Supporting Information

Cyclic Diaryl λ^3-chloranes: reagents and their C-C and C-O couplings with phenols *via* aryne intermediates

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Contents

General Remarks

All reactions were carried out under nitrogen atmosphere in flame-dried glassware. Liquids and solutions were transferred with syringes or cannula purged with nitrogen prior to use. Air- and moisture- sensitive materials were stored, protected and handled under an atmosphere of argon, with appropriate glassware. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone prior to use. Technical grade solvents for extraction and chromatography (cyclohexane and ethyl acetate) were used without purification. All reagents, if commercially available, were purchased from standard suppliers (Sigma Aldrich, ABCR, Fluorochem, TCI, Alfa Aesar and Apollo scientific) and used without further purification unless otherwise stated. Reactions were cooled using acetone / dry ice / liquid nitrogen baths and heated using an oil bath on a magnetic stirrer.

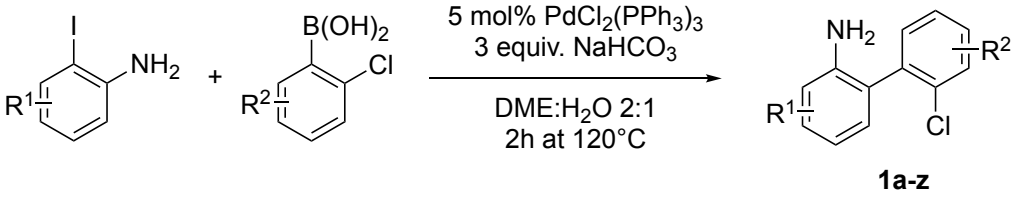
Chromatography: Analytical thin-layer chromatography (TLC) was performed using aluminum plates coated with silica (0.25 mm, Merck silica-gel 60-F254). Flash column chromatography was performed on VWR silica gel (40 – 63 μm) using the indicated solvents. Spots were visualized by UV light irradiation and/or by staining of the TLC plate with potassium permanganate ($KMnO_4$ (0.3 g), K_2CO_3 (20 g) and KOH (0.3 g) in water (300 mL)), followed by heating with a heat gun if necessary.

Analytical data: *NMR:* ^{1}H NMR (400 or 500 MHz), ^{19}F NMR (376 or 471 MHz) and ^{13}C NMR (101 or 126 MHz) spectra were recorded on Bruker Avance III HD 400 and 500 MHz instruments respectively. Chemical shifts are reported as δ-values in parts per million (ppm) and are referred to partially deuterated chloroform, DMSO or Acetone (chloroform $\delta[^{1}H] = 7.26$ ppm and $\delta[^{13}C] = 77.0$ ppm; DMSO $\delta[^{1}H] = 2.50$ ppm and $\delta[^{13}C] = 39.52$ ppm; Acetone $\delta[^{1}H] = 2.05$ ppm and $\delta[^{13}C] = 29.84$ ppm). The spectra were processed with MestreNova Mestrelab). Multiplicities were abbreviated as s (singlet), brs (broad signal), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublets of doublets). Coupling constants *J* were given in Hz. If not otherwise noted, the coupling constants given are either H-H or HF coupling constants for proton signals, and C-F and Si-F coupling constants for carbon and silicon signals. *HRMS:* High resolution mass spectrometry (HRMS) analysis were performed by the analytical facility at the University of Strasbourg. APCI-TOF-MS: MS experiments were performed on a Bruker Daltonics microTOF spectrometer (Bruker Daltonik GmgH, Bremen, Germany) equipped with an Agilent APCI source. Calibratio was performed using APCI/APPI calibrant solution (Agilent Technologies). Sample solutions were introduced into the spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, MA, USA) with a flow rate of 4 $\mu L.min^{-1}$. ESI-TOF-MS: MS experiments were performed on a Bruker Daltonics microTOF spectrometer (Bruker Daltonik GmgH, Bremen, Germany) equipped with an orthogonal electrospray (ESI) interface. Calibration was performed using Tuning mix (Agilent Technologies). Sample solutions were introduced into the spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, MA, USA) with a flow rate of 4 $\mu L.min^{-1}$. *X-Ray:*

The X-ray crystallographic structure analysis was performed by the radio-crystallographic facility at the Université de Strasbourg. The crystals were placed in oil, and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature N_2 stream. X-ray diffraction data collection was carried out on a Bruker PHOTON III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 37mm. The cell parameters were determined (APEX3 software) [1] from reflections taken from 1 set of 180 frames at 1s exposure. The structure was solved using the program SHELXT-2014 [2]. The refinement and all further calculations were carried out using SHELXL-2014 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 A semi-empirical absorption correction was applied using SADABS in APEX3 [1]; transmission factors: T_{min}/T_{max} = 0.7209/0.7458.

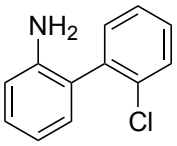
CCDC 2176956, 2176957, 2176958, 2176959 contain respectively the supplementary crystallographic data for compounds **2a**-BF_4, **2w**, **19** and **22**.

General procedure A: Synthesis of 2'-chloro-[1,1'-biphenyl]-2-amine 1a-z



SCHEME S-1

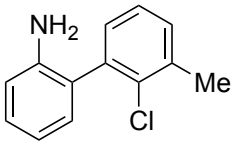
To a flame dried Schlenk was charged 2-iodoanilines (1 equiv), 2-chlorophenylboronic acid (1.05 to 1.2 equiv), dichlorobis(triphenylphosphine)palladium (3 mol%), and $NaHCO_3$ (3 equiv). The tube was evacuated and refilled with argon three times. Then DME (0.32 M) was added. The mixture was stirred at room temperature for 5 min then H_2O (2:1 DME:H_2O) was added. The resulting mixture was stirred at 120 °C for 2 hours. After being cooled to room temperature, the mixture was extracted with EtOAc. The extracts were combined, dried over Na_2SO_4, filtered and concentrated. The resulting crude product was purified by flash chromatography (Gradient Cyclohexane:EtOAc 9:1 to 7:3) yielding the desired product as pale orange-red solid. A subsequent distillation under a high vacuum (Kugelrohr, m.p. 70-90 °C; b.p. 150 – 260°C) guarantees the isolation of **1a**-**z** as a metal-free white solid.



2'-chloro-[1,1'-biphenyl]-2-amine 1a

Following the **GP-A** using 2-iodoaniline (4 g, 18.3 mmol) and 2-chlorophenylboronic acid (3.43 g, 22 mmol) **1a** was obtained as colorless solid in 82% yield (15 mmol, 3.06 g).

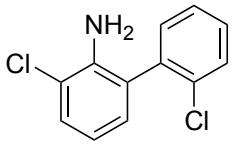
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H), 7.36 – 7.31 (m, 3H), 7.22 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.84 (td, *J* = 7.5, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.1, 1.2 Hz, 1H), 3.56 (brs, 2H). The spectral data correspond to the literature.[4]



2'-chloro-3-methyl-[1,1'-biphenyl]-2-amine 1d

Following the **GP-A** using 2-iodoaniline (380 mg, 1.73 mmol) and (2-chloro-3-methylphenyl)boronic acid (310 mg, 1.82 mmol) **1b** was obtained in 68% yield (1.17 mmol, 255 mg) as colorless oil.

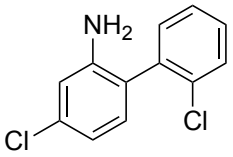
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 4H), 7.05 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.83 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.25 (brs, 2H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 138.1, 137.1, 134.0, 130.3, 130.3, 129.3, 128.9, 126.7, 126.1, 118.3, 115.5, 20.9. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{13}ClN^+$: 218.0731; found: 218.0718.



2',3-dichloro-[1,1'-biphenyl]-2-amine 1c

Following the **GP-A** using 2-chloro-6-iodoaniline (486 mg, 1.9 mmol) and 2-chlorophenylboronic acid (315 mg, 2 mmol) **1c** was obtained in 89% yield (1.71 mmol, 408 mg) as colorless oil.

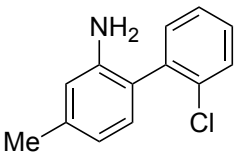
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.52 (m, 1H), 7.37 – 7.30 (m, 4H), 6.97 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.76 (t, *J* = 7.8 Hz, 1H), 3.96 (brs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.6, 137.1, 133.8, 131.7, 130.0, 129.4, 129.1, 128.8, 127.3, 126.1, 119.5, 118.0. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{12}H_{10}Cl_2N^+$: 238.0185; found: 238.0187.



2',4-dichloro-[1,1'-biphenyl]-2-amine 1d

Following the **GP-A** using 5-chloro-2-iodoaniline (486 mg, 1.92 mmol) and 2-chlorophenylboronic acid (315 mg, 2.01 mmol) **1d** was obtained in 73% yield (1.4 mmol, 333.6 mg) as colorless oil.

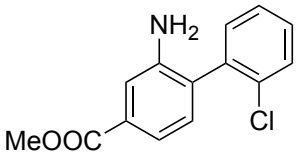
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H), 7.35 – 7.30 (m, 3H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.81 – 6.78 (m, 2H), 3.63 (brs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.0, 136.9, 134.6, 133.9, 131.9, 131.6, 130.1, 129.4, 127.4, 123.6, 118.3, 115.2. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{12}H_{10}Cl_2N$+: 238.0185; found: 238.0187.



2'-chloro-4-methyl-[1,1'-biphenyl]-2-amine 1e

Following the **GP-A** using 2-iodo-5-methylaniline (466 mg, 2 mmol) and 2-chlorophenylboronic acid (328 mg, 2.1 mmol) **1e** was obtained in 68% yield (1.37 mmol, 298 mg) as colorless oil.

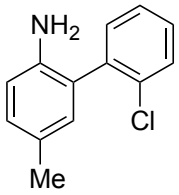
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H), 7.35 – 7.30 (m, 3H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.69 – 6.67 (m, 1H), 6.64 – 6.63 (brs, 1H), 3.51 (brs, 2H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 139.0, 137.9, 134.0, 132.0, 130.2, 129.8, 128.9, 127.1, 122.6, 119.2, 116.2, 21.3. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{13}ClN^+$: 218.0731; found: 218.0743.



methyl 2-amino-2'-chloro-[1,1'-biphenyl]-4-carboxylate 1f

Following the **GP-A** using methyl 3-amino-4-iodobenzoate (531 mg, 1.92 mmol) and 2-chlorophenylboronic acid (315 mg, 2.01 mmol) **1f** was obtained in 58% yield (1.11 mmol, 289 mg) as colorless oil.

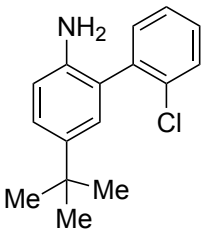
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 3H), 7.36 – 7.30 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 3.70 (brs, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 143.9, 137.0, 133.4, 131.4, 130.8, 130.5, 130.0, 129.5, 129.4, 127.3, 119.2, 116.3, 52.0. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{13}ClNO_2^+$: 262.0629; found: 262.0619.



2'-chloro-5-methyl-[1,1'-biphenyl]-2-amine 1g

Following the **GP-A** using 2-iodo-4-methylaniline (447 mg, 1.9 mmol) and 2-chlorophenylboronic acid (315 mg, 2.0 mmol) **1g** was obtained in 78% yield (1.49 mmol, 324 mg) as colorless oil.

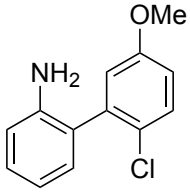
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 1H), 7.35 – 7.30 (m, 3H), 7.04 (ddd, *J* = 8.1, 2.3, 0.8 Hz, 1H), 6.89 (d, *J* = 2.6 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 3.45 (brs, 2H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.2, 138.1, 133.8, 131.9, 130.7, 129.8, 129.7, 128.9, 127.5, 127.1, 125.4, 115.7, 20.4. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{13}ClN^+$: 218.0731; found: 218.0735.



5-(tert-butyl)-2'-chloro-[1,1'-biphenyl]-2-amine 1h

Following the **GP-A** using 4-tert-butyl-2-iodoaniline (455 mg,1.65 mmol) and 2-chlorophenylboronic acid (271 mg, 1.74 mmol) **1h** was obtained in 94% yield (1.55 mmol, 402 mg) as colorless oil.

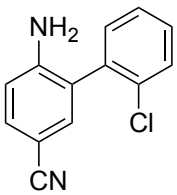
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 1H), 7.42 – 7.34 (m, 3H), 7.29 – 7.26 (m, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.50 (brs, 2H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 141.1, 138.4, 133.9, 131.9, 129.9, 128.8, 127.4, 127.1, 125.9, 124.9, 115.3, 34.0, 31.5 (3C). **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{16}H_{19}ClN^+$: 260.1201; found: 260.1205.



2'-chloro-5'-methoxy-[1,1'-biphenyl]-2-amine 1i

Following the **GP-A** using 2-iodoaniline (392 mg, 1.79 mmol) and (2-chloro-5-methoxyphenyl)boronic acid (350 mg, 1.88 mmol) **1i** was obtained in 88% yield (1.57 mmol, 365.9 mg) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 1H), 7.09 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 6.94 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.76 – 6.74 (m, 2H), 6.72 (td, *J* = 7.5, 1.2 Hz, 1H), 6.67 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.68 (s, 3H), 3.48 (brs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.5, 143.7, 138.7, 130.5, 130.2, 129.1, 125.3, 125.0, 118.2, 116.6, 115.5, 115.1, 55.5. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{13}ClNO^+$: 234.0680; found: 234.0684.

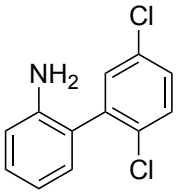


6-amino-2'-chloro-[1,1'-biphenyl]-3-carbonitrile 1j

Following the **GP-A** using 4-amino-3-iodobenzonitrile (488 mg, 2.0 mmol) and 2-chlorophenylboronic acid (328 mg, 2.1 mmol) **1j** was obtained in 73% yield (1.46 mmol, 335 mg) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 1H), 7.45 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.31 - 7.28 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 2H). **^{13}C NMR**

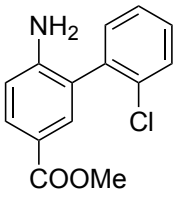
(101 MHz, $CDCl_3$) δ 147.9, 135.4, 134.7, 133.8, 133.2, 131.6, 130.2, 130.0, 127.6, 124.8, 119.9, 115.0, 100.2. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{10}ClN_2^+$: 229.0527; found: 229.0531.



2',5'-dichloro-[1,1'-biphenyl]-2-amine 1k

Following the **GP-A** using 2-iodoaniline (438 mg, 2.0 mmol) and 2,5-dichlorophenylboronic acid (401 mg, 2.1 mmol) **1k** was obtained in 64% yield (1.28 mmol, 305 mg) as colorless oil.

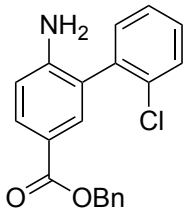
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.23 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.84 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 8.1, 1.2 Hz, 1H), 3.57 (brs, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 139.5, 132.9, 132.3, 131.8, 130.9, 130.2, 129.5, 129.0, 124.0, 118.4, 115.6. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{12}H_{10}Cl_2N^+$: 238.0185; found: 238.0187.



methyl 6-amino-2'-chloro-[1,1'-biphenyl]-3-carboxylate 1l

Following the **GP-A** using methyl 4-amino-3-iodobenzoate (531 mg, 1.9 mmol) and 2-chlorophenylboronic acid (315 mg, 2.0 mmol) **1l** was obtained in 79% yield (1.51 mmol, 395 mg) as colorless oil.

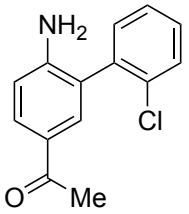
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.77 (d, *J* = 2.1 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.37 – 7.31 (m, 3H), 6.75 (d, *J* = 8.5 Hz, 1H), 3.98 (brs, 2H), 3.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 148.2, 136.7, 133.9, 132.5, 131.9, 131.1, 130.0, 129.5, 127.4, 124.0, 119.5, 114.3, 51.6. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{13}ClNO_2^+$: 262.0629; found: 262.0640.



benzyl 6-amino-2'-chloro-[1,1'-biphenyl]-3-carboxylate 1m

Following the **GP-A** using benzyl 4-amino-3-iodobenzoate (530 mg,1.5 mmol) and 2-chlorophenylboronic acid (246 mg, 1.58 mmol) **1m** was obtained in 63% yield (0.94 mmol, 318 mg) as colorless oil.

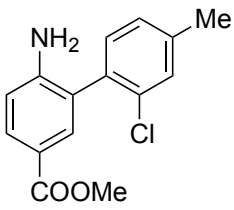
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.81 (d, *J* = 2.1 Hz, 1H),7.53 – 7.50 (m, 1H), 7.45 – 7.43 (m, 2H), 7.40 – 7.31 (m, 6H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.33 (s, 2H), 4.06 (brs, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 148.3, 136.6, 136.4, 133.9, 132.6, 131.9, 131.3, 129.9, 129.5, 128.5 (2C), 128.1 (2C), 128.0, 127.4, 124.0, 119.4, 114.3, 66.1. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{20}H_{17}ClNO_2^+$: 338.0942; found: 338.0951.



1-(6-amino-2'-chloro-[1,1'-biphenyl]-3-yl)ethan-1-one 1n

Following the **GP-A** using 1-(4-amino-3-iodophenyl)ethan-1-one (706 mg, 2.7 mmol) and 2-chlorophenylboronic acid (444 mg, 2.84 mmol) **1n** was obtained in 56% yield (1.52 mmol, 374 mg) as colorless oil.

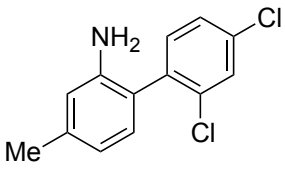
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.70 (d, *J* = 2.2 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.36 – 7.31 (m, 3H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.04 (brs, 2H), 2.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 148.5, 136.6, 133.8, 131.8, 131.8, 130.2, 130.0, 129.5, 127.5, 127.4, 123.8, 114.2, 26.0. **HRMS (ESI)**: m/z $[M+Na]^+$ calcd for $C_{14}H_{12}ClNNaO^+$: 268.0500; found: 268.0501.



methyl 6-amino-2'-chloro-4'-methyl-[1,1'-biphenyl]-3-carboxylate 1o

Following the **GP-A** using methyl 4-amino-3-iodobenzoate (532 mg,1.92 mmol) and (2-chloro-4-methylphenyl)boronic acid (343 mg, 2.04 mmol) **1o** was obtained in 47% yield (0.9 mmol, 249 mg) as colorless oil.

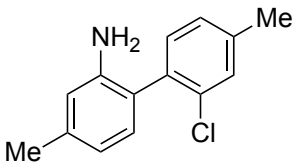
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.33 (brs, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.15 (ddd, *J* = 7.7, 1.7, 0.7 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 3.90 (brs, 2H), 3.84 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 148.4, 139.7, 133.6, 133.5, 132.7, 131.6, 131.0, 130.4, 128.2, 124.1, 119.5, 114.2, 51.6, 20.9. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{15}H_{15}ClNO_2^+$: 276.0786; found: 276.0791.



2',4'-dichloro-4-methyl-[1,1'-biphenyl]-2-amine 1p

Following the **GP-A** using 2-iodo-5-methylaniline (466 mg, 2 mmol) and 2,4-dichlorophenylboronic acid (457 mg, 2.4 mmol) **1p** was obtained in 65% yield (1.30 mmol, 328.5 mg) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.1 Hz, 1H), 7.32 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.68 – 6.66 (m, 1H), 6.62 (brs, 1H), 3.50 (brs, 2H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 139.4, 136.5, 134.8, 134.0, 132.8, 130.2, 129.6, 127.5, 121.3, 119.3, 116.2, 21.3. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{12}Cl_2N^+$: 252.0341; found: 252.0343.

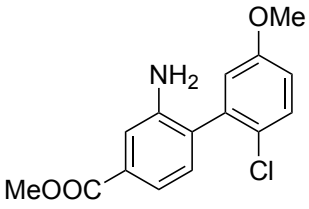


2'-chloro-4,4'-dimethyl-[1,1'-biphenyl]-2-amine 1q

Following the **GP-A** using 2-iodo-5-methylaniline (466 mg, 2 mmol) and (2-chloro-4-methylphenyl)boronic acid (357 mg, 2.1 mmol) **1q** was obtained in 32% yield (0.64 mmol, 148 mg) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 0.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.13 (ddd, *J* = 7.8, 1.8, 0.8 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.65 (ddd, *J* = 7.8, 1.7, 0.8 Hz, 1H), 6.62 (s, 1H),

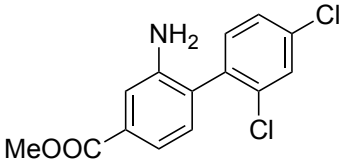
3.51 (brs, 2H), 2.38 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.7, 139.1, 138.9, 134.8, 133.6, 131.7, 130.4, 130.2, 128.0, 122.6, 119.2, 116.1, 21.3, 20.9. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{15}ClN^+$: 232.0888; found: 232.0876.



methyl 2-amino-2'-chloro-5'-methoxy-[1,1'-biphenyl]-4-carboxylate 1r

Following the **GP-A** using methyl 3-amino-4-iodobenzoate (554 mg, 2 mmol) and (2-chloro-5-methoxyphenyl)boronic acid (447 mg, 2.4 mmol) **1r** was obtained in 57% yield (1.14 mmol, 333.3 mg) as colorless oil.

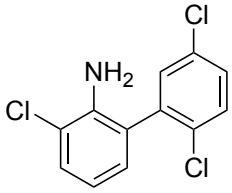
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 (d, *J* = 1.5 Hz, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.88 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.84 (d, *J* = 3.1 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.76 (brs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 158.5, 143.9, 137.7, 130.8, 130.7, 130.3, 129.4, 124.5, 119.1, 116.3, 116.2, 115.4, 55.5, 52.0. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{15}H_{15}ClNO_3^+$: 292.0735; found: 292.0742.



methyl 2-amino-2',4'-dichloro-[1,1'-biphenyl]-4-carboxylate 1s

Following the **GP-A** using 2methyl 3-amino-4-iodobenzoate (554 mg, 2 mmol) and 2,4-dichlorophenylboronic acid (458 mg, 2.4 mmol) **1s** was obtained in 64% yield (1.28 mmol, 380 mg) as colorless oil.

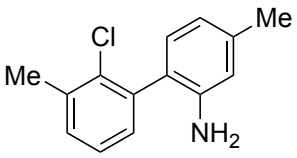
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.34 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 3.65 (brs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 143.9, 135.5, 134.7, 134.3, 132.3, 131.1, 130.5, 129.9, 128.1, 127.7, 119.2, 116.4, 52.1. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{12}Cl_2NO_2^+$: 296.0240; found: 296.0247.



2',3,5'-trichloro-[1,1'-biphenyl]-2-amine 1t

Following the **GP-A** using 2-iodoaniline (438 mg, 2.0 mmol) and 2,5-dichlorophenylboronic acid (401 mg, 2.1 mmol) **1t** was obtained in 64% yield (1.28 mmol, 305 mg) as colorless oil.

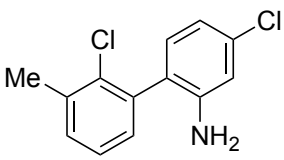
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.27 – 7.23 (m, 3H), 6.86 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.68 (t, *J* = 7.8 Hz, 1H), 3.89 (brs, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 138.7, 133.0, 132.2, 131.6, 131.1, 129.5 (2C), 128.7, 124.8, 119.6, 118.2. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{12}H_9Cl_3N^+$: 271.9795; found: 271.9795.



2'-chloro-3',4-dimethyl-[1,1'-biphenyl]-2-amine 1u

Following the **GP-A** using 2-iodo-5-methylaniline (651 mg, 2.79 mmol) and (2-chloro-3-methylphenyl)boronic acid (500 mg, 2.93 mmol) **1u** was obtained in 60% yield (1.67 mmol, 388 mg) as colorless oil.

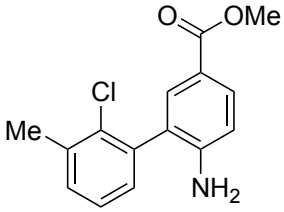
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.19 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.71 (ddd, *J* = 7.6, 1.7, 0.8 Hz, 1H), 6.67 (brs, 1H), 3.57 (brs, 2H), 2.50 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 138.8, 138.1, 137.0, 134.1, 130.2, 130.1, 129.4, 126.6, 123.3, 119.2, 116.1, 21.3, 20.9. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{15}ClN^+$: 232.0888; found: 232.0877.



2',4-dichloro-3'-methyl-[1,1'-biphenyl]-2-amine 1v

Following the **GP-A** using 5-Chloro-2-iodoaniline (556 mg, 2.24 mmol) and (2-chloro-3-methylphenyl)boronic acid (420 mg, 2.46 mmol) **1v** was obtained in 47% yield (1.05 mmol, 263.7 mg) as colorless oil.

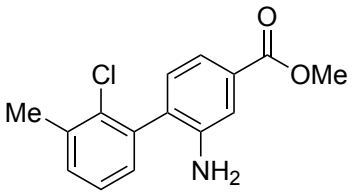
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 (ddd, *J* = 7.3, 2.0, 0.7 Hz, 1H), 6.95 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.80 – 6.77 (m, 2H), 3.61 (brs, 2H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 137.3, 137.0, 134.3, 134.0, 131.4, 130.6, 129.2, 126.8, 124.3, 118.2, 115.0, 20.9. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{12}Cl_2N^+$: 252.0341; found: 252.0345



methyl 6-amino-2'-chloro-3'-methyl-[1,1'-biphenyl]-3-carboxylate 1w

Following the **GP-A** using methyl 4-amino-3-iodobenzoate (650 mg, 2.35 mmol) and (2-chloro-3-methylphenyl)boronic acid (420 mg, 2.46 mmol) **1w** was obtained in 74% yield (1.74 mmol, 480.1 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.76 (d, *J* = 2.1 Hz, 1H), 7.29 (ddd, *J* = 7.5, 2.0, 0.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.15 (ddd, *J* = 7.3, 2.0, 0.6 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 3.95 (brs, 2H), 3.85 (s, 3H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 148.2, 137.3, 137.0, 134.0, 132.4, 131.0, 130.7, 129.3, 126.8, 124.9, 119.5, 114.2, 51.6, 20.8. **HRMS (ESI)**: m/z $[M+Na]^+$ calcd for $C_{15}H_{14}ClNNaO_2^+$: 298.0605; found: 298.0599.

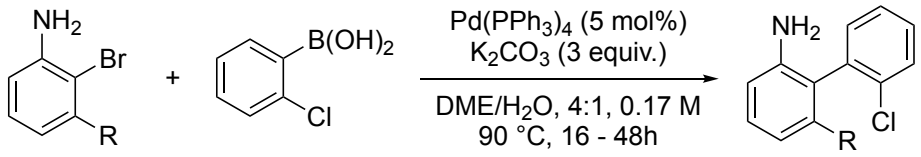


methyl 2-amino-2'-chloro-3'-methyl-[1,1'-biphenyl]-4-carboxylate 1x

Following the **GP-A** using methyl 3-amino-4-iodobenzoate (867 mg, 3.13 mmol) and (2-chloro-3-methylphenyl)boronic acid (560 mg, 3.29 mmol) **1x** was obtained in 69% yield (2.16 mmol, 596 mg) as colorless oil.

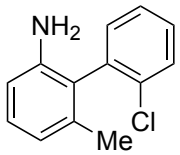
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.47 (d, *J* = 1.4 Hz, 1H), 7.29 (ddd, *J* = 7.5, 1.9, 0.8 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.14 (ddd, *J* = 7.3, 1.9, 0.7 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 143.7, 137.4, 137.2, 133.6, 130.8, 130.6, 130.4, 130.4, 128.8, 126.8, 119.4, 116.4, 52.1, 20.8. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{15}H_{15}ClNO_2^+$: 276.0786; found: 276.0783.

Synthesis of 2'-chloro-[1,1'-biphenyl]-2-amine 1b and 1c



SCHEME S-2

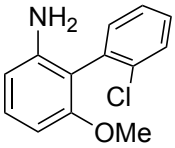
A 25-mL round bottom flask was charged with aniline (1 equiv.), (2-chlorophenyl)boronic acid (1.2 equiv), K_2CO_3 (3 equiv) and $Pd(PPh_3)_4$ (5 mol%), and it was then evacuated and backfilled with Argon three times. After adding dioxane and H_2O (5:1, 0.17 M), the resulting mixture was stirred at 90 ºC for 16h (**1b**) o 48h (**1c**). After the reaction was cooled down to room temperature, H_2O was added, and the resulting solution was extracted with EtOAc (3 times). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (cyclohexane : ethyl acetate) and further purified through distillation under a high vacuum (Kugelrohr) to afford the pure compound.



2'-chloro-6-methyl-[1,1'-biphenyl]-2-amine 1b

Following the procedure reported above using 2-bromo-3-methylaniline (372 mg, 2 mmol, 1 equiv.) **1b** was obtained in 48% as a white solid (0.96 mmol, 210 mg).

^{1}H NMR (400 MHz, CDCl3) δ 7.55 – 7.53 (m, 1H), 7.39 – 7.31 (m, 2H), 7.27 – 7.25 (m, 1H), 7.11 (t, J = 7.8 Hz, 1H), 6.72 (dt, J = 7.6, 0.9 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 1.97 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 143.7, 137.2, 136.8, 134.4, 131.7, 130.1, 129.1, 128.6, 127.6, 125.2, 120.0, 112.9, 20.1. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{13}ClN^+$: 218.0731; found: 218.0739.

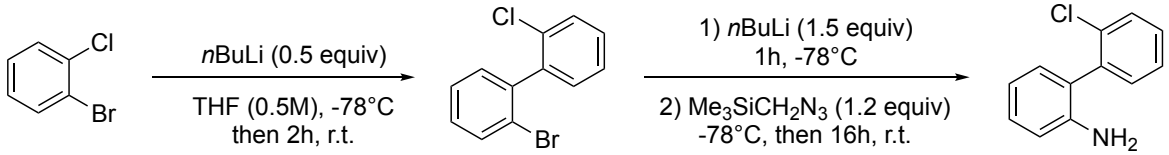


2'-chloro-6-methoxy-[1,1'-biphenyl]-2-amine 1c

Following the procedure reported above using 2-bromo-3-methoxyaniline (404 mg, 2 mmol, 1 equiv.) **1c** was obtained in 51% as a white solid (1.02 mmol, 238 mg).

^{1}H NMR (400 MHz, CDCl3) δ 7.55 – 7.53 (m, 1H), 7.37 – 7.30 (m, 3H), 7.18 (t, J = 8.2 Hz, 1H), 6.47 – 6.42 (m, 2H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 157.7, 145.0, 134.9, 134.1, 132.4, 129.8, 129.4, 128.9, 127.2, 113.9, 108.4, 101.0, 55.7. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{13}H_{13}ClNO^+$: 234.0680; found: 234.0664.

Transition metal-free preparation of the 2'-chloro-[1,1'-biphenyl]-2-amine 1a



step 1
5 mmol scale
78%

step 2
2 mmol scale
61%

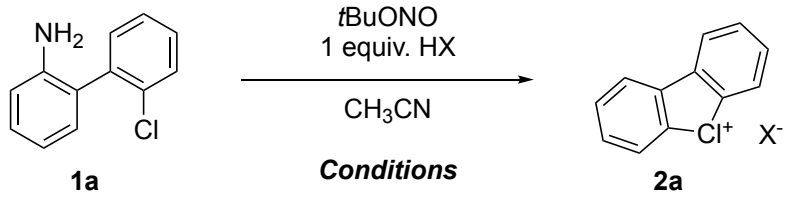
1a

SCHEME S-3

Step 1: A 50-mL round-bottom flask was charged with 1-bromo-2-chlorobenzene (957 mg, 5 mmol), the reaction flask was evacuated and backfilled with Argon 3 times, followed by the addition of dried THF (10 mL). A solution of *n*-BuLi (1.6 M, 1.56 mL, 2.5 mmol, 0.5 equiv) was added dropwise at -78 °C, and the reaction mixture was stirred at rt for 2 h. The reaction was quenched with a saturated solution of NH_4Cl (10 mL), extracted with EtOAc (3 x 10 mL) and washed with brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to give 2-bromo-2'-chloro-1,1'-biphenyl as pale yellow solid in 78% (522 mg, 1.95 mmol). The crude product was used for the next step without further purification.

Step 2: In a 25-mL round-bottom flask, the crude of 2-bromo-2'-chloro-1,1'-biphenyl (522 mg, 1.95 mmol) was redissolved in dried THF (4 mL) under Argon. A solution of *n*-BuLi (1.6 M, 1.88 mL, 3 mmol, 1.54 equiv) was added at -78 °C and the resulting mixture was stirred at -78 °C for 1 h. After adding (trimethylsily1)methyl azide (0.45 mL, 3 mmol, 1.54 equiv) at -78 °C, the resulting mixture was stirred overnight at room temperature. The reaction was quenched with a saturated solution of NH_4Cl (10 mL) and stirred for 20 min, extracted with EtOAc (3 x 20 mL) and washed with brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification was performed by flash column chromatography (CyH:EtOAC 8:1) to afford **1a** as colorless oil in 61% yield (242 mg, 1.19 mmol).

Optimization of the preparation of cyclic diaryl λ^3-chloranes



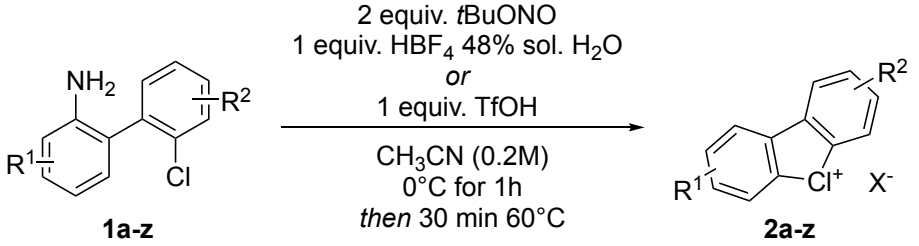
1a **2a**

To a solution of 2'-Chloro-[1,1'-biphenyl]-2-amine **1a** (1 equiv. 0.5 mmol) in CH_3CN at 0 °C *t*BuONO was added followed by the protic acid (1 equiv.). The mixture was stirred at the same temperature for 1h then, following the conditions of the **Table S-1** heated at the corresponding temperature for the indicated time. The cooled reaction was purged in cold Et_2O (Et_2O:CH_3CN 5:1) where a white solid precipitate. The product was collected through filtration and washed twice with Et_2O and dried under high vacuum.

TABLE S-1

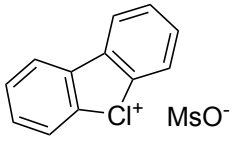
	HX	*tBuONO equiv.*	*Solvent (M)*	*Conditions*	*Yields*
1	MsOH	2	CH_3CN (0.1M)	1h @ 0°C + 30min @ 65°C	63%
2	HPF_6	2	CH_3CN (0.1M)	1h @ 0°C + 30min @ 65°C	58%
3	TfOH	2	CH_3CN (0.1M)	1h @ 0°C + 30min @ 65°C	52%
4	HBF_4	2	CH_3CN (0.1M)	1h @ 0°C + 30min @ 65°C	79%
5	HBF_4	2	CH_3CN (0.05M)	1h @ 0°C + 30min @ 65°C	66%
6	*HBF_4*	*2*	*CH_3CN (0.2M)*	*1h @ 0°C + 30min @ 65°C*	*76%*
7	HBF_4	1.2	CH_3CN (0.1M)	1h @ 0°C + 30min @ 65°C	73%
8	HBF_4	2	CH_3CN (0.1M)	1h @ 0°C + 1h @ 65°C	75%
9	HBF_4	2	CH_3CN (0.1M)	1h @ 0°C + 1h @ 45°C	66%
10	HBF_4	2	CH_3CN (0.1M)	1h @ 0°C + 1h @ r.t.	Traces

General procedure B: Preparation of cyclic diaryl λ^3-chloranes 2a-z



SCHEME S-4

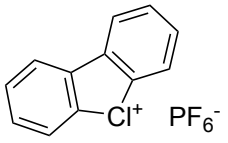
To a solution of 2'-Chloro-[1,1'-biphenyl]-2-amine **1a-z** (1 equiv. 0.5 mmol) in CH_3CN (2.5 mL, 0.2 M) at 0 °C, *t*BuONO (120 µL, 1 mmol, 2 equiv.) was added followed by the acid (*HBF_4* 48% H_2O sol.: 65 µL, 0.5 mmol, 1 equiv.; *TfOH*: 45 µL, 0.5 mmol, 1 equiv.). The mixture was stirred at the same temperature for 1h, then heated to 65 °C and stirred at the same temperature for 30 min. The cooled reaction was purged in cold Et_2O (Et_2O:CH_3CN 5:1) where a white solid precipitate. The desired product **2a-z** was collected through filtration and washed twice with Et_2O and dried under high vacuum.



dibenzo[b,d]chlorol-5-ium methanesulfonate 2a-OMs

Table S-1, Entry 1: Following the **GP-B** using **1a** (101 mg, 0.5 mmol) **2a**-OMs was obtained as white solid in 63% yield. (88.9 mg, 0.31 mmol).

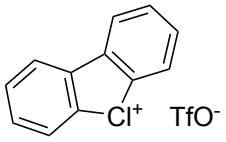
^{1}H NMR (500 MHz, DMSO) δ 8.69 – 8.67 (m, 4H), 8.03 – 8.00 (m, 2H), 7.97 – 7.94 (m, 2H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 140.0, 132.0 (2C), 131.7, 125.5, 123.0, 39.8. **HRMS (ESI)**: m/z $[M\text{-}MsO]^+$ calcd for $C_{12}H_8Cl^+$: 187.0309; found: 187.0306.



dibenzo[b,d]chlorol-5-ium hexafluorophosphate 2a-PF_6

Table S-1, Entry 2: Following the **GP-B** using **1a** (101 mg, 0.5 mmol) **2a**-PF_6 was obtained as white solid in 58% yield. (96.3 mg, 0.29 mmol).

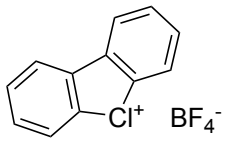
^{1}H NMR (400 MHz, DMSO) δ 8.69 – 8.65 (m, 4H), 8.03 – 7.99 (m, 2H), 7.98 – 7.93 (m, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 140.5, 132.5 (2C), 132.2, 126.0, 123.4. **^{19}F NMR** (377 MHz, DMSO) δ -70.2 (d, J = 711.2 Hz). **HRMS (ESI)**: m/z $[M\text{-}PF_6]^+$ calcd for $C_{12}H_8Cl^+$: 187.0309; found: 187.0304.



dibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2a-OTf

Table 1, Entry 3: Following the **GP-B** using **1a** (101 mg, 0.5 mmol) **2a**-OTf was obtained as white solid in 52% yield. (87.5 mg, 0.26 mmol). (15 mmol scale: 60%, 3.05 g).

^{1}H NMR (500 MHz, DMSO) δ 8.68 – 8.65 (m, 4H), 8.02 – 7.99 (m, 2H), 7.95 (ddd, *J* = 9.0, 7.2, 1.8 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 140.0, 132.0 (2C), 131.7, 125.5, 122.9. **^{19}F NMR** (377 MHz, DMSO) δ -77.7. **HRMS (ESI)**: m/z $[M\text{-}TfO]^+$ calcd for $C_{12}H_8Cl^+$: 187.0309; found: 187.0309.

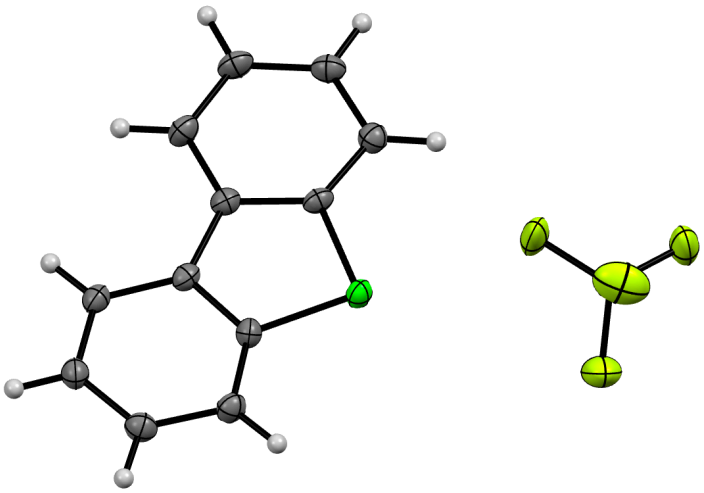


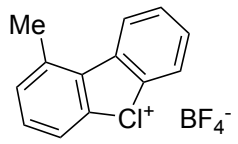
dibenzo[b,d]chlorol-5-ium tetrafluoroborate 2a-BF_4

Table S-1, Entry 4: Following the **GP-B** using **1a** (101 mg, 0.5 mmol) **2a-BF_4** was obtained as white solid in 79% yield. (107 mg, 0.39 mmol).

^{1}H NMR (500 MHz, DMSO) δ 8.67 – 8.65 (m, 4H), 8.02 – 7.99 (m, 2H), 7.97 – 7.93 (m, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 140.0, 132.0 (2C), 131.7, 125.5, 122.9. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{12}H_8Cl^+$: 187.0309; found: 187.0303.

X-ray suitable crystals of **2a**-BF_4 were obtained through vapor diffusion from DCM/Hexane (Ellipsoid probability at 50%) CCDC 2176956

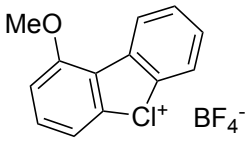




1-methyldibenzo[*b*,*d*]chlorol-5-ium tetrafluoroborate 2b

Following the **GP-B** using **1b** (109 mg, 0.5 mmol) **2b** was obtained as white solid in 49% yield. (71 mg, 0.25 mmol).

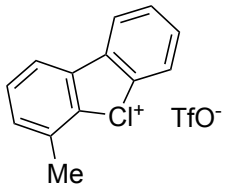
^{1}H NMR (400 MHz, DMSO) δ 8.71 (dd, J = 8.4, 1.3 Hz, 1H), 8.58 – 8.53 (m, 2H), 8.03 – 7.94 (m, 2H), 7.86 – 7.81 (m, 2H), 2.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 139.5, 138.8, 138.6, 133.9, 132.5, 131.8, 131.2, 131.1, 129.7, 127.9, 123.0, 120.4, 21.1. **^{19}F NMR** (377 MHz, DMSO) δ -148.2. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{10}H_{10}Cl^+$: 201.0466; found: 201.0473.



1-methoxydibenzo[*b*,*d*]chlorol-5-ium tetrafluoroborate 2c

Following the **GP-B** using **1c** (109 mg, 0.5 mmol) **2c** was obtained as white solid in 49% yield. (71 mg, 0.25 mmol).

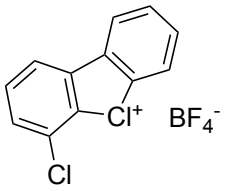
^{1}H NMR (400 MHz, DMSO) δ 8.65 (dd, J = 8.5, 1.2 Hz, 1H), 8.61 (dd, J = 7.7, 1.7 Hz, 1H), 8.24 (d, J = 8.7 Hz, 1H), 7.99 – 7.89 (m, 3H), 7.64 (d, J = 8.4 Hz, 1H), 4.17 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 158.2, 140.0, 139.0, 132.9, 132.2, 131.8, 131.3, 128.1, 123.1, 120.4, 114.7, 114.6, 57.7. **^{19}F NMR** (377 MHz, DMSO) δ -148.2. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{13}H_{10}ClO^+$:217.0415; found: 217.0418.



4-methyldibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2d

Following the **GP-B** using **1d** (255 mg, 1.17 mmol) **2d** was obtained as white solid in 58% yield. (237.7 mg, 0.68 mmol).

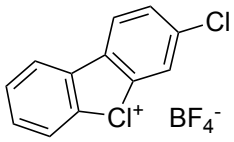
^{1}H NMR (400 MHz, DMSO) δ 8.71 – 8.66 (m, 2H), 8.54 – 8.51 (m, 1H), 8.04 (td, *J* = 7.5, 1.2 Hz, 1H), 8.00 – 7.92 (m, 2H), 7.85 – 7.82 (m, 1H), 2.75 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 140.4, 140.1, 132.9, 132.5, 132.3, 132.1, 132.0, 131.7, 131.6, 126.2, 123.3, 122.8, 19.0. **^{19}F NMR** (377 MHz, DMSO) δ -77.7. **HRMS (ESI)**: m/z $[M\text{-}OTf]^+$ calcd for $C_{13}H_{10}Cl^+$: 201.0466; found: 201.0462.



4-chlorodibenzo[b,d]chlorol-5-ium tetrafluoroborate 2e

Following the **GP-B** using **1e** (119 mg, 0.5 mmol) **2e** was obtained as white solid in 91% yield. (140 mg, 0.45 mmol).

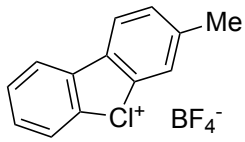
^{1}H NMR (500 MHz, DMSO) δ 8.40 (t, *J* = 8.2 Hz, 1H), 8.33 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.87 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.73 (td, *J* = 7.9, 1.8 Hz, 1H), 7.68 (td, *J* = 7.5, 1.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 143.1, 141.6, 136.5, 133.2, 132.6, 132.0, 131.9, 131.0, 131.0, 130.4, 128.5, 116.4. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{12}H_7Cl_2^+$: 220.9919; found: 220.9914.



3-chlorodibenzo[b,d]chlorol-5-ium tetrafluoroborate 2f

Following the **GP-B** using **1f** (119 mg, 0.5 mmol) **2f** was obtained as white solid in 66% yield. (101 mg, 0.33 mmol).

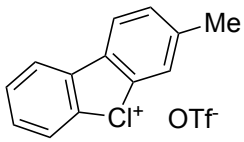
^{1}H NMR (500 MHz, DMSO) δ 8.80 (d, *J* = 2.0 Hz, 1H), 8.68 – 8.65 (m, 3H), 8.12 (dd, *J* = 8.5, 1.9 Hz, 1H), 8.01 (td, *J* = 7.5, 1.2 Hz, 1H), 7.97 (ddd, *J* = 9.0, 7.3, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 140.9, 139.4, 135.1, 132.3, 132.2, 131.9, 131.3, 131.2, 126.2, 125.7, 122.9, 122.8. **^{19}F NMR** (377 MHz, DMSO) δ -148.2. **HRMS (ESI)**: m/z [M-BF_4]$^+$ calcd for $C_{12}H_7Cl_2^+$: 220.9919; found: 220.9918.



3-methyldibenzo[b,d]chlorol-5-ium tetrafluoroborate 2g

Following the **GP-B** using **1g** (109 mg, 0.5 mmol) **2g** was obtained as white solid in 73% yield. (106 mg, 0.37 mmol).

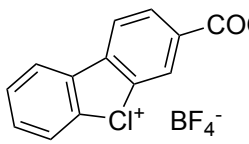
^{1}H NMR (500 MHz, DMSO) δ 8.61 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.56 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.49 (d, *J* = 7.9 Hz, 1H), 8.43 (s, 1H), 7.96 (td, *J* = 7.6, 1.2 Hz, 1H), 7.90 (ddd, *J* = 9.0, 7.3, 1.7 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 143.0, 140.0, 139.9, 132.6, 131.9, 131.7, 131.5, 129.3, 125.1, 124.9, 122.9, 122.4, 21.5. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z [M-BF_4]$^+$ calcd for $C_{13}H_{10}Cl^+$: 201.0466; found: 201.0457.



3-methyldibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2g-OTf

Following the **GP-B** using **1g** (43.5 mg, 0.2 mmol), *t*BuONO (48 μL, 0.4 mmol, 2 equiv.) and trifluoromethanesulfonic acid (18 μL, 0.2 mmol, 1 equiv.) **2g**-OTf was obtained as white solid in 62% yield. (43.4 mg, 0.12 mmol).

^{1}H NMR (500 MHz, DMSO) δ 8.63 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.46 (brs, 1H), 7.98 (td, *J* = 7.5, 1.1 Hz, 1H), 7.91 (ddd, *J* = 8.9, 7.3, 1.7 Hz, 1H), 7.84 (dt, *J* = 7.9, 1.1 Hz, 1H), 2.59 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 142.9, 140.1, 140.0, 132.6, 132.0, 131.7, 131.5, 129.3, 125.2, 125.0, 122.9, 122.5, 21.5. **^{19}F NMR** (377 MHz, DMSO) δ -77.74. **HRMS (ESI)**: m/z [M-OTf]$^+$ calcd for $C_{13}H_{10}Cl^+$: 201.0466; found: 201.0465.

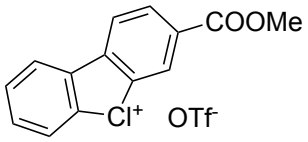


3-(methoxycarbonyl)dibenzo[b,d]chlorol-5-ium tetrafluoroborate 2h

Following the **GP-B** using **1h** (131 mg, 0.5 mmol) **2h** was obtained as white solid in 85% yield. (141 mg, 0.42 mmol).

^{1}H NMR (500 MHz, DMSO) δ 9.30 (d, *J* = 1.4 Hz, 1H), 8.79 (d, *J* = 8.2 Hz, 1H), 8.76 – 8.74 (m, 1H), 8.72 – 8.70 (m, 1H), 8.50 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.07 – 8.00 (m, 2H), 3.98 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 164.1, 141.4, 139.9, 136.2, 133.1, 132.1, 132.1, 131.9, 131.1, 126.3,

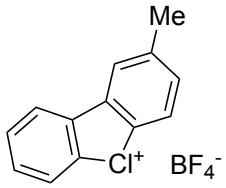
125.5, 124.0, 123.1, 53.2. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{14}H_{10}ClO_2^+$: 245.0364; found: 245.0356.



3-(methoxycarbonyl)dibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2h-OTf

Following the **GP-B** using **2h** (52.3 mg, 0.2 mmol), *t*BuONO (48 μL, 0.4 mmol, 2 equiv) and trifluoromethanesulfonic acid (18 μL, 0.2 mmol, 1 equiv.) **2h**-OTf was obtained as white solid in 62% yield. (43.4 mg, 0.12 mmol).

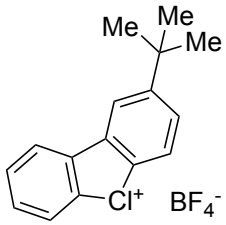
^{1}H NMR (400 MHz, DMSO) δ 9.30 (d, *J* = 1.5 Hz, 1H), 8.80 (d, *J* = 8.2 Hz, 1H), 8.76 (dd, *J* = 7.5, 2.1 Hz, 1H), 8.72 – 8.70 (m, 1H), 8.51 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.07 – 8.00 (m, 2H), 3.98 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 164.6, 141.9, 140.4, 136.6, 133.5, 132.6, 132.6, 132.4, 131.6, 126.8, 126.0, 124.5, 123.6, 53.6. **^{19}F NMR** (377 MHz, DMSO) δ -77.8. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{14}H_{10}ClO_2^+$: 245.0364; found: 245.0363.



2-methyldibenzo[b,d]chlorol-5-ium tetrafluoroborate 2i

Following the **GP-B** using **1i** (109 mg, 0.5 mmol) **2i** was obtained as white solid in 72% yield. (104 mg, 0.36 mmol).

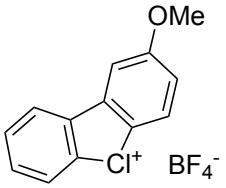
^{1}H NMR (500 MHz, DMSO) δ 8.64 – 8.62 (m, 1H), 8.58 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.50 – 8.48 (m, 2H), 7.99 (td, *J* = 7.6, 1.2 Hz, 1H), 7.93 (ddd, *J* = 9.0, 7.3, 1.7 Hz, 1H), 7.75 (dd, *J* = 9.0, 2.3 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 142.3, 140.2, 137.3, 132.7, 131.9 (2C), 131.7 (2C), 125.5, 125.3, 123.0, 122.4, 20.8. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{13}H_{10}Cl^+$: 201.0466; found: 201.0466.



2-(tert-butyl)dibenzo[b,d]chlorol-5-ium 2j

Following the **GP-B** using **1j** (186 mg, 0.5 mmol) **2j** was obtained as white solid in 76% yield. (126 mg, 0.38 mmol).

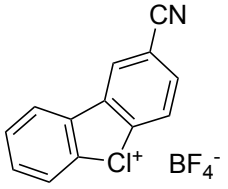
^{1}H NMR (400 MHz, DMSO) δ 8.80 (d, *J* = 7.8 Hz, 1H), 8.68 (brs, 1H), 8.64 (d, *J* = 8.6 Hz, 1H), 8.55 (d, *J* = 9.2 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.93 (ddd, *J* = 8.8, 7.3, 1.8 Hz, 1H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, DMSO) δ 155.3, 140.3, 137.3, 132.2, 131.8 (2C), 131.6, 129.5, 125.7, 122.9, 122.5, 122.3, 35.4, 31.0 (3C). **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{16}H_{16}Cl^+$: 243.0935; found: 243.0949.



2-methoxydibenzo[b,d]chlorol-5-ium tetrafluoroborate 2k

Following the **GP-B** using **1k** (117 mg, 0.5 mmol) **2k** was obtained as white solid in 81% yield. (124 mg, 0.41 mmol).

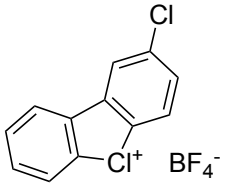
^{1}H NMR (500 MHz, DMSO) δ 8.68 (d, *J* = 7.8 Hz, 1H), 8.63 (d, *J* = 8.5 Hz, 1H), 8.50 (d, *J* = 9.6 Hz, 1H), 8.22 (d, *J* = 2.9 Hz, 1H), 8.00 (t, *J* = 7.5 Hz, 1H), 7.94 (ddd, *J* = 8.9, 7.3, 1.7 Hz, 1H), 7.49 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 161.8, 140.6, 133.6, 132.0, 132.0, 131.6, 130.8, 125.7, 123.7, 123.0, 118.9, 109.3, 56.6. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{13}H_{10}ClO^+$: 217.0415; found: 217.0412.



2-cyanodibenzo[b,d]chlorol-5-ium tetrafluoroborate 2l

Following the **GP-B** using **1l** (114 mg, 0.5 mmol) **2l** was obtained as white solid in 47% yield. (70 mg, 0.23 mmol).

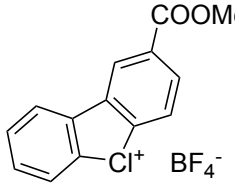
^{1}H NMR (500 MHz, DMSO) δ 9.30 (d, *J* = 2.0 Hz, 1H), 8.86 (d, *J* = 9.0 Hz, 1H), 8.71 – 8.69 (m, 2H), 8.40 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.06 (td, *J* = 7.4, 1.3 Hz, 1H), 8.02 (td, *J* = 7.9, 1.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 142.8, 141.2, 134.8, 133.5, 133.0, 132.0, 130.9, 129.5, 126.0, 124.3, 123.0, 117.1, 114.7. **^{19}F NMR** (377 MHz, DMSO) δ -148.2. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{13}H_7ClN^+$: 212.0262; found: 212.0264.



2-chlorodibenzo[b,d]chlorol-5-ium tetrafluoroborate 2m

Following the **GP-B** using **1m** (119 mg, 0.5 mmol) **2m** was obtained as white solid in 82% yield. (127 mg, 0.41 mmol).

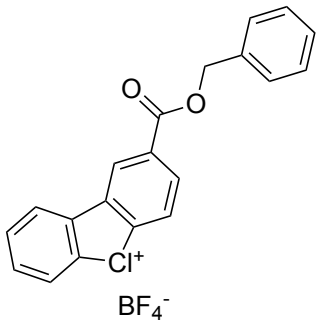
^{1}H NMR (400 MHz, DMSO) δ 8.90 (d, *J* = 2.4 Hz, 1H), 8.71 (dd, *J* = 7.6, 1.8 Hz, 1H), 8.68 – 8.65 (m, 2H), 8.05 - 7.96 (m, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 141.0, 137.9, 136.8, 134.1, 132.6, 131.8, 131.5, 131.2, 125.9, 125.2, 124.4, 123.0. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{12}H_7Cl_2^+$: 220.9919; found: 220.9925.



2-(methoxycarbonyl)dibenzo[b,d]chlorol-5-ium tetrafluoroborate 2n

Following the **GP-B** using **1n** (131 mg, 0.5 mmol) **2n** was obtained as white solid in 79% yield. (131 mg, 0.39 mmol).

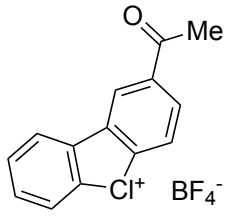
^{1}H NMR (500 MHz, DMSO) δ 9.15 (d, *J* = 2.0 Hz, 1H), 8.87 – 8.85 (m, 1H), 8.79 (d, *J* = 9.2 Hz, 1H), 8.69 – 8.67 (m, 1H), 8.44 (dd, *J* = 9.1, 2.1 Hz, 1H), 8.02 – 7.96 (m, 2H), 3.98 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 164.7, 142.9, 140.9, 132.9, 132.9, 132.5, 132.1, 131.8, 131.4, 126.2, 126.0, 123.6, 122.9, 53.1. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{14}H_{10}ClO_2^+$: 245.0364; found: 245.0360.



2-((benzyloxy)carbonyl)dibenzo[b,d]chlorol-5-ium 2o

Following the **GP-B** using **1o** (169 mg, 0.5 mmol) **2o** was obtained as white solid in 72% yield. (147 mg, 0.36 mmol).

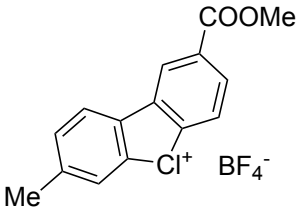
^{1}H NMR (400 MHz, DMSO) δ 9.19 (s, 1H), 8.89 (d, *J* = 6.8 Hz, 1H), 8.81 (d, *J* = 9.2 Hz, 1H), 8.69 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.49 (dd, *J* = 9.2, 1.7 Hz, 1H), 8.03 – 7.96 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.37 (m, 3H), 5.49 (s, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 164.1, 143.1, 140.9, 135.6, 132.9, 132.9, 132.5, 132.2, 131.8, 131.4, 128.6 (2C), 128.4, 128.2 (2C), 126.3, 126.0, 123.7, 122.9, 67.3. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{20}H_{14}ClO_2^+$: 321.0677; found: 321.0695.



2-acetyldibenzo[b,d]chlorol-5-ium tetrafluoroborate 2p

Following the **GP-B** using **1p** (123 mg, 0.5 mmol) **2p** was obtained as white solid in 82% yield. (129 mg, 0.41 mmol).

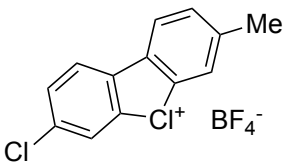
^{1}H NMR (500 MHz, DMSO) δ 9.18 (d, *J* = 2.0 Hz, 1H), 8.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.78 (d, *J* = 9.0 Hz, 1H), 8.69 (dd, *J* = 8.6, 1.1 Hz, 1H), 8.44 (dd, *J* = 9.1, 2.1 Hz, 1H), 8.04 (td, *J* = 7.6, 1.2 Hz, 1H), 7.99 (ddd, *J* = 8.9, 7.3, 1.7 Hz, 1H), 2.78 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 196.9, 142.7, 140.9, 139.3, 132.8, 132.5, 131.8, 131.6, 131.1, 126.0, 125.1, 123.4, 123.0, 27.3. **^{19}F NMR** (377 MHz, DMSO) δ -148.2. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{14}H_{10}ClO^+$: 229.0415; found: 229.0418.



2-(methoxycarbonyl)-7-methyldibenzo[b,d]chlorol-5-ium tetrafluoroborate 2q

Following the **GP-B** using **1q** (138 mg, 0.5 mmol) **2q** was obtained as white solid in 92% yield. (159.5 mg, 0.46 mmol).

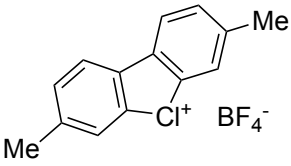
^{1}H NMR (500 MHz, DMSO) δ 9.10 (d, *J* = 2.0 Hz, 1H), 8.77 – 8.73 (m, 2H), 8.47 (brs, 1H), 8.41 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 3.98 (s, 3H), 2.59 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 164.7, 143.6, 142.8, 141.0, 132.9, 132.8, 132.7, 131.6, 128.7, 125.7, 125.6, 123.5, 122.4, 53.1, 21.6. **^{19}F NMR** (377 MHz, DMSO) δ -148.26. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{15}H_{12}ClO_2^+$: 259.0520; found: 259.0524.



3-chloro-7-methyldibenzo[b,d]chlorol-5-ium tetrafluoroborate 2r

Following the **GP-B** using **1r** (126 mg, 0.5 mmol) **2r** was obtained as white solid in 73% yield. (118 mg, 0.37 mmol).

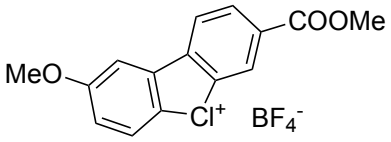
^{1}H NMR (500 MHz, DMSO) δ 8.77 (s, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 7.9 Hz, 1H), 8.45 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 143.3, 141.0, 139.2, 134.5, 132.7, 132.2, 131.3, 128.5, 125.9, 125.2, 122.8, 122.4, 21.6. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{13}H_9Cl_2^+$: 235.0076; found: 235.0070.



3,7-dimethyldibenzo[b,d]chlorol-5-ium tetrafluoroborate 2s

Following the **GP-B** using **1s** (116 mg, 0.5 mmol) **2s** was obtained as white solid in 62% yield. (92.5 mg, 0.31 mmol).

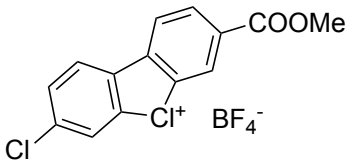
^{1}H NMR (500 MHz, DMSO) δ 8.46 (dd, *J* = 8.0, 1.3 Hz, 2H), 8.42 (s, 2H), 7.79 (dd, *J* = 8.0, 1.1 Hz, 2H), 2.56 (s, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 142.4, 139.9, 132.6, 129.3, 124.6, 122.4, 21.5. **^{19}F NMR** (377 MHz, DMSO) δ -148.2. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{14}H_{12}Cl^+$: 215.0622; found: 215.0616.



2-methoxy-7-(methoxycarbonyl)dibenzo[b,d]chlorol-5-ium tetrafluoroborate 2t

Following the **GP-B** using **1t** (146 mg, 0.5 mmol) **2t** was obtained as white solid in 77% yield. (140 mg, 0.39 mmol).

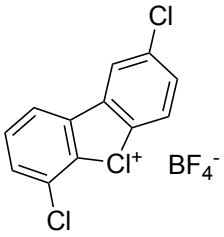
^{1}H NMR (500 MHz, DMSO) δ 9.22 (d, *J* = 1.4 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 8.52 (d, *J* = 9.6 Hz, 1H), 8.44 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.25 (d, *J* = 2.9 Hz, 1H), 7.53 (dd, *J* = 9.6, 2.9 Hz, 1H), 3.97 (s, 3H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 164.1, 161.9, 140.4, 136.1, 132.6, 132.1, 132.1, 132.0, 125.6, 124.1, 123.8, 120.2, 109.9, 56.7, 53.1. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{15}H_{12}ClO_3^+$: 275.0469; found: 275.0453.



3-chloro-7-(methoxycarbonyl)dibenzo[b,d]chlorol-5-ium tetrafluoroborate 2u

Following the **GP-B** using **1u** (148 mg, 0.5 mmol) **2u** was obtained as white solid in 50% yield. (91 mg, 0.25 mmol).

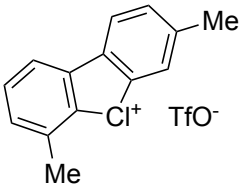
^{1}H NMR (500 MHz, DMSO) δ 9.28 (d, *J* = 1.5 Hz, 1H), 8.83 (d, *J* = 2.0 Hz, 1H), 8.80 – 8.76 (m, 2H), 8.50 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.98 (s, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 164.1, 140.8 (2C), 136.2, 135.3, 132.5, 132.3, 132.3, 130.5, 127.1, 125.8, 123.9, 123.0, 53.2. **^{19}F NMR** (377 MHz, DMSO) δ -148.3. **HRMS (ESI)**: m/z $[M\text{-}BF_4]^+$ calcd for $C_{14}H_9Cl_2O_2^+$: 278.9974; found: 278.9968.



2,6-dichlorodibenzo[b,d]chlorol-5-ium tetrafluoroborate 2v

Following the **GP-B** using **1v** (136 mg, 0.5 mmol) **2v** was obtained as white solid in 81% yield. (139 mg, 0.405 mmol).

^{1}H NMR (500 MHz, DMSO) δ 8.43 – 8.40 (m, 1H), 8.35 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.10 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.01 (d, *J* = 2.6 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.80 (dd, *J* = 8.7, 2.6 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 141.7, 141.3, 136.7, 132.8, 132.8, 132.7, 132.6, 132.4, 132.0, 130.9, 130.7, 116.3. **^{19}F NMR** (377 MHz, DMSO) δ -148.2. **HRMS (ESI)**: m/z [M-BF_4]$^+$ calcd for $C_{12}H_6Cl_3^+$: 254.9530; found: 254.9525.

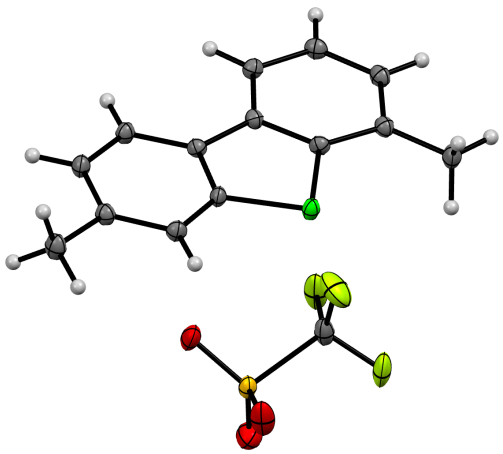


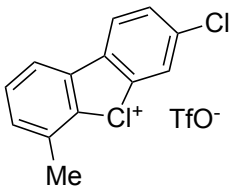
3,6-dimethyldibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2w

Following the **GP-B** using **1w** (388 mg, 1.67 mmol) **2w** was obtained as white solid in 56% yield. (343.6 mg, 0.94 mmol).

^{1}H NMR (400 MHz, DMSO) δ 8.57 (d, *J* = 8.1 Hz, 1H), 8.47 – 8.44 (m, 2H), 7.94 – 7.90 (m, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 2.74 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 143.4, 140.3, 140.2, 133.0, 132.5, 132.0, 131.7, 131.6, 129.8, 125.6, 122.9, 122.2, 21.5, 19.0. **^{19}F NMR** (377 MHz, DMSO) δ -77.7. **HRMS (ESI)**: m/z [M-OTf]$^+$ calcd for $C_{14}H_{12}Cl^+$: 215.0622; found: 215.0637.

X-ray suitable crystals of **2w** were obtained through vapor diffusion from DCM/Hexane (Ellipsoid probability at 50%) CCDC 2176957

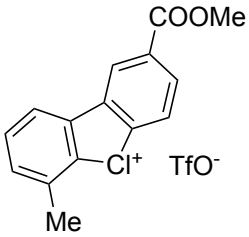




3-chloro-6-methyldibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2x

Following the **GP-B** using **1x** (596 mg, 2.16 mmol) **2x** was obtained as white solid in 42% yield. (169.7 mg, 0.44 mmol).

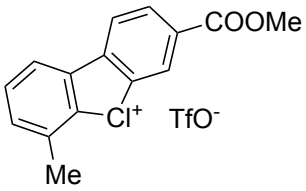
^{1}H NMR (400 MHz, DMSO) δ 8.83 (d, *J* = 1.9 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.55 – 8.52 (m, 1H), 8.17 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.95 (t, *J* = 7.6 Hz, 1H), 7.87 – 7.84 (m, 1H), 2.76 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 141.3, 139.2, 135.4, 133.2, 132.6, 132.2, 131.8, 131.8, 130.8, 126.9, 123.5, 122.6, 19.0. **^{19}F NMR** (377 MHz, DMSO) δ -77.7. **HRMS (ESI)**: m/z $[M\text{-}OTf]^+$ calcd for $C_{13}H_9Cl_2^+$: 235.0076; found: 235.0093.



2-(methoxycarbonyl)-6-methyldibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2y

Following the **GP-B** using **1y** (480 mg, 1.74 mmol) **2y** was obtained as white solid in 60% yield. (424.6 mg, 1.039 mmol).

^{1}H NMR (400 MHz, DMSO) δ 9.22 – 9.20 (m, 1H), 8.81 (d, *J* = 9.1 Hz, 1H), 8.75 – 8.73 (m, 1H), 8.48 (dd, *J* = 9.1, 2.0 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.88 – 7.86 (m, 1H), 3.99 (s, 3H), 2.76 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 164.6, 142.9, 141.2, 133.5, 133.3, 133.3, 132.5, 132.1, 131.7, 131.0, 126.7, 124.0, 123.4, 53.1, 19.0. **^{19}F NMR** (377 MHz, DMSO) δ -77.8. **HRMS (ESI)**: m/z $[M\text{-}OTf]^+$ calcd for $C_{15}H_{12}ClO_2^+$: 259.0520; found: 259.0538.

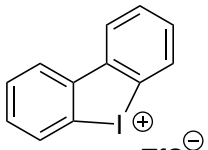


3-(methoxycarbonyl)-6-methyldibenzo[b,d]chlorol-5-ium trifluoromethanesulfonate 2z

Following the **GP-B** using **1z** (596 mg, 2.16 mmol) **2z** was obtained as white solid in 59% yield. (520 mg, 1.27 mmol).

^{1}H NMR (400 MHz, DMSO) δ 9.30 (s, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 8.61 (d, *J* = 7.7 Hz, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.3 Hz, 1H), 3.99 (s, 3H), 2.78 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 164.0, 141.6, 140.0, 136.6, 134.1, 132.5, 132.5, 132.2, 131.9, 130.7, 126.2, 124.2, 123.8, 53.2, 19.0. ^{19}F NMR (377 MHz, DMSO) δ -77.8. **HRMS (ESI)**: m/z $[M\text{-}OTf]^+$ calcd for $C_{15}H_{12}ClO_2^+$: 259.0520; found: 259.0518.

Preparation of cyclic diaryl λ^3-iodane **4a**-OTf



4a-OTf

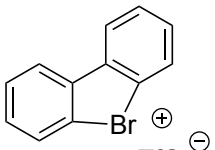
dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate 4a-OTf

Following a reported procedure[5]: To a stirred solution of 2-iodo-1,1'-biphenyl (1.1 g, 3.93 mmol) in anhydrous CH_2Cl_2 (10 mL, 0.4 M) was added *m*-CPBA (1.02 g, 5.89 mmol) and TfOH (1.04 mL, 11.78 mmol). The solution was stirred for 1 h at r.t. CH_2Cl_2 was removed by rotary evaporation before Et_2O (15 mL) was added, and the mixture was stirred for 20 min, and filtered. The collected solid was washed with Et_2O three times, dried in vacuo to afford **4a**-OTf (1.68g, 98% yield) as a white powder.

^{1}H NMR (400 MHz, DMSO) δ 8.50 (dd, *J* = 7.9, 1.5 Hz, 2H), 8.22 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.87 (td, *J* = 7.6, 1.1 Hz, 2H), 7.72 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 2H).

The spectral data correspond to the literature. [5]

Preparation of cyclic diaryl λ^3-bromane **3a**-OTf



3a-OTf

dibenzo[b,d]bromol-5-ium trifluoromethanesulfonate 3a-OTf

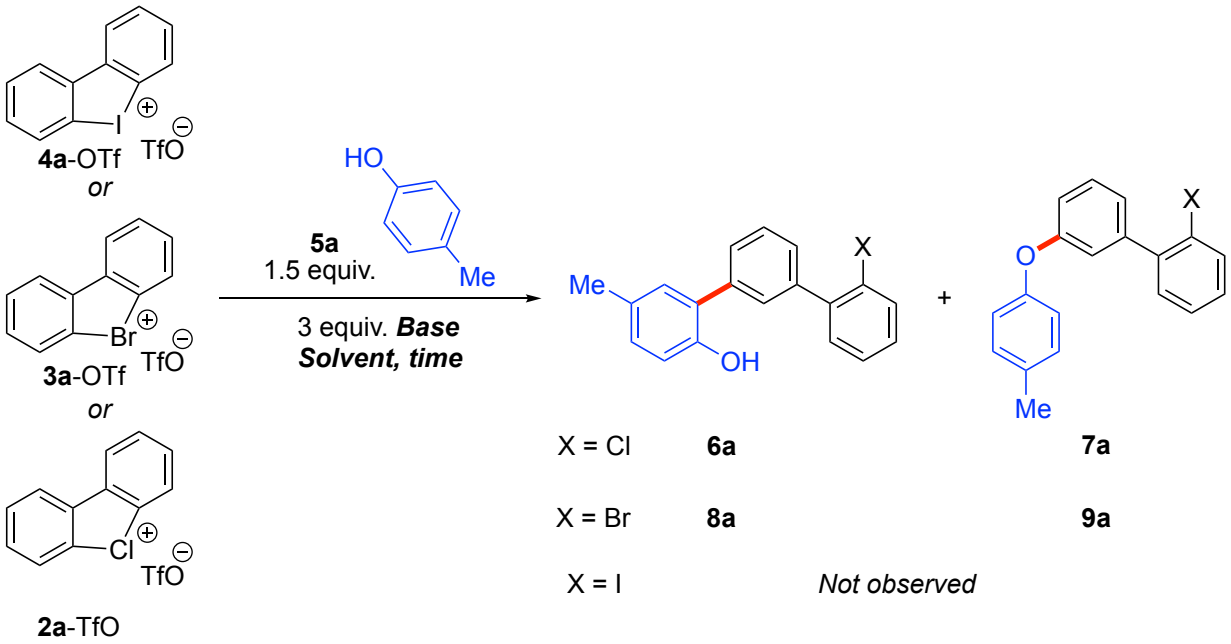
To a stirred solution of 2'-bromo-[1,1'-biphenyl]-2-amine (2 g, 8 mmol) in CH_3CN (40 mL, 0.2 M) was added *t*-butyl nitrite (1.9 mL, 16.1 mmol, 2 equiv.) and TfOH (1.4 mL, 16.1 mmol, 2 equiv.). The solution was stirred for 1 h at 0 °C then heated to 65 °C for 1h. The cooled reaction was purged in cold Et_2O (3:1 Et_2O:CH_3CN) where a white solid precipitate. The collected solid was washed with Et_2O three times, dried in vacuo to afford **3a**-OTf (1.8 g, 4.72 mmol, 59 %) as a white powder.

^{1}H NMR (400 MHz, DMSO) δ 8.59 (dd, *J* = 7.8, 1.6 Hz, 2H), 8.47 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.95 (td, *J* = 7.6, 1.1 Hz, 2H), 7.85 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 2H).

The spectral data correspond to the literature. [6]

Optimization of the reactions conditions:

Control Experiments

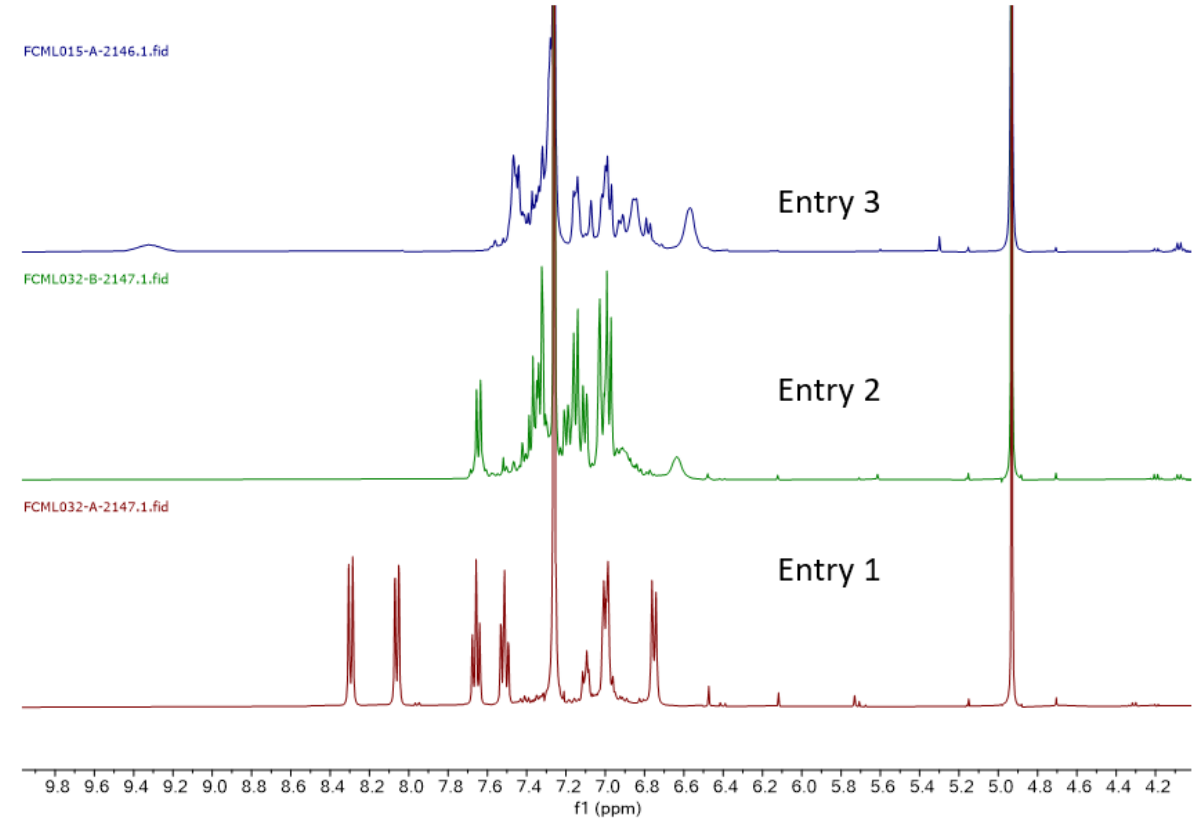


SCHEME S-5

To an oven dried tube equipped with magnetic stirring was charged the hypervalent compound **[X(III)OTf]** (0.15 mmol, 1 equiv.), the corresponding base (0.3 mmol), and the 4-MethylPhenol **5a** (24 mg, 0.23 mmol, 1.5 equiv.). The tube is degassed and back refilled with argon. Then the corresponding solvent was added, and the mixture was stirred at room temperature for the corresponding time.

TABLE S-2

Entry	*X(III)-OTf*	*Base*	*Time/Temperature*	*Solvent*	*Isolated Yield 6 or 8*	*Isolated Yield 7 or 9*
1	I(III)-OTf (**4a**-OTf)				No Conversion/Decomposition	
2	Br(III)-OTf (**3a**-OTf)	Cs_2CO_3	16h at r.t.	$CHCl_3$	15%	70%
3	Cl(III)-OTf (**2a**-TfO)				35%	35%
4	I(III)-OTf (**4a**-OTf)				No Conversion/Decomposition	
5	Br(III)-OTf (**3a**-OTf)	K_2CO_3	16h at r.t.	$CHCl_3$	26%	9%
6	Cl(III)-OTf (**2a**-TfO)				49%	Traces
7	I(III)-OTf (**4a**-OTf)				No Conversion/Decomposition	
8	Br(III)-OTf (**3a**-OTf)	K_2CO_3	3h at r.t.	H_2O	No Conversion/Decomposition	
9	Cl(III)-OTf (**2a**-TfO)				13%	60%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Entry 3
FCML032-B-2147.1.fid
Entry 2
FCML032-A-2147.1.fid
Entry 1
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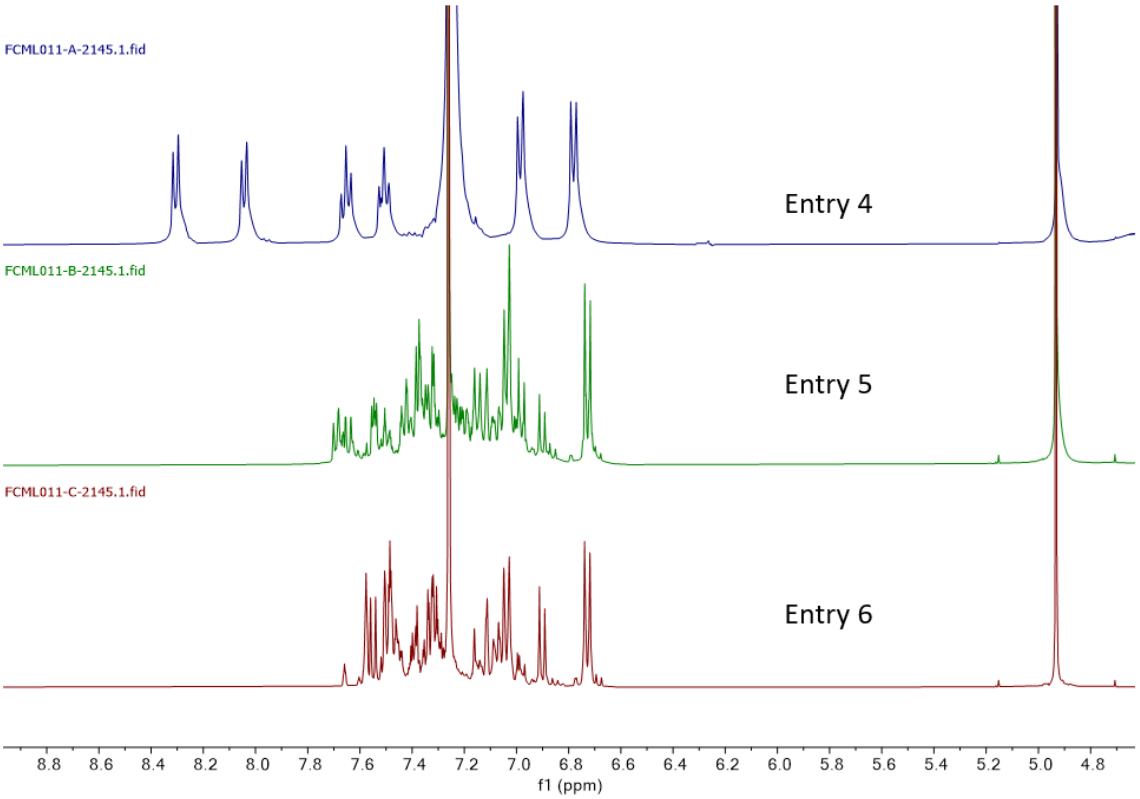
f1 (ppm)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Entry 5
FCML011-C-2145.1.fid
Entry 6
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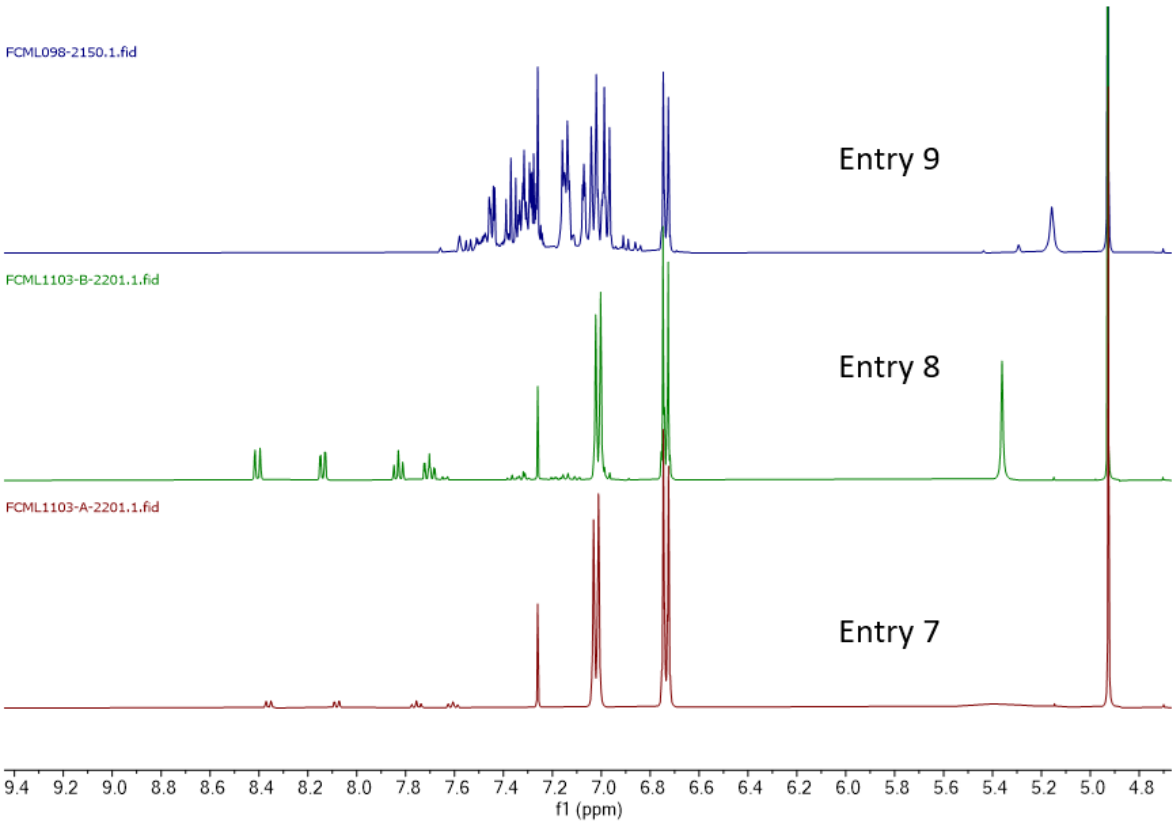
f1 (ppm)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Entry 8
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Entry 7
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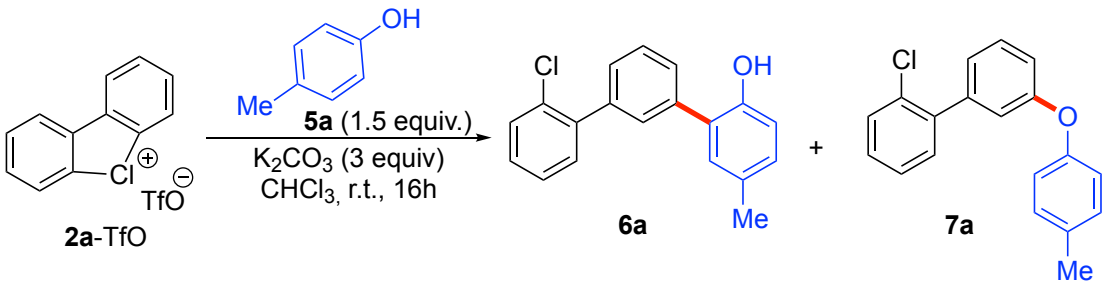
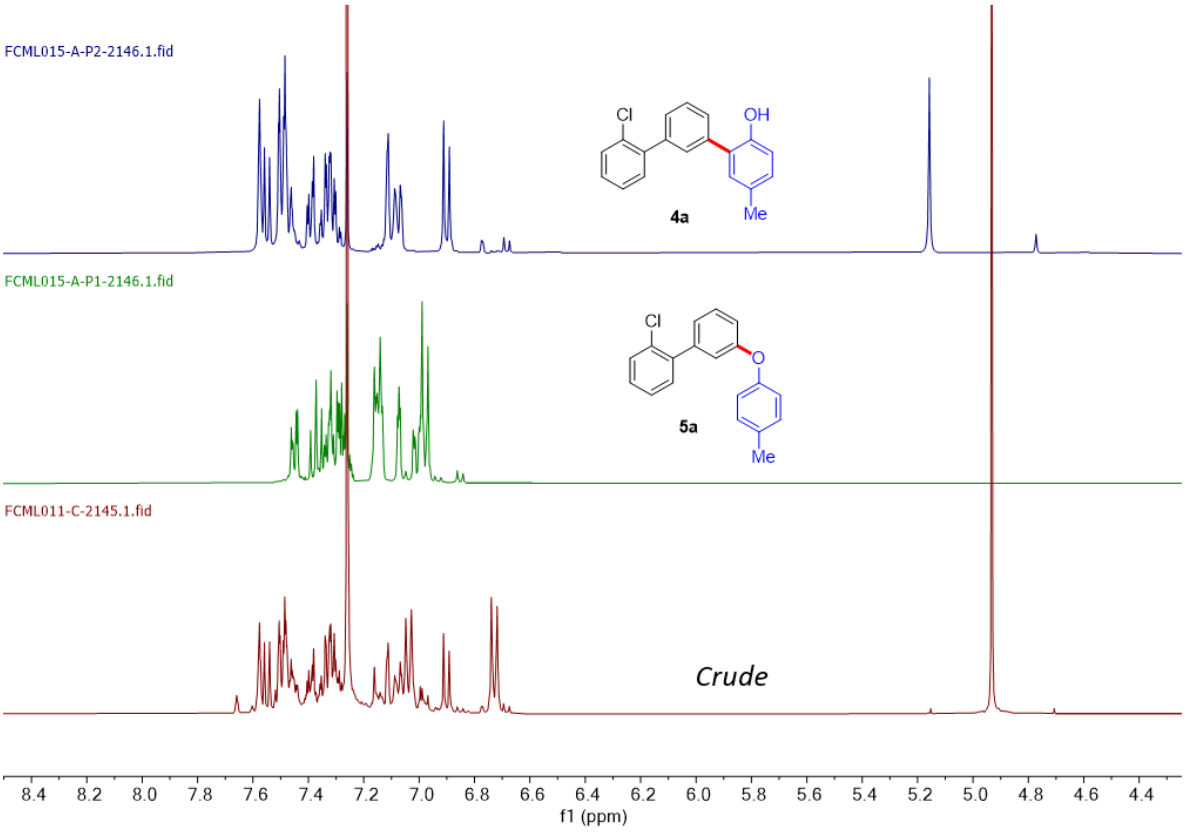
f1 (ppm)


OH
Me
5a (1.5 equiv.)
K2CO3 (3 equiv)
CHCl3, r.t., 16h
Cl
TfO
2a-TfO
Cl
OH
Me
6a
+
Cl
O
Me
7a

SCHEME S-6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4a
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Cl
O
5a
Me
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8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
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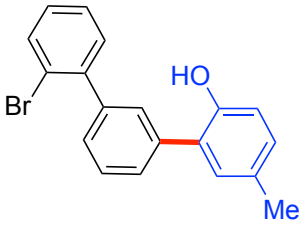
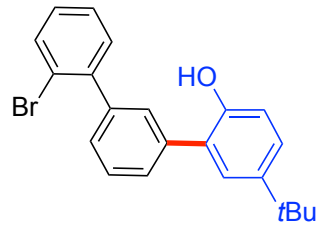
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
f1 (ppm)



2''-bromo-5-methyl-[1,1':3',1''-terphenyl]-2-ol 8a

Table S-2; Entry 5: **8a** was obtained as colorless oil in 26% yield. (13 mg, 0.039 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 86:14.

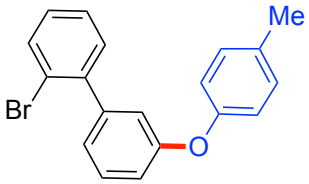
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.51 – 7.48 (m, 1H), 7.44 – 7.42 (m, 1H), 7.38 – 7.37 (m, 2H), 7.24 – 7.21 (m, 1H), 7.11 (d, *J* = 2.7 Hz, 1H), 7.07 (ddd, *J* = 8.2, 2.3, 0.7 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 5.18 (s, 1H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.3, 142.0, 141.9, 136.9, 133.2, 131.2, 130.7, 130.0 (2C), 129.8, 129.0, 129.0, 128.7, 128.3, 127.5, 127.4, 122.6, 115.7, 20.5. **HRMS (APCI)**: m/z $[M+H]^+$ calcd for $C_{19}H_{16}BrO^+$: 339.0379; found: 339.0383.



2''-bromo-5-(*tert*-butyl)-[1,1':3',1''-terphenyl]-2-ol 8b

Following the conditions of ***Table S-2***; **Entry 5: 8b** was obtained as colorless oil in 30% yield. (17 mg, 0.045 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 99:1.

^{1}H NMR (400 MHz, CDCl3) δ 7.65 – 7.63 (m, 1H), 7.53 – 7.45 (m, 3H), 7.39 (dt, J = 7.4, 1.6 Hz, 1H), 7.34 – 7.32 (m, 2H), 7.26 – 7.24 (m, 2H), 7.20 – 7.15 (m, 1H), 6.89 (d, J = 9.2 Hz, 1H), 5.18 (brs, 1H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz, CDCl3) δ 150.3, 143.7, 142.0, 141.9, 137.4, 133.3, 131.3, 130.2, 129.1, 129.0, 128.7, 128.4, 127.6, 127.2, 127.1, 126.3, 122.6, 115.5, 34.2, 31.6. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{21}BrO^+$: 380.0770; found: 380.0763.



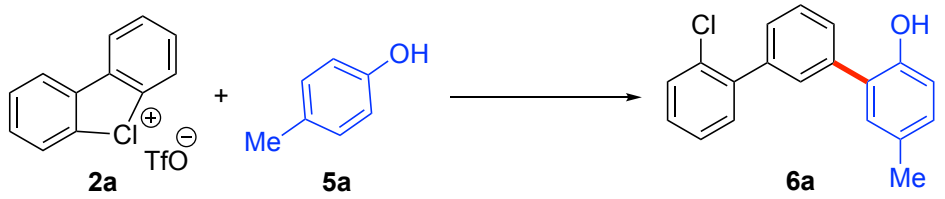
2-bromo-3'-(p-tolyloxy)-1,1'-biphenyl 9a

Table S-2; Entry 2: **9a** was obtained as colorless oil in 70% yield. (36 mg, 0.105 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 99:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.47 – 7.44 (m, 1H), 7.43 – 7.41 (m, 2H), 7.37 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.31 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 7.27 – 7.24 (m, 2H), 2.61 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4, 154.5, 142.6, 142.0, 133.1, 133.0, 131.1, 130.2 (2C), 129.2, 128.8, 127.3, 123.8, 122.5, 119.3, 119.2 (2C), 117.5, 20.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{15}BrO^+$: 338.0301; found: 338.0301.

Optimization of metal-free CDC C-C bond formation with cyclic diaryl λ^3-chloranes

Table S-3



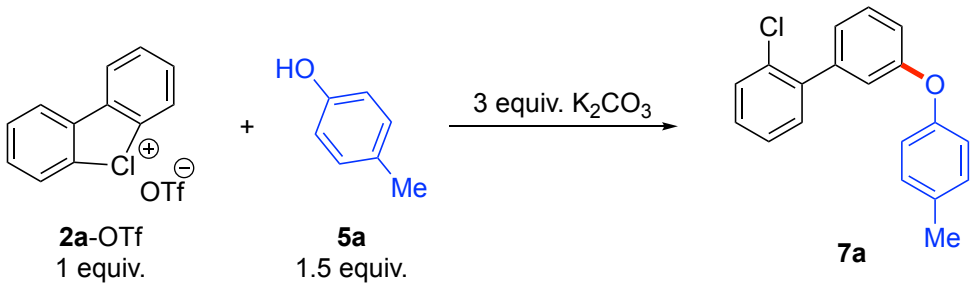
To an oven dry vial was charged **2a**-OTf (50.5 mg, 0.15 mmol, 1 equiv.) and the base. The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, **5a** was added followed by the desired solvent. The resulting mixture was stirred, and the conversion was verified by GCMS and TLC. The **^{1}H NMR** of the crude was recorded, yields were calculated using CH_2Br_2 as internal standard (20 µL, 0.284 mmol). ([a] Isolated yields)

2a	Eq of **2a**	Eq of **5a**	Base	Eq of base	Solvent (M)	Time;temp.	NMR Yield of **6a**%
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$	16h; r.t.	66% (49%)[a]
2a-OTf	1	1.5	-	-	$CHCl_3$	16h; r.t.	No Conversion
2a-BF_4	1	1.5	K_2CO_3	3	$CHCl_3$	16h; r.t.	61%
2a-PF_6	1	1.5	K_2CO_3	3	$CHCl_3$	16h; r.t.	62%
2a-OMs	1	1.5	K_2CO_3	3	$CHCl_3$	16h; r.t.	54%
2a-OTf	1	1.5	Cs_2CO_3	3	$CHCl_3$	16h; r.t.	47% (35%)[a]
2a-OTf	1	1.5	Li_2CO_3	3	$CHCl_3$	16h; r.t.	No Conv.
2a-OTf	1	1.5	Na_2CO_3	3	$CHCl_3$	16h; r.t.	57%
2a-OTf	1	1.5	$KHCO_3$	3	$CHCl_3$	16h; r.t.	37%
2a-OTf	1	1.5	KOH	3	$CHCl_3$	16h; r.t.	Decomposition
2a-OTf	1	1.5	KtBuO	3	$CHCl_3$	16h; r.t.	37%
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$ (0.05M)	16h; r.t.	64%
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$ (0.2M)	16h; r.t.	56%
2a-OTf	1	1.2	K_2CO_3	3	$CHCl_3$	16h; r.t.	63%
2a-OTf	1.2	1	K_2CO_3	3	$CHCl_3$	16h; r.t.	58%
2a-OTf	1	1.5	K_2CO_3	3	DCM	16h; r.t.	64%
2a-OTf	1	1.5	K_2CO_3	3	Acetone	16h; r.t.	Decomposition
2a-OTf	1	1.5	K_2CO_3	3	CH_3CN	16h; r.t.	18%
2a-OTf	1	1.5	K_2CO_3	3	Toluene	16h; r.t.	68% (45%)[a]
2a-OTf	1	1.5	K_2CO_3	3	Dioxane	16h; r.t.	
2a-OTf	1	1.5	K_2CO_3	3	DME	16h; r.t.	
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$	16h; 0°C	37%
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$	16h; 50°C	45%

2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$	16h; 30°C	37%
2a-OTf	1	1.5	K_2CO_3	1.5	$CHCl_3$	16h; r.t.	56%
2a-OTf	1	1.5	K_2CO_3	2	$CHCl_3$	16h; r.t.	62%
2a-OTf	1	1.5	K_2CO_3	5	$CHCl_3$	16h; r.t.	68%
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$	9h; r.t.	59%
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$	6h; r.t.	66%
2a-OTf	***1***	***1.5***	***K_2CO_3***	***3***	***$CHCl_3$***	***3h; r.t.***	***66%***
2a-OTf	1	1.5	K_2CO_3	3	$CHCl_3$	1.5h; r.t.	54%

Optimization of metal free C-O arylation of phenols with cyclic diaryl λ^3-chloride

Table S-4



2a-OTf
1 equiv.

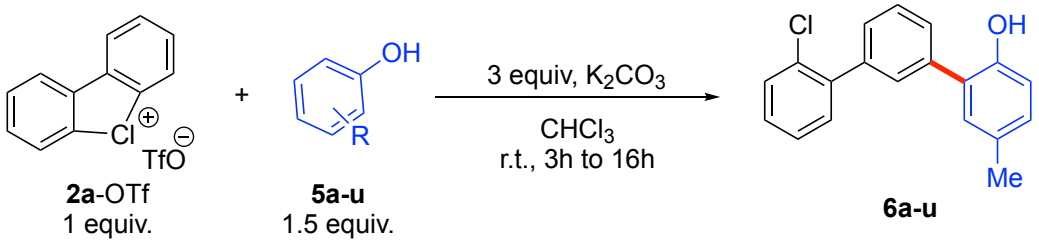
5a
1.5 equiv.

7a

To an oven dry vial was charged **2a**-OTf (50.5 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, the **5a** (24 mg, 0.23 mmol, 1.5 equiv.) was added followed by the solvent. The resulting mixture was stirred at room temperature for 16 hours at the desired temperature. The conversion was verified by GCMS and TLC. The mixture was extracted with EtOAc (3 mL x 3 times). The extracts were combined, dried over $MgSO_4$, filtered, and concentrated. The **^{1}H NMR** of the crude was recorded, yields were calculated using CH_2Br_2 as internal standard (20 µL, 0.284 mmol). ([a] Isolated yields)

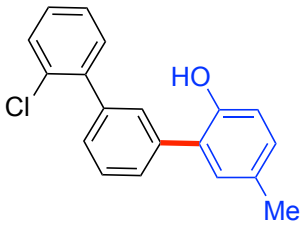
Base	Solvent (M)		time@temp.	NMR Yield of **7a**
K_2CO_3	H_2O	0.1M	16h; r.t.	84% (60%)
$KHCO_3$	H_2O	0.1M	16h; r.t.	51%
Li_2CO_3	H_2O	0.1M	16h; r.t.	76%
Na_2CO_3	H_2O	0.1M	16h; r.t.	72%
K_2CO_3	H_2O	0.2M	16h; r.t.	84%
K_2CO_3	H_2O	0.05M	16h; r.t.	80%
K_2CO_3	H_2O	0.1M	16h; 50°C	74%
K_2CO_3	H_2O (1mL) + Acetone (0.5mL)	0.1M	16h; r.t.	78%
K_2CO_3	H_2O (1mL) + CH_3CN (0.5mL)	0.1M	16h; r.t.	80%
-	H_2O (1mL) + CH_3CN (0.5mL)	0.1M	16h; r.t.	No conversion

General procedure C: Metal-free CDC C-C bond formation with cyclic diaryl λ^3-chloranes 5a-u



SCHEME S-7

To an oven dry vial was charged **2a**-OTf (50.5 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, the desired phenol **5a-u** (1.5 equiv) was added followed by $CHCl_3$ (1.5 mL, 0.1M or 1 mL, 0.15M as specify). The resulting heterogeneous mixture was stirred at room temperature for 3 to 16 hours. The conversion was verified by GCMS and TLC. The mixture was diluted with EtOAc (3 mL) and filtered. After removal of volatile components, the crude was purified through Prep-TLC.

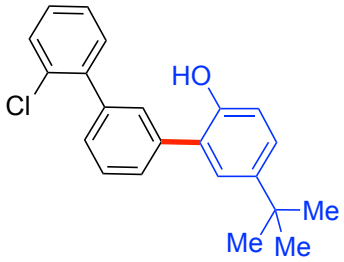


2''-chloro-5-methyl-[1,1':3',1''-terphenyl]-2-ol 6a

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and *p*-cresol **5a** (24 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6a** was obtained as colorless oil in 49% yield. (21.2 mg, 0.072 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 90:10.

3 mmol scale: To a round bottom flask was charged **2a**-OTf (1 g, 3 mmol), *p*-cresol **5a** (500 mg, 4.5 mmol) and K_2CO_3 (1.24 g, 9 mmol.) followed by $CHCl_3$ (20 mL, 0.15 M). The resulting mixture was stirred for 30 hours at room temperature. After a standard treatment **6a** was obtained as colorless oil in 64% yield. (567 mg, 1.92 mmol).

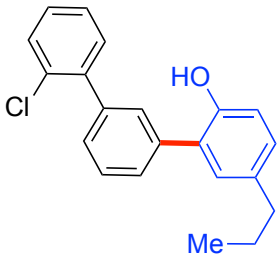
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.51 – 7.50 (m, 1H), 7.49 – 7.46 (m, 2H), 7.40 – 7.38 (m, 1H), 7.36 – 7.29 (m, 2H), 7.12 (d, *J* = 2.7 Hz, 1H), 7.08 (ddd, *J* = 8.2, 2.3, 0.8 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 5.18 (brs, 1H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.2, 140.2, 139.9, 137.0, 132.4, 131.3, 130.7, 130.1, 130.0, 130.0, 129.7, 129.0, 128.8, 128.8, 128.2, 127.4, 126.9, 115.7, 20.5. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{15}ClO^+$: 294.0806; found: 294.0787.



5-(tert-butyl)-2''-chloro-[1,1':3',1''-terphenyl]-2-ol 6b

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-tert-butylphenol **5b** (33.8 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6b** was obtained as colorless oil in 70% yield. (35.5 mg, 0.105 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 92:8.

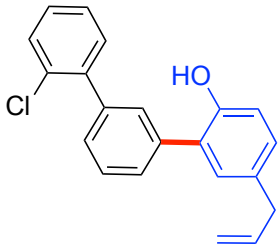
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, *J* = 1.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.36 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.31 – 7.25 (m, 4H), 6.90 (d, *J* = 9.2 Hz, 1H), 5.14 (brs, 1H), 1.29 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.2, 143.6, 140.2, 139.9, 137.4, 132.5, 131.4, 130.2, 130.1, 129.0, 128.8, 128.7, 128.3, 127.1, 127.1, 127.0, 126.2, 115.4, 34.2, 31.5 (3C). **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{21}ClO^+$: 336.1275; found: 336.1255.



2''-chloro-5-propyl-[1,1':3',1''-terphenyl]-2-ol 6c

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-propylphenol **5c** (31 µL, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6c** was obtained as colorless oil in 53% yield. (25.4 mg, 0.079 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 94:6.

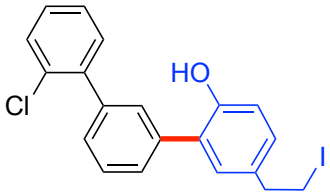
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (t, *J* = 1.8 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.66 – 7.61 (m, 3H), 7.54 (dd, *J* = 7.2, 2.3 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.26 (d, *J* = 2.3 Hz, 1H), 7.23 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 5.32 (brs, 1H), 2.73 (m, 2H), 1.79 (h, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.4, 140.2, 139.9, 137.2, 135.1, 132.5, 131.3, 130.1 (2C), 130.0, 129.2, 129.0, 128.8, 128.7, 128.3, 127.4, 126.9, 115.7, 37.2, 24.8, 13.8. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{21}H_{19}ClO^+$: 322.1119; found: 322.1116.



5-allyl-2''-chloro-[1,1':3',1''-terphenyl]-2-ol 6d

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-(prop-2-en-1-yl)phenol **5d** (30 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6d** was obtained as colorless oil in 64% yield. (30.7 mg, 0.096 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 92:8. (2 mmol scale: 190 mg, 0.6 mmol, 30%)

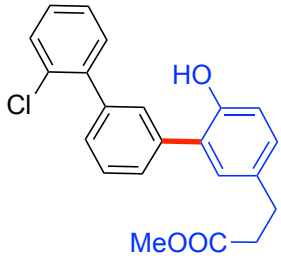
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (t, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.40 – 7.38 (m, 1H), 7.36 – 7.29 (m, 2H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 5.99 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.21 (brs, 1H), 5.12 – 5.05 (m, 2H), 3.37 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.8, 140.3, 139.9, 137.7, 137.0, 132.4, 132.4, 131.3, 130.3, 130.1, 130.0, 129.3, 129.0, 128.8 (2C), 128.3, 127.6, 126.9, 115.9, 115.7, 39.4. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{21}H_{17}ClO^+$: 320.0962; found: 320.0952.



2''-chloro-5-(2-iodoethyl)-[1,1':3',1''-terphenyl]-2-ol 6e

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-(2-iodoethyl)phenol **5e** (55.8 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6e** was obtained as colorless oil in 30% yield. (19.5 mg, 0.045 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 89:11.

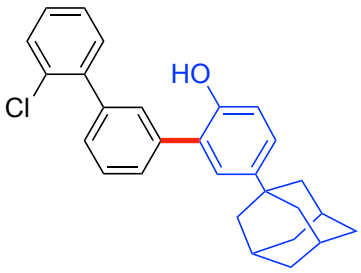
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.51 – 7.47 (m, 3H), 7.40 – 7.38 (m, 1H), 7.36 – 7.29 (m, 2H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 5.28 (s, 1H), 3.37 – 3.33 (m, 2H), 3.15 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 140.4, 139.8, 136.6, 133.1, 132.4, 131.3, 130.1, 130.1, 130.1, 129.1, 129.1, 129.0, 128.9, 128.2, 127.9, 127.0, 116.1, 39.6, 6.2. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{17}ClO^+$: 433.9929; found: 433.9910.



methyl 3-(2''-chloro-6-hydroxy-[1,1':3',1''-terphenyl]-3-yl)propanoate 6f

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and methyl 3-(4-hydroxyphenyl)propionate **5f** (41 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6f** was obtained as colorless oil in 57% yield. (31.6 mg, 0.086 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 90:10.

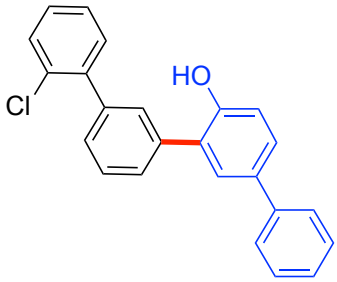
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.50 – 7.46 (m, 3H), 7.40 – 7.38 (m, 1H), 7.35 – 7.29 (m, 2H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 5.29 (brs, 1H), 3.67 (s, 3H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.65 – 2.62 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4, 151.0, 140.3, 139.9, 136.9, 132.8, 132.4, 131.3, 130.1, 130.0 (2C), 129.0, 129.0, 128.8, 128.8, 128.2, 127.7, 126.9, 116.0, 51.6, 36.0, 30.1. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{19}ClO_3^+$: 366.1017; found: 366.1007.



5-((3r,5r,7r)-adamantan-1-yl)-2''-chloro-[1,1':3',1''-terphenyl]-2-ol 6g

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-(adamantan-1-yl)phenol **5g** (51.4 mg, 0.23 mmol) in $CHCl_3$ (1 mL, 0.15 M) for 48 hours, **6g** was obtained as colorless oil in 72% yield. (45 mg, 0.108 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 95:5.

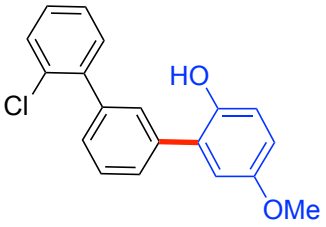
^{1}HNMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.51 – 7.45 (m, 3H), 7.40 – 7.37 (m, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.25 (m, 2H), 6.94 (d, *J* = 9.2 Hz, 1H), 5.17 (s, 1H), 2.09 – 2.07 (brs, 3H), 1.91 (d, *J* = 3.1 Hz, 6H), 1.77 -1.74 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 144.0, 140.2, 140.0, 137.5, 132.5, 131.4, 130.2, 130.0, 129.0, 128.8, 128.7, 128.3, 127.1, 126.9, 126.8, 125.7, 115.5, 43.4 (3C), 36.8 (3C), 35.7, 29.0 (3C). **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{28}H_{27}ClO^+$: 414.1745; found: 414.1754.



2'''-chloro-[1,1':3',1'':3'',1'''-quaterphenyl]-4'-ol 6h

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-phenylphenol **5h** (38 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6h** was obtained as colorless oil in 52% yield. (25.4 mg, 0.071 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 89:11.

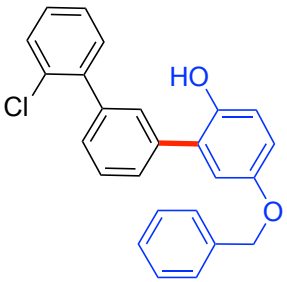
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.42 (m, 9H), 7.37 – 7.33 (m, 3H), 7.29 – 7.23 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.29 (brs, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.1, 140.6, 140.4, 139.8, 136.8, 134.1, 132.4, 131.3, 130.2, 130.1, 129.2, 129.0, 129.0, 128.9, 128.7 (2C), 128.3, 128.0, 127.9, 127.0, 126.8, 126.7 (2C), 116.4. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{24}H_{17}ClO^+$: 356.0962; found: 356.0943.



2''-chloro-5-methoxy-[1,1':3',1''-terphenyl]-2-ol 6i

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-Methoxyphenol **5i** (28 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6i** was obtained as colorless oil in 53% yield. (24.5 mg, 0.079 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 89:11.

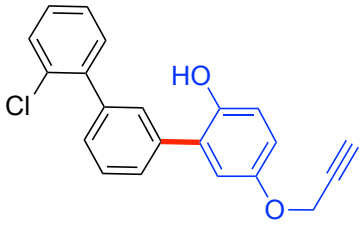
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.40 – 7.38 (m, 1H), 7.36 – 7.29 (m, 2H), 6.93 (dd, *J* = 8.7, 0.5 Hz, 1H), 6.87 (d, *J* = 2.9 Hz, 1H), 6.84 (dd, *J* = 8.6, 3.1 Hz, 1H), 4.98 (brs, 1H), 3.80 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.7, 146.5, 140.3, 139.8, 137.0, 132.4, 131.3, 130.1, 130.1, 129.1, 128.9, 128.8, 128.3, 128.2, 127.0, 116.7, 115.2, 114.8, 55.8. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{15}ClO_2^+$: 310.0755; found: 310.0742.



5-(benzyloxy)-2''-chloro-[1,1':3',1''-terphenyl]-2-ol 6j

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-(benzyloxy)phenol **5j** (45 mg, 0.23 mmol) in $CHCl_3$ (1 mL, 0.15 M) for 36 hours **6j** was obtained as pale yellow oil in 69% yield. (40 mg, 0.103 mmol). Regioselective ratio determined by **^{1}H-NMR** *m*:*o* = 92:8.

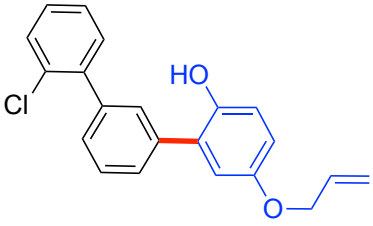
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.32 – 7.31 (m, 2H), 7.27 – 7.25 (m, 3H), 7.23 – 7.17 (m, 4H), 6.84 – 6.79 (m, 2H), 4.92 (s, 2H), 4.90 (brs, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.9, 146.7, 140.3, 139.8, 137.2, 136.9, 132.4, 131.3, 130.1, 130.0, 129.0, 128.9, 128.8, 128.5 (2C), 128.3, 128.2, 127.9, 127.5 (2C), 127.0, 116.7, 116.5, 115.8, 70.8. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{25}H_{19}ClO_2^+$: 386.1068; found: 386.1047.



2''-chloro-5-(prop-2-yn-1-yloxy)-[1,1':3',1''-terphenyl]-2-ol 6k

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-(prop-2-yn-1-yloxy)phenol **5k** (33 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6k** was obtained as colorless oil in 58% yield. (29 mg, 0.087 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 88:12.

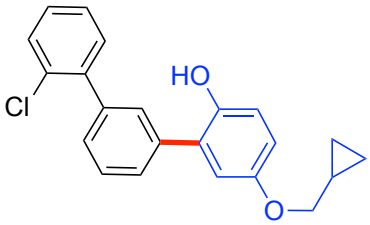
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.43 – 7.39 (m, 3H), 7.32 – 7.29 (m, 1H), 7.27 – 7.20 (m, 2H), 6.88 – 6.87 (m, 1H), 6.85 – 6.84 (m, 2H), 4.98 (brs, 1H), 4.59 (d, *J* = 2.4 Hz, 2H), 2.43 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 147.3, 140.3, 139.8, 136.7, 132.4, 131.3, 130.0 (2C), 129.1, 129.0, 128.8, 128.3, 128.2, 127.0, 116.8, 116.7, 116.1, 78.8, 75.4, 56.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{21}H_{15}ClO_2^+$: 334.0755; found: 334.0741.



5-(allyloxy)-2''-chloro-[1,1':3',1''-terphenyl]-2-ol 6l

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-(prop-2-en-1-yloxy)phenol **5l** (33.8 mg, 0.22 mmol) in $CHCl_3$ (1 mL, 0.15 M) for 32 hours, **6l** was obtained as pale yellow oil in 59% yield. (30 mg, 0.089 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 89:11.

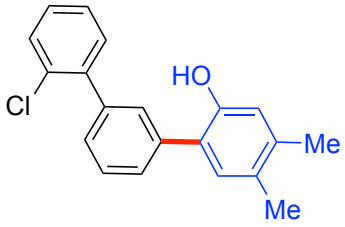
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, J = 1.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H), 7.28 – 7.26 (m, 1H), 7.24 – 7.17 (m, 2H), 6.81 – 6.78 (m, 2H), 6.75 – 6.72 (m, 1H), 5.95 (ddt, J = 17.3, 10.6, 5.3 Hz, 1H), 5.30 (dq, J = 17.3, 1.7 Hz, 1H), 5.16 (dq, J = 10.5, 1.5 Hz, 1H), 4.93 (brs, 1H), 4.40 (dt, J = 5.3, 1.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.6, 146.6, 140.2, 139.8, 136.9, 133.5, 132.4, 131.3, 130.1, 130.0, 129.0, 128.9, 128.8, 128.3, 128.2, 126.9, 117.6, 116.7, 116.4, 115.7, 69.6. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{21}H_{17}ClO_2^+$: 336.0912; found: 336.0892.



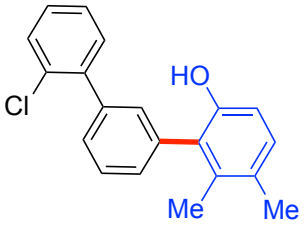
2''-chloro-5-(cyclopropylmethoxy)-[1,1':3',1''-terphenyl]-2-ol 6m

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-(cyclopropylmethoxy)phenol **5m** (37.0 mg, 0.22 mmol) in $CHCl_3$ (1 mL, 0.15 M) for 32 hours **6m** was obtained as pale yellow oil in 55% yield. (29 mg, 0.083 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 89:11.

^{1}H NMR (400 MHz, CDCl3) δ 7.51 – 7.50 (m, 1H), 7.50 – 7.46 (m, 1H), 7.44 – 7.38 (m, 3H), 7.32 – 7.30 (m, 1H), 7.28 – 7.20 (m, 2H), 6.85 – 6.75 (m, 3H), 4.97 (brs, 1H), 3.71 (d, J = 7.0 Hz, 2H), 1.24 – 1.14 (m, 1H), 0.58 – 0.53 (m, 2H), 0.28 – 0.24 (m, 2H). **^{13}C NMR** (101 MHz, CDCl3) δ 153.0, 146.5, 140.2, 139.8, 137.0, 132.4, 131.3, 130.1, 130.0, 129.0, 128.9, 128.8, 128.2, 128.2, 126.9, 116.7, 116.2, 115.7, 73.6, 10.4, 3.1 (2C). **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{19}ClO_2^+$: 350.1068; found: 350.1053.



4n

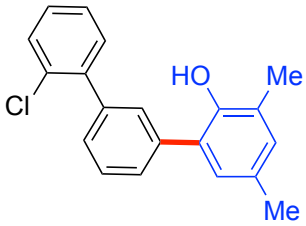


4n'

2''-chloro-4,5-dimethyl-[1,1':3',1''-terphenyl]-2-ol 6n and 2''-chloro-5,6-dimethyl-[1,1':3',1''-terphenyl]-2-ol 6n'

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 3,4-dimethylphenol **5n** (27.5 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6n** and **6n'** were obtained as colorless oil in 57% yield. (**^{1}HNMR** 1:1.1 mixture, 26.5 mg, 0.086 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 91:9.

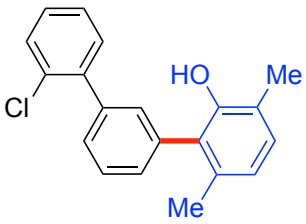
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.48 (m, 4H), 7.45 (dt, *J* = 7.3, 1.5 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.35 – 7.28 (m, 5H), 7.10 – 7.07 (m, 2H), 6.81 – 6.79 (m, 2H), 5.23 (s, 1H), 4.74 (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (126 MHz, CDCl3) δ 150.9, 150.3, 140.4, 140.1, 140.0, 139.8, 137.8, 137.1, 135.7, 135.4, 132.4 (2C), 131.6, 131.3, 131.2, 131.1, 130.1, 130.0, 130.0, 129.9, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7 (2C), 128.5, 128.5, 128.2, 127.9, 126.9 (2C), 125.0, 117.1, 112.1, 19.8, 19.6, 18.7, 17.3. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{17}ClO^+$: 308.0962; found: 308.0963.



2''-chloro-3,5-dimethyl-[1,1':3',1''-terphenyl]-2-ol 6o

Following the **GP-C** using **2a**-OTf (33.7 mg, 0.1 mmol) and 2,4-dimethylphenol **5o** (18.3 mg, 0.15 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6o** was obtained as colorless oil in 53% yield. (16.4 mg, 0.052 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 91:9.

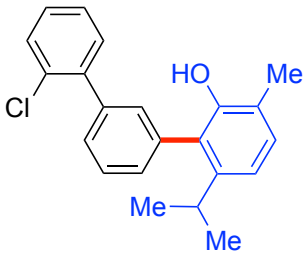
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.50 – 7.46 (m, 3H), 7.40 – 7.38 (m, 1H), 7.35 – 7.29 (m, 2H), 6.97 – 6.95 (m, 2H), 5.22 (brs, 1H), 2.29 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.4, 140.3, 139.9, 137.3, 132.5, 131.3, 131.3, 130.1, 130.0, 129.3, 129.1, 128.8, 128.7, 128.3, 128.1, 127.1, 126.9, 124.5, 20.4, 16.2. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{17}ClO^+$: 308.0962; found: 308.0956.



2''-chloro-3,6-dimethyl-[1,1':3',1''-terphenyl]-2-ol 6p

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 2,5-dimethylphenol **5p** (21 mg, 0.22 mmol) in $CHCl_3$ (1 mL, 0.15 M) **6p** was obtained as colorless oil in 76% yield. (35 mg, 0.114 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 99:1.

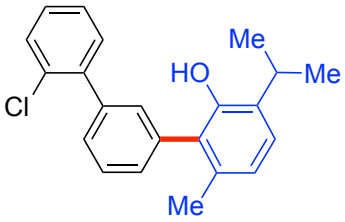
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.37 – 7.36 (m, 1H), 7.34 (dd, J = 7.4, 2.0 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.00 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 4.85 (s, 1H), 2.22 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 140.5, 139.8, 135.4, 134.4, 132.5, 131.5, 131.2, 130.0, 129.8, 129.5, 129.2, 129.1, 128.8, 127.2, 126.9, 121.5, 121.4, 20.3, 16.0. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{17}ClO^+$: 308.0962; found:308.0954.



2''-chloro-6-isopropyl-3-methyl-[1,1':3',1''-terphenyl]-2-ol 6q

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and isothymol **5q** (35 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6q** was obtained as colorless oil in 59% yield. (30 mg, 0.089 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 99:1.

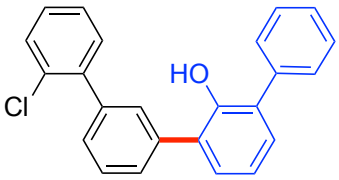
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (td, *J* = 7.6, 0.6 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.36 (td, *J* = 1.8, 0.6 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.30 – 7.22 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 4.72 (d, *J* = 0.6 Hz, 1H), 2.70 (hept, *J* = 6.9 Hz, 1H), 2.21 (s, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 145.5, 140.4, 139.8, 135.1, 132.5, 131.7, 131.2, 130.3, 130.1, 129.8, 129.2, 129.1, 128.8, 126.9, 126.3, 121.2, 116.7, 30.0, 24.1, 24.1, 15.9. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{21}ClO^+$: 336.1275; found: 336.1278.



2''-chloro-3-isopropyl-6-methyl-[1,1':3',1''-terphenyl]-2-ol 6r

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and thymol **5r** (33.8 mg, 0.22 mmol) in $CHCl_3$ (1 mL, 0.15 M) **6r** was obtained as colorless oil in 75% yield. (38 mg, 0.108 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 99:1.

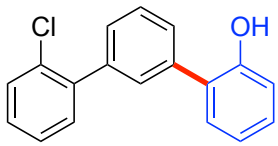
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (td, J = 7.6, 0.6 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.36 (td, J = 1.7, 0.5 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.28 – 7.20 (m, 3H), 7.07 (d, J = 7.9 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 4.84 (brs, 1H), 3.23 (hept, J = 6.9 Hz, 1H), 2.04 (d, J = 0.7 Hz, 3H), 1.21 (dd, J = 6.9, 3.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 140.6, 139.8, 135.4, 134.2, 132.5, 132.0, 131.6, 131.2, 130.0, 129.6, 129.3, 129.1, 128.8, 127.4, 126.9, 125.3, 121.6, 27.1, 22.7, 22.6, 20.3. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{21}ClO^+$: 336.1275; found: 336.1263.



2'''-chloro-[1,1':3',1'':3'',1'''-quaterphenyl]-2'-ol 6t

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 2-phenylphenol **5t** (38.3 mg, 0.23 mmol) in $CHCl_3$ (1 mL, 0.15 M) **6t** was obtained as pale-yellow oil in 52% yield. (28 mg, 0.078 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 96:4.

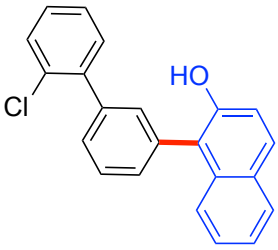
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (td, J = 1.8, 0.6 Hz, 1H), 7.80 – 7.71 (m, 4H), 7.69 – 7.64 (m, 4H), 7.60 – 7.57 (m, 2H), 7.54 – 7.45 (m, 4H), 7.26 (t, J = 7.6 Hz, 1H), 5.68 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 140.1, 139.8, 137.5, 137.3, 132.5, 131.4, 130.5, 130.0, 130.0, 130.0, 129.3 (2C), 128.9 (2C), 128.8, 128.7, 128.6, 128.6, 128.6, 128.4, 127.7, 126.9, 120.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{24}H_{17}ClO^+$: 356.0962; found: 356.0948.



2''-chloro-[1,1':3',1''-terphenyl]-2-ol 6s

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and phenol **5s** (21 mg, 0.23 mmol) in $CHCl_3$ (1 mL, 0.15 M) for 36 hours **6s** was obtained as single regioisomer as pale-yellow oil in 50% yield. (21 mg, 0.103 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 92:8.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.85 (m, 1H), 7.84 – 7.81 (m, 1H), 7.78 – 7.74 (m, 3H), 7.67 – 7.65 (m, 1H), 7.62 – 7.52 (m, 4H), 7.30 – 7.26 (m, 2H), 5.61 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 140.3, 139.9, 136.8, 132.4, 131.3, 130.3, 130.1, 130.0, 129.3, 129.1, 128.8, 128.8, 128.3, 127.8, 126.9, 120.9, 115.9. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{13}ClO^+$: 280.0649; found: 280.0665.

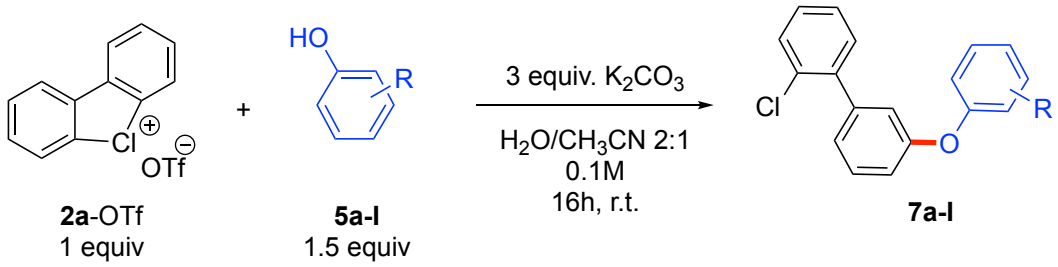


1-(2'-chloro-[1,1'-biphenyl]-3-yl)naphthalen-2-ol 6u

Following the **GP-C** using **2a**-OTf (50.5 mg, 0.15 mmol) and 2-naphthol **5u** (32 mg, 0.23 mmol) in $CHCl_3$ (1.5 mL, 0.1M) **6u** was obtained as colorless oil in 67% yield. (33 mg, 0.1 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 97:3.

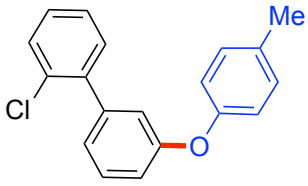
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.53 (t, *J* = 1.8 Hz, 1H), 7.51 – 7.49 (m, 1H), 7.47 – 7.45 (m, 1H), 7.43 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.37 – 7.34 (m, 1H), 7.33 - 7.24 (m, 4H), 5.28 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.2, 140.7, 139.7, 133.9, 133.2, 132.5, 132.3, 131.3, 130.3, 130.1, 129.6, 129.4, 129.4, 128.9, 128.9, 128.0, 127.0, 126.6, 124.6, 123.3, 120.6, 117.4. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{15}ClO^+$: 330.0806; found: 330.0790.

General procedure D: Metal free C-O arylation of phenols with cyclic diaryl λ^3-chloranes 7a-I



SCHEME S-8

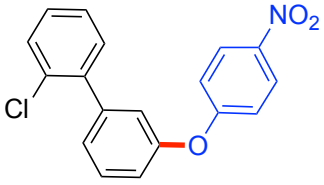
To a dry and metal-free vial was charged **2a**-OTf (50.5 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, the desired phenol **5a-I** (1.5 equiv) was added followed by H_2O/CH_3CN (2:1, 1.5 mL, 0.1M). The resulting homogeneous mixture was stirred at room temperature for 16 hours. The conversion was verified by GCMS and TLC. The mixture was extracted with EtOAc (3 mL x 3 times). The extracts were combined, dried over $MgSO_4$, and filtered. After removal of volatile components, the crude was purified through Prep-TLC.



2-chloro-3'-(p-tolyloxy)-1,1'-biphenyl 7a

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-Methylphenol **5a** (24.3 mg, 0.23 mmol) **7a** was obtained as colorless oil in 60% yield. (26.4 mg, 0.09 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 93:7.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.16 – 7.13 (m, 2H), 7.07 (dd, *J* = 2.5, 1.6 Hz, 1H), 7.01 (ddd, *J* = 8.1, 2.4, 1.1 Hz, 1H), 6.99 – 6.97 (m, 2H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.5, 154.5, 140.9, 139.9, 133.0, 132.4, 131.2, 130.3 (2C), 129.9, 129.3, 128.7, 126.8, 123.9, 119.3, 119.2 (2C), 117.4, 20.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{15}ClO^+$: 294.0806; found: 294.0803.

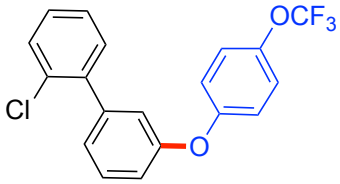


2-chloro-3'-(4-nitrophenoxy)-1,1'-biphenyl 7v

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-nitrophenol **5v** (31 mg, 0.23 mmol) **7v** was obtained as colorless oil in 51% yield. (25 mg, 0.077 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 94:6.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.36 (m, 2H), 7.68 – 7.63 (m, 2H), 7.53 – 7.44 (m, 4H), 7.36 (t, *J* = 2.0 Hz, 1H), 7.28 (ddd, *J* = 8.1, 2.4, 1.0 Hz, 1H), 7.27 – 7.23 (m, 2H). **^{13}C NMR** (101 MHz,

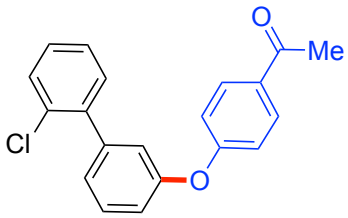
$CDCl_3$) δ 163.2, 154.3, 142.7, 141.6, 139.2, 132.3, 131.1, 130.1, 130.0, 129.1, 127.0, 126.4, 126.0 (2C), 121.6, 119.6, 117.2 (2C). **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{12}ClNO_3^+$: 325.0500; found: 325.0521.



2-chloro-3'-(4-(trifluoromethoxy)phenoxy)-1,1'-biphenyl 7w

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol) **7w** was obtained as colorless oil in 80% yield. (44 mg, 0.12 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 99:1.

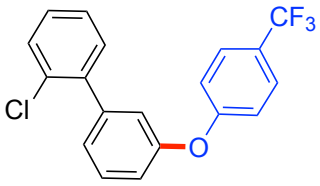
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.41 – 7.374 (m, 3H), 7.31 – 7.30 (m, 1H), 7.27 – 7.21 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 155.7, 144.5 (q, *J* = 1.8 Hz), 141.2, 139.6, 132.4, 131.2, 130.0, 129.6, 128.8, 126.9, 124.9, 122.6 (2C), 120.2, 120.6 (d, *J* = 243.9 Hz), 119.6 (2C), 118.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.2. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{12}ClF_3O_2^+$: 364.0472; found: 364.0491.



1-(4-((2'-chloro-[1,1'-biphenyl]-3-yl)oxy)phenyl)ethan-1-one 7x

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4'-hydroxyacetophenone **5x** (30.6 mg, 0.23 mmol) **7x** was obtained as colorless oil in 58% yield. (28.1 mg, 0.087 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 96:4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.39 – 7.35 (m, 2H), 7.27 – 7.17 (m, 5H), 7.09 – 7.08 (m, 1H), 7.012 – 6.97 (m, 2H), 2.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 161.8, 155.1, 141.3, 139.4, 132.4, 132.0, 131.1, 130.6 (2C), 130.0, 129.7, 128.9, 126.9, 125.6, 121.2, 119.2, 117.4 (2C), 26.4. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{20}H_{16}ClO_2^+$: 323.0833; found: 323.0834.

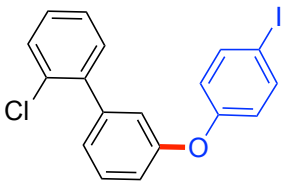


2-chloro-3'-(4-(trifluoromethyl)phenoxy)-1,1'-biphenyl 7y

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-trifluoromethylphenol **5y** (36.5 mg, 0.23 mmol) **7y** was obtained as colorless oil in 67% yield. (35 mg, 0.1 mmol). (1 gram scale: 572 mg, 1.64 mmol, 55 %). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H), 7.39 – 7.35 (m, 2H), 7.27 -7.16 (m, 4H), 7.07 (t, *J* = 2.1 Hz, 1H), 7.04 – 6.98 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 160.3, 155.4, 141.4, 139.5, 132.4, 131.2, 130.0, 129.7, 128.9, 127.2 (q, *J* = 3.7 Hz, 2C), 126.9, 126.4 – 120.2 (m, 1C),

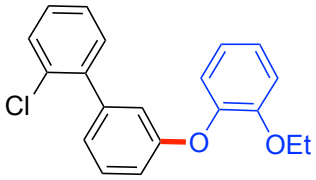
125.5, 121.0, 119.0, 118.0 (2C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{12}ClF_3O^+$: 348.0523; found: 348.0528.



2-chloro-3'-(4-iodophenoxy)-1,1'-biphenyl 7z

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4-iodophenol **5z** (49.5 mg, 0.23 mmol) **7z** was obtained as colorless oil in 62% yield. (37.7 mg, 0.093 mmol). (3 mmol scale reaction; 78%, 944 mg, 2.32 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 93:7.

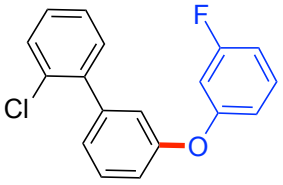
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.48 – 7.46 (m, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.22 – 7.20 (m, 1H), 7.11 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.04 (ddd, *J* = 8.1, 2.5, 1.1 Hz, 1H), 6.86 – 6.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.2, 156.2, 141.2, 139.6, 138.7 (2C), 132.4, 131.2, 130.0, 129.5, 128.8, 126.9, 124.8, 120.9 (2C), 120.1, 118.2, 86.1. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{12}ClIO^+$: 405.9616; found: 405.9617.



2-chloro-3'-(2-ethoxyphenoxy)-1,1'-biphenyl 7A

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 2-ethoxyphenol **5A** (28.5 µL, 0.23 mmol) **7A** was obtained as colorless oil in 41% yield. (20.1 mg, 0.062 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 91:9.

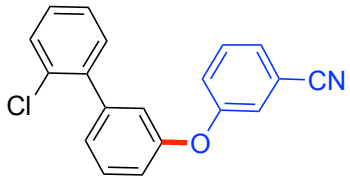
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.13 – 7.07 (m, 3H), 7.02 – 6.97 (m, 3H), 6.93 (ddd, *J* = 7.9, 7.3, 1.5 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 150.8, 145.2, 140.6, 140.1, 132.4, 131.2, 129.9, 129.0, 128.6, 126.7, 124.9, 123.4, 121.6, 121.2, 118.1, 116.3, 114.5, 64.5, 14.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{17}ClO_2^+$: 324.0912; found: 324.0932.



2-chloro-3'-(3-fluorophenoxy)-1,1'-biphenyl 7B

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 3-fluorophenol **5B** (20.3 µL, 0.23 mmol) **7B** was obtained as colorless oil in 48% yield. (21.6 mg, 0.072 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 95:5.

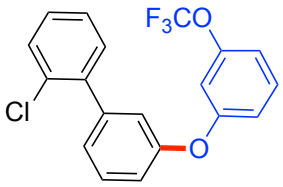
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 7.19 – 7.09 (m, 4H), 7.06 (ddd, *J* = 7.6, 1.7, 1.1 Hz, 1H), 6.98 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.90 (ddd, *J* = 8.2, 2.4, 1.1 Hz, 1H), 6.69 (m, 1H), 6.65 – 6.59 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.5 (d, *J* = 246.6 Hz), 155.9, 158.7 (d, *J* = 10.4 Hz), 141.2, 139.6, 132.4, 131.2, 130.5 (d, *J* = 10.0 Hz), 130.0, 129.5, 128.8, 126.9, 125.1, 120.5, 118.5, 114.1 (d, *J* = 3.2 Hz), 110.0 (d, *J* = 21.3 Hz), 106.2 (d, *J* = 24.5 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -110.9. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{12}ClFO^+$: 298.0555; found: 298.0545.



3-((2'-chloro-[1,1'-biphenyl]-3-yl)oxy)benzonitrile 7C

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 3-cyanophenol **5C** (27 mg, 0.23 mmol) **7C** was obtained as colorless oil in 65% yield. (30 mg, 0.098 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 90:10.

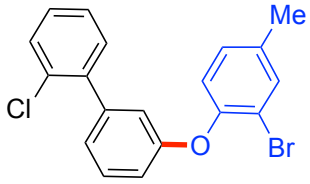
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 3H), 7.35 – 7.25 (m, 5H), 7.25 – 7.22 (m, 2H), 7.11 – 7.10 (m, 1H), 7.06 – 7.01 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 155.2, 141.5, 139.3, 132.3, 131.1, 130.7, 130.0, 129.8, 129.0, 126.9, 126.5, 125.7, 122.9, 121.3, 120.8, 118.8, 118.2, 113.6. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{12}ClNO^+$: 305.0602; found: 305.0607.



2-chloro-3'-(3-(trifluoromethoxy)phenoxy)-1,1'-biphenyl 7D

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 3-(trifluoromethoxy)phenol **5D** (29 µL, 0.23 mmol) **7D** was obtained as colorless oil in 52% yield. (28.2 mg, 0.077 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 91:9.

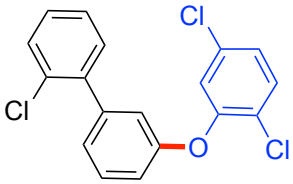
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.27 – 7.20 (m, 4H), 7.15 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.06 – 7.05 (m, 1H), 7.00 – 6.97 (m, 1H), 6.91 – 6.84 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5, 155.8, 150.2 (q, *J* = 1.8 Hz), 141.3, 139.6, 132.4, 131.2, 130.5, 130.0, 129.7, 128.9, 126.9, 125.3, 120.6 120.4 (q, *J* = 257.5 Hz), 118.6, 116.6, 115.2, 111.5. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.8. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{12}ClF_3O_2^+$: 364.0472; found: 364.0465.



3'-(2-bromo-4-methylphenoxy)-2-chloro-1,1'-biphenyl 7E

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 2-bromo-4-methylphenol **5E** (27 µL, 0.23 mmol) **7E** was obtained as colorless oil in 73% yield. (41 mg, 0.11 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 91:9.

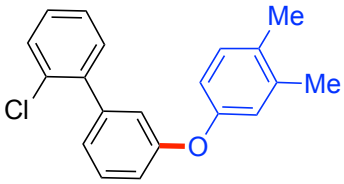
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.68 – 7.64 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 7.44 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 7.36 (ddd, *J* = 8.3, 2.2, 0.9 Hz, 1H), 7.30 – 7.29 (m, 1H), 7.28 – 7.24 (m, 2H), 2.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.0, 150.9, 140.9, 139.8, 135.3, 134.1, 132.4, 131.2, 129.9, 129.3, 129.3, 128.7, 126.8, 124.1, 121.0, 118.6, 116.7, 114.9, 20.4. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{14}BrClO^+$: 371.9911; found: 371.9919.



2-chloro-3'-(2,5-dichlorophenoxy)-1,1'-biphenyl 7F

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 2,5-dichlorophenol **5F** (36.7 mg, 0.23 mmol) **7F** was obtained as colorless oil in 65% yield. (34 mg, 0.097 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 94:6.

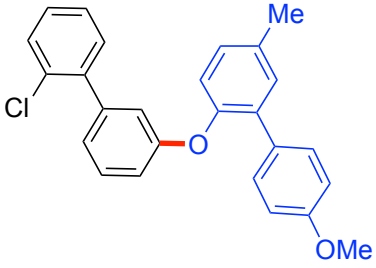
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.61 – 7.60 (m, 1H), 7.58 – 7.55 (m, 1H), 7.54 – 7.49 (m, 2H), 7.46 (ddd, *J* = 7.6, 1.7, 1.1 Hz, 1H), 7.32 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.29 – 7.25 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.7, 153.2, 141.3, 139.5, 133.1, 132.4, 131.3, 131.2, 130.0, 129.7, 128.9, 126.9, 125.2, 124.5, 123.8, 120.3, 119.7, 117.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{11}Cl_3O^+$: 347.9870; found: 347.9846.



2-chloro-3'-(3,4-dimethylphenoxy)-1,1'-biphenyl 7G

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 3,4-dimethylphenol **5G** (27.5 mg, 0.23 mmol) **7G** was obtained as colorless oil in 57% yield. (26.2 mg, 0.085 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 95:5.

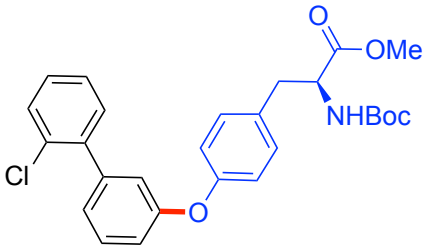
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.14 (m, 3H), 7.03 (ddd, *J* = 7.5, 1.7, 1.0 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.97 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.90 (ddd, *J* = 8.2, 2.5, 1.1 Hz, 1H), 6.78 (d, *J* = 2.7 Hz, 1H), 6.71 (dd, *J* = 8.2, 2.7 Hz, 1H), 2.13 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.5, 154.6, 140.9, 140.0, 138.2, 132.4, 131.7, 131.2, 130.6, 129.9, 129.2, 128.6, 126.8, 123.7, 120.6, 119.3, 117.4, 116.5, 19.9, 19.0. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{17}ClO^+$: 308.0962; found: 308.0940.



2-((2'-chloro-[1,1'-biphenyl]-3-yl)oxy)-4'-methoxy-5-methyl-1,1'-biphenyl 7H

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and 4'-methoxy-5-methyl-[1,1'-biphenyl]-2-ol **5H** (48 mg, 0.23 mmol) **7H** was obtained as colorless oil in 42% yield. (25.2 mg, 0.063 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 92:8.

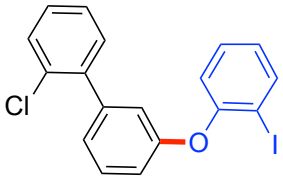
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.43 – 7.41 (m, 1H), 7.30 – 7.23 (m, 5H), 7.09 – 7.07 (m, 1H), 7.04 (ddd, *J* = 7.6, 1.6, 1.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.96 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.91 (ddd, *J* = 8.2, 2.4, 1.1 Hz, 1H), 6.90 – 6.87 (m, 2H), 3.79 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.8, 157.9, 150.8, 140.7, 140.0, 133.8, 133.3, 132.4, 131.6, 131.2, 130.2 (2C), 130.2, 129.9, 129.1, 128.8, 128.6, 126.7, 123.3, 120.7, 118.6, 116.8, 113.6 (2C), 55.2, 20.8. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{26}H_{21}ClO_2^+$: 400.1225; found: 400.1232.



methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-((2'-chloro-[1,1'-biphenyl]-3-yl)oxy)phenyl)propanoate 7I

Following the **GP-D** using **2a**-OTf (50.5 mg, 0.15 mmol) and Boc-L-tyrosine methyl ester **5I** (66 mg, 0.23 mmol) **7I** was obtained as colorless oil in 62% yield. (45 mg, 0.093 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.20 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.14 – 7.12 (m, 3H), 7.06 – 7.01 (m, 3H), 5.04 (d, *J* = 7.8 Hz, 1H), 4.63 – 4.58 (m, 1H), 3.73 (s, 3H), 3.15 – 3.02 (m, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 156.8, 156.1, 155.0, 141.0, 139.8, 132.4, 131.2, 130.9, 130.6 (2C), 129.9, 129.3, 128.7, 126.8, 124.3, 120.0, 118.9 (2C), 118.0, 79.9, 54.4, 52.2, 37.7, 28.3 (3C). **HRMS (ESI)**: m/z $[M+K]^+$ calcd for $C_{27}H_{28}ClKNO_5^+$: 520.1288; found: 520.1265.

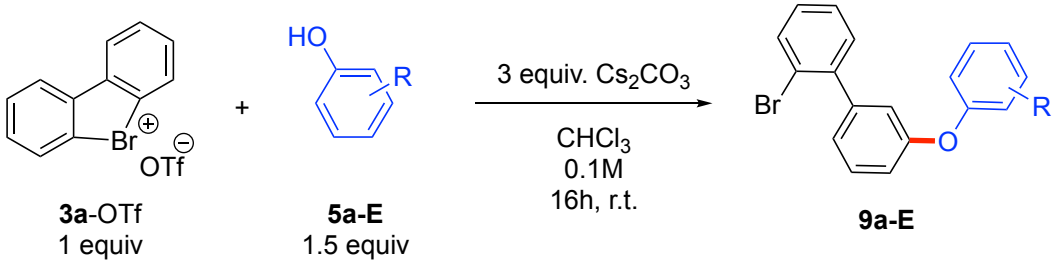


2-chloro-3'-(2-iodophenoxy)-1,1'-biphenyl 7J

Following the **GP-D** using **2a**-OTf (168 mg, 0.5 mmol), 2-iodophenol **5J** (165 mg, 0.75 mmol), K_2CO_3 (207 mg, 1.5 mmol) in H_2O:CH_3CN (2:1, 0.1 M) **7J** was obtained as colorless oil in 68% yield through flash chromatography (138 mg, 0.34 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 89:11.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.28 – 7.20 (m, 4H), 7.12 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 6.98 – 6.97 (m, 1H), 6.94 (ddd, *J* = 8.1, 2.4, 1.0 Hz, 1H), 6.91 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.80 (td, *J* = 7.6, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5, 156.4, 141.1, 139.9, 139.7, 132.4, 131.2, 130.0, 129.7, 129.4, 128.8, 126.8, 125.4, 124.6, 119.5, 119.5, 117.6, 88.9. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{12}ClIO^+$: 405.9616; found: 405.9605.

General procedure E: Metal free C-O arylation of phenols with cyclic diaryl λ^3-bromanes 9a-E



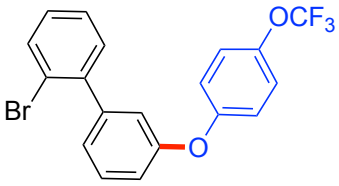
3a-OTf
1 equiv

5a-E
1.5 equiv

9a-E

SCHEME S-9

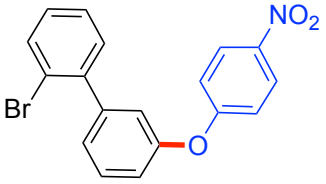
To a dry and metal-free vial was charged **3a**-OTf (57 mg, 0.15 mmol, 1 equiv.) and Cs_2CO_3 (146 mg, 0.45 mmol, 3 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, the desired phenol **3a-E** (1.5 equiv) was added followed by $CHCl_3$ (1.5 mL, 0.1M). The resulting heterogenous mixture was stirred at room temperature for 16 hours. The conversion was verified by GCMS and TLC. The mixture was diluted with EtOAc (3 mL) and filtered. After removal of volatile components, the crude was purified through Prep-TLC.



2-bromo-3'-(4-(trifluoromethoxy)phenoxy)-1,1'-biphenyl 9w

Following the **GP-E** using **3a**-OTf (57 mg, 0.15 mmol) and 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol) **9w** was obtained as colorless oil in 99% yield. (61 mg, 0.15 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 92:8.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.41 – 7.33 (m, 4H), 7.27 – 7.21 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 155.7, 144.5 (q, *J* = 2.0 Hz), 142.9, 141.7, 133.2, 131.1, 129.5, 129.0, 127.4, 124.8, 122.6 (2C), 122.5, 120.2, 120.5 (q, *J* = 256.6 Hz), 119.6 (2C), 118.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.2. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{12}BrF_3O_2^+$: 407.9967; found: 407.9943.

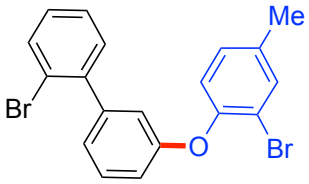


2-bromo-3'-(4-nitrophenoxy)-1,1'-biphenyl 9v

Following the **GP-E** using **3a**-OTf (57 mg, 0.15 mmol) and 4-nitrophenol **5v** (31 mg, 0.23 mmol) **9v** was obtained as colorless oil in 79% yield. (44 mg, 0.12 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.36 (m, 2H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.51 (m, 7.48 (m, 1H), 7.44 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.38 (ddd, *J* = 8.0, 6.9, 2.2 Hz, 1H), 7.32 – 7.31 (m, 1H), 7.28 (ddd, *J* = 8.1, 2.4, 1.0 Hz, 1H), 7.26 – 7.23 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 154.2, 143.3, 142.7, 141.2, 133.2, 131.0,

130.0, 129.2, 127.5, 126.3, 126.0 (2C), 122.4, 121.6, 119.6, 117.3 (2C). **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{12}BrNO_3^+$: 368.9995; found: 368.9990.

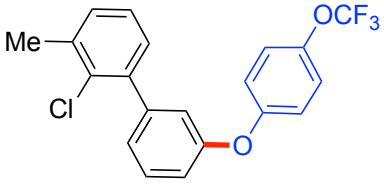


2-bromo-3'-(2-bromo-4-methylphenoxy)-1,1'-biphenyl 9E

Following the **GP-E** using **2z**-OTf (57 mg, 0.15 mmol) and 2-bromo-4-methylphenol **5E** (27 µL, 0.23 mmol) **9E** was obtained as colorless oil in 85% yield. (53 mg, 0.13 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* = 94:6.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 1H), 7.46 (dd, *J* = 2.1, 0.8 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.32 (m, 2H), 7.20 (ddd, *J* = 8.1, 6.3, 2.9 Hz, 1H), 7.13 (ddd, *J* = 7.6, 1.6, 1.0 Hz, 1H), 7.09 (ddd, *J* = 8.3, 2.1, 0.7 Hz, 1H), 7.02 – 6.97 (m, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.9, 150.9, 142.6, 141.8, 135.3, 134.1, 133.1, 131.1, 129.3, 129.3, 128.9, 127.3, 124.0, 122.5, 121.1, 118.5, 116.8, 114.9, 20.4. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{14}Br_2O^+$: 415.9406; found: 415.9383.

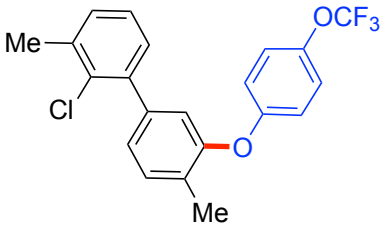
Unsymmetric Substrates



2-chloro-3-methyl-3'-(4-(trifluoromethoxy)phenoxy)-1,1'-biphenyl 7dw

Following the **GP-D** using **2d** (52.6 mg, 0.15 mmol) and 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol) **7dw** was obtained as colorless oil in 74% yield. (42 mg, 0.11 mmol).

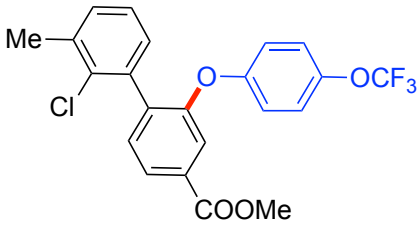
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 6.93 (m, 11H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 155.8, 144.5 (d, *J* = 2.2 Hz), 142.0, 140.1, 137.1, 132.6 (brs), 130.2, 129.5, 128.7, 126.2, 124.9, 120.5 (q, *J* = 256.8 Hz), 122.6 (2C), 120.3, 119.6 (2C), 118.0, 21.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.2. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{14}ClF_3O_2^+$: 378.0629; found: 378.0637.



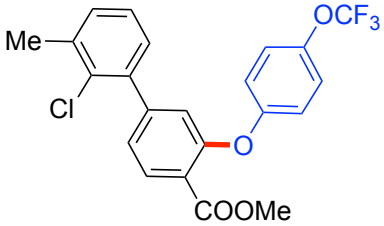
2-chloro-3,4'-dimethyl-3'-(4-(trifluoromethoxy)phenoxy)-1,1'-biphenyl 7ww

Following the **GP-D** using **2w** (55 mg, 0.15 mmol) and 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol) **7ww** was obtained as unique regioisomer as colorless oil in 71% yield. (42 mg, 0.11 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.51 – 7.49 (m, 1H), 7.46 – 7.41 (m, 5H), 7.30 (d, *J* = 1.7 Hz, 1H), 7.27 – 7.23 (m, 2H), 2.71 (s, 3H), 2.57 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 153.5, 143.9 (q, *J* = 2.2 Hz), 140.0, 139.4, 137.0, 132.7, 131.2, 130.0, 129.1, 128.7, 126.2, 125.5, 122.6 (2C), 121.0, 120.5 (d, *J* = 256.4 Hz), 118.1 (2C), 21.0, 15.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.3. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{21}H_{16}ClF_3O_2^+$: 392.0785; found: 392.0781.



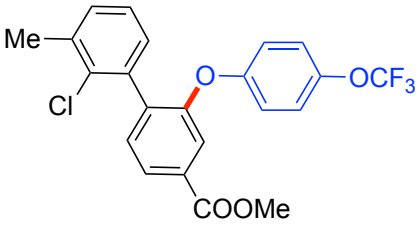
7zw



7zw'

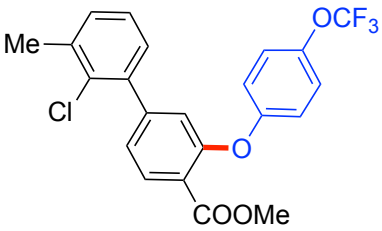
methyl 2'-chloro-3'-methyl-2-(4-(trifluoromethoxy)phenoxy)-[1,1'-biphenyl]-4-carboxylate 7zw and methyl 2'-chloro-3'-methyl-3-(4-(trifluoromethoxy)phenoxy)-[1,1'-biphenyl]-4-carboxylate 7zw'

Following the **GP-D** using **2z** (61 mg, 0.15 mmol) and 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol) **7zw** and **7zw'** were obtained in 78% total yield. Compounds separated by prep-TLC (Cy:EtOAc 9:1)



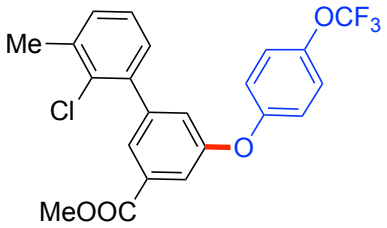
7zw - Colorless oil, 53% (35 mg, 0.08 mmol)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.07 (ddd, *J* = 7.5, 1.8, 0.8 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.97 – 6.94 (m, 3H), 6.79 (m, 2H), 3.76 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 155.2, 154.3, 144.6 (d, *J* = 1.8 Hz), 136.7, 136.5, 136.0, 133.4, 132.0, 131.3, 130.6, 128.7, 126.0, 124.6, 122.4 (2C), 120.4 (q, *J* = 256.8 Hz), 119.8 (2C), 119.7, 52.3, 20.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.3. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{16}ClF_3O_4^+$: 436.0684; found: 436.0691.

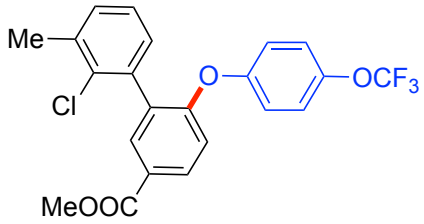


7zw' – Colorless oil, 24 % (15.8 mg, 0.036 mmol)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.27 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.25 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.13 (dd, *J* = 7.5, 2.4 Hz, 1H), 7.09 (d, *J* = 1.7 Hz, 1H), 7.02 – 6.99 (m, 2H), 3.84 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 156.2, 155.1, 145.9, 144.3 (m), 139.0, 137.3, 132.4, 131.7, 130.8, 128.4, 126.4, 125.3, 122.6 (2C), 122.5, 122.1, 118.7 (2C), 52.2, 20.9. (O***C***F3 not detected) **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.3. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{22}H_{17}ClF_3O_4^+$: 437.0762; found: 437.0743.



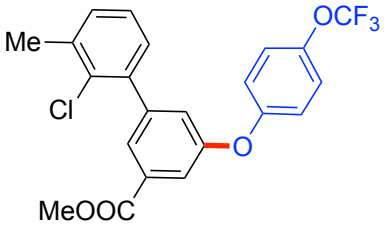
7yw



7yw'

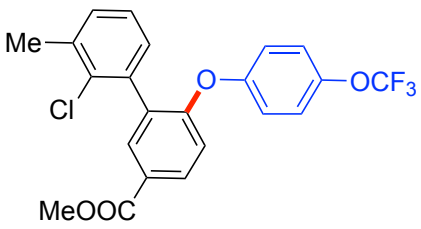
methyl 2'-chloro-3'-methyl-5-(4-(trifluoromethoxy)phenoxy)-[1,1'-biphenyl]-3-carboxylate 7yw and methyl 2'-chloro-3'-methyl-6-(4-(trifluoromethoxy)phenoxy)-[1,1'-biphenyl]-3-carboxylate 7yw'

Following the **GP-D** using **2y** (61 mg, 0.15 mmol) and 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol) **7yw** and **7yw'** were obtained in 80% total yield. Compounds separated by prep-TLC (Cy:EtOAc 9:1)



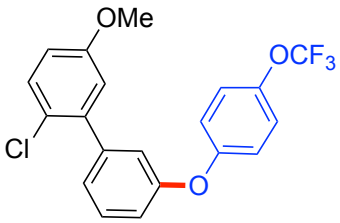
7yw – Colorless oil, 55% (35.8 mg, 0.082 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 1.5 Hz, 1H), 7.60 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.22 (dd, *J* = 2.4, 1.6 Hz, 1H), 7.20 – 7.17 (m, 1H), 7.15 – 7.11 (m, 3H), 7.09 (dd, *J* = 7.4, 2.3 Hz, 1H), 7.01 – 6.97 (m, 2H), 3.83 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 156.5, 155.2, 144.8 (q, *J* = 1.8 Hz), 142.2, 139.1, 137.2, 132.6, 131.8, 130.6, 128.6, 126.4, 126.0, 124.6, 122.7 (2C), 120.5 (q, *J* = 256.8 Hz), 119.8 (2C), 118.8, 52.4, 20.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.2. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{22}H_{16}ClF_3NaO_4^+$: 459.0581; found: 459.0563.

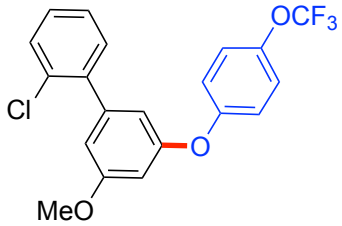


7yw' – Colorless oil, 26% (16.8 mg, 0.038 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.23 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.14 (m, 3H), 7.02 – 6.98 (m, 2H), 6.92 (d, *J* = 9.2 Hz, 1H), 3.91 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 158.6, 154.3, 145.2 (q, *J* = 2.2 Hz), 136.6, 136.2, 133.8, 133.5, 131.1, 131.0, 130.5, 129.0, 126.1, 125.0, 122.5 (2C), 120.9 (2C), 120.4 (q, *J* = 257.1 Hz), 116.9, 52.1, 20.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.3. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{22}H_{17}ClF_3O_4^+$: 437.0762; found: 437.0758.



7kw
Major
(M)

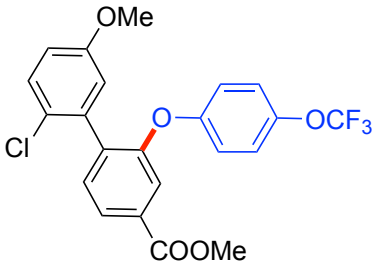


7kw'
Minor
(m)

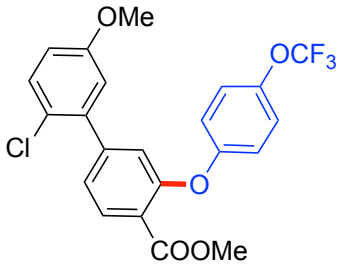
2-chloro-5-methoxy-3'-(4-(trifluoromethoxy)phenoxy)-1,1'-biphenyl 7kw and 2-chloro-3'-methoxy-5'-(4-(trifluoromethoxy)phenoxy)-1,1'-biphenyl 7kw'

Following the **GP-D** using **2k** (30.5 mg, 0.1 mmol) and 4-trifluoromethoxy phenol **5w** (19.5 µL, 0.15 mmol) **7kw** and **7kw'** were obtained as colorless oil in 81% yield. (32 mg, 0.081 mmol). **^{1}HNMR** ratio **7kw**:**7kw'** 73:27

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 1H, 1H m), 7.60 (t, *J* = 7.9 Hz, 1H, 1H M), 7.54 (d, *J* = 8.7 Hz, 1H, 1H M), 7.52 – 7.46 (m, 3H, 3H m), 7.41 – 7.37 (m, 5H, 3H M + 2H m), 7.31 (dd, *J* = 2.2, 1.9 Hz, 1H, 1H M), 7.27 – 7.21 (m, 5H, 3H M + 2H m), 7.06 (d, *J* = 2.9 Hz, 1H, 1H M), 7.02 (dd, *J* = 8.7, 3.1 Hz, 1H, 1H M), 6.94 (dd, *J* = 2.3, 1.3 Hz, 1H, 1H m), 6.87 (dd, *J* = 2.2, 1.3 Hz, 1H, 1H m), 6.79 (t, *J* = 2.3 Hz, 1H, 1H m), 4.01 (s, 3H, 3H m), 3.99 (s, 3H, 3H M). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6 (Cq m), 158.2 (Cq M), 157.4 (Cq m), 156.4 (Cq M), 155.7 (Cq M), 155.5 (Cq m), 144.6 (d, *J* = 2.1 H, 1Cq m), 144.5 (q, *J* = 2.1 Hz, 1Cq M), 141.8 (Cq m), 141.3 (Cq M), 140.4 (Cq M), 139.7 (Cq m), 132.3 (Cq M), 131.8 (Cq m), 131.0 (CH m), 130.7 (CH M), 130.0 (CH m), 129.6 (CH M), 128.9 (CH m), 126.8 (CH m), 124.8 (CH M), 123.7 (2CH m), 122.6 (2CH M), 120.8 (d, *J* = 297.1 Hz, C_{CF3} m), 120.5 (q, *J* = 256.8 Hz, C_{CF3} M), 120.1 (CH M), 119.8 (2CH m), 119.6 (2CH M), 118.2 (CH M), 116.5 (CH M), 114.5 (CH M), 112.4 (CH m), 110.6 (CH m), 104.3 (CH m), 55.6 (C_{OMe} M), 55.5 (C_{OMe} m). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.2, -58.2. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{14}ClF_3O_3^+$: 394.0578; found: 394.0581.



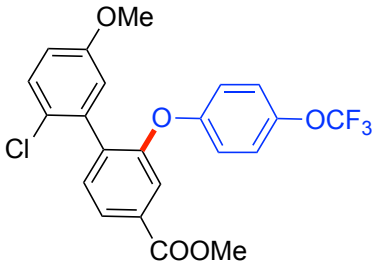
7tw



7tw'

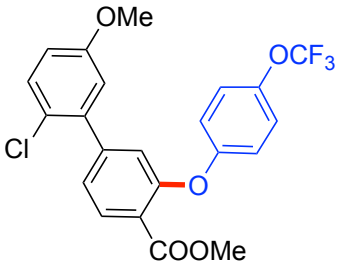
methyl 2'-chloro-5'-methoxy-2-(4-(trifluoromethoxy)phenoxy)-[1,1'-biphenyl]-4-carboxylate 7tw and methyl 2'-chloro-5'-methoxy-3-(4-(trifluoromethoxy)phenoxy)-[1,1'-biphenyl]-4-carboxylate 7tw'

Following the **GP-D** using **2t** (36 mg, 0.1 mmol) and 4-trifluoromethoxy phenol **5w** (19.5 µL, 0.15 mmol) **7tw** and **7tw'** were obtained in 62% total yield. Compounds separated by prep-TLC (Cy:EtOAc 15:1). **7tw**:**7tw'** 86:14



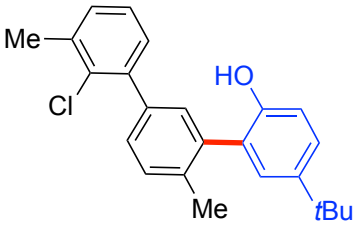
7tw – 53% (24 mg, 0.053 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.96 – 6.93 (m, 2H), 6.78 – 6.74 (m, 2H), 6.67 – 6.63 (m, 2H), 3.74 (s, 3H), 3.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 157.9, 155.2, 154.1, 144.6 (q, *J* = 2.1 Hz), 136.4, 135.8, 132.0, 131.6, 130.2, 124.7 (2C), 122.5 (2C), 120.4 (d, *J* = 256.8 Hz), 119.8, 119.6 (2C), 116.5, 115.1, 55.5, 52.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.27. **HRMS (ESI)**: m/z $[M+K]^+$ calcd for $C_{22}H_{16}ClF_3KO_5^+$: 491.0270; found: 491.0252.



7tw' – 9% (4 mg, 0.0088 mmol

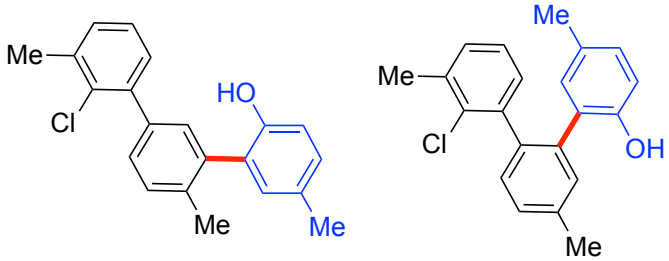
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.29 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.19 – 7.16 (m, 2H), 7.11 (d, *J* = 1.7 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.87 – 6.83 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 158.3, 156.1, 155.1, 145.1, 144.4 (m), 139.2, 131.8, 130.9, 125.1, 124.7 – 121.7 (m), 123.5, 122.6 (2C), 122.4, 122.3, 118.7 (2C), 116.4, 114.9, 55.6, 52.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.3. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{22}H_{17}ClF_3O_5^+$: 453.0711; found: 453.0693.



5-(tert-butyl)-2''-chloro-3'',6'-dimethyl-[1,1':3',1''-terphenyl]-2-ol 6wb

Following the **GP-C** using **2w** (55 mg, 0.15 mmol) and 4-tert-butylphenol **5b** (34 mg, 0.23 mmol) **6wb** was obtained in 52% yield (28.3 mg, 0.078 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* 87:13

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.46 (m, 2H), 7.42 – 7.42 (m, 1H), 7.35 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.24 (d, *J* = 2.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.84 (s, 1H), 2.51 (s, 3H), 2.30 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 143.1, 140.2, 138.3, 137.0, 136.6, 136.0, 132.7, 131.5, 130.4, 130.0, 129.3, 128.9, 127.2, 126.7, 126.2, 125.9, 114.8, 34.1, 31.6 (3C), 21.0, 19.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{24}H_{25}ClO^+$: 364.1588; found: 364.1597.

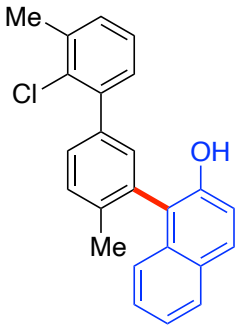


6wa major **6wa'** minor

2''-chloro-3'',5,6'-trimethyl-[1,1':3',1''-terphenyl]-2-ol 6wa and 2''-chloro-3'',5,5'-trimethyl-[1,1':2',1''-terphenyl]-2-ol 6wa'

Following the **GP-C** using **2w** (55 mg, 0.15 mmol) and p-cresol **5a** (24 mg, 0.23 mmol) **6wa** and **6wa'** were obtained in 59% yield (28.5 mg, 0.088 mmol). Regioselective ratio determined by **^{1}HNMR** *m*:*o* 74:26

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.39 (m, 2H, 2H M), 7.33 – 7.29 (m, 2H, 1H M, 2H m), 7.25 – 7.19 (m, 4H, 3H M, 1H m), 7.09 – 7.06 (m, 2H, 1H M, 1H m), 6.98 – 6.95 (m, 2H, 1H M, 1H m), 6.90 (d, *J* = 8.2 Hz, 1H, 1H M), 6.91 – 6.87 (m, 2H, 2H m), 6.79 (d, *J* = 2.2 Hz, 1H, 1H m), 6.67 (d, *J* = 8.2 Hz, 1H, 1H m), 4.81 (s, 1H, 1H m), 4.73 (s, 1H, 1H M), 2.45 (s, 6H, 3H M, 3H m), 2.35 (s, 3H, 3H m), 2.31 (s, 3H, 3H M), 2.25 (s, 3H, 3H M), 2.14 (s, 3H, 3H m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 140.2, 138.3, 137.0, 136.5, 135.6, 131.5, 131.3, 130.6, 130.3, 130.0, 129.6, 129.4, 128.9, 127.2, 126.2, 115.1, 21.0, 20.5, 20.4, 19.6. (**^{13}C NMR** only the Major product). **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{22}H_{19}ClO^+$: 322.1119; found: 322.1116.

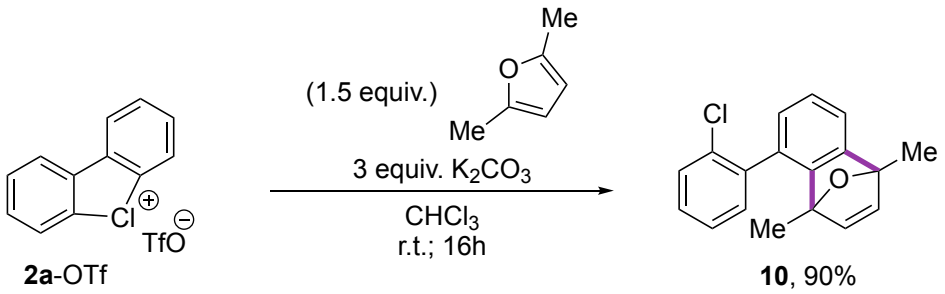


1-(2'-chloro-3',4-dimethyl-[1,1'-biphenyl]-3-yl)naphthalen-2-ol 6wu

Following the **GP-C** using **2u** (55 mg, 0.15 mmol) and 2-naphthol **5u** (32 mg, 0.23 mmol) **6wu** was obtained in 59% yield (32 mg, 0.089 mmol). Regioselective ratio determined by ^{1}**HNMR** *m*:*o* 83:17

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.51 – 7.51 (m, 2H), 7.40 – 7.39 (m, 2H), 7.36 – 7.31 (m, 3H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.23 – 7.21 (m, 2H), 5.08 (s, 1H), 2.45 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 140.1, 138.7, 138.1, 137.0, 133.0, 132.8, 132.7 (2C), 130.7, 130.0, 129.9, 129.5, 128.9, 128.8, 128.1, 126.6, 126.2, 124.5, 123.3, 119.9, 117.3, 21.0, 19.3. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{24}H_{19}ClO^+$: 358.1119; found: 358.1090.

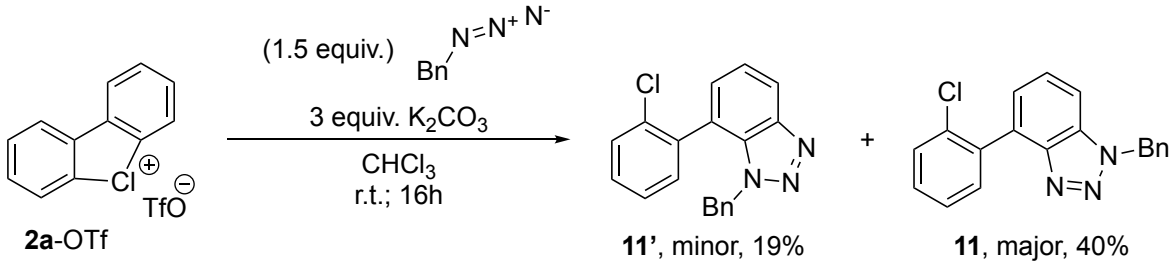
Cycloadditions with cyclic diaryl λ^3-chloranes



SCHEME S-10

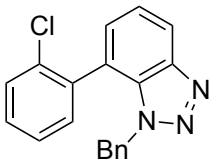
A vial was charged with **2a**-OTf (50.5 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, 2,5-dimethylfuran (24 μL, 0.23 mmol, 1.5 equiv) was added followed by $CHCl_3$ (1.5 mL, 0.1 M). The resulting heterogeneous mixture was stirred at room temperature for 16 hours. The conversion was controlled by GCMS and TLC. The mixture was diluted with EtOAc (3 mL) and filtered. After removal of volatile components, the crude was purified through Prep-TLC to afford the product as colorless oil in 90% yield (0.13 mmol, 38 mg). **10** has been obtained as mixture of two atropoisomers, **^{1}H NMR** ratio of 71:29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.7, 1.5 Hz, 1H, 1H m), 7.38 – 7.36 (m, 1H, 1H M), 7.29 – 7.18 (m, 5H, 2H m + 3H M), 7.09 (dd, J = 7.1, 1.0 Hz, 2H, 1H M + 1H m), 7.00 – 6.93 (m, 4H, 2H M + 2H m), 6.79 (dd, J = 7.8, 1.0 Hz, 1H, 1H m), 6.75 – 6.99 (m, 4H, 2H M + 2H m), 1.87 (s, 3H, 3H m), 1.85 (s, 3H, 3H M), 1.28 (s, 3H, 3H M), 1.25 (s, 3H, 3H m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.0, 152.7, 150.7, 149.9, 147.3, 146.6, 146.5, 145.8, 139.0, 138.6, 133.5, 133.3, 132.0, 131.9, 131.4, 131.1, 129.6, 129.0, 129.0, 128.8, 126.7, 126.7, 126.5, 126.1, 125.0, 124.2, 117.7, 117.6, 89.6, 89.6, 88.1, 87.9, 16.4, 16.0, 15.4, 15.2. **HRMS (APCI)**: m/z $[M+H^+]^+$ calcd for $C_{18}H_{16}ClO^+$: 283.0884; found: 283.0896.



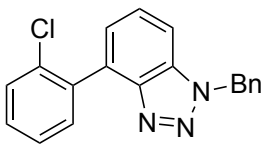
SCHEME S-11

To a dry vial were charged **2a**-OTf (50.5 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, Benzyl azide (30 mg, 0.23 mmol, 1.5 equiv.) was added followed by $CHCl_3$ (1.0 mL, 0.1 M). The resulting heterogeneous mixture was stirred at room temperature for 16 hours. The conversion was controlled by GCMS and TLC. The mixture was diluted with EtOAc (3 mL) and filtered. After removal of volatile components, the crude was purified through Prep-TLC to afford the pure products as colorless oil in 59% total yield.



1-benzyl-7-(2-chlorophenyl)-1*H*-benzo[*d*][1,2,3]triazole 11', (9 mg, 0.028 mmol, 19%)

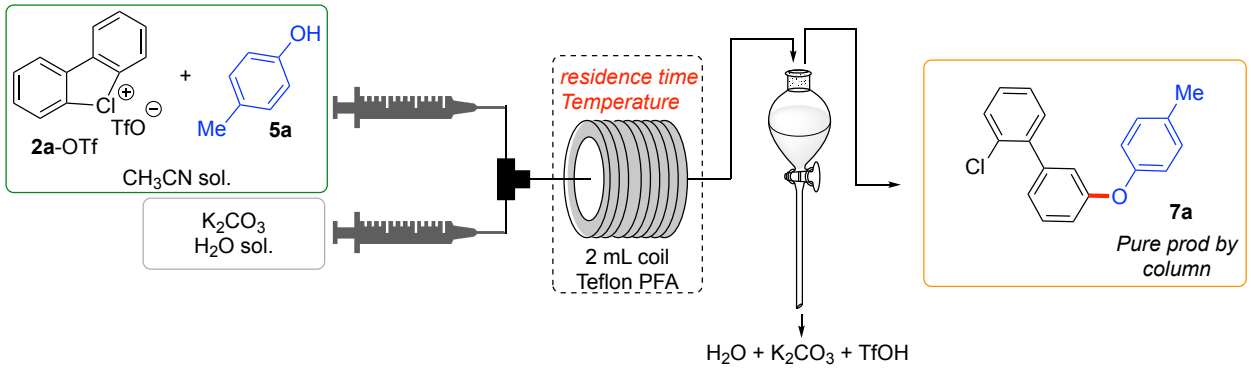
^{1}H NMR (400 MHz, CDCl3) δ 8.14 (dd, J = 8.3, 1.0 Hz, 1H), 7.48 (dd, J = 8.1, 1.3 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.22 (dd, J = 7.1, 1.0 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.07 – 7.03 (m, 2H), 7.18 (td, J = 7.5, 1.3 Hz, 1H), 6.97 (dd, J = 7.6, 1.7 Hz, 1H), 6.46 – 6.44 (m, 2H), 5.74 (d, J = 15.8 Hz, 1H), 5.35 (d, J = 15.9 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ 146.8, 136.1, 135.6, 134.2, 131.9, 130.6, 129.8, 129.3, 129.1, 128.3 (2C), 127.6, 126.7, 126.3 (2C), 123.8, 123.2, 119.9, 52.8. **HRMS (APCI)**: m/z $[M+H^+]^+$ calcd for $C_{18}H_{15}ClN_3^+$: 320.0949; found: 320.0946.



1-benzyl-4-(2-chlorophenyl)-1*H*-benzo[*d*][1,2,3]triazole 11, (19 mg, 0.059 mmol, 40%)

^{1}H NMR (400 MHz, CDCl3) δ 7.55 – 7.52 (m, 1H), 7.49 – 7.47 (m, 1H), 7.40 – 7.37 (m, 1H), 7.34 – 7.27 (m, 5H), 7.26 – 7.23 (m, 4H), 5.80 (s, 2H). **^{13}C NMR** (101 MHz, CDCl3) δ 144.9, 135.7, 134.7, 133.2, 133.1, 132.4, 131.3, 130.1, 129.4, 129.0 (2C), 128.5, 127.6 (2C), 127.0, 126.7, 125.1, 109.3, 52.4. **HRMS (APCI)**: m/z $[M+H^+]^+$ calcd for $C_{18}H_{15}ClN_3^+$: 320.0949; found: 320.0945.

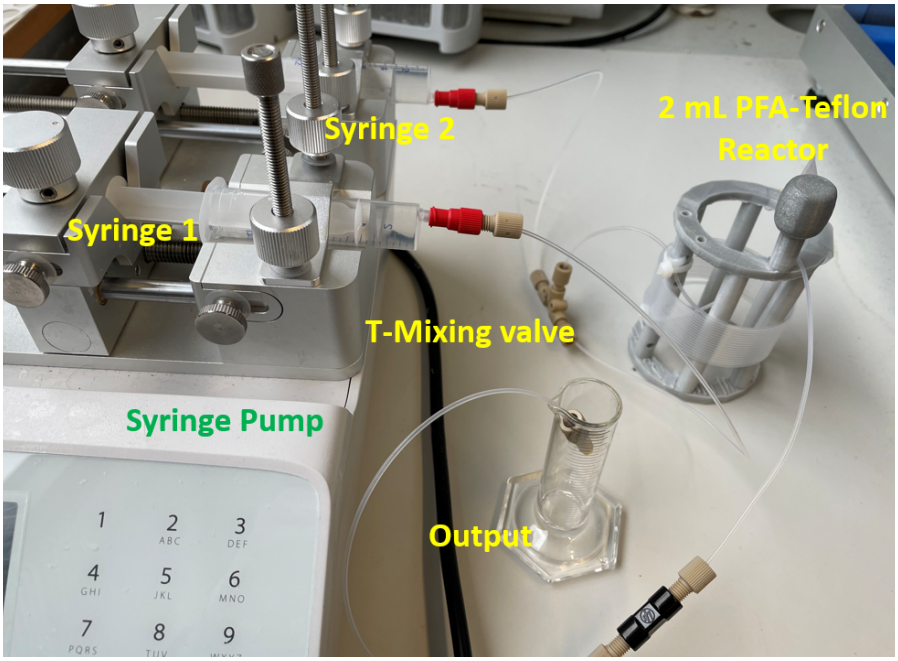
General procedure, Optimization and Set-up of metal free C-O arylation of phenols with cyclic diaryl λ^3-chloranes



SCHEME S-12

After the equilibration of the reactor, the solutions (1) **2a**-OTf (168 mg, 0.5 mmol, 1 equiv) and **5a** (81 mg, 0.75 mmol, 1.5 equiv. or 162 mg, 1.5 mmol, 3 equiv.) in CH_3CN (1.5 mL) and (2) K_2CO_3 (414 mg, 3 mmol, 6 equiv.) in H_2O (3 mL) were prepared separately and charged in syringes. The infusion proceeds under the corresponding reaction conditions reported below. The biphasic mixture was collected. The water phase was washed with EtOAc (3 times), the organic phases were collected, dried over Na_2SO_4 and concentered. The **^{1}H NMR** of the crude was recorded, yields were calculated using CH_2Br_2 as internal standard (20 µL, 0.284 mmol). The pure product was isolated by flash chromatography (Cyclohexane/EtOAc 95:5).

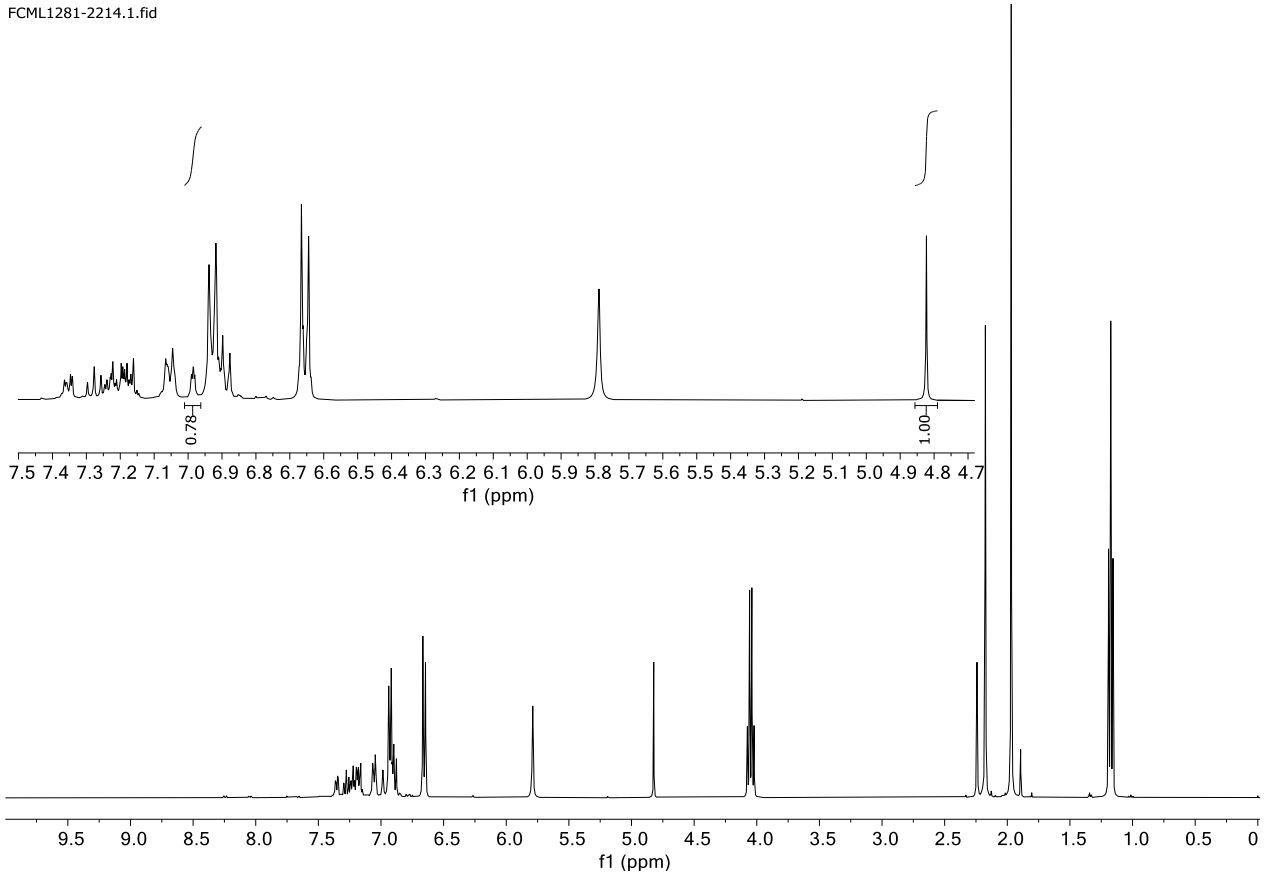
Entry	Syringe (1) or (2)	Mmol Phenols	Flow rate syringe (mL/min)	Flow Reactor (mL/min)	Temp. (°C)	Residence time (min)	NMR Yield % (Isolated yield)
1	(1) (2)	1.5	0.05 0.1	0.15	r.t.	13.3	48%
2	(1) (2)	1.5	0.03 0.06	0.09	r.t.	22.2	42%
3	(1) (2)	3	0.05 0.1	0.15	r.t.	13.3	89% (72%)



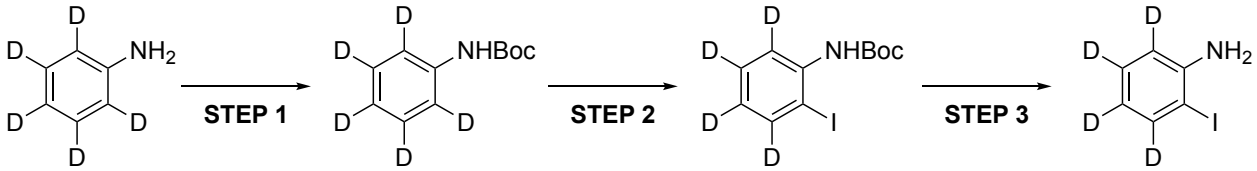
Set-Up: *Syringe pump*: Chemyx Fusion 4000; *Tubing*: Index Health & Science (1912L) PFA+ Tubing Natural 1/16" OD x .030" ID x 50ft; *Valve*: PEEK Low Pressure Tee Assembly 1/16" PEEK .020 thru hole; *Syringes*: 2mL, 6mL, 10mL, 20 mL NORM-JECT®

Reactor Configuration			
tube ID (mm)	radius (mm)	Volume tube (mL = cm^3)	lenght tube (cm)
0.75	0.0375	2	453

Crude **^{1}H NMR** of ***Entry 3***



Preparation of deuterated substrates:

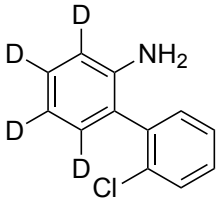


SCHEME S-13

Step 1: A solution of aniline-2,3,4,5,6-D_5 (1 mL, 11 mmol, 1 equiv) and *t*-butyl-dicarbonate (2.87 g, 13.2 mmol, 1.2 equiv) in dry THF (22 mL, M 0.5) was stirred at room temperature for 16h. The resulting mixture was concentrated and purified by flash chromatography column to obtain the *t*-butyl N-[(2,3,4,5,6-D_5)phenyl]carbamate as a white solid in quantitative yield. (2.15 g, 10.8 mmol).

Step 2: To a schlenk tube was added *t*-butyl N-[(2,3,4,5,6-$^2H_5$)phenyl]carbamate (g, 5.04 mmol, 1 equiv), $Pd(OAc)_2$ (1.19 g, 5.3 mmol, 1.05 equiv), dry TsOH (1.74 g, 10.08 mmol, 2 equiv) and dry MeOH (30 mL, 0.17 M). The resulting mixture was stirred for 24 hours at room temperature. NIS (1.2 g, 5.3 mmol, 1.05 equiv) was added and the reaction mixture was stirred for 30 minutes at room temperature. The resulting mixture was filtered through a pad of celite and concentrated. The residue was diluted with water, quenched with saturated aqueous $Na_2S_2O_3$ solution and extracted with ethyl acetate (3 times). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified through flash chromatography column yielding the *t*-butyl N-[2-iodo(3,4,5,6-$^2H_4$)phenyl]carbamate as colorless oil in 21% yield. (343 mg, 1.059 mmol).

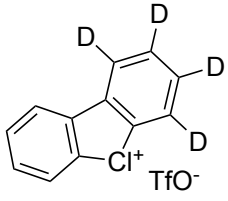
Step 3: To a solution of *t*-butyl N-[2-iodo(3,4,5,6-$^2H_4$)phenyl]carbamate (343 mg, 1.06 mmol, 1 equiv) in dry DCM (5 mL, 0.2 M) at 0 °C was added dropwise TFA (0.93 mL, 12.57 mmol, 12.7 equiv). The resulting mixture was stirred 3 hours at room temperature. The reaction was quenched with $NaHCO_3$ extracted with EtOAc, dried concentrated to yield the crude 2-iodo($^2H_4$)aniline as pale brown solid in quantitative yield. (219 mg, 0.98 mmol) The product was used without further purification.



2'-chloro-[1,1'-biphenyl]-3,4,5,6-d4-2-amine 1a-[D_4]

Following the **GP-A** using 2'-chloro-[1,1'-biphenyl]-3,4,5,6-d_4-2-amine (443 mg, 2 mmol) and 2-chlorophenylboronic acid (341 mg, 2.2 mmol) **1a-**[$D]_4$ was obtained as colorless solid in 58% yield (1.16 mmol, 241 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 1H), 7.35 – 7.31 (m, 3H), 3.38 (brs, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 137.9, 133.9, 131.9, 129.9, 129.0, 127.2, 125.2. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{12}H_7ClD_4N^+$: 208.0826; found: 208.0840.



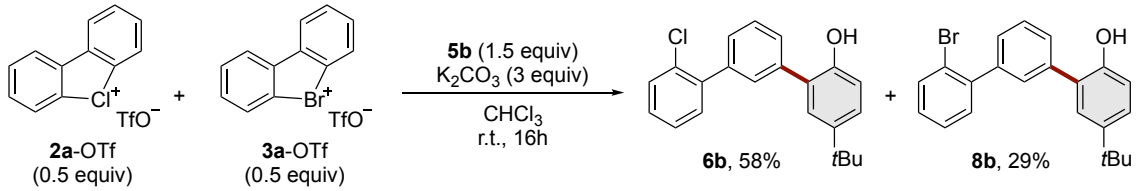
dibenzo[b,d]chlorol-5-ium-1,2,3,4-d$_4$ trifluoromethanesulfonate 2a-[$D]_4$-OTf

Following the **GP-B** using **1a**-[D_4] (241 mg, 1.16 mmol) and triflic acid (103 μL, 1.16 mmol) **2a**-[D_4]-OTf was obtained as white solid in 63% yield (0.73 mmol, 248 mg)

^{1}H NMR (400 MHz, DMSO) δ 8.69 – 8.65 (m, 2H), 8.01 (tdd, J = 7.5, 5.0, 1.1 Hz, 1H), 7.95 (ddd, J = 9.0, 7.4, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 140.1 (2C), 132.0 (3C), 131.7, 125.5, 122.9. **^{19}F NMR** (377 MHz, DMSO) δ -77.7. **HRMS (ESI)**: m/z $[M-TfO]^+$ calcd for $C_{12}H_4ClD_4^+$: 191.0560; found: 191.0560.

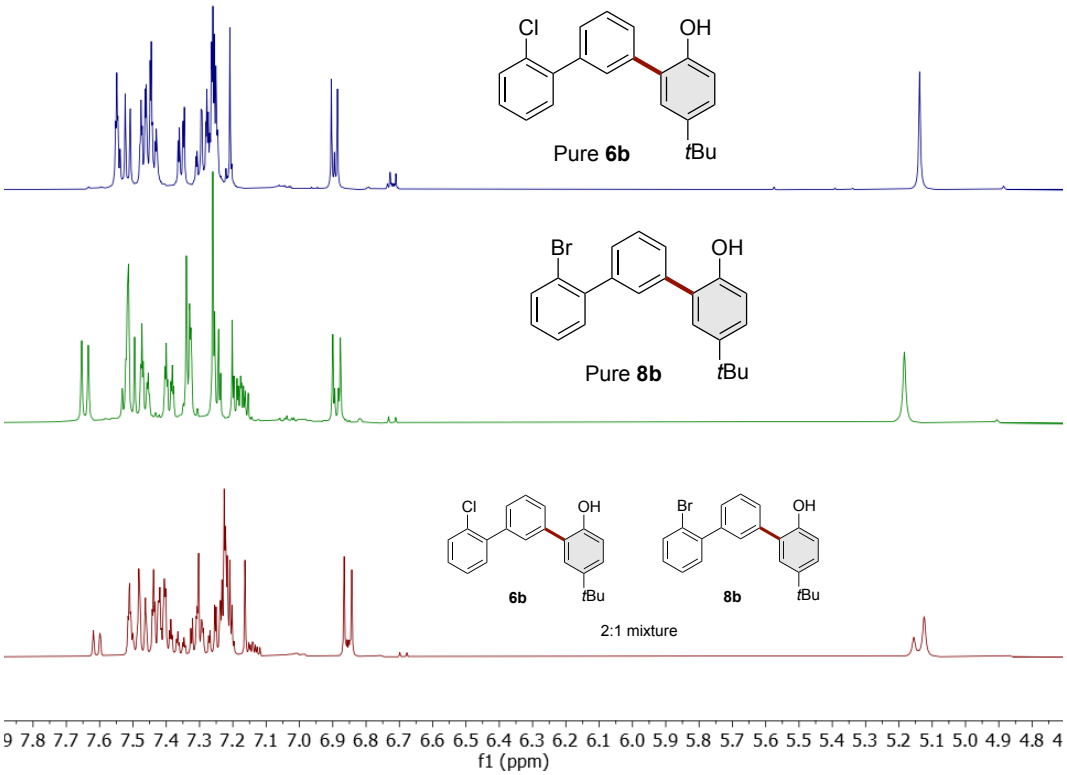
Mechanistic Investigations:

Competition experiments: Metal-free CDC C-C bond formation with cyclic diaryl λ^3-chloranes

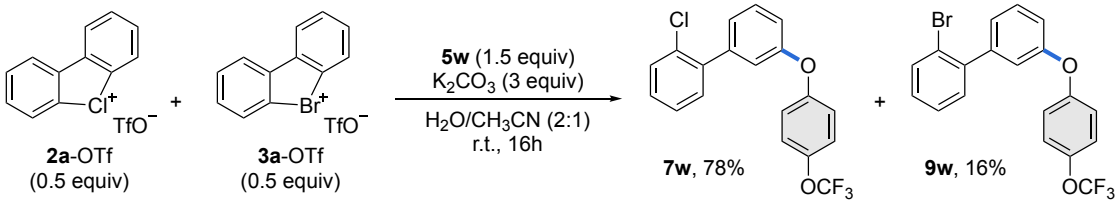


SCHEME S-14

An oven dried vial was charged with **2a**-OTf (25.3 mg, 0.075 mmol, 0.5 equiv.), **3a**-OTf (28.6 mg, 0.075 mmol, 0.5 equiv.), 4-(*tert*-butyl)phenol **5b** (33.8 mg, 0.23 mol, 1.5 equiv), and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv.). The vial was evacuated and back refilled with Argon three times. Subsequently, $CHCl_3$ (1.5 mL, 0.1M) was added. The resulting heterogeneous mixture was stirred at room temperature for 16 hours. The crude was purified through Prep-TLC (Cy:EtOAc 9:1) yielding **6b** and **8b** as a mixture (23 mg) with a ration of 2:1 form which yields were determinate.

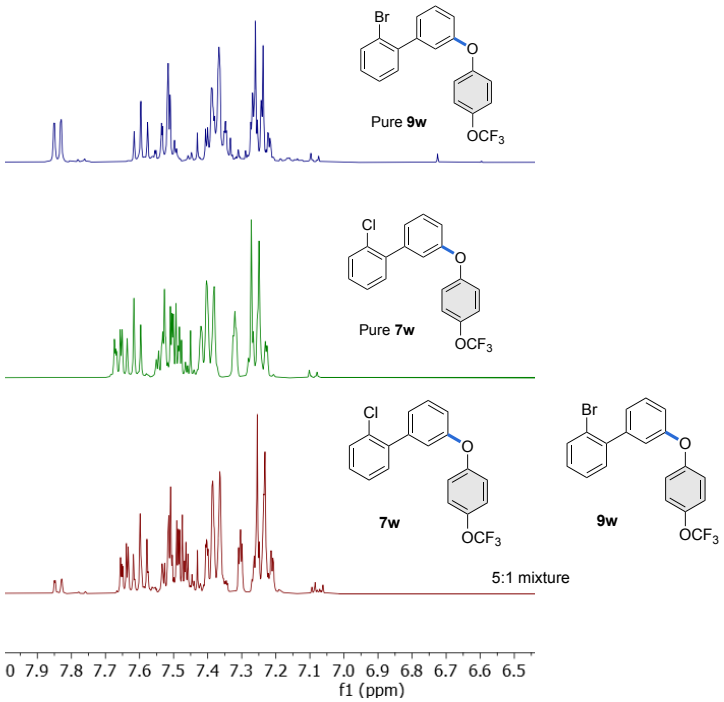


Competition experiments: Metal free C-O arylation of phenols with cyclic diaryl λ^3-chloranes

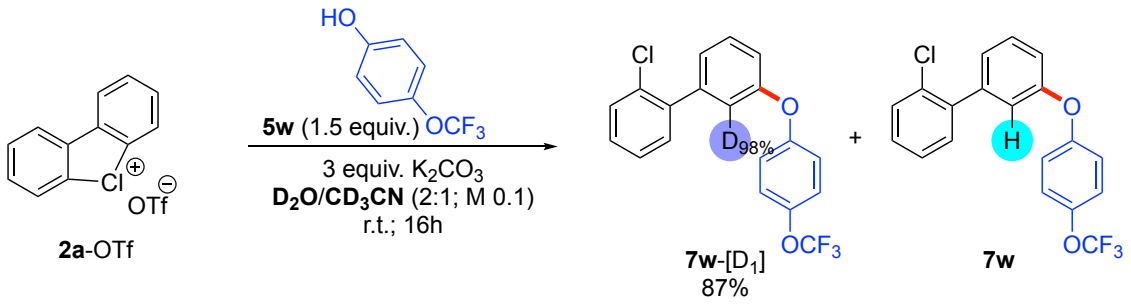


SCHEME S-15

An oven dried vial was charged with **2a**-OTf (25.3 mg, 0.075 mmol, 0.5 equiv.), **3a**-OTf (28.6 mg, 0.075 mmol, 0.5 equiv.), 4-(trifluoromethoxy)phenol **5w** (29.2 µL, 0.23 mol, 1.5 equiv.), and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv.). The vial was evacuated and back refilled with Argon three times. Subsequently, H_2O (1 mL) and CH_3CN (0.5 mL) were added. The resulting heterogeneous mixture was stirred at room temperature for 16 hours. The crude was purified through Prep-TLC (Cy:EtOAc 9:1) yielding **7w** and **9w** as a mixture (26 mg) with a ration of 5:1 form which yields were determined.



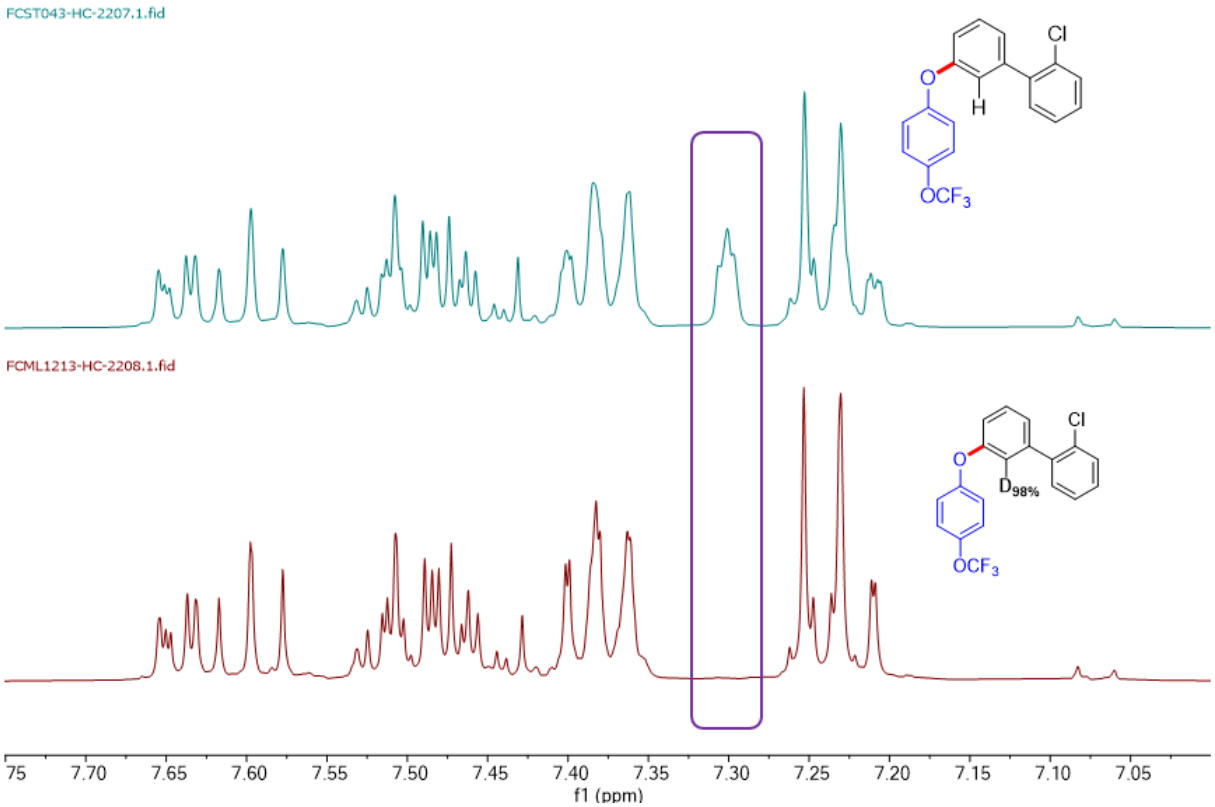
Deuterated solvent: Metal free C-O arylation of phenols with cyclic diaryl λ^3-chloranes

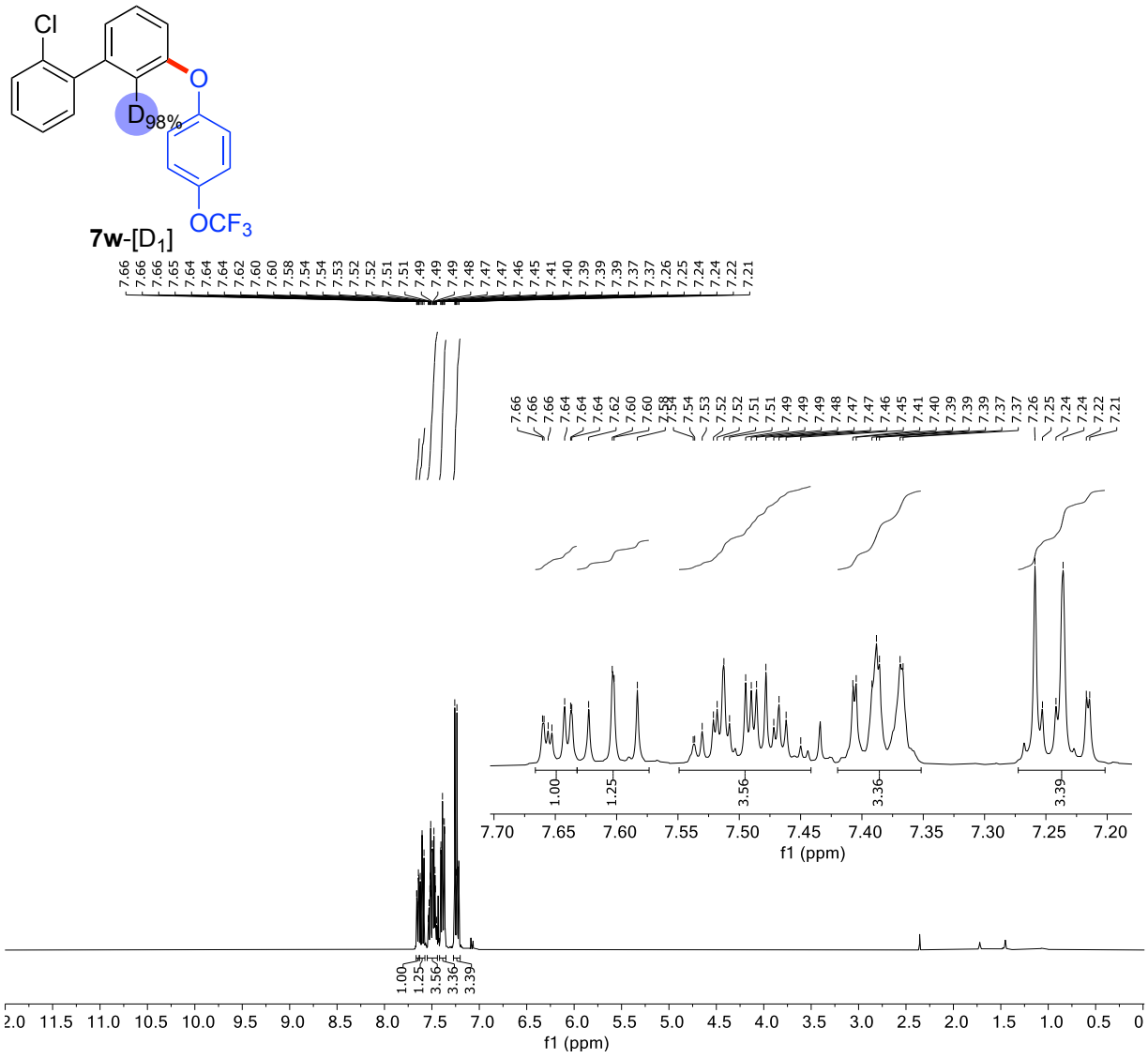


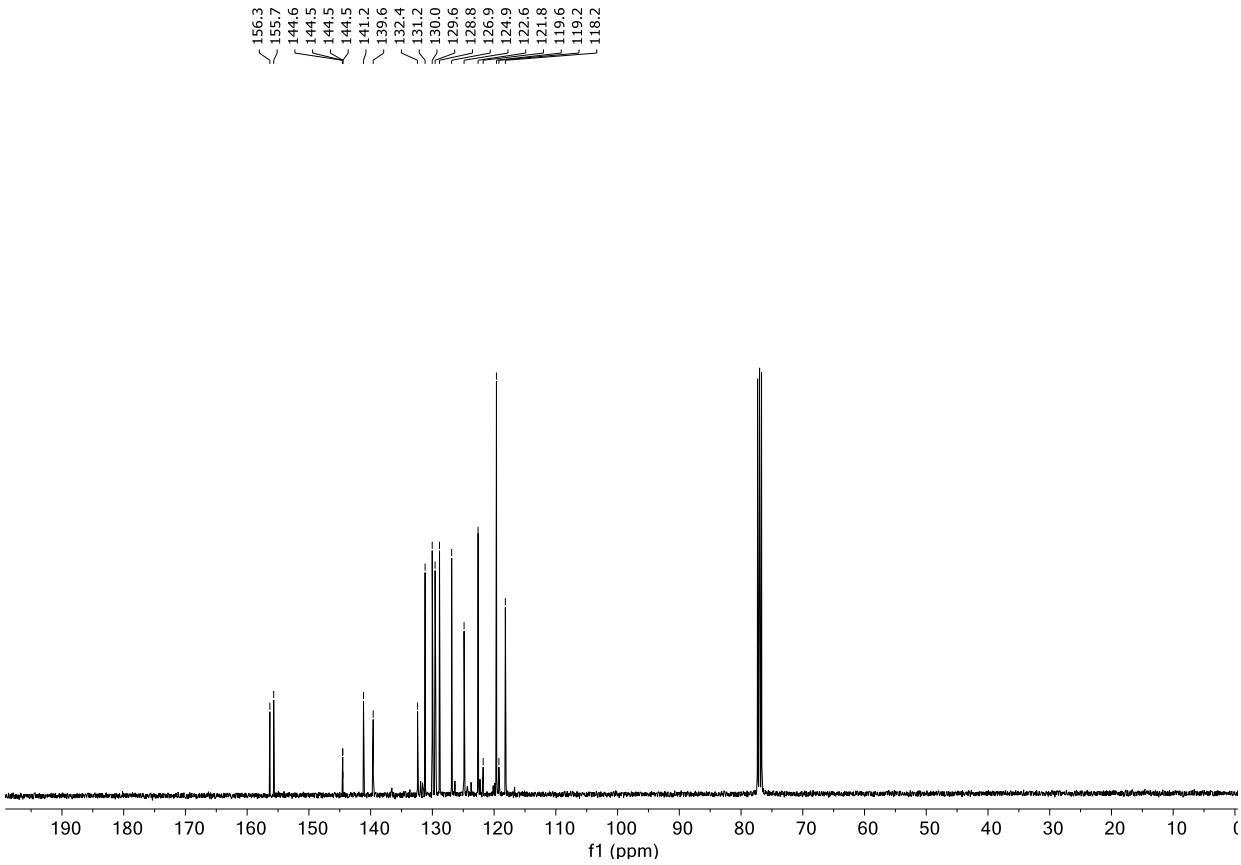
SCHEME S-16

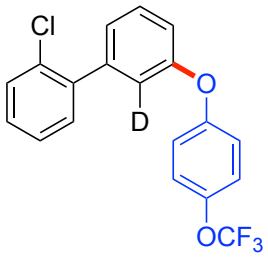
An oven dried vial was charged with **2a**-OTf (51 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv.). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol, 1.5 equiv.) was added followed by D_2O (1 mL) and CD_3CN (0.5 mL). The conversion was verified by GCMS and TLC. The mixture was extracted with EtOAc (3 mL x 3 times). The extracts were combined, dried over $MgSO_4$, and filtered. After removal of volatile components, the crude was purified through Prep-TLC (Cy:EtOAc 9:1) yielding **7w**-$[D]_1$ as colorless oil in 87% yield. (47.7 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.45 (m, 3H), 7.41 – 7.37 (m, 3H), 7.26 – 7.21 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 155.7, 144.5 (dd, J = 3.9, 1.7 Hz), 141.2, 139.6, 132.4, 131.2, 130.0, 129.6, 128.8, 126.9, 124.9, 122.6 (2C), 120.5 (q, J = 256.8 Hz), 119.6 (2C), 118.2. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{11}ClDF_3O_2^+$: 365.0535; found: 365.0529.

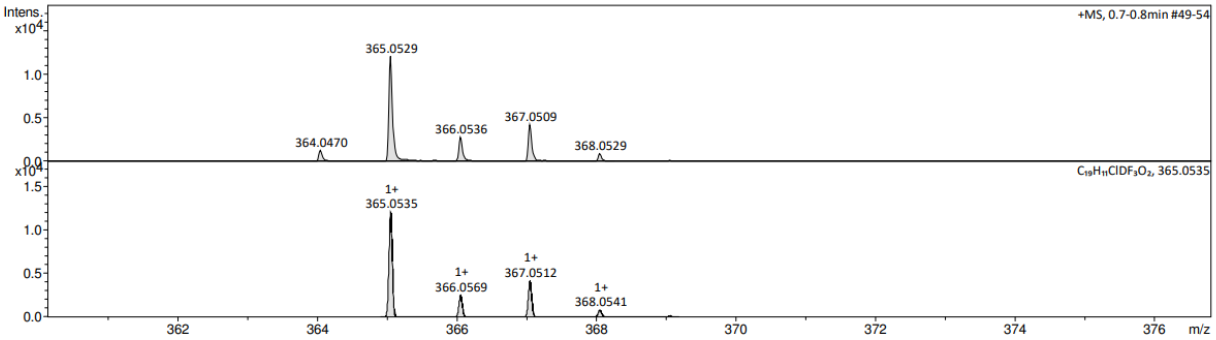

FCST043-HC-2207.1.fid
Cl
O
H
OCF3
FCML1213-HC-2208.1.fid
Cl
O
D98%
OCF3
75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
f1 (ppm)


Cl
O
D98%
OCF3
7w-[D1]
7.66 7.66 7.66 7.65 7.64 7.64 7.64 7.62 7.60 7.60 7.58 7.54 7.54 7.53 7.52 7.52 7.51 7.51 7.49 7.49 7.49 7.48 7.47 7.47 7.46 7.45 7.41 7.40 7.39 7.39 7.39 7.37 7.37 7.26 7.25 7.24 7.24 7.22 7.21
1.00 1.25 3.56 3.36 3.39
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


156.3
155.7
144.6
144.5
144.5
144.5
141.2
139.6
132.4
131.2
130.0
129.6
128.8
126.9
124.9
122.6
121.8
119.6
119.2
118.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

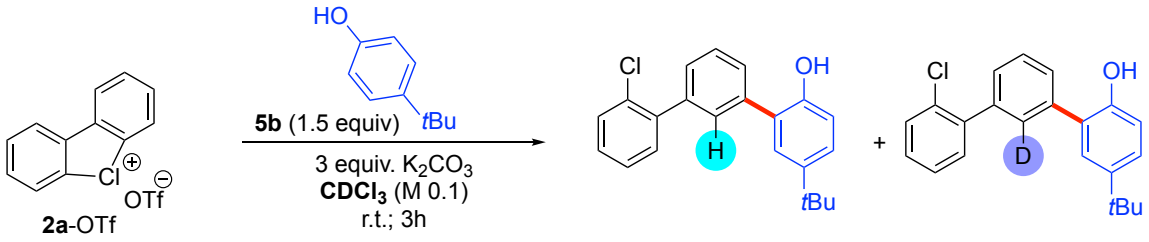


Chemical Formula: $C_{19}H_{11}DClF_3O_2$
Exact Mass: 365,0535



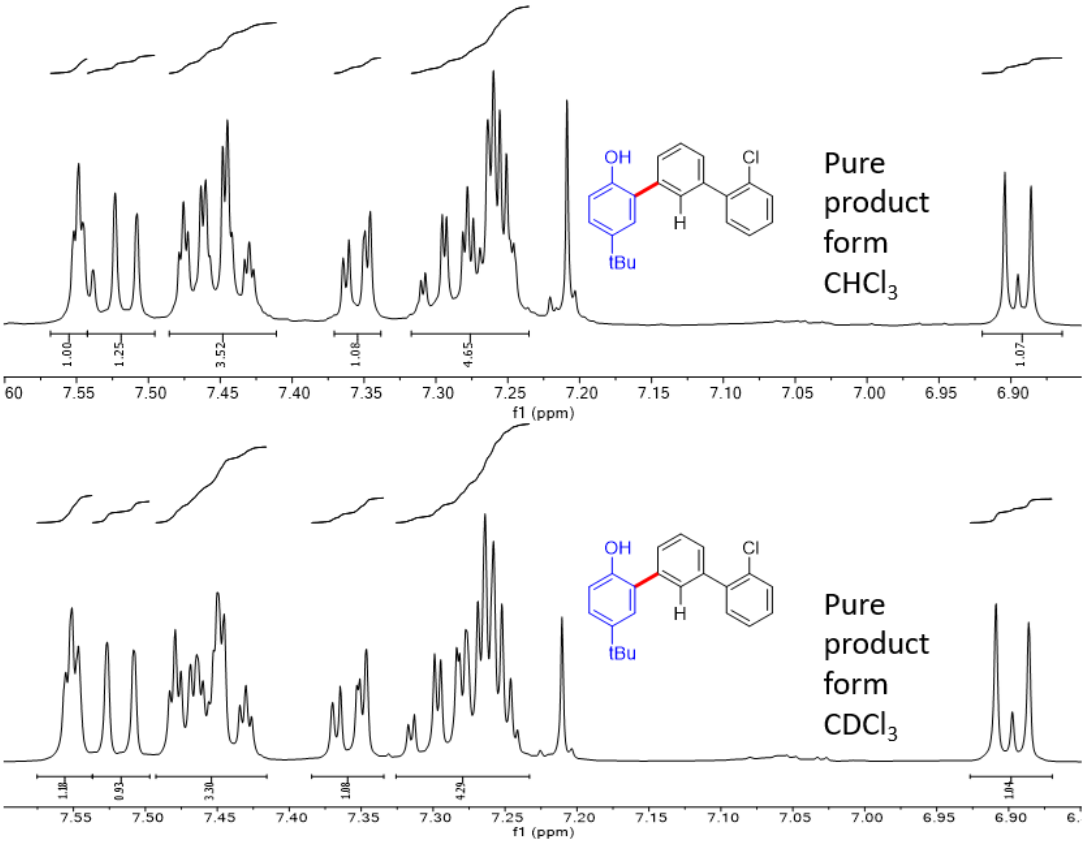
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
365.0529	1	C19H11ClDF3O2	365.0535	1.8	13.3	1	100.00	12.0	odd	ok

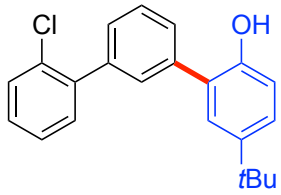
Deuterated solvent: Metal-free CDC C-C bond formation with cyclic diaryl λ^3-chloranes



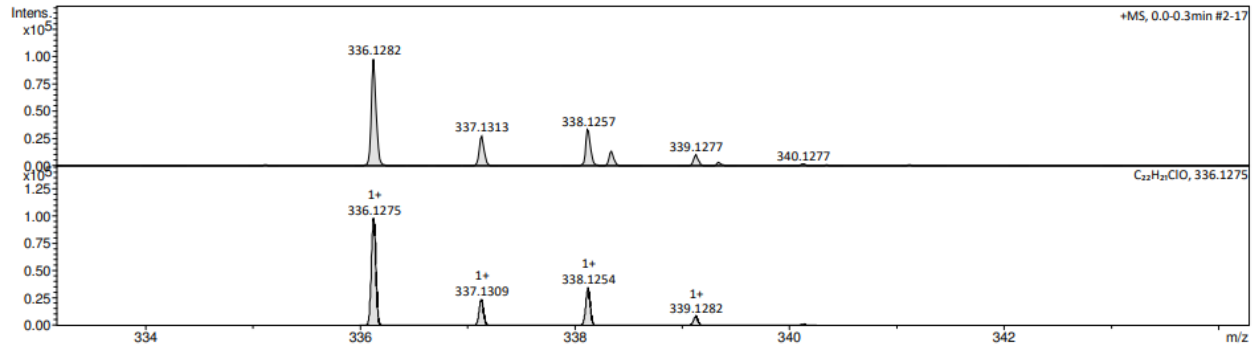
SCHEME S-17

To a dry and metal-free vial was charged **2a**-OTf (50.5 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv) and 4-*t*Butylphenol **5b** (34.5 mg, 0.22 mmol, 1.5 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, $CDCl_3$ (1.5 mL, 0.1M) was added. The resulting heterogeneous mixture was stirred at room temperature for 3 hours. The conversion was verified by GCMS and TLC. The mixture was diluted with EtOAc (3 mL) and filtered. After removal of volatile components, the crude was purified through Prep-TLC yielding **6b** as colorless oil in 40% (20 mg, 0.06 mmol). No deuteration has been observed. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{21}ClO^+$: 336.1275; found: 336.1282.





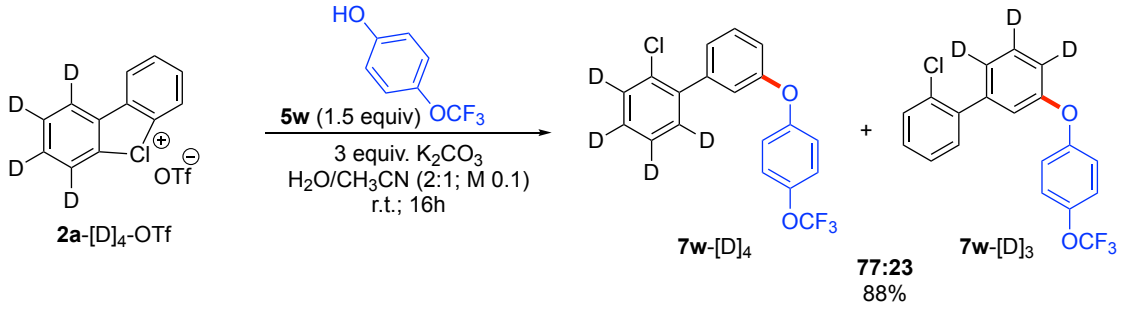
Chemical Formula: $C_{22}H_{21}ClO$
Exact Mass: 336,1275



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
336.1282	1	C22H21ClO	336.1275	-1.8	20.0	1	100.00	12.0	odd	ok

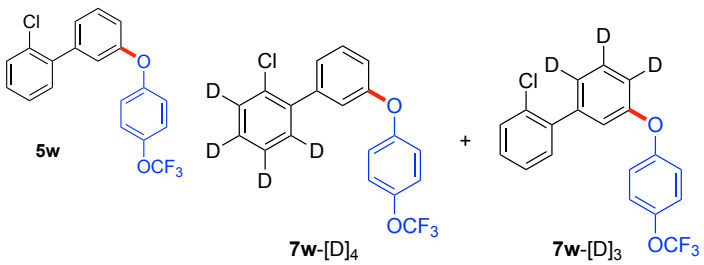
Deuterated Substrate:

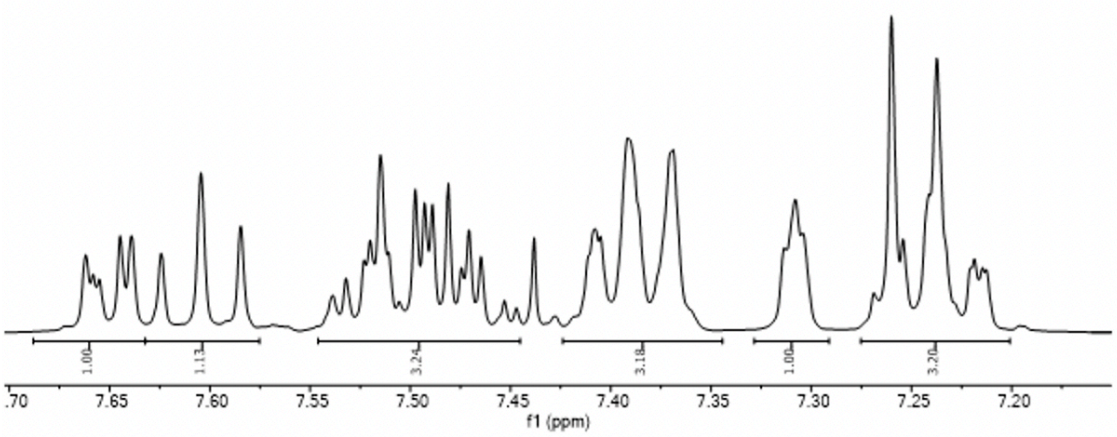
Metal free C-O arylation of phenols with cyclic diaryl λ^3-chloranes

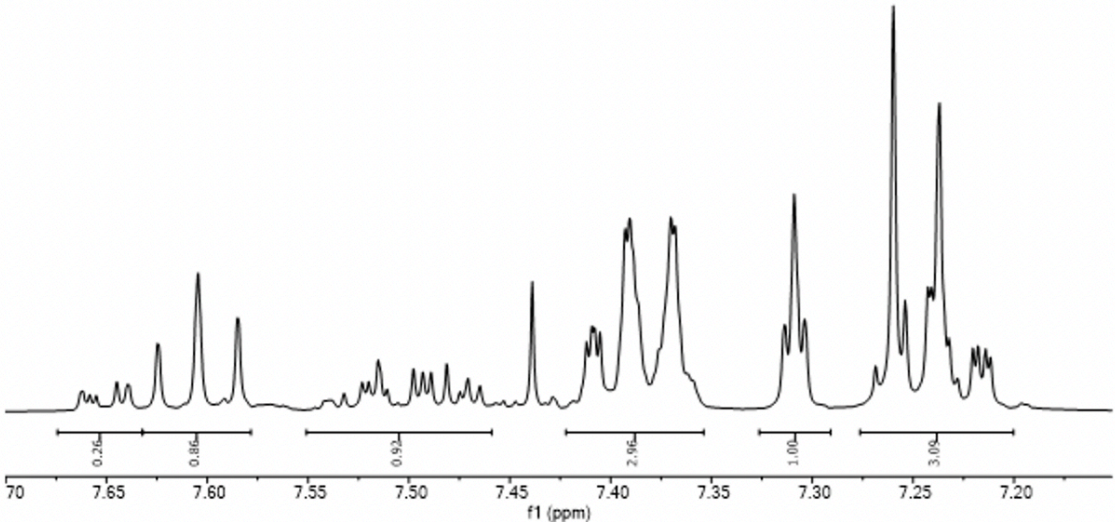


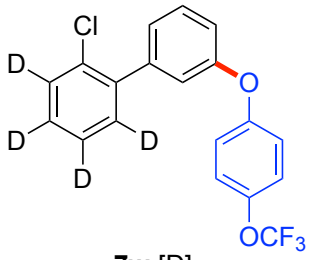
SCHEME S-18

To a dry and metal-free vial was charged **2a**-$[D]_4$-OTf (51 mg, 0.15 mmol, 1 equiv.) and K_2CO_3 (62 mg, 0.45 mmol, 3 equiv). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, 4-trifluoromethoxy phenol **5w** (29 µL, 0.23 mmol, 1.5 equiv) was added followed by H_2O (1 mL) and CH_3CN (0.5 mL). The conversion was verified by GCMS and TLC. The mixture was extracted with EtOAc (3 mL x 3 times). The extracts were combined, dried over $MgSO_4$, and filtered. After removal of volatile components, the crude was purified through Prep-TLC (Cy:EtOAc 9:1) yielding **7w**-$[D]_4$ and **5w**-$[D]_3$ as colorless oil in 88% yield. (48.7 mg, 0.13 mmol). The ratio has been determined by **^{1}H NMR** which resulted to be 77:23 **7w**-$[D]_4$ and **7w**-$[D]_3$. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_8ClD_4F_3O_2^+$: 368.0724; found: 368.0734.


Cl
O
OCF3
5w
Cl
D
D
D
D
O
OCF3
7w-[D]4
+
D
D
Cl
D
O
OCF3
7w-[D]3

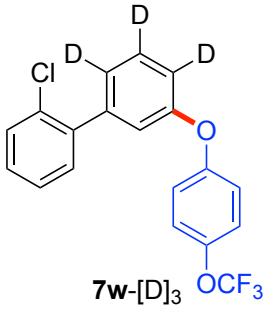

1.00
1.13
3.24
3.18
1.00
3.20
.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)


0.26
0.86
0.92
2.96
1.00
3.09
70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)



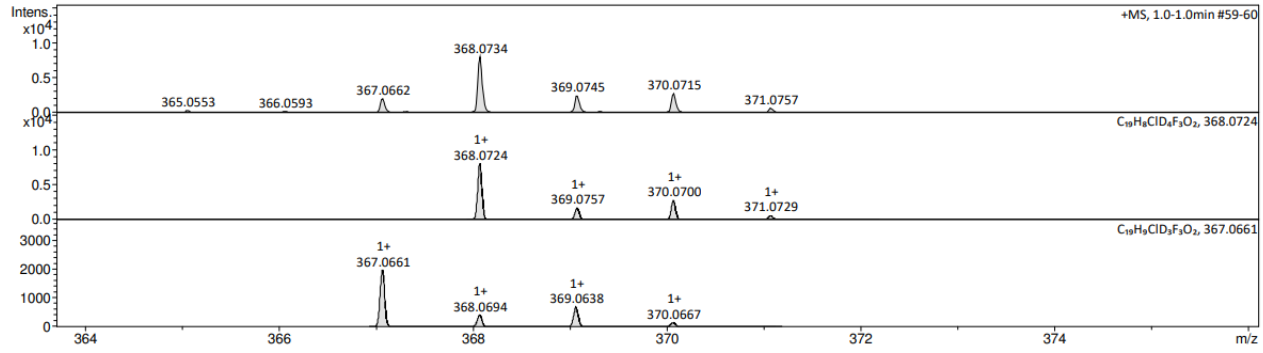
7w-$[D]_4$

Chemical Formula: $C_{19}H_8D_4ClF_3O_2$
Exact Mass: 368.0729



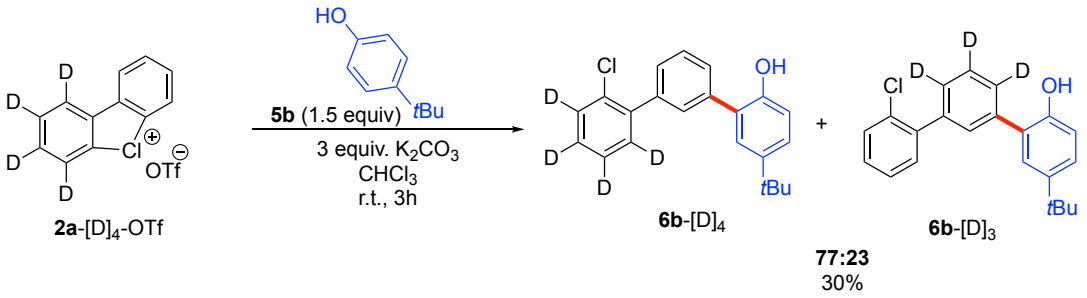
7w-$[D]_3$

Chemical Formula: $C_{19}H_9D_3ClF_3O_2$
Exact Mass: 367.0666



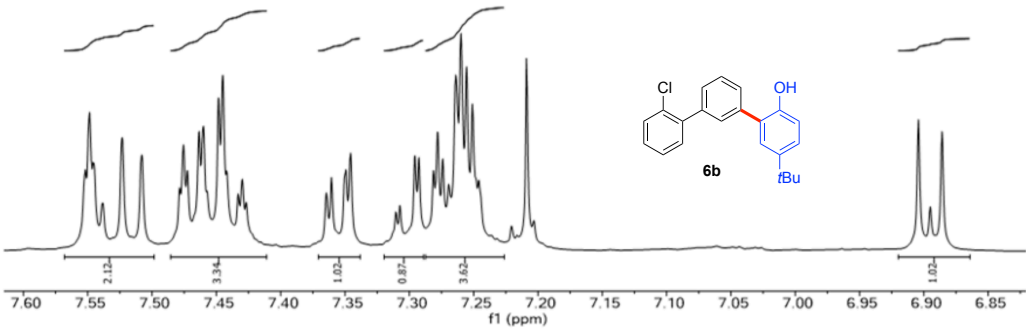
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
367.0662	1	C19H9ClD3F3O2	367.0661	-0.3	589.8	1	100.00	12.0	odd	ok
368.0734	1	C19H8ClD4F3O2	368.0724	-2.8	45.3	1	100.00	12.0	odd	ok

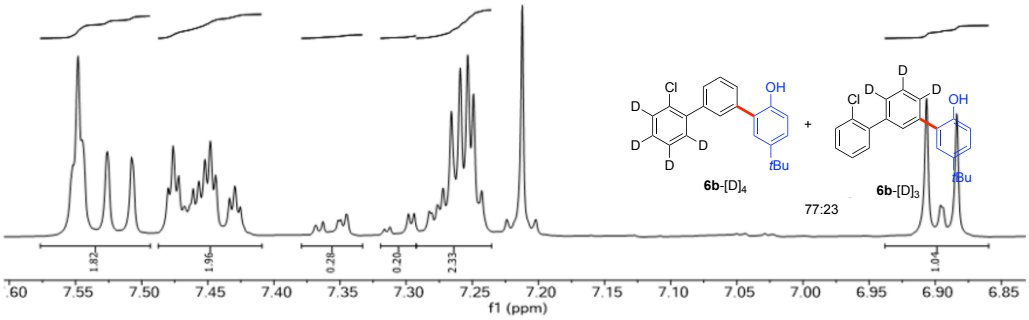
Metal-free CDC C-C bond formation with cyclic diaryl λ^3-chloranes

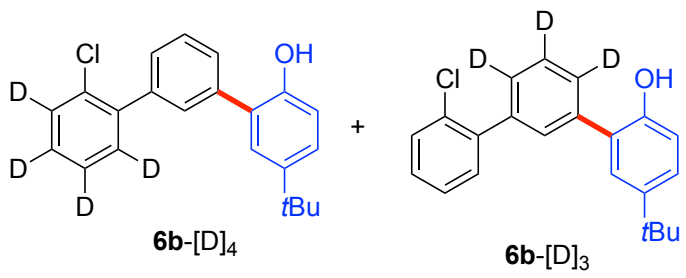


SCHEME S-19

To a dry and metal-free vial was charged **2a**-$[D]_4$-OTf (51 mg, 0.15 mmol, 1 equiv.), K_2CO_3 (62 mg, 0.45 mmol, 3 equiv.) and 4-*t*Butylphenol **5b** (34 mg, 0.23 mmol, 1.5 equiv.). The vial was evacuated and back refilled with Argon three times. Subsequently, under argon, $CHCl_3$ (1.5 mL) was added. The reaction was stirred for 3h at r.t. The conversion was verified by GCMS and TLC. The mixture was filtered and after removal of volatile components, the crude was purified through Prep-TLC (Cy:EtOAc 9:1) yielding **6b**-$[D]_4$ and **6b**-$[D]_3$ as colorless oil in 30% yield. (15.7 mg, 0.046 mmol The ratio has been determined by **^{1}H NMR** which resulted to be 77:23 **6b**-$[D]_4$ and **6b**-$[D]_3$. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{22}H_{17}ClD_4O^+$: 340.1527; found: 340.1539.


Cl
OH
6b
tBu
2.12
3.34
1.02
0.87
3.62
1.02
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
f1 (ppm)

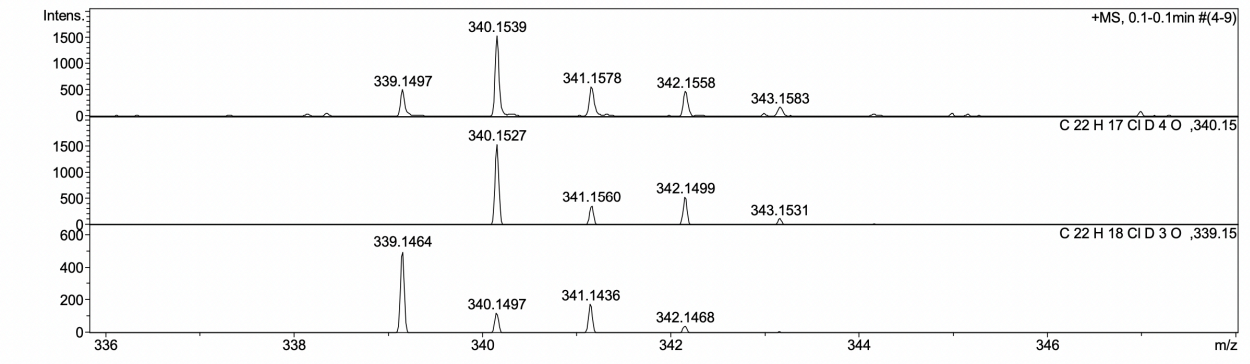

Cl
OH
D
D
D
D
tBu
6b-[D]4
+
Cl
D
D
D
OH
tBu
6b-[D]3
77:23
1.82
1.96
0.28
0.20
2.33
1.04
.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
f1 (ppm)



6b-$[D]_4$ **6b**-$[D]_3$

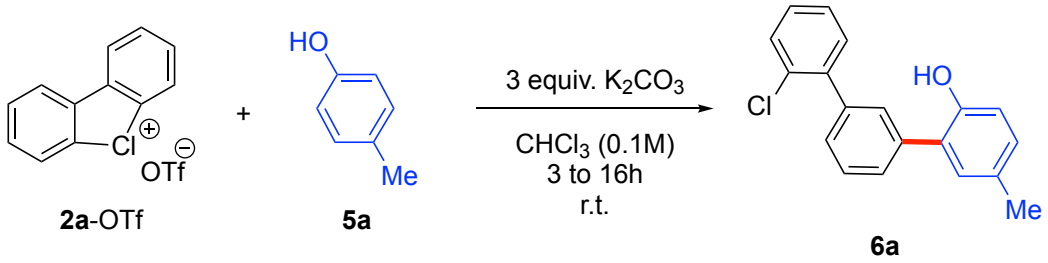
Chemical Formula: $C_{22}H_{17}D_4ClO$
Exact Mass: 340.1532

Chemical Formula: $C_{22}H_{18}D_3ClO$
Exact Mass: 339.1469



Kinetic Studies:

Metal-free CDC C-C bond formation with cyclic diaryl λ^3-chloranes



2a-OTf **5a** **6a**

SCHEME S-20

To a dry and metal-free vial was charged **2a**-OTf (101 mg, 0.3 mmol, 1 equiv.) and K_2CO_3 (124 mg, 0.9 mmol, 3 equiv) and 4-MethylPhenol **5a** (49 mg, 0.45 mmol, 1.5 equiv.). The vial was evacuated and back refilled with Argon three times. Subsequently, $CHCl_3$ (3 mL, 0.1 M) was added. The resulting heterogeneous mixture was stirred at room temperature. Samples (100 µL) was taken over the time, a solution (500 µL, 0.02 M) of internal standard in $CDCl_3$ (67.3 mg of 1,3,5-Trimethoxybenzene in 20 mL of $CDCl_3$) was added, then **^{1}HNMR** was recorded. The experiment was replicated three times.

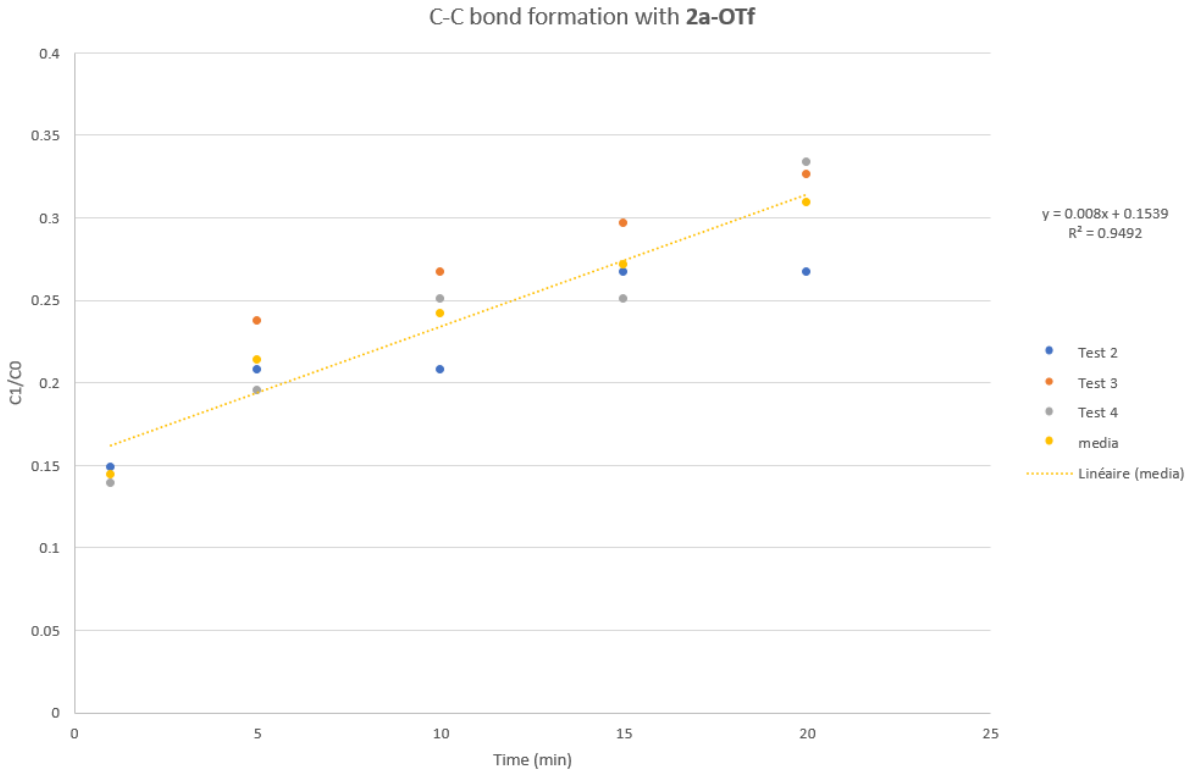
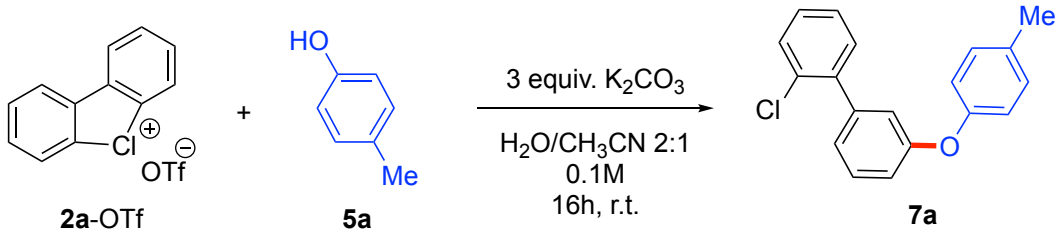


FIGURE S-1

Metal free C-O arylation of phenols with cyclic diaryl λ^3-chloranes



2a-OTf **5a** **7a**

SCHEME S-21

To a dry and metal-free vial was charged **2a**-OTf (101 mg, 0.3 mmol, 1 equiv.) and K_2CO_3 (124 mg, 0.9 mmol, 3 equiv) and 4-methylPhenol **5a** (49 mg, 0.45 mmol, 1.5 equiv.). The vial was evacuated and back refilled with Argon three times. Subsequently, CH_3CN/H_2O (0.5 mL and 1 mL respectively, 0.1 M) was added. The resulting heterogeneous mixture was stirred at room temperature. Samples (100 µL) was taken over the time, a solution (500 µL, 0.02 M) of internal standard in $CDCl_3$ (67.3 mg of 1,3,5-Trimethoxybenzene in 20 mL of $CDCl_3$) was added, then **^{1}HNMR** was recorded. The experiment was replicated three times.

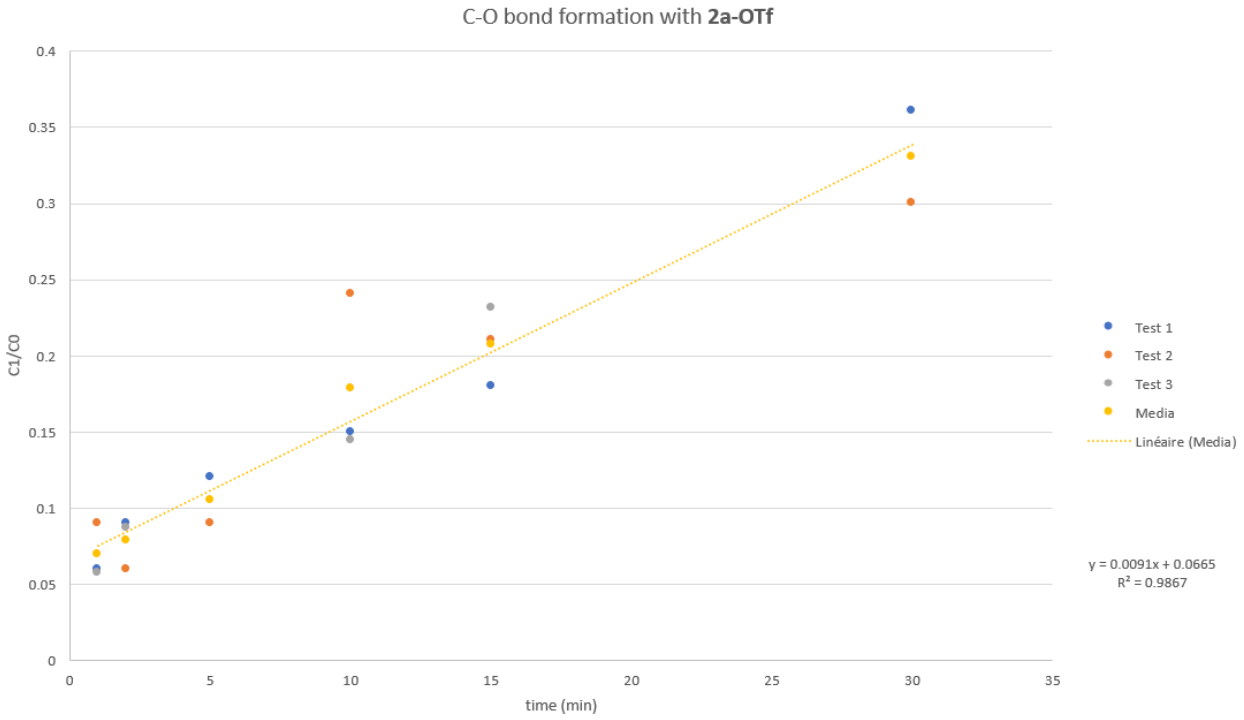


FIGURE S-2

Computational Data

All density functional theory (DFT) calculations were performed with the Gaussian 16, Rev. A.03, program package. [4] Geometry optimizations were performed at the ωB97X-D level of theory. [5] All atoms were described with a def2-TZVP basis set[6] in combination with SDD pseudopotential[7,8] for Br and I. Analytical frequency calculations were performed at the same level of theory to characterize all stationary points as intermediates (no imaginary frequencies) or transition states (exactly one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed at the same level of theory to confirm the intermediates linked by each transition state. The electronic energy was refined through single point calculations at the ωB97X-D level of theory, employing a def2-QZVPP basis set[6] in combination with SDD pseudopotential for Br and I. Unless stated otherwise, solvent effects were taken into consideration in single-point calculations through the use of the SMD solvation model (solvent = chloroform) to model $CHCl_3$.[9] *GoodVibes*[10] (v. 3.0.2) with quasi-harmonic entropy[11] and enthalpy[12] treatment (frequency cut-off value: 100 cm^{-1}) was used to obtain corrected Gibbs free energies and enthalpies at 298 K and 1 atm.

NBO charges were calculated with *Natural Atomic Orbitals and Natural Bond Orbitals Analysis* (NBO 7.0) software.[13]

3D-visualizations of optimized structures were rendered with *CYLview20*.[14]

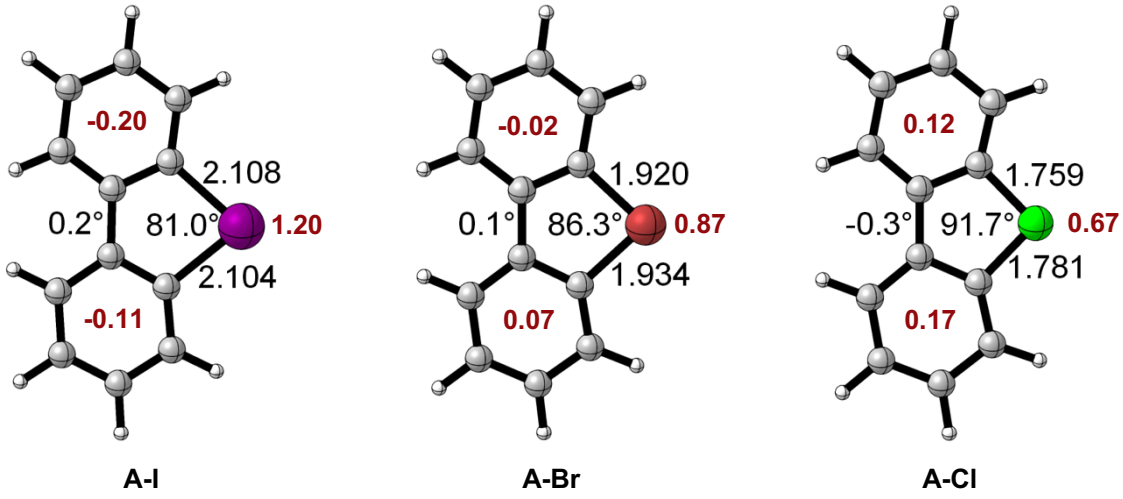


Figure S-3. Calculated geometries of hypervalent halonium species **A** (**2a**, **3a** and **4a**). Distances are given in Å and OTf^- was omitted for clarity. Values in red correspond to NBO charges.

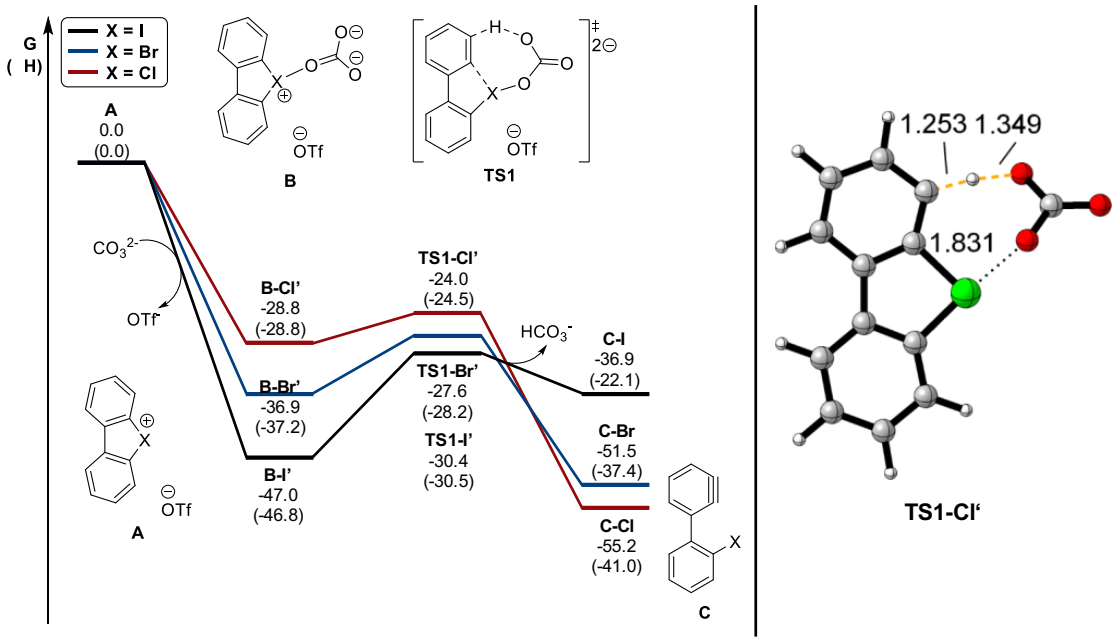


Figure S-4. Calculated energy diagram (in kcal mol^{-1}) for the formation of arynes **C** from hypervalent halonium **2a**, **3a** and **4a** in the abscence of OTf⁻. Distances are given in Å.

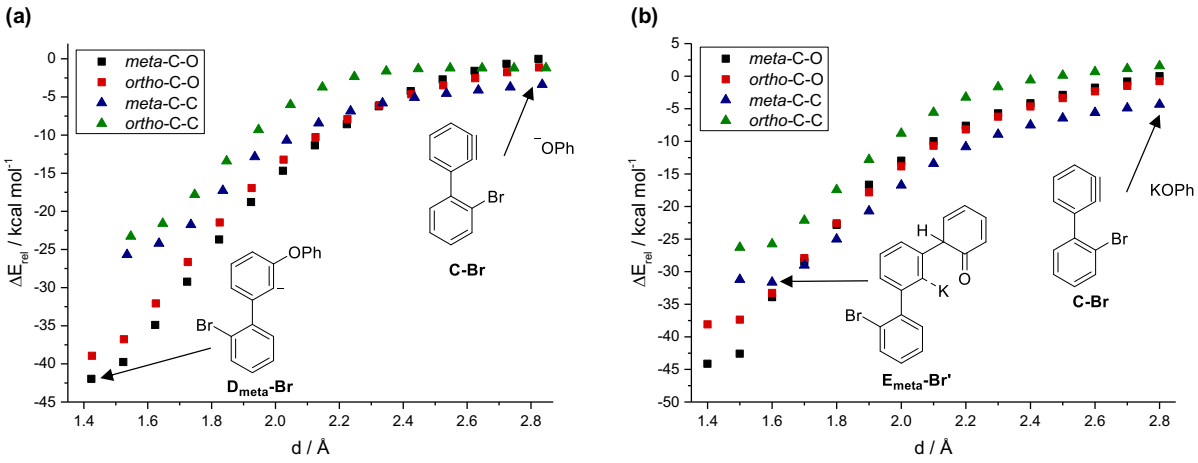


Figure S-5. Calculated energy profile (in kcal mol^{-1}) for C–O bond (black and red squares) and C–C bond (blue and green triangles) formation with bromine-substituted aryne and (a) phenolate and (b) potassium phenolate.

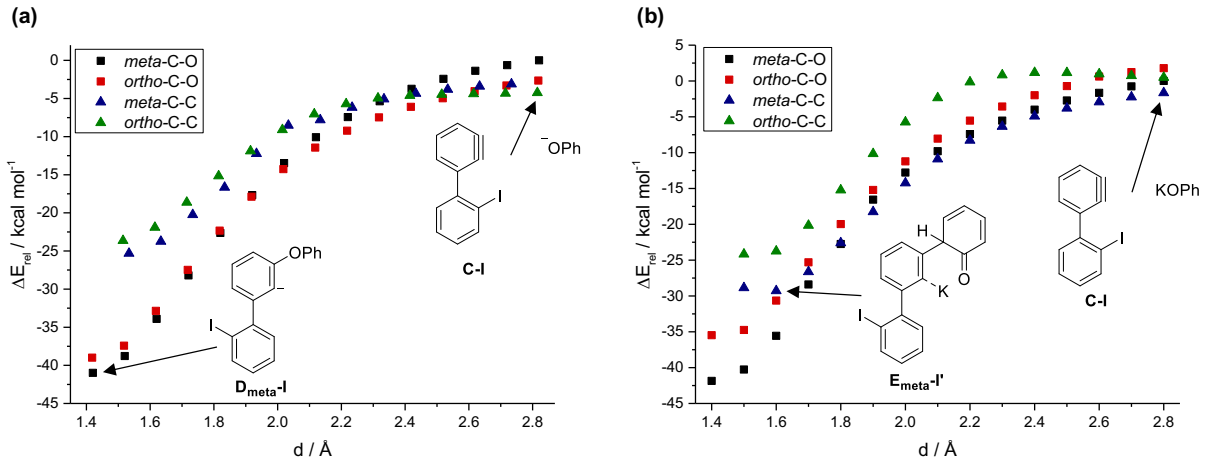


Figure S-6. Calculated energy profile (in kcal mol^{-1}) for C–O bond (black and red squares) and C–C bond (blue and green triangles) formation with iodine-substituted aryne and (a) phenolate and (b) potassium phenolate.

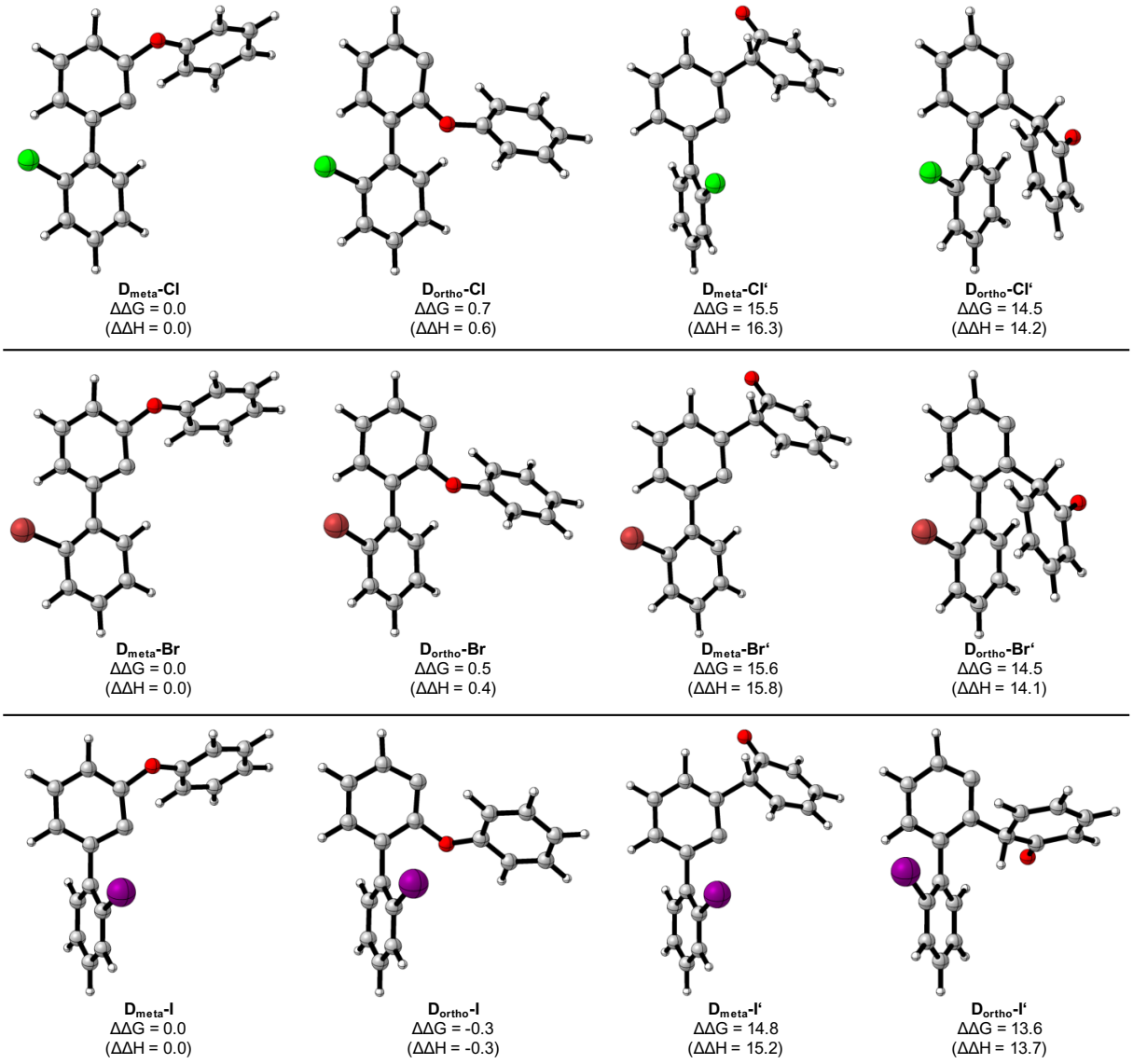


Figure S-7. Optimized geometries of C–O and C–C intermediates and energies relative to $\mathbf{D_{meta}}$ (in kcal mol^{-1}).

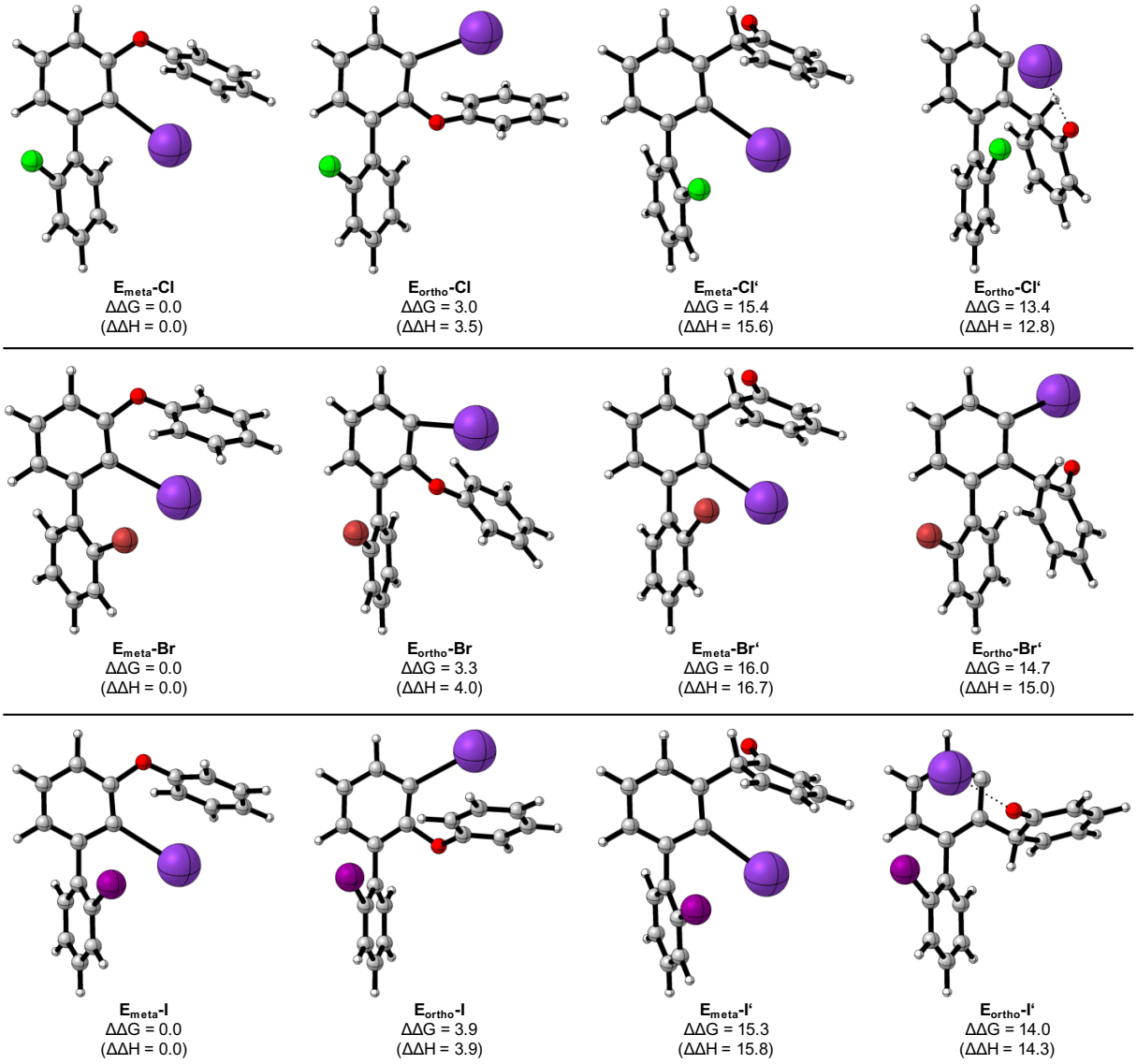


Figure S-8. Optimized geometries of C–O and C–C intermediates and energies relative to $\mathbf{E_{meta}}$ (in kcal mol^{-1}).

Summary of Energies

Structure	E_SPC (au)	qh-H_SPC (au)	T.qh-S (au)	qh-G(T)_SPC (au)	im. freq (cm^{-1})
Figure S-1					
A-I	-1435.122635	-1434.914348	0.065458	-1434.979806	--
A-Br	-1437.102785	-1436.894782	0.065578	-1436.960360	--
A-Cl	-1883.927110	-1883.718912	0.064304	-1883.783216	--
B-I	-1699.199483	-1698.973802	0.078187	-1699.051989	--
B-Br	-1701.167849	-1700.942224	0.077014	-1701.019238	--
B-Cl	-2147.980254	-2147.754480	0.076196	-2147.830675	--
TS1-I	-1699.168627	-1698.948784	0.077382	-1699.026166	-962.20
TS1-Br	-1701.147795	-1700.927837	0.076491	-1701.004328	-1093.07
TS1-Cl	-2147.969198	-2147.748308	0.075497	-2147.823805	-460.21
C-I	-472.790492	-472.632873	0.048780	-472.681653	--
C-Br	-474.795424	-474.637619	0.047906	-474.685525	--
C-Cl	-921.625570	-921.467451	0.046771	-921.514222	--
CO_3^{2-}	-264.005957	-263.987791	0.029664	-264.017455	--
HCO_3^-	-264.579846	-264.548667	0.030166	-264.578833	--
OTf^-	-961.791521	-961.755854	0.039721	-961.795574	--
Figure S-2					
B-I'	-737.411538	-737.220853	0.055782	-737.276635	--
B-Br'	-739.376583	-739.186070	0.055048	-739.241118	--
B-Cl'	-1186.187385	-1185.996765	0.054315	-1186.051080	--
TS1-I'	-737.379683	-737.194858	0.055223	-737.250081	-909.35
TS1-Br'	-739.356569	-739.171676	0.054558	-739.226234	-1115.15
TS1-Cl'	-1186.175424	-1185.989835	0.053562	-1186.043398	-799.71
Figure S-5					
D_{meta}-Cl	-1228.696181	-1228.438350	0.059112	-1228.497462	--

D_{ortho}-Cl	-1228.695131	-1228.437369	0.058953	-1228.496322	--
D_{meta}-Cl'	-1228.669230	-1228.412439	0.060332	-1228.472771	--
D_{ortho}-Cl'	-1228.672858	-1228.415655	0.058748	-1228.474403	--
D_{meta}-Br	-781.865704	-781.608451	0.060363	-781.668814	--
D_{ortho}-Br	-781.865066	-781.607810	0.060232	-781.668042	--
D_{meta}-Br'	-781.840359	-781.583275	0.060609	-781.643884	--
D_{ortho}-Br'	-781.842702	-781.585927	0.059761	-781.645688	--
D_{meta}-I	-779.859592	-779.602556	0.061164	-779.663720	--
D_{ortho}-I	-779.860084	-779.603082	0.061075	-779.664157	--
D_{meta}-I'	-779.834883	-779.578323	0.061764	-779.640087	--
D_{ortho}-I'	-779.837031	-779.580652	0.061389	-779.642041	--
PhO^-	-307.003778	-306.906607	0.035041	-306.941648	--
Figure S-6					
E_{meta}-Cl	-1828.604745	-1828.343397	0.063680	-1828.407077	--
E_{ortho}-Cl	-1828.599311	-1828.337893	0.064333	-1828.402227	--
E_{meta}-Cl'	-1828.579216	-1828.318497	0.064091	-1828.382588	--
E_{ortho}-Cl'	-1828.584125	-1828.323027	0.062646	-1828.385673	--
E_{meta}-Br	-1381.776519	-1381.515317	0.063925	-1381.579242	--
E_{ortho}-Br	-1381.770072	-1381.509019	0.065003	-1381.574021	--
E_{meta}-Br'	-1381.748984	-1381.488642	0.065141	-1381.553784	--
E_{ortho}-Br'	-1381.751745	-1381.491380	0.064434	-1381.555813	--
E_{meta}-I	-1379.772375	-1379.511554	0.065127	-1379.576681	--
E_{ortho}-I	-1379.766343	-1379.505272	0.065211	-1379.570482	--
E_{meta}-I'	-1379.746591	-1379.486412	0.065870	-1379.552281	--
E_{ortho}-I'	-1379.749194	-1379.488777	0.065536	-1379.554313	--
KOPh	-906.904773	-906.804209	0.040682	-906.844891	--

Cartesian Coordinates of Optimized Structures

A-I

C	4.058158	8.995946	4.508179
C	3.302435	7.852534	4.324647
H	2.806035	7.366240	5.154495
C	3.189522	7.333797	3.045787
H	2.602979	6.440017	2.879276
C	3.827049	7.959148	1.980789
H	3.734890	7.548710	0.983875
C	4.578782	9.101673	2.181096
H	5.067365	9.574089	1.339186
C	4.706802	9.642365	3.459185
C	5.471009	10.844304	3.803953
C	6.184926	11.632629	2.902894
H	6.202481	11.368490	1.853910
C	6.870534	12.750476	3.339135
H	7.419384	13.351179	2.625839
C	6.860828	13.109283	4.680904
H	7.399362	13.985975	5.015025
C	6.162516	12.350502	5.606394
H	6.140747	12.611411	6.654028
C	5.489298	11.241081	5.139376
C	3.078390	12.482232	9.479584
O	5.094273	11.475074	8.205541
O	5.137618	11.365659	10.640502
O	3.622219	9.933830	9.325844
S	4.370405	11.159448	9.459777
I	4.363316	9.950596	6.362241
F	2.330072	12.415109	8.371606
F	3.634753	13.689130	9.525324
F	2.279252	12.343373	10.529113

A-Br

C	-1.890678	-1.091783	-0.398157
C	-2.309008	-2.403452	-0.326204
C	-3.568414	-2.695901	-0.825138
C	-4.360787	-1.692446	-1.372907
C	-3.912205	-0.385554	-1.433121
C	-2.651061	-0.065303	-0.938801
C	-2.005540	1.241263	-0.914262
C	-2.518439	2.448231	-1.381612
C	-1.765551	3.603413	-1.278643
C	-0.497497	3.580617	-0.709942
C	0.047864	2.398225	-0.232275
C	-0.733625	1.276358	-0.360032
Br	-0.179320	-0.482737	0.222695
O	1.956163	0.450621	1.022472
S	3.065857	0.301249	0.059571
O	4.084103	1.293607	0.194358
O	2.593119	-0.007196	-1.264911
C	3.840854	-1.275276	0.636393
F	2.932975	-2.265763	0.622188
F	4.300155	-1.165459	1.878690
F	4.845544	-1.630952	-0.154949
H	1.029230	2.352121	0.215818
H	0.082382	4.490585	-0.636162
H	-2.169610	4.537073	-1.646810
H	-3.504644	2.477579	-1.825903
H	-4.538372	0.384495	-1.864278
H	-5.341111	-1.937891	-1.759140
H	-3.932589	-3.713788	-0.787621
H	-1.684737	-3.178695	0.097264

A-Cl

C	6.432980	3.286546	8.260948
C	5.801963	2.061818	8.119228
C	6.567410	1.000026	7.649967
C	7.902822	1.206304	7.351557
C	8.493873	2.456099	7.513859
C	7.756774	3.533641	7.980368
C	4.401249	2.106275	8.503298
C	3.983691	3.355593	8.934618
C	2.721393	3.688214	9.350753
C	1.799832	2.651412	9.331194
C	2.159422	1.374165	8.912809
C	3.449063	1.093155	8.497652
Cl	5.335780	4.514047	8.880799
O	3.877906	6.422217	9.881400
S	4.160971	6.394234	11.319649
O	4.417354	5.054561	11.797705
C	2.514038	6.813928	12.050815
F	2.108314	8.022644	11.672130
F	1.581420	5.930286	11.652344
F	2.556991	6.783157	13.378600
O	5.034210	7.428461	11.782671
H	2.483733	4.690645	9.673640
H	0.788066	2.850500	9.657029
H	1.418187	0.586133	8.913374
H	3.719854	0.096915	8.173838
H	6.120944	0.022694	7.523235

H	8.499889	0.380716	6.988038
H	9.540343	2.593790	7.278316
H	8.200932	4.509432	8.119166

B-I

C	3.092750	1.318749	0.030782
C	4.201744	2.142093	0.149015
H	5.181229	1.690910	0.221886
C	4.019568	3.516197	0.169919
H	4.880932	4.167339	0.262014
C	2.742087	4.053899	0.073446
H	2.601001	5.128661	0.089996
C	1.644587	3.221414	-0.044081
H	0.652899	3.649599	-0.118771
C	1.798380	1.833705	-0.067867
C	0.689920	0.875573	-0.190058
C	-0.659785	1.218858	-0.300428
H	-0.968681	2.257790	-0.300905
C	-1.624868	0.233983	-0.411861
H	-2.673773	0.494517	-0.500963
C	-1.244508	-1.105072	-0.412923
H	-2.012546	-1.864244	-0.500845
C	0.094973	-1.450145	-0.303286
H	0.376974	-2.499060	-0.305833
C	1.067245	-0.463965	-0.191965
C	-6.569757	-0.221035	0.923749
O	-5.000356	-1.376952	-0.778100
O	-6.990271	-0.242657	-1.627608
O	-5.107188	1.060907	-0.780789
S	-5.824973	-0.192701	-0.777634
I	3.245910	-0.803015	-0.012486
F	-5.635415	-0.176370	1.882481
F	-7.295290	-1.331632	1.134817
F	-7.391139	0.822403	1.128731
C	5.958015	-1.655980	0.197019
O	5.354652	-0.418757	0.178179
O	7.185056	-1.681329	0.300771
O	5.150507	-2.631764	0.102624

B-Br

C	-2.755137	-0.923509	-0.237909
C	-4.086008	-0.557856	-0.159873
C	-4.380546	0.797439	-0.122614
C	-3.366223	1.749012	-0.162556
C	-2.040142	1.362936	-0.241049
C	-1.719424	0.005946	-0.280235
C	-0.373182	-0.557062	-0.362134
C	0.823784	0.154741	-0.421029
C	2.016843	-0.543736	-0.494504
C	2.019436	-1.936245	-0.508511
C	0.826105	-2.645435	-0.451733
C	-0.366078	-1.945913	-0.378791
Br	-2.199076	-2.784129	-0.295057
O	3.074784	2.935429	-0.613630
S	2.160335	4.015256	-0.328806
O	0.758274	3.666878	-0.390355
O	2.505733	5.294040	-0.899277
C	2.420671	4.295326	1.487429
F	3.691099	4.635271	1.761944
F	2.143394	3.200980	2.206060
F	1.644016	5.283861	1.957588
H	0.829332	-3.730286	-0.464674
H	2.961030	-2.471919	-0.565543
H	2.942723	0.016018	-0.540405
H	0.839059	1.238946	-0.416593
H	-1.250324	2.105702	-0.270545
H	-3.610796	2.804187	-0.131749
H	-5.416175	1.111291	-0.061009
H	-4.842776	-1.329177	-0.130677
C	-4.164996	-4.709838	-0.226130
O	-4.199379	-3.343641	-0.201949
O	-5.248894	-5.305061	-0.181272
O	-3.002806	-5.222615	-0.293249

B-Cl

C	-0.420265	-1.850791	-0.381071
C	-0.351315	-0.469513	-0.367859
C	0.886415	0.164568	-0.433140
C	2.024911	-0.620510	-0.509131
C	1.936062	-2.012241	-0.519332
C	0.702637	-2.648359	-0.456146
C	-1.682150	0.112351	-0.280982
C	-2.693935	-0.840762	-0.236308
C	-4.033931	-0.518681	-0.152658
C	-4.351825	0.831688	-0.112726
C	-3.361462	1.810015	-0.155047
C	-2.025060	1.461621	-0.239181
Cl	-2.119309	-2.526652	-0.295314
O	-4.069724	-3.227759	-0.199121
C	-3.922536	-4.578535	-0.233616
O	-2.729751	-5.015368	-0.307905
O	-4.959970	-5.263338	-0.189901
O	0.753589	3.666941	-0.400852
S	2.152308	4.027167	-0.323390

C	2.386497	4.320006	1.494108
F	1.596677	5.305497	1.947442
O	3.076486	2.950654	-0.589656
O	2.495435	5.304024	-0.898342
F	3.650592	4.669945	1.783000
F	2.106849	3.227536	2.214849
H	0.610626	-3.728079	-0.464521
H	2.841010	-2.606570	-0.578542
H	2.988937	-0.130073	-0.559819
H	0.968188	1.245652	-0.432119
H	-1.247547	2.217569	-0.270897
H	-3.635707	2.857718	-0.121457
H	-5.393692	1.122571	-0.046702
H	-4.760262	-1.319956	-0.122679

TS1-I

C	3.133899	1.073843	0.103680
C	4.388664	1.599635	0.177718
H	5.526185	0.744811	-0.027296
C	4.395225	2.999512	0.220308
H	5.346651	3.523714	0.274759
C	3.223298	3.748982	0.183202
H	3.269026	4.833362	0.222308
C	1.987087	3.130000	0.073171
H	1.082658	3.723739	0.020679
C	1.910880	1.738336	0.018334
C	0.676701	0.959243	-0.150325
C	-0.606933	1.497622	-0.264302
H	-0.750637	2.570699	-0.219680
C	-1.705633	0.674223	-0.437865
H	-2.704294	1.086737	-0.529565
C	-1.539252	-0.705995	-0.499249
H	-2.413973	-1.330354	-0.638121
C	-0.270255	-1.253263	-0.384454
H	-0.144580	-2.330106	-0.428645
C	0.828505	-0.424093	-0.210924
C	-6.363699	-0.232342	0.945889
O	-4.957324	-1.219033	-0.987120
O	-7.073092	-0.132908	-1.540718
O	-5.160305	1.208787	-0.832402
S	-5.822666	-0.074864	-0.823222
I	2.859882	-1.072324	0.047231
F	-5.325916	-0.200142	1.791368
F	-7.016776	-1.384468	1.168725
F	-7.194398	0.760071	1.305327
C	6.193621	-1.195149	0.044241
O	5.003523	-1.463989	0.567644
O	7.048366	-2.071565	-0.058580
O	6.410649	0.042274	-0.326126

TS1-Br

C	1.122707	-0.487167	-0.204586
C	0.933461	0.886785	-0.147435
C	-0.360069	1.394110	-0.266004
C	-1.431108	0.534034	-0.438706
C	-1.221461	-0.841666	-0.493345
C	0.060812	-1.359018	-0.373515
C	2.171072	1.643359	0.019498
C	3.351067	0.913438	0.096533
C	4.631547	1.364395	0.165405
C	4.714523	2.760794	0.210935
C	3.585873	3.575381	0.182341
C	2.315661	3.027873	0.077044
Br	2.987493	-1.041276	0.041015
O	4.992448	-1.658066	0.560416
C	6.217558	-1.500112	0.072406
O	6.554818	-0.297295	-0.306674
O	6.991780	-2.459861	0.010861
O	-4.625246	-1.214990	-0.978815
S	-5.499739	-0.076996	-0.819993
O	-4.844696	1.210843	-0.829517
C	-6.044759	-0.234168	0.947687
F	-6.882643	0.753695	1.302366
F	-5.009036	-0.192985	1.795440
F	-6.690454	-1.389912	1.171111
O	-6.746827	-0.144191	-1.541802
H	5.648038	0.522654	-0.003847
H	5.695272	3.226144	0.261041
H	3.695099	4.654610	0.223576
H	1.440458	3.664675	0.029722
H	-0.530026	2.463773	-0.225422
H	-2.441645	0.915253	-0.536144
H	-2.078588	-1.489651	-0.631139
H	0.224585	-2.430196	-0.412447

TS1-Cl

C	3.566892	0.742465	0.069398
C	2.441581	1.554869	0.011241
C	2.657476	2.926682	0.090927
C	3.957691	3.395047	0.204732
C	5.034807	2.513330	0.221148
C	4.871719	1.127508	0.153302
C	1.190642	0.833746	-0.159257
C	1.398294	-0.532537	-0.223735

C	0.370550	-1.439331	-0.391631
C	-0.919746	-0.940948	-0.508148
C	-1.159015	0.431155	-0.449640
C	-0.110141	1.318131	-0.275109
Cl	3.111040	-1.016060	-0.015511
O	-4.287866	-1.226379	-0.980080
S	-5.159803	-0.087688	-0.809947
O	-4.500166	1.198432	-0.823502
C	-5.685674	-0.246781	0.962896
F	-6.330989	-1.401123	1.191046
F	-4.639430	-0.209344	1.798006
F	-6.516423	0.742697	1.328192
O	-6.413176	-0.149990	-1.519978
H	0.568056	-2.503652	-0.432021
H	-1.764853	-1.603900	-0.646138
H	-2.177909	0.789729	-0.546923
H	-0.300992	2.383884	-0.231076
H	1.817391	3.609731	0.057352
H	4.133349	4.464032	0.264750
H	6.043032	2.910773	0.283281
H	5.791287	0.325741	0.033790
C	6.326540	-1.770959	0.119995
O	5.053156	-1.827709	0.495607
O	7.022290	-2.800172	0.149524
O	6.787942	-0.614010	-0.251326

C-I

C	-2.271299	-2.821139	0.064547
C	-2.269297	-1.452470	-0.137940
C	-1.075447	-0.744372	-0.139846
C	0.145774	-1.393986	0.058984
C	0.110654	-2.774684	0.274508
C	-1.074011	-3.484563	0.275668
H	-1.061843	-4.552338	0.451188
H	1.040001	-3.293083	0.470744
C	1.450710	-0.709815	0.066033
C	1.742162	0.563939	0.504956
C	2.830363	1.149566	0.561847
C	4.047351	0.627025	0.177578
C	3.889773	-0.674352	-0.317584
C	2.648477	-1.312706	-0.372148
H	2.603538	-2.311723	-0.789253
H	4.761496	-1.206268	-0.680571
H	5.009166	1.118288	0.222954
I	-1.214670	1.337493	-0.466283
H	-3.202442	-0.930771	-0.298389
H	-3.209107	-3.361324	0.064780

C-Br

C	2.998332	1.783574	0.024643
C	2.647618	0.458978	-0.166281
C	1.313261	0.084393	-0.148741
C	0.296322	1.019580	0.054794
C	0.684007	2.346869	0.256860
C	2.010767	2.731188	0.240324
H	2.273040	3.767886	0.405835
H	-0.080722	3.086140	0.456020
C	-1.135058	0.675272	0.077540
C	-1.724790	-0.490175	0.515055
C	-2.919598	-0.801333	0.580385
C	-3.977243	0.002492	0.207257
C	-3.514224	1.231622	-0.280916
C	-2.155971	1.552775	-0.344889
H	-1.875146	2.514161	-0.758414
H	-4.234838	1.960746	-0.632593
H	-5.028767	-0.243395	0.256035
Br	0.932684	-1.764130	-0.430493
H	3.409148	-0.290061	-0.332273
H	4.042278	2.068526	0.011506

C-Cl

C	-3.362599	-0.811872	0.008970
C	-2.804109	0.436887	-0.195041
C	-1.426985	0.593595	-0.169716
C	-0.574328	-0.490326	0.054821
C	-1.169347	-1.735719	0.267342
C	-2.540746	-1.902924	0.243290
H	-2.967231	-2.881958	0.417605
H	-0.533254	-2.584997	0.480139
C	0.892540	-0.368644	0.085040
C	1.652279	0.692340	0.527779
C	2.880450	0.811307	0.594799
C	3.805293	-0.141537	0.221769
C	3.158940	-1.284547	-0.267927
C	1.767494	-1.392568	-0.335421
H	1.342094	-2.298789	-0.750344
H	3.759581	-2.115959	-0.617980
H	4.881814	-0.059265	0.272440
Cl	-0.799448	2.188699	-0.444783
H	-3.429564	1.299826	-0.377557
H	-4.438423	-0.927218	-0.009791

CO_3^{2-}

C	0.000009	0.000003	0.000125

O	-0.995874	0.832869	-0.000045
O	1.219227	0.446021	-0.000045
O	-0.223359	-1.278891	-0.000045

HCO^{3-}

C	-0.124479	-0.037190	-0.000072
O	-0.071437	-1.281977	0.000027
O	-1.069186	0.749436	0.000023
O	1.163076	0.586309	0.000023
H	1.749826	-0.173706	0.000037

OTf^-

C	0.906231	-0.000024	0.000001
F	1.409876	-1.000466	0.740004
F	1.409851	1.141091	0.496411
F	1.409900	-0.140604	-1.236431
S	-0.951324	-0.000013	0.000007
O	-1.262323	1.133138	-0.838212
O	-1.262280	-1.292494	-0.562206
O	-1.262224	0.159343	1.400457

B-I‘

C	0.138539	1.260587	-0.000013
C	-0.603155	2.432451	-0.000005
H	-1.681982	2.369758	-0.000009
C	0.059120	3.649738	0.000006
H	-0.514989	4.568324	0.000013
C	1.447420	3.693091	0.000008
H	1.962427	4.646472	0.000017
C	2.176645	2.518935	-0.000001
H	3.258725	2.563921	-0.000001
C	1.534672	1.279677	-0.000012
C	2.231374	-0.016175	-0.000024
C	3.617207	-0.179968	-0.000034
H	4.276804	0.679901	-0.000034
C	4.163664	-1.451276	-0.000047
H	5.240091	-1.575445	-0.000054
C	3.333808	-2.567397	-0.000050
H	3.765248	-3.561989	-0.000059
C	1.956731	-2.403759	-0.000042
H	1.317680	-3.281790	-0.000046
C	1.398231	-1.132491	-0.000030
I	-0.782326	-0.662326	-0.000023
C	-3.585020	-0.514936	-0.000029
O	-2.589575	0.446781	-0.000044
O	-4.744905	-0.122005	-0.000029
O	-3.137289	-1.705210	-0.000017

B-Br‘

C	-0.015164	1.183437	-0.000102
C	-0.808808	2.316941	-0.000067
C	-0.183022	3.554386	-0.000027
C	1.203905	3.648835	-0.000022
C	1.979301	2.503880	-0.000060
C	1.376334	1.247265	-0.000102
C	2.064008	-0.044082	-0.000154
C	3.440547	-0.261737	-0.000166
C	3.924233	-1.558878	-0.000222
C	3.043953	-2.637373	-0.000265
C	1.673388	-2.420879	-0.000251
C	1.189236	-1.122988	-0.000196
Br	-0.781108	-0.602949	-0.000156
H	0.988104	-3.261769	-0.000282
H	3.432795	-3.649162	-0.000308
H	4.993248	-1.735067	-0.000232
H	4.133491	0.571986	-0.000132
H	3.059882	2.581611	-0.000060
H	1.680750	4.621691	0.000009
H	-0.787619	4.453034	-0.000001
H	-1.883735	2.204737	-0.000072
C	-3.469863	-0.856491	-0.000120
O	-2.629368	0.236586	-0.000092
O	-2.870285	-1.977079	-0.000173
O	-4.677921	-0.632093	-0.000091

B-Cl‘

C	1.159291	-0.989122	-0.000183
C	2.092596	0.030181	-0.000155
C	3.449826	-0.279806	-0.000177
C	3.830368	-1.611717	-0.000226
C	2.874254	-2.626570	-0.000254
C	1.520664	-2.321150	-0.000232
C	1.431027	1.328027	-0.000105
C	0.041914	1.237065	-0.000097
C	-0.779862	2.348668	-0.000052
C	-0.169464	3.594200	-0.000014
C	1.216177	3.717671	-0.000021
C	2.017019	2.590326	-0.000066
Cl	-0.603396	-0.423215	-0.000148
O	-2.471167	0.278860	-0.000107
C	-3.238151	-0.863186	-0.000138
O	-4.462089	-0.701222	-0.000121
O	-2.593495	-1.954588	-0.000181
H	0.760486	-3.093907	-0.000253

H	3.192889	-3.662178	-0.000292
H	4.882722	-1.868683	-0.000243
H	4.199414	0.503220	-0.000155
H	3.096515	2.682460	-0.000072
H	1.670847	4.700932	0.000009
H	-0.789667	4.481936	0.000021
H	-1.851137	2.201576	-0.000048

TS1-I‘

C	-0.191270	1.082147	-0.090461
C	-1.301472	1.869679	-0.065368
H	-2.573116	1.248155	0.230619
C	-1.005794	3.238435	-0.062507
H	-1.821178	3.956729	-0.036316
C	0.300751	3.717205	-0.076895
H	0.488616	4.786176	-0.079345
C	1.376094	2.842277	-0.060850
H	2.388567	3.227252	-0.042379
C	1.147871	1.466605	-0.054516
C	2.188124	0.433642	0.026635
C	3.559520	0.681919	0.089555
H	3.929699	1.699566	0.066207
C	4.457010	-0.366943	0.186203
H	5.519771	-0.162017	0.236087
C	4.000719	-1.679445	0.219824
H	4.705780	-2.498515	0.298735
C	2.639598	-1.935936	0.153693
H	2.287033	-2.961812	0.175472
C	1.738983	-0.886745	0.057005
I	-0.407888	-1.073911	-0.131139
C	-3.583477	-0.520709	0.160905
O	-2.536735	-0.935690	-0.565800
O	-4.541539	-1.256742	0.343360
O	-3.518043	0.699870	0.620026

TS1-Br‘

C	-0.266481	0.934405	-0.090848
C	-1.407090	1.669367	-0.045940
C	-1.167314	3.047987	-0.028569
C	0.118588	3.581311	-0.048913
C	1.230691	2.752860	-0.050253
C	1.051384	1.371398	-0.057566
C	2.085304	0.343793	0.015001
C	3.463012	0.538520	0.079577
C	4.308971	-0.554206	0.168217
C	3.792584	-1.845545	0.191726
C	2.421377	-2.047614	0.123708
C	1.581890	-0.951785	0.039211
Br	-0.381796	-1.056670	-0.151528
H	2.016856	-3.053601	0.137285
H	4.461659	-2.694654	0.263398
H	5.380231	-0.401723	0.220008
H	3.873537	1.541087	0.063155
H	2.229840	3.171743	-0.032824
H	0.259069	4.656998	-0.039440
H	-2.013392	3.727579	0.015562
H	-2.561084	1.040752	0.216854
C	-3.501030	-0.817480	0.107756
O	-2.418161	-1.122541	-0.622418
O	-3.530318	0.374641	0.628516
O	-4.405211	-1.638060	0.232515

TS1-Cl‘

C	-0.321281	0.761527	-0.080879
C	0.967755	1.276821	-0.071190
C	1.087408	2.662756	-0.069075
C	-0.065196	3.432719	-0.049396
C	-1.321429	2.833491	-0.004826
C	-1.494722	1.446868	-0.017963
C	2.013709	0.269775	-0.009713
C	1.480860	-1.008161	0.024135
C	2.266052	-2.139637	0.097097
C	3.643050	-1.975099	0.149808
C	4.201146	-0.699991	0.119585
C	3.395632	0.424176	0.039370
Cl	-0.314223	-1.069091	-0.132116
H	1.817647	-3.125784	0.113689
H	4.286267	-2.844020	0.213615
H	5.277480	-0.586338	0.159839
H	3.836618	1.413437	0.017530
H	2.067086	3.125377	-0.070420
H	0.018114	4.513944	-0.044021
H	-2.202063	3.465094	0.053811
H	-2.557744	0.827120	0.218845
C	-3.450222	-1.093737	0.050360
O	-2.319407	-1.291173	-0.639535
O	-4.312024	-1.976874	0.067875
O	-3.572391	0.050010	0.651438

D_{meta}-Cl

C	-2.632045	-0.321511	1.275590
C	-2.530915	-0.434724	-0.097492
C	-1.279985	-0.447664	-0.704748
C	-0.093016	-0.355315	0.022604

C	-0.240492	-0.211351	1.407998
C	-1.472289	-0.201037	2.030854
H	-1.530667	-0.093711	3.107655
H	0.675561	-0.077073	1.969751
C	1.297225	-0.373563	-0.526556
C	2.209904	0.555801	0.006674
C	3.473626	0.428250	-0.542906
C	3.874771	-0.497050	-1.493396
C	2.934645	-1.406460	-1.961928
C	1.639709	-1.344322	-1.476463
H	0.907207	-2.061654	-1.830164
H	3.213118	-2.156628	-2.693542
H	4.898477	-0.511804	-1.853816
Cl	-1.288979	-0.513952	-2.458351
H	-3.416983	-0.499888	-0.715233
H	-3.607568	-0.313214	1.746886
O	4.501660	1.338460	-0.165233
C	4.916796	1.392973	1.105681
C	5.771391	2.447404	1.438209
C	4.595975	0.450274	2.084986
C	6.297140	2.553131	2.713360
H	6.006236	3.176150	0.672480
C	5.130237	0.570907	3.357155
H	3.916592	-0.352606	1.841262
C	5.982365	1.615672	3.688073
H	6.957655	3.380422	2.948572
H	4.868552	-0.168220	4.106193
H	6.389701	1.700498	4.688047

D_{ortho}-Cl

C	-2.875462	0.354194	0.301345
C	-2.368893	0.127692	-0.965120
C	-1.009229	-0.096142	-1.136681
C	-0.117526	-0.110234	-0.064973
C	-0.665030	0.126741	1.199456
C	-2.014026	0.357558	1.389190
H	-2.392112	0.543073	2.386975
H	0.008562	0.134876	2.047284
C	1.338606	-0.363930	-0.194765
C	2.293778	0.585396	0.184190
C	3.669894	0.437107	0.174561
C	4.054323	-0.834933	-0.281933
C	3.166510	-1.827372	-0.697070
C	1.802213	-1.595006	-0.653779
H	1.094068	-2.355978	-0.961988
H	3.533767	-2.788107	-1.049831
H	5.117353	-1.082198	-0.326482
Cl	-0.445469	-0.326927	-2.773105
H	-3.017315	0.131836	-1.831253
H	-3.935551	0.533000	0.433683
O	1.726971	1.845266	0.535580
C	1.839480	2.319312	1.780214
C	1.274288	3.575952	2.016603
C	2.423309	1.629608	2.845227
C	1.286893	4.125884	3.285099
H	0.824027	4.098294	1.181945
C	2.425834	2.195424	4.110351
H	2.895987	0.677092	2.657915
C	1.861347	3.440627	4.348215
H	0.840326	5.101025	3.445410
H	2.887006	1.648767	4.925469
H	1.873474	3.872206	5.341566

D_{meta}-Cl‘

C	3.334658	4.037428	2.745193
C	2.969184	4.169958	1.355337
C	3.233062	3.176292	0.498224
C	4.026212	1.966092	0.875563
C	4.526020	1.948633	2.317274
C	4.024130	2.985514	3.220354
C	3.210508	0.712732	0.533494
C	1.832249	0.901513	0.338138
C	1.150722	-0.287795	0.020035
C	1.765911	-1.535512	-0.090999
C	3.134430	-1.649516	0.110716
C	3.863915	-0.513825	0.427302
C	-0.330225	-0.232470	-0.145612
C	-0.980679	0.486704	-1.149236
C	-2.363912	0.534152	-1.245044
C	-3.147089	-0.152823	-0.332599
C	-2.533931	-0.891928	0.666853
C	-1.151871	-0.924788	0.747079
Cl	-0.074474	1.325570	-2.379108
H	2.890855	3.218847	-0.526453
H	-3.130885	-1.436148	1.389326
H	-0.667857	-1.486780	1.536782
H	1.182139	-2.418064	-0.342861
H	3.626012	-2.612017	0.019238
H	4.931959	-0.586427	0.606610
H	-2.818123	1.105725	-2.043930
H	-4.226975	-0.109908	-0.408170
H	4.942227	1.961690	0.267895
O	5.342319	1.125400	2.692187
H	2.398045	5.035362	1.043674

H	4.290868	2.893949	4.266083
H	3.025170	4.820122	3.432196

D_{ortho}-Cl‘

C	-1.244557	3.144131	1.687637
C	-0.271204	3.558870	0.698284
C	0.921821	2.960174	0.645021
C	1.327696	1.851678	1.552465
C	0.309355	1.487236	2.619141
C	-0.985722	2.184862	2.588349
C	1.925288	0.693351	0.719086
C	1.079589	-0.203085	0.044293
C	1.645213	-1.225814	-0.711863
C	3.024539	-1.315124	-0.810707
C	3.823500	-0.374491	-0.170095
C	3.330606	0.674628	0.626307
C	-0.406361	-0.129311	0.093641
C	-1.171334	0.529220	-0.868409
C	-2.554582	0.594872	-0.793128
C	-3.215805	-0.027667	0.251502
C	-2.487610	-0.718017	1.207419
C	-1.107174	-0.761750	1.122311
Cl	-0.404665	1.292995	-2.234599
H	1.660646	3.237772	-0.098170
H	-2.991820	-1.211610	2.029090
H	-0.529271	-1.271370	1.881883
H	1.000628	-1.930912	-1.226296
H	3.467046	-2.115319	-1.400082
H	4.902920	-0.472606	-0.303501
H	-3.102699	1.129493	-1.557516
H	-4.296121	0.025735	0.311508
O	0.553825	0.674672	3.491867
H	-0.537857	4.337308	-0.006054
H	-1.719625	1.871172	3.320559
H	-2.216066	3.628853	1.688069
H	2.216641	2.190187	2.099604

D_{meta}-Br

C	2.337003	1.211050	1.293844
C	2.241073	1.237369	-0.084370
C	1.010453	1.034134	-0.698664
C	-0.160274	0.808417	0.022635
C	-0.013820	0.758085	1.415492
C	1.196687	0.960140	2.046405
H	1.254255	0.917200	3.127760
H	-0.908478	0.520744	1.977585
C	-1.533959	0.601250	-0.529030
C	-2.294668	-0.448658	0.017119
C	-3.559040	-0.526795	-0.540816
C	-4.091938	0.311379	-1.507365
C	-3.301046	1.348584	-1.986241
C	-2.015247	1.493950	-1.494654
H	-1.397782	2.309086	-1.856181
H	-3.687806	2.036106	-2.730035
H	-5.103391	0.162295	-1.871798
Br	1.052783	0.994484	-2.624786
H	3.120698	1.399123	-0.692794
H	3.296438	1.370590	1.771299
O	-4.435996	-1.580098	-0.155441
C	-4.836670	-1.691675	1.116483
C	-5.507320	-2.869198	1.457558
C	-4.676152	-0.701342	2.088133
C	-6.010296	-3.049809	2.733483
H	-5.618265	-3.632670	0.697733
C	-5.185103	-0.897990	3.361232
H	-4.138301	0.200881	1.838959
C	-5.854660	-2.065772	3.700591
H	-6.526307	-3.972381	2.975460
H	-5.049337	-0.119973	4.104281
H	-6.243632	-2.208306	4.701325

D_{ortho}-Br

C	2.705320	0.652854	0.374948
C	2.183725	0.645688	-0.906174
C	0.808332	0.615102	-1.090513
C	-0.085252	0.602621	-0.022609
C	0.477813	0.604558	1.257509
C	1.843966	0.626770	1.462317
H	2.235988	0.619779	2.471925
H	-0.196610	0.576187	2.104343
C	-1.562569	0.592644	-0.163297
C	-2.336848	-0.491411	0.260839
C	-3.717172	-0.590843	0.243291
C	-4.315910	0.569822	-0.276132
C	-3.614051	1.683642	-0.736800
C	-2.230335	1.699990	-0.680408
H	-1.664165	2.558579	-1.023917
H	-4.142622	2.546098	-1.135686
H	-5.405380	0.622131	-0.334765
Br	0.178891	0.543624	-2.899641
H	2.838996	0.651634	-1.766676
H	3.778785	0.671292	0.518961
O	-1.556465	-1.609512	0.676645
C	-1.569138	-2.010565	1.951371

C	-0.777886	-3.121888	2.257474
C	-2.266114	-1.373097	2.980204
C	-0.680546	-3.579765	3.558251
H	-0.242437	-3.604907	1.449892
C	-2.155949	-1.845072	4.278695
H	-2.909459	-0.539413	2.741434
C	-1.367158	-2.944780	4.585535
H	-0.058614	-4.441905	3.772495
H	-2.707026	-1.341550	5.065315
H	-1.293008	-3.304507	5.604476

D_{meta}-Br‘

C	-3.089329	-3.564304	3.196495
C	-2.551046	-3.919115	1.904254
C	-2.871424	-3.194502	0.826192
C	-3.882910	-2.094582	0.855137
C	-4.549110	-1.873035	2.209570
C	-3.989463	-2.580439	3.363601
C	-3.242565	-0.807279	0.316532
C	-1.839704	-0.758647	0.305265
C	-1.318560	0.438956	-0.223100
C	-2.115879	1.502701	-0.650315
C	-3.496867	1.399325	-0.588417
C	-4.068290	0.229182	-0.111088
C	0.165843	0.591158	-0.237648
C	0.952993	1.039110	-1.296522
C	2.334722	1.162192	-1.203838
C	2.979454	0.825311	-0.028881
C	2.231457	0.349052	1.040593
C	0.861128	0.232529	0.925536
Br	0.204202	1.446346	-3.024689
H	-2.410544	-3.390029	-0.132200
H	2.720350	0.065544	1.965411
H	0.260325	-0.168852	1.732014
H	-1.669366	2.421261	-1.017365
H	-4.122358	2.225929	-0.907238
H	-5.147903	0.137781	-0.045962
H	2.898532	1.507200	-2.060136
H	4.056135	0.923040	0.043184
O	-5.532897	-1.163738	2.321343
H	-1.817656	-4.713244	1.842113
H	-4.386507	-2.319062	4.336770
H	-2.737372	-4.112840	4.065644
H	-4.706709	-2.377414	0.185082

D_{ortho}-Br‘

C	1.532325	-2.416815	1.761696
C	0.584171	-3.020853	0.848693
C	-0.680788	-2.592400	0.821594
C	-1.196336	-1.493153	1.683284
C	-0.193516	-0.928638	2.674910
C	1.182626	-1.445709	2.618029
C	-1.981598	-0.480055	0.816785
C	-1.297030	0.479019	0.051670
C	-2.029223	1.369766	-0.728101
C	-3.410532	1.266420	-0.762295
C	-4.044441	0.265570	-0.034152
C	-3.378695	-0.657025	0.792494
C	0.185689	0.604541	0.022721
C	0.990533	0.001729	-0.941687
C	2.371097	0.127903	-0.937448
C	2.986967	0.891034	0.040047
C	2.214307	1.530250	0.996419
C	0.838849	1.383130	0.981385
Br	0.210787	-1.014277	-2.364269
H	-1.404882	-3.012764	0.133018
H	2.681871	2.133567	1.764899
H	0.230898	1.853986	1.742499
H	-1.509378	2.122069	-1.312056
H	-3.983577	1.963201	-1.370233
H	-5.131632	0.207989	-0.119463
H	2.957589	-0.367060	-1.699592
H	4.066068	0.986732	0.046184
H	-2.006742	-1.912362	2.292875
O	-0.510462	-0.103435	3.511827
H	0.925205	-3.798054	0.175872
H	1.896805	-0.990406	3.293173
H	2.560370	-2.765333	1.740747

D_{meta}-I

C	-1.814492	-2.104162	1.223760
C	-1.782171	-0.964445	0.436788
C	-0.582632	-0.519193	-0.101332
C	0.619158	-1.186025	0.132906
C	0.549107	-2.340995	0.917844
C	-0.638822	-2.798417	1.460789
H	-0.644507	-3.692081	2.074119
H	1.473450	-2.871563	1.113067
C	1.946830	-0.742636	-0.385820
C	2.428157	0.513492	0.014499
C	3.690992	0.769371	-0.493144
C	4.436974	-0.061758	-1.317016
C	3.896914	-1.286583	-1.686693
C	2.643882	-1.634776	-1.208756

H	2.204154	-2.588952	-1.487019
H	4.447800	-1.956172	-2.337684
H	5.416322	0.247172	-1.668272
I	-0.671721	1.189505	-1.347876
H	-2.696030	-0.422823	0.231773
H	-2.753772	-2.442615	1.644512
O	4.320232	2.019708	-0.250510
C	4.502058	2.475868	0.995943
C	4.930329	3.800703	1.110743
C	4.349744	1.712232	2.154803
C	5.207891	4.347393	2.351019
H	5.036606	4.383981	0.204590
C	4.630882	2.274838	3.388790
H	3.983497	0.700255	2.075526
C	5.061632	3.589612	3.504854
H	5.538271	5.378238	2.415661
H	4.502221	1.670042	4.279496
H	5.272348	4.017687	4.477241

D_{ortho}-I

C	-2.187097	-2.379477	0.531897
C	-2.068536	-1.048894	0.166180
C	-0.812619	-0.492982	-0.031649
C	0.353814	-1.238076	0.132557
C	0.200370	-2.577555	0.495886
C	-1.044968	-3.147609	0.693775
H	-1.122759	-4.189789	0.979789
H	1.098905	-3.166426	0.631940
C	1.723060	-0.700061	-0.065999
C	2.365567	0.079987	0.901290
C	3.656219	0.576830	0.837458
C	4.294710	0.231274	-0.365335
C	3.722027	-0.543264	-1.373094
C	2.430006	-1.021138	-1.220938
H	1.959243	-1.628997	-1.986233
H	4.279161	-0.780897	-2.275914
H	5.318411	0.572154	-0.535623
I	-0.715145	1.532970	-0.625485
H	-2.954096	-0.442445	0.032496
H	-3.169407	-2.808570	0.688302
O	1.570453	0.242398	2.064454
C	1.424884	1.417158	2.695949
C	1.865281	2.652290	2.217922
C	0.718146	1.368660	3.899271
C	1.587523	3.801335	2.939085
H	2.445680	2.684959	1.309369
C	0.450006	2.526603	4.607990
H	0.381130	0.402879	4.254839
C	0.881805	3.757393	4.134415
H	1.937092	4.753685	2.555856
H	-0.103618	2.464586	5.538418
H	0.676154	4.665516	4.688136

D_{meta}-I‘

C	2.037859	4.254427	2.799238
C	1.580131	4.243647	1.430179
C	2.183711	3.457818	0.530758
C	3.417860	2.670944	0.837744
C	3.952928	2.838863	2.256645
C	3.119484	3.570735	3.211717
C	3.163972	1.199804	0.485927
C	1.821178	0.817583	0.338039
C	1.659828	-0.534347	-0.007290
C	2.719063	-1.427249	-0.180301
C	4.023950	-0.984657	-0.018249
C	4.248883	0.341963	0.318975
C	0.273787	-1.062011	-0.149860
C	-0.674932	-0.553449	-1.036511
C	-1.963600	-1.063996	-1.103564
C	-2.341214	-2.114825	-0.283247
C	-1.416678	-2.653307	0.597503
C	-0.136308	-2.131373	0.652912
I	-0.199246	0.997072	-2.401916
H	1.802754	3.371303	-0.477673
H	-1.694091	-3.474683	1.248057
H	0.584005	-2.536824	1.353264
H	2.531013	-2.462400	-0.455787
H	4.856930	-1.664615	-0.159807
H	5.262600	0.701346	0.464551
H	-2.671222	-0.645886	-1.807185
H	-3.350250	-2.505652	-0.337267
O	5.049653	2.411862	2.571862
H	0.690700	4.803465	1.170137
H	3.452769	3.583240	4.242148
H	1.471202	4.833289	3.523172
H	4.225209	3.046834	0.193556

D_{ortho}-I‘

C	-0.892743	3.239934	2.782392
C	-0.550874	3.562117	1.419712
C	-0.059040	2.610891	0.615326
C	0.010619	1.169494	1.004090
C	-0.216632	0.900505	2.492872
C	-0.734467	2.008286	3.299304

C	1.295897	0.563166	0.478704
C	1.309331	-0.709875	-0.102244
C	2.516358	-1.228949	-0.562907
C	3.667770	-0.465867	-0.448372
C	3.607348	0.806288	0.114714
C	2.429534	1.390134	0.606876
C	0.079825	-1.530670	-0.262859
C	-0.726428	-1.486900	-1.398863
C	-1.858899	-2.279214	-1.530119
C	-2.212354	-3.142897	-0.507499
C	-1.433964	-3.202464	0.638832
C	-0.308844	-2.406129	0.754053
I	-0.255494	-0.169318	-2.989697
H	0.262664	2.839260	-0.391955
H	-1.708654	-3.864281	1.451294
H	0.284269	-2.415382	1.657780
H	2.541188	-2.213806	-1.017417
H	4.611578	-0.868674	-0.809182
H	4.542349	1.367406	0.167519
H	-2.462806	-2.218594	-2.425375
H	-3.097603	-3.759449	-0.607414
O	-0.036240	-0.199537	2.980433
H	-0.625466	4.589873	1.086965
H	-0.940919	1.791778	4.340486
H	-1.260162	4.037774	3.421782
H	-0.869159	0.689476	0.538157

PhO^-

C	-1.004247	-0.011370	0.000015
C	-0.206728	-1.212153	0.000007
C	1.172945	-1.190122	0.000012
C	1.889431	0.007913	0.000016
C	1.156964	1.195801	0.000009
C	-0.223239	1.199578	0.000004
H	-0.770993	2.137480	-0.000006
H	1.686416	2.146609	0.000007
H	2.973249	0.015101	0.000025
H	1.715412	-2.133562	0.000014
H	-0.742793	-2.156796	0.000000
O	-2.262452	-0.020304	-0.000013

E_{meta}-Cl

C	-2.217959	0.003841	1.544371
C	-2.099462	0.456471	0.242590
C	-0.916394	0.256572	-0.458684
C	0.179654	-0.390794	0.110570
C	0.022898	-0.839639	1.426220
C	-1.148636	-0.651333	2.139836
H	-1.235280	-1.030646	3.150802
H	0.860971	-1.360344	1.875442
C	1.504308	-0.562735	-0.556436
C	2.589612	0.104172	0.029306
C	3.789928	-0.121104	-0.622736
C	3.966284	-0.924680	-1.737626
C	2.852936	-1.556753	-2.272375
C	1.611226	-1.374429	-1.686022
H	0.737841	-1.863892	-2.102348
H	2.957959	-2.191593	-3.143524
H	4.948026	-1.047541	-2.179339
Cl	-0.827060	0.894487	-2.075763
H	-2.919146	0.972021	-0.239627
H	-3.143501	0.155635	2.084768
O	4.967176	0.534384	-0.191253
C	4.991572	1.022311	1.064915
C	5.184652	2.386756	1.251764
C	4.875855	0.187583	2.177861
C	5.238780	2.916744	2.536195
H	5.284314	3.018313	0.378545
C	4.929338	0.721655	3.453644
H	4.729212	-0.872179	2.020067
C	5.098997	2.091830	3.643389
H	5.398915	3.979909	2.669304
H	4.848177	0.064252	4.311000
H	5.153862	2.502748	4.643360
K	2.017178	1.774860	2.109522

E_{ortho}-Cl

C	-3.039255	0.023994	0.132695
C	-2.439838	0.028985	-1.113763
C	-1.061801	-0.096829	-1.216606
C	-0.252018	-0.235291	-0.092004
C	-0.886186	-0.231656	1.150067
C	-2.257676	-0.104214	1.271008
H	-2.716505	-0.107221	2.251462
H	-0.272199	-0.334289	2.036466
C	1.223034	-0.387698	-0.163509
C	2.084519	0.607883	0.286287
C	3.471309	0.557172	0.311679
C	3.977150	-0.652303	-0.183274
C	3.176647	-1.687653	-0.661384
C	1.800055	-1.556149	-0.653082
H	1.162601	-2.351648	-1.019515
H	3.625353	-2.599438	-1.040469
H	5.054549	-0.809634	-0.214090

Cl	-0.360444	-0.049760	-2.809125
H	-3.031277	0.135026	-2.013011
H	-4.114422	0.122140	0.211305
O	1.432892	1.810311	0.681688
C	1.738277	2.349682	1.866114
C	1.667133	3.740255	1.976849
C	2.125537	1.596924	2.979149
C	2.008888	4.366468	3.166325
H	1.344056	4.308859	1.114070
C	2.464314	2.236495	4.161093
H	2.182989	0.520867	2.893910
C	2.424414	3.622588	4.263348
H	1.946422	5.445744	3.235873
H	2.760411	1.640993	5.016396
H	2.687658	4.112405	5.191567
K	4.747279	2.673676	1.519142

E_{meta}-Cl‘

C	3.189680	4.287451	2.293697
C	3.514338	4.168907	0.881375
C	3.920330	2.998451	0.379343
C	4.098769	1.762958	1.202075
C	3.796883	1.938155	2.687523
C	3.272518	3.245088	3.134763
C	3.276019	0.617727	0.607849
C	1.885708	0.792041	0.544507
C	1.198664	-0.291859	-0.023814
C	1.828357	-1.446933	-0.489637
C	3.205349	-1.559018	-0.405504
C	3.933862	-0.518967	0.151978
C	-0.292494	-0.247744	-0.066491
C	-1.036901	0.673009	-0.805310
C	-2.424649	0.707895	-0.775664
C	-3.116639	-0.201649	0.004505
C	-2.411922	-1.142654	0.740126
C	-1.028987	-1.157625	0.698165
Cl	-0.243557	1.834165	-1.854004
H	4.140031	2.901568	-0.677745
H	-2.940365	-1.864275	1.350163
H	-0.476610	-1.883339	1.282110
H	1.245677	-2.254981	-0.920936
H	3.706908	-2.448619	-0.766001
H	5.012938	-0.603795	0.233274
H	-2.952643	1.433195	-1.380465
H	-4.198503	-0.179345	0.025684
H	5.160003	1.487590	1.153847
O	4.017762	1.056533	3.485345
H	3.419446	5.042409	0.247782
H	3.034631	3.333267	4.187967
H	2.869952	5.255556	2.668226
K	0.375323	2.956028	1.189243

E_{ortho}-Cl‘

C	-3.083006	0.323985	-0.322379
C	-2.237555	0.709822	-1.347251
C	-0.871120	0.529002	-1.208430
C	-0.304582	-0.015226	-0.055881
C	-1.189307	-0.420765	0.942361
C	-2.556629	-0.253905	0.821761
H	-3.211170	-0.576432	1.621180
H	-0.775831	-0.872169	1.834096
C	1.161367	-0.190059	0.133120
C	1.927101	0.642478	0.972491
C	3.322190	0.514646	1.145714
C	3.885447	-0.566523	0.440906
C	3.163280	-1.408544	-0.400831
C	1.800058	-1.211787	-0.564732
H	1.223258	-1.851174	-1.222532
H	3.653094	-2.218475	-0.932935
H	4.953788	-0.757027	0.536826
Cl	0.125752	0.997523	-2.567659
H	-2.629274	1.147027	-2.255279
H	-4.150929	0.464729	-0.427633
C	1.261736	1.818675	1.700821
C	0.570932	2.809719	0.788063
C	0.502550	1.434605	2.921945
C	-0.733202	3.314779	1.186182
C	-0.680797	1.969416	3.233378
H	0.984523	0.711177	3.569573
C	-1.306156	2.913934	2.334917
H	-1.219401	4.009549	0.513718
H	-1.198565	1.690896	4.141969
H	-2.282203	3.303682	2.602523
O	1.119986	3.198963	-0.238926
H	2.141533	2.365974	2.077244
K	3.163122	1.920417	-1.329343

E_{meta}-Br

C	2.208700	1.027544	1.301110
C	1.608549	-0.204309	1.104142
C	0.338881	-0.267659	0.548246
C	-0.376659	0.869386	0.177190
C	0.269046	2.093061	0.377998
C	1.534925	2.180640	0.929167

H	1.995006	3.150448	1.071017
H	-0.263815	2.992996	0.096905
C	-1.761402	0.856621	-0.378104
C	-2.801734	0.405904	0.445948
C	-4.043540	0.479585	-0.164181
C	-4.301262	0.952376	-1.440358
C	-3.231286	1.399617	-2.201413
C	-1.952796	1.352574	-1.669772
H	-1.107845	1.691184	-2.260179
H	-3.395427	1.774005	-3.204228
H	-5.313227	0.969932	-1.827159
Br	-0.375754	-2.031952	0.252725
H	2.130079	-1.115759	1.363059
H	3.200174	1.079743	1.732186
O	-5.196550	0.089011	0.561992
C	-5.088744	-0.990169	1.355424
C	-4.486089	-2.176247	0.926547
C	-5.624633	-0.923295	2.639378
C	-4.402875	-3.259385	1.784495
H	-4.067082	-2.221818	-0.069237
C	-5.536757	-2.016513	3.492091
H	-6.098272	-0.002209	2.953519
C	-4.914784	-3.186289	3.077577
H	-3.936333	-4.174212	1.439389
H	-5.960746	-1.951645	4.486909
H	-4.852746	-4.039585	3.740434
K	-2.293307	-0.890192	2.825332

E_{ortho}-Br

C	2.476908	0.366945	0.788187
C	1.979799	-0.173282	-0.386075
C	0.625809	-0.081917	-0.665884
C	-0.263272	0.539868	0.207150
C	0.268699	1.082254	1.376653
C	1.618514	1.001823	1.670715
H	1.997013	1.429135	2.590359
H	-0.410659	1.564315	2.068470
C	-1.724723	0.633151	-0.033978
C	-2.562820	-0.475438	0.077835
C	-3.932531	-0.507507	-0.099925
C	-4.468507	0.751328	-0.416414
C	-3.699714	1.903850	-0.525351
C	-2.326177	1.848285	-0.333416
H	-1.714001	2.737226	-0.428820
H	-4.165506	2.853259	-0.766765
H	-5.539081	0.848806	-0.583457
Br	0.013940	-0.806662	-2.324731
H	2.641664	-0.660183	-1.088911
H	3.534685	0.292540	1.006037
O	-1.907668	-1.712362	0.380103
C	-1.588205	-1.983047	1.670131
C	-0.763752	-3.086067	1.885506
C	-2.073221	-1.255925	2.753751
C	-0.425903	-3.455141	3.175739
H	-0.371698	-3.616879	1.026630
C	-1.721530	-1.638591	4.040132
H	-2.710057	-0.399579	2.580536
C	-0.902806	-2.734568	4.262459
H	0.226345	-4.305465	3.332286
H	-2.096109	-1.065170	4.879208
H	-0.631874	-3.020507	5.270215
K	-4.176327	-3.181100	0.229203

E_{meta}-Br‘

C	2.846961	1.228869	0.446499
C	2.403371	0.194045	-0.358975
C	1.040299	-0.010060	-0.525386
C	0.080825	0.787345	0.097213
C	0.567912	1.829912	0.891099
C	1.921830	2.053601	1.068642
H	2.255649	2.871919	1.694190
H	-0.157031	2.466535	1.383158
C	-1.392453	0.570369	-0.008647
C	-1.944174	-0.553477	0.625478
C	-3.337680	-0.651052	0.504854
C	-4.118941	0.267860	-0.187722
C	-3.520731	1.363829	-0.789994
C	-2.148030	1.520845	-0.693784
H	-1.666407	2.373991	-1.161348
H	-4.118935	2.085764	-1.332121
H	-5.192489	0.131036	-0.268059
Br	0.516201	-1.435059	-1.705991
H	3.110482	-0.442473	-0.873556
H	3.909143	1.393296	0.574316
C	-4.014873	-1.858109	1.156923
C	-3.758026	-3.122494	0.339716
C	-3.632463	-1.959108	2.597798
C	-3.073945	-4.247338	1.008822
C	-3.102962	-3.056756	3.147345
H	-3.814946	-1.077242	3.200843
C	-2.819466	-4.221690	2.326819
H	-2.865037	-5.116977	0.397496
H	-2.867000	-3.091366	4.203849
H	-2.384565	-5.094245	2.805717

H	-5.101478	-1.708054	1.117930
O	-4.131701	-3.220532	-0.806482
K	-0.168651	-2.425812	1.483381

E_{ortho}-Br'

C	1.514581	-2.315998	2.253123
C	1.045802	-2.706610	0.947178
C	-0.186600	-2.371181	0.554698
C	-1.149973	-1.645513	1.427902
C	-0.596419	-1.214965	2.775374
C	0.756342	-1.616451	3.117666
C	-1.987407	-0.585752	0.697152
C	-1.338592	0.372892	-0.097160
C	-2.103449	1.287923	-0.812911
C	-3.483062	1.244253	-0.728160
C	-4.092164	0.300869	0.092613
C	-3.387891	-0.658673	0.838365
C	0.143185	0.488409	-0.163315
C	0.902309	0.113842	-1.271435
C	2.280630	0.239548	-1.290780
C	2.939286	0.750321	-0.183633
C	2.212508	1.144148	0.927171
C	0.834634	1.015944	0.927291
Br	0.063366	-0.644227	-2.812568
H	-0.546929	-2.634460	-0.432641
H	2.716331	1.551289	1.794506
H	0.261351	1.328854	1.791369
H	-1.609164	2.027227	-1.431940
H	-4.077825	1.951811	-1.296948
H	-5.181490	0.313317	0.136016
H	2.836603	-0.070898	-2.164621
H	4.017559	0.845515	-0.198950
H	-1.911534	-2.395733	1.698832
O	-1.288249	-0.588269	3.576288
H	1.712112	-3.247501	0.288717
H	1.129397	-1.306571	4.085462
H	2.525472	-2.587608	2.537033
K	-3.877988	-0.320919	3.463016

E_{meta}-I

C	-1.648024	-1.691529	1.454340
C	-1.550076	-0.544467	0.685180
C	-0.354912	-0.238910	0.045056
C	0.773230	-1.051665	0.156820
C	0.632475	-2.209658	0.927945
C	-0.550711	-2.530923	1.568723
H	-0.615761	-3.436319	2.159167
H	1.494939	-2.857694	1.023703
C	2.102842	-0.745214	-0.448410
C	2.804573	0.362492	0.046418
C	4.047719	0.522550	-0.541029
C	4.592732	-0.286912	-1.526123
C	3.845829	-1.363224	-1.979009
C	2.594415	-1.602966	-1.433345
H	2.002632	-2.443920	-1.779080
H	4.241012	-2.011575	-2.751235
H	5.574960	-0.074446	-1.931216
I	-0.347179	1.502822	-1.173854
H	-2.408598	0.102870	0.567524
H	-2.581214	-1.929284	1.948697
O	4.863195	1.626563	-0.194784
C	4.675737	2.205931	1.005772
C	4.410727	3.570921	1.052812
C	4.786209	1.487631	2.198256
C	4.236470	4.208741	2.275754
H	4.338772	4.114904	0.119953
C	4.609267	2.129307	3.411825
H	4.993961	0.427530	2.151340
C	4.321376	3.491790	3.460871
H	4.038194	5.273487	2.299257
H	4.704871	1.564696	4.331532
H	4.195802	3.990341	4.413407
K	1.611929	2.020275	1.886792

E_{ortho}-I

C	-2.282213	-2.374457	0.216318
C	-2.097686	-1.134024	-0.369864
C	-0.822383	-0.592960	-0.451096
C	0.289409	-1.267787	0.044863
C	0.073248	-2.515215	0.629314
C	-1.191707	-3.067851	0.716990
H	-1.326139	-4.039168	1.175968
H	0.930072	-3.048456	1.021531
C	1.671514	-0.728373	-0.028885
C	2.220582	0.025613	1.003798
C	3.497403	0.568761	1.037923
C	4.238441	0.284312	-0.117987
C	3.756931	-0.472033	-1.183619
C	2.471370	-0.981371	-1.138129
H	2.072658	-1.566065	-1.958554
H	4.381478	-0.665309	-2.048943
H	5.258704	0.657417	-0.204420
I	-0.613057	1.300572	-1.372951
H	-2.944518	-0.589350	-0.764046

H	-3.278023	-2.794617	0.278348
O	1.366289	0.161573	2.129975
C	1.322351	1.341917	2.763208
C	1.266789	2.561587	2.082745
C	1.312686	1.336564	4.157305
C	1.236107	3.748037	2.795559
H	1.257073	2.557097	1.001524
C	1.281382	2.533463	4.861659
H	1.336168	0.383166	4.669347
C	1.259235	3.747233	4.188129
H	1.183774	4.686991	2.257555
H	1.270108	2.514337	5.944781
H	1.226848	4.679180	4.737408
K	4.239094	2.257176	3.077153

E_{meta}-I‘

C	1.759160	4.374152	2.412954
C	2.024983	4.449671	0.985999
C	2.857630	3.577767	0.409277
C	3.581750	2.505618	1.158678
C	3.315690	2.487875	2.661015
C	2.318445	3.437799	3.195190
C	3.273372	1.144319	0.532519
C	1.933540	0.730913	0.529249
C	1.719659	-0.511253	-0.084767
C	2.737205	-1.287582	-0.639175
C	4.042217	-0.826719	-0.606282
C	4.311332	0.398515	-0.013994
C	0.330586	-1.056498	-0.090277
C	-0.729482	-0.508023	-0.812767
C	-2.020674	-1.016400	-0.729354
C	-2.281443	-2.106178	0.083978
C	-1.245776	-2.685610	0.801101
C	0.032595	-2.164819	0.708995
I	-0.429418	1.126748	-2.138676
H	3.037491	3.615385	-0.658979
H	-1.434246	-3.543231	1.434697
H	0.841800	-2.606756	1.277104
H	2.511792	-2.244618	-1.099254
H	4.843570	-1.416180	-1.034398
H	5.333344	0.762185	0.023844
H	-2.816761	-0.573125	-1.312194
H	-3.286632	-2.503280	0.144465
O	3.926663	1.752662	3.402114
H	1.533960	5.218656	0.402348
H	2.125153	3.384823	4.259882
H	1.083891	5.104534	2.849275
H	4.657071	2.699095	1.056925
K	-0.308346	1.989019	1.423570

E_{ortho}-I‘

C	-2.208991	-2.966804	-0.702641
C	-1.732358	-2.187478	-1.741704
C	-0.594075	-1.414171	-1.558385
C	0.093528	-1.391241	-0.348358
C	-0.410082	-2.196158	0.676930
C	-1.541698	-2.972389	0.512061
H	-1.901055	-3.582967	1.330394
H	0.119634	-2.202793	1.621319
C	1.311931	-0.581360	-0.079608
C	1.280435	0.587531	0.697579
C	2.423840	1.343759	1.037556
C	3.623551	0.800563	0.544996
C	3.694202	-0.339384	-0.256764
C	2.535536	-1.028803	-0.576813
H	2.572614	-1.924329	-1.185747
H	4.649557	-0.703328	-0.622924
H	4.564993	1.293348	0.787823
I	0.041645	-0.271484	-3.229878
H	-2.247386	-2.180839	-2.692334
H	-3.097744	-3.567111	-0.847478
C	-0.049391	1.123189	1.226917
C	-0.280171	2.559827	0.791212
C	-0.163738	0.890655	2.697669
C	-0.733156	3.517362	1.786962
C	-0.549564	1.835704	3.555030
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C	-0.849438	3.167967	3.078503
H	-0.931607	4.524441	1.443852
H	-0.622721	1.630515	4.614820
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H	-0.885972	0.577722	0.762939
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K	2.075205	2.341616	-1.582128

KOPh

C	0.068315	1.348671	-0.000036
C	-0.831342	0.259634	-0.000016
C	-0.252481	-1.028856	0.000013
C	1.119451	-1.207636	0.000038
C	1.984606	-0.120278	0.000028
C	1.438555	1.157497	-0.000012
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K	-4.380863	0.739206	0.000089

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H	3.057289	-0.265005	0.000047
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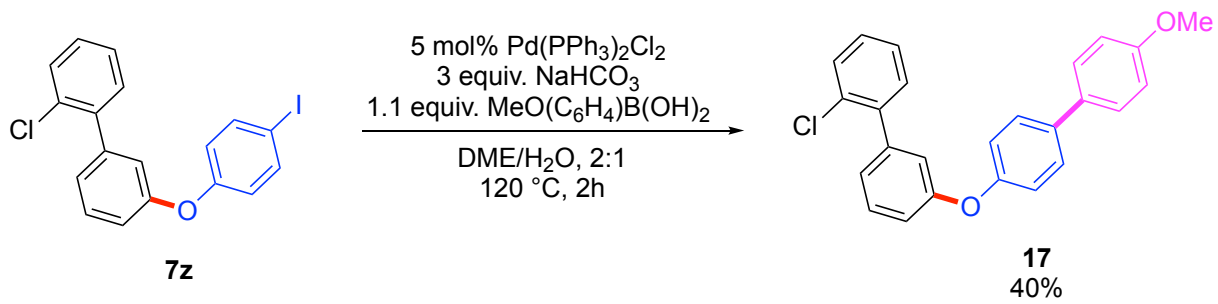
Post-Functionalization:

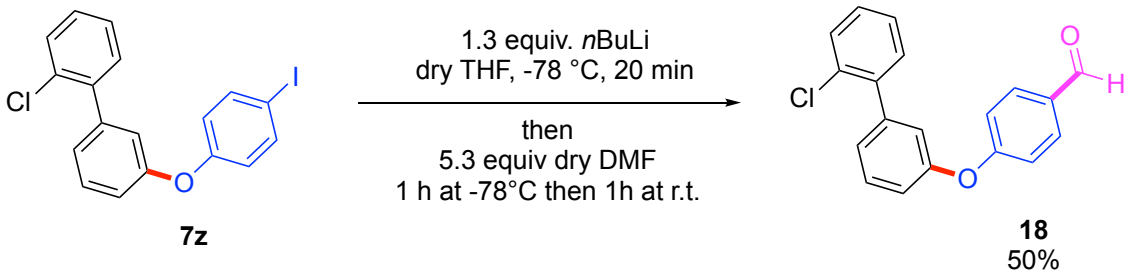


SCHEME S-22

2-chloro-3'-((4'-methoxy-[1,1'-biphenyl]-4-yl)oxy)-1,1'-biphenyl 17

A solution of **7z** (49 mg, 0.12 mmol, 1 equiv.), 4-methoxyphenylboronic acid (20 mg, 0.13 mmol, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (4 mg, 6 µmol, 5 mol%), and $NaHCO_3$ (30 mg, 0.36 mmol, 3 equiv.) in DME (500 µL) was stirred at room temperature for 5 min. Then, H_2O (240 µL) was added. The resulting mixture was sealed and stirred at 120 °C for 2 hours. After being cooled to room temperature, the mixture was extracted with EtOAc. The extracts were combined, dried over $MgSO_4$, and filtered. After removal of volatile components from the filtrate, the resulting crude product was purified by preparative TLC (Cy/EtOAc 9:1) yielding **17** in 40% (18.5 mg, 0.048 mmol) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 4H), 7.39 – 7.36 (m, 1H), 7.35 – 7.31 (m, 1H), 7.28 – 7.19 (m, 3H), 7.10 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.07 – 7.06 (m, 1H), 7.05 – 7.02 (m, 2H), 6.99 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 6.91 – 6.88 (m, 2H), 3.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 157.0, 156.1, 141.1, 139.8, 136.1, 133.1, 132.4, 131.2, 130.0, 129.4, 128.7, 128.0 (2C), 127.9 (2C), 126.8, 124.3, 119.9, 119.2 (2C), 117.9, 114.2 (2C), 55.3. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{25}H_{19}ClO_2^+$: 386.1068; found: 386.1024.

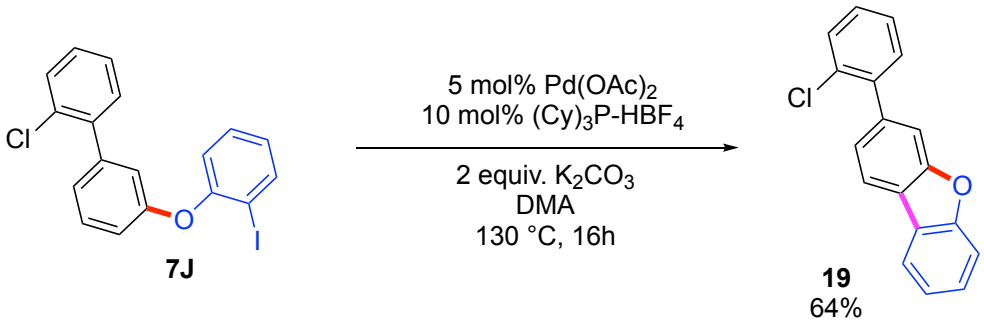


SCHEME S-23

4-((2'-chloro-[1,1'-biphenyl]-3-yl)oxy)benzaldehyde 18

To a solution of **7z** (50 mg, 0.12 mmol, 1 equiv.) in freshly distilled THF (1.3 mL, 0.1 M) at -78 °C a 1.6 M solution of *n*BuLi in hexanes (100 µL, 0.16 mmol, 1.3 equiv.) was added dropwise. The resulting solution was stirred for 30 min at -78 °C. Then dry DMF (50 µL, 0.65 mmol, 5.3 equiv.) was added dropwise. The solution was stirred at -78 °C for one hour than the cold bath was removed and the resulting mixture was stirred for 1h. The reaction was quenched with $NaHCO_3$ and water, then extracted with EtOAc. The organic phase was dried, filtered and concentrated. The crude was purified by preparative TLC (Cy:EtOAc 9:1) yielding **18** in 50% as colorless oil (18.5 mg, 0.06 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.36 – 7.28 (m, 4H), 7.19 (t, J = 2.0 Hz, 1H), 7.15 – 7.10 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 163.1, 154.8, 141.5, 139.4, 132.4, 132.0 (2C), 131.4, 131.2, 130.1, 129.9, 129.0, 127.0, 126.0, 121.5, 119.5, 117.8 (2C). **HRMS (APCI)**: m/z $[M+H]^+$ calcd for $C_{19}H_{14}ClO_2^+$: 309.0677; found: 309.0673.



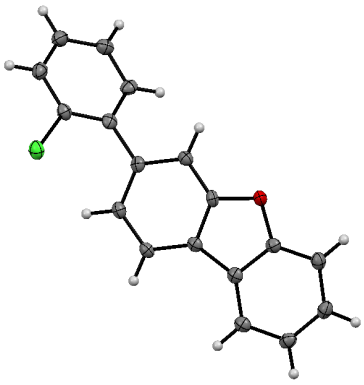
SCHEME S-24

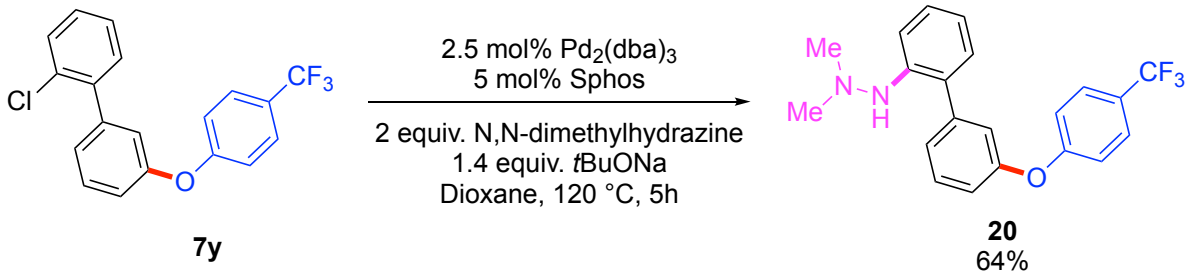
3-(2-chlorophenyl)dibenzo[b,d]furan 19

To an oven dried 7 mL vial equipped with a magnetic stirrer was charged with **7J** (50 mg, 0.12 mmol, 1 equiv) followed by $Pd(OAc)_2$ (1.4 mg, 6.1 µmol, 5 mol%), $(Cy)_3P\text{-}HBF_4$ (4.5 mg, 12 µmol, 10 mol%) and K_2CO_3 (34 mg, 0.25 mmol, 2 equiv). The vial was purged with argon, then degassed DMA (500 µL, M 0.24) was added. The resulting mixture was heated to 130 °C overnight. The crude mixture was then loaded directly onto silica and purified by flash chromatography (Cy/EtOAc 9:1) yielding **19** in 64% as colorless oil (22 mg, 0.079 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.58 (d, J = 1.1 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.36 (m, 1H), 7.35 – 7.33 (m, 2H), 7.29 – 7.20 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 155.9, 140.3, 138.5, 132.6, 131.6, 130.1, 128.7, 127.3, 126.9, 124.4, 124.0, 123.6, 122.8, 120.7, 120.1, 112.8, 111.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{18}H_{11}ClO^+$: 278.0493; found: 278.0507.

X-Ray suitable crystals of **19** were obtained through slow evaporation of acetone (Ellipsoid probability at 50%). CCDC 2176958



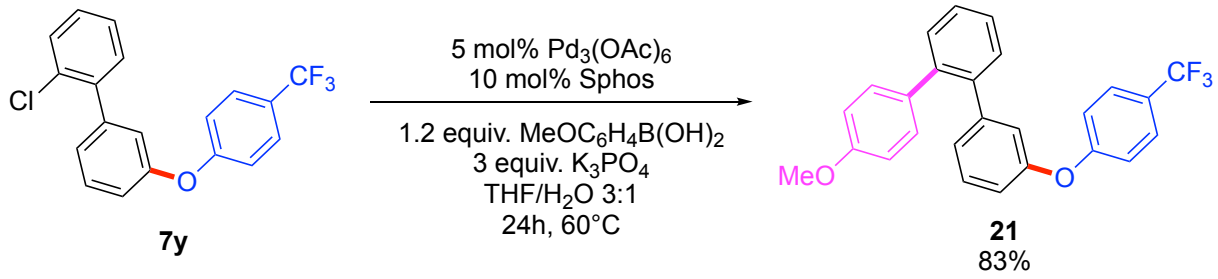


SCHEME S-25

1,1-dimethyl-2-(3'-(4-(trifluoromethyl)phenoxy)-[1,1'-biphenyl]-2-yl)hydrazine 20

A 7 mL reaction tube was charged with $Pd_2(dba)_3$ (2.3 mg, 2.5 µmol, 2.5 mol%) and Sphos (2.1 mg, 5 µmol, 5 mol%) followed by dioxane (200 µL). The resulting mixture was stirred at room temperature under argon for ten minutes. The compound **7y** (34.9 mg, 0.1 mmol) in 200 µL of dioxane, N,N-dimethylhydrazine (15 µL, 0.2 mmol, 2 equiv.) and *t*BuONa (13.5 mg, 1.4 mmol, 1.4 equiv.) were then added. The reaction mixture was stirred at 120 °C under argon for 5 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, Cy/EtOAc 10:1) to afford the product **20** in 64% as colorless oil (24 mg, 0.064 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.46 (t, J = 7.9 Hz, 1H), 7.33 (dd, J = 8.2, 1.5 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.23 (ddd, J = 7.6, 1.6, 1.0 Hz, 1H), 7.13 – 7.04 (m, 5H), 6.84 (td, J = 7.3, 1.5 Hz, 1H), 4.46 (s, 1H), 2.47 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1 (m), 156.3, 144.2, 141.2, 130.4, 130.0, 129.1, 127.2 (q, J = 3.9 Hz, 2C), 125.7, 125.1 125.2 (d, J = 33.0 Hz), 124.1 (q, J = 271.3 Hz), 120.3, 118.8, 118.3, 118.3 (2C), 113.9, 47.6 (2C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.8. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{21}H_{20}F_3N_2O^+$: 373.1522; found: 373.1505.

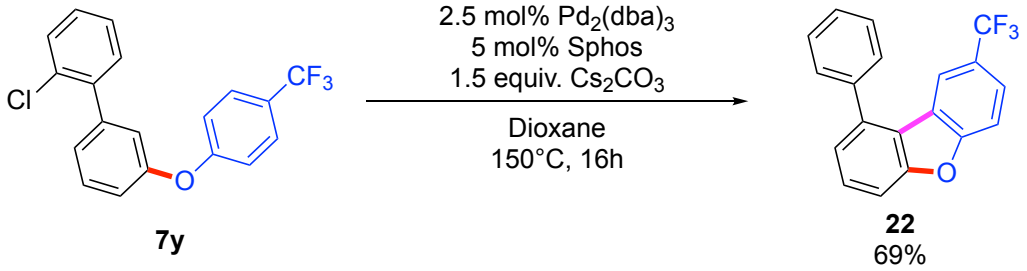


SCHEME S-26

4''-methoxy-3-(4-(trifluoromethyl)phenoxy)-1,1':2',1''-terphenyl 21

A 5 mL test tube was charged with $Pd_3(OAc)_6$ (4.1 mg, 0.018 mmol, 5 mol%) and S-Phos (14.8 mg, 0.036 mmol, 10 mol%), The vial was evacuated and back refilled with Ar three times. Then a mixture of THF-H_2O (3/1, 1 mL) was added. The resulting mixture was stirred for 10 min to generate the active catalyst solution. A 5 mL reaction tube was charged with **7y** (42 mg, 0.12 mmol, 1 equiv.), K_3PO_4 (76.4 mg, 0.36 mmol, 3 equiv), and 4-methoxyphenylboronic acid (21.8 mg, 0.144 mmol, 1.2 equiv), purged and filled with Ar three times. The active catalyst solution (0.33 mL) and the mixture of THF-H_2O (3/1, 0.9 mL) was added. The reaction mixture was stirred at 60 °C for 24 h. The crude mixture was diluted in DCM (2 mL), filtered through celite and washed with DCM (3x2 mL). After evaporating the solvent, the residue was purified by preparative TLC (Cyclohexane/ethyl acetate 10:1) to afford product **21** in 83% as colorless oil (42 mg, 0.1 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 9.1, 0.7 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.18 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.96 (ddd, *J* = 8.2, 2.5, 1.1 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.75 (dd, *J* = 9.2, 0.8 Hz, 2H), 6.70 (dd, *J* = 2.5, 1.4 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2 (d, *J* = 1.5 Hz), 158.4, 154.7, 143.9, 140.2, 139.5, 133.6, 131.0 (2C), 130.6, 130.3, 130.0, 127.9, 127.2, 126.9 (q, *J* = 3.7 Hz, 2C), 125.8, 124.6 (d, *J* = 271.4 Hz), 124.4 (q, *J* = 32.6 Hz), 121.7, 118.4, 117.4 (2C), 113.5 (2C), 55.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.7. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{26}H_{19}F_3O_2^+$: 420.1332; found: 420.1353.



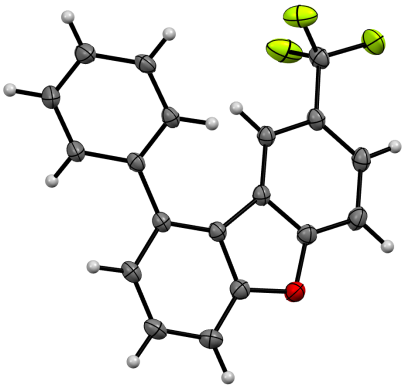
SCHEME S-27

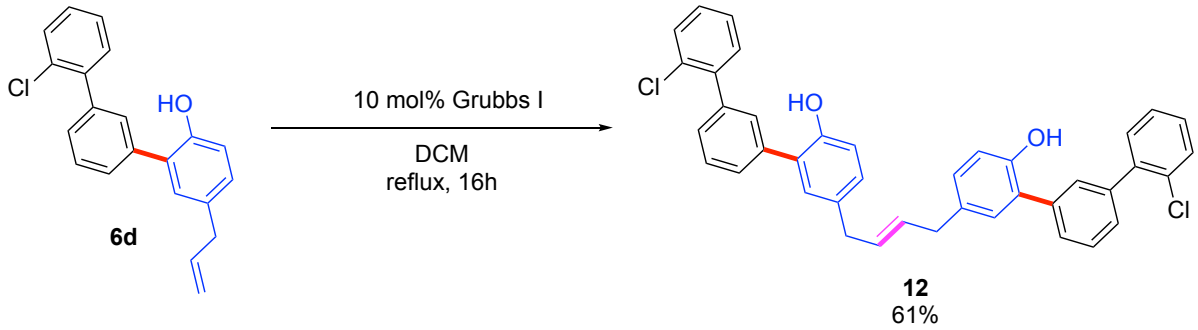
1-phenyl-8-(trifluoromethyl)dibenzo[b,d]furan 22

A 5 mL test tube was charged with $Pd_2(dba)_3$ (2.8 mg, 0.003 mmol, 2.5 mol%) and S-Phos (2.5 mg, 0.006 mmol, 5 mol%). The vial was evacuated and back refilled with Ar three times. Then dioxane (0.2 mL) was added. The mixture of was stirred for 10 min at room temperature. In the meantime, **7y** (42 mg, 0.12 mmol, 1 equiv.) was dissolved in dioxane (0.2 mL), the resulting solution was added to the catalytic reaction tube followed by Cs_2CO_3 (59 mg, 0.18 mmol, 1.5 equiv.). The resulting mixture was allowed to stir at 150°C for 16 hours. After cooling at room temperature, the crude was filtered, concentrated and purified through prep-TLC (Cy 100%) affording **22** (26 mg, 0.083 mmol) as white powder in 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (brs, 1H), 7.57 (dd, J = 8.7, 1.8 Hz, 1H), 7.55 – 7.42 (m, 8H), 7.22 (dd, J = 7.1, 1.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.8 - 157.7 (m), 157.0, 139.1, 138.3, 128.7 (4C), 128.4, 128.0, 124.9 (q, J = 32.3 Hz), 124.5, 124.4 (q, J = 271.8 Hz), 124.1, 124.1 - 124.0 (m), 120.9, 119.8 (q, J = 4.3 Hz), 119.9, 110.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.0. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{19}H_{11}F_3O^+$: 312.0757; found: 312.0732.

X-Ray suitable crystals of **22** were obtained through slow evaporation of chloroform (Ellipsoid probability at 50%) CCDC 2176959



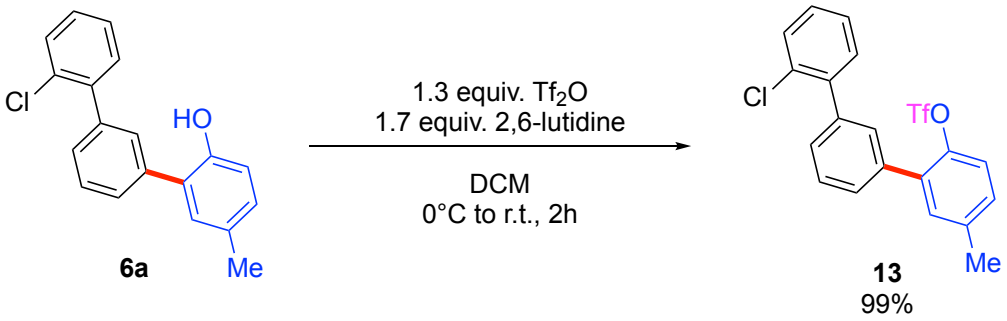


SCHEME S-28

(E)-5,5'''-(but-2-ene-1,4-diyl)bis(2''-chloro-[1,1':3',1''-terphenyl]-2-ol) 12

A 5 mL test tube was charged with **6d** (48 mg, 0.15 mmol, 1 equiv.) and Grubbs I catalyst (13 mg, 0.014 mmol, 10 mol%). The vial was evacuated and back refilled with Ar three times. Then DCM (0.75 mL, 0.2 M) was added. The resulting mixture was heated at reflux for 16 hours. The solvent was removed under reduced pressure and purified by prep-TLC (Cy:EtOAc 4:1) to afford **12** as pale yellow oil in 61% yield. (28 mg, 0.046 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 2H), 7.68 – 7.66 (m, 2H), 7.64 – 7.59 (m, 6H), 7.53 – 7.42 (m, 6H), 7.26 (d, *J* = 2.2 Hz, 2H), 7.23 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 5.84 (m, 2H), 5.35 (s, 2H), 3.49 – 3.48 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 140.2, 139.9, 137.0, 133.1, 132.4, 131.3, 130.5, 130.2, 130.1, 130.0, 129.2, 129.0, 128.8, 128.8, 128.3, 127.6, 126.9, 115.9, 38.1. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{40}H_{30}Cl_2O_2^+$: 612.1617; found: 612.1622.

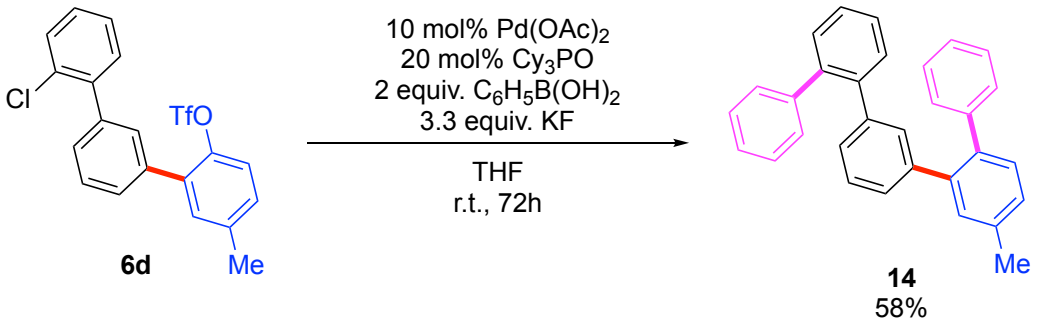


SCHEME S-29

2''-chloro-5-methyl-[1,1':3',1''-terphenyl]-2-yl trifluoromethanesulfonate 13

To a solution of **6a** (59 mg, 0.2 mmol, 1 equiv.) in dry CH_2Cl_2 (1 mL), 2,6-lutidine (40 µL, 0.34 mmol, 1.7 equiv.) was added. Then trifluoromethanesulfonic anhydride (43 µL, 0.26 mmol, 1.3 equiv.) was added dropwise at 0 °C followed by CH_2Cl_2 (200 µL). The solution was allowed to warm to room temperature and stirring was continued for 2 hours. The reaction was quenched with H_2O (1 mL) and the mixture was extracted with CH_2Cl_2 (1 mL x times). The organic layer was concentrated under reduced pressure. The residue was purified *via* filtration on silica gel using CH_2Cl_2 to afford **13** (85 mg, 0.2 mmol) as a colorless oil in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 5H), 7.34 – 7.32 (m, 1H), 7.28 – 7.19 (m, 4H), 7.16 – 7.13 (m, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 140.0, 139.6, 138.6, 135.6, 134.8, 132.5, 132.5, 131.4, 130.4, 129.9, 129.6, 129.3, 128.7, 128.5, 128.1, 126.9, 121.8, 20.9. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{20}H_{14}ClF_3O_3S^+$: 426.0299; found: 426.0298.

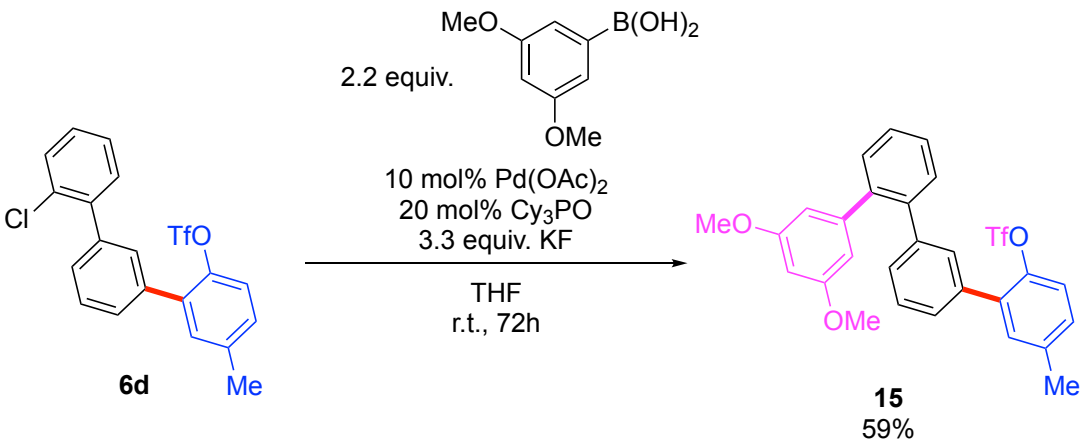


SCHEME S-30

4'-methyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl 14

A 5 mL reaction tube was charged with $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%), Cy_3P (5.6 mg, 0.02 mmol, 20 mol%), phenylboronic acid (24.3 mg, 0.2 mmol, 2 equiv) and KF (19.1 mg, 0.33 mmol, 3.3 equiv). The tube was evacuated and backfilled with Argon three times. Then a solution of the **6d** (42.7 mg, 0.1 mmol, 1 equiv.) in THF (0.2 mL, 0.5 M) was added by syringe. The resulting mixture was stirred at room temperature for 72 hours. The reaction was monitored by TLC and GC-MS. The crude was filtered through a pad of celite and washing with EtOAc (2 mL x 2 times) then concentrated *in vacuo*. The residue was purified by prep-TLC (Cy:DCM 3:1) to afford **14** as colorless oil in 58% yield. (23 mg, 0.058 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 3H), 7.31 – 7.19 (m, 9H), 7.14 – 7.06 (m, 5H), 6.99 (d, J = 7.4 Hz, 1H), 6.95 – 6.93 (m, 2H), 6.87 (dt, J = 7.4, 1.6 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 141.5, 141.2, 141.1, 140.6, 140.5, 140.2, 137.7, 137.1, 131.5, 131.3, 130.5, 130.5, 130.3, 130.0 (2C), 130.0 (2C), 128.1, 128.1, 127.9, 127.9 (2C), 127.8 (2C), 127.4 (2C), 127.2, 126.4, 126.2, 21.0. **HRMS (APCI)**: m/z $[M]^+$ calcd for $C_{31}H_{24}^+$: 396.1873; found: 396.1902.

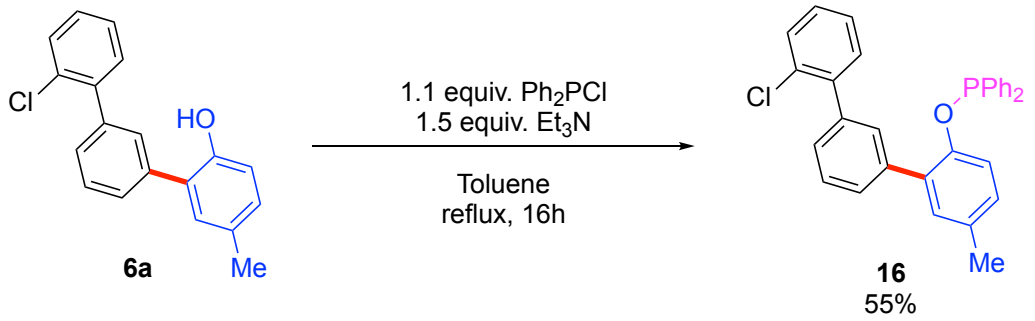


SCHEME S-31

3,5-dimethoxy-5'''-methyl-[1,1':2',1'':3'',1'''-quaterphenyl]-2'''-yl trifluoromethanesulfonate 15

A 5 mL reaction tube was charged with $Pd(OAc)_2$ (11 mg, 0.05 mmol, 10 mol%), Cy_3P (28 mg, 0.1 mmol, 20 mol%), 3,5-dimethoxyphenylboronic acid (218 mg, 1.2 mmol, 2.2 equiv) and KF (96 mg, 1.65 mmol, 3.3 equiv). The tube was evacuated and backfilled with Argon three times. Then a solution of the **6d** (213 mg, 0.5 mmol, 1 equiv.) in THF (1 mL, 0.5 M) was added by syringe. The resulting mixture was stirred at room temperature for 72 hours. The reaction was monitored by TLC and GC-MS. The crude was filtered through a pad of celite and washing with EtOAc (2 mL x 2 times) then concentrated *in vacuo*. The residue was purified by prep-TLC (Cy:DCM 3:1) to afford **15** as colorless oil in 59% yield. (155 mg, 0.29 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.54 – 7.51 (m, 1H), 7.50 – 7.46 (m, 2H), 7.41 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.27 (d, J = 8.1 Hz, 1H), 7.22 – 7.19 (m, 1H), 6.45 – 6.42 (m, 3H), 6.95 (d, J = 2.2 Hz, 1H), 3.68 (s, 6H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3 (2C), 144.7, 143.6, 141.7, 140.6, 139.8, 138.6, 135.3, 134.8, 132.6, 130.8, 130.4, 130.3, 129.3 (2C), 127.9, 127.8, 127.6, 127.4, 121.6, 108.1 (2C), 99.2, 55.1 (2C), 20.7. **^{19}F NMR** (377 MHz, CDCl3) δ -73.9. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{28}H_{24}F_3O_5S^+$: 529.1291; found: 529.1290.



SCHEME S-32

((2''-chloro-5-methyl-[1,1':3',1''-terphenyl]-2-yl)oxy)diphenylphosphane 16

A Schlenk tube under an atmosphere of nitrogen was charged with **6a** (30 mg, 0.1 mmol, 1 equiv.), chlorodiphenylphosphine (19 µL, 0.11 mmol, 1.1 equiv.), toluene (0.3 mL, 0.34 M) and triethylamine (21 µL, 0.15 mmol, 1.5 equiv.). The resultant mixture was then heated at reflux temperature overnight, allowed to cool to room temperature and the precipitated Et_3NHCl removed by filtration through a pad of Celite. The precipitate was washed with toluene (2 × 10 mL) and the combined organic fractions were then evaporated, the crude product was purified through prep-TLC (Cy:EtOAc 2:1) yielding **16** (30 mg, 0.063 mmol) as colorless oil in 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 9H), 7.39 – 7.33 (m, 3H), 7.28 – 7.19 (m, 7H), 7.10 – 7.09 (m, 1H), 7.00 (ddd, *J* = 8.3, 2.4, 0.8 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8 (d, *J* = 8.2 Hz), 140.2, 139.1, 137.9, 134.3, 132.8 (d, *J* = 5.7 Hz), 132.5, 132.1 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 10.4 Hz, 2C), 131.5, 131.4, 131.4, 130.6, 130.0, 130.0, 129.3, 128.9, 128.6, 128.4, 128.3 (d, *J* = 13.4 Hz, 2C), 127.7, 126.9, 121.2 (d, *J* = 3.5 Hz), 20.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.8.

Crystallographic data

2a-BF_4

Table 1. Crystal data and structure refinement for **2a**-BF_4.

Identification code	efcmla_a
Empirical formula	C12 H8 B Cl F4
Formula weight	274.44
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 11.1512(4) A alpha = 90 deg. b = 16.2741(7) A beta = 113.4590(14) deg. c = 13.1460(6) A gamma = 90 deg.
Volume	2188.49(16) A^3
Z, Calculated density	8, 1.666 Mg/m^3
Absorption coefficient	0.378 mm^-1
F(000)	1104
Crystal size	0.150 x 0.100 x 0.100 mm
Theta range for data collection	1.991 to 28.804 deg.
Limiting indices	-14<=h<=15, -21<=k<=22, -17<=l<=17
Reflections collected / unique	55828 / 5700 [R(int) = 0.0442]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6965
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5700 / 0 / 325

Goodness-of-fit on F^2 1.008

Final R indices [I>2sigma(I)] R1 = 0.0319, wR2 = 0.0786

R indices (all data) R1 = 0.0420, wR2 = 0.0862

Extinction coefficient n/a

Largest diff. peak and hole 0.619 and -0.500 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for efcmla_a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	1612(1)	3457(1)	5375(1)	19(1)
C(1)	2431(1)	3254(1)	4485(1)	18(1)
C(2)	2946(1)	3860(1)	4052(1)	21(1)
C(3)	3559(1)	3579(1)	3384(1)	22(1)
C(4)	3635(1)	2745(1)	3185(1)	22(1)
C(5)	3095(1)	2156(1)	3636(1)	20(1)
C(6)	2473(1)	2413(1)	4315(1)	18(1)
C(7)	1879(1)	1927(1)	4913(1)	18(1)
C(8)	1350(1)	2391(1)	5516(1)	18(1)
C(9)	713(1)	2091(1)	6144(1)	21(1)
C(10)	643(2)	1239(1)	6182(1)	24(1)
C(11)	1187(2)	744(1)	5617(1)	25(1)
C(12)	1787(2)	1075(1)	4971(1)	23(1)
Cl(2)	6831(1)	1441(1)	10158(1)	19(1)
C(13)	7583(1)	1858(1)	9306(1)	18(1)
C(14)	8195(1)	1380(1)	8796(1)	21(1)
C(15)	8745(1)	1819(1)	8179(1)	22(1)
C(16)	8662(1)	2671(1)	8100(1)	22(1)
C(17)	8019(1)	3122(1)	8623(1)	20(1)
C(18)	7463(1)	2708(1)	9257(1)	18(1)
C(19)	6798(1)	3034(1)	9918(1)	18(1)
C(20)	6387(1)	2435(1)	10461(1)	18(1)
C(21)	5727(1)	2561(1)	11133(1)	20(1)
C(22)	5485(2)	3381(1)	11284(1)	22(1)
C(23)	5888(2)	4012(1)	10776(1)	24(1)
C(24)	6531(2)	3848(1)	10090(1)	23(1)

B(1)	4824(2)	472(1)	1939(1)	20(1)
F(1)	5620(1)	616(1)	1371(1)	29(1)
F(2)	3715(1)	44(1)	1256(1)	35(1)
F(3)	5501(1)	20(1)	2889(1)	34(1)
F(4)	4446(1)	1224(1)	2228(1)	30(1)
B(2)	-101(2)	4577(1)	6925(1)	23(1)
F(5)	-702(1)	4994(1)	5932(1)	41(1)
F(6)	190(1)	3783(1)	6699(1)	41(1)
F(7)	1019(1)	4983(1)	7585(1)	50(1)
F(8)	-940(1)	4528(1)	7464(1)	37(1)

Table 3. Bond lengths [A] and angles [deg] for efcmla_a.

Cl(1)-C(1)	1.7791(14)
Cl(1)-C(8)	1.7814(13)
C(1)-C(2)	1.3739(19)
C(1)-C(6)	1.3908(18)
C(2)-C(3)	1.387(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.391(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.385(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3932(19)
C(5)-H(5)	0.9500
C(6)-C(7)	1.4488(19)
C(7)-C(8)	1.3851(19)
C(7)-C(12)	1.3950(19)
C(8)-C(9)	1.374(2)
C(9)-C(10)	1.391(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.388(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.382(2)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
Cl(2)-C(13)	1.7803(14)
Cl(2)-C(20)	1.7830(14)
C(13)-C(14)	1.373(2)
C(13)-C(18)	1.3889(19)
C(14)-C(15)	1.393(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.392(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.384(2)

C(16)-H(16)	0.9500
C(17)-C(18)	1.3936(19)
C(17)-H(17)	0.9500
C(18)-C(19)	1.4495(19)
C(19)-C(20)	1.3875(19)
C(19)-C(24)	1.3955(19)
C(20)-C(21)	1.3720(19)
C(21)-C(22)	1.391(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.394(2)
C(22)-H(22)	0.9500
C(23)-C(24)	1.384(2)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
B(1)-F(3)	1.3857(19)
B(1)-F(1)	1.3899(18)
B(1)-F(2)	1.3913(19)
B(1)-F(4)	1.3941(17)
B(2)-F(7)	1.374(2)
B(2)-F(8)	1.3823(19)
B(2)-F(5)	1.385(2)
B(2)-F(6)	1.3921(18)

C(1)-Cl(1)-C(8)	92.06(7)
C(2)-C(1)-C(6)	126.44(13)
C(2)-C(1)-Cl(1)	123.20(11)
C(6)-C(1)-Cl(1)	110.36(10)
C(1)-C(2)-C(3)	114.70(13)
C(1)-C(2)-H(2)	122.7
C(3)-C(2)-H(2)	122.7
C(2)-C(3)-C(4)	121.50(13)
C(2)-C(3)-H(3)	119.2
C(4)-C(3)-H(3)	119.2
C(5)-C(4)-C(3)	121.70(13)
C(5)-C(4)-H(4)	119.2
C(3)-C(4)-H(4)	119.2
C(4)-C(5)-C(6)	118.58(13)
C(4)-C(5)-H(5)	120.7
C(6)-C(5)-H(5)	120.7
C(1)-C(6)-C(5)	117.08(13)
C(1)-C(6)-C(7)	113.42(12)
C(5)-C(6)-C(7)	129.47(13)
C(8)-C(7)-C(12)	116.92(13)
C(8)-C(7)-C(6)	113.88(12)
C(12)-C(7)-C(6)	129.20(13)
C(9)-C(8)-C(7)	126.16(13)
C(9)-C(8)-Cl(1)	123.58(11)

C(7)-C(8)-Cl(1)	110.26(10)
C(8)-C(9)-C(10)	115.13(14)
C(8)-C(9)-H(9)	122.4
C(10)-C(9)-H(9)	122.4
C(11)-C(10)-C(9)	121.15(14)
C(11)-C(10)-H(10)	119.4
C(9)-C(10)-H(10)	119.4
C(12)-C(11)-C(10)	121.56(13)
C(12)-C(11)-H(11)	119.2
C(10)-C(11)-H(11)	119.2
C(11)-C(12)-C(7)	119.03(14)
C(11)-C(12)-H(12)	120.5
C(7)-C(12)-H(12)	120.5
C(13)-Cl(2)-C(20)	92.07(6)
C(14)-C(13)-C(18)	126.88(13)
C(14)-C(13)-Cl(2)	122.74(11)
C(18)-C(13)-Cl(2)	110.38(10)
C(13)-C(14)-C(15)	114.35(13)
C(13)-C(14)-H(14)	122.8
C(15)-C(14)-H(14)	122.8
C(16)-C(15)-C(14)	121.55(14)
C(16)-C(15)-H(15)	119.2
C(14)-C(15)-H(15)	119.2
C(17)-C(16)-C(15)	121.55(13)
C(17)-C(16)-H(16)	119.2
C(15)-C(16)-H(16)	119.2
C(16)-C(17)-C(18)	118.87(13)
C(16)-C(17)-H(17)	120.6
C(18)-C(17)-H(17)	120.6
C(13)-C(18)-C(17)	116.79(13)
C(13)-C(18)-C(19)	113.51(12)
C(17)-C(18)-C(19)	129.67(13)
C(20)-C(19)-C(24)	116.64(13)
C(20)-C(19)-C(18)	113.86(12)
C(24)-C(19)-C(18)	129.50(13)
C(21)-C(20)-C(19)	126.69(13)
C(21)-C(20)-Cl(2)	123.14(11)
C(19)-C(20)-Cl(2)	110.16(10)
C(20)-C(21)-C(22)	114.79(13)
C(20)-C(21)-H(21)	122.6
C(22)-C(21)-H(21)	122.6
C(21)-C(22)-C(23)	121.39(14)
C(21)-C(22)-H(22)	119.3
C(23)-C(22)-H(22)	119.3
C(24)-C(23)-C(22)	121.27(14)
C(24)-C(23)-H(23)	119.4
C(22)-C(23)-H(23)	119.4

C(23)-C(24)-C(19)	119.20(13)
C(23)-C(24)-H(24)	120.4
C(19)-C(24)-H(24)	120.4
F(3)-B(1)-F(1)	109.78(13)
F(3)-B(1)-F(2)	109.97(12)
F(1)-B(1)-F(2)	109.35(13)
F(3)-B(1)-F(4)	109.62(13)
F(1)-B(1)-F(4)	108.99(12)
F(2)-B(1)-F(4)	109.12(13)
F(7)-B(2)-F(8)	109.53(14)
F(7)-B(2)-F(5)	109.69(13)
F(8)-B(2)-F(5)	109.81(14)
F(7)-B(2)-F(6)	110.53(14)
F(8)-B(2)-F(6)	108.60(12)
F(5)-B(2)-F(6)	108.66(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for efcmla_a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	22(1)	14(1)	24(1)	-2(1)	12(1)	0(1)
C(1)	18(1)	18(1)	19(1)	-2(1)	9(1)	1(1)
C(2)	23(1)	16(1)	24(1)	-1(1)	9(1)	-1(1)
C(3)	23(1)	21(1)	24(1)	1(1)	10(1)	-2(1)
C(4)	22(1)	22(1)	21(1)	-1(1)	11(1)	2(1)
C(5)	21(1)	17(1)	21(1)	-1(1)	7(1)	2(1)
C(6)	17(1)	16(1)	18(1)	0(1)	4(1)	1(1)
C(7)	18(1)	16(1)	19(1)	1(1)	6(1)	0(1)
C(8)	19(1)	13(1)	21(1)	1(1)	6(1)	-1(1)
C(9)	21(1)	20(1)	22(1)	0(1)	9(1)	0(1)
C(10)	25(1)	22(1)	25(1)	4(1)	10(1)	-2(1)
C(11)	28(1)	16(1)	30(1)	3(1)	11(1)	-1(1)
C(12)	25(1)	15(1)	28(1)	-1(1)	10(1)	1(1)
Cl(2)	23(1)	14(1)	24(1)	2(1)	13(1)	0(1)
C(13)	19(1)	18(1)	20(1)	2(1)	9(1)	-2(1)
C(14)	20(1)	19(1)	24(1)	0(1)	9(1)	0(1)
C(15)	20(1)	24(1)	22(1)	0(1)	10(1)	0(1)
C(16)	22(1)	24(1)	20(1)	2(1)	10(1)	-4(1)

C(17)	23(1)	17(1)	20(1)	2(1)	8(1)	-3(1)
C(18)	18(1)	17(1)	18(1)	0(1)	6(1)	-2(1)
C(19)	19(1)	16(1)	17(1)	1(1)	6(1)	-1(1)
C(20)	20(1)	13(1)	19(1)	-1(1)	6(1)	0(1)
C(21)	20(1)	20(1)	20(1)	1(1)	9(1)	-1(1)
C(22)	25(1)	22(1)	21(1)	-1(1)	10(1)	1(1)
C(23)	30(1)	17(1)	25(1)	-2(1)	12(1)	1(1)
C(24)	28(1)	17(1)	23(1)	1(1)	10(1)	-2(1)
B(1)	27(1)	14(1)	25(1)	0(1)	16(1)	-1(1)
F(1)	36(1)	25(1)	38(1)	3(1)	26(1)	1(1)
F(2)	38(1)	30(1)	39(1)	-10(1)	17(1)	-14(1)
F(3)	52(1)	26(1)	27(1)	6(1)	19(1)	9(1)
F(4)	38(1)	18(1)	40(1)	-4(1)	23(1)	2(1)
B(2)	30(1)	16(1)	27(1)	1(1)	17(1)	1(1)
F(5)	51(1)	38(1)	37(1)	15(1)	22(1)	14(1)
F(6)	63(1)	19(1)	62(1)	2(1)	47(1)	8(1)
F(7)	47(1)	49(1)	47(1)	2(1)	12(1)	-24(1)
F(8)	54(1)	26(1)	49(1)	-2(1)	40(1)	-1(1)

2w

Table 1. Crystal data and structure refinement for jwdml220325.

Identification code	jwdml220325
Empirical formula	C15 H12 Cl F3 O3 S
Formula weight	364.76
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 6.8197(2) A alpha = 65.2470(10) deg. b = 9.9960(3) A beta = 87.4440(10) deg. c = 11.8872(3) A gamma = 79.7850(10) deg.
Volume	723.83(4) A^3
Z, Calculated density	2, 1.674 Mg/m^3
Absorption coefficient	0.454 mm^-1
F(000)	372
Crystal size	0.140 x 0.100 x 0.060 mm
Theta range for data collection	2.272 to 29.075 deg.
Limiting indices	-9<=h<=9, -13<=k<=13, -16<=l<=16
Reflections collected / unique	48653 / 3870 [R(int) = 0.0366]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.7209
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3870 / 0 / 210

Goodness-of-fit on F^2 1.052

Final R indices [I>2sigma(I)] R1 = 0.0344, wR2 = 0.0913

R indices (all data) R1 = 0.0393, wR2 = 0.0960

Extinction coefficient n/a

Largest diff. peak and hole 0.605 and -0.419 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for jwdml220325. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2581(2)	4315(2)	9424(1)	15(1)
C(2)	2465(2)	2831(2)	10160(1)	16(1)
C(3)	2333(2)	2515(2)	11425(1)	17(1)
C(4)	2313(2)	3612(2)	11859(1)	18(1)
C(5)	2390(2)	5095(2)	11062(1)	16(1)
C(6)	2528(2)	5473(2)	9792(1)	14(1)
C(7)	2583(2)	6921(2)	8767(1)	14(1)
C(8)	2502(2)	8327(2)	8771(1)	16(1)
C(9)	2499(2)	9569(2)	7649(1)	17(1)
C(10)	2585(2)	9465(2)	6506(1)	17(1)
C(11)	2696(2)	8070(2)	6476(1)	16(1)
C(12)	2684(2)	6877(2)	7613(1)	15(1)
C(13)	2437(2)	1695(2)	9648(2)	22(1)
C(14)	2498(3)	10853(2)	5313(1)	22(1)
C(15)	2084(3)	6175(2)	3939(1)	22(1)
O(1)	5348(2)	7227(2)	3268(1)	32(1)
O(2)	2365(2)	8914(1)	3354(1)	25(1)
O(3)	2679(2)	8006(1)	1730(1)	33(1)
F(1)	2921(2)	4927(1)	3826(1)	34(1)
F(2)	2253(2)	5901(1)	5134(1)	38(1)
F(3)	158(2)	6427(2)	3647(1)	45(1)
S(1)	3258(1)	7766(1)	2964(1)	17(1)
Cl(1)	2774(1)	5002(1)	7779(1)	16(1)

Table 3. Bond lengths [A] and angles [deg] for jwdml220325.

C(1)-C(2)	1.3854(19)
C(1)-C(6)	1.3935(19)
C(1)-Cl(1)	1.7882(14)
C(2)-C(3)	1.404(2)
C(2)-C(13)	1.500(2)
C(3)-C(4)	1.392(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.394(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3973(19)
C(5)-H(5)	0.9500
C(6)-C(7)	1.4559(19)
C(7)-C(12)	1.3894(19)
C(7)-C(8)	1.3989(19)
C(8)-C(9)	1.390(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.403(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.398(2)
C(10)-C(14)	1.507(2)
C(11)-C(12)	1.3783(19)
C(11)-H(11)	0.9500
C(12)-Cl(1)	1.7906(14)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-F(3)	1.326(2)
C(15)-F(1)	1.3343(19)
C(15)-F(2)	1.3356(17)
C(15)-S(1)	1.8274(16)
O(1)-S(1)	1.4366(13)
O(2)-S(1)	1.4412(11)
O(3)-S(1)	1.4445(12)

C(2)-C(1)-C(6)	128.04(13)
C(2)-C(1)-Cl(1)	121.79(11)
C(6)-C(1)-Cl(1)	110.17(10)
C(1)-C(2)-C(3)	113.02(13)
C(1)-C(2)-C(13)	123.24(13)
C(3)-C(2)-C(13)	123.73(13)
C(4)-C(3)-C(2)	121.93(13)
C(4)-C(3)-H(3)	119.0

C(2)-C(3)-H(3)	119.0
C(3)-C(4)-C(5)	122.03(13)
C(3)-C(4)-H(4)	119.0
C(5)-C(4)-H(4)	119.0
C(4)-C(5)-C(6)	118.49(13)
C(4)-C(5)-H(5)	120.8
C(6)-C(5)-H(5)	120.8
C(1)-C(6)-C(5)	116.47(12)
C(1)-C(6)-C(7)	113.73(12)
C(5)-C(6)-C(7)	129.78(13)
C(12)-C(7)-C(8)	116.20(13)
C(12)-C(7)-C(6)	113.73(12)
C(8)-C(7)-C(6)	130.06(13)
C(9)-C(8)-C(7)	119.16(13)
C(9)-C(8)-H(8)	120.4
C(7)-C(8)-H(8)	120.4
C(8)-C(9)-C(10)	122.33(13)
C(8)-C(9)-H(9)	118.8
C(10)-C(9)-H(9)	118.8
C(11)-C(10)-C(9)	119.71(13)
C(11)-C(10)-C(14)	119.97(13)
C(9)-C(10)-C(14)	120.29(13)
C(12)-C(11)-C(10)	115.63(13)
C(12)-C(11)-H(11)	122.2
C(10)-C(11)-H(11)	122.2
C(11)-C(12)-C(7)	126.97(13)
C(11)-C(12)-Cl(1)	122.77(11)
C(7)-C(12)-Cl(1)	110.26(10)
C(2)-C(13)-H(13A)	109.5
C(2)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(2)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
F(3)-C(15)-F(1)	107.60(13)
F(3)-C(15)-F(2)	107.78(14)
F(1)-C(15)-F(2)	107.24(13)
F(3)-C(15)-S(1)	111.30(11)
F(1)-C(15)-S(1)	111.75(11)
F(2)-C(15)-S(1)	110.96(11)
O(1)-S(1)-O(2)	115.15(8)

O(1)-S(1)-O(3)	114.41(9)
O(2)-S(1)-O(3)	115.53(8)
O(1)-S(1)-C(15)	103.95(8)
O(2)-S(1)-C(15)	102.94(7)
O(3)-S(1)-C(15)	102.37(7)
C(1)-Cl(1)-C(12)	92.06(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for jwdml220325. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	16(1)	16(1)	11(1)	-5(1)	0(1)	-3(1)
C(2)	17(1)	14(1)	16(1)	-5(1)	0(1)	-3(1)
C(3)	18(1)	14(1)	16(1)	-3(1)	0(1)	-3(1)
C(4)	19(1)	18(1)	13(1)	-4(1)	0(1)	-3(1)
C(5)	17(1)	16(1)	14(1)	-7(1)	0(1)	-3(1)
C(6)	14(1)	13(1)	14(1)	-5(1)	0(1)	-3(1)
C(7)	15(1)	14(1)	13(1)	-6(1)	0(1)	-3(1)
C(8)	20(1)	15(1)	15(1)	-8(1)	0(1)	-4(1)
C(9)	22(1)	14(1)	18(1)	-7(1)	0(1)	-4(1)
C(10)	19(1)	15(1)	15(1)	-5(1)	0(1)	-4(1)
C(11)	21(1)	16(1)	13(1)	-6(1)	1(1)	-3(1)
C(12)	19(1)	11(1)	15(1)	-7(1)	1(1)	-3(1)
C(13)	31(1)	15(1)	21(1)	-8(1)	3(1)	-6(1)
C(14)	32(1)	15(1)	15(1)	-4(1)	0(1)	-4(1)
C(15)	38(1)	17(1)	14(1)	-6(1)	2(1)	-10(1)
O(1)	26(1)	28(1)	44(1)	-18(1)	3(1)	-5(1)
O(2)	37(1)	14(1)	23(1)	-9(1)	5(1)	-3(1)
O(3)	62(1)	25(1)	12(1)	-5(1)	0(1)	-16(1)
F(1)	67(1)	15(1)	23(1)	-10(1)	4(1)	-12(1)
F(2)	81(1)	24(1)	12(1)	-7(1)	9(1)	-22(1)
F(3)	36(1)	44(1)	53(1)	-12(1)	3(1)	-22(1)
S(1)	27(1)	12(1)	13(1)	-5(1)	2(1)	-5(1)
Cl(1)	24(1)	13(1)	12(1)	-6(1)	2(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for jwdml220325.

	x	y	z	U(eq)
H(3)	2254	1523	12002	21
H(4)	2245	3343	12725	21
H(5)	2350	5831	11375	19
H(8)	2450	8432	9530	19
H(9)	2437	10523	7656	21
H(11)	2776	7952	5722	20
H(13A)	1253	1991	9103	32
H(13B)	2402	715	10331	32
H(13C)	3638	1636	9174	32
H(14A)	1133	11415	5146	33
H(14B)	2907	10567	4631	33
H(14C)	3399	11477	5385	33

Table 6. Torsion angles [deg] for jwdml220325.

C(6)-C(1)-C(2)-C(3)	-1.7(2)
Cl(1)-C(1)-C(2)-C(3)	179.67(10)
C(6)-C(1)-C(2)-C(13)	176.90(14)
Cl(1)-C(1)-C(2)-C(13)	-1.7(2)
C(1)-C(2)-C(3)-C(4)	0.3(2)
C(13)-C(2)-C(3)-C(4)	-178.33(14)
C(2)-C(3)-C(4)-C(5)	1.1(2)
C(3)-C(4)-C(5)-C(6)	-1.2(2)
C(2)-C(1)-C(6)-C(5)	1.7(2)
Cl(1)-C(1)-C(6)-C(5)	-179.63(10)
C(2)-C(1)-C(6)-C(7)	-177.01(14)
Cl(1)-C(1)-C(6)-C(7)	1.71(15)
C(4)-C(5)-C(6)-C(1)	-0.1(2)
C(4)-C(5)-C(6)-C(7)	178.34(14)
C(1)-C(6)-C(7)-C(12)	-0.22(18)
C(5)-C(6)-C(7)-C(12)	-178.66(14)
C(1)-C(6)-C(7)-C(8)	178.10(14)
C(5)-C(6)-C(7)-C(8)	-0.3(3)
C(12)-C(7)-C(8)-C(9)	0.9(2)
C(6)-C(7)-C(8)-C(9)	-177.42(14)
C(7)-C(8)-C(9)-C(10)	-0.3(2)
C(8)-C(9)-C(10)-C(11)	-0.6(2)
C(8)-C(9)-C(10)-C(14)	177.63(14)
C(9)-C(10)-C(11)-C(12)	0.9(2)

C(14)-C(10)-C(11)-C(12)	-177.34(13)
C(10)-C(11)-C(12)-C(7)	-0.3(2)
C(10)-C(11)-C(12)-Cl(1)	178.97(11)
C(8)-C(7)-C(12)-C(11)	-0.6(2)
C(6)-C(7)-C(12)-C(11)	178.01(14)
C(8)-C(7)-C(12)-Cl(1)	-179.94(10)
C(6)-C(7)-C(12)-Cl(1)	-1.37(15)
F(3)-C(15)-S(1)-O(1)	-171.66(12)
F(1)-C(15)-S(1)-O(1)	-51.33(13)
F(2)-C(15)-S(1)-O(1)	68.31(14)
F(3)-C(15)-S(1)-O(2)	67.91(13)
F(1)-C(15)-S(1)-O(2)	-171.76(11)
F(2)-C(15)-S(1)-O(2)	-52.11(14)
F(3)-C(15)-S(1)-O(3)	-52.30(14)
F(1)-C(15)-S(1)-O(3)	68.04(13)
F(2)-C(15)-S(1)-O(3)	-172.32(13)
C(2)-C(1)-Cl(1)-C(12)	176.72(12)
C(6)-C(1)-Cl(1)-C(12)	-2.09(11)
C(11)-C(12)-Cl(1)-C(1)	-177.44(13)
C(7)-C(12)-Cl(1)-C(1)	1.97(11)

Symmetry transformations used to generate equivalent atoms:

19

Table 1. Crystal data and structure refinement for **19**.

Identification code	jwdml220324
Empirical formula	C18 H11 Cl O
Formula weight	278.72
Temperature	120(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 3.8406(2) A alpha = 90 deg. b = 13.4224(8) A beta = 90 deg. c = 24.5771(15) A gamma = 90 deg.
Volume	1266.95(13) A^3
Z, Calculated density	4, 1.461 Mg/m^3
Absorption coefficient	2.579 mm^-1
F(000)	576
Crystal size	0.250 x 0.120 x 0.100 mm
Theta range for data collection	3.597 to 66.664 deg.
Limiting indices	-4<=h<=4, -15<=k<=15, -29<=l<=29
Reflections collected / unique	25318 / 2259 [R(int) = 0.0620]
Completeness to theta = 66.664	100.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.5309
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2259 / 0 / 182

Goodness-of-fit on F^2 1.100

Final R indices [I>2sigma(I)] R1 = 0.0277, wR2 = 0.0731

R indices (all data) R1 = 0.0279, wR2 = 0.0733

Absolute structure parameter 0.466(18)

Extinction coefficient n/a

Largest diff. peak and hole 0.454 and -0.244 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for jwdml220324. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6814(6)	1663(2)	7392(1)	20(1)
C(2)	6303(7)	1347(2)	7924(1)	25(1)
C(3)	4892(7)	1998(2)	8304(1)	26(1)
C(4)	4069(7)	2966(2)	8149(1)	24(1)
C(5)	4631(7)	3271(2)	7620(1)	23(1)
C(6)	6002(6)	2630(2)	7223(1)	20(1)
C(7)	6466(7)	3020(2)	6659(1)	18(1)
C(8)	7912(6)	3969(2)	6595(1)	19(1)
C(9)	8043(6)	4358(2)	6078(1)	18(1)
C(10)	8895(7)	5395(2)	5397(1)	19(1)
C(11)	9798(7)	6230(2)	5106(1)	23(1)
C(12)	9093(7)	6206(2)	4550(1)	24(1)
C(13)	7517(7)	5387(2)	4309(1)	23(1)
C(14)	6586(7)	4555(2)	4609(1)	21(1)
C(15)	7304(6)	4556(2)	5168(1)	19(1)
C(16)	6774(6)	3870(2)	5618(1)	18(1)
C(17)	5351(6)	2918(2)	5683(1)	18(1)
C(18)	5226(6)	2504(2)	6199(1)	20(1)
O(1)	9391(5)	5286(1)	5953(1)	20(1)
Cl(1)	8673(2)	800(1)	6945(1)	25(1)

Table 3. Bond lengths [A] and angles [deg] for jwdml220324.

C(1)-C(2)	1.389(3)
C(1)-C(6)	1.398(3)
C(1)-Cl(1)	1.749(2)
C(2)-C(3)	1.388(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.390(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.381(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.403(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.493(3)
C(7)-C(8)	1.397(3)
C(7)-C(18)	1.407(3)
C(8)-C(9)	1.376(3)
C(8)-H(8)	0.9500
C(9)-O(1)	1.384(3)
C(9)-C(16)	1.395(3)
C(10)-C(11)	1.373(3)
C(10)-O(1)	1.386(3)
C(10)-C(15)	1.400(3)
C(11)-C(12)	1.394(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.388(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.385(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.402(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.453(3)
C(16)-C(17)	1.399(3)
C(17)-C(18)	1.387(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500

C(2)-C(1)-C(6)	122.2(2)
C(2)-C(1)-Cl(1)	116.51(19)
C(6)-C(1)-Cl(1)	121.30(18)
C(3)-C(2)-C(1)	119.7(2)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	119.5(2)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(5)-C(4)-C(3)	119.9(2)
C(5)-C(4)-H(4)	120.0

C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	122.2(2)
C(4)-C(5)-H(5)	118.9
C(6)-C(5)-H(5)	118.9
C(1)-C(6)-C(5)	116.5(2)
C(1)-C(6)-C(7)	125.1(2)
C(5)-C(6)-C(7)	118.4(2)
C(8)-C(7)-C(18)	119.6(2)
C(8)-C(7)-C(6)	118.1(2)
C(18)-C(7)-C(6)	122.1(2)
C(9)-C(8)-C(7)	117.6(2)
C(9)-C(8)-H(8)	121.2
C(7)-C(8)-H(8)	121.2
C(8)-C(9)-O(1)	124.2(2)
C(8)-C(9)-C(16)	123.9(2)
O(1)-C(9)-C(16)	111.94(19)
C(11)-C(10)-O(1)	124.3(2)
C(11)-C(10)-C(15)	123.9(2)
O(1)-C(10)-C(15)	111.8(2)
C(10)-C(11)-C(12)	116.3(2)
C(10)-C(11)-H(11)	121.9
C(12)-C(11)-H(11)	121.9
C(13)-C(12)-C(11)	121.4(2)
C(13)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(14)-C(13)-C(12)	121.6(2)
C(14)-C(13)-H(13)	119.2
C(12)-C(13)-H(13)	119.2
C(13)-C(14)-C(15)	118.0(2)
C(13)-C(14)-H(14)	121.0
C(15)-C(14)-H(14)	121.0
C(10)-C(15)-C(14)	118.7(2)
C(10)-C(15)-C(16)	105.40(19)
C(14)-C(15)-C(16)	135.9(2)
C(9)-C(16)-C(17)	118.3(2)
C(9)-C(16)-C(15)	105.6(2)
C(17)-C(16)-C(15)	136.0(2)
C(18)-C(17)-C(16)	118.9(2)
C(18)-C(17)-H(17)	120.6
C(16)-C(17)-H(17)	120.6
C(17)-C(18)-C(7)	121.7(2)
C(17)-C(18)-H(18)	119.1
C(7)-C(18)-H(18)	119.1
C(9)-O(1)-C(10)	105.24(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for jwdml220324.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	16(1)	19(1)	25(1)	-1(1)	1(1)	-3(1)
C(2)	24(1)	23(1)	27(1)	5(1)	-4(1)	-5(1)
C(3)	29(1)	27(1)	21(1)	2(1)	-2(1)	-5(1)
C(4)	24(1)	27(1)	21(1)	-3(1)	0(1)	-1(1)
C(5)	20(1)	27(1)	21(1)	3(1)	-4(1)	-2(1)
C(6)	14(1)	22(1)	23(1)	1(1)	-3(1)	-3(1)
C(7)	15(1)	17(1)	22(1)	0(1)	0(1)	2(1)
C(8)	19(1)	18(1)	20(1)	-2(1)	-1(1)	1(1)
C(9)	17(1)	13(1)	24(1)	-1(1)	2(1)	0(1)
C(10)	19(1)	19(1)	19(1)	-1(1)	1(1)	3(1)
C(11)	24(1)	18(1)	25(1)	-1(1)	4(1)	0(1)
C(12)	28(1)	20(1)	24(1)	4(1)	5(1)	4(1)
C(13)	25(1)	25(1)	19(1)	1(1)	2(1)	5(1)
C(14)	18(1)	22(1)	22(1)	-3(1)	1(1)	2(1)
C(15)	16(1)	19(1)	21(1)	-1(1)	3(1)	4(1)
C(16)	16(1)	18(1)	19(1)	-2(1)	1(1)	3(1)
C(17)	16(1)	18(1)	21(1)	-4(1)	1(1)	0(1)
C(18)	18(1)	17(1)	24(1)	-1(1)	1(1)	-1(1)
O(1)	25(1)	15(1)	20(1)	-1(1)	0(1)	-3(1)
Cl(1)	26(1)	19(1)	30(1)	-2(1)	4(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic
displacement parameters (A^2 x 10^3) for jwdml220324.

	x	y	z	U(eq)
H(2)	6916	688	8028	30
H(3)	4491	1783	8667	31
H(4)	3121	3417	8407	29
H(5)	4071	3936	7521	27
H(8)	8773	4331	6899	23
H(11)	10844	6792	5275	27

H(12)	9704	6763	4332	29
H(13)	7068	5397	3929	28
H(14)	5492	4000	4441	25
H(17)	4484	2561	5378	22
H(18)	4279	1856	6245	24

Table 6. Torsion angles [deg] for jwdml220324.

C(6)-C(1)-C(2)-C(3)	1.0(4)
Cl(1)-C(1)-C(2)-C(3)	179.0(2)
C(1)-C(2)-C(3)-C(4)	-1.3(4)
C(2)-C(3)-C(4)-C(5)	0.5(4)
C(3)-C(4)-C(5)-C(6)	0.5(4)
C(2)-C(1)-C(6)-C(5)	0.0(4)
Cl(1)-C(1)-C(6)-C(5)	-177.89(19)
C(2)-C(1)-C(6)-C(7)	-179.7(2)
Cl(1)-C(1)-C(6)-C(7)	2.4(3)
C(4)-C(5)-C(6)-C(1)	-0.7(4)
C(4)-C(5)-C(6)-C(7)	179.0(2)
C(1)-C(6)-C(7)-C(8)	-136.0(3)
C(5)-C(6)-C(7)-C(8)	44.3(3)
C(1)-C(6)-C(7)-C(18)	49.6(4)
C(5)-C(6)-C(7)-C(18)	-130.1(3)
C(18)-C(7)-C(8)-C(9)	0.2(3)
C(6)-C(7)-C(8)-C(9)	-174.4(2)
C(7)-C(8)-C(9)-O(1)	179.9(2)
C(7)-C(8)-C(9)-C(16)	1.1(4)
O(1)-C(10)-C(11)-C(12)	-179.8(2)
C(15)-C(10)-C(11)-C(12)	-1.0(4)
C(10)-C(11)-C(12)-C(13)	0.9(4)
C(11)-C(12)-C(13)-C(14)	-0.2(4)
C(12)-C(13)-C(14)-C(15)	-0.5(4)
C(11)-C(10)-C(15)-C(14)	0.3(4)
O(1)-C(10)-C(15)-C(14)	179.3(2)
C(11)-C(10)-C(15)-C(16)	-179.1(2)
O(1)-C(10)-C(15)-C(16)	-0.1(3)
C(13)-C(14)-C(15)-C(10)	0.5(3)
C(13)-C(14)-C(15)-C(16)	179.6(3)
C(8)-C(9)-C(16)-C(17)	-1.5(4)
O(1)-C(9)-C(16)-C(17)	179.6(2)
C(8)-C(9)-C(16)-C(15)	177.7(2)
O(1)-C(9)-C(16)-C(15)	-1.2(3)
C(10)-C(15)-C(16)-C(9)	0.7(3)
C(14)-C(15)-C(16)-C(9)	-178.4(3)
C(10)-C(15)-C(16)-C(17)	179.8(3)

C(14)-C(15)-C(16)-C(17)	0.6(5)
C(9)-C(16)-C(17)-C(18)	0.7(3)
C(15)-C(16)-C(17)-C(18)	-178.3(3)
C(16)-C(17)-C(18)-C(7)	0.5(4)
C(8)-C(7)-C(18)-C(17)	-1.0(4)
C(6)-C(7)-C(18)-C(17)	173.3(2)
C(8)-C(9)-O(1)-C(10)	-177.8(2)
C(16)-C(9)-O(1)-C(10)	1.2(3)
C(11)-C(10)-O(1)-C(9)	178.4(2)
C(15)-C(10)-O(1)-C(9)	-0.6(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for jwdml220324 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

22

Table 1. Crystal data and structure refinement for **22**.

Identification code	jwdtst220422
Empirical formula	C19 H11 F3 O
Formula weight	312.28
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.6217(3) A alpha = 89.6190(10) deg. b = 10.1702(3) A beta = 78.1910(10) deg. c = 14.7670(5) A gamma = 83.7530(10) deg.
Volume	1405.86(8) A^3
Z, Calculated density	4, 1.475 Mg/m^3
Absorption coefficient	0.117 mm^-1
F(000)	640
Crystal size	0.250 x 0.220 x 0.200 mm
Theta range for data collection	2.015 to 29.176 deg.
Limiting indices	-13<=h<=13, -13<=k<=13, -20<=l<=20
Reflections collected / unique	84490 / 7592 [R(int) = 0.0283]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.7185
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7592 / 0 / 415

Goodness-of-fit on F^2 1.042

Final R indices [I>2sigma(I)] R1 = 0.0383, wR2 = 0.1050

R indices (all data) R1 = 0.0423, wR2 = 0.1093

Extinction coefficient n/a

Largest diff. peak and hole 0.426 and -0.403 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for jwdtst220422. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	1908(1)	1632(1)	3928(1)	19(1)
C(2)	1662(1)	3011(1)	3918(1)	23(1)
C(3)	1572(1)	3759(1)	4717(1)	29(1)
C(4)	1705(1)	3141(1)	5541(1)	31(1)
C(5)	1931(1)	1772(1)	5564(1)	29(1)
C(6)	2038(1)	1022(1)	4763(1)	23(1)
C(7)	1955(1)	828(1)	3086(1)	20(1)
C(8)	1195(1)	-278(1)	3161(1)	25(1)
C(9)	1148(1)	-1063(1)	2399(1)	30(1)
C(10)	1881(1)	-788(1)	1518(1)	29(1)
C(11)	2646(1)	297(1)	1452(1)	24(1)
C(12)	4091(1)	1748(1)	854(1)	23(1)
C(13)	5015(1)	2416(1)	218(1)	26(1)
C(14)	5540(1)	3495(1)	549(1)	25(1)
C(15)	5146(1)	3859(1)	1486(1)	21(1)
C(16)	4230(1)	3162(1)	2120(1)	20(1)
C(17)	3671(1)	2087(1)	1799(1)	20(1)
C(18)	2708(1)	1120(1)	2197(1)	20(1)
C(19)	5643(1)	5077(1)	1819(1)	25(1)
C(20)	6710(1)	1981(1)	3979(1)	20(1)
C(21)	8008(1)	2128(1)	4235(1)	21(1)
C(22)	8032(1)	2736(1)	5069(1)	24(1)
C(23)	6762(1)	3234(1)	5654(1)	31(1)
C(24)	5471(1)	3130(1)	5393(1)	34(1)
C(25)	5442(1)	2502(1)	4565(1)	26(1)
C(26)	6687(1)	1173(1)	3151(1)	19(1)

C(27)	5773(1)	179(1)	3232(1)	23(1)
C(28)	5785(1)	-697(1)	2504(1)	26(1)
C(29)	6716(1)	-618(1)	1657(1)	27(1)
C(30)	7599(1)	384(1)	1579(1)	23(1)
C(31)	9173(1)	1718(1)	967(1)	23(1)
C(32)	10161(1)	2310(1)	324(1)	27(1)
C(33)	10617(1)	3460(1)	607(1)	25(1)
C(34)	10087(1)	3972(1)	1504(1)	21(1)
C(35)	9111(1)	3348(1)	2149(1)	20(1)
C(36)	8643(1)	2188(1)	1877(1)	20(1)
C(37)	7615(1)	1285(1)	2289(1)	20(1)
C(38)	10497(1)	5281(1)	1756(1)	24(1)
O(1)	3479(1)	669(1)	632(1)	27(1)
O(2)	8560(1)	621(1)	776(1)	26(1)
F(1)	5966(1)	4936(1)	2660(1)	32(1)
F(2)	6801(1)	5453(1)	1249(1)	37(1)
F(3)	4629(1)	6124(1)	1898(1)	36(1)
F(4)	10713(1)	5337(1)	2621(1)	39(1)
F(5)	11670(1)	5621(1)	1202(1)	54(1)
F(6)	9471(1)	6275(1)	1720(1)	45(1)

Table 3. Bond lengths [A] and angles [deg] for jwdtst220422.

C(1)-C(2)	1.3966(13)
C(1)-C(6)	1.3996(13)
C(1)-C(7)	1.4822(13)
C(2)-C(3)	1.3897(15)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3893(18)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3872(17)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3906(15)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.3992(13)
C(7)-C(18)	1.4105(13)
C(8)-C(9)	1.3956(15)
C(8)-H(8)	0.9500
C(9)-C(10)	1.3893(16)
C(9)-H(9)	0.9500
C(10)-C(11)	1.3843(14)
C(10)-H(10)	0.9500
C(11)-O(1)	1.3830(12)
C(11)-C(18)	1.4013(14)

C(12)-O(1)	1.3721(12)
C(12)-C(13)	1.3840(14)
C(12)-C(17)	1.4052(13)
C(13)-C(14)	1.3871(15)
C(13)-H(13)	0.9500
C(14)-C(15)	1.4000(14)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3938(12)
C(15)-C(19)	1.4964(14)
C(16)-C(17)	1.3962(13)
C(16)-H(16)	0.9500
C(17)-C(18)	1.4625(13)
C(19)-F(2)	1.3419(11)
C(19)-F(1)	1.3432(12)
C(19)-F(3)	1.3516(13)
C(20)-C(25)	1.3967(13)
C(20)-C(21)	1.3998(13)
C(20)-C(26)	1.4828(13)
C(21)-C(22)	1.3875(14)
C(21)-H(21)	0.9500
C(22)-C(23)	1.3909(15)
C(22)-H(22)	0.9500
C(23)-C(24)	1.3889(16)
C(23)-H(23)	0.9500
C(24)-C(25)	1.3902(15)
C(24)-H(24)	0.9500
C(25)-H(25)	0.9500
C(26)-C(27)	1.3999(13)
C(26)-C(37)	1.4096(13)
C(27)-C(28)	1.3979(15)
C(27)-H(27)	0.9500
C(28)-C(29)	1.3893(15)
C(28)-H(28)	0.9500
C(29)-C(30)	1.3850(14)
C(29)-H(29)	0.9500
C(30)-O(2)	1.3840(12)
C(30)-C(37)	1.4009(13)
C(31)-O(2)	1.3735(12)
C(31)-C(32)	1.3838(14)
C(31)-C(36)	1.4043(13)
C(32)-C(33)	1.3880(15)
C(32)-H(32)	0.9500
C(33)-C(34)	1.4008(14)
C(33)-H(33)	0.9500
C(34)-C(35)	1.3955(13)
C(34)-C(38)	1.4984(14)
C(35)-C(36)	1.3970(13)

C(35)-H(35)	0.9500
C(36)-C(37)	1.4611(13)
C(38)-F(5)	1.3294(12)
C(38)-F(4)	1.3387(12)
C(38)-F(6)	1.3428(13)

C(2)-C(1)-C(6)	118.37(9)
C(2)-C(1)-C(7)	120.92(9)
C(6)-C(1)-C(7)	120.63(9)
C(3)-C(2)-C(1)	120.77(10)
C(3)-C(2)-H(2)	119.6
C(1)-C(2)-H(2)	119.6
C(4)-C(3)-C(2)	120.28(10)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	119.59(10)
C(5)-C(4)-H(4)	120.2
C(3)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	120.20(10)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(5)-C(6)-C(1)	120.78(10)
C(5)-C(6)-H(6)	119.6
C(1)-C(6)-H(6)	119.6
C(8)-C(7)-C(18)	117.09(9)
C(8)-C(7)-C(1)	118.95(8)
C(18)-C(7)-C(1)	123.95(8)
C(9)-C(8)-C(7)	122.56(9)
C(9)-C(8)-H(8)	118.7
C(7)-C(8)-H(8)	118.7
C(10)-C(9)-C(8)	121.11(10)
C(10)-C(9)-H(9)	119.4
C(8)-C(9)-H(9)	119.4
C(11)-C(10)-C(9)	115.93(10)
C(11)-C(10)-H(10)	122.0
C(9)-C(10)-H(10)	122.0
O(1)-C(11)-C(10)	123.05(9)
O(1)-C(11)-C(18)	112.11(8)
C(10)-C(11)-C(18)	124.82(10)
O(1)-C(12)-C(13)	123.70(9)
O(1)-C(12)-C(17)	112.03(8)
C(13)-C(12)-C(17)	124.27(10)
C(12)-C(13)-C(14)	116.88(9)
C(12)-C(13)-H(13)	121.6
C(14)-C(13)-H(13)	121.6
C(13)-C(14)-C(15)	120.34(9)
C(13)-C(14)-H(14)	119.8

C(15)-C(14)-H(14)	119.8
C(16)-C(15)-C(14)	122.04(9)
C(16)-C(15)-C(19)	118.22(9)
C(14)-C(15)-C(19)	119.64(9)
C(15)-C(16)-C(17)	118.51(9)
C(15)-C(16)-H(16)	120.7
C(17)-C(16)-H(16)	120.7
C(16)-C(17)-C(12)	117.94(9)
C(16)-C(17)-C(18)	136.76(9)
C(12)-C(17)-C(18)	105.29(8)
C(11)-C(18)-C(7)	118.49(9)
C(11)-C(18)-C(17)	104.95(8)
C(7)-C(18)-C(17)	136.49(9)
F(2)-C(19)-F(1)	106.90(8)
F(2)-C(19)-F(3)	106.00(8)
F(1)-C(19)-F(3)	105.72(9)
F(2)-C(19)-C(15)	113.07(9)
F(1)-C(19)-C(15)	112.77(8)
F(3)-C(19)-C(15)	111.84(9)
C(25)-C(20)-C(21)	118.63(9)
C(25)-C(20)-C(26)	120.95(8)
C(21)-C(20)-C(26)	120.14(8)
C(22)-C(21)-C(20)	120.64(9)
C(22)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
C(21)-C(22)-C(23)	120.28(9)
C(21)-C(22)-H(22)	119.9
C(23)-C(22)-H(22)	119.9
C(24)-C(23)-C(22)	119.48(10)
C(24)-C(23)-H(23)	120.3
C(22)-C(23)-H(23)	120.3
C(23)-C(24)-C(25)	120.39(10)
C(23)-C(24)-H(24)	119.8
C(25)-C(24)-H(24)	119.8
C(24)-C(25)-C(20)	120.53(9)
C(24)-C(25)-H(25)	119.7
C(20)-C(25)-H(25)	119.7
C(27)-C(26)-C(37)	117.22(9)
C(27)-C(26)-C(20)	119.21(8)
C(37)-C(26)-C(20)	123.42(8)
C(28)-C(27)-C(26)	122.31(9)
C(28)-C(27)-H(27)	118.8
C(26)-C(27)-H(27)	118.8
C(29)-C(28)-C(27)	121.14(9)
C(29)-C(28)-H(28)	119.4
C(27)-C(28)-H(28)	119.4
C(30)-C(29)-C(28)	116.07(10)

C(30)-C(29)-H(29)	122.0
C(28)-C(29)-H(29)	122.0
O(2)-C(30)-C(29)	123.43(9)
O(2)-C(30)-C(37)	111.95(8)
C(29)-C(30)-C(37)	124.61(9)
O(2)-C(31)-C(32)	123.71(9)
O(2)-C(31)-C(36)	112.02(8)
C(32)-C(31)-C(36)	124.24(9)
C(31)-C(32)-C(33)	116.77(9)
C(31)-C(32)-H(32)	121.6
C(33)-C(32)-H(32)	121.6
C(32)-C(33)-C(34)	120.48(9)
C(32)-C(33)-H(33)	119.8
C(34)-C(33)-H(33)	119.8
C(35)-C(34)-C(33)	122.00(9)
C(35)-C(34)-C(38)	118.95(9)
C(33)-C(34)-C(38)	118.90(9)
C(34)-C(35)-C(36)	118.29(9)
C(34)-C(35)-H(35)	120.9
C(36)-C(35)-H(35)	120.9
C(35)-C(36)-C(31)	118.20(9)
C(35)-C(36)-C(37)	136.43(9)
C(31)-C(36)-C(37)	105.27(8)
C(30)-C(37)-C(26)	118.63(9)
C(30)-C(37)-C(36)	105.11(8)
C(26)-C(37)-C(36)	136.20(9)
F(5)-C(38)-F(4)	106.76(9)
F(5)-C(38)-F(6)	105.83(9)
F(4)-C(38)-F(6)	104.49(9)
F(5)-C(38)-C(34)	113.47(9)
F(4)-C(38)-C(34)	113.40(8)
F(6)-C(38)-C(34)	112.17(9)
C(12)-O(1)-C(11)	105.61(8)
C(31)-O(2)-C(30)	105.60(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for jwdtst220422.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	14(1)	20(1)	22(1)	2(1)	-1(1)	-5(1)
C(2)	16(1)	21(1)	29(1)	4(1)	2(1)	-4(1)
C(3)	19(1)	24(1)	40(1)	-6(1)	4(1)	-7(1)
C(4)	18(1)	43(1)	31(1)	-11(1)	2(1)	-9(1)
C(5)	19(1)	44(1)	23(1)	3(1)	-2(1)	-9(1)
C(6)	18(1)	25(1)	26(1)	6(1)	-2(1)	-6(1)
C(7)	16(1)	19(1)	24(1)	2(1)	-2(1)	-4(1)
C(8)	22(1)	22(1)	29(1)	2(1)	-1(1)	-8(1)
C(9)	28(1)	25(1)	36(1)	-2(1)	-3(1)	-11(1)
C(10)	29(1)	28(1)	31(1)	-5(1)	-4(1)	-9(1)
C(11)	22(1)	26(1)	23(1)	0(1)	-2(1)	-5(1)
C(12)	23(1)	24(1)	22(1)	1(1)	-3(1)	-4(1)
C(13)	28(1)	30(1)	19(1)	2(1)	1(1)	-4(1)
C(14)	23(1)	27(1)	22(1)	6(1)	2(1)	-4(1)
C(15)	18(1)	22(1)	22(1)	5(1)	-1(1)	-4(1)
C(16)	18(1)	22(1)	19(1)	4(1)	-1(1)	-4(1)
C(17)	17(1)	21(1)	19(1)	4(1)	-2(1)	-3(1)
C(18)	17(1)	20(1)	22(1)	2(1)	-4(1)	-3(1)
C(19)	22(1)	27(1)	24(1)	5(1)	0(1)	-8(1)
C(20)	19(1)	20(1)	20(1)	3(1)	-2(1)	-6(1)
C(21)	18(1)	20(1)	25(1)	4(1)	-2(1)	-6(1)
C(22)	22(1)	25(1)	27(1)	3(1)	-6(1)	-11(1)
C(23)	30(1)	38(1)	24(1)	-5(1)	-1(1)	-15(1)
C(24)	22(1)	47(1)	29(1)	-10(1)	4(1)	-11(1)
C(25)	18(1)	35(1)	26(1)	-3(1)	0(1)	-8(1)
C(26)	16(1)	20(1)	22(1)	2(1)	-4(1)	-3(1)
C(27)	19(1)	24(1)	27(1)	4(1)	-4(1)	-7(1)
C(28)	24(1)	23(1)	33(1)	2(1)	-9(1)	-8(1)
C(29)	28(1)	24(1)	30(1)	-2(1)	-7(1)	-7(1)
C(30)	23(1)	22(1)	23(1)	0(1)	-3(1)	-3(1)
C(31)	24(1)	21(1)	23(1)	0(1)	-2(1)	-3(1)
C(32)	29(1)	27(1)	21(1)	-1(1)	3(1)	-3(1)
C(33)	24(1)	26(1)	23(1)	5(1)	2(1)	-4(1)
C(34)	19(1)	21(1)	23(1)	4(1)	-2(1)	-4(1)
C(35)	19(1)	20(1)	20(1)	2(1)	-1(1)	-3(1)
C(36)	18(1)	20(1)	21(1)	2(1)	-1(1)	-2(1)
C(37)	18(1)	19(1)	22(1)	2(1)	-3(1)	-3(1)
C(38)	25(1)	24(1)	24(1)	7(1)	-2(1)	-8(1)

O(1)	29(1)	29(1)	22(1)	-2(1)	-2(1)	-8(1)
O(2)	30(1)	25(1)	23(1)	-3(1)	0(1)	-7(1)
F(1)	38(1)	35(1)	26(1)	3(1)	-7(1)	-14(1)
F(2)	33(1)	45(1)	33(1)	4(1)	5(1)	-23(1)
F(3)	37(1)	22(1)	48(1)	2(1)	-7(1)	-3(1)
F(4)	63(1)	28(1)	32(1)	7(1)	-20(1)	-15(1)
F(5)	51(1)	57(1)	48(1)	-11(1)	18(1)	-38(1)
F(6)	50(1)	20(1)	74(1)	4(1)	-32(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for jwdtst220422.

	x	y	z	U(eq)
H(2)	1555	3442	3360	27
H(3)	1419	4696	4698	35
H(4)	1641	3654	6087	37
H(5)	2012	1345	6127	34
H(6)	2203	86	4783	27
H(8)	692	-504	3754	30
H(9)	605	-1797	2483	36
H(10)	1857	-1313	992	35
H(13)	5278	2149	-414	32
H(14)	6171	3989	136	30
H(16)	3992	3414	2756	24
H(21)	8881	1808	3834	25
H(22)	8919	2813	5241	29
H(23)	6778	3642	6228	37
H(24)	4602	3490	5782	40
H(25)	4552	2427	4396	32
H(27)	5120	96	3802	28
H(28)	5146	-1358	2590	31
H(29)	6746	-1216	1160	32
H(32)	10511	1948	-281	32
H(33)	11293	3903	189	30
H(35)	8774	3702	2758	24

Table 6. Torsion angles [deg] for jwdtst220422.

C(6)-C(1)-C(2)-C(3)	1.01(14)
C(7)-C(1)-C(2)-C(3)	177.88(9)
C(1)-C(2)-C(3)-C(4)	-0.96(15)
C(2)-C(3)-C(4)-C(5)	0.11(15)
C(3)-C(4)-C(5)-C(6)	0.67(15)
C(4)-C(5)-C(6)-C(1)	-0.62(15)
C(2)-C(1)-C(6)-C(5)	-0.22(14)
C(7)-C(1)-C(6)-C(5)	-177.10(9)
C(2)-C(1)-C(7)-C(8)	-133.26(10)
C(6)-C(1)-C(7)-C(8)	43.55(13)
C(2)-C(1)-C(7)-C(18)	45.71(13)
C(6)-C(1)-C(7)-C(18)	-137.49(10)
C(18)-C(7)-C(8)-C(9)	-1.06(15)
C(1)-C(7)-C(8)-C(9)	177.98(10)
C(7)-C(8)-C(9)-C(10)	0.93(17)
C(8)-C(9)-C(10)-C(11)	0.05(17)
C(9)-C(10)-C(11)-O(1)	177.26(10)
C(9)-C(10)-C(11)-C(18)	-0.88(17)
O(1)-C(12)-C(13)-C(14)	179.63(9)
C(17)-C(12)-C(13)-C(14)	-0.51(16)
C(12)-C(13)-C(14)-C(15)	0.58(15)
C(13)-C(14)-C(15)-C(16)	0.35(15)
C(13)-C(14)-C(15)-C(19)	-175.91(10)
C(14)-C(15)-C(16)-C(17)	-1.38(15)
C(19)-C(15)-C(16)-C(17)	174.93(9)
C(15)-C(16)-C(17)-C(12)	1.42(14)
C(15)-C(16)-C(17)-C(18)	-179.65(10)
O(1)-C(12)-C(17)-C(16)	179.37(8)
C(13)-C(12)-C(17)-C(16)	-0.51(15)
O(1)-C(12)-C(17)-C(18)	0.12(11)
C(13)-C(12)-C(17)-C(18)	-179.75(10)
O(1)-C(11)-C(18)-C(7)	-177.58(8)
C(10)-C(11)-C(18)-C(7)	0.73(16)
O(1)-C(11)-C(18)-C(17)	-0.12(11)
C(10)-C(11)-C(18)-C(17)	178.19(10)
C(8)-C(7)-C(18)-C(11)	0.25(14)
C(1)-C(7)-C(18)-C(11)	-178.73(9)
C(8)-C(7)-C(18)-C(17)	-176.18(10)
C(1)-C(7)-C(18)-C(17)	4.84(17)
C(16)-C(17)-C(18)-C(11)	-179.03(11)
C(12)-C(17)-C(18)-C(11)	0.00(10)
C(16)-C(17)-C(18)-C(7)	-2.3(2)
C(12)-C(17)-C(18)-C(7)	176.75(11)
C(16)-C(15)-C(19)-F(2)	162.29(9)

C(14)-C(15)-C(19)-F(2)	-21.30(14)
C(16)-C(15)-C(19)-F(1)	40.86(13)
C(14)-C(15)-C(19)-F(1)	-142.73(9)
C(16)-C(15)-C(19)-F(3)	-78.14(11)
C(14)-C(15)-C(19)-F(3)	98.27(11)
C(25)-C(20)-C(21)-C(22)	2.31(14)
C(26)-C(20)-C(21)-C(22)	-171.70(9)
C(20)-C(21)-C(22)-C(23)	-1.37(15)
C(21)-C(22)-C(23)-C(24)	-0.66(17)
C(22)-C(23)-C(24)-C(25)	1.72(19)
C(23)-C(24)-C(25)-C(20)	-0.75(18)
C(21)-C(20)-C(25)-C(24)	-1.26(16)
C(26)-C(20)-C(25)-C(24)	172.70(10)
C(25)-C(20)-C(26)-C(27)	-45.60(13)
C(21)-C(20)-C(26)-C(27)	128.27(10)
C(25)-C(20)-C(26)-C(37)	139.02(10)
C(21)-C(20)-C(26)-C(37)	-47.11(13)
C(37)-C(26)-C(27)-C(28)	1.51(14)
C(20)-C(26)-C(27)-C(28)	-174.16(9)
C(26)-C(27)-C(28)-C(29)	-0.09(16)
C(27)-C(28)-C(29)-C(30)	-1.00(16)
C(28)-C(29)-C(30)-O(2)	-178.29(10)
C(28)-C(29)-C(30)-C(37)	0.68(16)
O(2)-C(31)-C(32)-C(33)	176.19(10)
C(36)-C(31)-C(32)-C(33)	-1.58(16)
C(31)-C(32)-C(33)-C(34)	0.16(16)
C(32)-C(33)-C(34)-C(35)	1.11(16)
C(32)-C(33)-C(34)-C(38)	-174.31(10)
C(33)-C(34)-C(35)-C(36)	-1.00(15)
C(38)-C(34)-C(35)-C(36)	174.42(9)
C(34)-C(35)-C(36)-C(31)	-0.35(14)
C(34)-C(35)-C(36)-C(37)	-176.02(10)
O(2)-C(31)-C(36)-C(35)	-176.31(8)
C(32)-C(31)-C(36)-C(35)	1.69(16)
O(2)-C(31)-C(36)-C(37)	0.60(11)
C(32)-C(31)-C(36)-C(37)	178.60(10)
O(2)-C(30)-C(37)-C(26)	179.80(8)
C(29)-C(30)-C(37)-C(26)	0.73(15)
O(2)-C(30)-C(37)-C(36)	2.11(11)
C(29)-C(30)-C(37)-C(36)	-176.96(10)
C(27)-C(26)-C(37)-C(30)	-1.77(13)
C(20)-C(26)-C(37)-C(30)	173.69(9)
C(27)-C(26)-C(37)-C(36)	175.00(10)
C(20)-C(26)-C(37)-C(36)	-9.53(17)
C(35)-C(36)-C(37)-C(30)	174.46(11)
C(31)-C(36)-C(37)-C(30)	-1.59(10)
C(35)-C(36)-C(37)-C(26)	-2.6(2)

C(31)-C(36)-C(37)-C(26)	-178.66(11)
C(35)-C(34)-C(38)-F(5)	164.07(10)
C(33)-C(34)-C(38)-F(5)	-20.37(14)
C(35)-C(34)-C(38)-F(4)	42.03(13)
C(33)-C(34)-C(38)-F(4)	-142.41(10)
C(35)-C(34)-C(38)-F(6)	-76.06(12)
C(33)-C(34)-C(38)-F(6)	99.50(11)
C(13)-C(12)-O(1)-C(11)	179.68(10)
C(17)-C(12)-O(1)-C(11)	-0.20(11)
C(10)-C(11)-O(1)-C(12)	-178.15(10)
C(18)-C(11)-O(1)-C(12)	0.20(11)
C(32)-C(31)-O(2)-C(30)	-177.35(10)
C(36)-C(31)-O(2)-C(30)	0.66(11)
C(29)-C(30)-O(2)-C(31)	177.33(10)
C(37)-C(30)-O(2)-C(31)	-1.76(11)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for jwdtst220422 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

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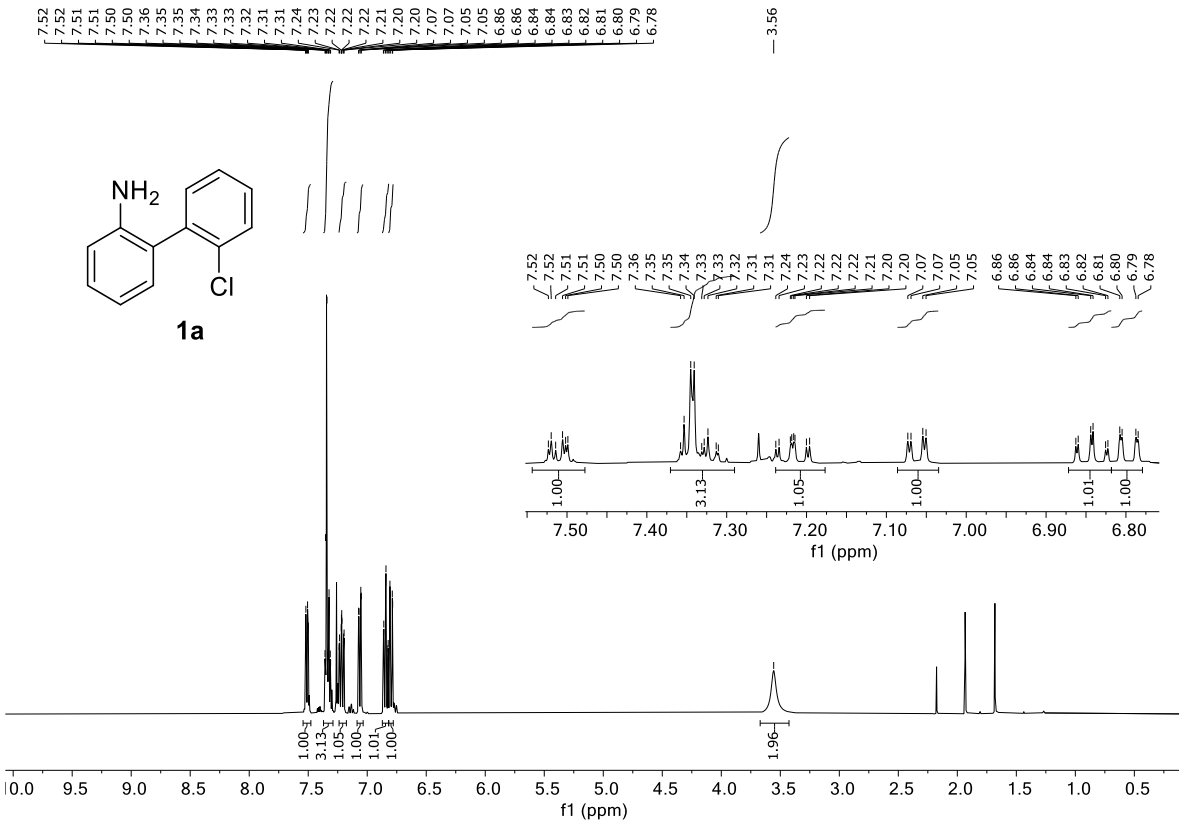
Copy of NMR spectra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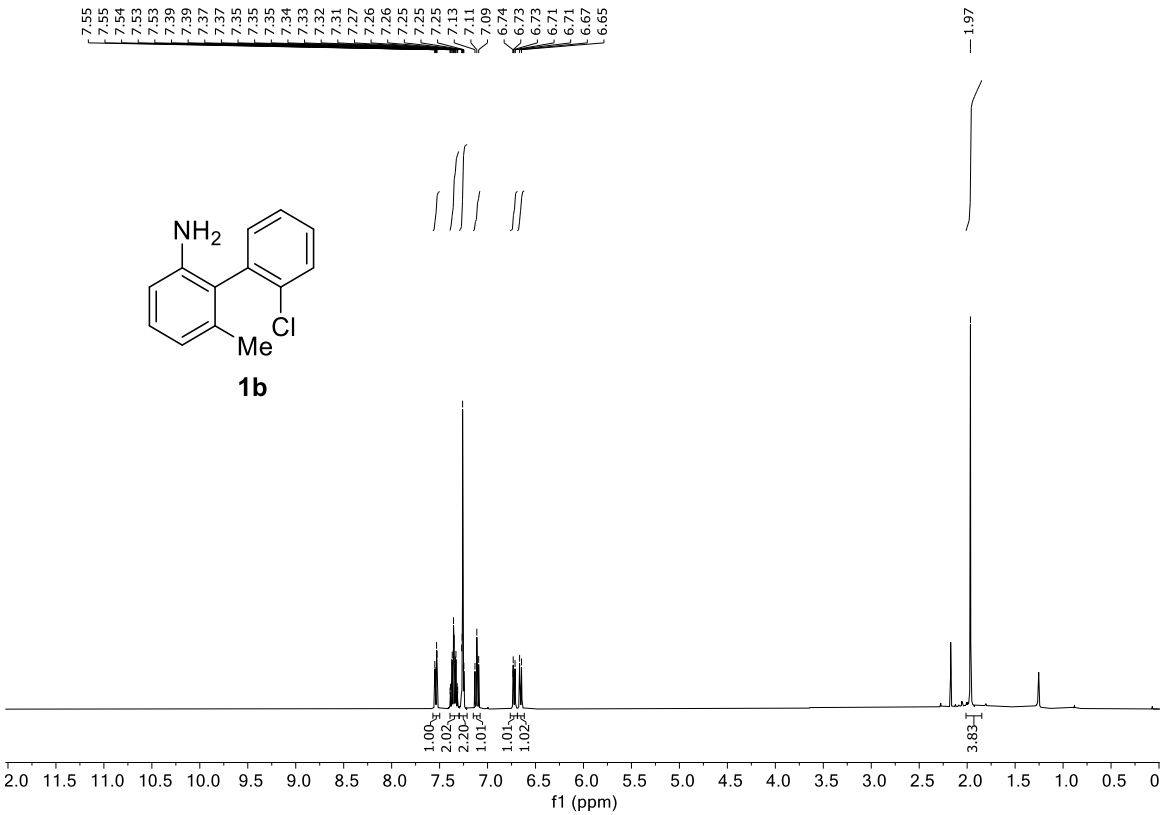
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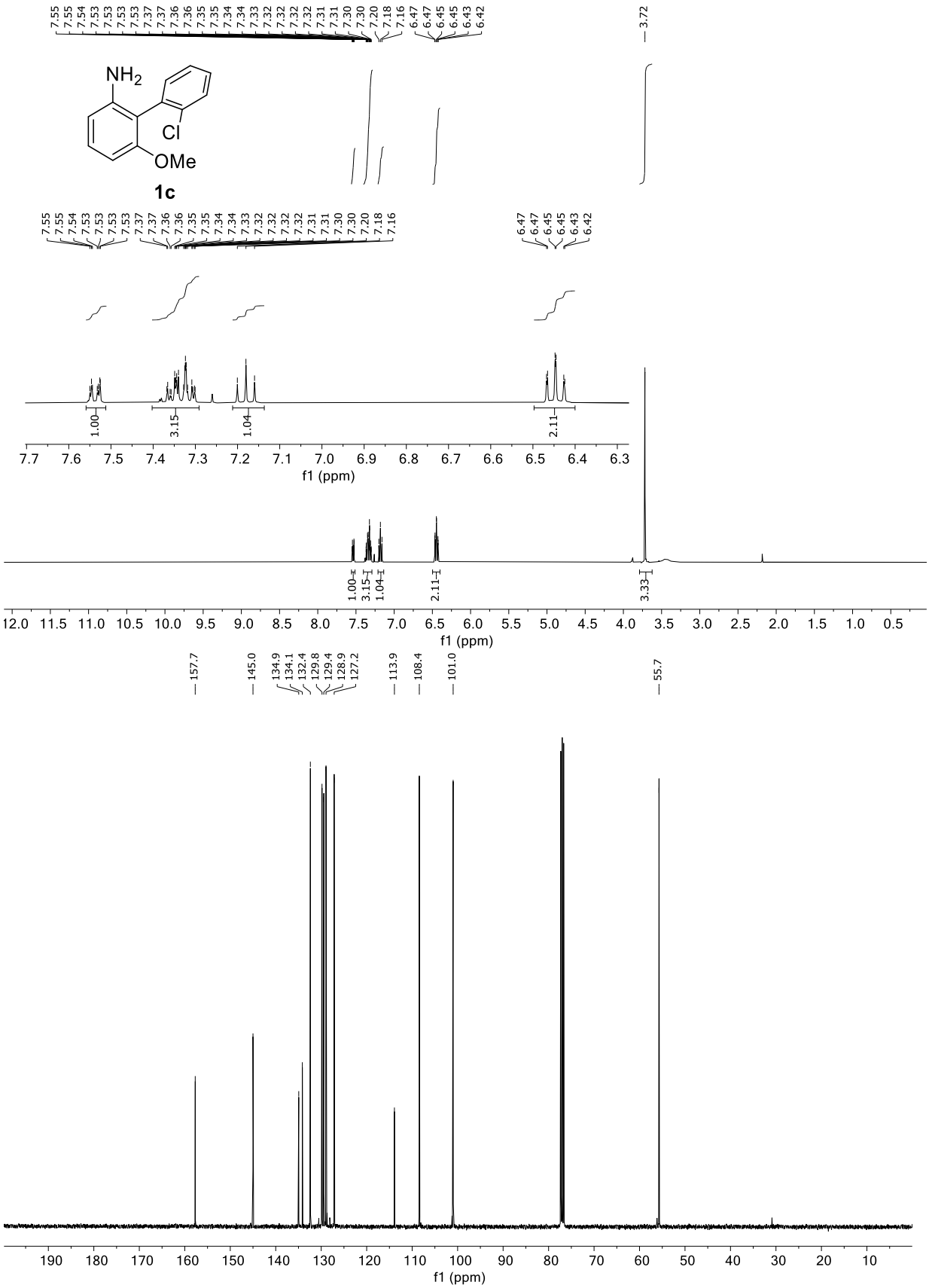
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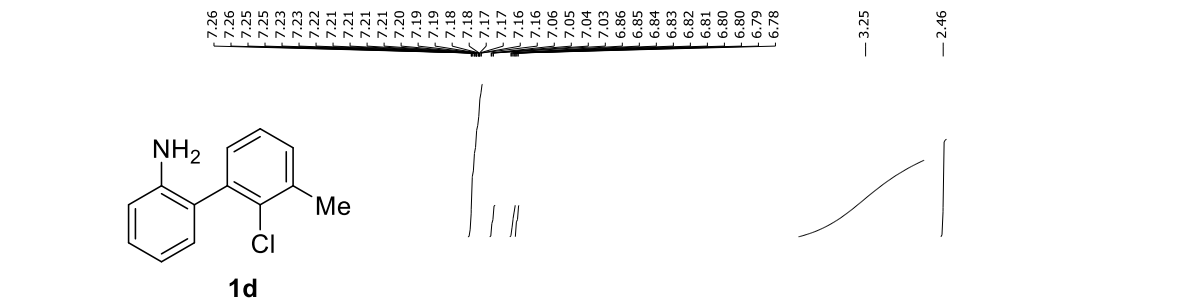
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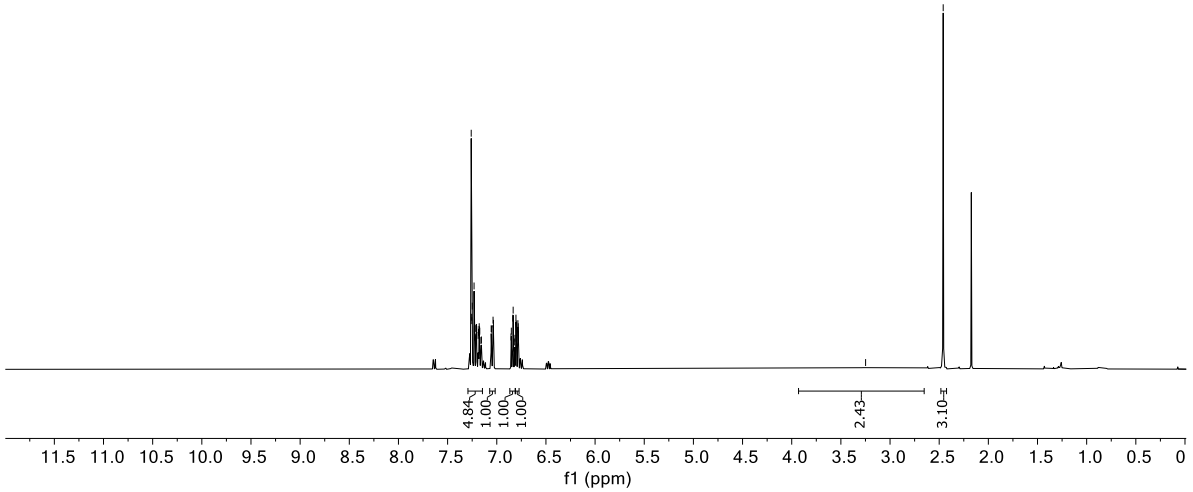
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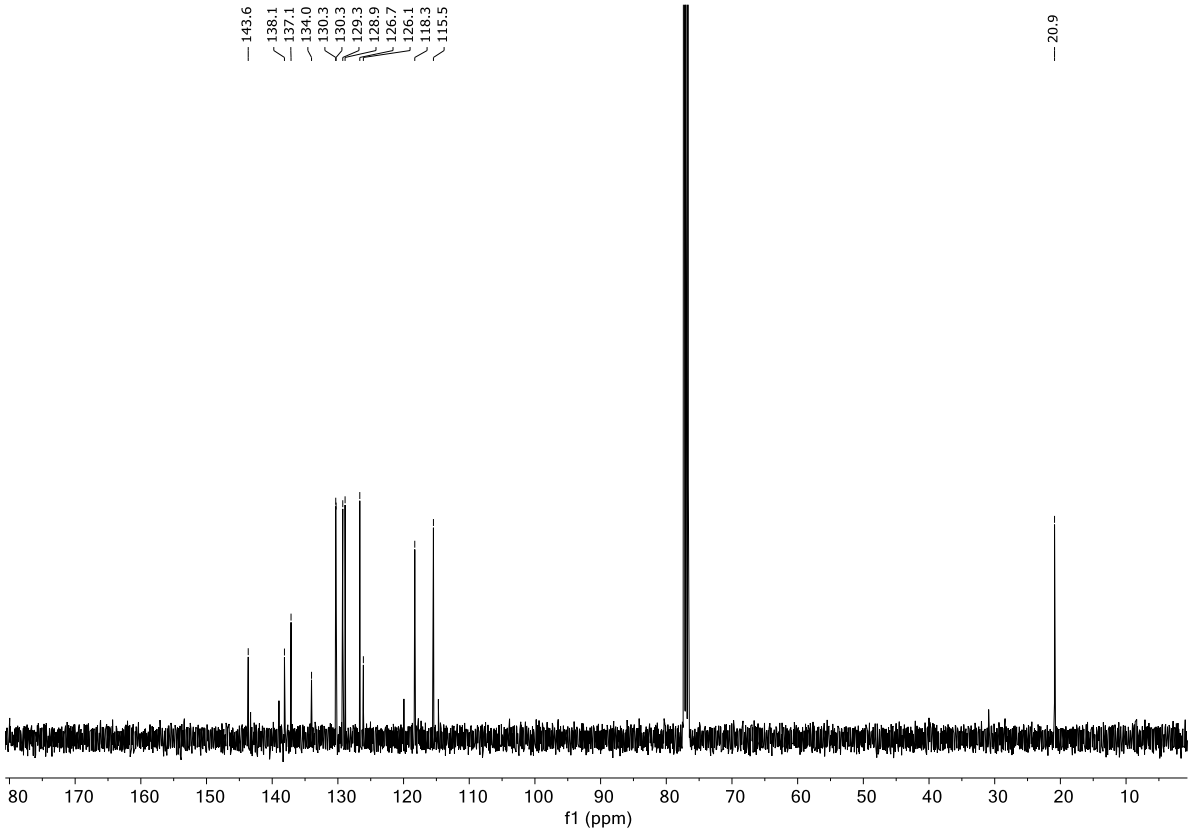
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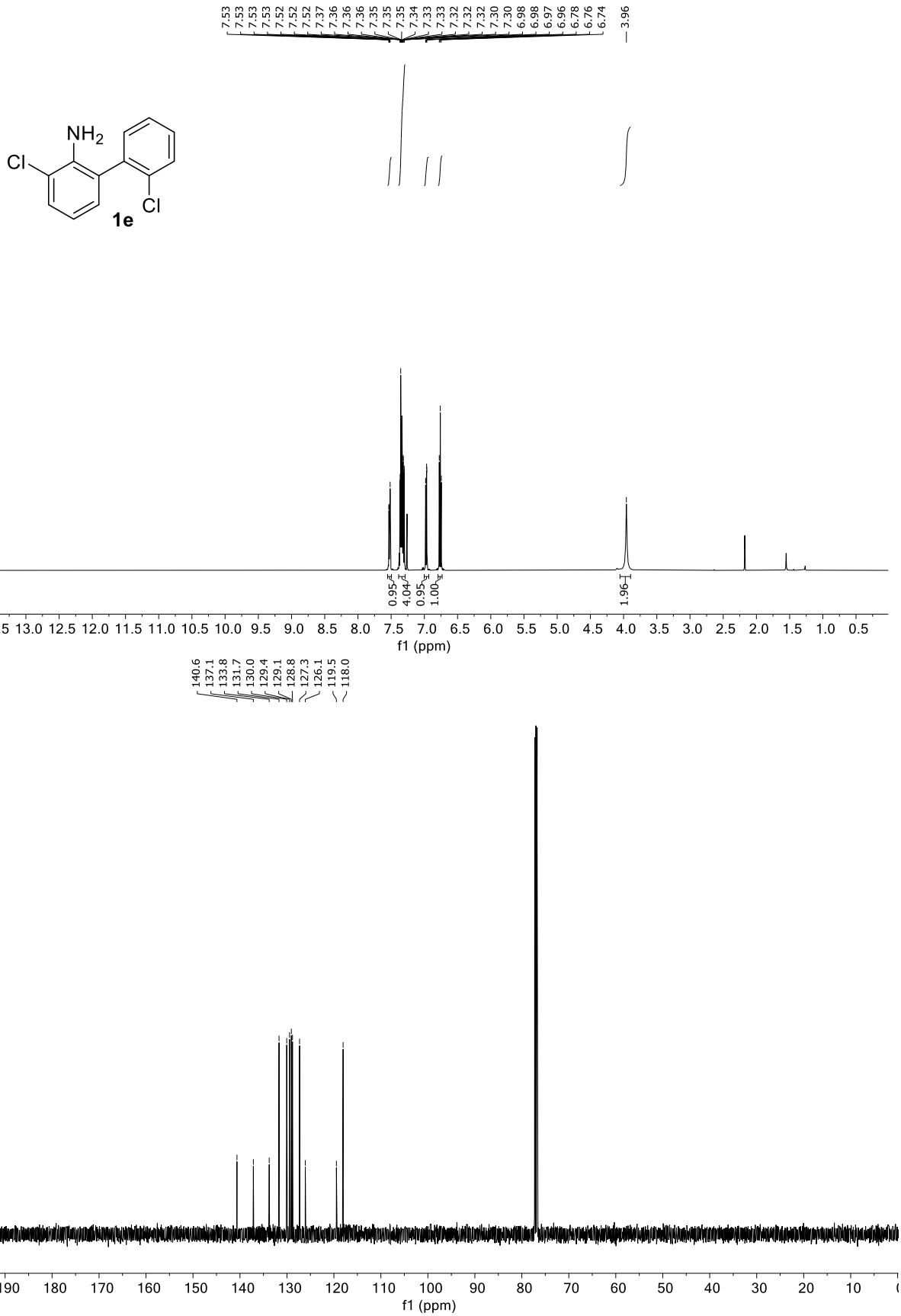
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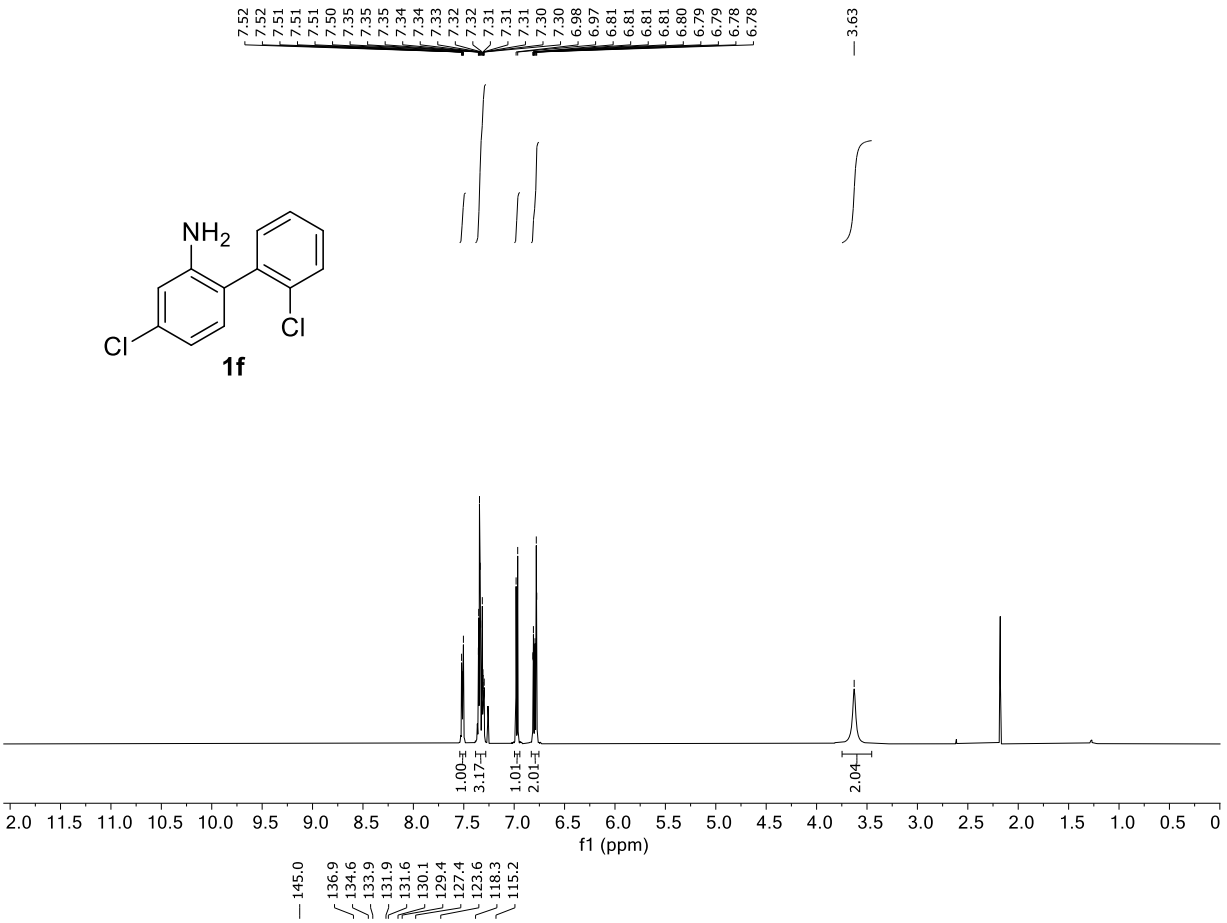
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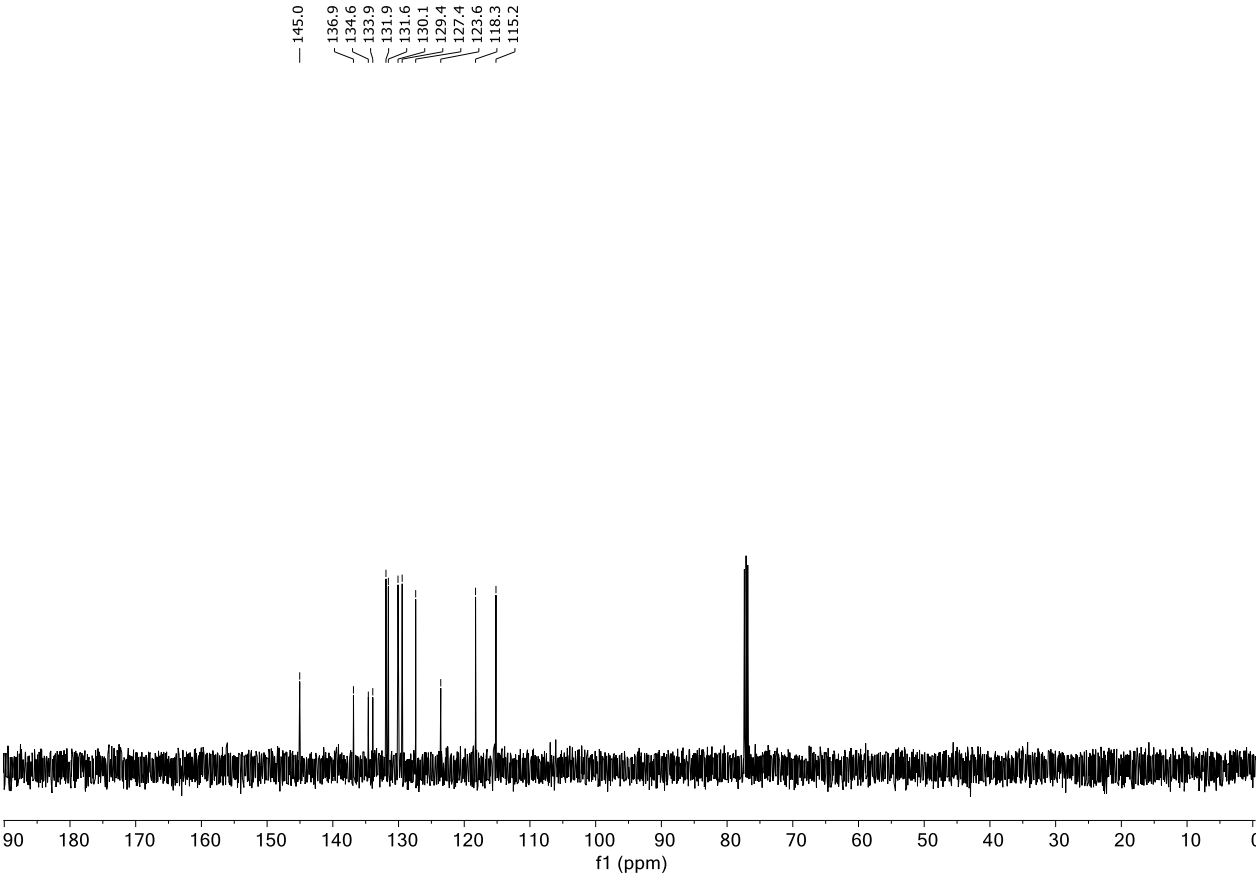
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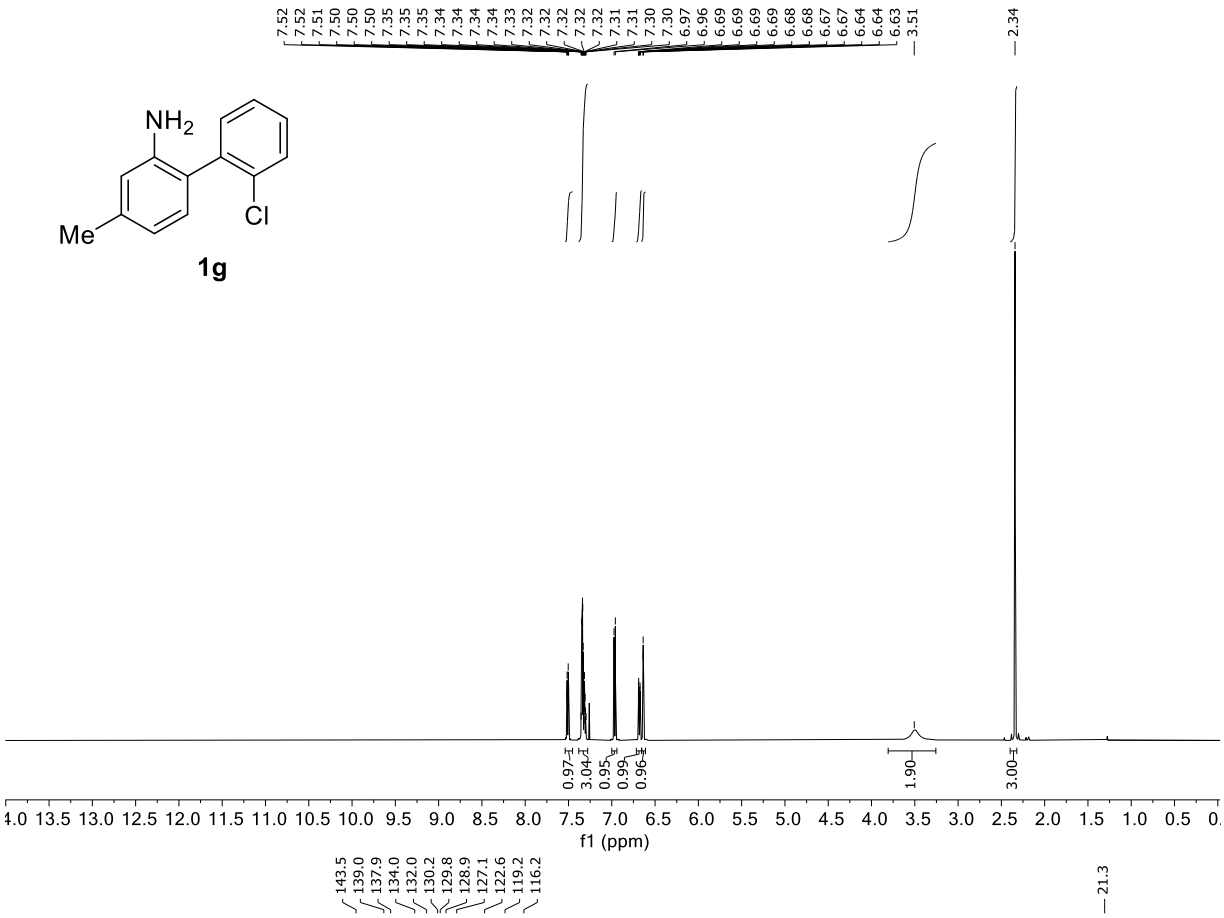
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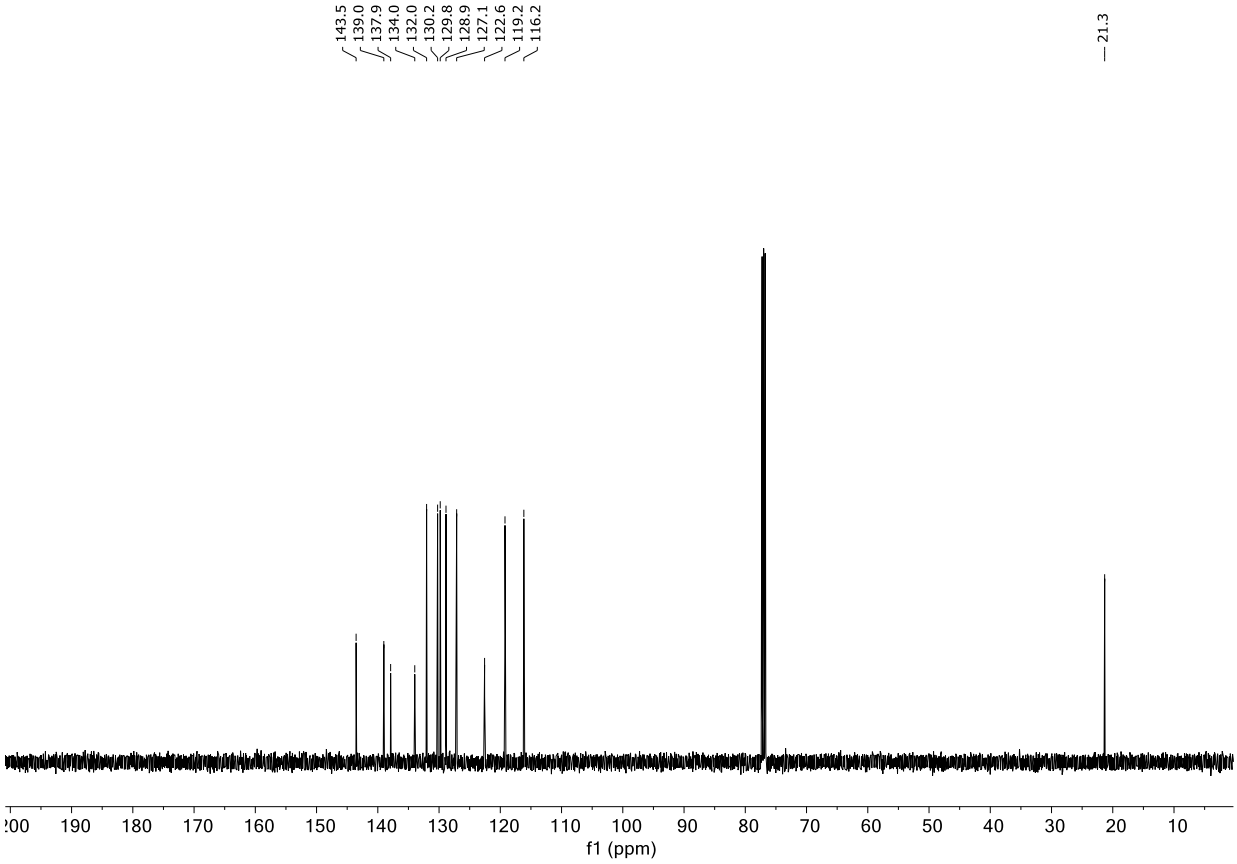
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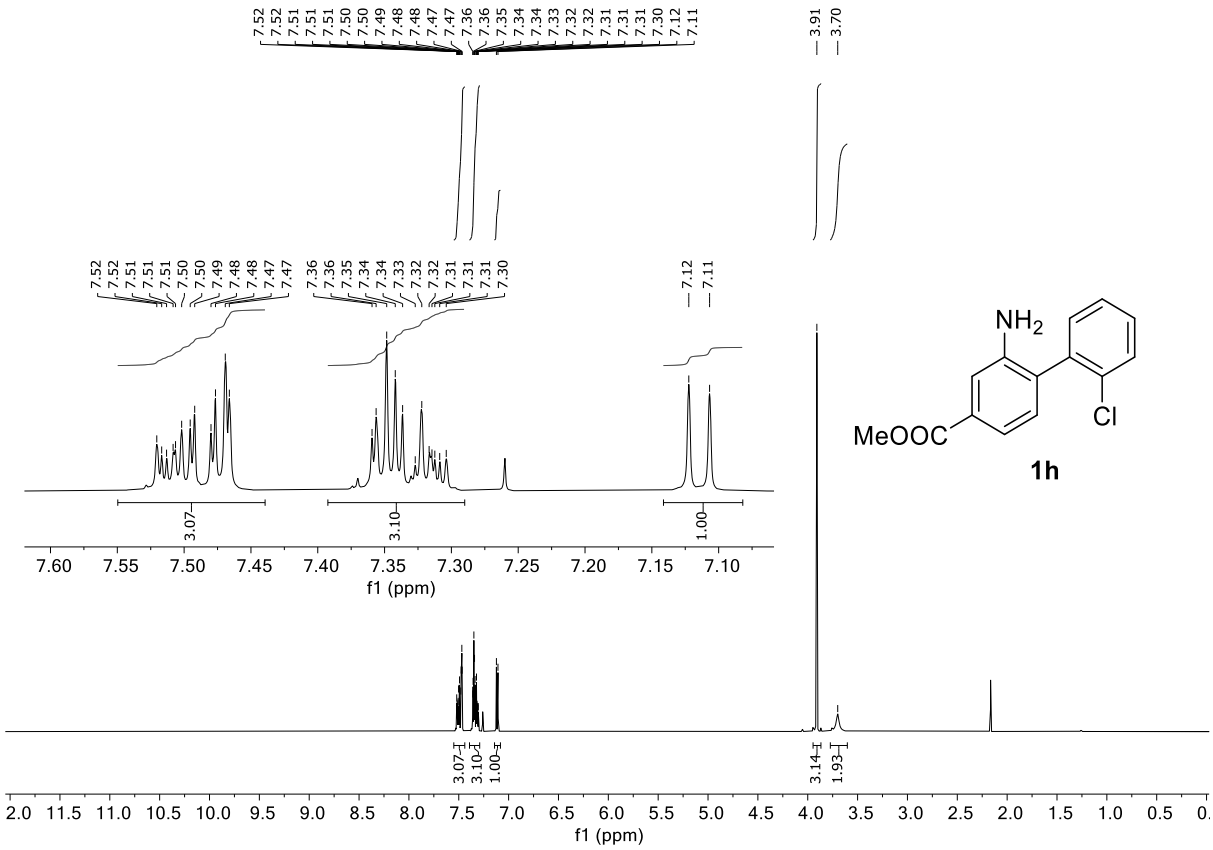
f1 (ppm)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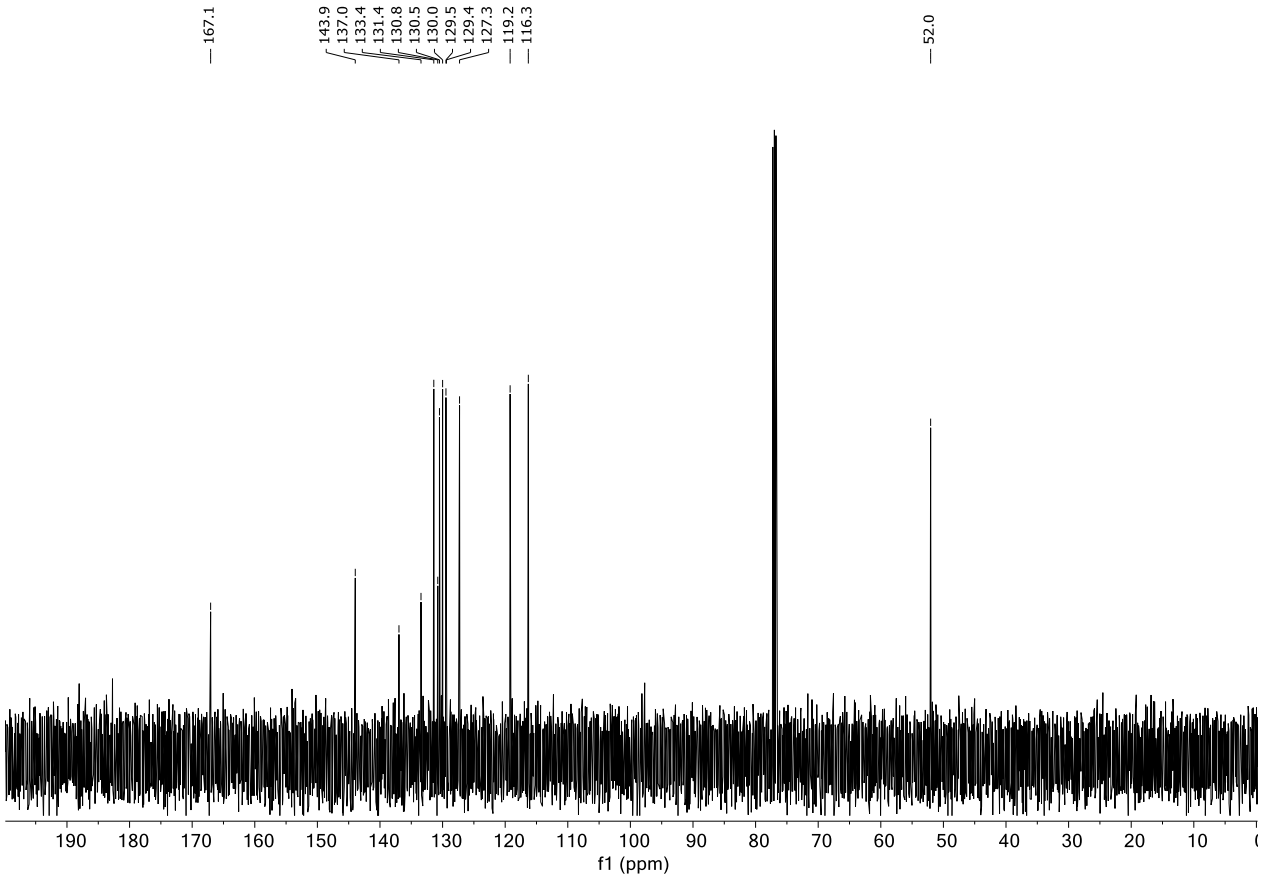
3.91 3.70
3.07
3.10
1.00
3.14
1.93
f1 (ppm)
NH2
Cl
MeOOC
1h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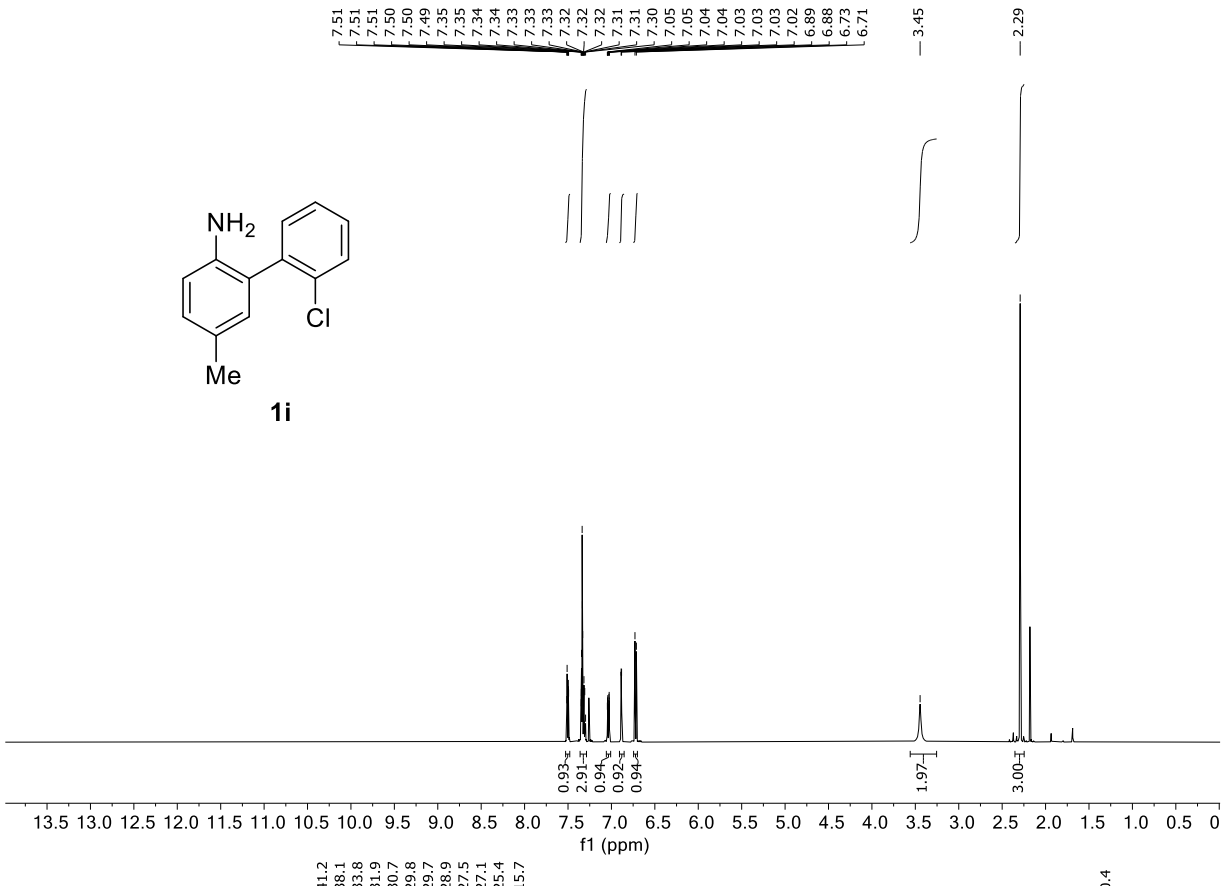
119.2 116.3
52.0
f1 (ppm)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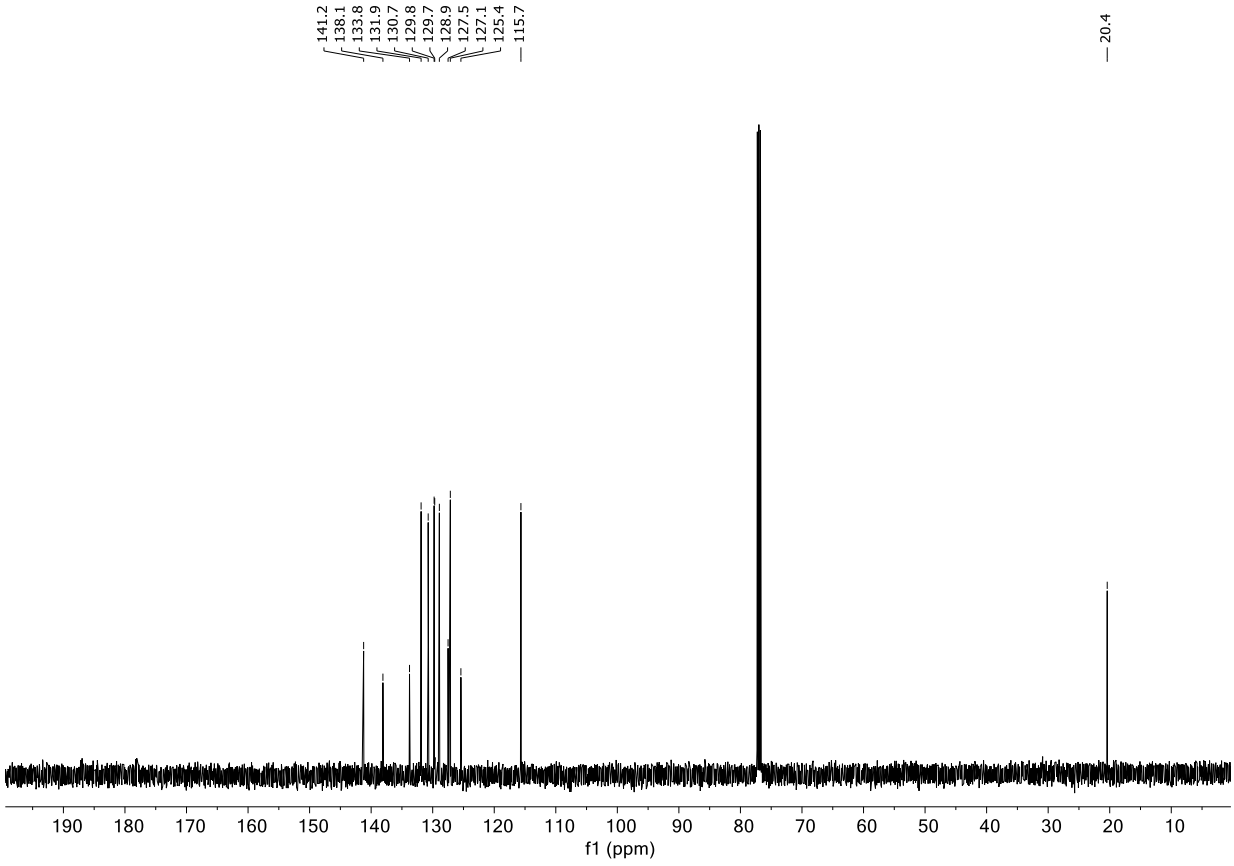
7.32
7.31
7.31
7.30
7.05
7.05
7.04
7.04
7.03
7.03
7.03
7.02
6.89
6.88
6.73
6.71
3.45
2.29
NH2
Cl
Me
1i
0.93
2.91
0.94
0.92
0.94
1.97
3.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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138.1
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129.8
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128.9
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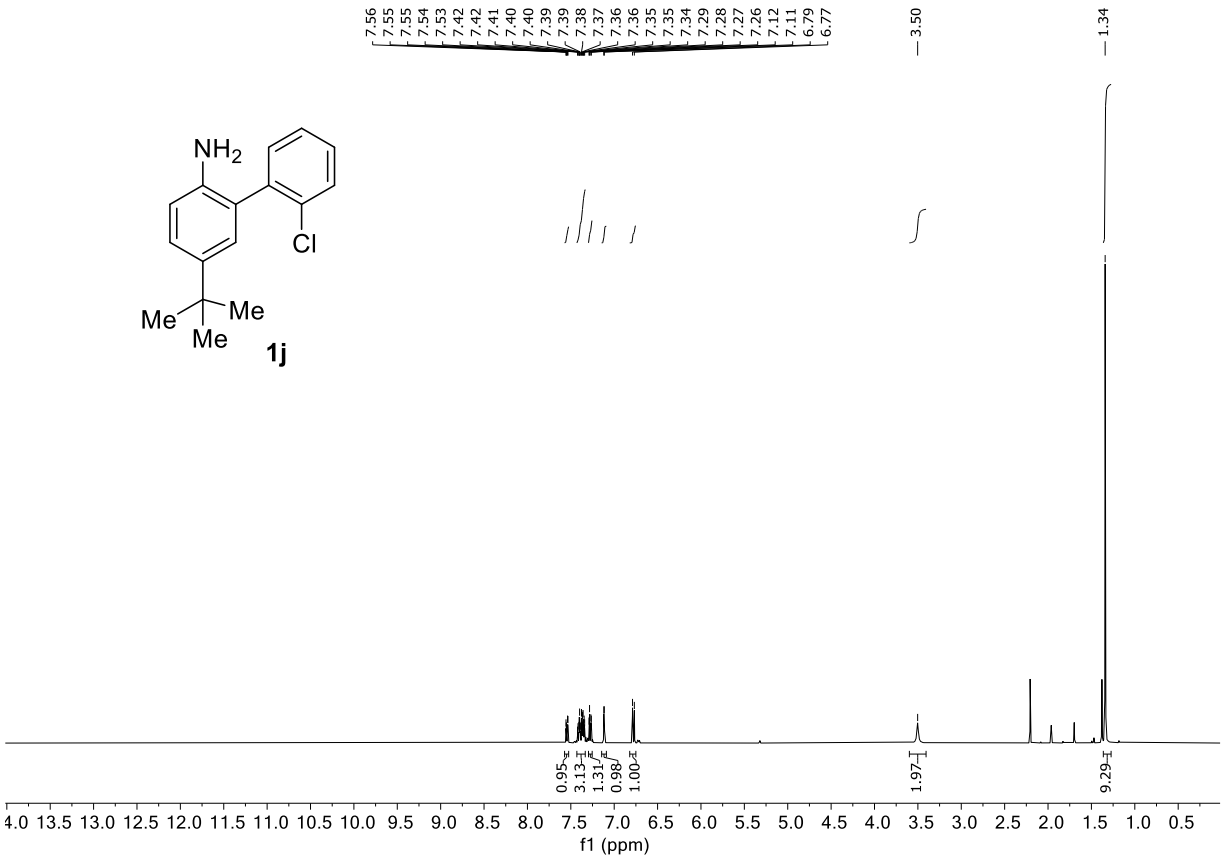
127.1
125.4
115.7
20.4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.36
7.36
7.35
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7.34
7.29
7.28
7.27
7.26
7.12
7.11
6.79
6.77
3.50
1.34
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Cl
Me
Me
Me
1j
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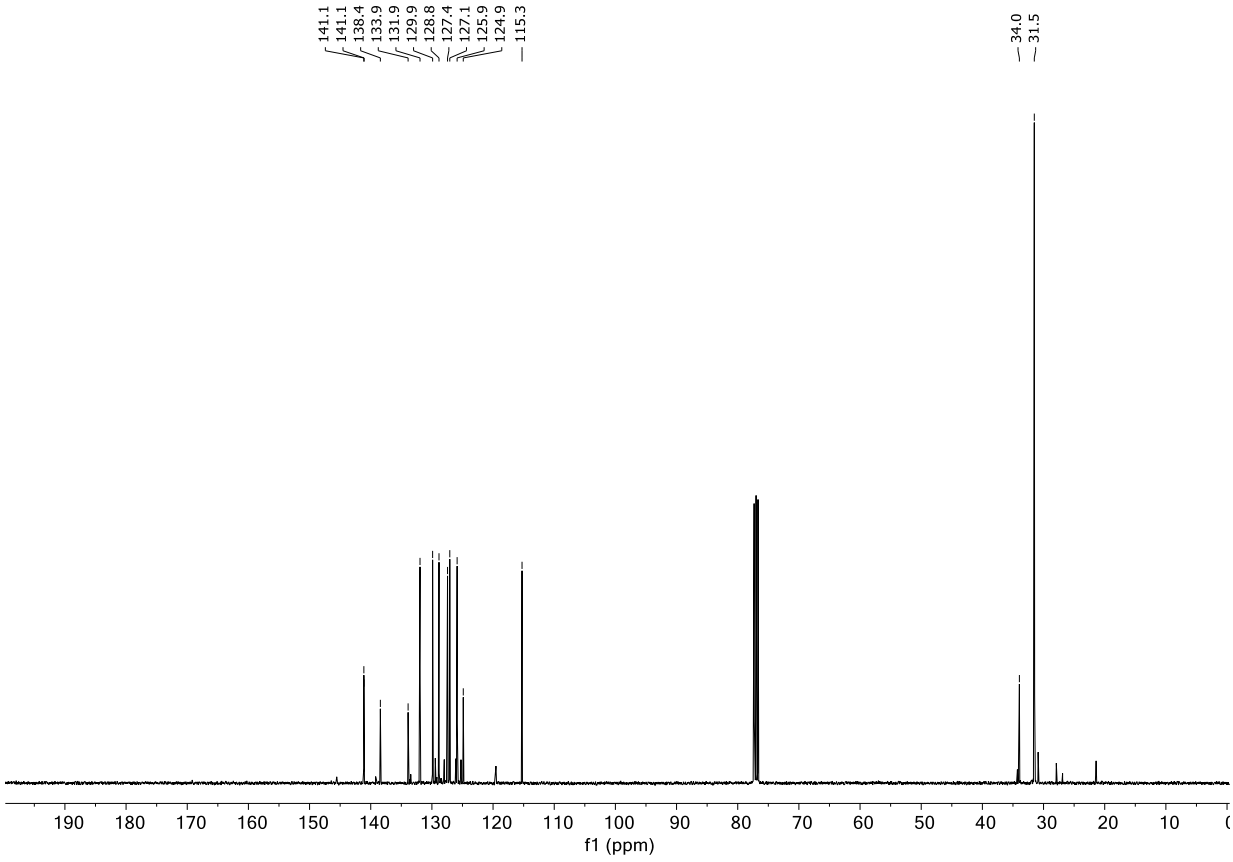
3.13
1.31
0.98
1.00
1.97
9.29
f1 (ppm)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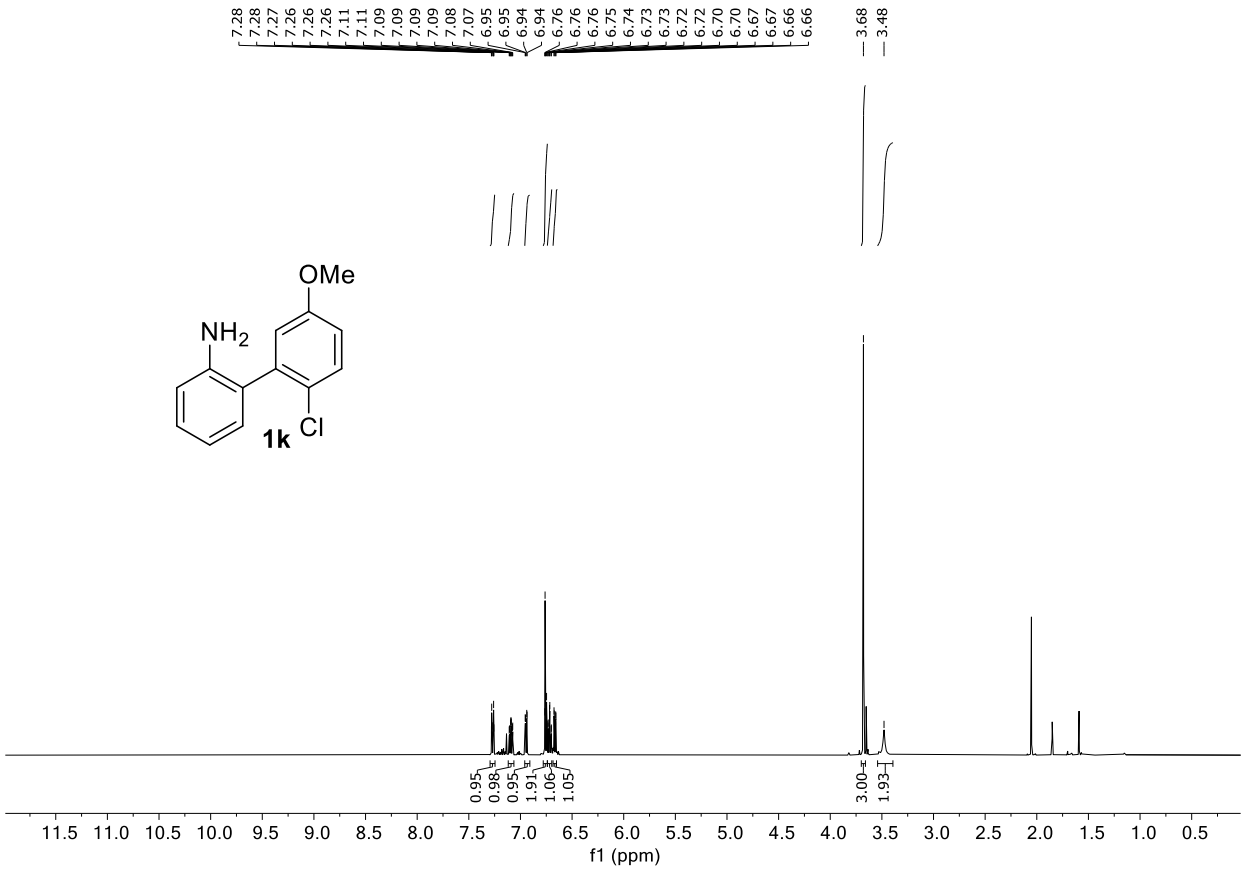
127.1
125.9
124.9
115.3
34.0
31.5
f1 (ppm)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7.09
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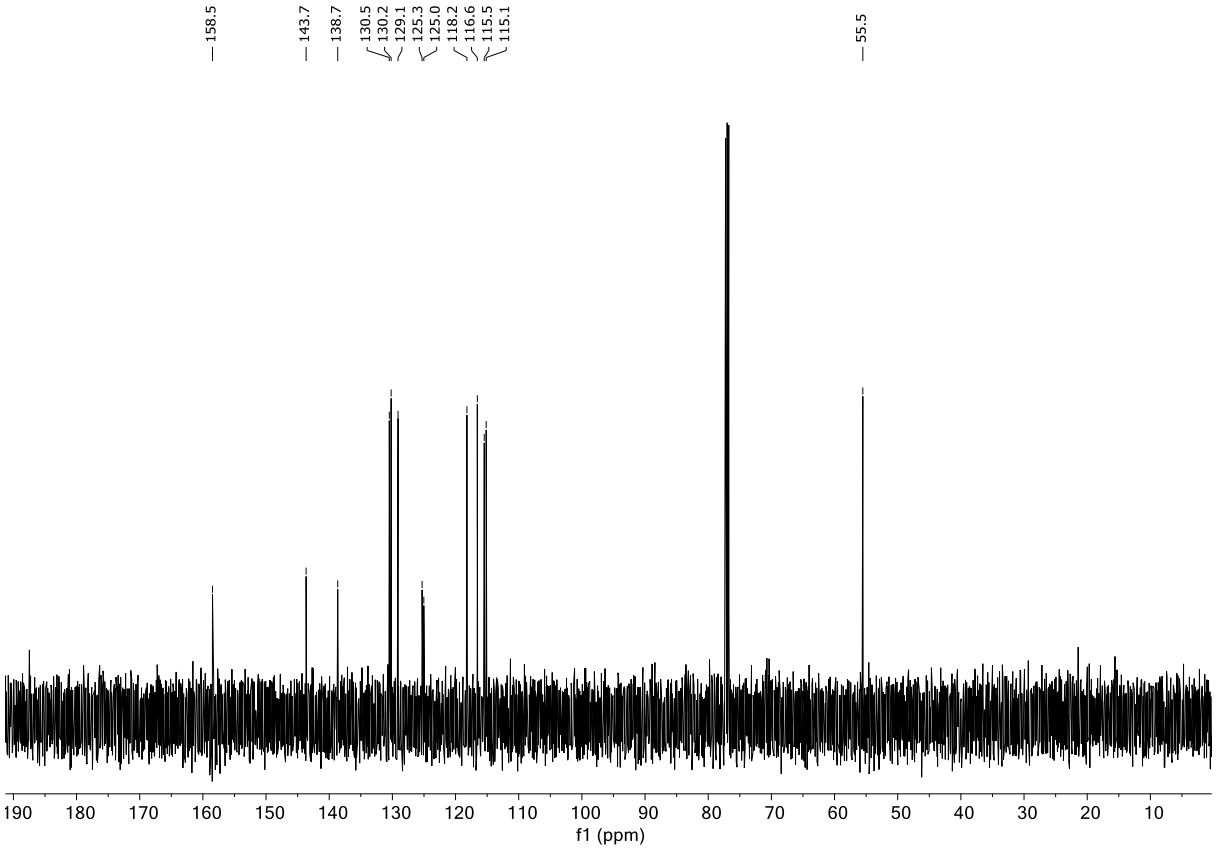
7.07
6.95
6.95
6.94
6.94
6.76
6.76
6.76
6.75
6.74
6.73
6.73
6.72
6.72
6.70
6.70
6.67
6.67
6.66
6.66
3.68
3.48
OMe
NH2
Cl
1k
0.95
0.98
0.95
1.91
1.06
1.05
3.00
1.93
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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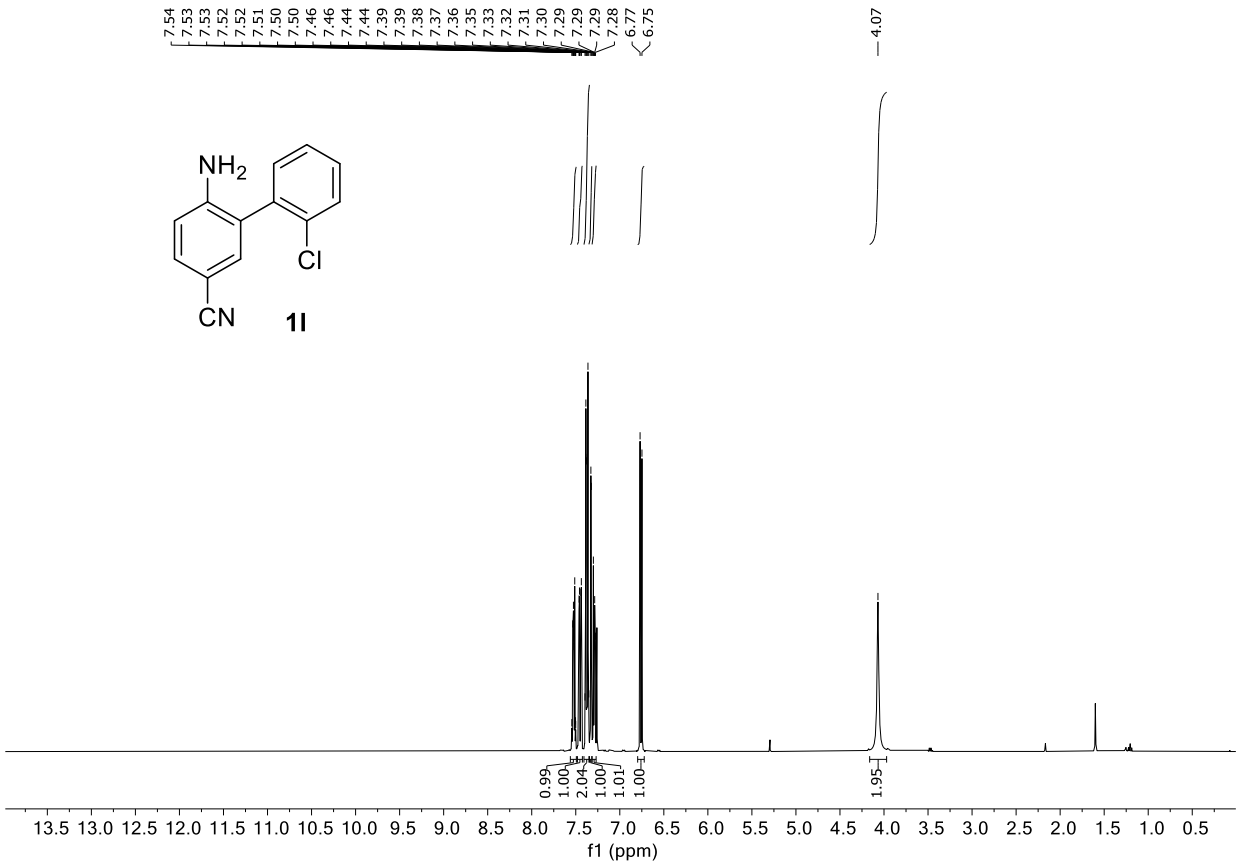
130.5
130.2
129.1
125.3
125.0
118.2
116.6
115.5
115.1
55.5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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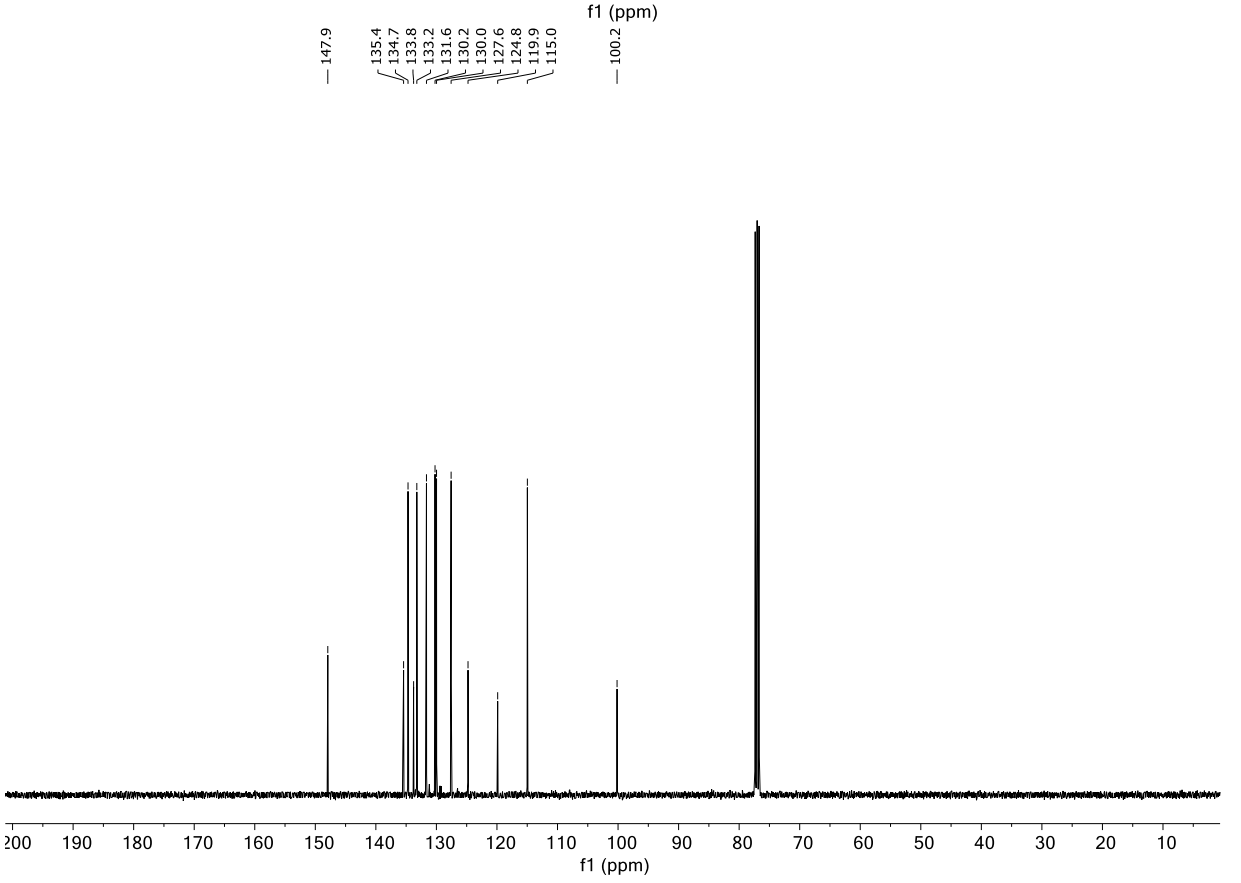
7.39
7.39
7.38
7.37
7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.29
7.29
7.28
6.77
6.75
4.07
NH2
Cl
CN
1l
0.99
1.00
2.04
1.00
1.01
1.00
1.95
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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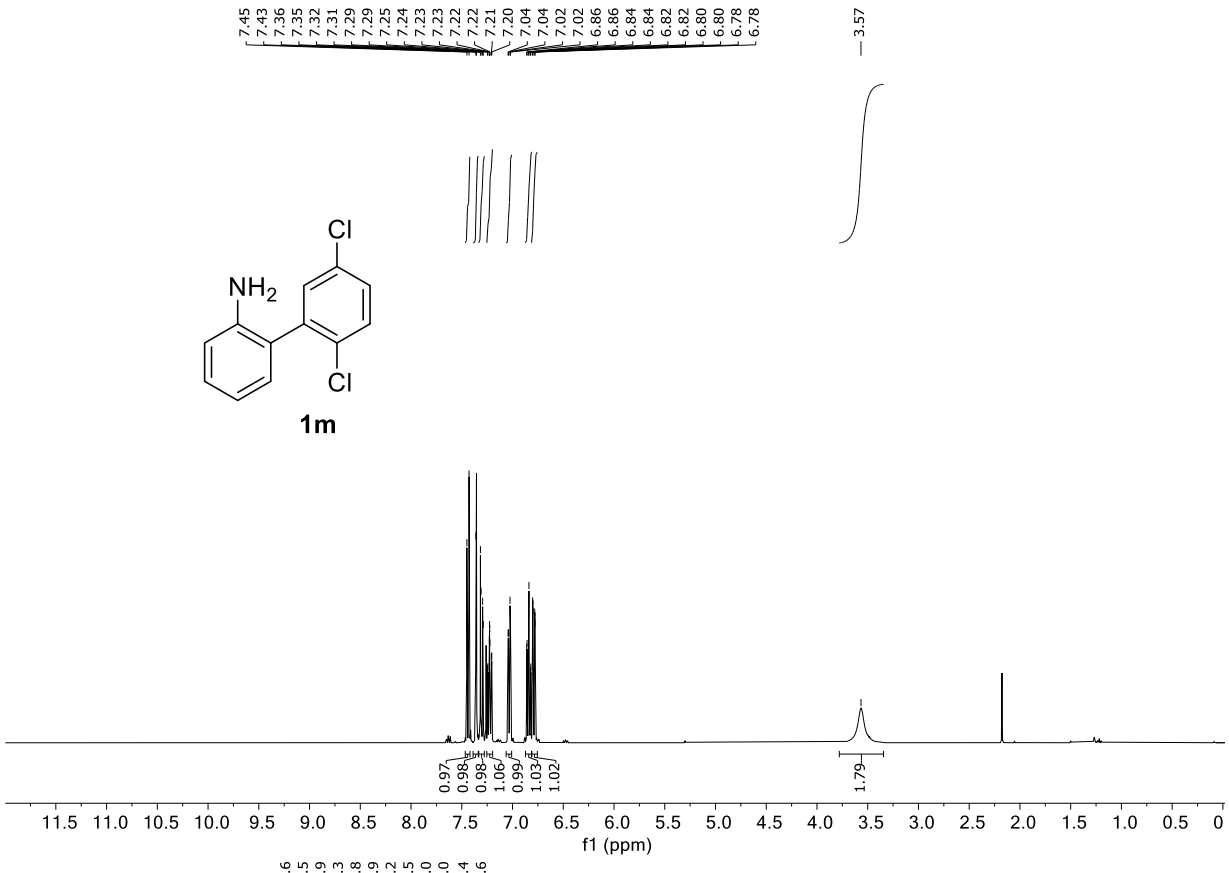
135.4
134.7
133.8
133.2
131.6
130.2
130.0
127.6
124.8
119.9
115.0
100.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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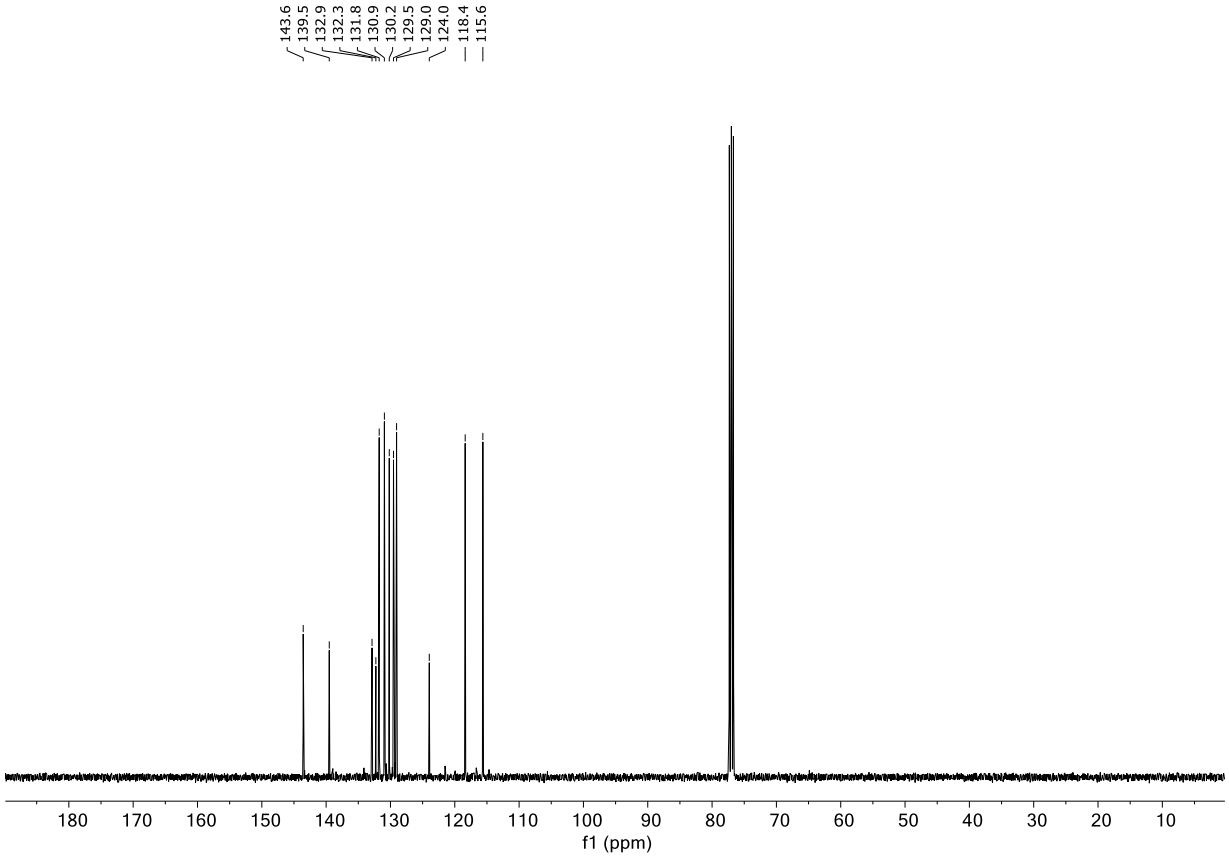
7.22
7.22
7.21
7.20
7.04
7.04
7.02
7.02
6.86
6.86
6.84
6.84
6.82
6.82
6.80
6.80
6.78
6.78
3.57
Cl
NH2
Cl
1m
0.97
0.98
0.98
1.06
0.99
1.03
1.02
1.79
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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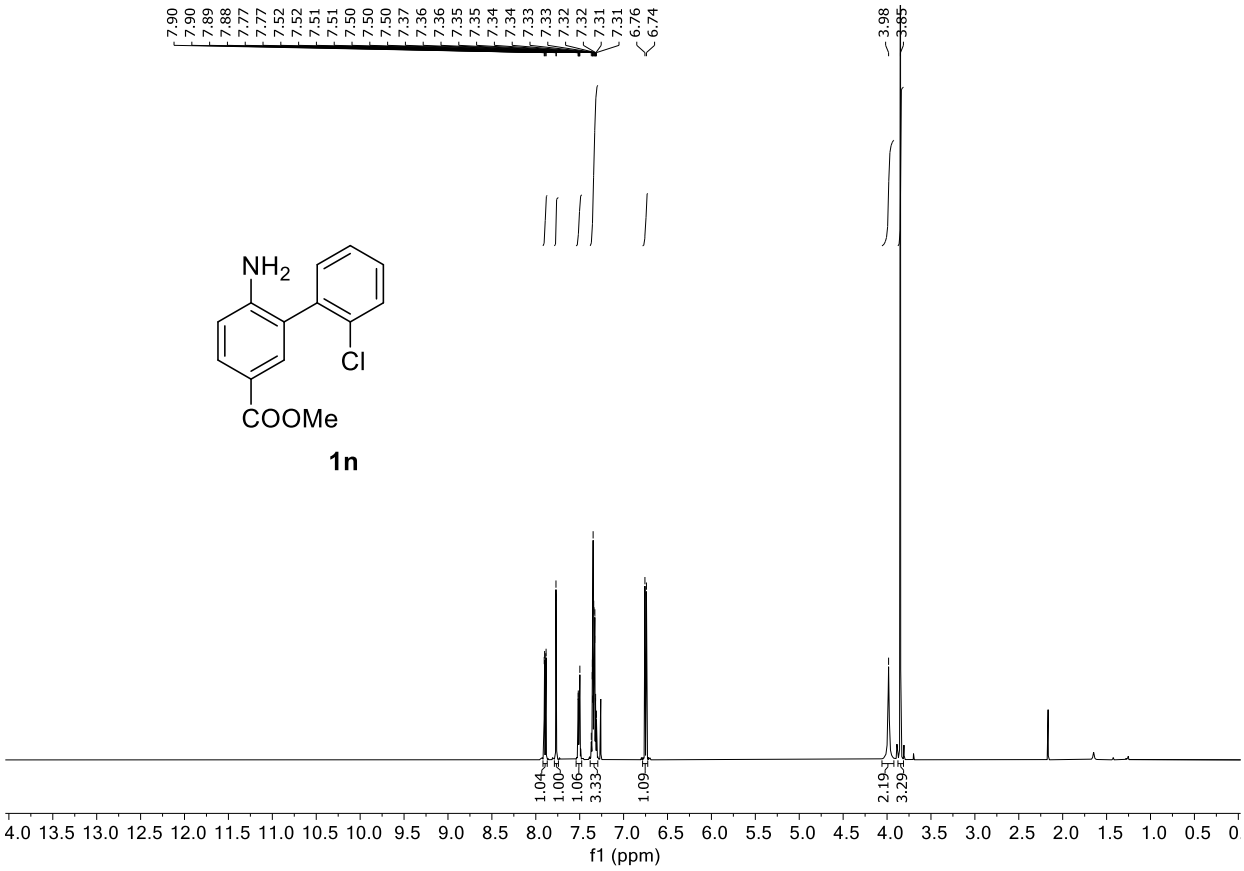
139.5
132.9
132.3
131.8
130.9
130.2
129.5
129.0
124.0
118.4
115.6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.50
7.50
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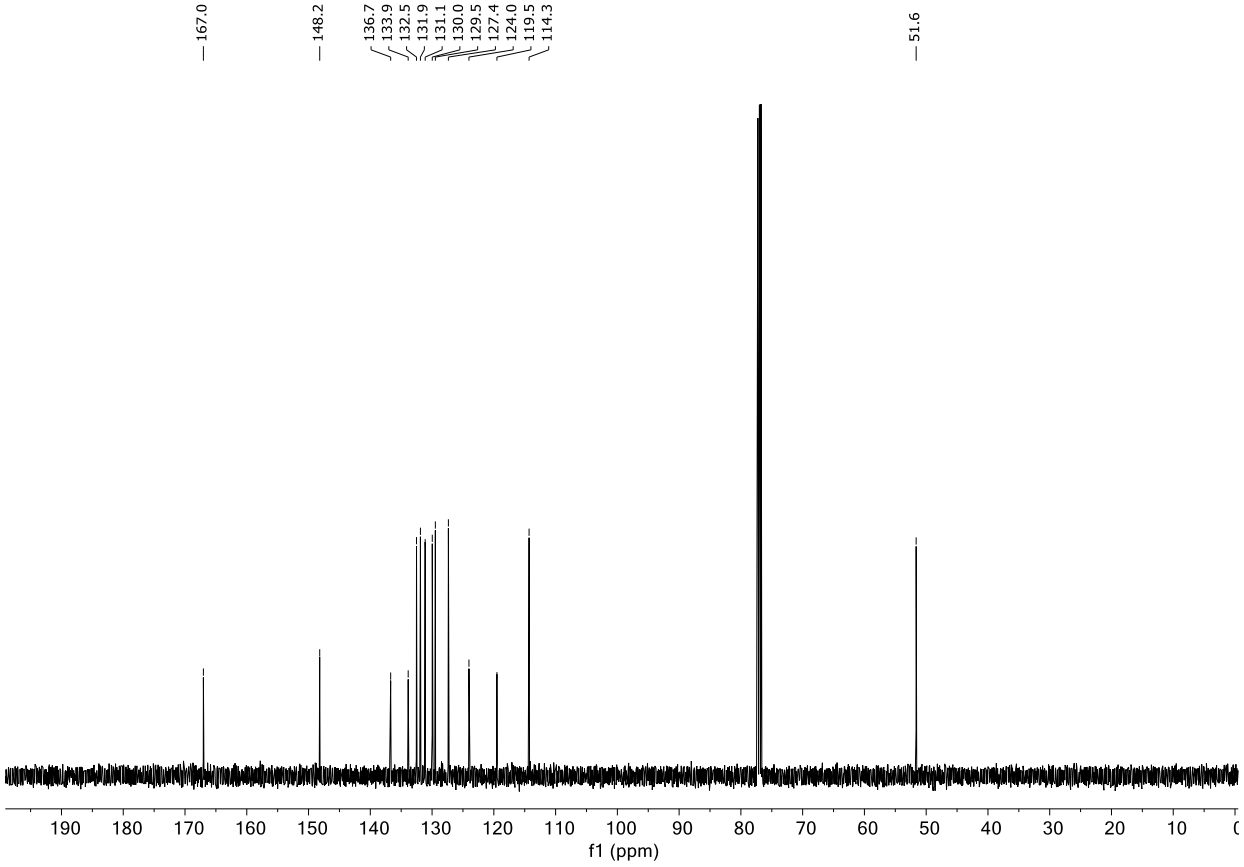
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
6.76
6.74
3.98
3.85
NH2
Cl
COOMe
1n
1.04
1.00
1.06
3.33
1.09
2.19
3.29
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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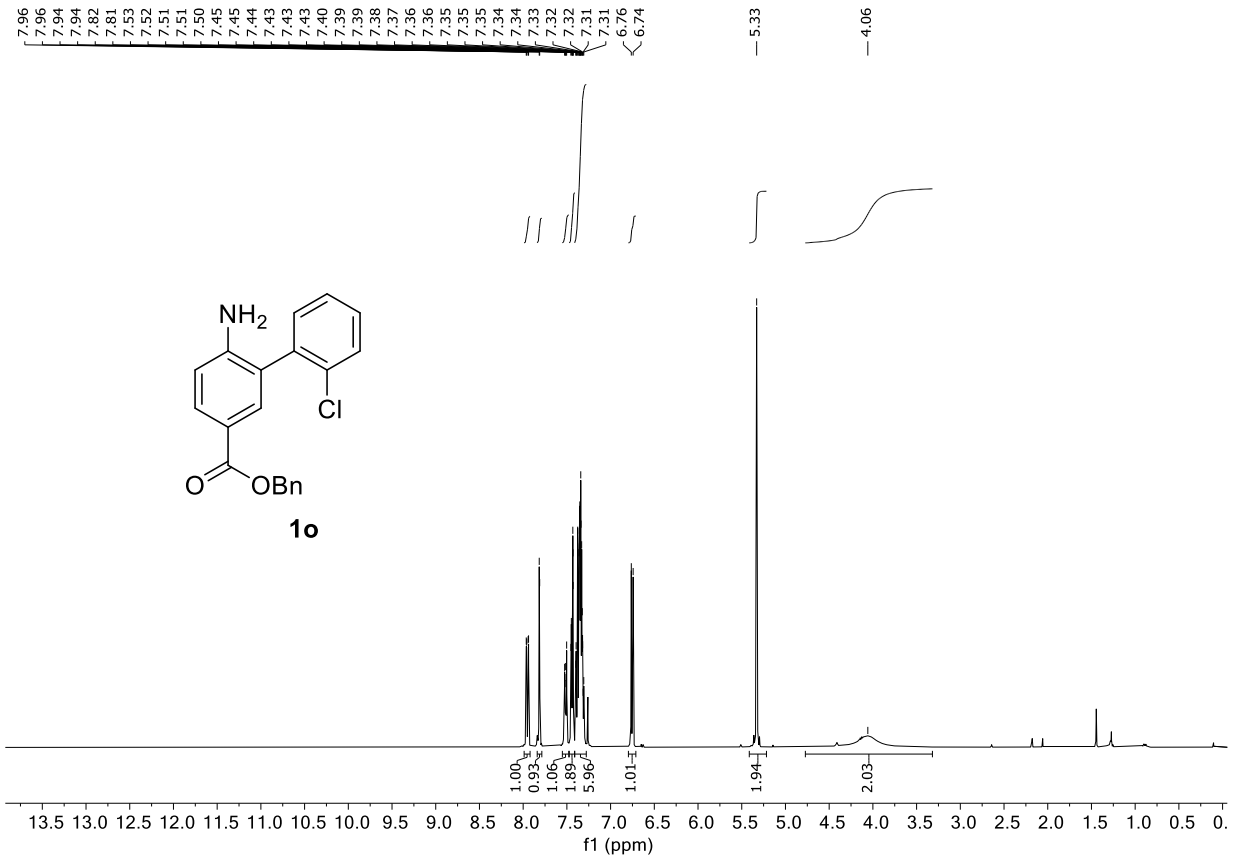
148.2
136.7
133.9
132.5
131.9
131.1
130.0
129.5
127.4
124.0
119.5
114.3
51.6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.40
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7.36
7.36
7.35
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7.33
7.32
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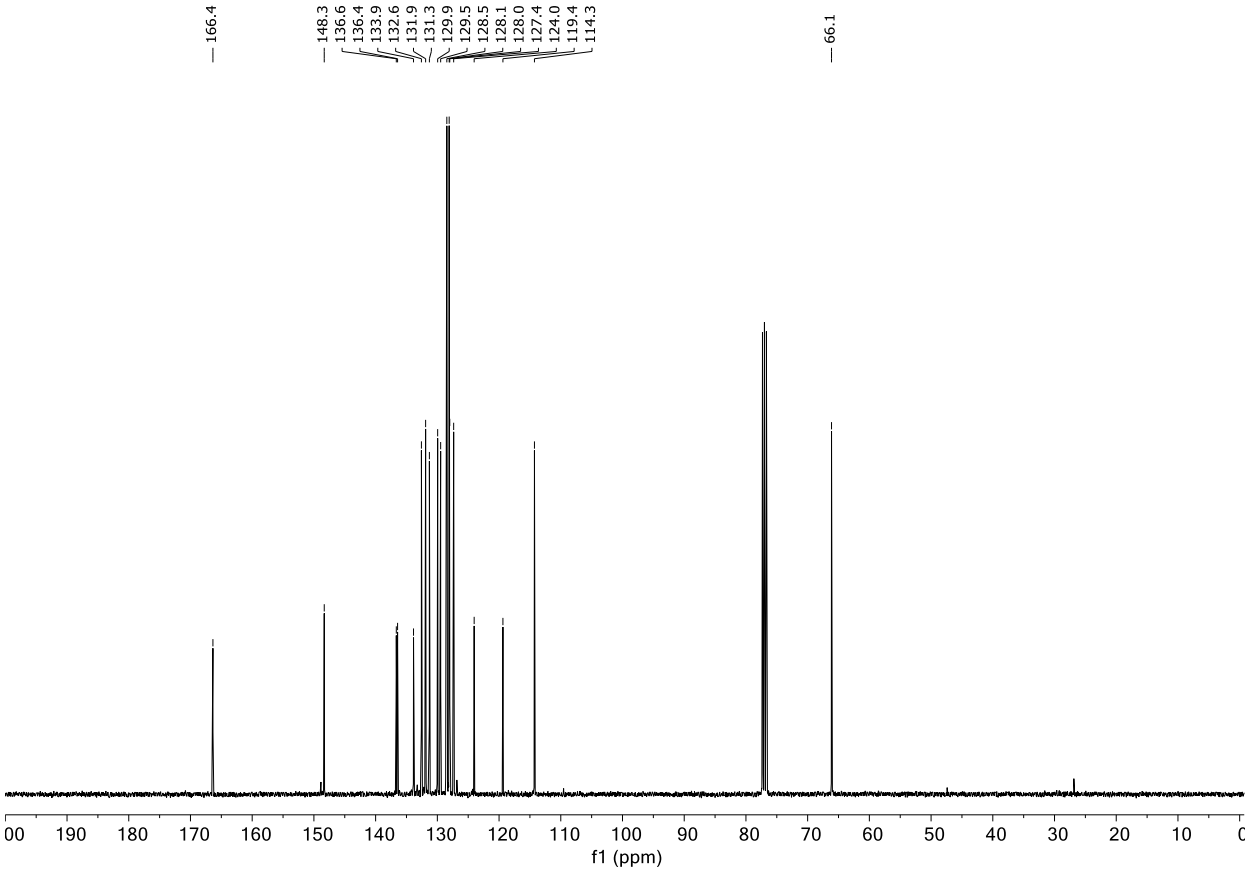
7.31
7.31
6.76
6.74
5.33
4.06
NH2
Cl
O
OBn
1o
1.00
0.93
1.06
1.89
5.96
1.01
1.94
2.03
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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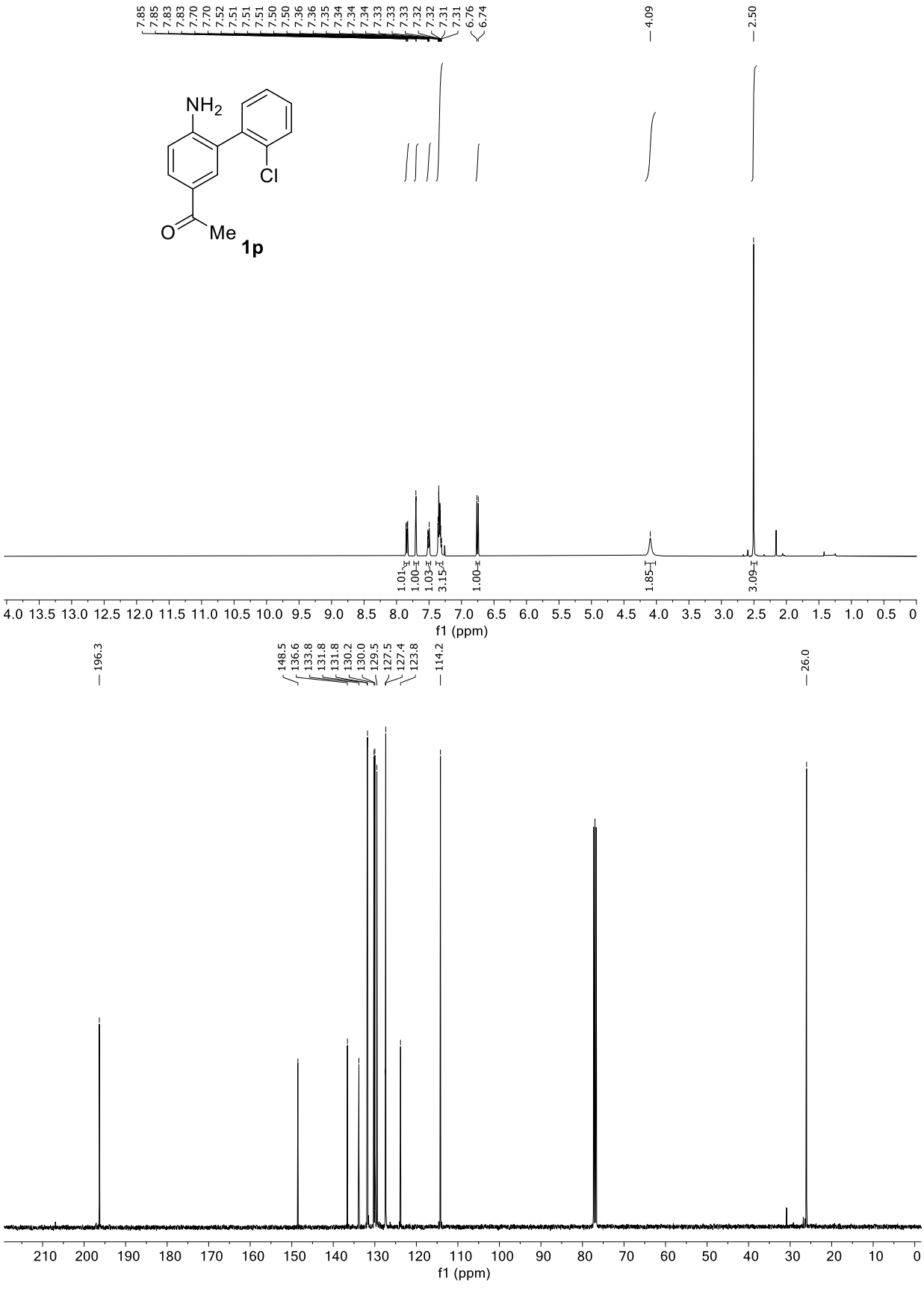
132.6
131.9
131.3
129.9
129.5
128.5
128.1
128.0
127.4
124.0
119.4
114.3
66.1
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.35
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7.33
7.33
7.33
7.32
7.32
7.31
7.31
6.76
6.74
4.09
2.50
NH2
Cl
O
Me
1p
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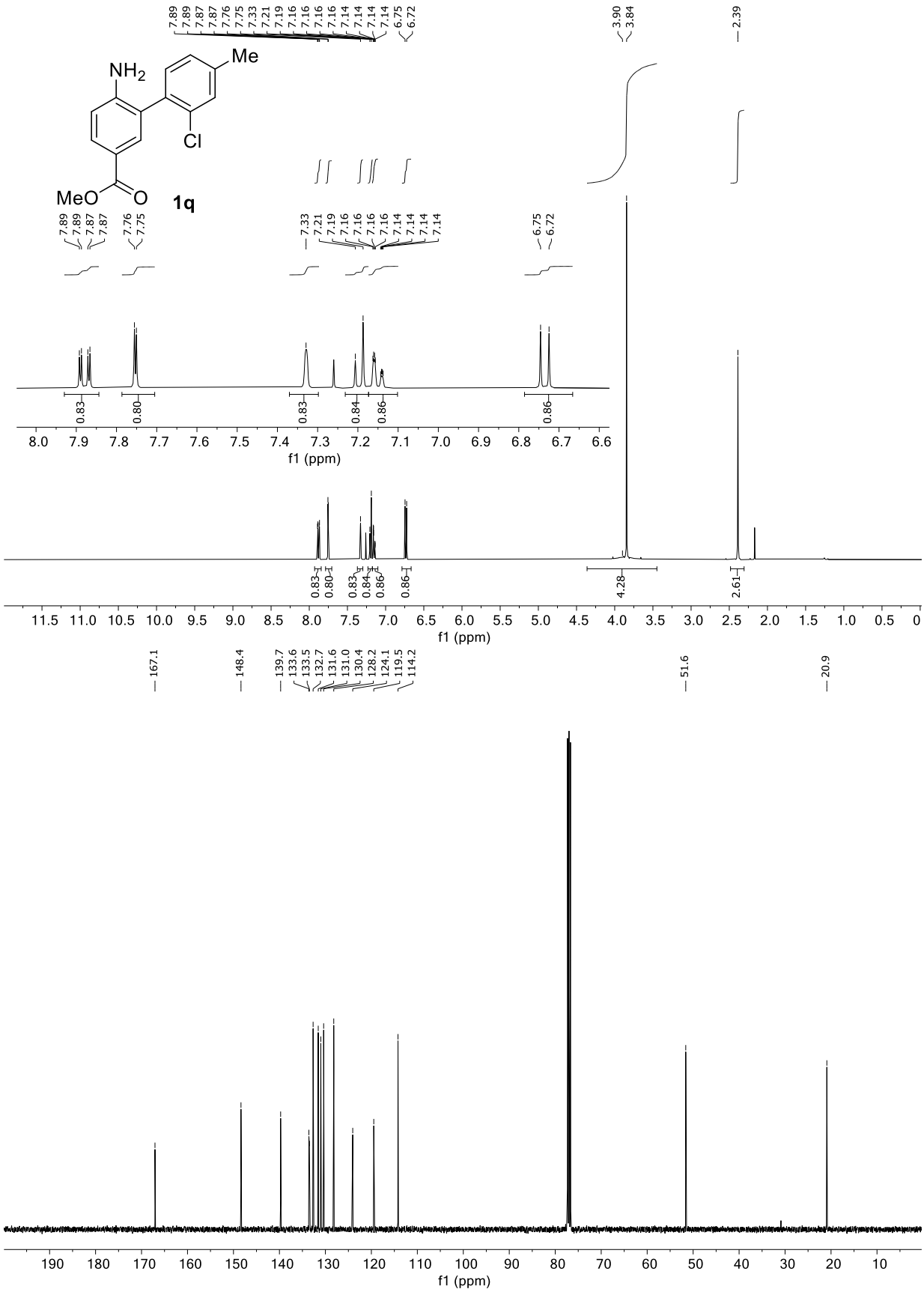
1.00
1.03
3.15
1.00
1.85
3.09
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)
196.3
148.5
136.6
133.8
131.8
131.8
130.2
130.0
129.5
127.5
127.4
123.8
114.2
26.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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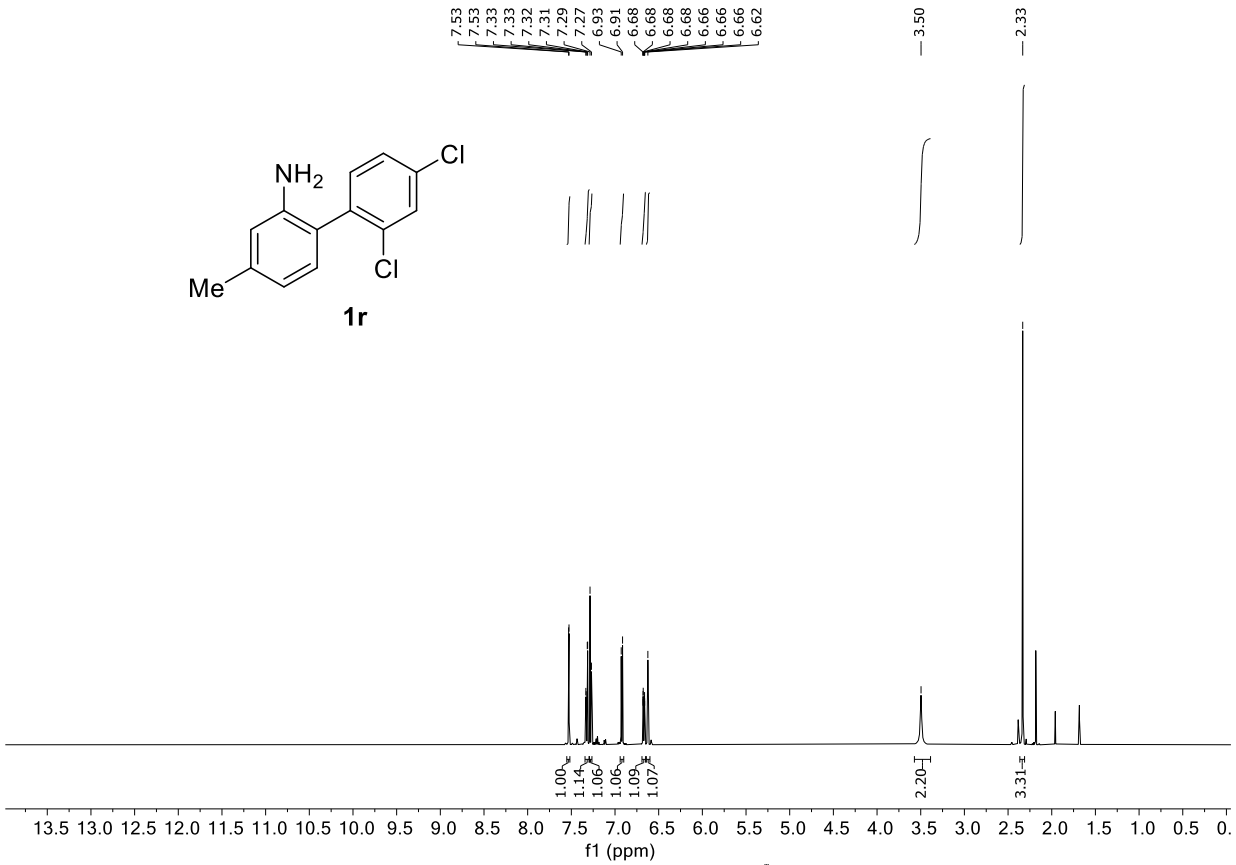
Me
Cl
MeO
O
O
1q
f1 (ppm)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6.68
6.66
6.66
6.66
6.62
3.50
2.33
NH2
Cl
Cl
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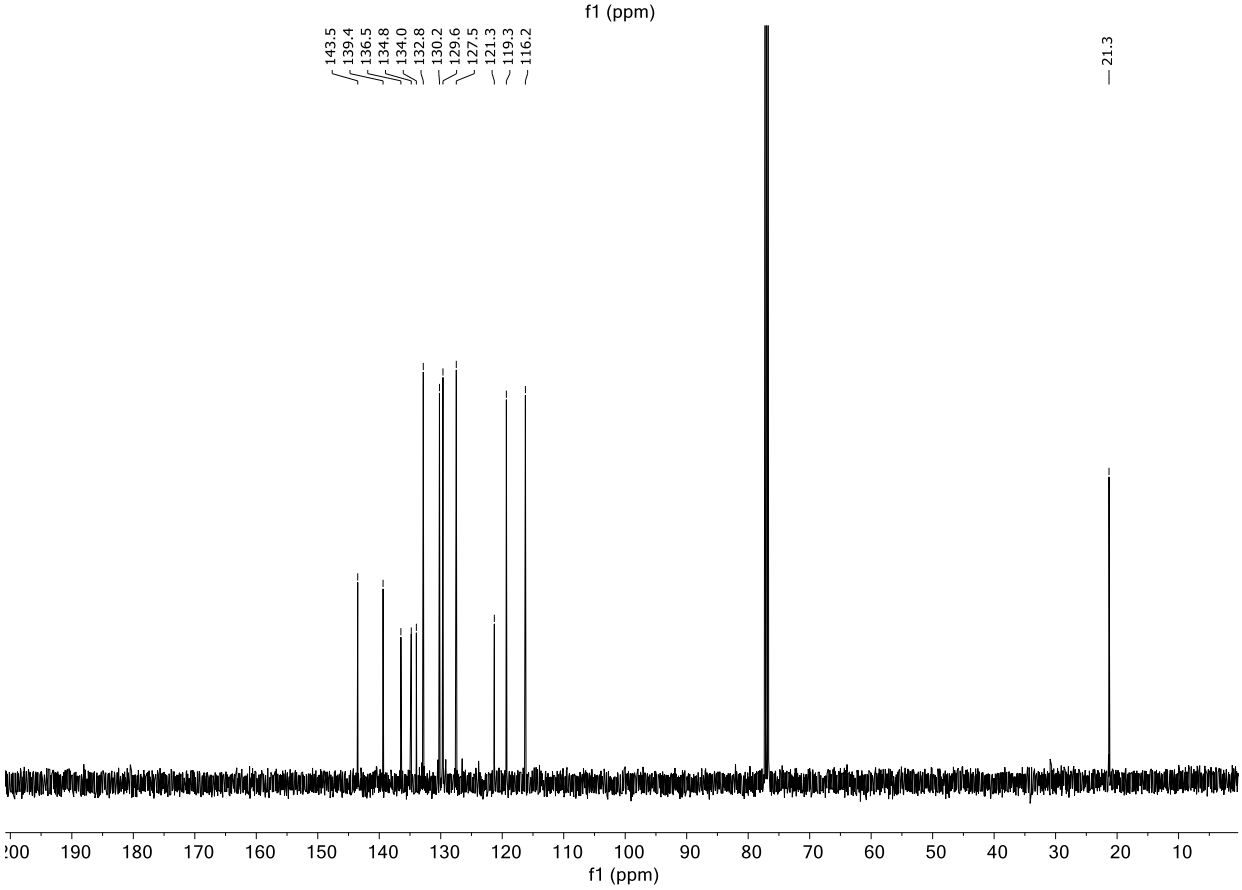
1.06
1.09
1.07
2.20
3.31
f1 (ppm)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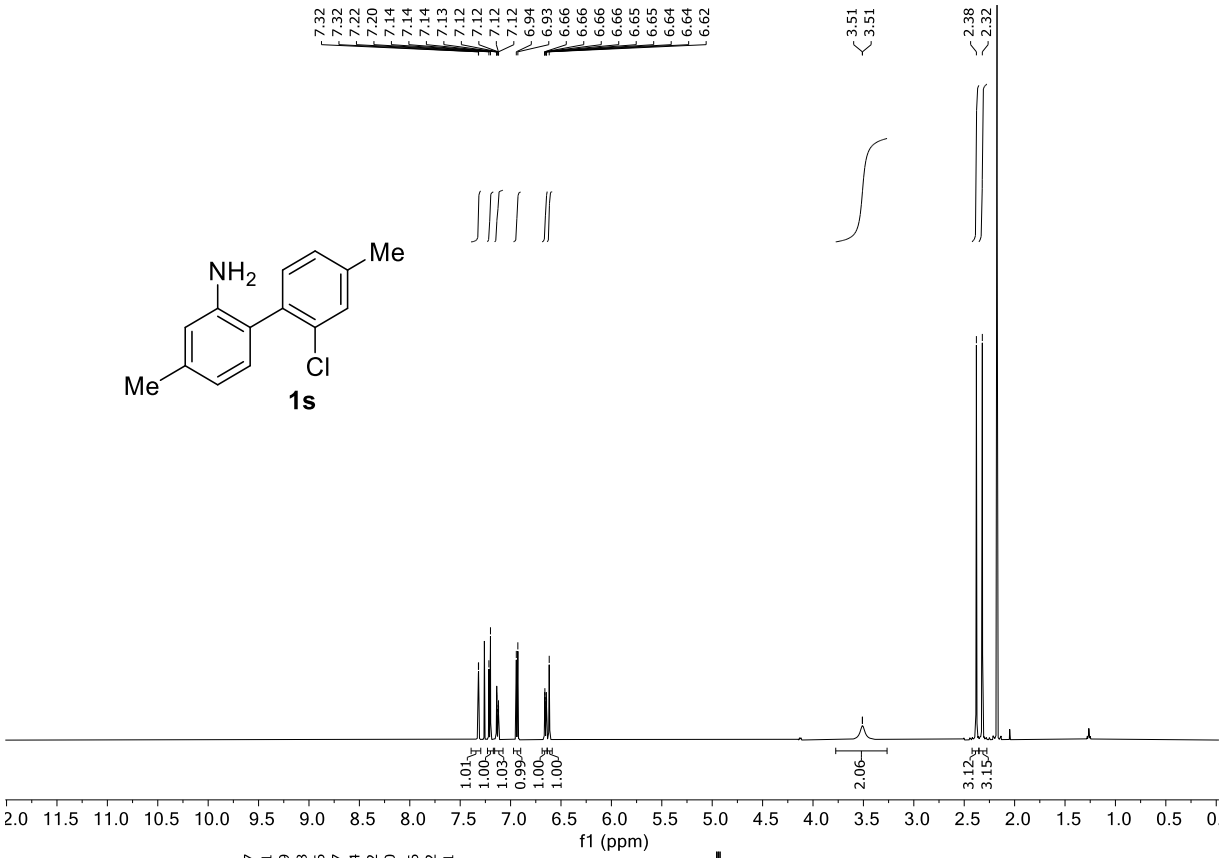
130.2
129.6
127.5
121.3
119.3
116.2
21.3
f1 (ppm)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6.66
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6.64
6.62
3.51
3.51
2.38
2.32
NH2
Me
Cl
Me
1s
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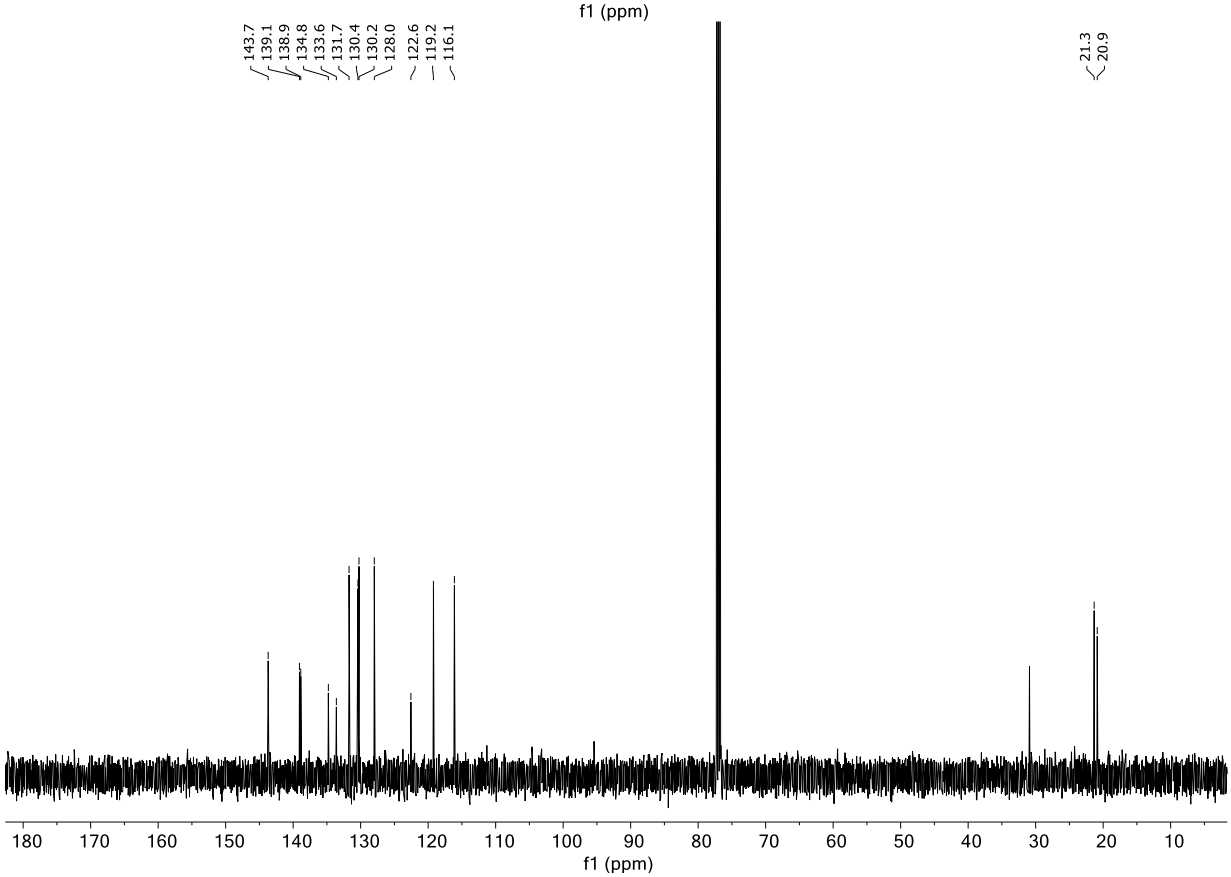
1.00
1.03
0.99
1.00
1.00
2.06
3.12
3.15
f1 (ppm)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133.6
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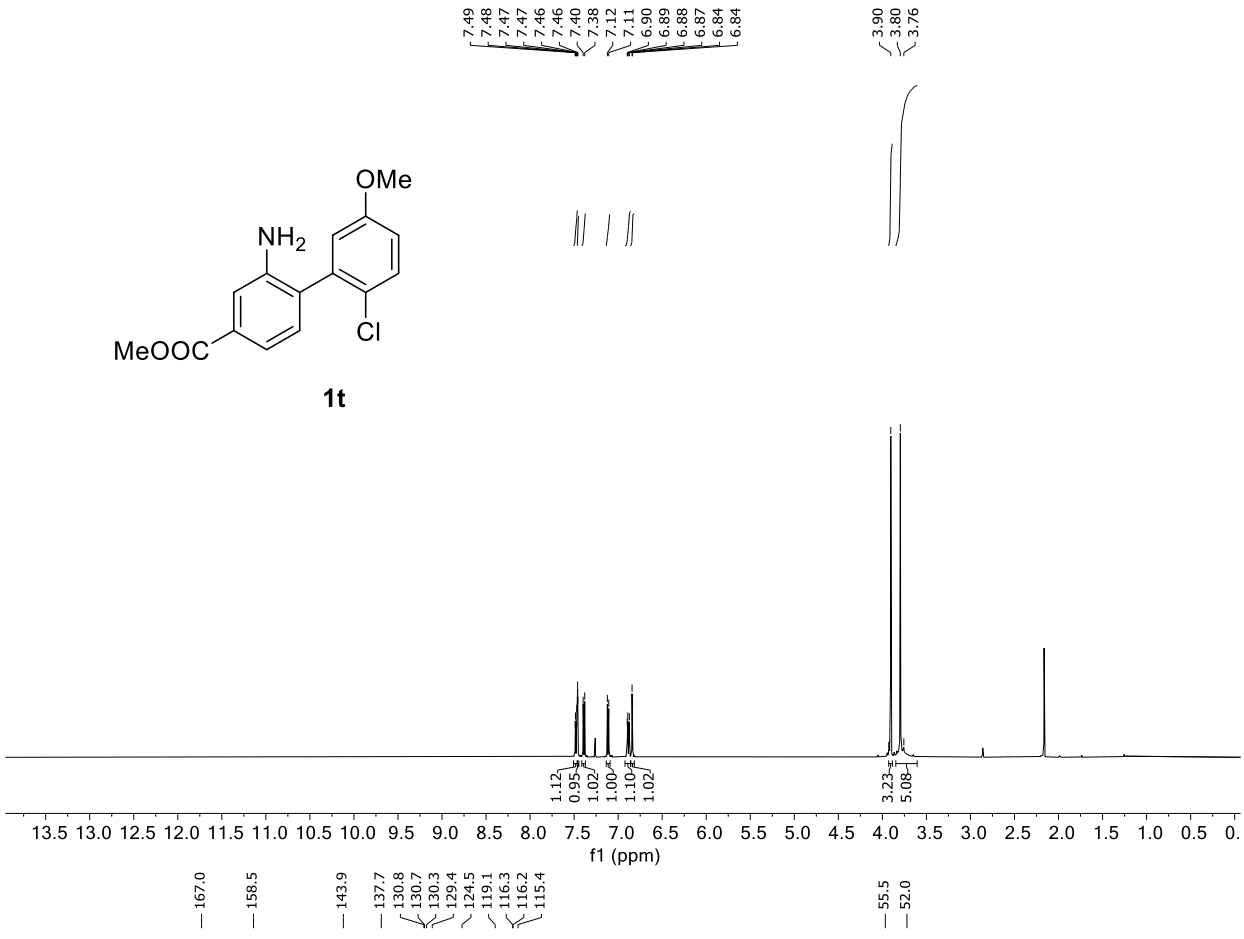
130.4
130.2
128.0
122.6
119.2
116.1
21.3
20.9
f1 (ppm)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7.11
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6.89
6.88
6.87
6.84
6.84
3.90
3.80
3.76
OMe
NH2
Cl
MeOOC
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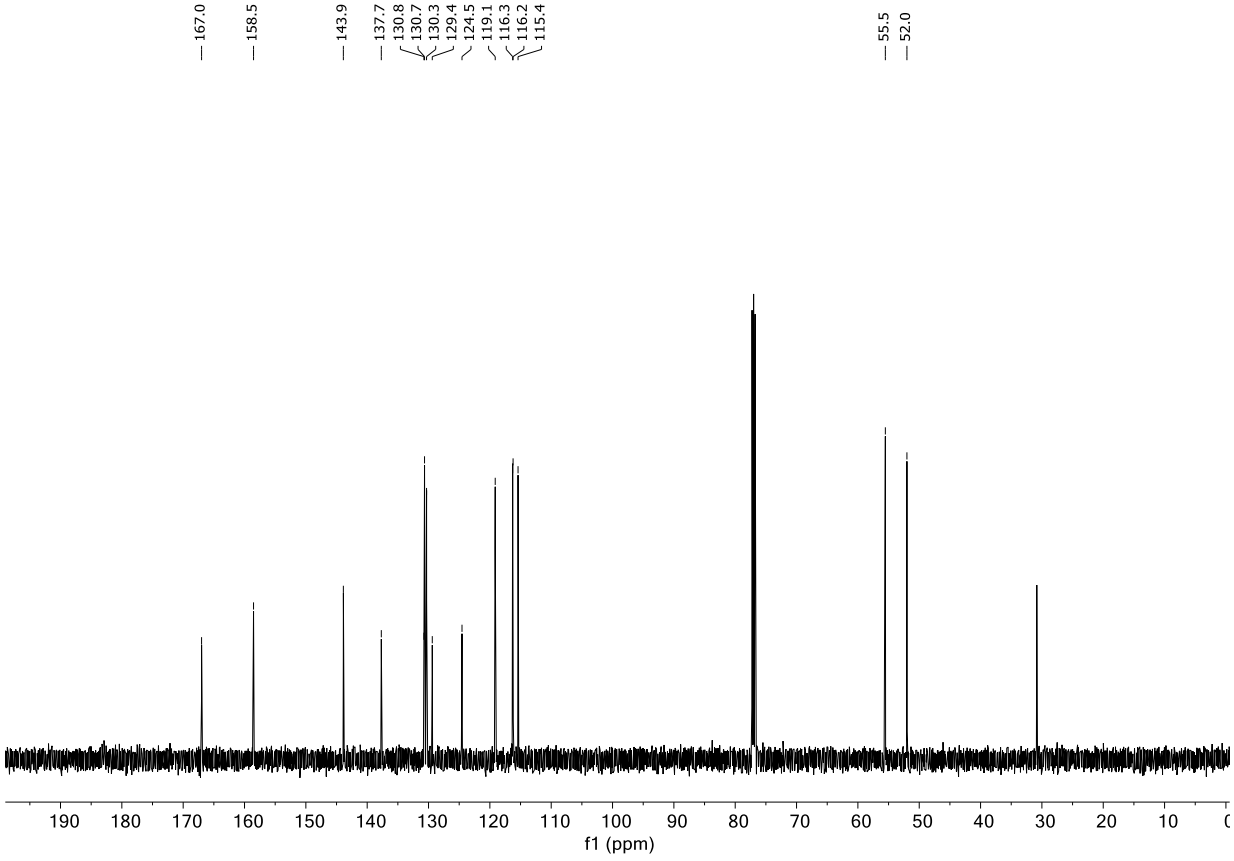
0.95
1.02
1.00
1.10
1.02
3.23
5.08
f1 (ppm)

1t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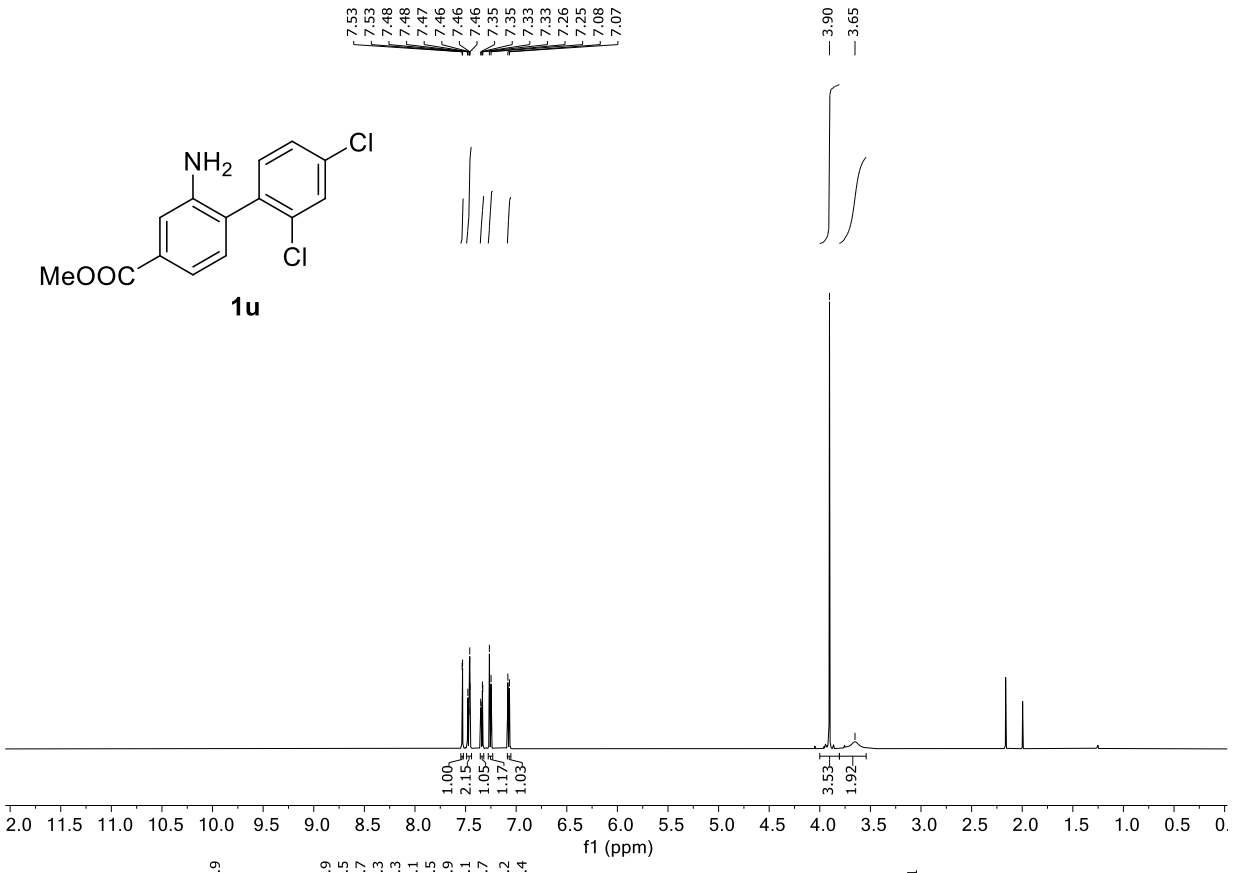
158.5
143.9
137.7
130.8
130.7
130.3
129.4
124.5
119.1
116.3
116.2
115.4
55.5
52.0
f1 (ppm)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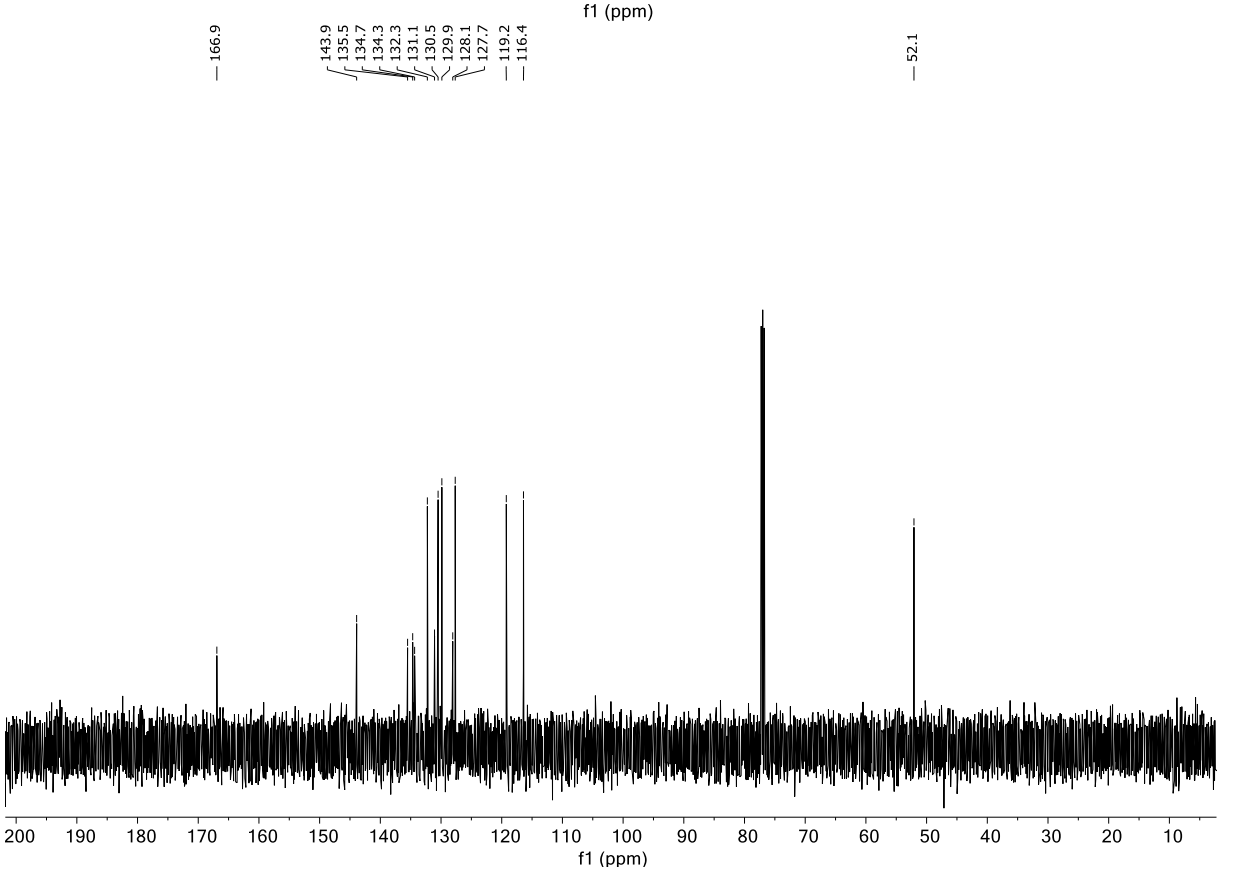
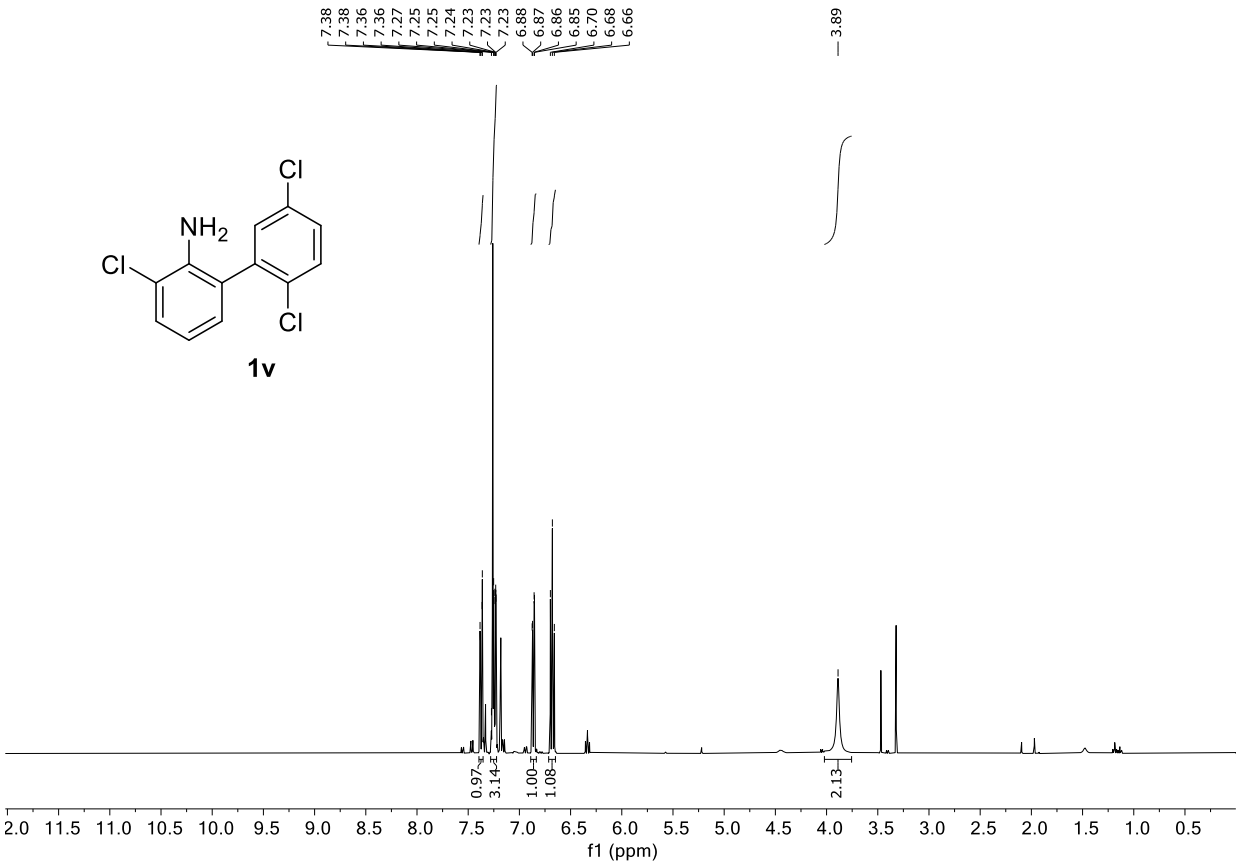
7.46
7.46
7.35
7.35
7.33
7.33
7.26
7.25
7.08
7.07
3.90
3.65
NH2
Cl
Cl
MeOOC
1u
1.00
2.15
1.05
1.17
1.03
3.53
1.92
f1 (ppm)


166.9
143.9
135.5
134.7
134.3
132.3
131.1
130.5
129.9
128.1
127.7
119.2
116.4
52.1
f1 (ppm)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7.24
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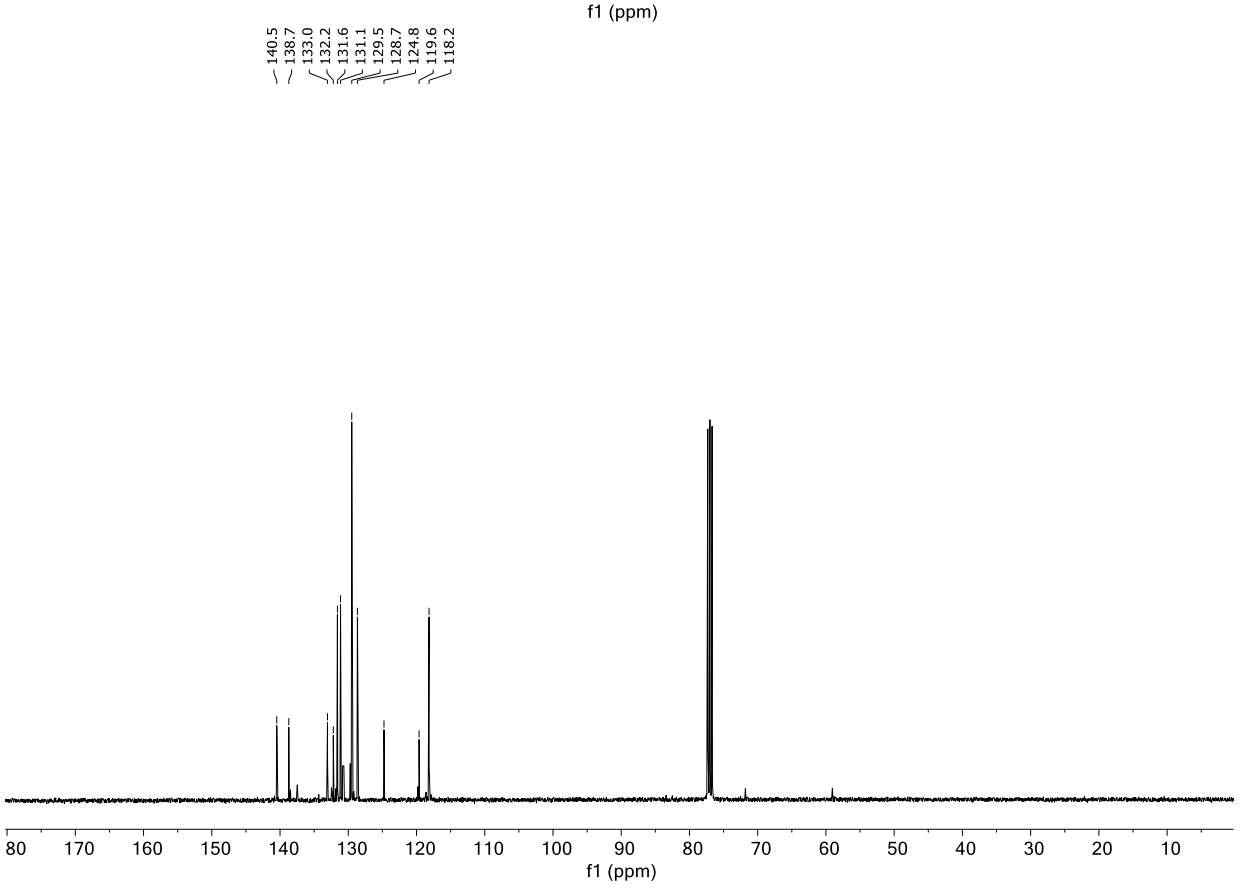
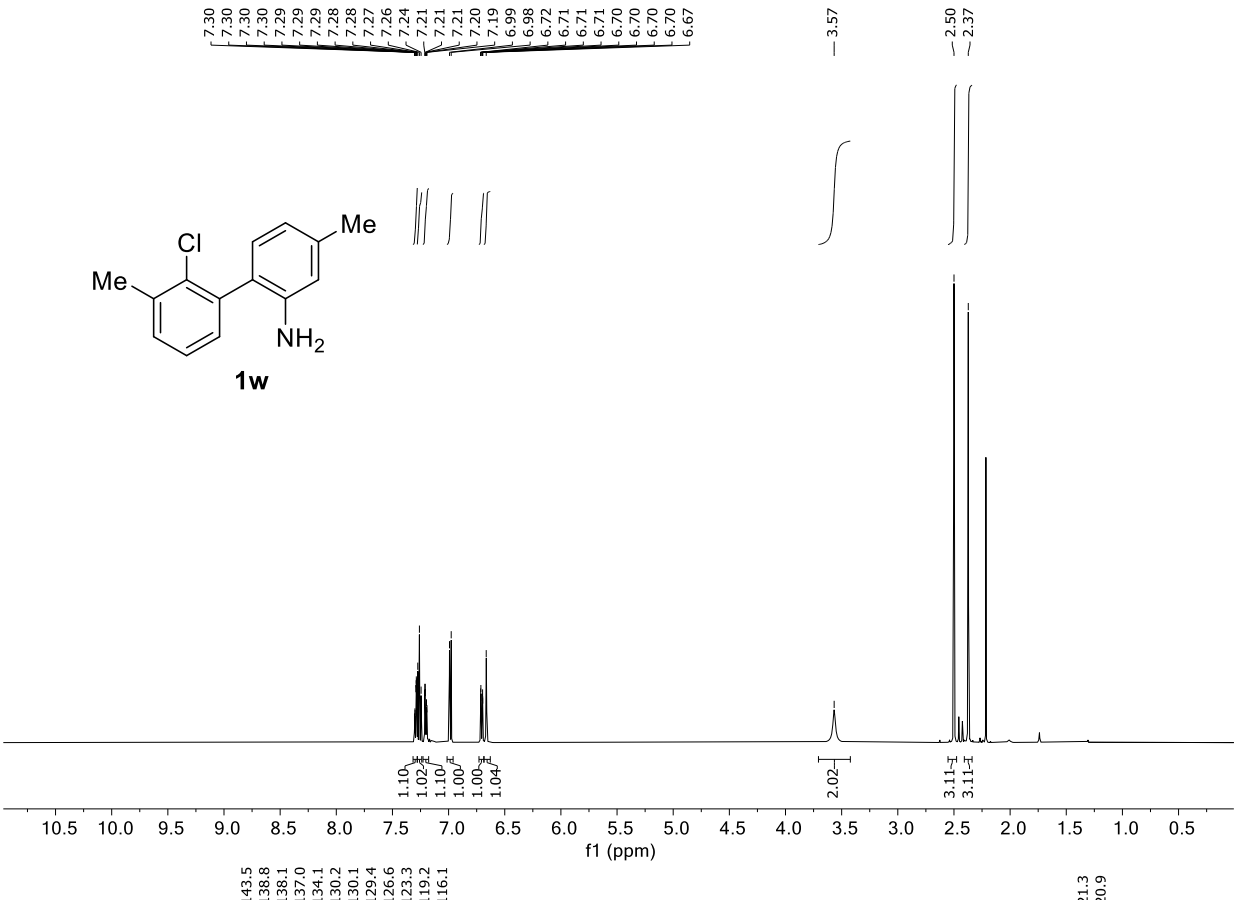
7.23
7.23
6.88
6.87
6.86
6.85
6.70
6.68
6.66
3.89
Cl
NH2
Cl
Cl
0.97
3.14
1.00
1.08
2.13
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

1v


140.5
138.7
133.0
132.2
131.6
131.1
129.5
128.7
124.8
119.6
118.2
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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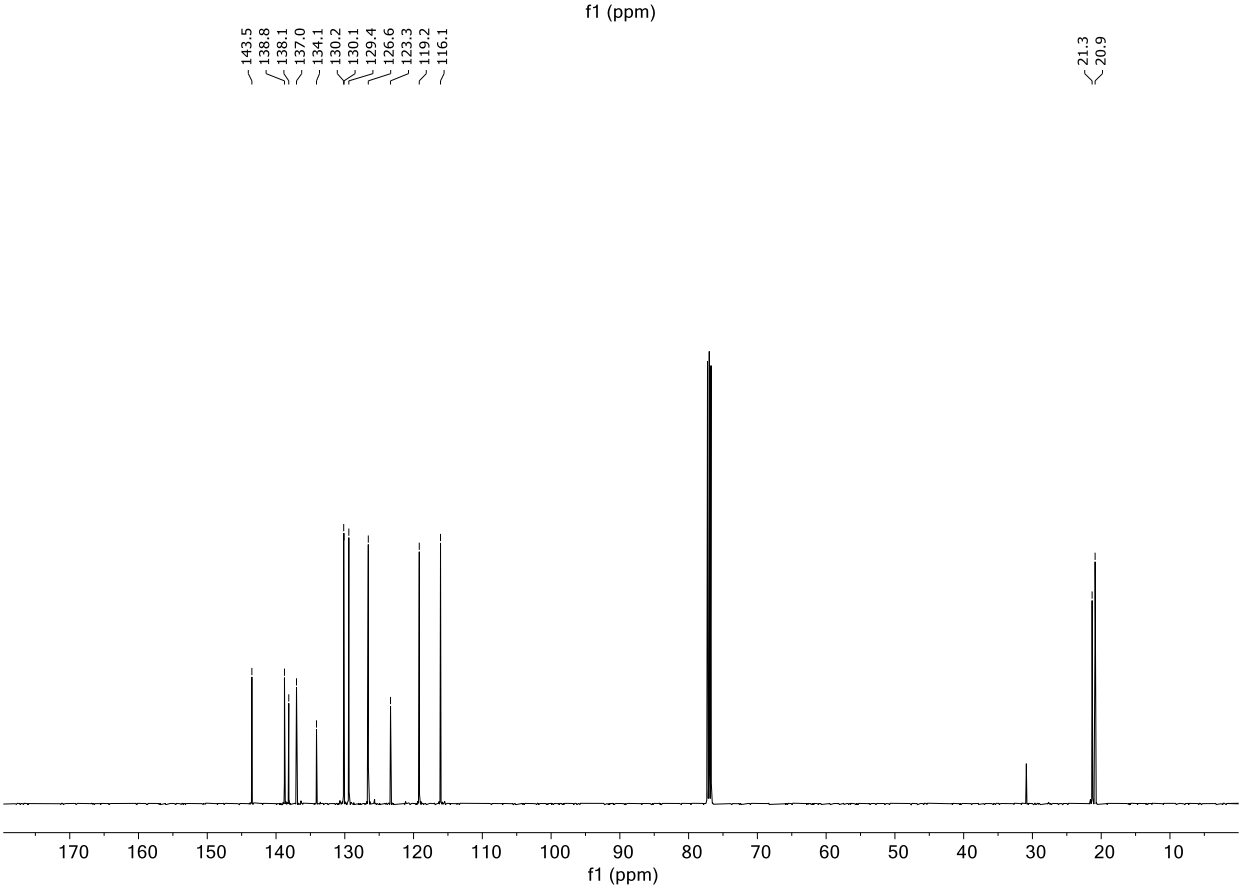
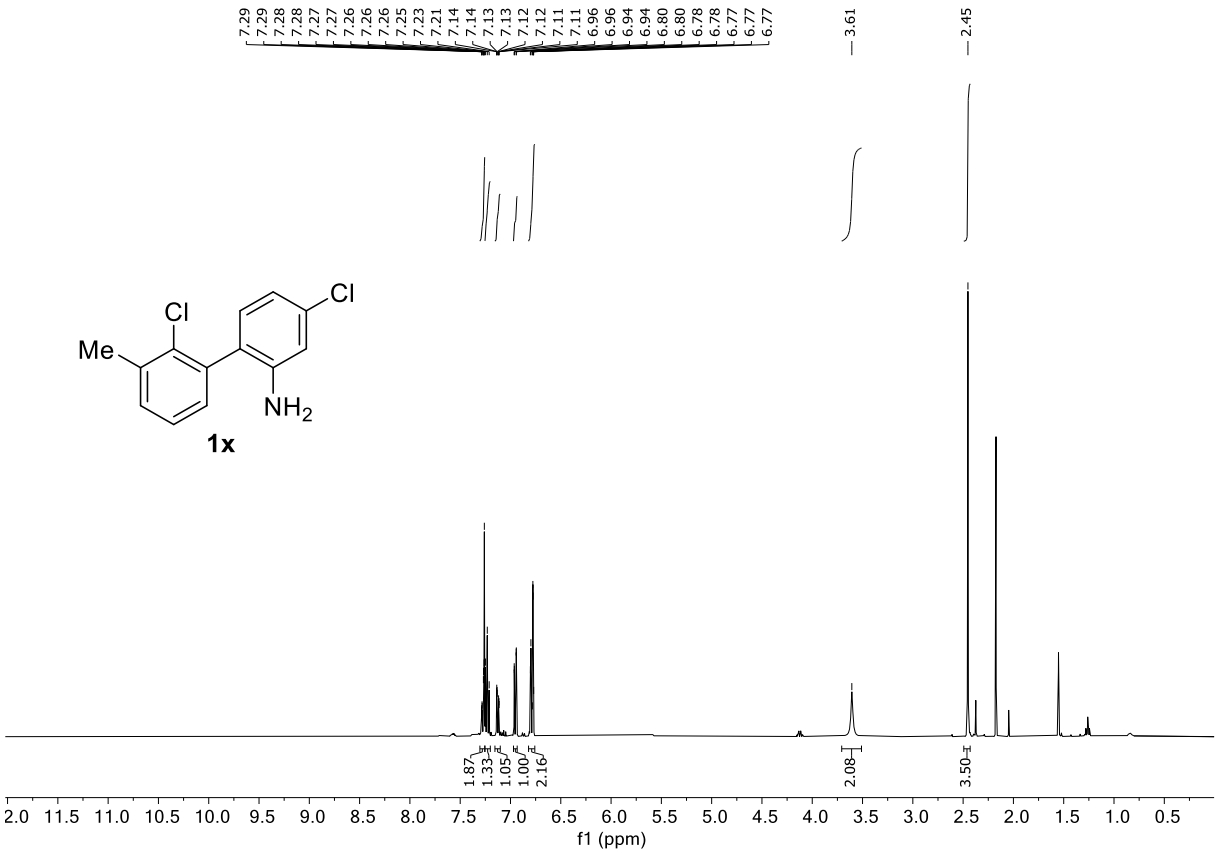
7.27
7.26
7.24
7.21
7.21
7.21
7.20
7.19
6.99
6.98
6.72
6.71
6.71
6.71
6.70
6.70
6.70
6.70
6.67
3.57
2.50
2.37
Cl
Me
Me
NH2
1w
1.10
1.02
1.10
1.00
1.00
1.04
2.02
3.11
3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


143.5
138.8
138.1
137.0
134.1
130.2
130.1
129.4
126.6
123.3
119.2
116.1
21.3
20.9
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.26
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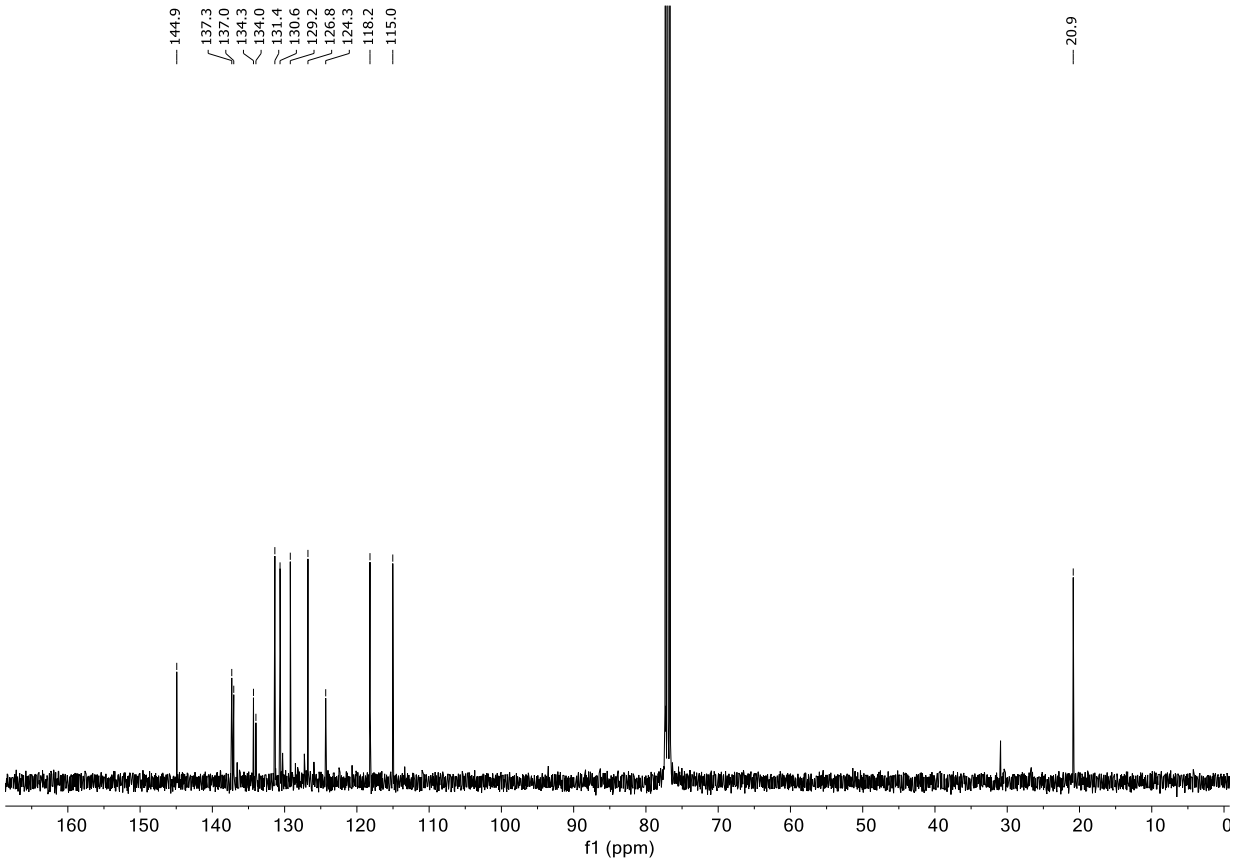
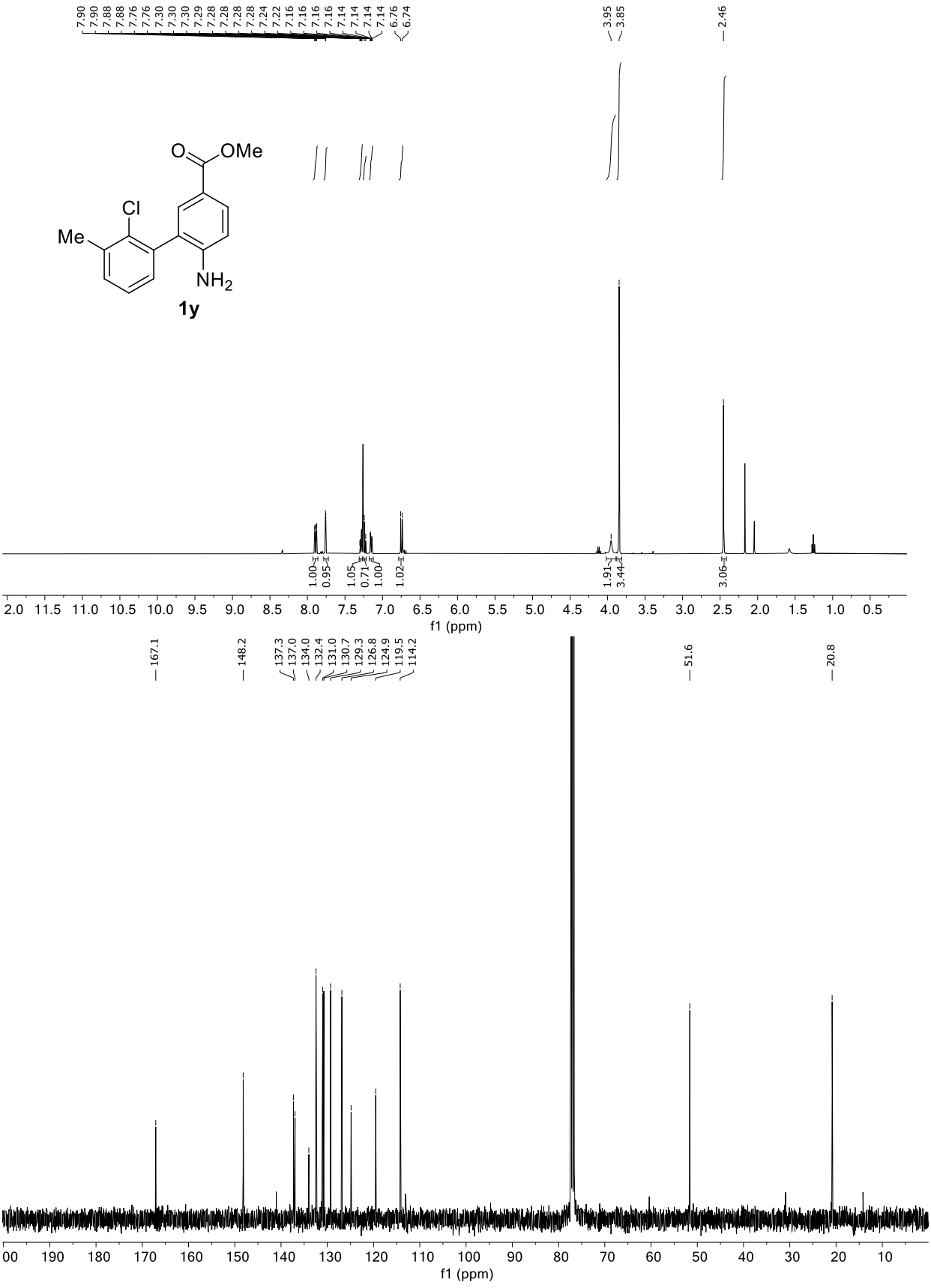
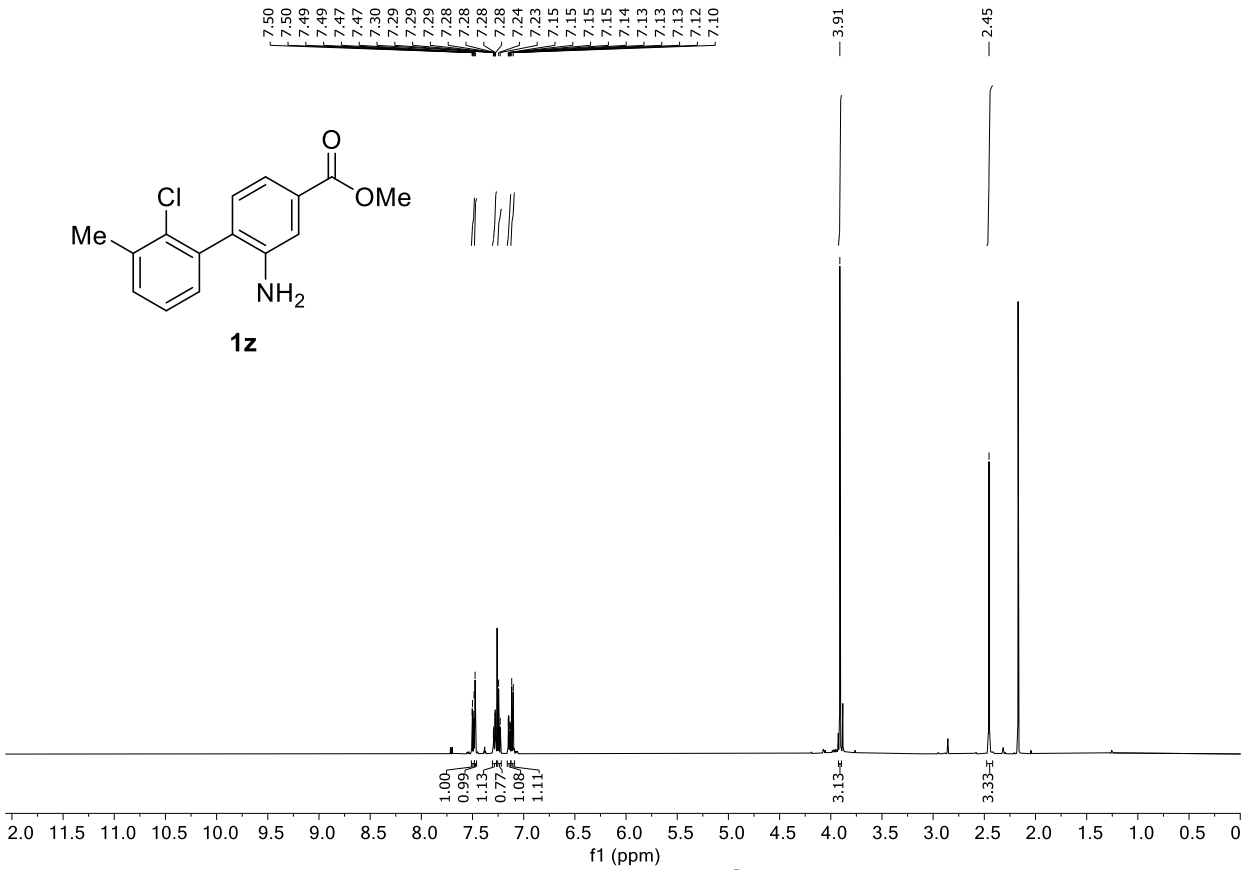
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
6.96
6.96
6.94
6.94
6.80
6.80
6.78
6.78
6.77
6.77
6.77
3.61
2.45
Cl
Cl
Me
NH2
1x
1.87
1.33
1.05
1.00
2.16
2.08
3.50
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


144.9
137.3
137.0
134.3
134.0
131.4
130.6
129.2
126.8
124.3
118.2
115.0
20.9
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.90
7.90
7.88
7.88
7.76
7.76
7.30
7.30
7.30
7.29
7.28
7.28
7.28
7.28
7.24
7.22
7.16
7.16
7.16
7.14
7.14
7.14
7.14
6.76
6.74
3.95
3.85
2.46
O
OMe
Cl
Me
NH2
1y
1.00
0.95
1.05
0.71
1.00
1.02
1.91
3.44
3.06
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
167.1
148.2
137.3
137.0
134.0
132.4
131.0
130.7
129.3
126.8
124.9
119.5
114.2
51.6
20.8
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.49
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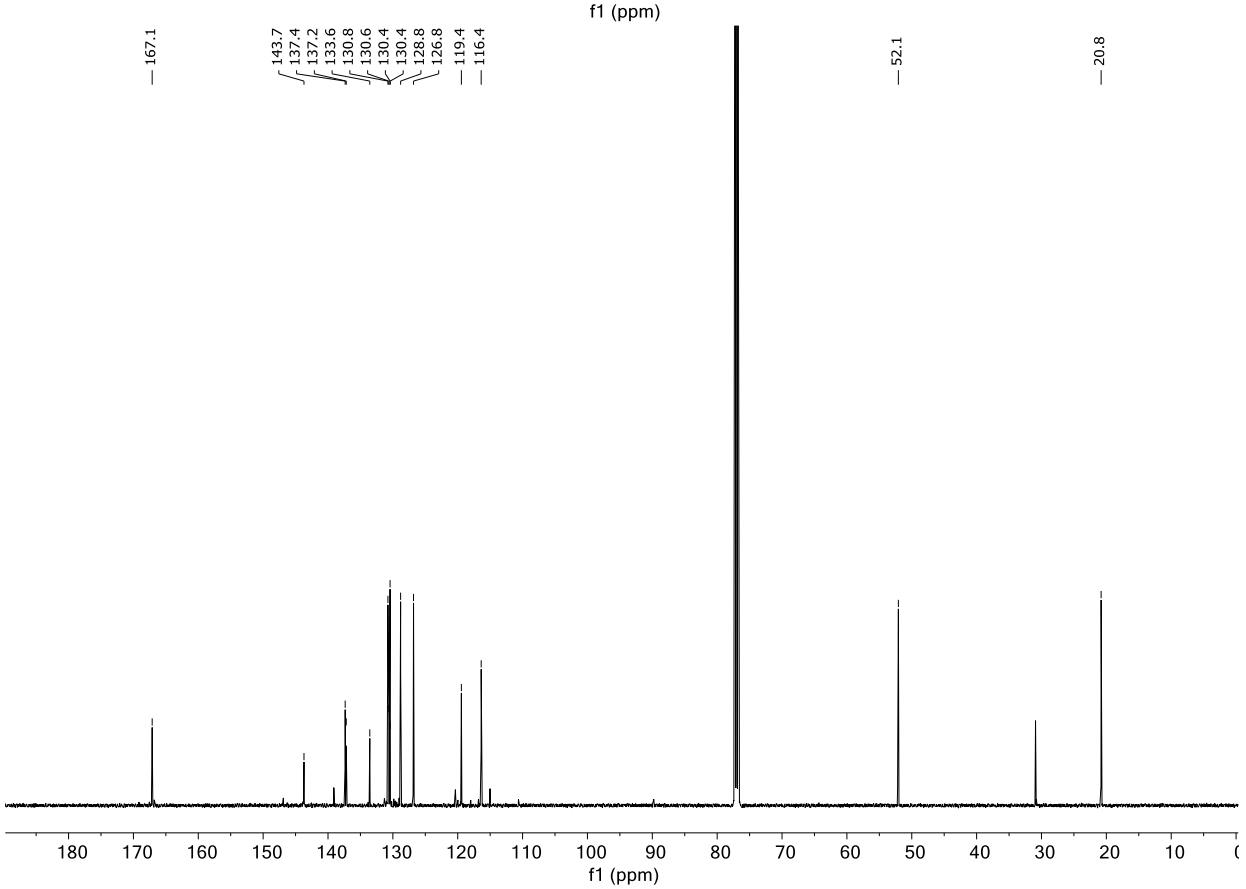
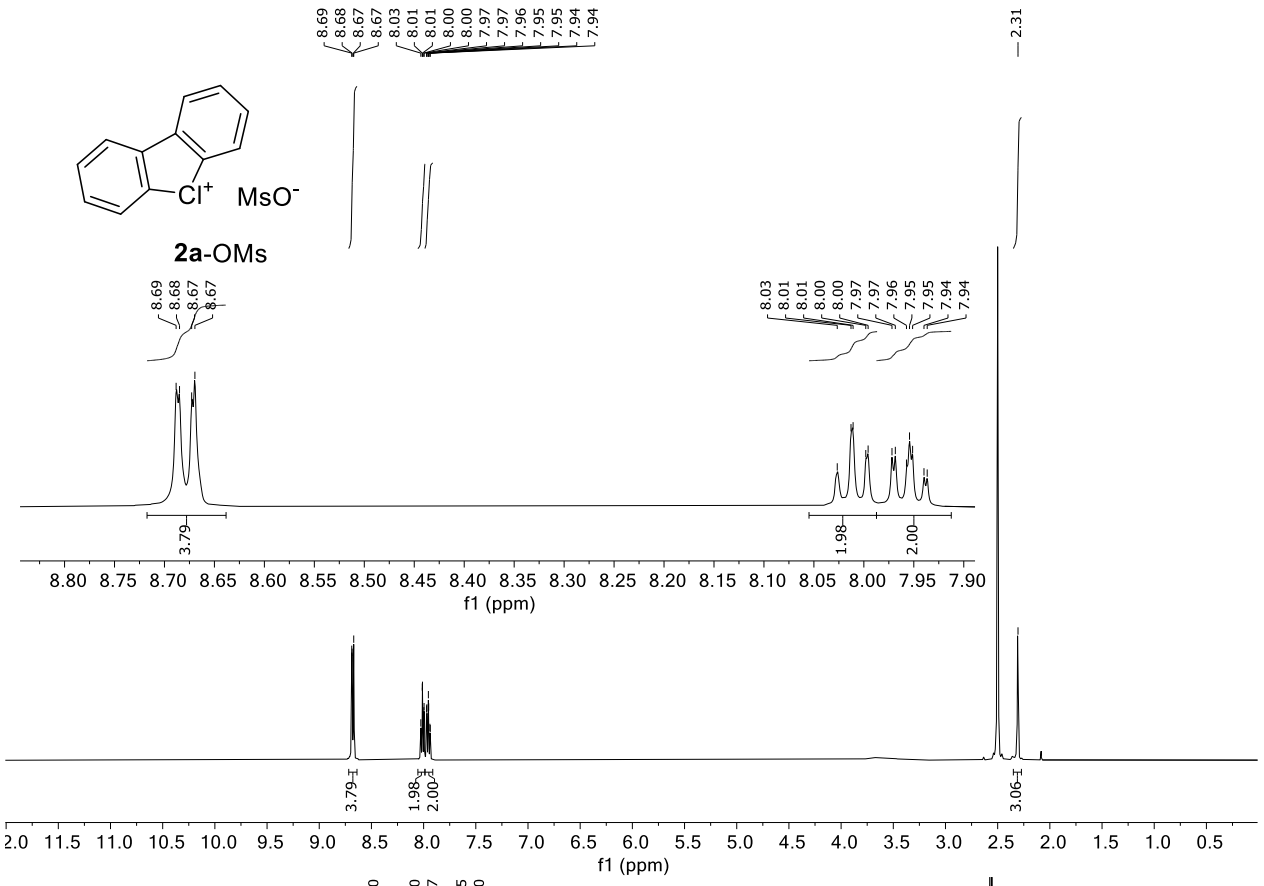
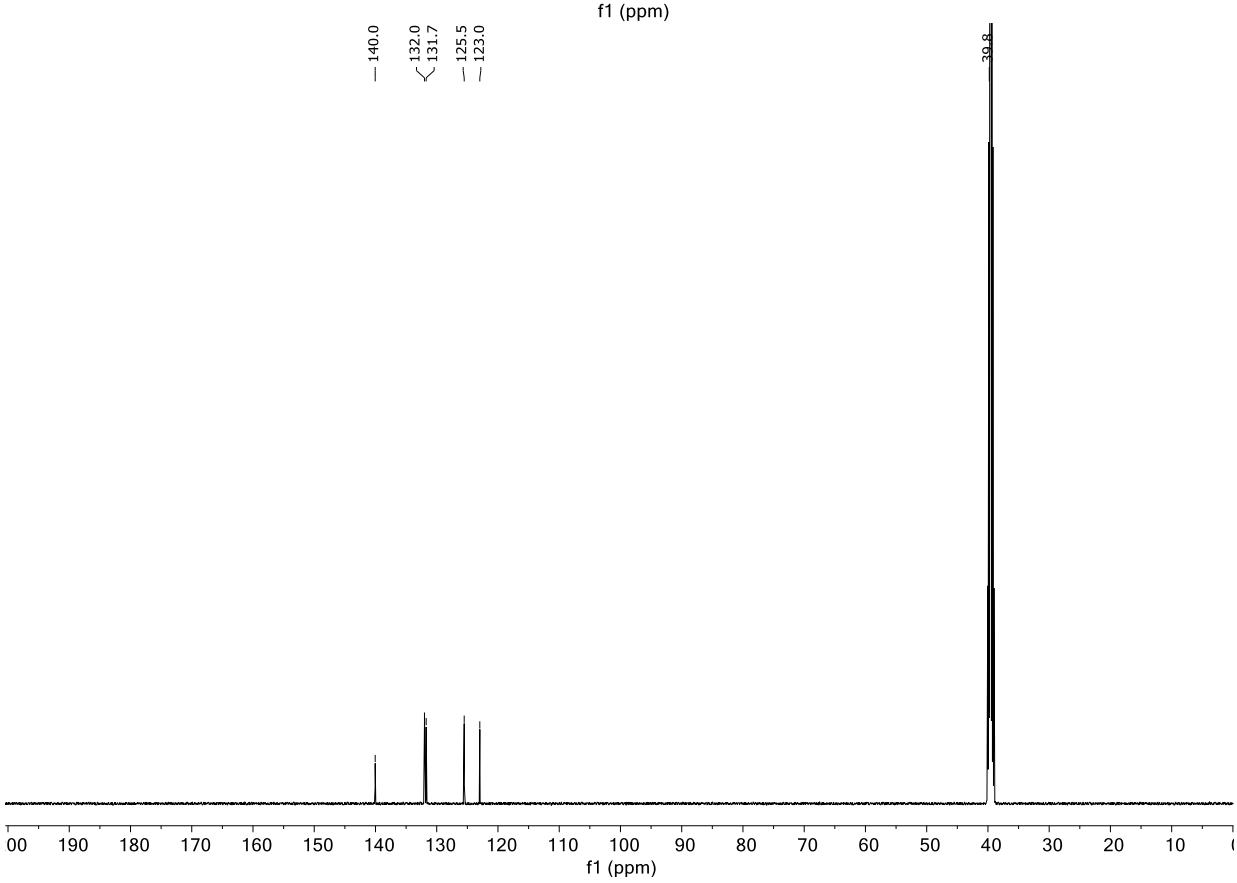
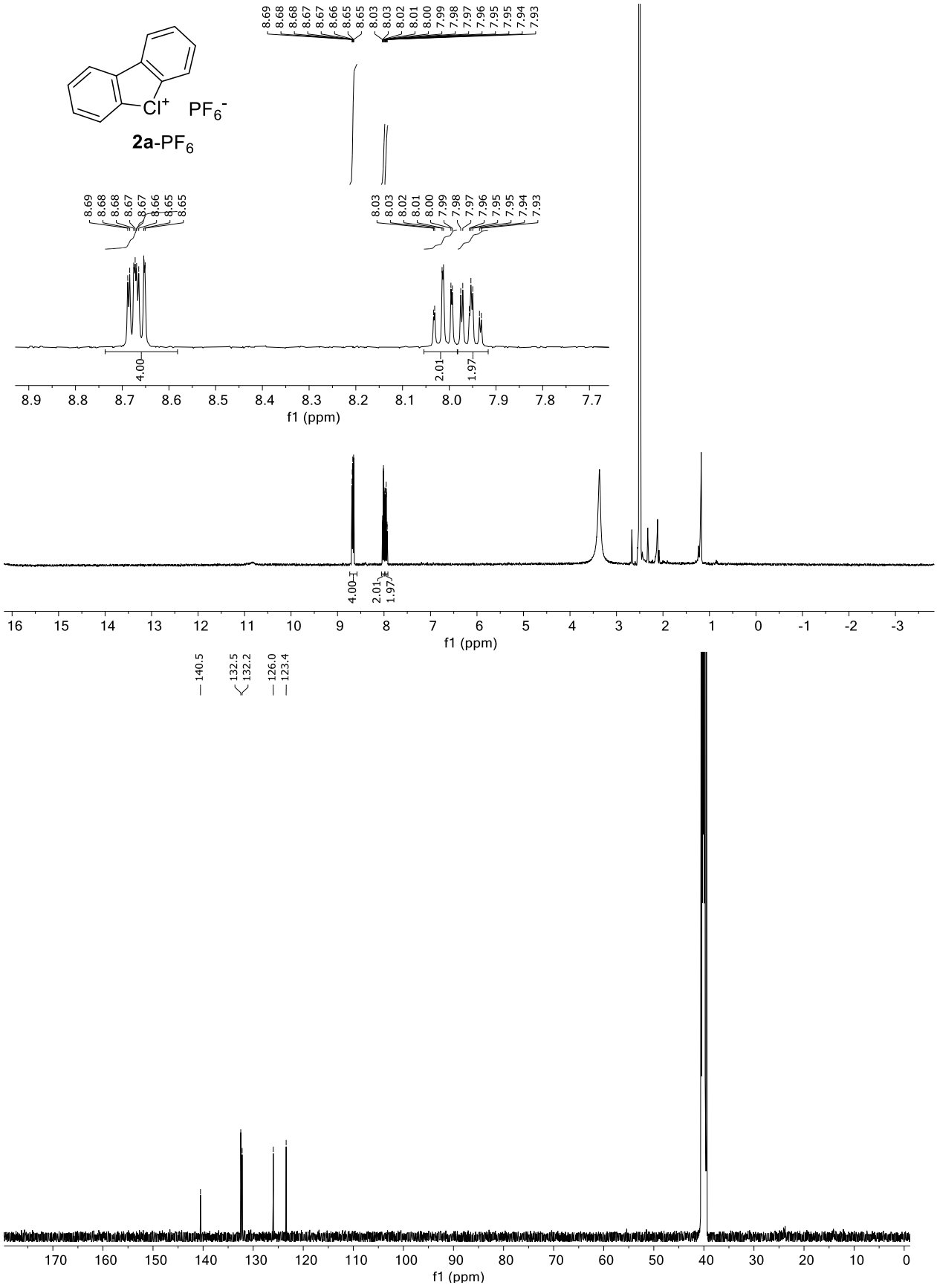
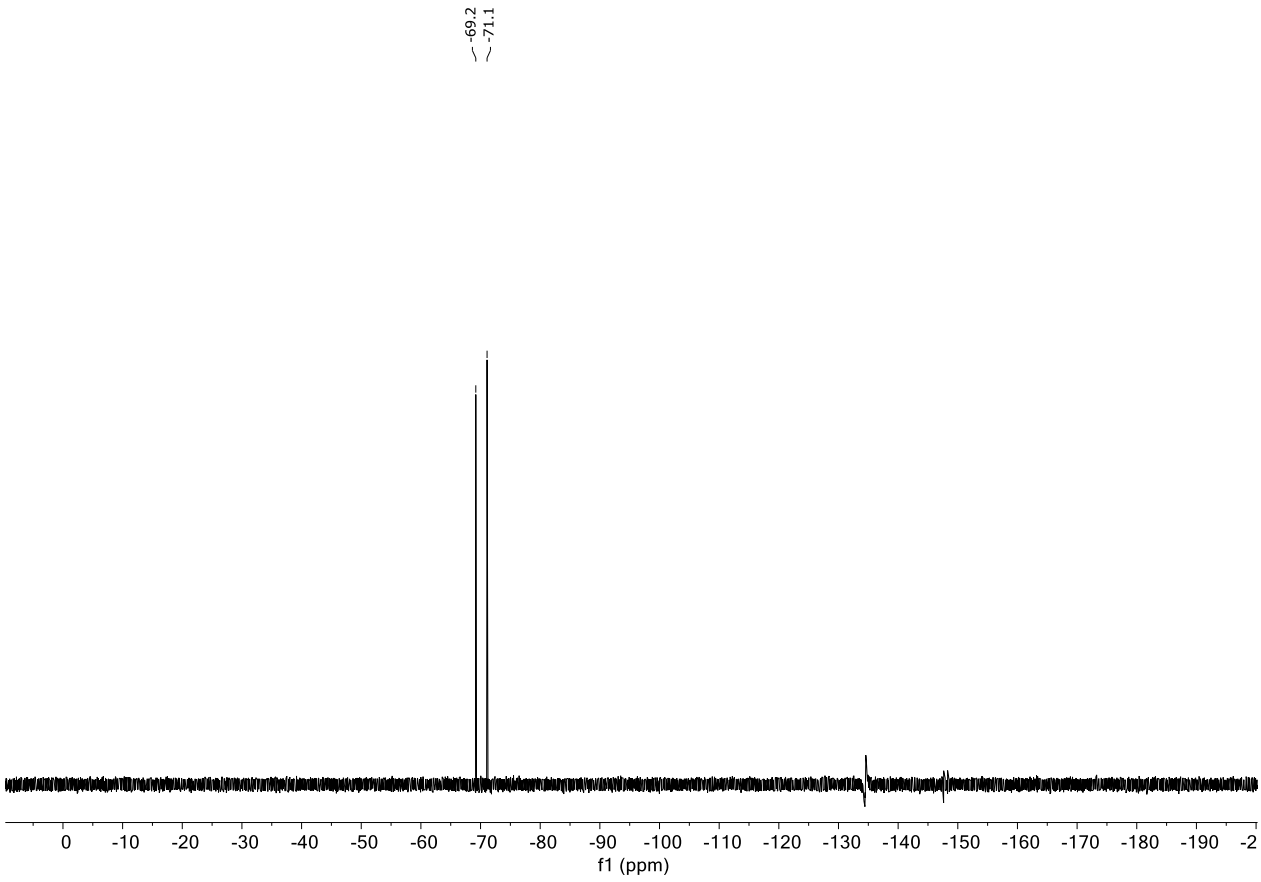
7.47
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.28
7.24
7.23
7.15
7.15
7.15
7.15
7.14
7.13
7.13
7.13
7.12
7.10
3.91
2.45
O
OMe
Cl
Me
NH2
1z
1.00
0.99
1.13
0.77
1.08
1.11
3.13
3.33
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

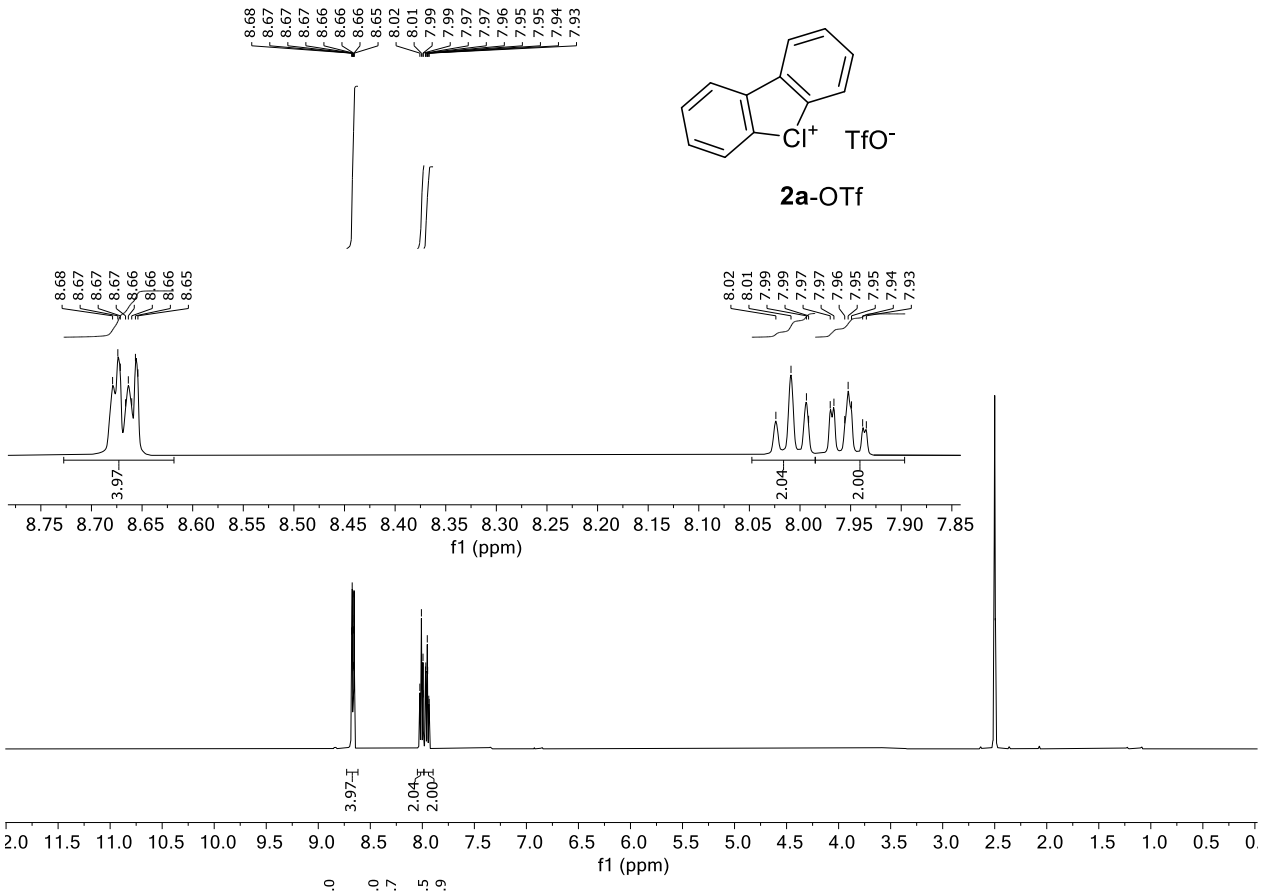

167.1
143.7
137.4
137.2
133.6
130.8
130.6
130.4
130.4
128.8
126.8
119.4
116.4
52.1
20.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

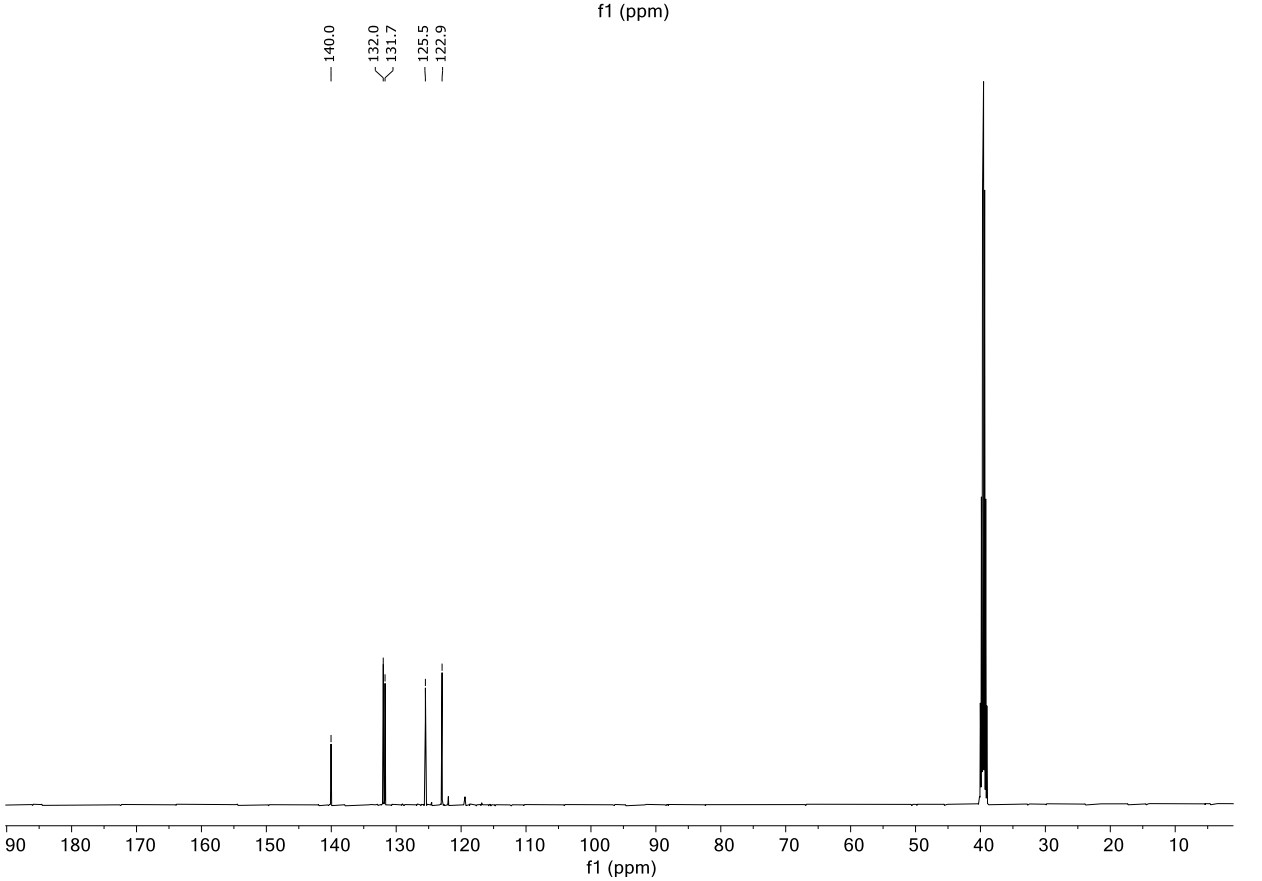

8.69
8.68
8.67
8.67
8.03
8.01
8.01
8.00
8.00
7.97
7.97
7.96
7.95
7.95
7.94
7.94
2.31
Cl+
MsO-
2a-OMs
3.79
1.98
2.00
3.06
f1 (ppm)

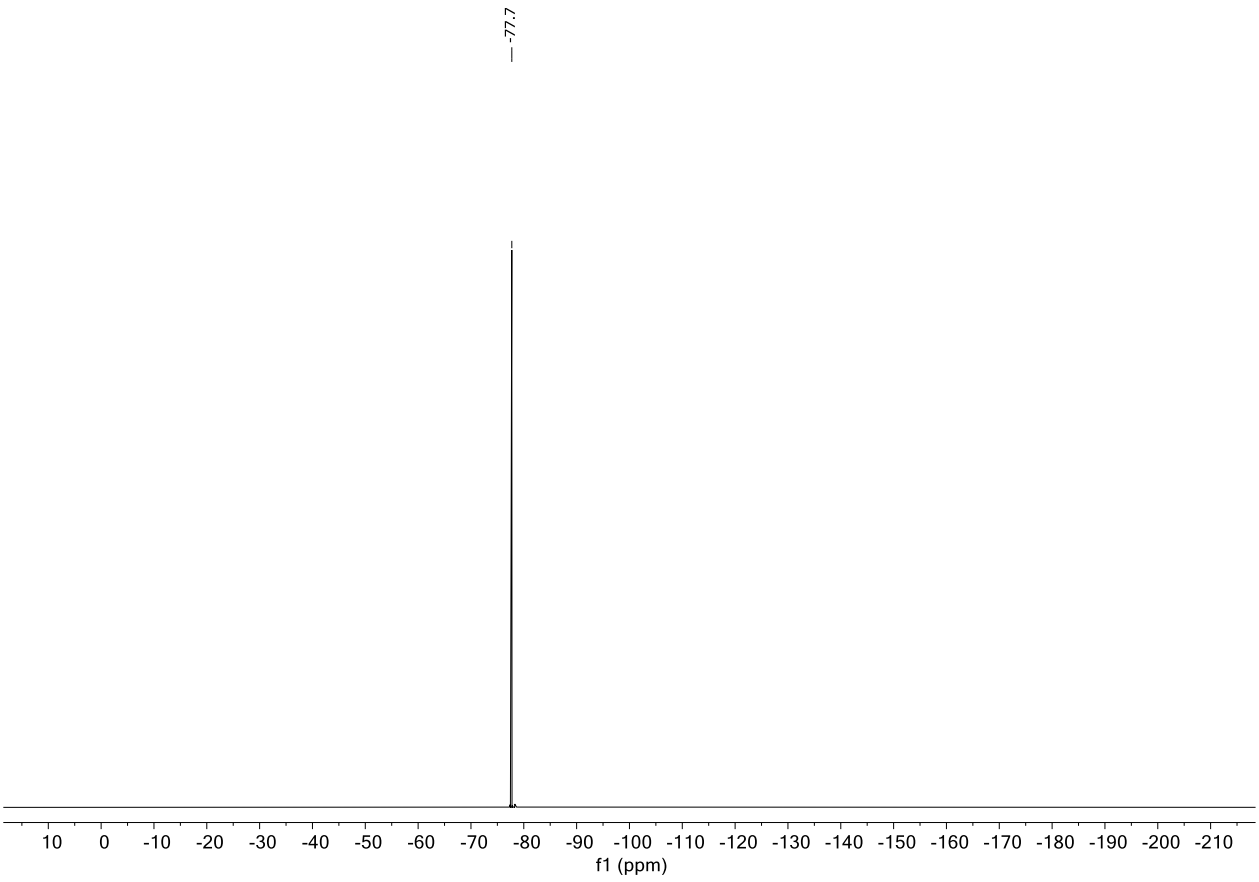

140.0
132.0
131.7
125.5
123.0
30.8
f1 (ppm)

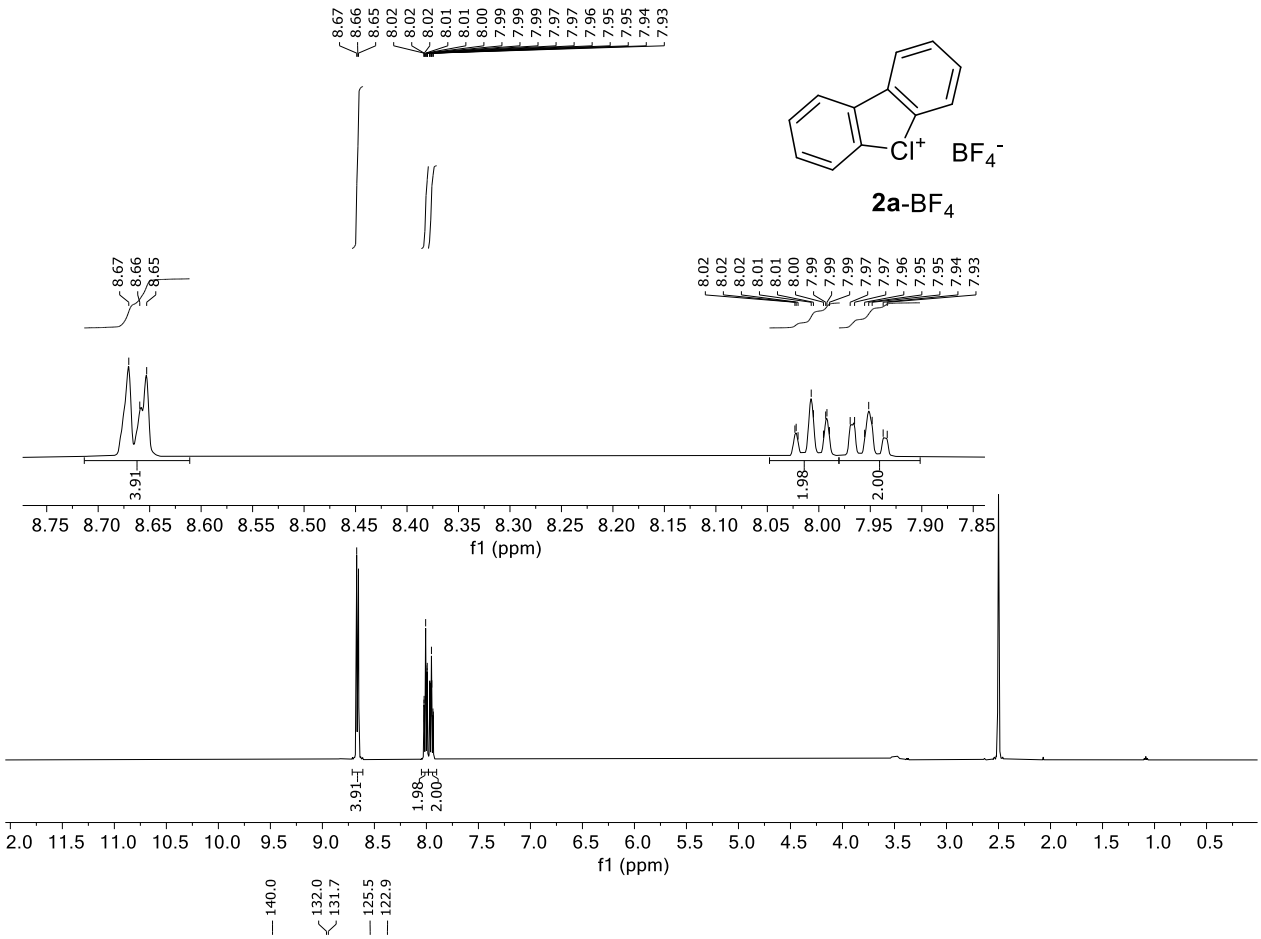

Cl+ PF6-
2a-PF6
f1 (ppm)
f1 (ppm)
f1 (ppm)


-69.2
-71.1
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)


8.68 8.67 8.67 8.67 8.66 8.66 8.66 8.65 8.02 8.01 7.99 7.99 7.97 7.97 7.96 7.95 7.95 7.94 7.93
Cl+ TfO-
2a-OTf
3.97
2.04
2.00
f1 (ppm)


140.0 132.0 131.7 125.5 122.9
f1 (ppm)


-77.7
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)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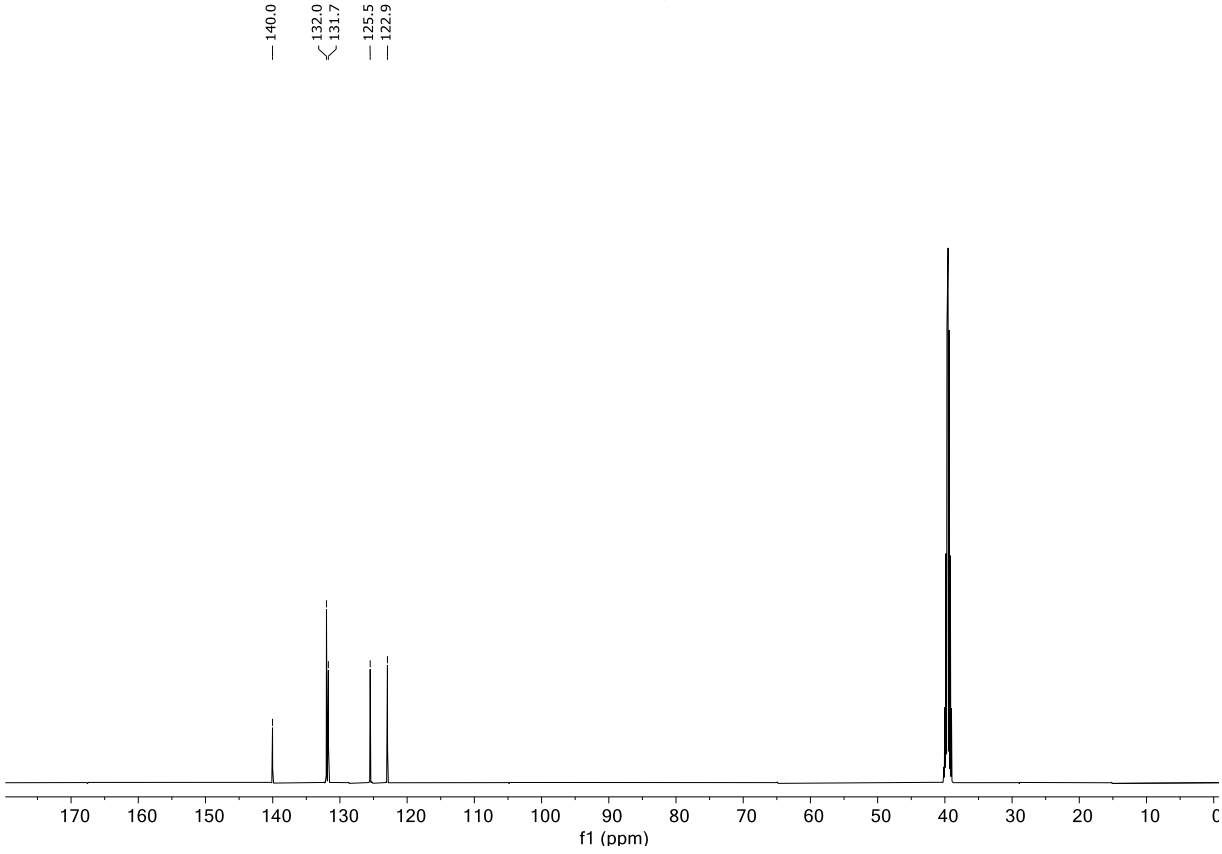
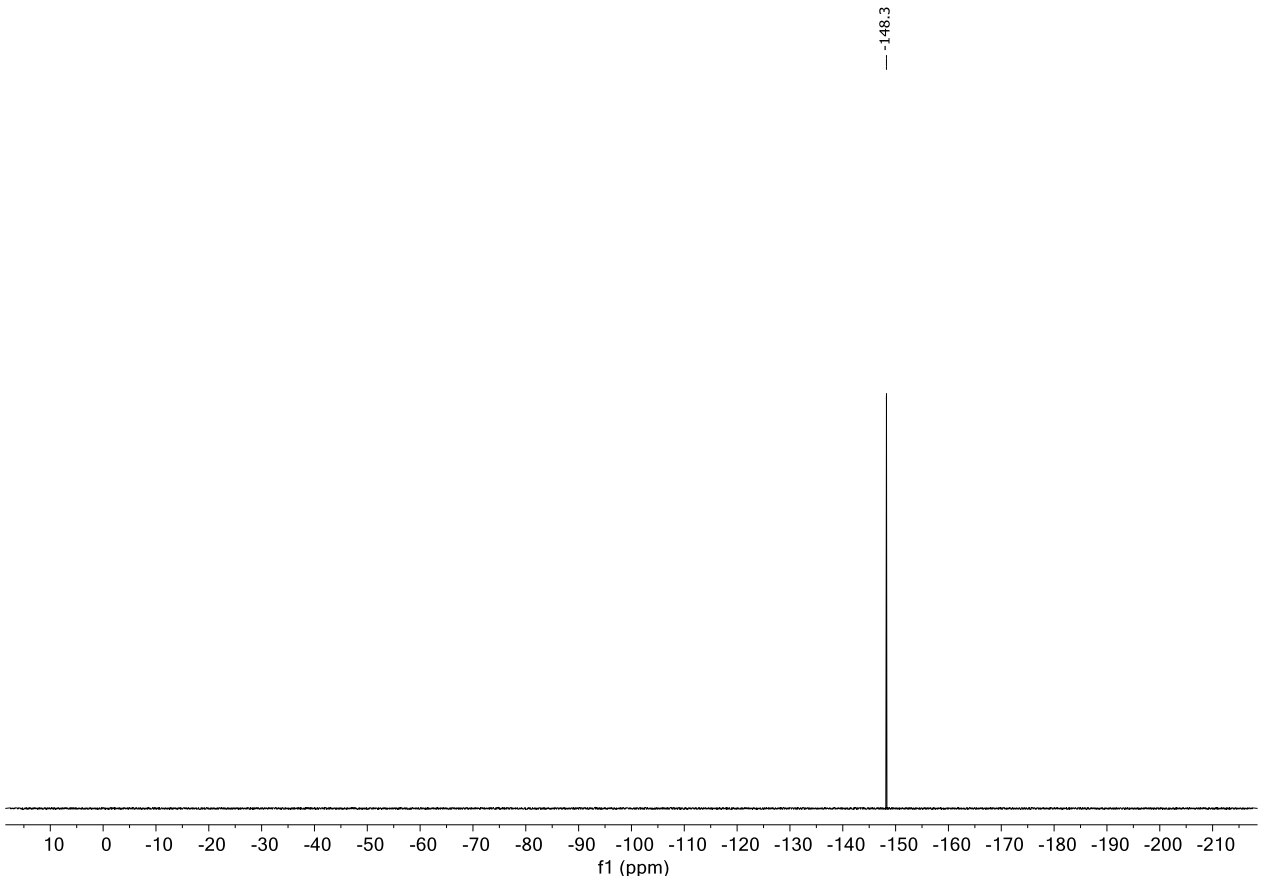
8.66
8.65
8.02
8.02
8.02
8.01
8.01
8.00
7.99
7.99
7.99
7.97
7.97
7.96
7.95
7.95
7.94
7.93
Cl+
BF4-
2a-BF4
3.91
1.98
2.00
f1 (ppm)


140.0
132.0
131.7
125.5
122.9
f1 (ppm)


-148.3
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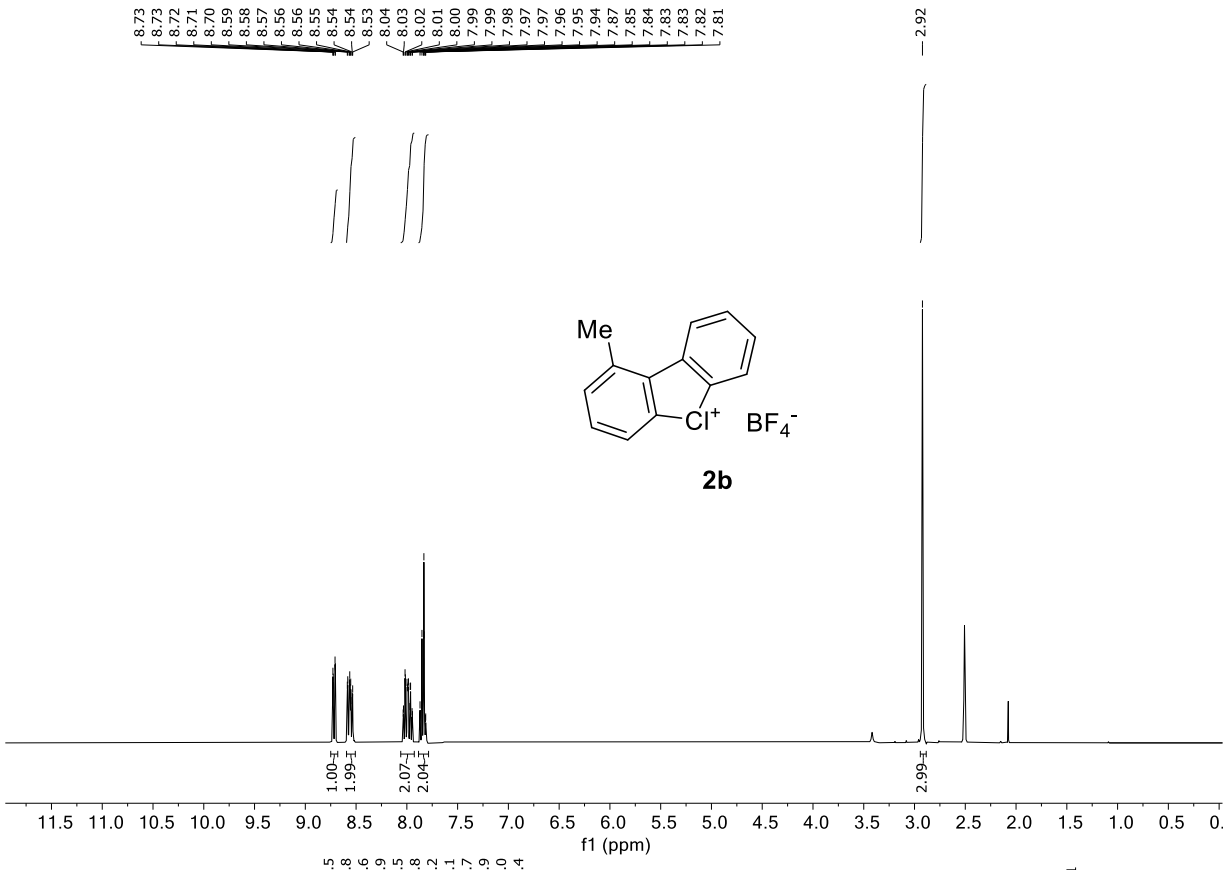
f1 (ppm)


8.73
8.73
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8.70
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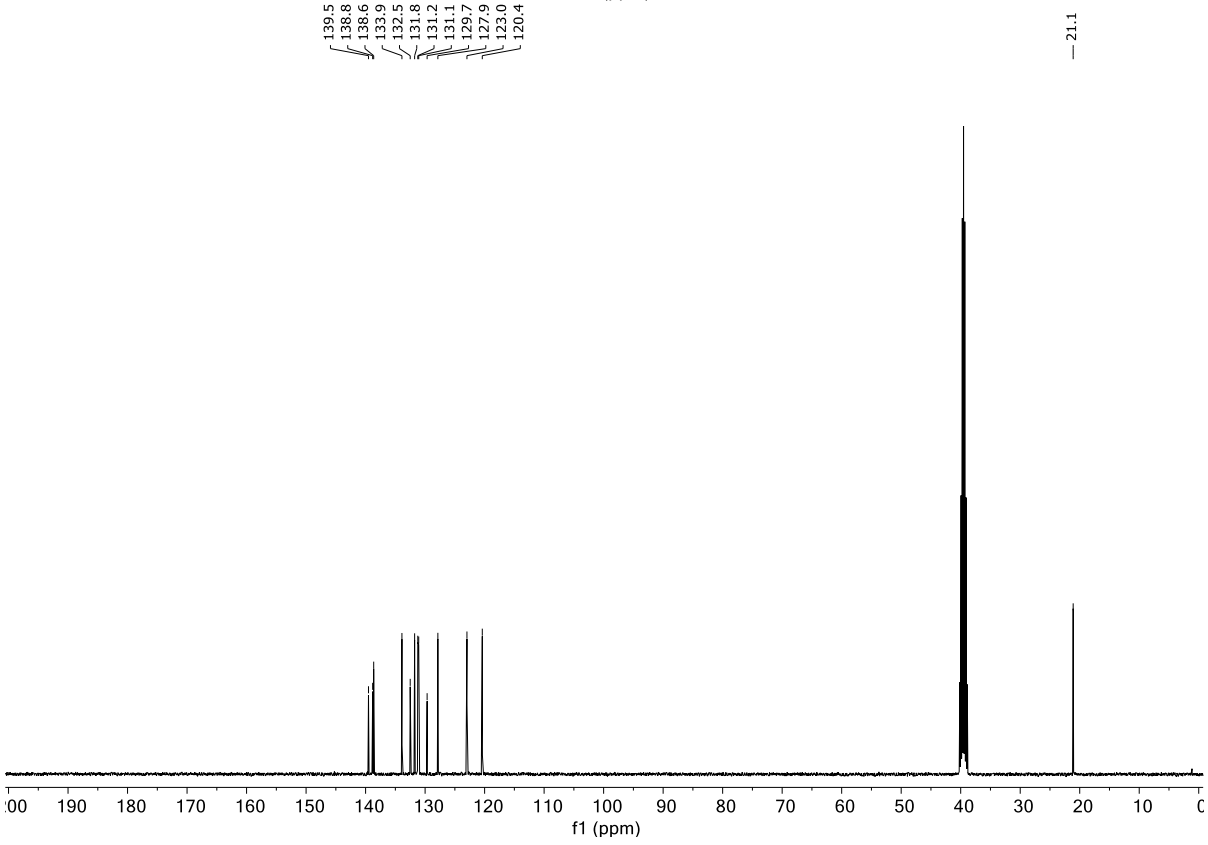
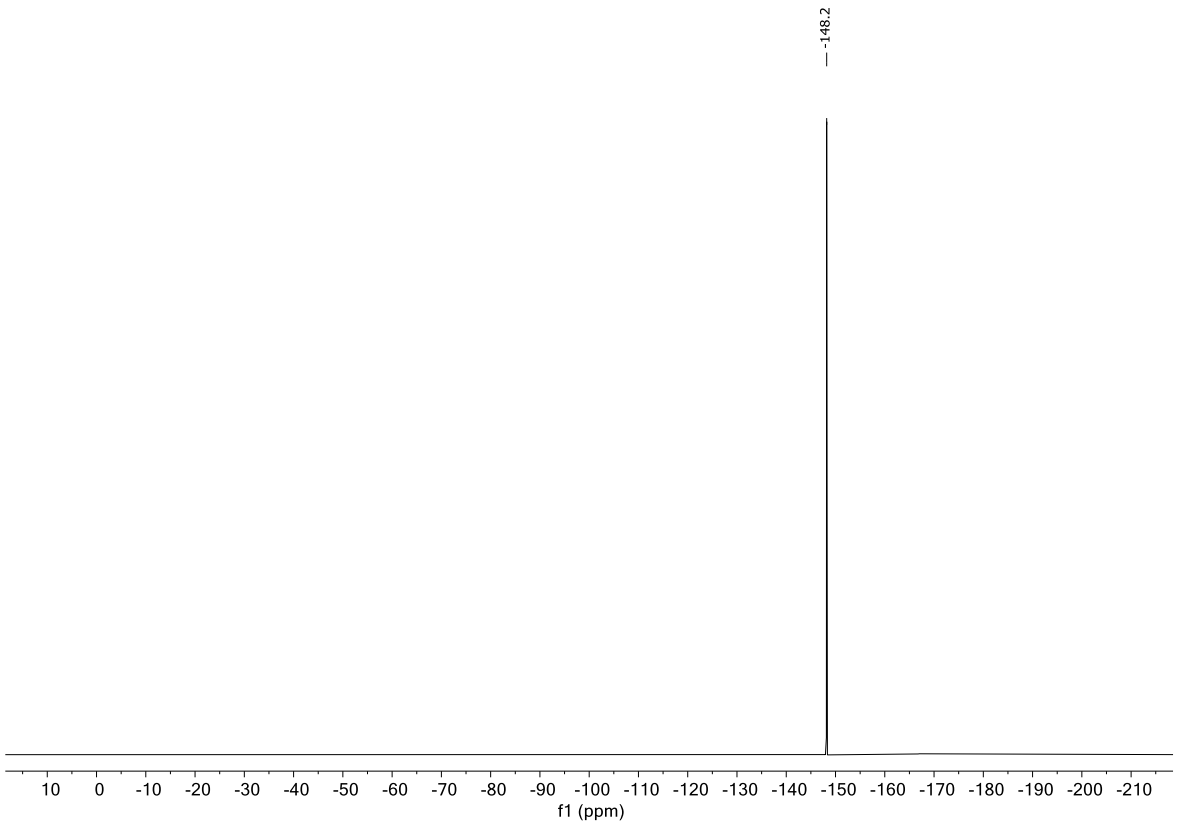
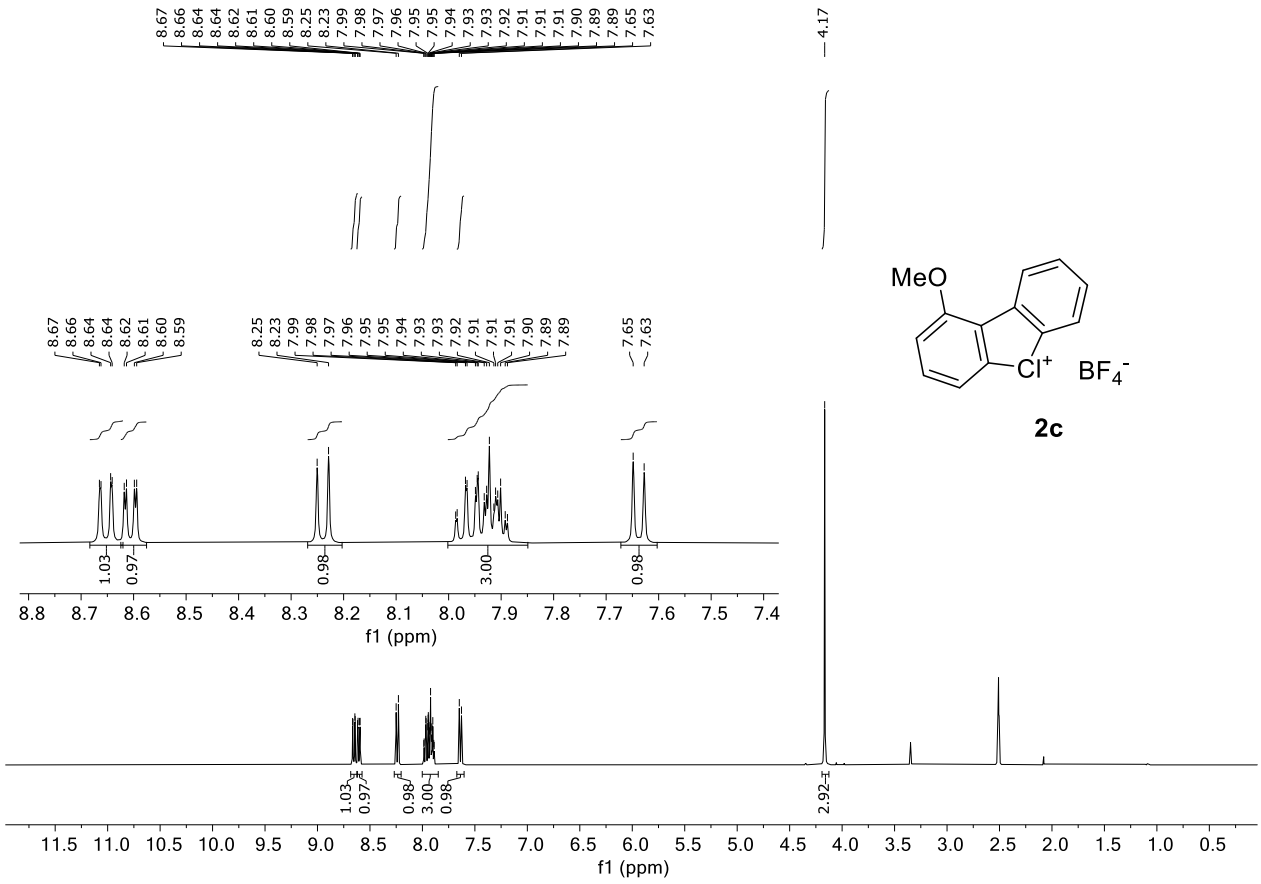
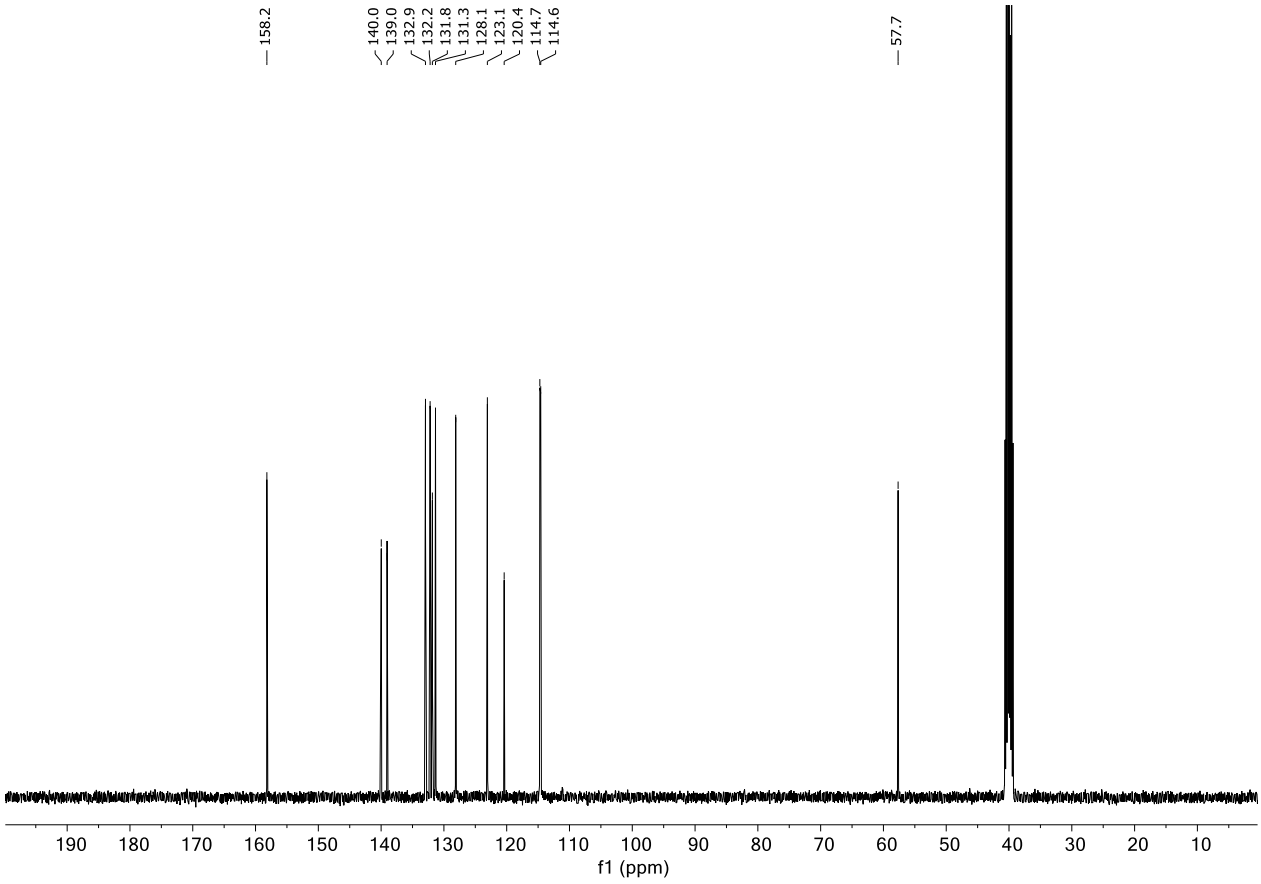
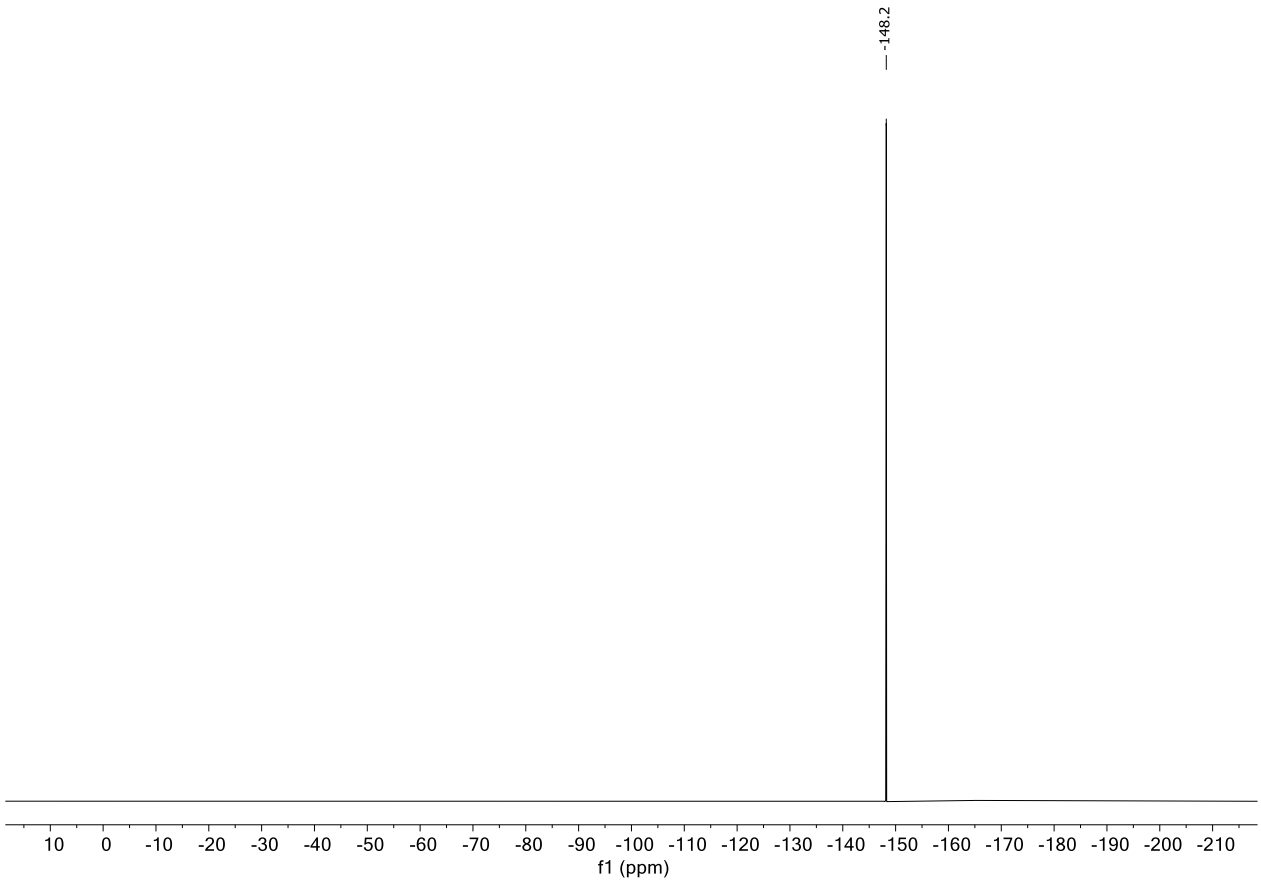
8.58
8.57
8.56
8.56
8.55
8.54
8.54
8.53
8.04
8.03
8.02
8.01
8.00
7.99
7.99
7.98
7.97
7.97
7.96
7.95
7.94
7.87
7.85
7.84
7.83
7.83
7.82
7.81
2.92
Me
Cl+
BF4-
2b
1.00
1.99
2.07
2.04
2.99
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

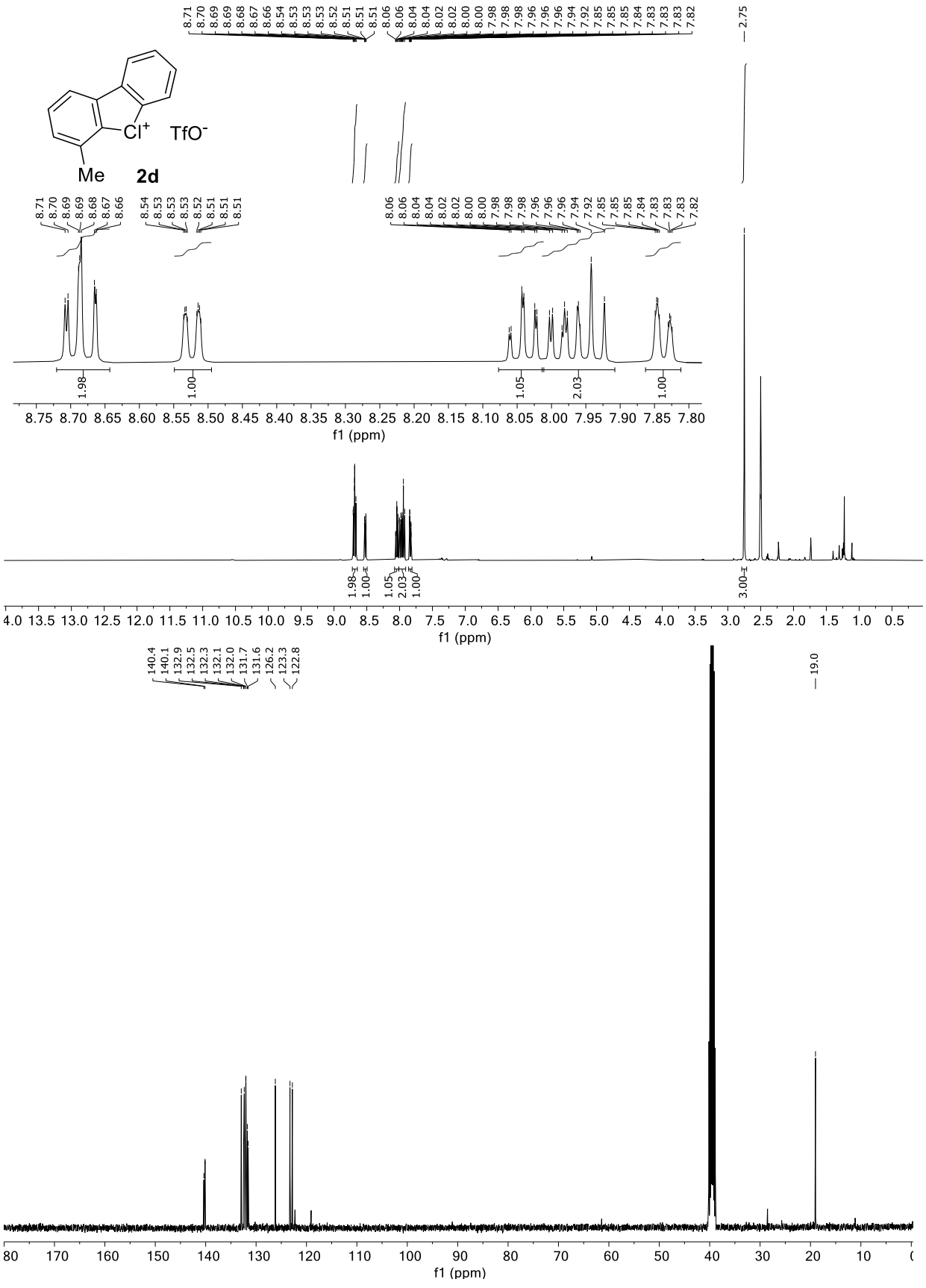

139.5
138.8
138.6
133.9
132.5
131.8
131.2
131.1
129.7
127.9
123.0
120.4
21.1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

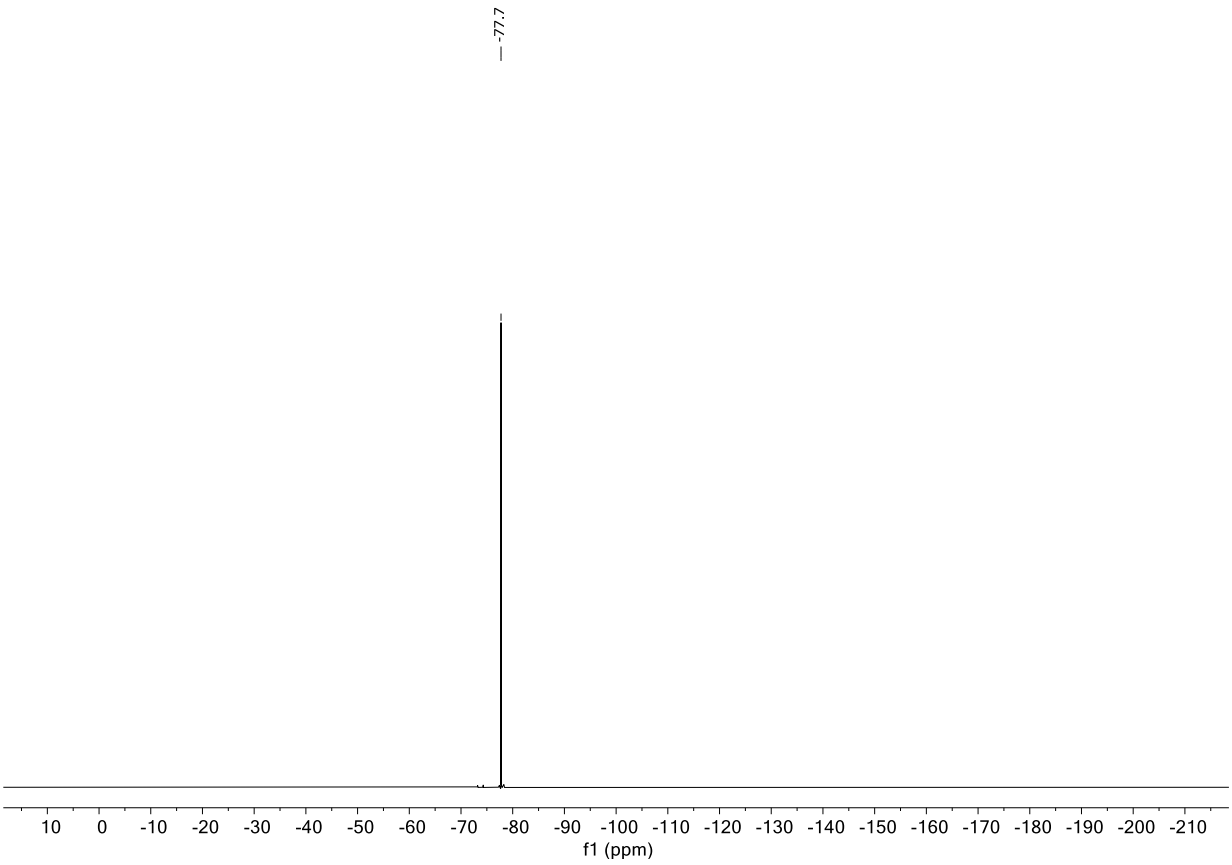

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

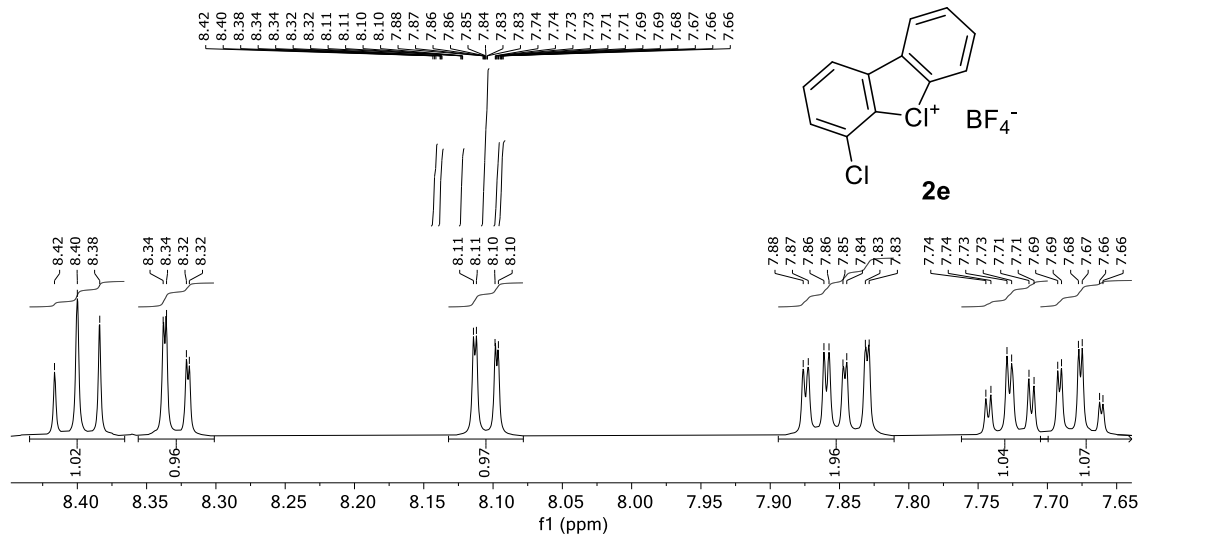

MeO
Cl+
BF4-
2c
f1 (ppm)
f1 (ppm)

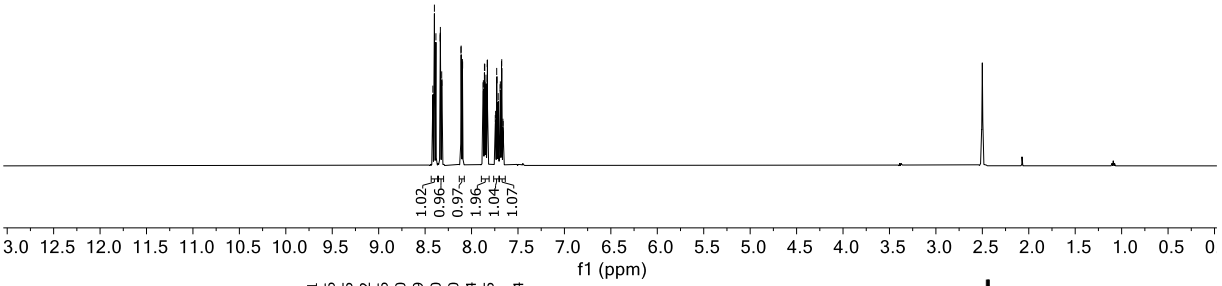

158.2
140.0
139.0
132.9
132.2
131.8
131.3
128.1
123.1
120.4
114.7
114.6
57.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

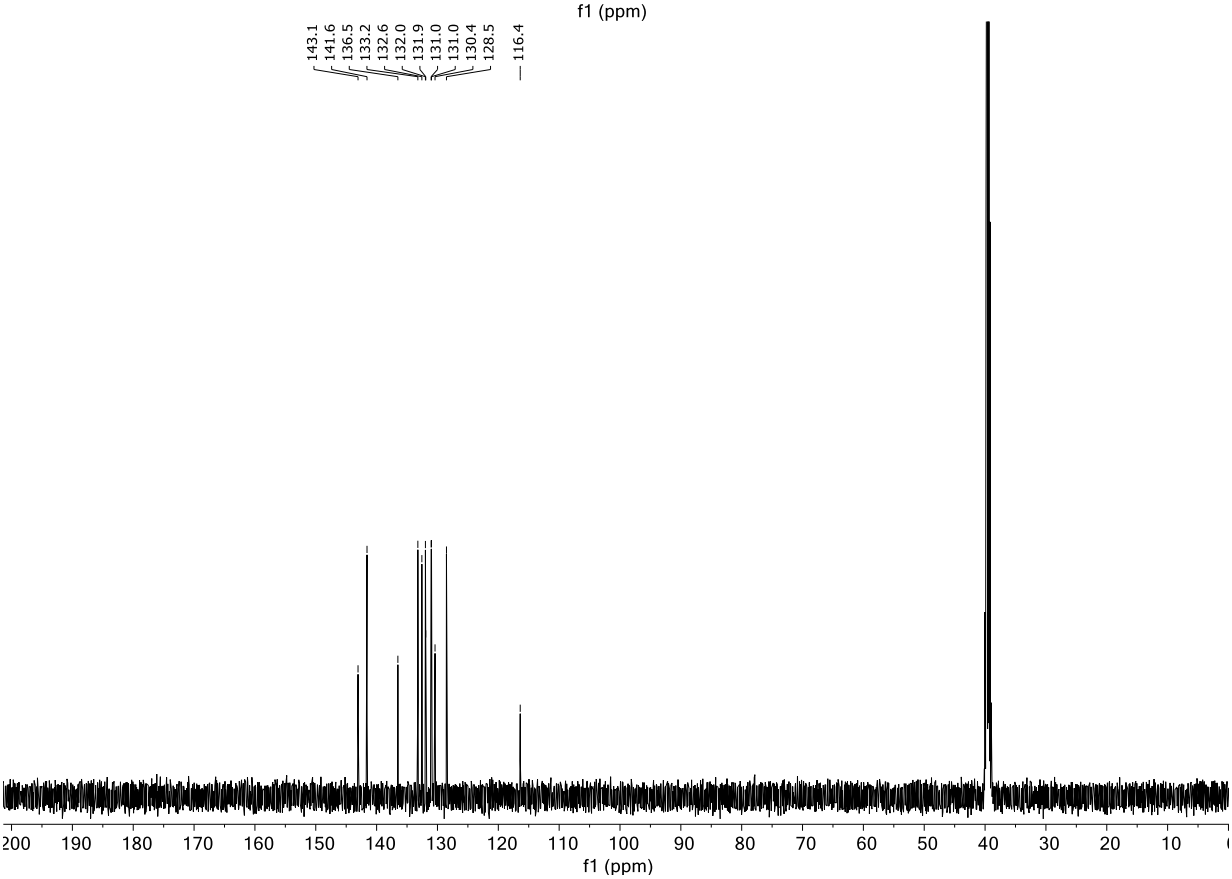

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

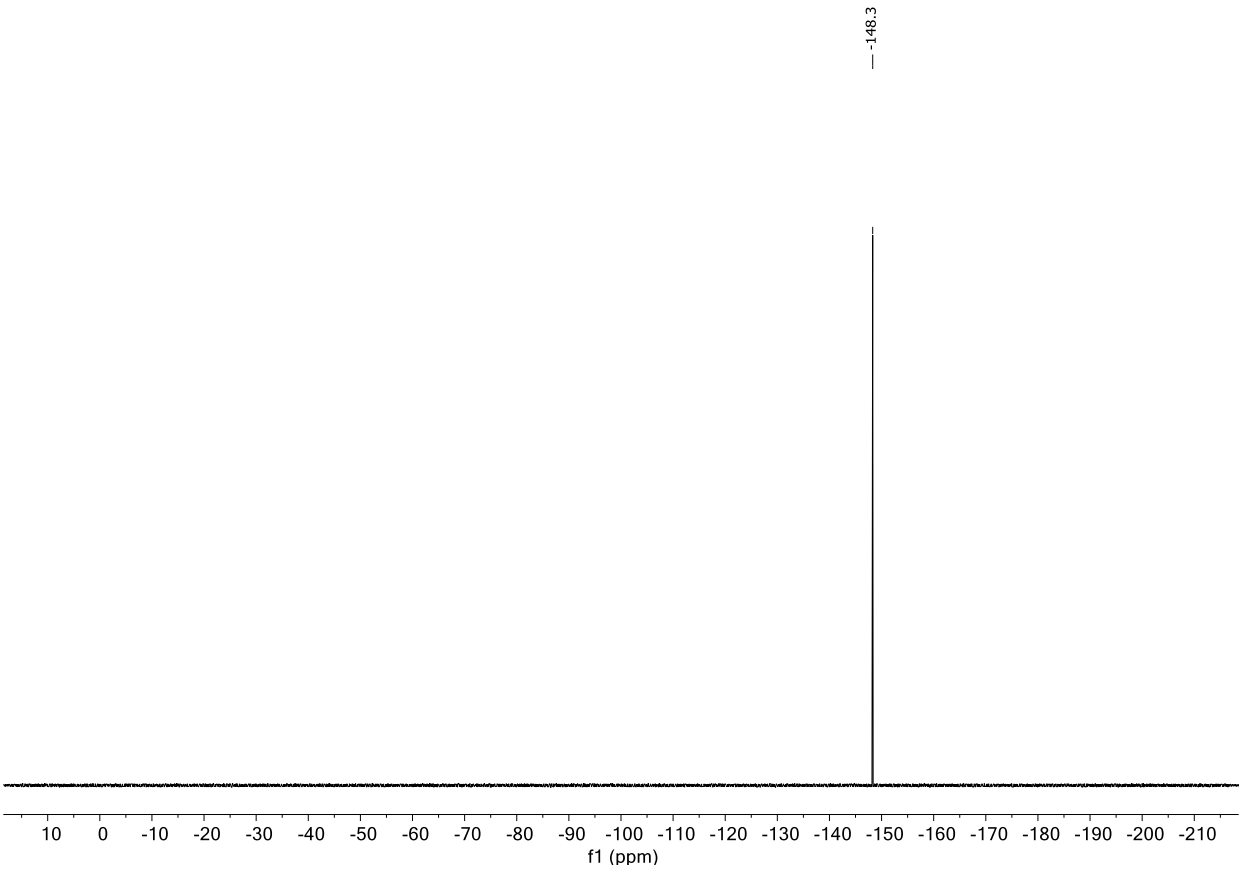

Cl+
TfO-
Me
2d
f1 (ppm)
f1 (ppm)
f1 (ppm)

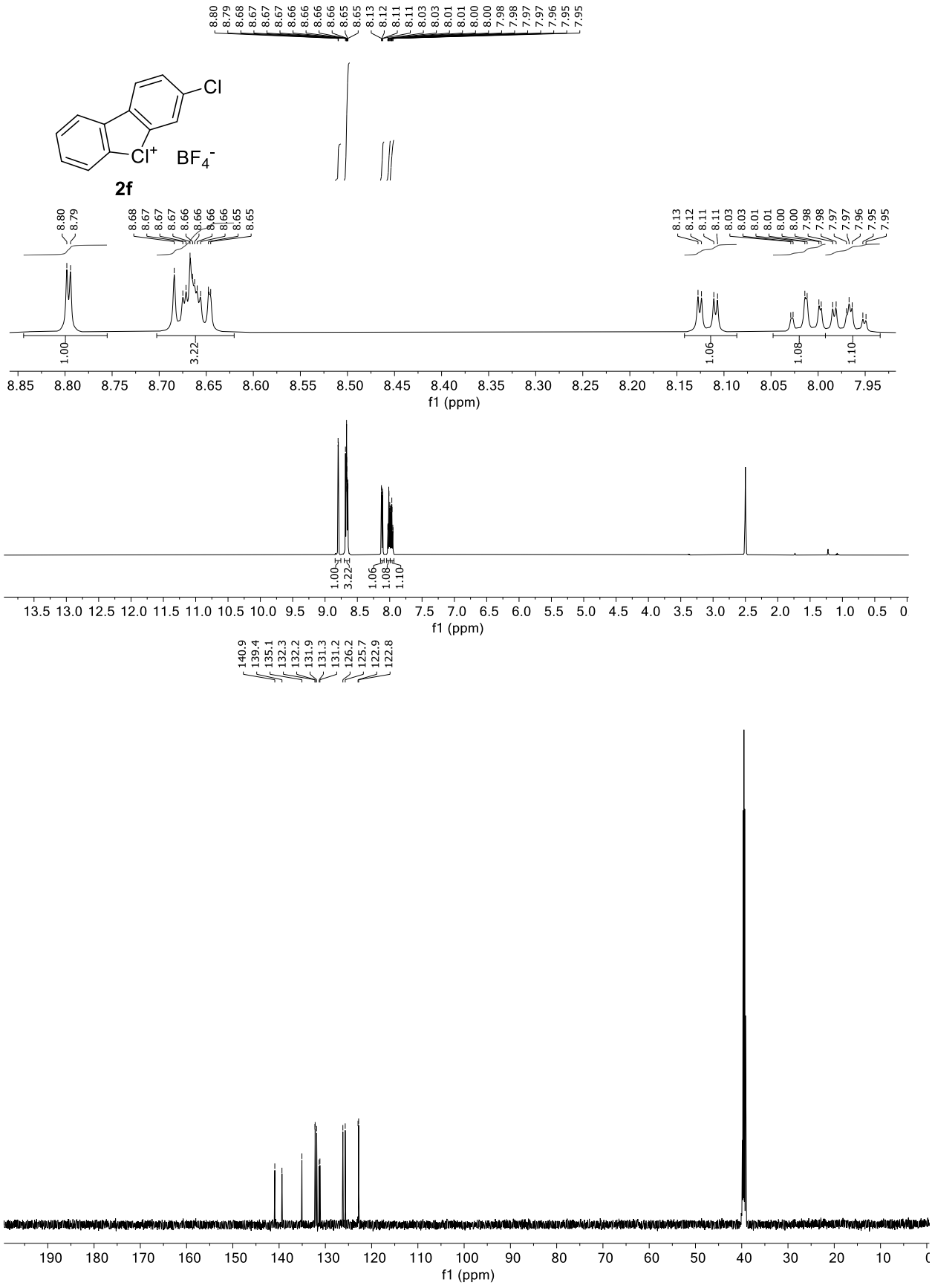

-77.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

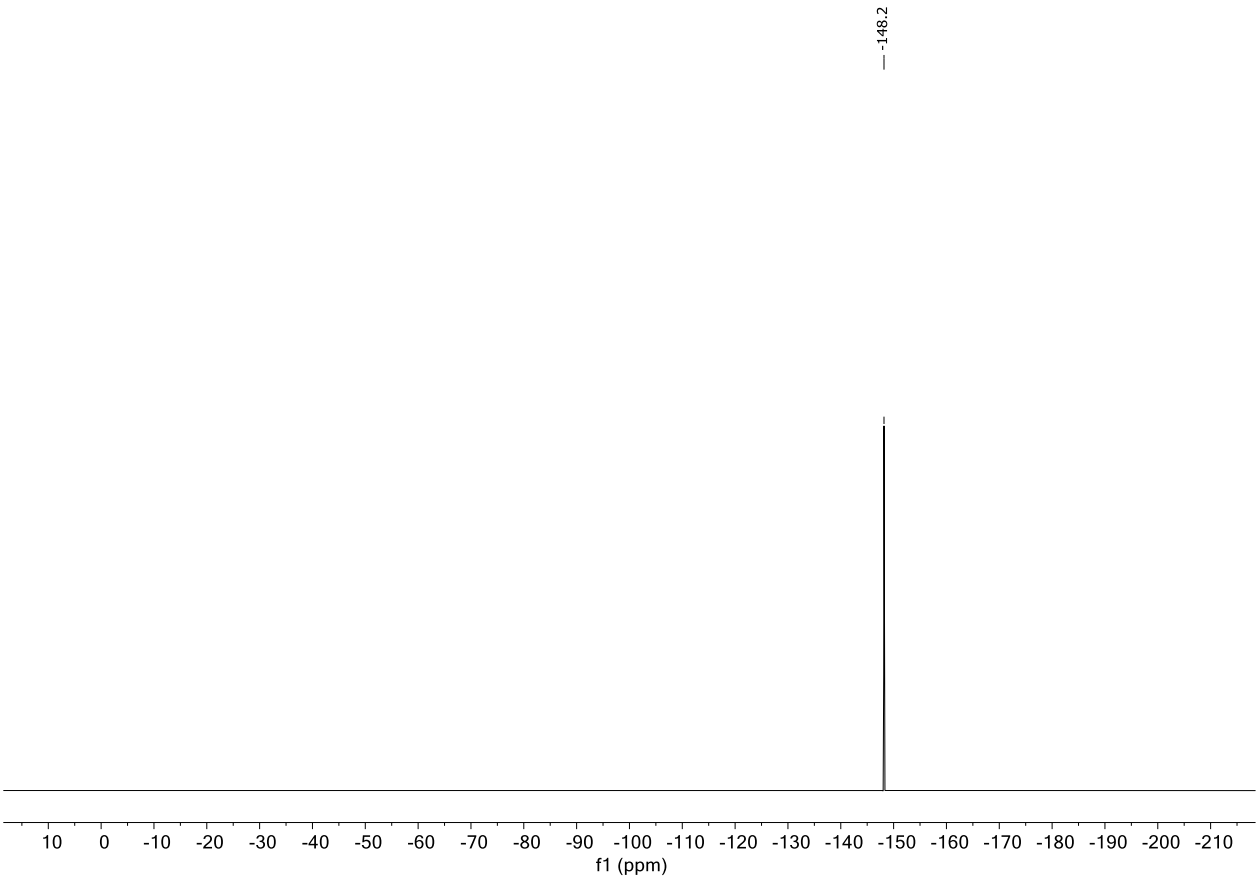

8.42 8.40 8.38 8.34 8.34 8.32 8.32 8.11 8.11 8.10 8.10 7.88 7.87 7.86 7.86 7.85 7.84 7.83 7.83 7.74 7.74 7.73 7.73 7.71 7.71 7.69 7.69 7.68 7.67 7.66 7.66
Cl+ BF4-
Cl
2e
1.02 0.96 0.97 1.96 1.04 1.07
8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65
f1 (ppm)

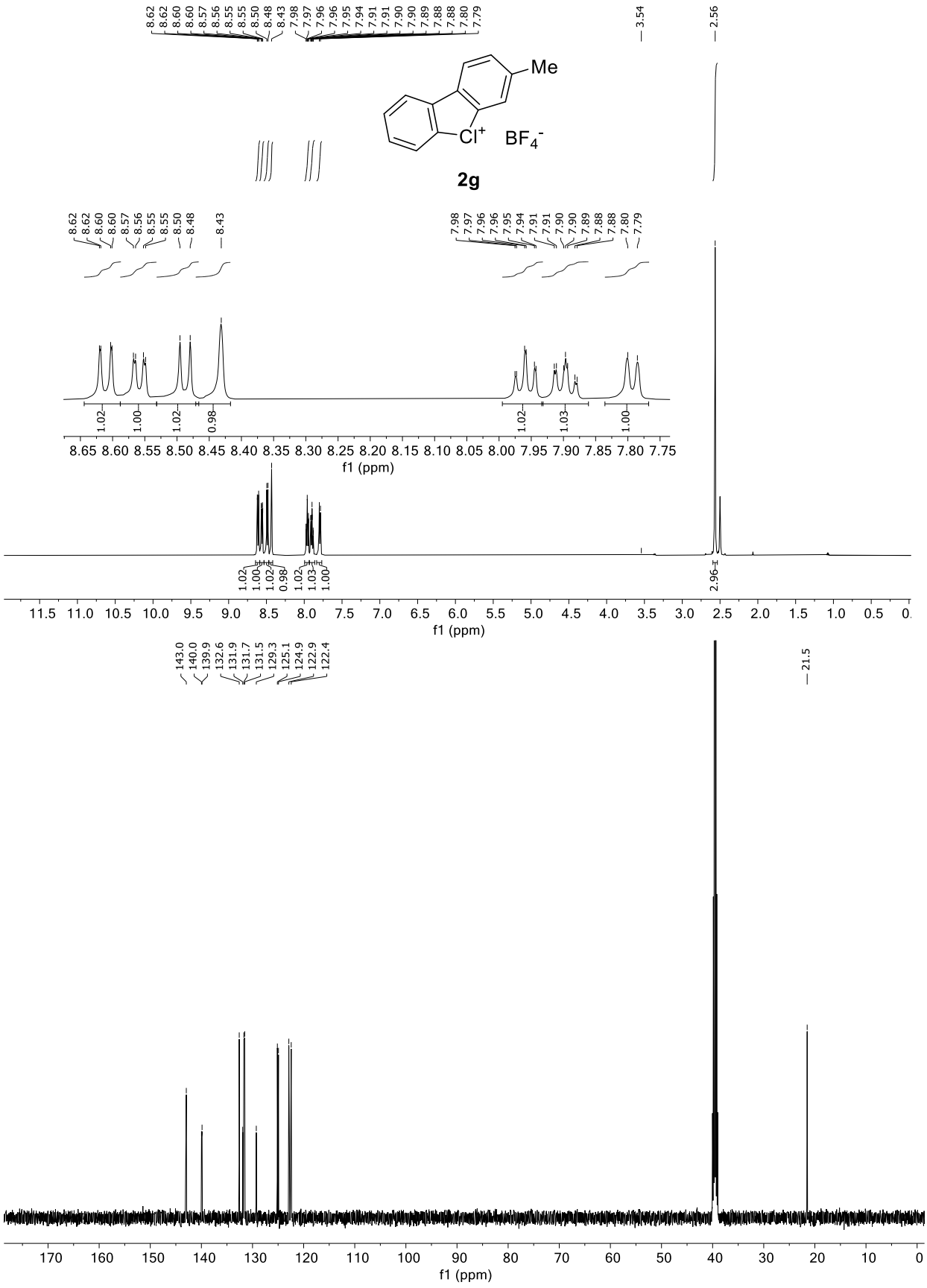

1.02 0.96 0.97 1.96 1.04 1.07
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

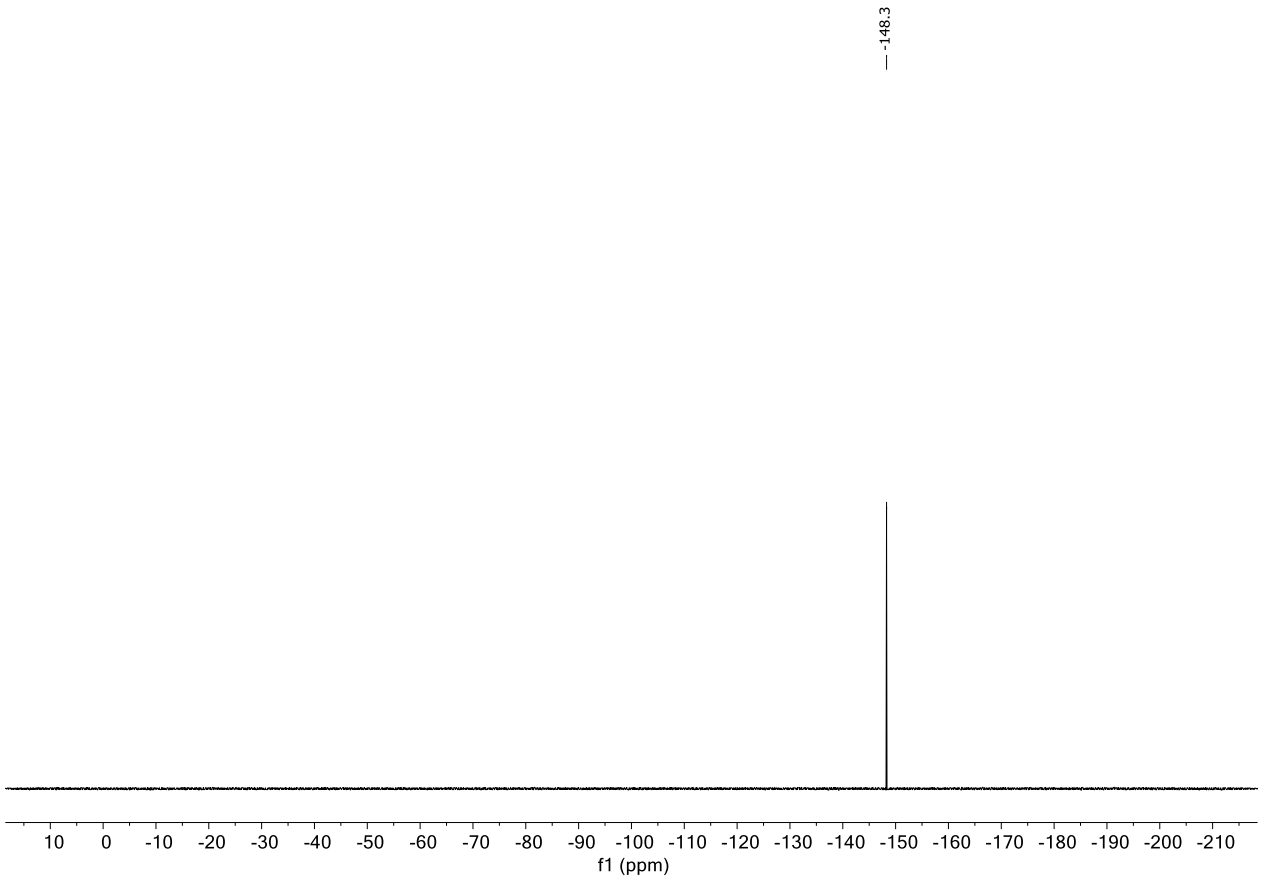

143.1 141.6 136.5 133.2 132.6 132.0 131.9 131.0 131.0 130.4 128.5 116.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

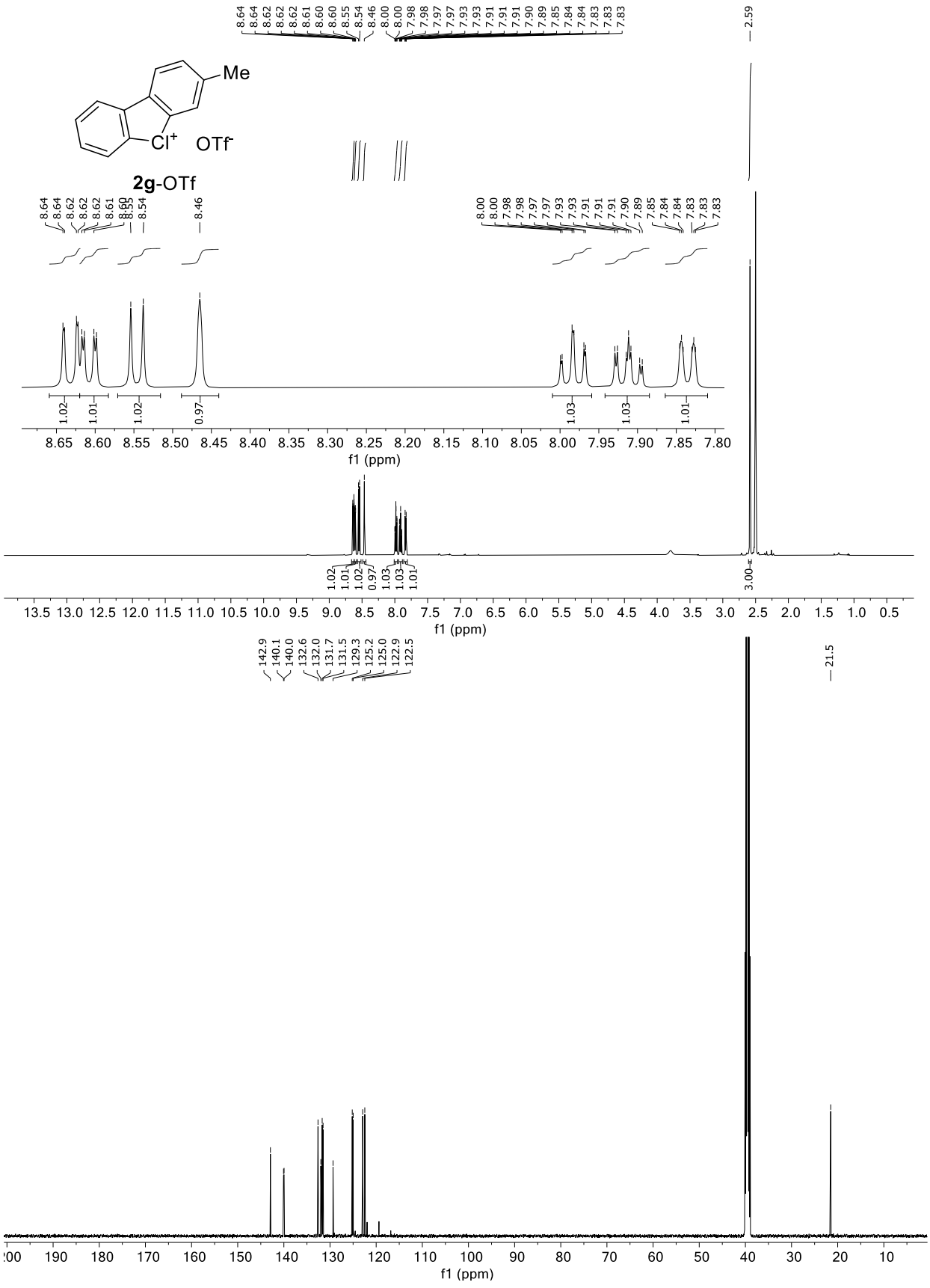

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

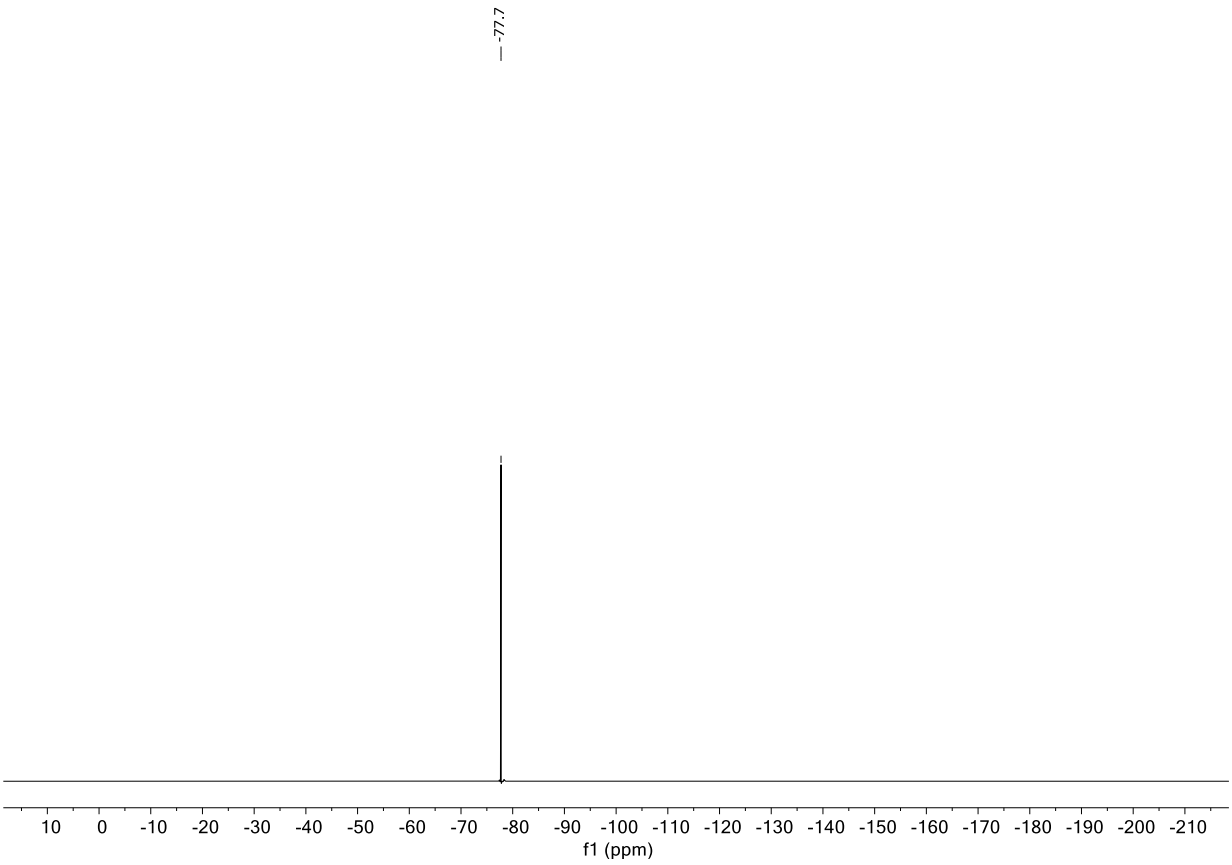

Cl
Cl+
BF4-
2f
f1 (ppm)
f1 (ppm)
f1 (ppm)

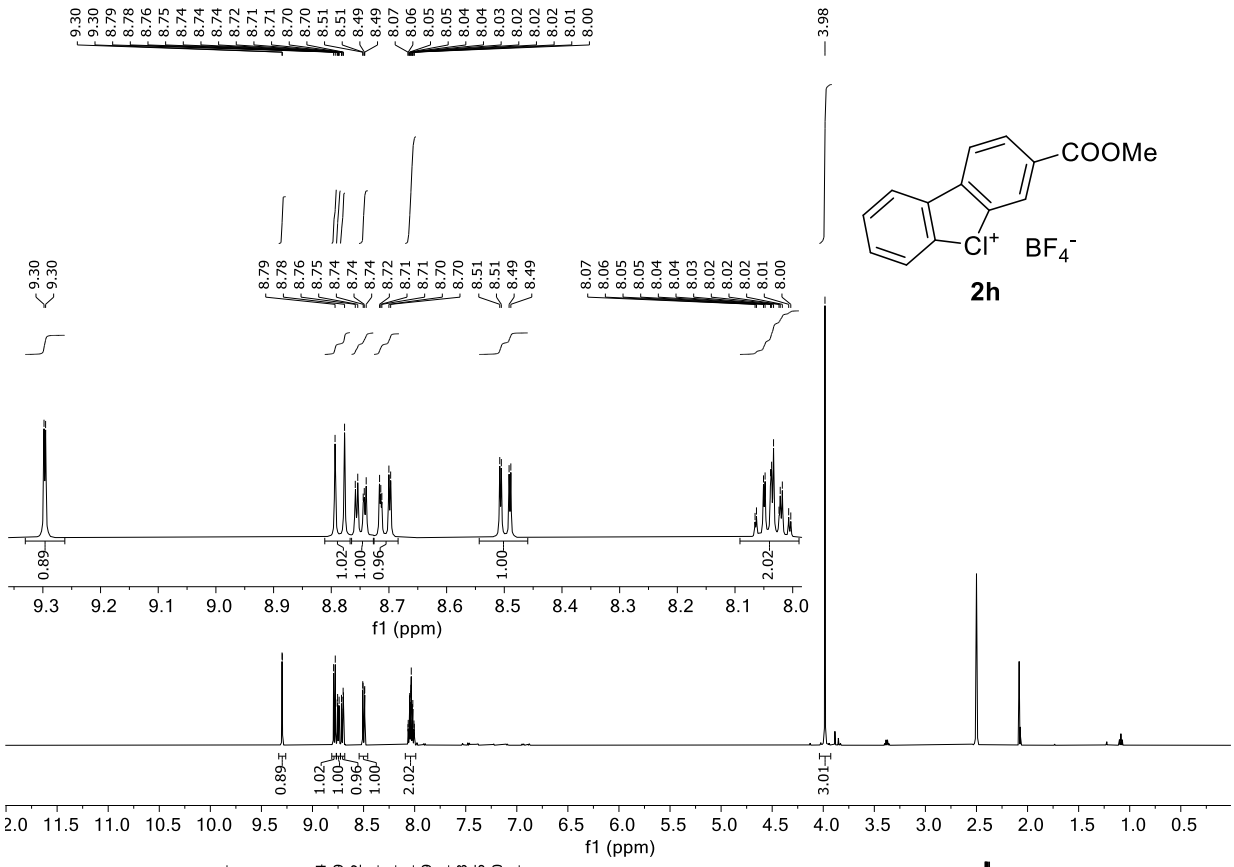

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

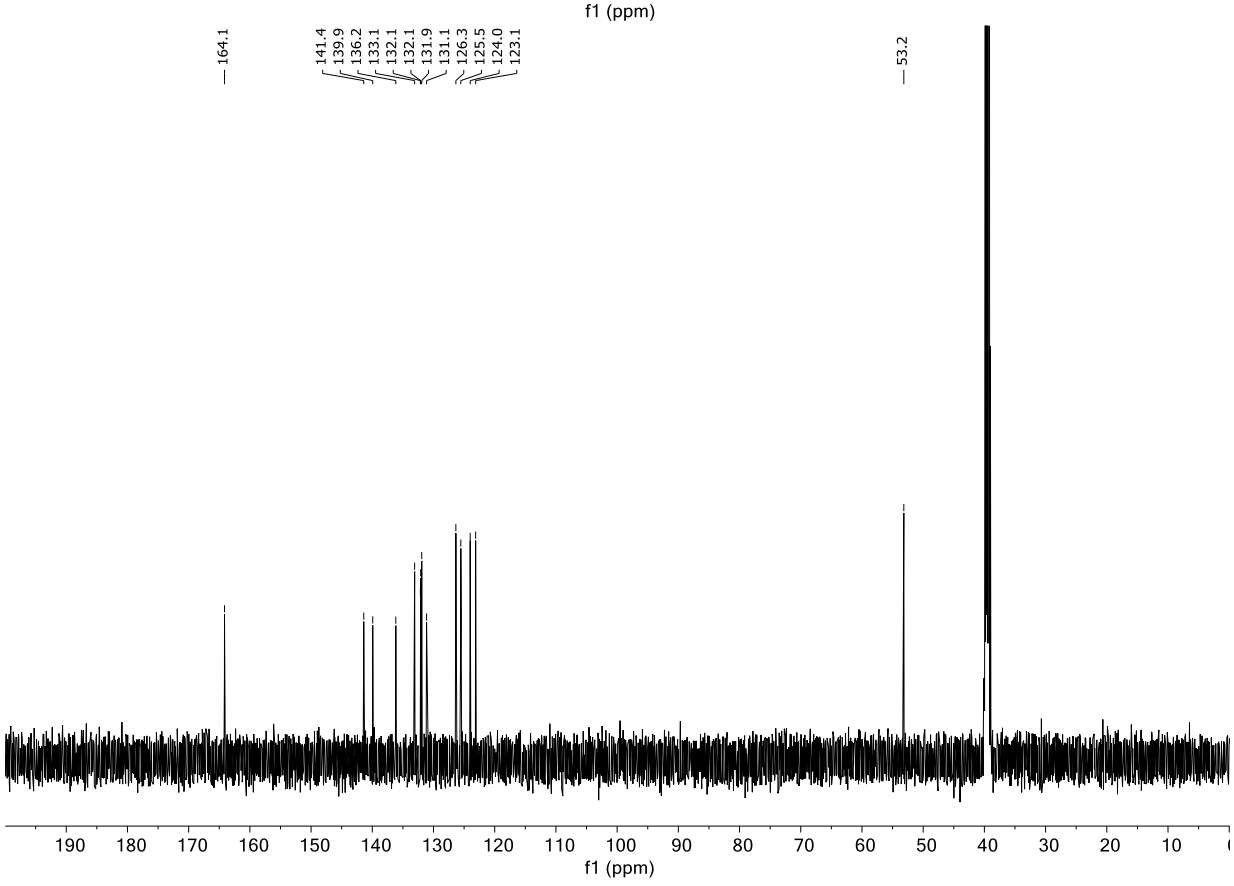

8.62 8.62 8.60 8.60 8.57 8.56 8.55 8.55 8.50 8.48 8.43 7.98 7.97 7.96 7.96 7.95 7.94 7.91 7.90 7.90 7.89 7.88 7.88 7.80 7.79
3.54
2.56
Me
Cl+
BF4-
2g
1.02 1.00 1.02 0.98 1.02 1.03 1.00
f1 (ppm)
2.96
143.0 140.0 139.9 132.6 131.9 131.7 131.5 129.3 125.1 124.9 122.9 122.4
21.5
f1 (ppm)

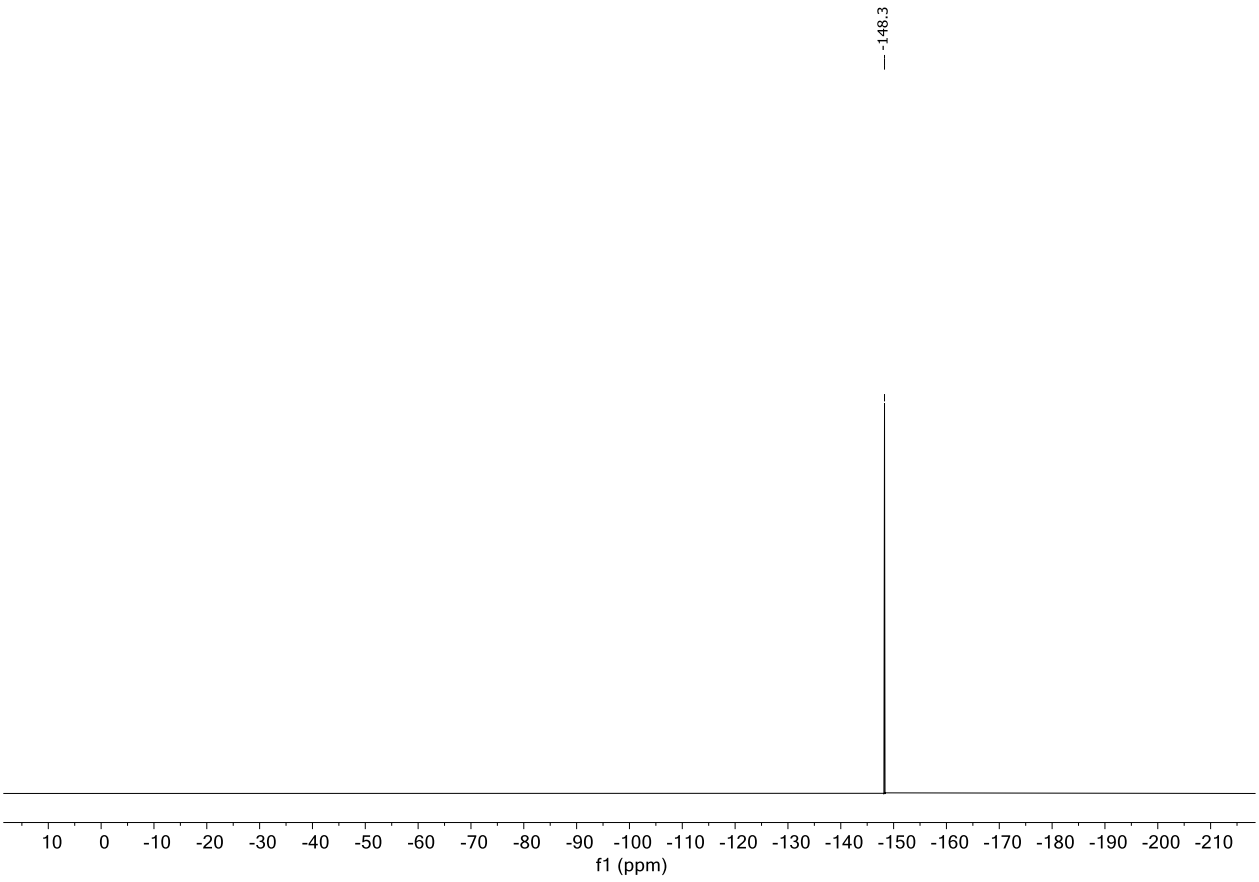

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

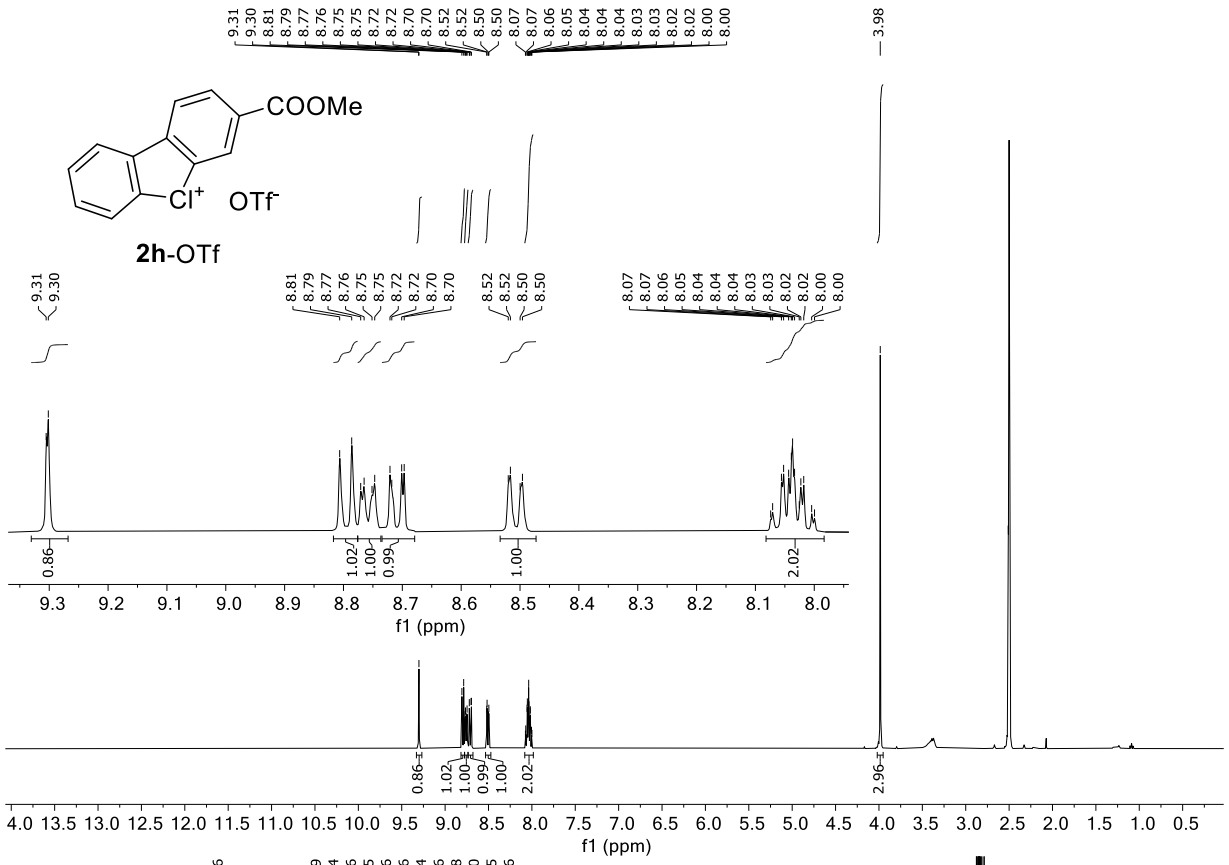

Me
Cl+
OTf-
2g-OTf
f1 (ppm)
f1 (ppm)
f1 (ppm)

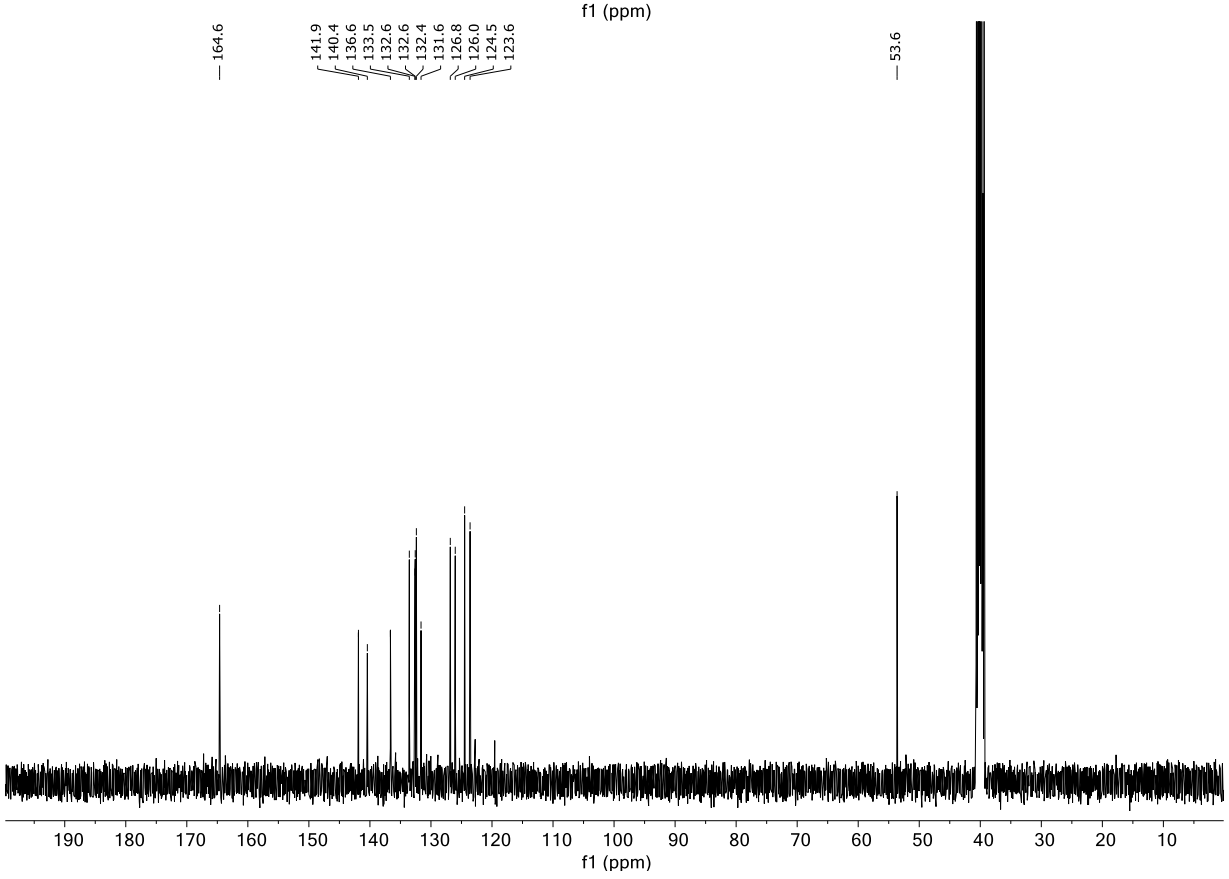

-77.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

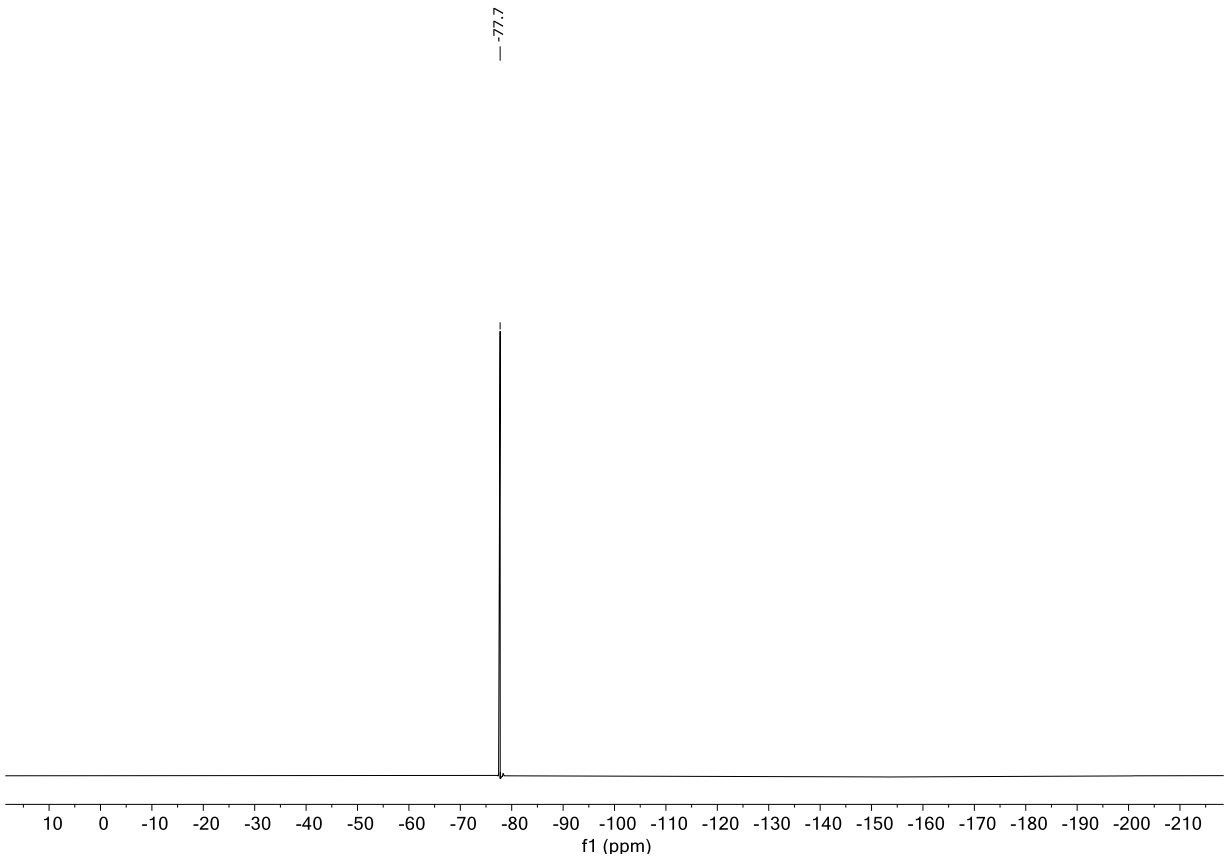

COOMe
Cl+
BF4-
2h
f1 (ppm)


f1 (ppm)


-148.3
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)


COOMe
Cl+
OTf-
2h-OTf
f1 (ppm)


f1 (ppm)


-77.7
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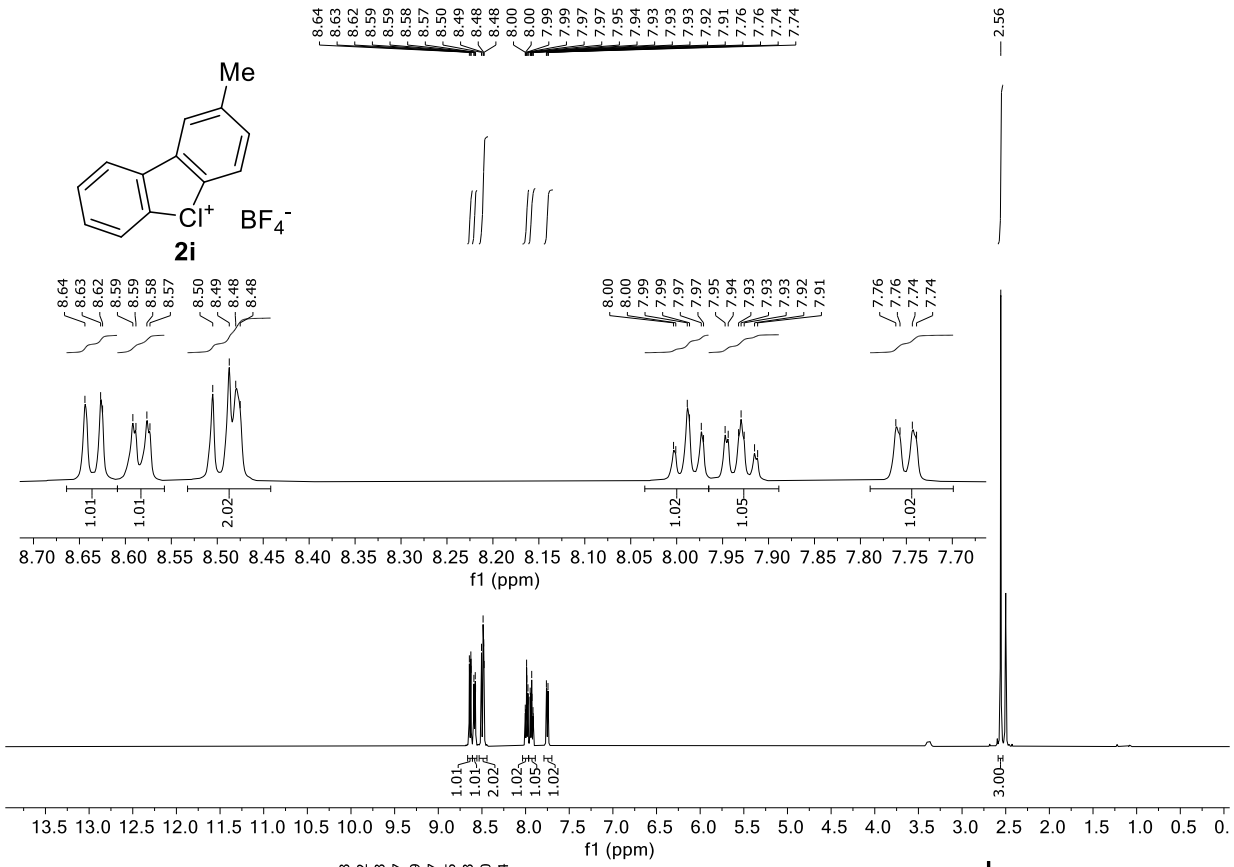
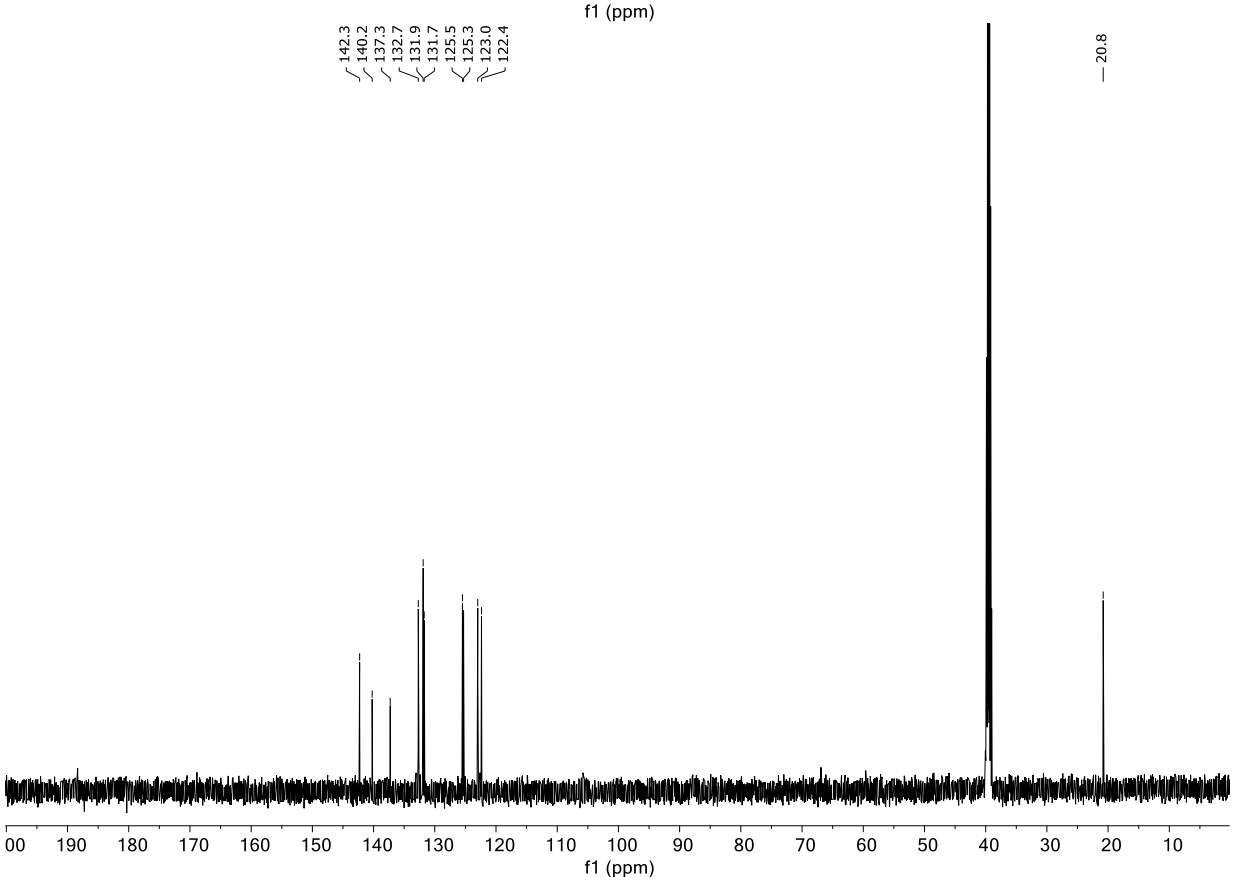
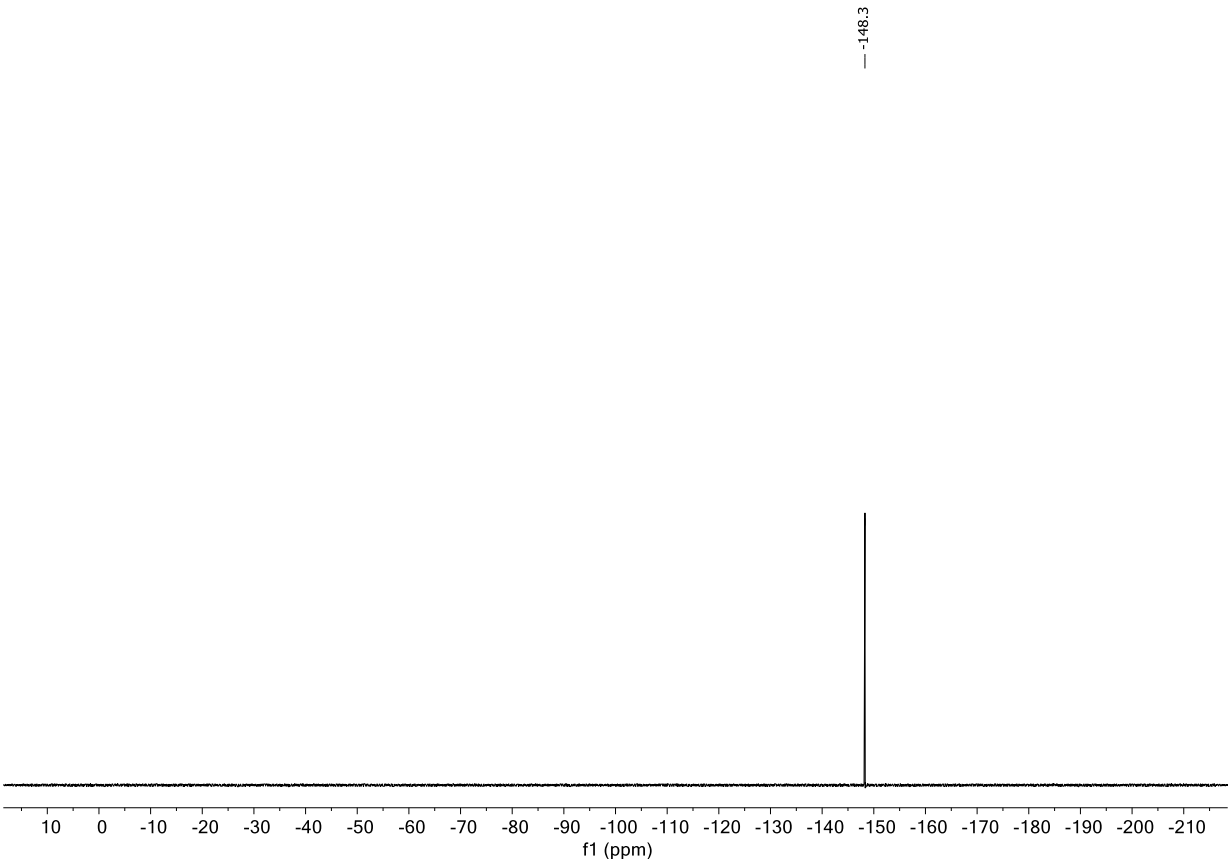
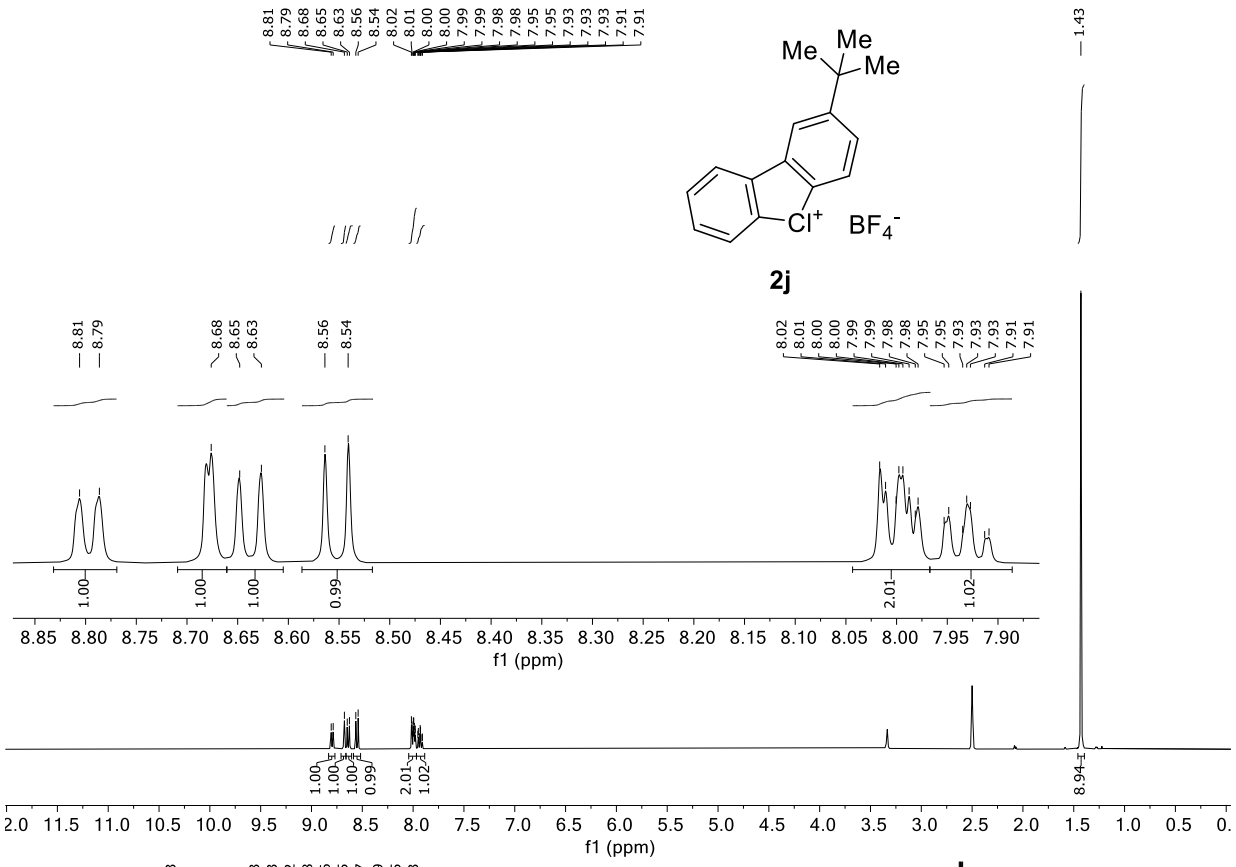
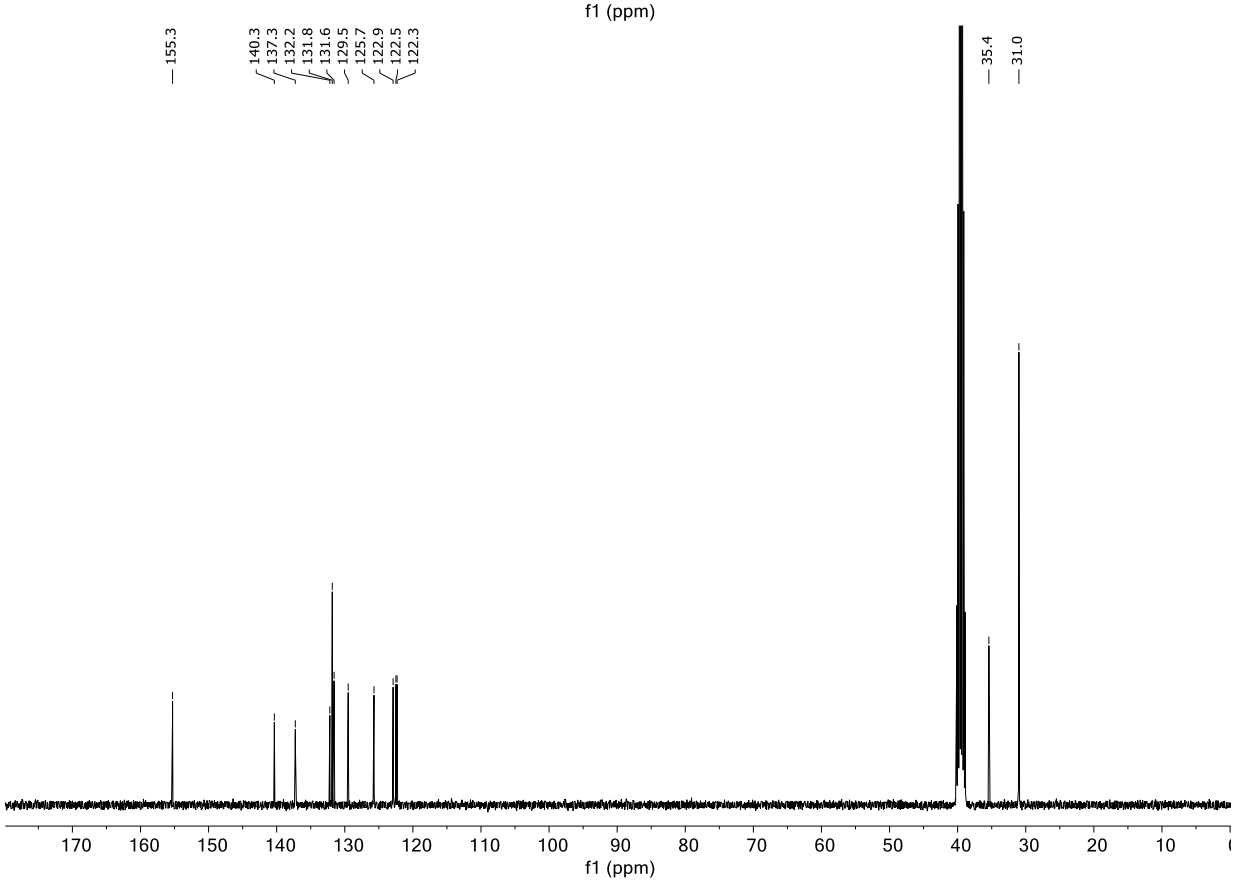
f1 (ppm)

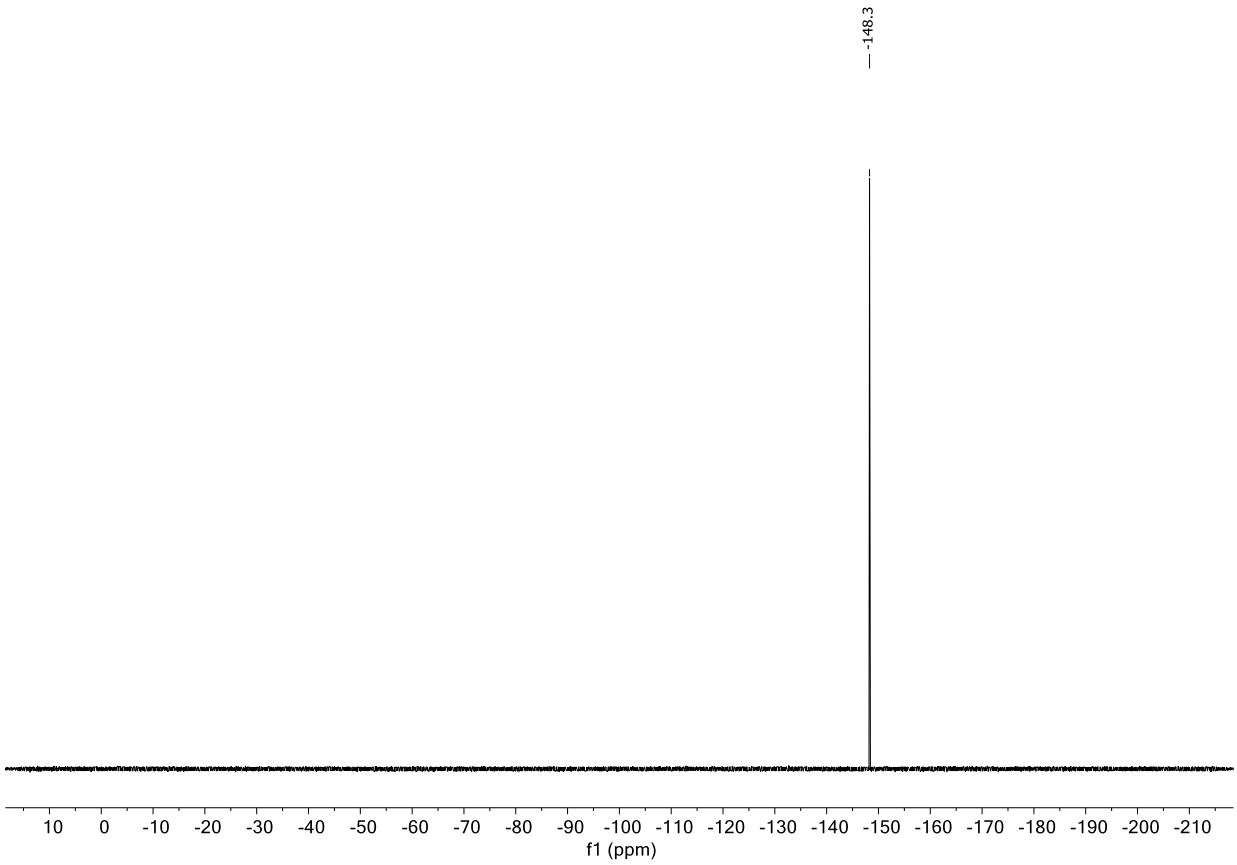

Me
Cl+
BF4-
2i
f1 (ppm)

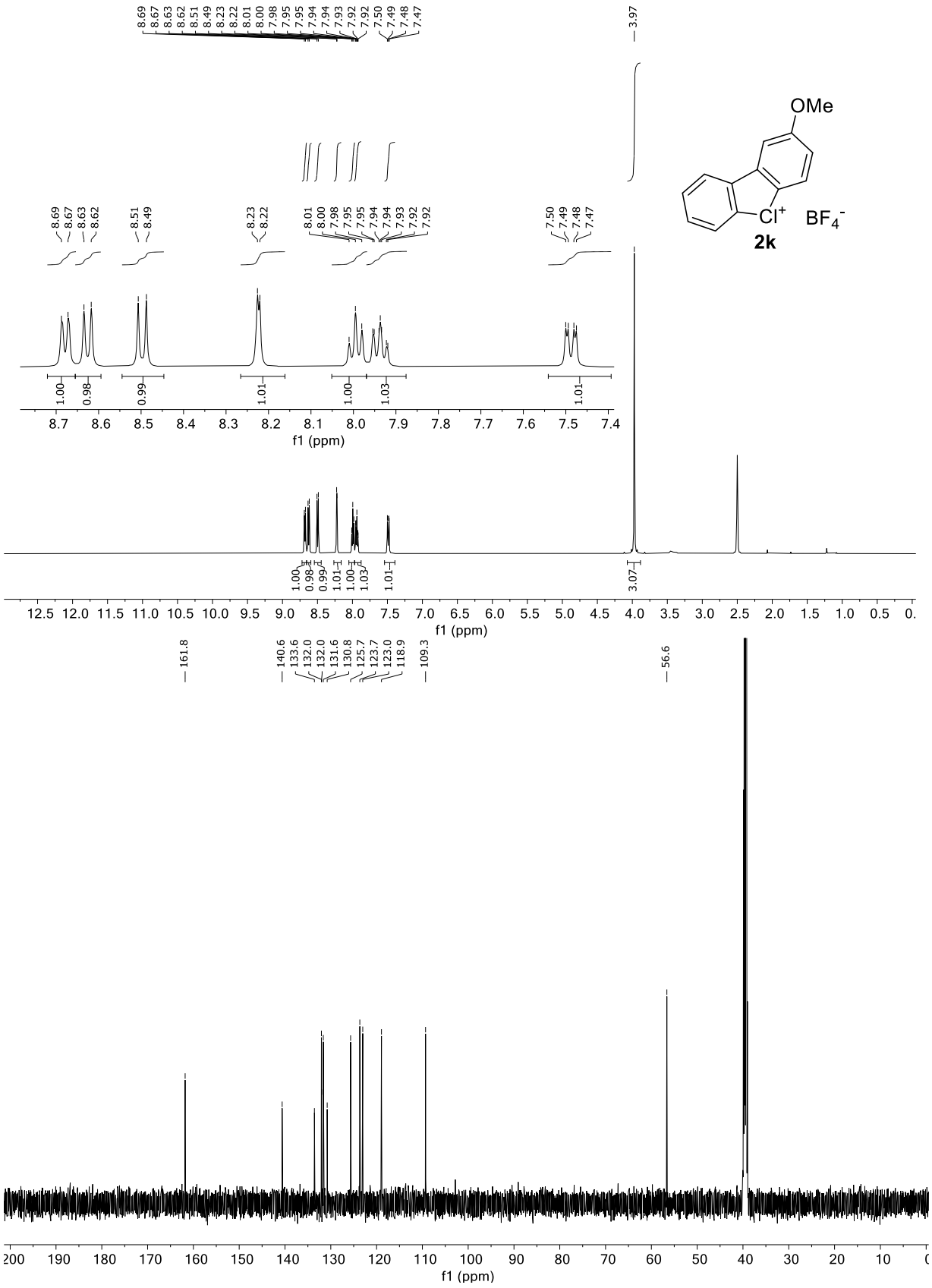

f1 (ppm)

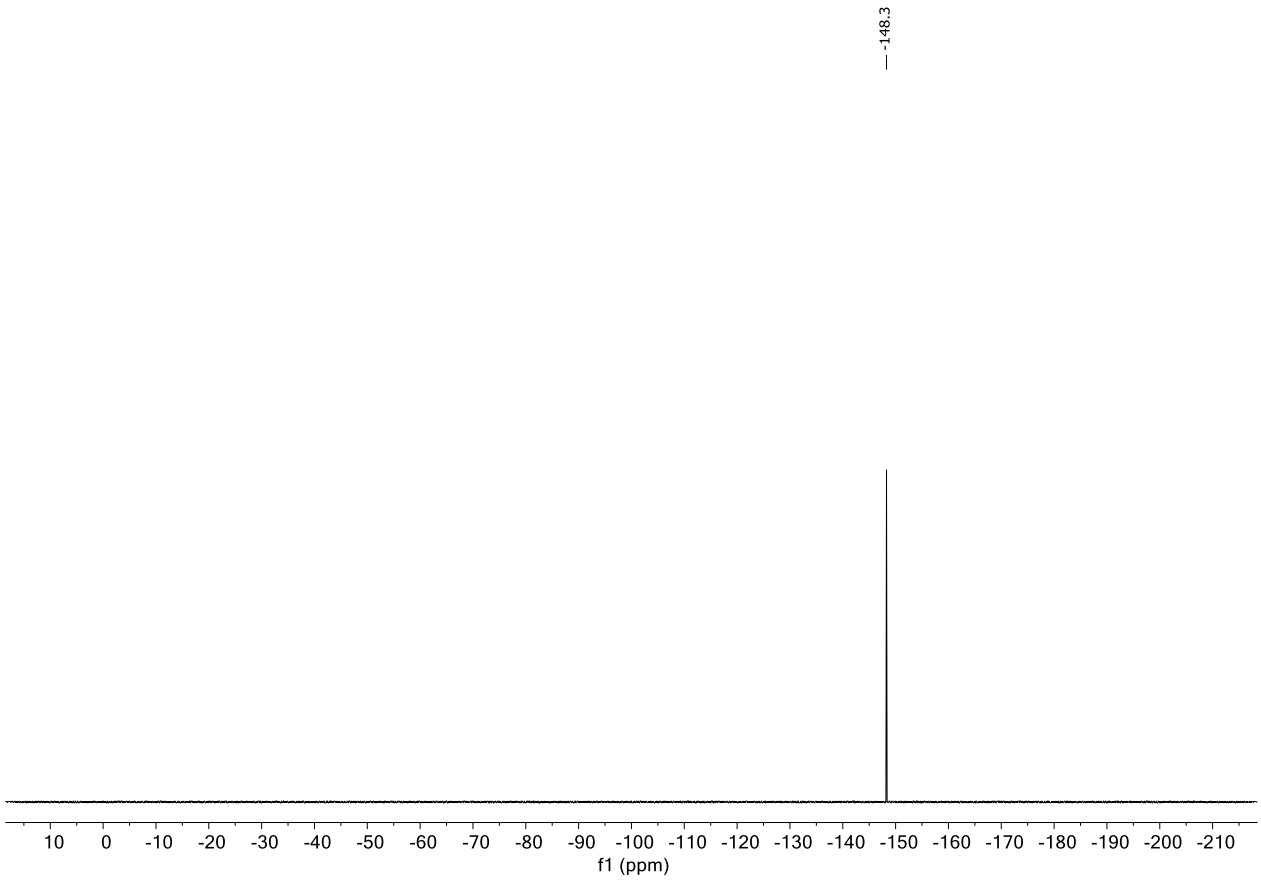

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

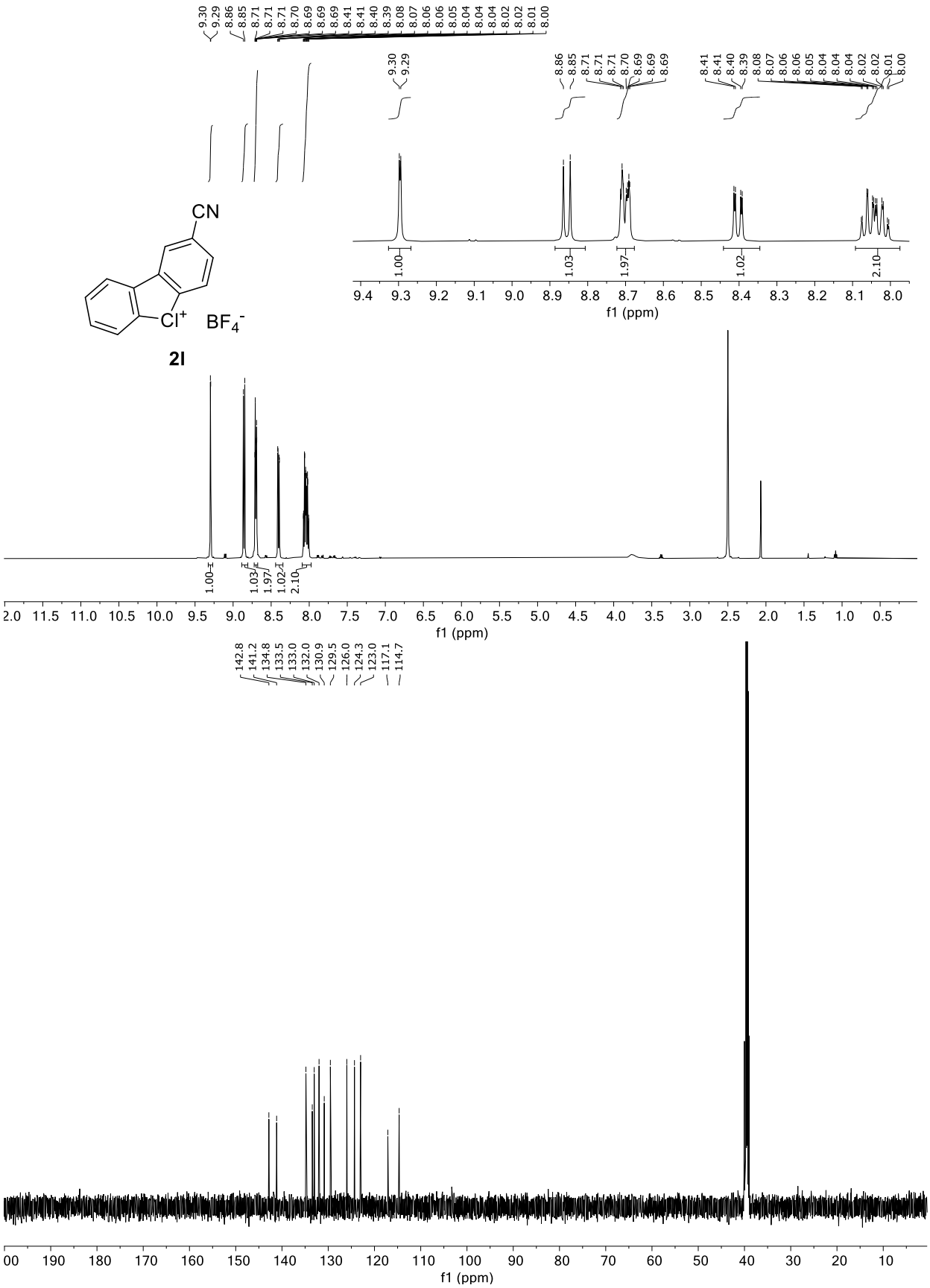

8.81
8.79
8.68
8.65
8.63
8.56
8.54
8.02
8.01
8.00
8.00
7.99
7.99
7.98
7.98
7.95
7.95
7.93
7.93
7.93
7.91
7.91
1.43
Me
Me
Me
Cl+
BF4-
2j
1.00
1.00
1.00
0.99
2.01
1.02
f1 (ppm)
1.00
1.00
1.00
0.99
2.01
1.02
8.94
f1 (ppm)

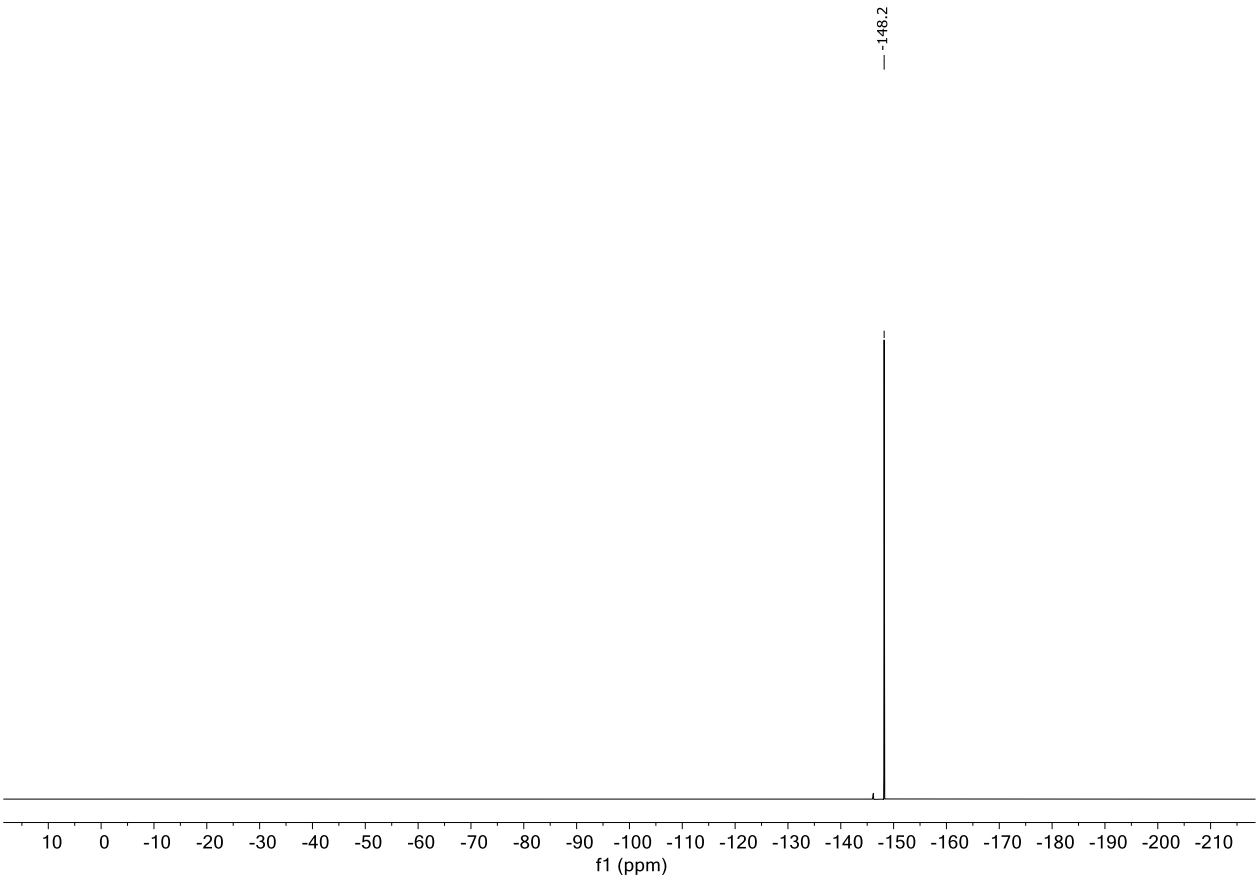

155.3
140.3
137.3
132.2
131.8
131.6
129.5
125.7
122.9
122.5
122.3
35.4
31.0
f1 (ppm)

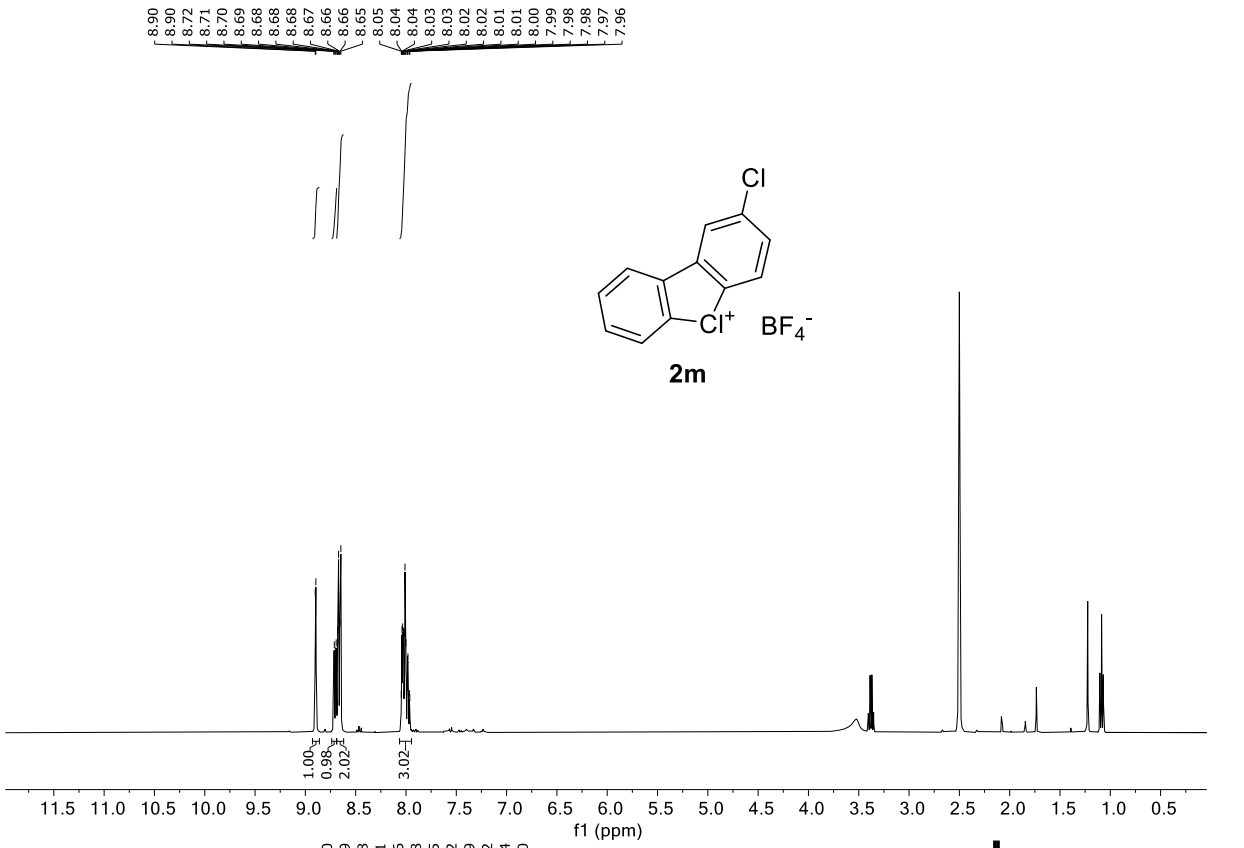

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


OMe
Cl+
BF4-
2k
f1 (ppm)
f1 (ppm)
f1 (ppm)

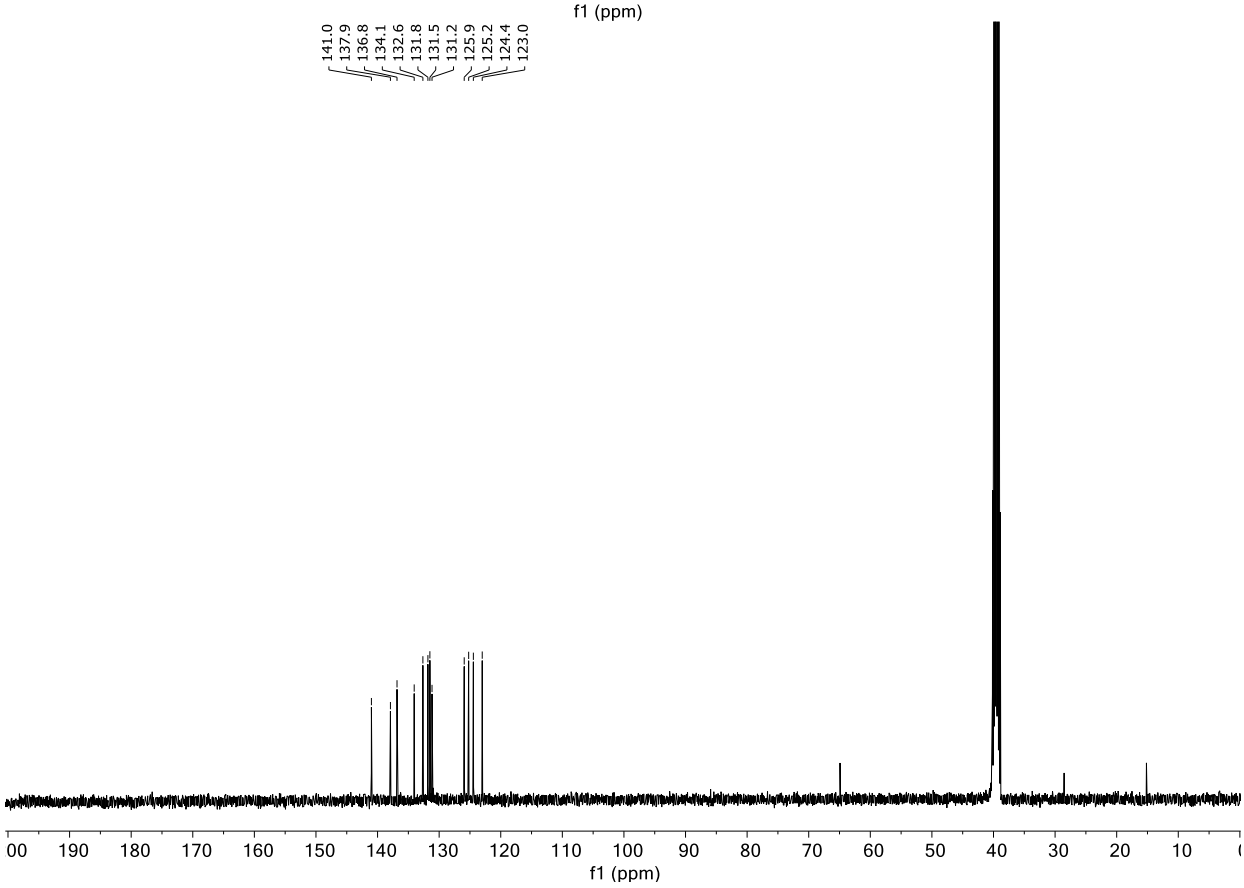

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

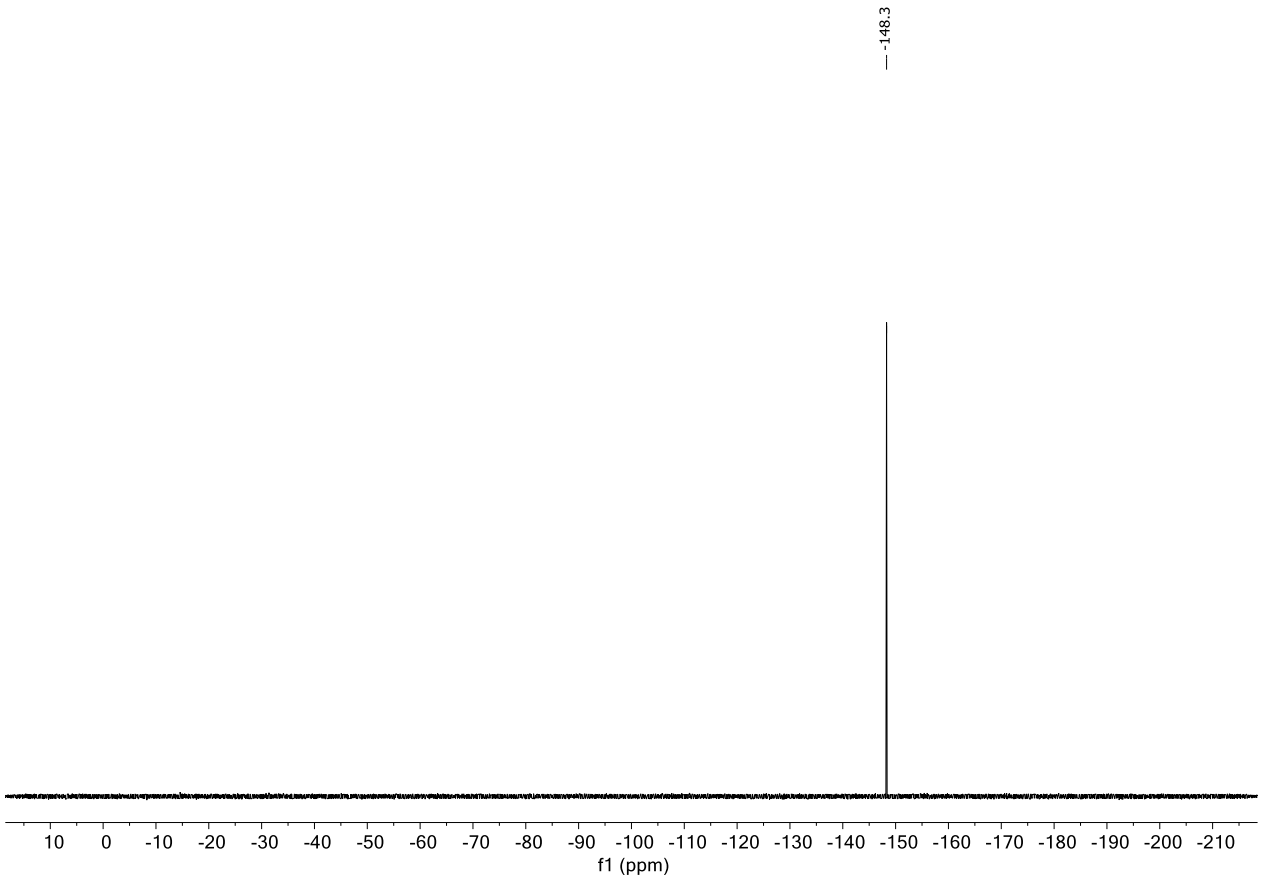

9.30
9.29
8.86
8.85
8.71
8.71
8.71
8.70
8.69
8.69
8.69
8.41
8.41
8.40
8.39
8.08
8.07
8.06
8.06
8.05
8.04
8.04
8.04
8.02
8.02
8.01
8.00
CN
Cl+
BF4-
2I
1.00
1.03
1.97
1.02
2.10
f1 (ppm)
142.8
141.2
134.8
133.5
133.0
132.0
130.9
129.5
126.0
124.3
123.0
117.1
114.7

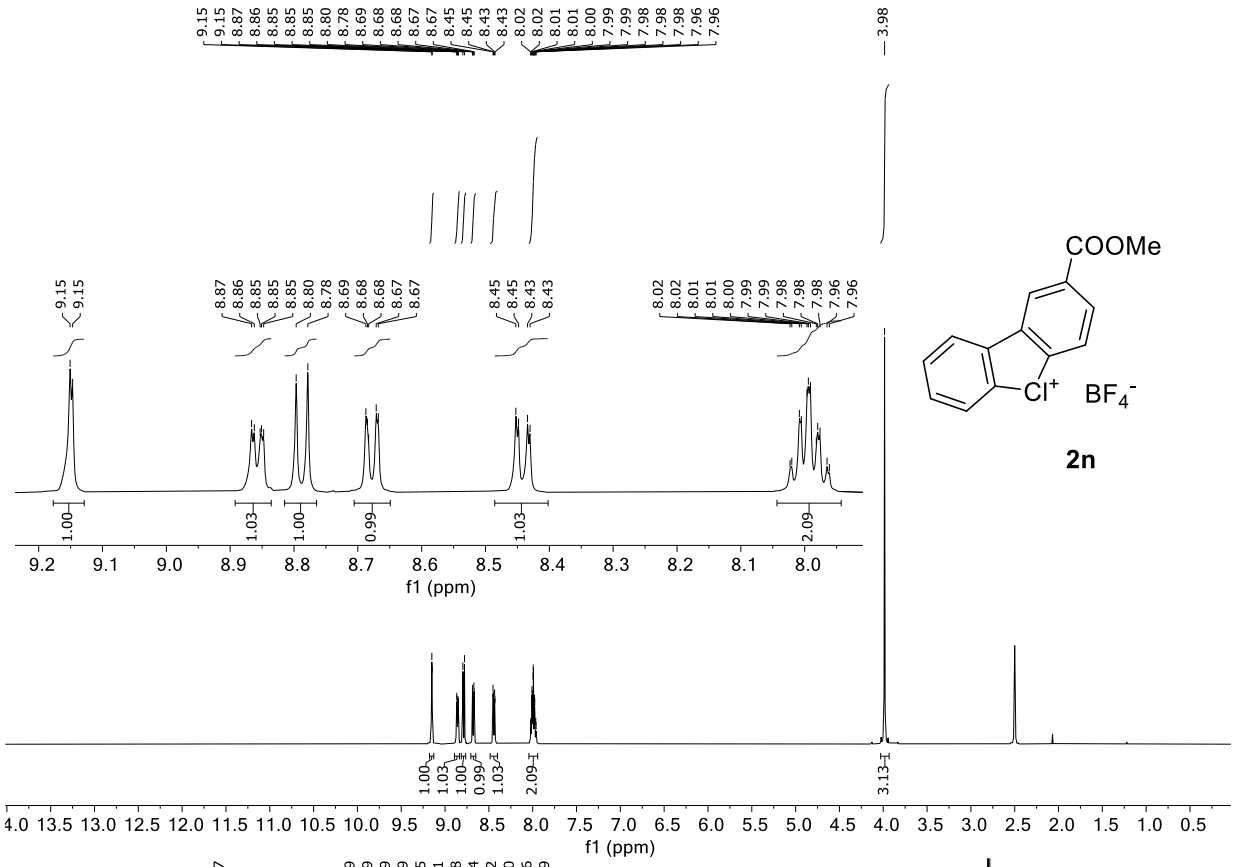

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

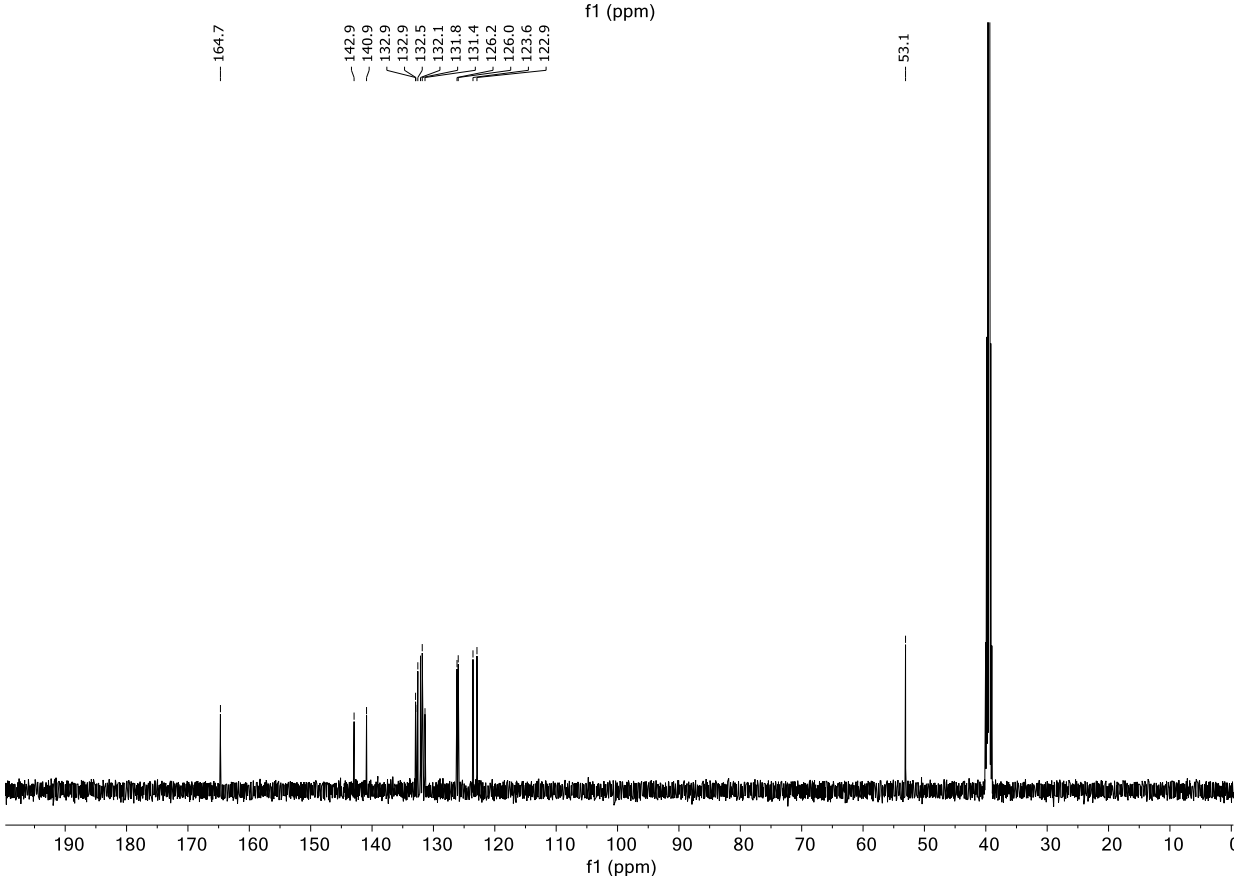

8.90
8.90
8.72
8.71
8.70
8.69
8.68
8.68
8.68
8.67
8.66
8.66
8.65
8.05
8.04
8.04
8.03
8.03
8.02
8.02
8.01
8.01
8.00
7.99
7.98
7.98
7.97
7.96
Cl
Cl+
BF4-
1.00
0.98
2.02
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

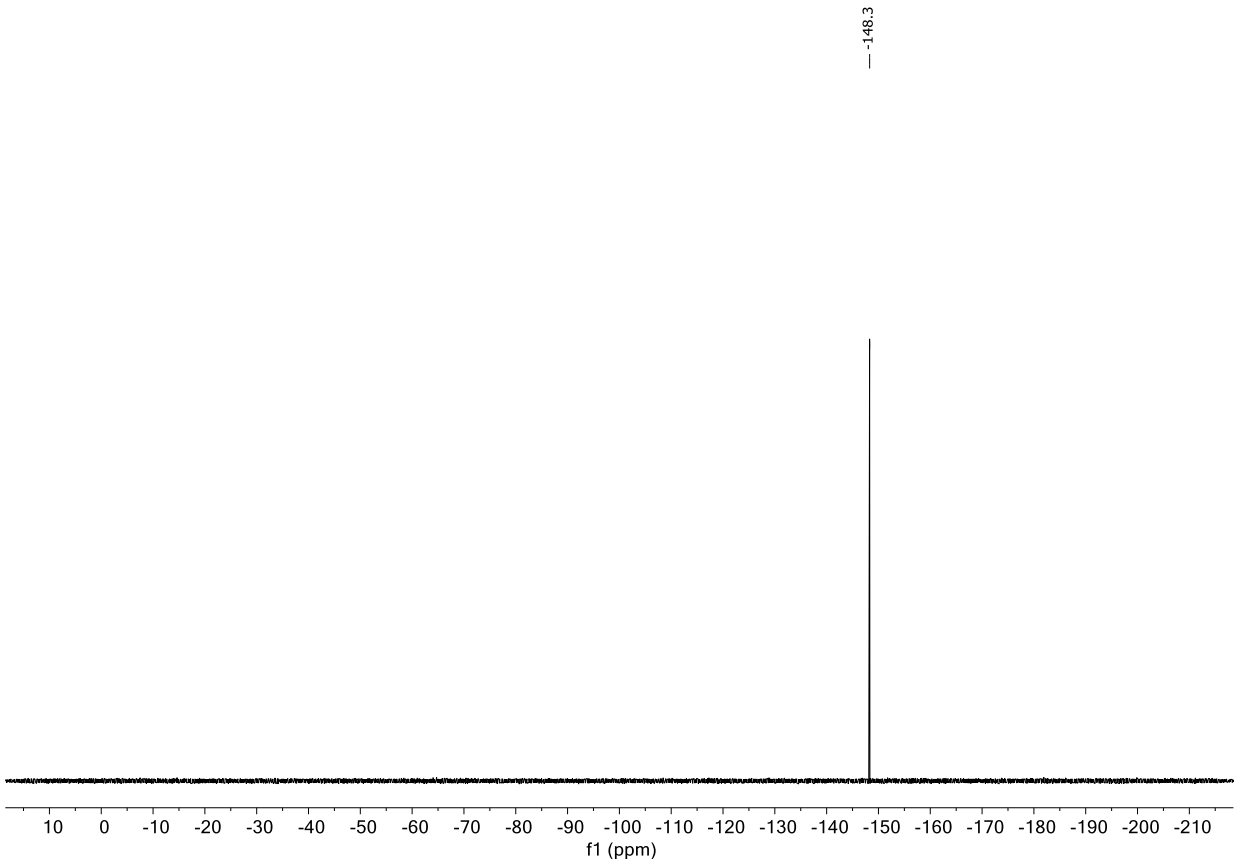
2m

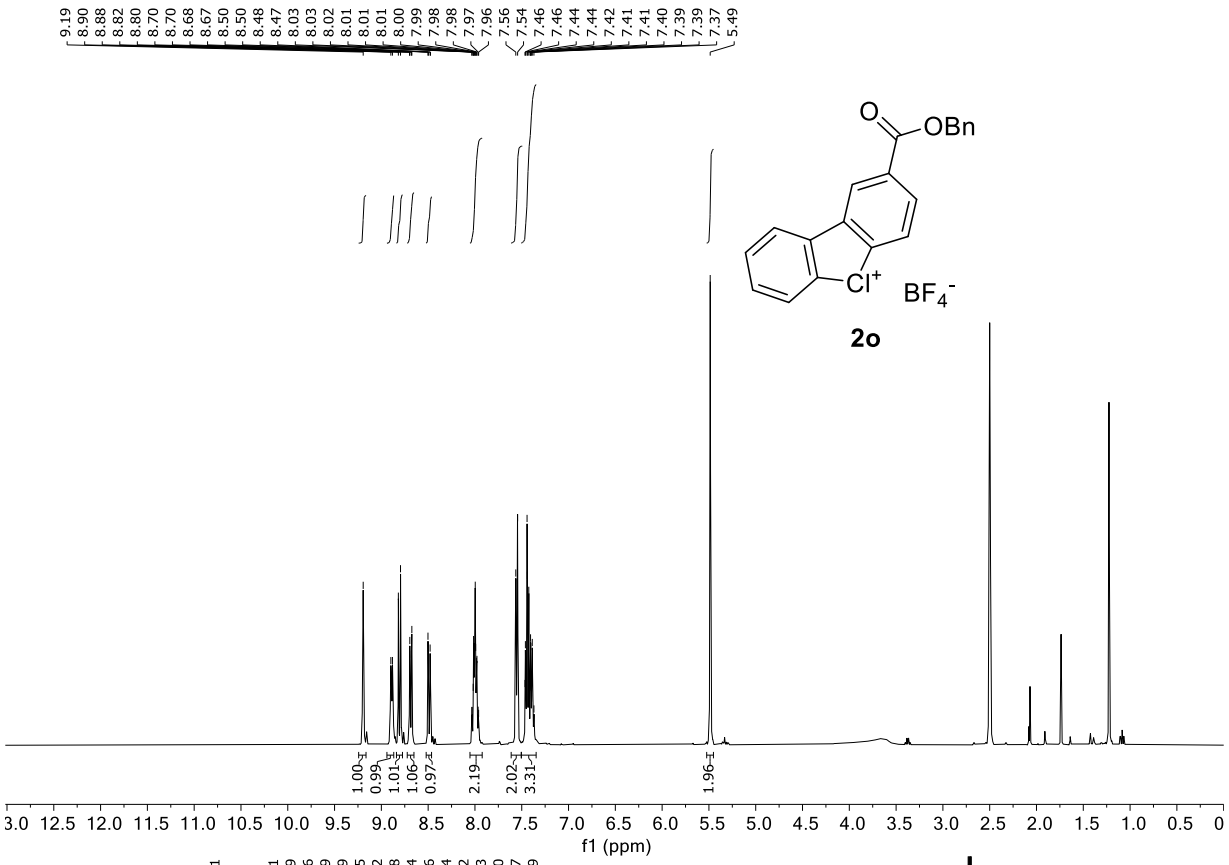

141.0
137.9
136.8
134.1
132.6
131.8
131.5
131.2
125.9
125.2
124.4
123.0
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

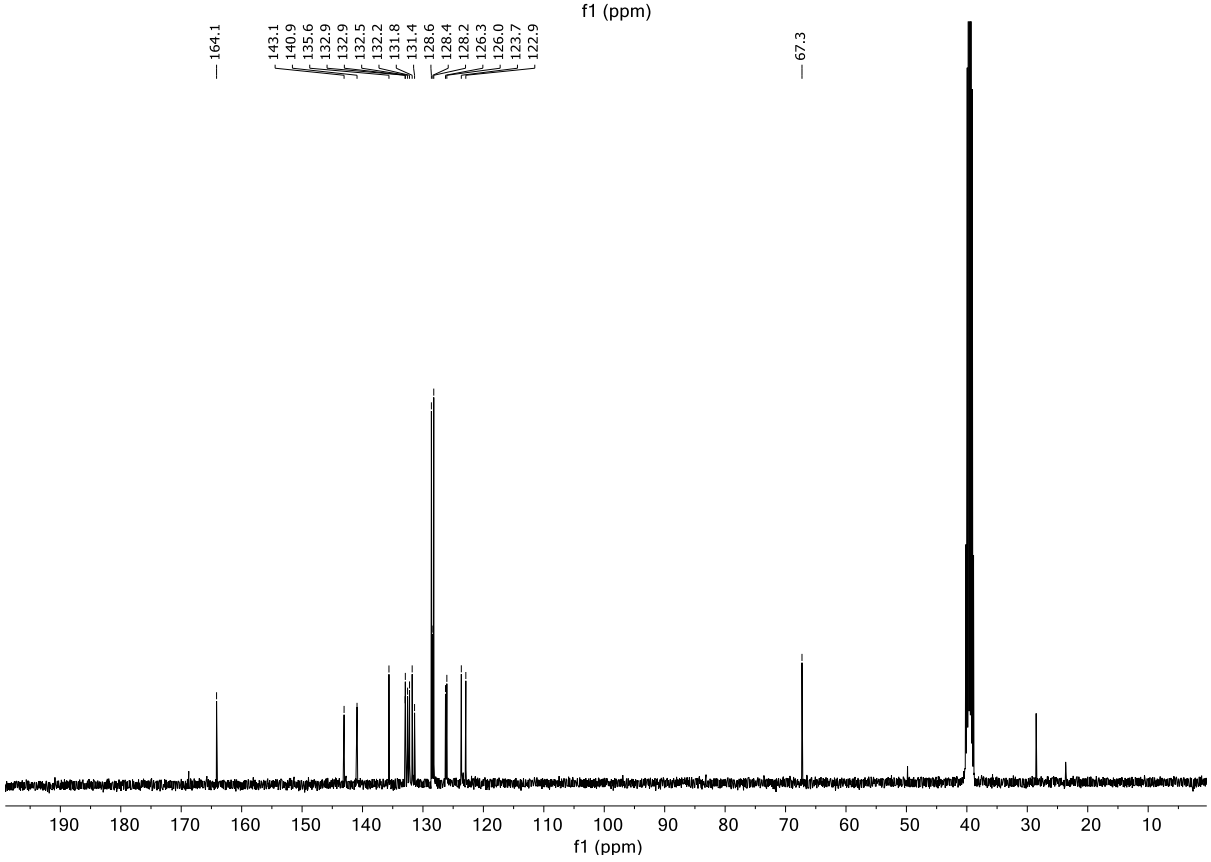

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

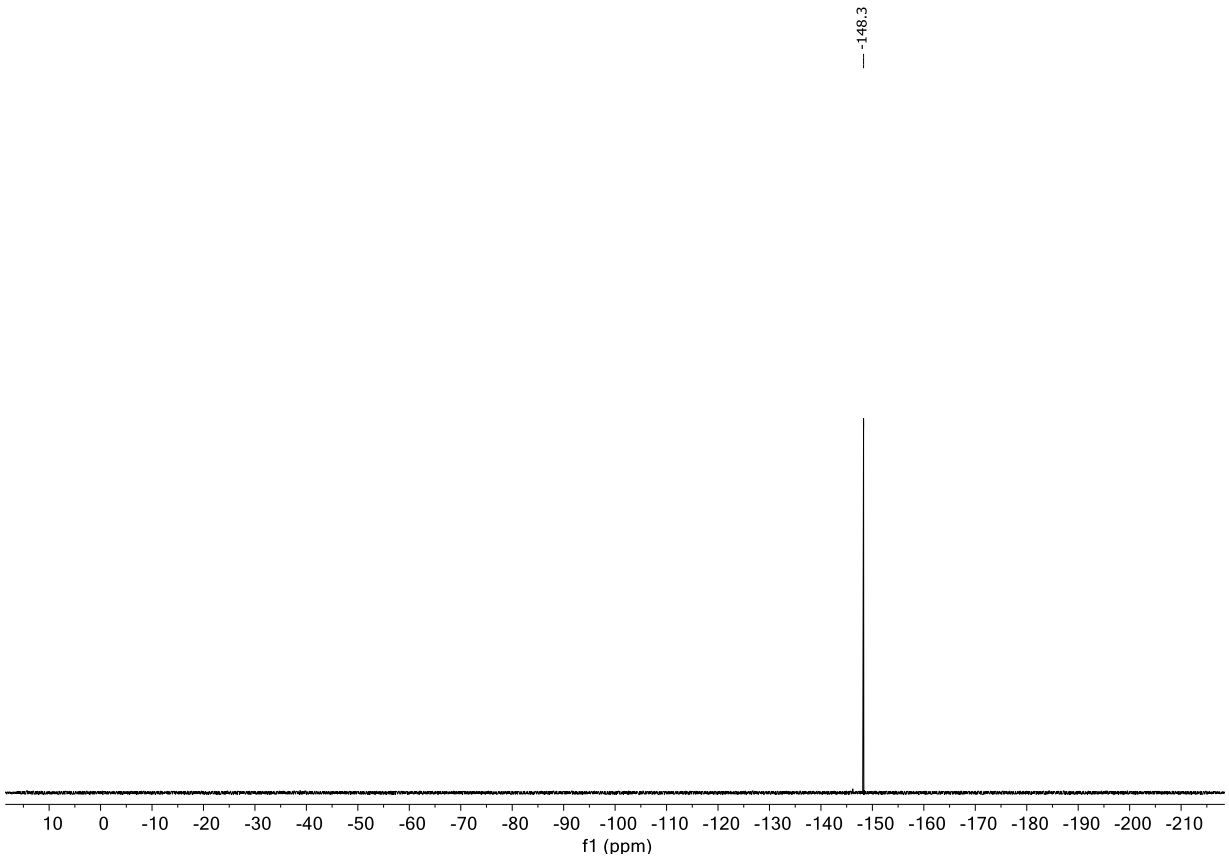

9.15
9.15
8.87
8.86
8.85
8.85
8.85
8.85
8.80
8.78
8.69
8.68
8.68
8.67
8.67
8.45
8.45
8.43
8.43
8.02
8.02
8.01
8.01
8.00
7.99
7.99
7.98
7.98
7.98
7.96
7.96
3.98
COOMe
Cl+
BF4-
2n
1.00
1.03
1.00
0.99
1.03
2.09
3.13
f1 (ppm)

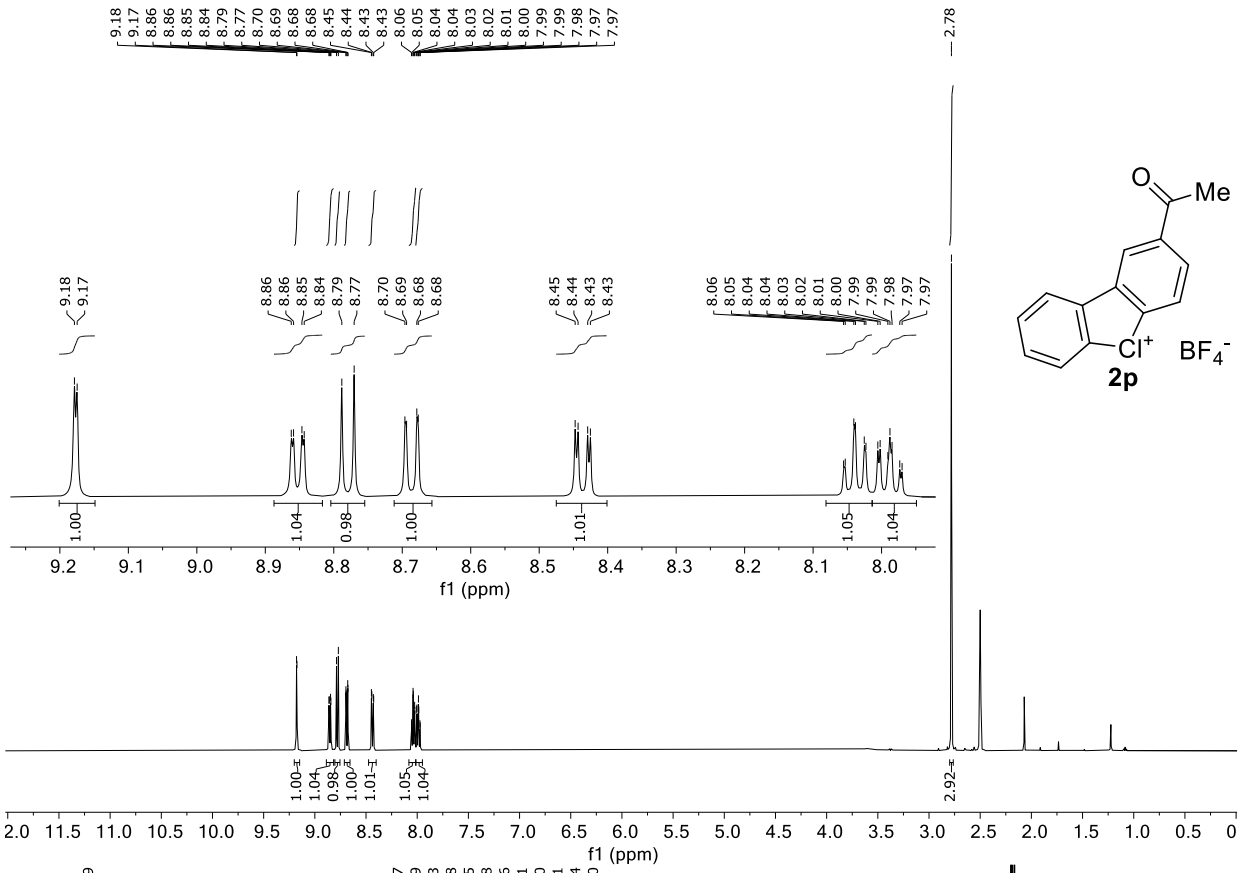

164.7
142.9
140.9
132.9
132.9
132.5
132.1
131.8
131.4
126.2
126.0
123.6
122.9
53.1
f1 (ppm)

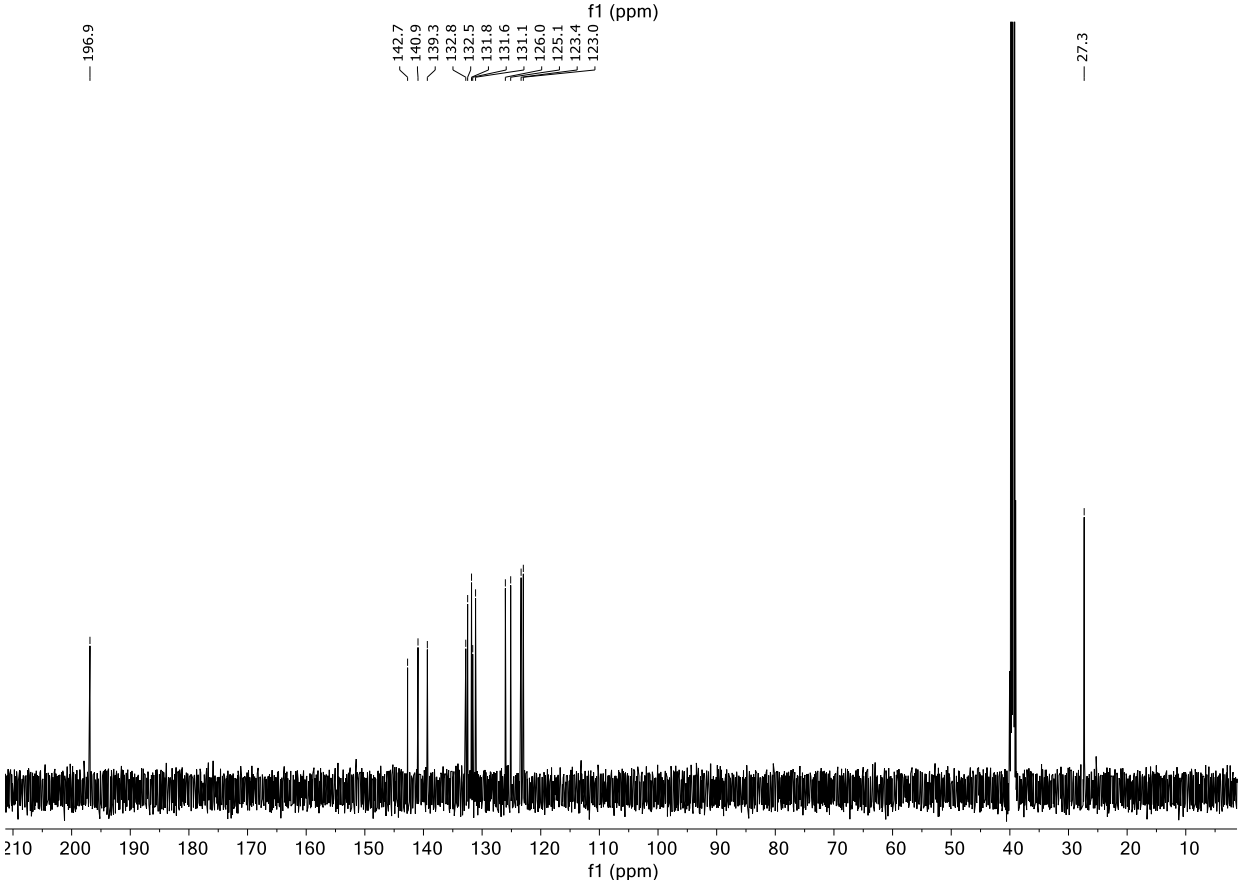

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

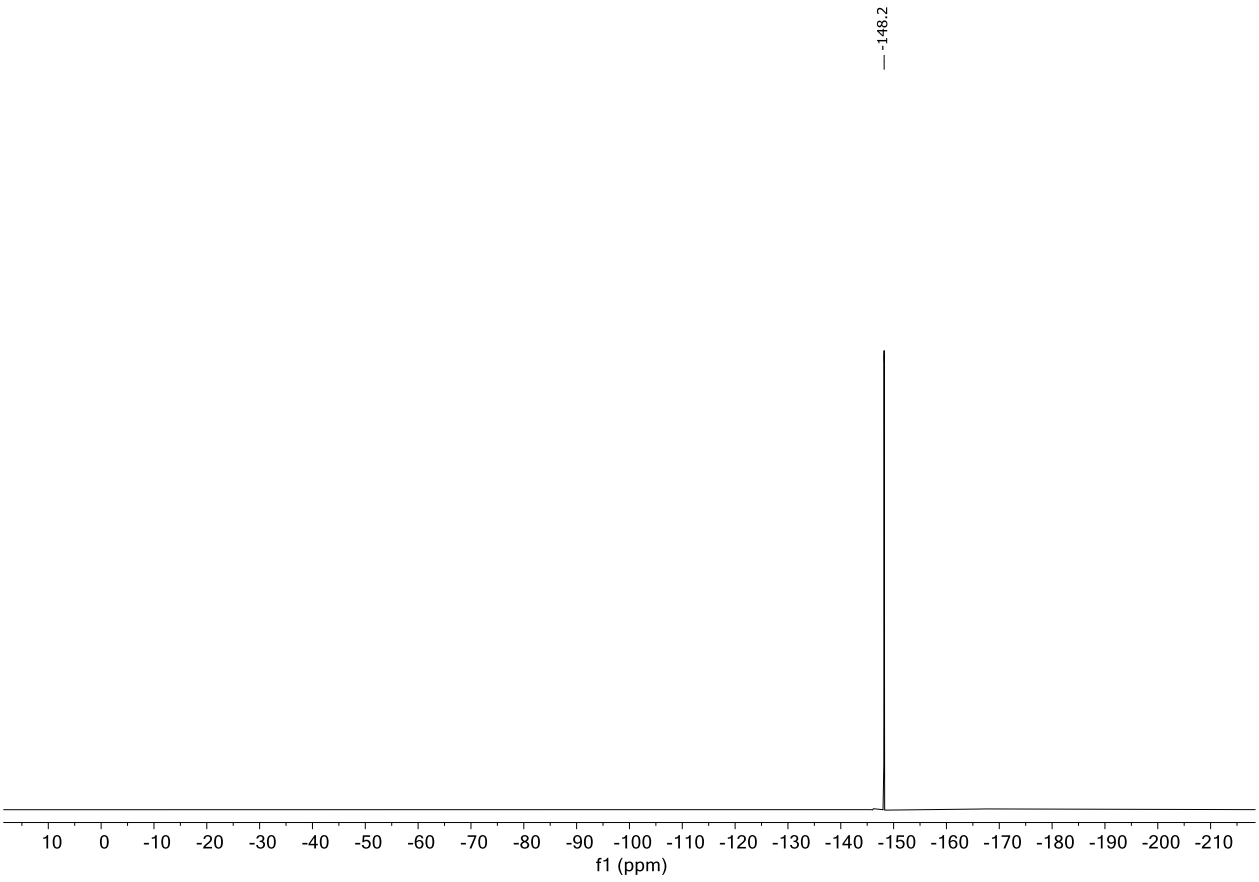

9.19
8.90
8.88
8.82
8.80
8.70
8.70
8.68
8.67
8.50
8.50
8.48
8.47
8.03
8.03
8.02
8.01
8.01
8.01
8.00
7.99
7.98
7.98
7.97
7.96
7.56
7.54
7.46
7.46
7.44
7.44
7.42
7.41
7.41
7.40
7.39
7.39
7.37
5.49
O
OBn
Cl+
BF4-
2o
1.00
0.99
1.01
1.06
0.97
2.19
2.02
3.31
1.96
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

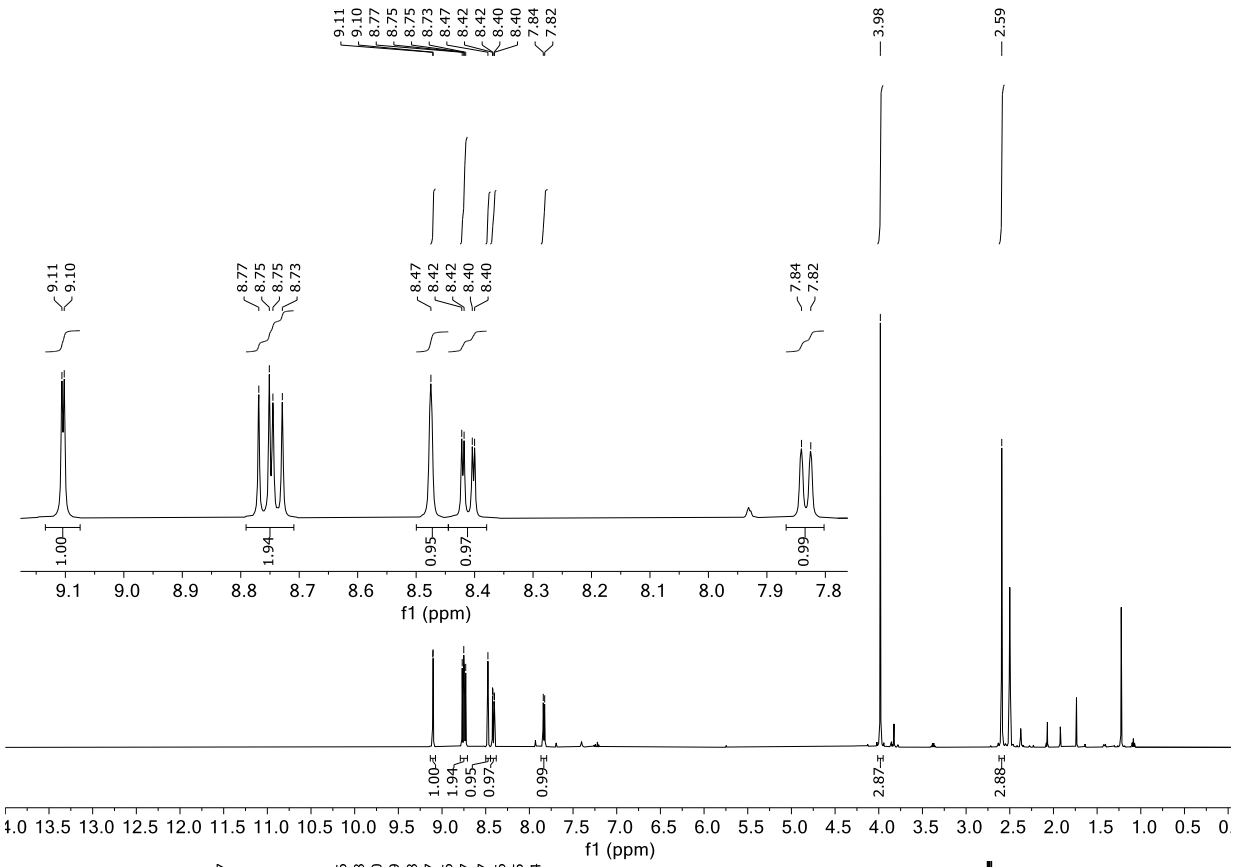

164.1
143.1
140.9
135.6
132.9
132.9
132.5
132.2
131.8
131.4
128.6
128.4
128.2
126.3
126.0
123.7
122.9
67.3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

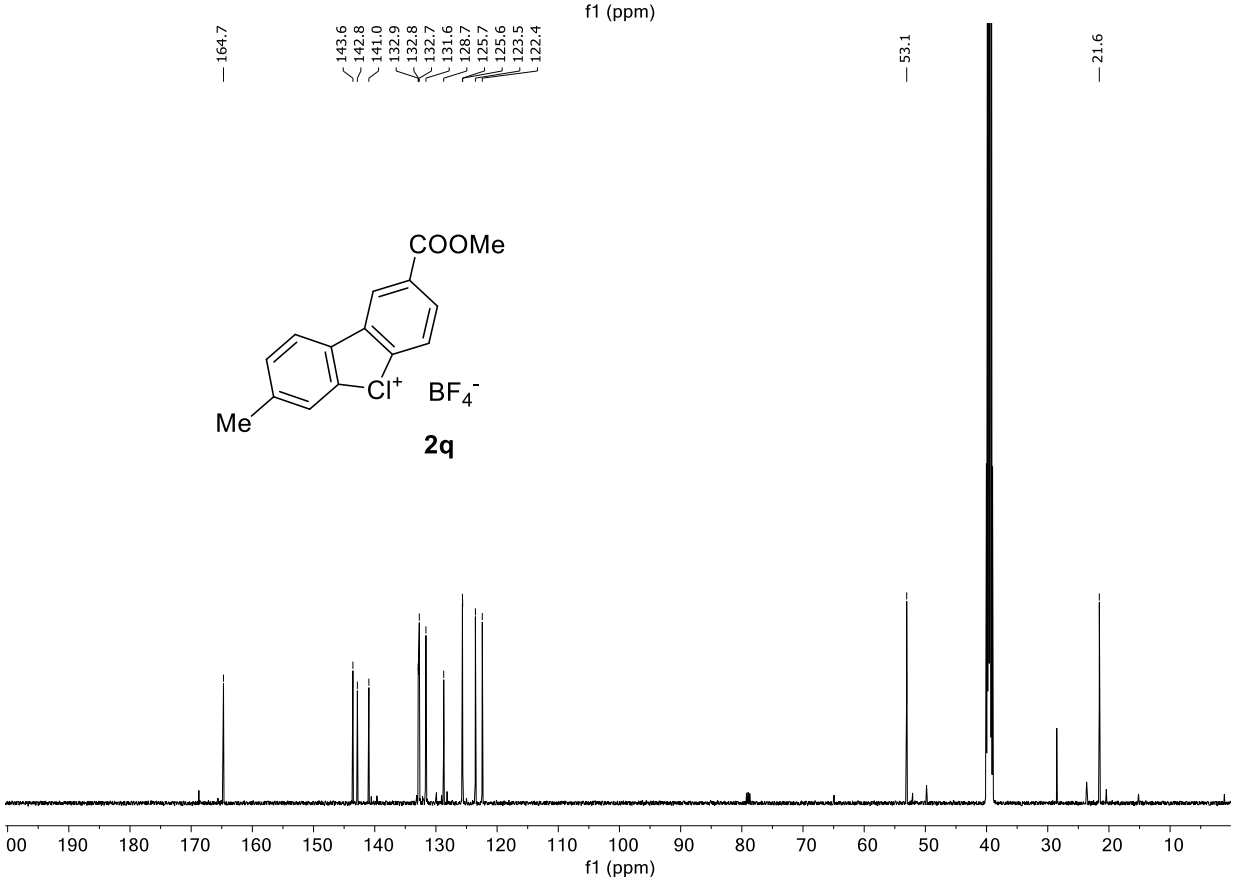

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

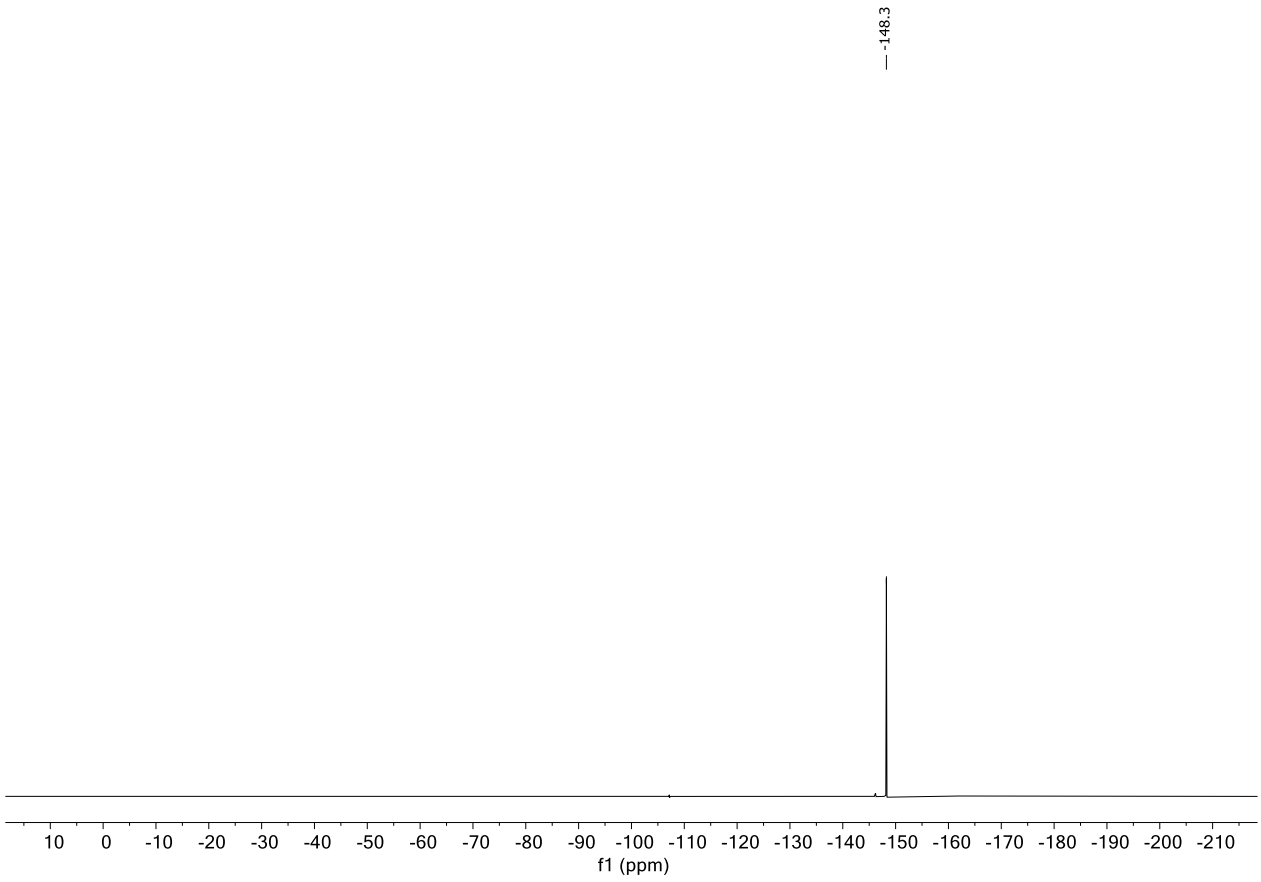

9.18
9.17
8.86
8.86
8.85
8.84
8.79
8.77
8.70
8.69
8.68
8.68
8.45
8.44
8.43
8.43
8.06
8.05
8.04
8.04
8.03
8.02
8.01
8.00
7.99
7.99
7.98
7.97
7.97
2.78
1.00
1.04
0.98
1.00
1.01
1.05
1.04
2.92
f1 (ppm)
O
Me
Cl+
BF4-
2p

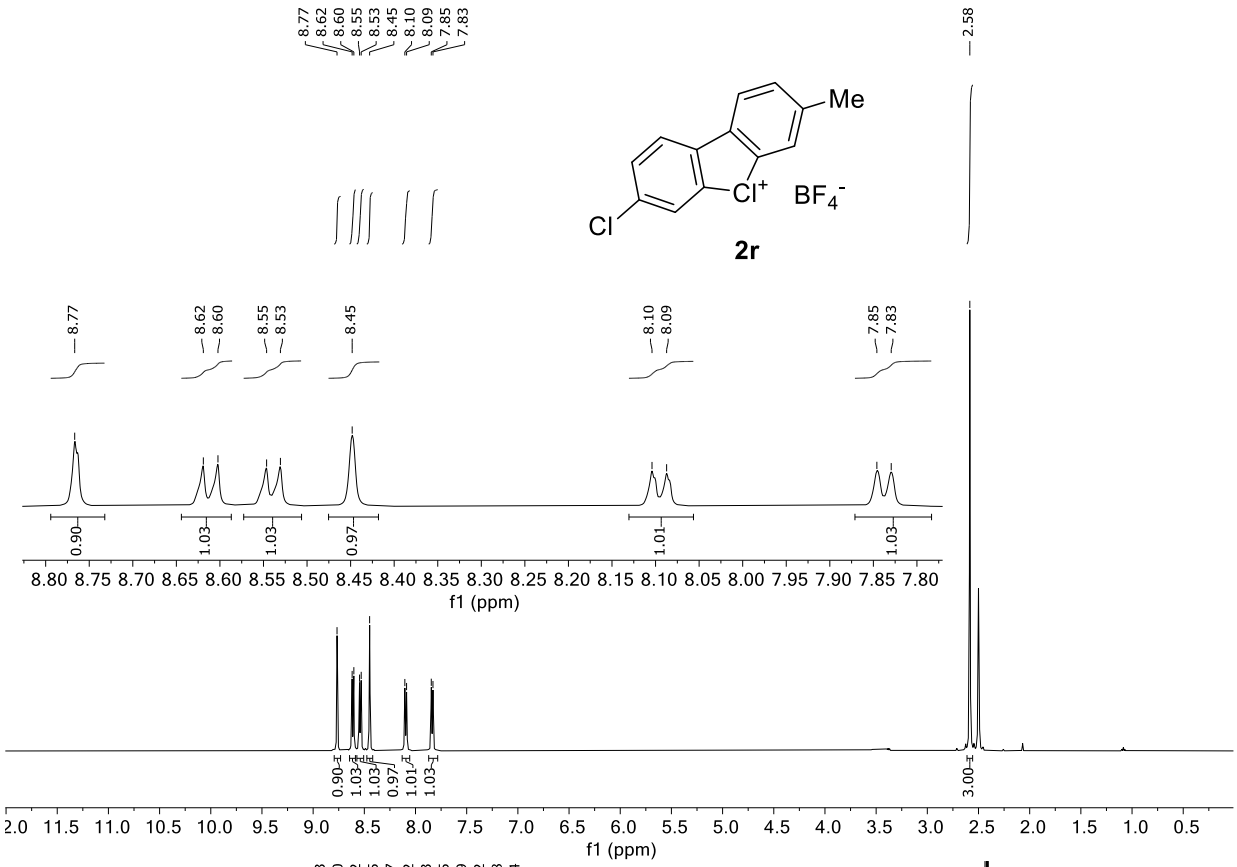

196.9
142.7
140.9
139.3
132.8
132.5
131.8
131.6
131.1
126.0
125.1
123.4
123.0
27.3
f1 (ppm)

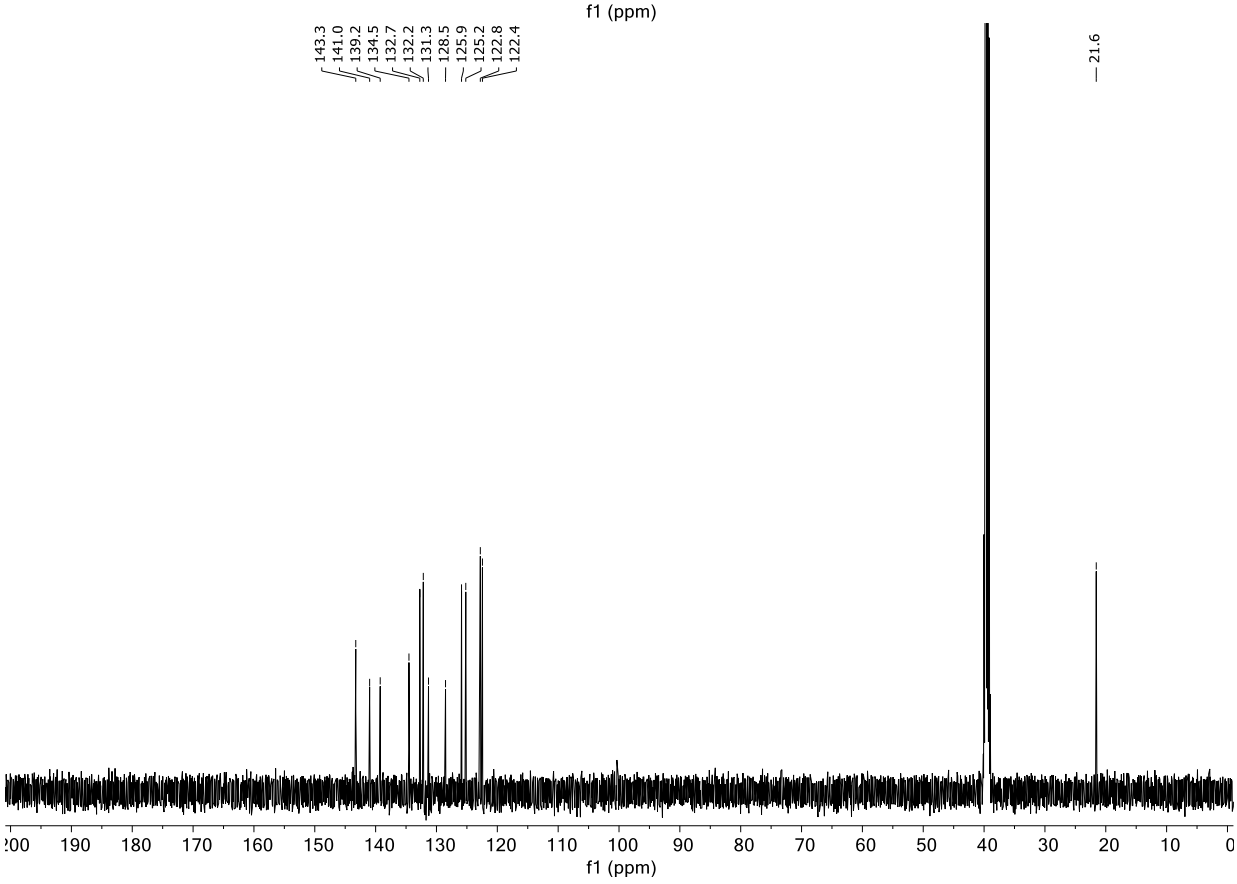

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

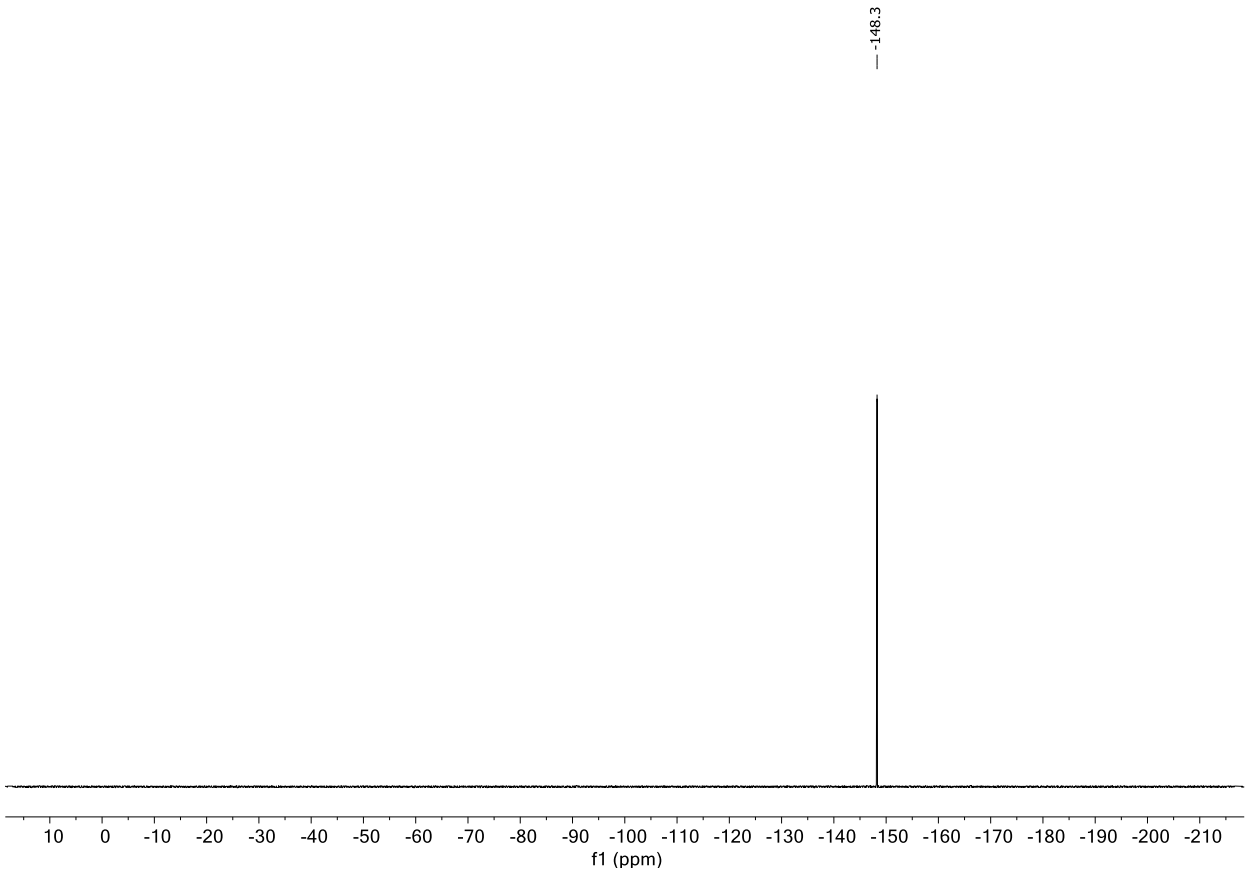

9.11
9.10
8.77
8.75
8.75
8.73
8.47
8.42
8.42
8.40
7.84
7.82
3.98
2.59
1.00
1.94
0.95
0.97
0.99
2.87
2.88
f1 (ppm)

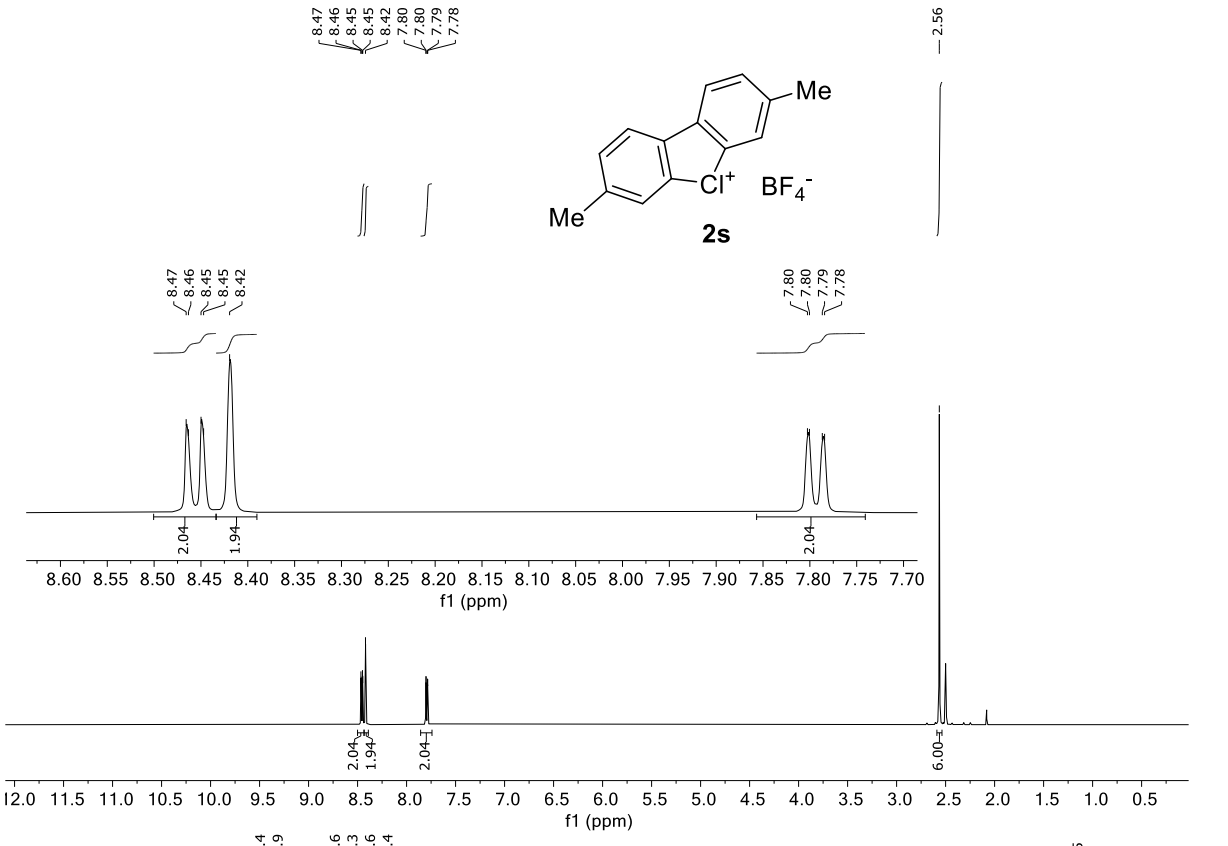

164.7
143.6
142.8
141.0
132.9
132.8
132.7
131.6
128.7
125.7
125.6
123.5
122.4
53.1
21.6
COOMe
Cl+
BF4-
Me
2q
f1 (ppm)

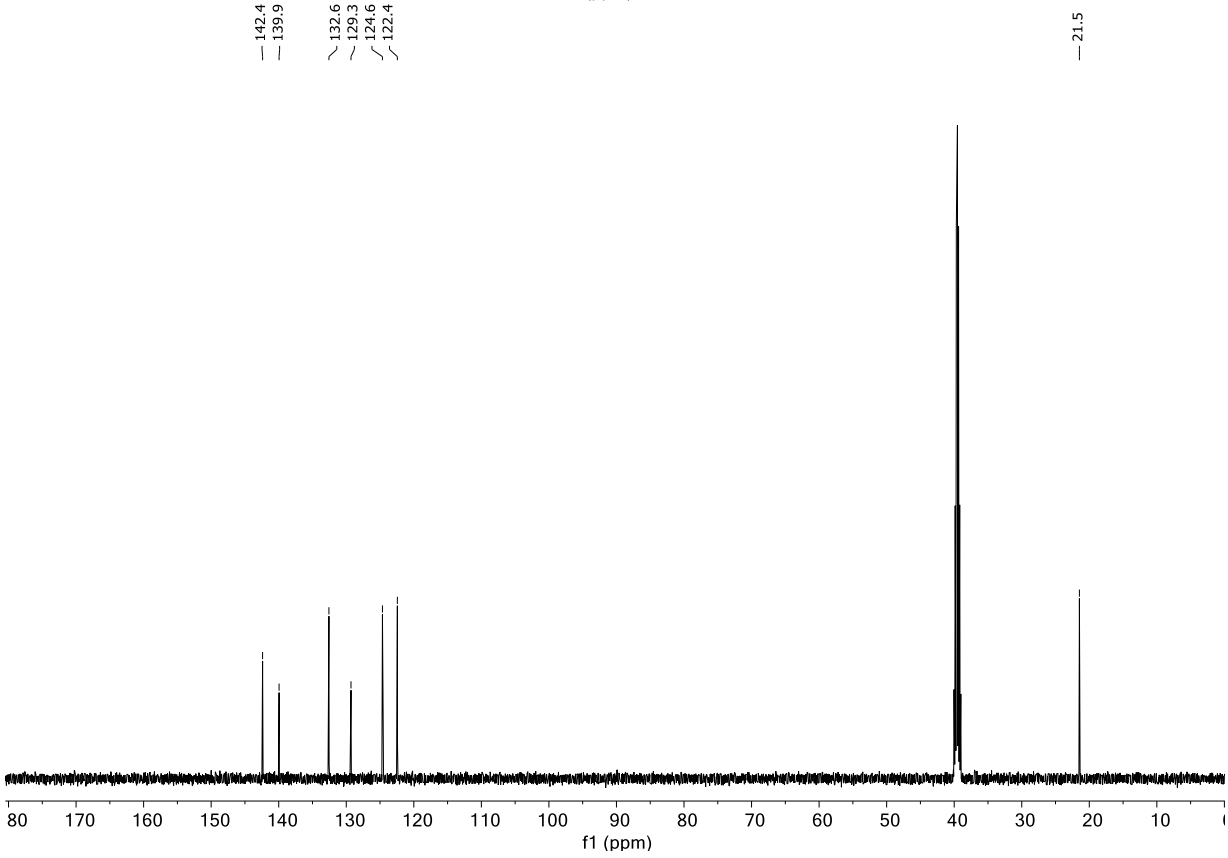

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

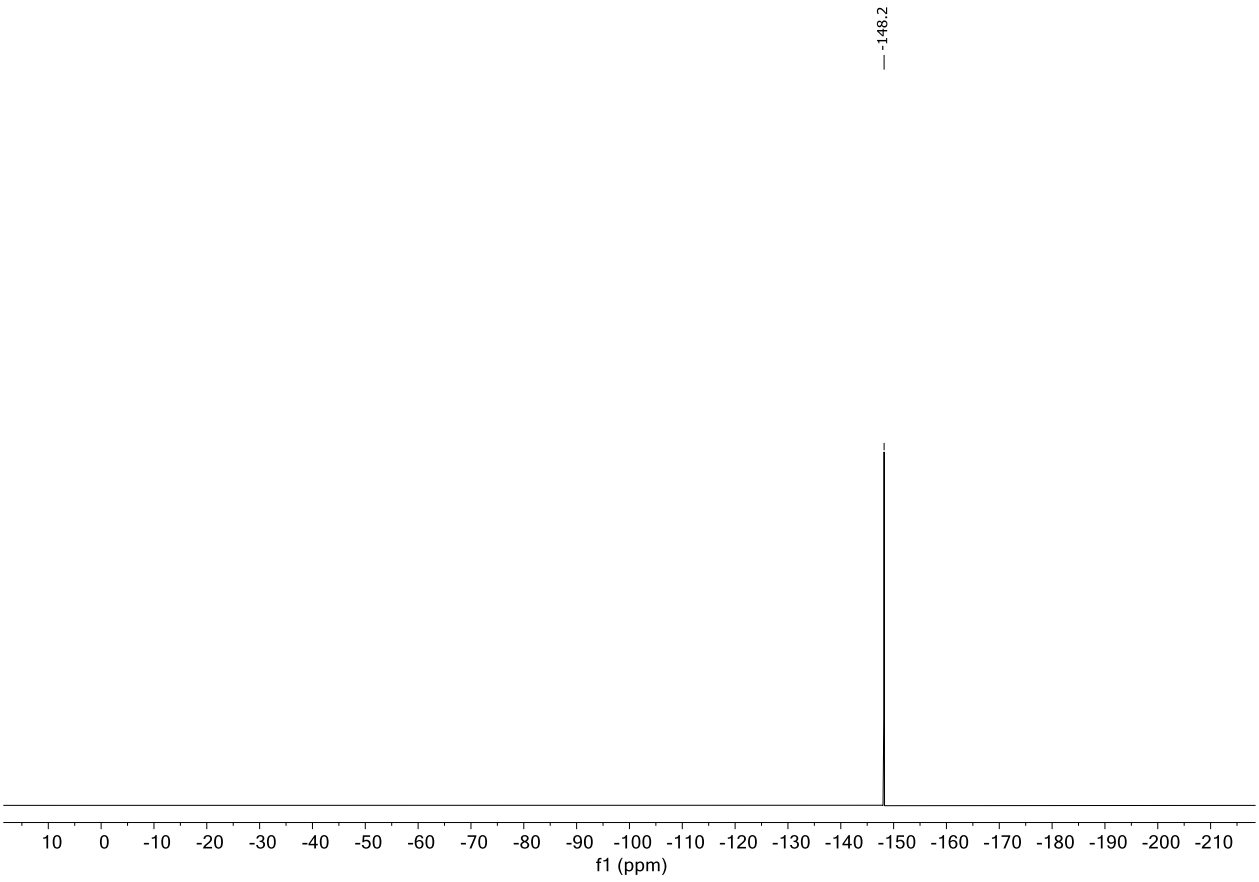

8.77
8.62
8.60
8.55
8.53
8.45
8.10
8.09
7.85
7.83
2.58
Me
Cl
Cl+
BF4-
2r
0.90
1.03
1.03
0.97
1.01
1.03
3.00
f1 (ppm)

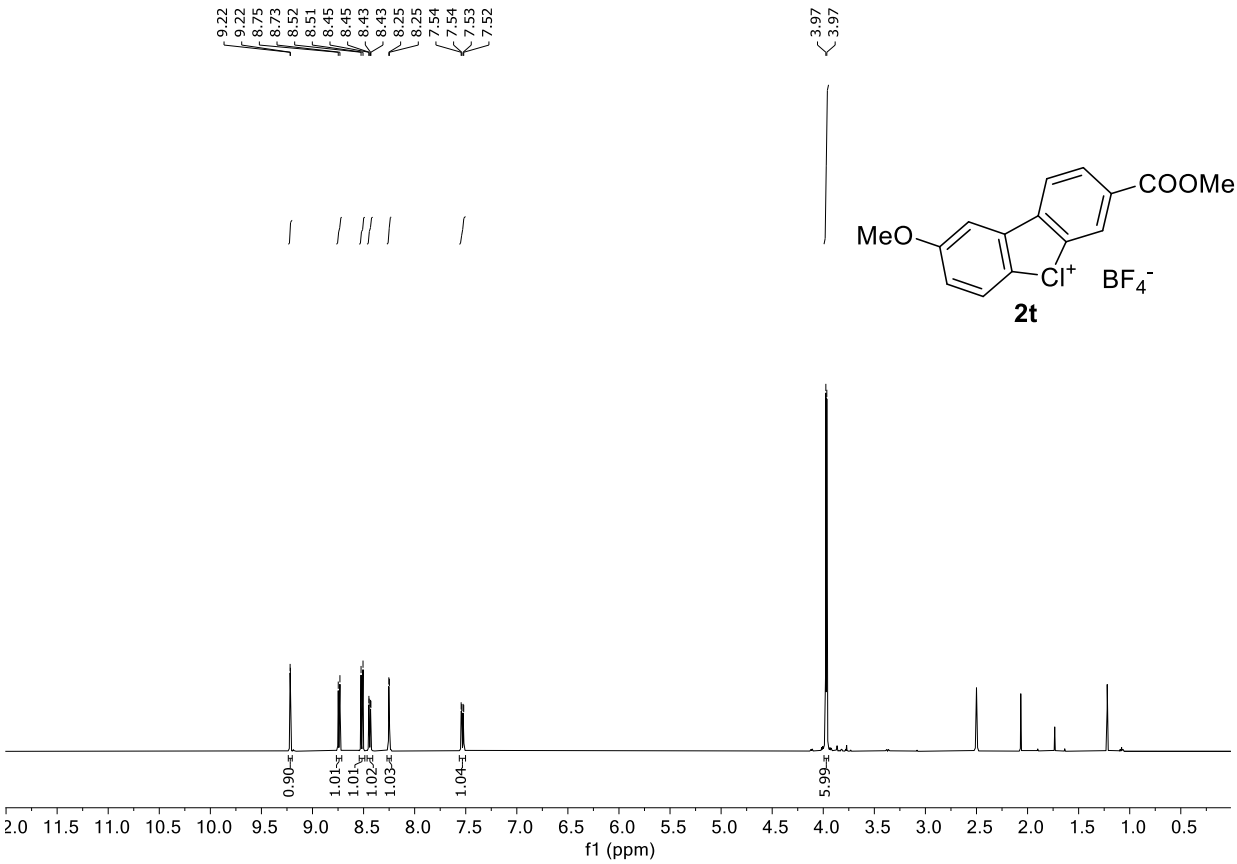

143.3
141.0
139.2
134.5
132.7
132.2
131.3
128.5
125.9
125.2
122.8
122.4
21.6
f1 (ppm)

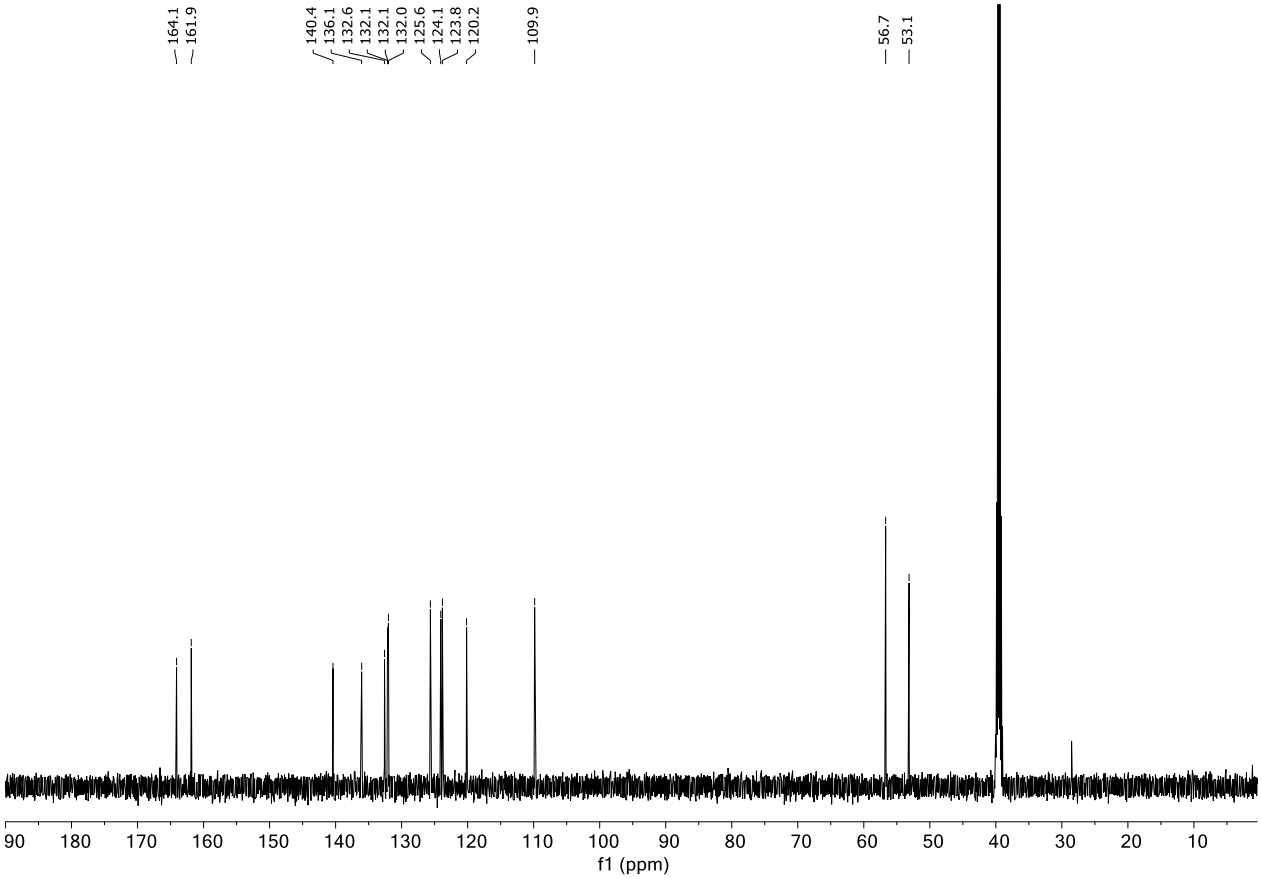

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

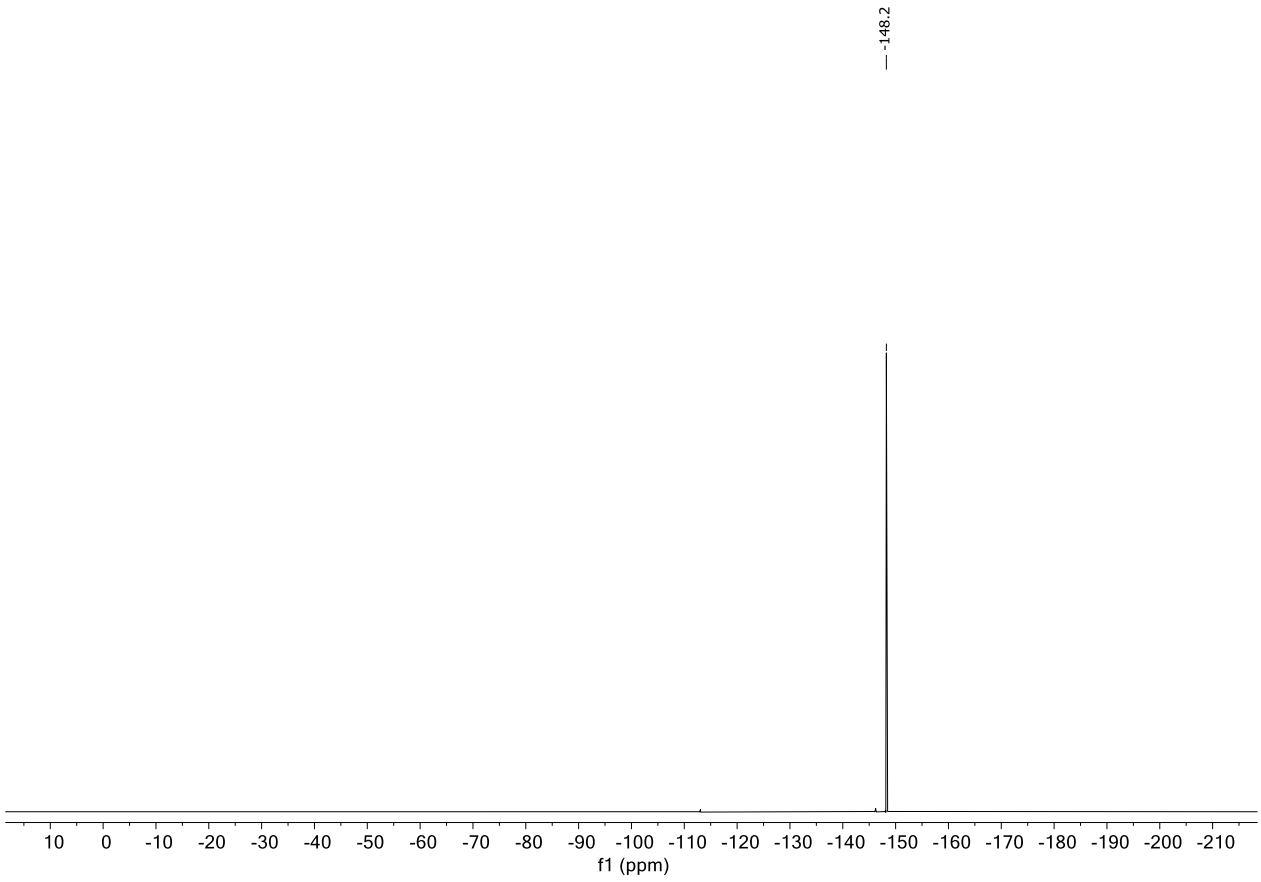

8.47
8.46
8.45
8.45
8.42
7.80
7.80
7.79
7.78
2.56
Me
Cl+
BF4-
Me
2s
2.04
1.94
2.04
6.00
f1 (ppm)

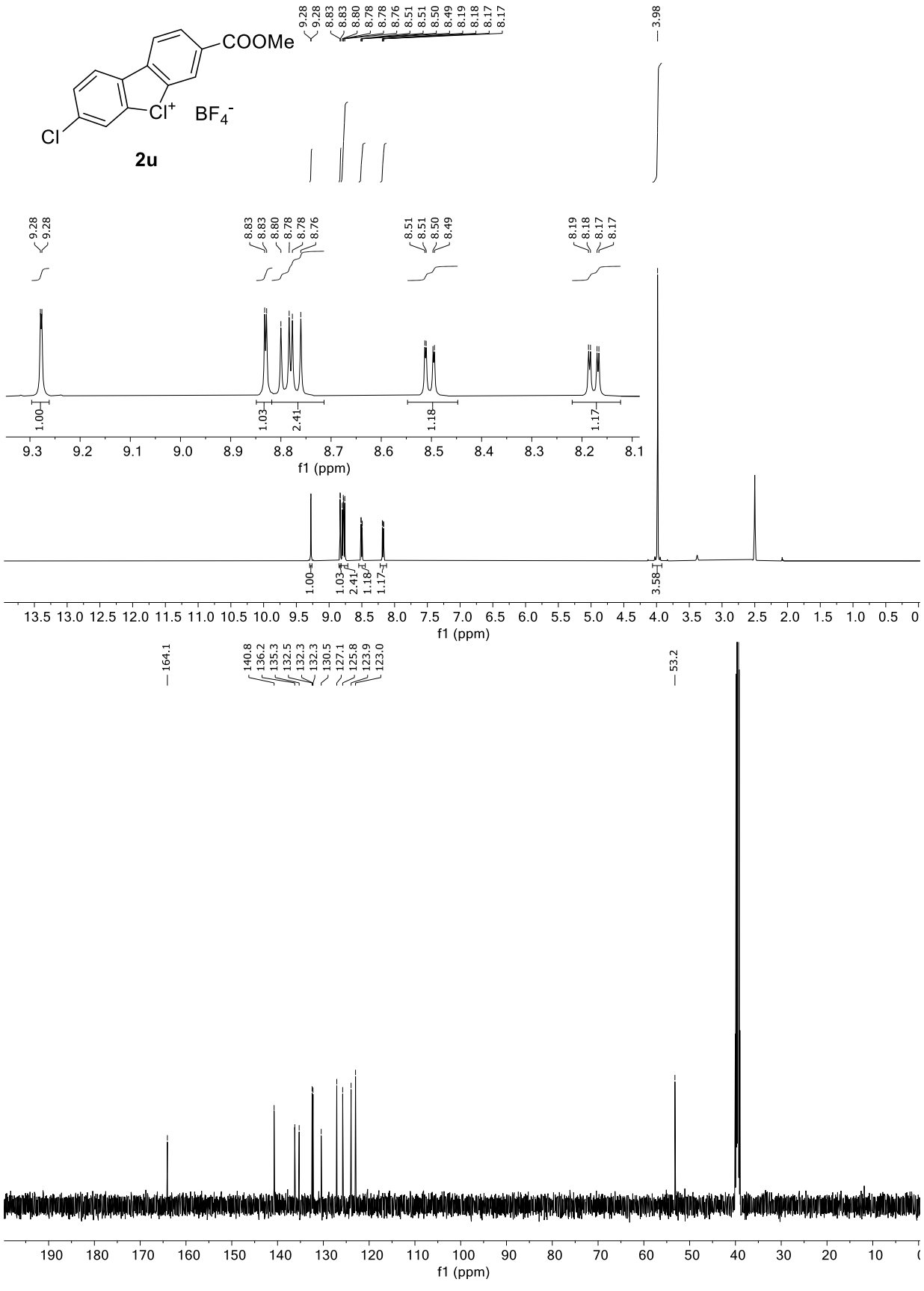

142.4
139.9
132.6
129.3
124.6
122.4
21.5
f1 (ppm)

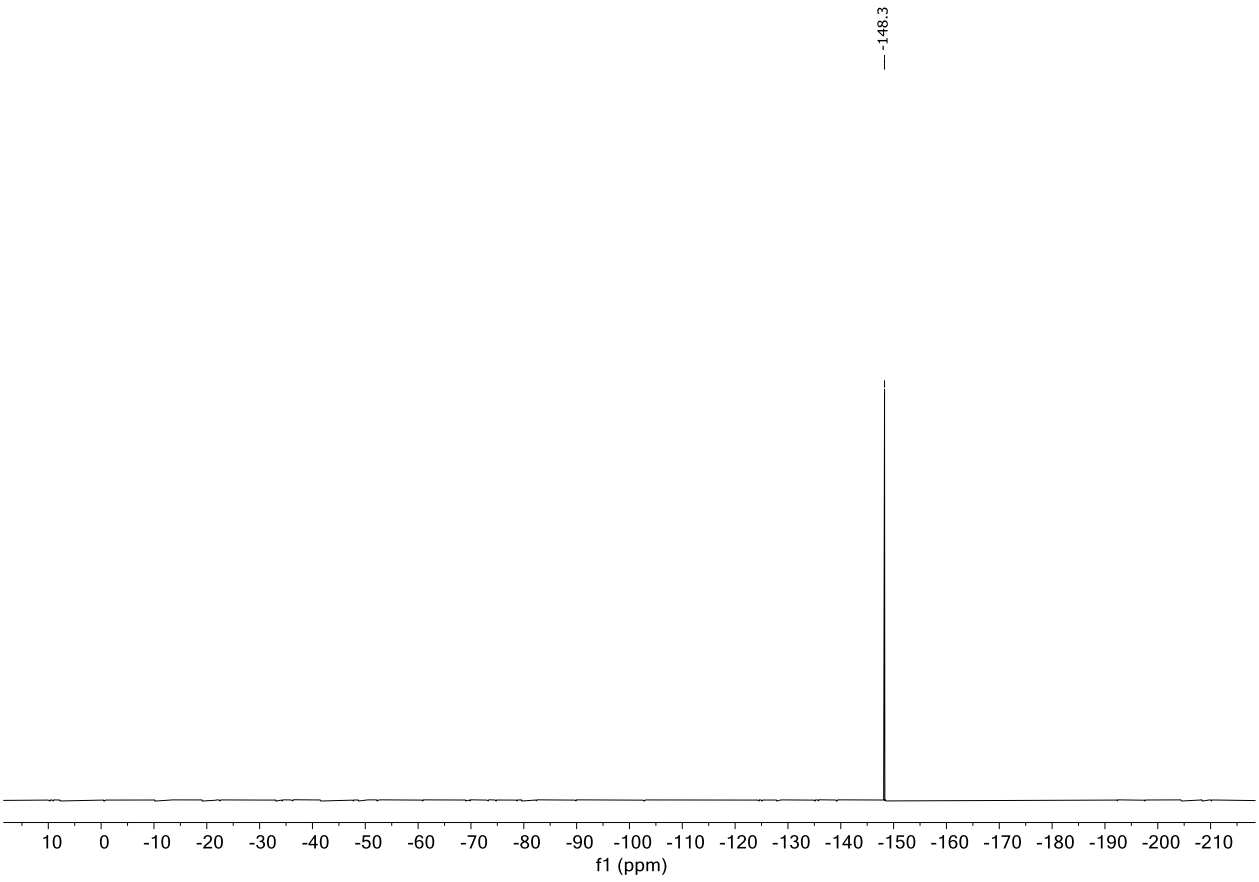

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

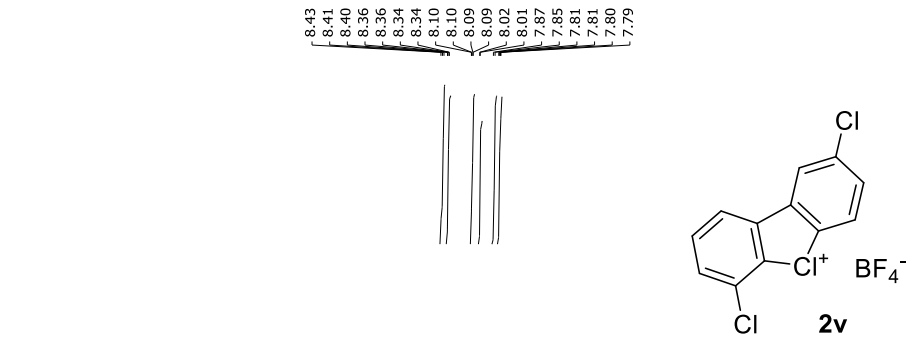

9.22
9.22
8.75
8.73
8.52
8.51
8.45
8.45
8.43
8.43
8.25
8.25
7.54
7.54
7.53
7.52
3.97
3.97
COOMe
MeO
Cl+
BF4-
2t
0.90
1.01
1.01
1.02
1.03
1.04
5.99
f1 (ppm)

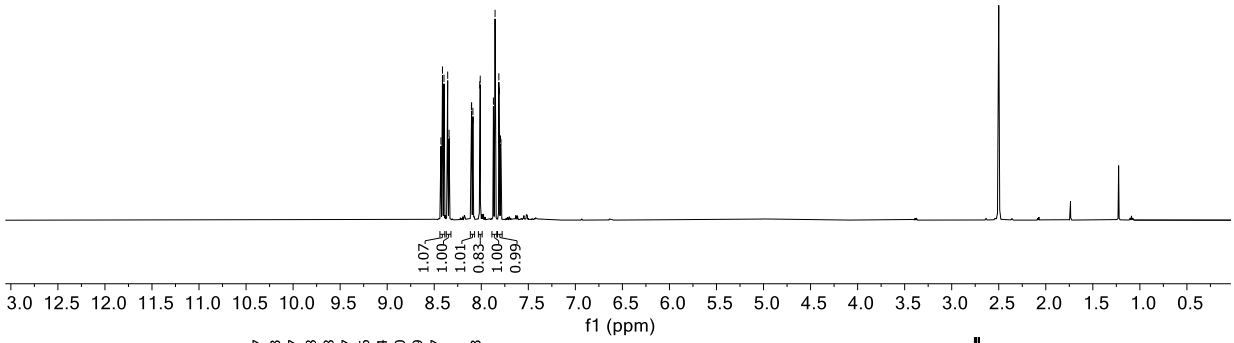

164.1
161.9
140.4
136.1
132.6
132.1
132.1
132.0
125.6
124.1
123.8
120.2
109.9
56.7
53.1
f1 (ppm)

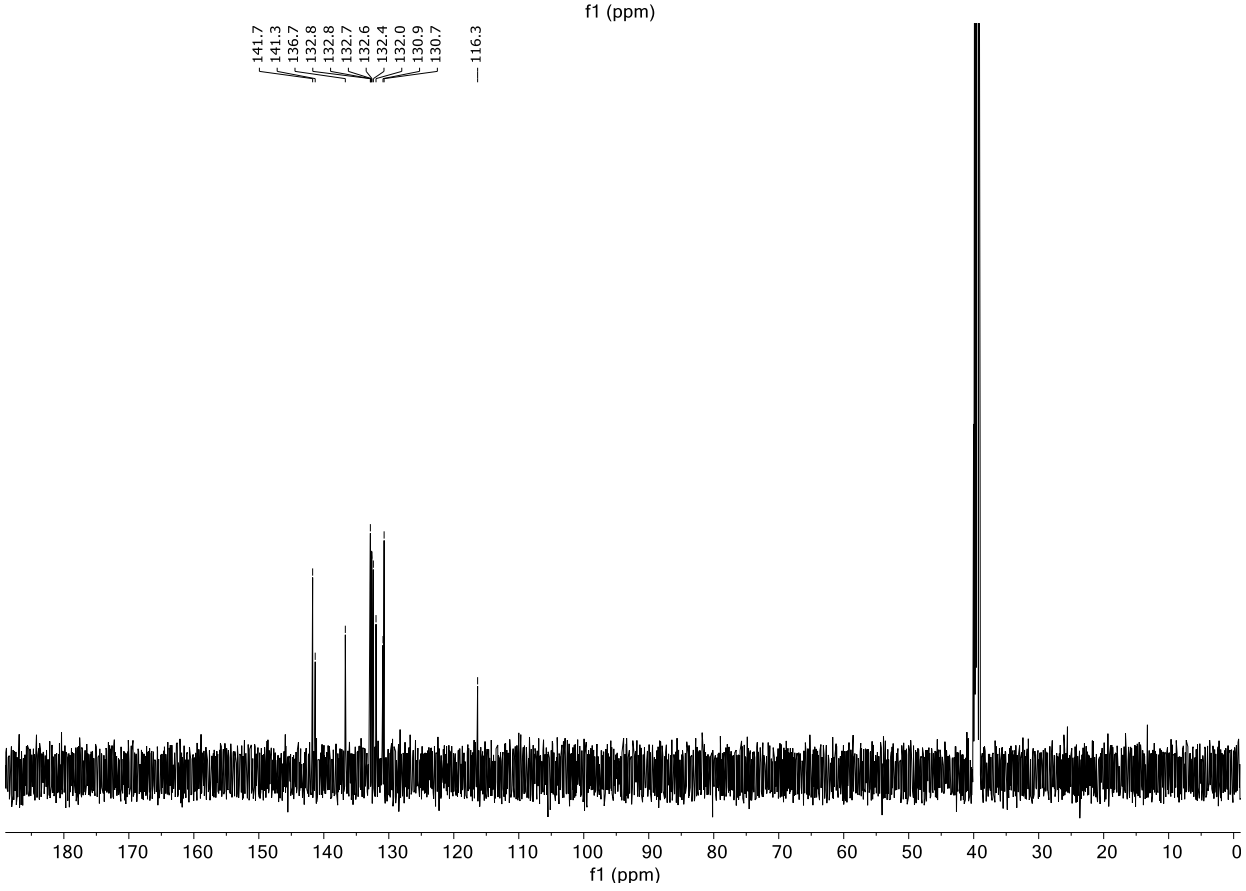

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

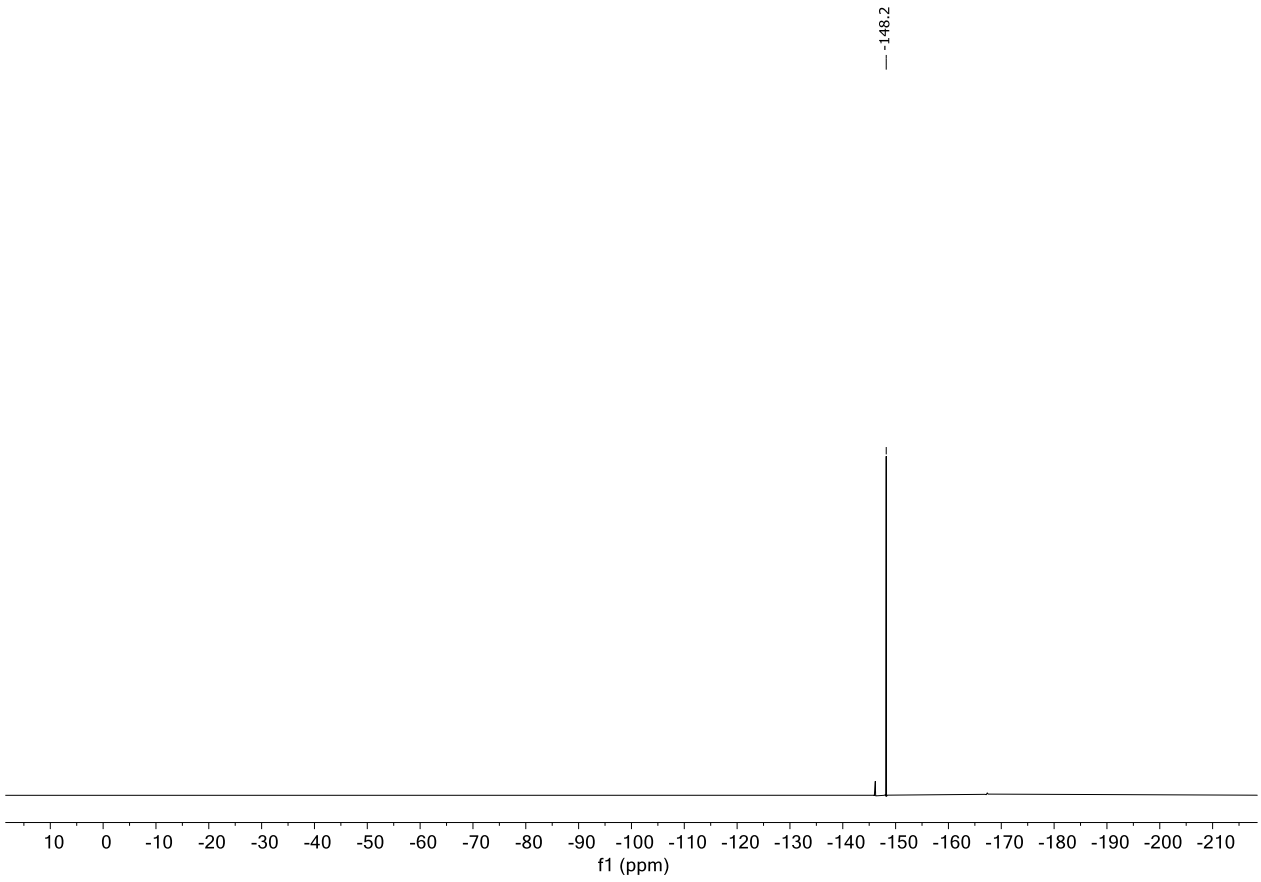

COOMe
Cl
Cl+
BF4-
2u
f1 (ppm)
f1 (ppm)
f1 (ppm)

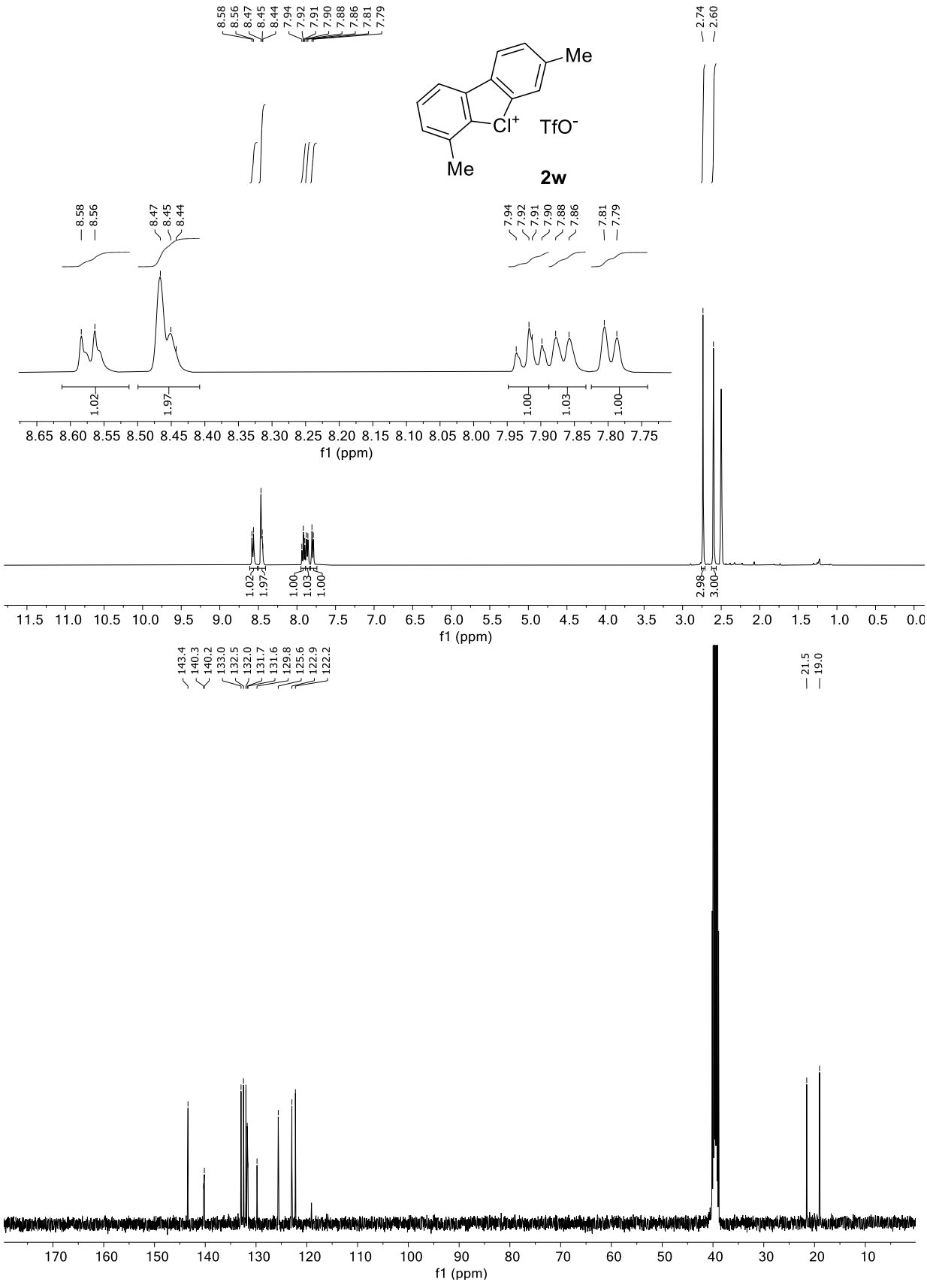

-148.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

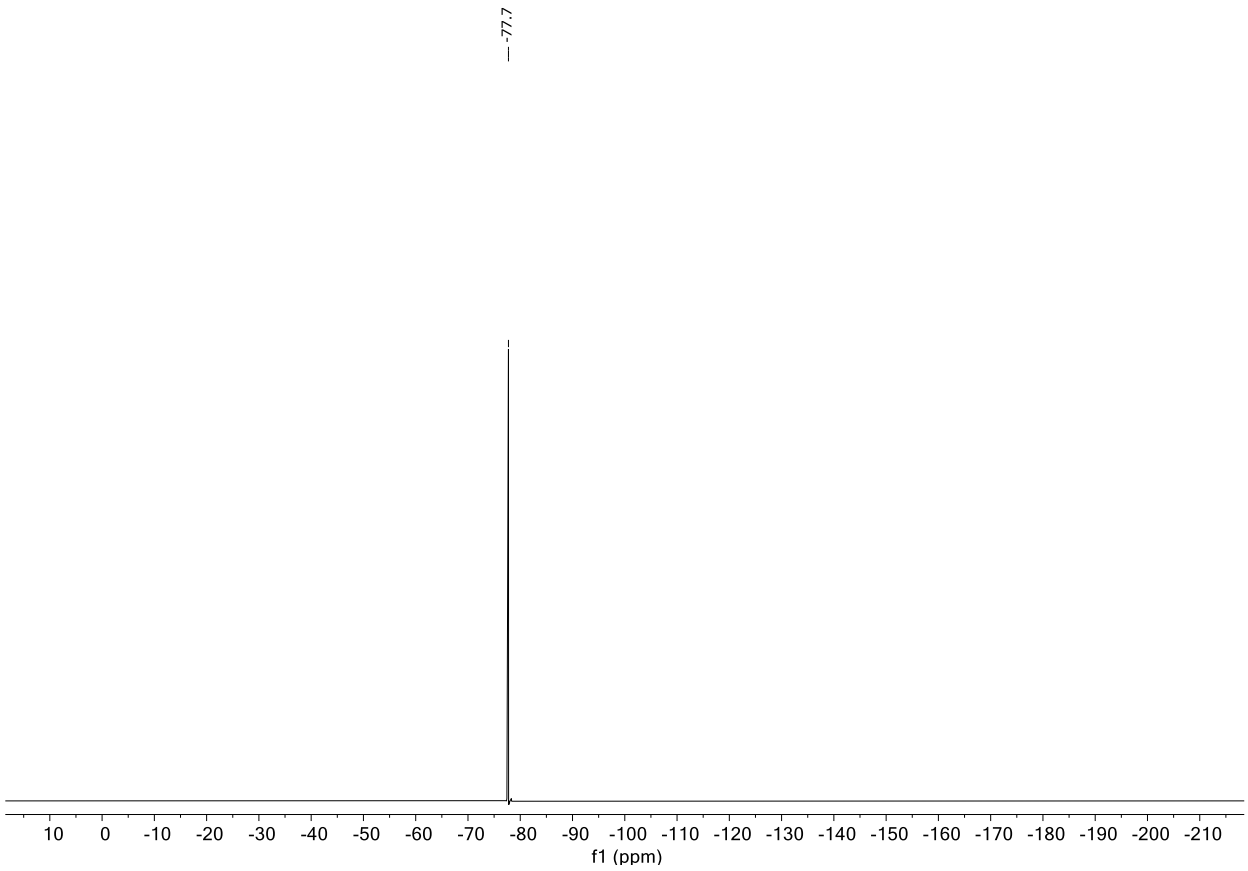

8.43
8.41
8.40
8.36
8.36
8.34
8.34
8.34
8.10
8.10
8.09
8.09
8.09
8.02
8.01
7.87
7.85
7.81
7.81
7.80
7.79
Cl
Cl+
BF4-
Cl
2v

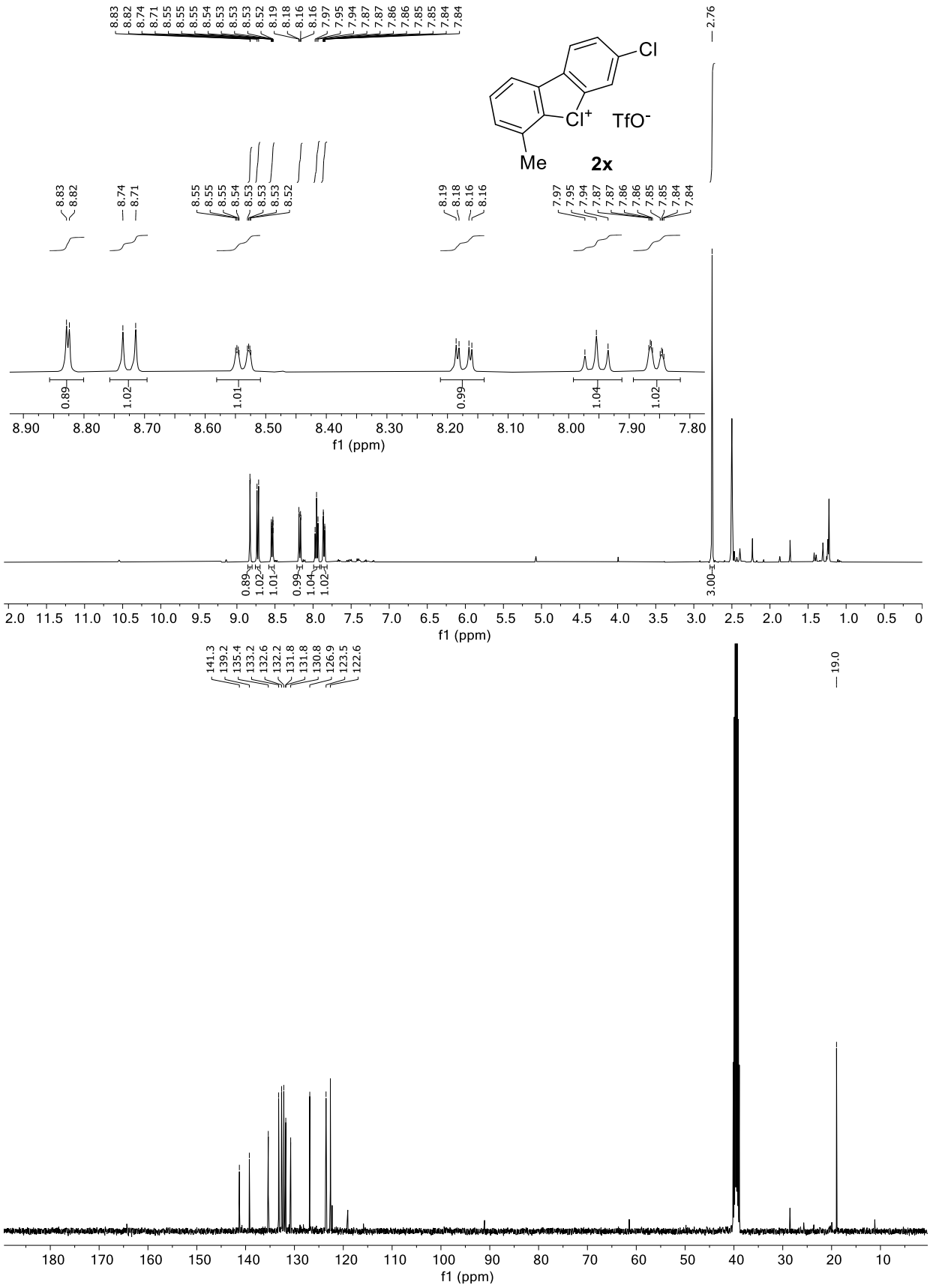

1.07
1.00
1.01
0.83
1.00
0.99
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

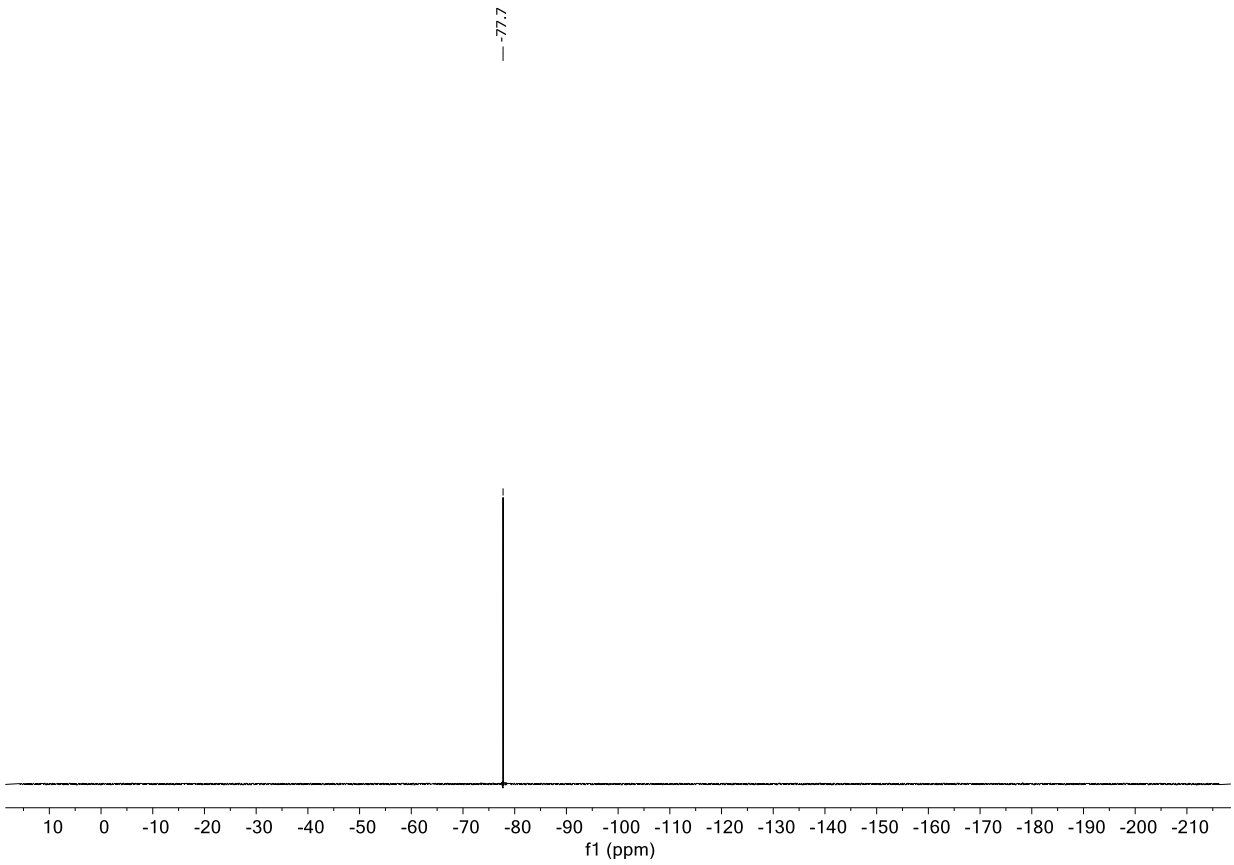

141.7
141.3
136.7
132.8
132.8
132.7
132.6
132.4
132.0
130.9
130.7
116.3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

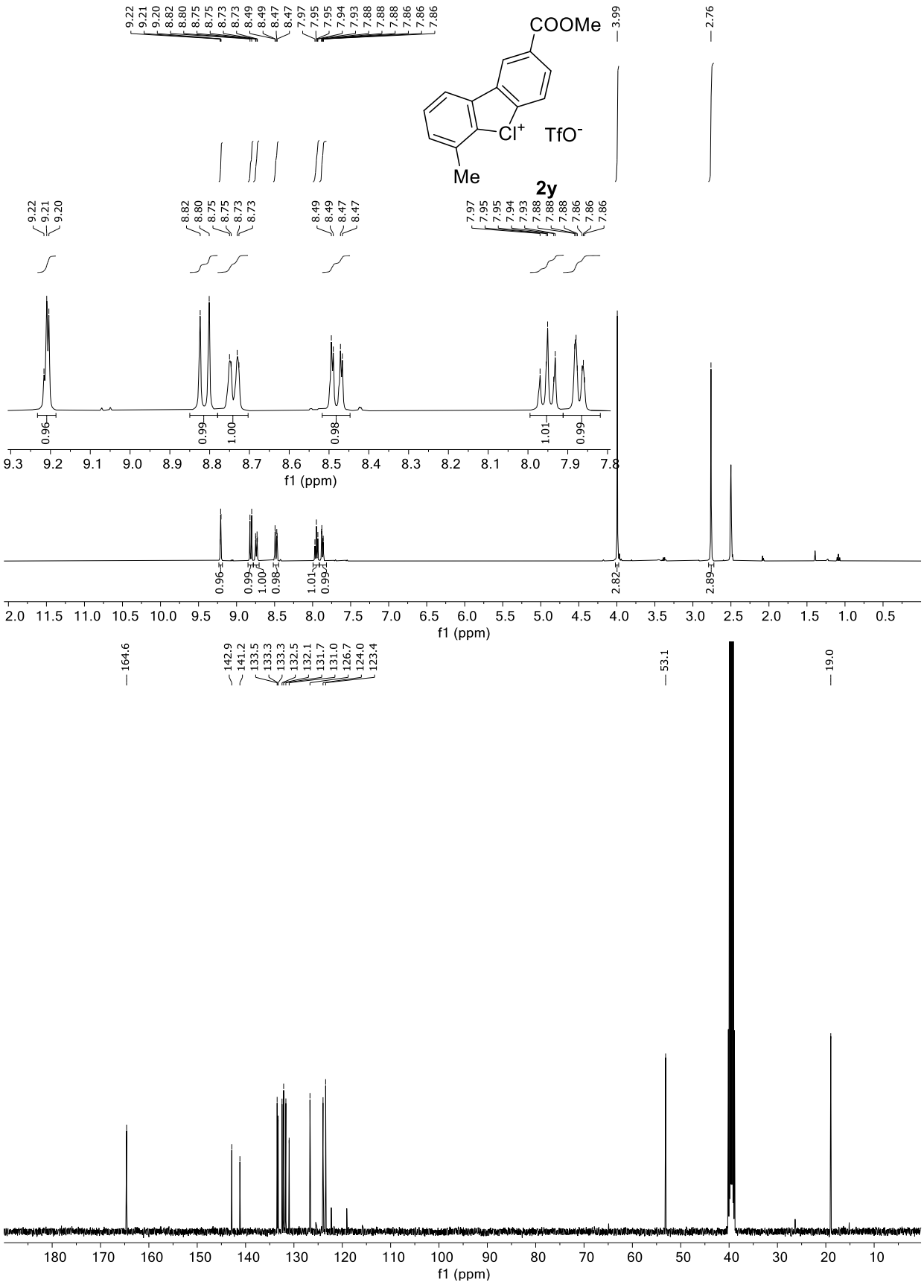

-148.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

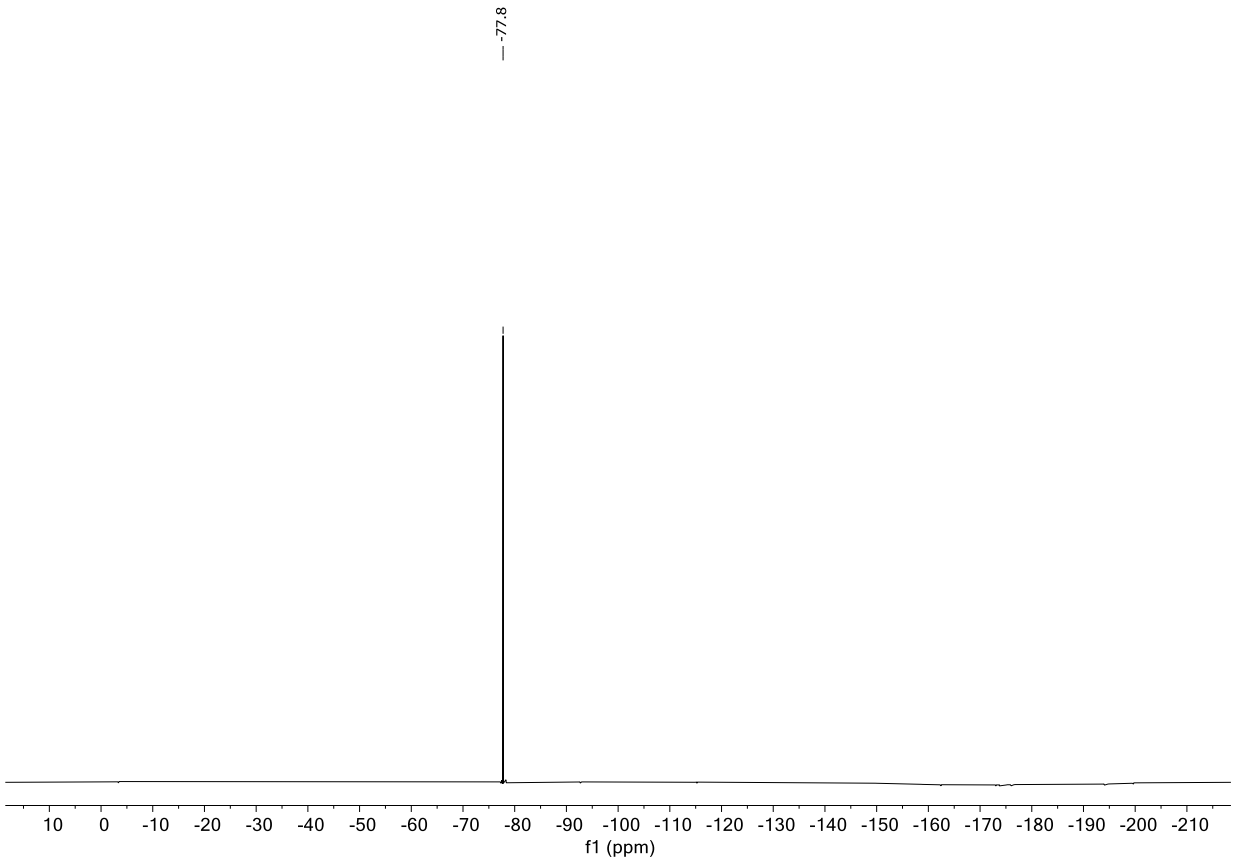

8.58
8.56
8.47
8.45
8.44
7.94
7.92
7.91
7.90
7.88
7.86
7.81
7.79
2.74
2.60
Me
Cl+
TfO-
Me
2w
1.02
1.97
1.00
1.03
1.00
f1 (ppm)
2.98
3.00
143.4
140.3
140.2
133.0
132.5
132.0
131.7
131.6
129.8
125.6
122.9
122.2
21.5
19.0
f1 (ppm)

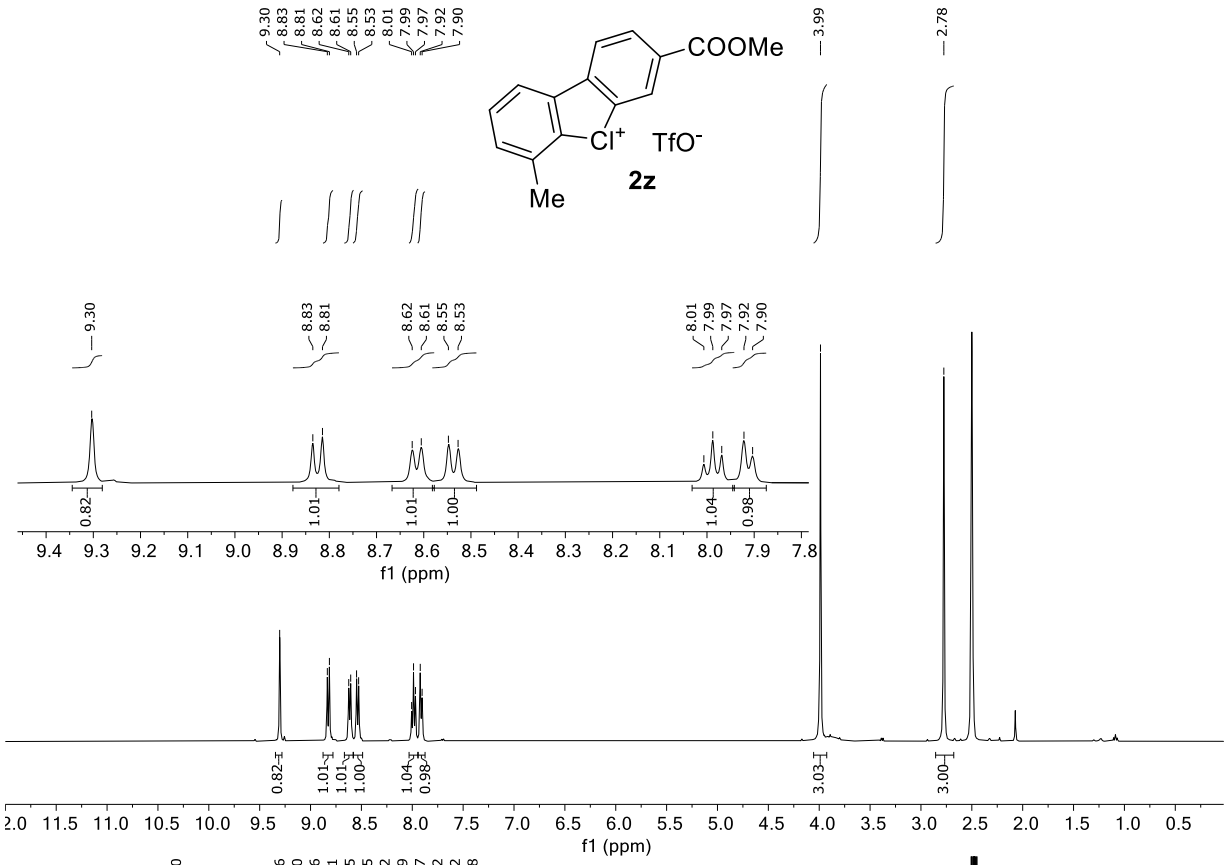

-77.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

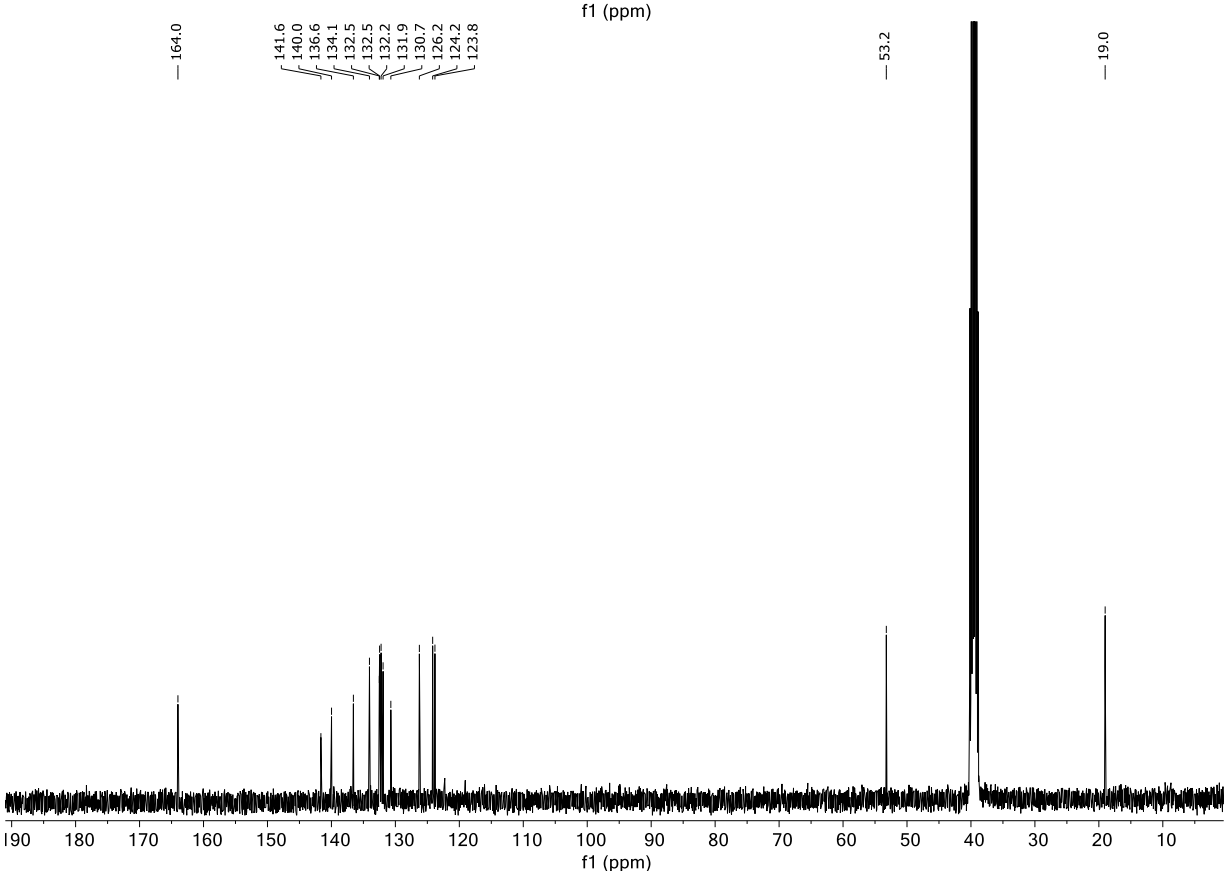

Cl
Cl+
TfO-
Me
2x
f1 (ppm)
f1 (ppm)
f1 (ppm)

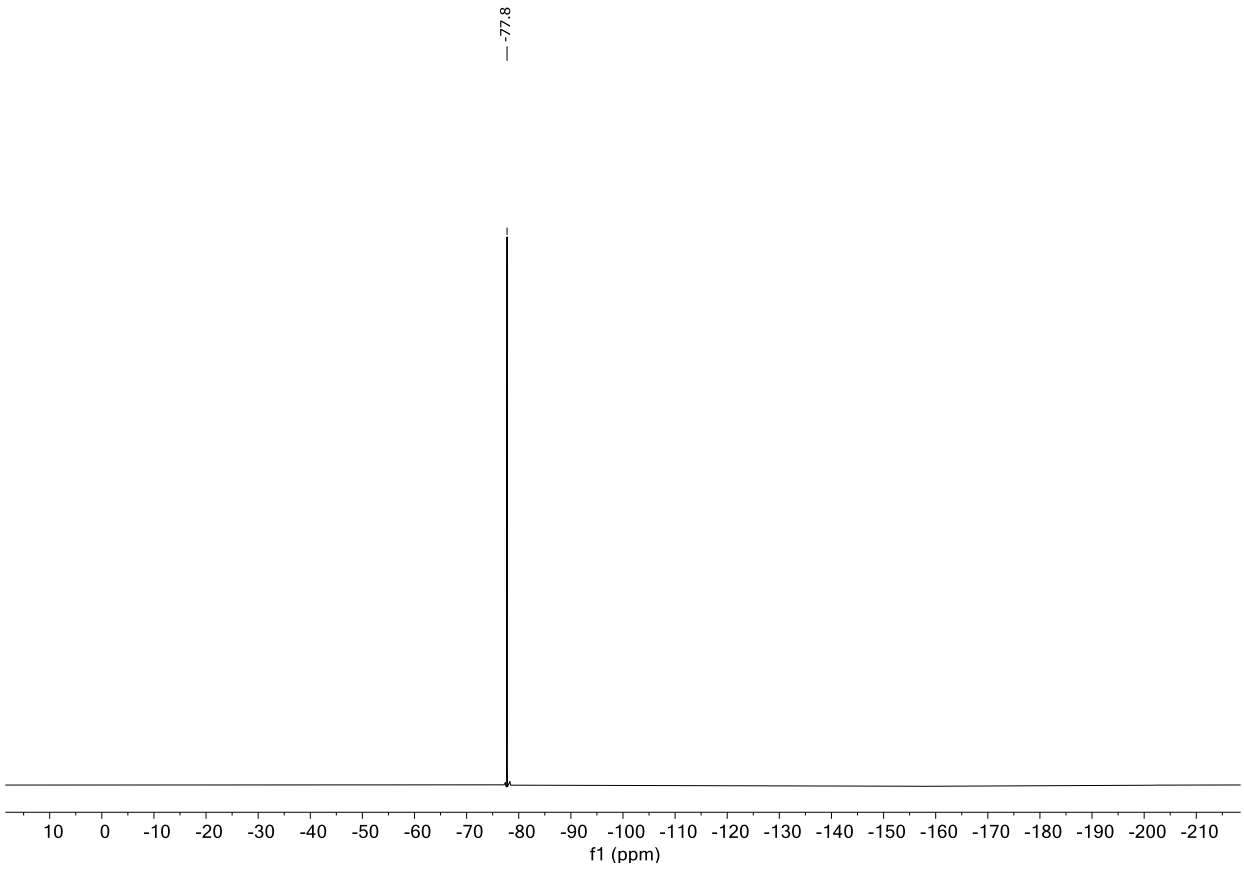

-77.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

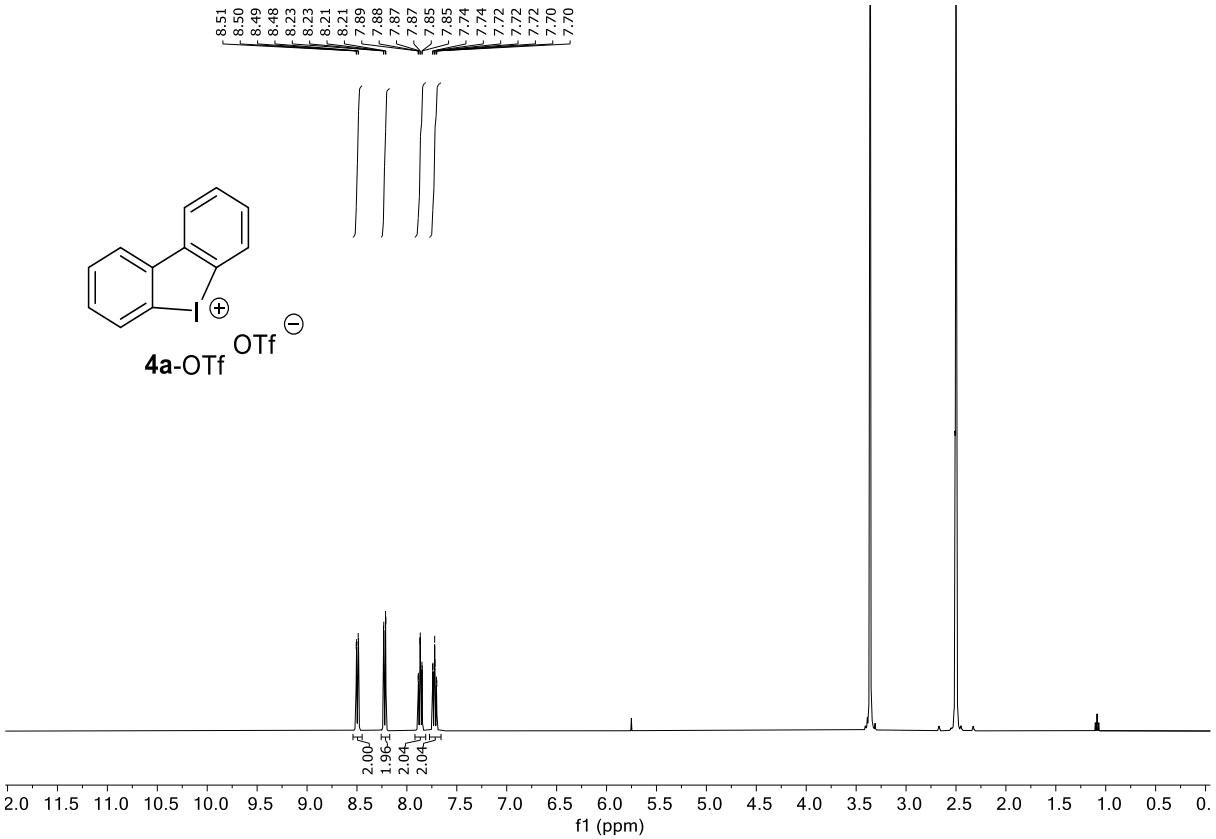

COOMe
Cl+
TfO-
Me
2y
f1 (ppm)


-77.8
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)

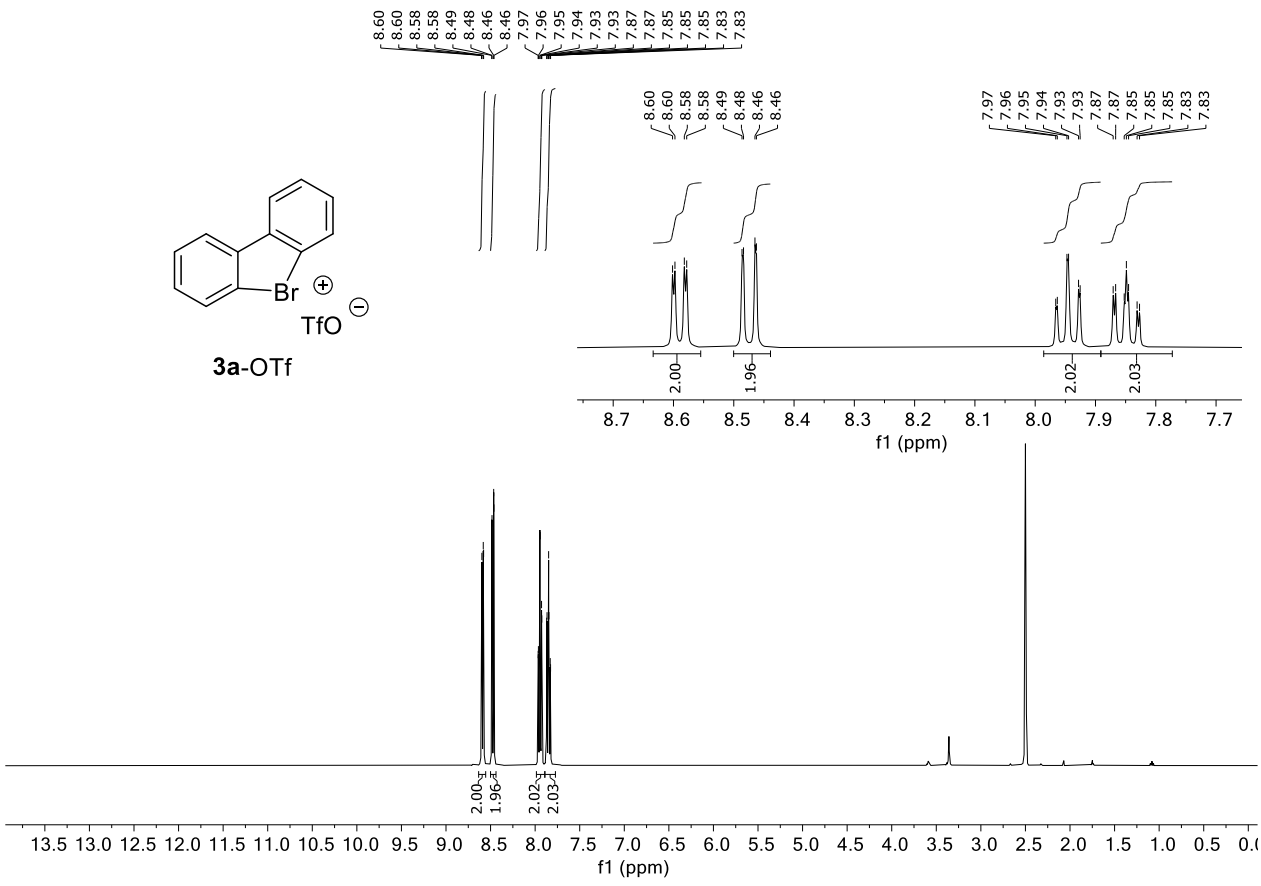

9.30
8.83
8.81
8.62
8.61
8.55
8.53
8.01
7.99
7.97
7.92
7.90
3.99
2.78
COOMe
Cl+
TfO-
Me
2z
0.82
1.01
1.01
1.00
1.04
0.98
3.03
3.00
f1 (ppm)


164.0
141.6
140.0
136.6
134.1
132.5
132.5
132.2
131.9
130.7
126.2
124.2
123.8
53.2
19.0
f1 (ppm)

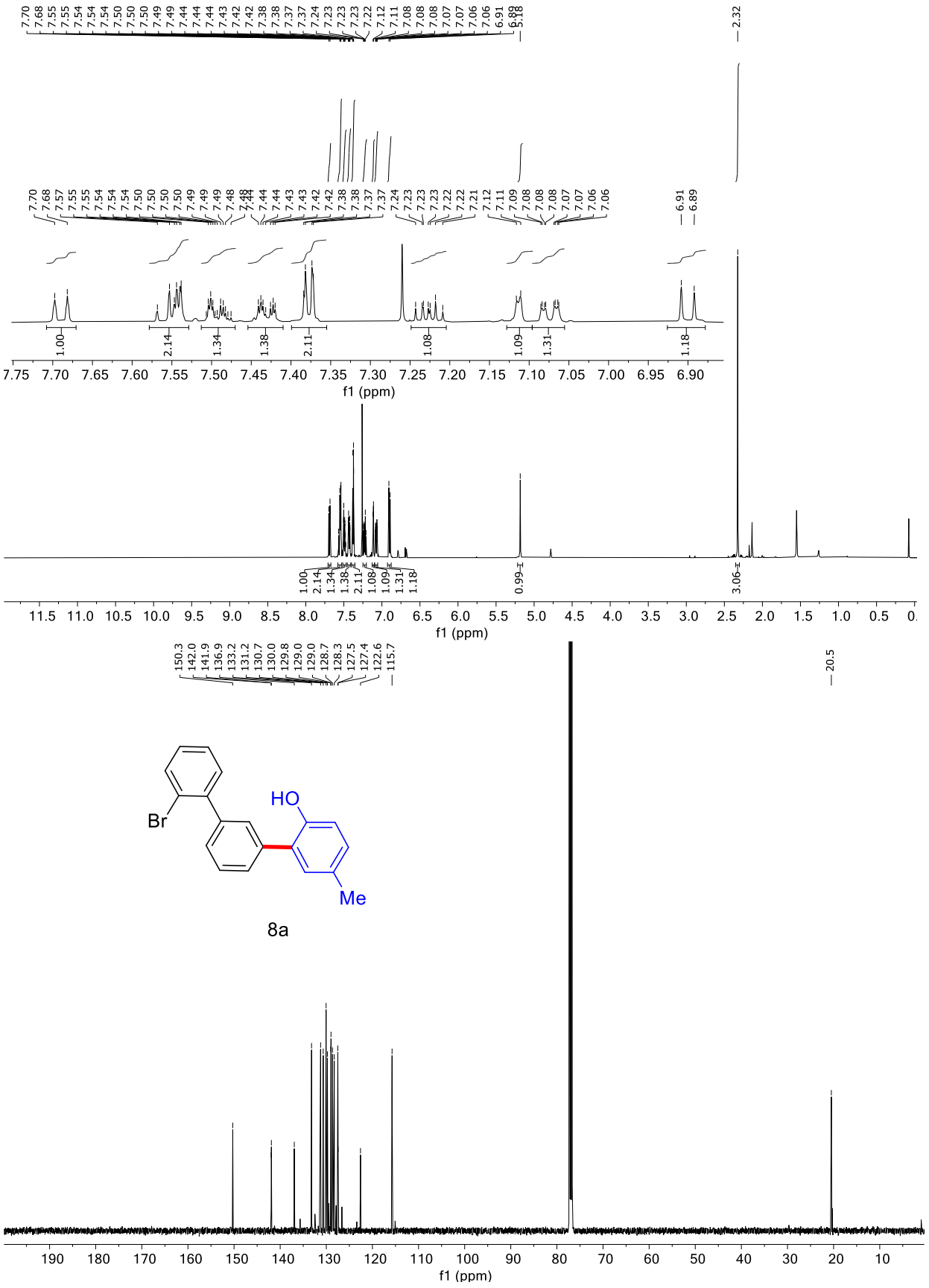

-77.8
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.51
8.50
8.49
8.48
8.23
8.23
8.21
8.21
7.89
7.88
7.87
7.87
7.85
7.85
7.74
7.74
7.72
7.72
7.72
7.70
7.70
I
OTf
2.00
1.96
2.04
2.04
f1 (ppm)

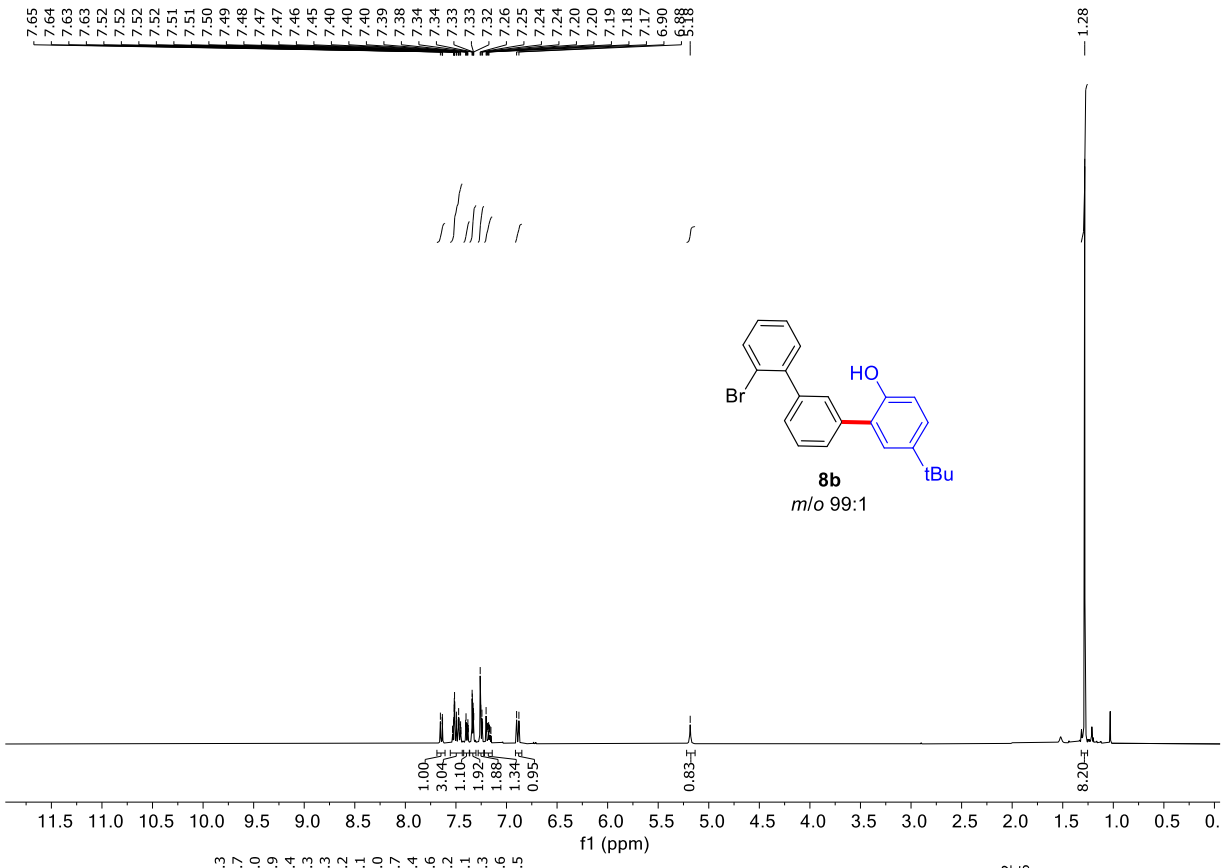
4a-OTf

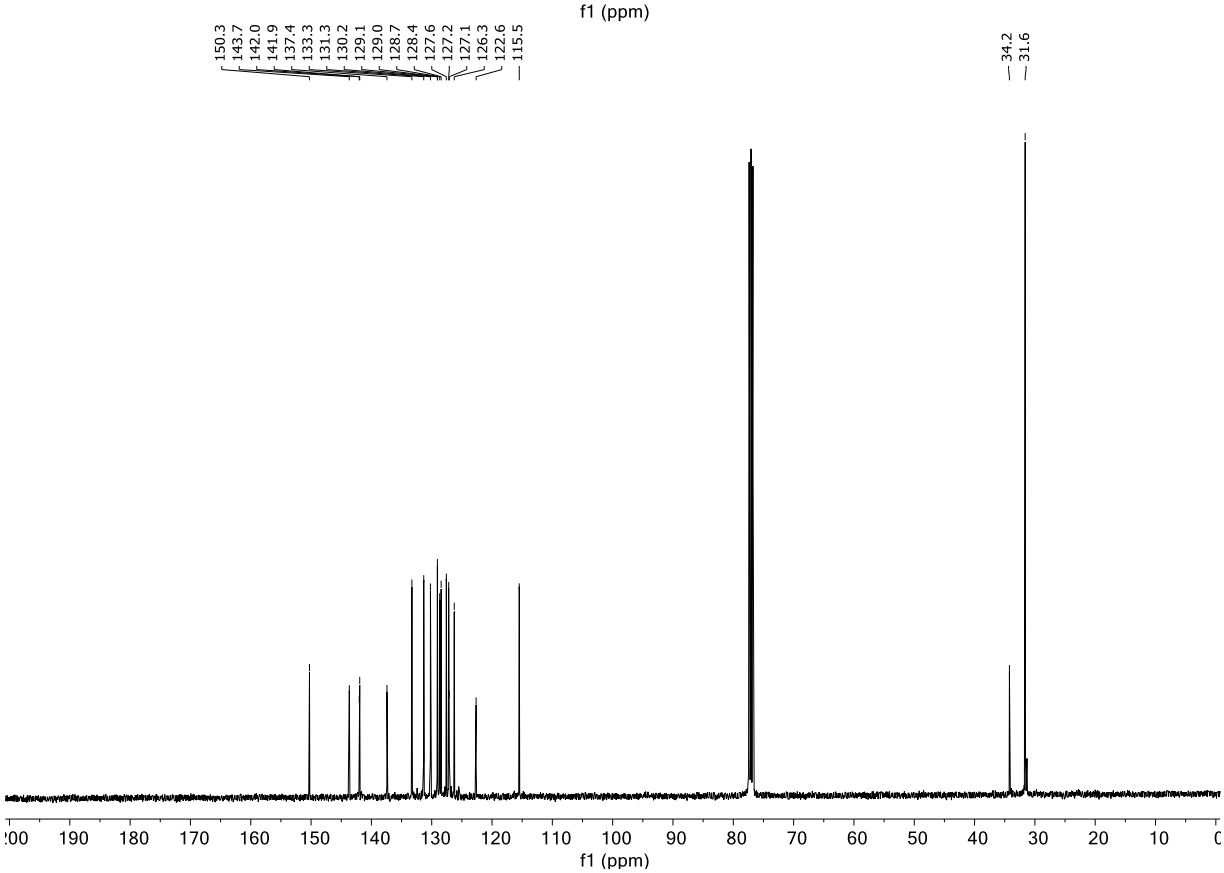

8.60
8.60
8.58
8.58
8.49
8.48
8.46
8.46
7.97
7.96
7.95
7.94
7.93
7.93
7.87
7.85
7.85
7.83
7.83
Br
TfO
2.00
1.96
2.02
2.03
f1 (ppm)

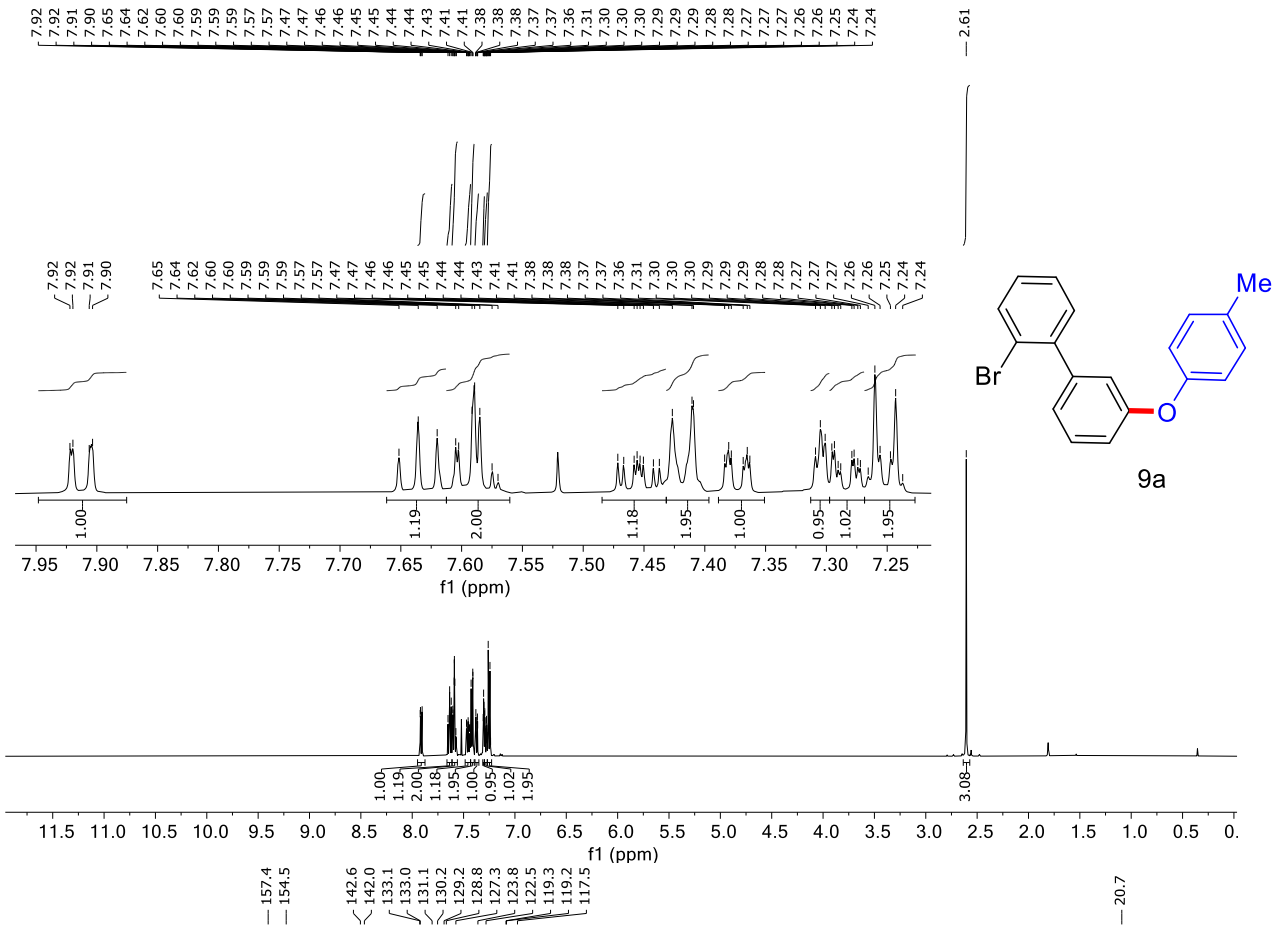
3a-OTf

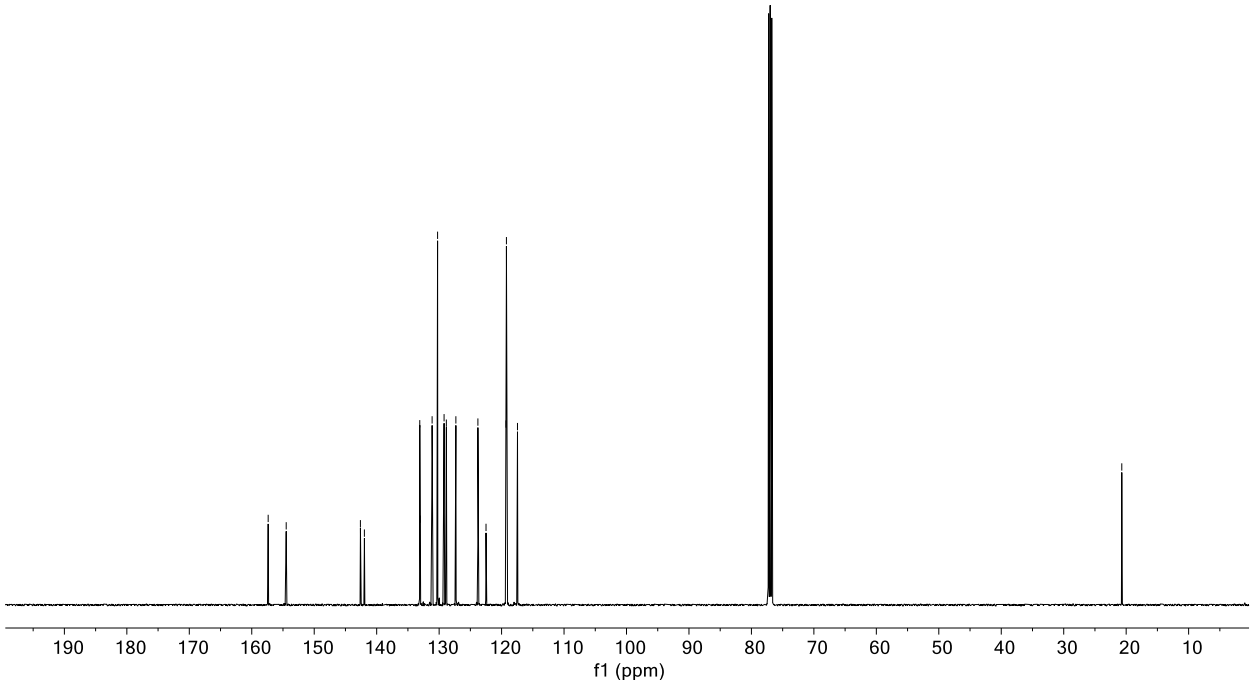


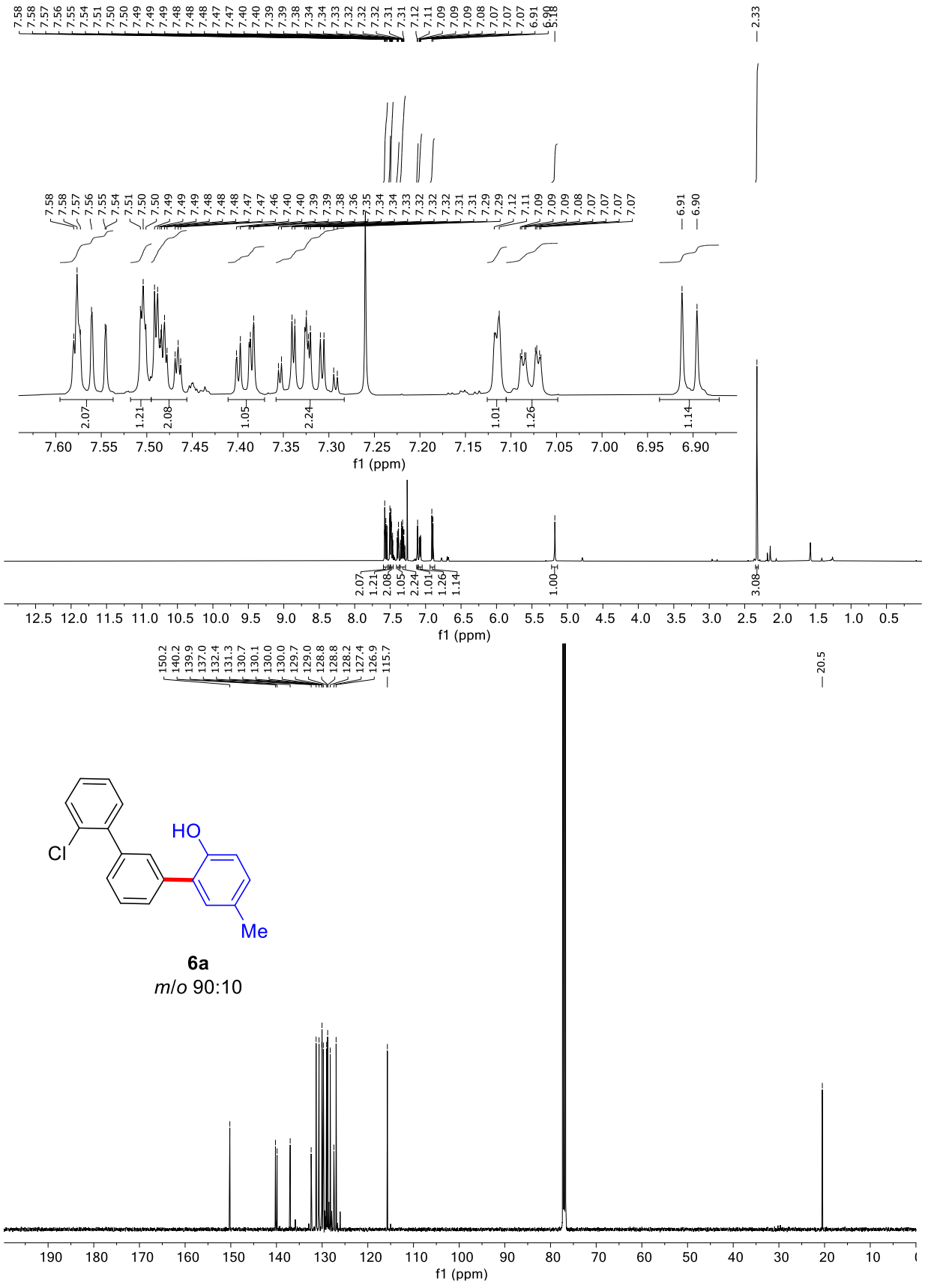
8a

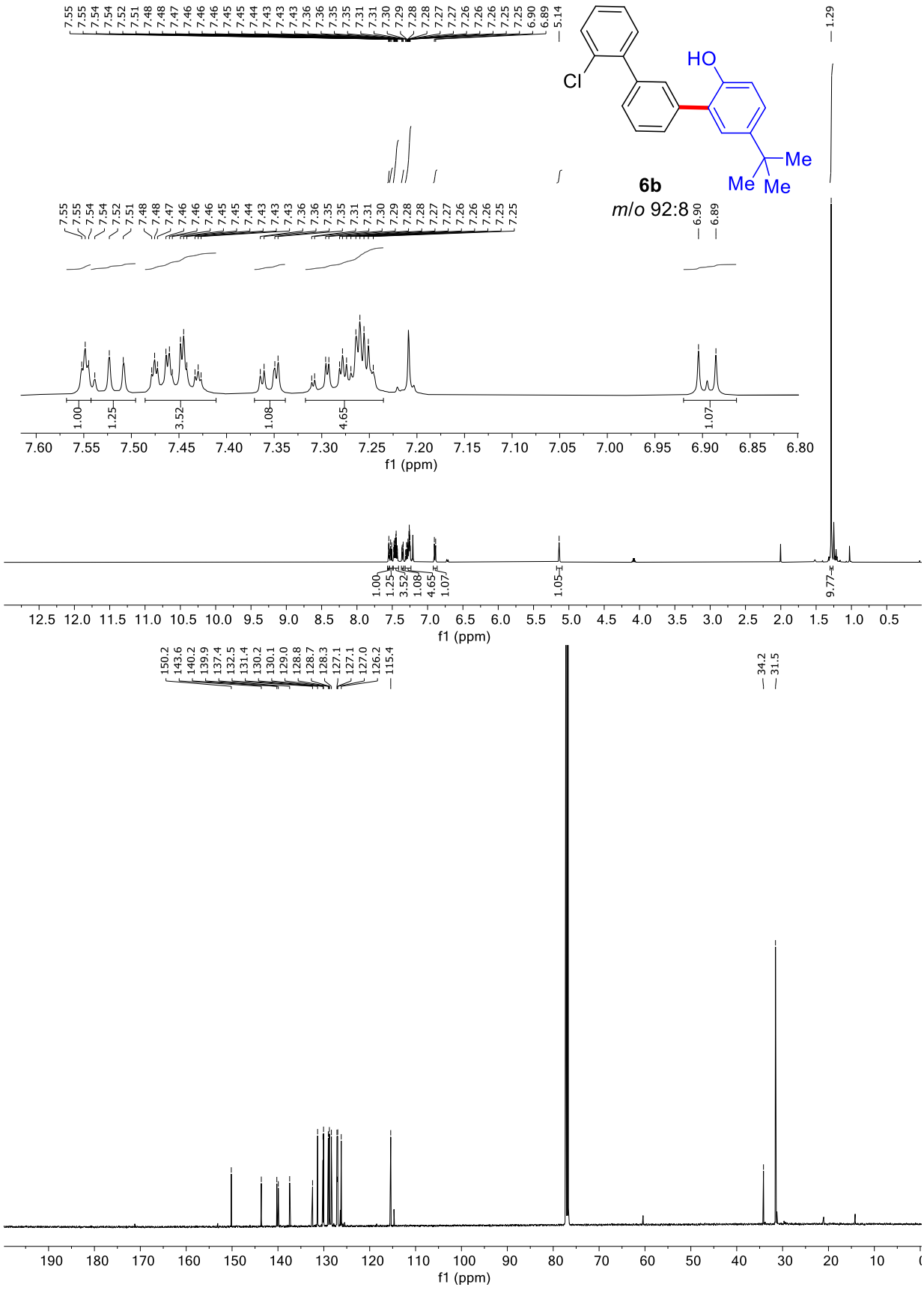

7.65
7.64
7.63
7.63
7.52
7.52
7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.40
7.40
7.40
7.39
7.38
7.34
7.33
7.33
7.32
7.26
7.25
7.24
7.24
7.20
7.20
7.19
7.18
7.17
6.90
6.88
5.18
1.28
HO
Br
tBu
8b
m/o 99:1
1.00
3.04
1.10
1.92
1.88
1.34
0.95
0.83
8.20
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

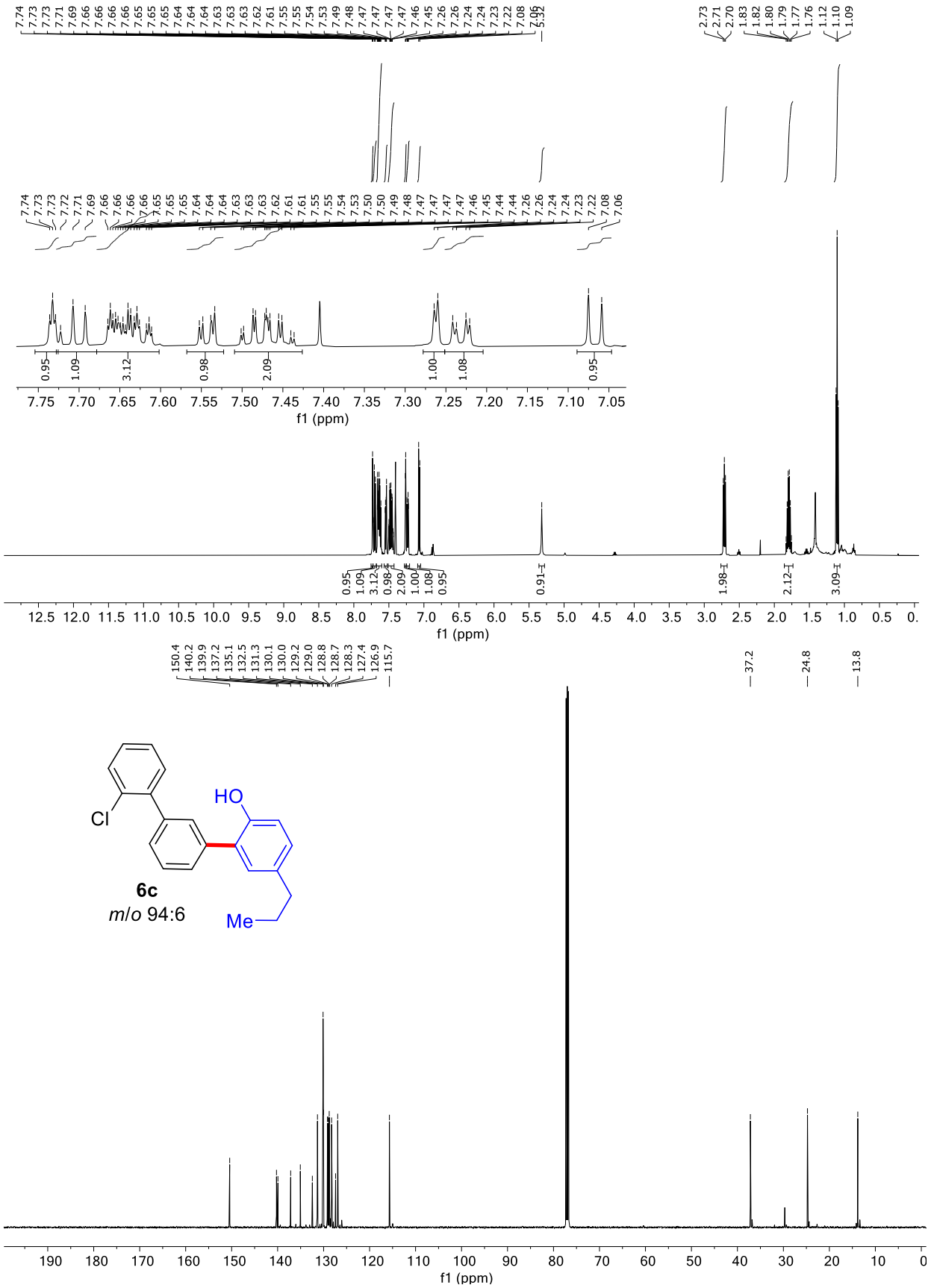

150.3
143.7
142.0
141.9
137.4
133.3
131.3
130.2
129.1
129.0
128.7
128.4
127.6
127.2
127.1
126.3
122.6
115.5
34.2
31.6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

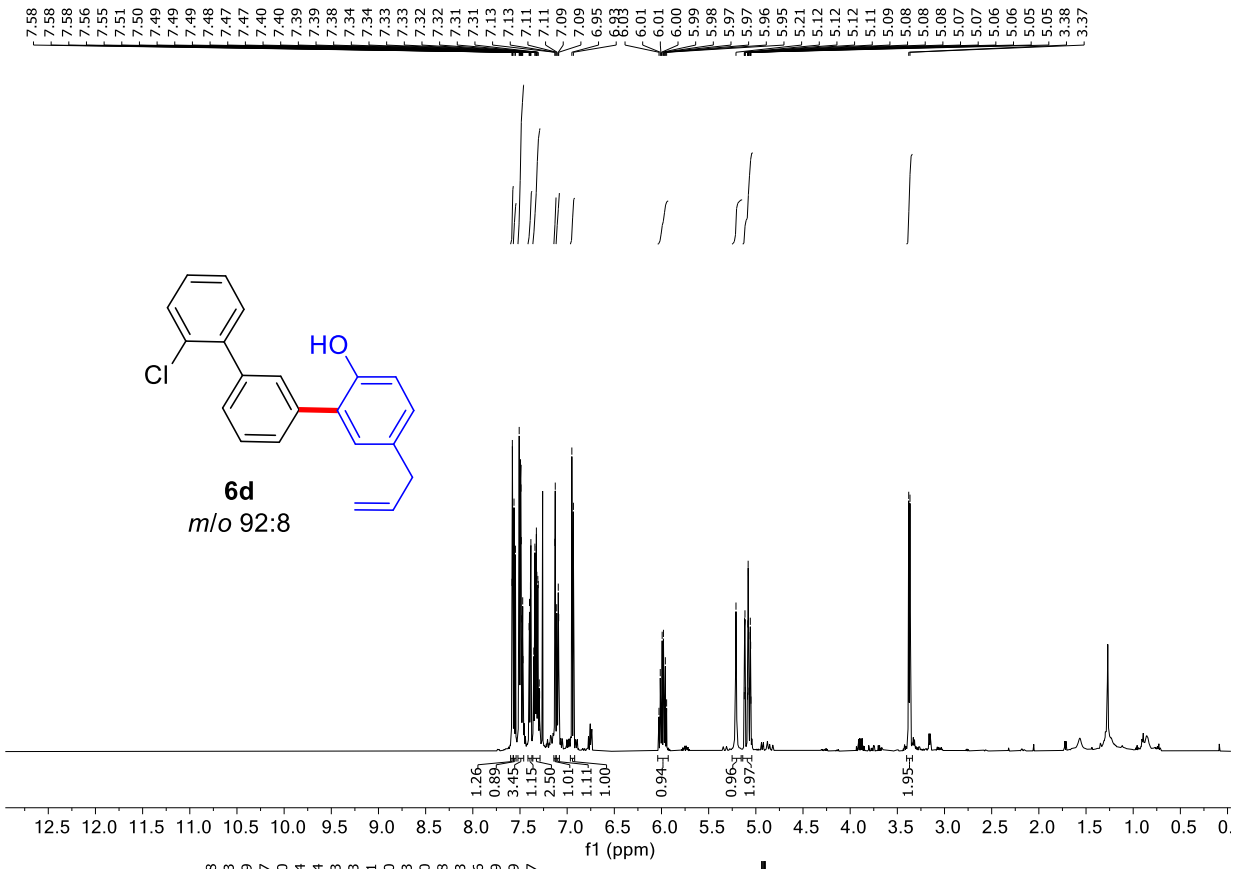

Br
O
Me
9a
f1 (ppm)


f1 (ppm)

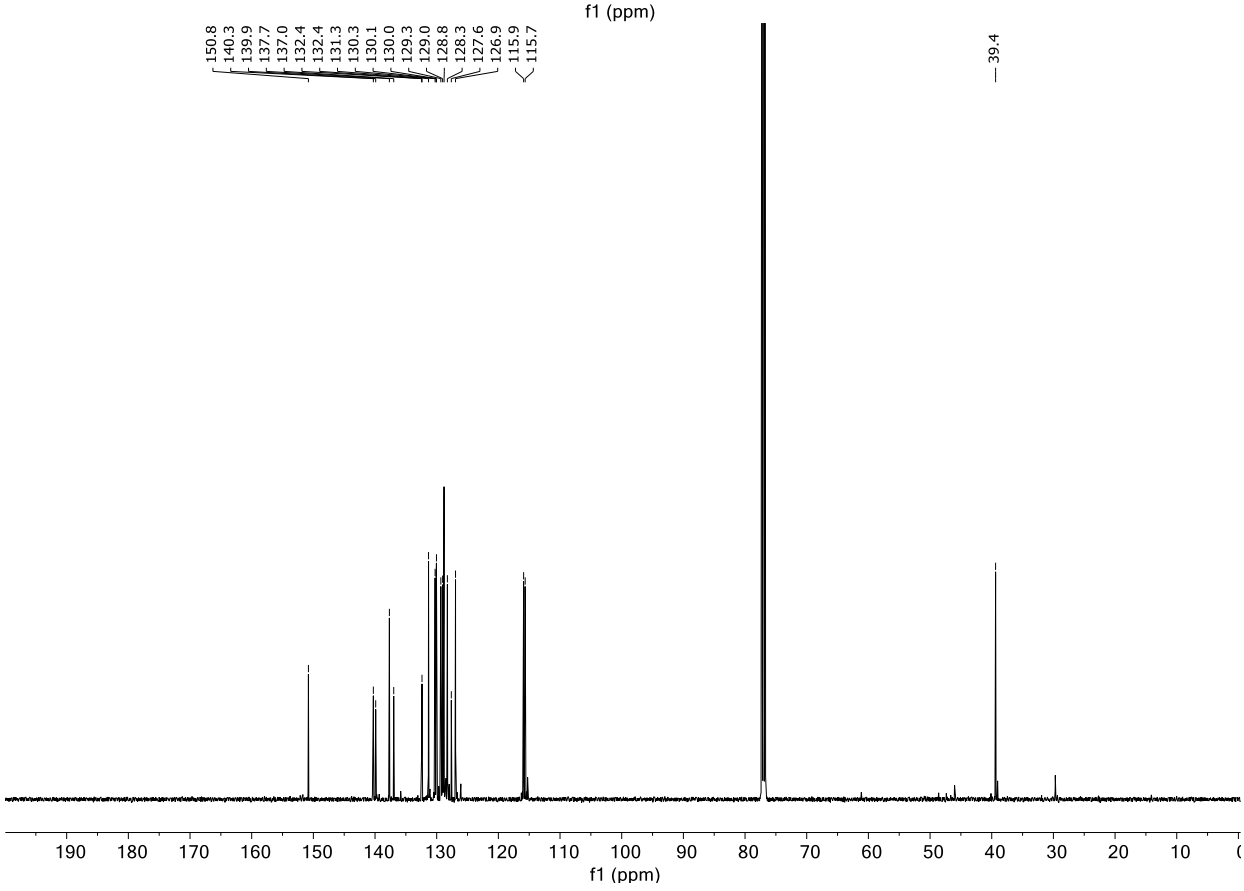

HO
Cl
Me
6a
m/o 90:10
f1 (ppm)

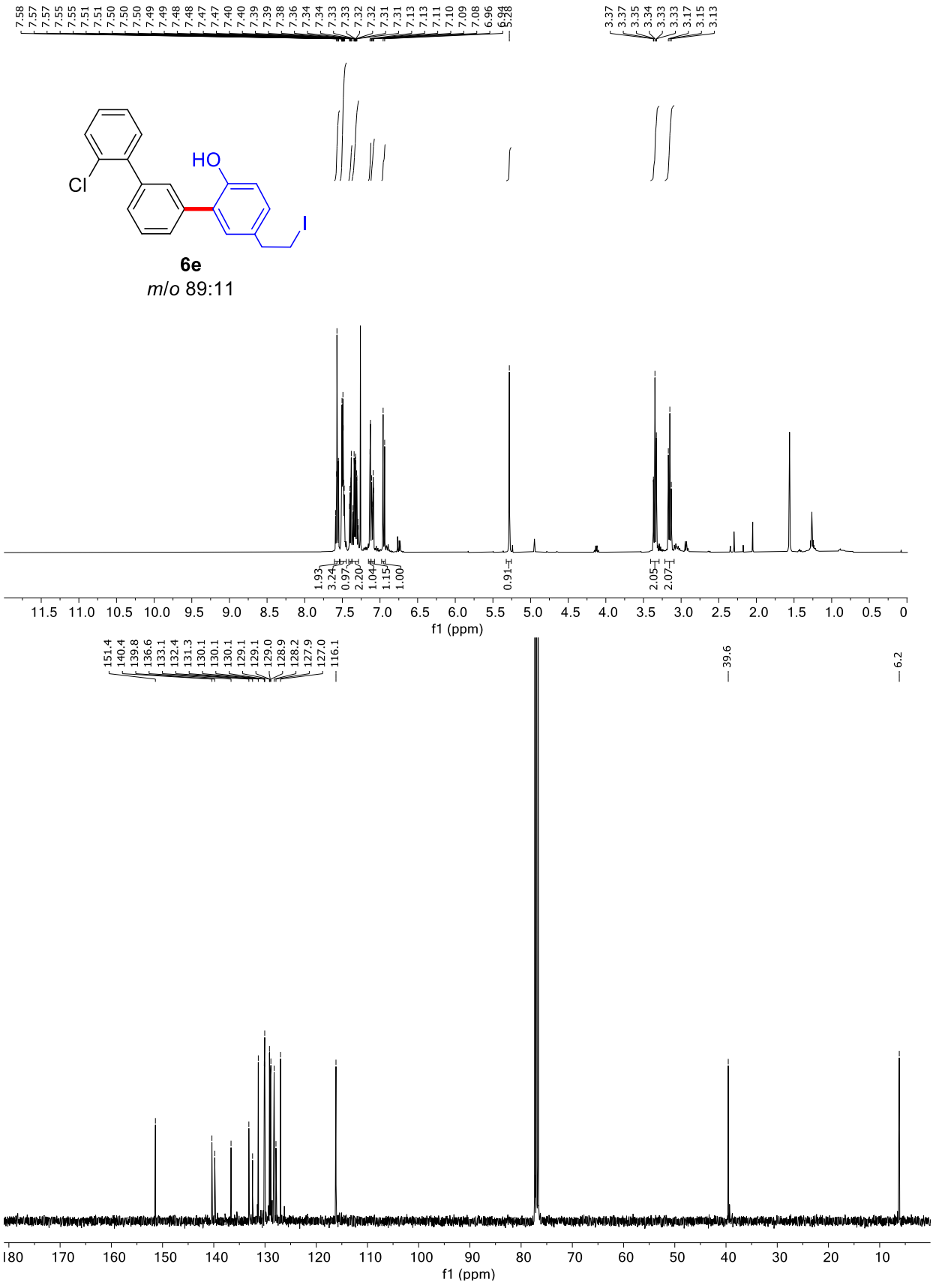

Cl
HO
Me
Me
Me
6b
m/o 92:8
f1 (ppm)
f1 (ppm)
f1 (ppm)


Cl
HO
Me
6c
m/o 94:6
f1 (ppm)



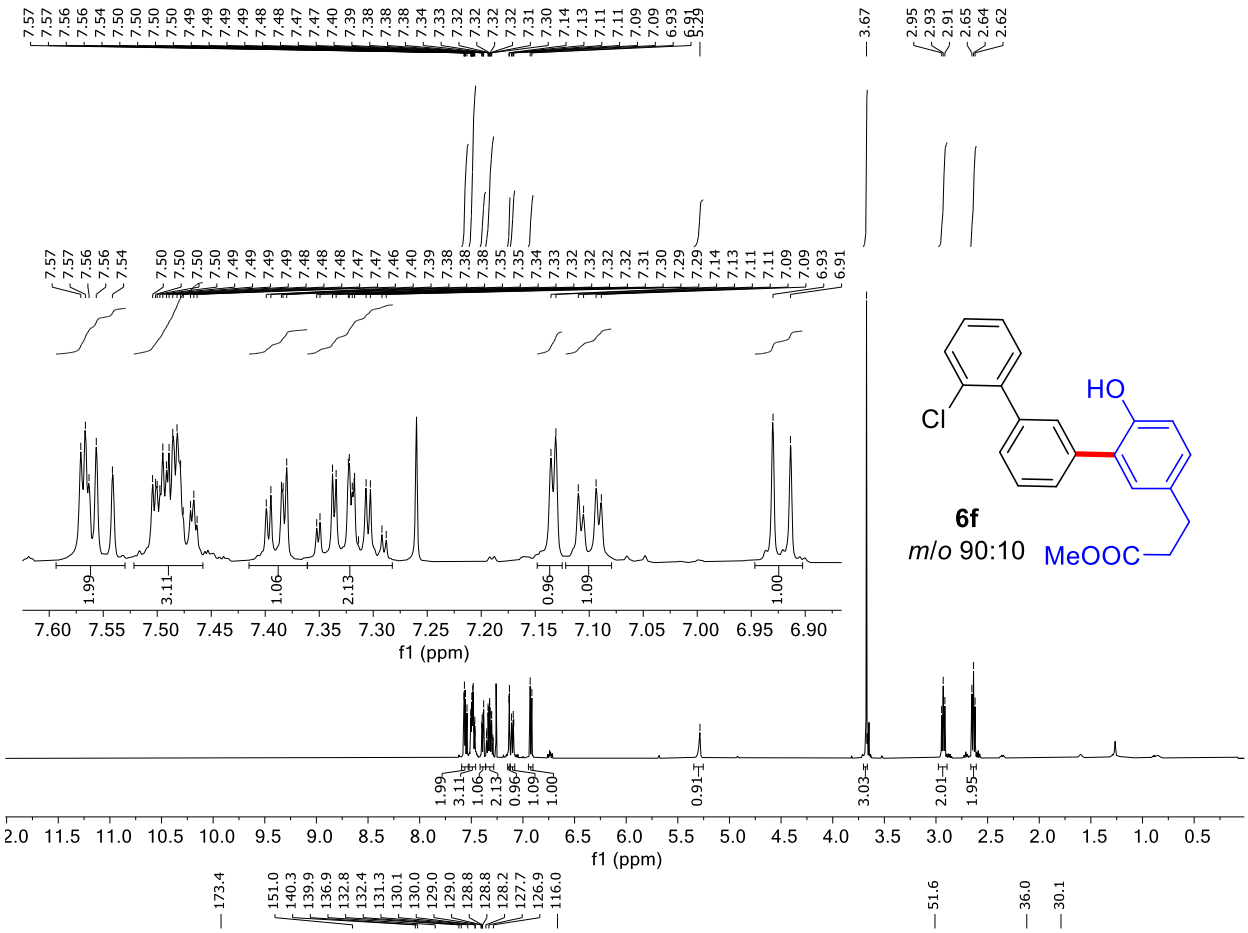
6d
m/o 92:8

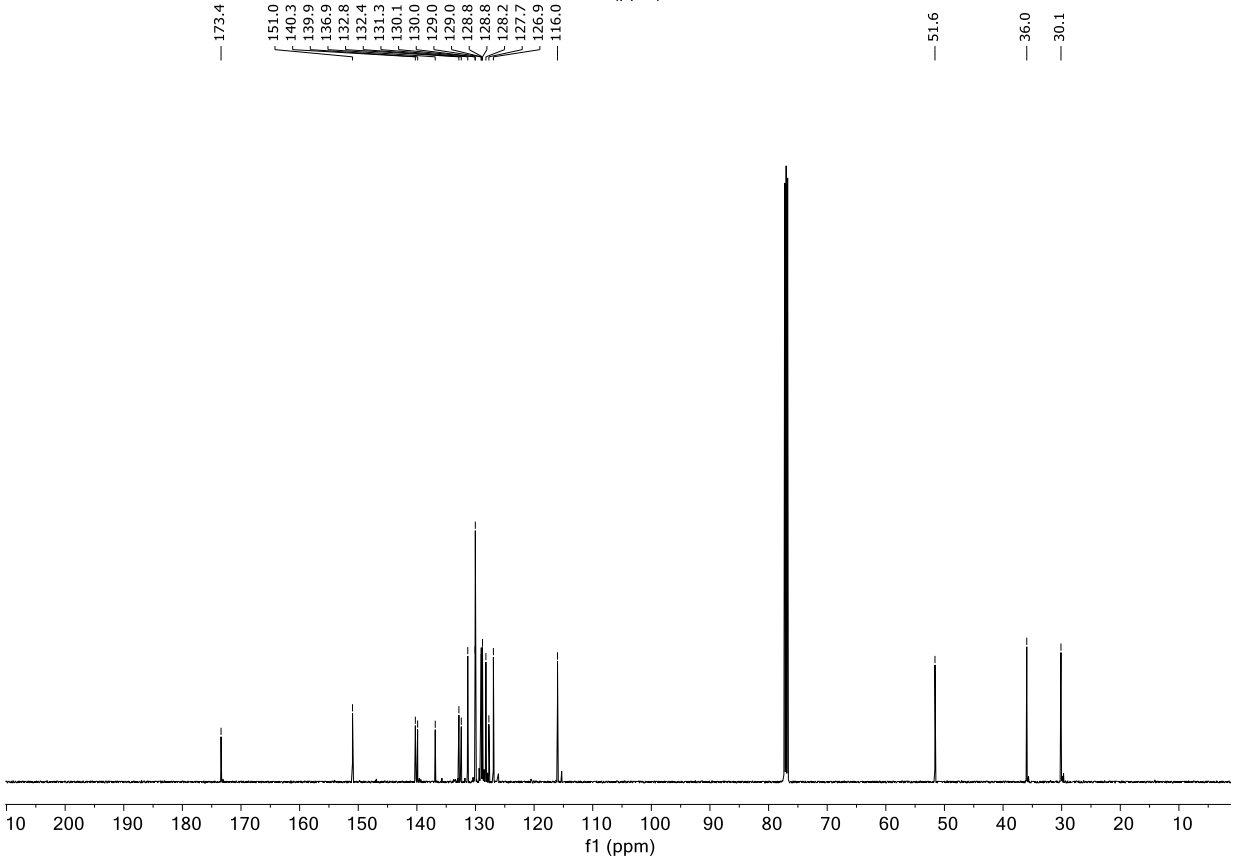


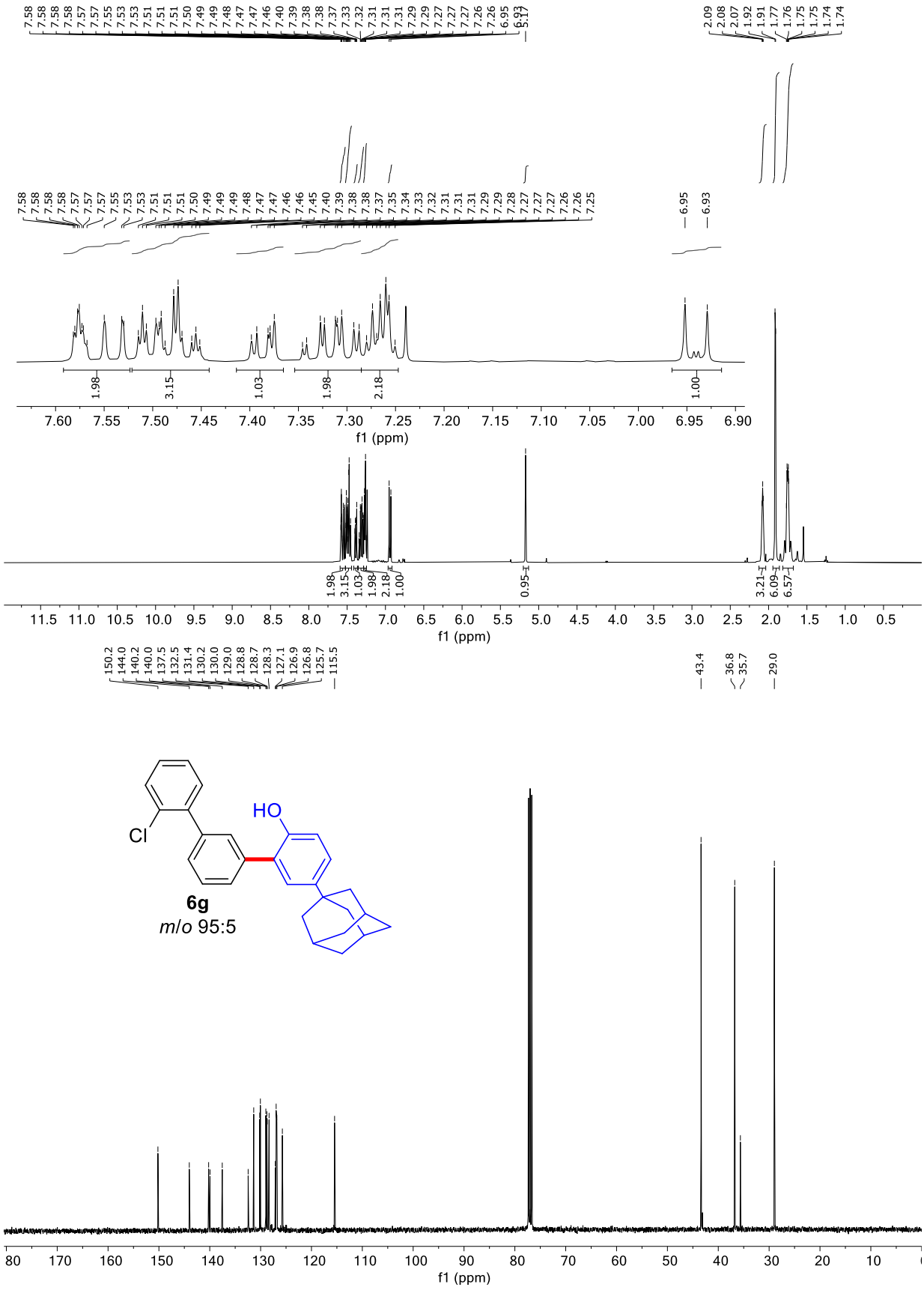


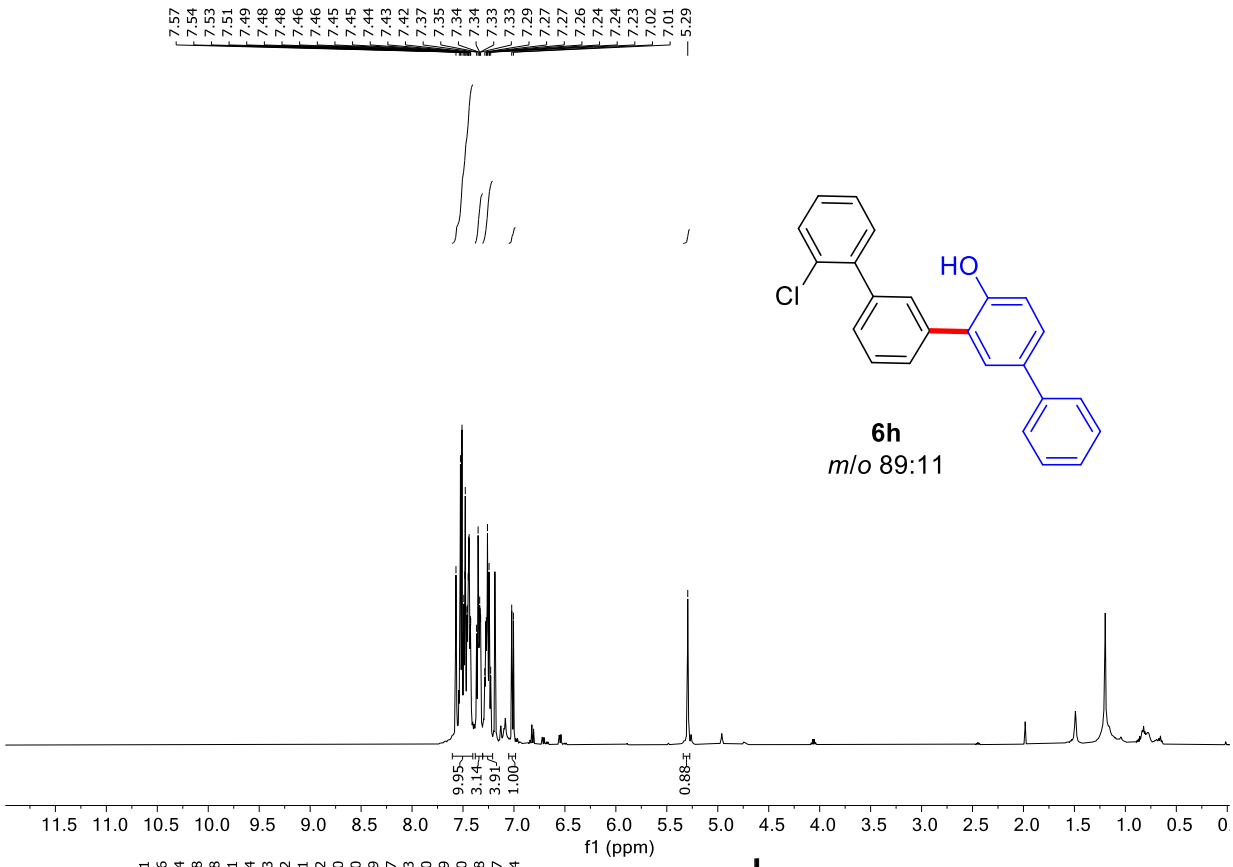
6e

m/o 89:11


Cl
HO
MeOOC
6f
m/o 90:10
f1 (ppm)

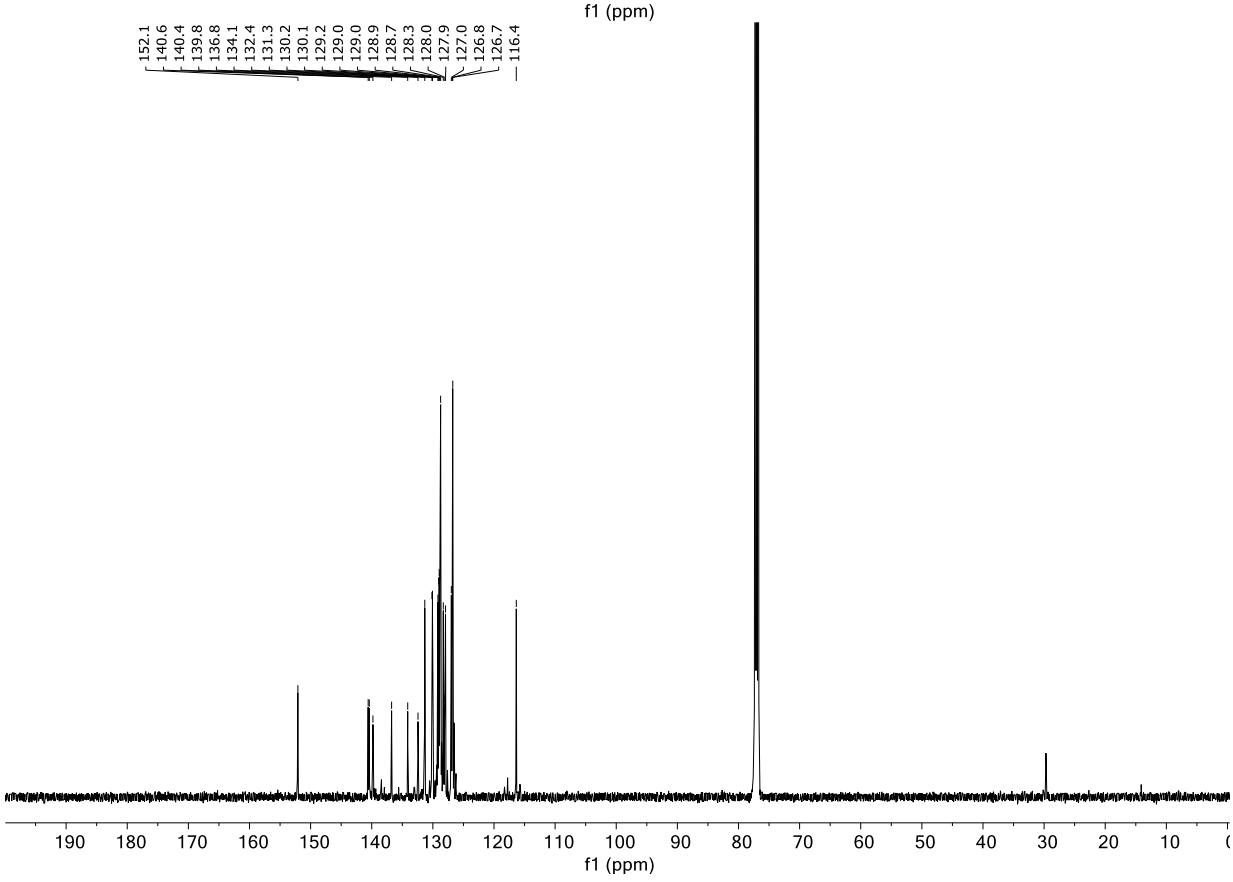

f1 (ppm)

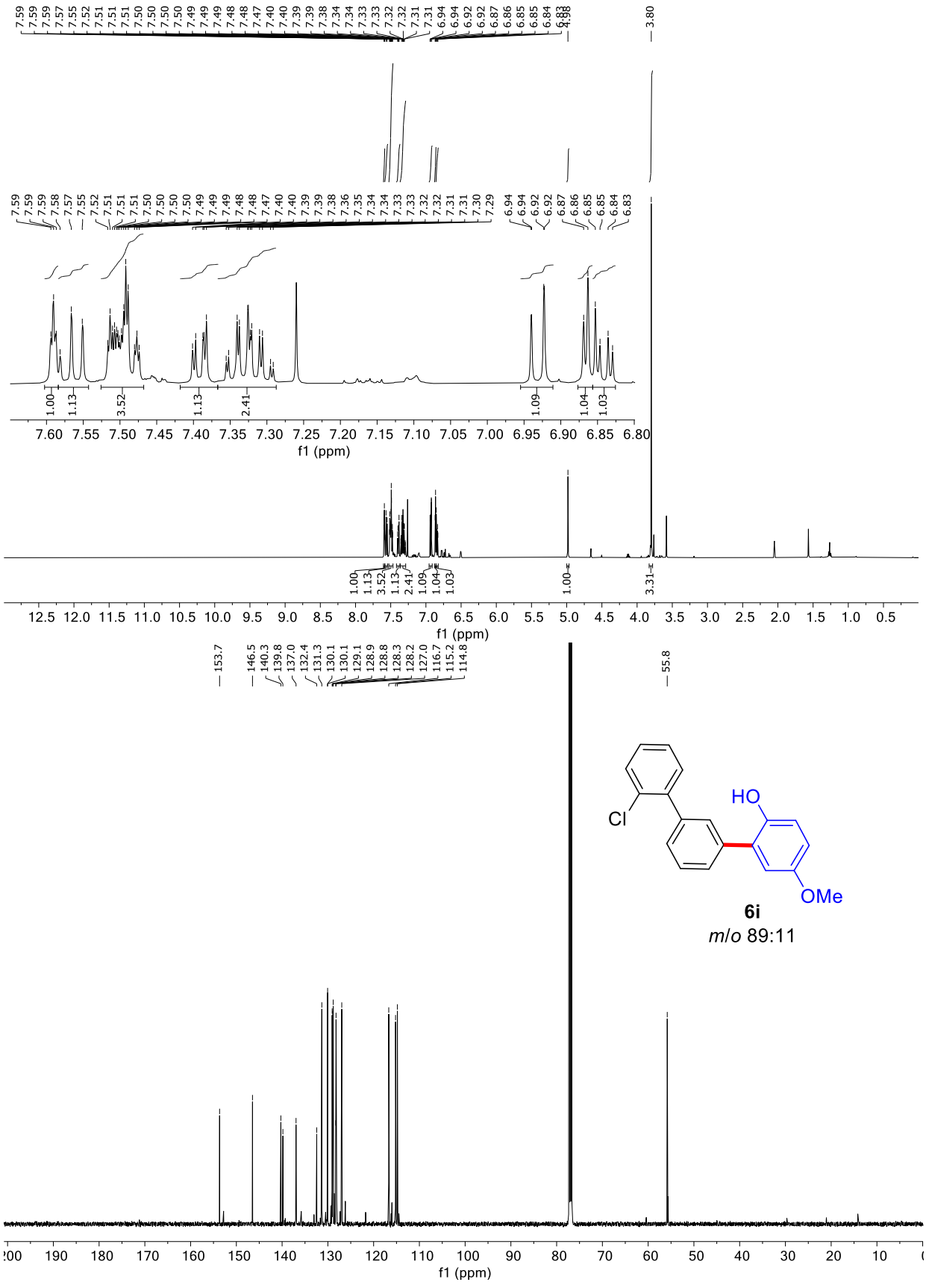

HO
Cl
6g
m/o 95:5
f1 (ppm)


7.57
7.54
7.53
7.51
7.49
7.48
7.48
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.37
7.35
7.34
7.34
7.33
7.33
7.29
7.27
7.27
7.26
7.24
7.24
7.23
7.02
7.01
5.29
Cl
HO
9.95
3.14
3.91
1.00
0.88
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

6h

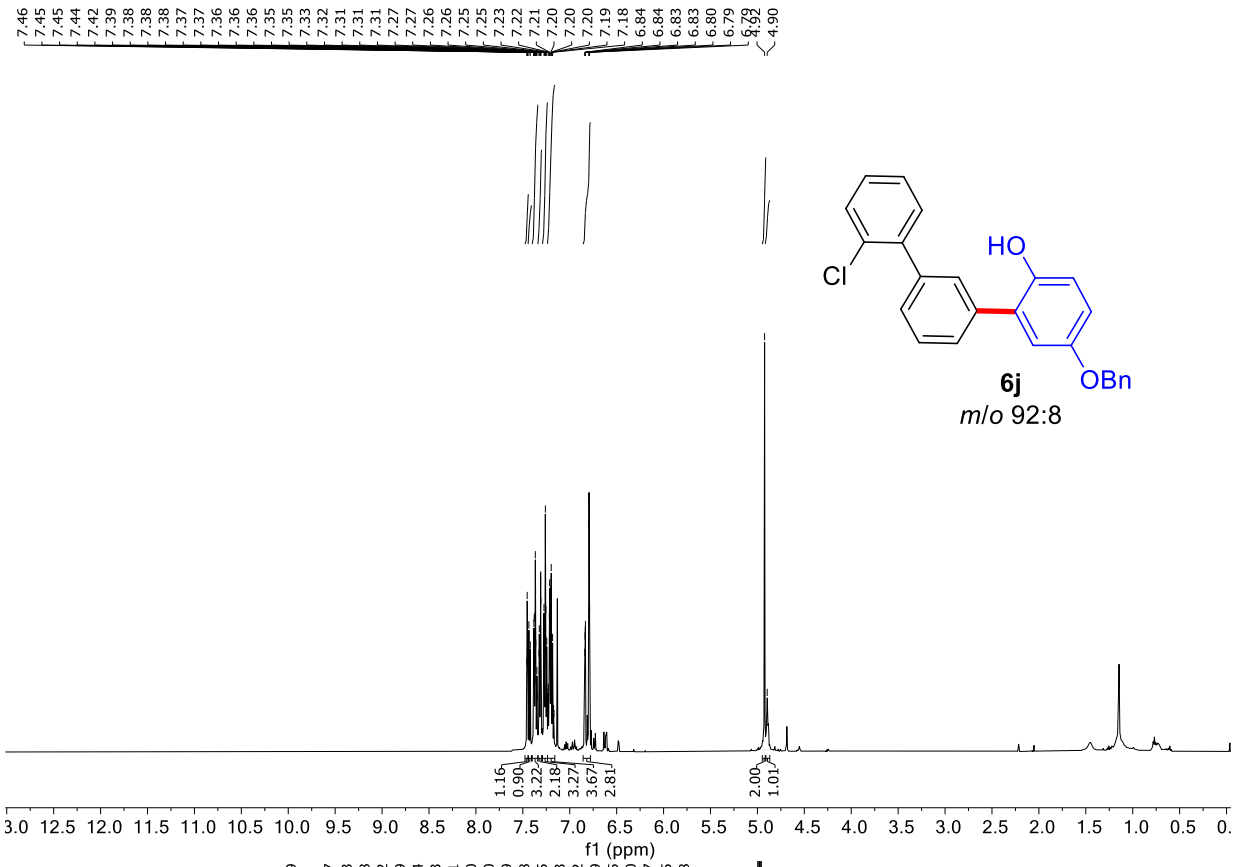
m/o 89:11

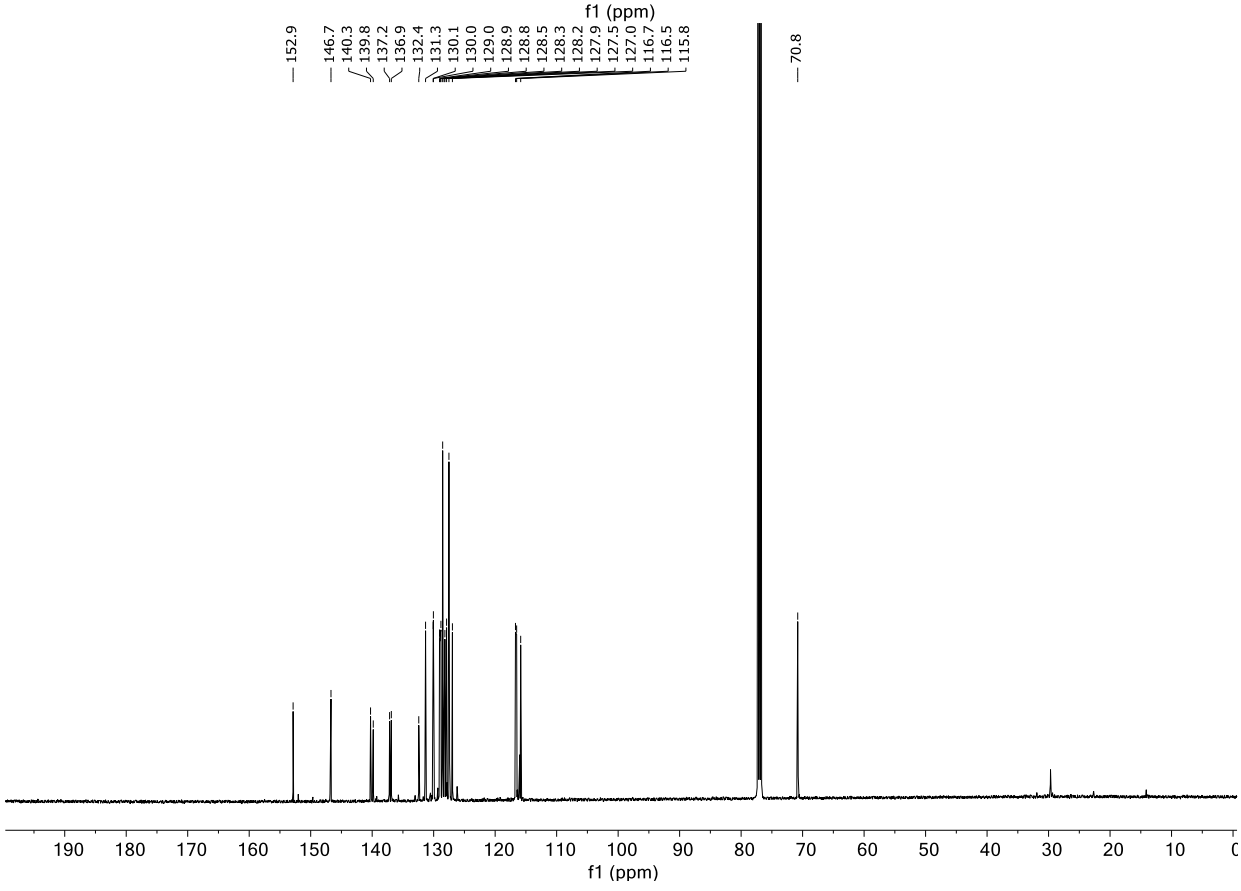

152.1
140.6
140.4
139.8
136.8
134.1
132.4
131.3
130.2
130.1
129.2
129.0
129.0
129.0
128.9
128.7
128.3
128.0
127.9
127.0
126.8
126.7
116.4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

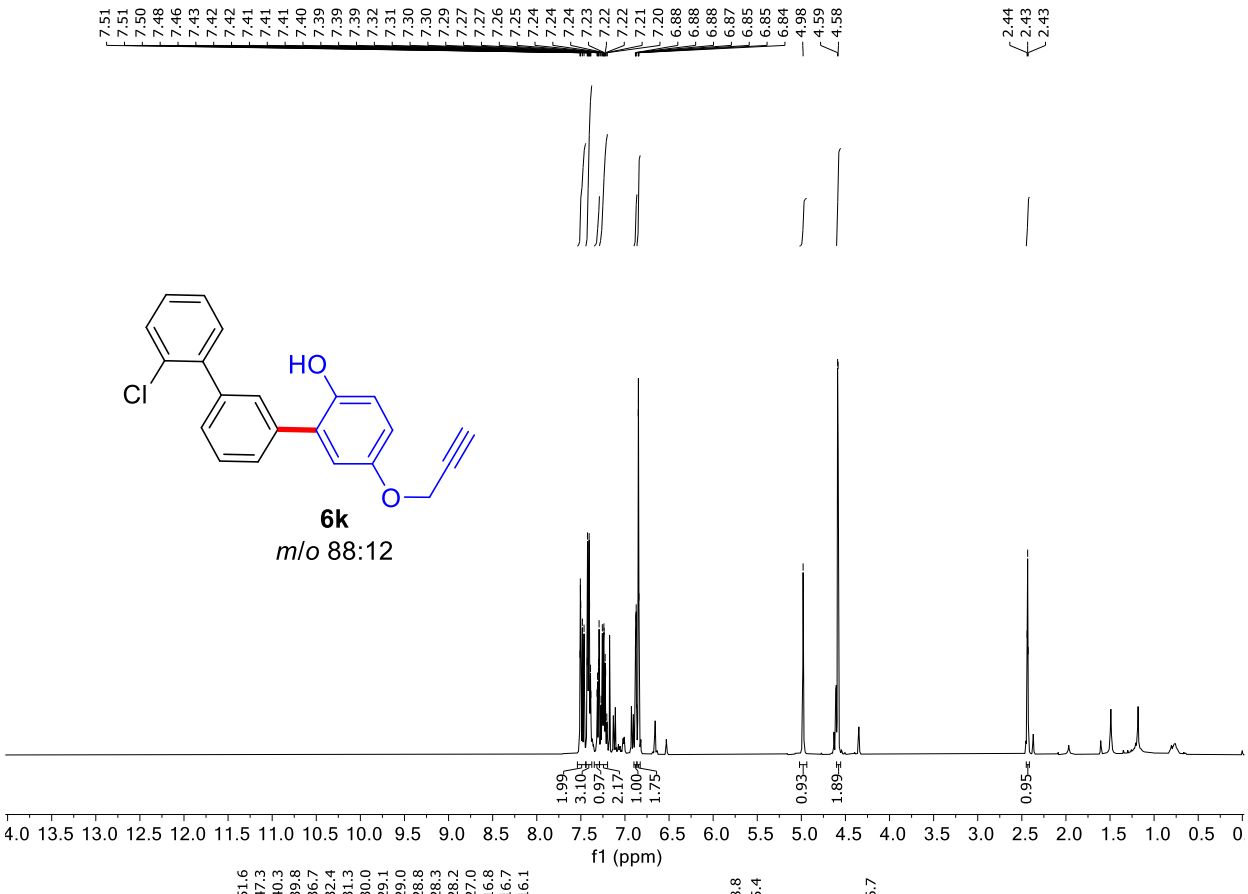


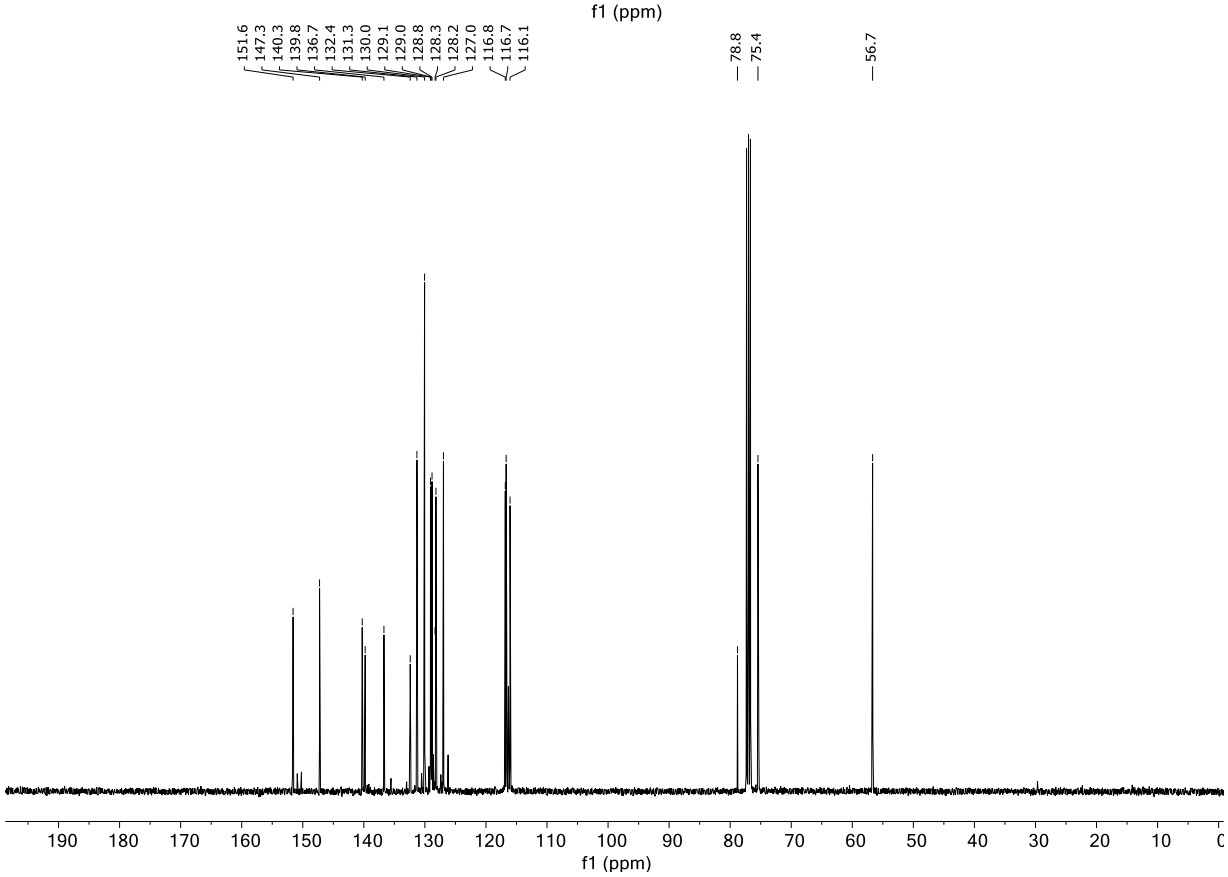
6i

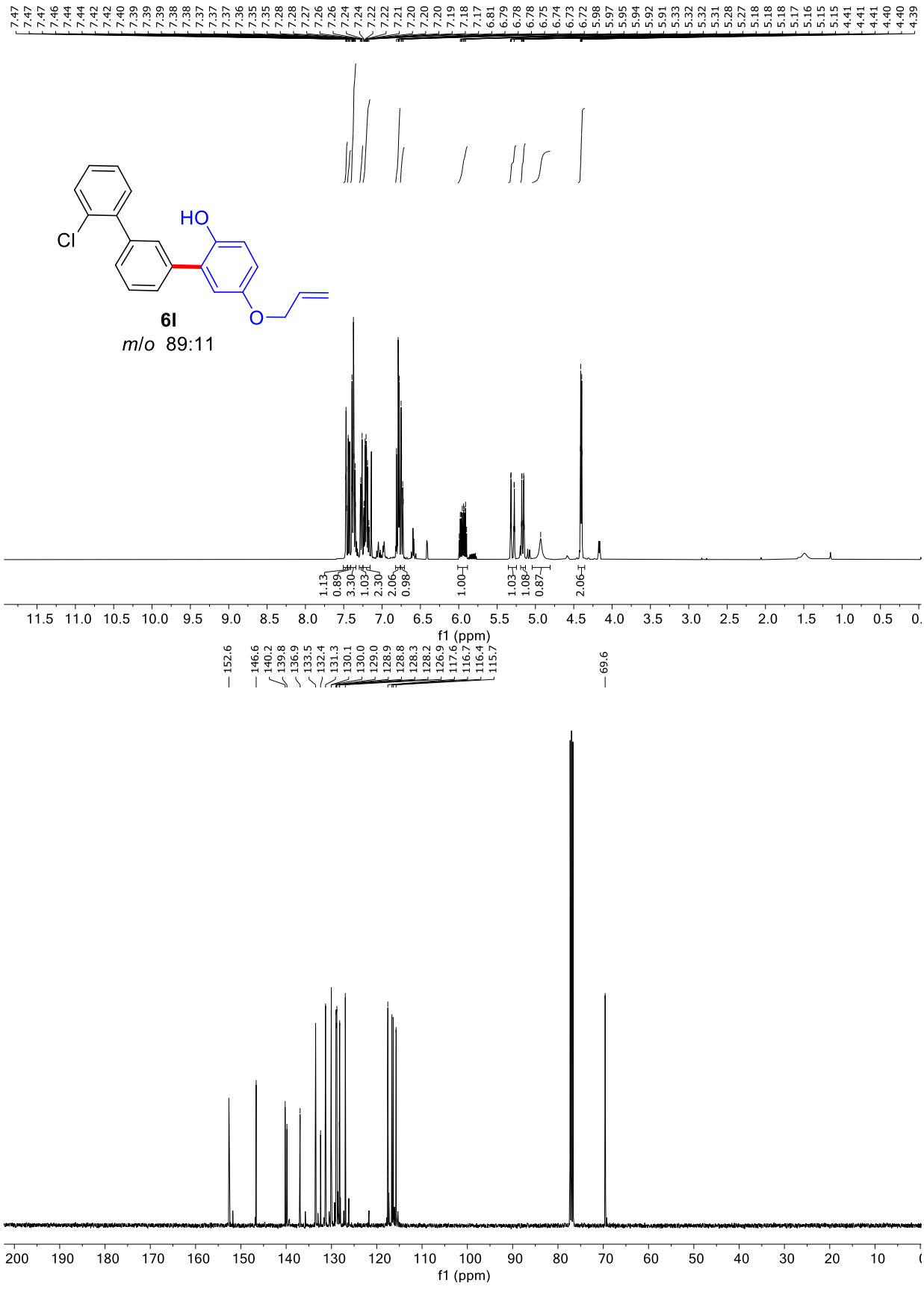
m/o 89:11

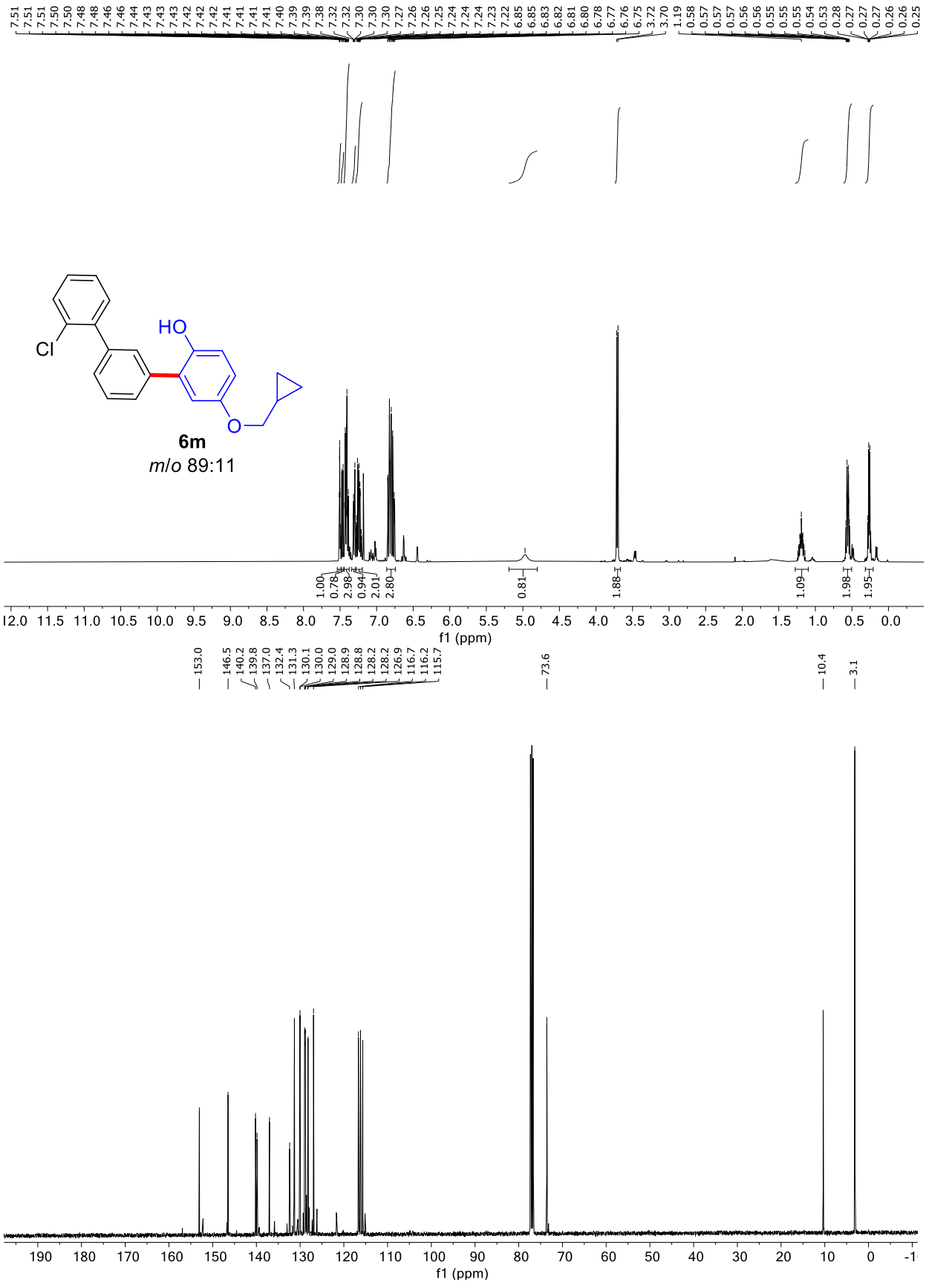

7.46 7.45 7.45 7.44 7.42 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.33 7.32 7.31 7.31 7.31 7.27 7.27 7.26 7.26 7.25 7.25 7.23 7.22 7.21 7.20 7.20 7.20 7.19 7.18 6.84 6.84 6.83 6.83 6.80 6.79 6.79 4.92 4.90
1.16 0.90 3.22 2.18 3.27 3.67 2.81 2.00 1.01
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)
Cl
HO
OBn
6j
m/o 92:8

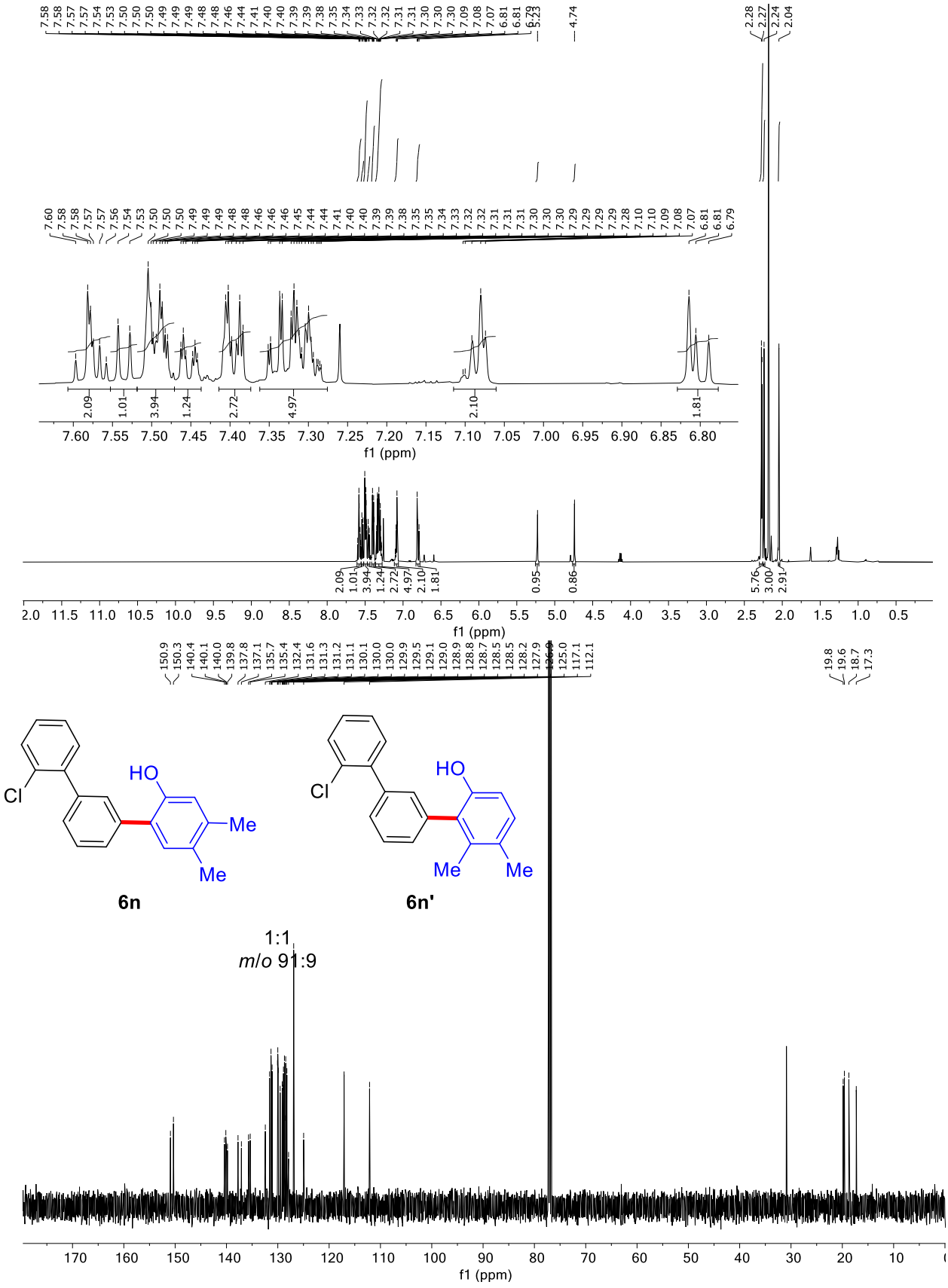

152.9 146.7 140.3 139.8 137.2 136.9 132.4 131.3 130.1 130.0 129.0 128.9 128.8 128.5 128.3 128.2 127.9 127.5 127.0 116.7 116.5 115.8 70.8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

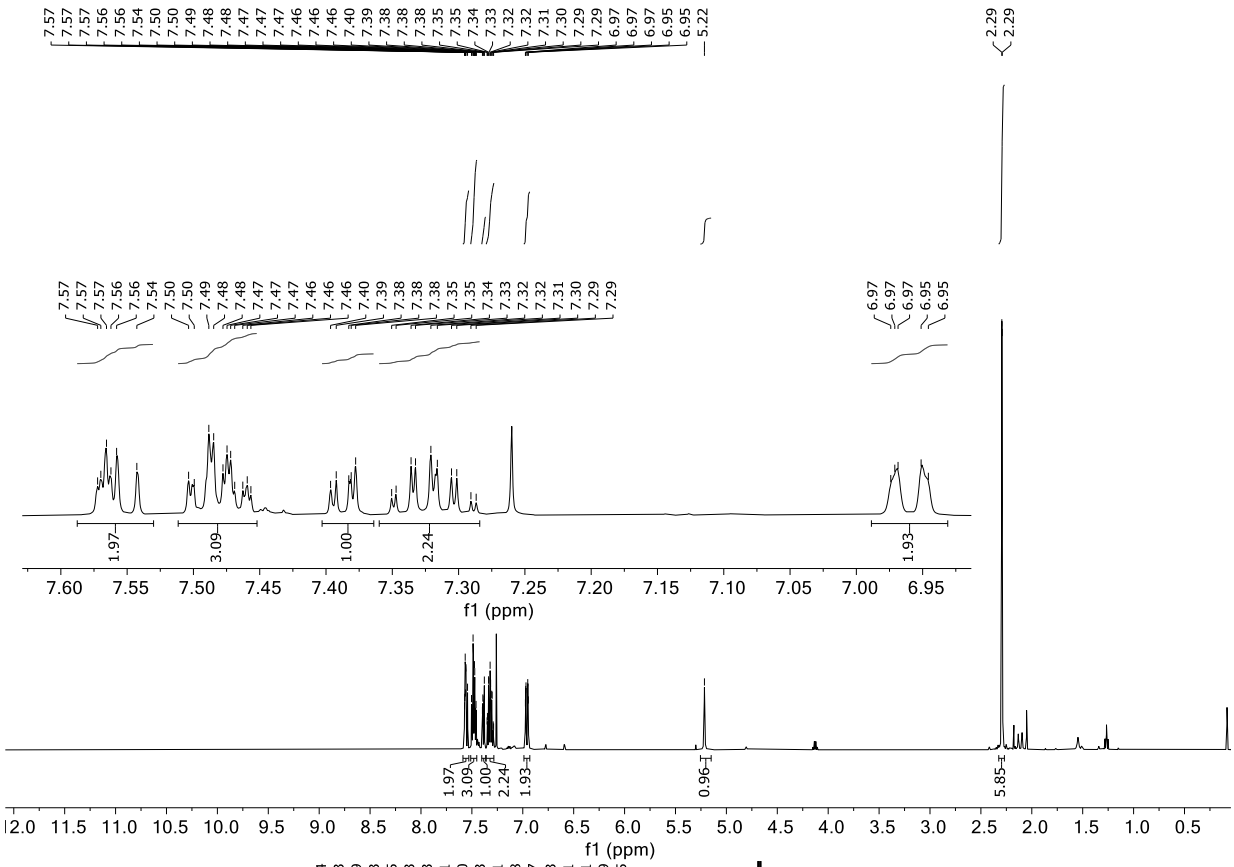

7.51
7.51
7.50
7.48
7.46
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.39
7.39
7.39
7.32
7.31
7.30
7.30
7.29
7.27
7.27
7.26
7.25
7.24
7.24
7.24
7.23
7.22
7.22
7.21
7.20
6.88
6.88
6.88
6.87
6.85
6.85
6.84
4.98
4.59
4.58
2.44
2.43
2.43
HO
Cl
O
6k
m/o 88:12
1.99
3.10
0.97
2.17
1.00
1.75
0.93
1.89
0.95
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

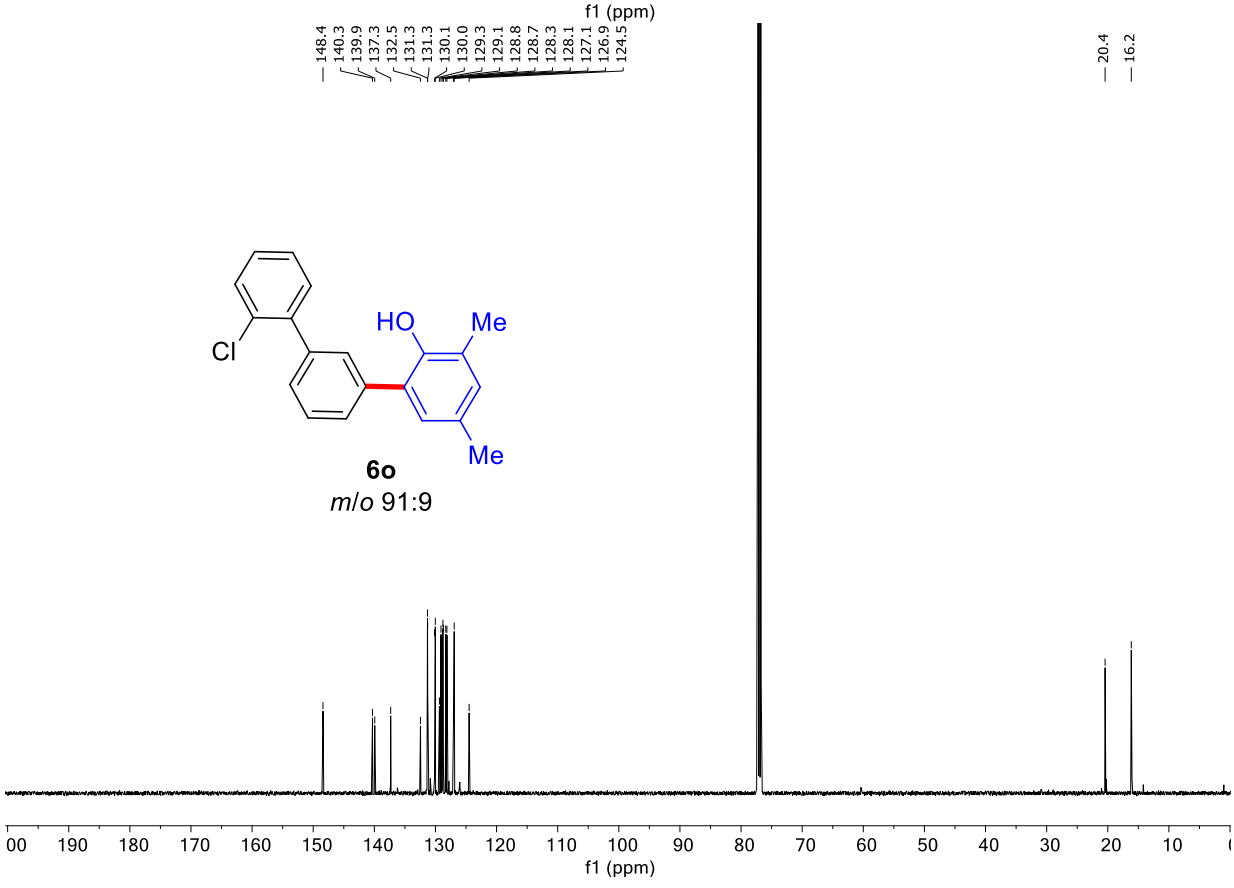

151.6
147.3
140.3
139.8
136.7
132.4
131.3
130.0
129.1
129.0
128.8
128.3
128.2
127.0
116.8
116.7
116.1
78.8
75.4
56.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


HO
Cl
O
6l
m/o 89:11
f1 (ppm)
f1 (ppm)


HO
Cl
O
6m
m/o 89:11
f1 (ppm)
f1 (ppm)

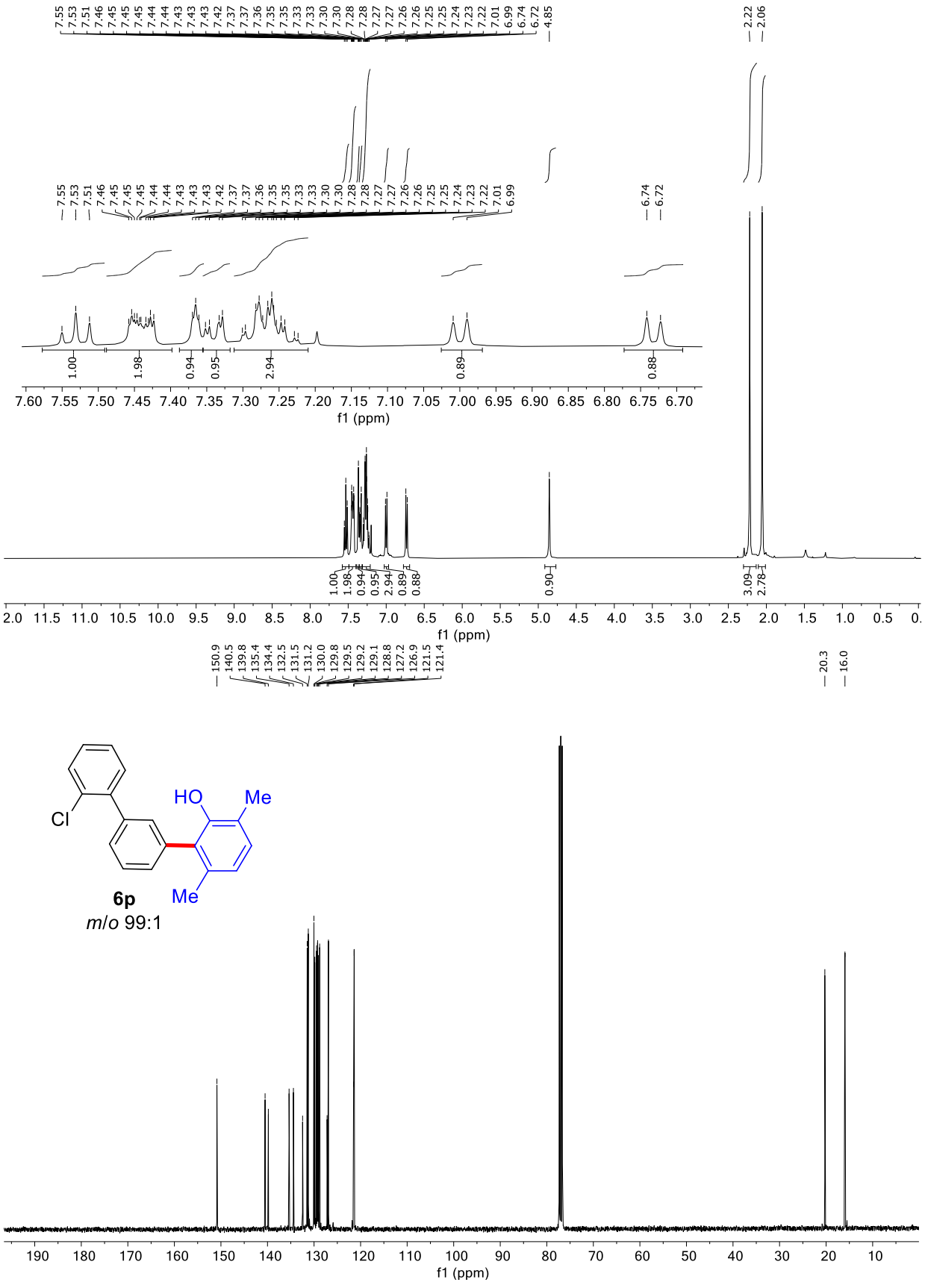

6n
6n'
1:1
m/o 91:9
f1 (ppm)

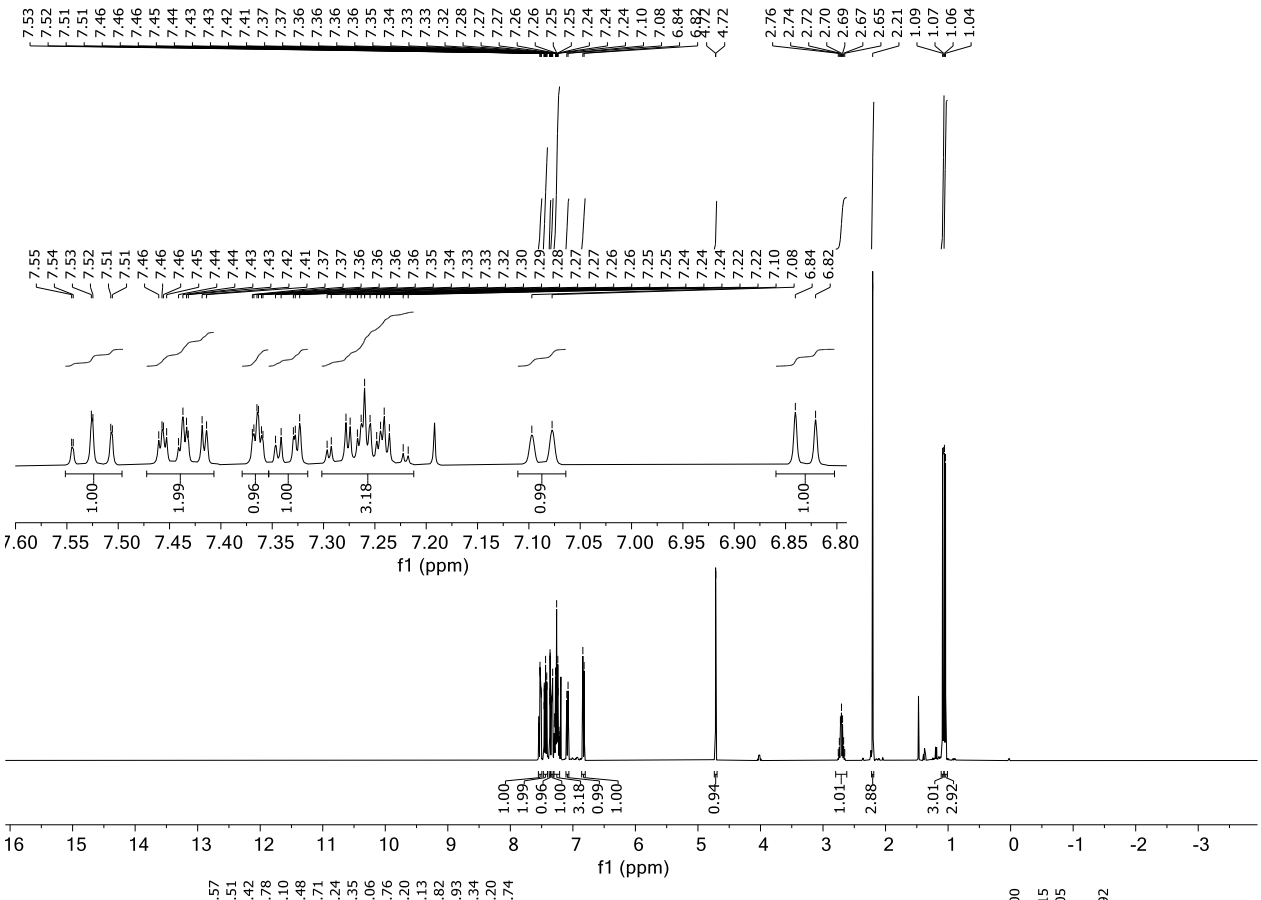


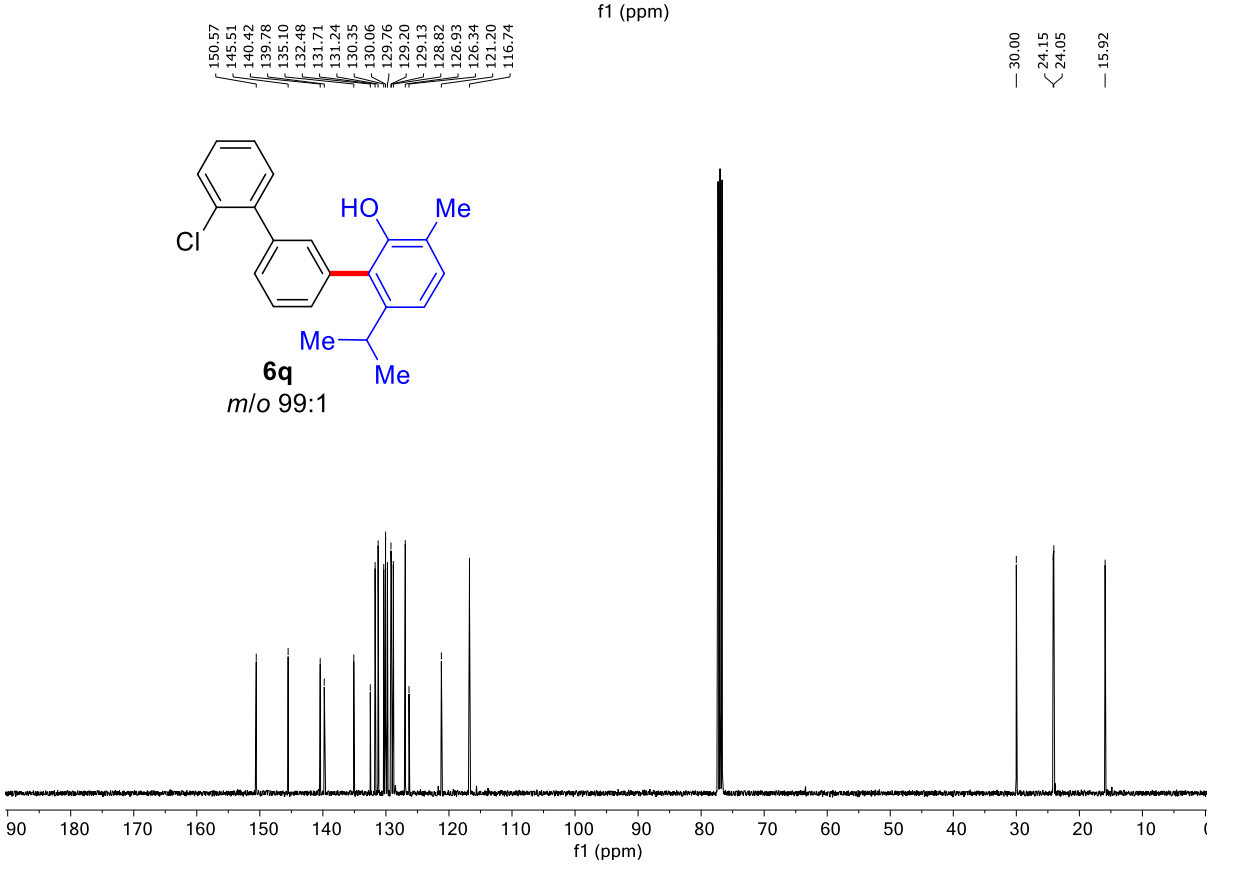


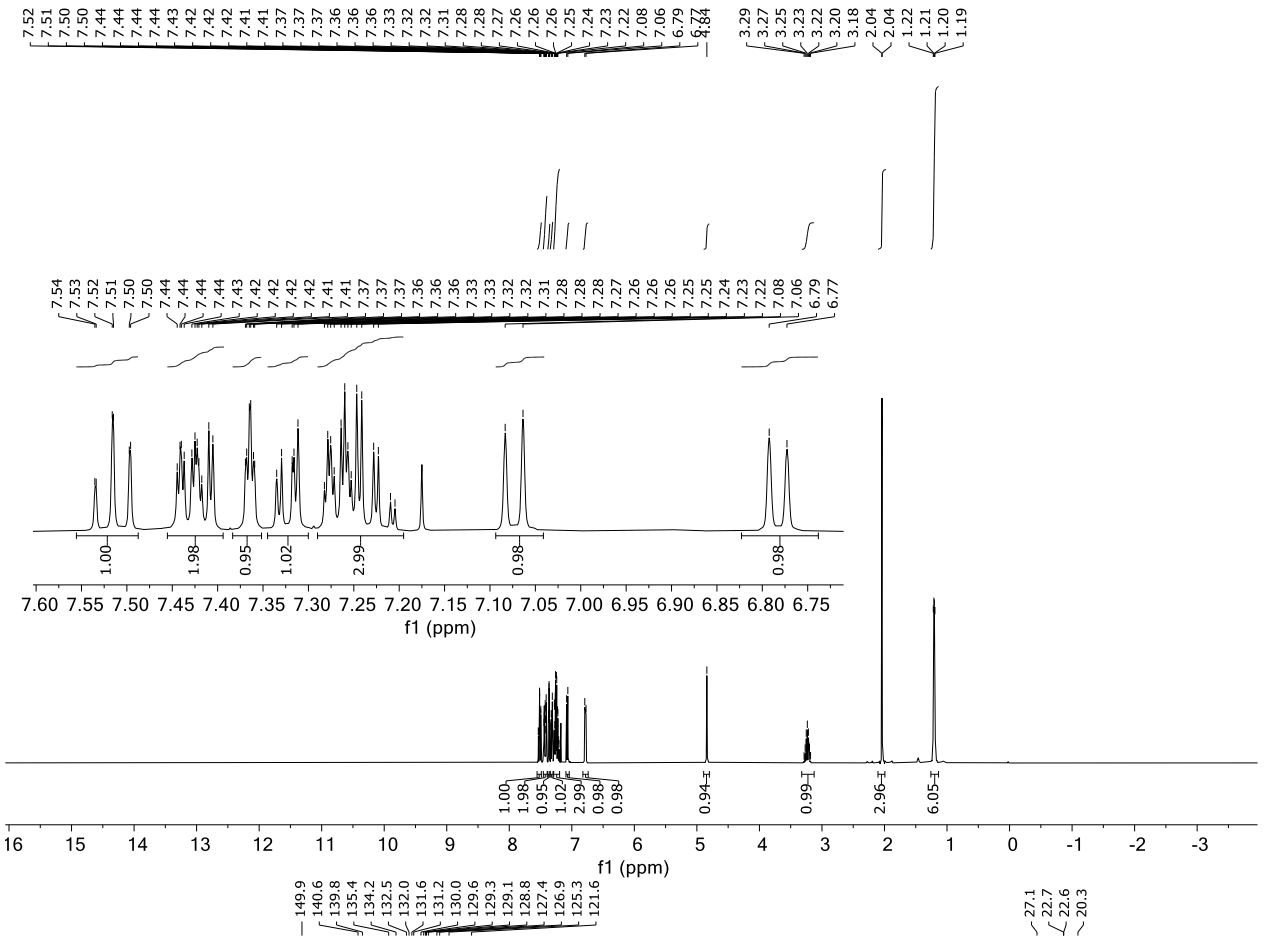
6o

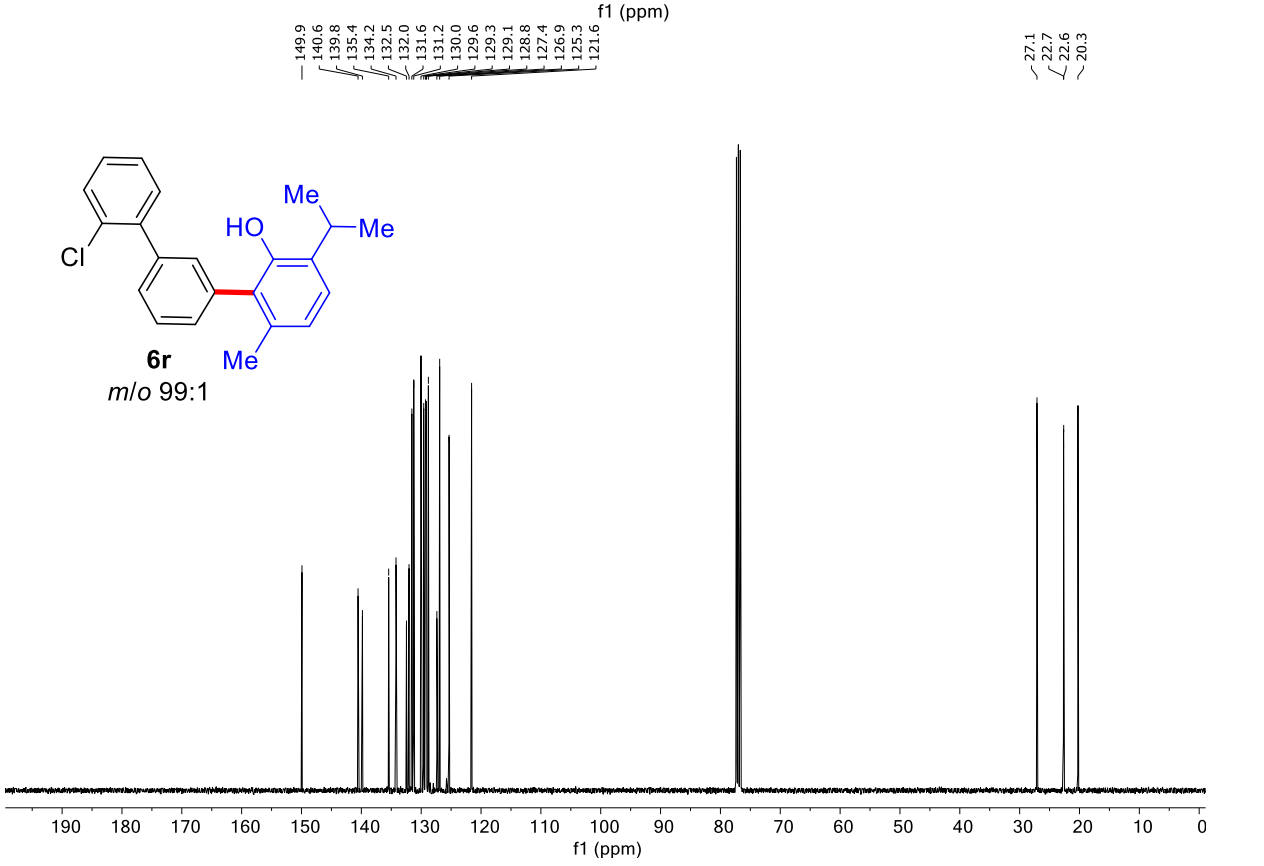
m/*o* 91:9

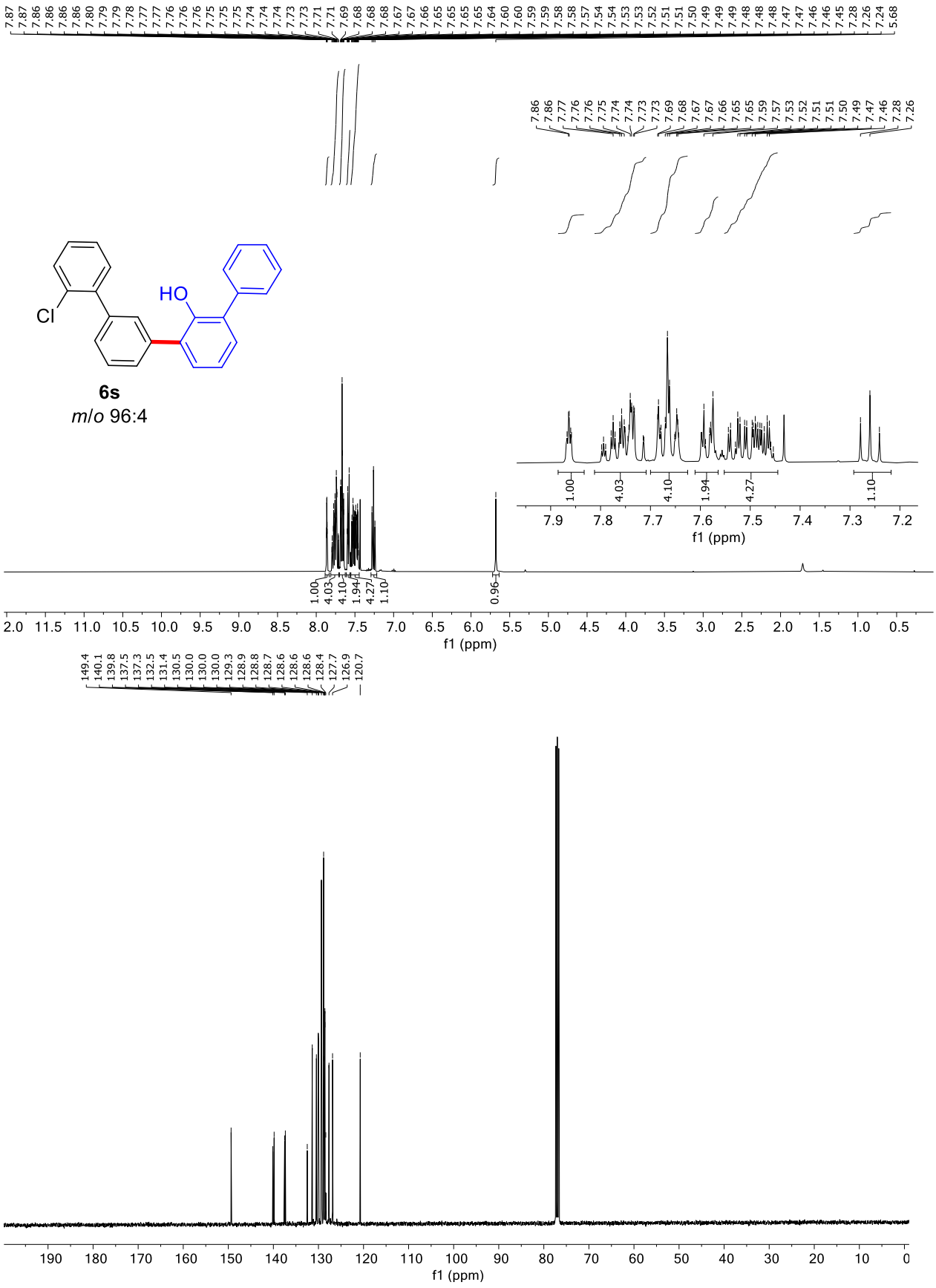

7.55 7.53 7.51 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.37 7.37 7.36 7.35 7.35 7.33 7.33 7.30 7.30 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.01 6.99 6.74 6.72 4.85
2.22 2.06
1.00 1.98 0.94 0.95 2.94 0.89 0.88
0.90
3.09 2.78
f1 (ppm)
150.9 140.5 139.8 135.4 134.4 132.5 131.5 131.2 130.0 129.8 129.5 129.2 129.1 128.8 127.2 126.9 121.5 121.4
20.3 16.0
Cl
HO
Me
Me
6p
m/o 99:1
f1 (ppm)


f1 (ppm)

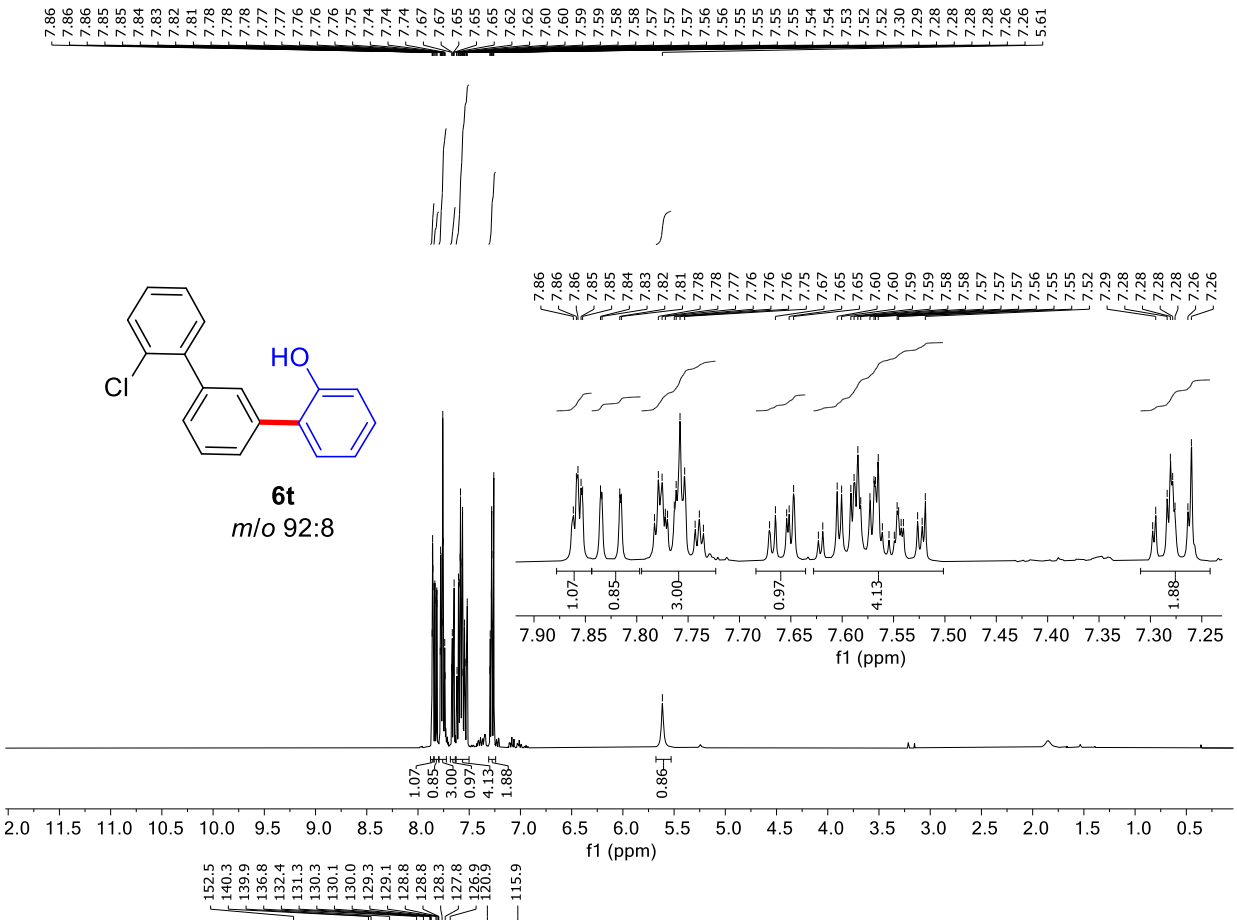

HO
Me
Cl
Me
Me
6q
m/o 99:1
f1 (ppm)

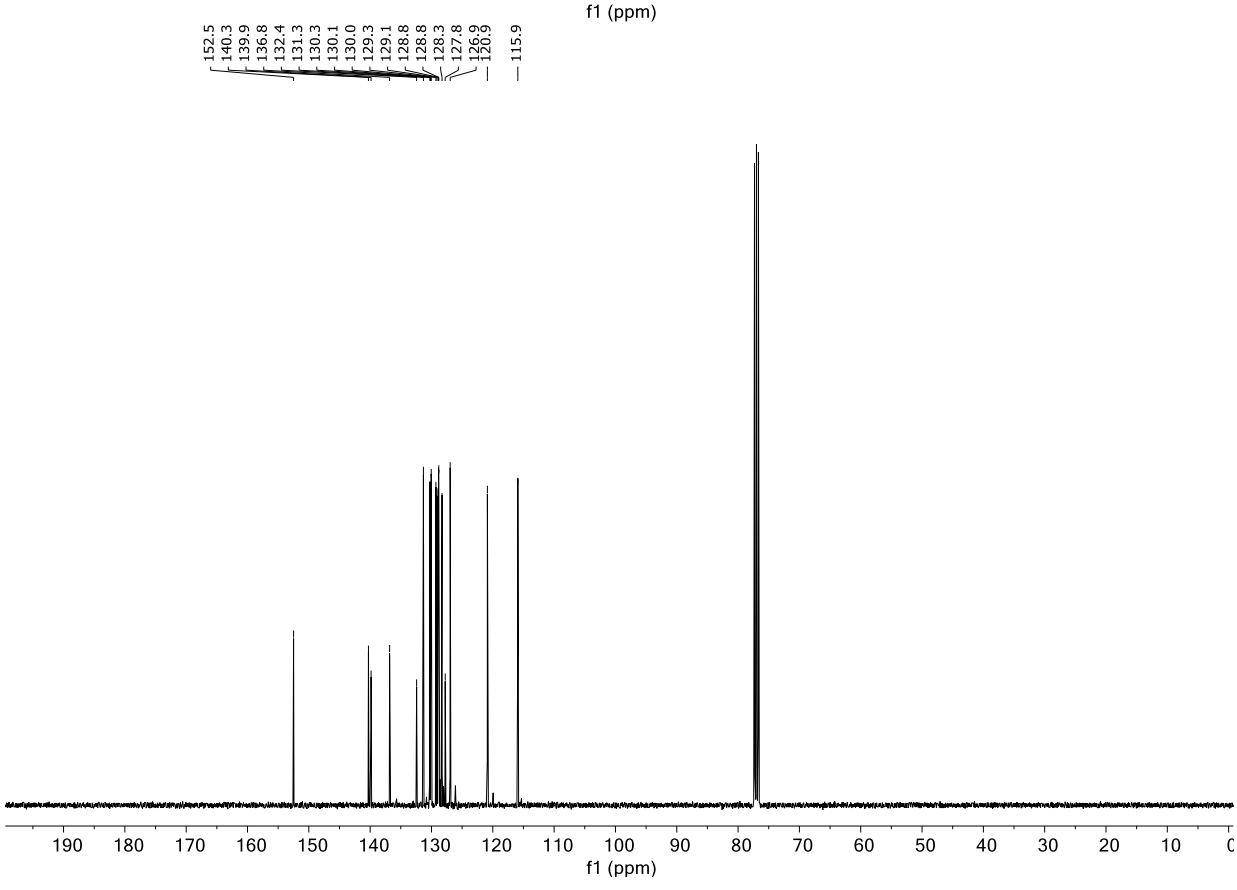

7.52 7.51 7.50 7.50 7.50 7.44 7.44 7.44 7.43 7.42 7.42 7.42 7.41 7.41 7.37 7.37 7.37 7.36 7.36 7.36 7.33 7.32 7.32 7.31 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.08 7.06 6.79 6.77 4.84
3.29 3.27 3.25 3.23 3.22 3.20 3.18 2.04 2.04 1.22 1.21 1.20 1.19
1.00 1.98 0.95 1.02 2.99 0.98 0.98
0.94 0.99 2.96 6.05
f1 (ppm)

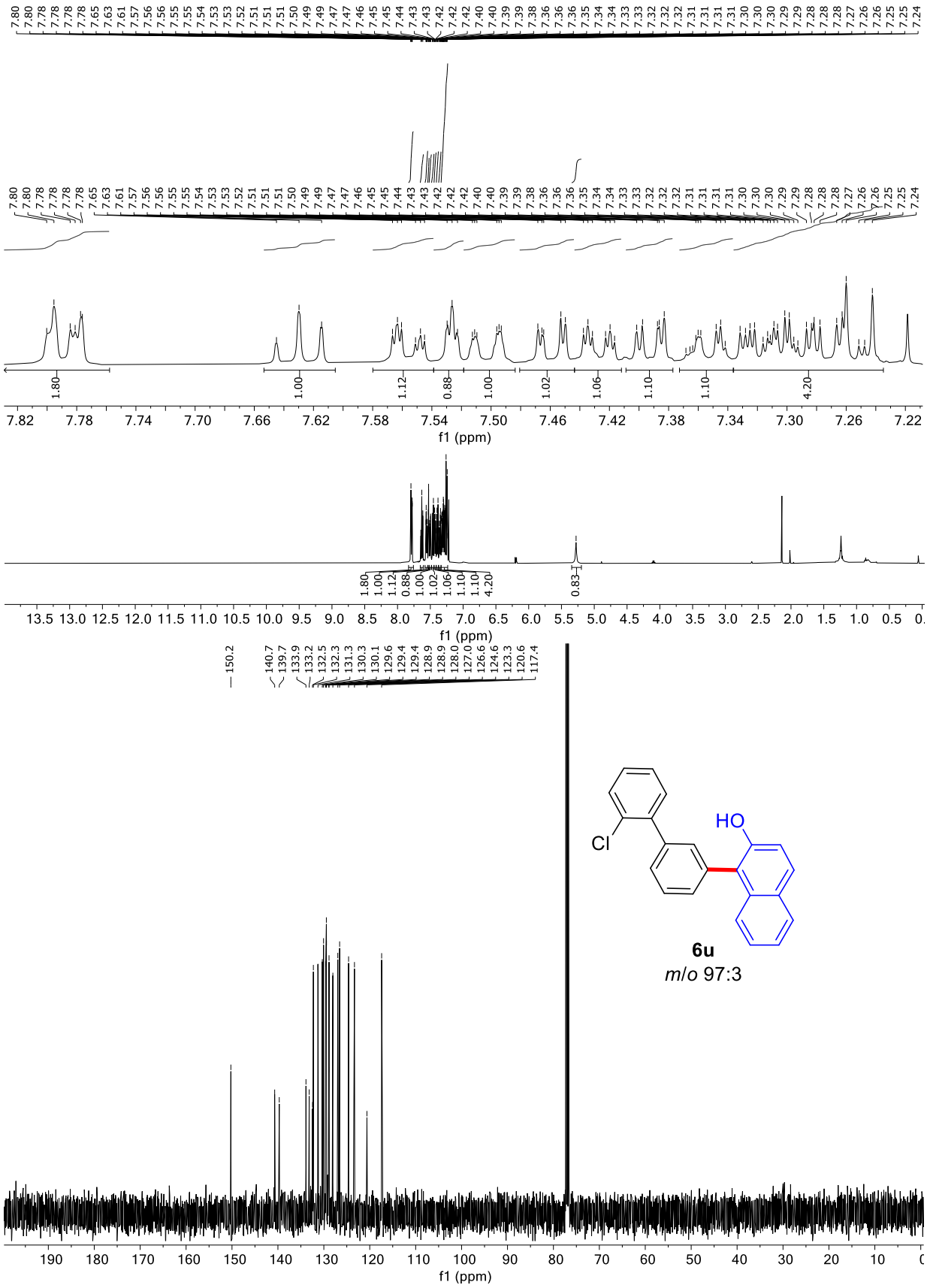

149.9 140.6 139.8 135.4 134.2 132.5 132.0 131.6 131.2 130.0 129.6 129.3 129.1 128.8 127.4 126.9 125.3 121.6
27.1 22.7 22.6 20.3
Cl
HO
Me
Me
Me
6r
m/o 99:1
f1 (ppm)


HO
Cl
6s
m/o 96:4
f1 (ppm)

f1 (ppm)

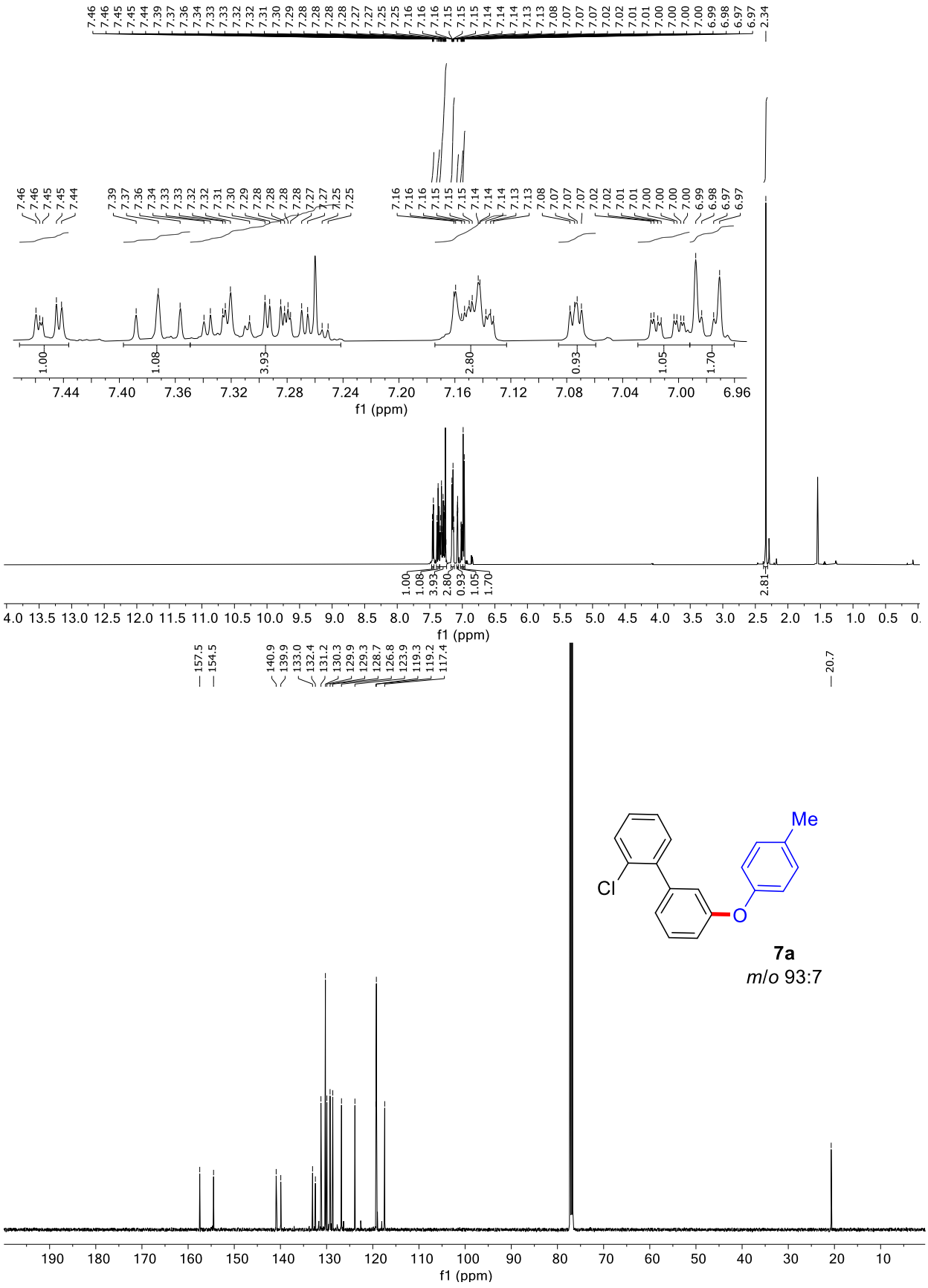

HO
Cl
6t
m/o 92:8
f1 (ppm)

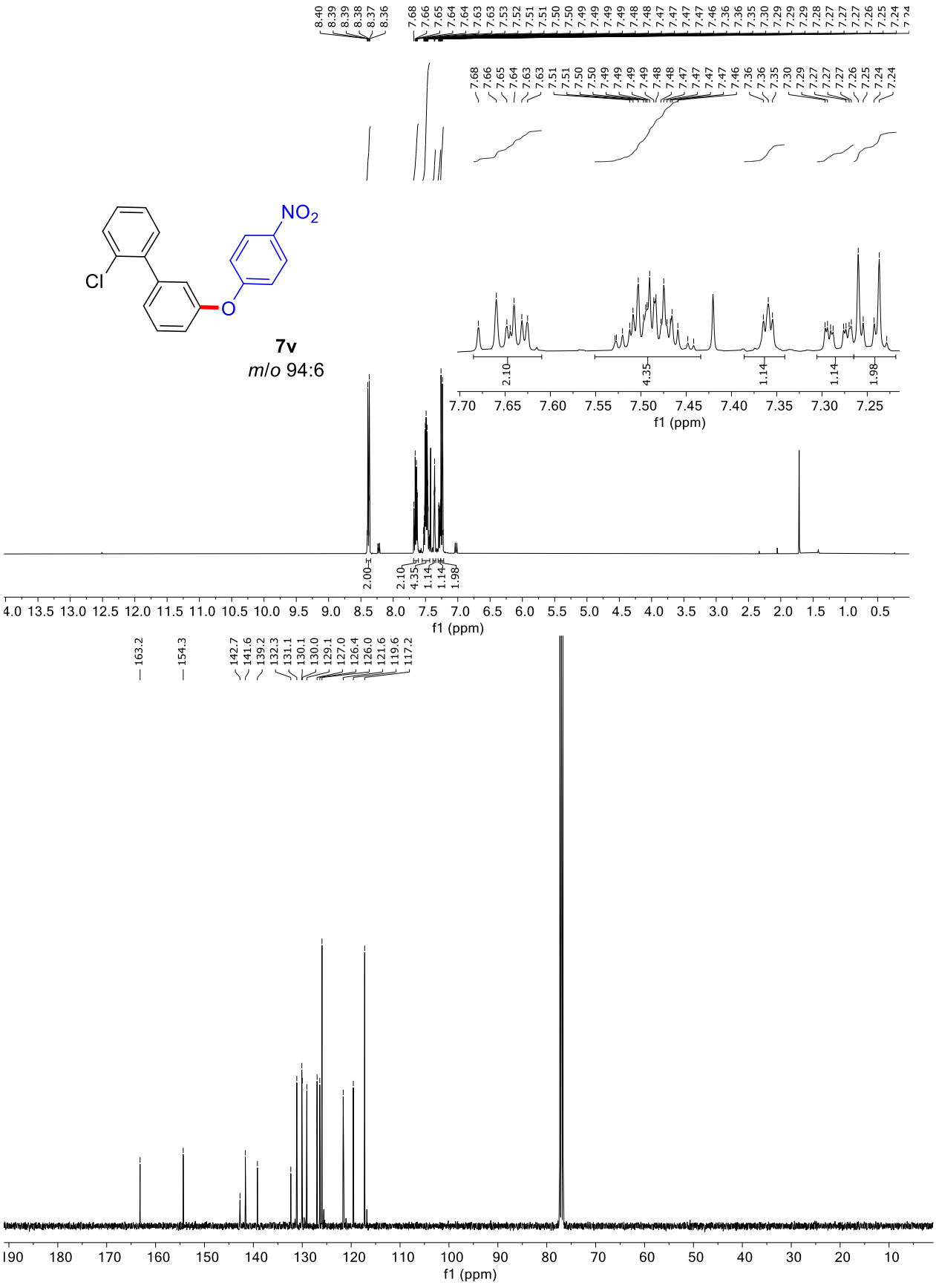

f1 (ppm)

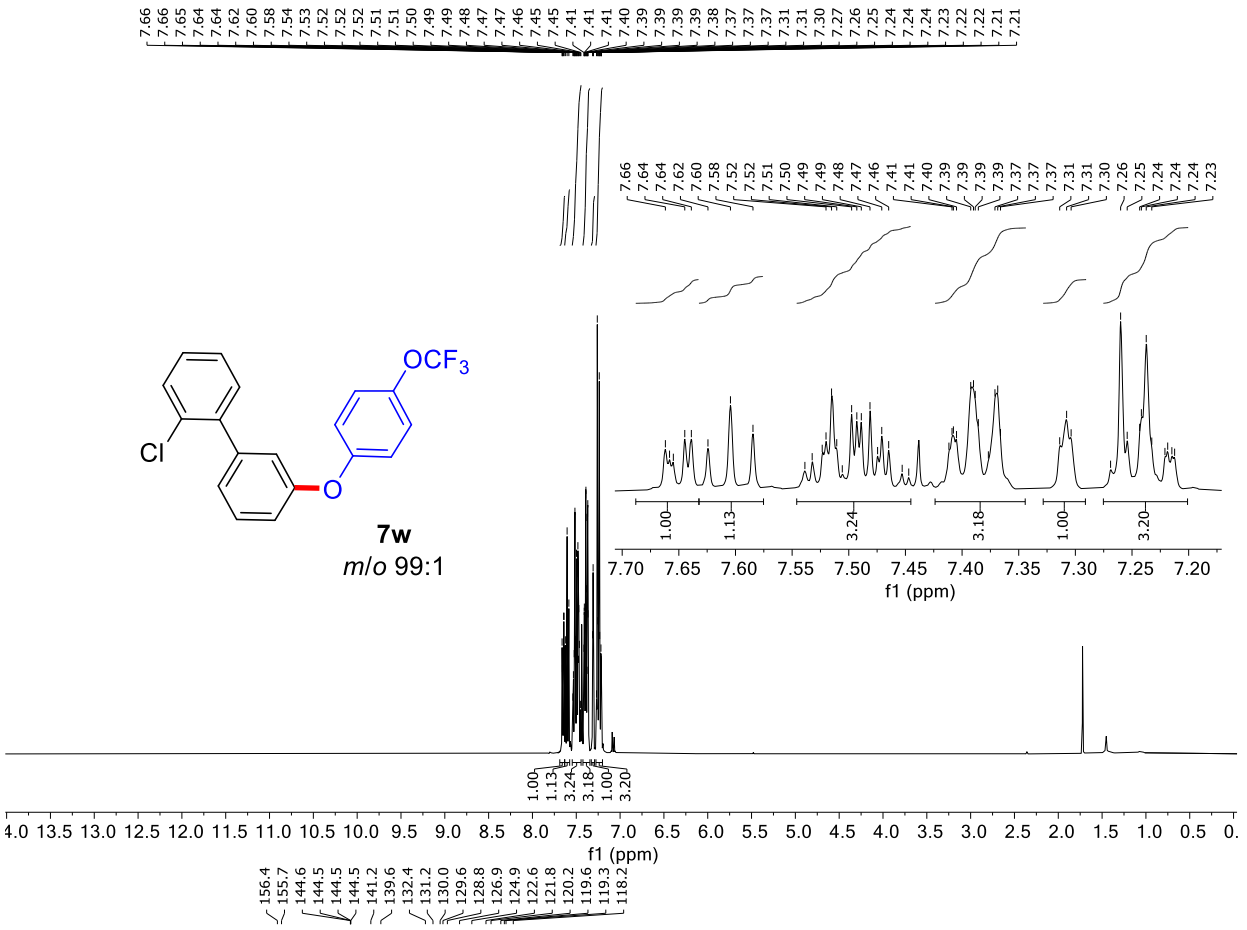


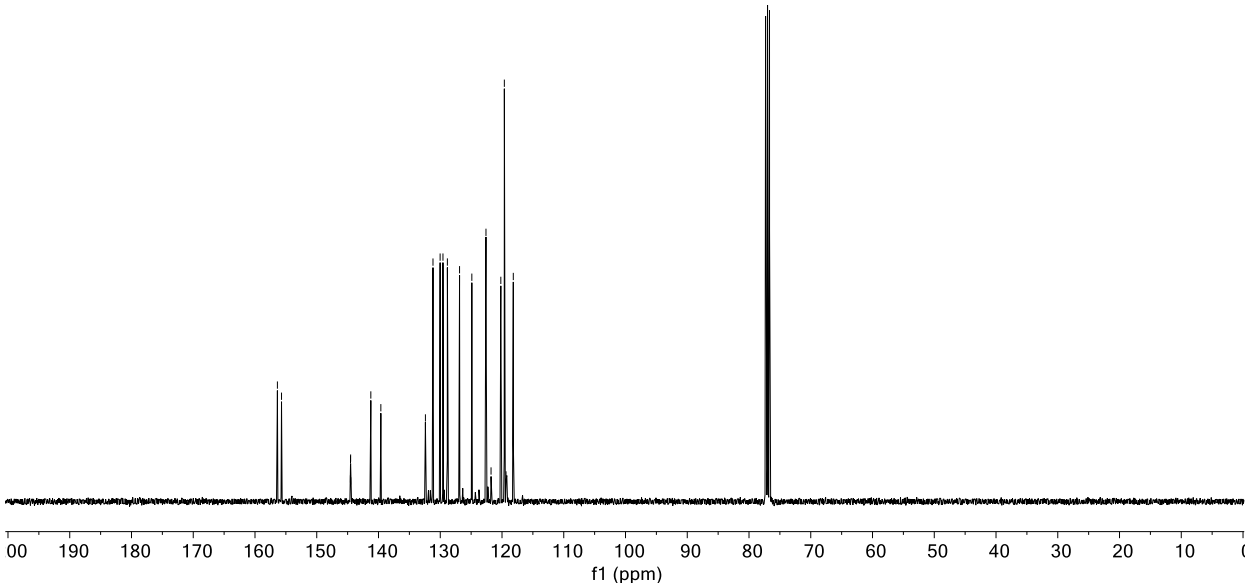
6u

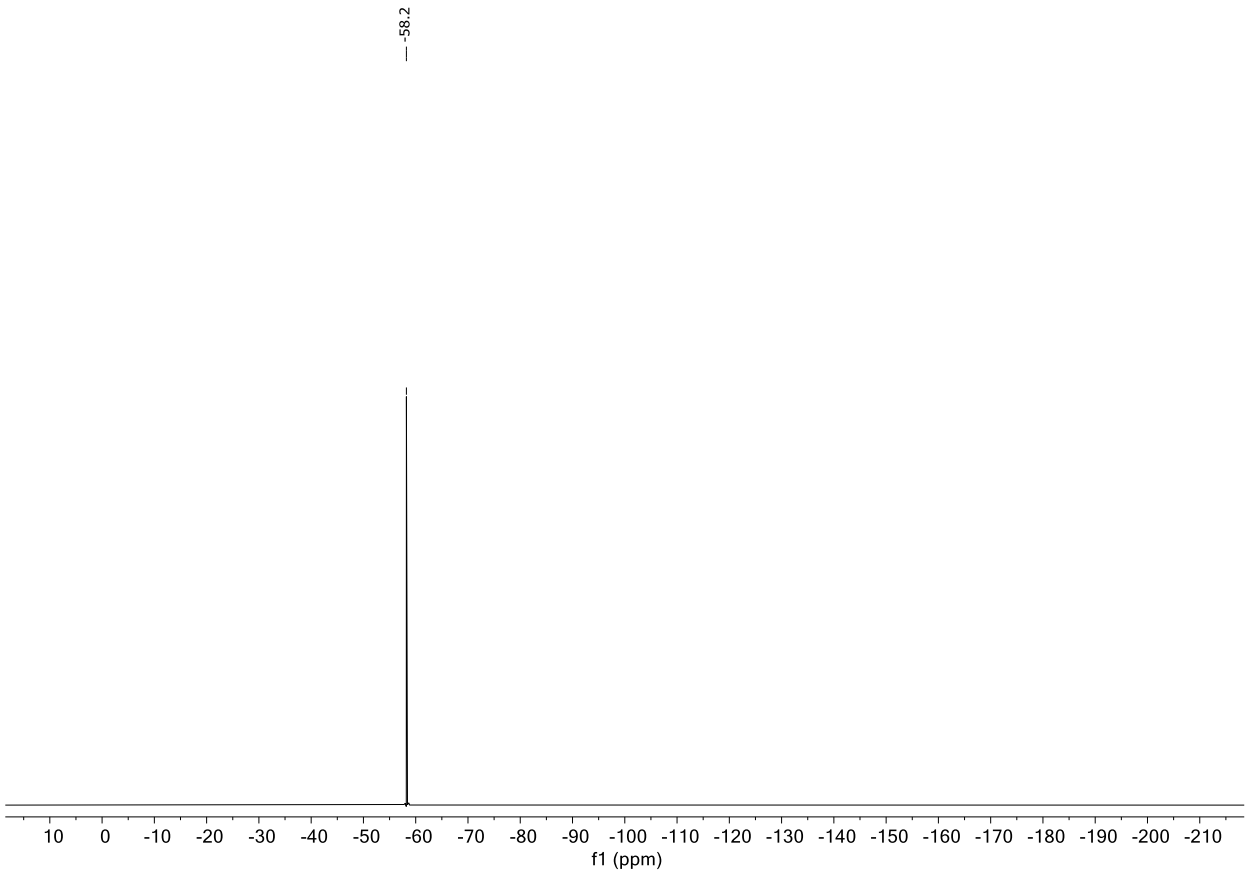
m/o 97:3

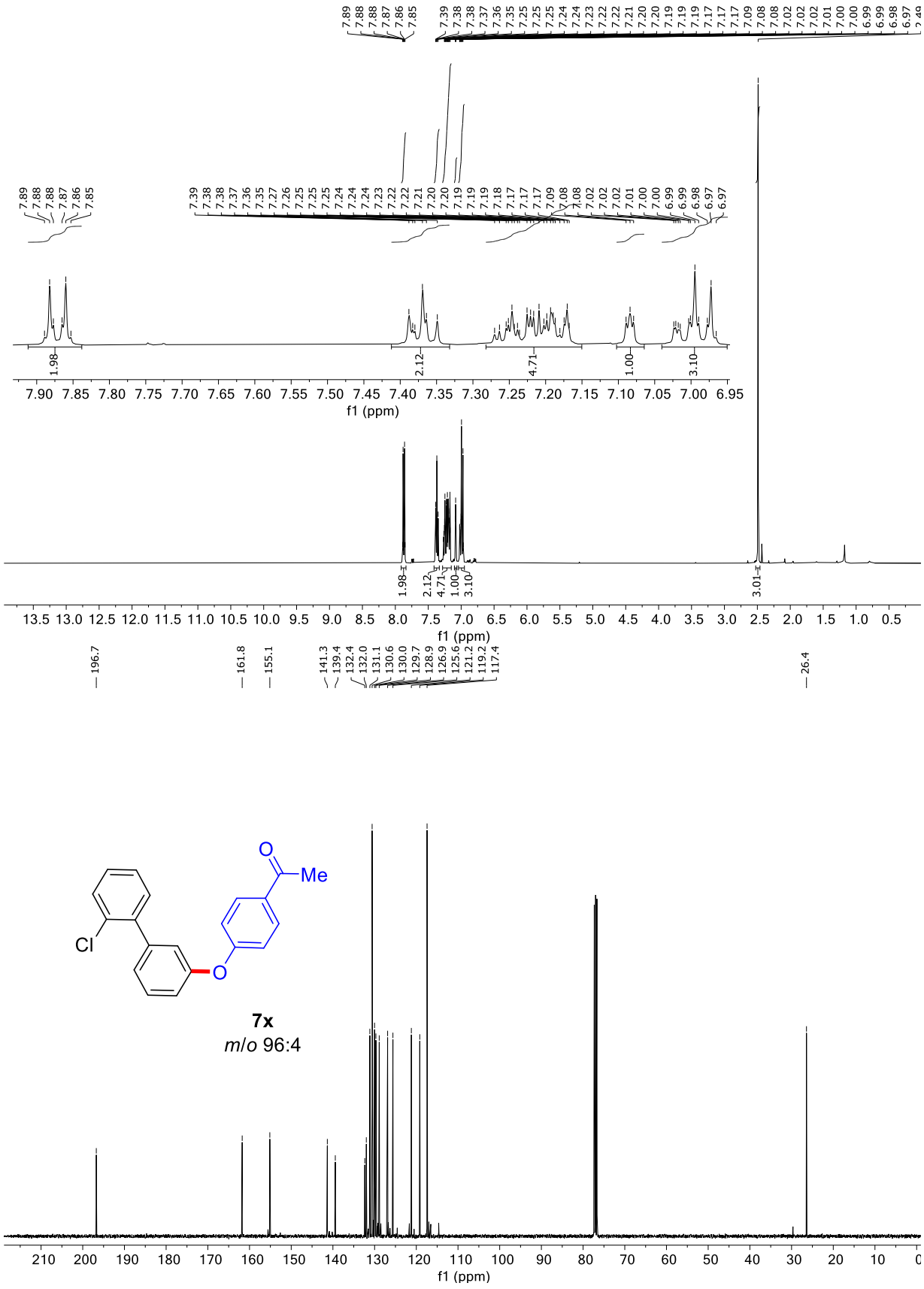

7.46 7.46 7.45 7.45 7.44 7.39 7.37 7.36 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.29 7.28 7.28 7.28 7.27 7.27 7.25 7.25 7.16 7.16 7.16 7.15 7.15 7.15 7.14 7.14 7.14 7.13 7.13 7.08 7.07 7.07 7.07 7.02 7.02 7.01 7.01 7.00 7.00 7.00 7.00 6.99 6.98 6.97 6.97 2.34
1.00 1.08 3.93 2.80 0.93 1.05 1.70
7.44 7.40 7.36 7.32 7.28 7.24 7.20 7.16 7.12 7.08 7.04 7.00 6.96
f1 (ppm)
2.81
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
157.5 154.5 140.9 139.9 133.0 132.4 131.2 130.3 129.9 129.3 128.7 126.8 123.9 119.3 119.2 117.4 20.7
Cl
O
Me
7a
m/o 93:7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

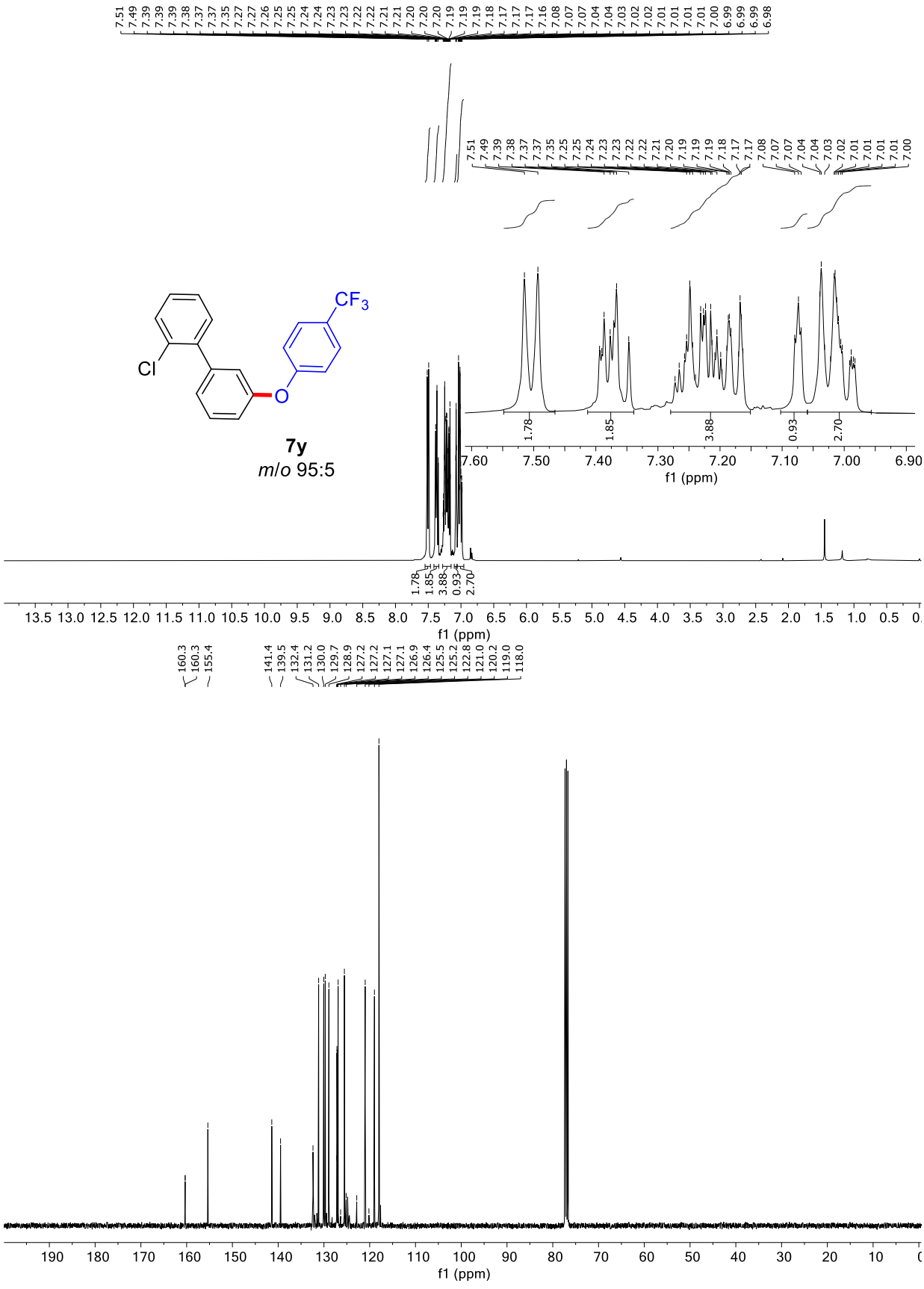

NO2
Cl
O
7v
m/o 94:6
f1 (ppm)

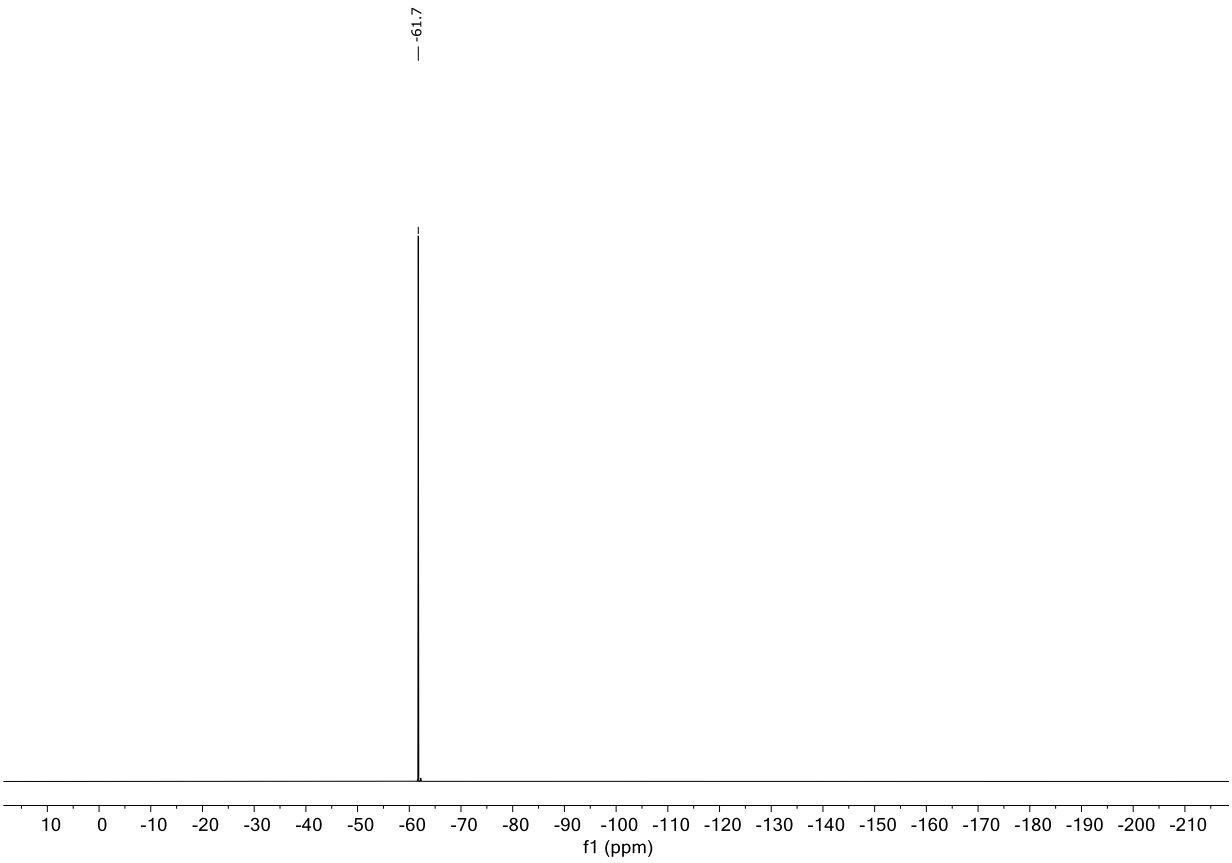

OCF3
Cl
O
7w
m/o 99:1
f1 (ppm)

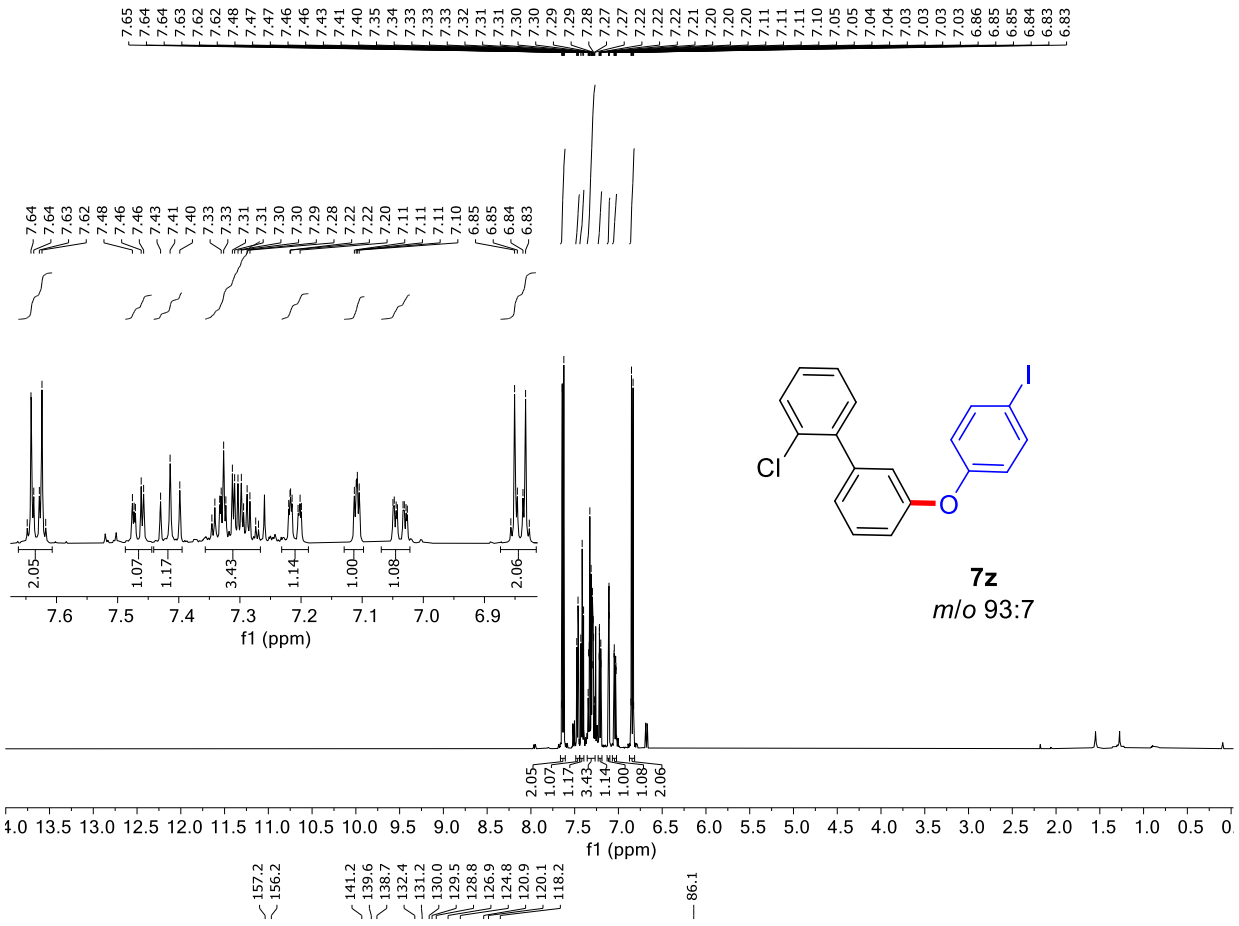

f1 (ppm)

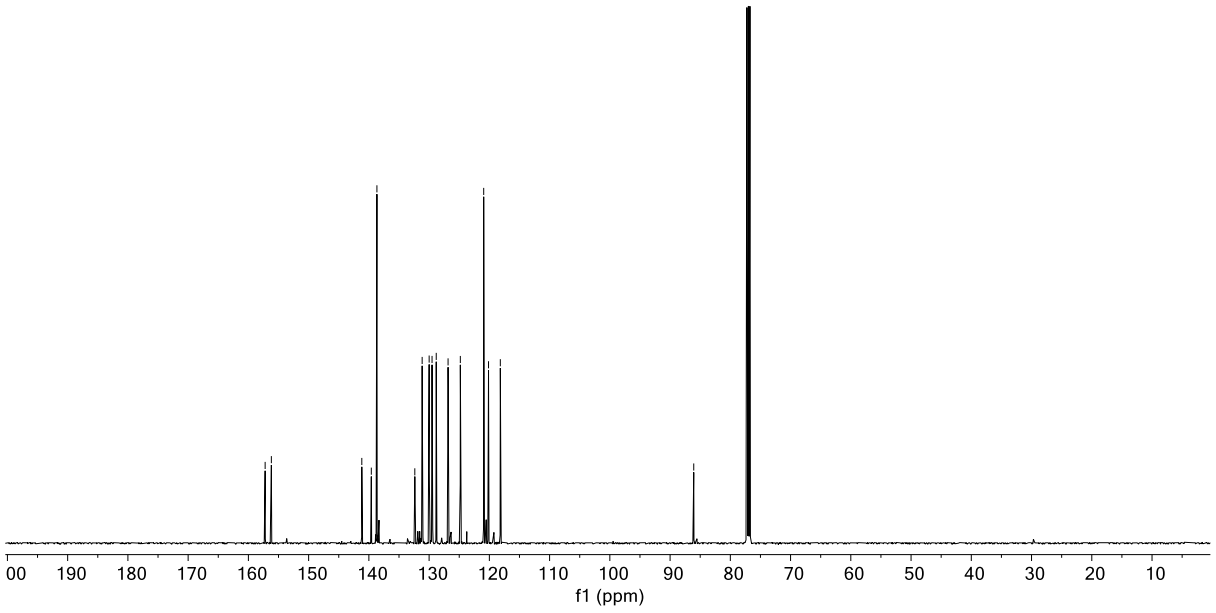

-58.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

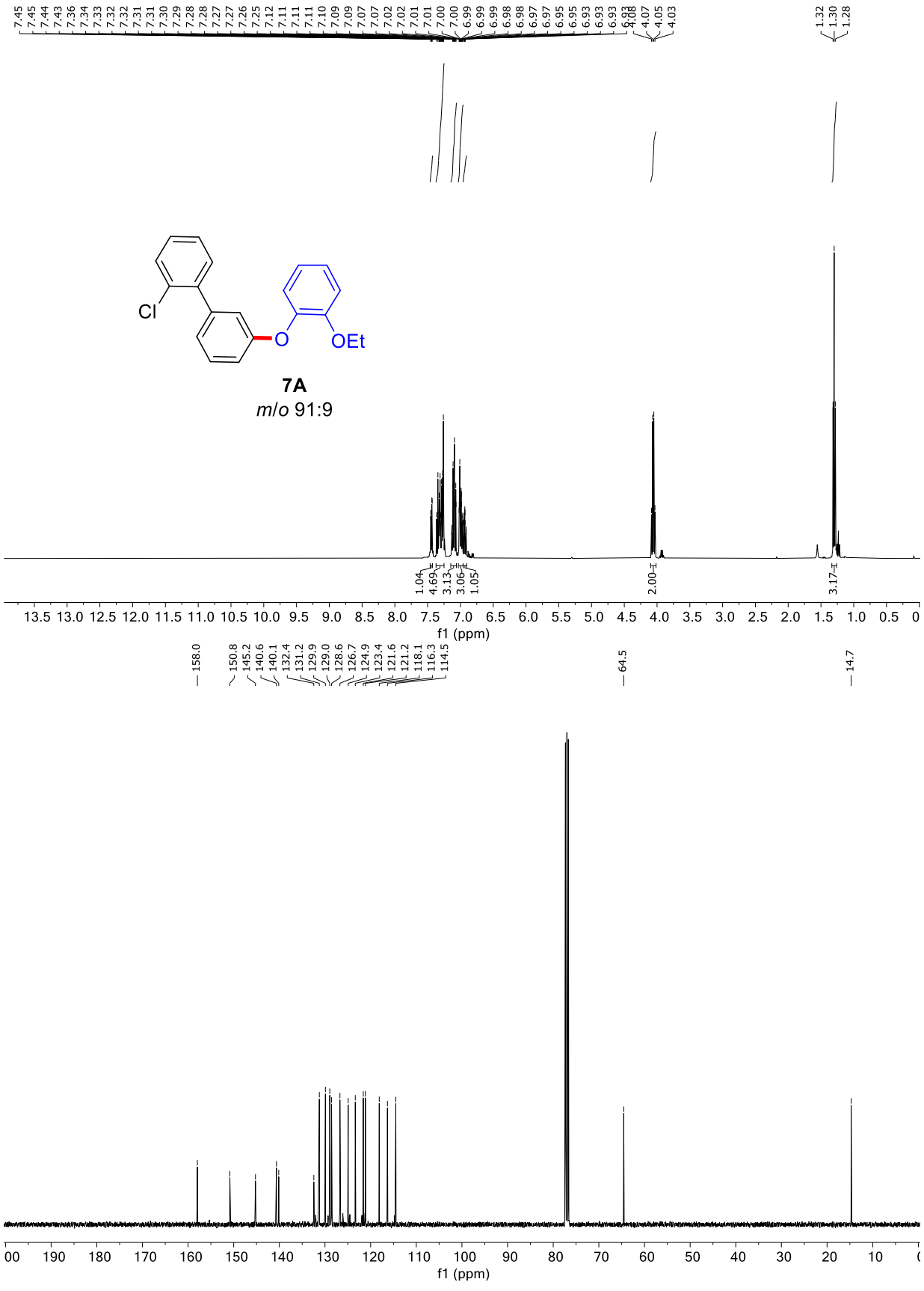

f1 (ppm)
f1 (ppm)
f1 (ppm)
O
Me
Cl
O
7x
m/o 96:4

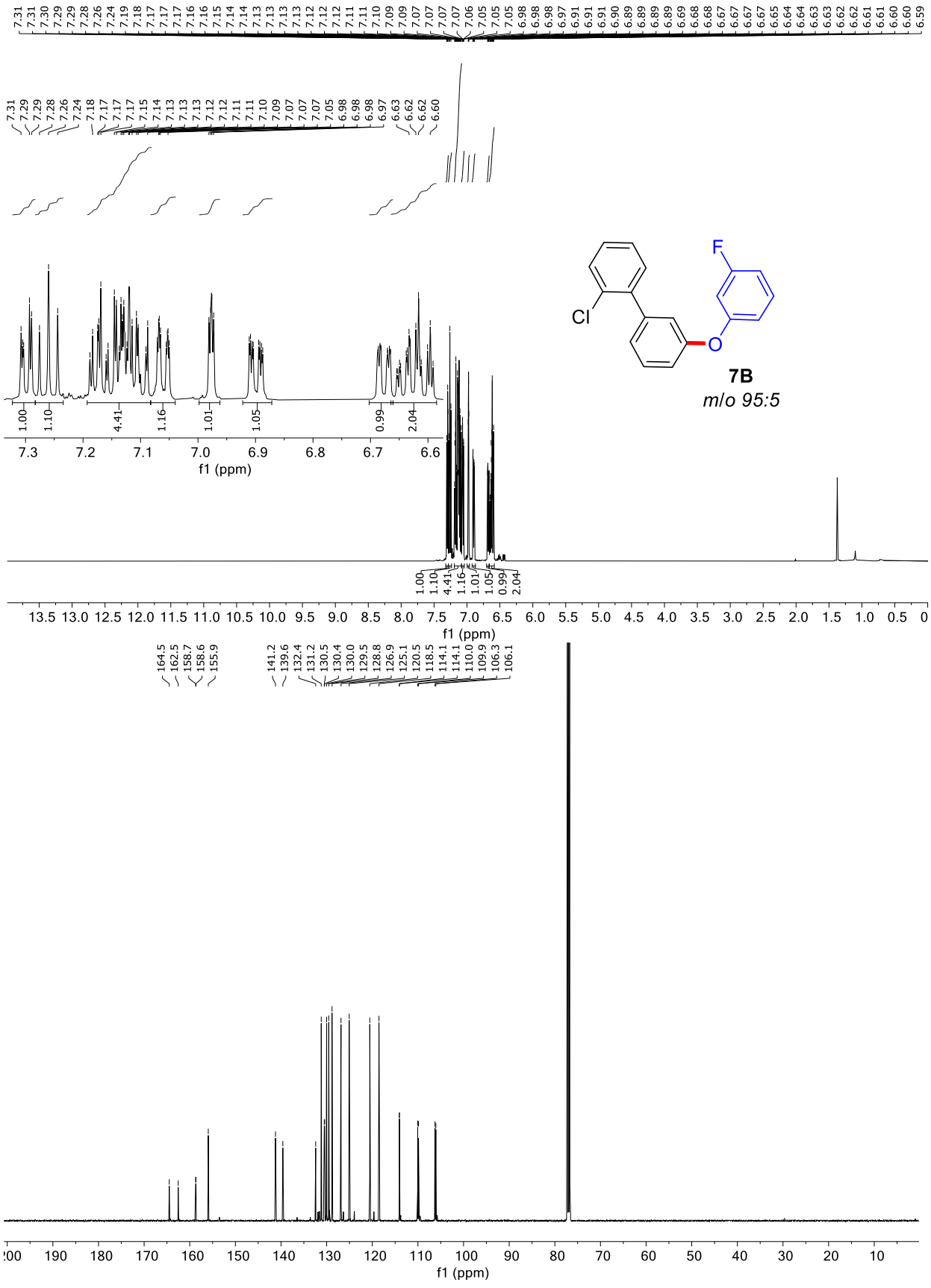

Cl
O
CF3
7y
m/o 95:5
f1 (ppm)

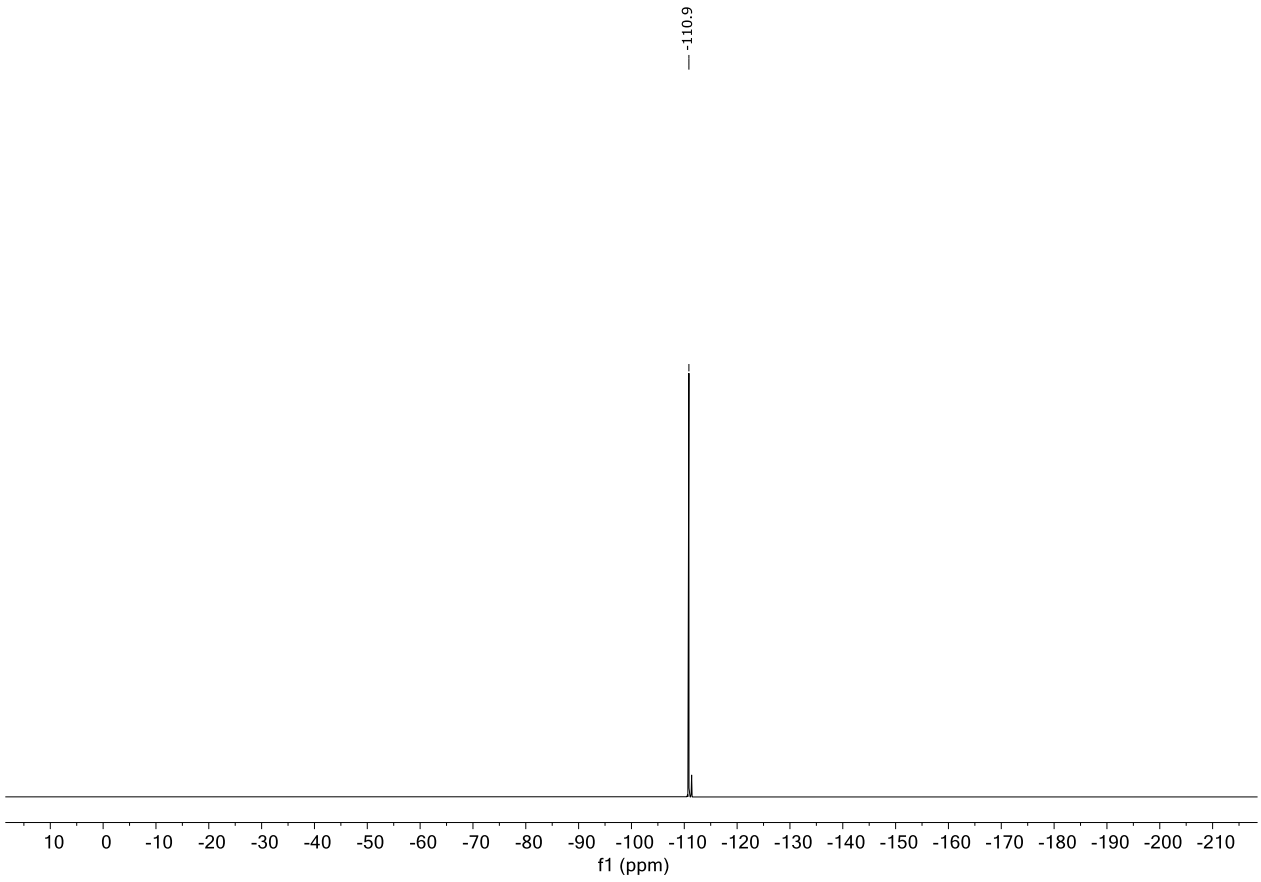

-61.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

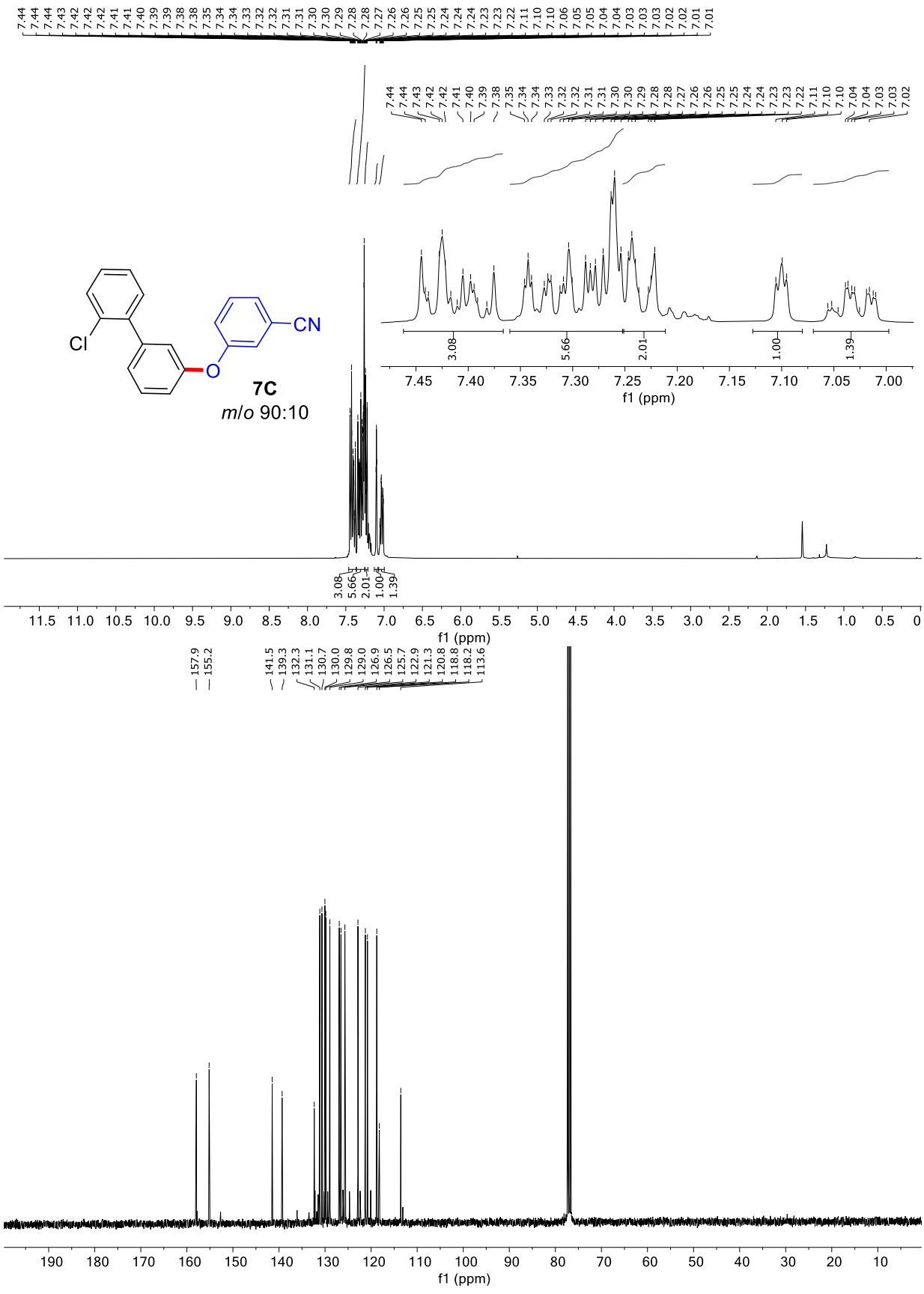

7.65 7.64 7.64 7.63 7.62 7.62 7.48 7.47 7.47 7.46 7.46 7.43 7.41 7.40 7.35 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.22 7.22 7.22 7.21 7.20 7.20 7.20 7.11 7.11 7.11 7.10 7.05 7.05 7.04 7.04 7.03 7.03 7.03 7.03 6.86 6.85 6.85 6.84 6.83 6.83
7.64 7.64 7.63 7.62 7.48 7.46 7.46 7.43 7.41 7.40 7.33 7.33 7.31 7.31 7.30 7.30 7.29 7.28 7.22 7.22 7.20 7.11 7.11 7.10 6.85 6.85 6.84 6.83
2.05 1.07 1.17 3.43 1.14 1.00 1.08 2.06
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
Cl
I
O
7z
m/o 93:7
2.05 1.07 1.17 3.43 1.14 1.00 1.08 2.06
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

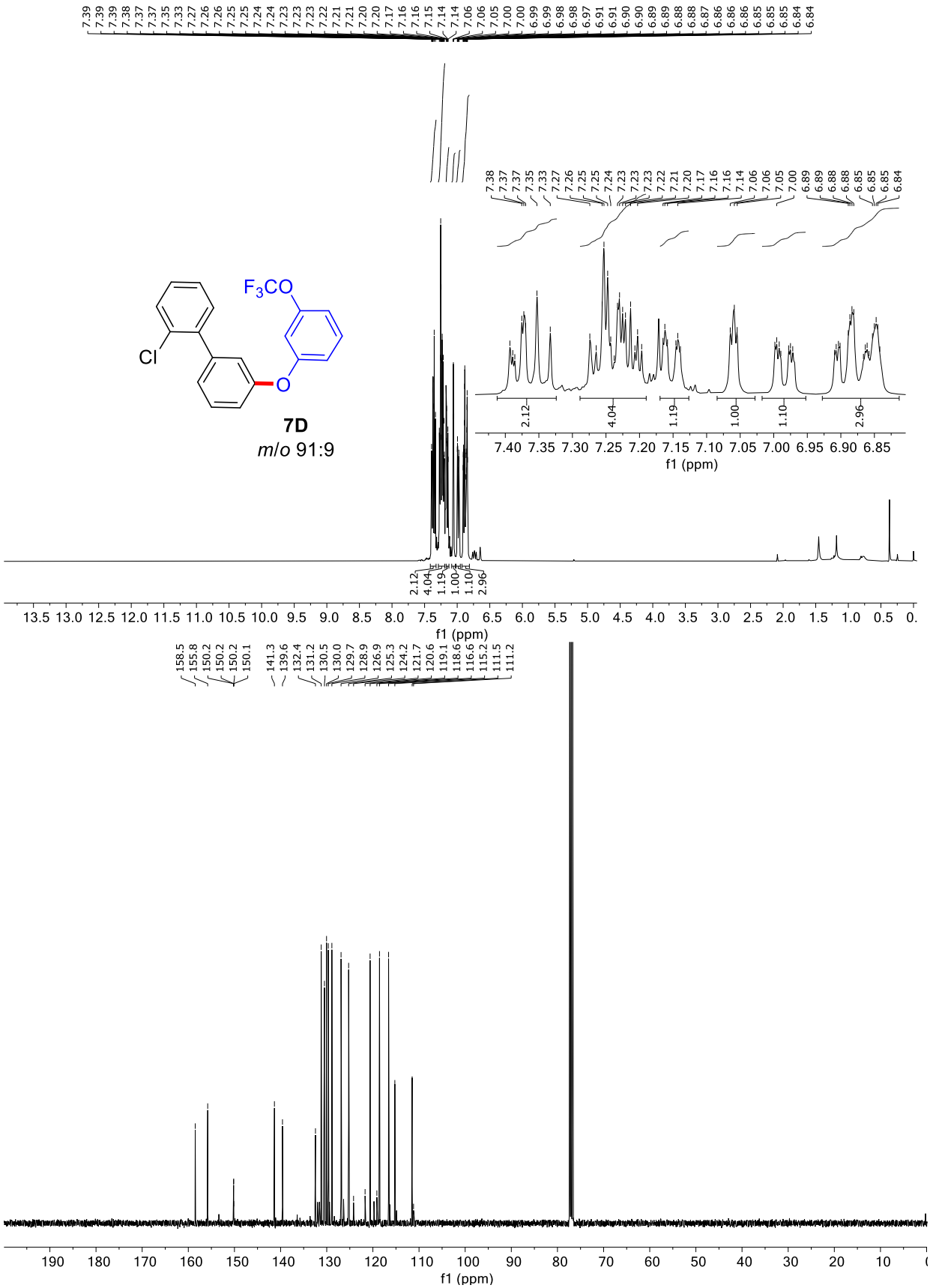

157.2 156.2 141.2 139.6 138.7 132.4 131.2 130.0 129.5 128.8 126.9 124.8 120.9 120.1 118.2 86.1
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

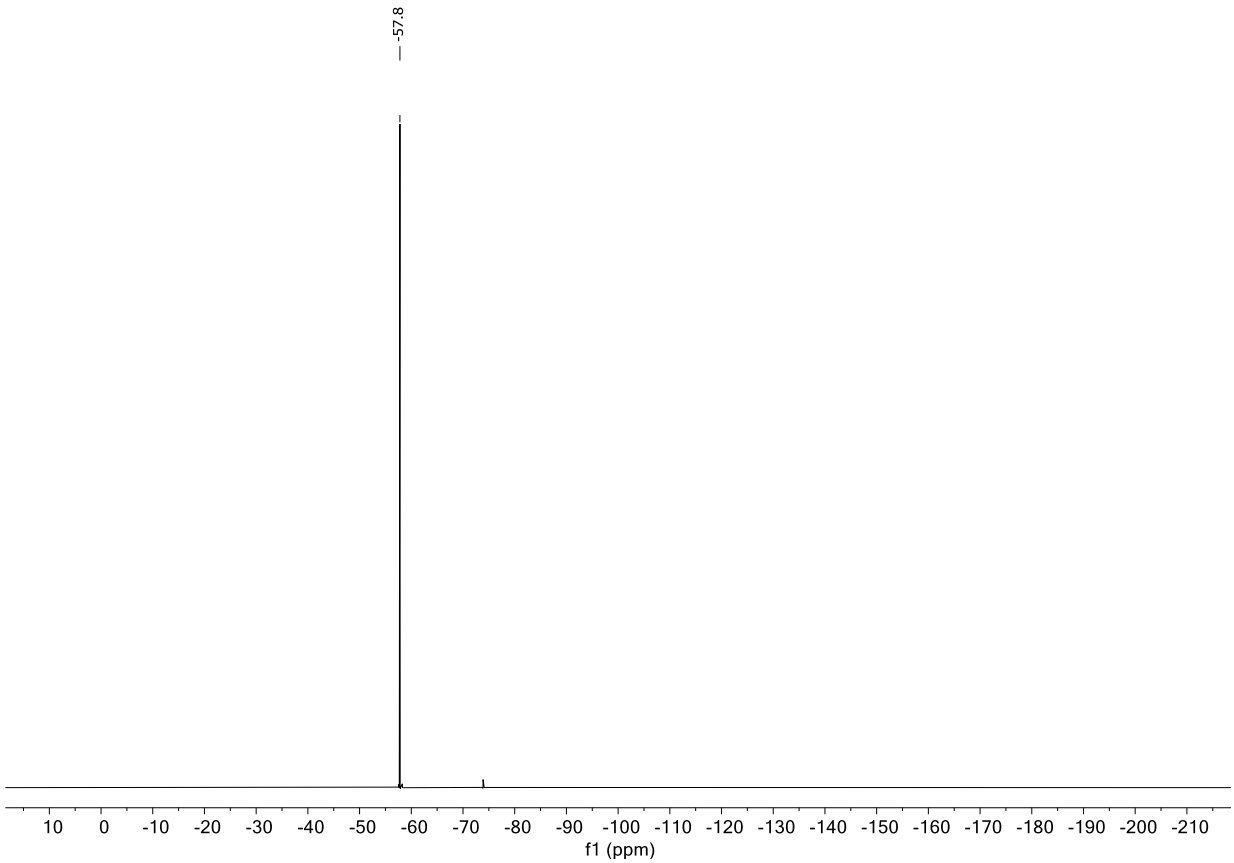

Cl
O
OEt
7A
m/o 91:9
f1 (ppm)
f1 (ppm)

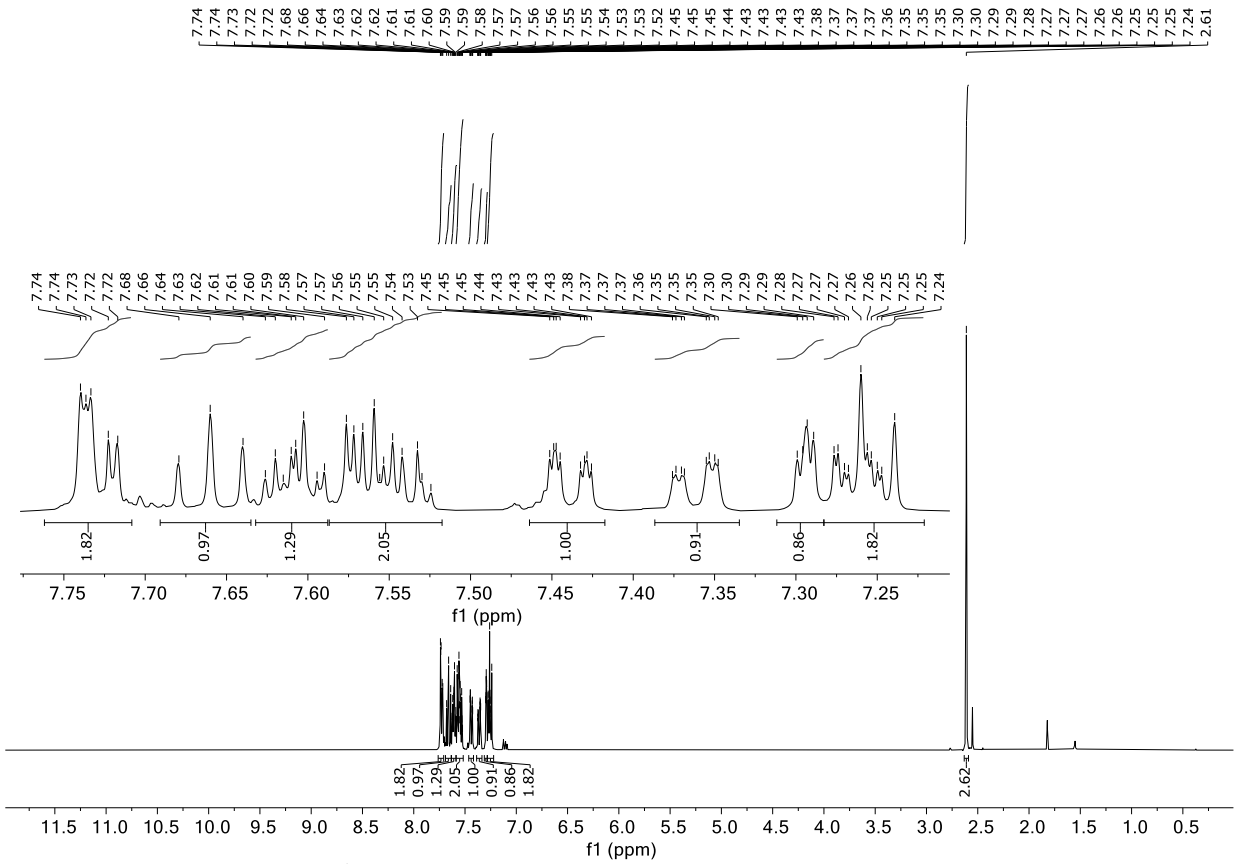

F
Cl
O
7B
m/o 95:5
f1 (ppm)

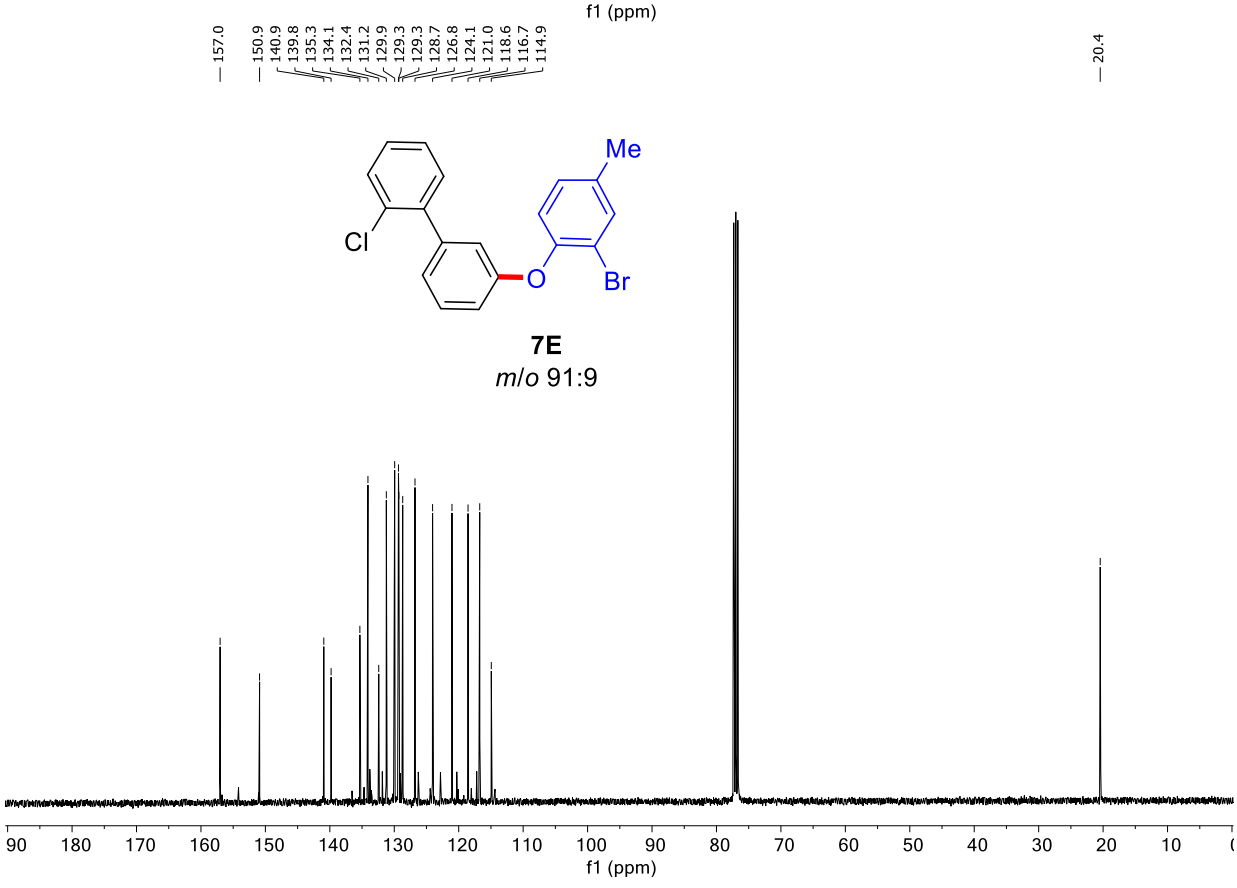

-110.9
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


Cl
CN
O
7C
m/o 90:10
f1 (ppm)


F3CO
Cl
O
7D
m/o 91:9
f1 (ppm)

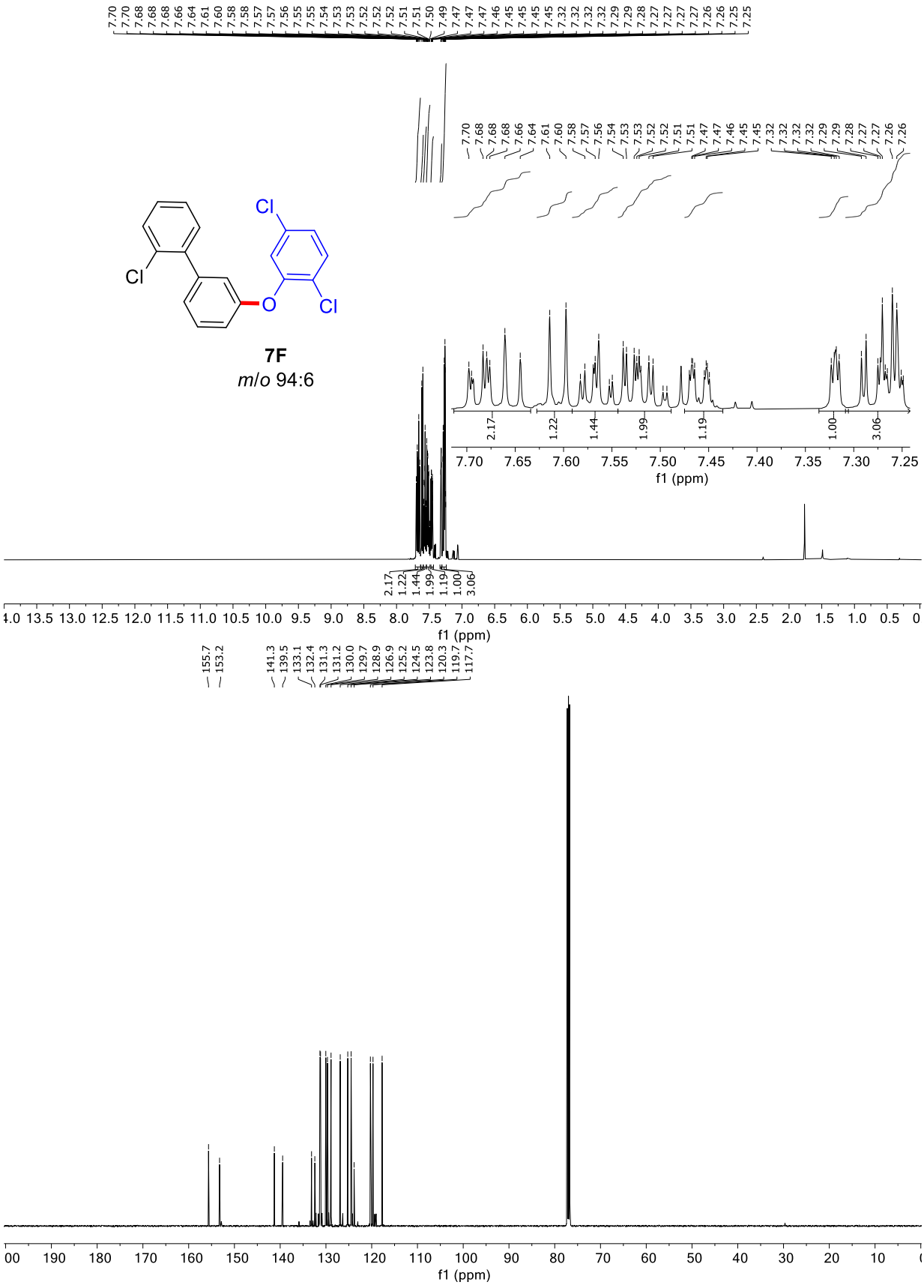

-57.8
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

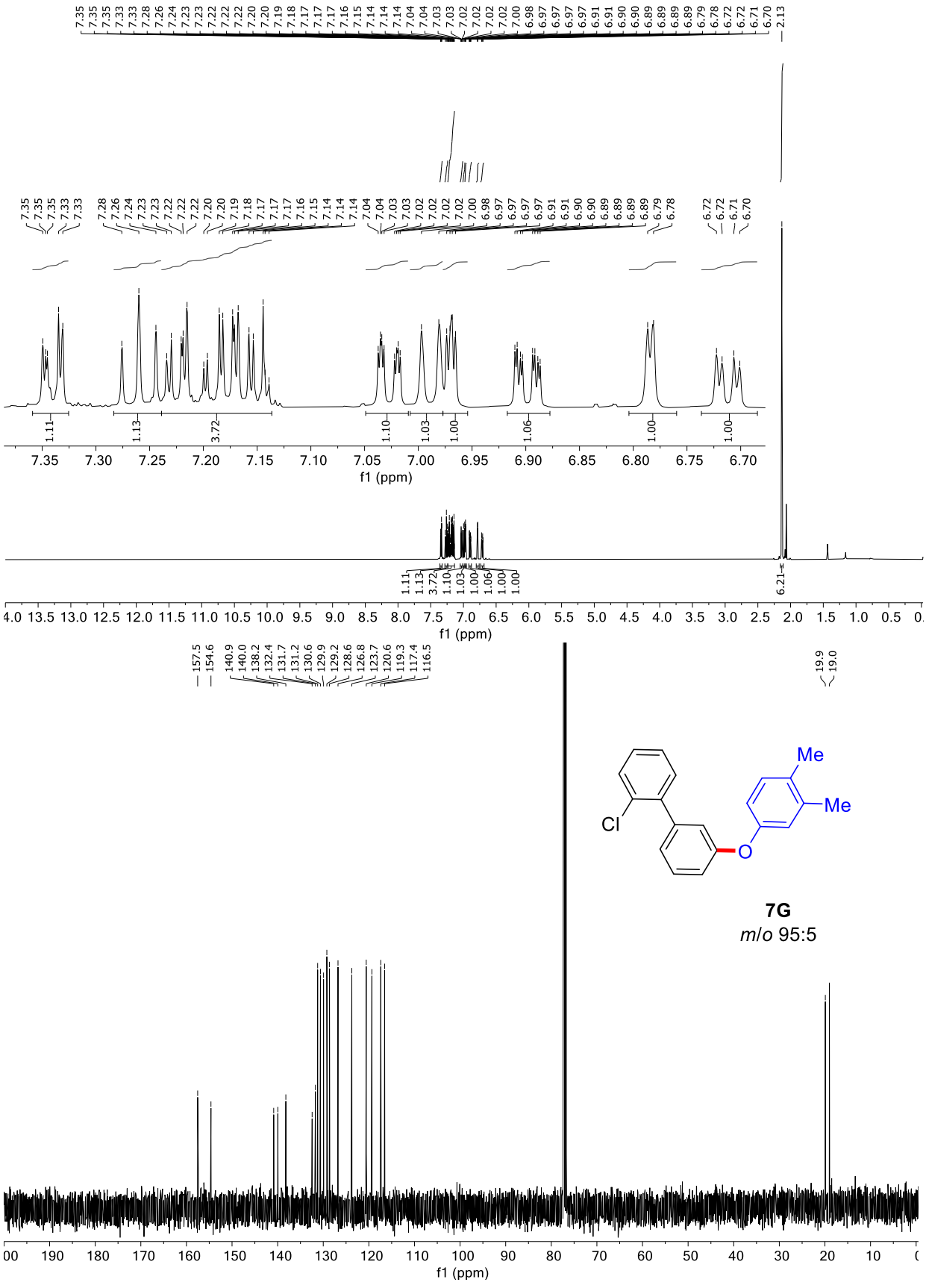




7E

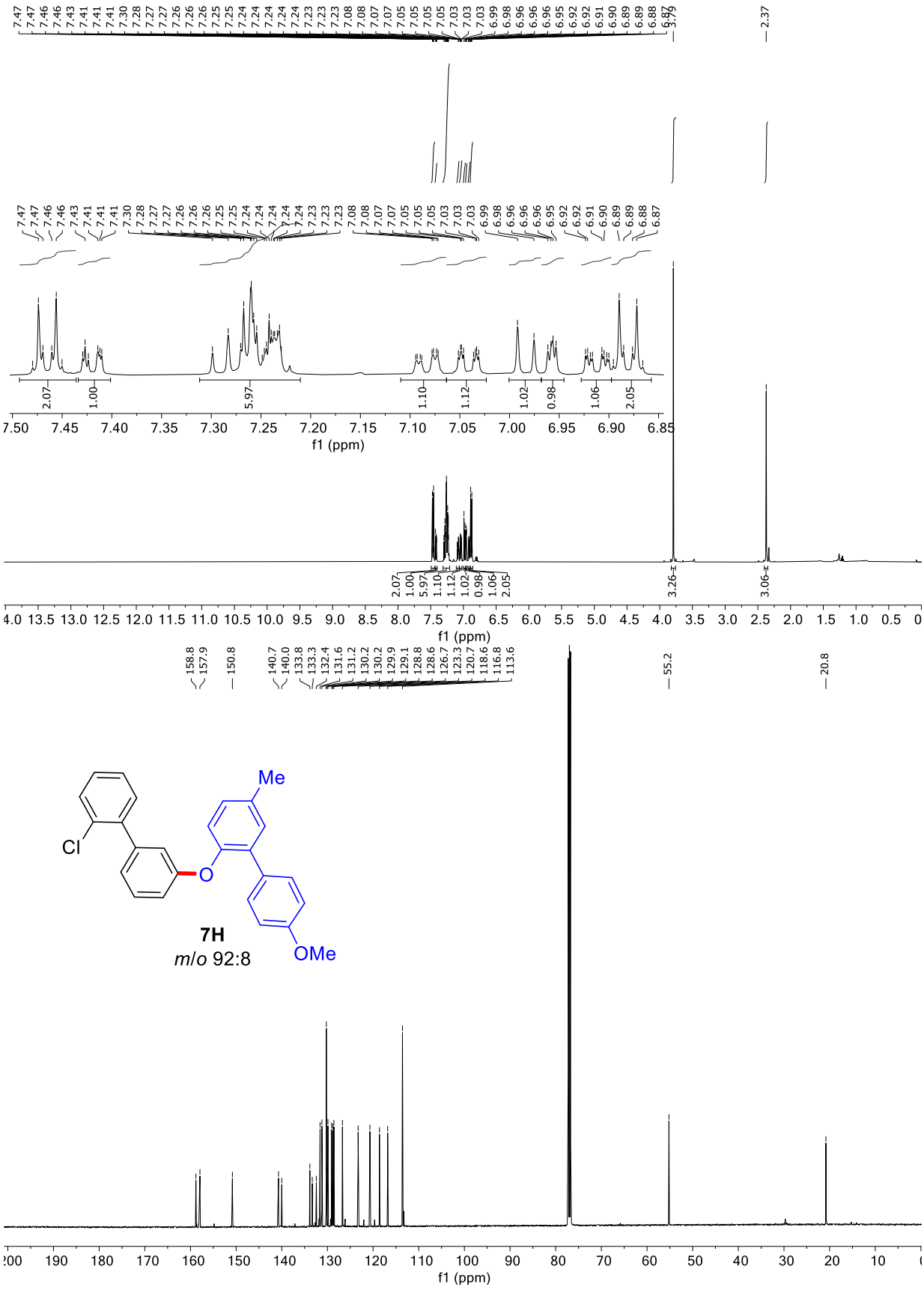
m/o 91:9

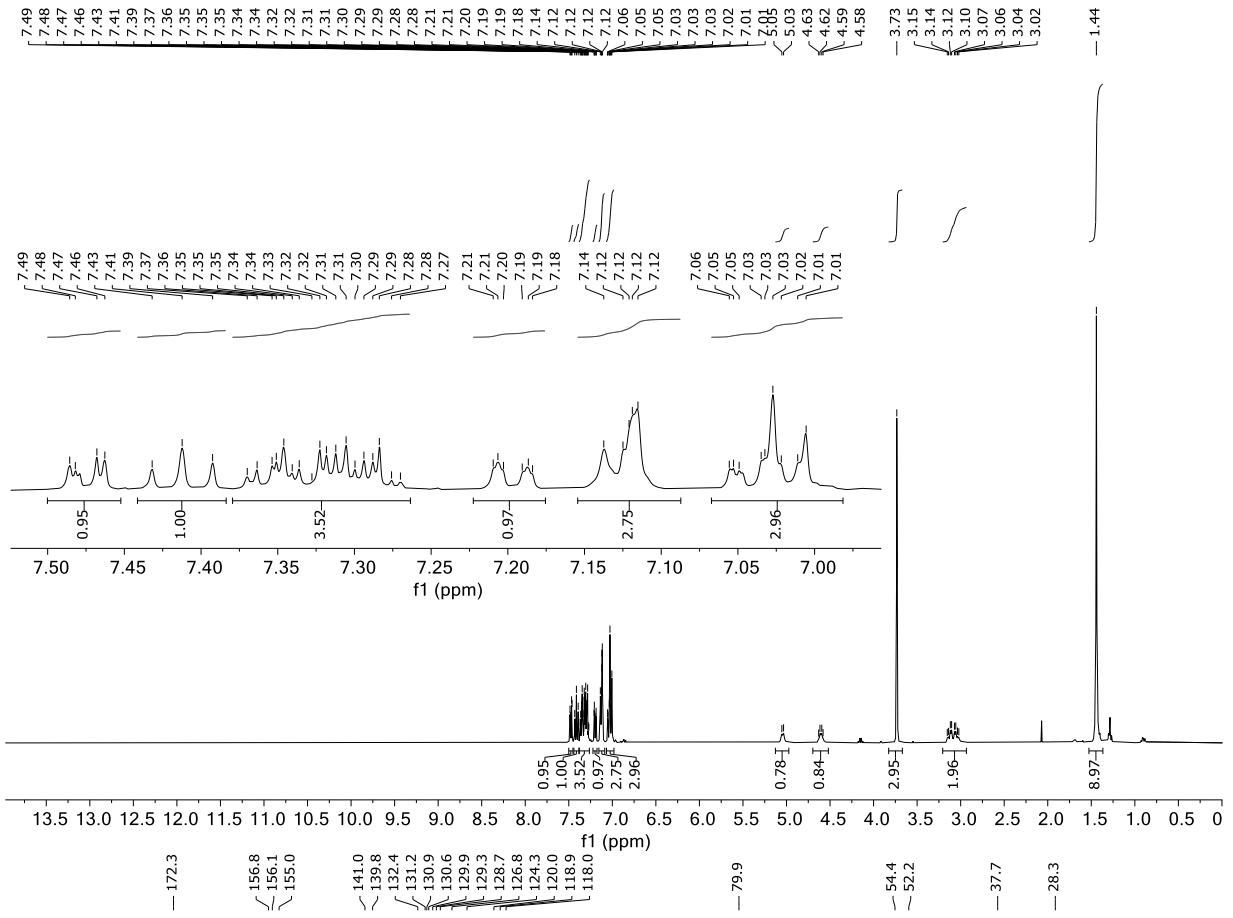

7.70 7.70 7.68 7.68 7.68 7.66 7.64 7.61 7.60 7.58 7.58 7.57 7.57 7.56 7.55 7.55 7.54 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.50 7.49 7.47 7.47 7.47 7.46 7.45 7.45 7.45 7.32 7.32 7.32 7.29 7.29 7.28 7.27 7.27 7.27 7.27 7.26 7.25 7.25
Cl
Cl
O
Cl
7F
m/o 94:6
2.17 1.22 1.44 1.99 1.19 1.00 3.06
f1 (ppm)
155.7 153.2 141.3 139.5 133.1 132.4 131.3 131.2 130.0 129.7 128.9 126.9 125.2 124.5 123.8 120.3 119.7 117.7
f1 (ppm)

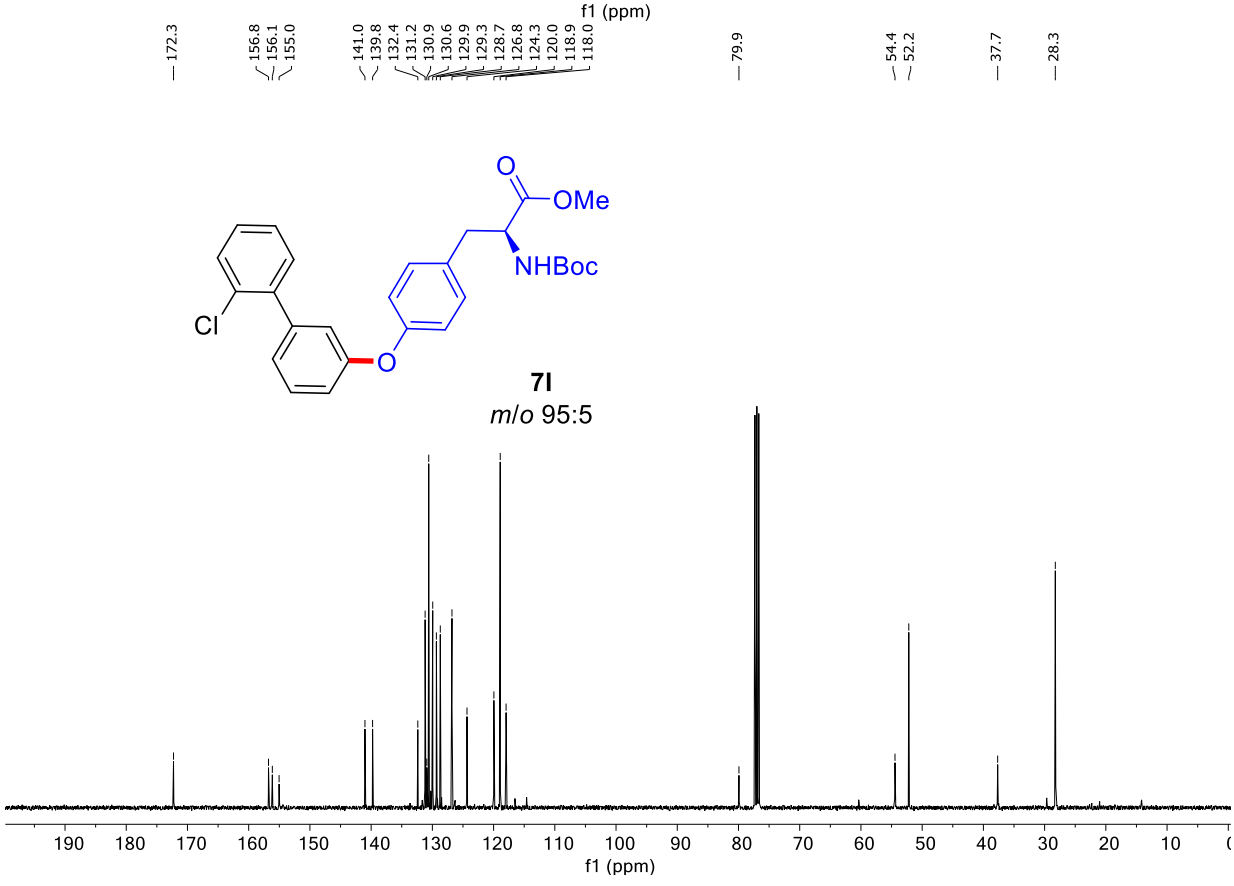


7G

m/o 95:5

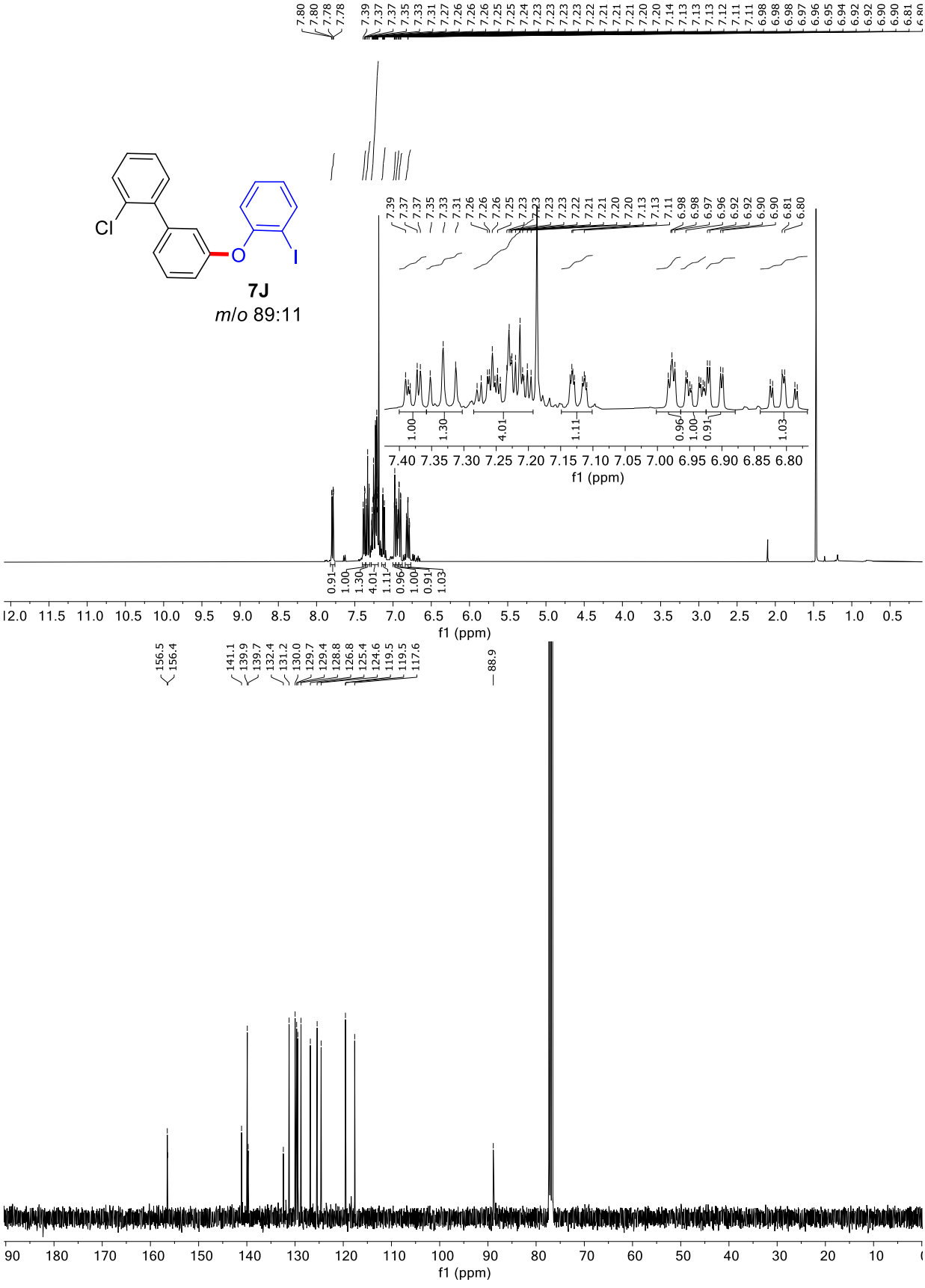

Me
Cl
O
OMe
7H
m/o 92:8
f1 (ppm)

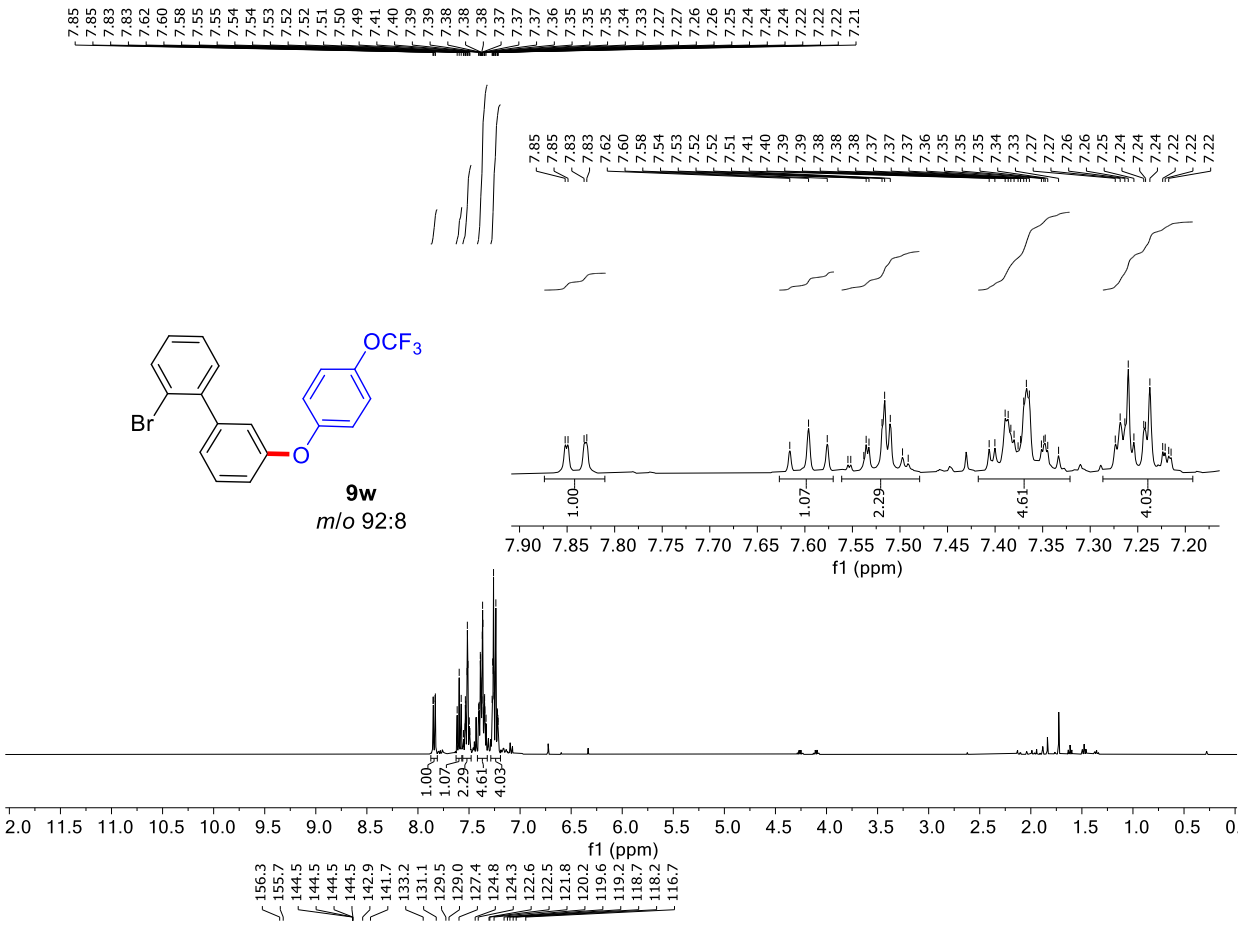


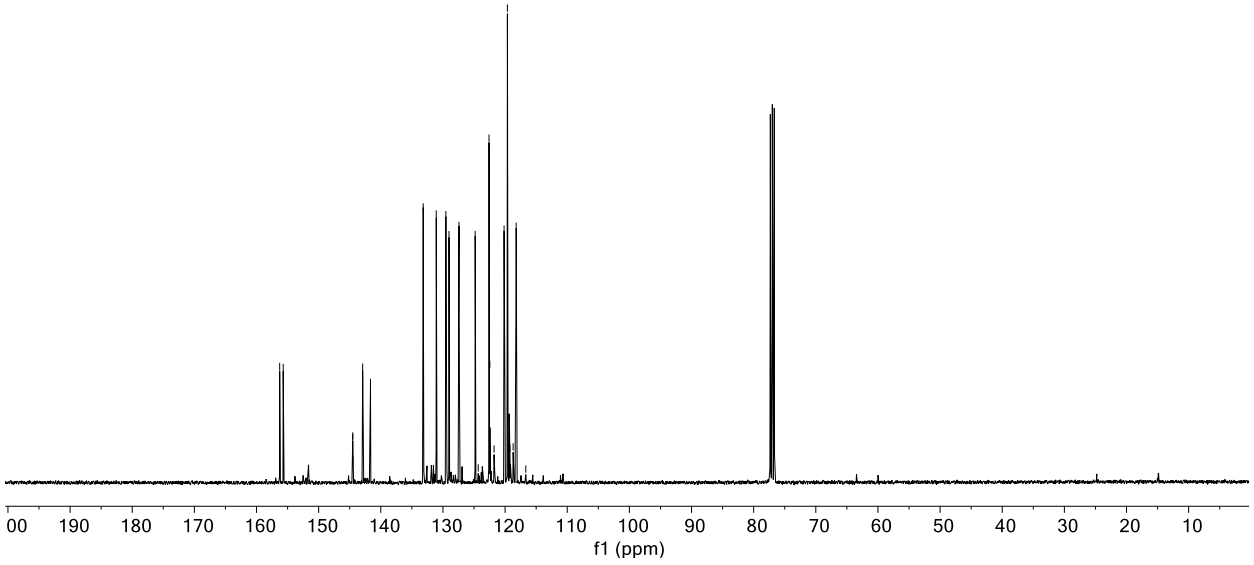


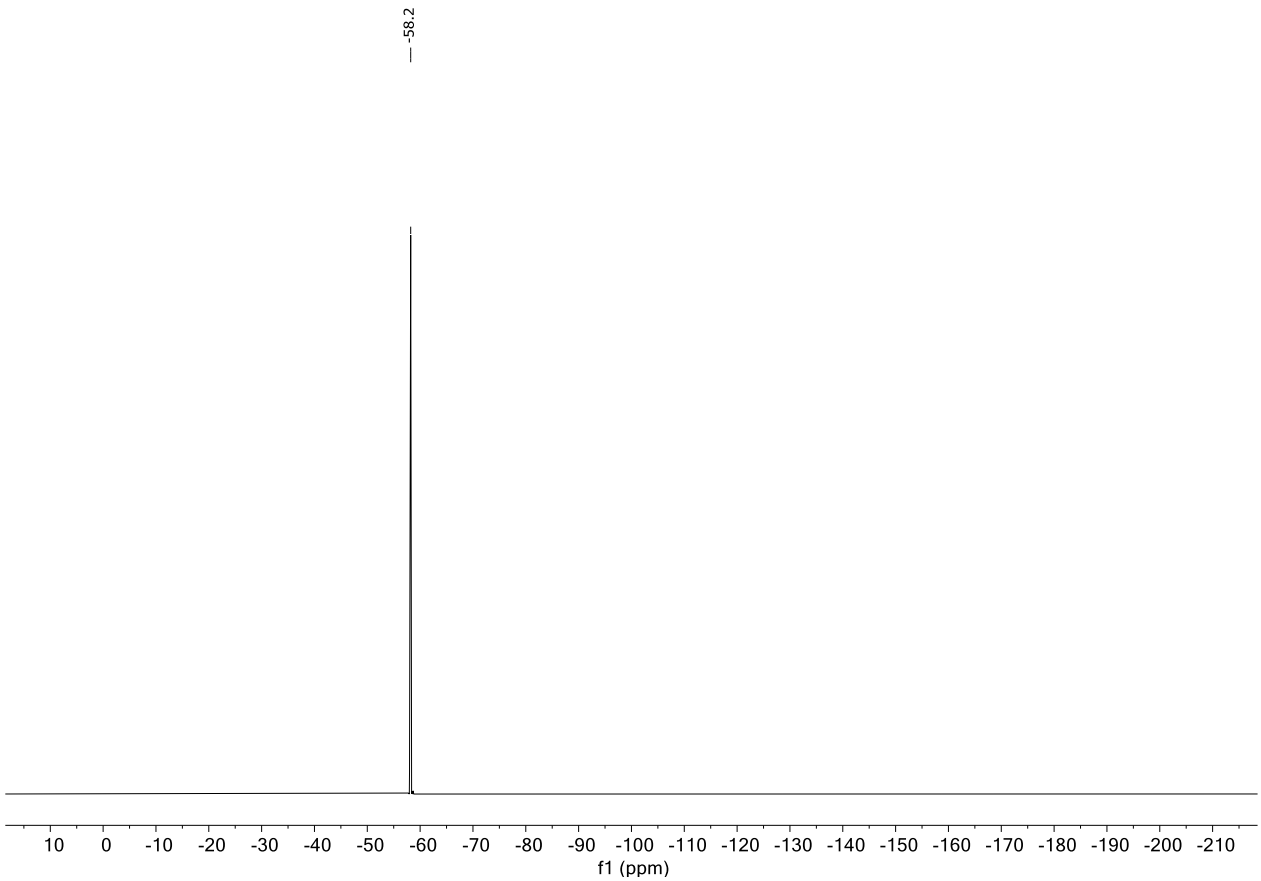
7l

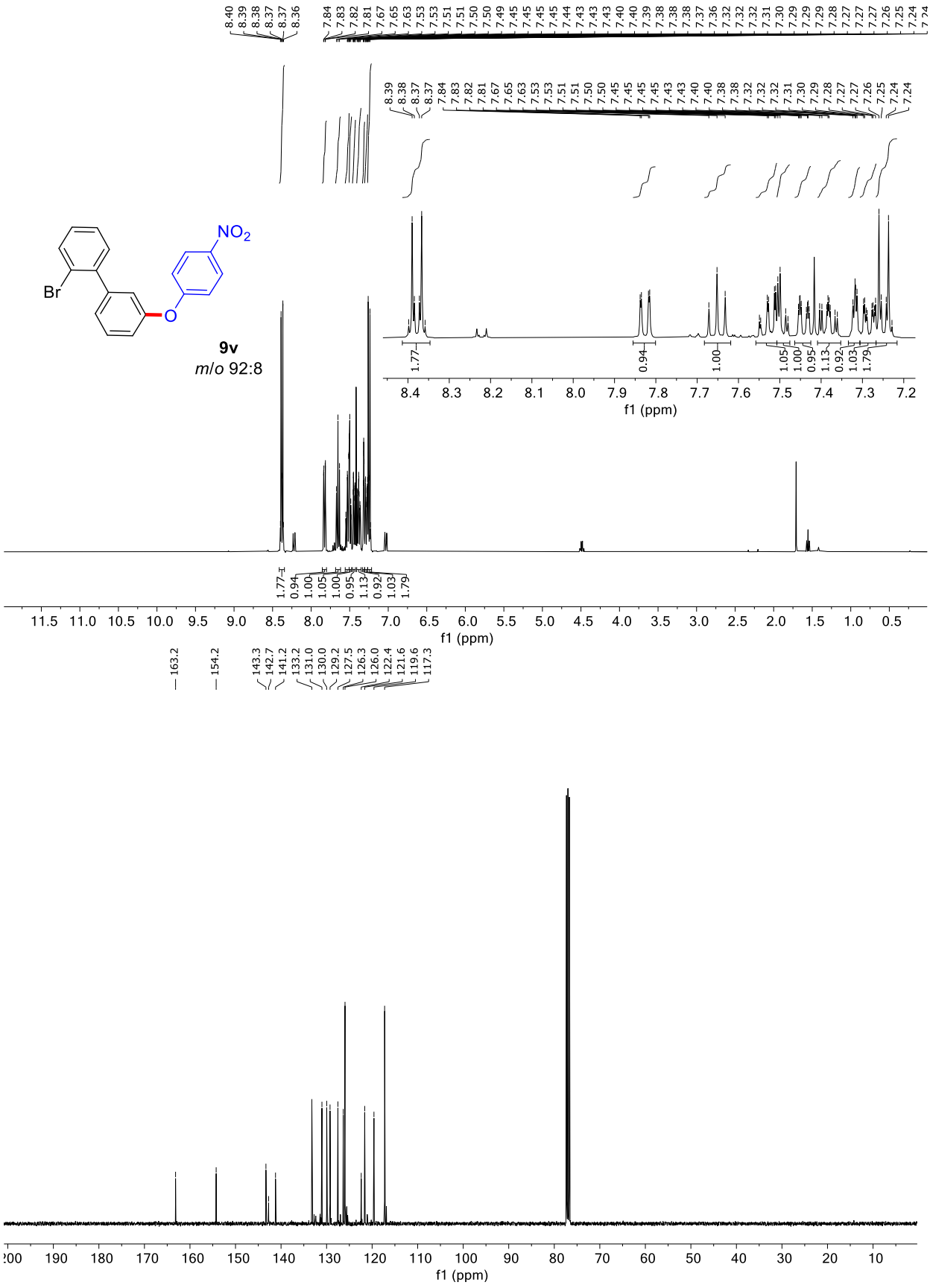
m/o 95:5

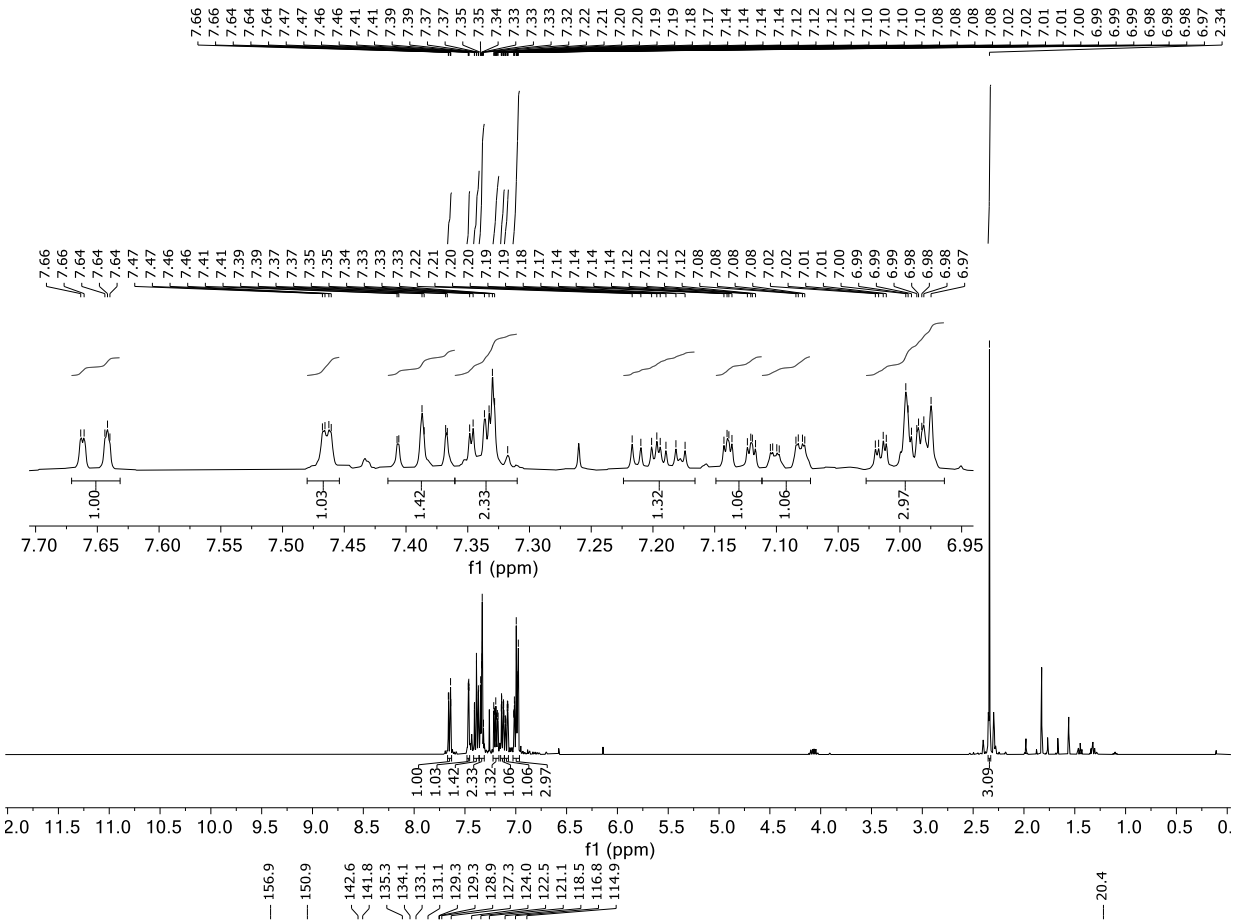

Cl
O
I
7J
m/o 89:11
f1 (ppm)
f1 (ppm)
f1 (ppm)

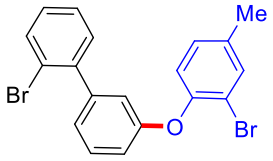

Br
O
OCF3
9w
m/o 92:8
f1 (ppm)


f1 (ppm)


-58.2
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)

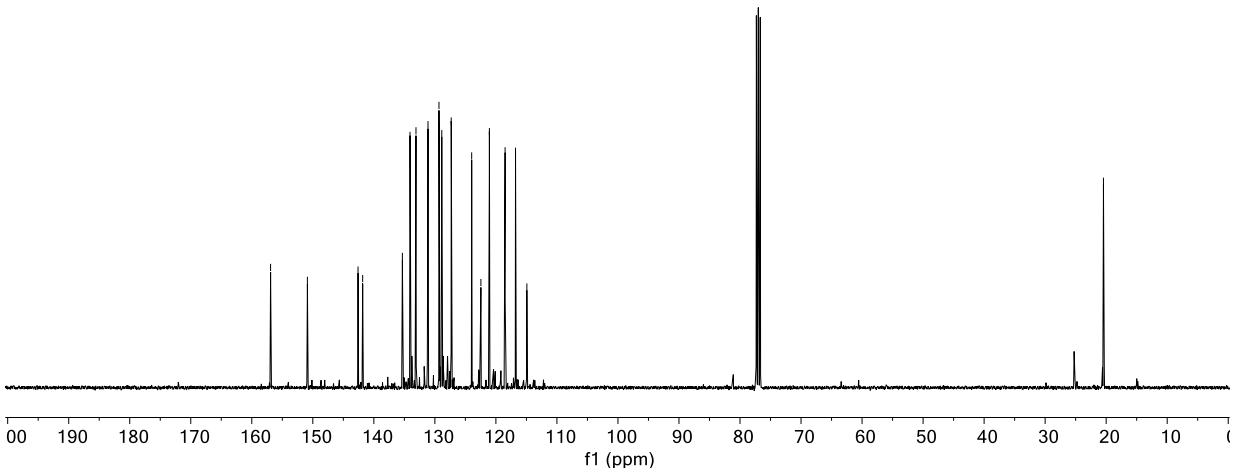

NO2
Br
O
9v
m/o 92:8
f1 (ppm)

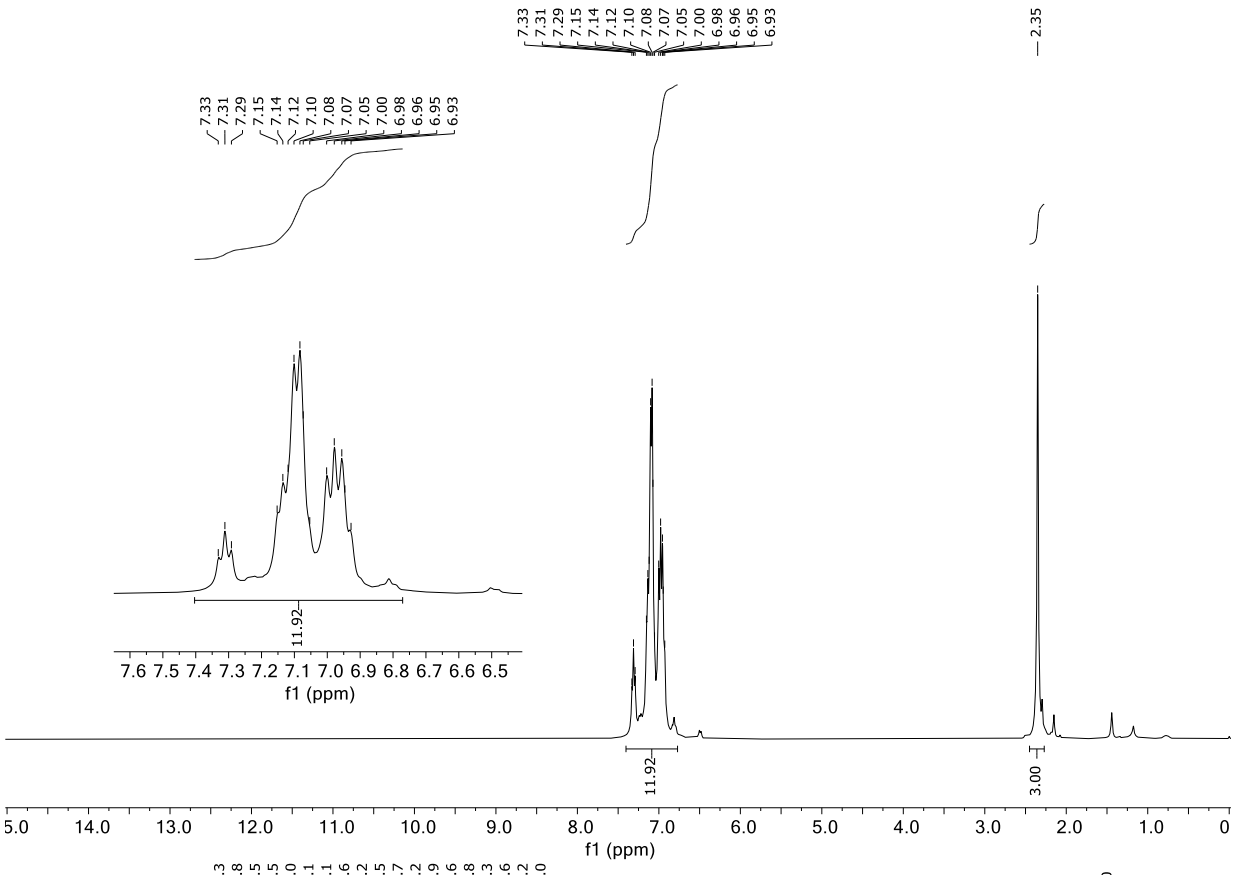

7.66 7.66 7.64 7.64 7.64 7.47 7.47 7.46 7.46 7.41 7.41 7.39 7.39 7.37 7.37 7.35 7.35 7.34 7.33 7.33 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.14 7.14 7.14 7.14 7.12 7.12 7.12 7.12 7.08 7.08 7.08 7.08 7.02 7.02 7.01 7.01 7.00 6.99 6.99 6.98 6.98 6.97
1.00 1.03 1.42 2.33 1.32 1.06 1.06 2.97
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95
f1 (ppm)
1.00 1.03 1.42 2.33 1.32 1.06 2.97 3.09
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
156.9 150.9 142.6 141.8 135.3 134.1 133.1 131.1 129.3 129.3 128.9 127.3 124.0 122.5 121.1 118.5 116.8 114.9
20.4

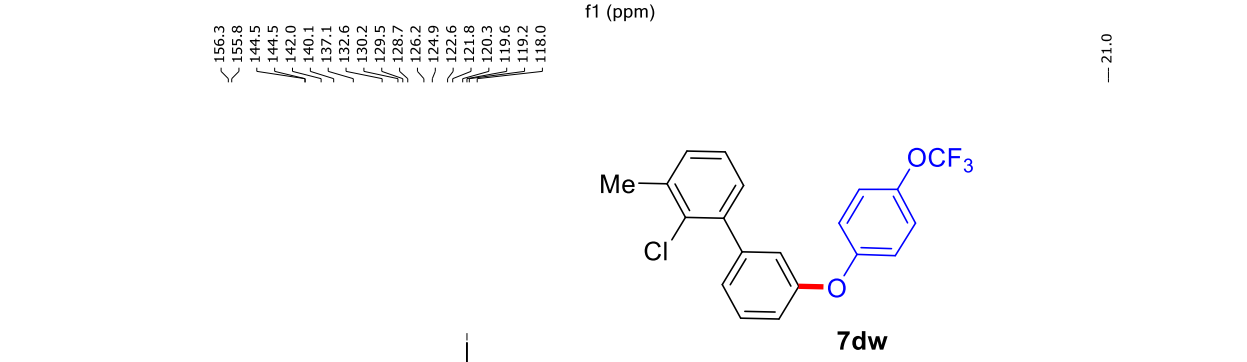

Me
Br
O
Br

9E

m/o 94:6

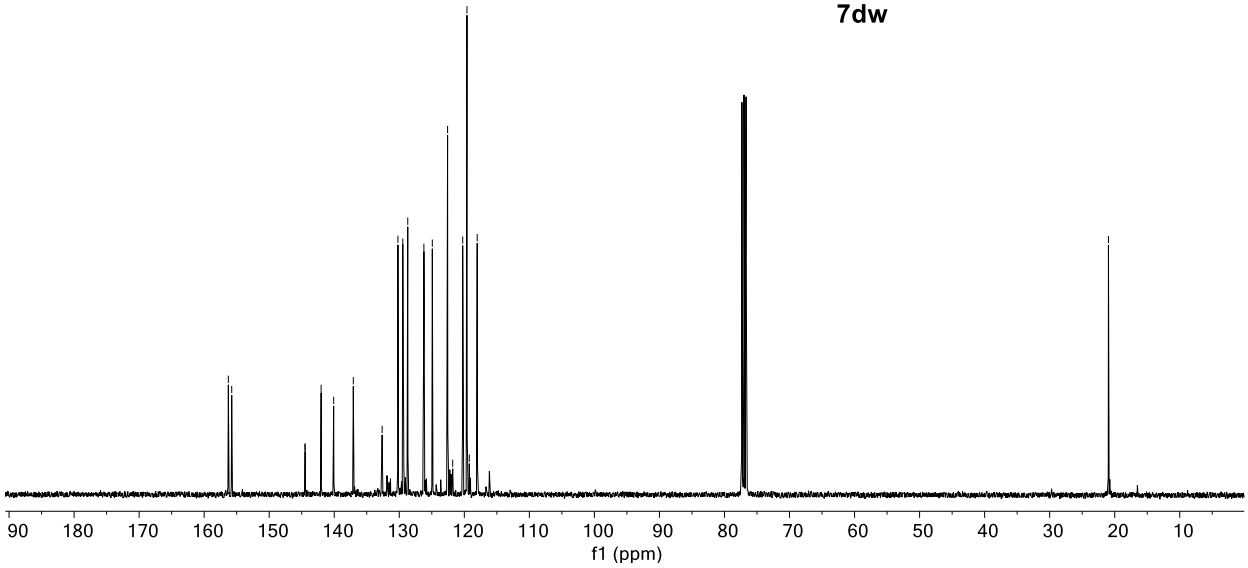

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

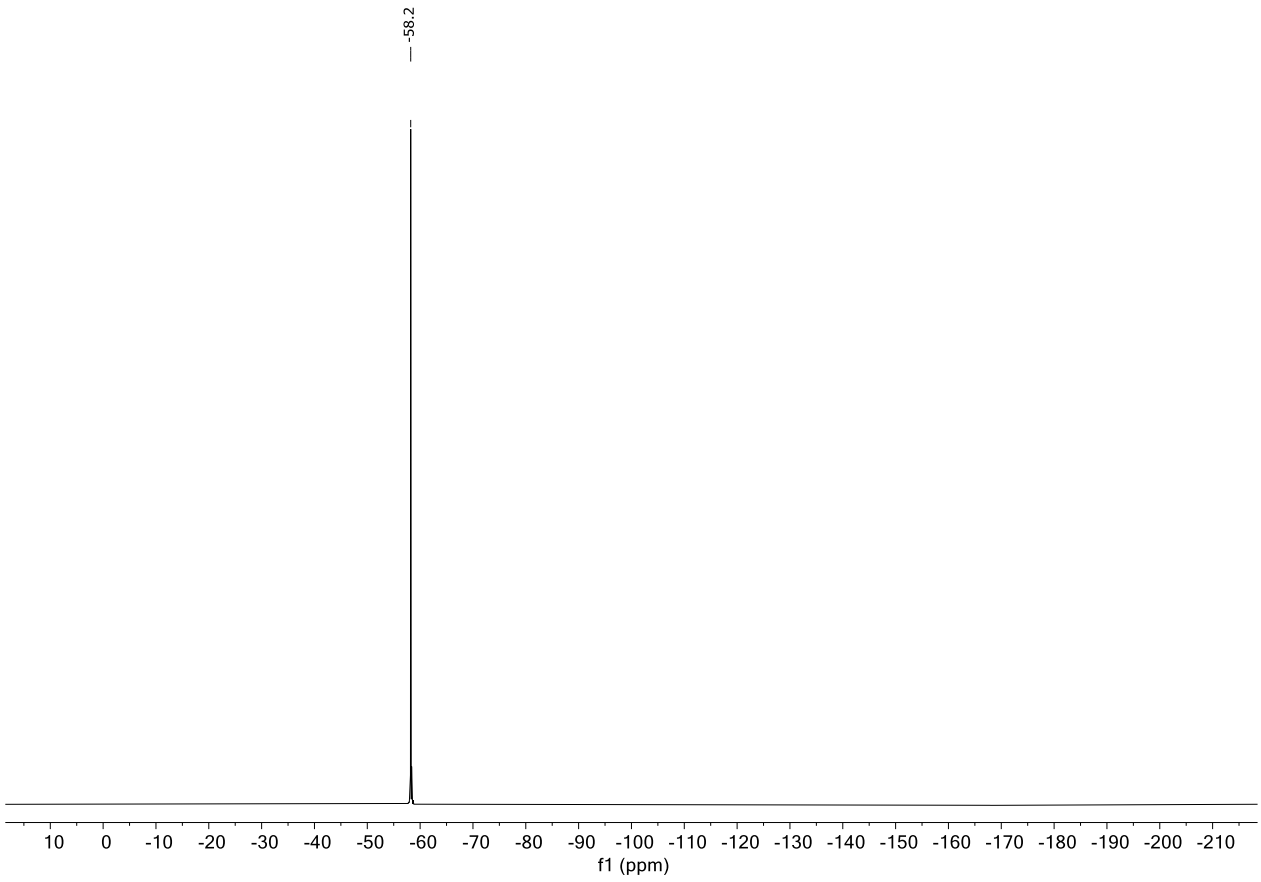

7.33
7.31
7.29
7.15
7.14
7.12
7.10
7.08
7.07
7.05
7.00
6.98
6.96
6.95
6.93
2.35
11.92
3.00
f1 (ppm)

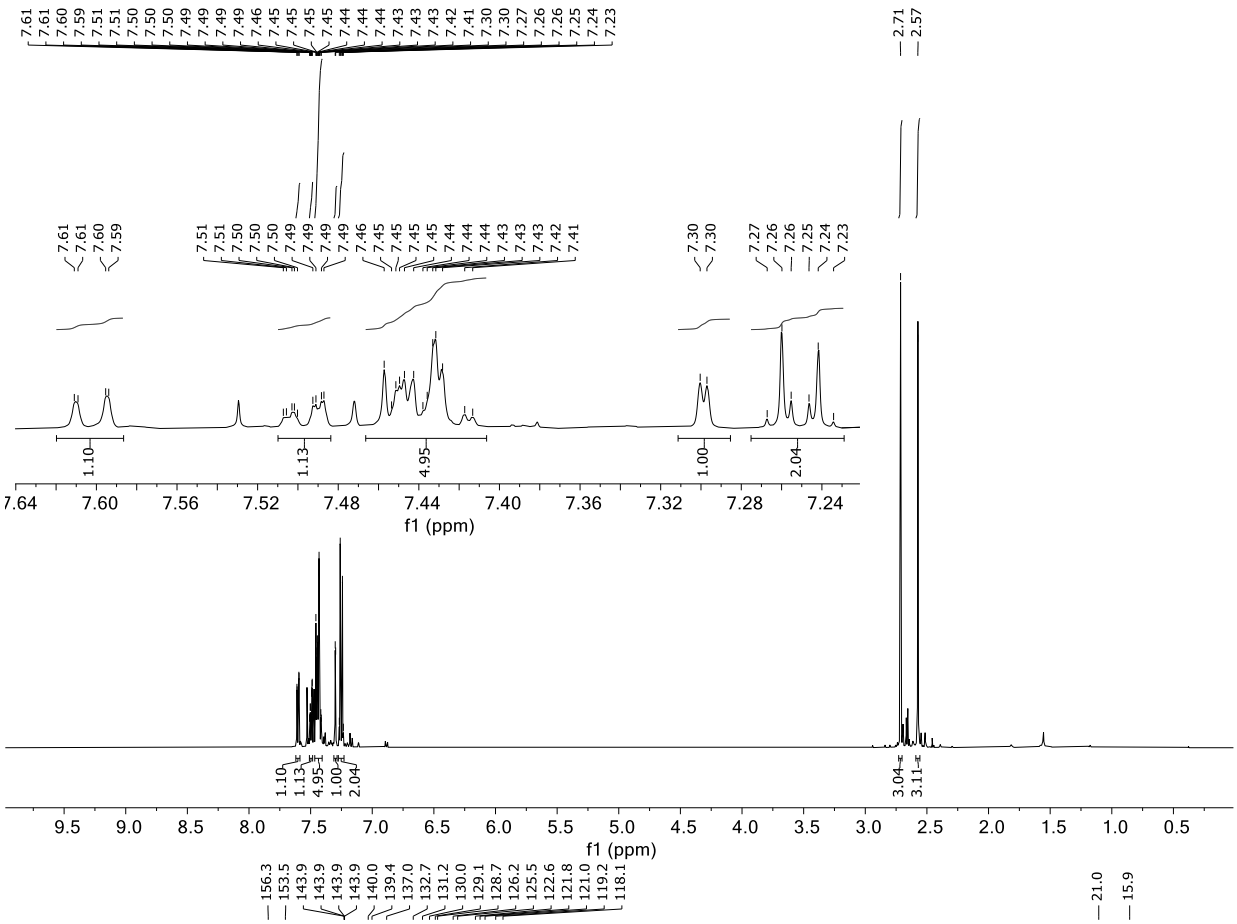

156.3
155.8
144.5
144.5
142.0
140.1
137.1
132.6
130.2
129.5
128.7
126.2
124.9
122.6
121.8
120.3
119.6
119.2
118.0
21.0
f1 (ppm)

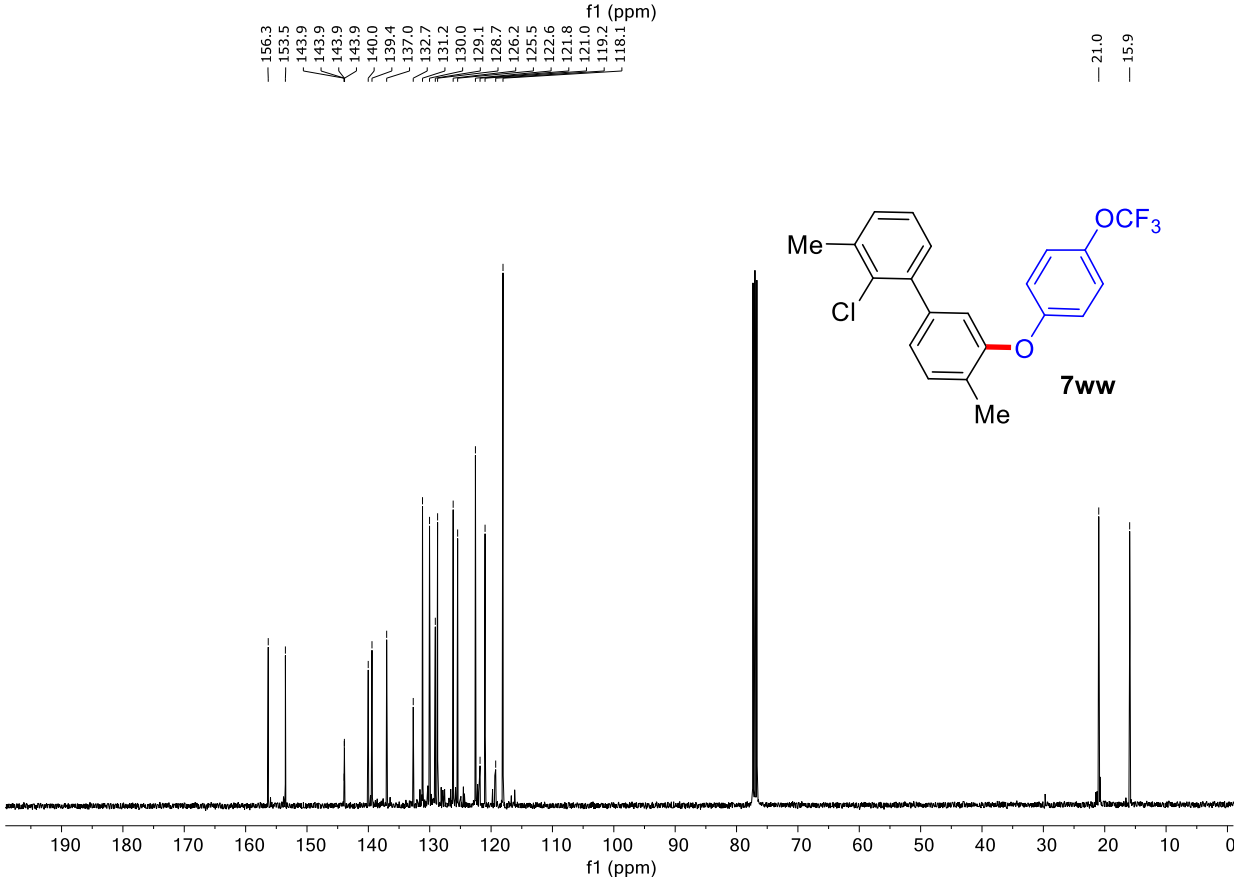
Me
Cl
O
OCF3

7dw


f1 (ppm)

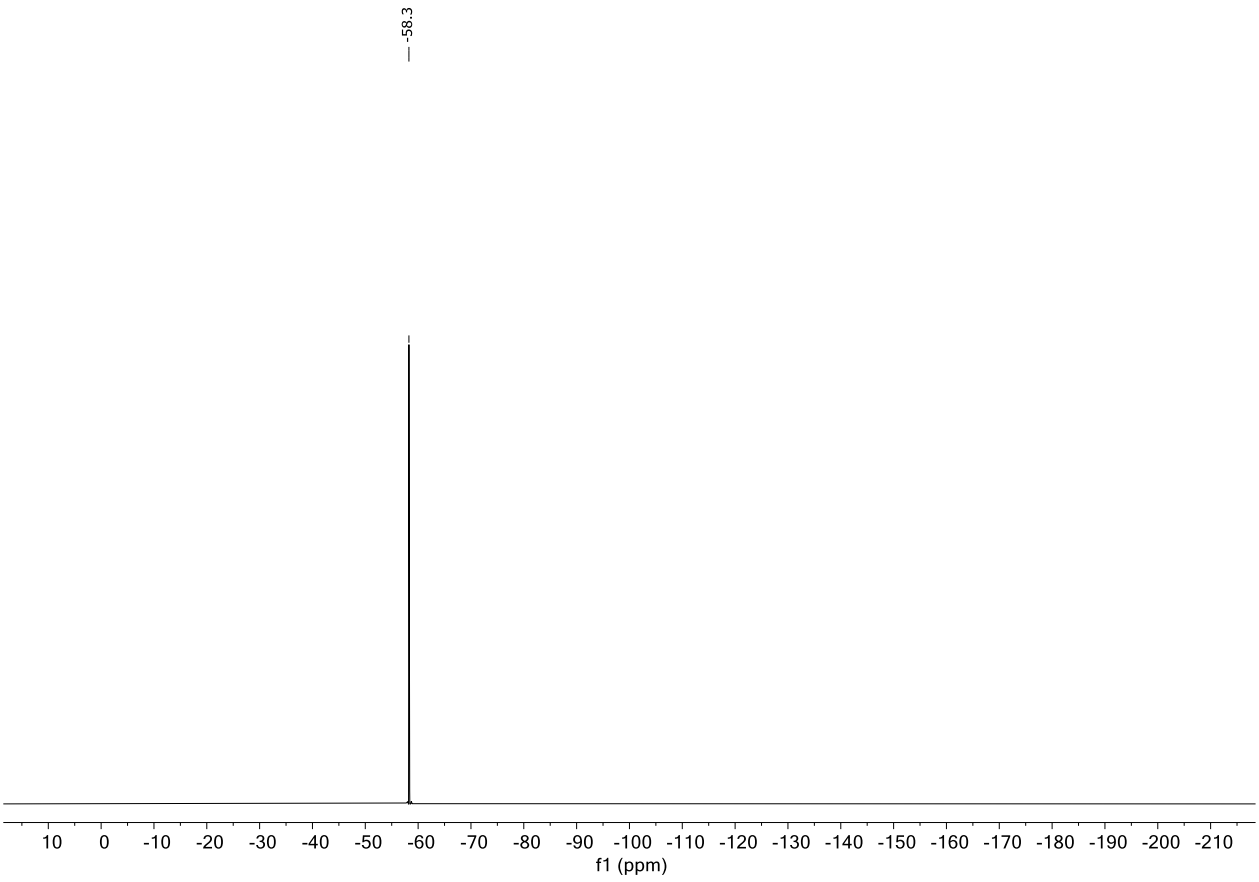

-58.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

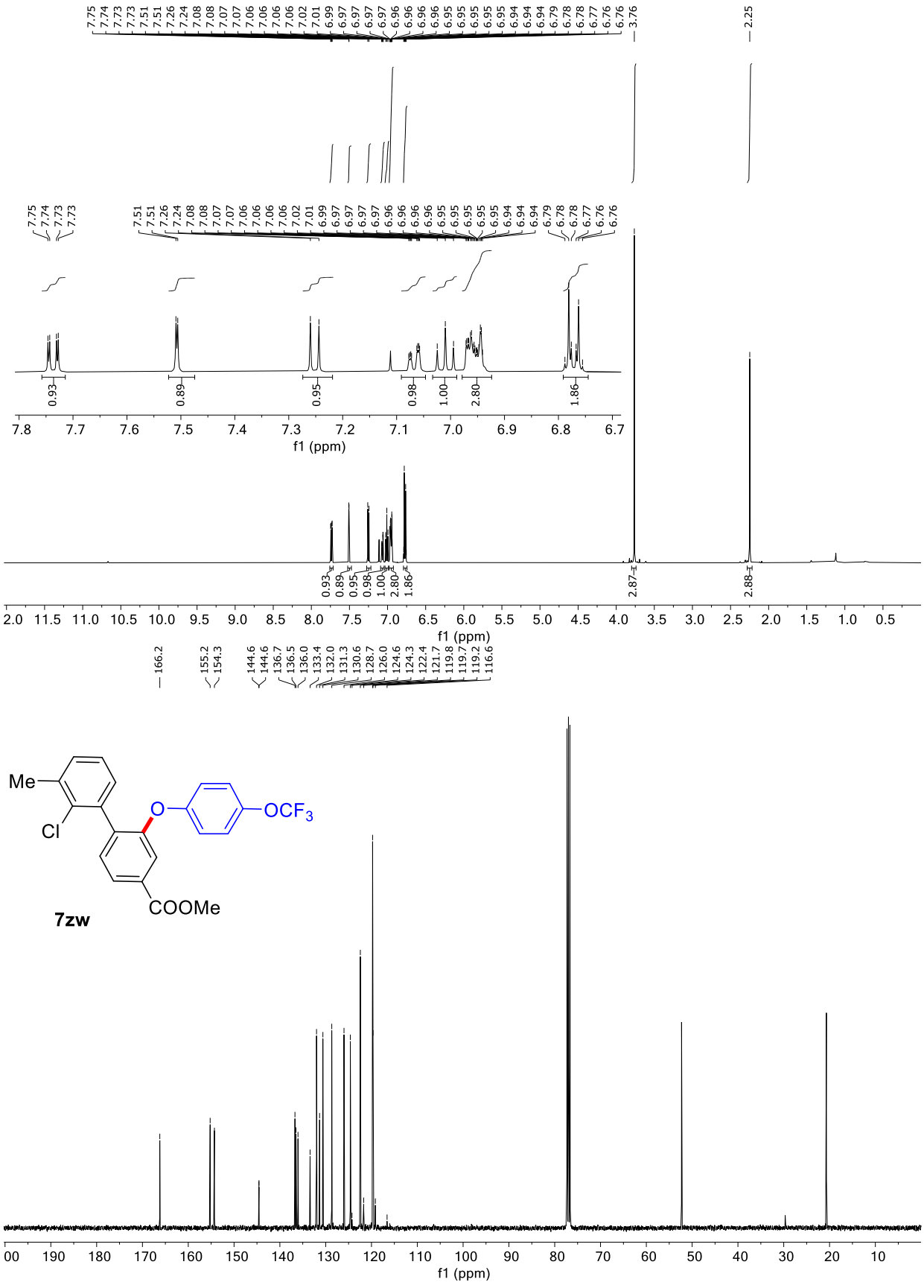

7.61 7.61 7.60 7.59 7.51 7.51 7.50 7.50 7.50 7.49 7.49 7.49 7.49 7.46 7.45 7.45 7.45 7.45 7.44 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.30 7.30 7.27 7.26 7.26 7.25 7.24 7.23
2.71 2.57
1.10 1.13 4.95 1.00 2.04
3.04 3.11
f1 (ppm)

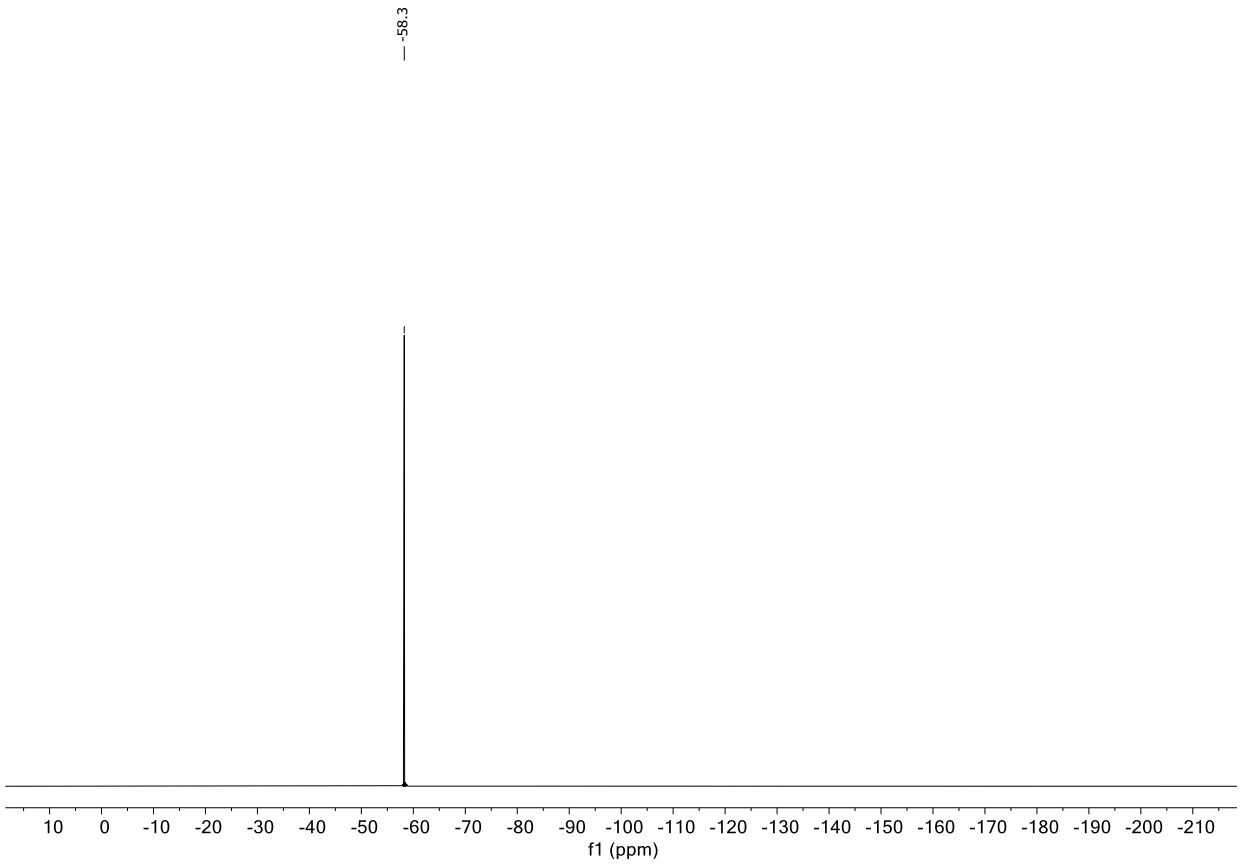

156.3 153.5 143.9 143.9 143.9 143.9 140.0 139.4 137.0 132.7 131.2 130.0 129.1 128.7 126.2 125.5 122.6 121.8 121.0 119.2 118.1
21.0 15.9
f1 (ppm)

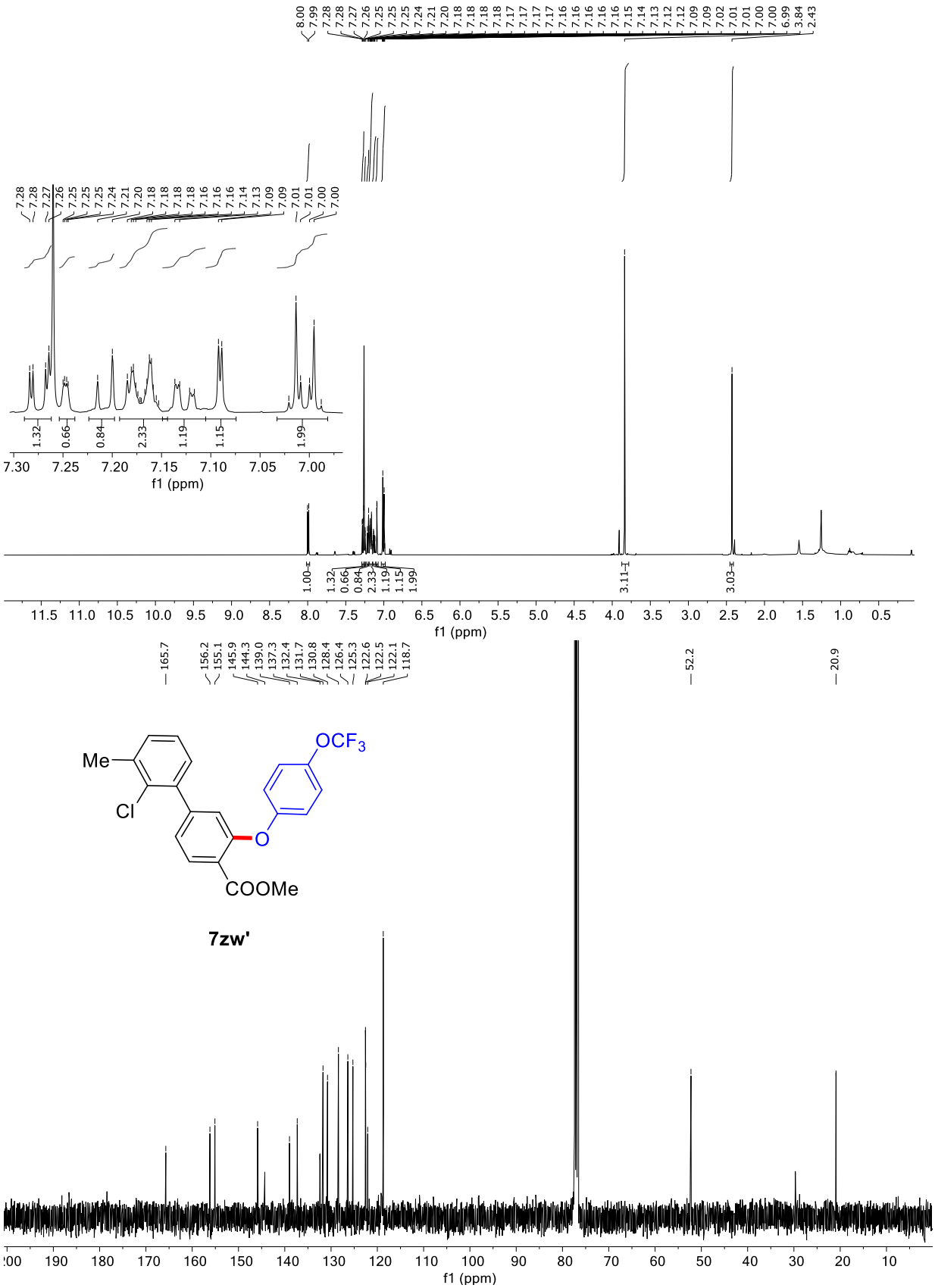
Me
Cl
O
OCF3
Me

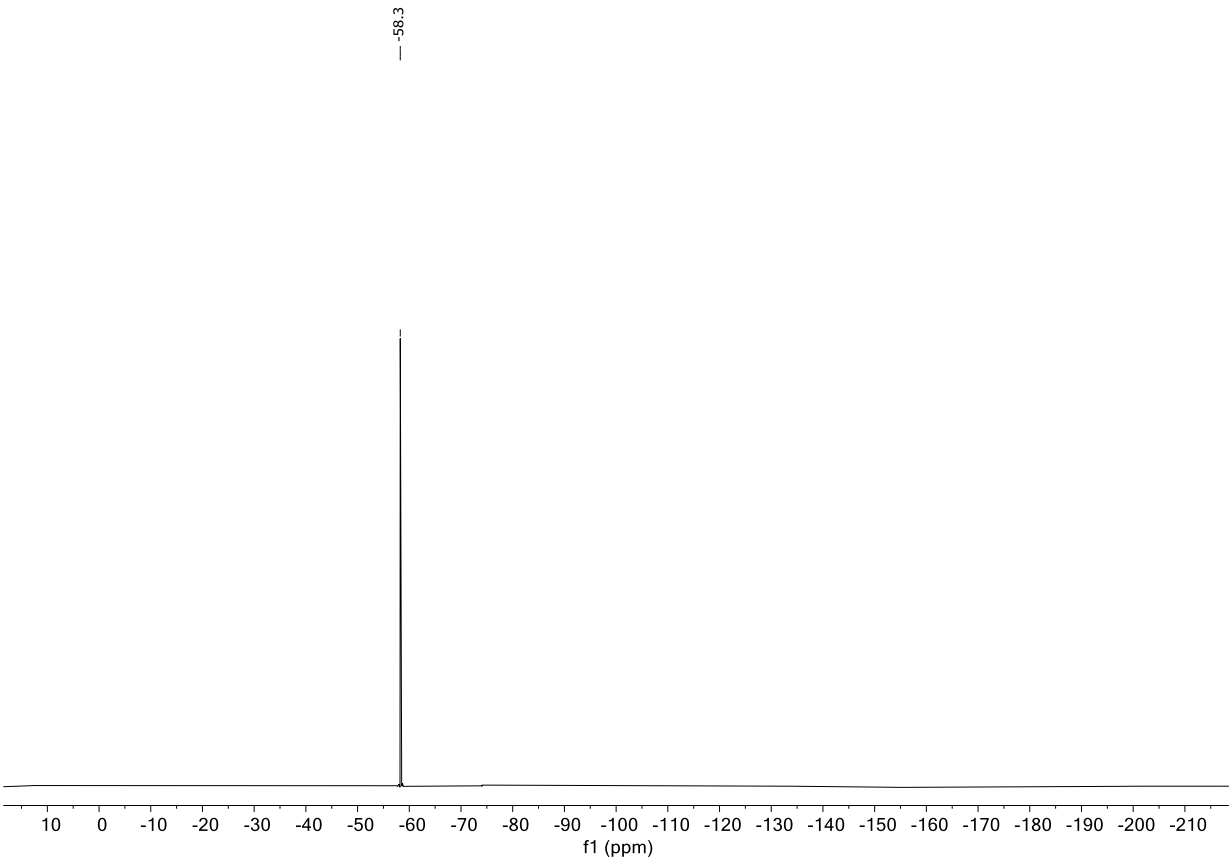
7ww

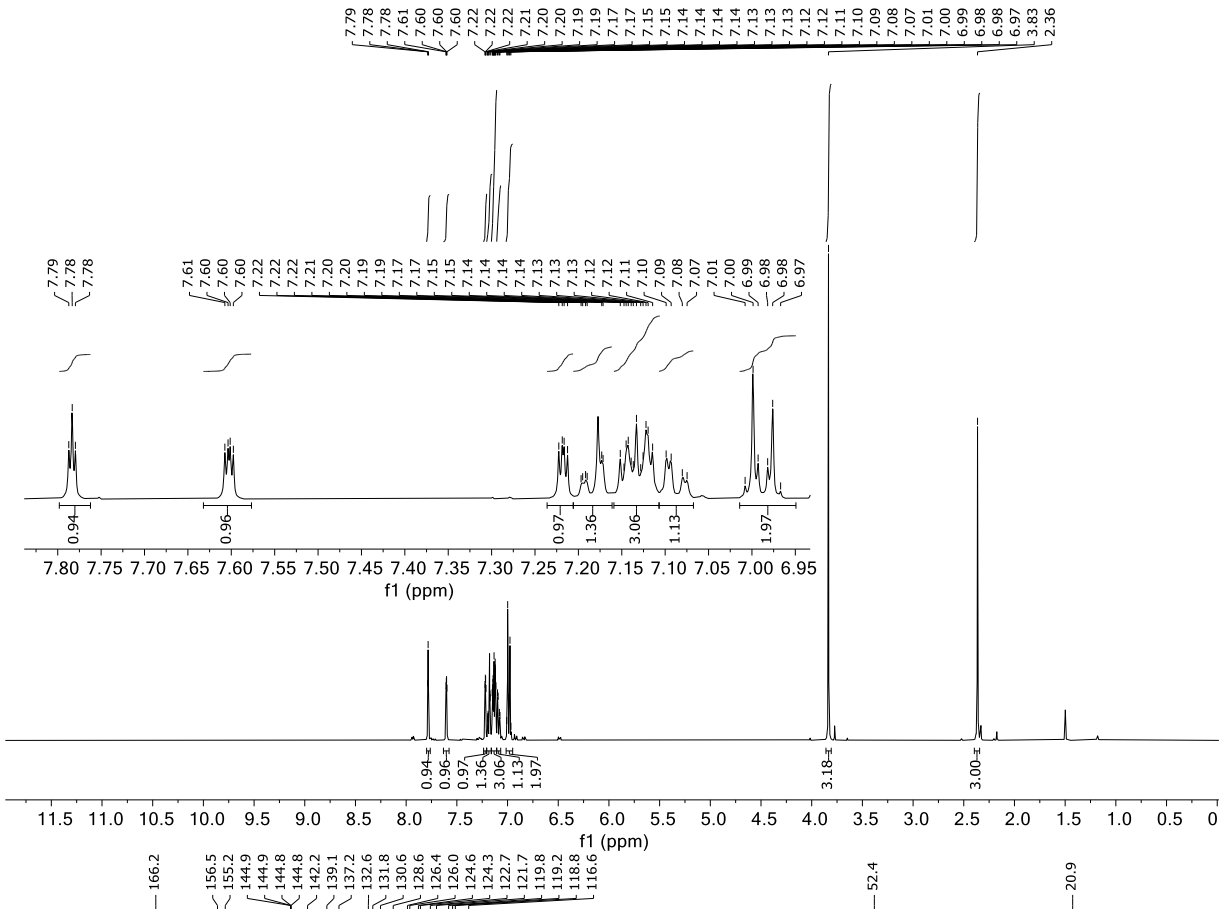

-58.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

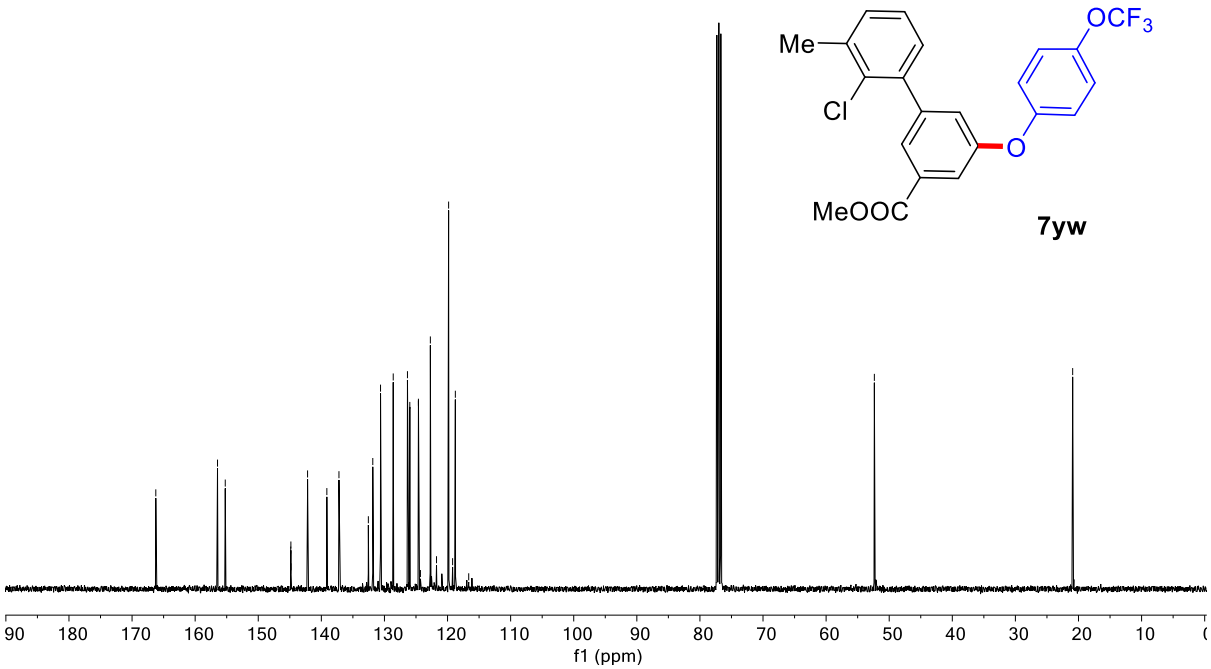

7.75 7.74 7.73 7.73 7.51 7.51 7.26 7.24 7.08 7.08 7.07 7.07 7.06 7.06 7.06 7.06 7.06 7.02 7.01 6.99 6.97 6.97 6.97 6.97 6.96 6.96 6.96 6.96 6.95 6.95 6.95 6.95 6.94 6.94 6.94 6.94 6.79 6.78 6.78 6.77 6.76 6.76 6.76 3.76 2.25
0.93 0.89 0.95 0.98 1.00 2.80 1.86
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
0.93 0.89 0.95 0.98 1.00 2.80 1.86 2.87 2.88
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
166.2 155.2 154.3 144.6 144.6 136.7 136.5 136.0 133.4 132.0 131.3 130.6 128.7 126.0 124.6 124.3 122.4 121.7 119.8 119.7 119.2 116.6
Me
Cl
O
OCF3
COOMe
7zw
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-58.3
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)

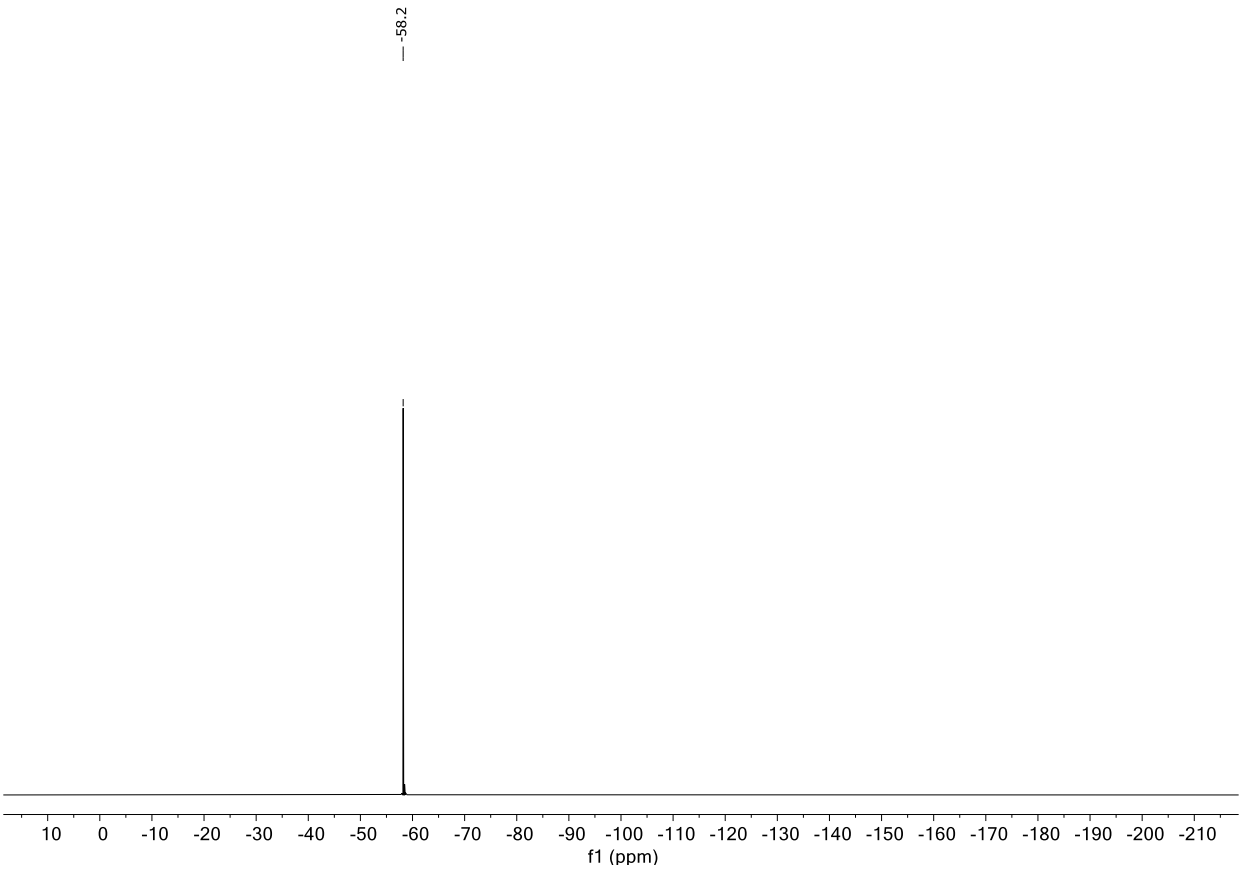

Me
Cl
O
OCF3
COOMe
7zw'
f1 (ppm)

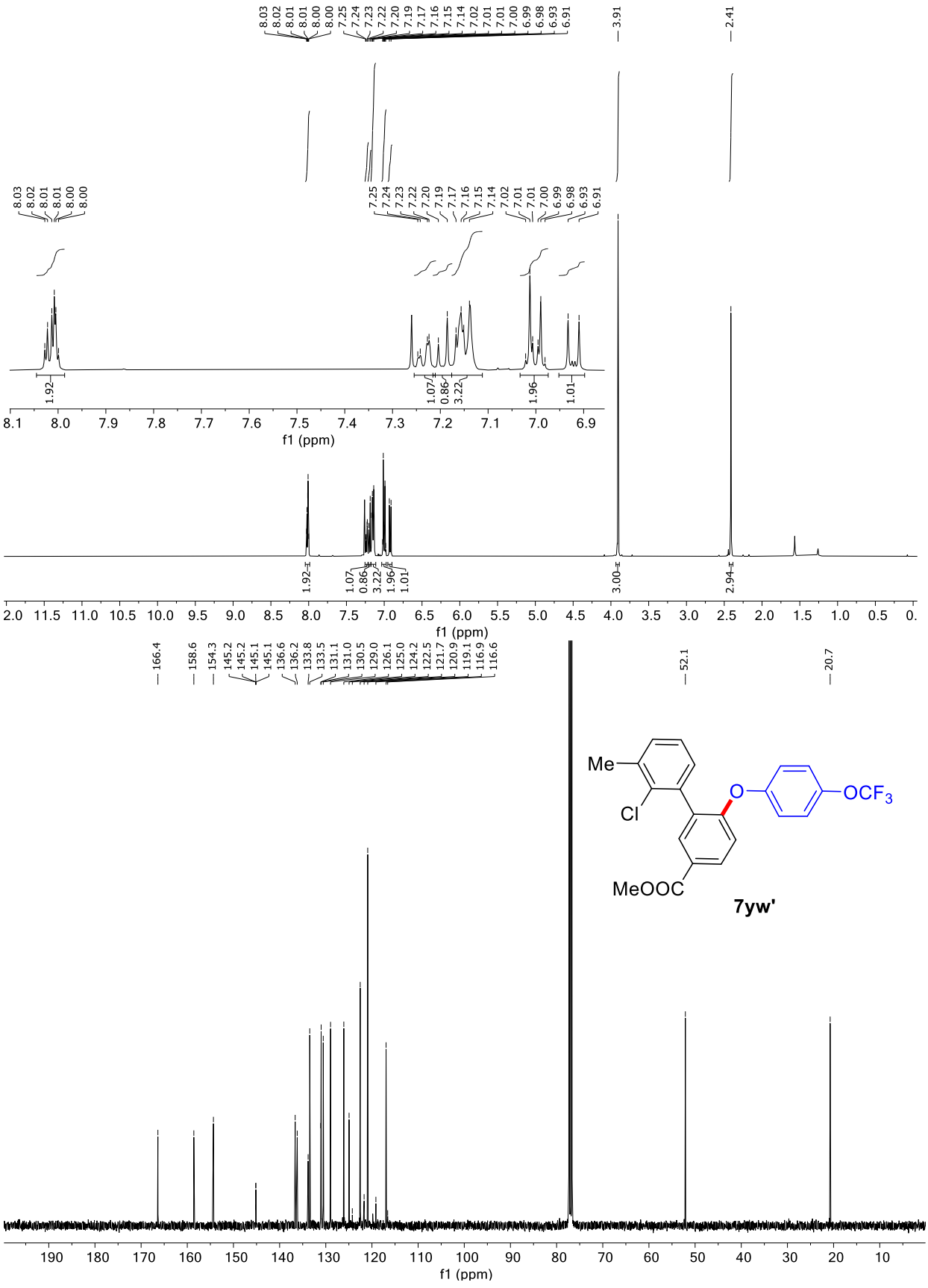

-58.3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

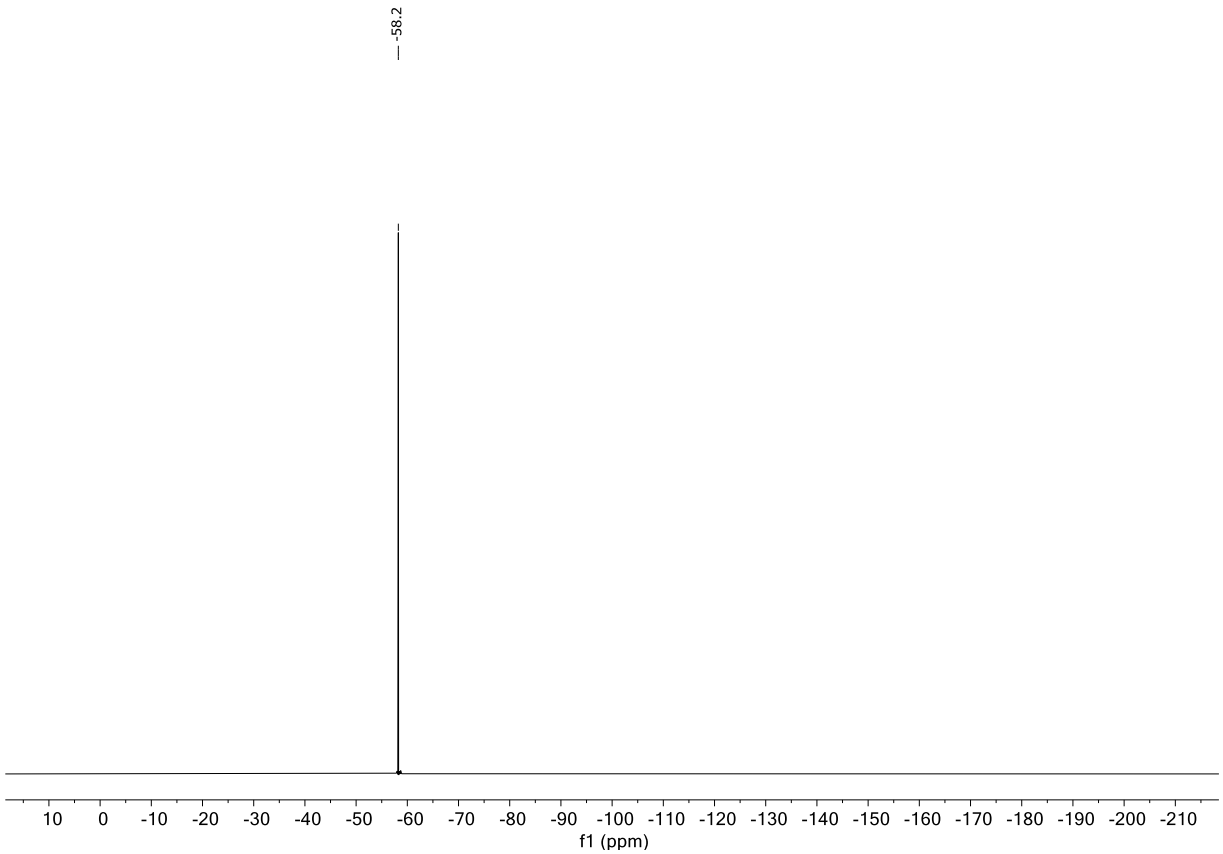


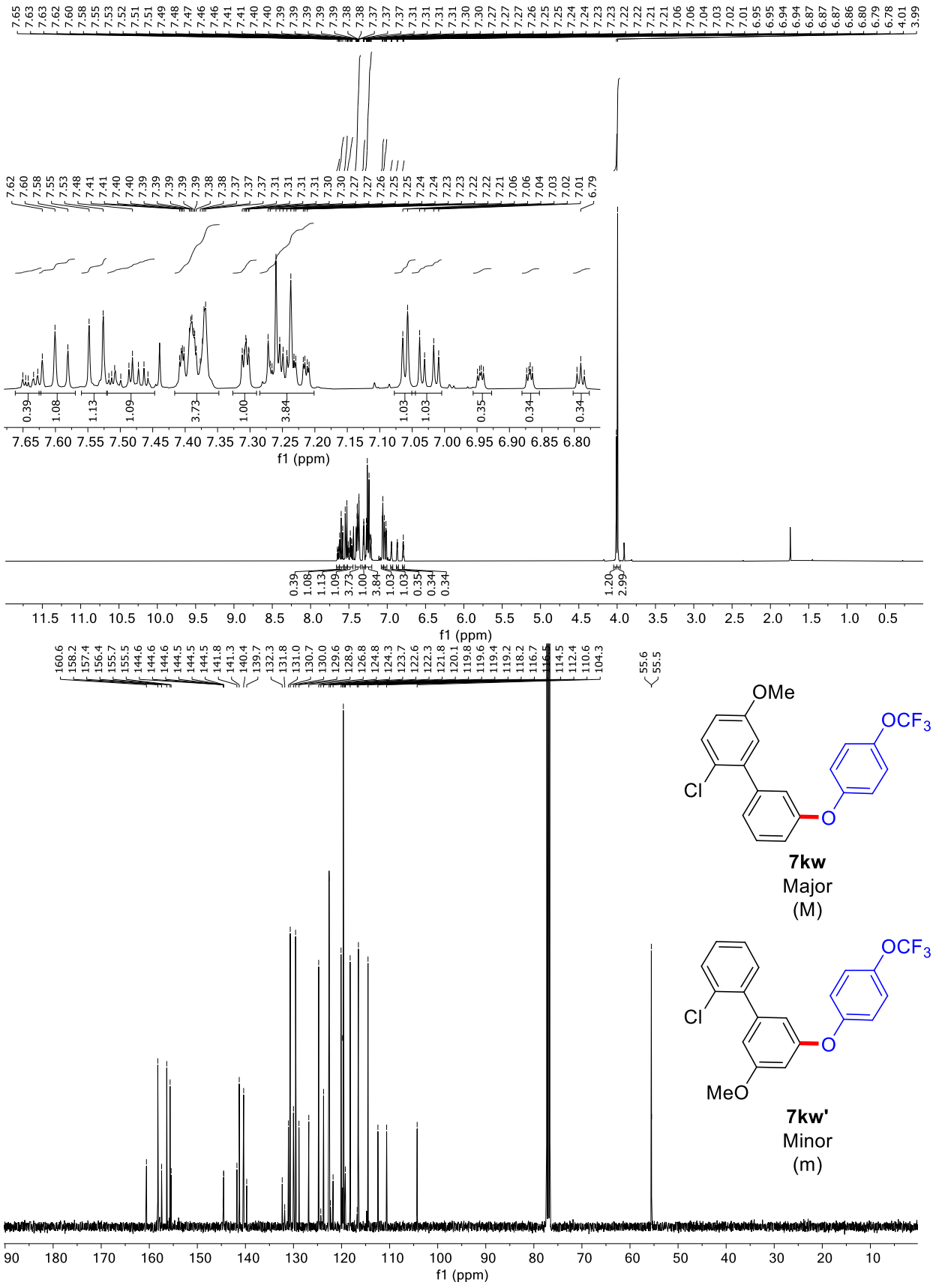


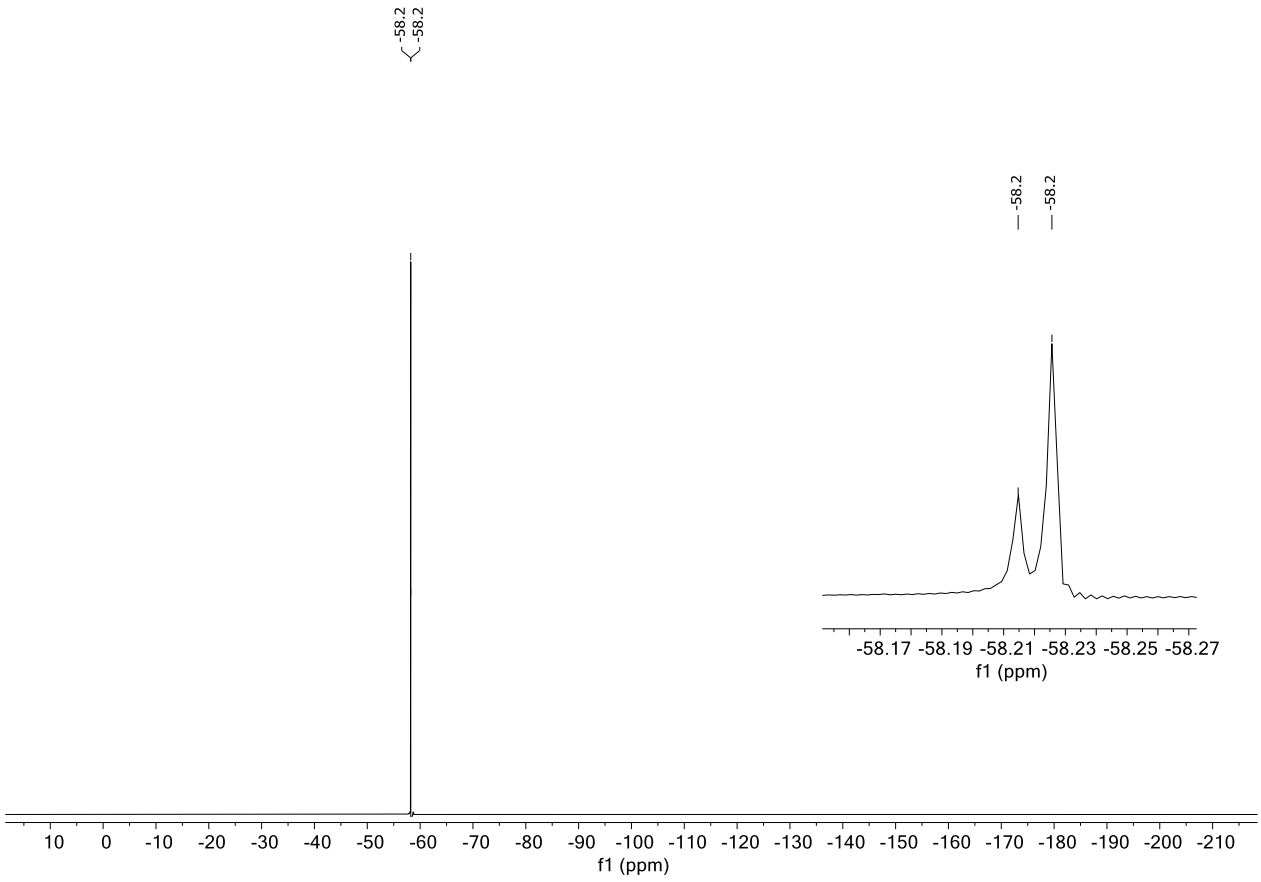
7yw

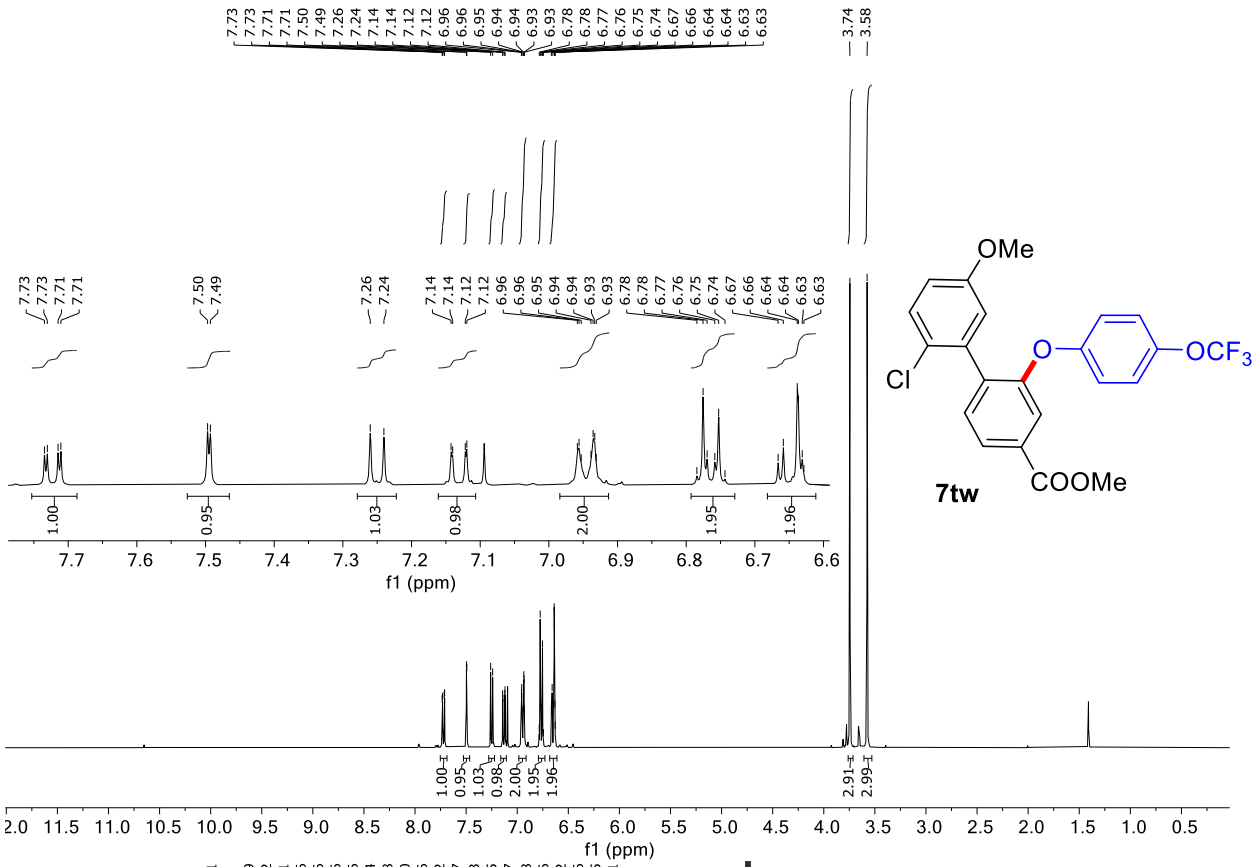

-58.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

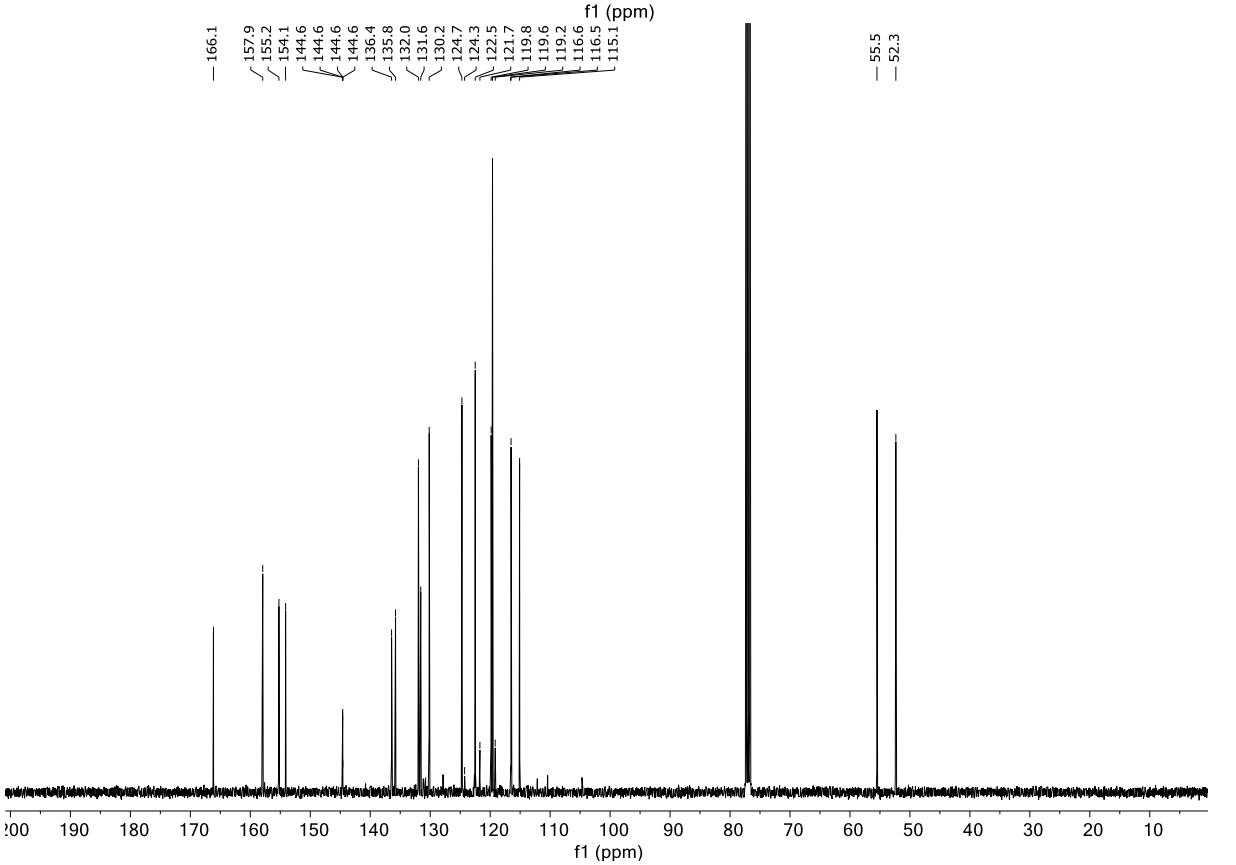

8.03
8.02
8.01
8.01
8.00
8.00
7.25
7.24
7.23
7.22
7.20
7.19
7.17
7.16
7.15
7.14
7.02
7.01
7.01
7.00
6.99
6.98
6.93
6.91
3.91
2.41
1.92
1.07
0.86
3.22
1.96
1.01
3.00
2.94
f1 (ppm)
166.4
158.6
154.3
145.2
145.2
145.1
145.1
136.6
136.2
133.8
133.5
131.1
131.0
130.5
129.0
126.1
125.0
124.2
122.5
121.7
120.9
119.1
116.9
116.6
52.1
20.7
Me
Cl
O
OCF3
MeOOC
7yw'

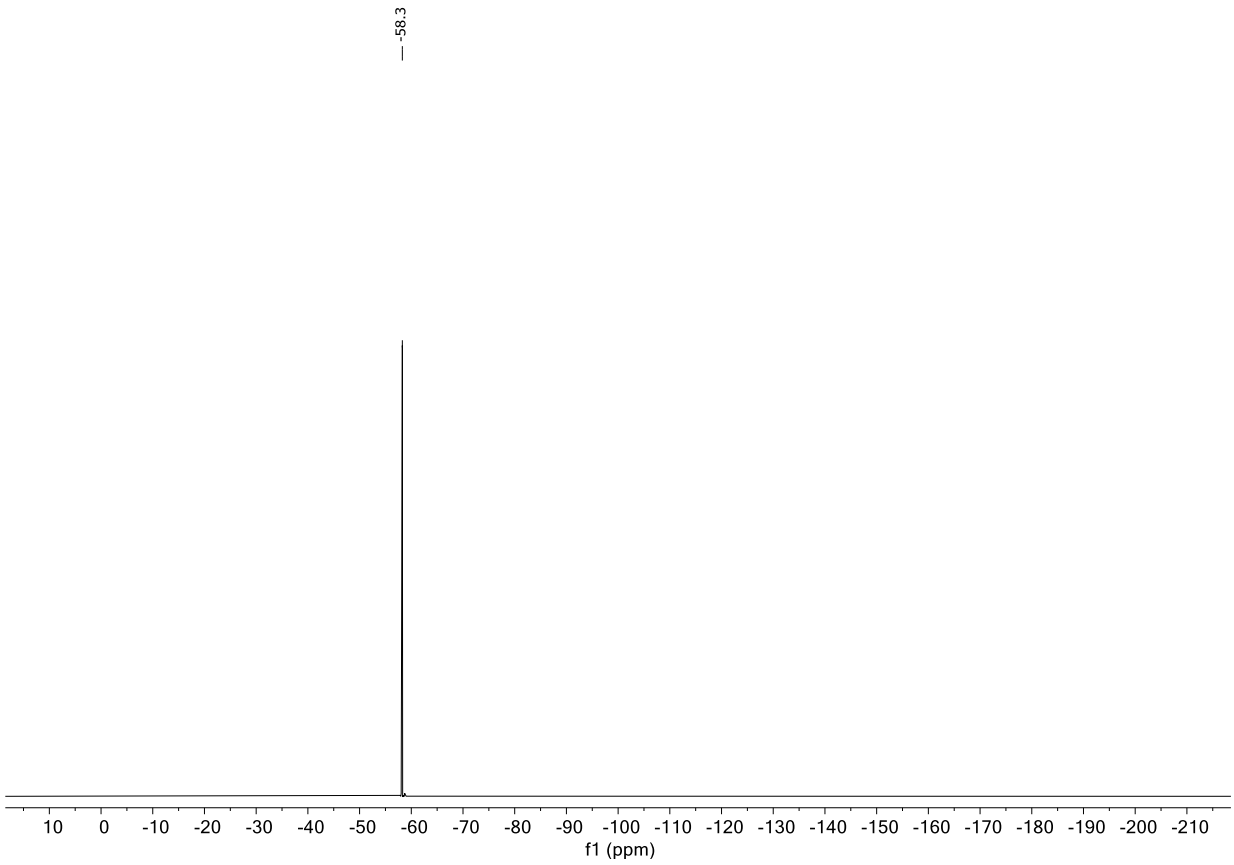

-58.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

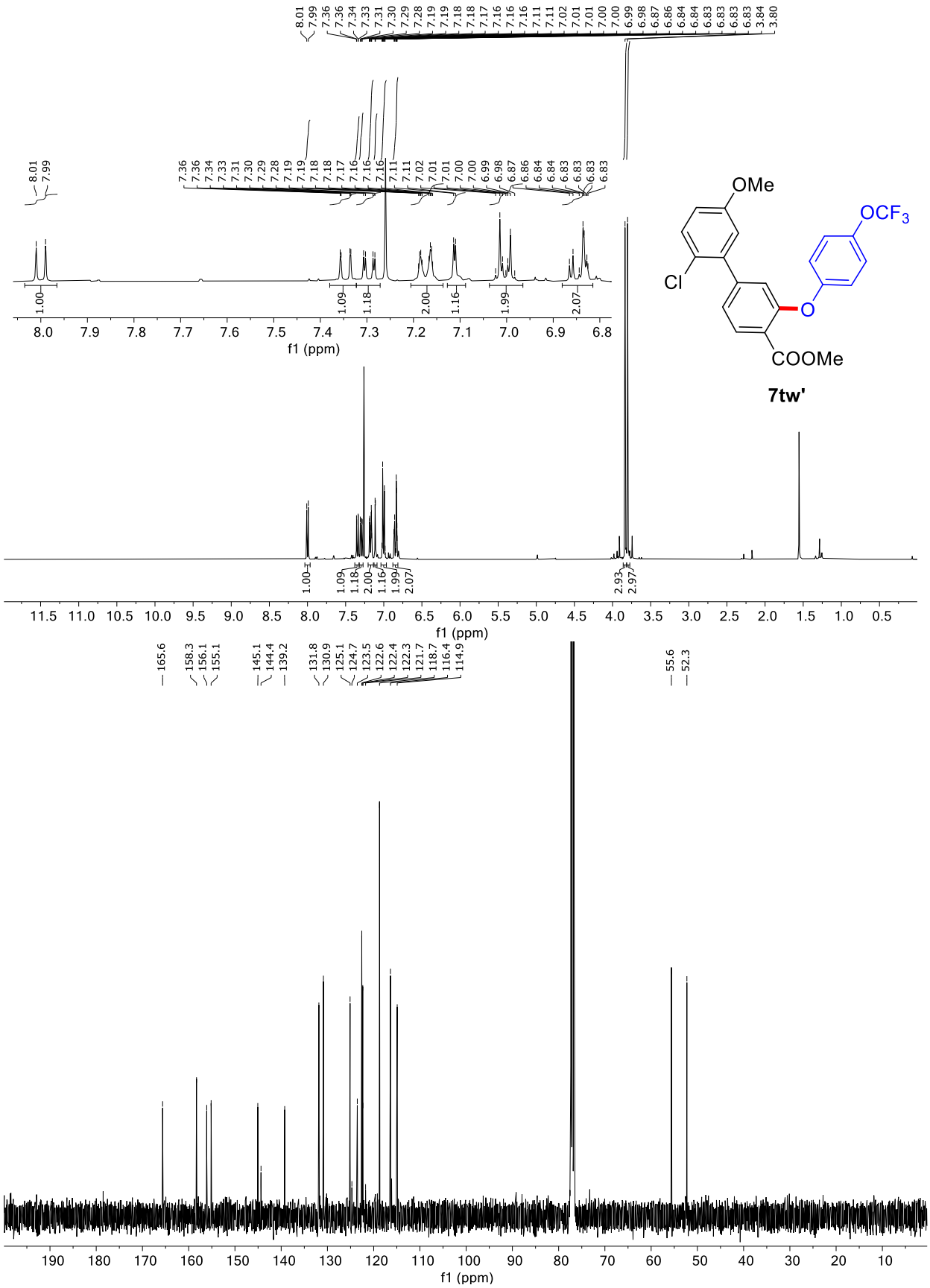

f1 (ppm)
OMe
OCF3
Cl
O
7kw
Major
(M)
OCF3
Cl
O
MeO
7kw'
Minor
(m)

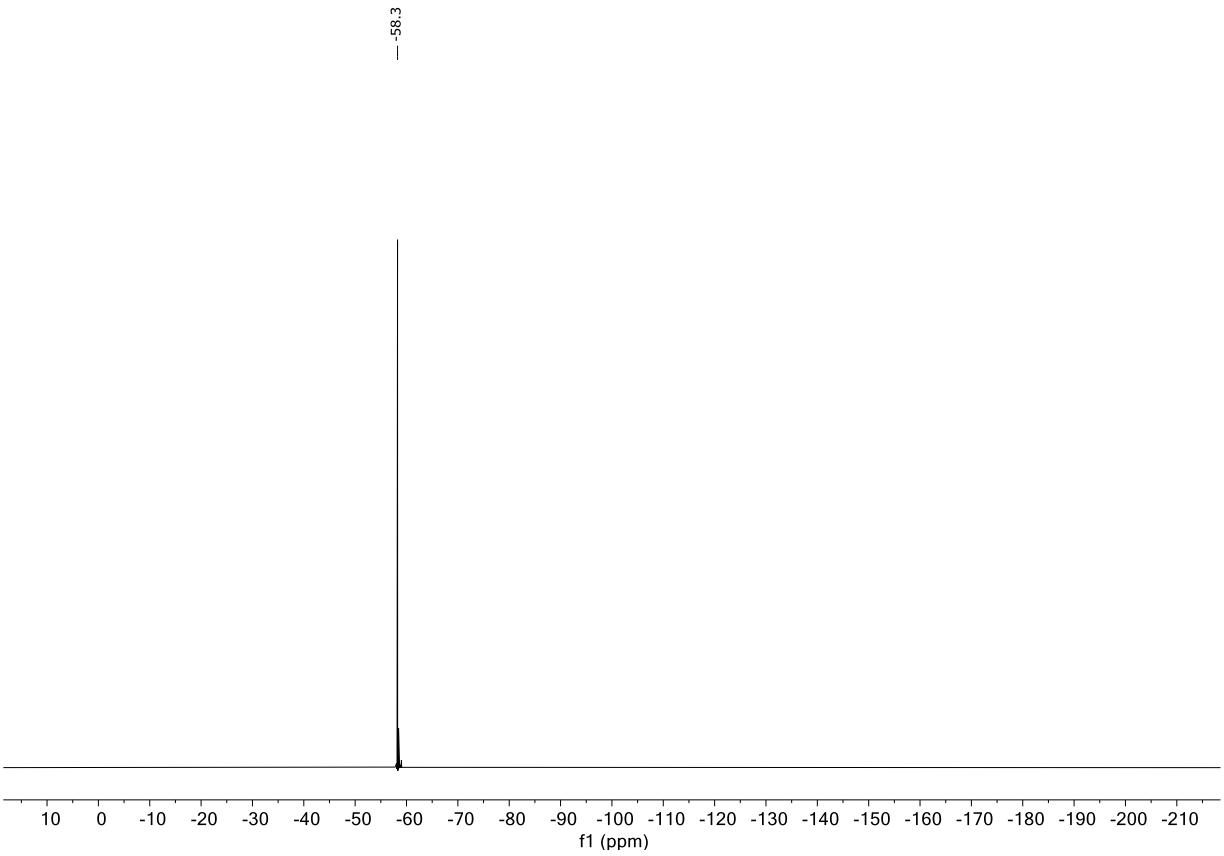

-58.2
-58.2
-58.2
-58.2
-58.17 -58.19 -58.21 -58.23 -58.25 -58.27
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

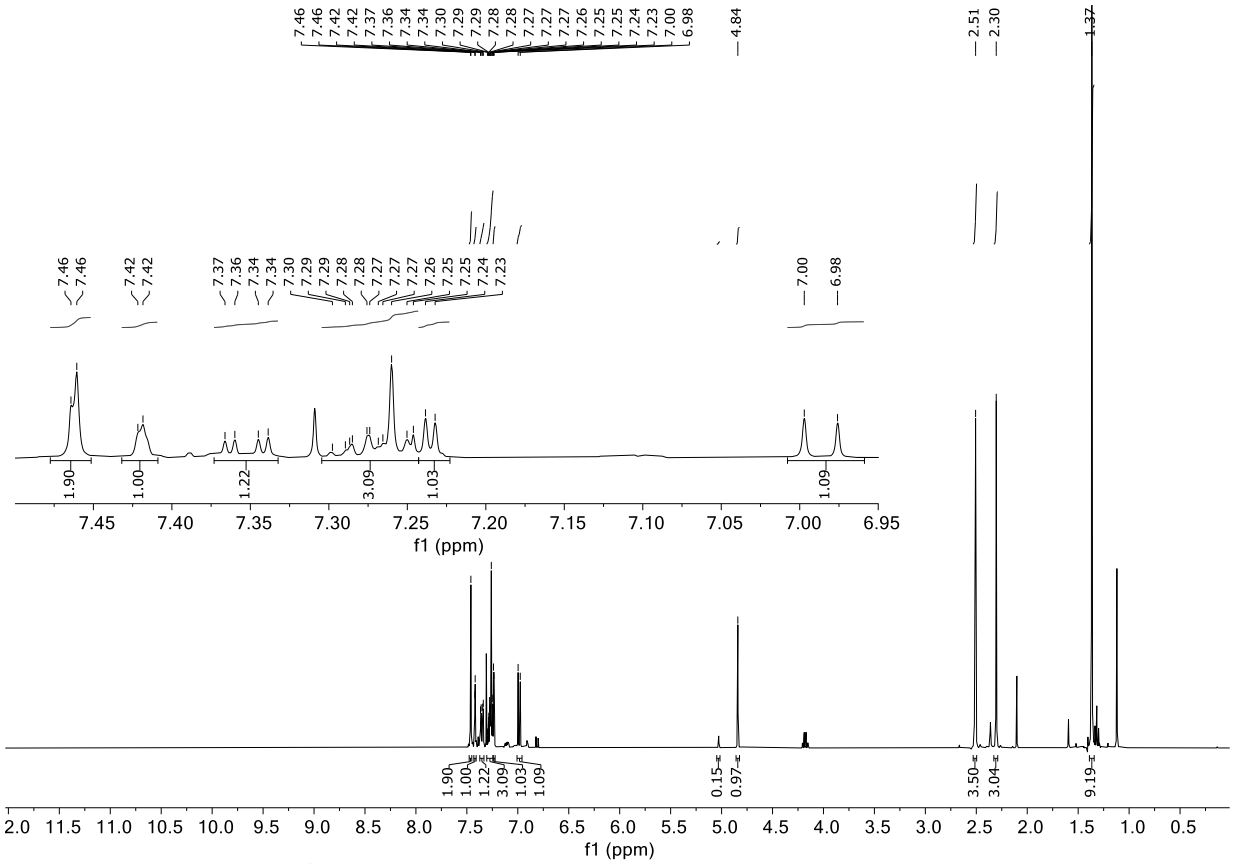

OMe
Cl
O
OCF3
COOMe
7tw
f1 (ppm)


f1 (ppm)


-58.3
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)

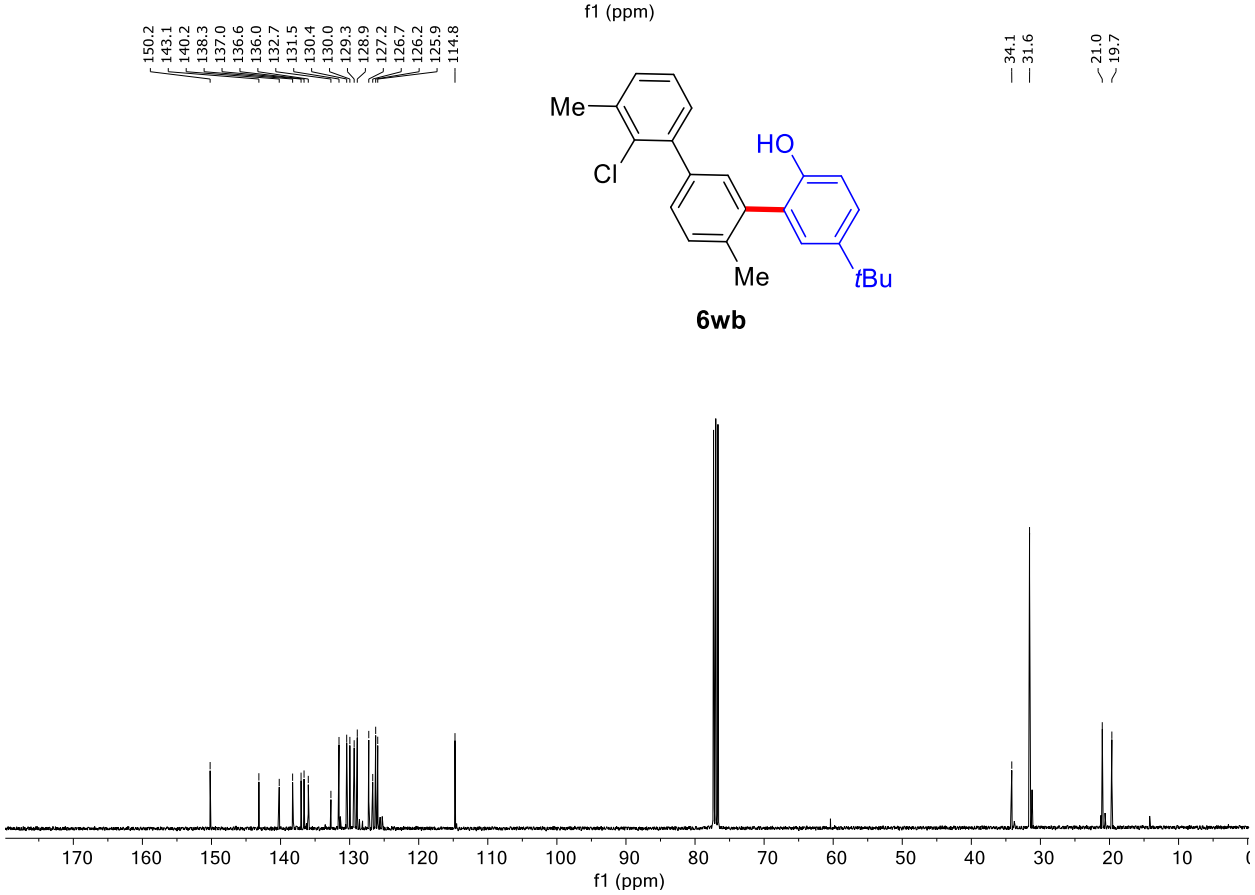

OMe
OCF3
Cl
O
COOMe
7tw'
f1 (ppm)

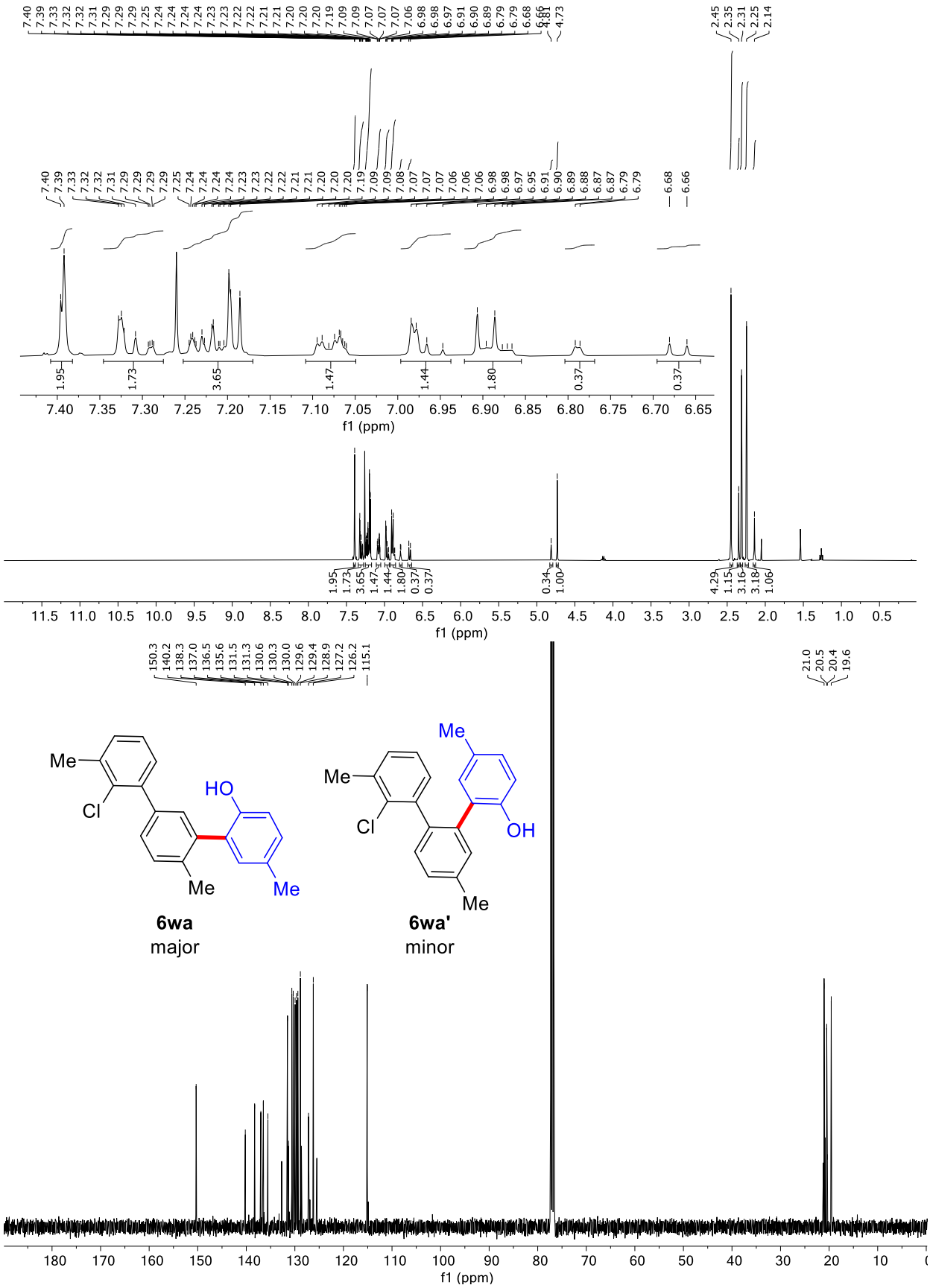

-58.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

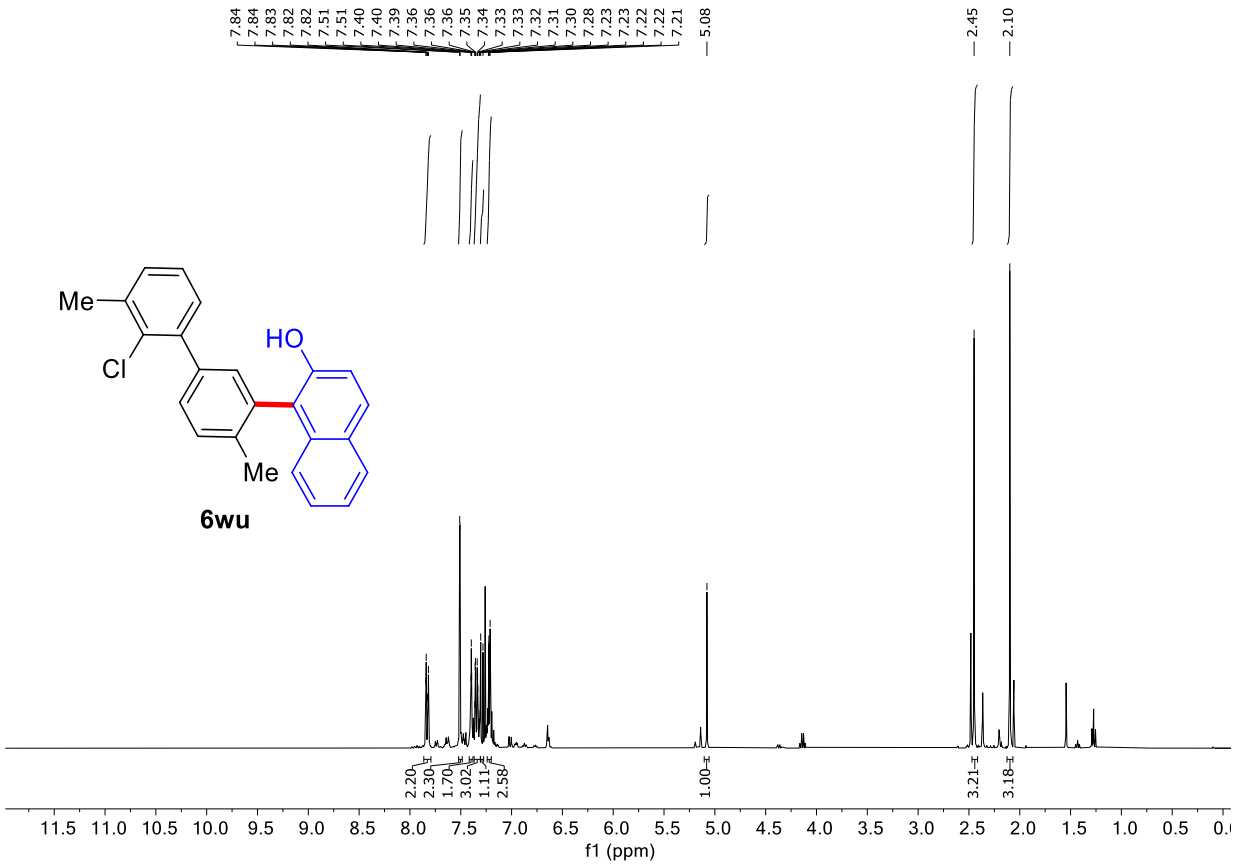

7.46
7.46
7.42
7.42
7.37
7.36
7.34
7.34
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.00
6.98
4.84
2.51
2.30
1.37
1.90
1.00
1.22
3.09
1.03
1.09
0.15
0.97
3.50
3.04
9.19
f1 (ppm)

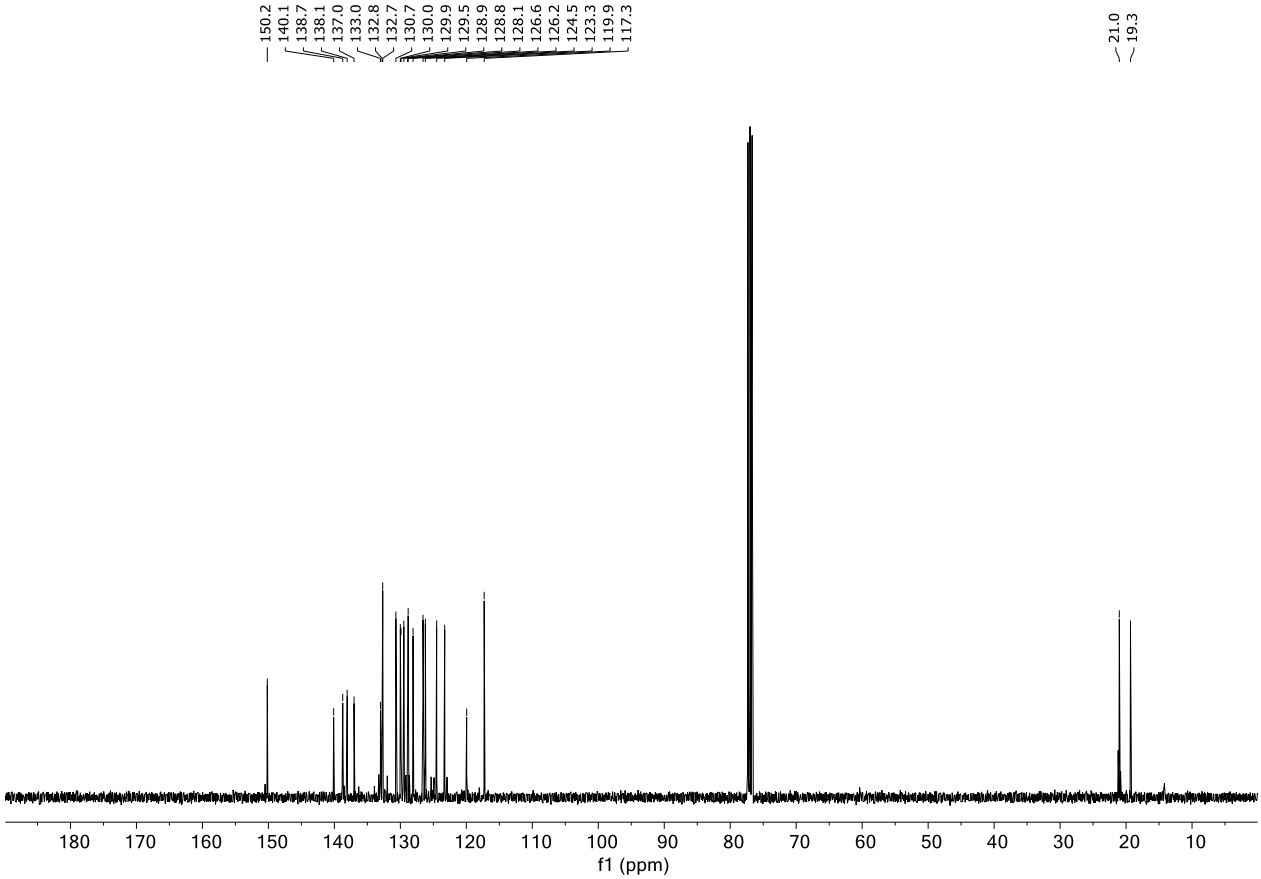
Me
Cl
HO
Me
tBu

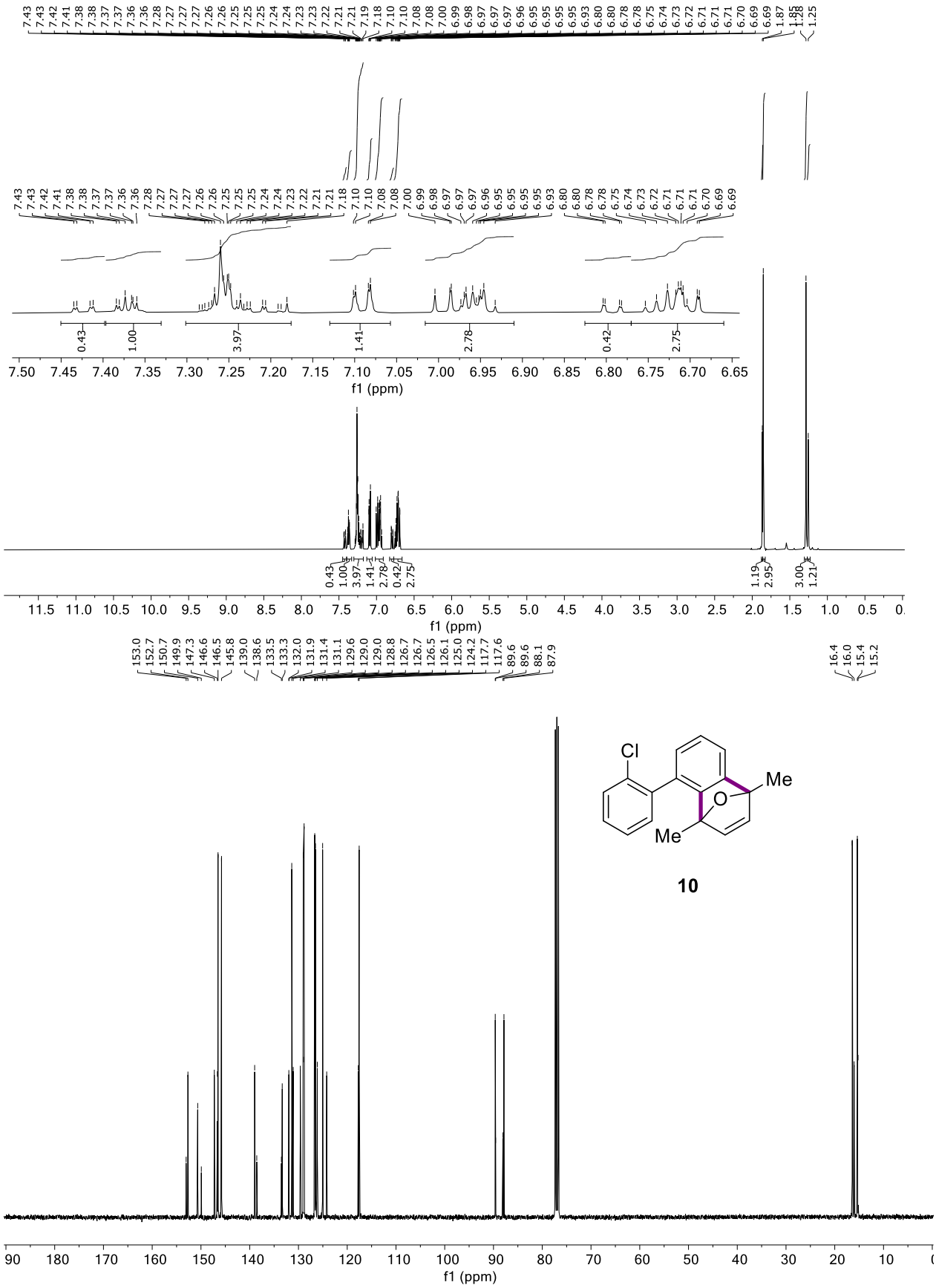
6wb

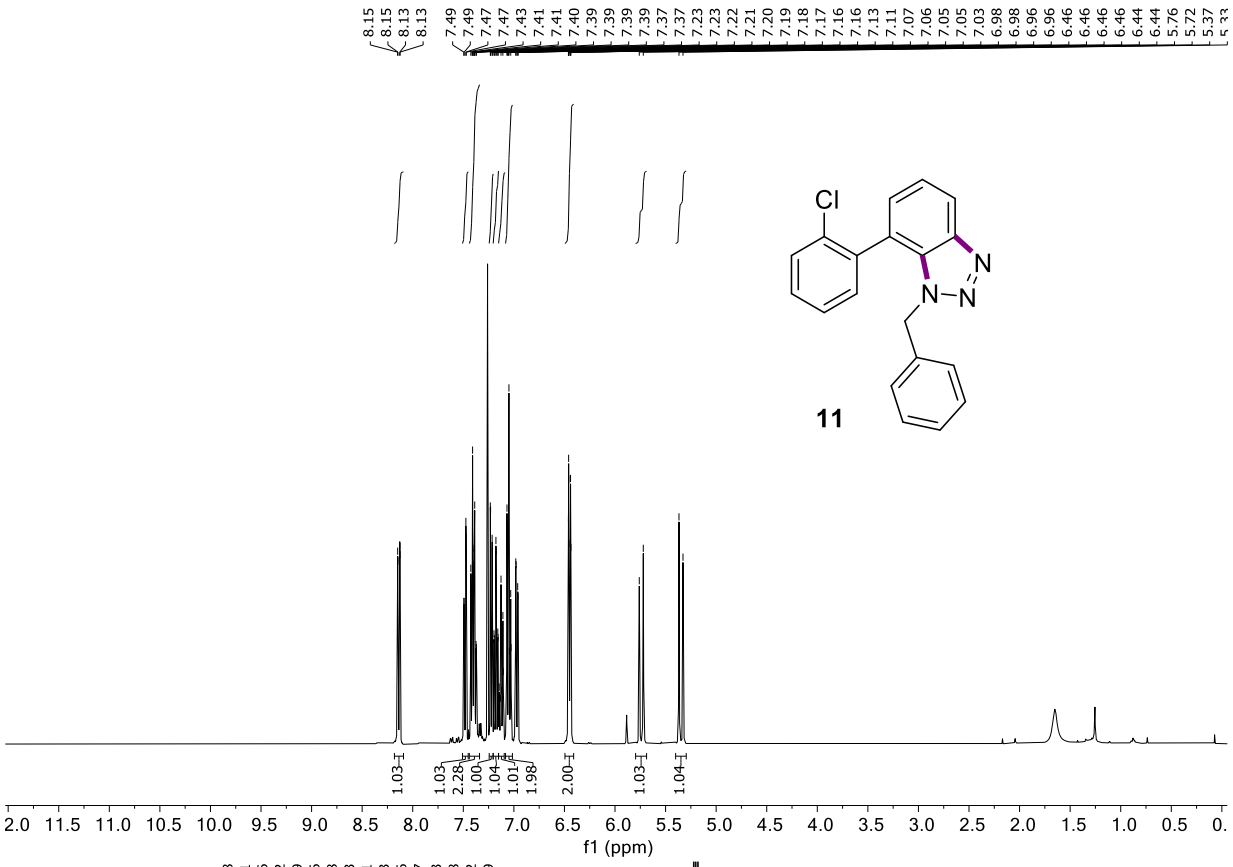

150.2
143.1
140.2
138.3
137.0
136.6
136.0
132.7
131.5
130.4
130.0
129.3
128.9
127.2
126.7
126.2
125.9
114.8
34.1
31.6
21.0
19.7
f1 (ppm)

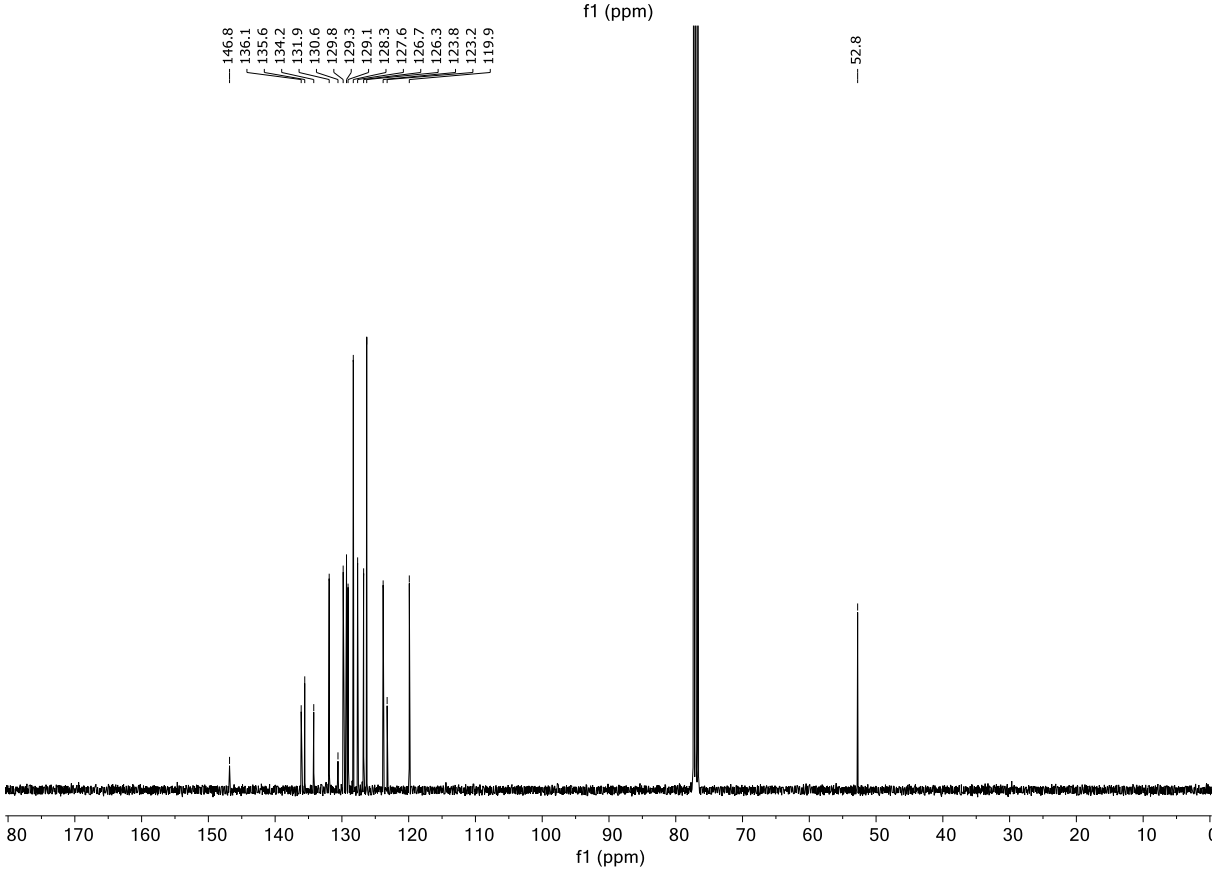

f1 (ppm)
Me
Cl
HO
Me
Me
6wa
major
Me
Me
Cl
OH
Me
6wa'
minor

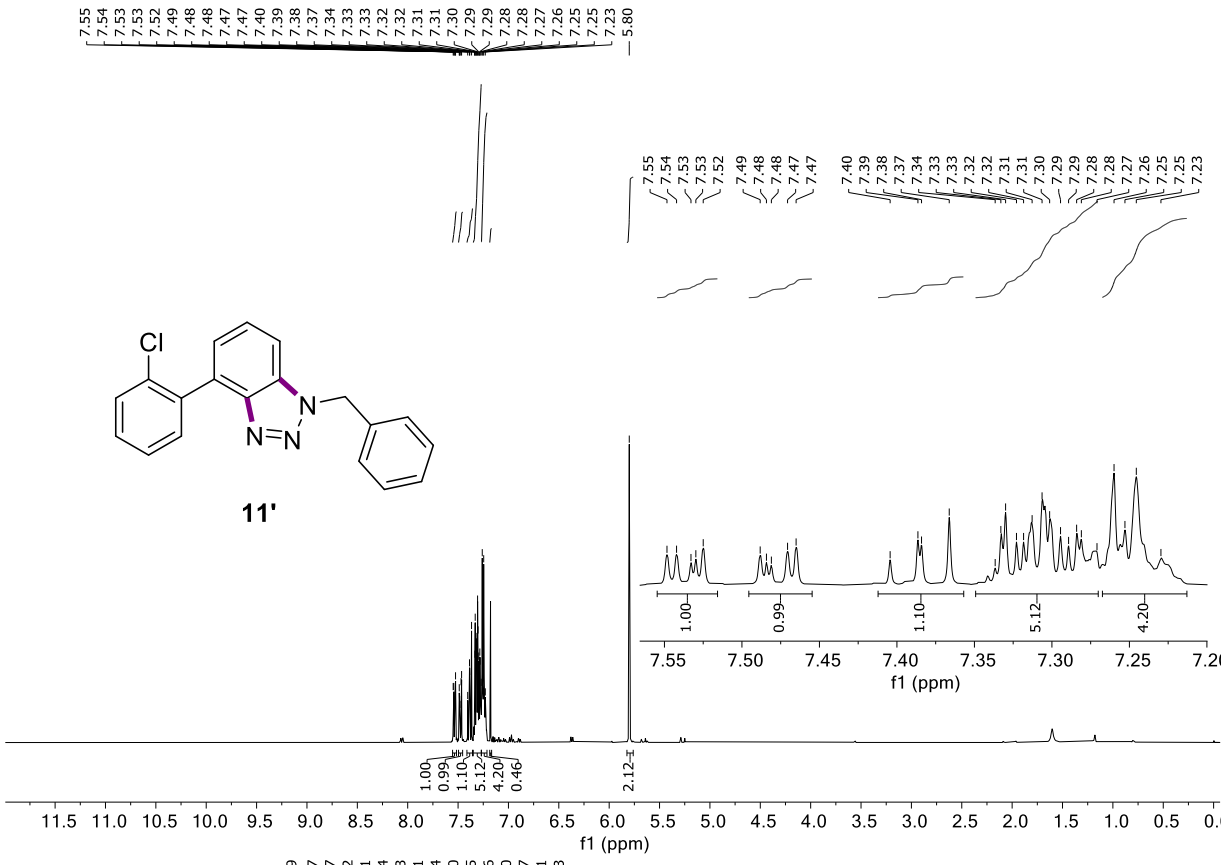

7.84
7.84
7.83
7.82
7.82
7.51
7.51
7.40
7.40
7.39
7.36
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.28
7.23
7.23
7.22
7.22
7.21
5.08
2.45
2.10
Me
Cl
HO
Me
6wu
2.20
2.30
1.70
3.02
1.11
2.58
1.00
3.21
3.18
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

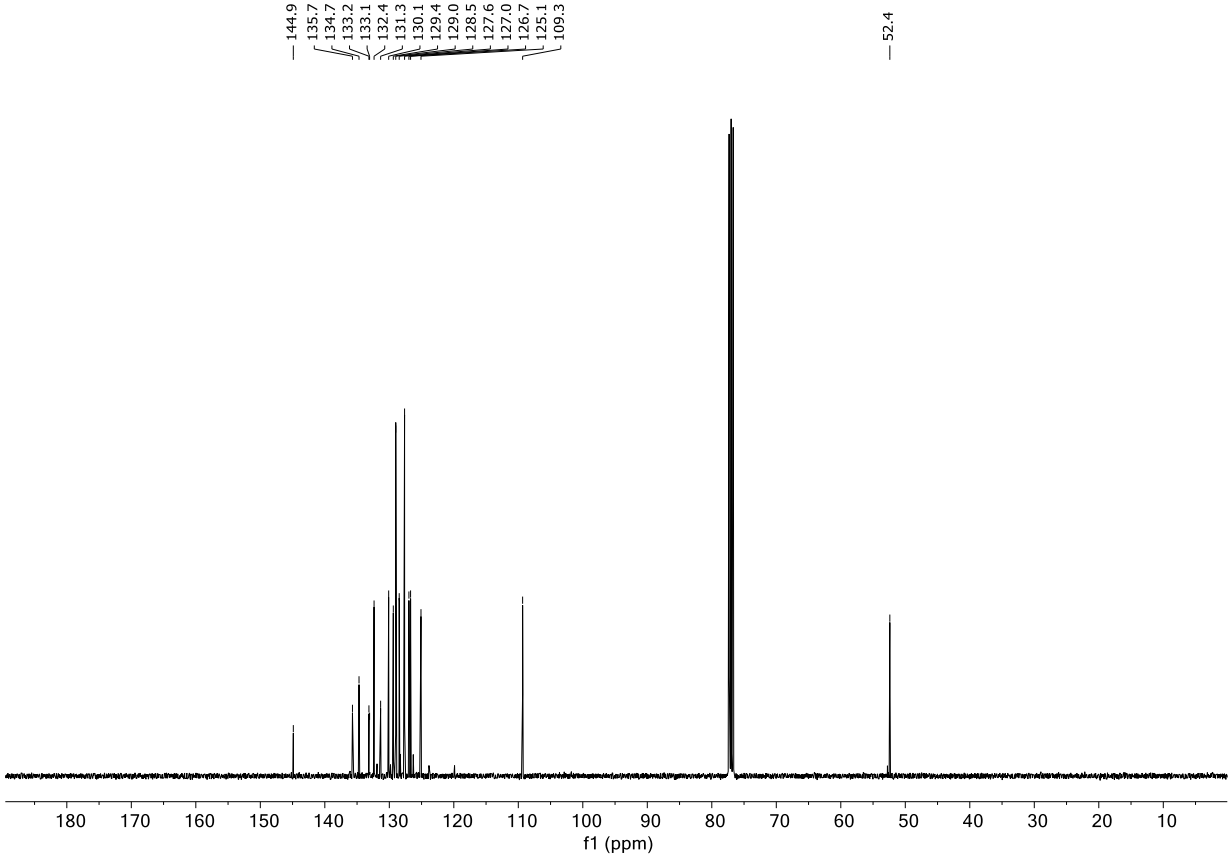

150.2
140.1
138.7
138.1
137.0
133.0
132.8
132.7
130.7
130.0
129.9
129.5
128.9
128.8
128.1
126.6
126.2
124.5
123.3
119.9
117.3
21.0
19.3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

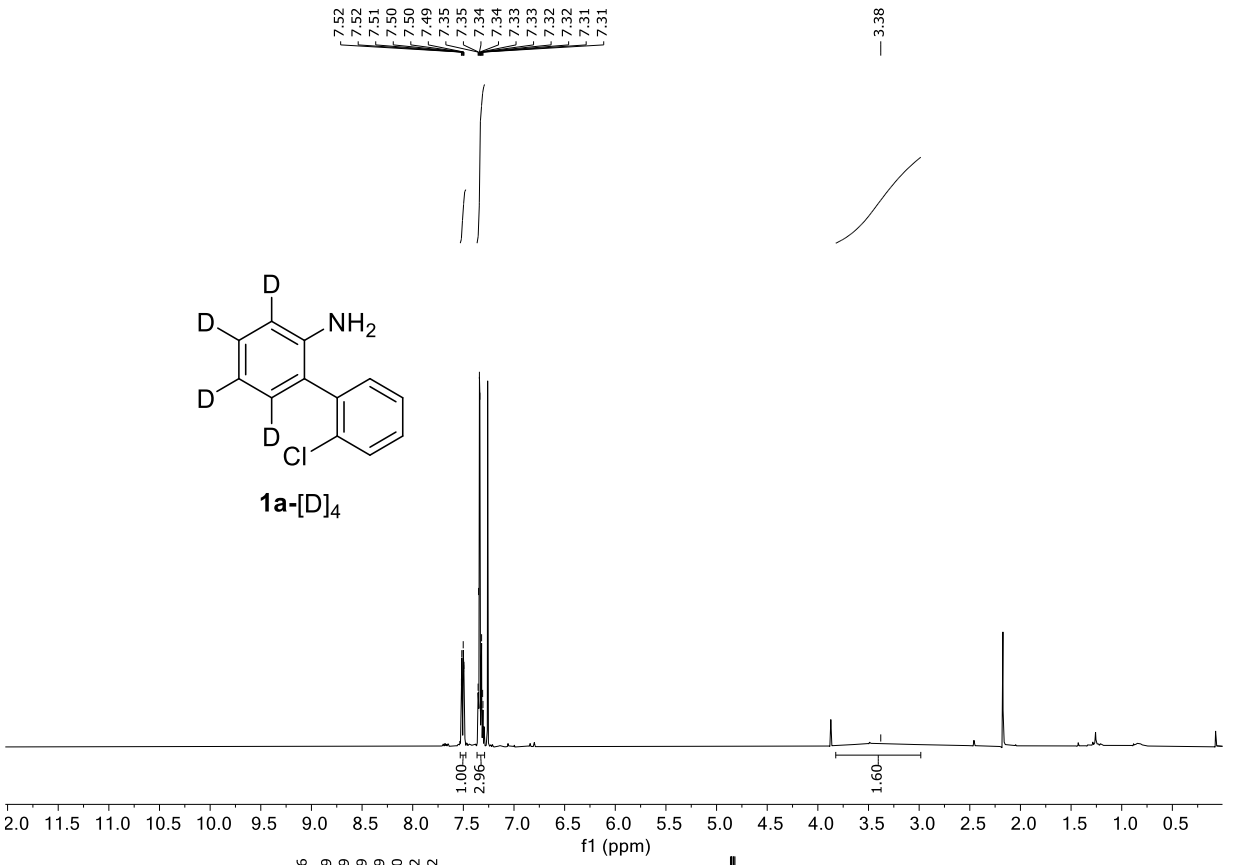

Cl
Me
O
Me
10
f1 (ppm)

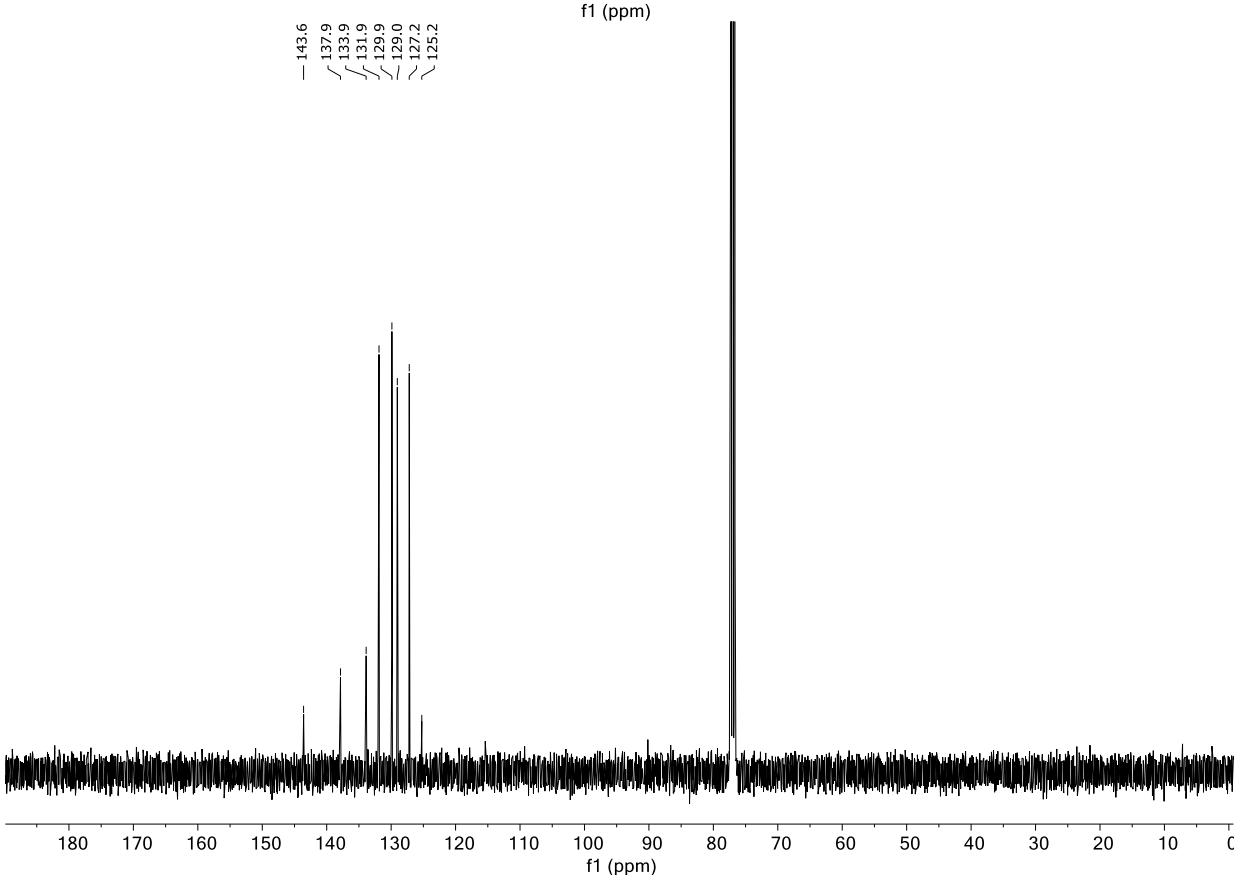

8.15
8.15
8.13
8.13
7.49
7.49
7.47
7.47
7.43
7.41
7.41
7.40
7.39
7.39
7.39
7.39
7.37
7.37
7.23
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.16
7.13
7.11
7.07
7.06
7.05
7.05
7.03
6.98
6.98
6.96
6.96
6.46
6.46
6.46
6.46
6.44
6.44
5.76
5.72
5.37
Cl
N
N–N
11
1.03
1.03
2.28
1.00
1.04
1.01
1.98
2.00
1.03
1.04
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

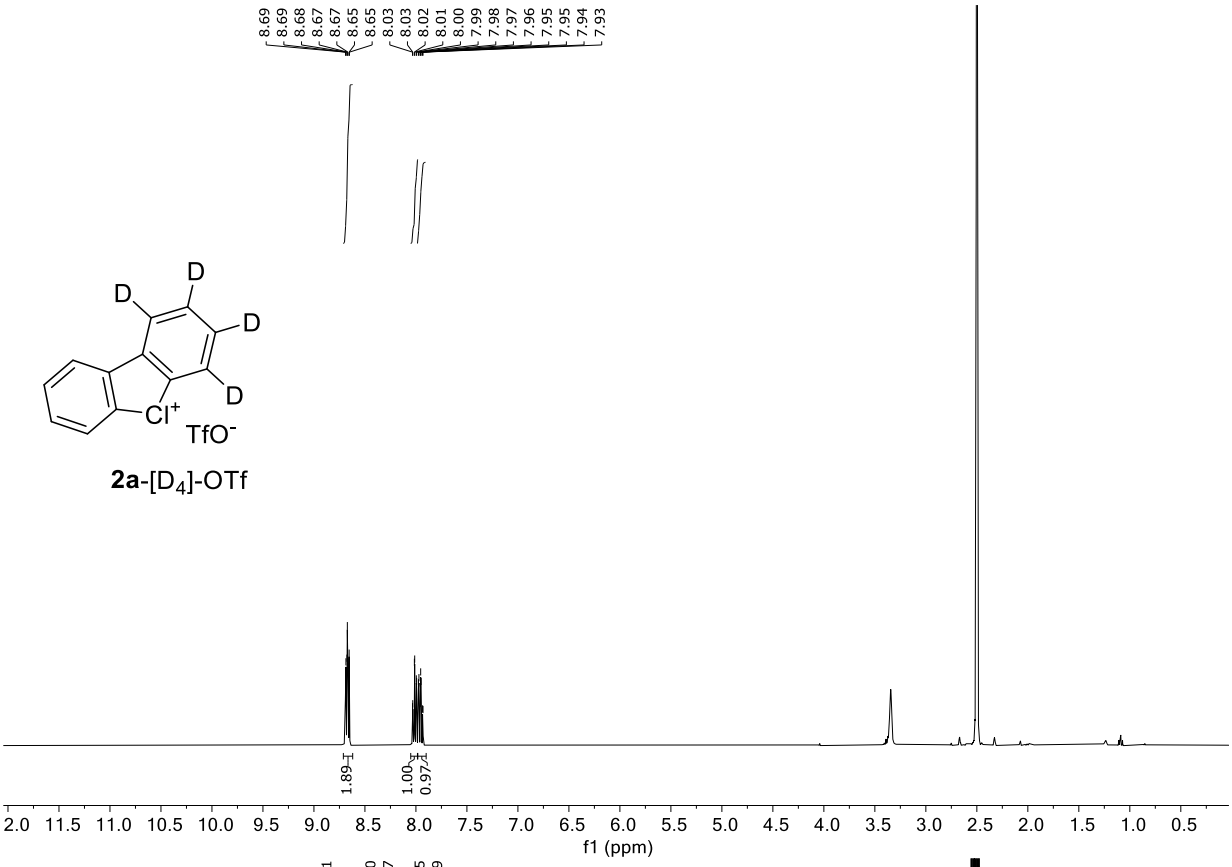

146.8
136.1
135.6
134.2
131.9
130.6
129.8
129.3
129.1
128.3
127.6
126.7
126.3
123.8
123.2
119.9
52.8
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.55 7.54 7.53 7.53 7.52 7.49 7.48 7.48 7.47 7.47 7.40 7.39 7.38 7.37 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.25 7.23 5.80
Cl
N
N=N
11'
1.00 0.99 1.10 5.12 4.20
7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
1.00 0.99 1.10 5.12 4.20 0.46 2.12
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

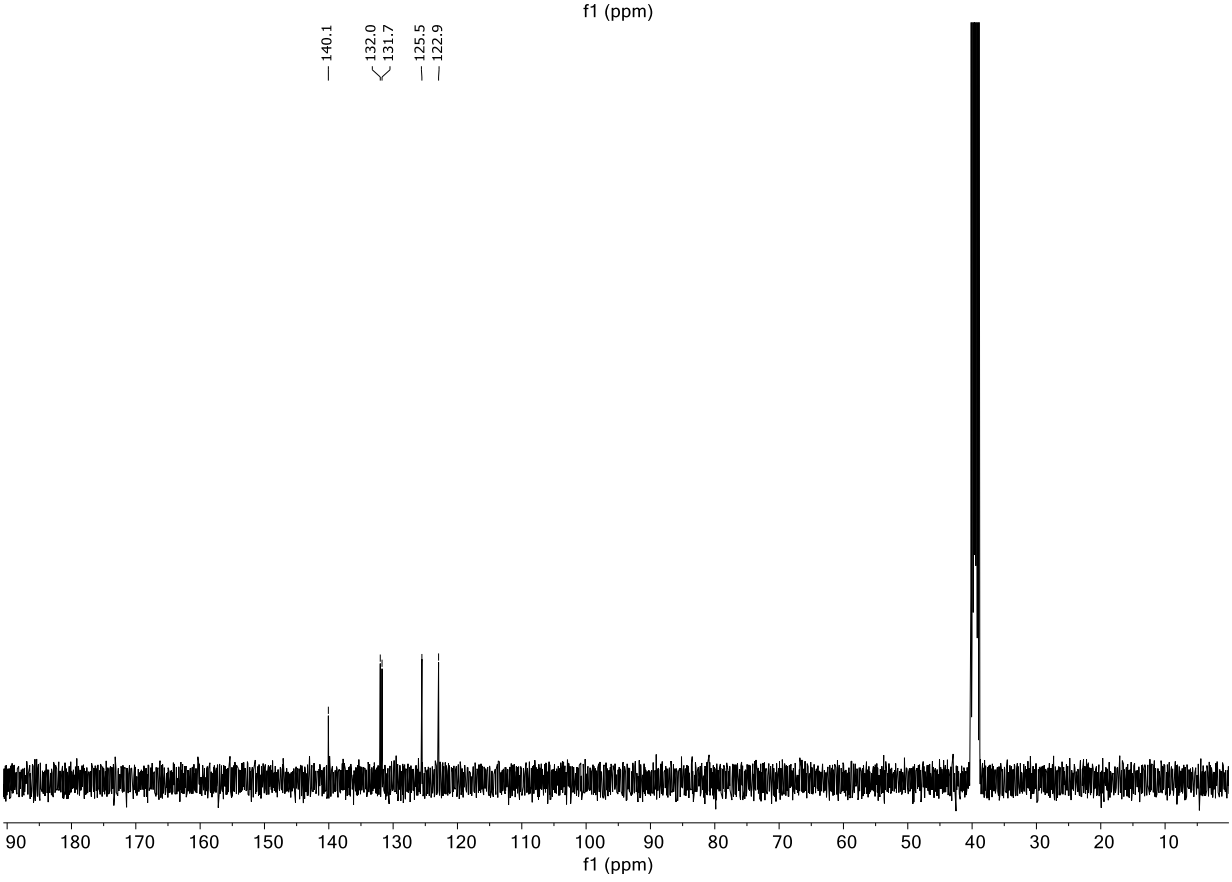

144.9 135.7 134.7 133.2 133.1 132.4 131.3 130.1 129.4 129.0 128.5 127.6 127.0 126.7 125.1 109.3
52.4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

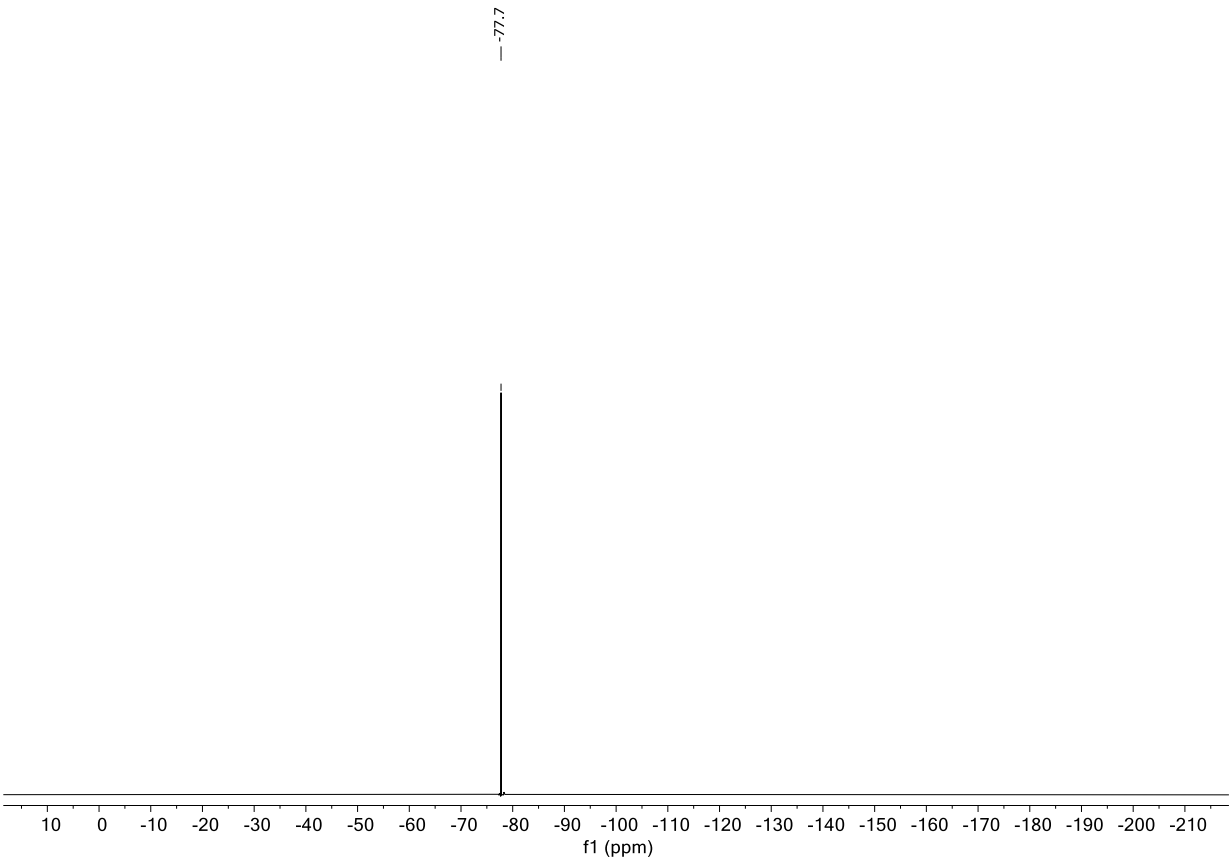

7.52
7.52
7.51
7.50
7.50
7.49
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
3.38
D
D
NH2
D
D
Cl
1a-[D]4
1.00
2.96
1.60
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

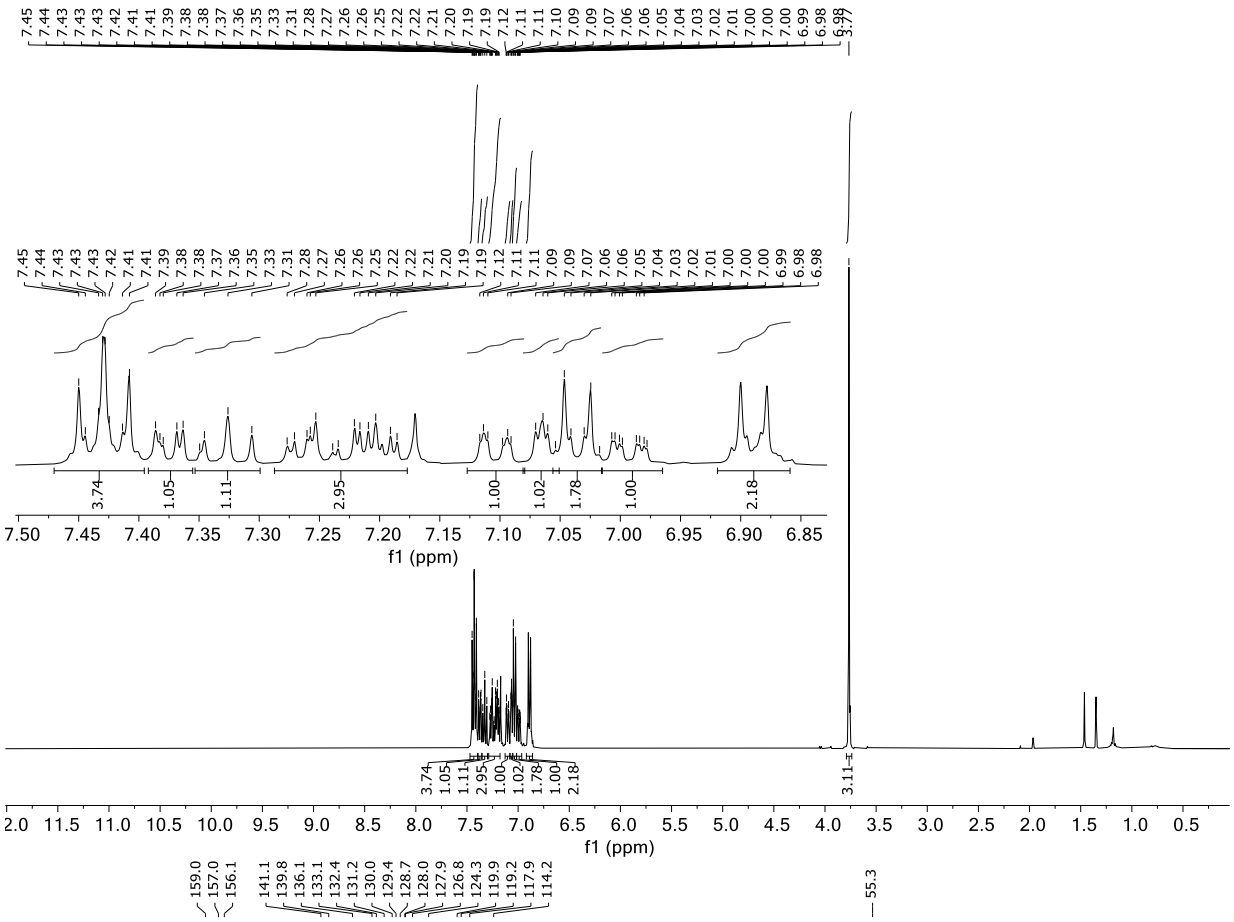

143.6
137.9
133.9
131.9
129.9
129.0
127.2
125.2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

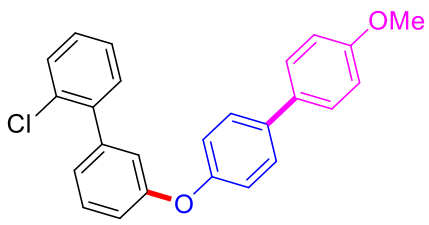

8.69
8.69
8.68
8.67
8.67
8.65
8.65
8.03
8.03
8.02
8.01
8.00
7.99
7.98
7.97
7.96
7.95
7.95
7.94
7.93
D
D
D
D
D
Cl+
TfO-
1.89
1.00
0.97
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

2a-[D_4]-OTf

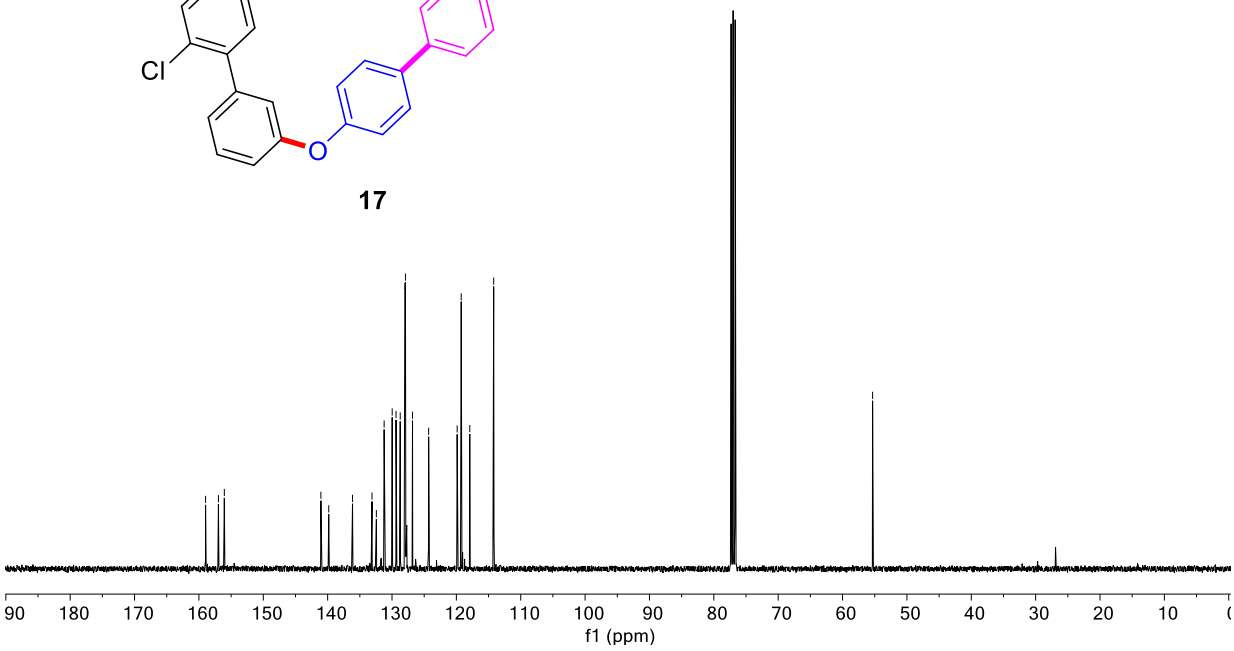

140.1
132.0
131.7
125.5
122.9
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

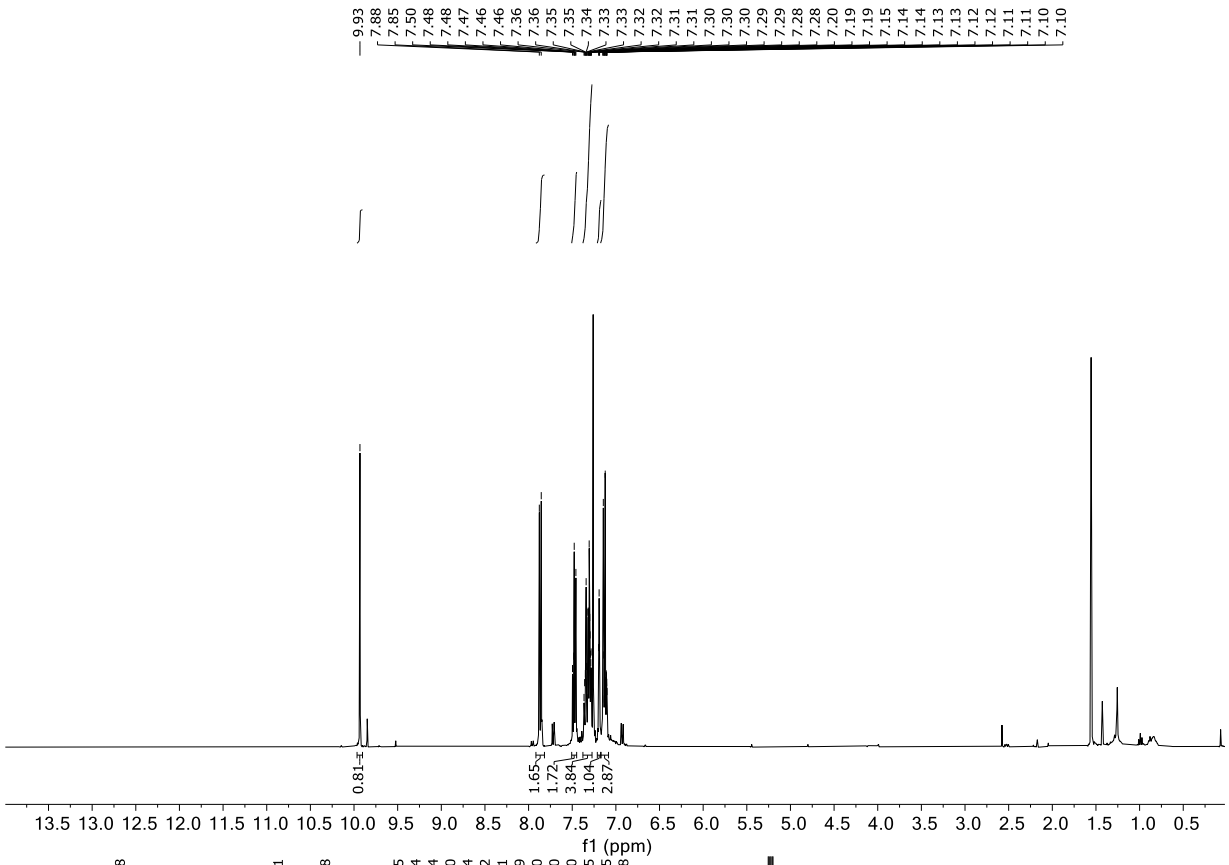

-77.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

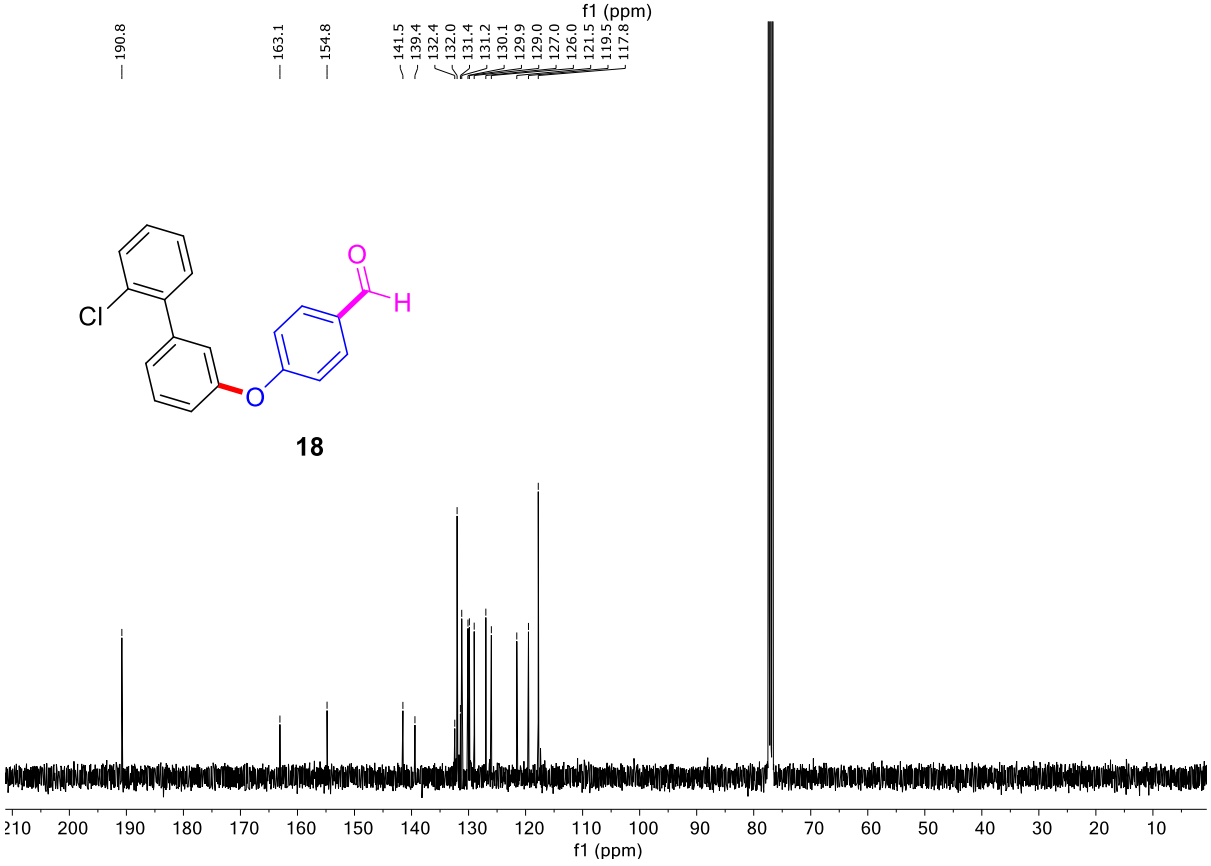


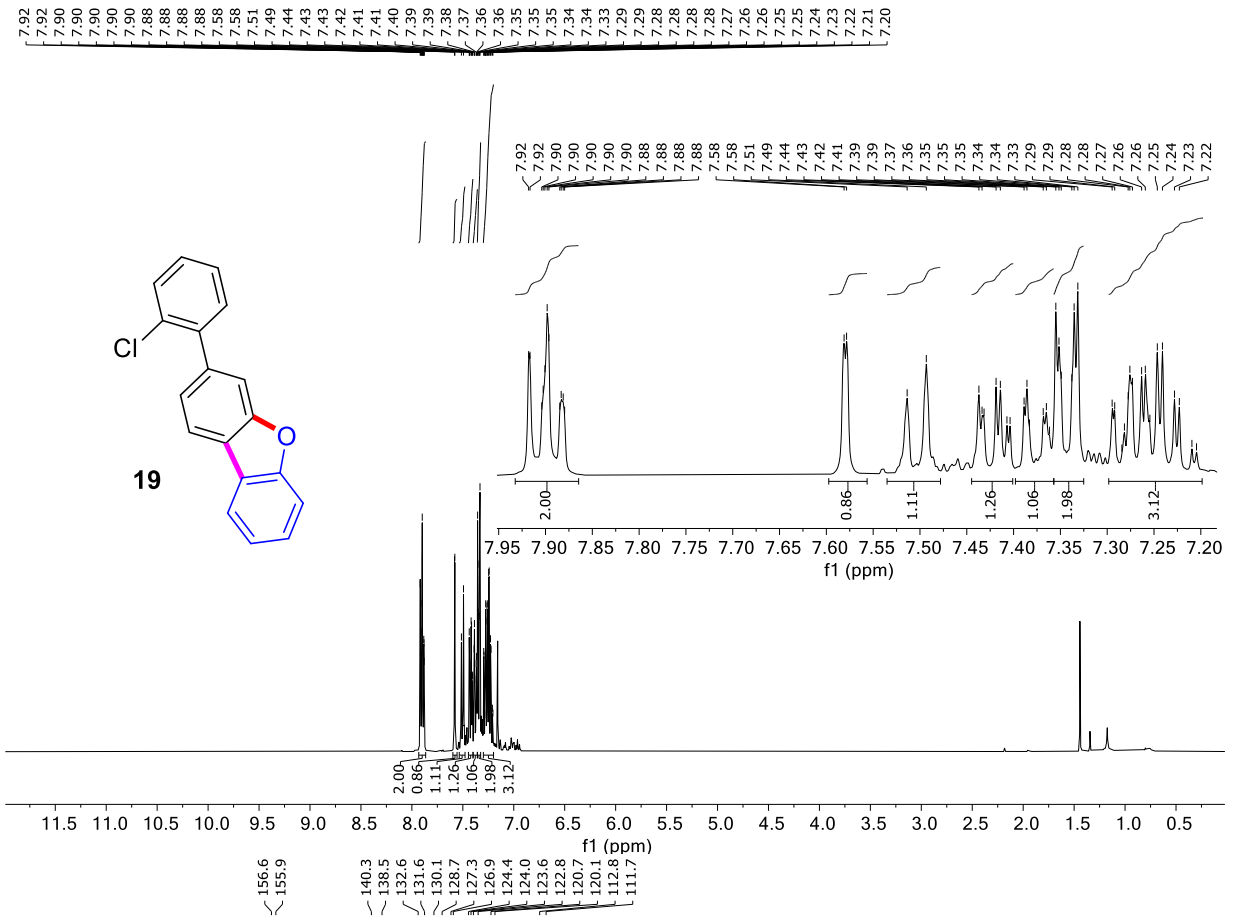


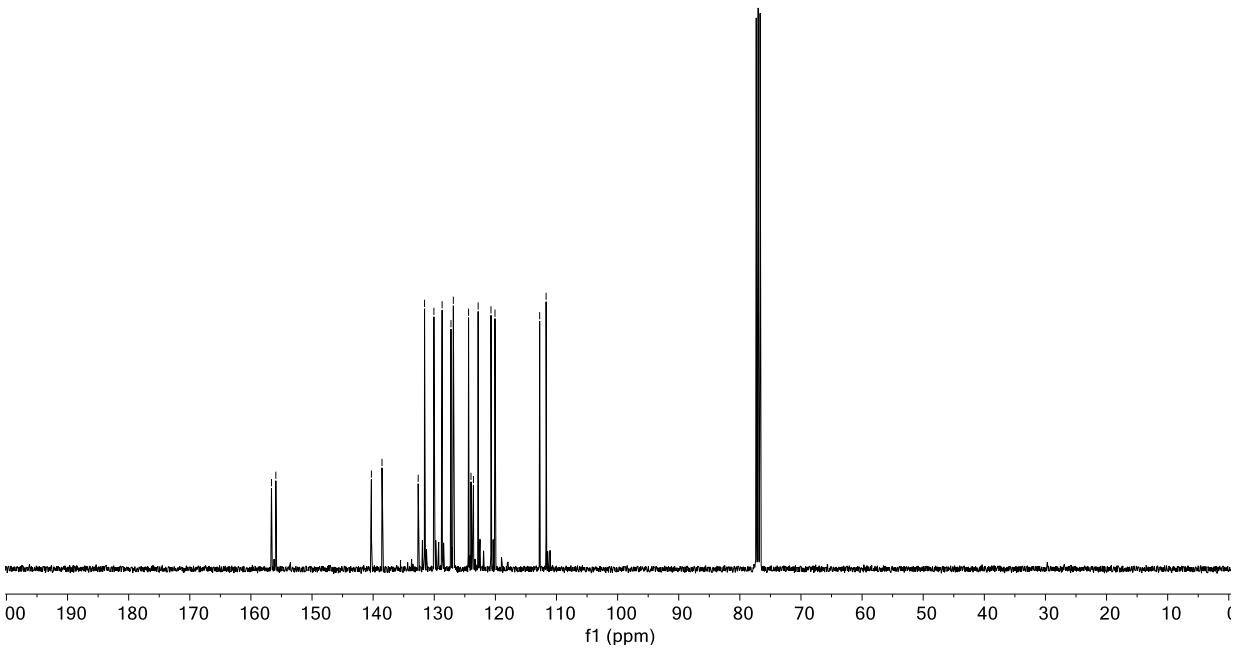
17

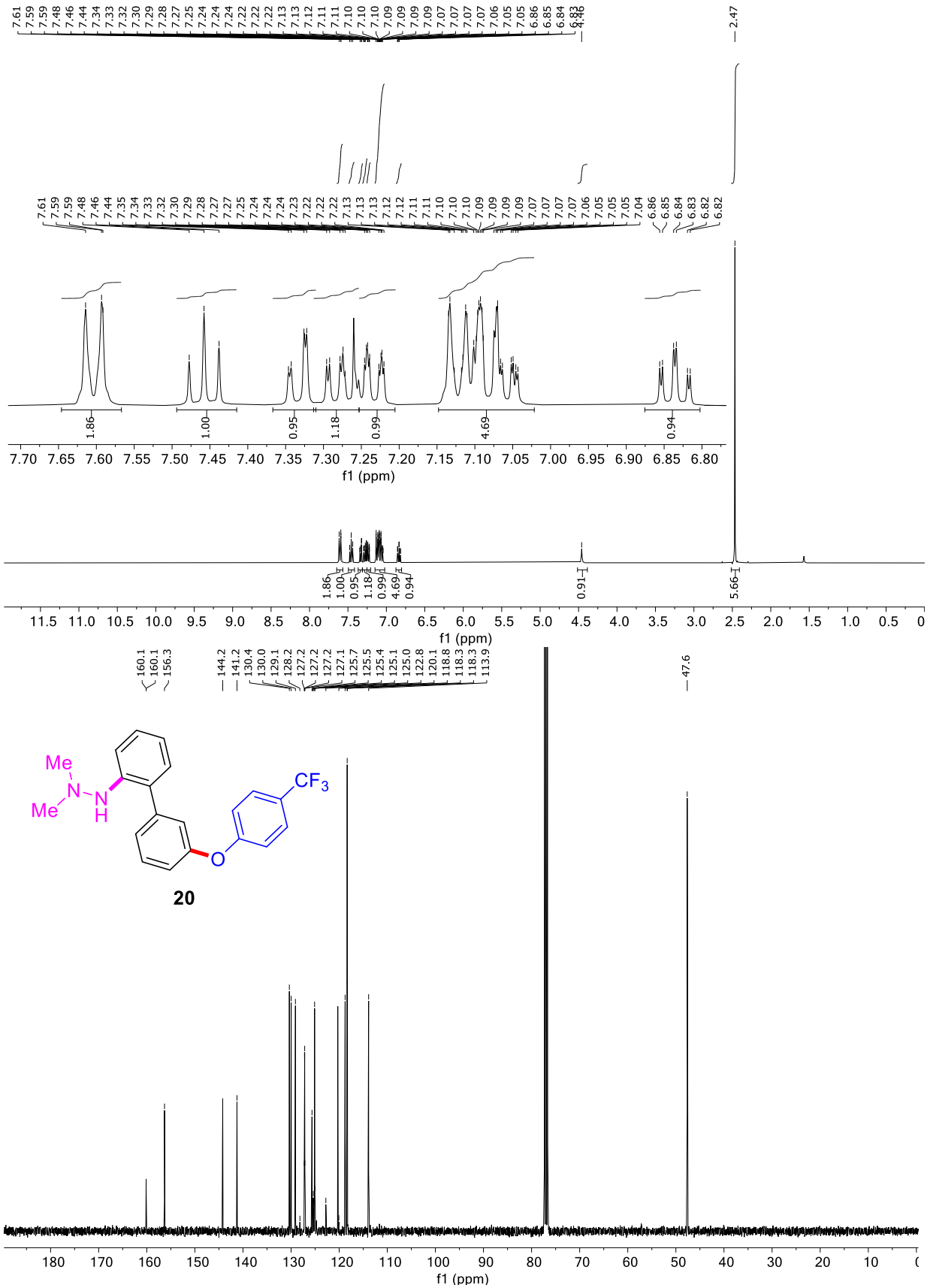


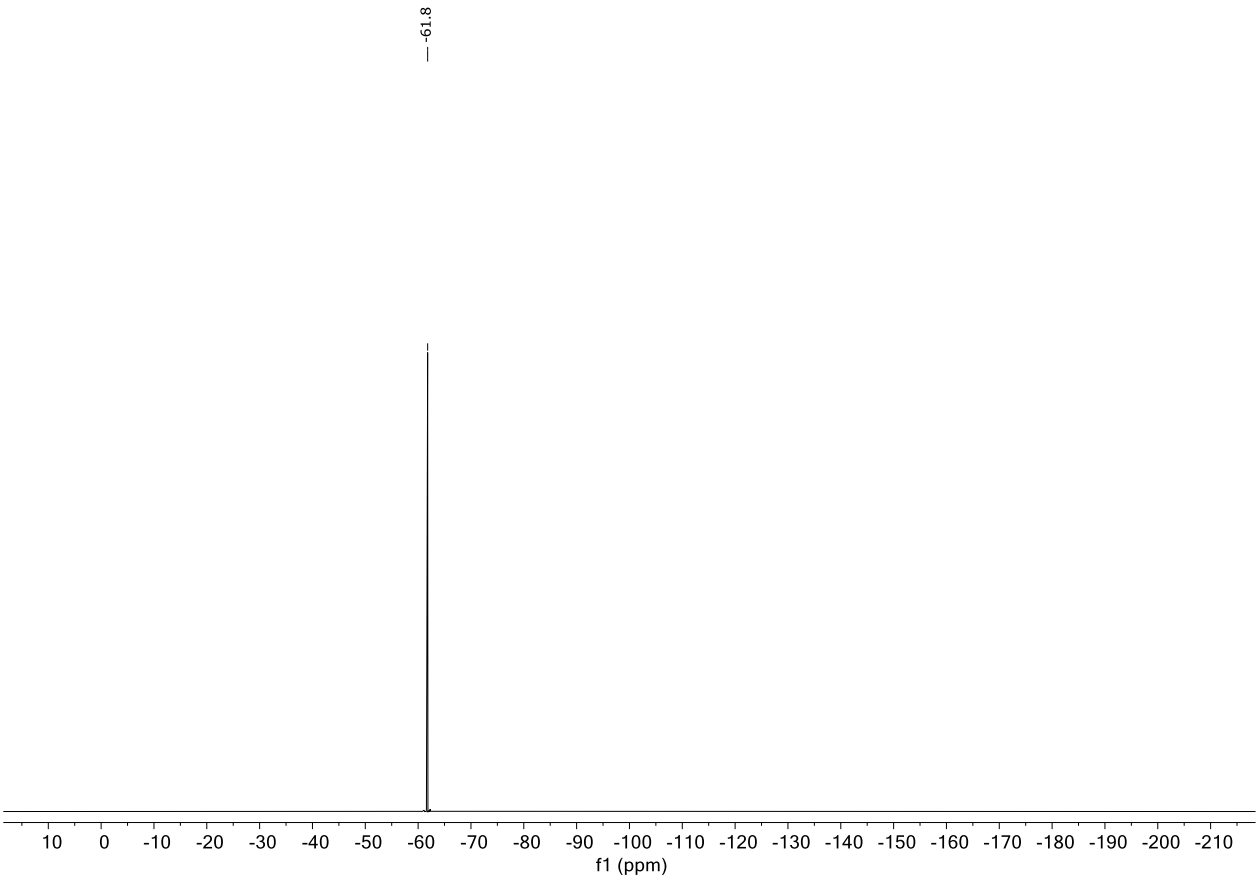

9.93
7.88
7.85
7.50
7.48
7.48
7.47
7.46
7.46
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.20
7.19
7.19
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.10
0.81
1.65
1.72
3.84
1.04
2.87
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

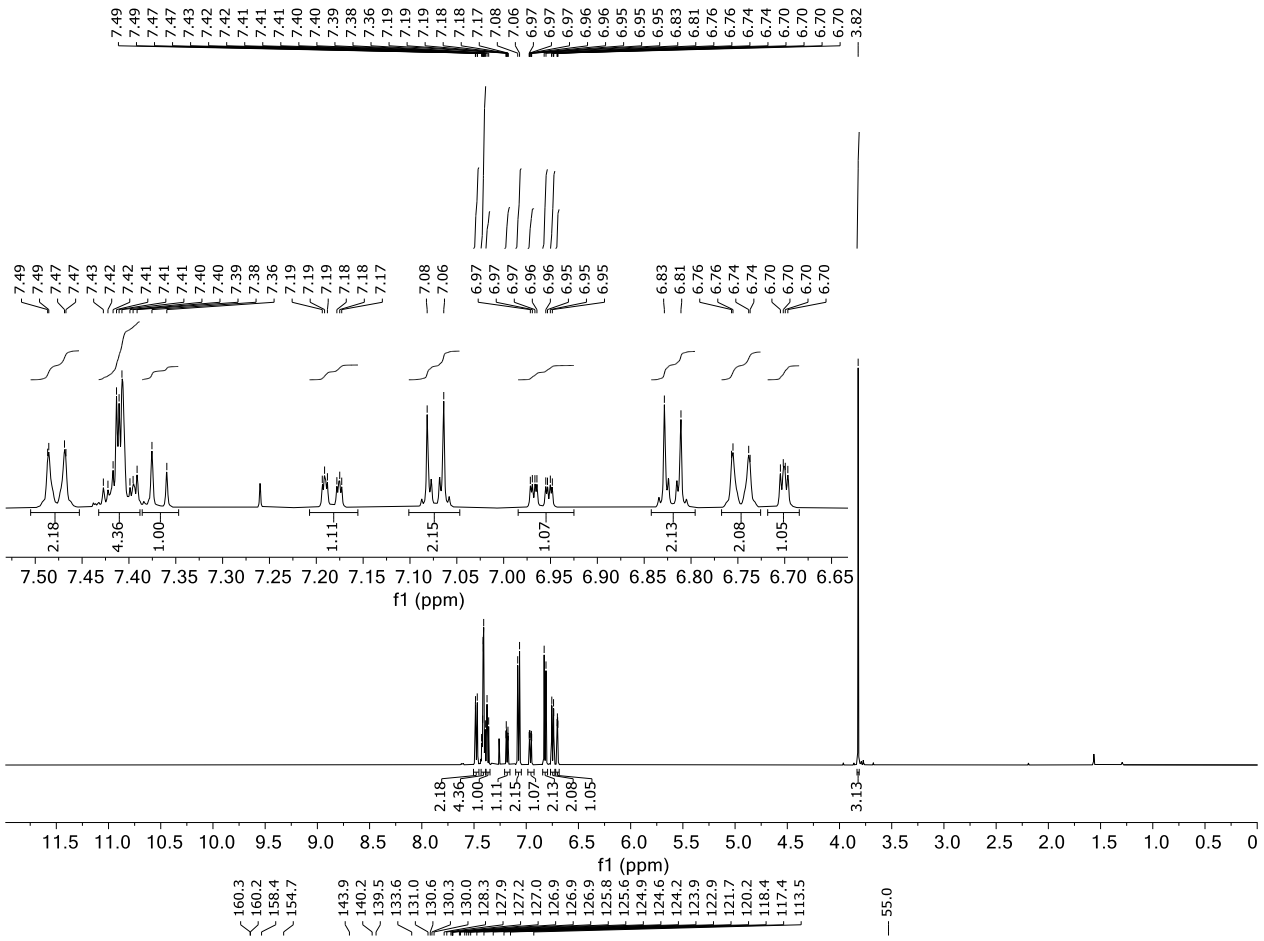

190.8
163.1
154.8
141.5
139.4
132.4
132.0
131.4
131.2
130.1
129.9
129.0
127.0
126.0
121.5
119.5
117.8
Cl
O
H
O
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

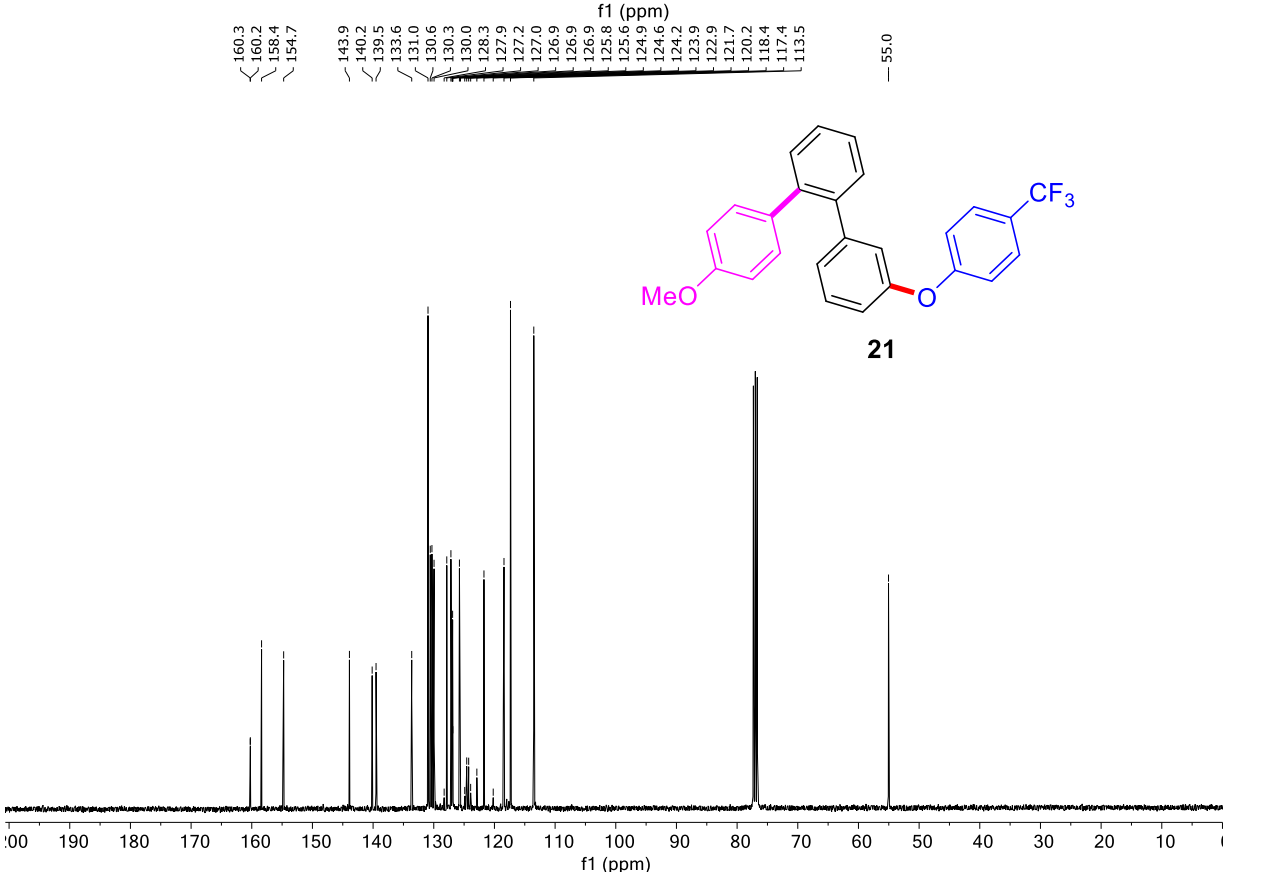

Cl
O
19
f1 (ppm)


f1 (ppm)

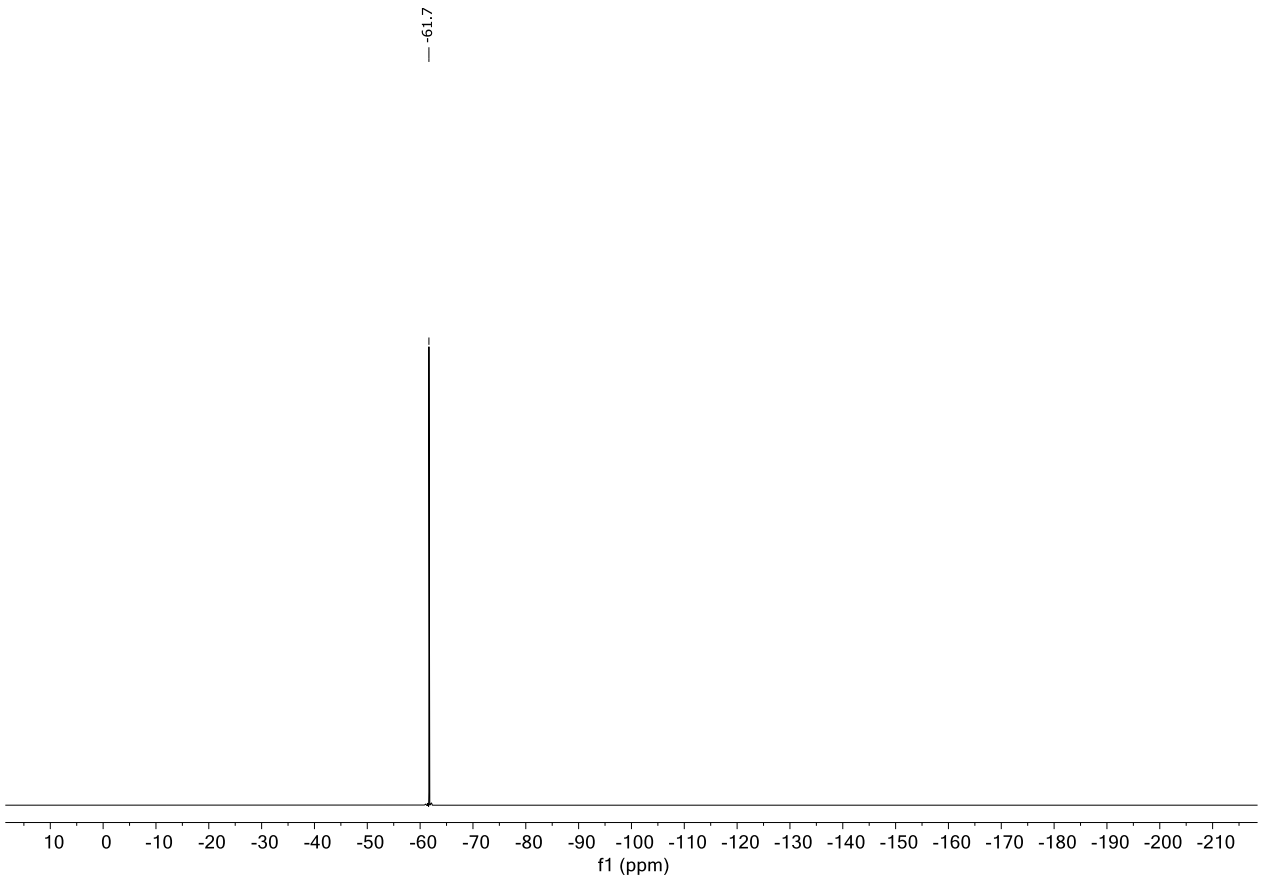

Me
N
N
H
Me
CF3
O
20
f1 (ppm)

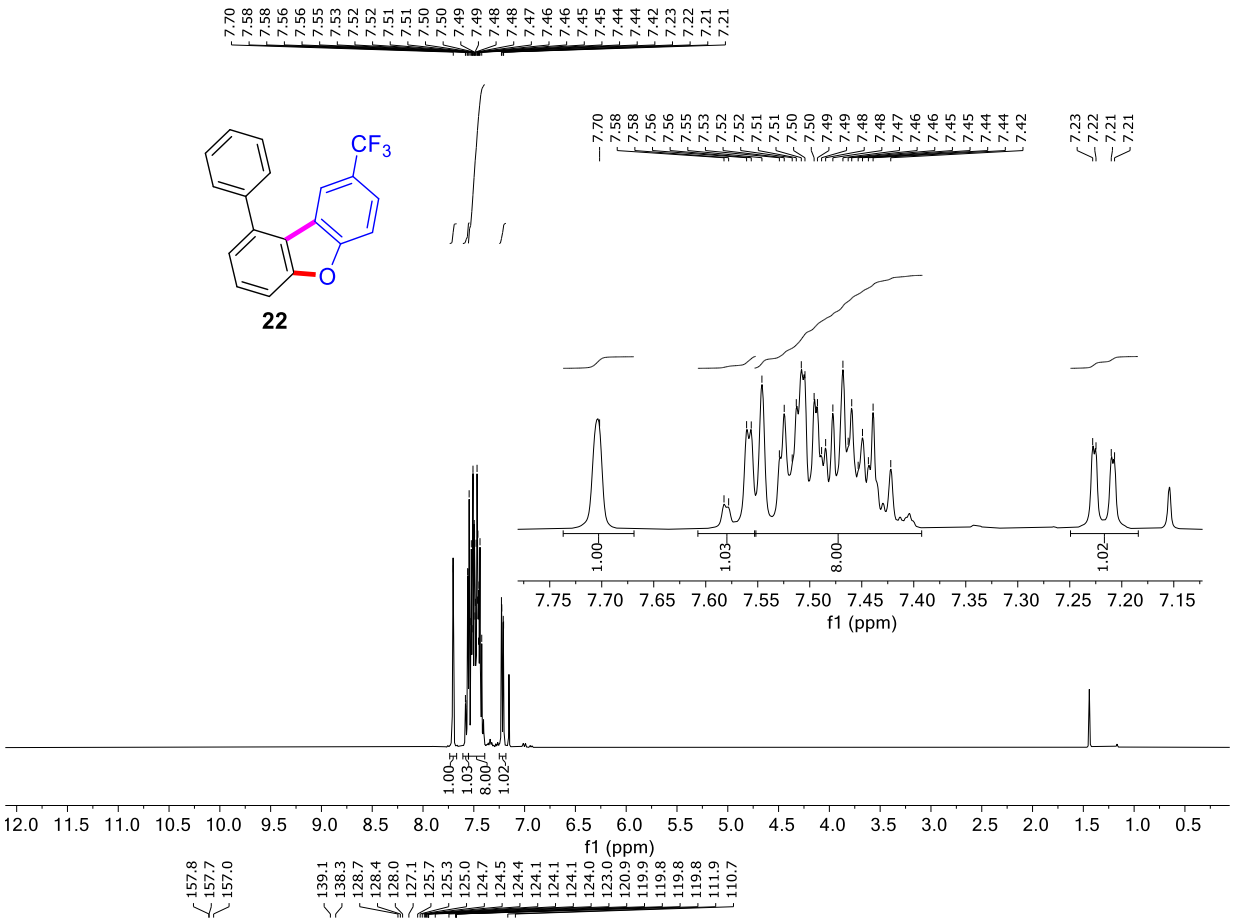

-61.8
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

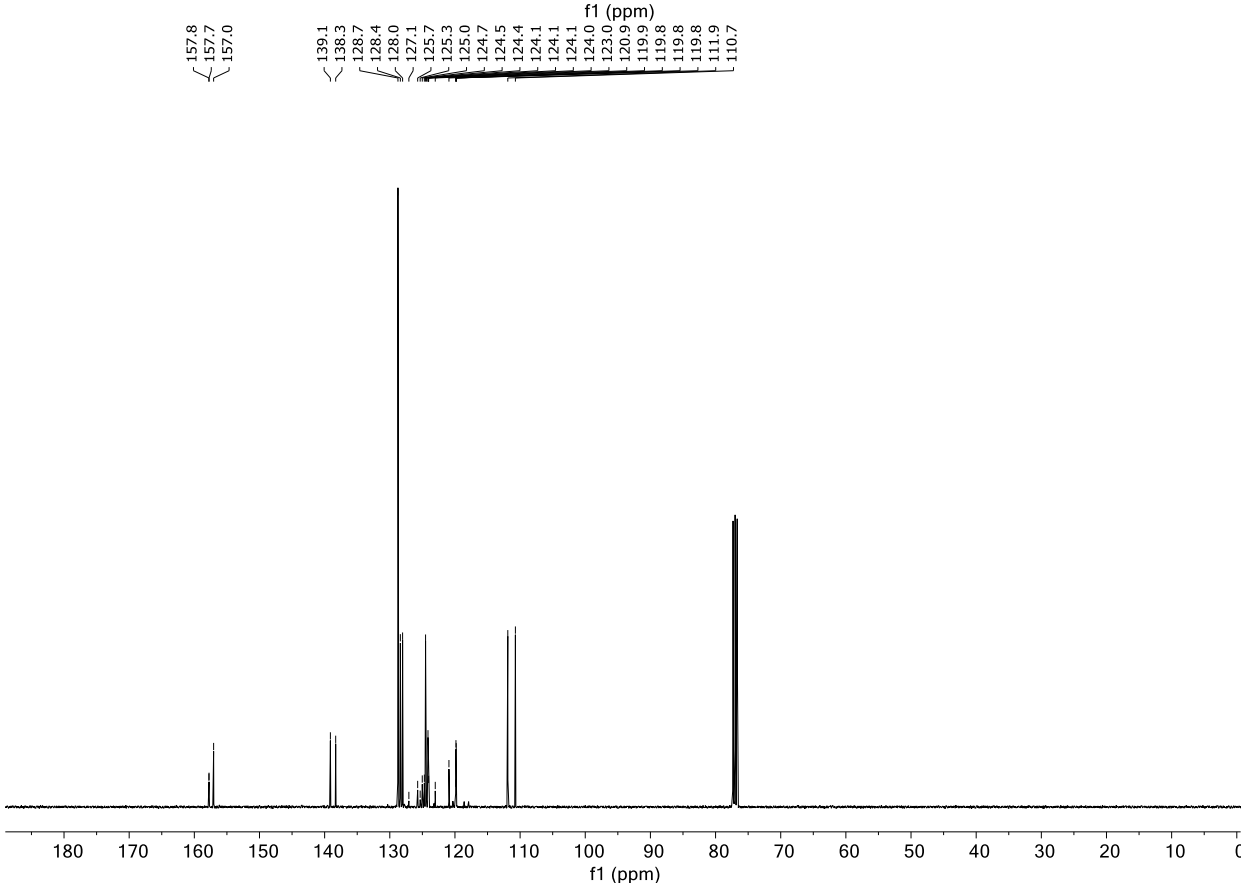


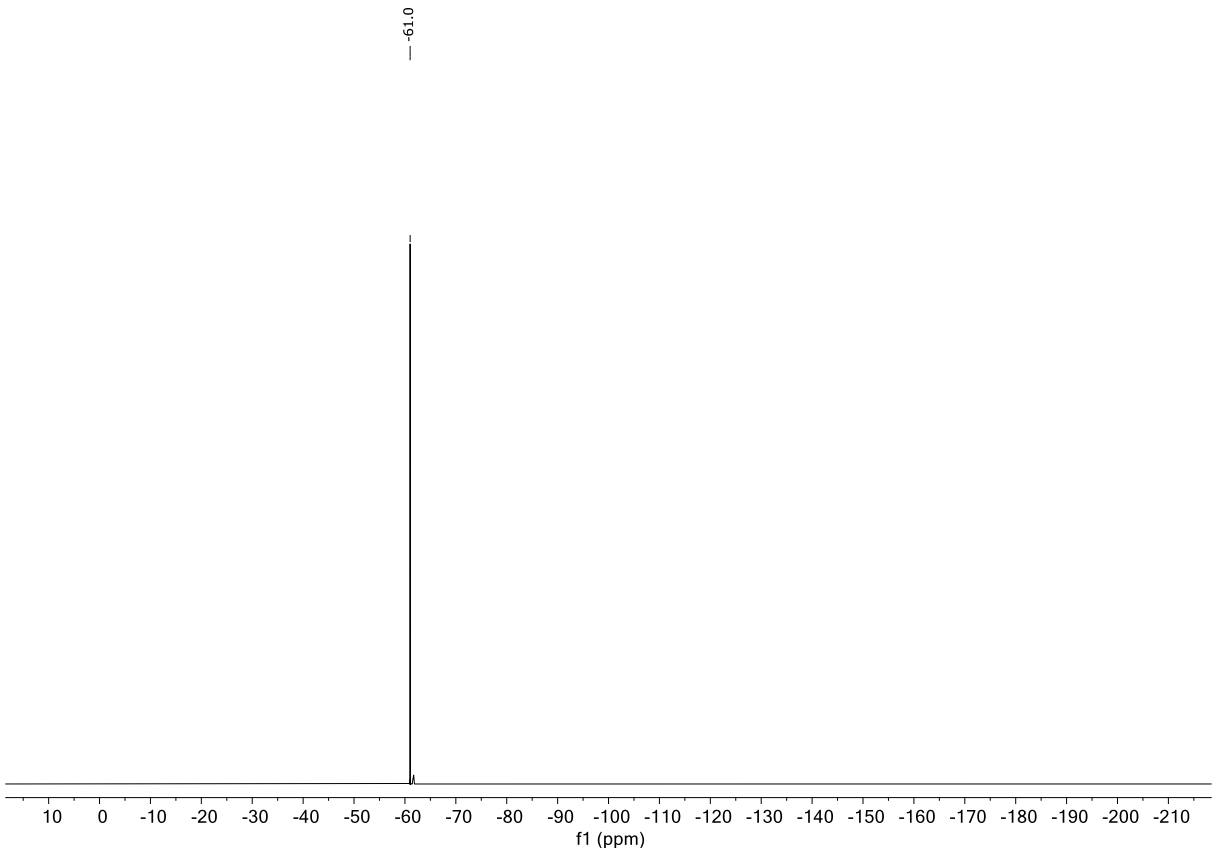


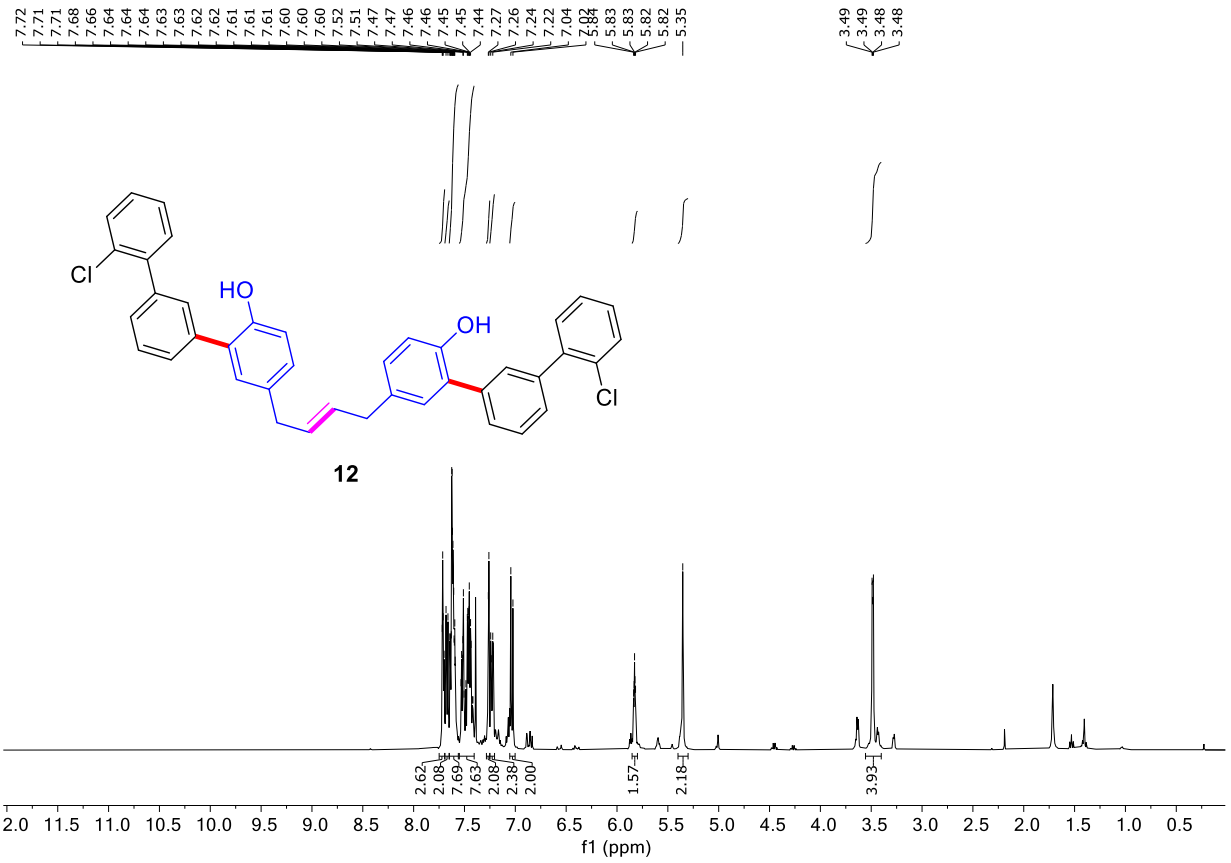
21

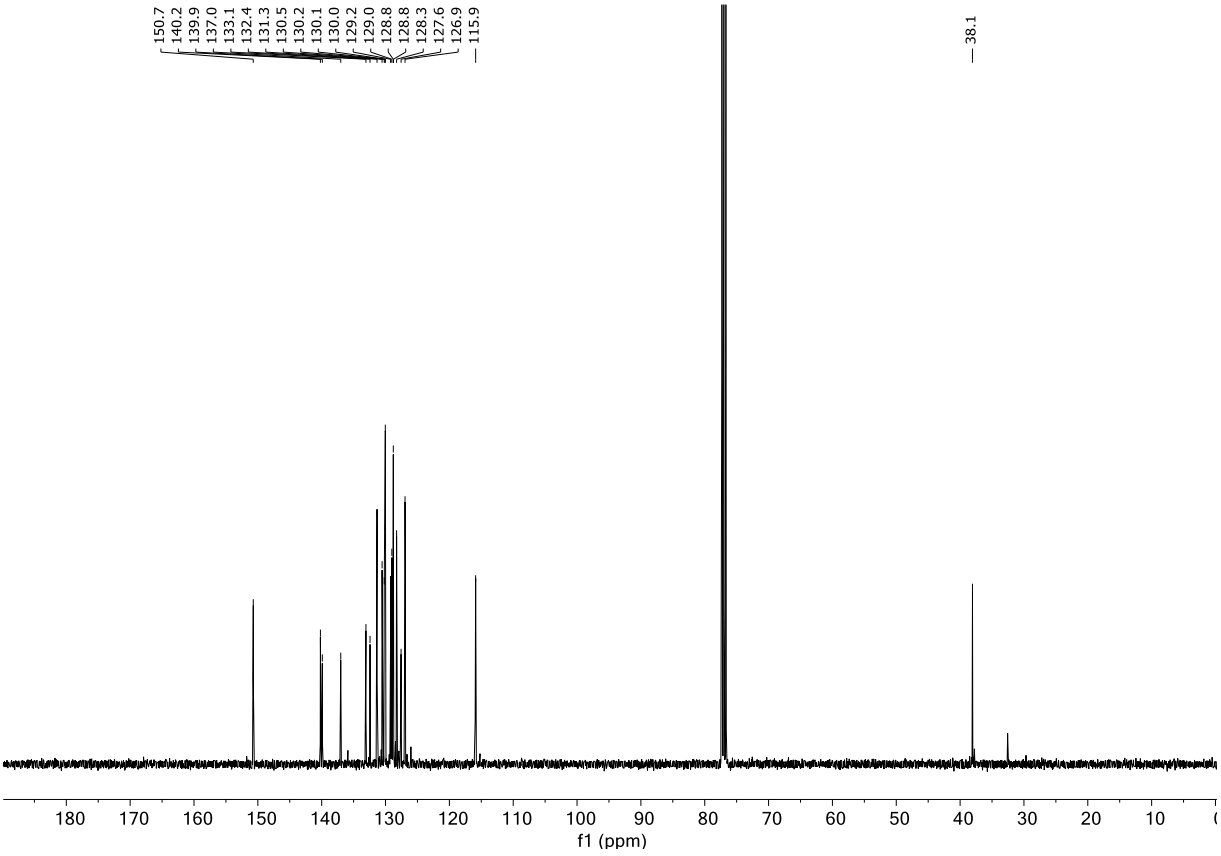

-61.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

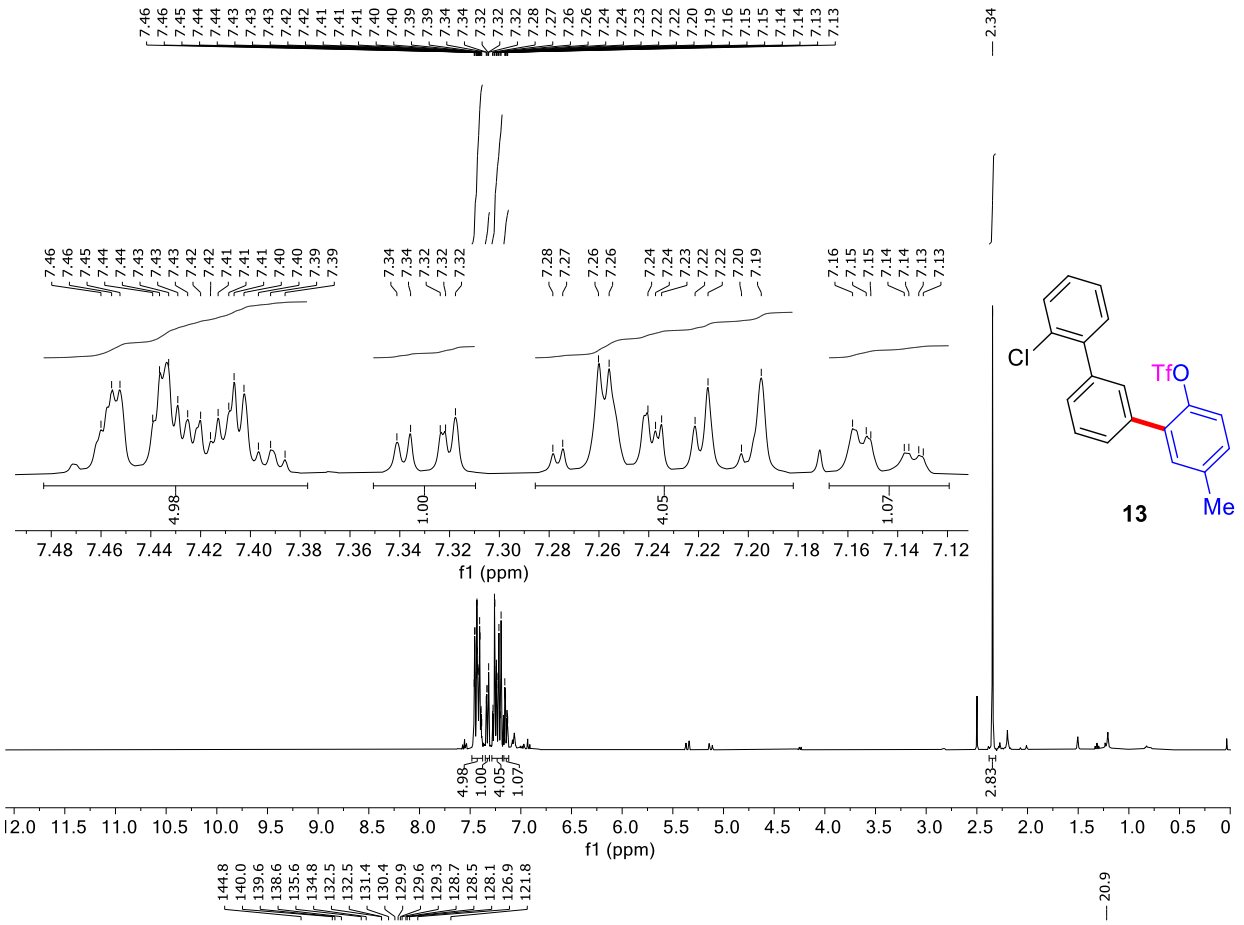

7.70 7.58 7.58 7.56 7.56 7.55 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.42 7.23 7.22 7.21 7.21
CF3
O
22
1.00 1.03 8.00 1.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)

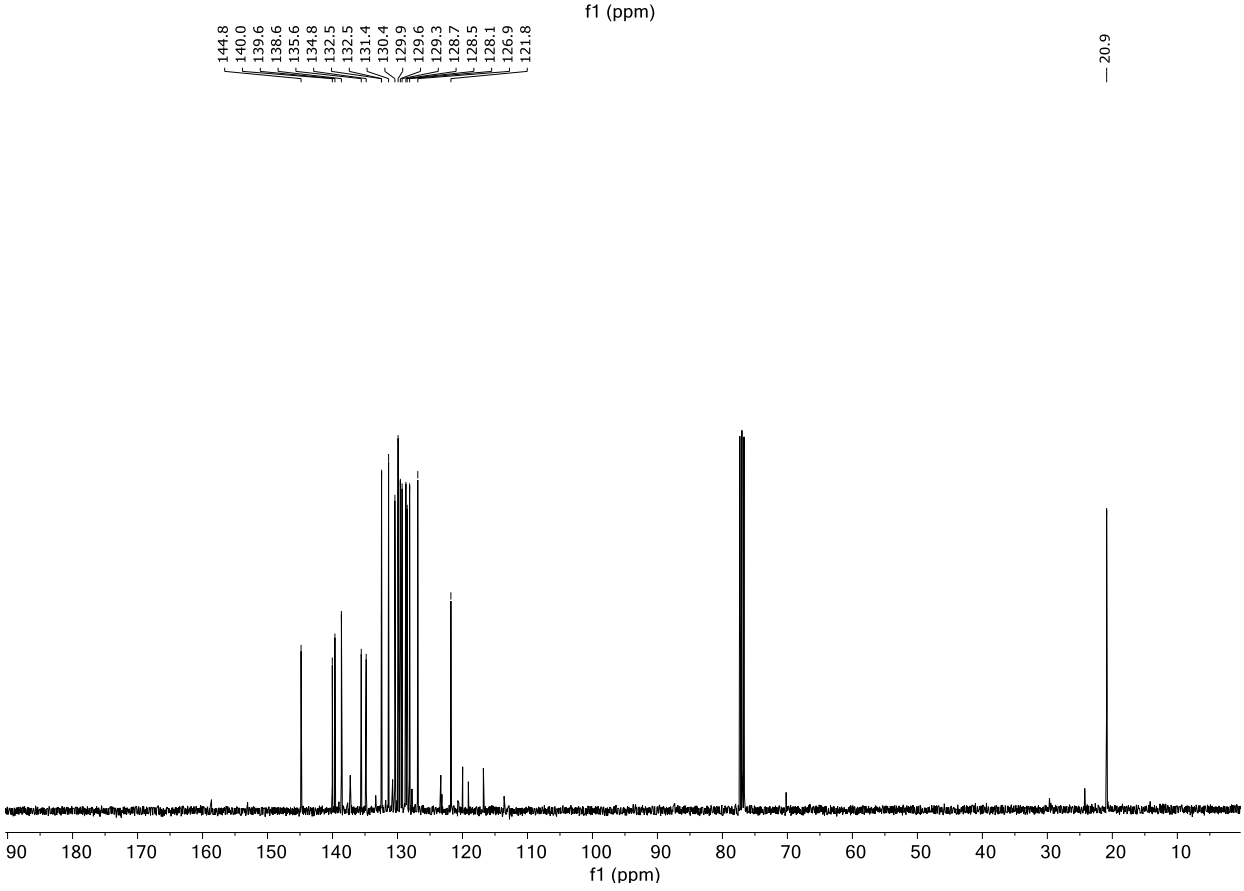

157.8 157.7 157.0 139.1 138.3 128.7 128.4 128.0 127.1 125.7 125.3 125.0 124.7 124.5 124.4 124.1 124.1 124.1 124.0 123.0 120.9 119.9 119.8 119.8 119.8 111.9 110.7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

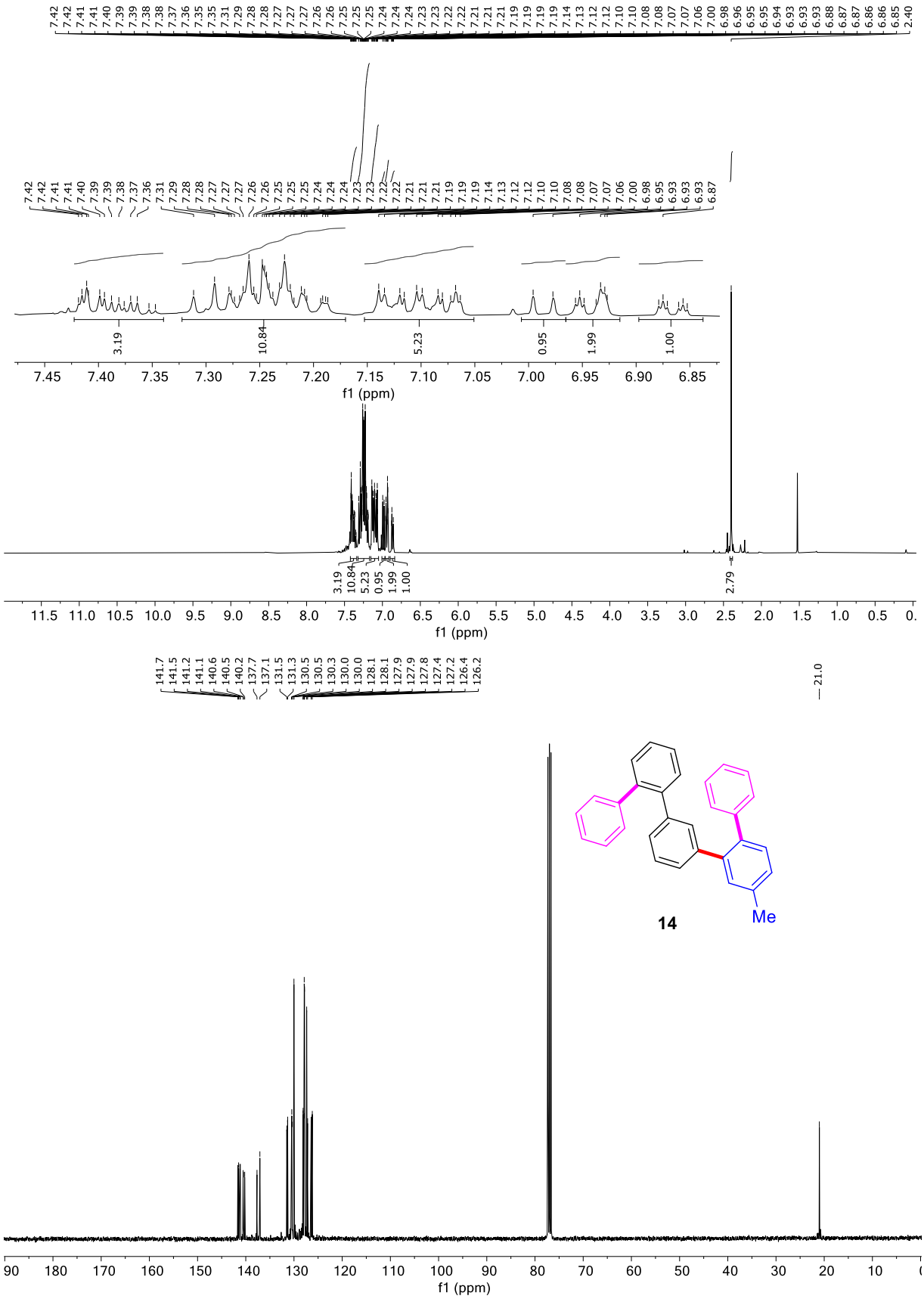

-61.0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

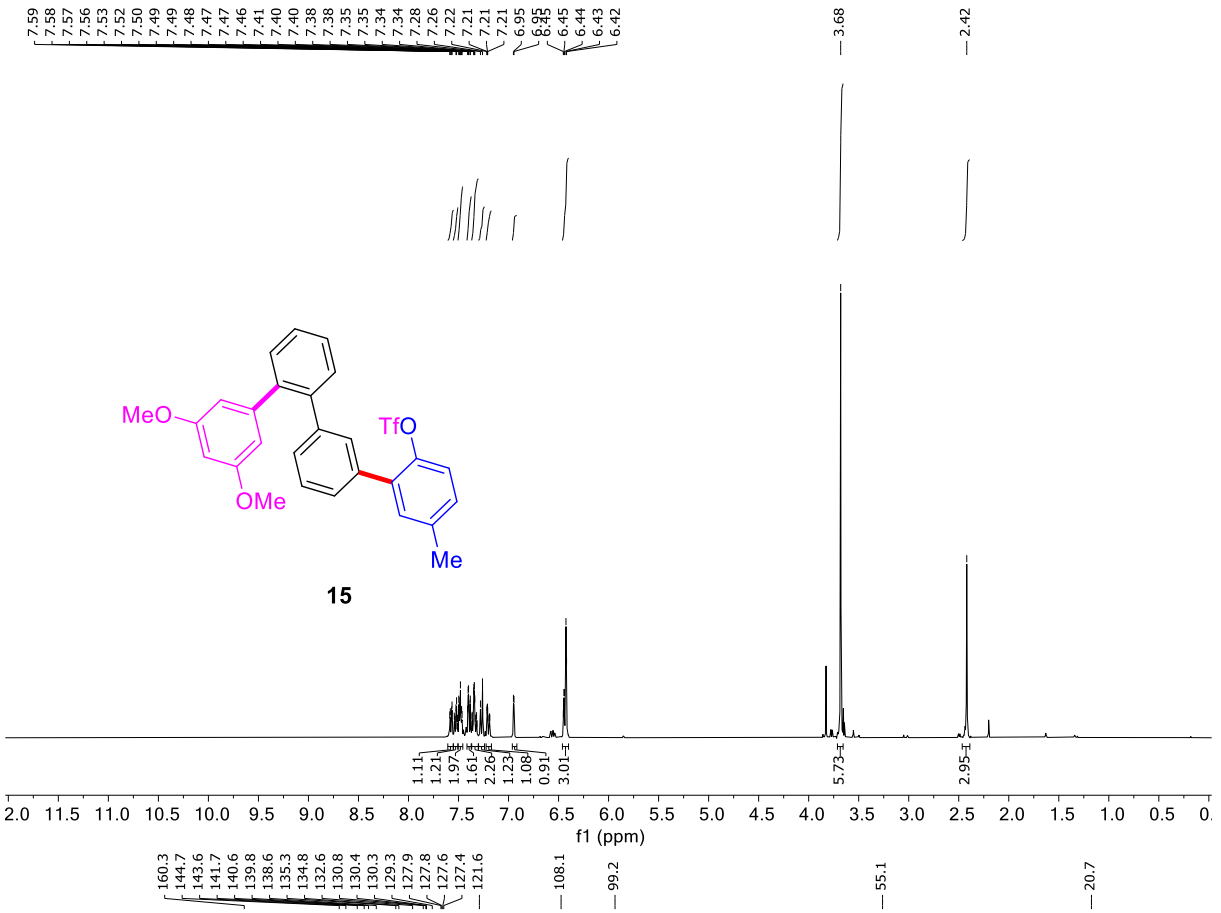

7.72
7.71
7.71
7.68
7.66
7.64
7.64
7.64
7.63
7.62
7.62
7.61
7.61
7.61
7.60
7.60
7.60
7.52
7.51
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.27
7.26
7.24
7.22
7.04
5.84
5.83
5.83
5.82
5.82
5.35
3.49
3.49
3.48
3.48
Cl
HO
OH
Cl
12
2.62
2.08
7.69
7.63
2.08
2.38
2.00
1.57
2.18
3.93
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

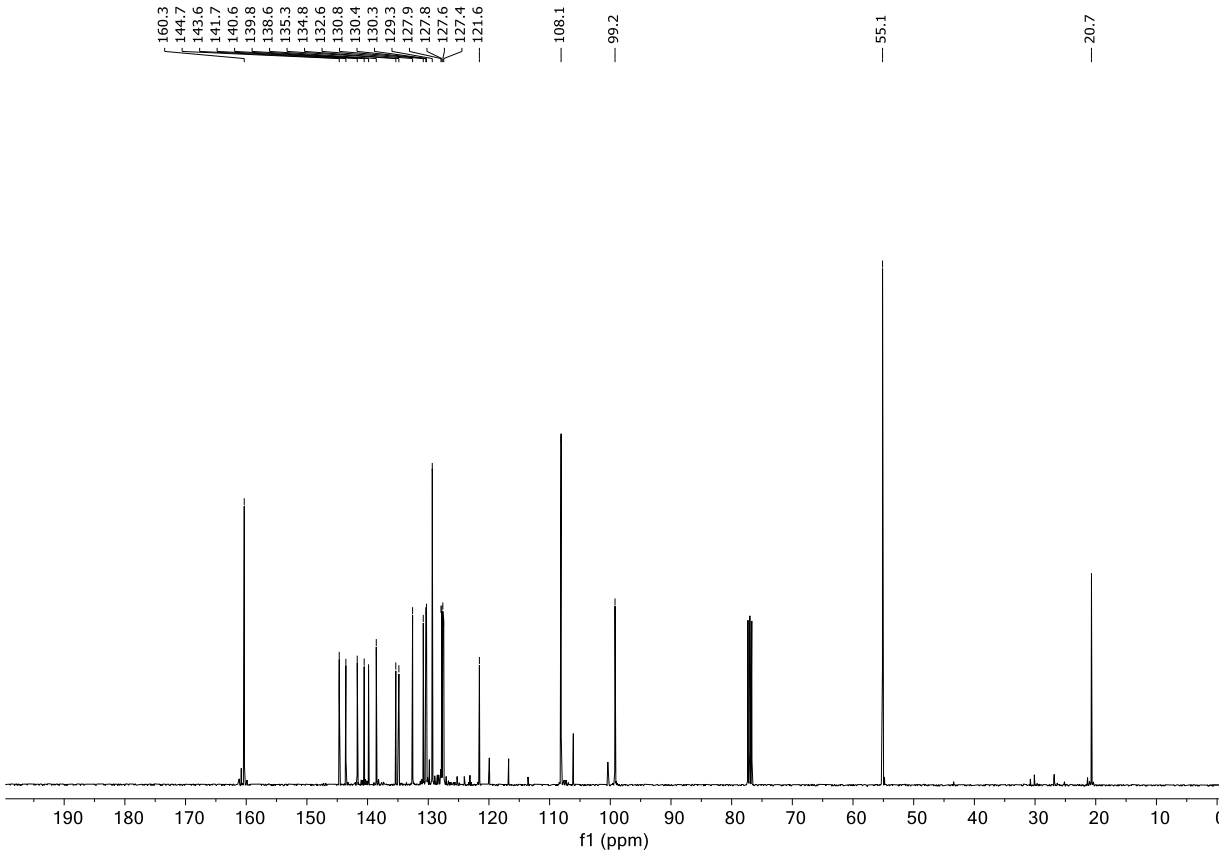

150.7
140.2
139.9
137.0
133.1
132.4
131.3
130.5
130.2
130.1
130.0
129.2
129.0
128.8
128.8
128.3
127.6
126.9
115.9
38.1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

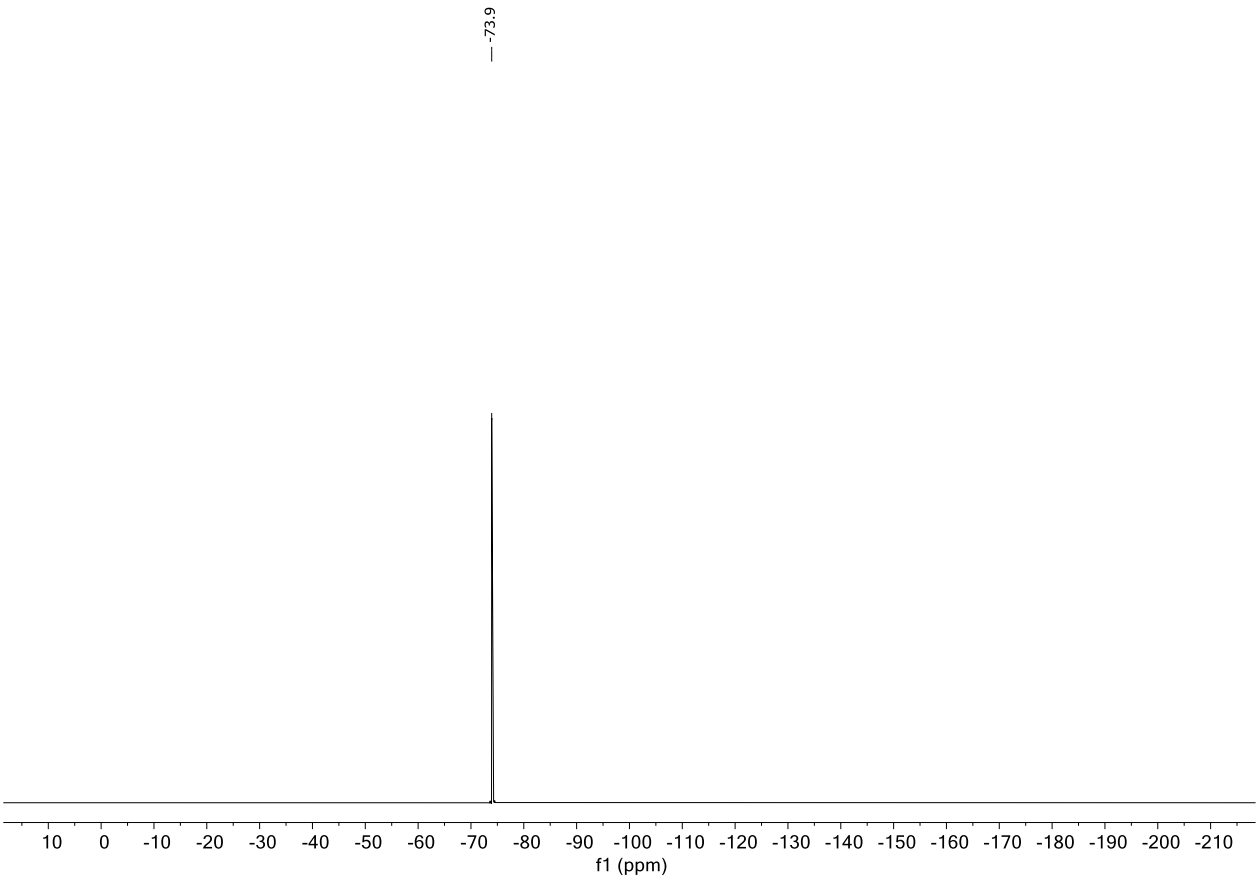

7.46 7.46 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.34 7.34 7.32 7.32 7.32 7.28 7.27 7.26 7.26 7.24 7.24 7.23 7.22 7.22 7.20 7.19 7.16 7.15 7.15 7.14 7.14 7.13 7.13
2.34
4.98
1.00
4.05
1.07
2.83
f1 (ppm)
Cl
TfO
Me
13

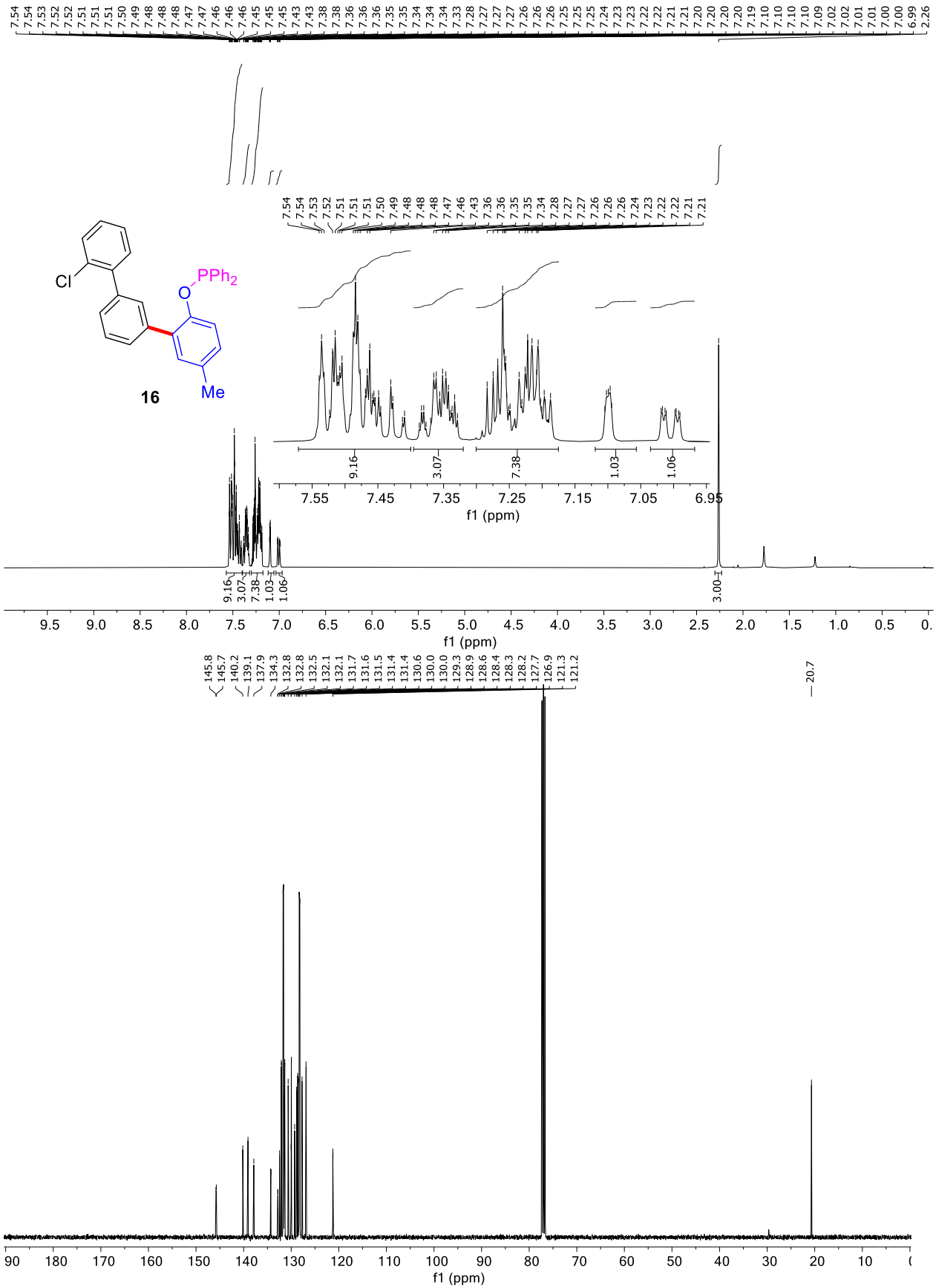

144.8 140.0 139.6 138.6 135.6 134.8 132.5 132.5 131.4 130.4 129.9 129.6 129.3 128.7 128.5 128.1 126.9 121.8
20.9
f1 (ppm)

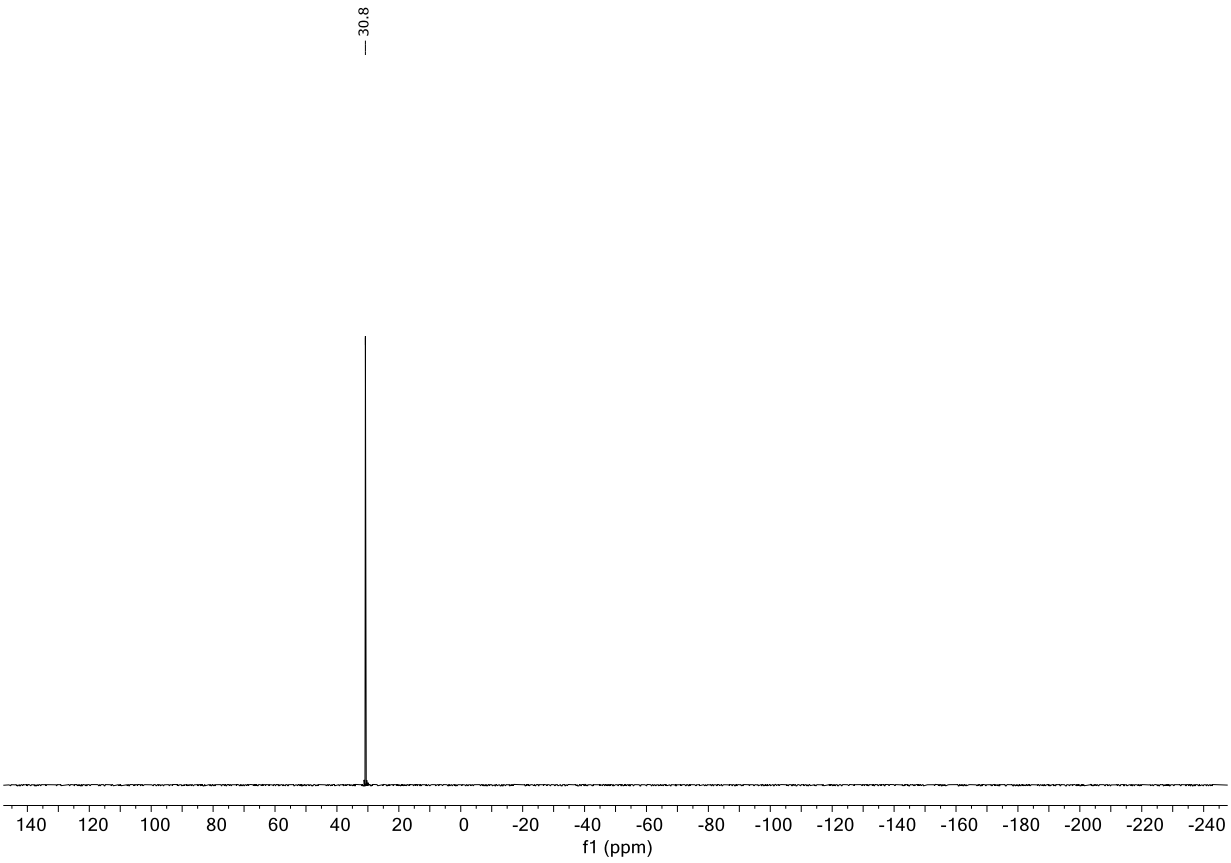

f1 (ppm)
Me
14


MeO
OMe
TfO
Me
15
f1 (ppm)


f1 (ppm)


-73.9
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)


Cl
PPh2
O
Me
16
f1 (ppm)
f1 (ppm)
f1 (ppm)


30.8
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)