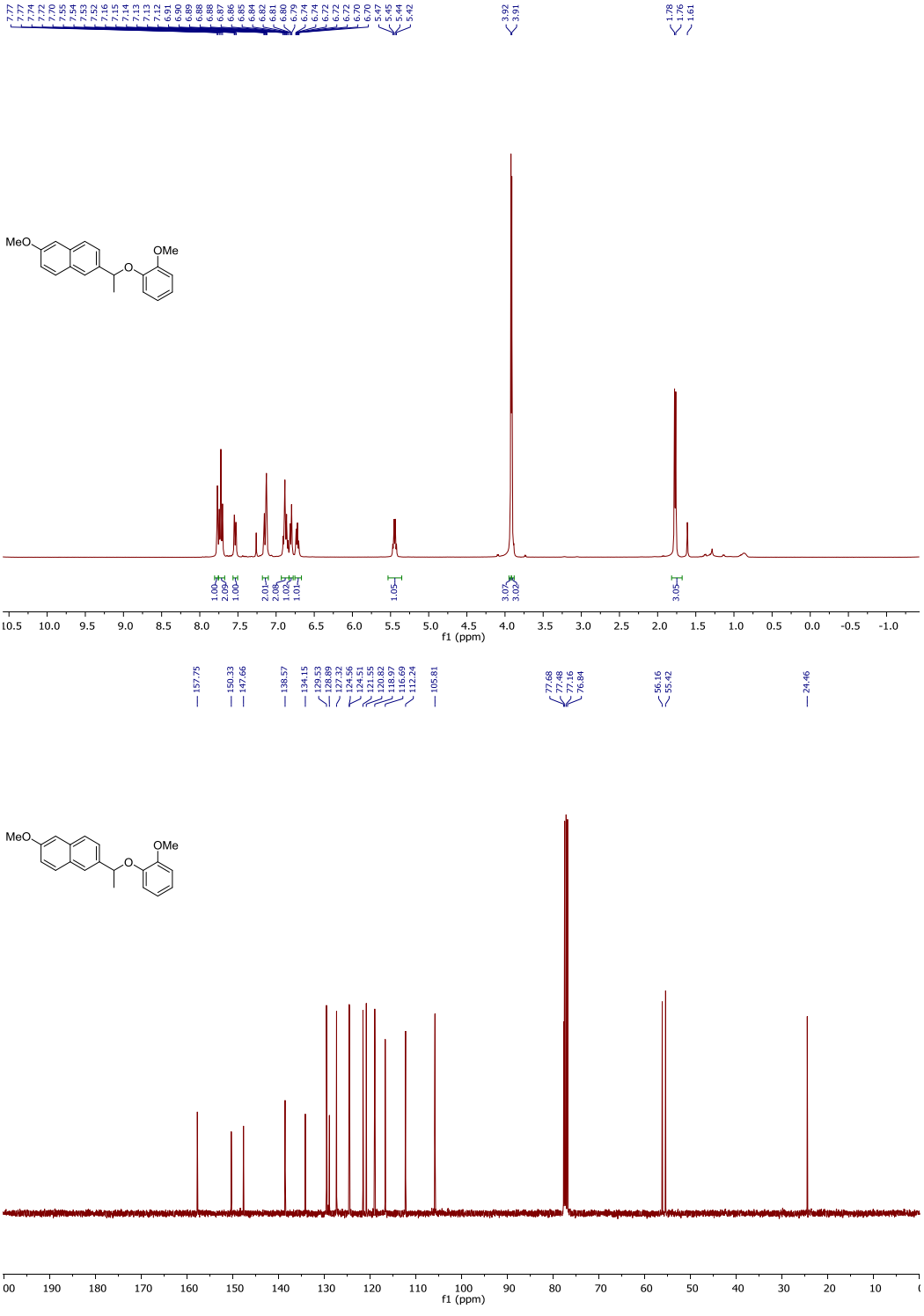


Figure S54. NMR spectra of 7k

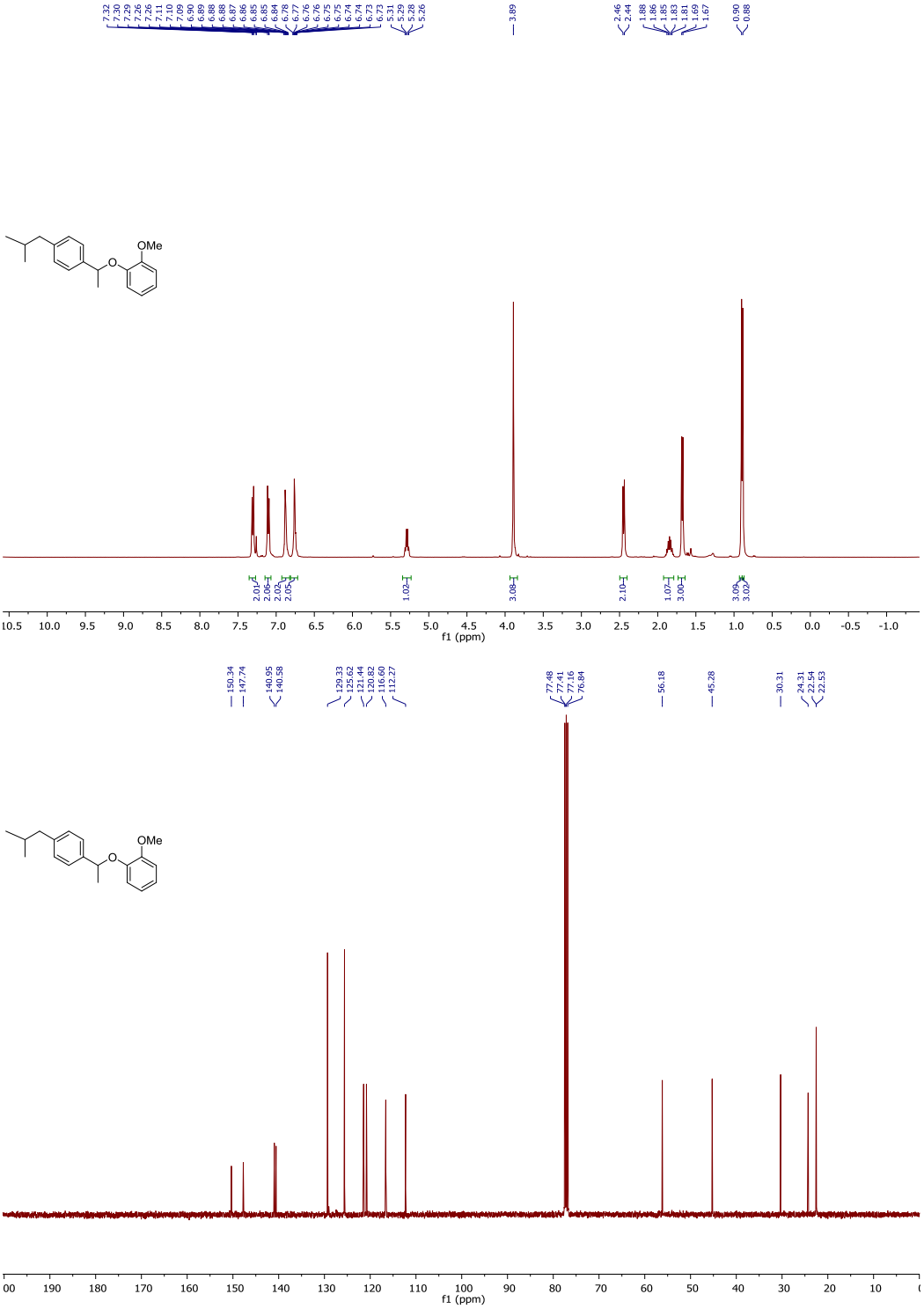


Figure S55. NMR spectra of 7l

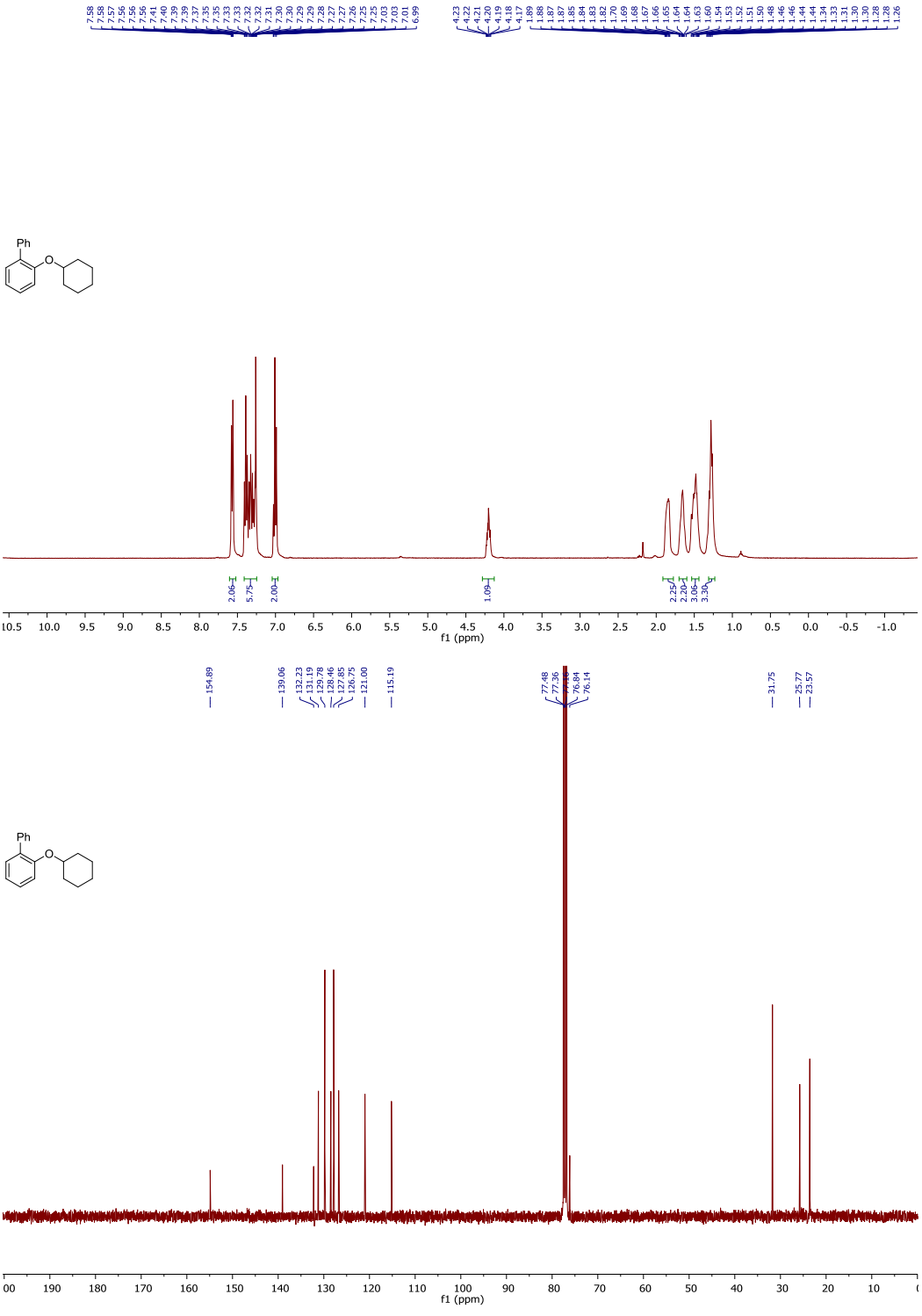


Figure S56. NMR spectra of 7m

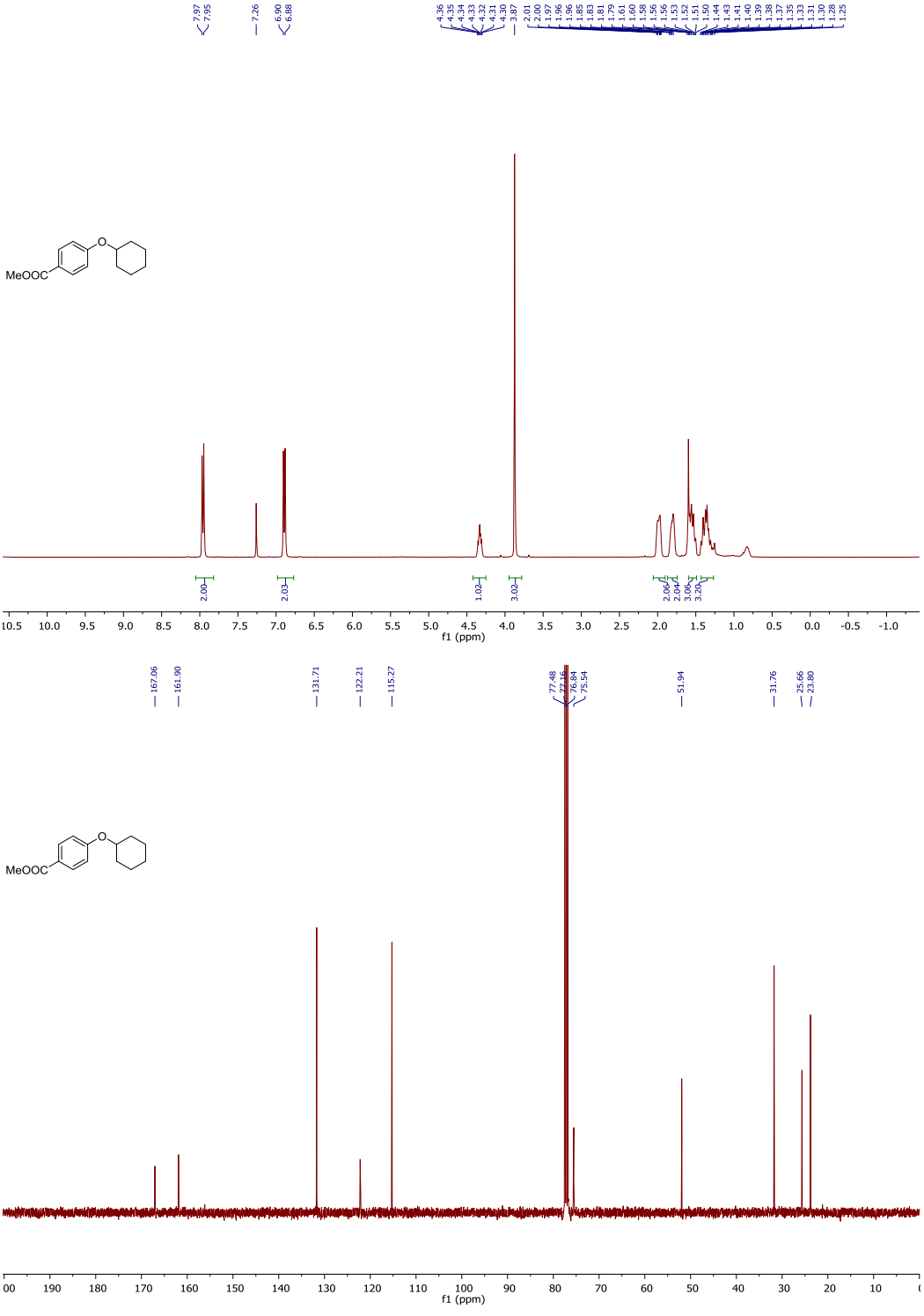
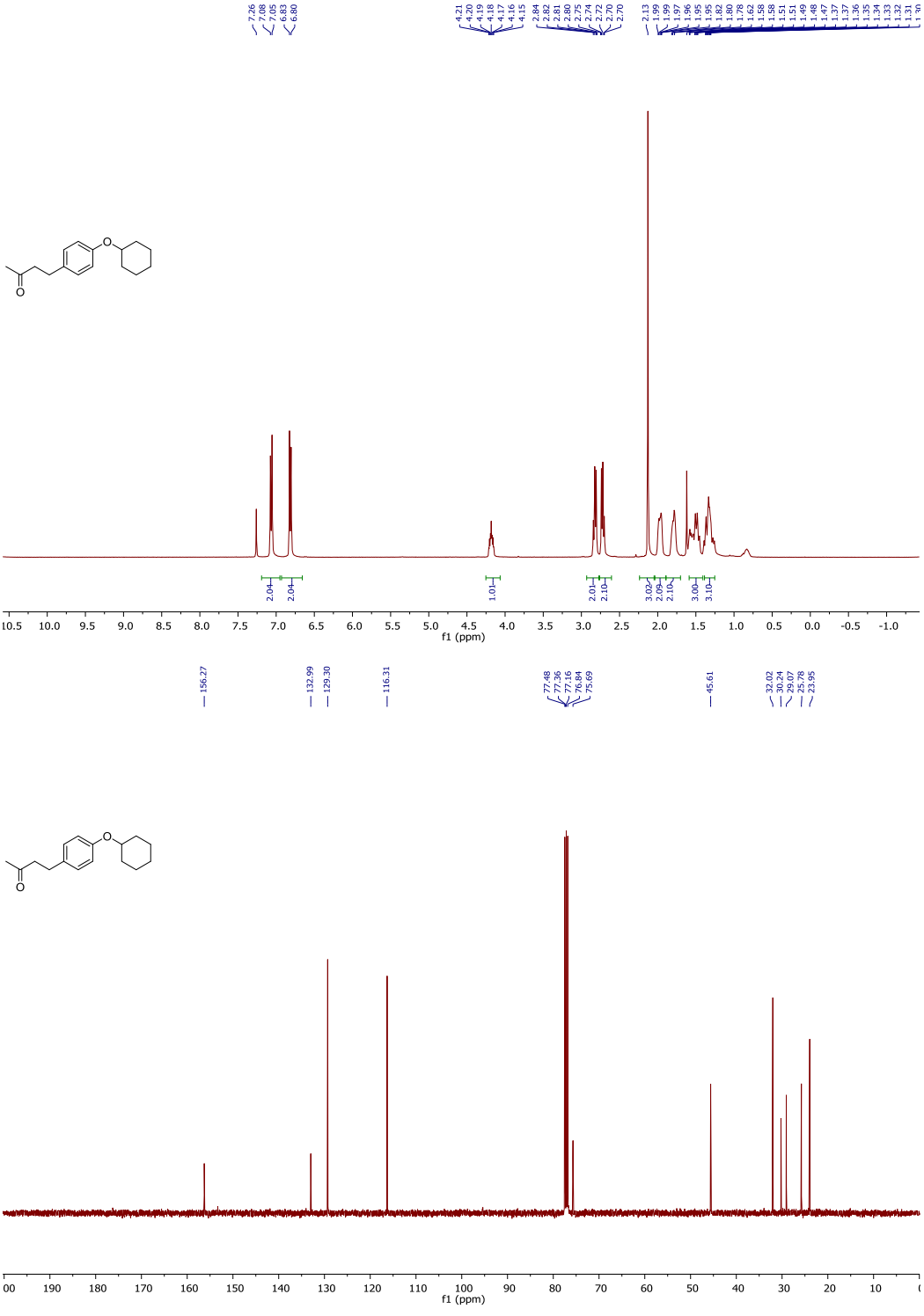


Figure S57. NMR spectra of 7n



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