Supporting Information

Cobalt-catalyzed regio- and diastereoselective carbocyclization/arylation of 1,5-bisallenes

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1. General Information

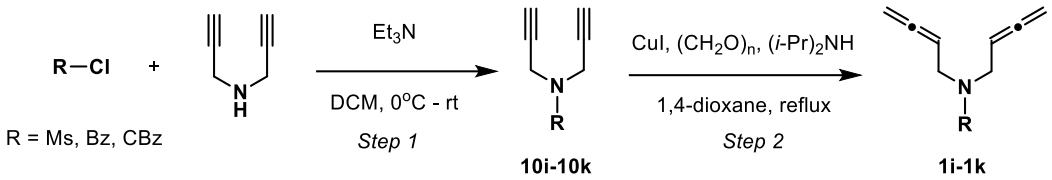
All reagents were purchased and used without further purification unless otherwise specified. Flash column chromatography was performed over silica gel (300-400 mesh) purchased from Shanghai Titan Scientific Co., Ltd. Anhydrous tetrahydrofuran (THF), *tert*-Butyl methyl ether (MTBE), acetone, dimethyl sulfoxide (DMSO), 1,4-dioxane, toluene, acetonitrile (CH_3CN) and 2-Methyltetrahydrofuran (2-Me-THF) were purchased from Shanghai Titan Scientific Co., Ltd. and used as received. $CoCl_2$ and $CoBr_2$ were purchased from Alfa Aesar. $Co(OAc)_2$ was purchased from Sigma-Aldrich. $Co(acac)_2$ was purchased from TCI Chemicals. $CoCl_2(PPh_3)_2$ and $CoCl(PPh_3)_3$ were purchased from Shanghai Bide Pharmatech Co., Ltd. $Co_2(CO)_8$ was purchased from Shanghai Titan Scientific Co., Ltd.

^1H, ^{13}C, ^{19}F NMR spectra were collected on a Bruker AV 400 MHz and 600 MHz NMR spectrometer using residue solvent peaks as an internal standard (^1H NMR: $CDCl_3$ at 7.26 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J* (Hz), and integration. High resolution mass spectra were acquired by Agilent 6545 Accurate-Mass Q-TOF LC/MS System. X-ray structure was determined on a Bruker D8 Venture X-ray Diffraction meter.

2. Substrate Preparation

Bisallenes **1a-1c**,[1] **1d**,[2] **1e-1h**,[1] **1l**,[3] **1m**[1], **1n**[4], **1o**[5], and **1p**[6] are known compounds. They were prepared according to the literatures. Other substrates were prepared according to the following procedures, which were unoptimized.

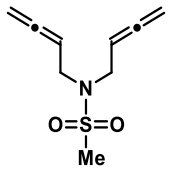
General procedure A: Synthesis bisallenes 1i-1k



Step 1: In an oven-dried 100 mL round-bottom flask equipped with a magnetic stirrer, a mixture of dipropargylamine (1.2 equiv, 12 mmol), triethylamine (1.4 equiv, 14 mmol) and DCM (20 mL) was stirred at room temperature for 10 minutes. R-Cl (1.0 equiv, 10 mmol) was then added dropwise at 0 °C and the reaction mixture was stirred overnight and allowed to warm to room temperature. The solids were filtered off and the filtrate was concentrated under reduced pressure. The crude was mixed with water and extracted with DCM. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude diyne product **10** was directly used in the next step without further purification.

Step 2: In an oven-dried 100 mL round-bottom charged with diyne **10** (1.0 equiv, 10 mmol), paraformaldehyde (5.0 equiv, 50 mmol) and CuI (1.0 equiv, 10 mmol) was evacuated and backfilled with N_2 for three times. Then, diisopropylamine (4.0 equiv, 40 mmol) and 1,4-dioxane (50 mL) were added and the resulting mixture was stirred at reflux for 16 h until completion (TLC monitoring). The reaction mixture was allowed to cool to room temperature, concentrated under reduced pressure. The resulting crude was purified by column chromatography (SiO_2) to afford the corresponding bisallenes **1i-1k**.

***N*,*N*-di(buta-2,3-dien-1-yl)methanesulfonamide (1i)**



1i

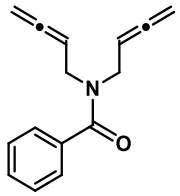
General procedure A, R_f = 0.5 (PE/EA = 5/1), yellow oil (425.1 mg, 21% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 5.19 – 5.10 (m, 2H), 4.87 – 4.82 (m, 4H), 3.94 – 3.91 (m, 4H), 2.89 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 209.7, 85.8, 76.6, 45.3, 40.3.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_9H_{13}NNaO_2S^{\oplus}$ 222.0559, found 222.0564.

***N*,*N*-di(buta-2,3-dien-1-yl)benzamide (1j)**



1j

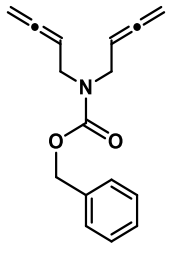
General procedure A, R_f = 0.5 (PE/EA = 5/1), yellow oil (351.8 mg, 16% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 – 7.34 (m, 5H), 5.38 – 4.99 (m, 2H), 4.90 – 4.73 (m, 4H), 4.24 – 3.73 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 209.1, 171.6, 136.2, 129.6, 128.4, 126.7, 86.6, 76.9, 45.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{15}NNaO^{\oplus}$ 248.1046, found 248.1052.

Benzyl di(buta-2,3-dien-1-yl)carbamate (1k)



1k

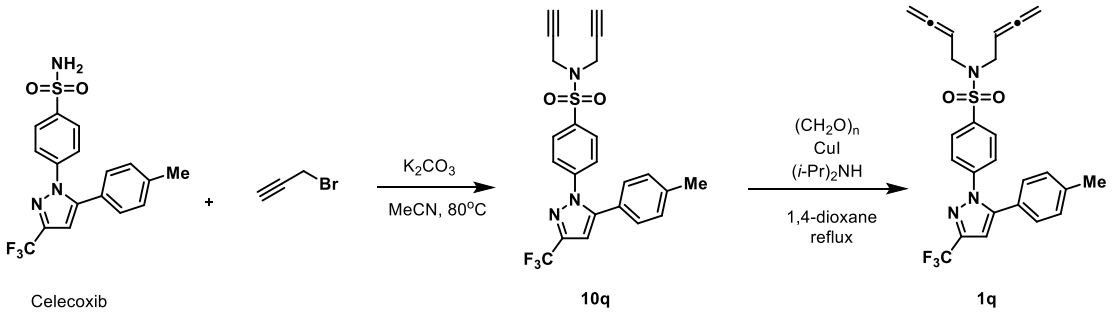
General procedure A, R_f = 0.8 (PE/EA = 5/1), colorless oil (1.1 g, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.39 – 7.29 (m, 5H), 5.18 – 5.04 (m, 4H), 4.80 – 4.68 (m, 4H), 4.00 – 3.86 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 209.0, 155.8, 136.7, 128.4, 127.9, 127.8, 86.8, 76.3, 67.1, 45.3.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{17}NNaO_2^{\oplus}$ 278.1151, found 278.1156.

Synthesis bisallene **1q**:

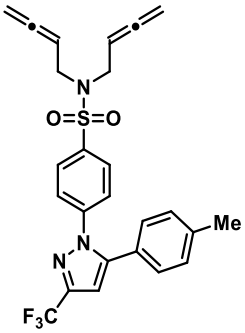


Celecoxib **10q** **1q**

Step1: An oven-dried 50 mL round-bottom flask charged with Celecoxib (1.0 equiv, 5 mmol), 3-Bromopropyne (3.0 equiv, 15 mmol), K_2CO_3 (3.0 equiv, 15 mmol), and MeCN (10 mL) was refluxed at 80 °C in oil bath for 12 h. The reaction mixture was allowed to cool to room temperature, concentrated under reduced pressure. The resulting crude was purified by column chromatography (SiO_2) to afford the corresponding product **10q**.

Step2: In an oven-dried 100 mL round-bottom charged with diyne **10q** (1.0 equiv, 4.7 mmol), paraformaldehyde (5.0 equiv, 23.5 mmol) and CuI (1.0 equiv, 4.7 mmol) was evacuated and backfilled with N_2 for three times. Then, diisopropylamine (4.0 equiv, 18.8 mmol) and 1,4-dioxane (24 mL) were added and the resulting mixture was stirred at reflux for 16 h until completion (TLC monitoring). The reaction mixture was allowed to cool to room temperature, concentrated under reduced pressure. The resulting crude was purified by column chromatography (SiO_2) to afford the corresponding bisallene **1q**.

***N,N*-di(buta-2,3-dien-1-yl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (1q)**



1q

R_f = 0.5 (PE/EA = 10/1), yellow oil (1.6 g, 70% yield).

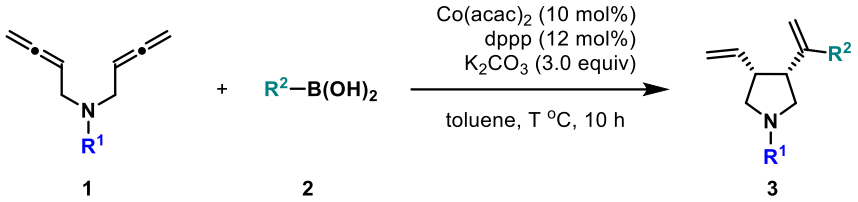
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 4.96– 4.87 (m, 1H), 4.77 – 4.70 (m, 4H), 3.93 – 3.87 (m, 4H), 2.38 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 209.7, 145.2, 144.1 (q, *J* = 38.3 Hz), 142.4, 140.1, 139.8, 129.7, 128.7, 128.1, 125.7, 125.6, 121.5 (q, *J* = 267.7 Hz), 106.2, 85.3, 76.5, 45.7, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.4.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{25}H_{22}F_3N_3NaO_2S^{\oplus}$ 508.1277, found 508.1288.

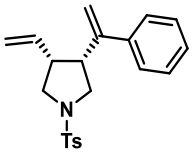
3. Substrate Scope of 1,5-Bisallenes



Condition A: In a glove box, an oven-dried 4-mL vial was charged with bisallene **1** (0.2 mmol, 1.0 equiv), arylboronic acid **2** (0.6 mmol, 3.0 equiv), K_2CO_3 (0.6 mmol, 3.0 equiv), $Co(acac)_2$ (0.02 mmol, 0.1 equiv), dppp (0.024 mmol, 0.12 equiv) and toluene (2.0 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at 70 °C for 10 h. Then the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography to give the desired product **3**.

Condition B: In a glove box, an oven-dried 4-mL vial was charged with bisallene **1** (0.2 mmol, 1.0 equiv), arylboronic acid **2** (0.6 mmol, 3.0 equiv), K_2CO_3 (0.6 mmol, 3.0 equiv), $Co(acac)_2$ (0.02 mmol, 0.1 equiv), dppp (0.024 mmol, 0.12 equiv) and toluene (2.0 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at 80 °C for 10 h. Then the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography to give the desired product **3**.

3-(1-Phenylvinyl)-1-tosyl-4-vinylpyrrolidine (3aa)



3aa

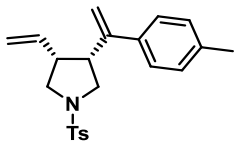
Condition A, R_f = 0.4 (PE/EA = 10/1), yellow oil (59 mg, 84% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.24 – 7.20 (m, 2H), 5.30 – 5.21 (m, 2H), 4.88 (d, *J* = 1.4 Hz, 1H), 4.80 (d, *J* = 10.4 Hz, 1H), 4.63 – 4.55 (m, 1H), 3.67 (dd, *J* = 9.5, 6.9 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.41 (t, *J* = 9.6 Hz, 1H), 3.37 – 3.30 (m, 2H), 2.79 -2.73 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 145.6, 143.5, 141.4, 134.5, 134.3, 129.7, 128.3, 127.6, 127.5, 126.4, 116.7, 114.0, 52.3, 49.7, 45.8, 44.3, 21.5.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{23}NNaO_2S^{\oplus}$ 376.1342, found 376.1353.

3-(1-(*p*-Tolyl)vinyl)-1-tosyl-4-vinylpyrrolidine (3ab)



3ab

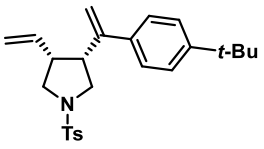
Condition B, R_f = 0.3 (PE/EA = 10/1), colorless oil (48.1 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.05 (m, 4H), 5.29 – 5.19 (m, 2H), 4.84 – 4.77 (m, 2H), 4.59 (d, *J* = 17.2 Hz, 1H), 3.66 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.40 (t, *J* = 9.6 Hz, 1H), 3.36 – 3.27 (m, 2H), 2.80 -2.72 (m, 1H), 2.45 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.3, 143.4, 138.5, 137.4, 134.5, 134.2, 129.7, 129.0, 127.5, 126.2, 116.6, 113.2, 52.2, 49.7, 45.8, 44.3, 21.5, 21.1.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{25}NNaO_2S^{\oplus}$ 390.1498, found 390.1509.

3-(1-(4-(*tert*-Butyl)phenyl)vinyl)-1-tosyl-4-vinylpyrrolidine (3ac)



3ac

Condition B, R_f = 0.4 (PE/EA = 10/1), white solid (50.1 mg, 61% yield).

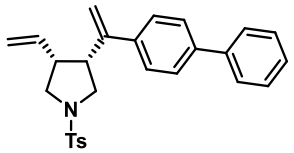
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.32 – 5.23 (m, 2H), 4.85 –

4.80 (m, 2H), 4.65 – 4.58 (m, 1H), 3.66 (dd, *J* = 9.5, 6.9 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.42 – 3.28 (m, 3H), 2.83 – 2.75 (m, 1H), 2.46 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 150.7, 145.2, 143.4, 138.4, 134.6, 134.3, 129.7, 127.5, 125.9, 125.2, 116.6, 113.3, 52.2, 49.8, 45.8, 44.2, 34.5, 31.3, 21.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{25}H_{31}NNaO_2S^{\oplus}$ 432.1968, found 432.1984.

3-(1-([1,1'-Biphenyl]-4-yl)vinyl)-1-tosyl-4-vinylpyrrolidine (3ad)



3ad

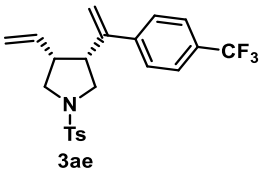
Condition A, R_f = 0.3 (PE/EA = 10/1), white solid (50.2 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 8.2 Hz, 2H), 7.58 (dd, *J* = 8.4, 2H), 7.52 (dd, *J* = 8.3, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.27 (m, 5H), 5.40 – 5.18 (m, 2H), 4.91 (s, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.63 (d, *J* = 17.2 Hz, 1H), 3.69 (dd, *J* = 9.1, 6.5 Hz, 1H), 3.52 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.44 (t, *J* = 9.3 Hz, 1H), 3.40 – 3.31 (m, 2H), 2.91 -2.75 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 145.1, 143.5, 140.4, 140.3, 134.5, 134.2, 129.8, 128.8, 127.5, 127.4, 127.0, 126.9, 126.7, 116.8, 113.9, 52.3, 49.8, 45.8, 44.4, 21.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{27}H_{27}NNaO_2S^{\oplus}$ 452.1655, found 452.1663.

1-Tosyl-3-(1-(4-(trifluoromethyl)phenyl)vinyl)-4-vinylpyrrolidine (3ae)



3ae

Condition B, R_f = 0.3 (PE/EA = 10/1), white solid (44.7 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.41 – 7.29 (m, 4H), 5.32 (s, 1H), 5.27 – 5.16 (m, 1H), 4.99 (s, 1H), 4.80 (d, *J* =

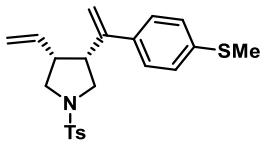
10.2 Hz, 1H), 4.58 (d, *J* = 17.0 Hz, 1H), 3.73 – 3.64 (m, 1H), 3.55 – 3.47 (m, 1H), 3.43 (t, *J* = 9.3 Hz, 1H), 3.38 – 3.29 (m, 2H), 2.77 – 2.69 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.0, 144.6, 143.6, 134.2, 134.0, 129.8, 129.6 (q, *J* = 32.3 Hz), 127.4, 126.7, 125.2 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 270.3 Hz), 117.1, 115.8, 52.3, 49.7, 45.6, 44.4, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.5.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{22}F_3NNaO_2S^{\oplus}$ 444.1216, found 444.1225.

3-(1-(4-(Methylthio)phenyl)vinyl)-1-tosyl-4-vinylpyrrolidine (3af)



3af

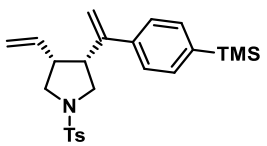
Condition B, R_f = 0.4 (PE/EA = 10/1), white solid (29.3 mg, 37% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.80 – 7.74 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.18 – 7.13 (m, 4H), 5.26 – 5.18 (m, 2H), 4.85 (d, *J* = 1.5 Hz, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.59 (dt, *J* = 17.1, 1.2 Hz, 1H), 3.66 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.40 (t, *J* = 9.5 Hz, 1H), 3.36 – 3.27 (m, 2H), 2.79 – 2.72 (m, 1H), 2.47 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 144.8, 143.5, 138.0, 137.9, 134.4, 134.1, 129.7, 127.4, 126.7, 126.2, 116.7, 113.5, 52.2, 49.7, 45.6, 44.3, 21.6, 15.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{25}NNaO_2S_2^{\oplus}$ 422.1219, found 422.1227.

1-Tosyl-3-(1-(4-(trimethylsilyl)phenyl)vinyl)-4-vinylpyrrolidine (3ag)



3ag

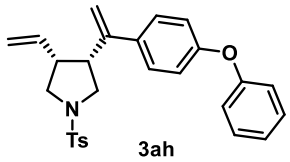
Condition B, R_f = 0.4 (PE/EA = 10/1), white solid (52.3 mg, 62% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.33 – 5.26 (m, 2H), 4.89 (d, *J* = 1.1 Hz, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.64 (d, *J* = 17.2 Hz, 1H), 3.67 (dd, *J* = 9.5, 6.9 Hz, 1H), 3.50 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.43 – 3.31 (m, 3H), 2.83 – 2.76 (m, 1H), 2.46 (s, 3H), 0.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.5, 143.5, 141.7, 139.9, 134.5, 134.3, 133.3, 129.7, 127.5, 125.6, 116.7, 114.0, 52.2, 49.8, 45.8, 44.3, 21.5, -1.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{24}H_{31}NNaO_2SSi^{\oplus}$ 448.1752, found 448.1752.

3-(1-(4-Phenoxyphenyl)vinyl)-1-tosyl-4-vinylpyrrolidine (3ah)



3ah

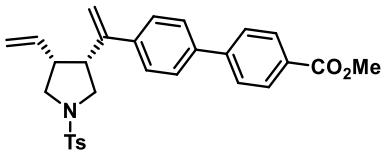
Condition B, R_f = 0.5 (PE/EA = 10/1), colorless oil (50.9 mg, 57% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.22 – 7.07 (m, 3H), 7.04 – 6.97 (m, 2H), 6.93 – 6.90 (m, 2H), 5.29 – 5.21 (m, 2H), 4.85 (d, *J* = 1.3 Hz, 1H), 4.81 (d, *J* = 10.4 Hz, 1H), 4.61 (d, *J* = 17.1 Hz, 1H), 3.67 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.50 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.40 (t, *J* = 9.5 Hz, 1H), 3.35 (dd, *J* = 10.2, 2.9 Hz, 1H), 3.33 – 3.26 (m, 1H), 2.80 – 2.74 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 156.9, 156.8, 144.7, 143.5, 136.3, 134.4, 134.1, 129.8, 129.7, 127.7, 127.4, 123.5, 119.0, 118.4, 116.7, 113.4, 52.2, 49.7, 45.8, 44.3, 21.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{27}H_{27}NNaO_3S^{\oplus}$ 468.1604, found 468.1623.

Methyl 4'-(1-(1-tosyl-4-vinylpyrrolidin-3-yl)vinyl)-[1,1'-biphenyl]-4-carboxylate (3ai)



3ai

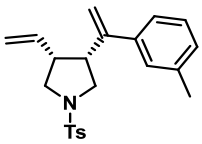
Condition B, R_f = 0.5 (PE/EA = 10/1), white solid (40.2 mg, 41% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.12 – 8.07 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.66 – 7.63 (m, 2H), 7.58 – 7.55 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.32 (m, 2H), 5.34 (s, 1H), 5.30 – 5.22 (m, 1H), 4.94 (d, *J* = 1.3 Hz, 1H), 4.82 (d, *J* = 10.5 Hz, 1H), 4.64 – 4.59 (m, 1H), 3.94 (s, 3H), 3.70 (dd, *J* = 9.4, 6.7 Hz, 1H), 3.52 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.44 (t, *J* = 9.4 Hz, 1H), 3.40 - 3.35 (m, 2H), 2.84 – 2.77 (m, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.9, 145.0, 144.8, 143.5, 141.2, 139.2, 134.4, 134.2, 130.1, 129.8, 129.0, 127.5, 127.1, 126.9, 126.8, 116.8, 114.4, 52.3, 52.1, 49.8, 45.7, 44.4, 21.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{29}H_{29}NNaO_4S^{\oplus}$ 510.1710, found 510.1719.

3-(1-(*m*-Tolyl)vinyl)-1-tosyl-4-vinylpyrrolidine (3aj)



3aj

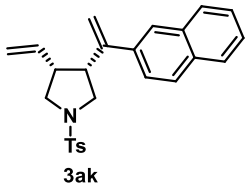
Condition B, R_f = 0.4 (PE/EA = 10/1), colorless oil (42.7 mg, 58% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.19 – 6.99 (m, 4H), 5.31 – 5.20 (m, 2H), 4.88 – 4.78 (m, 2H), 4.61 (d, *J* = 17.2 Hz, 1H), 3.66 (dd, *J* = 9.5, 6.9 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.43 – 3.27 (m, 3H), 2.80 - 2.7 (m, 1H), 2.46 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 145.6, 143.5, 141.4, 137.8, 134.5, 134.2, 129.7, 128.4, 128.2, 127.4, 127.0, 123.5, 116.6, 113.8, 52.2, 49.7, 45.8, 44.2, 21.6, 21.4.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{25}NNaO_2S^{\oplus}$ 390.1498, found 390.1509.

3-(1-(Naphthalen-2-yl)vinyl)-1-tosyl-4-vinylpyrrolidine (3ak)



3ak

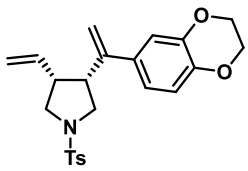
Condition A, R_f = 0.4 (PE/EA = 10/1), white solid (59.3 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 – 7.62 (m, 6H), 7.49 – 7.43 (m, 2H), 7.41 – 7.33 (m, 3H), 5.40 (s, 1H), 5.34 – 5.21 (m, 1H), 4.98 (s, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.56 (d, *J* = 17.1 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.58 – 3.44 (m, 3H), 3.41 - 3.32 (m, 1H), 2.86 – 2.77 (m, 1H), 2.47 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 145.5, 143.5, 138.7, 134.5, 134.3, 133.2, 132.8, 129.8, 128.04, 127.95, 127.54, 127.48, 126.3, 126.0, 125.0, 124.8, 116.8, 114.5, 52.3, 49.8, 45.8, 44.4, 21.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{25}H_{25}NNaO_2S^{\oplus}$ 426.1498, found 426.1508.

3-(1-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)vinyl)-1-tosyl-4-vinylpyrrolidine (3al)



3al

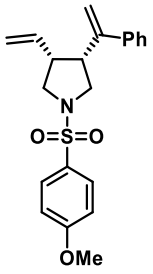
Condition B, R_f = 0.5 (PE/EA = 10/1), white solid (32.3 mg, 39% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.79 – 7.74 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 6.81 – 6.70 (m, 3H), 5.29 – 5.22 (m, 1H), 5.19 (s, 1H), 4.82 (d, *J* = 10.5 Hz, 1H), 4.78 (d, *J* = 1.3 Hz, 1H), 4.63 (dt, *J* = 17.2, 1.2 Hz, 1H), 4.25 (s, 4H), 3.64 (dd, *J* = 9.7, 7.0 Hz, 1H), 3.47 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.40 – 3.34 (m, 2H), 3.25 – 3.18 (m, 1H), 2.81 - 2.74 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 144.5, 143.5, 143.2, 143.1, 134.9, 134.5, 134.1, 129.7, 127.4, 119.5, 117.0, 116.6, 115.1, 112.9, 64.4, 64.3, 52.2, 49.6, 45.7, 44.2, 21.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{23}H_{25}NNaO_4S^{\oplus}$ 434.1397, found 434.1405.

1-((4-Methoxyphenyl)sulfonyl)-3-(1-phenylvinyl)-4-vinylpyrrolidine (3ba)



3ba

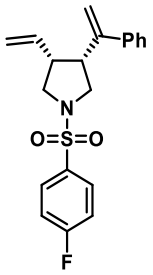
Condition B, R_f = 0.2 (PE/EA = 10/1), colorless oil (60.7 mg, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.87 – 7.77 (m, 2H), 7.31 – 7.26 (m, 3H), 7.24 – 7.21 (m, 2H), 7.05 – 7.00 (m, 2H), 5.31 – 5.22 (m, 2H), 4.88 (d, *J* = 1.3 Hz, 1H), 4.81 (d, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 17.1 Hz, 1H), 3.89 (s, 3H), 3.66 (dd, *J* = 9.4, 6.8 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.40 (t, *J* = 9.5 Hz, 1H), 3.38 – 3.30 (m, 2H), 2.80 - 2.74 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 163.0, 145.7, 141.5, 134.6, 129.6, 129.3, 128.3, 127.6, 126.4, 116.7, 114.3, 114.0, 55.6, 52.4, 49.8, 46.0, 44.4.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{23}NNaO_3S^{\oplus}$ 392.1291, found 392.1301.

1-((4-Fluorophenyl)sulfonyl)-3-(1-phenylvinyl)-4-vinylpyrrolidine (3ca)



3ca

Condition A, R_f = 0.4 (PE/EA = 10/1), white solid (53.9 mg, 76% yield).

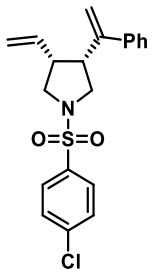
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.99 – 7.86 (m, 2H), 7.31 - 7.21 (m, 7H), 5.31 – 5.21 (m, 2H), 4.88 (s, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.60 (d, *J* = 17.1 Hz, 1H), 3.68 (dd, *J* = 8.8, 6.3 Hz, 1H), 3.50 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.43 – 3.32 (m, 3H), 2.83 – 2.72 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.2 (d, *J* = 253.2 Hz), 145.4, 141.3, 134.2, 133.5 (d, *J* = 3.4 Hz), 130.0 (d, *J* = 9.1 Hz), 128.3, 127.7, 126.4, 116.9, 116.4 (d, *J* = 22.3 Hz), 114.0, 52.3, 49.7, 45.9, 44.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -105.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{20}FNNaO_2S^{\oplus}$ 380.1091, found 380.1098.

1-((4-Chlorophenyl)sulfonyl)-3-(1-phenylvinyl)-4-vinylpyrrolidine (3da)



3da

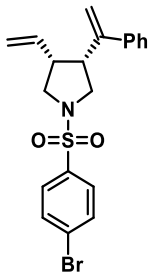
Condition B, R_f = 0.4 (PE/EA = 10/1), white solid (59.8 mg, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.85 – 7.80 (m, 2H), 7.57 – 7.50 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 – 7.21 (m, 2H), 5.32 – 5.22 (m, 2H), 4.88 (d, *J* = 1.4 Hz, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 4.61 (d, *J* = 17.1 Hz, 1H), 3.67 (dd, *J* = 9.3, 6.7 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.42 (t, *J* = 9.4 Hz, 1H), 3.39 – 3.34 (m, 2H), 2.81 – 2.76 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 145.4, 141.3, 139.2, 135.9, 134.2, 129.4, 128.8, 128.3, 127.7, 126.4, 116.9, 114.1, 52.3, 49.7, 45.9, 44.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{20}ClNNaO_2S^{\oplus}$ 396.0795, found 396.0805.

1-((4-Bromophenyl)sulfonyl)-3-(1-phenylvinyl)-4-vinylpyrrolidine (3ea)



3ea

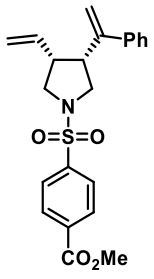
Condition B, R_f = 0.4 (PE/EA = 10/1), white solid (67.3 mg, 81% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.78 – 7.72 (m, 2H), 7.72 – 7.68 (m, 2H), 7.32 – 7.21 (m, 5H), 5.32 – 5.22 (m, 2H), 4.88 (d, *J* = 1.5 Hz, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 4.61 (dt, *J* = 17.1, 1.1 Hz, 1H), 3.67 (dd, *J* = 9.3, 6.7 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.2 Hz, 1H), 3.42 (t, *J* = 9.4 Hz, 1H), 3.39 – 3.32 (m, 2H), 2.83 - 2.72 (m, 1H).

^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 145.4, 141.3, 136.4, 134.2, 132.4, 128.8, 128.3, 127.7, 126.4, 116.9, 114.1, 52.3, 49.7, 45.9, 44.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{20}{}^{79}BrNNaO_2S^{\oplus}$ 440.0290, found 440.0297.

Methyl 4-((3-(1-phenylvinyl)-4-vinylpyrrolidin-1-yl)sulfonyl)benzoate (3fa)



3fa

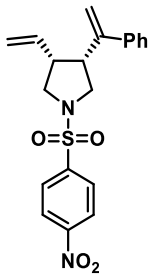
Condition B, R_f = 0.2 (PE/EA = 10/1), white solid (60.6 mg, 76 % yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.24 – 8.18 (m, 2H), 7.98 – 7.91 (m, 2H), 7.30 – 7.25 (m, 3H), 7.23 – 7.20 (m, 2H), 5.31 – 5.21 (m, 2H), 4.87 (d, *J* = 1.4 Hz, 1H), 4.82 (d, *J* = 10.4 Hz, 1H), 4.61 (d, *J* = 17.1 Hz, 1H), 3.97 (s, 3H), 3.70 (dd, *J* = 9.5, 6.9 Hz, 1H), 3.52 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.43 (t, *J* = 9.5 Hz, 1H), 3.40 – 3.32 (m, 2H), 2.84 - 2.78 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 165.7, 145.3, 141.23, 141.21, 134.1, 133.9, 130.4, 128.3, 127.7, 127.3, 126.4, 117.0, 114.1, 52.7, 52.3, 49.7, 45.9, 44.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{23}NNaO_4S^{\oplus}$ 420.1240, found 420.1252.

1-((4-Nitrophenyl)sulfonyl)-3-(1-phenylvinyl)-4-vinylpyrrolidine (3ga)



3ga

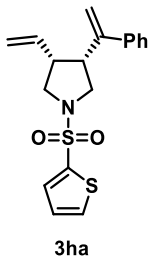
Condition A, R_f = 0.3 (PE/EA = 10/1), white solid (59.7 mg, 78% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.47 – 8.37 (m, 2H), 8.11 – 8.03 (m, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 5.32 – 5.22 (m, 2H), 4.88 (d, *J* = 1.4 Hz, 1H), 4.85 (d, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 17.2 Hz, 1H), 3.72 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.53 (dd, *J* = 10.2, 6.2 Hz, 1H), 3.48 – 3.38 (m, 3H), 2.85 – 2.79 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 150.1, 145.2, 143.4, 141.1, 133.8, 128.42, 128.38, 127.8, 126.4, 124.4, 117.2, 114.2, 52.4, 49.7, 45.9, 44.1.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{20}H_{21}N_2O_4S^{\oplus}$ 385.1217, found 385.1224.

3-(1-Phenylvinyl)-1-(thiophen-2-ylsulfonyl)-4-vinylpyrrolidine (3ha)



3ha

Condition A, R_f = 0.3 (PE/EA = 10/1), colorless oil (51.7 mg, 75% yield).

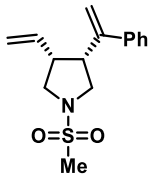
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.67 – 7.60 (m, 2H), 7.31 – 7.17 (m, 6H), 5.31 – 5.20 (m, 2H), 4.91 (d, *J* = 1.5 Hz, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.60 (dt, *J* = 17.2, 1.1 Hz, 1H), 3.72 (dd, *J* = 9.8, 7.0 Hz, 1H), 3.54 (dd, *J* = 10.4, 6.3 Hz, 1H), 3.48 (t, *J*

= 9.8 Hz, 1H), 3.40 (dd, *J* = 10.4, 2.7 Hz, 1H), 3.38 – 3.33 (m, 1H), 2.81 - 2.75 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.4, 141.3, 137.1, 134.2, 132.1, 131.7, 128.3, 127.7, 127.6, 126.4, 116.8, 114.1, 52.5, 49.9, 45.9, 44.3.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{19}NNaO_2S_2^{\oplus}$ 368.0749, found 368.0757.

1-(Methylsulfonyl)-3-(1-phenylvinyl)-4-vinylpyrrolidine (3ia)



3ia

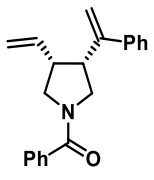
Condition B, R_f = 0.3 (PE/EA = 10/1), white solid (50.1 mg, 90% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.36 – 7.27 (m, 5H), 5.65 - 5.54 (m, 1H), 5.34 (s, 1H), 5.03 – 4.99 (m, 2H), 4.84 (dt, *J* = 17.1, 1.1 Hz, 1H), 3.72 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.61 – 3.54 (m, 2H), 3.54 – 3.50 (m, 1H), 3.44 (dd, *J* = 10.1, 2.6 Hz, 1H), 2.96 – 2.91 (m, 1H), 2.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 145.4, 141.4, 134.4, 128.4, 127.7, 126.5, 117.1, 114.2, 52.3, 49.5, 46.3, 44.4, 35.6.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{19}NNaO_2S^{\oplus}$ 300.1029, found 300.1036.

Phenyl(3-(1-phenylvinyl)-4-vinylpyrrolidin-1-yl)methanone (3ja)



3ja

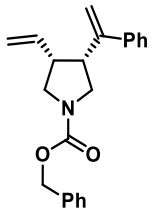
Condition B, R_f = 0.3 (PE/EA = 10/1), white solid (32.3 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.59 – 7.26 (m, 10H), 5.68 – 5.50 (m, 1H), 5.39 – 5.27 (m, 1H), 5.14 – 4.68 (m, 3H), 4.08 – 3.75 (m, 2H), 3.74 – 3.58 (m, 2H), 3.53 – 3.42 (m, 1H), 3.03 – 2.81 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 170.0, 146.1, 141.8, 136.8, 134.9, 130.0, 128.4, 128.3, 127.6, 127.1, 126.5, 116.6, 113.9, 52.8, 49.5, 45.8, 43.9.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{21}NNaO^{\oplus}$ 326.1515, found 326.1522.

Benzyl 3-(1-phenylvinyl)-4-vinylpyrrolidine-1-carboxylate (3ka)



3ka

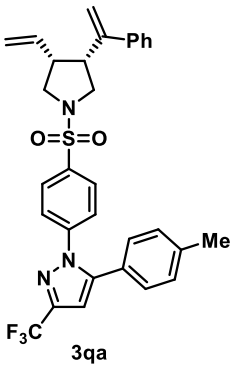
Condition A, R_f = 0.4 (PE/EA = 10/1), colorless oil (29.2 mg, 44% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.42 – 7.33 (m, 4H), 7.33 – 7.26 (m, 6H), 5.62 - 5.53 (m, 1H), 5.34 – 5.29 (m, 1H), 5.24 – 5.13 (m, 2H), 5.03 - 4.90 (m, 2H), 4.83 - 4.72 (m, 1H), 3.85 - 3.74 (m, 1H), 3.65 – 3.42 (m, 4H), 2.90 - 2.81 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.9, 146.1, 141.8, 136.9, 135.1, 128.5, 127.9, 127.8, 127.6, 126.5, 116.3, 113.8, 66.8, 50.8, 50.7, 48.1, 45.6, 43.9.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{23}NNaO_2^{\oplus}$ 356.1621, found 356.1628.

1-(4-((3-(1-Phenylvinyl)-4-vinylpyrrolidin-1-yl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole (3qa)



3qa

Condition B, R_f = 0.4 (PE/EA = 10/1), colorless oil (56.9 mg, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.90 – 7.84 (m, 2H), 7.54 – 7.50 (m, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.22 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.76 (s, 1H), 5.31 – 5.23 (m, 2H), 4.89 – 4.82 (m, 2H), 4.63 (d, *J* = 17.1 Hz, 1H), 3.66 (dd, *J* = 9.2, 6.6 Hz, 1H), 3.48 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.43 – 3.32 (m, 3H), 2.82 – 2.73 (m, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 145.4, 145.3, 144.1 (q, *J* = 38.2 Hz), 142.6, 141.2, 139.8, 136.8, 134.1, 129.7, 128.7, 128.4, 128.3, 127.7, 126.4, 125.7, 125.6, 121.0 (q, *J* = 267.9 Hz), 117.0, 114.0, 106.3, 52.4, 49.7, 45.9, 44.2, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.4.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{31}H_{28}F_3N_3NaO_2S^{\oplus}$ 586.1747, found 586.1754.

4. X-ray Crystal Structure of 3ga

The structure of product **3ga** was determined by X-ray diffraction. The X-ray crystallography data have been deposited in Cambridge Crystallography Data Center (CCDC 2355016). The structure of other products was assumed by analogy.

The single crystal sample for X-ray analysis was obtained by recrystallization from a mixed solvent of ethyl acetate and petroleum ether by slow evaporation. A suitable crystal was selected and the data were collected on a d8 venture system (Cu kα, λ = 1.54178 Å). The crystal was kept at 298(2) K during data collection.

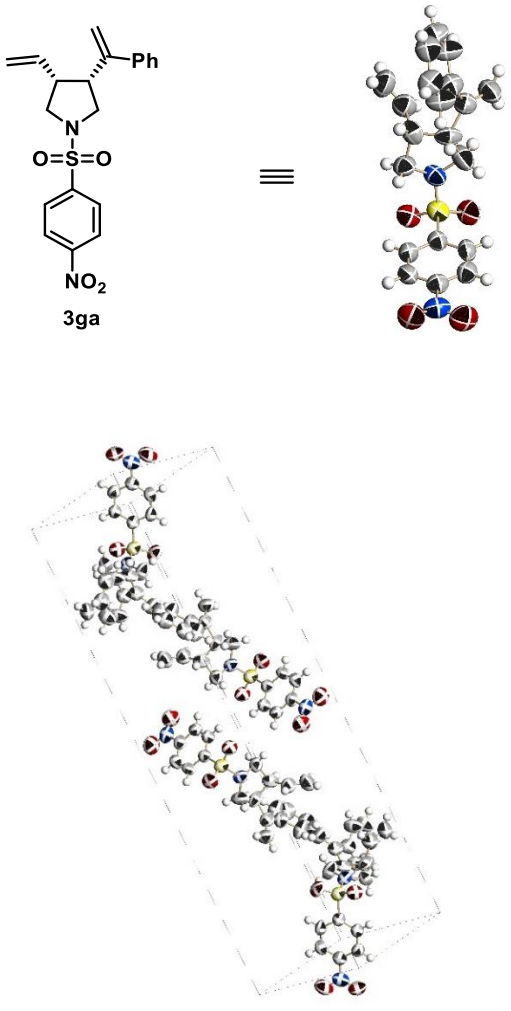


Figure S1. Thermal ellipsoids are shown at 50% probability for **3ga**

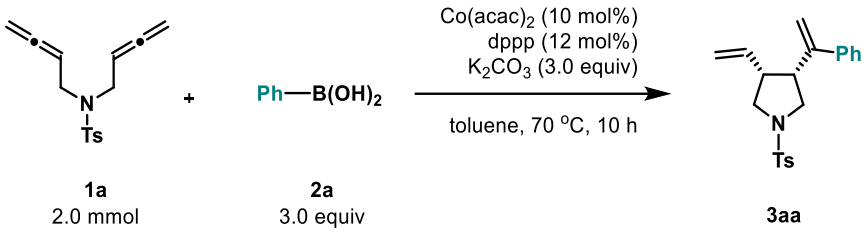
Table S1. Crystal data and structure refinement for 3ga.

Identification code	**3ga**	
Chemical formula	$C_{20}H_{20}N_2O_4S$	
Formula weight	384.44 g/mol	
Temperature	298(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 8.2866(2) Å	α = 90°
	b = 34.0670(8) Å	β = 110.1470(10)°
	c = 7.2733(2) Å	γ = 90°
Volume	1927.62(8) $Å^3$	
Z	4	
Density (calculated)	1.325 g/cm^3	
Absorption coefficient	1.731 mm^{-1}	
F(000)	808	
Diffractometer	d8 venture	
Theta range for data collection	2.59 to 65.19°	
Index ranges	-9<=h<=9, -40<=k<=40, -8<=l<=8	
Reflections collected	36354	
Independent reflections	3299 [R(int) = 0.0881]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	

Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	3299 / 0 / 244	
Goodness-of-fit on F2	1.061	
Δ/σmax	0.004	
Final R indices	2039 data; I>2σ(I)	R1 = 0.1037, wR2 = 0.2767
	all data	R1 = 0.1513, wR2 = 0.3121
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1411P)^2+3.1967P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.755 and -0.299 eÅ^{-3}	
R.M.S. deviation from mean	0.070 eÅ^{-3}	

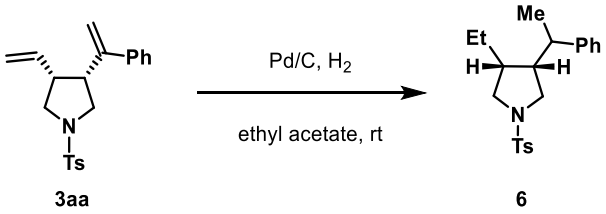
5. Scale-up Reaction and Product Transformations

2.0-mmol Scale Reaction



In a glove box, a 100-mL oven-dried Schlenk flask was charged with bisallene **1a** (550 mg, 2.0 mmol, 1.0 equiv), phenylboronic acid **2a** (732 mg, 6.0 mmol, 3.0 equiv), and K_2CO_3 (828 mg, 6.0 mmol, 3.0 equiv), $Co(acac)_2$ (52 mg, 0.2 mmol, 0.1 equiv), dppp (100 mg, 0.24 mmol, 0.12 equiv) and toluene (20 mL). The flask was capped and removed from the glove box. The reaction mixture was placed in a pre-heated oil bath and stirred at 70 °C for 10 h. Then the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography to afford the product **3aa** as a yellow oil (eluent: PE/EA = 10:1, 537.5 mg, 76% yield).

Product Transformation



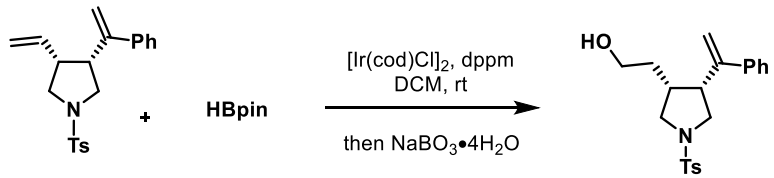
3-Ethyl-4-1-phenylethyl-1-tosylpyrrolidine (6) An oven-dried 10-mL flask charged with **3aa** (70.6 mg, 0.2 mmol) and 10% Pd/C (7 mg) was evacuated and backfilled with H_2 for three times. Then ethyl acetate (5 mL) was added and the mixture was stirred at room temperature under a hydrogen atmosphere for 5 h. When the reaction was completed as monitored by TLC, ethyl acetate was added, and then the mixture was passed through a membrane filter. After filtration and concentrated *in vacuo*, the residue was purified by silica gel flash

column chromatography to afford the product **6** as a colorless oil (eluent: PE/EA = 10:1, 51.9 mg, 73% yield, dr = 15:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.64 – 7.59 (m, 2H), 7.31 – 7.19 (m, 5H), 7.09 – 7.05 (m, 2H), 3.43 (d, *J* = 10.3 Hz, 1H), 3.24 – 3.19 (m, 1H), 2.91 – 2.86 (m, 1H), 2.72 – 2.66 (m, 1H), 2.57 – 2.50 (m, 1H), 2.43 (s, 3H), 2.19 – 2.10 (m, 1H), 2.04 – 1.97 (m, 1H), 1.46 – 1.35 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 7.3 Hz, 3H), 0.74 – 0.64 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 145.3, 143.1, 134.2, 129.5, 128.6, 127.2, 126.7, 126.6, 51.8, 50.3, 49.5, 41.4, 38.8, 21.5, 20.6, 18.1, 12.2.

HRMS (ESI-TOF): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{27}NNaO_2S^{\oplus}$ 380.1655, found 380.1664.



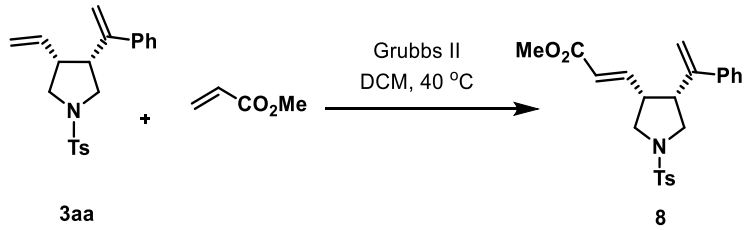
3aa 7

2-(4-(1-Phenylvinyl)-1-tosylpyrrolidin-3-yl) ethan-1-ol (7) In a glove box, $[Ir(cod)Cl]_2$ (6.7 mg, 0.01 mmol), bis(diphenylphosphino)methane (dppm) (7.7 mg, 0.02 mmol), and dichloromethane (1.0 mL) were added to a 4 mL vial containing a magnetic stir bar, and the mixture was stirred at room temperature for 30 min. A solution of **3aa** (70.6 mg, 0.2 mmol) and HBpin (127.9 mg, 1.0 mmol) in dichloromethane (1.0 mL) was added, and the vial sealed with a plastic cap. The mixture was stirred at room temperature overnight. The reaction mixture was concentrated when the reaction was completed as monitored by TLC. Then the $NaBO_3.4H_2O$ (153 mg, 1.5 mmol) and THF/H_2O (1 mL/1 mL) were added to the mixture. After the mixture was stirred for 4 h, followed by the addition of H_2O. The reaction mixture was extracted with ethyl acetate (3×10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography to afford the product **7** as a colorless oil (eluent: PE/EA = 10:1 to 5:1, 37.8 mg, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.26 (m, 5H), 5.32 (s, 1H), 4.92 (s, 1H), 3.62 (t, *J* = 8.3 Hz, 1H), 3.46 – 3.38 (m, 2H), 3.37 – 3.28 (m, 3H), 3.27 – 3.20 (m, 1H), 2.45 (s, 3H), 2.26 – 2.16 (m, 1H), 1.29 – 1.22 (m, 1H), 0.99 – 0.78 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 146.0, 143.5, 141.5, 134.1, 129.7, 128.5, 127.8, 127.4, 126.2, 114.5, 60.9, 51.9, 50.0, 45.4, 37.3, 30.2, 21.5.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{21}H_{26}NO_3S^{\oplus}$ 372.1628, found 372.1634.



3aa 8

Methyl (*E*)-3-(4-(1-phenylvinyl)-1-tosylpyrrolidin-3-yl)acrylate (8) An oven-dried 10-mL flask charged with **3aa** (35.3 mg, 0.1 mmol) and Grubbs catalyst Ⅱ (25.5 mg, 0.03 mmol) was evacuated and backfilled with N_2 for three times. Then methyl acrylate (300.2 μL, 3.33 mmol) and CH_2Cl_2 (0.5 mL) were added and the reaction mixture was stirred at 40 °C for 24 h. Next, the mixture was concentrated *in vacuo* and the residue was purified by silica gel flash column chromatography to afford the product **8** as a brown oil (eluent: PE/EA = 10:1, 16.6 mg, 40% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.19 (d, *J* = 6.7 Hz, 2H), 6.38 – 6.31 (m, 1H), 5.31 – 5.25 (m, 2H), 4.90 (s, 1H), 3.75 – 3.71 (m, 1H), 3.65 (s, 3H), 3.56 – 3.51 (m, 1H), 3.47 – 3.41 (m, 2H), 3.34 (dd, *J* = 10.5, 2.4 Hz, 1H), 2.93 – 2.88 (m, 1H), 2.47 (s, 3H).

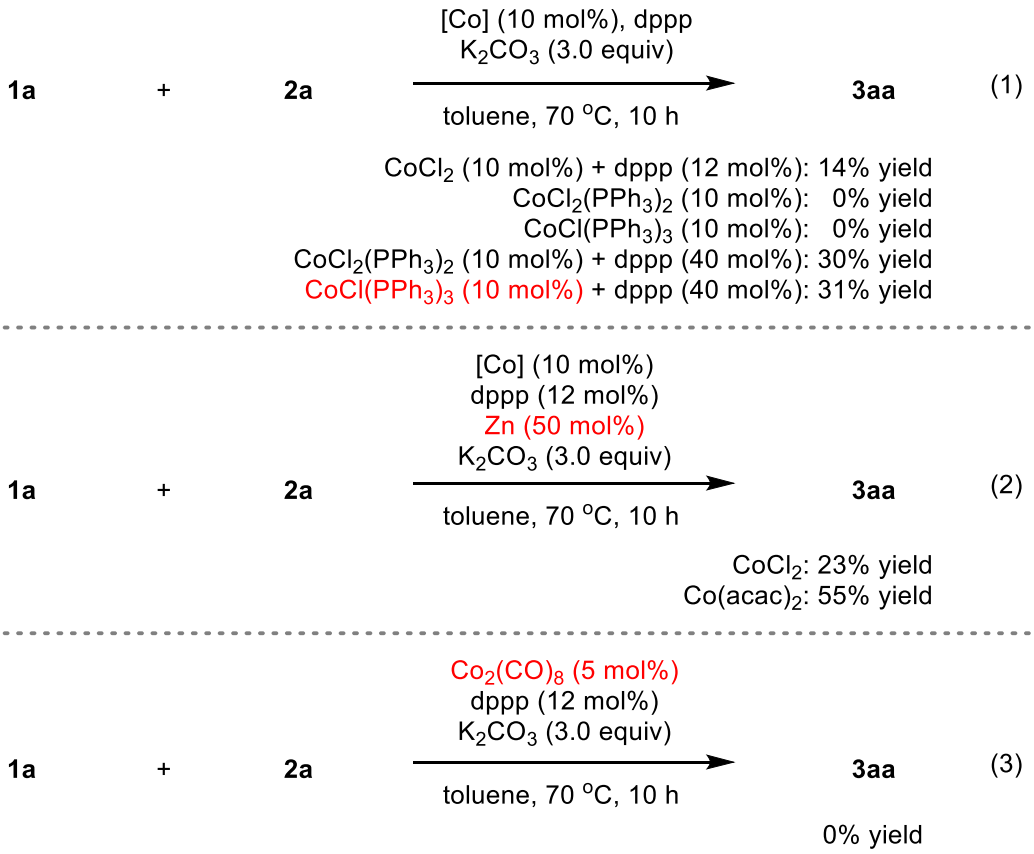
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 166.0, 144.6, 144.5, 143.9, 140.9, 133.7, 129.9, 128.5, 127.9, 127.4, 126.3, 122.6, 114.6, 51.9, 51.5, 49.5, 46.0, 42.9, 21.6.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{23}H_{26}NO_4S^{\oplus}$ 412.1577, found 412.1582.

6. Mechanistic Experiments and Possible Catalytic Cycle

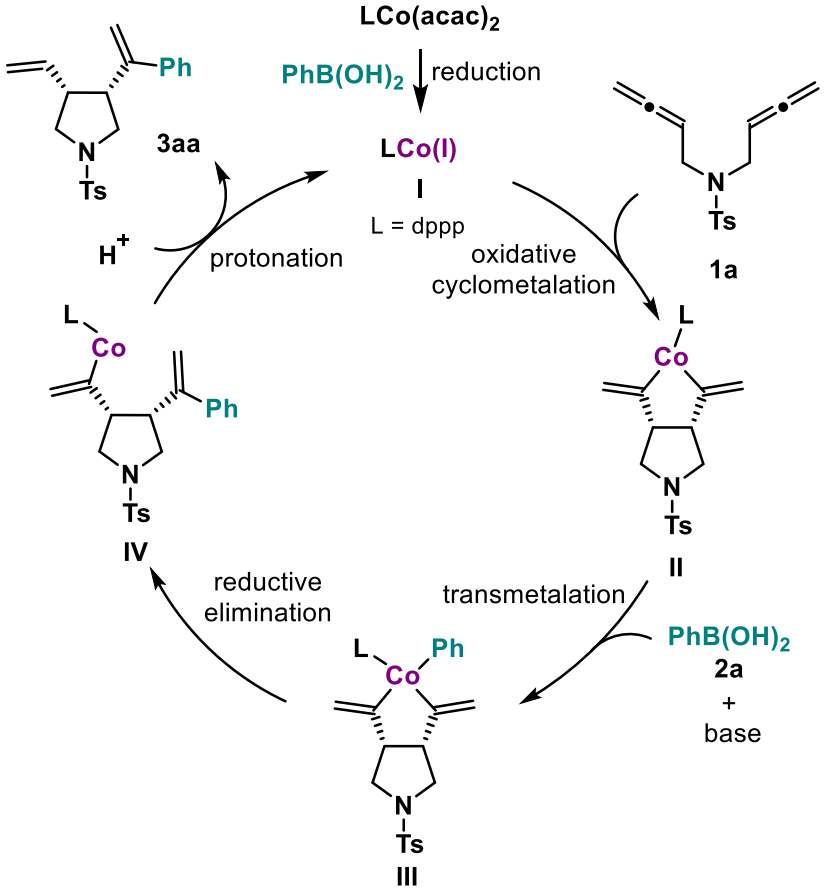
Mechanistic Experiments:

In a glove box, an oven-dried 4-mL vial was charged with bisallene **1a** (0.05 mmol, 1.0 equiv), phenyl boronic acid **2a** (0.15 mmol, 3.0 equiv), K_2CO_3 (0.15 mmol, 3.0 equiv), catalyst (10 mol% base on metal), dppp, additive, and toluene (0.5 mL). The vial was capped and removed from the glove box. The reaction mixture was stirred at 70 °C for 10 h. Then the reaction mixture was cooled to room temperature, diluted with H_2O (5 mL), and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Finally, the residue was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.



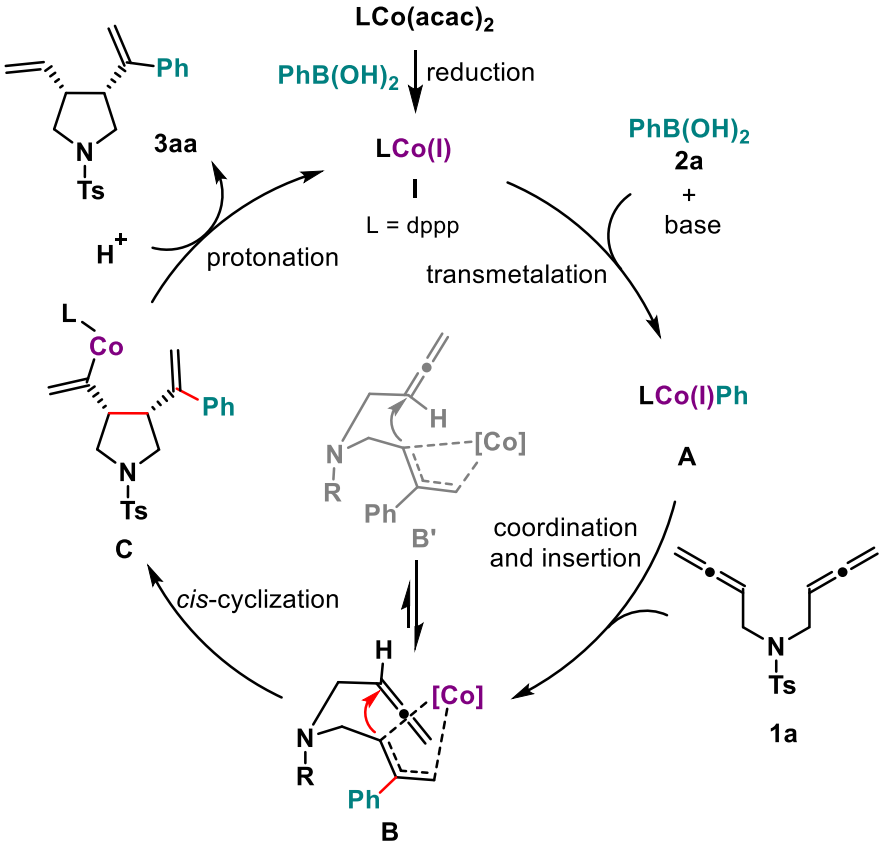
Possible Catalytic Cycle:

In light of the excellent regio- and diastereoselectivities observed in this reaction, along with the mechanistic studies, a potential catalytic cycle involving Co(I)/Co(III) is proposed. At first, with the assistance of boronic acid, Co(II) is reduced to Co(I), which is regarded as the catalytically active species of this reaction. Next, this Co(I) complex undergoes oxidative cyclometalation with bisallene **1a** to afford the Co(III) complex **II**, which subsequently proceeds transmetalation with phenyl boronic acid to yield the cobalt complex **III**. Then, the cobalt complex **III** undergoes reductive elimination to form the Co(I) complex **IV**. Finally, the protonation of Co(I) complex **IV** results in the formation of *cis* five-membered ring product **3aa** and the regeneration of Co(I) complex **I**.



Apart from the Co(I)/Co(III) catalytic cycle, the stepwise arylative cyclization process involving Co(I) cannot be excluded, which is illustrated below. Firstly,

Co(II) was reduced to Co(I) complex, which then underwent transmetalation with phenyl boronic acid to yield Co(I) complex **A**. Next, the coordination and regioselective insertion of bisallene **1a** into aryl cobalt complex **A** led to allylic cobalt complex **B** or **B′**. Complex **B** proceeded intramolecular *cis*-cyclization to afford the *cis*-cyclic alkenyl cobalt complex **C**, which underwent protonation to form the *cis*-product **3aa** and regenerate the Co(I) complex. In contrast, the *trans*-cyclization product through allylic cobalt complex **B′** was not detected.



7. References

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[3] A. Artigas, J. Vila, A. Lledó, M. Solà, A. Pla-Quintana and A. Roglans, *Org. Lett.*, 2019, **21**, 6608−6613.

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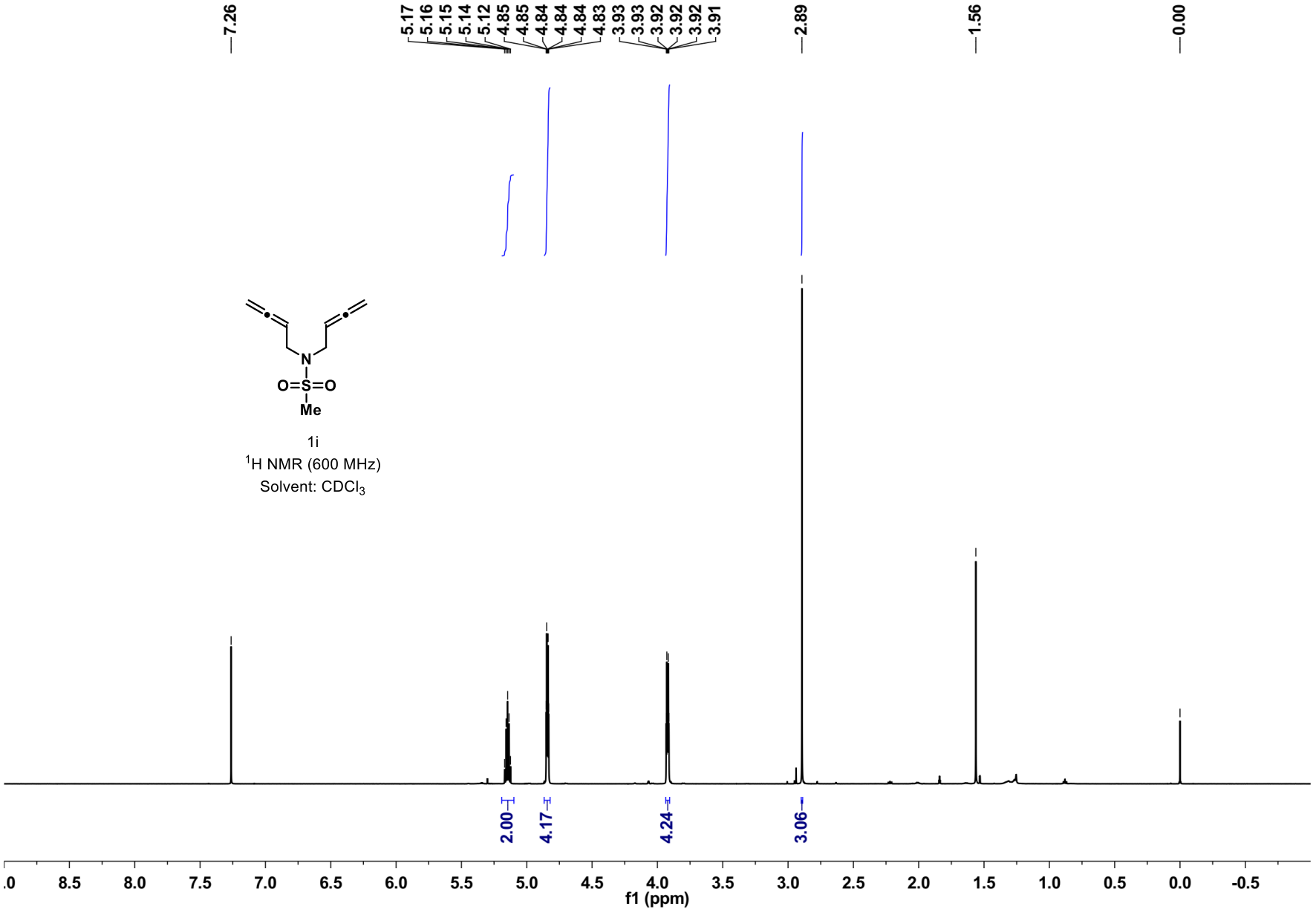
8. NMR Spectra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5.12
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4.85
4.84
4.84
4.84
4.83
3.93
3.93
3.92
3.92
3.92
3.91
2.89
1.56
0.00
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1i
1H NMR (600 MHz)
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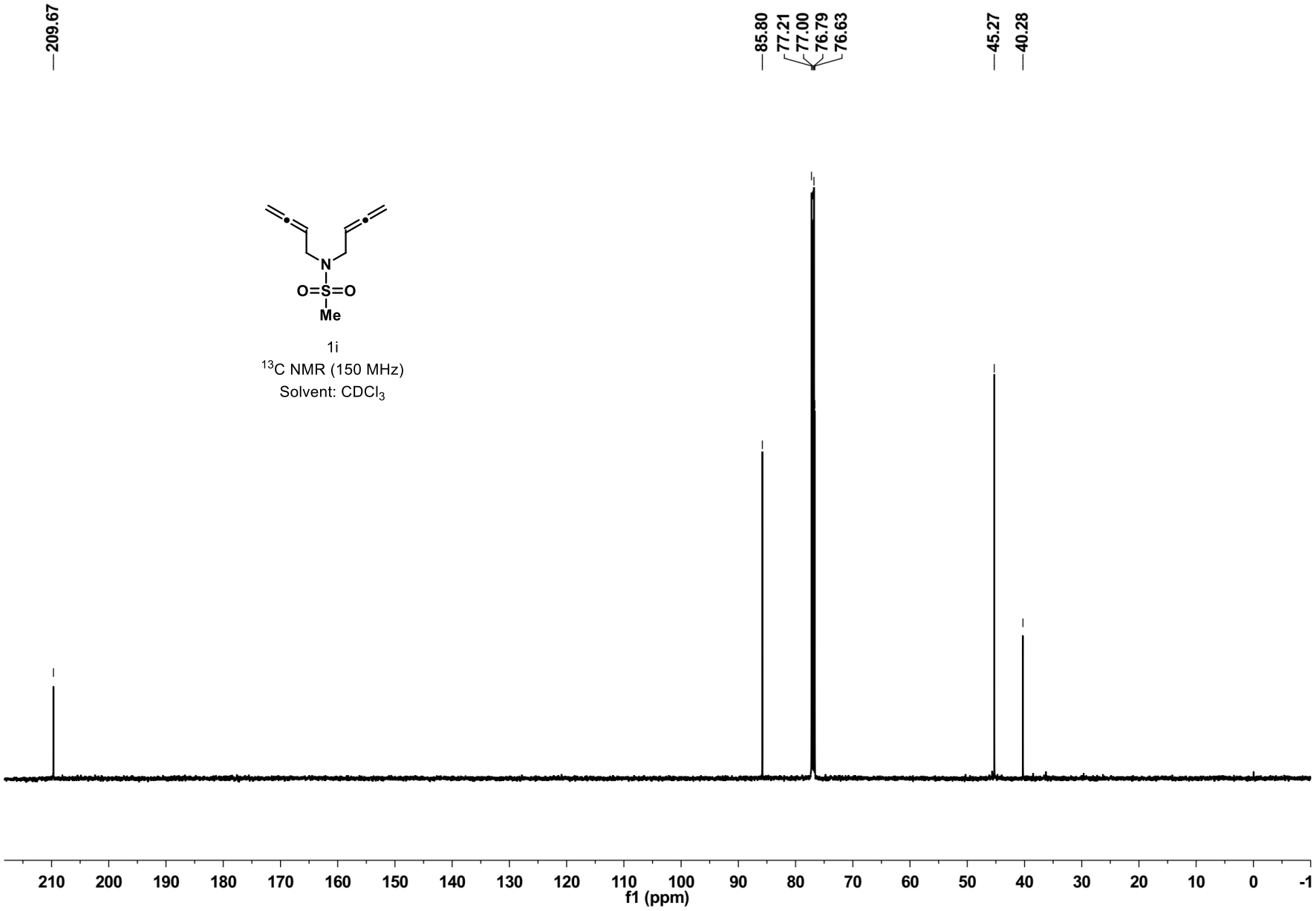
f1 (ppm)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Me
1i
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Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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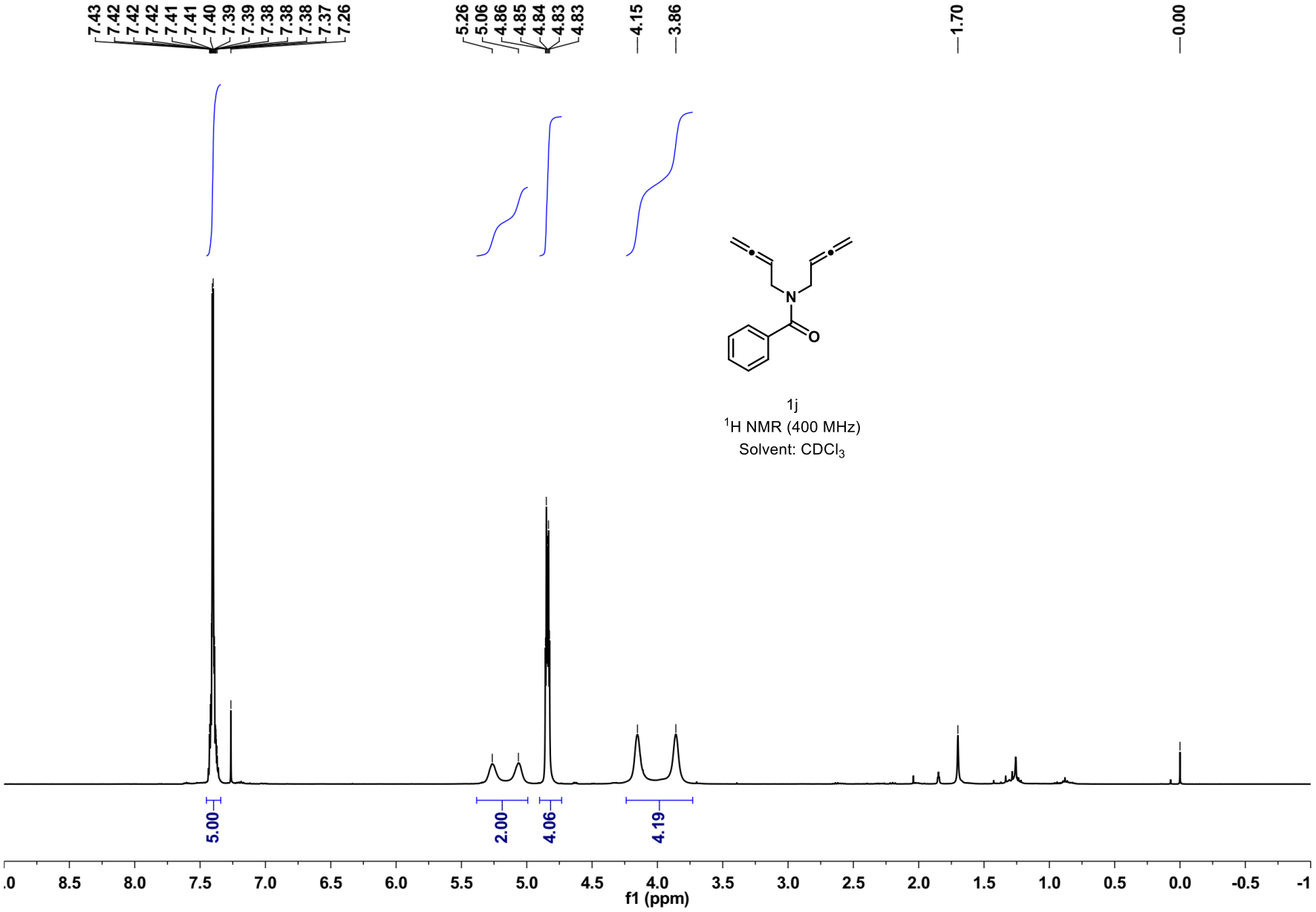
0
-1
f1 (ppm)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7.26
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4.85
4.84
4.83
4.83
4.15
3.86
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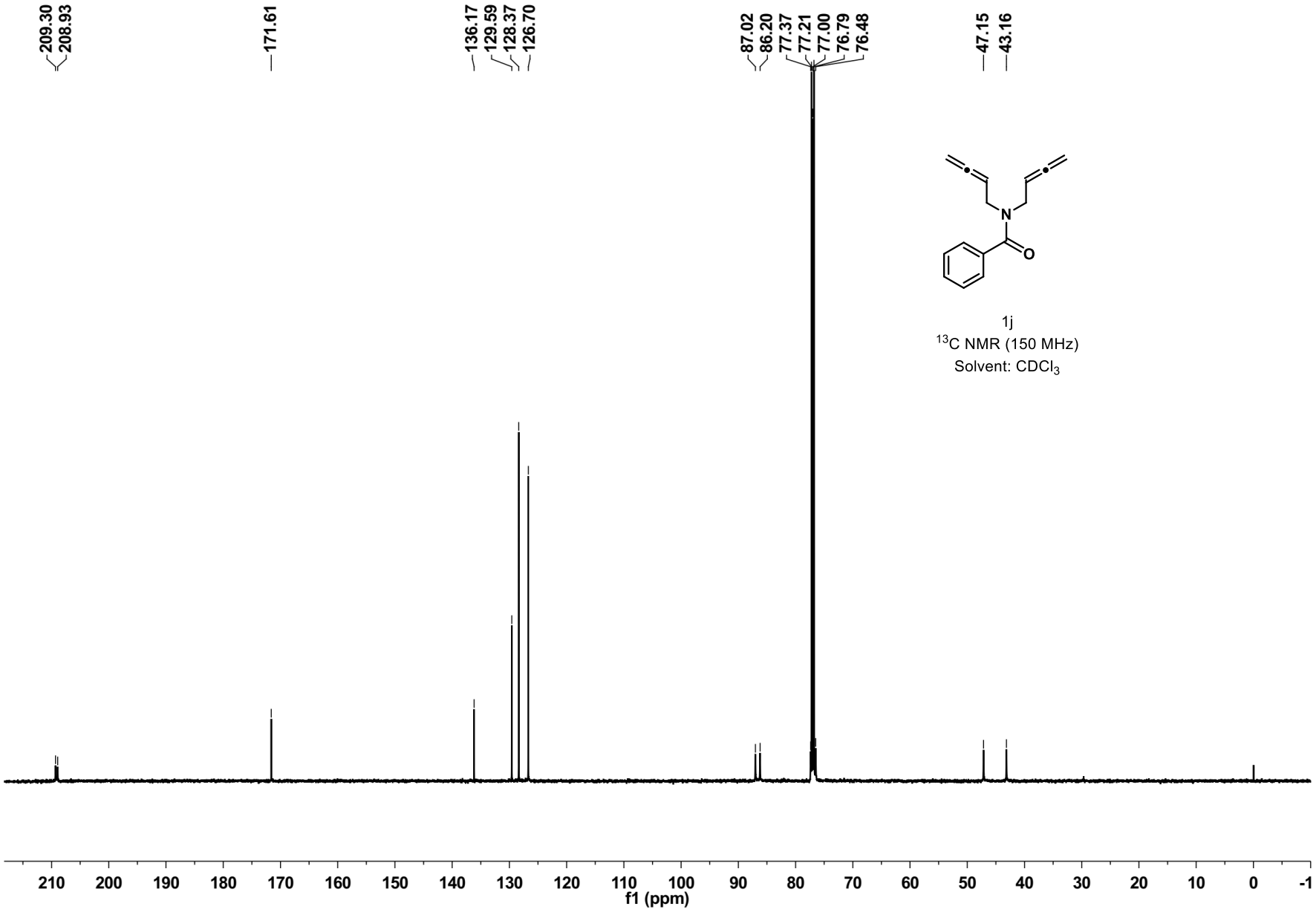
4.19
f1 (ppm)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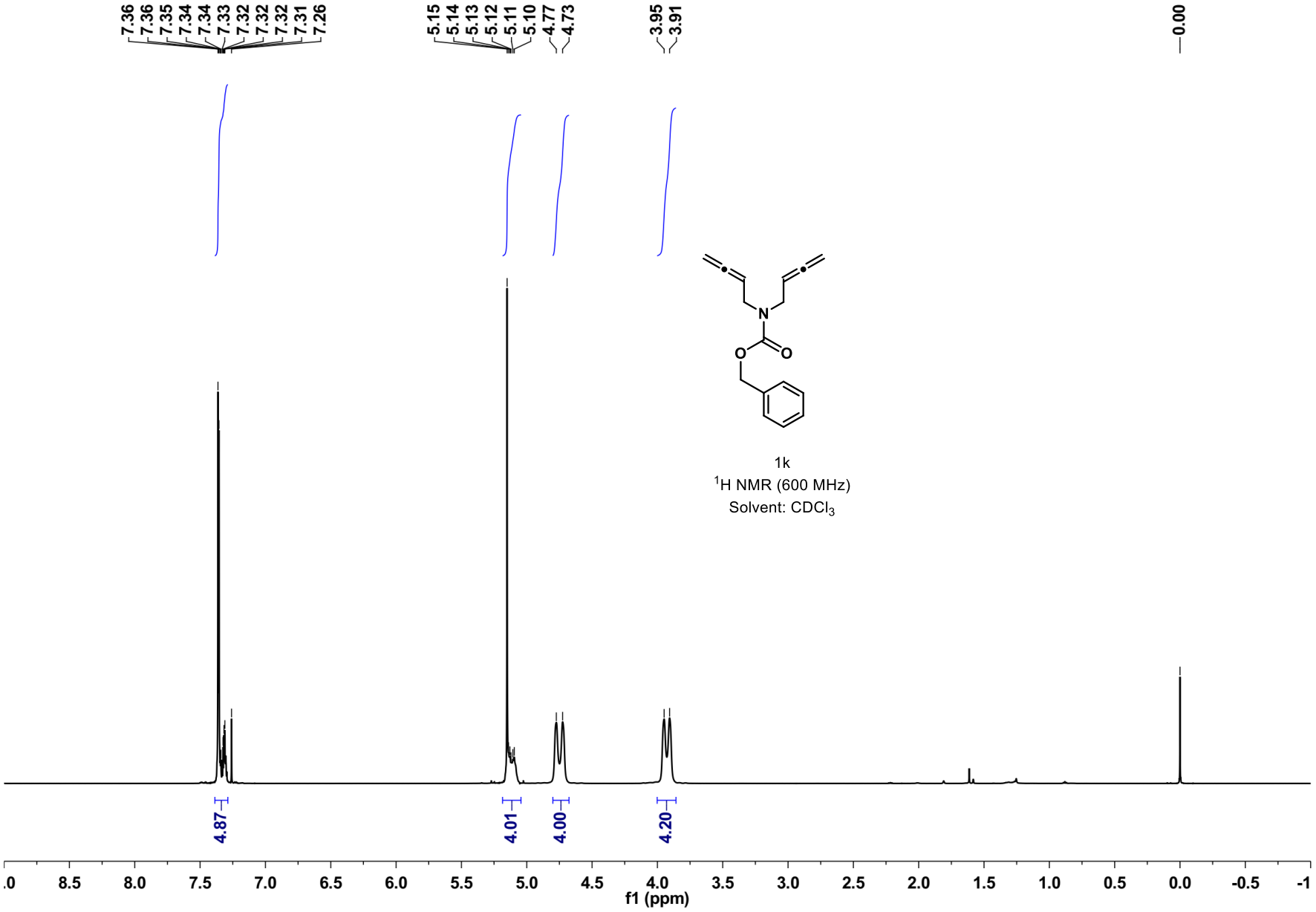
76.79
76.48
47.15
43.16
N
O
1j
13C NMR (150 MHz)
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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5.12
5.11
5.10
4.77
4.73
3.95
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0.00
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1k
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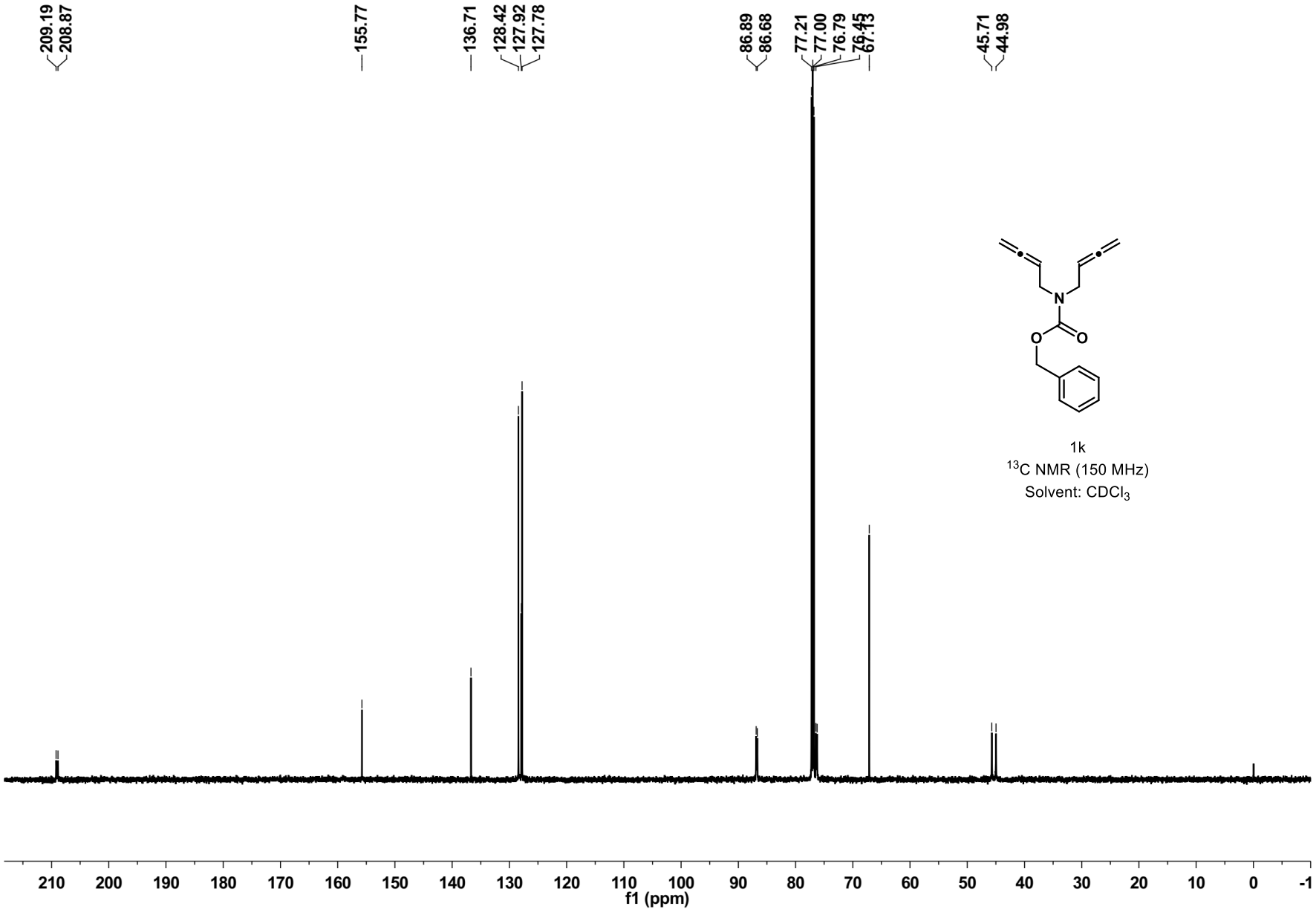
4.87
4.01
4.00
4.20
f1 (ppm)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67.13
45.71
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N
O
O
1k
13C NMR (150 MHz)
Solvent: CDCl3
210
200
190
180
170
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150
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120
110
100
90
80
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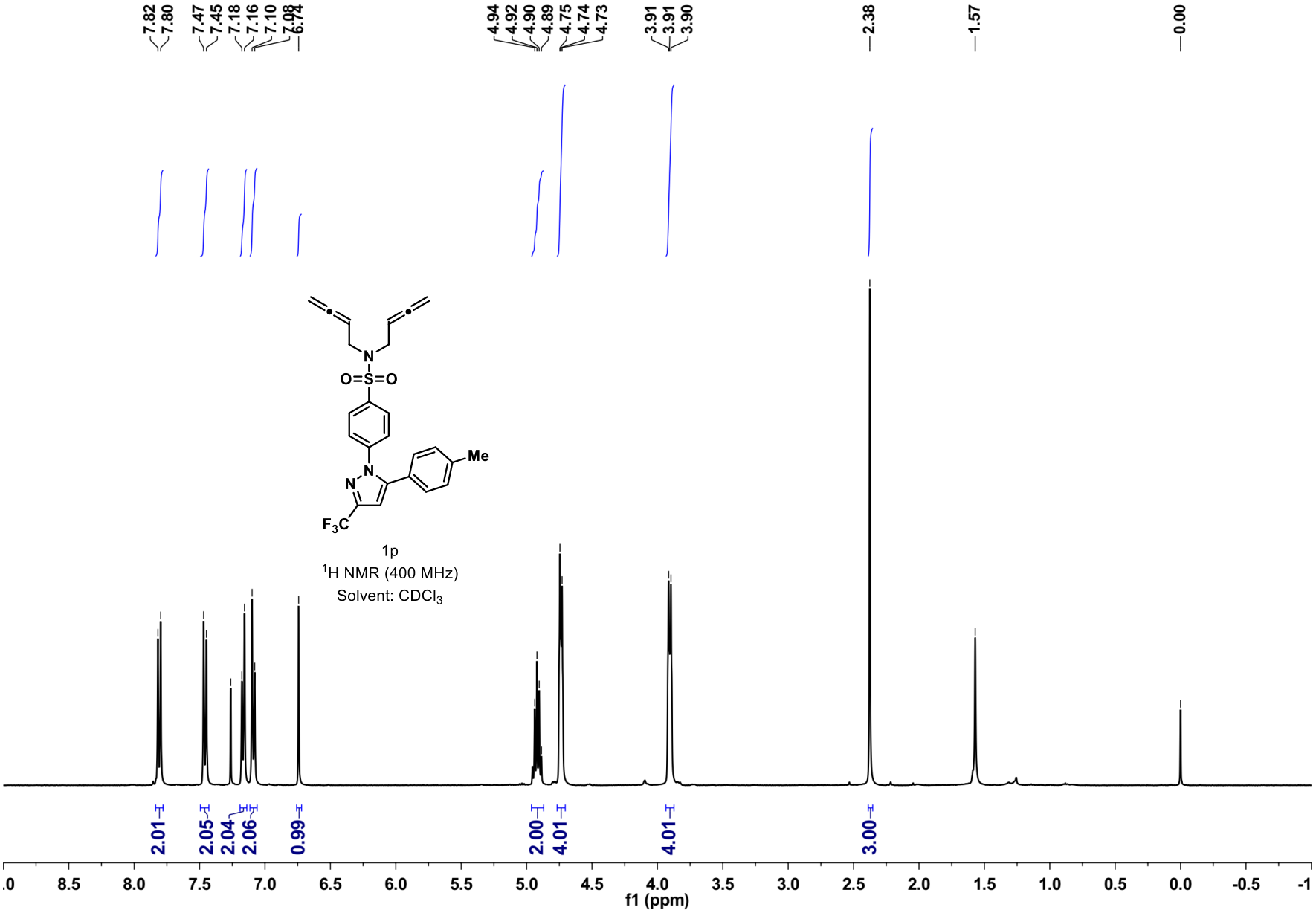
50
40
30
20
10
0
-1
f1 (ppm)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4.74
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3.91
3.91
3.90
2.38
1.57
0.00
Me
1p
1H NMR (400 MHz)
Solvent: CDCl3
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2.06
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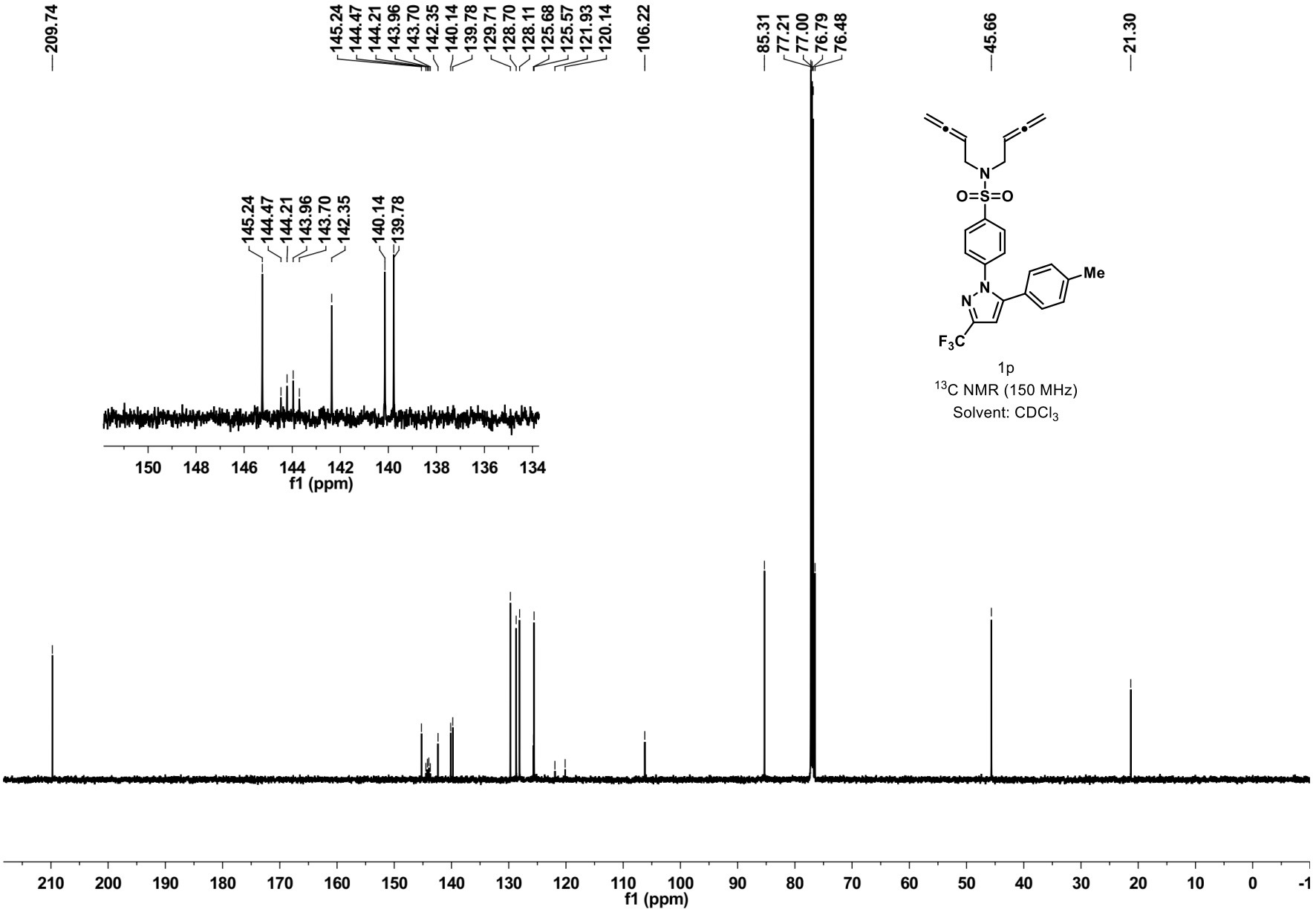
f1 (ppm)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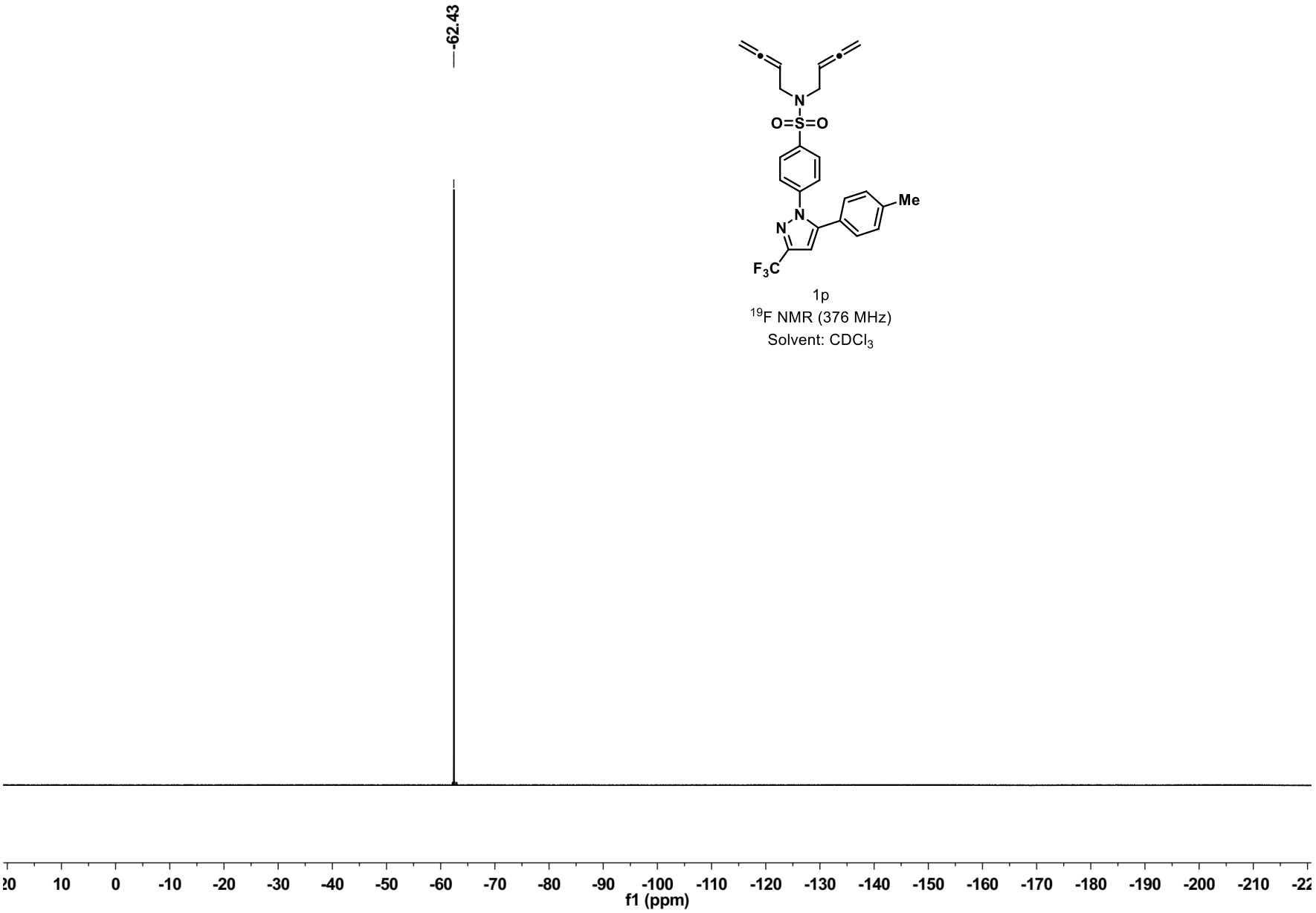
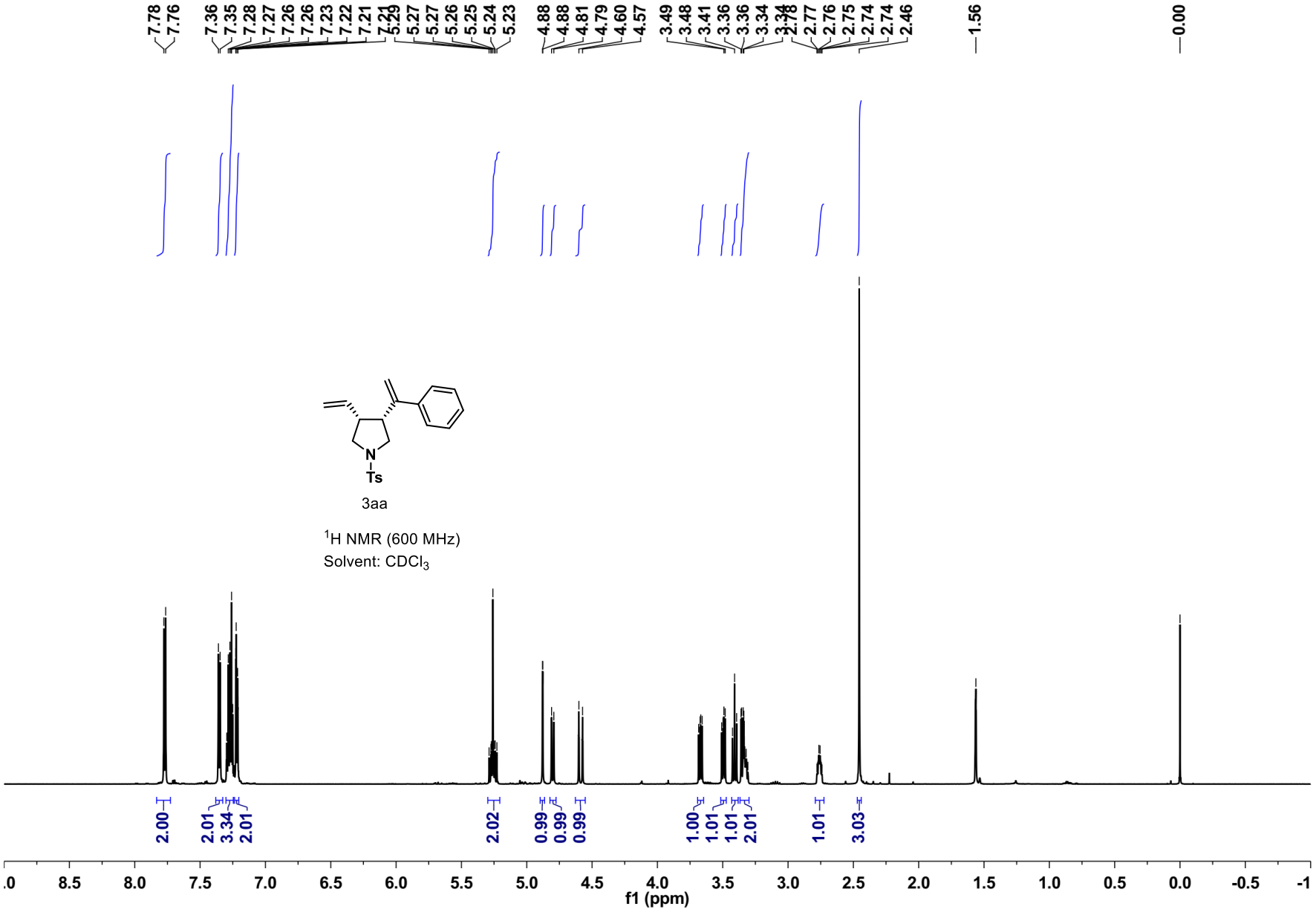
121.93
120.14
106.22
85.31
77.21
77.00
76.79
76.48
45.66
21.30
f1 (ppm)
1p
13C NMR (150 MHz)
Solvent: CDCl3
Me
F3C



1p

^{19}F NMR (376 MHz)

Solvent: $CDCl_3$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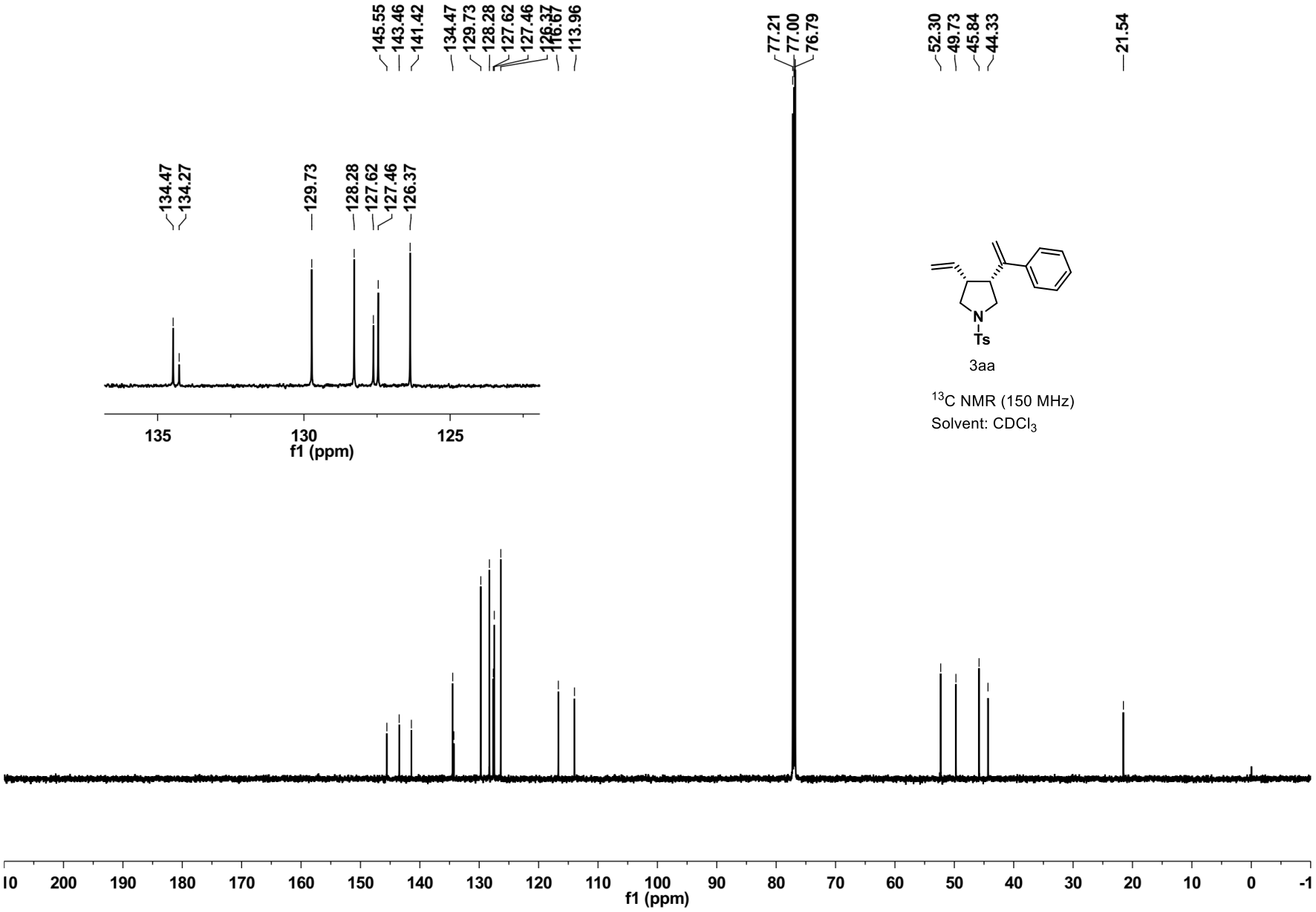
7.76
7.36
7.35
7.28
7.27
7.26
7.26
7.23
7.22
7.21
5.29
5.27
5.27
5.26
5.25
5.24
5.23
4.88
4.88
4.81
4.79
4.60
4.57
3.49
3.48
3.41
3.36
3.36
3.34
2.78
2.77
2.76
2.75
2.74
2.74
2.46
1.56
0.00
N
Ts
3aa
1H NMR (600 MHz)
Solvent: CDCl3
2.00
2.01
3.34
2.01
2.02
0.99
0.99
0.99
1.00
1.01
1.01
2.01
1.01
3.03
f1 (ppm)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141.42
134.47
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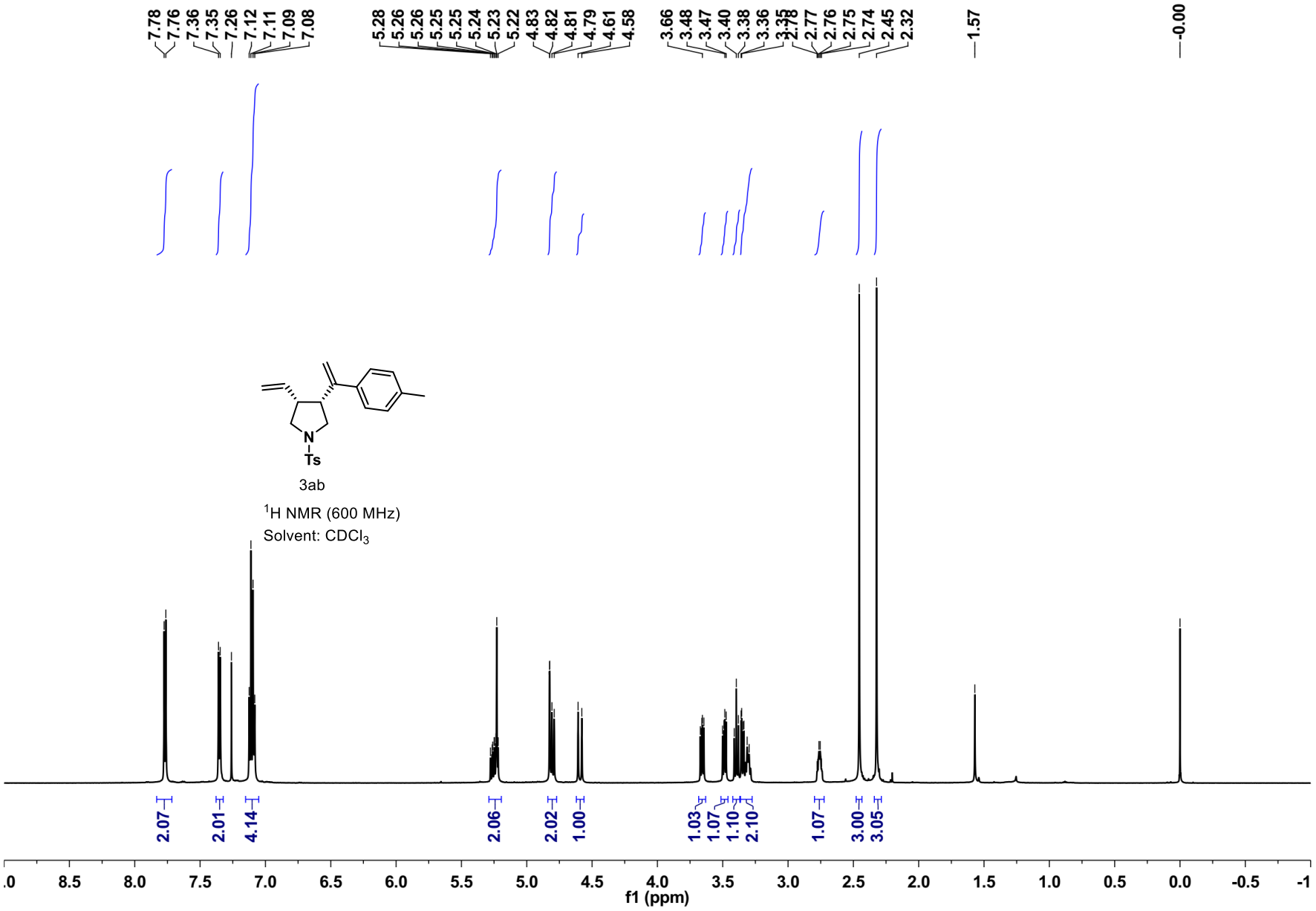
128.28
127.62
127.46
126.37
116.67
113.96
77.21
77.00
76.79
52.30
49.73
45.84
44.33
21.54
134.47
134.27
129.73
128.28
127.62
127.46
126.37
135
130
125
f1 (ppm)
N
Ts
3aa
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)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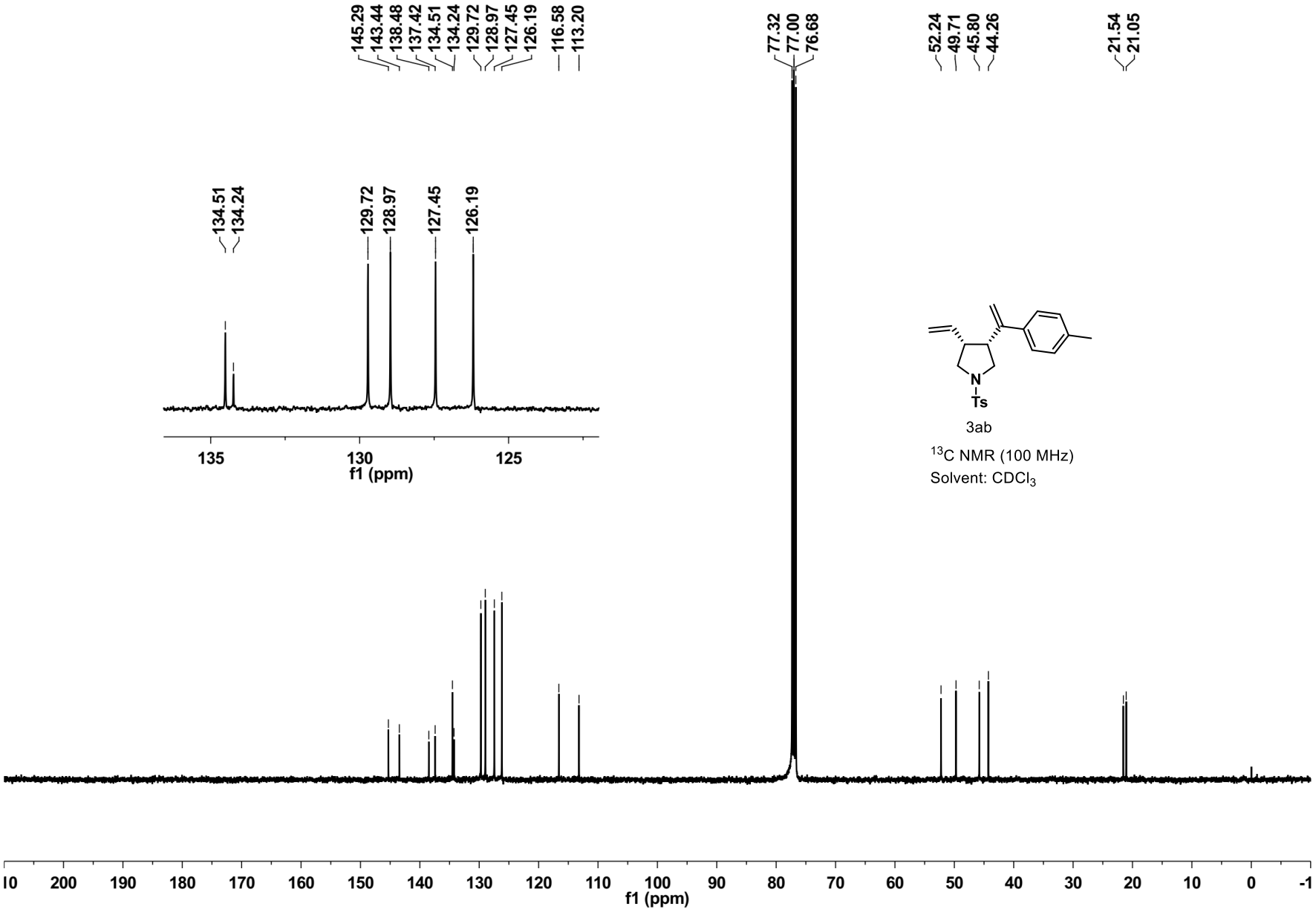
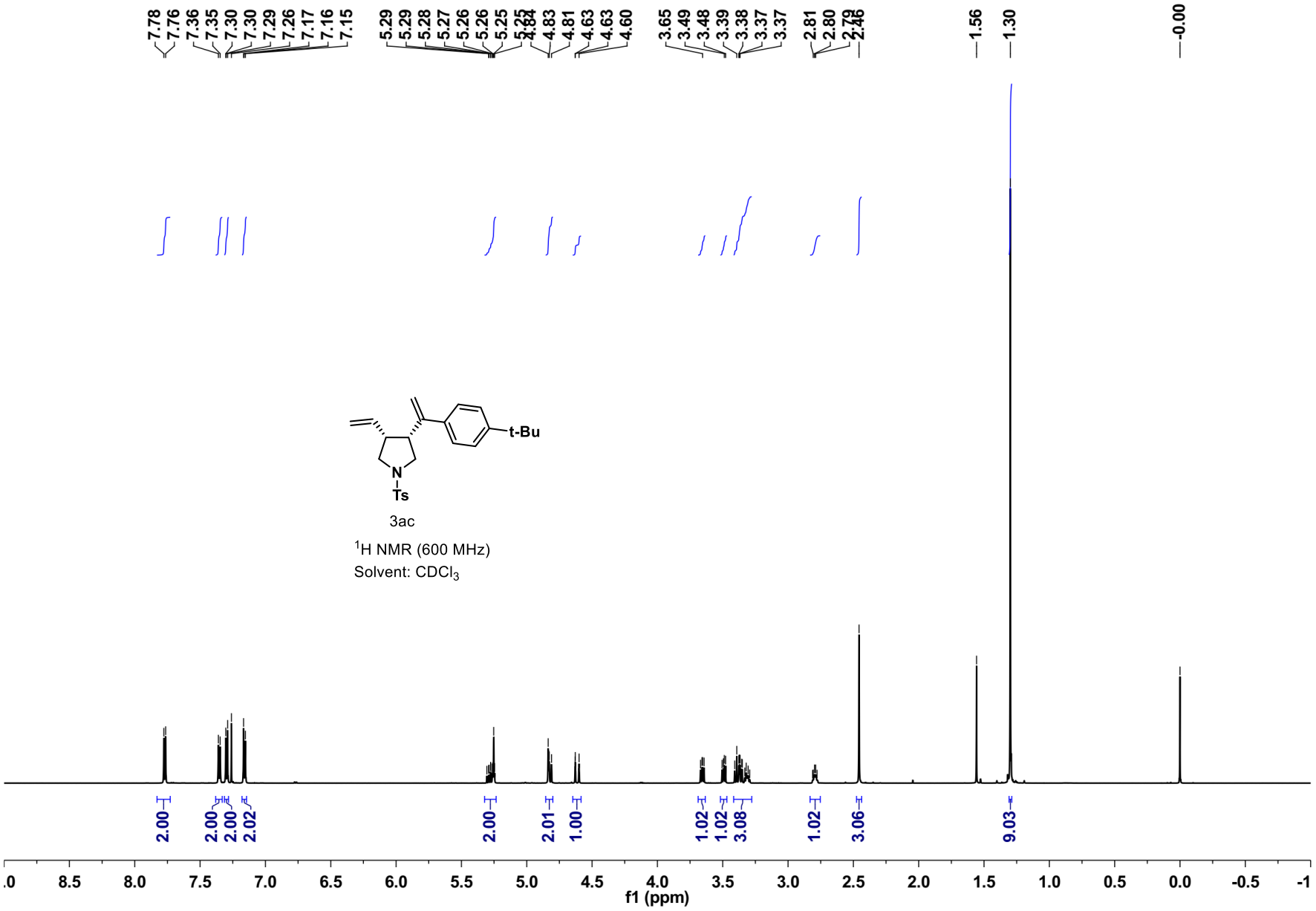
7.76
7.36
7.35
7.26
7.12
7.11
7.09
7.08
5.28
5.26
5.26
5.25
5.25
5.24
5.23
5.22
4.83
4.82
4.81
4.79
4.61
4.58
3.66
3.48
3.47
3.40
3.38
3.36
2.78
2.77
2.76
2.75
2.74
2.45
2.32
1.57
-0.00
N
Ts
3ab
1H NMR (600 MHz)
Solvent: CDCl3
2.07
2.01
4.14
2.06
2.02
1.00
1.03
1.07
1.10
2.10
1.07
3.00
3.05
f1 (ppm)


145.29
143.44
138.48
137.42
134.51
134.24
129.72
128.97
127.45
126.19
116.58
113.20
77.32
77.00
76.68
52.24
49.71
45.80
44.26
21.54
21.05
134.51
134.24
129.72
128.97
127.45
126.19
135
130
125
f1 (ppm)
N
Ts
3ab
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)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7.76
7.36
7.35
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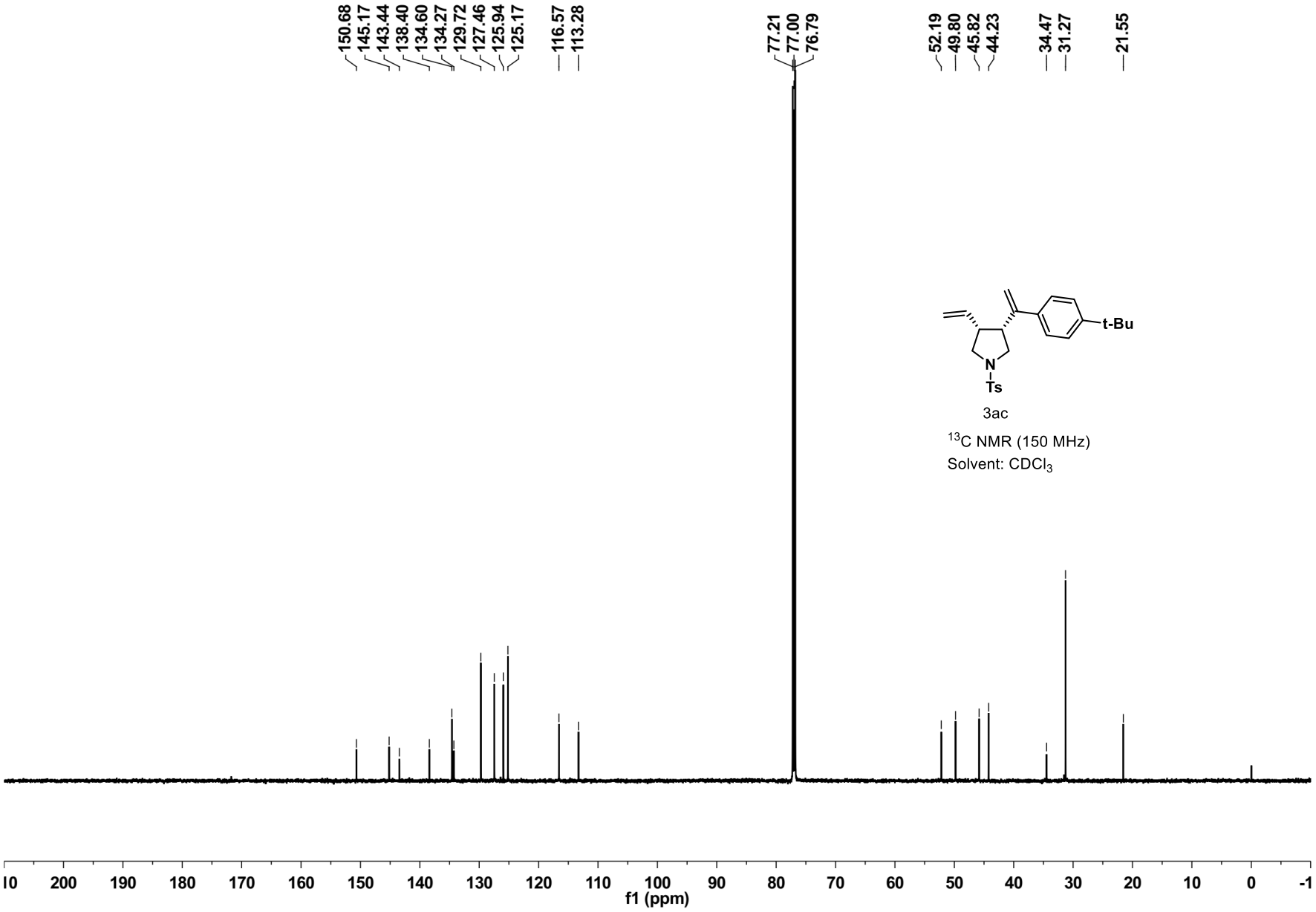
7.30
7.29
7.26
7.17
7.16
7.15
5.29
5.29
5.28
5.27
5.26
5.26
5.25
4.84
4.83
4.81
4.63
4.63
4.60
3.65
3.49
3.48
3.39
3.38
3.37
3.37
2.81
2.80
2.79
2.46
1.56
1.30
-0.00
t-Bu
N
Ts
3ac
1H NMR (600 MHz)
Solvent: CDCl3
2.00
2.00
2.00
2.02
2.00
2.01
1.00
1.02
1.02
3.08
1.02
3.06
9.03
f1 (ppm)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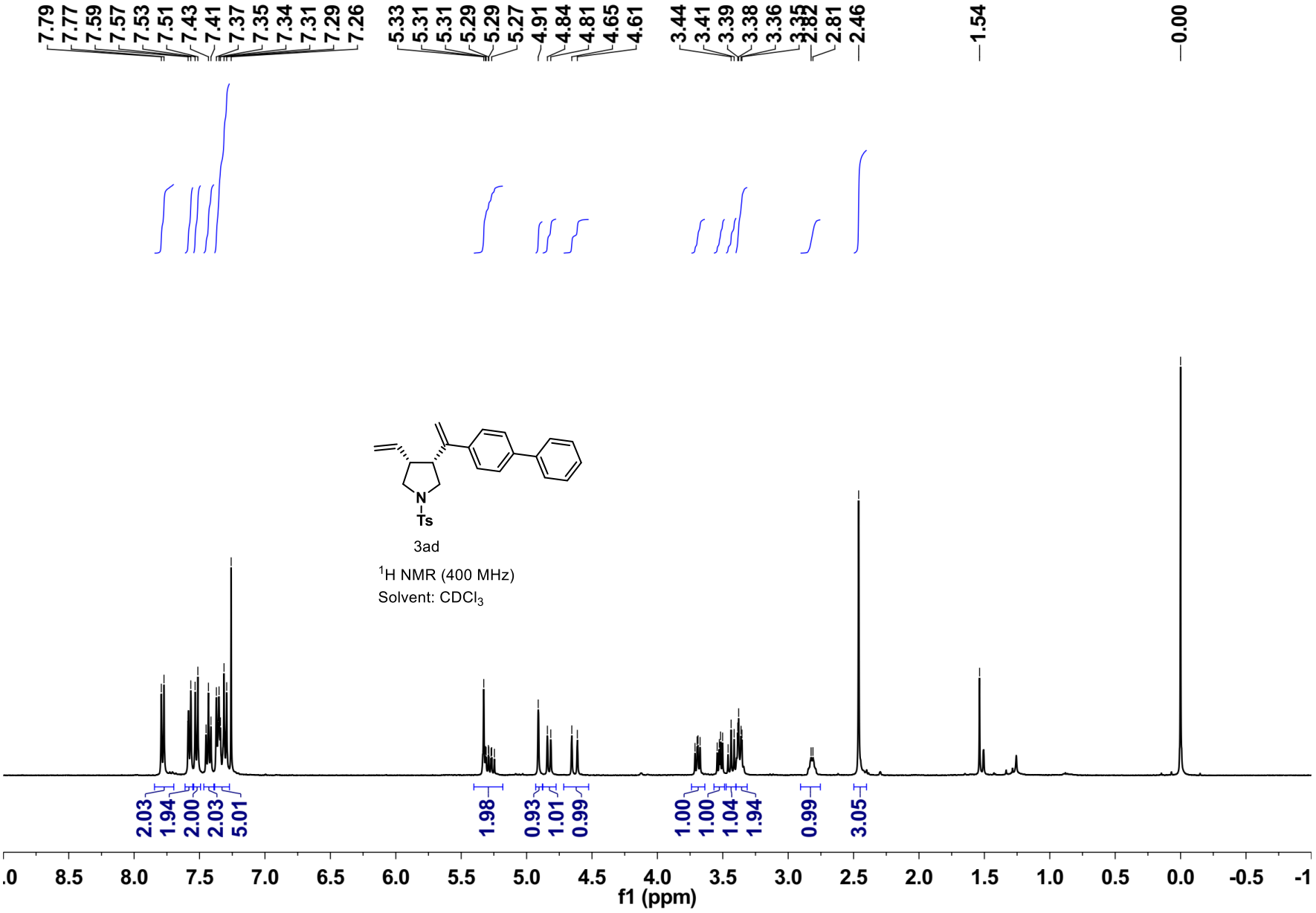
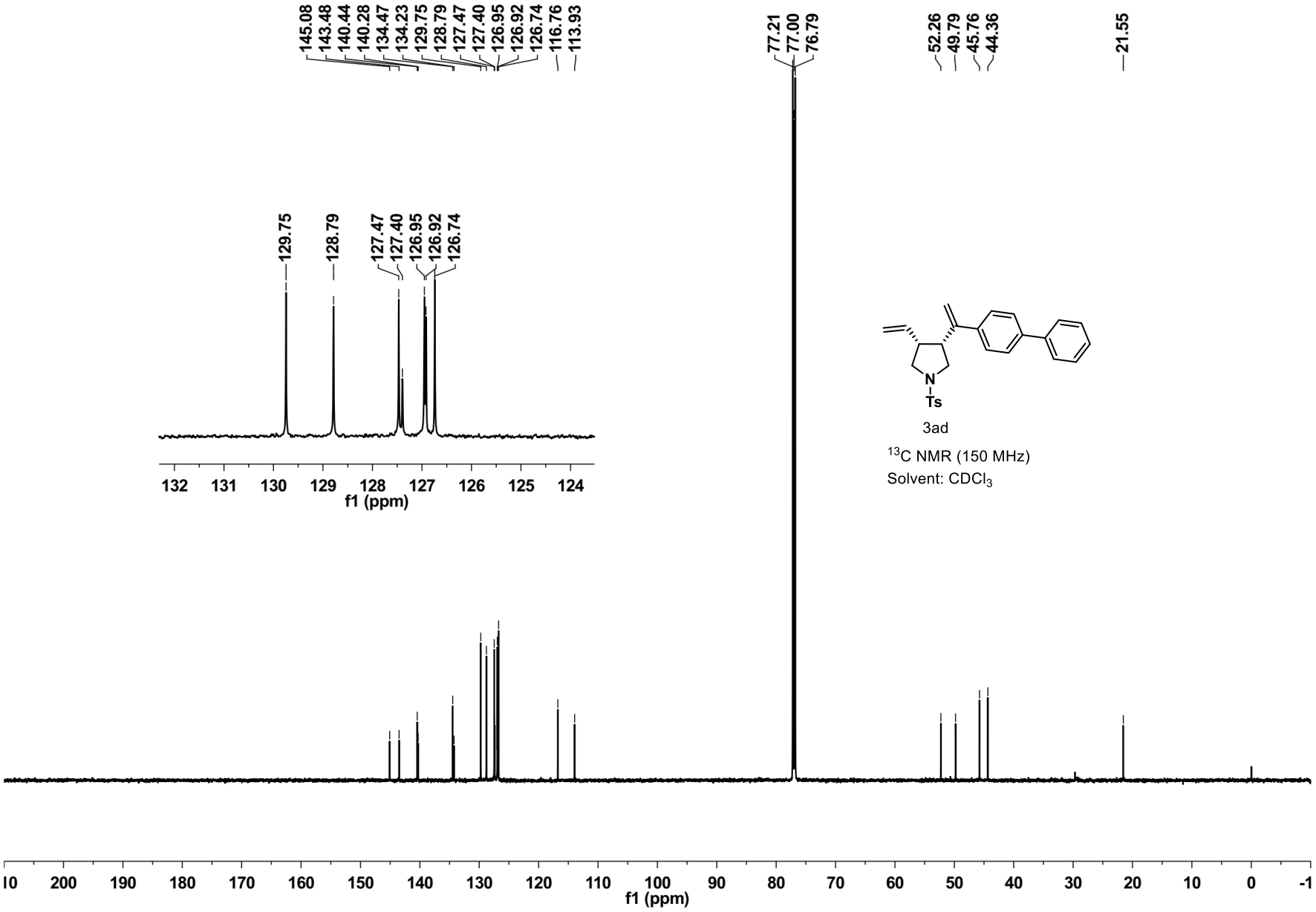
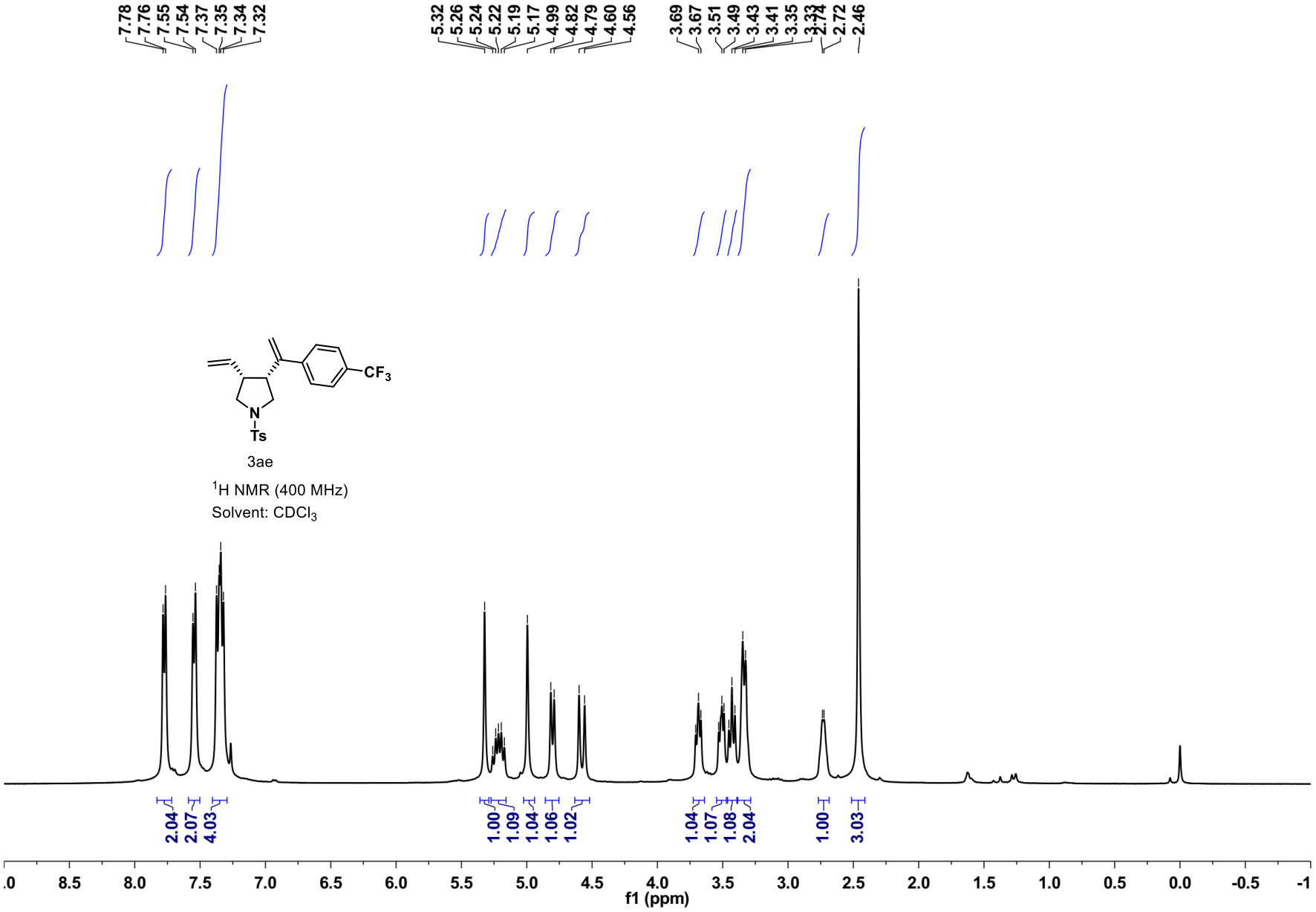
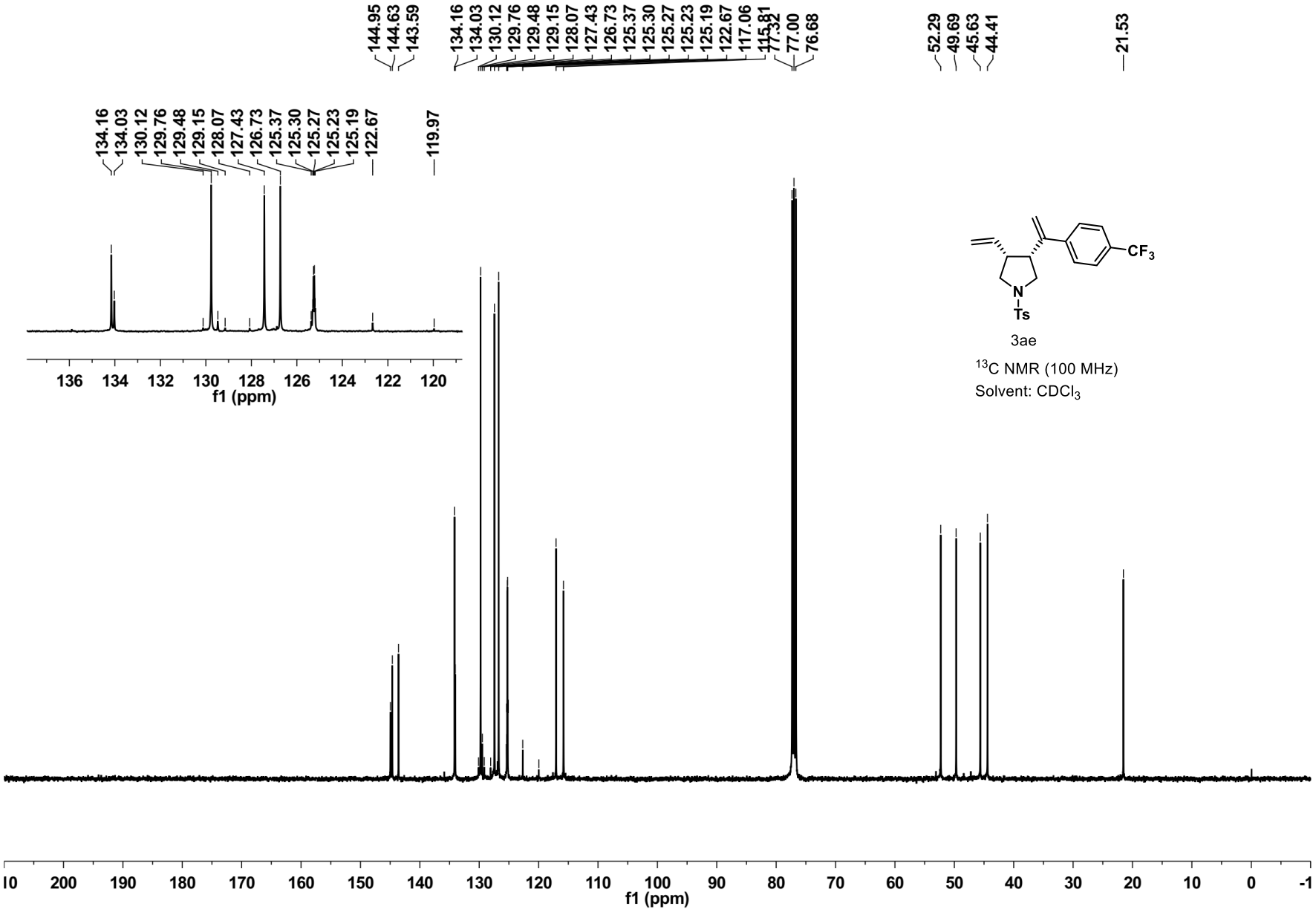
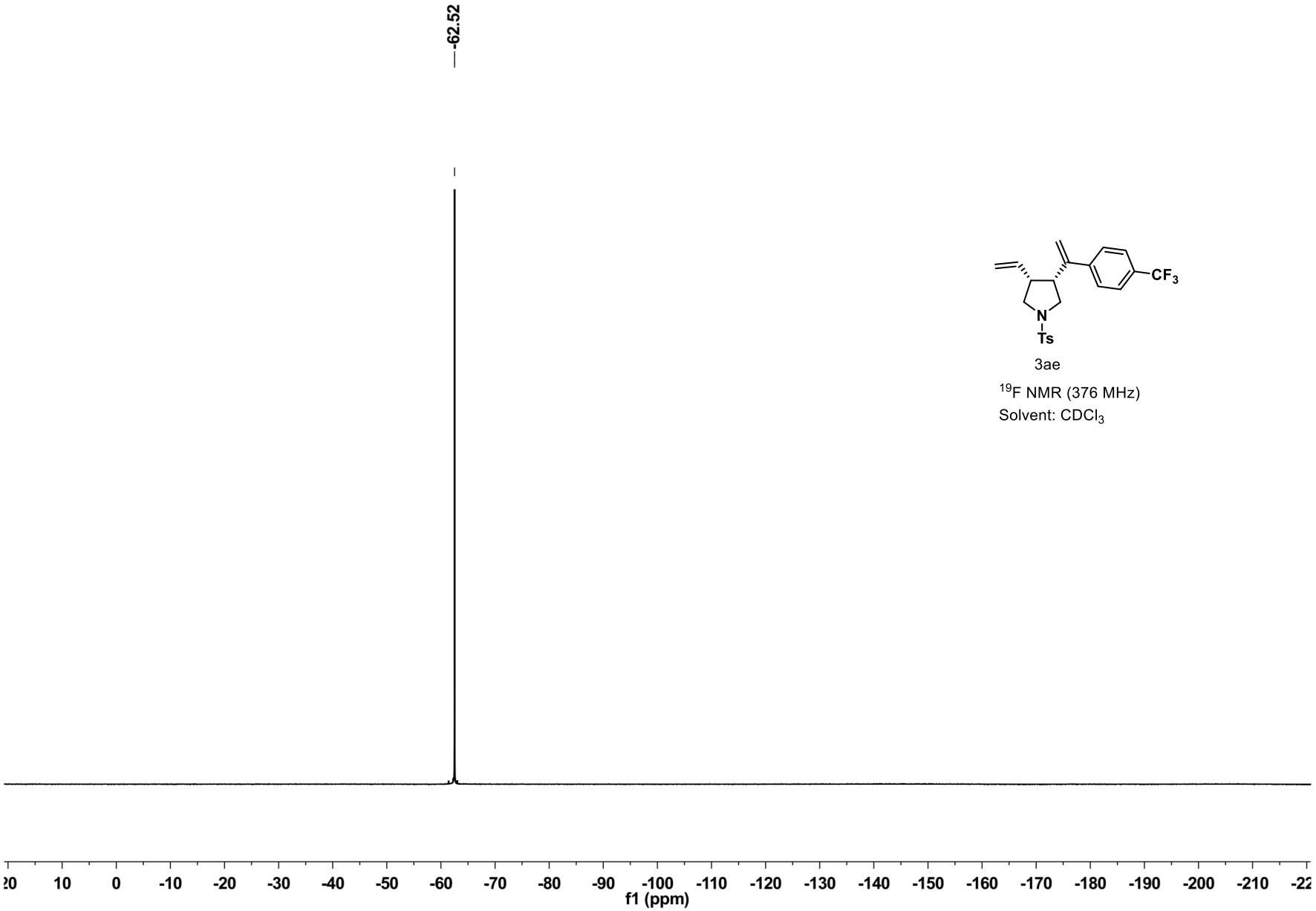
145.17
143.44
138.40
134.60
134.27
129.72
127.46
125.94
125.17
116.57
113.28
77.21
77.00
76.79
52.19
49.80
45.82
44.23
34.47
31.27
21.55
t-Bu
N
Ts
3ac
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)

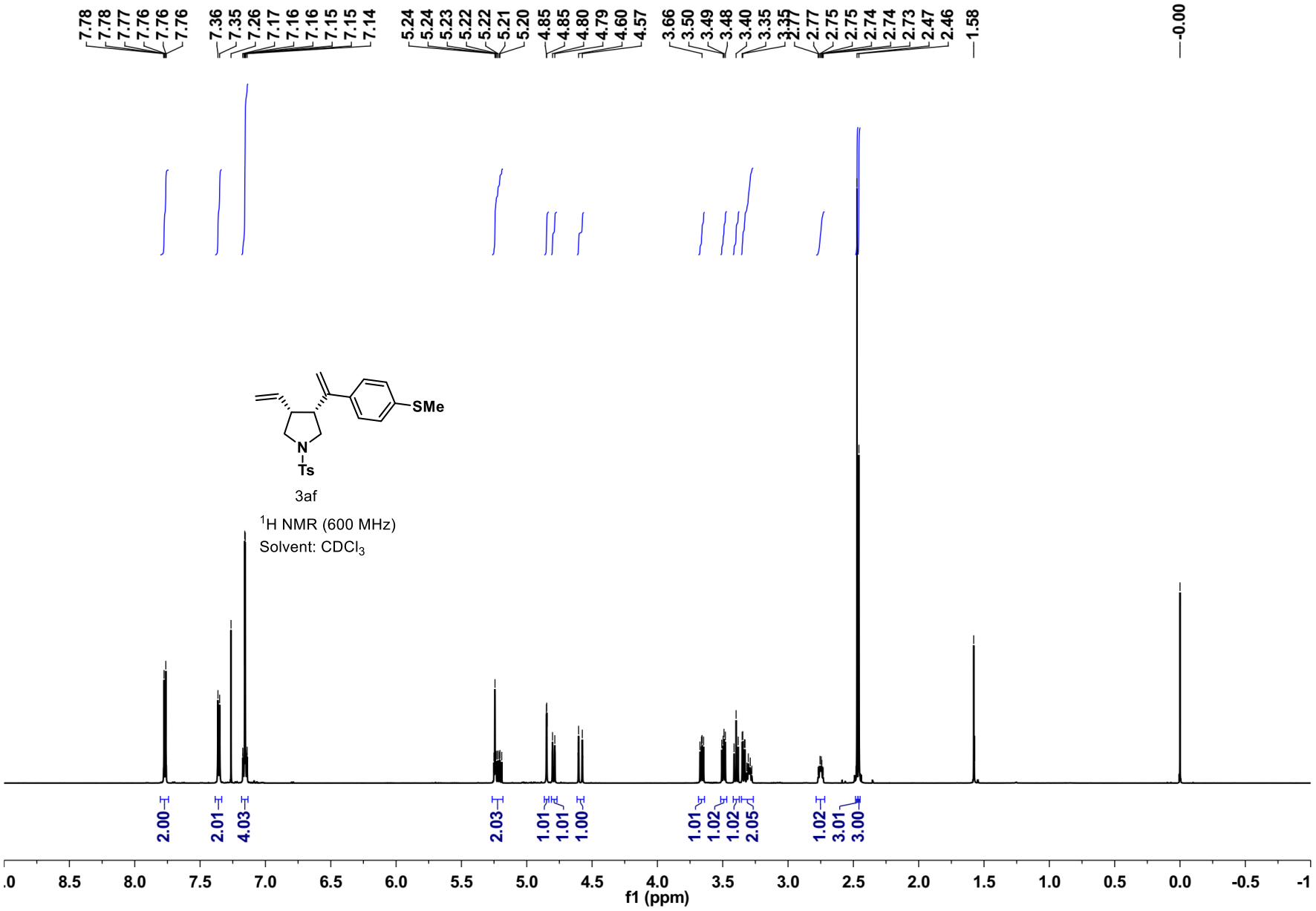

7.79
7.77
7.59
7.57
7.53
7.51
7.43
7.41
7.37
7.35
7.34
7.31
7.29
7.26
5.33
5.31
5.31
5.29
5.29
5.27
4.91
4.84
4.81
4.65
4.61
3.44
3.41
3.39
3.38
3.36
2.82
2.81
2.46
1.54
0.00
N
Ts
3ad
1H NMR (400 MHz)
Solvent: CDCl3
2.03
1.94
2.00
2.03
5.01
1.98
0.93
1.01
0.99
1.00
1.00
1.04
1.94
0.99
3.05
f1 (ppm)


145.08
143.48
140.44
140.28
134.47
134.23
129.75
128.79
127.47
127.40
126.95
126.92
126.74
116.76
113.93
77.21
77.00
76.79
52.26
49.79
45.76
44.36
21.55
129.75
128.79
127.47
127.40
126.95
126.92
126.74
132 131 130 129 128 127 126 125 124
f1 (ppm)
N
Ts
3ad
13C NMR (150 MHz)
Solvent: CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.78
7.76
7.55
7.54
7.37
7.35
7.34
7.32
5.32
5.26
5.24
5.22
5.19
5.17
4.99
4.82
4.79
4.60
4.56
3.69
3.67
3.51
3.49
3.43
3.41
3.35
3.33
2.72
2.46
CF3
N
Ts
3ae
1H NMR (400 MHz)
Solvent: CDCl3
2.04
2.07
4.03
1.00
1.09
1.04
1.06
1.02
1.04
1.07
1.08
2.04
1.00
3.03
f1 (ppm)


144.95
144.63
143.59
134.16
134.03
130.12
129.76
129.48
129.15
128.07
127.43
126.73
125.37
125.30
125.27
125.23
125.19
122.67
117.06
115.81
77.32
77.00
76.68
52.29
49.69
45.63
44.41
21.53
119.97
CF3
N
Ts
3ae
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


-62.52
CF3
N
Ts
3ae
19F NMR (376 MHz)
Solvent: CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)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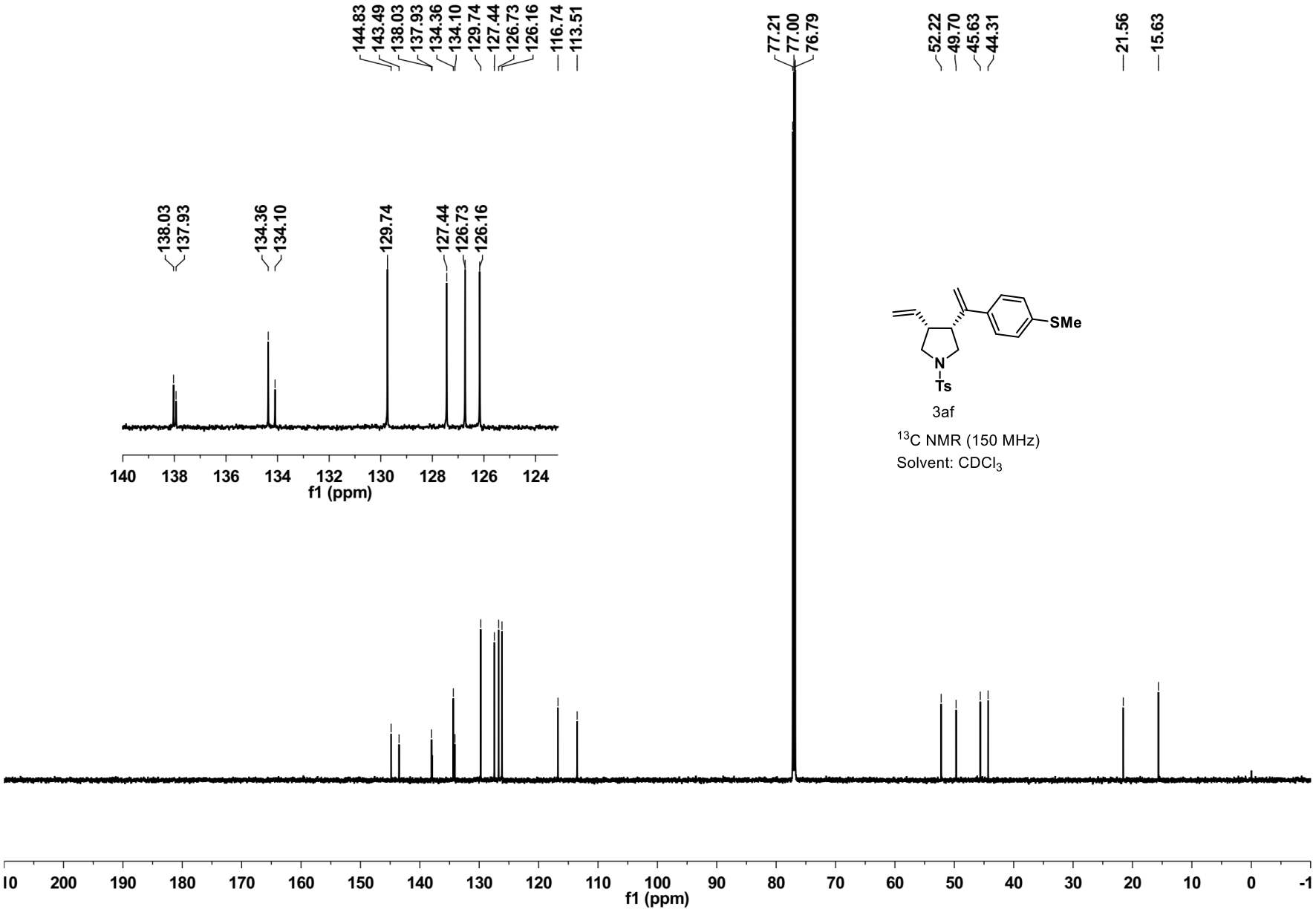
7.78
7.77
7.76
7.76
7.76
7.36
7.35
7.26
7.17
7.16
7.16
7.15
7.15
7.14
5.24
5.24
5.23
5.22
5.22
5.21
5.20
4.85
4.85
4.80
4.79
4.60
4.57
3.66
3.50
3.49
3.48
3.40
3.35
3.35
2.77
2.77
2.75
2.75
2.74
2.74
2.73
2.47
2.46
1.58
-0.00
SMe
N
Ts
3af
1H NMR (600 MHz)
Solvent: CDCl3
2.00
2.01
4.03
2.03
1.01
1.01
1.00
1.01
1.02
1.02
2.05
1.02
3.01
3.00
f1 (ppm)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138.03
137.93
134.36
134.10
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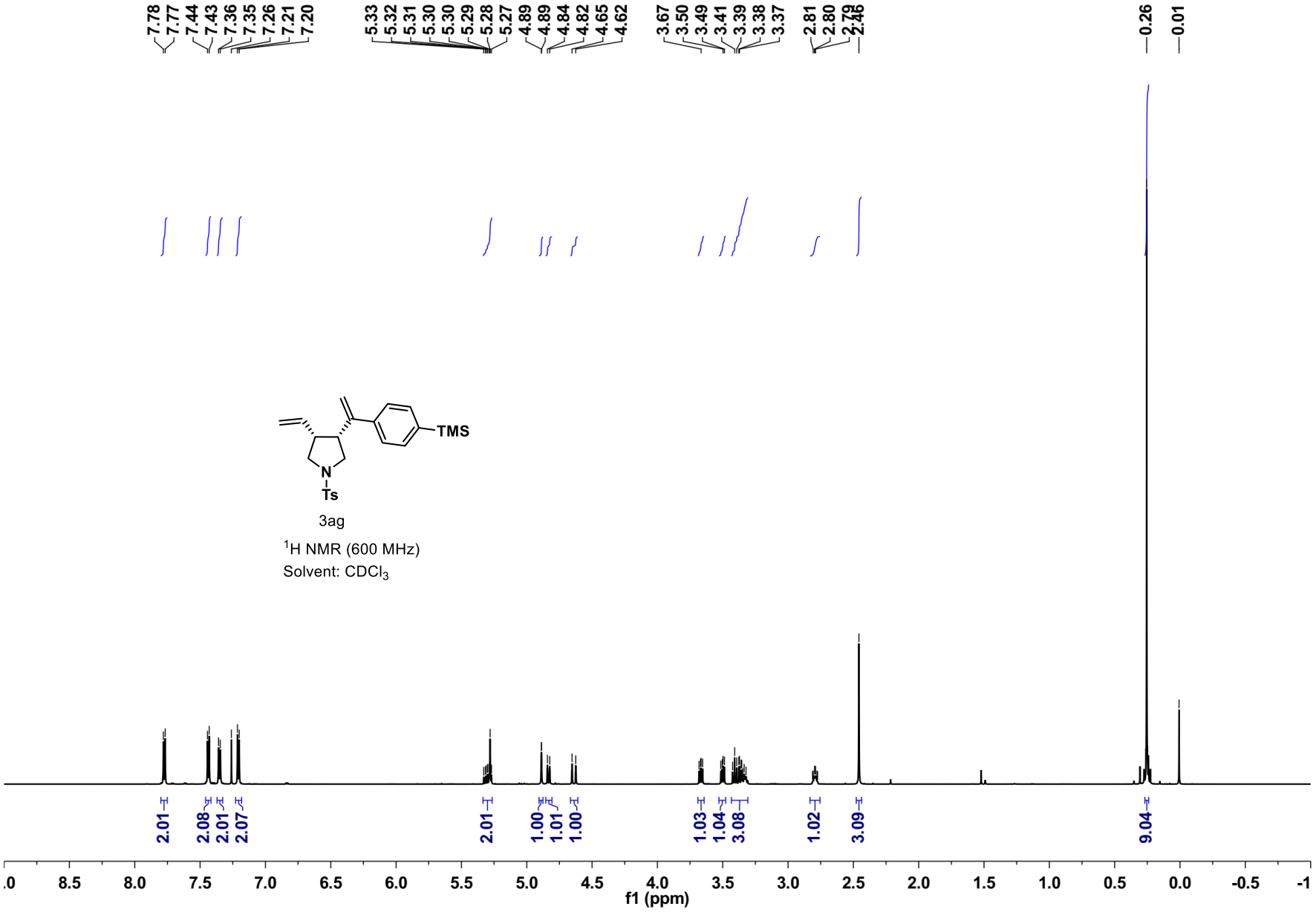
127.44
126.73
126.16
116.74
113.51
77.21
77.00
76.79
52.22
49.70
45.63
44.31
21.56
15.63
138.03
137.93
134.36
134.10
129.74
127.44
126.73
126.16
140 138 136 134 132 130 128 126 124
f1 (ppm)
SMe
N
Ts
3af
13C NMR (150 MHz)
Solvent: CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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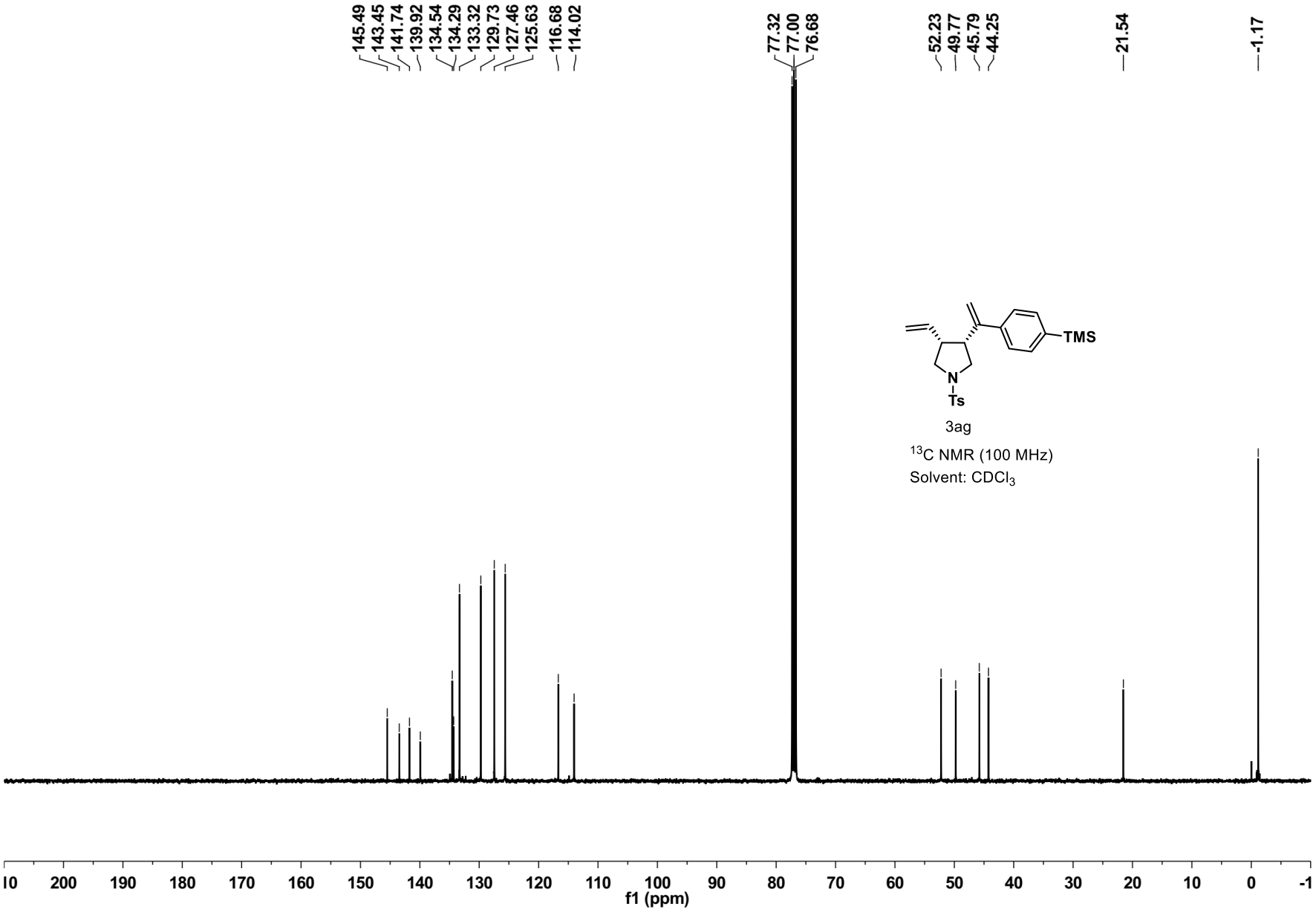
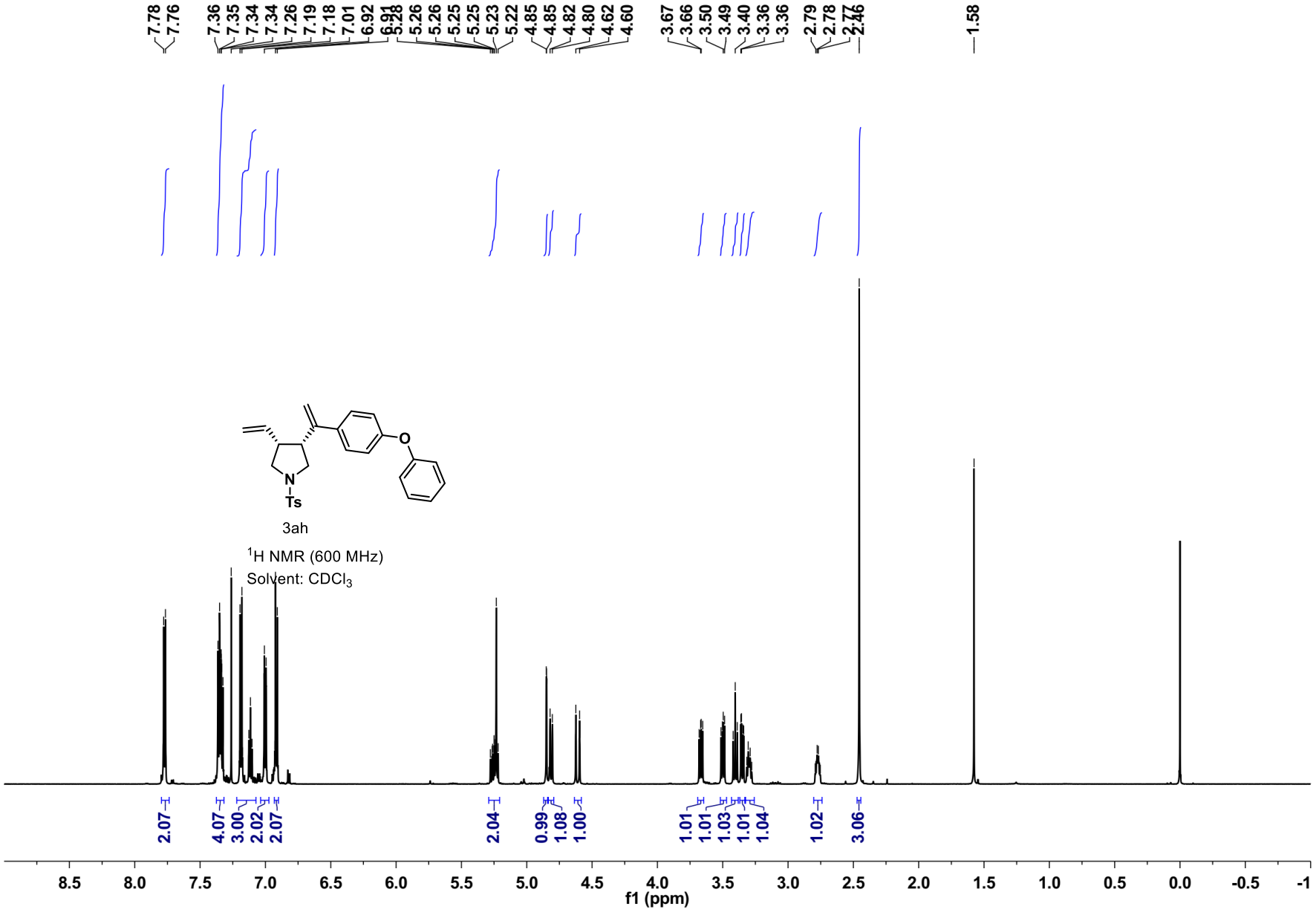
7.77
7.44
7.43
7.36
7.35
7.26
7.21
7.20
5.33
5.32
5.31
5.30
5.30
5.29
5.28
5.27
4.89
4.89
4.84
4.82
4.65
4.62
3.67
3.50
3.49
3.41
3.39
3.38
3.37
2.81
2.80
2.79
2.46
0.26
0.01
TMS
N
Ts
3ag
1H NMR (600 MHz)
Solvent: CDCl3
2.01
2.08
2.01
2.07
2.01
1.00
1.01
1.00
1.03
1.04
3.08
1.02
3.09
9.04
f1 (ppm)


145.49
143.45
141.74
139.92
134.54
134.29
133.32
129.73
127.46
125.63
116.68
114.02
77.32
77.00
76.68
52.23
49.77
45.79
44.25
21.54
-1.17
TMS
N
Ts
3ag
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)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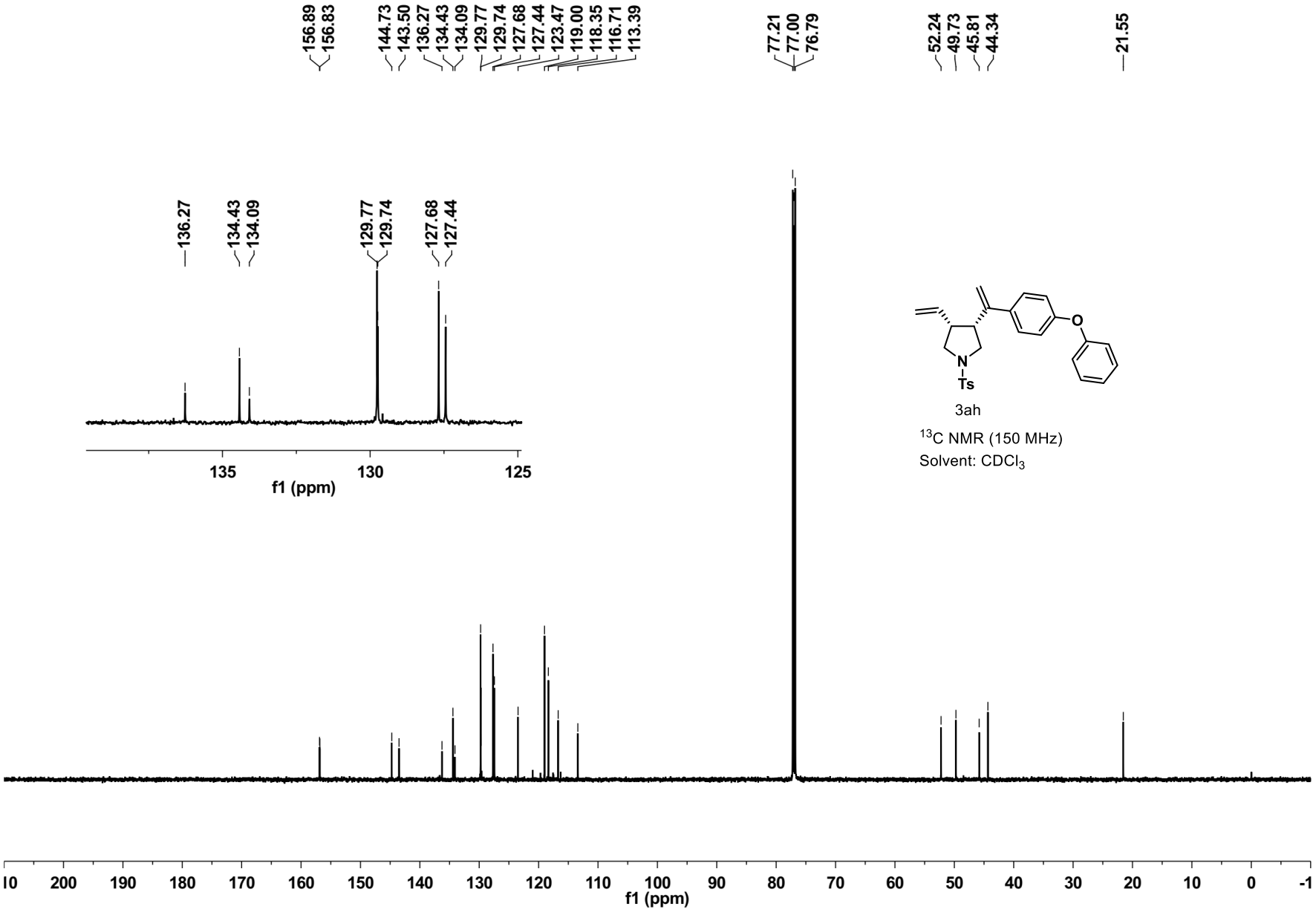
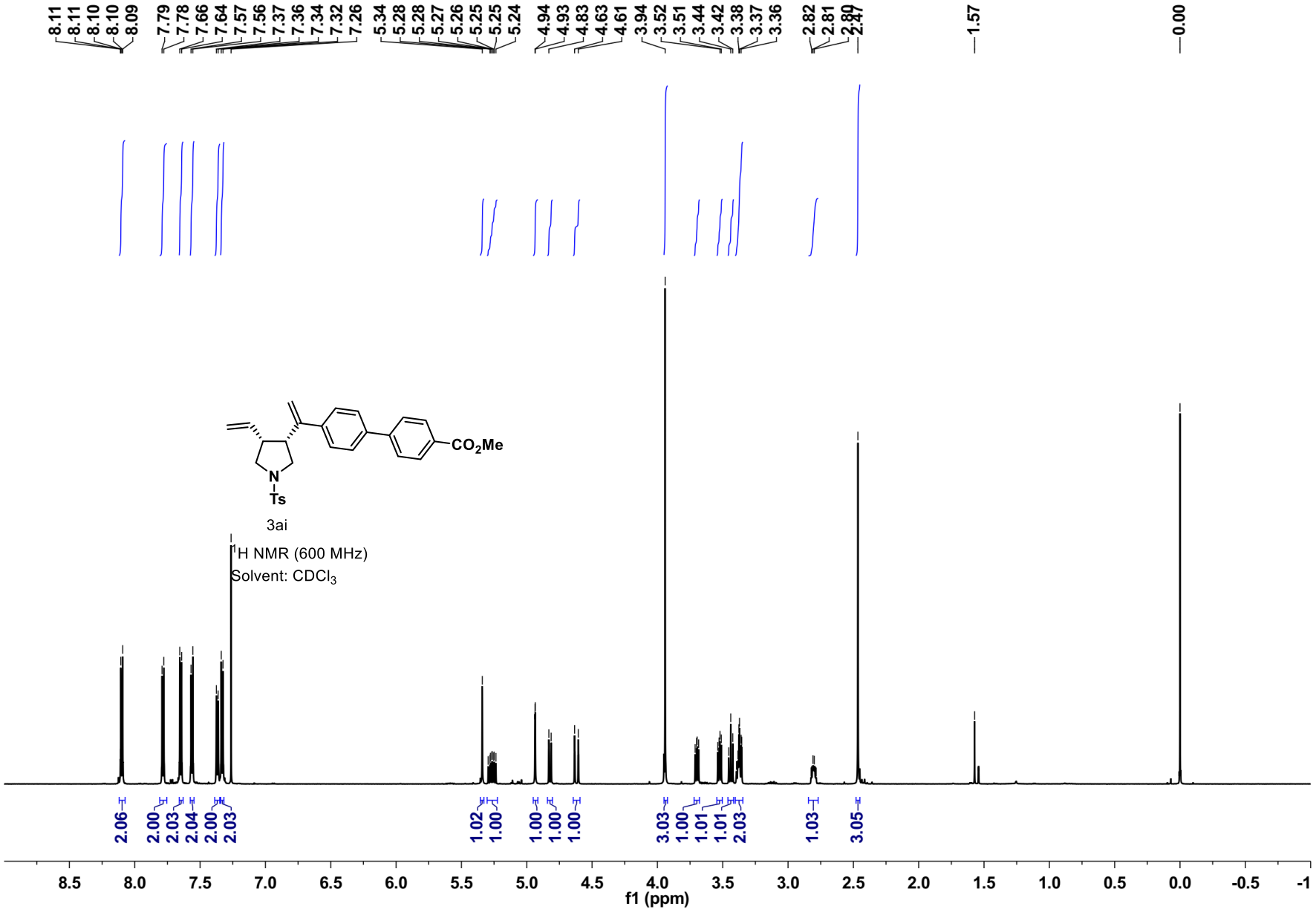
7.76
7.36
7.35
7.34
7.34
7.26
7.19
7.18
7.01
6.92
6.91
5.28
5.26
5.26
5.25
5.25
5.23
5.22
4.85
4.85
4.82
4.80
4.62
4.60
3.67
3.66
3.50
3.49
3.40
3.36
3.36
2.79
2.78
2.77
2.76
1.58
O
N
Ts
3ah
1H NMR (600 MHz)
Solvent: CDCl3
2.07
4.07
3.00
2.02
2.07
2.04
0.99
1.08
1.00
1.01
1.01
1.03
1.01
1.04
1.02
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


156.89
156.83
144.73
143.50
136.27
134.43
134.09
129.77
129.74
127.68
127.44
123.47
119.00
118.35
116.71
113.39
77.21
77.00
76.79
52.24
49.73
45.81
44.34
21.55
136.27
134.43
134.09
129.77
129.74
127.68
127.44
135
130
125
f1 (ppm)
N
Ts
O
3ah
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)


8.11
8.11
8.10
8.10
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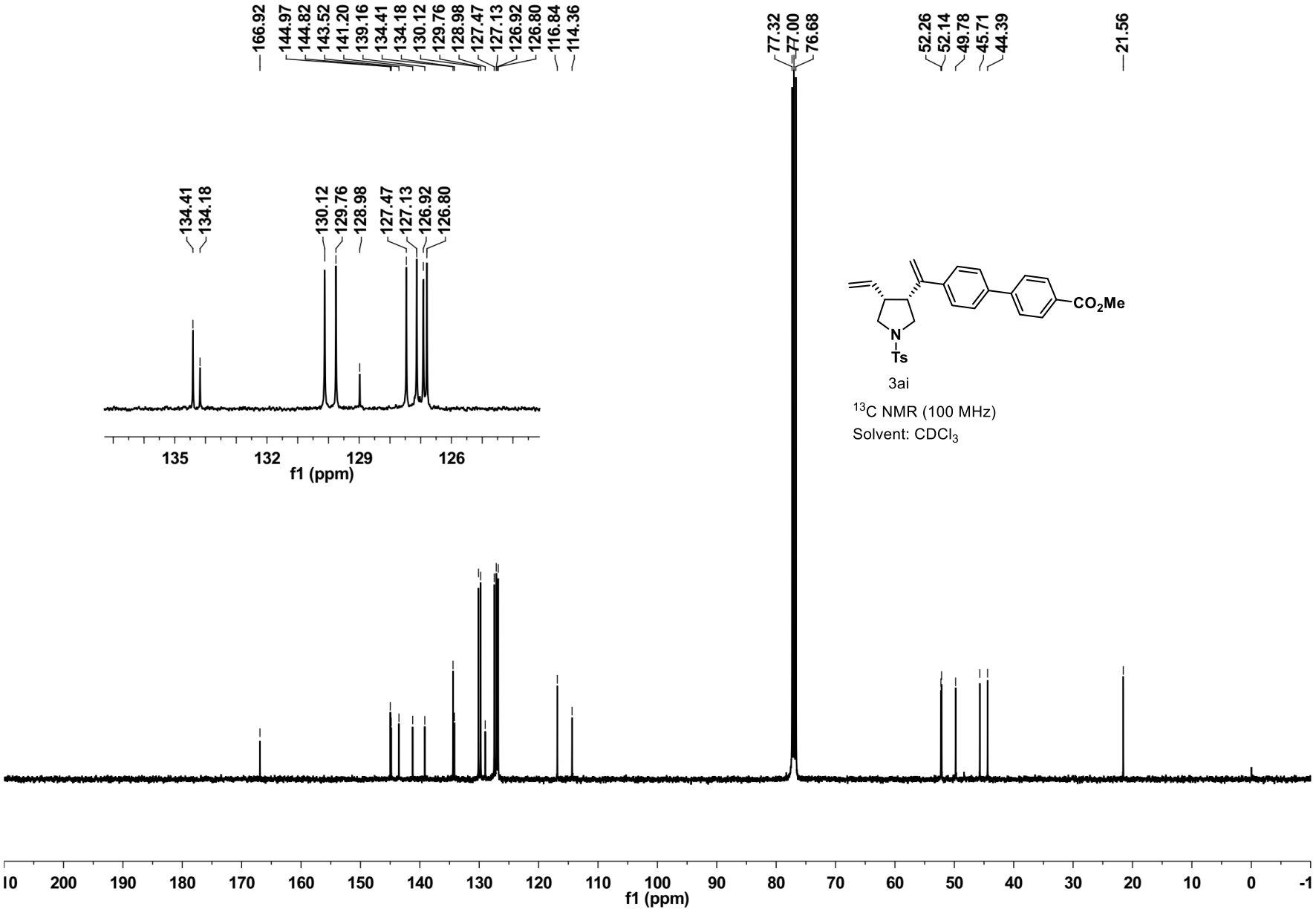
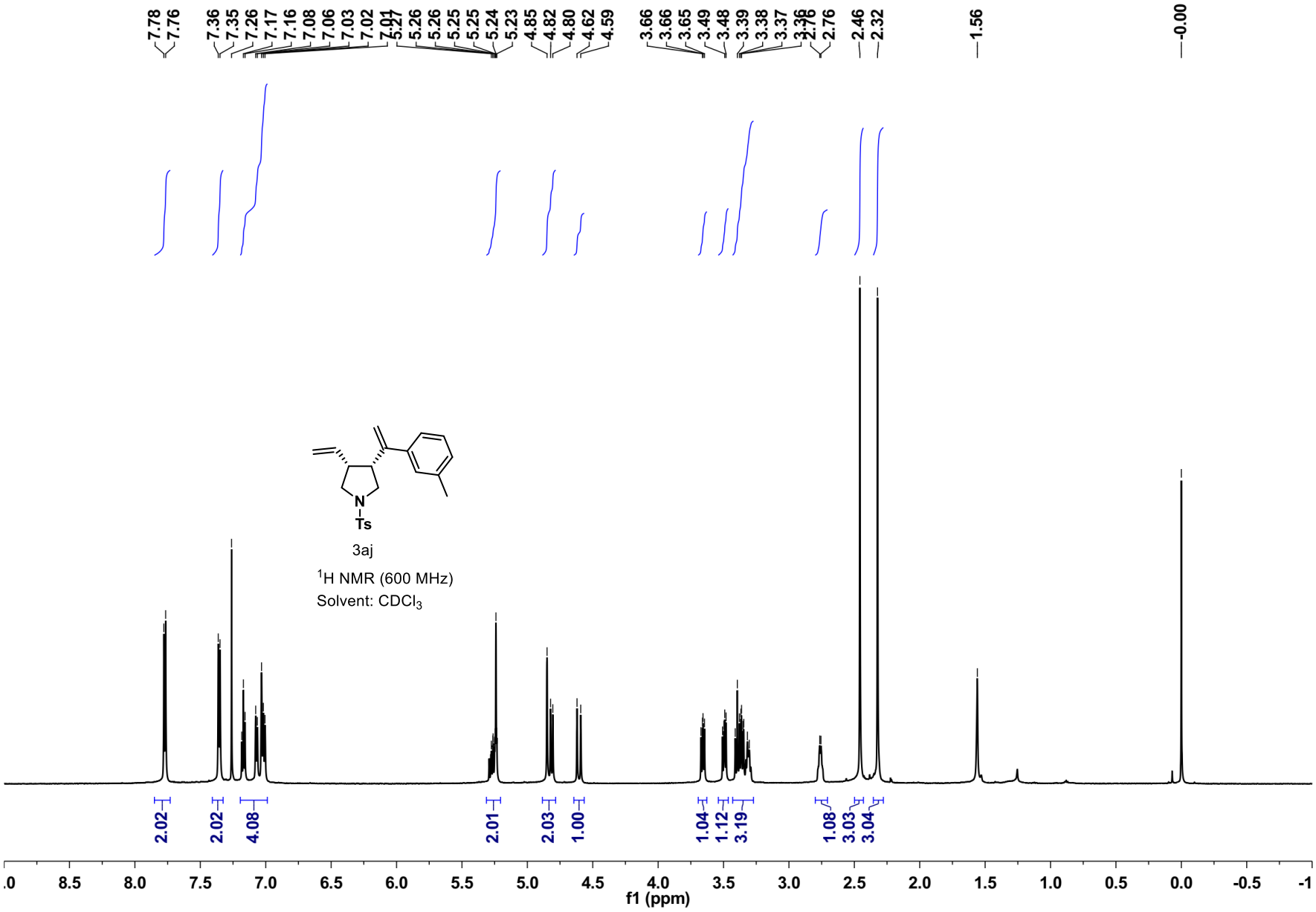
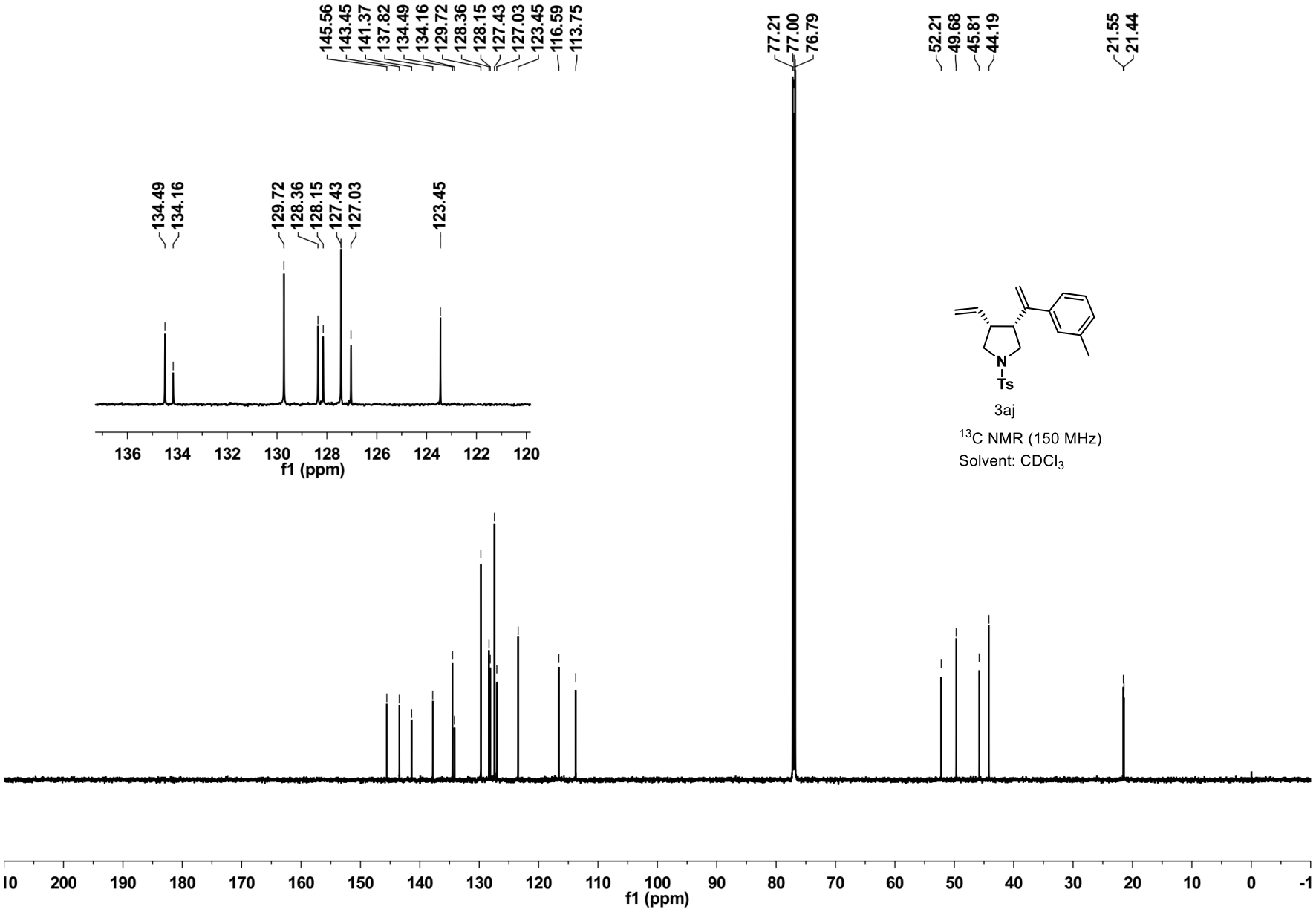
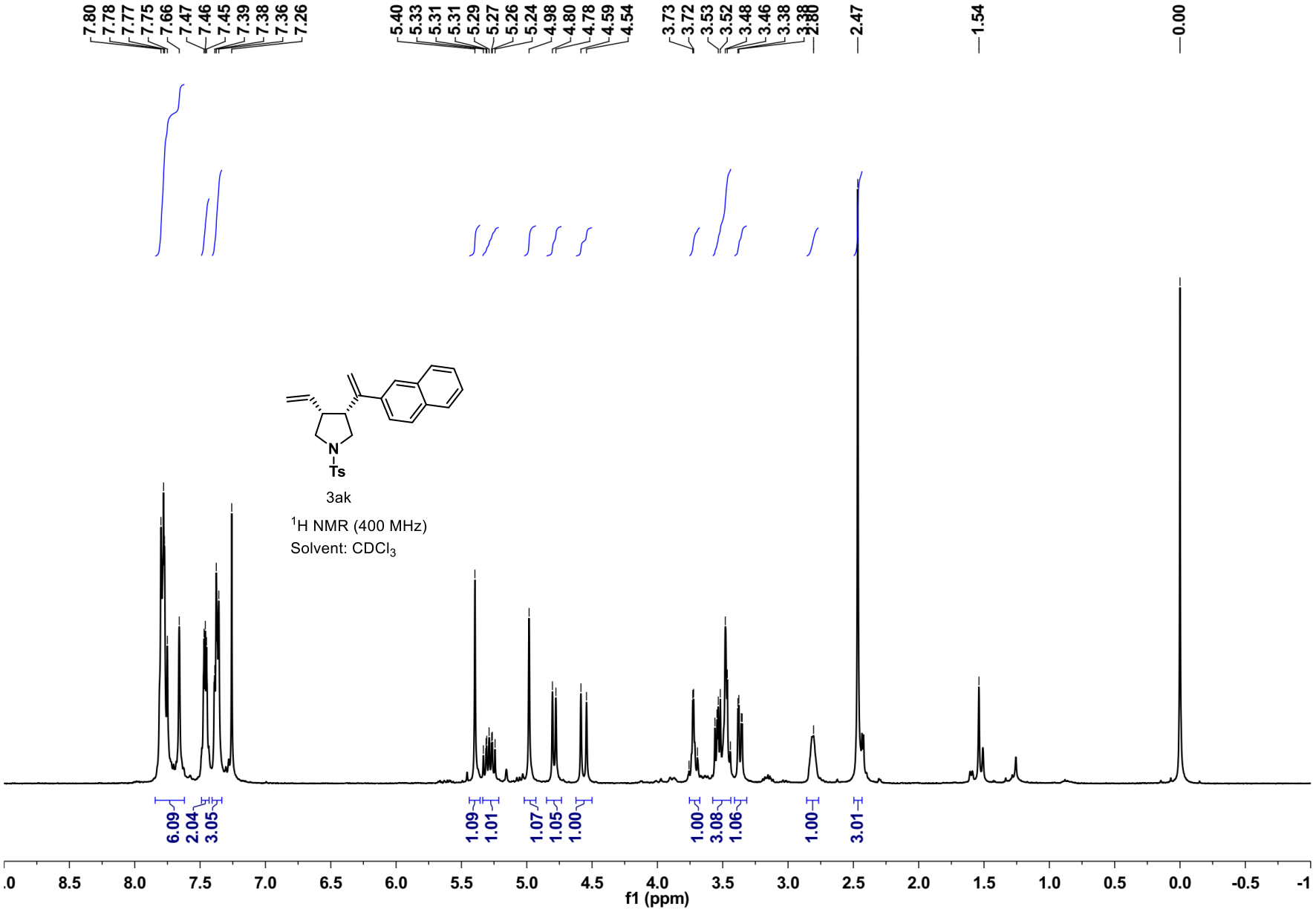
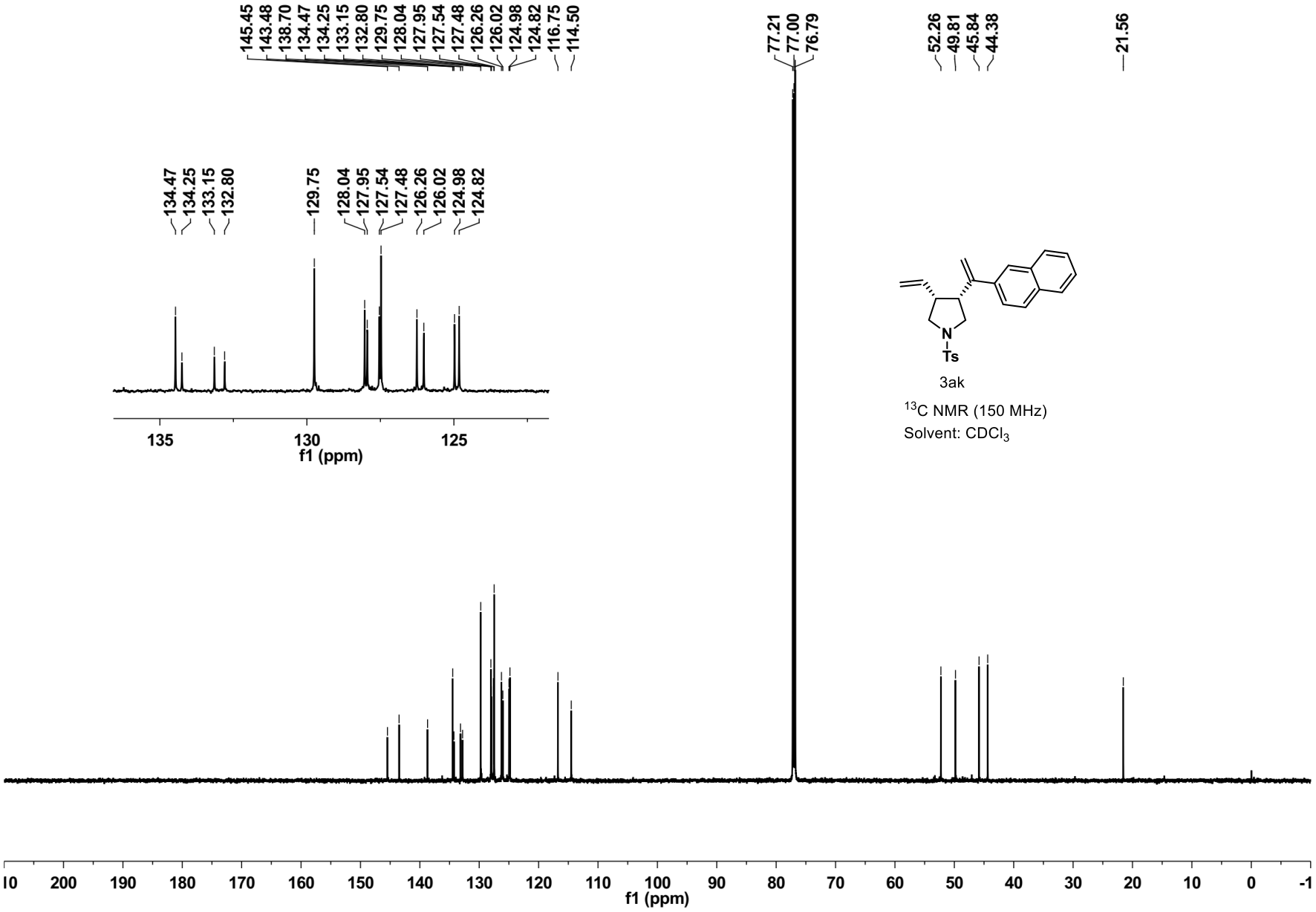
7.79
7.78
7.66
7.64
7.57
7.56
7.37
7.36
7.34
7.32
7.26
5.34
5.28
5.28
5.27
5.26
5.25
5.25
5.24
4.94
4.93
4.83
4.63
4.61
3.94
3.52
3.51
3.44
3.42
3.38
3.37
3.36
2.82
2.81
2.80
2.47
1.57
0.00
CO2Me
N
Ts
3ai
1H NMR (600 MHz)
Solvent: CDCl3
2.06
2.00
2.03
2.04
2.00
2.03
1.02
1.00
1.00
1.00
1.00
3.03
1.00
1.01
1.01
2.03
1.03
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

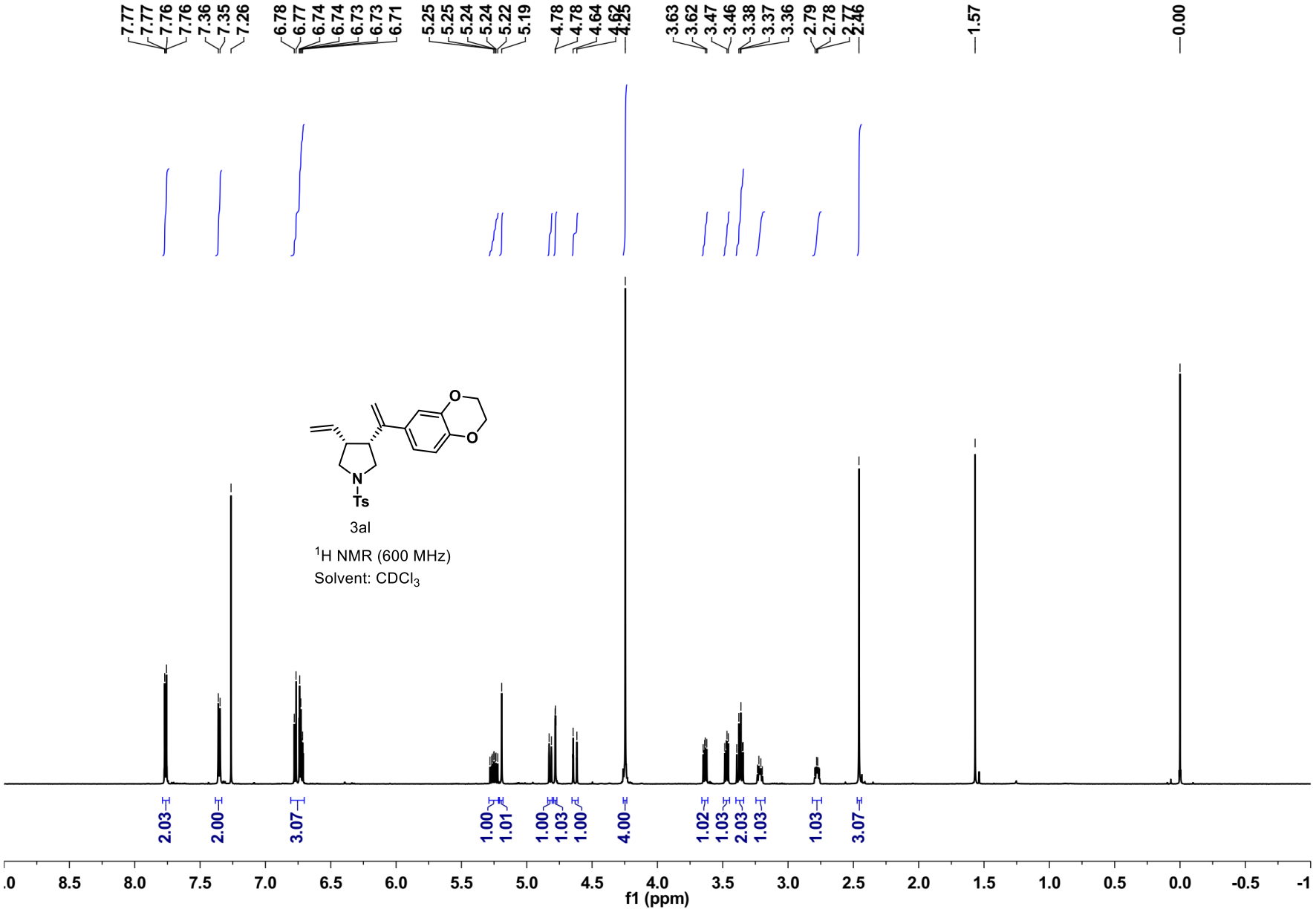

166.92
144.97
144.82
143.52
141.20
139.16
134.41
134.18
130.12
129.76
128.98
127.47
127.13
126.92
126.80
116.84
114.36
77.32
77.00
76.68
52.26
52.14
49.78
45.71
44.39
21.56
CO2Me
N
Ts
3ai
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

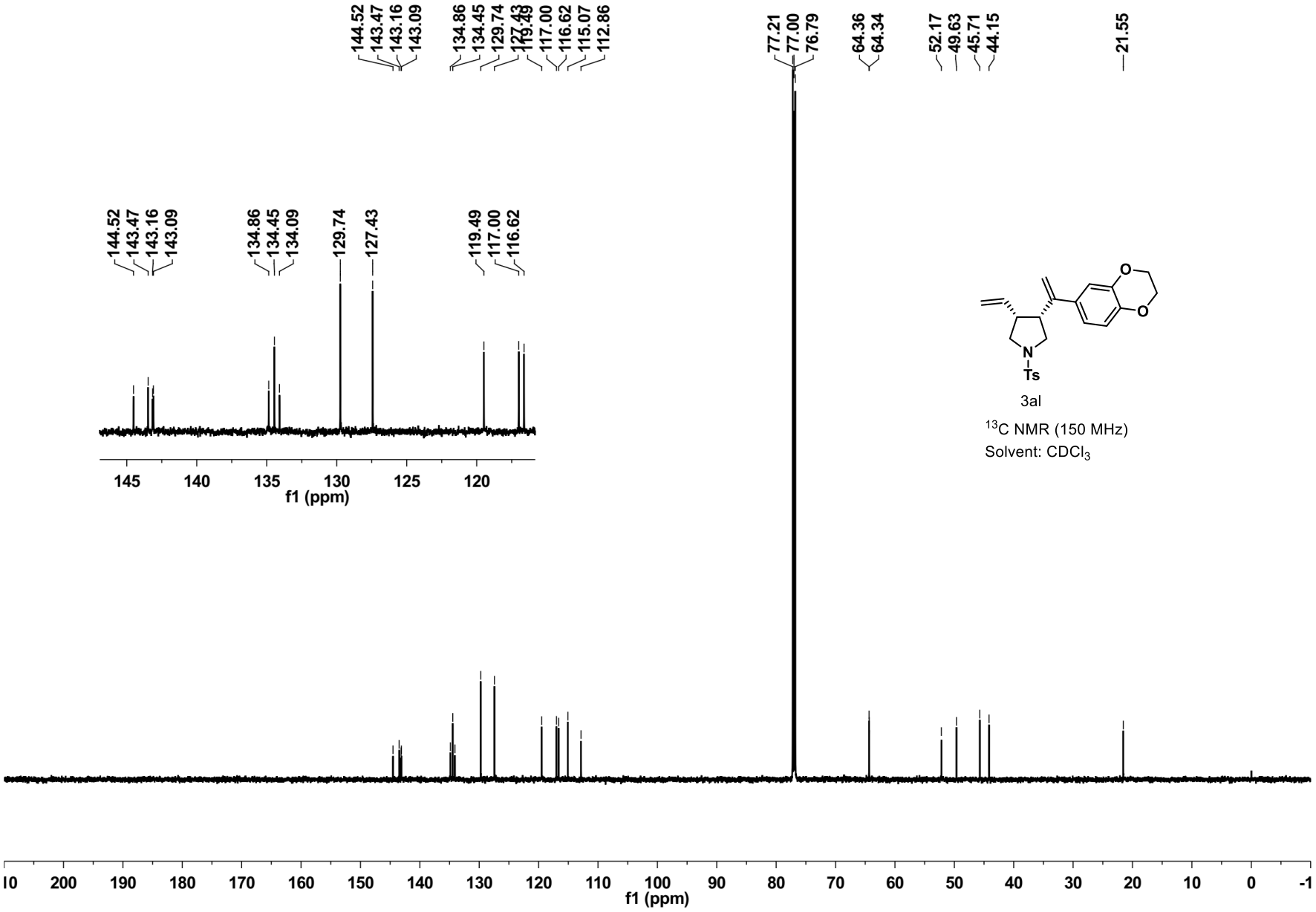

7.78
7.76
7.36
7.35
7.26
7.17
7.16
7.08
7.06
7.03
7.02
7.01
5.27
5.26
5.26
5.25
5.25
5.24
5.23
4.85
4.82
4.80
4.62
4.59
3.66
3.66
3.65
3.49
3.48
3.39
3.38
3.37
2.76
2.76
2.46
2.32
1.56
-0.00
N
Ts
3aj
1H NMR (600 MHz)
Solvent: CDCl3
2.02
2.02
4.08
2.01
2.03
1.00
1.04
1.12
3.19
1.08
3.03
3.04
f1 (ppm)

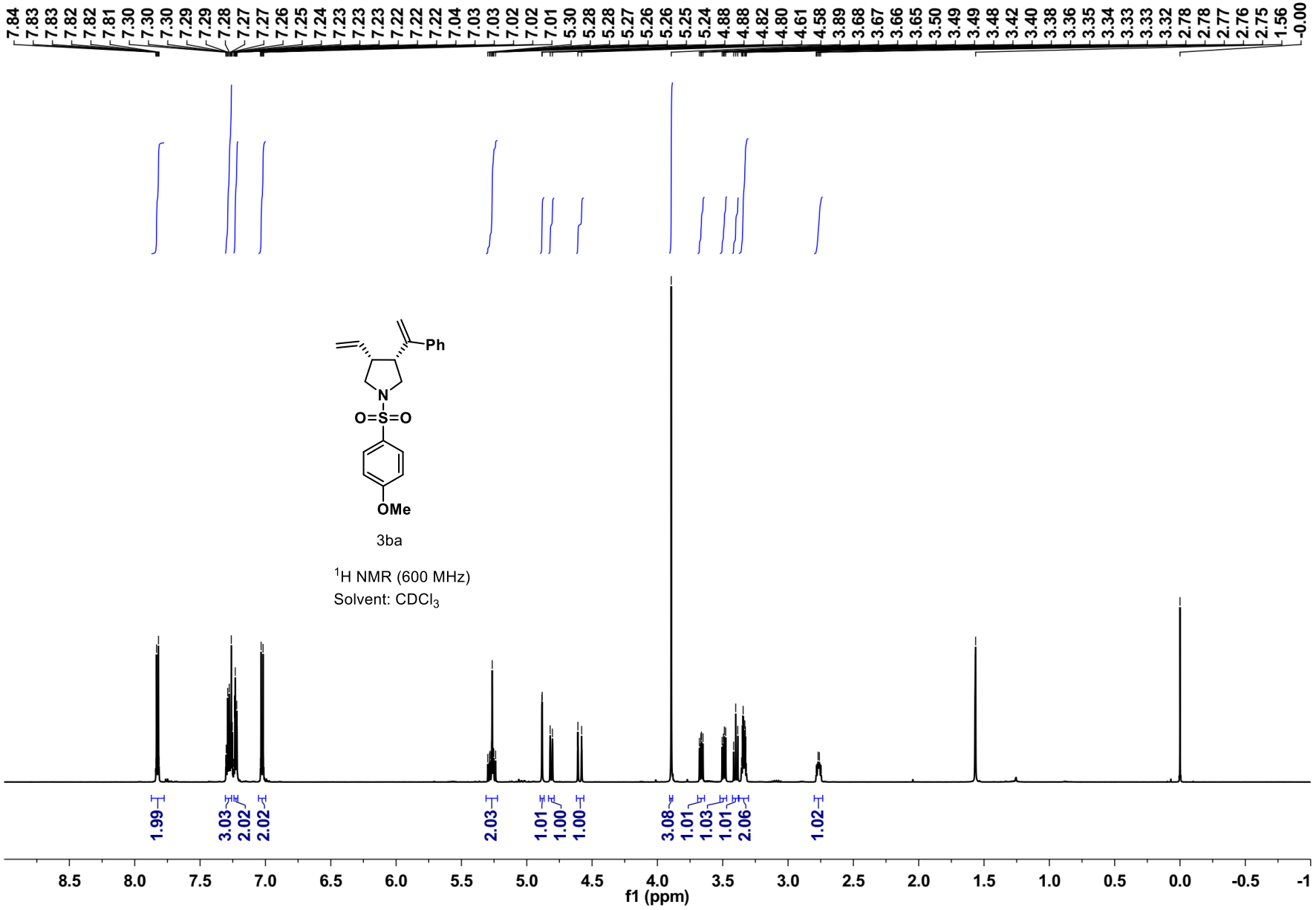

145.56
143.45
141.37
137.82
134.49
134.16
129.72
128.36
128.15
127.43
127.03
123.45
116.59
113.75
77.21
77.00
76.79
52.21
49.68
45.81
44.19
21.55
21.44
134.49
134.16
129.72
128.36
128.15
127.43
127.03
123.45
136 134 132 130 128 126 124 122 120
f1 (ppm)
N
Ts
3aj
13C NMR (150 MHz)
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

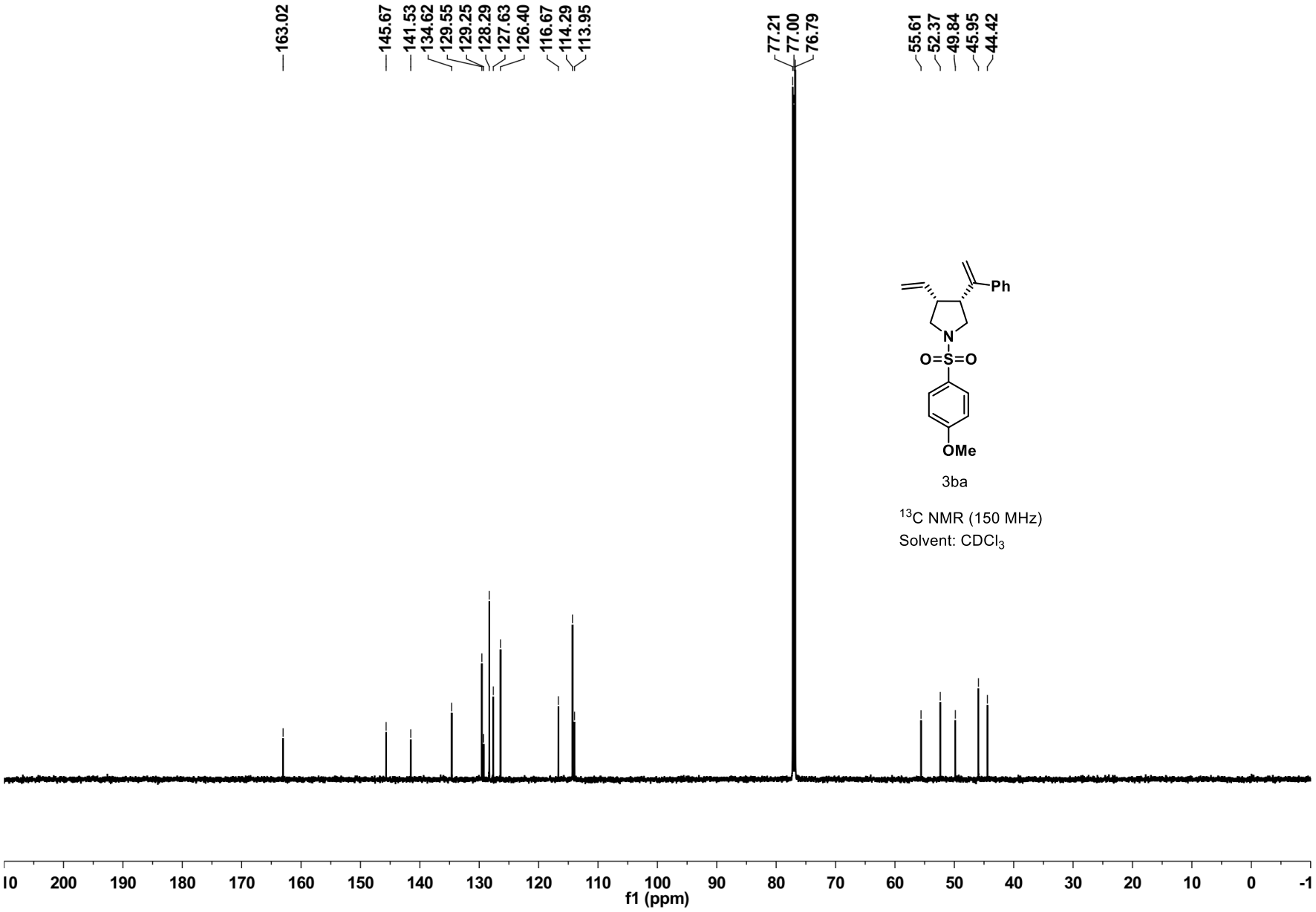

7.80
7.78
7.77
7.75
7.66
7.47
7.46
7.45
7.39
7.38
7.36
7.26
5.40
5.33
5.31
5.31
5.29
5.27
5.26
5.24
4.98
4.80
4.78
4.59
4.54
3.73
3.72
3.53
3.52
3.48
3.46
3.38
2.47
1.54
0.00
N
Ts
3ak
1H NMR (400 MHz)
Solvent: CDCl3
6.09
2.04
3.05
1.09
1.01
1.07
1.05
1.00
1.00
3.08
1.06
1.00
3.01
f1 (ppm)

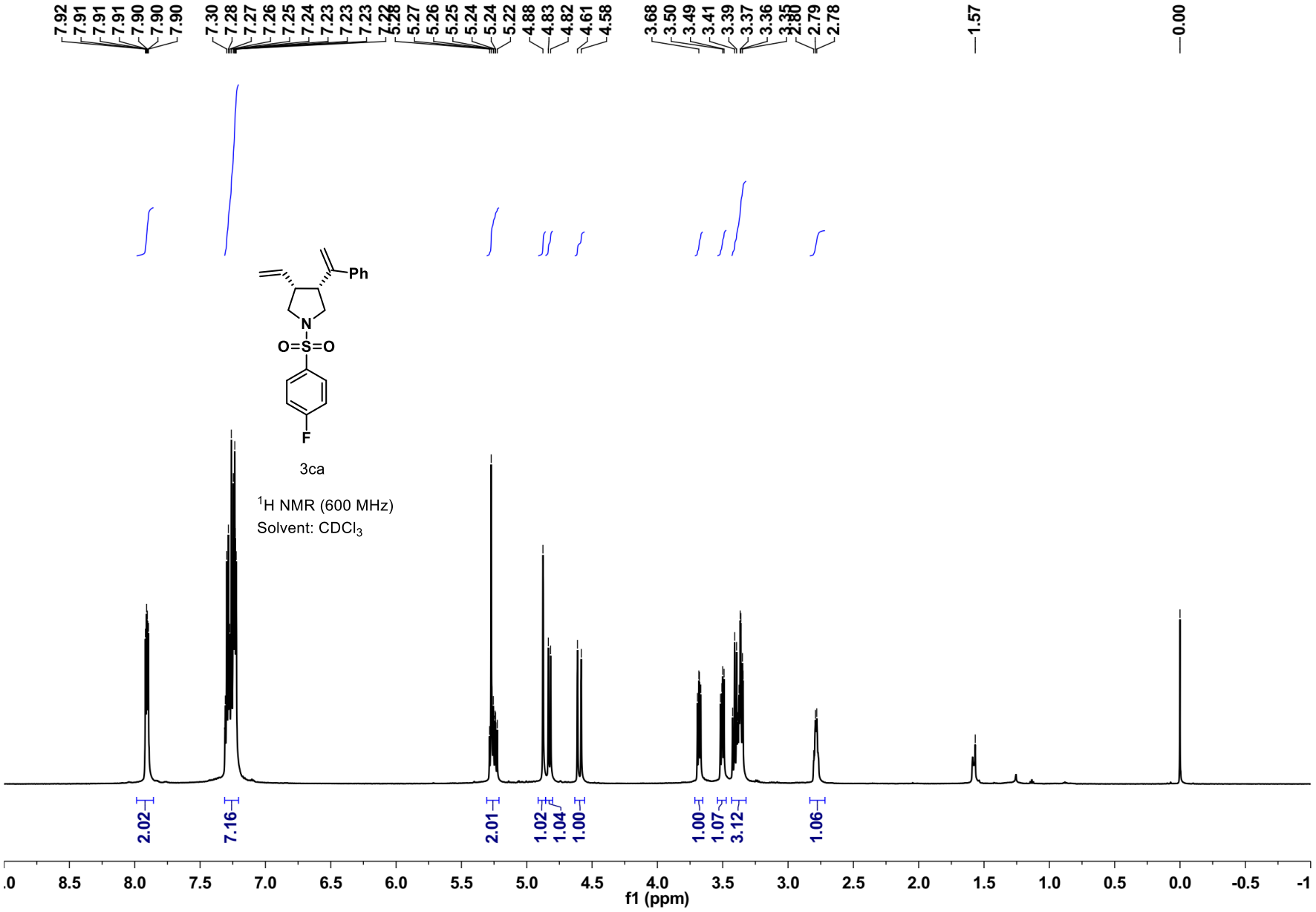

145.45
143.48
138.70
134.47
134.25
133.15
132.80
129.75
128.04
127.95
127.54
127.48
126.26
126.02
124.98
124.82
116.75
114.50
77.21
77.00
76.79
52.26
49.81
45.84
44.38
21.56
N
Ts
3ak
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)

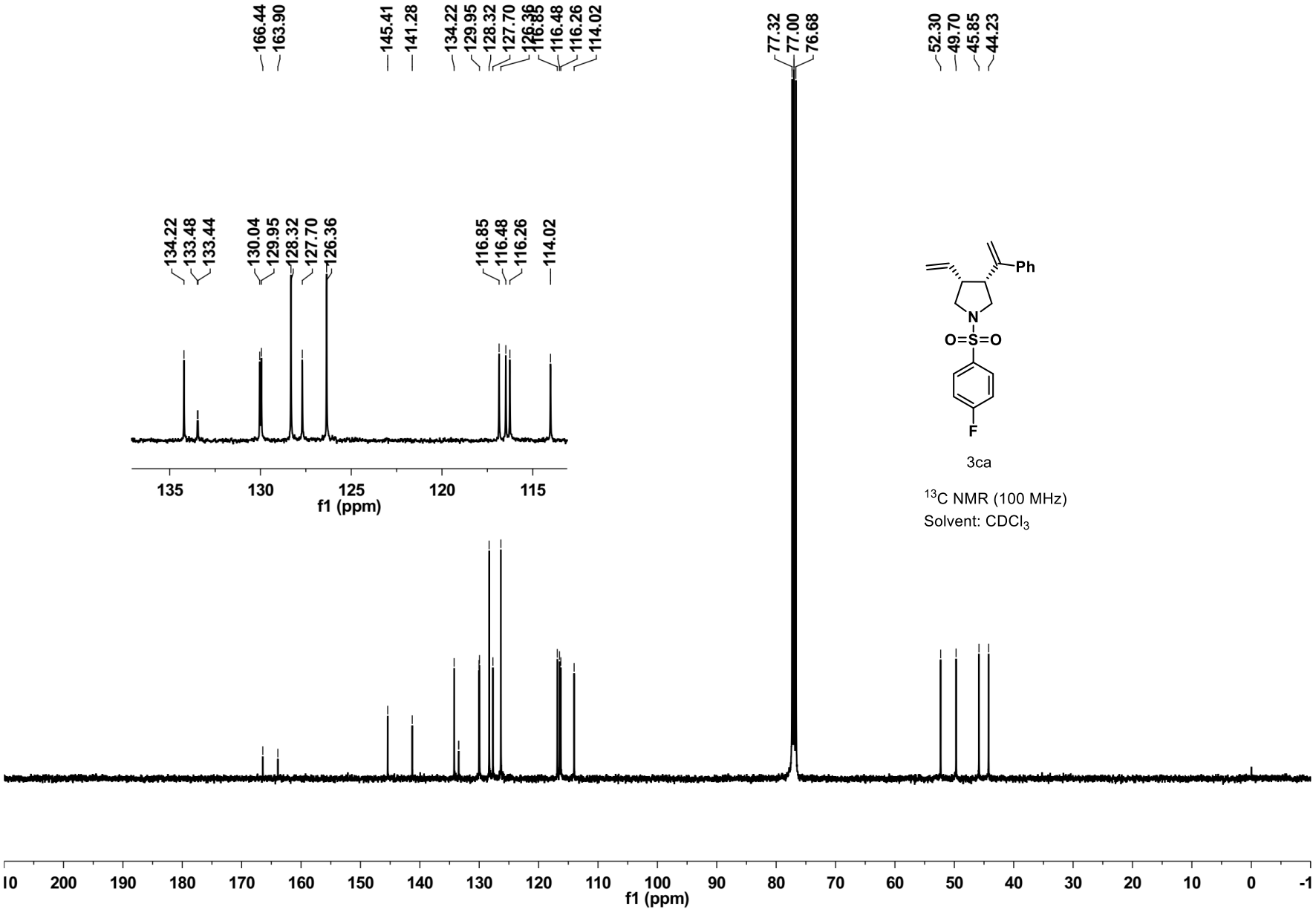

7.77
7.77
7.76
7.76
7.36
7.35
7.26
6.78
6.77
6.74
6.74
6.73
6.73
6.71
5.25
5.25
5.24
5.24
5.22
5.19
4.78
4.78
4.64
4.62
4.25
3.63
3.62
3.47
3.46
3.38
3.37
3.36
2.79
2.78
2.77
2.76
1.57
0.00
O
O
N
Ts
3al
1H NMR (600 MHz)
Solvent: CDCl3
2.03
2.00
3.07
1.00
1.01
1.00
1.03
1.00
4.00
1.02
1.03
2.03
1.03
1.03
3.07
f1 (ppm)

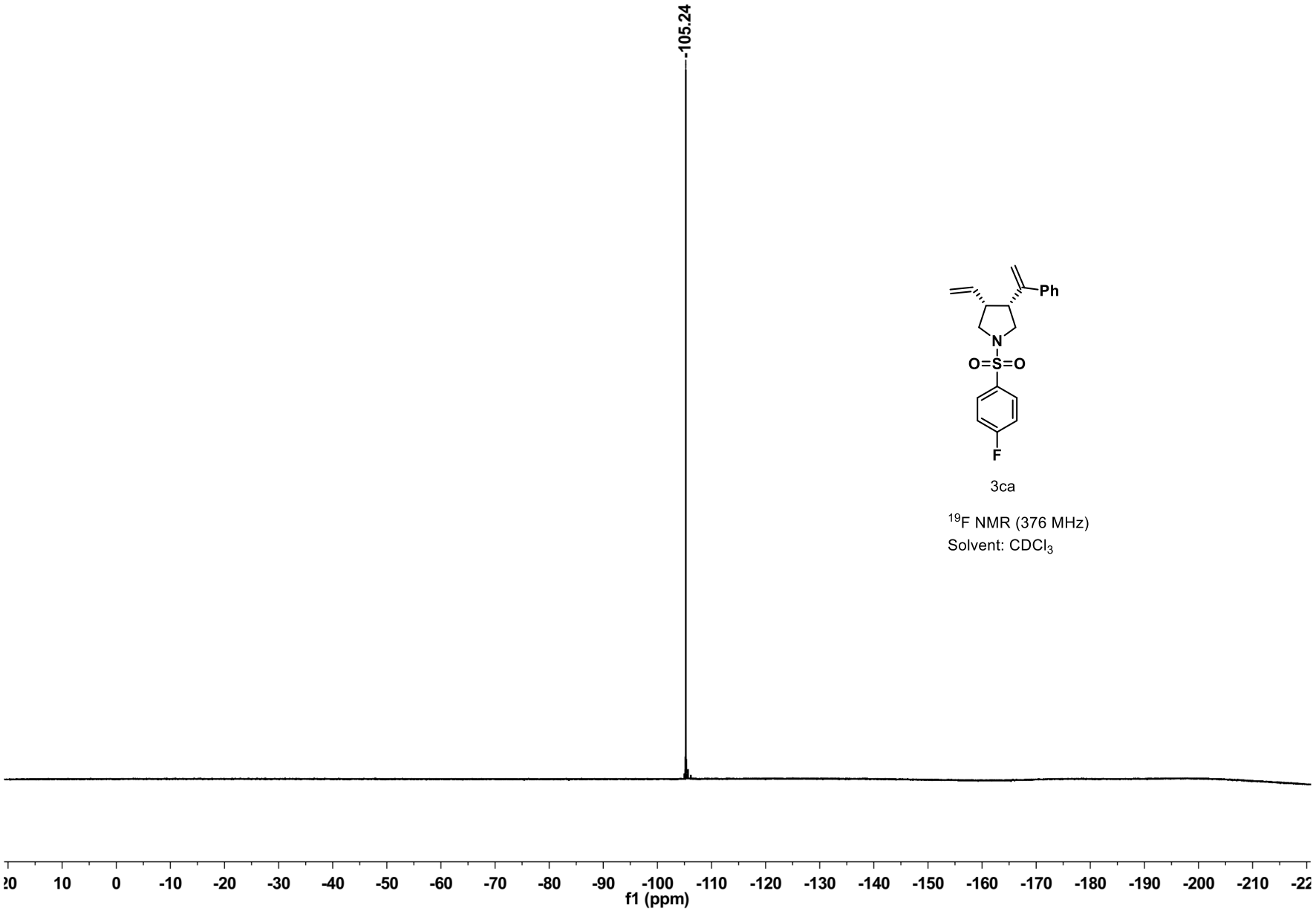

144.52
143.47
143.16
143.09
134.86
134.45
129.74
127.43
119.49
117.00
116.62
115.07
112.86
77.21
77.00
76.79
64.36
64.34
52.17
49.63
45.71
44.15
21.55
144.52
143.47
143.16
143.09
134.86
134.45
134.09
129.74
127.43
119.49
117.00
116.62
145
140
135
130
125
120
f1 (ppm)
O
O
N
Ts
3al
^{13}C NMR (150 MHz)
Solvent: $CDCl_3$
f1 (ppm)

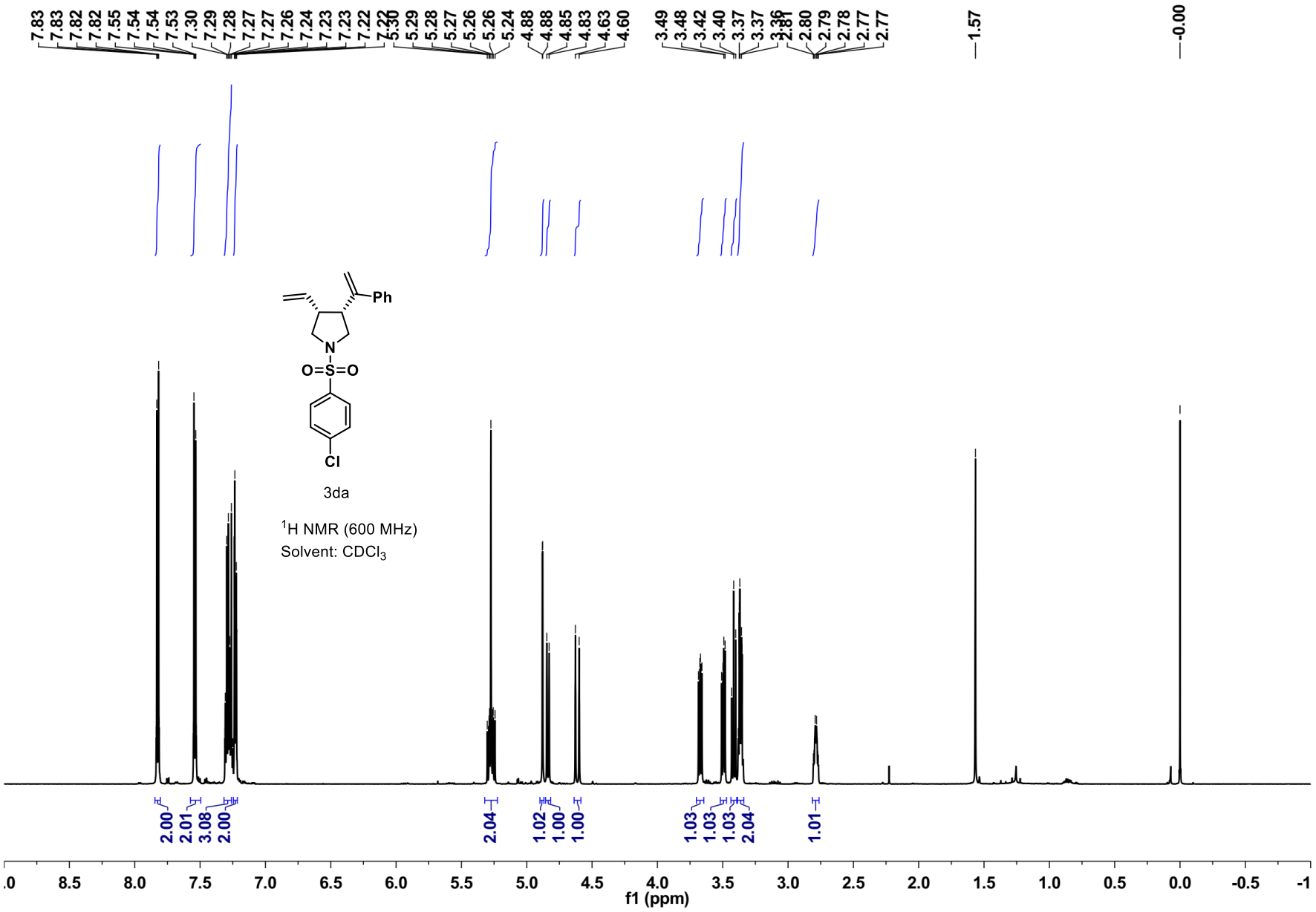

7.84 7.83 7.83 7.82 7.82 7.81 7.30 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.23 7.23 7.22 7.22 7.22 7.04 7.03 7.03 7.02 7.02 7.01 5.30 5.28 5.28 5.27 5.26 5.26 5.25 5.24 4.88 4.88 4.82 4.80 4.61 4.58 3.89 3.68 3.67 3.66 3.65 3.50 3.49 3.49 3.48 3.42 3.40 3.38 3.36 3.35 3.34 3.33 3.33 3.32 2.78 2.78 2.77 2.76 2.75 1.56 -0.00
Ph
N
O=S=O
OMe
3ba
1H NMR (600 MHz)
Solvent: CDCl3
1.99 3.03 2.02 2.02 2.03 1.01 1.00 1.00 3.08 1.01 1.03 1.01 2.06 1.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

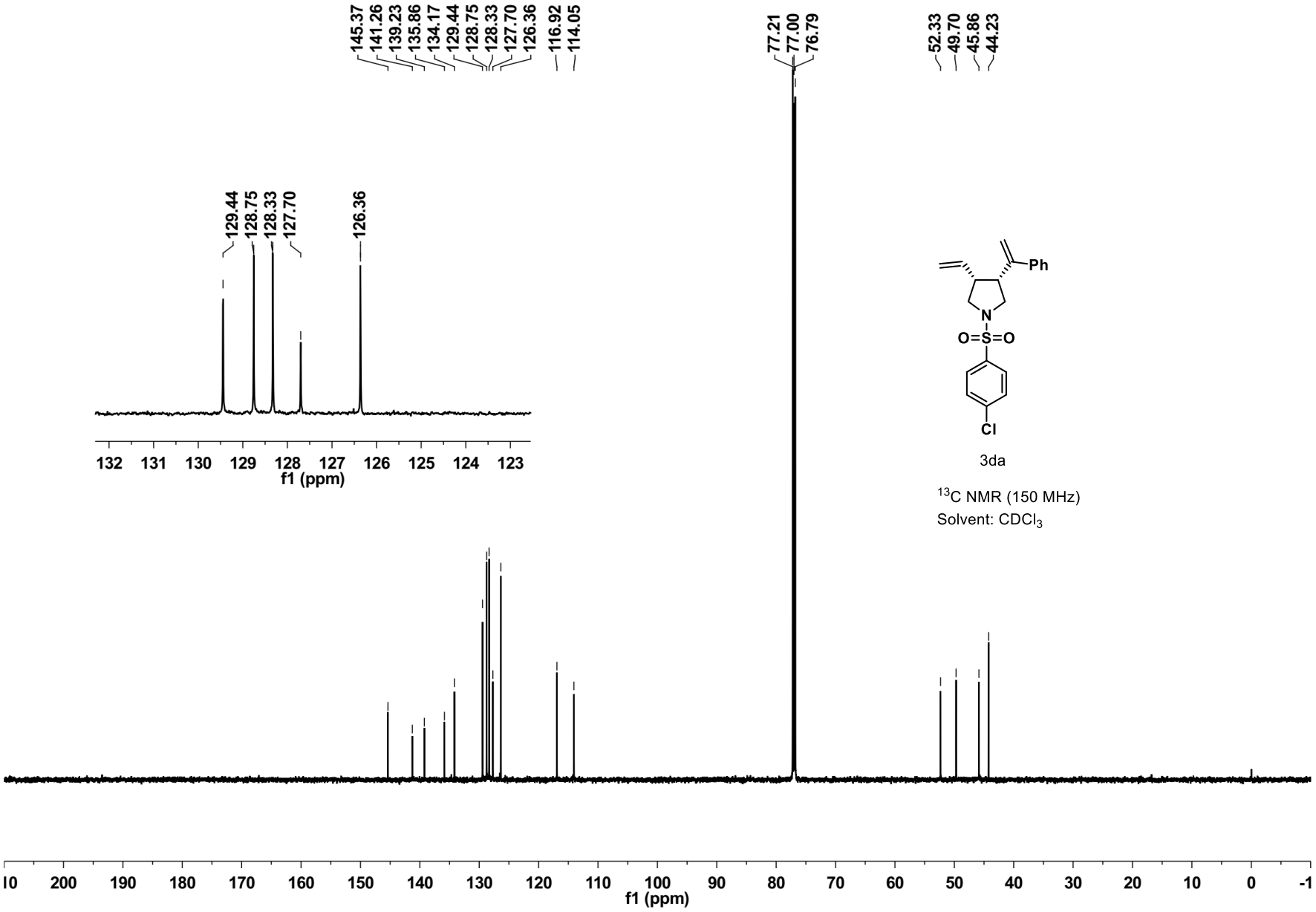

163.02
145.67
141.53
134.62
129.55
129.25
128.29
127.63
126.40
116.67
114.29
113.95
77.21
77.00
76.79
55.61
52.37
49.84
45.95
44.42
Ph
N
O=S=O
OMe
3ba
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)

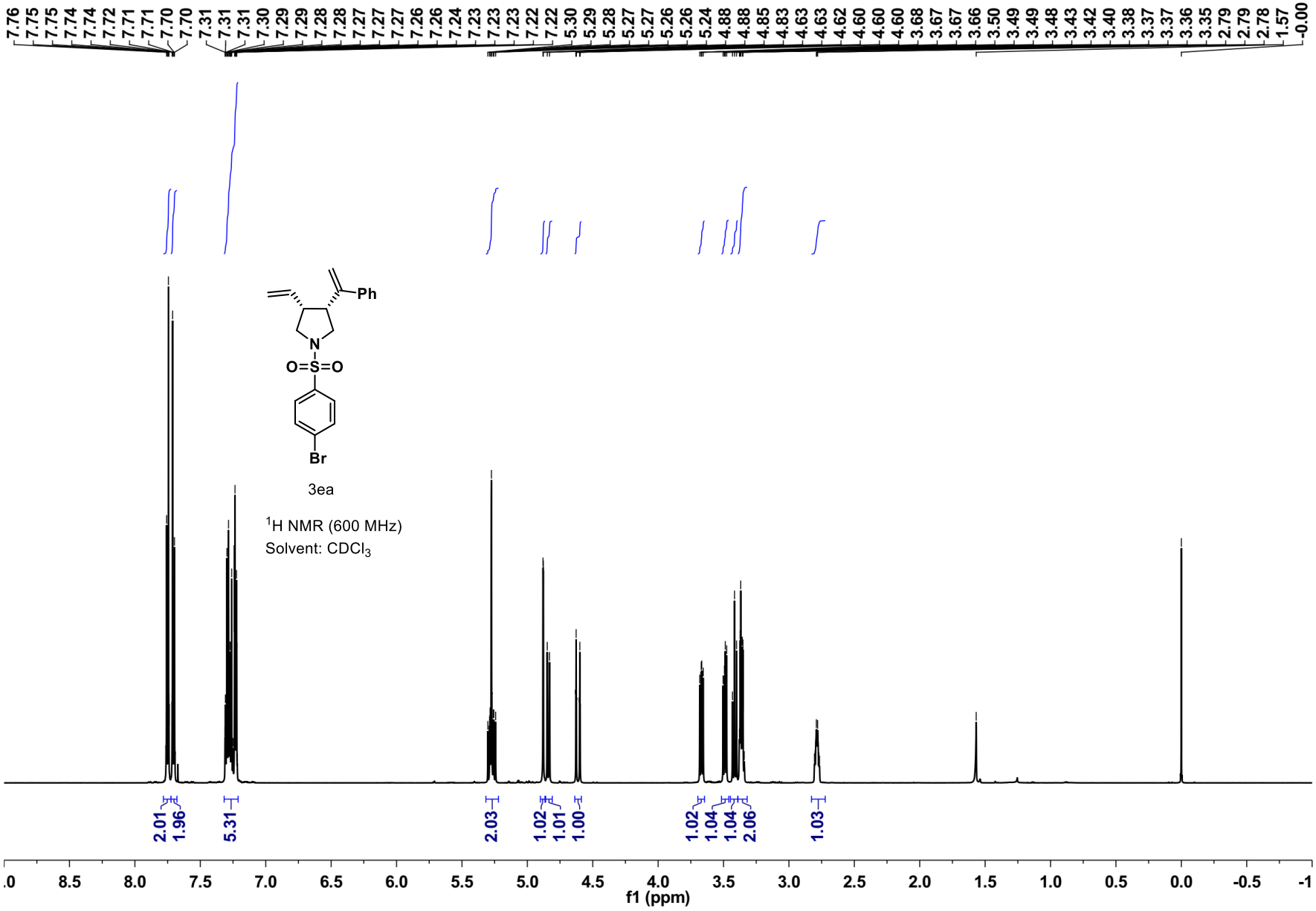

7.92
7.91
7.91
7.91
7.90
7.90
7.90
7.30
7.28
7.27
7.26
7.25
7.24
7.23
7.23
7.23
7.22
5.28
5.27
5.26
5.25
5.24
5.24
5.22
4.88
4.83
4.82
4.61
4.58
3.68
3.50
3.49
3.41
3.39
3.37
3.36
3.35
2.80
2.79
2.78
1.57
0.00
Ph
N
O=S=O
F
3ca
1H NMR (600 MHz)
Solvent: CDCl3
2.02
7.16
2.01
1.02
1.04
1.00
1.00
1.07
3.12
1.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

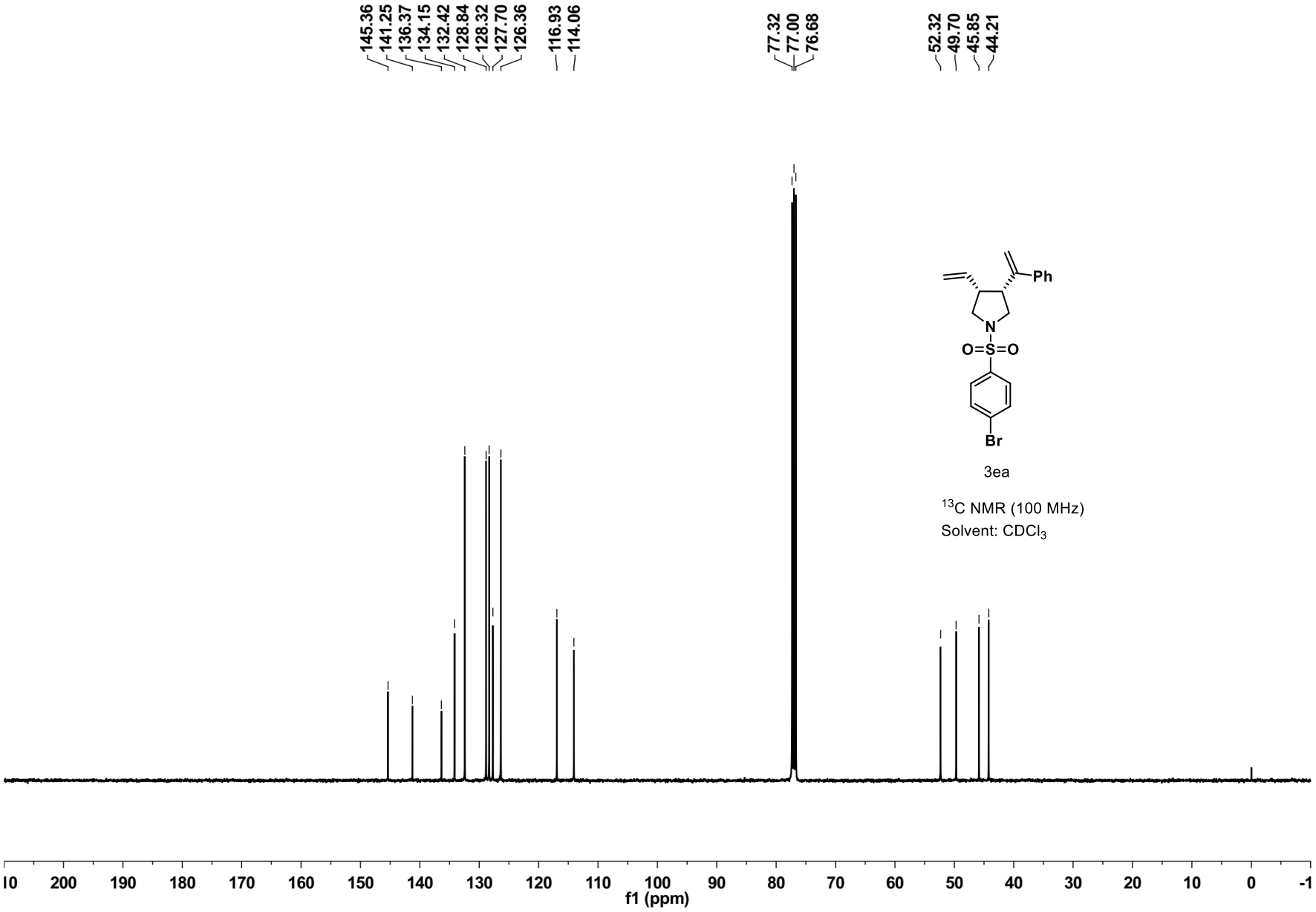

166.44
163.90
145.41
141.28
134.22
129.95
128.32
127.70
126.36
116.85
116.48
116.26
114.02
77.32
77.00
76.68
52.30
49.70
45.85
44.23
134.22
133.48
133.44
130.04
129.95
128.32
127.70
126.36
116.85
116.48
116.26
114.02
135
130
125
120
115
f1 (ppm)
Ph
N
O=S=O
F
3ca
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

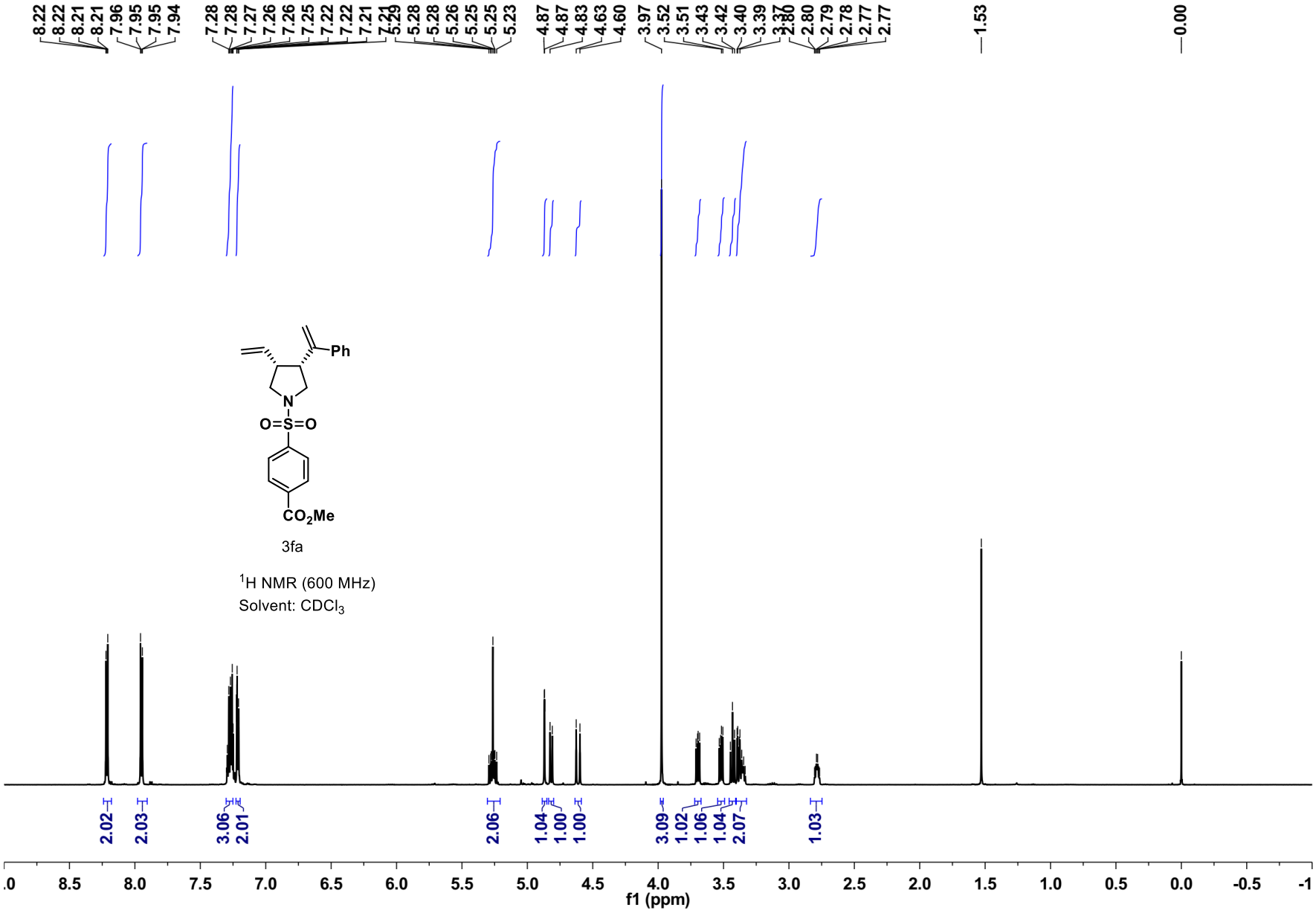

-105.24
Ph
N
O=S=O
F
3ca
^{19}F NMR (376 MHz)
Solvent: $CDCl_3$
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.83
7.83
7.82
7.82
7.55
7.54
7.54
7.53
7.30
7.29
7.28
7.27
7.27
7.26
7.24
7.23
7.23
7.22
7.22
5.30
5.29
5.28
5.27
5.26
5.26
5.24
4.88
4.88
4.85
4.83
4.63
4.60
3.49
3.48
3.42
3.40
3.37
3.37
3.36
2.81
2.80
2.79
2.78
2.77
2.77
1.57
-0.00
Ph
N
O=S=O
Cl
3da
1H NMR (600 MHz)
Solvent: CDCl3
2.00
2.01
3.08
2.00
2.04
1.02
1.00
1.00
1.03
1.03
1.03
2.04
1.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


145.37
141.26
139.23
135.86
134.17
129.44
128.75
128.33
127.70
126.36
116.92
114.05
77.21
77.00
76.79
52.33
49.70
45.86
44.23
129.44
128.75
128.33
127.70
126.36
132 131 130 129 128 127 126 125 124 123
f1 (ppm)
Ph
N
O=S=O
Cl
3da
13C NMR (150 MHz)
Solvent: CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Ph
N
O=S=O
Br
3ea
1H NMR (600 MHz)
Solvent: CDCl3
f1 (ppm)


145.36
141.25
136.37
134.15
132.42
128.84
128.32
127.70
126.36
116.93
114.06
77.32
77.00
76.68
52.32
49.70
45.85
44.21
Ph
N
O=S=O
Br
3ea
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


8.22
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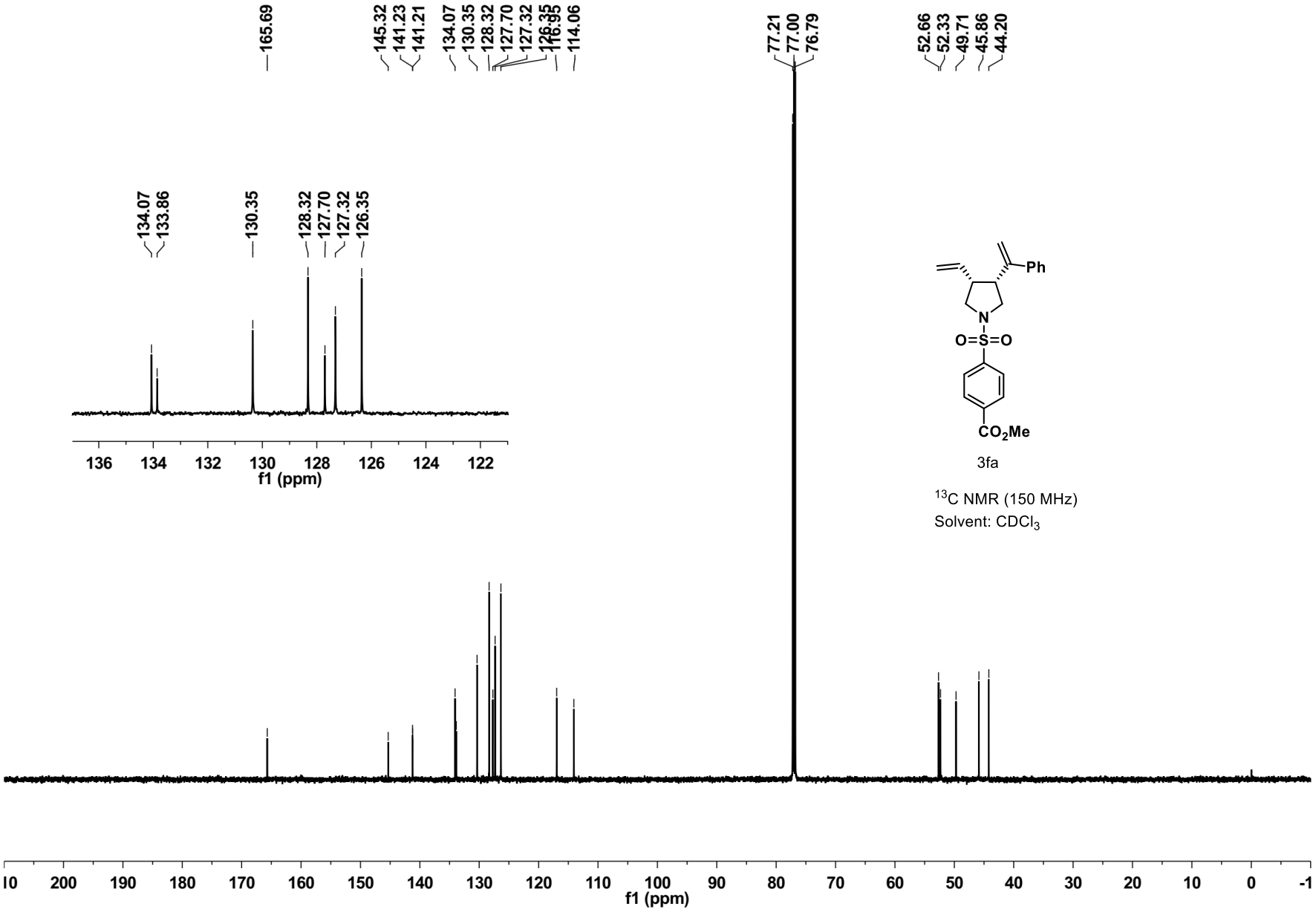
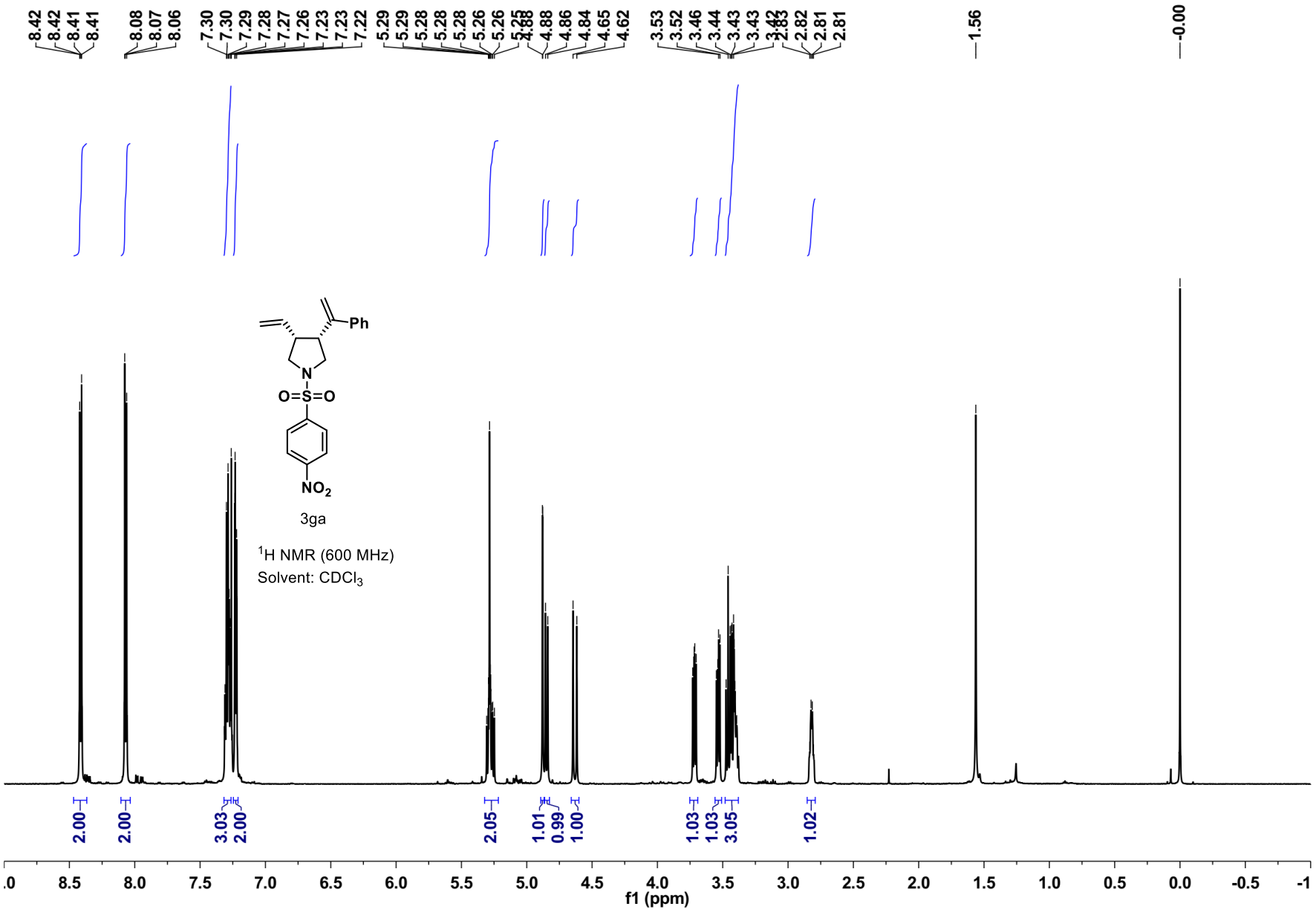
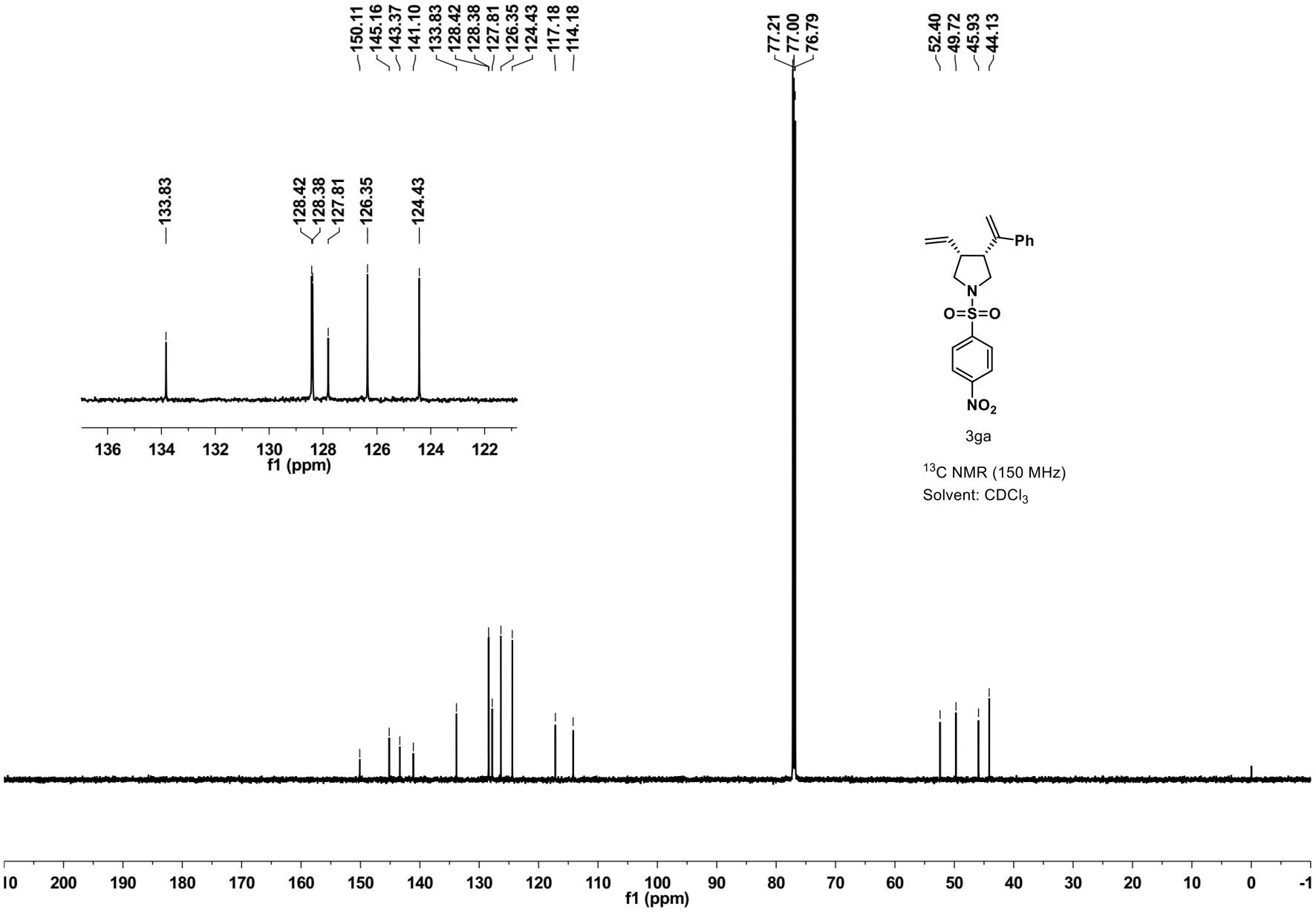
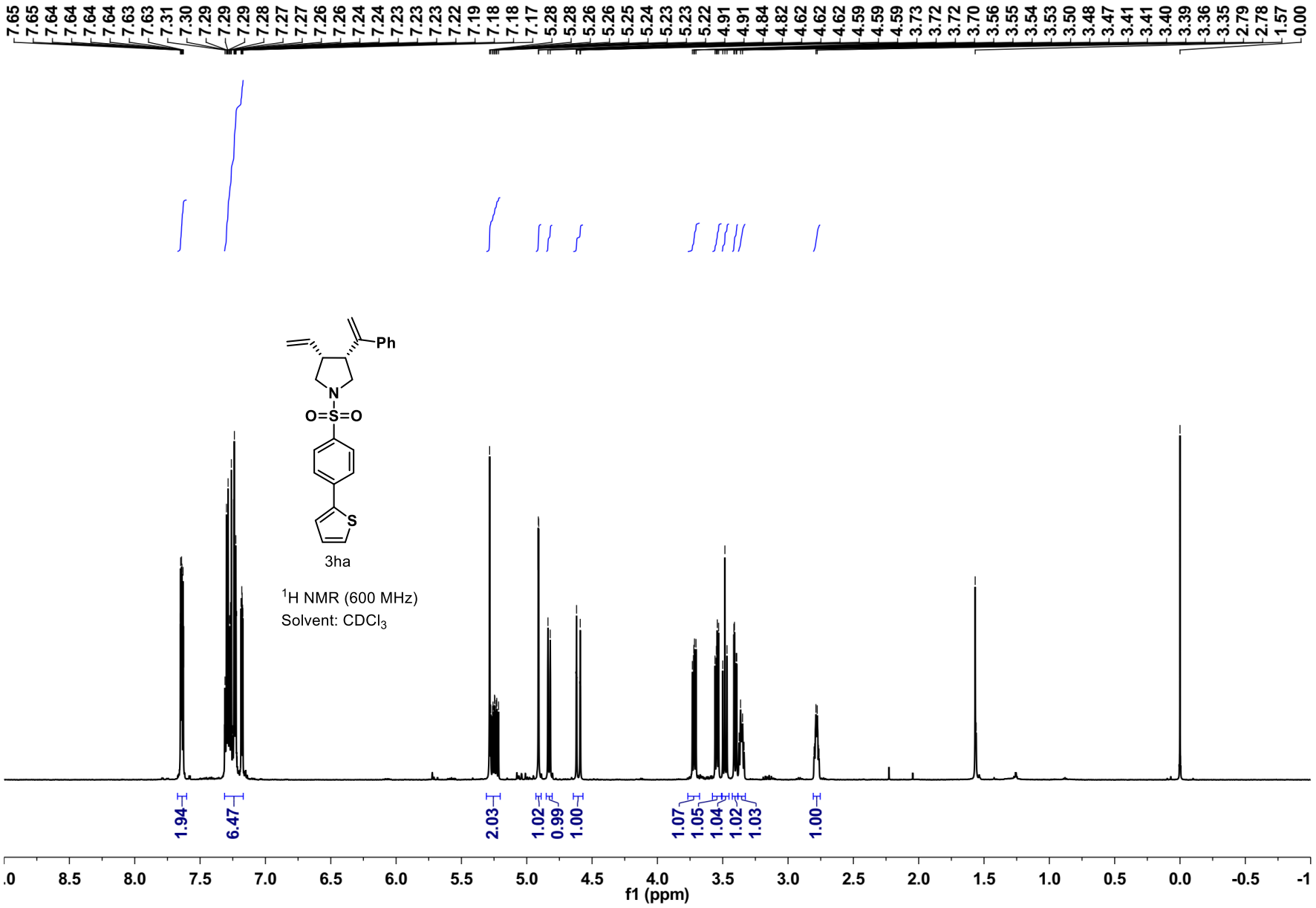
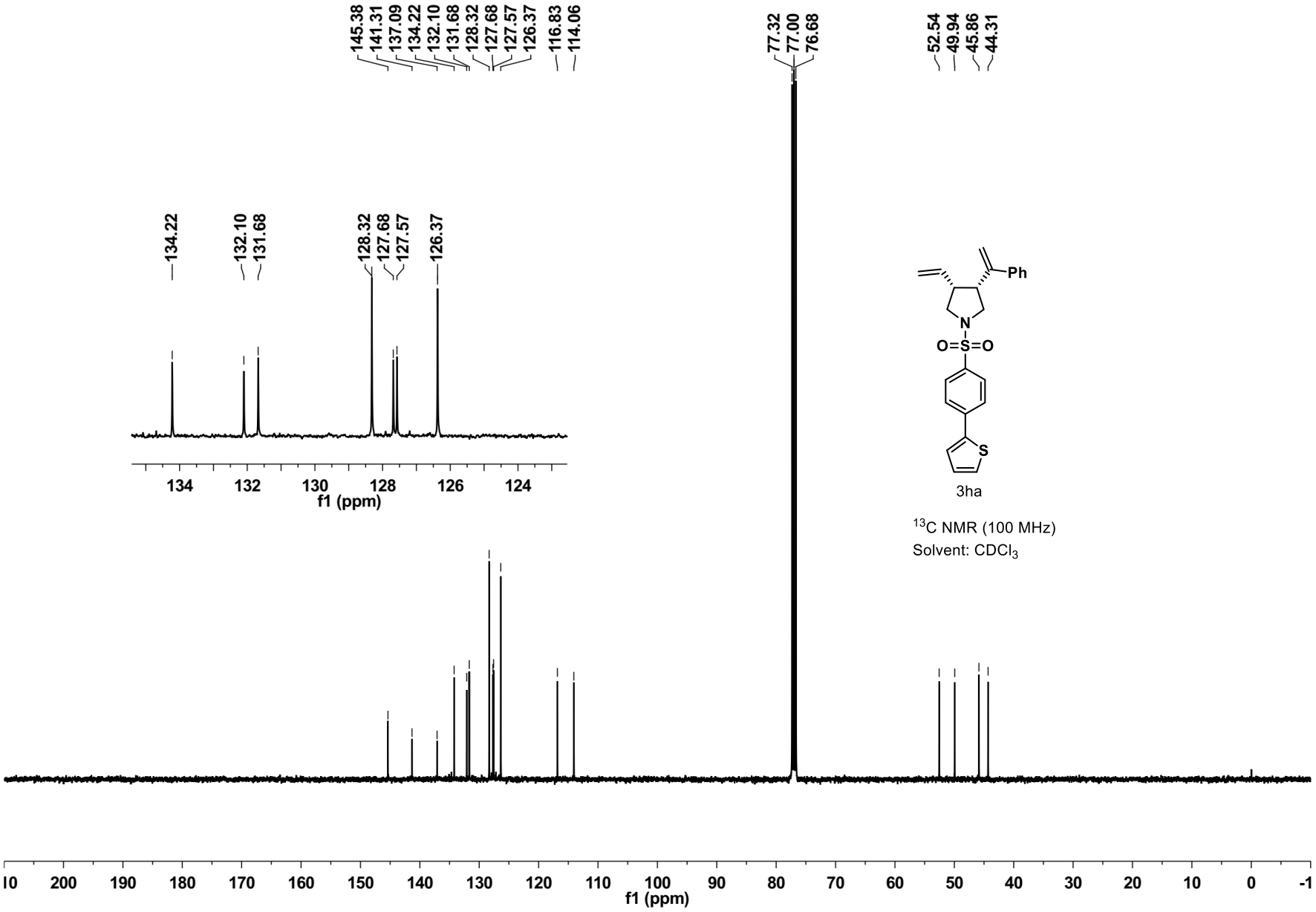
8.21
8.21
7.96
7.95
7.95
7.94
7.28
7.28
7.27
7.26
7.26
7.25
7.22
7.22
7.21
7.21
5.29
5.28
5.28
5.26
5.25
5.25
5.23
4.87
4.87
4.83
4.63
4.60
3.97
3.52
3.51
3.43
3.42
3.40
3.39
3.37
2.80
2.80
2.79
2.78
2.77
2.77
1.53
0.00
Ph
N
O=S=O
CO2Me
3fa
1H NMR (600 MHz)
Solvent: CDCl3
2.02
2.03
3.06
2.01
2.06
1.04
1.00
1.00
3.09
1.02
1.06
1.04
2.07
1.03
f1 (ppm)

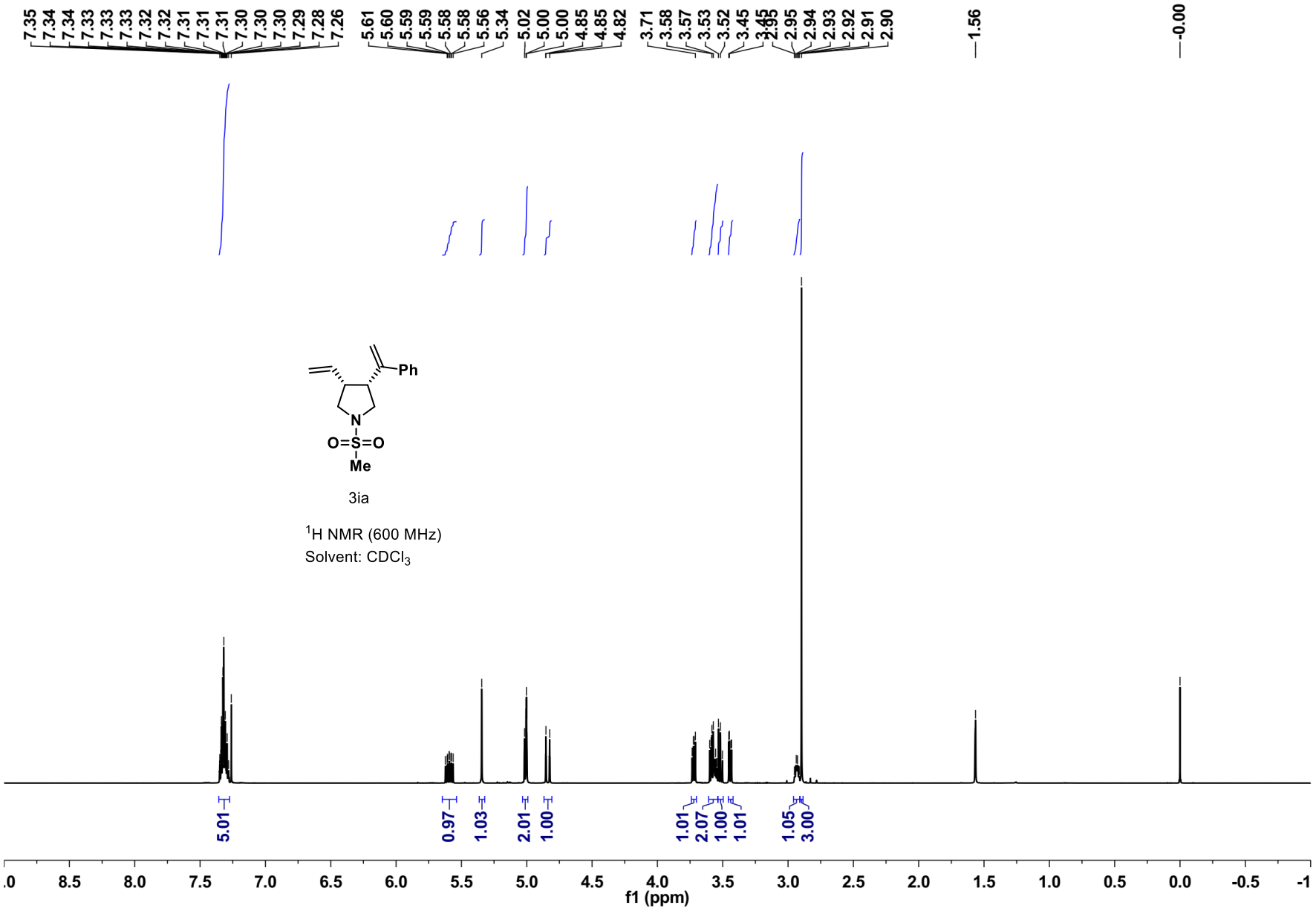

165.69
145.32
141.23
141.21
134.07
130.35
128.32
127.70
127.32
126.35
116.95
114.06
77.21
77.00
76.79
52.66
52.33
49.71
45.86
44.20
134.07
133.86
130.35
128.32
127.70
127.32
126.35
136
134
132
130
128
126
124
122
f1 (ppm)
Ph
N
O=S=O
CO2Me
3fa
13C NMR (150 MHz)
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

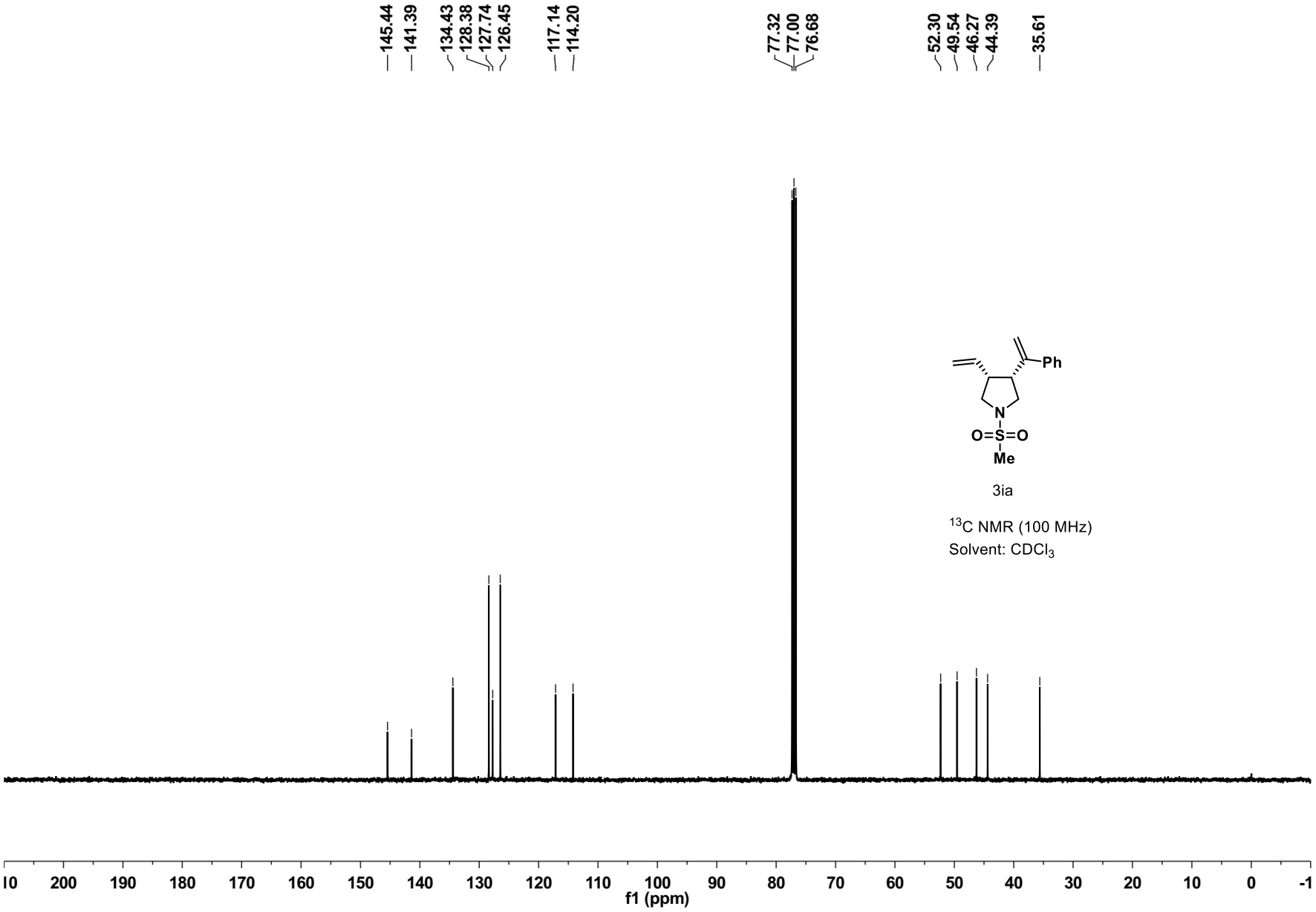

8.42
8.42
8.41
8.41
8.08
8.07
8.06
7.30
7.30
7.29
7.28
7.27
7.26
7.23
7.23
7.22
5.29
5.29
5.28
5.28
5.28
5.26
5.26
5.25
4.88
4.88
4.86
4.84
4.65
4.62
3.53
3.52
3.46
3.44
3.43
3.43
3.42
2.83
2.82
2.81
2.81
1.56
-0.00
Ph
N
O=S=O
NO2
3ga
1H NMR (600 MHz)
Solvent: CDCl3
2.00
2.00
3.03
2.00
2.05
1.01
0.99
1.00
1.03
1.03
3.05
1.02
f1 (ppm)

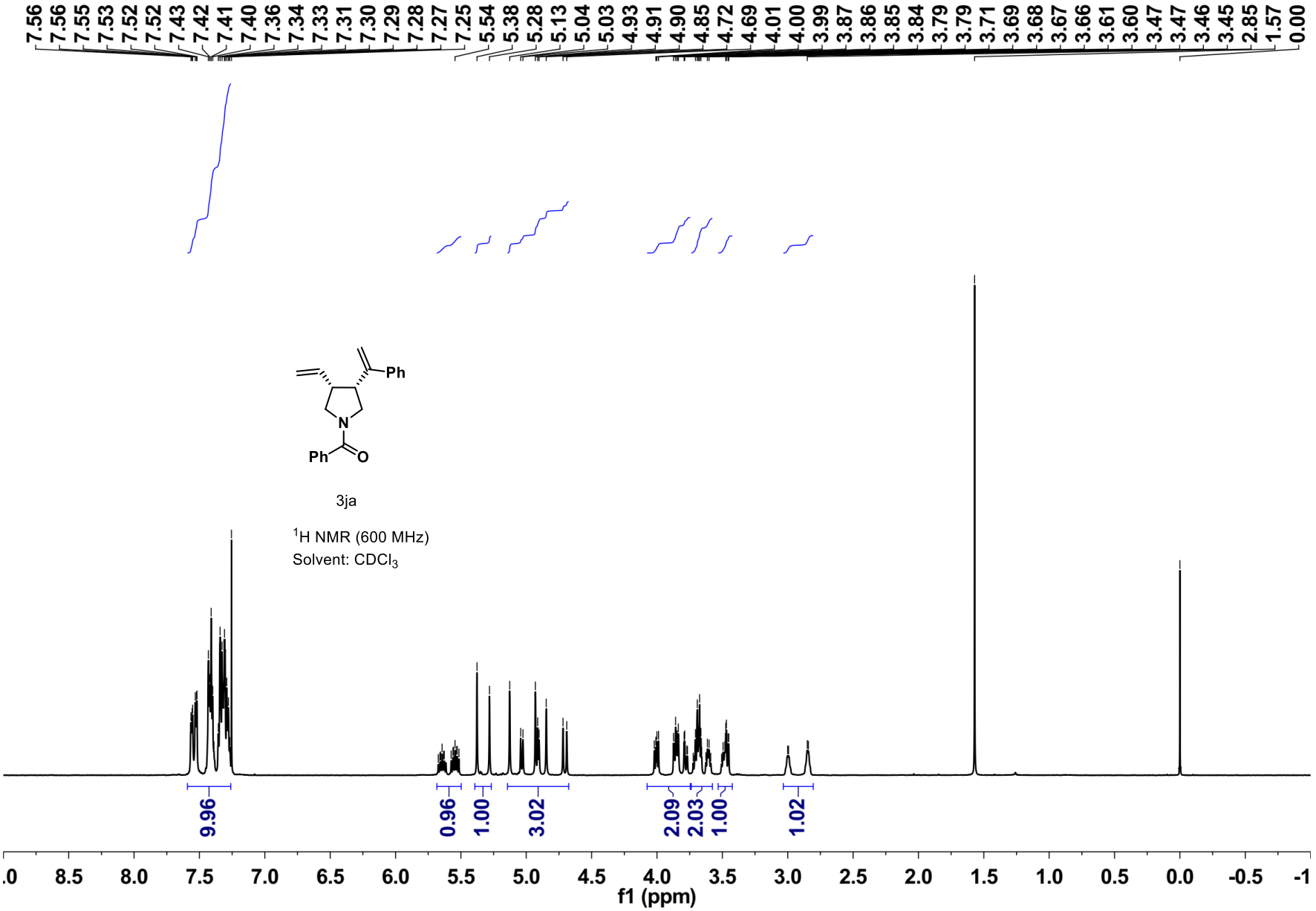

150.11
145.16
143.37
141.10
133.83
128.42
128.38
127.81
126.35
124.43
117.18
114.18
77.21
77.00
76.79
52.40
49.72
45.93
44.13
f1 (ppm)
Ph
N
O=S=O
NO2
3ga
13C NMR (150 MHz)
Solvent: CDCl3

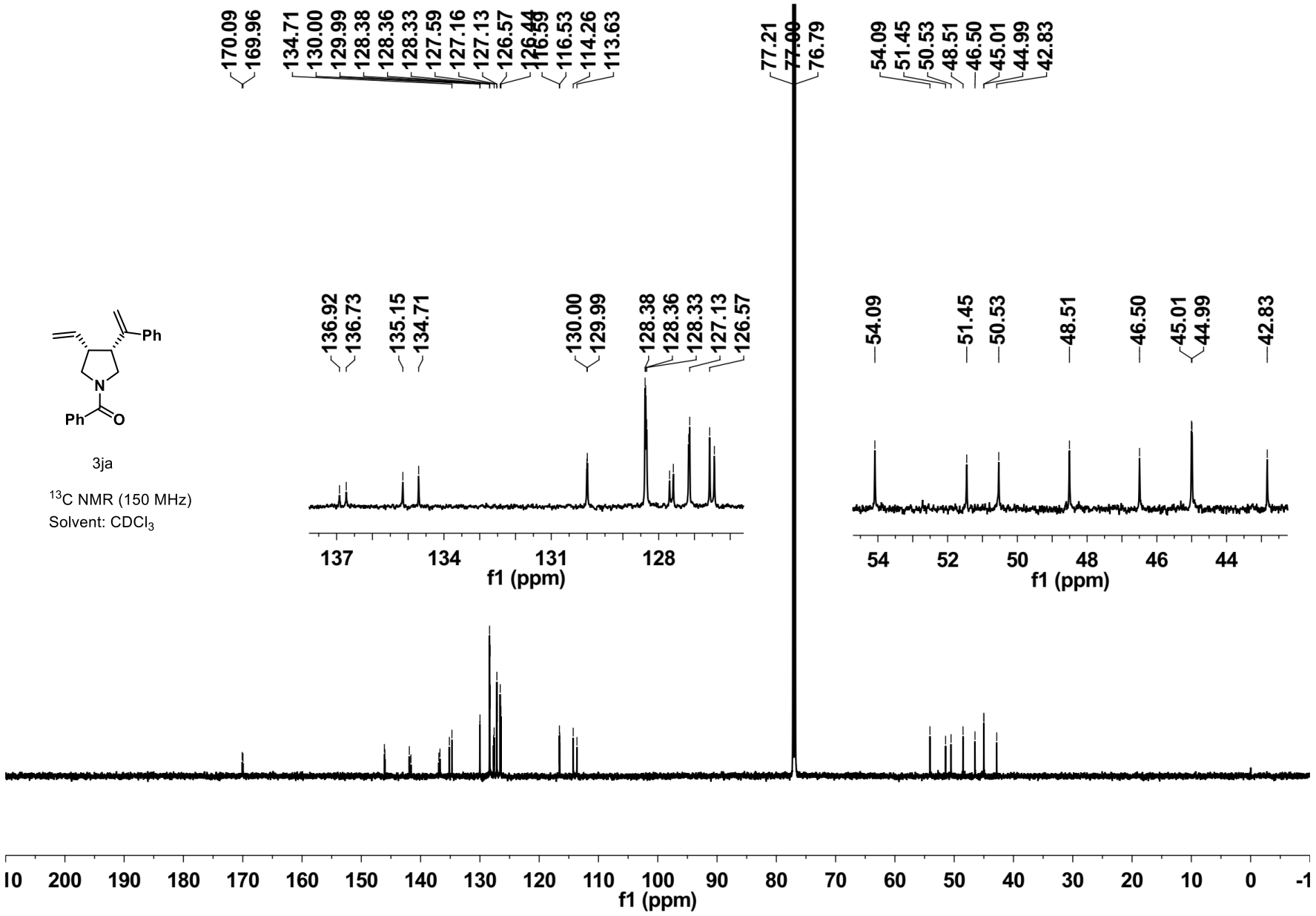

7.65 7.65 7.64 7.64 7.64 7.64 7.63 7.63 7.31 7.30 7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.24 7.24 7.23 7.23 7.23 7.22 7.19 7.18 7.18 7.17 5.28 5.28 5.26 5.26 5.25 5.24 5.23 5.23 5.22 4.91 4.91 4.84 4.82 4.62 4.62 4.62 4.59 4.59 4.59 3.73 3.72 3.72 3.70 3.56 3.55 3.54 3.53 3.50 3.48 3.47 3.41 3.41 3.40 3.39 3.36 3.35 2.79 2.78 1.57 0.00
Ph
N
O=S=O
S
3ha
1H NMR (600 MHz)
Solvent: CDCl3
1.94 6.47 2.03 1.02 0.99 1.00 1.07 1.05 1.04 1.02 1.03 1.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

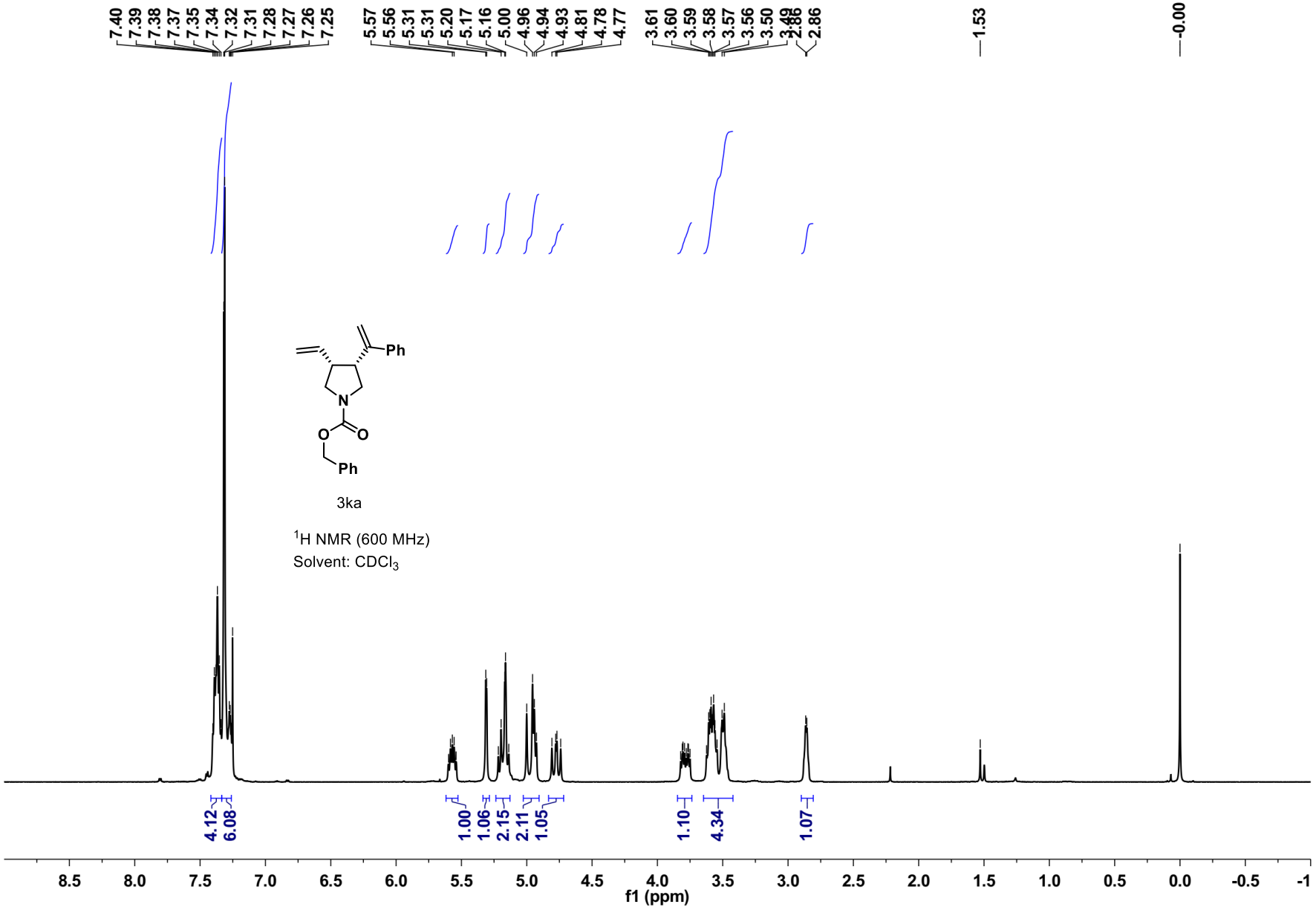

145.38
141.31
137.09
134.22
132.10
131.68
128.32
127.68
127.57
126.37
116.83
114.06
77.32
77.00
76.68
52.54
49.94
45.86
44.31
134.22
132.10
131.68
128.32
127.68
127.57
126.37
134
132
130
128
126
124
f1 (ppm)
Ph
N
O=S=O
S
3ha
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

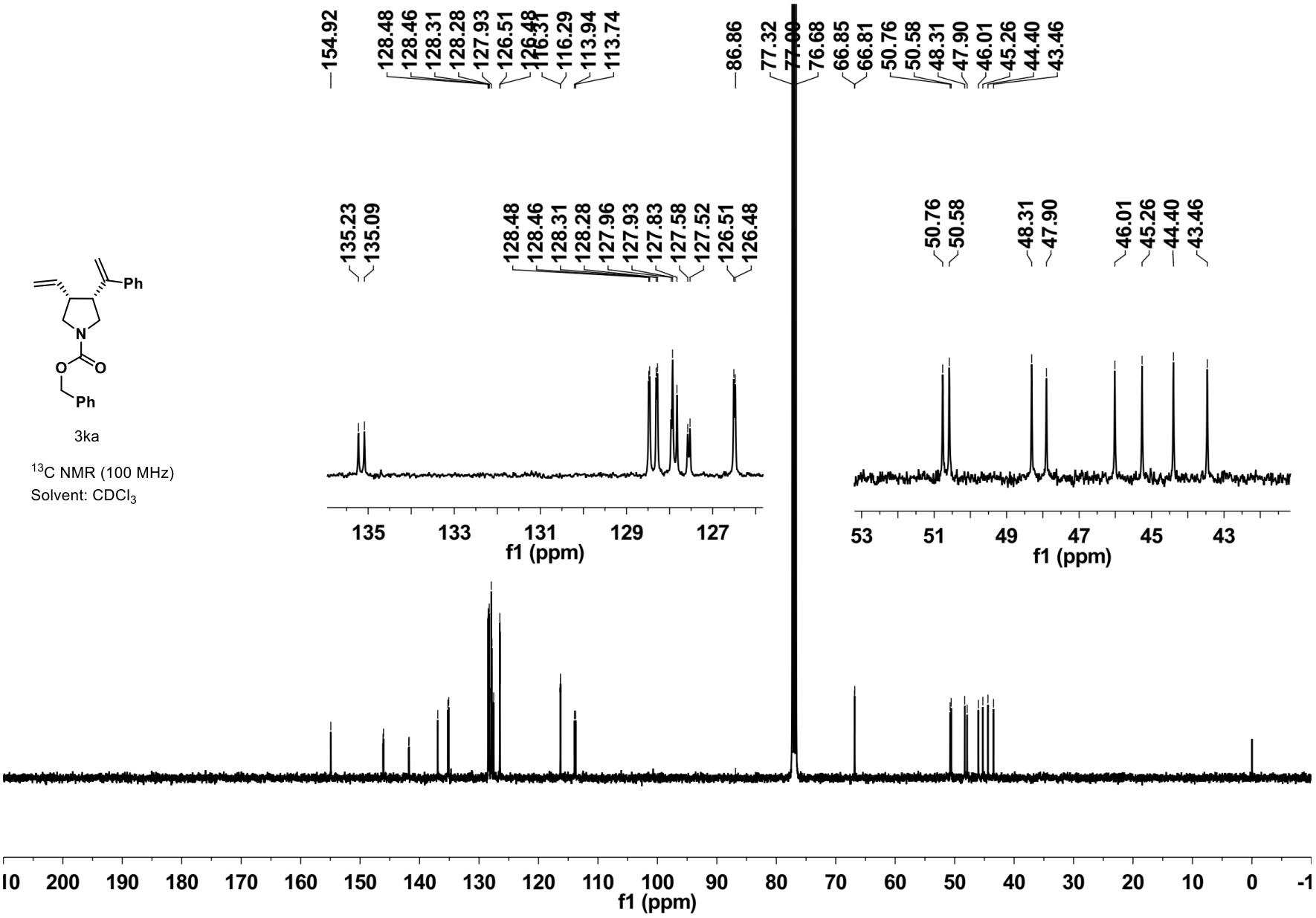

7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.26
5.61 5.60 5.59 5.59 5.58 5.58 5.56 5.34
5.02 5.00 5.00 4.85 4.85 4.82
3.71 3.58 3.57 3.53 3.52 3.45 2.95 2.95 2.94 2.93 2.92 2.91 2.90
1.56
-0.00
Ph
N
O=S=O
Me
3ia
1H NMR (600 MHz)
Solvent: CDCl3
5.01
0.97
1.03
2.01
1.00
1.01
2.07
1.00
1.01
1.05
3.00
f1 (ppm)

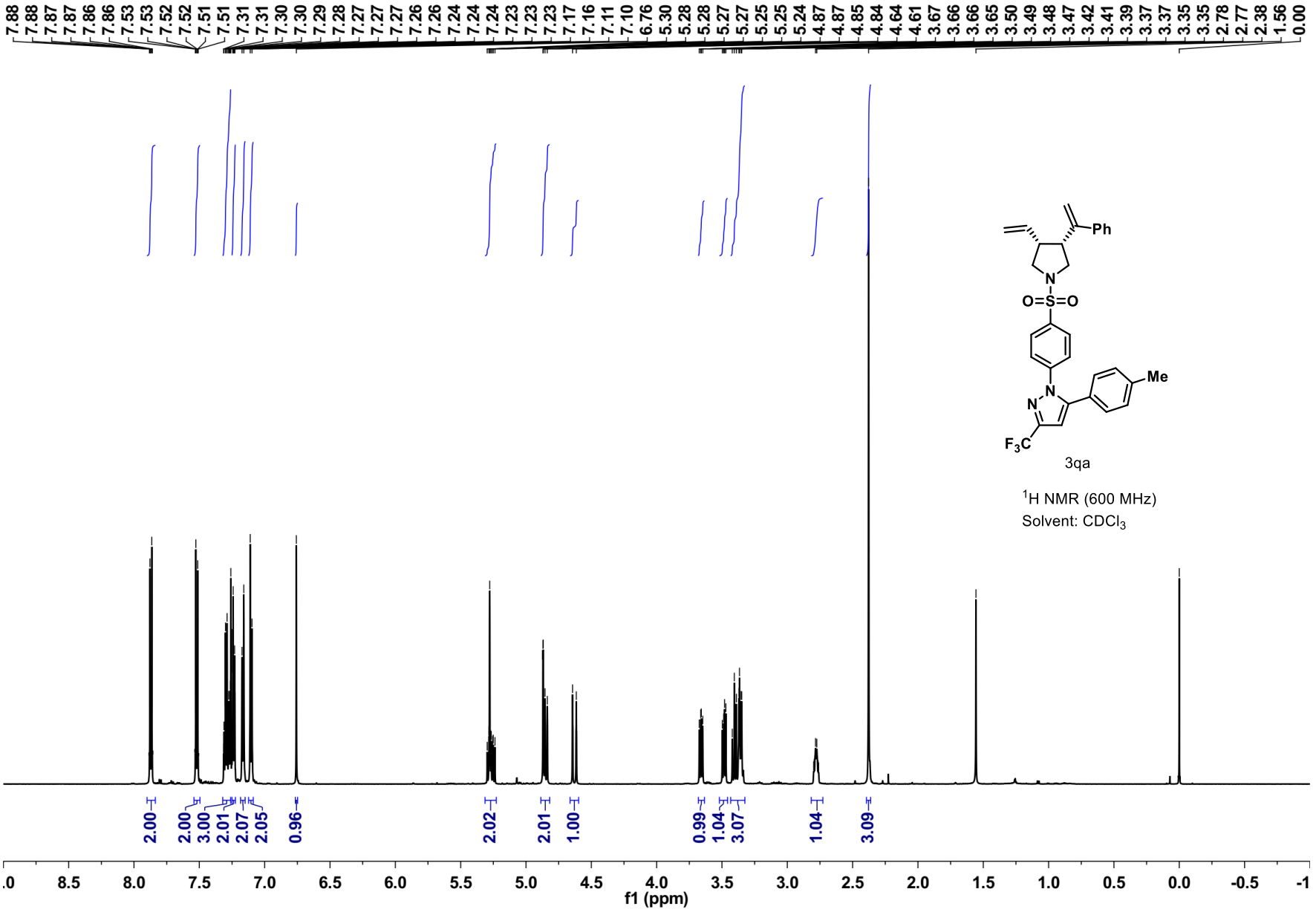

145.44
141.39
134.43
128.38
127.74
126.45
117.14
114.20
77.32
77.00
76.68
52.30
49.54
46.27
44.39
35.61
Ph
N
O=S=O
Me
3ia
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

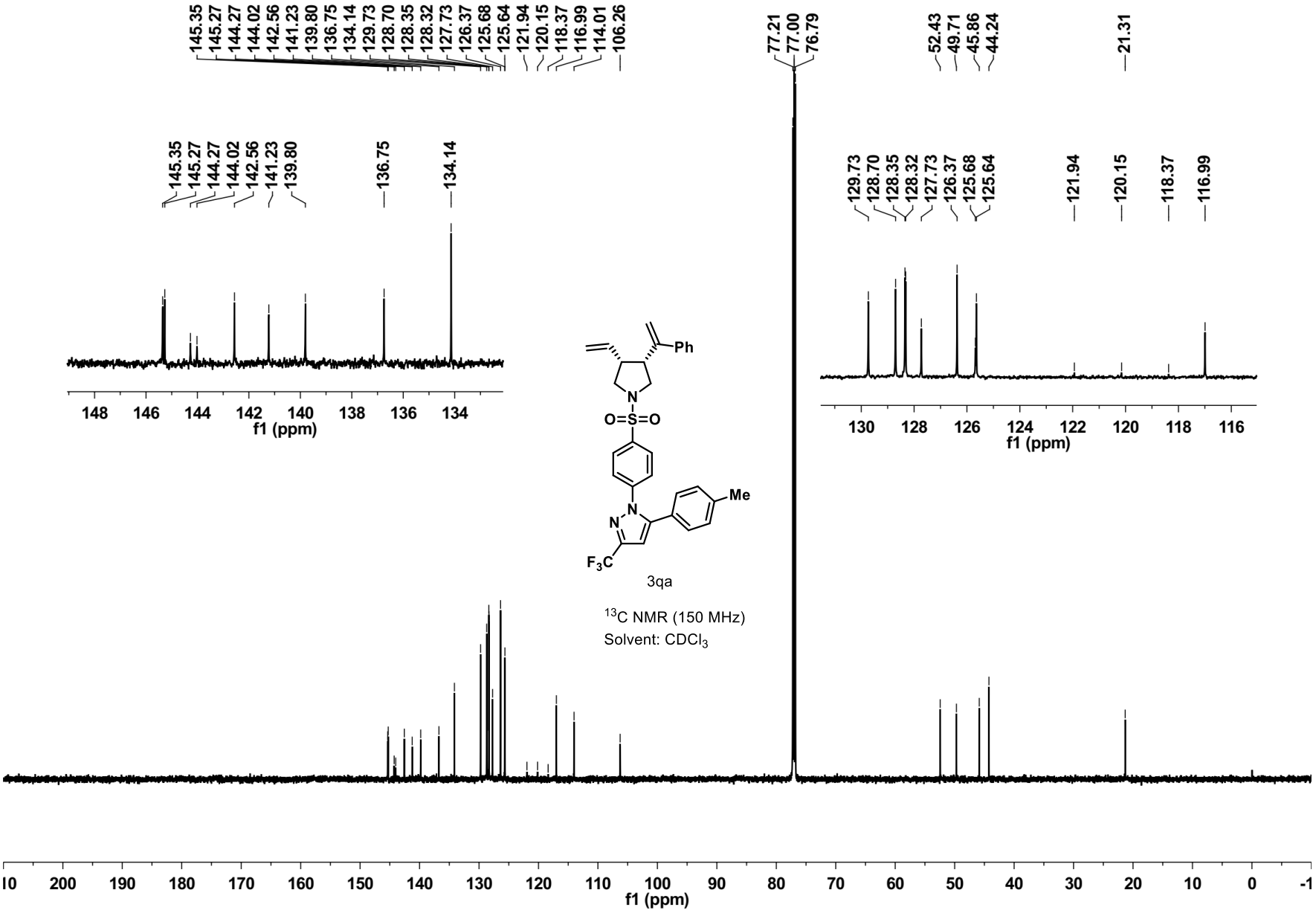

7.56 7.56 7.55 7.53 7.52 7.52 7.43 7.42 7.41 7.40 7.36 7.34 7.33 7.31 7.30 7.29 7.28 7.27 7.25 5.54 5.38 5.28 5.13 5.04 5.03 4.93 4.91 4.90 4.85 4.72 4.69 4.01 4.00 3.99 3.87 3.86 3.85 3.84 3.79 3.79 3.71 3.69 3.68 3.67 3.66 3.61 3.60 3.47 3.47 3.46 3.45 2.85 1.57 0.00
Ph
N
Ph
O
3ja
1H NMR (600 MHz)
Solvent: CDCl3
9.96
0.96
1.00
3.02
2.09
2.03
1.00
1.02
f1 (ppm)

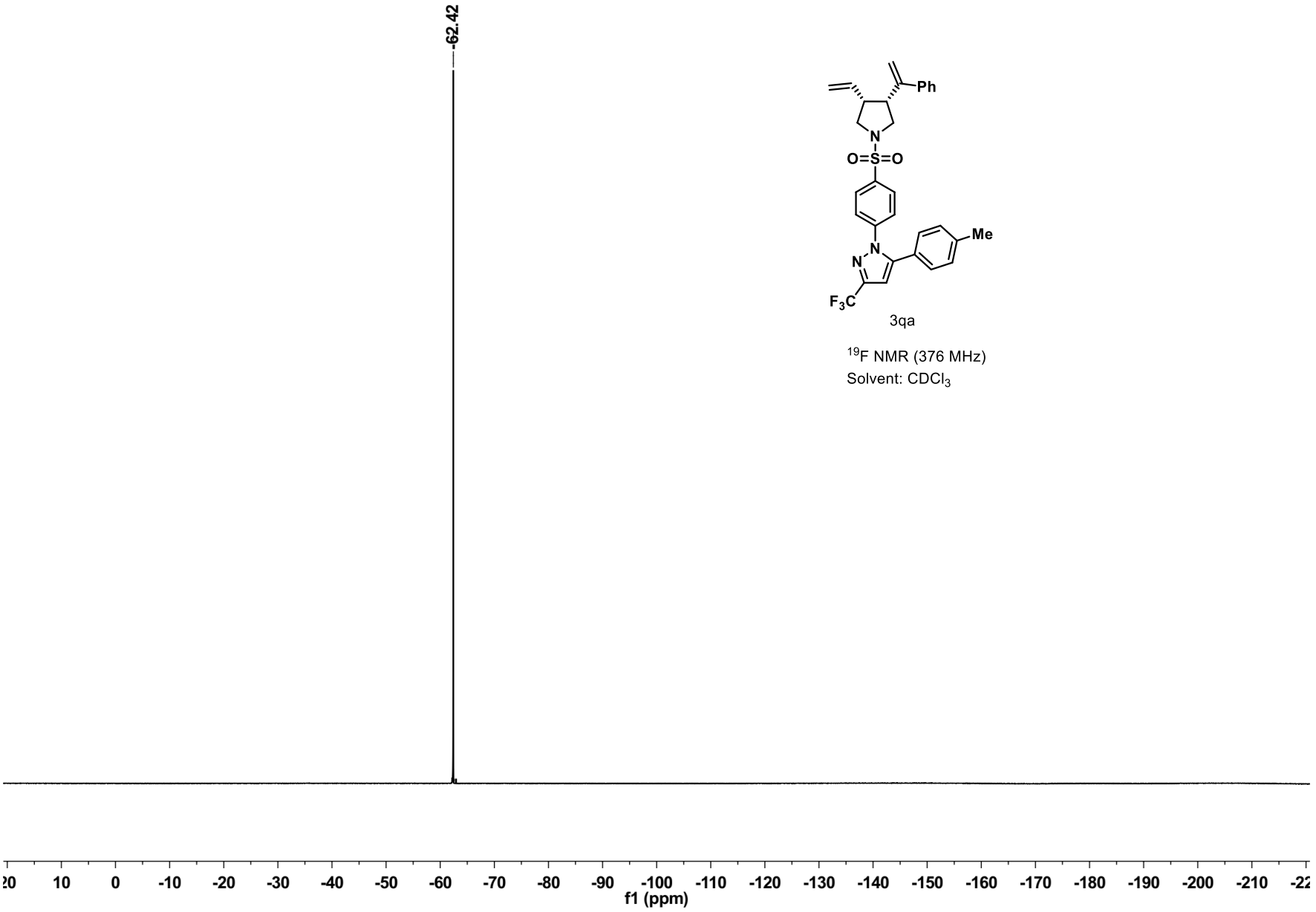

170.09
169.96
134.71
130.00
129.99
128.38
128.36
128.33
127.59
127.16
127.13
126.57
116.53
114.26
113.63
77.21
76.79
54.09
51.45
50.53
48.51
46.50
45.01
44.99
42.83
Ph
N
Ph
O
3ja
13C NMR (150 MHz)
Solvent: CDCl3
136.92
136.73
135.15
134.71
130.00
129.99
128.38
128.36
128.33
127.13
126.57
137
134
131
128
f1 (ppm)
54.09
51.45
50.53
48.51
46.50
45.01
44.99
42.83
54
52
50
48
46
44
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

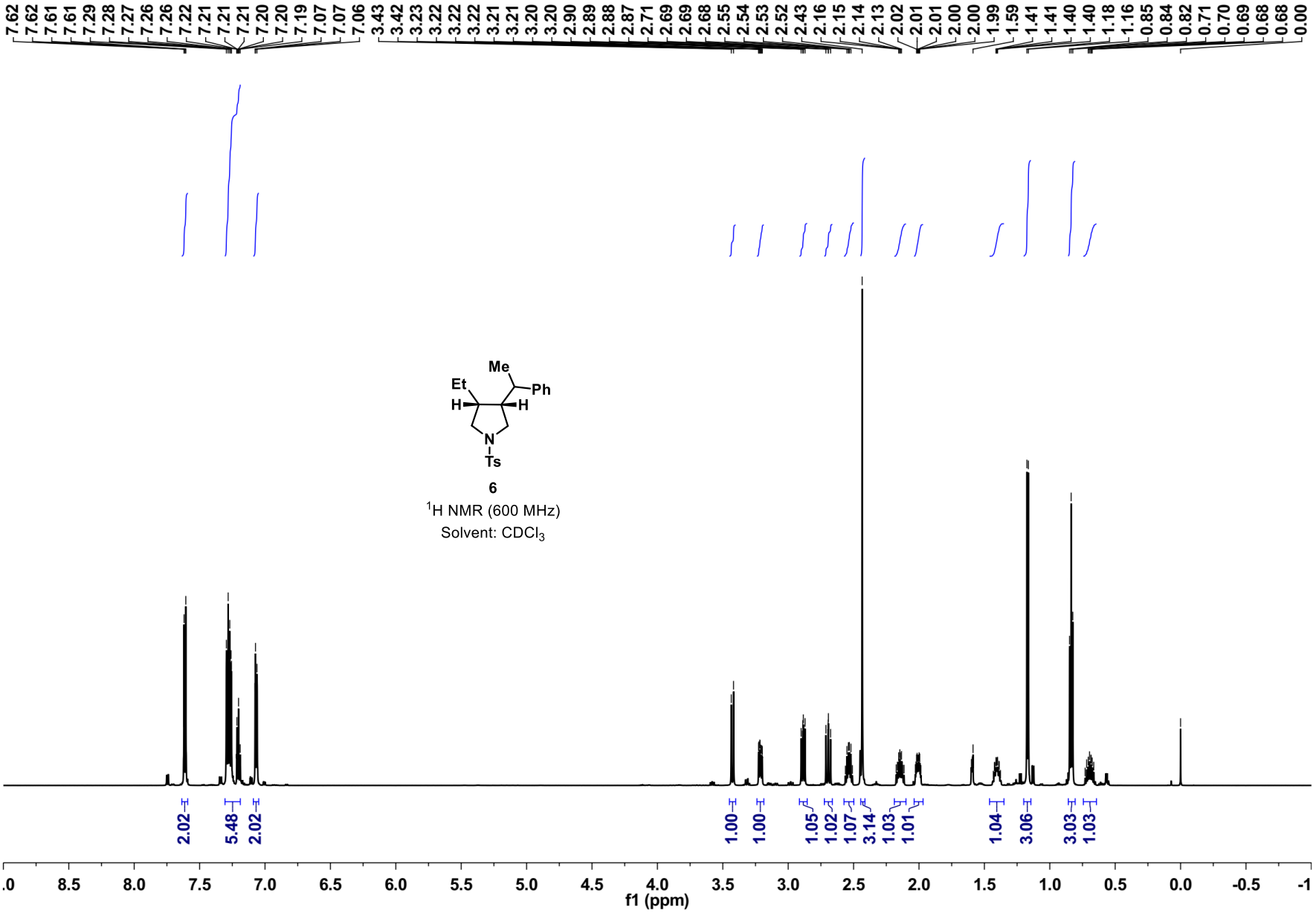

7.40
7.39
7.38
7.37
7.35
7.34
7.32
7.31
7.28
7.27
7.26
7.25
5.57
5.56
5.31
5.31
5.20
5.17
5.16
5.00
4.96
4.94
4.93
4.81
4.78
4.77
3.61
3.60
3.59
3.58
3.57
3.56
3.50
2.86
1.53
0.00
Ph
N
O
O
Ph
3ka
1H NMR (600 MHz)
Solvent: CDCl3
4.12
6.08
1.00
1.06
2.15
2.11
1.05
1.10
4.34
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

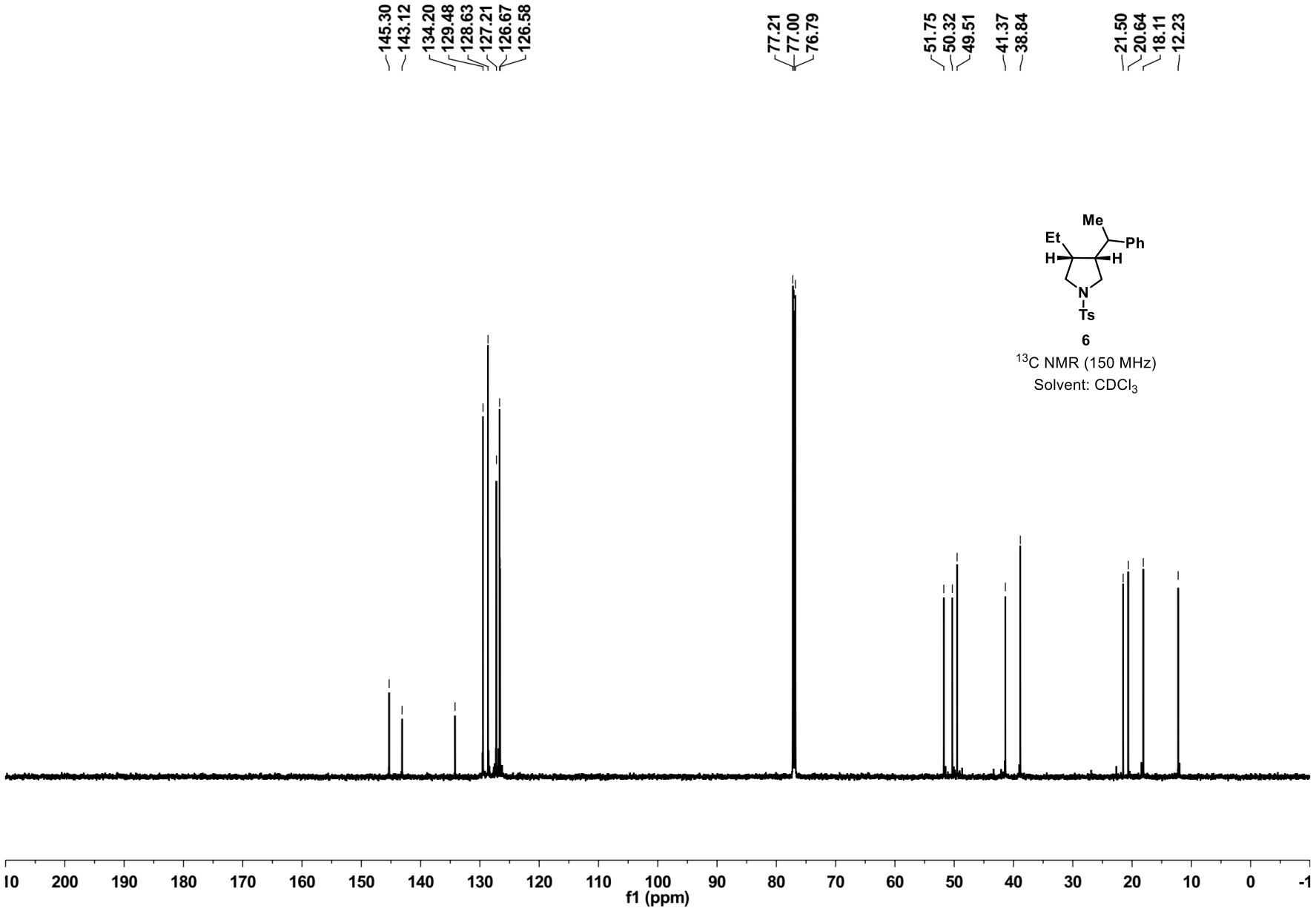

154.92
128.48
128.46
128.31
128.28
127.93
126.51
126.48
116.31
116.29
113.94
113.74
86.86
77.32
77.00
76.68
66.85
66.81
50.76
50.58
48.31
47.90
46.01
45.26
44.40
43.46
135.23
135.09
128.48
128.46
128.31
128.28
127.96
127.93
127.83
127.58
127.52
126.51
126.48
50.76
50.58
48.31
47.90
46.01
45.26
44.40
43.46
135
133
131
129
127
f1 (ppm)
53
51
49
47
45
43
f1 (ppm)
Ph
N
O
O
Ph
3ka
13C NMR (100 MHz)
Solvent: CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

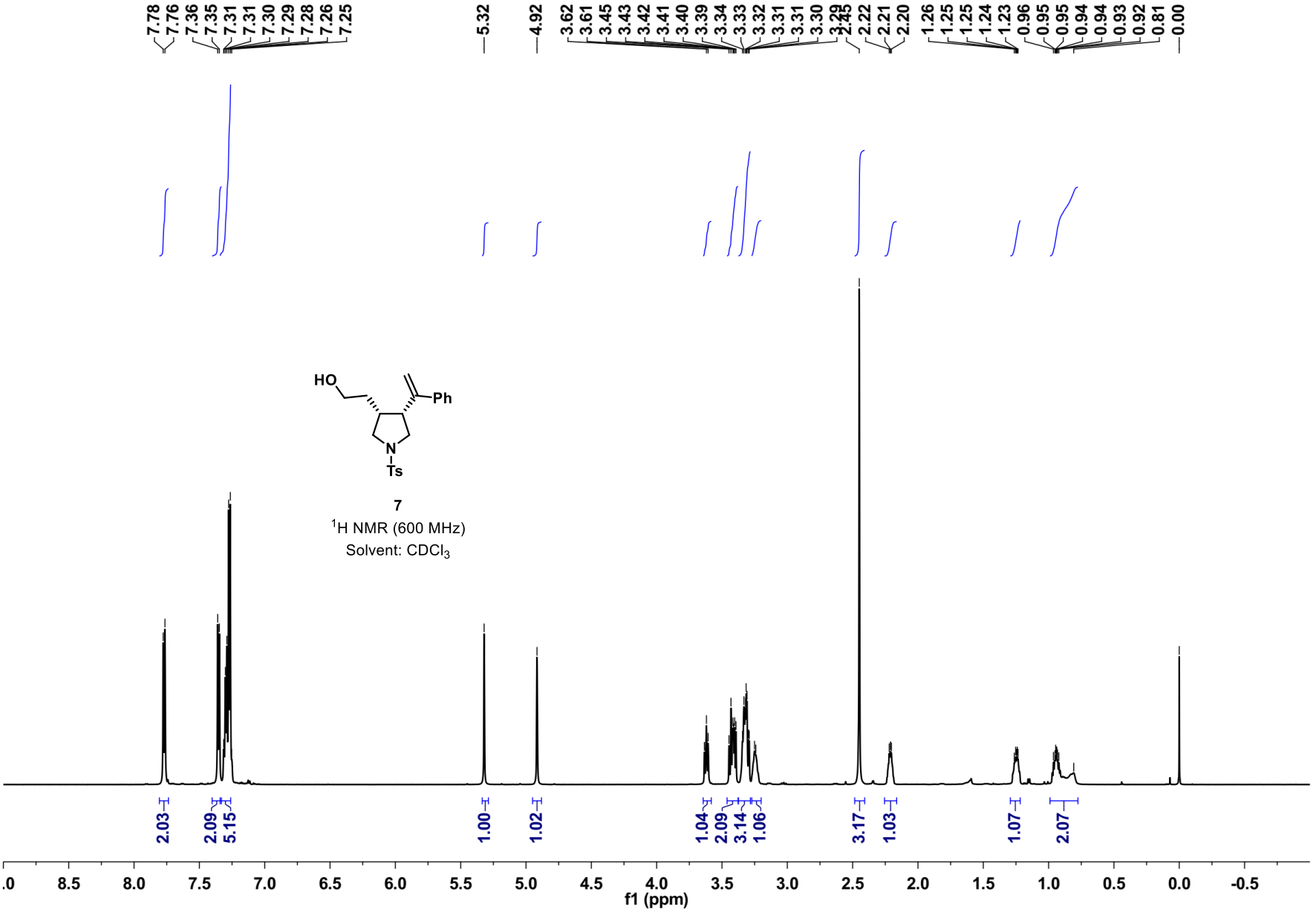

7.88 7.88 7.87 7.87 7.86 7.86 7.53 7.53 7.52 7.52 7.51 7.51 7.31 7.31 7.30 7.30 7.29 7.28 7.27 7.27 7.27 7.26 7.26 7.24 7.24 7.24 7.23 7.23 7.23 7.17 7.16 7.11 7.10 6.76 5.30 5.28 5.28 5.27 5.25 5.25 5.24 4.87 4.87 4.85 4.84 4.64 4.61 3.67 3.66 3.66 3.65 3.50 3.49 3.48 3.47 3.42 3.41 3.39 3.37 3.37 3.35 3.35 2.78 2.77 2.38 1.56 0.00
Ph
N
O=S=O
N
N
Me
F3C
3qa
1H NMR (600 MHz)
Solvent: CDCl3
2.00 2.00 3.00 2.01 2.07 2.05 0.96 2.02 2.01 1.00 0.99 1.04 3.07 1.04 3.09
f1 (ppm)

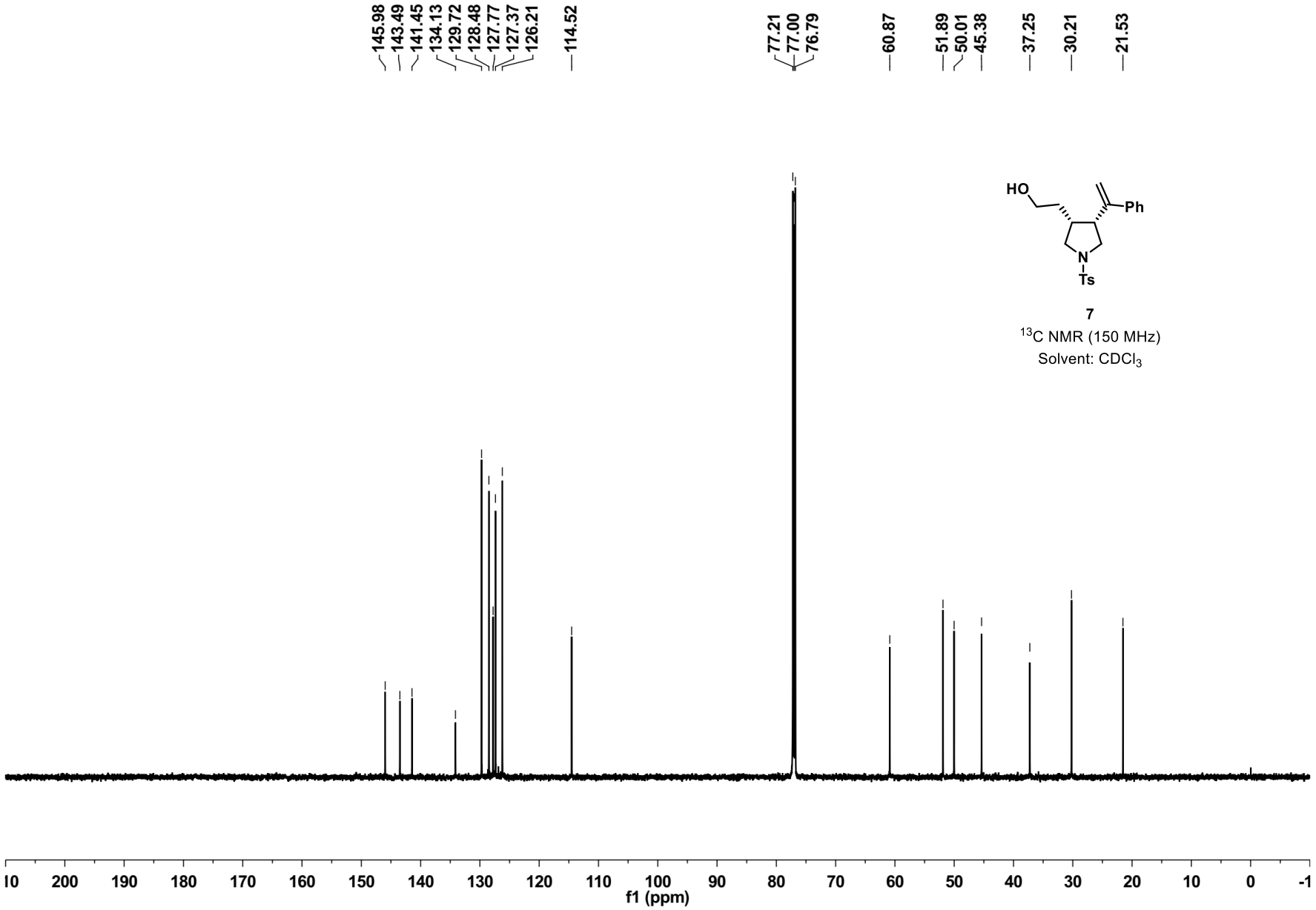

145.35
145.27
144.27
144.02
142.56
141.23
139.80
136.75
134.14
129.73
128.70
128.35
128.32
127.73
126.37
125.68
125.64
121.94
120.15
118.37
116.99
114.01
106.26
77.21
77.00
76.79
52.43
49.71
45.86
44.24
21.31
Ph
Me
O=S=O
N
F3C
3qa
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)

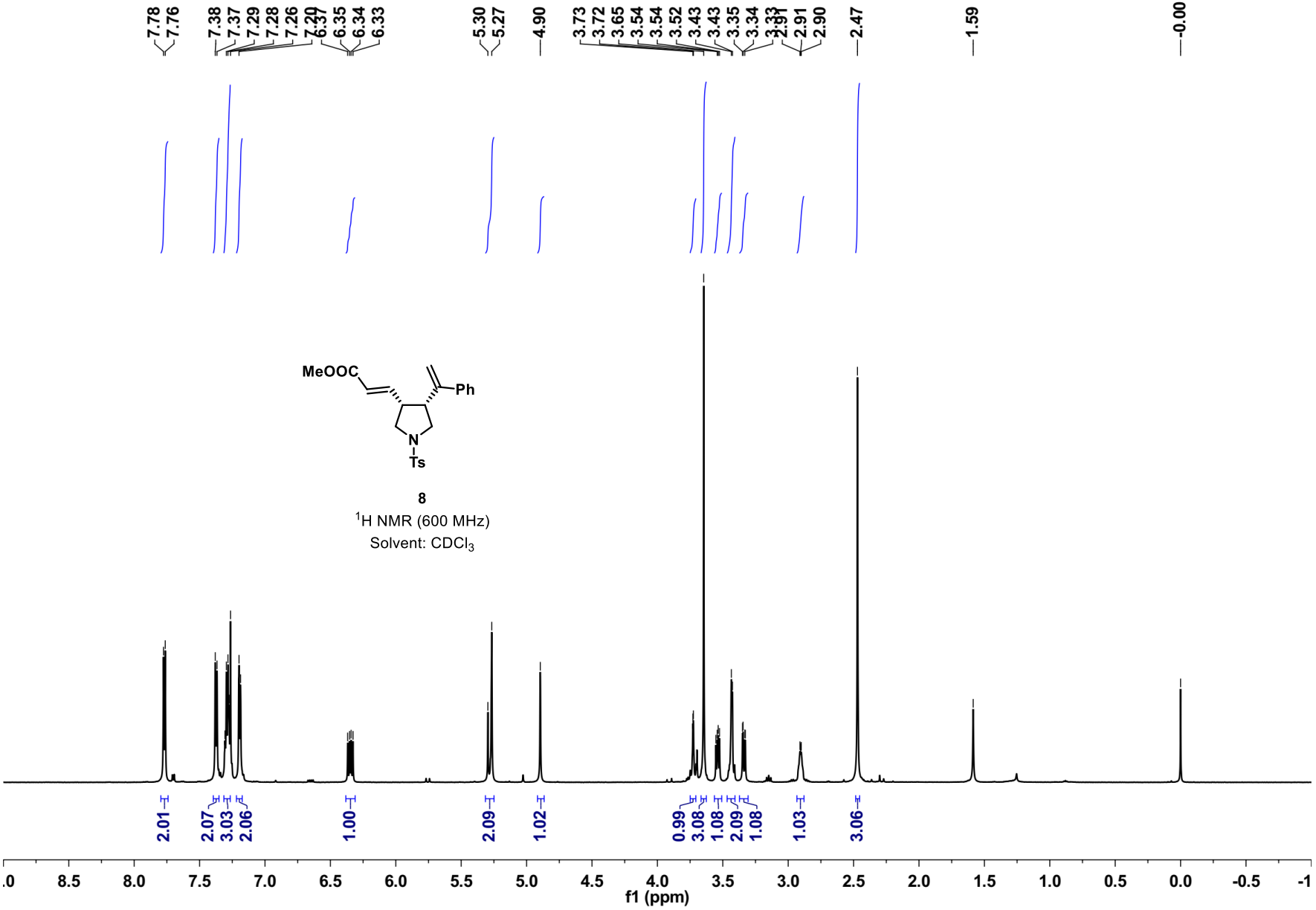

-62.42
Ph
N
O=S=O
Me
N
N
F3C
3qa
19F NMR (376 MHz)
Solvent: CDCl3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

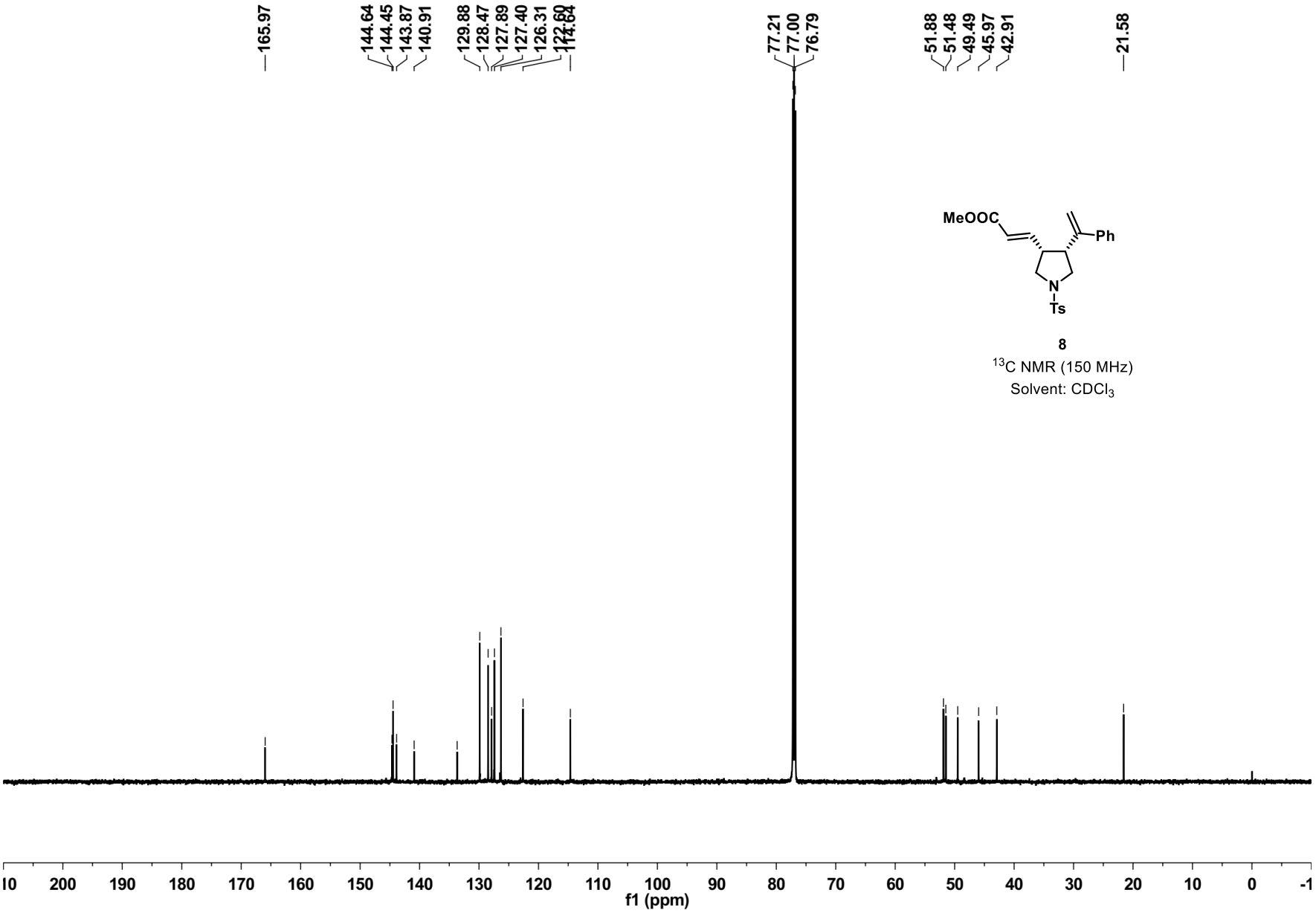

7.62 7.62 7.61 7.61 7.29 7.28 7.27 7.26 7.26 7.22 7.21 7.21 7.21 7.20 7.20 7.19 7.07 7.07 7.06
3.43 3.42 3.23 3.22 3.22 3.22 3.21 3.21 3.20 3.20 2.90 2.89 2.88 2.87 2.71 2.69 2.69 2.68 2.55 2.54 2.53 2.52 2.43 2.16 2.15 2.14 2.13 2.02 2.01 2.01 2.00 2.00 1.99 1.59 1.41 1.41 1.40 1.40 1.18 1.16 0.85 0.84 0.82 0.71 0.70 0.69 0.68 0.68 0.00
Me
Et
Ph
H
H
N
Ts
6
1H NMR (600 MHz)
Solvent: CDCl3
2.02 5.48 2.02 1.00 1.00 1.05 1.02 1.07 3.14 1.03 1.01 1.04 3.06 3.03 1.03
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


145.30
143.12
134.20
129.48
128.63
127.21
126.67
126.58
77.21
77.00
76.79
51.75
50.32
49.51
41.37
38.84
21.50
20.64
18.11
12.23
Me
Et
Ph
H
H
N
Ts
6
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)


7.78
7.76
7.36
7.35
7.31
7.31
7.30
7.29
7.28
7.26
7.25
5.32
4.92
3.62
3.61
3.45
3.43
3.42
3.41
3.40
3.39
3.34
3.33
3.32
3.31
3.31
3.30
2.22
2.21
2.20
1.26
1.25
1.25
1.24
1.23
0.96
0.95
0.95
0.94
0.94
0.93
0.92
0.81
0.00
HO
Ph
N
Ts
7
1H NMR (600 MHz)
Solvent: CDCl3
2.03
2.09
5.15
1.00
1.02
1.04
2.09
3.14
1.06
3.17
1.03
1.07
2.07
f1 (ppm)


145.98
143.49
141.45
134.13
129.72
128.48
127.77
127.37
126.21
114.52
77.21
77.00
76.79
60.87
51.89
50.01
45.38
37.25
30.21
21.53
HO
Ph
N
Ts
7
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)


7.78
7.76
7.38
7.37
7.29
7.28
7.26
6.35
6.34
6.33
5.30
5.27
4.90
3.73
3.72
3.65
3.54
3.54
3.52
3.43
3.43
3.35
3.34
2.91
2.90
2.47
1.59
-0.00
MeOOC
Ph
N
Ts
8
1H NMR (600 MHz)
Solvent: CDCl3
2.01
2.07
3.03
2.06
1.00
2.09
1.02
0.99
3.08
1.08
2.09
1.08
1.03
3.06
f1 (ppm)


165.97
144.64
144.45
143.87
140.91
129.88
128.47
127.89
127.40
126.31
77.21
77.00
76.79
51.88
51.48
49.49
45.97
42.91
21.58
MeOOC
Ph
N
Ts
8
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)