

Supporting Information

Stereoselective Synthesis of Trifluoromethyl-substituted 2*H*-Furan-Amines from Enaminones

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General methods and optimization of reaction conditions:

All reactions were carried out in flame or oven-dried glassware under argon atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 - 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with I₂. NMR spectra were recorded at room temperature on 400 MHz Bruker spectrometers and 400 MHz Joel spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for ¹H NMR spectra and 77.0 ppm for ¹³C NMR spectra in CDCl₃). Chemical shift (δ) is reported in ppm, coupling constants (*J*) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premier TM mass spectrometer.

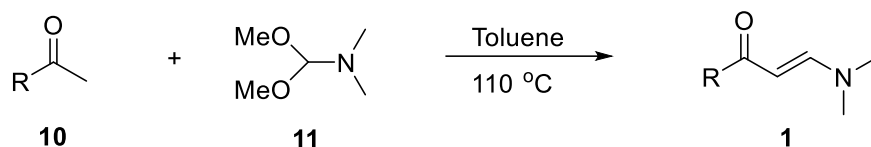
Table 1. Optimization of reaction conditions.^a

Entry	Metal	Base	Solvent	Conv. (%) ^b
1	Rh ₂ (OAc) ₄	KO ^t Bu	toluene	5
2	FeCl ₂	KO ^t Bu	toluene	2
3	CuCl	KO ^t Bu	toluene	65
4	CuBr	KO ^t Bu	toluene	62
5	CuI	KO ^t Bu	toluene	48
6	Cu(OAc) ₂	KO ^t Bu	toluene	71
7	CuCl ₂	KO ^t Bu	toluene	72
8	CuCl ₂	K ₃ PO ₄	toluene	61
9	CuCl ₂	K ₂ CO ₃	toluene	71
10	CuCl ₂	DBU	toluene	-
11	CuCl ₂	Et ₃ N	toluene	-
12	CuCl ₂	KO ^t Bu	CH ₂ Cl ₂	81
13	CuCl ₂	KO ^t Bu	DCE	33
14	CuCl ₂	KO ^t Bu	PhCl	66
15	CuCl ₂ ^c	KO ^t Bu	CH ₂ Cl ₂	82
16	CuCl ₂ ^c	KO ^t Bu	CH ₂ Cl ₂	86 ^d /87 ^e

^aExperiments were performed with **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.20 mmol, 2.0 equiv.), catalyst (20 mol %) and base (0.21 mmol, 2.1 equiv.) in solvent (4 mL) with stirring at 80 °C under Ar atmosphere until **1a** was completely consumed. ^bYields were determined by ¹H NMR with tetrachloroethane as an internal standard. ^c5 mol % catalyst loading. ^d**2a** (0.25 mmol, 2.5 equiv.), base (0.26 mmol, 2.6 equiv.). ^eIsolated yields. DCE = dichloroethane.

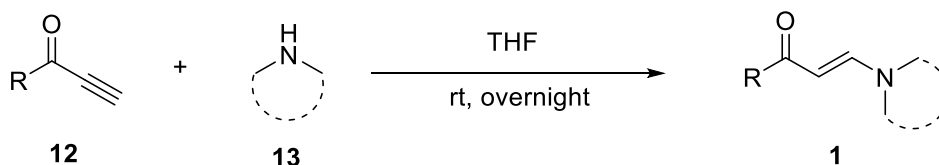
General procedure for enaminones and their spectral datas:

General procedure A for the synthesis of enaminones¹:



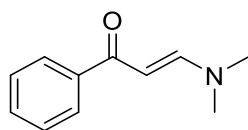
To a stirred solution of ketone **10** (5.0 mmol, 1.0 equiv.) in toluene (5 mL), 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 1.4 equiv.) was added and stirred at 110 °C. After completion of the reaction (monitored by TLC), it was quenched with water, extracted with ethyl acetate and dried with anhydrous Na₂SO₄. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography (hexane: ethyl acetate = 1 : 1) to give the desired product.

General procedure B for the synthesis of enaminones²:



To a stirred solution of **12** (5.0 mmol, 1.0 equiv.) in THF (10 mL), amine **13** (12.0 mmol, 2.4 equiv.) was added dropwise and stirred at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture is concentrated under reduced pressure and purified by column chromatography (hexane : ethyl acetate = 2 : 1) to give the desired product.

(*E*)-3-(Dimethylamino)-1-phenylprop-2-en-1-one (**1a**):



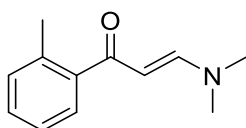
The title compound was prepared from acetophenone **10a** (5.0 mmol, 600.8 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general

1. Y. Jiang, V. Y. K. Zhong, L. Emmanuvel and C.-M. Park, *Chem. Commun.*, 2012, **48**, 3133-3135.

2. L. Šenica, U. Grošelj, M. Kasunič, D. Kočar, B. Stanovnik and J. Svete, *Eur. J. Org. Chem.*, 2014, **15**, 3067-3071.

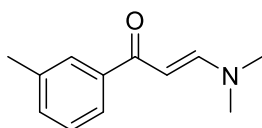
procedure A. The product was obtained as yellow solid in 98% yield (857.0 mg), Mp.90 – 91 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.89 (m, 2H), 7.79 (d, *J* = 12.4 Hz, 1H), 7.46 – 7.39 (m, 3H), 5.71 (d, *J* = 12.4 Hz, 1H), 3.12 (s, 3H), 2.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 188.6, 154.1, 140.4, 130.8, 128.0, 127.4, 92.1, 45.0, 37.2; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₁H₁₄NO⁺: 176.1075. Found: 176.1075.

(*E*)-3-(Dimethylamino)-1-(*o*-tolyl)prop-2-en-1-one (1b):



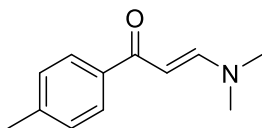
The title compound was prepared from 1-(*o*-tolyl)ethan-1-one **10b** (5.0 mmol, 670.9 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow brown oil in 82% yield (775.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.15 (m, 5H), 5.33 (d, *J* = 12.8 Hz, 1H), 3.03 (s, 3H), 2.84 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.4, 154.8, 141.8, 135.1, 130.4, 128.4, 126.8, 125.0, 97.7, 44.8, 36.9, 19.6; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₂H₁₆NO⁺: 190.1232. Found: 190.1232.

(*E*)-3-(Dimethylamino)-1-(*m*-tolyl)prop-2-en-1-one (1c):



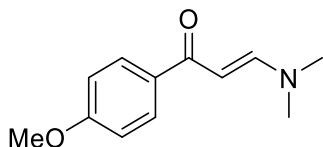
The title compound was prepared from 1-(*m*-tolyl)ethan-1-one **10c** (5.0 mmol, 670.9 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 65% yield (614.6 mg), Mp.35 – 37 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 12.4 Hz, 1H), 7.71(s, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.24 (m, 2H), 5.70 (d, *J* = 12.4 Hz, 1H), 3.10 (s, 3H), 2.90 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 188.7, 154.0, 140.4, 137.6, 131.5, 127.9, 127.8, 124.4, 92.1, 44.8, 37.1, 21.3; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₂H₁₆NO: 190.1232. Found: 190.1230.

(*E*)-3-(Dimethylamino)-1-(*p*-tolyl)prop-2-en-1-one (1d):



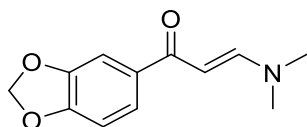
The title compound was prepared from 1-(*p*-tolyl)ethan-1-one **10d** (5.0 mmol, 670.9 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 76% yield (718.6 mg), Mp.87 – 89 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82 - 7.77 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.72 (d, *J* = 12.4 Hz, 1H), 3.11 (s, 3H), 2.94 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 188.4, 154.0, 141.2, 137.8, 128.8, 127.6, 92.1, 21.4; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₂H₁₆NO⁺: 190.1232. Found: 190.1228.

(*E*)-3-(Dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (1e):



The title compound was prepared from 1-(4-methoxyphenyl)ethan-1-one **10e** (5.0 mmol, 750.9 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 82% yield (840.5 mg), Mp.90 – 91 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.87 (m, 2H), 7.77 (d, *J* = 12.4 Hz, 1H), 6.90 – 6.87 (m, 2H), 5.69 (d, *J* = 12.4 Hz, 1H), 3.82 (s, 3H), 3.06 – 2.92 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 187.3, 161.9, 153.7, 133.0, 129.4, 113.2, 91.6, 55.3; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₂H₁₆NO₂⁺: 206.1181. Found: 206.1182.

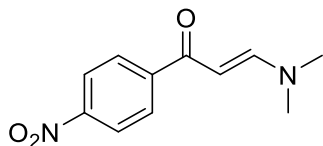
(*E*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-3-(dimethylamino)prop-2-en-1-one (1f):



The title compound was prepared from 1-(benzo[*d*][1,3]dioxol-5-yl)ethan-1-one **10f** (5.0 mmol, 820.8 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 65% yield (962.0 mg), Mp.127 – 129 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 12.3 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.45 – 7.42 (m, 1H), 6.82 (d, *J* = 8.12 Hz, 1H); 6.01 (s, 2H), 5.65 (d, *J* = 12.3 Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 186.9, 154.0, 149.9, 147.6, 135.1,

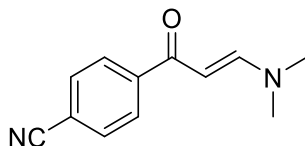
122.5, 107.9, 107.6, 101.4, 91.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{14}NO_3^+$: 220.0974. Found: 220.0977.

(E)-3-(Dimethylamino)-1-(4-nitrophenyl)prop-2-en-1-one (1g):



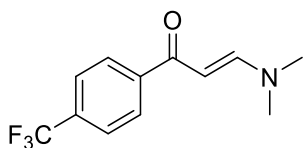
The title compound was prepared from 1-(4-nitrophenyl)ethan-1-one **10g** (5.0 mmol, 825.8 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 67% yield (737.5 mg), Mp.148 – 149 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.23 (m, 2H), 8.01 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 12.4 Hz, 1H), 5.68 (d, J = 12.0 Hz, 1H), 3.21 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 155.2, 149.0, 146.0, 128.3, 123.3, 91.9, 45.3, 37.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}N_2O_3^+$: 221.0926. Found: 221.0932.

(E)-4-(3-(Dimethylamino)acryloyl)benzonitrile (1h):



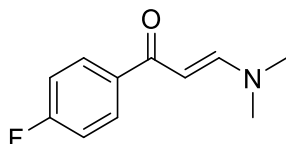
The title compound was prepared from 4-acetylbenzonitrile **10h** (5.0 mmol, 725.8 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 82% yield (820.0 mg), Mp.117 – 118 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 12.2 Hz, 1H), 7.71 – 7.69 (m, 2H), 5.66 (d, J = 12.2, 1H), 3.19 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 155.1, 144.3, 132.1, 128.0, 118.6, 114.0, 91.7, 45.3, 37.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_2O^+$: 201.1028. Found: 201.1026.

(E)-3-(Dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1i)



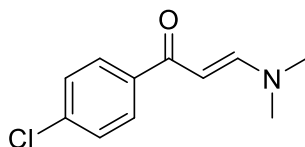
The title compound was prepared from 1-(4-(trifluoromethyl)phenyl)ethan-1-one **10i** (5.0 mmol, 940.8 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 76% yield (923.4 mg), Mp. 107 – 109 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 12.2 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 5.68 (d, *J* = 12.2 Hz, 1H), 3.18 (s, 3H), 2.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.1, 154.8, 143.6, 132.2 (d, *J* = 32.5 Hz), 127.7, 125.1 (t, *J* = 3.6 Hz), 122.6, 91.9, 45.2, 37.3; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₂H₁₃F₃NO⁺: 244.0949. Found: 244.0952.

(*E*)-3-(Dimethylamino)-1-(4-fluorophenyl)prop-2-en-1-one (1j):



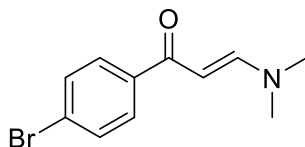
The title compound was prepared from 1-(4-fluorophenyl)ethan-1-one **10j** (5.0 mmol, 690.7 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 88% yield (849.2 mg), Mp. 83 – 84 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.90 (m, 2H), 7.81 (d, *J* = 12.4 Hz, 1H), 7.10 – 7.05 (m, 2H), 5.67 (d, *J* = 12.4 Hz, 1H), 3.15 (s, 3H), 2.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.0, 165.7, 154.3, 136.6 (*J* = 3.0 Hz), 129.7 (*J* = 9.0 Hz), 114.9 (*J* = 21 Hz), 91.6, 45.0, 37.2; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₁H₁₃FNO⁺: 194.0981. Found: 194.0984.

(*E*)-1-(4-Chlorophenyl)-3-(dimethylamino)prop-2-en-1-one (1k):



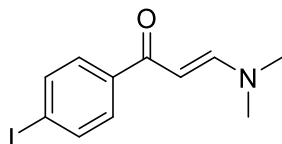
The title compound was prepared from 1-(4-chlorophenyl)ethan-1-one **10k** (5.0 mmol, 773.0 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 83% yield (867.4 mg), Mp. 88 – 89 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.83 (m, 2H), 7.80 (d, *J* = 12.4 Hz, 1H), 7.39 – 7.35 (m, 2H), 5.66 (d, *J* = 12.4 Hz, 1H), 3.15 (s, 3H), 2.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.1, 154.5, 138.8, 136.9, 128.9, 128.2, 91.6; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₁H₁₃ClNO⁺: 210.0686. Found: 210.0690.

(E)-1-(4-Bromophenyl)-3-(dimethylamino)prop-2-en-1-one (1l):



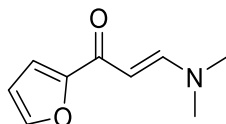
The title compound was prepared from 1-(4-bromophenyl)ethan-1-one **10l** (5.0 mmol, 995.3 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 84% yield (1062.0 mg), Mp. 82 – 83 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 12.4 Hz, 1H), 7.78 – 7.76 (m, 2H), 7.54 – 7.52 (m, 2H), 5.65 (d, *J* = 12.0 Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.1, 154.5, 139.2, 131.2, 129.1, 125.4, 91.6, 45.0, 37.3; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₁H₁₃BrNO⁺: 254.0181. Found: 254.0184.

(E)-3-(Dimethylamino)-1-(4-iodophenyl)prop-2-en-1-one (1m):



The title compound was prepared from 1-(4-iodophenyl)ethan-1-one **10m** (5.0 mmol, 1230.3 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 65% yield (978.5 mg), Mp. 121 – 122 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 12.4 Hz, 1H), 7.75 – 7.73 (m, 2H), 7.63 – 7.61 (m, 2H), 5.64 (d, *J* = 12.4 Hz, 1H), 3.12 (s, 3H), 2.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.1, 154.4, 139.7, 137.1, 129.0, 97.7, 91.4, 45.0, 37.2; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₁H₁₃INO⁺: 302.0042. Found: 302.0039.

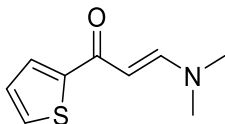
(E)-3-(Dimethylamino)-1-(furan-2-yl)prop-2-en-1-one (1n):



The title compound was prepared from 1-(furan-2-yl)ethan-1-one **10n** (5.0 mmol, 550.6 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 81% yield (668.3 mg), Mp. 80 – 81 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 12.4 Hz, 1H), 7.49 (s, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 6.48 (s, 1H), 5.68 (d, *J* = 12.8 Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H); ¹³C NMR (100 MHz,

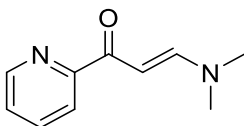
CDCl_3) δ 177.4, 154.7, 153.5, 144.1, 113.3, 111.7, 91.4, 44.9, 37.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{12}\text{NO}_2^+$: 166.0868. Found: 166.0869.

(E)-3-(Dimethylamino)-1-(thiophen-2-yl)prop-2-en-1-one (1o):



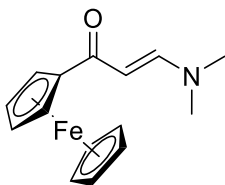
The title compound was prepared from 1-(thiophen-2-yl)ethan-1-one **10o** (5.0 mmol, 630.9 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 79% yield (715.0 mg), Mp. 117 – 118 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 12.4 Hz, 1H), 7.62 – 7.61 (m, 1H), 7.47 – 7.45 (m, 1H), 7.08 – 7.06 (m, 1H), 5.62 (d, J = 12.0 Hz, 1H), 3.10 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.6, 153.4, 147.3, 130.0, 128.2, 127.4, 91.5, 44.8, 37.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{12}\text{NOS}^+$: 182.0640. Found: 182.0640.

(E)-3-(Dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (1p):



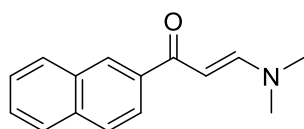
The title compound was prepared from 1-(pyridin-2-yl)ethan-1-one **10p** (5.0 mmol, 605.7 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as black solid in 71% yield (625.0 mg), Mp. 124 – 125 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.64 – 8.62 (m, 1H), 8.15 (d, J = 10.4 Hz, 1H), 7.92 (d, J = 12.7 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.38 – 7.34 (m, 1H), 6.45 (d, J = 12.7 Hz, 1H), 3.18 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.0, 155.5, 154.1, 147.7, 136.1, 124.8, 121.2, 90.4, 44.5, 36.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}^+$: 177.1028. Found: 177.1030.

(E)-3-(dimethylamino)-1-ferrocenyl -2-en-1-one (1q):



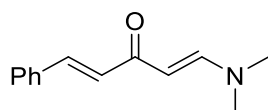
The title compound was prepared from acetylferrocene **10q** (5.0 mmol, 1140.4 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as red solid in 34% yield (481.4 mg), Mp. 65 – 66 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 12.5 Hz, 1H), 5.37 (d, *J* = 12.5 Hz, 1H), 4.78 (s, 2H), 4.38 (s, 2H), 4.16 (s, 5H), 3.00 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 191.7, 151.6, 93.1, 82.5, 70.9, 69.8, 69.0; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₅H₁₈FeNO⁺: 284.0732. Found: 284.0733.

(*E*)-3-(Dimethylamino)-1-(naphthalen-2-yl)prop-2-en-1-one (1r):



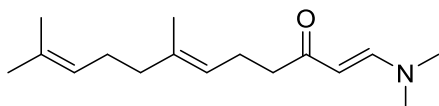
The title compound was prepared from 1-(naphthalen-2-yl)ethan-1-one **10r** (5.0 mmol, 851.1 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 77% yield (866.5 mg), Mp. 113 – 114 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 1H), 8.03 – 8.00 (m, 1H), 7.95 – 7.93 (m, 1H), 7.88 – 7.84 (m, 3H), 7.55 – 7.48 (m, 2H), 5.87 (d, *J* = 12.4 Hz, 1H), 3.06 (d, *J* = 70.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 188.4, 154.2, 137.8, 134.7, 132.7, 129.1, 127.7, 127.6, 127.1, 126.1, 124.6, 92.3, 45.0, 37.3; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₅H₁₆NO⁺: 226.1232. Found: 226.1233.

(1*E*, 4*E*)-1-(Dimethylamino)-5-phenylpenta-1,4-dien-3-one (1s):



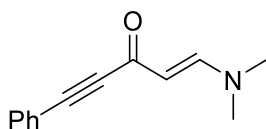
The title compound was prepared from (*E*)-4-phenylbut-3-en-2-one **10s** (5.0 mmol, 731.0 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 78% yield (784.0 mg), Mp. 99 – 100 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 12.4 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.38 – 7.32 (m, 3H), 6.79 (d, *J* = 12.8 Hz, 1H), 5.28 (d, *J* = 12.8 Hz, 1H), 3.12 (s, 3H), 2.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 186.2, 153.3, 138.3, 135.7, 129.1, 128.6, 128.2, 127.8, 96.3, 44.9, 37.2; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₃H₁₆NO⁺: 202.1232. Found: 202.1229.

(1*E*, 6*E*)-1-(Dimethylamino)-6,11-dimethyldodeca-1,6,10-trien-3-one (1t):



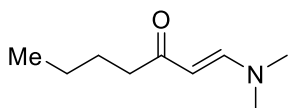
The title compound was prepared from (*E*)-6,10-dimethylundeca-5,9-dien-2-one **10t** (5.0 mmol, 971.6 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow oil in 72% yield (899.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 12.8$ Hz, 1H), 5.17 – 5.03 (m, 2H), 5.03 (d, $J = 12.4$ Hz, 1H), 3.00 – 2.84 (m, 6H), 2.36 – 2.29 (m, 4H), 2.06 – 2.03 (m, 3H), 1.99 – 1.97 (m, 1H), 1.62 – 1.59 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 197.5, 152.1, 135.5, 135.3, 131.3, 131.1, 124.4, 124.2, 123.6, 95.7, 41.5, 39.6, 31.8, 26.6, 26.5, 25.6, 24.2, 24.1, 23.3, 17.5, 17.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{28}\text{NO}^+$: 250.2171. Found: 250.2177.

(*E*)-1-(Dimethylamino)-5-phenylpent-1-en-4-yn-3-one (1u):



The title compound was prepared from 4-phenylbut-3-yn-2-one **10u** (5.0 mmol, 720.9 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as brown solid in 87% yield (865.8 mg), Mp.86 – 87 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 12.8$ Hz, 1H), 7.56 – 7.54 (m, 2H), 7.39 – 7.33 (m, 3H), 5.31 (d, $J = 12.7$ Hz, 1H), 3.16 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.1, 132.3, 129.6, 128.4, 121.3, 101.9, 45.3, 37.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{14}\text{NO}^+$: 200.1075. Found: 200.1075.

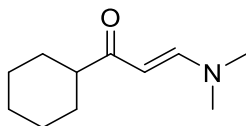
(*E*)-1-(Dimethylamino)hept-1-en-3-one (1v):



The title compound was prepared from hexan-2-one **10v** (5.0 mmol, 500.8 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as brown oil in 52% yield (403.0 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 12.7$ Hz, 1H), 5.04 (d, $J = 12.7$ Hz, 1H), 3.03 – 2.84 (m, 6H), 2.35 – 2.31 (m, 2H), 1.62 – 1.54 (m, 2H), 1.38 – 1.31 (m, 2H), 0.93 – 0.87 (m, 3H); ^{13}C NMR (100

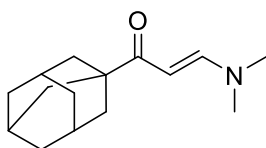
MHz, CDCl₃) δ 198.2, 152.1, 95.5, 44.4, 41.3, 36.8, 28.0, 22.5, 13.8; HRMS (ESI) m/z [M+H]⁺: Calcd for C₉H₁₈NO⁺: 156.1388. Found: 156.1285.

(E)-1-Cyclohexyl-3-(dimethylamino)prop-2-en-1-one (1w):



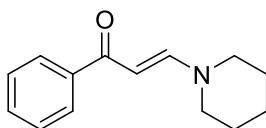
The title compound was prepared from 1-cyclohexylethan-1-one **10w** (5.0 mmol, 631.0 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 14% yield (127.4 mg), Mp. 41 – 42 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 12.4 Hz, 1H), 5.05 (d, J = 12.4 Hz, 1H), 3.05 (s, 3H), 2.83 (s, 3H), 2.30 – 2.24 (m, 1H), 1.80 – 1.76 (m, 4H), 1.68 – 1.65 (m, 1H), 1.44 – 1.15 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 200.8, 151.9, 93.6, 49.6, 44.2, 36.5, 29.3, 25.6; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₁H₂₀NO⁺: 182.1545. Found: 182.1548.

(E)-1-(Adamantan-1-yl)-3-(dimethylamino)prop-2-en-1-one (1x)



The title compound was prepared from 1-(adamantan-1-yl)ethan-1-one **10x** (5.0 mmol, 891.4 mg) and 1,1-dimethoxy-*N,N*-dimethylmethanamine **11** (7.0 mmol, 834.1 mg) according to the general procedure A. The product was obtained as yellow solid in 34% yield (397.8 mg), Mp. 117 – 118 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 12.4 Hz, 1H), 5.24 (d, J = 12.4 Hz, 1H), 2.87 (s, 6H), 2.02 (s, 3H), 1.83 (d, J = 2.8 Hz, 6H), 1.66 – 1.63 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 203.1, 153.3, 90.1, 44.0, 39.4, 36.9, 28.4; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₅H₂₄NO⁺: 234.1858. Found: 234.1858.

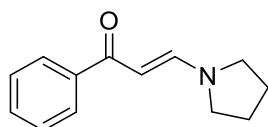
(E)-1-Phenyl-3-(piperidin-1-yl)prop-2-en-1-one (1y):



The title compound was prepared from 1-phenylprop-2-yn-1-one **12** (5.0 mmol, 650.8 mg) and piperidine **13y** (12.0 mmol, 1021.8 mg) according to the general procedure B. The product was

obtained as yellow solid in 85% yield (914.0 mg), Mp. 93 – 95 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.87 (m, 2H), 7.78 (d, J = 12.5 Hz, 1H), 7.46 – 7.38 (m, 3H), 5.82 (d, J = 12.5 Hz, 1H), 3.36 (s, 4H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.9, 153.0, 140.7, 130.7, 128.0, 127.3, 91.1, 54.8, 23.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{18}\text{NO}^+$: 216.1388. Found: 216.1390.

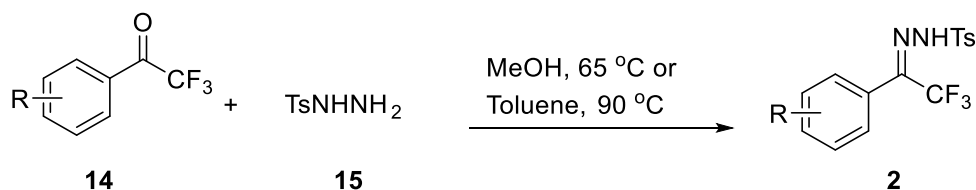
(*E*)-1-Phenyl-3-(pyrrolidin-1-yl)prop-2-en-1-one (1z**):**



The title compound was prepared from 1-phenylprop-2-yn-1-one **12** (5.0 mmol, 650.8 mg) and pyrrolidine **13z** (12.0 mmol, 853.4 mg) according to the general procedure B. The product was obtained as yellow solid in 87% yield (642.0 mg), Mp. 121 – 123 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 12.4 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.47 – 7.38 (m, 3H), 5.68 (d, J = 12.4 Hz, 1H), 3.55 (d, J = 5.5 Hz, 2H), 3.27 (s, 2H), 2.04 – 1.92 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.3, 149.8, 140.5, 130.6, 128.0, 127.4, 92.9, 52.2, 46.9, 25.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{16}\text{NO}^+$: 202.1232. Found: 202.1230.

General procedure for the synthesis of trifluoromethylated *N*-tosylhydrazones:

N-Tosylhydrazones were prepared according to the literature procedure³.

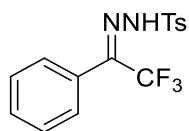


To a round bottom flask surmounted with a reflux condenser was added *N*-tosylhydrazide **15** (5.0 mmol, 1.0 equiv.) and the minimum quantity of solvent (either methanol or toluene according to individual substrates) needed to dissolve the hydrazide at reflux (approximately 1.5 M). Subsequently the reaction was cooled to room temperature and trifluoroacetophenone **14** (5.0 mmol, 1.0 equiv.) was added in one portion. The reaction

3. X. Wang, Y. Xu, Y. Deng, Y. Zhou, J. Feng, G. Ji, Y. Zhang and J. Wang, *Chem. Eur. J.* 2014, **20**, 961-965.

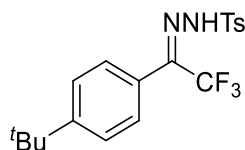
mixture was then stirred at 65 °C (MeOH) or 90 °C (Toluene) over 4-16 h (monitor by TLC). The solution was cooled down to 0 °C, at which point the product precipitated out of solution in most cases (precipitation can be induced by addition of pentane). The precipitate was collected by vacuum filtration and washed with pentane, in which case it was used without further purification. If no precipitation occurred, the solvent was removed under reduced pressure and the residue used in the next step without further purification.

(Z)-4-Methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (2a):



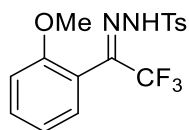
The title compound was prepared from 2,2,2-trifluoro-1-phenylethan-1-one **14a** (5.0 mmol, 870.6 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 82% yield (1403.6 mg), Mp. 161 – 162 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.50 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.22 (m, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 141.6 (q, *J* = 36.2 Hz), 134.5, 131.6, 130.0, 129.9, 128.2, 128.0, 125.2, 119.9 (q, *J* = 274.8 Hz), 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.33; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₅H₁₄F₃N₂O₂S⁺: 343.0728. Found: 343.0730.

(Z)-*N'*-(1-(4-(*Tert*-butyl)phenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (2b):



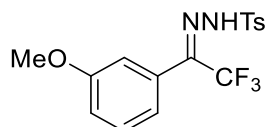
The title compound was prepared from 1-(4-(*tert*-butyl)phenyl)-2,2,2-trifluoroethan-1-one **14b** (5.0 mmol, 1151.2 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 60% yield (1195.3 mg), Mp. 145 – 146 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 2.45 (s, 3H), 1.33 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 144.9, 141.9 (q, *J* = 35.6 Hz), 134.6, 129.8, 128.0, 127.9, 127.0, 122.2, 120.0 (q, *J* = 275.0 Hz), 35.0, 31.0, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.32; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₂₂F₃N₂O₂S⁺: 399.1354. Found: 399.1359.

(Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(2-methoxyphenyl)ethylidene)benzenesulfonohydrazide (2c):



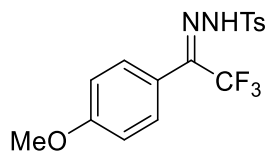
The title compound was prepared from 2,2,2-trifluoro-1-(2-methoxyphenyl)ethan-1-one **14c** (5.0 mmol, 1020.8 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 46% yield (856.4 mg), Mp.148 – 149 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 3.65 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 144.7, 139.5, 134.9, 133.2, 129.7, 129.6, 128.0, 121.8, 120.1 (q, *J* = 275.2 Hz), 114.2, 111.8, 55.8, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.17; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₆H₁₆F₃N₂O₃S⁺: 373.0834. Found: 373.0883.

(Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(3-methoxyphenyl)ethylidene)benzenesulfonohydrazide (2d):



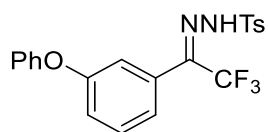
The title compound was prepared from 2,2,2-trifluoro-1-(3-methoxyphenyl)ethan-1-one **14d** (5.0 mmol, 1020.8 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 52% yield (968.1 mg), Mp.141 – 142 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.06 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 3.82 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 145.0 141.3 (q, *J* = 35.7 Hz), 134.5, 131.3, 129.9, 128.0, 126.3, 120.0, 119.9 (d, *J* = 274.8 Hz), 117.0, 113.5, 55.5, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.32; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₆H₁₆F₃N₂O₃S⁺: 373.0834. Found: 373.0883.

(Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (2e):



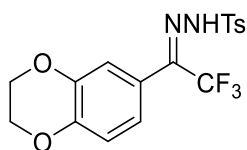
The title compound was prepared from 2,2,2-trifluoro-1-(4-methoxyphenyl)ethan-1-one **14e** (5.0 mmol, 1020.8 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 40% yield (744.7 mg), Mp.147 – 148 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 144.9, 141.6 (q, *J* = 35.6 Hz), 134.5, 129.8, 128.0, 120.0 (d, *J* = 275.0 Hz), 118.7, 116.9, 115.4, 55.5, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.31; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₆H₁₆F₃N₂O₃S⁺: 373.0834. Found: 373.0883.

(Z)-4-Methyl-*N'*-(2,2,2-trifluoro-1-(3-phenoxyphenyl)ethylidene)benzenesulfonohydrazide (2f):



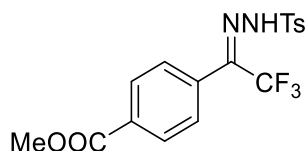
The title compound was prepared from 2,2,2-trifluoro-1-(3-phenoxyphenyl)ethan-1-one **14f** (5.0 mmol, 1331.1 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 47% yield (1020.7 mg), Mp.157 – 158 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 7.23 – 7.17 (m, 1H), 7.13 – 7.09 (m, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.85 – 6.82 (m, 1H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 155.5, 145.0, 140.8 (q, *J* = 35.8 Hz), 134.4, 131.6, 130.2, 129.9, 128.0, 126.6, 124.6, 122.1, 120.7, 119.8 (d, *J* = 274.6 Hz), 119.7, 117.4, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.28; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₁H₁₈F₃N₂O₃S⁺: 435.0998. Found: 435.0990.

(Z)-*N'*-(1-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (2g):



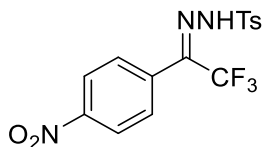
The title compound was prepared from 1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2,2,2-trifluoroethan-1-one **14g** (5.0 mmol, 1160.8 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 62% yield (1240.0 mg), Mp. 99 – 100 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.75 (d, *J* = 1.9 Hz, 1H), 6.71 (dd, *J* = 8.3, 2.0 Hz, 1H), 4.32 – 4.28 (m, 4H), 2.45 (s, 3H); ¹³C NMR (100 MHz, DMSO-D₆) δ 146.1, 144.6, 144.2, 135.8, 130.2, 128.0, 122.2, 120.8 (q, *J* = 275.3 Hz), 119.6, 118.5, 117.9, 64.9, 64.6, 21.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.21; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₁₆F₃N₂O₄S⁺: 401.0783. Found: 401.0780.

Methyl (Z)-4-(2,2,2-trifluoro-1-(2-tosylhydrazono)ethyl)benzoate (2h):



The title compound was prepared from methyl 4-(2,2,2-trifluoroacetyl)benzoate **14h** (5.0 mmol, 1160.8 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 80% yield (1601.2 mg), Mp. 142 – 143 °C. ¹H NMR (400 MHz, DMSO-D₆) δ 11.77 (br, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, DMSO-D₆) δ 166.1, 144.6, 135.7, 132.0, 131.6, 130.4, 130.3, 129.6, 127.8, 120.6 (d, *J* = 274.9 Hz), 53.0, 21.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -67.87; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₁₆F₃N₂O₄S⁺: 401.0783. Found: 401.0783.

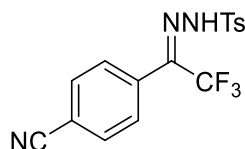
(Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(4-nitrophenyl)ethylidene)benzenesulfonohydrazide (2i):



The title compound was prepared from 2,2,2-trifluoro-1-(4-nitrophenyl)ethan-1-one **14i** (5.0 mmol, 1095.6 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 37% yield (716.5 mg), Mp. 157 – 158 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.39 – 8.34 (m, 2H), 8.12 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃)

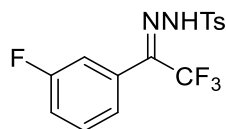
δ 149.6, 145.5, 138.8 (q, J = 36.5 Hz), 134.1, 131.6, 130.1, 130.0, 128.1, 125.1, 119.7 (d, J = 274.6 Hz), 21.8; ^{19}F NMR (376 MHz, CDCl_3) δ -67.71; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{N}_3\text{O}_4\text{S}^+$: 388.0579. Found: 388.0580.

(Z)-N'-(1-(4-Cyanophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (2j):



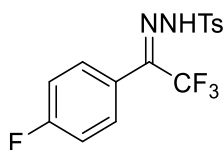
The title compound was prepared from 4-(2,2,2-trifluoroacetyl)benzonitrile **14j** (5.0 mmol, 995.7 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 52% yield (955.1 mg), Mp.152 – 153 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.82 (br, 1H), 8.03 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 144.7, 135.8, 133.7, 131.8, 130.4, 129.9, 127.9, 126.1, 120.6 (d, J = 274.7 Hz), 118.7, 114.0, 21.6; ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -66.29; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}_3\text{O}_2\text{S}^+$: 368.0681. Found: 368.0681.

(Z)-4-Methyl-N'-(2,2,2-trifluoro-1-(3-fluorophenyl)ethylidene)benzenesulfonohydrazide (2k):



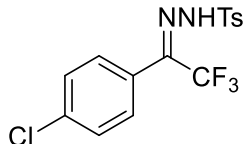
The title compound was prepared from 2,2,2-trifluoro-1-(3-fluorophenyl)ethan-1-one **14k** (5.0 mmol, 960.6 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 58% yield (1044.9 mg), Mp.135 – 136 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.05 (d, J = 7.7 Hz, 1H), 6.99 – 6.95 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 161.9, 145.2, 134.3, 132.0 (d, J = 8.2 Hz), 129.9, 128.0, 127.0 (d, J = 7.7 Hz), 124.0 (d, J = 3.6 Hz), 119.8 (d, J = 274.8 Hz), 118.9 (d, J = 20.9 Hz), 115.6 (d, J = 23.1 Hz), 21.7; ^{19}F NMR (376 MHz, CDCl_3) δ -68.21, -108.49, -108.51, -108.52, -108.53, -108.54, -108.55; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{13}\text{F}_4\text{N}_2\text{O}_2\text{S}^+$: 361.0634. Found: 361.0630.

(Z)-4-Methyl-*N'*-(2,2,2-trifluoro-1-(4-fluorophenyl)ethylidene)benzenesulfonohydrazide (2l):



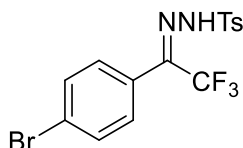
The title compound was prepared from 2,2,2-trifluoro-1-(4-fluorophenyl)ethan-1-one **14l** (5.0 mmol, 960.6 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 51% yield (918.8 mg), Mp. 135 – 136 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 140.5 (q, *J* = 36.2 Hz), 139.3, 134.3, 129.9, 129.7, 128.0, 124.5, 119.7 (d, *J* = 275.0 Hz), 98.5, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.22, -115.43; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₅H₁₃F₄N₂O₂S⁺: 361.0634. Found: 361.0630.

(Z)-*N'*-(1-(4-Chlorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (2m):



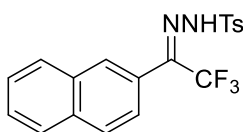
The title compound was prepared from 1-(4-chlorophenyl)-2,2,2-trifluoroethan-1-one **14m** (5.0 mmol, 1042.8 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 59% yield (1111.5 mg), Mp. 105 – 106 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 140.0 (q, *J* = 35.9 Hz), 138.1, 134.3, 130.4, 129.9, 129.7, 128.0, 123.5, 119.8 (d, *J* = 274.9 Hz), 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.24; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₅H₁₃ClF₃N₂O₂S⁺: 377.0338. Found: 377.0342.

(Z)-*N'*-(1-(4-Bromophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (2n):



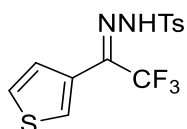
The title compound was prepared from 1-(4-bromophenyl)-2,2,2-trifluoroethan-1-one **14n** (5.0 mmol, 1265.1 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 71% yield (1495.3 mg), Mp.154 – 155 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 140.2 (q, *J* = 36.2 Hz), 134.3, 133.4, 133.1, 129.9, 128.0, 126.4, 123.9, 119.7 (d, *J* = 274.9 Hz), 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.23; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₅H₁₃BrF₃N₂O₂S⁺: 420.9833. Found: 420.9827.

(Z)-4-Methyl-*N'*-(2,2,2-trifluoro-1-(naphthalen-2-yl)ethyldene)benzenesulfonohydrazide (2o):



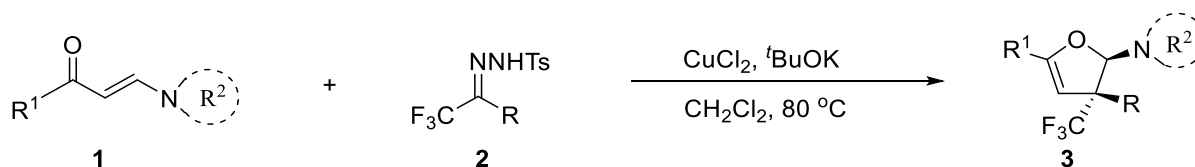
The title compound was prepared from 2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-one **14o** (5.0 mmol, 1120.9 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 83% yield (1628.4 mg), Mp.166 – 167 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.84 – 7.77 (m, 3H), 7.67 – 7.57 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.25 (m, 1H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 141.6 (q, *J* = 35.5 Hz), 134.5, 134.1, 132.9, 130.2, 129.9, 128.9, 128.5, 128.4, 128.1, 128.0, 127.6, 123.8, 122.4, 120.1 (d, *J* = 275.3 Hz), 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -67.98; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₁₆F₃N₂O₂S⁺: 393.0885. Found: 393.0888.

(Z)-4-Methyl-*N'*-(2,2,2-trifluoro-1-(thiophen-3-yl)ethyldene)benzenesulfonohydrazide (2p):



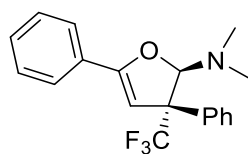
The title compound was prepared from 2,2,2-trifluoro-1-(thiophen-3-yl)ethan-1-one **14p** (5.0 mmol, 900.7 mg) and *N*-tosylhydrazide **15** (5.0 mmol, 931.2 mg) according to the general procedure. The product was obtained as white solid in 46% yield (818.6 mg), Mp. 134 – 135 °C. ¹H NMR (400 MHz, DMSO-D6) δ 11.63 (s, 1H), 8.04 – 8.00 (m, 1H), 7.80 – 7.76 (m, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.25 (m, 1H), 2.39 (s, 3H); ¹³C NMR (100 MHz, DMSO-D6) δ 144.6, 135.6, 131.1, 130.2, 128.4, 128.2, 127.1, 126.2, 122.1, 119.4, 21.6; ¹⁹F NMR (376 MHz, DMSO-D6) δ -66.68; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₃H₁₂F₃N₂O₂S⁺: 349.0248. Found: 349.0246.

General procedure for 2*H*-furans and their spectral data:



A mixture of **1** (0.2 mmol, 1.0 equiv.), **2** (0.5 mmol, 2.5 equiv.), CuCl₂ (0.01 mmol, 5 mol %), KO^tBu (0.52 mmol, 2.6 equiv.) and CH₂Cl₂ (4 mL) was sealed in a Schlenk tube under Ar protection at 80 °C and the mixture was stirred for 24 h or until the **1** was consumed completely. Then the reaction mixture was filtered by diatomite and concentrated under reduced pressure and purified by column chromatography (Et₃N : PE = 1:20) to give the desired product **3**.

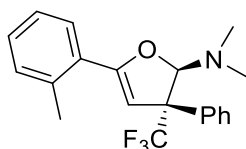
(2*R*,3*S*)-*N,N*-Dimethyl-3,5-diphenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (**3aa**):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow oil in 87% yield (58.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.72 (m, 2H), 7.58 – 7.56 (m, 2H), 7.45 – 7.37 (m, 3H), 7.36 – 7.30 (m, 3H), 5.80 (s, 1H), 5.78 (s, 1H), 2.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 133.4, 130.1, 129.7, 129.5, 128.4, 127.9, 127.3, 126.9 (q, *J* = 283.6 Hz), 125.7, 100.4 (q, *J* = 2.9 Hz), 91.4 (d, *J* = 1.4 Hz), 62.7 (q, *J* = 25.3 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.50;

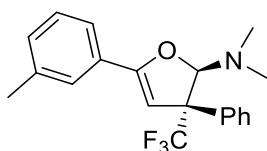
Selected IR (KBr) ν (cm⁻¹): 3061, 2947, 2850, 2797, 1686, 1645, 1599, 1579, 1494, 1449, 1152, 1048, 734, 697; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₉H₁₉F₃NO⁺: 334.1419. Found: 334.1411.

(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-(*o*-tolyl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ba):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(*o*-tolyl)prop-2-en-1-one **1b** (0.2 mmol, 37.9 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow solid in 50% yield (34.7 mg), Mp. 47 – 48 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.55 (m, 3H), 7.38 – 7.31 (m, 3H), 7.30 – 7.20 (m, 3H), 5.75 (s, 1H), 5.50 (s, 1H), 2.53 (s, 3H), 2.14 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 136.7, 133.5, 131.2, 130.1, 130.1, 129.2, 128.5, 127.9, 127.4, 126.9 (q, *J* = 283.4 Hz), 125.7, 99.9 (q, *J* = 3.1 Hz), 95.4 (d, *J* = 2.0 Hz), 62.8 (q, *J* = 25.1 Hz), 39.9, 21.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.53; Selected IR (KBr) ν (cm⁻¹): 2948, 2850, 1653, 1493, 1450, 1339, 1171, 1152, 1028, 950, 747; HRMS (ESI) m/z [M+H]⁺: Calcd for C₂₀H₂₁F₃NO⁺: 348.1575. Found: 348.1573.

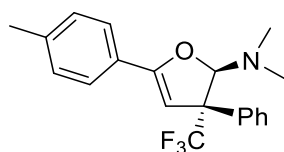
(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-(*m*-tolyl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ca):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(*m*-tolyl)prop-2-en-1-one **1c** (0.2 mmol, 37.9 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow solid in 90% yield (62.5 mg), Mp. 45 – 46 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.50 (m, 4H), 7.37 – 7.27 (m, 4H), 7.23

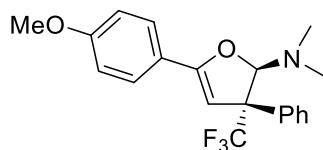
– 7.18 (m, 1H), 5.78 (s, 1H), 5.76 (s, 1H), 2.40 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 138.1, 133.4, 130.3, 130.1, 129.7, 128.4, 127.9, 127.3, 126.9 (q, $J = 283.6$ Hz), 126.3, 122.9, 100.3 (d, $J = 3.0$ Hz), 91.3 (d, $J = 1.7$ Hz), 62.6 (q, $J = 25.2$ Hz), 39.7, 21.4; ^{19}F NMR (376 MHz, CDCl_3) δ -74.53; Selected IR (KBr) ν (cm^{-1}): 2947, 2797, 1646, 1601, 1580, 1491, 1450, 1346, 1152, 1055, 790, 741, 696; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_3\text{NO}^+$: 348.1575. Found: 348.1573.

(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-(*p*-tolyl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3da):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(*p*-tolyl)prop-2-en-1-one **1d** (0.2 mmol, 37.9 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, $R_f = 0.7$). The product was obtained as yellow solid in 85% yield (59.1 mg), Mp : 77–78 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.67–7.63 (m, 2H), 7.62–7.56 (m, 2H), 7.38–7.33 (m, 3H), 7.26–7.21 (m, 2H), 5.80 (s, 1H), 5.74 (s, 1H), 2.41 (s, 3H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 139.6, 133.5, 130.2, 129.1, 127.9, 127.3, 127.0, 126.9 (q, $J = 283.7$ Hz), 125.6, 100.2 (q, $J = 2.9$ Hz), 90.6 (d, $J = 1.7$ Hz), 62.7 (q, $J = 25.2$ Hz), 39.7, 21.4; ^{19}F NMR (376 MHz, CDCl_3) δ -74.38; Selected IR (KBr) ν (cm^{-1}): 3030, 2947, 2850, 2797, 1645, 1511, 1450, 1346, 1257, 1150, 1047, 949, 746, 696; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_3\text{NO}^+$: 348.1575. Found: 348.1573.

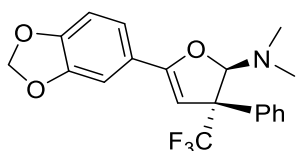
(2*R*,3*S*)-5-(4-Methoxyphenyl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ea):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one **1e** (0.2 mmol, 41.1 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl_2 (0.01 mmol, 1.7

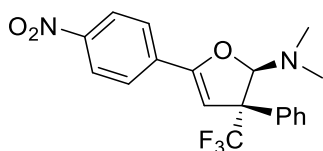
mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow oil in 85% yield (61.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.65 (m, 2H), 7.60 – 7.55 (m, 2H), 7.35 – 7.30 (m, 3H), 6.95 – 6.88 (m, 2H), 5.76 (s, 1H), 5.63 (s, 1H), 3.84 (s, 3H), 2.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 158.1, 133.6, 130.2, 127.9, 127.3, 127.2, 127.0 (q, *J* = 283.6 Hz), 122.4, 113.8, 100.2 (q, *J* = 3.0 Hz), 89.5 (d, *J* = 1.8 Hz), 62.7 (q, *J* = 25.2 Hz), 55.4, 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.57; Selected IR (KBr) ν (cm⁻¹): 2947, 2840, 2797, 1647, 1609, 1512, 1450, 1302, 1254, 1151, 1049, 949, 746, 696; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₀H₂₁F₃NO₂⁺: 364.1524. Found: 364.1521.

(2*R*,3*S*)-5-(Benzo[*d*][1,3]dioxol-4-yl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3fa):



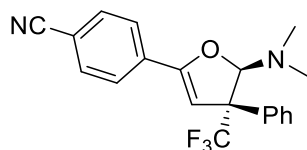
The title compound was prepared from (*E*)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-(dimethylamino)prop-2-en-1-one **1f** (0.2 mmol, 43.9 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as white solid in 86% yield (64.9 mg), Mp. 100 – 101 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.53 (m, 2H), 7.35 – 7.32 (m, 3H), 7.29 – 7.25 (m, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.00 (s, 2H), 5.76 (s, 1H), 5.62 (s, 1H), 2.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.0, 148.8, 147.9, 133.5, 130.3, 128.0, 127.4, 127.0 (q, *J* = 281.6 Hz), 124.0, 120.1, 108.4, 106.3, 101.5, 100.4 (d, *J* = 1.8 Hz), 90.2, 62.8 (q, *J* = 25.0 Hz), 39.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.59; Selected IR (KBr) ν (cm⁻¹): 2947, 2895, 2796, 1647, 1504, 1489, 1450, 1371, 1257, 1153, 1040, 812, 744, 697; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₀H₁₉F₃NO₃⁺: 378.1317. Found: 378.1308.

(2*R*,3*S*)-*N,N*-Dimethyl-5-(4-nitrophenyl)-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ga):



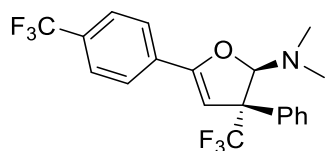
The title compound was prepared from (*E*)-3-(dimethylamino)-1-(4-nitrophenyl)prop-2-en-1-one **1g** (0.2 mmol, 44.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as yellow solid in 80% yield (60.5 mg), Mp. 77 – 78 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.31 – 8.25 (m, 2H), 7.93 – 7.85 (m, 2H), 7.59 – 7.52 (m, 2H), 7.40 – 7.32 (m, 3H), 6.00 (s, 1H), 5.86 (s, 1H), 2.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 148.1, 135.7, 132.7, 130.0, 128.2, 127.5, 126.6 (q, *J* = 283.8 Hz), 126.5, 123.8, 101.2 (q, *J* = 2.9 Hz), 95.6 (d, *J* = 1.8 Hz), 62.8 (q, *J* = 25.4 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.33; Selected IR (KBr) ν (cm⁻¹): 2949, 2852, 1642, 1596, 1523, 1450, 1345, 1154, 1048, 950, 744, 696; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₁₈F₃N₂O₃⁺: 379.1270. Found: 379.1275.

4-((4*S*,5*R*)-5-(Dimethylamino)-4-phenyl-4-(trifluoromethyl)-4,5-dihydrofuran-2-yl)benzonitrile (3ha):



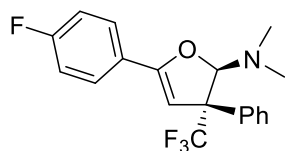
The title compound was prepared from (*E*)-4-(3-(dimethylamino)acryloyl)benzonitrile **1h** (0.2 mmol, 40.1 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.5). The product was obtained as white solid in 78% yield (55.9 mg), Mp. 121 – 122 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.78 (m, 2H), 7.73 – 7.67 (m, 2H), 7.57 – 7.52 (m, 2H), 7.39 – 7.33 (m, 3H), 5.93 (s, 1H), 5.84 (s, 1H), 2.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 156.5, 133.9, 132.7, 132.3, 130.0, 128.2, 127.5, 126.6 (q, *J* = 283.7 Hz), 126.2, 118.6, 112.8, 101.0 (q, *J* = 3.0 Hz), 94.8 (d, *J* = 2.0 Hz), 62.7 (q, *J* = 25.4 Hz), 39.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.38; Selected IR (KBr) ν (cm⁻¹): 2949, 2850, 2798, 2228, 1641, 1607, 1500, 1450, 1346, 1153, 1047, 950, 750, 696; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₀H₁₈F₃N₂O⁺: 359.1371. Found: 359.1372.

(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-3-(trifluoromethyl)-5-(4-(trifluoromethyl)phenyl)-2,3-dihydrofuran-2-amine (3ia):



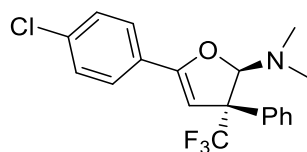
The title compound was prepared from (*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one **1i** (0.2 mmol, 48.7 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow oil in 77% yield (61.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.37 – 7.33 (m, 3H), 5.90 (s, 1H), 5.83 (s, 1H), 2.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 157.0, 133.1 (d, *J* = 1.2 Hz), 133.0, 131.2 (q, *J* = 32.4 Hz), 130.1, 128.1, 127.3, 126.7 (q, *J* = 281.8 Hz), 126.0, 125.5 (q, *J* = 3.9 Hz), 125.0 (q, *J* = 270.5 Hz), 100.9 (q, *J* = 2.8 Hz), 93.6, 62.7 (q, *J* = 25.2 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.72, -74.47; Selected IR (KBr) ν (cm⁻¹): 2990, 1355, 1259, 1165, 1128, 1066, 849, 750, 698; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₀H₁₈F₆NO⁺: 402.1293. Found: 402.1294.

(2*R*,3*S*)-5-(4-Fluorophenyl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ja):



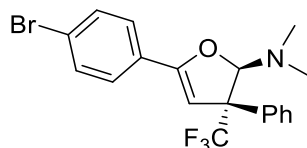
The title compound was prepared from (*E*)-3-(dimethylamino)-1-(4-fluorophenyl)prop-2-en-1-one **1j** (0.2 mmol, 38.6 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow solid in 92% yield (64.6 mg), Mp.42 – 43 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.68 (m, 2H), 7.58 – 7.53 (m, 2H), 7.36 – 7.32 (m, 3H), 7.13 – 7.06 (m, 2H), 5.79 (s, 1H), 5.71(s, 1H), 2.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4 (d, *J* = 249.4 Hz), 157.4, 133.3, 130.1, 128.0, 127.7 (d, *J* = 8.4 Hz), 127.4, 126.8 (q, *J* = 283.9 Hz), 126.0 (d, *J* = 3.4 Hz), 115.5 (d, *J* = 21.9 Hz), 100.6 (q, *J* = 3.0 Hz), 91.1, 62.7 (q, *J* = 25.3 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.56, -111.09; Selected IR (KBr) ν (cm⁻¹): 2951, 2851, 2799, 1649, 1605, 1508, 1450, 1259, 1232, 1154, 1047, 950, 806, 748, 697; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₁₈F₄NO⁺: 352.1325. Found: 352.1325.

(2*R*,3*S*)-5-(4-Chlorophenyl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ka):



The title compound was prepared from (*E*)-1-(4-chlorophenyl)-3-(dimethylamino)prop-2-en-1-one **1k** (0.2 mmol, 41.9 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow solid in 90% yield (66.2 mg), Mp.47 – 48 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 2H), 7.58 – 7.52 (m, 2H), 7.40 – 7.33 (m, 5H), 5.79 (s, 1H), 5.76 (s, 1H), 2.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 135.3, 133.2, 130.1, 128.7, 128.2, 128.0, 127.4, 127.0, 126.8 (q, *J* = 281.2 Hz), 100.6 (q, *J* = 2.9 Hz), 92.0 (d, *J* = 1.3 Hz), 62.7 (q, *J* = 25.0 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.51; Selected IR (KBr) ν (cm⁻¹): 2947, 2850, 2797, 1646, 1597, 1490, 1450, 1255, 1153, 1047, 950, 809, 746, 696; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₁₈ClF₃NO⁺: 368.1029. Found: 368.1025.

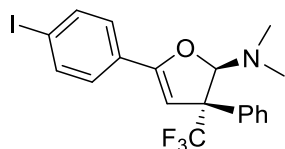
(2*R*,3*S*)-5-(4-Bromophenyl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3la):



The title compound was prepared from (*E*)-1-(4-bromophenyl)-3-(dimethylamino)prop-2-en-1-one **1l** (0.2 mmol, 50.8 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as white solid in 88% yield (72.5 mg), Mp.49 - 50 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.72 (m, 2H), 7.61 – 7.56 (m, 2H), 7.46 – 7.39 (m, 3H), 7.37 – 7.33 (m, 3H), 5.80 (s, 1H), 5.78 (s, 1H), 2.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 133.4, 130.2, 129.8, 129.5, 128.5, 128.0, 127.3, 126.9 (q, *J* = 281.9 Hz), 125.7, 100.4 (q, *J* = 2.8 Hz), 91.5, 62.4 (q, *J* = 24.9 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.48; Selected IR (KBr) ν (cm⁻¹): 3061, 2947, 2849, 2797, 1646, 1495, 1450, 1347, 1259,

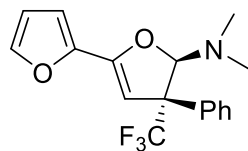
1152, 1048, 949, 814, 749, 697, 579; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}BrF_3NO^+$: 412.0524. Found: 412.0529.

(2*R*,3*S*)-5-(4-Iodophenyl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ma):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(4-iodophenyl)prop-2-en-1-one **1m** (0.2 mmol, 60.2 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), $CuCl_2$ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as white solid in 76% yield (69.8 mg), Mp 77 – 78 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.60 – 7.53 (m, 2H), 7.50 – 7.44 (m, 2H), 7.38 – 7.33 (m, 3H), 5.83 – 5.80 (m, 2H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 137.6, 133.1, 130.1, 129.2, 128.0, 127.3, 127.4, 126.7 (q, J = 282.0 Hz), 100.6 (q, J = 2.8 Hz), 95.4, 92.2 (q, J = 1.2 Hz), 62.7 (q, J = 25.1 Hz), 39.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.45; Selected IR (KBr) ν (cm^{-1}): 2946, 2849, 2797, 1644, 1484, 1449, 1396, 1257, 1153, 1045, 1005, 949, 893, 808, 746, 703, 478; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{18}F_3INO^+$: 460.0385. Found: 460.0385.

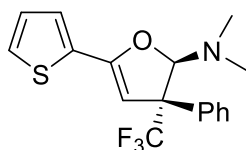
(4*S*,5*R*)-*N,N*-Dimethyl-4-phenyl-4-(trifluoromethyl)-4,5-dihydro-[2,2'-bifuran]-5-amine (3na):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(furan-2-yl)prop-2-en-1-one **1n** (0.2 mmol, 33.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), $CuCl_2$ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as red oil in 49% yield (31.7 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.50 – 7.48 (m, 1H), 7.37 – 7.32 (m, 3H), 6.67 (d, J = 3.4 Hz, 1H), 6.48 (dd, J_1 = 3.4 Hz, J_2 = 1.8 Hz, 1H), 5.80 (s, 1H), 5.73 (s, 1H), 2.12 (s, 6H);

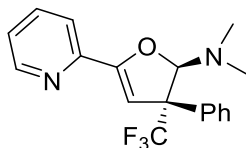
^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 145.5, 143.5, 133.2, 130.1, 128.0, 127.4, 126.8 (q, J = 283.7 Hz), 111.3, 109.1, 101.2 (q, J = 2.9 Hz), 91.3 (d, J = 1.8 Hz), 62.4 (q, J = 25.3 Hz), 39.6; ^{19}F NMR (376 MHz, CDCl_3) δ -74.45; Selected IR (KBr) ν (cm^{-1}): 3063, 2925, 1735, 1671, 1570, 1467, 1398, 1259, 1236, 1168, 763, 699, 592; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{NO}_2^+$: 324.1211. Found: 324.1205.

(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-(thiophen-2-yl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (30a):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(thiophen-2-yl)prop-2-en-1-one **1o** (0.2 mmol, 36.3 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as yellow oil in 63% yield (42.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.52 (m, 2H), 7.41 (dd, J = 3.7, 1.2 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.07 (dd, J = 5.0, 3.6 Hz, 1H), 5.78 (s, 1H), 5.65 (s, 1H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 133.3, 132.7, 130.2, 128.1, 127.6, 127.4, 126.9 (d, J = 283.7 Hz), 126.6, 126.1, 101.0 (d, J = 2.6 Hz), 91.1, 62.9 (q, J = 25.4 Hz), 39.7; ^{19}F NMR (376 MHz, CD_3OD) δ -74.49; Selected IR (KBr) ν (cm^{-1}): 2947, 1483, 1449, 1396, 1258, 1152, 1046, 1005, 949, 807, 748, 702; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{NOS}^+$: 340.0983. Found: 340.0980.

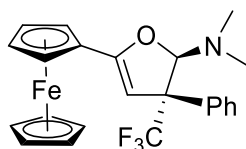
(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3pa):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one **1p** (0.2 mmol, 35.3 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as red solid in 71% yield (47.5 mg), Mp.72

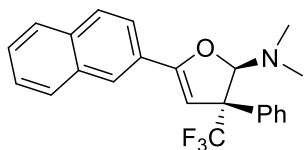
– 73 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.70 – 8.66 (m, 1H), 7.79 – 7.73 (m, 1H), 7.71 – 7.67 (m, 1H), 7.64 – 7.57 (m, 2H), 7.37 – 7.32 (m, 3H), 7.31 – 7.27 (m, 1H), 6.31 (s, 1H), 5.88 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6, 149.8, 148.6, 136.7, 133.1, 130.2, 128.0, 127.4, 126.7 (q, $J = 281.7$ Hz), 123.9, 120.3, 101.3 (q, $J = 2.9$ Hz), 95.3 (d, $J = 1.3$ Hz), 62.6 (q, $J = 25.1$ Hz), 39.7; ^{19}F NMR (376 MHz, CDCl_3) δ -74.31; Selected IR (KBr) ν (cm^{-1}): 3061, 2948, 1735, 1583, 1450, 1354, 1259, 1154, 1058, 950, 750, 704; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$: 335.1371. Found: 335.1373.

(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-(ferrocene-2-yl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3qa):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-ferrocenyl -2-en-1-one **1q** (0.2 mmol, 56.6 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as red oil in 52% yield (45.8 mg). ^1H NMR (400 MHz, CD_3OD) δ 7.57 – 7.55 (m, 2H), 7.32 – 7.30 (m, 3H), 5.72 (s, 1H), 5.51 (s, 1H), 4.66 – 4.65 (m, 1H), 4.59 – 4.58 (m, 1H), 4.33 – 4.29 (m, 2H), 4.17 (s, 5H), 2.09 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 133.8, 130.3, 127.9, 127.3, 126.8 (q, $J = 283.6$ Hz), 100.0 (d, $J = 2.4$ Hz), 89.1, 74.1, 69.7, 69.5, 69.1, 67.1, 66.6, 62.7 (q, $J = 25.1$ Hz), 39.9; ^{19}F NMR (376 MHz, CD_3OD) δ -75.62; Selected IR (KBr) ν (cm^{-1}): 3061, 2946, 2850, 2797, 1645, 1585, 1484, 1450, 1396, 1258, 1234, 1152, 1046, 1005, 949, 810, 747, 697, 480; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{23}\text{H}_{23}\text{F}_3\text{FeNO}^+$: 442.1128. Found: 442.1132.

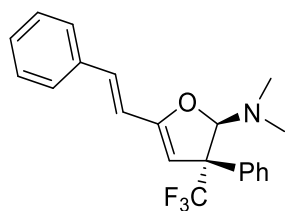
(2*R*,3*S*)-*N,N*-Dimethyl-5-(naphthalen-2-yl)-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ra):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-(naphthalen-2-yl)prop-2-en-1-one **1r** (0.2 mmol, 45.1 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-

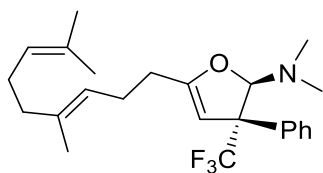
phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as clear oil in 86% yield (65.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.25 – 8.22 (m, 1H), 7.95 – 7.79 (m, 4H), 7.66 – 7.60 (m, 2H), 7.56 – 7.50 (m, 2H), 7.40 – 7.35 (m, 3H), 5.91 (s, 1H), 5.86 (s, 1H), 2.16 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 133.8, 133.4, 133.1, 130.2, 128.6, 128.2, 128.0, 127.8, 127.4, 127.0, 126.9 (q, *J* = 282.1 Hz), 126.8, 126.6, 125.0, 123.4, 100.5 (q, *J* = 2.8 Hz), 92.3 (d, *J* = 1.2 Hz), 62.8 (q, *J* = 25.1 Hz), 39.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.41; Selected IR (KBr) ν (cm⁻¹): 3060, 2981, 2947, 2849, 1645, 1450, 1363, 1260, 1152, 1047, 949, 815, 750, 696, 475; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₃H₂₁F₃NO⁺: 384.1575. Found: 384.1579.

(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-((*E*)-styryl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3sa):



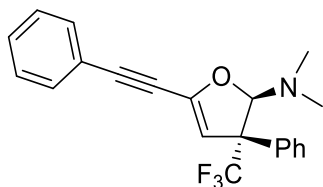
The title compound was prepared from (1*E*,4*E*)-1-(dimethylamino)-5-phenylpenta-1,4-dien-3-one **1s** (0.2 mmol, 40.3 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow solid in 70% yield (50.3 mg), Mp.59 – 60 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.47 (m, 4H), 7.40 – 7.27 (m, 6H), 7.09 (d, *J* = 16.0 Hz, 1H), 6.68 (d, *J* = 16.1 Hz, 1H), 5.74 (s, 1H), 5.46 (s, 1H), 2.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 157.4, 136.1, 133.3, 132.4, 130.1, 128.7, 128.4, 127.9, 127.3, 127.0, 126.8 (q, *J* = 281.9 Hz), 116.1, 100.4 (q, *J* = 2.9 Hz), 96.8 (d, *J* = 1.3 Hz), 62.5 (q, *J* = 25.1 Hz), 39.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.33; Selected IR (KBr) ν (cm⁻¹): 3060, 2947, 2950, 2797, 1649, 1604, 1449, 1397, 1259, 1152, 1046, 951, 809, 749, 694; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₁H₂₁F₃NO⁺: 360.1575. Found: 360.1569.

(2*R*,3*S*)-5-((*E*)-4,8-Dimethylnona-3,7-dien-1-yl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ta):



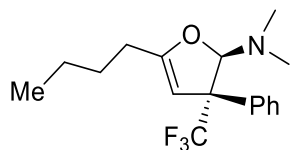
The title compound was prepared from (1*E*,6*E*)-1-(dimethylamino)-7,11-dimethyldodeca-1,6,10-trien-3-one **1t** (0.2 mmol, 49.9 mg), (Z)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as clear oil in 57% yield (46.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.46 (m, 2H), 7.31 – 7.29 (m, 3H), 5.58 (s, 1H), 5.21 – 5.07 (m, 2H), 5.04 (s, 1H), 2.33 – 2.26 (m, 4H), 2.10 – 1.96 (m, 10H), 1.70 – 1.58 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 136.1, 133.8, 131.4, 130.1, 127.7, 127.2, 127.0 (d, *J* = 283.3 Hz), 124.2, 123.0, 100.2 (q, *J* = 3.2 Hz), 91.7 (d, *J* = 1.9 Hz), 62.2 (q, *J* = 25.0 Hz), 39.7, 28.3, 26.7, 25.7, 25.1, 17.7, 16.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.81; Selected IR (KBr) ν (cm⁻¹): 2924, 1723, 1669, 1449, 1376, 1260, 1152, 1048, 951, 808, 749, 698; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₄H₃₃F₃NO⁺: 408.2514. Found: 408.2515.

(2*R*,3*S*)-*N,N*-Dimethyl-3-phenyl-5-(phenylethynyl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ua):



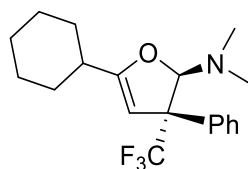
The title compound was prepared from (*E*)-1-(dimethylamino)-5-phenylpent-1-en-4-yn-3-one **1u** (0.2 mmol, 39.9 mg), (Z)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as white solid in 54% yield (38.6 mg), Mp. 63 - 64 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.53 (m, 2H), 7.52 – 7.48 (m, 2H), 7.39 – 7.32 (m, 6H), 5.78 (s, 1H), 5.74 (s, 1H), 2.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 142.3, 132.6, 132.0, 130.0, 129.3, 128.4, 128.1, 127.4, 126.5 (q, *J* = 283.6 Hz), 121.4, 102.9 (d, *J* = 1.7 Hz), 101.0 (q, *J* = 3.0 Hz), 92.6, 79.0, 62.3 (q, *J* = 25.4 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.28; Selected IR (KBr) ν (cm⁻¹): 2989, 1449, 1260, 1155, 952, 750, 691; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₁H₁₉F₃NO⁺: 358.1419. Found: 358.1414.

(2*R*,3*S*)-5-Butyl-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3va):



The title compound was prepared from (*E*)-1-(dimethylamino)hept-1-en-3-one **1v** (0.2 mmol, 31.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.8). The product was obtained as clear oil in 71% yield (44.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.47 (m, 2H), 7.33 – 7.29 (m, 3H), 5.57 (s, 1H), 5.03 (s, 1H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.04 (s, 6H), 1.64 – 1.55 (m, 2H), 1.45 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.4, 133.8, 130.2, 127.7, 127.2, 127.0 (q, *J* = 283.1 Hz), 100.1 (d, *J* = 3.0 Hz), 91.4 (d, *J* = 1.9 Hz), 62.2 (q, *J* = 25.0 Hz), 39.7, 28.8, 28.0, 22.5, 14.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.92; Selected IR (KBr) ν (cm⁻¹): 3063, 2961, 2874, 1721, 1669, 1449, 1240, 1162, 1047, 760, 749, 699; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₂₃F₃NO⁺: 314.1732. Found: 314.1727.

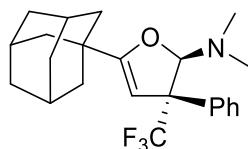
(2*R*,3*S*)-5-Cyclohexyl-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3wa):



The title compound was prepared from (*E*)-1-cyclohexyl-3-(dimethylamino)prop-2-en-1-one **1w** (0.2 mmol, 36.3 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.8). The product was obtained as clear oil in 68% yield (46.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.47 (m, 2H), 7.32 – 7.29 (m, 3H), 5.55 (s, 1H), 4.99 (s, 1H), 2.28 – 2.18 (m, 1H), 2.07 – 2.02 (m, 6H), 2.00 – 1.92 (m, 2H), 1.84 – 1.75 (m, 2H), 1.73 – 1.66 (m, 1H), 1.45 – 1.20 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 133.9, 130.2, 127.7, 127.1, 127.0 (q, *J* = 281.6 Hz), 99.6 (q, *J* = 2.8 Hz), 89.2 (d, *J* = 1.5 Hz), 62.0, (q, *J* = 24.8 Hz), 39.7, 37.5, 30.7, 30.3, 26.1, 25.9, 25.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -75.09; Selected IR (KBr) ν

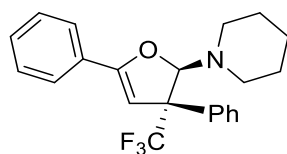
(cm⁻¹): 2930, 2854, 1449, 1258, 1195, 1152, 1084, 952, 750, 696; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₉H₂₅F₃NO⁺: 340.1888. Found: 340.1880.

(2*R*,3*S*)-5-((1*r*,3*R*,5*S*)-Adamantan-1-yl)-*N,N*-dimethyl-3-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3xa):



The title compound was prepared from (*E*)-1-(adamantan-1-yl)-3-(dimethylamino)prop-2-en-1-one **1x** (0.2 mmol, 46.7 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.8). The product was obtained as clear oil in 30% yield (23.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.47 (m, 2H), 7.32 – 7.28 (m, 3H), 5.53 (s, 1H), 4.92 (s, 1H), 2.03 (s, 9H), 1.92 – 1.83 (m, 6H), 1.79 – 1.69 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 134.0, 130.3, 127.7, 127.2, 127.1 (q, *J* = 283.3 Hz), 99.4 (q, *J* = 2.9 Hz), 87.9, 61.9 (q, *J* = 25.0 Hz), 40.0, 39.8, 36.9, 35.0, 28.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -75.11; Selected IR (KBr) ν (cm⁻¹): 2906, 2851, 1653, 1452, 1258, 1170, 1151, 1044, 950, 809, 749, 696; HRMS (ESI) m/z [M+H]⁺: Calcd for C₂₃H₂₉F₃NO⁺: 392.2201. Found: 392.2202.

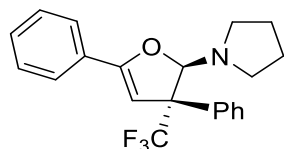
1-((2*R*,3*S*)-3,5-Diphenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-yl)piperidine (3ya):



The title compound was prepared from (*E*)-1-phenyl-3-(piperidin-1-yl)prop-2-en-1-one **1y** (0.2 mmol, 43.1 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow oil in 63% yield (47.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.69 (m, 2H), 7.62 – 7.56 (m, 2H), 7.43 – 7.37 (m, 3H), 7.35 – 7.31 (m, 3H), 5.78 (s, 1H), 5.73 (s, 1H), 2.59 – 2.37 (m, 4H), 1.31 – 1.16 (m, 4H), 1.09 – 0.91 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 133.6, 130.3, 129.9, 129.4, 128.4, 127.8, 127.1, 127.0 (q, *J* = 283.7 Hz), 125.7, 101.1 (q, *J* = 3.0 Hz), 91.7 (d, *J* = 1.8 Hz), 62.6 (q, *J* =

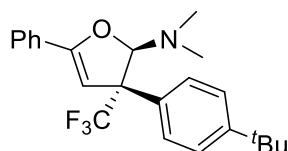
25.3 Hz), 49.0, 25.3, 24.0; ^{19}F NMR (376 MHz, CDCl_3) δ -74.36; Selected IR (KBr) ν (cm^{-1}): 3060, 2935, 2854, 1494, 1449, 1345, 1259, 1171, 1153, 1056, 952, 749, 692; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{22}\text{H}_{23}\text{F}_3\text{NO}^+$: 374.1732. Found: 374.1729.

1-((2*R*,3*S*)-3,5-Diphenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-yl)pyrrolidine (3a):



The title compound was prepared from (*E*)-1-phenyl-3-(pyrrolidin-1-yl)prop-2-en-1-one **1z** (0.2 mmol, 40.3 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide **2a** (0.5 mmol, 171.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as white solid in 76% yield (54.6 mg), Mp.40 – 41 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.70 (m, 2H), 7.60 – 7.55 (m, 2H), 7.42 – 7.37 (m, 3H), 7.34 – 7.30 (m, 3H), 6.07 (s, 1H), 5.73 (s, 1H), 2.68 – 2.60 (m, 2H), 2.36 – 2.28 (m, 2H), 1.54 – 1.4 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 133.9, 130.1, 129.8, 129.4, 128.4, 127.8, 127.1, 126.9 (q, J = 283.9 Hz), 125.7, 97.2 (d, J = 1.8 Hz), 91.1, 62.6 (q, J = 25.0 Hz), 47.1, 24.4; ^{19}F NMR (376 MHz, CDCl_3) δ -73.98; Selected IR (KBr) ν (cm^{-1}): 3060, 2935, 2854, 1646, 1495, 1449, 1346, 1259, 1171, 1153, 1056, 953, 749, 698; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{NO}^+$: 360.1575. Found: 360.1572.

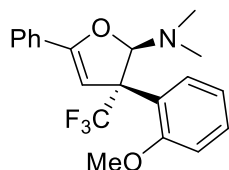
(2*R*,3*S*)-3-(4-(*Tert*-butyl)phenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ab):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-*N'*-(1-(4-(*tert*-butyl)phenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide **2b** (0.5 mmol, 199.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow solid in 94% yield (73.2 mg), Mp.65 - 66 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.73 (m, 2H), 7.52 – 7.47 (m, 2H), 7.45 – 7.34 (m, 5H), 5.80 (s, 1H), 5.78 (s, 1H), 2.14 (s, 6H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.2, 150.8,

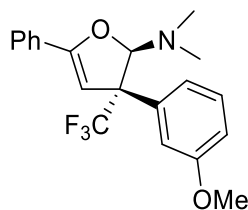
130.2, 130.0, 129.8, 129.5, 128.5, 127.1 (d, $J = 283.8$ Hz), 125.8, 124.4, 100.4 (d, $J = 2.3$ Hz), 91.8, 62.4 (q, $J = 25.3$ Hz), 39.8, 34.6, 31.4; ^{19}F NMR (376 MHz, CDCl_3) δ -74.42; Selected IR (KBr) ν (cm^{-1}): 3058, 2964, 2904, 2870, 2797, 1648, 1602, 1495, 1450, 1399, 1347, 1259, 1154, 1048, 1024, 821, 749, 686, 584; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{23}\text{H}_{27}\text{F}_3\text{NO}^+$: 390.2045. Found: 390.2048.

(2*R*,3*S*)-3-(2-Methoxyphenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ac):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(2-methoxyphenyl)ethylidene)benzenesulfonohydrazide **2c** (0.5 mmol, 186.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as white solid in 88% yield (63.9 mg), Mp. 110 – 111 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (dd, $J = 8.0, 1.6$ Hz, 2H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.41 – 7.31 (m, 4H), 6.97 – 6.93 (m, 2H), 5.89 (s, 1H), 5.83 (s, 1H), 3.83 (s, 3H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 157.8, 130.9, 130.0, 129.8, 129.4, 128.5, 127.1 (q, $J = 284.5$ Hz), 125.8, 122.2, 120.1, 112.8, 99.6, 92.6, 62.7 (q, $J = 26.8$ Hz), 56.0, 40.0; ^{19}F NMR (376 MHz, CDCl_3) δ -73.83; Selected IR (KBr) ν (cm^{-1}): 3061, 2993, 2942, 2838, 2795, 1641, 1600, 1493, 1449, 1342, 1258, 1155, 1041, 948, 751, 688; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_3\text{NO}_2^+$: 364.1524. Found: 364.1525.

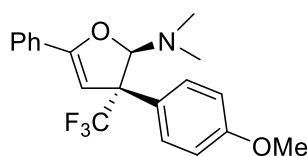
(2*R*,3*S*)-3-(3-Methoxyphenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ad):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(3-

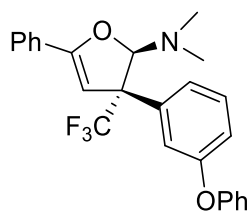
methoxyphenyl)ethylidene)benzenesulfonohydrazide **2d** (0.5 mmol, 186.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as white solid in 81% yield (58.9 mg), Mp. 57 – 58 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.70 (m, 2H), 7.45 – 7.37 (m, 3H), 7.30 – 7.22 (m, 1H), 7.20 – 7.12 (m, 2H), 6.92 – 6.87 (m, 1H), 5.78 (s, 1H), 5.73 (s, 1H), 3.82 (s, 3H), 2.14 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 158.4, 135.0, 129.8, 129.6, 128.6, 128.3, 126.9 (d, *J* = 283.7 Hz), 125.8, 122.7, 117.2, 112.7, 100.5 (d, *J* = 2.9 Hz), 91.6 (d, *J* = 1.8 Hz), 62.7 (q, *J* = 25.2 Hz), 55.4, 39.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.34; Selected IR (KBr) ν (cm⁻¹): 2953, 2851, 2797, 1721, 1647, 1602, 1583, 1493, 1450, 1347, 1261, 1172, 1151, 1046, 955, 747, 696; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₀H₂₁F₃NO₂⁺: 364.1524. Found: 364.1525.

(2*R*,3*S*)-3-(4-Methoxyphenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ae):



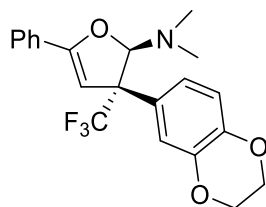
The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide **2e** (0.5 mmol, 186.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow oil in 63% yield (45.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.70 (m, 2H), 7.52 – 7.45 (m, 2H), 7.43 – 7.37 (m, 3H), 6.90 – 6.84 (m, 2H), 5.76 (s, 1H), 5.73 (s, 1H), 3.82 (s, 3H), 2.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 158.1, 131.2, 129.8, 129.4, 128.4, 126.9 (q, *J* = 283.9 Hz), 125.7, 125.3, 112.7, 100.3 (d, *J* = 3.0 Hz), 91.7 (d, *J* = 1.5 Hz), 61.9 (q, *J* = 25.4 Hz), 55.2, 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.86; Selected IR (KBr) ν (cm⁻¹): 2939, 2839, 1515, 1493, 1449, 1257, 1153, 1045, 950, 822, 749, 688; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₀H₂₁F₃NO₂⁺: 364.1524. Found: 364.1525.

(2*R*,3*S*)-*N,N*-Dimethyl-3-(3-phenoxyphenyl)-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3af):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(3-phenoxyphenyl)ethylidene)benzenesulfonohydrazide **2f** (0.5 mmol, 217.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as clear oil in 72% yield (61.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.69 (m, 2H), 7.42 – 7.37 (m, 3H), 7.35 – 7.28 (m, 5H), 7.12 – 7.06 (m, 1H), 7.01 – 6.96 (m, 3H), 5.74 (s, 1H), 5.72 (s, 1H), 2.15 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.6, 157.6, 155.7, 135.4, 129.8, 129.7, 129.6, 128.6, 128.5, 126.8 (q, *J* = 283.8 Hz), 125.8, 125.3, 123.0, 122.6, 119.1, 118.2, 100.3 (d, *J* = 2.0 Hz), 91.3, 62.7 (q, *J* = 25.4 Hz), 39.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.35; Selected IR (KBr) ν (cm⁻¹): 3063, 2946, 2851, 2797, 1646, 1852, 1488, 1450, 1244, 1174, 1148, 1046, 904, 740, 694; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₅H₂₃F₃NO₂⁺: 426.1681. Found: 426.1684.

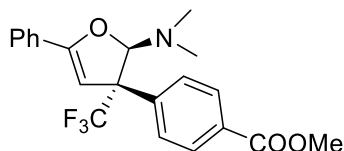
(2*R*,3*S*)-3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ag):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-*N'*-(1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide **2g** (0.5 mmol, 200.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as clear oil in 85% yield (66.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.69 (m, 2H), 7.42 – 7.37 (m, 3H), 7.10 – 7.08 (m, 1H), 7.05 – 7.02 (m, 1H), 6.83 – 6.80 (m, 1H), 5.73 (s, 1H), 5.67 (s, 1H), 4.27 (s, 4H), 2.15 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 143.4, 142.5, 129.8, 128.5, 126.9 (q, *J* = 283.5 Hz), 126.5, 125.8, 125.5, 123.4, 119.5, 116.1, 100.4, 91.8, 64.5, 64.4, 62.1 (q, *J* = 24.9 Hz), 39.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.58; Selected IR (KBr) ν (cm⁻¹): 2978, 1510, 1307, 1250,

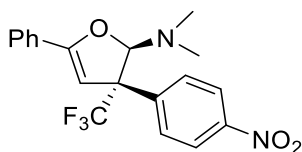
1171, 1069, 1047, 898, 749; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{21}F_3NO_3^+$: 392.1474. Found: 392.1480.

Methyl 4-((2*R*,3*S*)-2-(dimethylamino)-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-3-yl)benzoate (3ah):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), methyl (*Z*)-4-(2,2,2-trifluoro-1-(2-tosylhydrazono)ethyl)benzoate **2h** (0.5 mmol, 200.2 mg), $CuCl_2$ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as clear oil in 39% yield (30.5 mg). 1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.76 – 7.71 (m, 2H), 7.69 – 7.64 (m, 2H), 7.44 – 7.39 (m, 3H), 5.81 (s, 1H), 5.78 (s, 1H), 3.93 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 158.8, 138.7, 130.4, 129.8, 129.6, 128.6, 128.5, 126.7 (q, J = 283.7 Hz), 125.8, 100.4 (d, J = 3.1 Hz), 90.9, 63.0 (q, J = 25.3 Hz), 52.3, 39.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.12; Selected IR (KBr) ν (cm^{-1}): 3175, 2955, 1726, 1598, 1438, 1362, 1278, 1195, 1171, 1078, 999, 876, 748, 562; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{21}F_3NO_3^+$: 392.1474. Found: 392.1476.

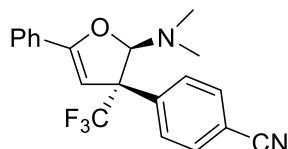
(2*R*,3*S*)-*N,N*-Dimethyl-3-(4-nitrophenyl)-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ai):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(4-nitrophenyl)ethylidene)benzenesulfonohydrazide **2i** (0.5 mmol, 193.7 mg), $CuCl_2$ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as yellow oil in 44% yield (33.3 mg). 1H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 2H), 7.80 – 7.71 (m, 4H), 7.45 – 7.41 (m, 3H), 5.82 (s, 1H), 5.75 (s, 1H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 147.7, 141.0, 131.4, 130.0, 129.3, 128.6, 126.4 (q, J = 284.2 Hz), 125.9, 122.4, 100.2 (d, J = 22.2 Hz), 90.2,

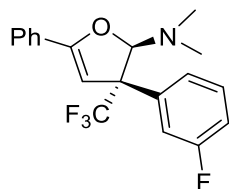
63.1 (q, $J = 25.4$ Hz), 39.8; ^{19}F NMR (376 MHz, CDCl_3) δ -74.00; Selected IR (KBr) ν (cm^{-1}): 2949, 1599, 1523, 1350, 1258, 1172, 1047, 749, 693; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_3^+$: 379.1270. Found: 379.1266.

4-((2*R*,3*S*)-2-(Dimethylamino)-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-3-yl)benzonitrile (3aj):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-*N'*-(1-(4-cyanophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide **2j** (0.5 mmol, 183.7 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.6). The product was obtained as white solid in 57% yield (40.9 mg), Mp 86 – 87 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.61 (m, 4H), 7.59 – 7.54 (m, 2H), 7.37 – 7.32 (m, 3H), 5.72 (s, 1H), 5.65 (s, 1H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 139.0, 136.6, 131.1, 130.0, 129.3, 128.6, 126.5 (q, $J = 283.8$ Hz), 125.9, 118.7, 112.1, 100.2 (d, $J = 1.9$ Hz), 90.2, 63.0 (q, $J = 25.7$ Hz), 39.8; ^{19}F NMR (376 MHz, CDCl_3) δ -74.07; Selected IR (KBr) ν (cm^{-1}): 2952, 2229, 11726, 1492, 1450, 1259, 1153, 1047, 822, 748, 697; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{NO}_2^+$: 359.1371. Found: 359.1375.

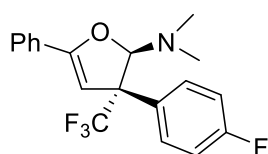
(2*R*,3*S*)-3-(3-Fluorophenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ak):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(3-fluorophenyl)ethylidene)benzenesulfonohydrazide **2k** (0.5 mmol, 180.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as clear oil in 76% yield (53.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.70 (m, 2H), 7.44 – 7.38 (m, 3H), 7.37 – 7.27 (m,

3H), 7.09 – 7.02 (m, 1H), 5.78 (s, 1H), 5.70 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 160.8, 158.8, 136.0 (d, $J = 7.3$ Hz), 129.7, 129.6, 128.7 (d, $J = 8.0$ Hz), 128.6, 126.7 (q, $J = 283.7$ Hz), 125.8, 117.7 (d, $J = 23.2$ Hz), 115.1 (d, $J = 20.9$ Hz), 100.4 (d, $J = 2.5$ Hz), 91.1, 62.7 (q, $J = 26.2$ Hz), 39.8; ^{19}F NMR (376 MHz, CDCl_3) δ -74.32, -113.75; Selected IR (KBr) ν (cm^{-1}): 2947, 1588, 1492, 1347, 1262, 1243, 1177, 1146, 12046, 748, 693; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_4\text{NO}^+$: 352.1325. Found: 352.1326.

(2*R*,3*S*)-3-(4-Fluorophenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3al):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(4-fluorophenyl)ethylidene)benzenesulfonohydrazide **2l** (0.5 mmol, 180.2 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as white solid in 66% yield (46.4 mg), Mp.56 – 57 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.65 (m, 4H), 7.44 – 7.38 (m, 3H), 7.33 – 7.28 (m, 2H), 5.76 (s, 1H), 5.69 (s, 1H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 136.6, 133.3, 132.2, 129.8, 129.6, 128.6, 126.7 (q, $J = 283.6$ Hz), 125.8, 100.2 (d, $J = 2.3$ Hz), 94.5, 90.9, 62.6 (q, $J = 25.5$ Hz), 39.8; ^{19}F NMR (376 MHz, CDCl_3) δ -74.45; Selected IR (KBr) ν (cm^{-1}): 2945, 1560, 1486, 1449, 1393, 1346, 1258, 1153, 1046, 952, 807, 749; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_4\text{NO}^+$: 352.1325. Found: 352.1326.

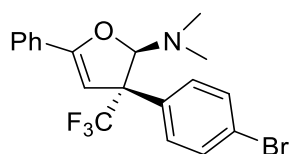
(2*R*,3*S*)-3-(4-Chlorophenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3am):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-*N'*-(1-(4-chlorophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide **2m** (0.5 mmol, 188.4 mg), CuCl_2 (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH_2Cl_2 (4 mL) according to the general procedure (EA/PE =

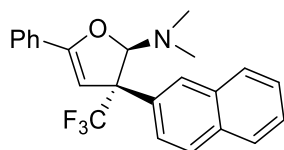
5%, Rf = 0.7). The product was obtained as white solid in 70% yield (51.5 mg), Mp.57 – 58 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.68 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.35 – 7.29 (m, 2H), 5.77 (s, 1H), 5.71 (s, 1H), 2.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.6, 134.2, 132.0, 131.5, 129.7, 129.6, 128.5, 127.6, 126.7 (q, *J* = 283.9 Hz), 125.7, 100.2 (d, *J* = 3.1 Hz), 91.0 (d, *J* = 1.9 Hz), 62.4 (q, *J* = 25.3 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.61; Selected IR (KBr) ν (cm⁻¹): 2948, 2851, 2798, 1646, 1597, 1494, 1258, 1172, 1153, 1096, 1047, 953, 814, 741, 697, 579; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₁₈ClF₃NO⁺: 368.1029. Found: 368.1032.

(2*R*,3*S*)-3-(4-Bromophenyl)-*N,N*-dimethyl-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3an):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-*N'*-(1-(4-bromophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonylhydrazide **2n** (0.5 mmol, 210.6 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, Rf = 0.7). The product was obtained as white solid in 46% yield (37.9 mg), Mp.62 – 63 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.68 (m, 2H), 7.50 – 7.38 (m, 7H), 5.76 (s, 1H), 5.71 (s, 1H), 2.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 132.6, 131.9, 130.5, 129.7, 129.5, 128.5, 126.6 (q, *J* = 283.7 Hz), 125.7, 122.5, 100.2 (d, *J* = 3.0 Hz), 90.9 (d, *J* = 1.9 Hz), 62.4 (q, *J* = 25.5 Hz), 39.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.59; Selected IR (KBr) ν (cm⁻¹): 2947, 1653, 1589, 1491, 1449, 1397, 1347, 1257, 1171, 1154, 1046, 952, 810, 740, 691, 579, 511; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₁₈BrF₃NO⁺: 412.0524. Found: 412.0529.

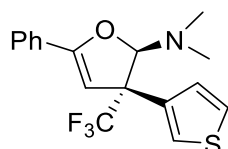
(2*R*,3*S*)-*N,N*-Dimethyl-3-(naphthalen-2-yl)-5-phenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ao):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(naphthalen-2-

yl)ethylidene)benzenesulfonohydrazide **2o** (0.5 mmol, 196.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow oil in 96% yield (73.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 8.01 (m, 1H), 7.87 – 7.82 (m, 2H), 7.81 – 7.76 (m, 3H), 7.71 – 7.68 (m, 1H), 7.50 – 7.48 (m, 2H), 7.45 – 7.38 (m, 3H), 5.92 (s, 1H), 5.88 (s, 1H), 2.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.6, 132.9, 132.7, 131.5, 131.4, 129.9, 129.7, 129.2, 128.6, 128.5, 128.4, 127.6, 127.1 (q, *J* = 284.3 Hz), 126.6, 126.0, 125.9, 100.5 (d, *J* = 2.4 Hz), 91.7, 63.0 (q, *J* = 25.3 Hz), 39.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.00; Selected IR (KBr) ν (cm⁻¹): 2946, 1449, 1248, 1171, 1151, 1048, 813, 748, 688, 476; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₂₃H₂₁F₃NO⁺: 384.1575. Found: 384.1580.

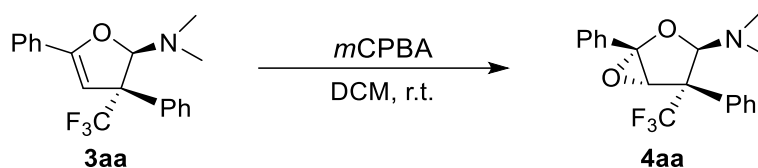
(2*R*,3*S*)-*N,N*-Dimethyl-5-phenyl-3-(thiophen-3-yl)-3-(trifluoromethyl)-2,3-dihydrofuran-2-amine (3ap):



The title compound was prepared from (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 35.0 mg), (*Z*)-4-methyl-*N'*-(2,2,2-trifluoro-1-(thiophen-3-yl)ethylidene)benzenesulfonohydrazide **2p** (0.5 mmol, 174.2 mg), CuCl₂ (0.01 mmol, 1.7 mg), KO^tBu (0.52 mmol, 58.3 mg) in CH₂Cl₂ (4 mL) according to the general procedure (EA/PE = 5%, R_f = 0.7). The product was obtained as yellow oil in 57% yield (38.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.69 (m, 2H), 7.41 – 7.39 (m, 4H), 7.29 – 7.27 (m, 1H), 7.23 – 7.21 (m, 1H), 5.73 (s, 1H), 5.65 (s, 1H), 2.17 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 134.0, 129.7, 129.5, 129.4, 128.5, 126.5 (d, *J* = 283.0 Hz), 125.7, 125.3, 124.0, 100.1 (d, *J* = 2.5 Hz), 92.3, 60.5 (q, *J* = 26.1 Hz), 39.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -75.25; Selected IR (KBr) ν (cm⁻¹): 2946, 1735, 1654, 1449, 1413, 1259, 1169, 1048, 749, 698; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₁₇F₃NOS⁺: 340.0983. Found: 340.0977.

General procedure for applications and their spectral data

(1*R*,3*R*,4*R*,5*S*)-*N,N*-Dimethyl-1,4-diphenyl-4-(trifluoromethyl)-2,6-dioxabicyclo[3.1.0]hexan-3-amine (4aa):



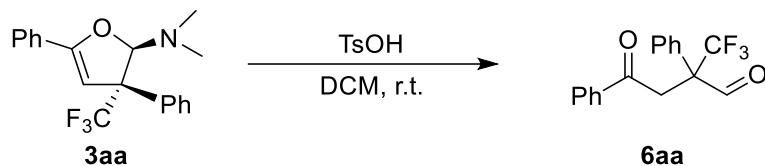
A solution of **3aa** (0.2 mmol, 66.7 mg) and *m*CPBA (0.3 mmol, 51.8 mg) was kept at r.t. for 3 h. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography to afford the product **4aa** as white solid in 93% yield (64.9 mg) (MeOH/DCM = 5%, *R*_f = 0.4), Mp.85 – 86 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 7.65 (m, 4H), 7.48 – 7.43(m, 3H), 7.38 – 7.33 (m, 3H), 5.85 (s, 1H), 5.82 (s, 1H), 3.37 (s, 3H), 2.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 130.7, 130.4, 129.4, 129.0, 127.8, 127.7, 126.2 (q, *J* = 284.4 Hz), 125.7, 102.3 (d, *J* = 2.0 Hz), 96.9 (d, *J* = 2.0 Hz), 65.3 (q, *J* = 26.2 Hz), 61.7, 50.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -71.01; Selected IR (KBr) ν (cm⁻¹): 3061, 2962, 1666, 1496, 1449, 1284, 1256, 1181, 1153, 1074, 1008, 758, 716, 697; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₉H₁₉F₃NO₂⁺: 350.1368. Found: 350.1362.

***N*-((2*R*,3*S*)-3,5-Diphenyl-3-(trifluoromethyl)-2,3-dihydrofuran-2-yl)-*N*-methylnitrous amide (**5aa**):**



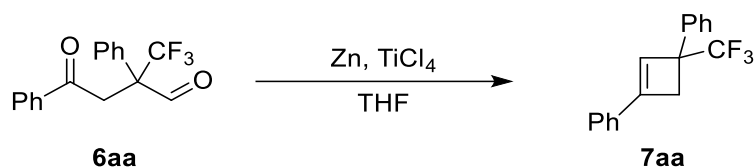
A solution of **3aa** (0.2 mmol, 66.7 mg) and TEMPO (0.02 mmol, 3 mg) in MeCN (2 mL) was mixed fully, then *tert*-Butyl nitrite (0.3 mmol, 36 ul) was added dropwise under air atmosphere. The reaction solution was stirred under room temperature. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography to afford the product **5aa** as white solid in 75% yield (52.3 mg) (EA/PE = 10%, *R*_f = 0.3), Mp.127 – 128 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.71 (m, 2H), 7.64 (s, 1H), 7.48 – 7.44 (m, 3H), 7.37 – 7.32 (m, 5H), 5.99 (s, 1H), 2.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 131.7, 130.6, 129.3, 129.1, 128.8, 128.7, 128.2, 126.3(q, *J* = 283.7 Hz), 126.0, 95.6 (d, *J* = 2.1 Hz), 92.6, 64.1 (q, *J* = 26.6 Hz), 27.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -73.40; Selected IR (KBr) ν (cm⁻¹): 2966, 1477, 1449, 1374, 1259, 1182, 1156, 1010, 749, 712; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₈H₁₆F₃N₂O₂⁺: 349.1164. Found: 349.1166.

4-Oxo-2,4-diphenyl-2-(trifluoromethyl)butanal (**6aa**):



A solution of **3aa** (0.2 mmol, 66.7 mg) and TsOH·H₂O (0.2 mmol, 38.0 mg) in DCM (2 mL) was mixed fully at room temperature. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography to afford the product **6aa** as white solid in 99% yield (60.6 mg) (EA/PE = 5%, R_f = 0.5), Mp.84 – 85 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.24 – 10.20 (m, 1H), 8.00 – 7.96 (m, 2H), 7.67 – 7.61 (m, 1H), 7.54 – 7.48 (m, 2H), 7.43 – 7.39 (m, 5H), 4.31 (d, *J* = 18.0 Hz, 1H), 4.20 (d, *J* = 18.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 194.7, 135.4, 134.2, 131.7, 129.0, 129.0, 128.9, 128.3, 128.0, 124.8 (d, *J* = 284.4 Hz), 59.4 (q, *J* = 23.2 Hz), 41.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -68.39; Selected IR (KBr) ν (cm⁻¹): 2965, 1734, 1685, 1597, 1449, 1356, 1244, 1171, 1001, 750, 701; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₁₄F₃O₂⁺: 307.0946. Found: 307.0946.

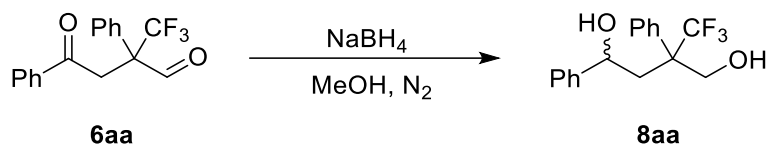
(3-(Trifluoromethyl)cyclobut-1-ene-1,3-diyl)dibenzene (**7aa**):



In a flame-dried flask, dry THF (2 mL) was added to zinc dust (1.6 mmol, 104.6 mg). The flask was cooled in an ice bath, and titanium tetrachloride (1M) (0.8 mmol, 0.8 mL) was added dropwise. A yellow cloud formed and the solution became dark blue. After 15 min, a solution of **6aa** (0.2 mmol, 61.3 mg) in THF (1 mL) was added to the reaction mixture. The reaction mixture was then heated to reflux for 3 h. After cooling the reaction to ambient temperature, 5 mL water was added and gas evolution was seen. After the bubbling subsided, the mixture was extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, dried over MgSO₄, filtered and the solvent was removed *in vacuo*. The resulting brown oil was purified by column chromatography to give **7aa** as yellow solid in 42% yield (23.1 mg) (EA/PE = 5%, R_f = 0.7), Mp.65 – 66 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.45 (m, 2H), 7.44 – 7.31 (m, 8H), 6.67 (d, *J* = 1.0 Hz, 1H), 3.51 (d, *J* = 13.0 Hz, 1H), 3.08 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (100 MHz,

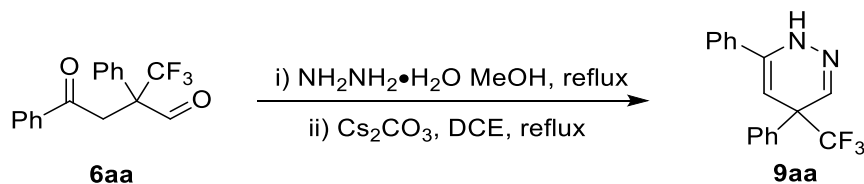
CDCl₃) δ 149.0, 137.2, 133.0, 129.1, 128.7, 128.6, 128.2, 127.7, 126.6 (q, J = 126.6 Hz), 125.1, 123.6 (q, J = 2.8 Hz), 52.0 (q, J = 28.9 Hz), 37.9 (q, J = 2.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.12; Selected IR (KBr) ν (cm⁻¹): 2931, 1448, 1295, 1148, 1007, 868, 749, 698; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₇H₁₄F₃⁺: 275.1048. Found: 275.1045.

1,3-Diphenyl-3-(trifluoromethyl)butane-1,4-diol (**8aa**):



To a solution of **6aa** (0.20 mmol, 61.3 mg) in MeOH (2 mL) was added NaBH₄ (0.4 mmol, 83.2 mg) at room temperature and the reaction mixture was stirred at the same temperature for 30 min under nitrogen atmosphere. The mixture was poured into H₂O (5 mL) and extracted with EtOAc (10 mL). The organic layer was washed with brine (10 mL) and dried with Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography to give **8aa** as colorless oil in 95% yield (58.9 mg) (EA/PE = 10%, R_f = 0.3). ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.43 (m, 2H), 7.38 – 7.27 (m, 8H), 5.18 (d, J = 9.7 Hz, 1H), 4.46 – 4.31 (m, 2H), 3.88 (m, 1H), 3.03 (s, 1H), 2.59 – 2.51 (m, 1H), 2.40 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 144.7, 137.2, 131.8, 129.1, 129.0, 128.9, 128.6, 128.2, 128.0, 125.5, 125.4, 71.6, 60.5 (d, J = 3.1 Hz), 52.1 (q, J = 21.7 Hz), 42.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -74.12; Selected IR (KBr) ν (cm⁻¹): 2968, 1492, 1449, 1275, 1261, 1144, 1058, 749, 699; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₇H₁₈F₃O₂⁺: 311.1259. Found: 311.1258.

4,6-Diphenyl-4-(trifluoromethyl)-1,4-dihydropyridazine (**9aa**):

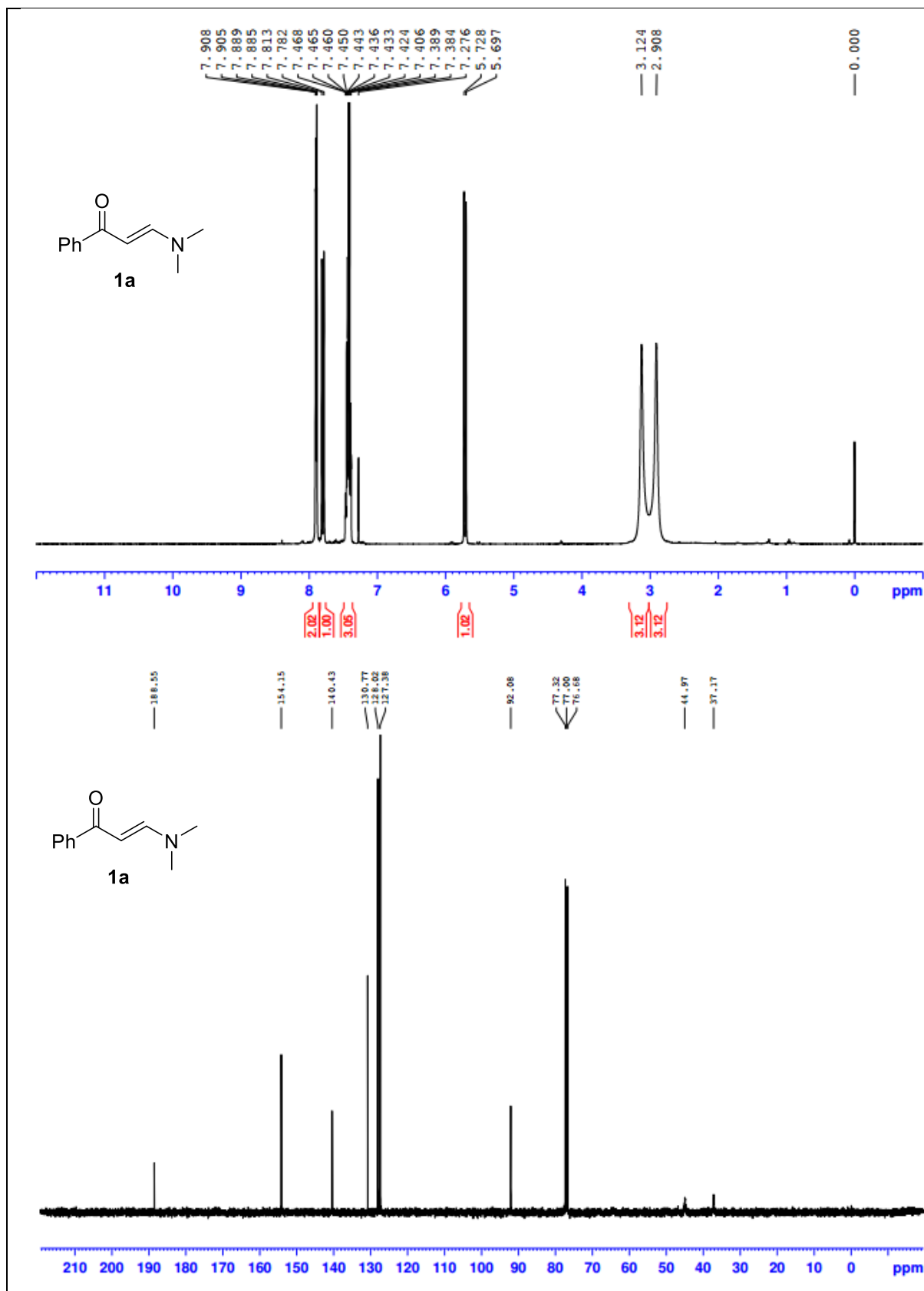


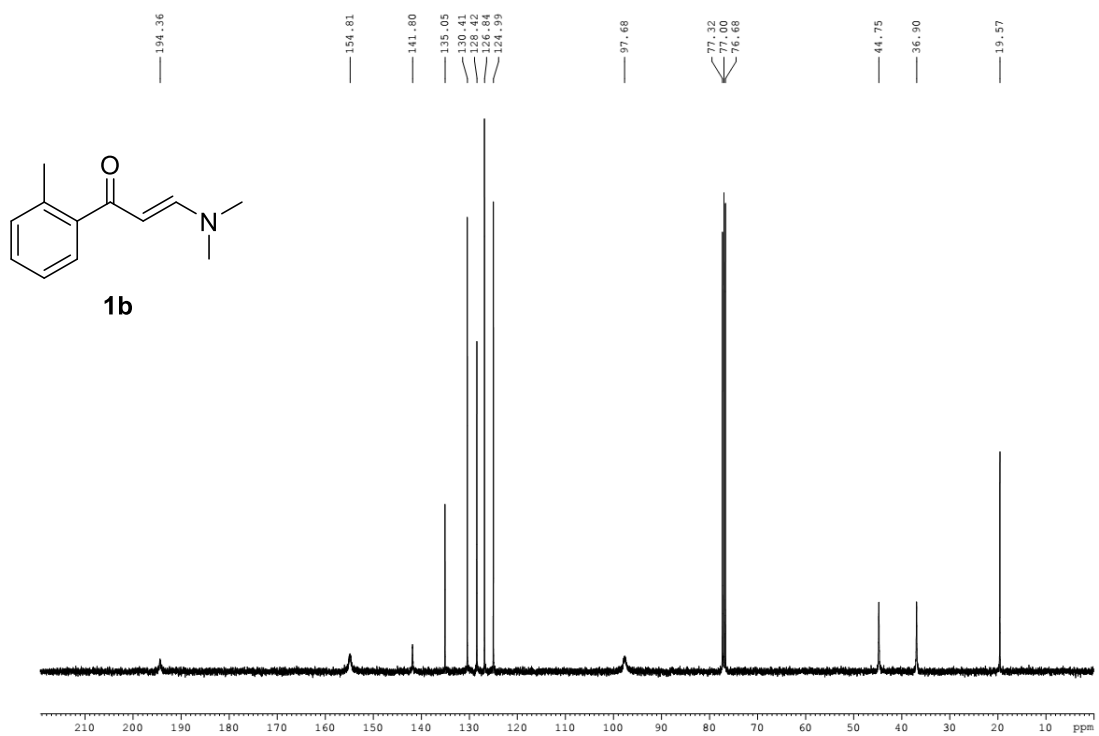
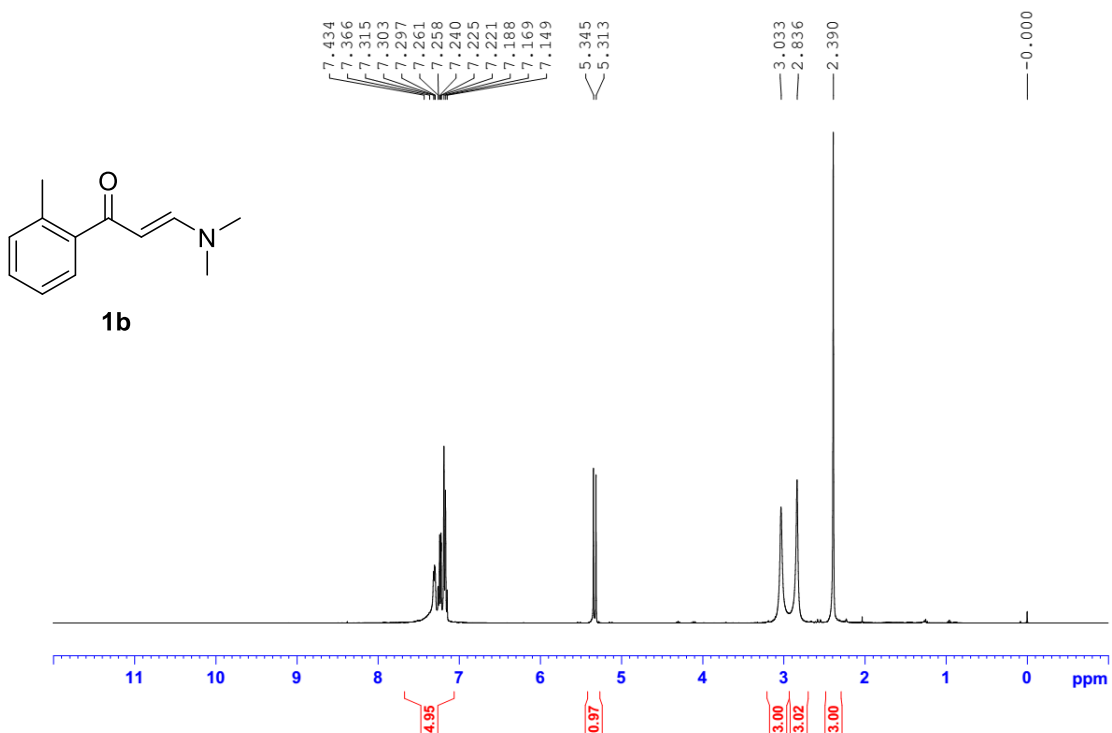
Step 1: To a flask was added **6aa** (0.2 mmol, 61.3 mg) and methanol (2 mL), the mixture was heated to 60 °C and stirred until **6aa** was dissolved. Then N₂H₄ • H₂O (0.44 mmol, 22mg) was added. After approximately 2 h, the reaction was completed (TLC), solvent was removed under vacuum and the solid was used without further purification.

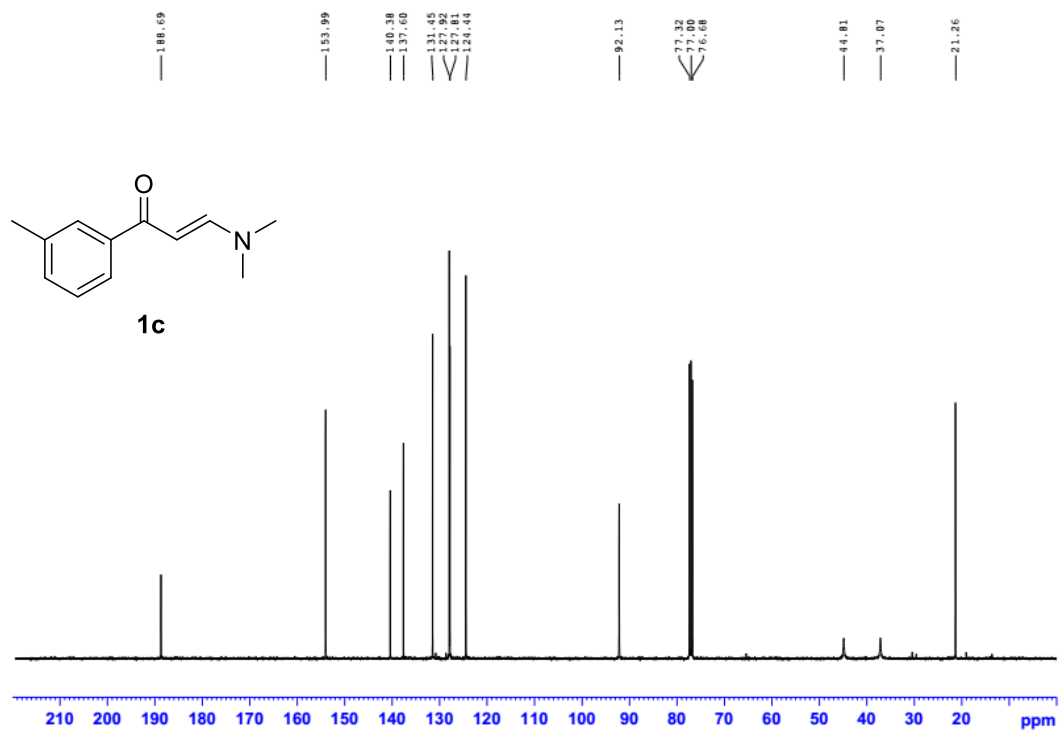
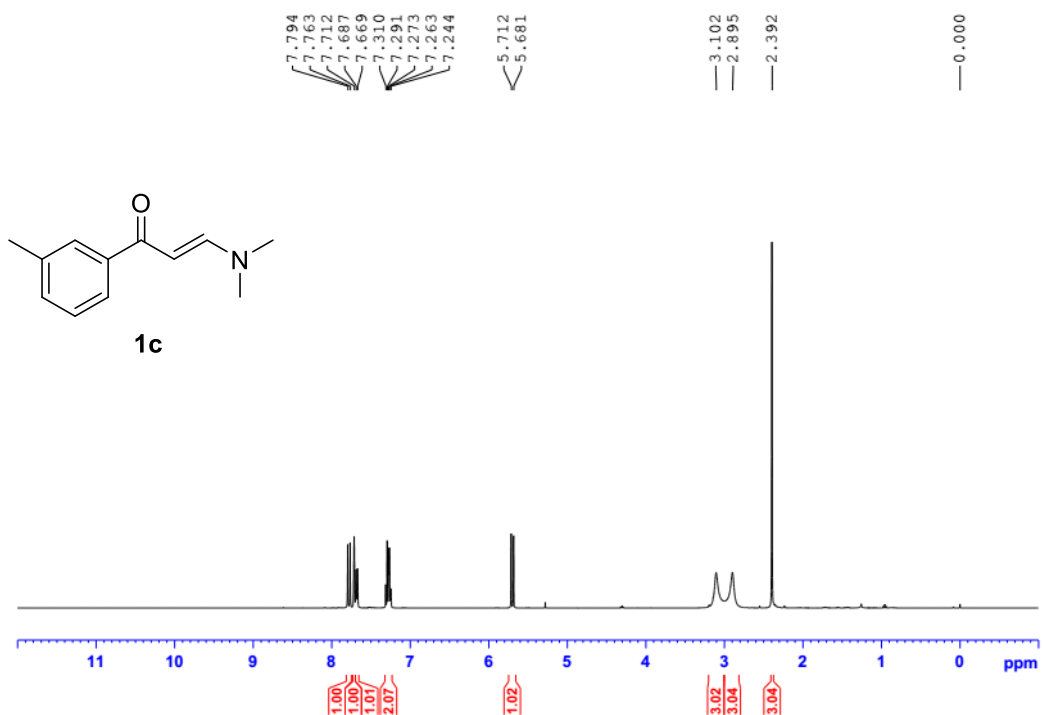
Step 2: Under argon atmosphere, the crude product of step 1, Cs₂CO₃ (0.6 mmol, 195.5 mg), and DCE (4 mL) were added to a 10 mL sealed tube. The resulting solution was stirred at reflux

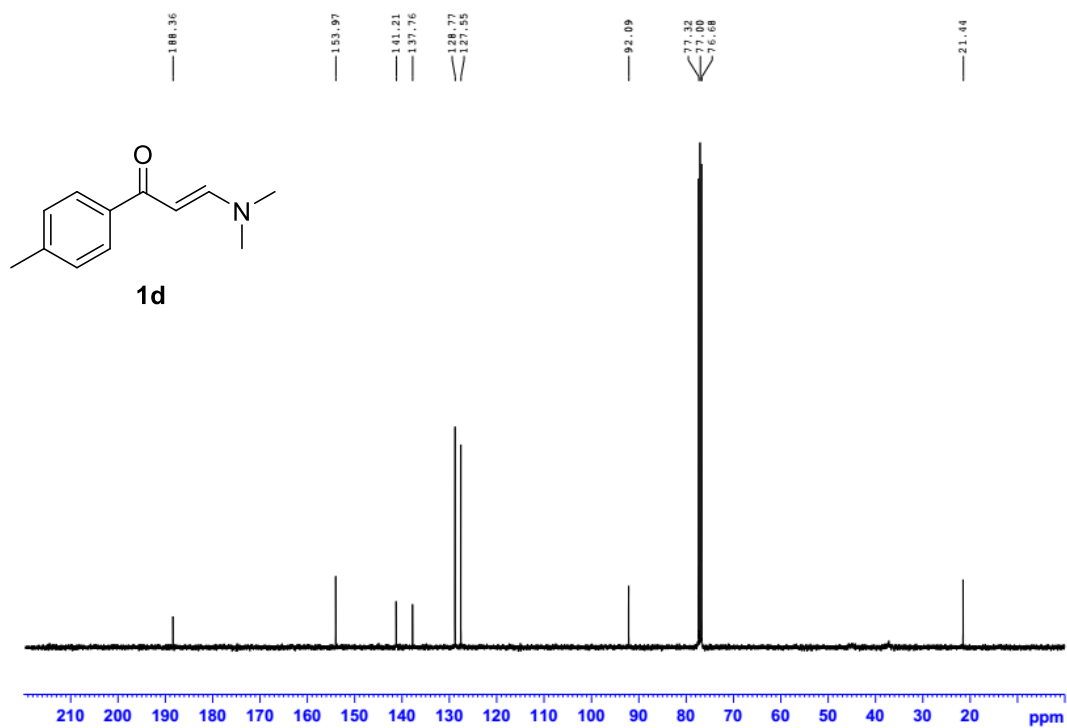
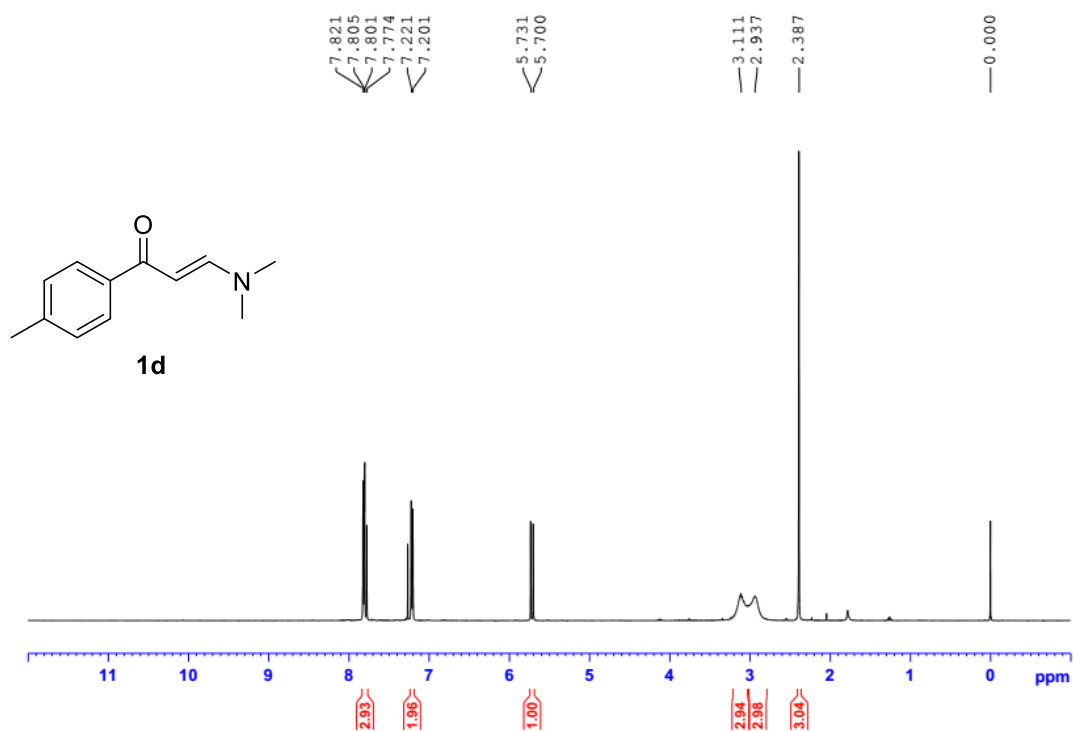
for 12 h. The mixture was then cooled to room temperature and solvent was removed under vacuum. The crude residue was purified by column chromatography to afford product **9aa** as white solid in (two steps yield: 94%, EA/PE = 10%, R_f = 0.3). Mp. 81 - 82 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.54 – 7.47 (m, 4H), 7.46 – 7.38 (m, 5H), 7.35 – 7.30 (m, 1H), 6.90 – 6.89 (m, 1H), 5.13 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 139.6, 134.1, 130.2, 129.7, 129.1, 128.8, 128.1, 127.5, 125.8, 125.5 (q, J = 283.5 Hz), 90.3 (d, J = 2.6 Hz), 48.2 (q, J = 27.4 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -72.03; Selected IR (KBr) ν (cm^{-1}): 2966, 1691, 1460, 1275, 1260, 1153, 750, 695; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_2^+$: 303.1104. Found: 303.1103.

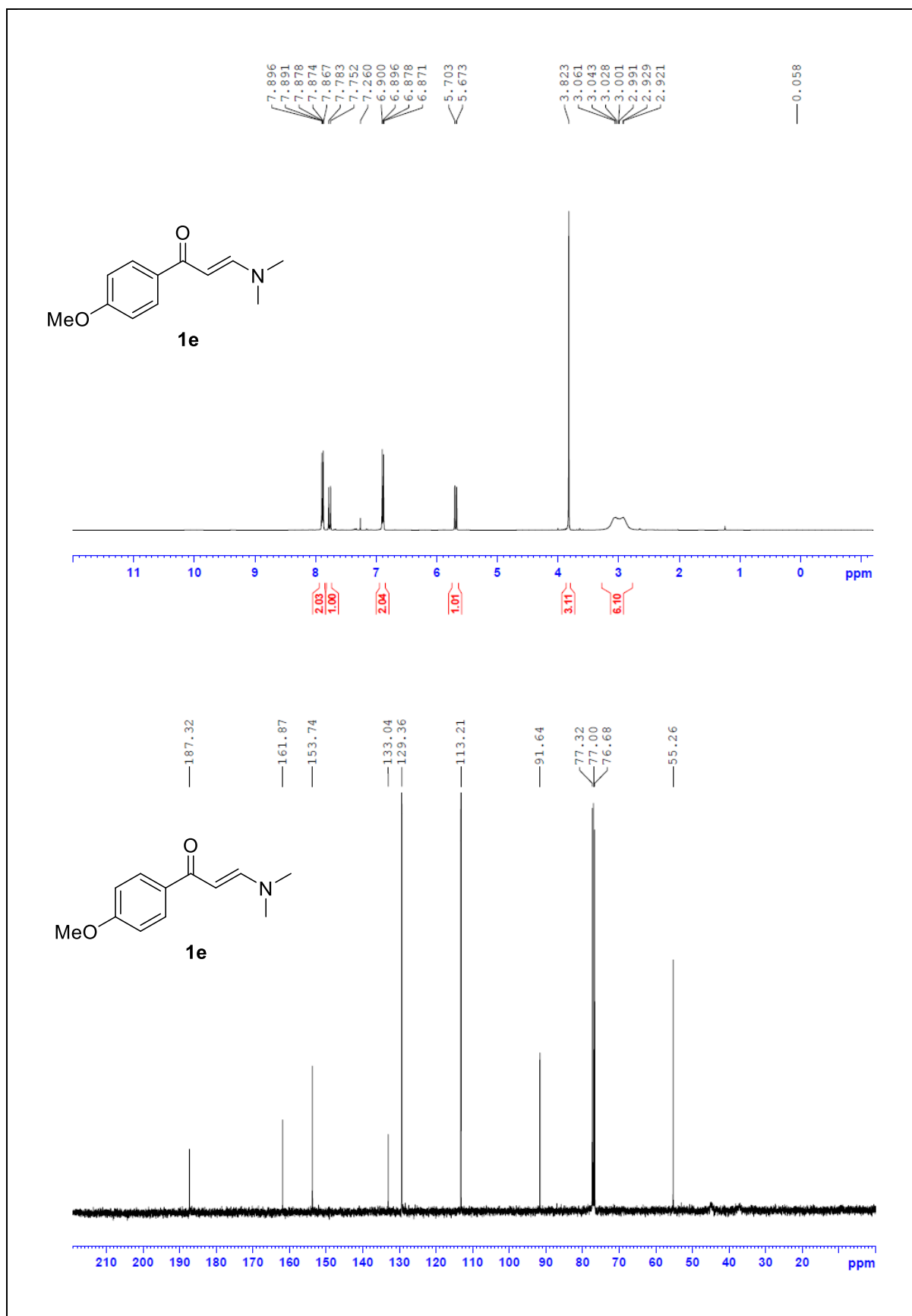
NMR Spectra for enaminones

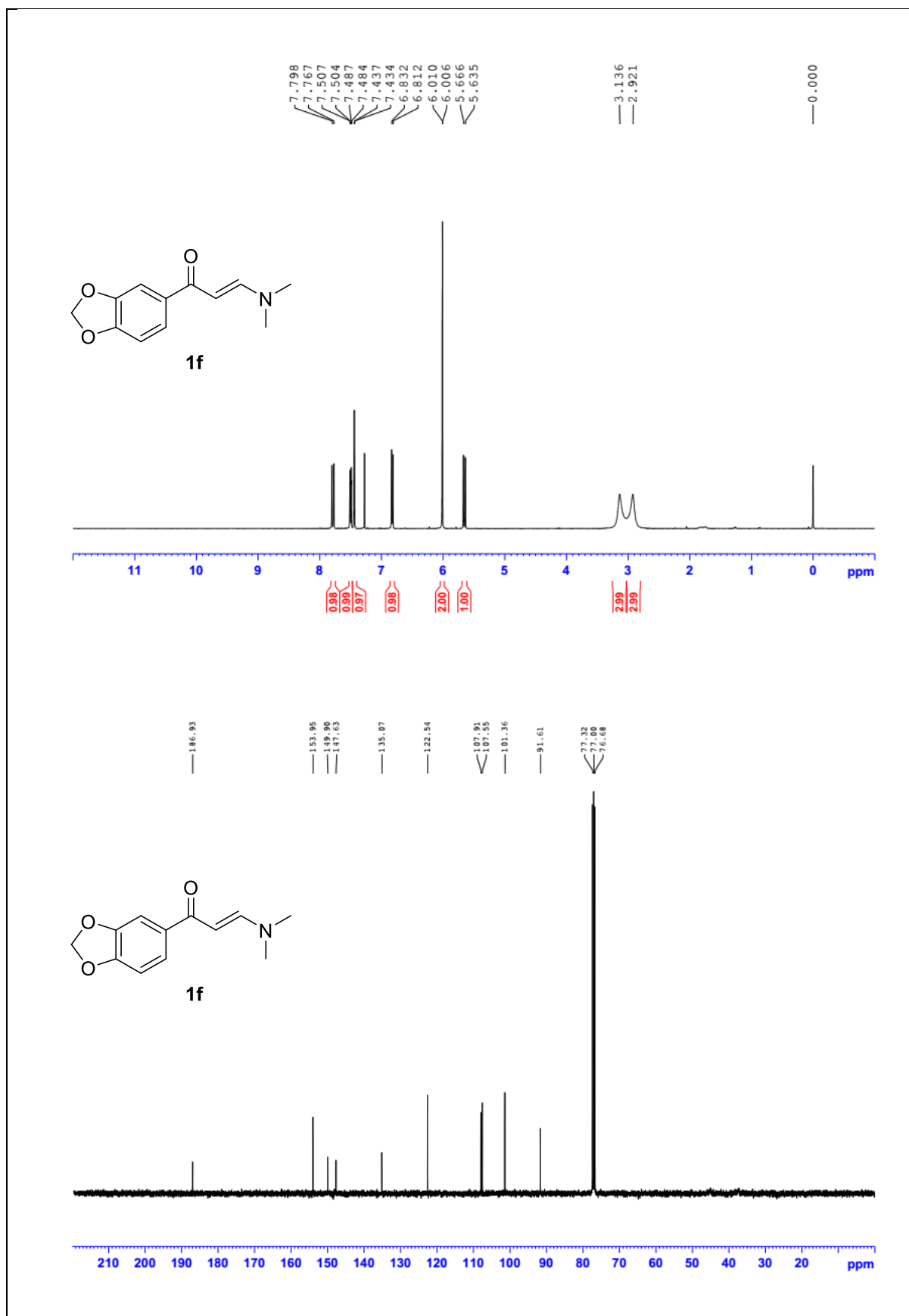


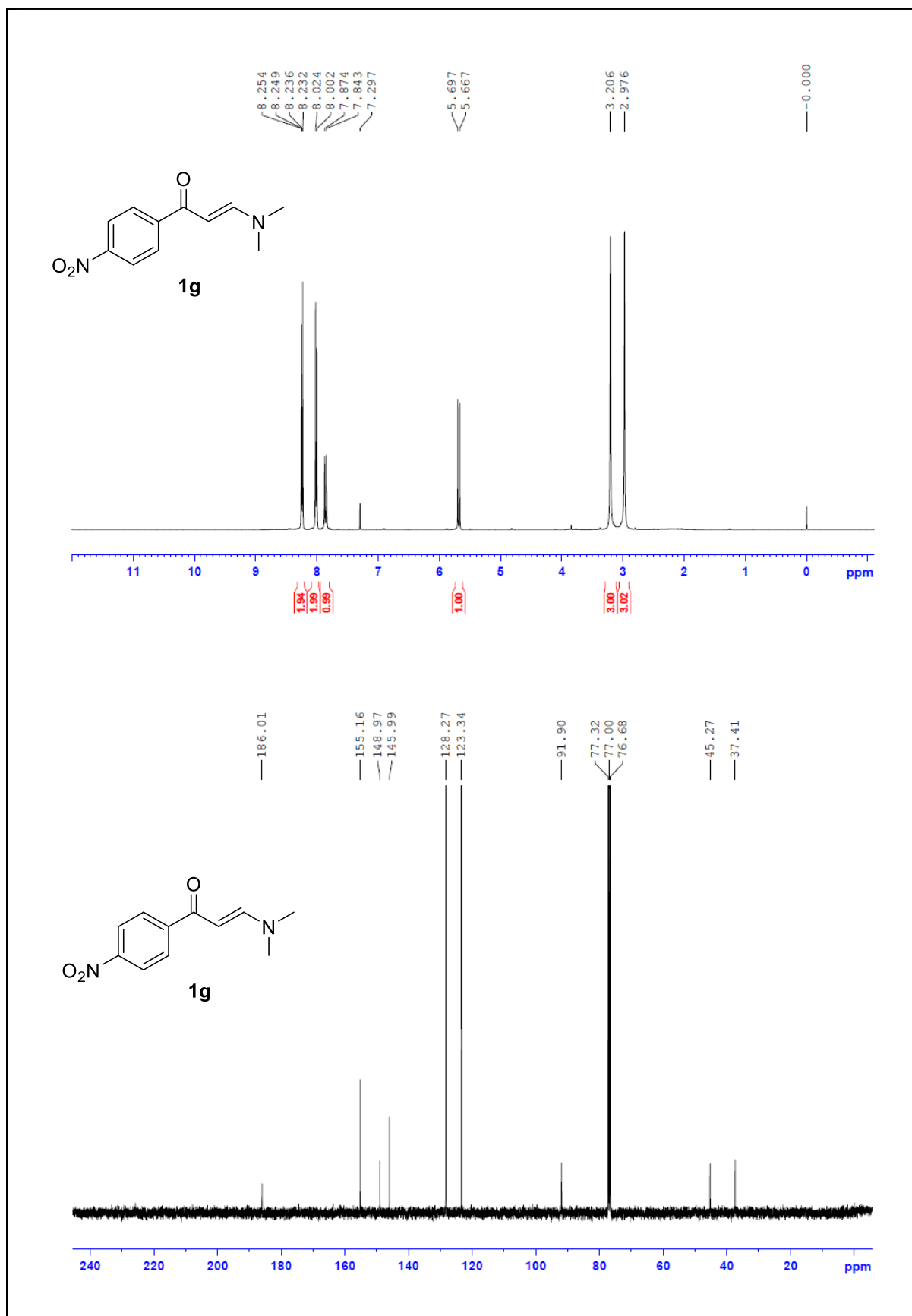


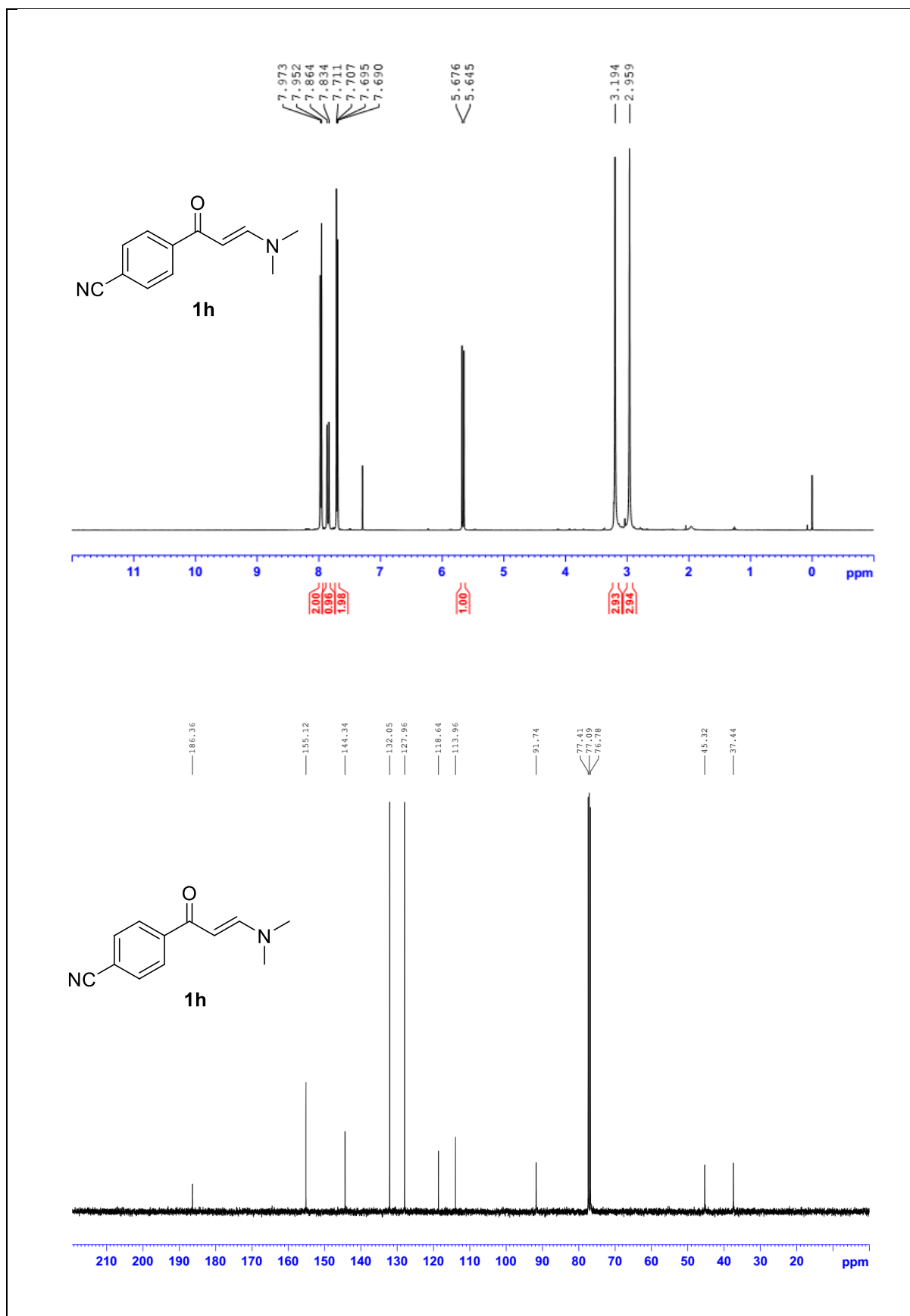


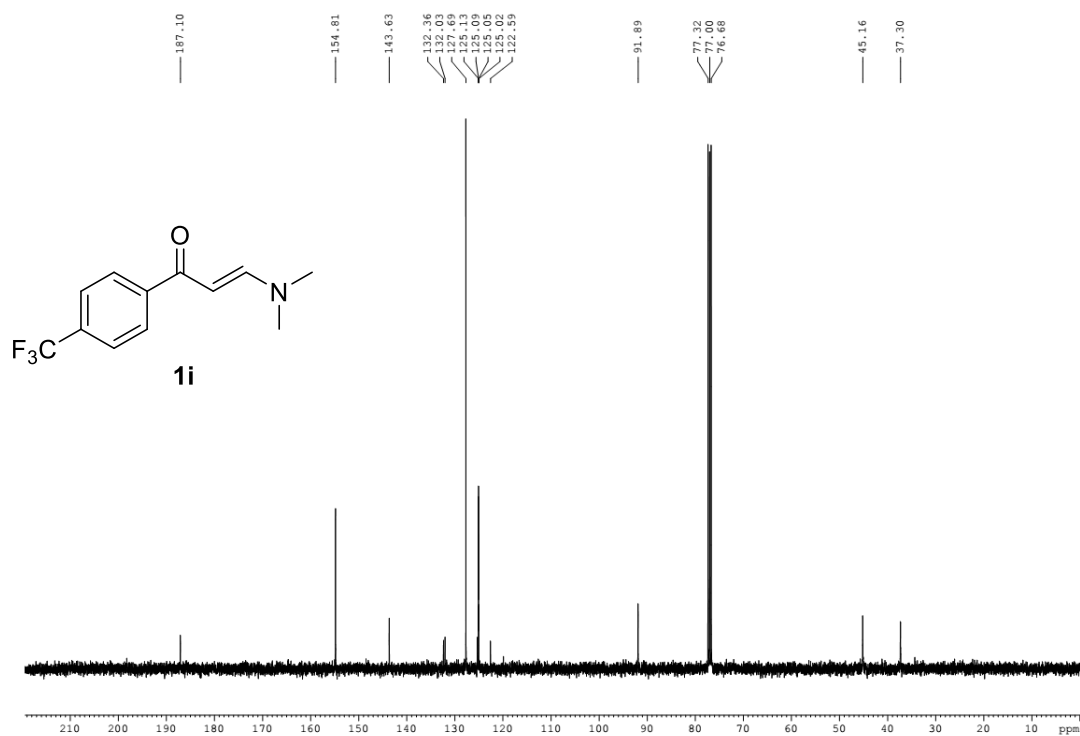
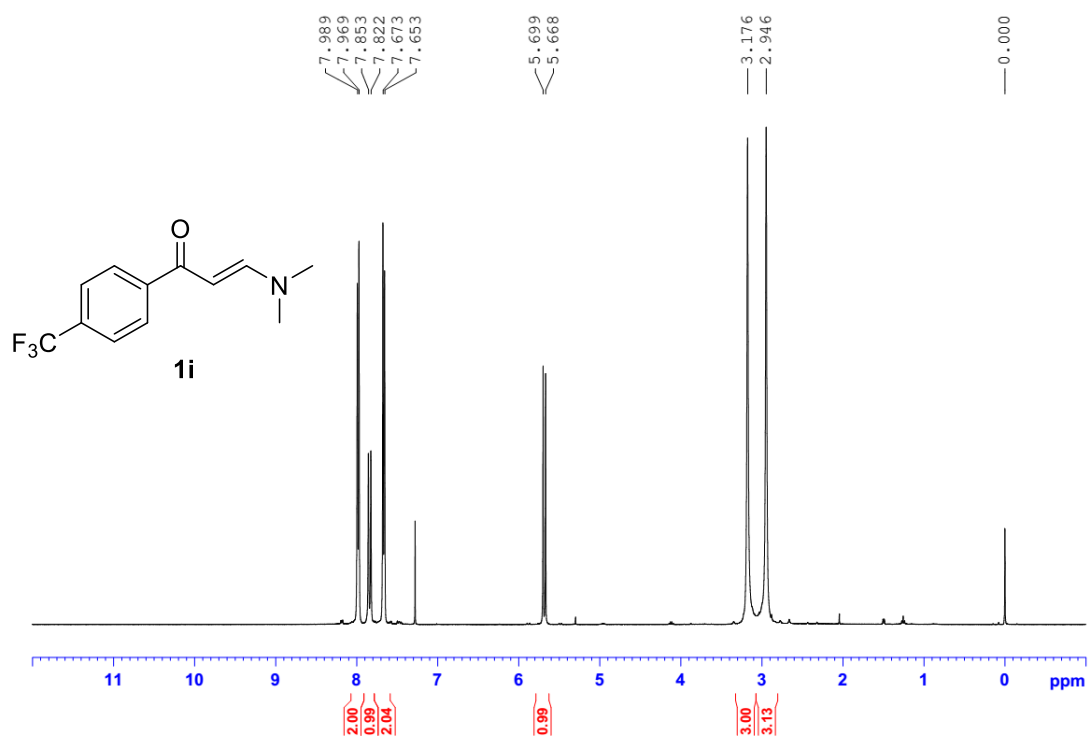


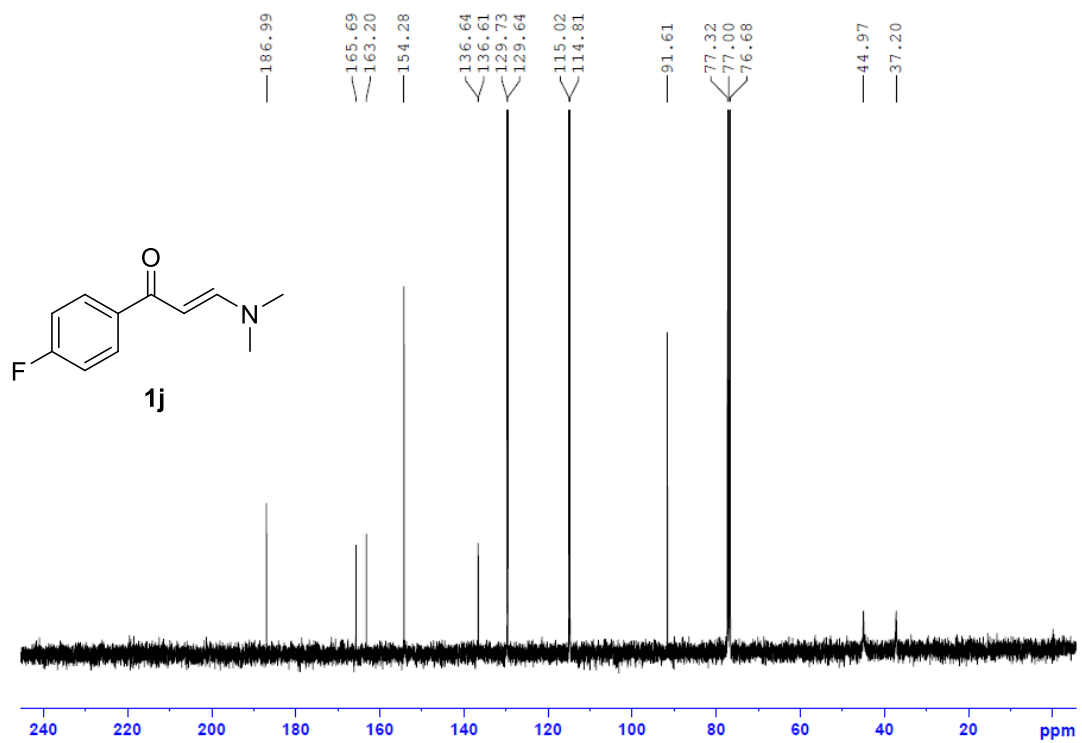
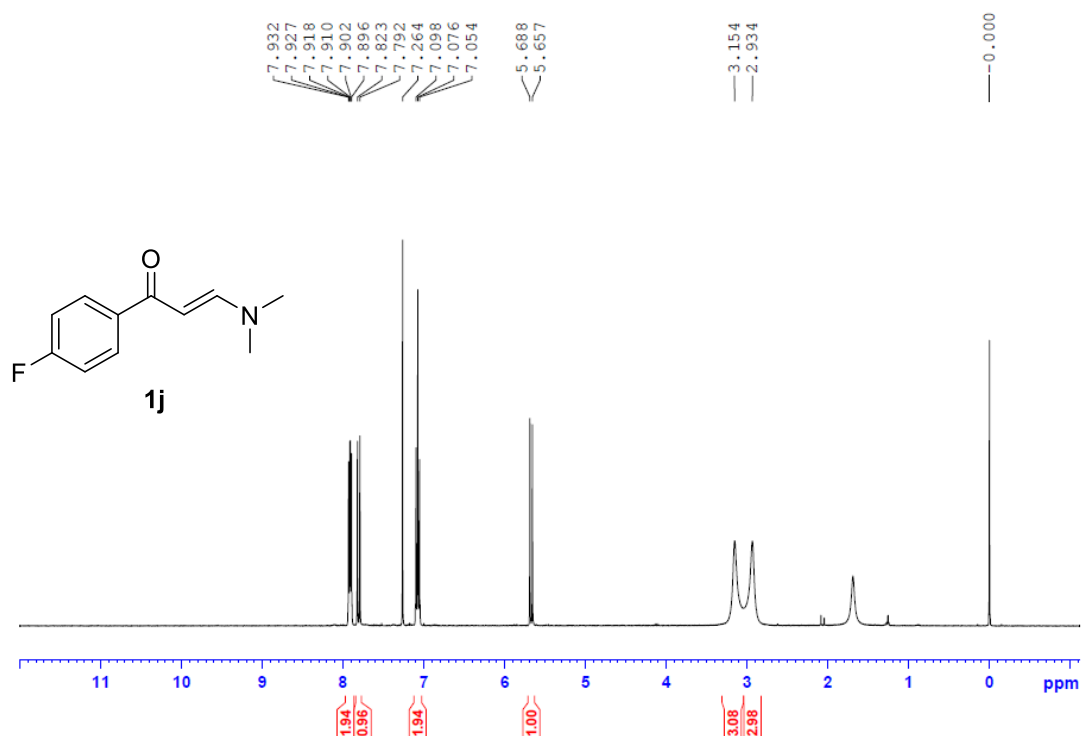


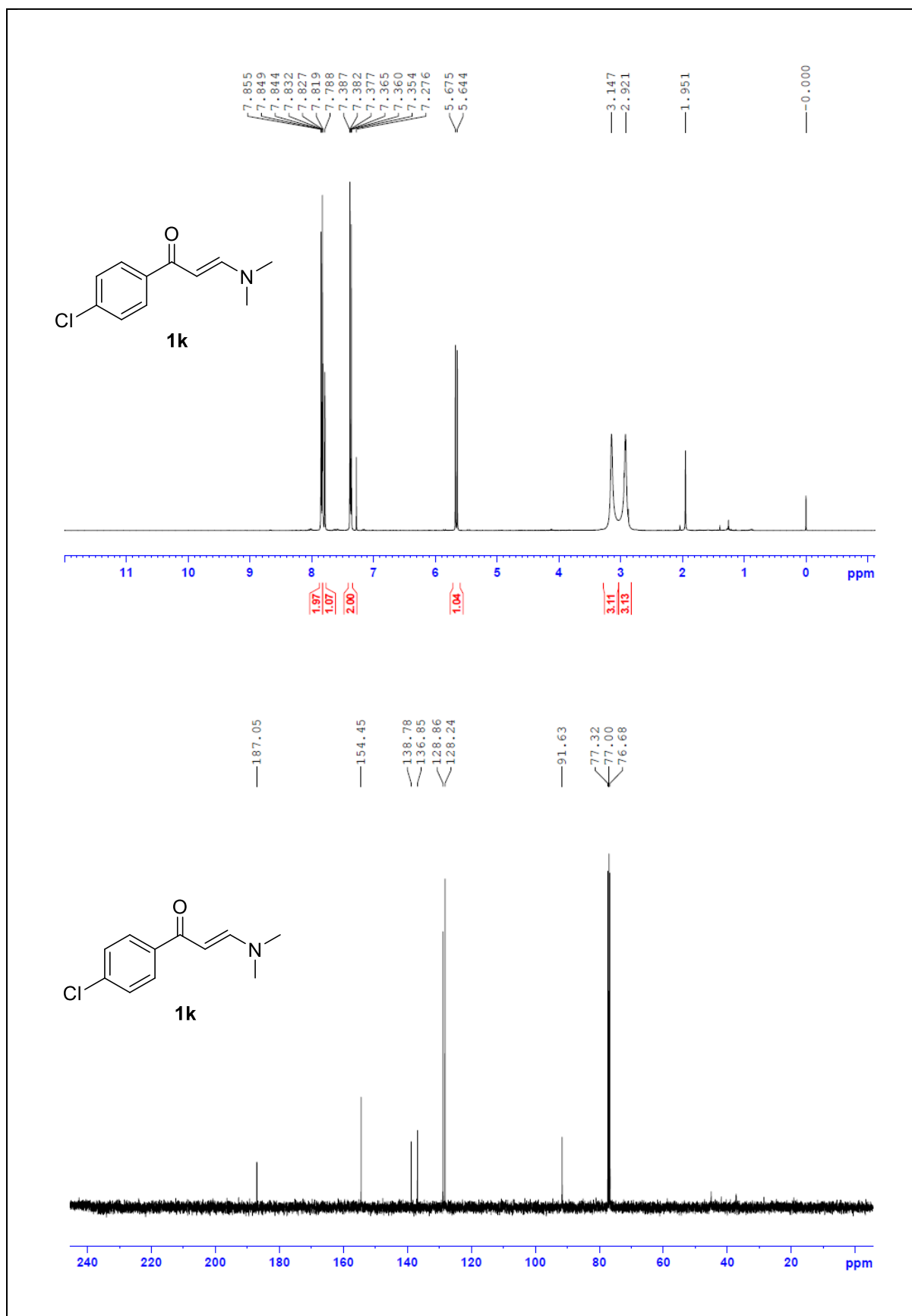


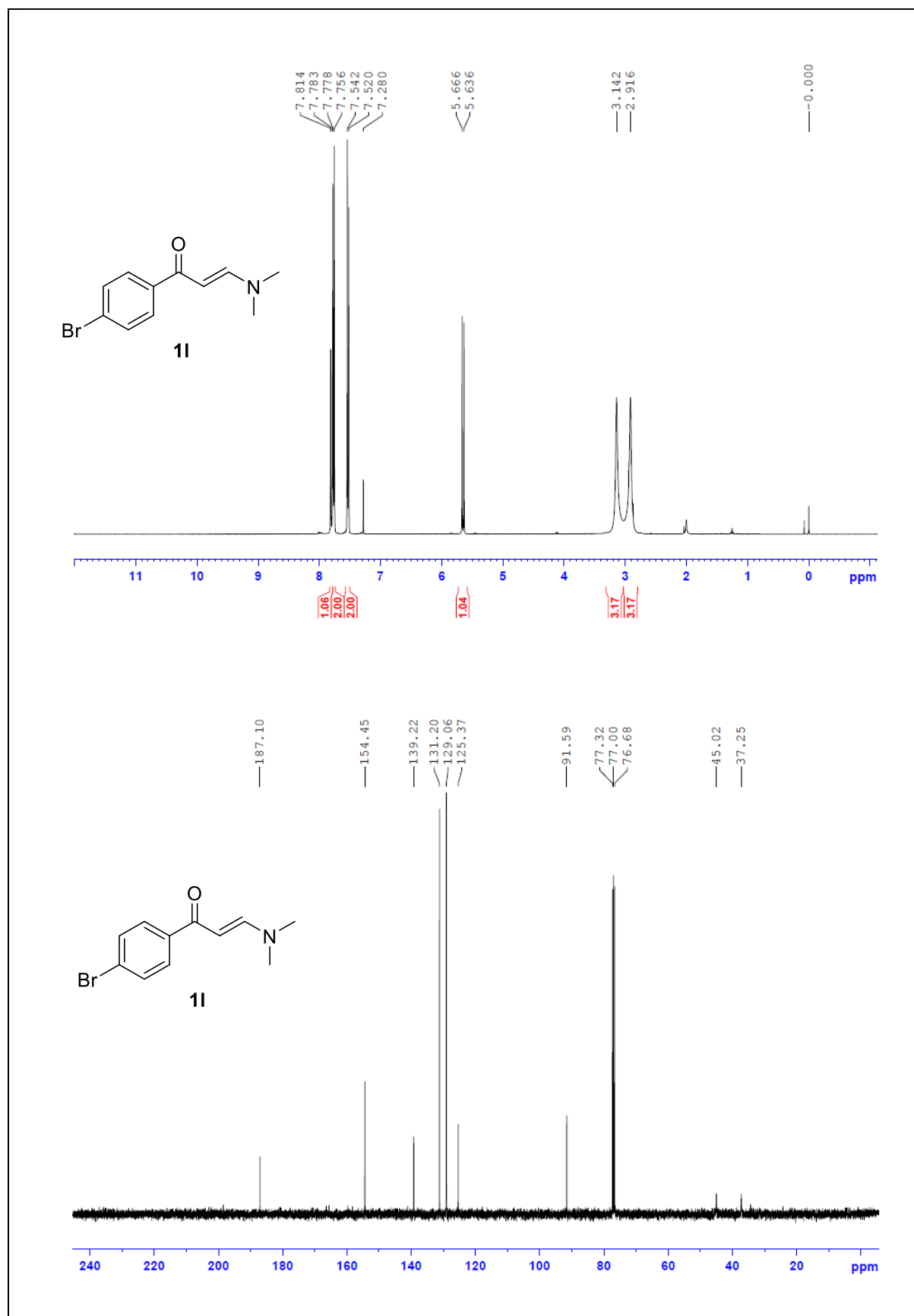


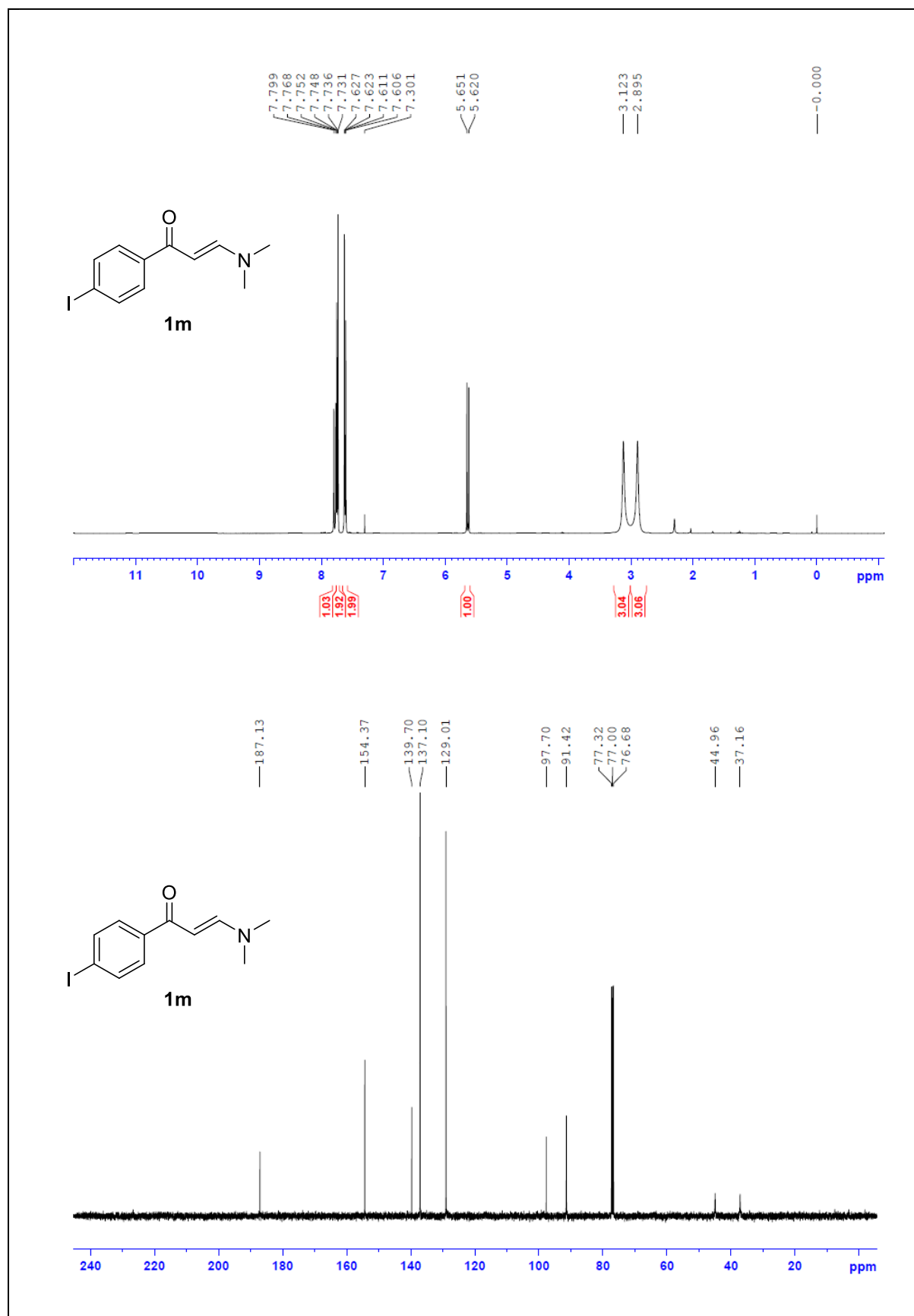


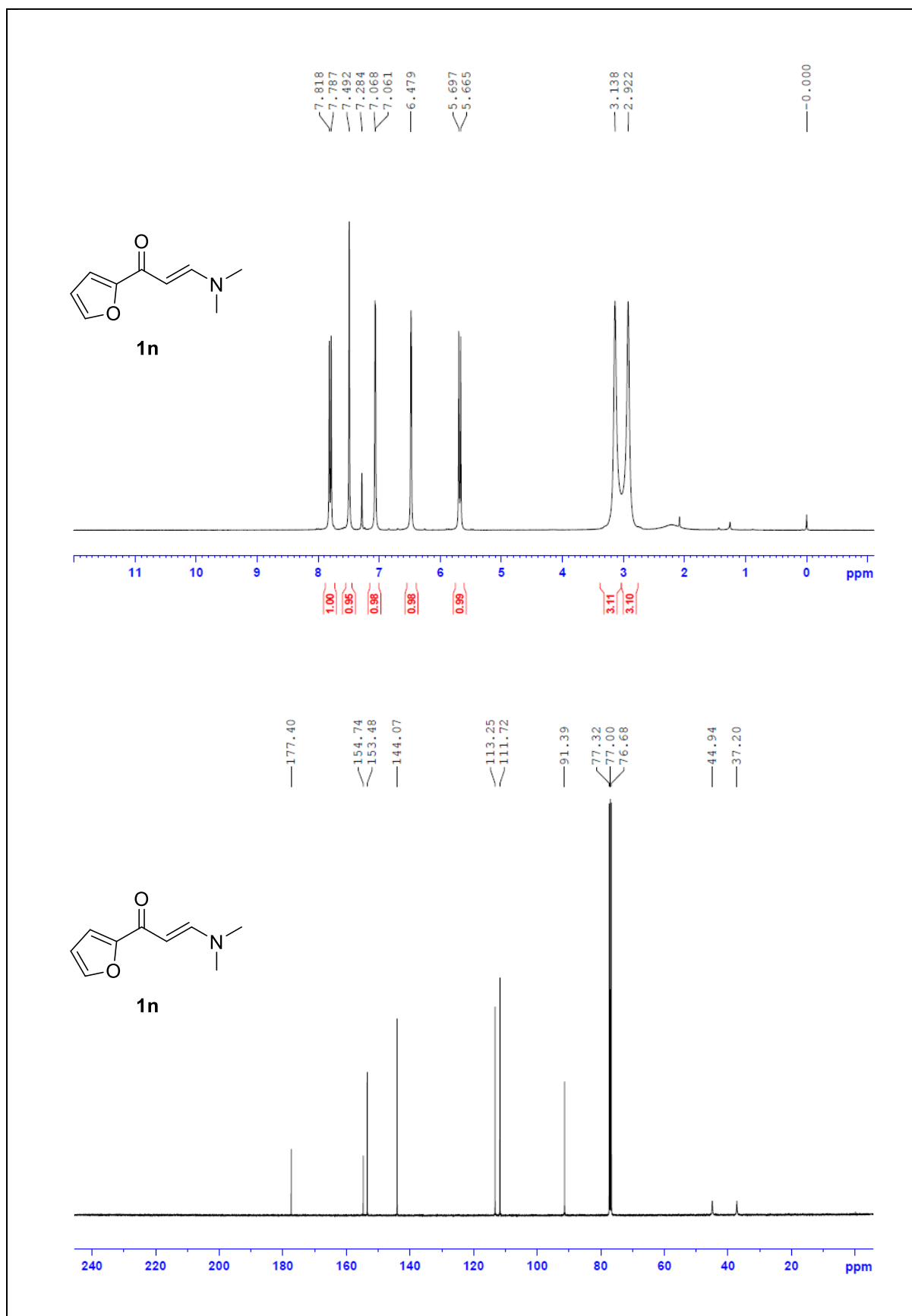


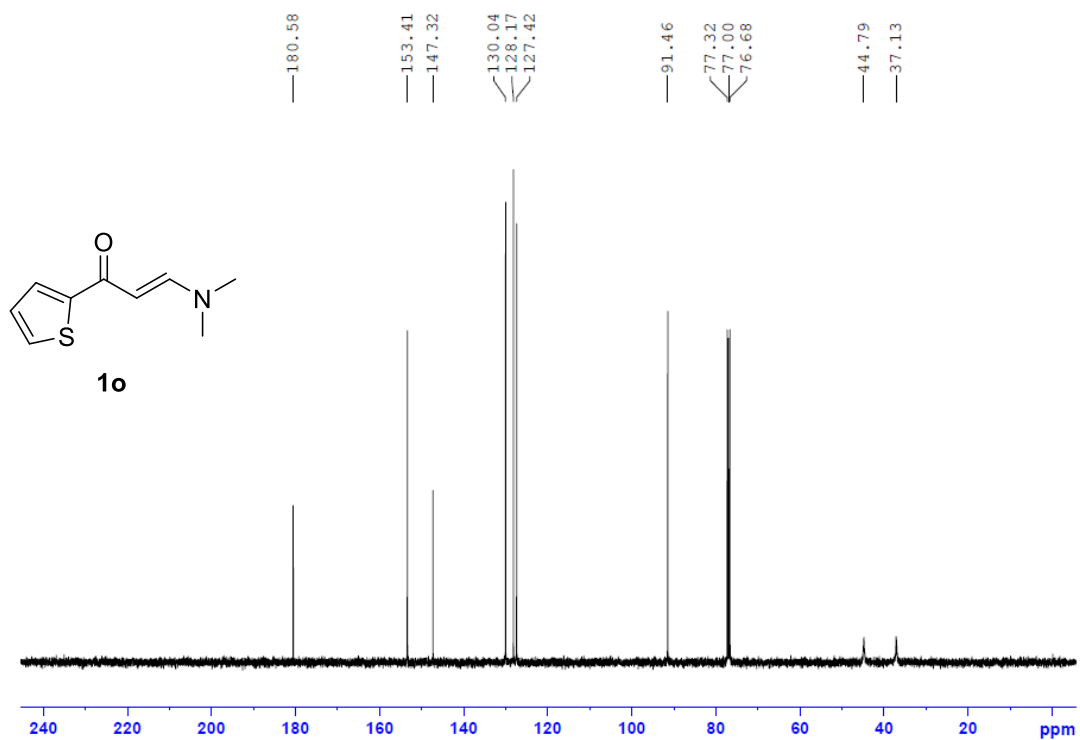
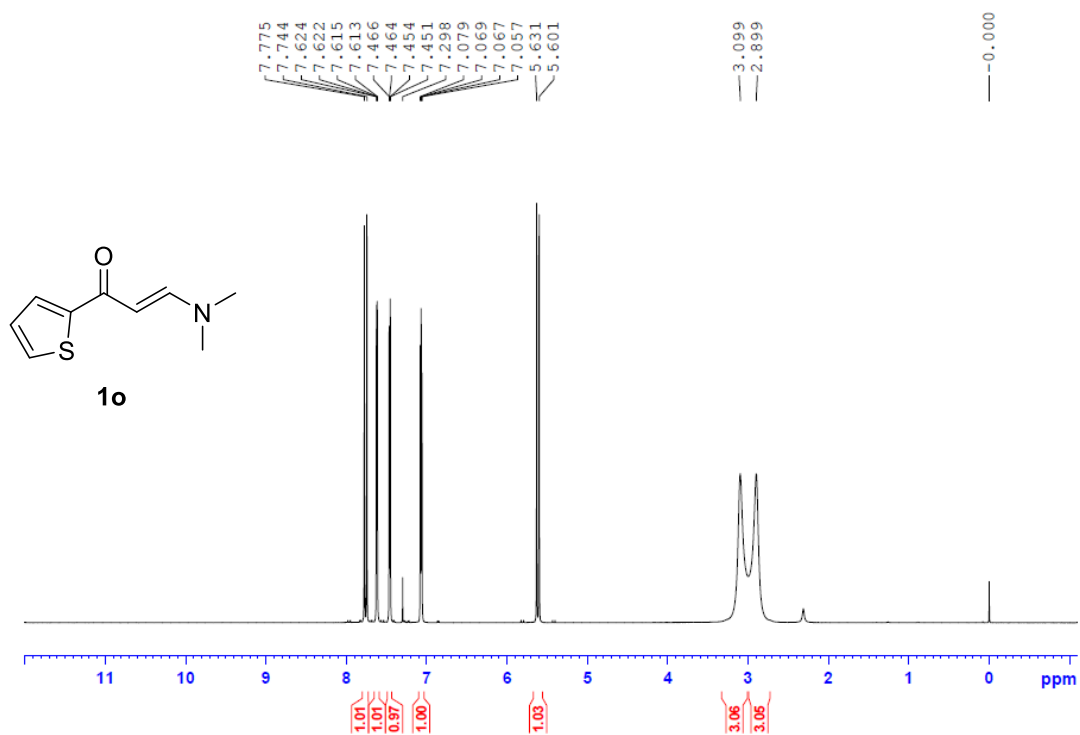


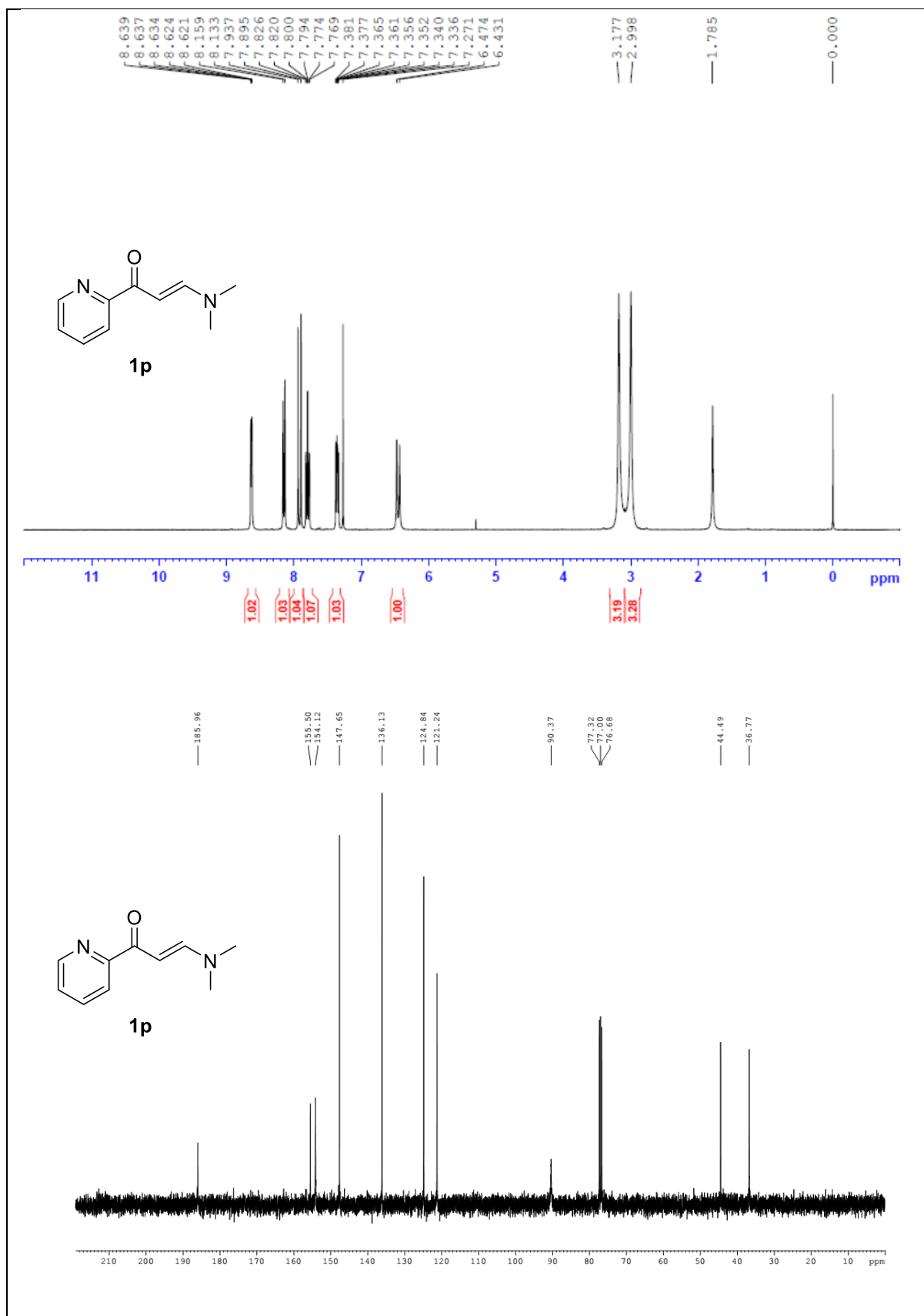


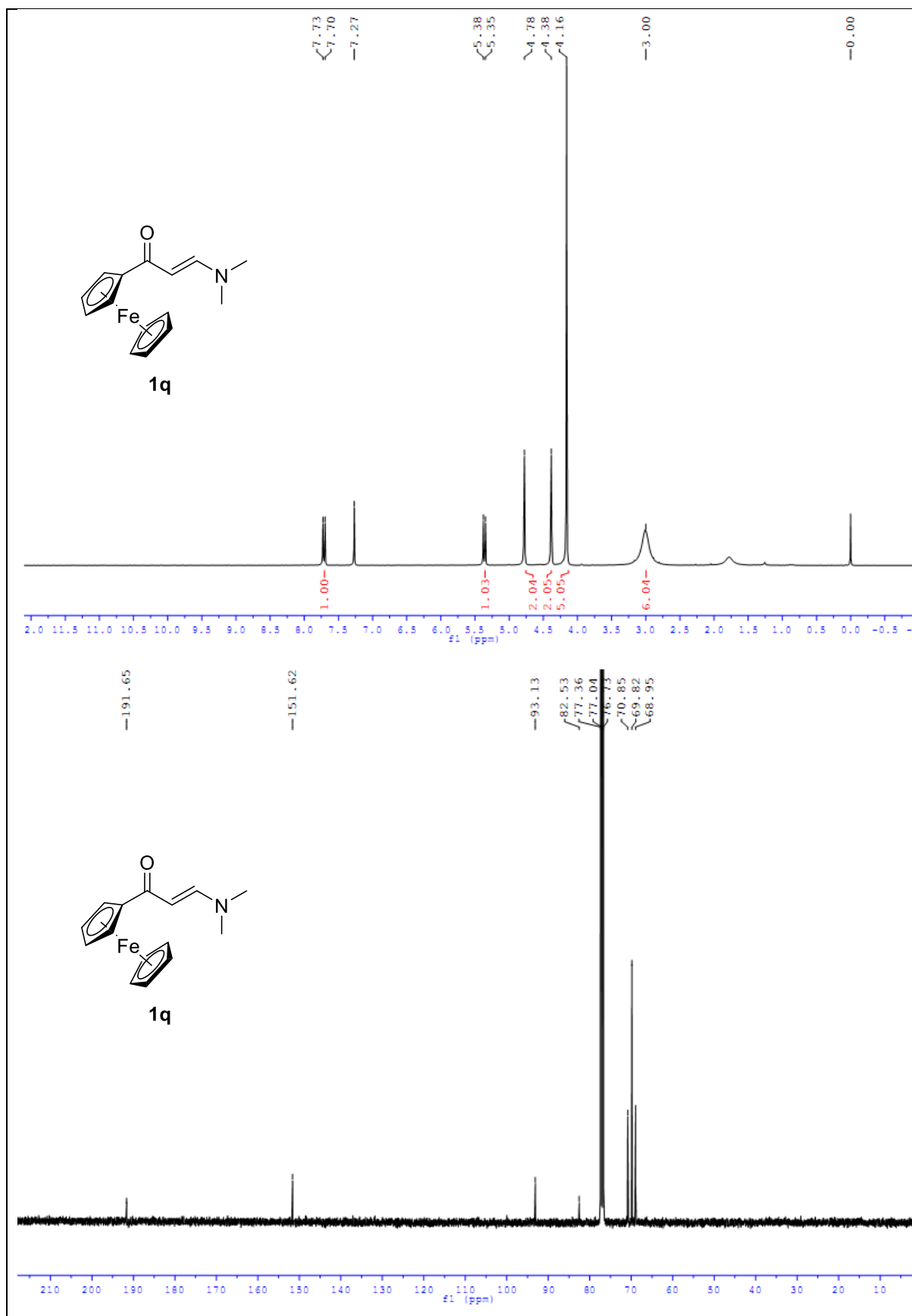


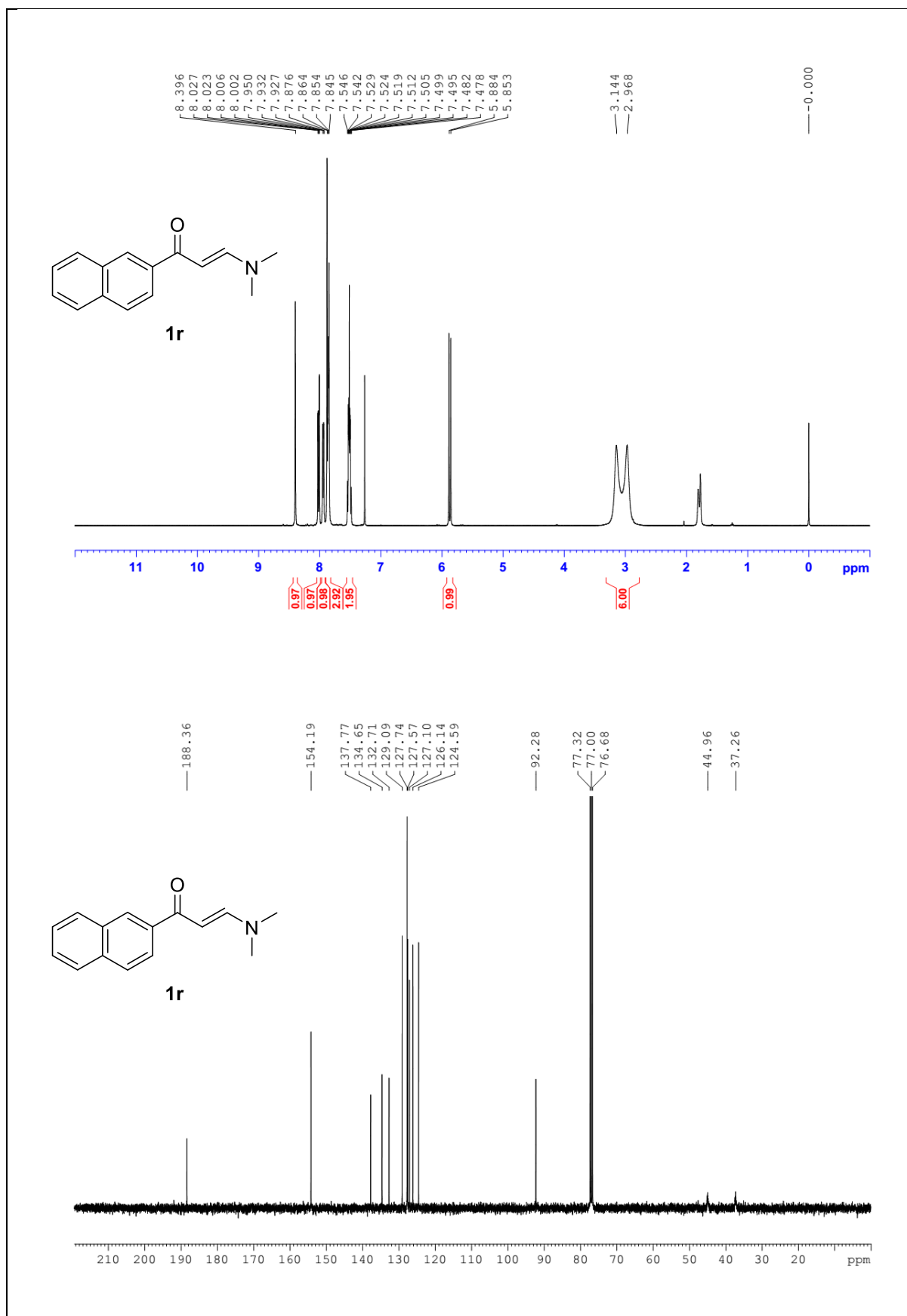


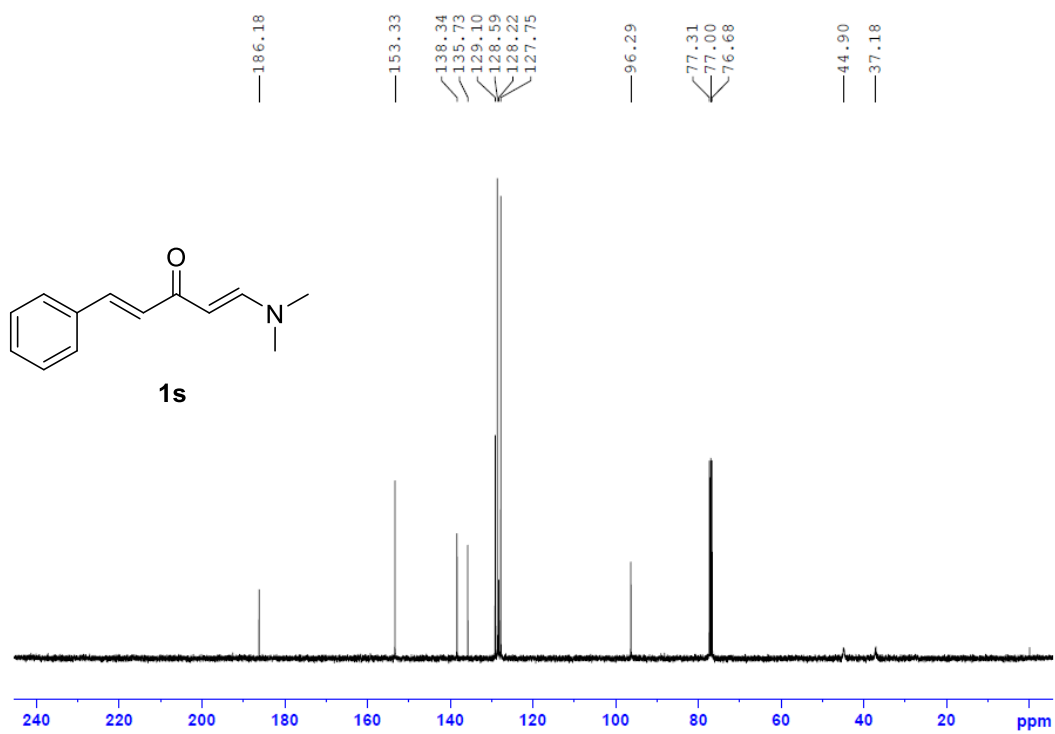
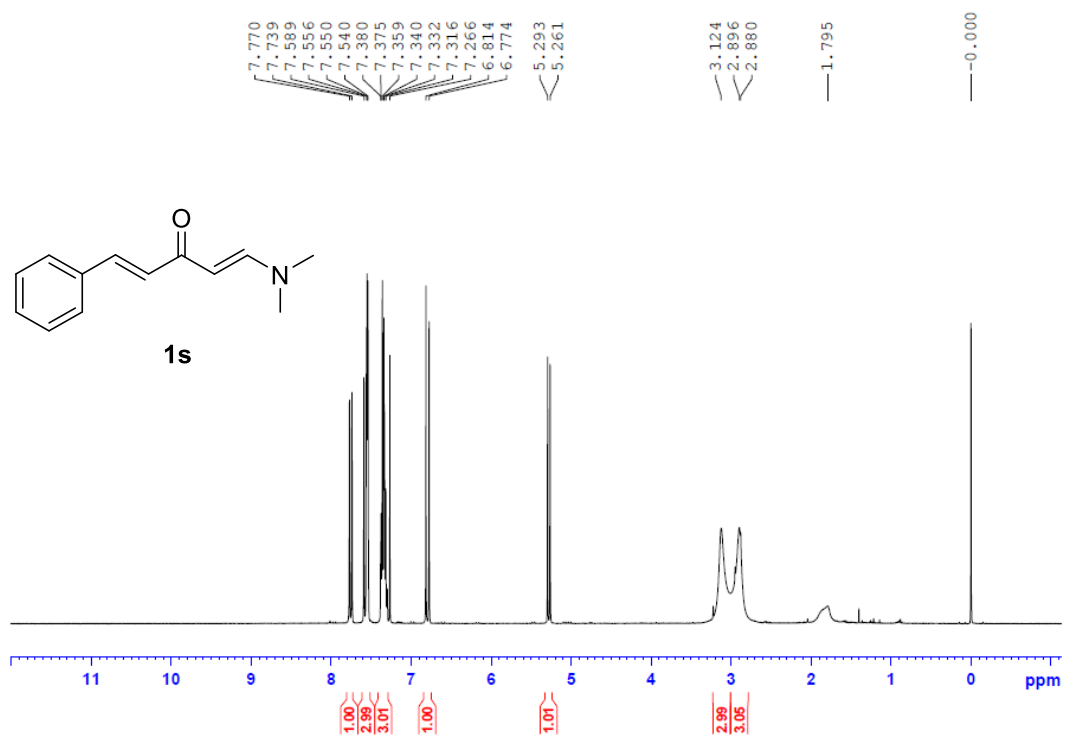


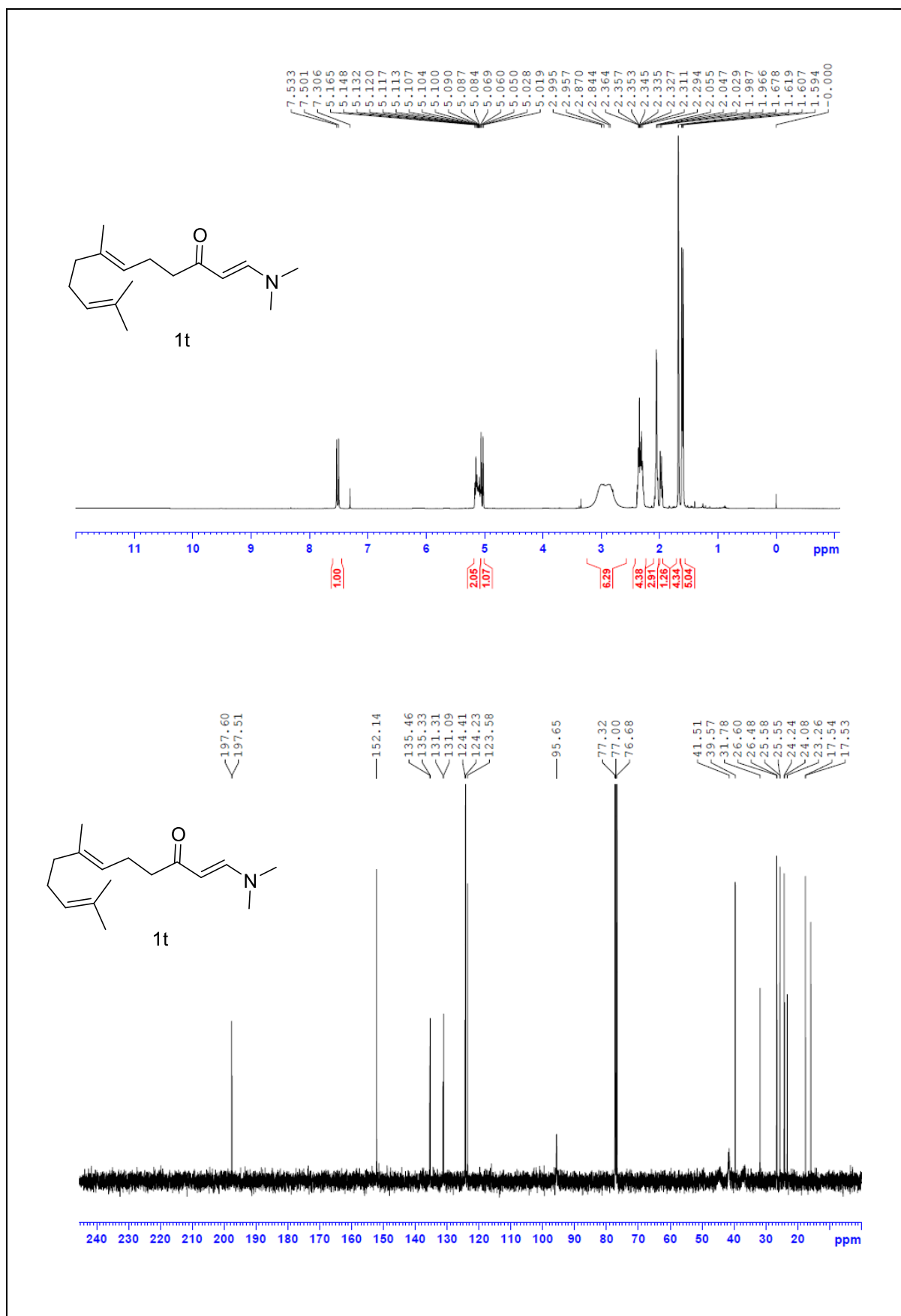


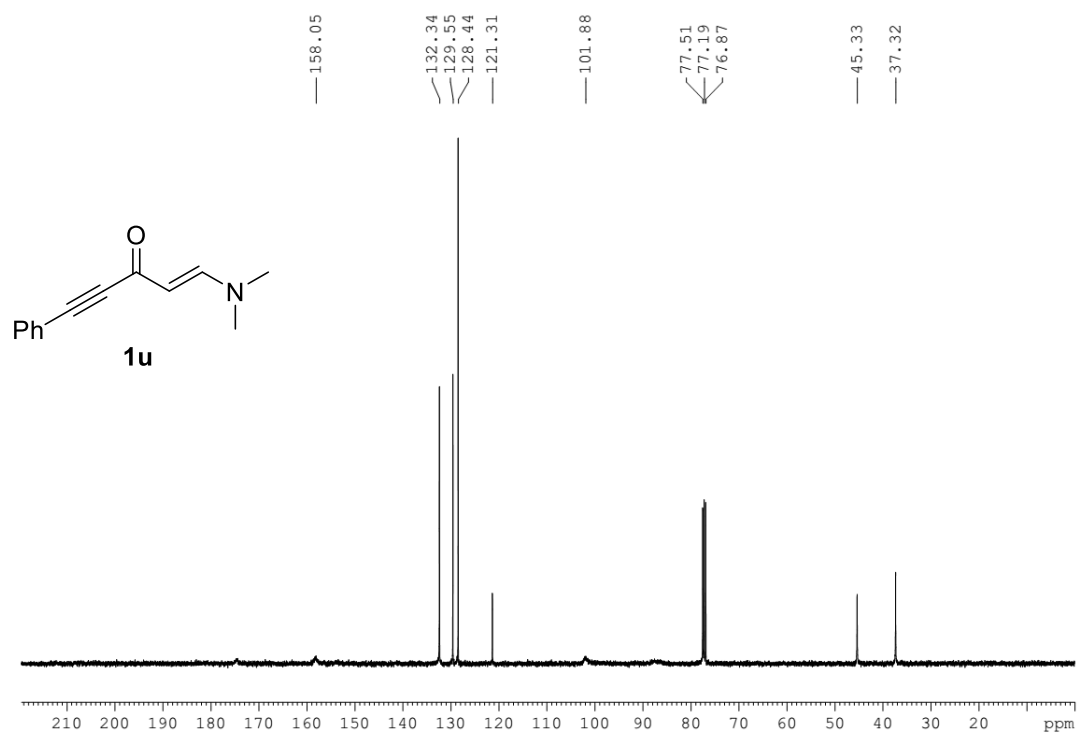
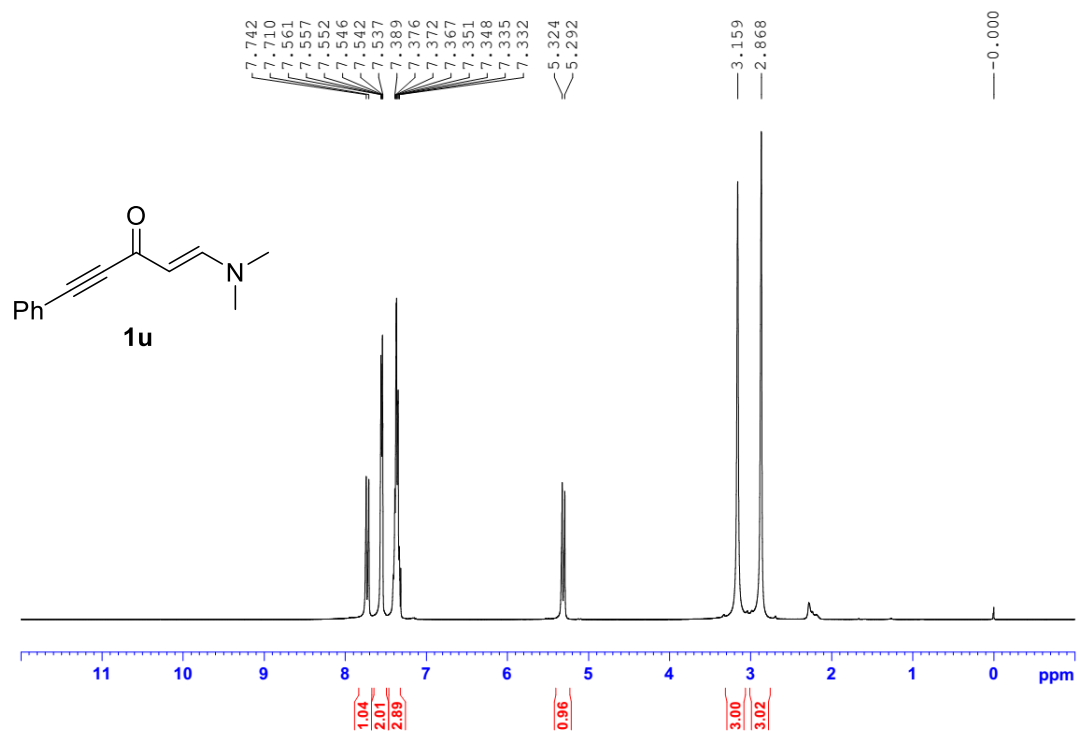


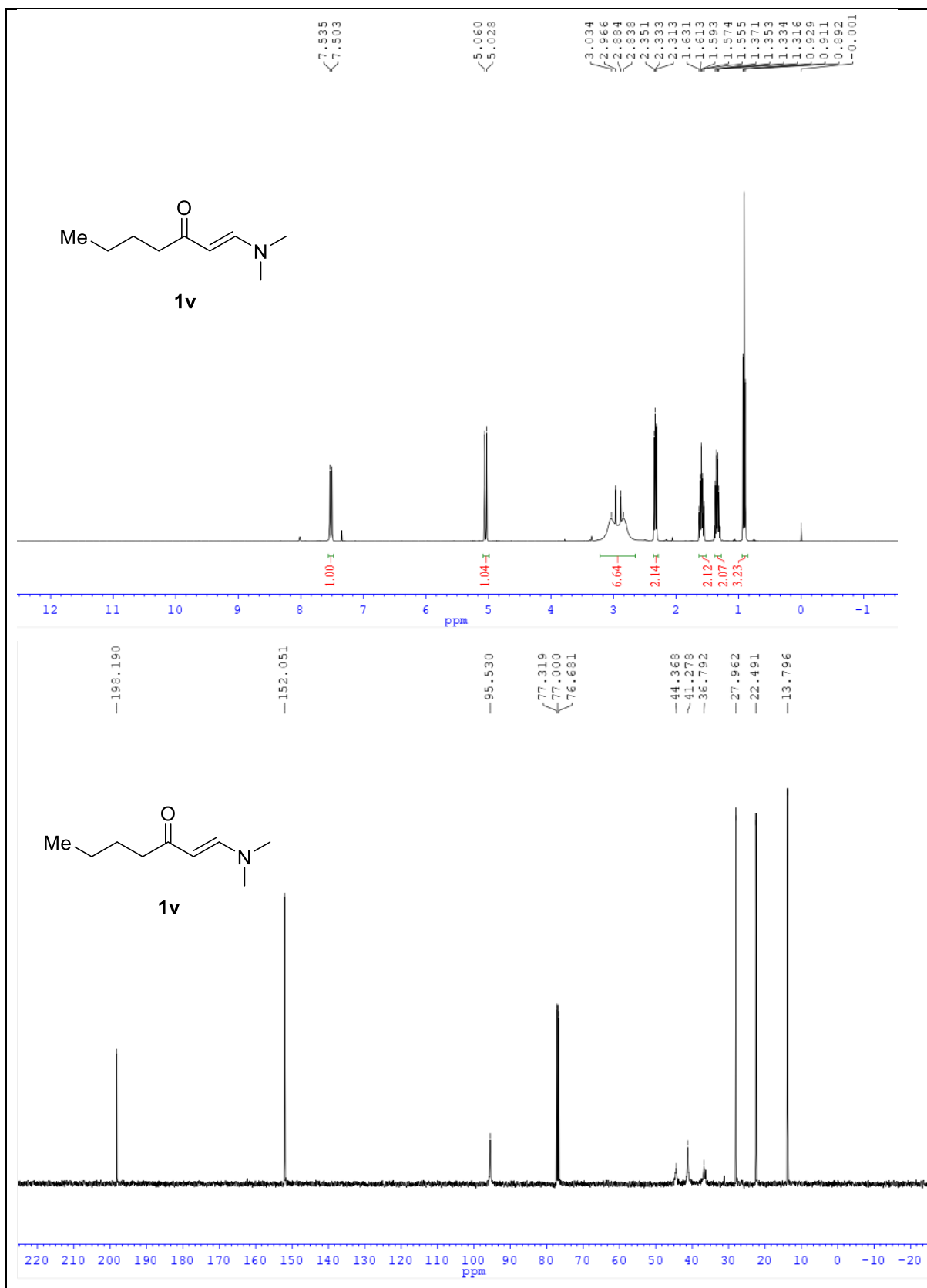


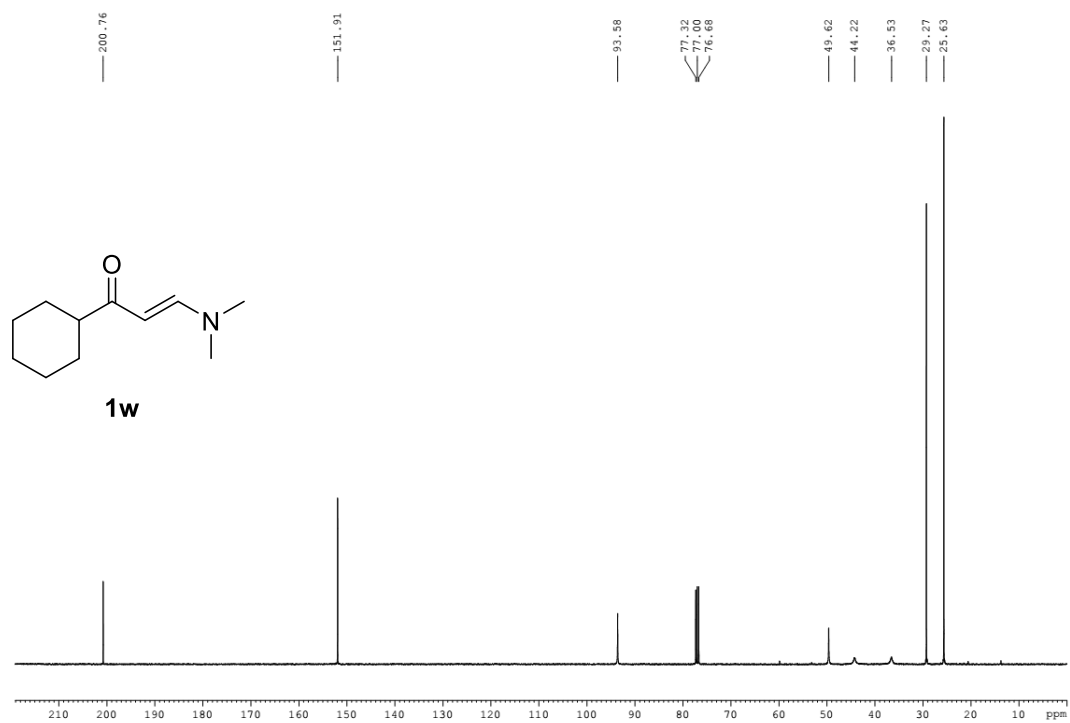
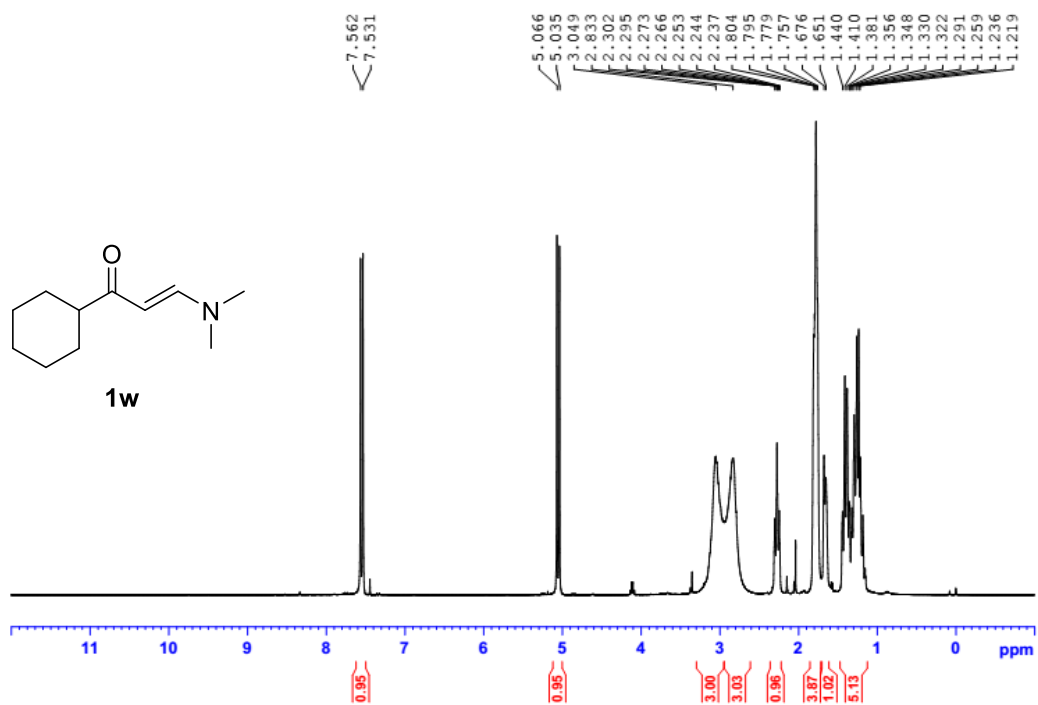


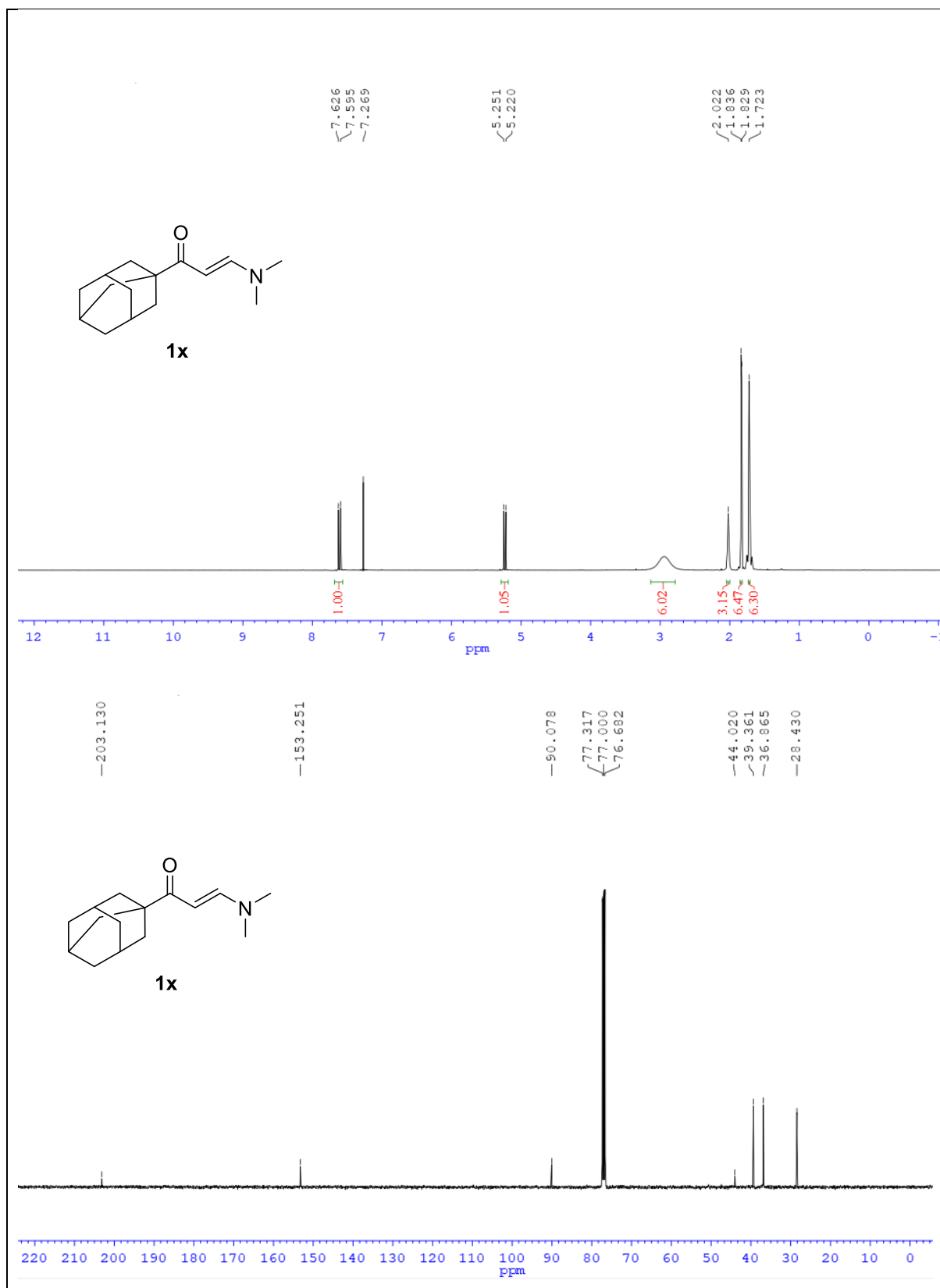


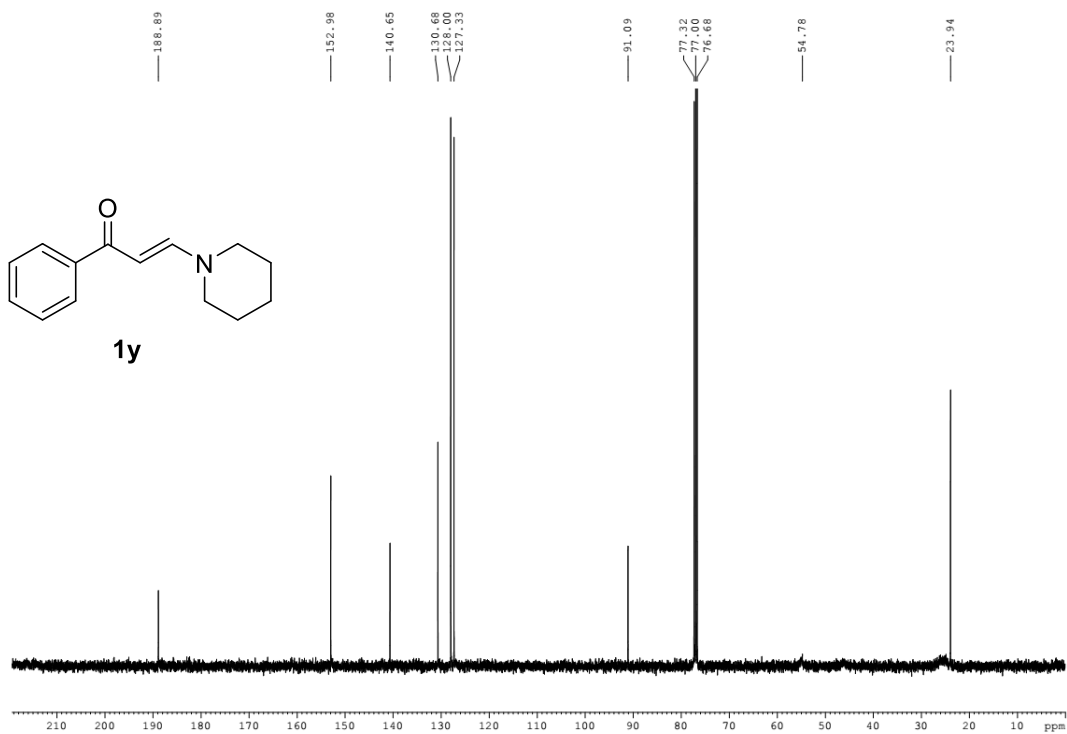
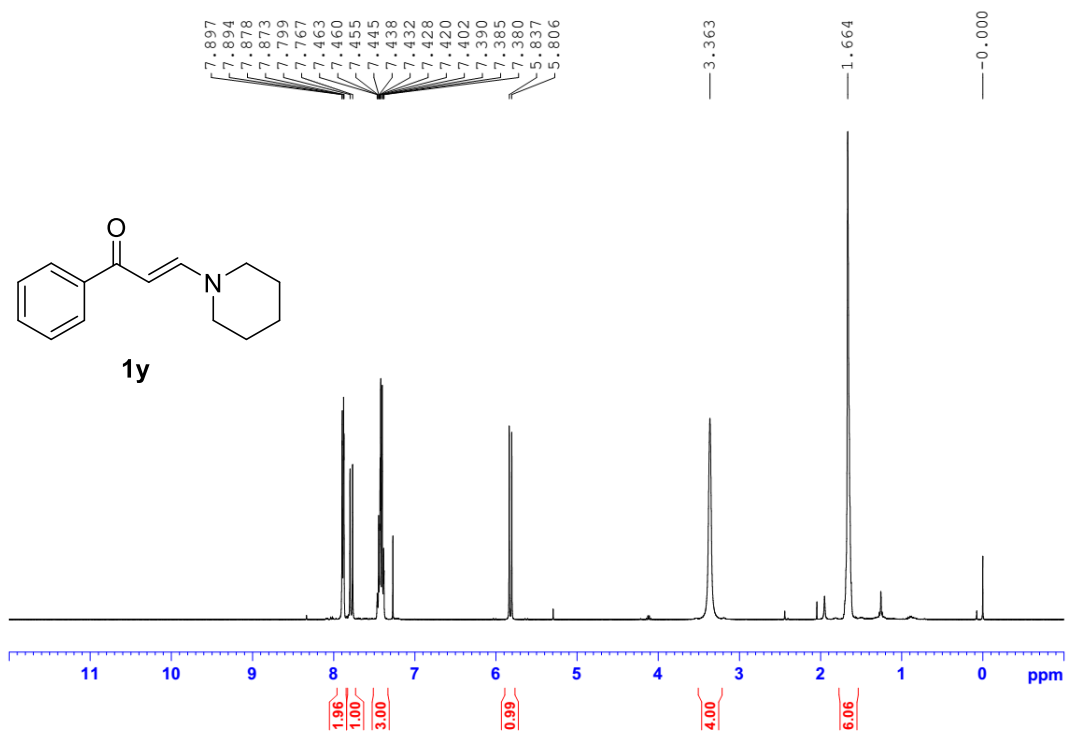


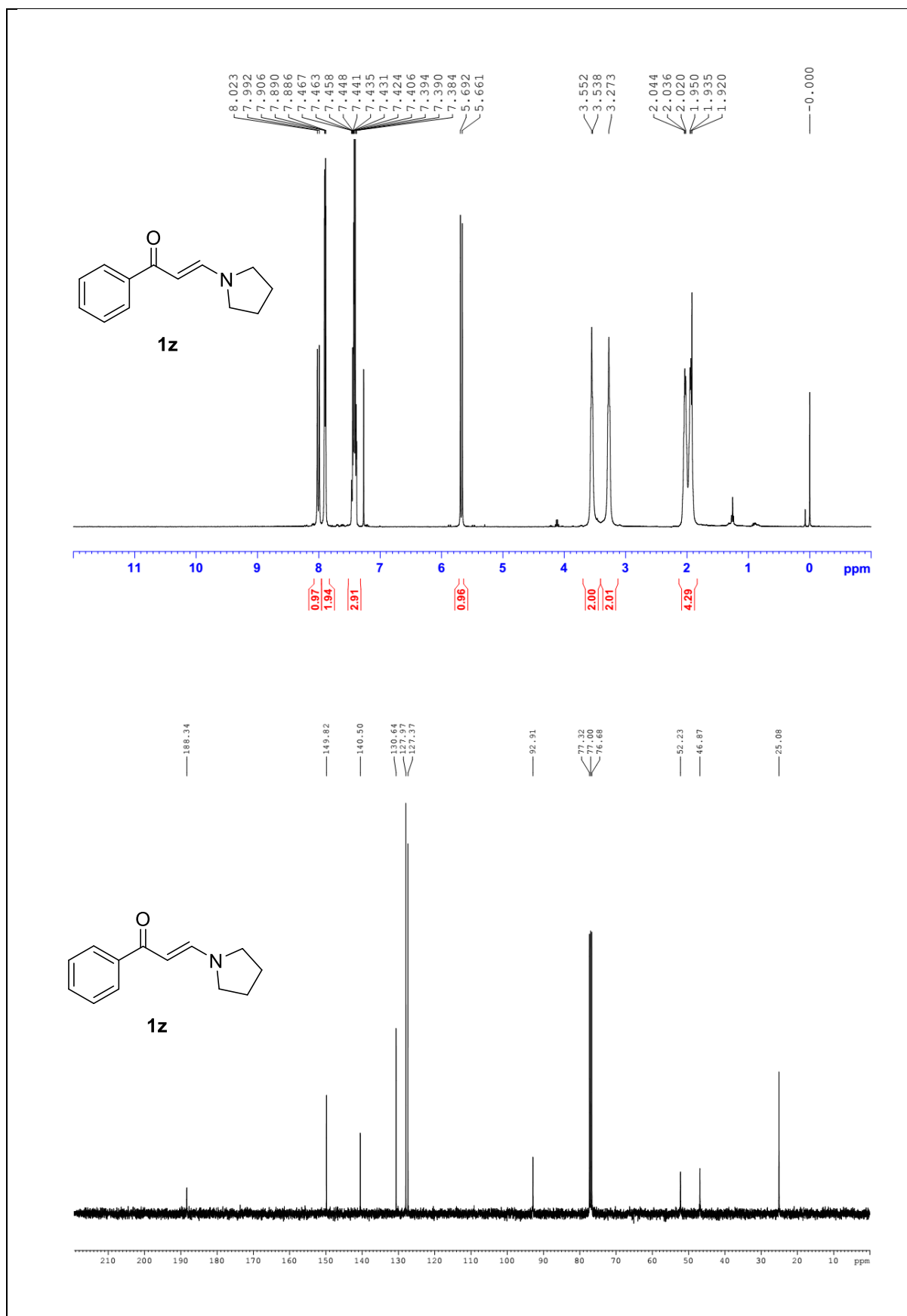




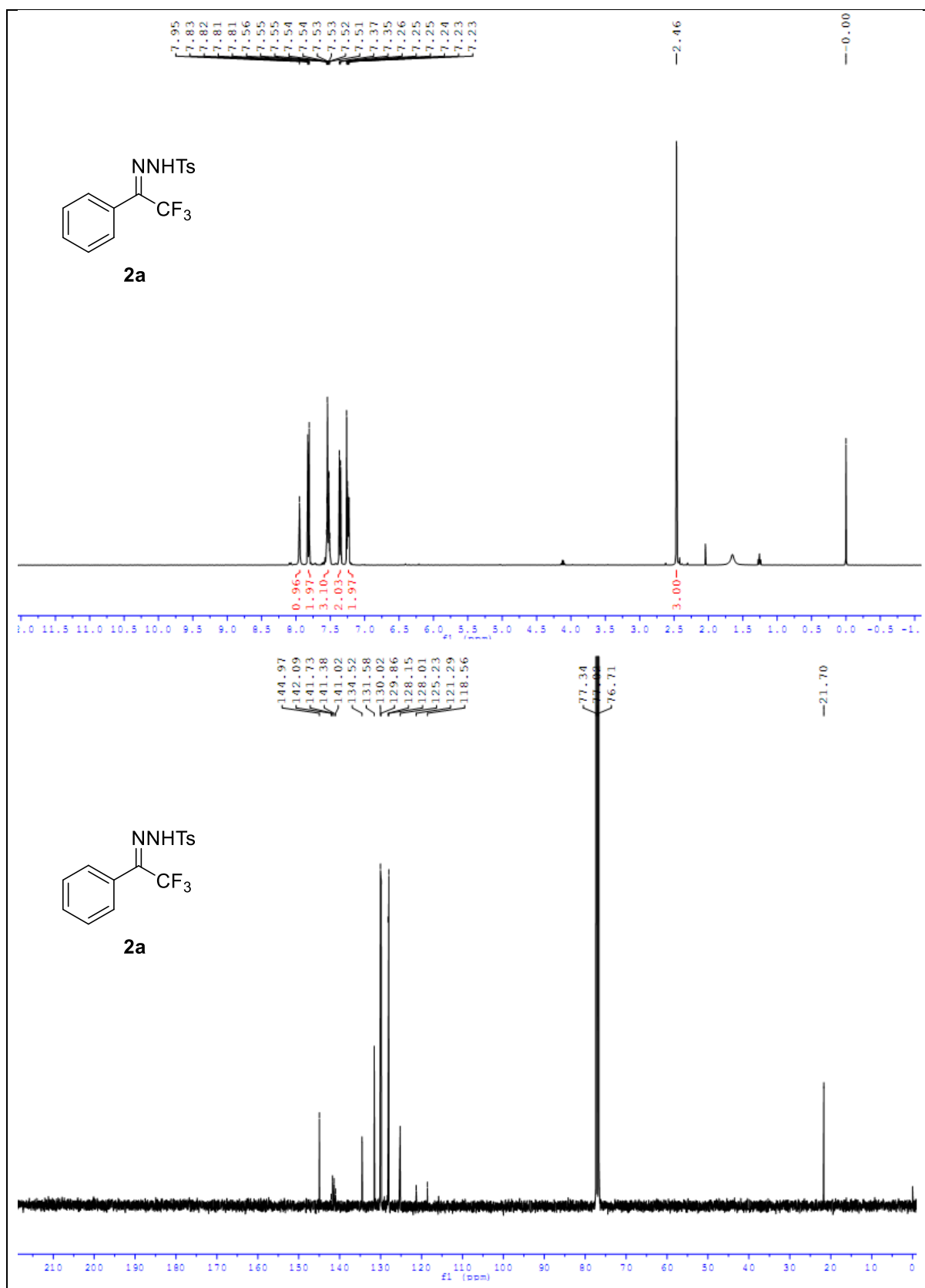


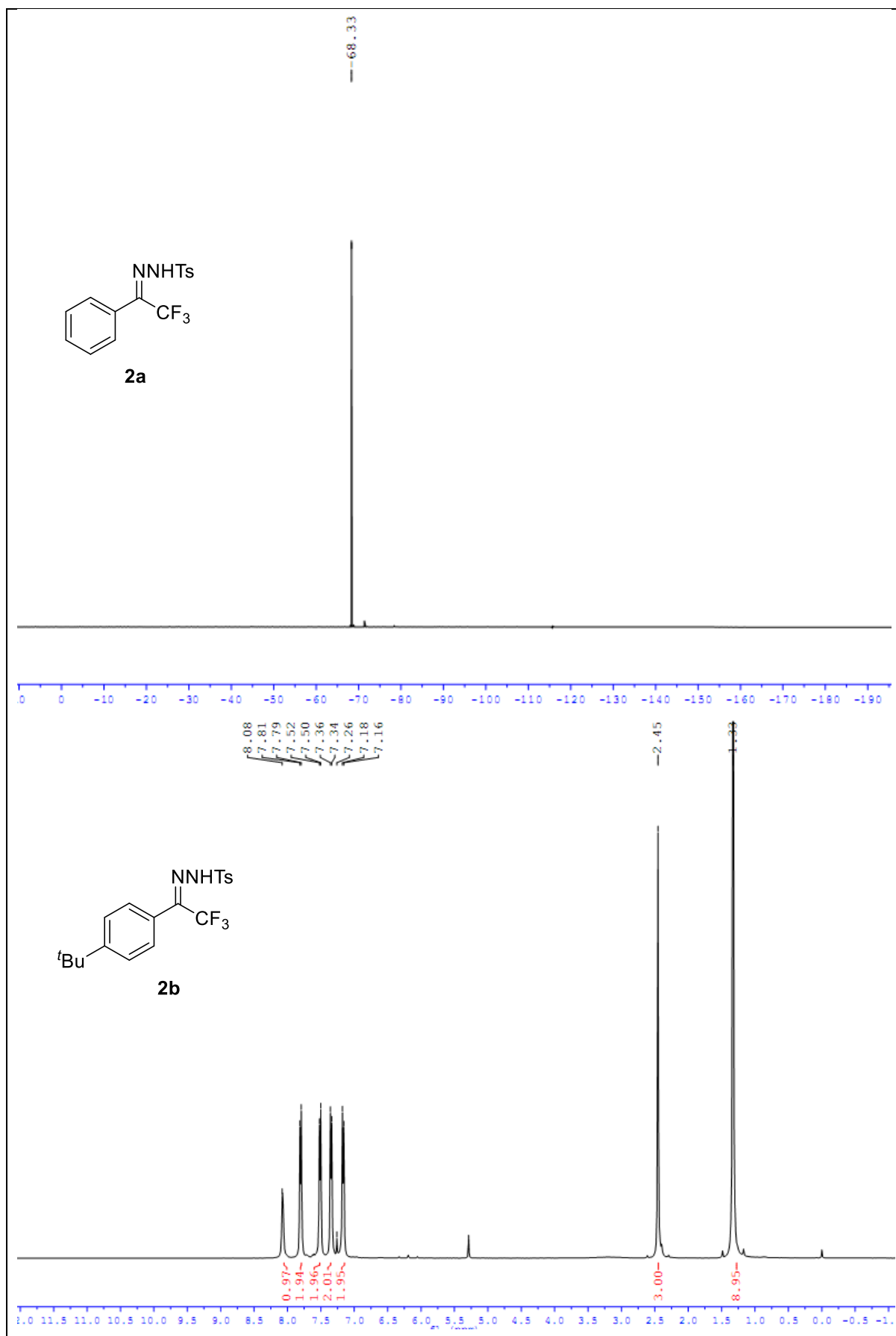


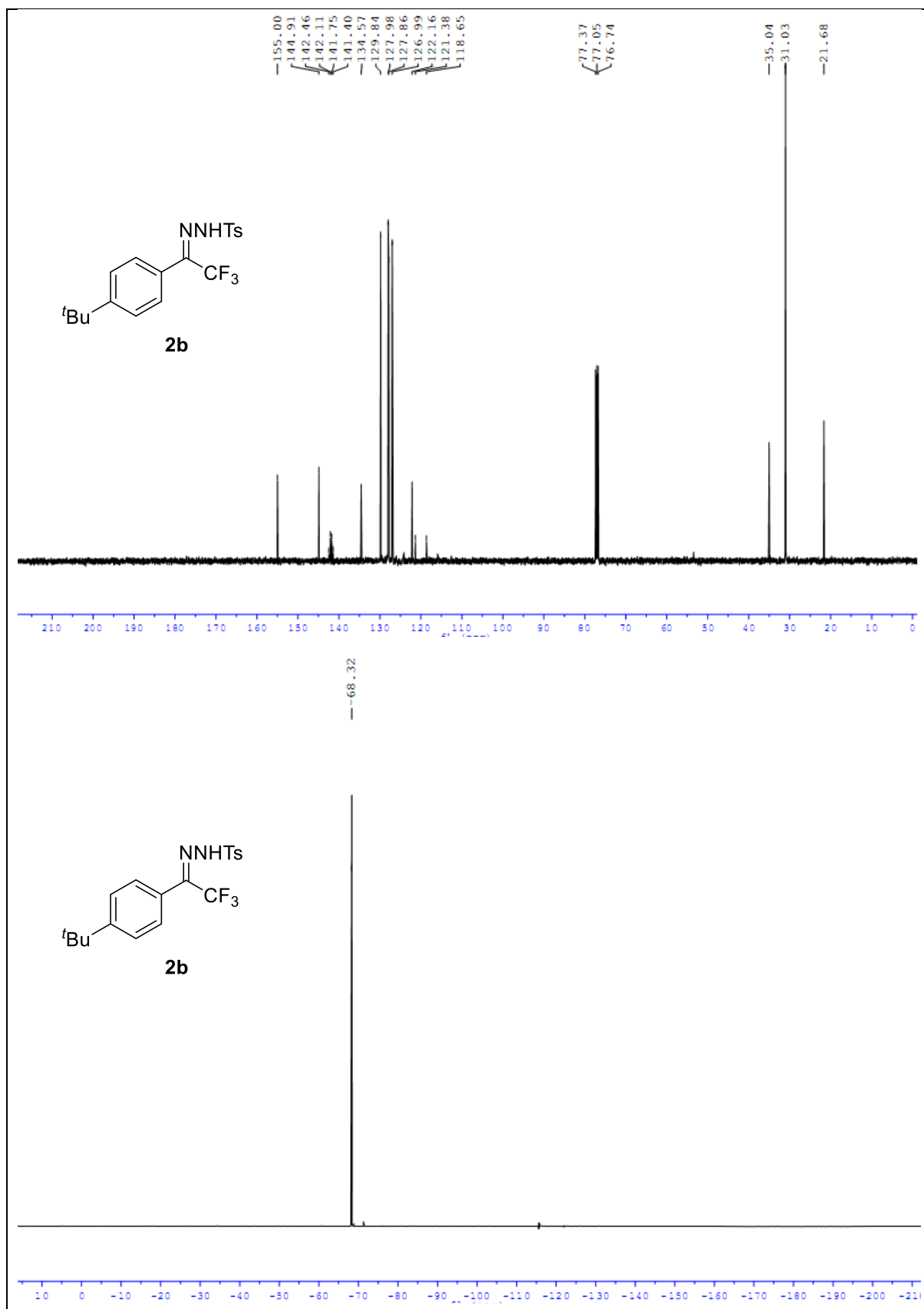


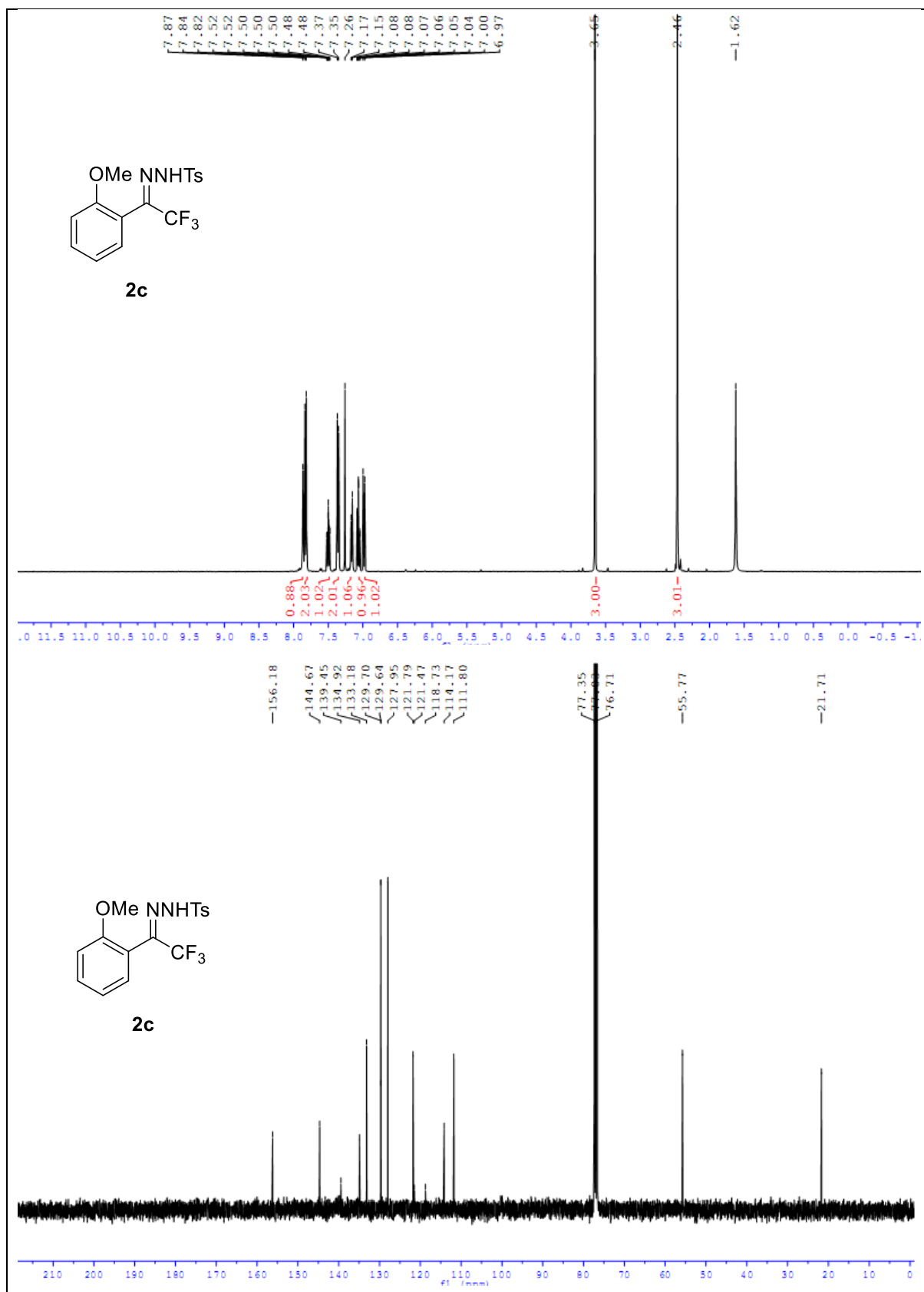


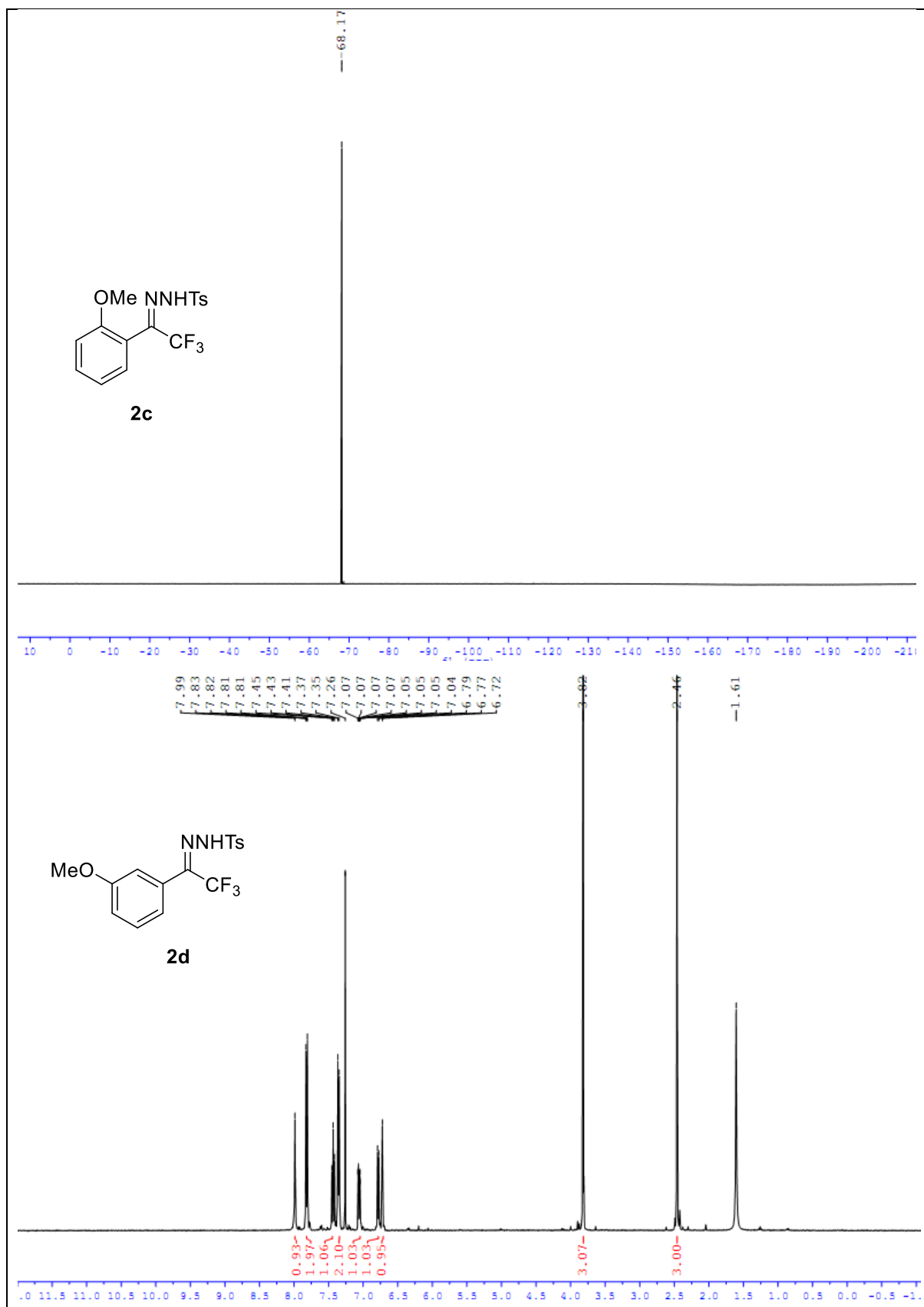
NMR Spectra for trifluoromethylated *N*-tosylhydrazones

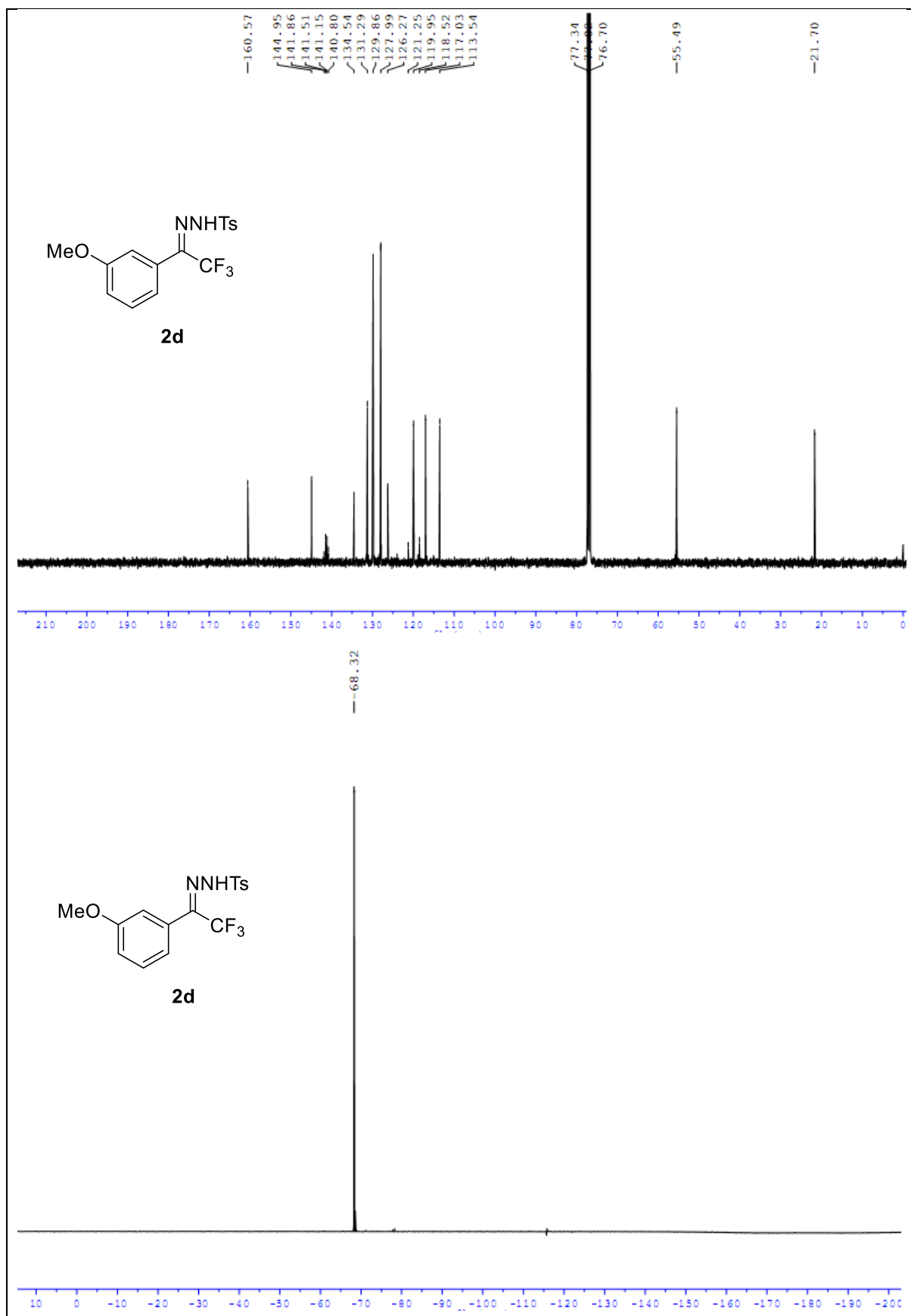


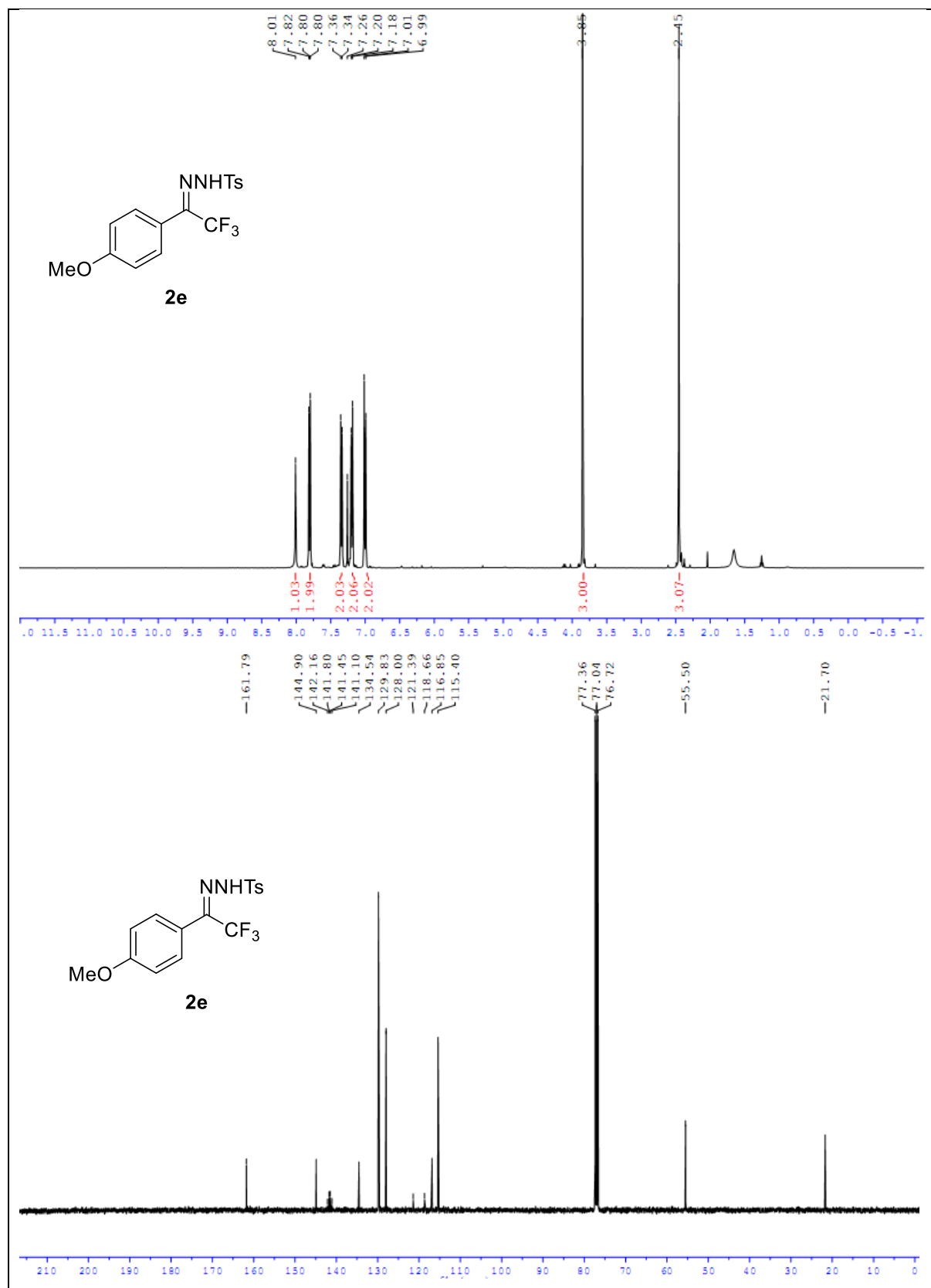


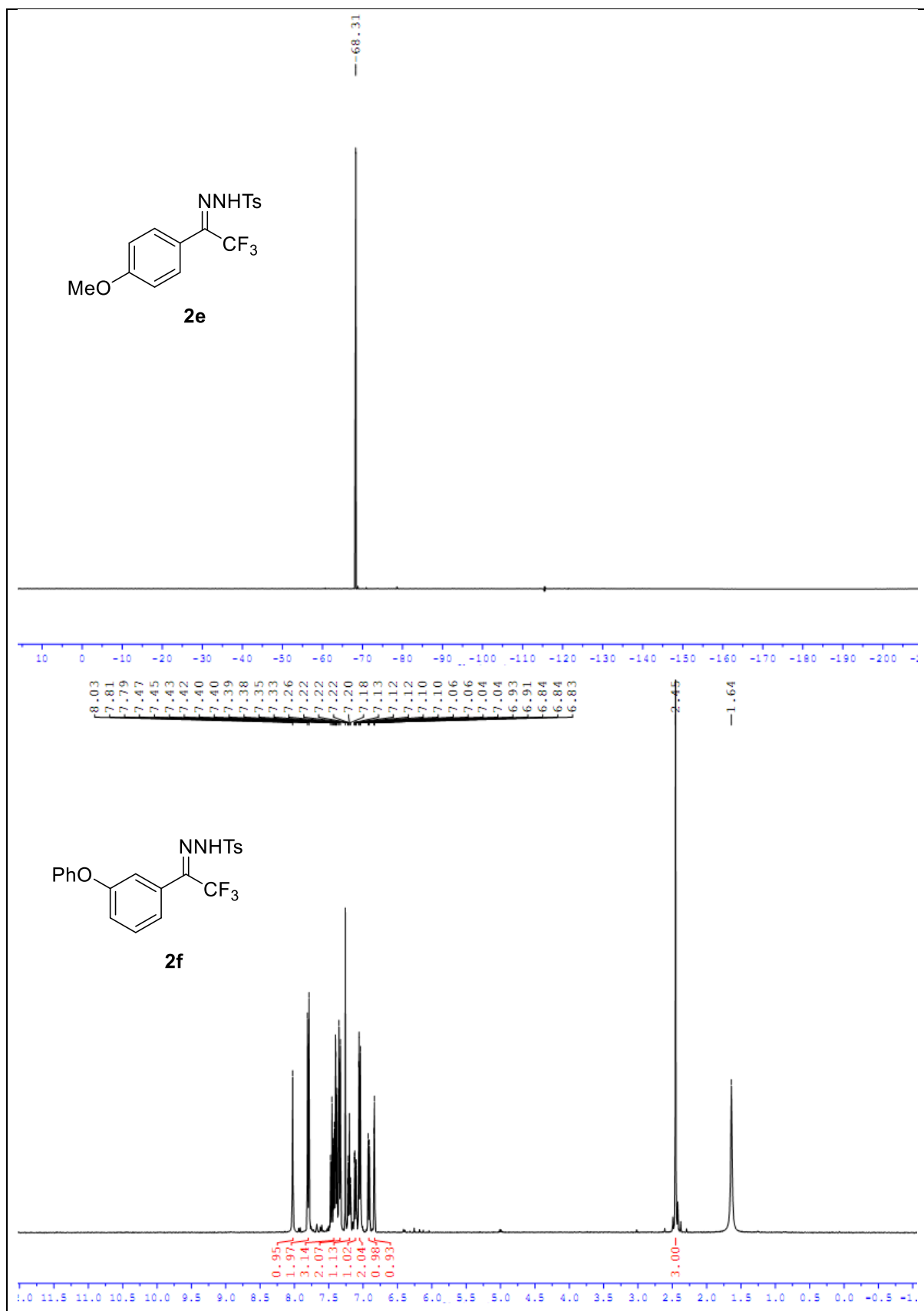


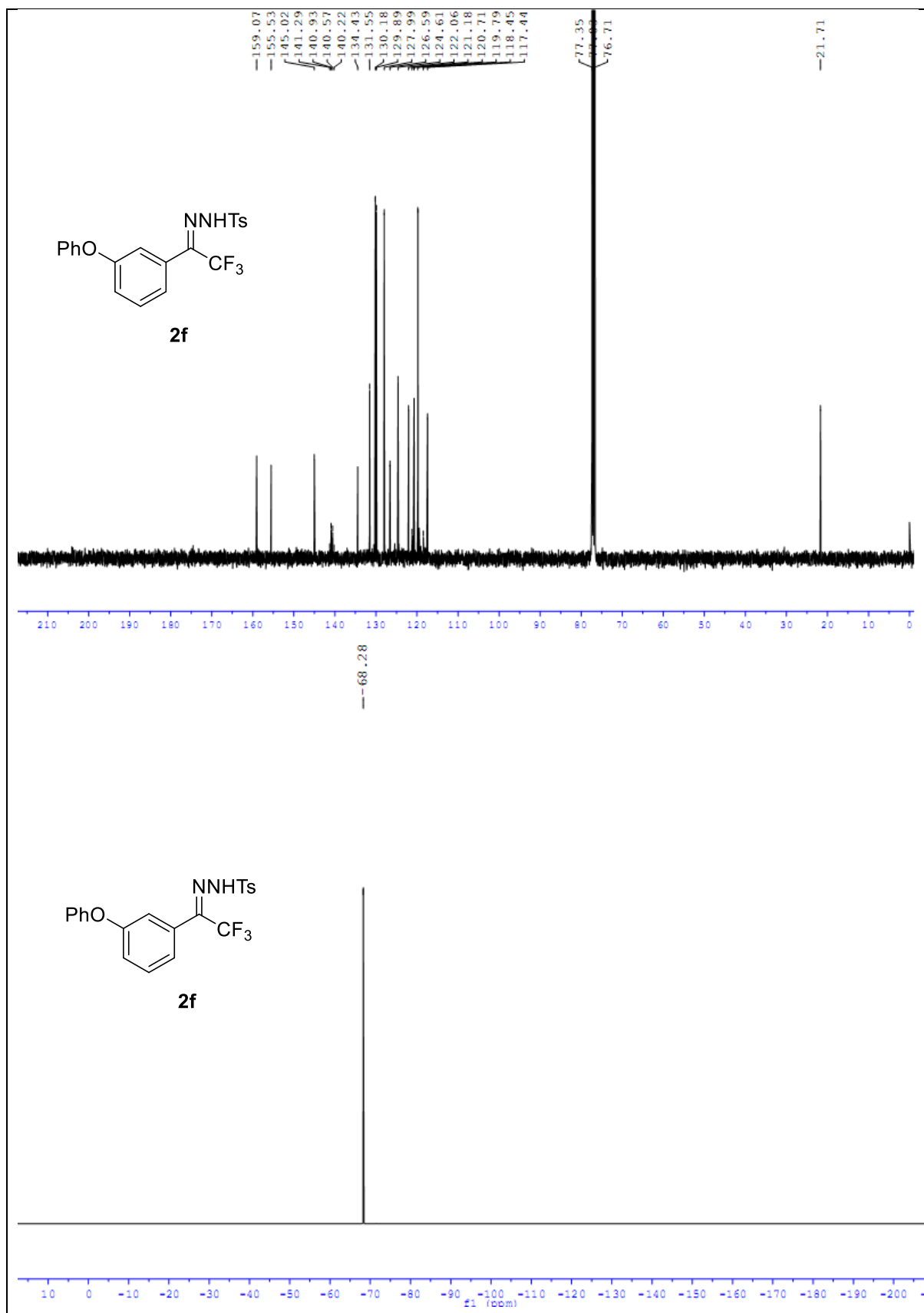


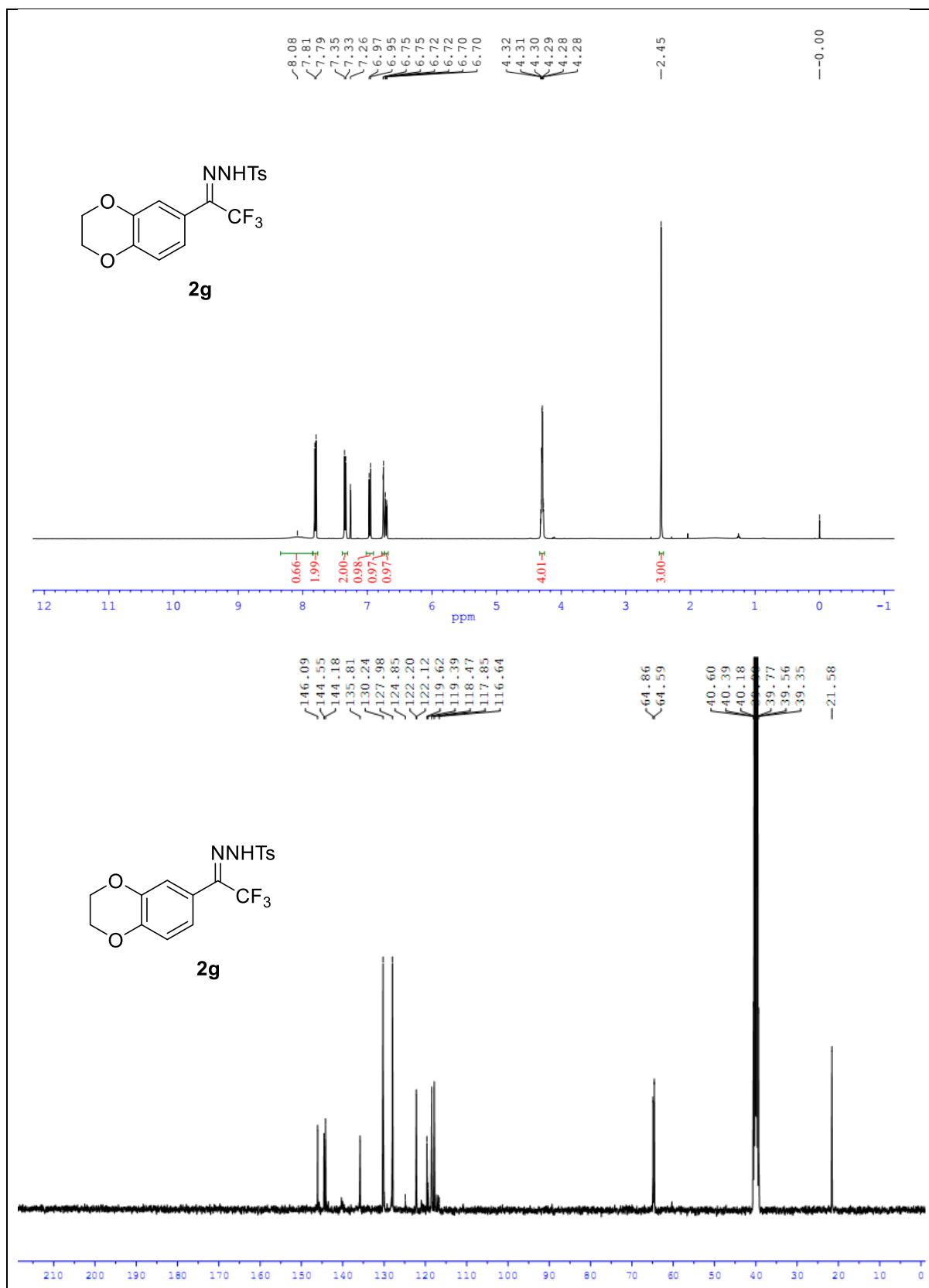


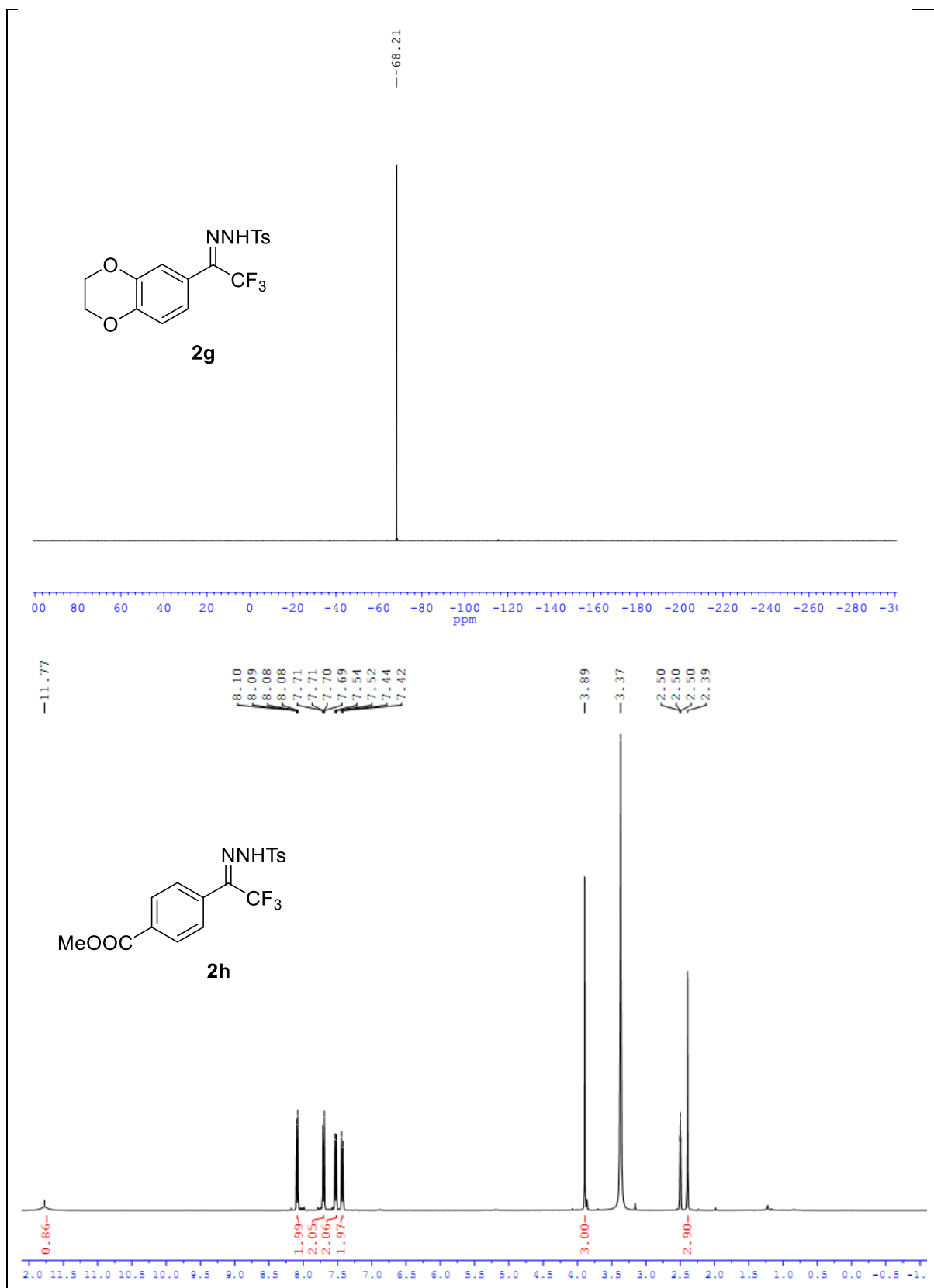


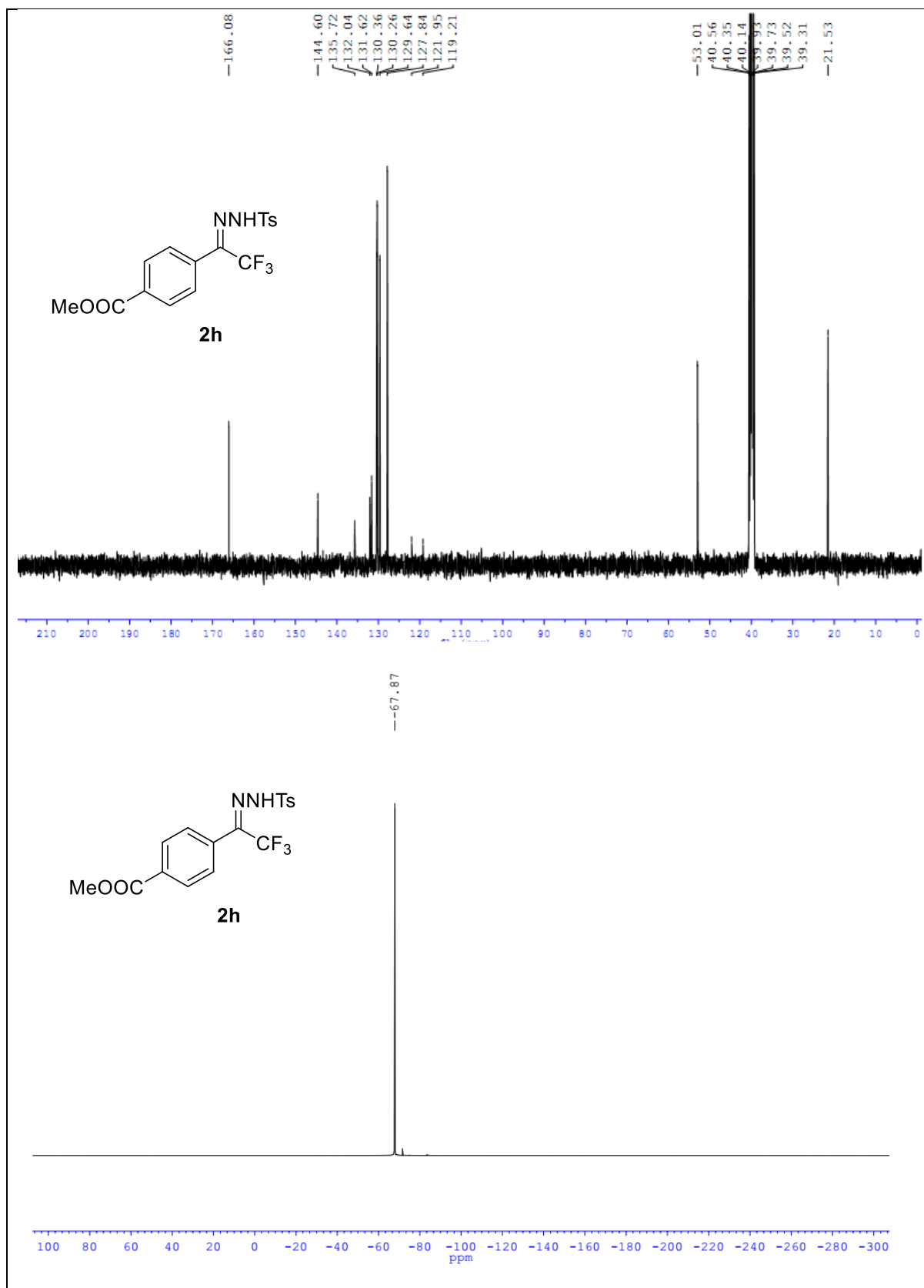


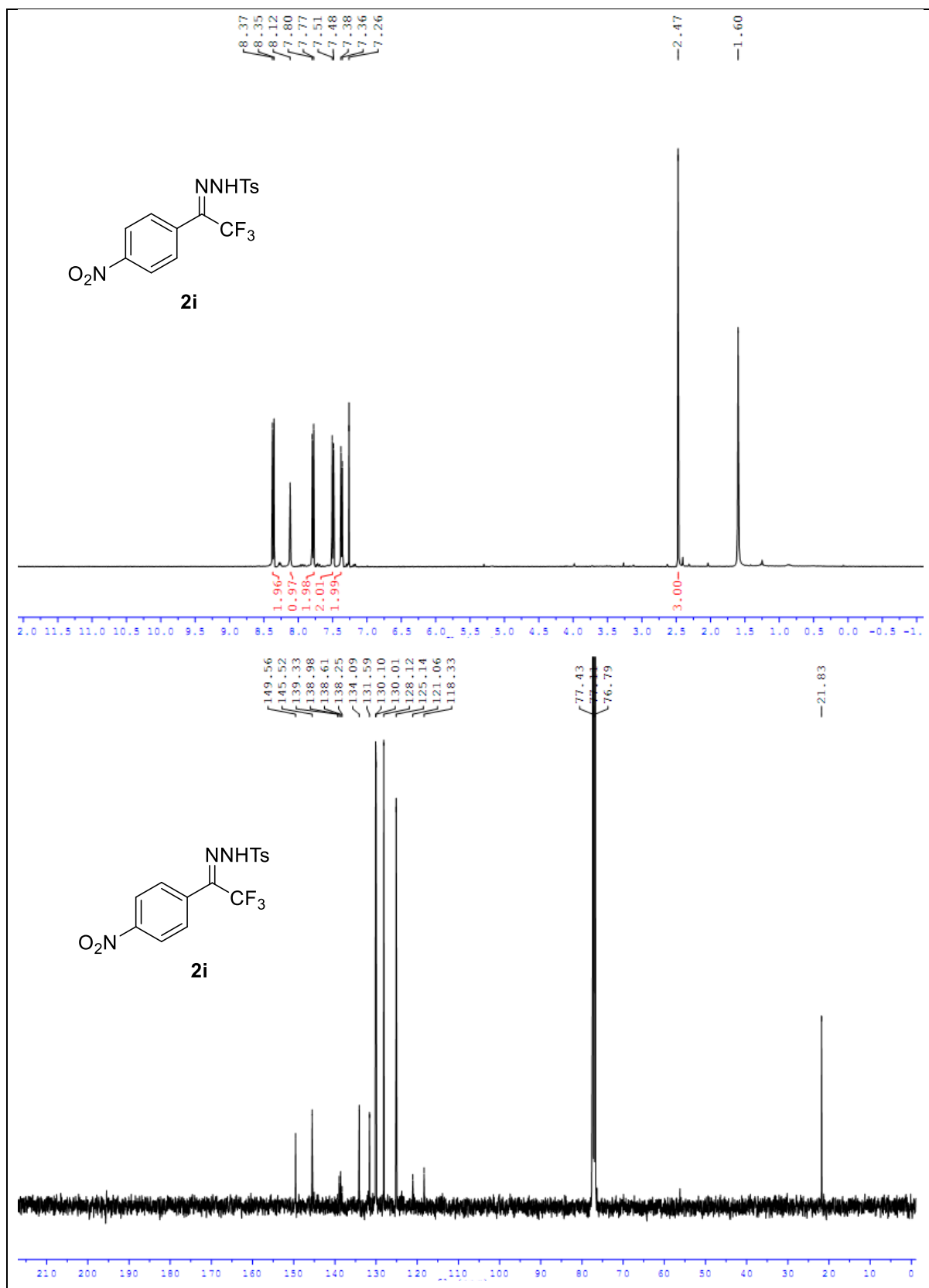


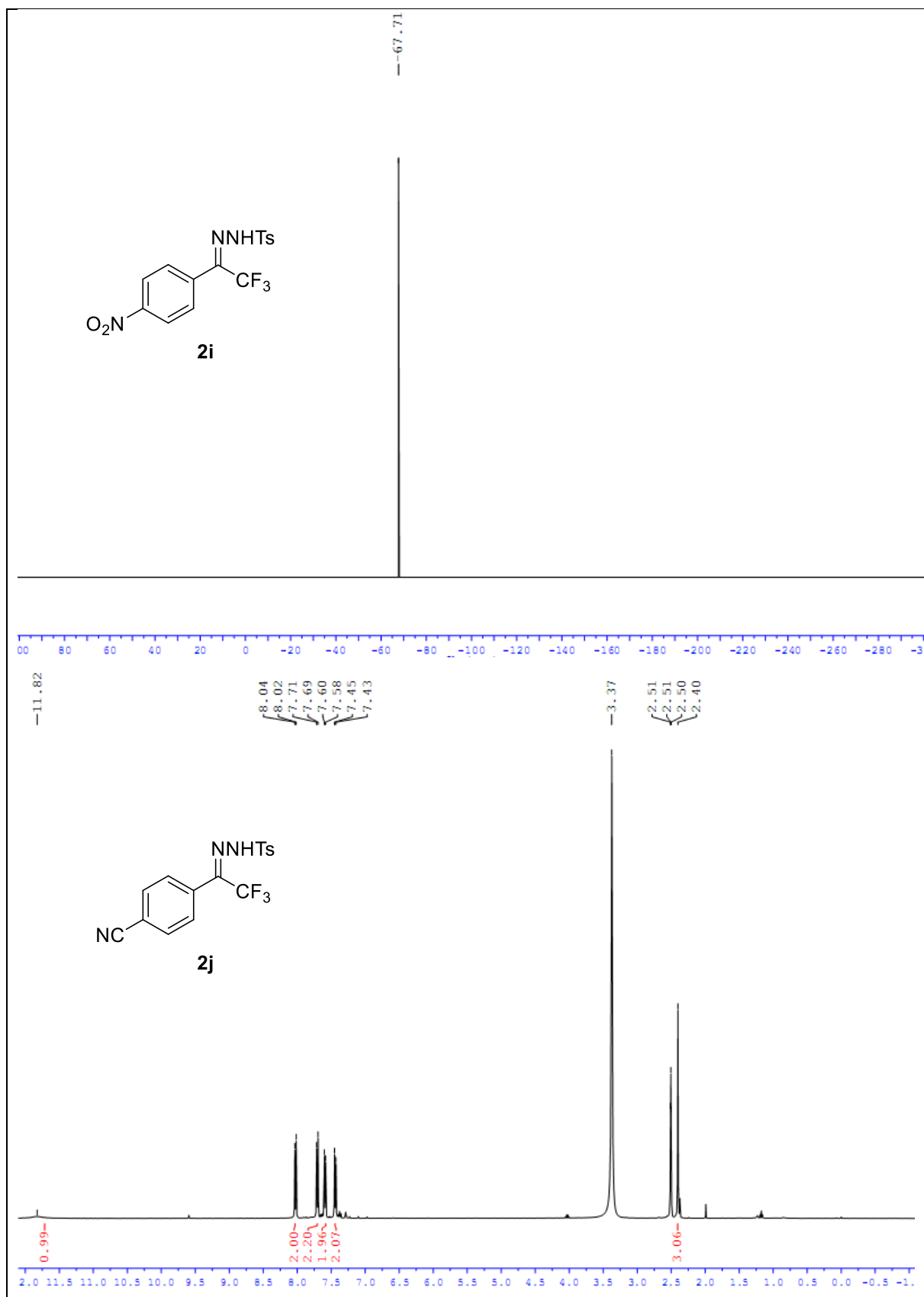


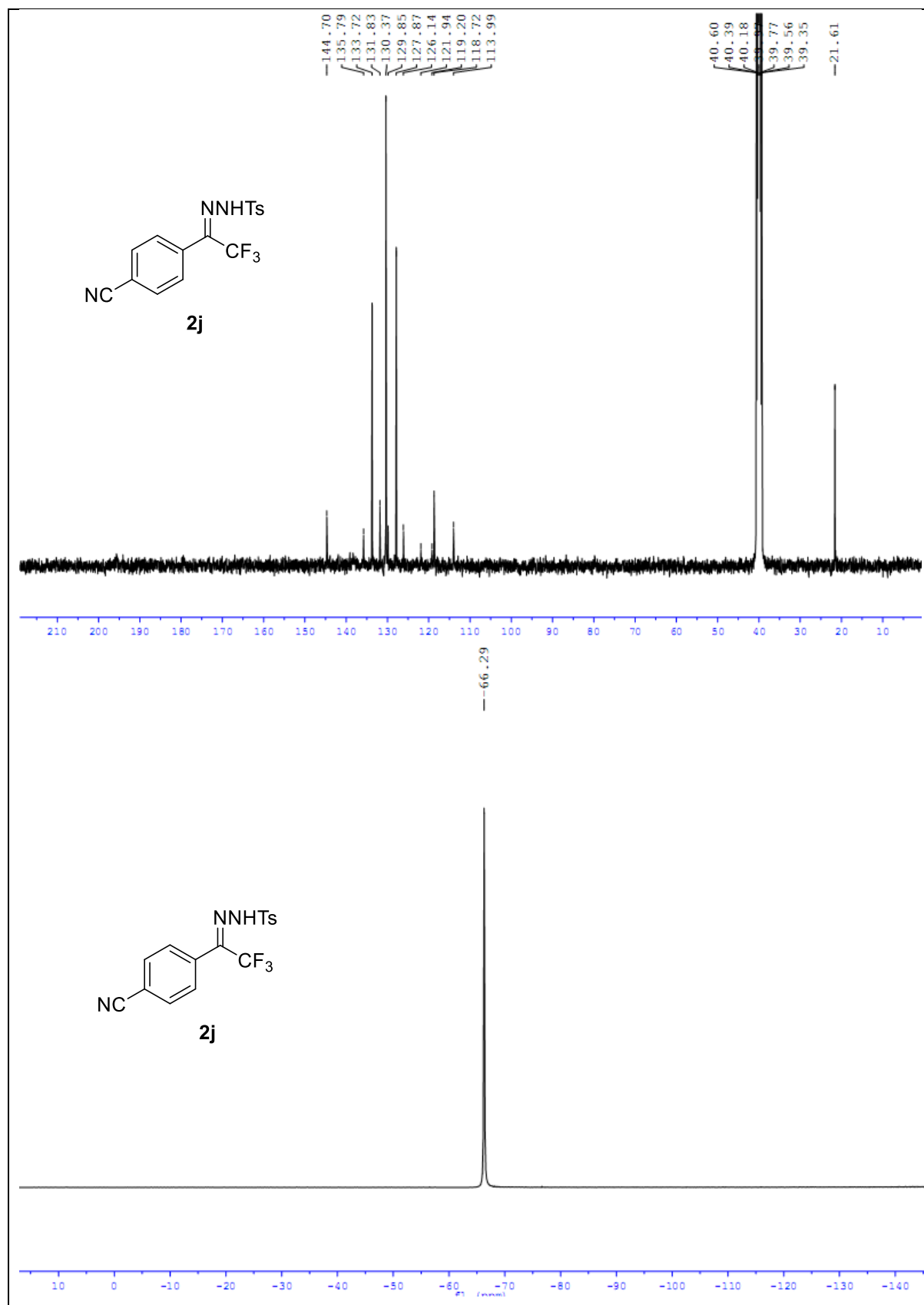


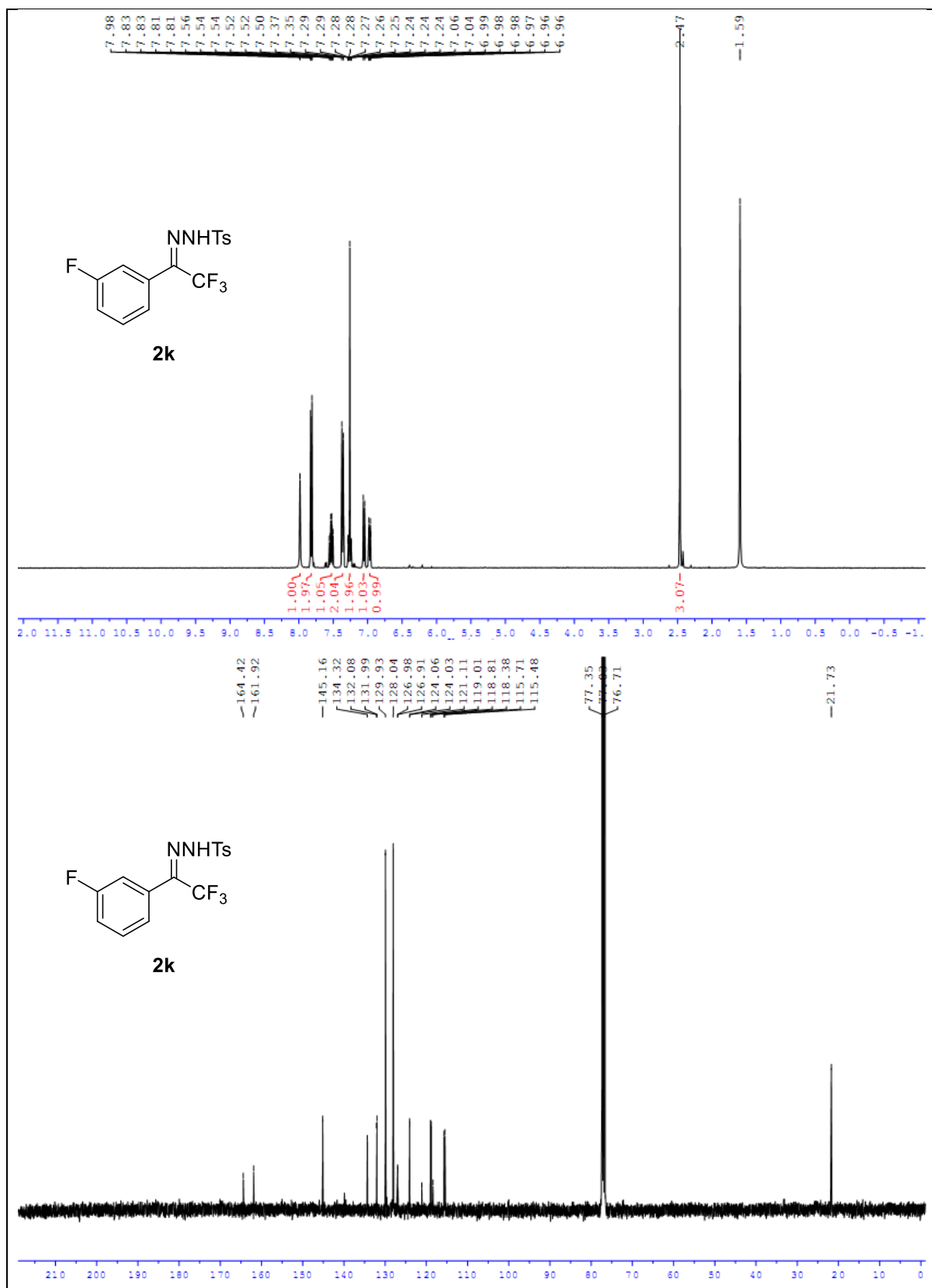


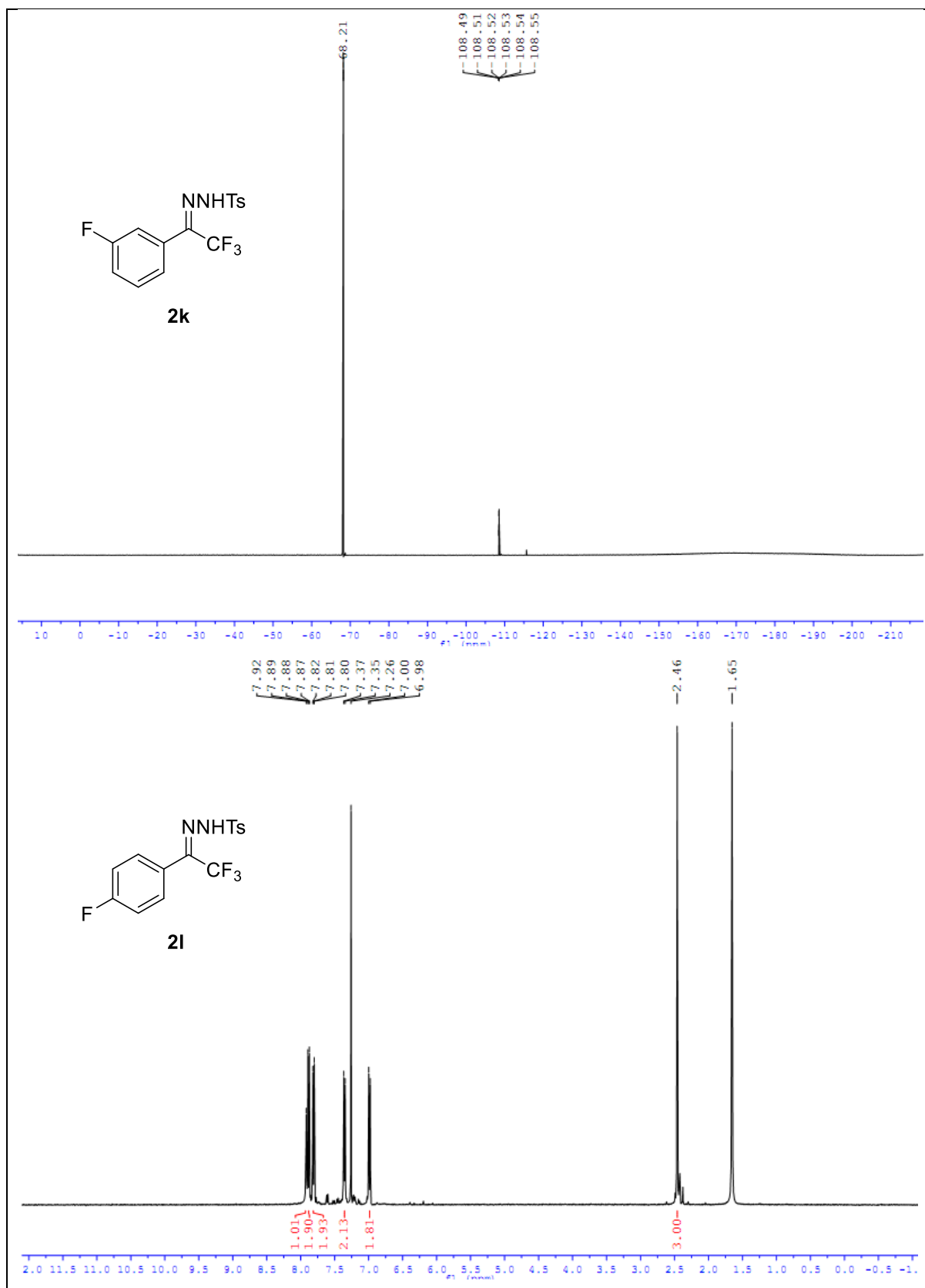


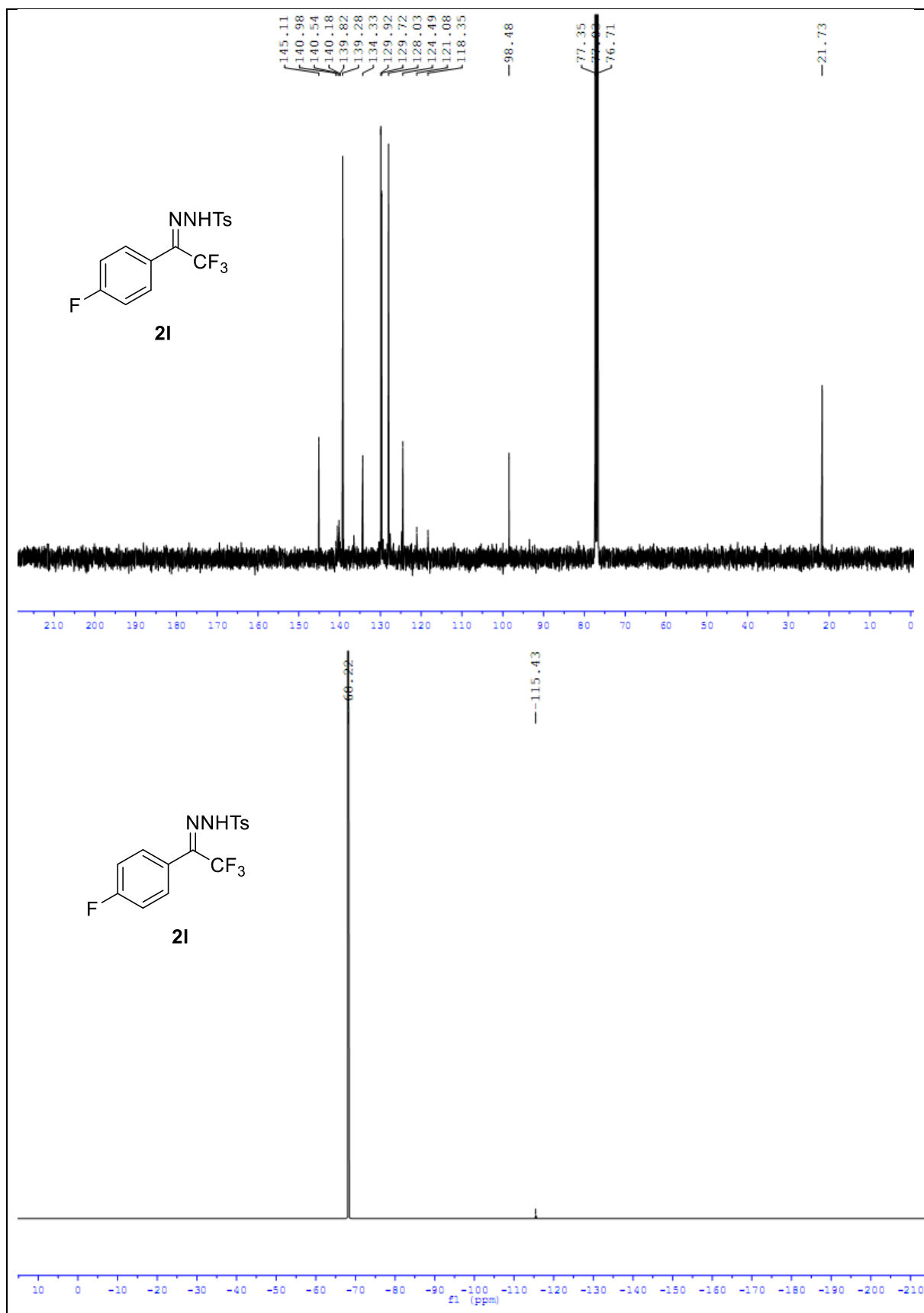


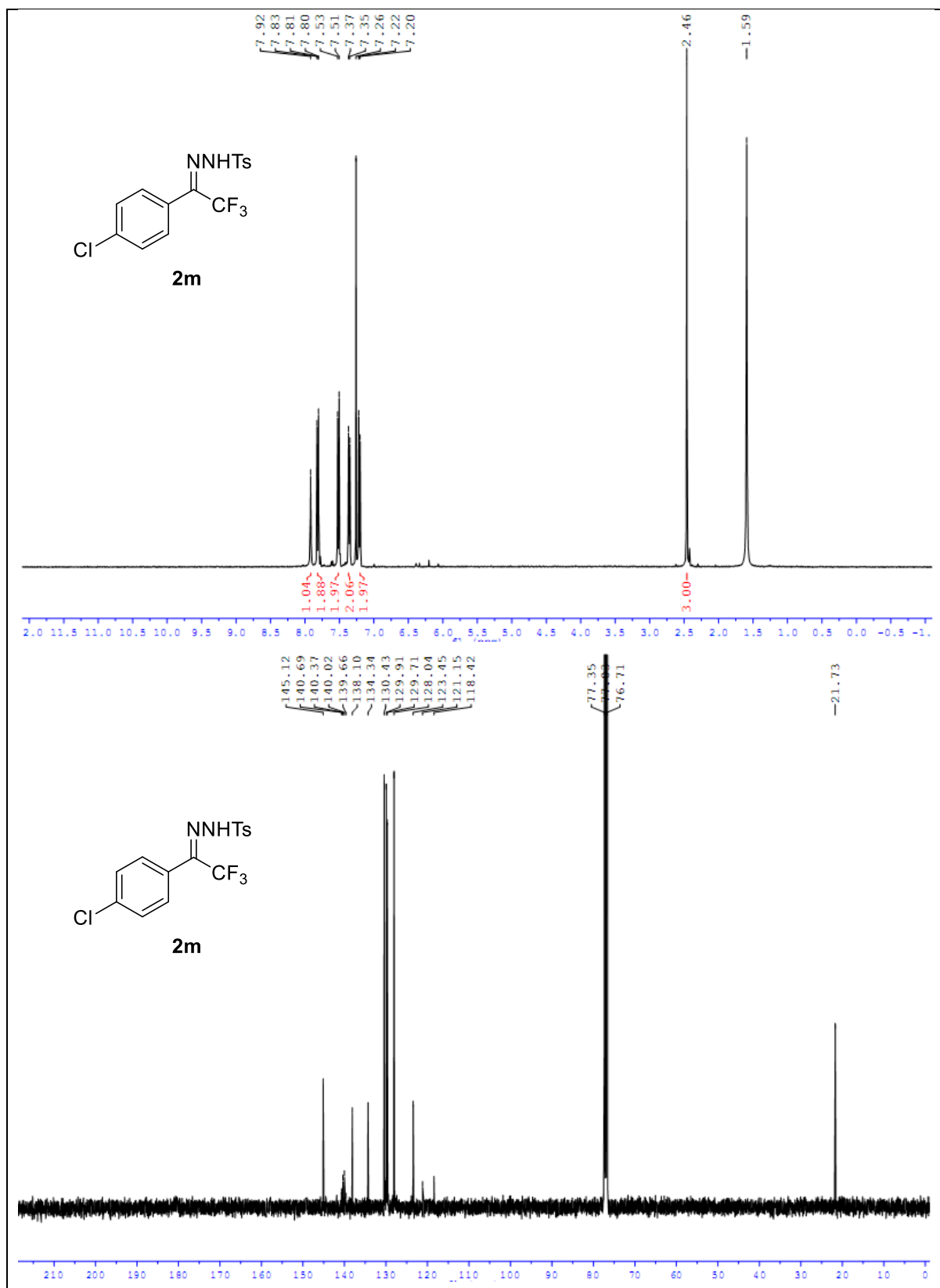


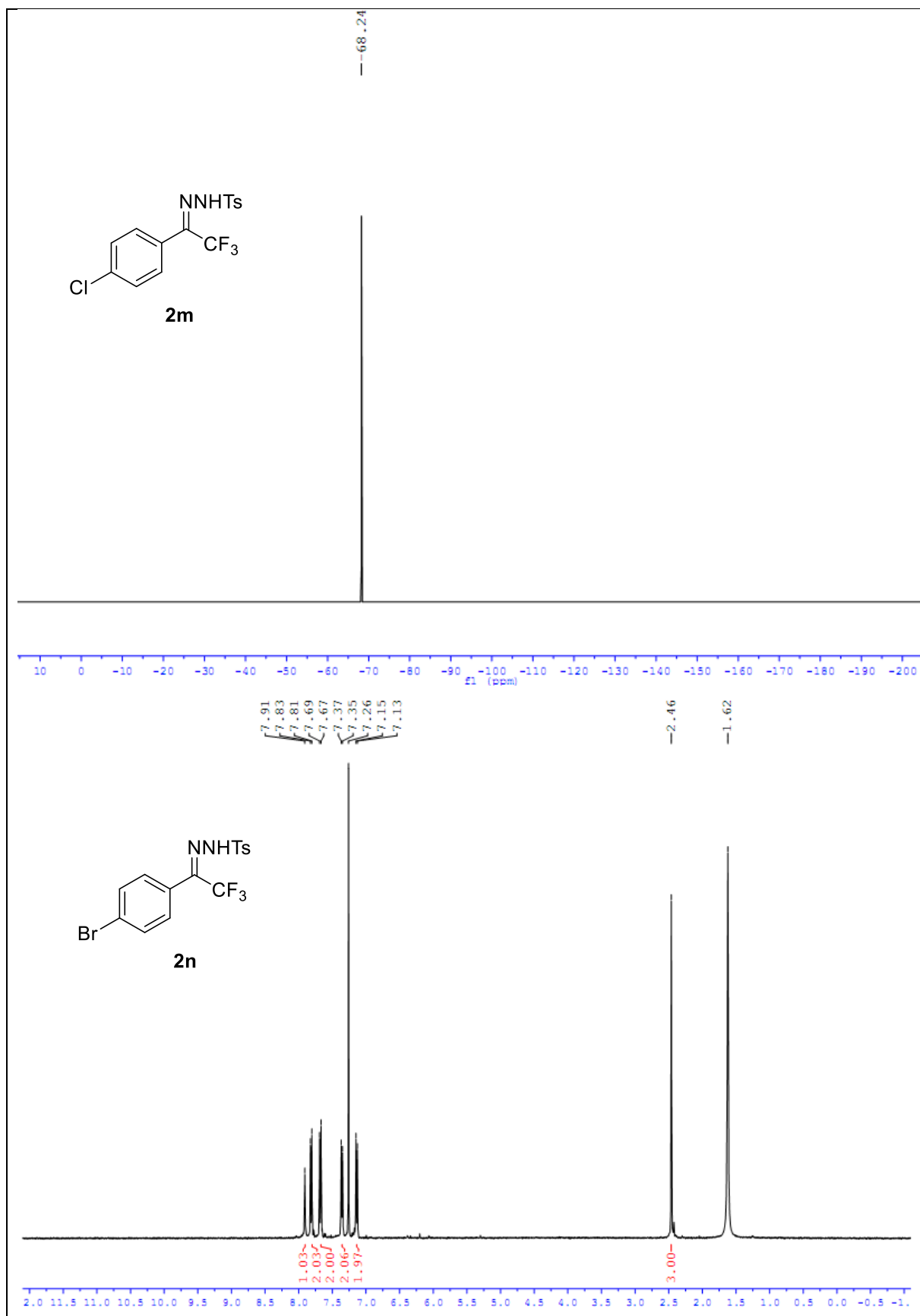


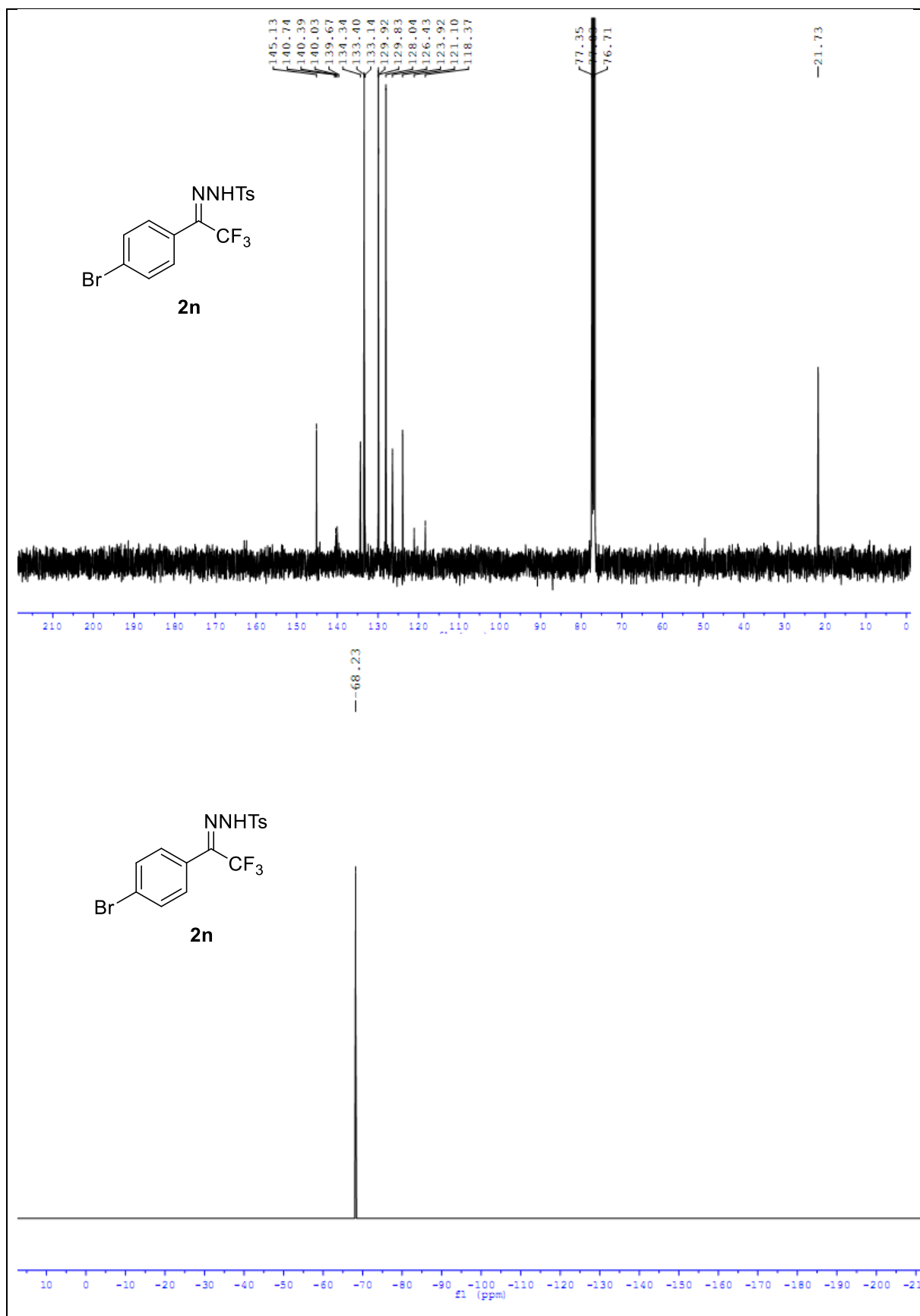


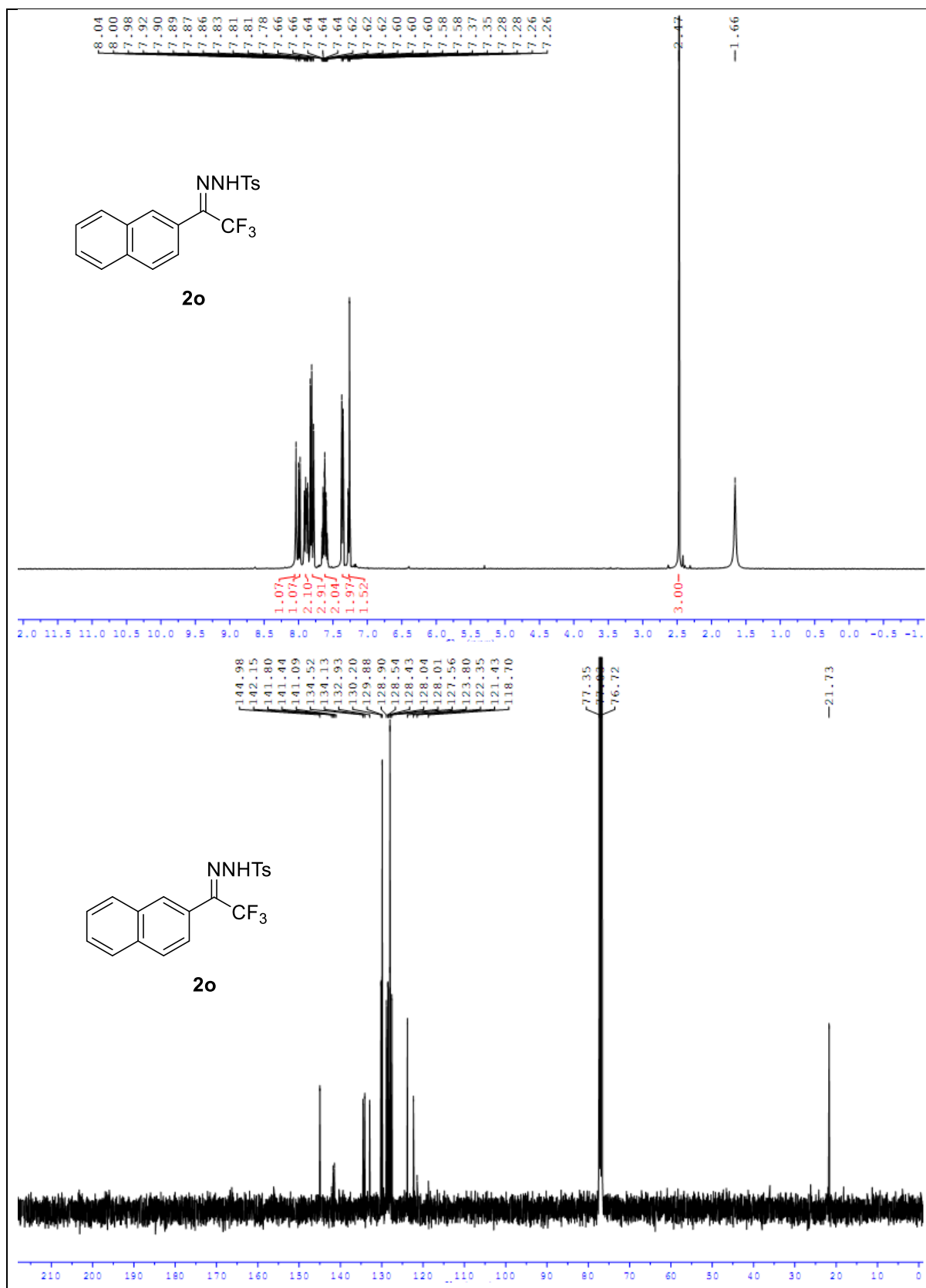


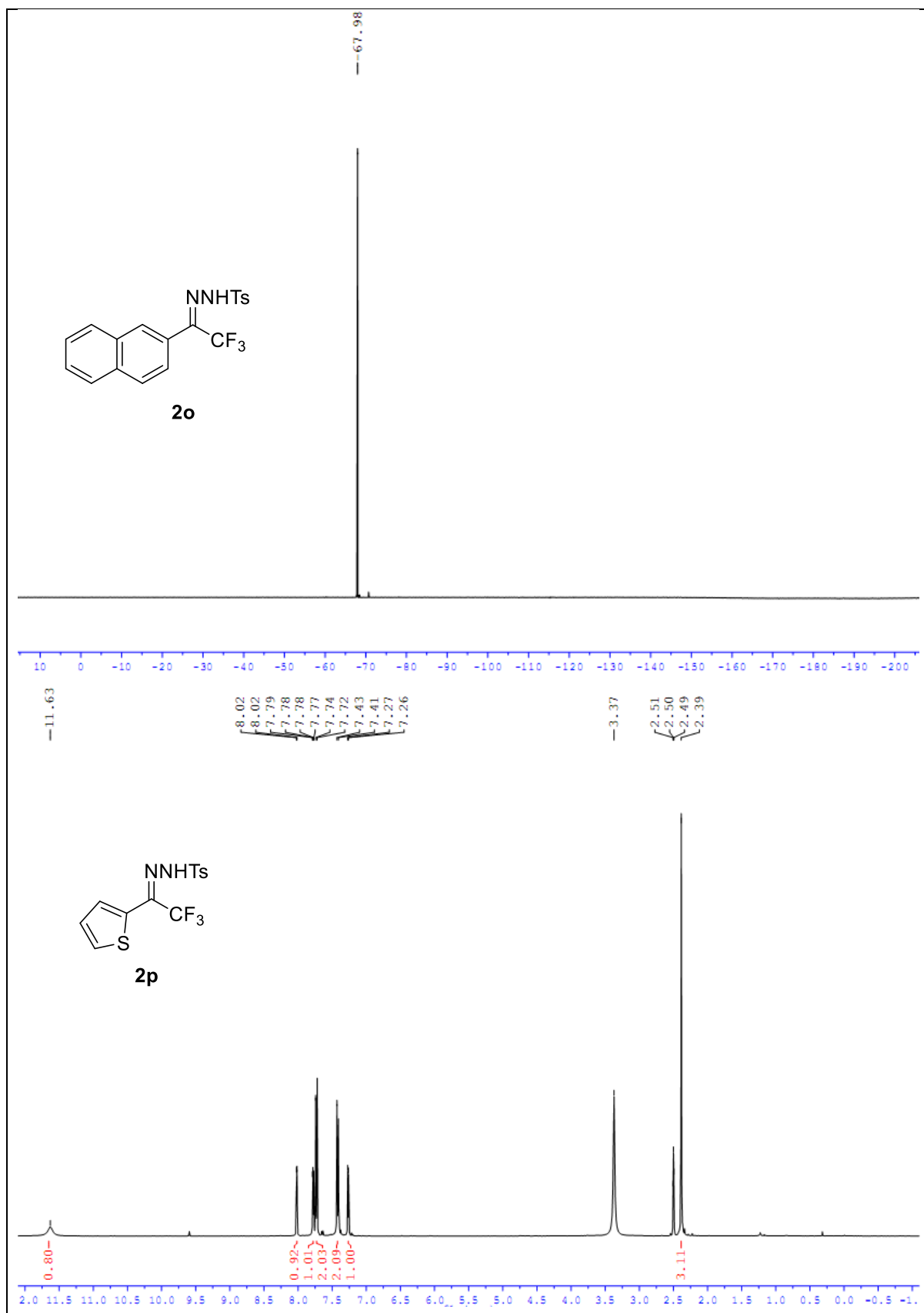


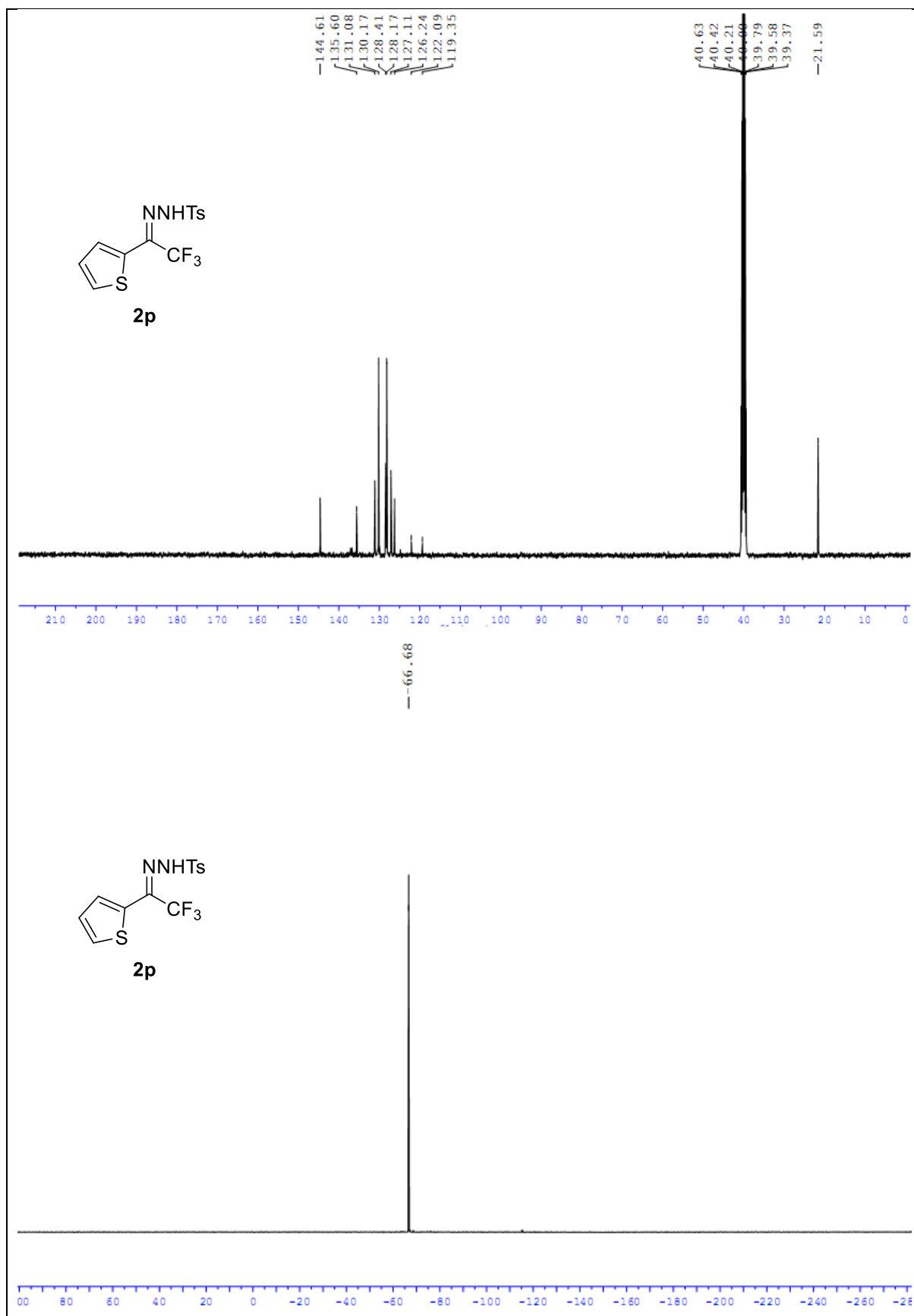




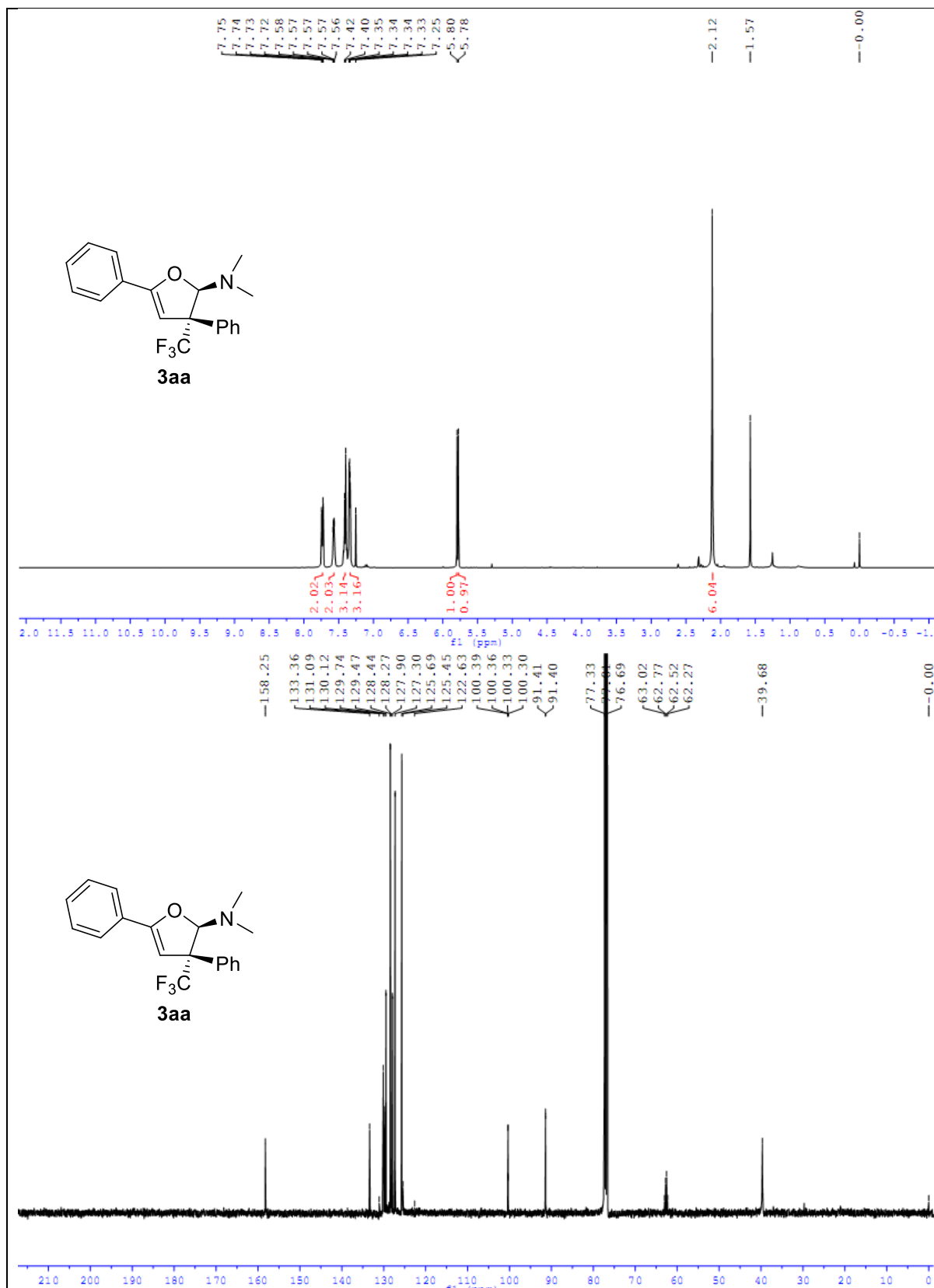


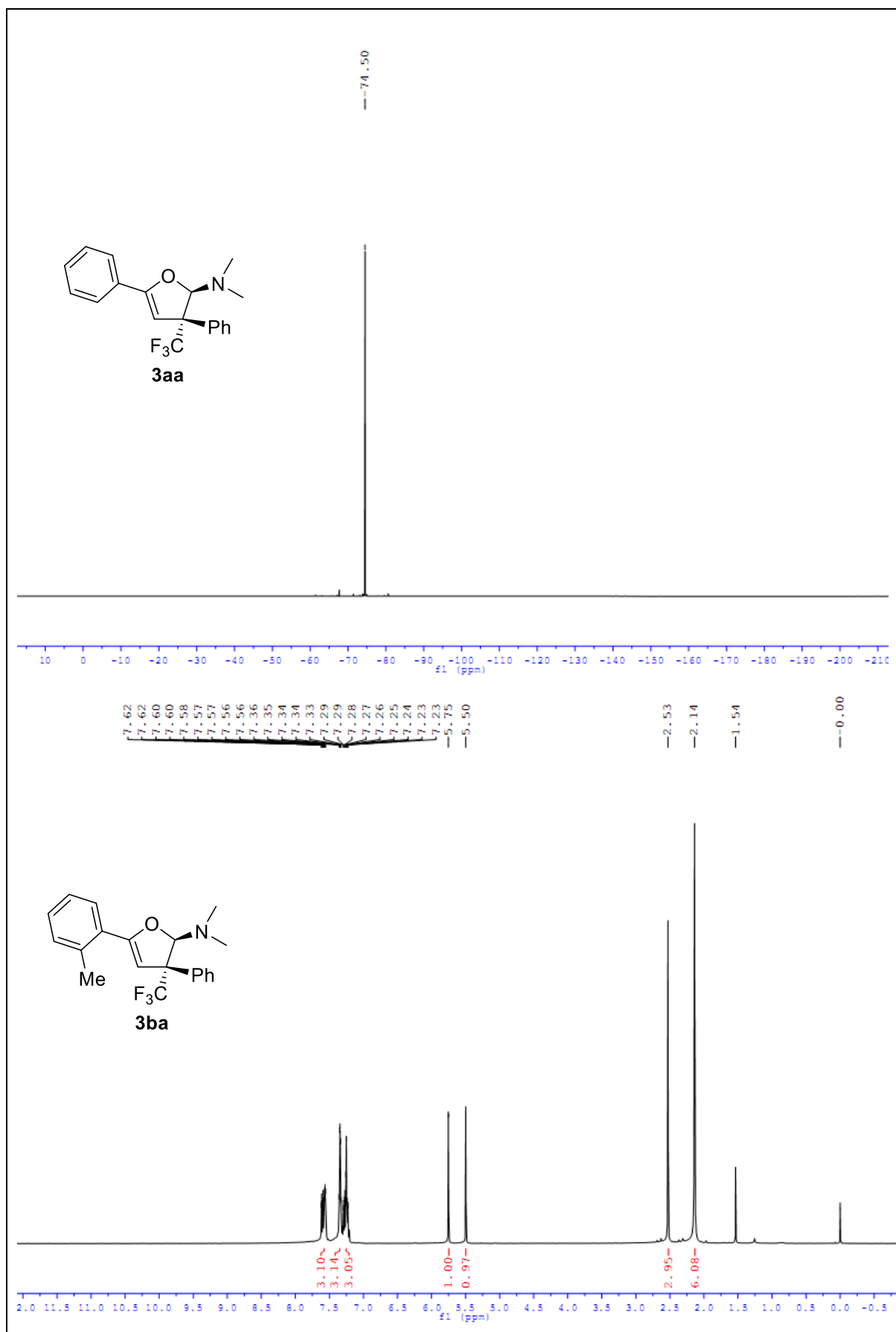


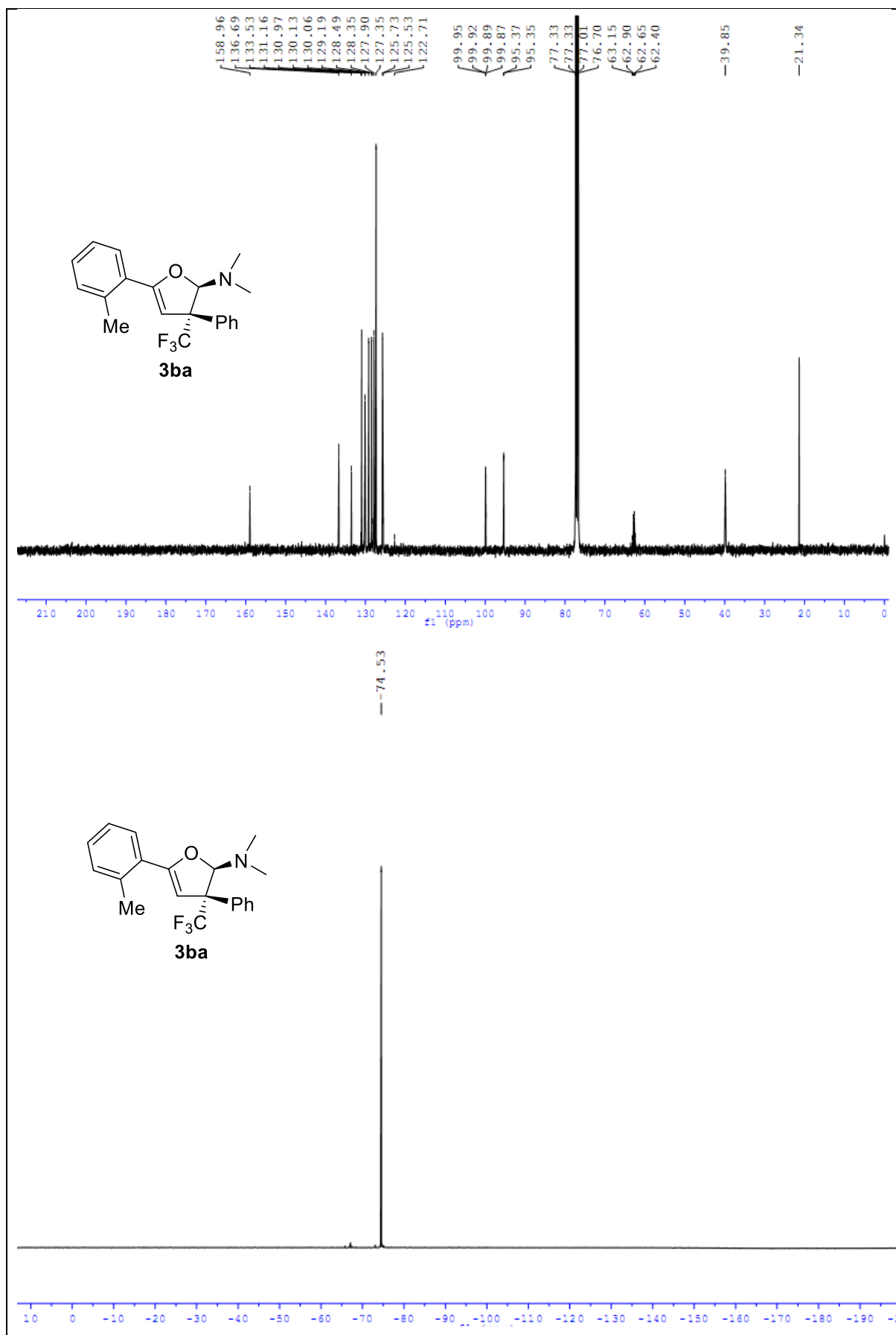


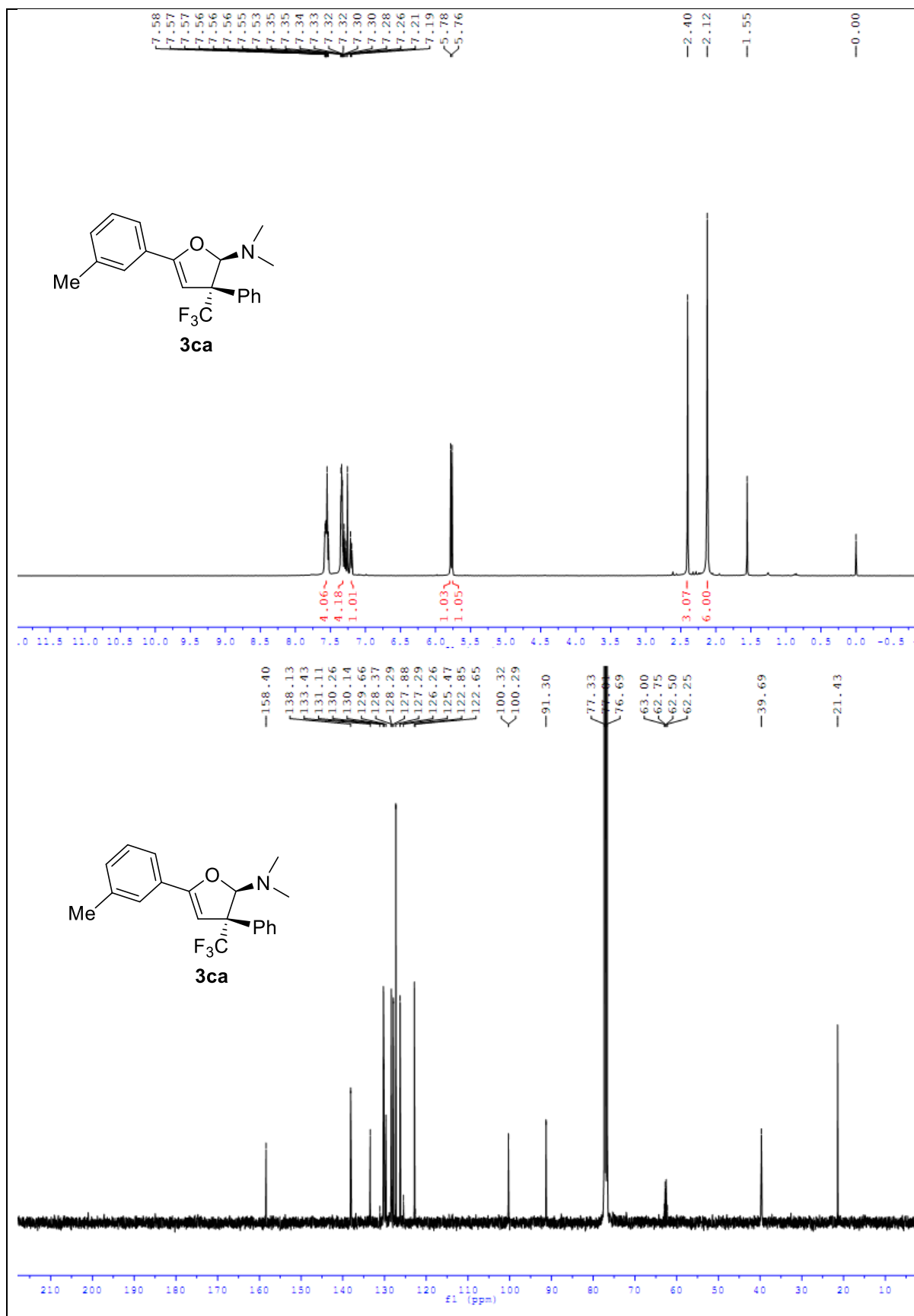


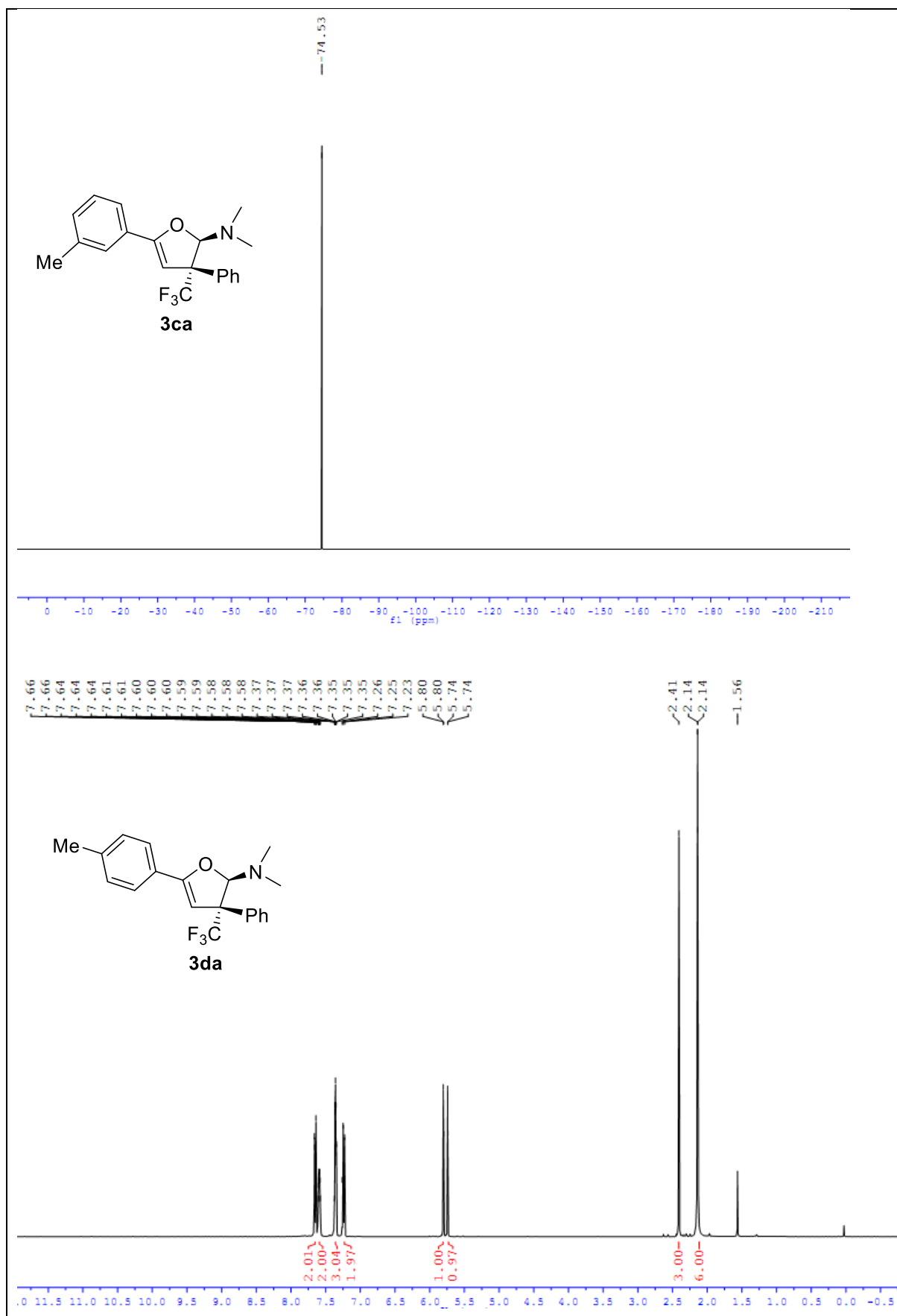
NMR spectra of 2*H*-furans

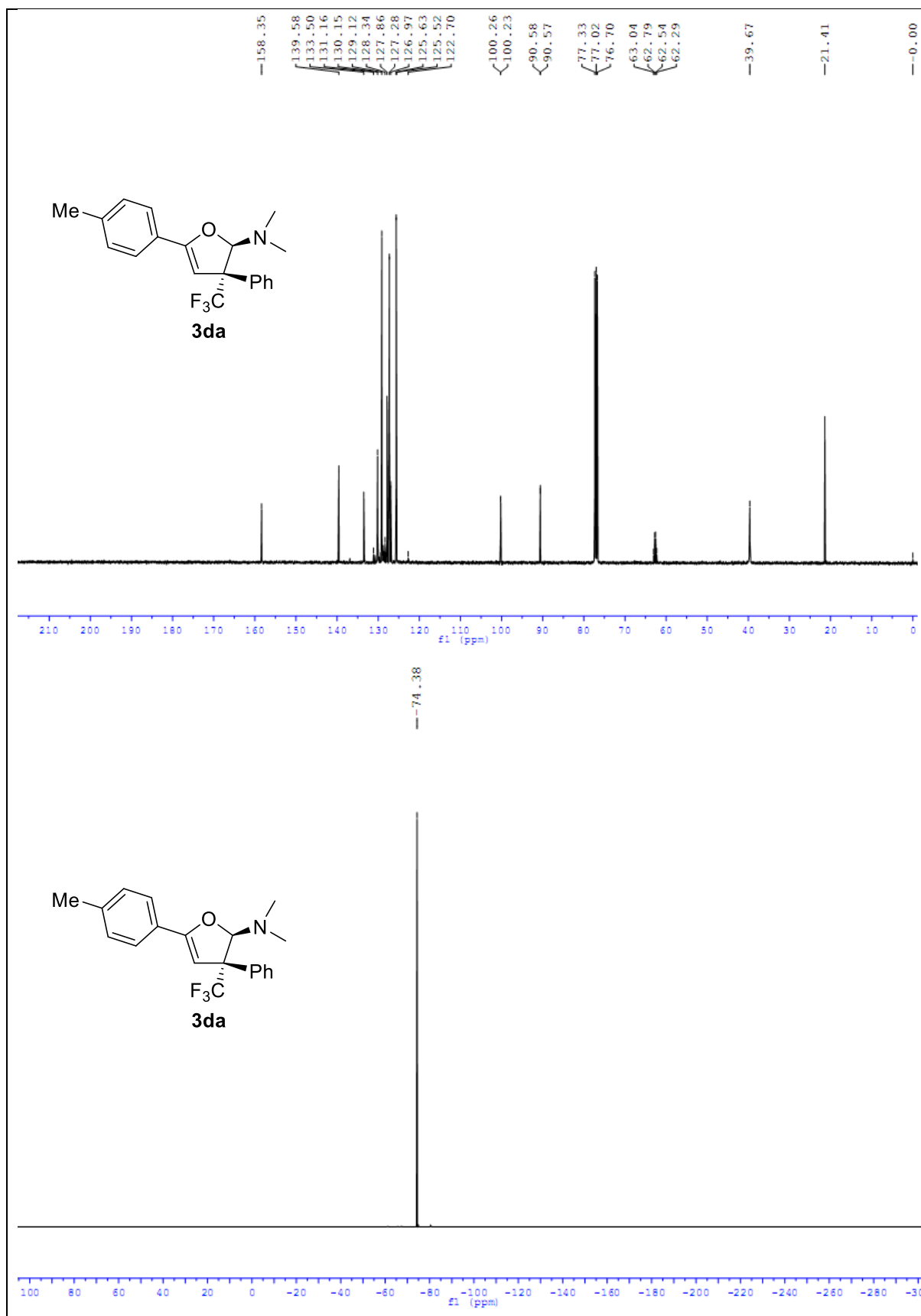


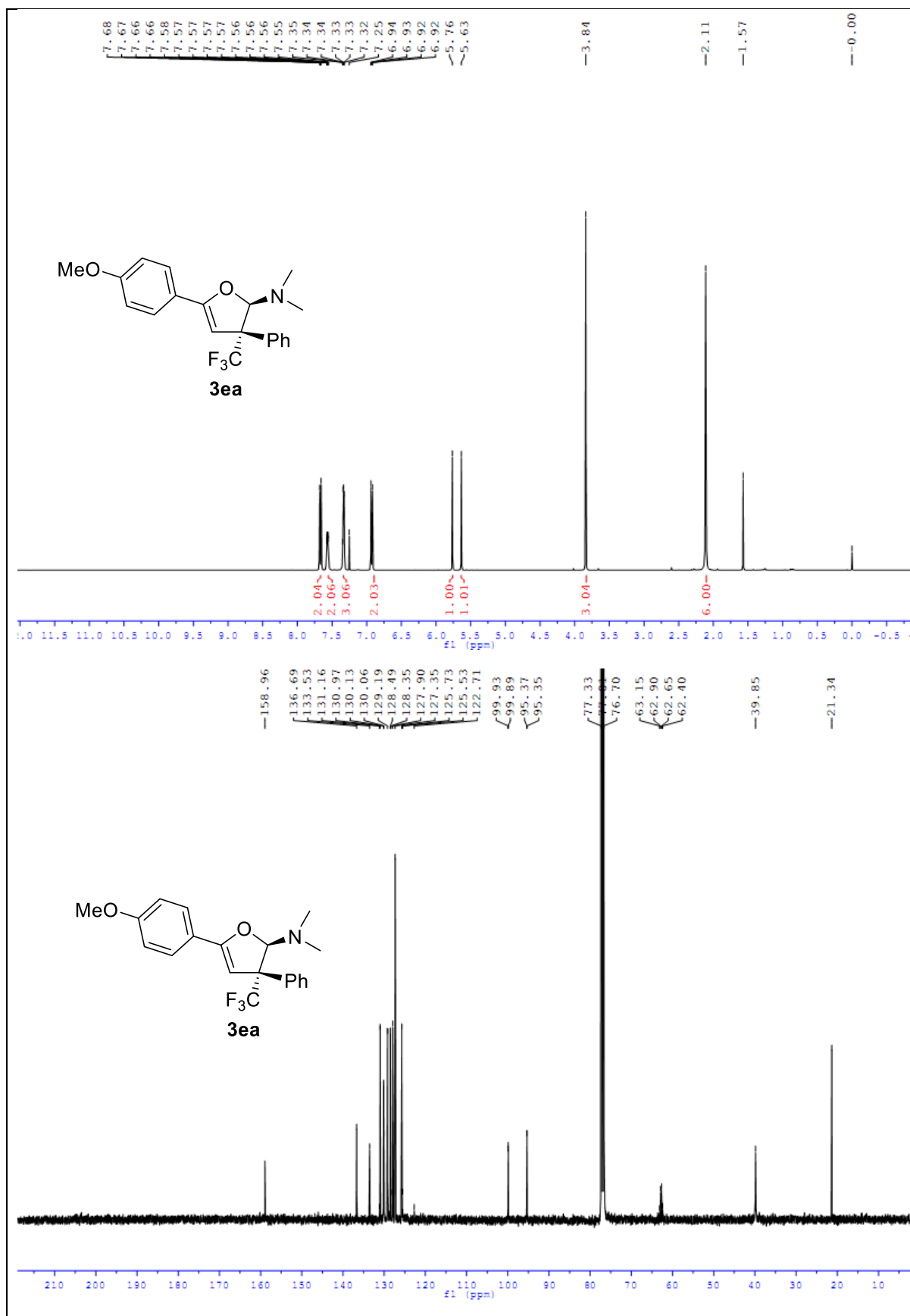


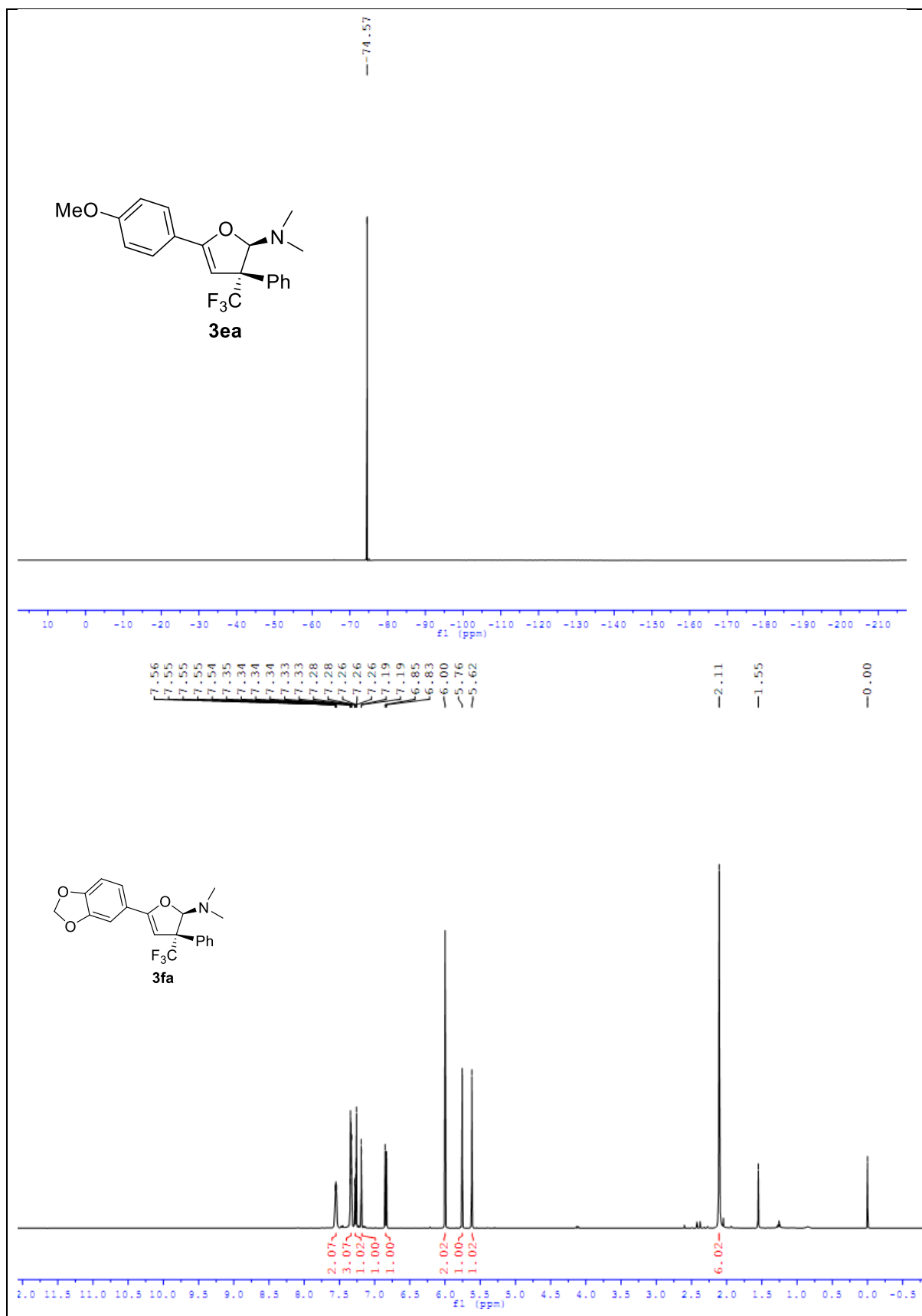


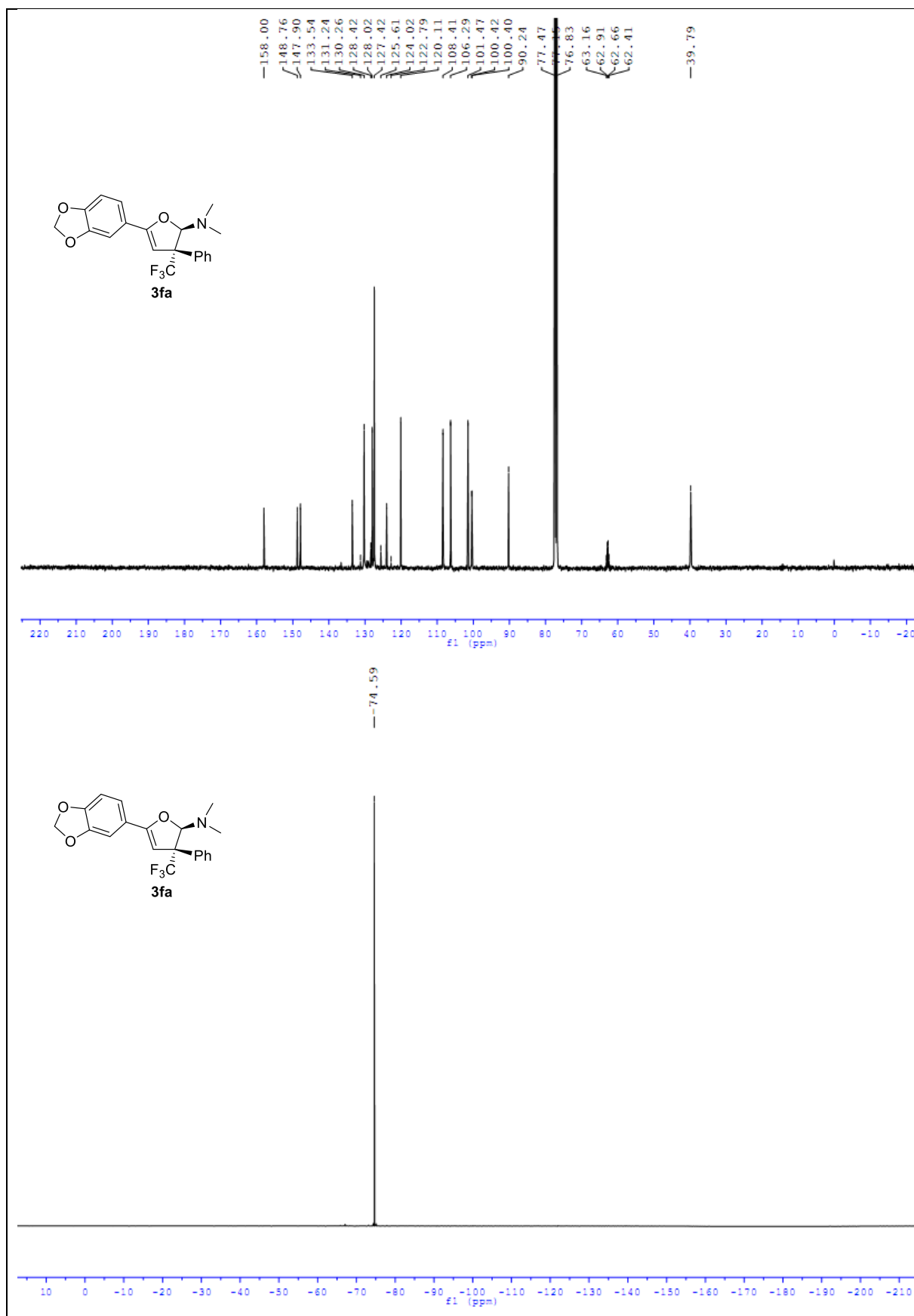


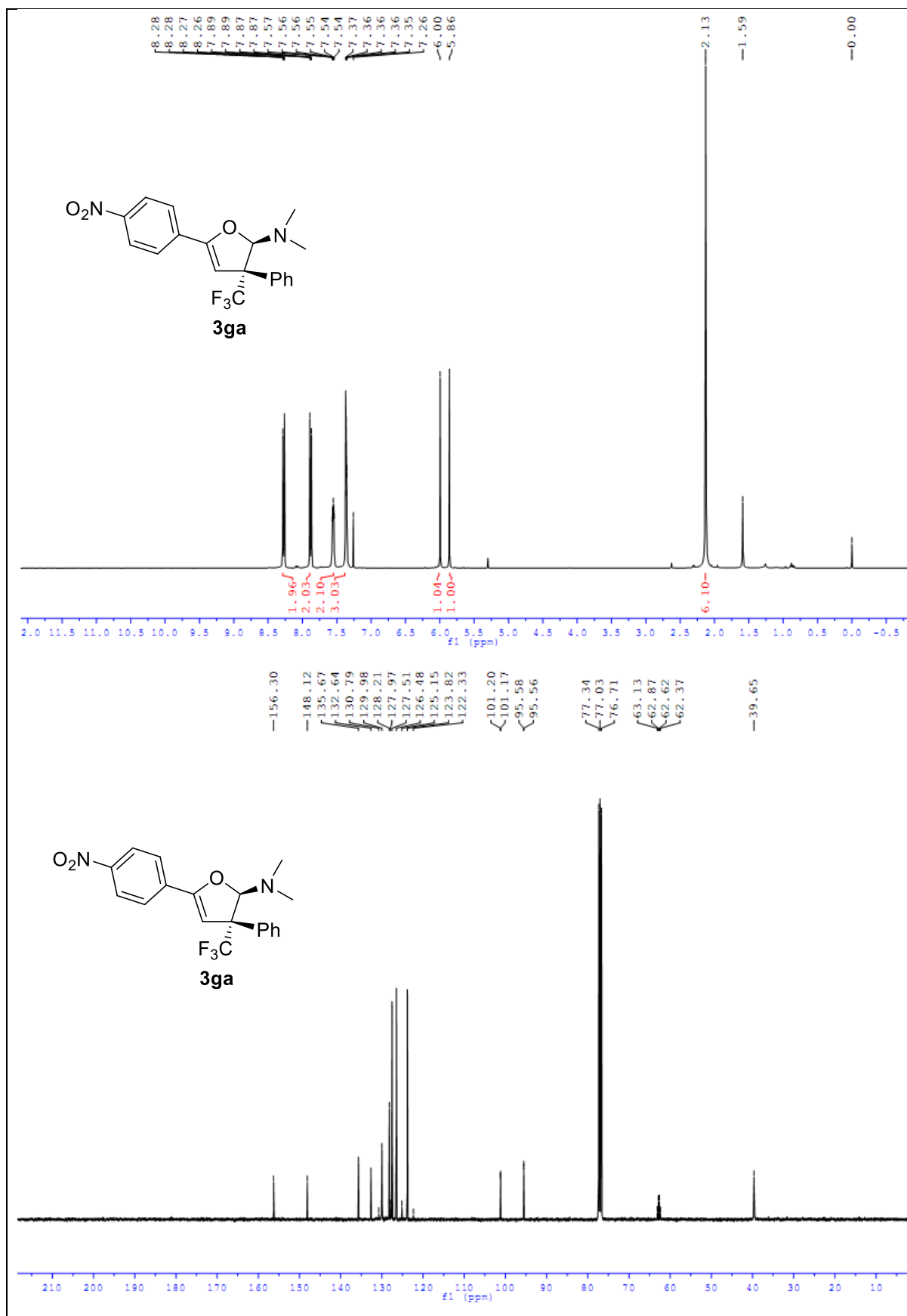


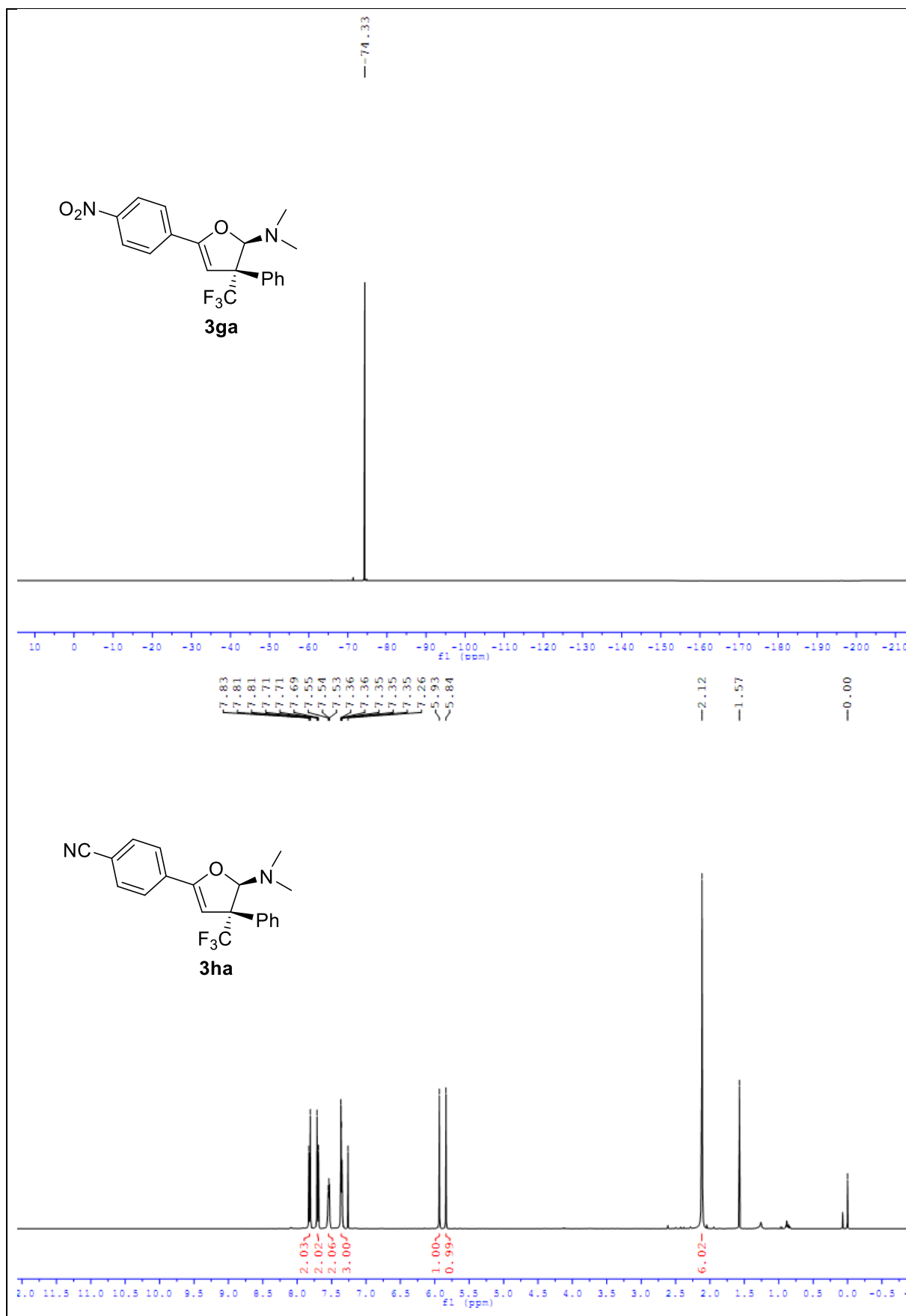


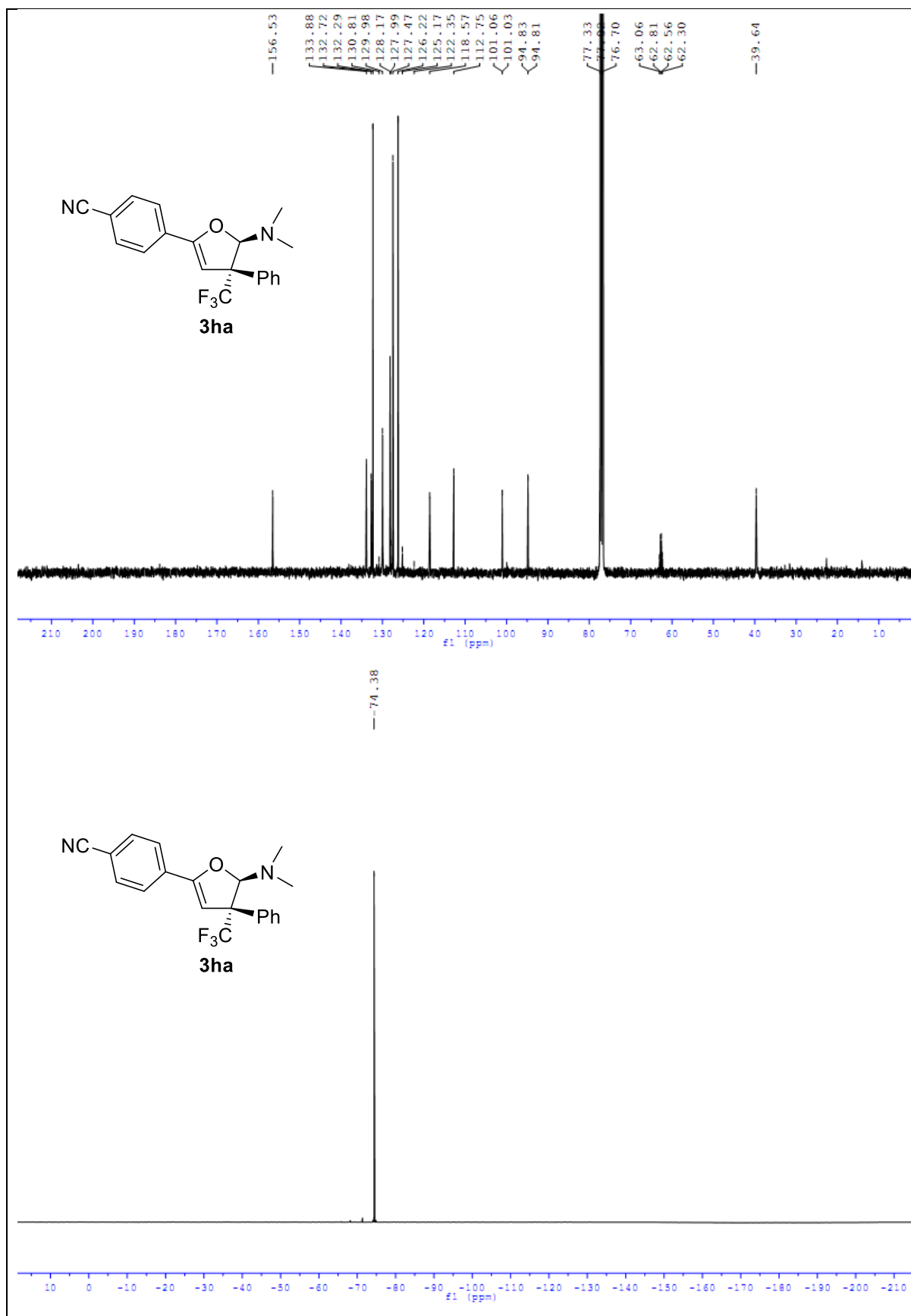


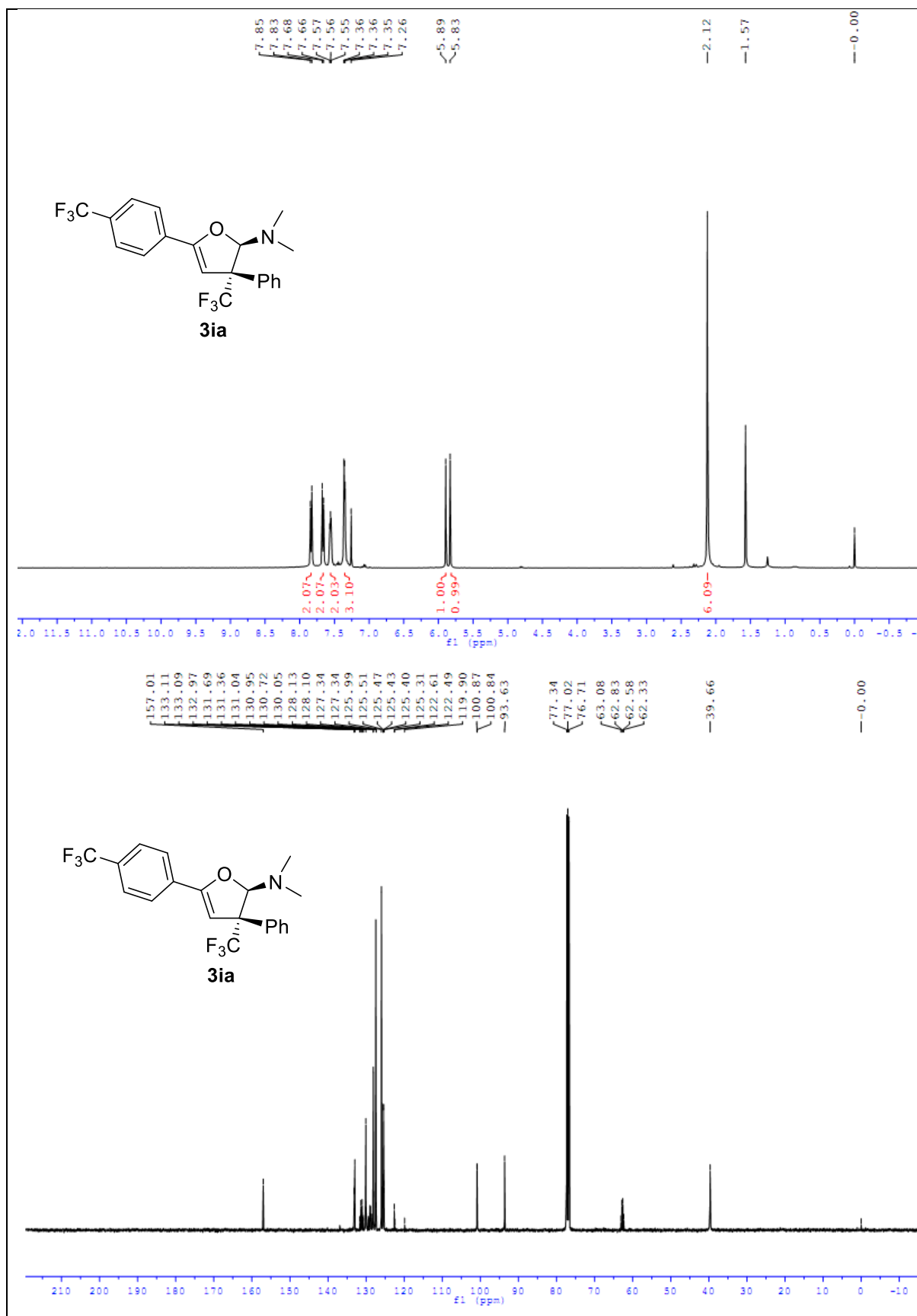


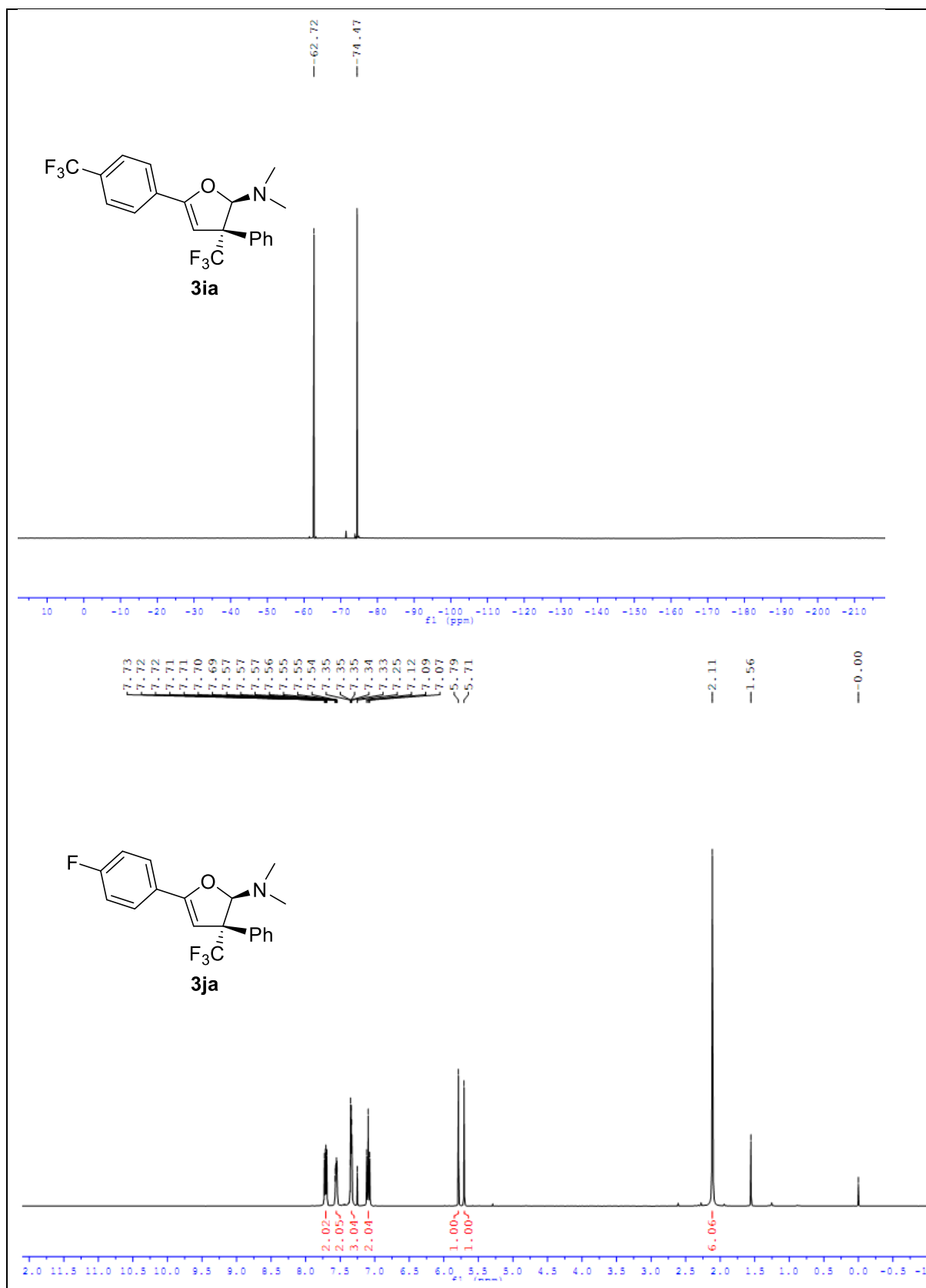


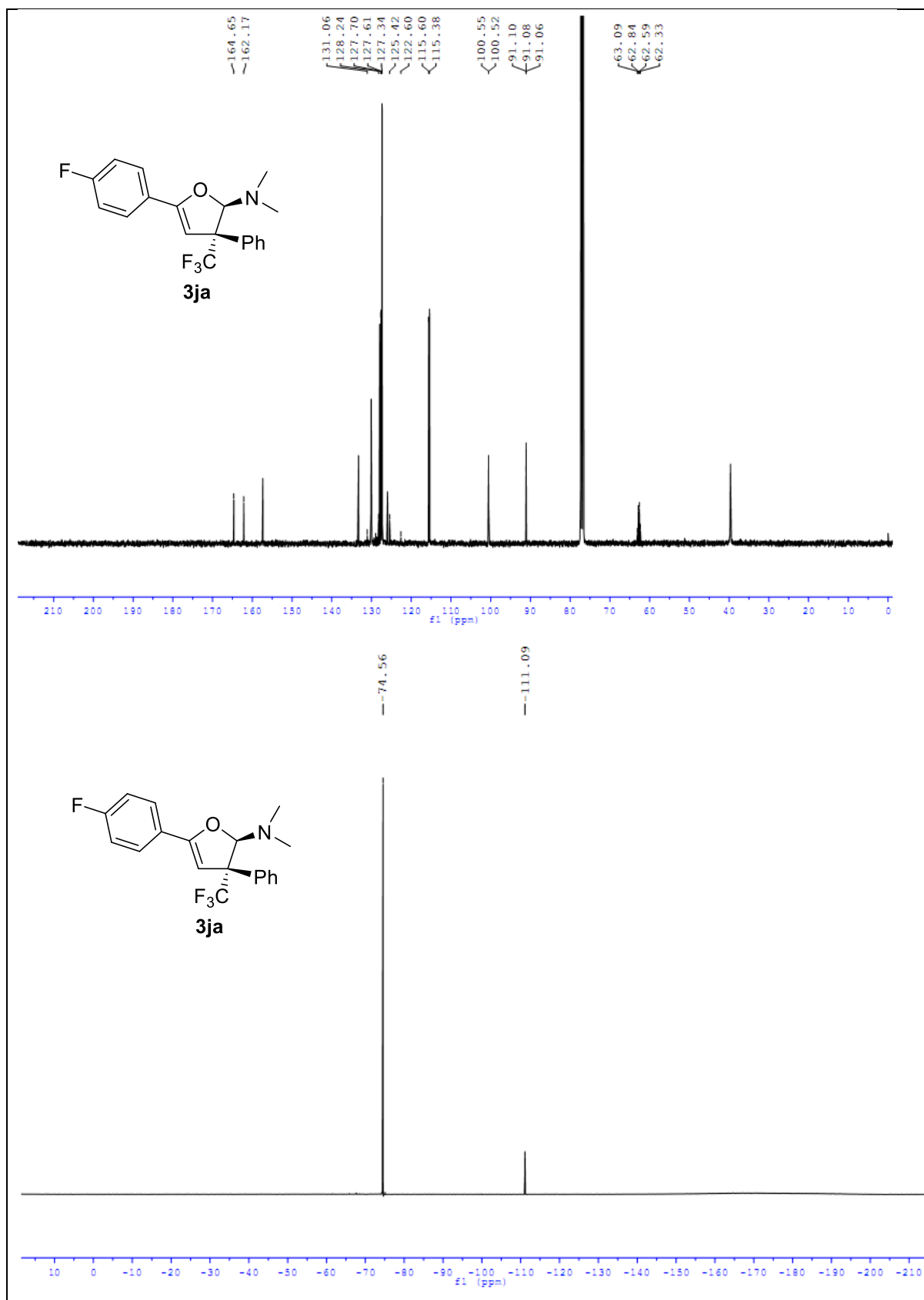


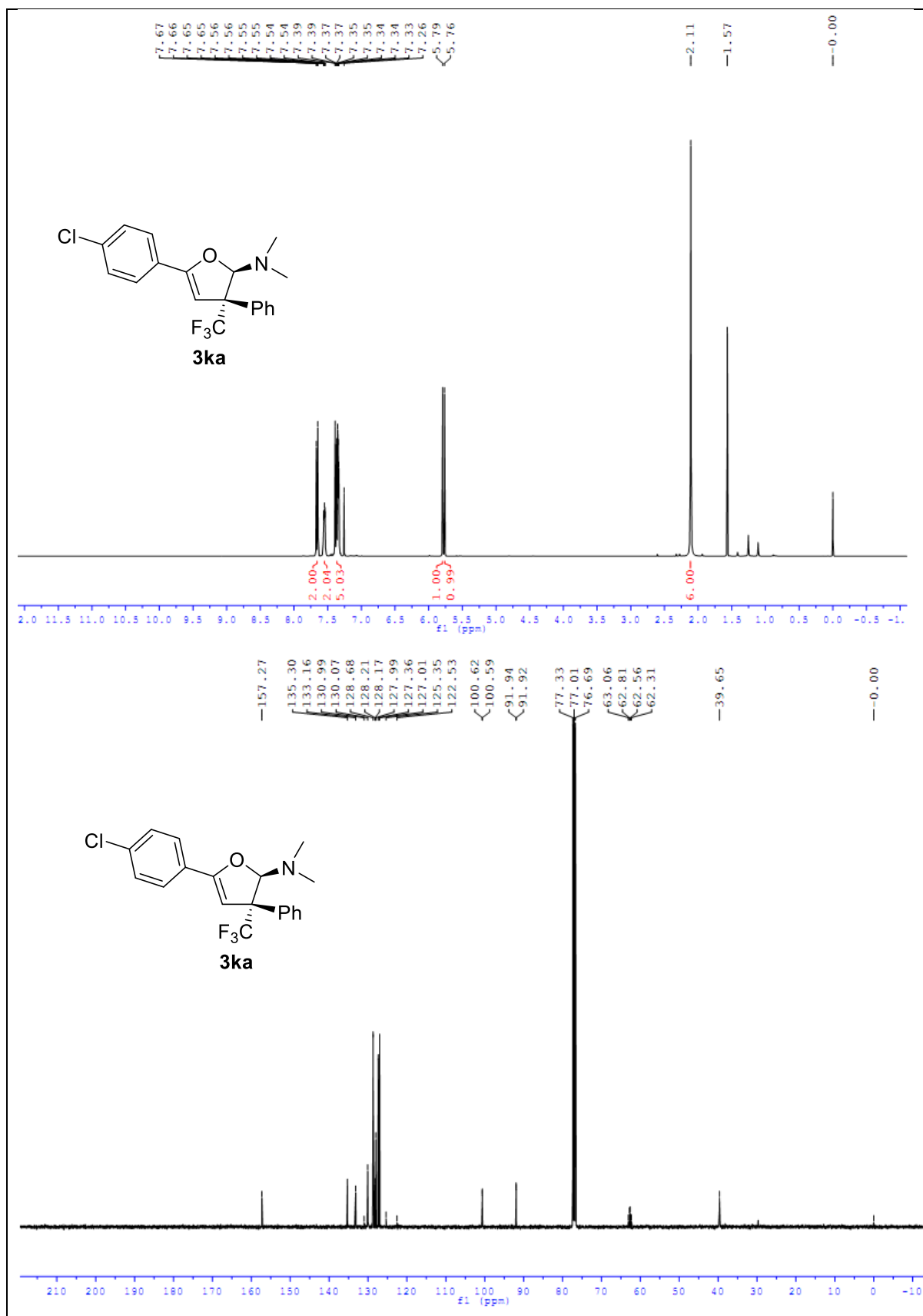


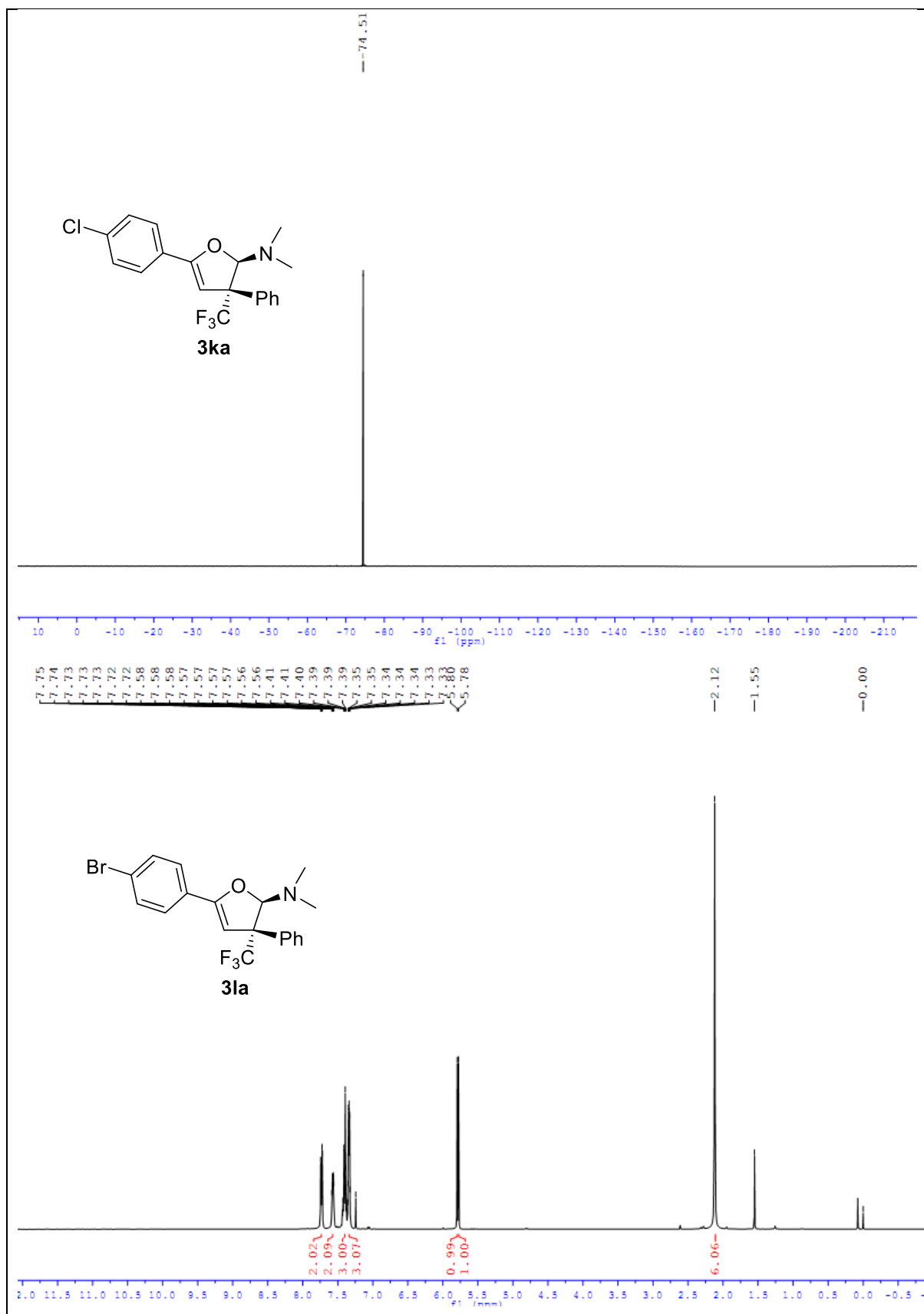


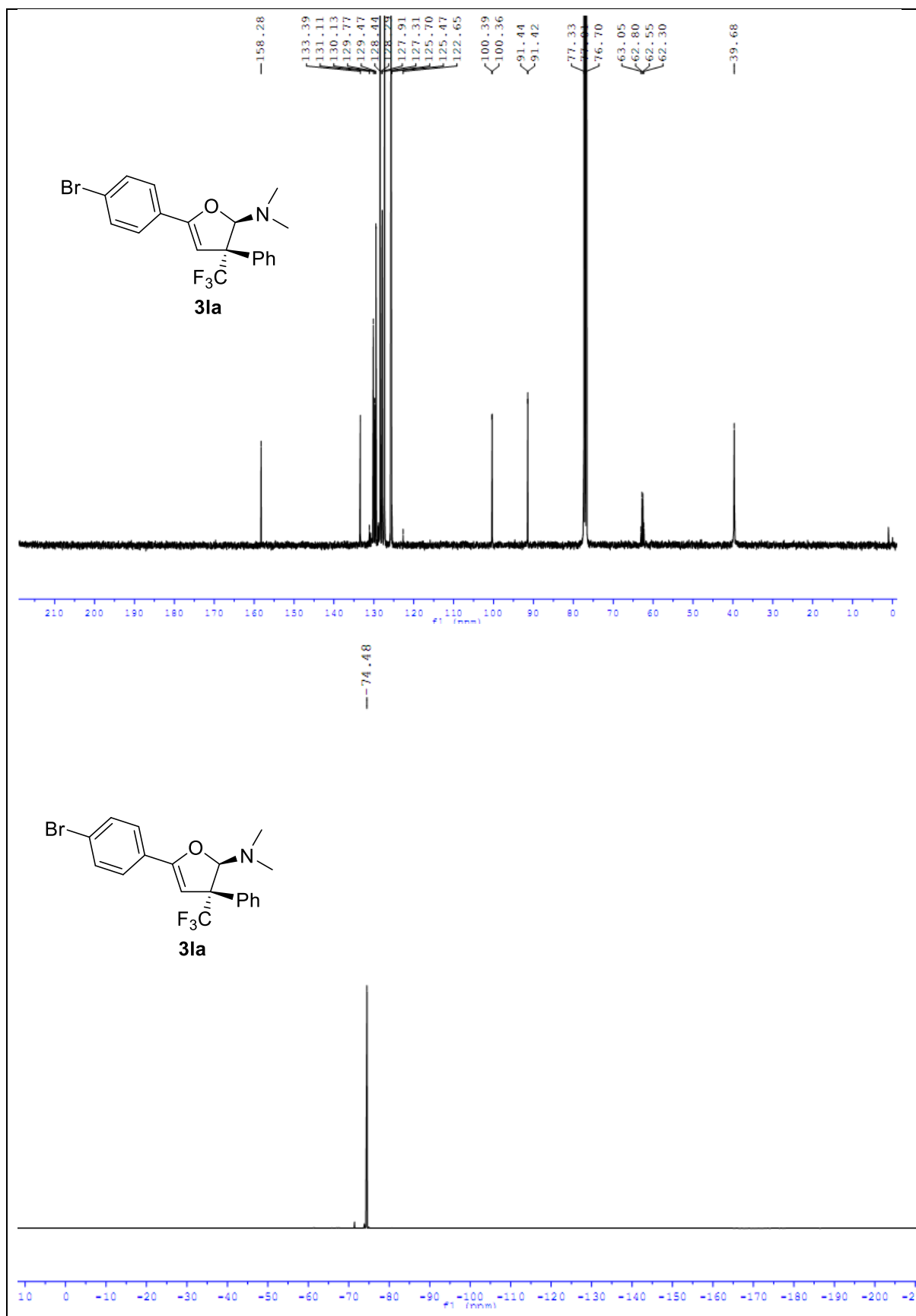


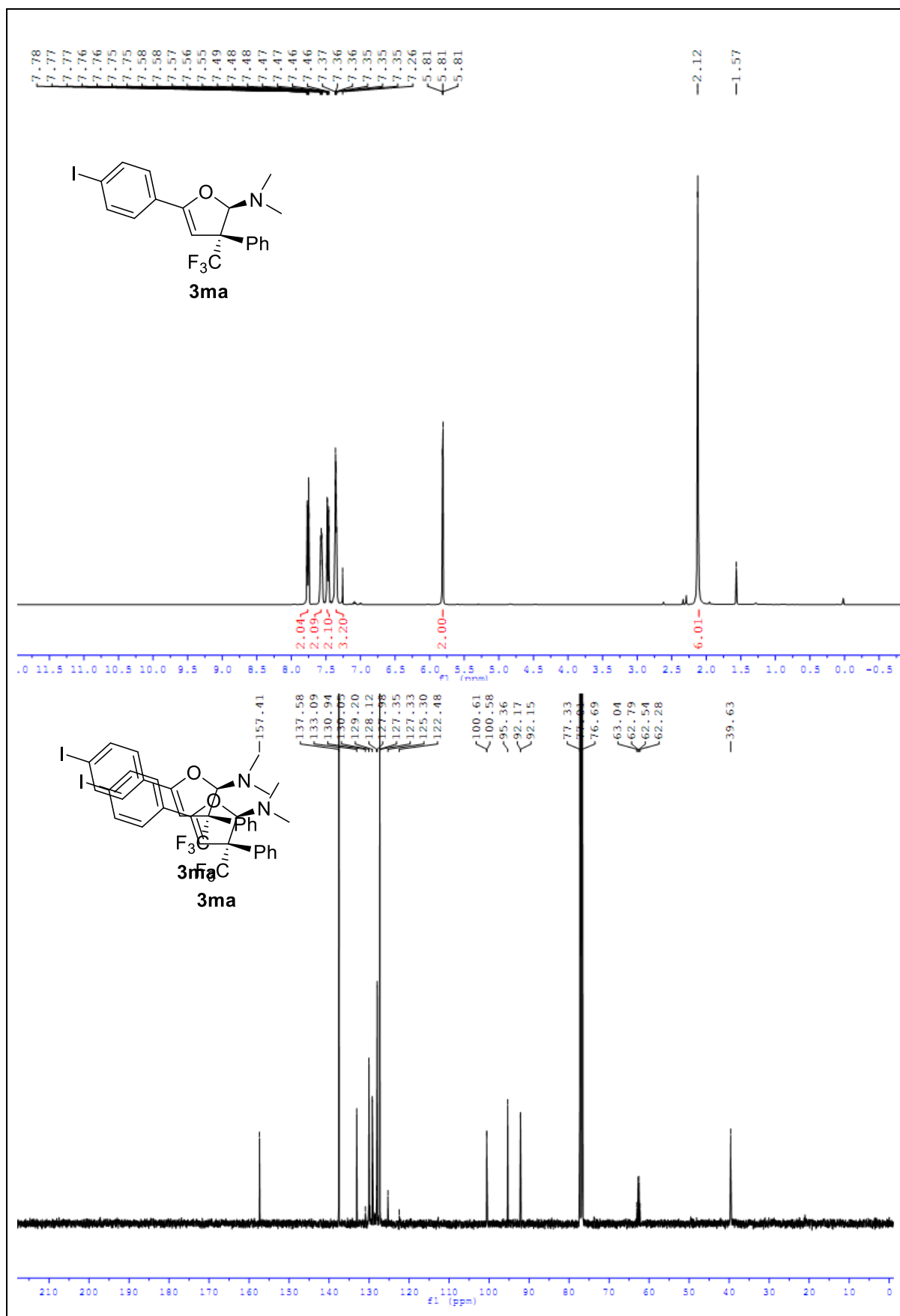


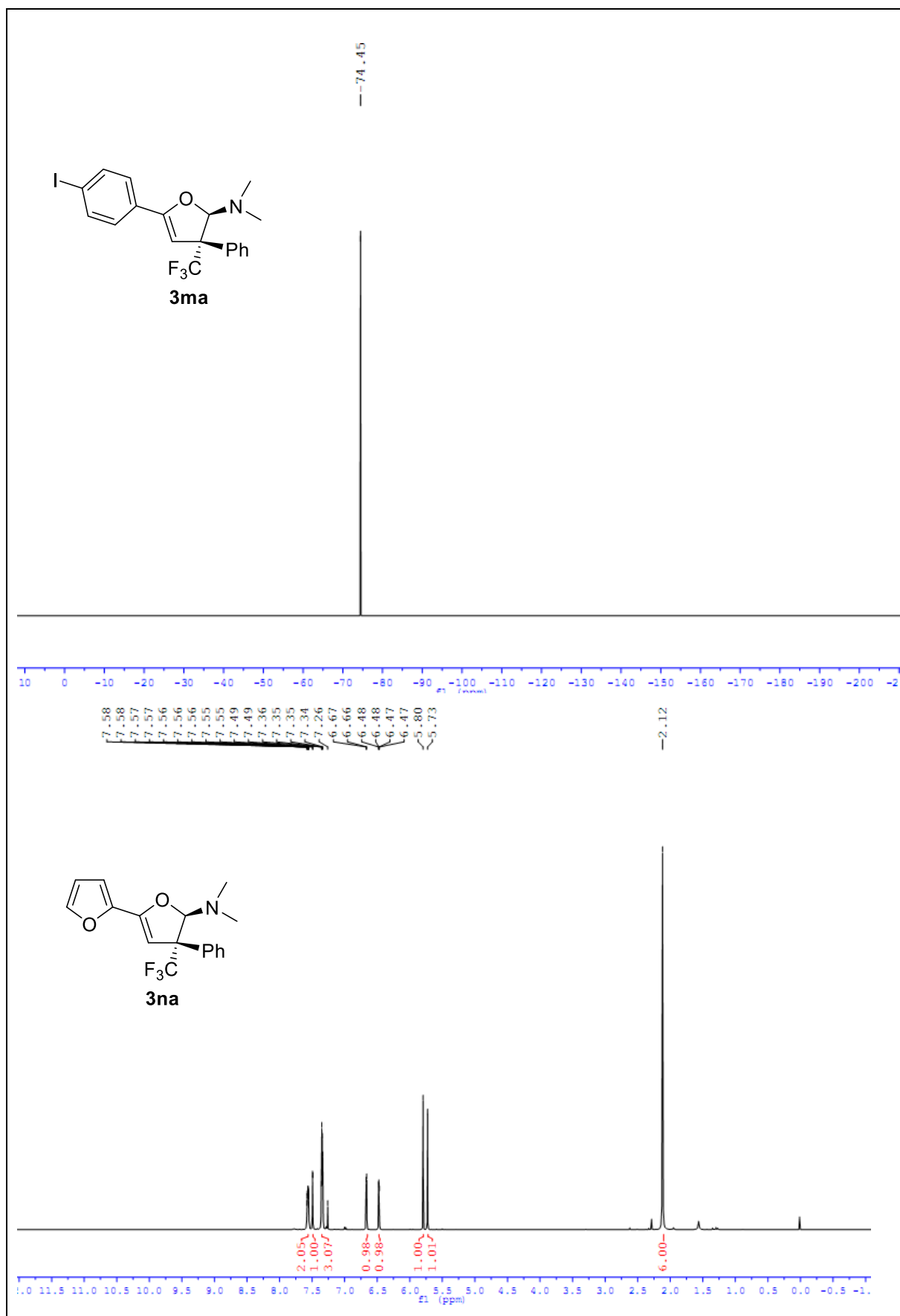


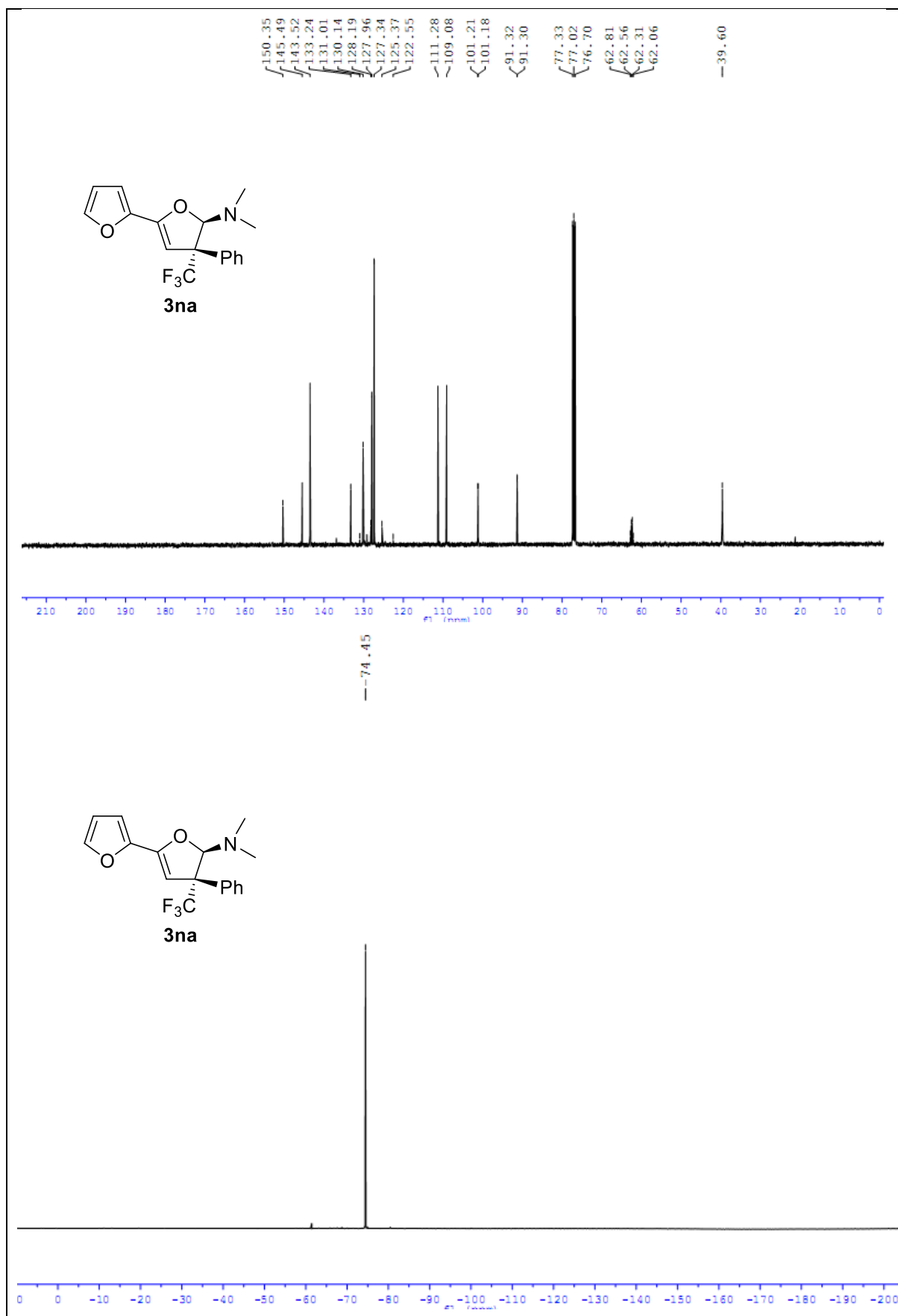


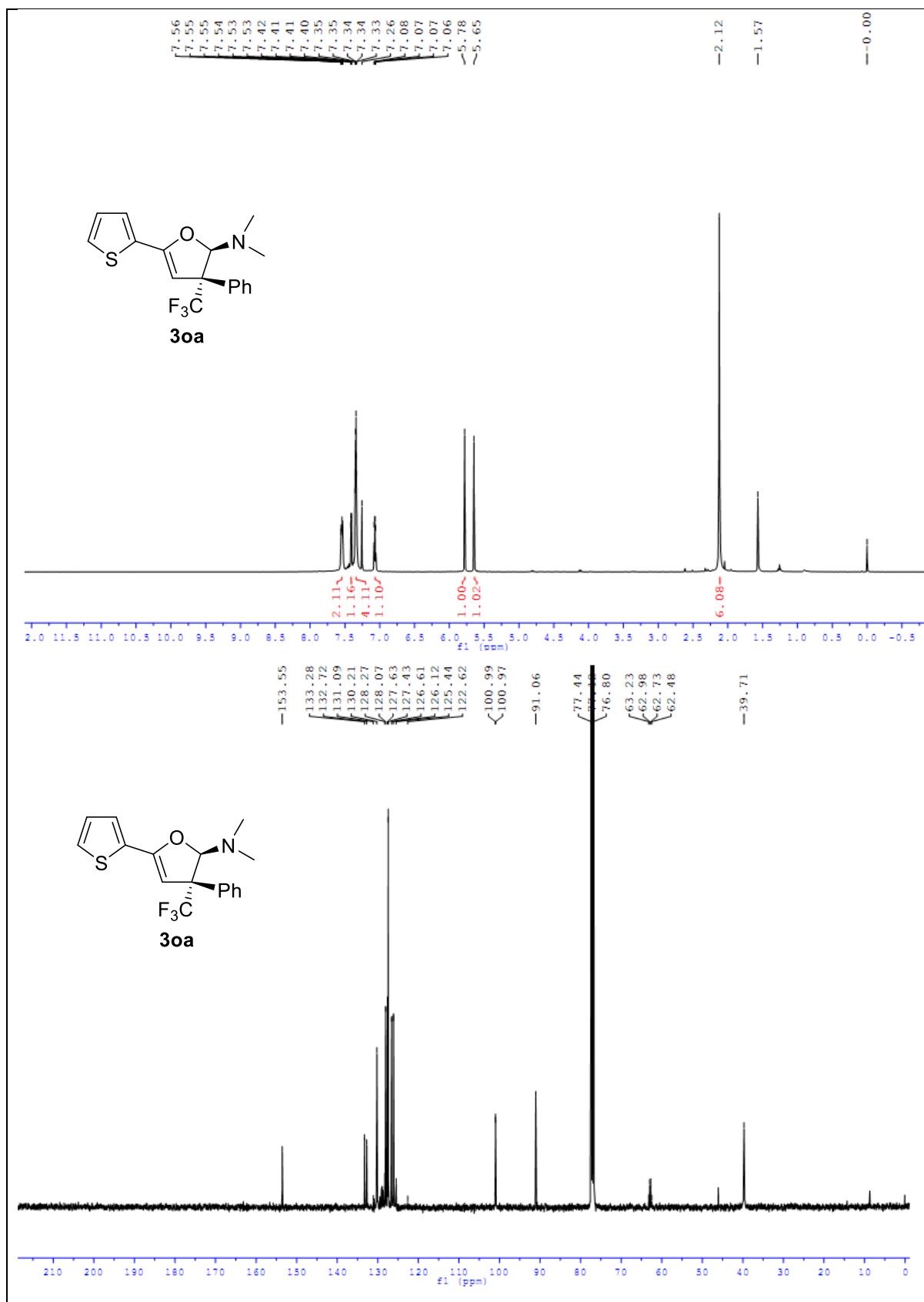




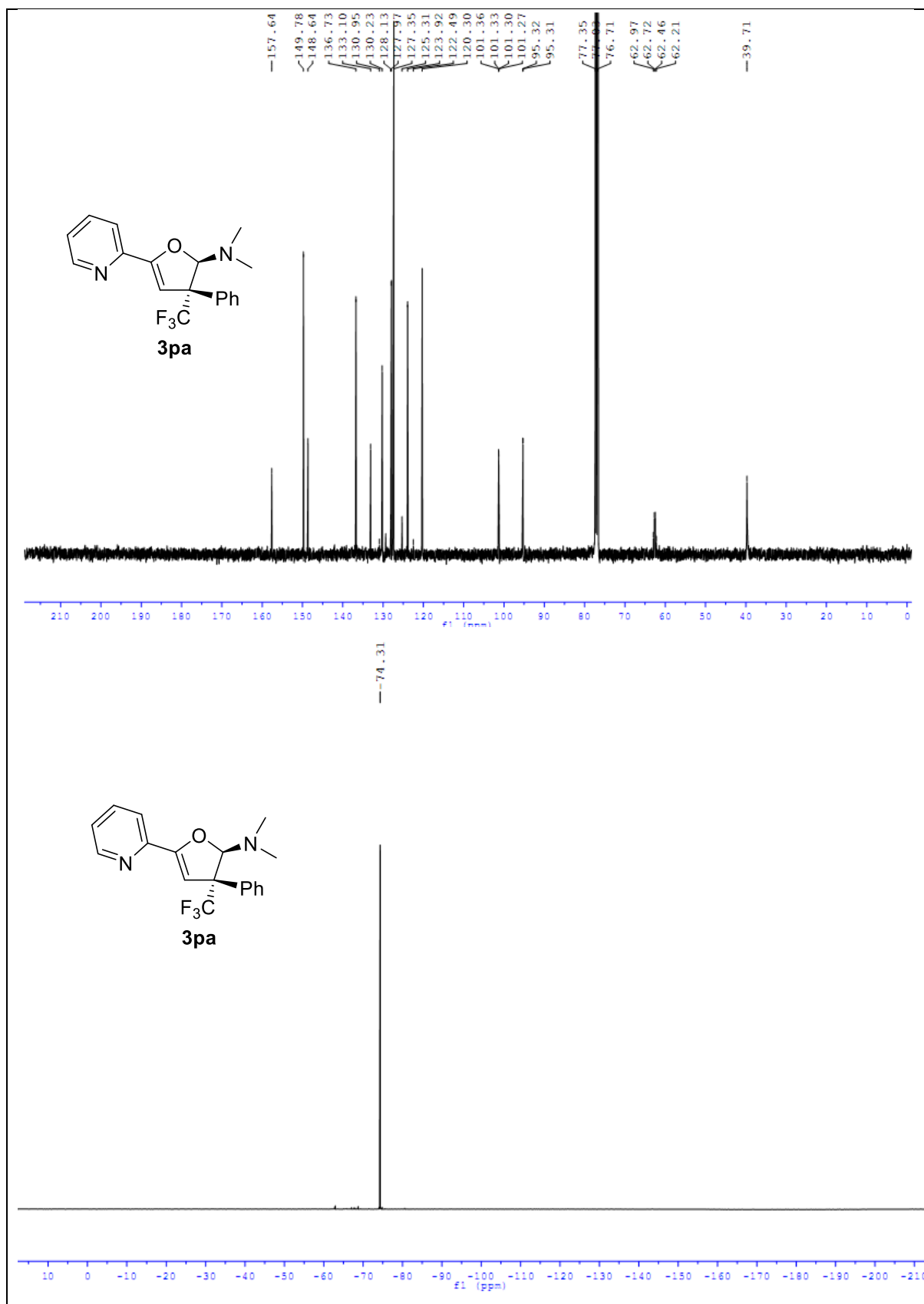


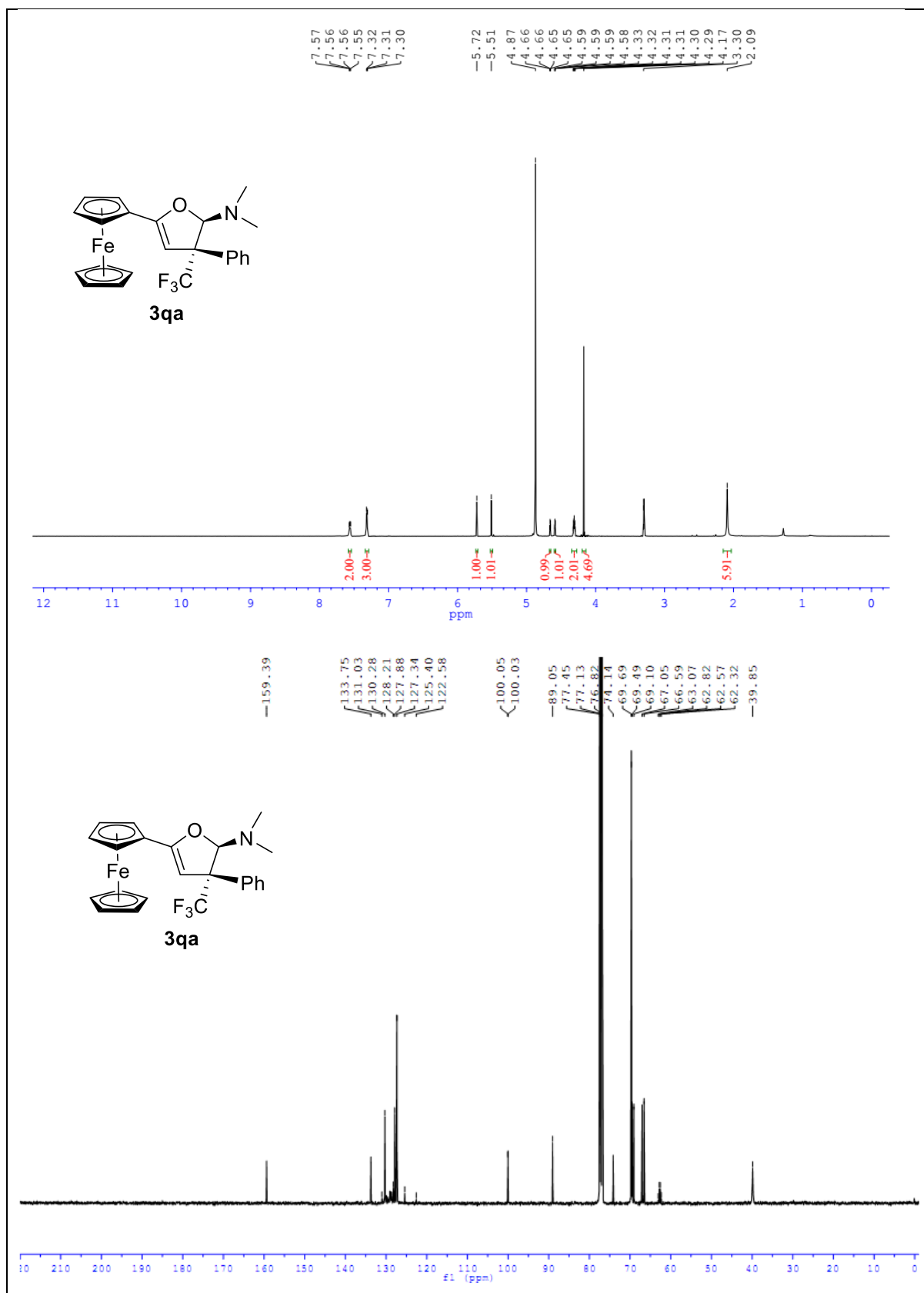


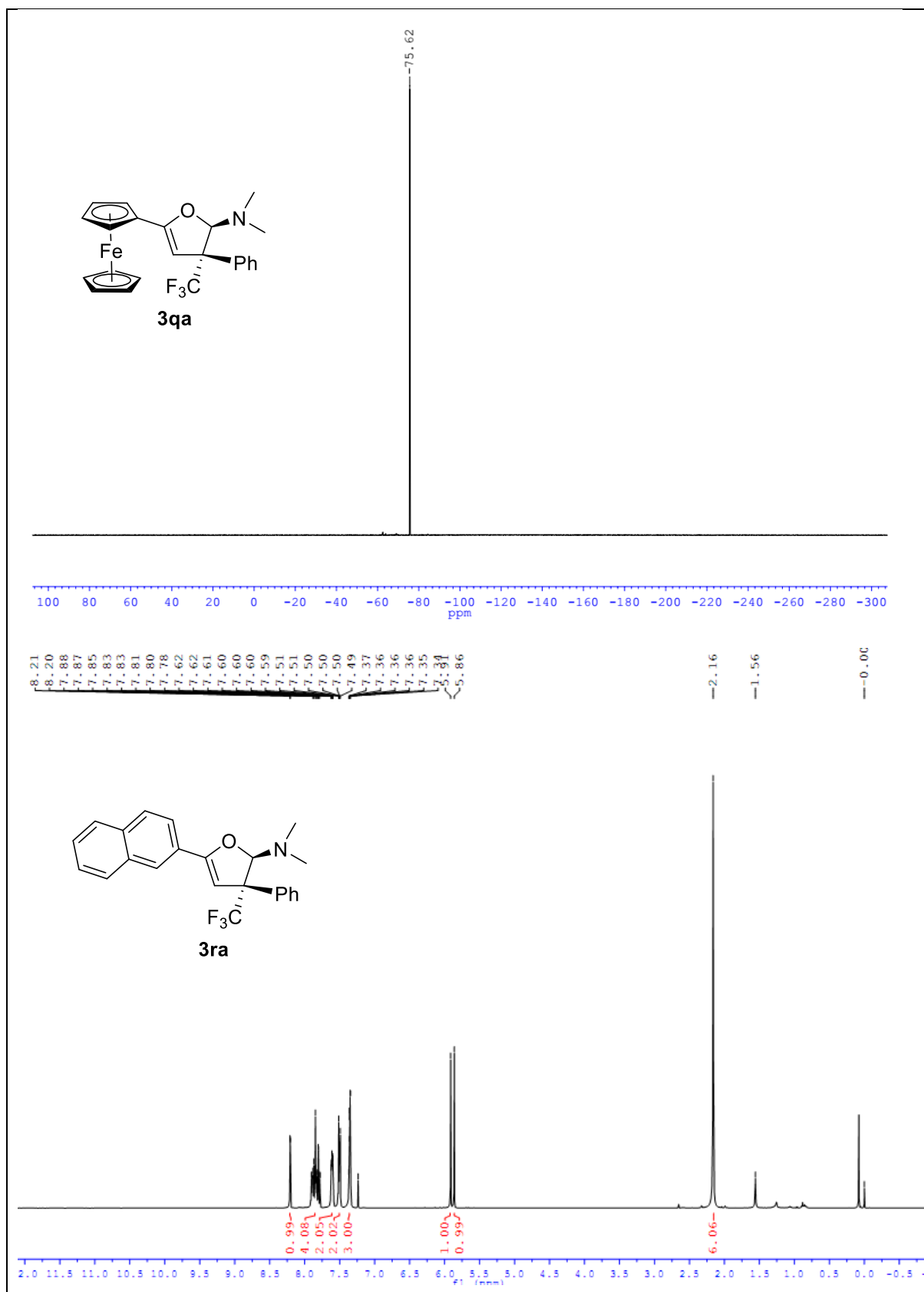


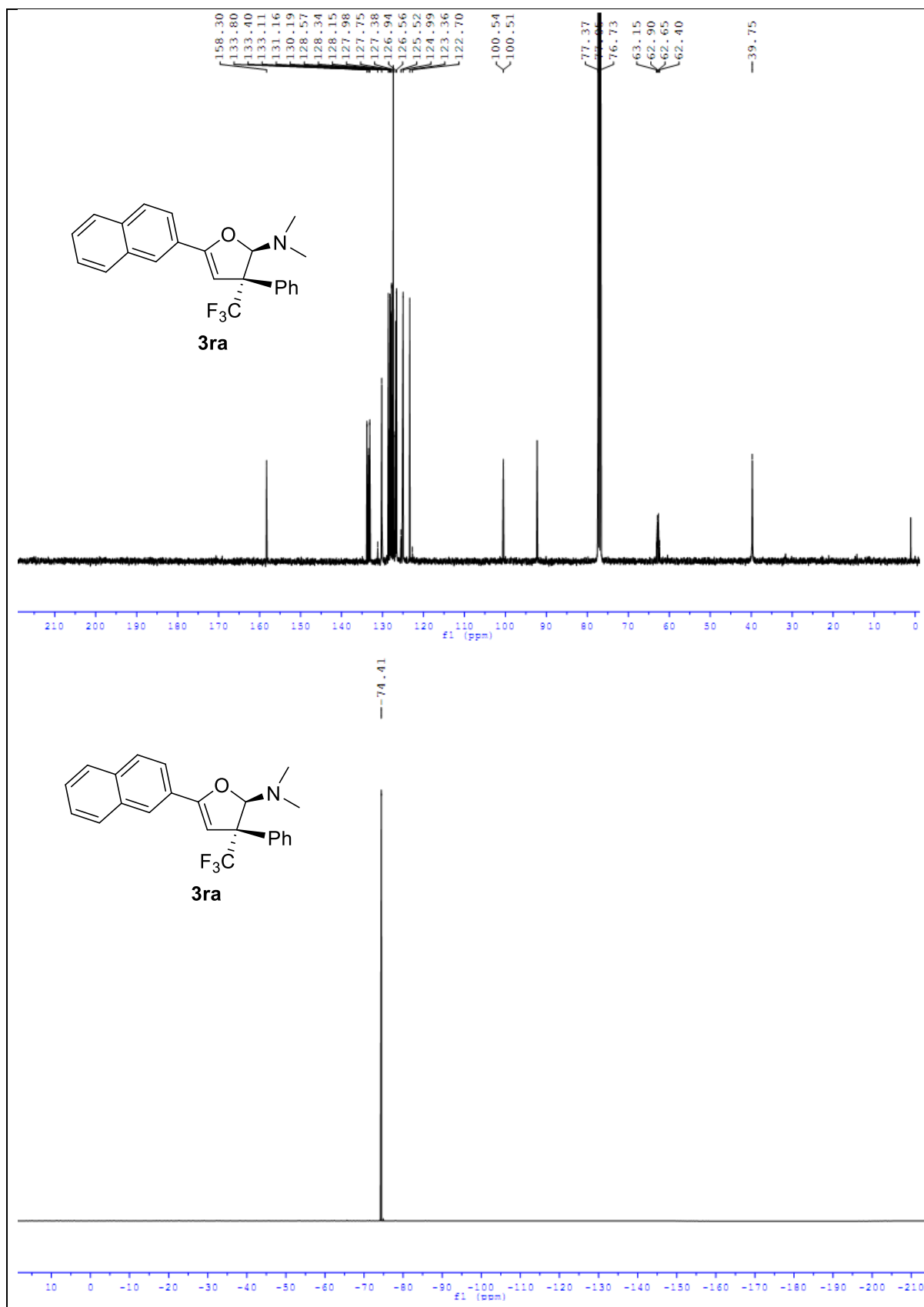


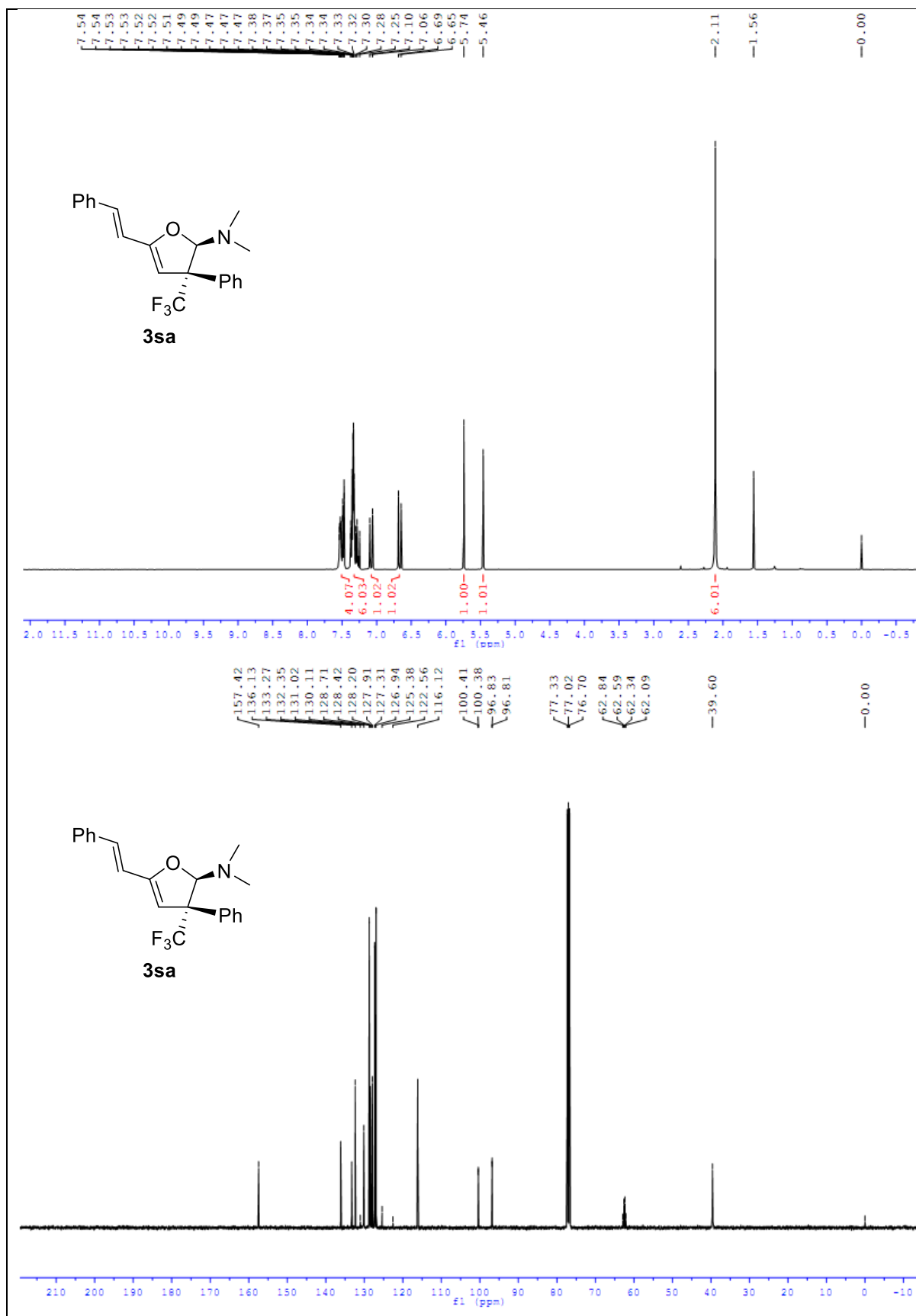


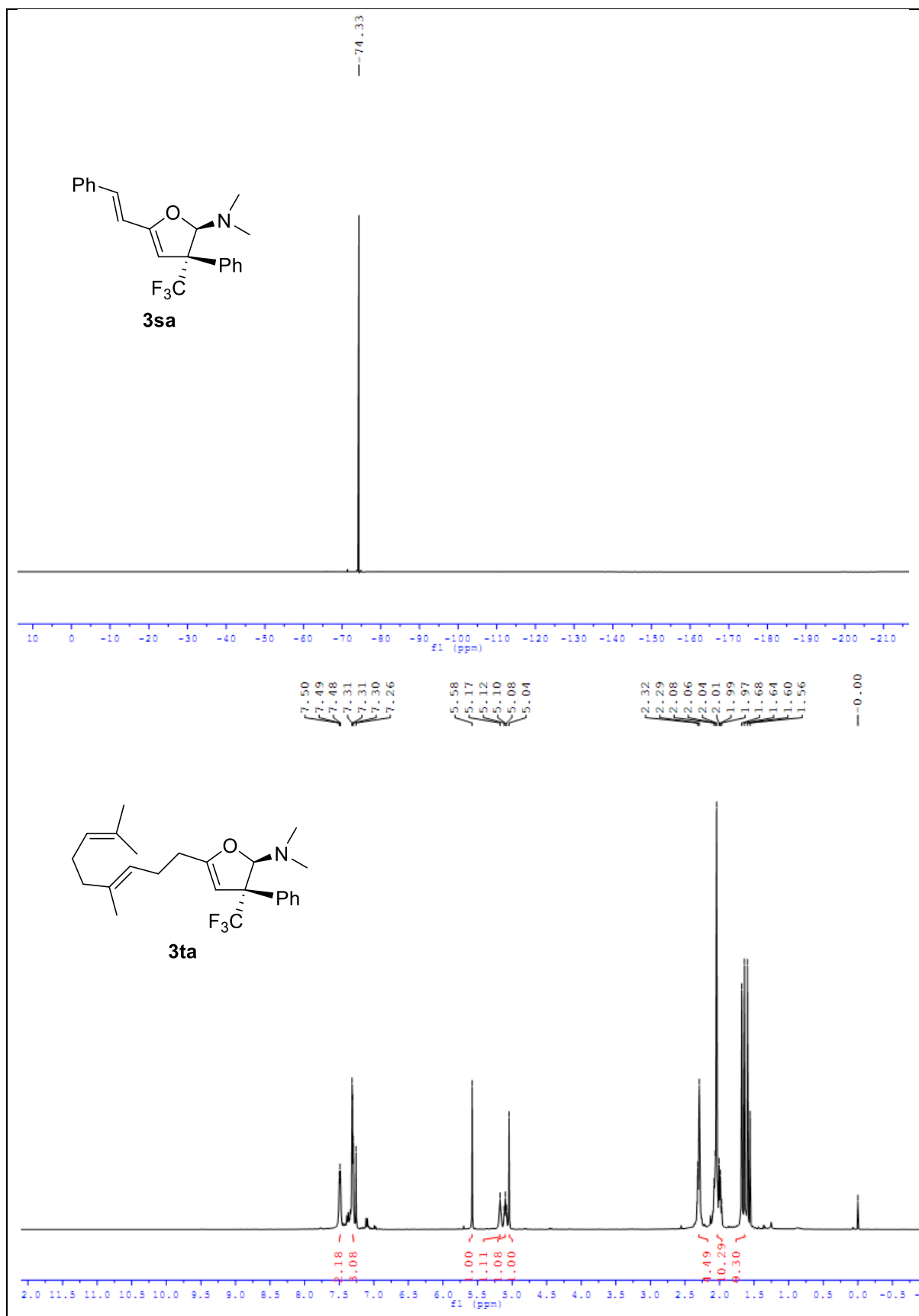


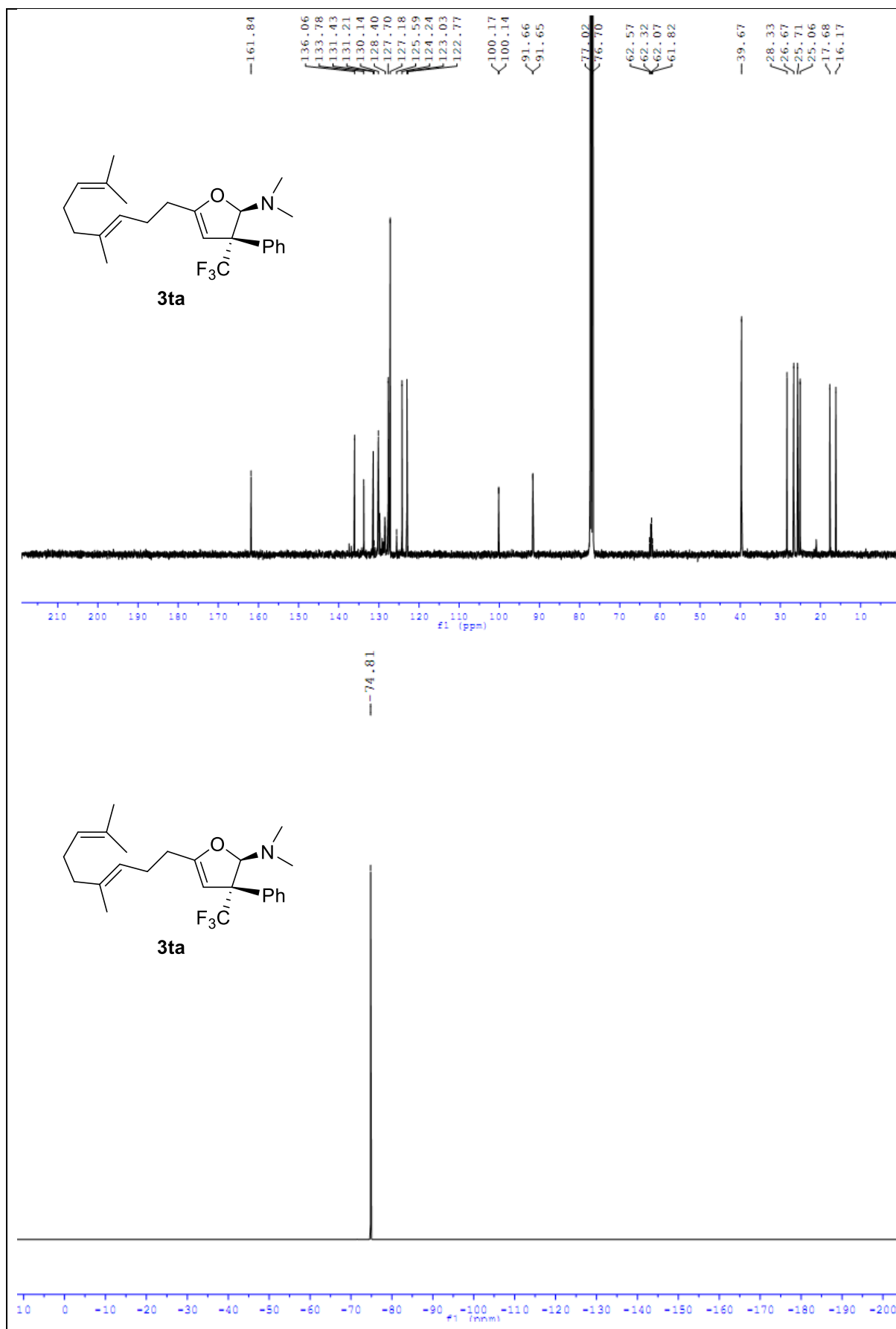


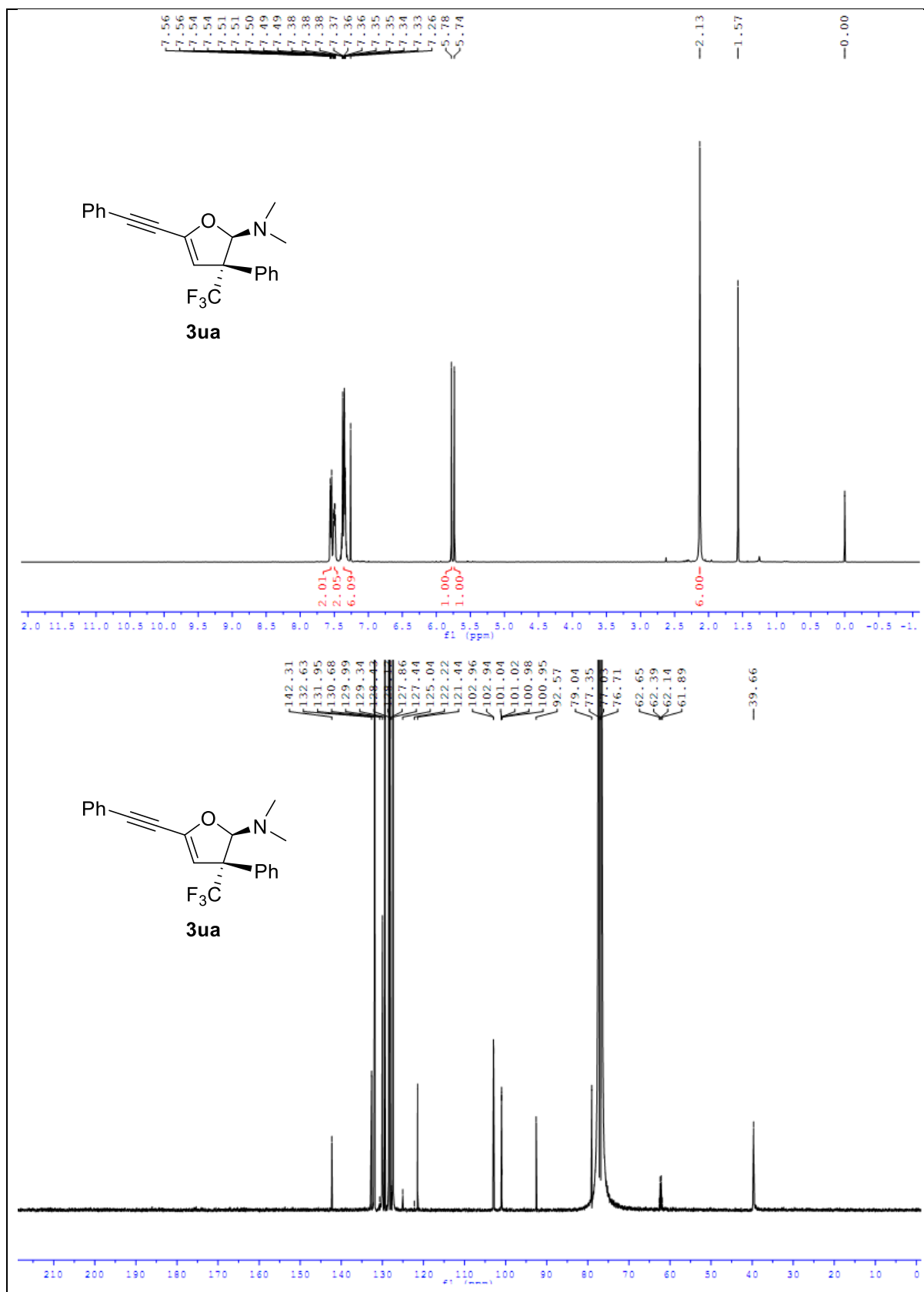


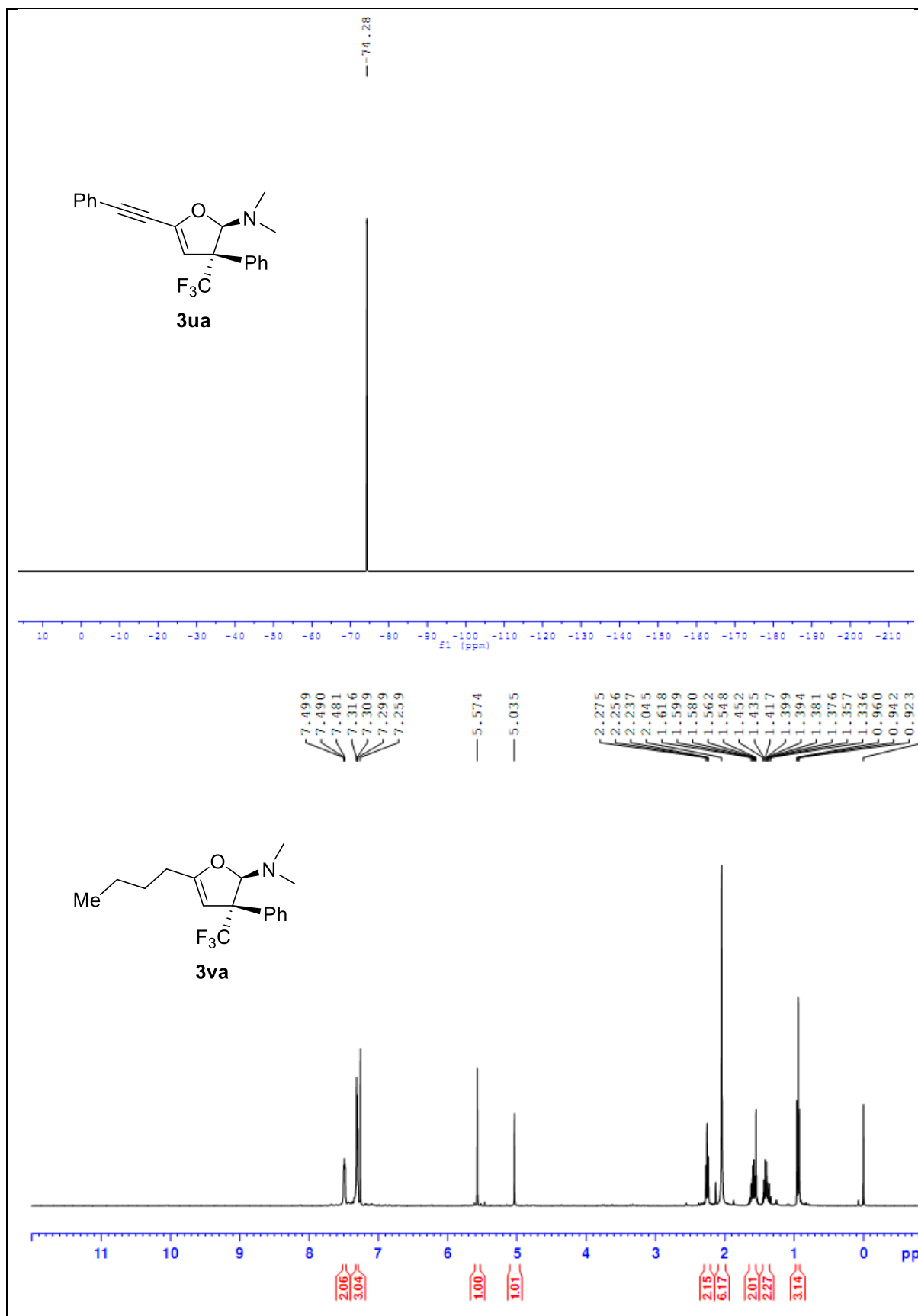


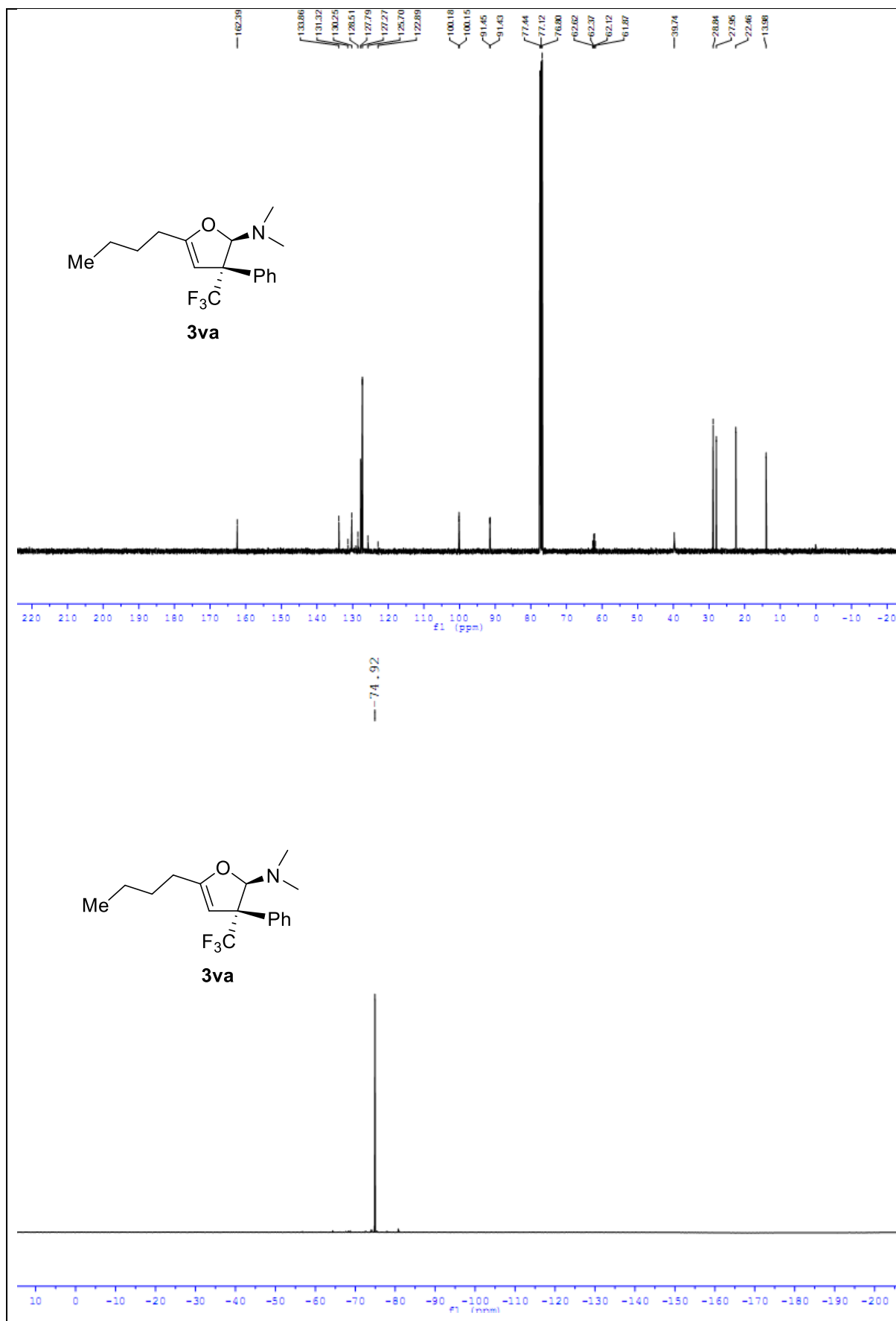


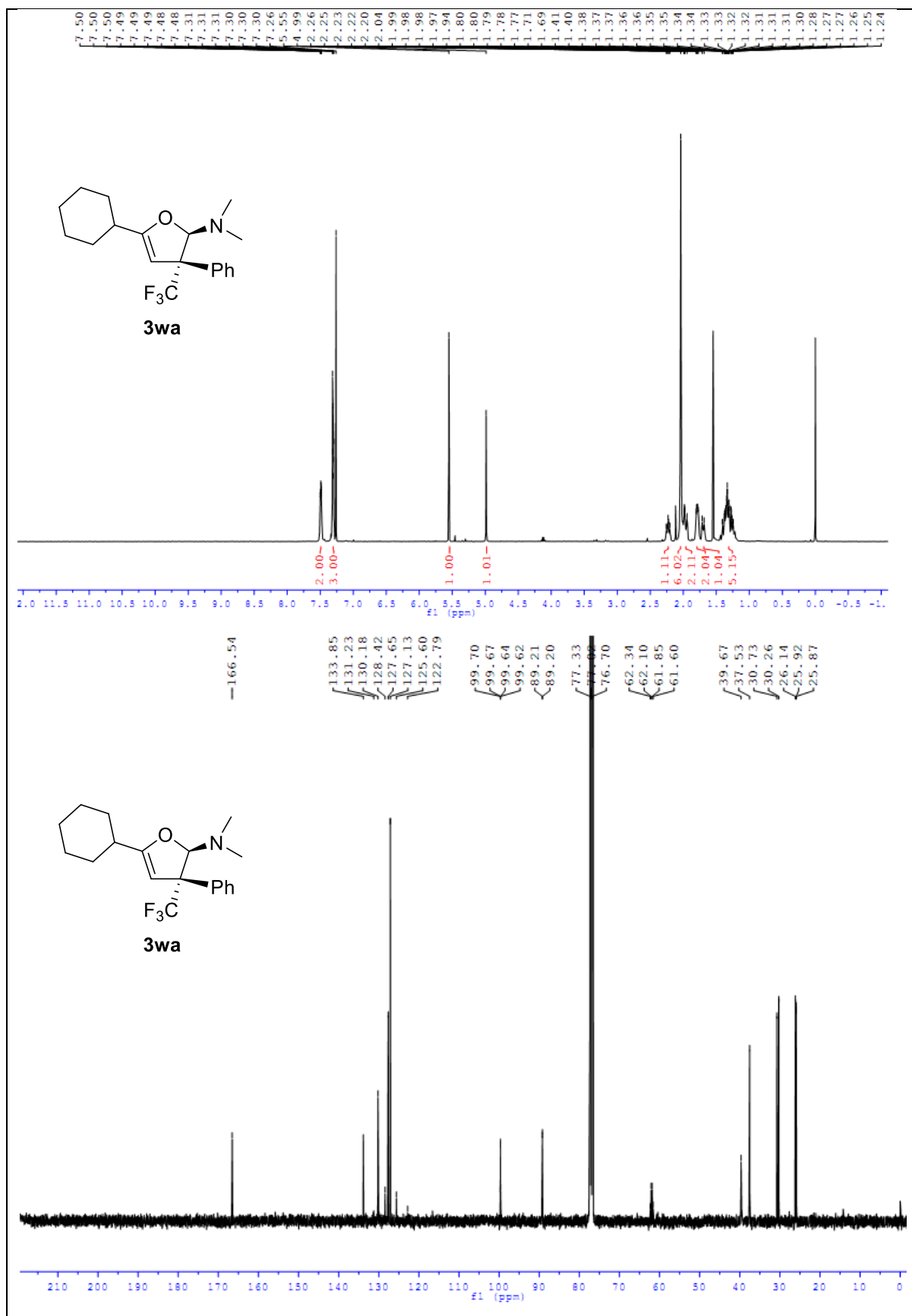


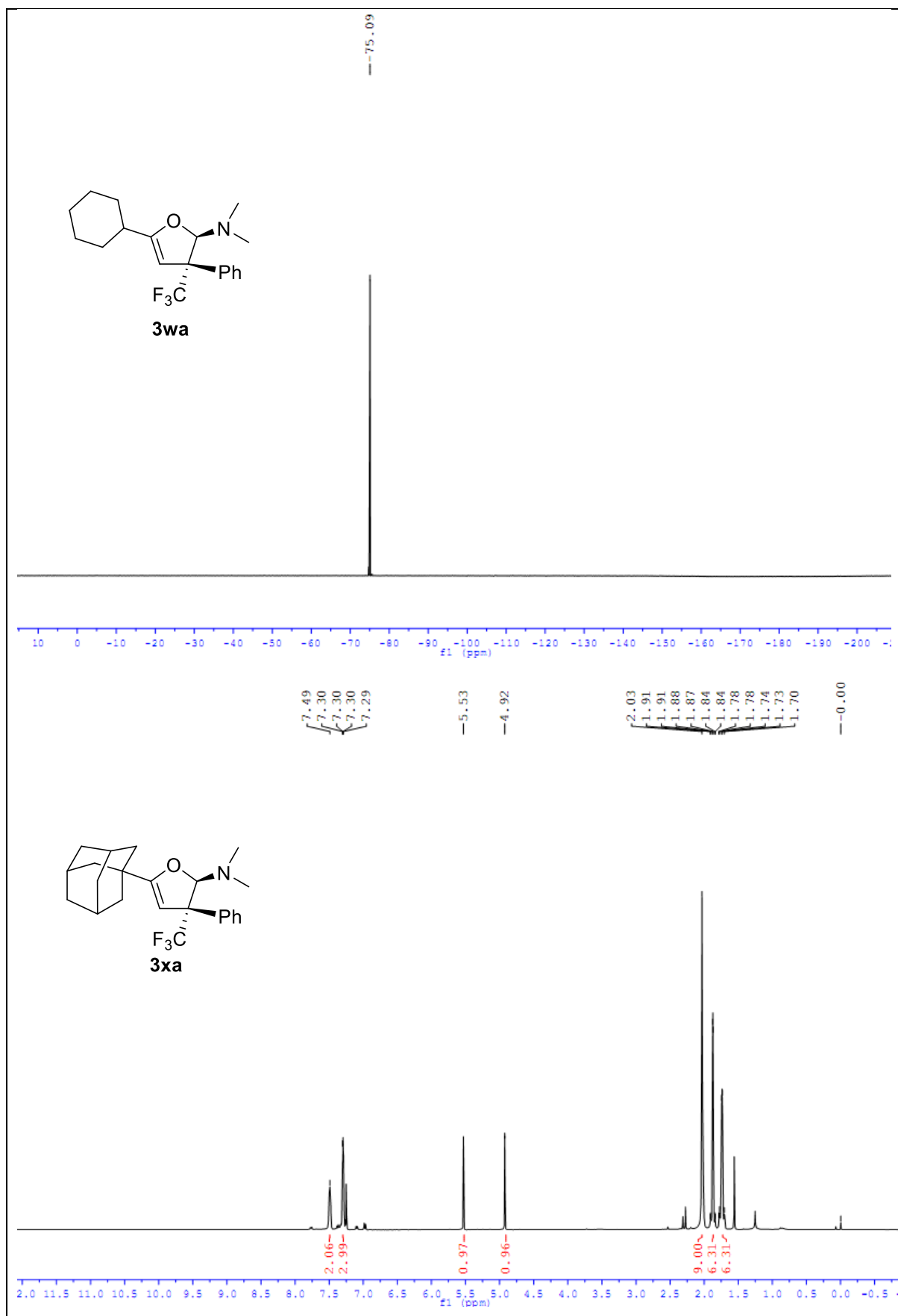


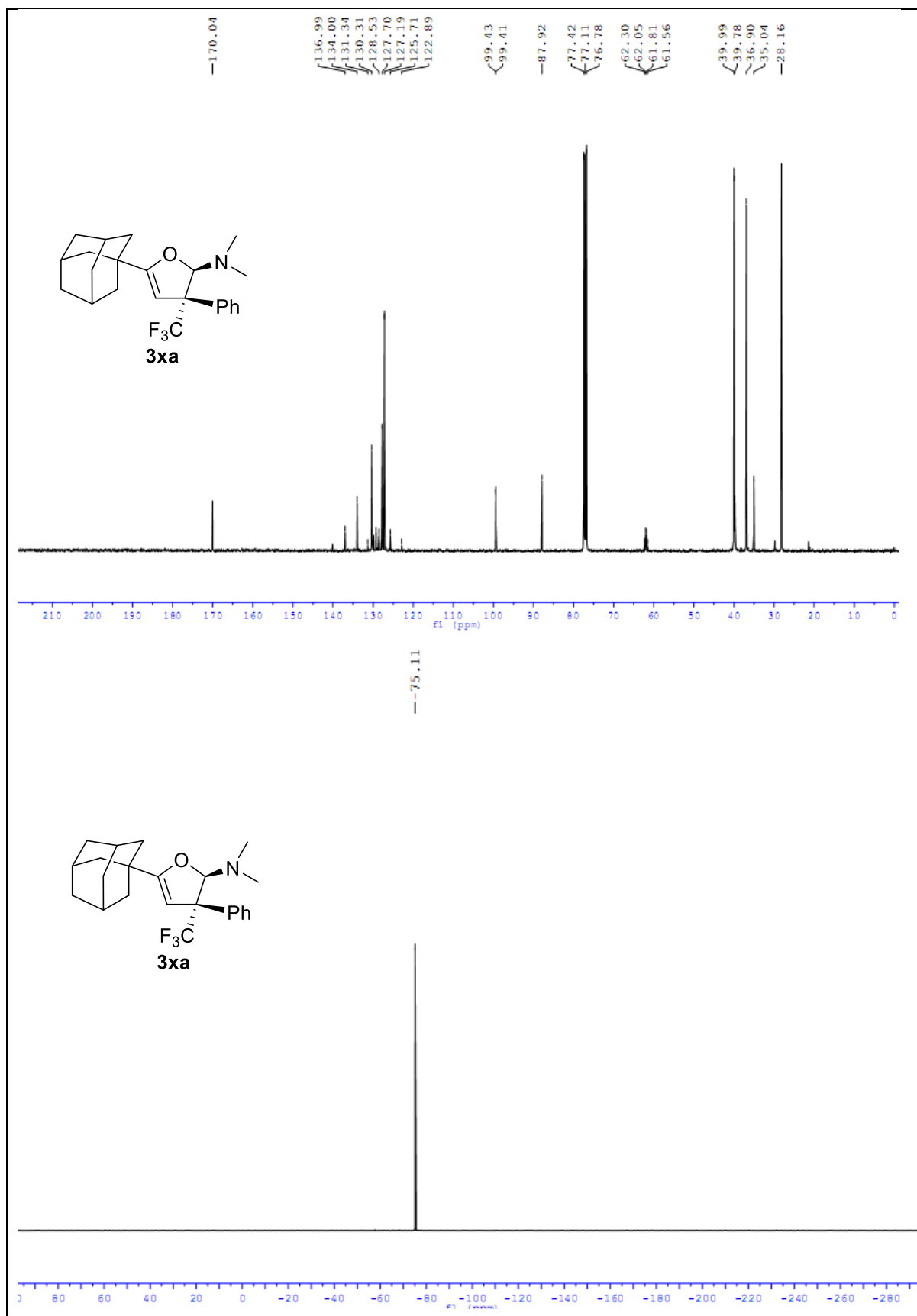


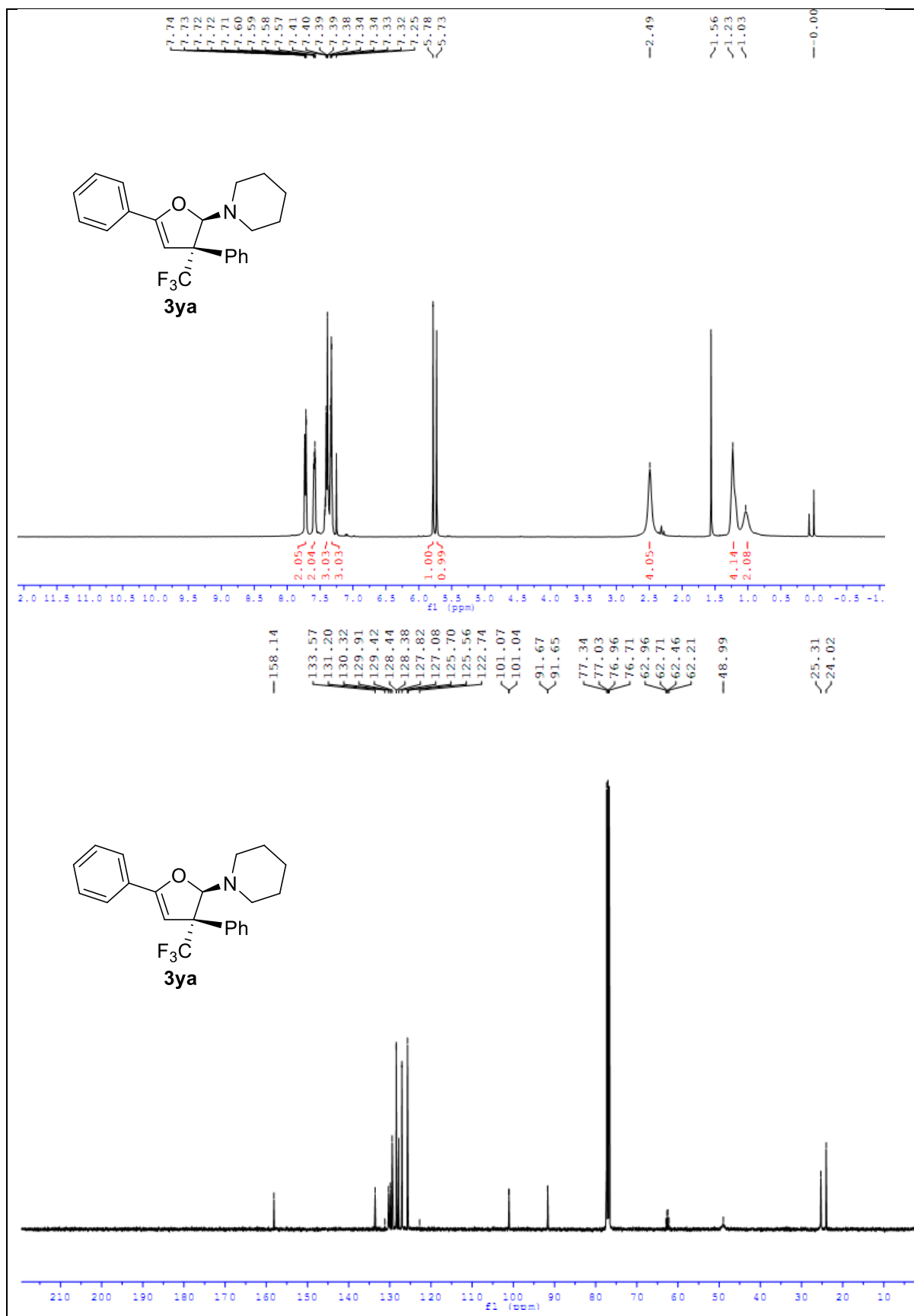


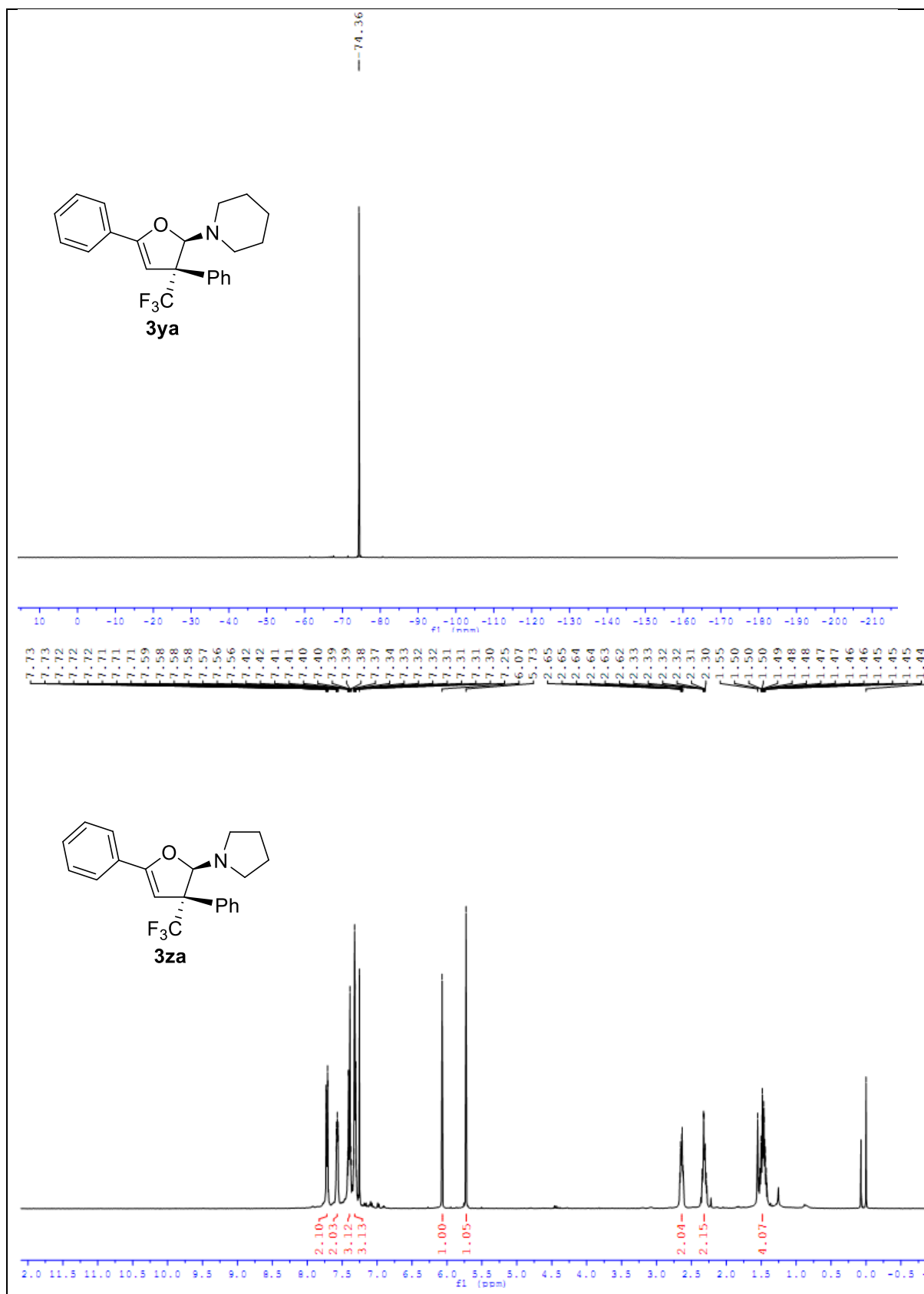


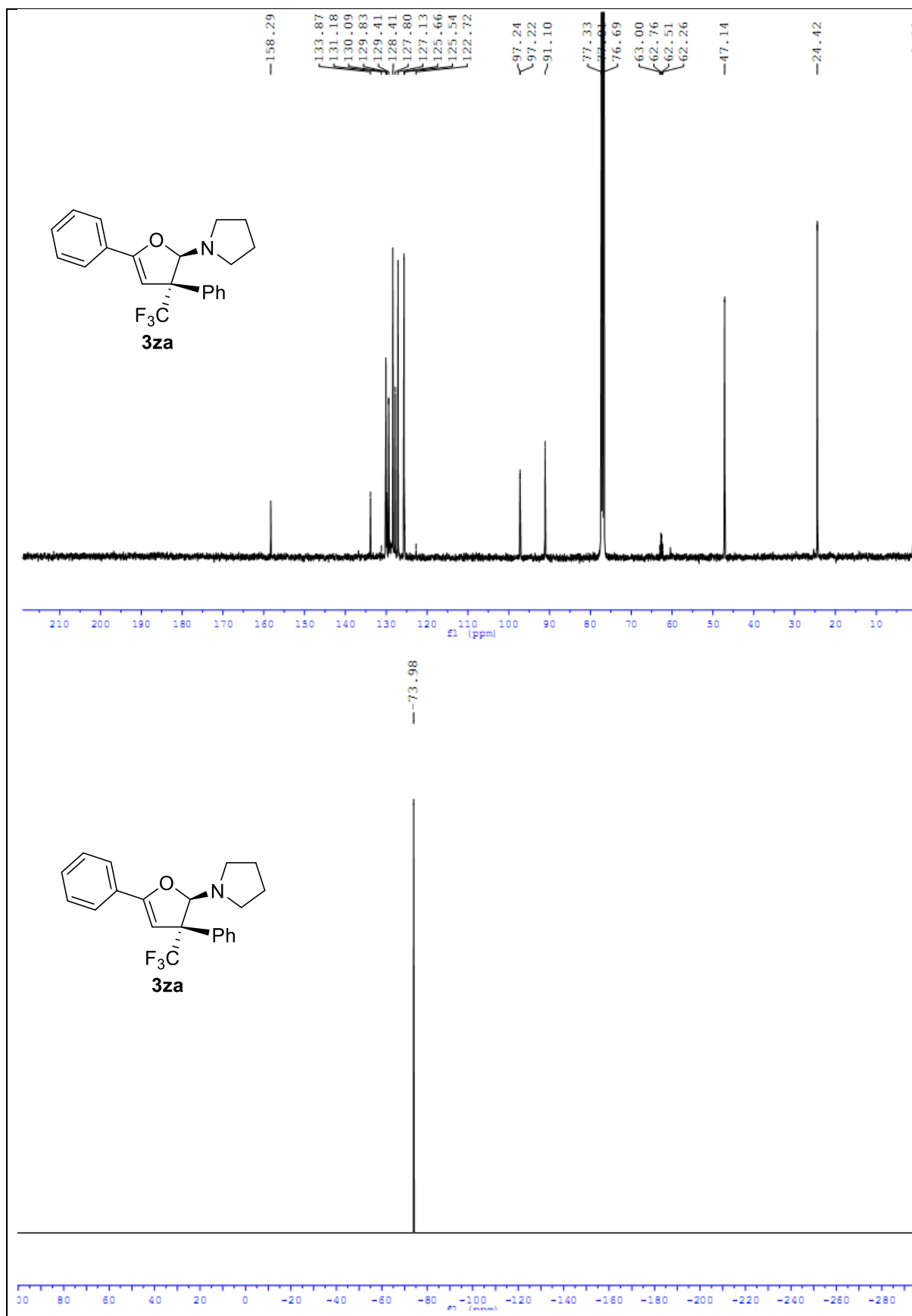


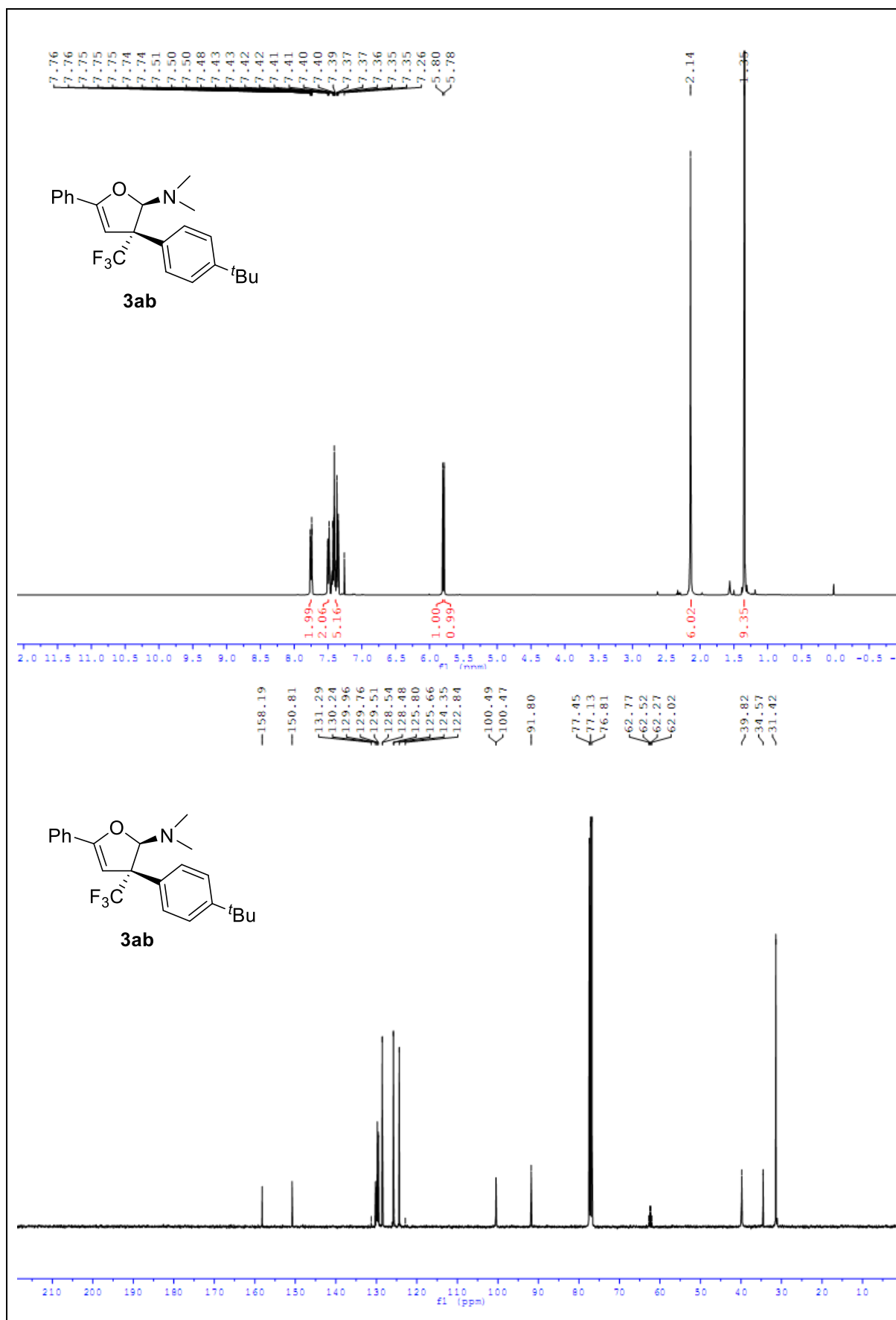


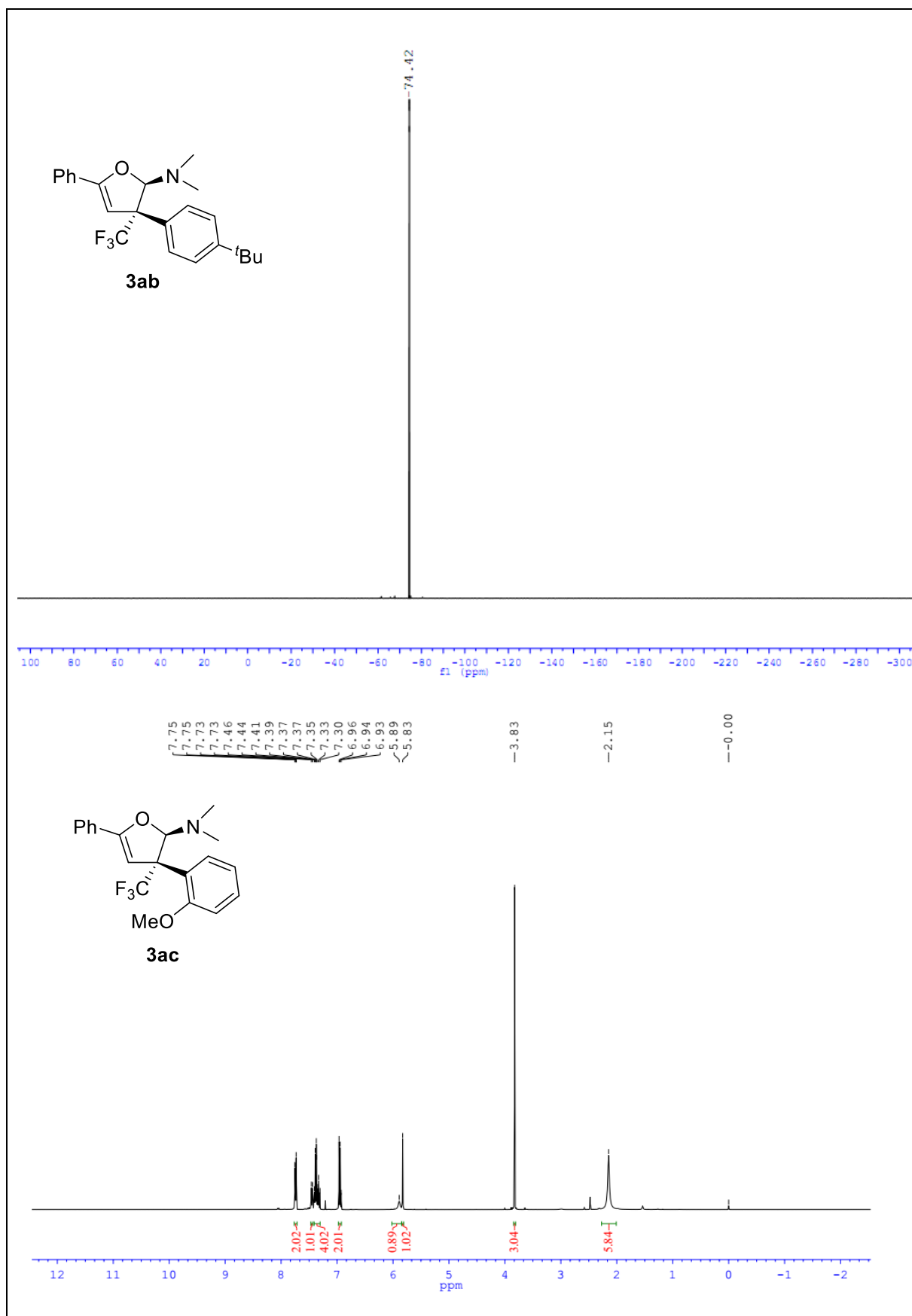


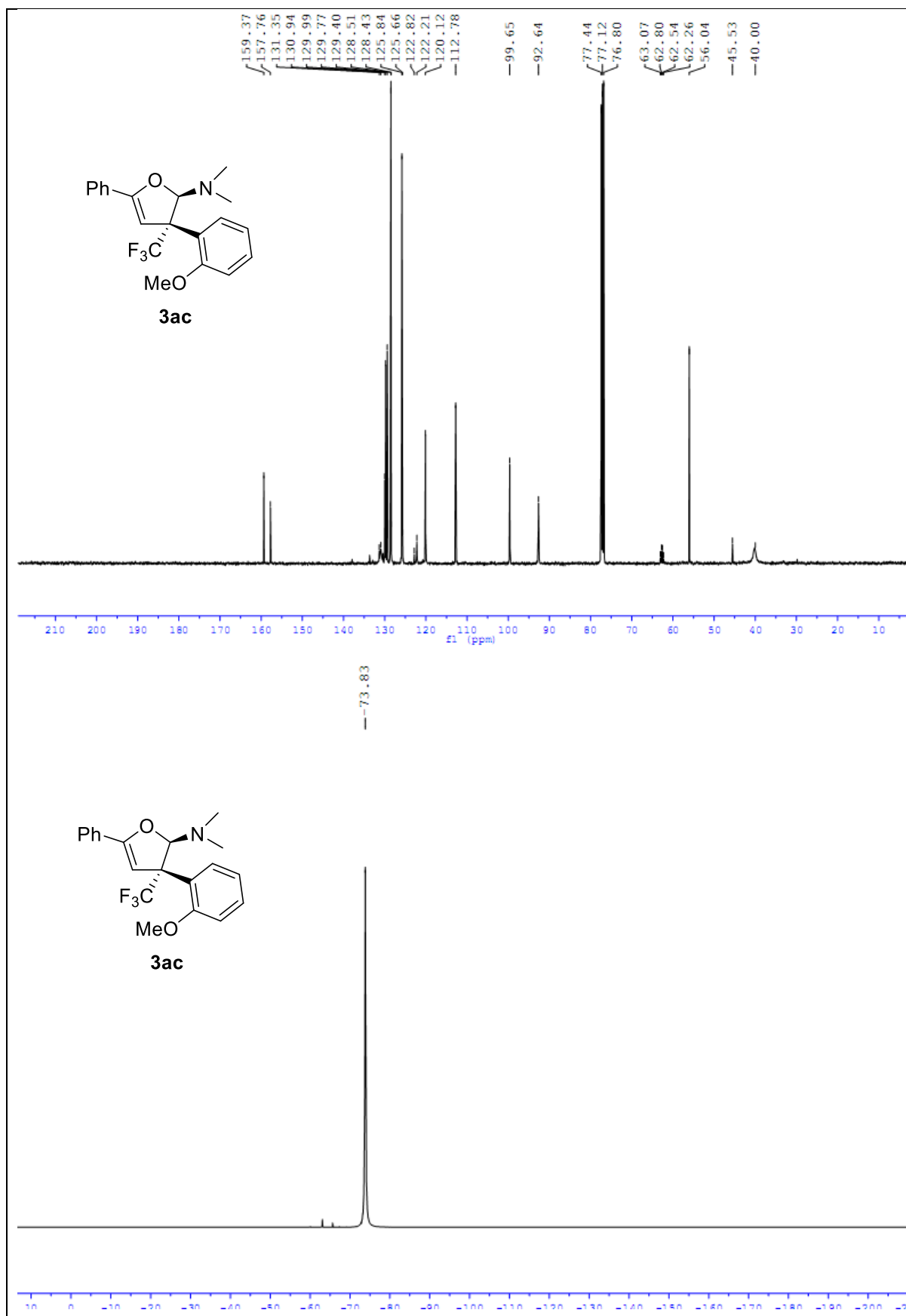


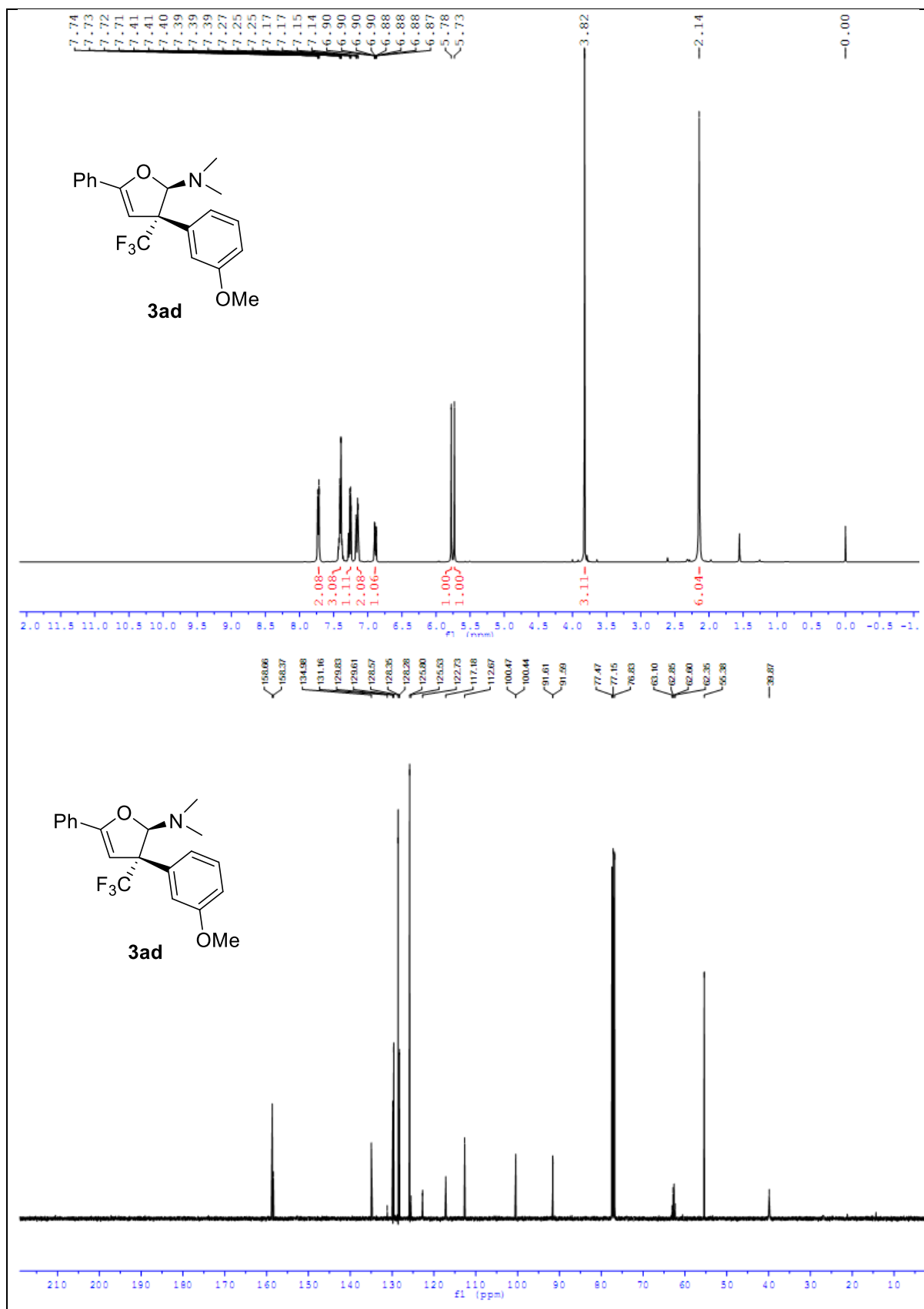


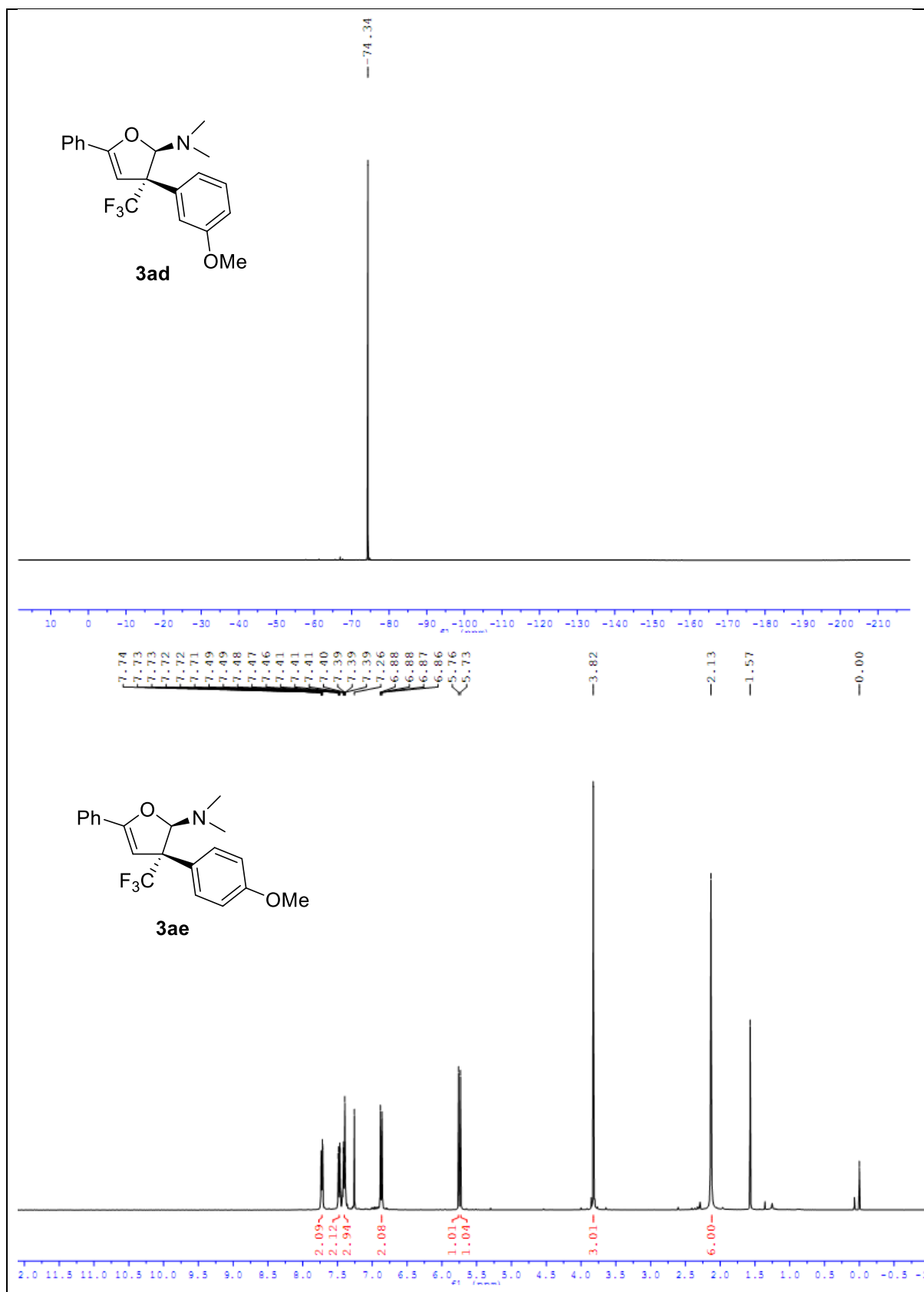


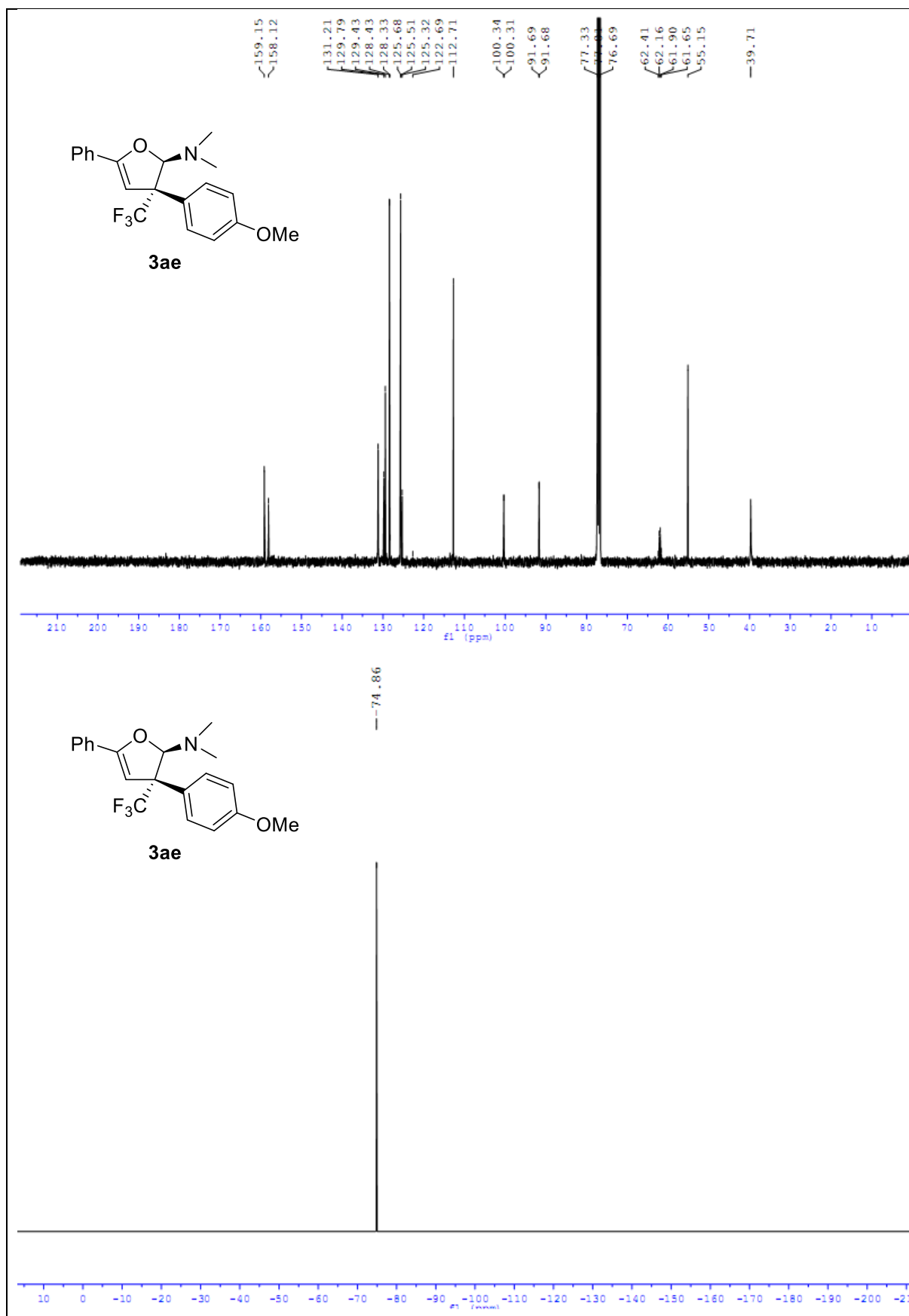


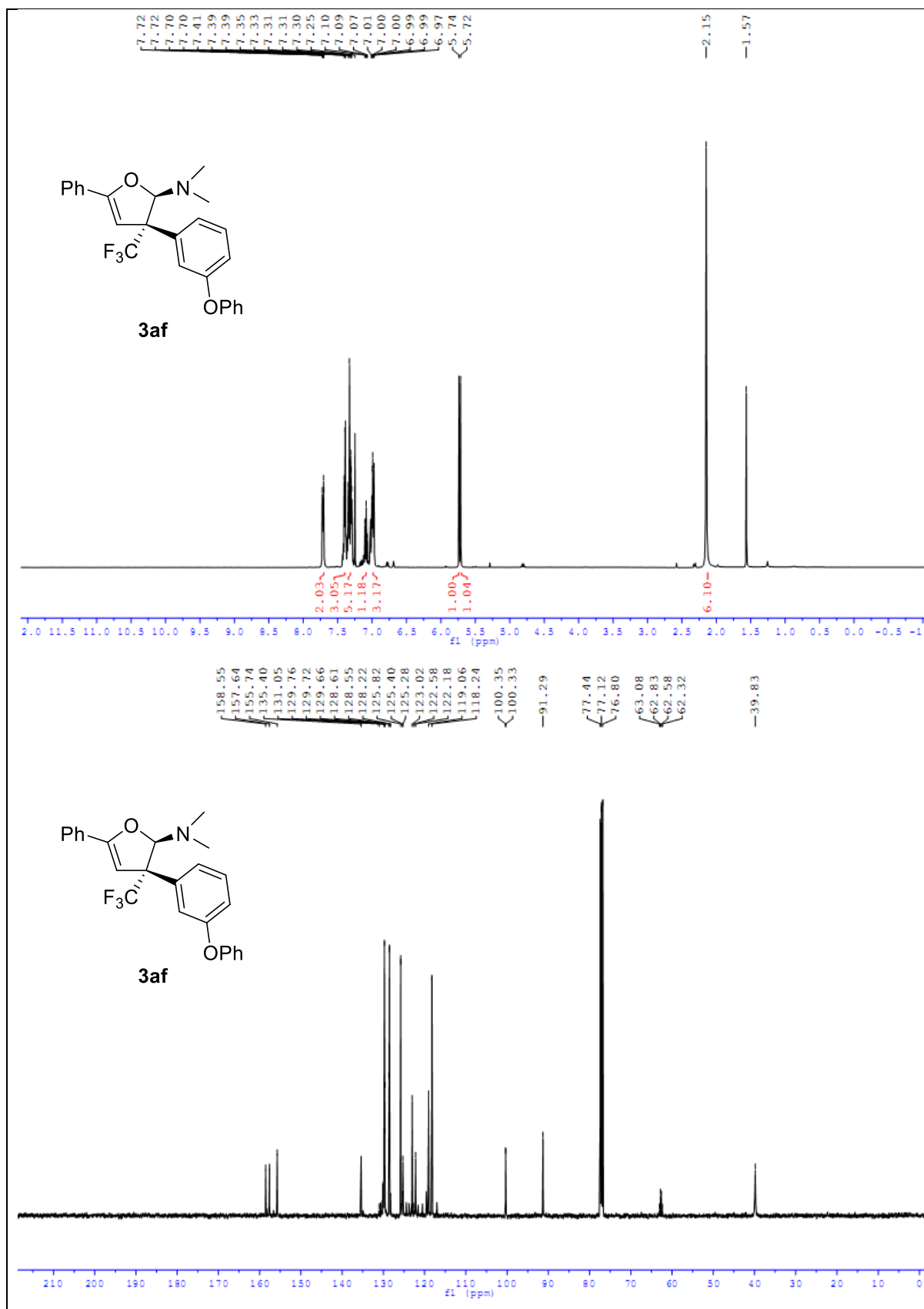


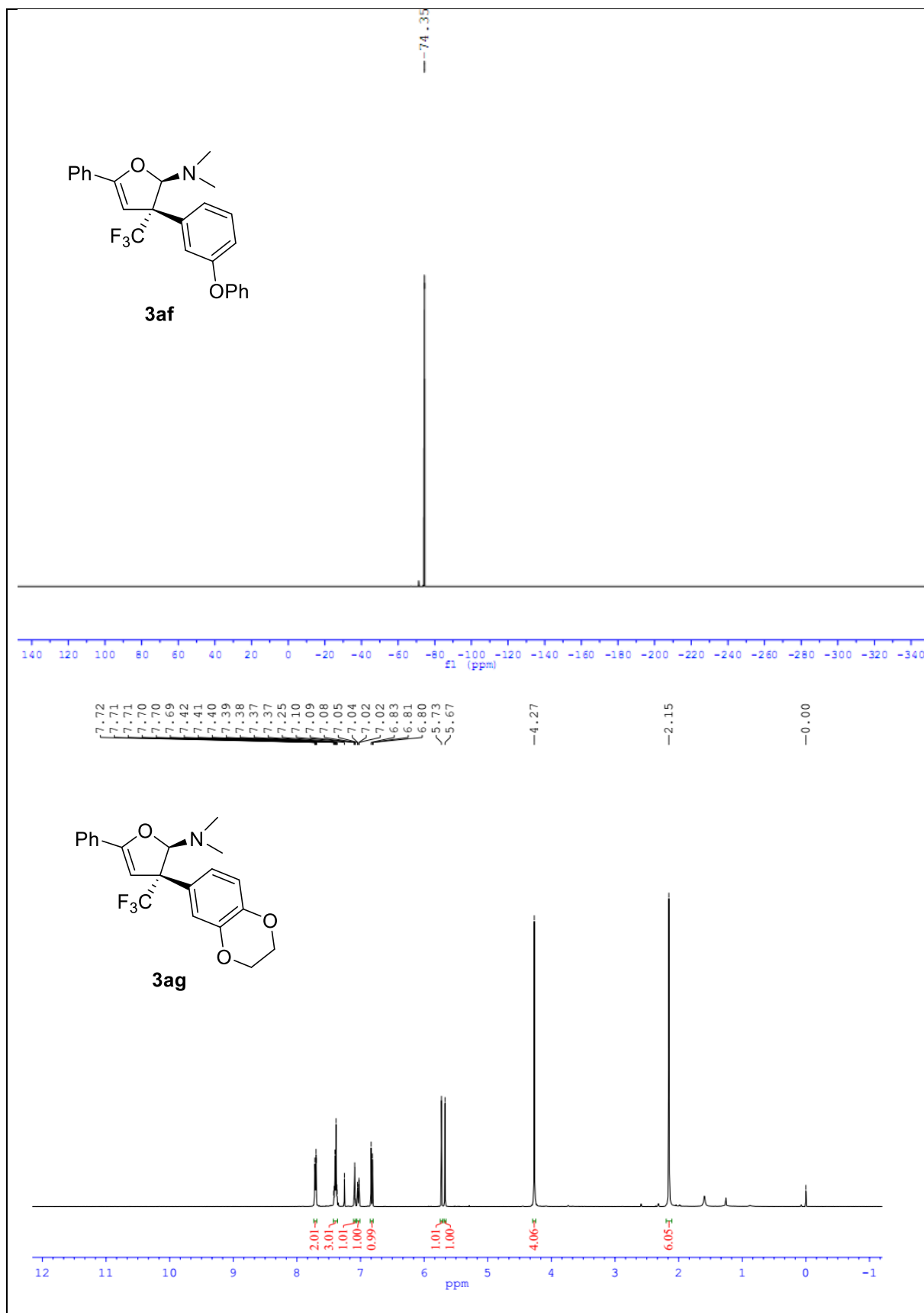


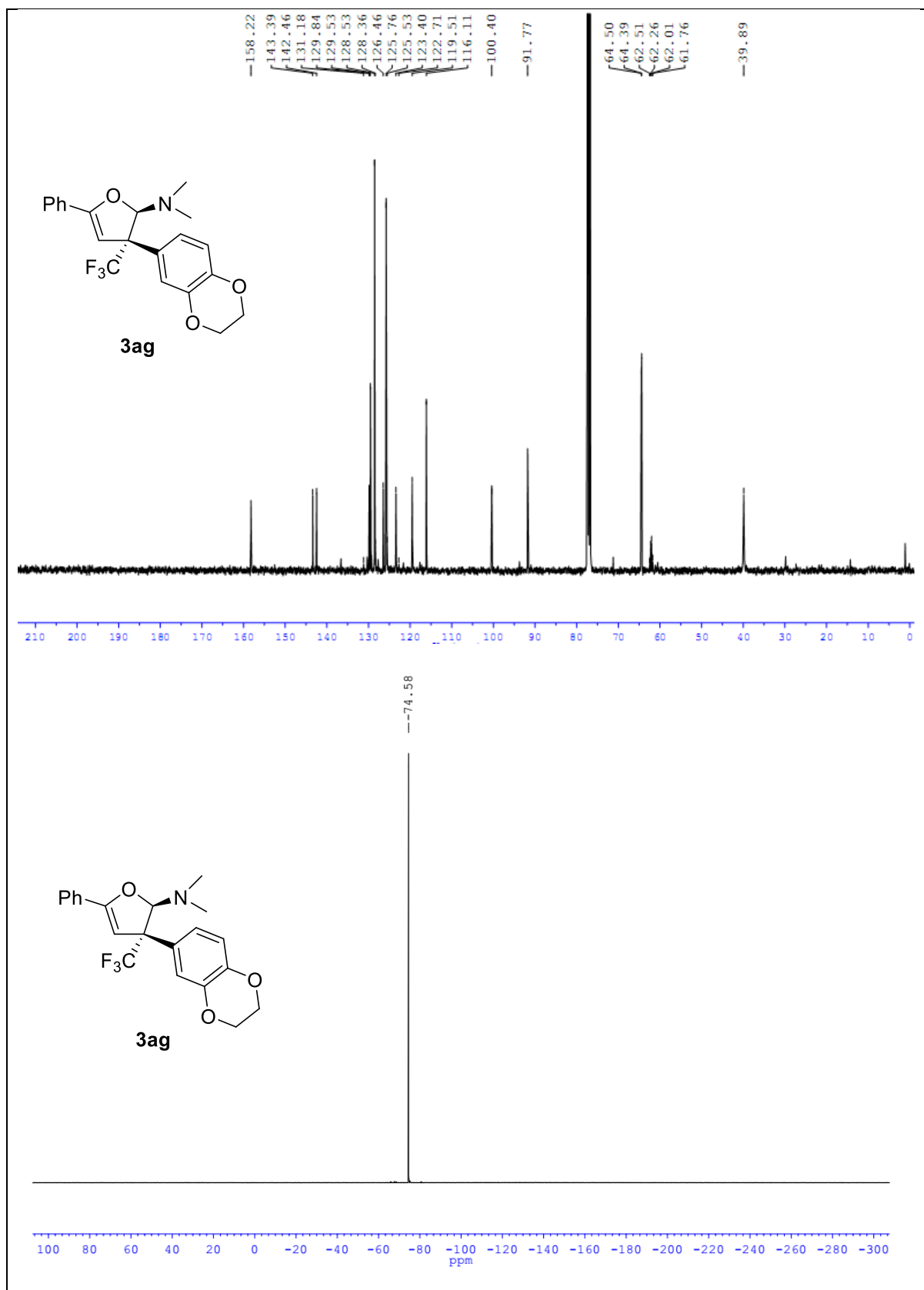


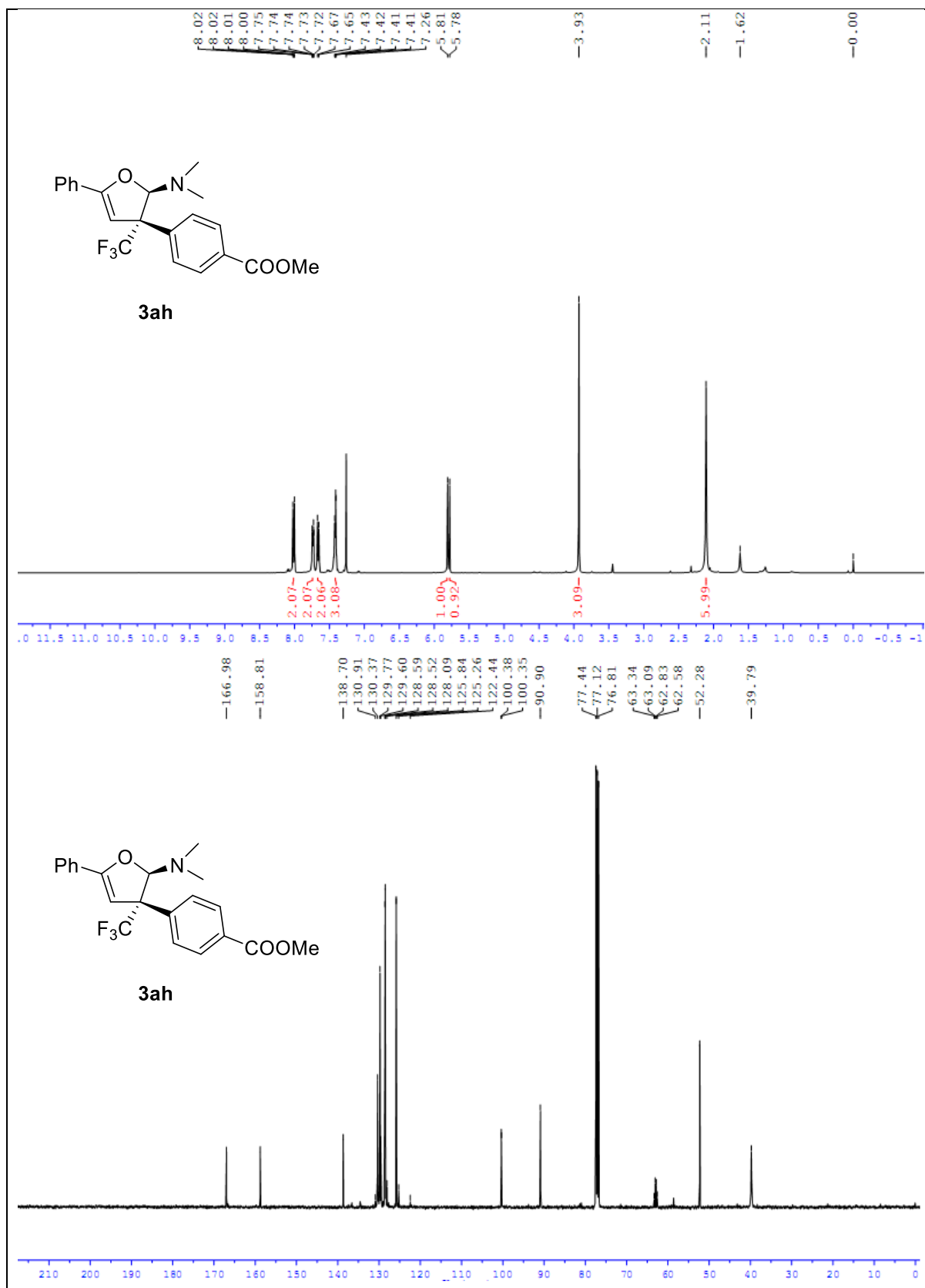


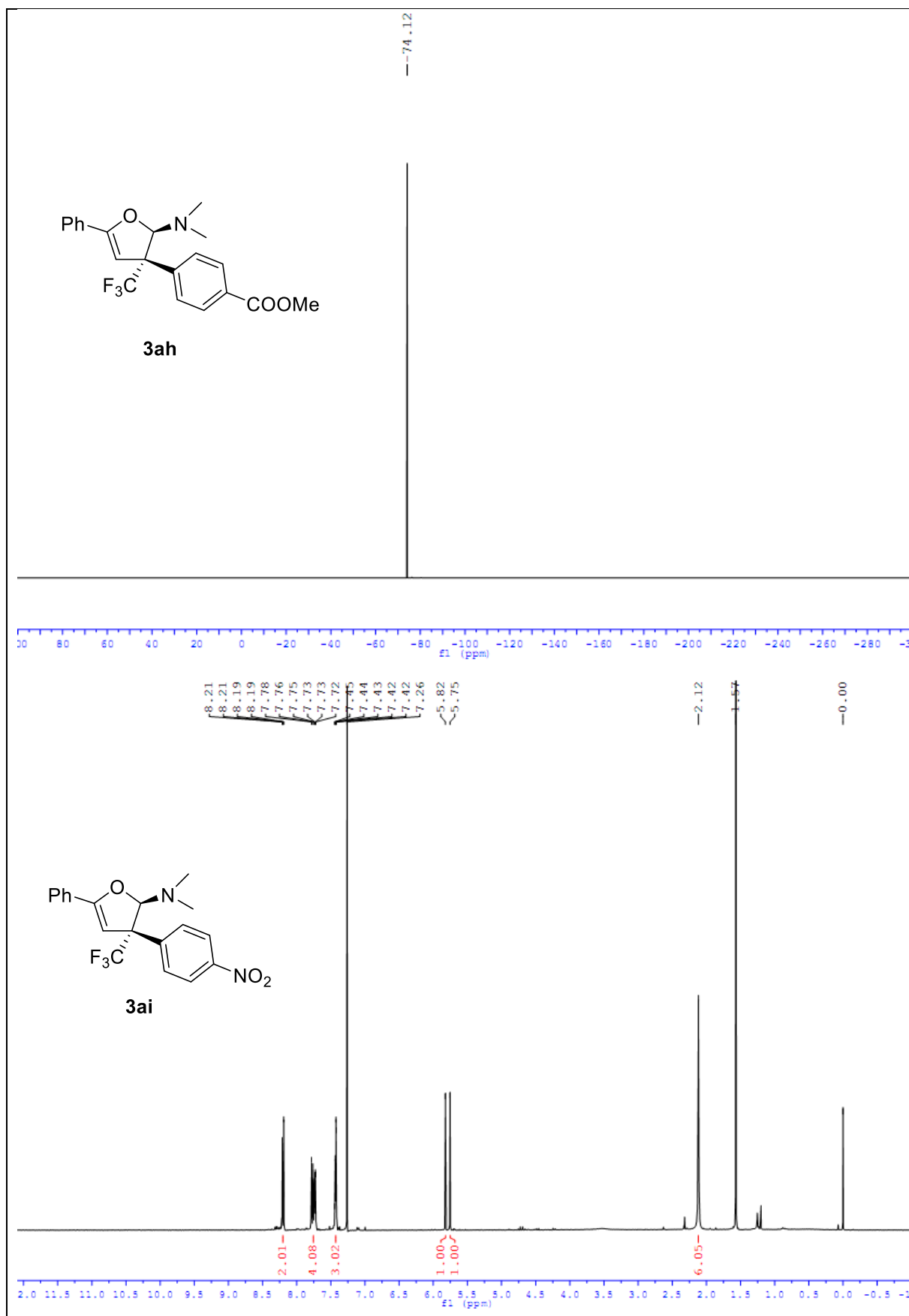


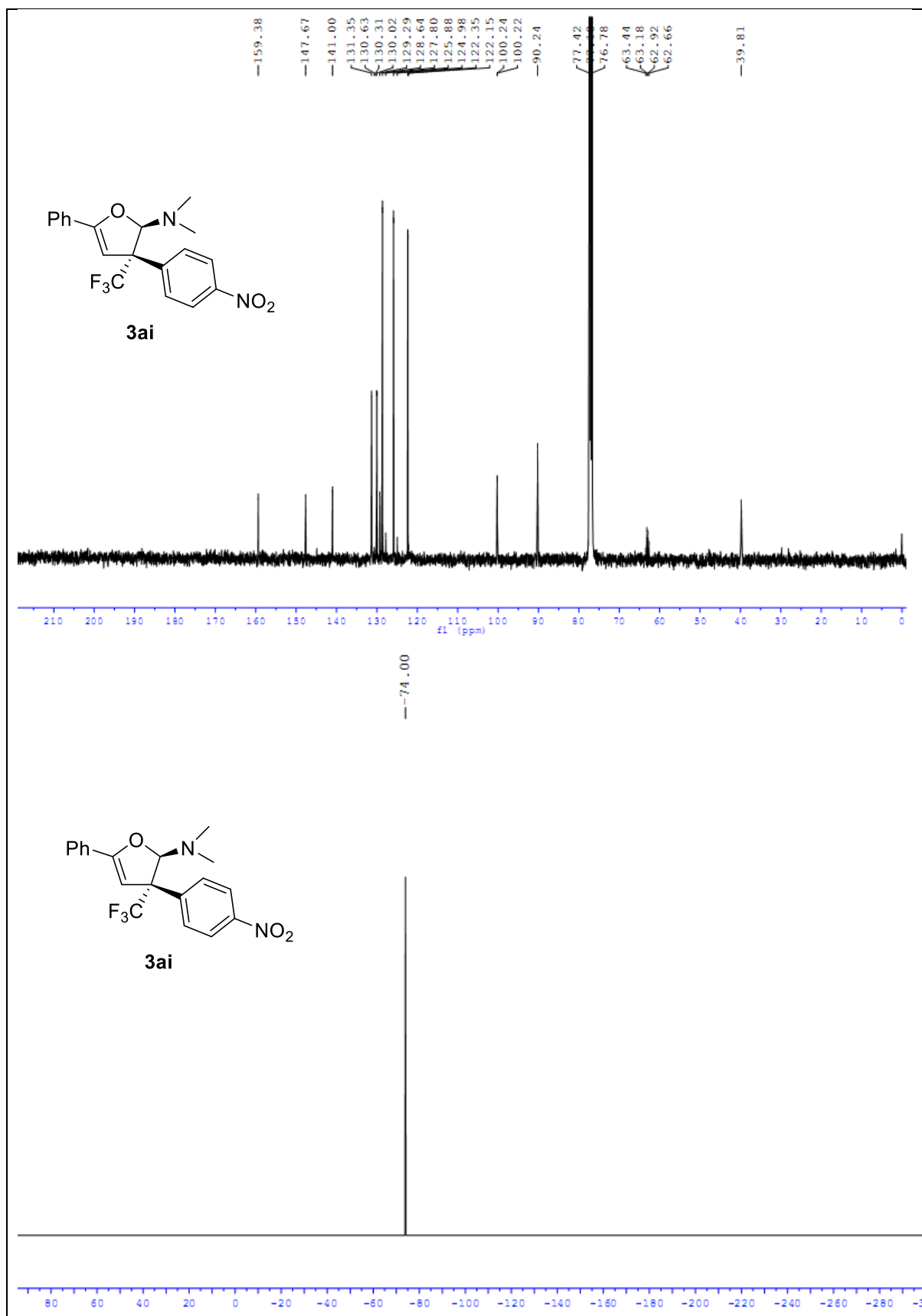


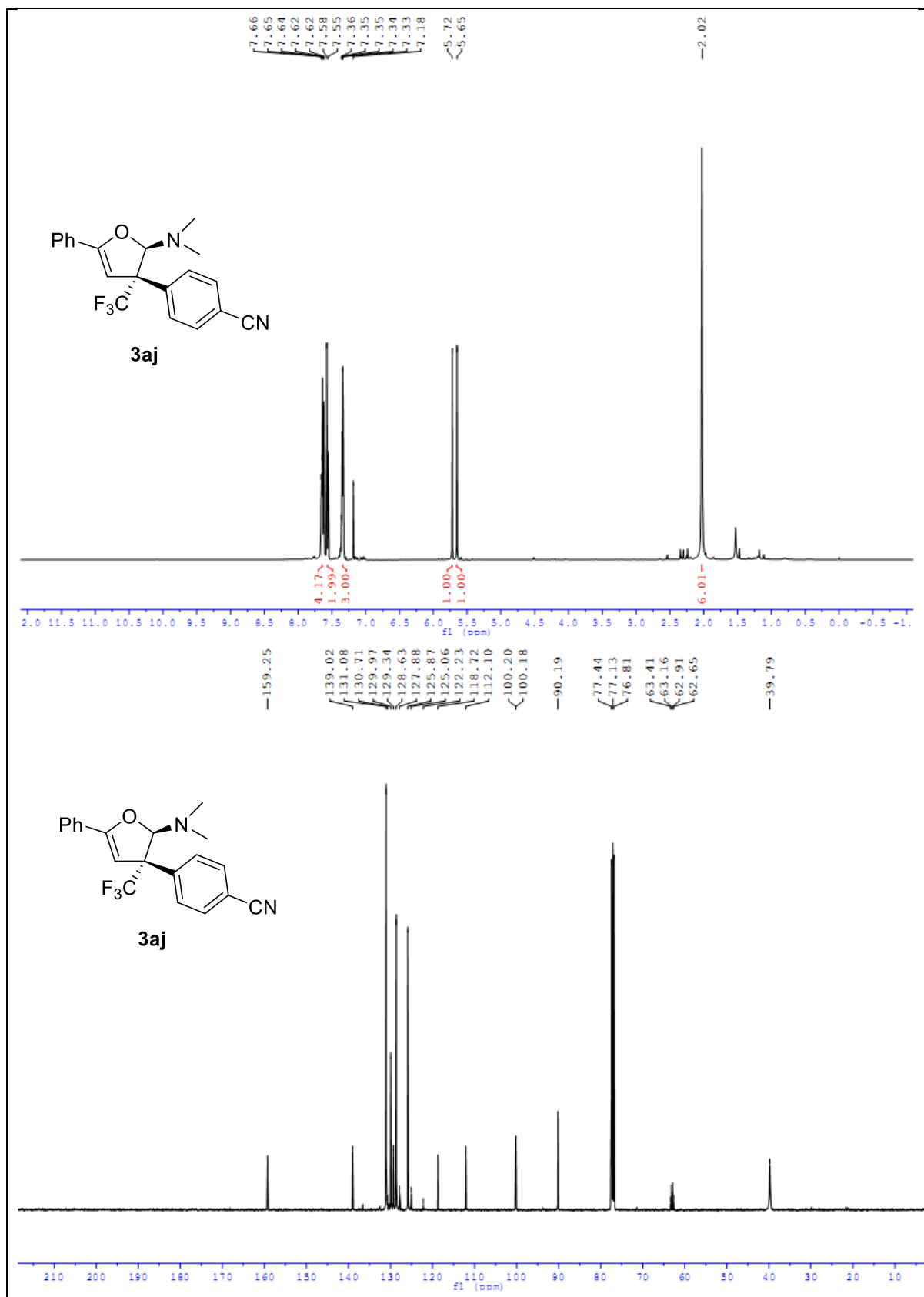


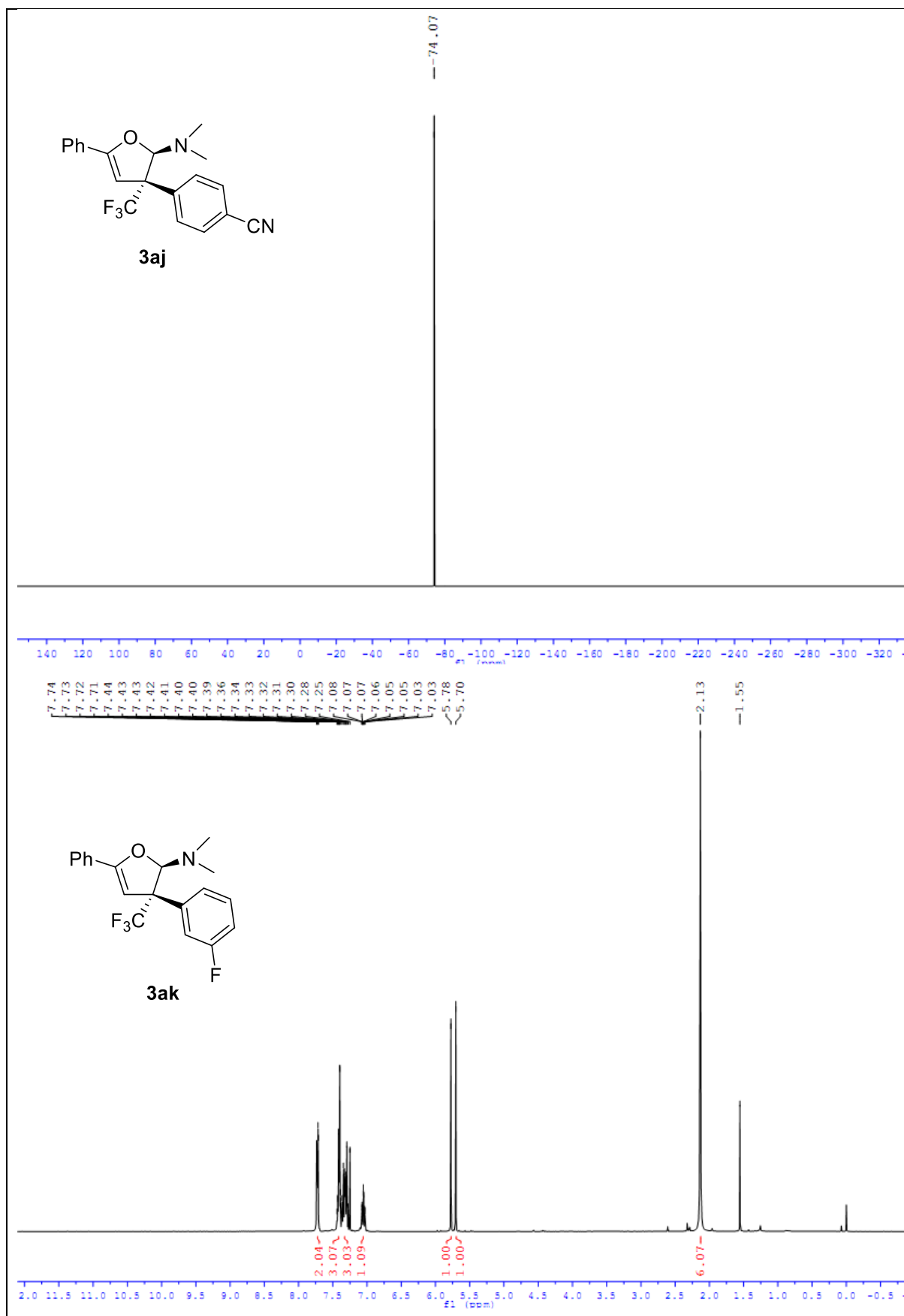


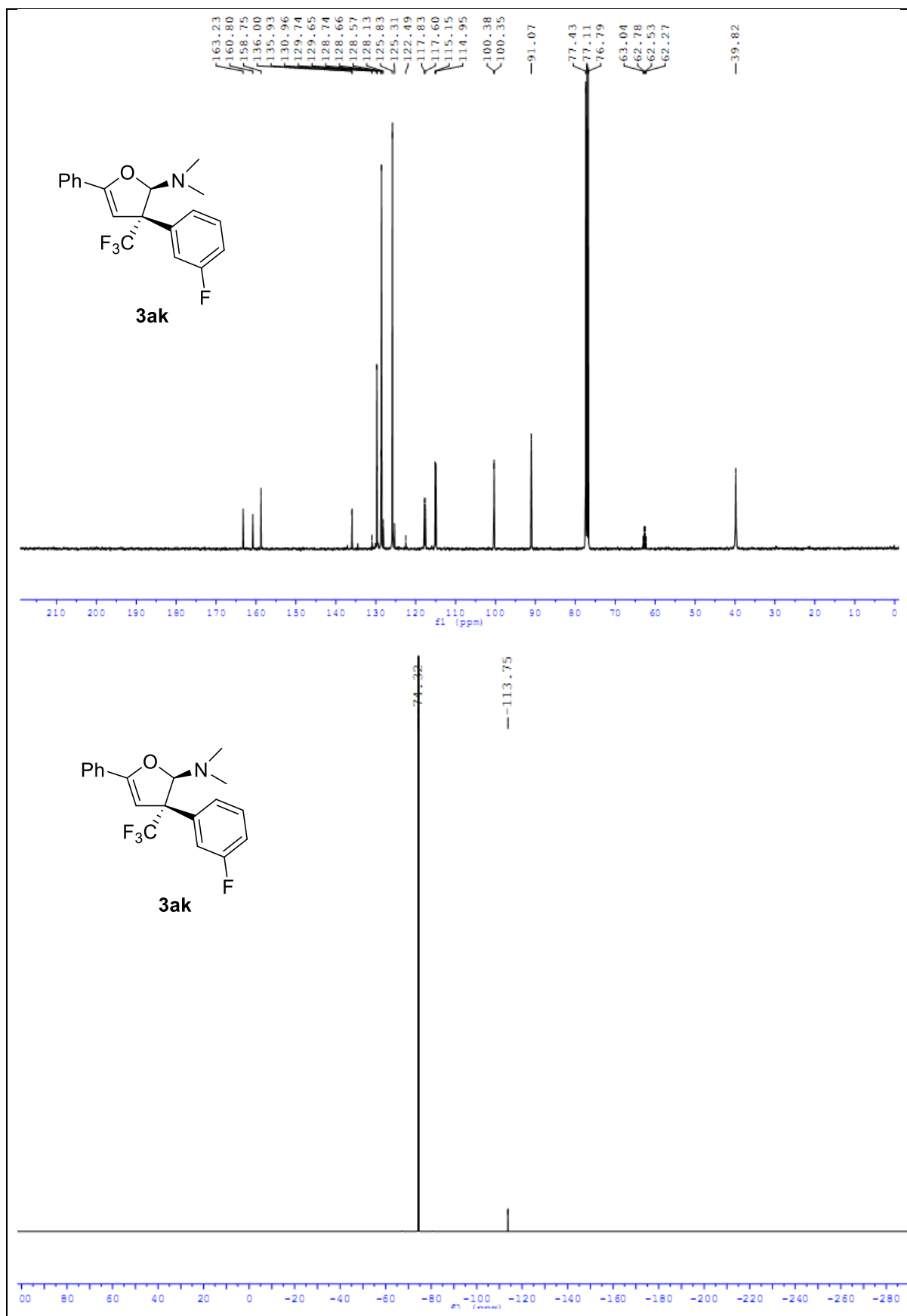


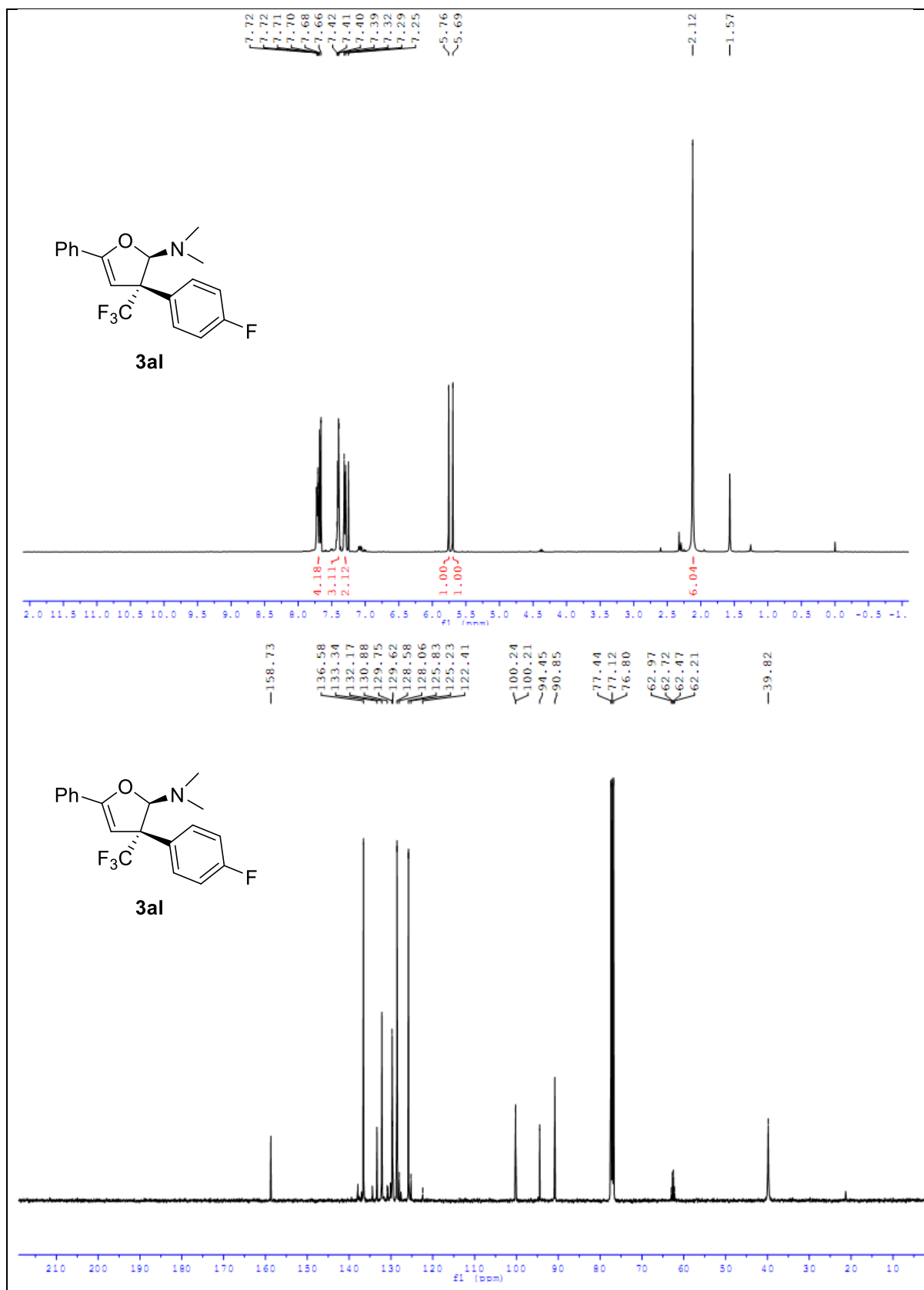


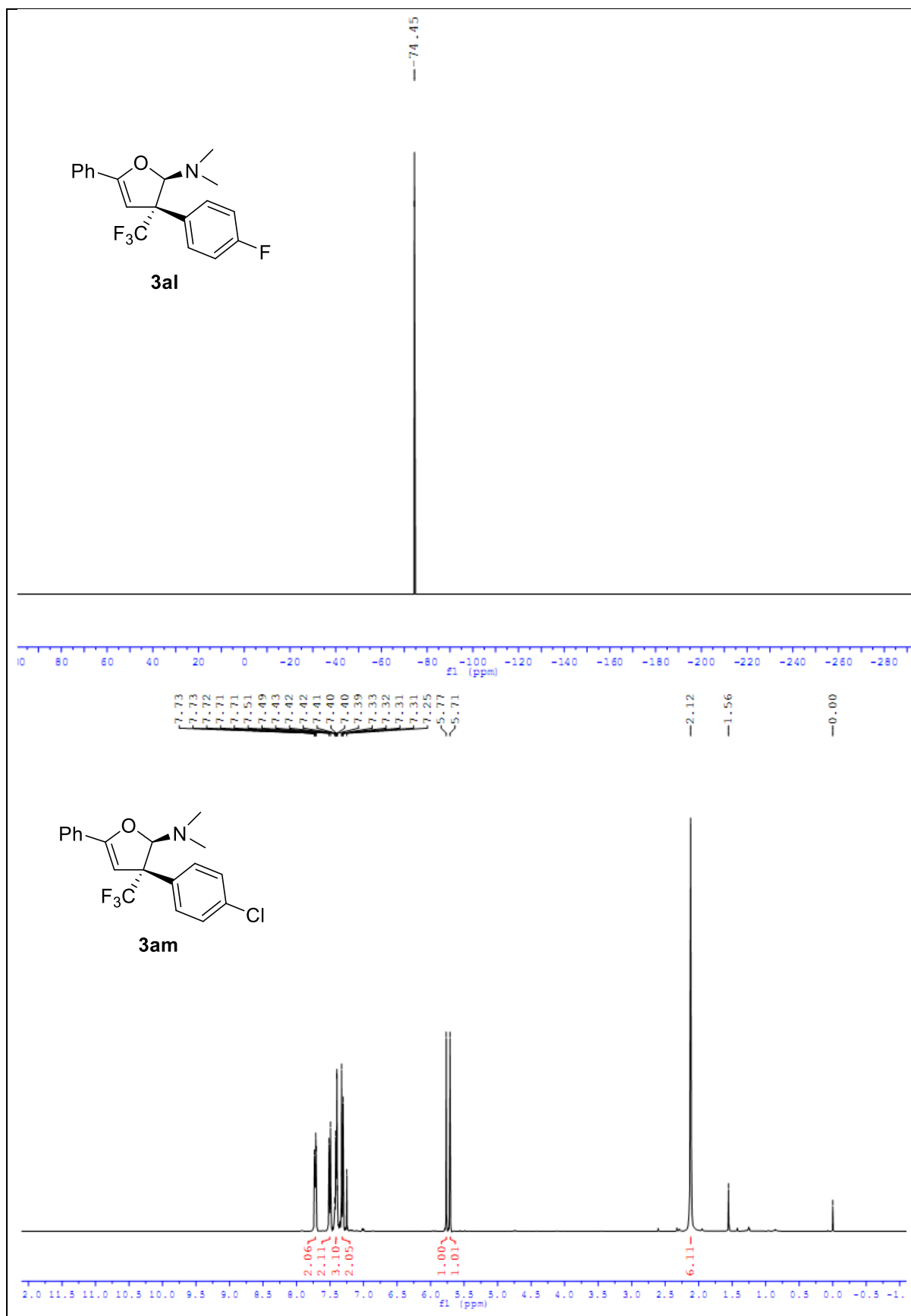


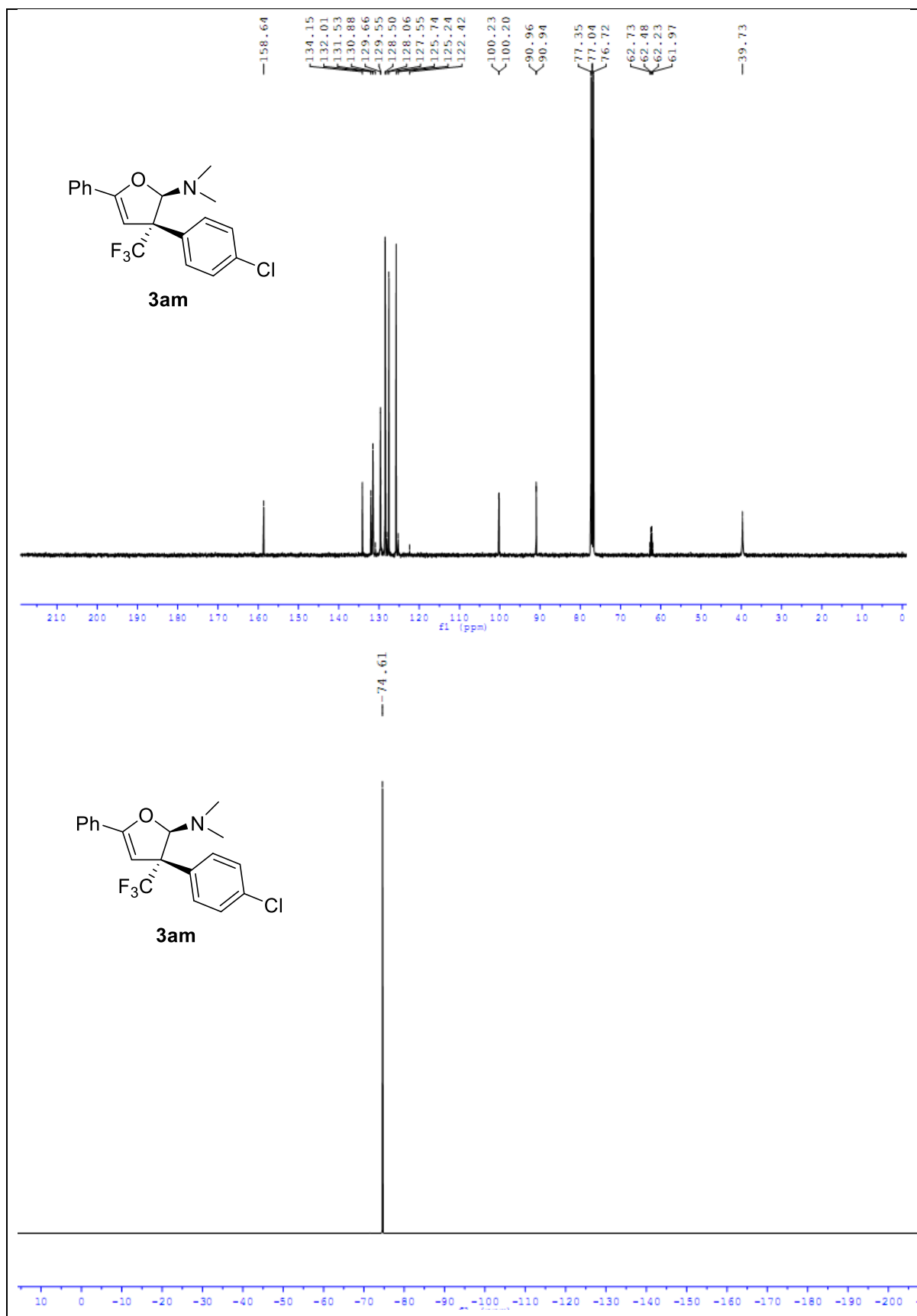


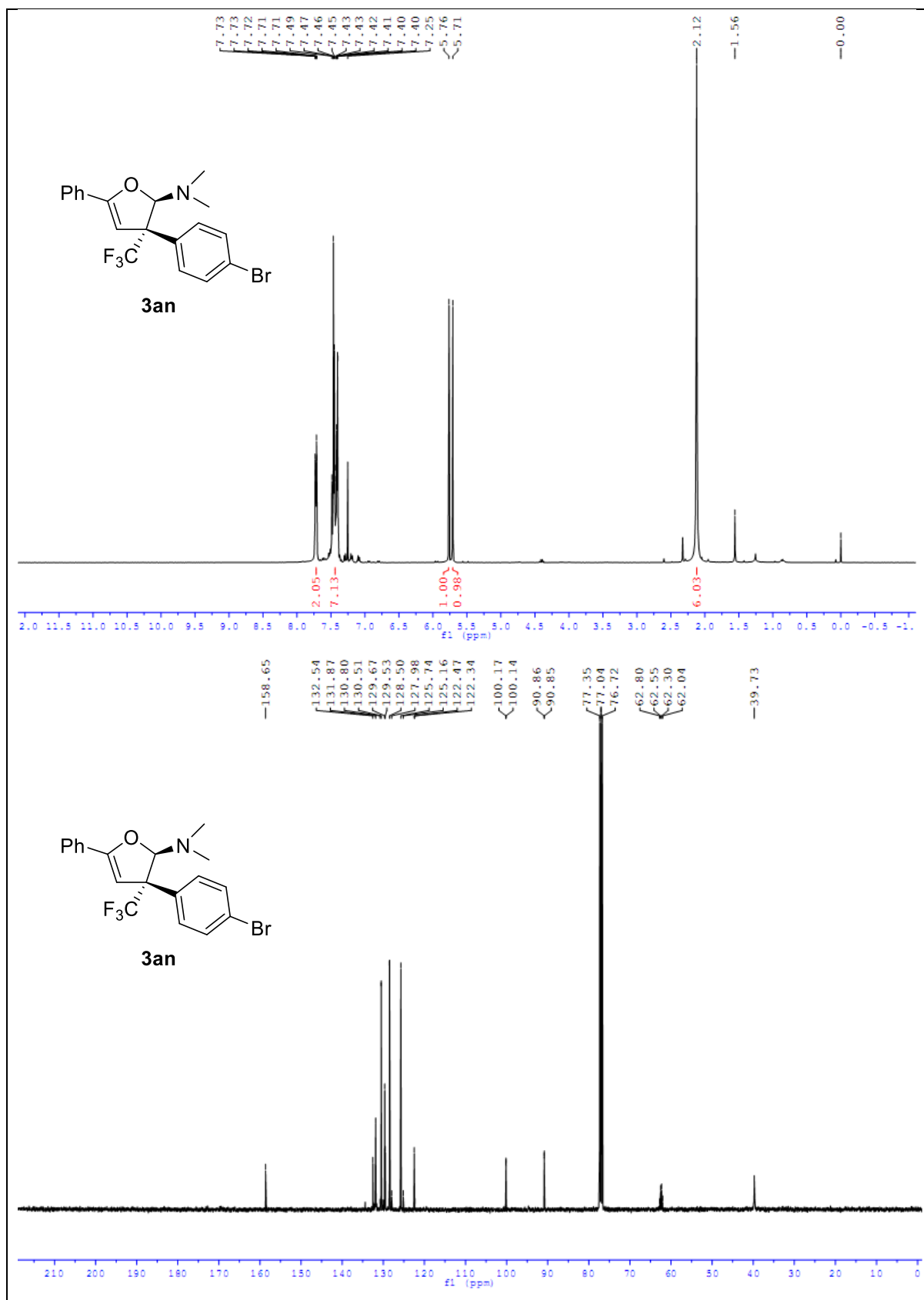


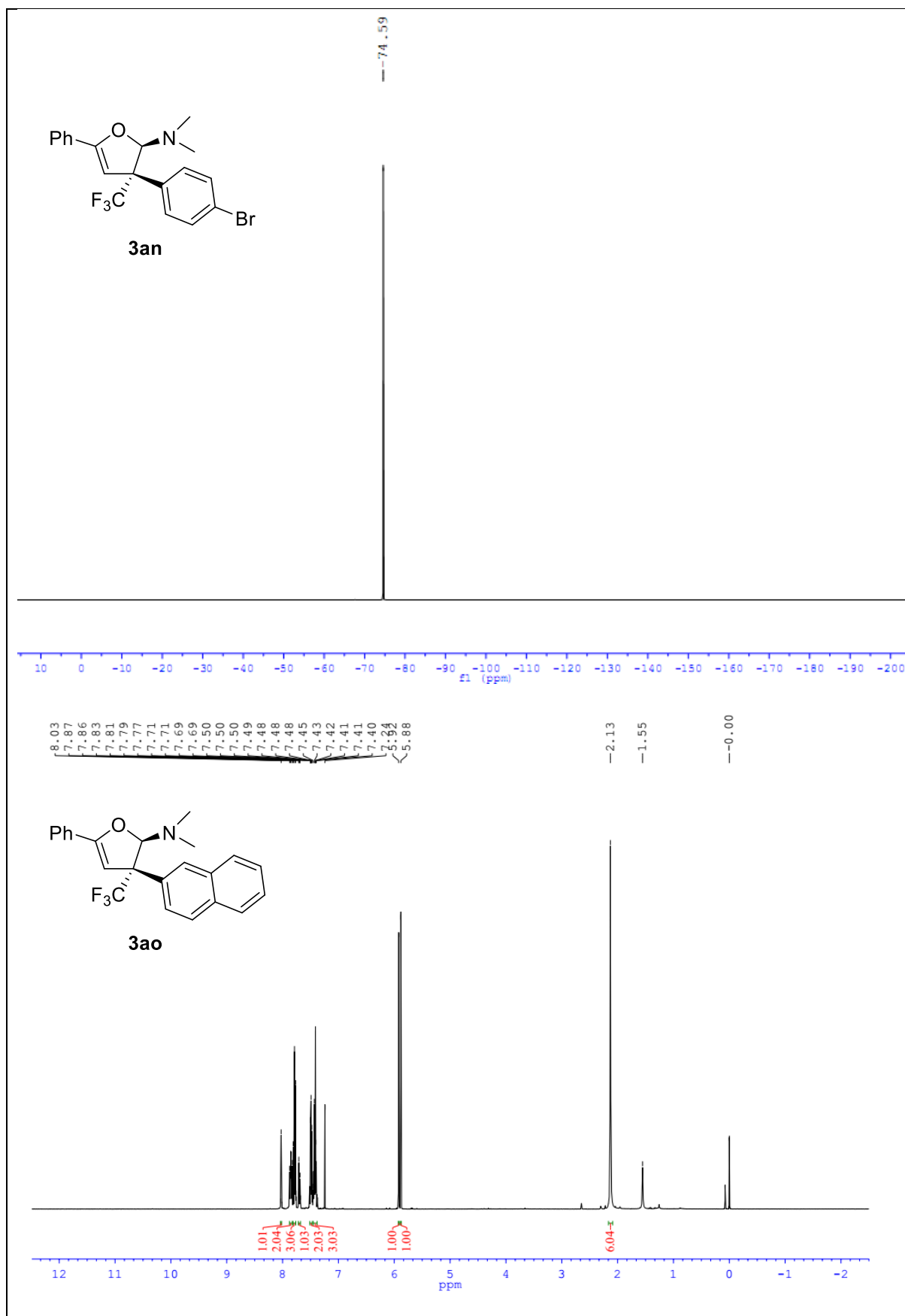


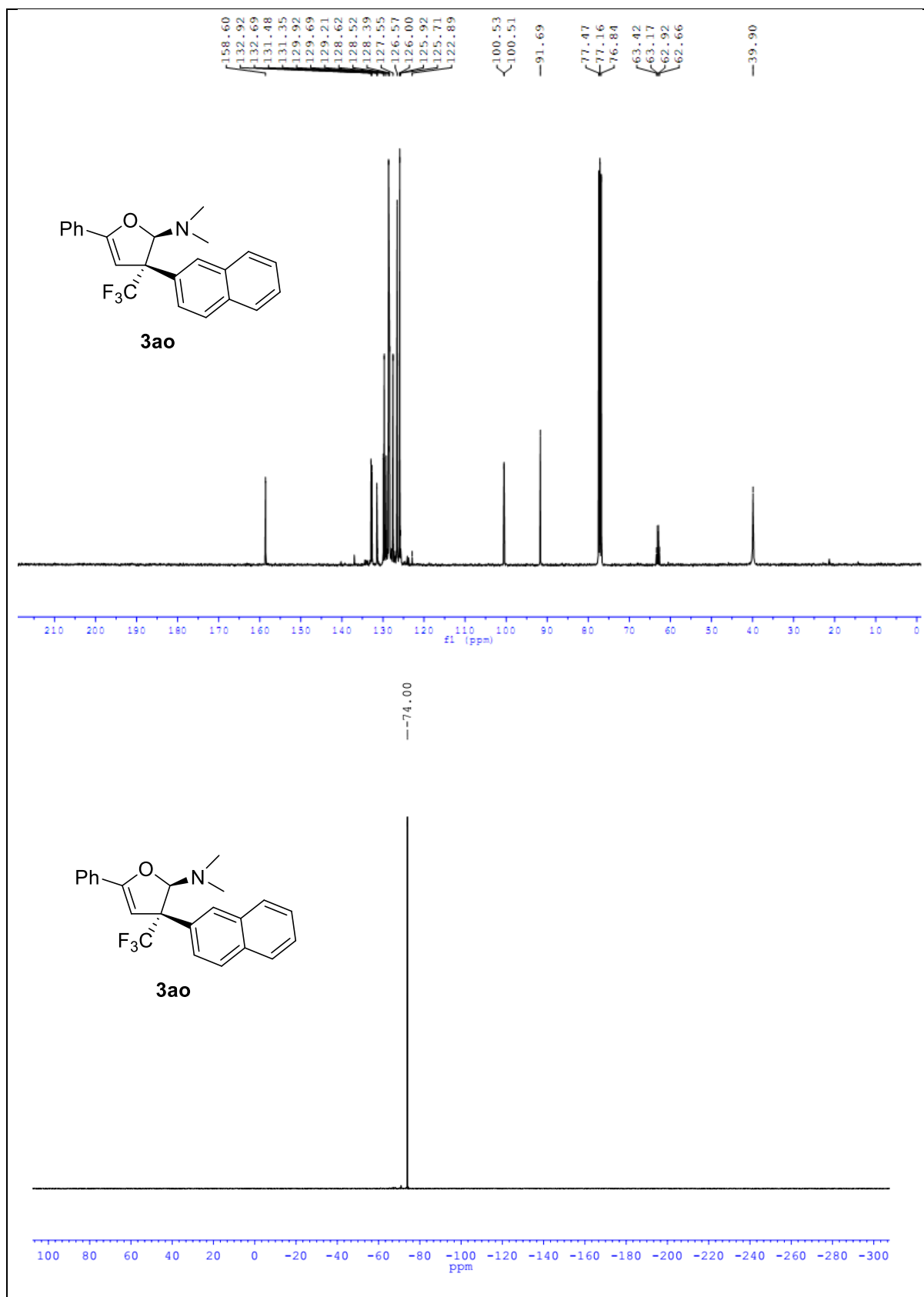


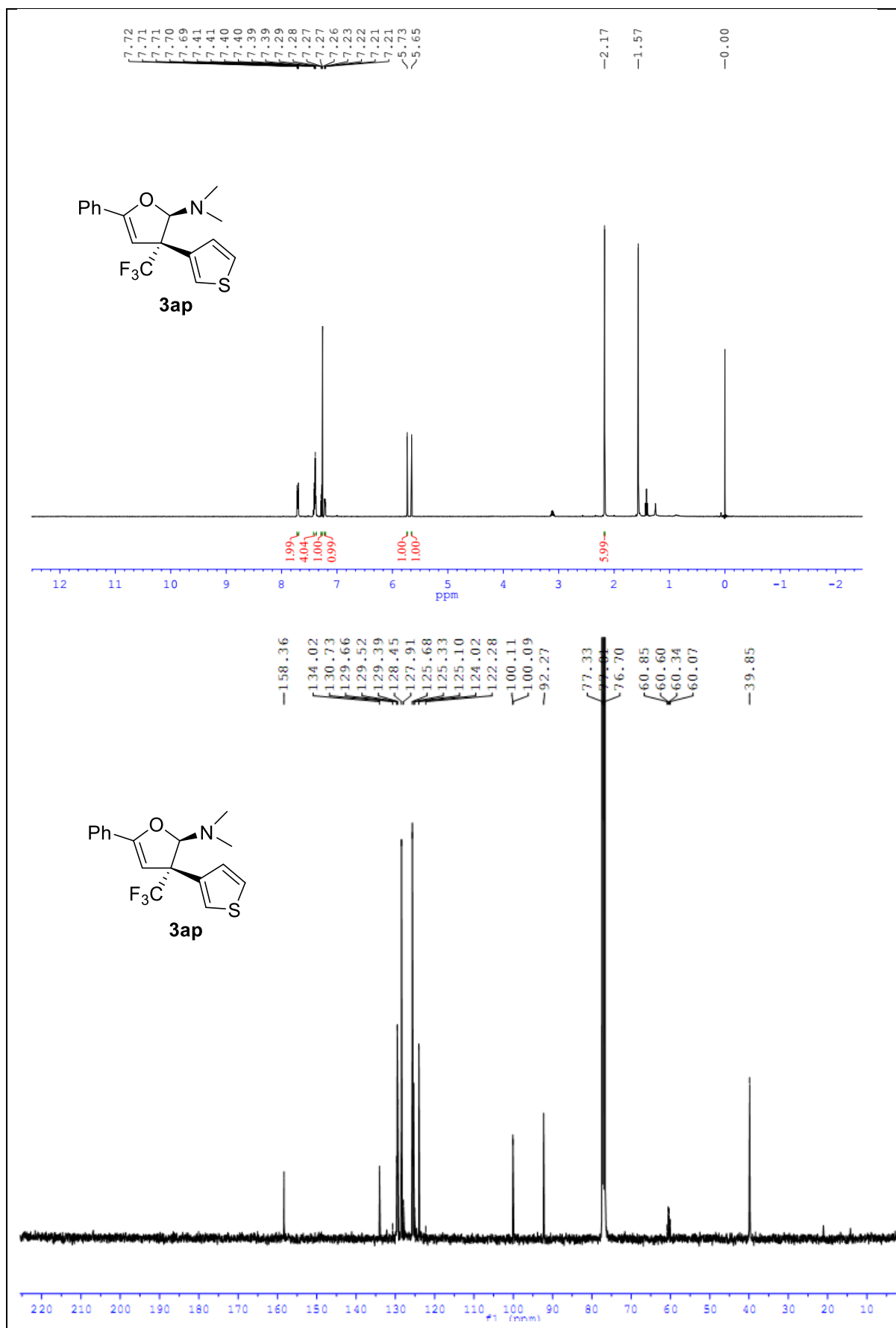


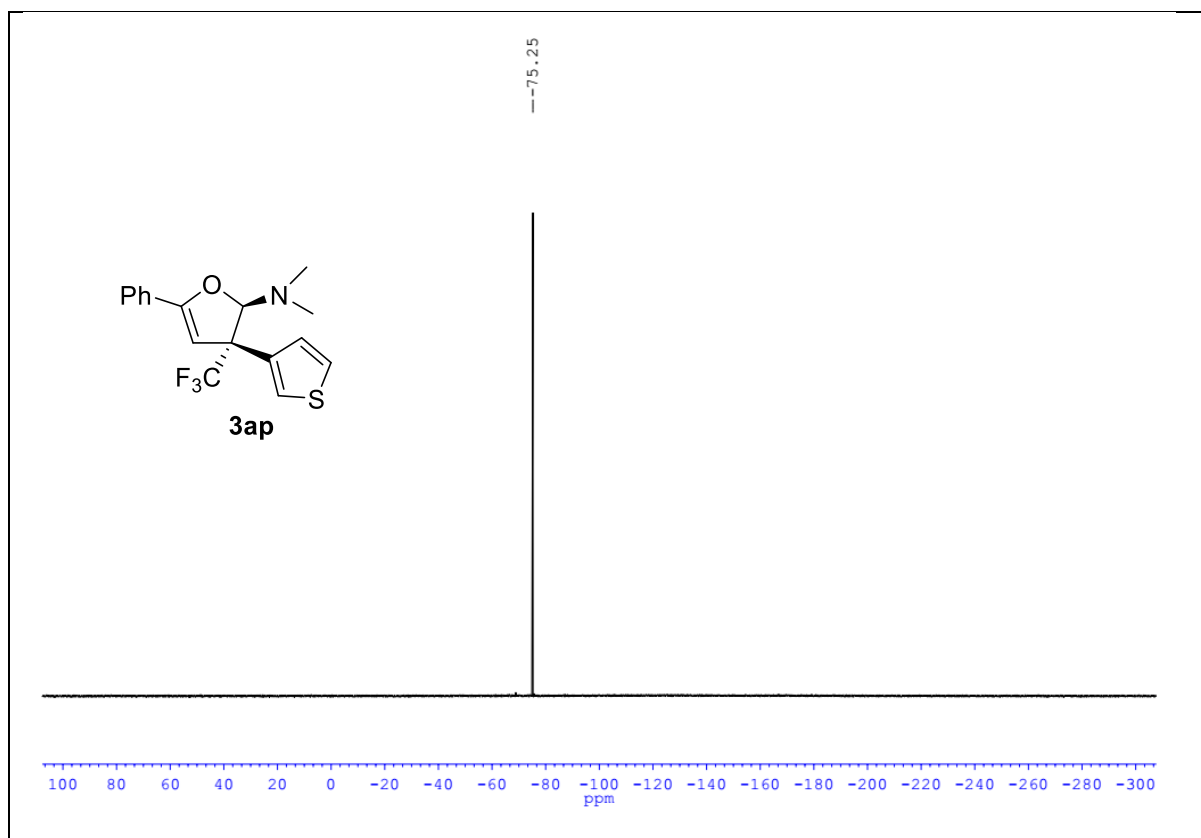












NMR Spectral for 2*H*-Furan applications

