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Methods

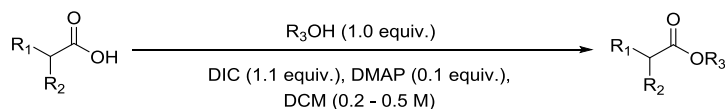
General Analytical Information

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

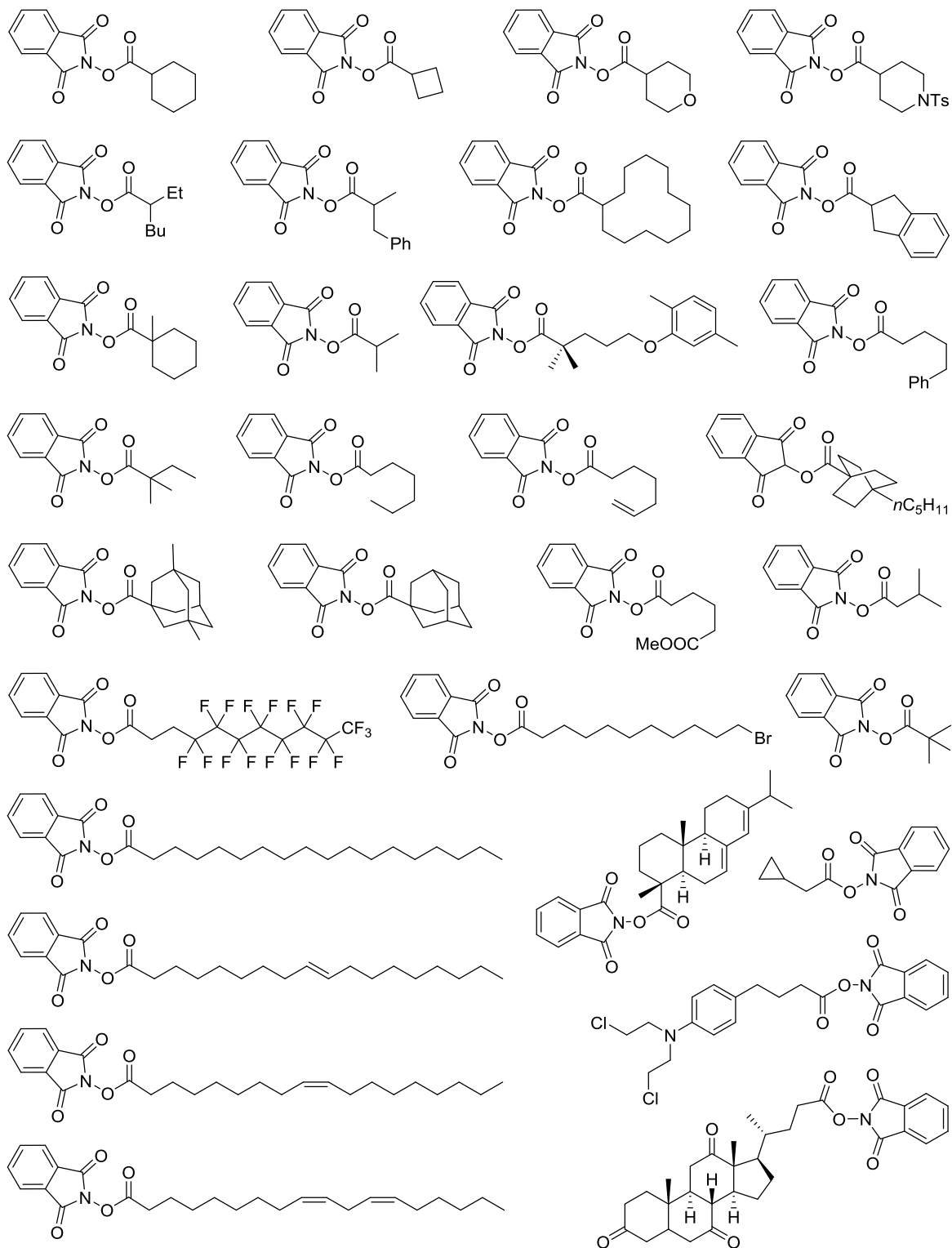
All manipulations for the decarboxylative $\text{C}(\text{sp}^3)\text{-N}$ cross coupling via synergetic photoredox and copper catalyzed reactions were set up in a 15 mL Teflon-screw capped test tubes (unless otherwise noted) under an inert nitrogen (N_2) atmosphere using glove-box techniques. The test 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). Notably, the silica gel used for the purification of amine products were pre-neutralized with 5% triethylamine in hexanes solution prior to the usage, in order to minimize the product loss. The eluents for column chromatography were presented as ratios of solvent volumes. Yields reported in the publication are of isolated materials unless otherwise noted.

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.

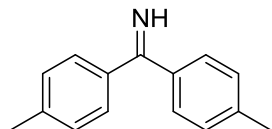
The preparation and spectral data of the following NHPI esters have been reported.^[2]



Preparation of benzophenone imine derivatives

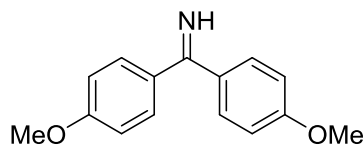
Note: The imines prepared below are sensitive to hydrolysis and contain small amounts of the corresponding ketones as impurities. To prevent further hydrolysis, these compounds were stored in a nitrogen-filled glovebox. Benzophenone imine **2a** is commercially available from Tokyo Chemical Industry (TCI) Co., Ltd, catalogue number: B1912.

4,4'-Dimethylbenzophenone imine (**2b**)



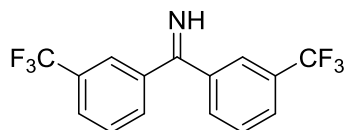
Dry magnesium turnings (365 mg, 15.0 mmol, 1.50 equiv), dry THF (20 ml), and a magnetic stir bar were placed in a nitrogen-filled flask, and the flask was connected to a reflux condenser. 4-bromotoluene (1.84 ml, 2.57 g, 15.0 mmol, 1.50 equiv) was dissolved in THF (3 ml), and a small amount of this solution was transferred to the reaction flask. The reaction was initiated with a single iodine crystal. The remaining aryl bromide solution was slowly transferred to the reaction flask. The syringe was rinsed with THF (3 ml), and the mixture was stirred at ambient temperature for 2.5 h at which time the majority of the magnesium was visibly consumed. The reaction mixture was then cooled to 0 °C. A solution of *p*-tolunitrile (1.20 ml, 1.17 g, 9.99 mmol) in THF (7 ml) was added to the flask, and the syringe rinsed with THF (3 ml). The reaction mixture was heated at reflux for 20 h, then cooled to 0 °C, and then quenched with dry methanol (3 ml). The reaction mixture was diluted with hexanes (30 ml), filtered through a pad of Celite, and concentrated at reduced pressure. The yellow oil was purified by column chromatography (5 % ethyl acetate gradient and 5% triethylamine in hexanes on pre-neutralized silica) to give the title compound as a pale yellow oil (1.54 g, 74% yield). The ¹H NMR spectrum was consistent with the spectrum reported in the literature.^[3]

4,4'-Dimethoxybenzophenone imine(**2c**)



Methoxyphenylmagnesium bromide (16 ml, 1.0M, 16 mmol, 1.1 equiv) in THF was transferred to a 100 ml nitrogen-filled flask fitted with a reflux condenser, and the solution was cooled to 0 °C. A solution of 4-methoxybenzonitrile (2.00 g, 15.0 mmol) in dry THF (9 ml) was added to the flask, and the syringe rinsed with THF (3 ml). The reaction mixture was heated at reflux for 17 h, then cooled to 0 °C, and then quenched with dry methanol (3 ml). The reaction mixture was diluted with hexanes (20 ml), filtered through a pad of Celite, and concentrated at reduced pressure. The yellow solid was purified by column chromatography (0 to 50% ethyl acetate gradient and 5% triethylamine in hexanes on prebasified silica) to give the title compound as an off-white powder (2.19 g, 61% yield). The ¹H NMR spectrum was consistent with the spectrum reported in the literature.^[3]

Bis(3-(trifluoromethyl)phenyl)methanimine (2d)



Dry magnesium turnings (370 mg, 15.2 mmol, 1.49 equiv), dry THF (10 ml), and a magnetic stir bar were placed in a nitrogen-filled flask, and the flask was connected to a reflux condenser. 3-Bromobenzotrifluoride (2.10 ml, 3.38 g, 15.0 mmol, 1.47 equiv) was dissolved in THF (3 ml), and a small amount of this solution was transferred to the reaction flask. The reaction was initiated with a single iodine crystal. The remaining aryl bromide solution was slowly transferred to the reaction flask. The syringe was rinsed with THF (3 ml) and the mixture was heated at reflux until the majority of the magnesium was visibly consumed. The reaction mixture was then cooled to 0 °C. A solution of 3-trifluoromethylbenzonitrile (1.37 ml, 1.75 g, 10.2 mmol) in THF (2 ml) was added to the flask, and the syringe rinsed twice with THF (2 ml). The reaction mixture was heated at reflux for 4 h, then cooled to 0 °C, and then quenched with dry methanol (2 ml). The reaction mixture was diluted with hexanes (50 ml), neutralized with sodium bicarbonate, filtered through a pad of Celite, and concentrated at reduced pressure. The red oil was purified by short path distillation (vapor temperature 110-130 °C at approximately 0.20 Torr) as a colorless oil (2.39 g, 75% yield).

¹H NMR (400 MHz, Chloroform-*d*): δ 7.86 (s, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 175.7, 139.5, 131.7, 131.4 (q, $J = 32.3$ Hz), 129.4, 127.5 (q, $J = 4.0$ Hz), 125.2, 123.8 (q, $J = 273.7$ Hz).

^{19}F NMR (376 MHz, Chloroform-*d*): δ -62.8.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{10}\text{F}_6\text{N}^+$ 318.0712; Found 318.0715.

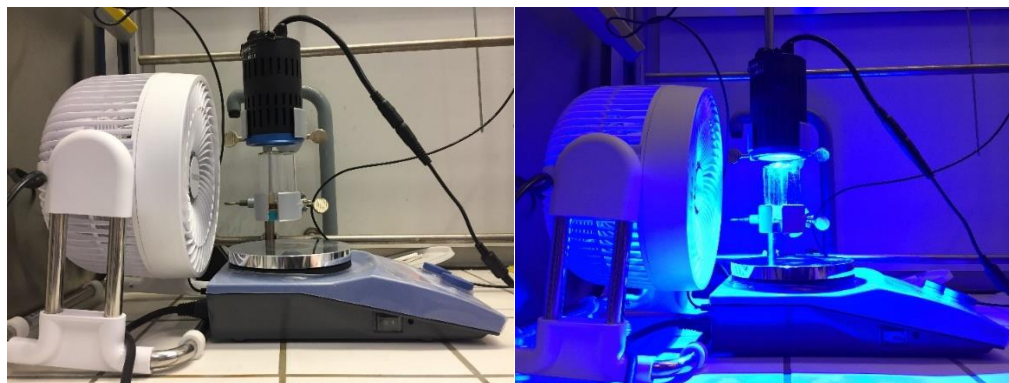
The spectral data was consistent with the data reported in the literature.^[3]

General procedure for visible-light-mediated decarboxylative amination of benzophenone imines with secondary and tertiary NHPI esters (General Procedure B)

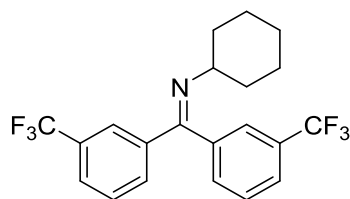
An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with secondary or tertiary NHPI ester (1 equiv.), **2a** or **2d** (2 equiv), [Ir(dtbbpy)(ppy)₂](PF₆) (1 mol%), Cu(MeCN)₄PF₆ (20 mol%), dimethylacetamide (DMA, 0.1 M), Cs₂CO₃ (2 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 the reaction, the resulting reaction mixture was directly purified by column chromatography (notably, the silica gel used for the purification were pre-neutralized with 5% triethylamine in hexanes solution prior to the usage, in order to minimize the product loss).

General procedure for visible-light-mediated decarboxylative amination of benzophenone imines 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 primary NHPI ester (2 equiv.), **2a** or **2d** (1 equiv), [Ir(dtbbpy)(ppy)₂](PF₆) (1 mol%), Cu(MeCN)₄PF₆ (20 mol%), MeCN (0.1 M), diisopropylamine (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 16 h. After the reaction, the resulting reaction mixture was directly purified by column chromatography (notably, the silica gel used for the purification were pre-neutralized with 5% triethylamine in hexanes solution prior to the usage, in order to minimize the product loss).



***N*-cyclohexyl-3,3'-bis(trifluoromethyl)benzophenone imine (3a)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 56 mg (70%) of the title compound **3a**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.58 (m, 3H), 7.47 – 7.40 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 3.14 (tt, *J* = 9.4, 4.5 Hz, 1H), 1.83 – 1.72 (m, 2H), 1.69 – 1.54 (m, 5H), 1.27 – 1.12 (m, 3H).

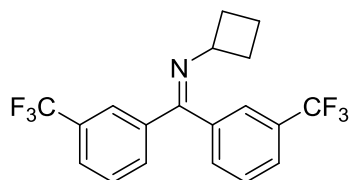
¹³C NMR (101 MHz, Chloroform-*d*): δ 162.5, 140.5, 137.3, 131.8, 131.2, 129.5, 128.8, 131.4 (q, *J* = 32.6 Hz), 130.9 (q, *J* = 32.4 Hz), 126.6 (q, *J* = 3.7 Hz), 125.6 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.3 Hz), 124.0 (q, *J* = 272.5 Hz), 62.0, 34.0, 25.7, 24.3.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.63, -62.74.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₀F₆N⁺ 400.1494; Found 400.1495.

***N*-cyclobutyl-3,3'-bis(trifluoromethyl)benzophenone imine (3b)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 42 mg (56%) of the title compound **3b**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.98 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.57 (m, 3H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.39 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 3.93 (p, *J* = 7.7 Hz, 1H), 2.38 – 2.21 (m, 2H), 2.15 – 2.03 (m, 2H), 1.96 – 1.82 (m, 1H), 1.79 – 1.64 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 163.47, 140.13, 137.47, 131.85, 131.32 (q, *J* = 32.7 Hz), 131.28, 130.97 (q, *J* = 32.5 Hz), 129.37, 128.84, 126.82 (q, *J* = 3.8 Hz), 125.82 (q, *J* = 3.7 Hz),

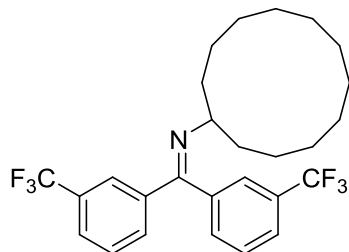
124.92 (q, $J = 3.8$ Hz), 124.71 (q, $J = 3.8$ Hz), 124.12 (q, $J = 272.5$ Hz), 123.93 (q, $J = 272.6$ Hz), 57.52, 31.43, 16.23.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.66, -62.77.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{16}\text{F}_6\text{N}^+$ 372.1181; Found 372.1176.

***N*-cyclododecyl-3,3'-bis(trifluoromethyl)benzophenone imine (3c)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 58 mg (60%) of the title compound **3c**.

^1H NMR (400 MHz, Chloroform- d): δ 7.96 (s, 1H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.70 – 7.58 (m, 3H), 7.49 – 7.39 (m, 2H), 7.35 (d, $J = 7.6$ Hz, 1H), 3.53 – 3.25 (m, 1H), 1.88 – 1.73 (m, 2H), 1.41 – 1.08 (m, 17H), 0.90 – 0.75 (m, 3H).

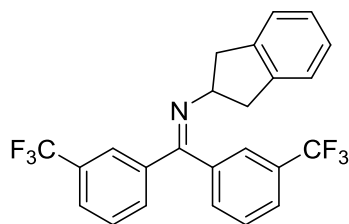
^{13}C NMR (101 MHz, Chloroform- d): δ 163.44, 140.28, 137.87, 131.78, 131.41 (q, $J = 32.6$ Hz), 131.30, 130.91 (q, $J = 32.4$ Hz), 129.48, 128.82, 126.68 (q, $J = 3.6$ Hz), 125.56 (q, $J = 3.5$ Hz), 124.85 (q, $J = 3.9$ Hz), 124.75 (q, $J = 3.9$ Hz), 124.14 (q, $J = 272.6$ Hz), 123.94 (q, $J = 272.6$ Hz), 58.13, 31.83, 23.99, 23.73, 23.21, 22.34, 22.04.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.59, -62.83.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{32}\text{F}_6\text{N}^+$ 484.2433; Found 484.2428.

***N*-(2,3-dihydro-1*H*-inden-2-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (3d)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 63 mg (73%) of the title compound **3d**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.98 (d, J = 2.1 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 7.8, 5.4 Hz, 3H), 7.50 – 7.39 (m, 3H), 7.23 – 7.13 (m, 4H), 4.19 (q, J = 7.3 Hz, 1H), 3.21 (dd, J = 15.5, 7.0 Hz, 2H), 3.02 (dd, J = 15.5, 7.6 Hz, 2H).

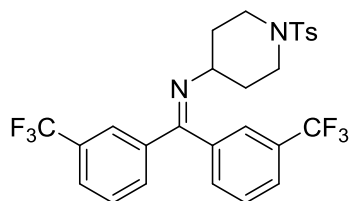
¹³C NMR (101 MHz, Chloroform-*d*): δ 164.43, 141.93, 139.95, 137.25, 131.94, 131.57 (q, J = 32.8 Hz), 131.20, 130.98 (q, J = 32.5 Hz), 129.61, 128.88, 126.95 (q, J = 4.0 Hz), 126.67, 125.89 (q, J = 3.7 Hz), 125.01 (q, J = 4.0 Hz), 124.58, 124.10 (q, J = 272.5 Hz), 123.90 (q, J = 272.5 Hz), 63.65, 41.33.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.64, -62.72.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z : $[M + H]^+$ Calcd for C₂₄H₁₈F₆N⁺ 434.1338; Found 434.1333.

***N*-(1-tosylpiperidin-4-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (**3e**)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using 0 to 30% ethyl acetate gradient in hexanes as an eluent to afford 68 mg (61%) of the title compound **3e**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.87 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.68 – 7.57 (m, 4H), 7.49 (d, J = 7.9 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.36 – 7.26 (m, 4H), 3.57 (dt, J = 10.6, 4.7 Hz, 2H), 3.21 (s, 1H), 2.64 (ddd, J = 12.1, 9.3, 3.2 Hz, 2H), 2.43 (s, 3H).

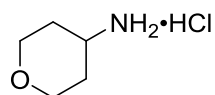
¹³C NMR (101 MHz, Chloroform-*d*): δ 163.73, 143.54, 139.57, 136.56, 133.21, 131.75, 131.52 (q, J = 32.9 Hz), 130.87 (q, J = 29.8 Hz), 130.73, 129.62, 129.59, 128.76, 127.71, 126.94 (q, J = 3.3 Hz), 125.83 (q, J = 3.6 Hz), 124.59 (q, J = 3.5 Hz), 124.03 (q, J = 3.8 Hz), 123.85 (q, J = 272.5 Hz), 123.65 (q, J = 272.5 Hz), 57.23, 43.66, 32.18, 21.50.

¹⁹F NMR (376 MHz, Chloroform-*d*): -62.75, -62.80.

Physical State: white solid.

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}F_6N_2O_2S^+$ 555.1535; Found 555.1546.

(Tetrahydro-2H-pyran-4-yl)amine hydrochloride (3f)



The corresponding NHPI ester (0.5 mmol) and **2d** (1.0 mmol) was directly transformed to the amine hydrochloride following the General Procedure B and D, the title compound **3f** was obtained in 50% (34 mg) overall yield.

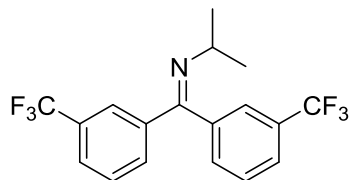
¹H NMR (400 MHz, Methanol-*d*₄): δ 4.92 (s, 3H), 4.03 (dd, $J = 12.0, 4.7$ Hz, 2H), 3.52 – 3.34 (m, 3H), 2.11 – 1.82 (m, 2H), 1.68 (qd, $J = 12.2, 4.7$ Hz, 2H).

¹³C NMR (101 MHz, Methanol-*d*₄): δ 67.74, 49.60, 32.79.

Physical State: white solid.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.^[4]

***N*-isopropyl-3,3'-bis(trifluoromethyl)benzophenone imine (3g)**



Following the General Procedure B with the corresponding NHPI ester (0.3 mmol) and **2d** (0.6 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 48 mg (45%) of the title compound **3g**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.96 (s, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.68 – 7.57 (m, 3H), 7.47 – 7.39 (m, 2H), 7.36 (d, $J = 7.6$ Hz, 1H), 3.47 (p, $J = 6.2$ Hz, 1H), 1.19 (s, 3H), 1.17 (s, 3H).

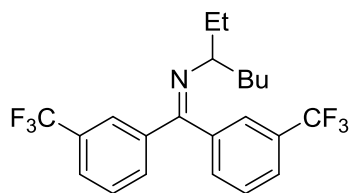
¹³C NMR (101 MHz, Chloroform-*d*): δ 162.37, 140.36, 137.32, 131.81, 131.46 (q, $J = 32.7$ Hz), 131.10, 130.93 (q, $J = 33.6$ Hz), 129.50, 128.81, 126.71 (q, $J = 3.9$ Hz), 125.66 (q, $J = 3.8$ Hz), 124.87 (q, $J = 4.0$ Hz), 124.41 (q, $J = 3.8$ Hz), 124.14 (q, $J = 272.4$ Hz), 123.94 (q, $J = 272.4$ Hz), 53.62, 23.96.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.63, -62.75.

Physical State: yellow oil.

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}F_6N^+$ 360.1181; Found 360.1176.

***N*-(heptan-3-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (3h)**



Following the General Procedure B with the corresponding NHPI ester (0.3 mmol) and **2d** (0.6 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 62 mg (50%) of the title compound **3h**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.70 – 7.57 (m, 3H), 7.48 – 7.39 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 3.09 (dt, *J* = 11.8, 5.8 Hz, 1H), 1.67 – 1.52 (m, 4H), 1.26 – 1.09 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H).

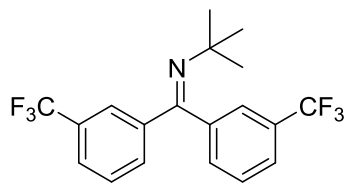
¹³C NMR (101 MHz, Chloroform-*d*): δ 163.19, 140.44, 137.70, 131.77, 131.50, 131.27 (q, *J* = 32.7 Hz), 130.92 (q, *J* = 32.4 Hz), 129.30, 128.83, 126.65 (q, *J* = 3.7 Hz), 125.45 (q, *J* = 3.7 Hz), 124.99 (q, *J* = 3.8 Hz), 124.87 (q, *J* = 3.9 Hz), 124.10 (q, *J* = 260.2 Hz), 123.97 (q, *J* = 272.5 Hz), 77.48, 77.16, 76.84, 64.13, 36.09, 29.51, 28.98, 22.95, 14.15, 11.20.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.61, -62.83.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₄F₆N⁺ 416.1807; Found 416.1814.

***N*-tert-butyl-3,3'-bis(trifluoromethyl)benzophenone imine (4a)**



Following the General Procedure B with the corresponding NHPI ester (0.3 mmol) and **2d** (0.6 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 50 mg (45%) of the title compound **4a**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.94 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 1.17 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 160.23, 142.01, 139.97, 131.80, 131.51, 130.90 (q, *J* = 32.7 Hz), 130.76 (q, *J* = 32.3 Hz), 128.85, 128.65, 126.38 (q, *J* = 3.7 Hz), 125.35 (q, *J* = 3.8 Hz),

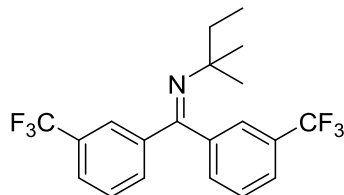
125.23 (q, $J = 3.8$ Hz), 124.59 (q, $J = 4.0$ Hz), 124.21 (q, $J = 272.4$ Hz), 123.89 (q, $J = 272.4$ Hz), 57.71, 31.65.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.65, -62.79.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_6\text{N}^+$ 374.1338; Found 374.1340.

***N*-tert-pentyl-3,3'-bis(trifluoromethyl)benzophenone imine (4b)**



Following the General Procedure B with the corresponding NHPI ester (0.3 mmol) and **2d** (0.6 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 59 mg (51%) of the title compound **4b**.

^1H NMR (400 MHz, Chloroform- d): δ 7.92 (s, 1H), 7.71 (d, $J = 7.9$ Hz, 1H), 7.64 – 7.51 (m, 3H), 7.47 (s, 1H), 7.40 (t, $J = 7.4$ Hz, 2H), 1.61 (q, $J = 7.4$ Hz, 2H), 1.02 (s, 6H), 0.96 (t, $J = 7.4$ Hz, 3H).

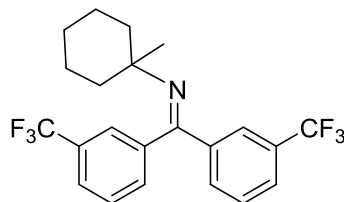
^{13}C NMR (101 MHz, Chloroform- d): 160.26, 142.12, 140.18, 131.73, 131.44, 130.85 (q, $J = 32.7$ Hz), 130.74 (q, $J = 32.3$ Hz), 128.81, 128.65, 126.33, 125.33, 125.17 (q, $J = 3.8$ Hz), 124.55 (q, $J = 3.7$ Hz), 124.21 (q, $J = 272.4$ Hz), 123.89 (q, $J = 272.4$ Hz), 60.12, 38.50, 28.48, 9.18.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.69, -62.79.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{F}_6\text{N}^+$ 388.1494; Found 388.1506.

***N*-(1-methylcyclohexyl)-3,3'-bis(trifluoromethyl)benzophenone imine (4c)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 50 mg (61%) of the title compound **4c**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.93 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 18.6, 7.6 Hz, 3H), 7.48 (s, 1H), 7.44 – 7.37 (m, 2H), 1.70 – 1.52 (m, 5H), 1.45 (ddd, *J* = 14.3, 6.7, 3.3 Hz, 2H), 1.30 (td, *J* = 10.0, 5.3 Hz, 3H), 1.02 (s, 3H).

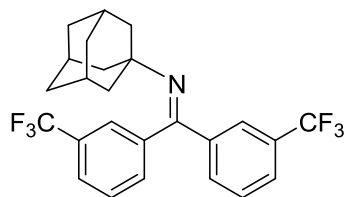
¹³C NMR (101 MHz, Chloroform-*d*): δ 160.40, 142.17, 140.34, 131.45, 131.40, 130.85 (q, *J* = 32.7 Hz), 130.75 (q, *J* = 32.3 Hz), 128.83, 128.66, 125.37 (q, *J* = 3.7 Hz), 125.33 (q, *J* = 3.7 Hz), 124.92 (q, *J* = 3.7 Hz), 124.52 (q, *J* = 3.7 Hz), 124.20 (q, *J* = 272.4 Hz), 123.94 (q, *J* = 272.4 Hz), 59.44, 40.49, 28.30, 26.00, 22.96.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.67, -62.79.

Physical State: pale yellow oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₂F₆N⁺ 414.1651; Found 414.1650.

***N*-(adamantan-1-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (4d)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 51 mg (56%) of the title compound **4d**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.94 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.48 (m, 3H), 7.47 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 1.99 (q, *J* = 3.2 Hz, 3H), 1.70 – 1.51 (m, 12H).

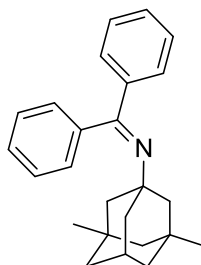
¹³C NMR (101 MHz, Chloroform-*d*): δ 159.46, 142.21, 140.48, 131.68, 131.50, 130.72 (q, *J* = 32.3 Hz), 130.73 (q, *J* = 32.6 Hz), 128.74, 128.61, 126.31 (q, *J* = 3.4 Hz), 125.29 (q, *J* = 4.2 Hz), 125.14 (q, *J* = 3.8 Hz), 124.58 (q, *J* = 4.1 Hz), δ 124.22 (q, *J* = 272.7.2 Hz), 123.97 (q, *J* = 272.7.2 Hz), 58.84, 44.36, 36.43, 29.77.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.63, -62.73.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₅H₂₄F₆N⁺ 452.1807; Found 452.1810.

***N*-(3,5-dimethyladamantan-1-yl)-benzophenone imine (4e)**



Following the General Procedure B with the corresponding NHPI ester (0.3 mmol) and **2a** (0.6 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 44 mg (43%) of the title compound **4e**.

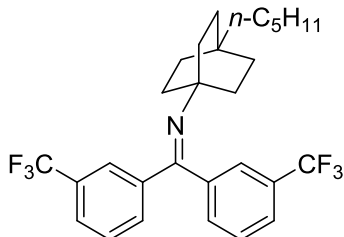
¹H NMR (400 MHz, Chloroform-*d*): δ 7.58 – 7.49 (m, 2H), 7.42 – 7.33 (m, 3H), 7.33 – 7.22 (m, 4H), 7.23 – 7.13 (m, 2H), 2.06 – 1.97 (m, 1H), 1.51 (d, J = 3.3 Hz, 2H), 1.39 (s, 4H), 1.20 (d, J = 3.1 Hz, 4H), 1.05 (s, 2H), 0.76 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 163.14, 142.29, 140.45, 129.38, 128.45, 128.17, 127.97, 127.90, 127.76, 60.02, 50.73, 50.67, 42.85, 42.47, 32.50, 30.67, 30.57.

Physical State: colorless oil.

HRMS (APCI/QTOF) m/z : $[M + H]^+$ Calcd for C₂₅H₃₀N⁺ 344.2373; Found 344.2369.

***N*-(4-pentylbicyclo[2.2.2]octan-1-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (4f)**



Following the General Procedure B with the corresponding NHPI ester (0.3 mmol) and **2d** (0.6 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using 0 to 20% ethyl acetate gradient in hexanes as an eluent to afford 58 mg (39%) of the title compound **4f**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.91 (s, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.50 – 7.45 (m, 1H), 7.42 (s, 1H), 7.38 (t, J = 7.5 Hz, 2H), 1.65 – 1.55 (m, 6H), 1.40 – 1.31 (m, 6H), 1.26 (q, J = 7.3 Hz, 2H), 1.21 – 1.09 (m, 4H), 1.04 – 0.96 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 160.14, 142.11, 140.56, 131.85, 131.47, 130.80 (q, J = 32.6 Hz), 130.71 (q, J = 32.3 Hz), 128.81, 128.60, 126.30 (q, J = 3.8 Hz), 125.26 (q, J = 3.4 Hz),

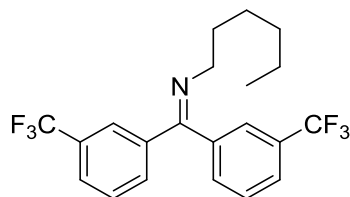
125.16 (q, $J = 3.4$ Hz), 124.56 (q, $J = 4.1$ Hz), 124.20 (q, $J = 272.4$ Hz), 123.96 (q, $J = 272.4$ Hz), 58.74, 41.38, 33.82, 32.94, 31.71, 30.80, 23.54, 22.81, 14.21.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.65, -62.70.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{32}\text{F}_6\text{N}^+$ 496.2433; Found 496.2432.

***N*-hexyl-3,3'-bis(trifluoromethyl)benzophenone imine (5a)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 79 mg (99%) of the title compound **5a**.

^1H NMR (400 MHz, Chloroform- d): δ 7.95 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 1H), 7.64 (t, $J = 7.7$ Hz, 3H), 7.49 – 7.40 (m, 2H), 7.36 (d, $J = 7.6$ Hz, 1H), 3.35 (t, $J = 7.0$ Hz, 2H), 1.75 – 1.65 (m, 2H), 1.31 – 1.23 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H).

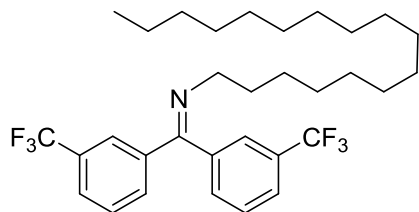
^{13}C NMR (101 MHz, Chloroform- d): δ 164.70, 140.19, 137.04, 131.72, 131.64, 131.33, 131.15, 130.82, 129.52, 128.86, 126.79 (q, $J = 4.6$ Hz), 125.76 (q, $J = 3.6$ Hz), 125.47, 125.28, 124.80 (q, $J = 3.8$ Hz), 124.68 (q, $J = 3.8$ Hz), 122.76, 122.57, 54.36, 31.74, 31.13, 27.30, 22.71, 14.15.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.67, -62.74.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{F}_6\text{N}^+$ 402.1651; Found 402.1658.

***N*-heptadecyl-3,3'-bis(trifluoromethyl)benzophenone imine (5b)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 89 mg (80%) of the title compound **5b**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 3H), 7.50 – 7.39 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 3.35 (t, *J* = 7.0 Hz, 2H), 1.69 (p, *J* = 7.1 Hz, 2H), 1.33 – 1.20 (m, 28H), 0.88 (t, *J* = 6.7 Hz, 3H).

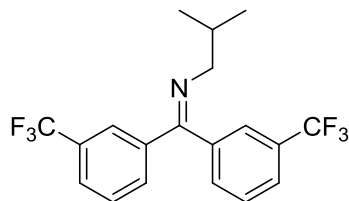
¹³C NMR (101 MHz, Chloroform-*d*): δ 164.68, 140.20, 137.05, 131.72, 131.49 (q, *J* = 32.4 Hz), 131.33, 130.99 (q, *J* = 32.5 Hz), 129.52, 128.85, 126.78 (q, *J* = 3.9 Hz), 125.76 (q, *J* = 3.8 Hz), 124.80 (q, *J* = 3.9 Hz), 124.69 (q, *J* = 3.8 Hz), 124.12 (q, *J* = 272.5 Hz), 123.93 (q, *J* = 272.6 Hz), 54.37, 32.09, 31.18, 29.86, 29.82, 29.77, 29.72, 29.56, 29.53, 27.63, 22.85, 14.27.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.67, -62.74.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₃₂H₄₄F₆N⁺ 556.3372; Found 556.3376.

***N*-isobutyl-3,3'-bis(trifluoromethyl)benzophenone imine (5c)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 68 mg (91%) of the title compound **5c**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 3H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.41 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 3.17 (d, *J* = 6.6 Hz, 2H), 2.13 – 1.97 (m, 1H), 0.95 (s, 3H), 0.93 (s, 3H).

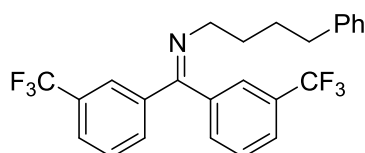
¹³C NMR (101 MHz, Chloroform-*d*): δ 137.11, 131.71, 131.41, 131.32, 131.14, 130.82, 129.53, 128.86, 125.47, 125.29, 124.77, 124.73, 122.76, 122.58, 61.94, 30.28, 20.89.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.69, -62.73.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₈F₆N⁺ 374.1338; Found 374.1332.

***N*-(5-phenylpentyl)-3,3'-bis(trifluoromethyl)benzophenone imine (5d)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 83 mg (92%) of the title compound **5d**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.99 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.72 – 7.61 (m, 3H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 3.41 (t, *J* = 6.6 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.66 (m, 4H).

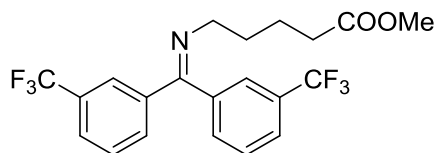
¹³C NMR (101 MHz, Chloroform-*d*): δ 164.85, 142.47, 140.12, 136.98, 131.72, 131.50 (q, *J* = 32.9 Hz), 131.30, 130.98 (q, *J* = 32.4 Hz), 129.56, 128.86, 128.51, 128.42, 126.82 (q, *J* = 3.7 Hz), 125.85, 125.79 (q, *J* = 3.8 Hz), 124.78 (q, *J* = 3.9 Hz), 124.64 (q, *J* = 3.8 Hz), 124.11 (q, *J* = 272.4 Hz), 123.91 (q, *J* = 272.4 Hz), 54.12, 35.79, 30.76, 29.33.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.65, -62.70.

Physical State: yellow oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₅H₂₂F₆N⁺ 450.1651; Found 450.1657.

Methyl 6-((bis(3-(trifluoromethyl)phenyl)methylene)amino)hexanoate (**5e**)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using 0 to 30% ethyl acetate gradient in hexanes as an eluent to afford 62 mg (72%) of the title compound **5e**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 8.3 Hz, 3H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.42 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 3.65 (d, *J* = 1.2 Hz, 3H), 3.36 (t, *J* = 6.3 Hz, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.80 – 1.65 (m, 4H).

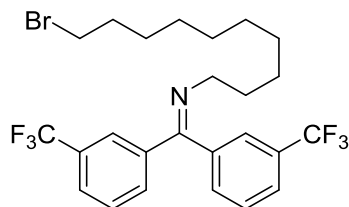
¹³C NMR (101 MHz, Chloroform-*d*): δ 174.09, 165.13, 139.99, 136.90, 131.74, 131.57 (q, *J* = 34.4 Hz), 131.26, 131.00 (q, *J* = 32.5 Hz), 129.62, 128.89, 125.87 (q, *J* = 3.9 Hz), 124.79 (q, *J* = 4.2 Hz), 124.58 (q, *J* = 3.8 Hz), 124.09 (q, *J* = 272.5 Hz), 123.89 (q, *J* = 272.5 Hz), 53.76, 51.65, 33.97, 30.61, 23.03.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.68, -62.73.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}F_6NO_2^+$ 432.1393; Found 432.1388.

***N*-(10-bromodecyl)-3,3'-bis(trifluoromethyl)benzophenone imine (5f)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 83 mg (78%) of the title compound **5f**.

1H NMR (400 MHz, Chloroform-*d*): δ 7.96 (s, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.64 (t, J = 8.1 Hz, 3H), 7.49 – 7.40 (m, 2H), 7.36 (d, J = 7.6 Hz, 1H), 3.40 (t, J = 6.8 Hz, 2H), 3.35 (t, J = 7.0 Hz, 2H), 1.84 (p, J = 6.9 Hz, 2H), 1.73 – 1.65 (m, 2H), 1.28 (d, J = 10.8 Hz, 12H).

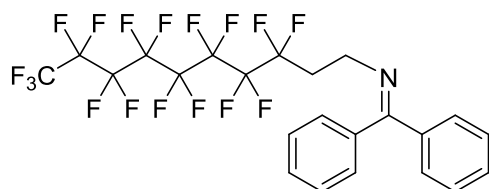
^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.68, 140.19, 137.04, 131.72, 131.47 (q, J = 30.4 Hz), 131.32, 130.97 (q, J = 32.4 Hz), 129.52, 128.85, 126.76 (q, J = 3.7 Hz), 125.74 (q, J = 3.7 Hz), 124.76 (q, J = 3.9 Hz), 124.66 (q, J = 3.8 Hz), 124.11 (q, J = 272.5 Hz), 123.92 (q, J = 272.5 Hz), 54.33, 34.15, 32.96, 31.14, 29.54, 29.49, 29.47, 28.87, 28.29, 27.58.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -62.66, -62.72.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}BrF_6N^+$ 536.1382; Found 536.1387.

***N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)-benzophenone imine (5g)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2a** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 66 mg (53%) of the title compound **5g**.

1H NMR (400 MHz, Chloroform-*d*): δ 7.66 – 7.57 (m, 2H), 7.54 – 7.30 (m, 6H), 7.22 – 7.12 (m, 2H), 3.66 (t, J = 7.5 Hz, 2H), 2.72 – 2.40 (m, 2H).

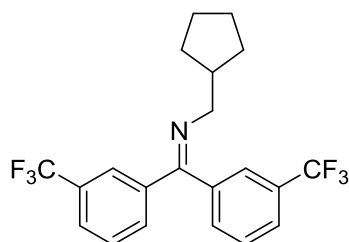
¹³C NMR (101 MHz, Chloroform-*d*): δ 170.10, 139.57, 136.48, 130.43, 128.90, 128.86, 128.57, 128.29, 127.64, 45.72 (t, *J* = 3.9 Hz), 32.86 (t, *J* = 21.1 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -80.84 (t, *J* = 10.0 Hz), -113.70 (t, *J* = 13.1 Hz), -121.70, -121.96, -122.76, -123.67, -126.15.

Physical State: yellow oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₃H₁₅F₁₇N⁺ 628.0928; Found 628.0928.

***N*-(cyclopentylmethyl)-3,3'-bis(trifluoromethyl)benzophenone imine (5h)**



Following the General Procedure C with the corresponding NHPI ester (derived from 6-heptenoic acid, 0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 52 mg (65%) of the title compound **5h**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 3H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 3.31 (d, *J* = 6.9 Hz, 2H), 2.27 (hept, *J* = 7.5 Hz, 1H), 1.90 – 1.69 (m, 2H), 1.61 – 1.50 (m, 4H), 1.29 – 1.14 (m, 2H).

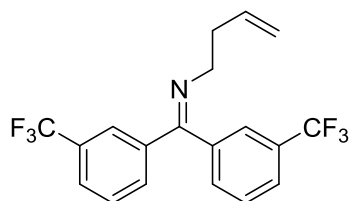
¹³C NMR (101 MHz, Chloroform-*d*): δ 164.43, 140.29, 137.16, 131.71, 131.47 (q, *J* = 32.6 Hz), 131.44, 130.96 (q, *J* = 32.4 Hz), 129.52, 128.84, 126.74 (q, *J* = 3.8 Hz), 125.72 (q, *J* = 3.7 Hz), 124.13 (q, *J* = 272.5 Hz), 123.94 (q, *J* = 272.5 Hz), 59.40, 41.56, 30.84, 25.30.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.68, -62.72.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₀F₆N⁺ 400.1494; Found 400.1505.

***N*-(but-3-en-1-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (5i)**



Following the General Procedure C with the corresponding NHPI ester (derived from cyclopropylacetic acid, 0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 28 mg (38%) of the title compound **5i**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.64 (td, *J* = 7.7, 3.9 Hz, 3H), 7.51 – 7.39 (m, 2H), 7.37 (d, *J* = 7.7 Hz, 1H), 5.80 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.14 – 4.92 (m, 2H), 3.44 (t, *J* = 7.0 Hz, 2H), 2.48 (q, *J* = 7.0 Hz, 2H).

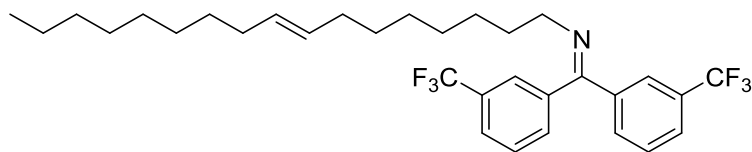
¹³C NMR (101 MHz, Chloroform-*d*): δ 165.23, 140.09, 136.90, 136.40, 131.76, 131.67, 131.34, 131.16, 130.84, 129.56, 128.87, 126.94, 126.91, 126.87, 125.87, 125.83, 125.45, 125.26, 124.87, 124.83, 124.78, 124.74, 124.70, 122.74, 122.55, 116.38, 53.84, 35.51.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.69, -62.75.

Physical State: light yellow oil.

HRMS (APCI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₆F₆N⁺ 372.1181; Found 372.1187.

(*E*)-N-(heptadec-8-en-1-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (6a)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 94 mg (85%) of the title compound **6a**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.95 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 3H), 7.49 – 7.41 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 5.37 (t, *J* = 4.0 Hz, 2H), 3.35 (t, *J* = 7.0 Hz, 2H), 1.95 (p, *J* = 5.1, 4.4 Hz, 4H), 1.75 – 1.63 (m, 2H), 1.33 – 1.23 (m, 20H), 0.87 (t, *J* = 6.6 Hz, 3H).

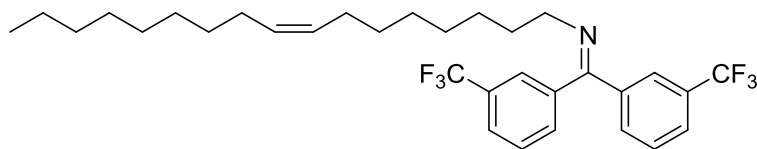
¹³C NMR (101 MHz, Chloroform-*d*): δ 164.69, 140.20, 137.05, 131.71, 131.48 (q, *J* = 32.7 Hz), 131.32, 130.98 (q, *J* = 32.5 Hz), 130.59, 130.39, 129.91 (q, *J* = 272.5 Hz), 129.52, 128.85, 126.78 (q, *J* = 3.6 Hz), 125.75 (q, *J* = 3.7 Hz), 124.79 (q, *J* = 3.8 Hz), 124.68 (q, *J* = 3.8 Hz), 124.11 (q, *J* = 272.5 Hz), 54.36, 32.76, 32.72, 32.05, 31.17, 29.85, 29.81, 29.73, 29.64, 29.47, 29.42, 29.34, 29.20, 27.60, 22.83, 14.26.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.67, -62.73.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{42}F_6N^+$ 554.3216; Found 554.3212.

(Z)-N-(heptadec-8-en-1-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (6b)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 90 mg (82%) of the title compound **6b**.

1H NMR (400 MHz, Chloroform-*d*): δ 7.96 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 1H), 7.64 (t, $J = 6.4$ Hz, 3H), 7.49 – 7.40 (m, 2H), 7.36 (d, $J = 7.6$ Hz, 1H), 5.42 – 5.24 (m, 2H), 3.36 (t, $J = 7.0$ Hz, 2H), 2.01 (q, $J = 6.6$ Hz, 4H), 1.70 (p, $J = 7.0$ Hz, 2H), 1.28 (d, $J = 11.5$ Hz, 20H), 0.88 (t, $J = 6.7$ Hz, 3H).

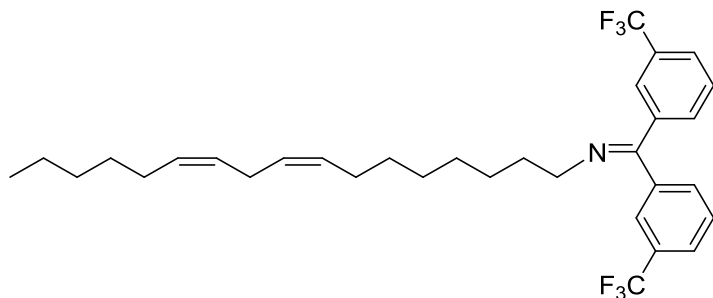
^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.68, 140.20, 137.07, 131.71, 131.49 (q, $J = 34.6$ Hz), 131.33, 130.99 (q, $J = 32.5$ Hz), 130.11, 129.92, 129.52, 128.85, 126.77 (q, $J = 3.7$ Hz), 125.75 (q, $J = 3.7$ Hz), 124.79 (q, $J = 3.9$ Hz), 124.68 (q, $J = 3.8$ Hz), 124.12 (q, $J = 272.5$ Hz), 123.92 (q, $J = 272.5$ Hz), 54.36, 32.06, 31.19, 29.93, 29.87, 29.68, 29.48, 29.36, 27.62, 27.37, 27.34, 22.84, 14.24.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -62.68, -62.75.

Physical State: colorless oil.

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{42}F_6N^+$ 554.3216; Found 554.3213.

N-((8Z,11Z)-heptadeca-8,11-dien-1-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (6c)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 89 mg (81%) of the title compound **6c**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.97 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 6.4 Hz, 3H), 7.49 – 7.40 (m, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 5.35 (m, 4H), 3.36 (t, *J* = 7.0 Hz, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.05 (q, *J* = 7.1 Hz, 4H), 1.69 (q, *J* = 7.1 Hz, 2H), 1.43 – 1.15 (m, 17H), 0.89 (t, *J* = 6.8 Hz, 3H).

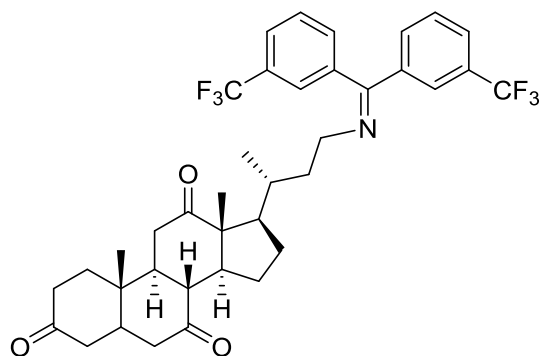
¹³C NMR (101 MHz, Chloroform-*d*): δ 164.69, 140.19, 131.71, 131.50 (q, *J* = 32.5 Hz), 131.32, 130.99 (q, *J* = 32.5 Hz), 130.34, 130.21, 129.52, 128.85, 128.16, 128.06, 126.78 (q, *J* = 3.7 Hz), 125.75 (q, *J* = 3.6 Hz), 124.79 (q, *J* = 3.8 Hz), 124.67 (q, *J* = 3.8 Hz), 124.13 (q, *J* = 272.5 Hz), 123.93 (q, *J* = 272.5 Hz), 54.35, 31.68, 31.18, 29.86, 29.76, 29.50, 29.47, 29.36, 27.61, 27.35, 25.78, 22.72, 14.20.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.68, -62.74.

Physical State: pale yellow oil.

HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₃₂H₄₀F₆N⁺ 552.3059; Found 552.3072.

(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-((bis(3-(trifluoromethyl)phenyl)methylene)amino)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (6d)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 69 mg (51%) of the title compound **6d**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.96 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 3.55 – 3.37 (m, 1H), 3.39 – 3.21 (m, 1H), 2.95 – 2.75 (m, 3H), 2.39 – 1.74 (m, 16H), 1.60 (td, *J* = 14.3, 5.1 Hz, 1H), 1.50 – 1.20 (m, 8H), 1.12 (d, *J* = 6.5 Hz, 2H), 1.05 (s, 3H), 0.75 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 164.76, 156.99, 140.13, 136.89, 131.69, 131.42 (q, *J* = 31.0 Hz), 131.27, 130.91 (q, *J* = 32.4 Hz), 129.54, 128.85, 126.74 (q, *J* = 3.7 Hz), 125.79 (q, *J* =

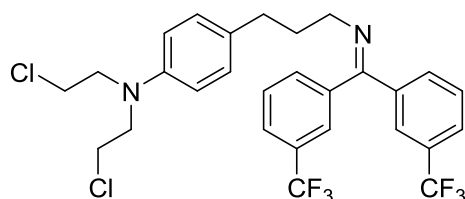
3.7 Hz), 124.69 (q, $J = 3.9$ Hz), 124.54 (q, $J = 3.8$ Hz), 124.07 (d, $J = 272.5$ Hz), 123.87 (d, $J = 272.5$ Hz), 60.49, 57.02, 51.97, 51.81, 49.08, 46.94, 45.92, 45.62, 45.09, 42.89, 42.25, 38.72, 36.72, 36.59, 36.11, 35.37, 34.36, 27.76, 25.22, 23.61, 21.99, 19.21, 14.30, 11.91.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.68, -62.69.

Physical State: white solid.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{38}\text{H}_{42}\text{F}_6\text{NO}_3^+$ 674.3063; Found 674.3066.

(3-(4-(bis(2-chloroethyl)amino)phenyl)propyl) 3,3'-bis(trifluoromethyl)benzophenone imine (6e)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and **2d** (0.2 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 79 mg (69%) of the title compound **6e**.

^1H NMR (400 MHz, Chloroform- d): δ 7.97 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 1H), 7.64 (dt, $J = 15.8$, 7.6 Hz, 3H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.41 (s, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.05 (d, $J = 8.4$ Hz, 2H), 6.60 (d, $J = 8.6$ Hz, 2H), 3.73 – 3.57 (m, 8H), 3.38 (t, $J = 6.8$ Hz, 2H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.00 (p, $J = 7.2$ Hz, 2H).

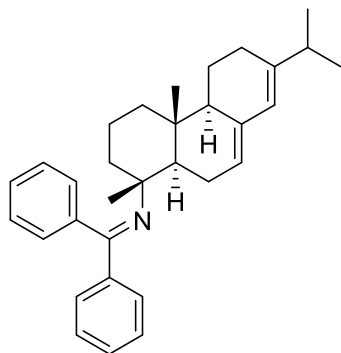
^{13}C NMR (101 MHz, Chloroform- d): δ 164.98, 144.34, 140.11, 136.96, 131.71, 131.45 (q, $J = 32.5$ Hz), 131.29, 131.19, 130.99 (q, $J = 32.5$ Hz), 129.73, 129.52, 128.88, 126.84 (q, $J = 3.8$ Hz), 125.76 (q, $J = 3.8$ Hz), 124.78 (q, $J = 3.9$ Hz), 124.60 (q, $J = 3.8$ Hz), 124.10 (q, $J = 272.5$ Hz), 123.89 (q, $J = 272.5$ Hz), 112.31, 53.77, 53.55, 40.67, 32.83, 32.55.

^{19}F NMR (376 MHz, Chloroform- d): δ -62.65, -62.66.

Physical State: yellow oil.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{27}\text{Cl}_2\text{F}_6\text{N}_2^+$ 575.1450; Found 575.1457.

***N*-((1*R*,4*aR*,4*bR*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,4*b*,5,6,10,10*a*-decahydrophenanthren-1-yl)-1,1-diphenylmethanimine (**6f**)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2a** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 43 mg (49%, *d.r.*=10.1:1) of the title compound **6f**.

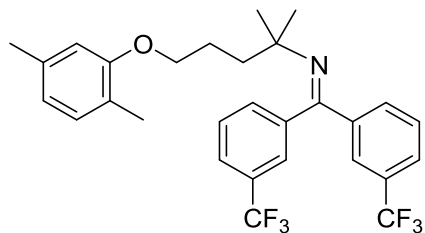
¹H NMR (400 MHz, Chloroform-*d*): δ 7.54 – 7.46 (m, 2H), 7.41 – 7.32 (m, 3H), 7.27 (q, *J* = 6.6 Hz, 4H), 7.20 – 7.11 (m, 2H), 5.84 (s, 1H), 5.54 (d, *J* = 5.1 Hz, 1H), 2.61 (dd, *J* = 12.6, 4.6 Hz, 1H), 2.24 (p, *J* = 7.0 Hz, 1H), 2.04 (td, *J* = 19.5, 9.8 Hz, 5H), 1.83 – 1.74 (m, 2H), 1.56 – 1.02 (m, 12H), 0.98 (s, 3H), 0.82 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 162.19, 145.10, 142.54, 140.48, 135.53, 129.31, 128.66, 128.14, 127.94, 127.90, 127.85, 127.81, 127.74, 122.71, 122.37, 61.84, 53.54, 51.52, 40.39, 38.40, 35.62, 35.07, 27.74, 27.72, 24.81, 22.85, 21.77, 21.59, 21.04, 19.70, 14.01.

Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [*M* + *H*]⁺ Calcd for C₃₂H₄₀N⁺ 438.3155; Found 438.3158.

***N*-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)-3,3'-bis(trifluoromethyl)benzophenone imine (**6g**)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and **2d** (0.4 mmol). The crude product was purified by column chromatography (with pre-neutralized silica gel) using hexanes as an eluent to afford 52 mg (50%) of the title compound **6g**.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.90 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.49 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.70 – 6.61 (m, 2H), 3.99 (t, *J* = 6.3 Hz, 2H), 2.31 (s, 3H), 2.20 (s, 3H), 2.02 – 1.89 (m, 2H), 1.84 – 1.73 (m, 2H), 1.08 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 160.52, 157.21, 141.94, 140.01, 136.61, 131.70, 131.41, 130.42, 131.00 (q, *J* = 16.0 Hz), 130.67 (q, *J* = 15.7 Hz), 128.90, 128.69, 126.45 (q, *J* = 3.7 Hz), 125.52, 125.40 (q, *J* = 3.8 Hz), 125.28, 125.16 (q, *J* = 3.8 Hz), 124.56 (q, *J* = 4.0 Hz), 123.73, 122.82, 122.57, 120.78, 112.17, 68.49, 59.69, 42.91, 28.91, 25.12, 21.54, 15.92.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.66, -62.75.

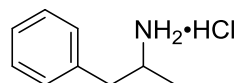
Physical State: colorless oil.

HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₉H₃₀F₆NO⁺ 522.2226; Found 522.2231.

General procedure for acid hydrolysis of imine products to corresponding ammonium chloride salt (General Procedure D)

An 25 mL flask equipped with a Teflon-coated magnetic stir bar, imine product (0.2 mmol) was dissolved in methanol (3 ml). $\text{HCl}_{(\text{aq})}$ (1.0 M, 1.5 equiv) was added dropwise to the reaction mixture with stirring. After 1 h, the reaction mixture was diluted with ether (~5 ml) and filtered through a plug of glass wool, which was rinsed with ether (1 ml) for 3 times. The volatile materials were evaporated at reduced pressure. Ether and water (~5 ml each) were added to residue, the organic layer was removed, the aqueous layer was washed again with ether (2 ml), and the combined organic layers were extracted with water (2 ml). The volatile materials were removed from the combined aqueous layers at reduced pressure. The crude ammonium chloride salt was dissolved in DCM (3 ml) and filtered through a plug of Na_2SO_4 . Addition of hexanes (~8 ml) at 0 °C caused a precipitate to form, which was collected by filtration, washed with cold hexanes (2 ml) for 2 times, and dried under vacuum to give the desired compound.

Amphetamine hydrochloride (**7a**)



Following the General Procedure B and D with the corresponding NHPI ester (0.4 mmol) and **2d** (0.8 mmol), the title compound **7a** was obtained in 60% (41 mg) overall yield.

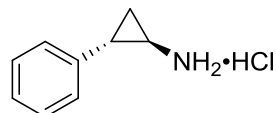
¹H NMR (400 MHz, Chloroform-*d*): δ 8.50 (s, 3H), 7.46 – 7.04 (m, 5H), 3.75 – 3.41 (m, 1H), 3.27 (dd, J = 13.4, 5.4 Hz, 1H), 2.89 (dd, J = 13.4, 9.1 Hz, 1H), 1.41 (d, J = 6.5 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 135.87, 129.46, 129.03, 127.43, 49.94, 41.27, 18.32.

Physical State: white solid.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.^[5]

trans-2-Phenylcyclopropylamine hydrochloride (**7b**)



Following the General Procedure B and D with the corresponding NHPI ester (0.5 mmol) and **2d** (1.0 mmol), the title compound **7b** was obtained in 41% (35 mg) overall yield.

¹H NMR (400 MHz, Chloroform-*d*): δ 8.76 (s, 3H), 7.36 – 7.08 (m, 5H), 2.94 – 2.79 (m, 1H), 2.68 (ddd, J = 10.3, 6.7, 3.5 Hz, 1H), 1.69 (ddd, J = 10.6, 6.7, 4.3 Hz, 1H), 1.26 (q, J = 6.8 Hz, 1H).

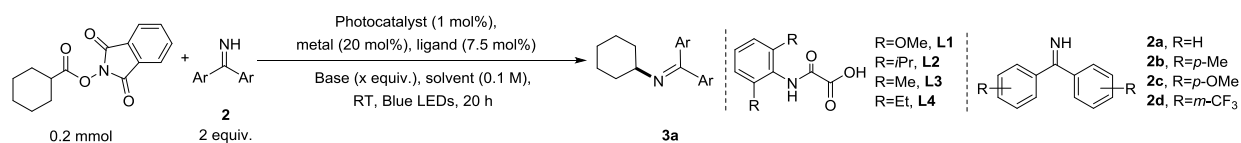
¹³C NMR (101 MHz, Chloroform-*d*): δ 138.06, 128.76, 127.04, 126.85, 31.01, 21.99, 13.57.

Physical State: white solid.

The ¹H NMR and ¹³C NMR spectra were consistent with the spectrum reported in the literature.^[6]

Tables

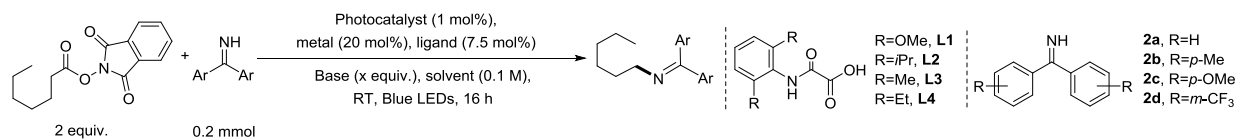
Table S1. Optimization of reaction parameters for secondary and tertiary NHPI ester



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	30%
2	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	L2	Et ₃ N (5 equiv.)	MeCN	25%
3	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	L3	Et ₃ N (5 equiv.)	MeCN	20%
4	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	L4	Et ₃ N (5 equiv.)	MeCN	26%
5	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	PCy ₃	Et ₃ N (5 equiv.)	MeCN	31%
6	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	dtbbpy	Et ₃ N (5 equiv.)	MeCN	12%
7	2a	Ru(bpy) ₃ (PF ₆) ₂	CuBr	none	Et ₃ N (5 equiv.)	MeCN	25%
8	2a	Ru(bpy) ₃ (PF ₆) ₂	CuCl	none	Et ₃ N (5 equiv.)	MeCN	30%
9	2a	Ru(bpy) ₃ (PF ₆) ₂	CuTC	none	Et ₃ N (5 equiv.)	MeCN	11%
10	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	Et ₃ N (5 equiv.)	MeCN	32%
11	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	MeCN	19%
12	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	39%
13	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	K ₂ CO ₃ (2 equiv.)	DMA	trace
14	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	KO ^t Bu (2 equiv.)	DMA	trace
15	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	Diisopropylamine (2 equiv.)	MeCN	16%
16	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	DBU (2 equiv.) ^c	MeCN	trace
17	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	BTMG (2 equiv.) ^d	MeCN	14%
18	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMF	27%
19	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DCM	19%
20	2a	Ru(bpy) ₃ (PF ₆) ₂	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	THF	trace
21	2a	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	40%
22	2a	Ir(ppy) ₃	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	37%
23	2a	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	49%
24	2b	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	33%
25	2c	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	20%
26	2d	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	70%
27 ^b	2d	Ir[(ppy) ₂ (dtbbpy)](PF ₆)	Cu(MeCN) ₄ (PF ₆)	none	Cs ₂ CO ₃ (2 equiv.)	DMA	56%

^aCorrected GC yield. ^b1-Adamantyl NHPI ester as electrophile. ^c1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). ^d2-tert-Butyl-1,1,3,3-tetramethylguanidine (BTMG).

Table S2. Optimization of reaction parameters for primary NHPI ester



Entry	Nucleophile	Photocatalyst	Metal	Ligand	Base	Solvent	GC yield ^a
1	2a	Ru(bpy) ₃ PF ₆	CuCl	no ligand	Et ₃ N (3 equiv.)	MeCN	52%
2	2a	Ru(bpy) ₃ PF ₆	CuCl	L1	Et ₃ N (3 equiv.)	MeCN	49%
3	2a	Ru(bpy) ₃ PF ₆	CuCl	L2	Et ₃ N (3 equiv.)	MeCN	46%
4	2a	Ru(bpy) ₃ PF ₆	CuCl	L3	Et ₃ N (3 equiv.)	MeCN	38%
5	2a	Ru(bpy) ₃ PF ₆	CuCl	L4	Et ₃ N (3 equiv.)	MeCN	48%
6	2a	Ru(bpy) ₃ PF ₆	CuCl	PCy ₃	Et ₃ N (3 equiv.)	MeCN	44%
7	2d	Ru(bpy) ₃ PF ₆	CuCl	no ligand	Et ₃ N (3 equiv.)	MeCN	76%
8	2d	Ru(bpy) ₃ PF ₆	CuCl	no ligand	Cs ₂ CO ₃ (2 equiv.)	DMA	8%
9	2d	Ir(ppy) ₃	CuCl	no ligand	Et ₃ N (3 equiv.)	MeCN	59%
10	2d	Ir[(ppy) ₂ (dtbbpy)]PF ₆	CuCl	no ligand	Et ₃ N (3 equiv.)	MeCN	22%
11	2d	Ru(bpy) ₃ PF ₆	Cu(MeCN) ₄ PF ₆	no ligand	Et ₃ N (3 equiv.)	MeCN	70%
12	2d	Ru(bpy) ₃ PF ₆	Cu(MeCN) ₄ PF ₆	no ligand	<i>N,N</i> -Diisopropylethylamine (2 equiv.)	MeCN	8%
13	2d	Ir[(ppy) ₂ (dtbbpy)]PF ₆	Cu(MeCN) ₄ PF ₆	no ligand	<i>N,N</i> -Diisopropylethylamine (2 equiv.)	MeCN	34%
14	2d	Ir[(ppy) ₂ (dtbbpy)]PF ₆	Cu(MeCN) ₄ PF ₆	no ligand	Diisopropylamine (2 equiv.)	MeCN	99%
15	2d	Ir[(ppy) ₂ (dtbbpy)]PF ₆	CuCl	no ligand	Diisopropylamine (2 equiv.)	MeCN	48%

^aCorrected GC yield using *n*-dodecane as an internal standard

Figures

Figure S1. Alternative mechanistic pathway

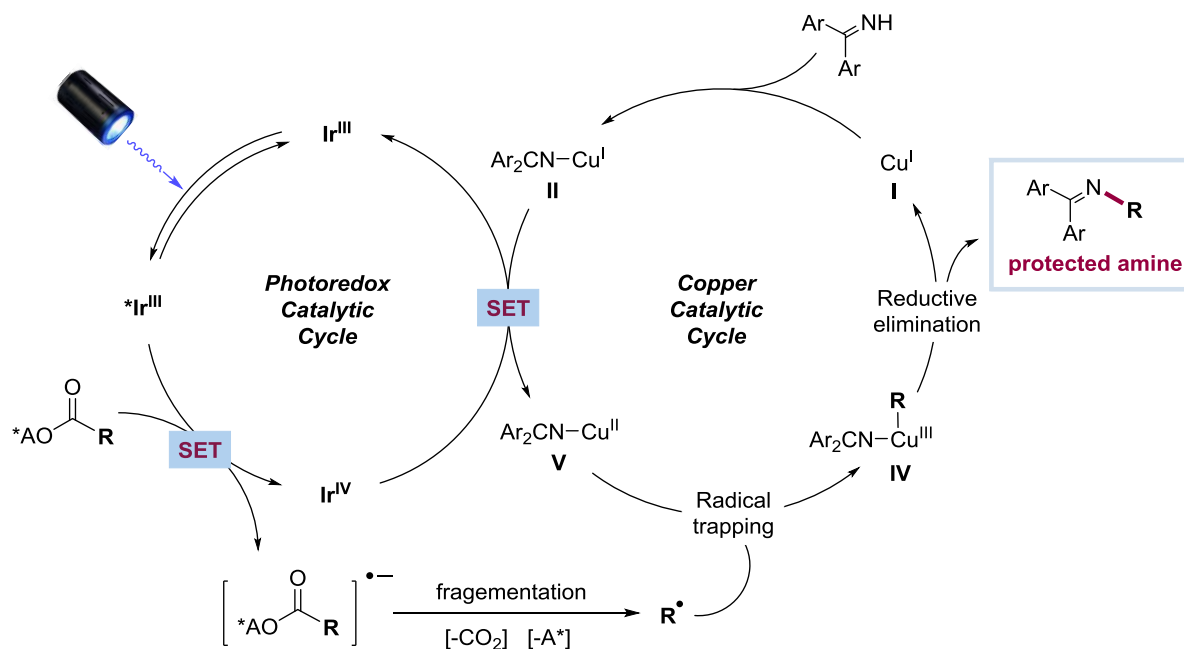
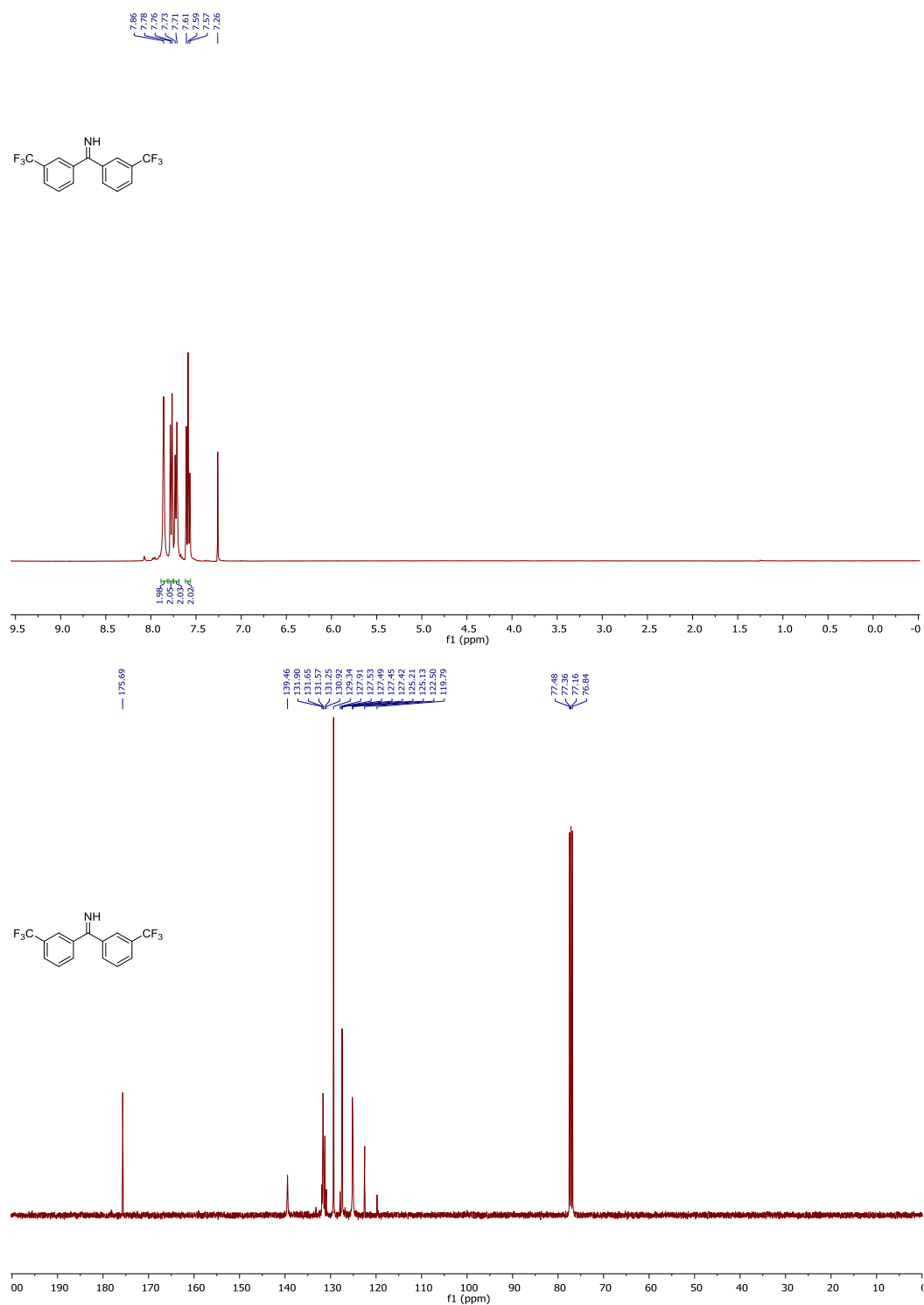


Figure S2. NMR spectra of 2d



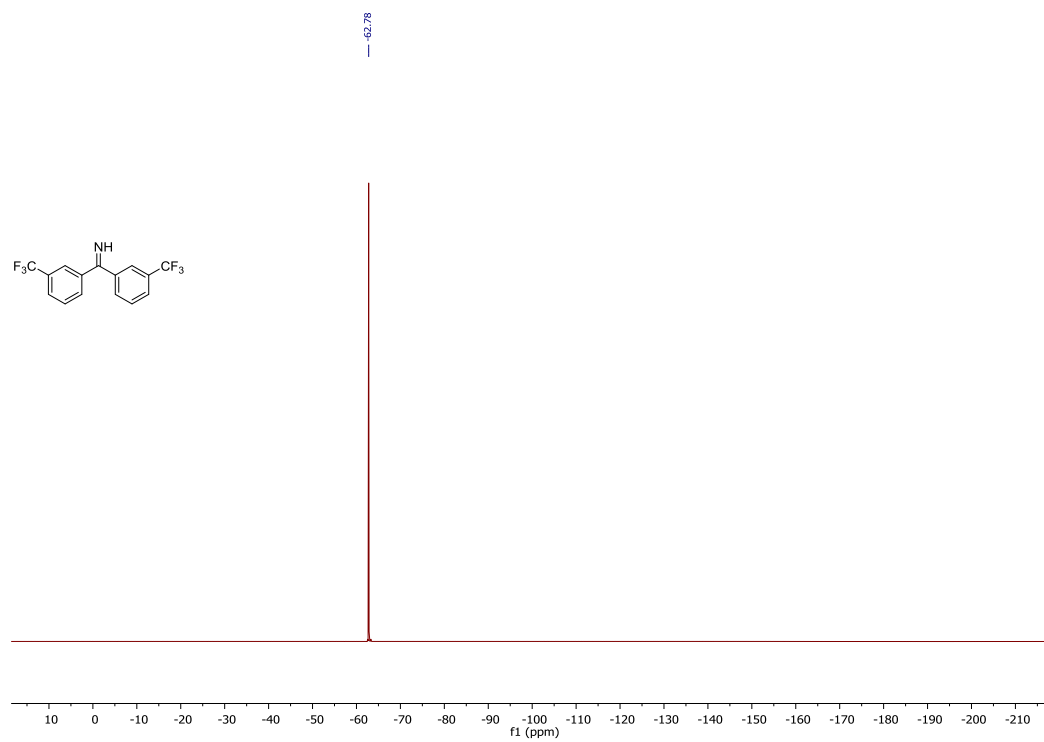
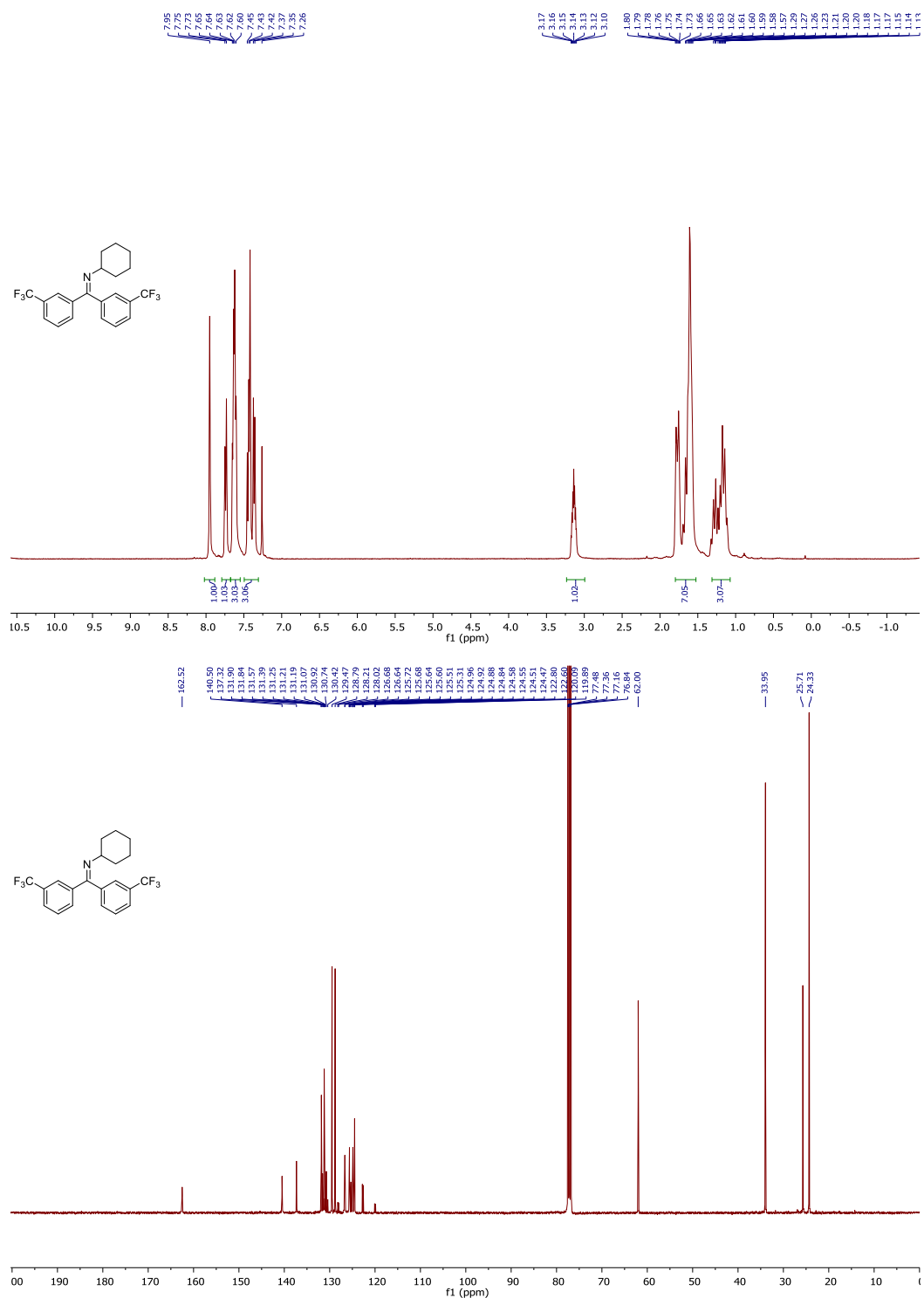


Figure S3. NMR spectra of 3a



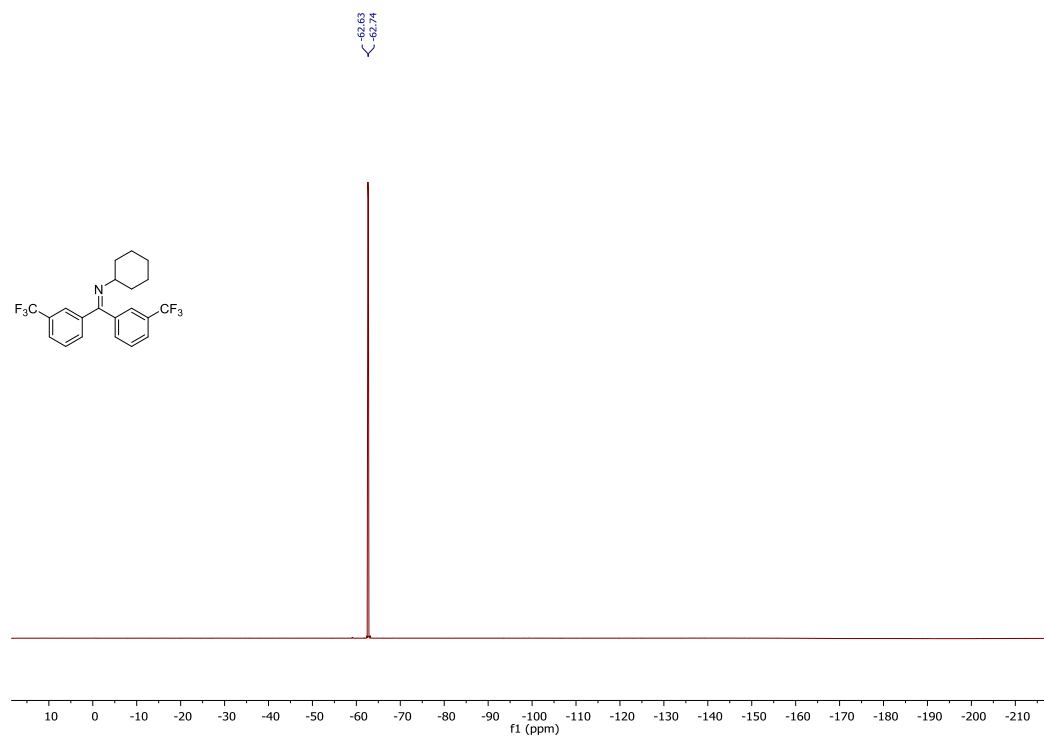
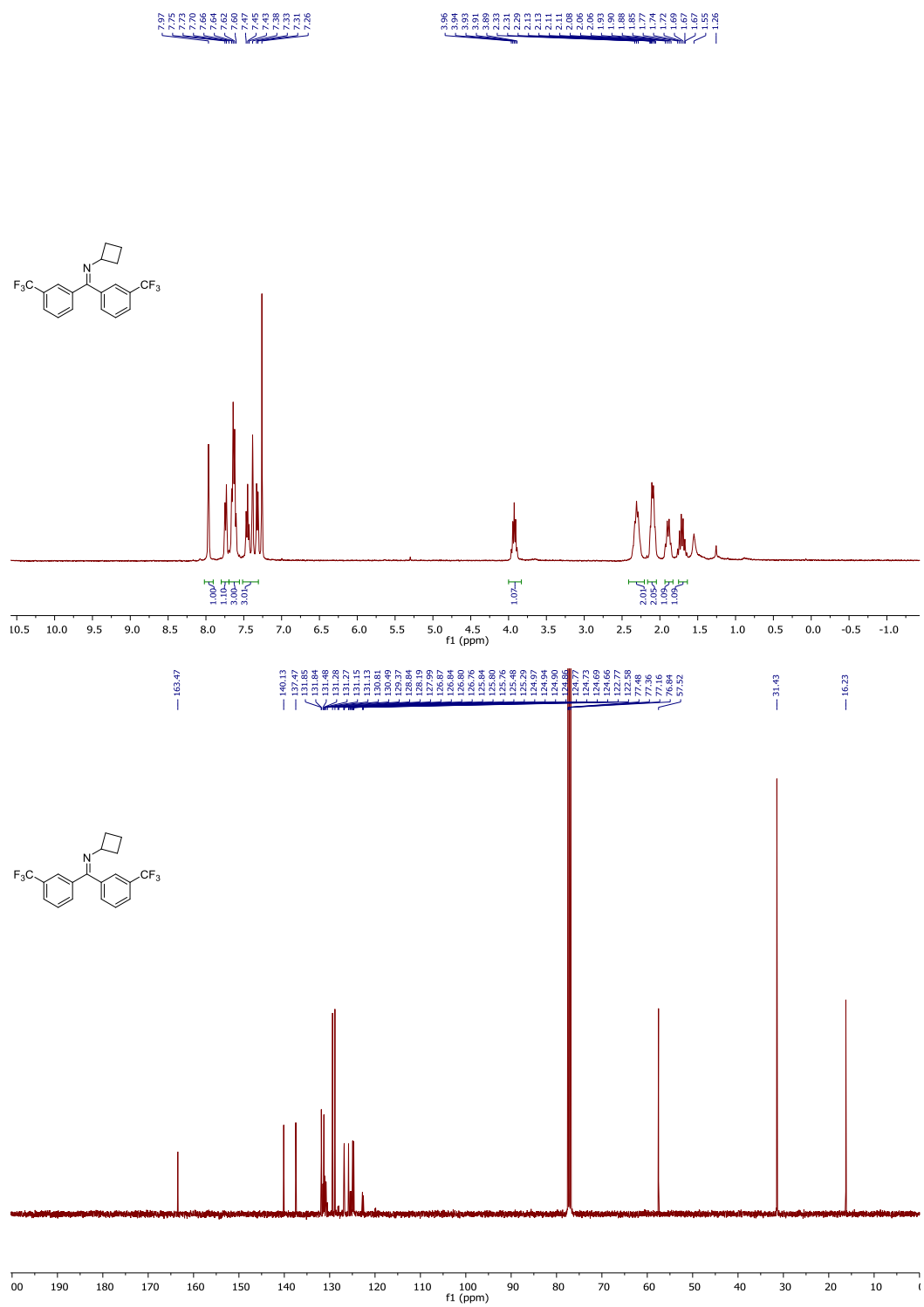


Figure S4. NMR spectra of 3b



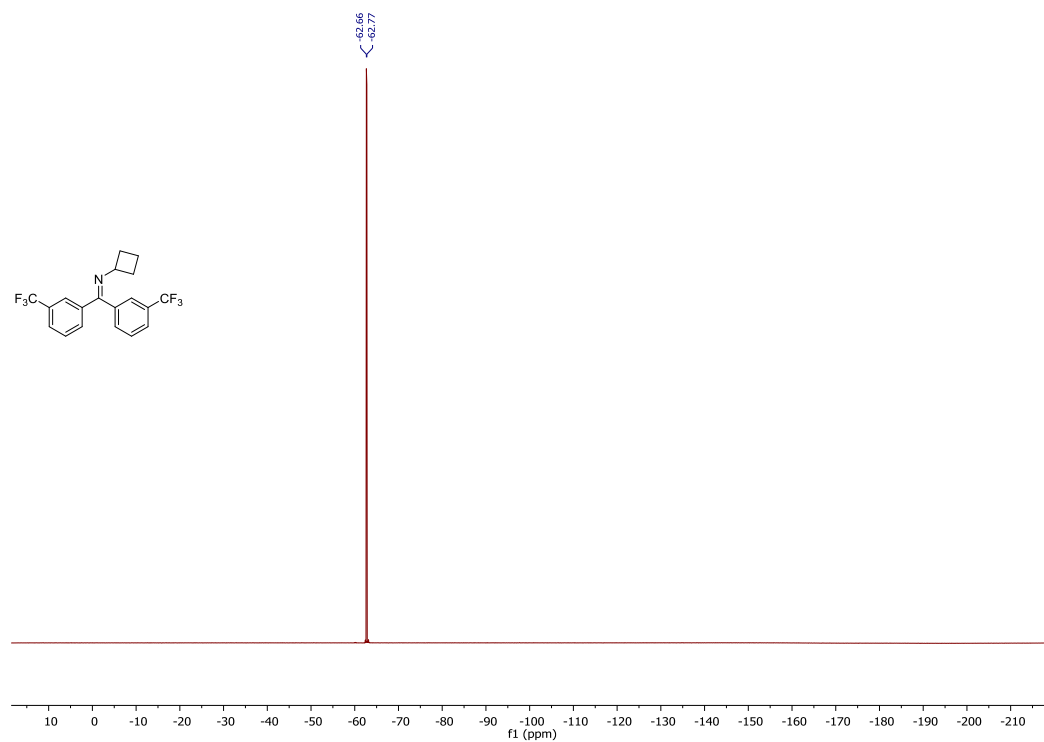
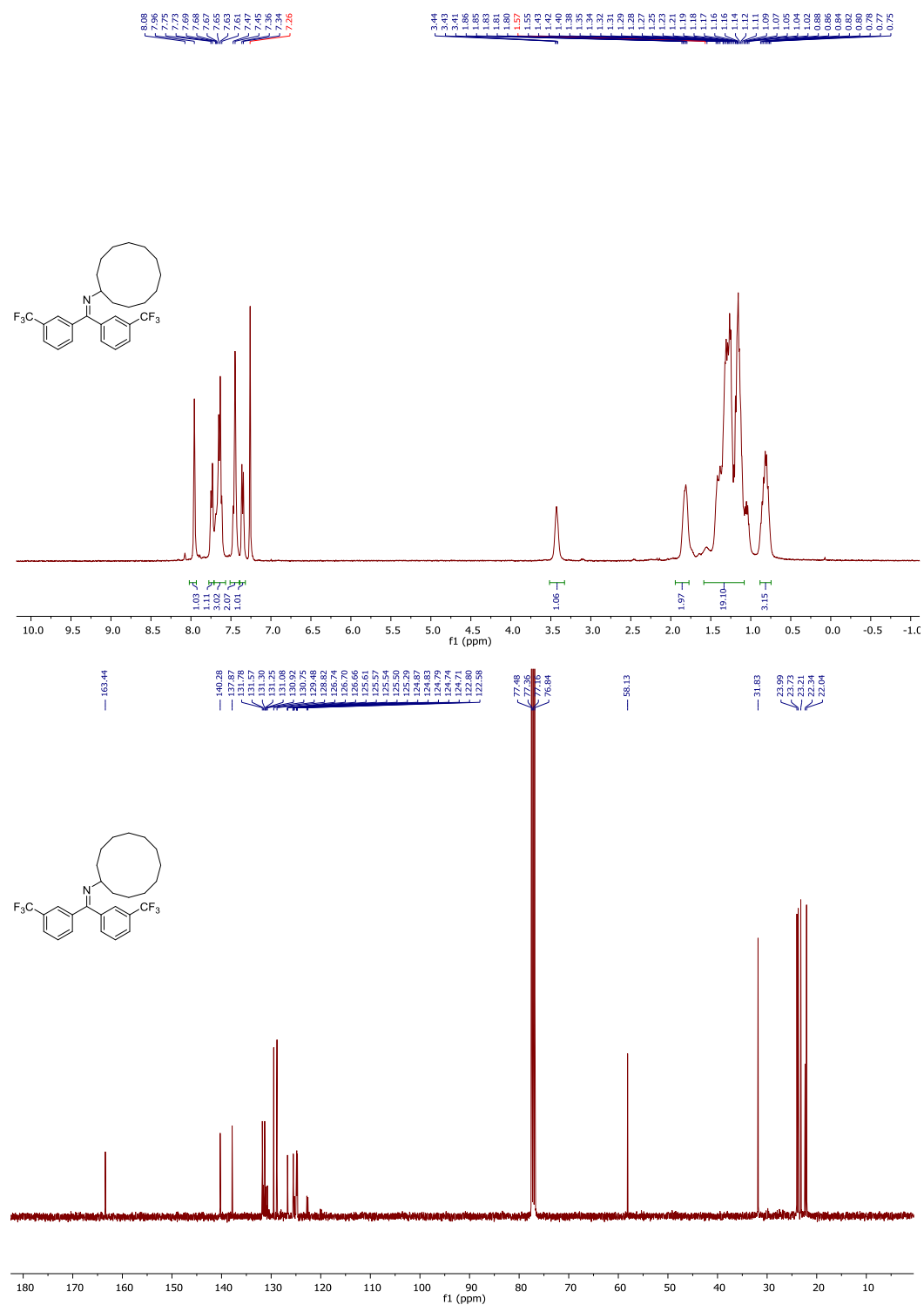


Figure S5. NMR spectra of 3c



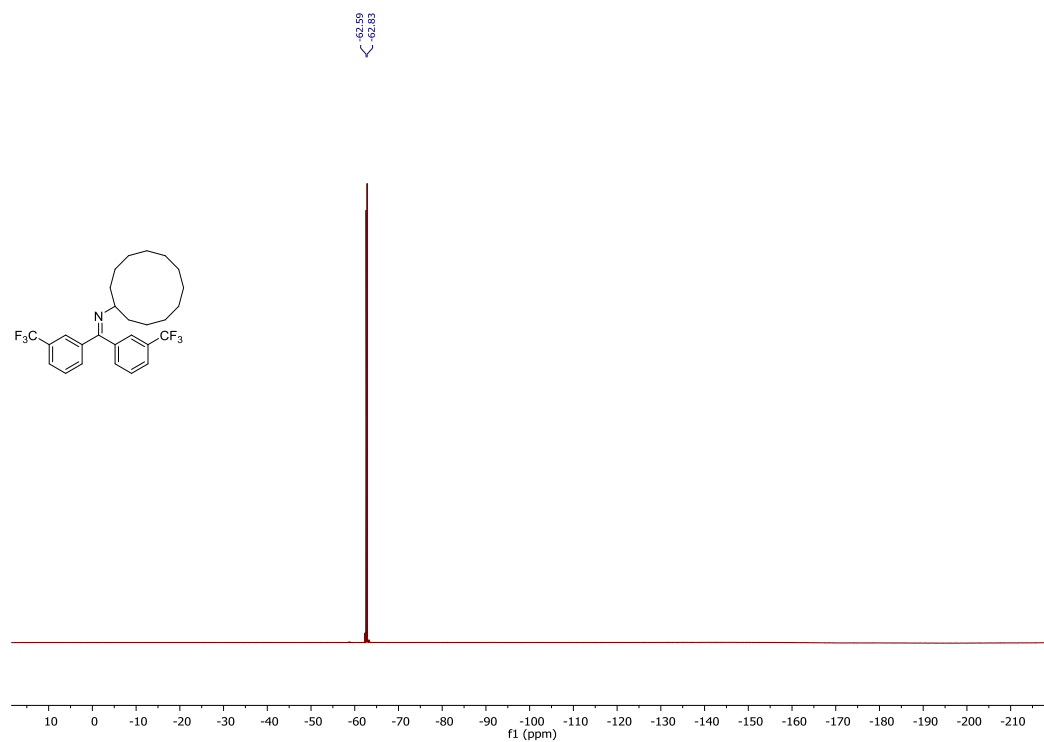
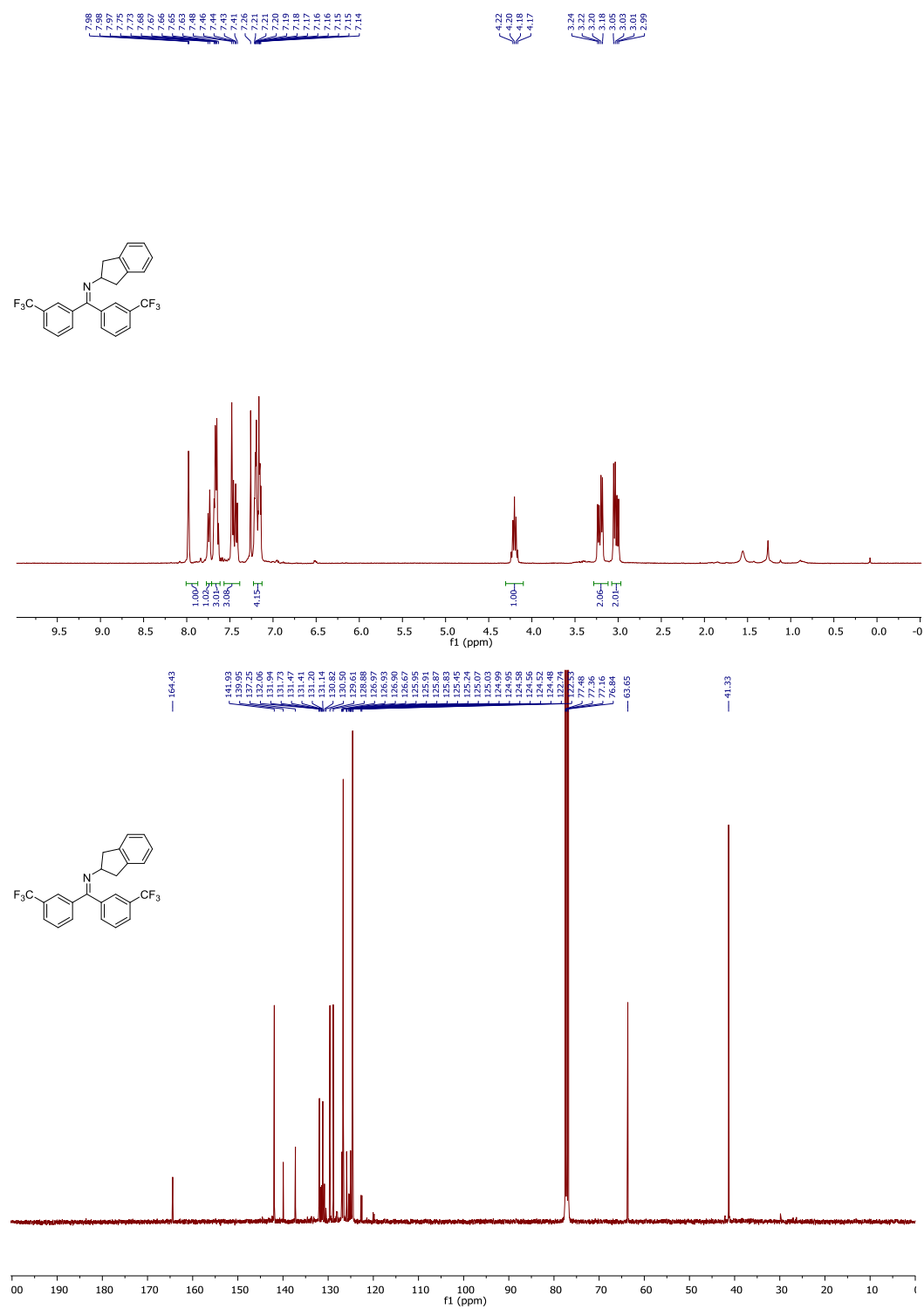


Figure S6. NMR spectra of 3d



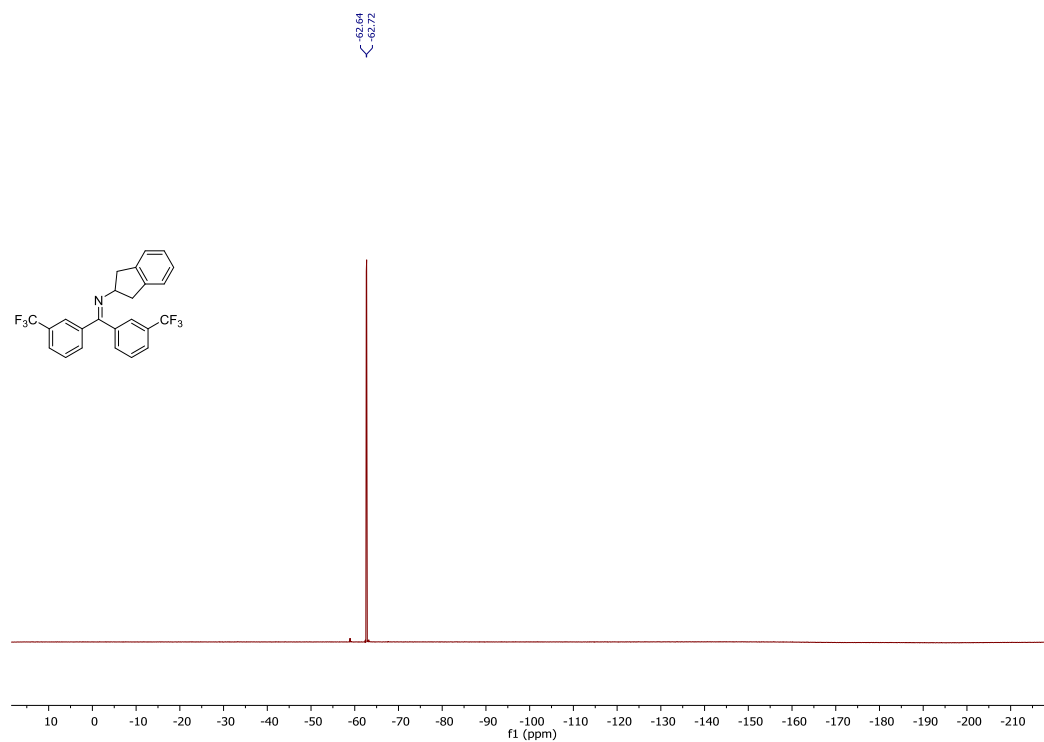
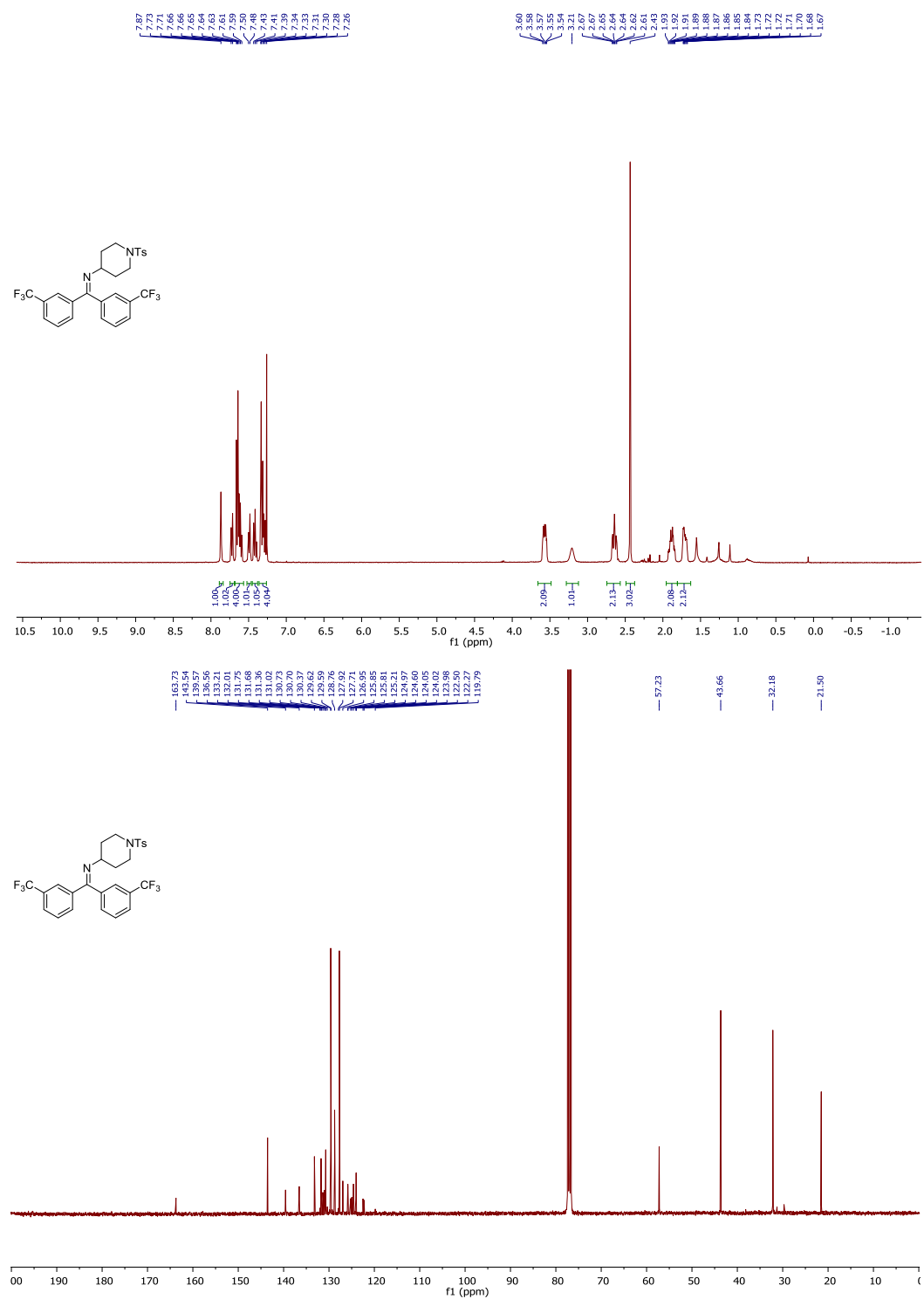


Figure S7. NMR spectra of 3e



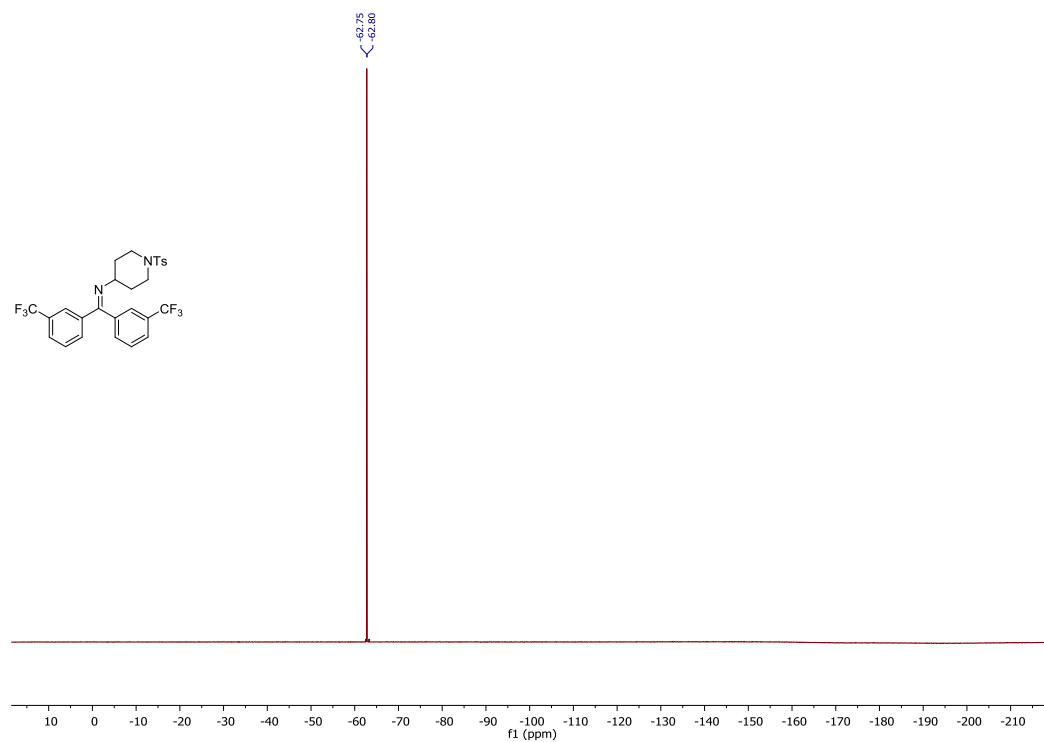


Figure S8. NMR spectra of 3f

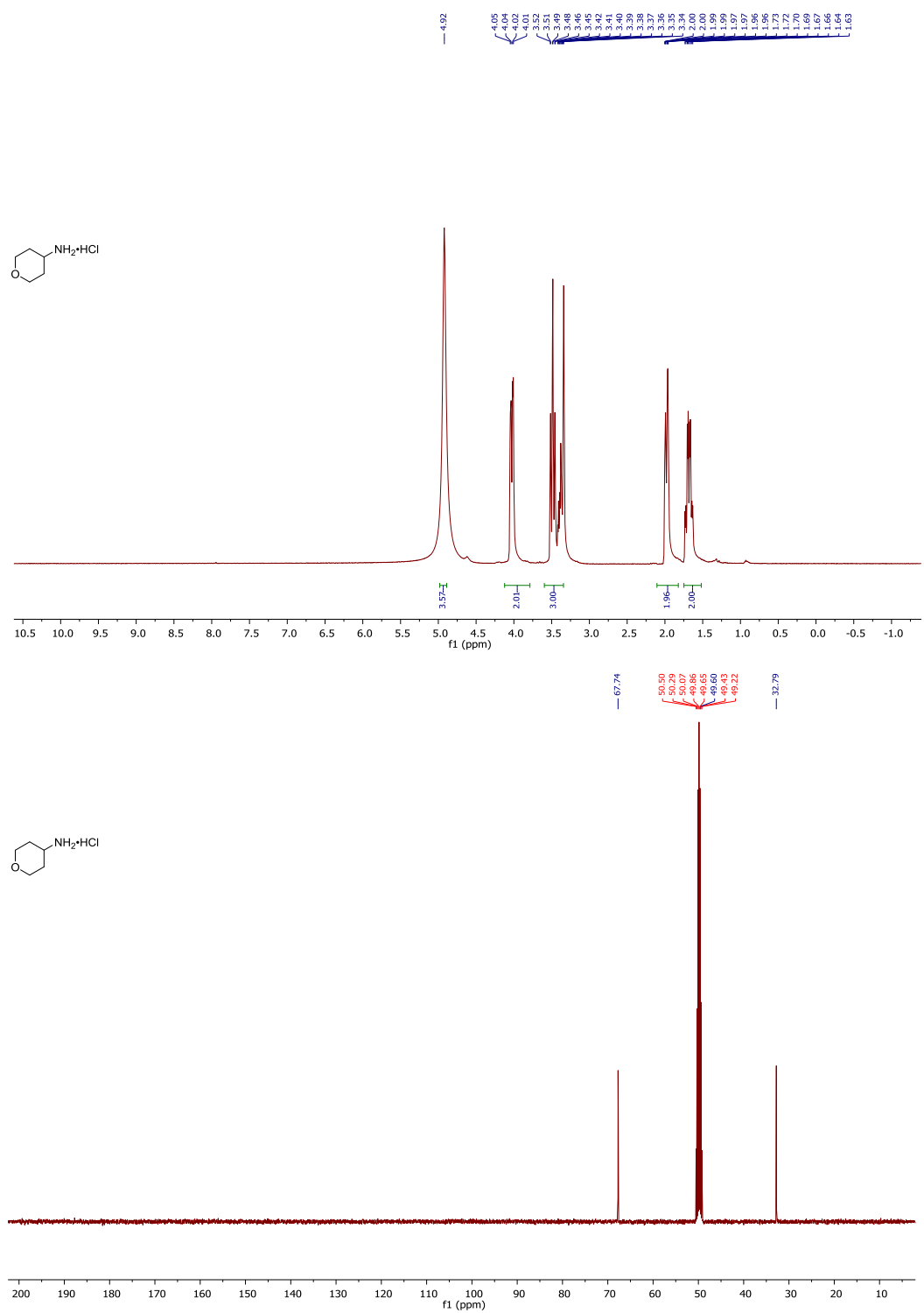
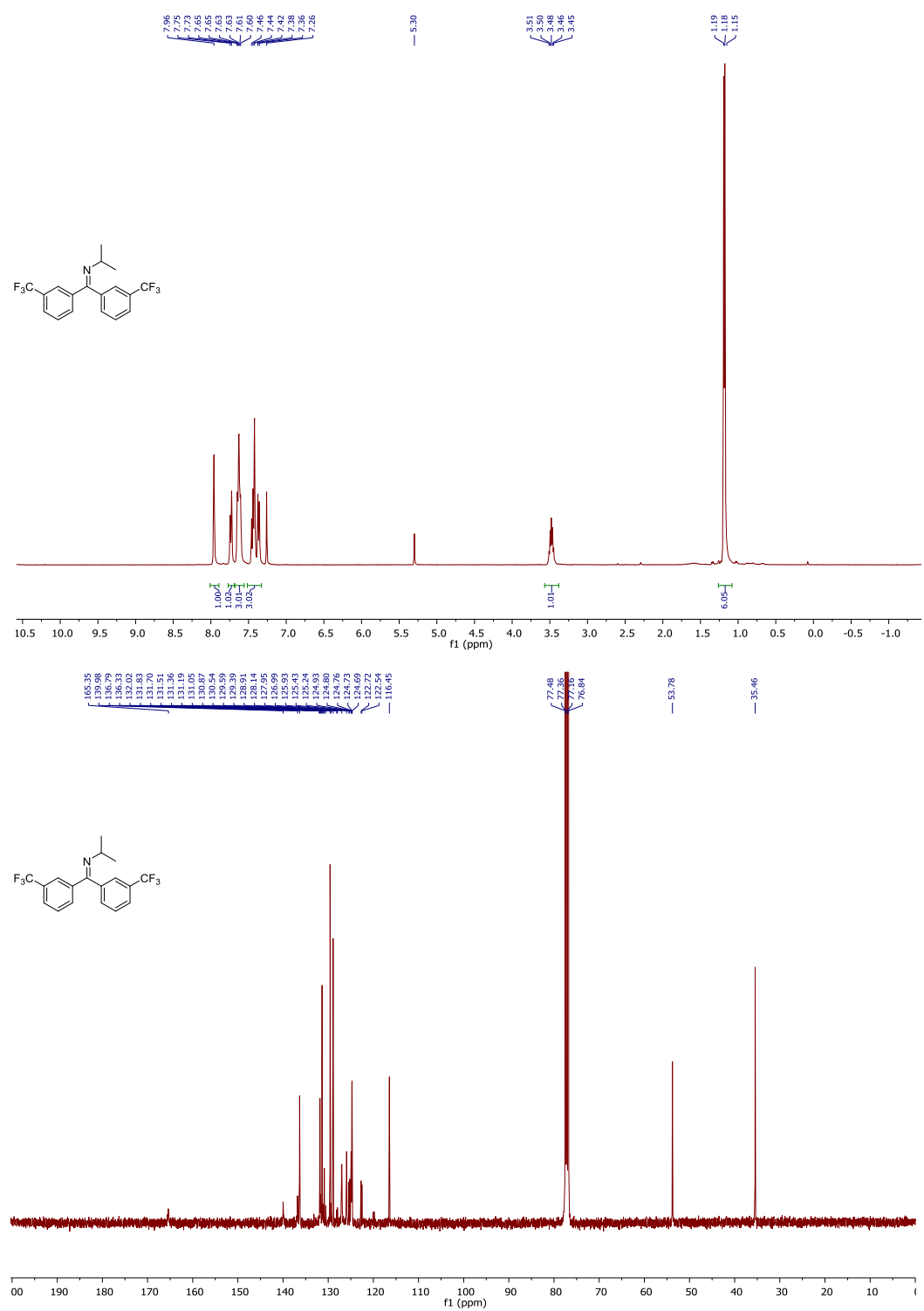
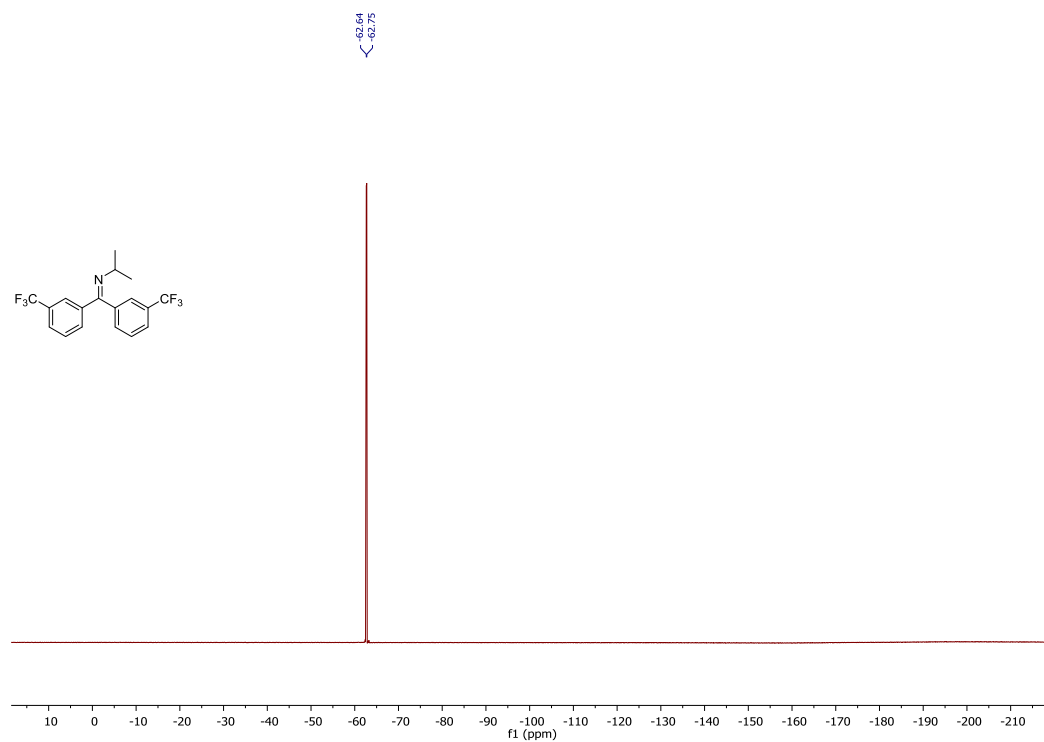


Figure S9. NMR spectra of 3g





Chemical structure: CC(C)=N(c1ccc(F)(F)F)c2ccc(F)(F)F

¹H NMR spectrum (top):

- Chemical shift range: 0.75 to 7.95 ppm.
- Integration values: 1.01, 2.02, 1.06, 1.00, 4.04, 4.07, 7.01.

¹³C NMR spectrum (bottom):

- Chemical shift range: 11.20 to 163.19 ppm.

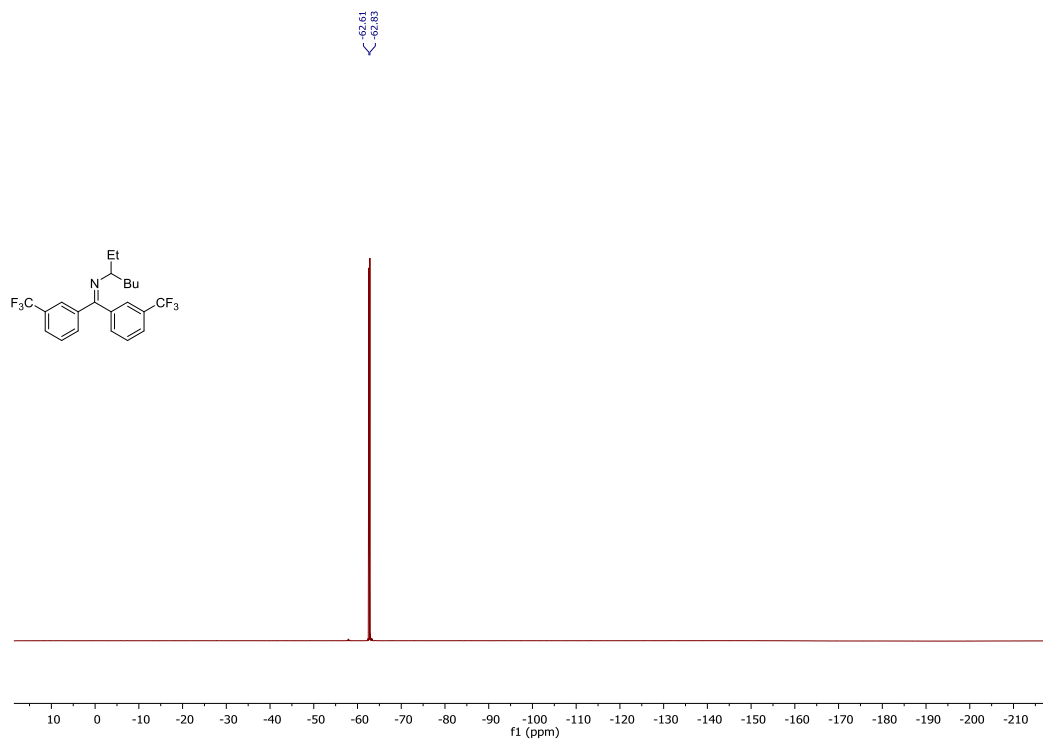
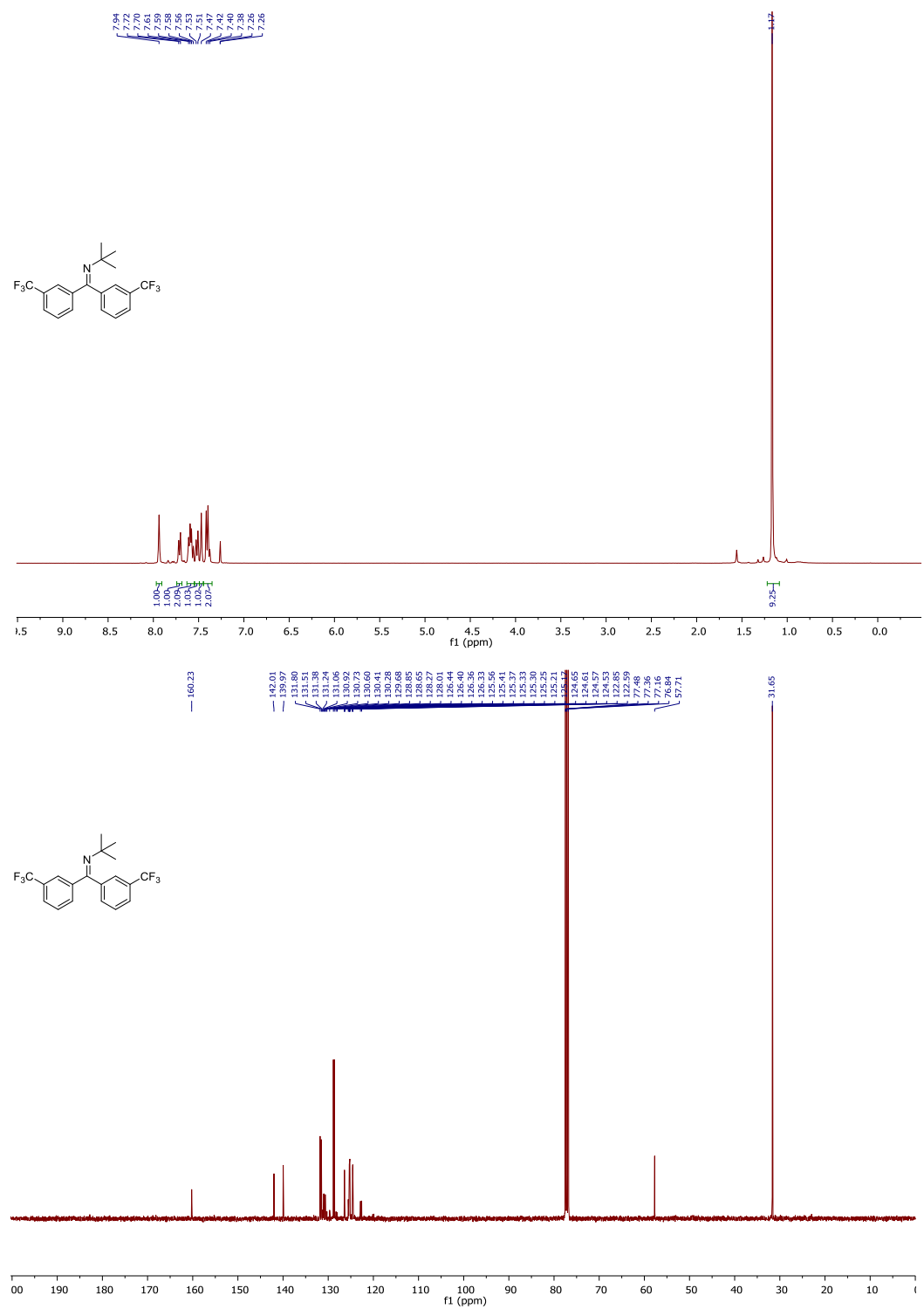


Figure S11. NMR spectra of 4a



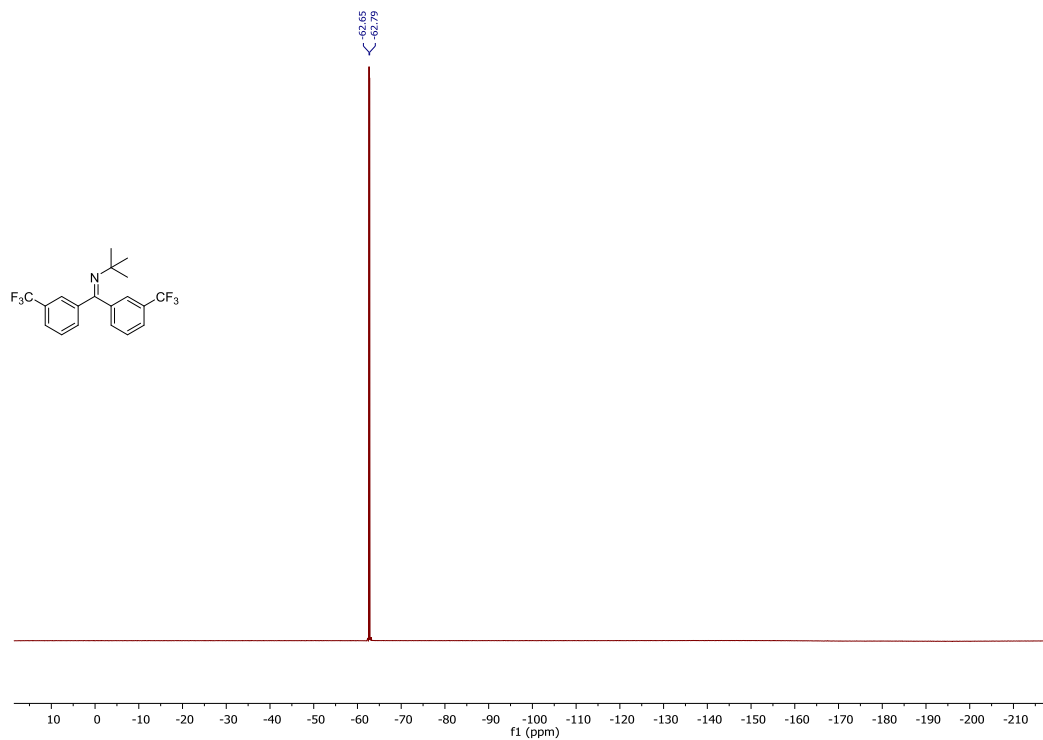
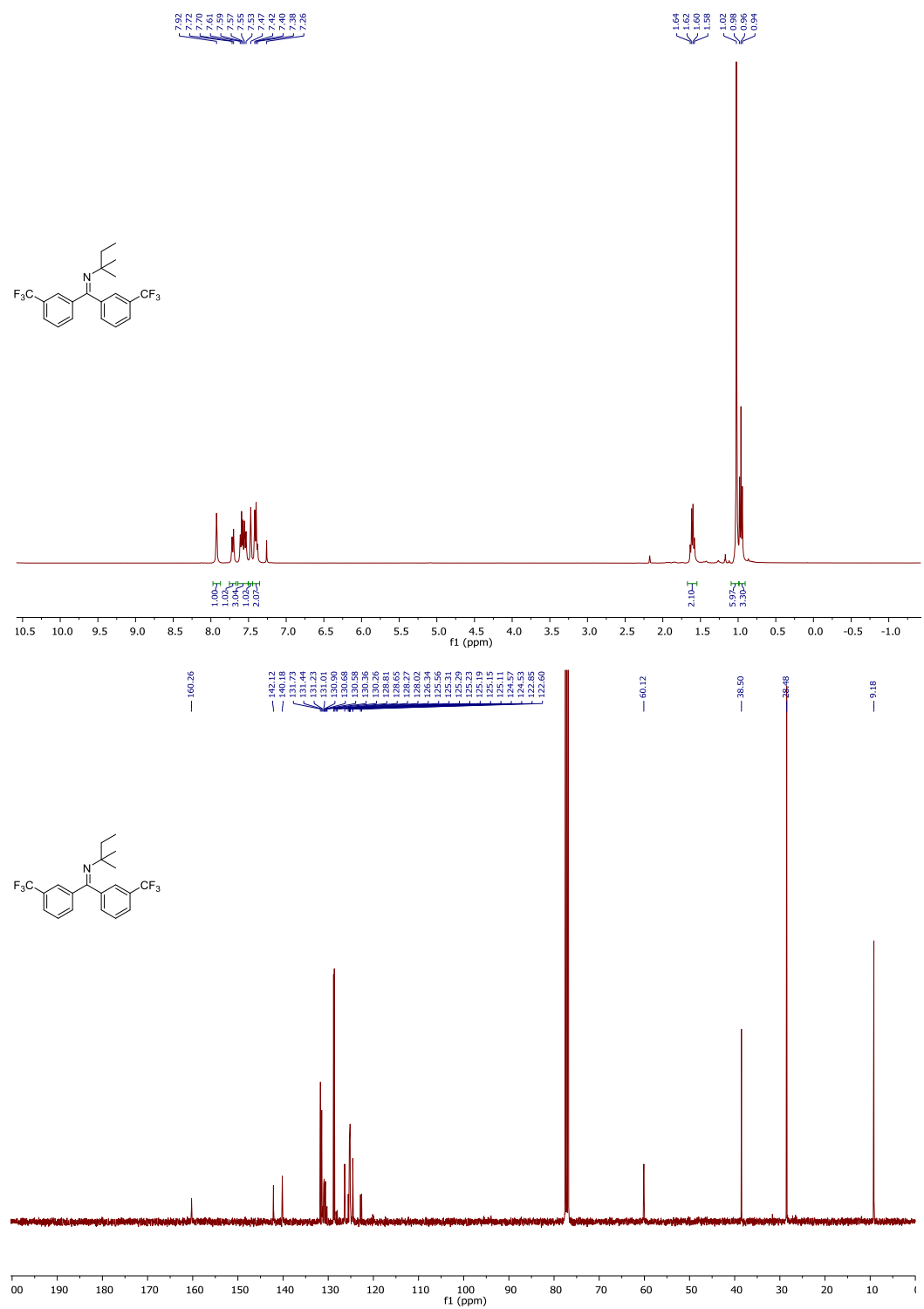


Figure S12. NMR spectra of 4b



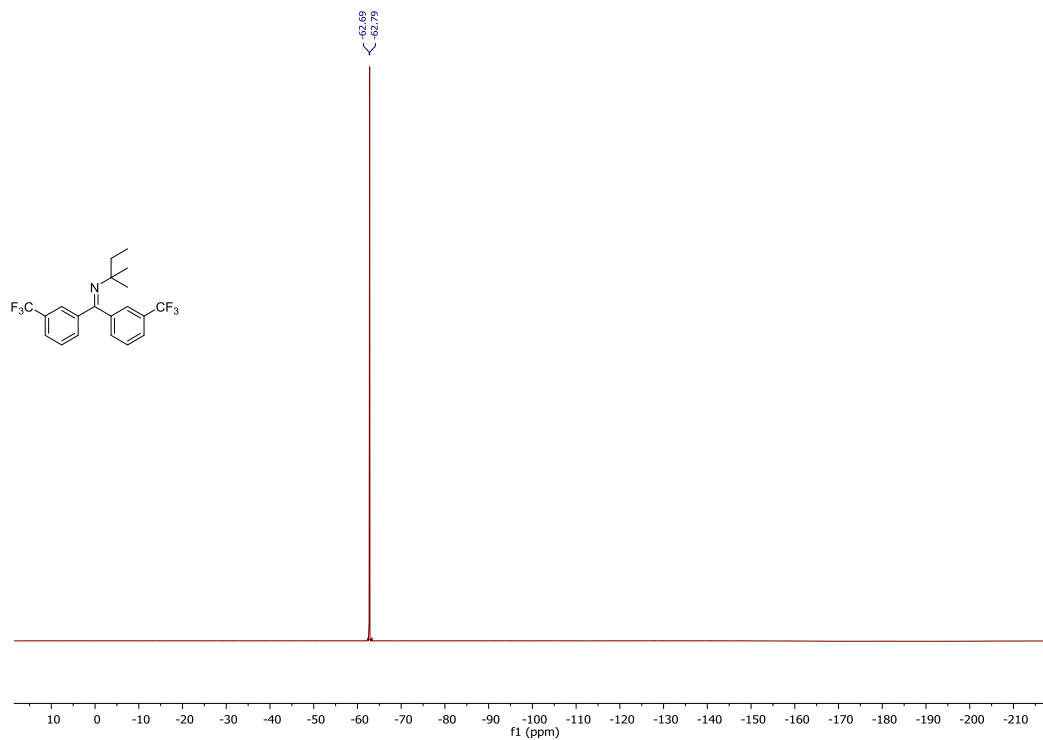
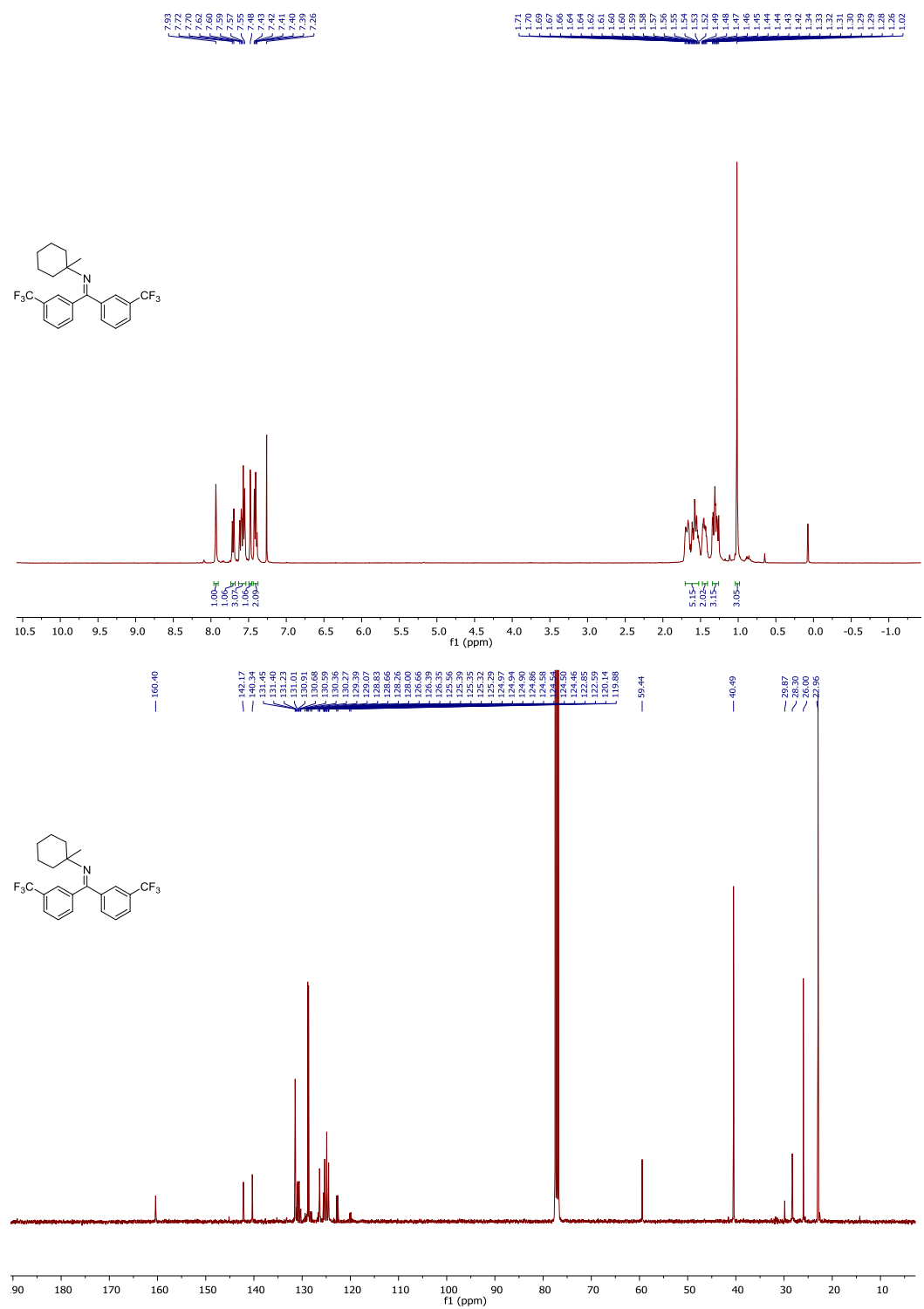


Figure S13. NMR spectra of 4c



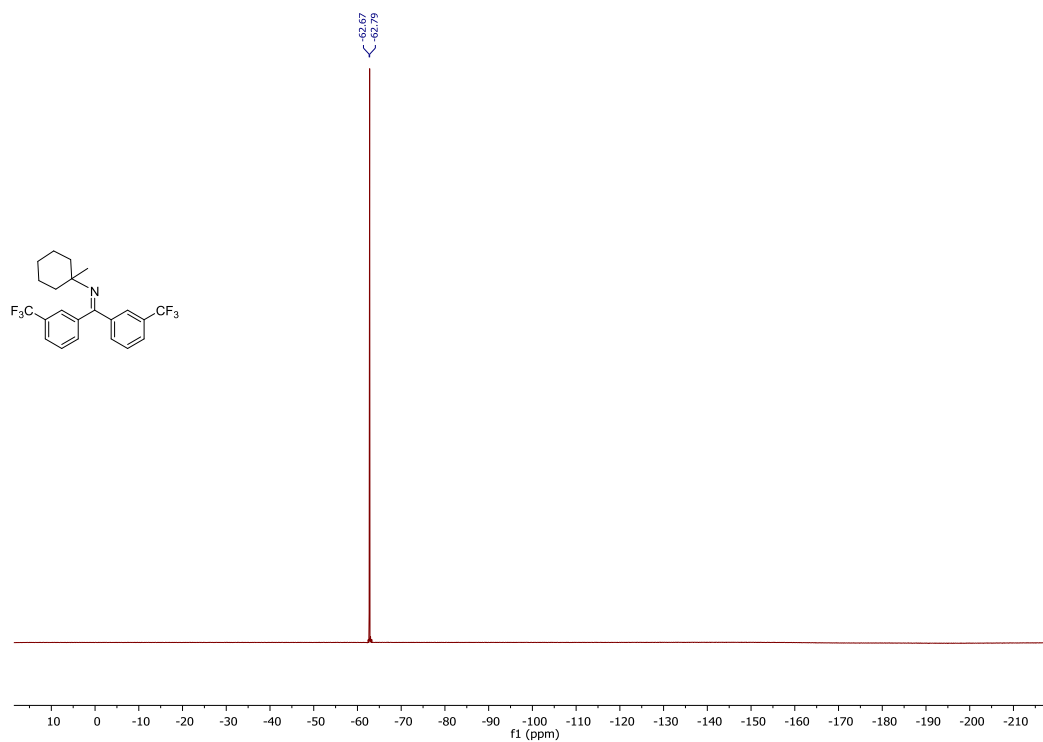
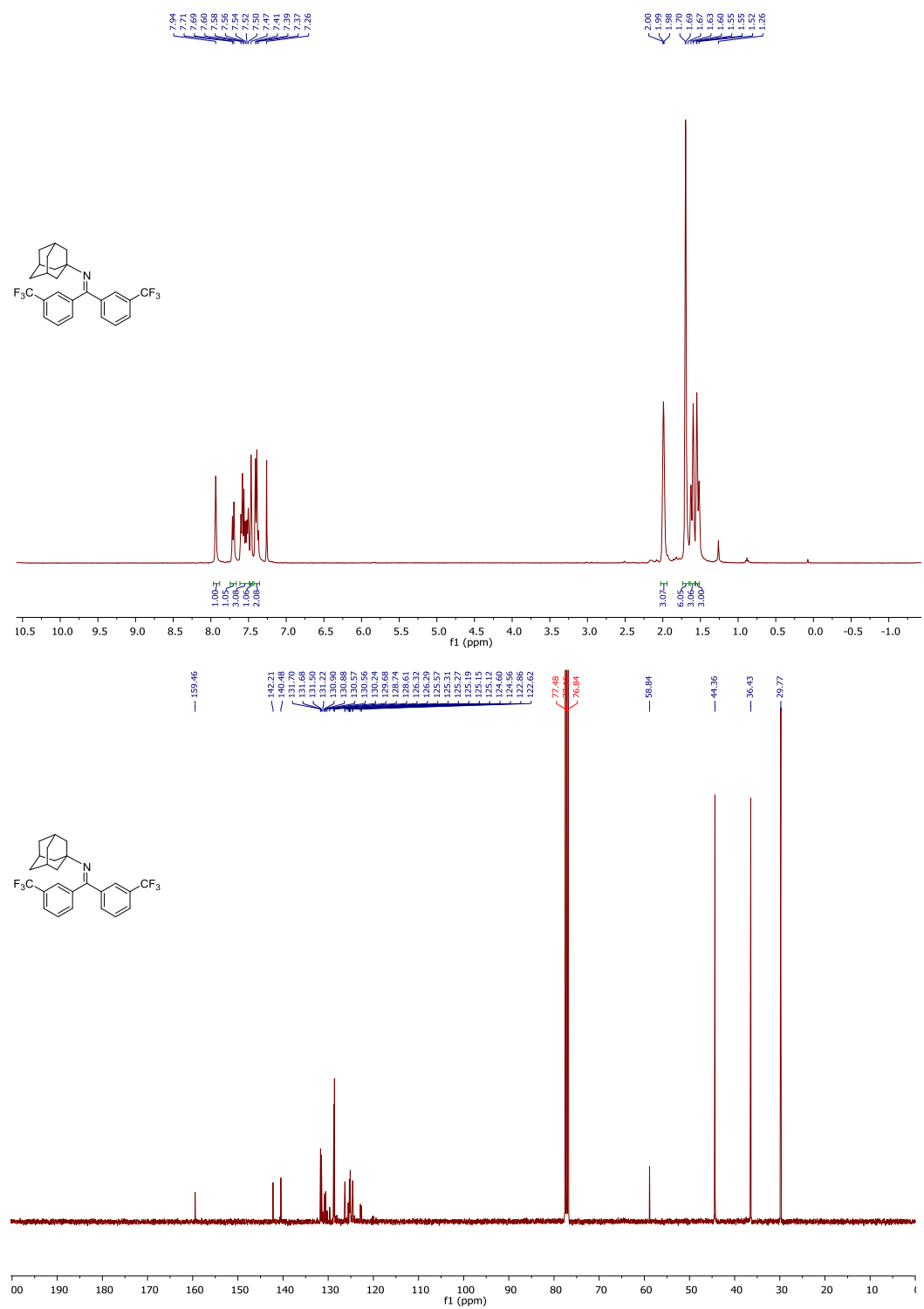


Figure S14. NMR spectra of 4d



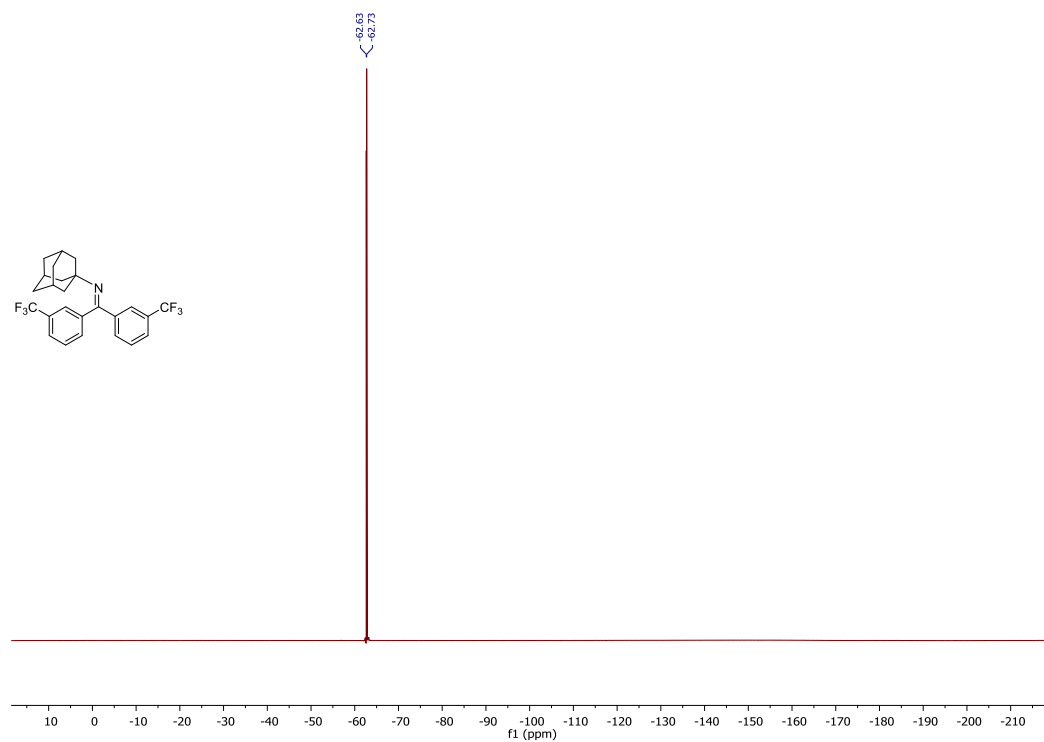


Figure S15. NMR spectra of 4e

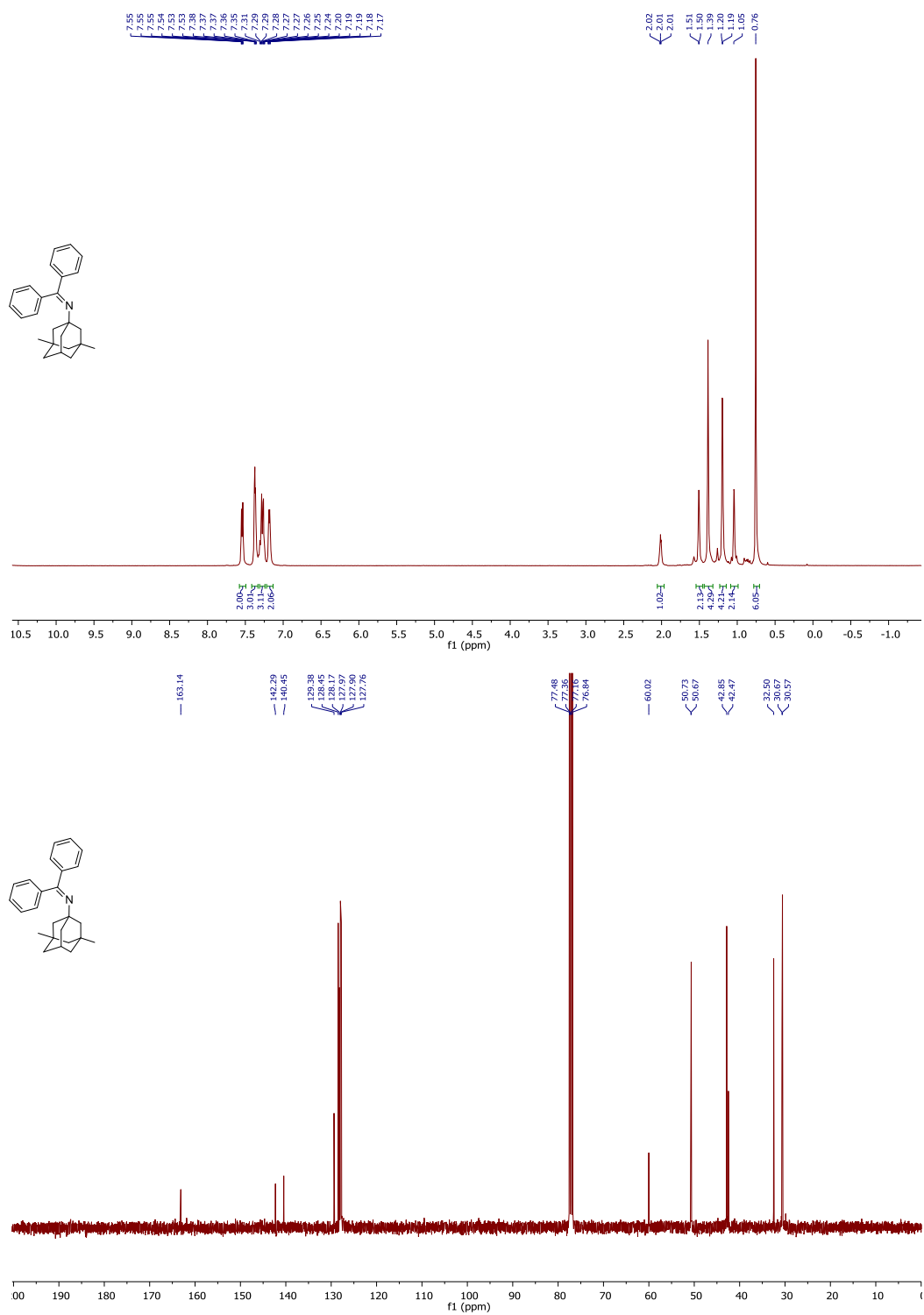
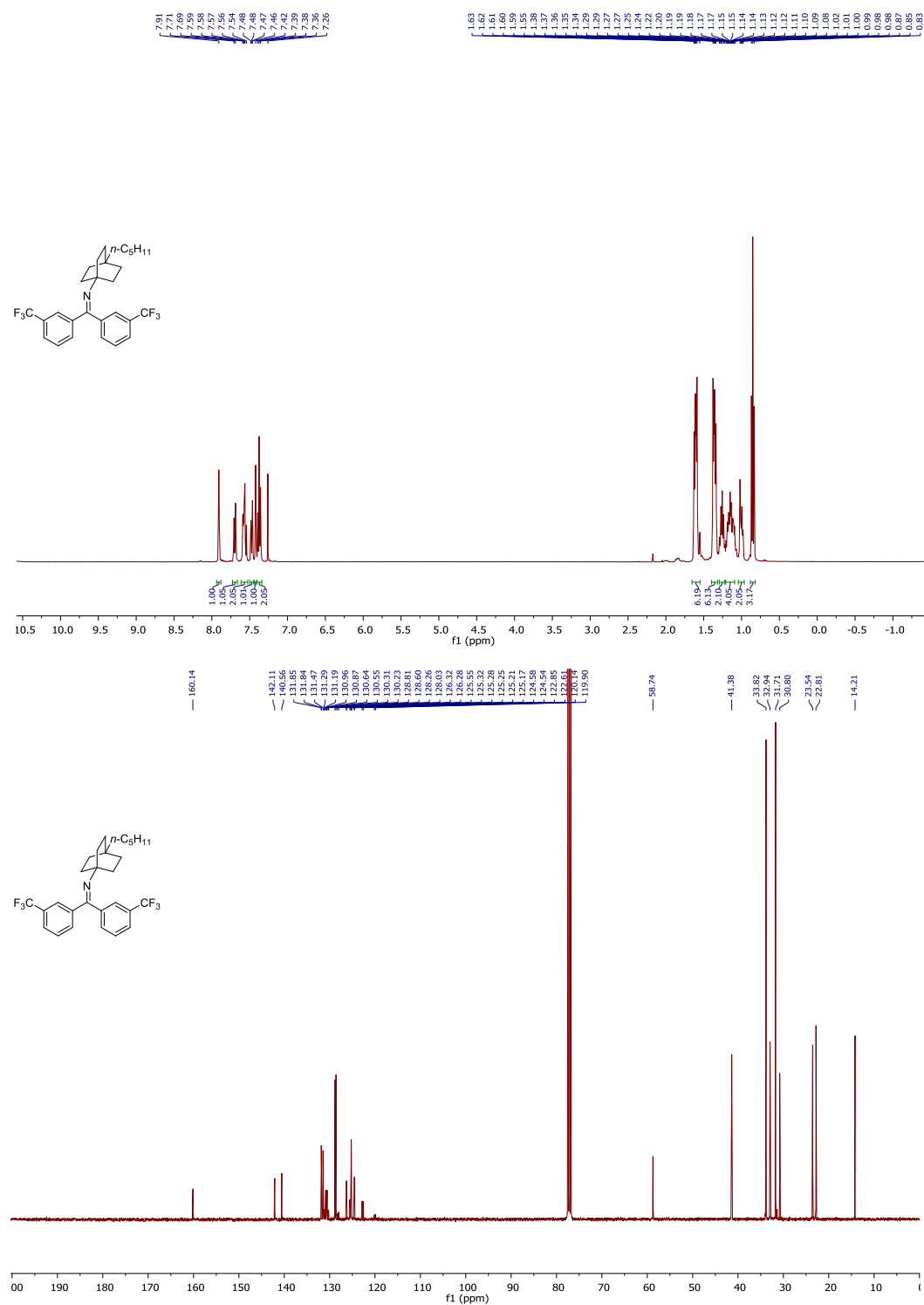


Figure S16. NMR spectra of 4f



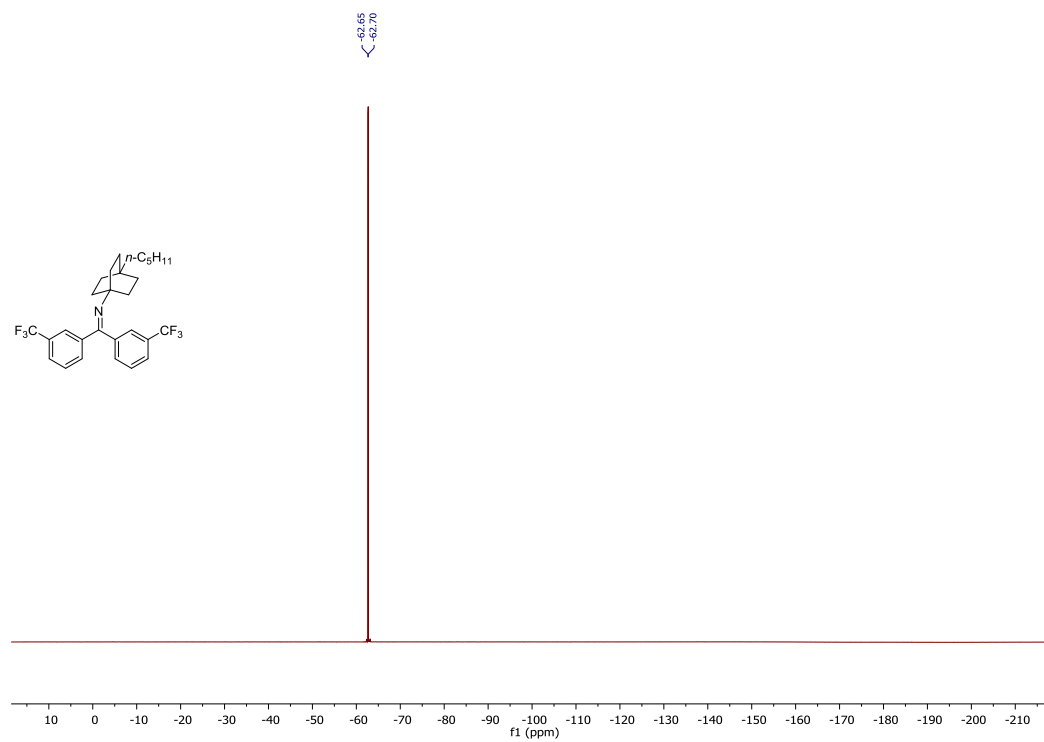
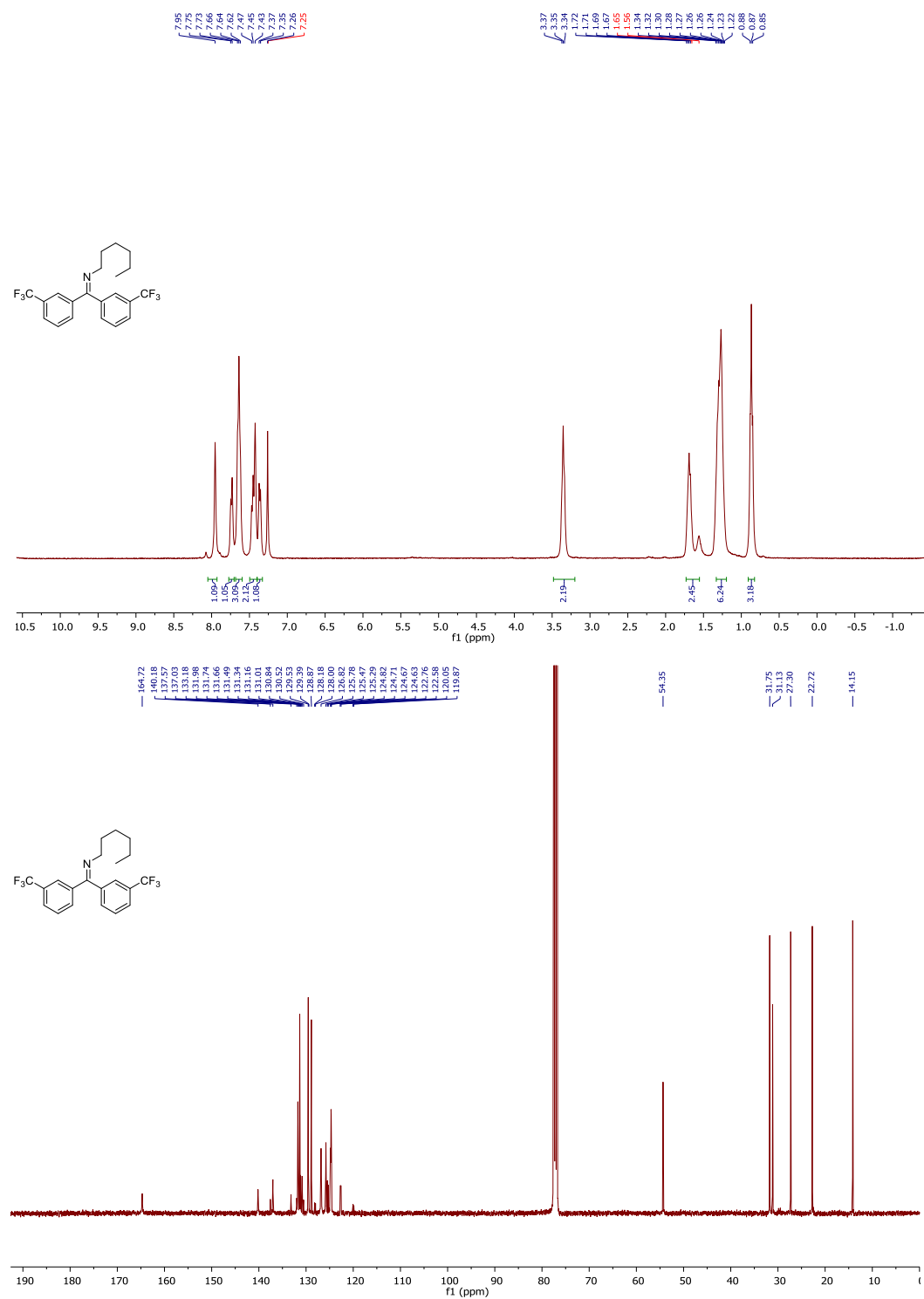


Figure S17. NMR spectra of 5a



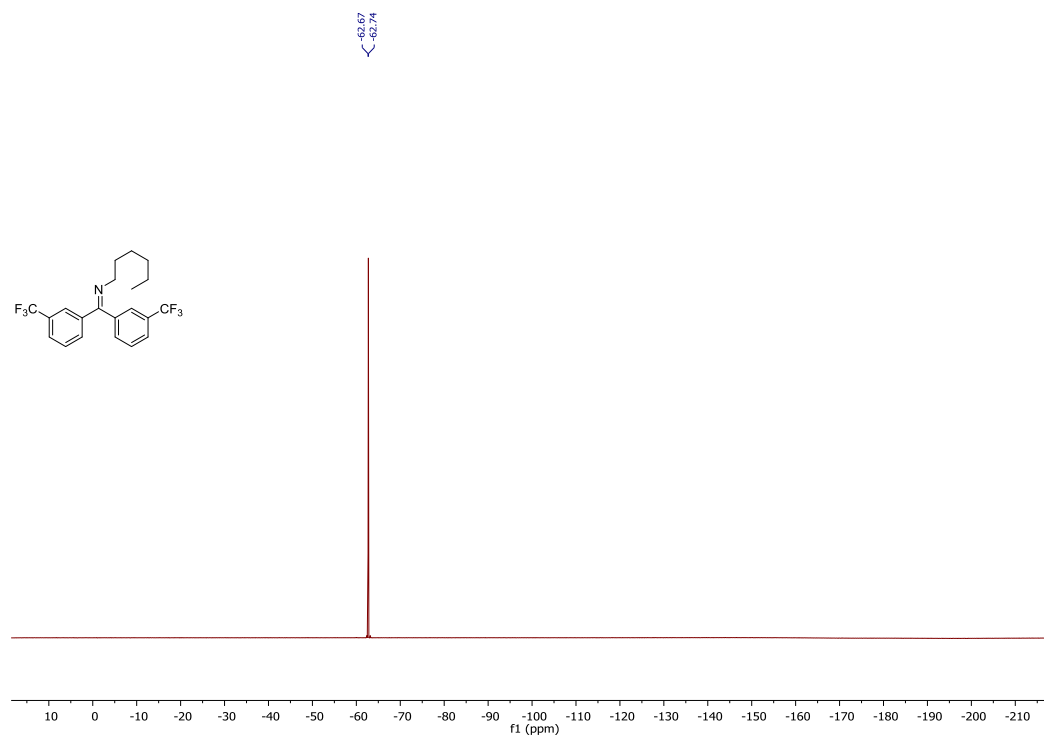


Figure S18. NMR spectra of 5b

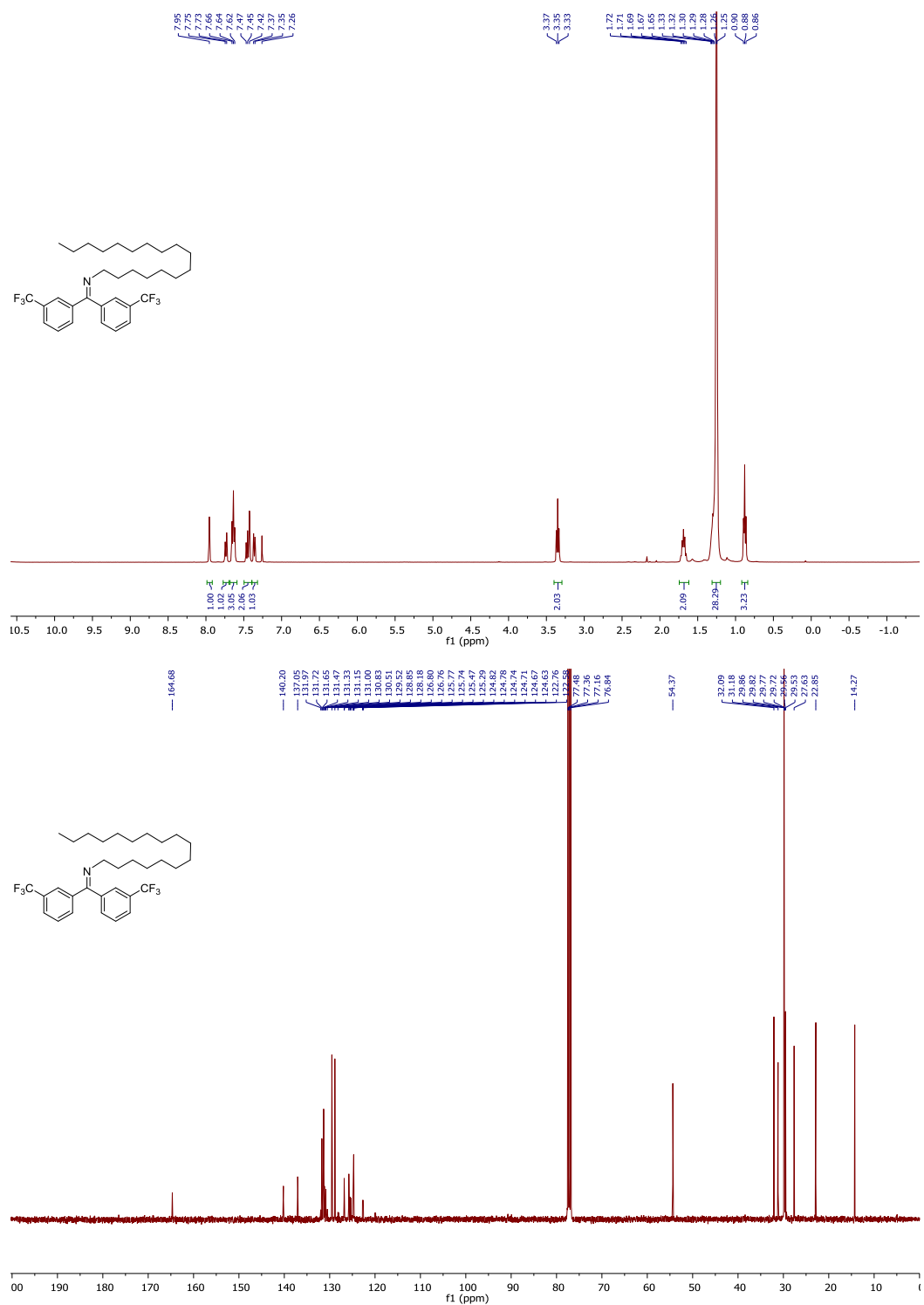
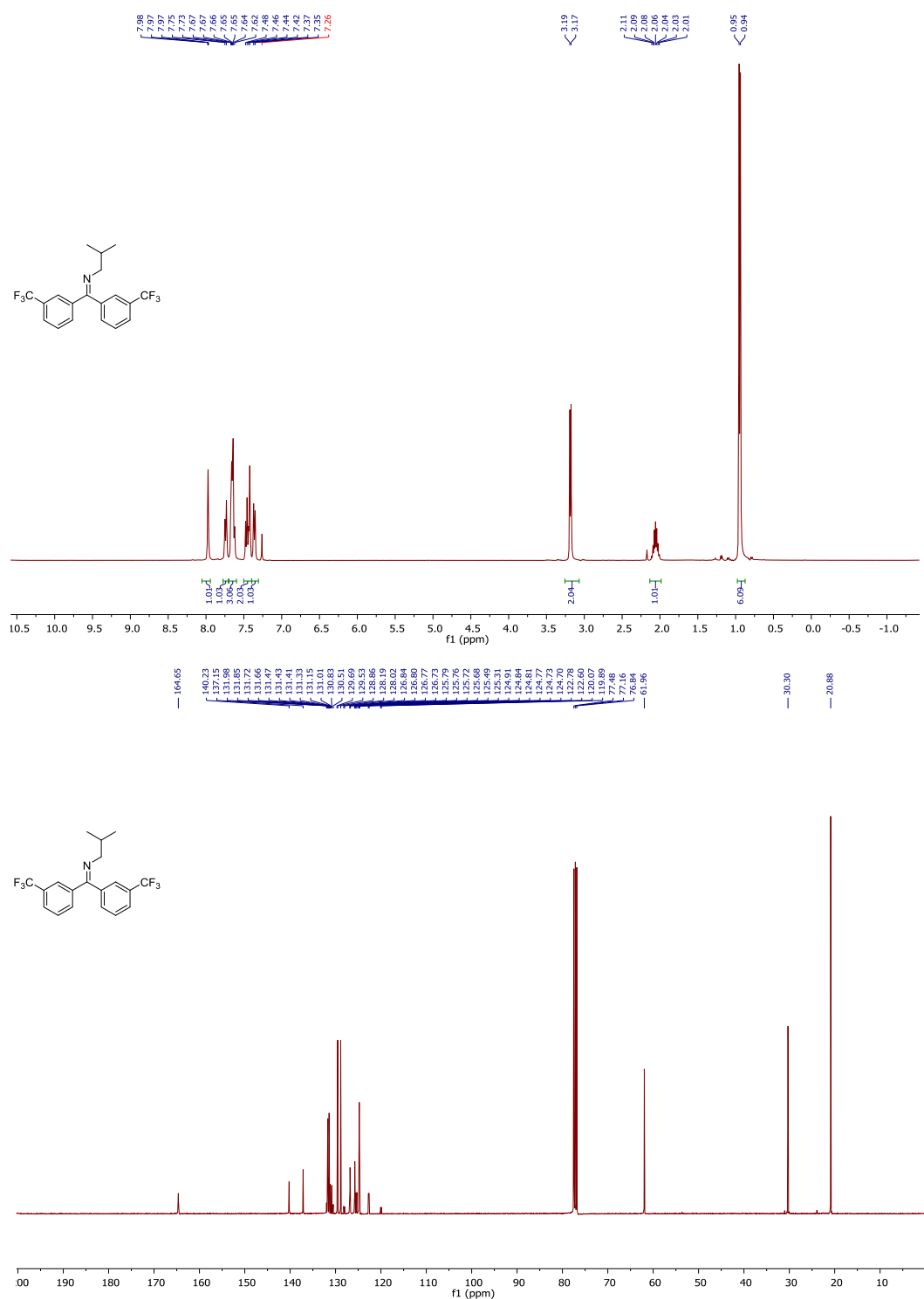




Figure S19. NMR spectra of 5c



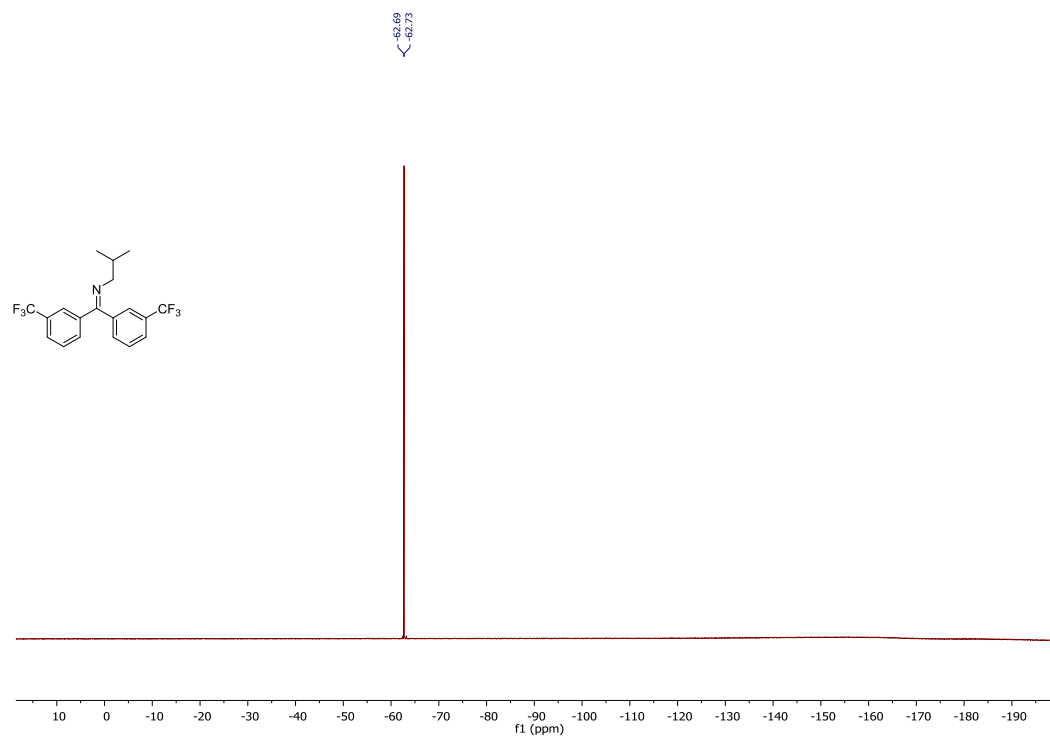
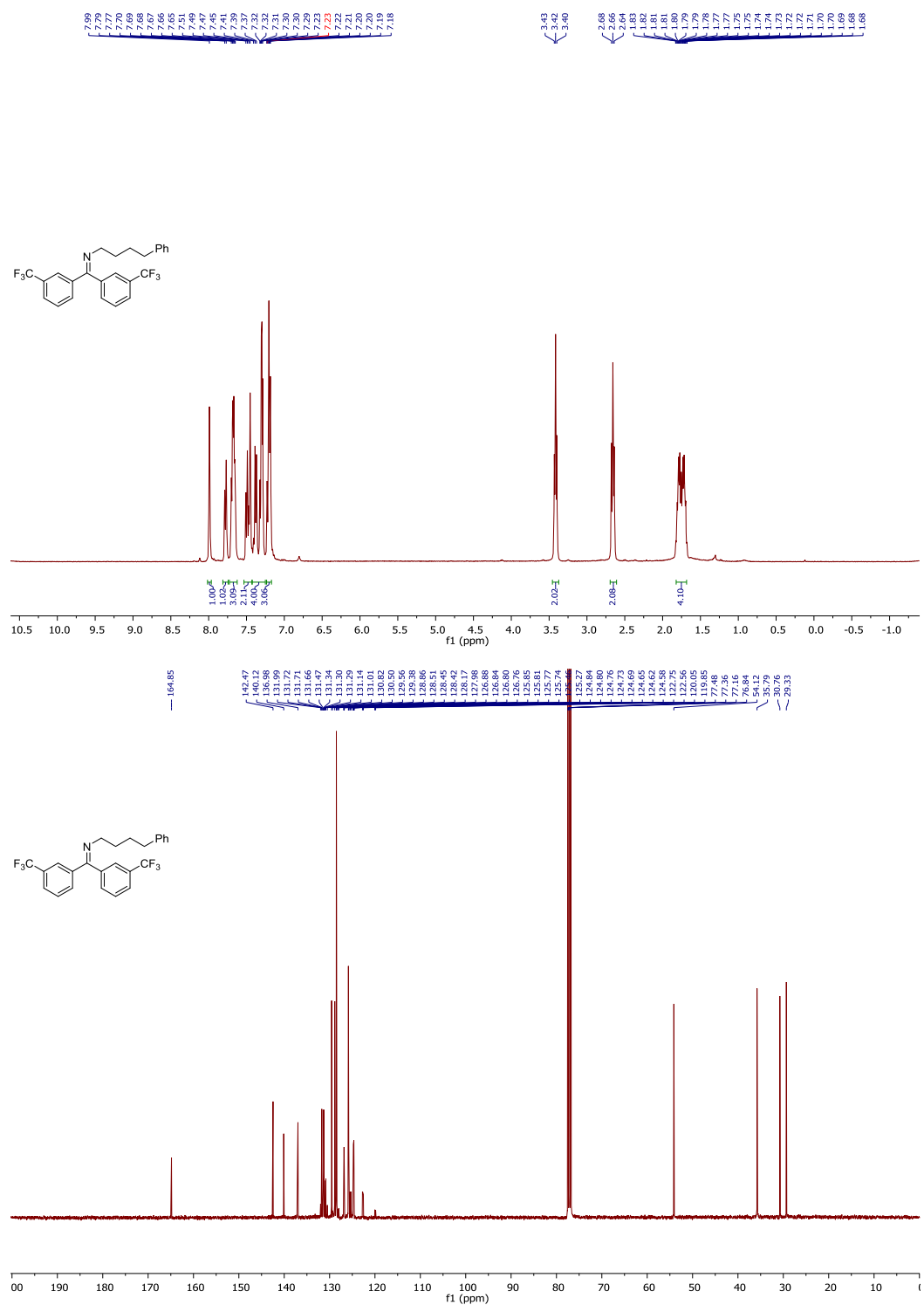


Figure S20. NMR spectra of 5d



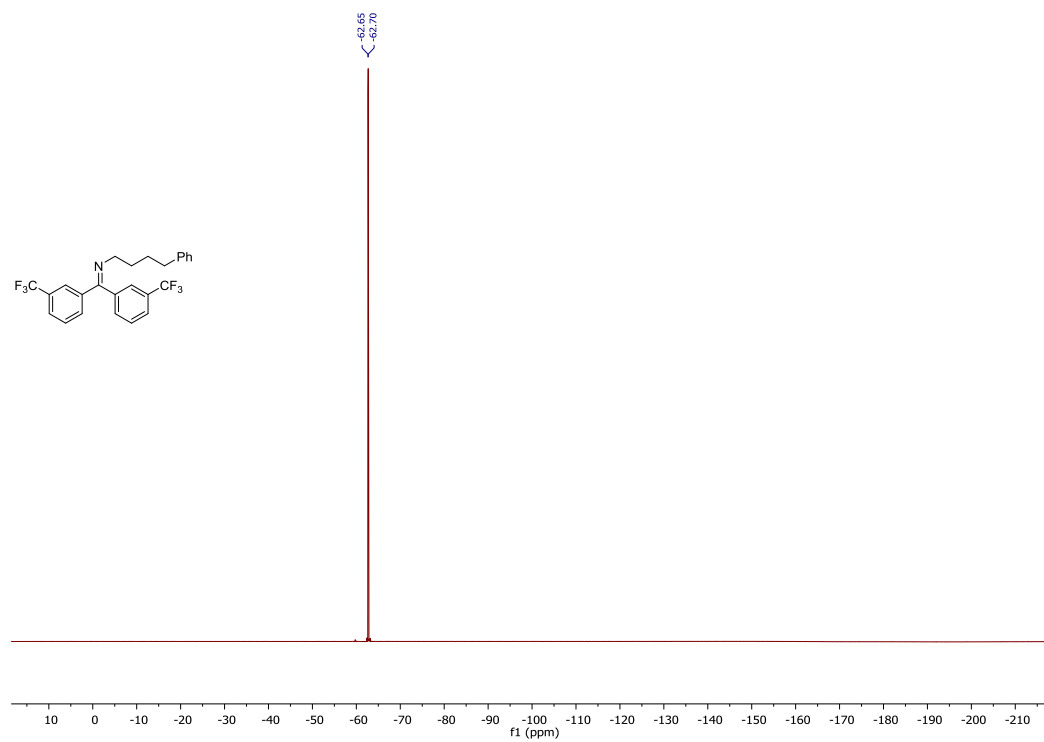
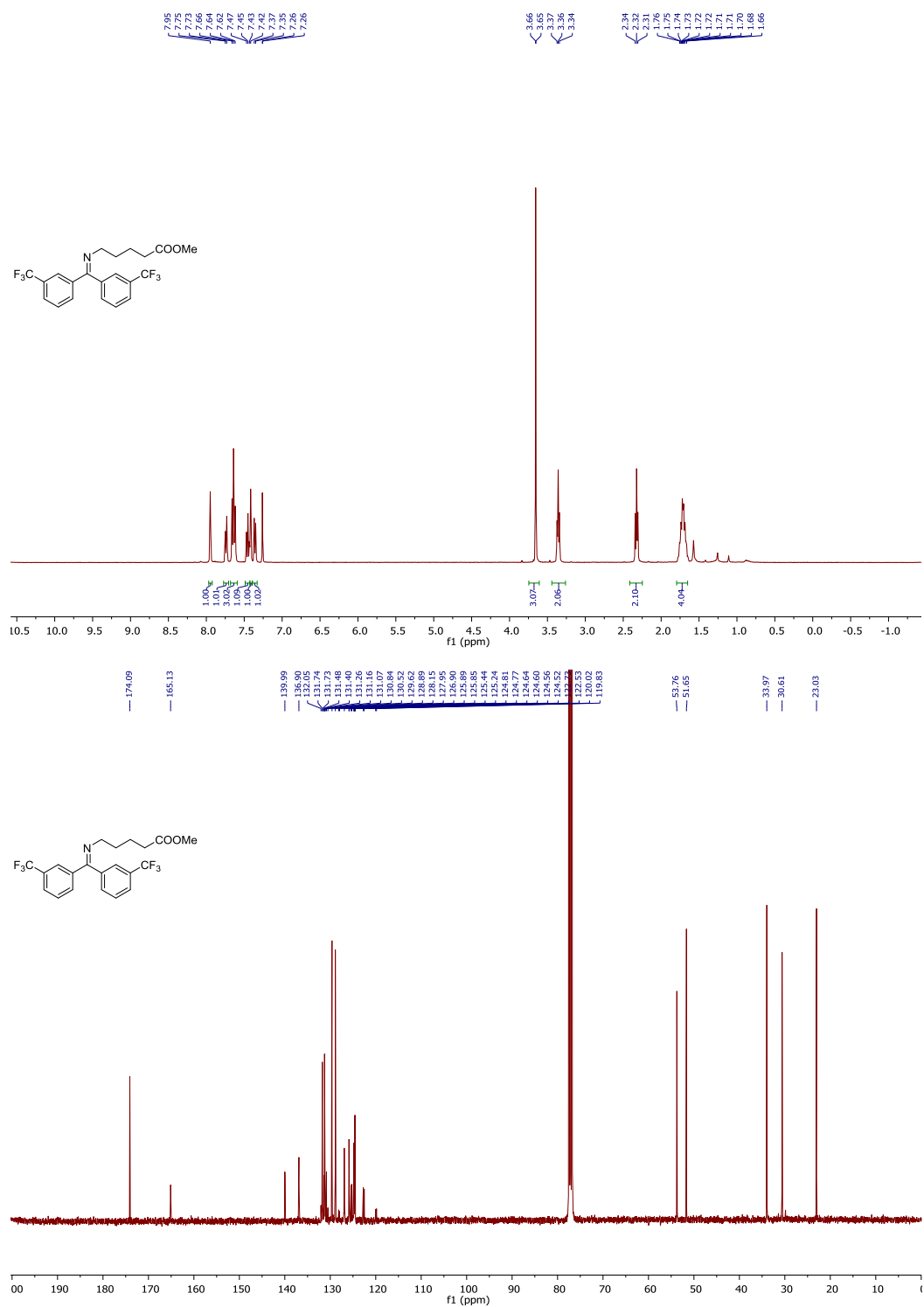


Figure S21. NMR spectra of 5e



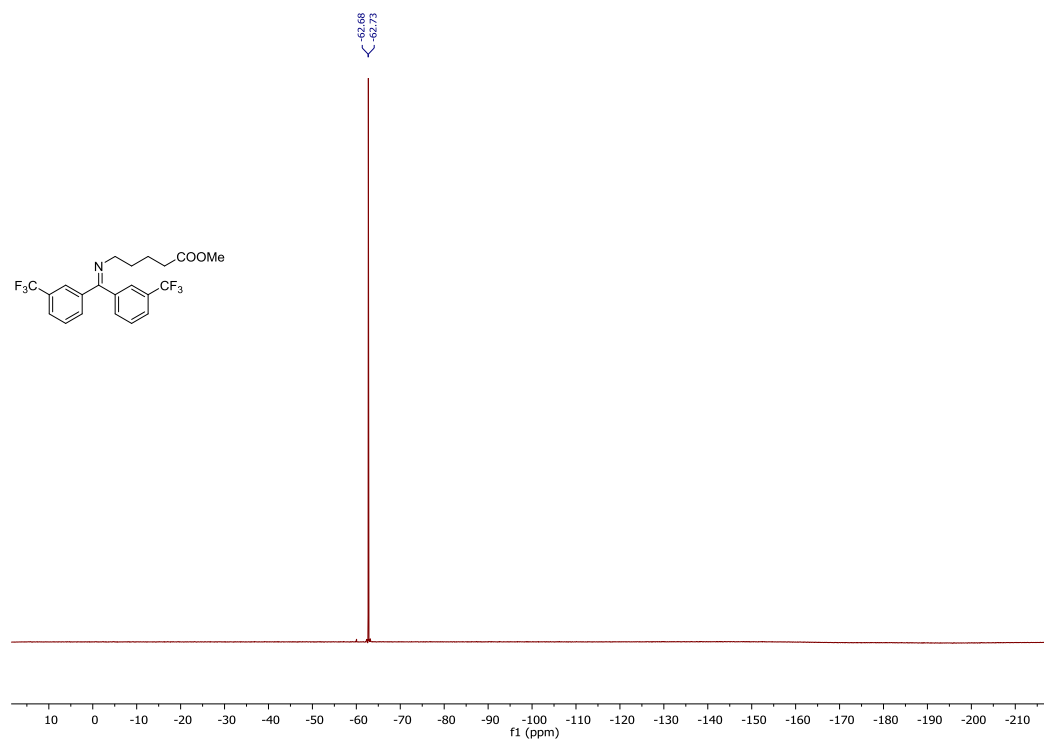
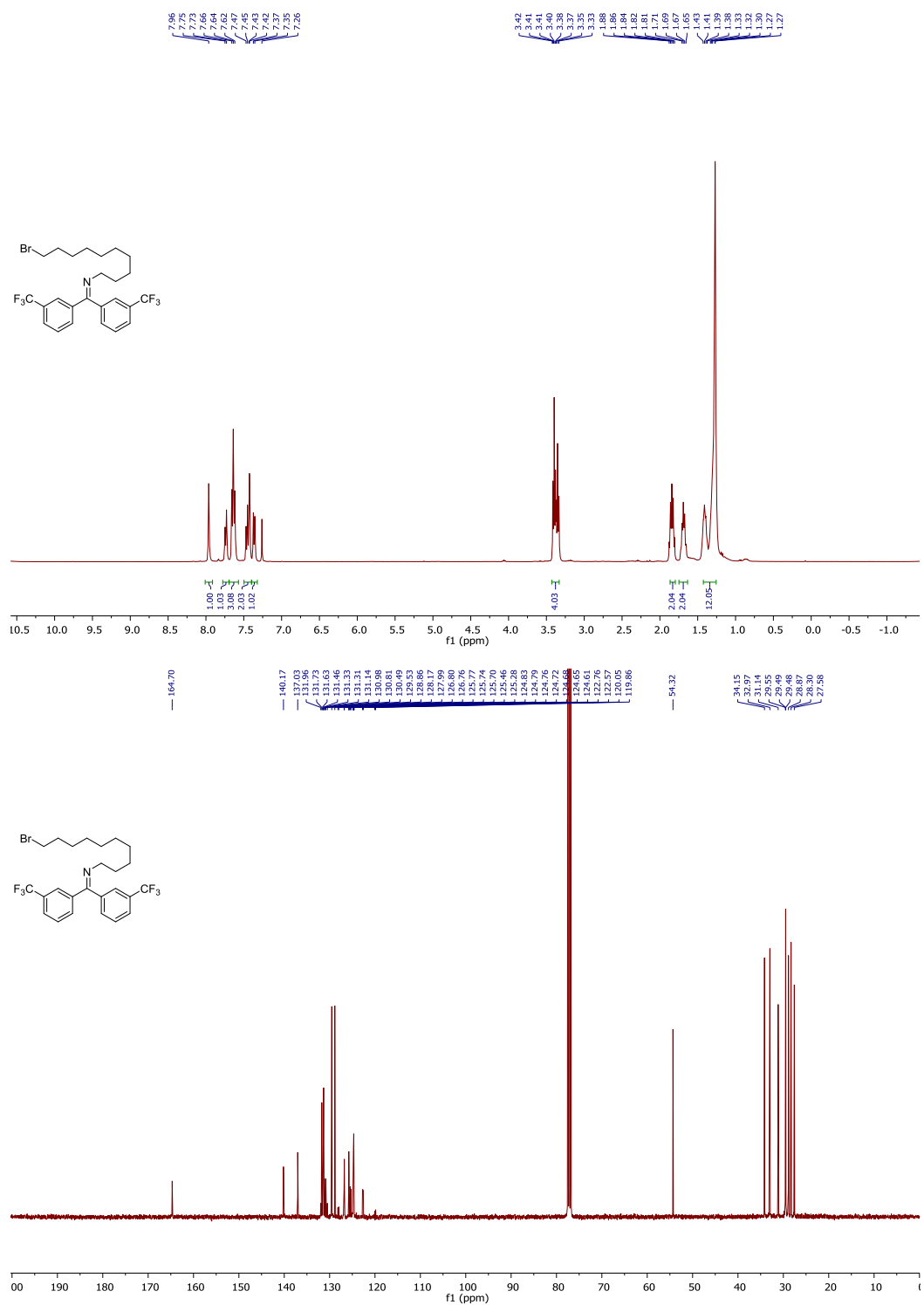


Figure S22. NMR spectra of 5f



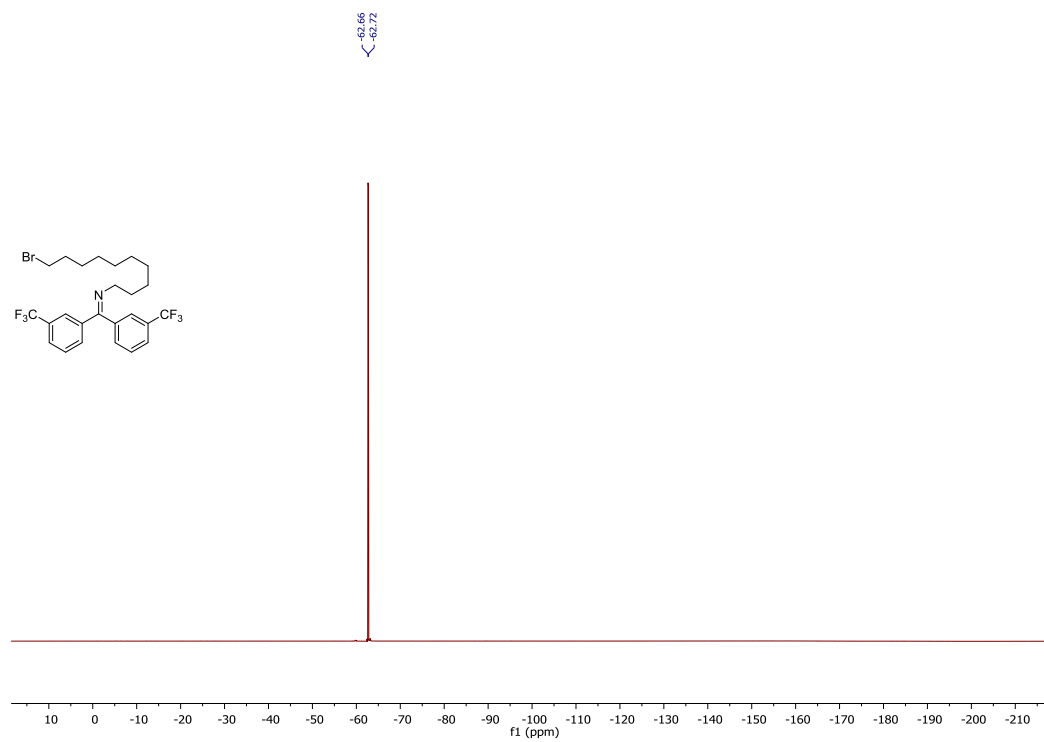
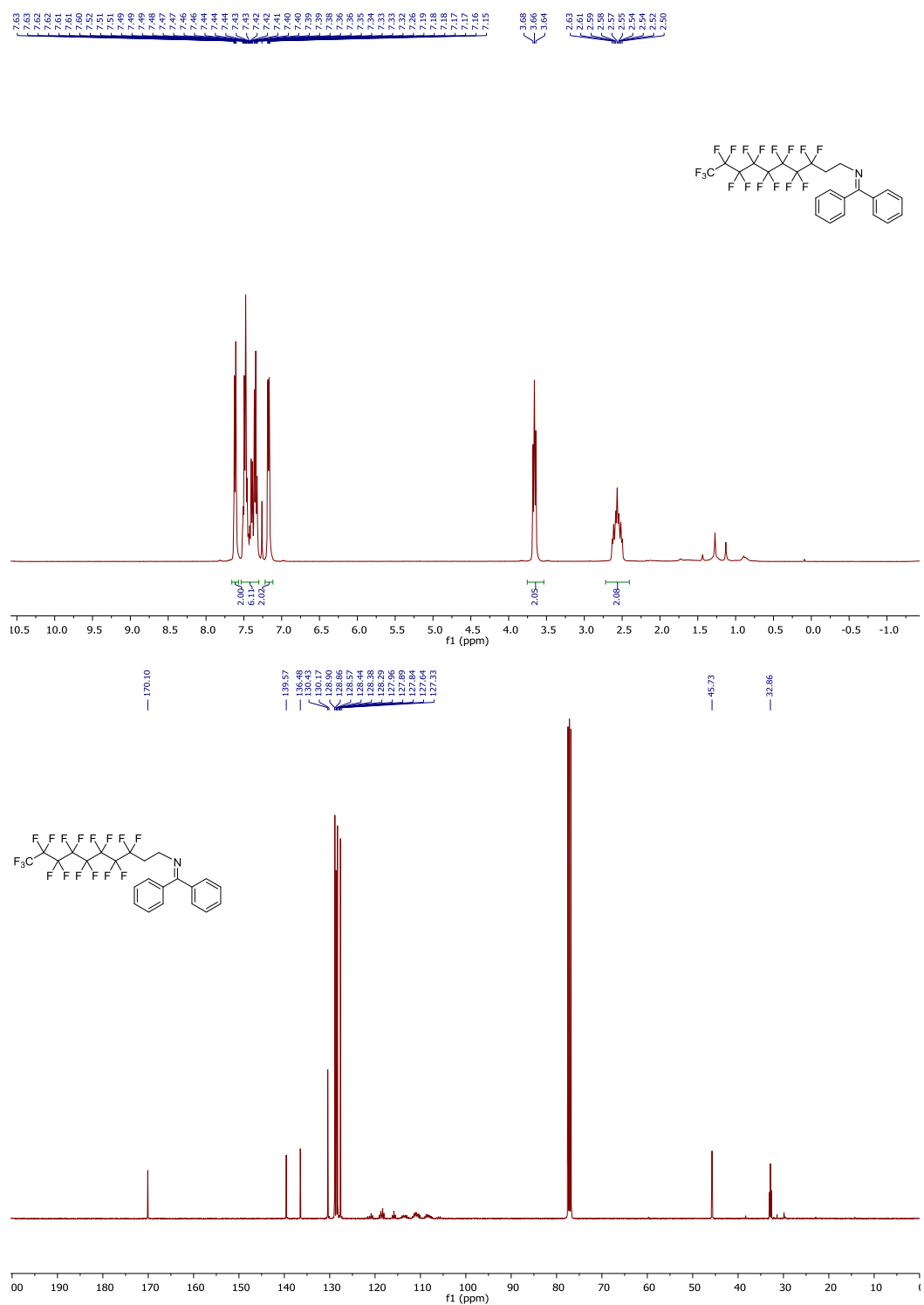


Figure S23. NMR spectra of 5g



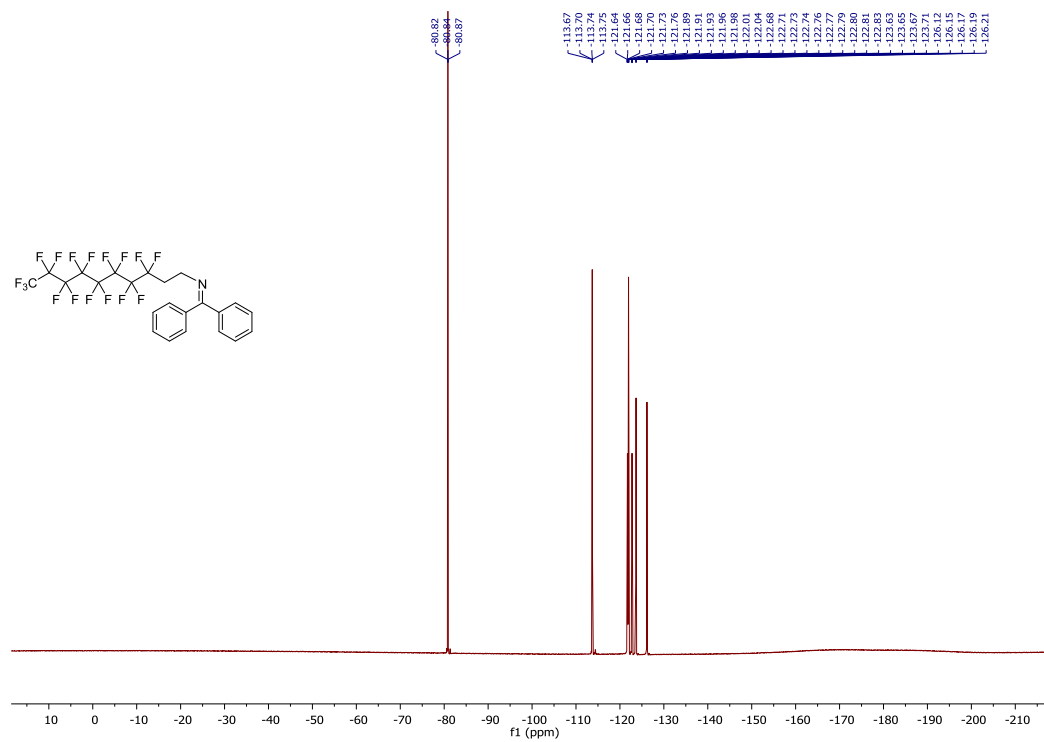
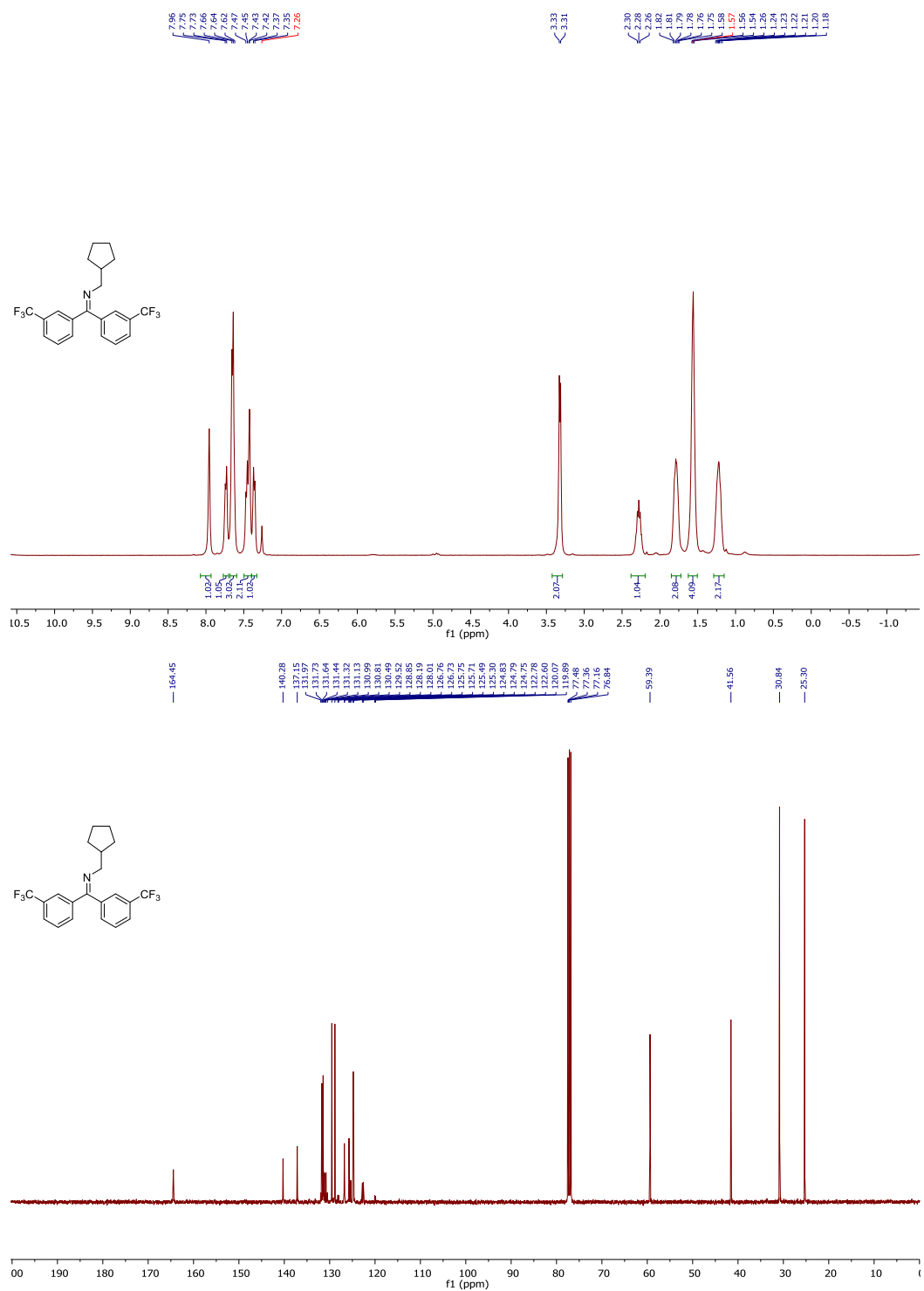


Figure S24. NMR spectra of 5h



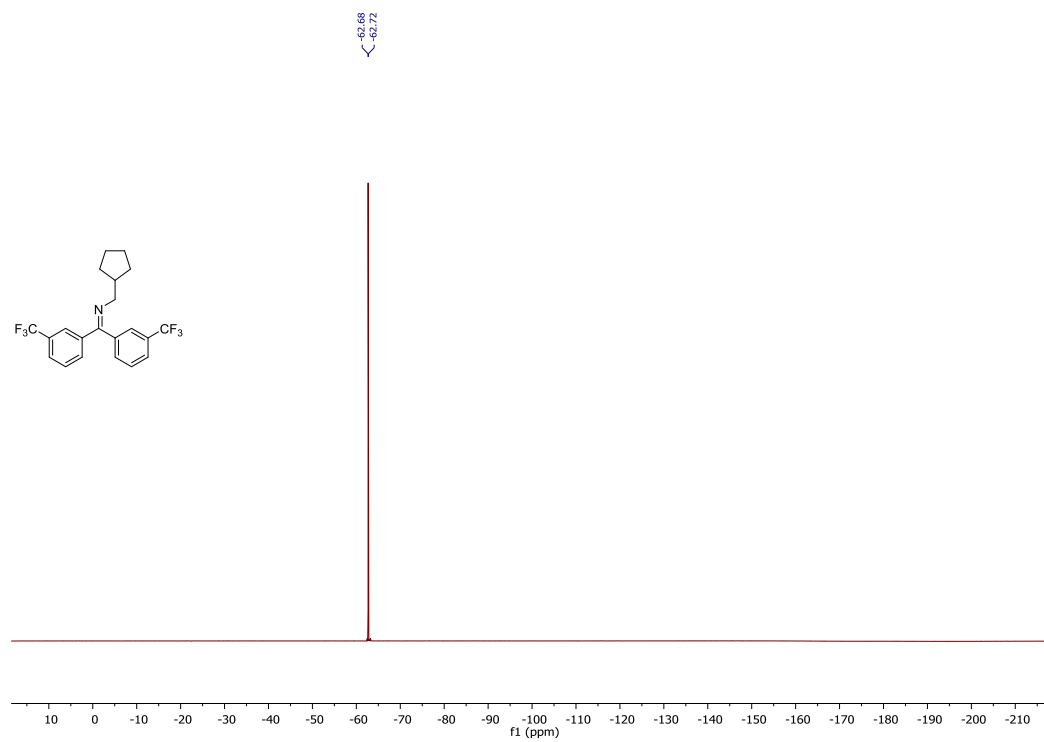
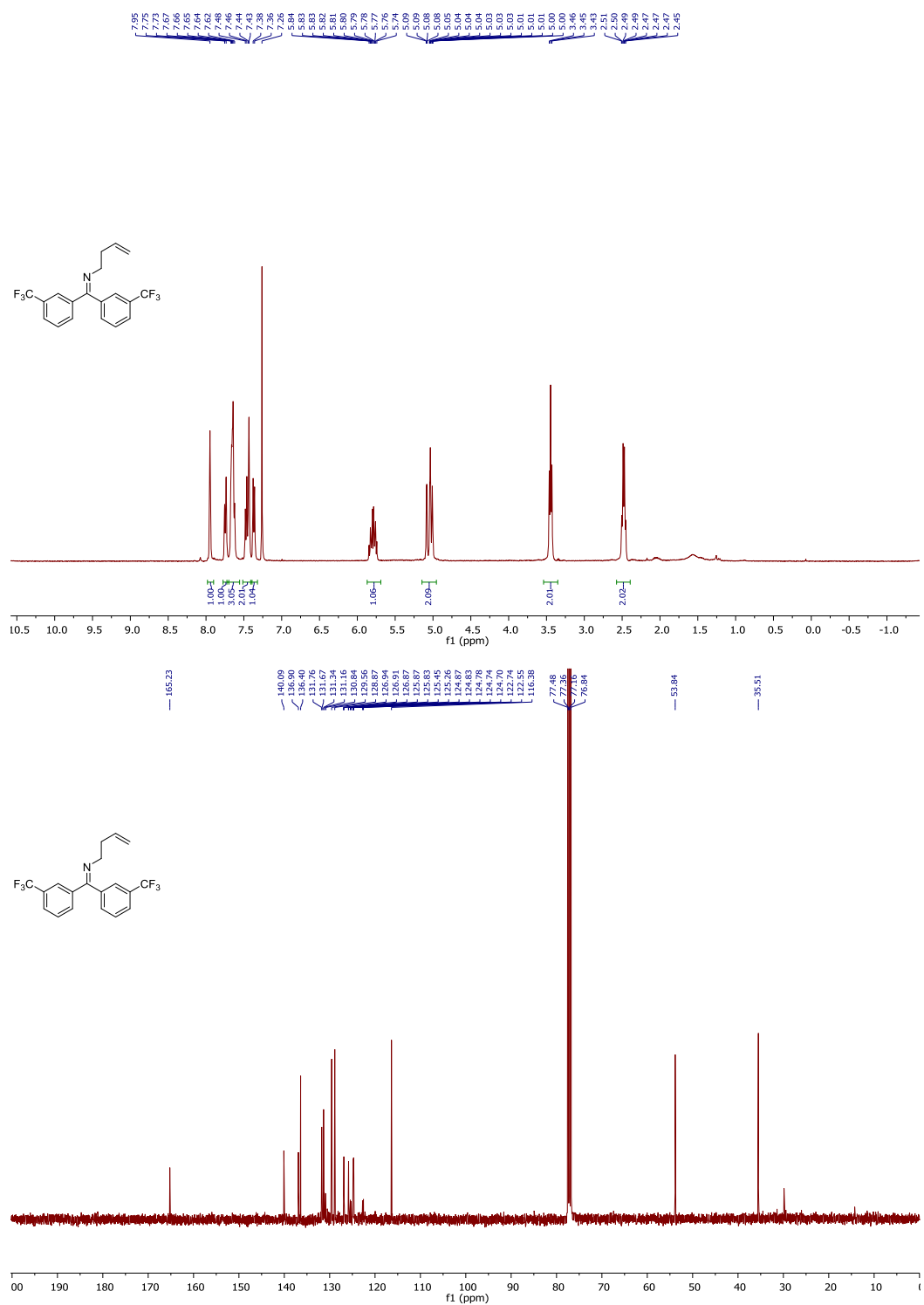


Figure S25. NMR spectra of 5i



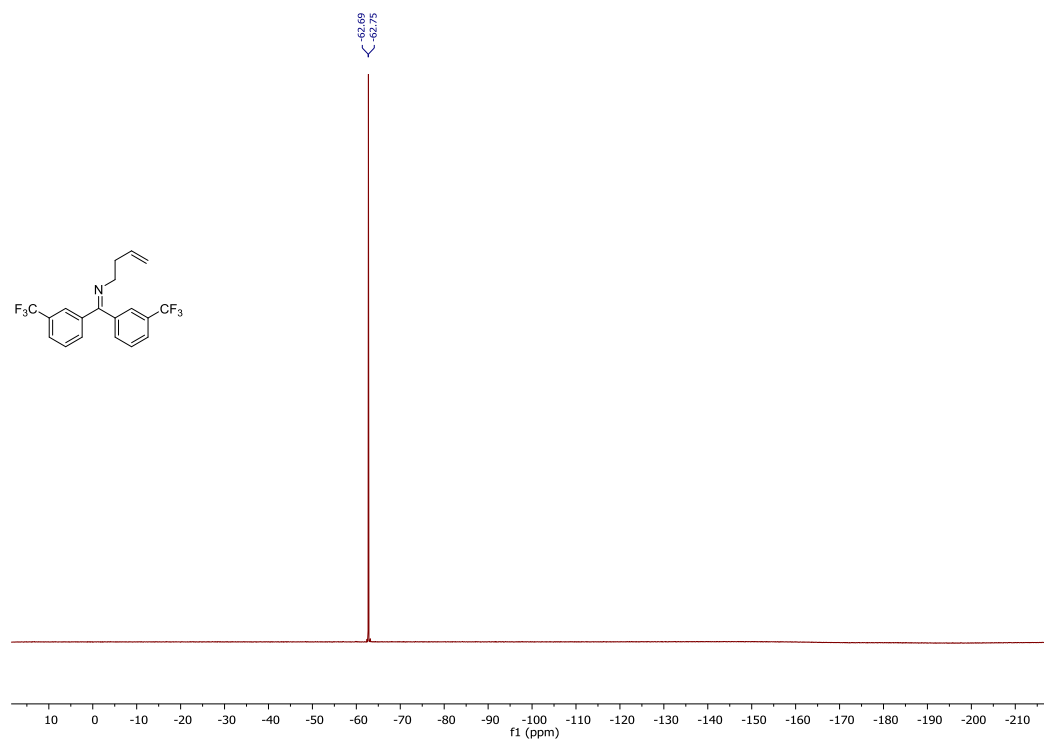
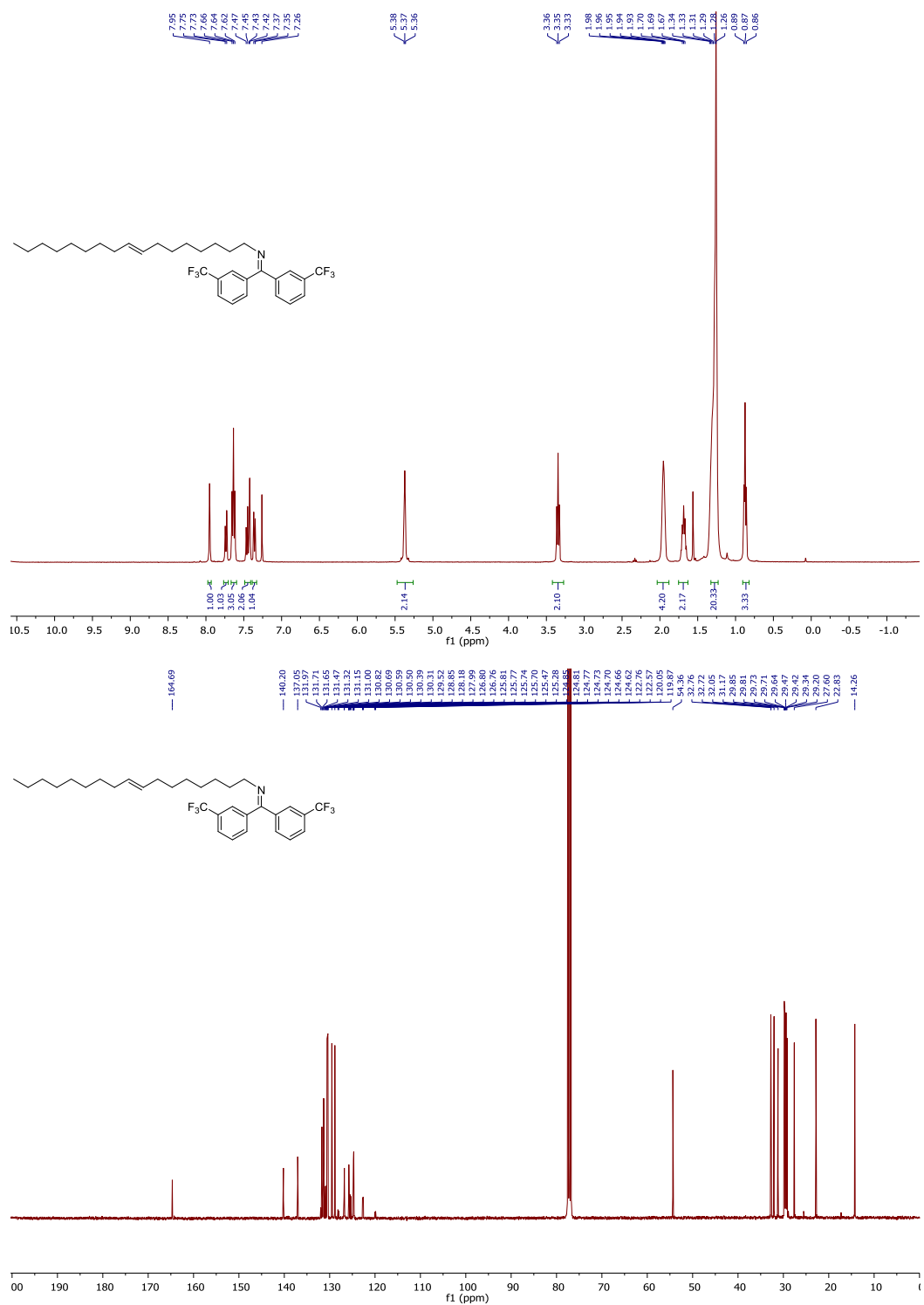


Figure S26. NMR spectra of 6a



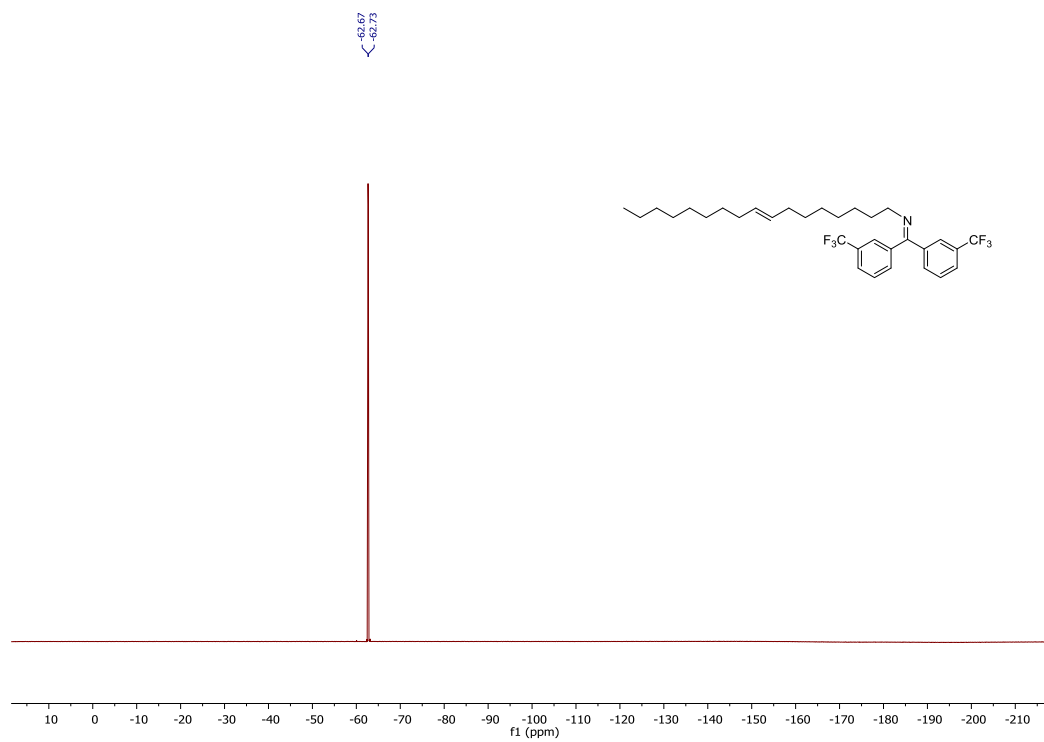
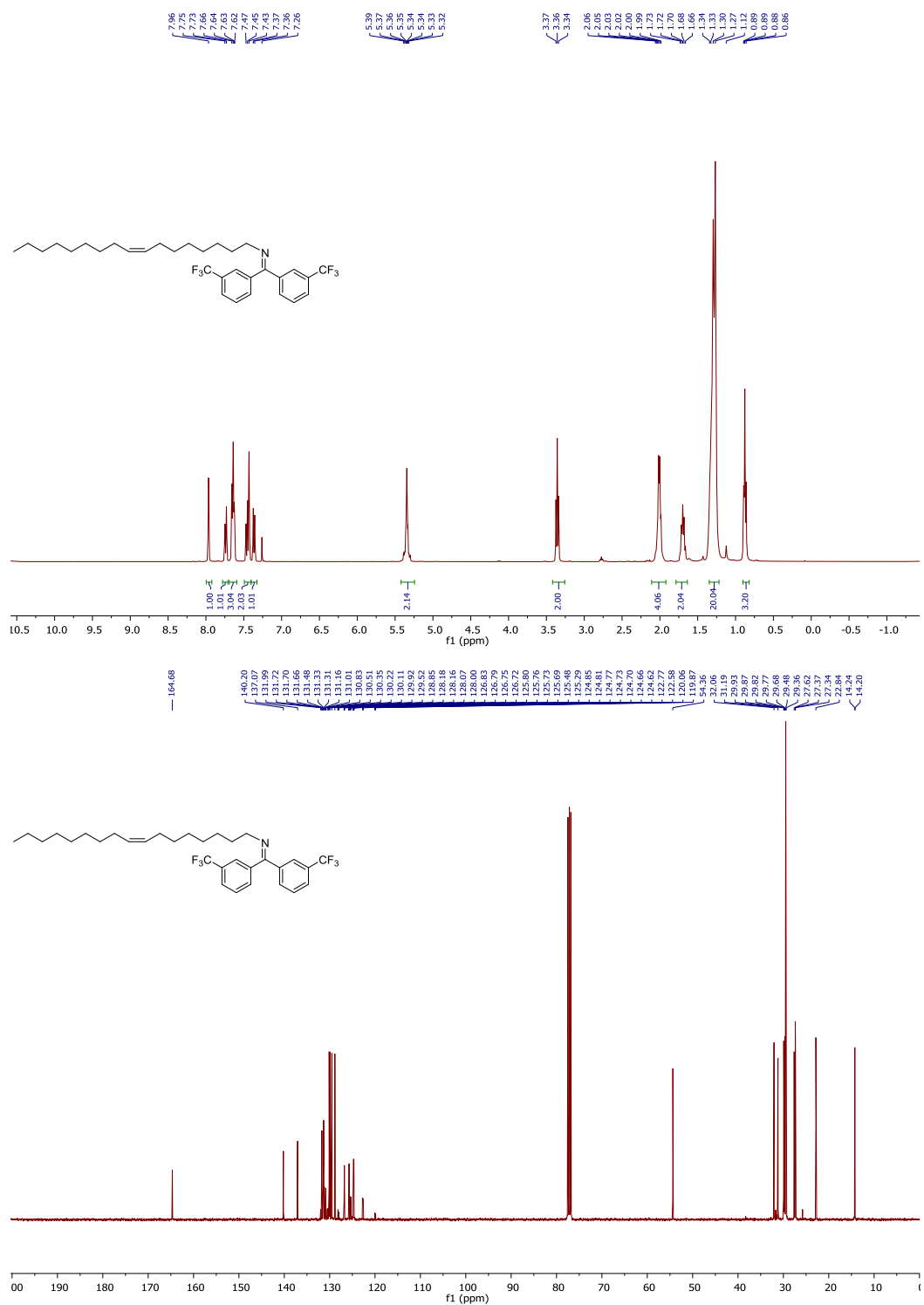


Figure S27. NMR spectra of 6b



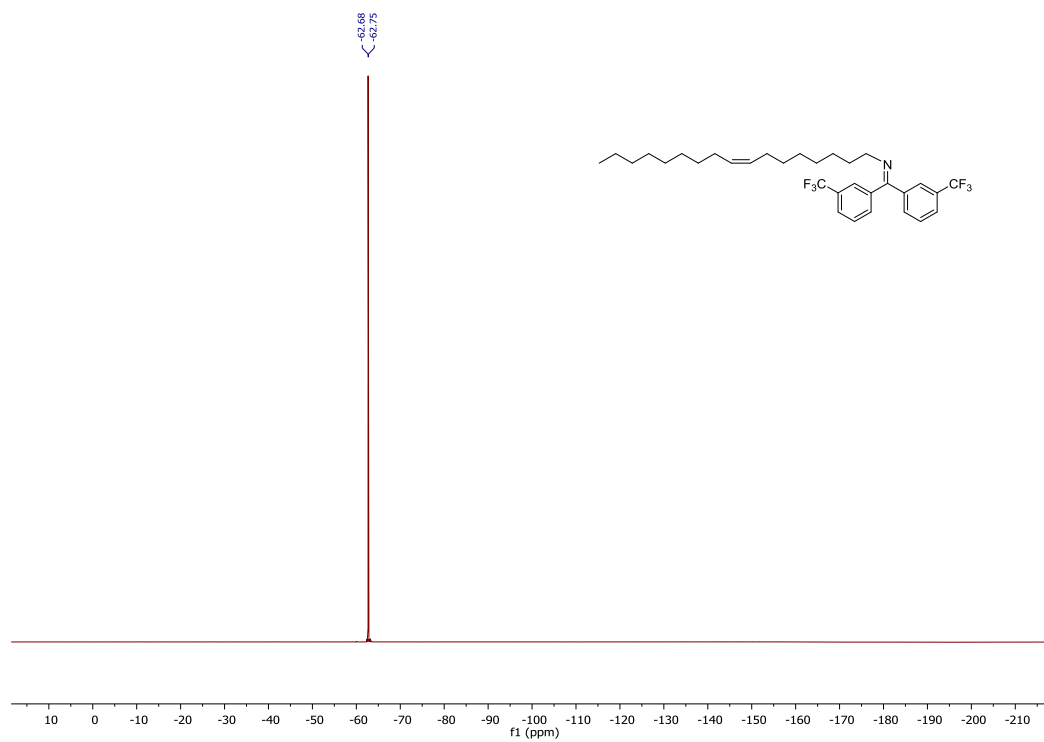
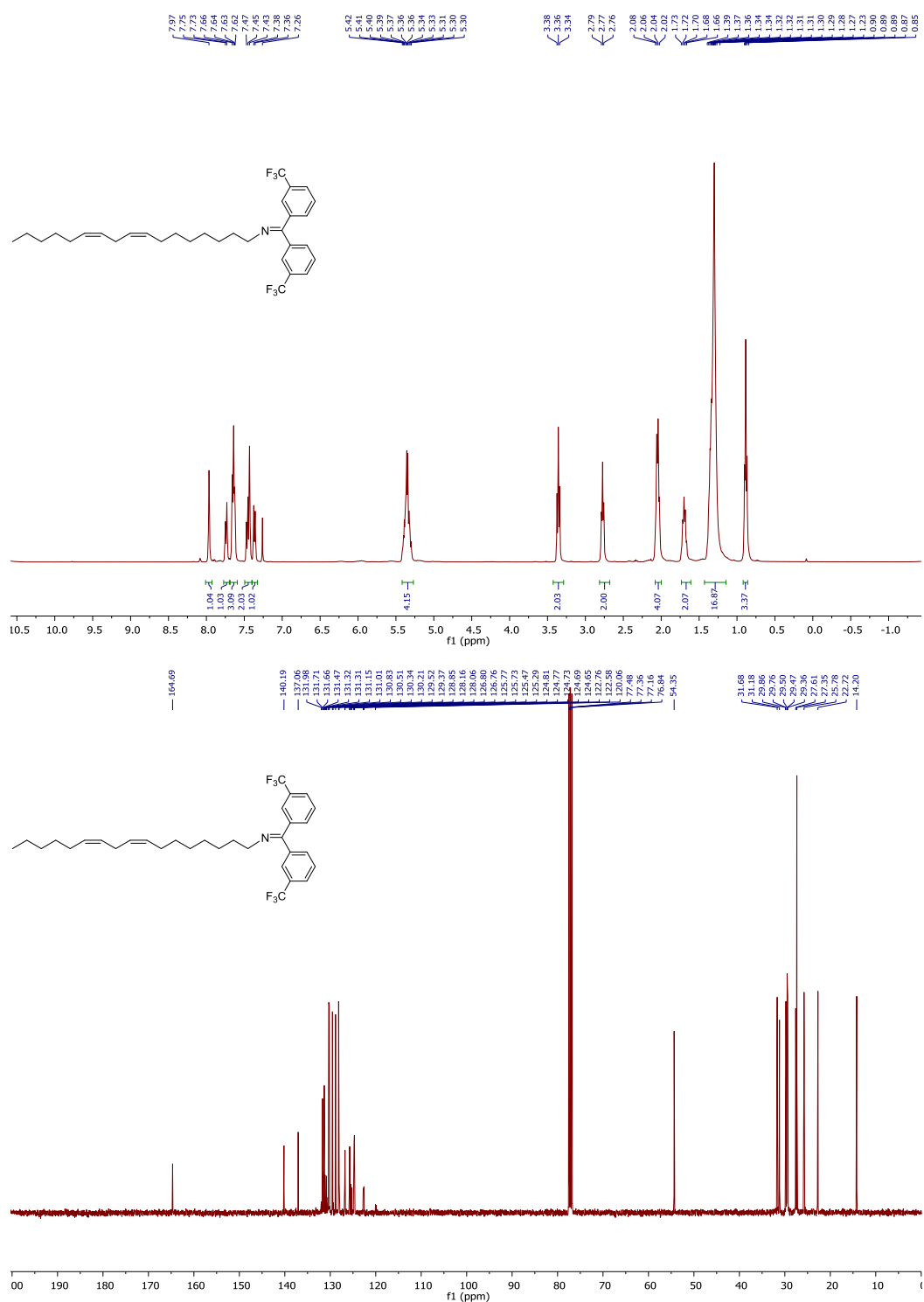
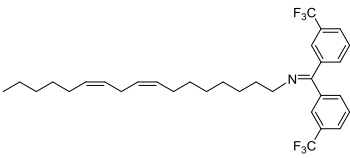


Figure S28. NMR spectra of 6c





Chemical structure of compound 10:

CC12CCC(=O)C1(C)CCC(=O)C2C(C)CCN=C(c1ccc(C(F)(F)F)cc1)c3ccc(C(F)(F)F)cc3

¹H NMR (400 MHz, CDCl₃) data:

Chemical Shift (ppm)	Integration
10.40 (s, 1H)	1.00
8.00 (s, 1H)	1.00
7.70 (s, 1H)	1.00
7.50 (s, 1H)	1.00
7.30 (s, 1H)	1.00
7.10 (s, 1H)	1.00
4.10 (s, 2H)	0.95
3.50 (s, 2H)	0.99
3.00 (s, 2H)	1.00
2.50 (s, 2H)	3.15
2.00 (s, 2H)	16.00
1.80 (s, 2H)	1.12
1.60 (s, 2H)	1.12
1.40 (s, 2H)	2.37
1.20 (s, 2H)	3.02
1.00 (s, 2H)	3.04

¹³C NMR (100 MHz, CDCl₃) data:

Chemical Shift (ppm)
171.24
164.76
156.99
144.18
140.13
138.69
134.31
131.90
131.69
131.27
131.40
131.27
131.25
131.08
130.92
130.75
130.75
129.54
128.85
128.13
127.84
126.79
126.75
125.72
125.68
125.85
125.81
125.81
125.74
125.42
125.23
125.23
124.71
124.67
124.65
124.60
124.56
124.52
124.52
122.53
120.01
119.01
112.85
60.49
51.97
51.81
49.08
48.92
45.52
45.62
45.69
45.69
42.25
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27.76
25.22
21.66
21.99
19.21
14.30
11.91

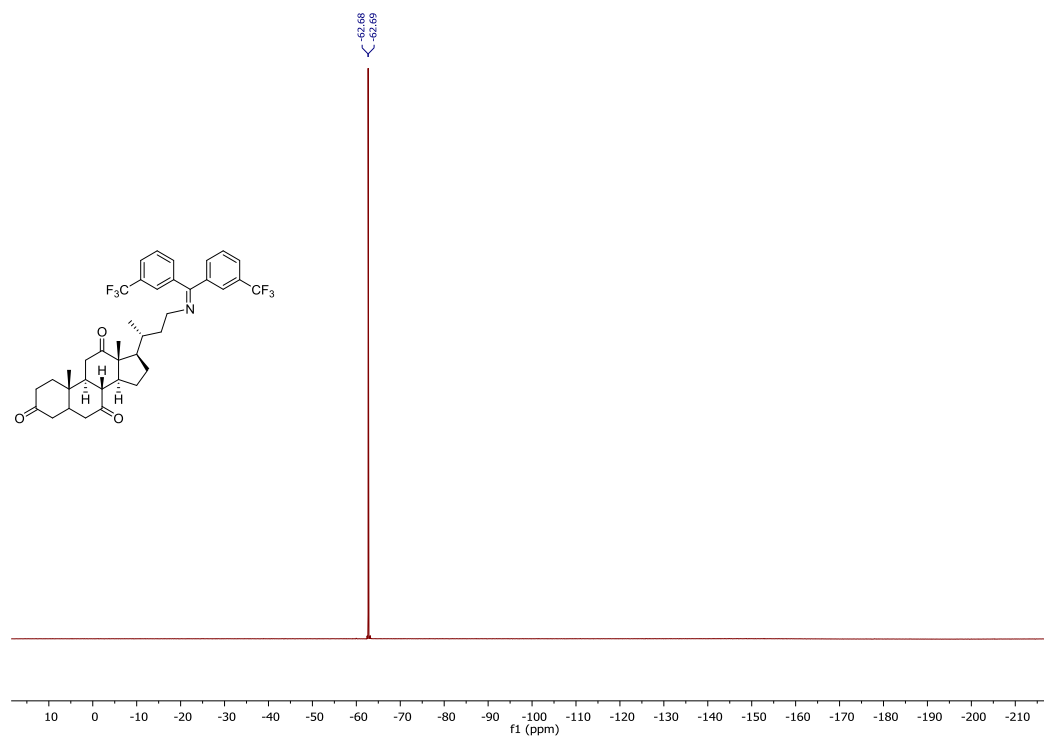
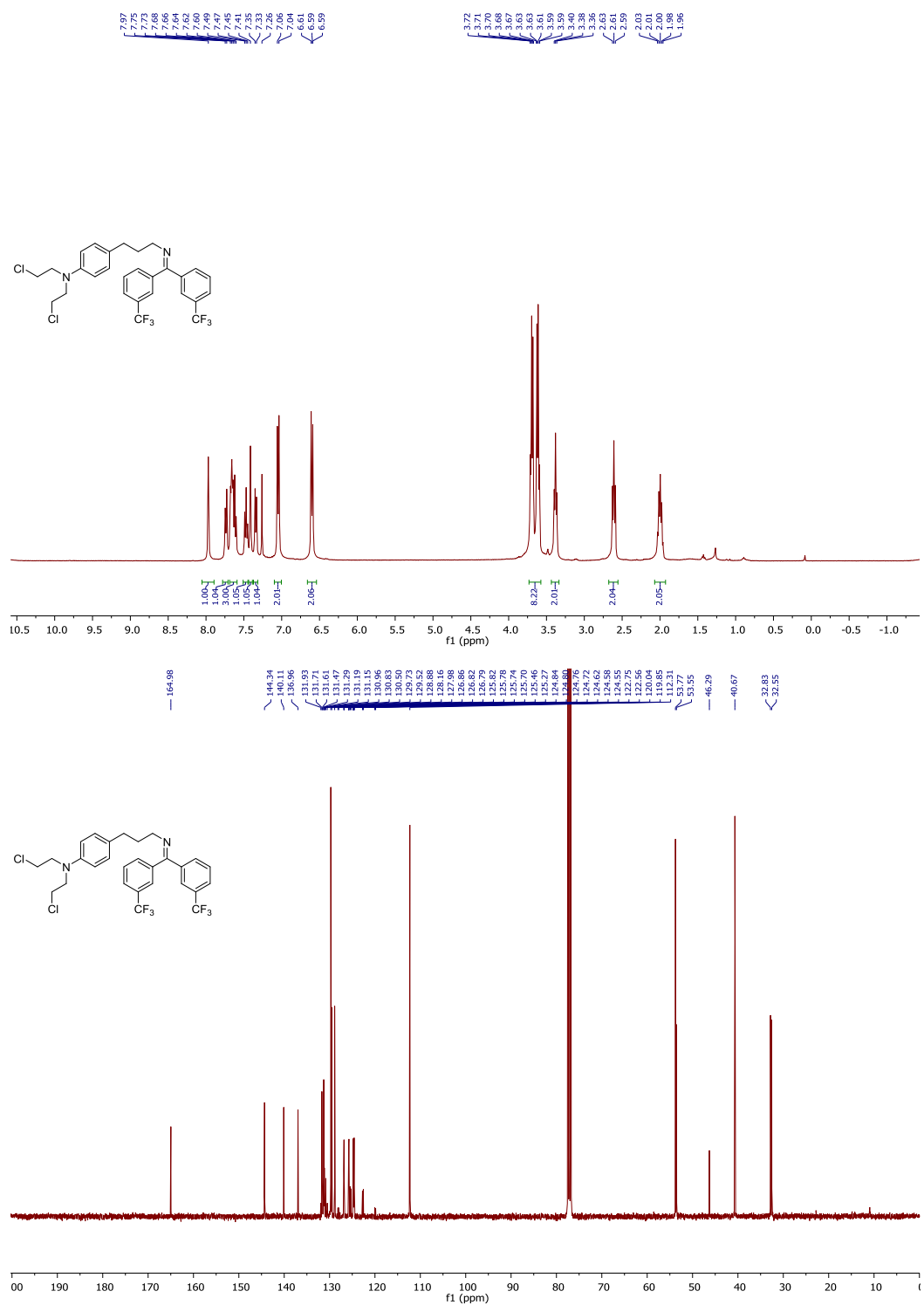


Figure S30. NMR spectra of 6e



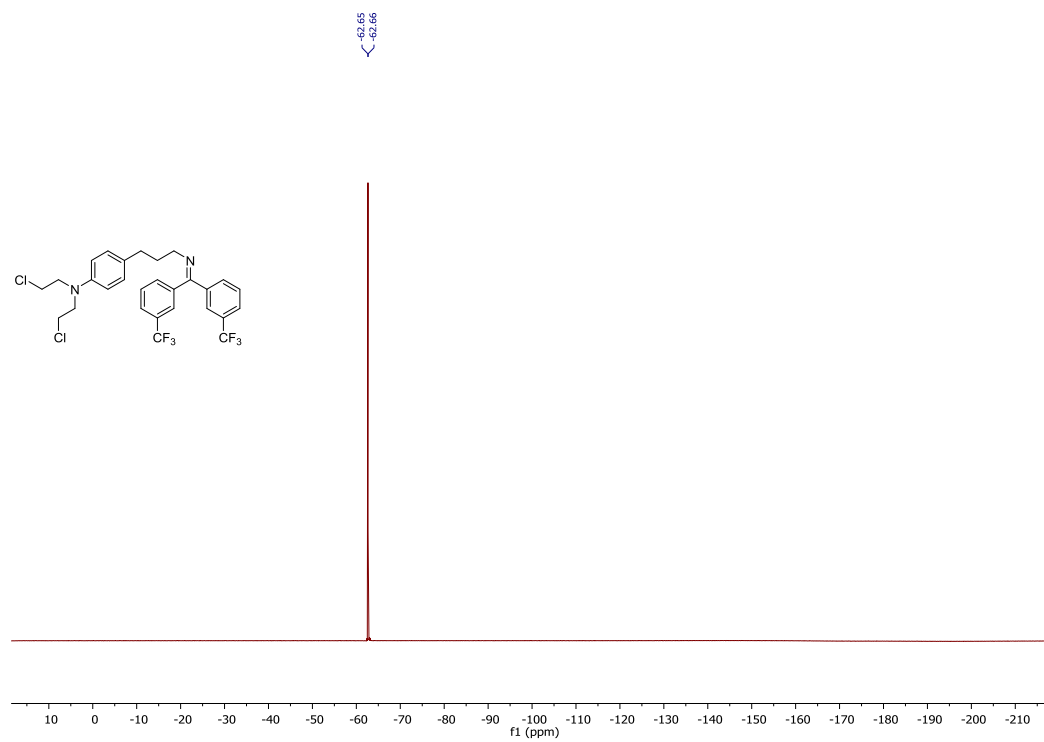


Figure S31. NMR spectra of 6f

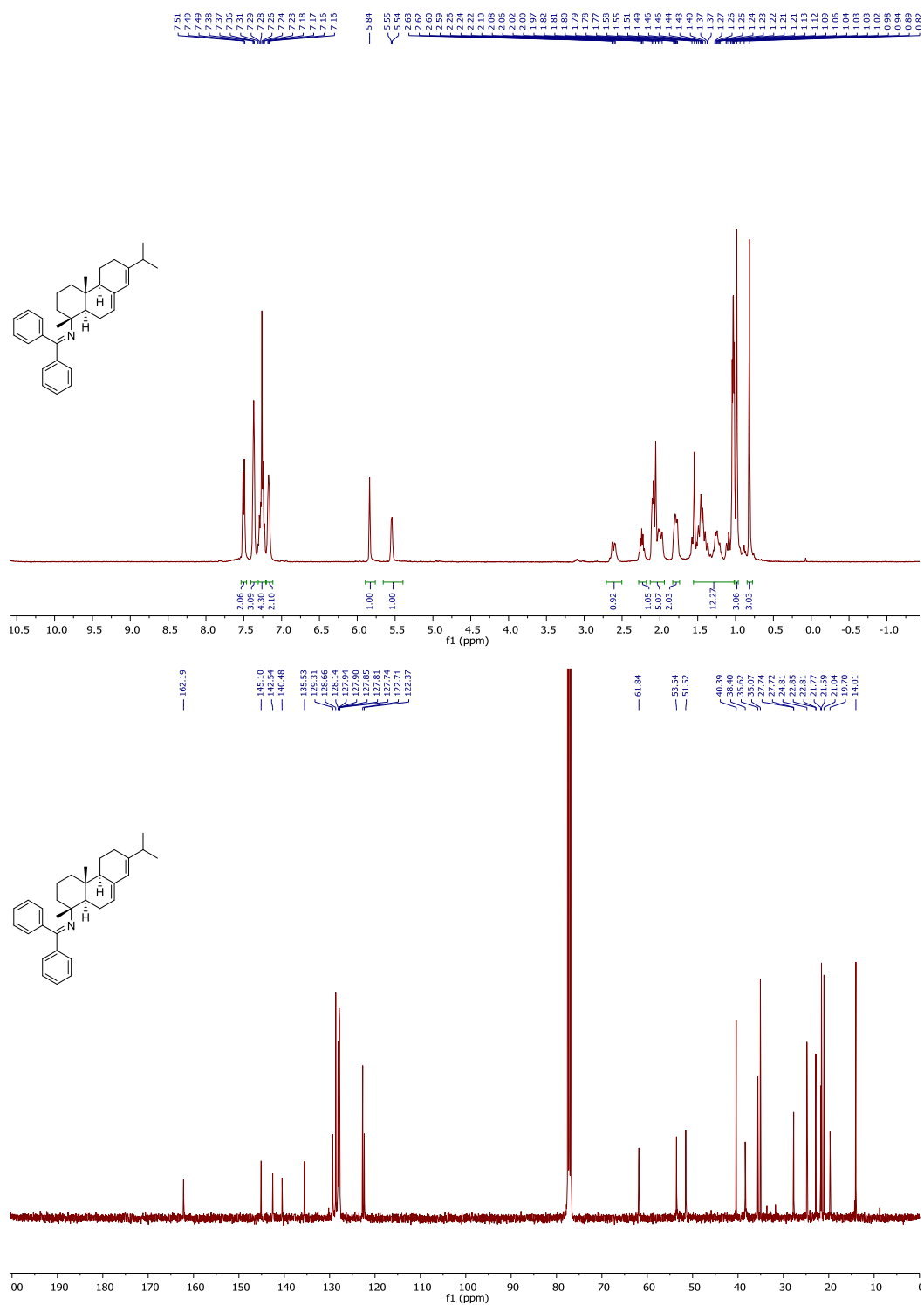
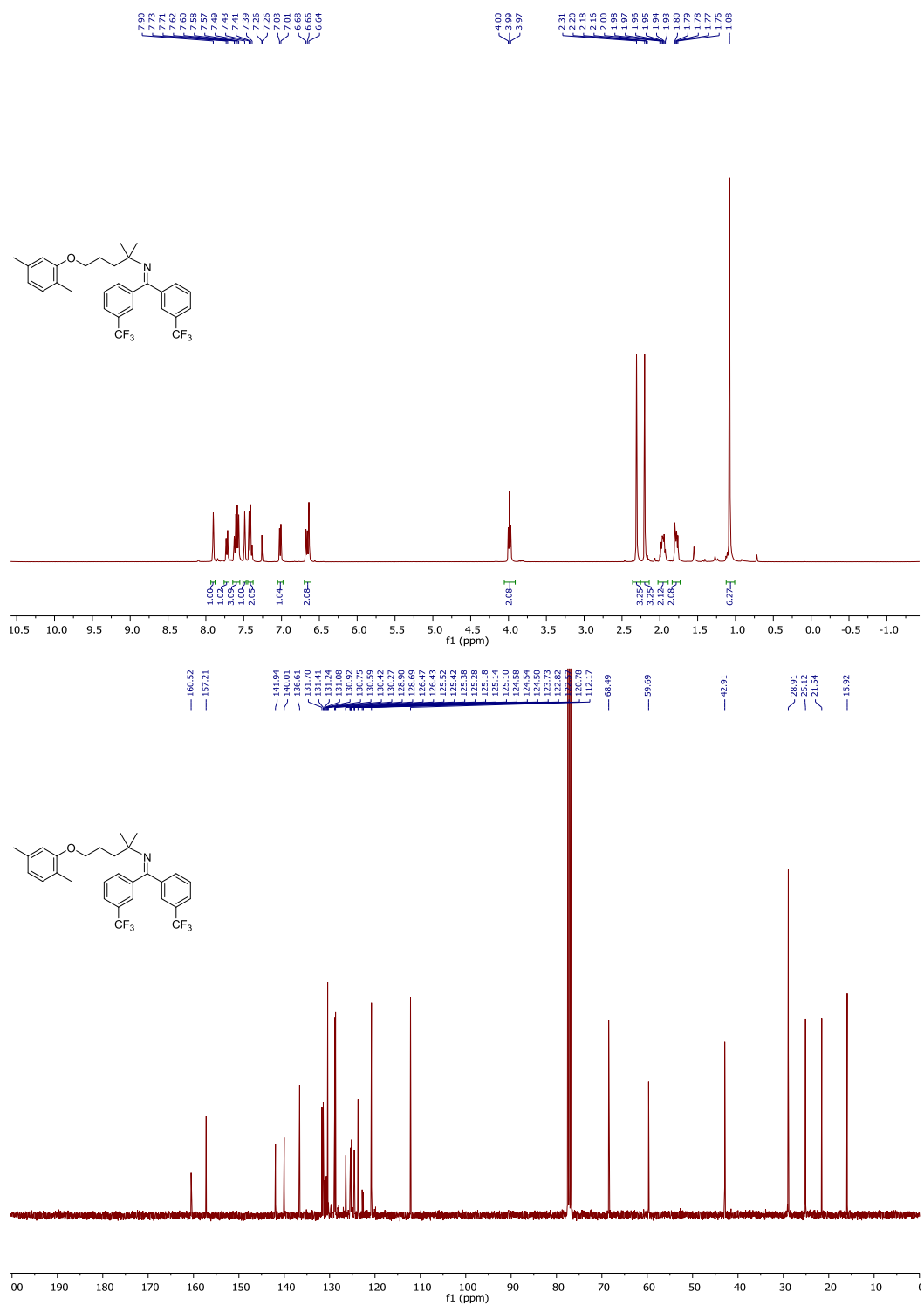


Figure S32. NMR spectra of 6g



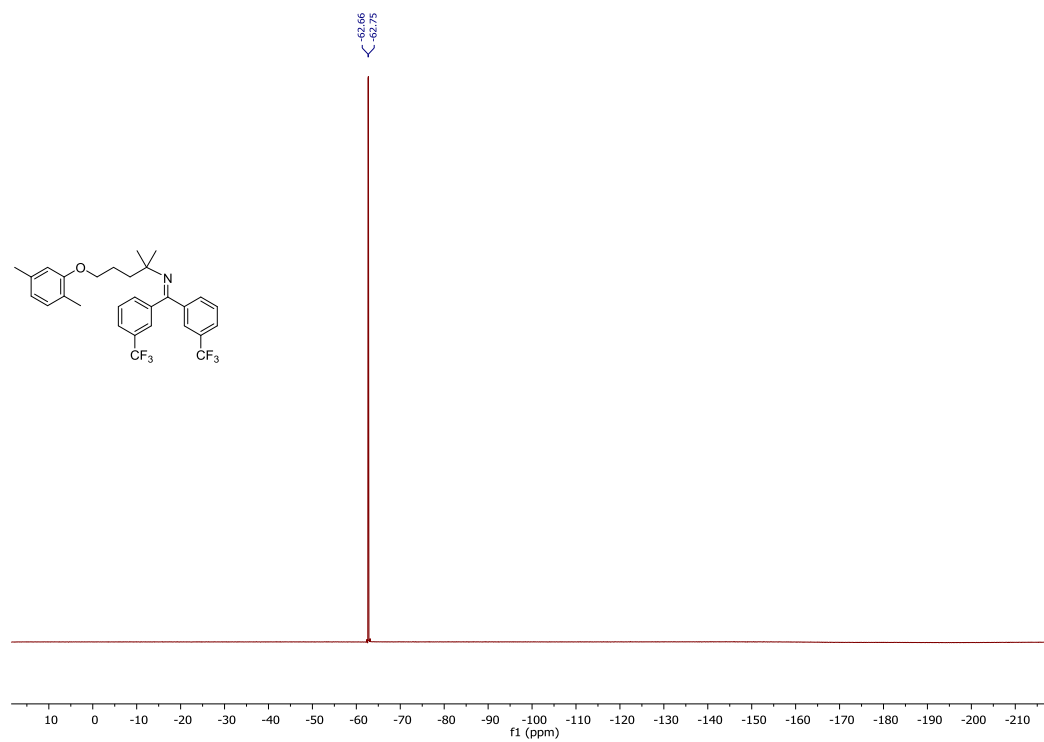
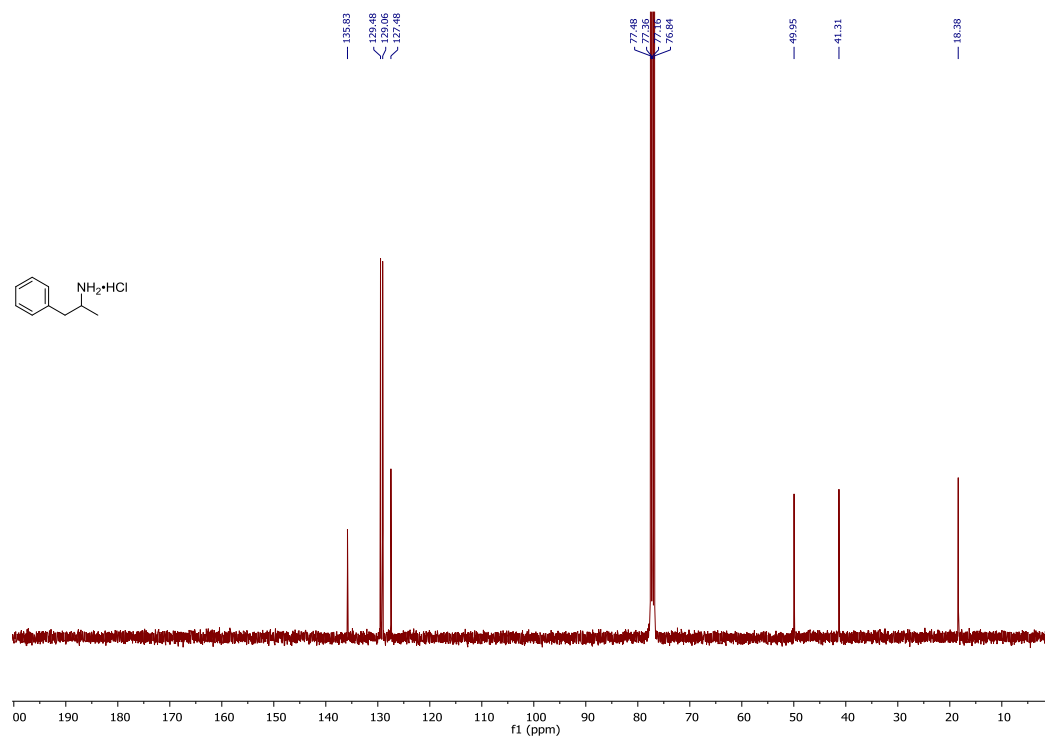
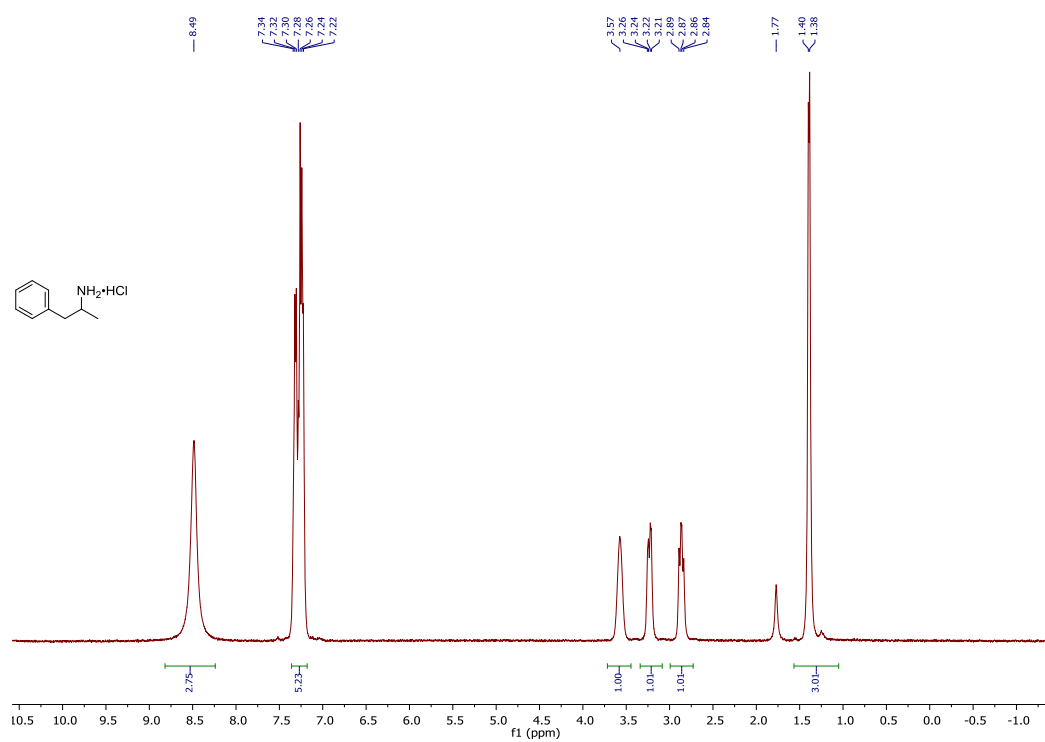
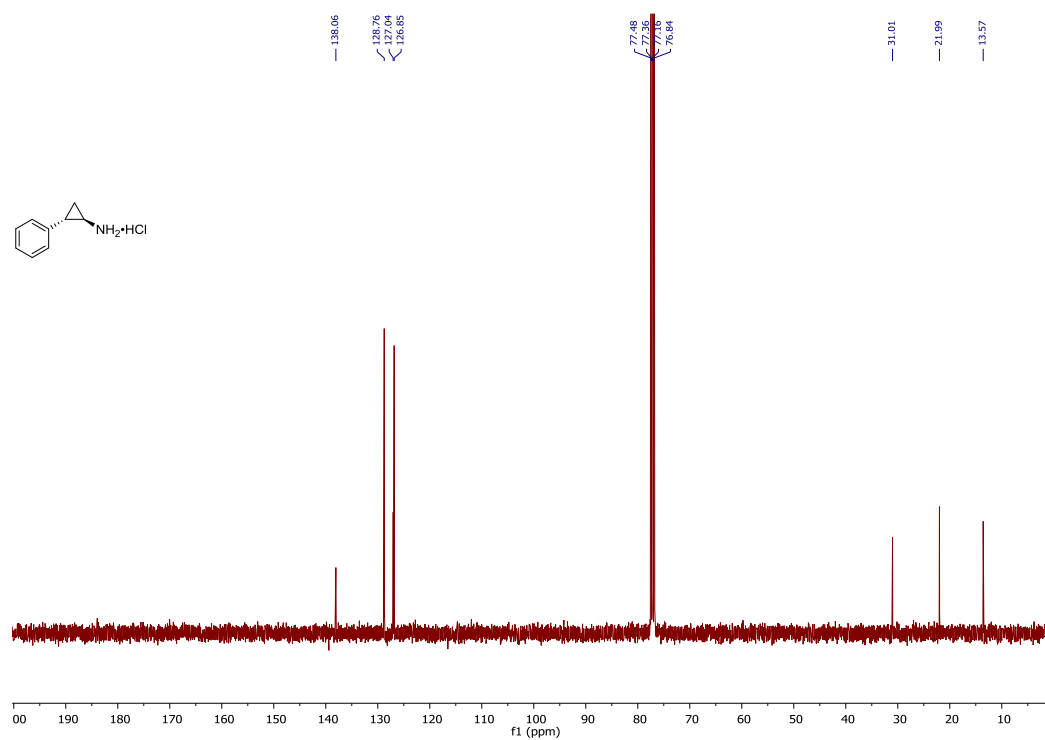


Figure S33. NMR spectra of 7a





References

- [1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.
- [2] a) C. Li, J. Wang, L. M. Barton, S. Yu, M. Tian, D. S. Peters, M. Kumar, A. W. Yu, K. A. Johnson, A. K. Chatterjee, M. Yan, P. S. Baran, *Science* **2017**, *356*, eaam7355; b) R. Mao, A. Frey, J. Balon, X. Hu, *Nat. Catal.* **2018**, *1*, 120-126; c) W. Zhao, R. P. Wurz, J. C. Peters, G. C. Fu, *J. Am. Chem. Soc.* **2017**, *139*, 12153–12156.
- [3] D. M. Peacock, C. B. Roos, J. F. Hartwig, *ACS Cent Sci* **2016**, *2*, 647-652.
- [4] R. P. Frutos, T. G. Tampone, J. A. Mulder, S. Rodriguez, N. K. Yee, B.-S. Yang, C. H. Senanayake, *Org. Process Res. Dev.* **2016**, *20*, 982-988.
- [5] M. Kitamura, T. Suga, S. Chiba, K. Narasaka, *Org. Lett.* **2004**, 4619–4621.
- [6] S. Miyamura, M. Araki, T. Suzuki, J. Yamaguchi, K. Itami, *Angew. Chem., Int. Ed.* **2015**, *54*, 846-851; *Angew.Chem.* **2015**, *127*,860-865.