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# Supporting Information



69451 Weinheim, Germany

# Rh-Catalyzed Transannulation of Pyridotriazoles with Alkynes and Nitriles

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## Content

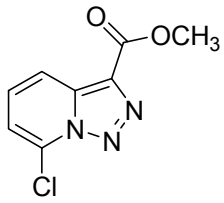
## General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instruments. (+) and (-) represent positive and negative intensities of signals in $^{13}C$ DEPT-135 experiments. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle silica gel (Kieselgel 60, 63-200 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Melting points were determined using a Thomas Hoover capillary melting point apparatus and are uncorrected. Anhydrous solvents were purchased from Aldrich and stored over calcium hydride. Alkynes, nitriles and Rh(II) carboxylates were commercially available and purchased from Aldrich, Strem Chemicals Inc., Alfa Aesar or Acros Organics, or synthesized via known literature procedures.

## Starting Materials. Preparation of [1,2,3]Triazolo[1,5-a]pyridines

***Note**: All the pyridotriazoles employed in this work demonstrated long shelf life (were stored at room temeperature for several months) and did NOT reveal any signs of spontaneous decomposition.*

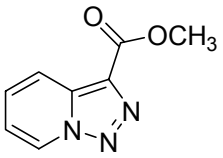
***Methyl 7-chloro[1,2,3]triazolo[1,5-a]pyridine-3-carboxylate*** **(3b)** was prepared via the diazotransfer reaction[1] on methyl (6-chloropyridin-2-yl)acetate synthesized according to the procedure by Davies and co-workers.[2] To a stirred solution of methyl (6-chloropyridin-2-yl)acetate (3.8 g, 20.5 mmol) and DBU (3.4 ml, 22.6 mmol) in 100 ml of dry acetonitrile, *p*-ABSA (5.2 g, 20.5 mmol) was added at room temperature in small portions over a 5 min period. The resulting yellow solution was stirred overnight and, after removal of solvent the residue was taken up into 150 ml of dichloromethane, washed with water and brine, and dried over sodium sulfate. Flash Silica chromatography (1:2 EtOAc/Hexanes) gave the product as yellowish solid. Yield: 4.1 g (19.4 mmol, 95%).




**3b**: $^1H$ NMR (500 MHz, DMSO-$d_6$) δ 8.19 (d, *J*=8.44 Hz, 1 H), 7.76 (t, *J*=8.07 Hz, 1 H), 7.66 (d, *J*=6.79 Hz, 1 H), 3.94 (s, 3 H); $^{13}C$ NMR (126 MHz, DMSO-$d_6$) δ 161.28, 136.86, 131.91 (+), 130.02, 127.79, 117.78 (+, 2C), 52.44 (+); FT IR (KBr): 3513, 3065, 1704, 1627, 1508, 1450 $cm^{-1}$; mp 147°C (dichloromethane – hexanes); HR EI MS *m/z* 211.0154, Calcd for $C_8H_6ClN_3O_2$ 211.01485.

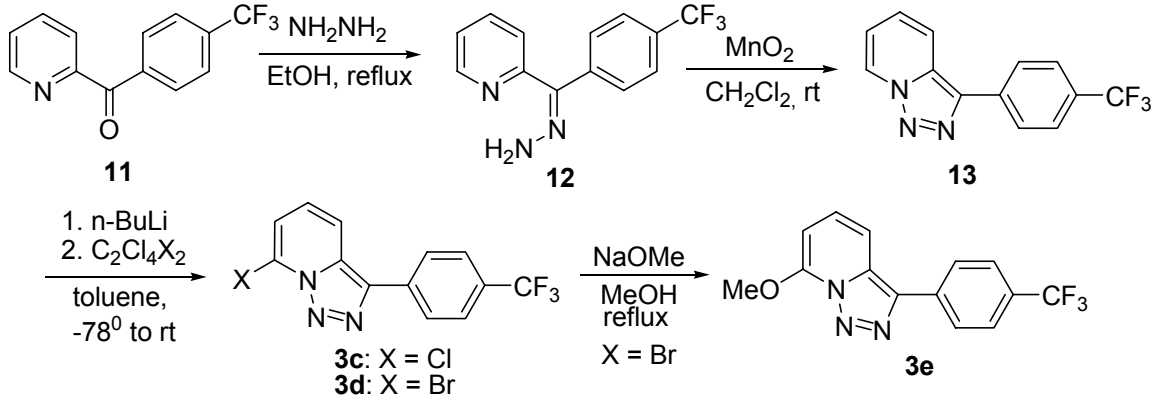
[1] (a) Regitz, M. *Angew. Chem., Int. Ed. Engl*. **1967**, *6*, 733; (b) Davies, H. M. L.; Cantrell, W. R., Jr.; Romines, K. R.; Baum, J. S. *Org. Synth.* **1992**, *70*, 93.
[2] Davies, H. M. L.; Townsend, R. J. . *J. Org. Chem.* **2001**, *66*, 6595.

***Methyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate*** **(3a)** (prepared analogously to **3b** from commercially available methyl pyridine-2-ylacetate).

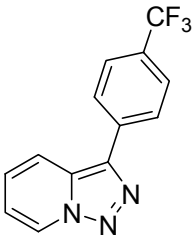


**3a**: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J*=6.96 Hz, 1 H), 8.29 (d, *J*=9.02 Hz, 1 H), 7.54 – 7.58 (m, 1 H), 7.17 (td, *J*=6.99, 1.04 Hz, 1 H), 4.05 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.15, 135.12, 129.24 (+), 125.94, 119.32 (+), 116.41 (+), 52.11 (+); FT IR (KBr): 3394, 3091, 2952, 1633, 1608, 1597, 1485 cm$^{-1}$; mp 140-141°C.

Compounds **3c-d** were prepared from the 2-pyridylketone **11** as shown in the scheme below. Hydrazone **12** was oxidized with manganese(IV) oxide[3] (Aldrich, <5 micron, activated) to give triazolopyridine **13**. Introduction of halogen to C-7 nucleophilic substitution of bromine with methoxide were done according to literature procedures:[4]



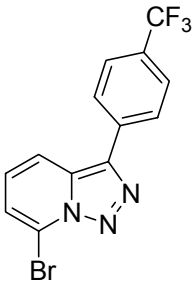

***3-[4-(Trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine*** **(13).** To a solution of pyridin-2-yl[4-(trifluoromethyl)phenyl]methanone **11**[5] (1.26 g, 5.0 mmol) in 5 ml of ethanol, hydrazine monohydrate (0.75 g, 15.0 mmol) was added. The reaction mixture was refluxed overnight, quenched with 50 ml of water, and extracted with EtOAc (2 x 50ml). The extract was washed with water and brine and dried over sodium sulfate. Removal of solvent afforded the crude hydrazone, which was dissolved in 25 ml of dichloromethane, and $MnO_2$ (1.7 g, 10.0 mmol) was added to this solution in one portion. The reaction mixture was stirred for 24h at room temperature. The inorganic solid was then filtered off, the solvent removed, and the residue was purified via flash Silica chromatography to afford 1.17 g (4.45 mmol, 89%) of 3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine **13** as yellowish crystalline solid.



**13**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.78 (dt, *J*=7.06, 0.96 Hz, 1 H), 8.05 - 8.15 (m, 2 H), 8.01 (dt, *J*=8.99, 1.10 Hz, 1 H), 7.66 - 7.83 (m, 2 H), 7.38 (ddd, *J*=8.99, 6.60, 0.92 Hz, 1 H), 7.06 (td, *J*=6.88, 1.10 Hz, 1 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 136.39, 135.00, 130.78, 129.59 (q, $J_{FC}$ = 32.37 Hz ), 126.55 (+, 3C), 125.96 (+, q, $J_{FC}$ = 2.77 Hz, 2C), 125.91 (+), 124.15 (q, $J_{FC}$ = 271.88 Hz), 118.06 (+), 115.56 (+); mp 178-179°C (MeOH).

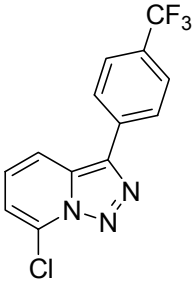
[3] Abarca, B.; Ballesteros, R.; Chadlaoui, M. *Tetrahedron* **2004**, *60*, 5785.
[4] Abarca, B.; Ballesteros, R.; Mojarred, F.; Jones, G.; Mouat, D. J. *J. Chem. Soc., Perkin Trans. I*, **1987**, 1865.
[5] Buschauer, A. *Arch. Pharm.* **1989**, *322*, 165.

***7-Bromo-3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine*** **(3d).** To a stirred solution of 3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine **13** (1.32 g, 5.0 mmol) in 25 ml of dry toluene cooled to -78° under inert atmosphere, *n*-BuLi (5.5 mmol, 2.1 ml of 2.6M solution in hexanes) was added slowly over a 5 min period. The reaction mixture was then allowed to warm to room temperature, stirred for 30 min, and again cooled to -78°C. A solution of dibromotetrachloroethane (DBTCE) (1.95 g, 6.0 mmol) in 10 ml was added slowly to the reaction mixture, which then was warmed up to room temperature, stirred overnight, and quenched with 50 ml of saturated $NH_4Cl$ solution. The aqueous layer was extracted with dichloromethane (2 x 50ml), and the combined organic fractions were washed with water and brine and dried over sodium sulfate. After removal of solvents in vacuo, the residue was purified via flash Silica chromatography (1:20 EtOAc/Toluene) to give 1.41 g (4.12 mmol, 82%) of 7-bromo-3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine **3d** as colorless crystalline solid.



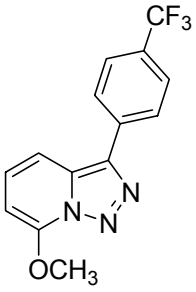

**3d**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J*=8.07 Hz, 2 H), 8.02 (dd, *J*=8.44, 1.28 Hz, 1 H), 7.77 (d, *J*=8.25 Hz, 2 H), 7.18 - 7.40 (m, 2 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 138.06, 134.68, 132.31, 130.00 (q, $J_{FC}$ = 33.29 Hz), 126.99 (+), 126.87 (+, 2C), 126.04 (+, q, $J_{FC}$ = 2.77 Hz, 2 C), 124.08 (q, $J_{FC}$ = 270.96 Hz), 119.73 (+), 116.93 (+), 116.06; mp 204°C (dec); FT-IR (KBr): 3091, 1618, 1521, 1496, 1425, 1318 cm$^{-1}$; HR EI MS *m/z* 340.9773, Calcd for $C_{13}H_7BrF_3N_3$ 340.97754.

***7-Chloro-3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine*** **(3c)** (prepared analogously to **3d** using hexachloroethane instead of DBTCE).




**3c**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J*=8.07 Hz, 2 H), 7.99 (dd, *J*=8.99, 0.92 Hz, 1 H), 7.77 (d, *J*=8.25 Hz, 2 H), 7.38 (dd, *J*=8.89, 7.06 Hz, 1 H), 7.26 (s, 1 H), 7.16 (dd, *J*=7.15, 0.92 Hz, 1 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 137.93, 134.54, 132.45, 130.15, 128.23, 126.93 (+), 126.87 (+, 2C), 126.04 (+, q, $J_{FC}$ = 2.77 Hz), 124.09 (q, $J_{FC}$ = 271.88 Hz), 116.38 (+), 115.52 (+); mp 199-200°C (dec.) (hexane-dichloromethane); FT-IR (KBr): 3095, 1620, 1523, 1500, 1317 cm$^{-1}$; HR EI MS *m/z* 297.0282, Calcd for $C_{13}H_7ClF_3N_3$ 297.02806.

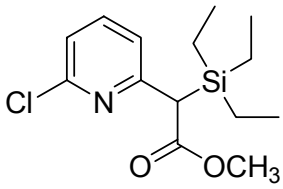
***7-Methoxy-3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine*** **(3e).** A freshly prepared from 0.138 g (6.0 mmol) of sodium and 12 ml of dry methanol solution of sodium methoxide was added under inert atmosphere to 0.684 g (2.0 mmol) of 7-bromo-3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine . The resulting mixture was refluxed for 1h, methanol was removed in vacuo, 20 ml of water was added to the residue, and the separated precipitate was filtered, thoroughly washed with water and dried on air. The product was additionally purified via flash Silica chromatography (1:1 EtOAc/Hexanes) to afford 0.438 g (1.5mmol, 75%) of 7-methoxy-3-[4-(trifluoromethyl)phenyl][1,2,3]triazolo[1,5-a]pyridine **3e** as white crystalline solid.




**3e**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.99 - 8.19 (m, 2 H), 7.67 - 7.85 (m, 2 H), 7.63 (dd, *J*=8.89, 0.64 Hz, 1 H), 7.39 (dd, *J*=8.80, 7.34 Hz, 1 H), 6.32 (dd, *J*=7.37, 0.36 Hz, 1 H), 4.25 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 149.87, 136.32, 135.14, 132.43, 129.41 (q, $J_{FC}$ = 32.37 Hz), 128.43 (+), 126.56 (+, 2C), 125.87 (+, q, $J_{FC}$ = 2.77 Hz, 2C), 124.19 (q, $J_{FC}$ = 271.88 Hz), 109.42 (+), 91.64 (+), 57.21 (+); FT-IR (KBr): 3129, 3086, 2843, 1633, 1617, 1540, 1428, 1336 cm$^{-1}$; mp 183°C (dec.); HR EI MS *m/z* 293.07811, Calcd for $C_{14}H_{10}F_3N_3O$ 293.07760.

## Initial Experiments

**$Rh_2(OAc)_4$-Catalyzed Decomposition of Triazole 3b in a Presence of Triethylsilane.**[6] To an oven dried 3 ml Wheaton vial was added methyl 7-chloro[1,2,3]triazolo[1,5-a]pyridine-3-carboxylate (**3b**) (0.106 g, 0.5 mmol) and $Rh_2(OAc)_4$ (2.2 mg, 0.005 mmol) under $N_2$ atmosphere. One ml of dry dichloromethane and 0.164 ml (0.116 g, 1.0 mmol) of triethylsilane were added sequentially to the same vial and the reaction mixture was stirred at room temperature for 2h, when judged complete by TLC analysis. Flash Silica chromatography (1:15 EtOAc/Hexanes, 1% (v/v) triethylamine) was then directly applied to the reaction mixture to afford 0.132 g (4.40 mmol, 88%) of methyl (6-chloropyridin-2-yl)triethylsilylacetate **4** as colorless oil.



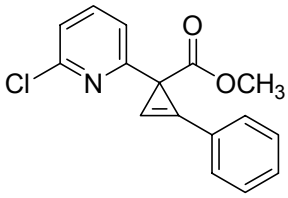

**4**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J*=7.89, 0.92 Hz, 1 H), 7.57 (t, *J*=7.79 Hz, 1 H), 7.11 (dd, *J*=7.70, 0.92 Hz, 1 H), 3.94 (s, 1 H), 3.69 (s, 3 H), 0.90 (t, *J*=7.89 Hz, 9 H), 0.60 (q, *J*=7.89 Hz, 6 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 172.66, 158.20, 149.89, 138.49 (+), 121.40 (+), 121.02 (+), 51.49 (+), 45.90(+), 6.95 (+, 3C), 2.82 (-, 3C).

**$Rh_2(OAc)_4$-Catalyzed Reaction of Triazole 3b with Phenylacetylene.** To an oven dried 5 ml Wheaton vial was added methyl 7-chloro[1,2,3]triazolo[1,5-a]pyridine-3-carboxylate (**3b**) (0.212 g, 1.0 mmol) and $Rh_2(OAc)_4$ (2.2 mg, 0.005 mmol) under $N_2$ atmosphere. Two ml of dry dichloromethane and phenylacetylene (0.306 g, 3.0 mmol) were added sequentially to the same vial and the reaction mixture was stirred at room temperature for 2h, when judged

[6] Bagheri, V.; Doyle, M.; Taunton, J.; Claxton, E. *J. Org. Chem*. **1988**, *53*, 6185-6160.

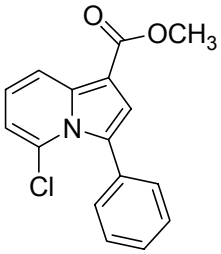
complete by TLC analysis. The reaction mixture was filtered through a layer of Silica (dichloromethane – eluent), all the solvents were removed in vacuo, and the residue was purified via flash Silica chromatography (1:10 EtOAc/Hexanes) to afford 0.194 g (0.68 mmol, 68%) of methyl 1-(6-chloropyridin-2-yl)-2-phenylcycloprop-2-ene-1-carboxylate **5** as yellow oil and 0.080 g (0.28 mmol, 28%) of methyl 5-chloro-3-phenylindolizine-1-carboxylate **6a** as white crystalline.

***Methyl 1-(6-chloropyridin-2-yl)-2-phenylcycloprop-2-ene-1-carboxylate* (5)**



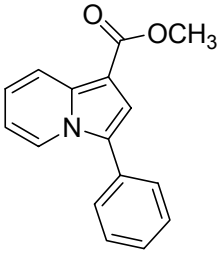

**5**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J*=7.75, 1.61 Hz, 2 H), 7.57 (t, *J*=7.75 Hz, 1 H), 7.48 (dd, *J*=7.75, 0.73 Hz, 1 H), 7.36 - 7.46 (m, 3 H), 7.20 (s, 1 H), 7.15 (dd, *J*=7.75, 0.73 Hz, 1 H), 3.71 (s, 3 H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.94, 160.69, 150.54, 138.63 (+), 130.19 (+), 130.11 (+, 2C), 128.86 (+, 2C), 124.95, 122.18 (+), 121.91 (+), 115.54, 98.25 (+,) 52.32 (+), 35.28; HR EI MS *m/z* 285.0547, Calcd for $C_{16}H_{12}ClNO_2$ 285.0557.

***Methyl 5-chloro-3-phenylindolizine-1-carboxylate* (6a)**




**6a**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J*=8.92, 1.32 Hz, 1 H), 7.29 - 7.43 (m, 5 H), 7.20 (s, 1 H), 6.98 (dd, *J*=9.06, 7.02 Hz, 1 H), 6.74 (dd, *J*=7.16, 1.32 Hz, 1 H), 3.88 (s, 3 H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.93, 138.77, 133.62, 131.01 (+, 2C), 128.09, 127.96 (+), 127.66, 127.04 (+, 2C), 121.99 (+), 119.51 (+), 118.52 (+), 114.75 (+), 104.60, 51.11 (+); mp 110°C (dichloromethane-hexane); HR EI MS *m/z* 285.0556 Calcd for $C_{16}H_{12}ClNO_2$ 285.05566.

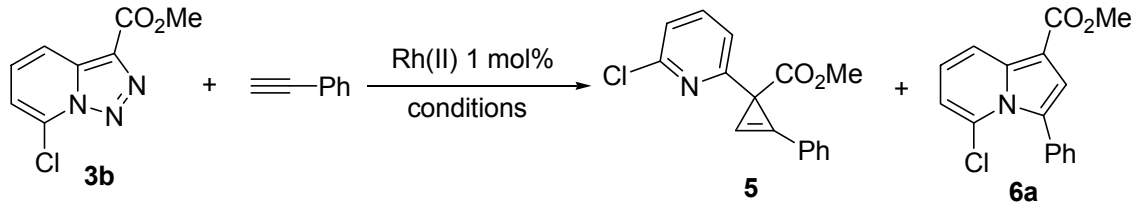
***Methyl 3-phenylindolizine-1-carboxylate* (14)** (prepared via reduction of **6a**[7] for 2D NMR studies and as a demonstration of a feasibility of chlorine removal). To an oven dried 1 ml Wheaton vial was added methyl 5-chloro-3-phenylindolizine-1-carboxylate (**6a**) (0.057 g, 0.2 mmol) and 0.070 g (0.096 ml, 0.6 mmol) of triethylsilane under $N_2$ atmosphere. Palladium(II)chloride (3.5 mg, 0.02 mmol) was added to the same vial under flow of argon, and reaction mixture was stirred for 12h at room temperature, when judged complete by TLC analysis. Flash Silica chromatography (1:5 EtOAc/Hexanes) afforded 0.050 g (0.2 mmol, 100%) of methyl 3-phenylindolizine-1-carboxylate (**14**) as white crystalline.




**14**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.29 - 8.33 (m, 1 H), 8.25 - 8.29 (m, 1 H), 7.46 - 7.60 (m, 4 H), 7.36 - 7.45 (m, 1 H), 7.30 (s, 1 H), 7.09 (ddd, *J*=8.99, 6.60, 1.10 Hz, 1 H), 6.72 (td, *J*=6.88, 1.28 Hz, 1 H), 3.92 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.41, 136.44, 131.23, 129.12 (+, 2C), 128.64 (+, 2C), 128.05 (+), 126.50, 123.38 (+), 122.36 (+), 120.14 (+), 116.03 (+), 112.66 (+), 103.89, 50.97 (+); mp 107-108°C (dichloromethane-hexane).

[7] Boukherroub, R.; Chatgilialoglu, C.; Manuel, G. *Organometallics* **1996**, *15*, 1508.

## Optimization of Chemoselectivity




**Optimization Procedure.** To an oven dried 1 ml Wheaton vial was added methyl 7-chloro[1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **3b** (0.021 g, 0.1 mmol) and Rh(II) carboxylate ( 0.001 mmol) under $N_2$ atmosphere. Phenylacetylene (0.051 g, 0.3 mmol) was then added, followed by 0.2 ml of dry solvent and the reaction mixture was stirred at temperature defined in Table 1 until judged complete by TLC analysis. The reaction mixture was filtered through a layer of Silica (dichloromethane – eluent), the solvents were removed in vacuo and the residue was analyzed by $^1$H NMR using dibromomethane as an internal standard. Selected results are summarized in Table 1.

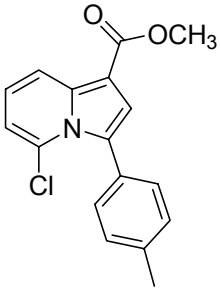
**Table 1**

| Rh catalyst | conditions | **5**:**6a** ratio | **6a**,% yield |
|---|---|---|---|
| $Rh_2(OAc)_4$ | DCM, rt, 2h | 2.4:1 | 28 |
| $Rh_2(CAPY)_4$ | DCM, $45^0$, 2h | NR | NR |
| $Rh_2(MEPY)_4$ | DCM, $45^0$, 2h | NR | NR |
| $Rh_2(CF_3COO)_4$ | DCM, rt, 12h | 1:11 | <5 |
| $Rh_2(PTPA)_4$ | DCM, rt, 2h | 4:1 | 19 |
| $Rh_2$(*S*-TBSP)$_4$ | DCM, rt, 2h | 11:1 | 8 |
| $Rh_2$(*S*-DOSP)$_4$ | DCM, rt, 2h | 11:1 | 8 |
| $Rh_2$(*S*-DOSP)$_4$ | toluene, rt, 2h | 19:1 | <5 |
| $Rh_2(C_3F_7COO)_4$ | DCM, rt, 3h | 1:10 | 81 |
| $Rh_2(C_3F_7COO)_4$ | DCE, $80^0$, 2h | 1:10 | 65 |

## $Rh_2(C_3F_7COO)_4$-Catalyzed Transannulation with Alkynes

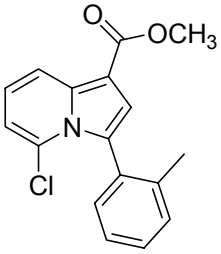
**Typical Preparative Procedure.** To an oven dried 5 ml Wheaton vial was added methyl 7-chloro[1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **3b** (0.106 g, 0.5 mmol) and $Rh_2(C_3F_7COO)_4$ (5.3 mg, 0.005 mmol) under $N_2$ atmosphere. Phenylacetylene (0.153 g, 1.5 mmol) was then added followed by 1 ml of dry dichloromethane, and the reaction mixture was stirred at room temperature for 3.5h, when judged complete by TLC analysis. The reaction mixture was filtered through a layer of Silica (dichloromethane – eluent), the solvents were removed, and the residue was purified via flash Silica chromatography (1:10 EtOAc/Hexanes) to afford 0.111 g (0.39 mmol, 78%) of methyl 5-chloro-3-phenylindolizine-1-carboxylate **6a** as white crystalline solid (see page S 6 for analytical data).

***Methyl 5-chloro-3-(4-methylphenyl)indolizine-1-carboxylate*** **(6b)**



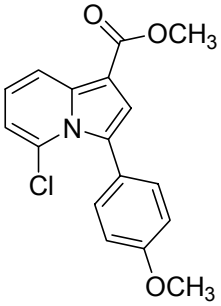
**6b**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J*=8.99, 1.10 Hz, 1 H), 7.29 (d, *J*=7.89 Hz, 2 H), 7.20 (s, 1 H), 7.18 (d, *J*=7.70 Hz, 2 H), 6.99 (dd, *J*=8.80, 7.15 Hz, 1 H), 6.75 (d, *J*=6.97 Hz, 1 H), 3.91 (s, 3 H), 2.43 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.99, 138.74, 137.88, 130.96 (+, 2C), 130.73, 128.21, 127.78 (+, 2C), 121.86 (+), 119.41 (+), 118.54 (+), 114.70 (+), 104.53, 51.11 (+), 21.39; mp 124°C (dichloromethane-hexane); HR EI MS *m/z* 299.0718, Calcd for $C_{17}H_{14}ClNO_2$ 299.0714.

***Methyl 5-chloro-3-(2-methylphenyl)indolizine-1-carboxylate*** **(6c)**



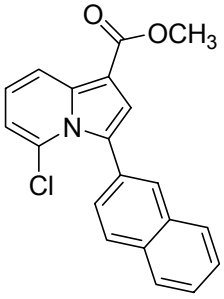
**6c**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J*=8.99, 1.28 Hz, 1 H), 7.29 - 7.39 (m, 2 H), 7.14 - 7.25 (m, 3 H), 6.99 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.74 (dd, *J*=7.06, 1.19 Hz, 1 H), 3.91 (s, 3 H), 2.03 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.04, 139.54, 138.52, 133.64, 131.60 (+), 128.92 (+), 128.78 (+), 127.47, 127.27, 124.73 (+), 121.91 (+), 118.64 (+), 118.61 (+), 114.42 (+), 104.40, 51.12 (+), 20.23 (+); yellowish oil; HR EI MS *m/z* 299.0705 Calcd for $C_{17}H_{14}ClN_2$ 299.0713.

***Methyl 5-chloro-3-(4-methoxyphenyl)indolizine-1-carboxylate*** **(6d)**



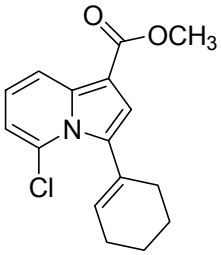
**6d**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J*=8.89, 1.19 Hz, 1 H), 7.28 - 7.35 (m, 2 H), 7.19 (s, 1 H), 6.98 (dd, *J*=8.99, 7.15 Hz, 1 H), 6.87 - 6.93 (m, 2 H), 6.74 (dd, *J*=7.06, 1.19 Hz, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.00, 159.54, 138.67, 132.38 (+, 2C), 127.95, 127.73, 125.95, 121.82 (+), 119.32 (+), 118.53 (+), 114.69 (+), 112.48 (+, 2C), 104.37, 55.31 (+), 51.10 (+); mp 124-125°C (dichloromethane-hexane); Found: C 64.52, H 4.53; Calcd for $C_{17}H_{14}ClNO_3$: C 64.67, H 4.47.

***Methyl 5-chloro-3-(2-naphthyl)indolizine-1-carboxylate*** **(6e)**



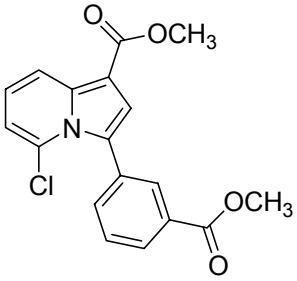
**6e**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.37 (dd, *J*=8.99, 1.28 Hz, 1 H), 7.85 - 7.93 (m, 3 H), 7.83 (d, *J*=8.62 Hz, 1 H), 7.50 - 7.58 (m, 3 H), 7.32 (s, 1 H), 7.03 (dd, *J*=8.99, 7.15 Hz, 1 H), 6.79 (d, *J*=6.79 Hz, 1 H), 3.93 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.95, 138.98, 132.76 , 132.35, 131.19, 129.52 (+, 2C), 129.17 (+), 128.14, 128.04 (+), 127.81, 127.70 (+), 126.46 (+), 126.18 (+), 122.11 (+), 119.98 (+), 118.62 (+), 114.77 (+), 104.78, 51.16 (+); mp 154-155°C (hexane-dichloromethane); Found: C 71.27, H 4.18; Calcd for $C_{20}H_{14}ClNO_2$: C 71.54, H 4.20.

***Methyl 5-chloro-3-cyclohex-1-en-1-ylindolizine-1-carboxylate*** **(6f)**



**6f**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.35 (dd, *J*=8.99, 1.28 Hz, 1 H), 8.00 - 8.14 (m, 2 H), 7.54 - 7.67 (m, 1 H), 7.38 - 7.54 (m, 1 H), 7.26 (s, 1 H), 7.03 (dd, *J*=8.99, 7.15 Hz, 1 H), 6.79 (dd, *J*=7.15, 1.10 Hz, 1 H), 3.93 (s, 3 H), 3.91 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.82, 164.81, 138.99, 135.07 (+), 133.98, 131.84 (+), 129.08 (+), 127.53, 127.21 (+), 126.78, 122.25 (+), 119.94 (+), 118.64 (+), 114.93 (+), 109.59, 104.91, 52.27 (+), 51.18 (+); HR EI MS *m/z* 343.0624 Calcd for $C_{18}H_{14}ClNO_4$ 343.0611.

***Methyl 5-chloro-3-[3-(methoxycarbonyl)phenyl]indolizine-1-carboxylate*** **(6g)**

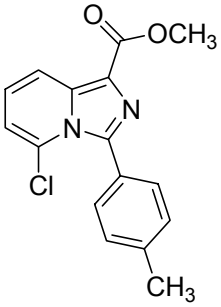


**6g**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J*=8.99, 1.28 Hz, 1 H), 7.02 (s, 1 H), 6.92 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.73 (dd, *J*=7.06, 1.19 Hz, 1 H), 5.84 (s, 1 H), 3.88 (s, 3 H), 1.49 - 2.48 (m, 8 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.05, 138.45, 131.30, 130.92, 127.50, 121.59 (+), 118.41 (+), 117.40 (+), 114.23 (+), 103.96, 51.01 (+), 32.54 (-), 25.67 (-), 22.53 (-), 21.76 (-); mp 106°C (hexane-dichloromethane); Found: C 66.19, H 5.65; Calcd for $C_{16}H_{16}ClNO_2$: C 66.32, H 5.57.

## $Rh_2(OAc)_4$-Catalyzed Transannulation with Nitriles

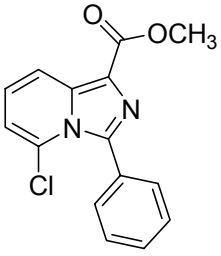
**Typical Preparative Procedure.** To an oven dried 3 ml Wheaton vial, equipped with mini-inert valve, was added methyl 7-chloro[1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **3b** (0.106 g, 0.5 mmol) and $Rh_2(OAc)_4$ (2.2 mg, 0.005 mmol) under $N_2$ atmosphere. *p*-Tolylnitrile (0.176 g, 0.180 ml, 1.5 mmol) was then added to the same vial, followed by 1 ml of dry toluene and the reaction mixture was stirred at 60° for 1h, when judged complete by TLC analysis. Flash Silica chromatography (1:2 EtOAc/Hexanes, 1 % (v/v) triethylamine) was then directly applied to the reaction mixture to afford 0.134 g (0.45 mmol, 89%) of methyl 5-chloro-3-(4-methylphenyl)imidazo[1,5-*a*]pyridine-1-carboxylate **7a** as white crystalline solid.

***Methyl 5-chloro-3-(4-methylphenyl)imidazo[1,5-a]pyridine-1-carboxylate* (7a)**



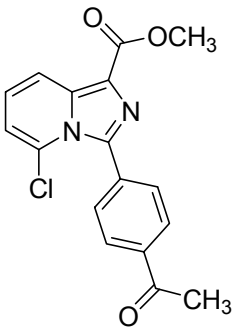

**7a**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J*=8.99 Hz, 1 H), 7.41 (d, *J*=8.07 Hz, 2 H), 7.20 (d, *J*=7.89 Hz, 2 H), 7.04 (dd, *J*=8.99, 7.15 Hz, 1 H), 6.79 (d, *J*=6.79 Hz, 1 H), 3.98 (s, 3 H), 2.41 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.63, 140.20, 139.39, 137.50, 131.07 (+, 2C), 128.73, 127.91 (+, 2C), 126.23, 124.24 (+), 121.60, 118.46 (+), 115.92 (+), 109.59, 51.71 (+), 21.51 (+); FT-IR (KBr): 3071, 2951, 2921, 1690, 1625, 1542, 1494, 1441 cm$^{-1}$; mp 248°C (hexane-dichloromethane); HR EI MS *m/z* 300.0671, Calcd for $C_{16}H_{13}ClN_2O_2$ 300.06656.

***Methyl 5-chloro-3-phenylimidazo[1,5-a]pyridine-1-carboxylate* (7b)**



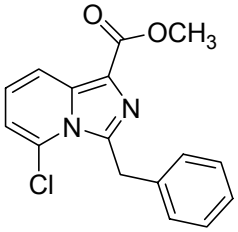

**7b**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J*=9.08, 1.01 Hz, 1 H), 7.50 - 7.57 (m, 2 H), 7.35 - 7.49 (m, 3 H), 7.06 (dd, *J*=9.17, 6.97 Hz, 1 H), 6.81 (dd, *J*=6.97, 1.10 Hz, 1 H), 3.98 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.59, 139.98, 137.51, 131.70, 131.21 (+, 2C), 129.39 (+), 127.23 (+, 2C), 126.15, 124.35 (+), 121.70, 118.50 (+), 115.99 (+), 51.75 (+); mp 194°C (hexane-dichloromethane); HR EI MS *m/z* 286.0502, Calcd for $C_{15}H_{11}ClN_2O_2$ 286.05091.

***Methyl 3-(4-acetylphenyl)-5-chloroimidazo[1,5-a]pyridine-1-carboxylate* (7c)**



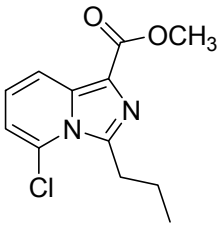

**7c**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J*=9.08, 0.83 Hz, 1 H), 7.89 - 8.11 (m, 2 H), 7.66 (s, 2 H), 7.11 (dd, *J*=9.08, 7.06 Hz, 1 H), 6.87 (dd, *J*=6.97, 0.92 Hz, 1 H), 3.99 (s, 3 H), 2.66 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 197.62, 163.39, 138.66, 137.73, 137.40, 136.17, 131.46 (+, 2C), 127.12 (+, 2C), 125.89, 124.68 (+), 122.28, 118.64 (+), 116.34 (+), 51.86 (+), 26.77 (+); mp 217°C (hexane-dichloromethane).

***Methyl 3-benzyl-5-chloroimidazo[1,5-a]pyridine-1-carboxylate*** **(7d)**



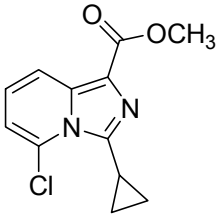
**7d**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J*=9.08, 1.01 Hz, 1 H), 7.13 - 7.34 (m, 3 H), 7.04 (d, *J*=6.97 Hz, 2 H), 6.96 (dd, *J*=9.17, 6.97 Hz, 1 H), 6.71 (dd, *J*=6.97, 1.10 Hz, 1 H), 4.88 (s, 2 H), 4.01 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.53, 139.47, 138.37, 138.16, 128.56 (+, 2C), 127.96 (+, 2C), 126.46 (+), 125.70, 124.22 (+), 121.03, 118.50 (+), 115.67 (+), 51.77 (+), 36.61 (-); mp 131°C (hexane-dichloromethane); HR EI MS *m/z* 300.0680, Calcd for $C_{16}H_{13}ClN_2O_2$ 300.06656.

***Methyl 5-chloro-3-propylimidazo[1,5-a]pyridine-1-carboxylate*** **(7e)**



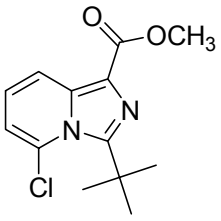
**7e**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J*=8.99 Hz, 1 H), 6.92 (dd, *J*=8.89, 7.06 Hz, 1 H), 6.75 (d, *J*=6.60 Hz, 1 H), 3.95 (s, 3 H), 3.40 (s, 2 H), 1.49 - 2.15 (m, 2 H), 1.01 (t, *J*=7.34 Hz, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.54, 142.18, 137.83, 125.59, 123.73 (+), 120.59, 118.58 (+, 2C), 115.55 (+), 51.65 (+, 2C), 32.91 (-), 23.66 (-), 13.82 (+); mp 113°C (hexane-dichloromethane); HR EI MS *m/z* 252.0658, Calcd for $C_{12}H_{13}ClN_2O_2$ 252.06656.

***Methyl 5-chloro-3-cyclopropylimidazo[1,5-a]pyridine-1-carboxylate*** **(7f)**



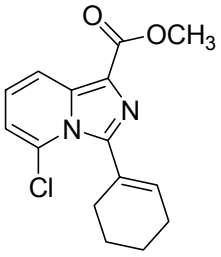
**7f**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J*=9.08, 1.01 Hz, 1H), 6.94 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.76 (dd, *J*=6.97, 0.92 Hz, 1 H), 3.94 (s, 3 H), 2.56 - 2.86 (m, 1 H), 1.16 - 1.38 (m, 2 H), 0.99 - 1.16 (m, 2 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.50, 142.97, 138.13, 126.34, 124.00 (+), 119.99, 118.48 (+), 115.41 (+), 51.65 (+), 11.62 (+), 8.95 (-, 2 C); mp 109-110°C (hexane-dichloromethane); HR EI MS *m/z* 250.0500, Calcd for $C_{12}H_{11}ClN_2O_2$ 250.05091.

***Methyl 3-tert-butyl-5-chloroimidazo[1,5-a]pyridine-1-carboxylate*** **(7g)**



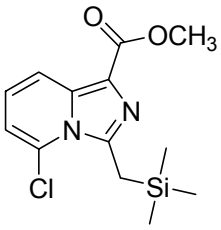
**7g**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J*=8.89, 1.38 Hz, 1 H), 6.96 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.86 (dd, *J*=6.79, 1.28 Hz, 1 H), 3.97 (s, 3 H), 1.72 (s, 9 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.74, 149.17, 139.69, 125.23, 123.51 (+), 119.64, 119.01 (+), 117.09 (+), 51.74 (+), 35.47, 32.26 (+, 3C). HR EI MS *m/z* 266.0828, Calcd for $C_{12}H_{11}ClN_2O_2$ 266.08221.

***Methyl 5-chloro-3-cyclohex-1-en-1-ylimidazo[1,5-a]pyridine-1-carboxylate* (7h)**



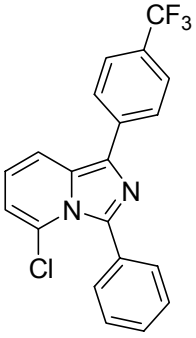
**7h**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J*=9.08, 1.01 Hz, 1 H), 7.00 (dd, *J*=9.08, 6.88 Hz, 1 H), 6.79 (dd, *J*=6.97, 1.10 Hz, 1 H), 5.91 - 6.16 (m, 1 H), 3.97 (s, 3 H), 2.31 - 2.60 (m, 2 H), 2.13 - 2.33 (m, 2 H), 1.63 - 1.90 (m, 4 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.62, 141.85, 137.12, 134.34 (+), 129.78, 126.00, 124.05 (+), 120.99, 118.31 (+), 115.51 (+), 51.62 (+), 30.74 (-), 25.43 (-), 22.33 (-), 21.40 (-); mp 188-189°C (hexane-dichloromethane); HR EI MS *m/z* 290.0827, Calcd for $C_{15}H_{15}ClN_2O_2$ 290.08221.

***Methyl 3-(trimethylsilyl)methyl-5-chloroimidazo[1,5-a]pyridine-1-carboxylate* (7i)**



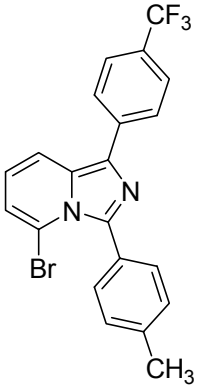
**7i:** $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J*=8.99, 1.10 Hz, 1 H), 6.85 (dd, *J*=9.17, 6.97 Hz, 1 H), 6.67 (dd, *J*=6.97, 1.10 Hz, 1 H), 3.94 (s, 3 H), 3.09 (s, 2 H), 0.06 (s, 9 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.70, 141.50, 137.48, 125.31, 123.10 (+), 120.61, 118.81 (+), 115.47 (+), 51.54 (+), 21.36 (-), -1.19 (+, 3C); mp 81°C.

***5-Chloro-3-phenyl-1-[4-(trifluoromethyl)phenyl]imidazo[1,5-a]pyridine* (7j)**



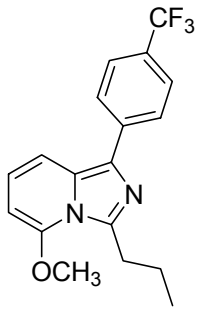
**7j**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J*=8.07 Hz, 2 H), 7.84 (d, *J*=8.80 Hz, 1 H), 7.71 (d, *J*=8.25 Hz, 2 H), 7.60 (s, 2 H), 7.39 - 7.54 (m, 3 H), 6.82 (dd, *J*=9.17, 6.79 Hz, 1 H), 6.69 (d, *J*=6.42 Hz, 1 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.83, 137.93, 132.37, 131.12 (+, 2C), 130.81, 130.43, 129.10 (+), 128.62 (q, $J_{FC}$ = 32.37 Hz), 127.31 (+, 2C), 127.12 (+, 2C), 125.67 (+, q, $J_{FC}$ = 2.77 Hz, 2C), 125.34, 124.42 (q, $J_{FC}$ = 271.88 Hz), 120.64 (+), 117.22 (+), 114.96 (+); mp 130-131°C (hexane-dichloromethane); HR EI MS *m/z* 372.0630, Calcd for $C_{20}H_{12}ClF_3N_3$ 372.06411.

***5-Bromo-3-(4-methylphenyl)-1-[4-(trifluoromethyl)phenyl]imidazo[1,5-a]pyridine* (7k)**

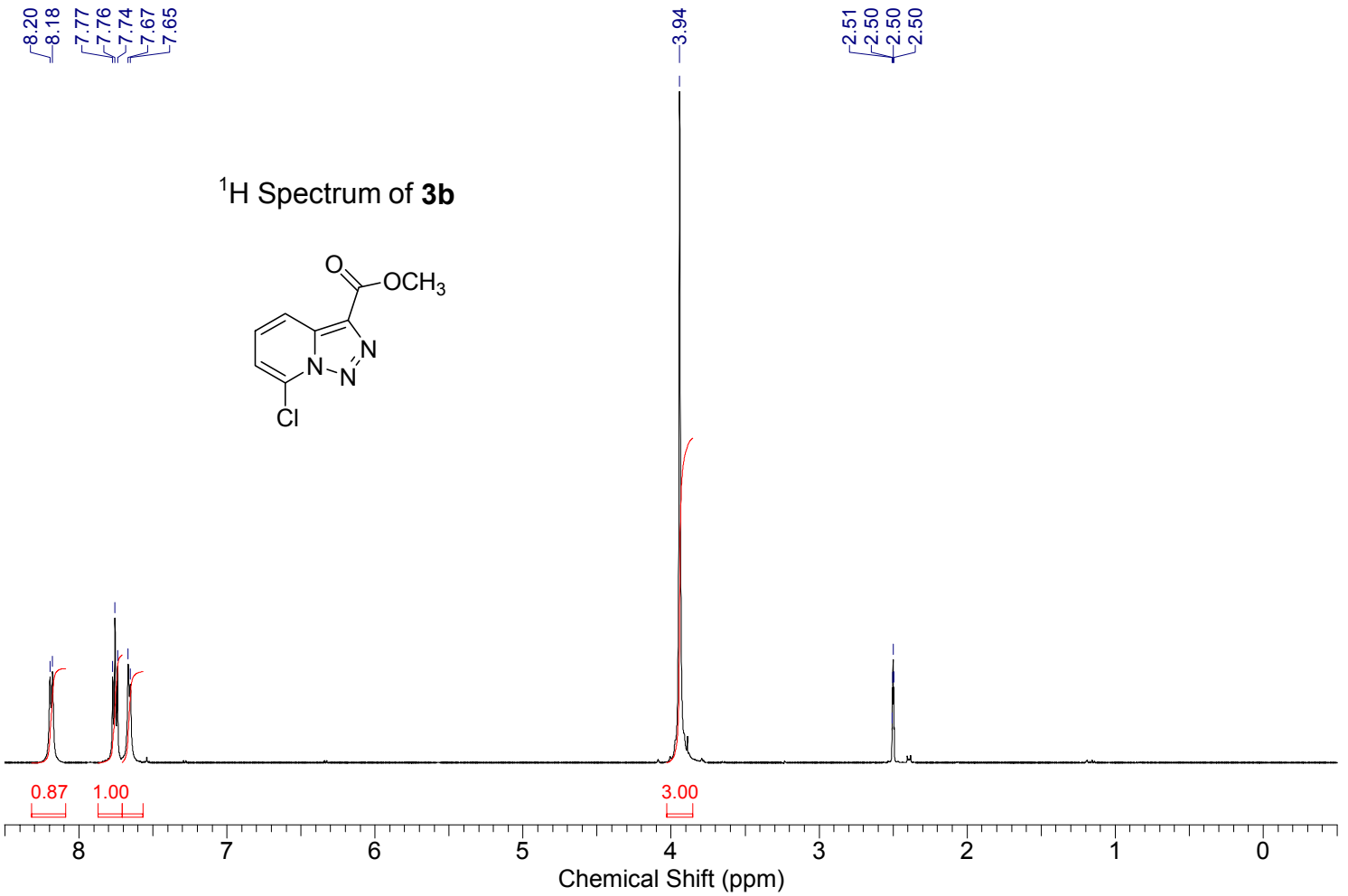


**7k**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J*=8.07 Hz, 2 H), 7.87 (dd, *J*=9.17, 0.73 Hz, 1 H), 7.70 (d, *J*=8.25 Hz, 2 H), 7.47 (d, *J*=8.07 Hz, 2 H), 7.26 (s, 2 H), 6.89 (dd, *J*=6.69, 0.64 Hz, 1 H), 6.71 (dd, *J*=9.17, 6.79 Hz, 1 H), 2.45 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 140.97, 139.45, 138.12 (+, 2C), 131.46 (+, 2C), 130.53, 130.42, 129.28, 128.66 (q, $J_{FC}$ = 32.37 Hz), 128.13, 127.25 (+, 2C), 125.76 (+, q, $J_{FC}$ = 2.77 Hz, 2 C), 124.51 (q, $J_{FC}$ = 271.88 Hz), 120.70 (+), 120.00 (+), 117.90 (+), 112.55, 21.66 (+); mp 158°C (hexane-dichloromethane); HR EI MS *m/z* 430.0282, Calcd for $C_{21}H_{14}BrF_3N_2$ 430.02925.

***5-Methoxy-3-propyl-1-[4-(trifluoromethyl)phenyl]imidazo[1,5-a]pyridine* (7l)**

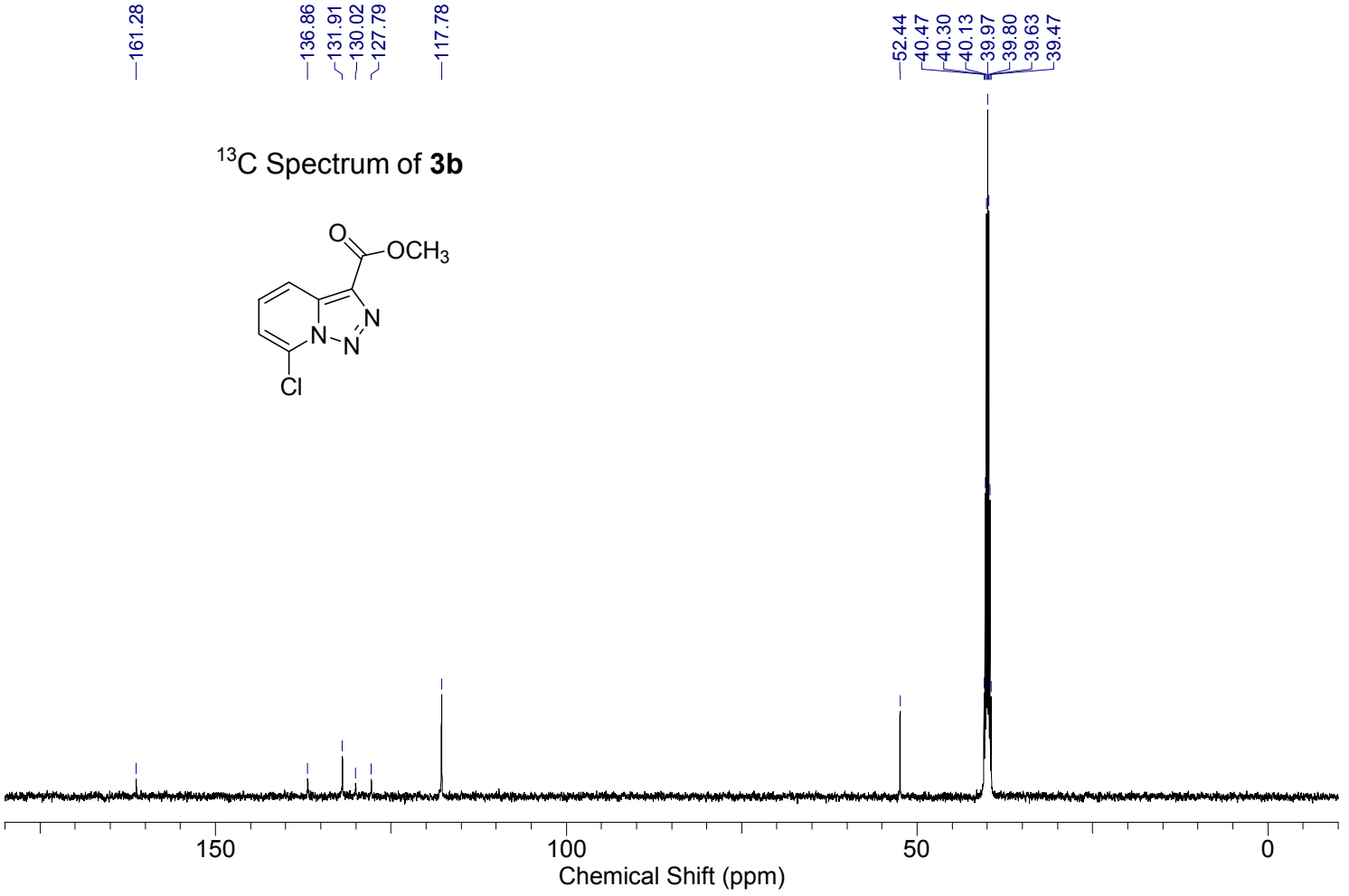



**7l**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.83 - 8.10 (m, 2 H), 7.55 - 7.76 (m, 2 H), 7.35 (dd, *J*=9.08, 0.64 Hz, 1 H), 6.75 (dd, *J*=9.17, 7.15 Hz, 1 H), 5.73 (d, *J*=6.97 Hz, 1 H), 4.02 (s, 3 H), 3.12 - 3.45 (m, 2 H), 1.71 - 1.98 (m, 2 H), 1.04 (t, *J*=7.43 Hz, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 150.07, 140.63, 138.97, 130.06, 127.63, 127.35 (q, $J_{FC}$ = 32.37 Hz), 126.25 (+, 2C), 125.64, 125.46 (+, q, $J_{FC}$ = 2.77 Hz, 2C), 124.56 (q, $J_{FC}$ = 271.88 Hz), 121.75 (+), 110.44 (+), 87.31 (+), 56.13 (+), 33.02 (-), 23.35 (-), 14.01 (+); mp 75-76°C.

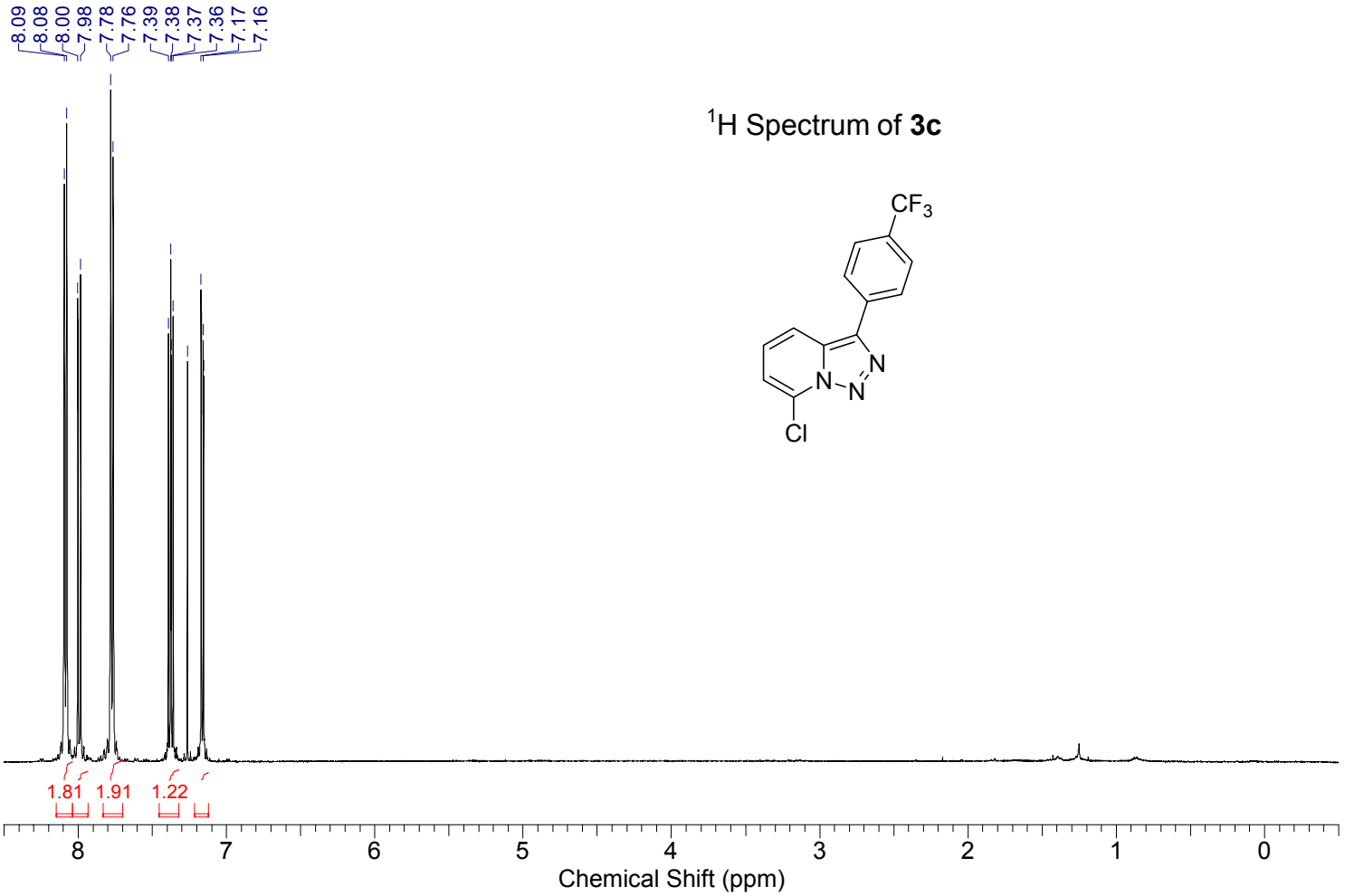



$^{1}$H Spectrum of **3b**



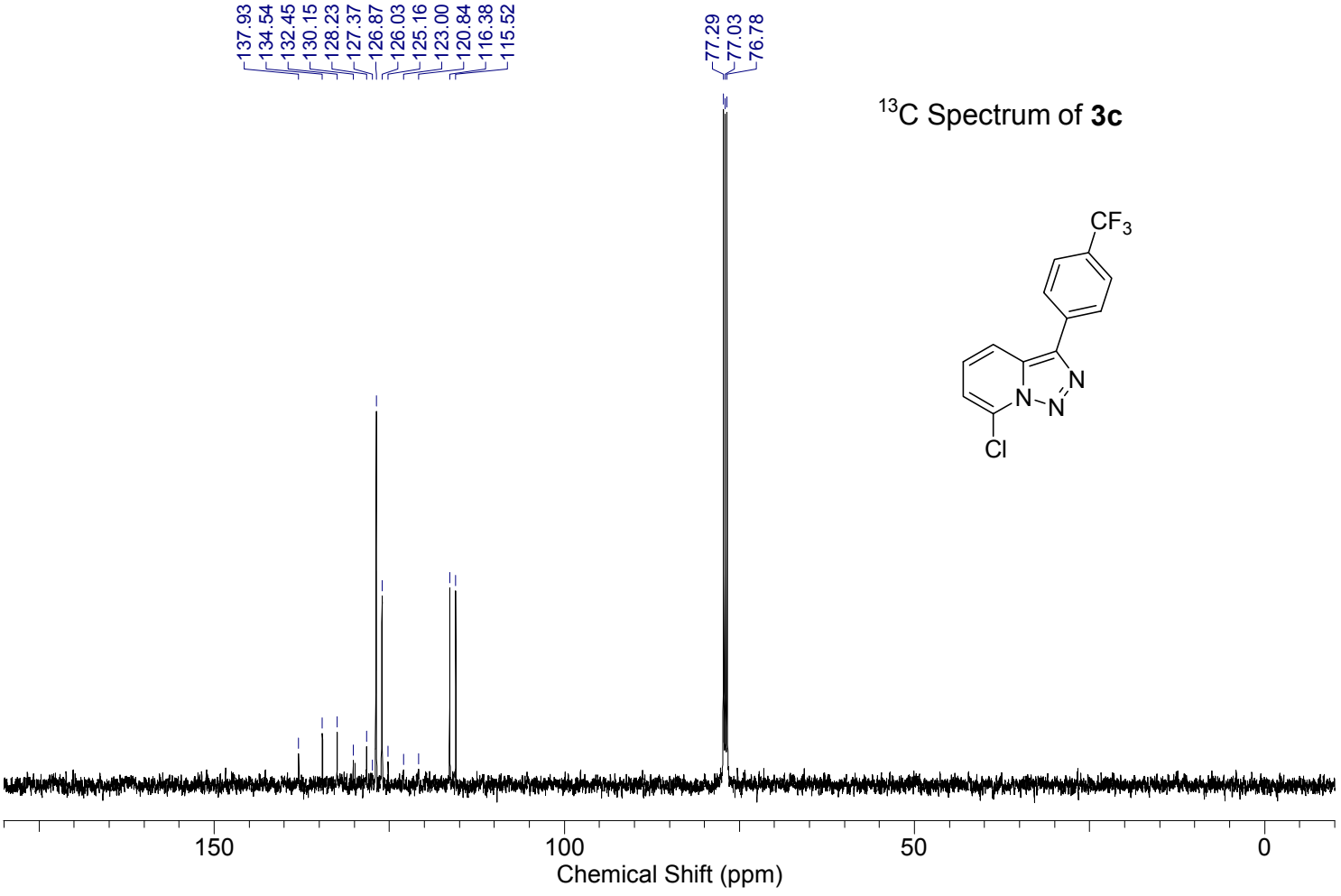




$^{13}$C Spectrum of **3b**

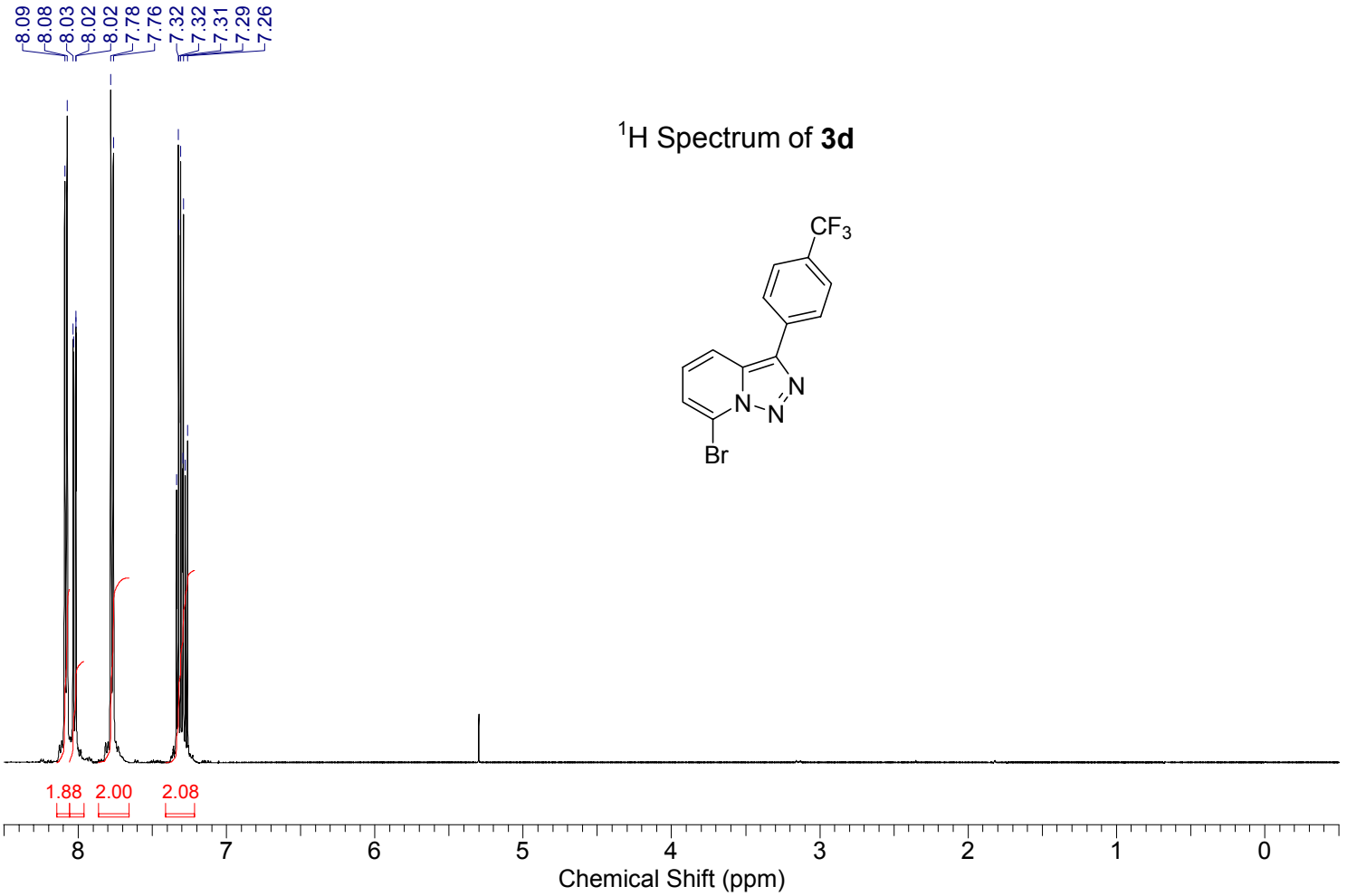



$^{1}$H Spectrum of **3c**



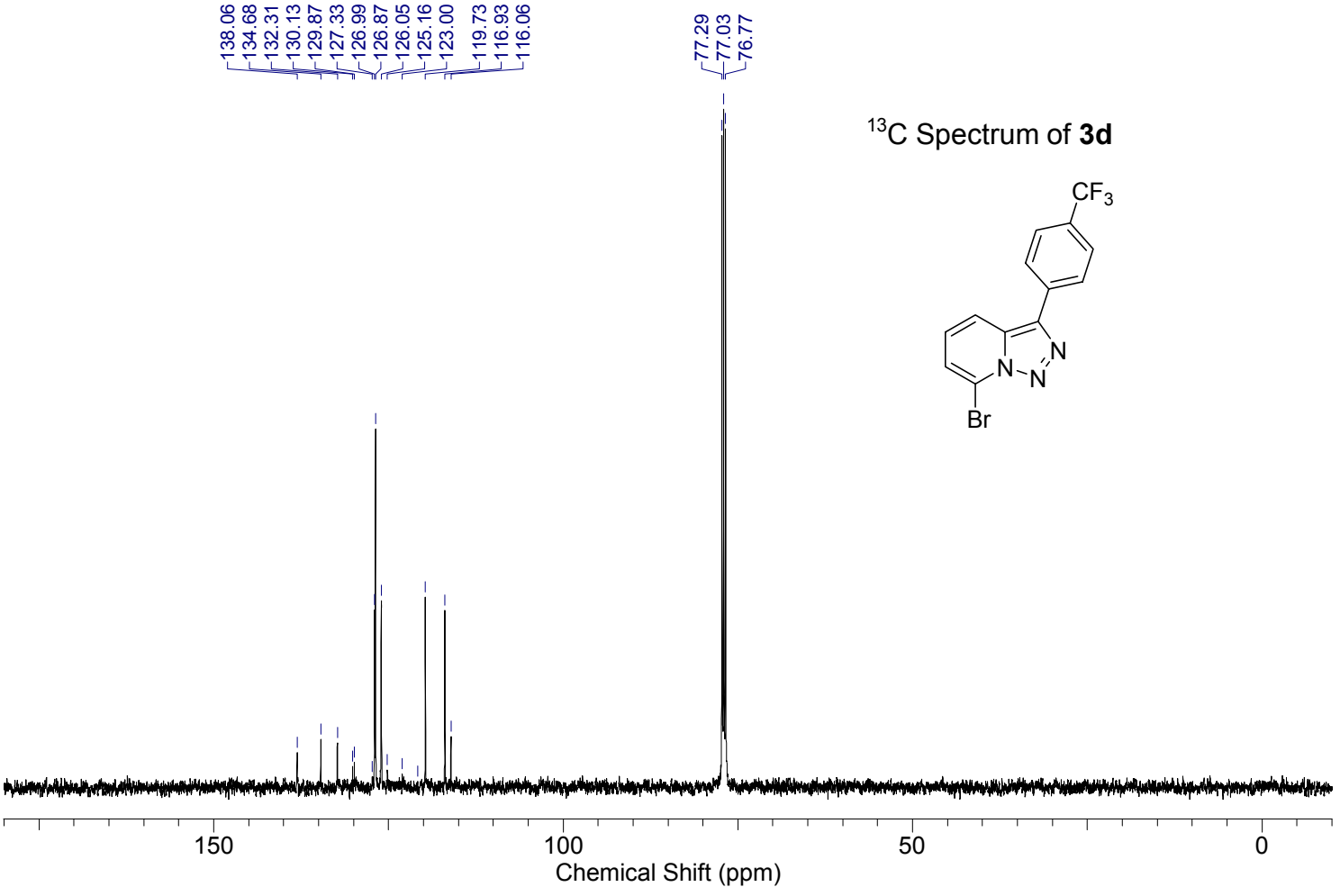




$^{13}$C Spectrum of **3c**

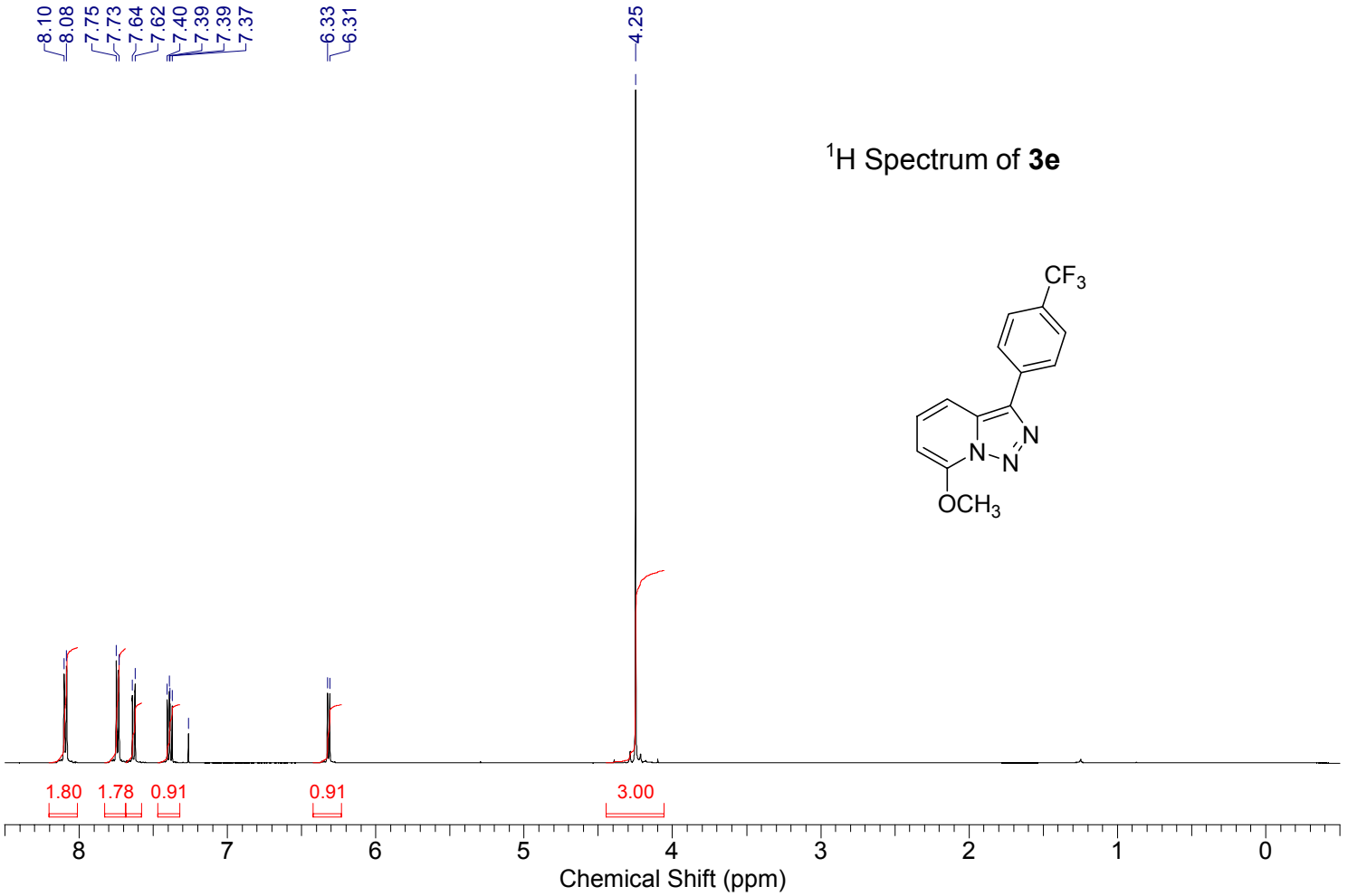


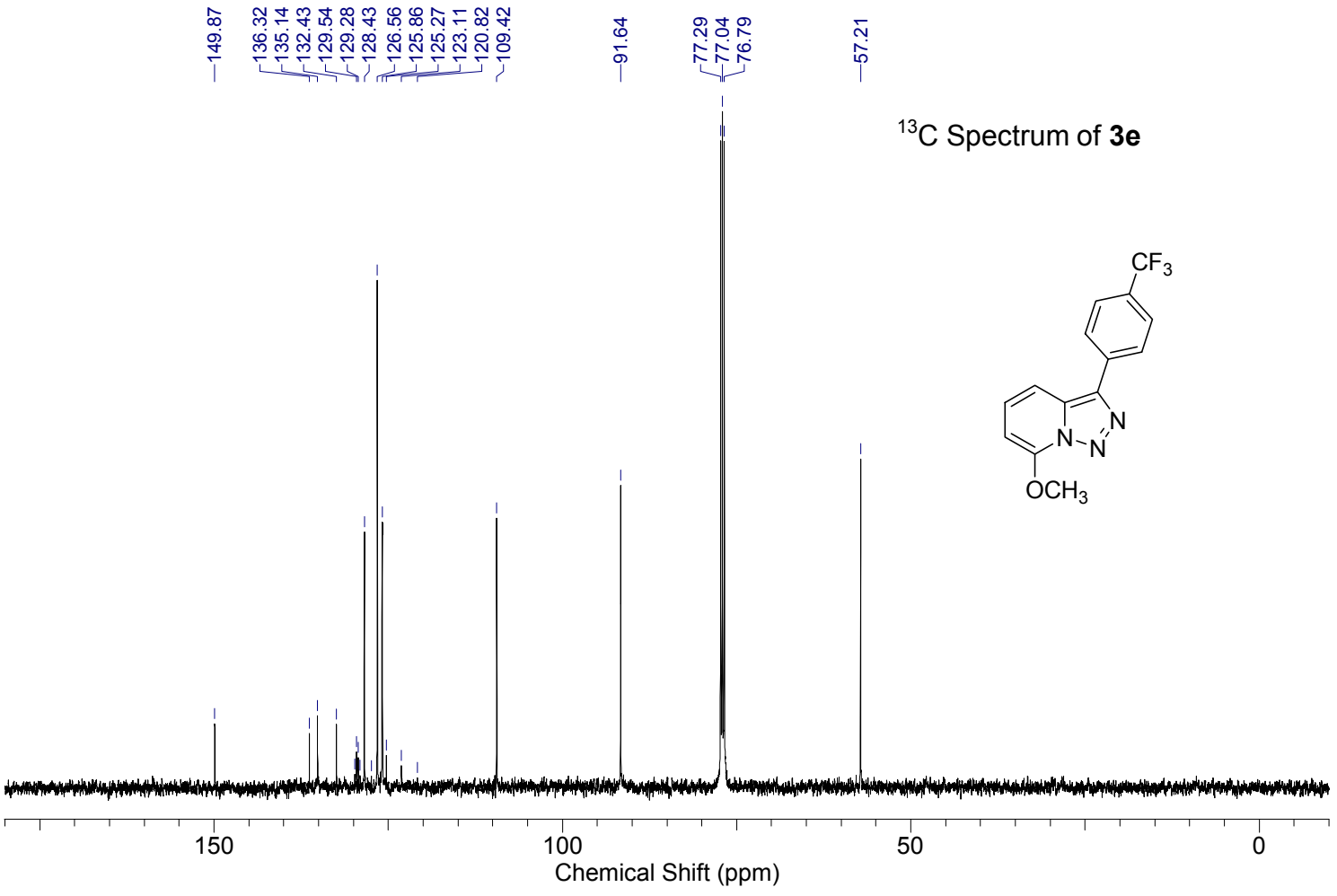

$^{1}$H Spectrum of **3d**

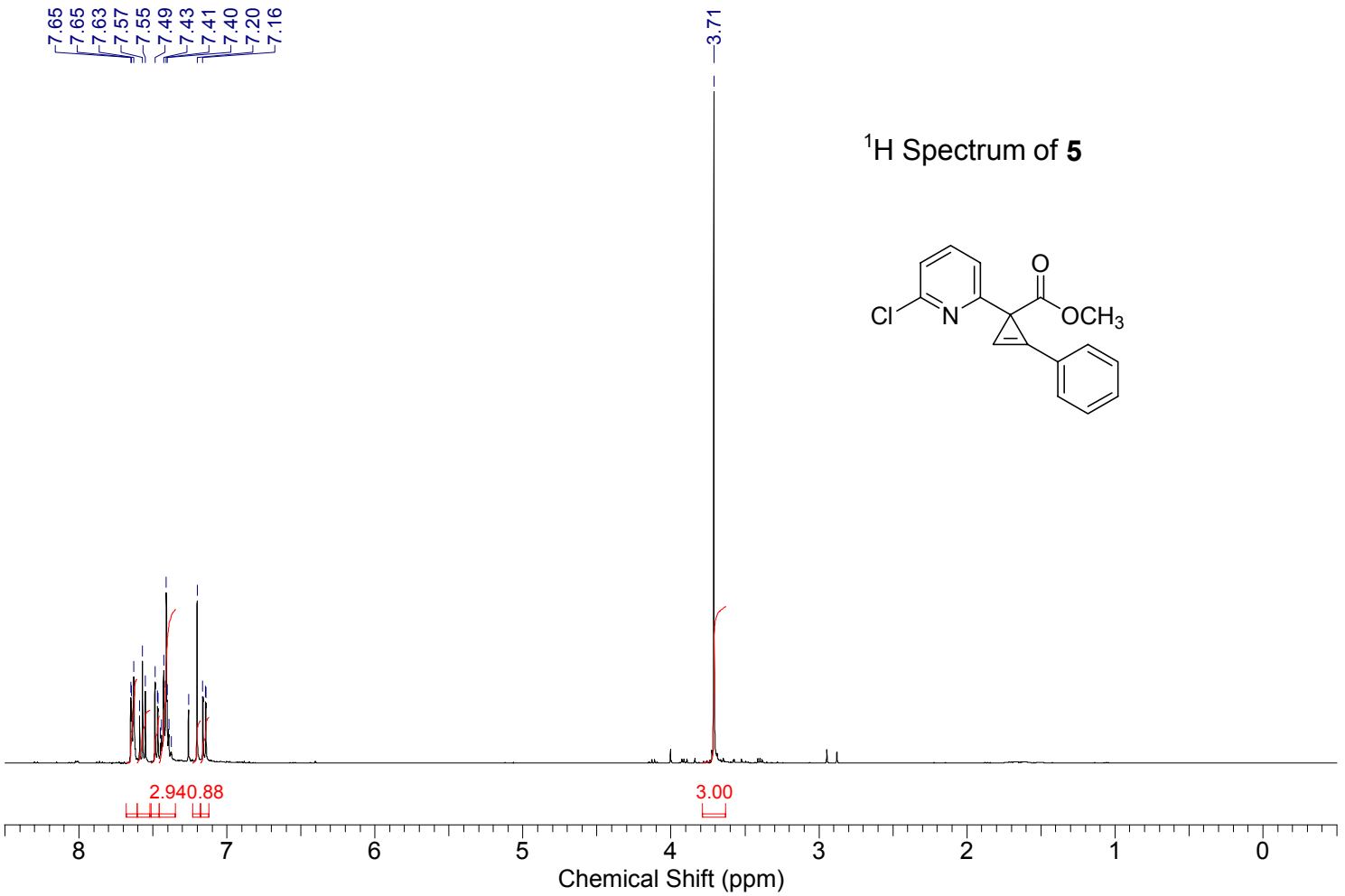



$^{13}$C Spectrum of **3d**

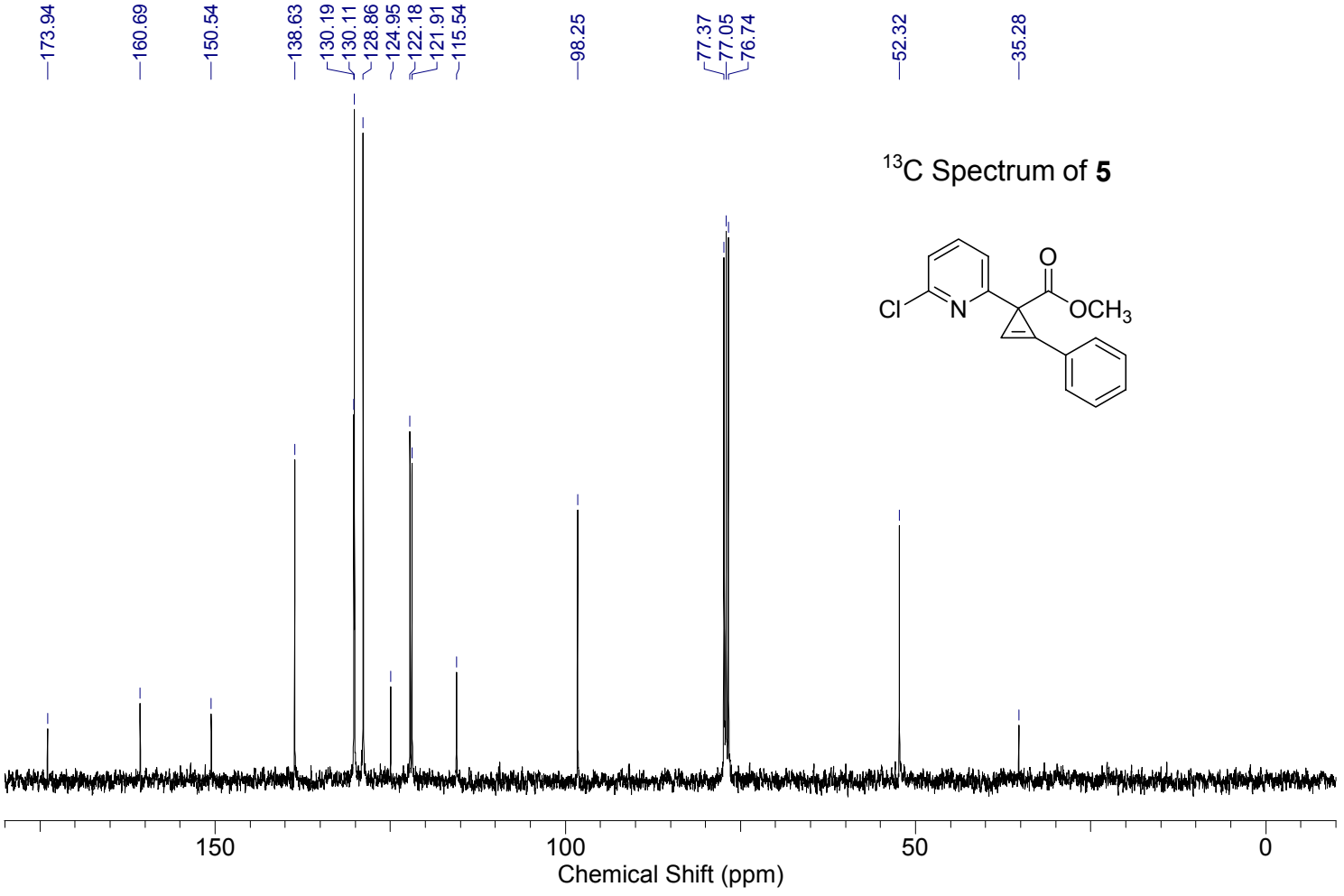

8.10
8.08
7.75
7.73
7.64
7.62
7.40
7.39
7.39
7.37
6.33
6.31
4.25
1H Spectrum of 3e
CF3
N
N
N
OCH3
1.80
1.78
0.91
0.91
3.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


149.87
136.32
135.14
132.43
129.54
129.28
128.43
126.56
125.86
125.27
123.11
120.82
109.42
91.64
77.29
77.04
76.79
57.21
13C Spectrum of 3e
CF3
N
N
N
OCH3
150
100
50
0
Chemical Shift (ppm)

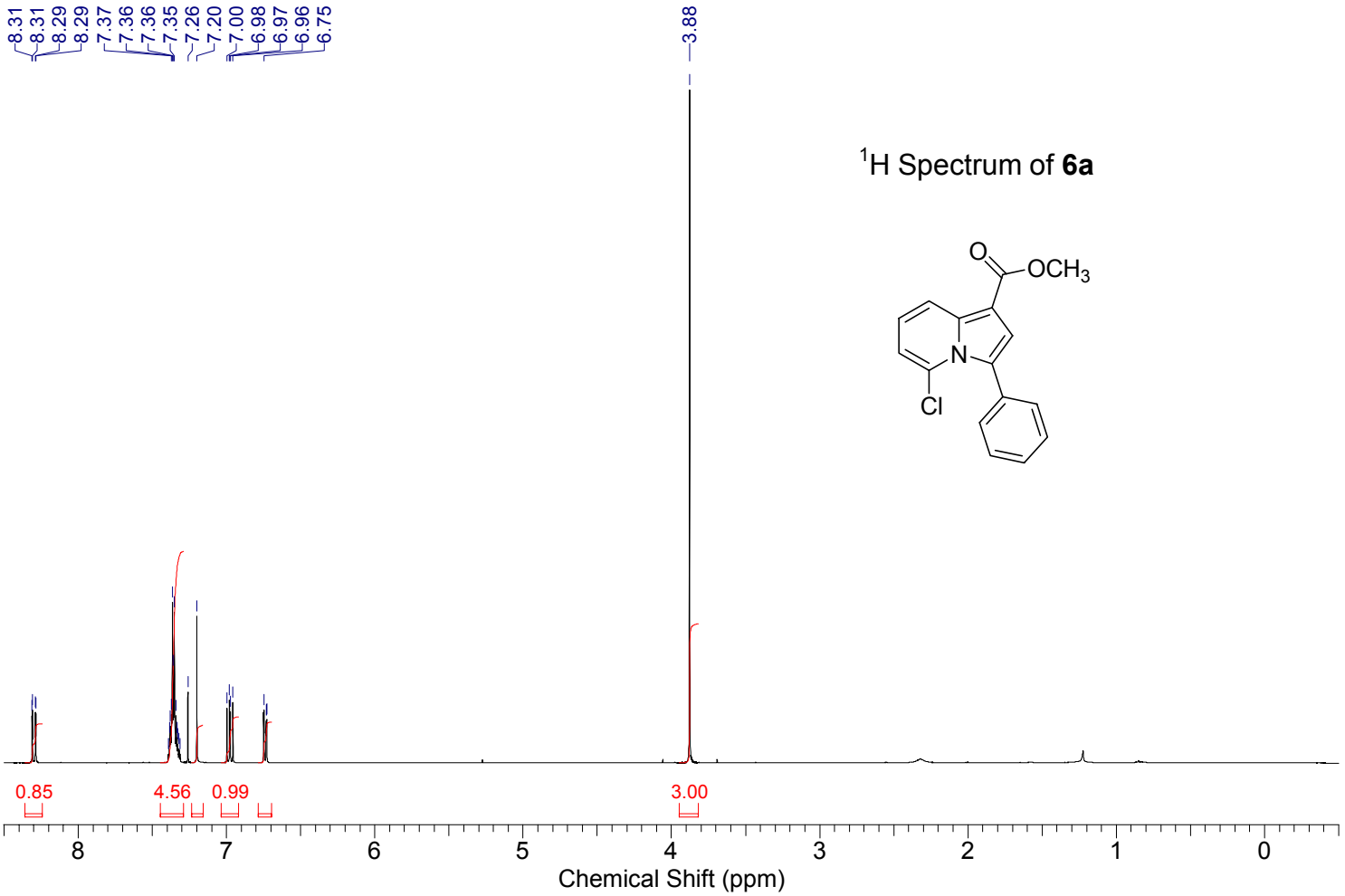



$^{1}$H Spectrum of **5**



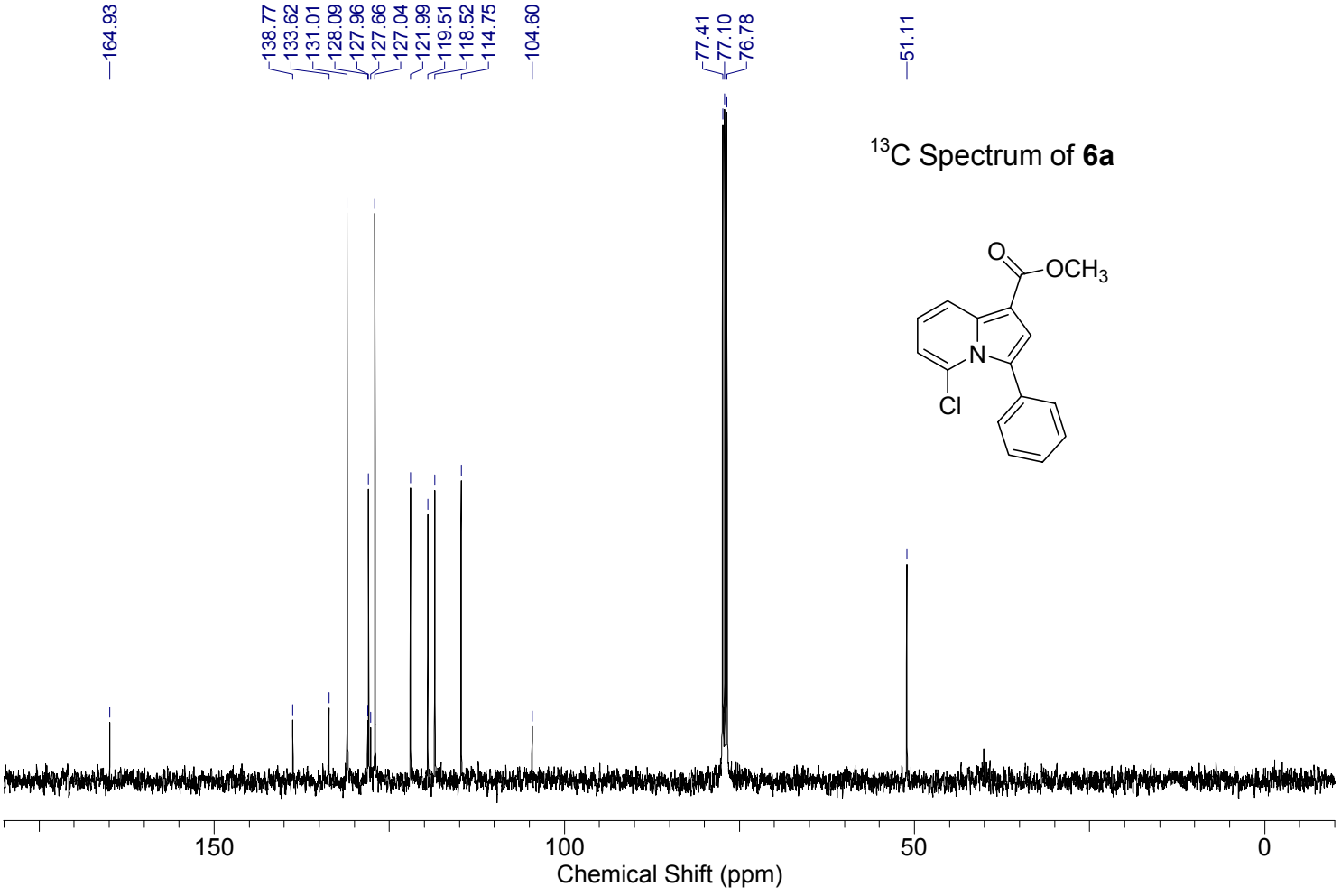




$^{13}$C Spectrum of **5**

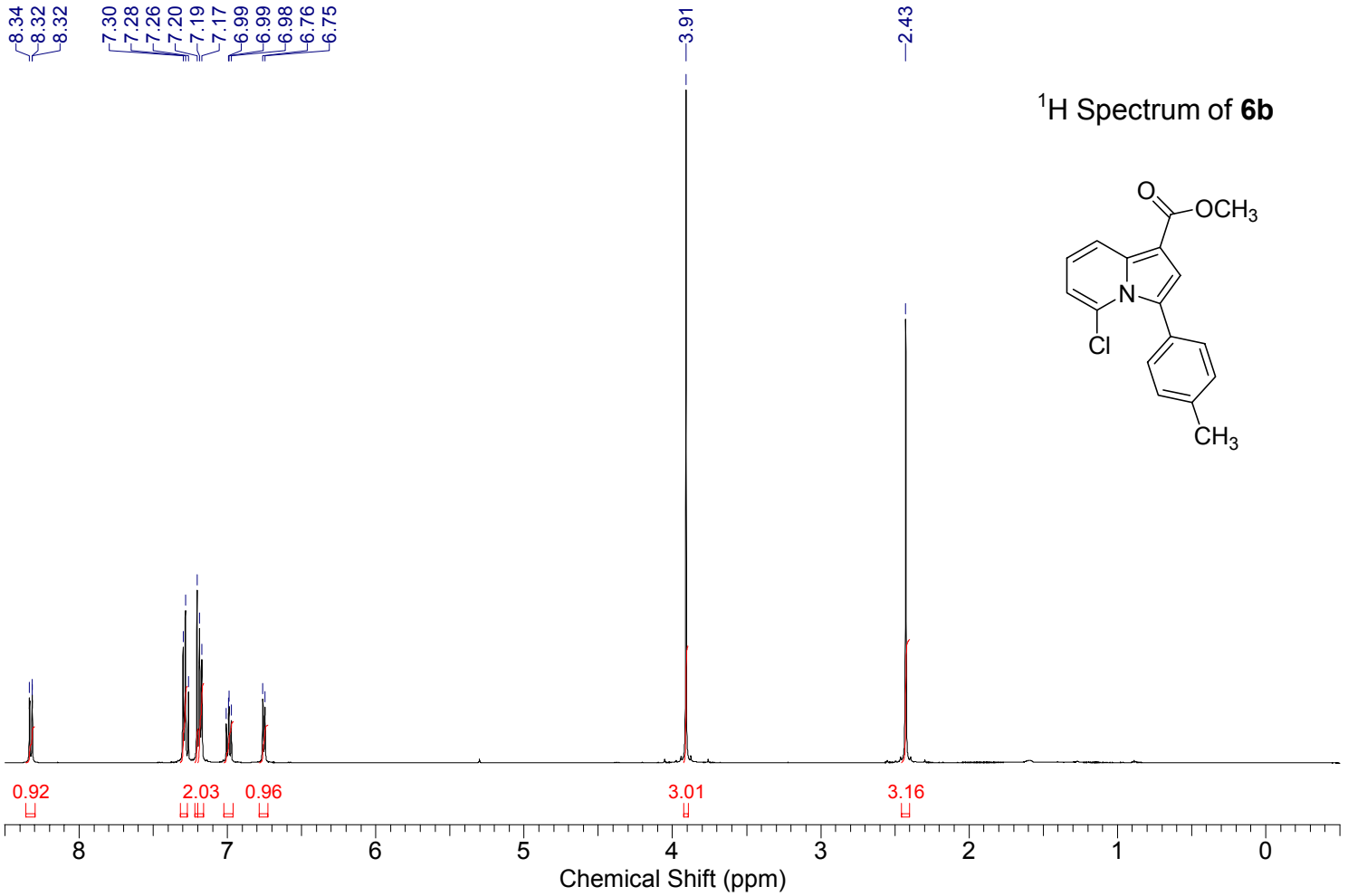



$^{1}$H Spectrum of **6a**



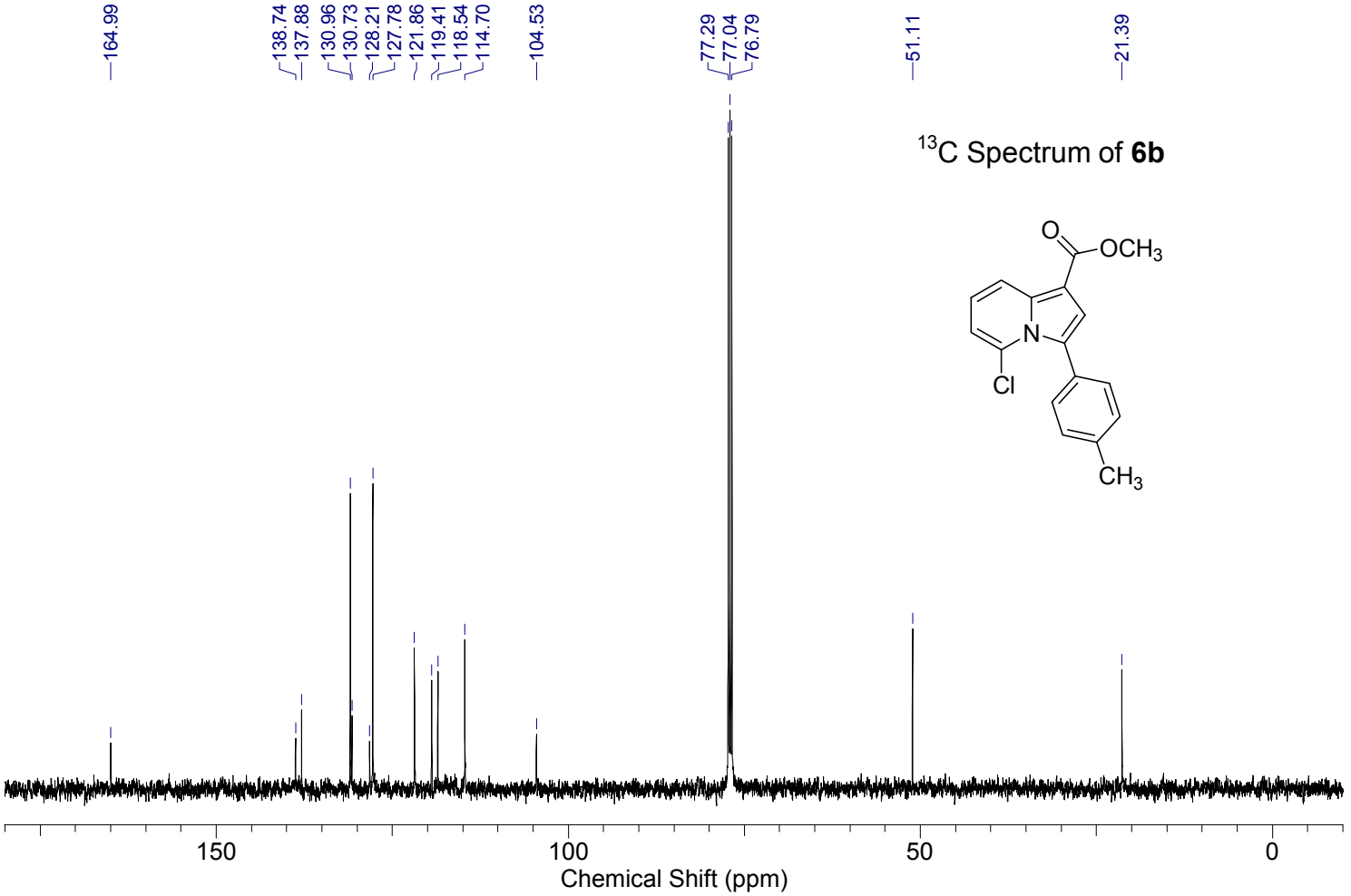




$^{13}$C Spectrum of **6a**

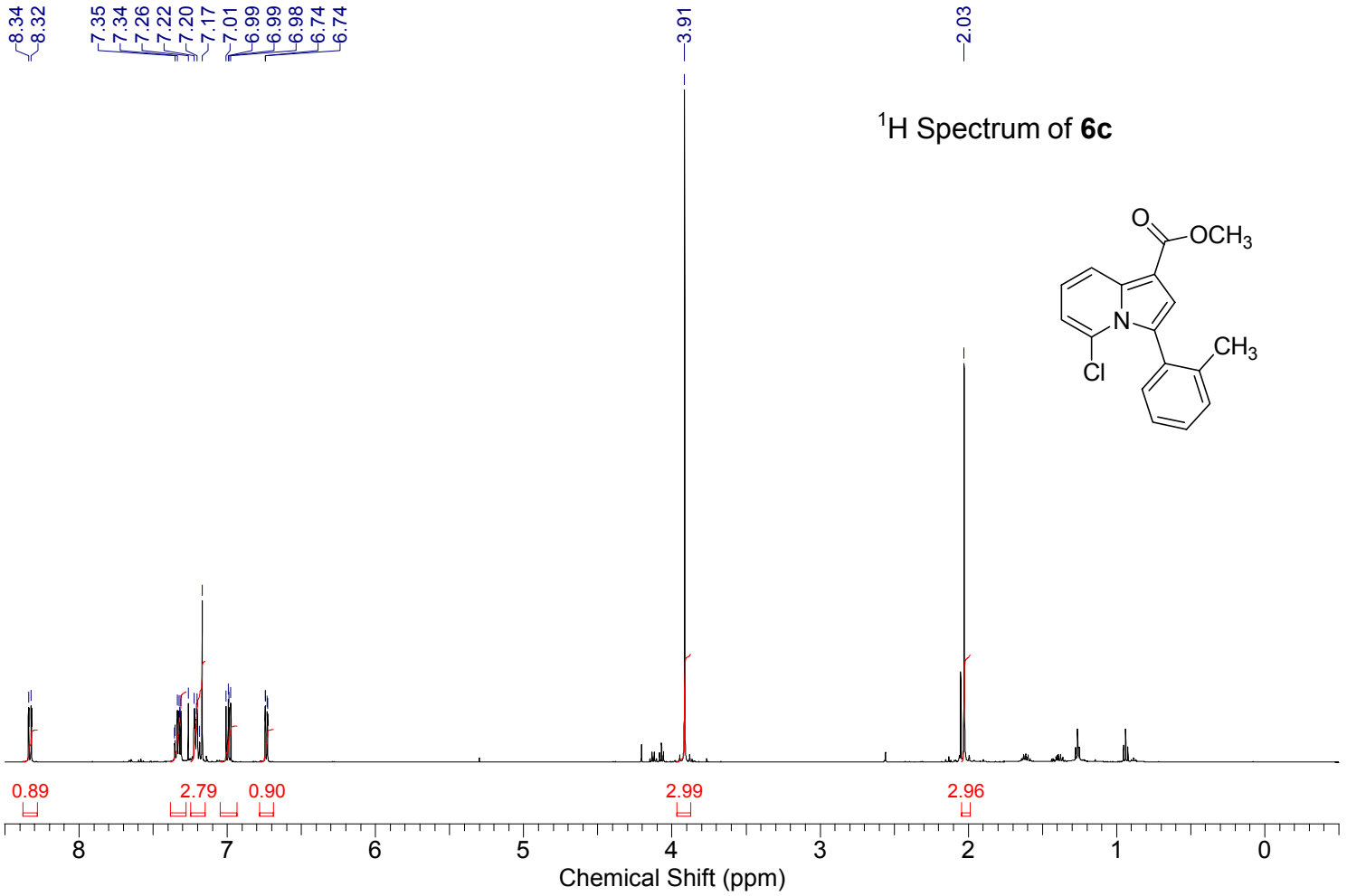



$^{1}$H Spectrum of **6b**



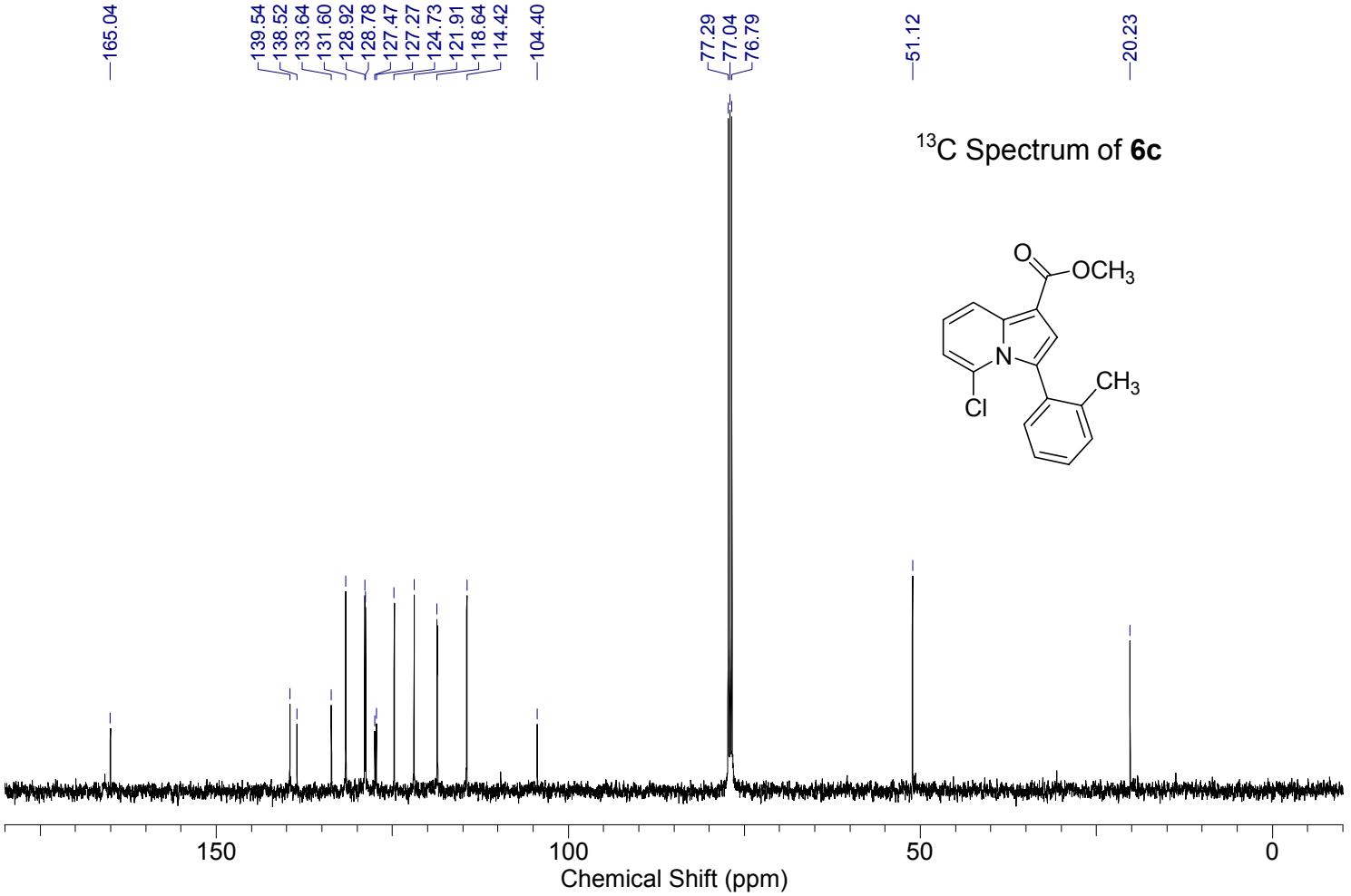




$^{13}$C Spectrum of **6b**

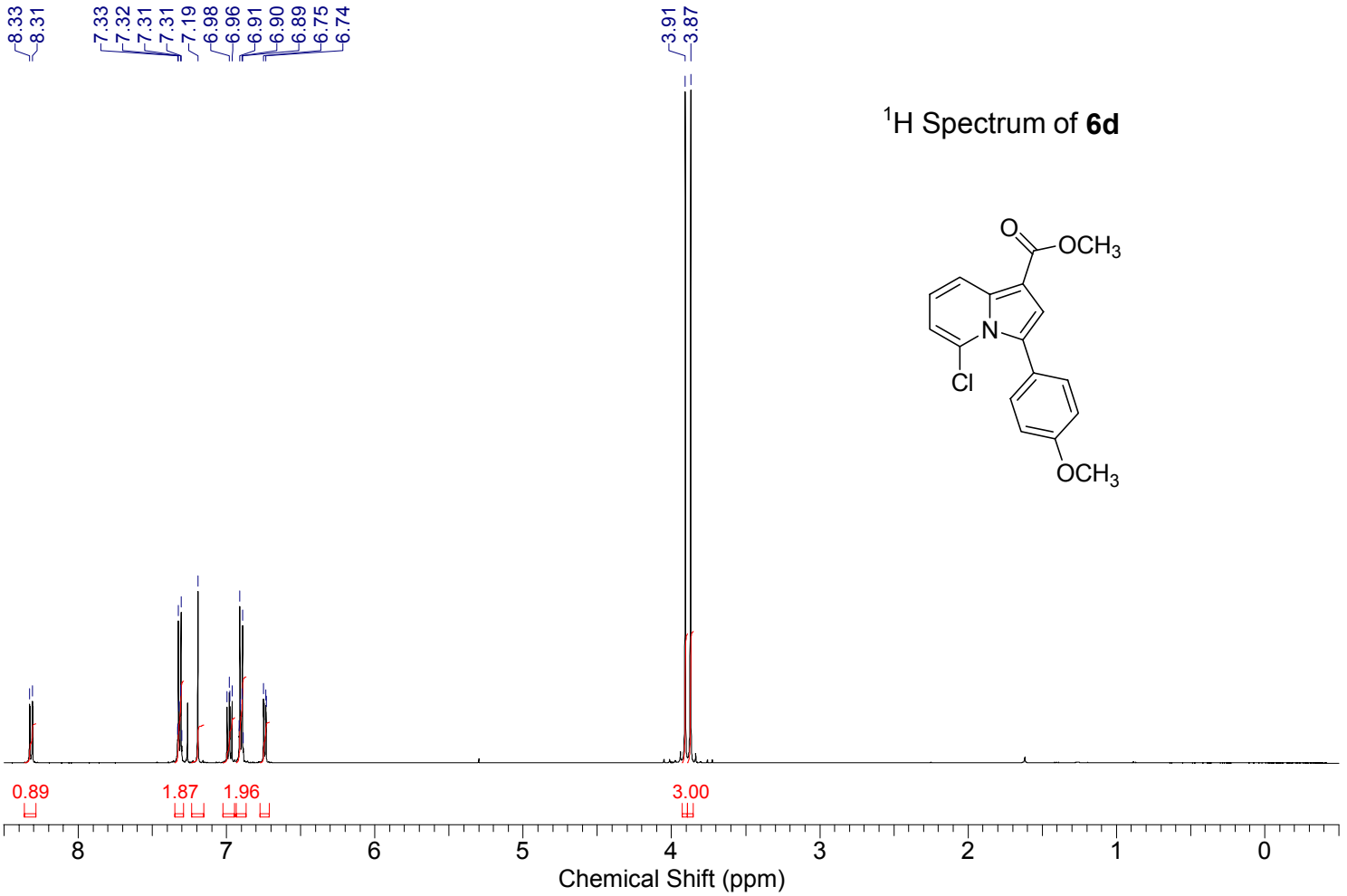



$^{1}$H Spectrum of **6c**



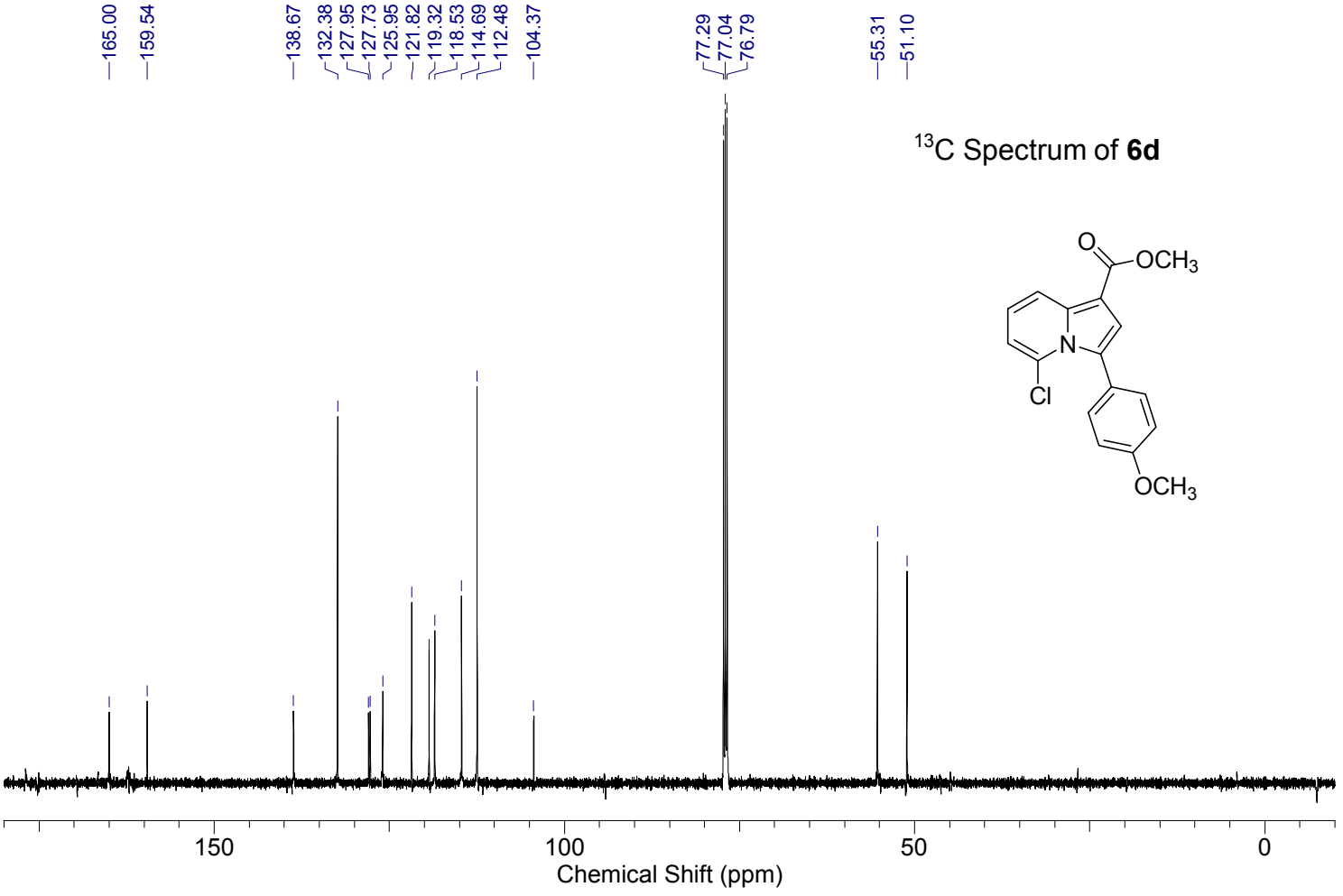




$^{13}$C Spectrum of **6c**

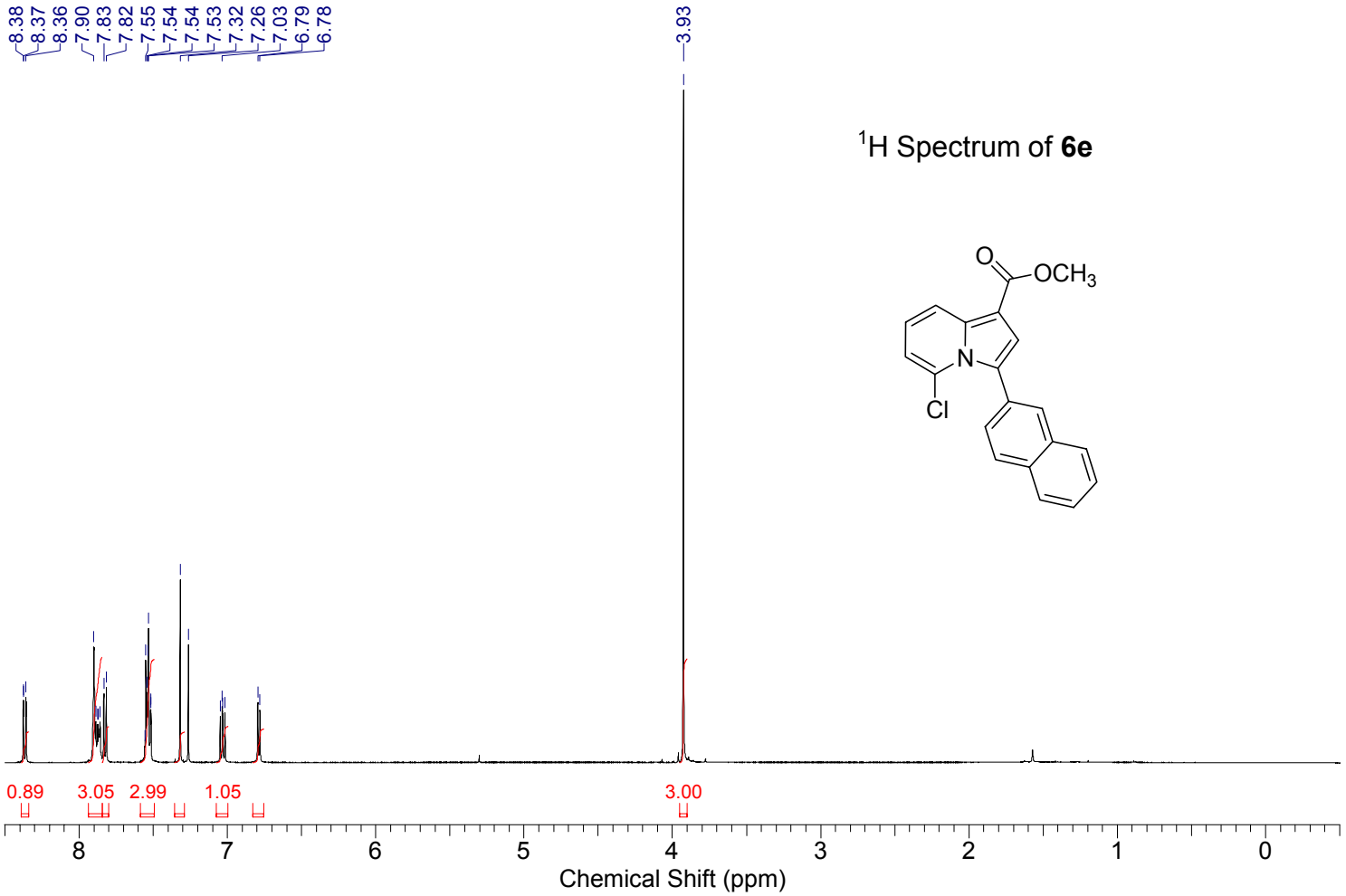



$^{1}$H Spectrum of **6d**



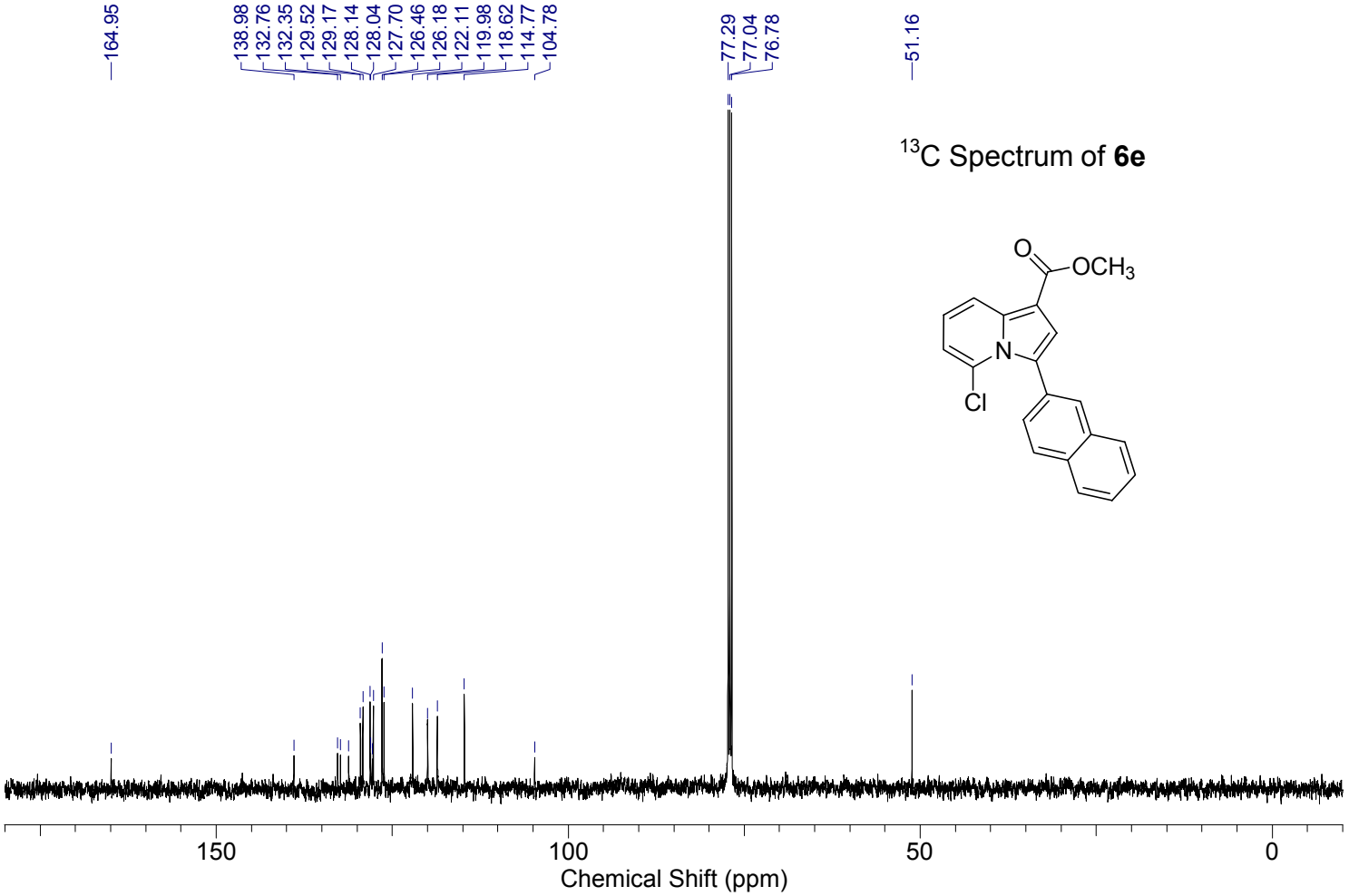




$^{13}$C Spectrum of **6d**

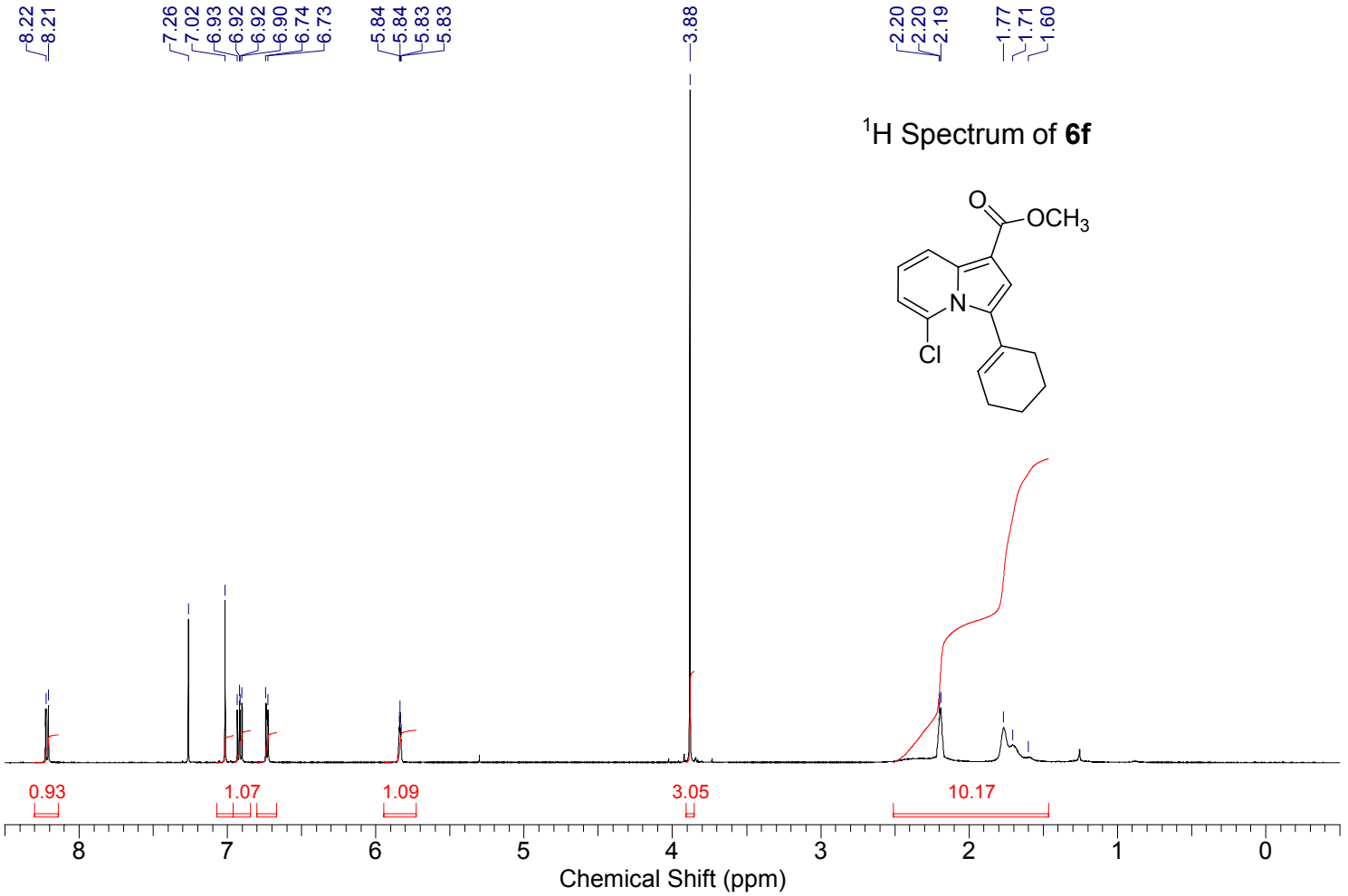


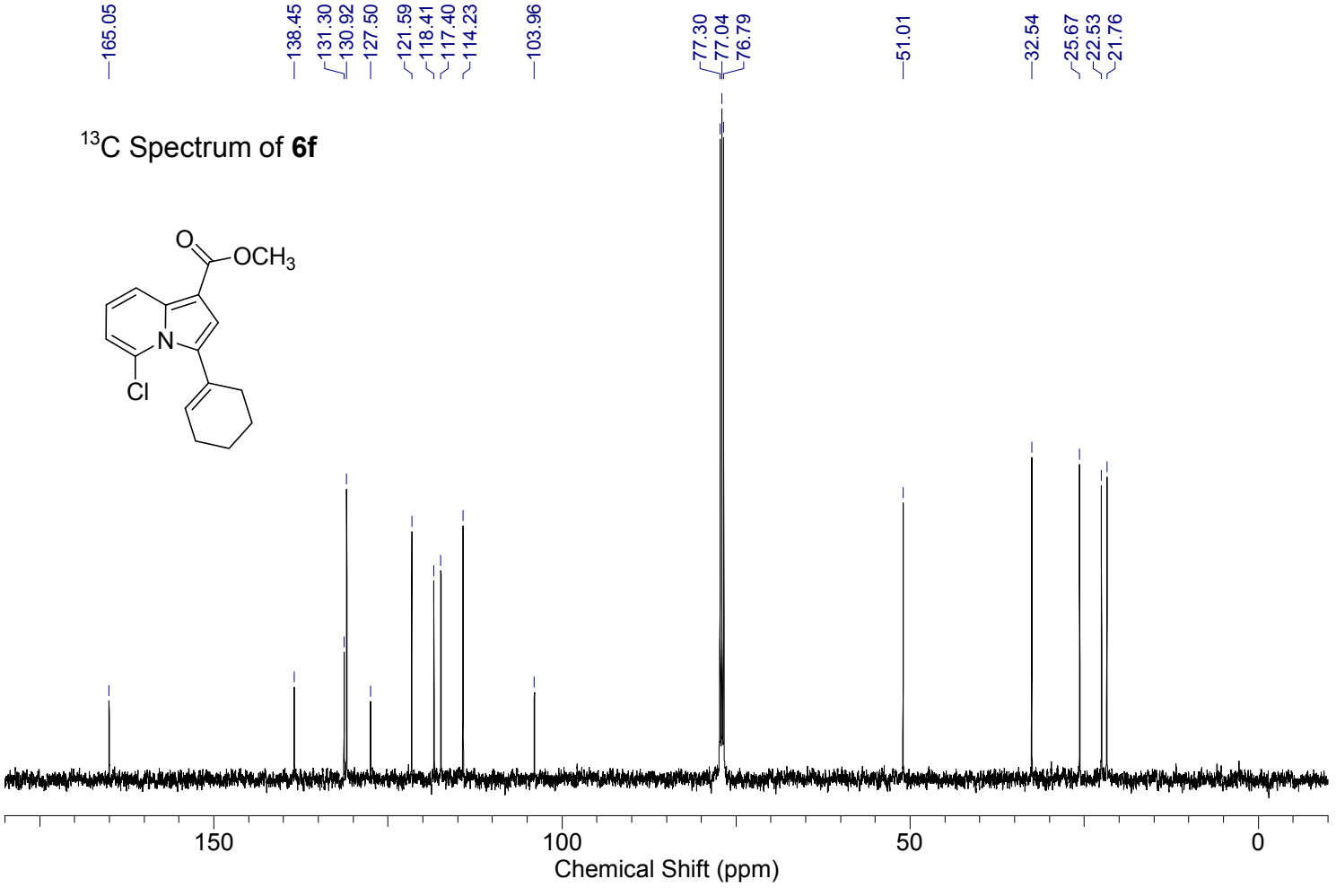

$^{1}$H Spectrum of **6e**

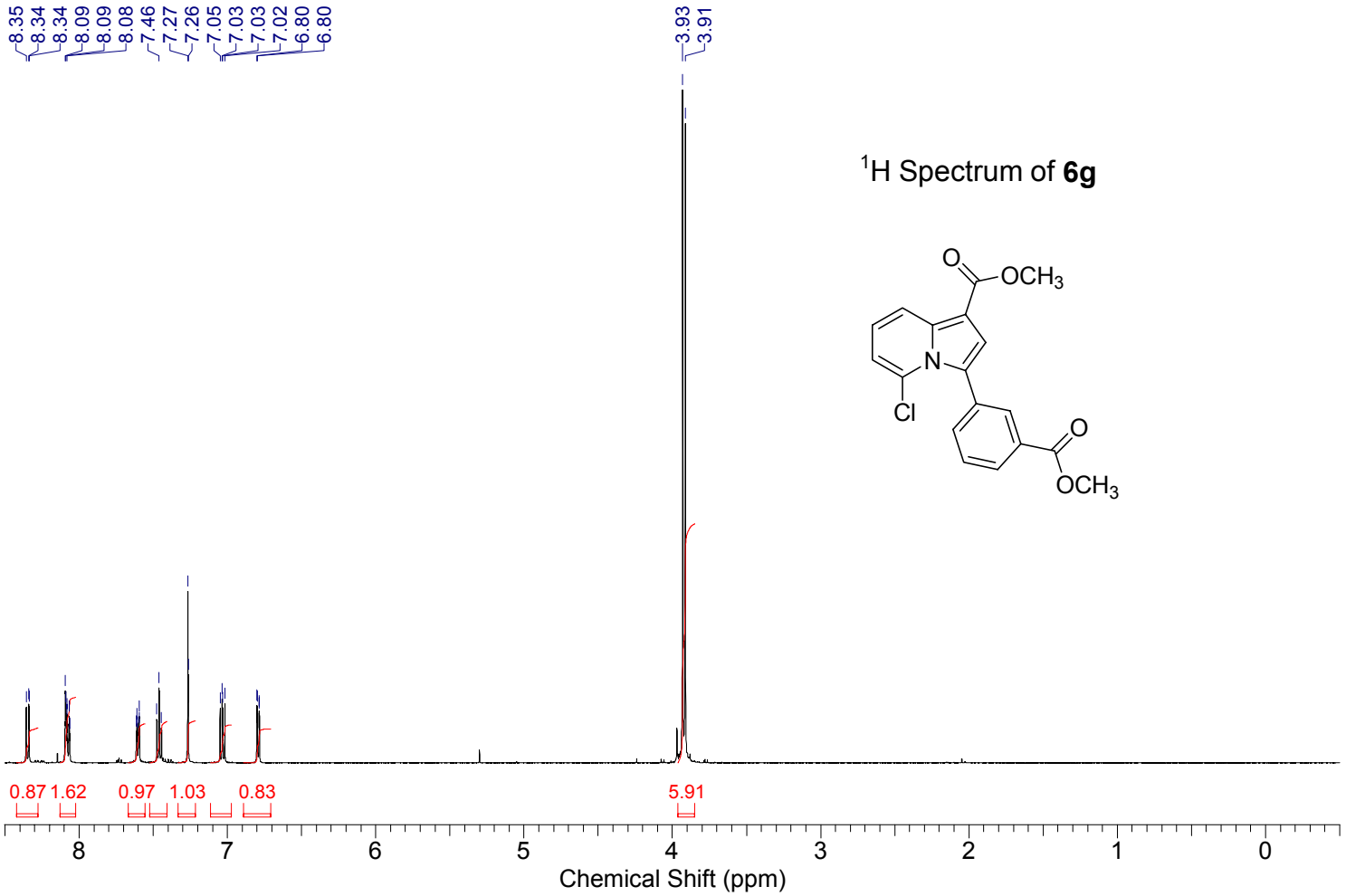



$^{13}$C Spectrum of **6e**

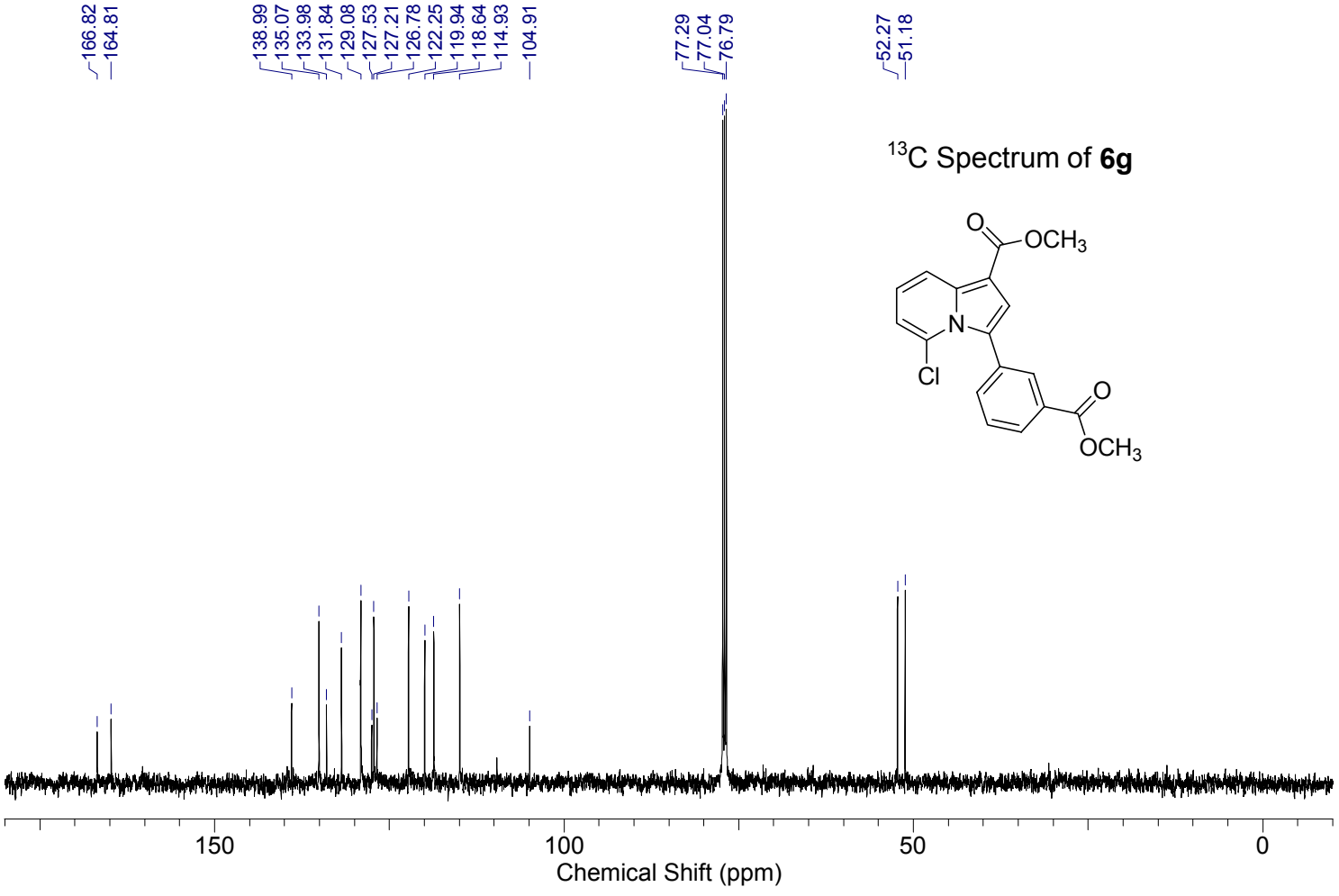

8.22
8.21
7.26
7.02
6.93
6.92
6.92
6.90
6.74
6.73
5.84
5.84
5.83
5.83
3.88
2.20
2.20
2.19
1.77
1.71
1.60
$^{1}$H Spectrum of **6f**
O
OCH$_3$
N
Cl
0.93
1.07
1.09
3.05
10.17
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


165.05
138.45
131.30
130.92
127.50
121.59
118.41
117.40
114.23
103.96
77.30
77.04
76.79
51.01
32.54
25.67
22.53
21.76
$^{13}$C Spectrum of **6f**
O
OCH$_3$
N
Cl
150
100
50
0
Chemical Shift (ppm)

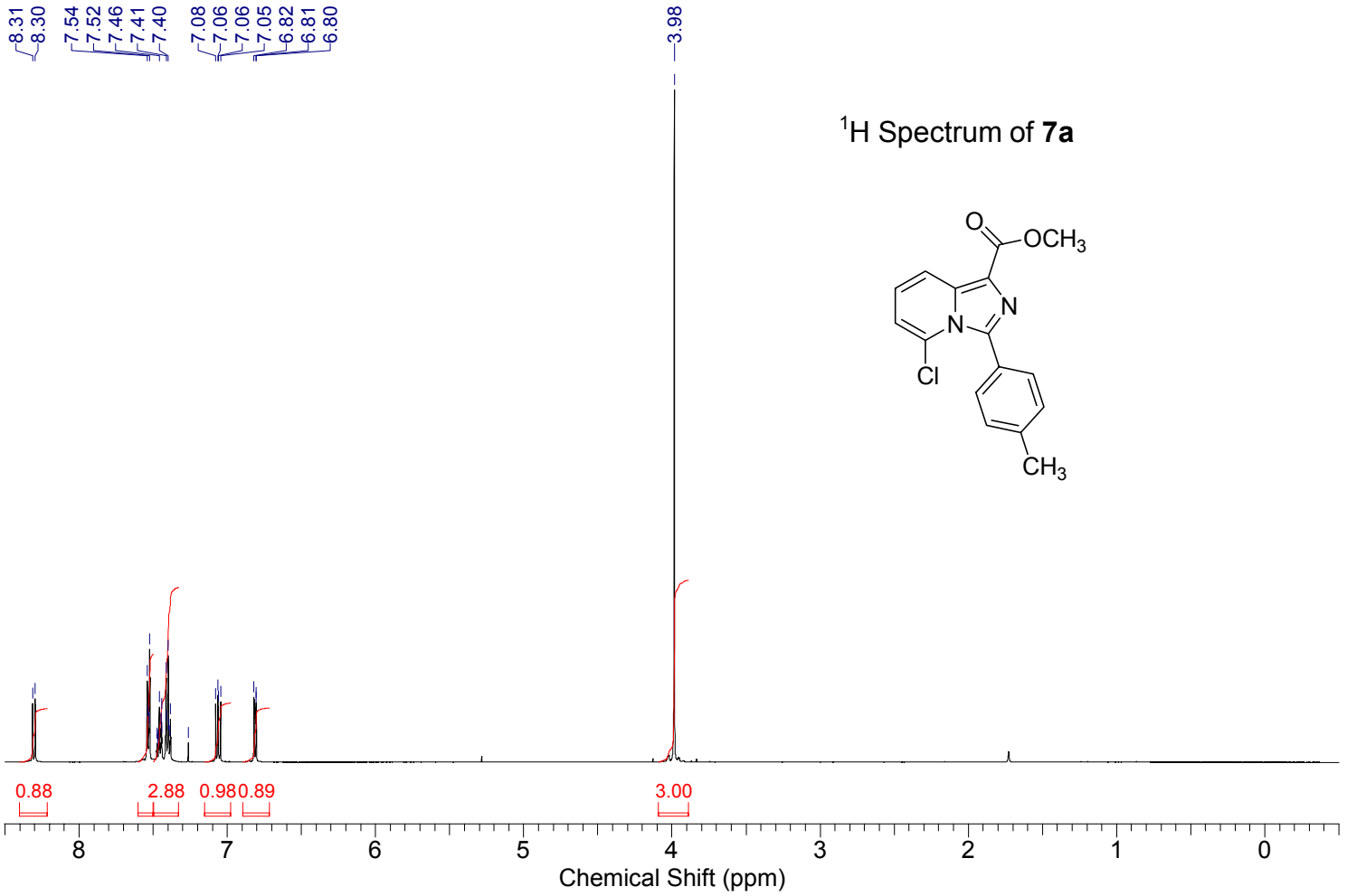



$^{1}$H Spectrum of **6g**



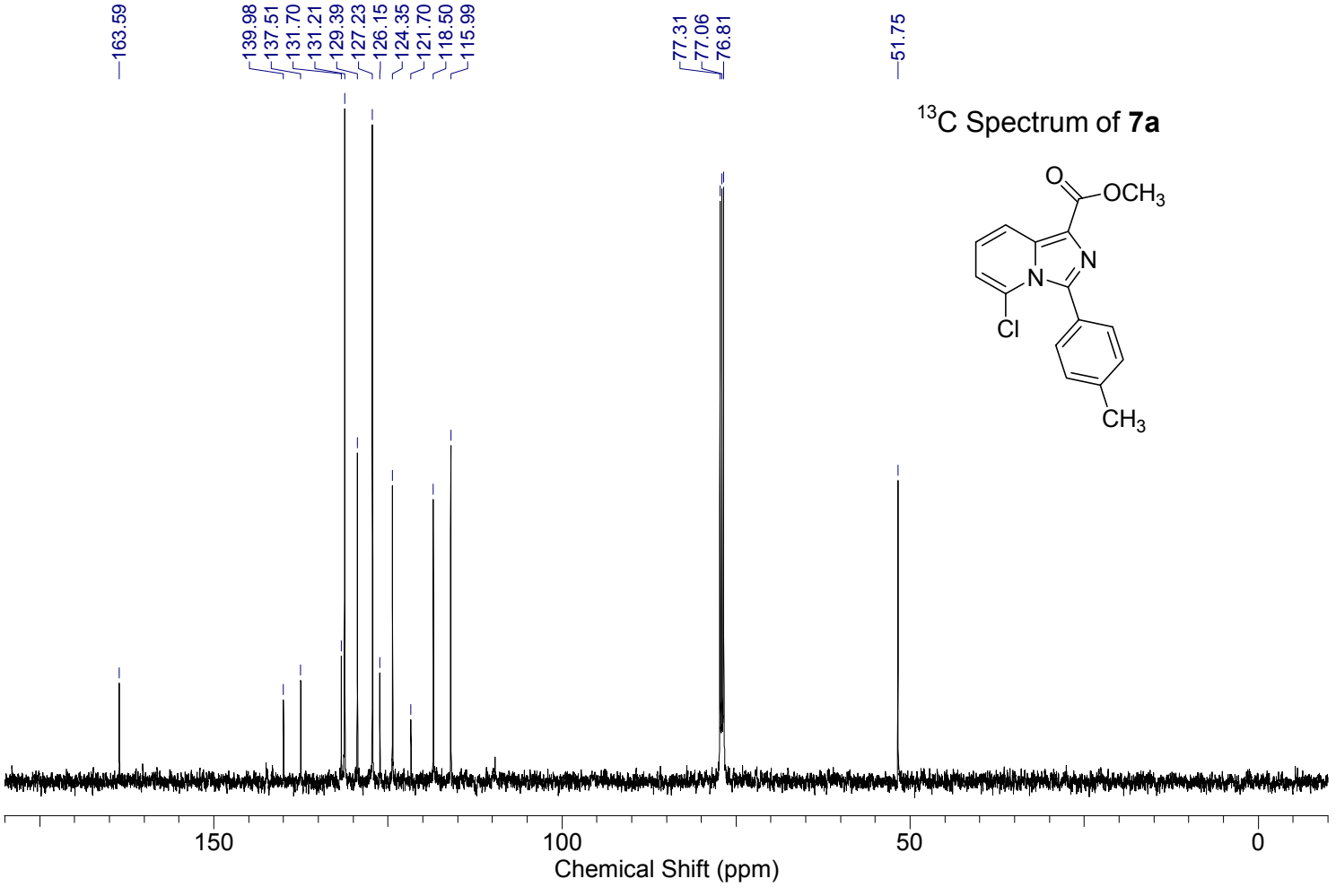




$^{13}$C Spectrum of **6g**

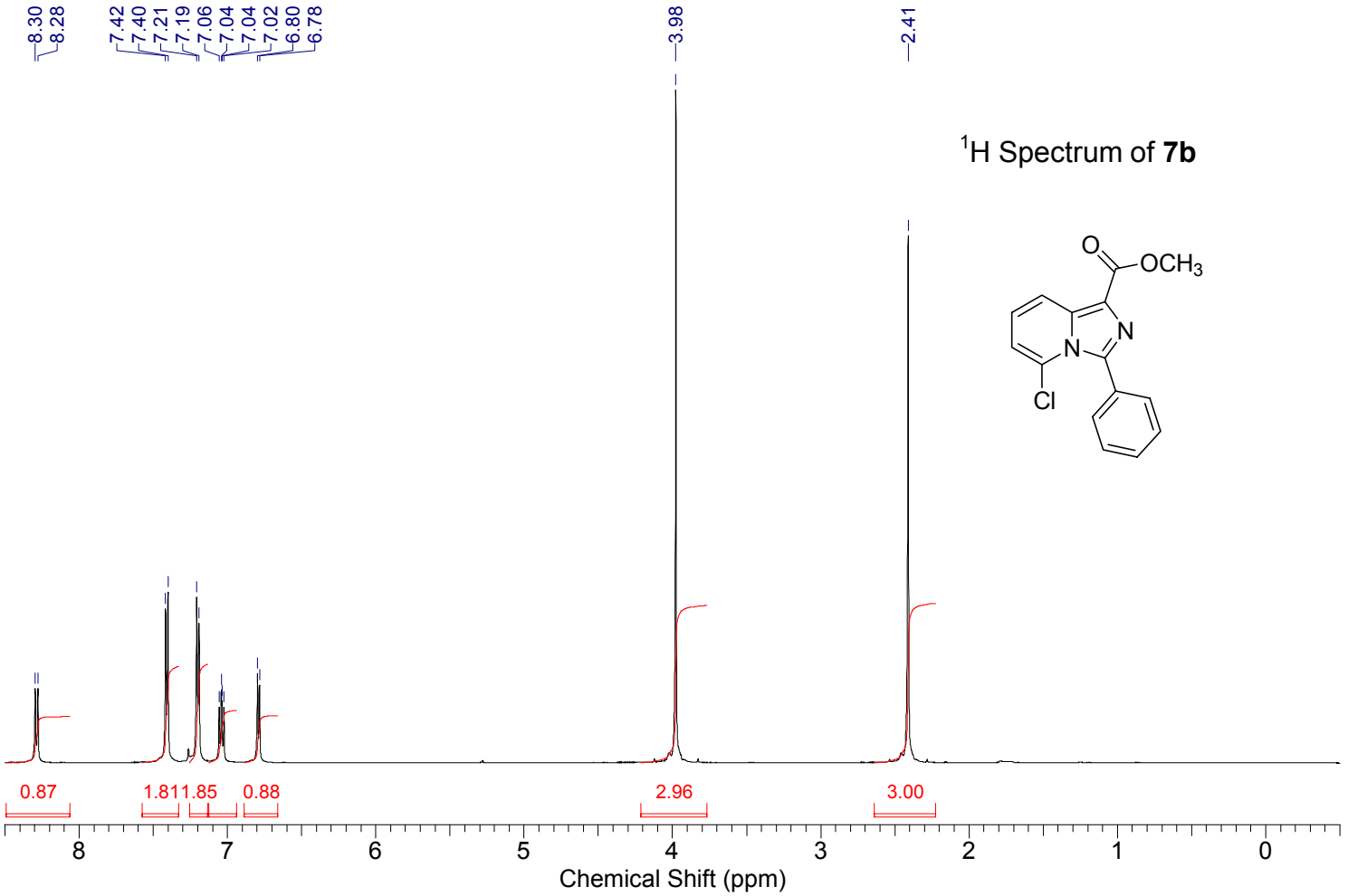



$^{1}$H Spectrum of **7a**



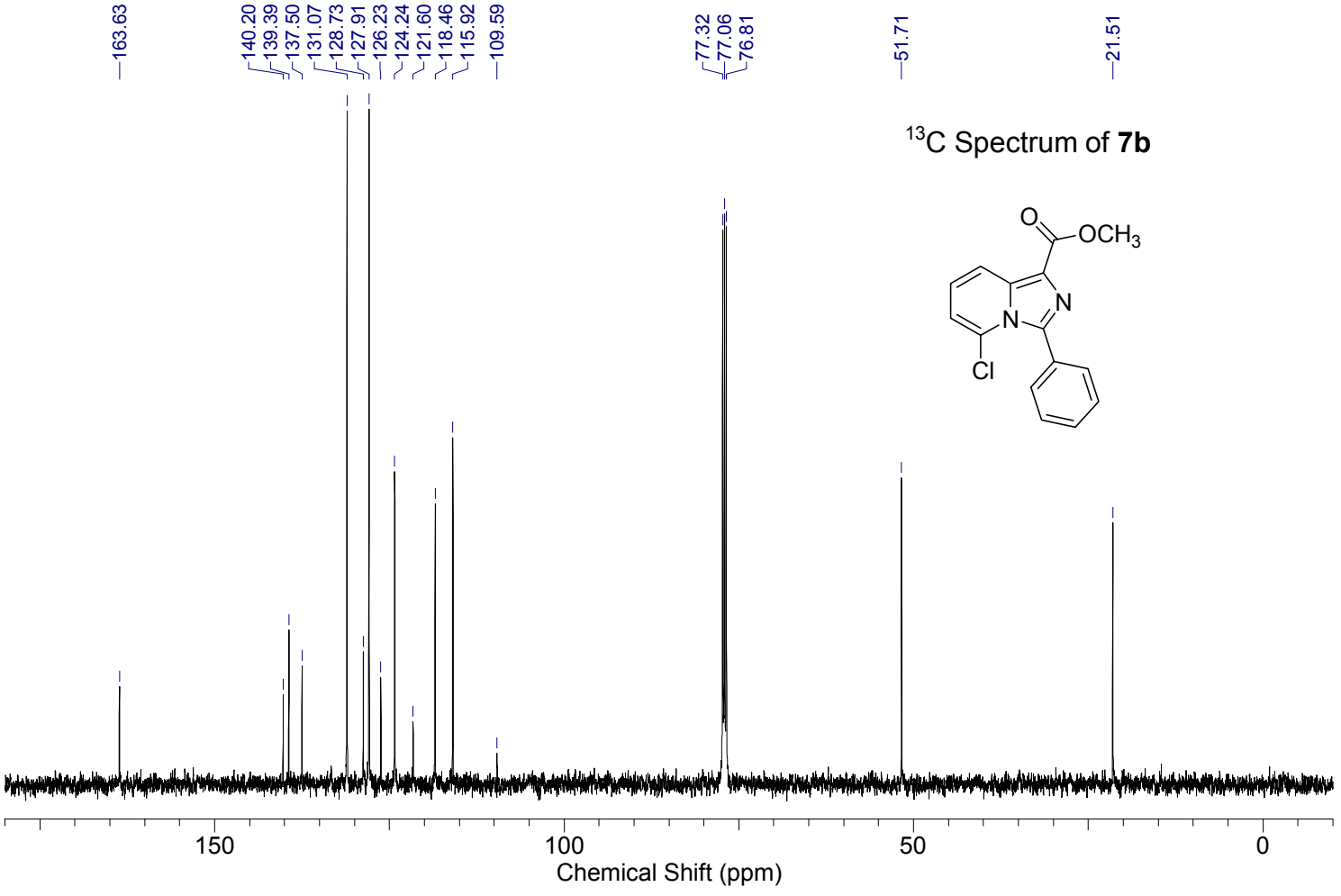




$^{13}$C Spectrum of **7a**

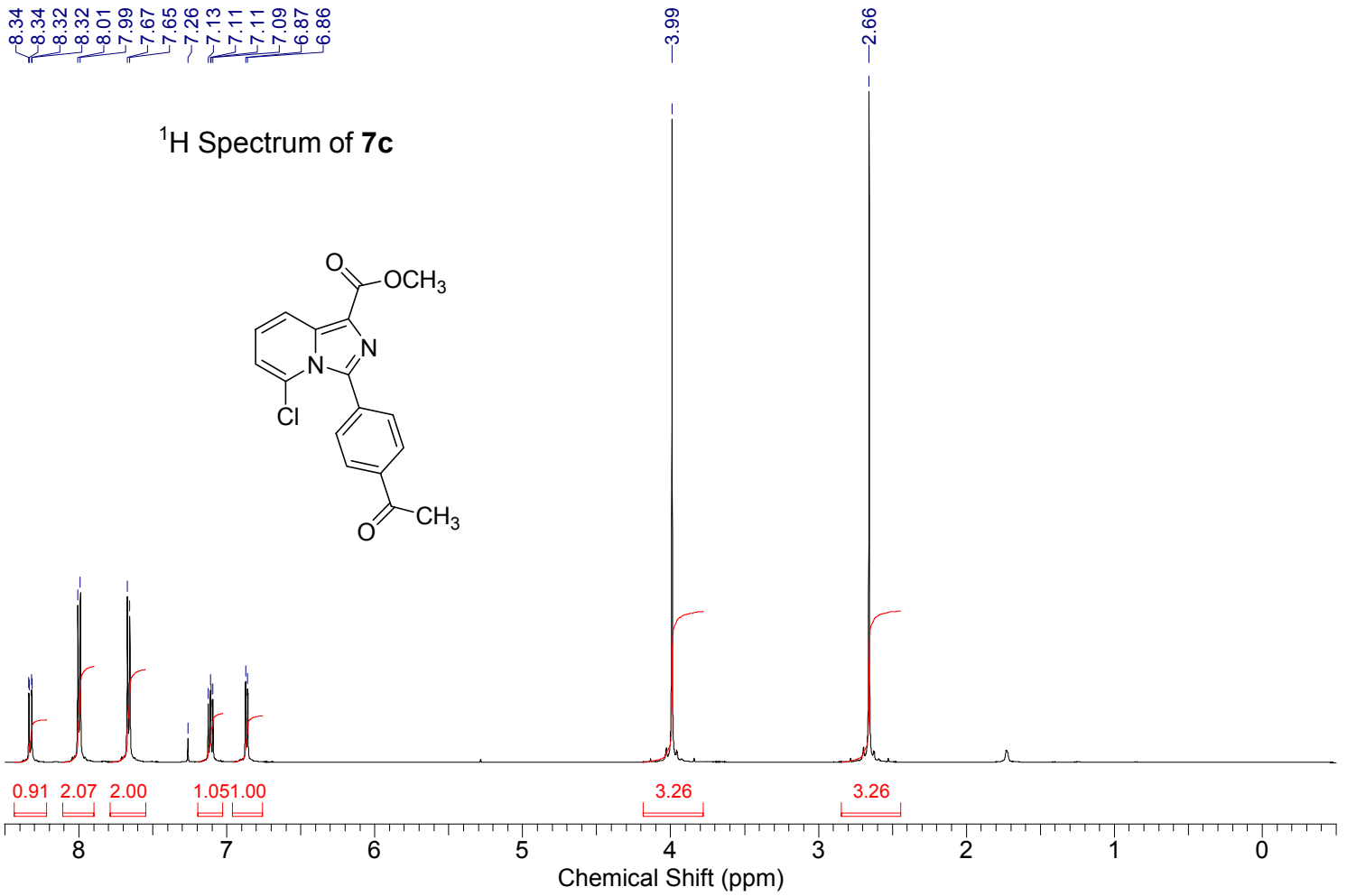


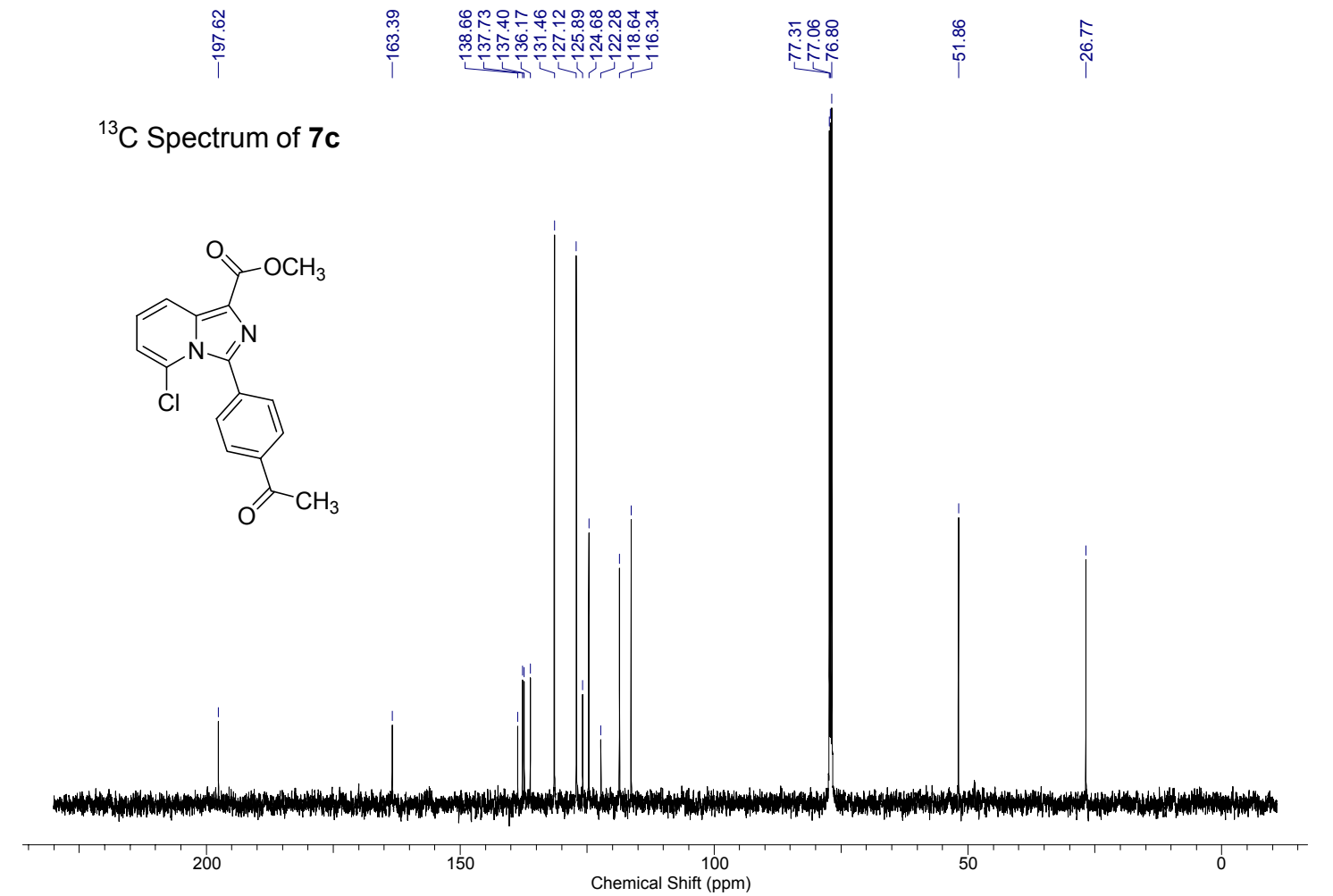

$^{1}$H Spectrum of **7b**

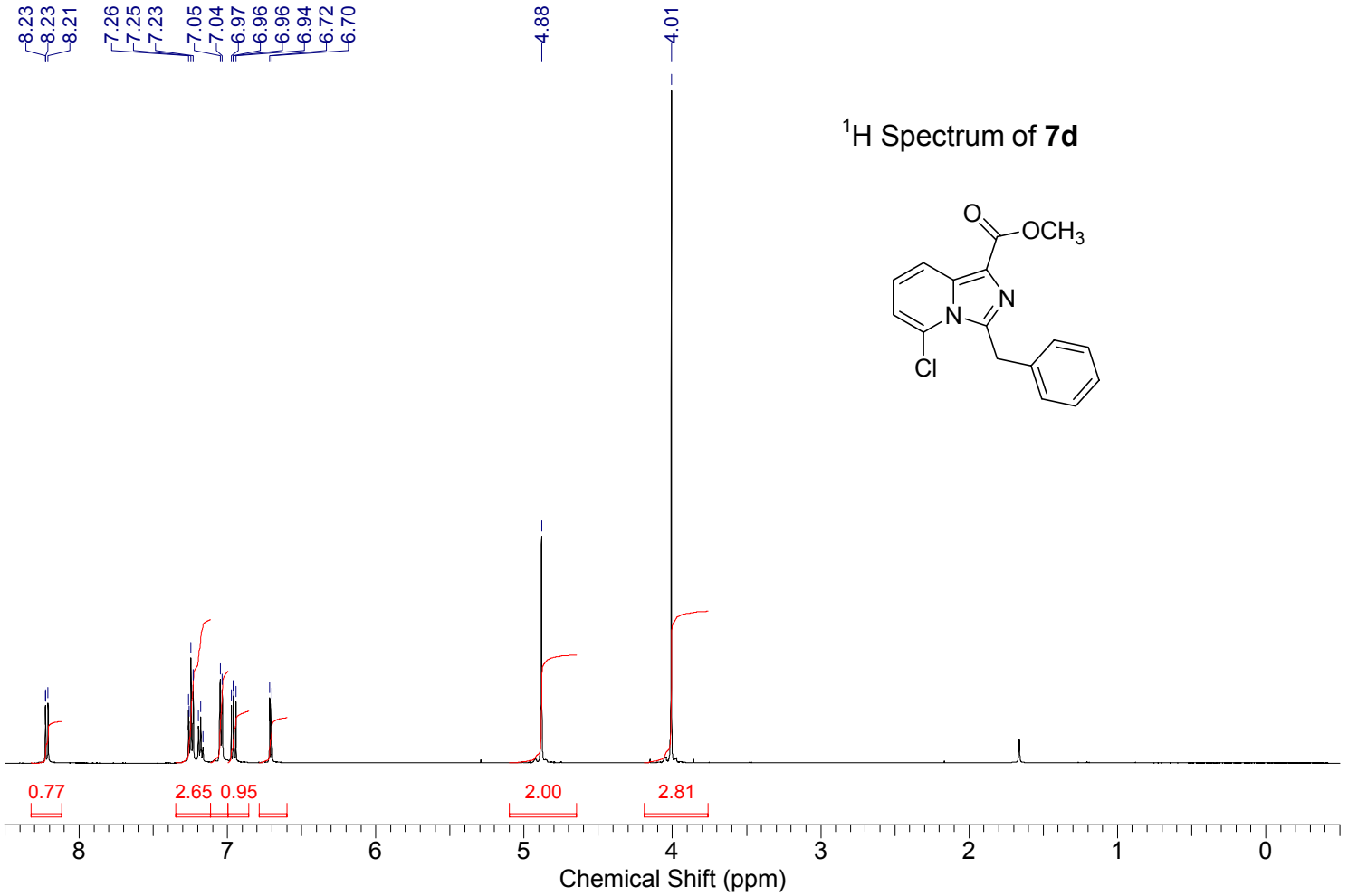



$^{13}$C Spectrum of **7b**

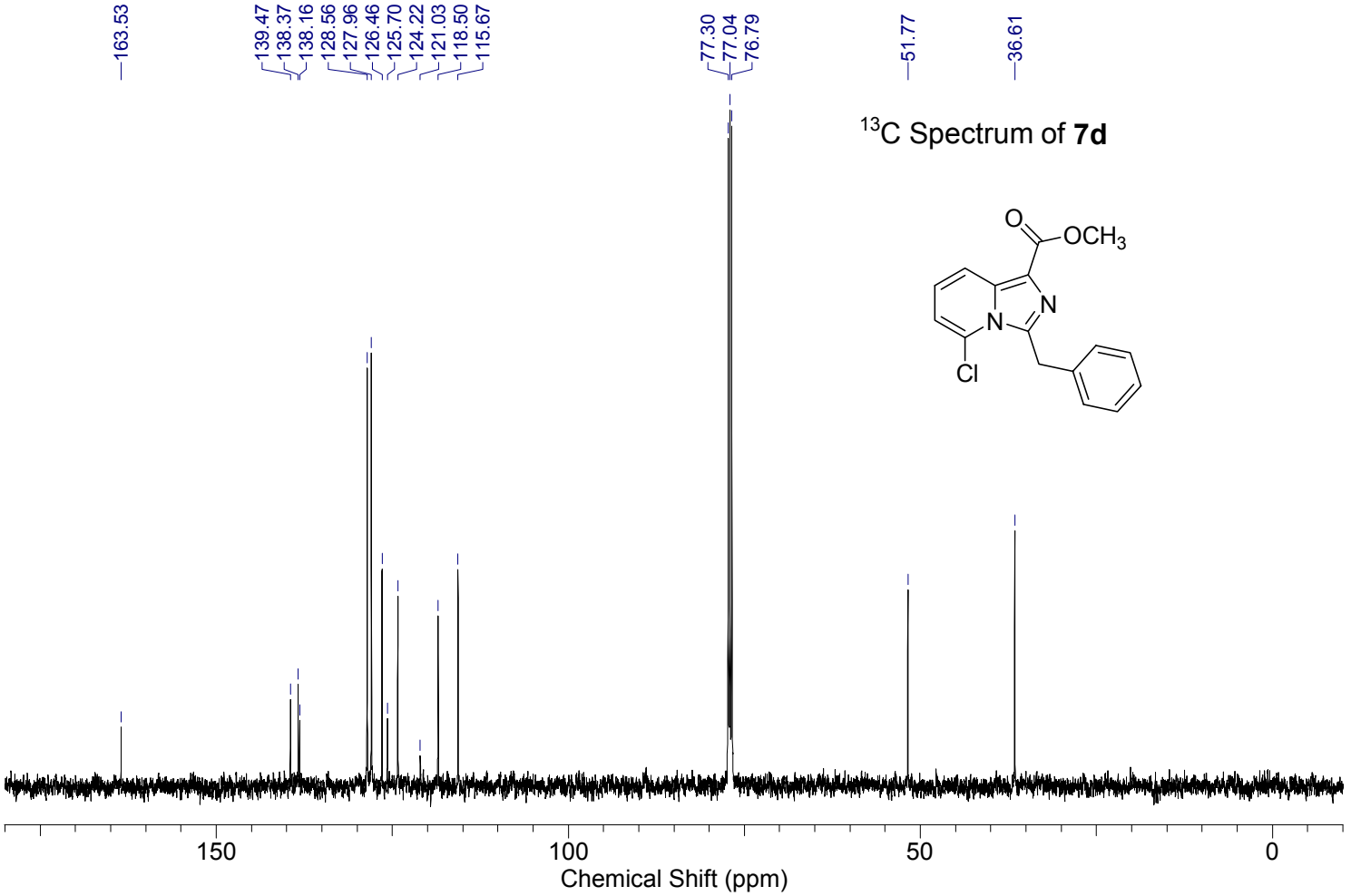

8.34
8.34
8.32
8.32
8.01
7.99
7.67
7.65
7.26
7.13
7.11
7.11
7.09
6.87
6.86
3.99
2.66
$^1$H Spectrum of **7c**
O
OCH$_3$
N
N
Cl
O
CH$_3$
0.91
2.07
2.00
1.05
1.00
3.26
3.26
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


197.62
163.39
138.66
137.73
137.40
136.17
131.46
127.12
125.89
124.68
122.28
118.64
116.34
77.31
77.06
76.80
51.86
26.77
$^{13}$C Spectrum of **7c**
O
OCH$_3$
N
N
Cl
O
CH$_3$
200
150
100
50
0
Chemical Shift (ppm)

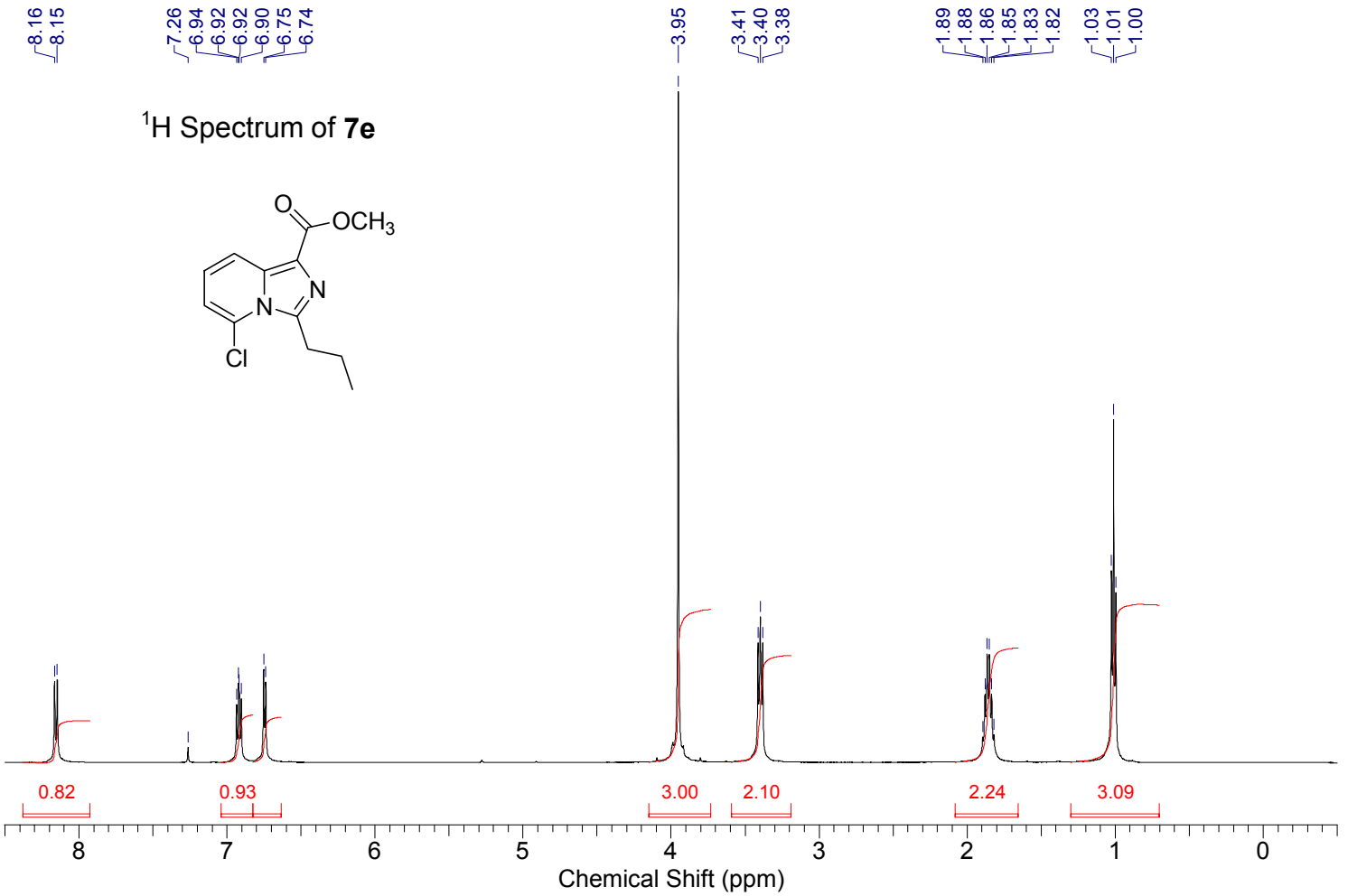


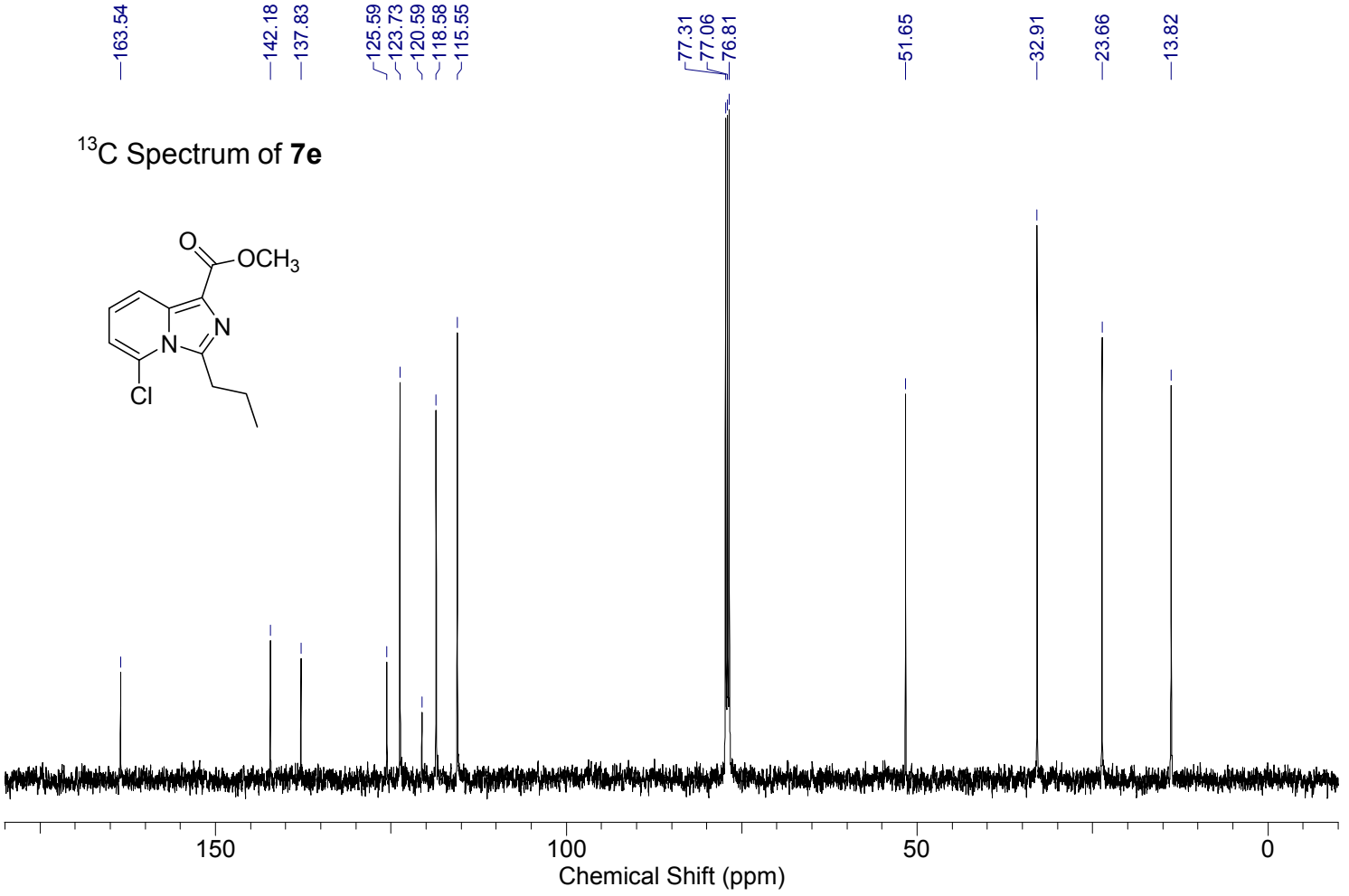

$^{1}$H Spectrum of **7d**

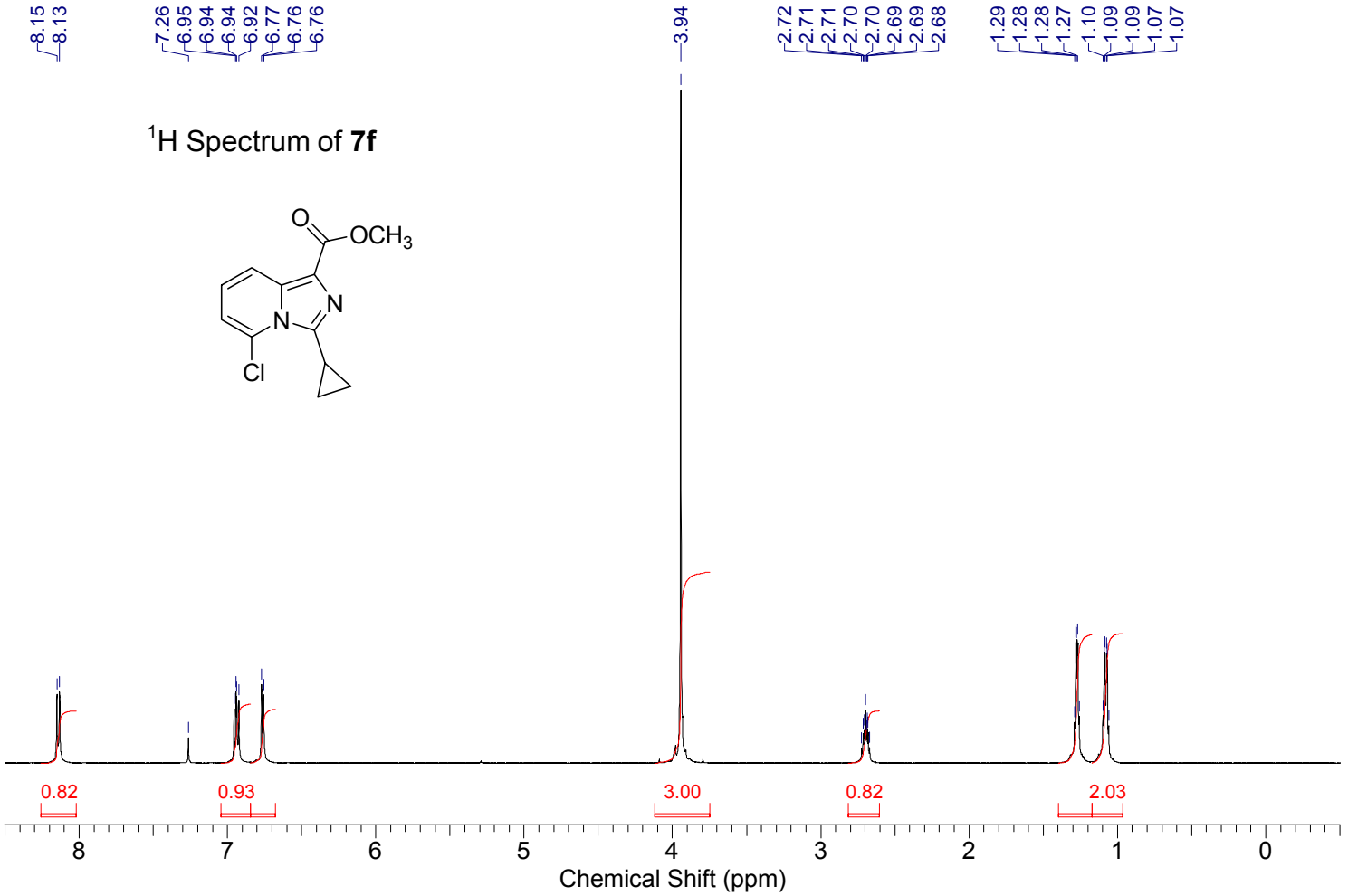


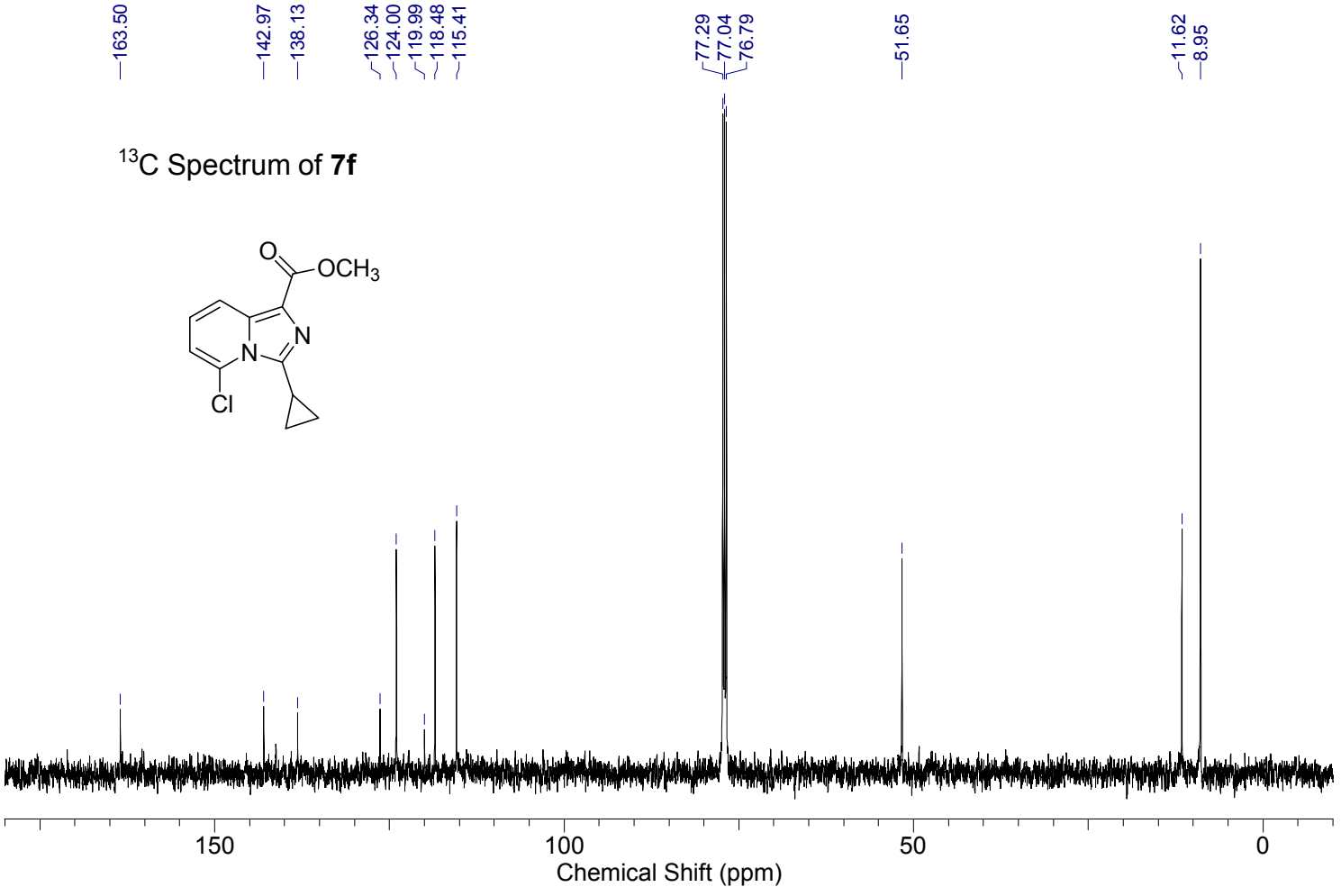



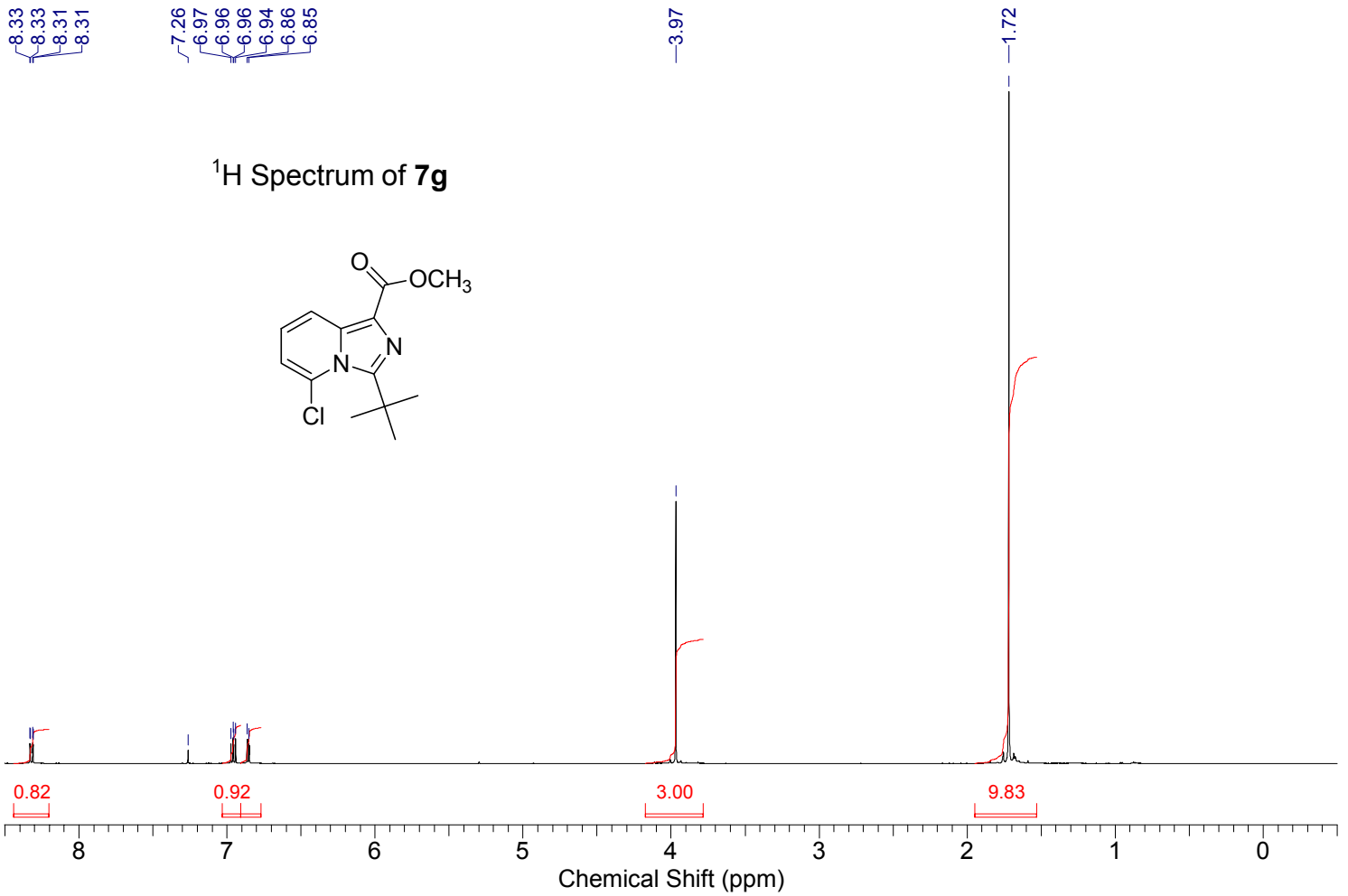

$^{13}$C Spectrum of **7d**


8.16
8.15
7.26
6.94
6.92
6.92
6.90
6.75
6.74
3.95
3.41
3.40
3.38
1.89
1.88
1.86
1.85
1.83
1.82
1.03
1.01
1.00
$^{1}$H Spectrum of **7e**
O
OCH$_3$
N
N
Cl
0.82
0.93
3.00
2.10
2.24
3.09
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


163.54
142.18
137.83
125.59
123.73
120.59
118.58
115.55
77.31
77.06
76.81
51.65
32.91
23.66
13.82
$^{13}$C Spectrum of **7e**
O
OCH$_3$
N
N
Cl
150
100
50
0
Chemical Shift (ppm)

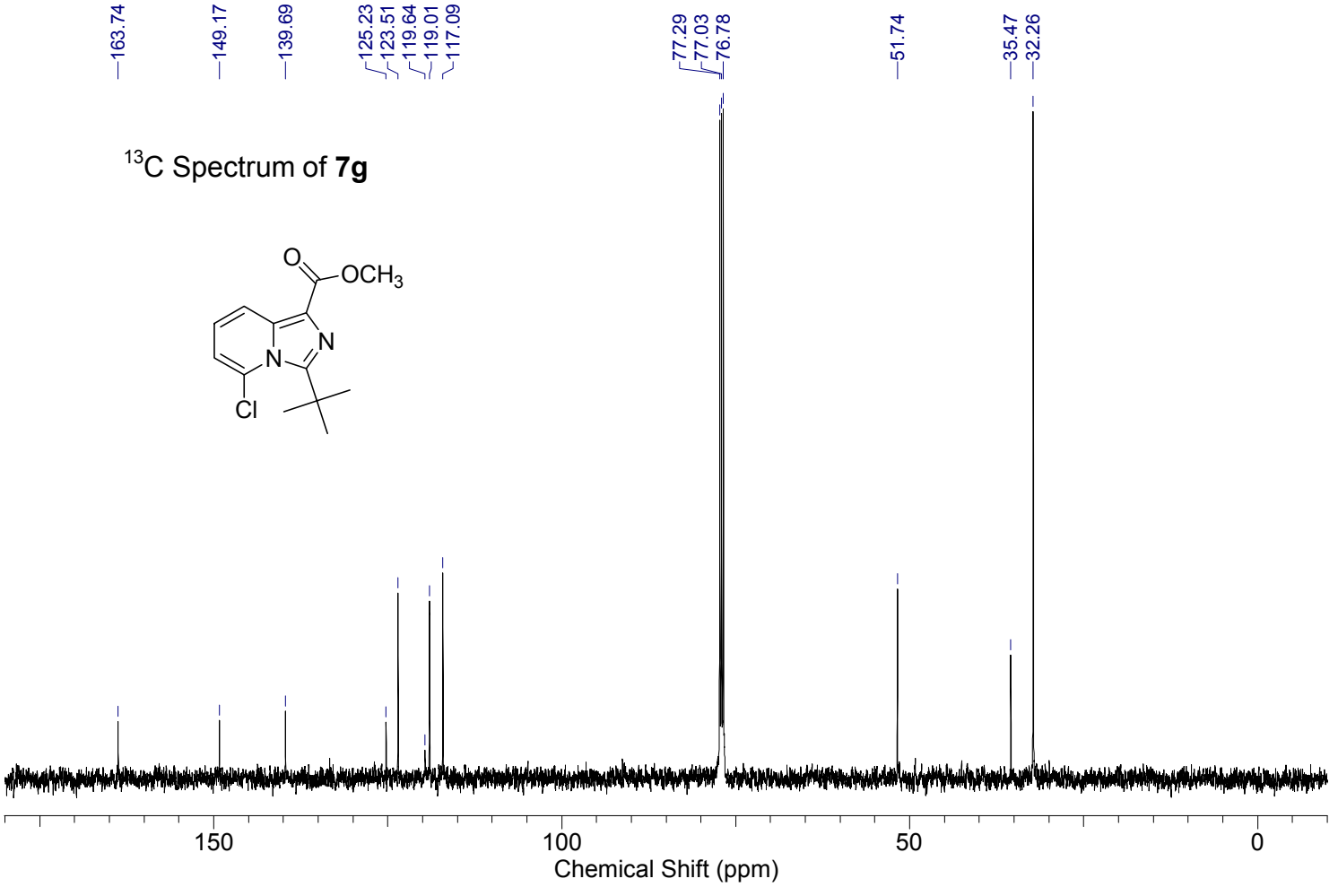

8.15
8.13
7.26
6.95
6.94
6.94
6.92
6.77
6.76
6.76
3.94
2.72
2.71
2.71
2.70
2.70
2.69
2.69
2.68
1.29
1.28
1.28
1.27
1.10
1.09
1.09
1.07
1.07
1H Spectrum of 7f
O
OCH3
N
N
Cl
0.82
0.93
3.00
0.82
2.03
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


163.50
142.97
138.13
126.34
124.00
119.99
118.48
115.41
77.29
77.04
76.79
51.65
11.62
8.95
13C Spectrum of 7f
O
OCH3
N
N
Cl
150
100
50
0
Chemical Shift (ppm)

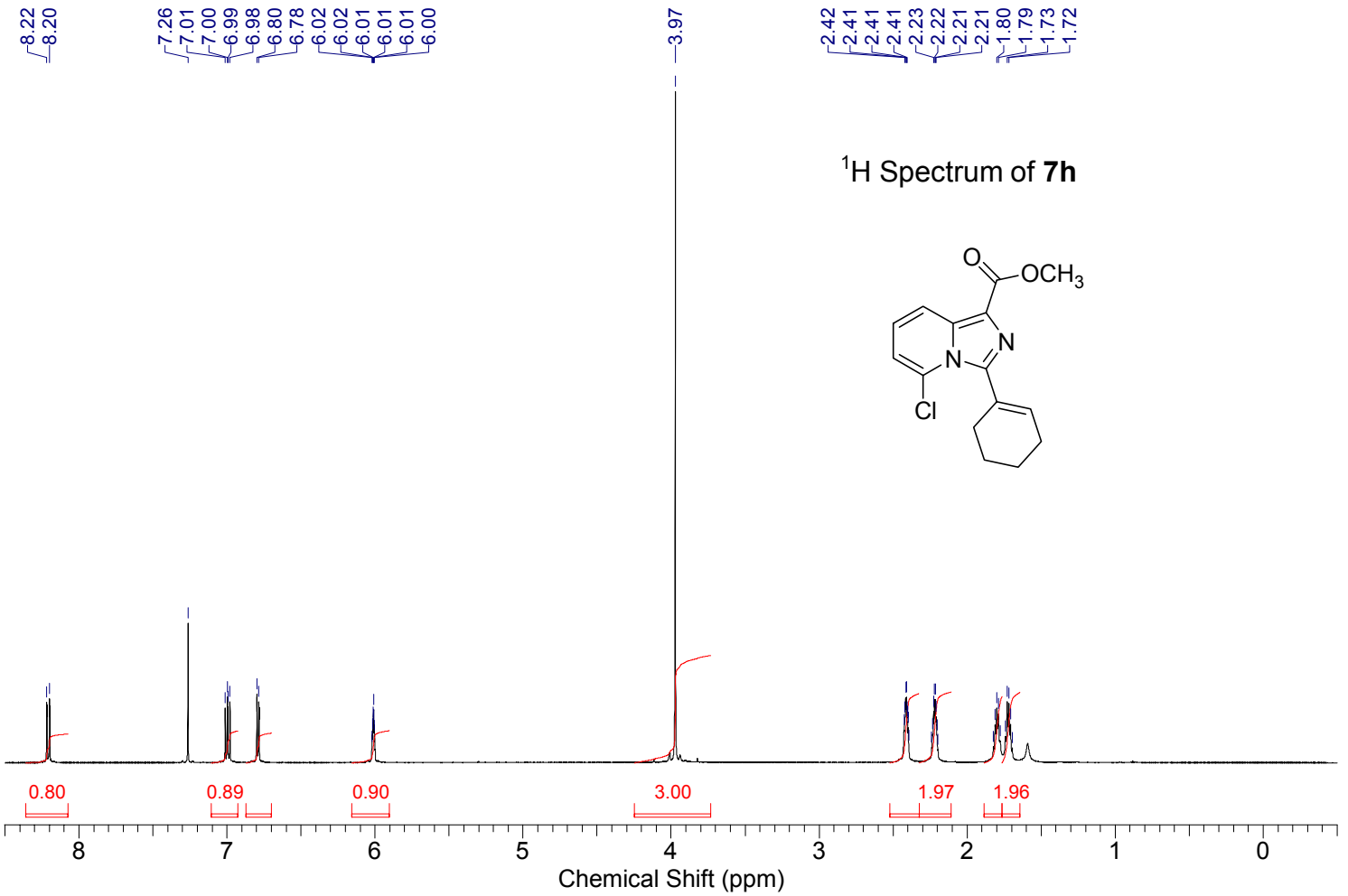



$^{1}$H Spectrum of **7g**



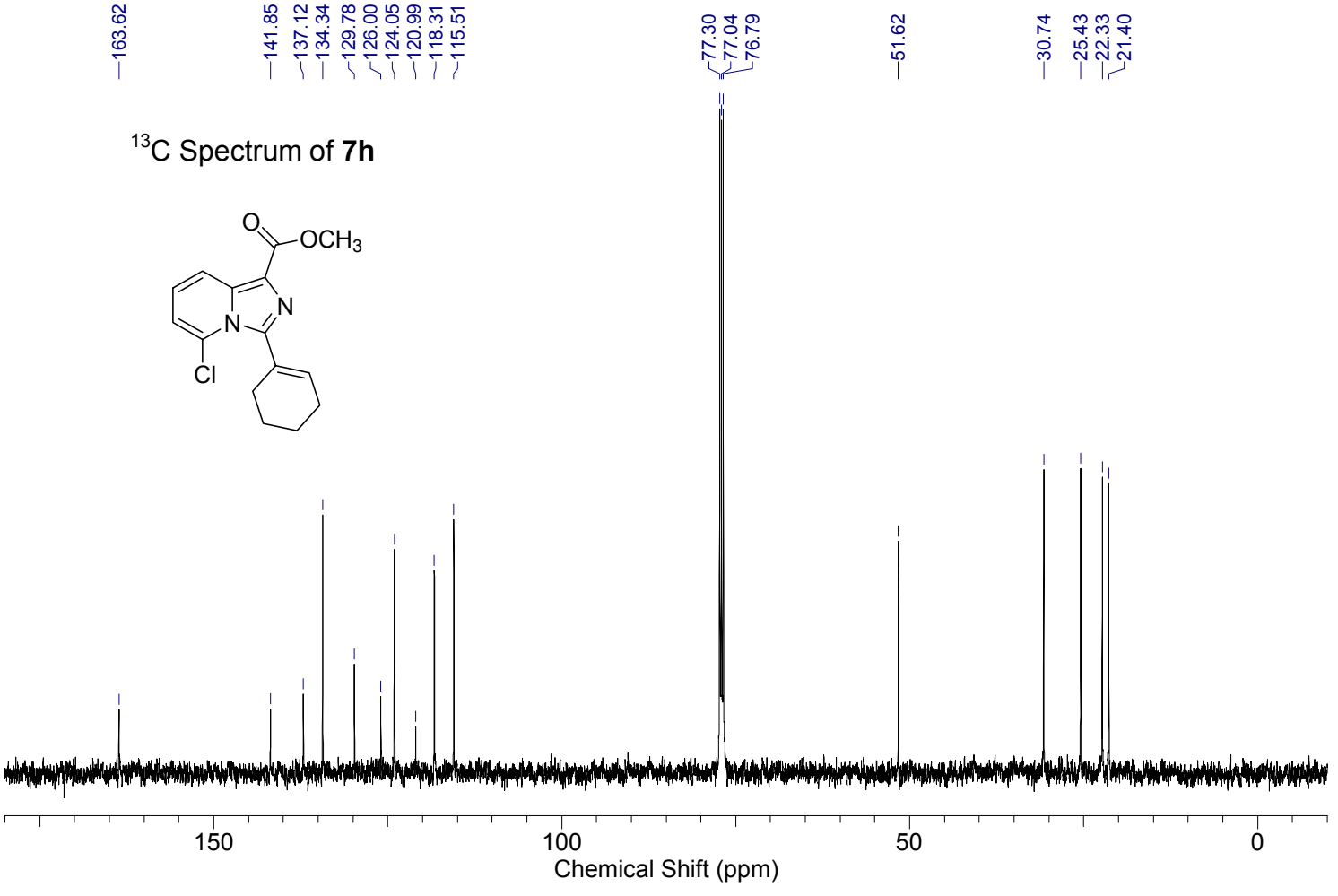




$^{13}$C Spectrum of **7g**

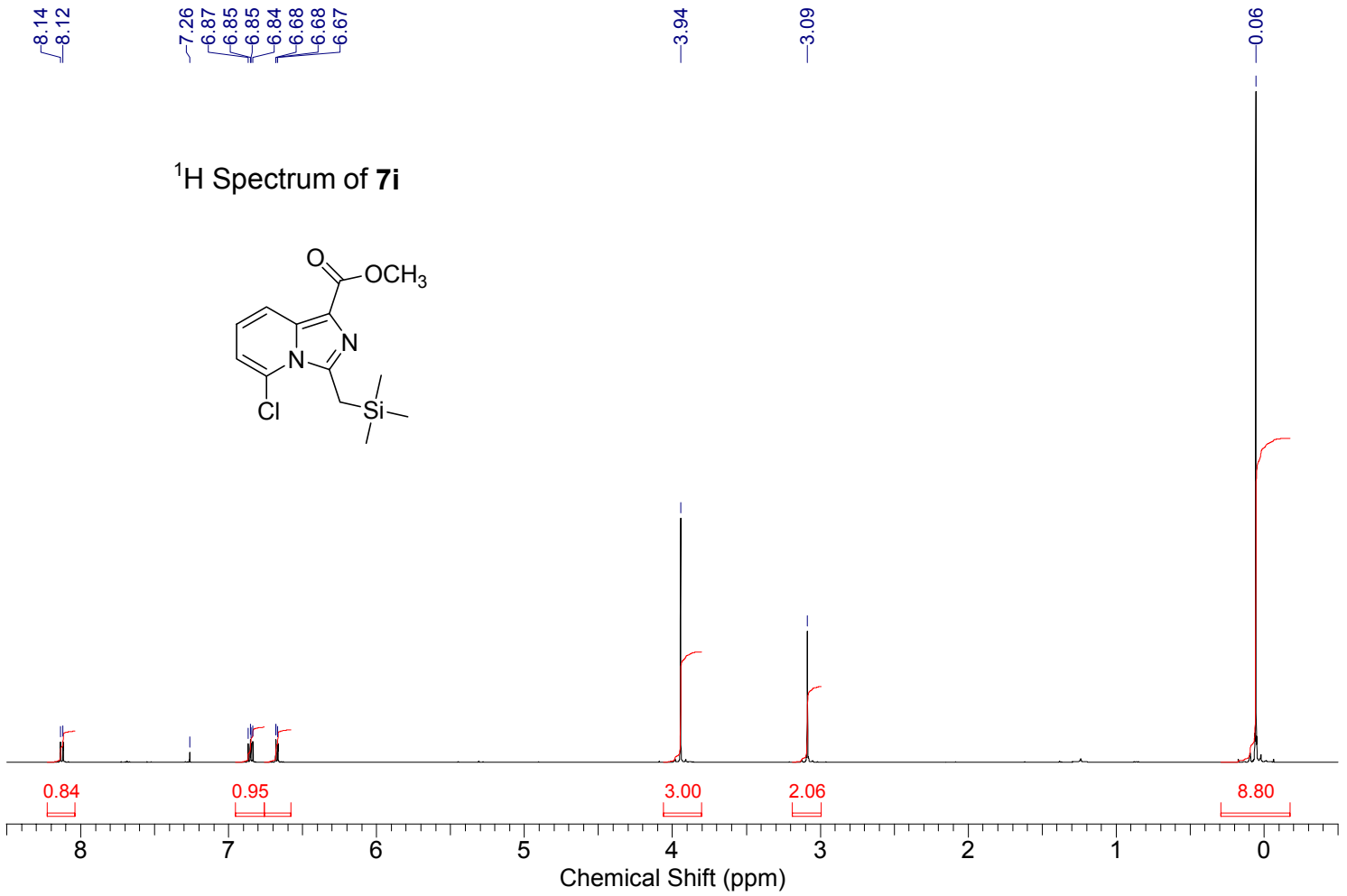



$^{1}$H Spectrum of **7h**



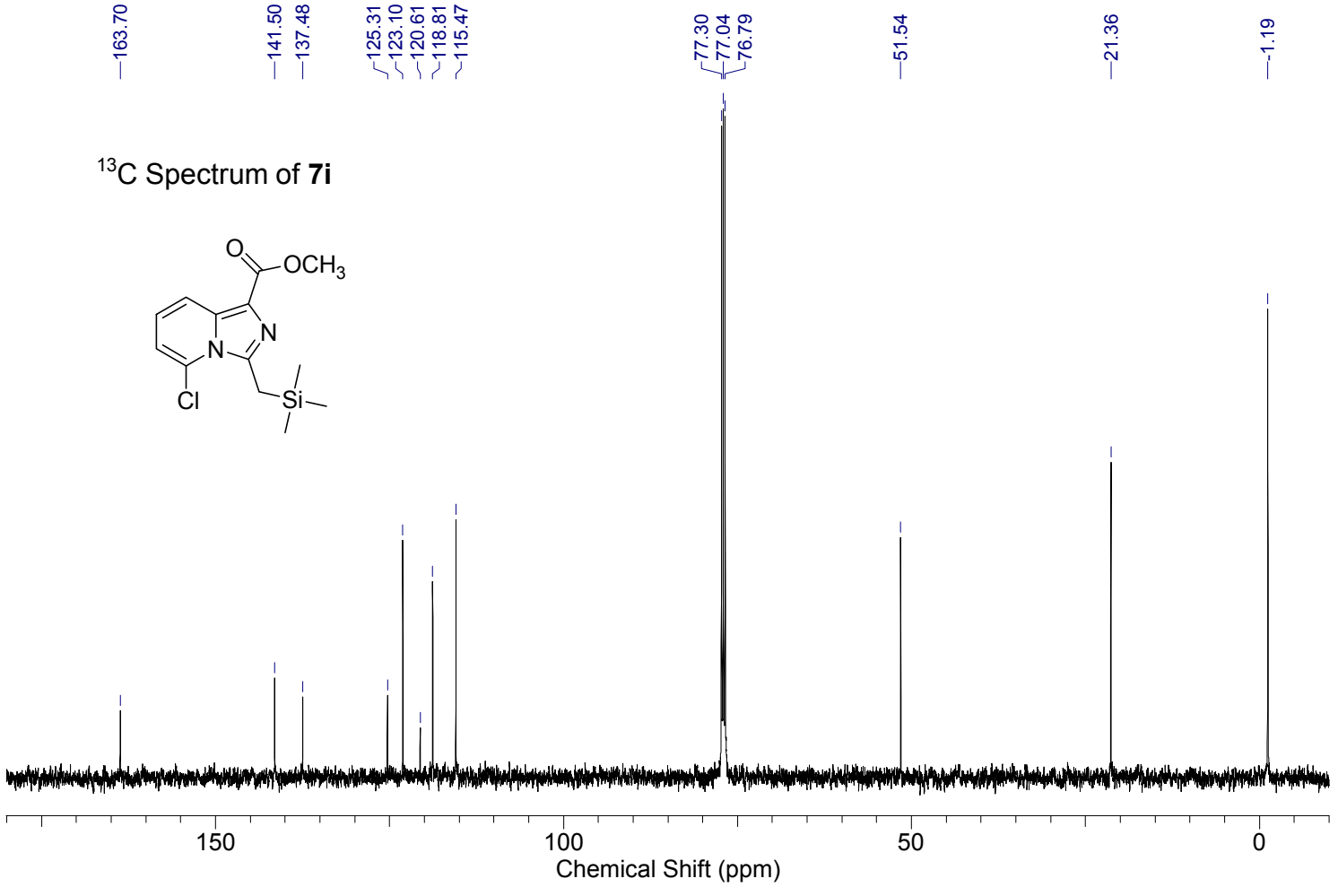




$^{13}$C Spectrum of **7h**

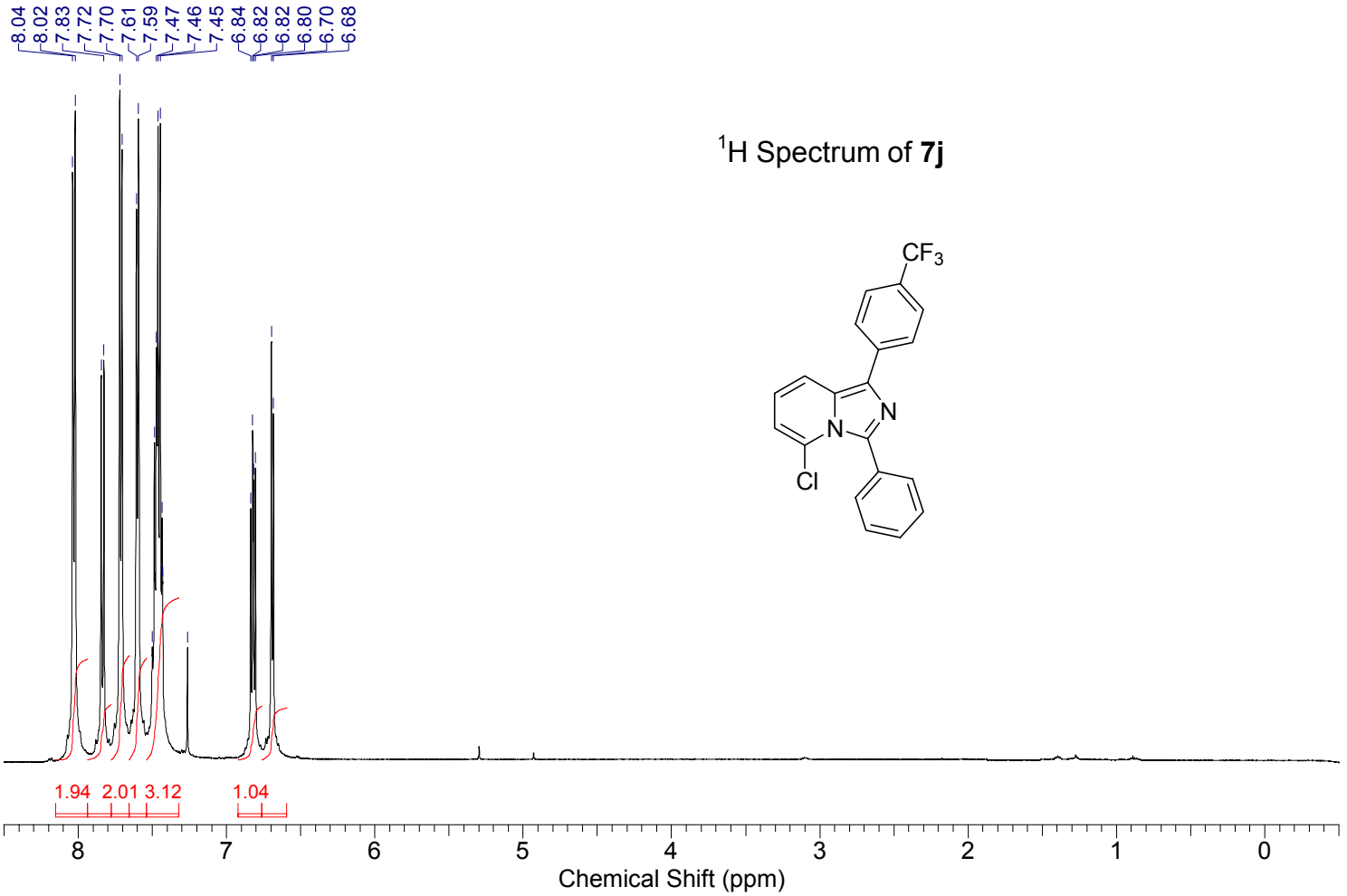



$^{1}$H Spectrum of **7i**



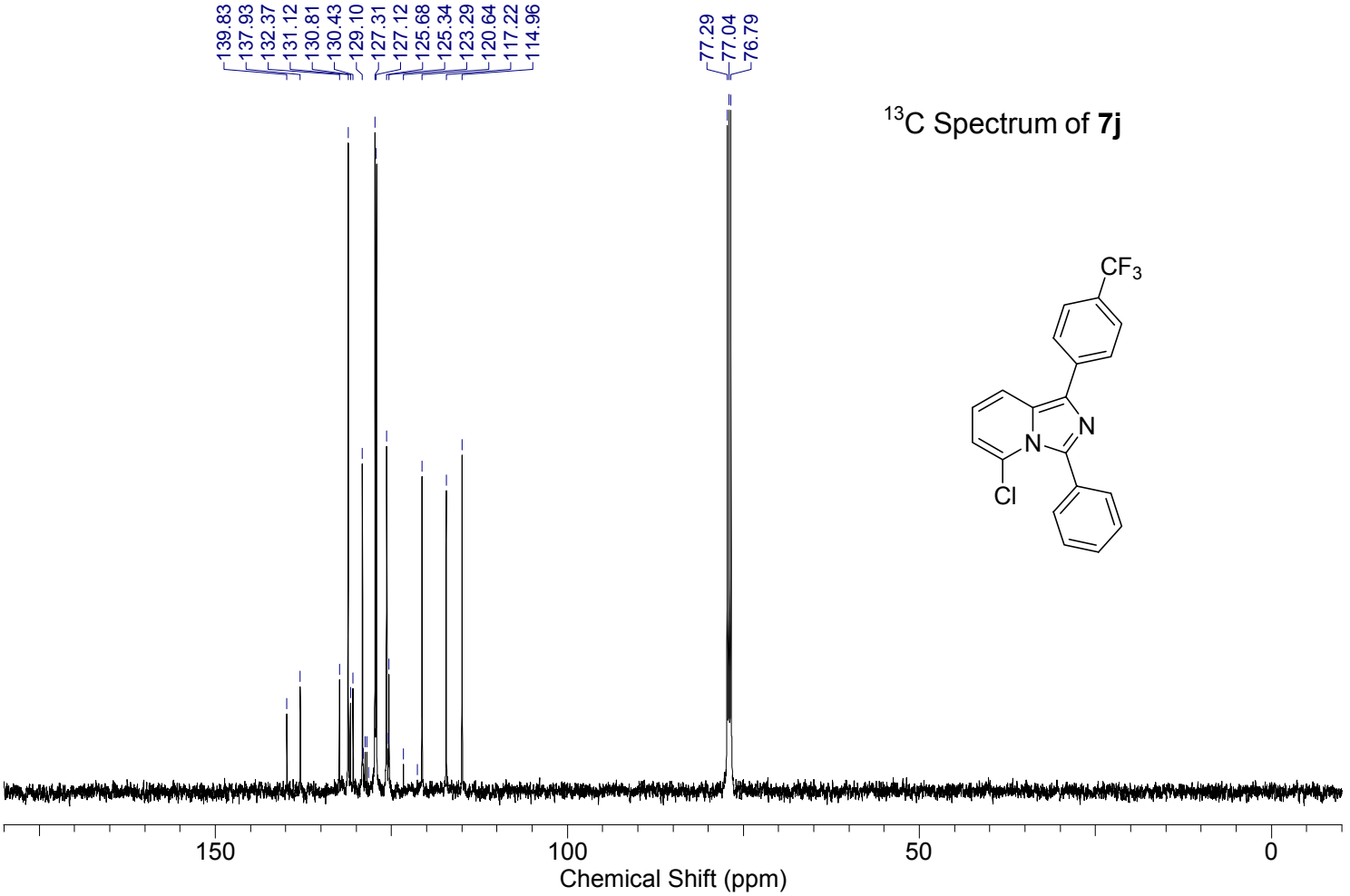




$^{13}$C Spectrum of **7i**

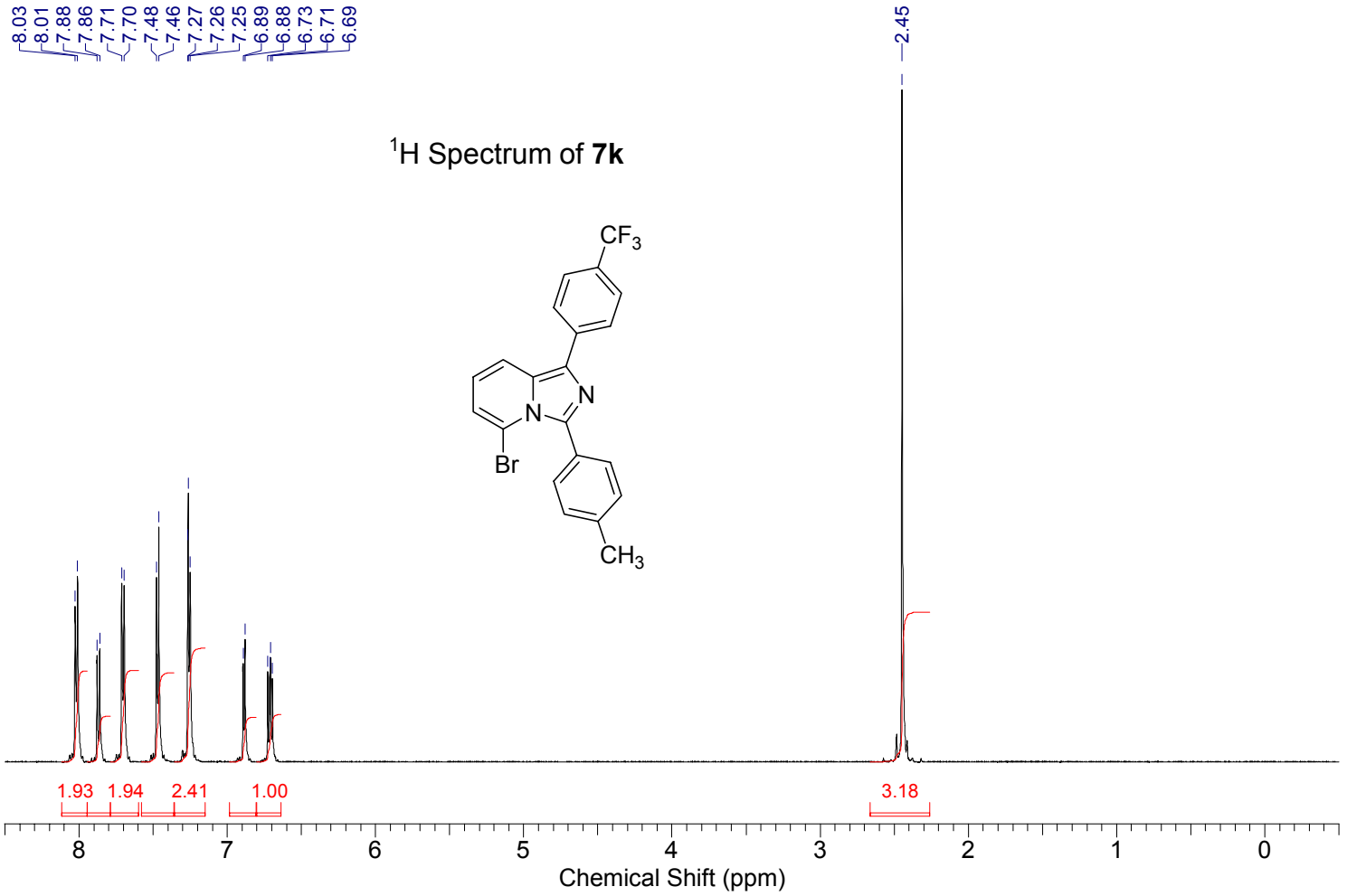


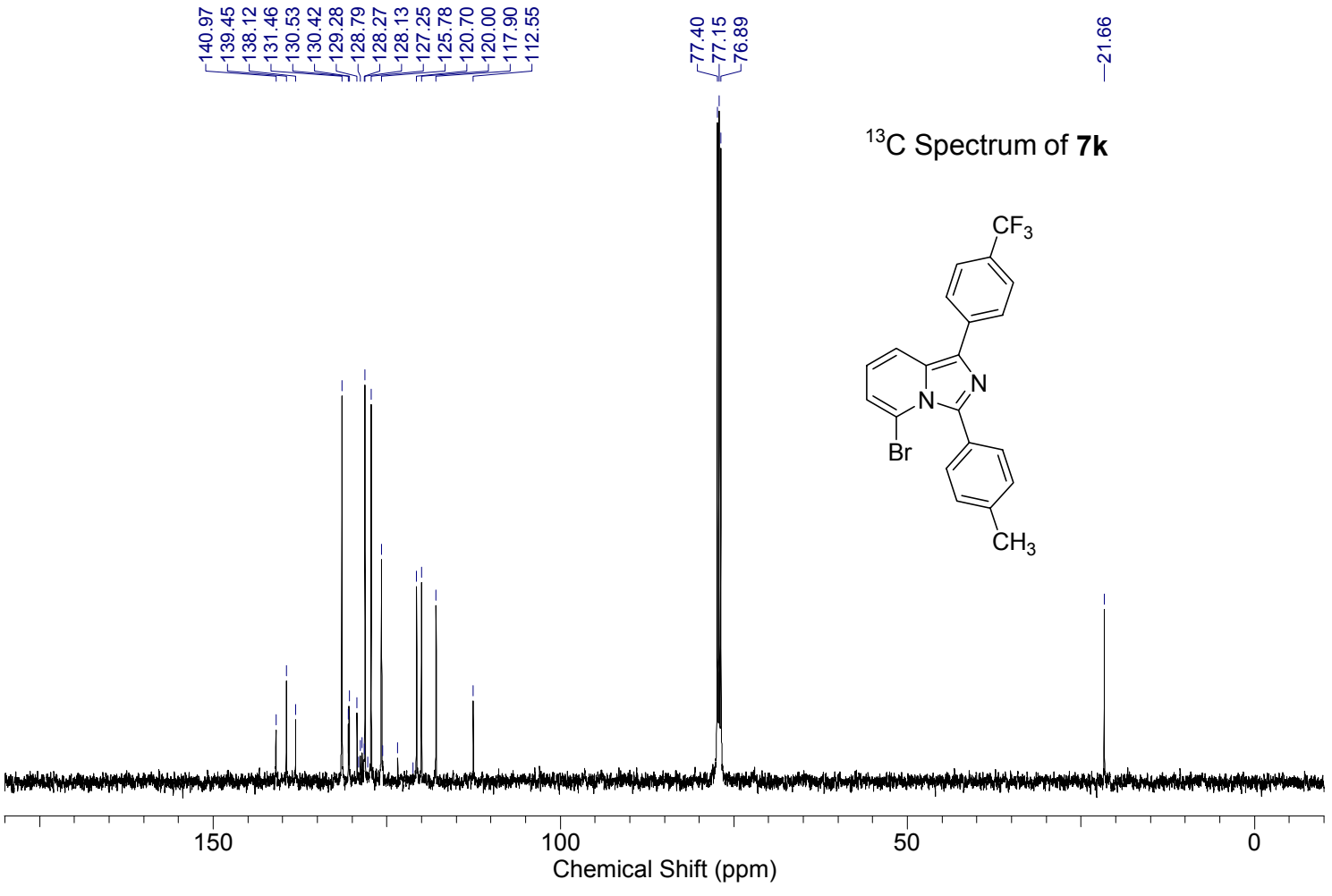

$^{1}$H Spectrum of **7j**

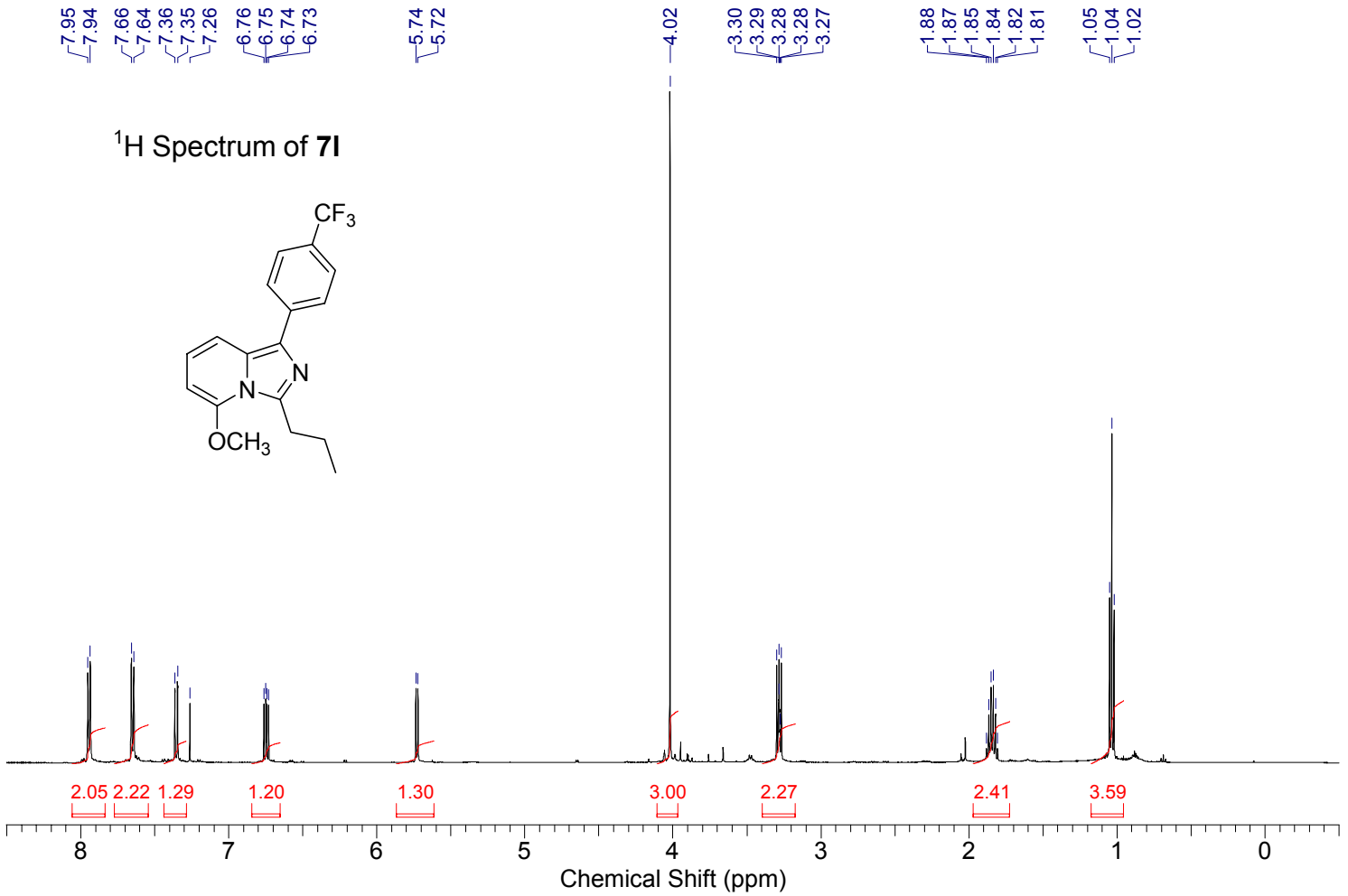


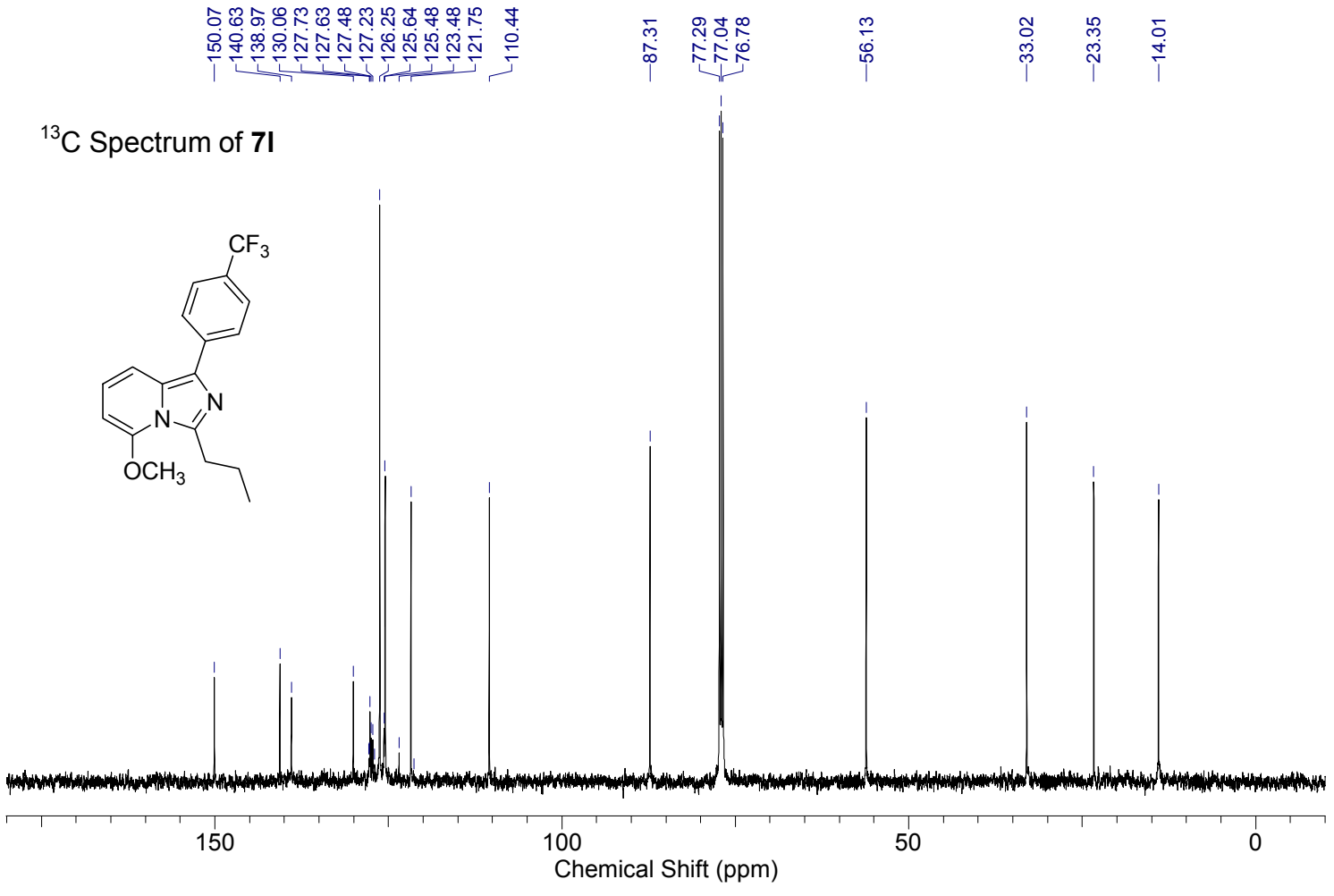




$^{13}$C Spectrum of **7j**


8.03
8.01
7.88
7.86
7.71
7.70
7.48
7.46
7.27
7.26
7.25
6.89
6.88
6.73
6.71
6.69
2.45
1H Spectrum of 7k
CF3
N
N
Br
CH3
1.93
1.94
2.41
1.00
3.18
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


140.97
139.45
138.12
131.46
130.53
130.42
129.28
128.79
128.27
128.13
127.25
125.78
120.70
120.00
117.90
112.55
77.40
77.15
76.89
21.66
13C Spectrum of 7k
CF3
N
N
Br
CH3
150
100
50
0
Chemical Shift (ppm)


7.95
7.94
7.66
7.64
7.36
7.35
7.26
6.76
6.75
6.74
6.73
5.74
5.72
4.02
3.30
3.29
3.28
3.28
3.27
1.88
1.87
1.85
1.84
1.82
1.81
1.05
1.04
1.02
1H Spectrum of 7I
CF3
N
N
OCH3
2.05 2.22 1.29 1.20 1.30 3.00 2.27 2.41 3.59
8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)


150.07
140.63
138.97
130.06
127.73
127.63
127.48
127.23
126.25
125.64
125.48
123.48
121.75
110.44
87.31
77.29
77.04
76.78
56.13
33.02
23.35
14.01
13C Spectrum of 7I
CF3
N
N
OCH3
150 100 50 0
Chemical Shift (ppm)