

Trifluoromethylation of Pyridines through Skeletal Rearrangement

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Supporting Information

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1. General Methods

Nuclear magnetic resonance spectra were acquired on either 500 MHz (Bruker® AVII+ 500, Bruker AVIII HD 500) or 400 MHz (Bruker AVIII HD 400, Bruker AVIII 400). All ¹H NMR spectra are reported in parts per million (ppm) and were measured relative to the signals at 7.26 ppm (CDCl₃), 2.05 ppm (Acetone-d₆). All ¹³C NMR spectra were reported in ppm relative to residual CDCl₃ (77.16 ppm), and were obtained with ¹H-decoupling. All ¹⁹F chemical shifts were unadjusted from raw data. Data for ¹H NMR are described as follows: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad signal), coupling constant (Hz), and integration.

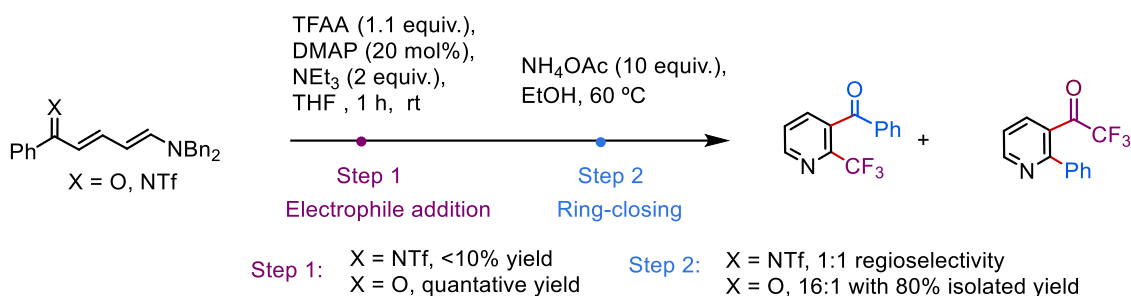
High resolution mass spectra were obtained on ThermoFisher Scientific Q-Exactive™, Thermo Scientific Exactive plus EMR, and Agilent 6530 Q-TOF instruments, using either electrospray ionisation (ESI), atmospheric-pressure chemical ionisation (APCI) as ionisation methods in the positive and negative mode.

Flash column chromatography was carried out by using re-used 10g, 25g, or 50g Biotage® Snap Ultra or Biotage Sfär Silica cartridges on a Biotage Isolera Four automated column, using 35-70 μ m, 60 Å silica gel for chromatography from ThermoFisher Scientific® or 40-63 μ m 60 Å silica gel from Sigma Aldrich.

Melting points (mp) were recorded on a Griffin melting point apparatus to the nearest degree and are uncorrected.

All air and/or moisture-sensitive reactions were performed under an atmosphere of dry nitrogen using anhydrous solvents. All solvents for air-sensitive reactions were degassed by bubbling N₂ on the Schlenk line. All commercially available reagents and solvents were used as received without further purification.

2. Reaction Optimization

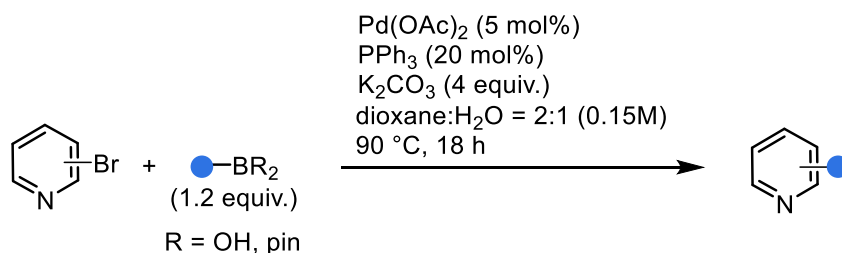


Entry	Variation from standard condition	Yield (%)
1	None	80
2	Without DMAP in Step 1	0
3	60 °C instead of r.t. in Step 1	77
4	0 °C instead of r.t. in Step 1	80
5	overnight instead of 1 h in Step 1	80

Table 1: All reactions were carried out on a 0.1 mmol scale, isolated yields.

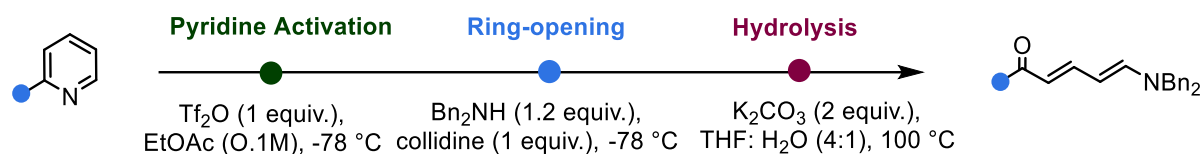
3. General Synthetic Procedures

General Procedure A: Suzuki coupling of bromopyridines and (hetero)aryl boronic acids



To the reaction vessel was added respective bromopyridines (1 equiv.), appropriate boronic acid/boronic pinacol ester (1.2 equiv.), K₂CO₃ (4 equiv.), Pd(OAc)₂ (5 mol%), and PPh₃ (20 mol%), and the vessel was evacuated and refilled with N₂ three times on a Schlenk line. A 2:1 mixture of 1,4-dioxane and water (0.15 M), previously degassed by bubbling through N₂ for 5 minutes, was added, and the resulting biphasic mixture was heated to 90 °C, while stirring for 18 h. The mixture was allowed to cool to room temperature, diluted with H₂O, and extracted three times with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated in vacuo to yield the crude product, which was purified by silica column chromatography.

General Procedure B: Synthesis of Zincke ketone



a) An oven-dried microwave vial containing pyridine substrate (1.0 equiv.) was evacuated and backfilled 3 times with nitrogen. EtOAc (0.1 M) was added (*pyridine substrates with low boiling points were added after EtOAc*). The reaction vial was cooled to $-78\text{ }^{\circ}\text{C}$, and Tf₂O (1.0 equiv.) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before dibenzylamine (1.2 equiv.) was added dropwise as a solution (1.0 M in EtOAc) followed by collidine (1.0 equiv.). The reaction was stirred for a further 30 minutes at $-78\text{ }^{\circ}\text{C}$. The cooling bath was removed, and the reaction was allowed to warm to room temperature while stirring for approximately 30 minutes.

b) The solvent was removed in vacuo, and K₂CO₃ (2.0 equiv.) and a 2:1 mixture of THF: H₂O (0.1M) were added. The reaction mixture was stirred at 100 °C for 18-24 hours. The organic layer was separated. The aqueous layer was washed with EtOAc (3 ×). The mixture was allowed to cool to room temperature, diluted with H₂O, and extracted three times with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated in vacuo to yield the crude product, which was purified by silica column chromatography.

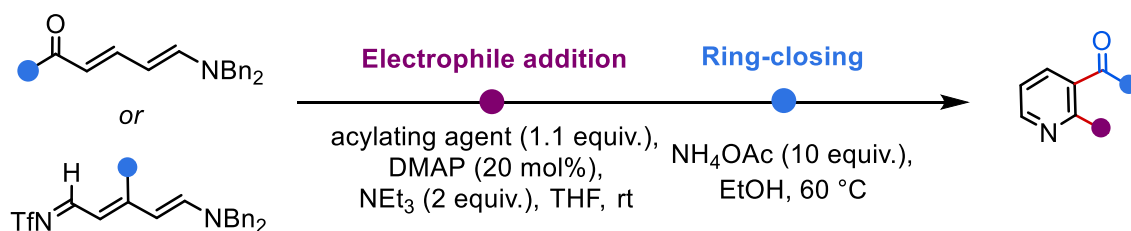
General Procedure C: Synthesis of Zincke imine



An oven-dried microwave vial containing pyridine substrate (1.0 equiv.) was evacuated and backfilled 3 times with nitrogen; EtOAc (0.1 M) was added to it. The reaction vial was cooled to $-78\text{ }^{\circ}\text{C}$, and Tf₂O (1.0 equiv.) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before dibenzylamine (1.2 equiv.) was added dropwise as a solution (1.0 M in EtOAc) followed by collidine (1.0 equiv.). The reaction was stirred for a further 30 minutes at $-78\text{ }^{\circ}\text{C}$. The cooling bath was removed, and the reaction was allowed to warm to room temperature while stirring for approximately 30 minutes. The reaction was diluted with EtOAc and washed with H₂O (3 ×), followed by brine (2 ×). The organic extract was dried over Na₂SO₄ and filtered.

After filtration, the organic extract was dissolved in 1-2 mL DCM and added dropwise to excess hexane (*approx.* 100 mL per 1.0 mmol) and, was kept overnight in a $-20\text{ }^{\circ}\text{C}$ fridge. Then, the excess hexane was decanted off, and the residual solid/oil was washed with hexane, redissolved in DCM and concentrated *in vacuo*, to provide the pure Zincke imine product.

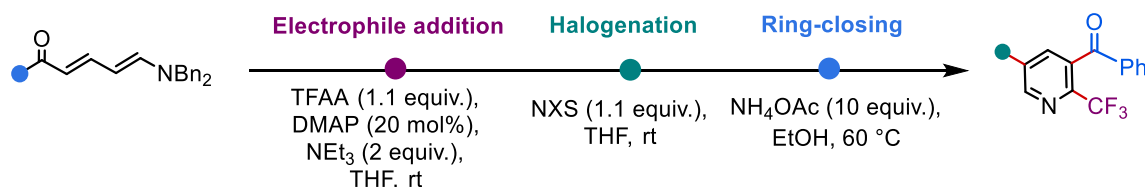
General Procedure D: Skeletal rearrangement



a) An oven-dried microwave vial containing Zincke ketone substrate (1.0 equiv.), DMAP (20 mol%) and Et_3N (2.0 equiv.) were taken in dry THF (0.1 M). The acylating reagent (1.1 equiv.) was added to it. The reaction was stirred at room temperature for 1-2 hours. However, for disubstituted arene bearing Zincke ketones (15i and 15j), the reaction was performed at 0 °C. For Zincke imines (1 equiv.), 1.2 equivalents of TFAA were used at 40 °C.

b) NH_4OAc (10.0 equiv.) and EtOH (0.05 M) were added. The reaction mixture was stirred at 60 °C for 2-4 hours and then concentrated under reduced pressure. The residue was redissolved with water (8 mL) and DCM (30 mL) and extracted with DCM (10 mL \times 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The crude product was then purified by flash column chromatography to afford the rearrangement product.

General Procedure E: Sequential functionalization (incorporating C5 halogenation)



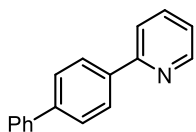
a) To the solution of 2-phenyl Zincke ketone (1.0 equiv.) in dry THF (0.1 M), DMAP (20 mol%) and Et_3N (2.0 equiv.) were added. Subsequently, trifluoroacetic anhydride (0.22 mmol, 1.1 equiv.). The reaction was stirred at room temperature for 1-2 hours.

b) *N*-halo succinimide (1.1 equiv.) was added to the above. The reaction mixture was stirred at room temperature for 1 h. However, for fluorination, NFSI (2 equiv.) was added to the above, and the reaction was stirred overnight.

c) NH_4OAc (10.0 equiv.) and EtOH (0.05 M) were added. The reaction mixture was stirred at 60 °C for 2-4 hours and then concentrated under reduced pressure. The residue was redissolved with water (8 mL) and DCM (30 mL) and extracted with DCM (10 mL \times 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The crude product was then purified by flash column chromatography to afford the rearranged trisubstituted product.

5. Synthesis of Pyridine Starting Materials

2-([1,1'-biphenyl]-4-yl)pyridine (S1)



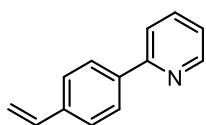
Prepared according to *General Procedure A* using 2-bromopyridine (0.24 mL, 2.5 mmol), 4-biphenylboronic acid (594.1 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) in 1,4-dioxane (10 mL) and water (5 mL) to yield the titled compound as a white solid (439 mg, 76%).

1H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.61 (m, 1H), 8.07 – 7.94 (m, 2H), 7.78 – 7.54 (m, 6H), 7.46 – 7.27 (m, 2H), 7.24 – 7.17 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 148.7, 141.0, 139.7, 137.1, 136.2, 128.0, 126.7, 126.5, 126.3, 121.3, 119.7.

The data are consistent with the literature.^[1]

2-(4-vinylphenyl)pyridine (S2)



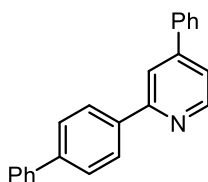
Prepared according to *General Procedure A* using 2-bromopyridine (0.24 mL, 2.5 mmol), 4-vinylphenylboronic acid (443.9 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) in 1,4-dioxane (10 mL) and water (5 mL) to yield the titled compound as a colourless oil (407.5 mg, 90%).

1H NMR (400 MHz, $CDCl_3$) δ 8.69 (dt, J = 4.9, 1.6 Hz, 1H), 8.02 – 7.94 (m, 2H), 7.77 – 7.72 (m, 2H), 7.56 – 7.49 (m, 2H), 7.22 (ddd, J = 5.8, 4.9, 2.8 Hz, 1H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.83 (dd, J = 17.6, 0.9 Hz, 1H), 5.31 (dd, J = 10.9, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 149.8, 138.7, 138.3, 136.9, 136.5, 127.2, 126.8, 122.2, 120.6, 114.7.

The data are consistent with the literature.^[1]

2-([1,1'-biphenyl]-4-yl)-4-phenylpyridine (S3)

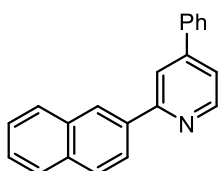


Prepared according to *General Procedure A* using 2-bromo-4-phenylpyridine (585 mg, 2.5 mmol), 4-biphenylboronic acid (594.1 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as a pale yellow solid (729.13 mg, 95%).

1H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 5.1 Hz, 1H), 8.05 (d, J = 7.9 Hz, 2H), 7.88 (s, 1H), 7.68 – 7.53 (m, 6H), 7.42 (t, J = 7.3 Hz, 2H), 7.37 (t, J = 7.4 Hz, 4H), 7.27 (t, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 150.1, 149.5, 141.9, 140.6, 138.5, 138.2, 129.2, 129.2, 128.9, 127.6, 127.5, 127.5, 127.2, 120.4, 118.8, 115.9.

The data are consistent with the literature.^[2]

2-(naphthalen-2-yl)-4-phenylpyridine (S4)

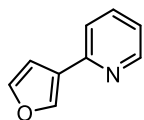


Prepared according to *General Procedure A* using 2-bromo-4-phenylpyridine (585 mg, 2.5 mmol), 2-naphthylboronic acid (516 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as yellow oil (576 mg, 82%).

1H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, J = 5.1 Hz, 1H), 8.56 (d, J = 1.9 Hz, 1H), 8.21 (dd, J = 8.6, 1.8 Hz, 1H), 8.08 (d, J = 1.7 Hz, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.93 – 7.87 (m, 1H), 7.77 – 7.70 (m, 2H), 7.56 – 7.51 (m, 4H), 7.48 (dd, J = 6.4, 3.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 150.2, 149.6, 138.6, 136.7, 133.8, 133.6, 129.3, 129.2, 128.9, 128.6, 127.8, 127.2, 126.7, 126.6, 126.5, 124.8, 120.5, 119.2.

The data are consistent with the literature.^[2]

2-(furan-3-yl)pyridine (S5)



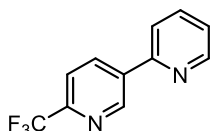
Prepared according to *General Procedure A* using 2-bromopyridine (0.24 mL, 2.5 mmol), 3-furylboronic acid (335.7 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as a colourless liquid (275.6 mg, 76%).

1H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, $J = 4.9, 2.0, 1.0$ Hz, 1H), 8.03 (q, $J = 1.3$ Hz, 1H), 7.67 (td, $J = 7.7, 1.9$ Hz, 1H), 7.52 – 7.41 (m, 2H), 7.14 (dddt, $J = 6.0, 4.8, 1.9, 1.1$ Hz, 1H), 6.90 (dd, $J = 1.9, 0.9$ Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 149.7, 144.0, 141.3, 136.8, 127.1, 121.9, 120.2, 108.7.

The data are consistent with the literature.^[1]

6'-(trifluoromethyl)-2,3'-bipyridine (S6)



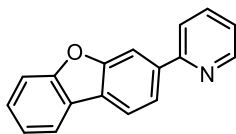
Prepared according to *General Procedure A* using 2-bromopyridine (0.24 mL, 2.5 mmol), (6-(Trifluoromethyl)pyridin-3-yl)boronic acid (572.8 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as a white solid (487.33 mg, 87%).

1H NMR (400 MHz, $CDCl_3$) δ 9.32 – 9.26 (m, 1H), 8.81 – 8.73 (m, 1H), 8.57 – 8.47 (m, 1H), 7.83 (m, 3H), 7.37 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 150.3, 148.4, 148.1 (q, $J = 34.7$ Hz), 137.4, 135.7, 123.7, 121.6 (q, $J = 274.1$ Hz), 121.0, 120.5.

The data are consistent with the literature.^[4]

2-(dibenzo[b,d]furan-3-yl)pyridine (S7)



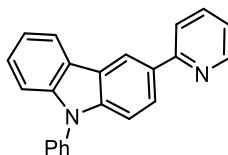
Prepared according to *General Procedure A* using 2-bromopyridine (0.24 mL, 2.5 mmol), 2-(Dibenzo[b,d]furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (882.45 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as a white solid (557.6 mg, 91%).

1H NMR (400 MHz, $CDCl_3$) δ 8.77 – 8.72 (m, 1H), 8.24 (t, $J = 1.1$ Hz, 1H), 8.03 (t, $J = 1.2$ Hz, 2H), 7.99 (d, $J = 7.6$ Hz, 1H), 7.86 – 7.76 (m, 2H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.52 – 7.44 (m, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.30 – 7.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 157.1, 157.0, 149.8, 138.8, 137.1, 127.6, 125.1, 124.1, 123.0, 122.4, 121.9, 121.0, 121.0, 120.9, 111.9, 110.3.

The data are consistent with the literature.^[3]

9-phenyl-3-(pyridin-2-yl)-9H-carbazole (S8)



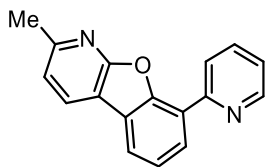
Prepared according to *General Procedure A* using 2-bromopyridine (0.24 mL, 2.5 mmol) 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1.1 g, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as a white solid (736 mg, 92%).

1H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.74 (d, $J = 4.8$ Hz, 1H), 8.24 (d, $J = 7.8$ Hz, 1H), 8.07 (d, $J = 8.7$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.78 (t, $J = 7.8$ Hz, 1H), 7.70 – 7.56 (m, 4H), 7.54 – 7.40 (m, 4H), 7.32 (dt, $J = 8.1, 4.0$ Hz, 1H), 7.24 (d, $J = 13.1$ Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 149.6, 141.5, 137.6, 136.8, 131.6, 130.0, 127.6, 127.1, 126.3, 125.2, 124.0, 123.7, 121.4, 120.7, 120.4, 119.2, 110.0.

The data are consistent with the literature.^[1]

2-methyl-8-(pyridin-2-yl)benzofuro[2,3-b]pyridine (S9)

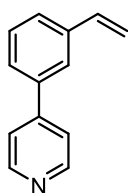


Prepared according to *General Procedure A* using 2-bromopyridine (0.24 mL, 2.5 mmol), 2-Methyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzofuro[2,3-b]pyridine (927.4 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as an off-white solid (585.2 mg, 90%).

1H NMR (400 MHz, $CDCl_3$) δ 8.76 (qd, $J = 2.9, 1.2$ Hz, 1H), 8.53 (m, 1H), 8.37 (dt, $J = 7.9, 1.6$ Hz, 1H), 8.16 (dd, $J = 7.8, 2.9$ Hz, 1H), 7.99 – 7.90 (m, 1H), 7.83 (tt, $J = 8.2, 1.5$ Hz, 1H), 7.51 (d, $J = 2.8$ Hz, 1H), 7.28 (tdd, $J = 7.8, 3.6, 2.1$ Hz, 1H), 7.21 (dd, $J = 7.7, 2.7$ Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 155.5, 151.9, 150.8, 148.6, 135.8, 128.9, 126.7, 123.7, 123.3, 122.8, 122.5, 121.6, 120.4, 118.0, 112.6, 23.7.

The data are consistent with the literature.^[1]

4-(3-vinylphenyl)pyridine (S10)



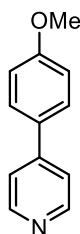
Prepared according to *General Procedure A* using 4-bromopyridine hydrochloride (487.5 mg, 2.5 mmol), 3-vinylphenylboronic acid (444 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as yellow oil (400 mg, 88%).

1H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.52 (m, 2H), 7.65 (d, $J = 1.8$ Hz, 1H), 7.58 – 7.39 (m, 5H), 6.79 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.84 (dd, $J = 17.6, 0.8$ Hz, 1H), 5.34 (dd, $J = 10.9, 0.8$ Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 138.5, 138.3, 136.3, 129.4, 126.9, 126.5, 125.0, 121.9, 115.0.

The data are consistent with the literature.

4-(4-methoxyphenyl)pyridine (S11)



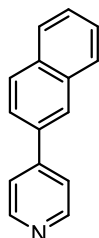
Prepared according to *General Procedure A* using 4-bromopyridine hydrochloride (487.5 mg, 2.5 mmol), 4-methoxyphenylboronic acid (456 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as a pale yellow solid (393.1 mg, 85%).

1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 2H), 7.62 – 7.55 (m, 2H), 7.49 (d, $J = 5.1$ Hz, 2H), 7.00 (d, $J = 8.6$ Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 149.6, 148.4, 130.2, 128.3, 121.3, 114.7, 55.5.

The data are consistent with the literature.^[5]

4-(naphthalen-2-yl)pyridine (S12)



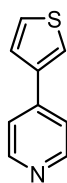
Prepared according to *General Procedure A* using 4-bromopyridine hydrochloride (487.5 mg, 2.5 mmol), 2-naphthylboronic acid (516 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as a white solid (400 mg, 78%).

1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, $J = 5.9$ Hz, 2H), 8.07 (s, 1H), 7.94 – 7.82 (m, 3H), 7.74 – 7.66 (m, 1H), 7.58 (d, $J = 5.1$ Hz, 2H), 7.53 (dt, $J = 6.2, 3.6$ Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 148.3, 135.2, 133.4, 129.0, 128.5, 127.7, 126.9, 126.7, 126.4, 124.5, 121.8.

The data are consistent with the literature.^[6]

4-(thiophen-3-yl)pyridine (S13)



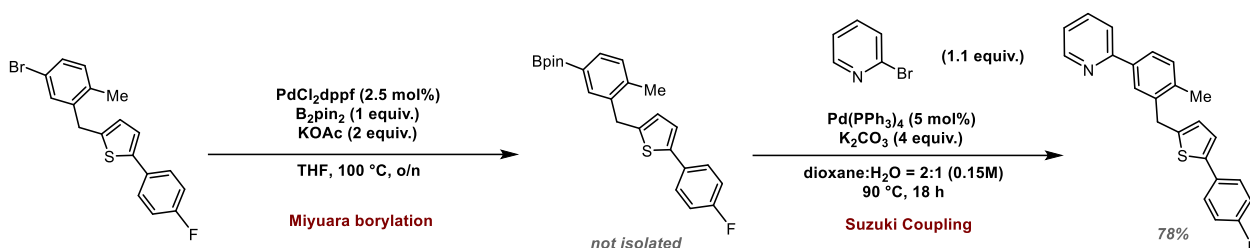
Prepared according to *General Procedure A* using 4-bromopyridine hydrochloride (487.5 mg, 2.5 mmol), 3-thienylboronic acid (384 mg, 3 mmol), K_2CO_3 (1.382 g, 10 mmol), $Pd(OAc)_2$ (28.06 mg, 0.125 mmol) and PPh_3 (131.2 mg, 0.5 mmol) to yield the titled compound as an off-white solid (322 mg, 80%).

1H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.60 (m, 2H), 7.69 (dd, J = 2.6, 1.7 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.46 – 7.44 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 142.9, 139.3, 127.2, 125.7, 123.3, 120.9.

The data are consistent with the literature.^[6]

2-(3-((5-(4-fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)pyridine (S14)



Step 1 (Miyuara borylation): In an oven-dried microwave vial, 2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (1.1 g, 3 mmol) was added with $PdCl_2 \cdot dppf$ (54.88 mg, 0.075 mmol, 2.5 mol%), $KOAc$ (588.9 mg, 6 mmol, 2.0 equiv.), and B_2pin_2 (761.8 mg, 3 mmol, 1.0 equiv.). The vial was evacuated and backfilled 3 times with nitrogen, and then dry THF (15 mL) was added to it. The reaction mixture was heated to 90 °C while stirring overnight. The mixture was allowed to cool to room temperature, diluted with H_2O , and extracted three times with $EtOAc$. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to yield the crude product, which was used for the next step without purification.

Step 2 (Suzuki coupling): To the reaction vessel with crude product, 2-bromopyridine (0.32 mL, 3.3 mmol, 1.1 equiv.), K_2CO_3 (1.65 g, 12 mmol, 4 equiv.), and $Pd(PPh_3)_4$ (173.3 mg, 0.15 mmol, 5 mol%) were added, and the vessel was evacuated and refilled with N_2 three times on a Schlenk line. A 2:1 mixture of 1,4-dioxane (12 mL) and water (6 mL), previously degassed by bubbling through N_2 for 5 minutes, was added, and the resulting biphasic mixture was heated to 90 °C while stirring for 18 h. The mixture was allowed to cool to room temperature, diluted with H_2O , and extracted three times with $EtOAc$. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to yield the crude product, which was purified by silica column chromatography to yield the titled compound as a white solid (850 mg, 78%).

1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.8 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.82 (dd, J = 7.9, 2.0 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.47 (ddd, J = 8.7, 5.4, 2.7 Hz, 2H), 7.30 (d, J = 7.9 Hz, 1H), 7.21 (td, J = 4.6, 2.3 Hz, 1H), 7.06 – 6.96 (m, 3H), 6.70 (d, J = 3.6 Hz, 1H), 4.22 (s, 2H), 2.38 (s, 3H).

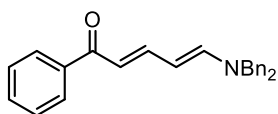
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.21.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 246.5 Hz), 157.3, 149.6, 143.5, 141.6, 138.7, 137.7, 137.4, 137.0, 131.0 (d, J = 3.4 Hz), 128.3, 127.2 (d, J = 8.0 Hz), 125.8 (d, J = 48.7 Hz), 125.6, 122.8, 122.1, 120.6, 115.9, 115.8, 34.5, 19.5.

HRMS (+APCI): Calculated for: $C_{23}H_{19}FN$ $[M+H]^+$ 360.1222, found 360.1216.

6. Synthesis of Zincke ketones

(2E,4E)-5-(dibenzylamino)-1-phenylpenta-2,4-dien-1-one (15b)



Prepared according to *General Procedure B* using 2-phenylpyridine (155.2 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (289.4 mg, 82%).

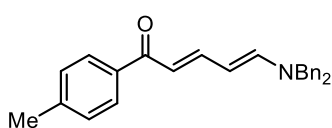
¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.0 Hz, 2H), 7.68 (dd, *J* = 14.2, 11.7 Hz, 1H), 7.49 – 7.30 (m, 9H), 7.19 (d, *J* = 7.1 Hz, 4H), 7.14 (d, *J* = 12.7 Hz, 1H), 6.61 (d, *J* = 14.3 Hz, 1H), 5.56 (t, *J* = 12.2 Hz, 1H), 4.36 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 189.8, 152.3, 148.9, 139.9, 136.1, 131.4, 129.0, 128.3, 128.0, 127.5, 113.8, 98.9.

HRMS (+APCI): Calculated for: C₂₅H₂₄NO [M+H]⁺ 354.1858, found 354.1850.

The data are consistent with the literature.^[1,7]

(2E,4E)-5-(dibenzylamino)-1-(*p*-tolyl)penta-2,4-dien-1-one (15c)



Prepared according to *General Procedure B* using 2-(*p*-tolyl)pyridine (0.17mL, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (290 mg, 79%).

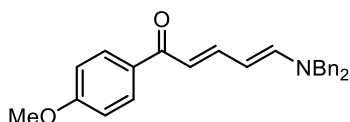
¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.66 (dd, *J* = 14.3, 11.6 Hz, 1H), 7.45 – 7.31 (m, 6H), 7.23 – 7.18 (m, 6H), 7.13 (d, *J* = 12.8 Hz, 1H), 6.62 (d, *J* = 14.2 Hz, 1H), 5.54 (t, *J* = 12.2 Hz, 1H), 4.35 (s, 4H), 2.39 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 189.4, 152.1, 148.4, 142.0, 137.2, 136.2, 129.0, 129.0, 128.2, 128.0, 127.6, 113.8, 98.9, 21.7.

HRMS (+APCI): Calculated for: C₂₆H₂₆NO [M+H]⁺ 368.2014, found 368.2014.

The data are consistent with the literature.^[1]

(2E,4E)-5-(dibenzylamino)-1-(4-methoxyphenyl)penta-2,4-dien-1-one (15d)



Prepared according to *General Procedure B* using 2-(4-methoxyphenyl)pyridine (185.3 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (264.2 mg, 70%).

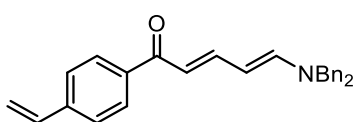
¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.88 (m, 2H), 7.66 (dd, *J* = 14.2, 11.6 Hz, 1H), 7.39 – 7.29 (m, 6H), 7.24 – 7.16 (m, 4H), 7.13 (d, *J* = 12.8 Hz, 1H), 6.93 – 6.88 (m, 2H), 6.62 (d, *J* = 14.2 Hz, 1H), 5.54 (t, *J* = 12.2 Hz, 1H), 4.35 (s, 4H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 188.3, 162.5, 152.0, 148.0, 136.2, 132.6, 130.1, 129.0, 128.0, 127.6, 113.5, 98.9, 55.5.

HRMS (+APCI): Calculated for: C₂₆H₂₆NO₂ [M+H]⁺ 384.1964, found 384.1958.

The data are consistent with the literature.^[1]

(2E,4E)-5-(dibenzylamino)-1-(4-vinylphenyl)penta-2,4-dien-1-one (15e)



Prepared according to *General Procedure B* using 2-(4-vinylphenyl)pyridine (181.1 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (276.8 mg, 73%).

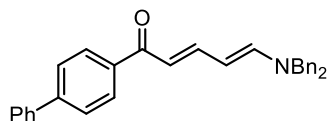
¹H NMR (500 MHz, CDCl₃) δ 7.92 – 7.86 (m, 2H), 7.67 (dd, *J* = 14.2, 11.6 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.28 (m, 6H), 7.19 (dd, *J* = 6.9, 1.8 Hz, 4H), 7.15 (d, *J* = 12.8 Hz, 1H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.61 (d, *J* = 14.3 Hz, 1H), 5.83 (d, *J* = 17.7 Hz, 1H), 5.56 (t, *J* = 12.2 Hz, 1H), 5.33 (d, *J* = 11.1 Hz, 1H), 4.36 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 189.0, 152.4, 148.8, 140.6, 139.2, 136.4, 136.1, 129.0, 128.4, 128.0, 127.6, 126.2, 115.7, 113.7, 99.0.

HRMS (+APCI): Calculated for: C₂₇H₂₆NO [M+H]⁺ 380.2014, found 380.2002.

Melting Point: 98 – 100 °C.

(2E,4E)-1-([1,1'-biphenyl]-4-yl)-5-(dibenzylamino)penta-2,4-dien-1-one (15f)



Prepared according to *General Procedure B* using 2-([1,1'-biphenyl]-4-yl)pyridine (231.1 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (321.9 mg, 75%).

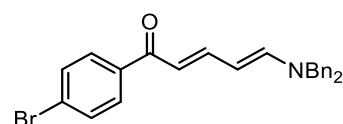
¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.78 – 7.59 (m, 5H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.35 (dt, *J* = 13.0, 6.9 Hz, 7H), 7.18 (dd, *J* = 16.1, 10.0 Hz, 5H), 6.66 (d, *J* = 14.2 Hz, 1H), 5.58 (t, *J* = 12.2 Hz, 1H), 4.37 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 189.2, 152.4, 148.9, 144.2, 140.5, 138.7, 136.1, 129.1, 129.0, 128.6, 128.1, 127.9, 127.6, 127.4, 127.0, 113.7, 99.0.

HRMS (+APCI): Calculated for: C₃₁H₂₈NO [M+H]⁺ 430.2171, found 430.2169.

The data are consistent with the literature.^[1]

(2E,4E)-1-(4-bromophenyl)-5-(dibenzylamino)penta-2,4-dien-1-one (15g)



Prepared according to *General Procedure B* using 2-(4-bromophenyl)pyridine (234.1 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (310.4 mg, 72%).

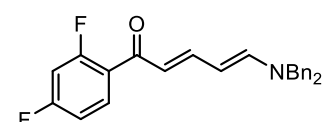
¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.67 (dd, *J* = 14.2, 11.7 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.34 (dq, *J* = 14.3, 7.1 Hz, 6H), 7.21 – 7.13 (m, 5H), 6.54 (d, *J* = 14.2 Hz, 1H), 5.55 (t, *J* = 12.2 Hz, 1H), 4.36 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 188.4, 152.8, 149.5, 138.7, 135.9, 131.6, 129.7, 129.1, 128.1, 127.6, 126.2, 113.1, 99.0.

HRMS (+APCI): Calculated for: C₂₅H₂₃BrNO [M+H]⁺ 432.0963, found 432.0964.

The data are consistent with the literature.^[1]

(2E,4E)-5-(dibenzylamino)-1-(2,4-difluorophenyl)penta-2,4-dien-1-one (15h)



Prepared according to *General Procedure B* using 2-(2,4-difluorophenyl)pyridine (0.15 mL, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (233.5 mg, 60%).

¹H NMR (500 MHz, CDCl₃) δ 7.78 (td, *J* = 8.5, 6.7 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.35 (dp, *J* = 14.3, 6.9 Hz, 6H), 7.18 (d, *J* = 7.4 Hz, 4H), 7.14 (d, *J* = 12.7 Hz, 1H), 6.91 (td, *J* = 8.2, 2.4 Hz, 1H), 6.81 (ddd, *J* = 11.0, 8.8, 2.4 Hz, 1H), 6.42 (dd, *J* = 14.3, 2.9 Hz, 1H), 5.55 (t, *J* = 12.2 Hz, 1H), 4.35 (s, 4H).

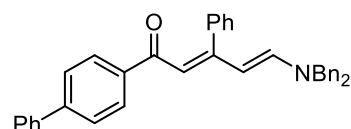
¹⁹F NMR (376 MHz, CDCl₃) δ -106.05, -107.18.

¹³C NMR (101 MHz, CDCl₃) δ 186.4 (d, *J* = 3.2 Hz), 164.1 (dd, *J* = 313.7, 12.0 Hz), 161.6 (dd, *J* = 315.0, 12.2 Hz), 153.0, 149.7, 135.9, 132.5 (dd, *J* = 10.2, 4.8 Hz), 129.0, 128.1, 127.6, 125.2 (dd, *J* = 14.3, 3.7 Hz), 117.2 (d, *J* = 6.8 Hz), 111.6 (dd, *J* = 21.1, 3.6 Hz), 104.4 (dd, *J* = 27.6, 25.2 Hz), 99.0.

HRMS (+APCI): Calculated for: C₂₅H₂₂F₂NO [M+H]⁺ 390.1669, found 390.1666.

The data are consistent with the literature.^[1]

(2Z,4E)-1-([1,1'-biphenyl]-4-yl)-5-(dibenzylamino)-3-phenylpenta-2,4-dien-1-one (15i)



Prepared according to *General Procedure B* using 2-([1,1'-biphenyl]-4-yl)-4-phenylpyridine (307 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (257.7 mg, 51%).

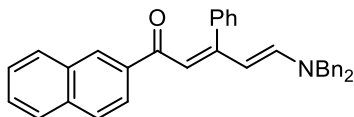
¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 13.5 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 4H), 7.36 (d, *J* = 7.1 Hz, 6H), 7.31 (d, *J* = 5.5 Hz, 3H), 7.25 (d, *J* = 7.5 Hz, 4H), 7.13 (d, *J* = 19.8 Hz, 5H), 6.89 (d, *J* = 13.4 Hz, 1H), 6.25 (s, 1H), 4.36 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 189.2, 160.9, 153.9, 143.7, 142.3, 140.6, 140.5, 136.2, 130.5, 129.2, 128.9, 128.3, 128.2, 128.2, 127.9, 127.8, 127.3, 127.0, 111.3, 99.7.

HRMS (+APCI): Calculated for: C₃₇H₃₂NO [M+H]⁺ 506.2484, found 506.2467.

Melting Point: 88 – 90 °C.

(2Z,4E)-5-(dibenzylamino)-1-(naphthalen-2-yl)-3-phenylpenta-2,4-dien-1-one (15j)



Prepared according to *General Procedure B* using 2-(naphthalen-2-yl)-4-phenylpyridine (281 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (220.4 mg, 46%).

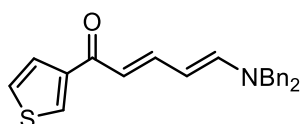
¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 1.7 Hz, 1H), 8.07 – 8.04 (m, 1H), 7.96 – 7.82 (m, 5H), 7.53 – 7.47 (m, 5H), 7.44 – 7.41 (m, 2H), 7.36 (t, *J* = 7.0 Hz, 5H), 7.32 (d, *J* = 1.5 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.00 (d, *J* = 13.5 Hz, 1H), 6.47 (s, 1H), 4.36 (s, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 189.4, 160.9, 153.9, 142.3, 138.9, 136.1, 134.7, 132.8, 130.2, 129.3, 129.2, 128.8, 128.2, 128.1, 127.9, 127.9, 127.6, 127.3, 126.2, 124.7, 111.3, 99.6.

HRMS (+APCI): C₃₅H₃₀NO [M+H]⁺ 480.2327, found 480.2324.

Melting Point: 88 – 90 °C.

(2E,4E)-5-(dibenzylamino)-1-(thiophen-3-yl)penta-2,4-dien-1-one (15k)



Prepared according to *General Procedure B* using 2-(3-thienyl)pyridine (0.15 mL, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (233.7 mg, 65%).

¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.65 (dd, *J* = 14.3, 11.7 Hz, 1H), 7.56 (dt, *J* = 6.4, 3.2 Hz, 1H), 7.39 – 7.30 (m, 6H), 7.29 – 7.26 (m, 1H), 7.23 – 7.17 (m, 4H), 7.13 (d, *J* = 12.7 Hz, 1H), 6.48 (d, *J* = 14.2 Hz, 1H), 5.52 (t, *J* = 12.2 Hz, 1H), 4.35 (s, 4H).

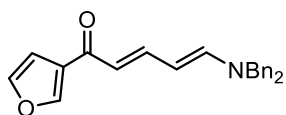
¹³C NMR (126 MHz, CDCl₃) δ 183.7, 152.2, 148.1, 144.5, 136.1, 129.7, 129.0, 128.0, 127.5, 125.7, 114.5, 98.7.

HRMS (+APCI): Calculated for: C₂₃H₂₂NOS [M+H]⁺ 360.1422, found 360.1421.

Melting Point: 92 – 94 °C.

The data are consistent with the literature.^[1]

(2E,4E)-5-(dibenzylamino)-1-(furan-3-yl)penta-2,4-dien-1-one (15l)



Prepared according to *General Procedure B* using 2-(furan-3-yl)pyridine (145 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (195.5 mg, 57%).

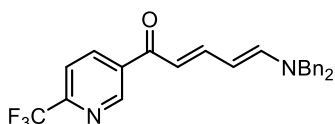
¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.62 (t, *J* = 12.9 Hz, 1H), 7.36 (td, *J* = 13.4, 6.6 Hz, 7H), 7.19 (d, *J* = 7.2 Hz, 4H), 7.12 (d, *J* = 12.9 Hz, 1H), 6.80 (s, 1H), 6.27 (d, *J* = 14.3 Hz, 1H), 5.47 (t, *J* = 12.2 Hz, 1H), 4.35 (s, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 183.8, 152.2, 147.4, 145.8, 143.6, 136.1, 129.2, 129.0, 128.0, 127.6, 114.9, 109.4, 98.4.

HRMS (+APCI): Calculated for: C₂₃H₂₂NO₂ [M+H]⁺ 344.1651, found 344.1647.

The data are consistent with the literature.^[1]

(2E,4E)-5-(dibenzylamino)-1-(6-(trifluoromethyl)pyridin-3-yl)penta-2,4-dien-1-one (15m)



Prepared according to *General Procedure B* using 6'-(trifluoromethyl)-2,3'-bipyridine (224 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow oil (177.3 mg, 42%).

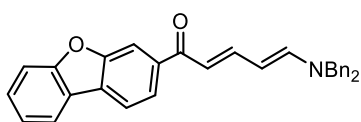
¹H NMR (400 MHz, Acetone) δ 9.15 (d, *J* = 2.0 Hz, 1H), 8.45 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.92 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.72 (dd, *J* = 14.1, 11.8 Hz, 1H), 7.64 (d, *J* = 12.6 Hz, 1H), 7.43–7.29 (m, 10H), 6.61 (d, *J* = 14.1 Hz, 1H), 5.66 (t, *J* = 12.2 Hz, 1H), 4.55 (s, 4H).

¹⁹F NMR (376 MHz, CDCl₃) δ -68.48.

¹³C NMR (101 MHz, CDCl₃) δ 186.2, 154.3, 151.4, 149.6 (q, *J* = 33.9 Hz), 137.7, 137.0, 135.5, 130.5, 129.2, 128.3, 127.6, 121.5 (q, *J* = 274.4 Hz), 120.3 (d, *J* = 2.7 Hz), 112.3, 99.3.

HRMS (+APCI): Calculated for: C₂₅H₂₂F₃N₂O [M+H]⁺ 423.1684, found 423.1676.

(2E,4E)-1-(dibenzo[b,d]furan-3-yl)-5-(dibenzylamino)penta-2,4-dien-1-one (15n)



Prepared according to *General Procedure B* using 2-(dibenzo[b,d]furan-3-yl)pyridine (245.3 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (243.75 mg, 55%).

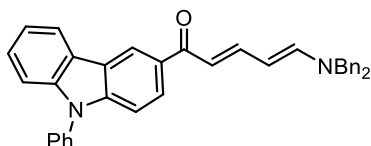
¹H NMR (400 MHz, CDCl₃) δ 8.14 (t, *J* = 1.0 Hz, 1H), 8.00–7.95 (m, 3H), 7.74 (dd, *J* = 14.1, 11.7 Hz, 1H), 7.59 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.49 (ddt, *J* = 8.4, 7.1, 1.2 Hz, 1H), 7.40–7.31 (m, 7H), 7.23–7.16 (m, 5H), 6.71 (d, *J* = 14.2 Hz, 1H), 5.60 (t, *J* = 12.2 Hz, 1H), 4.38 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 188.9, 157.4, 156.2, 152.6, 149.2, 139.2, 136.0, 130.5, 129.1, 128.1, 127.6, 127.2, 123.9, 123.1, 123.0, 121.3, 120.3, 113.7, 112.0, 111.5, 99.1

HRMS (+APCI): Calculated for: C₃₁H₂₆NO₂ [M+H]⁺ 444.1964, found 444.1960.

Melting Point: 96–98 °C.

(2E,4E)-5-(dibenzylamino)-1-(9-phenyl-9H-carbazol-3-yl)penta-2,4-dien-1-one (15o)



Prepared according to *General Procedure B* using 9-phenyl-3-(pyridin-2-yl)-9H-carbazole (320.4 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as an orange solid (300.7 mg, 58%).

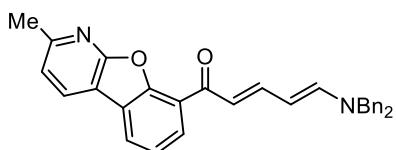
¹H NMR (500 MHz, CDCl₃) δ 8.82 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.12–8.03 (m, 1H), 7.77 (dd, *J* = 14.2, 11.6 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42–7.35 (m, 7H), 7.33 (t, *J* = 7.0 Hz, 3H), 7.22 (d, *J* = 7.4 Hz, 4H), 7.17 (d, *J* = 12.8 Hz, 1H), 6.87 (d, *J* = 14.2 Hz, 1H), 5.63 (t, *J* = 12.2 Hz, 1H), 4.37 (s, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 189.0, 151.8, 147.8, 143.0, 141.7, 137.3, 136.2, 132.1, 130.1, 129.0, 127.9, 127.9, 127.5, 127.2, 126.7, 126.4, 123.8, 123.2, 121.2, 120.7, 120.7, 114.0, 110.2, 109.3, 99.0.

HRMS (+APCI): Calculated for: C₃₇H₃₁N₂O [M+H]⁺ 519.2436, found 519.2441.

The data are consistent with the literature.^[1]

(2E,4E)-5-(dibenzylamino)-1-(2-methylbenzofuro[2,3-b]pyridin-7-yl)penta-2,4-dien-1-one (15p)



Prepared according to *General Procedure B* using 2-methyl-7-(pyridin-2-yl)benzofuro[2,3-b]pyridine (261 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as an orange solid (265.75 mg, 58%).

¹H NMR (500 MHz, CDCl₃) δ 8.13 (td, *J* = 6.0, 2.9 Hz, 2H), 7.97 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.84 (dd, *J* = 14.2, 11.8 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24–7.16 (m, 7H), 5.75 (t, *J* = 12.2 Hz, 1H), 4.38 (s, 4H), 2.69 (s, 3H).

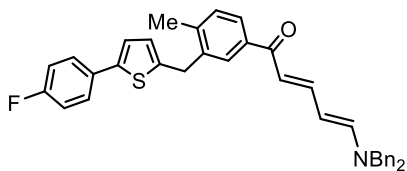
¹³C NMR (101 MHz, CDCl₃) δ 186.0, 163.0, 156.7, 153.0, 152.3, 149.5, 136.0, 130.0, 129.1, 129.0, 128.0, 127.6,

125.5, 123.8, 123.6, 123.4, 119.2, 117.3, 113.5, 99.8, 24.6.

HRMS (+APCI): Calculated for: C₃₁H₂₇O₂N₂ [M+H]⁺ 459.2073, found 459.2067.

The data are consistent with the literature.^[1]

(2E,4E)-5-(dibenzylamino)-1-(3-((5-(4-fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)penta-2,4-dien-1-one (15q)



Prepared according to *General Procedure B* using 2-(3-((5-(4-fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)pyridine (360 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), collidine (132 μL, 1 mmol), and K₂CO₃ (276.4 mg, 2 mmol) to yield the titled compound as a yellow solid (334.2 mg, 60%).

¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 1.9 Hz, 1H), 7.75 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.67 (dd, *J* = 14.2, 11.6 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.36 (dd, *J* = 8.0, 6.2 Hz, 4H), 7.32 (d, *J* = 7.1 Hz, 2H), 7.25 – 7.14 (m, 5H), 7.13 (d, *J* = 12.7 Hz, 1H), 7.04 – 6.98 (m, 3H), 6.65 (d, *J* = 3.6 Hz, 1H), 6.61 (d, *J* = 14.3 Hz, 1H), 5.55 (t, *J* = 12.2 Hz, 1H), 4.34 (s, 4H), 4.16 (s, 2H), 2.35 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -115.21.

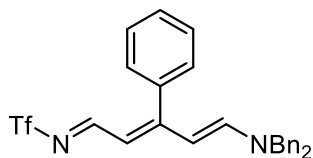
¹³C NMR (126 MHz, CDCl₃) δ 189.4, 162.2 (d, *J* = 246.6 Hz), 152.3, 148.7, 143.3, 141.6, 140.6, 138.1 (d, *J* = 9.8 Hz), 136.1, 130.6, 129.5, 129.0, 128.0, 127.6, 127.2 (d, *J* = 7.9 Hz), 126.9, 126.1, 122.8, 115.8 (d, *J* = 21.9 Hz), 113.8, 99.0, 34.4, 19.7.

HRMS (+APCI): Calculated for: C₃₇H₃₃FNOS [M+H]⁺ 558.2267, found 558.2259.

Melting Point: 98 – 99 °C.

7. Synthesis of Zincke Imines

N-((1E,2Z,4E)-5-(dibenzylamino)-3-phenylpenta-2,4-dien-1-ylidene)-1,1,1-trifluoromethanesulfonamide (15r)



Prepared according to *General Procedure C* using 4-phenylpyridine (154 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), and collidine (132 μL, 1 mmol) to yield the titled compound as an yellow solid (397 mg, 82%)

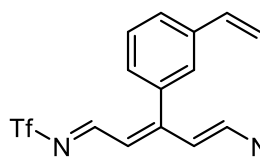
¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 11.4 Hz, 1H), 7.44 – 7.35 (m, 10H), 7.20 (dd, *J* = 19.9, 6.8 Hz, 4H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 11.4 Hz, 1H), 5.97 (d, *J* = 12.4 Hz, 1H), 4.52 (s, 2H), 4.33 (s, 2H).

¹⁹F NMR (376 MHz, CDCl₃) δ -77.81.

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 173.4, 157.0, 134.8, 133.8, 133.7, 130.6, 129.8, 129.6, 129.4, 129.2, 129.1, 128.1, 127.4, 120.0 (q, *J* = 323.8 Hz), 117.7, 105.6, 60.3, 52.0.

The data are consistent with the literature.^[7]

N-((1E,2Z,4E)-5-(dibenzylamino)-3-(3-vinylphenyl)penta-2,4-dien-1-ylidene)-1,1,1-trifluoromethanesulfonamide (15s)



Prepared according to *General Procedure C* using 4-(3-vinylphenyl)pyridine (245.3 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), and collidine (132 μL, 1 mmol) to yield the titled compound as an orange solid (423.8 mg, 82%).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 11.4 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.34 (m, 8H), 7.25 – 7.12 (m, 4H), 7.06 – 7.02 (m, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.31 (d, *J* = 11.3 Hz, 1H), 5.97 (d, *J* = 12.5 Hz, 1H), 5.78 (d, *J* = 17.5 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H), 4.52 (s, 2H), 4.33 (s, 2H).

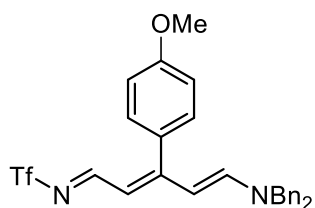
¹⁹F NMR (376 MHz, CDCl₃) δ -77.81.

¹³C NMR (101 MHz, CDCl₃) δ 174.6, 173.4, 156.8, 138.0, 136.0, 133.8, 133.7, 130.6, 129.4, 129.1, 129.1, 129.0, 128.9, 128.7, 128.2, 127.6, 127.4, 120.0 (q, *J* = 324.2 Hz), 117.6, 115.5, 105.5, 60.2, 52.1.

HRMS (+APCI): Calculated for: C₂₈H₂₆F₃N₂O₂S [M+H]⁺ 511.1667, found 511.1662.

Melting Point: 98 – 100 °C.

***N*-((1*E*,2*Z*,4*E*)-5-(dibenzylamino)-3-(4-methoxyphenyl)penta-2,4-dien-1-ylidene)-1,1,1-trifluoromethanesulfonamide (15t)**



Prepared according to *General Procedure C* using 4-(4-methoxyphenyl)pyridine (245.3 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), and collidine (132 μL, 1 mmol) to yield the titled compound as a yellow solid (421.6 mg, 82%).

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 10.7 Hz, 1H), 7.38 (p, *J* = 7.9 Hz, 7H), 7.18 (d, *J* = 7.4 Hz, 4H), 7.10 – 7.05 (m, 2H), 6.94 – 6.89 (m, 2H), 6.29 (d, *J* = 11.6 Hz, 1H), 5.95 (d, *J* = 12.5 Hz, 1H), 4.51 (s, 2H), 4.36 (s, 2H), 3.86 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -77.81.

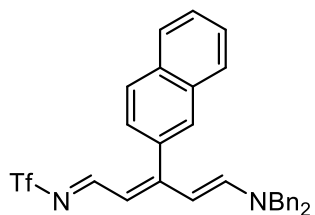
¹³C NMR (101 MHz, CDCl₃) δ 174.9, 173.3, 157.1, 134.0, 133.7, 131.4, 129.4, 129.1, 128.7, 128.5, 128.3, 128.1, 127.7, 127.4, 126.9, 120.1 (q, *J* = 323.2 Hz), 114.2, 105.6, 60.3, 55.5, 52.0.

HRMS (+APCI): Calculated for: C₂₇H₂₆F₃N₂O₃S [M+H]⁺ 515.1616, found 515.1611.

Melting Point: 100 – 120 °C.

***N*-((1*E*,2*Z*,4*E*)-5-(dibenzylamino)-3-(naphthalen-2-yl)penta-2,4-dien-1-ylidene)-1,1,1-trifluoromethanesulfonamide (15u)**

Prepared according to *General Procedure C* using 4-(naphthalen-2-yl)pyridine (205.1 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), and collidine (132 μL, 1 mmol) to yield the titled compound as an orange solid (461 mg, 86%).



¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 12.2 Hz, 1H), 7.92 – 7.82 (m, 4H), 7.71 (s, 1H), 7.58 (h, *J* = 5.9 Hz, 3H), 7.38 (ddt, *J* = 19.1, 9.1, 4.7 Hz, 6H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.03 – 6.94 (m, 2H), 6.40 (d, *J* = 11.3 Hz, 1H), 6.04 (d, *J* = 12.5 Hz, 1H), 4.53 (s, 2H), 4.27 (s, 2H).

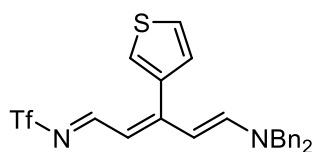
¹⁹F NMR (376 MHz, CDCl₃) δ -77.97.

¹³C NMR (126 MHz, CDCl₃) δ 174.9, 173.4, 159.3, 157.1, 150.2, 133.6, 132.7, 129.4, 129.3, 129.0, 128.7, 128.5, 128.2, 128.0, 127.4, 127.1, 127.0, 124.6, 122.0, 120.0 (q, *J* = 322.4 Hz), 117.8, 105.8, 60.2, 52.2.

HRMS (+APCI): Calculated for: C₂₇H₂₆F₃N₂O₃S [M+H]⁺ 535.1665, found 535.1649.

Melting Point: 100 – 120 °C.

***N*-((1*E*,2*Z*,4*E*)-5-(dibenzylamino)-3-(thiophen-3-yl)penta-2,4-dien-1-ylidene)-1,1,1-trifluoromethanesulfonamide (15v)**



Prepared according to *General Procedure C* using 4-(thiophen-3-yl)pyridine (161 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (179 μL, 1.2 mmol), and collidine (132 μL, 1 mmol) to yield the titled compound as a yellow solid (392 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 10.5 Hz, 1H), 7.45 – 7.33 (m, 9H), 7.18 (d, *J* = 7.1 Hz, 2H), 7.12 – 7.03 (m, 3H), 6.30 (d, *J* = 11.0 Hz, 1H), 5.94 (d, *J* = 12.4 Hz, 1H), 4.53 (s, 2H), 4.40 (s, 2H).

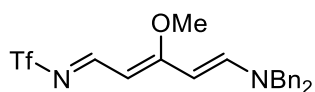
¹⁹F NMR (376 MHz, CDCl₃) δ -77.76.

¹³C NMR (101 MHz, CDCl₃) δ 172.9, 169.1, 156.5, 133.9, 133.7, 130.6, 129.5, 129.1, 129.0, 128.7, 128.3, 127.4, 127.0, 125.8, 120.0 (q, *J* = 323.8 Hz), 117.6, 105.3, 60.3, 52.2.

HRMS (+APCI): Calculated for: C₂₄H₂₂F₂N₂O₂S₂ [M+H]⁺ 491.1075, found 491.1059.

Melting Point: 88 – 90 °C.

***N*-((1*E*,2*Z*,4*E*)-5-(dibenzylamino)-3-methoxypenta-2,4-dien-1-ylidene)-1,1,1-trifluoromethanesulfonamide(15w)**



Prepared according to *General Procedure C* using 4-methoxypyridine (109.1 mg, 1 mmol), Tf₂O (169 μL, 1 mmol), Bn₂NH (150 μL, 1 mmol), and collidine (132 μL, 1 mmol) to yield the titled compound as a greenish-yellow oil (262.9 mg, 60%).

¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, *J* = 11.4 Hz, 1H), 7.95 (d, *J* = 12.3 Hz, 1H), 7.43 – 7.32 (m, 6H), 7.22 – 7.14 (m, 4H), 5.80 (d, *J* = 11.4 Hz, 1H), 5.57 (d, *J* = 12.4 Hz, 1H), 4.55 (s, 2H), 4.41 (s, 2H), 3.89 (s, 3H).

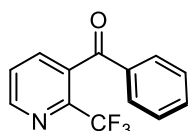
¹⁹F NMR (376 MHz, CDCl₃) δ -77.88.

¹³C NMR (101 MHz, CDCl₃) δ 168.8, 166.0, 153.1, 130.7, 129.3, 129.1, 128.8, 128.4, 127.9, 127.9, 127.3, 120.0 (q, *J* = 322.8 Hz), 97.1, 87.3, 60.4, 57.1, 51.5.

HRMS (+APCI): Calculated for: C₂₁H₂₂F₃N₂O₃S [M+H]⁺ 439.1303, found 439.1295.

8. Synthesis of Rearranged Pyridine Products

phenyl(2-(trifluoromethyl)pyridin-3-yl)methanone (17a)



Prepared according to *General Procedure D* using corresponding Zincke ketone (70 mg, 0.2 mmol), TFAA (32 μL, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a colorless oil (43 mg, 80%).

Gram-scale reaction

Prepared according to *General Procedure C* using corresponding Zincke ketone (1.1 g, 3 mmol), TFAA (0.46 mL, 3.3 mmol), DMAP (73.3 mg, 0.6 mmol), NEt₃ (0.84 mL, 0.6 mmol), and NH₄OAc (2.34 g, 30 mmol) to yield the titled compound as a colorless oil (620 mg, 80%).

Telescope reaction

Step 1: Prepared according to *General Procedure B* using 2-phenylpyridine (31.04 mg, 0.2 mmol), Tf₂O (33.9 μL, 0.2 mmol), Bn₂NH (35.8 μL, 0.24 mmol), collidine (26.4 μL, 0.2 mmol), and K₂CO₃ (55.3 mg, 0.4 mmol) to yield the crude product. The organic layer was separated, and the aqueous layer was washed with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was dried under vacuum.

Step 2: Prepared according to *General Procedure C* using the crude product, TFAA (67.8 μL, 0.4 mmol), DMAP (9.76 mg, 0.08 mmol), NEt₃ (111.6 μL, 0.8 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a colorless oil (60%).

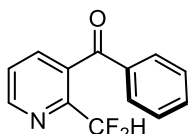
¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J* = 4.0 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.66 – 7.56 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 2H).

¹⁹F NMR (377 MHz, CDCl₃) δ -63.27.

¹³C NMR (101 MHz, CDCl₃) δ 193.4, 150.4, 144.9 (q, *J* = 34.9 Hz), 136.7, 135.9, 134.5, 130.1, 128.9, 126.0, 121.3 (q, *J* = 275.5 Hz).

HRMS (+APCI): Calculated for: C₁₃H₉F₃NO [M+H]⁺ 252.0636, found 252.0634.

(2-(difluoromethyl)pyridin-3-yl)(phenyl)methanone (17b)



Prepared according to *General Procedure D* using corresponding Zincke ketone (70 mg, 0.2 mmol), difluoroacetic anhydride (29 μL, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a colorless oil (37 mg, 75%).

¹H NMR (400 MHz, CDCl₃) δ 8.84 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.82 – 7.75 (m, 3H), 7.69 – 7.59 (m, 1H), 7.53 – 7.43 (m, 3H), 6.84 (t, *J* = 54.6 Hz, 1H).

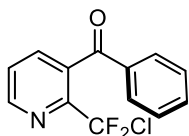
¹⁹F NMR (377 MHz, CDCl₃) δ -115.05.

¹³C NMR (101 MHz, CDCl₃) δ 194.6, 150.8, 150.2 (t, *J* = 23.6 Hz), 137.1, 136.3, 134.3, 134.0 (t, *J* = 2.2 Hz), 130.3,

128.9, 124.7, 112.2 (t, $J = 241.7$ Hz).

HRMS (+APCI): Calculated for: $C_{13}H_{10}F_2NO$ $[M+H]^+$ $[M+H]^+$ 234.0730, found 234.0718.

(2-(chlorodifluoromethyl)pyridin-3-yl)(phenyl)methanone (17c)



Prepared according to *General Procedure D* using corresponding Zincke ketone (70 mg, 0.2 mmol), chlorodifluoroacetic anhydride (40 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a colorless oil (48 mg, 85%).

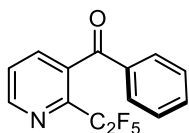
1H NMR (400 MHz, $CDCl_3$) δ 8.88 – 8.83 (m, 1H), 7.78 – 7.71 (m, 3H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.56 (dd, $J = 7.8, 4.7$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -51.20.

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 150.3, 149.0 (t, $J = 29.2$ Hz), 136.7, 136.0, 134.5, 133.0, 130.2, 128.9, 125.5, 124.4 (t, $J = 291.5$ Hz).

HRMS (+APCI): Calculated for: $C_{13}H_9ClF_2NO$ $[M+H]^+$ 268.0335, found 268.0327.

(2-(perfluoroethyl)pyridin-3-yl)(phenyl)methanone (17d)



Prepared according to *General Procedure D* using corresponding Zincke ketone (70 mg, 0.2 mmol), pentafluoropropionic anhydride (46 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a colorless oil (35 mg, 55%).

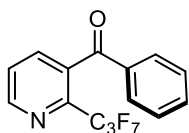
1H NMR (400 MHz, $CDCl_3$) δ 8.90 – 8.84 (m, 1H), 7.79 – 7.71 (m, 3H), 7.66 – 7.57 (m, 2H), 7.48 (t, $J = 7.8$ Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -81.6, -110.13.

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 150.2, 144.6 (t, $J = 26.3$ Hz), 136.6, 136.2, 136.0, 134.5, 130.1, 128.9, 125.7, 118.8 (qt, $J = 288.4, 36.9$ Hz), 111.9 (tq, $J = 257.4, 38.3$ Hz).

HRMS (+APCI): Calculated for: $C_{14}H_9F_5NO$ $[M+H]^+$ 302.0599, found 302.0598.

(2-(perfluoropropyl)pyridin-3-yl)(phenyl)methanone (17e)



Prepared according to *General Procedure D* using corresponding Zincke ketone (70 mg, 0.2 mmol), heptafluorobutyric anhydride (57 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a colorless oil (34 mg, 46%).

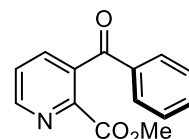
1H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, $J = 4.6$ Hz, 1H), 7.74 (t, $J = 6.2$ Hz, 3H), 7.64 – 7.57 (m, 2H), 7.47 (t, $J = 7.8$ Hz, 2H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -80.2, -108.0, -124.51.

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 150.2, 144.6 (t, $J = 26.5$ Hz), 136.5, 136.3, 136.1, 134.4, 130.1, 128.9, 125.7, 117.9 (qt, $J = 288.4, 33.9$ Hz), 113.5 (tt, $J = 258.3, 31.3$ Hz), 109.0 (tq, $J = 264.6, 37.8$ Hz).

HRMS (+APCI): Calculated for: $C_{15}H_9F_7NO$ $[M+H]^+$ 352.0567, found 352.0580.

methyl 3-benzoylpicolinate (17f)



Prepared according to *General Procedure D* using corresponding Zincke ketone (70 mg, 0.2 mmol), methyl oxalyl chloride (22 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (26 mg, 51%).

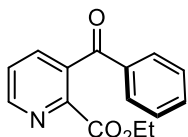
1H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, $J = 4.7, 1.6$ Hz, 1H), 7.81 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.77 – 7.71 (m, 2H), 7.62 – 7.55 (m, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 165.2, 150.5, 146.3, 138.0, 136.6, 136.5, 133.7, 129.4, 128.9, 126.3, 53.1.

HRMS (+APCI): Calculated for: $C_{14}H_{12}NO_3$ $[M+H]^+$ 242.0812, found 242.0809.

Melting point: 102-106 °C.

ethyl 3-benzoylpicolinate (17g)



Prepared according to *General Procedure D* using corresponding Zincke ketone (70 mg, 0.2 mmol), ethyl oxalyl chloride (22 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (25 mg, 51%).

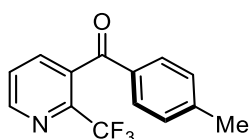
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.87 (dd, $J = 4.7, 1.6$ Hz, 1H), 7.81 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.77 – 7.72 (m, 2H), 7.63 – 7.55 (m, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 4.22 (q, $J = 7.1$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.8, 164.7, 150.6, 146.7, 137.8, 136.7, 136.5, 133.7, 129.5, 128.9, 126.1, 62.6, 13.9.

HRMS (+APCI): Calculated for: $\text{C}_{15}\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 256.0968, found 256.0980.

Melting point: 102-106 $^\circ\text{C}$.

p-tolyl(2-(trifluoromethyl)pyridin-3-yl)methanone (17h)



Prepared according to *General Procedure D* using corresponding Zincke ketone (73.5 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow oil (40.3 mg, 76%).

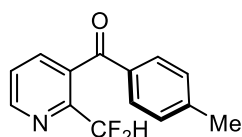
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.84 (dd, $J = 4.7, 1.6$ Hz, 1H), 7.77 (d, $J = 6.2$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.60 (dd, $J = 7.8, 4.8$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 2.43 (s, 3H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.34.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.1, 150.3, 145.8, 144.9 (q, $J = 34.8$ Hz), 136.7, 134.8, 133.5, 129.7, 125.9, 121.3 (q, $J = 275.5$ Hz), 21.9.

HRMS (+APCI): Calculated for: $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 266.0793, found 266.0787.

(2-(difluoromethyl)pyridin-3-yl)(*p*-tolyl)methanone (17i)



Prepared according to *General Procedure D* using corresponding Zincke ketone (73.5 mg, 0.2 mmol), difluoroacetic anhydride (29 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a colourless oil (36 mg, 73%).

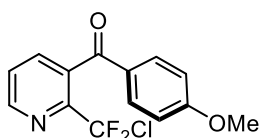
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.84 – 8.80 (m, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.67 (d, $J = 7.9$ Hz, 2H), 7.50 (dd, $J = 7.8, 4.8$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 6.81 (t, $J = 54.6$ Hz, 1H), 2.43 (s, 3H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -115.03.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.2, 150.7, 150.2 (t, $J = 23.6$ Hz), 145.5, 136.9, 134.3 (t, $J = 2.4$ Hz), 134.0, 130.5, 129.6, 124.6, 112.4 (t, $J = 241.7$ Hz), 21.9.

HRMS (+APCI): Calculated for: $\text{C}_{14}\text{H}_{12}\text{F}_2\text{NO}$ $[\text{M}+\text{H}]^+$ 248.0887, found 248.0887.

(2-(chlorodifluoromethyl)pyridin-3-yl)(4-methoxyphenyl)methanone (17j)



Prepared according to *General Procedure D* using corresponding Zincke ketone (76.6 mg, 0.2 mmol), chlorodifluoroacetic anhydride (40 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (39.2 mg, 66%).

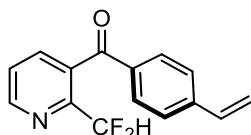
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.84 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.76 – 7.69 (m, 3H), 7.55 (dd, $J = 7.8, 4.7$ Hz, 1H), 6.97 – 6.92 (m, 2H), 3.88 (s, 3H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -51.35.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 192.1, 164.7, 150.1, 148.9 (t, $J = 29.1$ Hz), 136.7, 133.3, 132.6, 129.1, 125.5, 124.4 (t, $J = 291.5$ Hz), 114.2, 55.8.

HRMS (+APCI): Calculated for: $\text{C}_{14}\text{H}_{10}\text{ClF}_2\text{NO}_2$ $[\text{M}+\text{H}]^+$ 298.0446, found 298.0444.

(2-(difluoromethyl)pyridin-3-yl)(4-vinylphenyl)methanone (17k)



Prepared according to *General Procedure D* using corresponding Zincke ketone (75.8 mg, 0.2 mmol), difluoroacetic anhydride (29 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a colourless oil (37.3 mg, 72%).

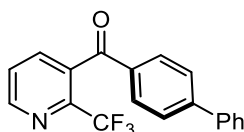
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.82 (dd, $J = 4.9, 1.6$ Hz, 1H), 7.78 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.76 – 7.72 (m, 2H), 7.52 – 7.48 (m, 3H), 6.94 – 6.70 (m, 2H), 5.90 (d, $J = 17.6$ Hz, 1H), 5.44 (d, $J = 10.8$ Hz, 1H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -114.93.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.9, 143.3, 136.9, 135.8, 135.5, 134.1 (t, $J = 2.3$ Hz), 130.7, 126.6, 124.6 (d, $J = 1.8$ Hz), 117.9, 112.4 (t, $J = 241.8$ Hz).

HRMS (+APCI): Calculated for: $\text{C}_{15}\text{H}_{12}\text{F}_2\text{NO}$ $[\text{M}+\text{H}]^+$ 260.0887, found 260.0878.

[1,1'-biphenyl]-4-yl(2-(trifluoromethyl)pyridin-3-yl)methanone (17l)



Prepared according to *General Procedure D* using corresponding Zincke ketone (85.8 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a pale-yellow solid (36 mg, 55%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.88 (dd, $J = 4.9, 1.6$ Hz, 1H), 7.84 – 7.81 (m, 3H), 7.72 – 7.69 (m, 2H), 7.63 (dt, $J = 6.2, 1.5$ Hz, 3H), 7.50 – 7.47 (m, 2H), 7.43 (d, $J = 6.0$ Hz, 1H).

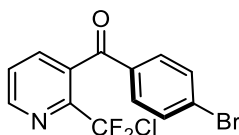
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.27.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.0, 150.4, 147.3, 145.0 (q, $J = 34.8$ Hz), 139.6, 136.7, 134.7, 130.8, 129.2, 128.8, 127.6, 127.5, 126.0, 121.4 (q, $J = 275.6$ Hz).

HRMS (+APCI): Calculated for: $\text{C}_{19}\text{H}_{13}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 328.0949, found 328.0947.

Melting Point: 112 – 114 $^\circ\text{C}$.

(4-bromophenyl)(2-(chlorodifluoromethyl)pyridin-3-yl)methanone (17m)



Prepared according to *General Procedure D* using corresponding Zincke ketone (85 mg, 0.2 mmol), chlorodifluoroacetic anhydride (40 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as an orange solid (44.1 mg, 64%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.86 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.72 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.65 – 7.55 (m, 5H).

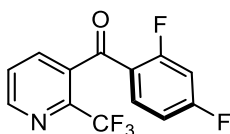
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -51.22.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 192.6, 150.5, 149.0 (t, $J = 29.3$ Hz), 136.6, 134.8, 132.5, 132.3, 131.5, 130.1, 125.6, 124.3 (t, $J = 291.2$ Hz).

HRMS (+APCI): Calculated for: $\text{C}_{13}\text{H}_7\text{BrClF}_2\text{NO}$ $[\text{M}+\text{H}]^+$ 345.9446, found 345.9441.

Melting Point: 58 – 60 $^\circ\text{C}$.

(2,4-difluorophenyl)(2-(trifluoromethyl)pyridin-3-yl)methanone (17n)



Prepared according to *General Procedure D* using corresponding Zincke ketone (77.8 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow oil (39 mg, 68%).

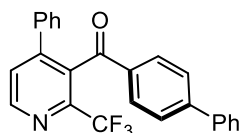
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.84 – 8.80 (m, 1H), 7.97 (td, $J = 8.6, 6.4$ Hz, 1H), 7.78 – 7.73 (m, 1H), 7.59 (dd, $J = 7.9, 4.7$ Hz, 1H), 7.05 – 7.02 (m, 1H), 6.83 (ddd, $J = 10.9, 8.5, 2.5$ Hz, 1H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.49, -98.14, -103.54.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 188.8, 166.4 (dd, $J = 392.7, 12.7$ Hz), 163.8 (dd, $J = 393.7, 12.7$ Hz), 150.4, 144.0 (td, $J = 36.0, 34.1$ Hz), 136.2, 135.7 (d, $J = 2.4$ Hz), 133.6 (dd, $J = 10.7, 2.4$ Hz), 126.2, 121.3 (dd, $J = 9.7, 3.6$ Hz), 121.3 (q, $J = 275.3$ Hz), 112.8 (dd, $J = 21.9, 3.5$ Hz), 105.3 (t, $J = 25.8$ Hz).

HRMS (+APCI): Calculated for: $\text{C}_{13}\text{H}_7\text{F}_5\text{NO}$ $[\text{M}+\text{H}]^+$ 288.0448, found 288.0439.

[1,1'-biphenyl]-4-yl(4-phenyl-2-(trifluoromethyl)pyridin-3-yl)methanone (17o)



Prepared according to *General Procedure D* using corresponding Zincke ketone (101 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a red solid (42 mg, 53%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.89 (d, $J = 5.0$ Hz, 1H), 7.64 – 7.57 (m, 4H), 7.57 – 7.50 (m, 5H), 7.46 – 7.41 (m, 3H), 7.41 – 7.36 (m, 2H), 7.27 (d, $J = 1.0$ Hz, 1H).

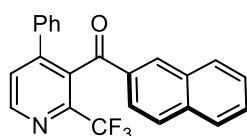
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.46.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.6, 150.1, 149.8, 146.5, 145.2 (q, $J = 34.2$ Hz), 139.6, 136.4, 135.4, 133.4, 130.0, 129.3, 129.1, 128.9, 128.7, 128.6, 127.4, 127.4, 127.2, 121.6 (q, $J = 276.3$ Hz).

HRMS (+APCI): Calculated for: $\text{C}_{25}\text{H}_{17}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 404.1262, found 404.1265.

Melting Point: 98 – 100 $^\circ\text{C}$.

naphthalen-2-yl(4-phenyl-2-(trifluoromethyl)pyridin-3-yl)methanone (17p)



Prepared according to *General Procedure D* using corresponding Zincke ketone (95.8 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a brown solid (38 mg, 51%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.91 (d, $J = 4.9$ Hz, 1H), 7.93 (s, 1H), 7.78 (dd, $J = 8.1, 6.5$ Hz, 2H), 7.76 – 7.73 (m, 2H), 7.61 (d, $J = 5.0$ Hz, 1H), 7.59 – 7.54 (m, 1H), 7.49 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.26 – 7.22 (m, 2H), 7.18 (dq, $J = 6.3, 3.5$ Hz, 3H).

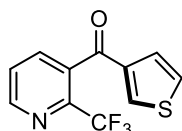
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.44.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.0, 150.2, 149.9, 145.3 (q, $J = 34.2$ Hz), 136.4, 135.9, 134.1, 133.4, 132.3, 132.2, 129.8, 129.2, 129.2, 128.8, 128.7, 127.9, 127.5, 127.0, 124.0, 121.6 (q, $J = 276.3$ Hz).

HRMS (+APCI): Calculated for: $\text{C}_{23}\text{H}_{15}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 378.1106, found 378.1089.

Melting Point: 94 – 96 $^\circ\text{C}$.

thiophen-3-yl(2-(trifluoromethyl)pyridin-3-yl)methanone (17q)



Prepared according to *General Procedure D* using corresponding Zincke ketone (71.8 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow oil (31.9 mg, 62%).

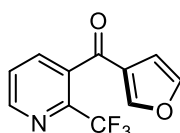
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.85 (d, $J = 4.7$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.73 (dt, $J = 2.7, 1.1$ Hz, 1H), 7.61 (dd, $J = 7.8, 4.8$ Hz, 1H), 7.56 (d, $J = 5.1$ Hz, 1H), 7.42 – 7.39 (m, 1H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.26.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 186.8, 150.5, 144.7 (q, $J = 35.0$ Hz), 141.6, 136.5, 136.3, 134.9, 127.5, 127.4, 126.0, 121.3 (q, $J = 275.7$ Hz).

HRMS (+APCI): Calculated for: $\text{C}_{11}\text{H}_7\text{F}_3\text{NOS}$ $[\text{M}+\text{H}]^+$ 258.0200, found 258.0197.

furan-3-yl(2-(trifluoromethyl)pyridin-3-yl)methanone (17r)



Prepared according to *General Procedure D* using corresponding Zincke ketone (68.6 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow oil (25.1 mg, 52%).

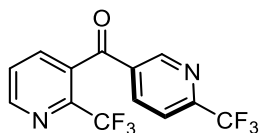
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.85 (d, $J = 4.7$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.73 (dt, $J = 2.7, 1.1$ Hz, 1H), 7.61 (dd, $J = 7.8, 4.8$ Hz, 1H), 7.56 (d, $J = 5.1$ Hz, 1H), 7.42 – 7.39 (m, 1H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.26.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 186.7, 150.6, 150.2, 145.2, 144.8 (d, $J = 35.1$ Hz), 136.4, 134.8, 127.9, 126.0, 121.3 (q, $J = 275.6$ Hz), 109.0.

HRMS (+APCI): Calculated for: $\text{C}_{11}\text{H}_7\text{F}_3\text{NO}_2$ $[\text{M}+\text{H}]^+$ 242.0429, found 242.0419.

(2-(trifluoromethyl)pyridin-3-yl)(6-(trifluoromethyl)pyridin-3-yl)methanone (17s)



Prepared according to *General Procedure D* using corresponding Zincke ketone (84.43 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μ L, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow oil (37.1 mg, 58%).

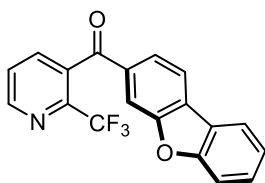
¹H NMR (500 MHz, CDCl₃) δ 8.99 (d, J = 2.1 Hz, 1H), 8.94 (dd, J = 4.8, 1.5 Hz, 1H), 8.29 (dd, J = 8.2, 2.2 Hz, 1H), 7.85 (dd, J = 8.2, 0.9 Hz, 1H), 7.83 (dd, J = 7.8, 1.6 Hz, 1H), 7.69 (dd, J = 7.8, 4.8 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -63.05, -68.35.

¹³C NMR (101 MHz, CDCl₃) δ 191.1, 152.3 (q, J = 35.4 Hz), 151.4, 151.2, 145.1 (q, J = 35.2 Hz), 138.6, 136.6, 133.5, 132.8, 126.3, 121.1 (q, J = 275.6 Hz), 121.0 (q, J = 274.9 Hz), 120.8 (d, J = 2.7 Hz).

HRMS (+APCI): Calculated for: C₁₃H₇F₆N₂O [M+H]⁺ 321.0463, found 321.0455.

dibenzo[b,d]furan-3-yl(2-(trifluoromethyl)pyridin-3-yl)methanone (17t)



Prepared according to *General Procedure D* using corresponding Zincke ketone (88.6 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μ L, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (30 mg, 44%).

¹H NMR (400 MHz, CDCl₃) δ 8.91 (dd, J = 4.8, 1.6 Hz, 1H), 8.02 (ddd, J = 7.8, 3.0, 2.0 Hz, 2H), 7.98 (d, J = 1.5 Hz, 1H), 7.86 (dd, J = 7.8, 1.6 Hz, 1H), 7.75 (dd, J = 8.1, 1.5 Hz, 1H), 7.68 – 7.53 (m, 3H), 7.41 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H).

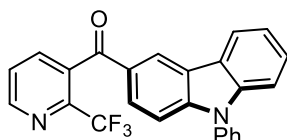
¹⁹F NMR (376 MHz, CDCl₃) δ -63.26.

¹³C NMR (101 MHz, CDCl₃) δ 192.8, 158.0, 155.8, 150.5, 145.0 (q, J = 34.8 Hz), 136.7, 134.8, 134.7, 130.1, 129.4, 126.0, 125.1, 123.6, 123.1, 121.9, 121.4 (q, J = 275.6 Hz), 120.9, 113.6, 112.3.

HRMS (+APCI): Calculated for: C₁₉H₁₁F₃NO₂ [M+H]⁺ 342.0742, found 342.0726.

Melting Point: 118 – 120 °C.

(9-phenyl-9H-carbazol-3-yl)(2-(trifluoromethyl)pyridin-3-yl)methanone (17u)



Prepared according to *General Procedure D* using corresponding Zincke ketone (103.7 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μ L, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (34.1 mg, 41%).

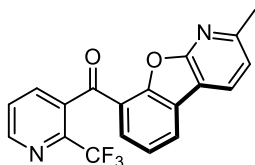
¹H NMR (400 MHz, CDCl₃) δ 8.90 (dd, J = 4.8, 1.6 Hz, 1H), 8.54 (d, J = 1.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.87 (ddd, J = 10.7, 8.2, 1.7 Hz, 2H), 7.67 – 7.61 (m, 3H), 7.55 (d, J = 7.8 Hz, 3H), 7.48 – 7.45 (m, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.37 – 7.32 (m, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -63.30.

¹³C NMR (101 MHz, CDCl₃) δ 192.9, 150.2, 144.9 (d, J = 34.7 Hz), 144.4, 142.1, 136.9, 136.7, 135.4, 130.3, 128.6, 128.4, 127.3, 126.0, 124.0, 123.5, 123.3, 121.5 (d, J = 275.3 Hz), 121.4, 120.8, 110.6, 110.0.

HRMS (+APCI): Calculated for: C₂₅H₁₆F₃N₂O [M+H]⁺ 417.1215, found 417.1207.

2-methylbenzofuro[2,3-b]pyridin-8-yl(2-(trifluoromethyl)pyridin-3-yl)methanone (17v)



Prepared according to *General Procedure D* using corresponding Zincke ketone (91.6 mg, 0.2 mmol), TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μ L, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (48.4 mg, 68%).

¹H NMR (500 MHz, CDCl₃) δ 8.90 (d, J = 4.7 Hz, 1H), 8.15 (dd, J = 7.8, 2.3 Hz, 2H), 7.99 – 7.94 (m, 1H), 7.88 (dd, J = 7.9, 1.5 Hz, 1H), 7.64 (dd, J = 7.8, 4.7 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 2.62 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -63.29.

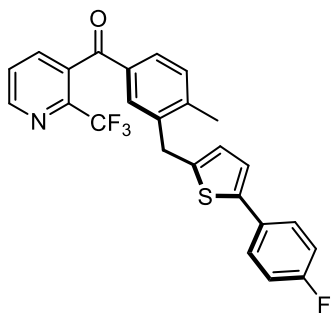
¹³C NMR (101 MHz, CDCl₃) δ 190.3, 163.1, 157.8, 152.9, 150.6, 144.6 (q, J = 34.9 Hz), 136.5, 136.0, 130.2, 129.4, 127.0, 126.2, 124.7, 123.5, 121.5, 121.4 (q, J = 275.6 Hz), 119.8, 112.5, 24.6.

HRMS (+APCI): Calculated for: C₁₉H₁₂F₃N₂O₂ [M+H]⁺ 357.0851, found 357.0858.

Melting Point: 190 – 192 °C.

(3-((5-(4-fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)(2-(trifluoromethyl)pyridin-3-yl)methanone (17w)

Prepared according to *General Procedure D* using corresponding Zincke ketone (111.4 mg, 0.2 mmol), TFAA (32 μL, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a pale-yellow oil (41 mg, 45%).



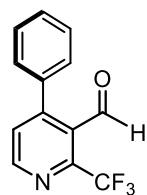
¹H NMR (500 MHz, CDCl₃) δ 8.82 (d, *J* = 4.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.46 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.08 – 6.98 (m, 3H), 6.64 (d, *J* = 3.5 Hz, 1H), 4.15 (s, 2H), 2.41 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -63.25, -114.85.

¹³C NMR (101 MHz, CDCl₃) δ 193.0, 162.3 (d, *J* = 247.0 Hz), 150.3, 144.8 (q, *J* = 35.0 Hz), 144.3, 142.0, 141.9, 139.2, 136.7, 134.7, 134.3, 131.1 (d, *J* = 7.4 Hz), 130.8 (d, *J* = 3.4 Hz), 129.1, 127.3 (d, *J* = 8.0 Hz), 126.5, 125.9, 122.5, 121.3 (q, *J* = 275.6 Hz), 116.0, 115.8, 34.1, 20.1.

HRMS (+APCI): Calculated for: C₂₅H₁₈F₄NOS [M+H]⁺ 456.1045, found 456.1044.

4-phenyl-2-(trifluoromethyl)nicotinaldehyde (19a)



Prepared according to *General Procedure D* using corresponding Zincke imine (96.8 mg, 0.2 mmol), TFAA (35 μL, 0.24 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (16.1 mg, 32%).

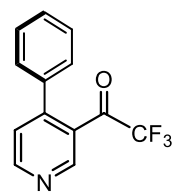
¹H NMR (400 MHz, CDCl₃) δ 10.20 (d, *J* = 1.9 Hz, 1H), 8.83 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 5.0 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.33 (dd, *J* = 6.7, 2.9 Hz, 2H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.16

¹³C NMR (101 MHz, CDCl₃) δ 190.8, 152.7, 150.6, 146.1 (q, *J* = 35.5 Hz), 135.3, 130.6, 129.9, 129.4, 129.2, 128.2, 121.4 (q, *J* = 276.1 Hz).

HRMS (+APCI): Calculated for: C₁₃H₉F₃NO [M+H]⁺ 252.0636, found 252.0620.

Melting Point: 64 – 66 °C.



The non-rearranged product, **2,2,2-trifluoro-1-(4-phenylpyridin-3-yl)ethan-1-one 20a** was isolated by flash column chromatography (30% EA:Hexane) as yellow oil (33.1 mg, 66%).

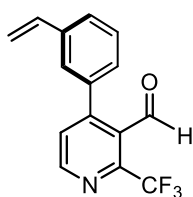
¹H NMR (500 MHz, CDCl₃) δ 8.88 (s, 1H), 8.82 (d, *J* = 5.1 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.31 – 7.27 (m, 2H).

¹⁹F NMR (376 MHz, CDCl₃) δ -73.71.

¹³C NMR (101 MHz, CDCl₃) δ 185.0 (q, *J* = 37.7 Hz), 153.0, 151.2, 149.0, 136.9, 129.7, 129.2, 128.4, 125.5, 115.6 (q, *J* = 291.8 Hz).

HRMS (+APCI): Calculated for: C₁₃H₉F₃NO [M+H]⁺ 252.0636, found 252.0619.

2-(trifluoromethyl)-4-(3-vinylphenyl)nicotinaldehyde (19b)



Prepared according to *General Procedure D* using corresponding Zincke imine (102 mg, 0.2 mmol), TFAA (35 μL, 0.24 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (18.8 mg, 34%).

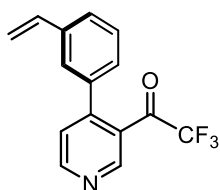
¹H NMR (400 MHz, CDCl₃) δ 10.24 (s, 1H), 8.89 – 8.83 (m, 1H), 7.67 – 7.45 (m, 3H), 7.35 – 7.20 (m, 1H), 6.78 (d, *J* = 19.6 Hz, 1H), 5.84 (d, *J* = 17.3 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.19

¹³C NMR (101 MHz, CDCl₃) δ 190.6, 152.5, 150.6, 146.1 (d, *J* = 35.7 Hz), 145.6, 138.6, 135.8, 130.6, 129.4, 128.6, 128.1, 127.5, 127.1, 121.4 (d, *J* = 275.8 Hz), 116.0.

HRMS (+APCI): Calculated for: C₁₅H₁₁F₃NO [M+H]⁺ 278.0714, found 278.0779.

Melting Point: 66 – 68 °C.



The non-rearranged product, **2,2,2-trifluoro-1-(4-(3-vinylphenyl)pyridin-3-yl)ethan-1-one 20b** was isolated by flash column chromatography (30% EA:Hexane) as yellow oil (35.5 mg, 64%).

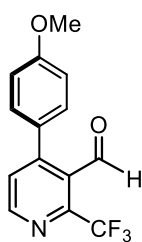
¹H NMR (500 MHz, CDCl₃) δ 8.89 (s, 1H), 8.84 (d, *J* = 5.2 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.37 (s, 1H), 7.32 (t, *J* = 1.8 Hz, 1H), 7.17 (dt, *J* = 7.6, 1.5 Hz, 1H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.79 (d, *J* = 17.6 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -73.66.

¹³C NMR (101 MHz, CDCl₃) δ 184.9 (q, *J* = 37.4 Hz), 152.8, 151.3, 148.9 (q, *J* = 2.8 Hz), 138.7, 137.1, 136.0, 129.5, 127.7, 127.5, 126.2, 125.5, 115.6, 115.6 (q, *J* = 292.0 Hz).

HRMS (+APCI): Calculated for: C₁₅H₁₁F₃NO [M+H]⁺ 278.0714, found 278.0776.

4-(4-methoxyphenyl)-2-(trifluoromethyl)nicotinaldehyde (19c)



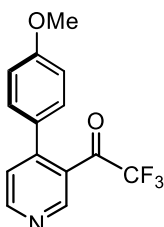
Prepared according to *General Procedure D* using corresponding Zincke imine (102.8 mg, 0.2 mmol), TFAA (35 μL, 0.24 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow oil (15.7 mg, 28%).

¹H NMR (400 MHz, CDCl₃) δ 10.11 (d, *J* = 1.6 Hz, 1H), 8.72 (d, *J* = 4.9 Hz, 1H), 7.50 (d, *J* = 4.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.81 (d, *J* = 1.0 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.20.

¹³C NMR (101 MHz, CDCl₃) δ 191.0, 161.1, 152.3, 150.4, 145.9 (q, *J* = 35.4 Hz), 131.0, 130.4, 128.0, 127.3, 121.4 (d, *J* = 275.9 Hz), 114.7, 55.6.

HRMS (+APCI): Calculated for: C₁₄H₁₁F₃NO₂ [M+H]⁺ 282.0742, found 282.0725.



The non-rearranged product, **2,2,2-trifluoro-1-(4-(4-methoxyphenyl)pyridin-3-yl)ethan-1-one 20c** was isolated by flash column chromatography (30% EA:Hexane) as yellow oil (38.2 mg, 68%).

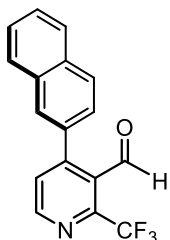
¹H NMR (400 MHz, CDCl₃) δ 8.91 – 8.64 (m, 2H), 7.41 (d, *J* = 4.8 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.00 – 6.95 (m, 2H), 3.84 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -73.70.

¹³C NMR (101 MHz, CDCl₃) δ 185.8 (q, *J* = 37.2 Hz), 160.9, 153.1, 150.4, 149.3, 129.9, 129.2, 125.0, 115.6 (q, *J* = 291.7 Hz), 114.8, 55.5.

HRMS (+APCI): Calculated for: C₁₄H₁₁F₃NO₂ [M+H]⁺ 282.0742, found 282.0730.

4-(naphthalen-2-yl)-2-(trifluoromethyl)nicotinaldehyde (19d)



Prepared according to *General Procedure D* using corresponding Zincke imine (106.8 mg, 0.2 mmol), TFAA (35 μL, 0.24 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (19.9 mg, 33%).

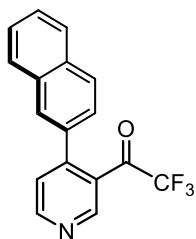
¹H NMR (400 MHz, CDCl₃) δ 10.25 (d, *J* = 1.9 Hz, 1H), 8.86 (d, *J* = 5.0 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.80 (d, *J* = 1.9 Hz, 1H), 7.67 (d, *J* = 5.0 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.43 (dd, *J* = 8.4, 1.9 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.11.

¹³C NMR (101 MHz, CDCl₃) δ 190.6, 152.6, 150.6, 146.3 (q, *J* = 35.2 Hz), 133.4, 133.0, 132.8, 130.7, 129.4, 129.2, 128.5, 128.4, 128.0, 127.7, 127.5, 126.2, 121.5 (q, *J* = 276.0 Hz).

HRMS (+APCI): Calculated for: C₁₇H₁₁F₃NO [M+H]⁺ 302.0793, found 302.0798.

Melting Point: 92 – 94 °C.



The non-rearranged product, **2,2,2-trifluoro-1-(4-(naphthalen-2-yl)pyridin-3-yl)ethan-1-one 20d** was isolated by flash column chromatography (30% EA:Hexane) as yellow oil (39.7 mg, 66%).

¹H NMR (400 MHz, CDCl₃) δ 8.95 (s, 1H), 8.86 (d, *J* = 5.2 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.76 (s, 1H), 7.56 (dt, *J* = 10.8, 6.0 Hz, 3H), 7.44 – 7.36 (m, 1H).

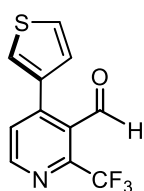
¹⁹F NMR (376 MHz, CDCl₃) δ -73.45.

¹³C NMR (101 MHz, CDCl₃) δ 185.0 (q, *J* = 37.1 Hz), 153.2, 151.1, 149.4 (q, *J* = 2.6 Hz), 134.4,

133.4, 133.2, 129.2, 128.6, 128.5, 128.2, 128.0, 127.5, 127.2, 125.7, 125.5, 115.7 (q, *J* = 291.8 Hz).

HRMS (+APCI): Calculated for: C₁₇H₁₁F₃NO [M+H]⁺ 302.0793, found 302.0788.

4-(thiophen-3-yl)-2-(trifluoromethyl)nicotinaldehyde (19e)



Prepared according to *General Procedure D* using corresponding Zincke imine (98 mg, 0.2 mmol), TFAA (35 μL, 0.24 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (18.5 mg, 36%).

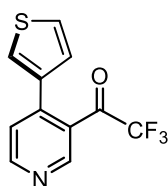
¹H NMR (400 MHz, CDCl₃) δ 10.27 (d, *J* = 1.9 Hz, 1H), 8.80 (d, *J* = 5.1 Hz, 1H), 7.62 (d, *J* = 5.1 Hz, 1H), 7.51 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.43 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.18 (dd, *J* = 5.0, 1.4 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.23.

¹³C NMR (101 MHz, CDCl₃) δ 191.1, 150.6, 146.6, 146.0 (d, *J* = 35.5 Hz), 135.7, 130.5, 128.3, 127.8, 127.6, 127.5, 121.4 (d, *J* = 276.0 Hz).

HRMS (+APCI): Calculated for: C₁₁H₇F₃NOS [M+H]⁺ 257.0200, found 258.0181.

Melting Point: 62 – 64 °C.



The non-rearranged product, **2,2,2-trifluoro-1-(4-(thiophen-3-yl)pyridin-3-yl)ethan-1-one 20e** was isolated by flash column chromatography (30% EA:Hexane) as yellow oil (33.7 mg, 62%).

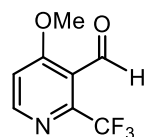
¹H NMR (400 MHz, CDCl₃) 8.82 (s, 2H), 7.52 – 7.44 (m, 2H), 7.38 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.11 (d, *J* = 1.4 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -74.00.

¹³C NMR (101 MHz, CDCl₃) δ 185.4 (d, *J* = 37.3 Hz), 153.0, 148.8, 145.2, 137.3, 127.8, 127.4, 126.2, 124.9, 119.5 (q, *J* = 319.4 Hz).

HRMS (+APCI): Calculated for: C₁₁H₇F₃NOS [M+H]⁺ 257.0200, found 258.0185.

4-methoxy-2-(trifluoromethyl)nicotinaldehyde (19f)



Prepared according to *General Procedure D* using corresponding Zincke imine (87.6 mg, 0.2 mmol), TFAA (35 μL, 0.24 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol), and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a white solid (14.8 mg, 36%).

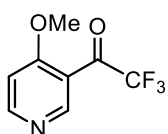
¹H NMR (400 MHz, CDCl₃) δ 10.47 (d, *J* = 2.0 Hz, 1H), 8.66 (d, *J* = 5.5 Hz, 2H), 7.13 (d, *J* = 5.4 Hz, 1H), 4.01 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.51

¹³C NMR (101 MHz, CDCl₃) δ 188.3, 166.7, 153.2, 147.7 (q, *J* = 35.2 Hz), 121.3, 121.2 (q, *J* = 275.8 Hz), 110.2, 56.8.

HRMS (+APCI): Calculated for: C₁₁H₇F₃NOS [M+H]⁺ 206.0429, found 206.0427.

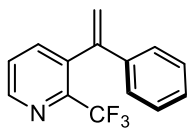
Melting Point: 74 – 76 °C.



Due to the volatile nature of the non-rearranged compound, **2,2,2-trifluoro-1-(4-methoxy-3-pyridinyl)ethan-1-one 20f** could not be isolated.

9. Product Derivatization

3-(1-phenylvinyl)-2-(trifluoromethyl)pyridine (21)



To the microwave vial was added phenyl(2-(trifluoromethyl)pyridin-3-yl)methanone (51 mg, 0.2 mmol), evacuated and backfilled 3 times with nitrogen. Dry THF (2 mL, 0.1 M) was added as solvent, followed by Tebbe reagent (68.3 mg, 0.24 mmol), and the reaction mixture was stirred at 60 °C overnight. The reaction mixture was cooled and quenched with NaHCO₃ aqueous solution.

The mixture was filtered through filter paper, and the residue was washed with DCM. The solution obtained was concentrated under reduced pressure. The residue was redissolved in water (8 mL) and DCM (30 mL) and then extracted with DCM (10 mL × 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (Hex: EtOAc = 10:1 ~ 10:5) to afford the 3-alkenyl pyridine as a yellow liquid (46 mg, 90% yield).

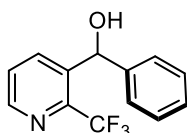
¹H NMR (400 MHz, CDCl₃) δ 8.72 (dd, *J* = 4.7, 1.2 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.50 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.24 – 7.20 (m, 2H), 5.94 (s, 1H), 5.27 (s, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.40.

¹³C NMR (101 MHz, CDCl₃) δ 148.4, 145.9 (q, *J* = 32.6 Hz), 144.3, 140.4, 139.4, 136.8, 128.6, 128.3, 126.7, 126.0, 121.9 (d, *J* = 275.9 Hz), 117.1.

HRMS (+APCI): Calculated for: C₁₄H₁₁F₃N [M+H]⁺ 250.0838, found 250.0848.

phenyl(2-(trifluoromethyl)pyridin-3-yl)methanol (22)



To the microwave vial was added phenyl(2-(trifluoromethyl)pyridin-3-yl)methanone (51 mg, 0.2 mmol), and NaBH₄ (15.2 mg, 0.4 mmol), evacuated and backfilled 3 times with nitrogen.

Butanol (0.1M) was added as a solvent. The reaction mixture was stirred at 120 °C overnight.

The reaction was cooled down to room temperature. To this mixture was slowly added water (10 mL) and then extracted with EtOAc (10 mL × 3). The combined organic layers were washed

with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was then purified by flash column chromatography (Hex: EtOAc = 10:1 ~ 10:5) to afford the 3-benzyl pyridine as a colorless liquid (41 mg, 90% yield).

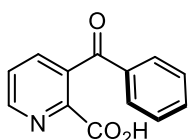
¹H NMR (400 MHz, CDCl₃) δ 8.62 – 8.58 (m, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.39 – 7.27 (m, 5H), 6.34 (s, 1H), 2.66 (s, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -61.80.

¹³C NMR (101 MHz, CDCl₃) δ 148.2, 144.5 (q, *J* = 33.3 Hz), 142.0, 138.6, 138.2, 128.8, 128.2, 127.0, 126.6, 122.3 (q, *J* = 275.7 Hz), 69.9 (d, *J* = 3.0 Hz).

HRMS (+APCI): Calculated for: C₁₃H₁₁F₃NO [M+H]⁺ 254.0787, found 254.0779.

3-benzoylpicolinic acid (23)



Ethyl 3-benzoylpicolinate (46 mg, 0.2 mmol) was taken in a microwave vial with THF (1 mL) solvent. Aq. NaOH solution (1 mL, 1.0 M) was added slowly at 0 °C. The reaction mixture was stirred at room temperature for 2 hours. The starting material consumption was monitored with TLC. Then, the reaction was neutralized by 1M HCl solution and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated

under reduced pressure. The crude product was then purified by flash column chromatography (Hex: EtOAc = 10:1 ~ 10:5) to afford the 3-benzoyl picolinic acid as an orange solid (40 mg, 85% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J* = 2.5 Hz, 1H), 8.60 – 8.10 (bs, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.78 – 7.66 (m, 3H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H).

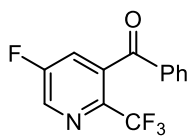
¹³C NMR (101 MHz, CDCl₃) δ 194.2, 163.7, 149.0, 144.1, 138.4, 137.4, 136.4, 133.9, 129.5, 128.8, 127.5.

HRMS (+APCI): Calculated for: C₁₃H₁₀NO₃ [M+H]⁺ 228.0655, found 228.0657.

The data are consistent with the literature.^[8]

10. Sequentially functionalized Pyridine Products

(5-fluoro-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (24a)



Prepared according to *General Procedure E* using corresponding Zincke ketone (70 mg, 0.2 mmol) and TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), NFSI (126.1 mg, 0.4 mmol), and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a colorless oil (23 mg, 40%).

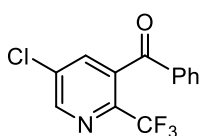
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.69 (d, J = 2.6 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.56 – 7.47 (m, 3H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.56, -120.1.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.5, 159.8 (d, J = 262.6 Hz), 141.0 (dq, J = 35.8, 4.2 Hz), 139.2 (d, J = 20.2 Hz), 136.4 (d, J = 3.0 Hz), 135.4, 134.9, 130.2, 129.1, 123.4 (d, J = 20.2 Hz), 121.0 (q, J = 275.7 Hz).

HRMS (+APCI): Calculated for: $\text{C}_{13}\text{H}_8\text{F}_4\text{NO}$ [$\text{M}+\text{H}$] $^+$ 270.0537, found 270.0537.

(5-chloro-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (24b)



Prepared according to *General Procedure E* using corresponding Zincke ketone (70 mg, 0.2 mmol) and TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), *N*-chlorosuccinamide (29.4 mg, 0.22 mmol) and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a white solid (26 mg, 45%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.79 (d, J = 2.1 Hz, 1H), 7.80 – 7.72 (m, 3H), 7.67 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H).

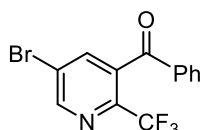
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.05.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.7, 149.4, 143.0 (q, J = 35.4 Hz), 136.1, 135.5, 135.5, 135.0, 134.9, 130.2, 129.1, 121.1 (q, J = 275.7).

HRMS (+APCI): Calculated for: $\text{C}_{13}\text{H}_8\text{ClF}_3\text{NO}$ [$\text{M}+\text{H}$] $^+$ 286.0241, found 286.0233.

Melting point: 116 – 118 $^\circ\text{C}$.

(5-bromo-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (24c)



Prepared according to *General Procedure E* using corresponding Zincke ketone (70 mg, 0.2 mmol) and TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), *N*-bromosuccinamide (39.2 mg, 0.22 mmol) and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (25 mg, 36%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.89 (d, J = 1.9 Hz, 1H), 7.91 (d, J = 1.9 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.71 – 7.62 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H).

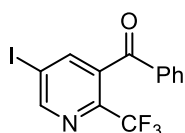
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.18.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.6, 151.7, 143.4 (q, J = 35.5 Hz), 138.9, 135.7, 135.5, 134.9, 130.2, 129.1, 123.7, 121.2 (q, J = 276.7 Hz).

HRMS (+APCI): Calculated for: $\text{C}_{13}\text{H}_8\text{BrF}_3\text{NO}$ [$\text{M}+\text{H}$] $^+$ 329.9736, found 329.9745.

Melting point: 124 – 128 $^\circ\text{C}$.

(5-iodo-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (24d)



Prepared according to *General Procedure E* using corresponding Zincke ketone (70 mg, 0.2 mmol) and TFAA (32 μ L, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt_3 (55.8 μ L, 0.4 mmol), *N*-iodosuccinamide (49.5 mg, 0.22 mmol) with additive TFA (16.9 μ L, 0.22 mmol) and NH_4OAc (155.7 mg, 2 mmol) to yield the titled compound as a white solid (32 mg, 40%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.05 (d, J = 1.6 Hz, 1H), 8.09 (d, J = 1.5 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.69 – 7.62 (m, 1H), 7.55 – 7.45 (m, 2H).

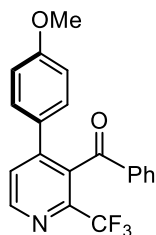
$^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -63.36.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.7, 156.6, 144.4, 143.8 (q, J = 35.4 Hz), 135.8, 135.5, 134.8, 130.2, 129.1, 121.3 (q, J = 275.6 Hz), 96.4.

HRMS (+APCI): Calculated for: C₁₃H₈F₃NO [M+H]⁺ 377.9597, found 377.9583.

Melting point: 102 - 108 °C.

(4-(4-methoxyphenyl)-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (25a)



Prepared according to *General Procedure F* using corresponding Zincke ketone (70 mg, 0.2 mmol), 4-iodoanisole (56.2 mg, 0.24 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), K₂CO₃ (55.3 mg, 0.4 mmol), TFAA (32 μL, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol) and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (54 mg, 35%).

¹H NMR (400 MHz, CDCl₃) δ 8.82 (d, J = 5.0 Hz, 1H), 7.54 (t, J = 5.5 Hz, 3H), 7.45 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.7 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 8.7 Hz, 2H), 3.72 (s, 3H).

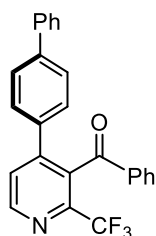
¹⁹F NMR (377 MHz, CDCl₃) δ -62.48.

¹³C NMR (101 MHz, CDCl₃) δ 194.5, 160.3, 149.8, 149.7, 145.1 (q, J = 34.3 Hz), 136.6, 134.0, 133.2, 130.3, 129.4, 128.7, 128.6, 127.4, 121.6 (q, J = 276.7 Hz), 114.2, 55.3.

HRMS (+APCI): Calculated for: C₂₀H₁₅F₃NO₂ [M+H]⁺ 358.1050, found 358.1054.

Melting point: 142 - 150 °C.

(4-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (25b)



Prepared according to *General Procedure F* using corresponding Zincke ketone (70 mg, 0.2 mmol), 4-iodo-1,1'-biphenyl (67.2 mg, 0.24 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), K₂CO₃ (55.3 mg, 0.4 mmol), TFAA (32 μL, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol) and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (62 mg, 36%).

¹H NMR (500 MHz, CDCl₃) δ 8.77 (d, J = 4.4 Hz, 1H), 7.48 (d, J = 8.5 Hz, 3H), 7.44 - 7.27 (m, 7H), 7.27 - 7.13 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 194.2, 149.8, 149.7, 145.2 (q, J = 34.0 Hz), 141.9, 139.8, 136.7, 135.2,

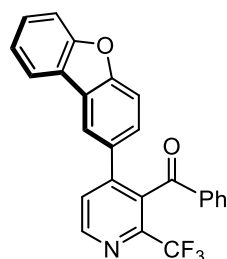
134.0, 133.3, 129.4, 129.3, 129.0, 128.6, 128.0, 127.3 (2C overlap), 127.1, 121.5 (q, J = 277.2 Hz).

¹⁹F NMR (471 MHz, CDCl₃) δ -62.41.

HRMS (+APCI): Calculated for: C₂₅H₁₇F₃NO [M+H]⁺ 404.1257, found 404.1253.

Melting point: 180 - 186 °C.

(4-(dibenzo[b,d]furan-2-yl)-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (25c)



Prepared according to *General Procedure F* using corresponding Zincke ketone (70 mg, 0.2 mmol), 2-bromo dibenzo[b,d]furan (59.3 mg, 0.24 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), K₂CO₃ (55.3 mg, 0.4 mmol), TFAA (32 μL, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol) and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (57 mg, 32%).

¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, J = 5.0 Hz, 1H), 7.74 - 7.67 (m, 2H), 7.52 (d, J = 5.0 Hz, 1H), 7.45 (d, J = 7.3 Hz, 2H), 7.41 - 7.17 (m, 6H), 7.16 - 7.09 (m, 2H).

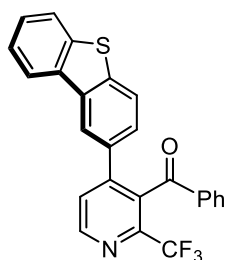
¹⁹F NMR (376 MHz, CDCl₃) δ -62.36.

¹³C NMR (101 MHz, CDCl₃) δ 194.3, 156.6, 156.2, 149.9, 149.7, 145.1 (q, J = 238 34.3 Hz), 136.5, 134.0, 133.5, 131.0, 129.2, 128.6, 128.0, 127.9, 127.7, 124.7, 123.4, 123.2, 121.5 (q, J = 276.7 Hz), 121.4, 120.9, 111.9, 111.9.

HRMS (+APCI): Calculated for: C₂₅H₁₅F₃NO₂ [M+H]⁺ 418.1050, found 418.1040.

Melting point: 146 - 148 °C.

(4-(dibenzo[b,d]thiophen-2-yl)-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (25d)



Prepared according to *General Procedure F* using corresponding Zincke ketone (70 mg, 0.2 mmol), 2-bromodibenzothiophene (63.2 mg, 0.24 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), K₂CO₃ (55.3 mg, 0.4 mmol), TFAA (32 μL, 0.22 mmol), DMAP (4.88 mg, 0.04 mmol), NEt₃ (55.8 μL, 0.4 mmol) and NH₄OAc (155.7 mg, 2 mmol) to yield the titled compound as a yellow solid (56 mg, 31%).

¹H NMR (400 MHz, CDCl₃) δ 8.92 (d, *J* = 4.7 Hz, 1H), 8.03 (s, 1H), 8.01 – 7.97 (m, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 4.8 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 2H).

¹⁹F NMR (377 MHz, CDCl₃) δ -62.39.

¹³C NMR (101 MHz, CDCl₃) δ 194.9, 149.8, 149.8, 145.2 (q, *J* = 34.3 Hz), 140.5, 139.9, 136.7, 135.7, 134.9, 134.1, 133.5, 132.6, 129.3, 128.7, 127.7, 127.4, 126.9, 124.8, 123.2, 123.0, 122.1, 121.8, 120.1 (q, *J* = 276.7 Hz).

HRMS (+APCI): Calculated for: C₂₅H₁₅F₃NOS [M+H]⁺ 434.0821, found 434.0822.

Melting point: 188 – 192 °C.

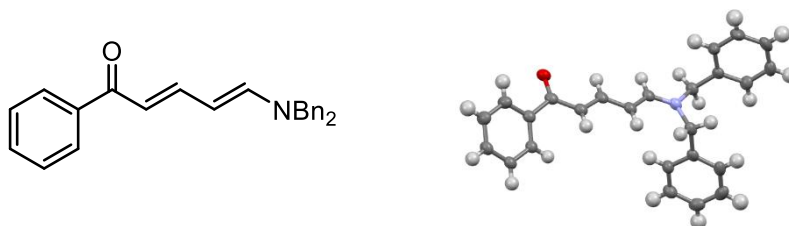
11. X-Ray Crystallography

All data collections, crystal structure determinations, and refinements were done by the X-ray crystallography service (Dr. Avantika Hasija) at The University of Manchester.

Crystallographic data for 15b, 17j, 17l, 17m, 17t, 17v, 23, 24b, 24c, 25a, and 25d have been deposited in the Cambridge Crystallographic Data Centre, with deposition numbers *CCDC 2487297 (14a)*, *CCDC 2515794 (17j)*, *CCDC 2487303 (17l)*, *CCDC 2515794 (17m)*, *CCDC 2478546 (17t)*, *CCDC 2515793 (17v)*, *CCDC 2487299 (23)*, *CCDC 2475756 (24b)*, *CCDC 2475750 (24c)*, *CCDC 2475751 (25a)*, and *CCDC 2475672 (25d)*, are available free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

X-Ray structure of (2E,4E)-5-(dibenzylamino)-1-phenylpenta-2,4-dien-1-one (15b)

CCDC Deposition Number: 2487297



Bond precision:	C-C = 0.0022 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=10.2927(1)	b=20.50005(19)	c=18.53109(19)
	alpha=90	beta=90.1212(9)	gamma=90

	Calculated	Reported
Volume	3910.07(7)	3910.07(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C ₂₅ H ₂₃ N O	C ₂₅ H ₂₃ N O
Sum formula	C ₂₅ H ₂₃ N O	C ₂₅ H ₂₃ N O
Mr	353.44	353.44
Dx, g cm ⁻³	1.201	1.201
Z	8	8

Mu (mm-1)	0.561	0.561
F000	1504.0	1504.0
F000'	1508.05	
h,k,lmax	12,24,22	12,24,22
Nref	6901	6625
Tmin,Tmax	0.966,0.976	0.931,1.000
Tmin'	0.960	

Correction method= #

Reported T Limits: Tmin=0.931 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 0.960

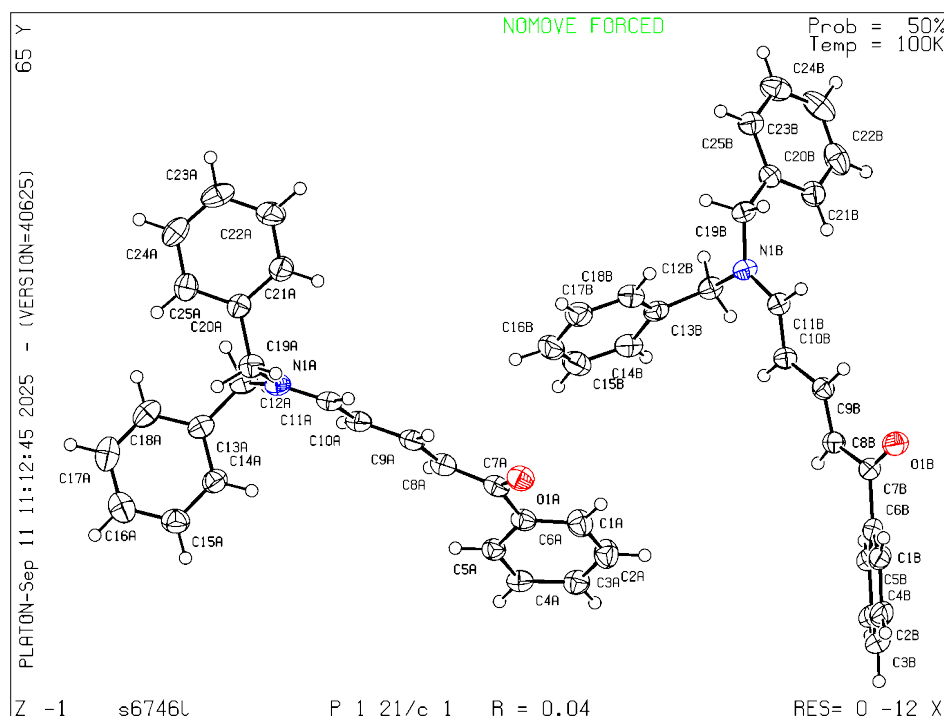
Theta(max)= 66.599

R(reflections)= 0.0405(5486)

wR2(reflections)= 0.1047(6625)

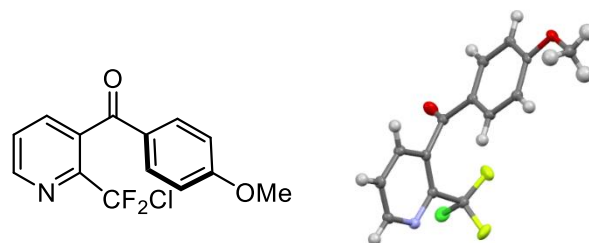
S = 1.019

Npar= 487



X-Ray structure of 2-(chlorodifluoromethyl)pyridin-3-yl(4-methoxyphenyl)methanone (17j)

CCDC Deposition Number: 2515794



Bond precision:	C-C = 0.0018 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=10.69639(17)	b=11.34198(17)	c=21.1345(3)
	alpha=90	beta=90	gamma=90

	Calculated	Reported
Volume	2564.00(7)	2564.00(7)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C14 H10 Cl F2 N O2	C14 H10 Cl F2 N O2
Sum formula	C14 H10 Cl F2 N O2	C14 H10 Cl F2 N O2
Mr	297.68	297.68
Dx,g cm-3	1.542	1.542
Z	8	8
Mu (mm-1)	2.896	2.896
F000	1216.0	1216.0
F000'	1223.01	
h,k,lmax	13,14,26	13,14,26
Nref	2743	2640
Tmin,Tmax	0.630,0.796	0.608,1.000
Tmin'	0.468	

Correction method= #

Reported T Limits: Tmin=0.608 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 0.962

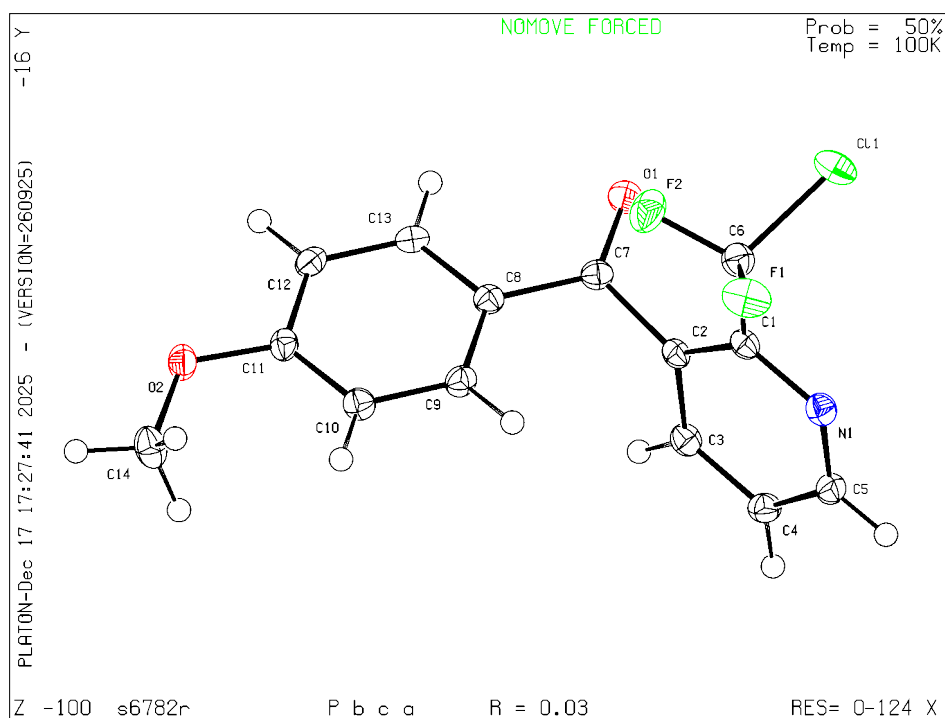
Theta(max)= 77.911

R(reflections)= 0.0296(2375)

wR2(reflections)= 0.0799(2640)

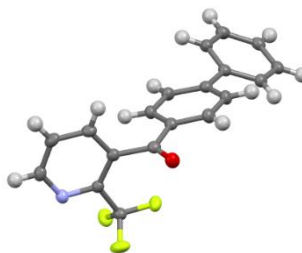
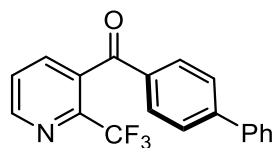
S = 1.085

Npar= 182



X-Ray structure of [1,1'-biphenyl]-4-yl(2-(trifluoromethyl)pyridin-3-yl)methanone (17l)

CCDC Deposition Number: 2487303



Bond precision:	C-C = 0.0031 A	Wavelength=1.54184	Temperature:100 K
Cell:	a=31.5336(3)	b=35.2182(4)	c=8.0829(1)
	alpha=90	beta=90	gamma=90

	Calculated	Reported
Volume	8976.52(17)	8976.52(17)
Space group	A b a 2	A e a 2
Hall group	A 2 -2ac	A 2 -2ac
Moiety formula	C ₁₉ H ₁₂ F ₃ N O	C ₁₉ H ₁₂ F ₃ N O
Sum formula	C ₁₉ H ₁₂ F ₃ N O	C ₁₉ H ₁₂ F ₃ N O
Mr	327.30	327.30
Dx,g cm-3	1.453	1.453
Z	24	24
Mu (mm-1)	0.986	0.986
F000	4032.0	4032.0
F000'	4046.85	
h,k,lmax	39,44,10	39,44,10
Nref	9575[5142]	9357
Tmin,Tmax	0.899,0.943	0.822,1.000
Tmin'	0.774	

Correction method= #

Reported T Limits: Tmin=0.822 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.82/0.98

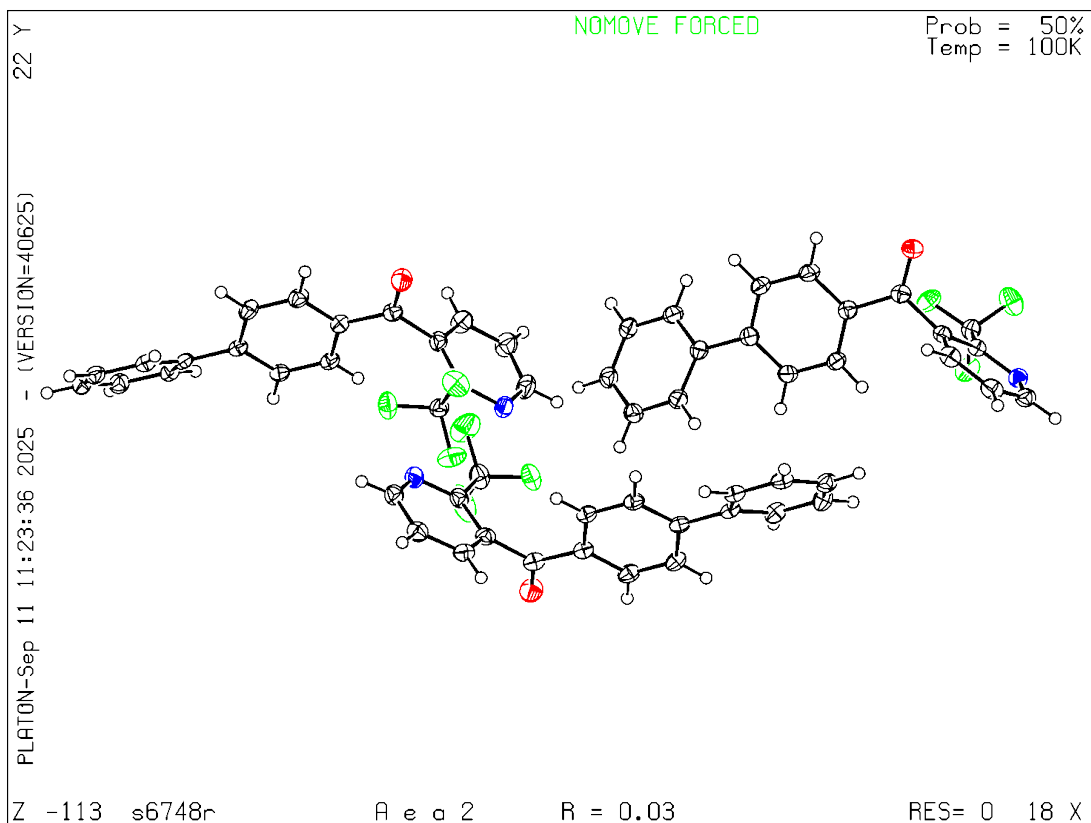
Theta(max)= 77.821

R(reflections)= 0.0324(8633)

wR2(reflections)= 0.0790(9357)

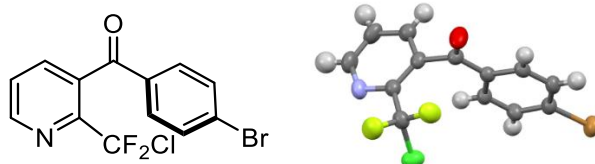
S = 1.037

Npar= 649



X-Ray structure of (4-bromophenyl)(2-(chlorodifluoromethyl)pyridin-3-yl)methanone (17m)

CCDC Deposition Number: 2515792



Bond precision:	C-C = 0.0062 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=8.0757(3)	b=10.1580(4)	c=16.3029(5)
	alpha=85.467(3)	beta=78.465(3)	gamma=88.991(3)

	Calculated	Reported
Volume	1306.26(8)	1306.27(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₁₃ H ₇ Br Cl F ₂ N O	C ₁₃ H ₇ Br Cl F ₂ N O
Sum formula	C ₁₃ H ₇ Br Cl F ₂ N O	C ₁₃ H ₇ Br Cl F ₂ N O
Mr	346.55	346.56
Dx, g cm ⁻³	1.762	1.762
Z	4	4
Mu (mm ⁻¹)	6.335	6.334
F000	680.0	680.0
F000'	680.56	
h,k,lmax	10,12,20	9,12,20
Nref	5564	5108

Tmin,Tmax	0.636,0.881	0.665,0.929
Tmin'	0.471	

Correction method= #

Reported T Limits: Tmin=0.665 Tmax=0.929

AbsCorr = GAUSSIAN

Data completeness= 0.918

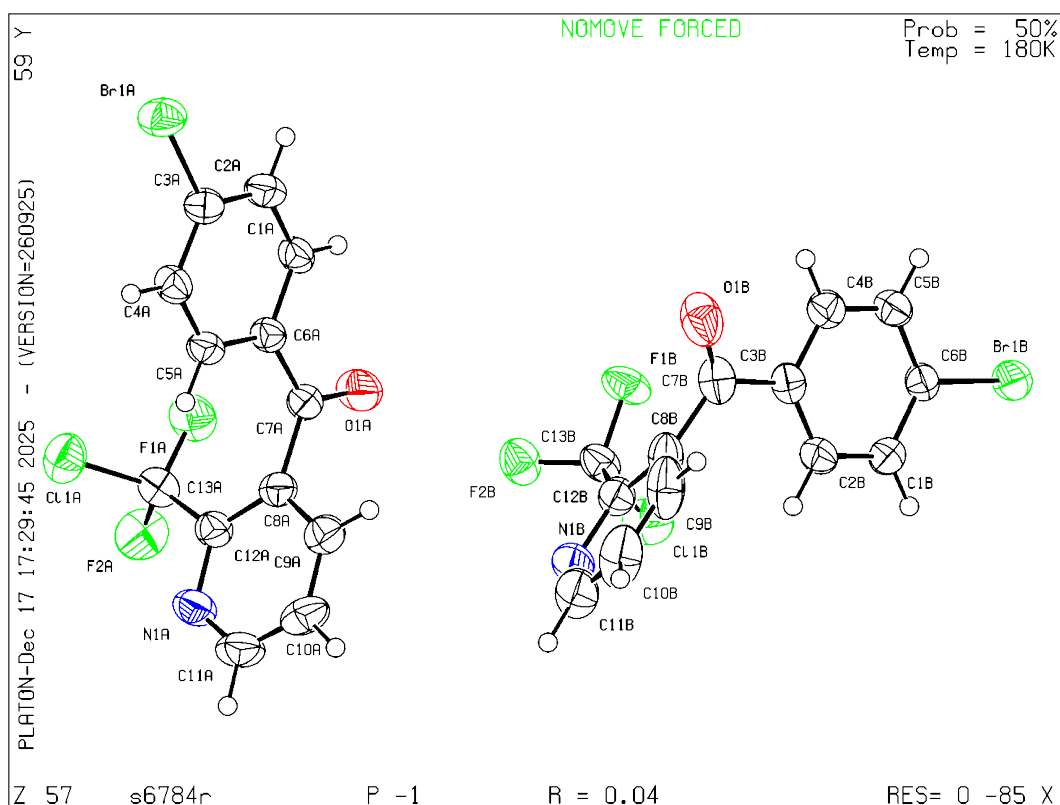
Theta(max)= 77.571

R(reflections)= 0.0441(4059)

wR2(reflections)= 0.1187(5108)

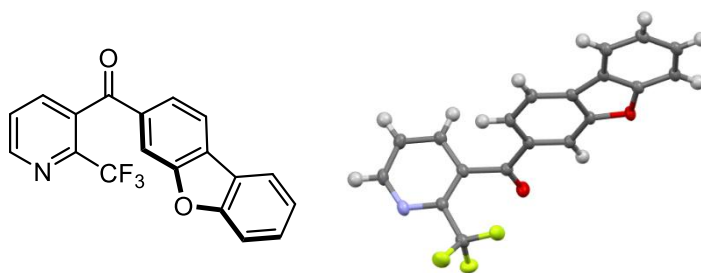
S = 1.029

Npar= 343



X-Ray structure of dibenzo[b,d]furan-3-yl(2-(trifluoromethyl)pyridin-3-yl)methanone (17t)

CCDC Deposition Number: 2478546



Bond precision:	C-C = 0.0023 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=6.3172(3)	b=9.4347(4)	c=13.0054(5)
	alpha=104.381(3)	beta=101.852(4)	gamma=95.556(4)

	Calculated	Reported
Volume	725.85(6)	725.85(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₁₉ H ₁₀ F ₃ N O ₂	C ₁₉ H ₁₀ F ₃ N O ₂
Sum formula	C ₁₉ H ₁₀ F ₃ N O ₂	C ₁₉ H ₁₀ F ₃ N O ₂
Mr	341.28	341.28
Dx,g cm-3	1.561	1.561
Z	2	2
Mu (mm-1)	1.099	1.099
F000	348.0	348.0
F000'	349.34	
h,k,lmax	8,11,16	8,11,16
Nref	3083	2906
Tmin,Tmax	0.917,0.960	0.878,1.000
Tmin'	0.859	

Correction method= #

Reported T Limits: Tmin=0.878 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 0.943

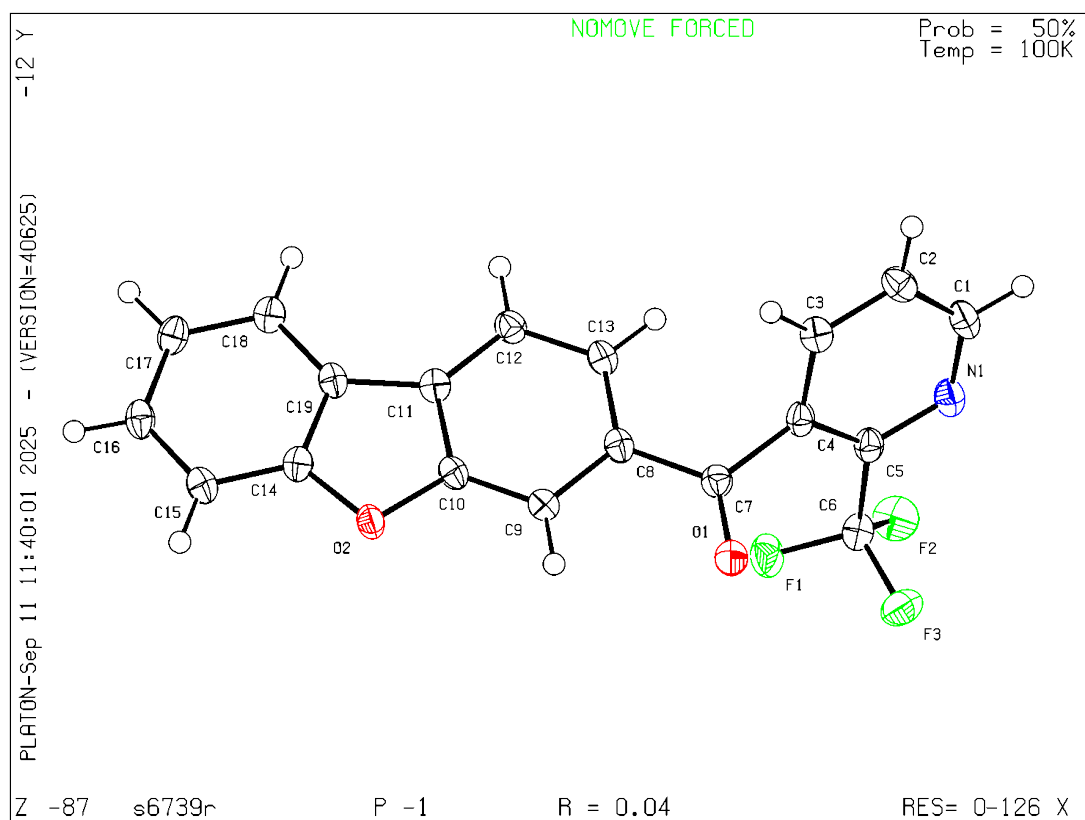
Theta(max)= 77.783

R(reflections)= 0.0405(2422)

wR2(reflections)= 0.1091(2906)

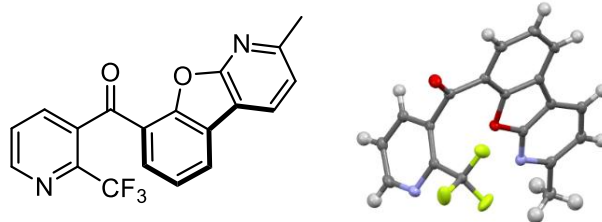
S = 1.048

Npar= 226



X-Ray structure of (4-bromophenyl)(2-(chlorodifluoromethyl)pyridin-3-yl)methanone (17v)

CCDC Deposition Number: 2515793



Bond precision:	C-C = 0.0018 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=14.7181(2)	b=7.14966(9)	c=15.2683(2)
	alpha=90	beta=108.6911(14)	gamma=90

	Calculated	Reported
Volume	1521.94(4)	1521.94(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H11 F3 N2 O2	C19 H11 F3 N2 O2
Sum formula	C19 H11 F3 N2 O2	C19 H11 F3 N2 O2
Mr	356.30	356.30
Dx,g cm-3	1.555	1.555
Z	4	4
Mu (mm-1)	1.094	1.094
F000	728.0	728.0
F000'	730.77	
h,k,lmax	18,9,19	18,8,18
Nref	3235	3120
Tmin,Tmax	0.826,0.885	0.924,0.992
Tmin'	0.826	

Correction method= #

Reported T Limits: Tmin=0.924 Tmax=0.992

AbsCorr = GAUSSIAN

Data completeness= 0.964

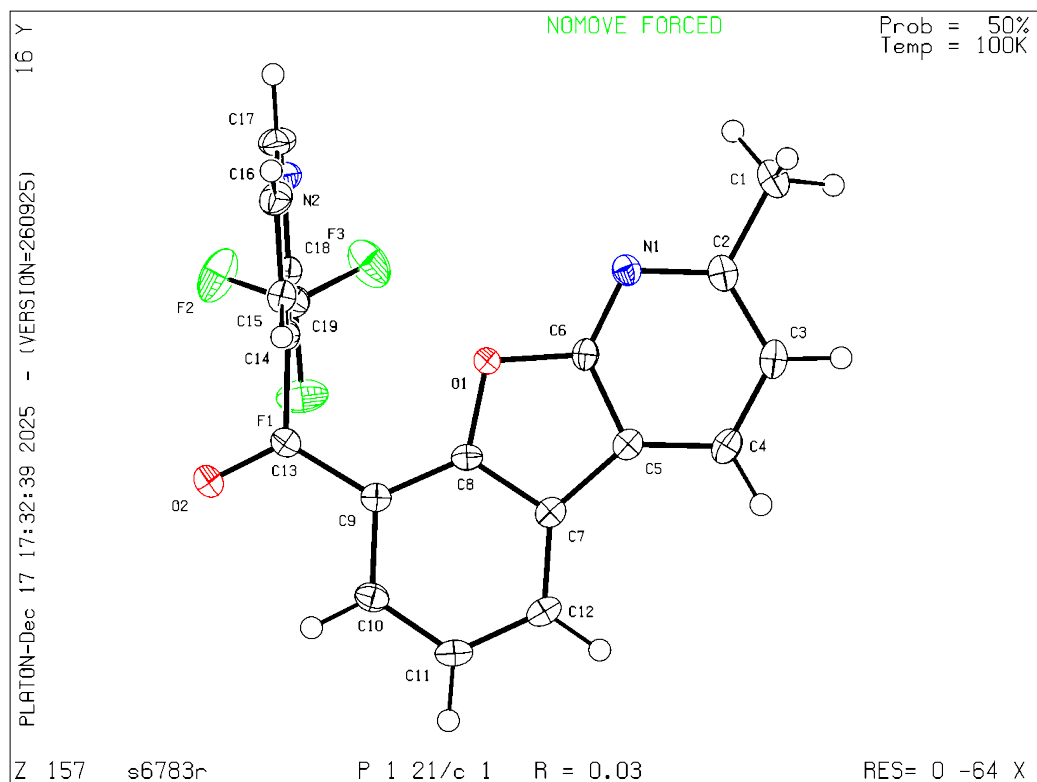
Theta(max)= 77.602

R(reflections)= 0.0330(2863)

wR2(reflections)= 0.0856(3120)

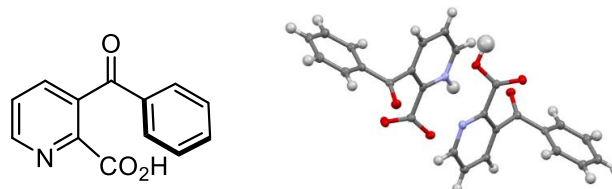
S = 1.043

Npar= 236



X-Ray structure of 3-benzoylpicolinic acid (23)

CCDC Deposition Number: 2487299



Bond precision:	C-C = 0.0035 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=6.0757(1)	b=24.4204(5)	c=7.3631(2)
	alpha=90	beta=111.530(3)	gamma=90

	Calculated	Reported
Volume	1016.24(4)	1016.24(4)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C ₁₃ H ₉ N O ₃	C ₁₃ H ₉ N O ₃
Sum formula	C ₁₃ H ₉ N O ₃	C ₁₃ H ₉ N O ₃
Mr	227.21	227.21
Dx, g cm ⁻³	1.485	1.485
Z	4	4
Mu (mm ⁻¹)	0.889	0.889
F000	472.0	472.0
F000'	473.58	
h,k,lmax	7,30,9	7,30,9
Nref	4262[2183]	3162

Tmin,Tmax	0.867,0.940	0.655,1.000
Tmin'	0.867	

Correction method= #

Reported T Limits: Tmin=0.655 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 1.45/0.74

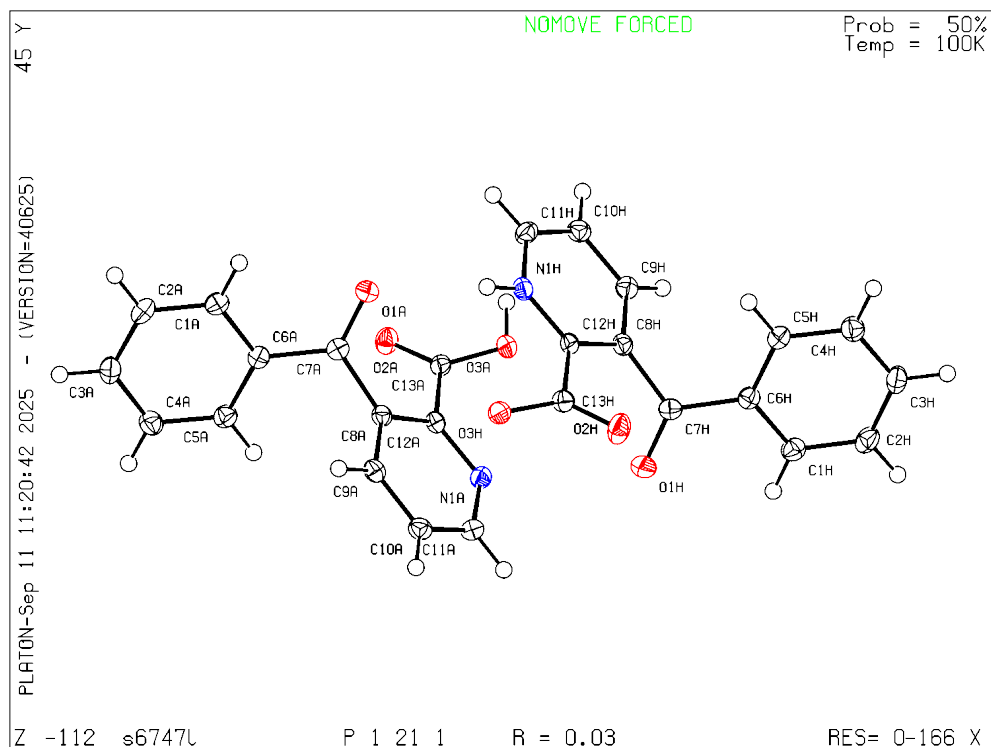
Theta(max)= 76.177

R(reflections)= 0.0288(3073)

wR2(reflections)= 0.0794(3162)

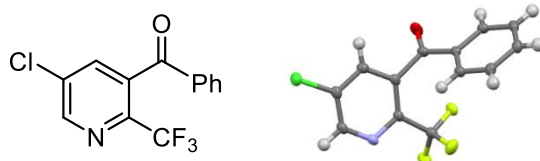
S = 1.063

Npar= 315



X-Ray structure of (5-chloro-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (24b)

CCDC Deposition Number: 2475756



Bond precision:	C-C = 0.0030 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=9.6528(4)	b=7.5835(3)	c=16.5958(6)
	alpha=90	beta=105.477(4)	gamma=90

	Calculated	Reported
Volume	1170.79(8)	1170.79(7)
Space group	P 21/c	P 1 21/c 1

Hall group	-P 2ybc	-P 2ybc
Moiety formula	C13 H7 Cl F3 N O	C13 H7 Cl F3 N O
Sum formula	C13 H7 Cl F3 N O	C13 H7 Cl F3 N O
Mr	285.65	285.65
Dx,g cm-3	1.621	1.621
Z	4	4
Mu (mm-1)	3.206	3.206
F000	576.0	576.0
F000'	579.53	
h,k,lmax	12,9,21	12,9,20
Nref	2496	2353
Tmin,Tmax	0.760,0.914	0.740,1.000
Tmin'	0.608	

Correction method= #

Reported T Limits: Tmin=0.740 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 0.943

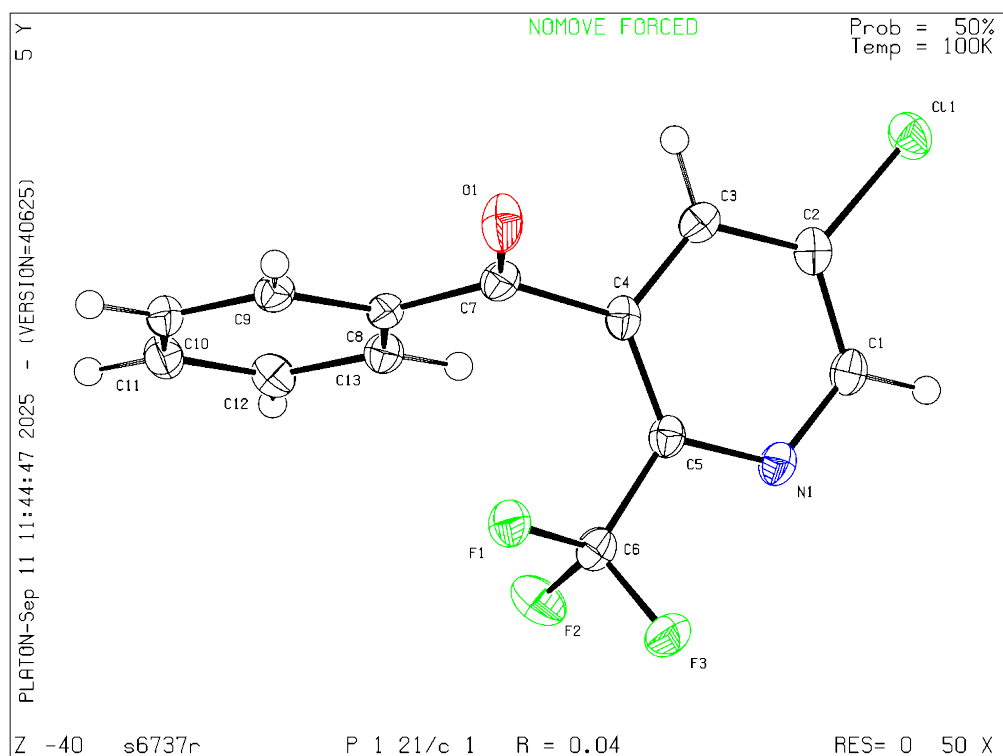
Theta(max)= 77.377

R(reflections)= 0.0390(1919)

wR2(reflections)= 0.0972(2353)

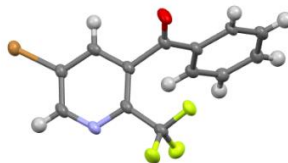
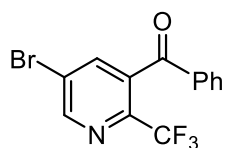
S = 1.057

Npar= 172



X-Ray structure of (5-bromo-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (24c)

CCDC Deposition Number: 2475750



Bond precision:	C-C = 0.0051 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=9.7276(3)	b=7.63087(19)	c=16.6784(5)
	alpha=90	beta=105.133(3)	gamma=90

	Calculated	Reported
Volume	1195.11(6)	1195.11(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C13 H7 Br F3 N O	C13 H7 Br F3 N O
Sum formula	C13 H7 Br F3 N O	C13 H7 Br F3 N O
Mr	330.10	330.10
Dx,g cm ⁻³	1.835	1.835
Z	4	4
Mu (mm ⁻¹)	5.002	5.002
F000	648.0	648.0
F000'	647.36	
h,k,lmax	12,9,21	12,9,20
Nref	2559	2423
Tmin,Tmax	0.728,0.878	0.571,1.000
Tmin'	0.327	

Correction method= #

Reported T Limits: Tmin=0.571 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 0.947

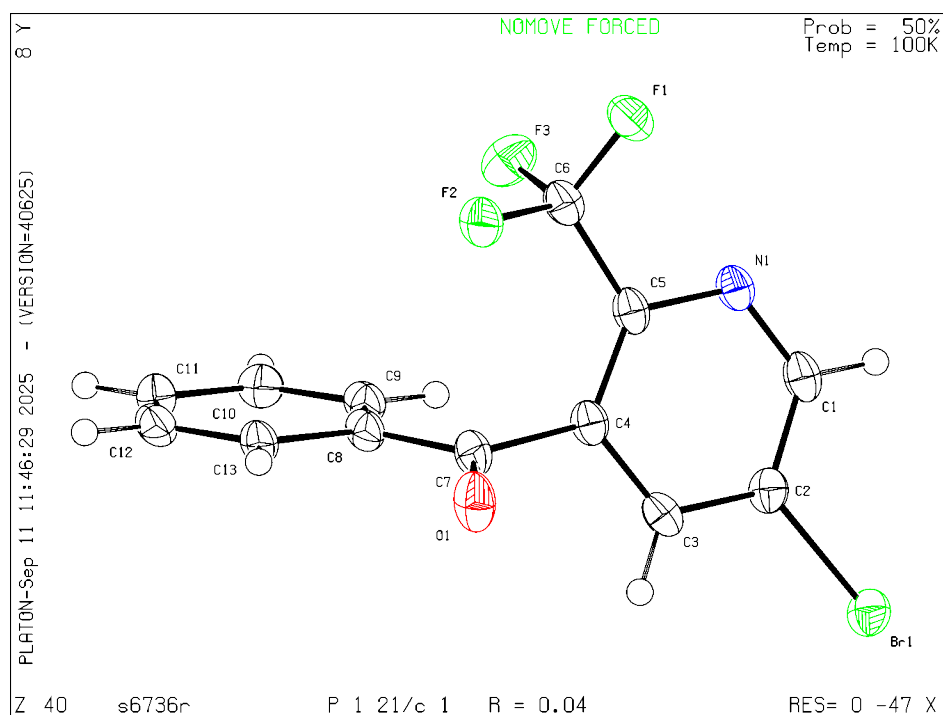
Theta(max)= 78.071

R(reflections)= 0.0430(2057)

wR2(reflections)= 0.1198(2423)

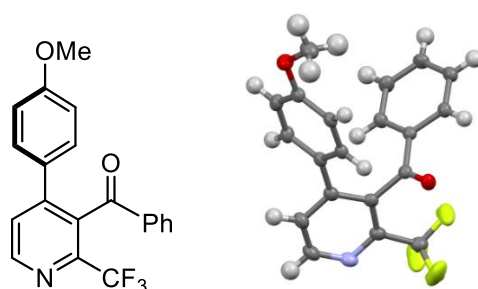
S = 1.081

Npar= 172



X-Ray structure of (4-(4-methoxyphenyl)-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (25a)

CCDC Deposition Number: 2475751



Bond precision:	C-C = 0.0020 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=8.3940(2)	b=21.4396(5)	c=9.3120(2)
	alpha=90	beta=90.923(2)	gamma=90

	Calculated	Reported
Volume	1675.61(7)	1675.62(7)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C ₂₀ H ₁₄ F ₃ N O ₂	C ₂₀ H ₁₄ F ₃ N O ₂
Sum formula	C ₂₀ H ₁₄ F ₃ N O ₂	C ₂₀ H ₁₄ F ₃ N O ₂
Mr	357.32	357.32
Dx, g cm ⁻³	1.416	1.416
Z	4	4
Mu (mm ⁻¹)	0.974	0.974
F000	736.0	736.0
F000'	738.74	
h,k,lmax	10,27,11	10,26,11
Nref	3516	3432

Tmin,Tmax	0.962,0.968	0.968,1.000
Tmin'	0.953	

Correction method= #

Reported T Limits: Tmin=0.968 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 0.976

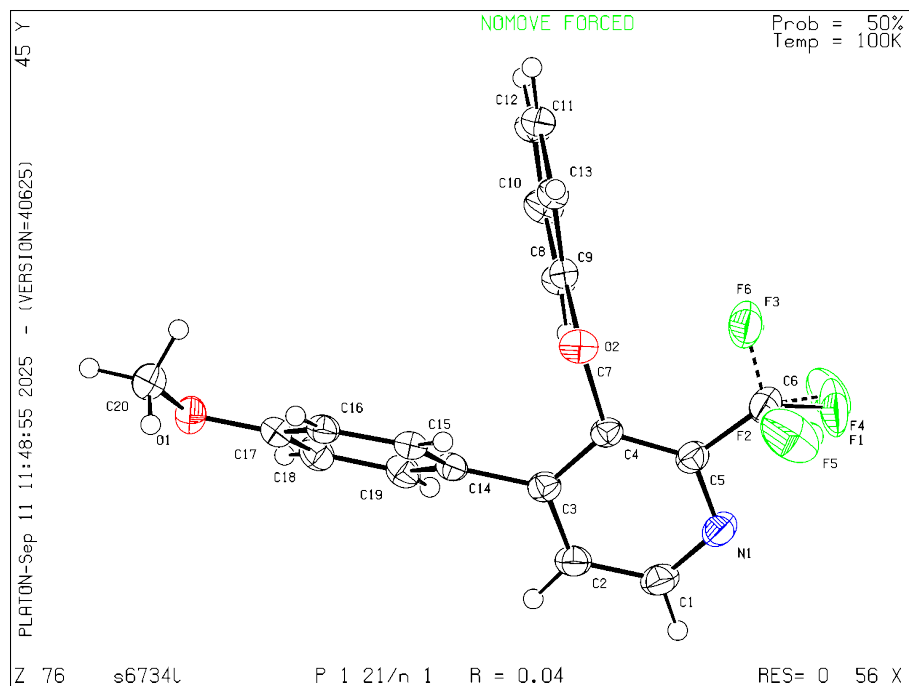
Theta(max)= 76.359

R(reflections)= 0.0374(2824)

wR2(reflections)= 0.1015(3432)

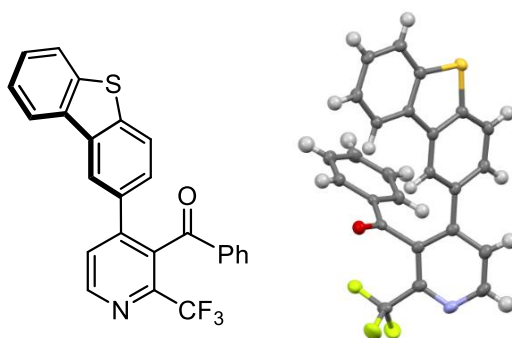
S = 1.051

Npar= 265



X-Ray structure of (4-(dibenzo[*b,d*]furan-2-yl)-2-(trifluoromethyl)pyridin-3-yl)(phenyl)methanone (25d)

CCDC Deposition Number: 2475672



Bond precision:	C-C = 0.0023 Å	Wavelength=1.54184	Temperature:100 K
Cell:	a=8.36426(13)	b=25.5739(4)	c=9.21252(14)
	alpha=90	beta=91.2344(14)	gamma=90

	Calculated	Reported
Volume	1970.16(5)	1970.16(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C ₂₅ H ₁₄ F ₃ N O S	C ₂₅ H ₁₄ F ₃ N O S
Sum formula	C ₂₅ H ₁₄ F ₃ N O S	C ₂₅ H ₁₄ F ₃ N O S
Mr	433.43	433.43
Dx,g cm ⁻³	1.461	1.461
Z	4	4
Mu (mm ⁻¹)	1.867	1.867
F000	888.0	888.0
F000'	892.23	
h,k,lmax	10,32,11	10,32,11
Nref	4213	4032
Tmin,Tmax	0.845,0.906	0.874,0.978
Tmin'	0.814	

Correction method= #

Reported T Limits: Tmin=0.874 Tmax=1.000

AbsCorr = GAUSSIAN

Data completeness= 0.957

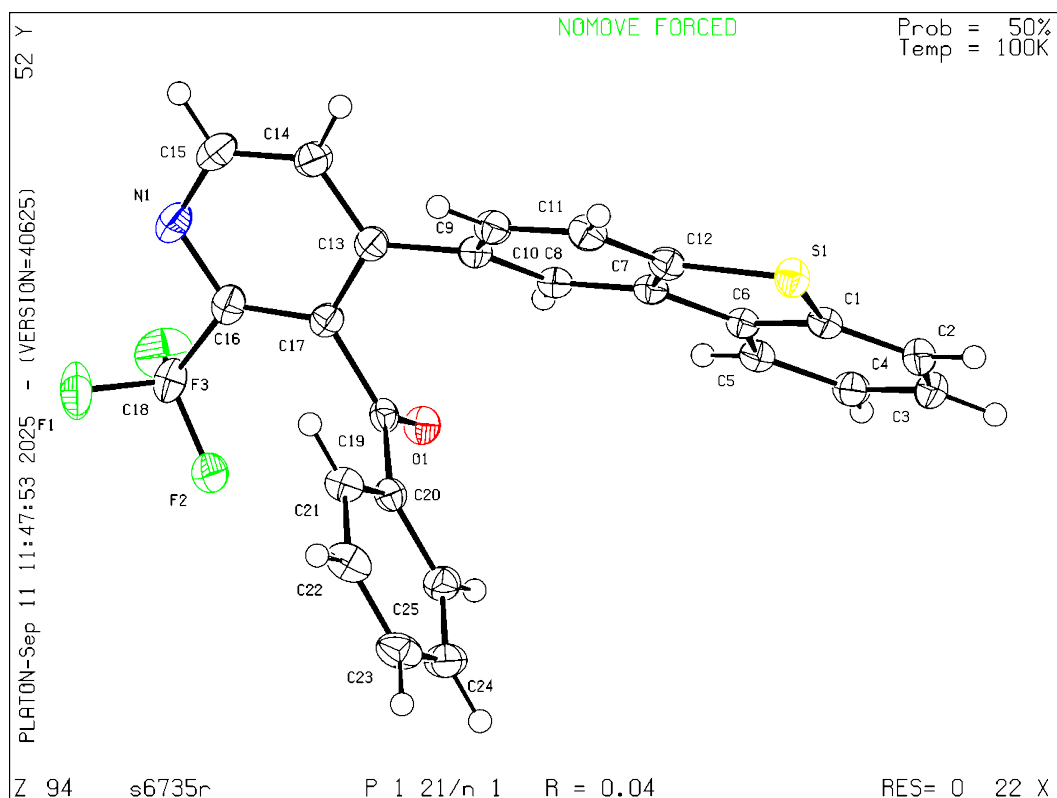
Theta(max)= 77.990

R(reflections)= 0.0375(3333)

wR2(reflections)= 0.0943(4032)

S = 1.048

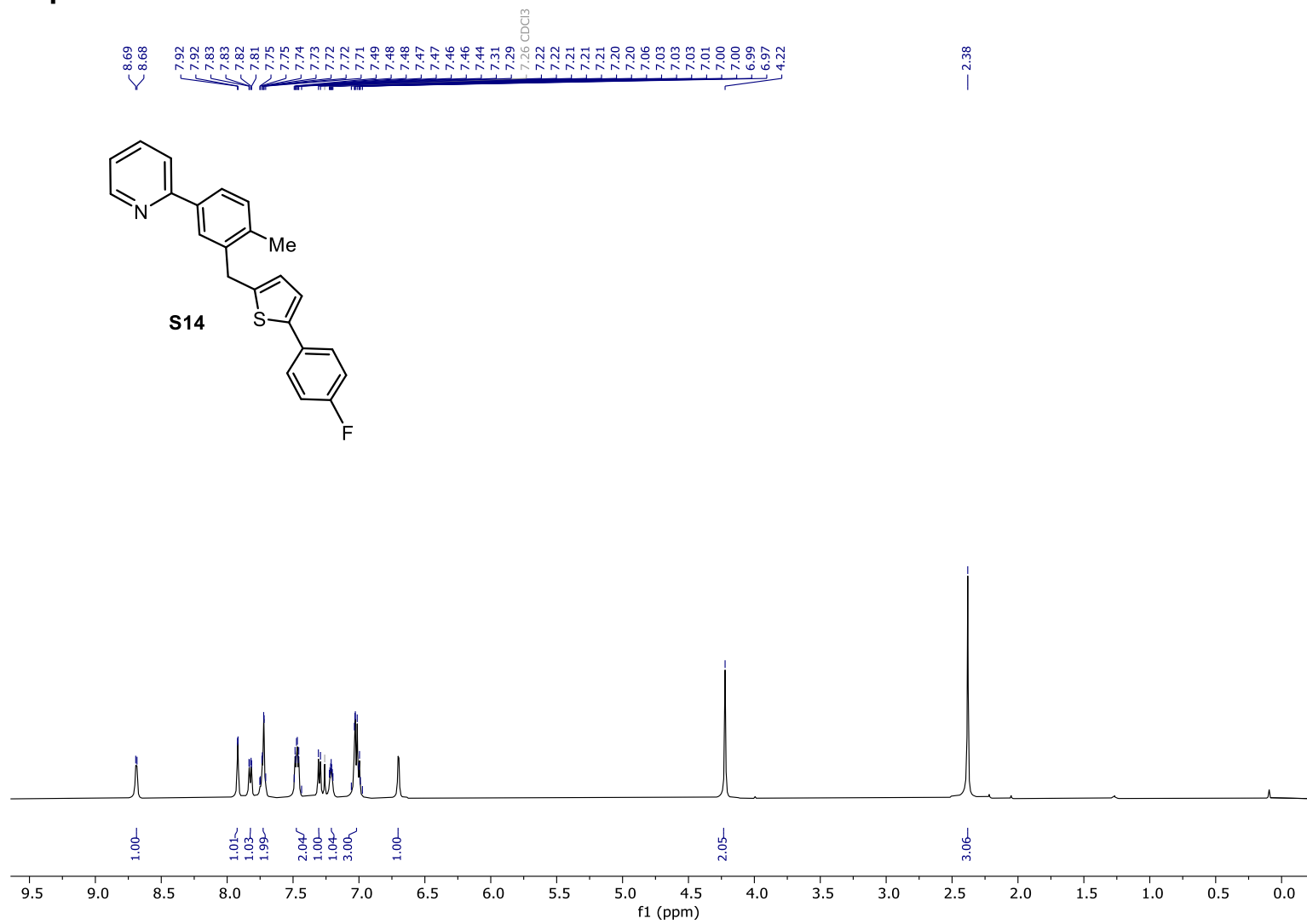
Npar= 280

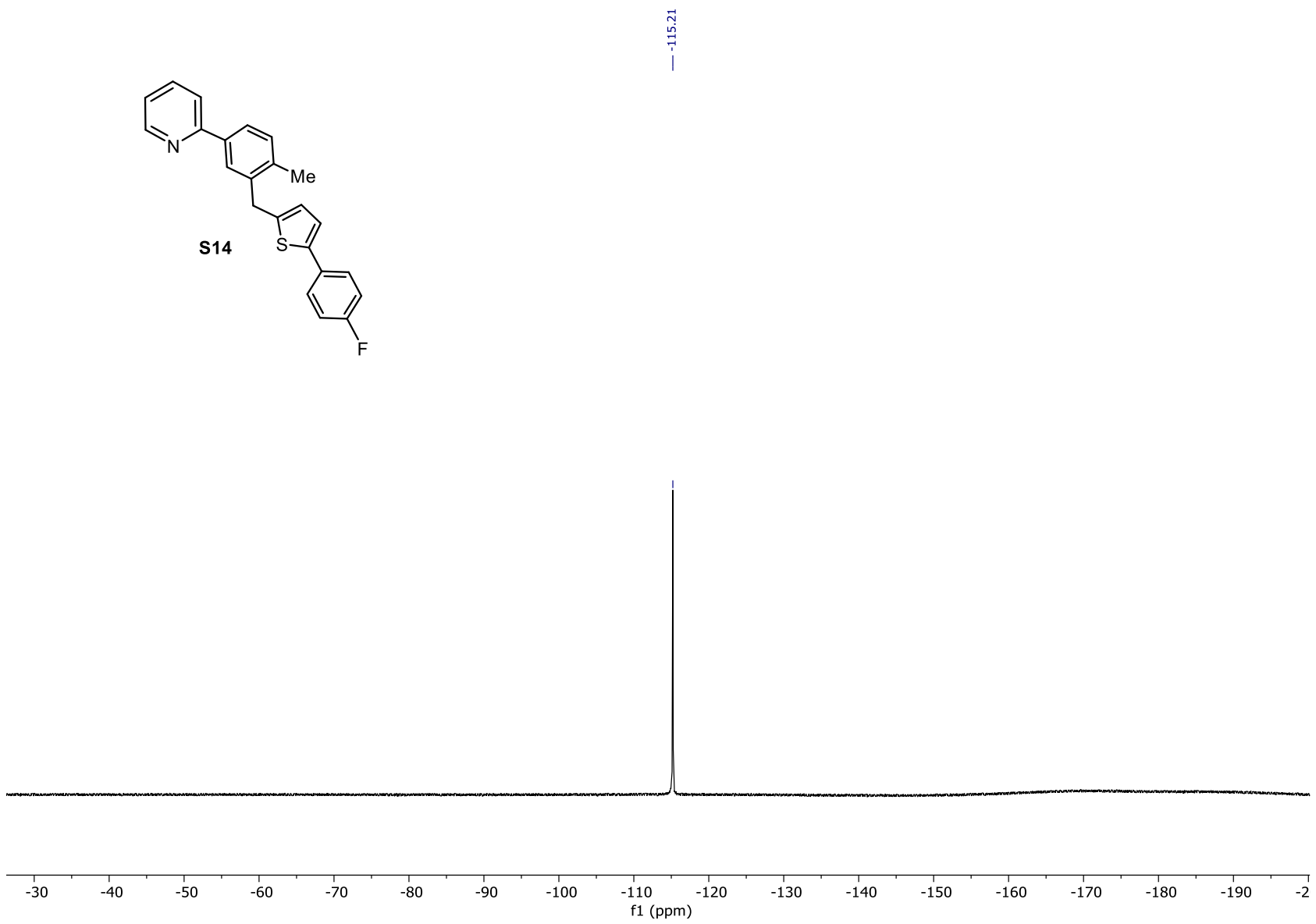
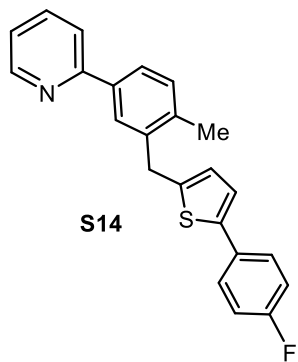


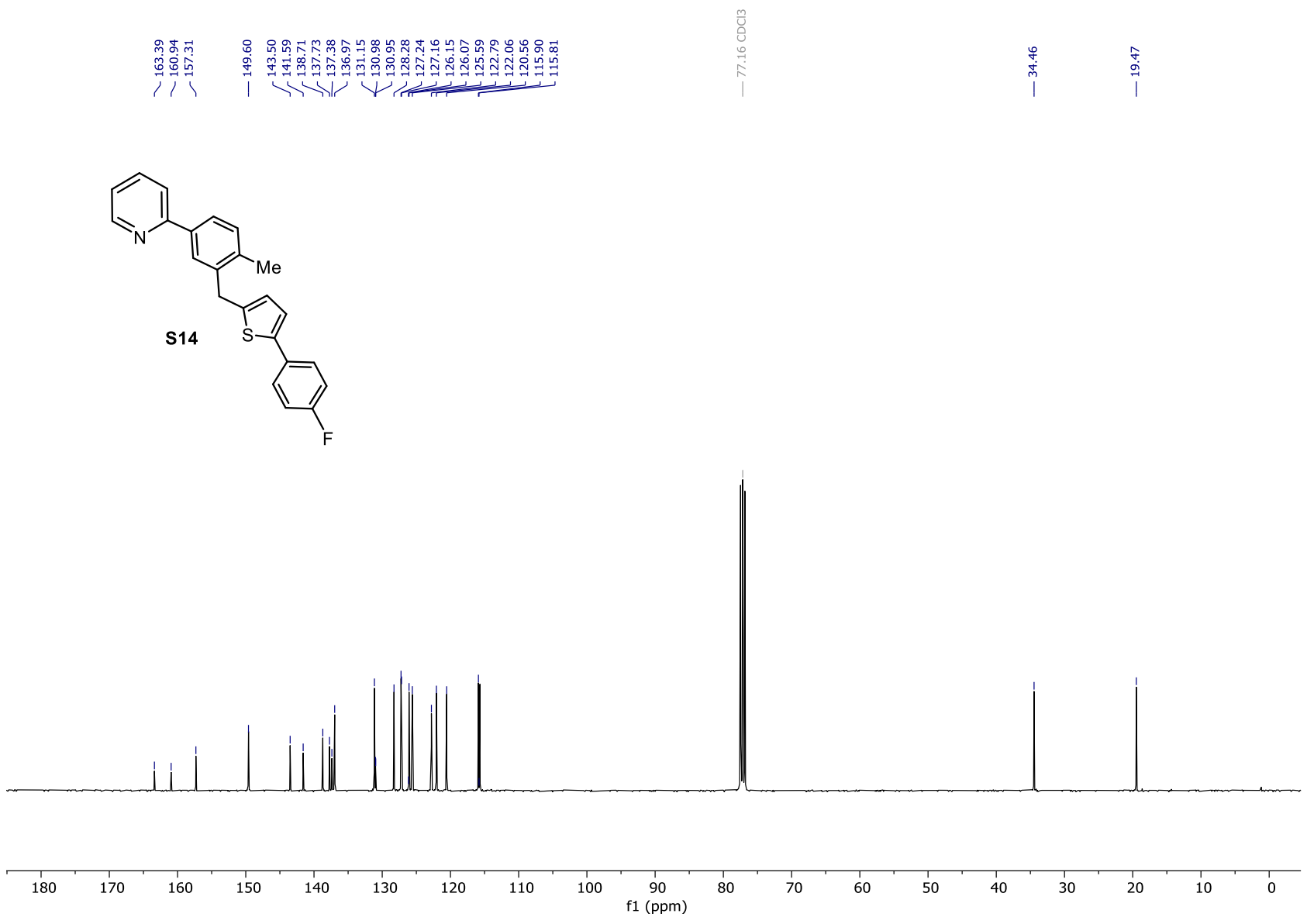
12. References

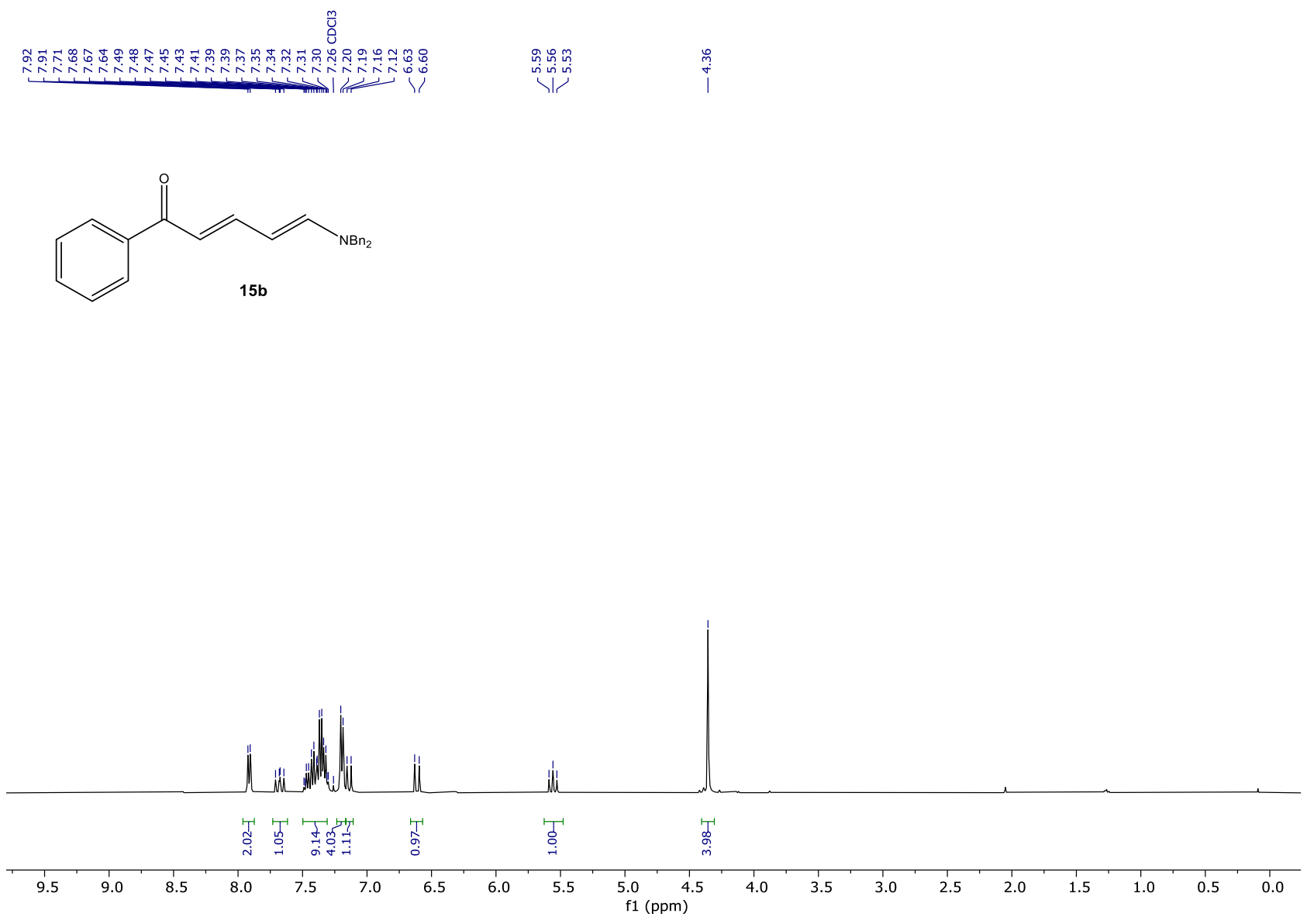
1. Z. Liu and M. F. Greaney, *Angew. Chem. Int. Ed.*, 2025, **64**, e202512321.
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4. S. Bhowmick, A. Awasthi, K. Tiwari, P. Yadav and D. K. Tiwari, *Org. Lett.*, 2025, **27**, 2289–2294.
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6. X. Duan, R. Sun, J. Tang, S. Li, X. Zheng, R. Li, H. Chen, H. Fu and M. Yuan, *J. Org. Chem.*, 2022, **87**, 7975–7988.
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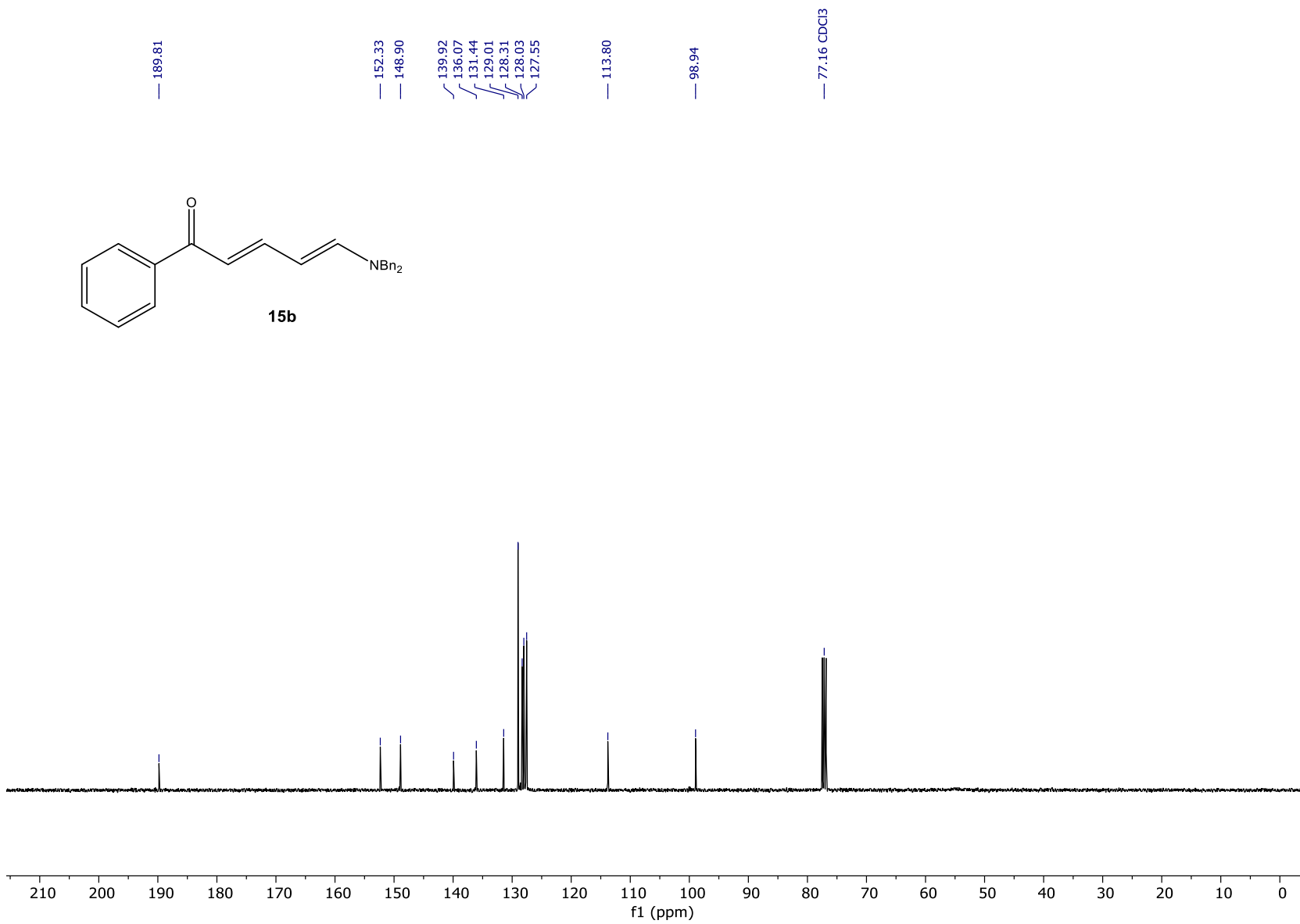
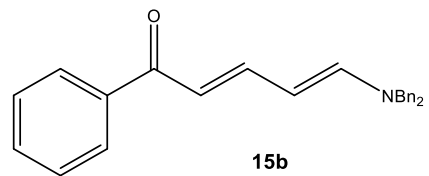
13. NMR Spectra

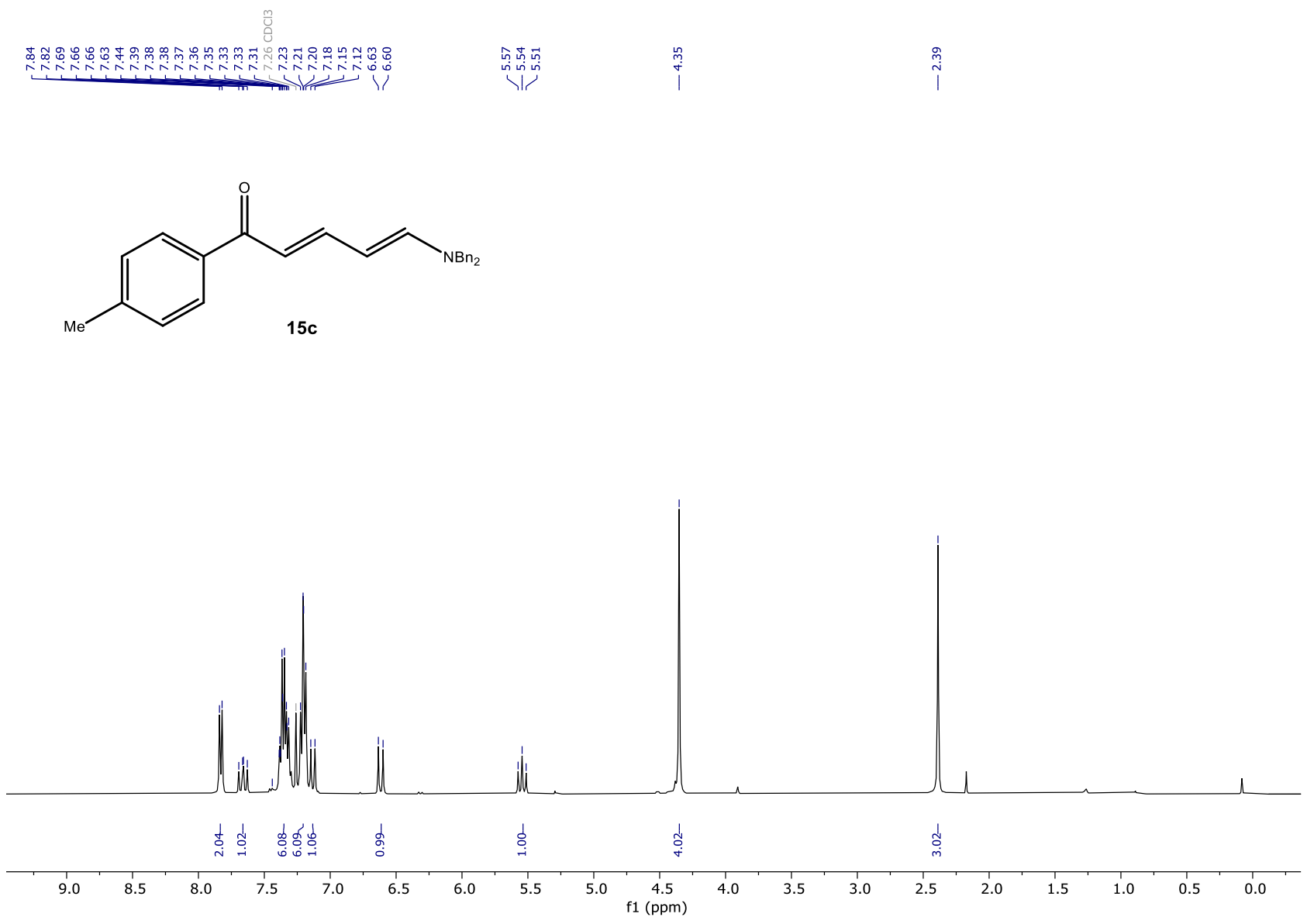


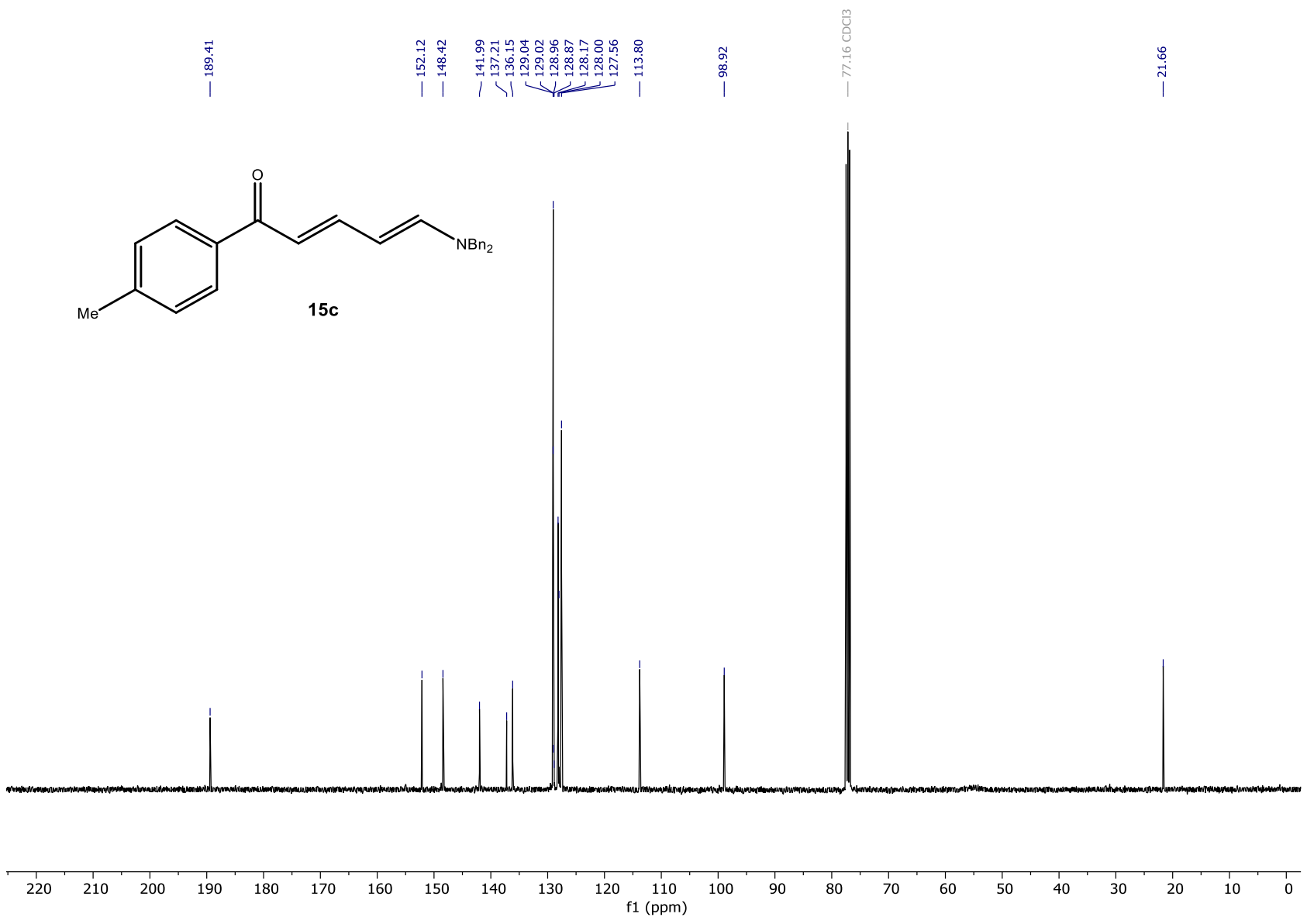


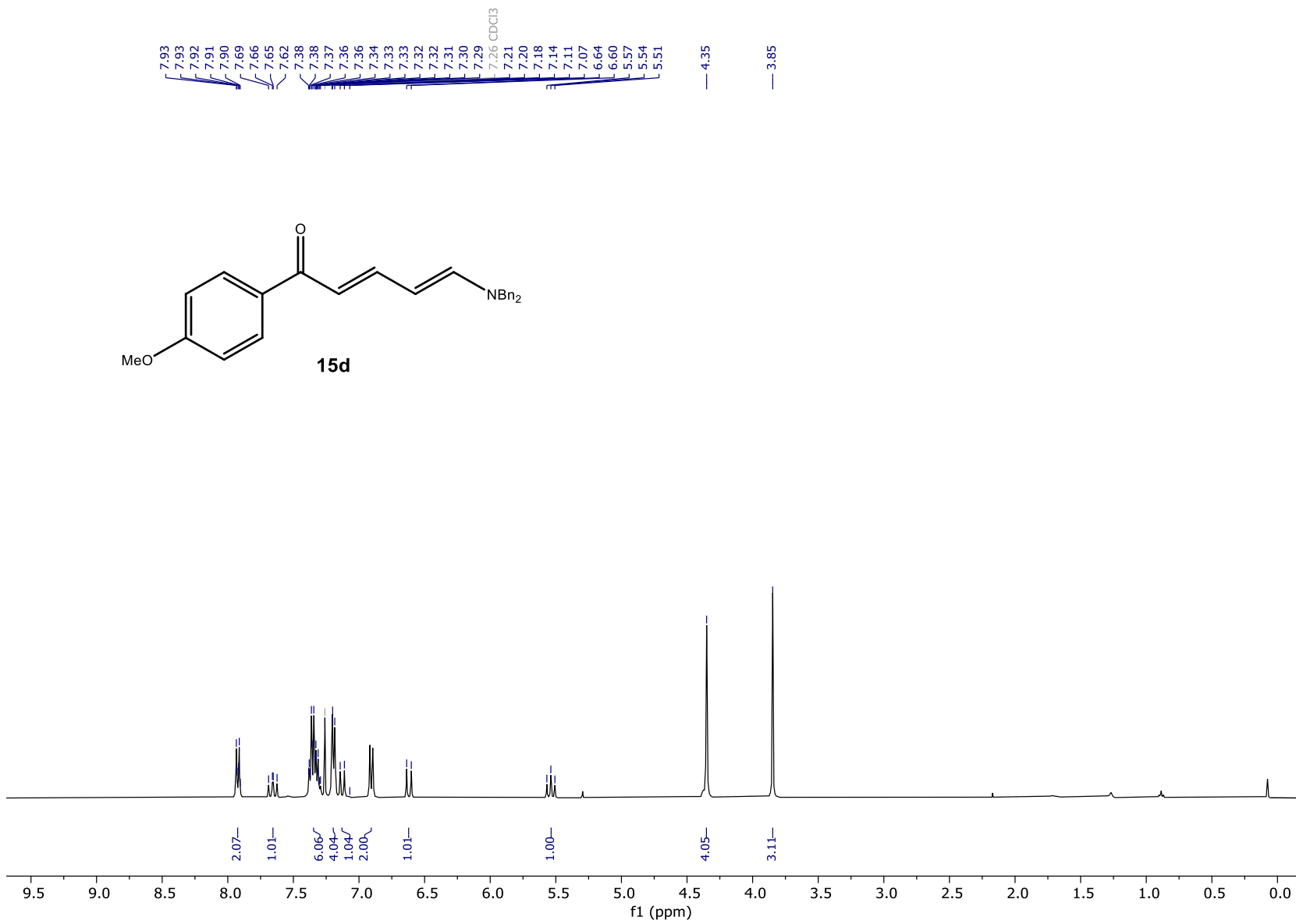
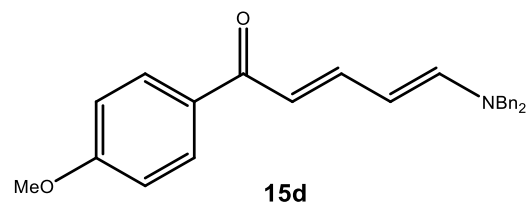


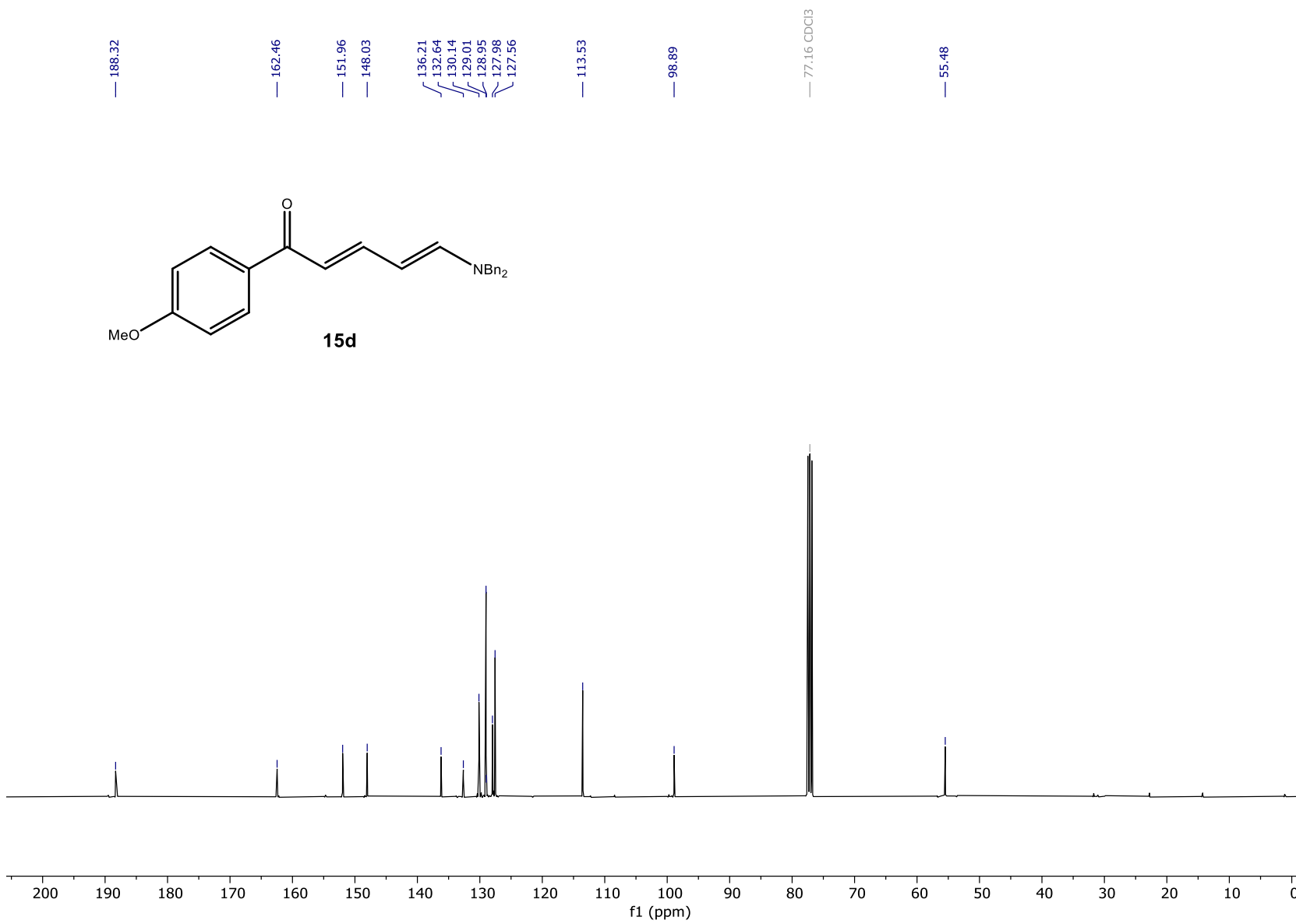
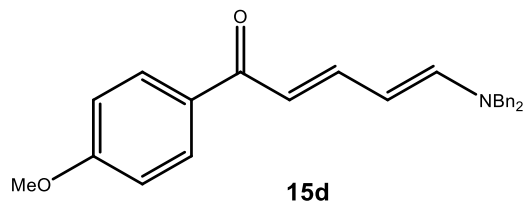




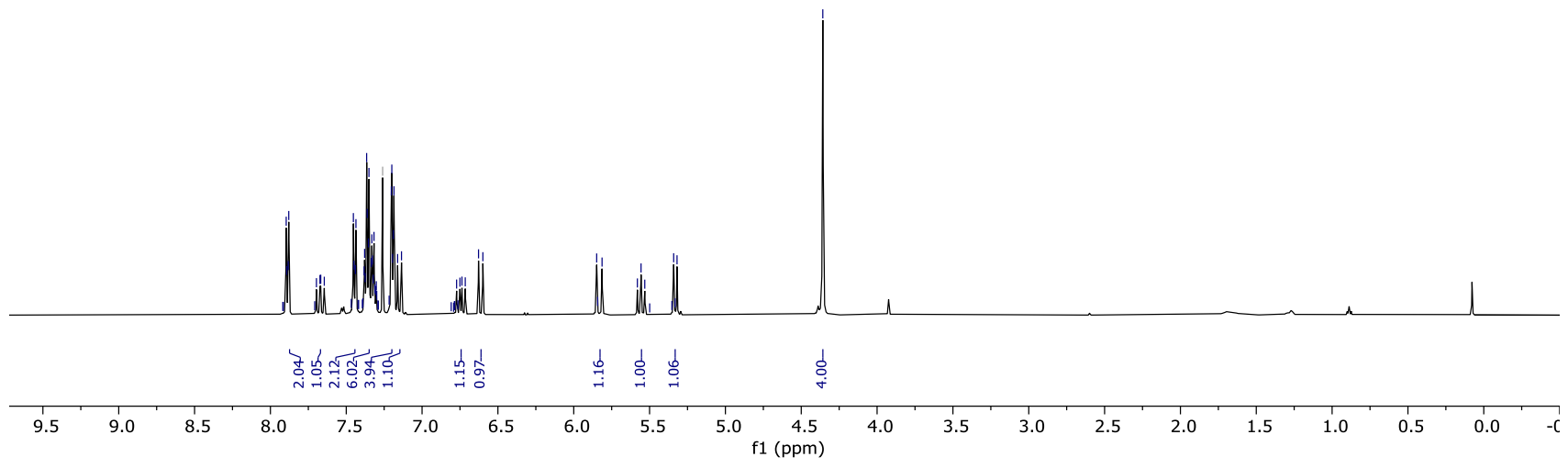
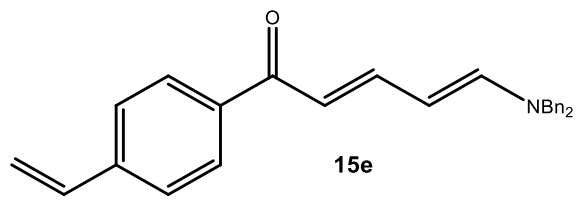


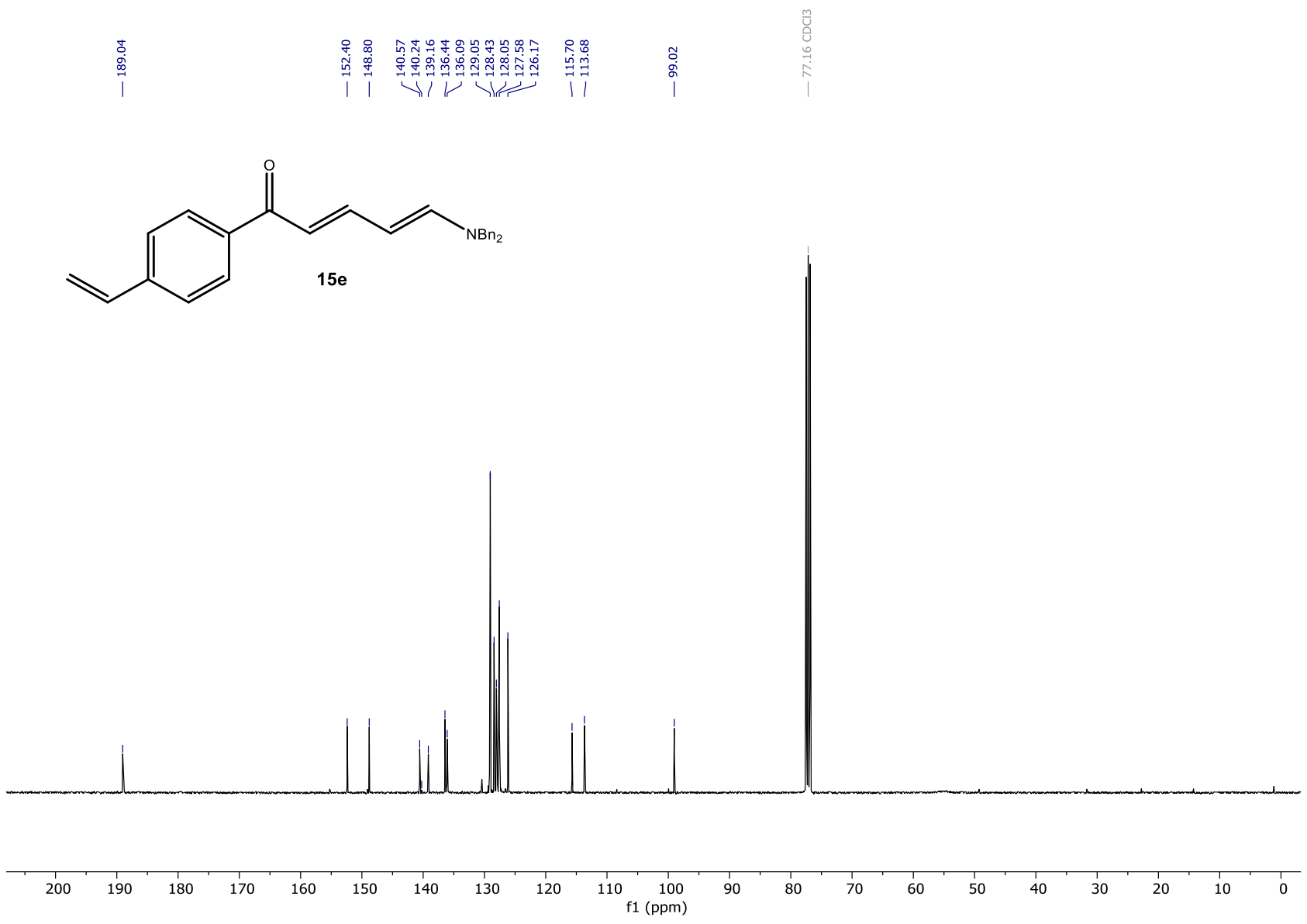


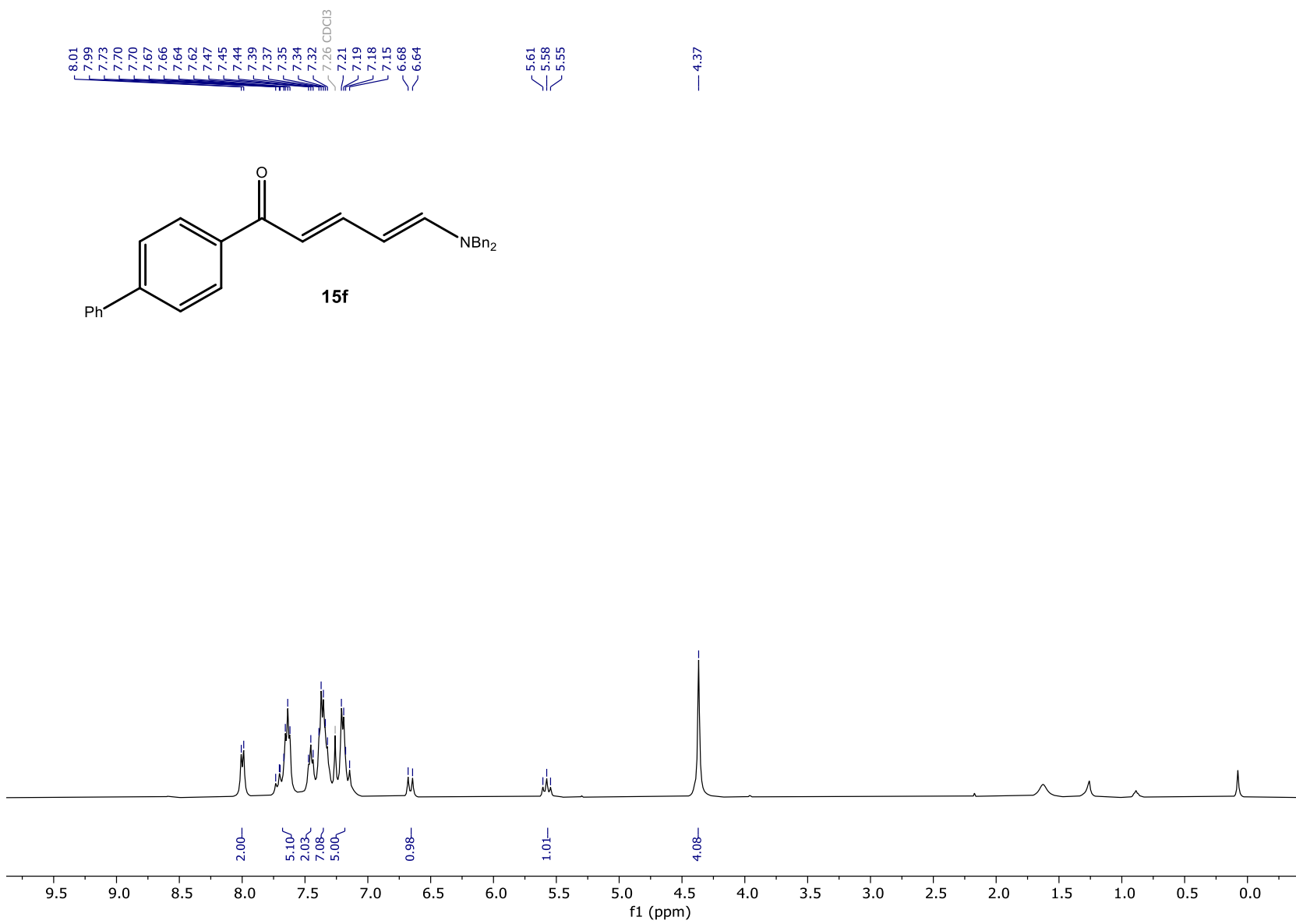


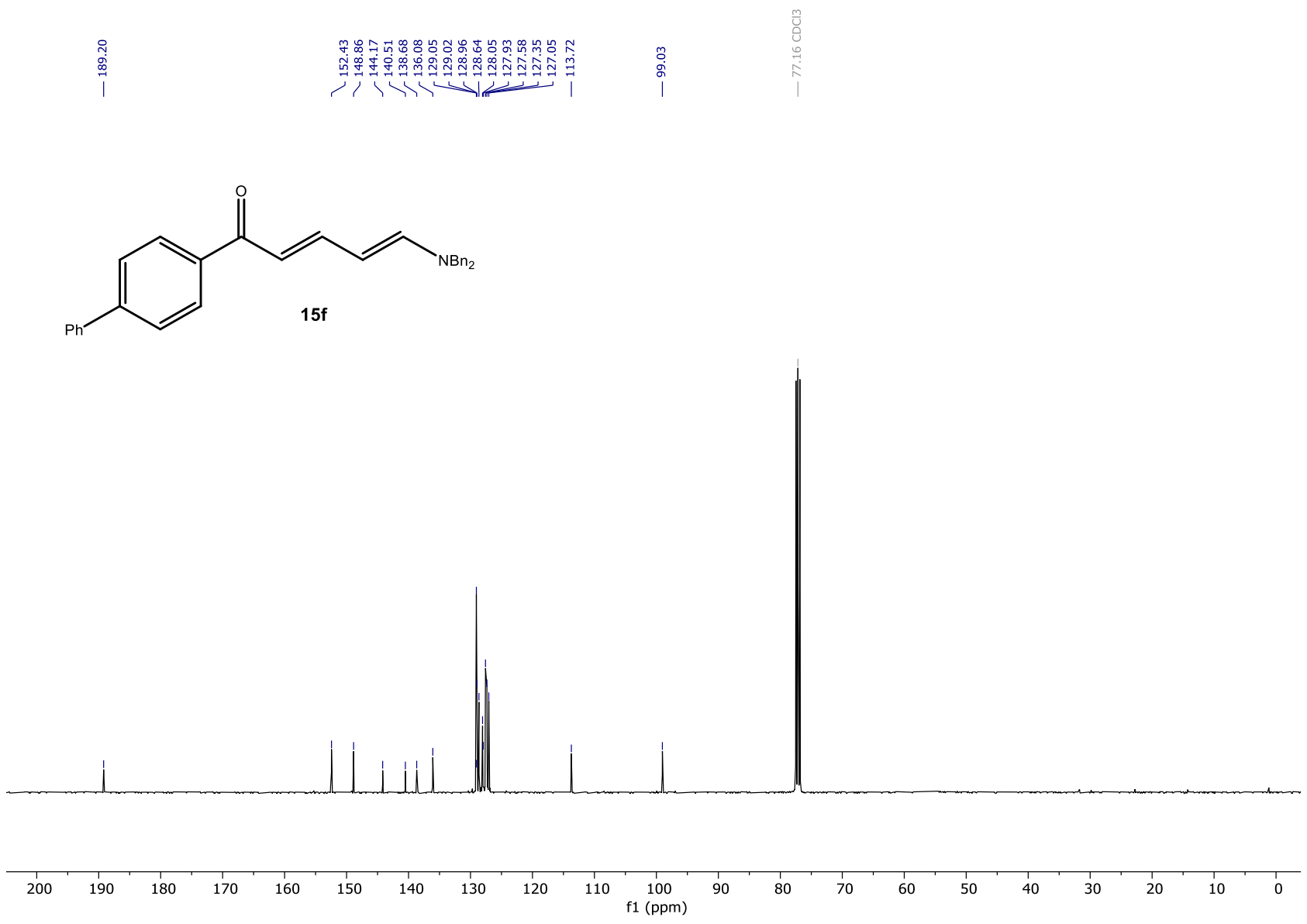


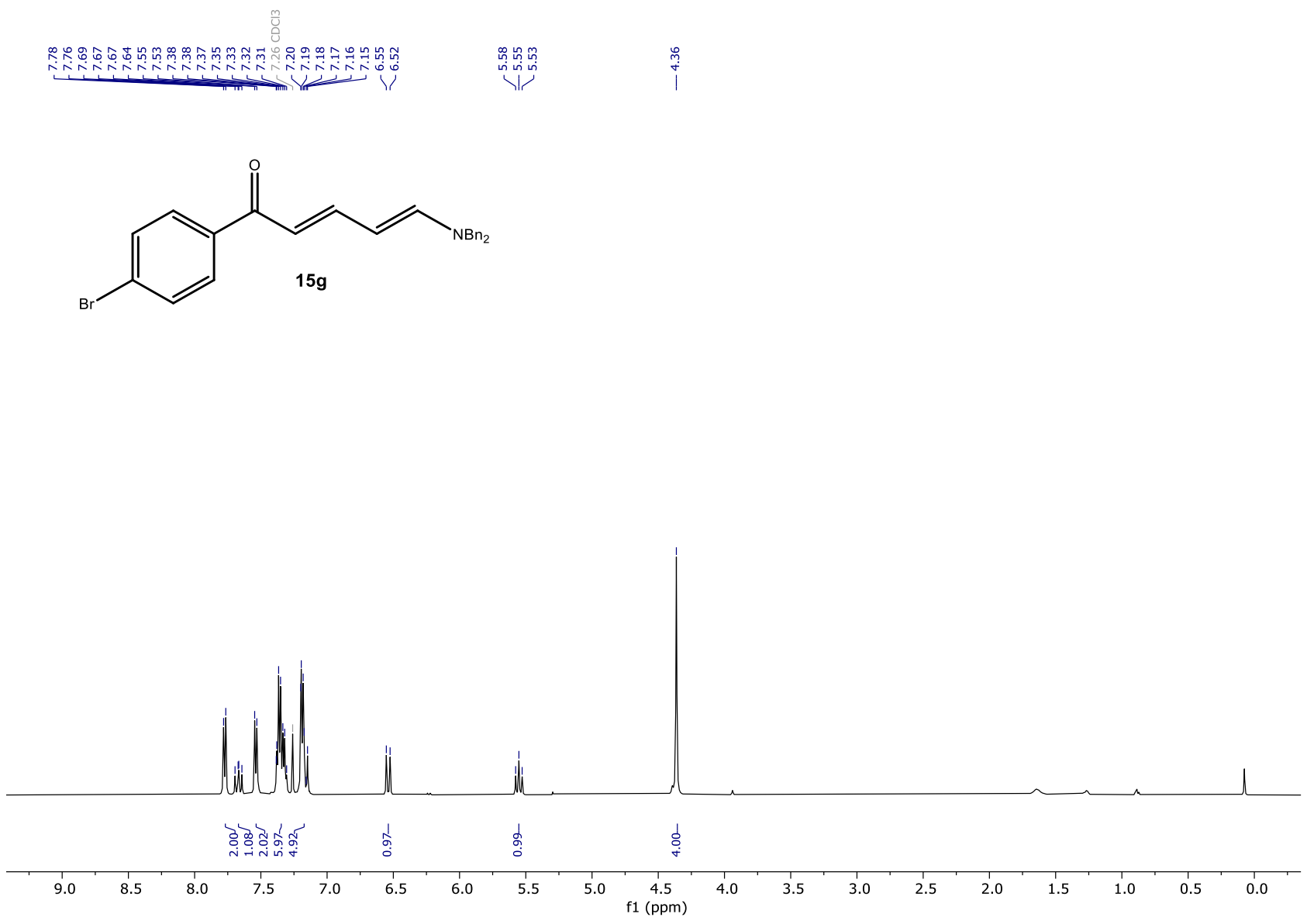
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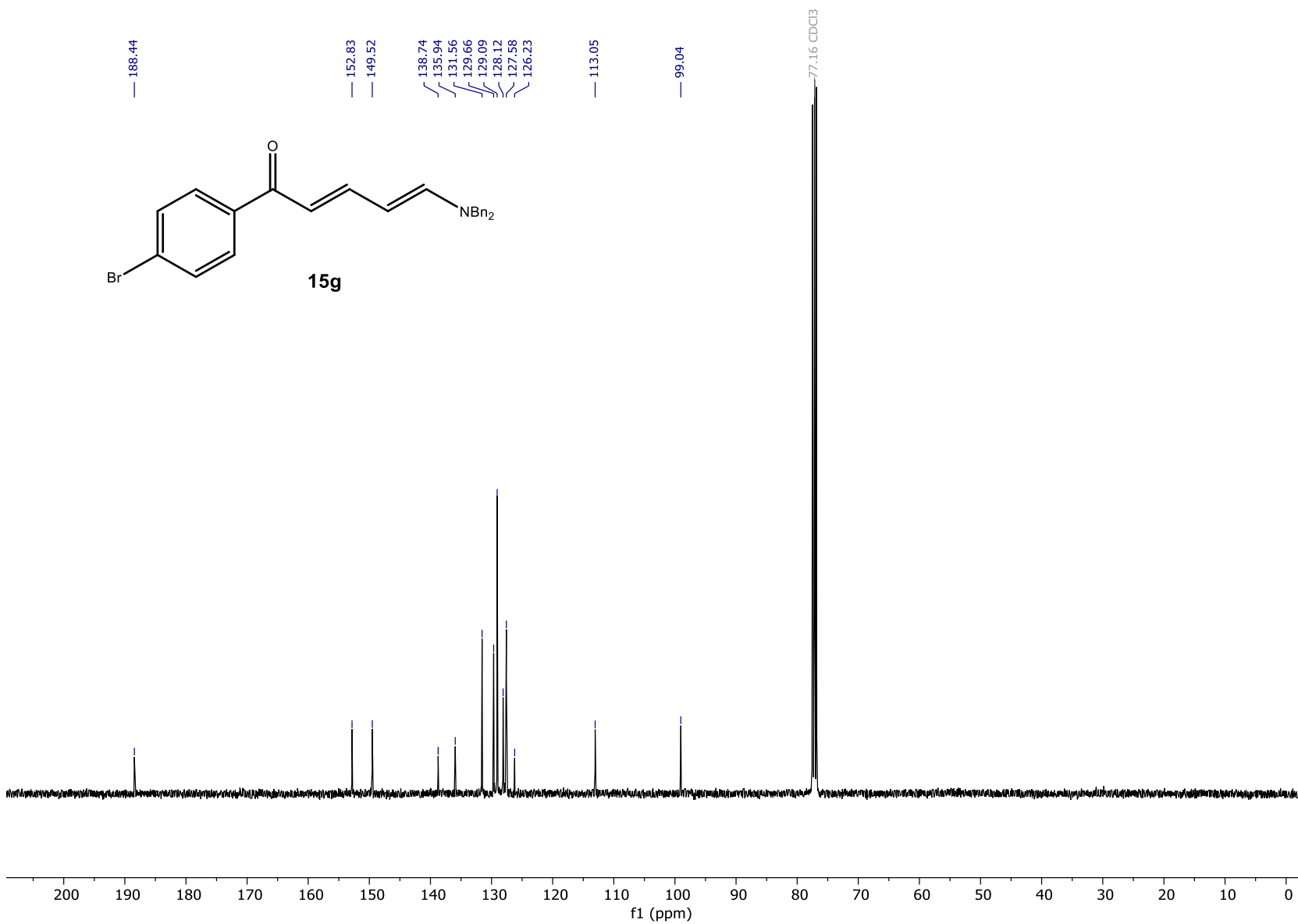
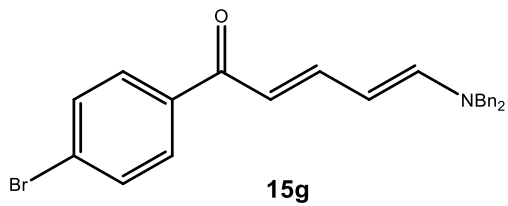


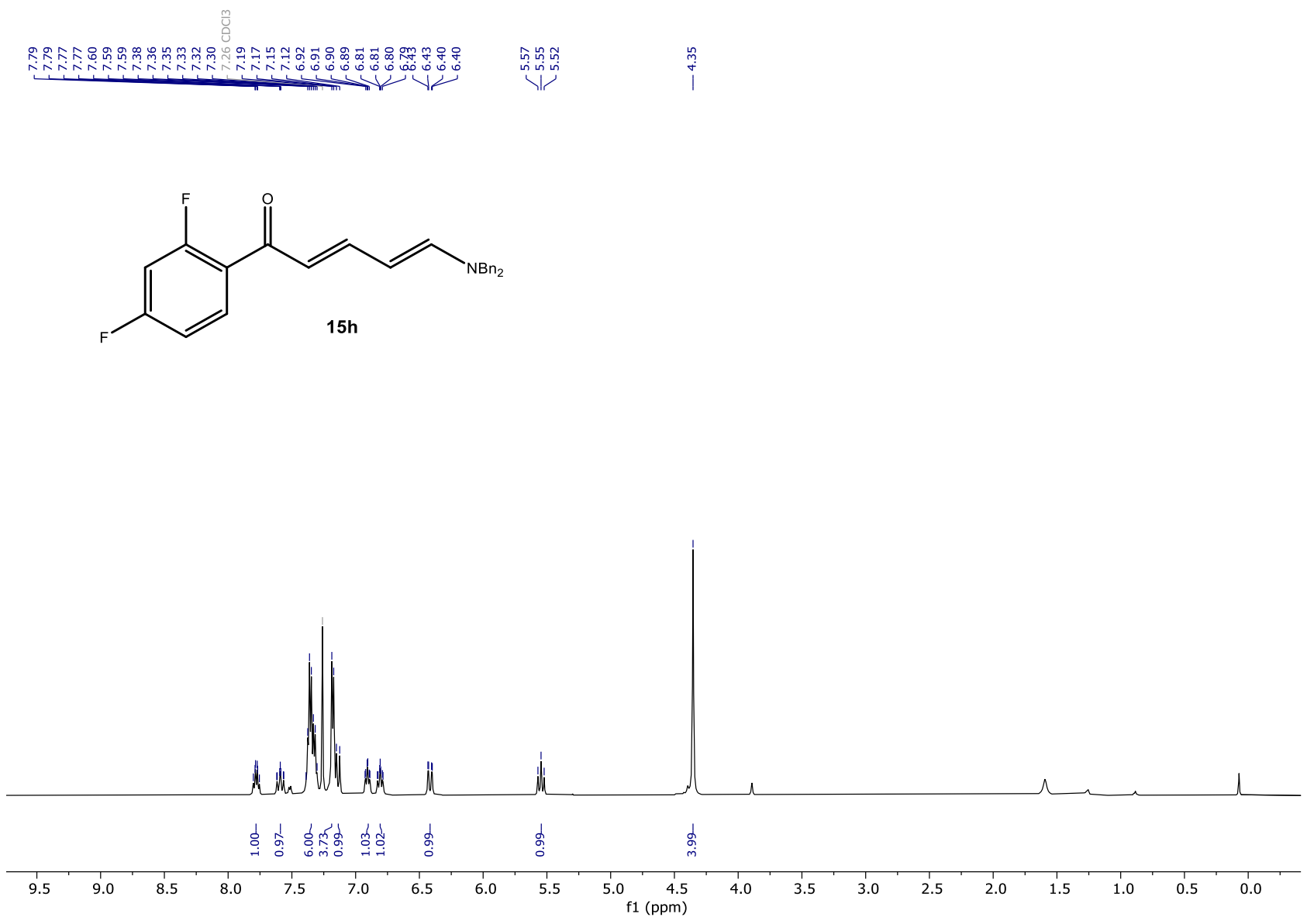


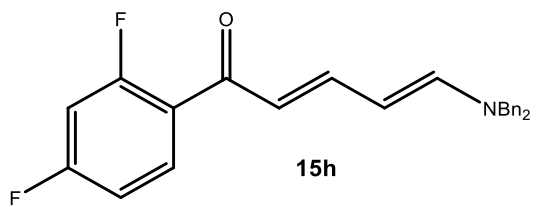




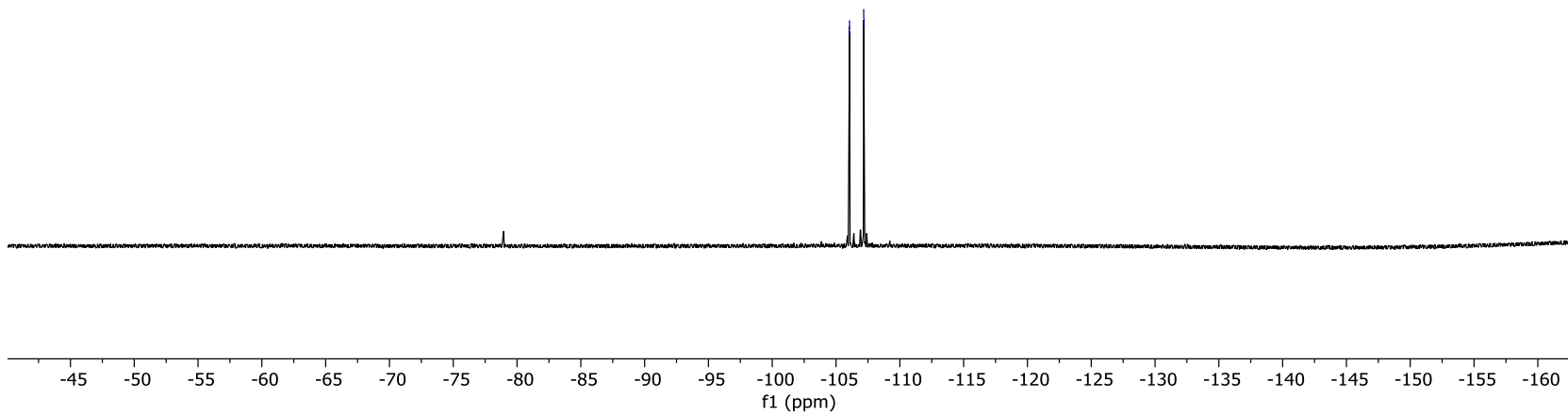


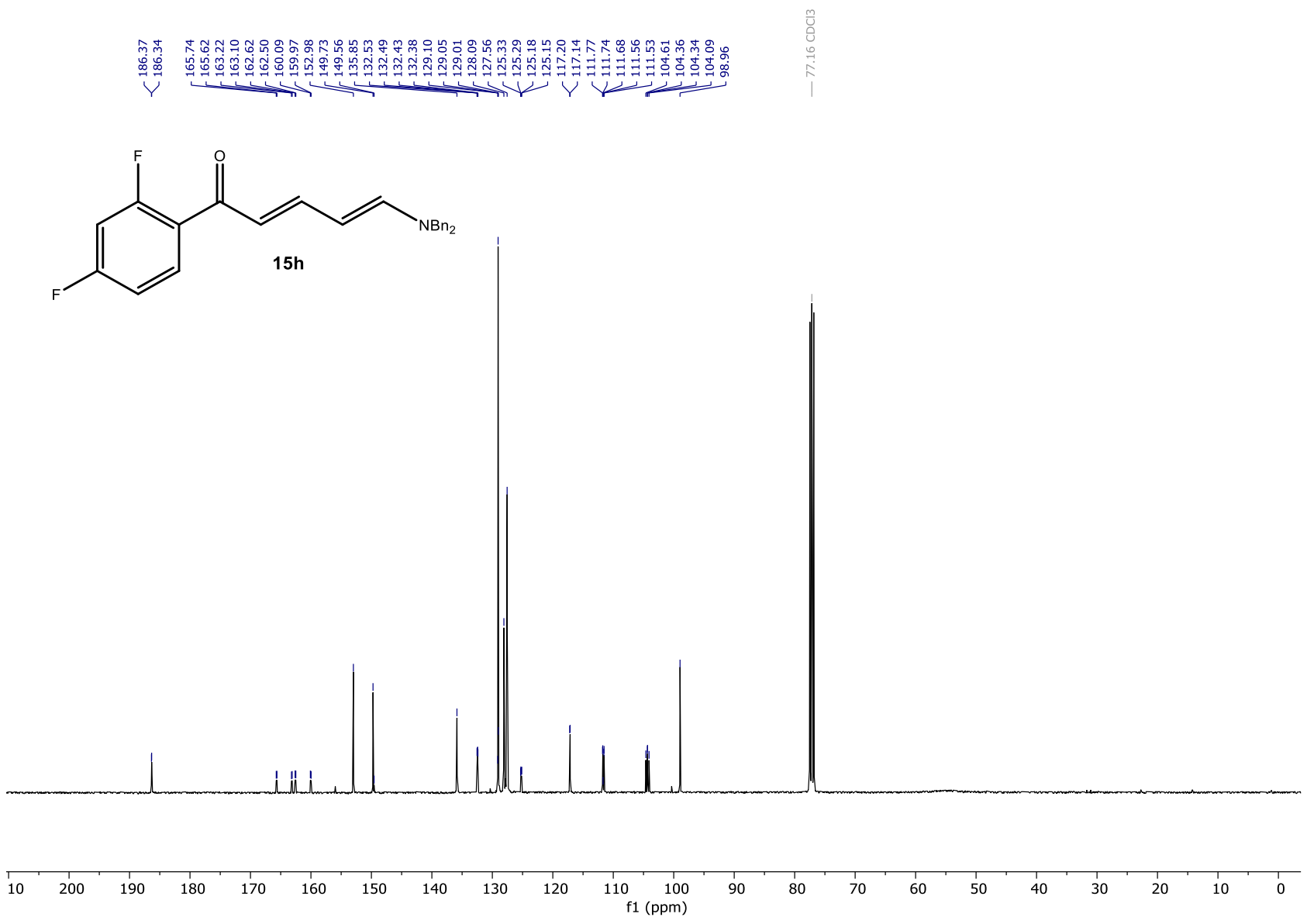


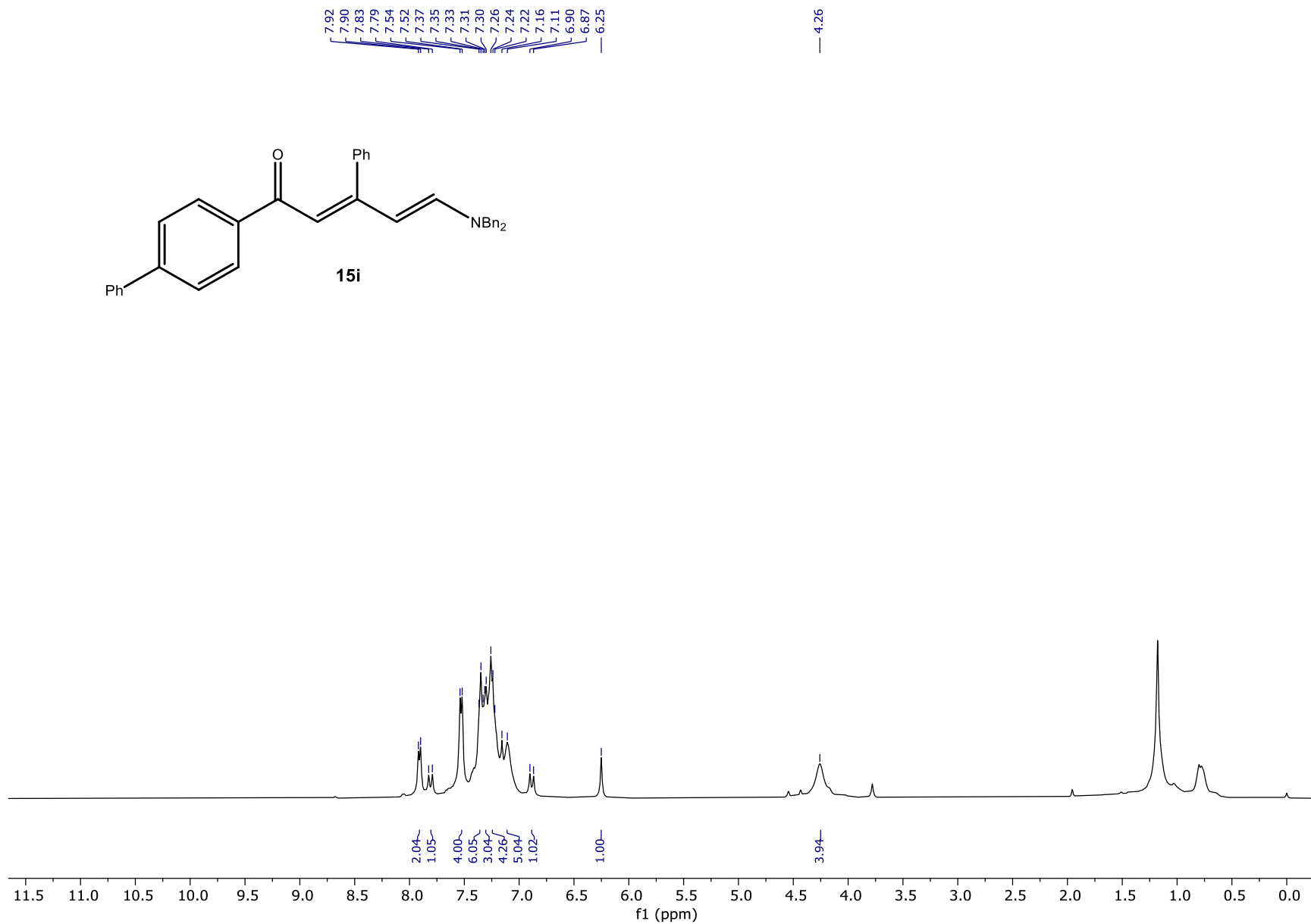
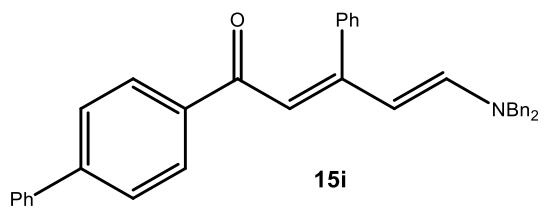


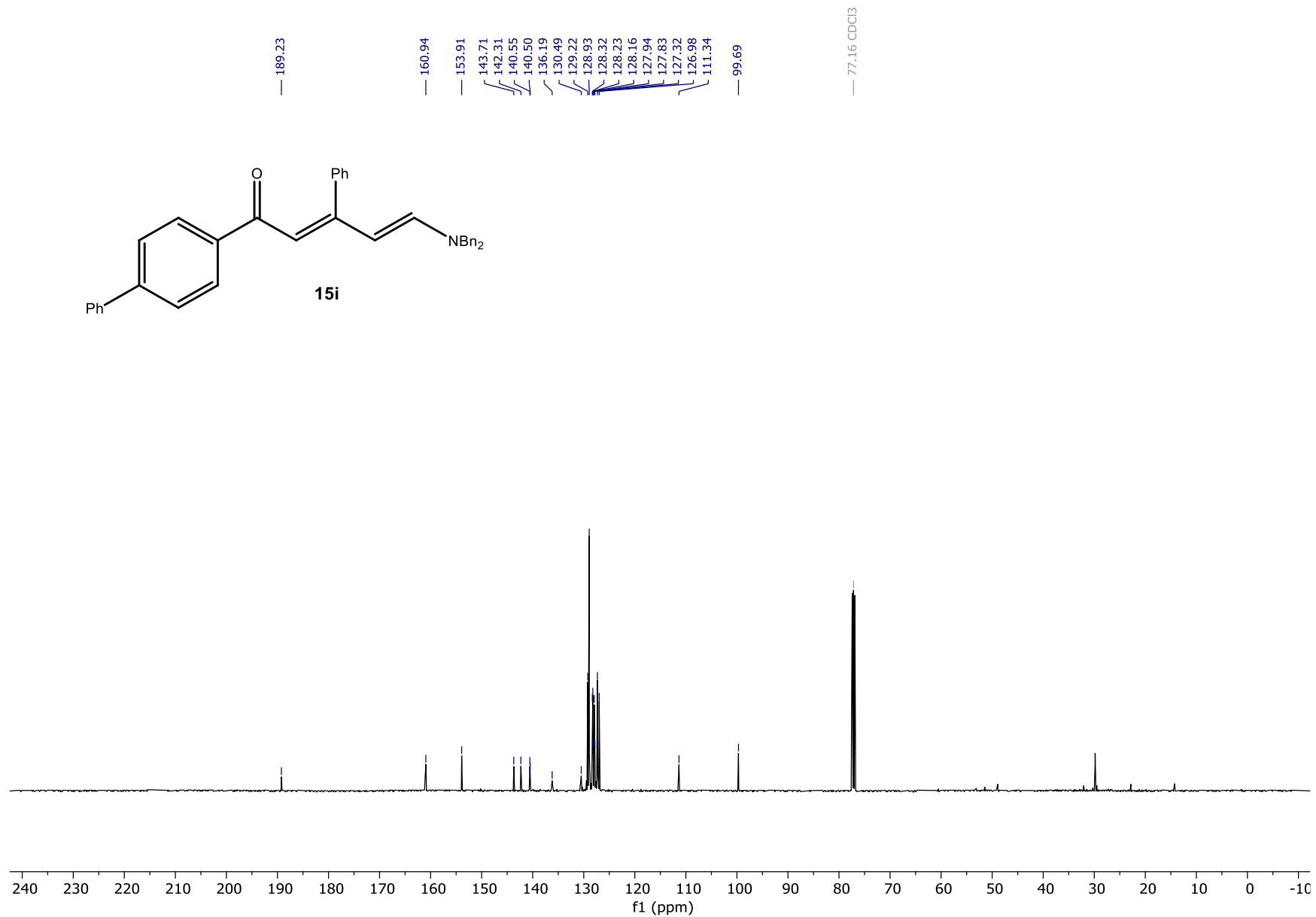
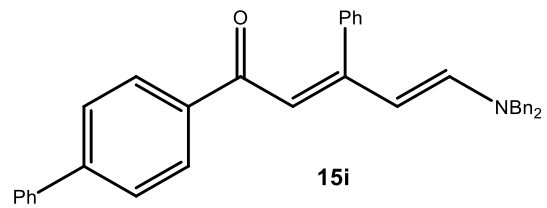


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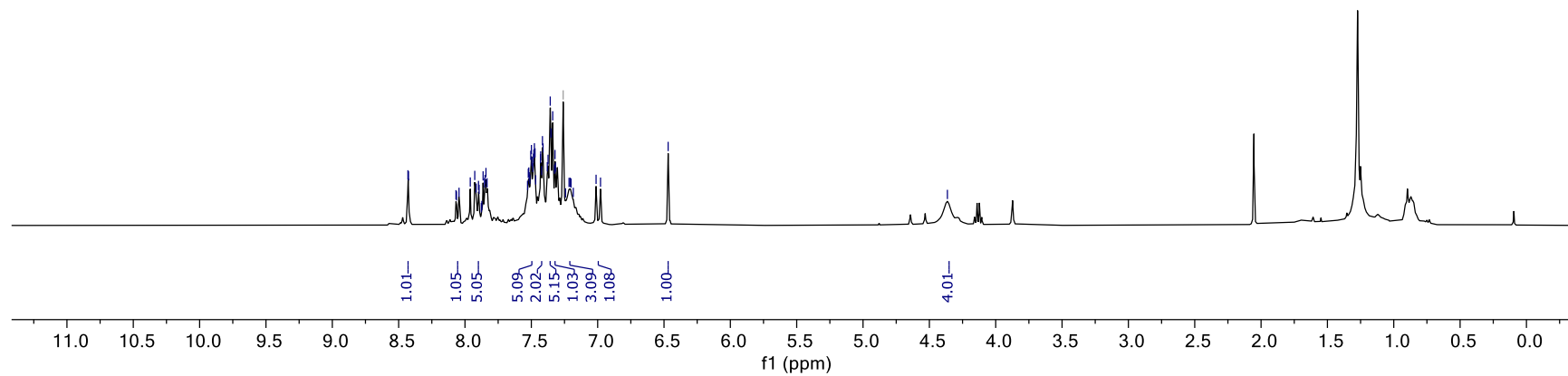
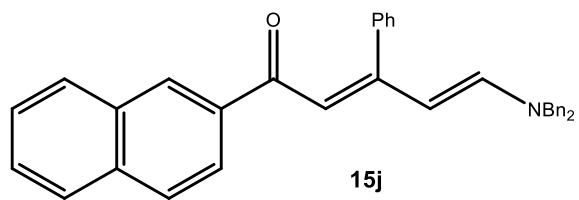


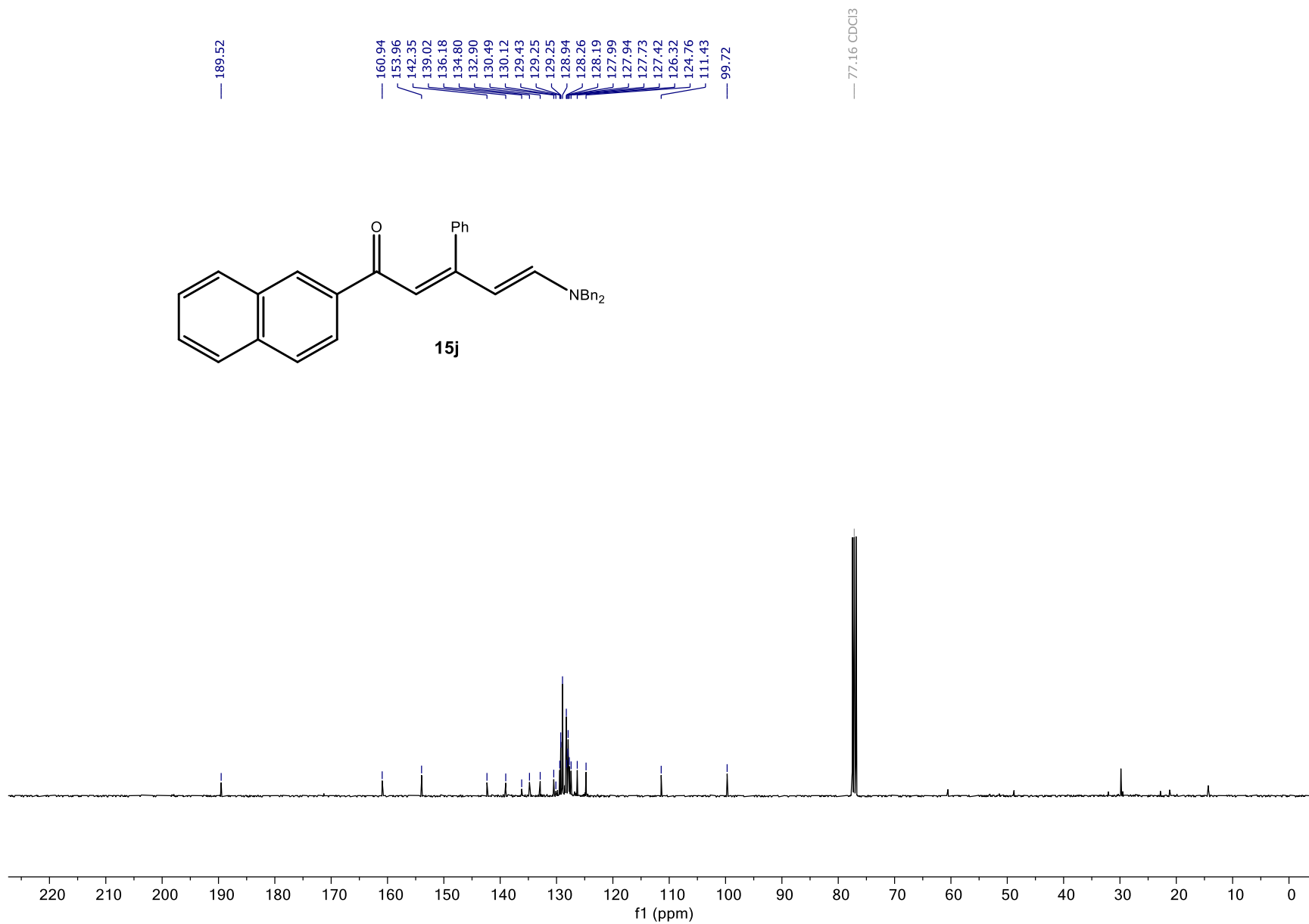
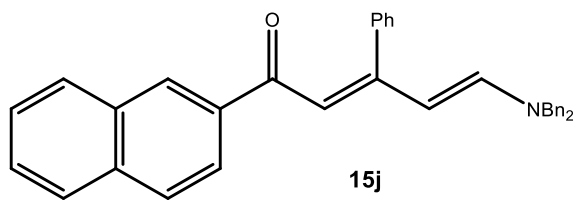


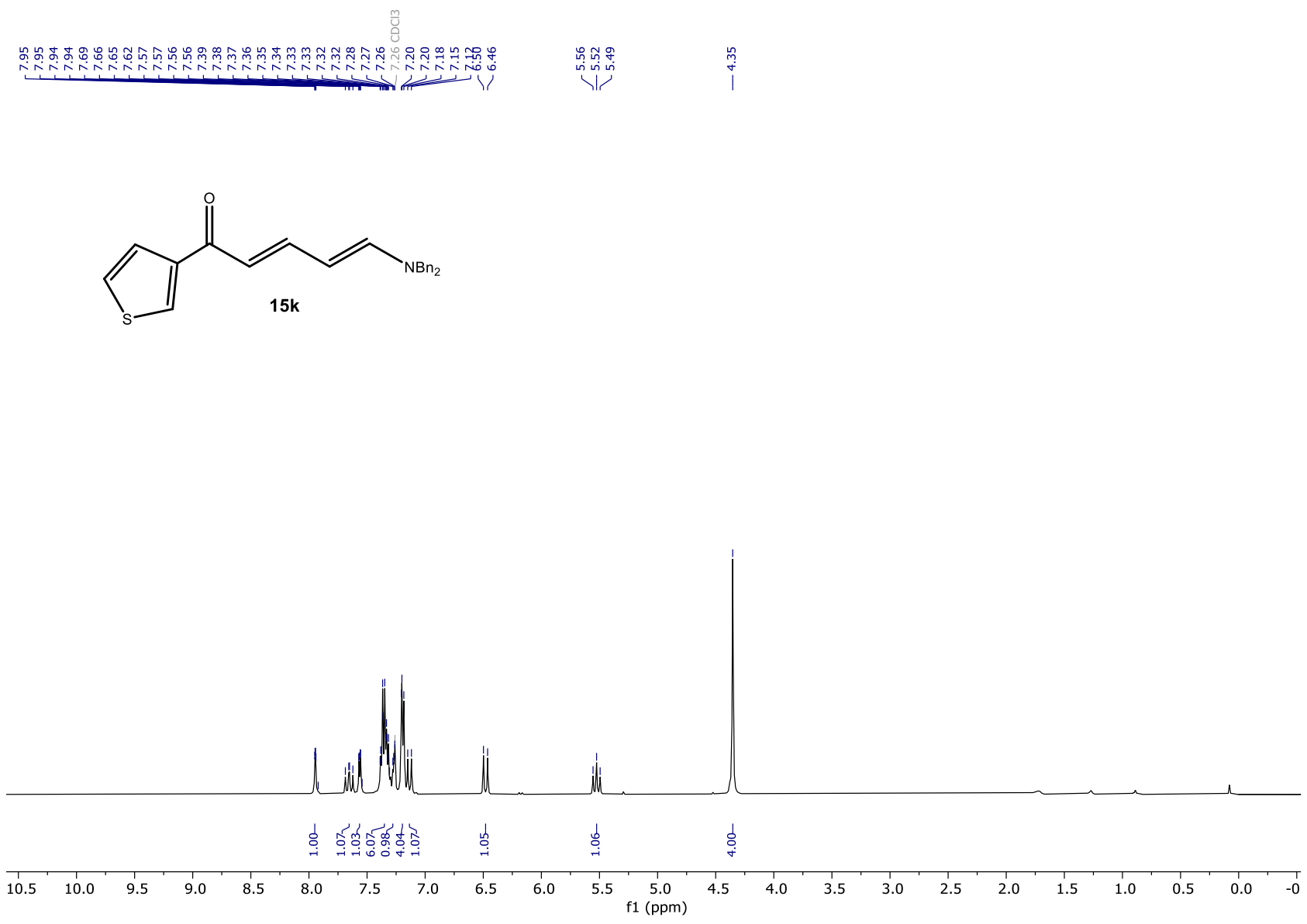


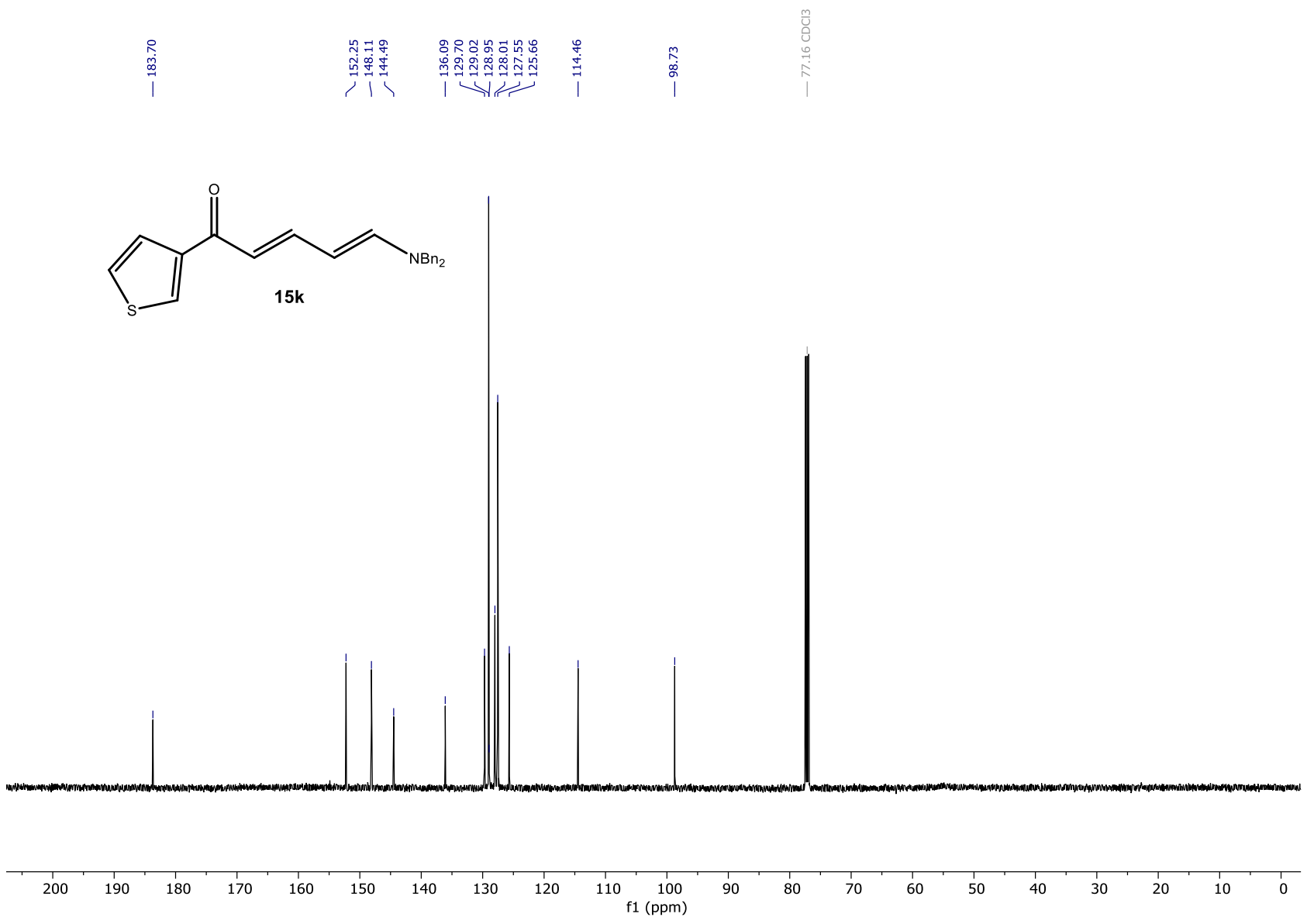


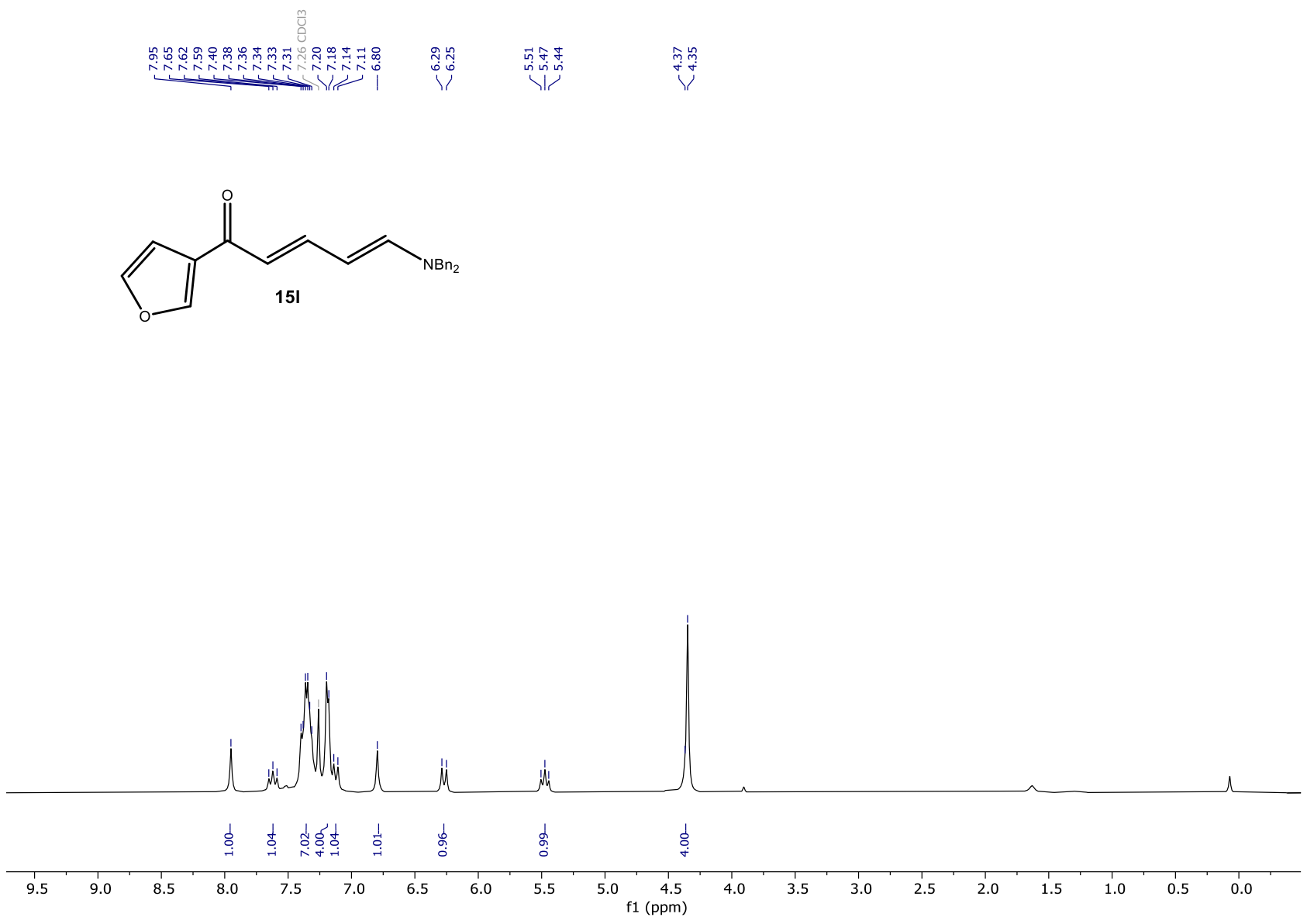
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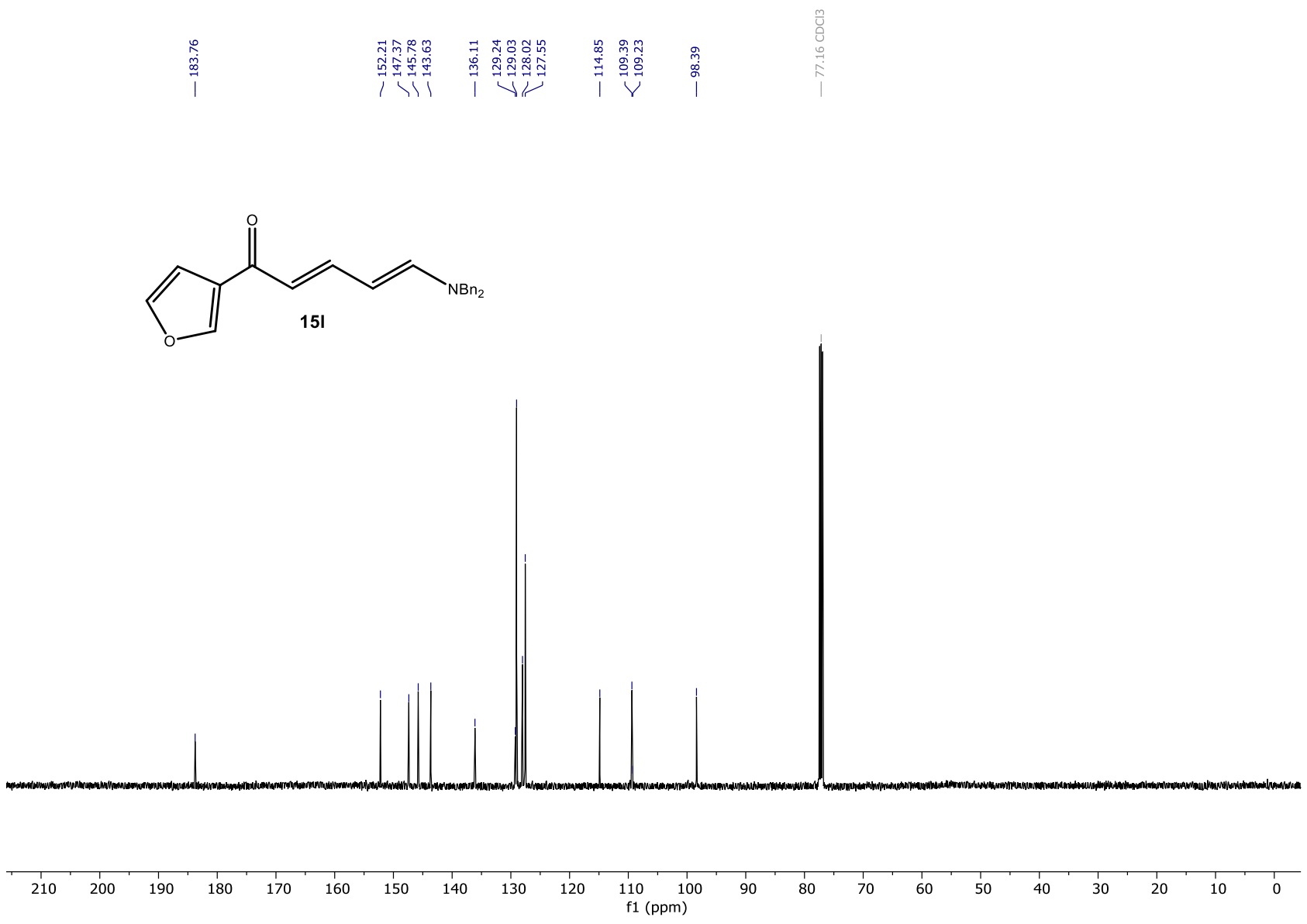


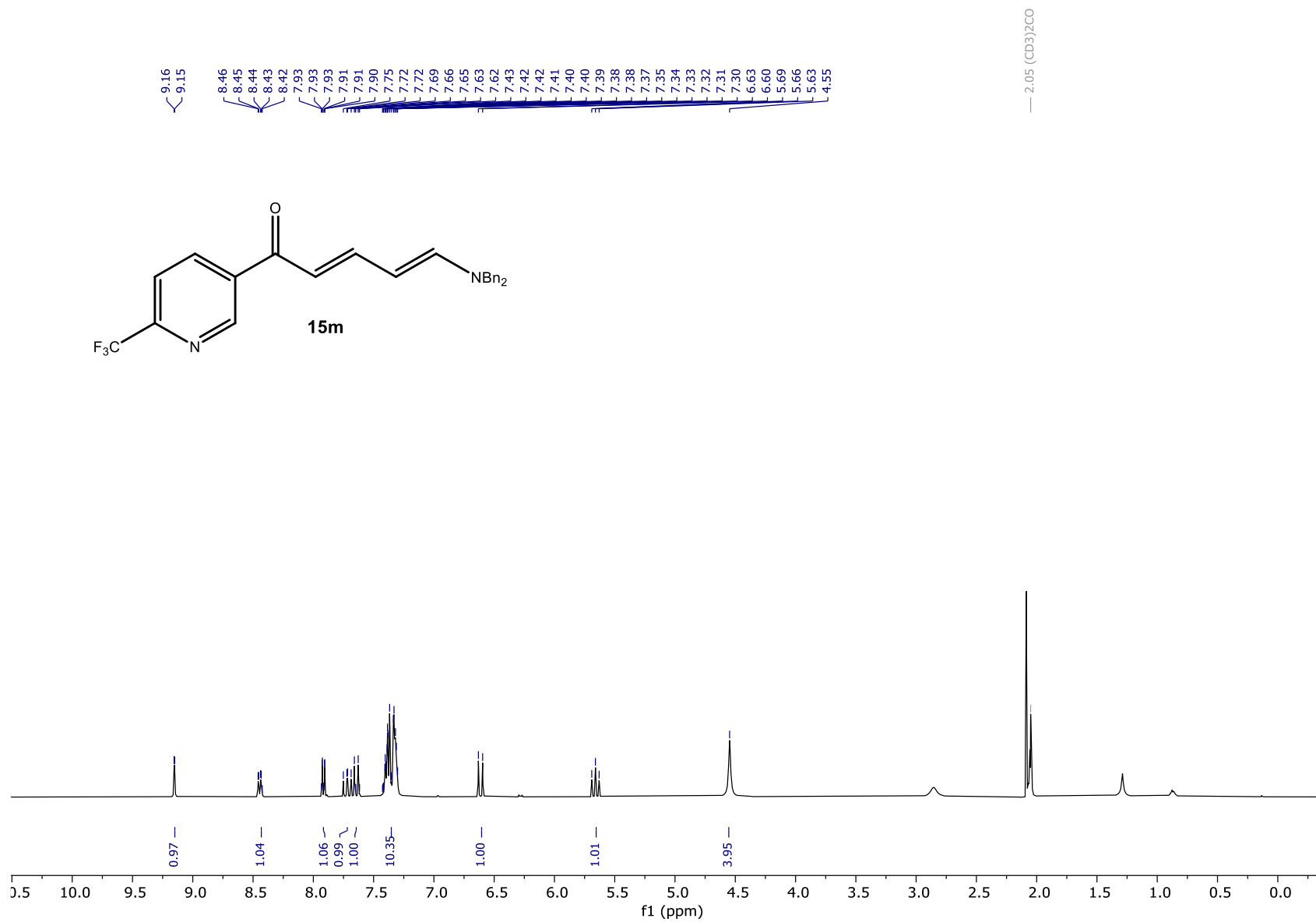


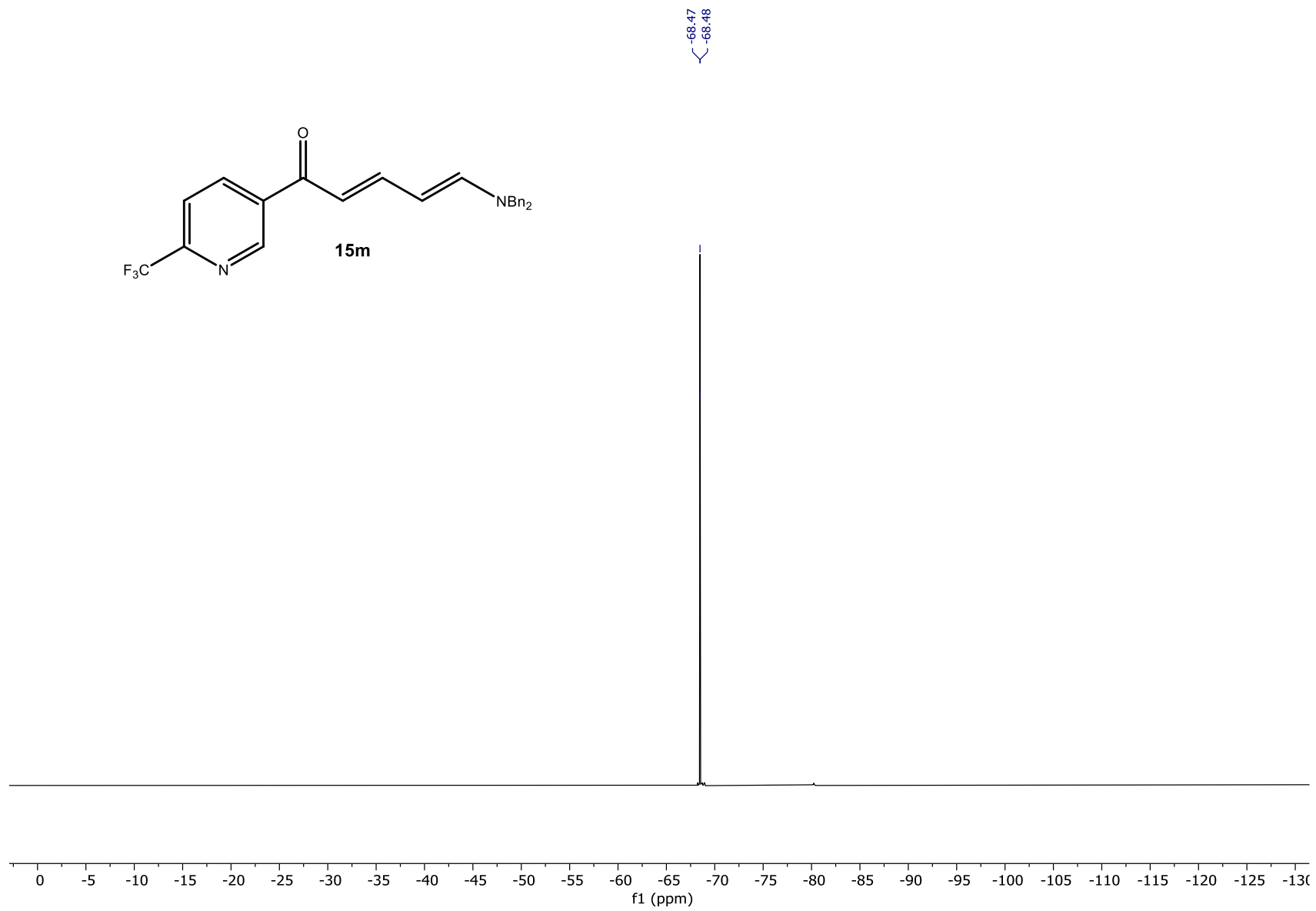
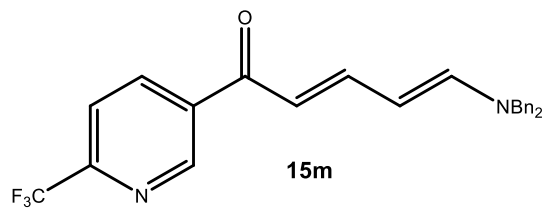


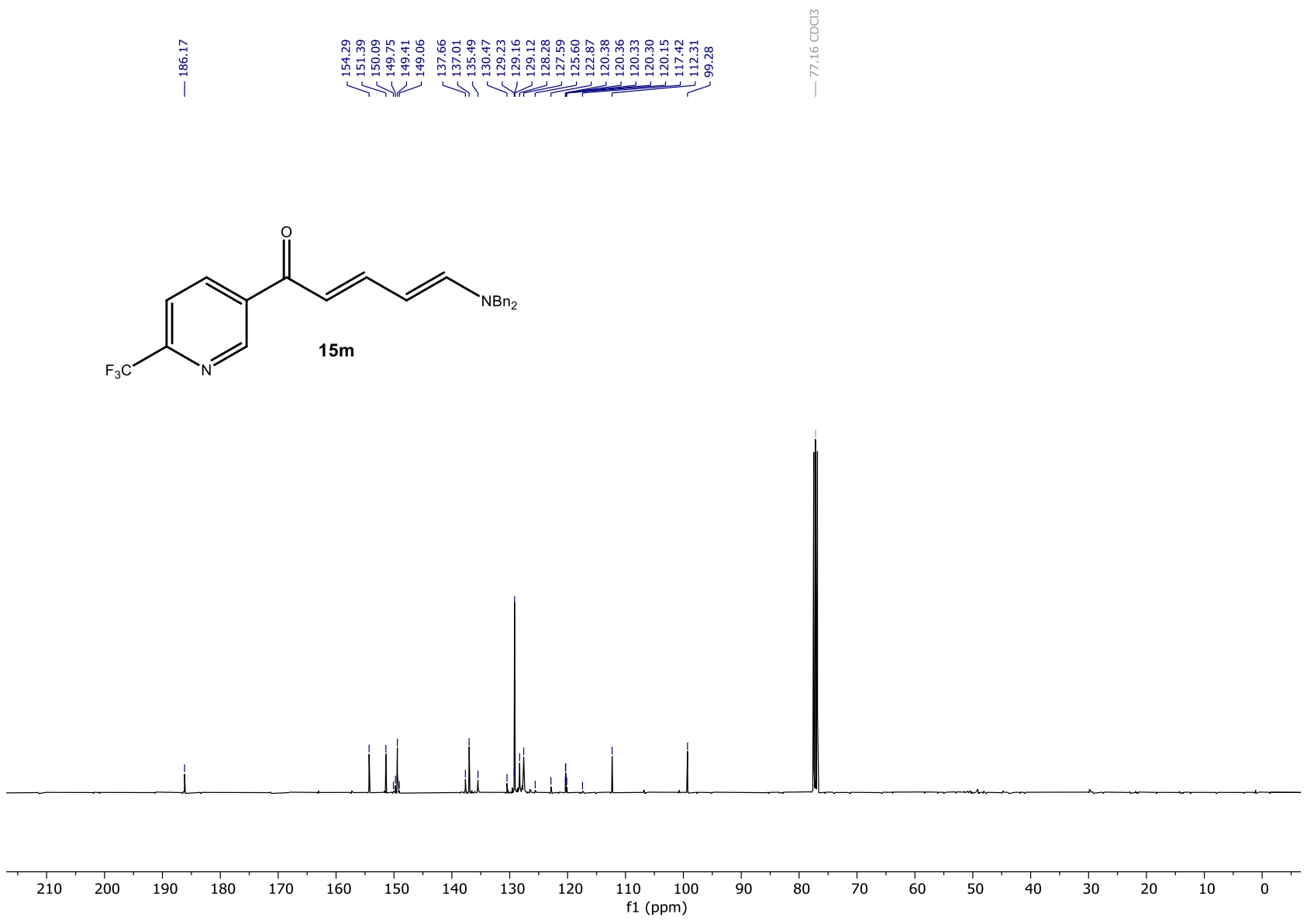




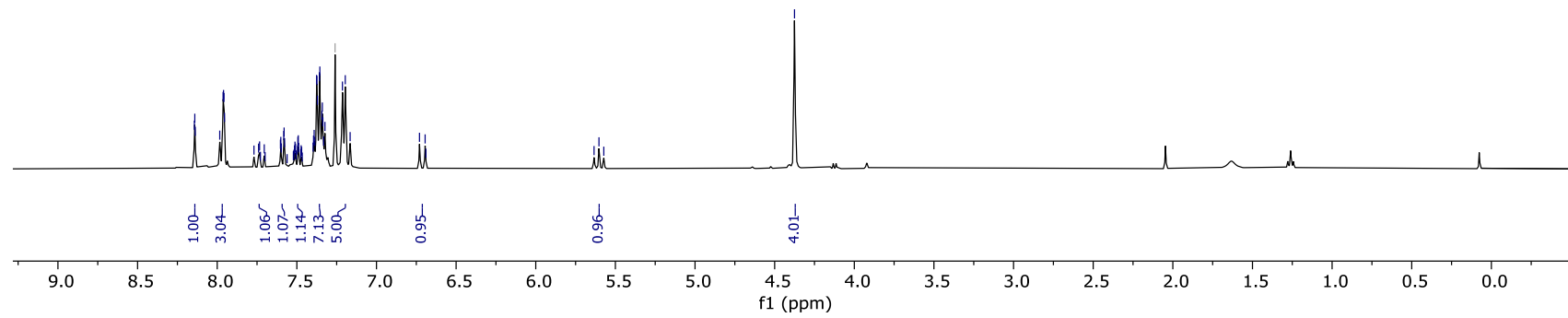
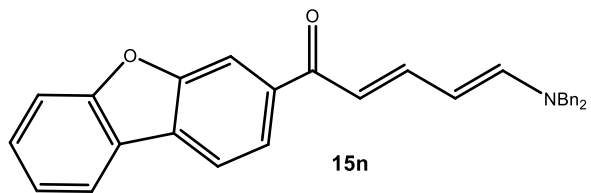


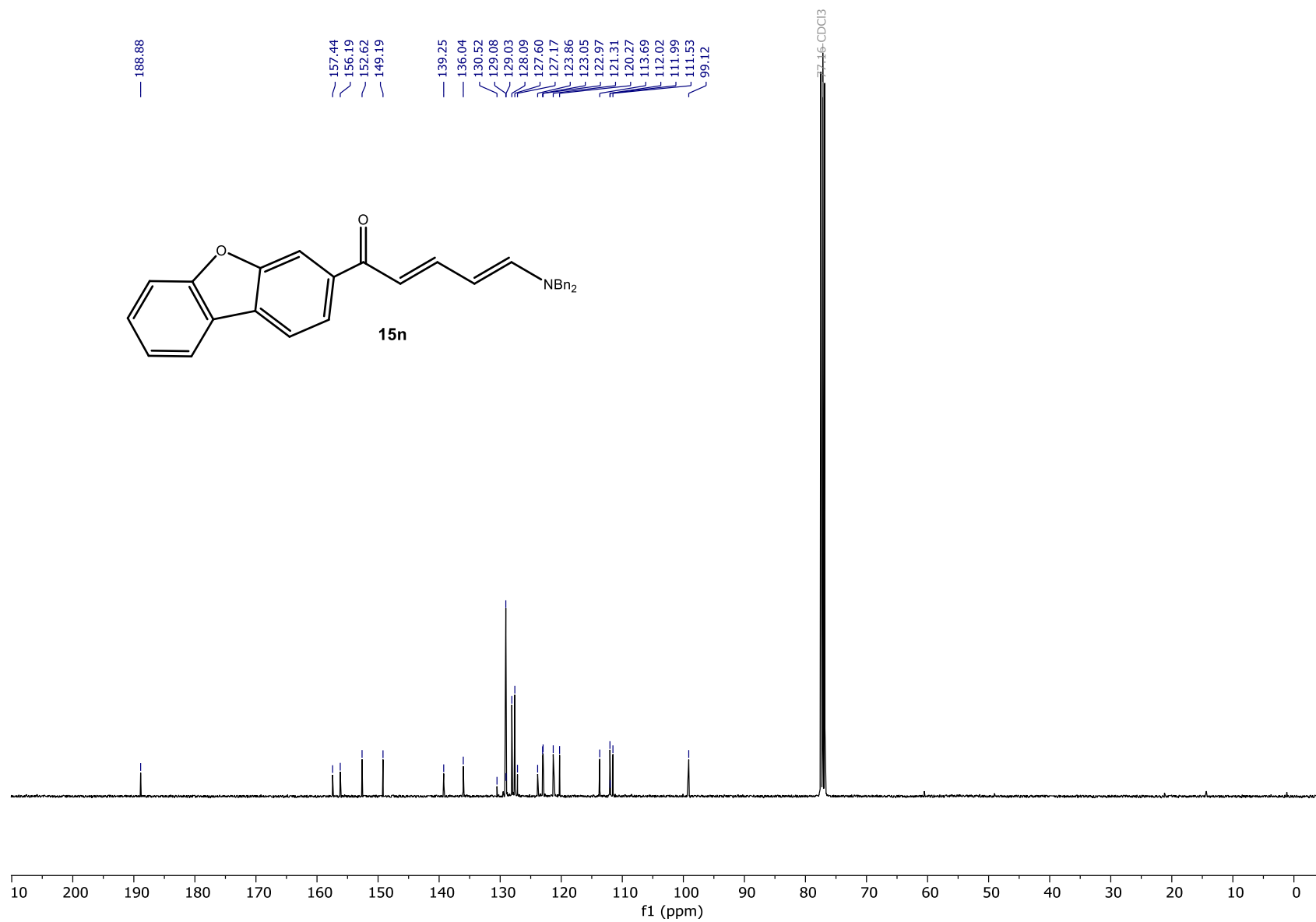


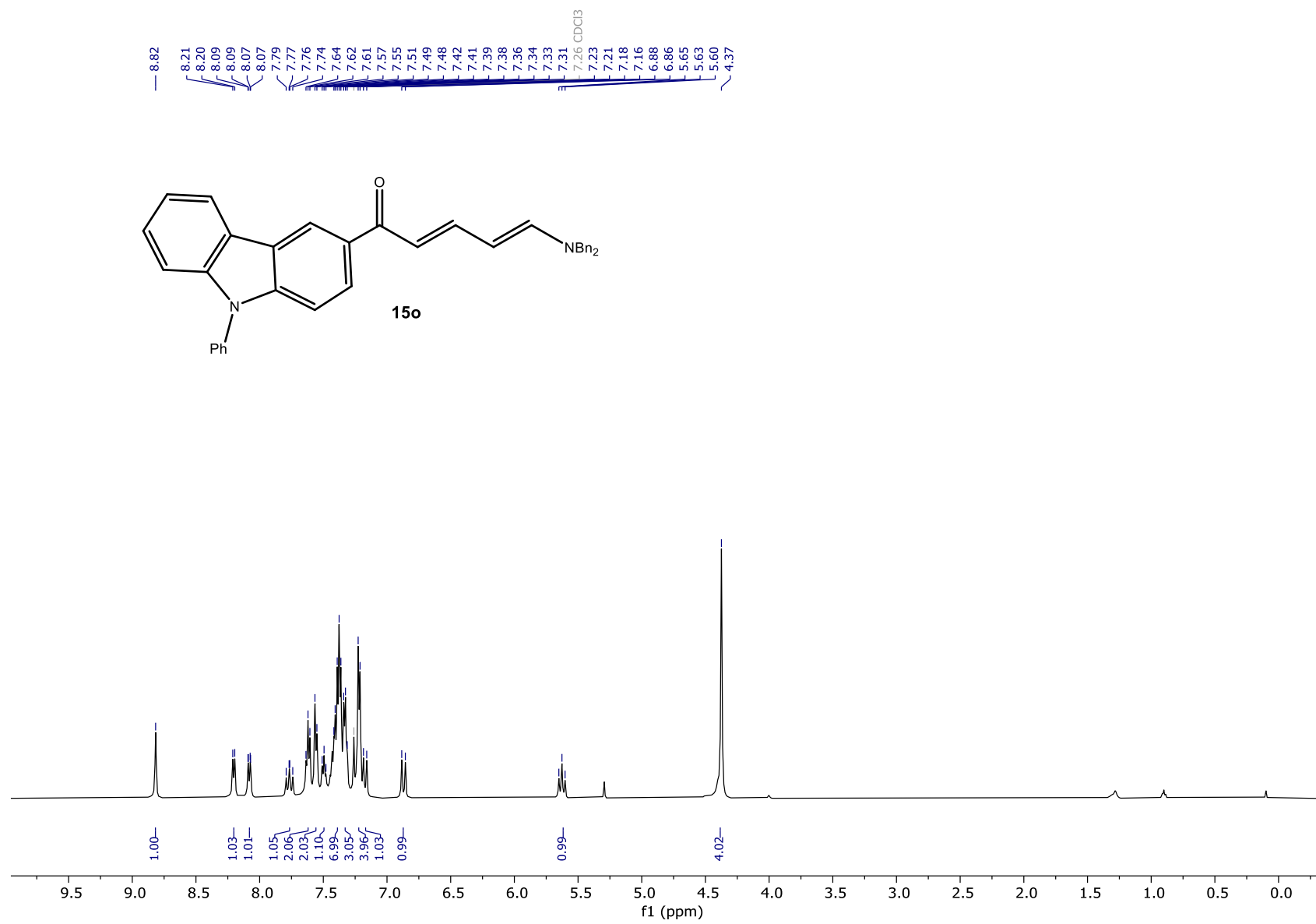


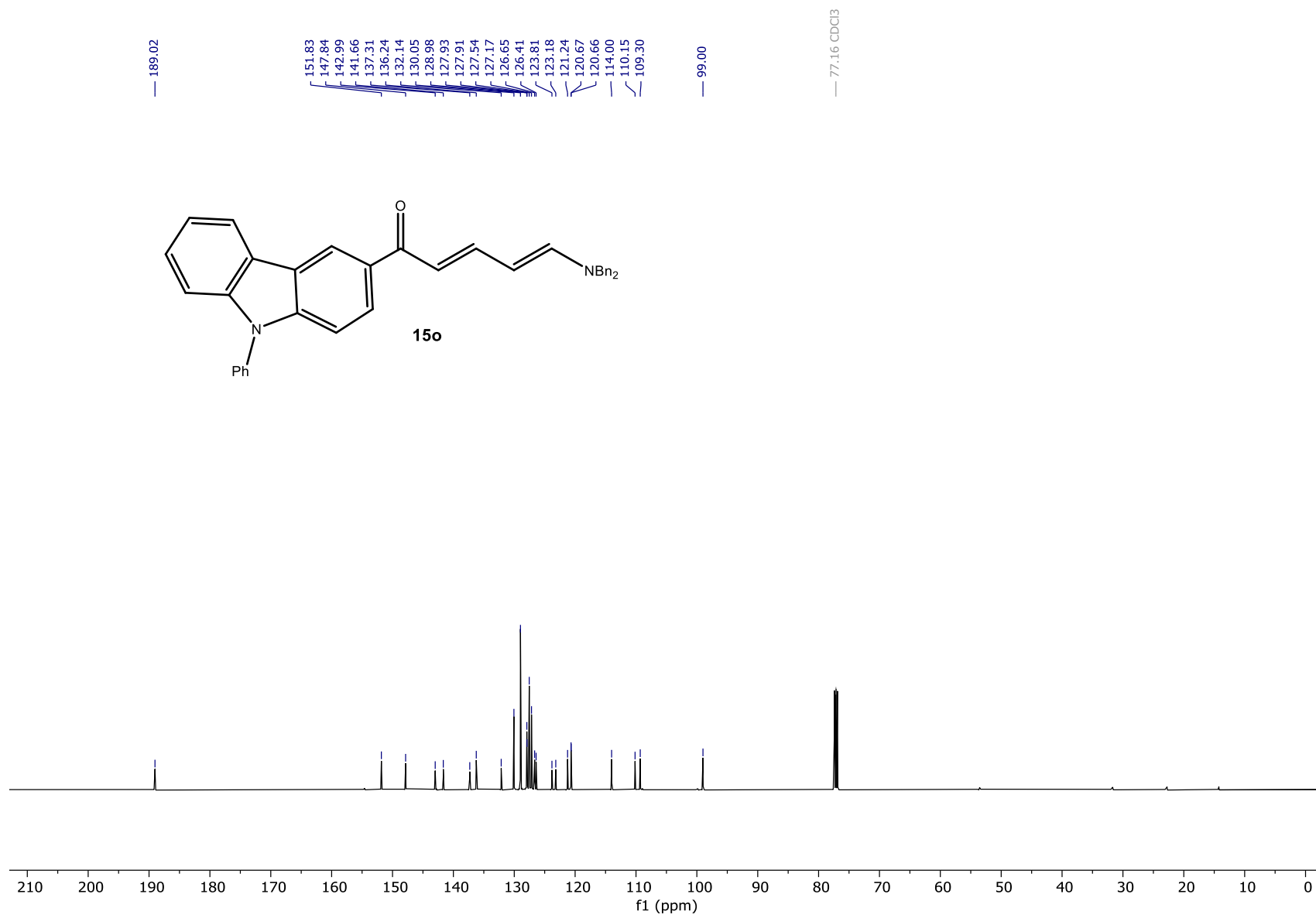


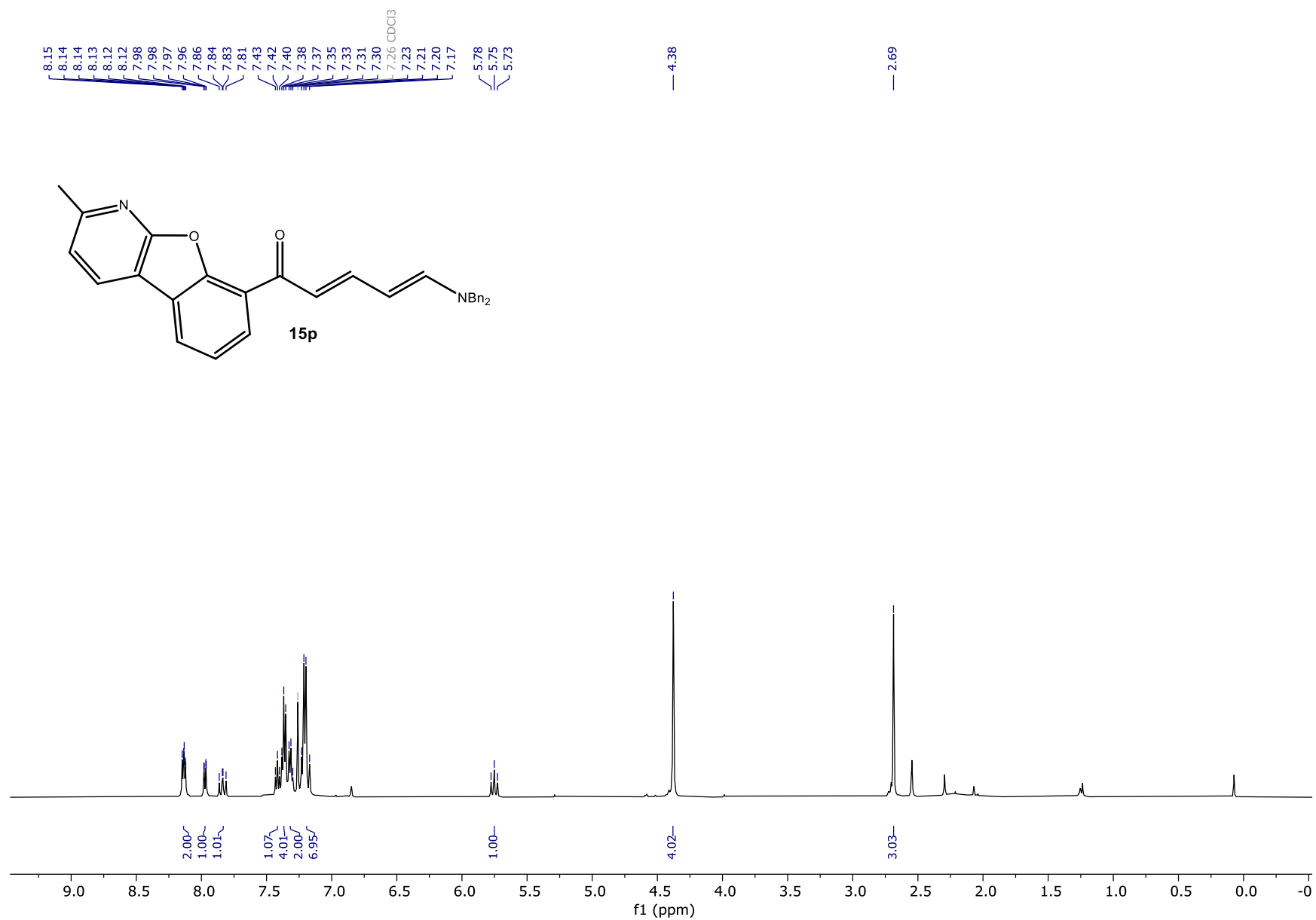
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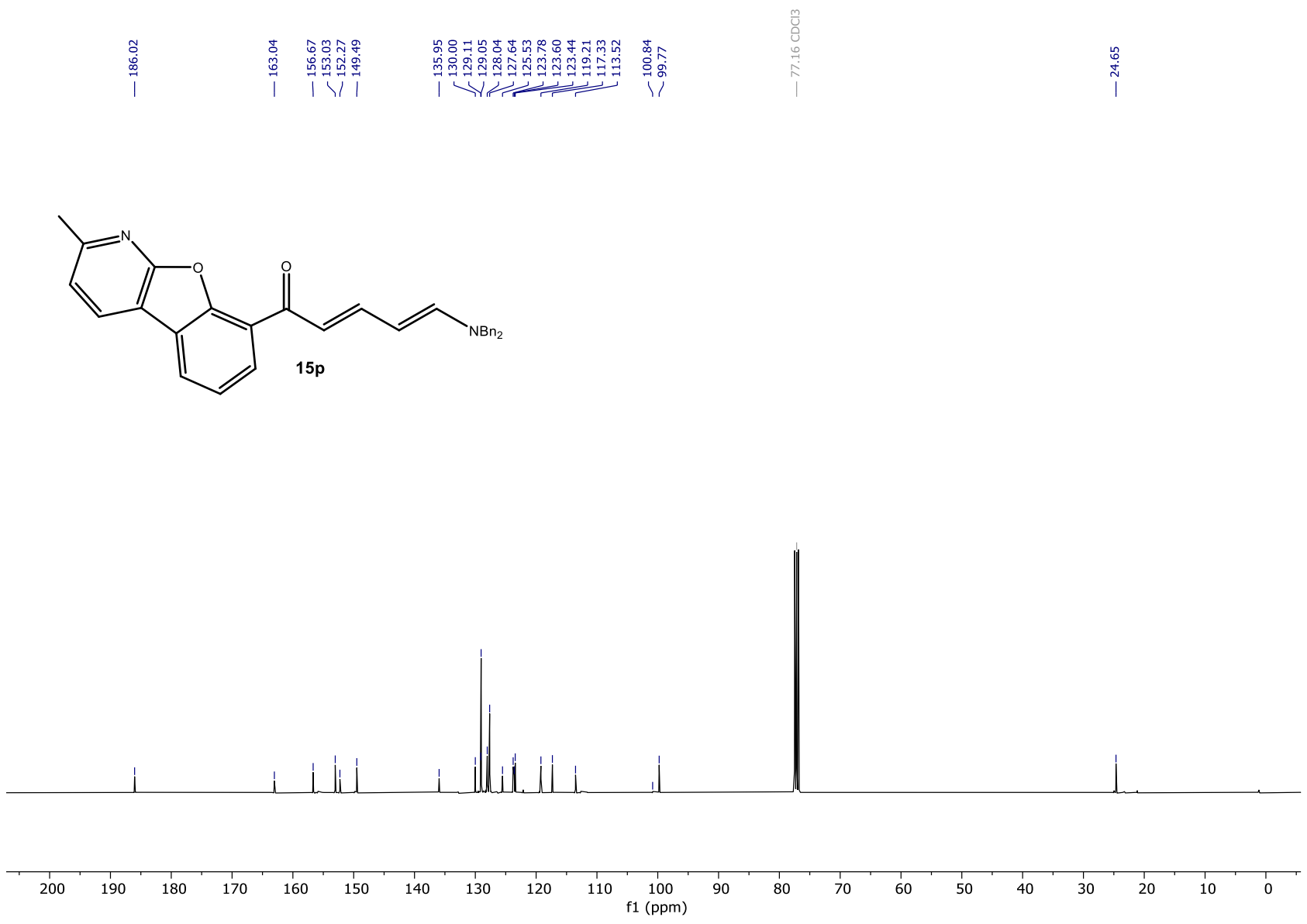


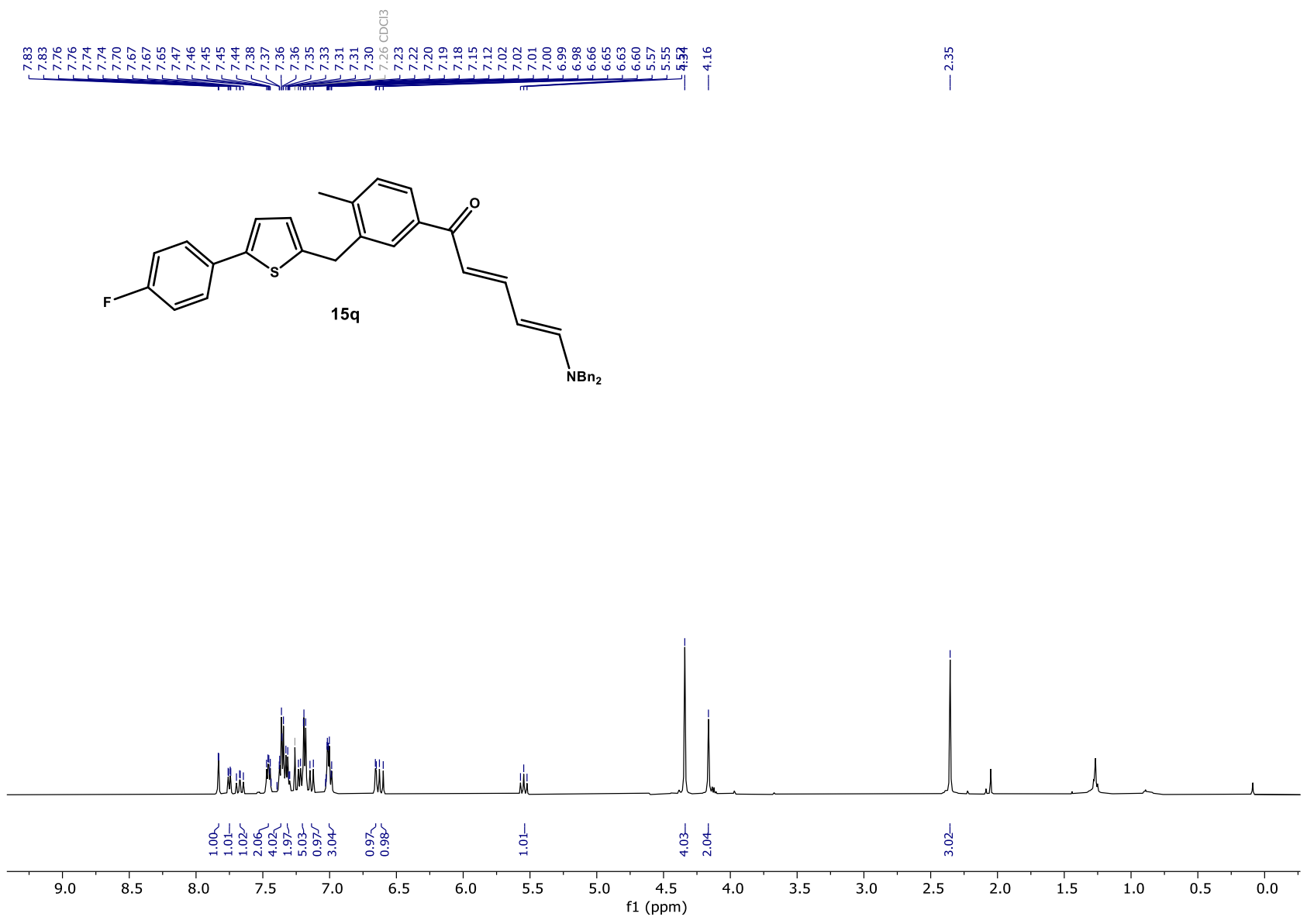


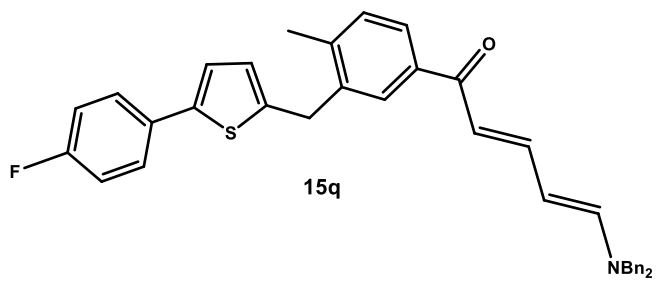




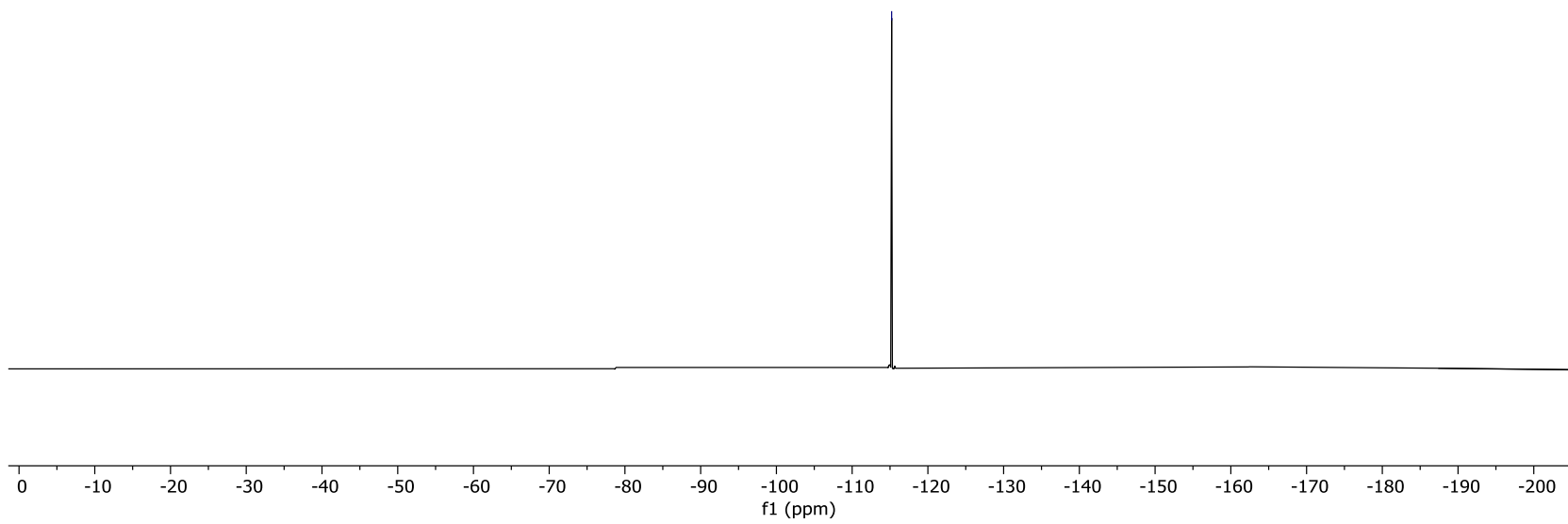


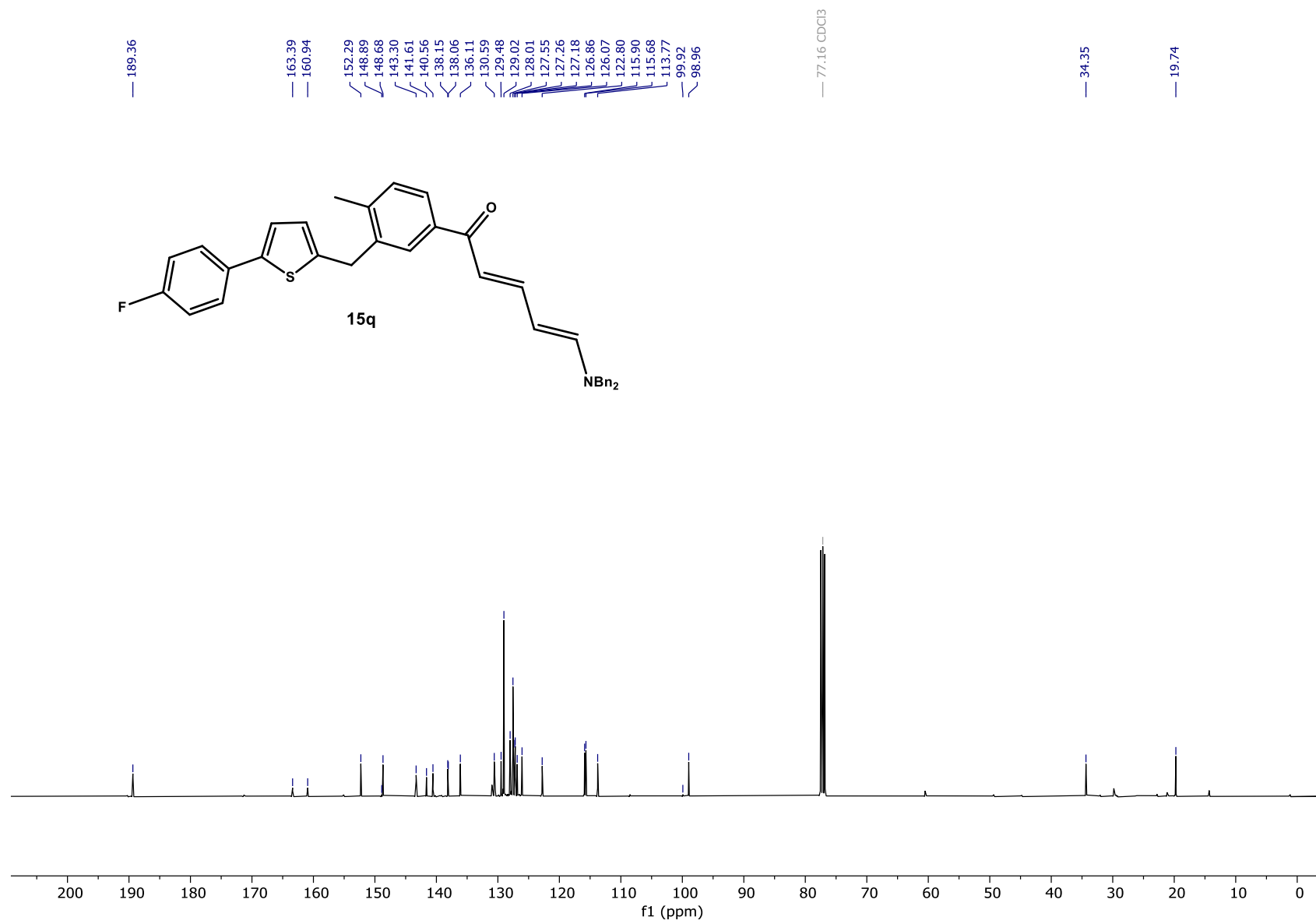


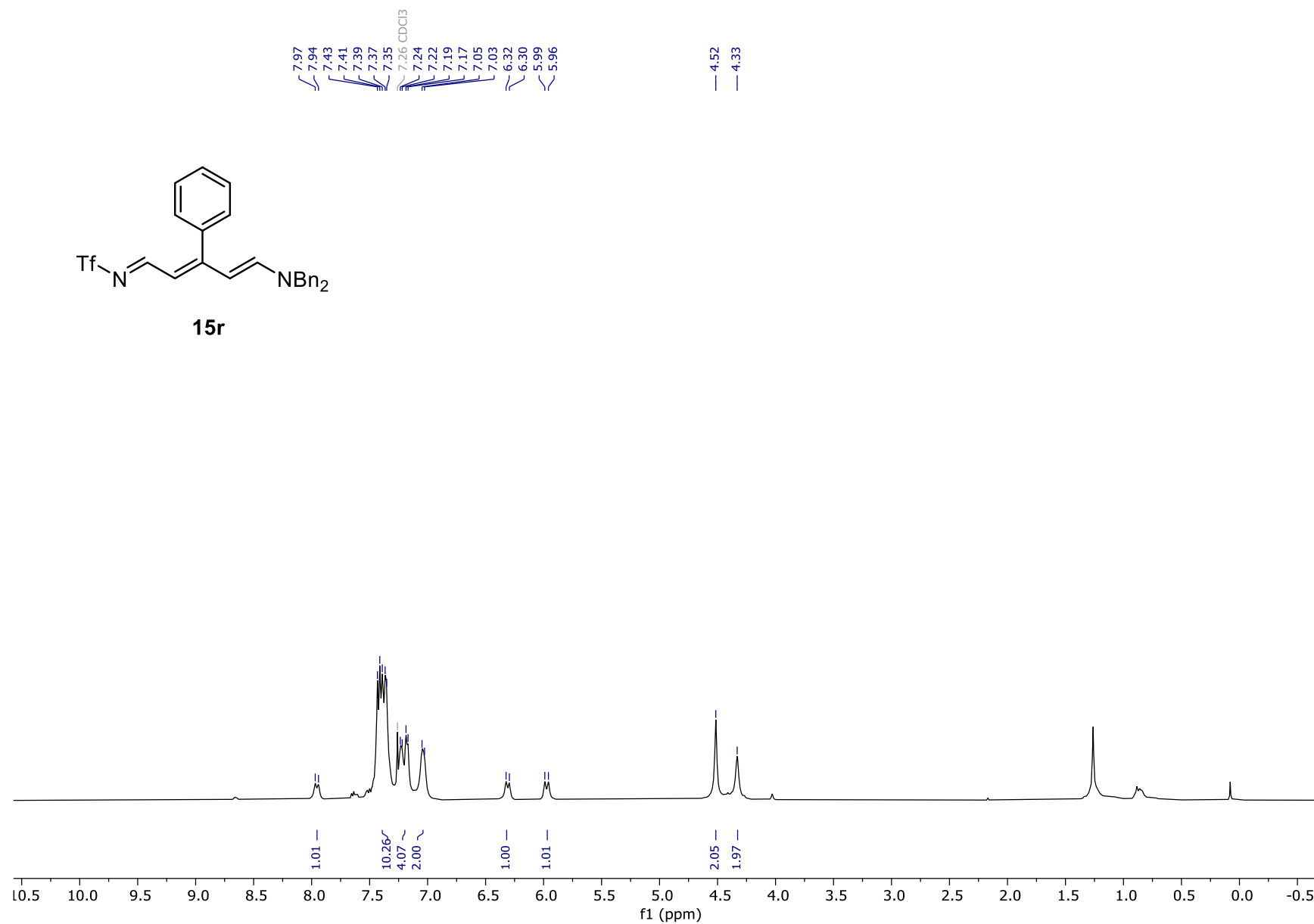
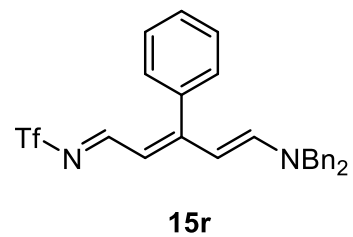


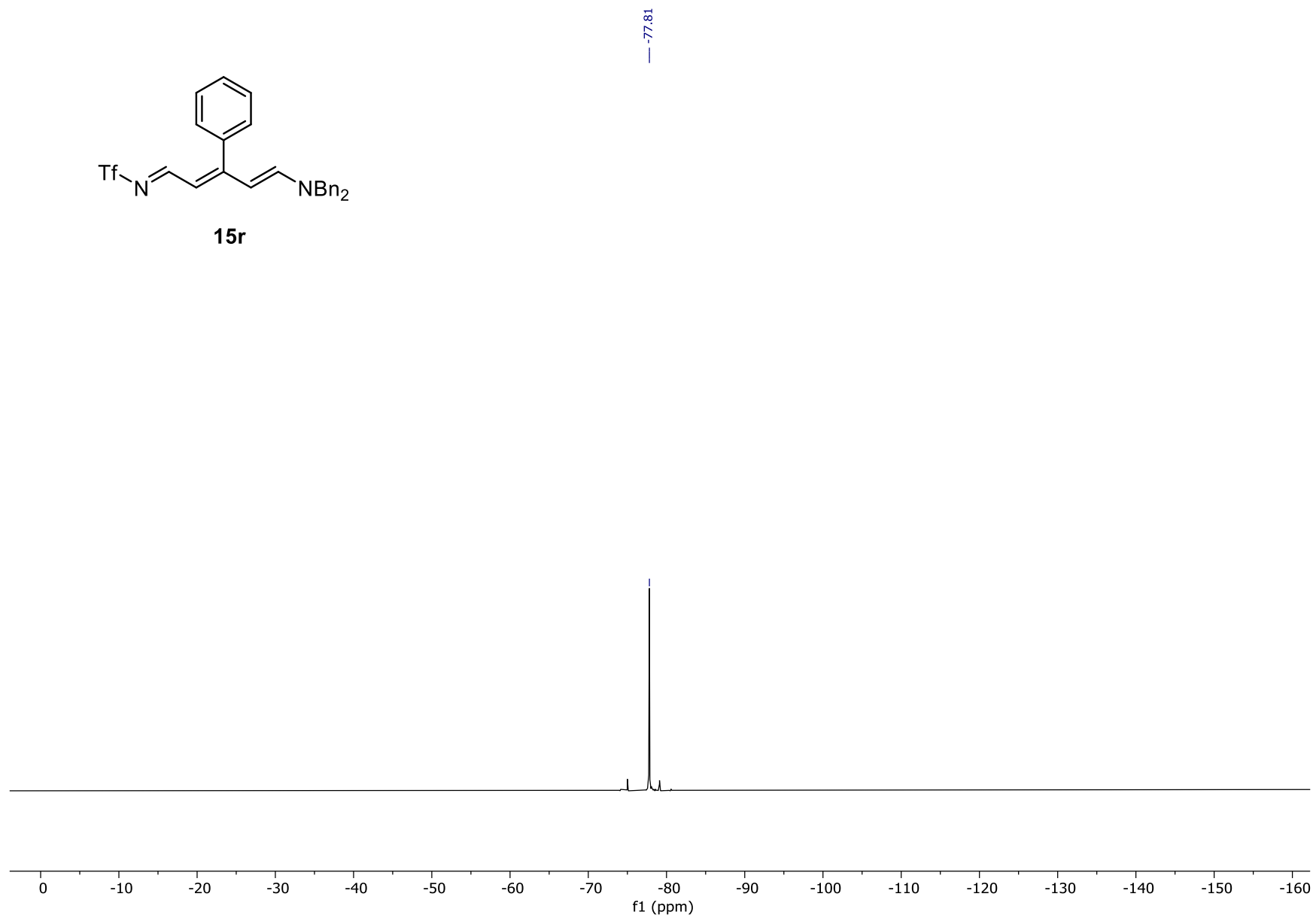
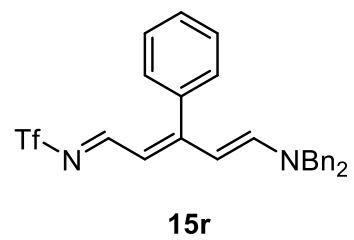


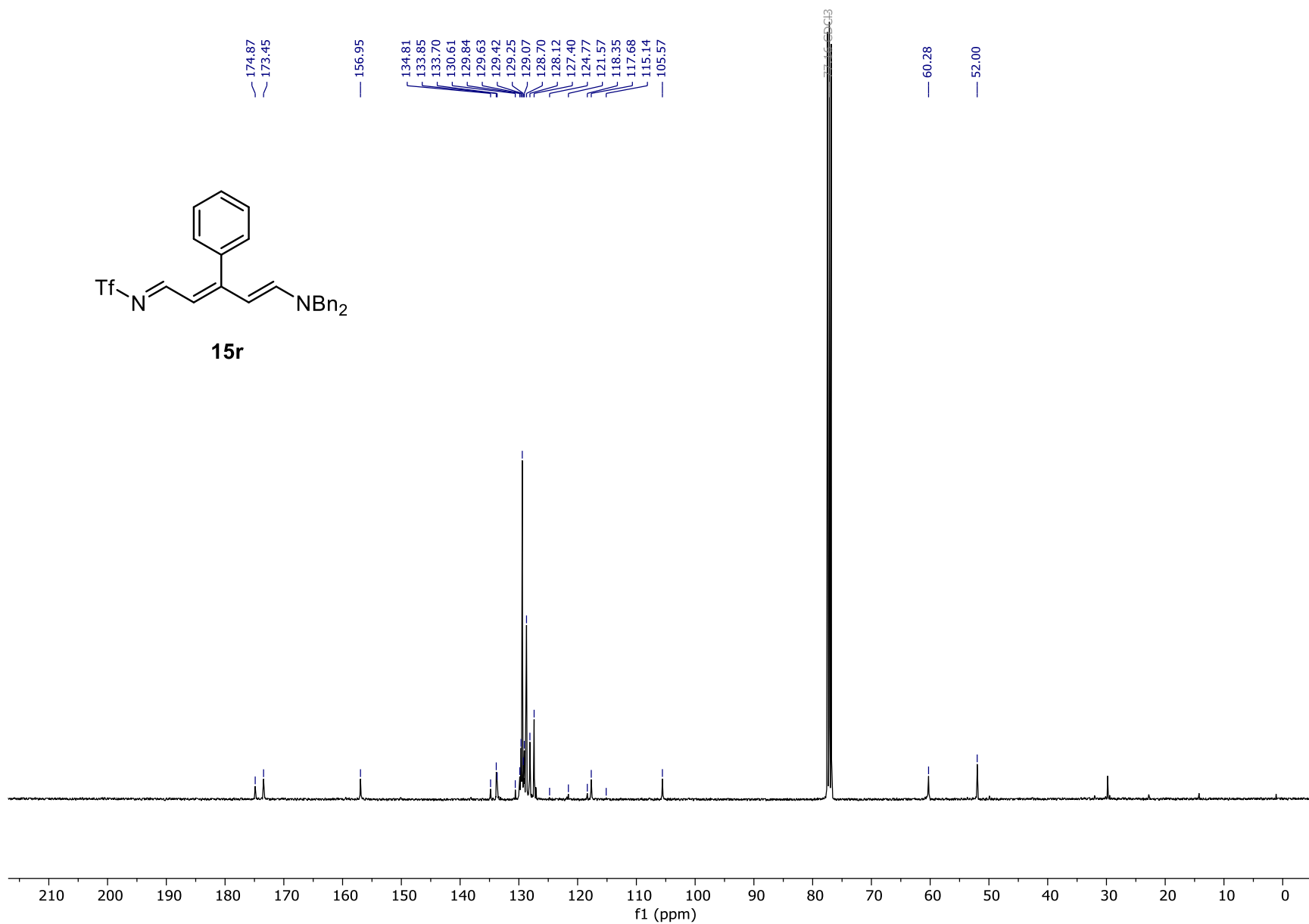
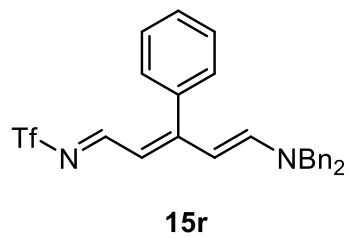
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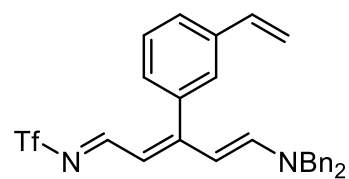




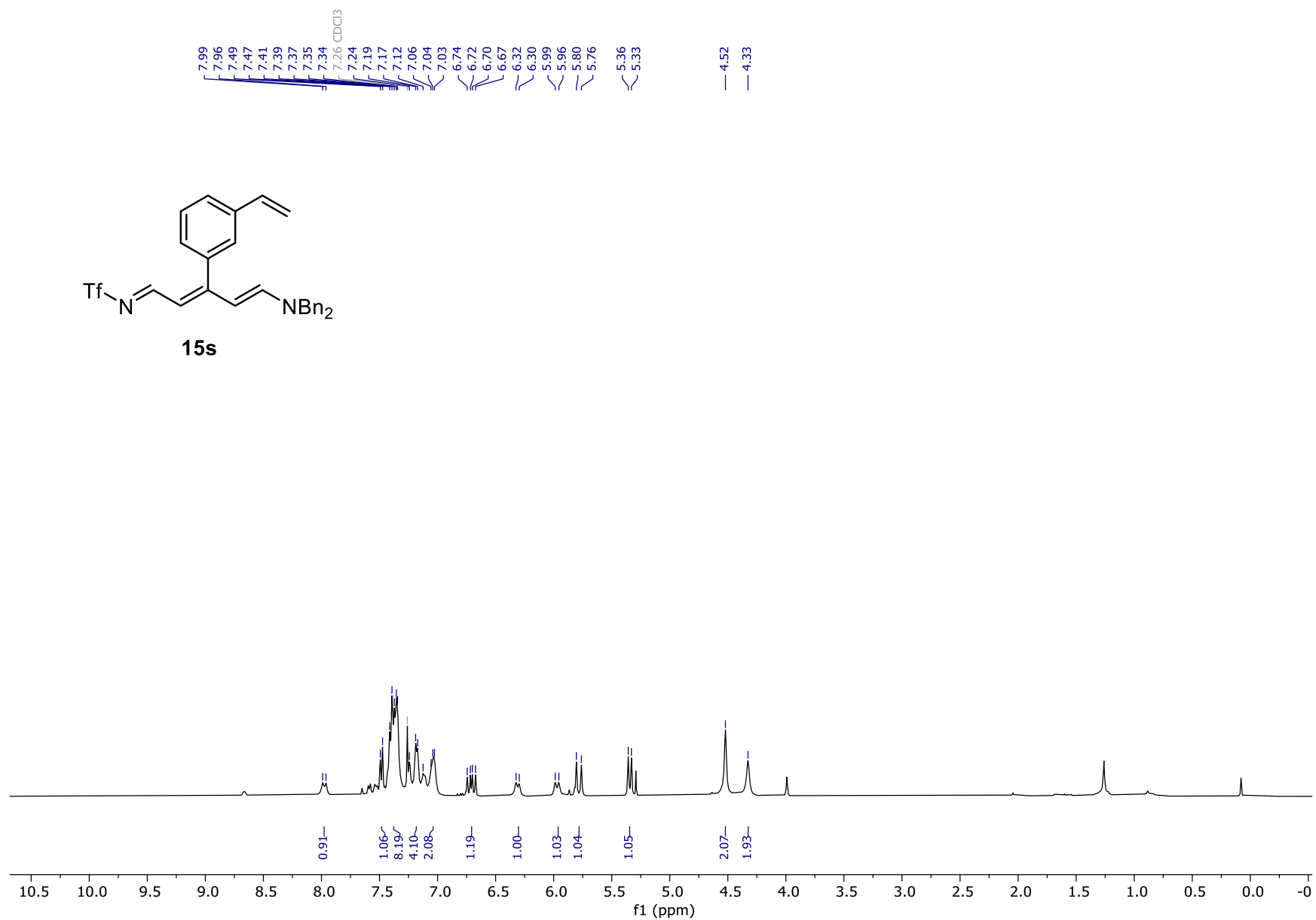


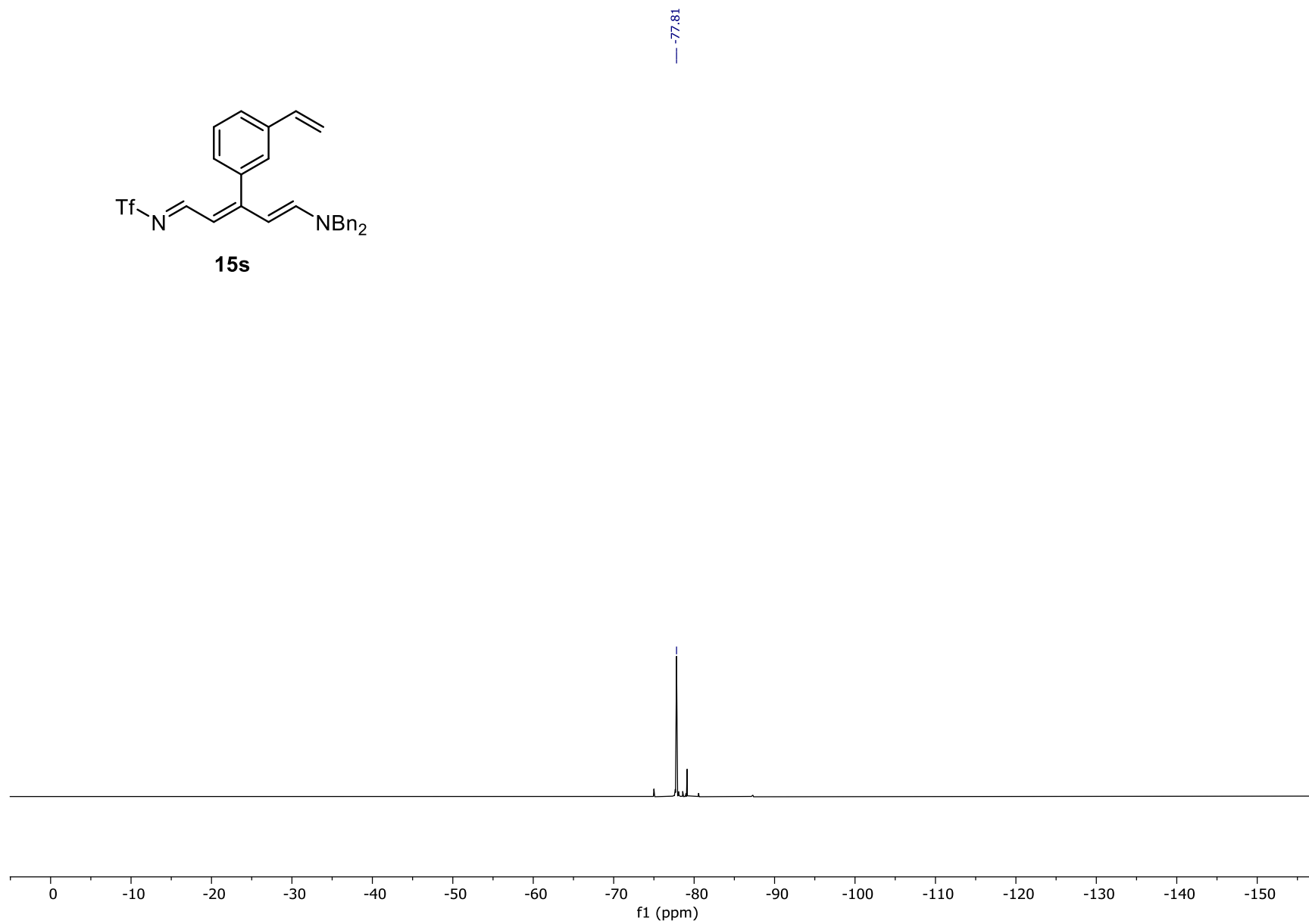
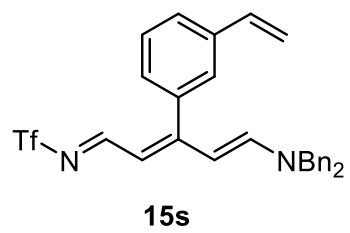


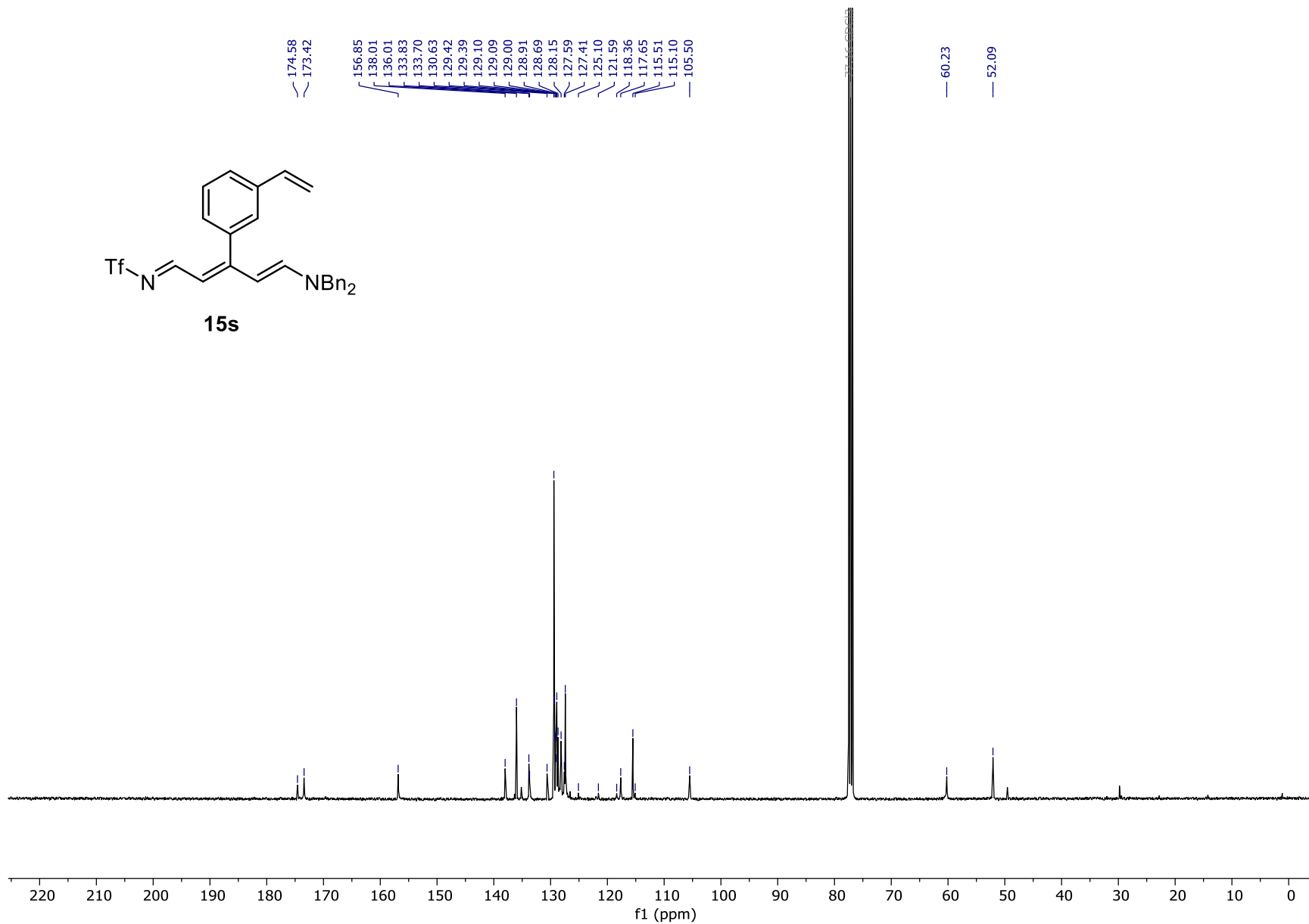
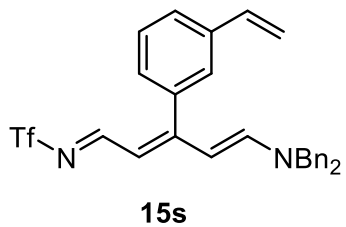


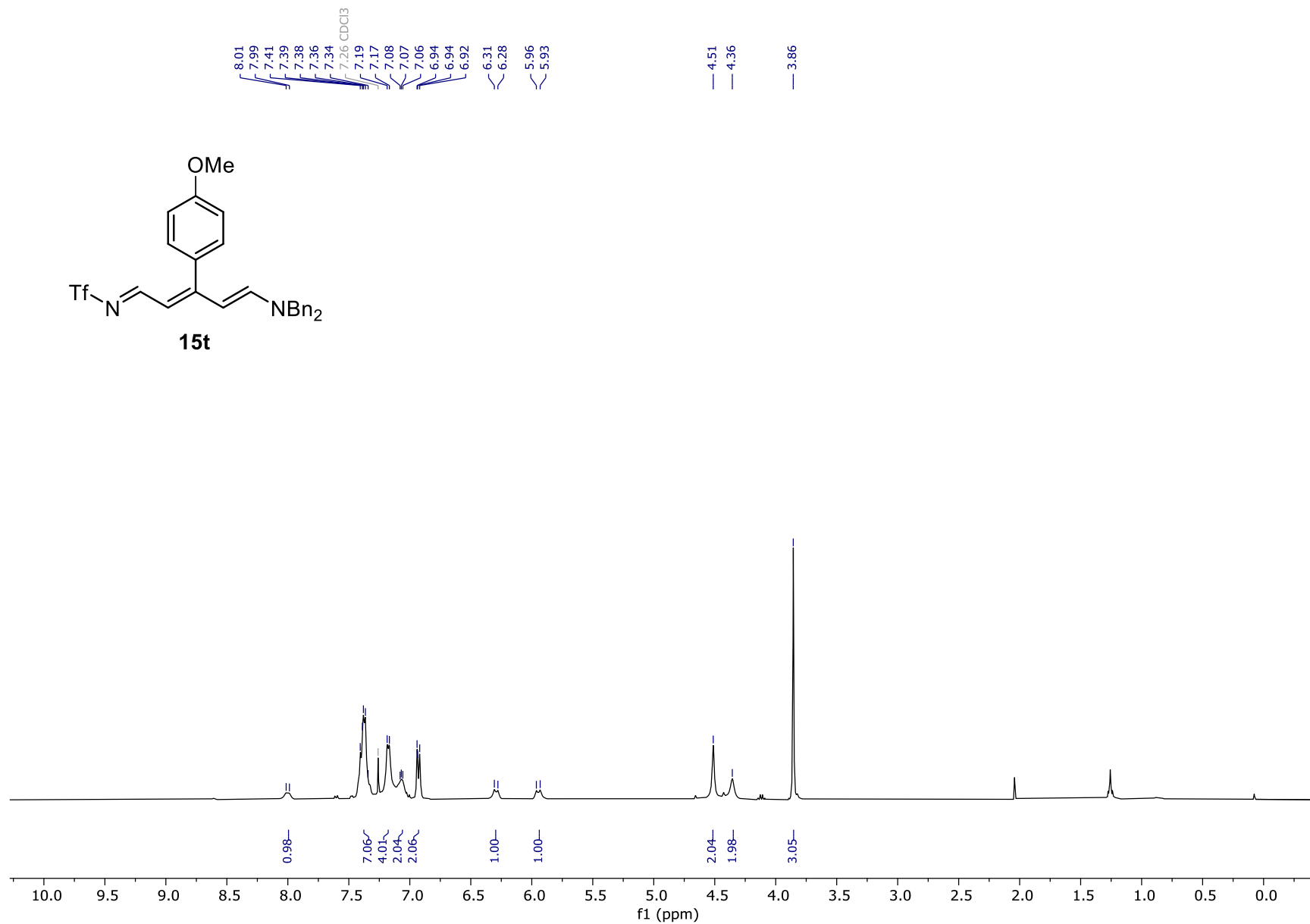
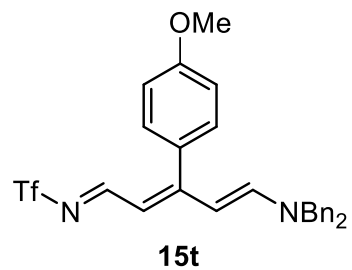


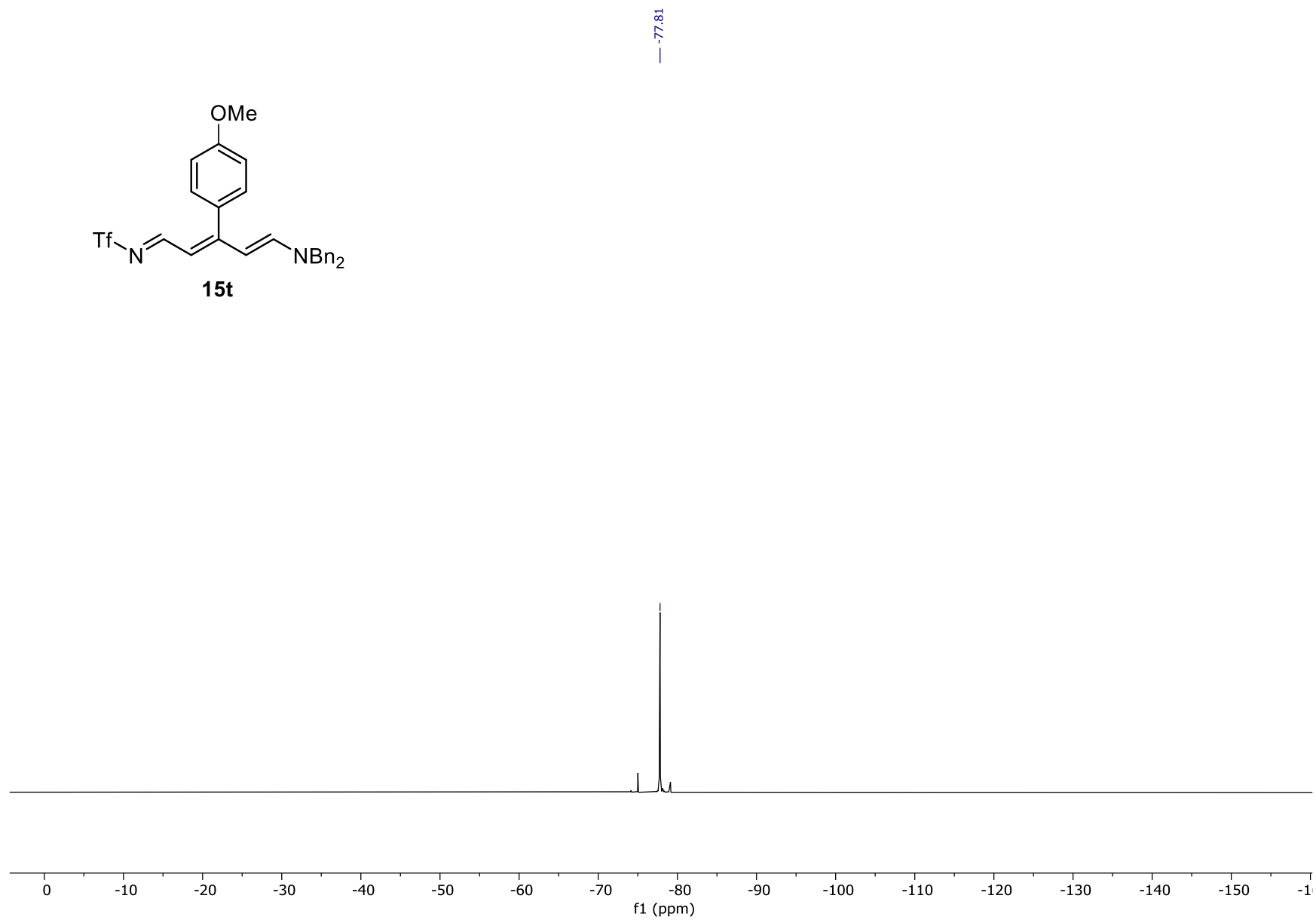
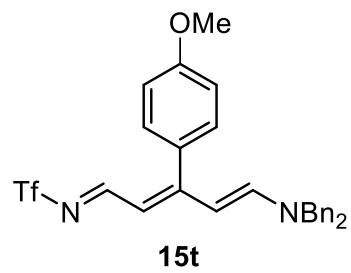
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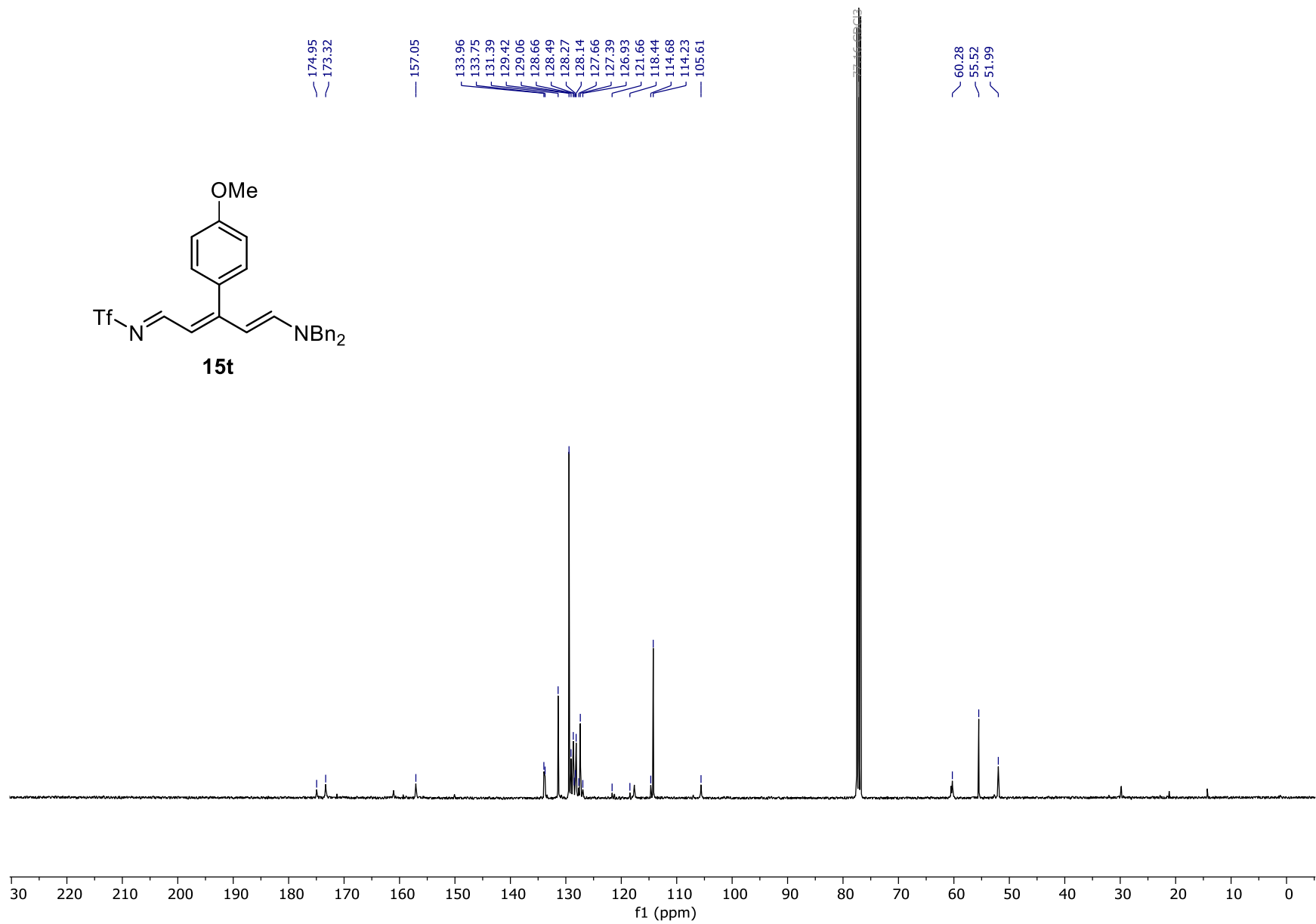
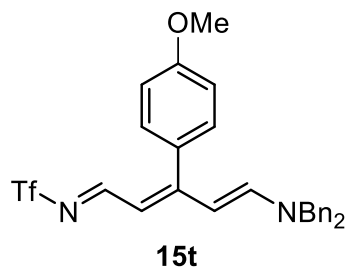




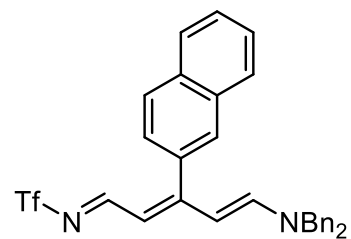




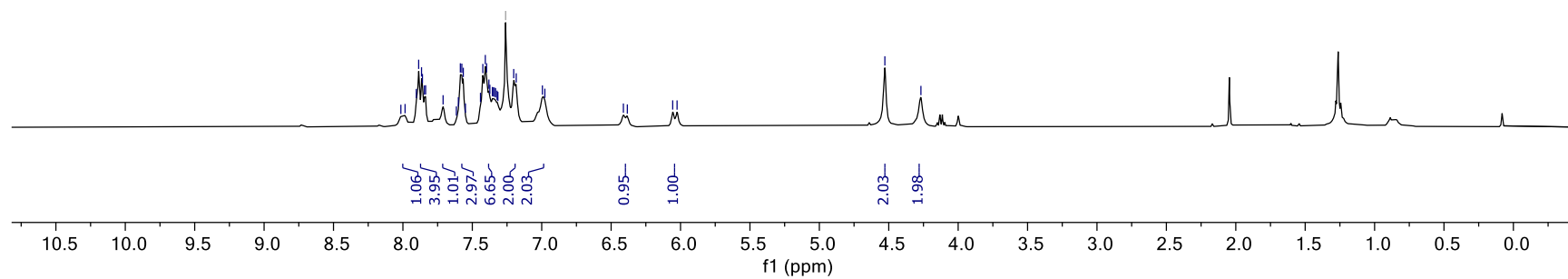


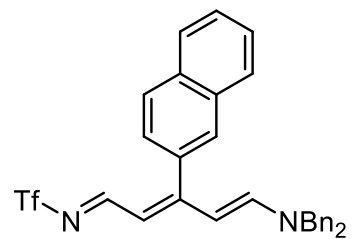


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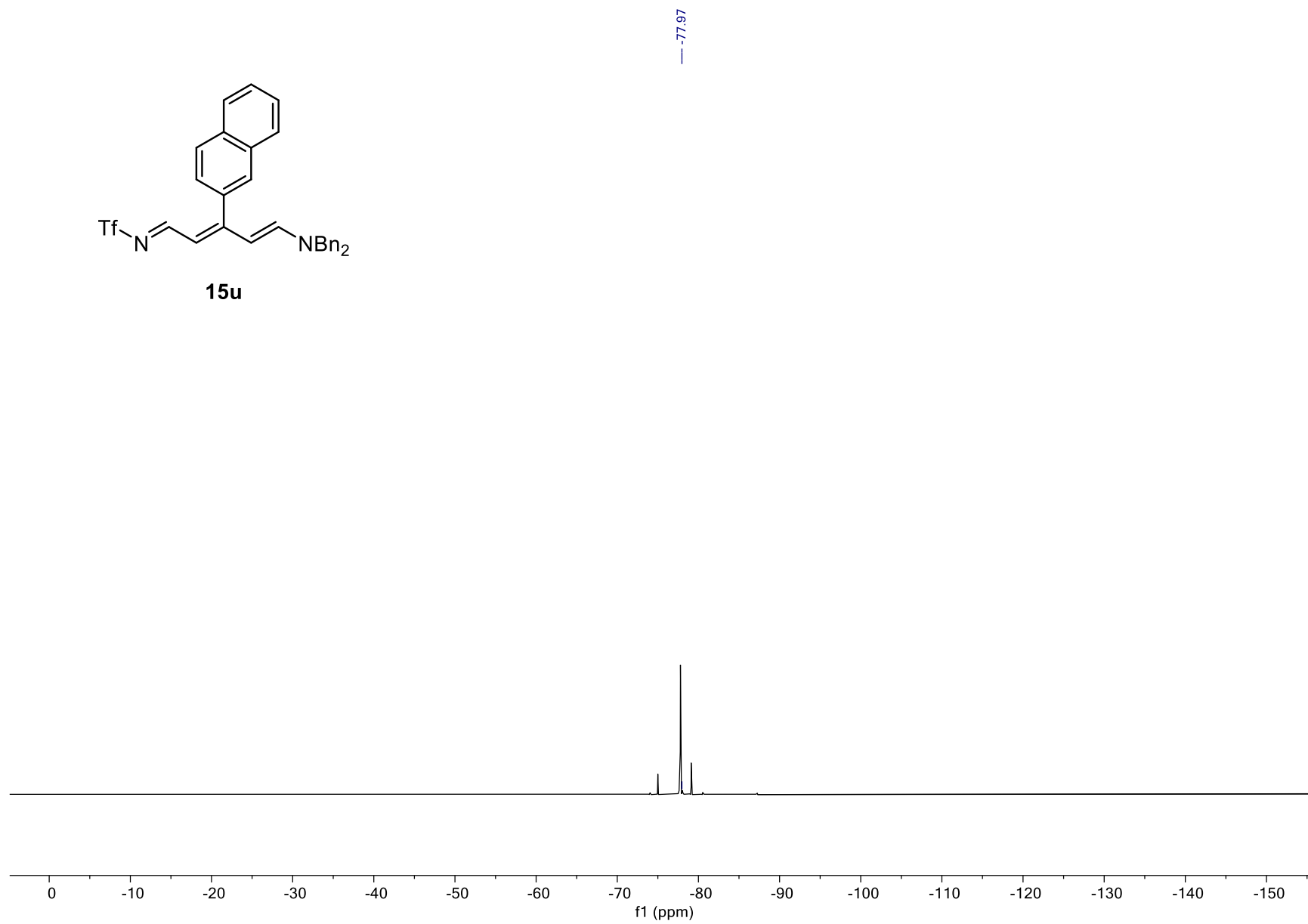


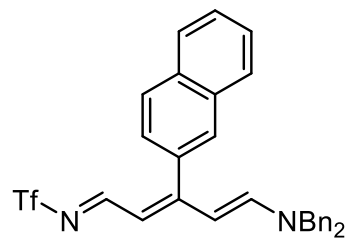
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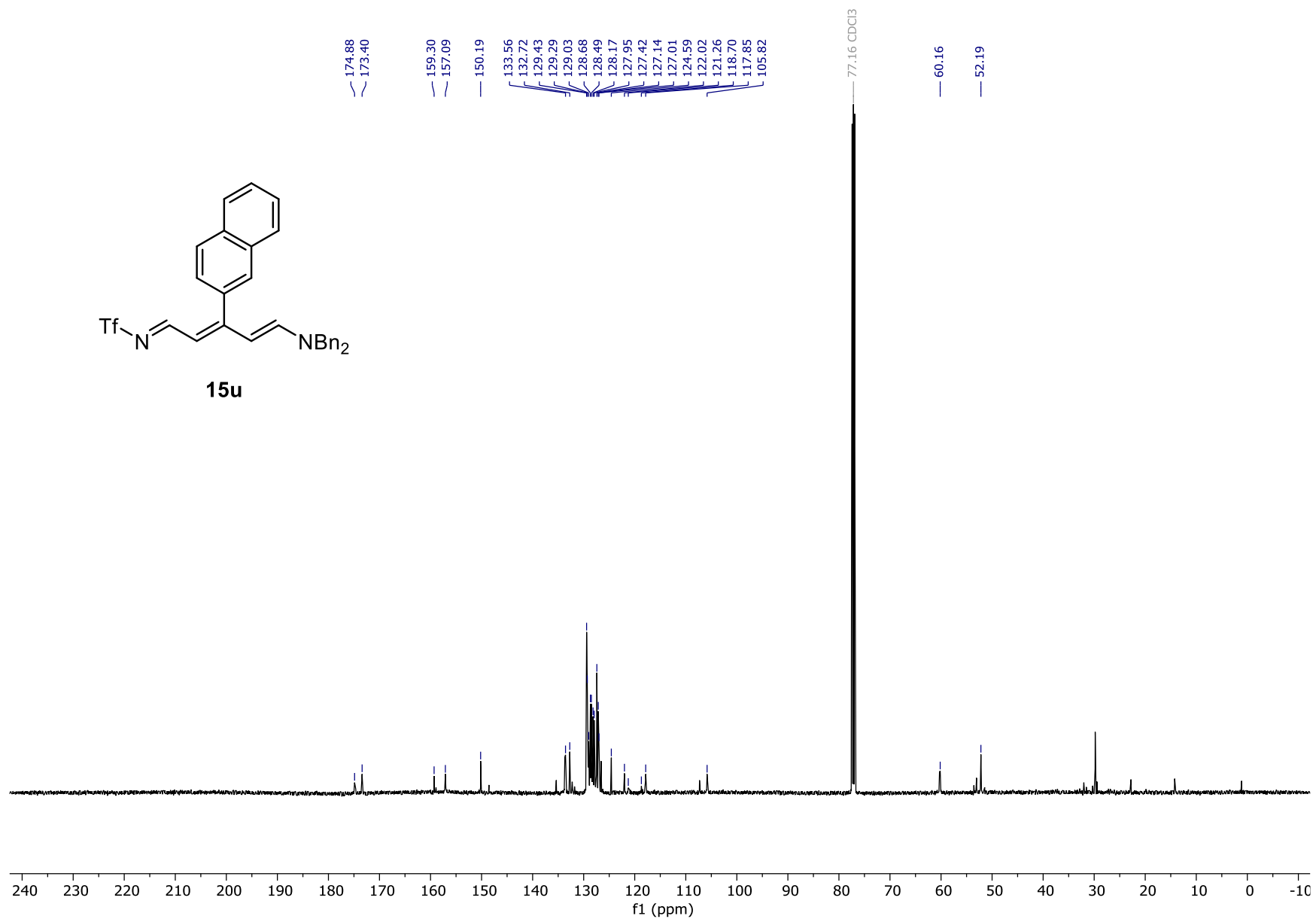


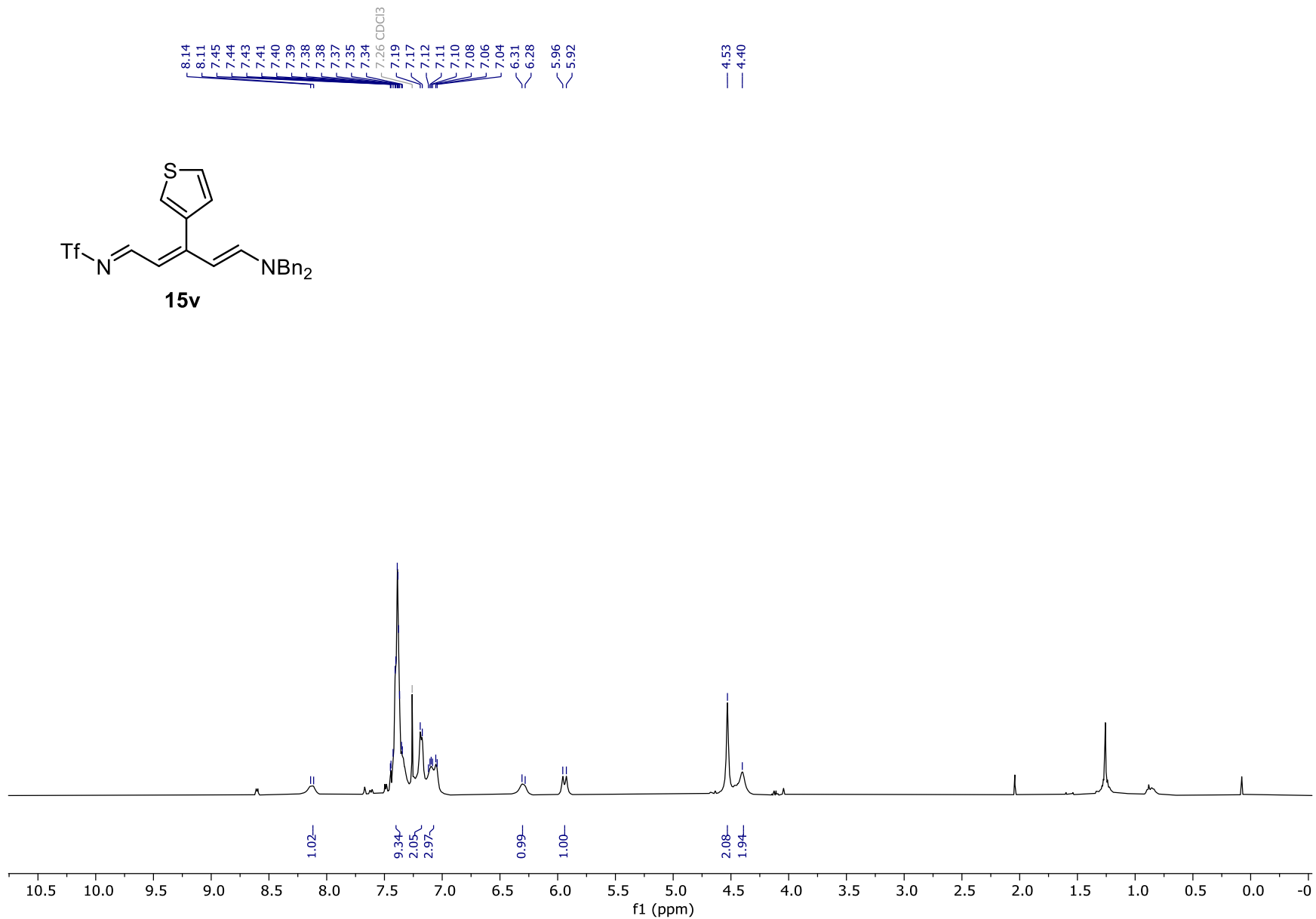
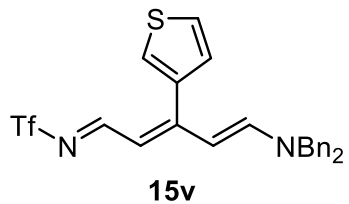
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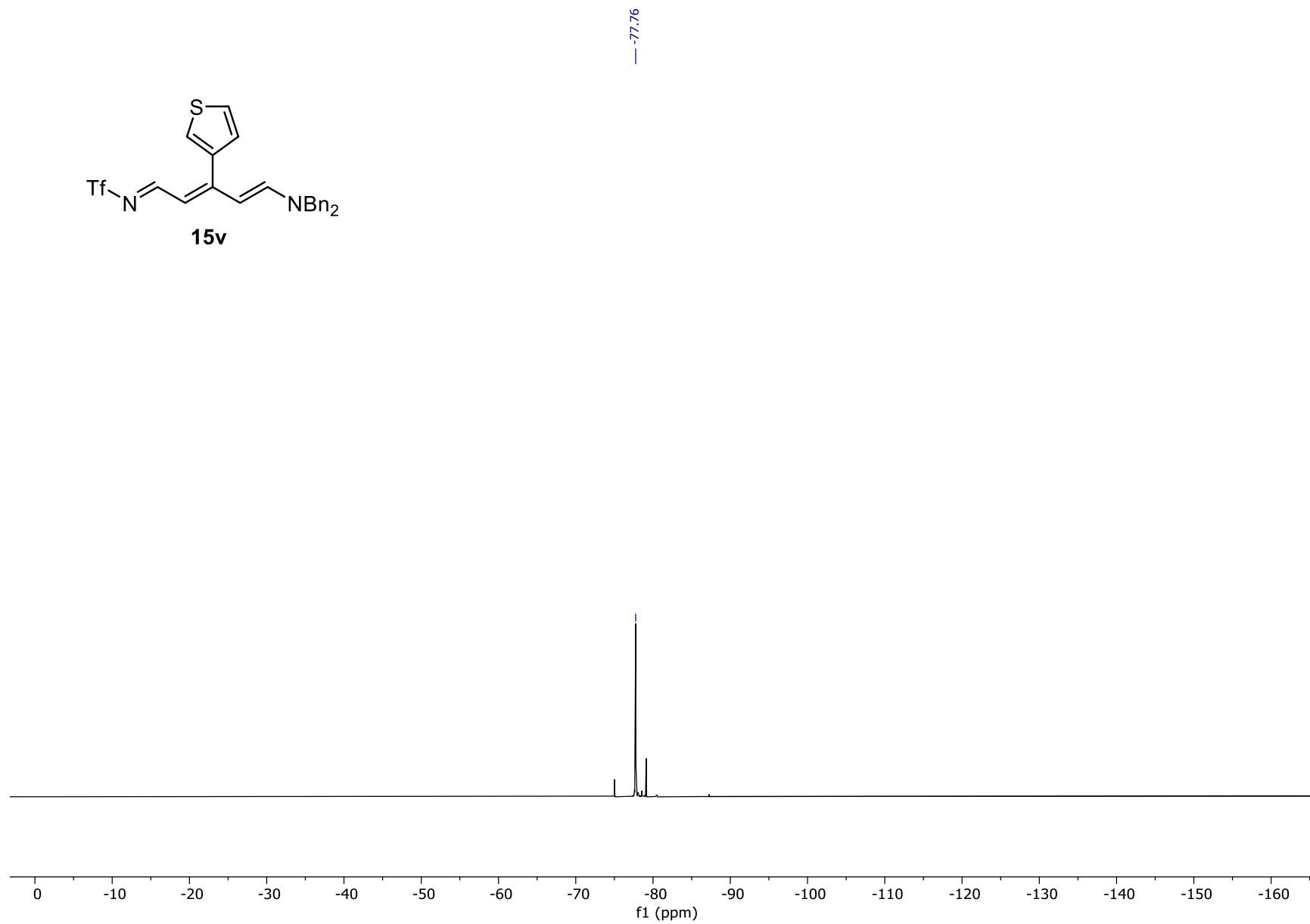
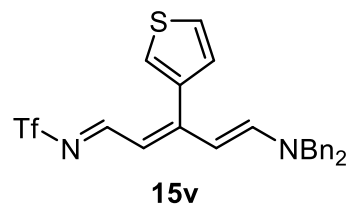


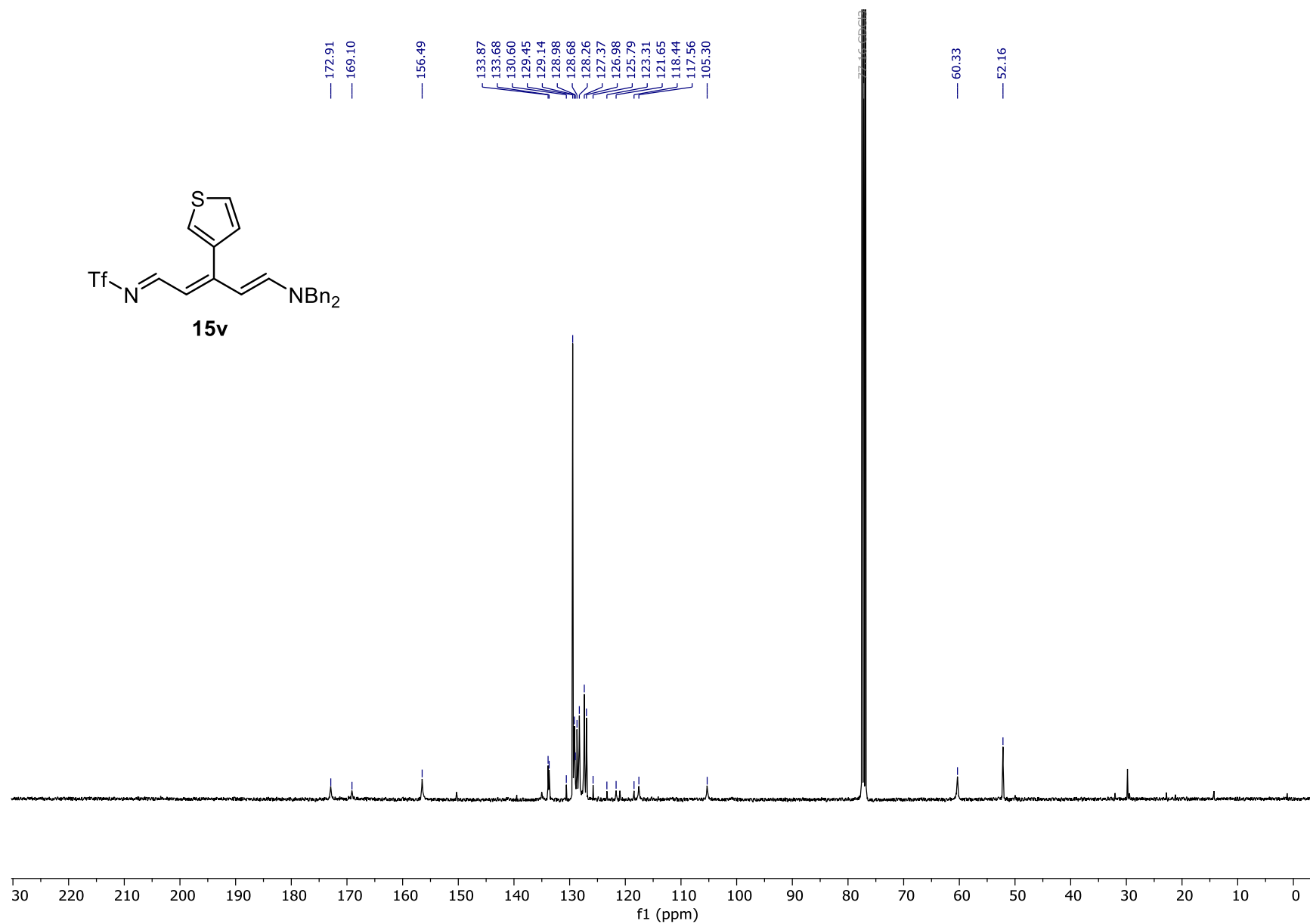
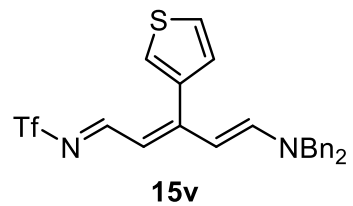


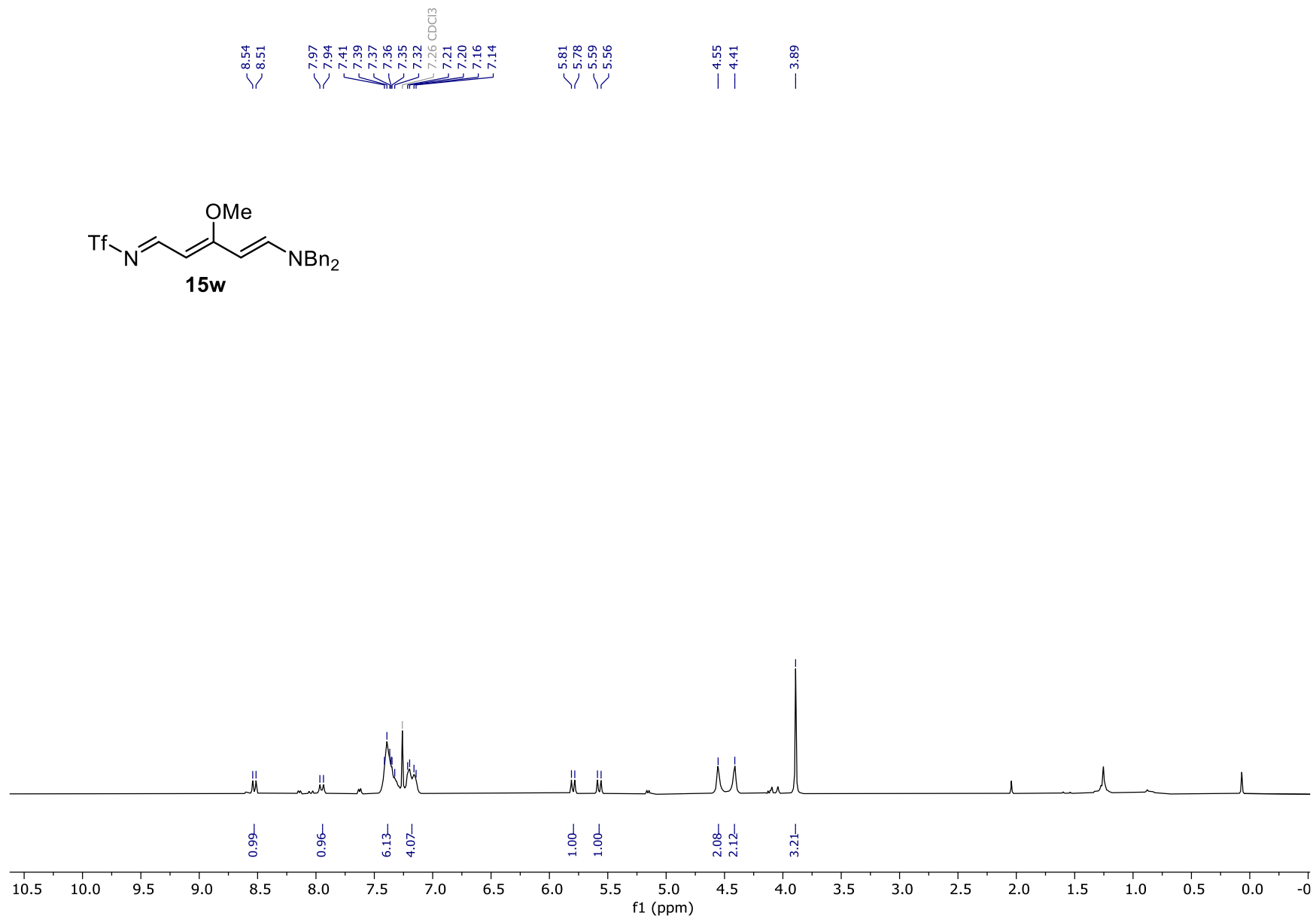
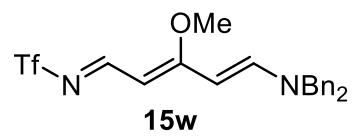
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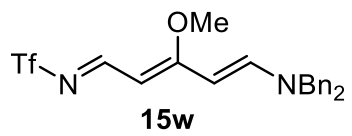




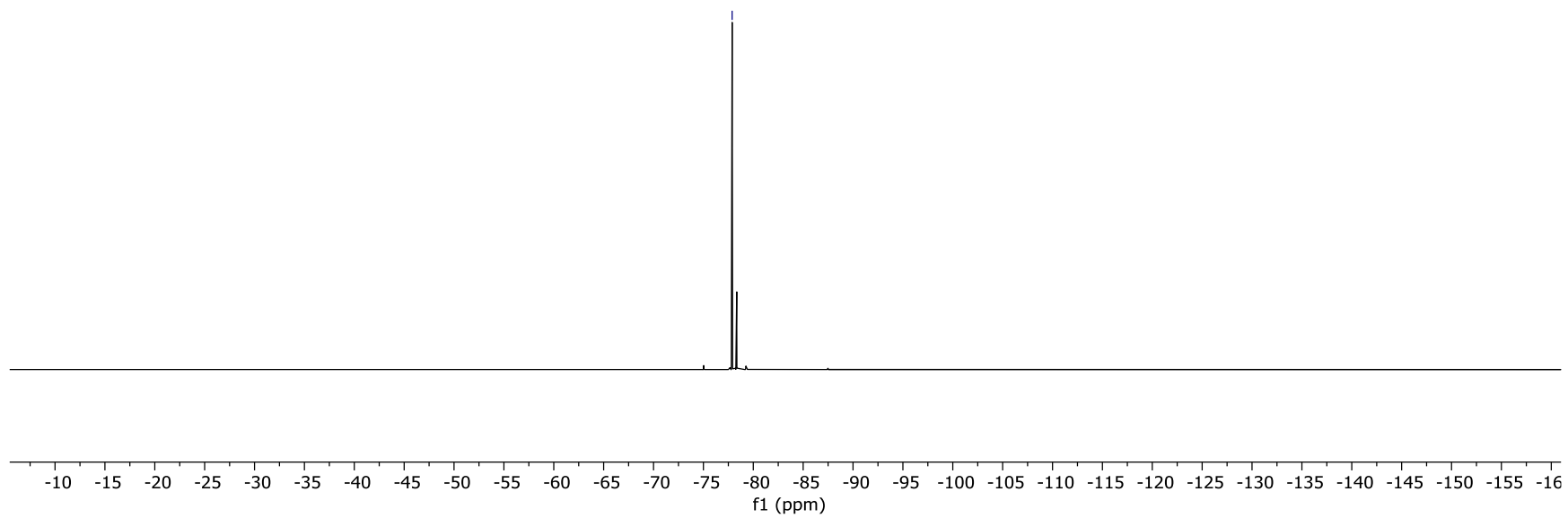


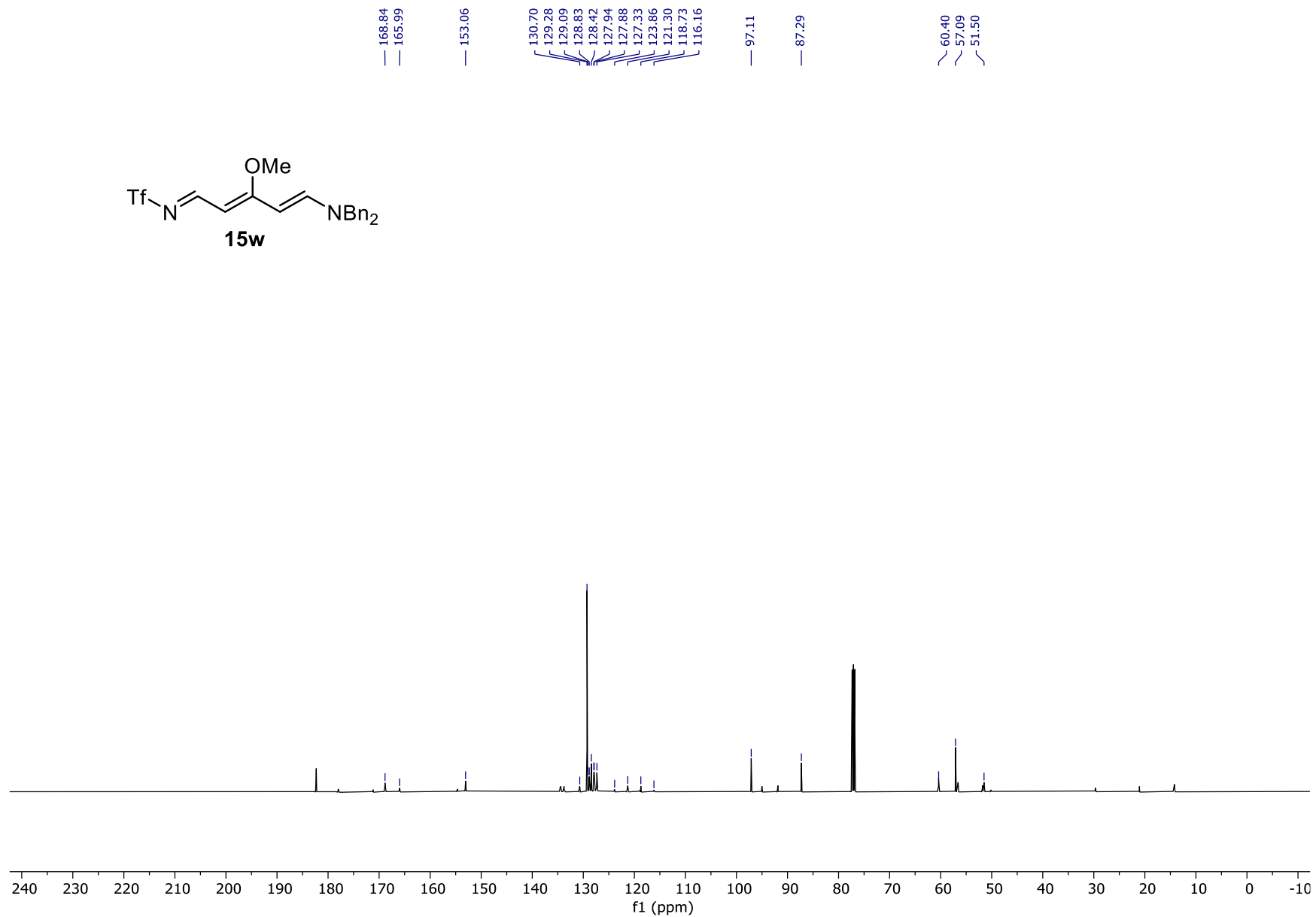
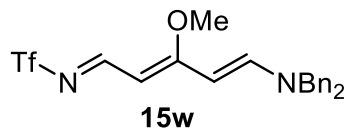


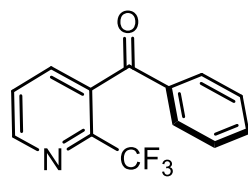




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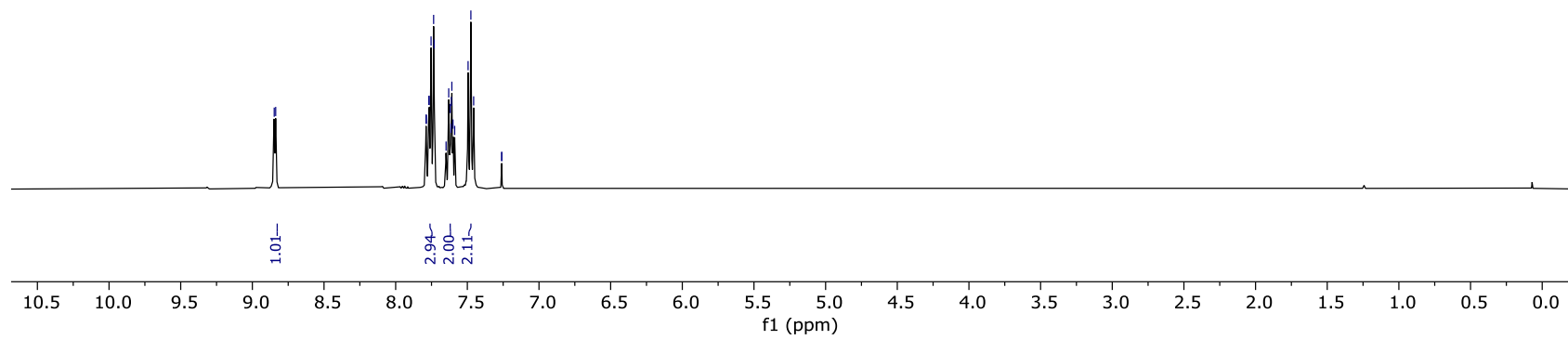


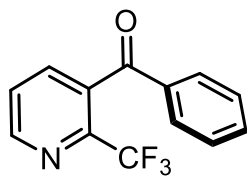




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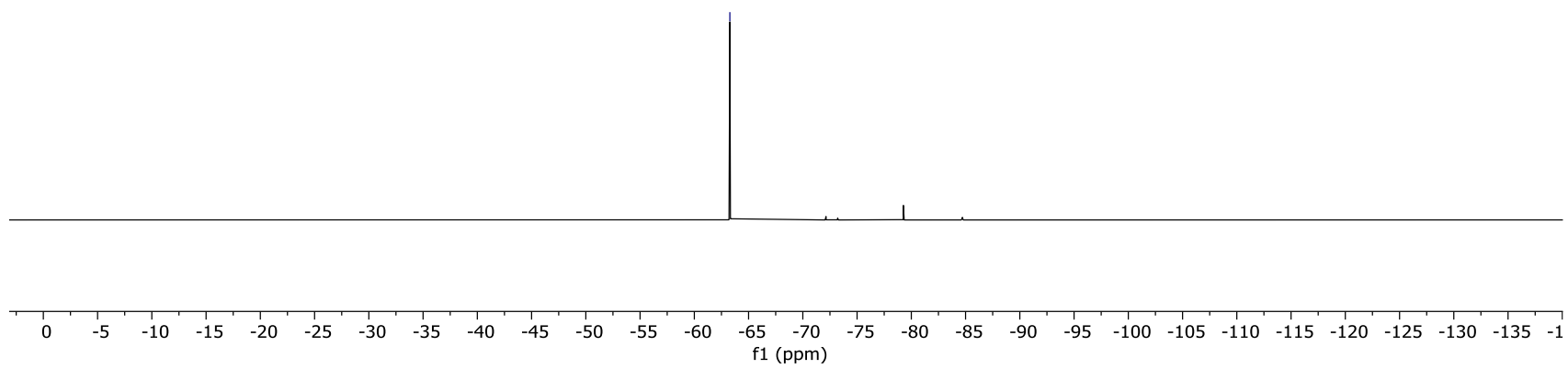
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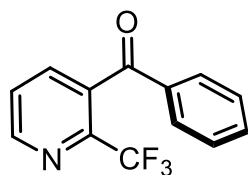
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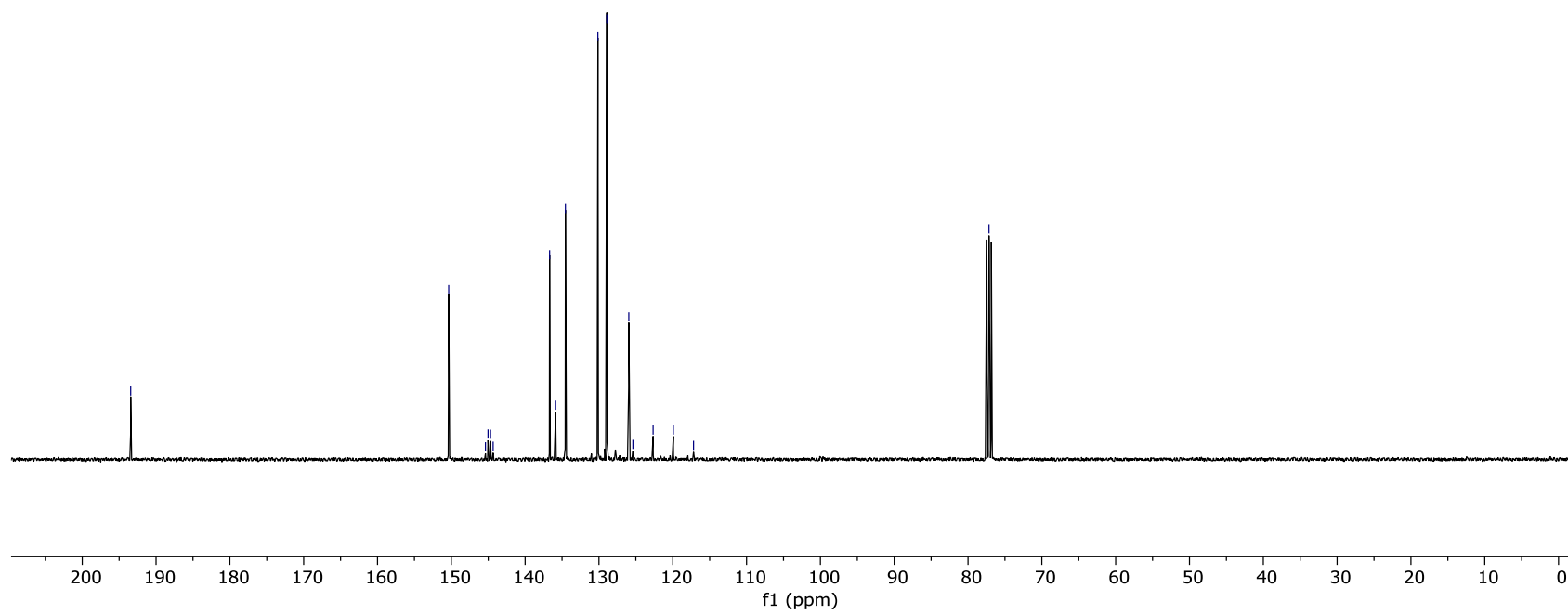
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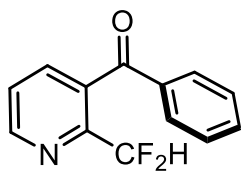
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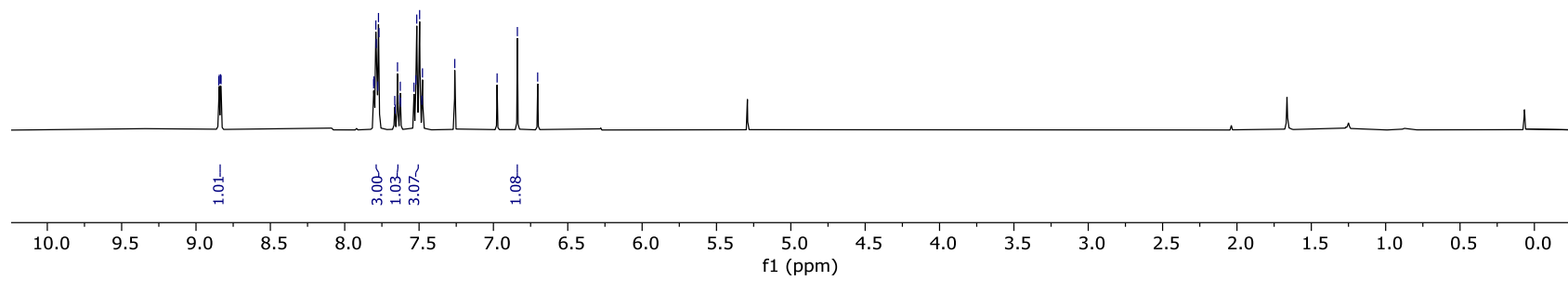
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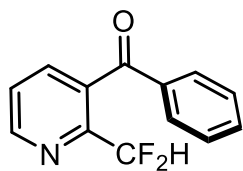


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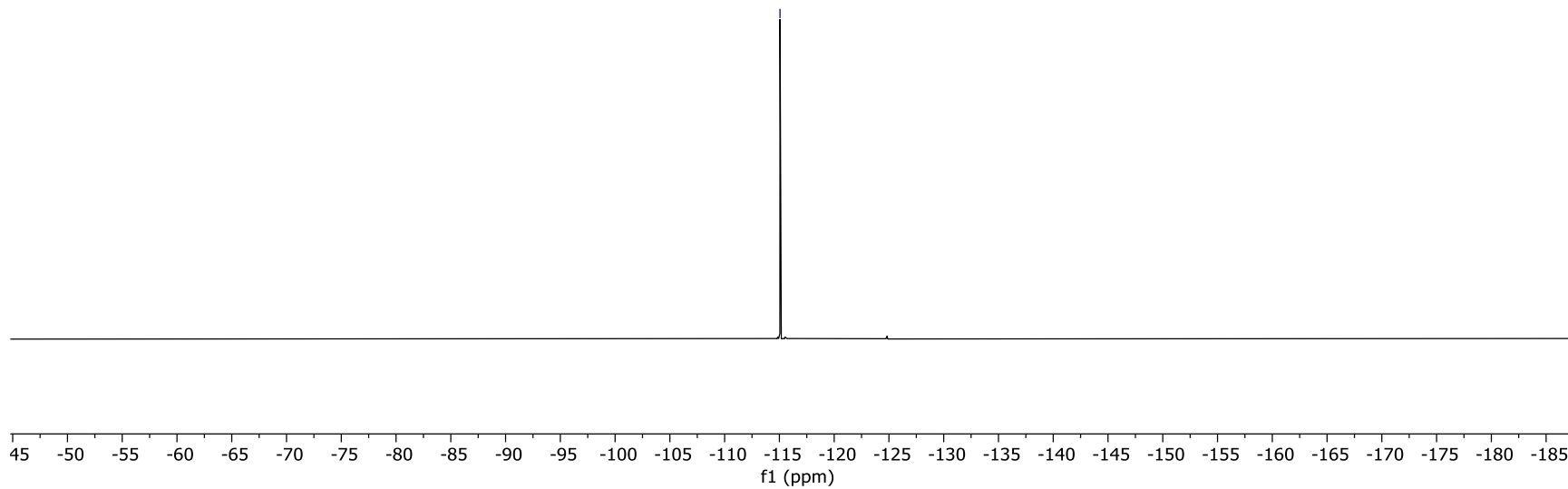
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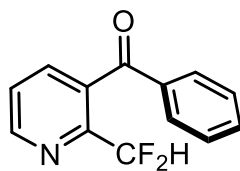




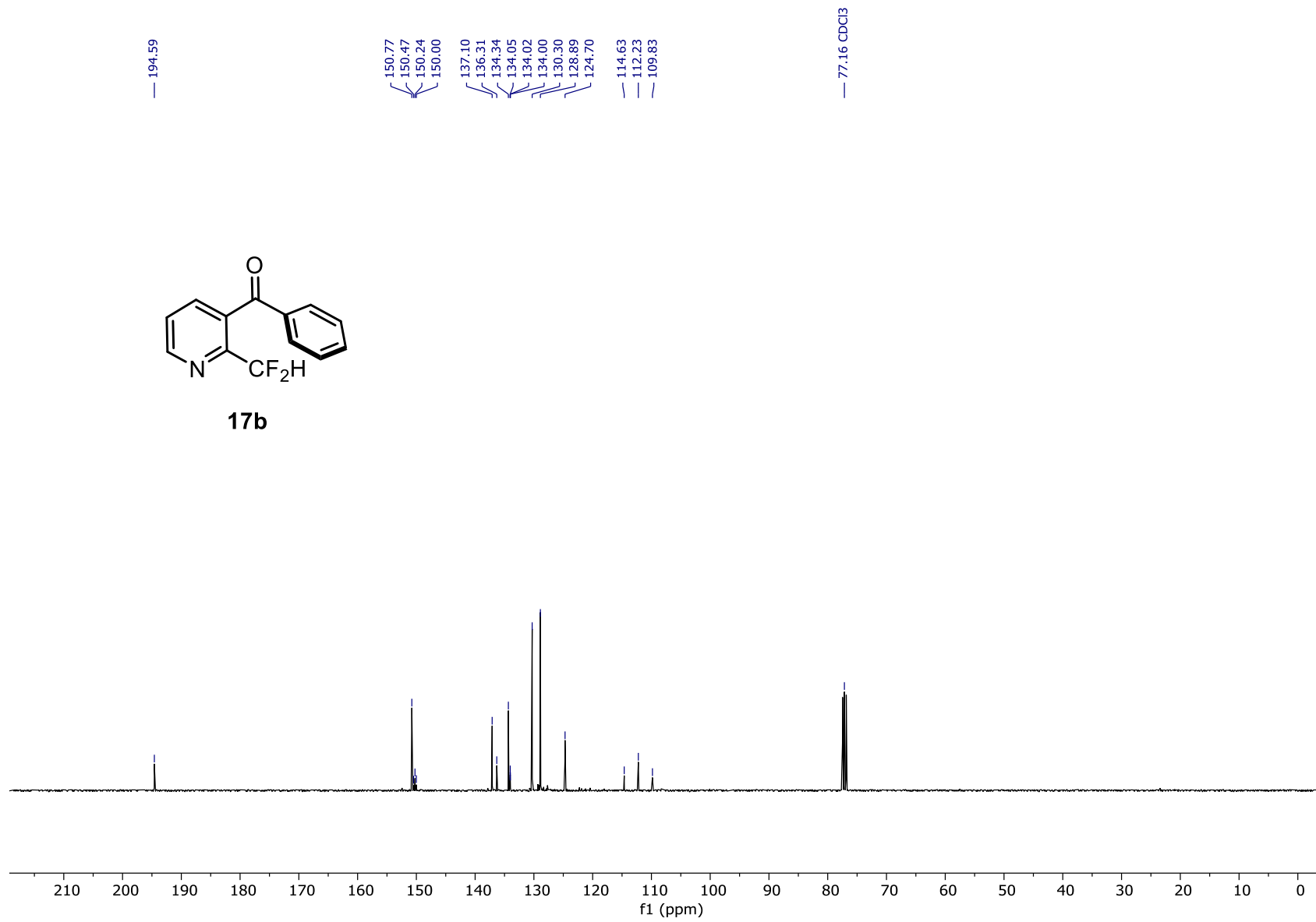
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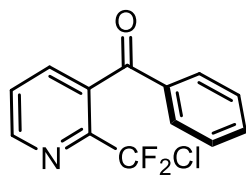




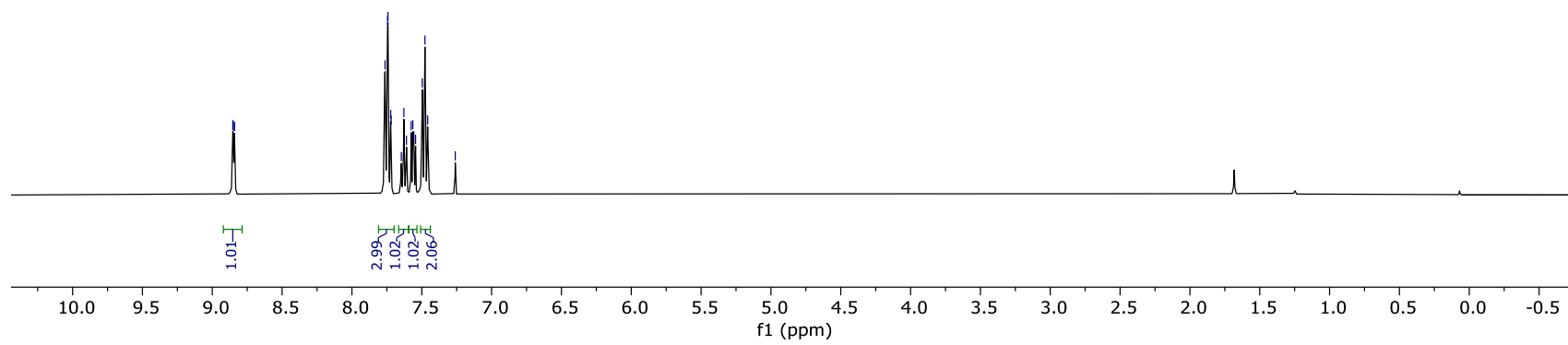
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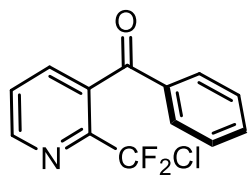


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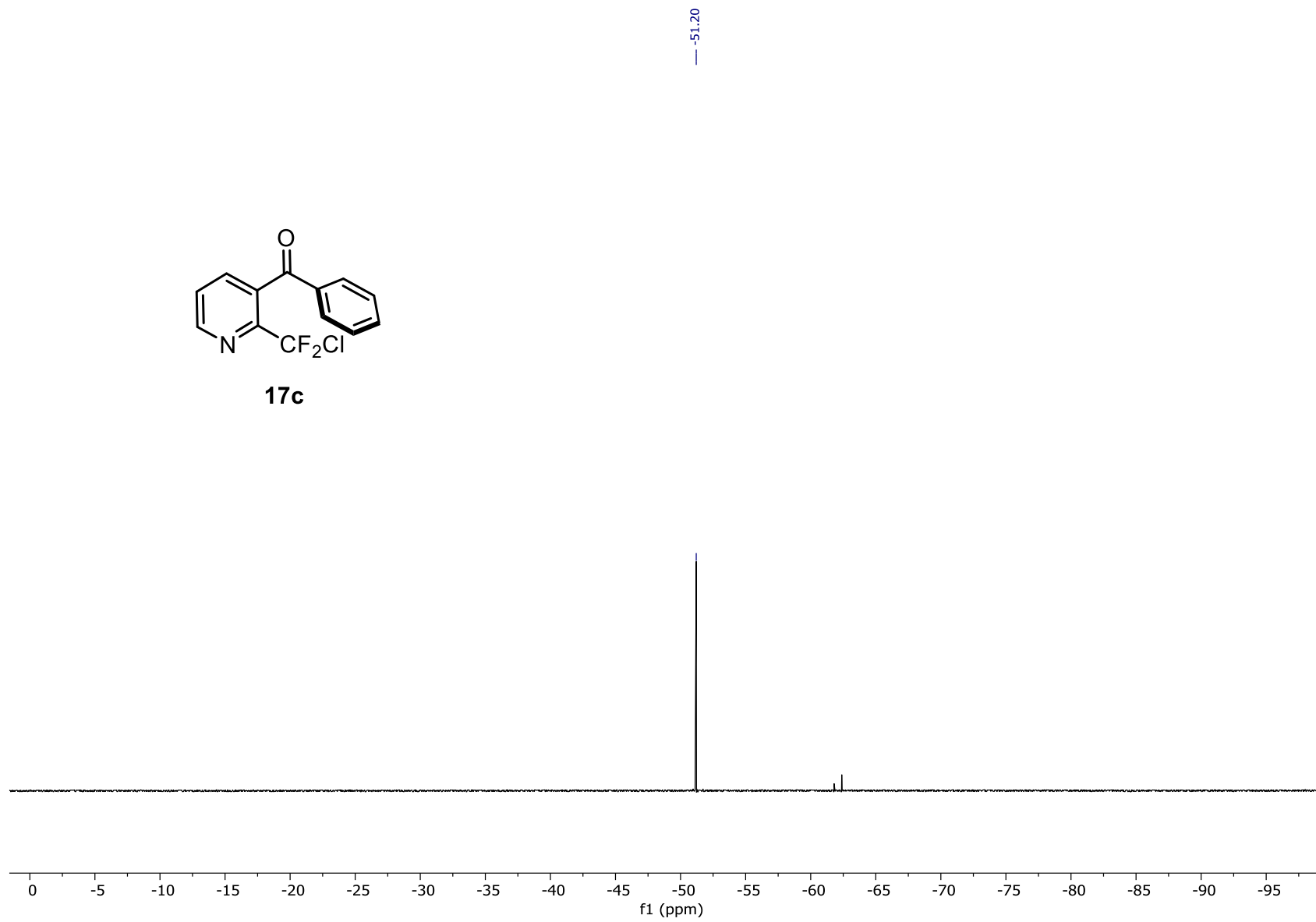


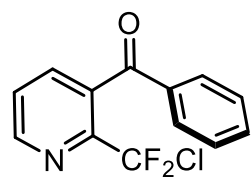
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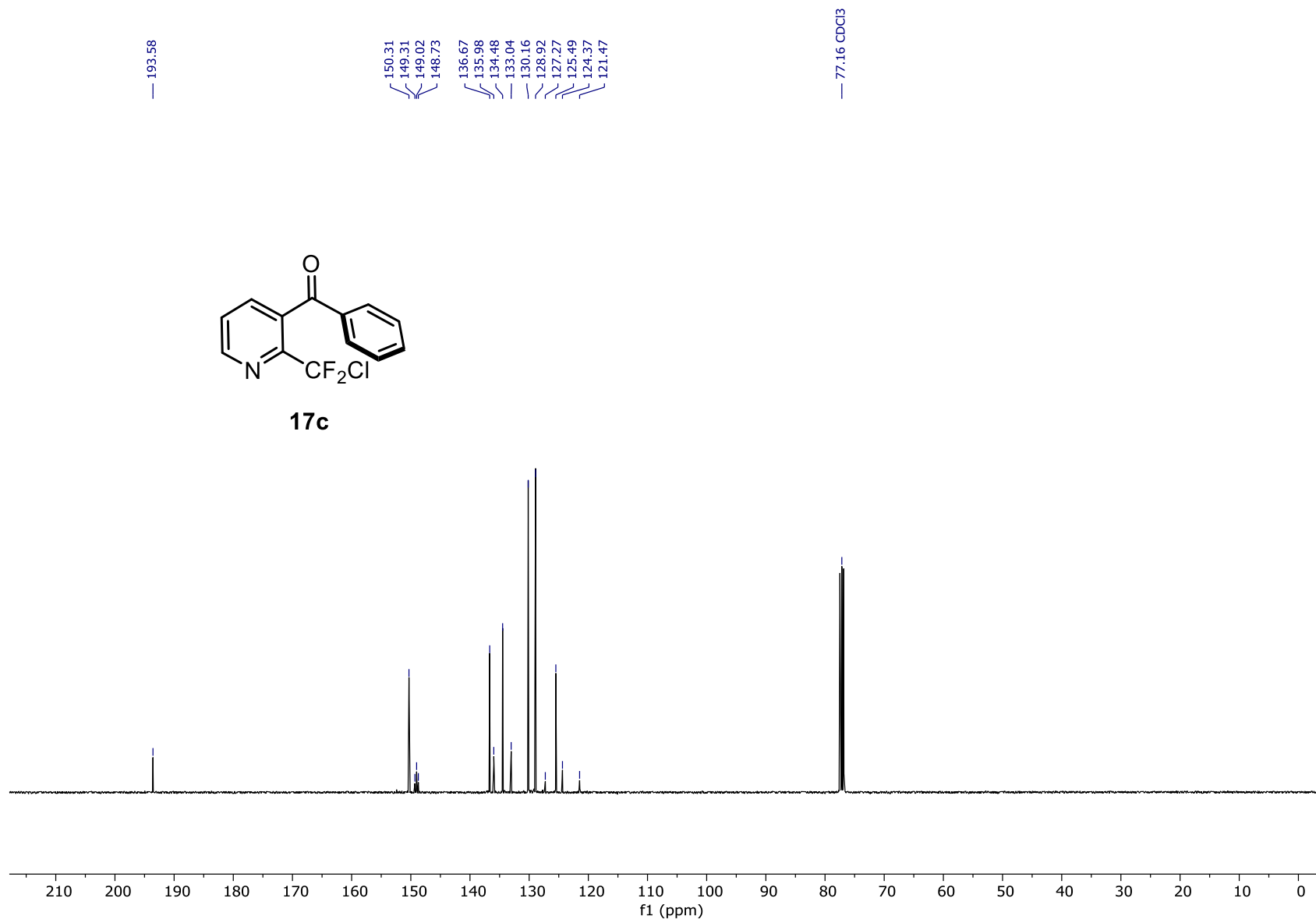


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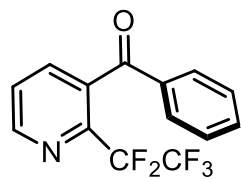




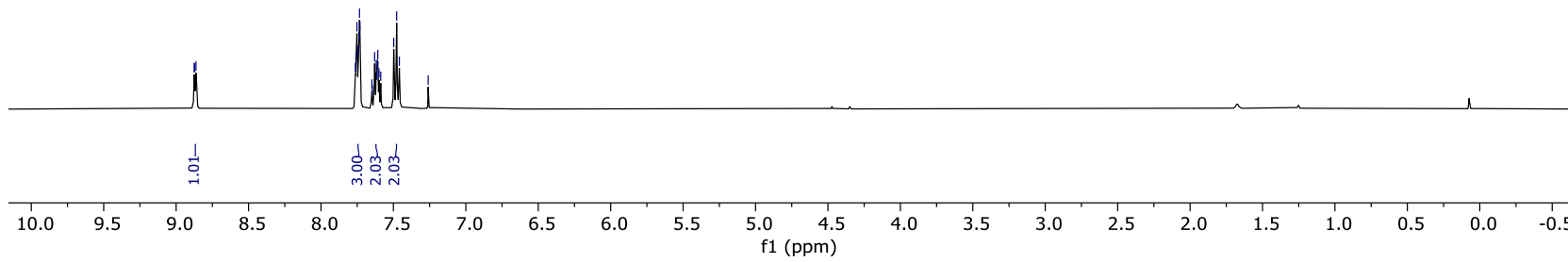
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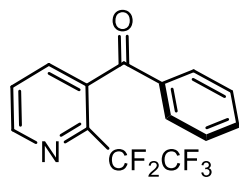


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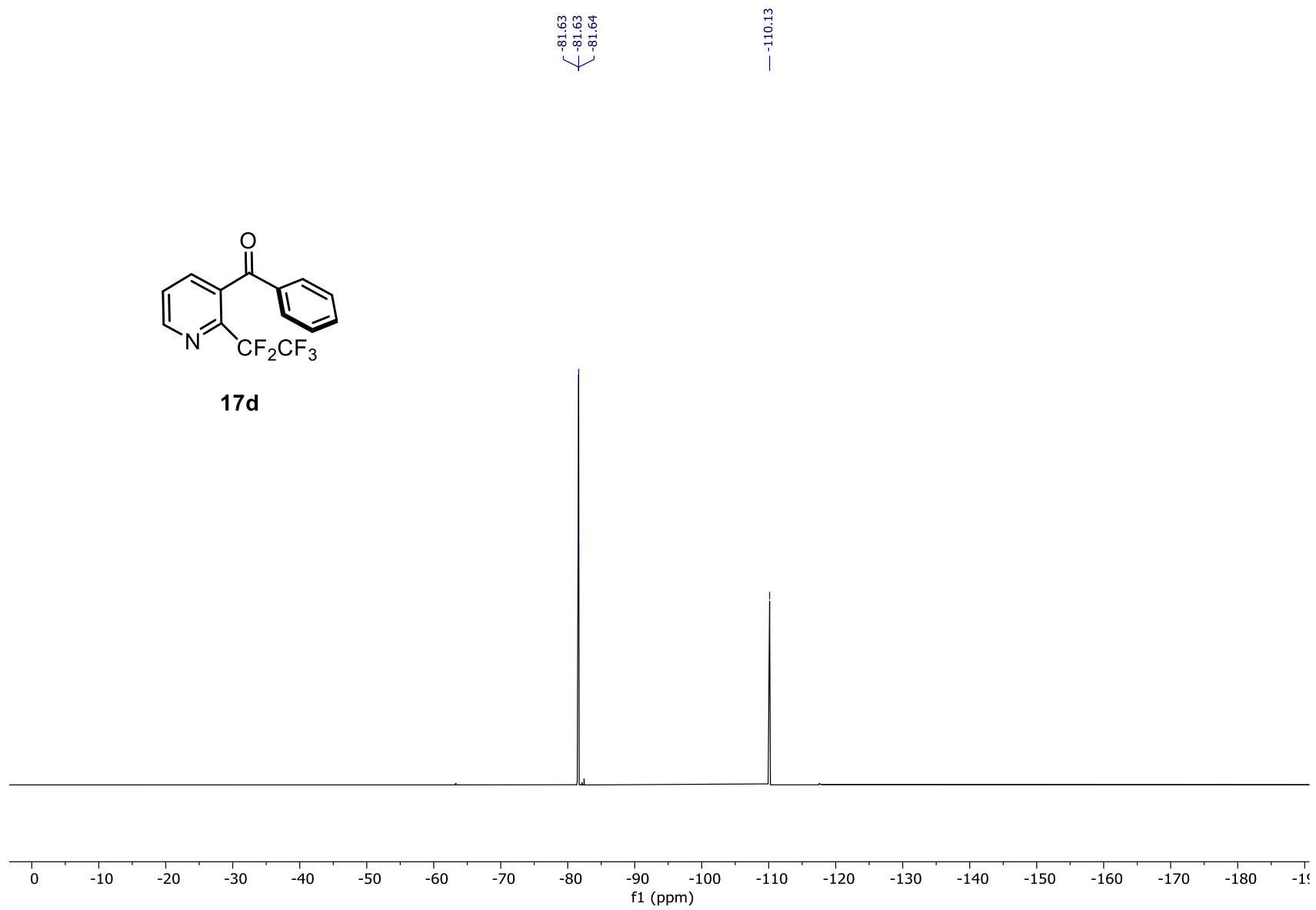


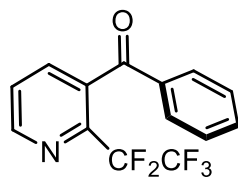
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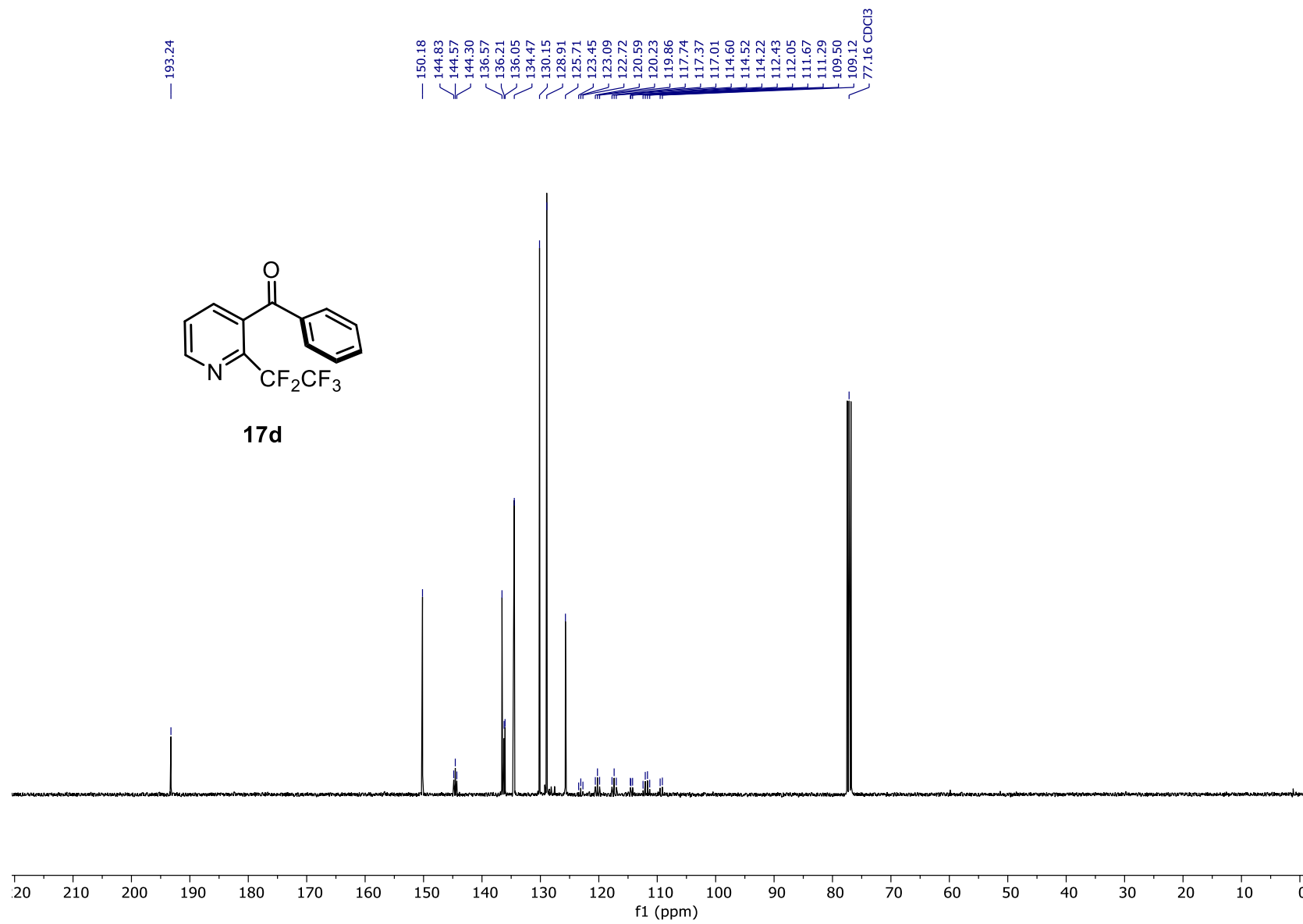


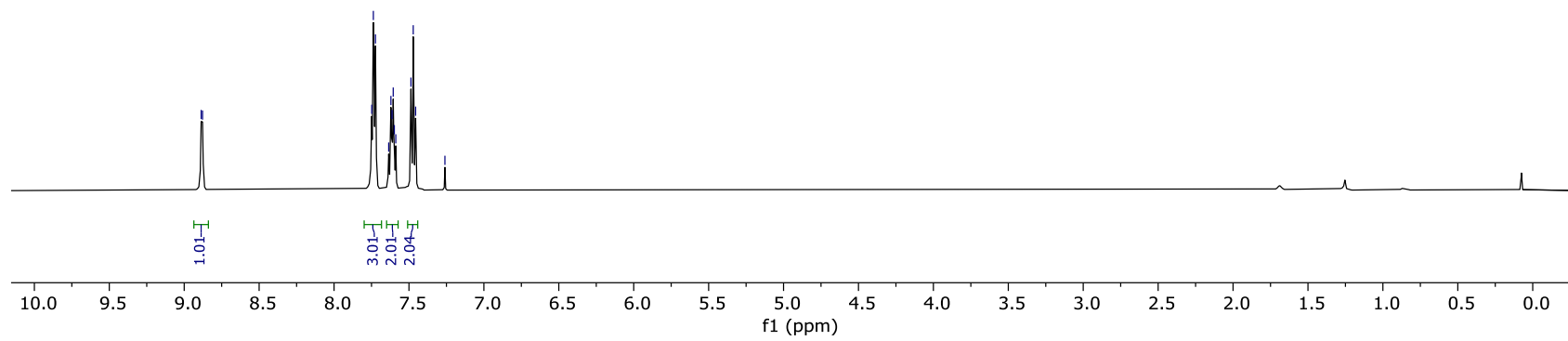
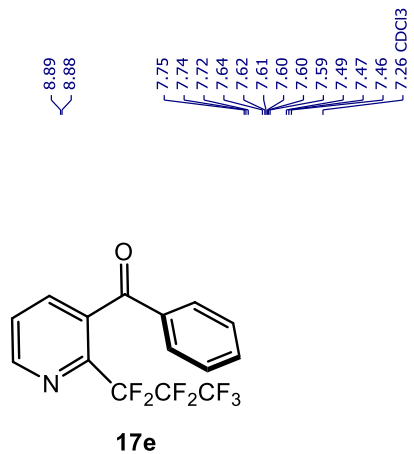
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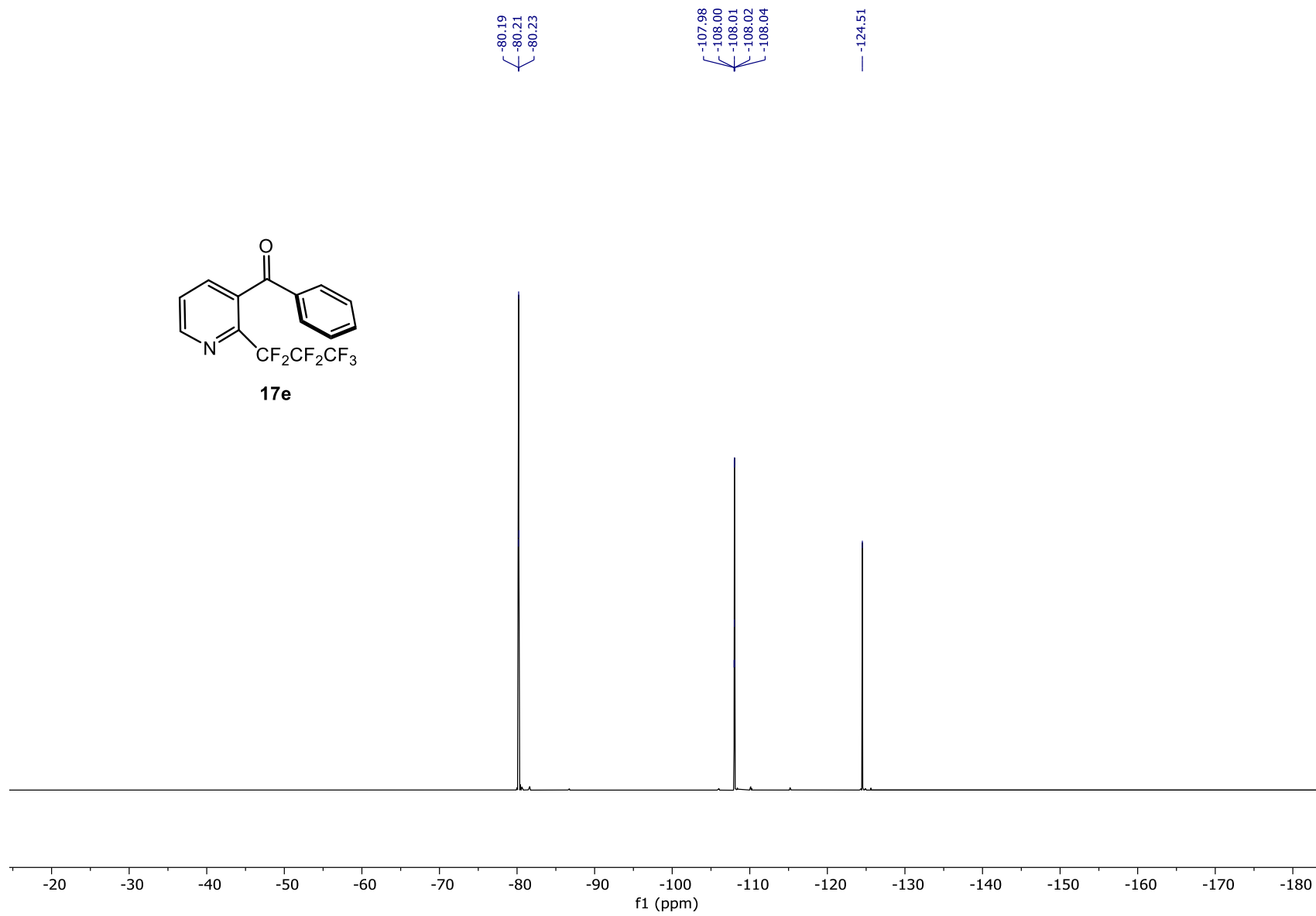
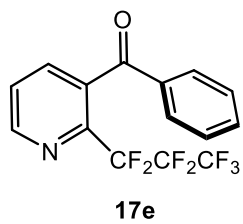


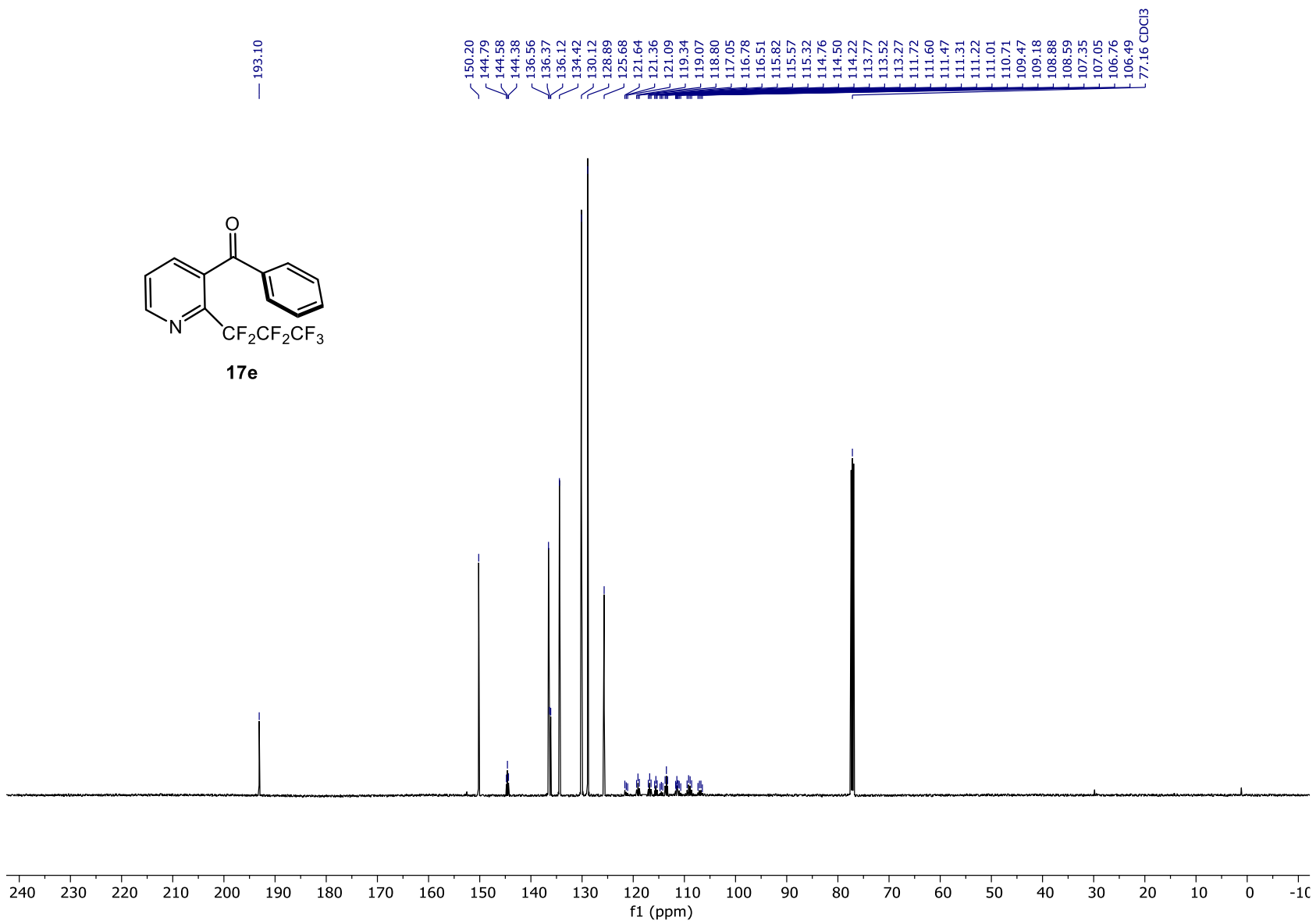
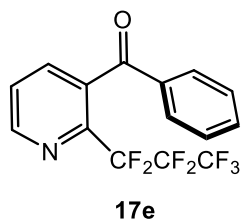


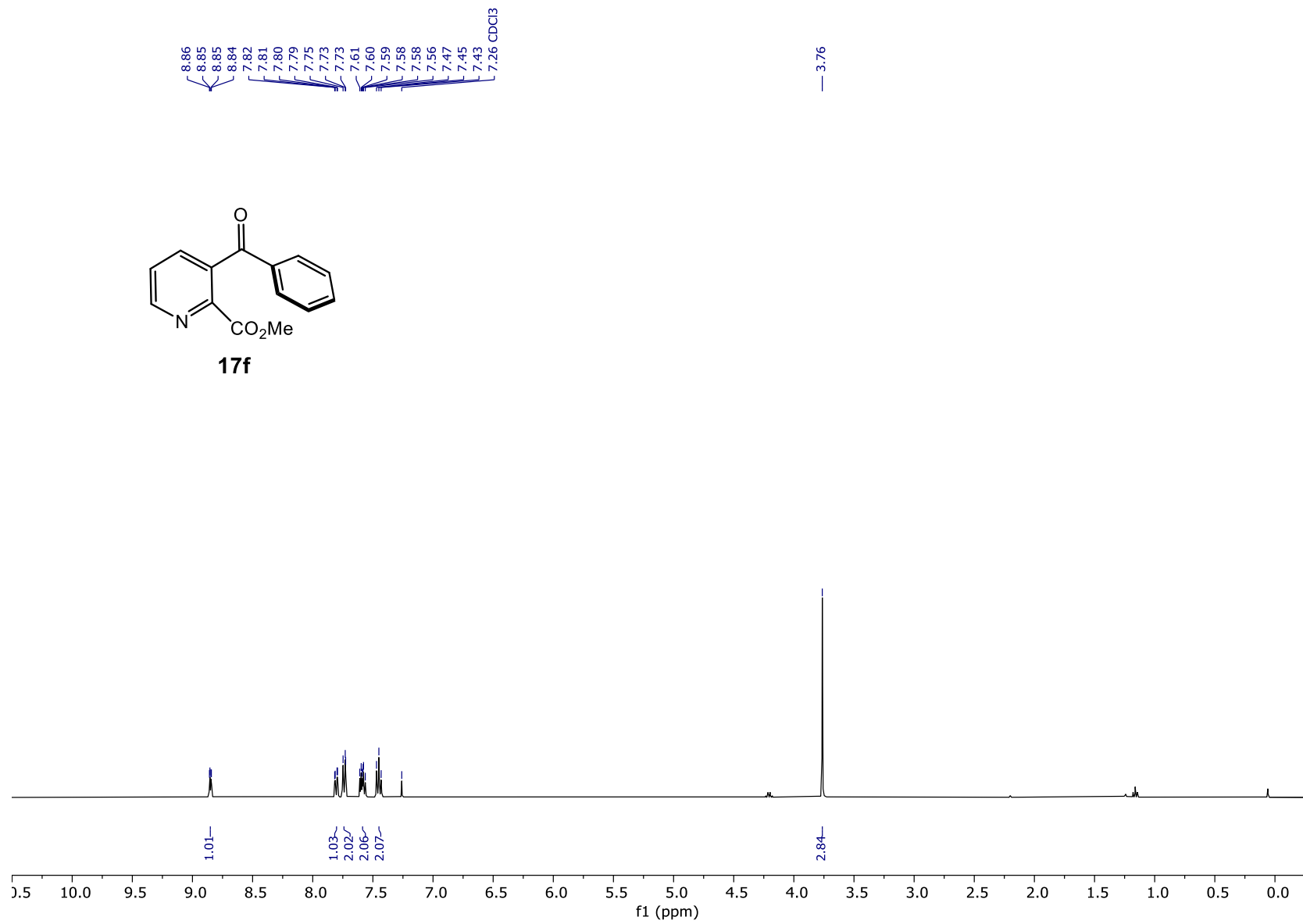
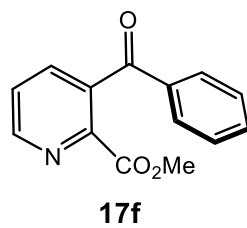
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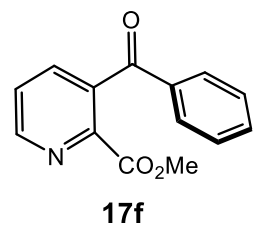
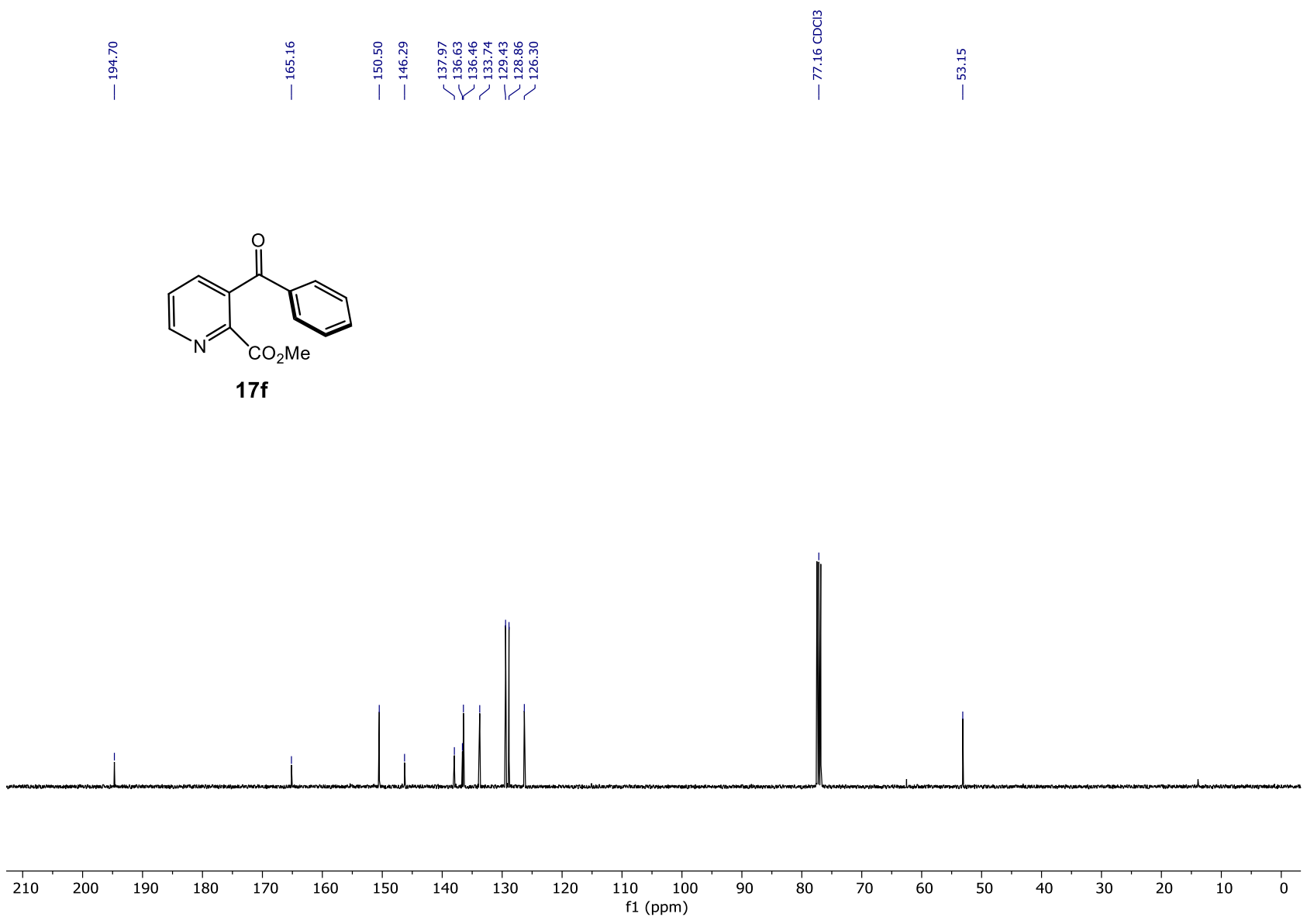








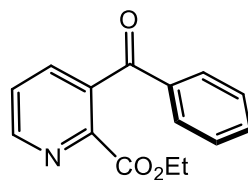




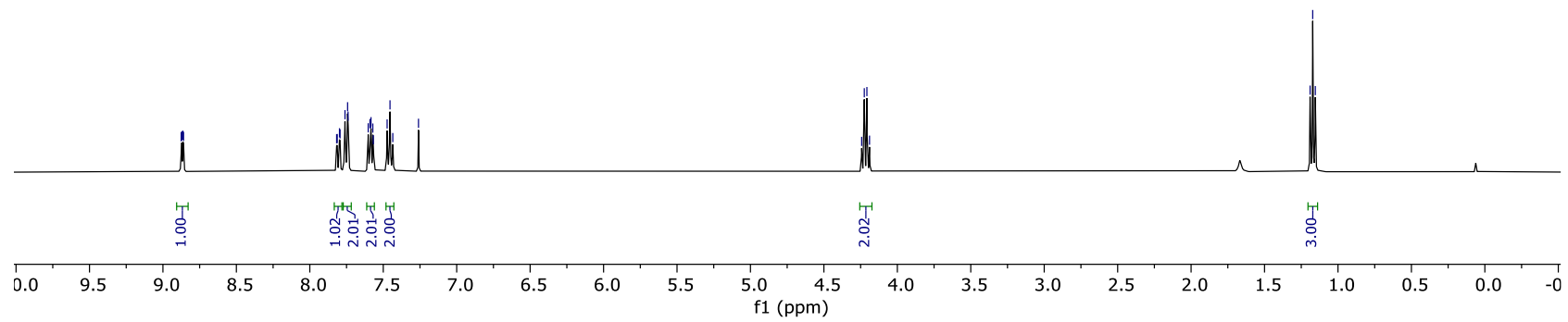
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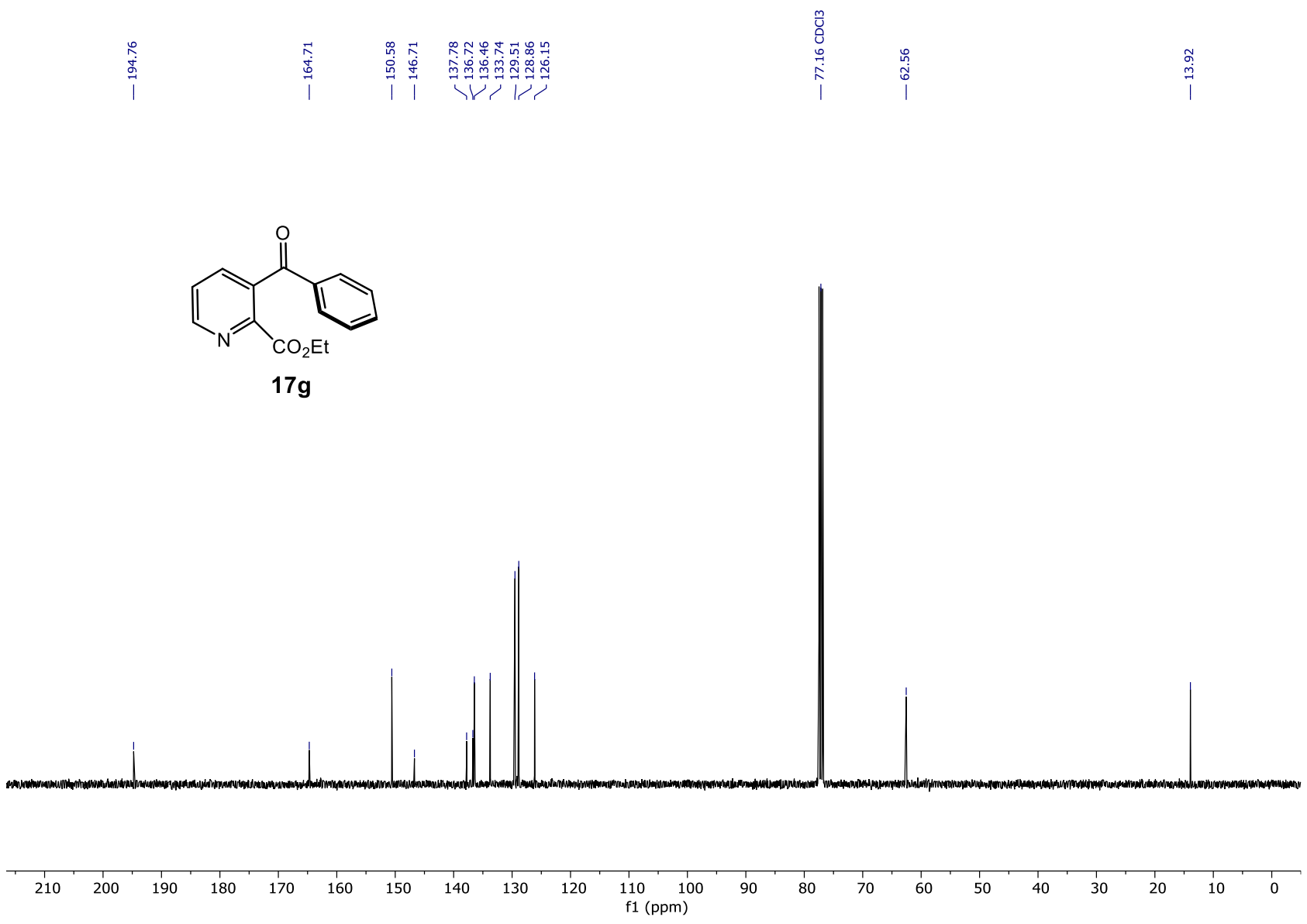
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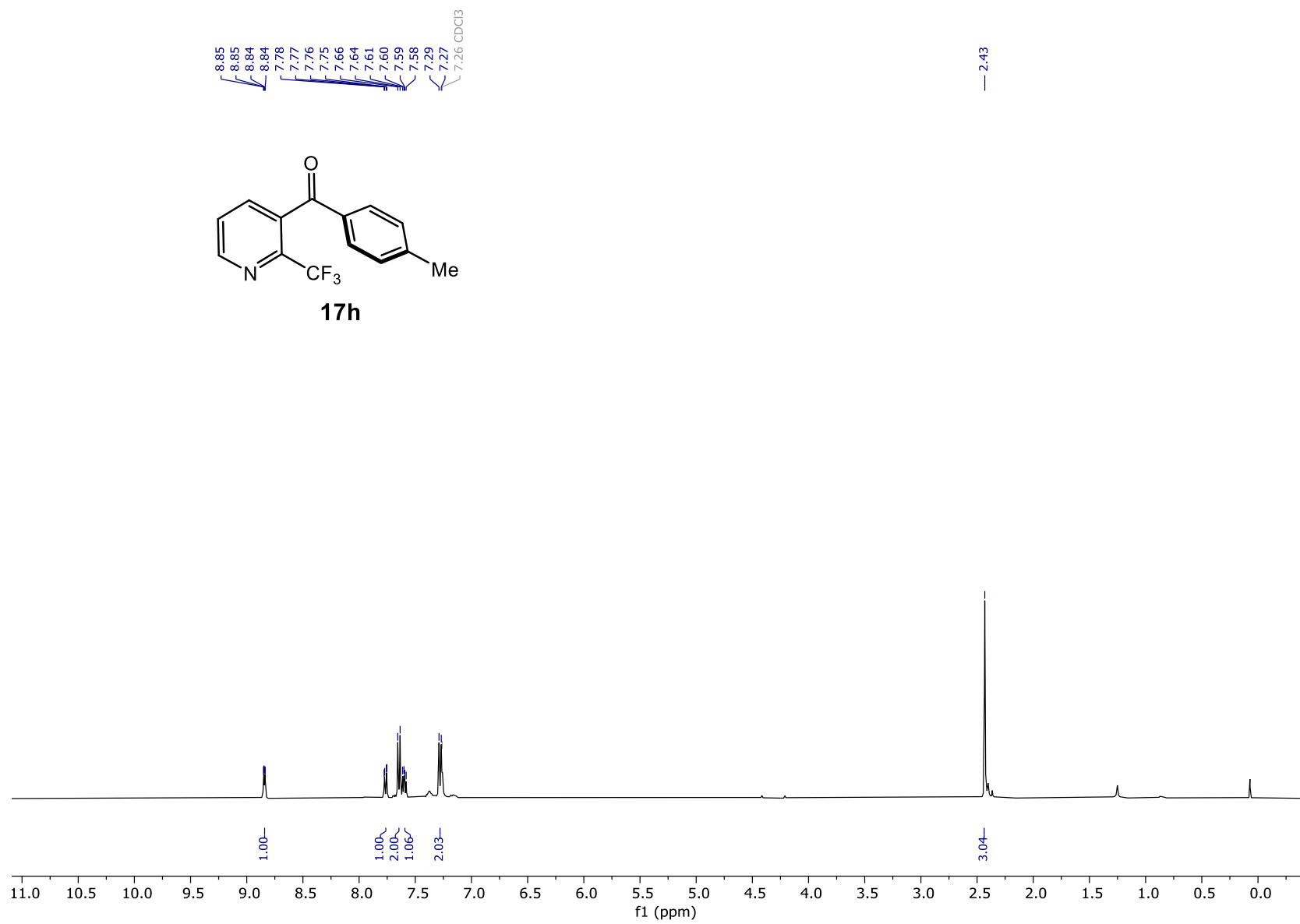
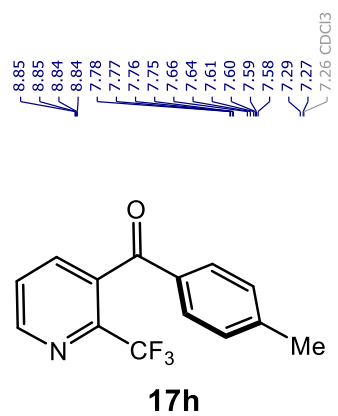
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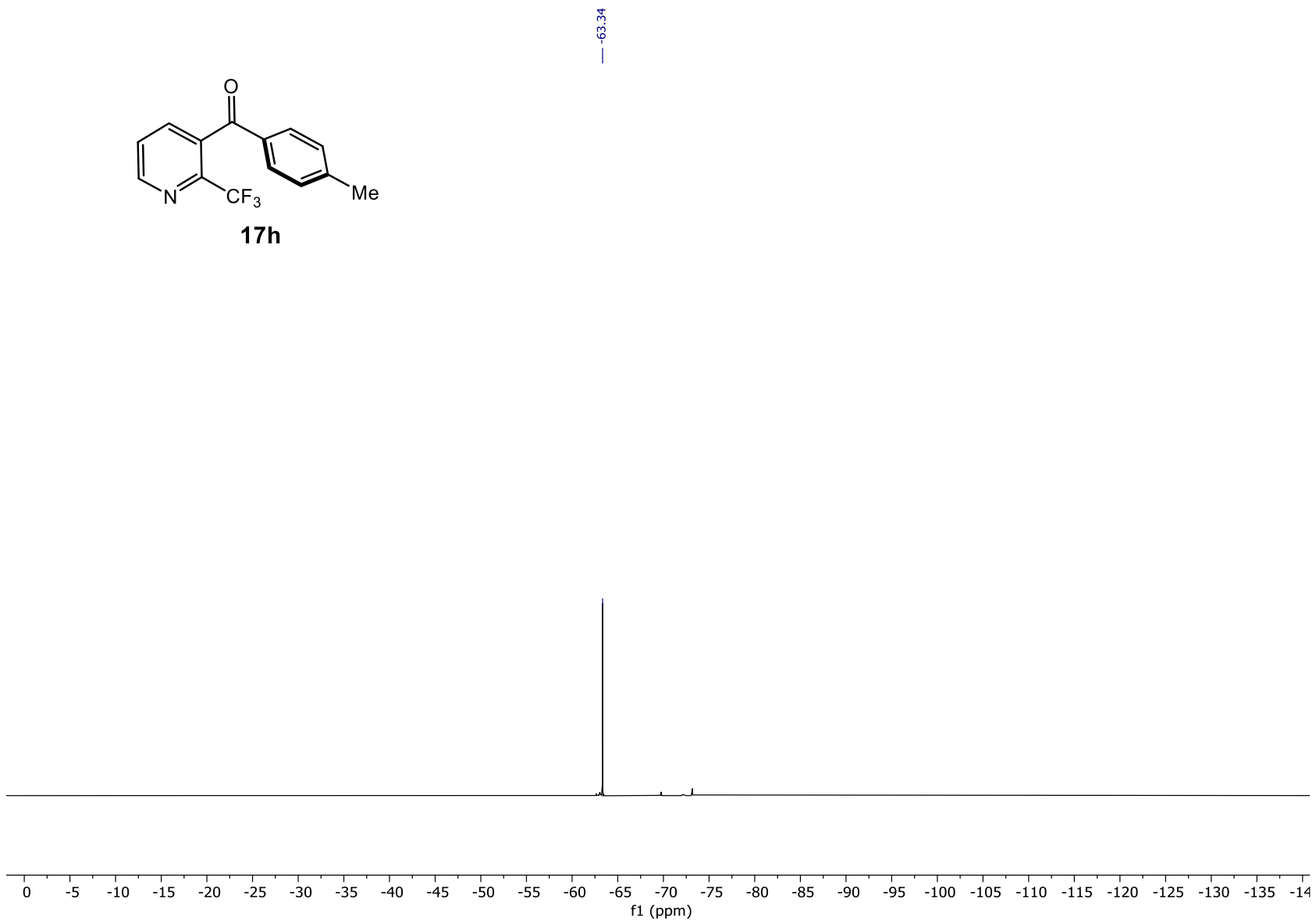
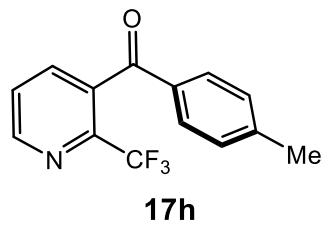


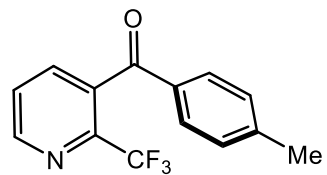
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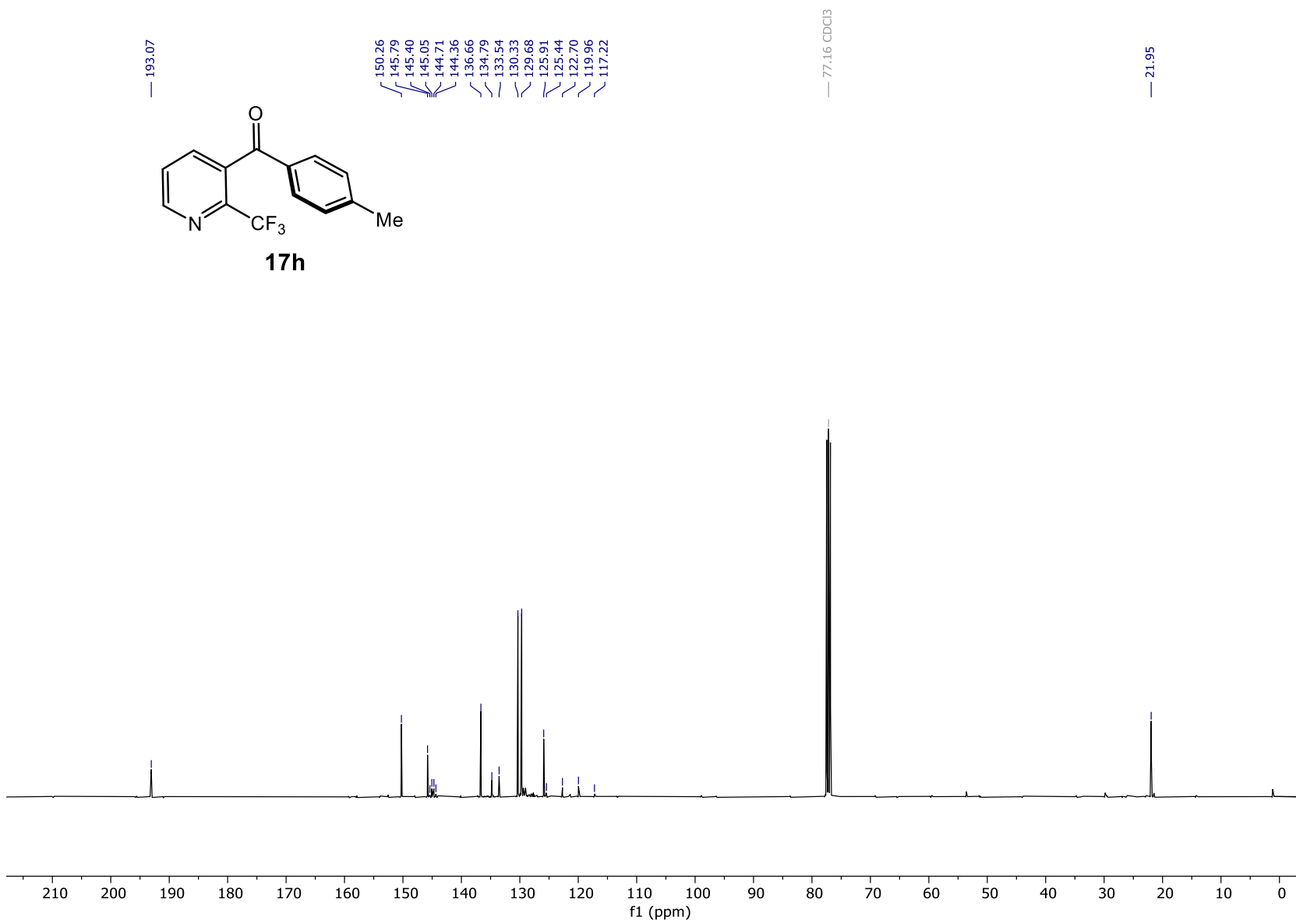




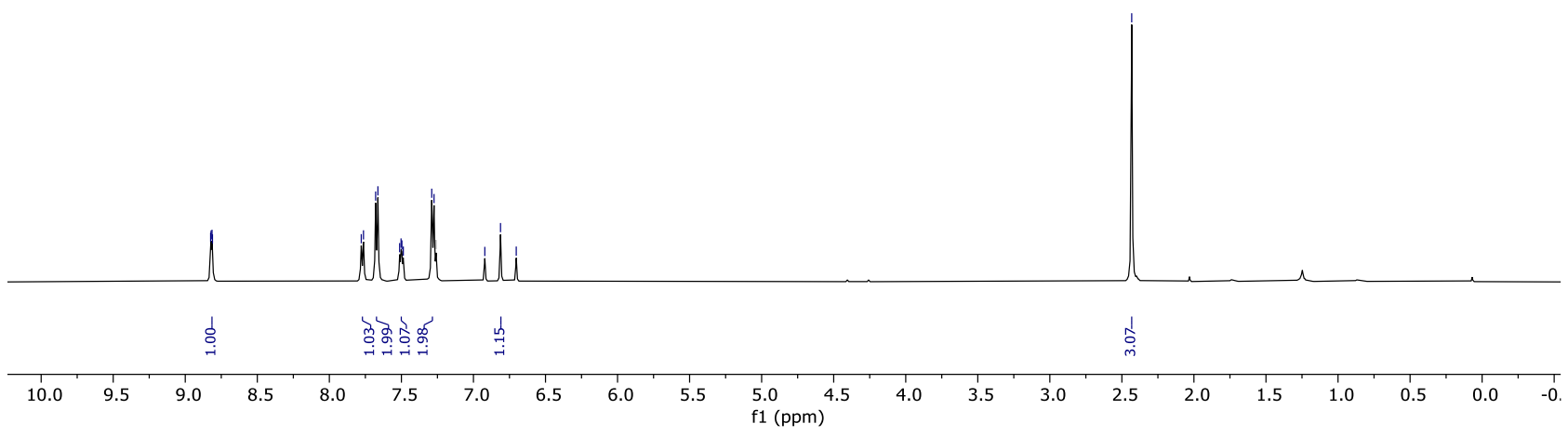
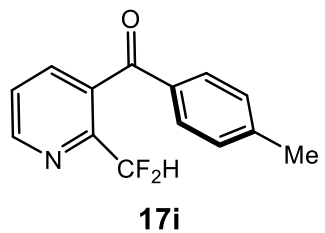


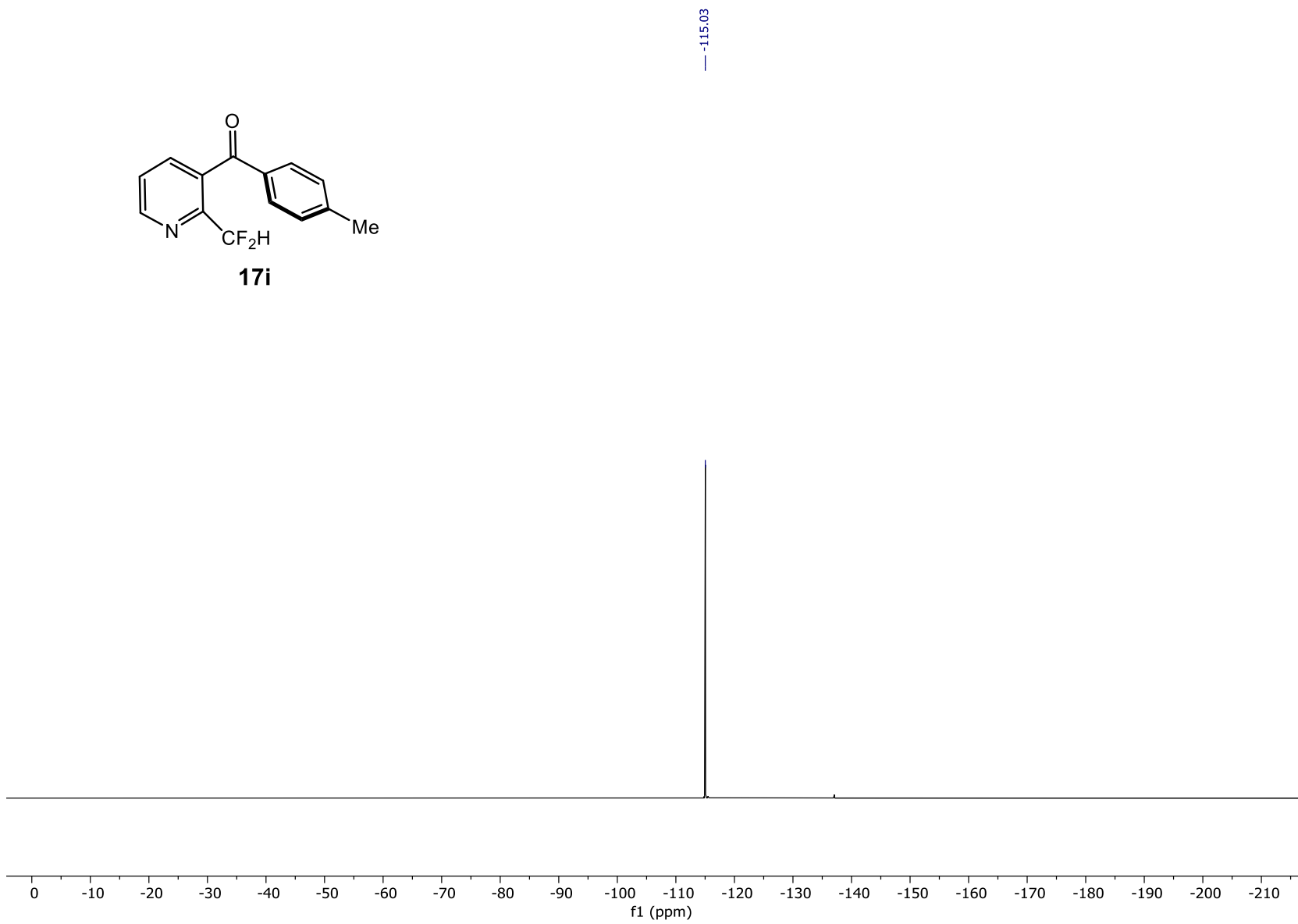
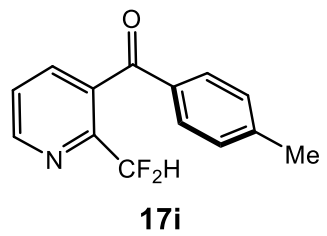


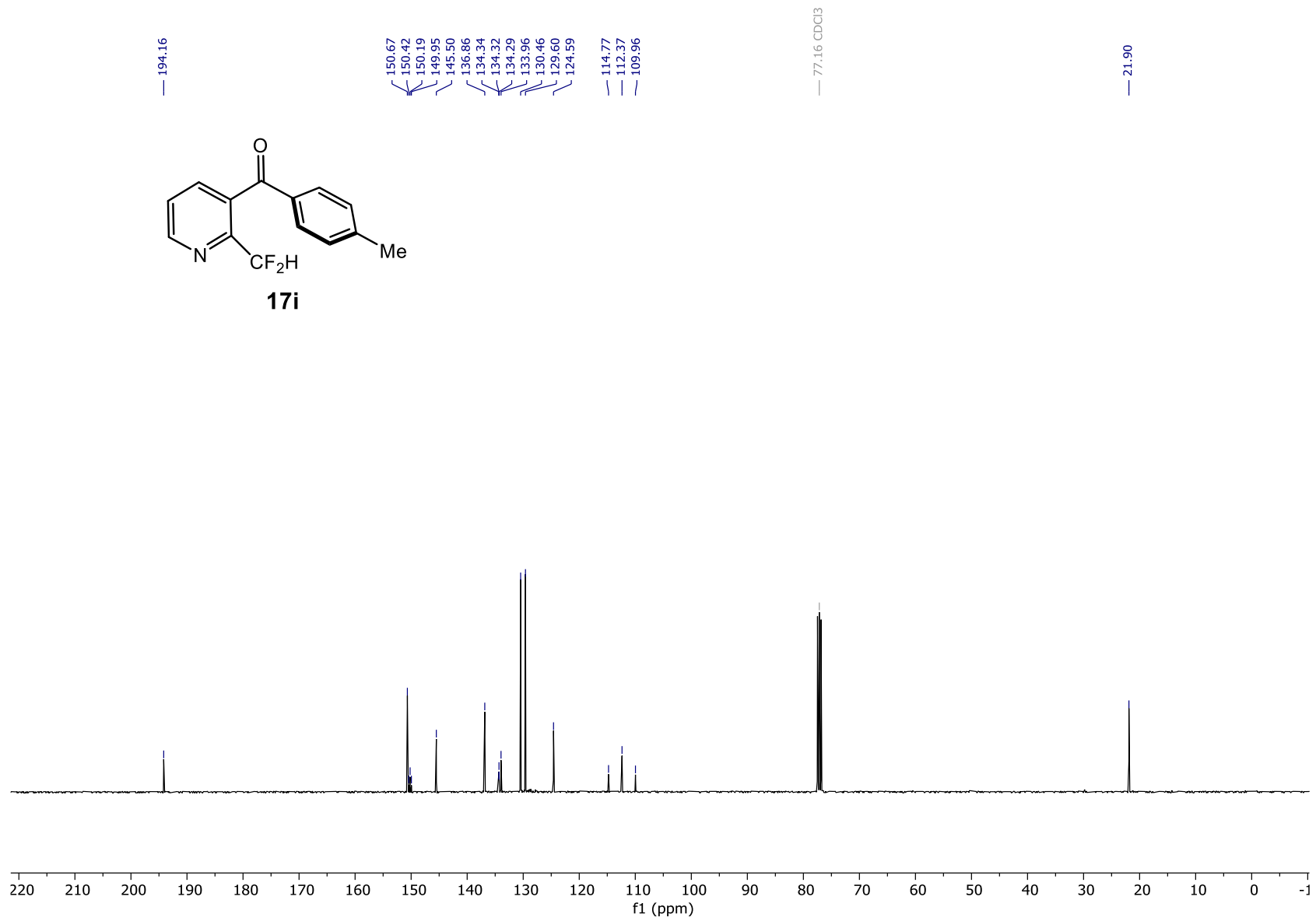
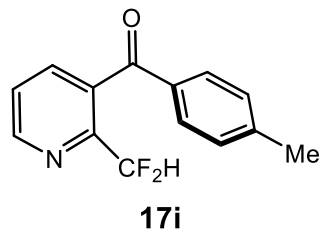
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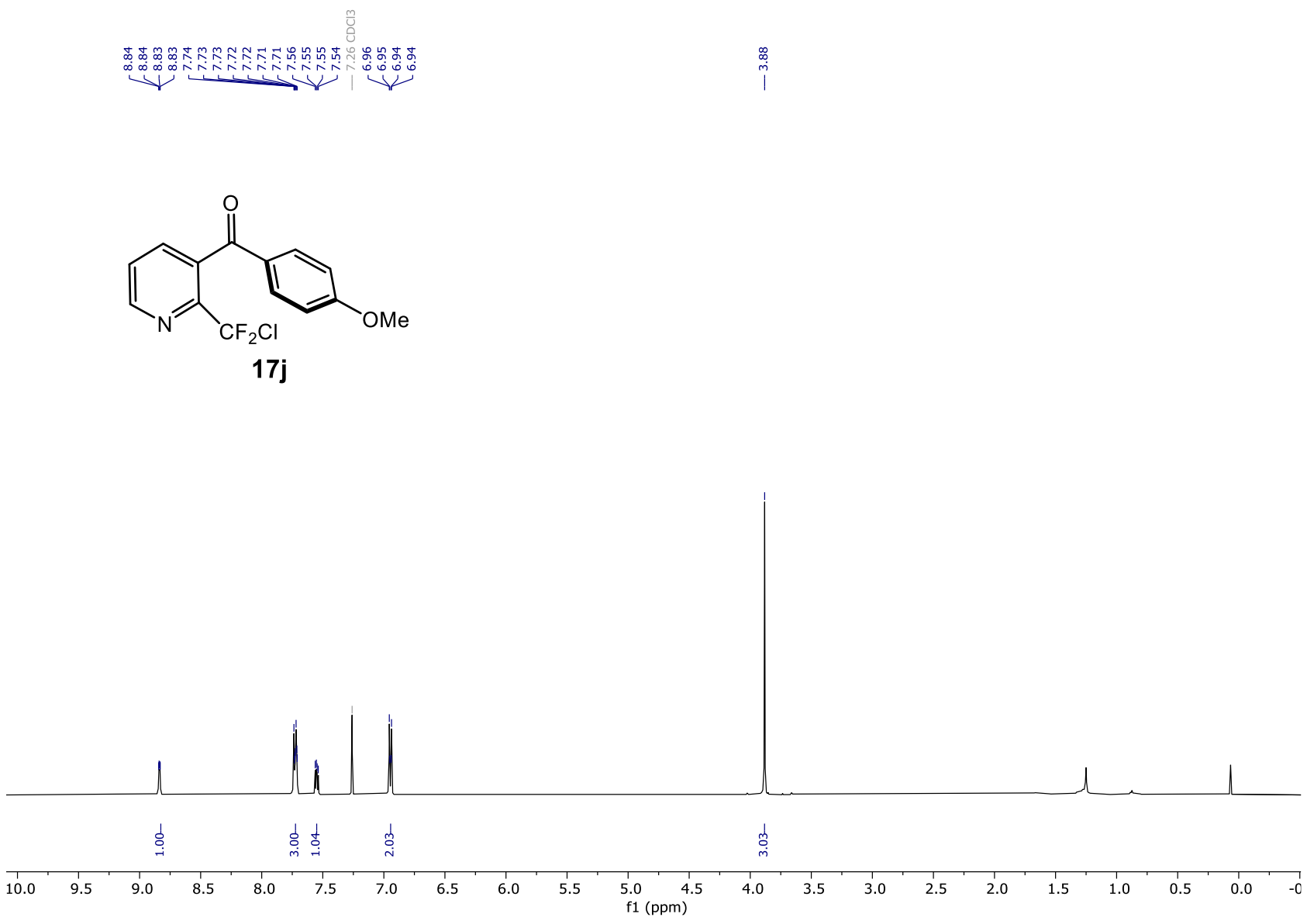


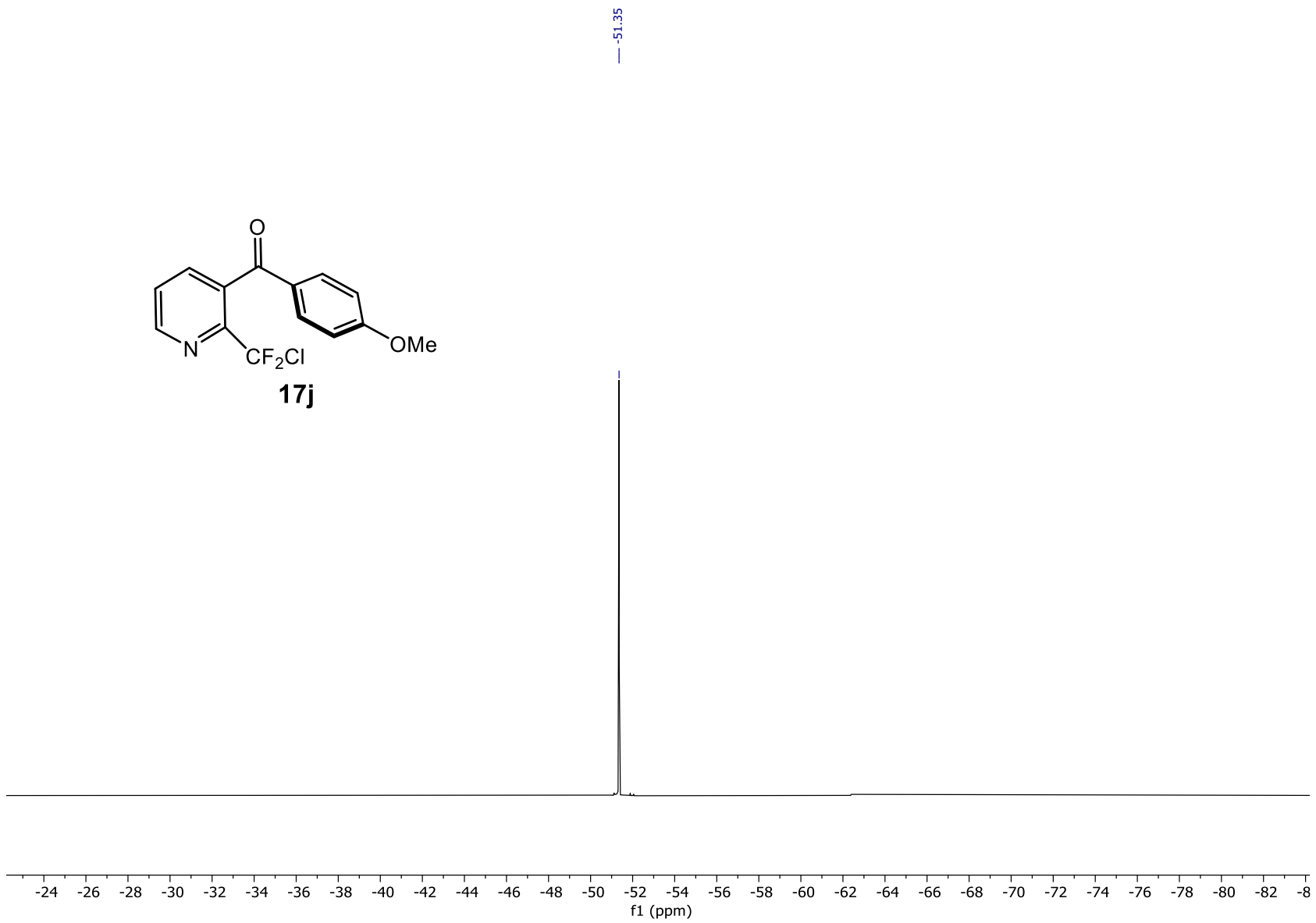
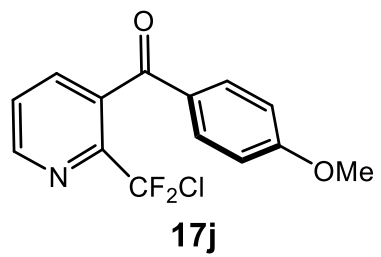
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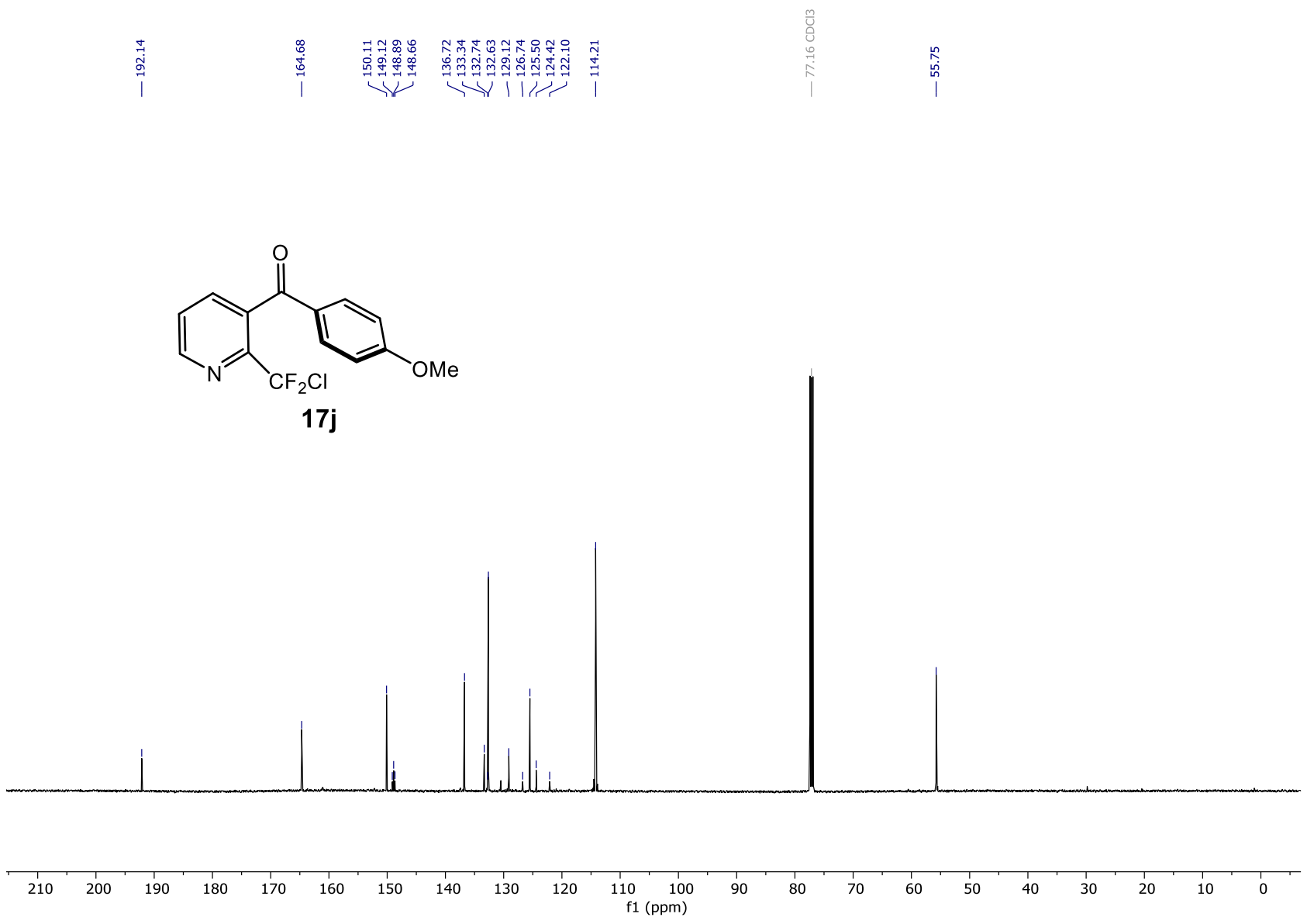


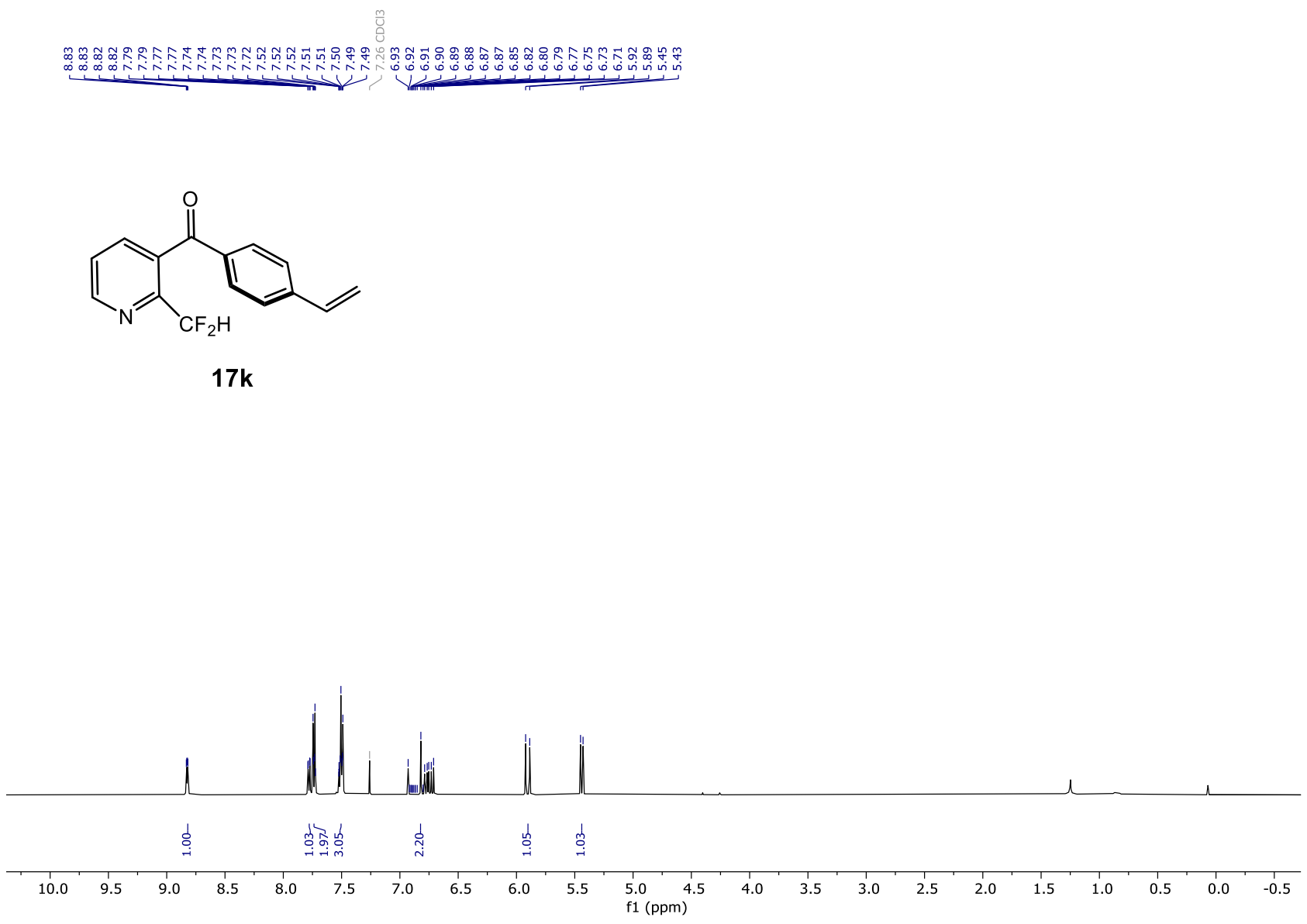


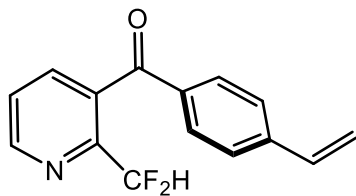




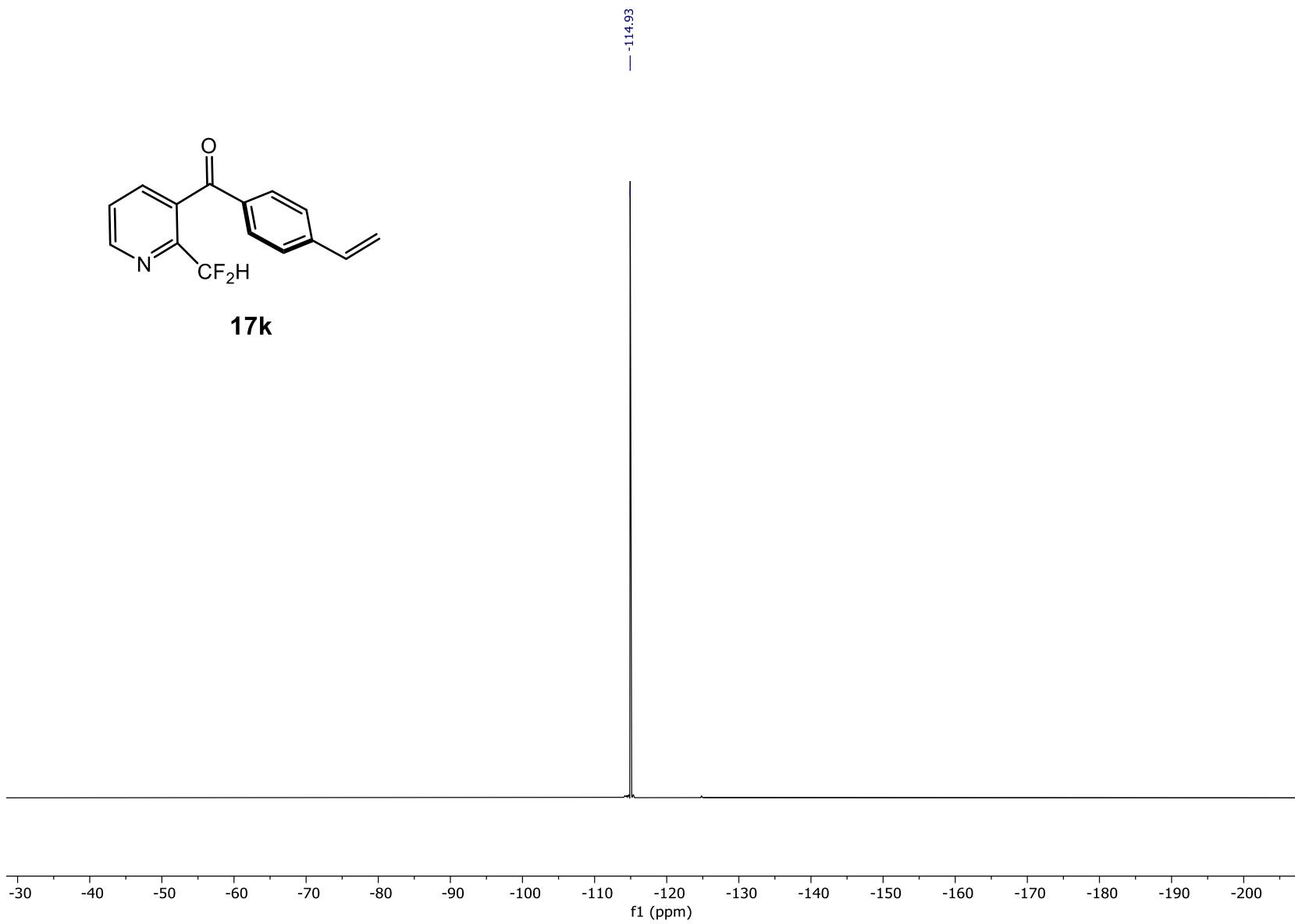


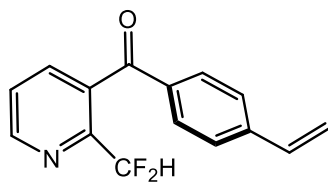




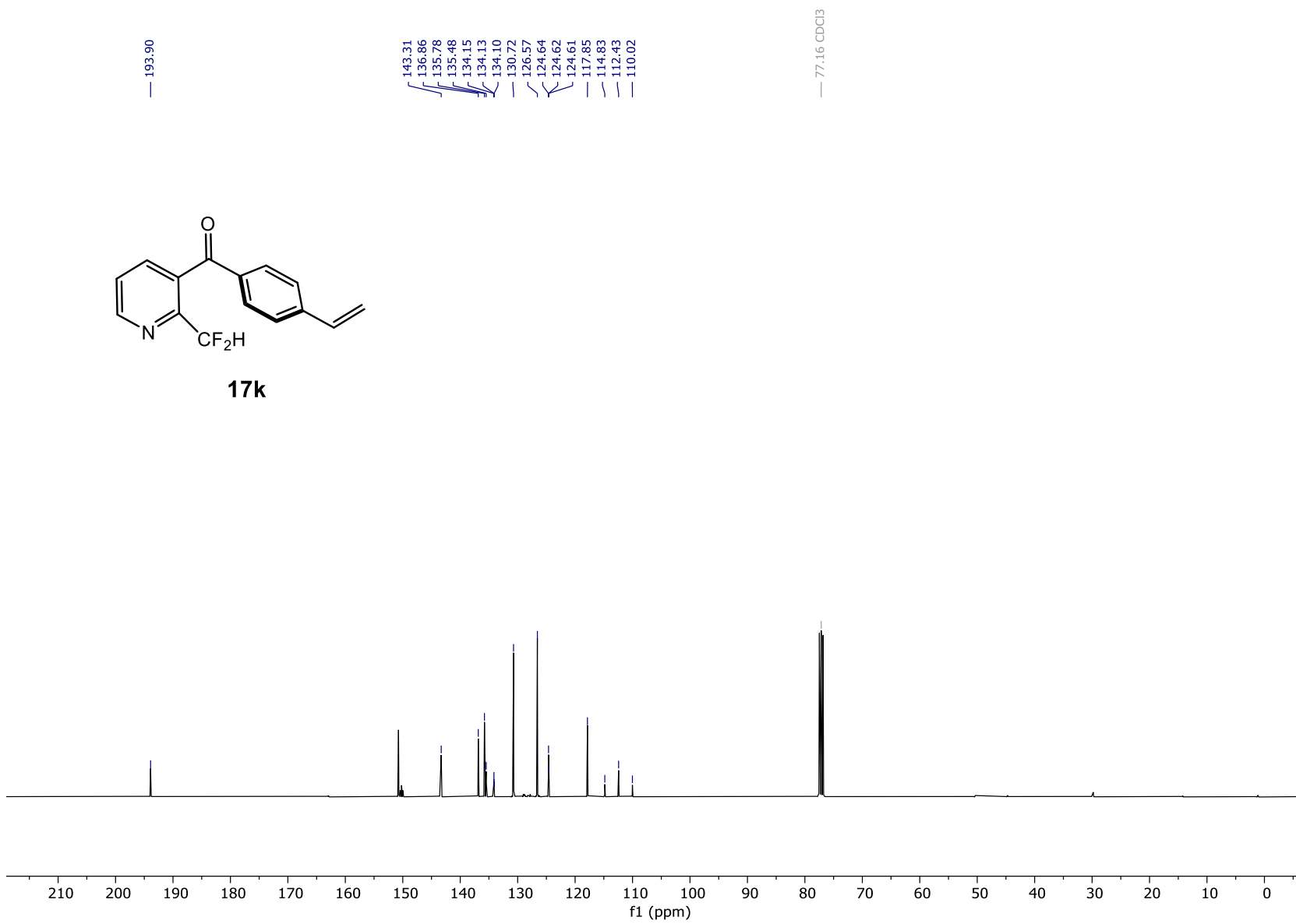


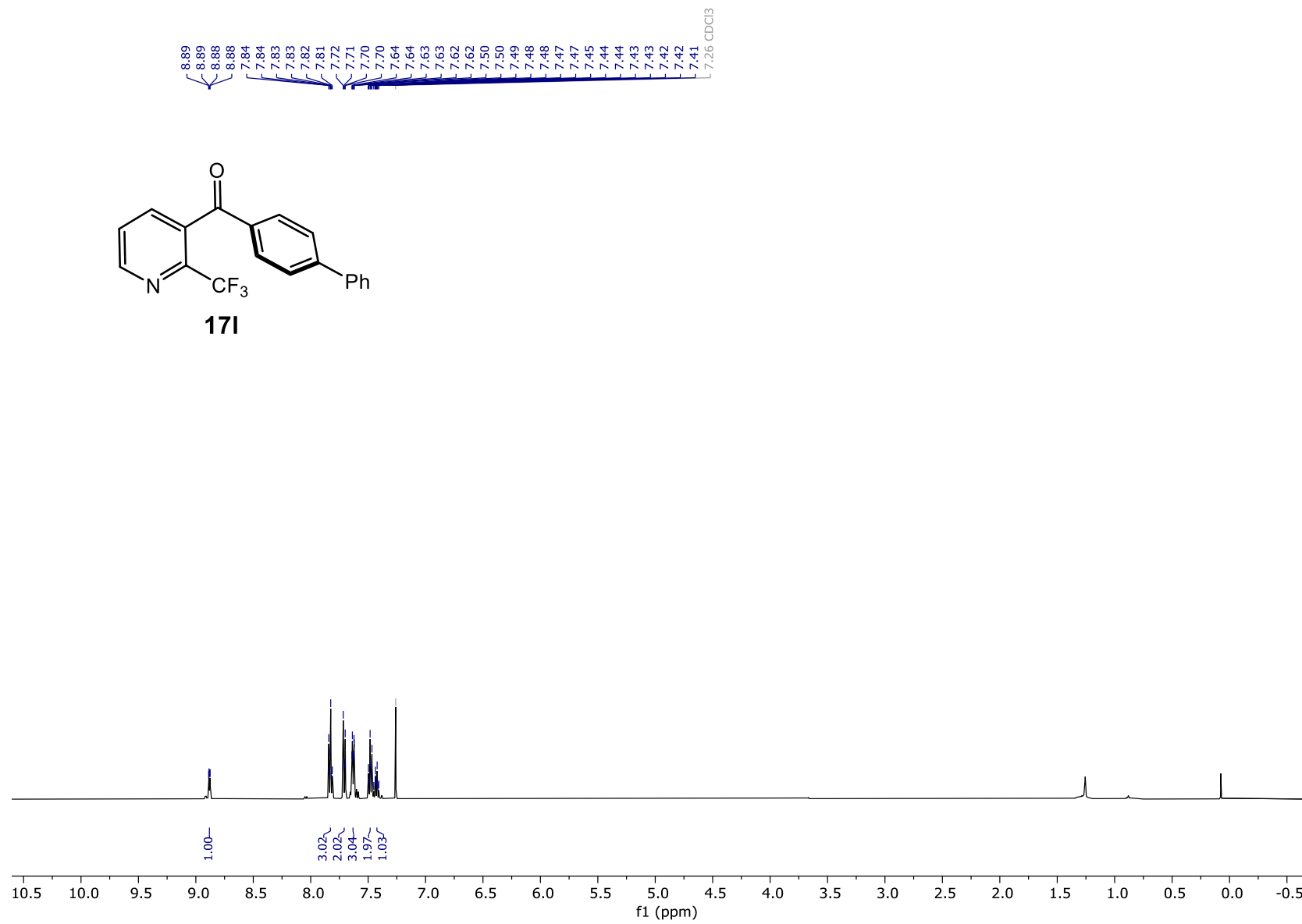
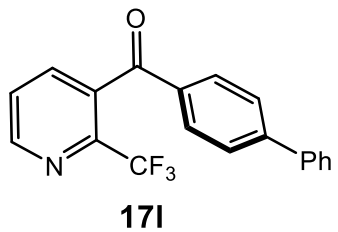
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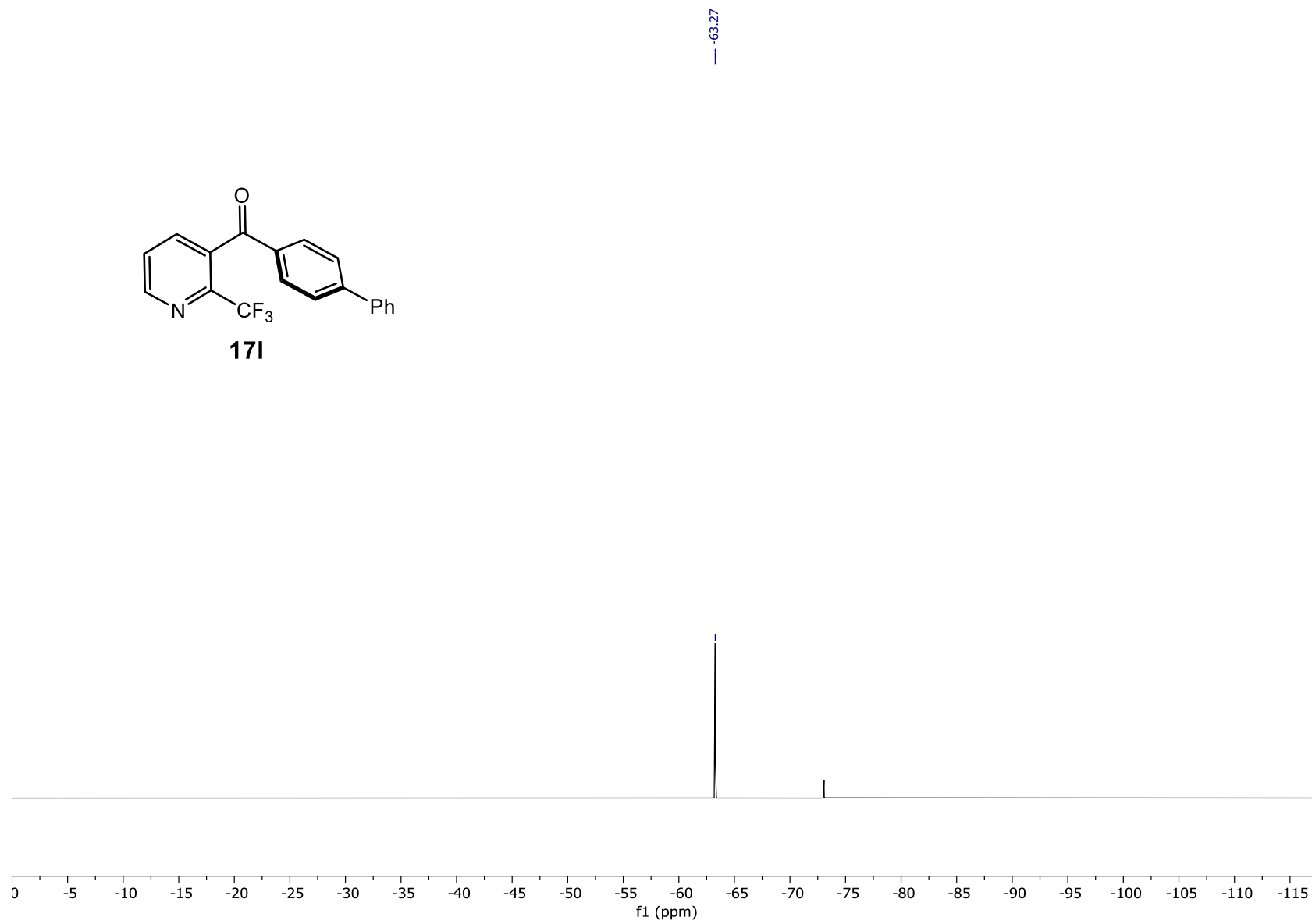
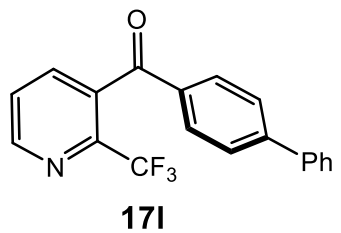


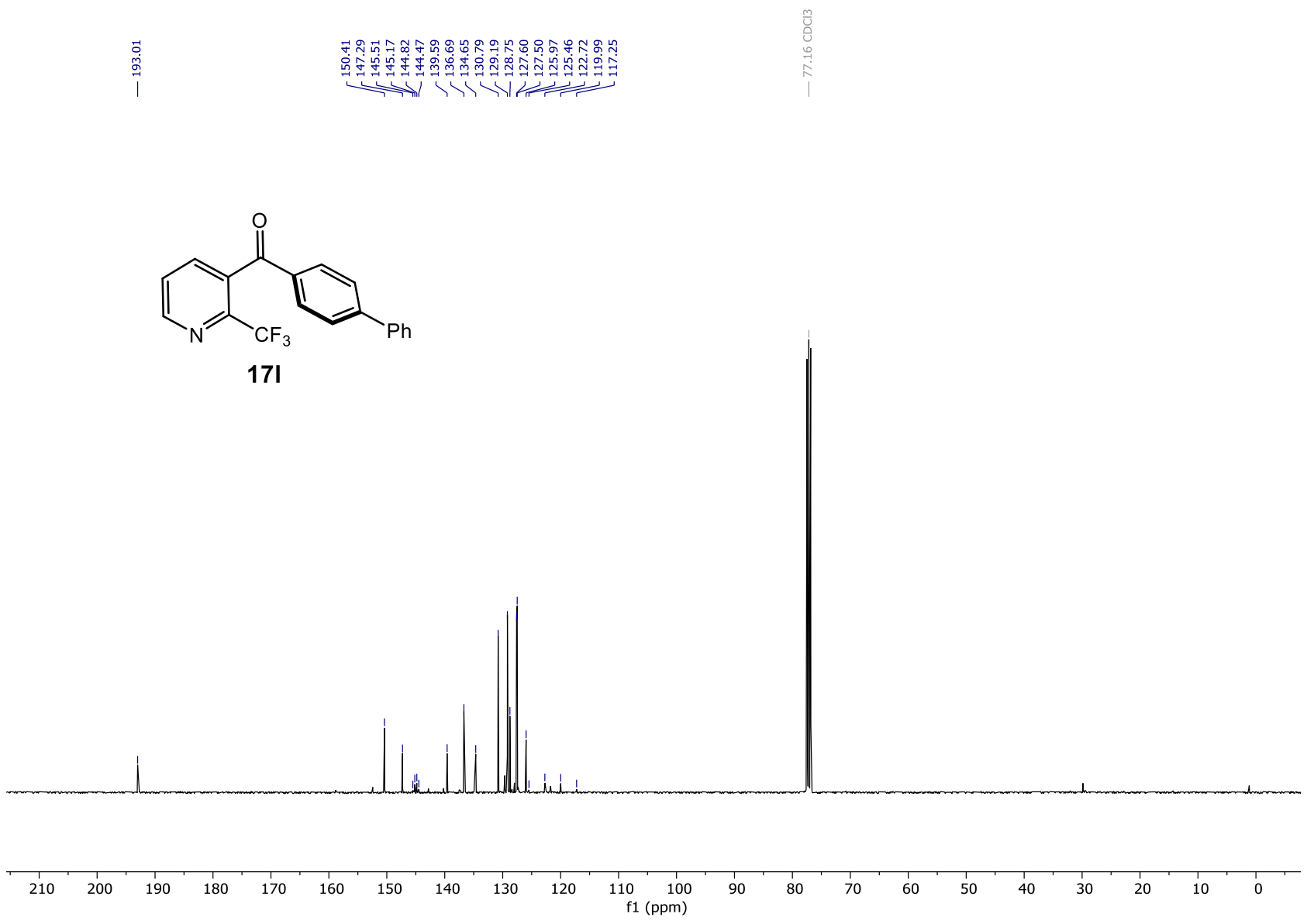


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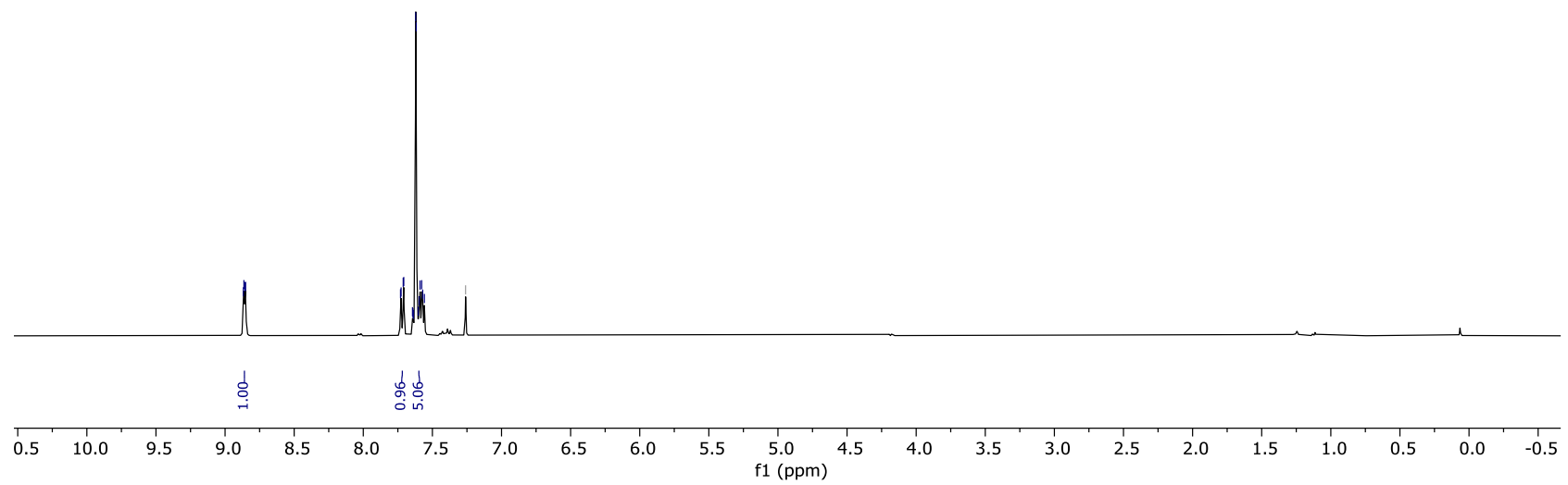
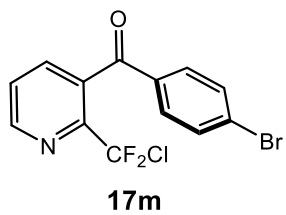


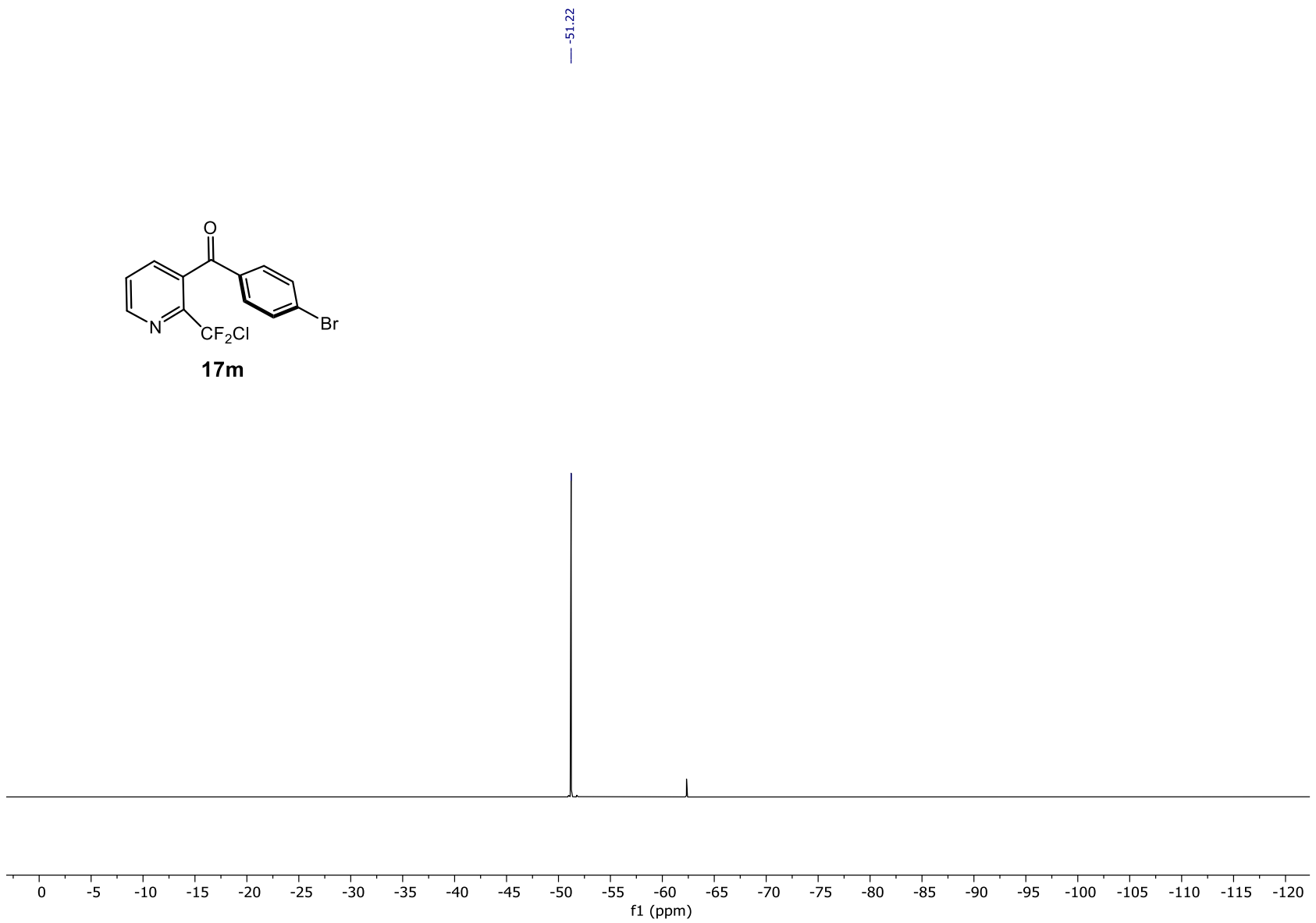
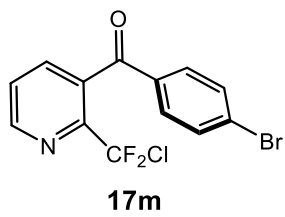


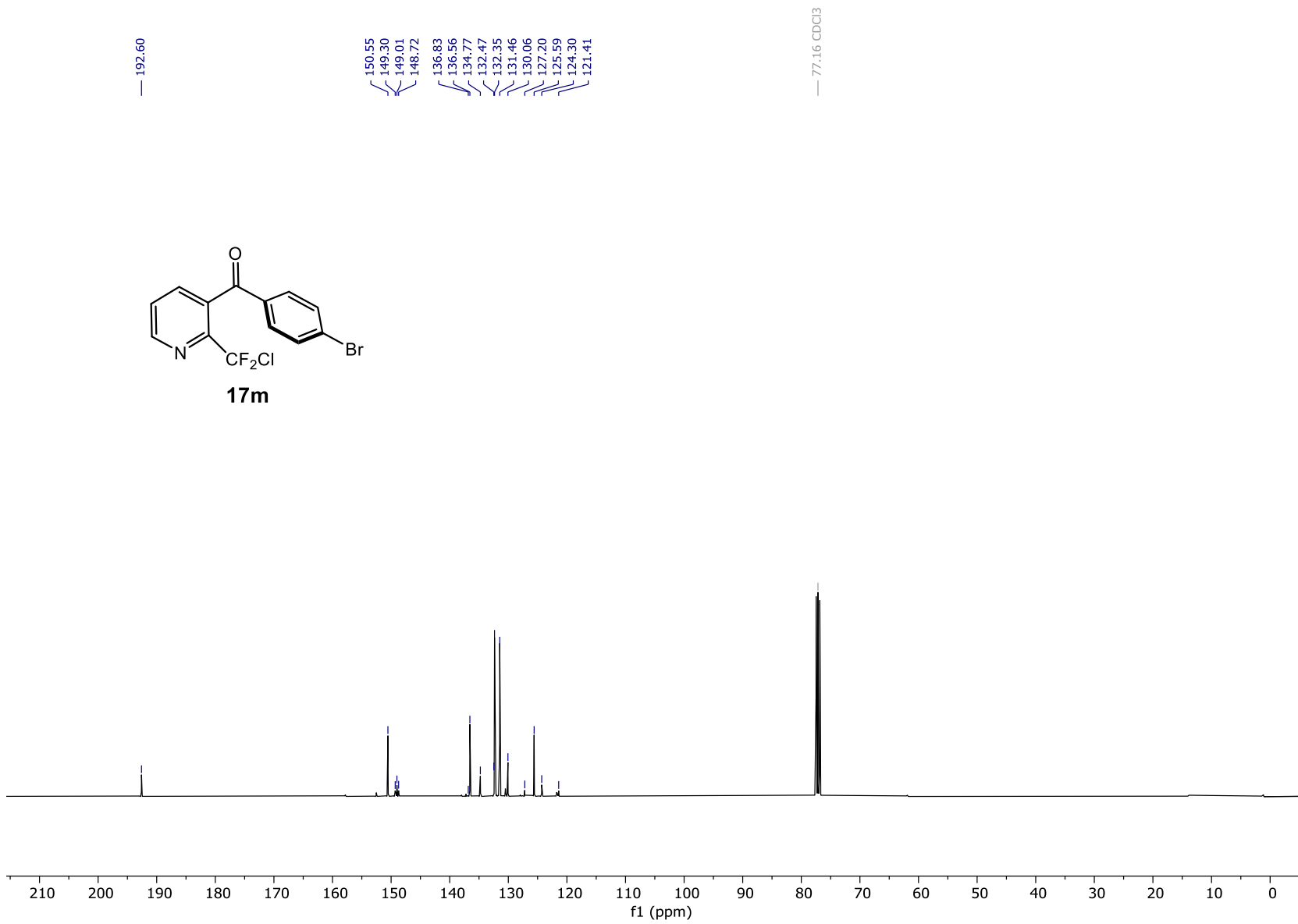
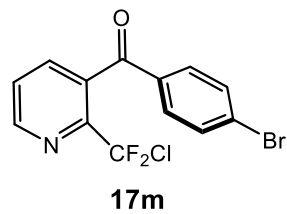




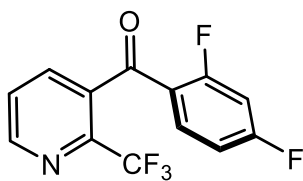
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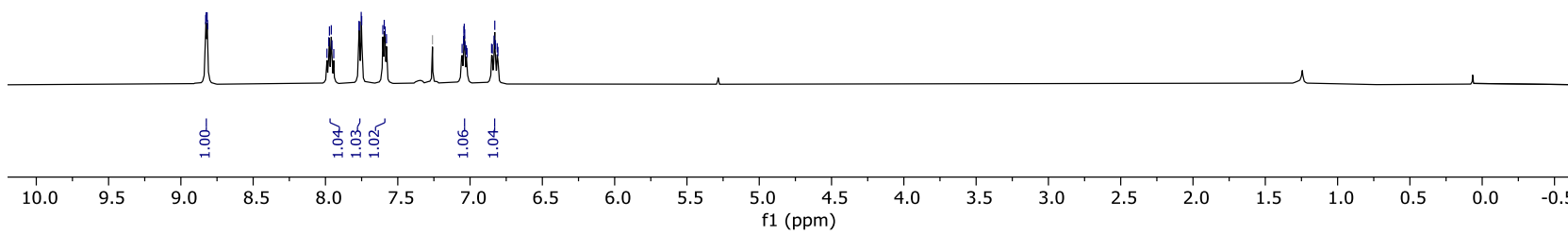


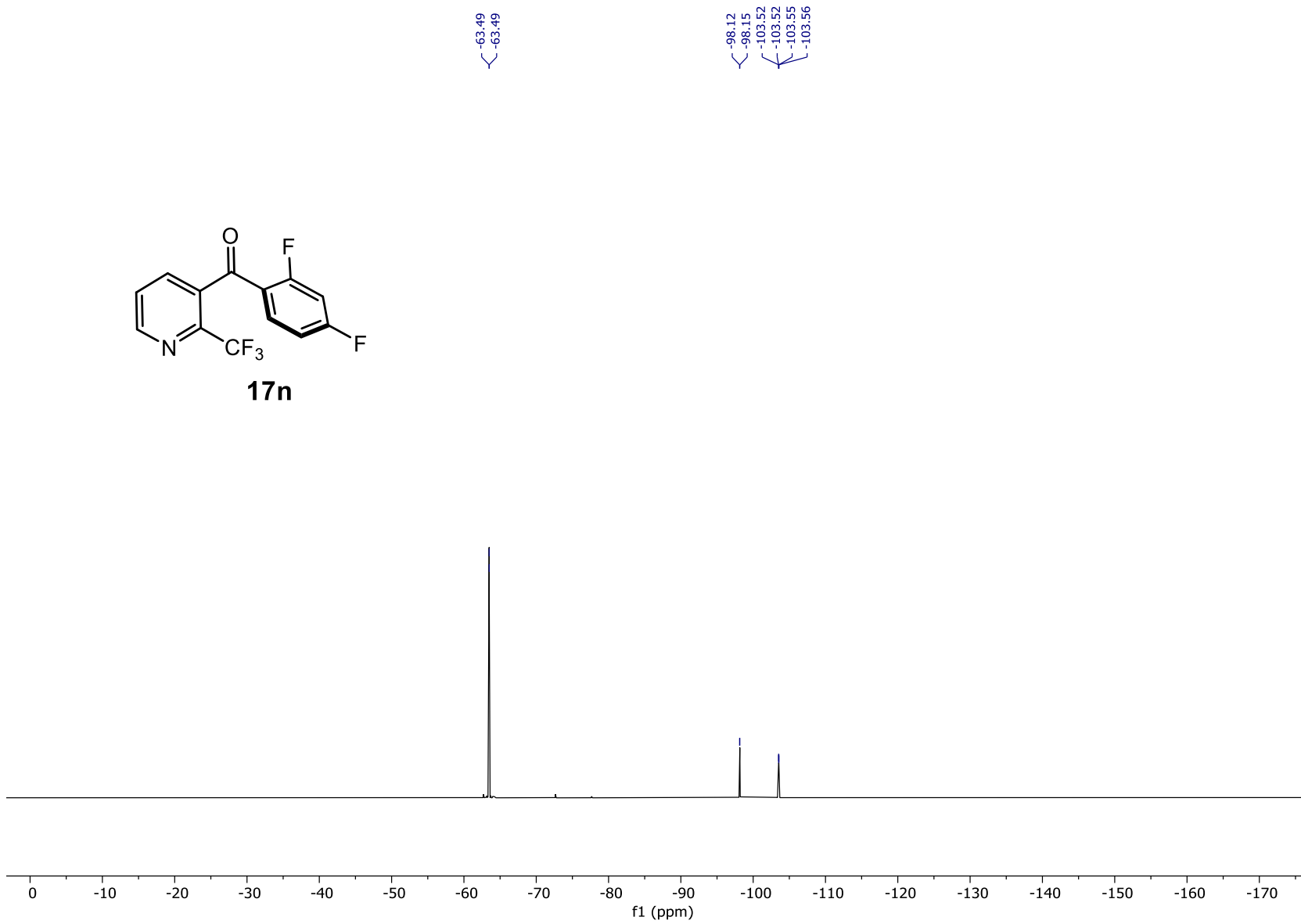
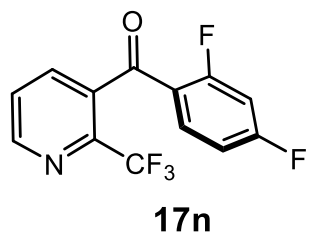


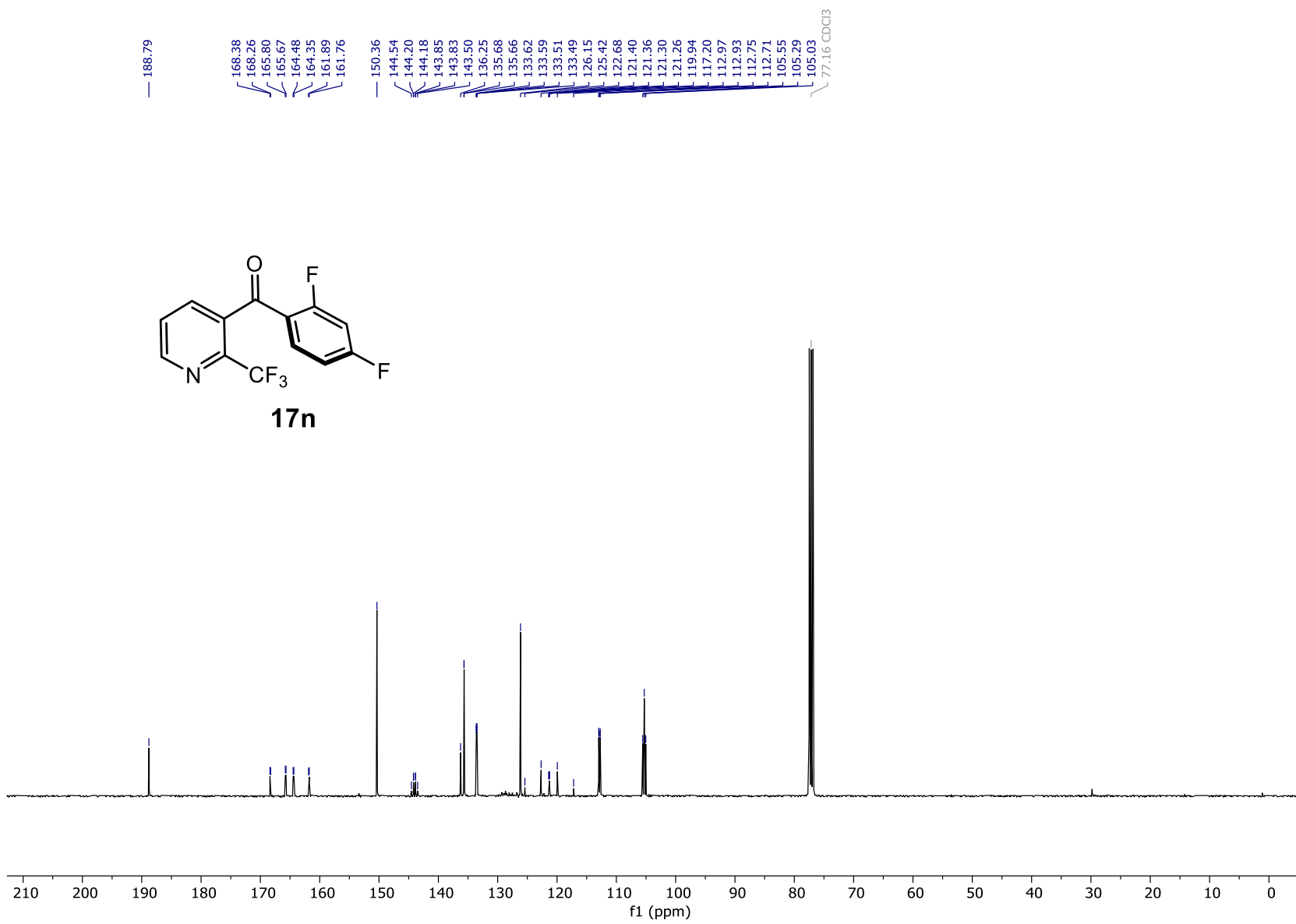
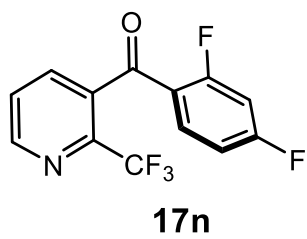
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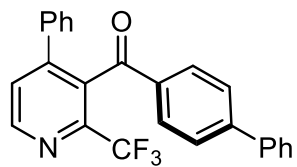


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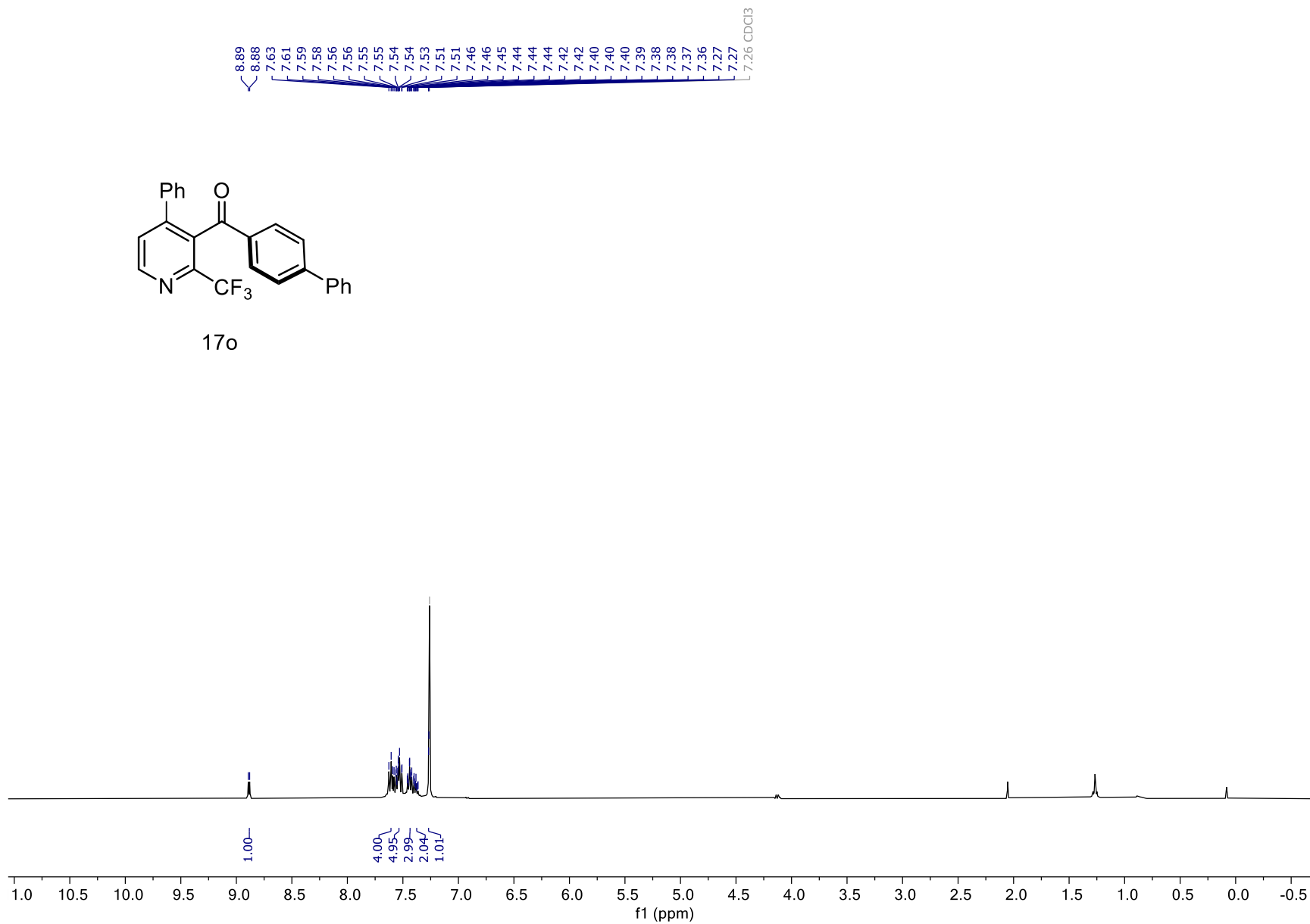


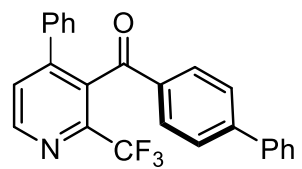






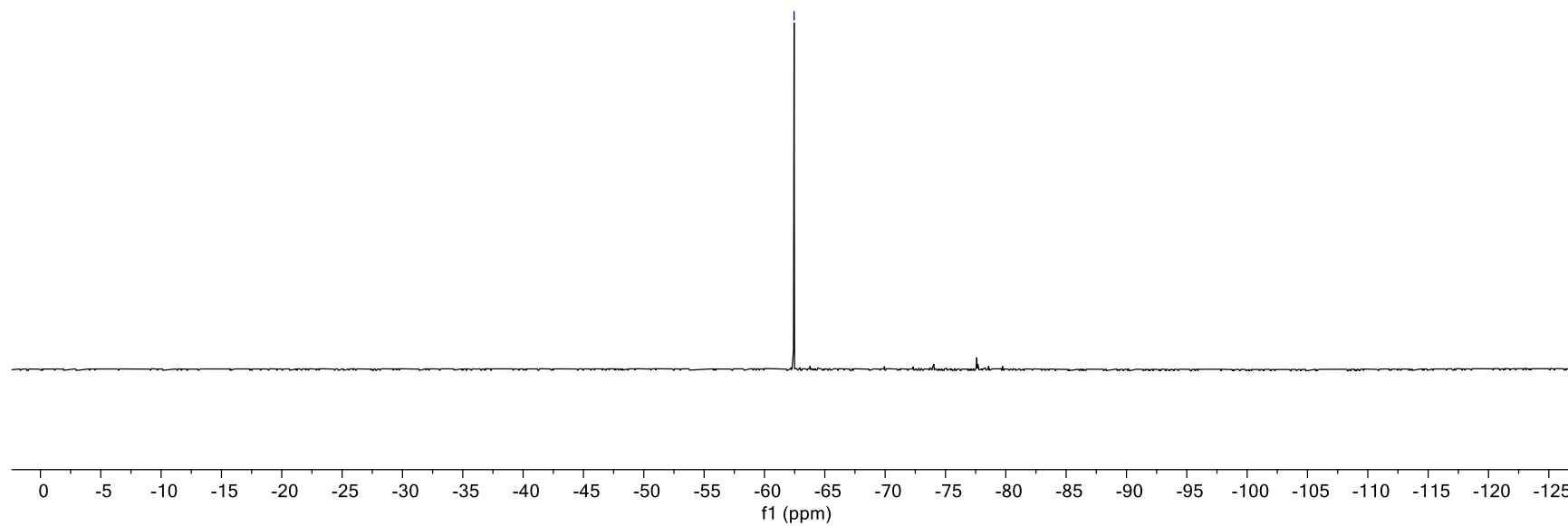
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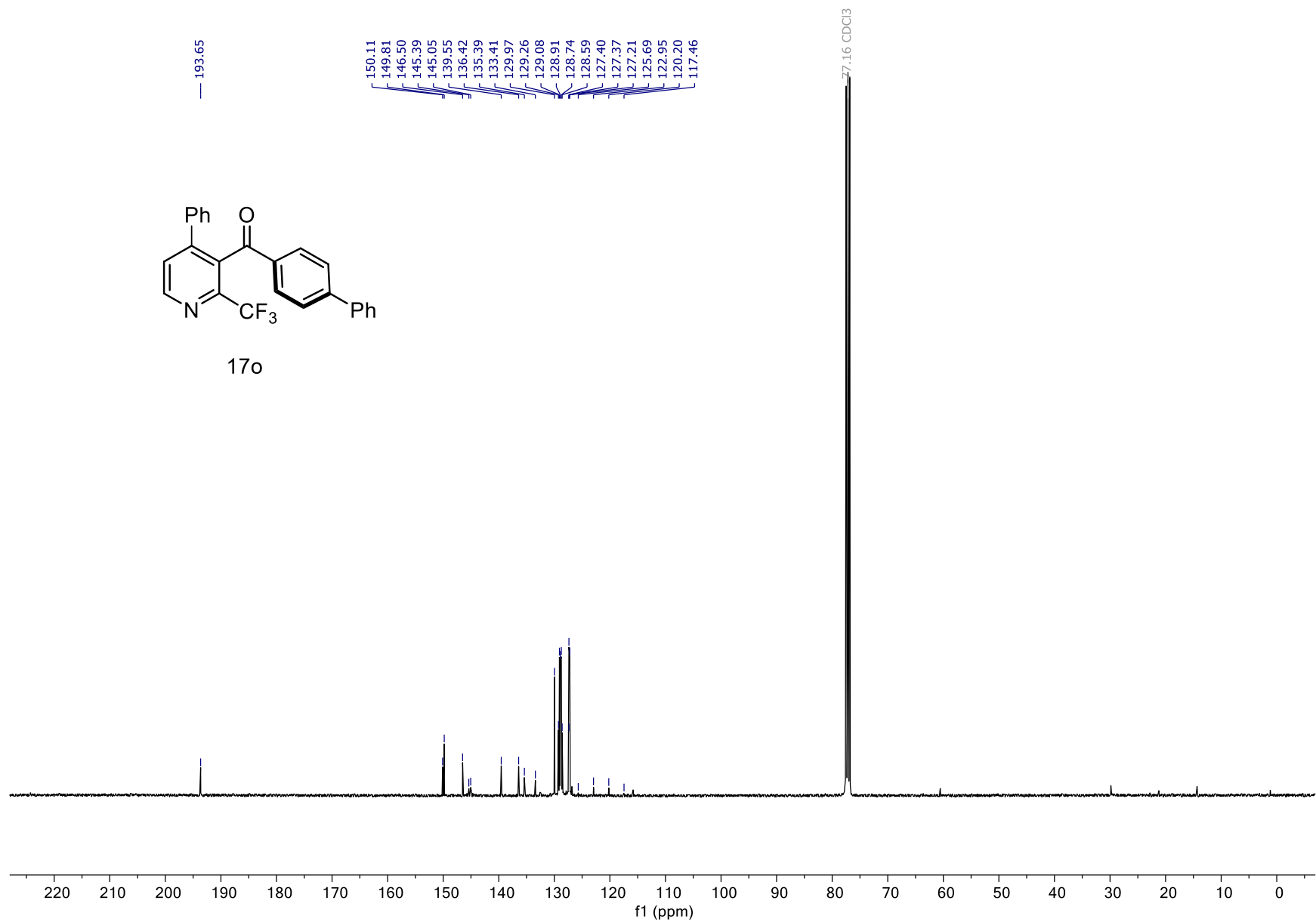


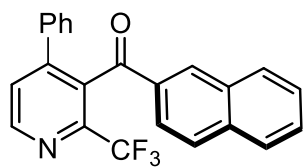


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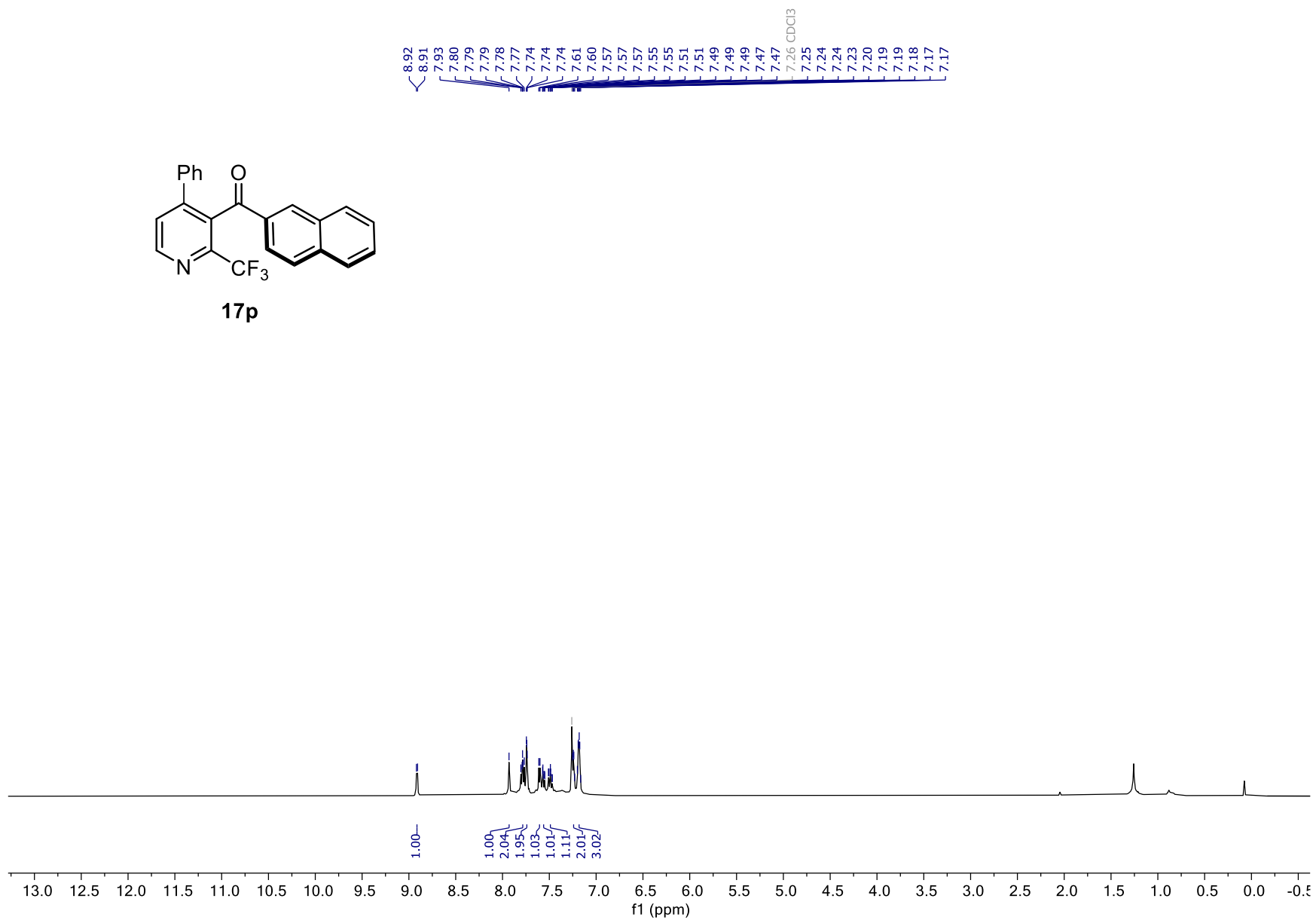
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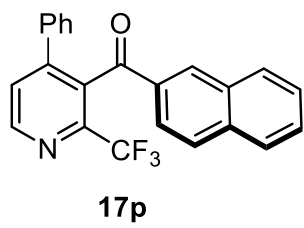




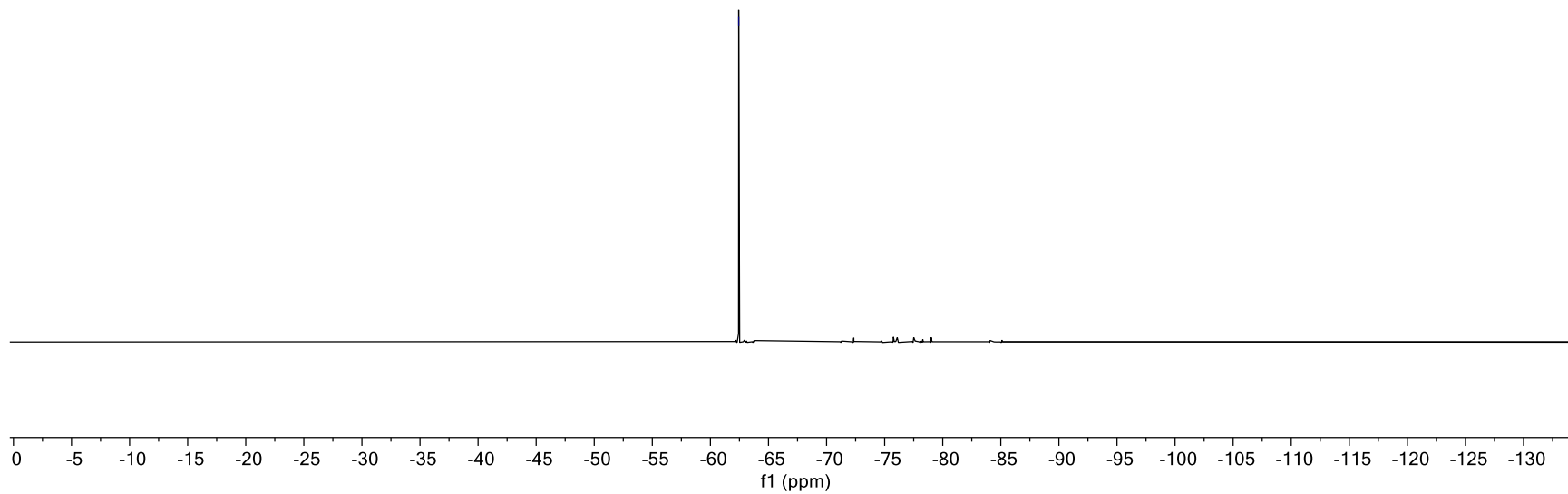


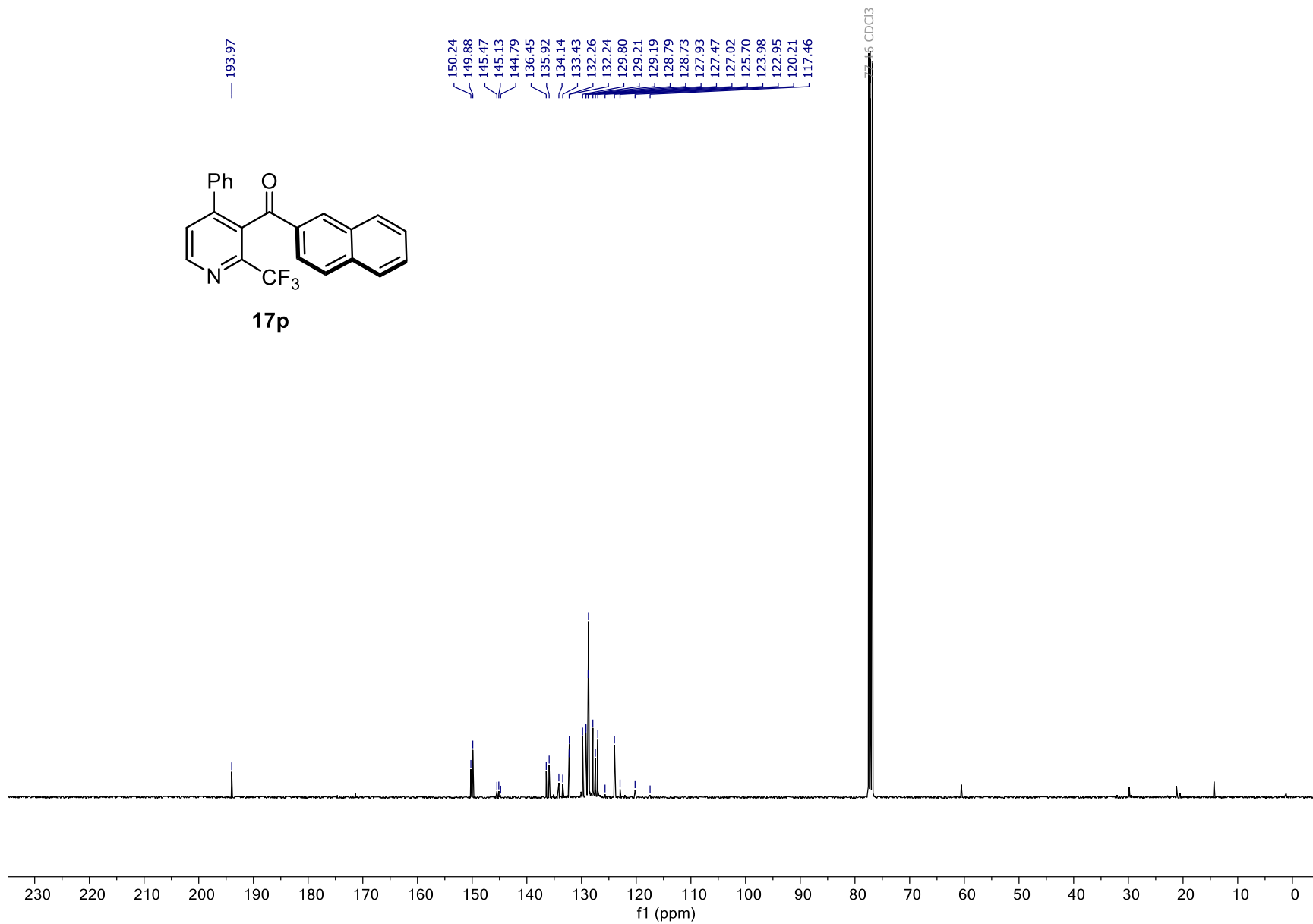
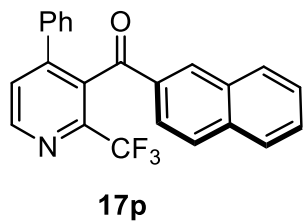
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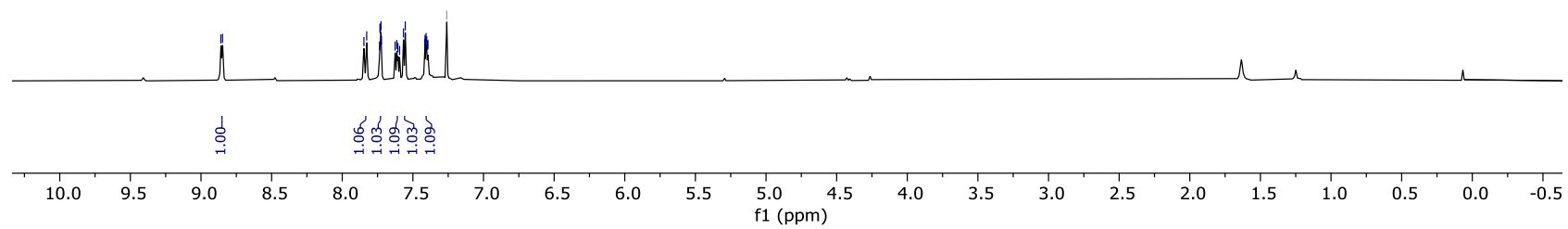
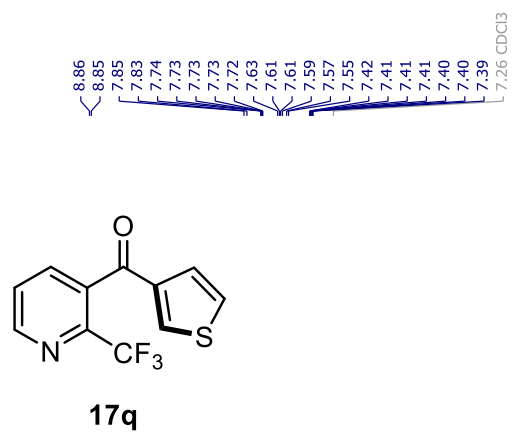


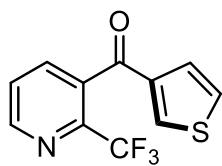


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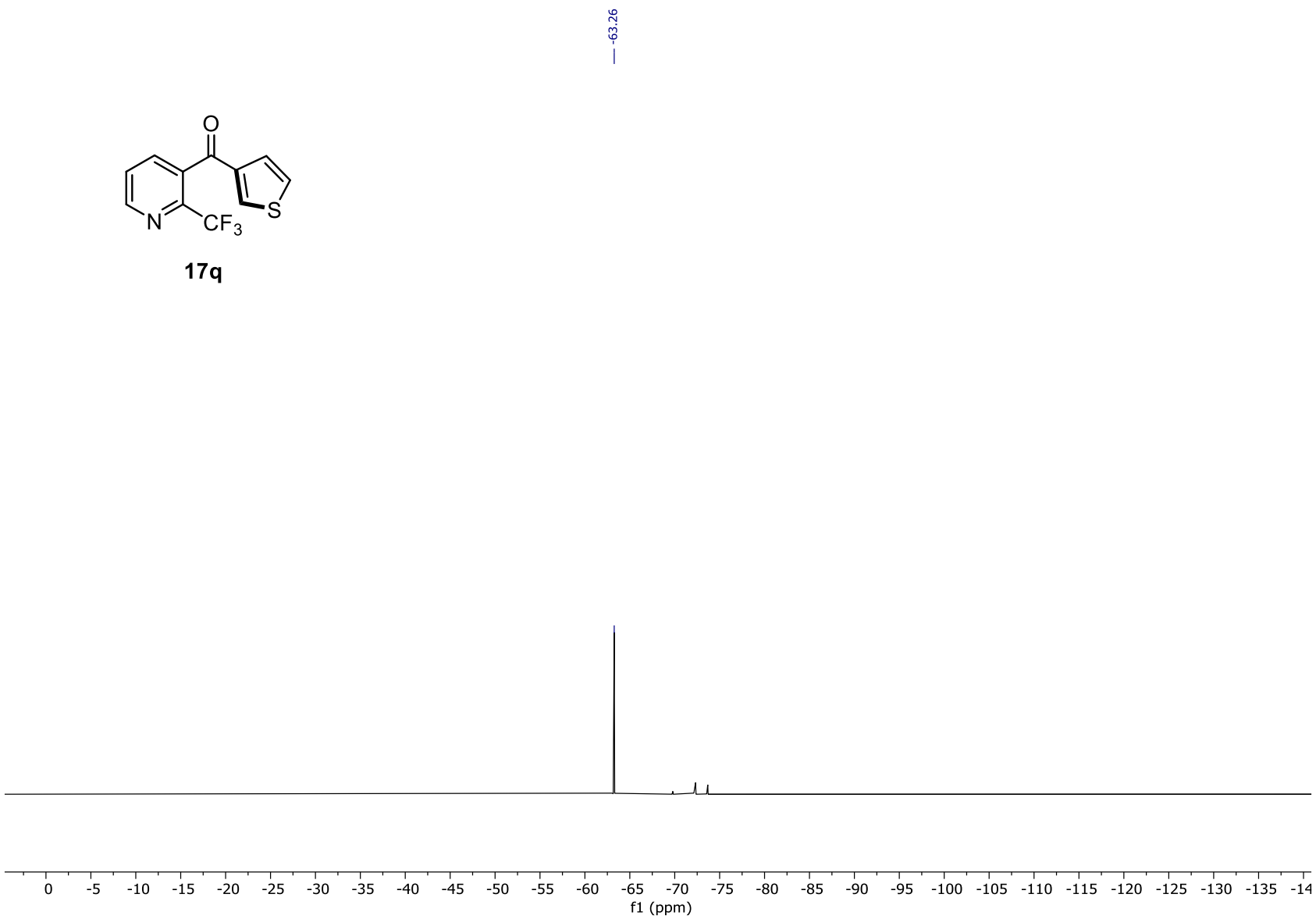


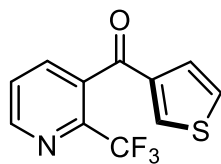




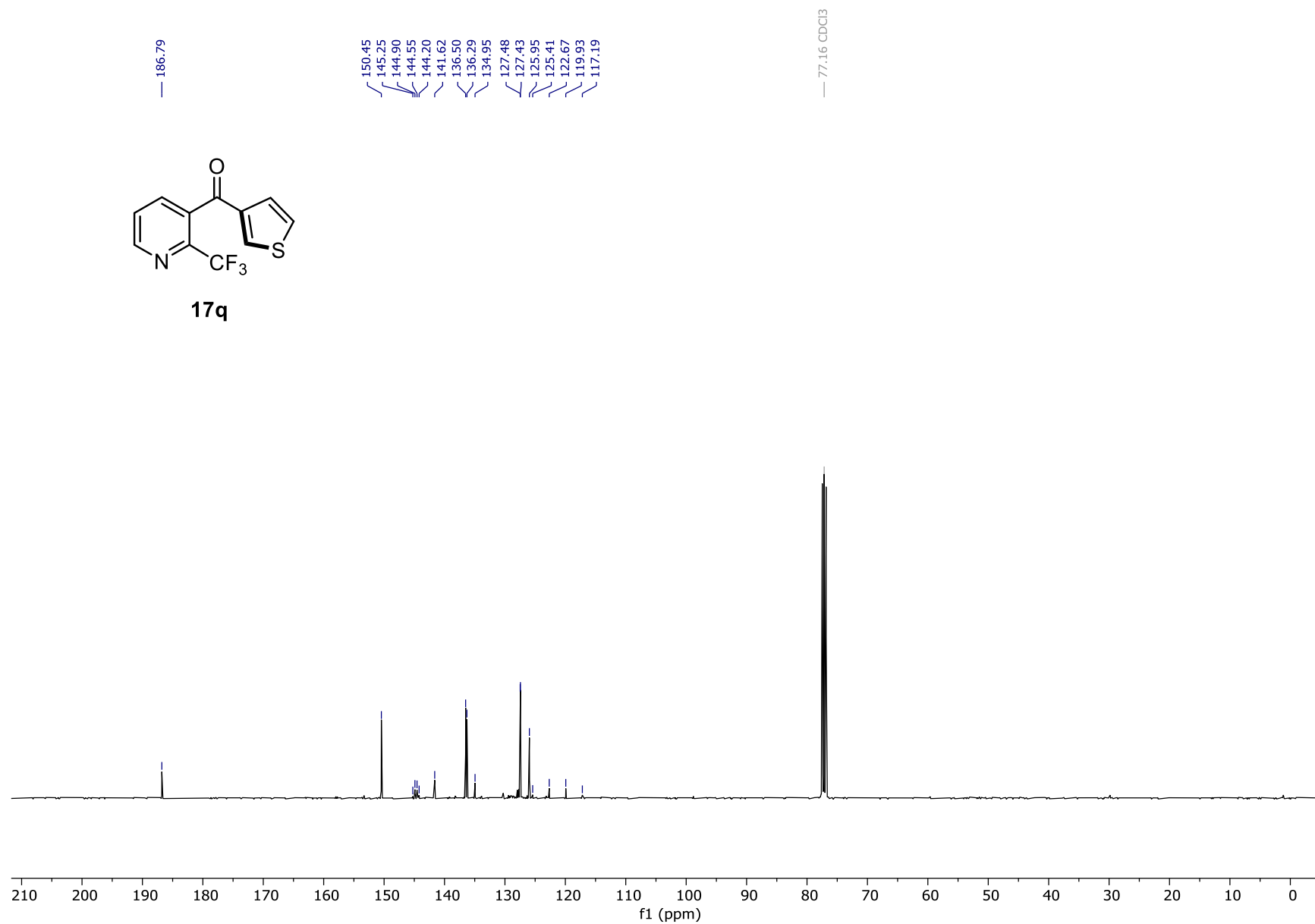


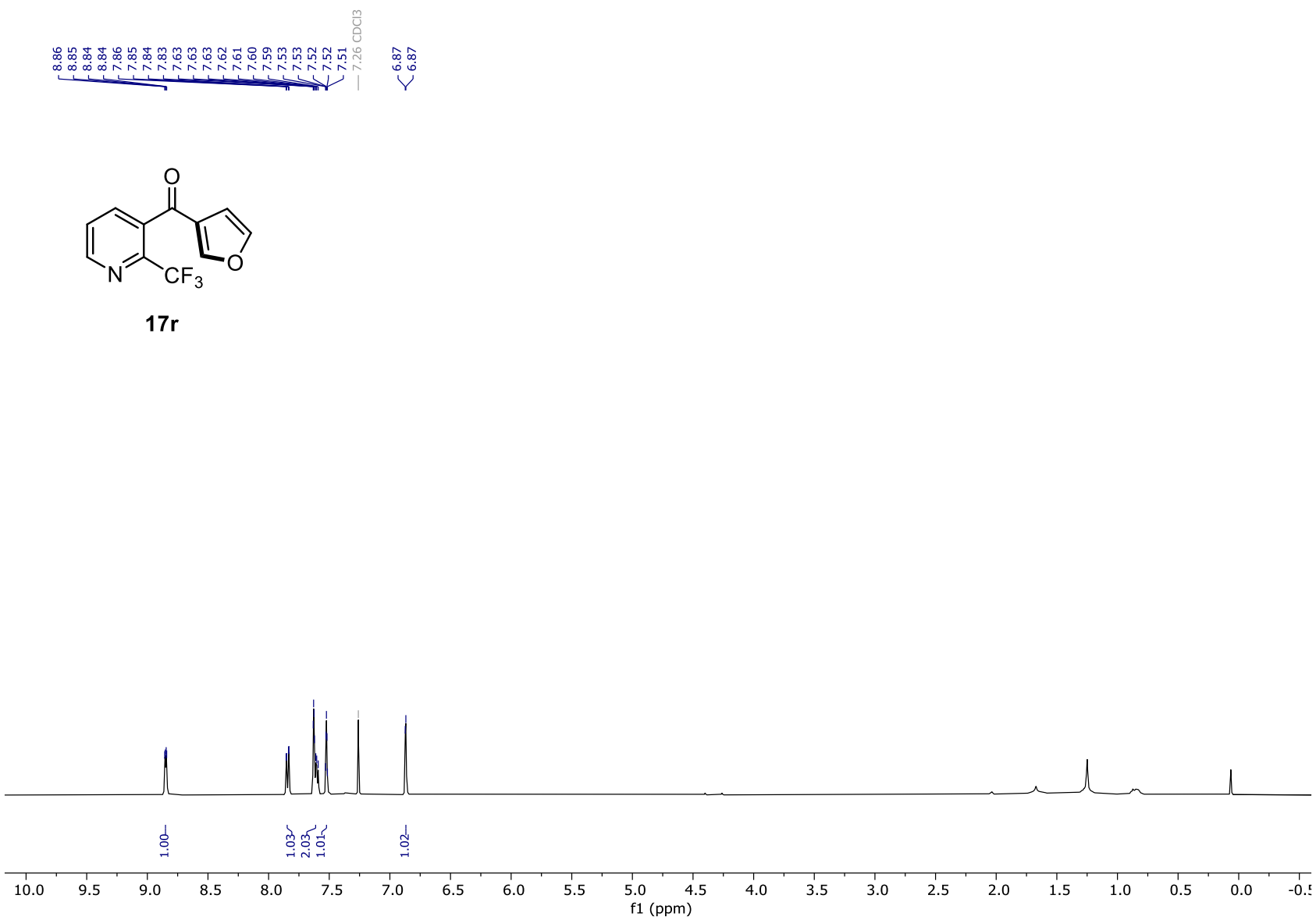
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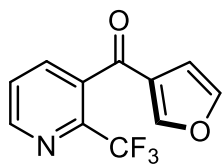




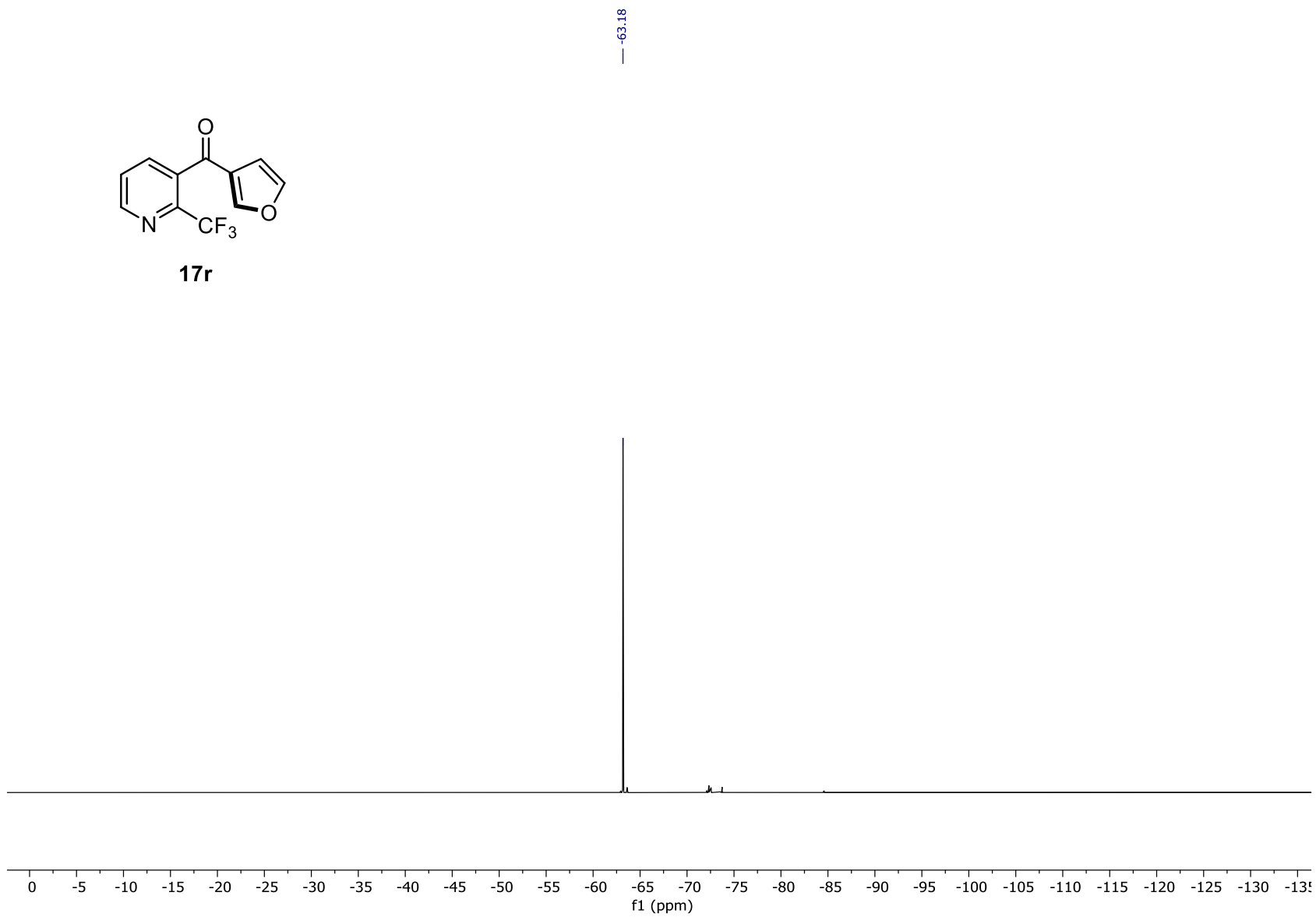
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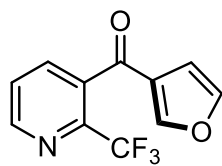




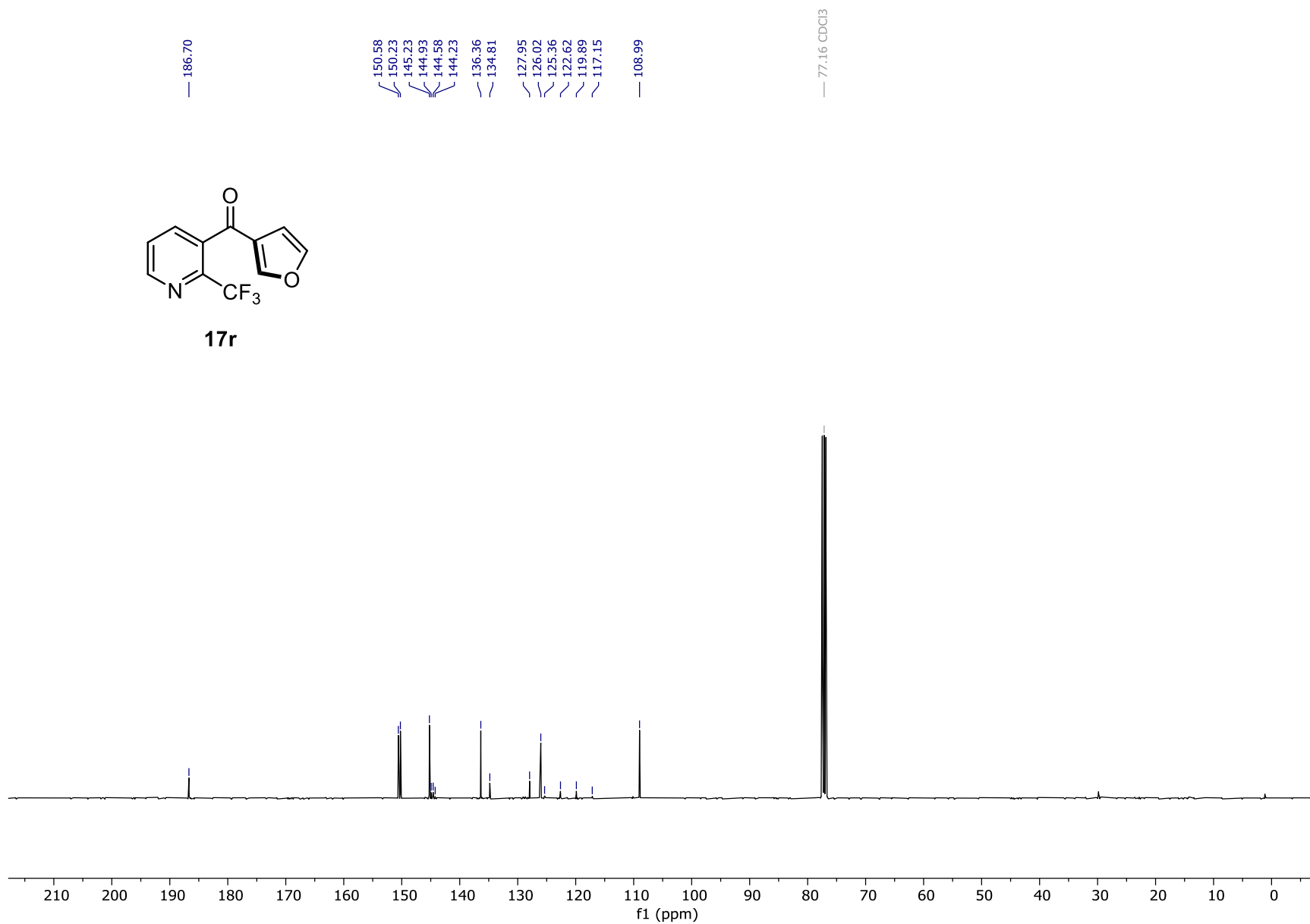


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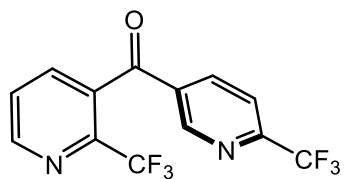




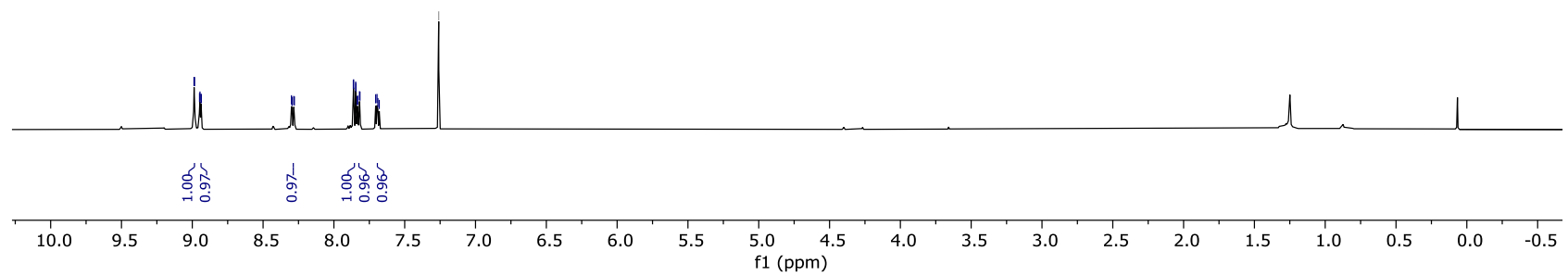
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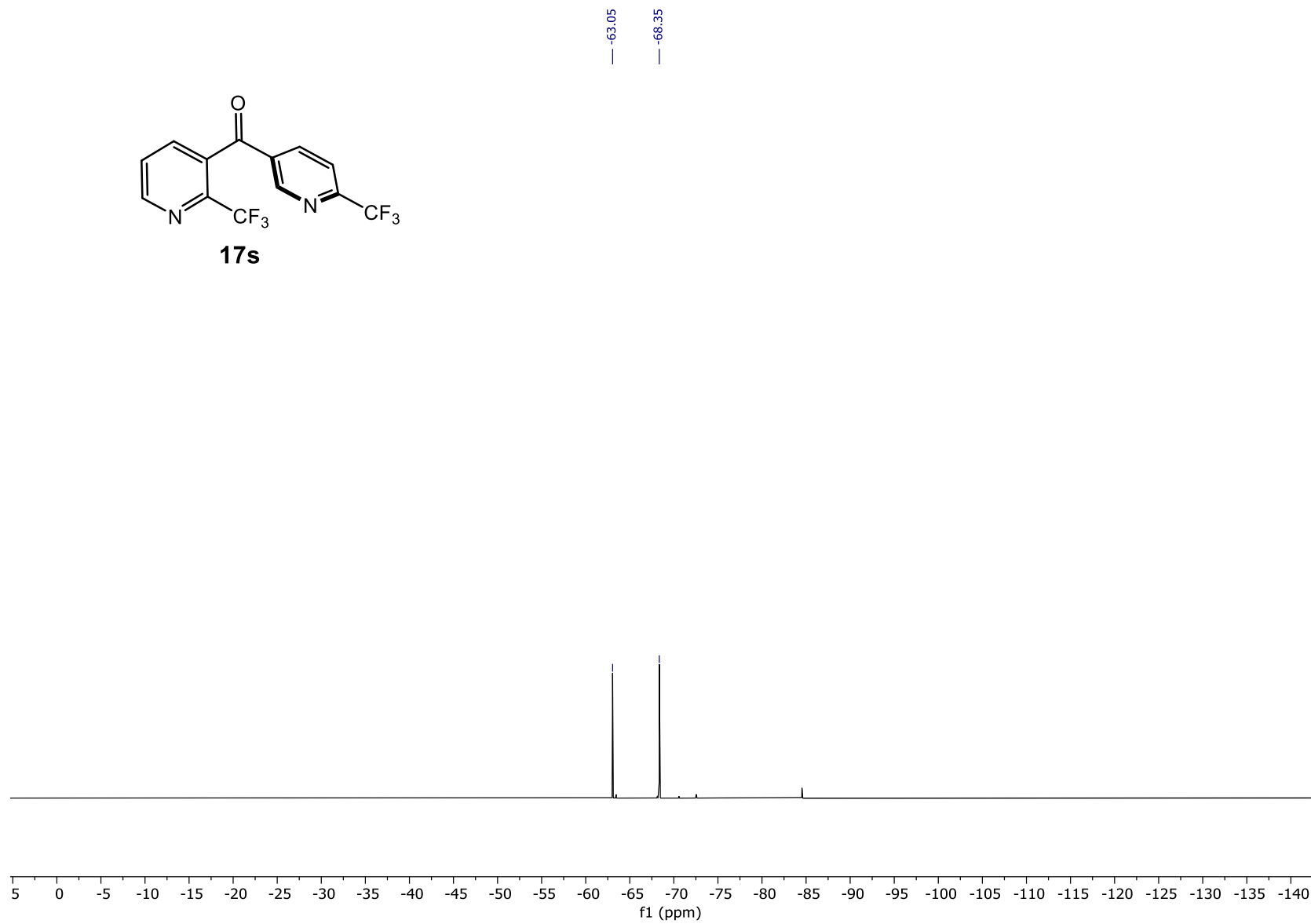
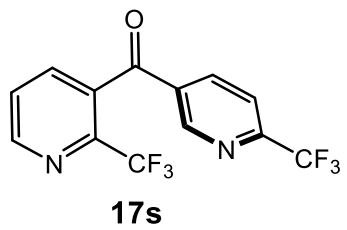


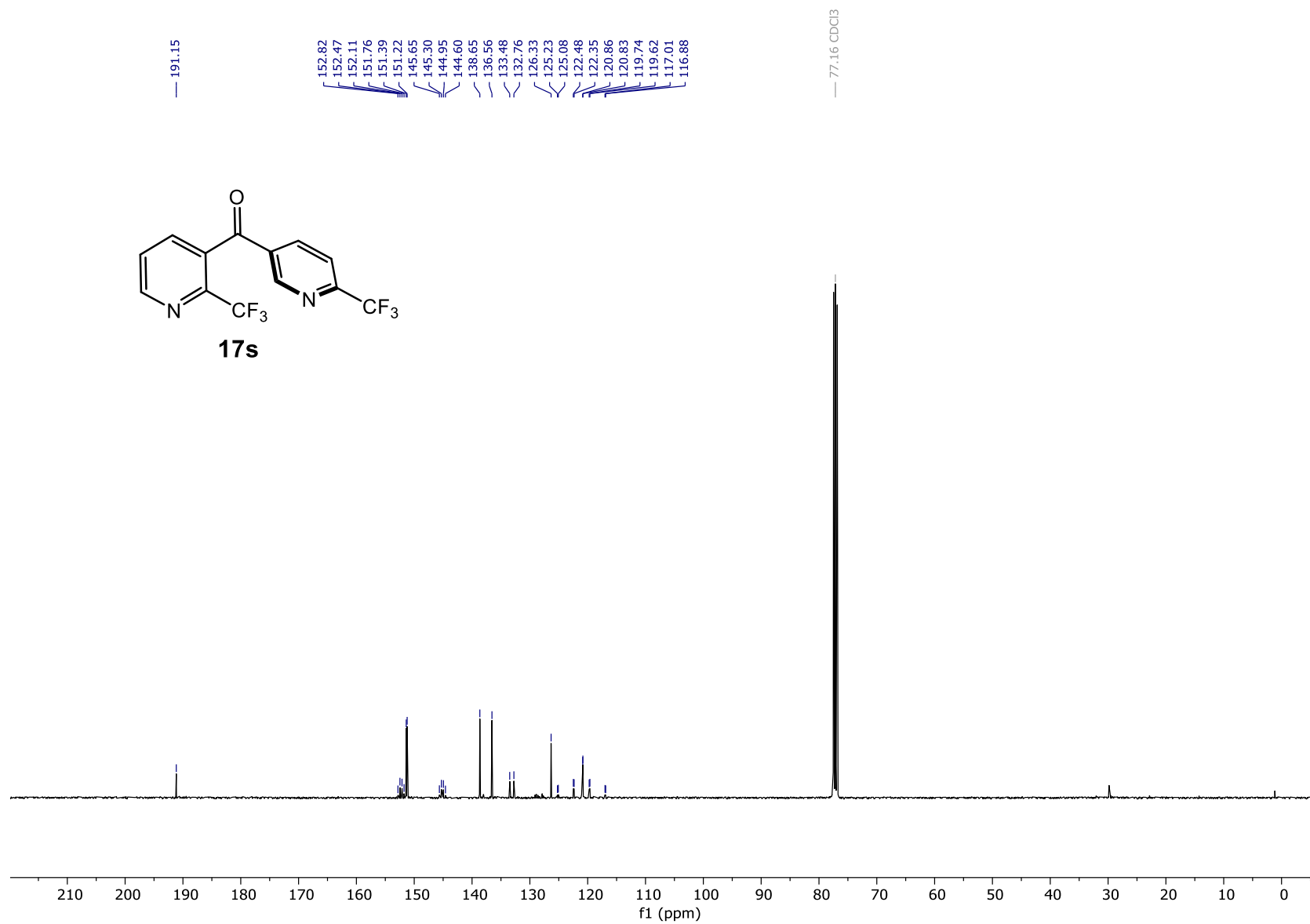
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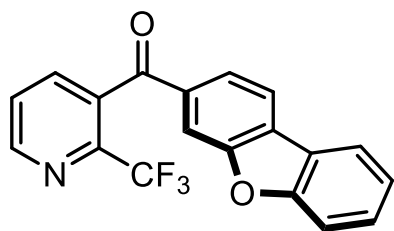


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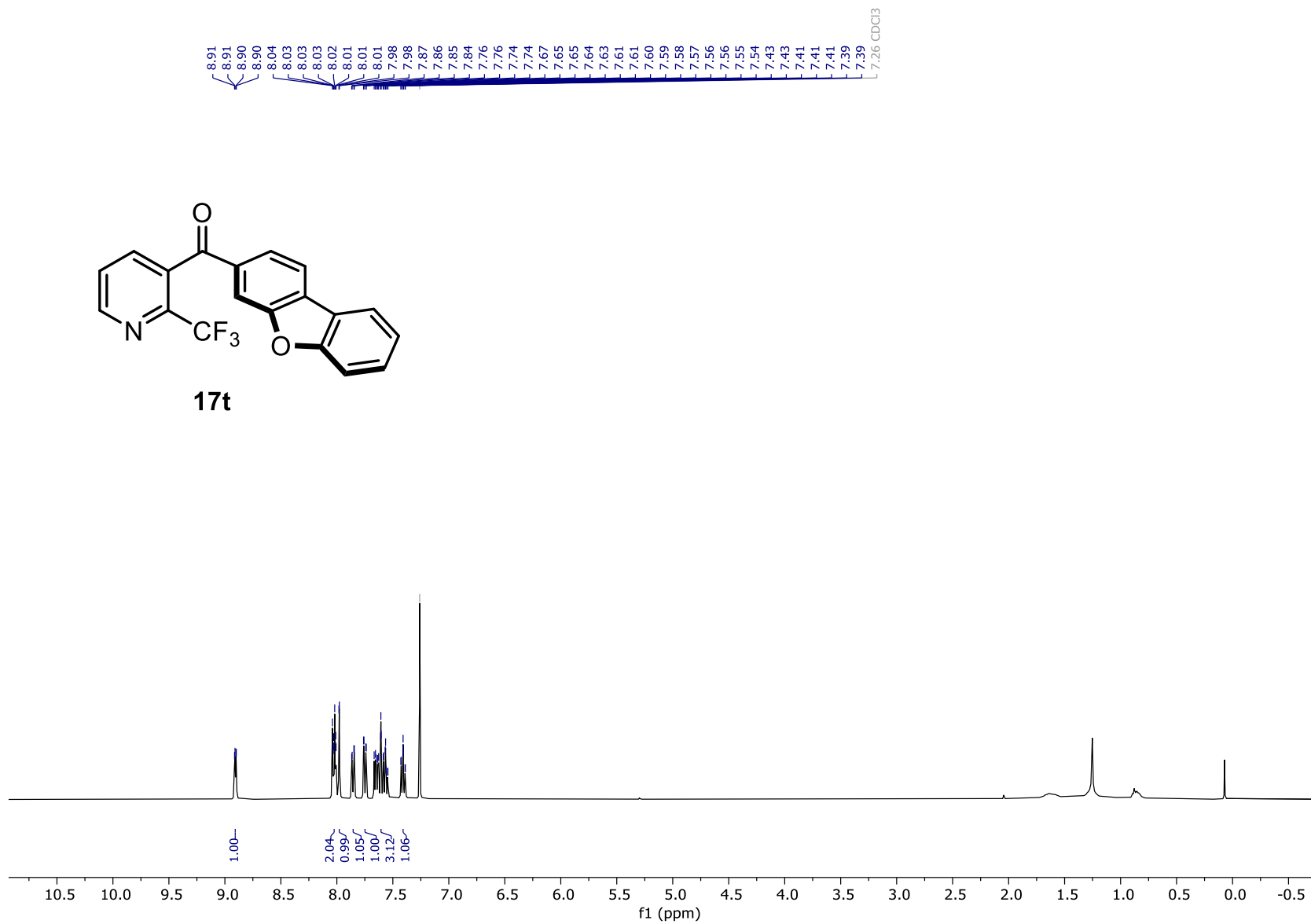


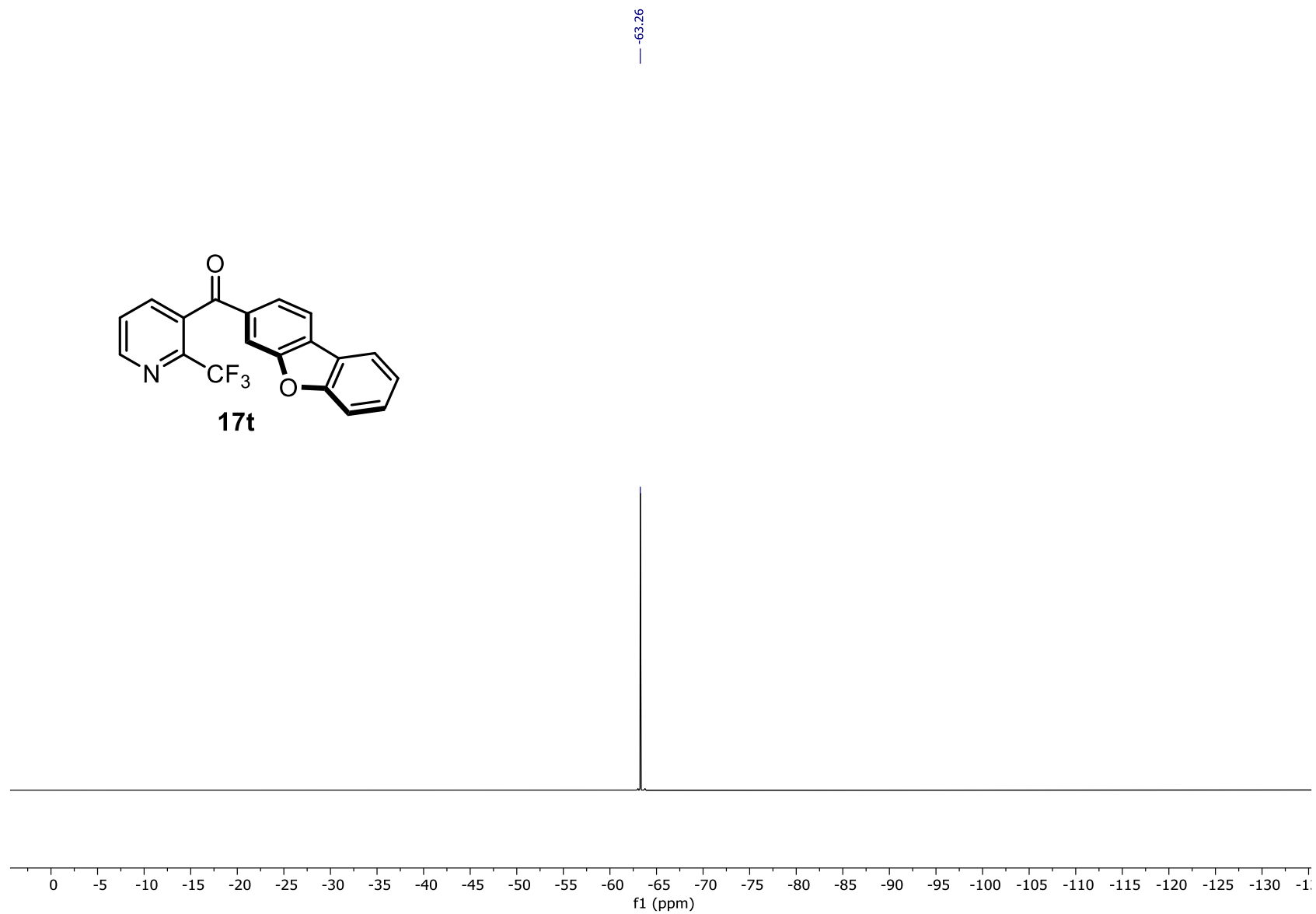
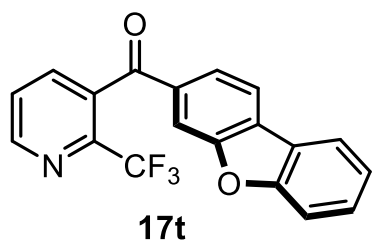


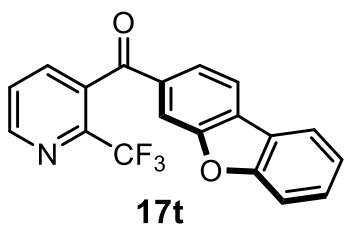
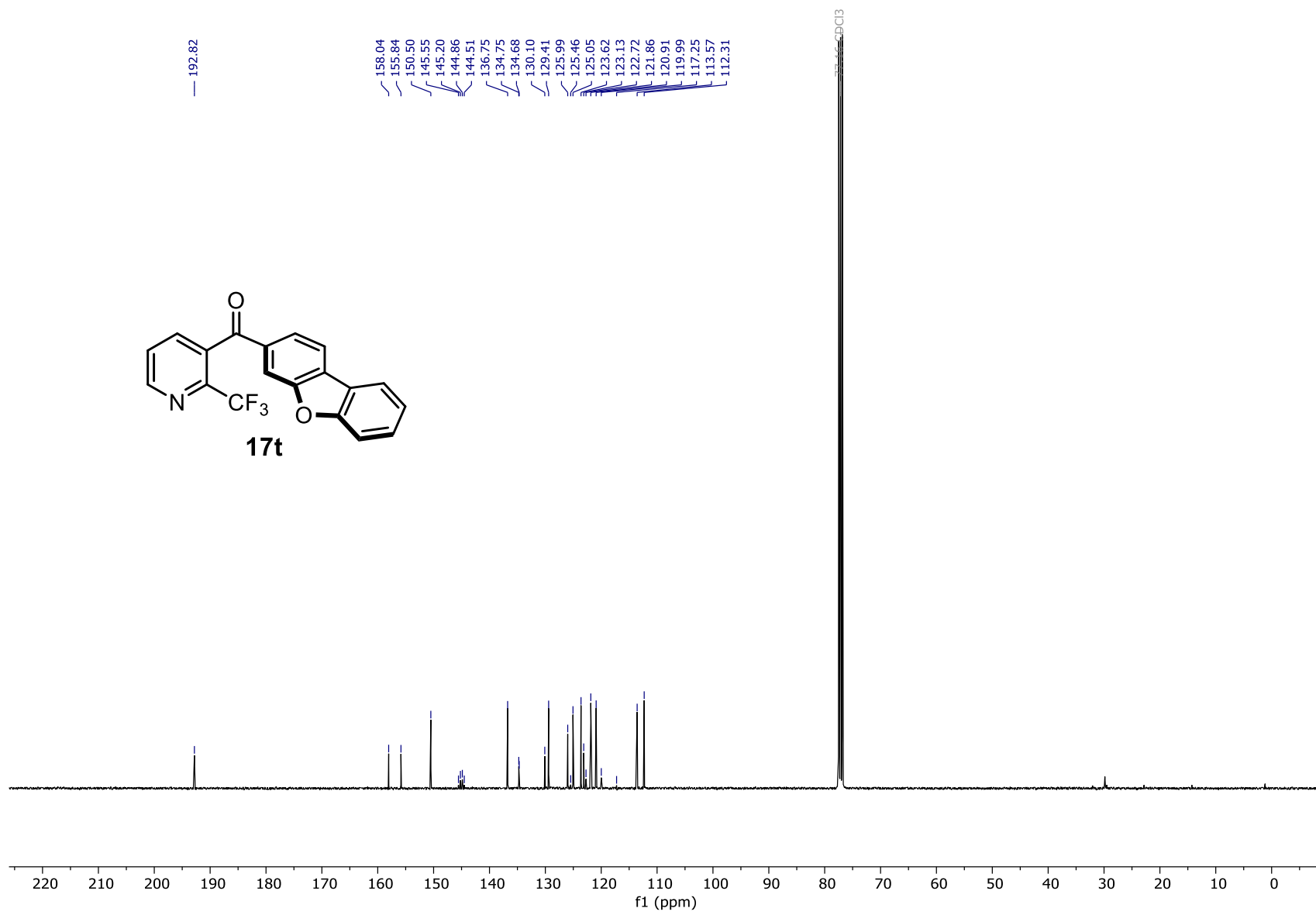


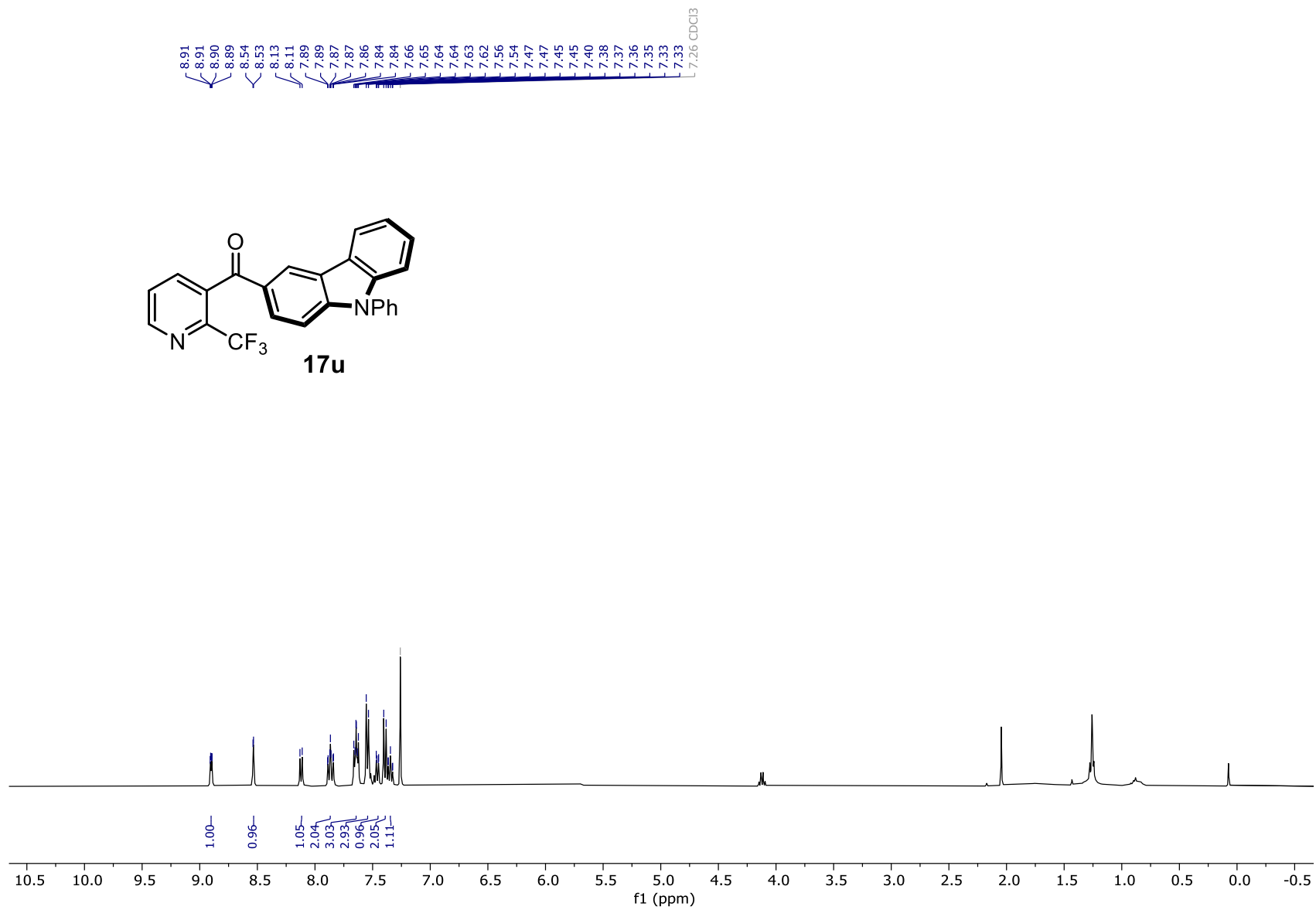


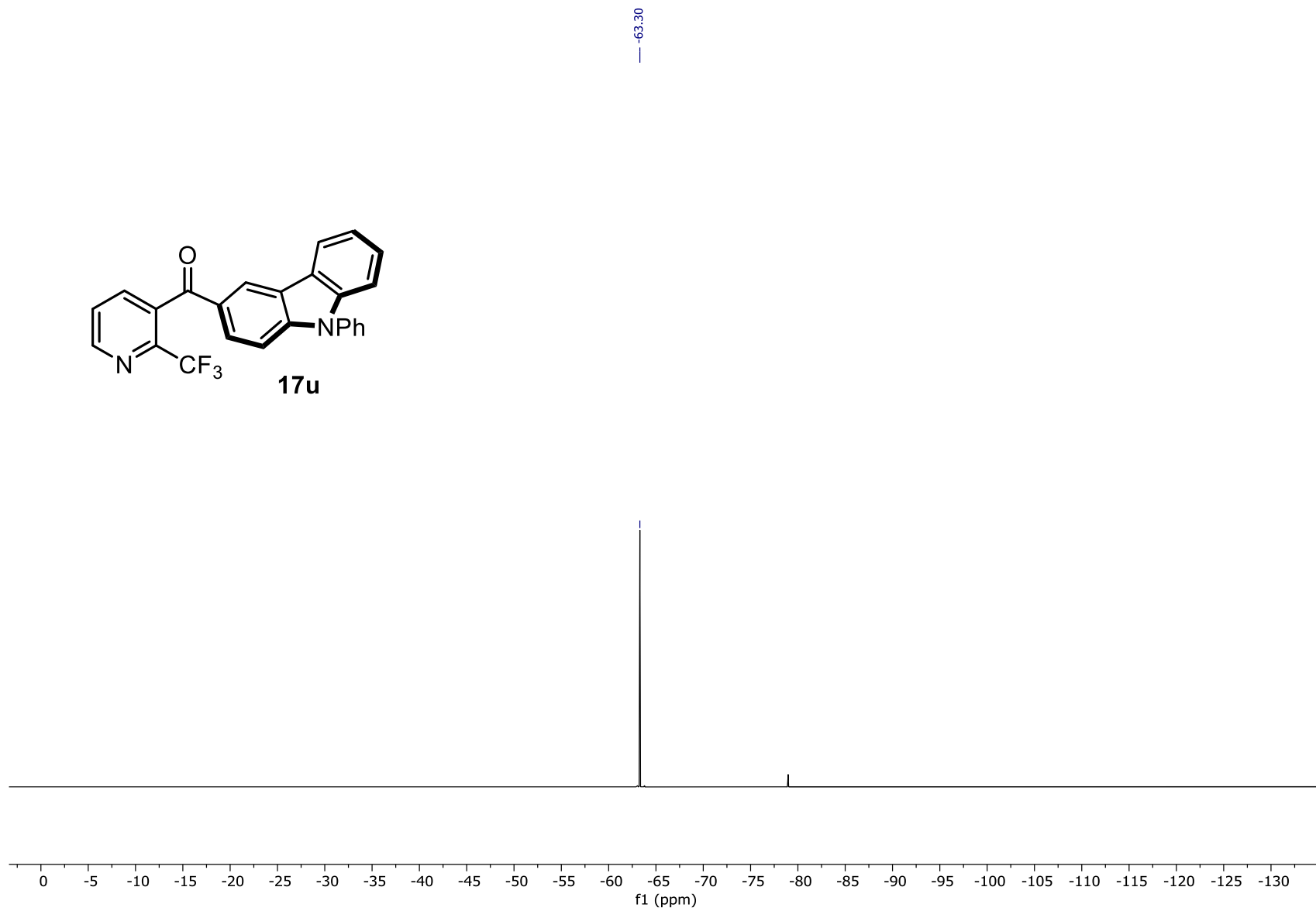
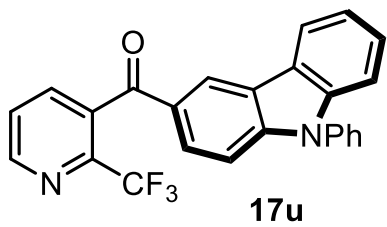
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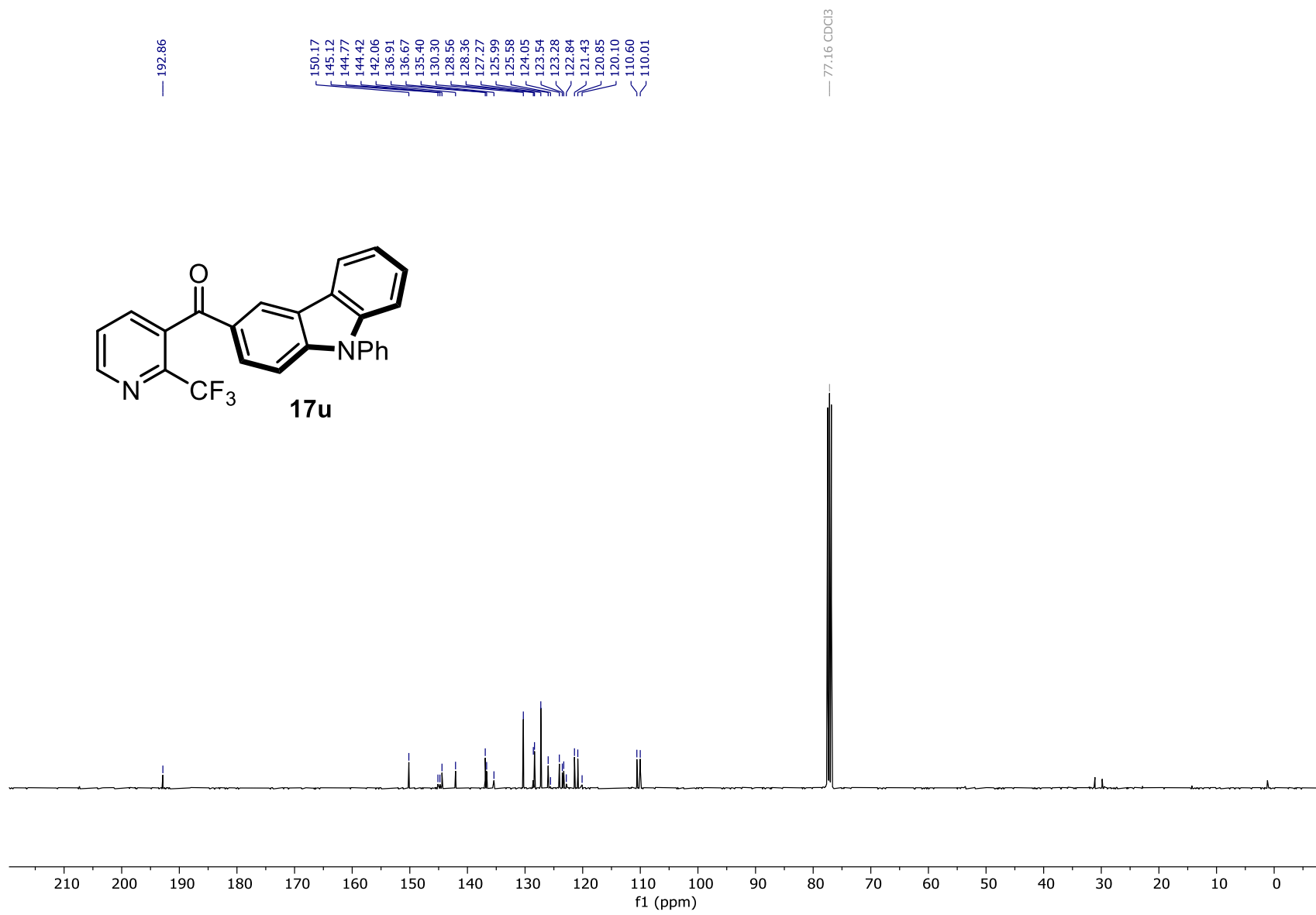


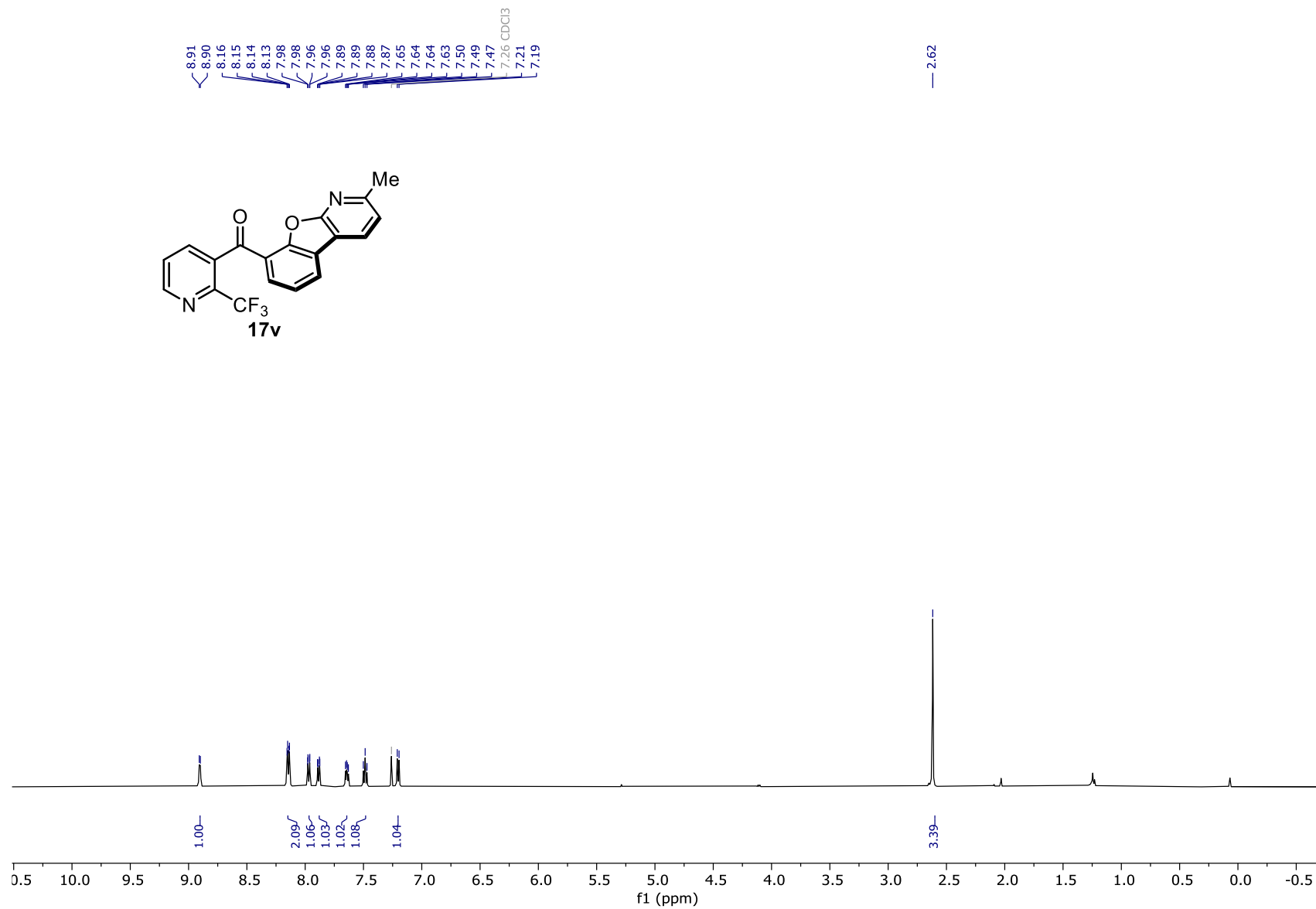
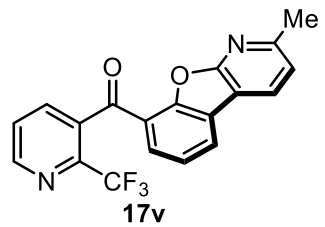


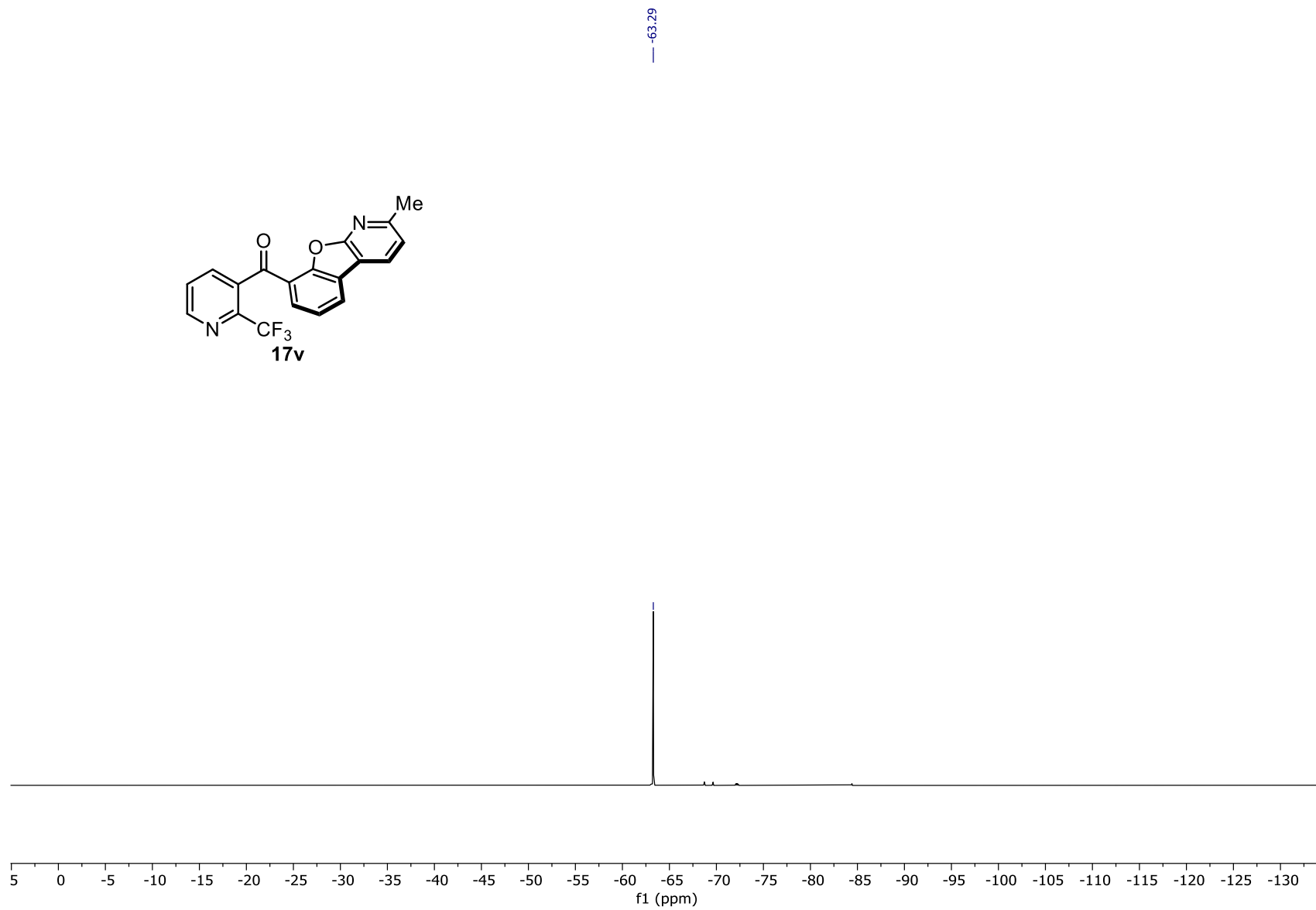
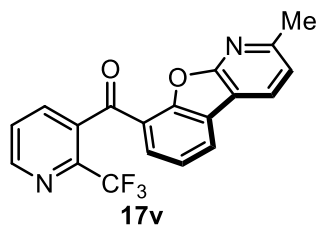


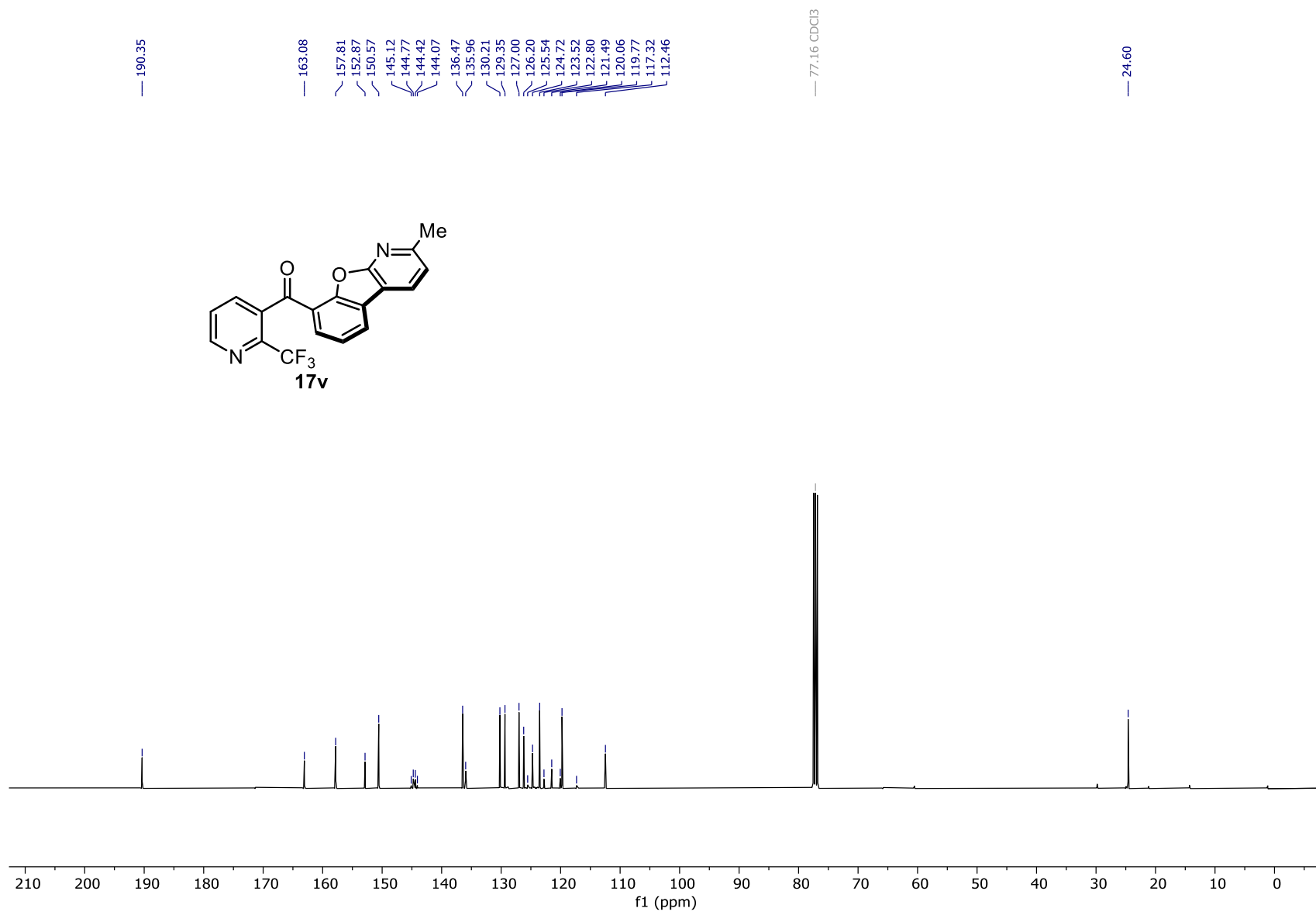


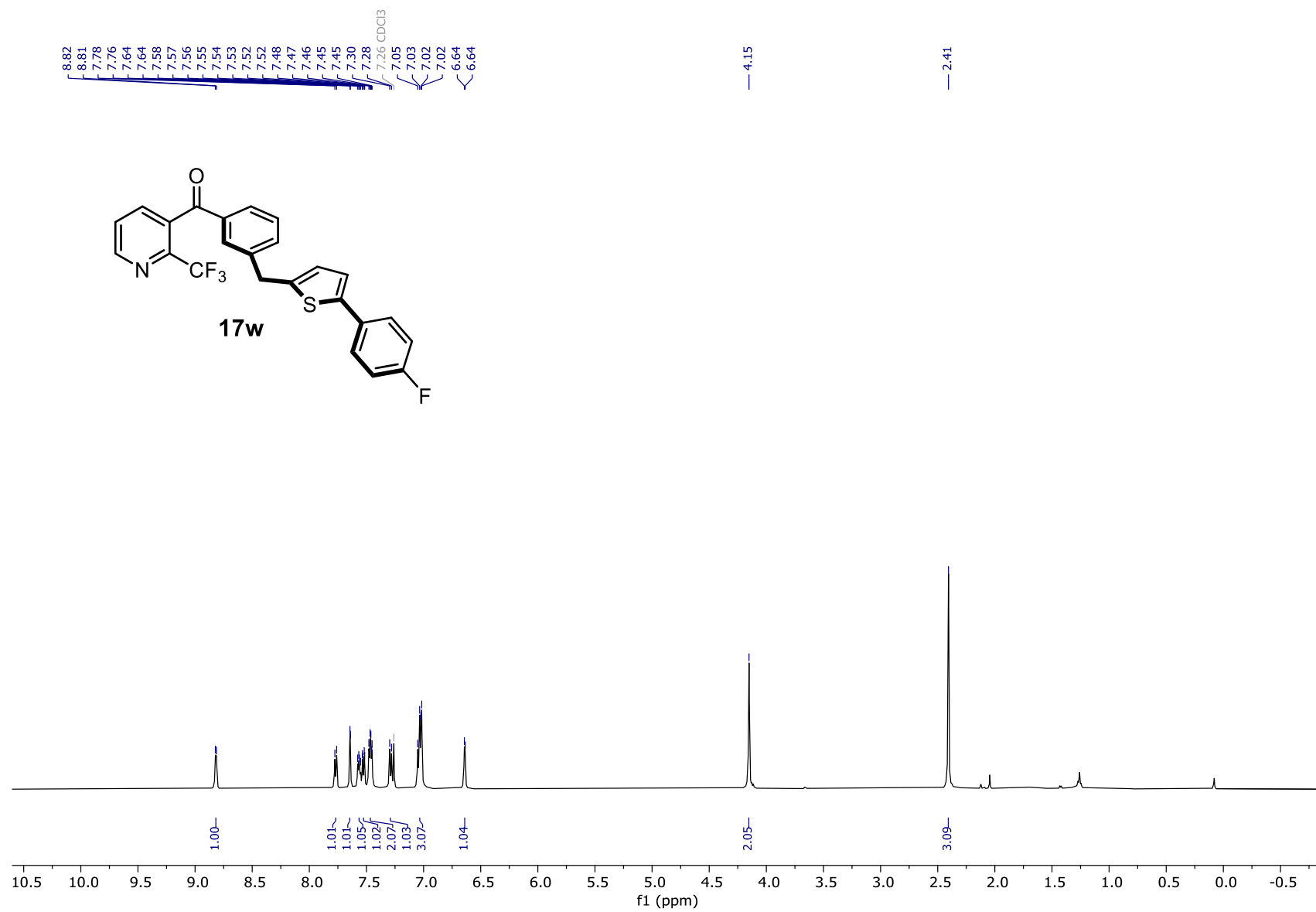


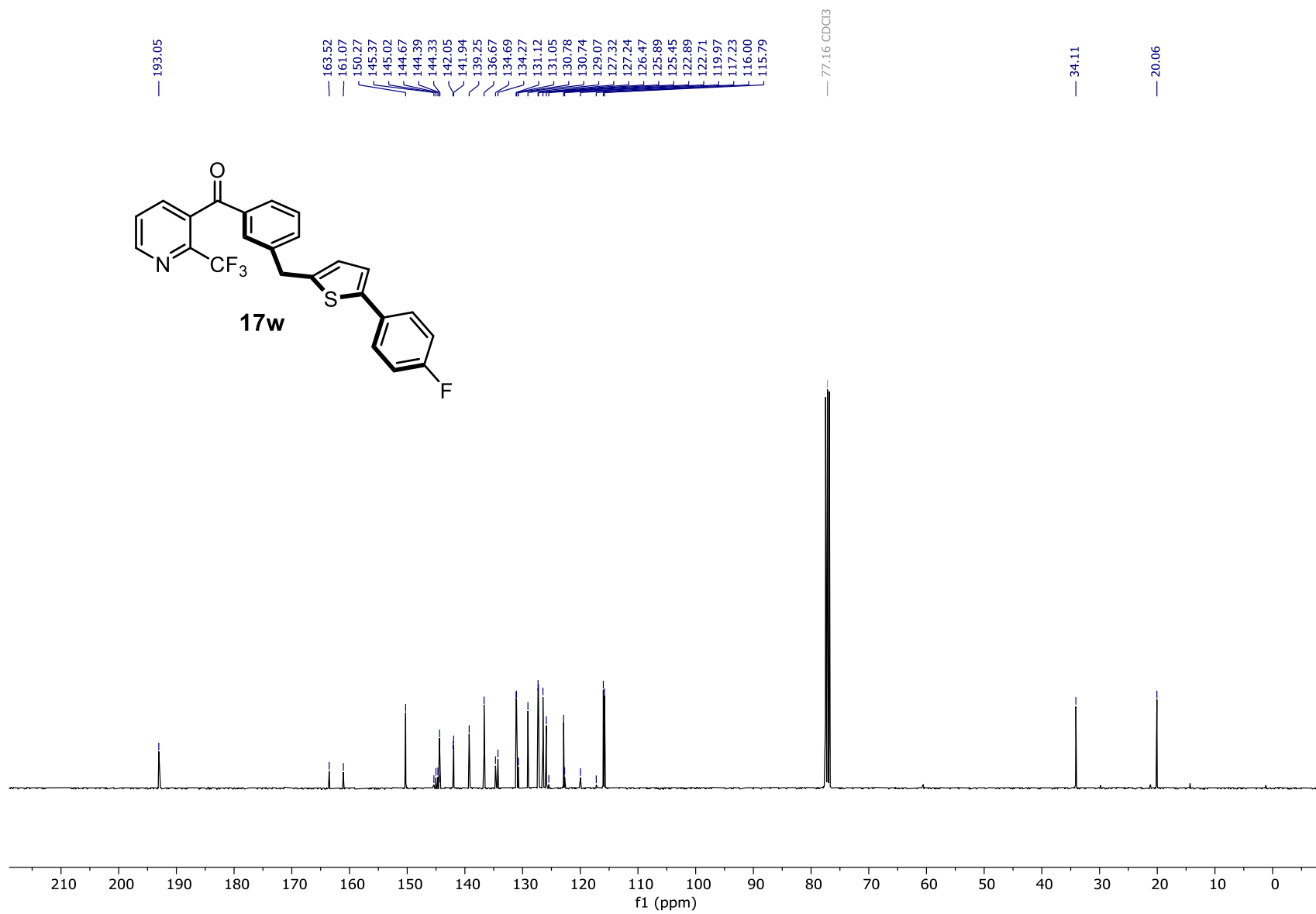


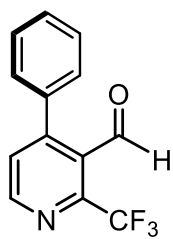




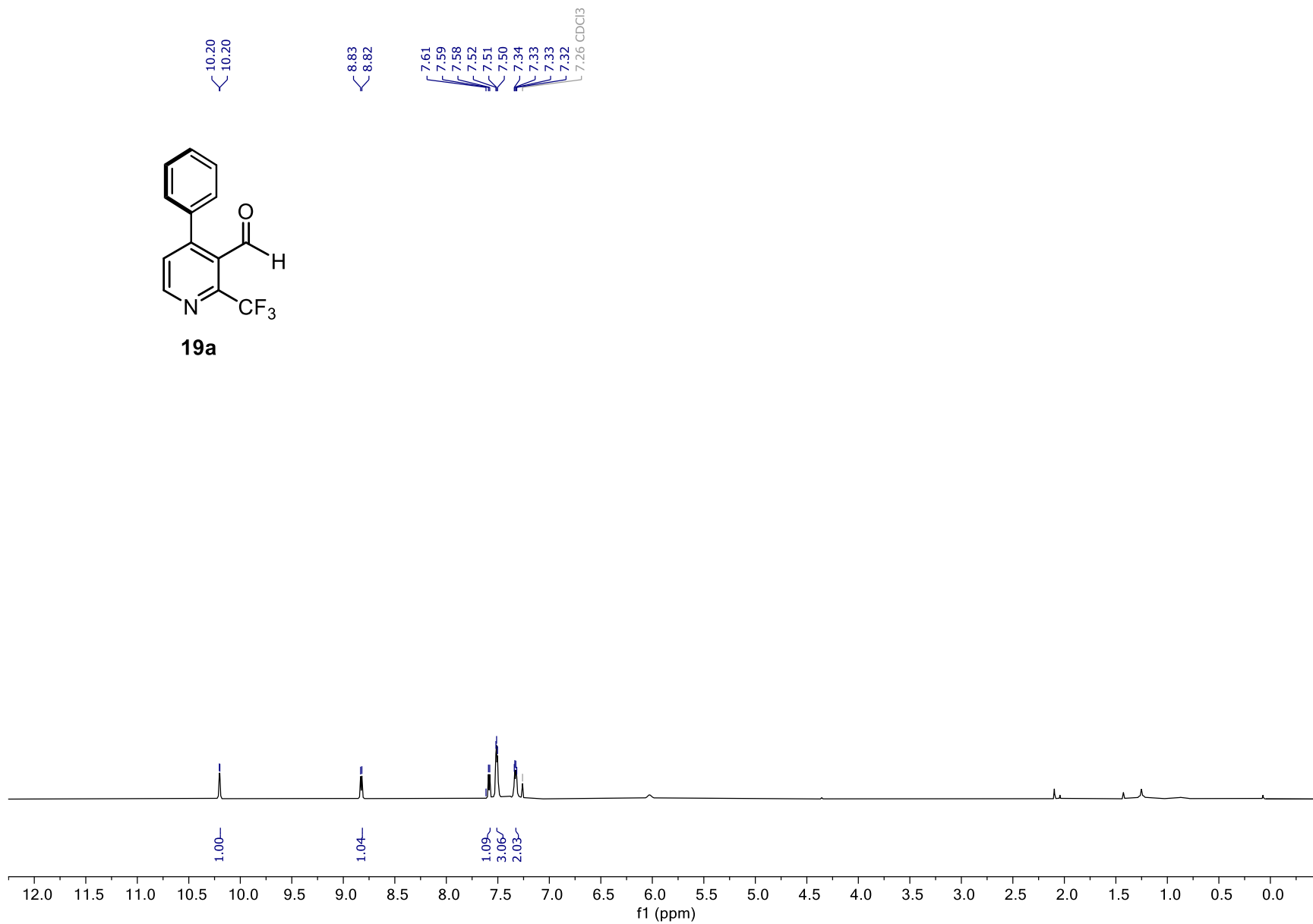


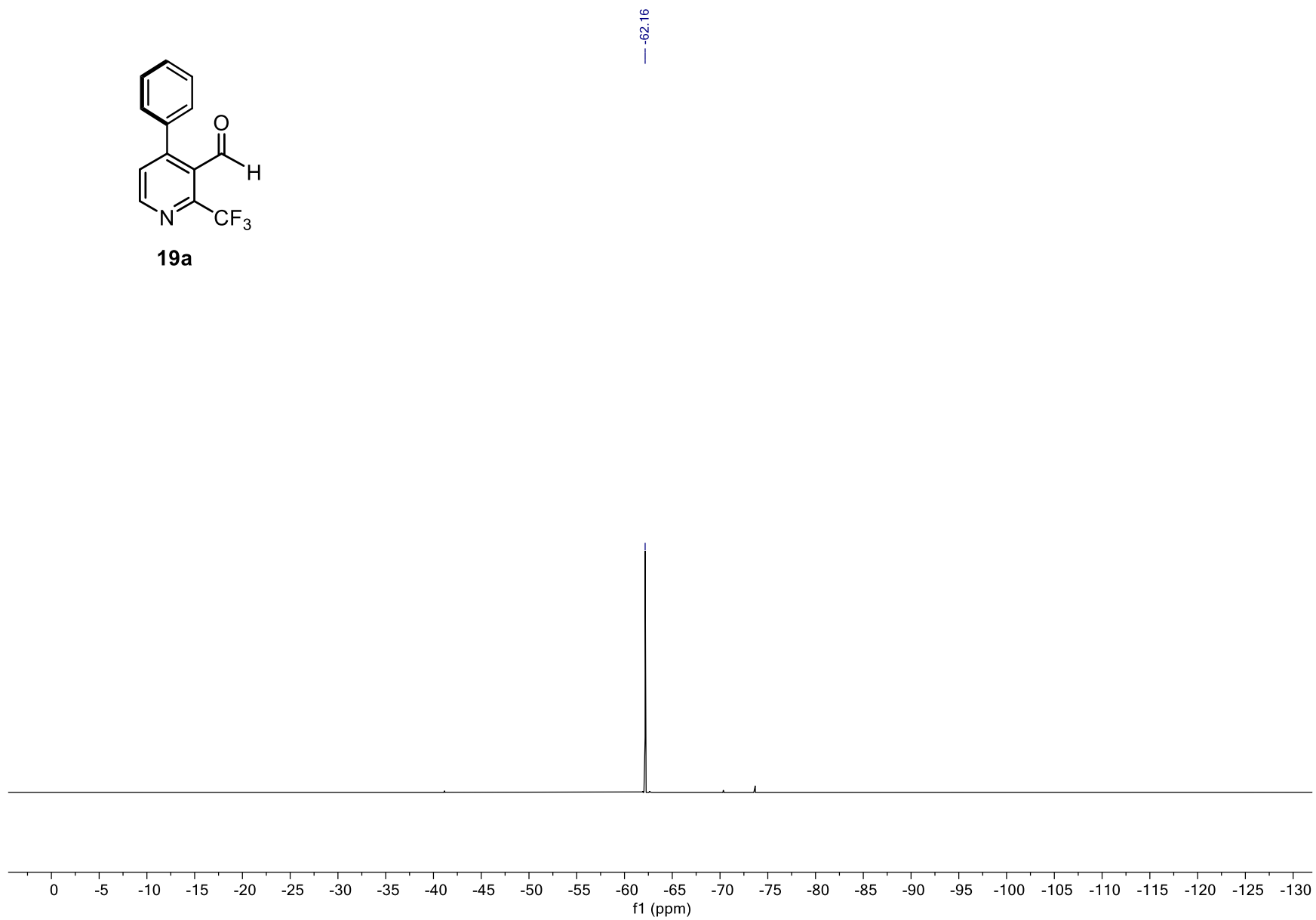
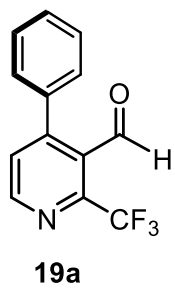


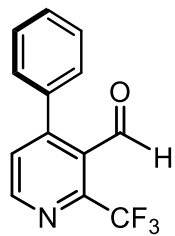




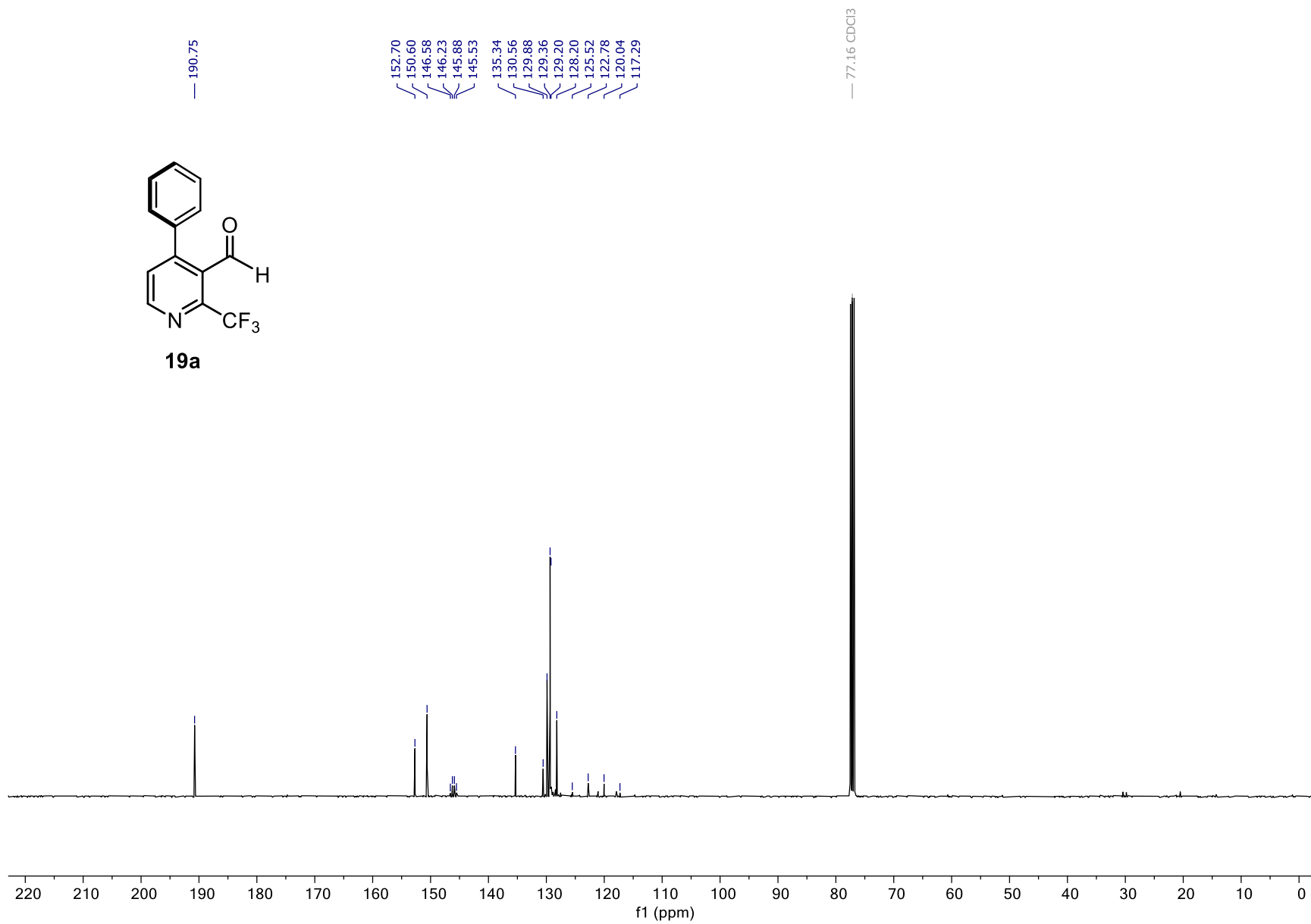
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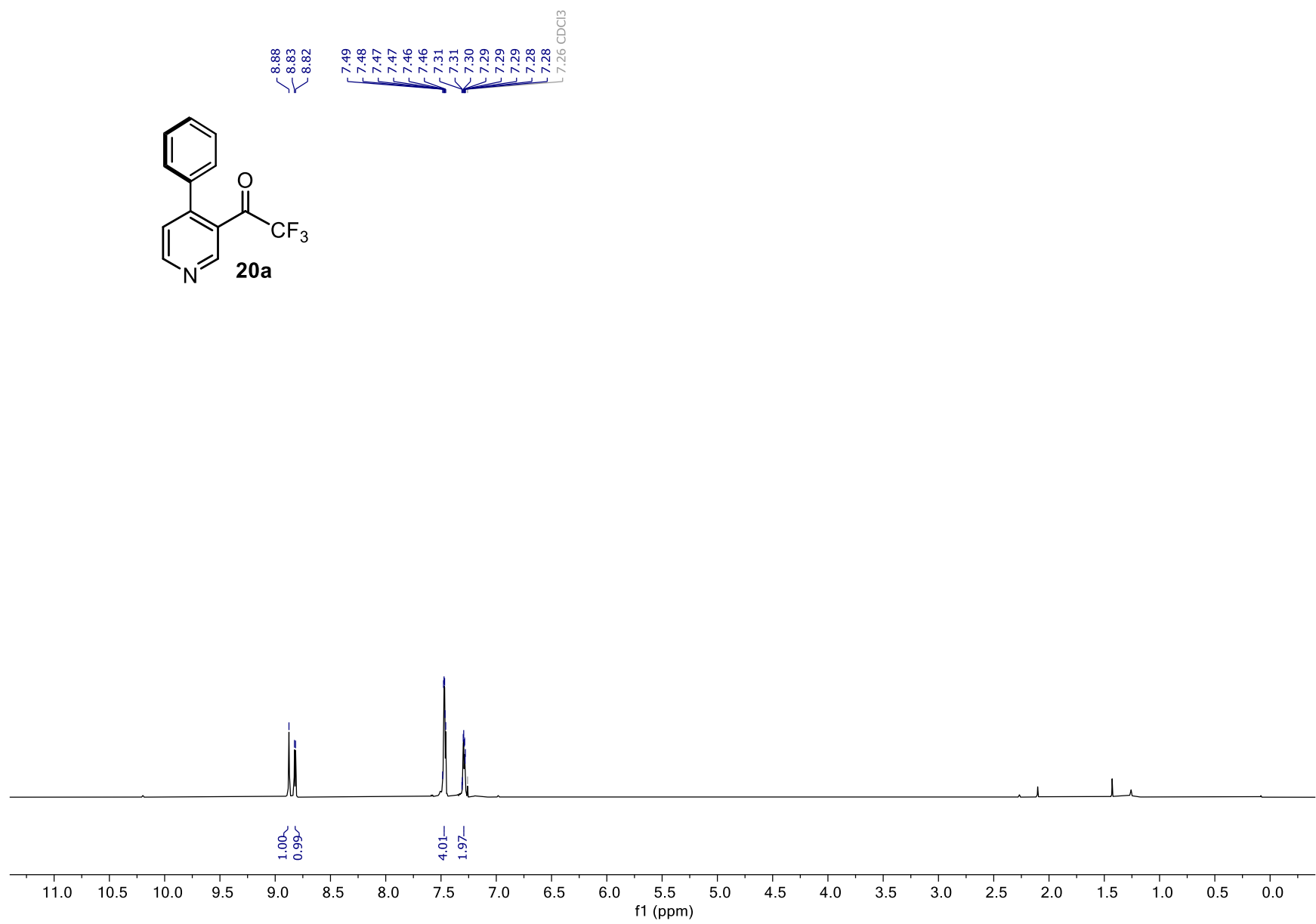


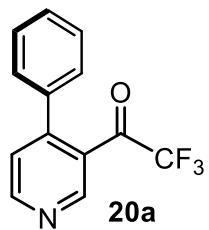




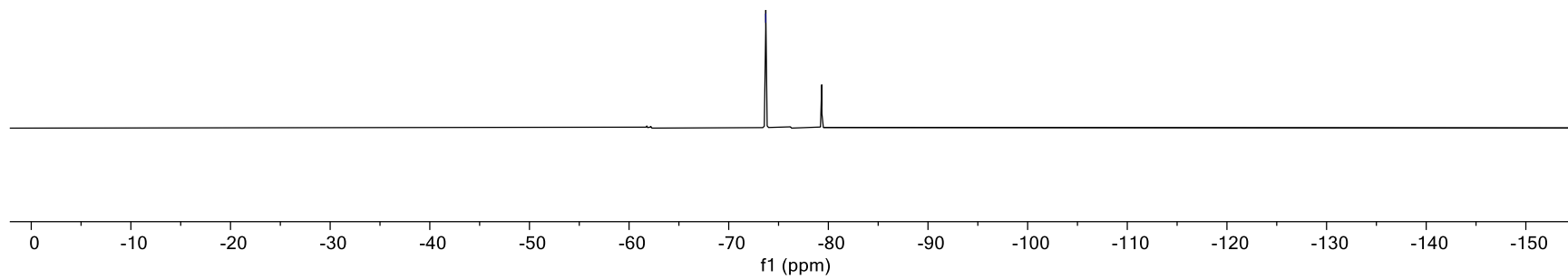
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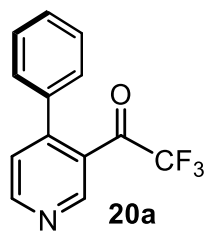






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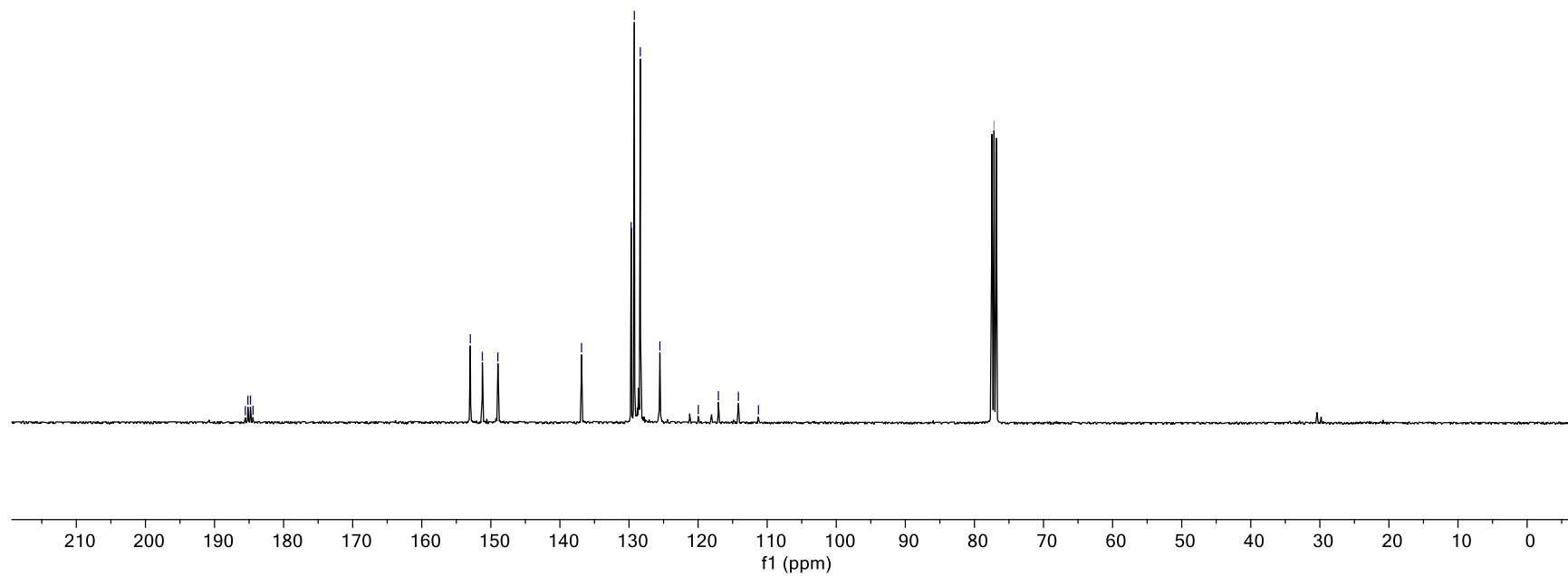
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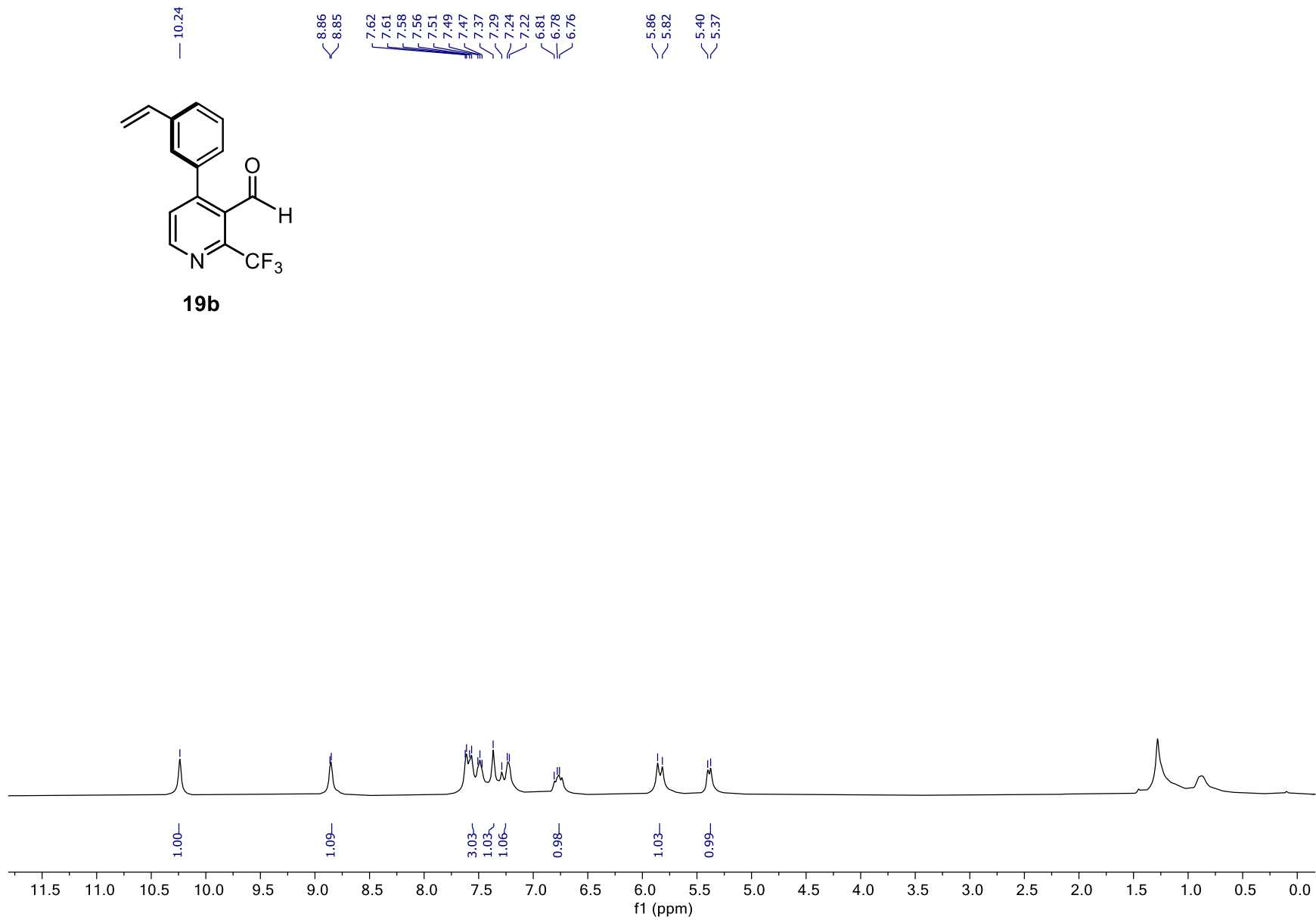
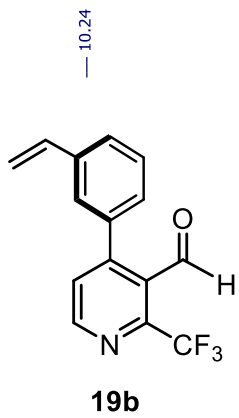
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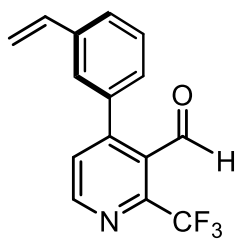
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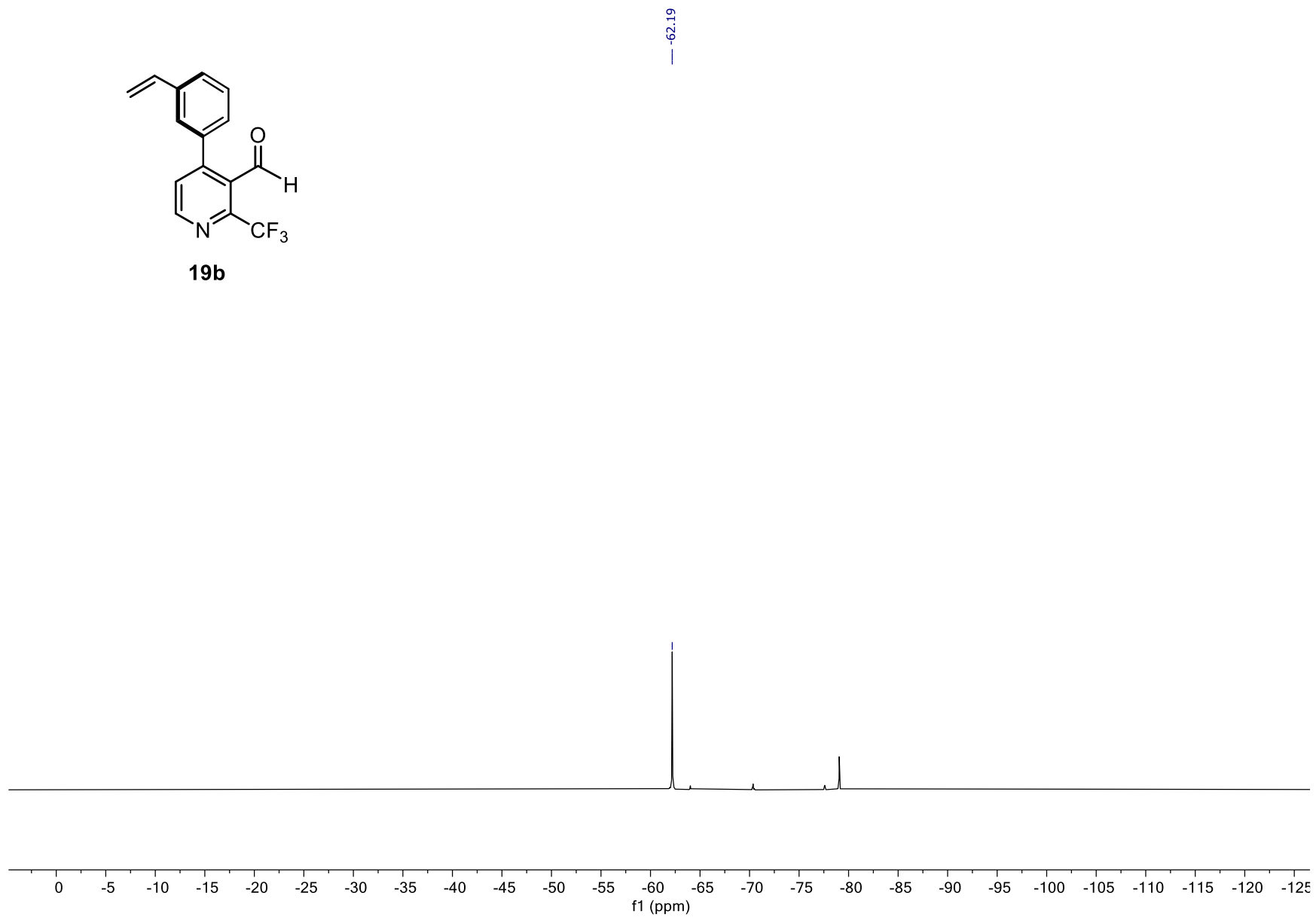
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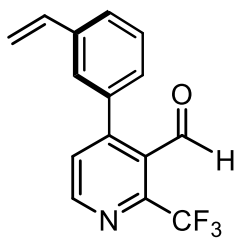




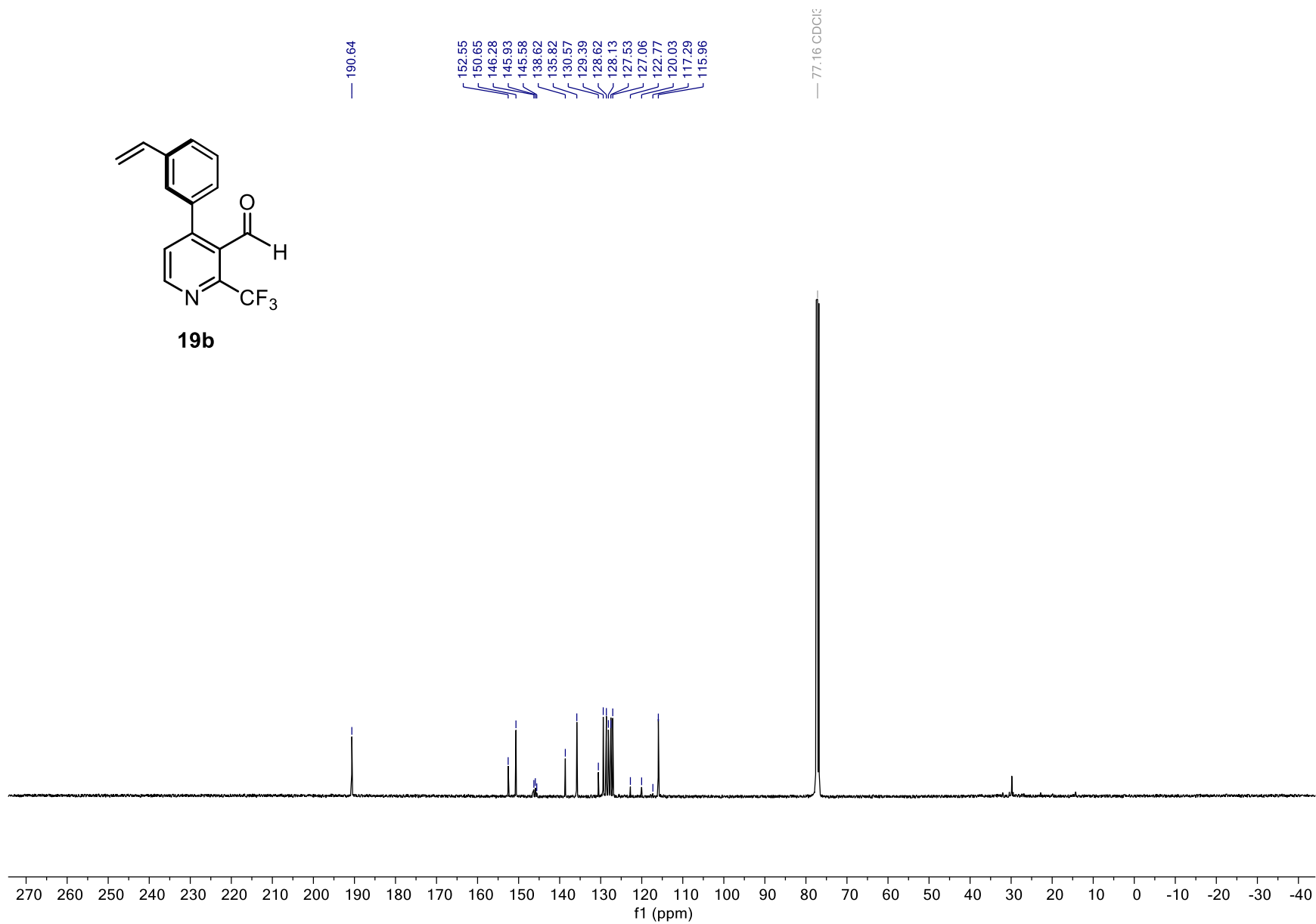


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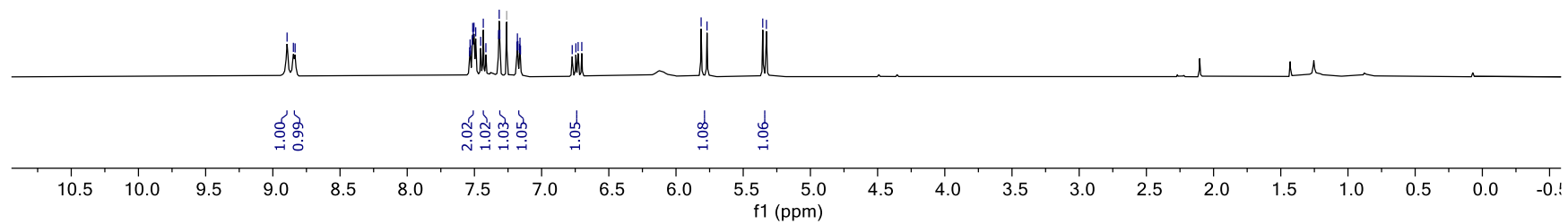
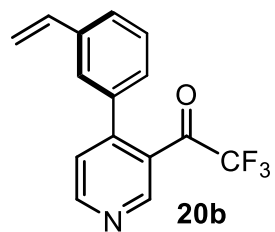


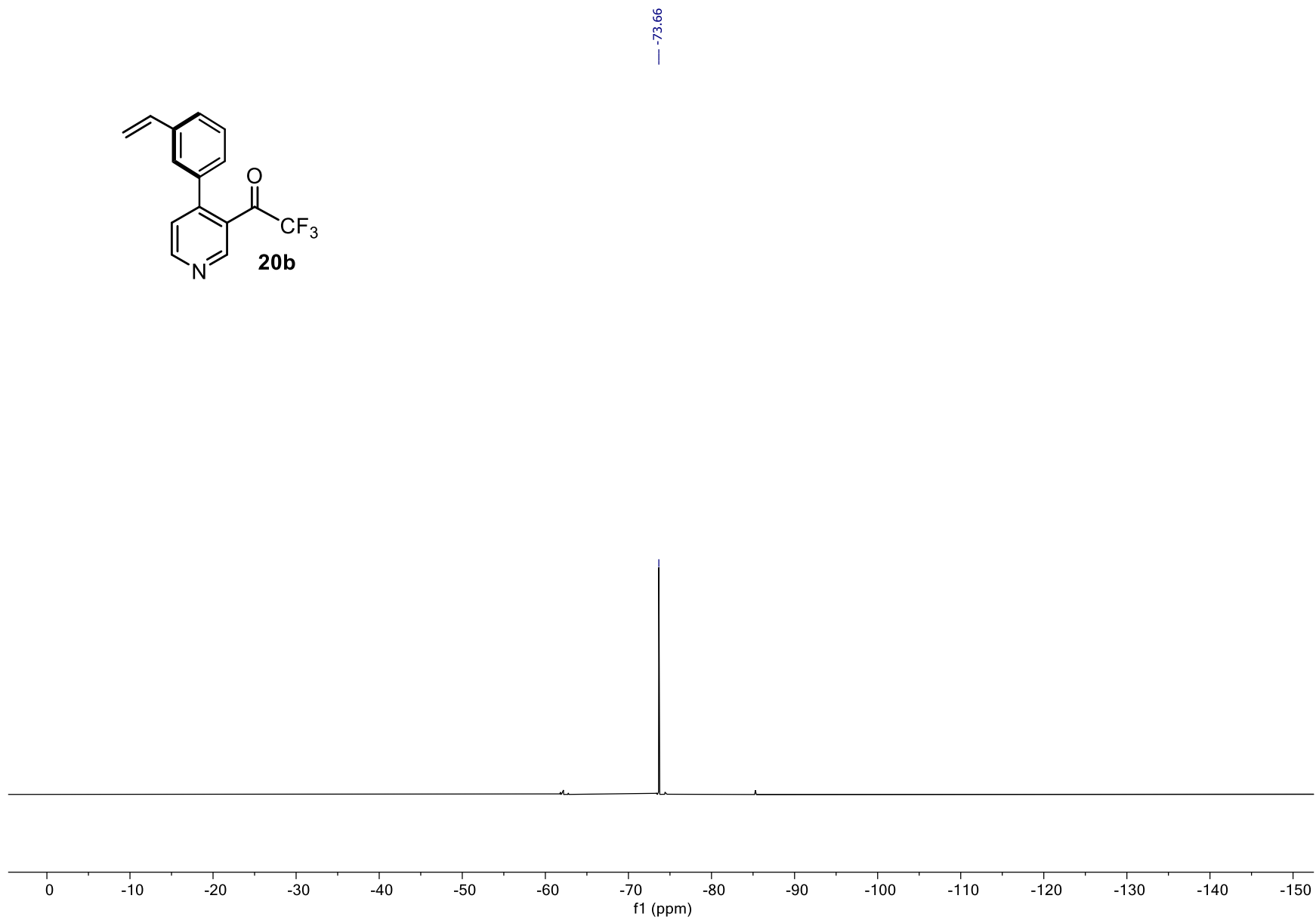
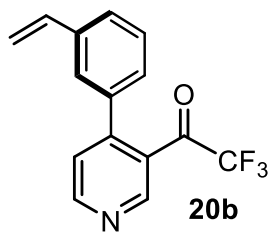


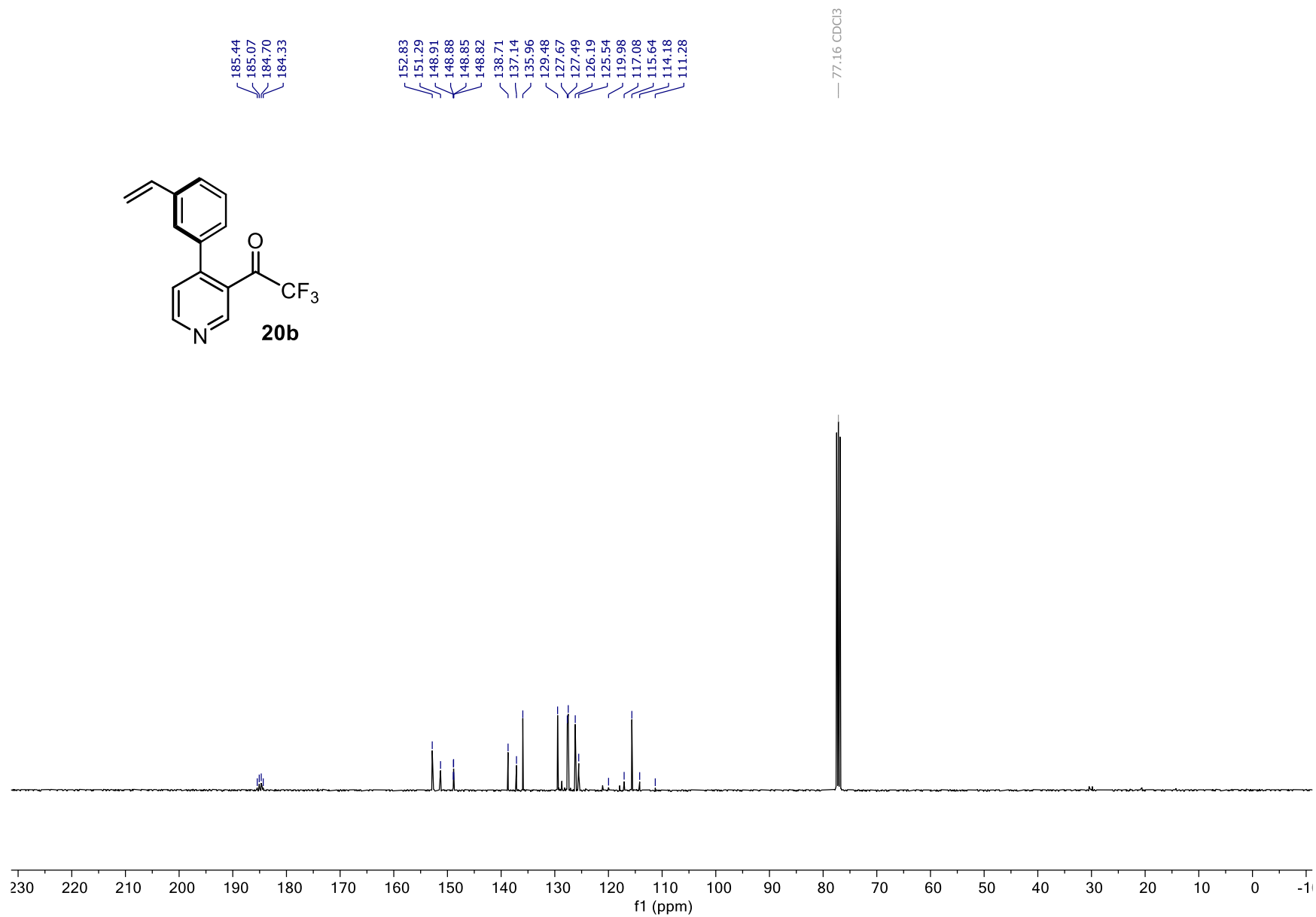
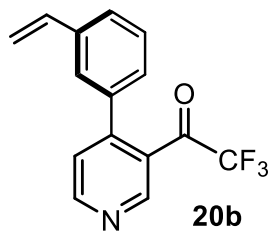
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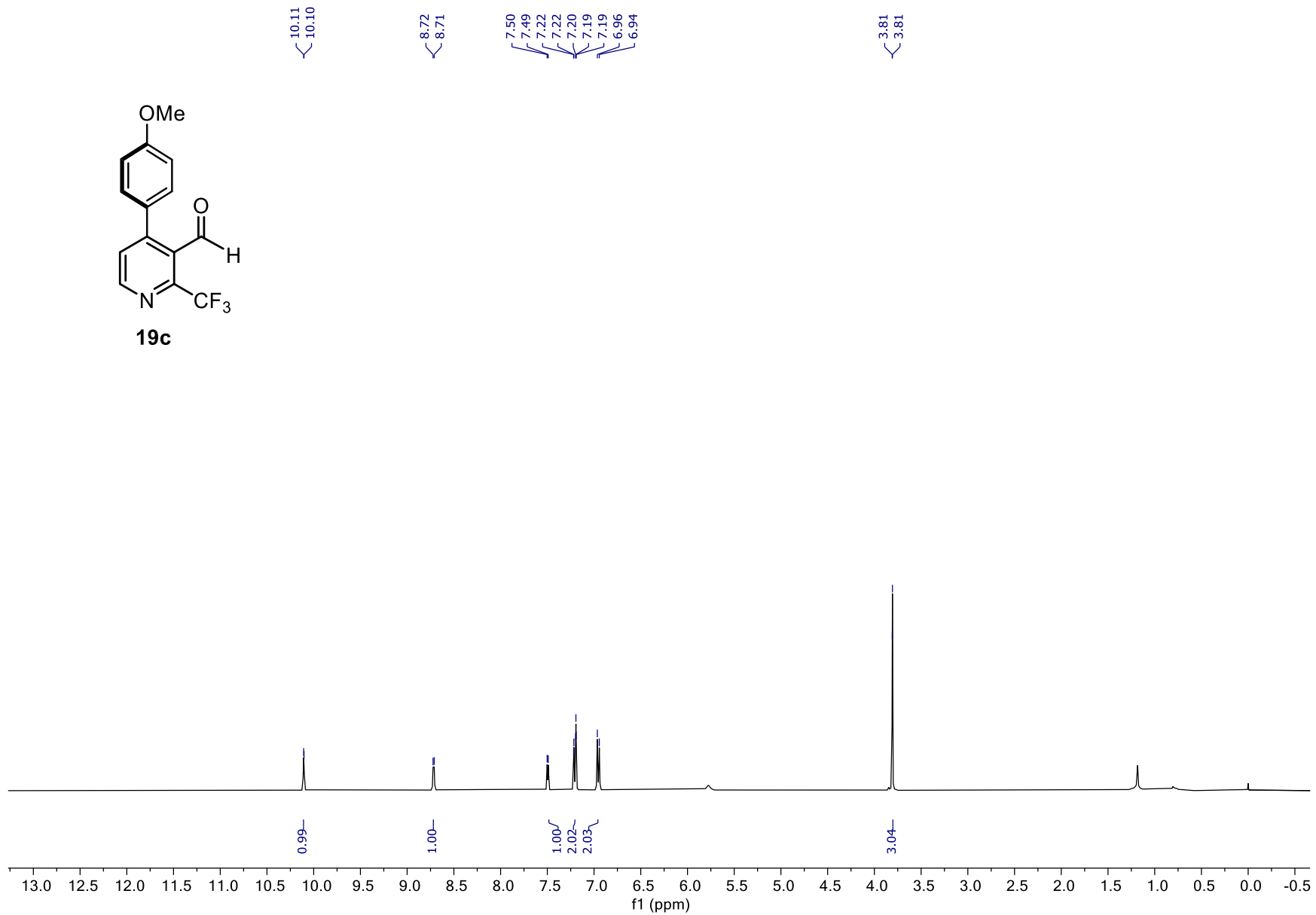
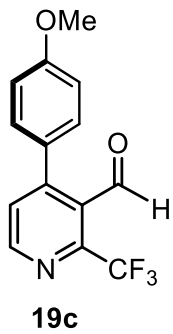


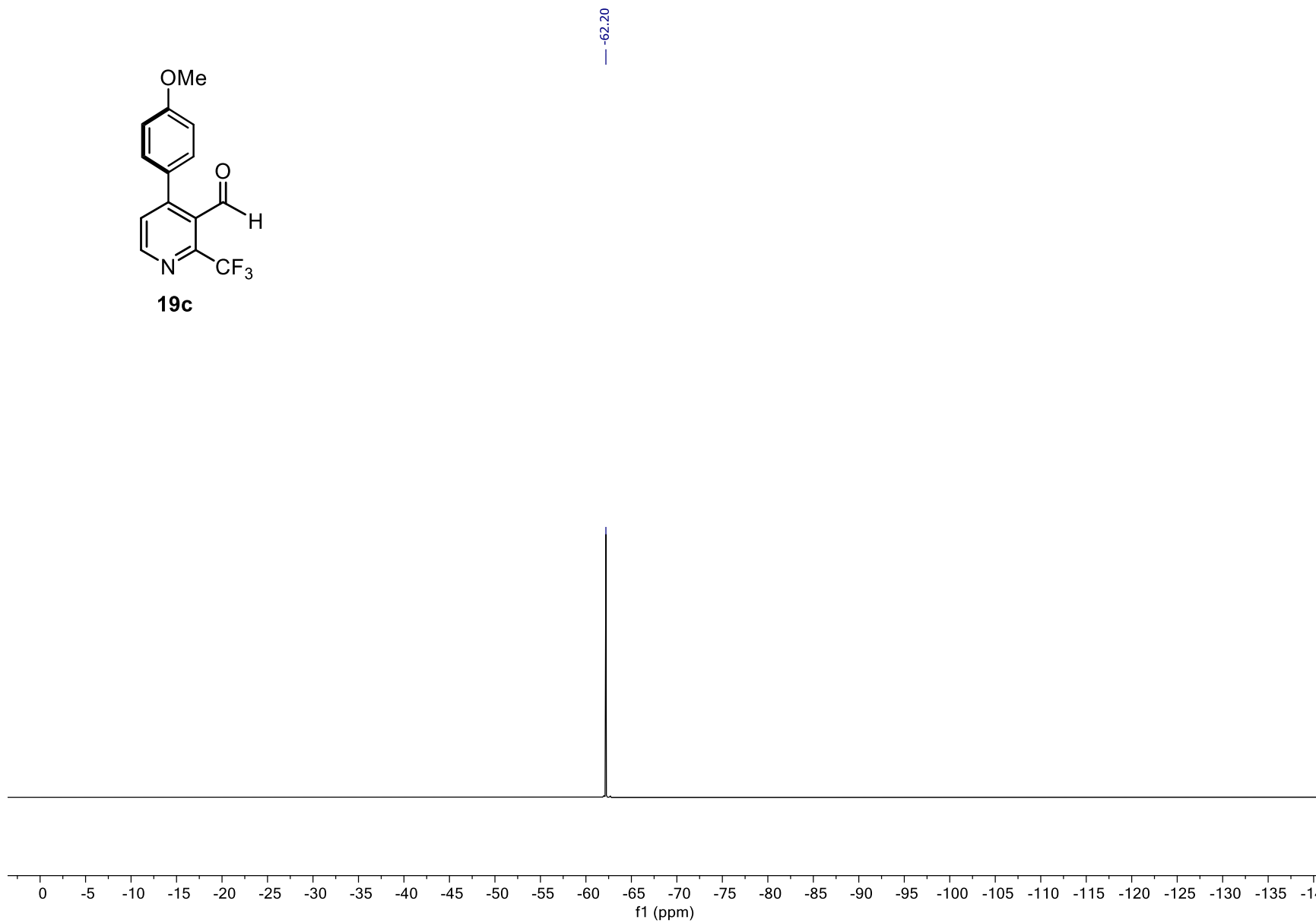
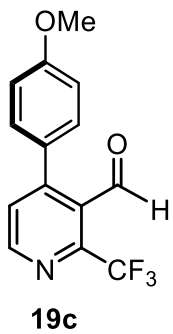
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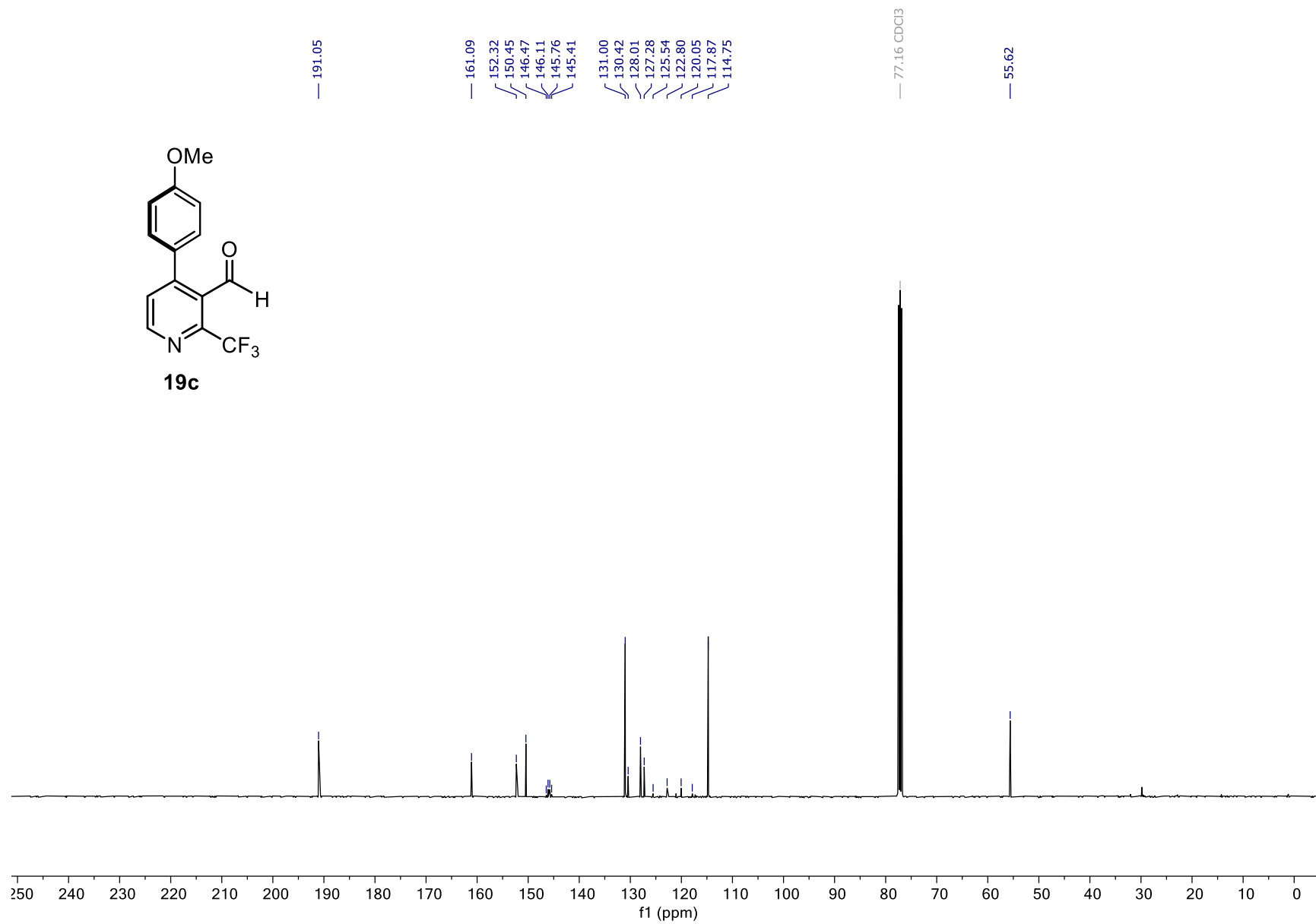
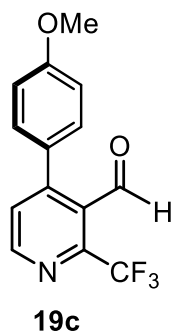


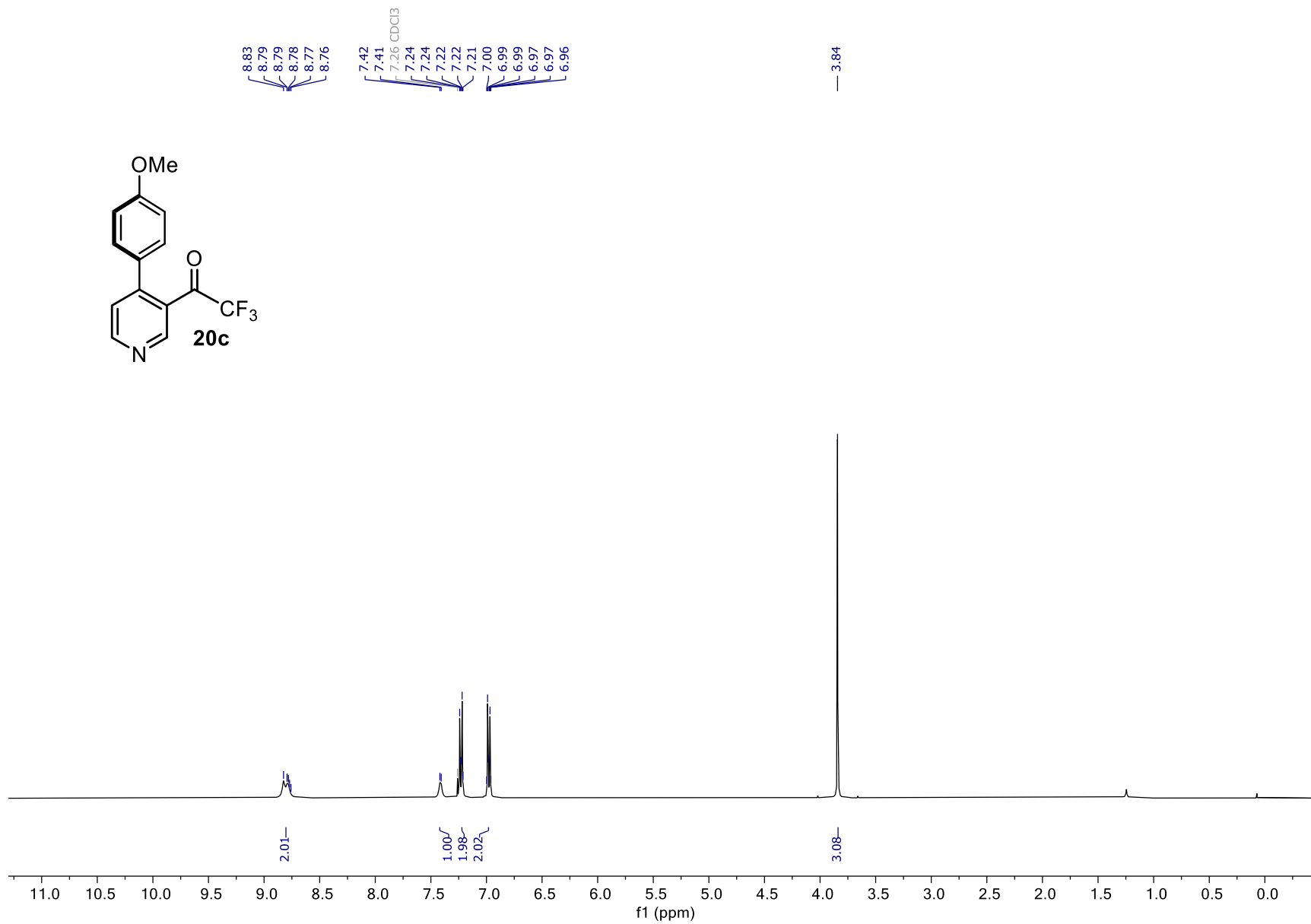
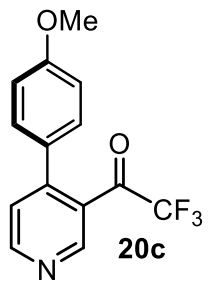


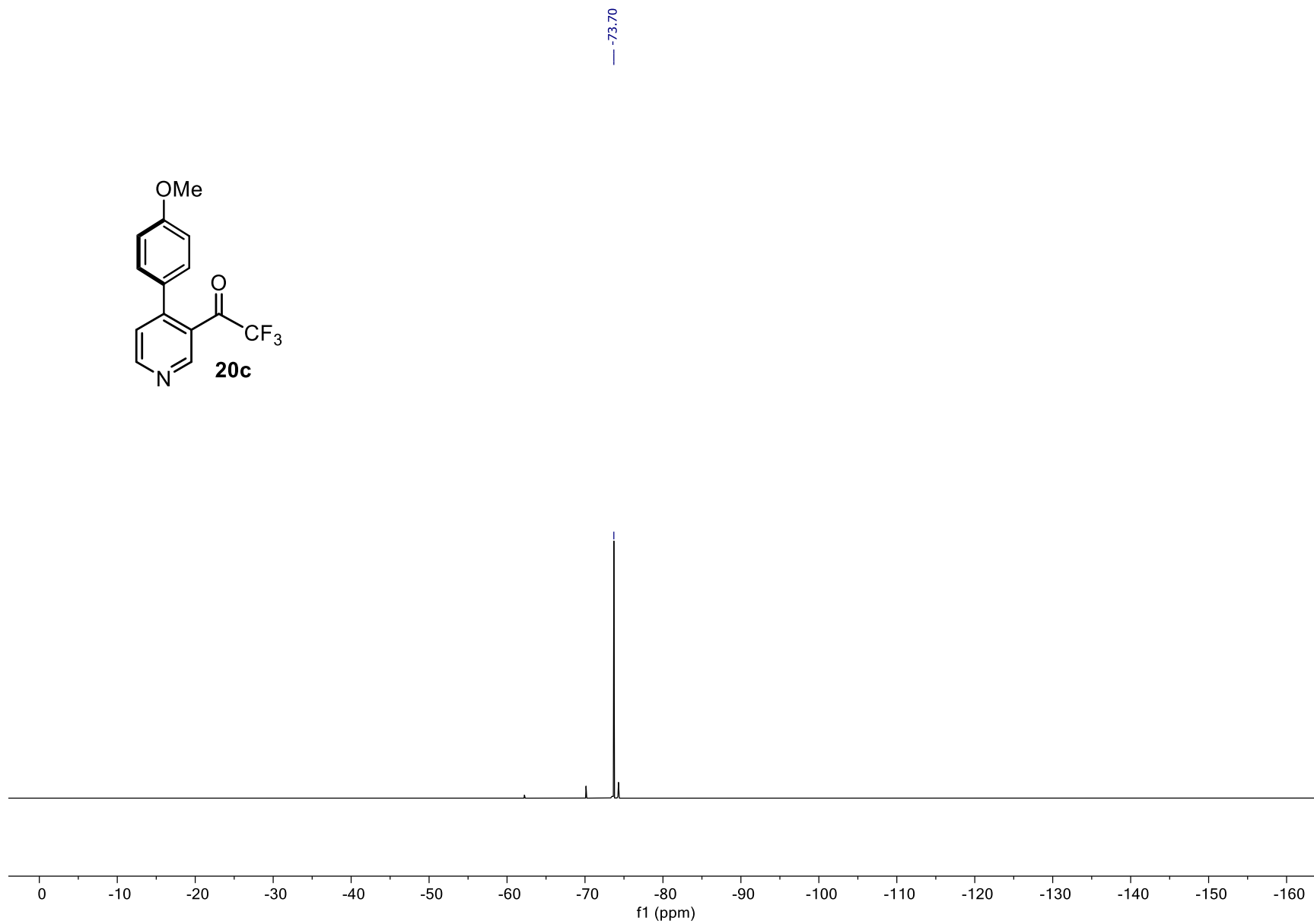
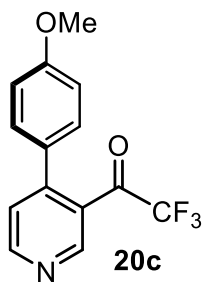


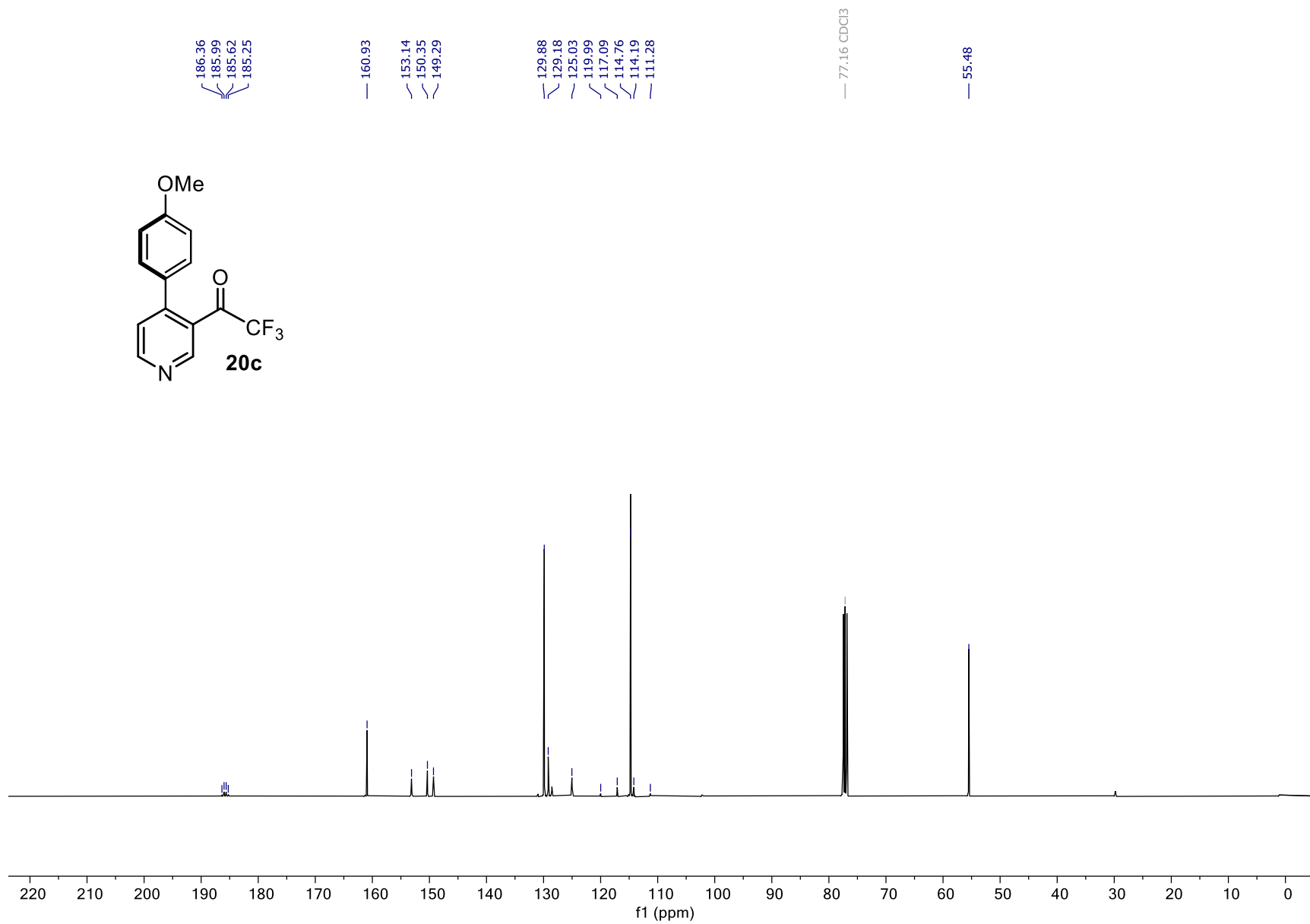
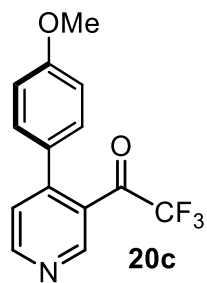


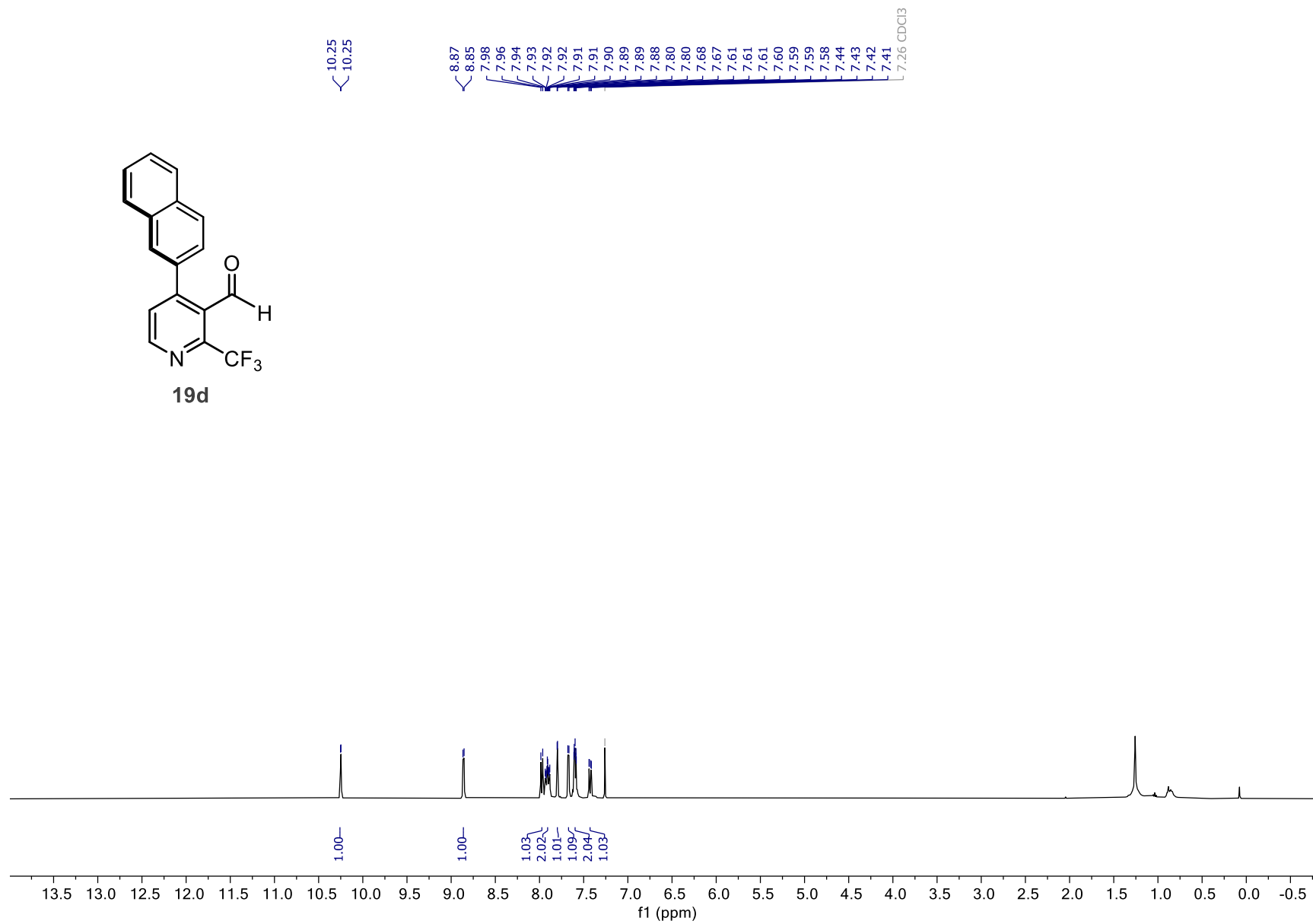
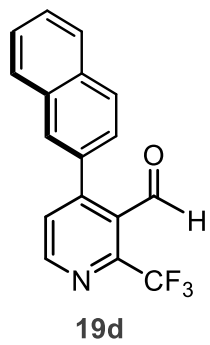


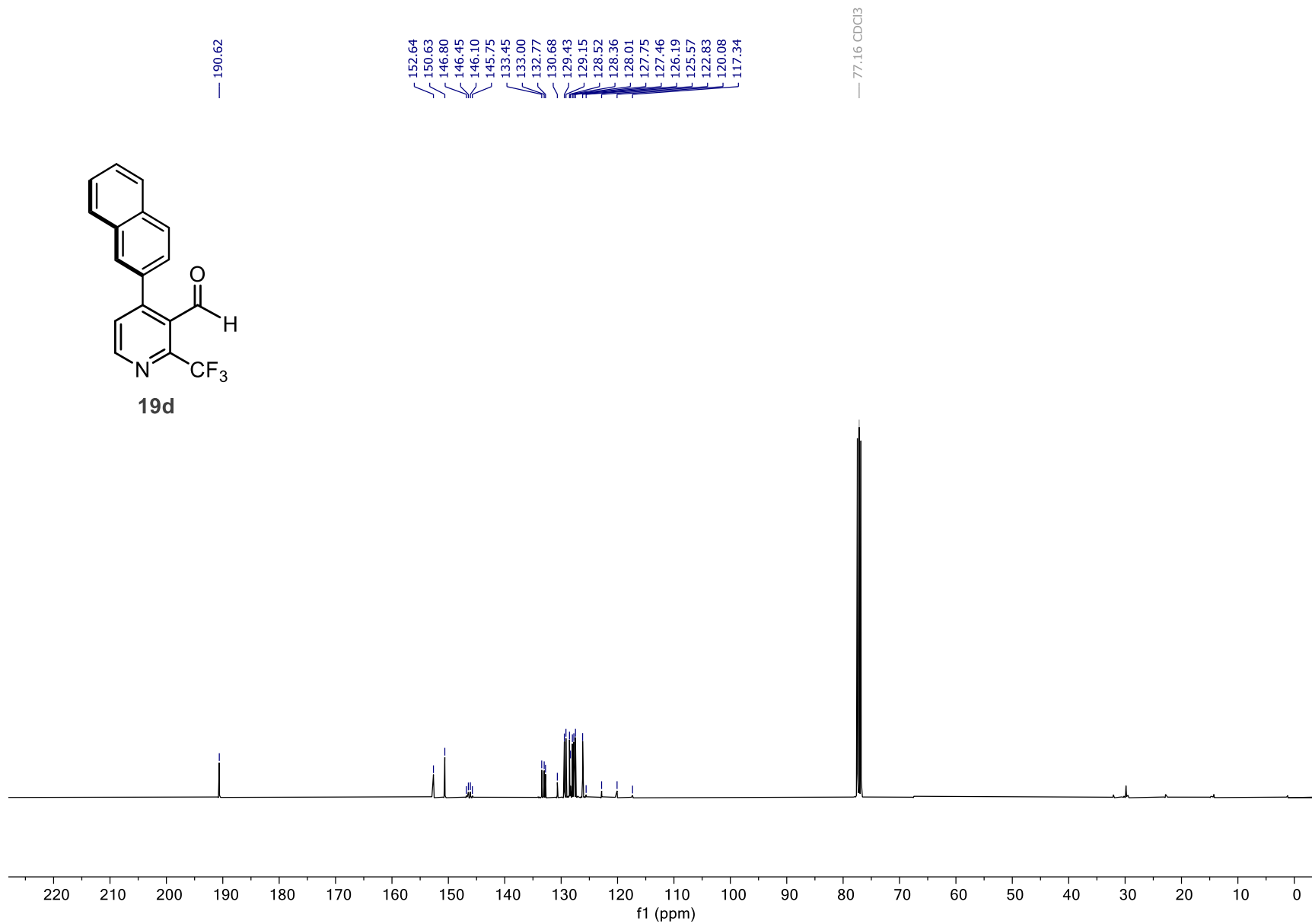
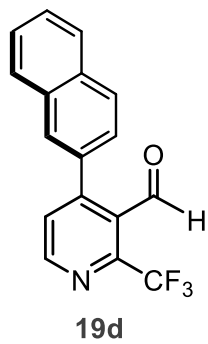


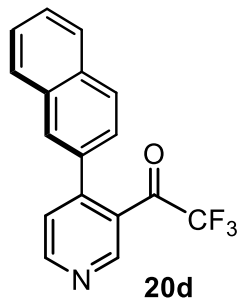




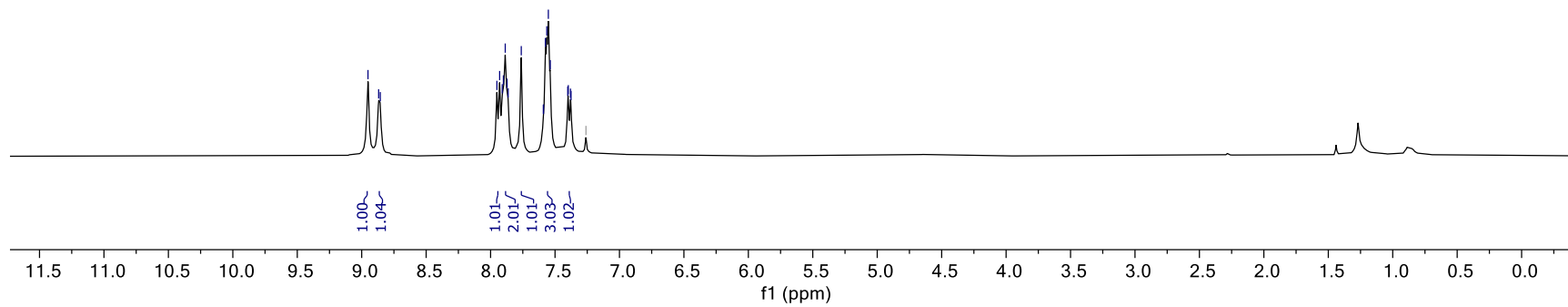


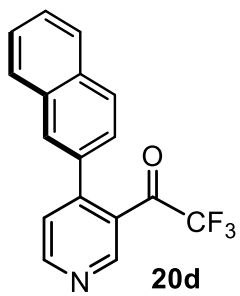




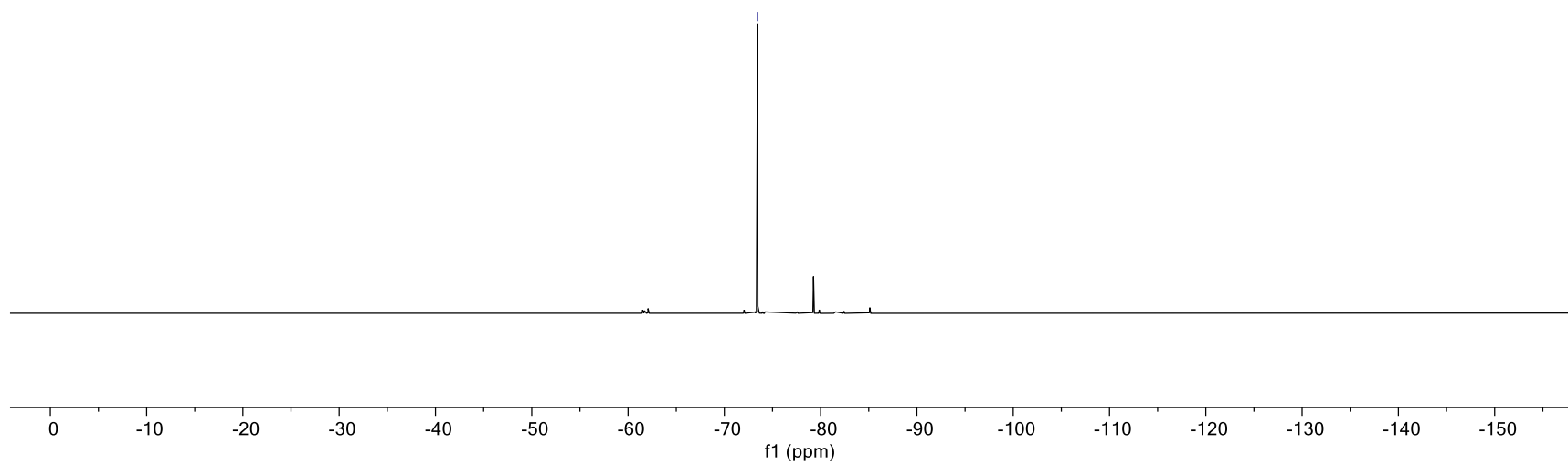


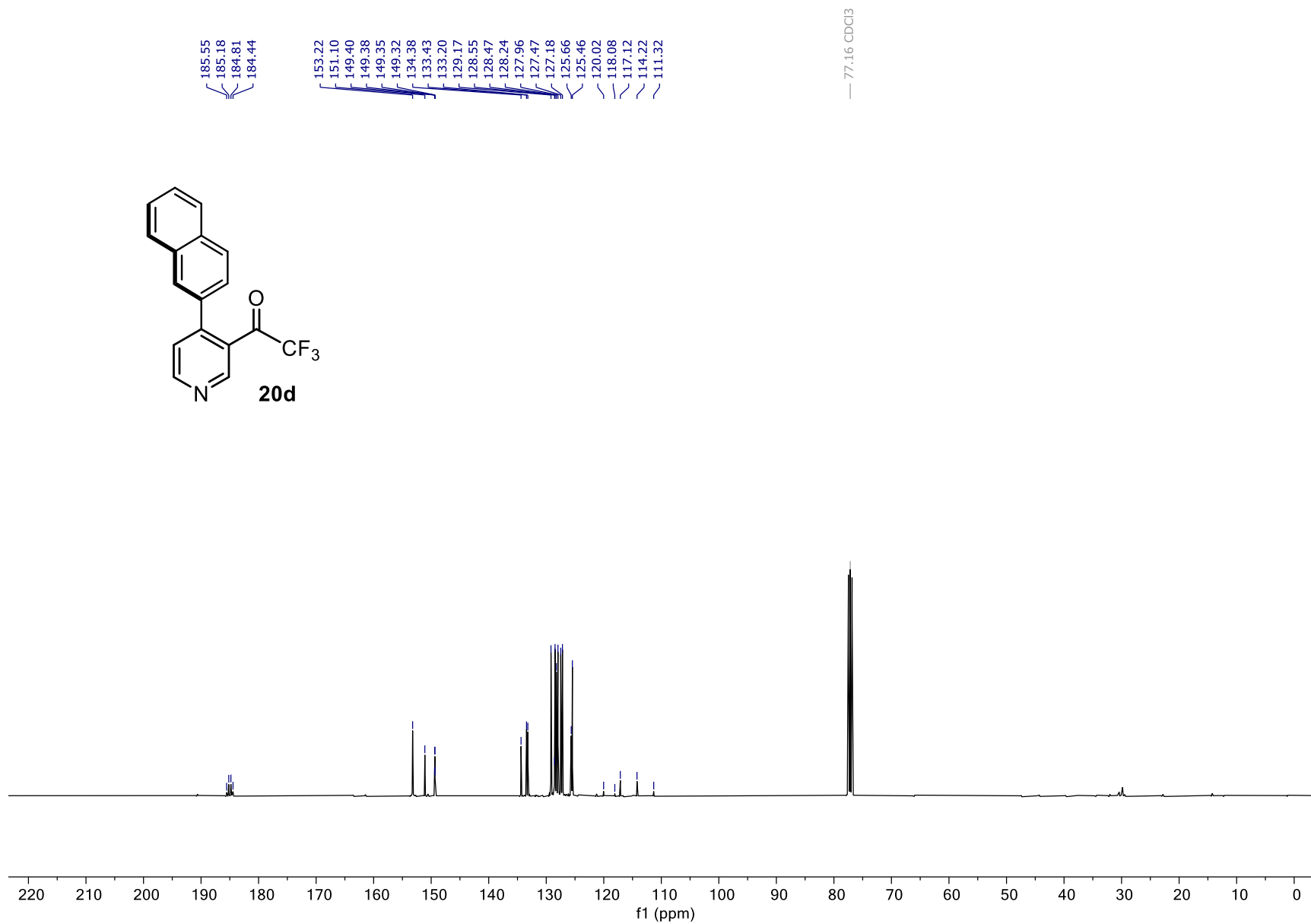
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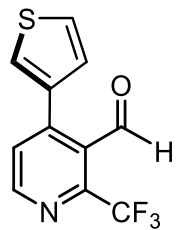




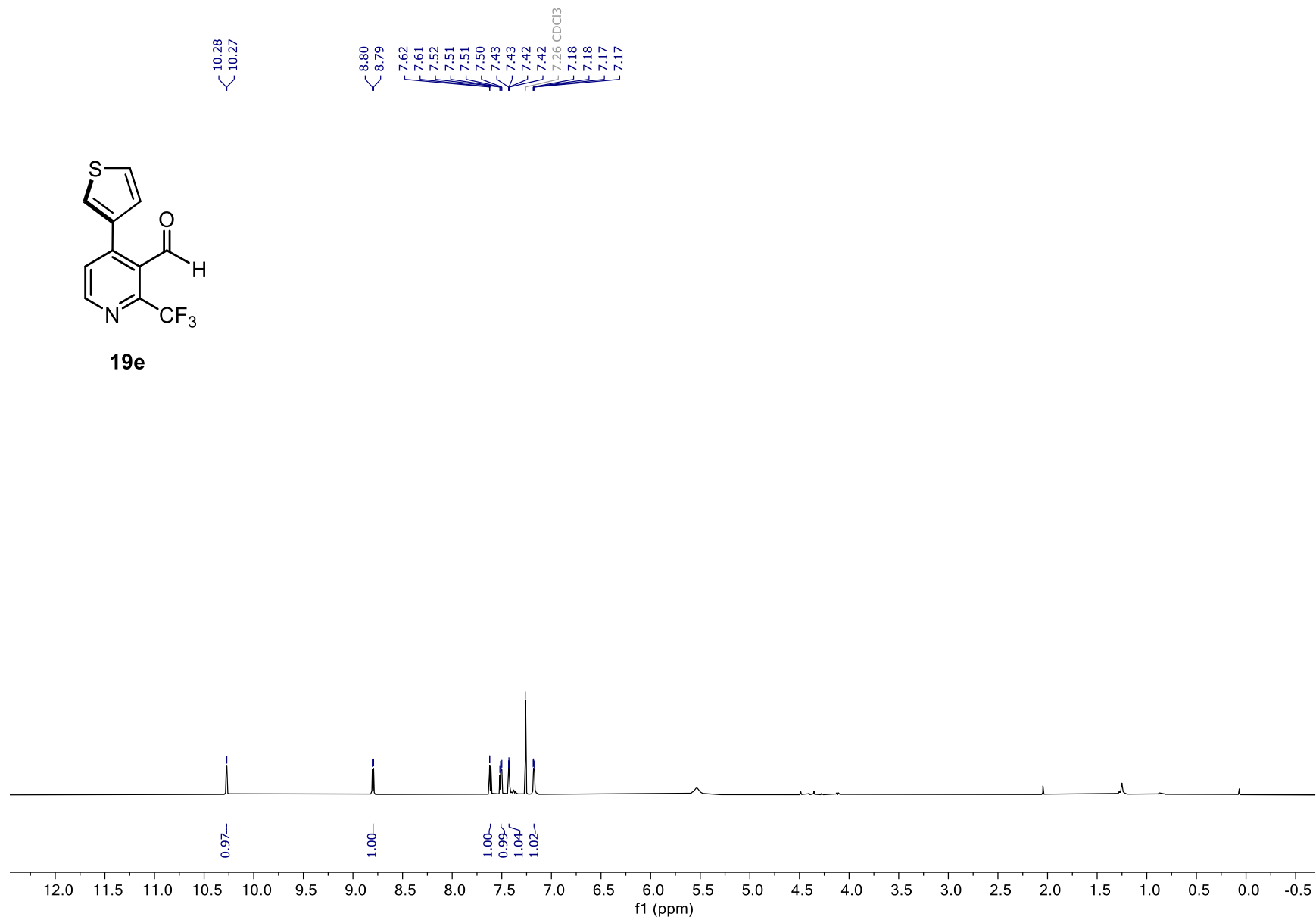
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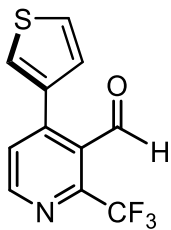




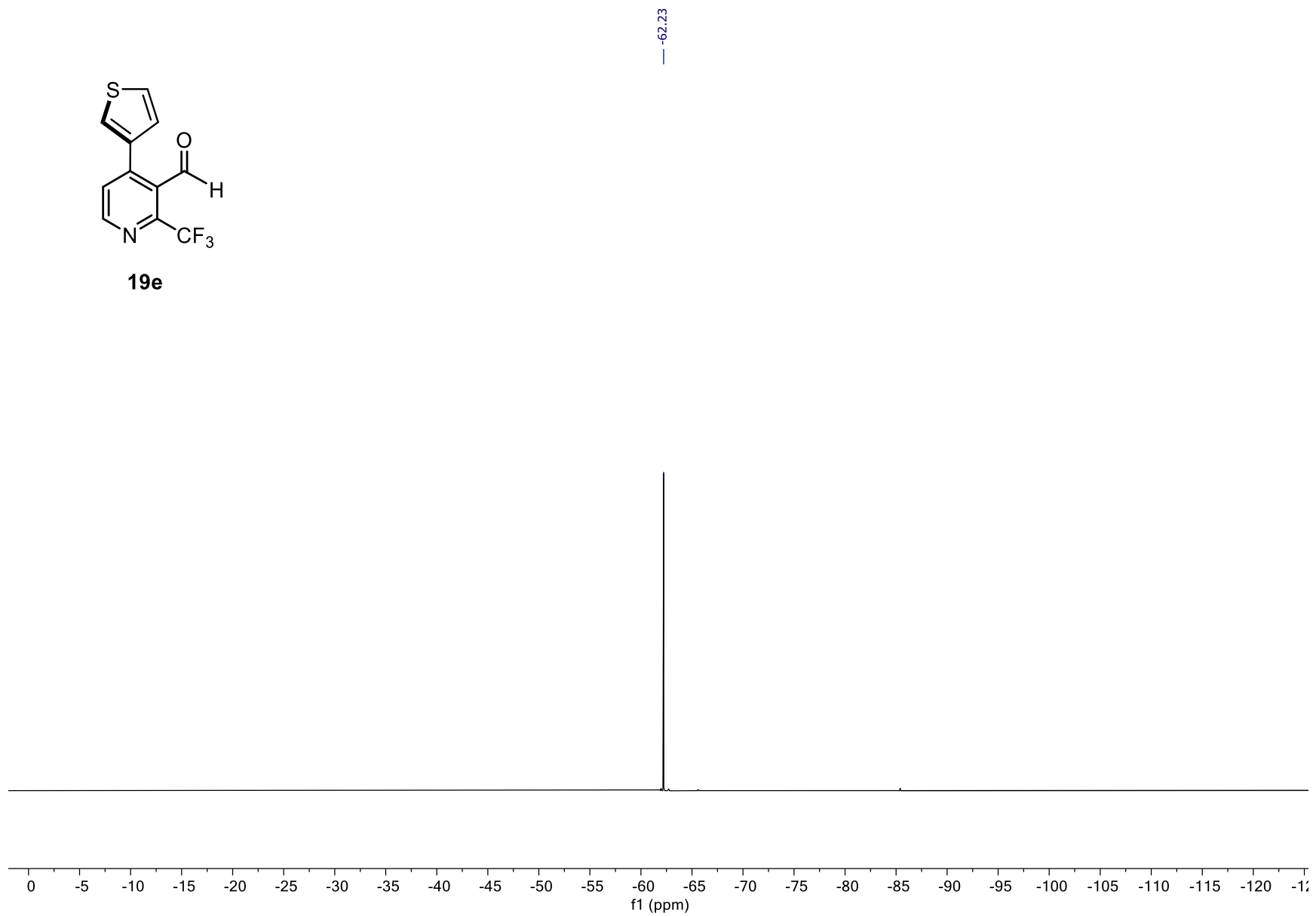


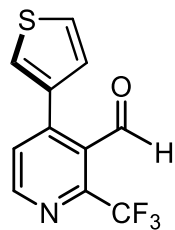
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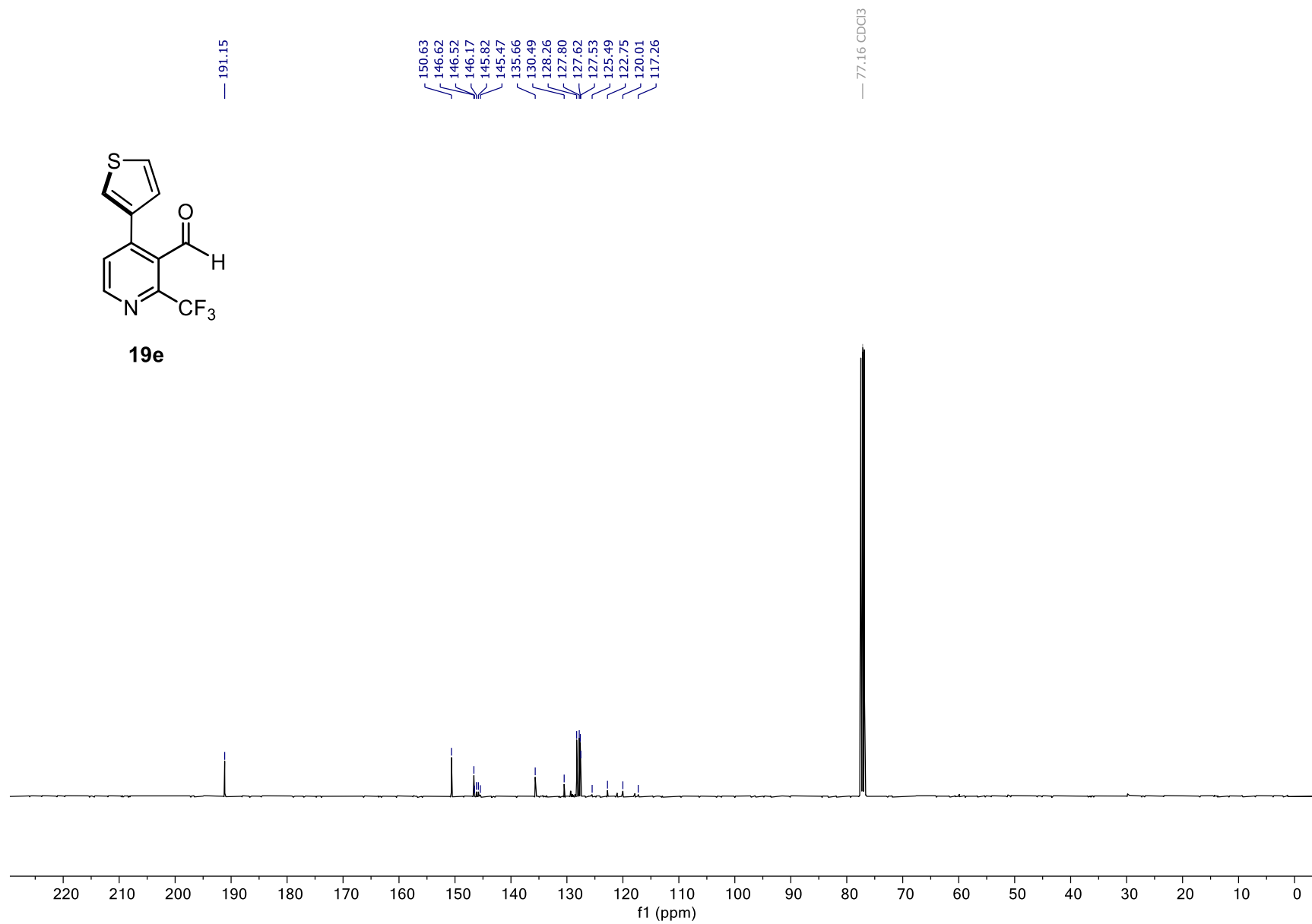


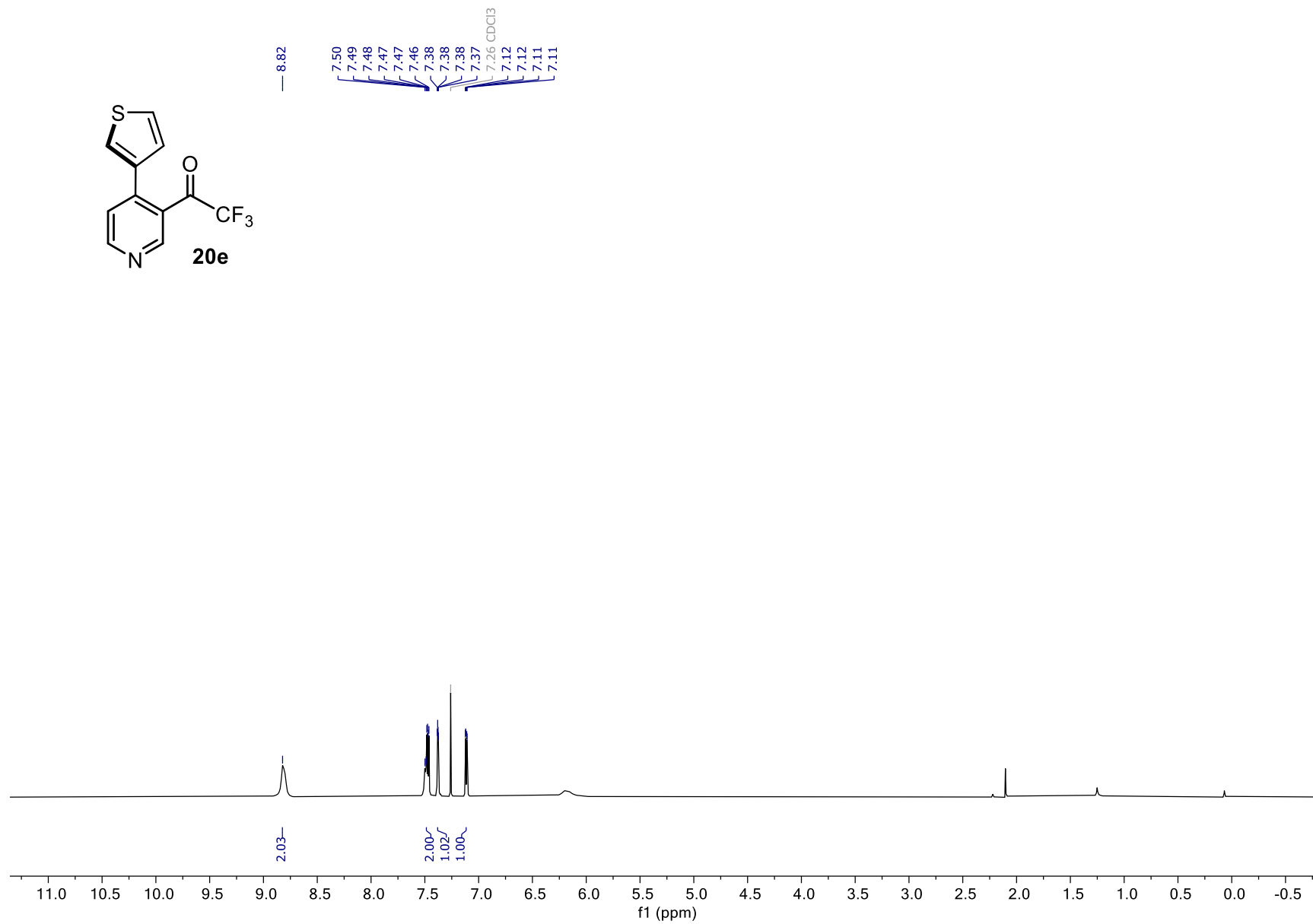
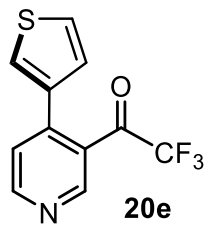
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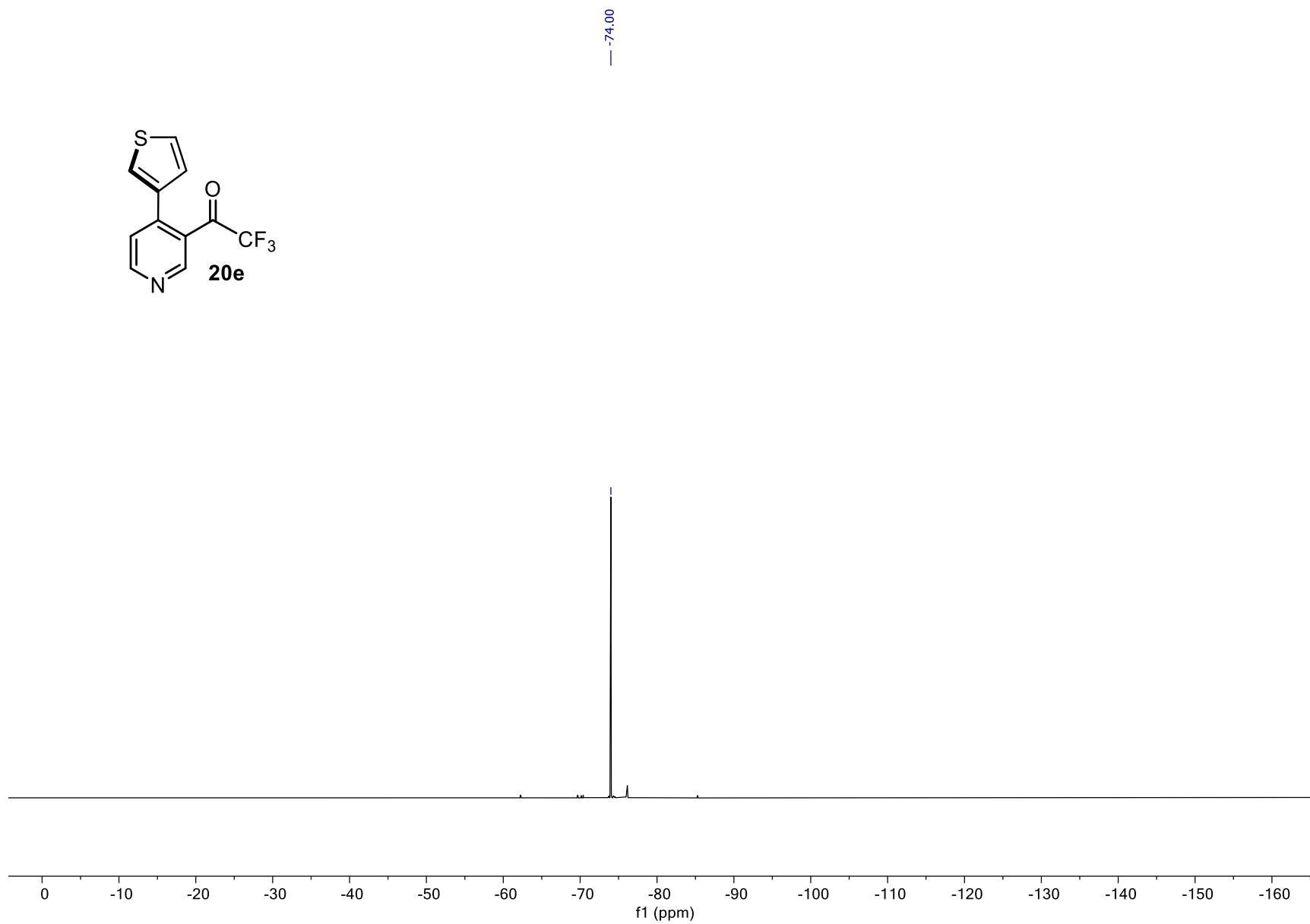
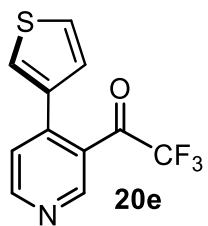


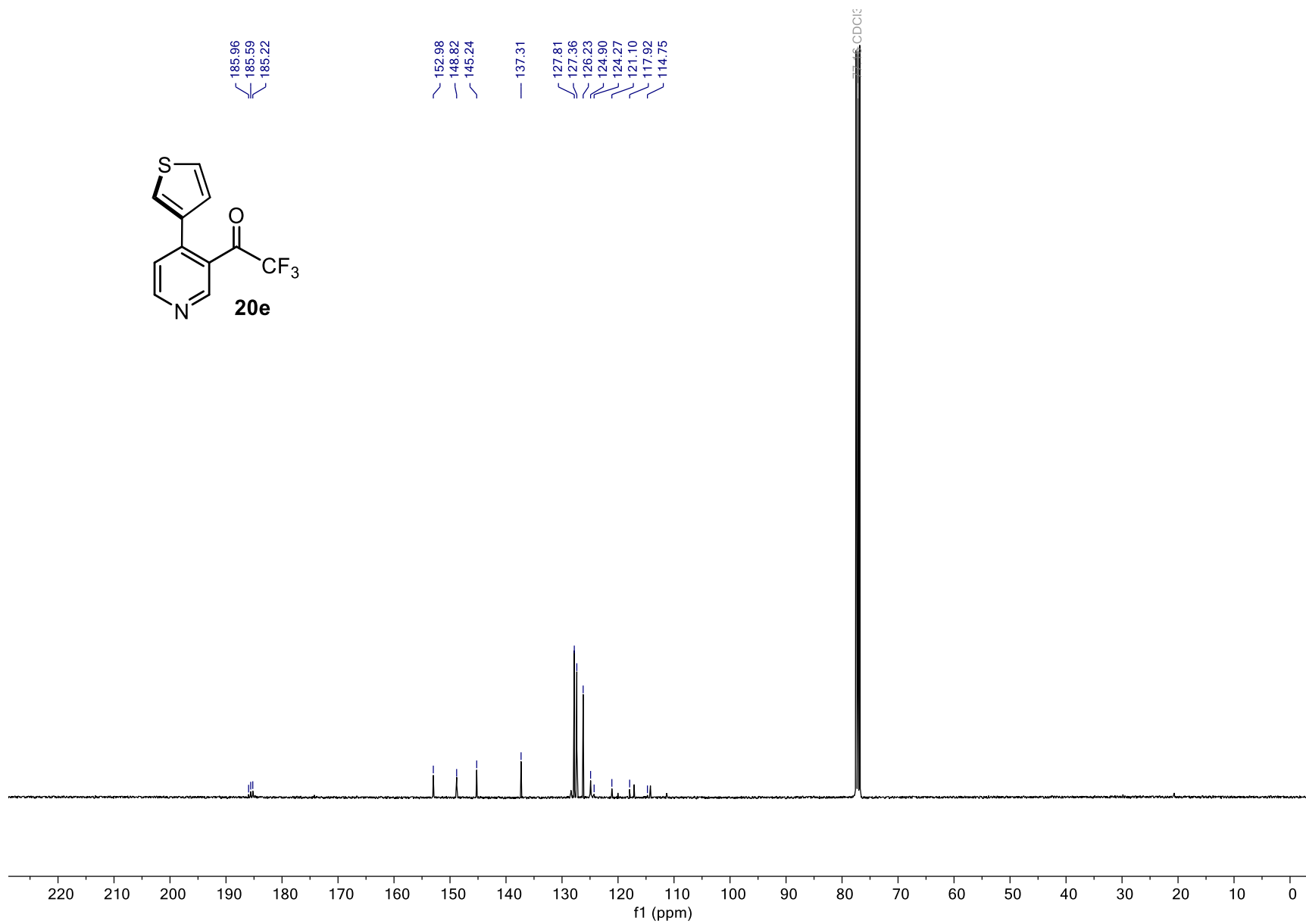
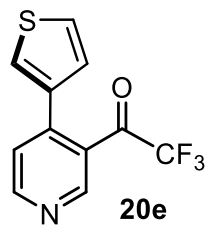


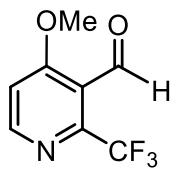
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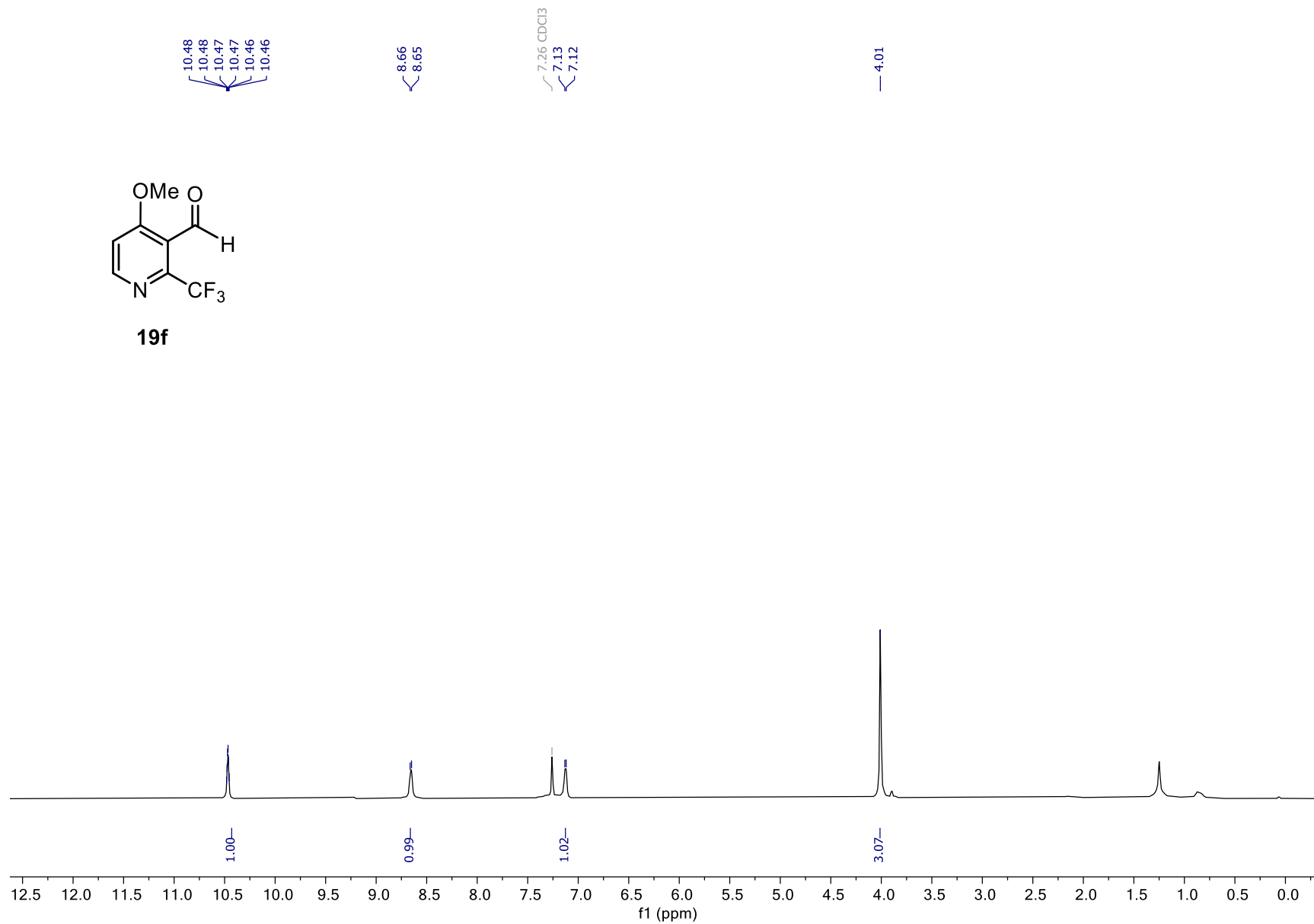


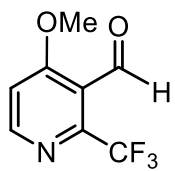






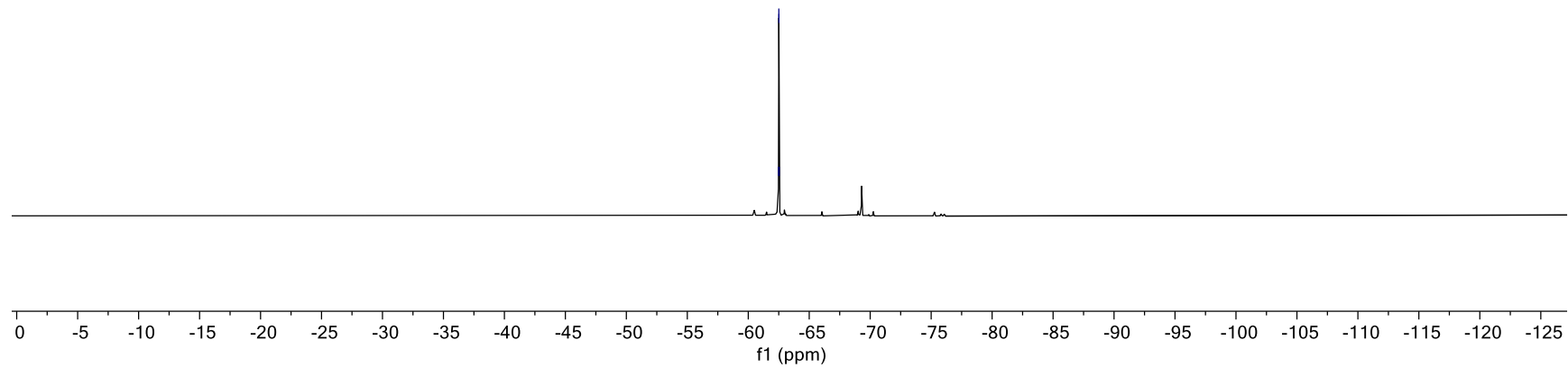
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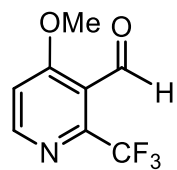




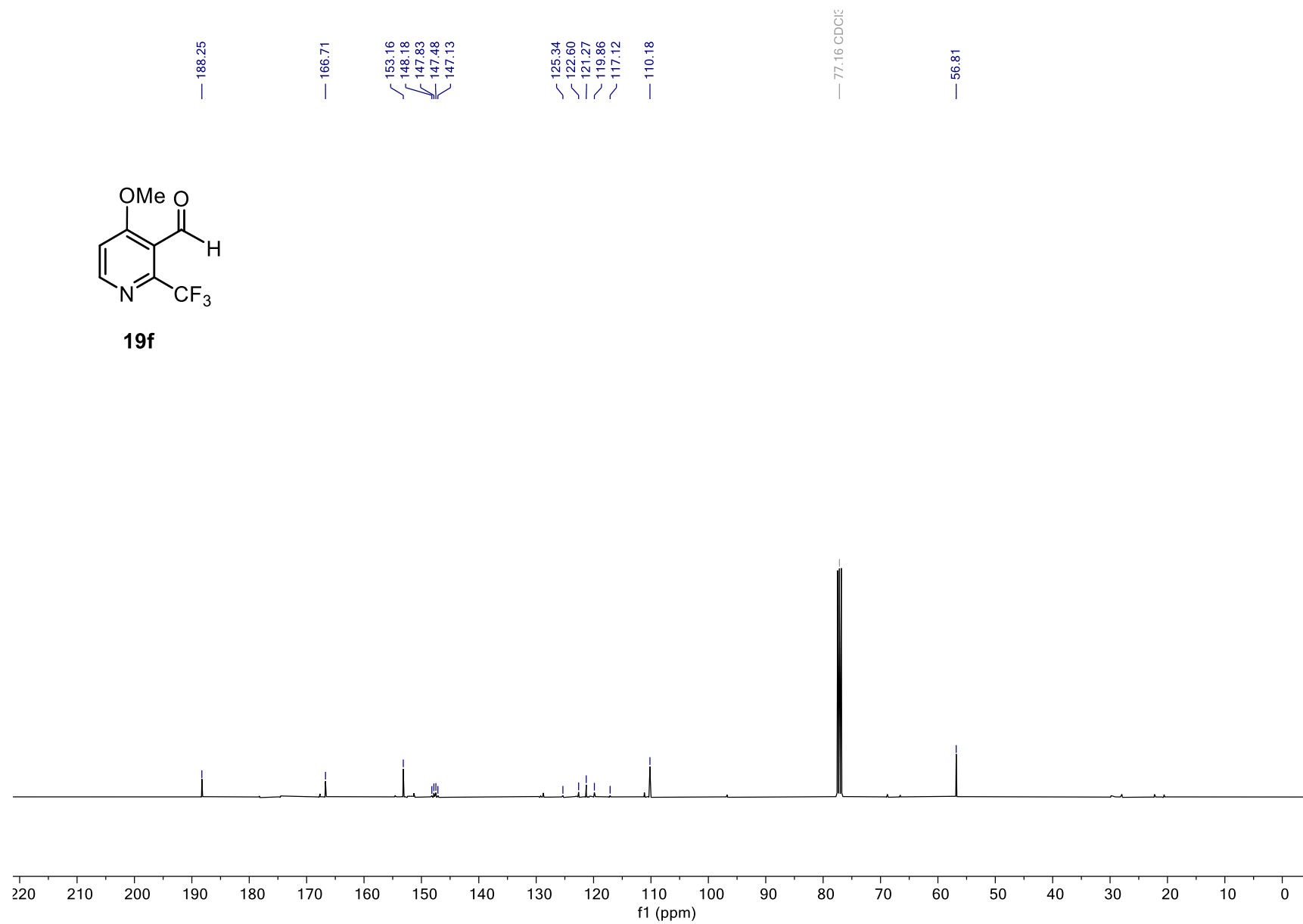
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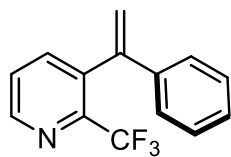




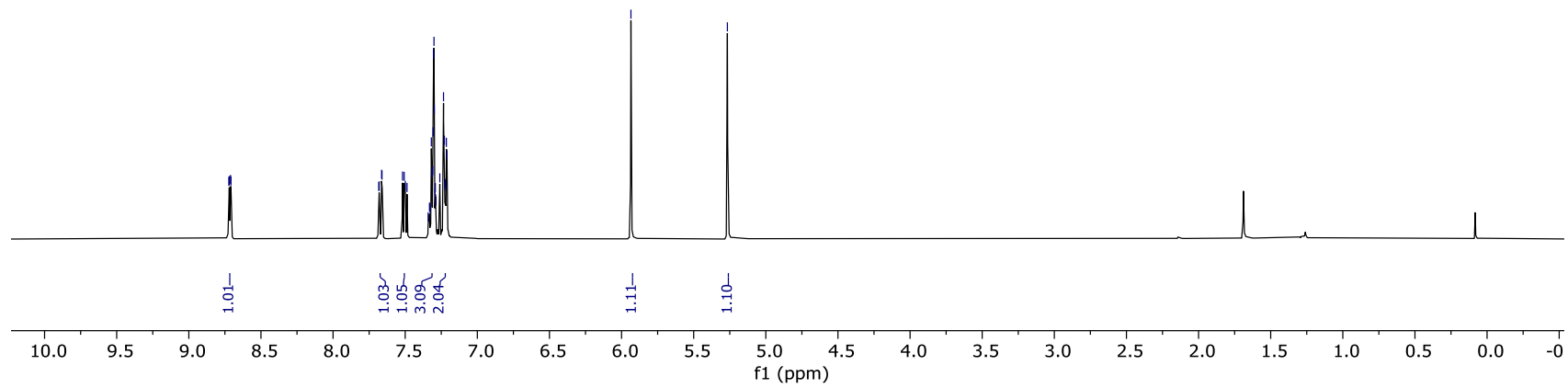
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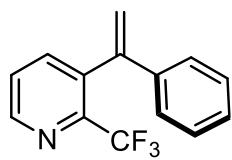


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5.27

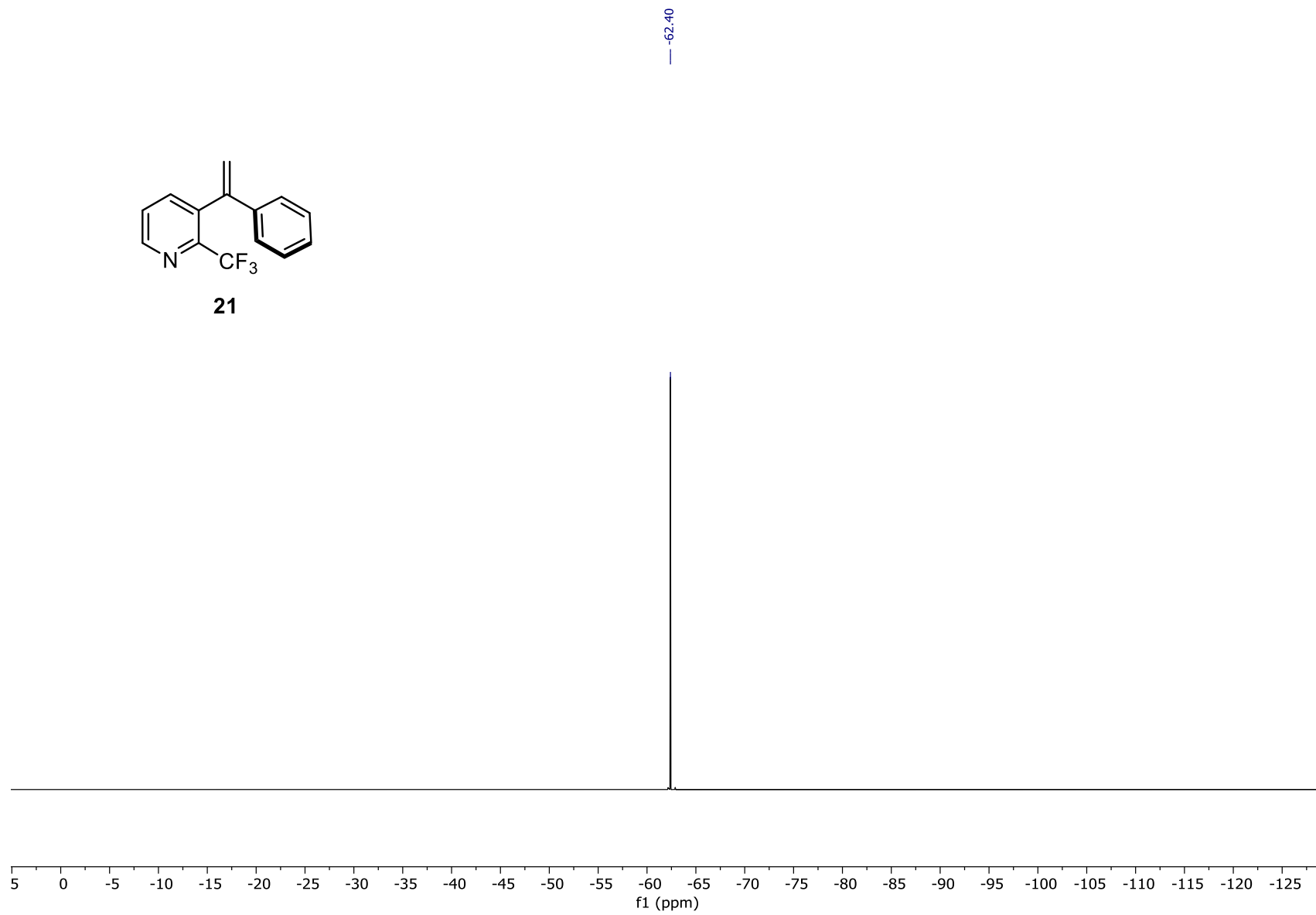


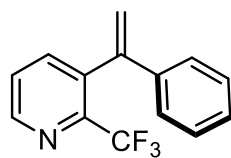
21





21

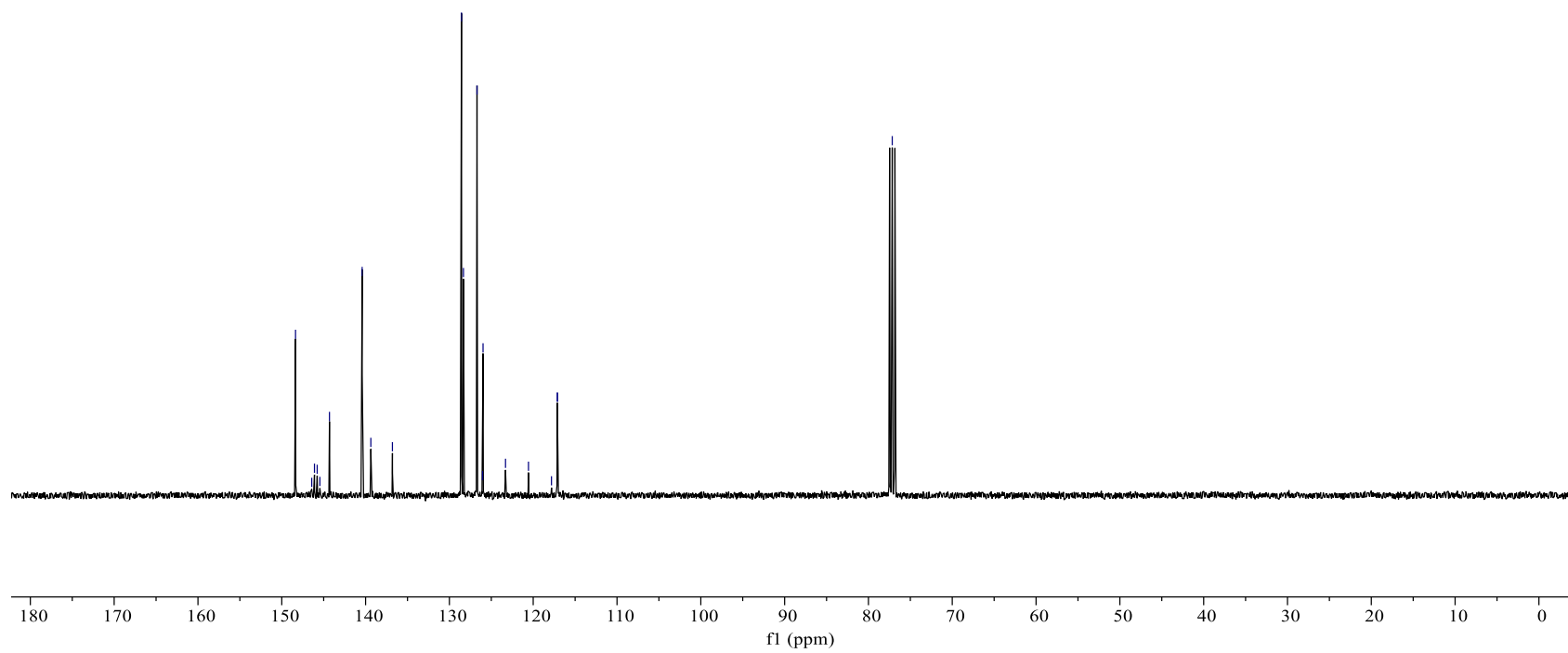


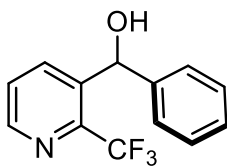


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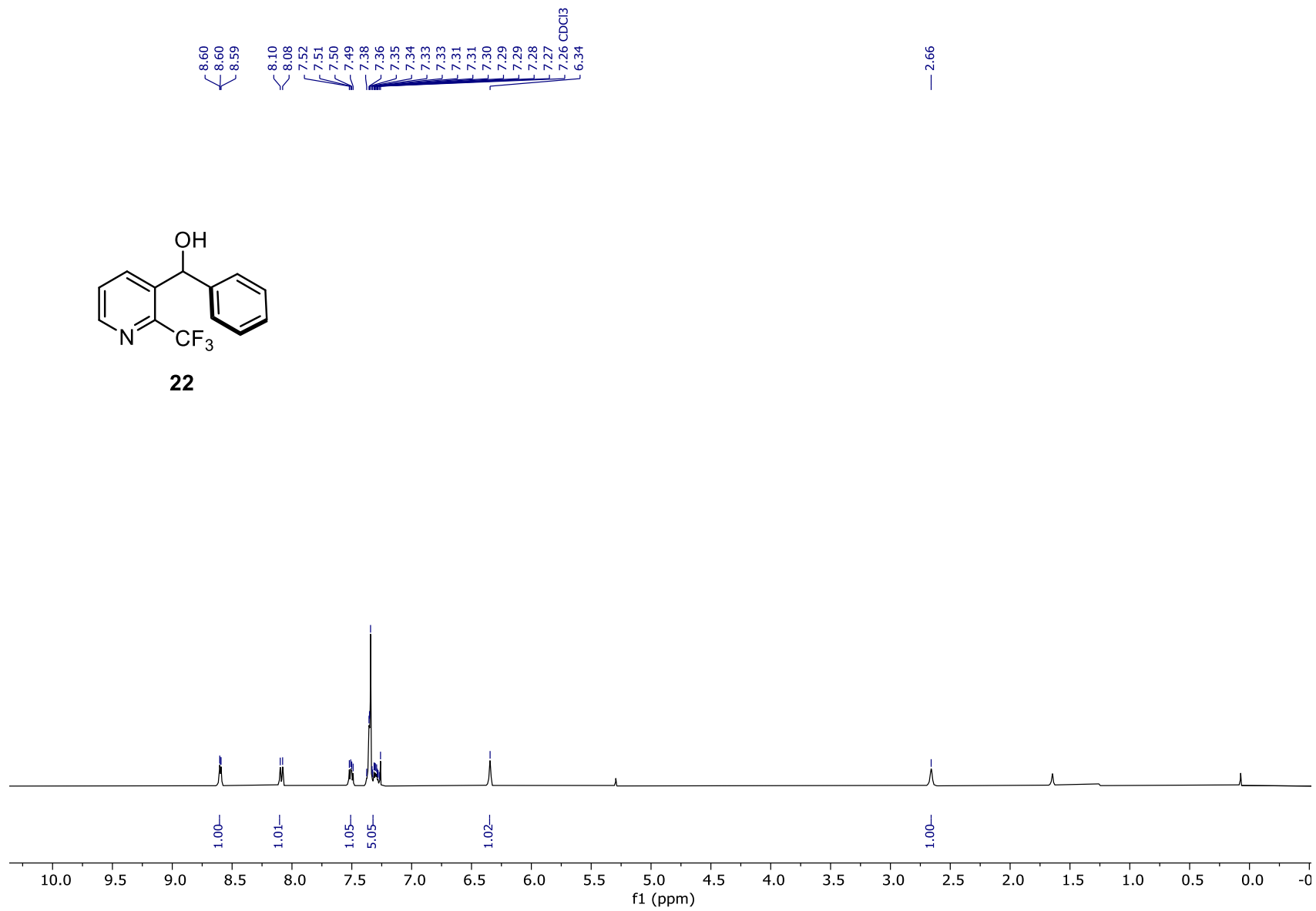
148.4
146.4
146.1
145.8
145.5
144.3
140.4
139.4
136.8
128.6
128.3
126.7
126.0
123.3
120.6
117.8
117.1
117.1

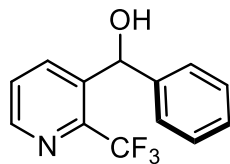
— 77.2 CDCl₃



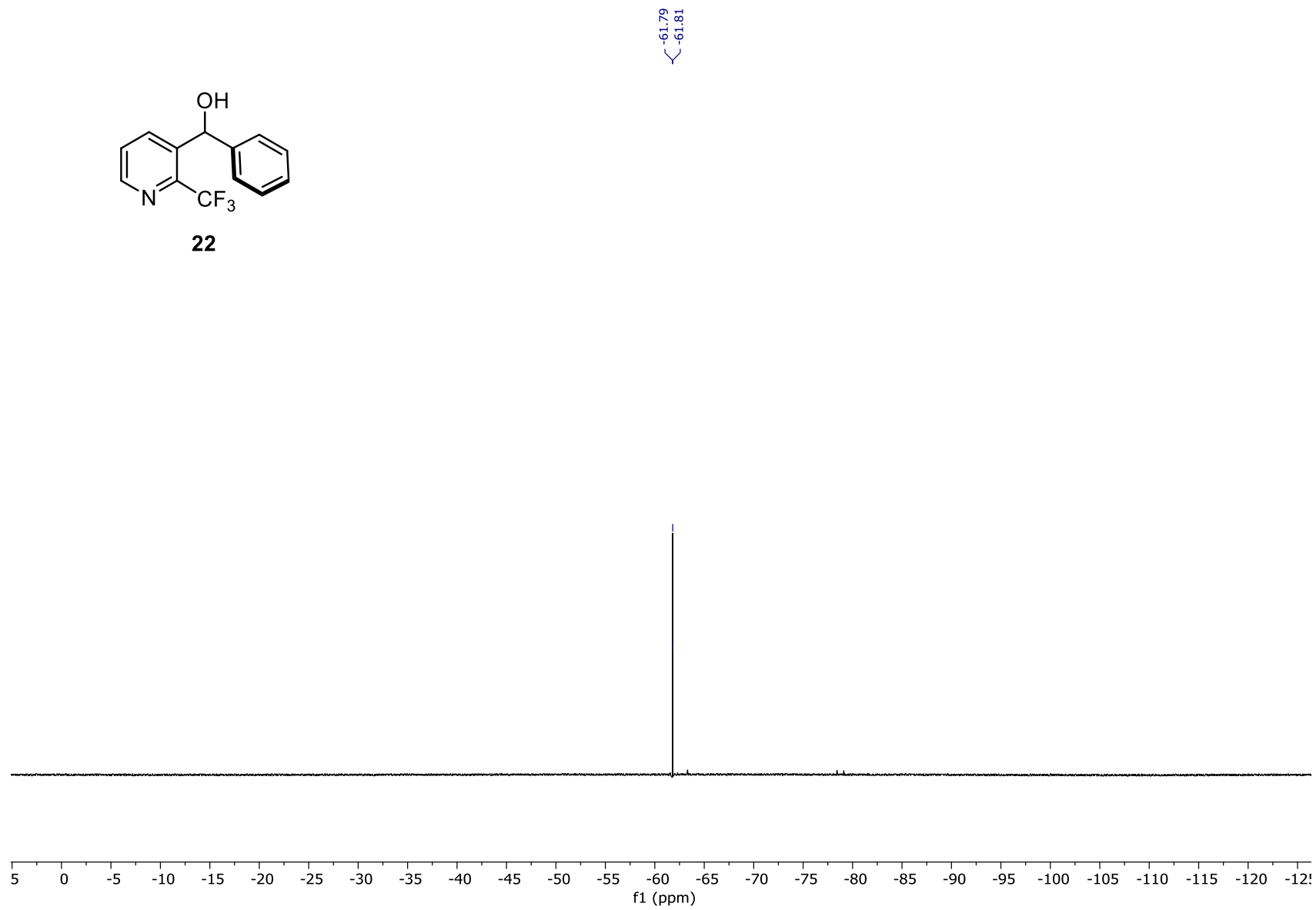


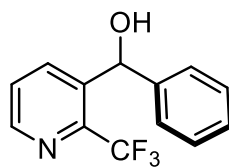
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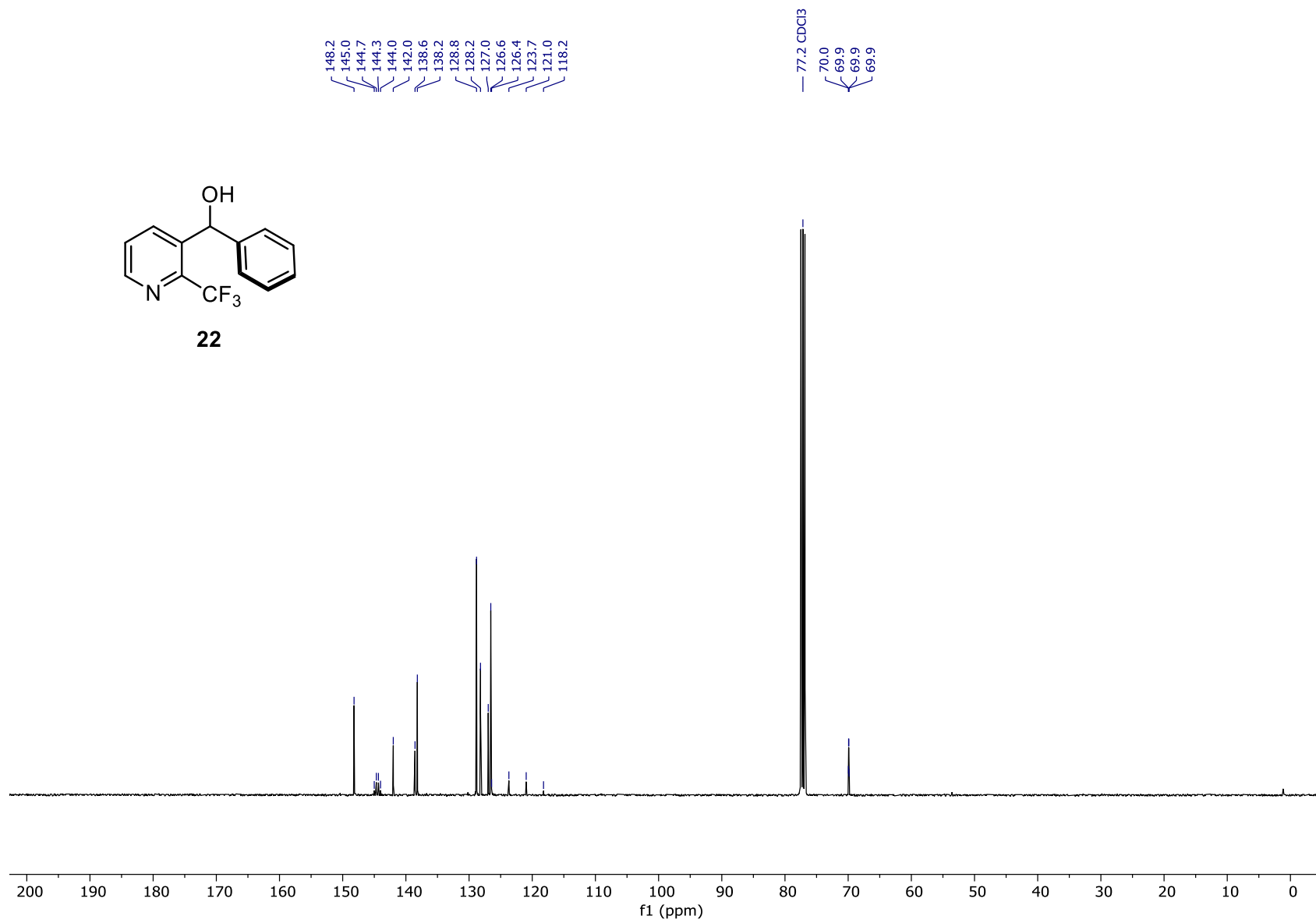


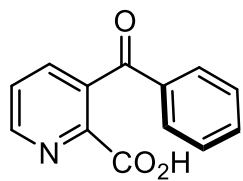
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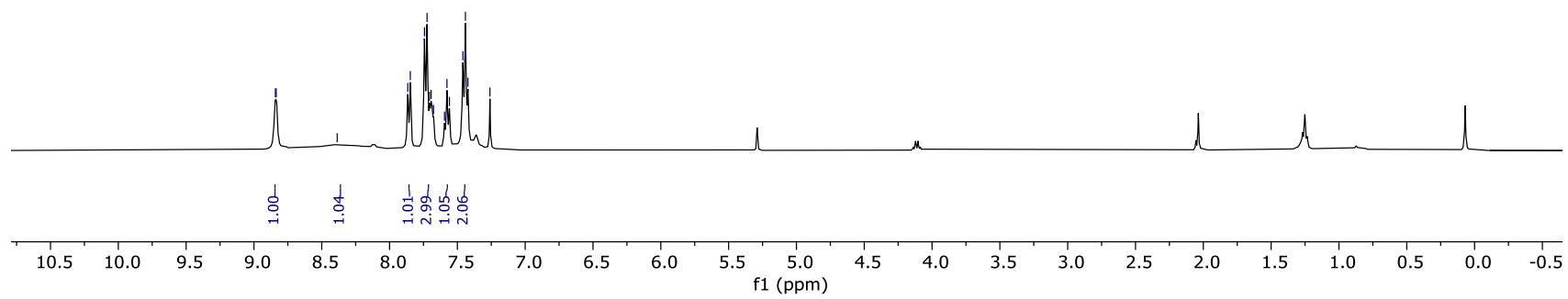
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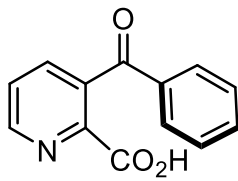




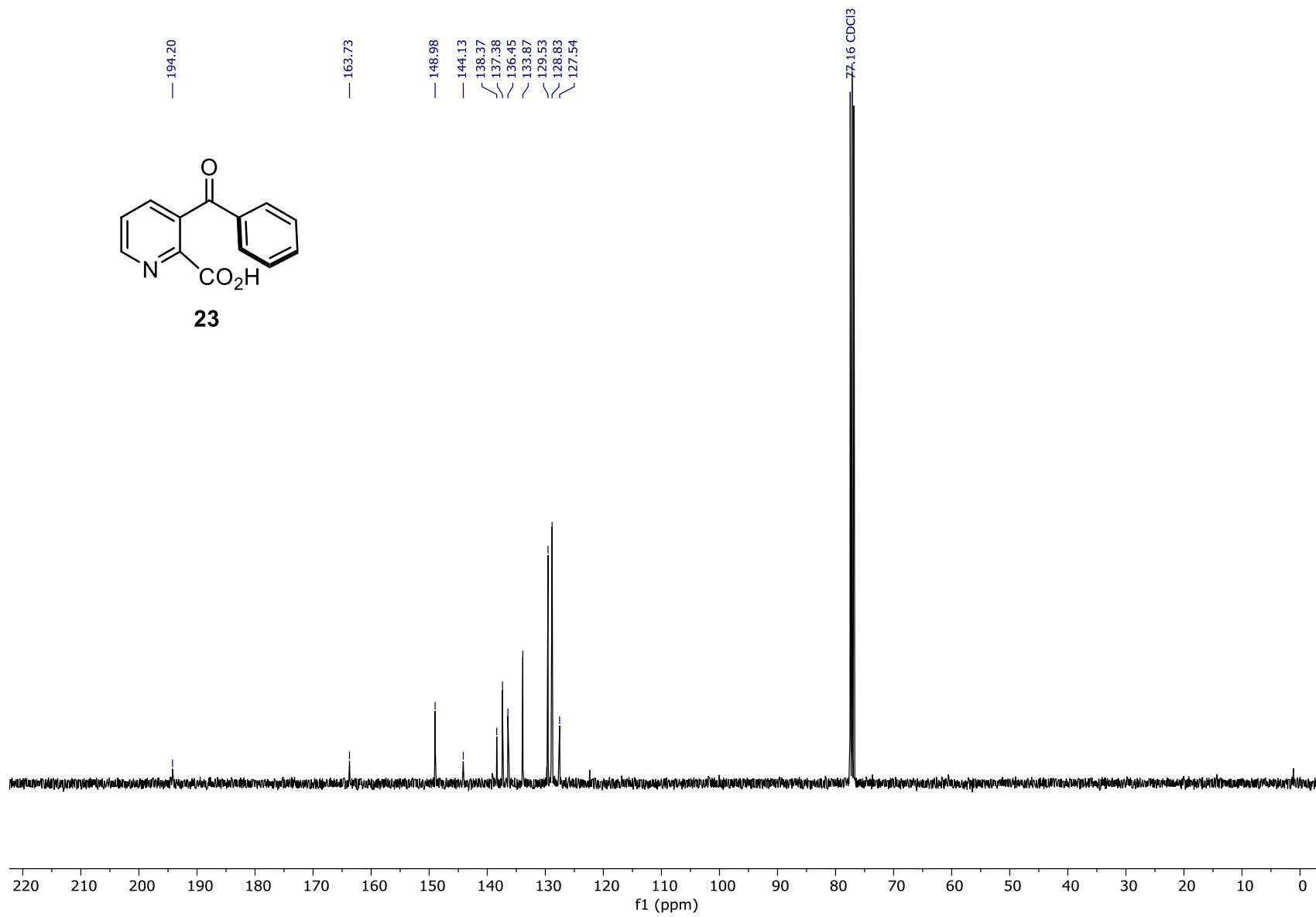
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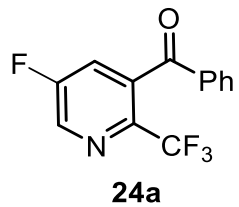
8.84
8.84
8.39
7.87
7.85
7.74
7.72
7.71
7.69
7.68
7.59
7.58
7.56
7.46
7.44
7.42
7.26 CDCl₃



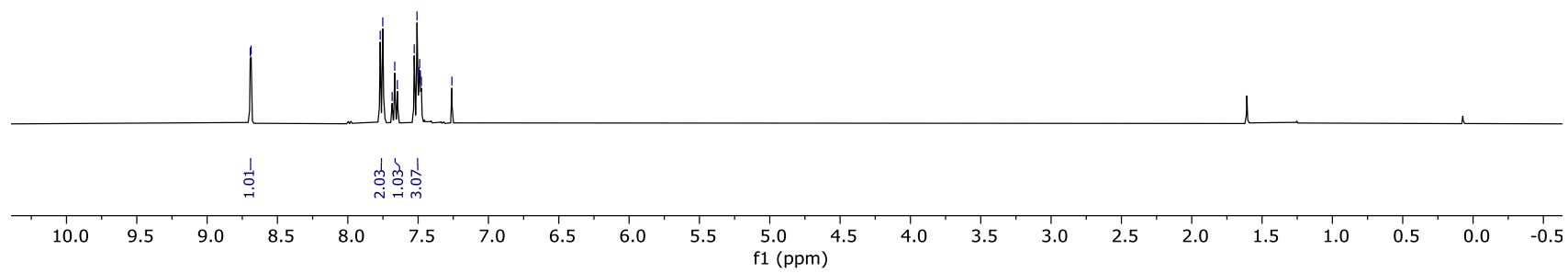


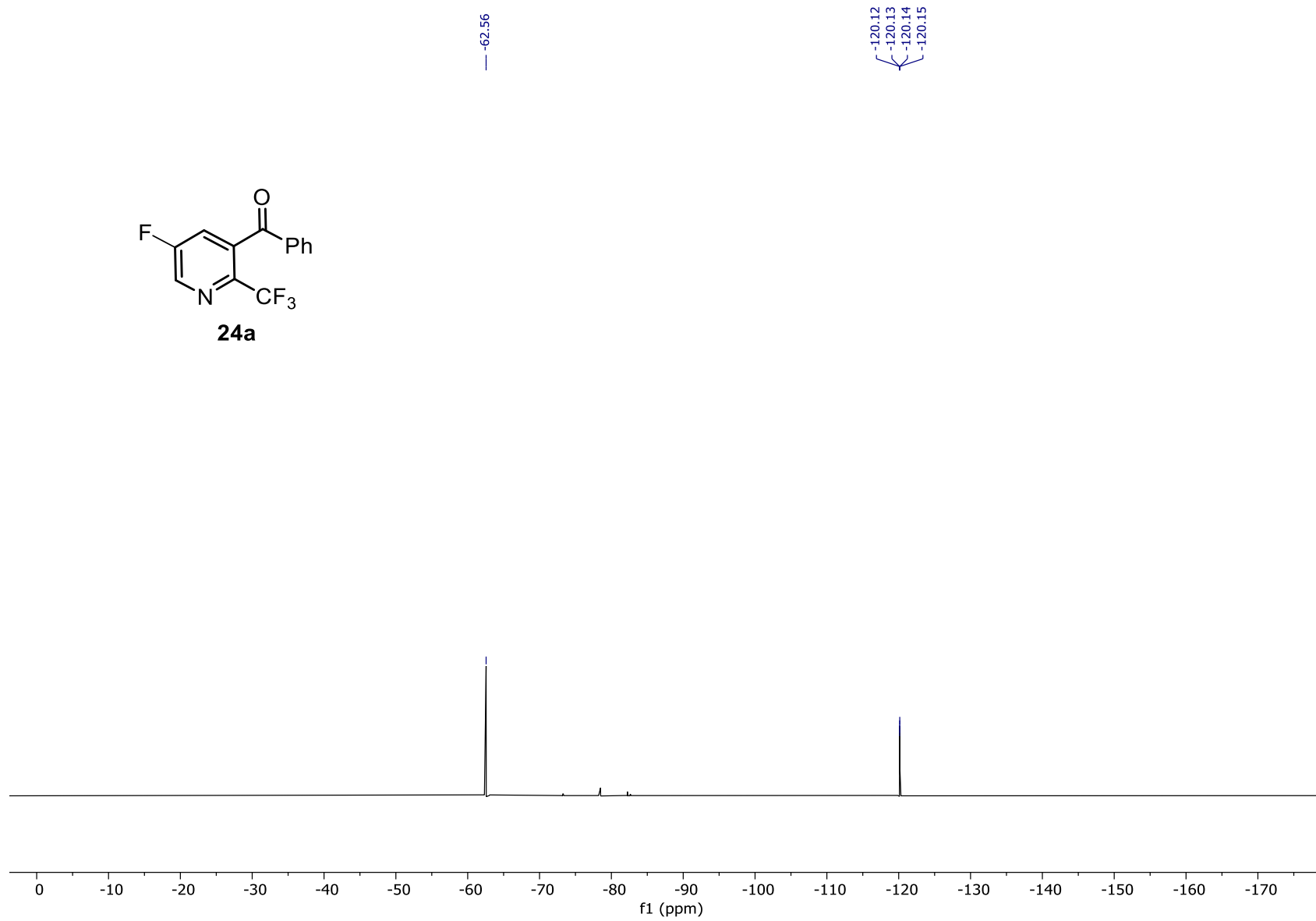
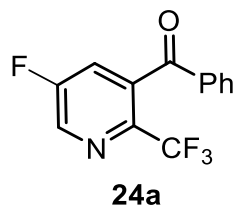
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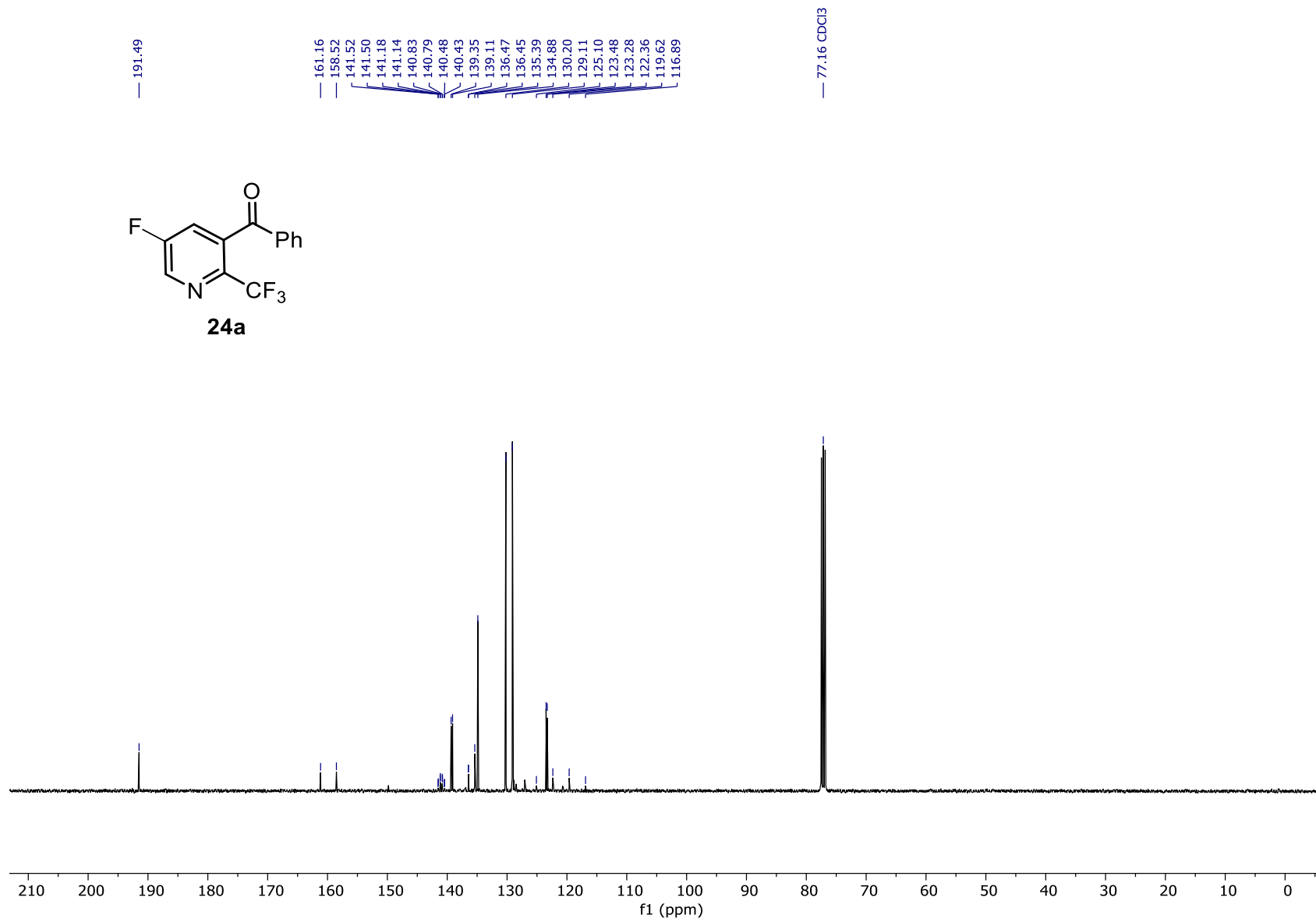
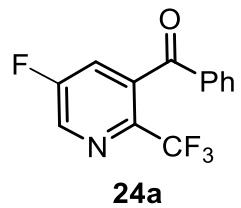


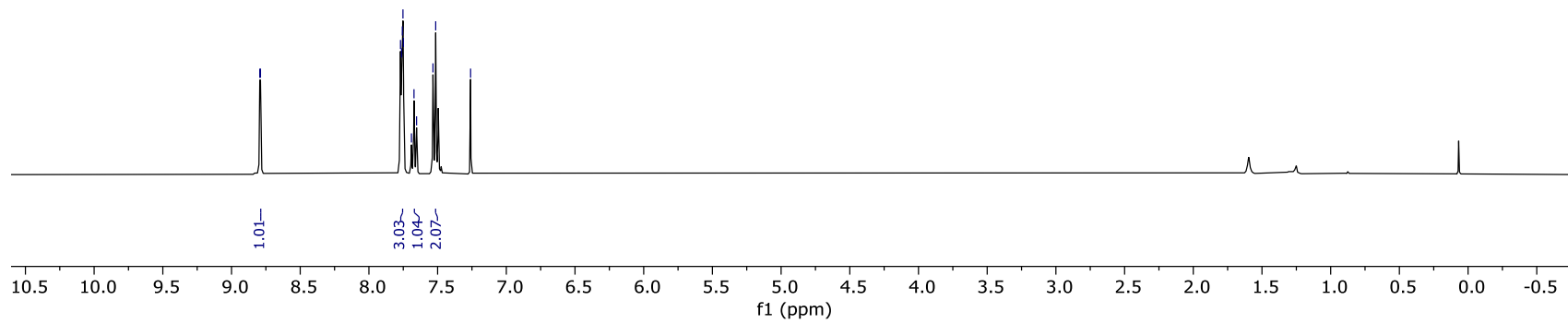
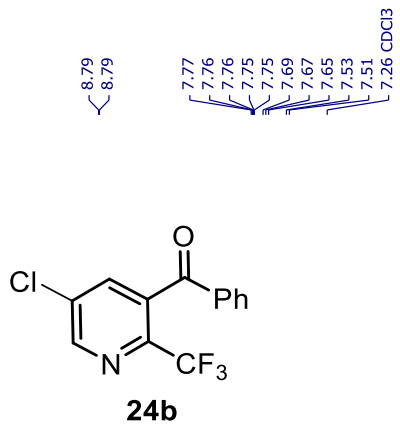


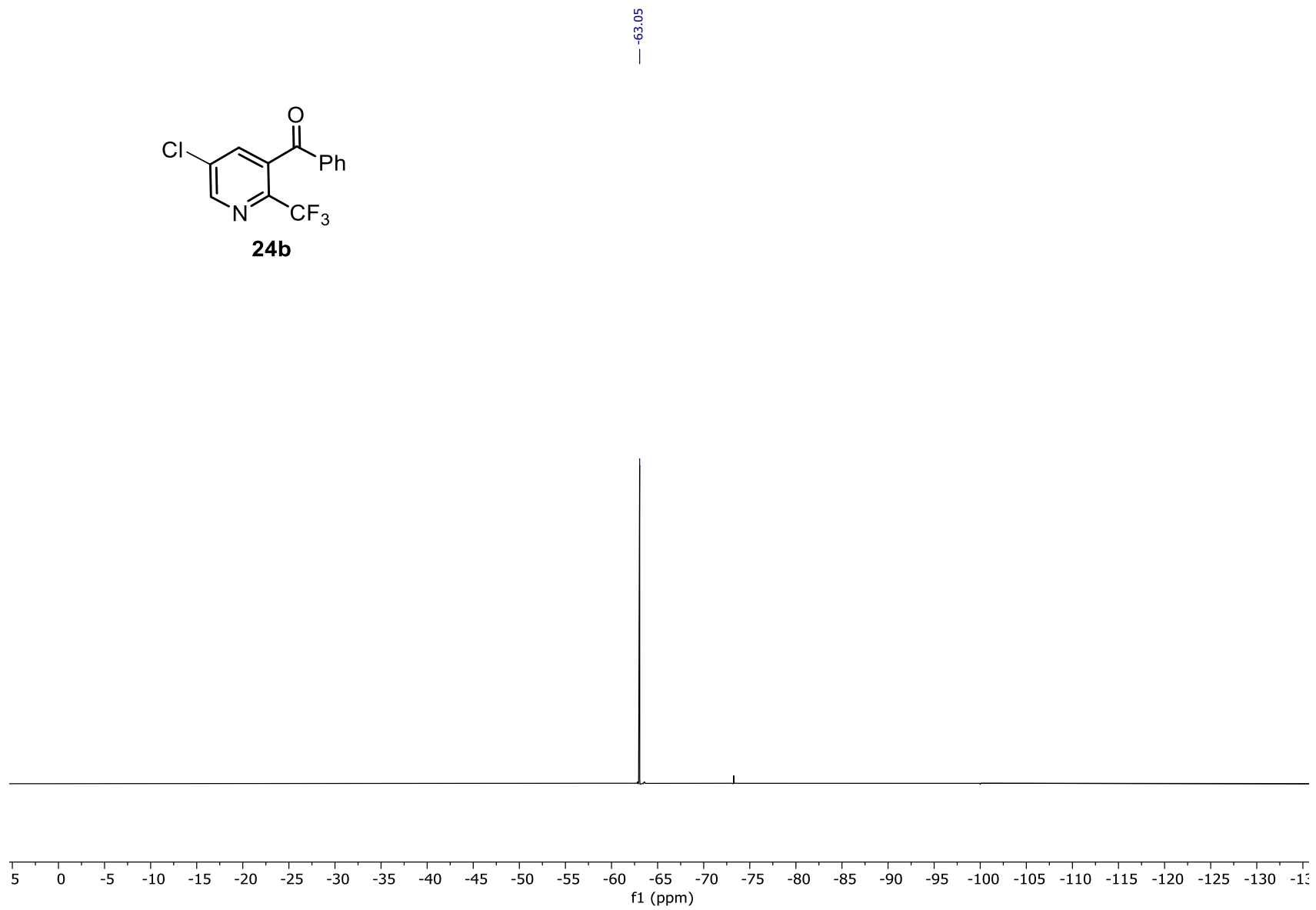
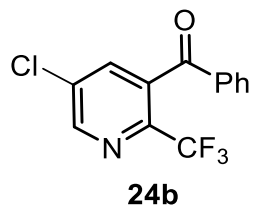
8.69
8.69
7.77
7.75
7.75
7.68
7.67
7.65
7.53
7.51
7.49
7.49
7.48
7.48
7.26 CDCl₃

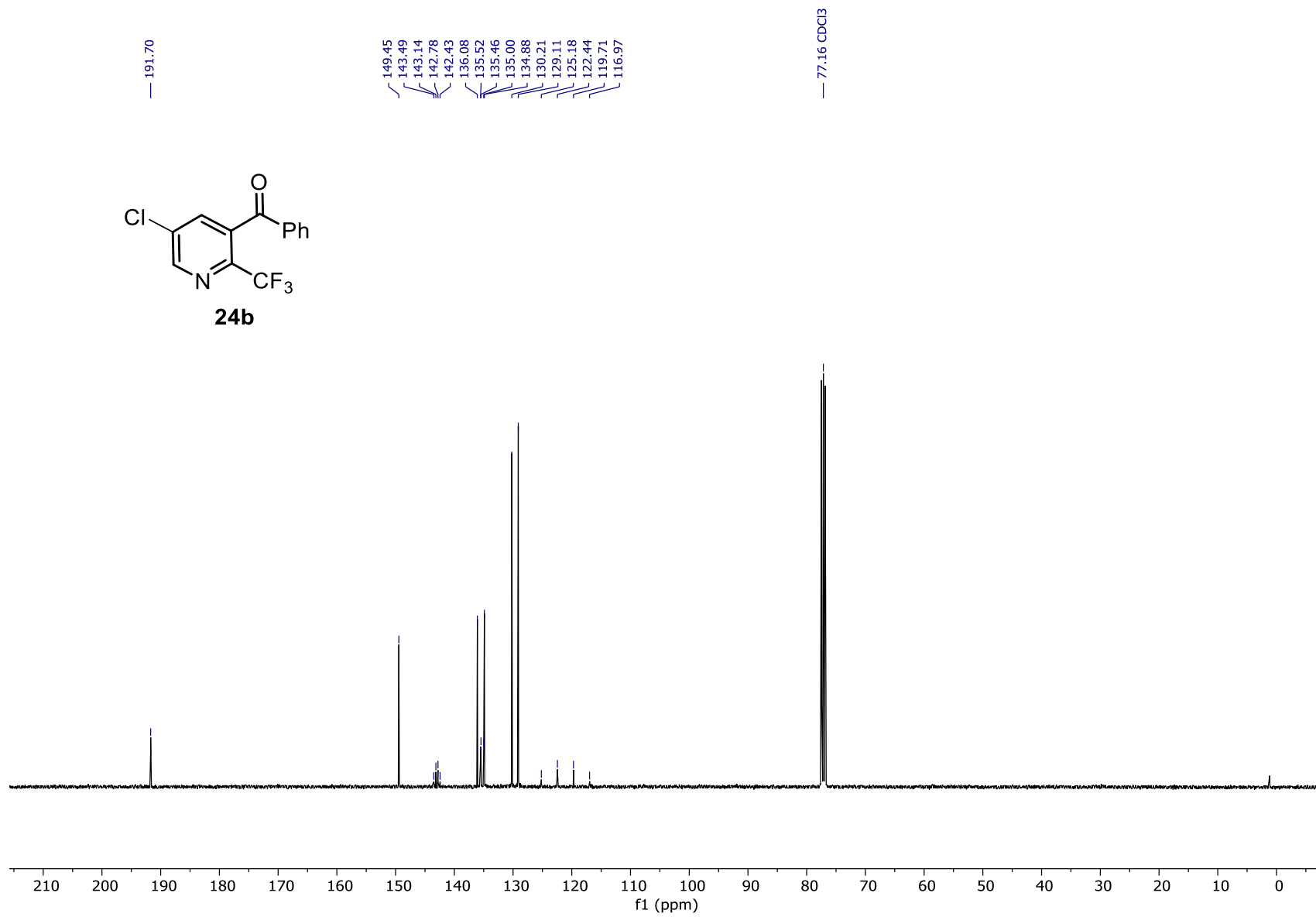
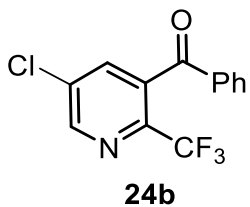


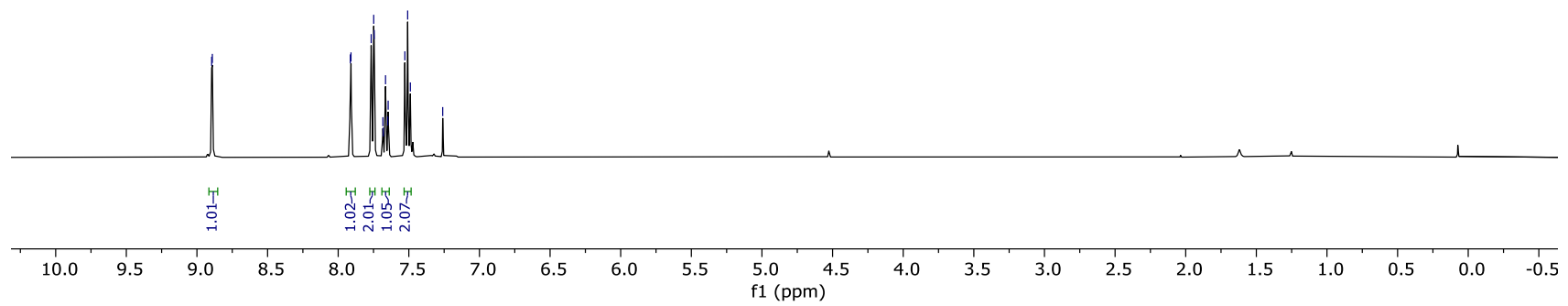
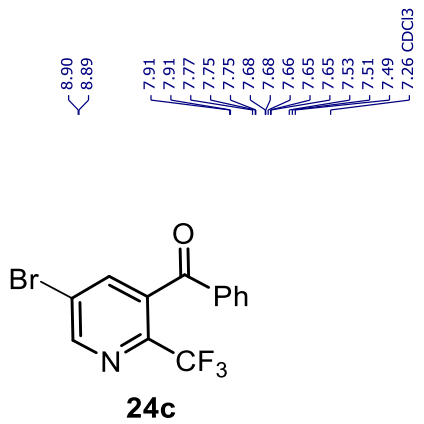


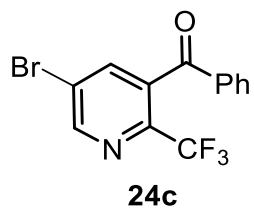




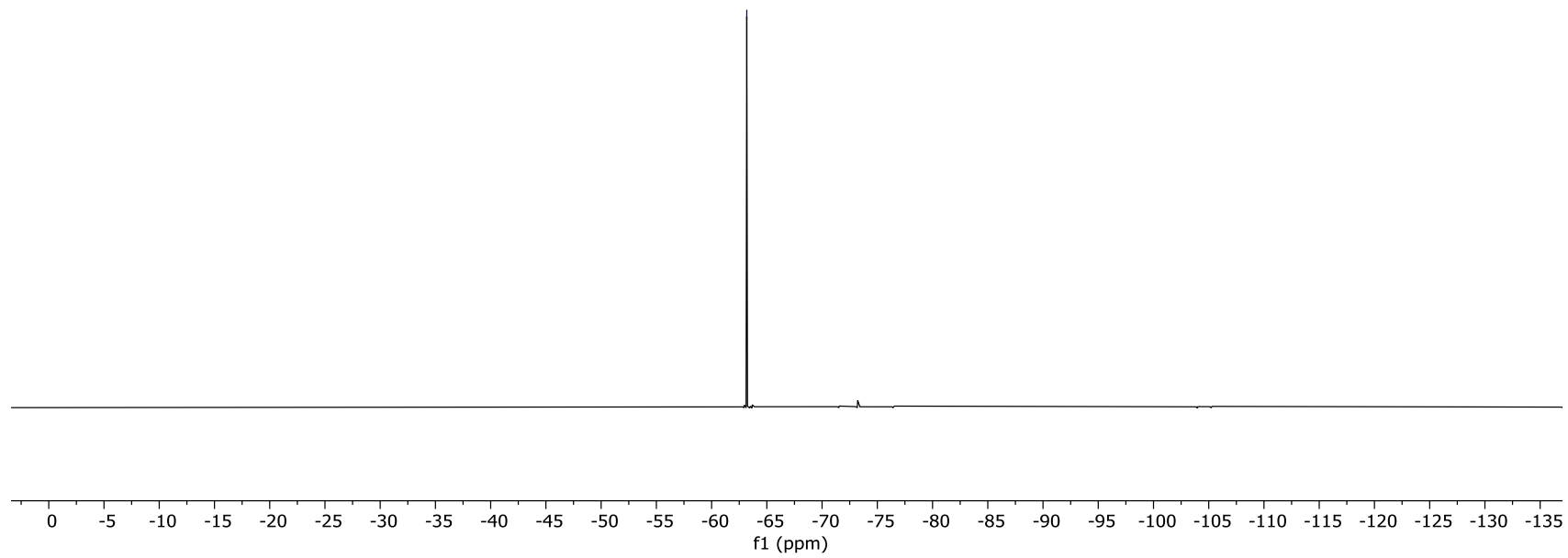


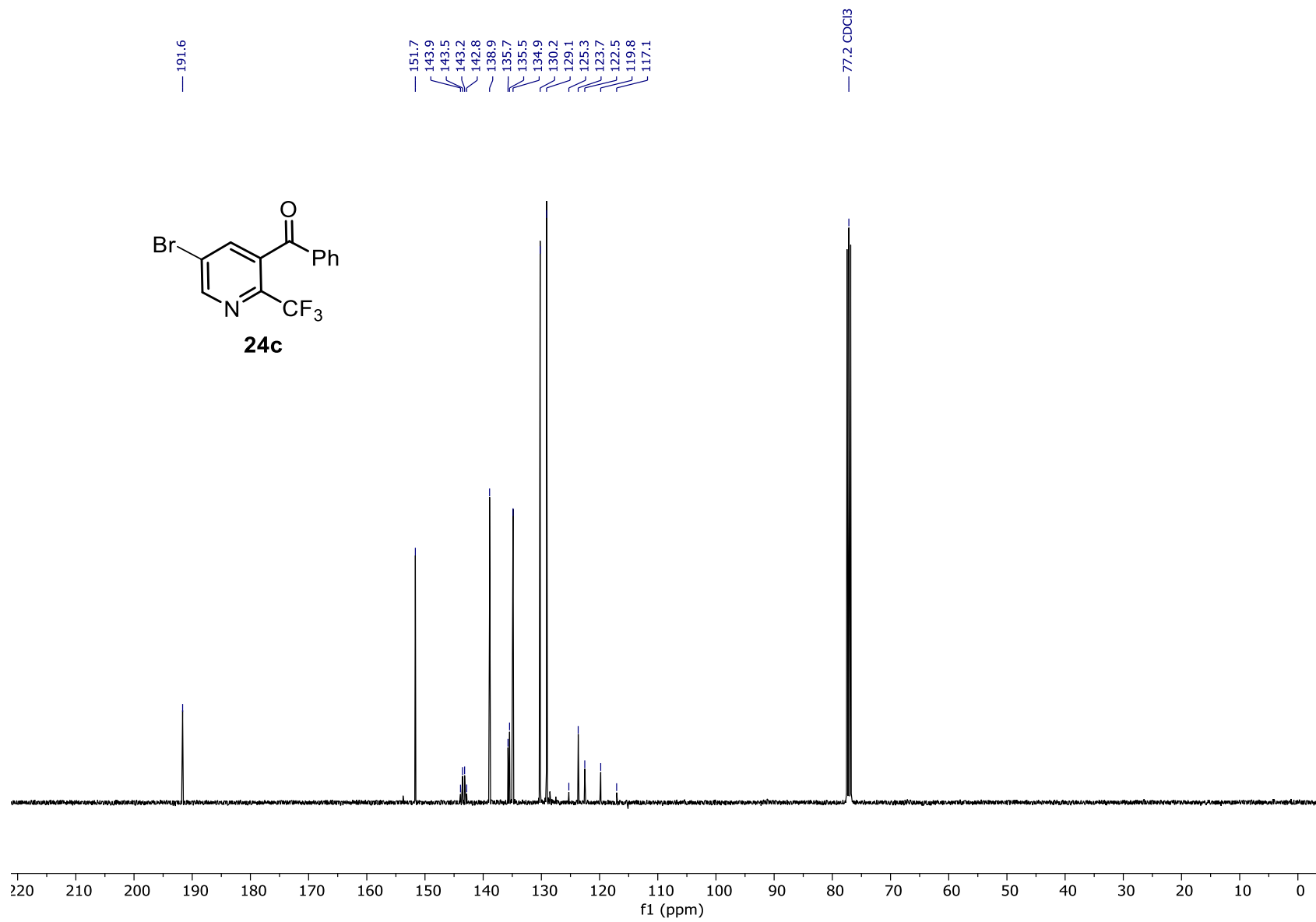


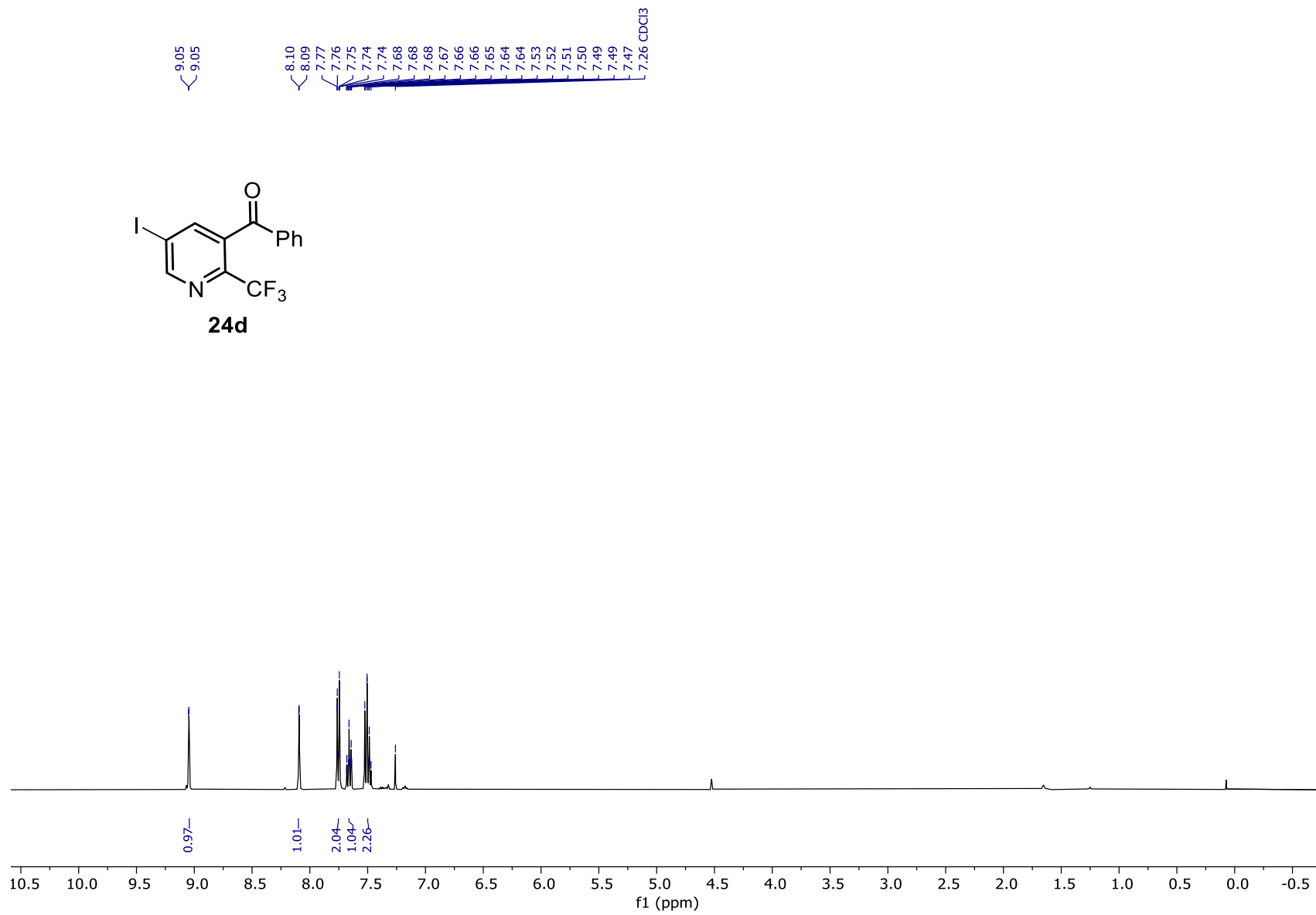
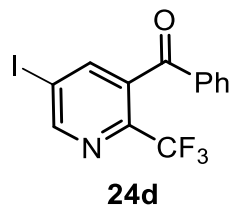


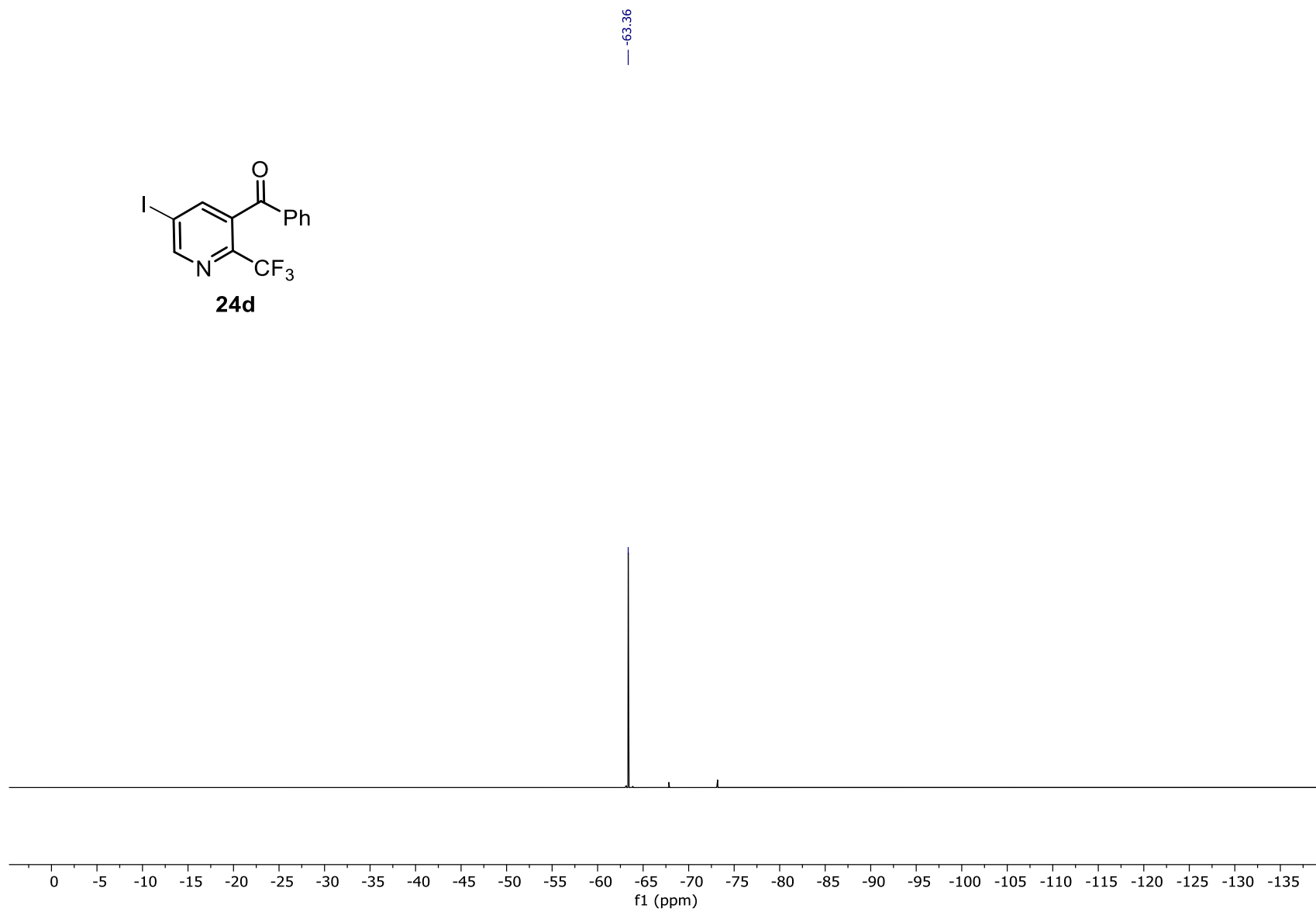
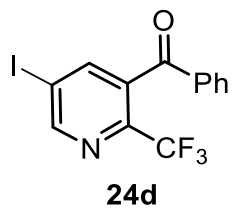


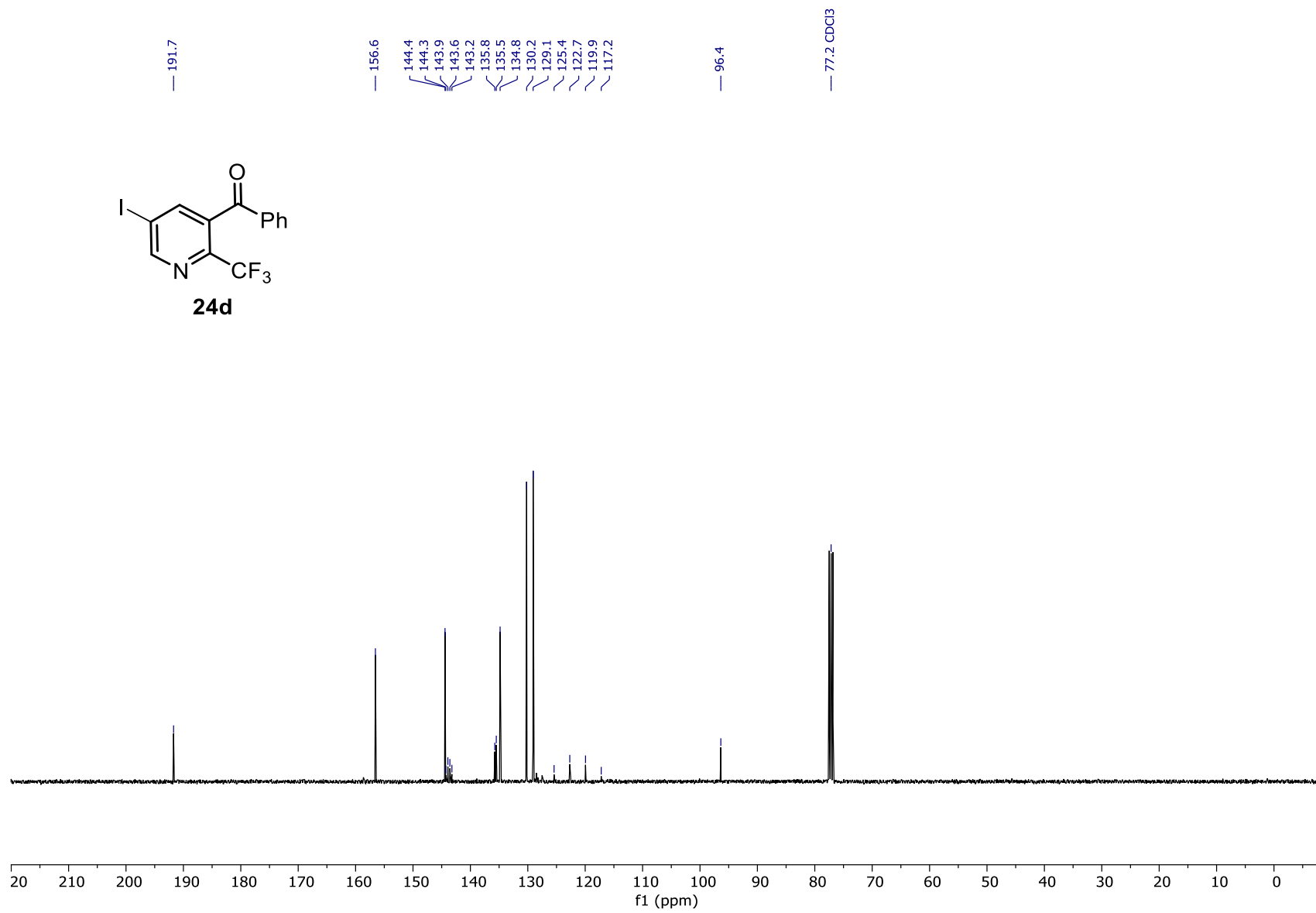
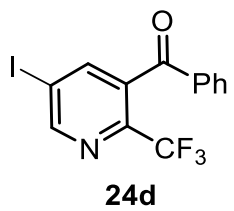
— 63.18

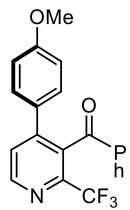




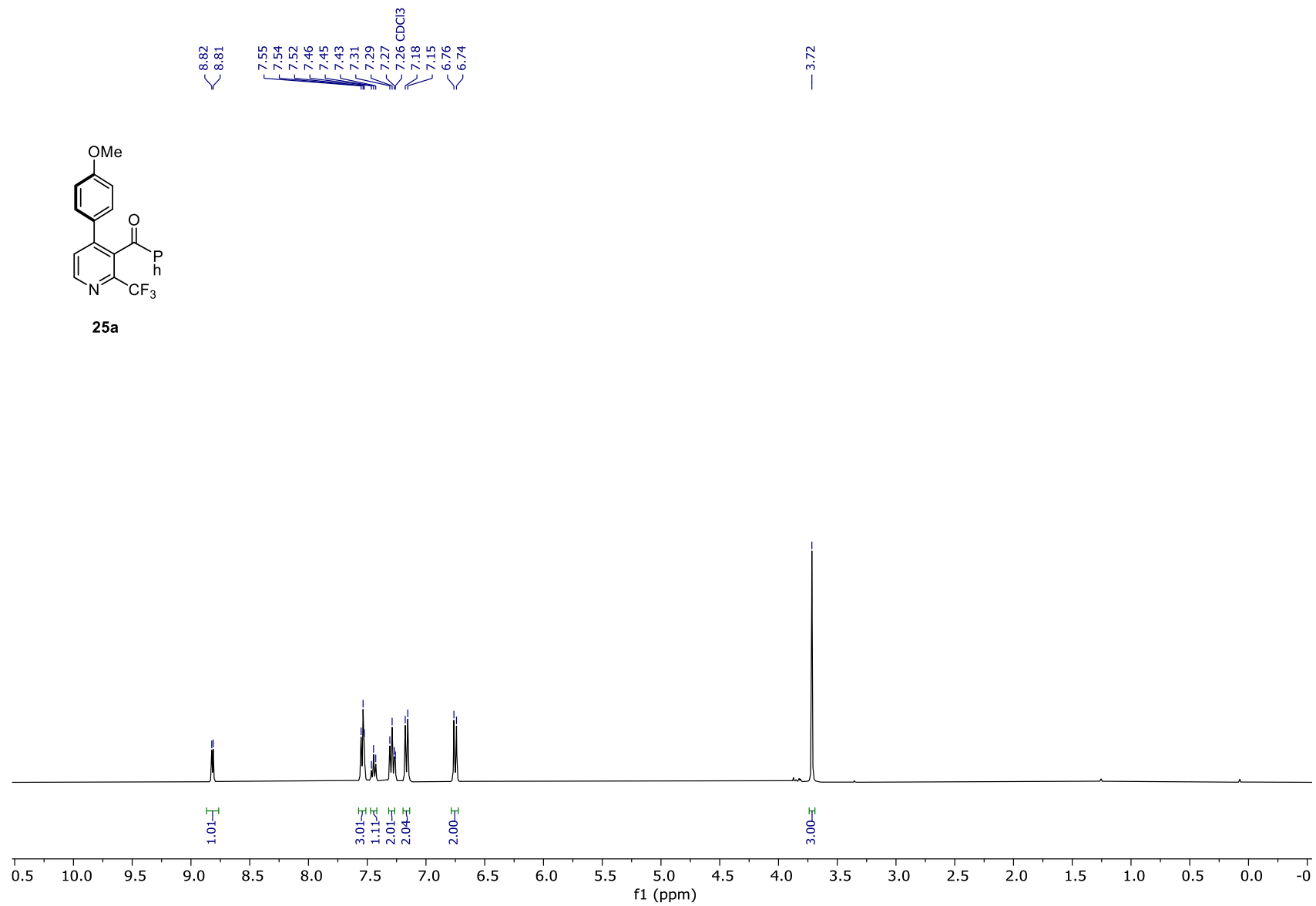


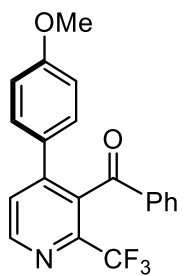




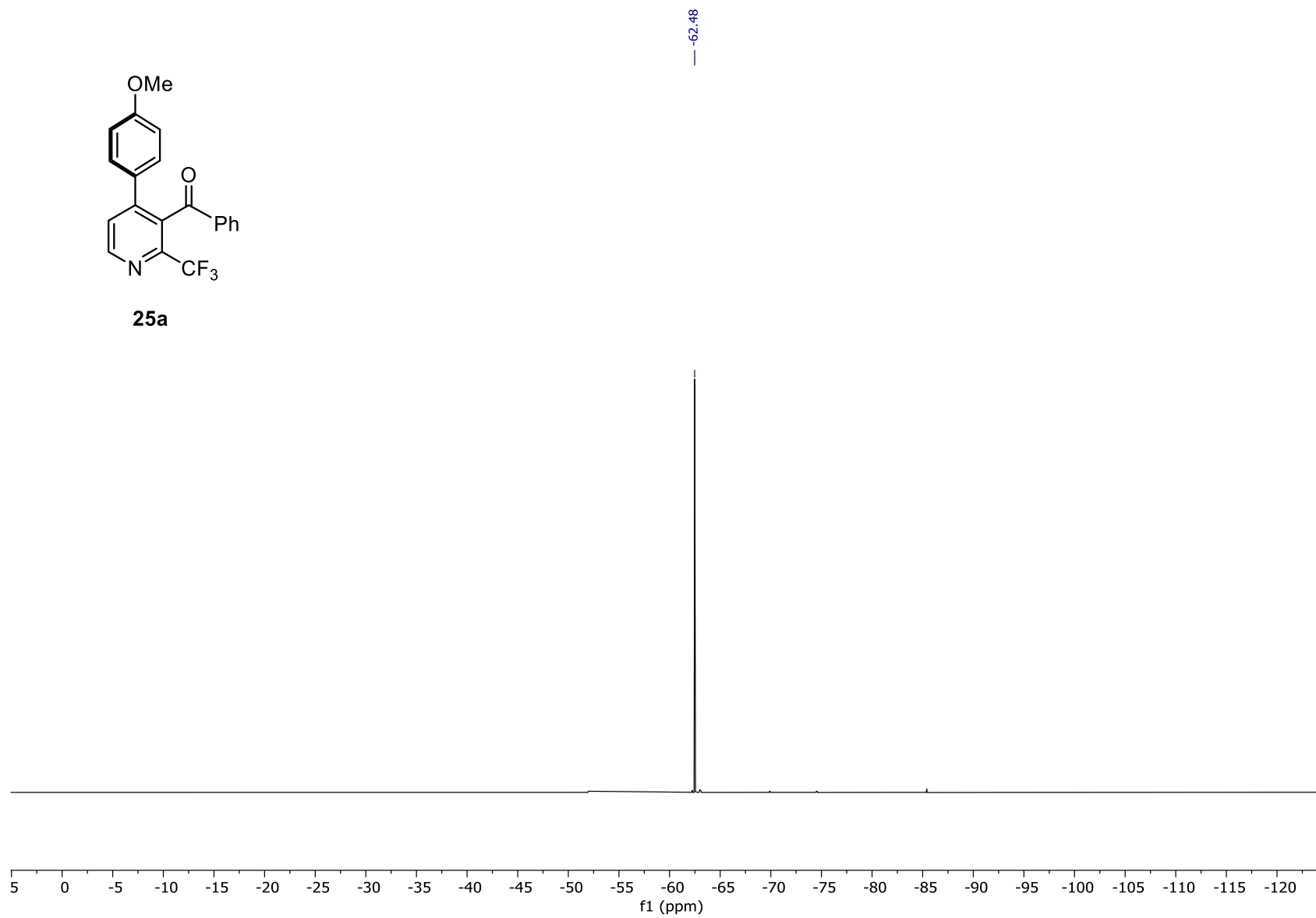


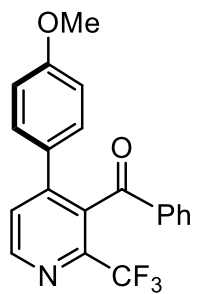
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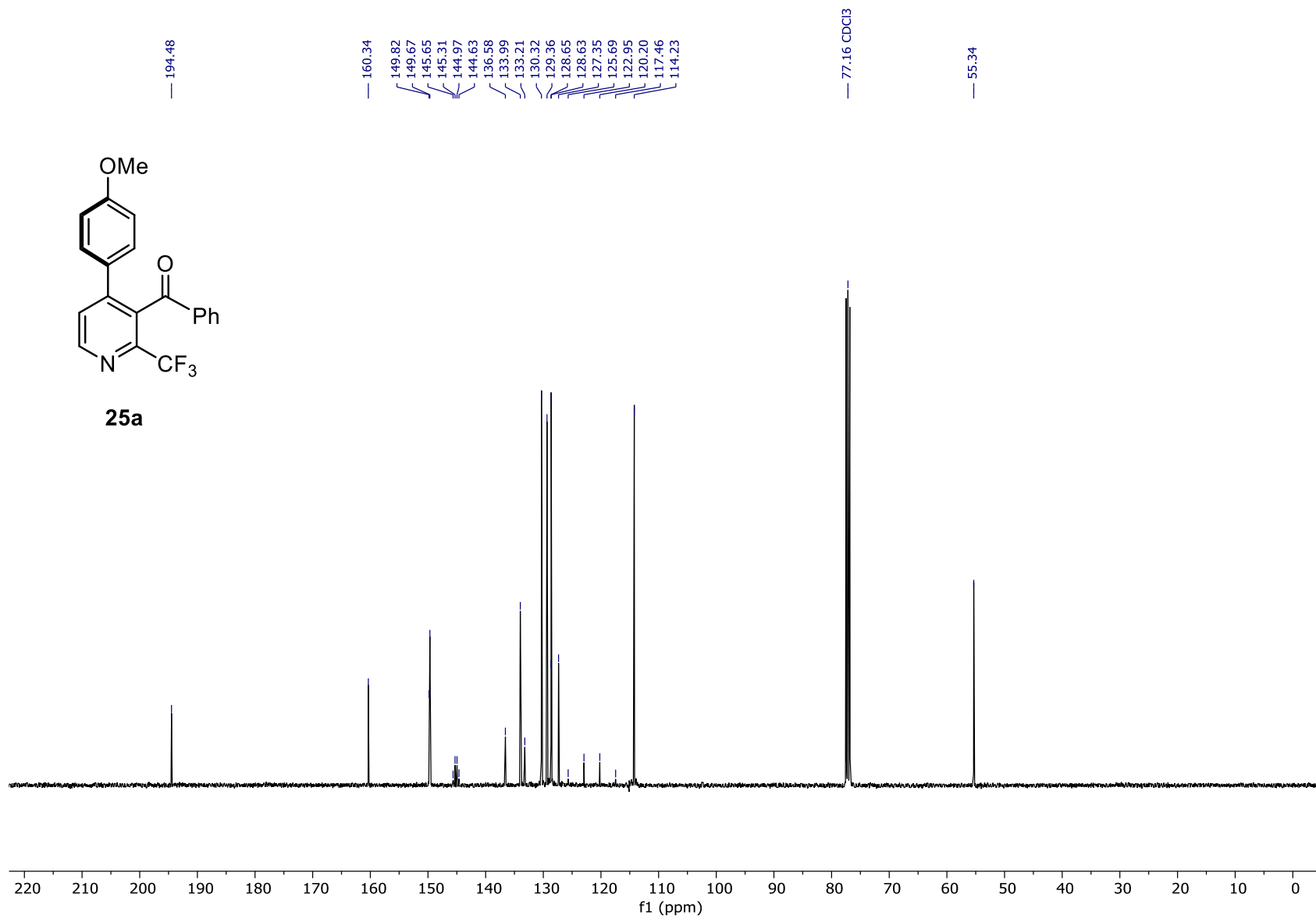


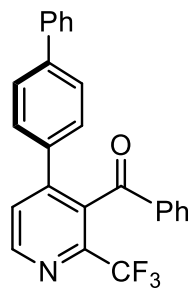
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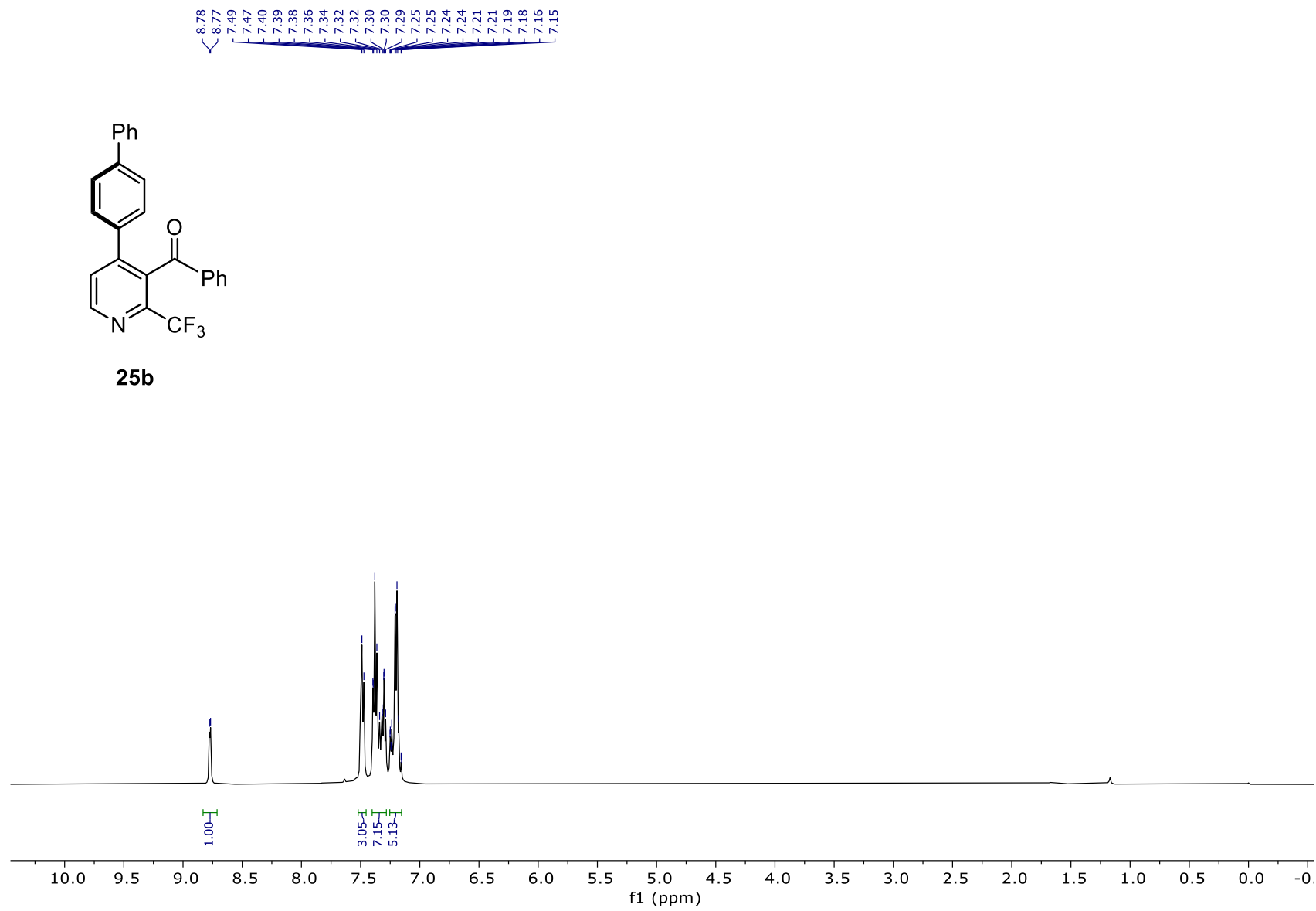


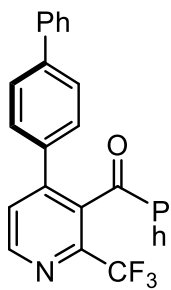
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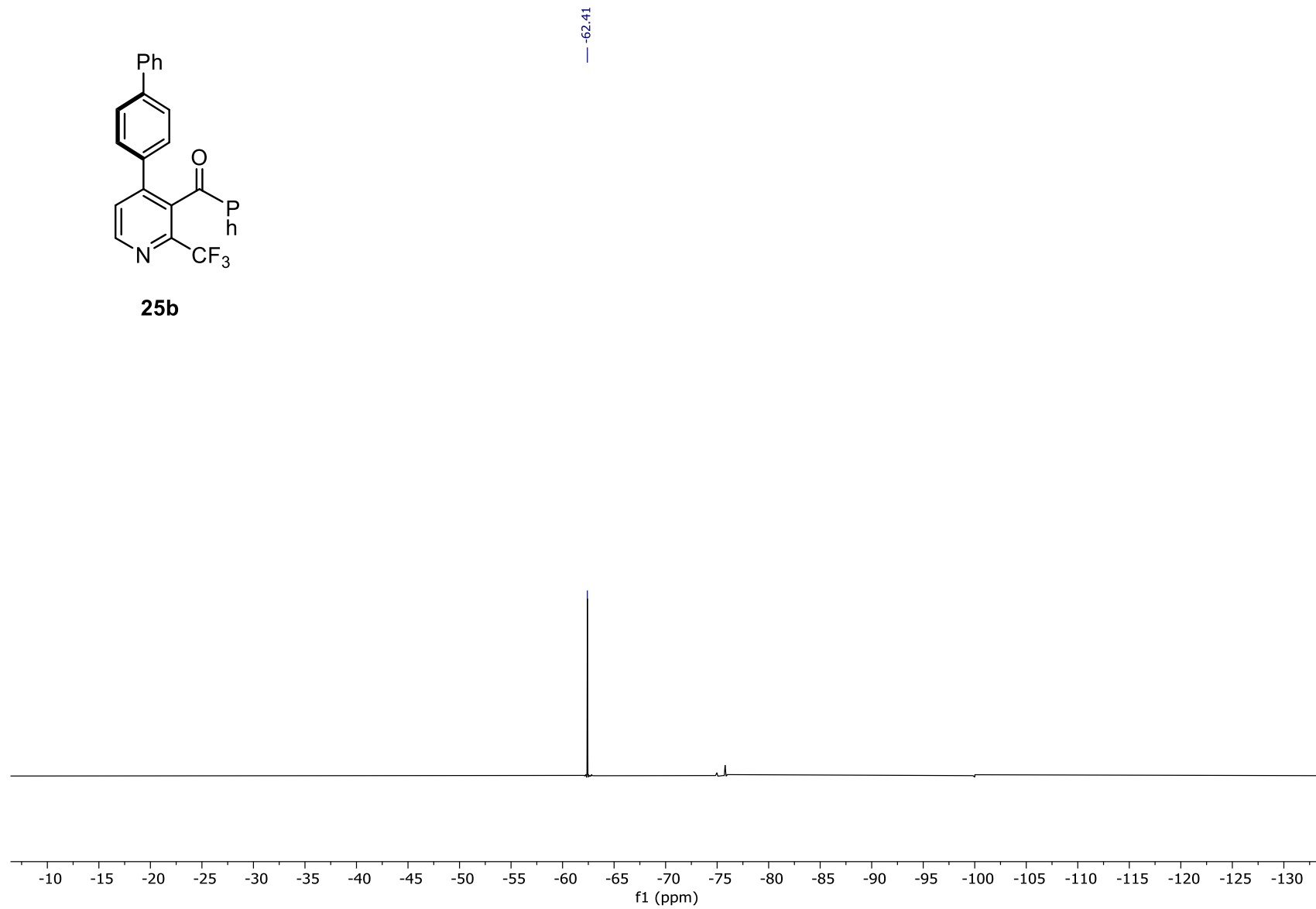


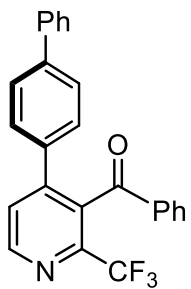
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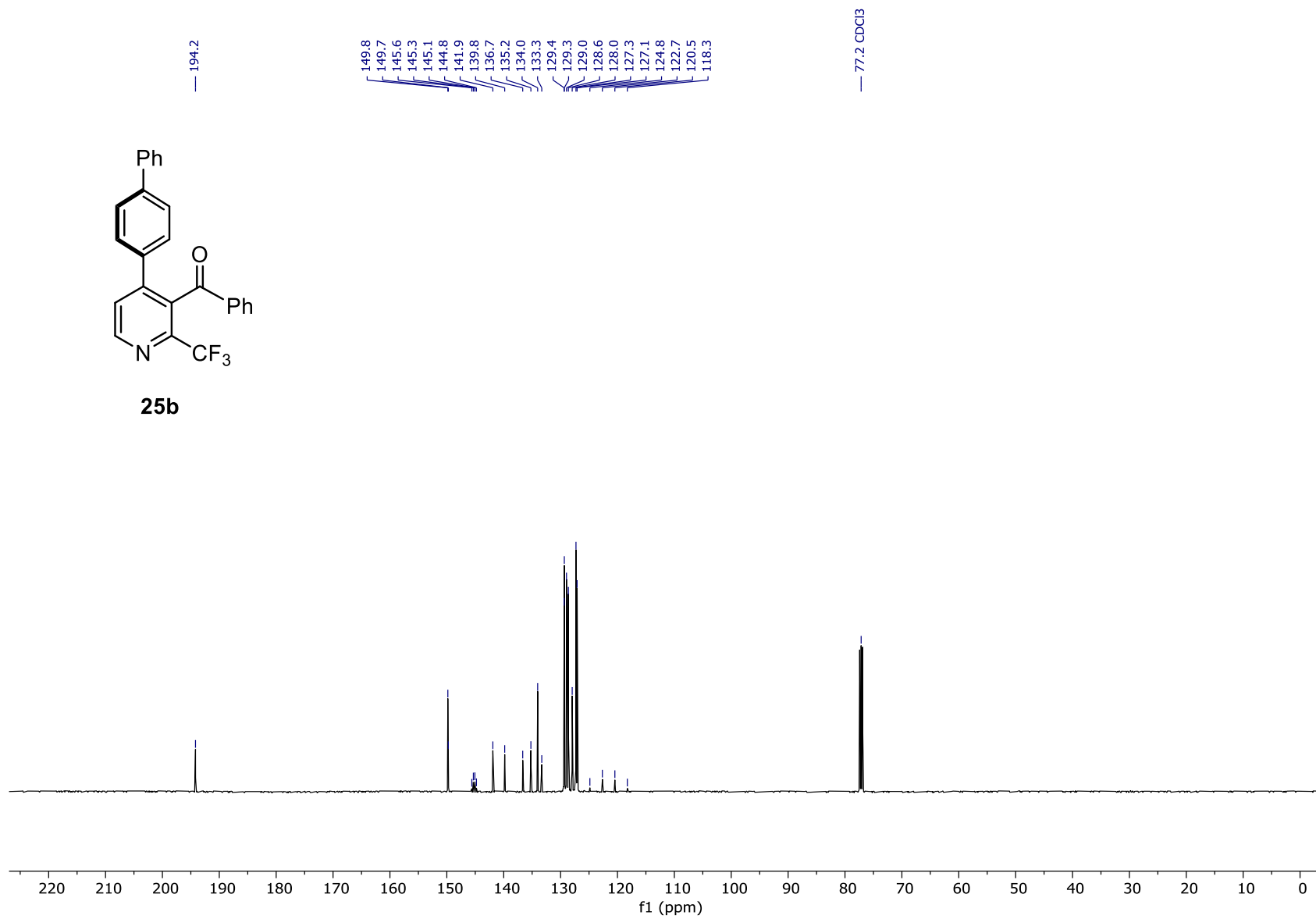


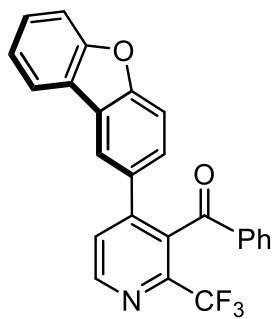
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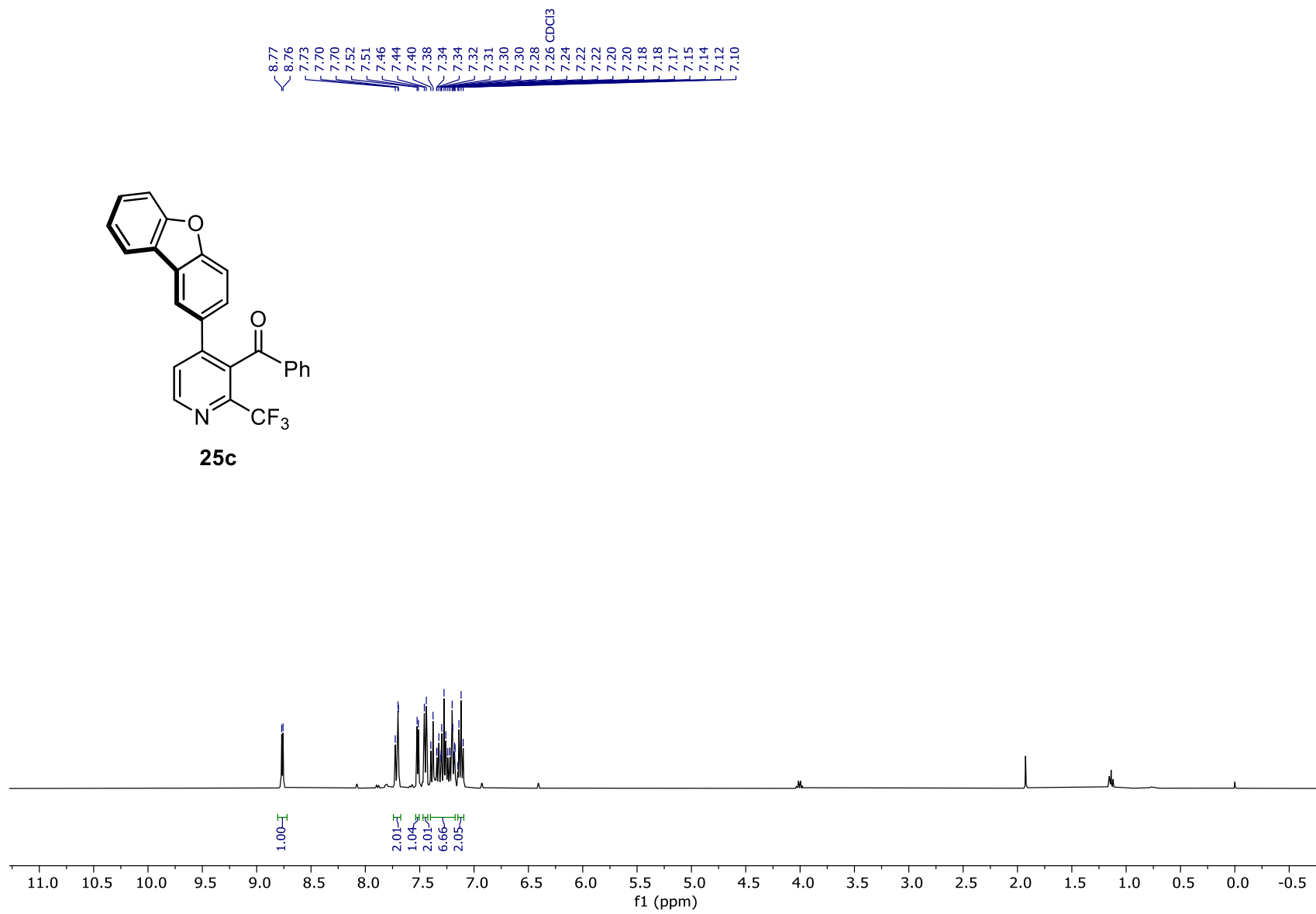


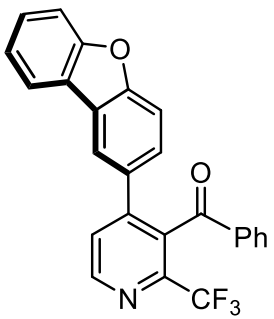
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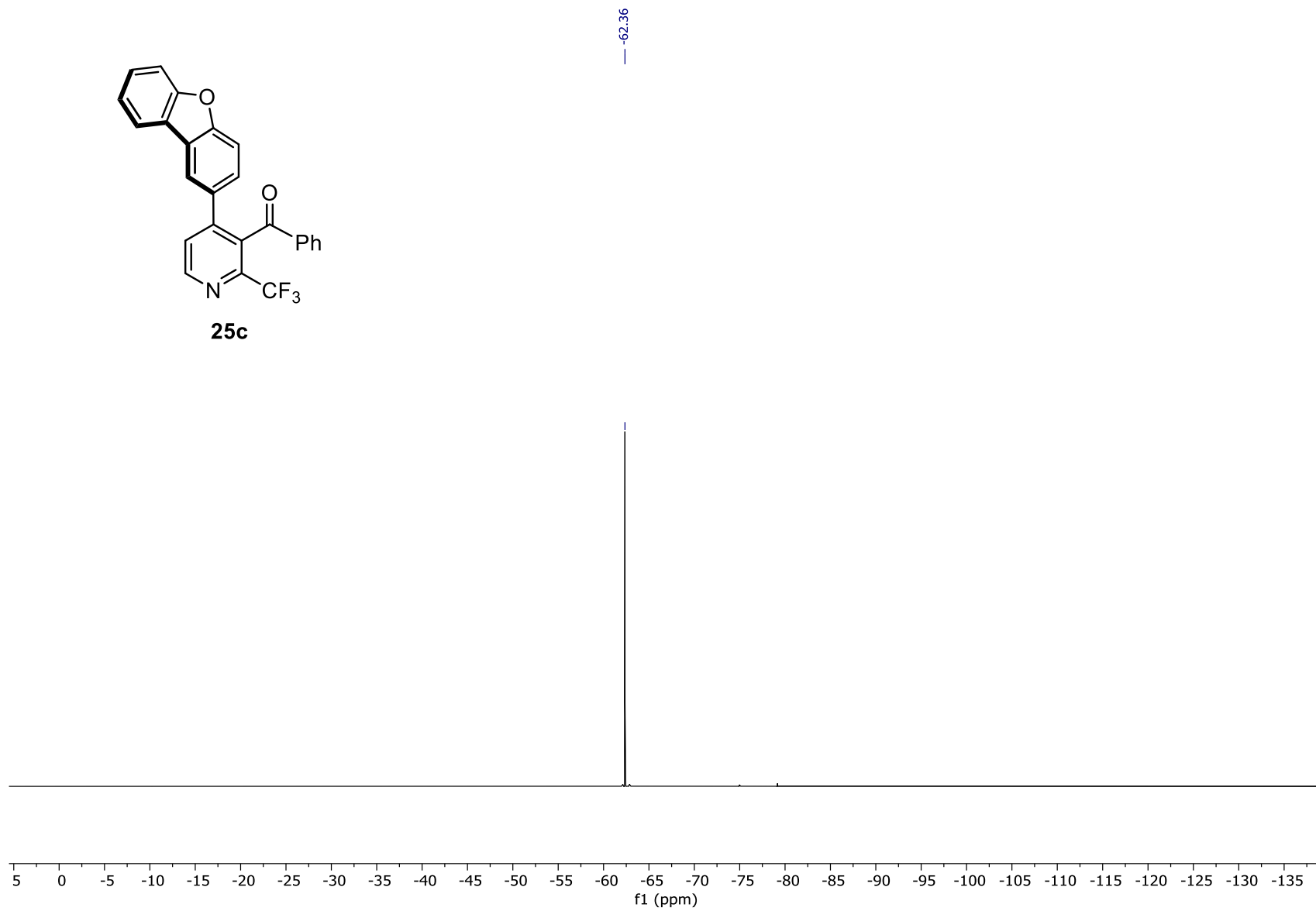


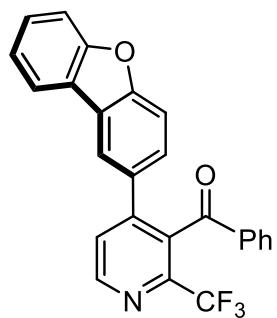
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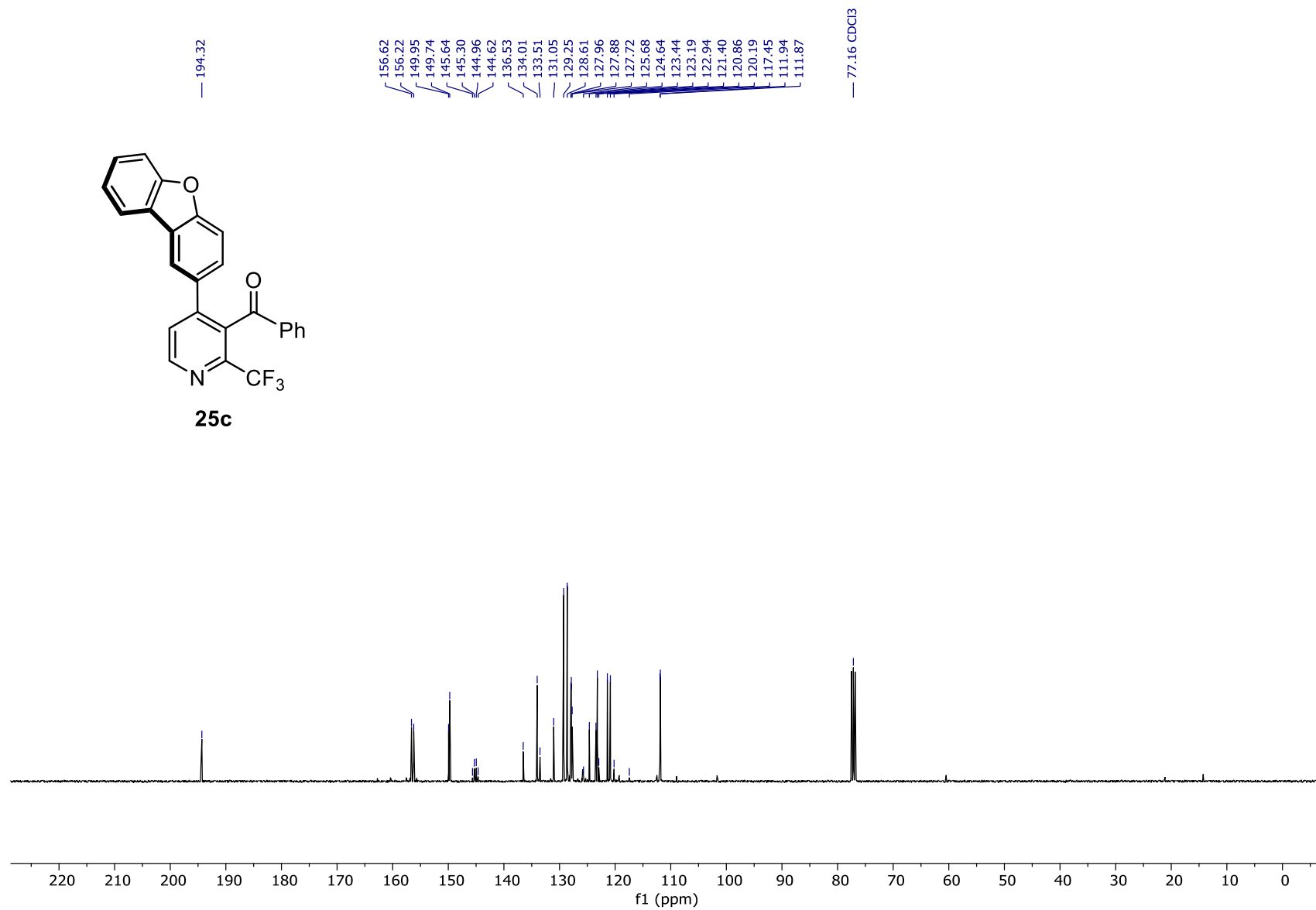


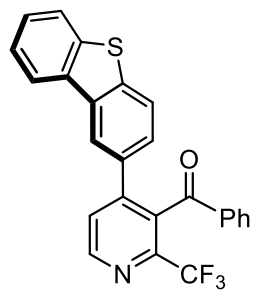
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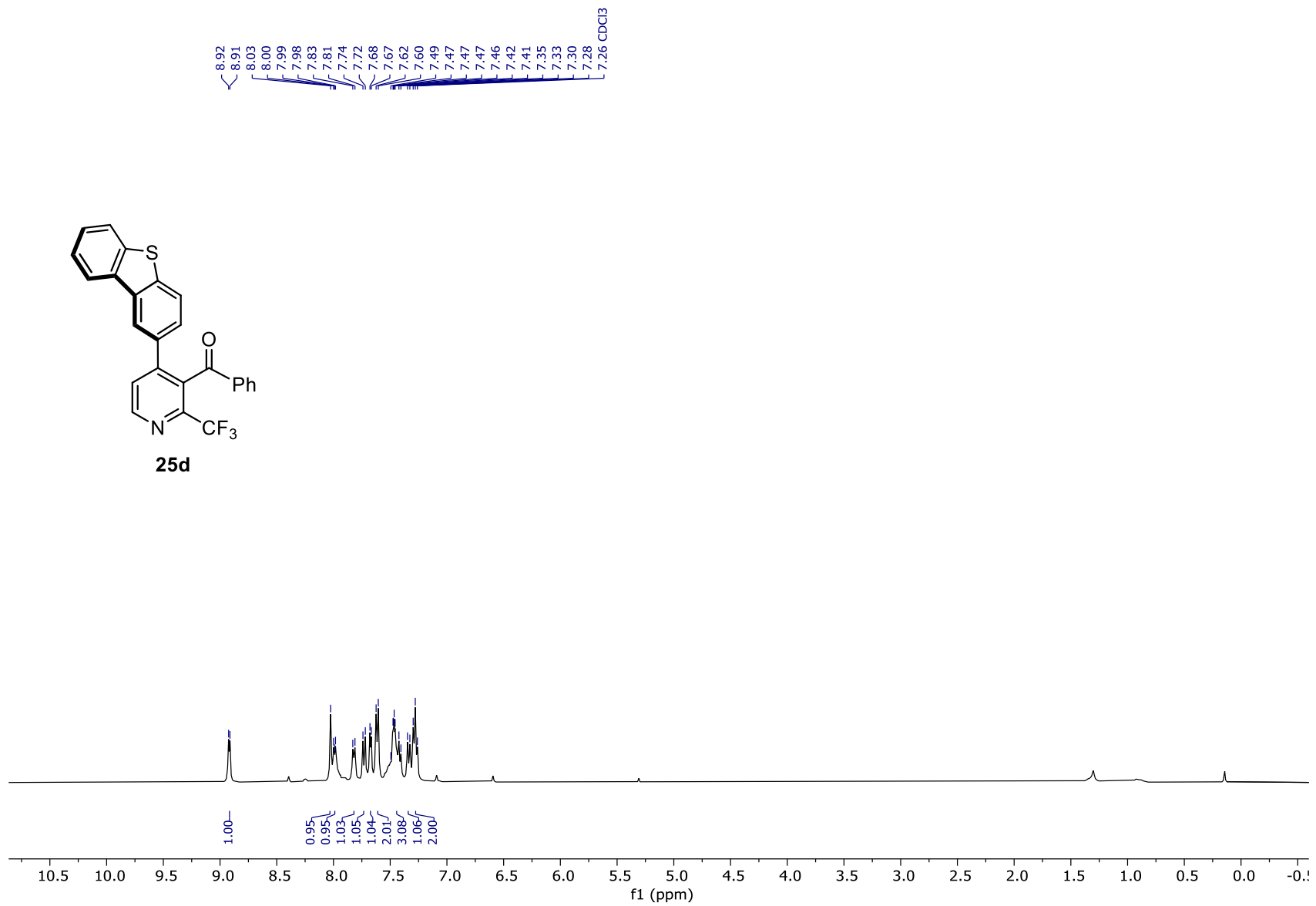


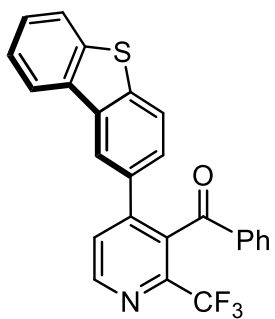
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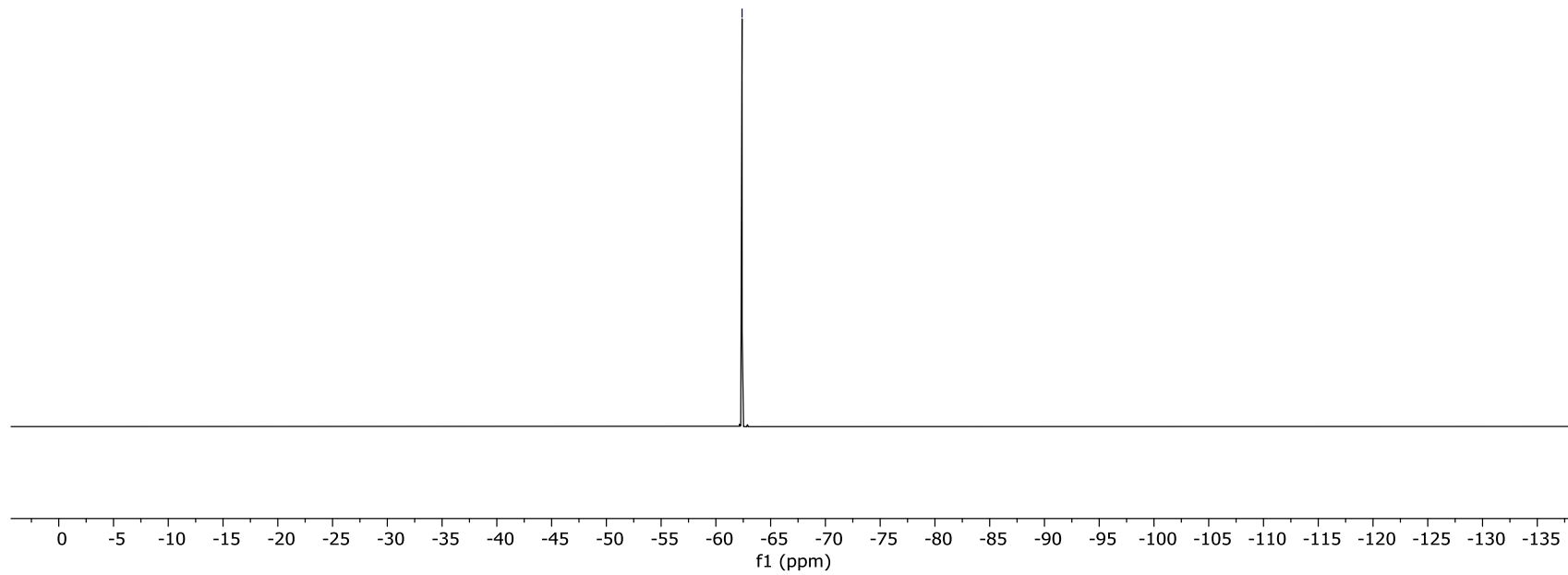
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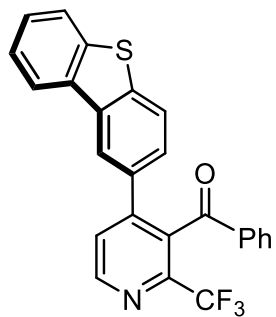




25d

-62.39





25d

