Supporting Information for

Oxidative [3+2]-annulation of nitroalkenes and azolium ylides in the presence of Cu(II): efficient synthesis of [5,5]-annulated *N*-fused heterocycles

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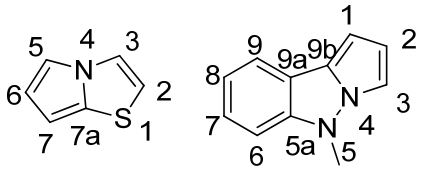
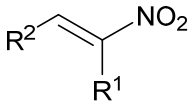
General experimental.

All reactions were performed in oven-dried (150 °C) glassware. Most of the chemicals were acquired from commercial sources and used as received. Starting nitroalkenes were prepared by literature procedures: **1a,**[s1] **1b**,[s2] **1c-1d**,[s1] **1e-1f**,[s3] **1g**,[s4] **1h-1i**,[s5] **1j**,[s6] **1k**,[s4] **1l**.[s7] Other starting materials were prepared according to the literature procedures: **2a**,[s3] **2f**.[s4] TLC were performed on silica coated on aluminium with UV254 indicator. Visualization was accomplished with UV. Column chromatography was performed on silica (0.04–0.063 mm, 60 Å). NMR spectra were recorded at the 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR), and 282 MHz (^{19}F NMR) frequencies. Multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), br (broad). High resolution mass spectra were acquired at TOF spectrometer using electrospray ionization (ESI). Positions of pyrrolo[2,1-b]thiazole and pyrrolo[1,2-b]indazole rings are numerated according to IUPAC as shown. Assignment was made on the basis of 2D NMR (COSY, HSQC, HMBC) for compounds **3c**, **5a, 5b, 5e, 5f, 7f**.

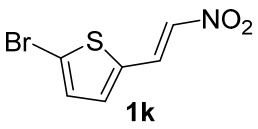


For the salts **2** and **6** intensities of CH_2-group signals can be reduced due to their high acidity that causes proton exchange with water in DMSO-d_6. More significant decrease of CH_2-group intensity is attributed to higher acidity (e.g. for compound **2c**).

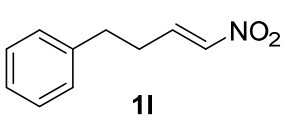
List of starting reagents:



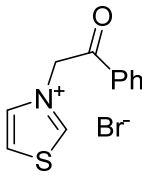
1a, R^1 = F, R^2 = 4-Cl-C_6H_4-
1b, R^1 = F, R^2 = 2-Cl-C_6H_4-
1c, R^1 = F, R^2 = 4-MeO-C_6H_4-
1d, R^1 = F, R^2 = 4-NO_2-C_6H_4-
1e, R^1 = CO_2Et, R^2 = 4-Cl-C_6H_4-
1f, R^1 = CO_2Et, R^2 = 2-Br-C_6H_4-
1g, R^1 = H, R^2 = 4-Cl-C_6H_4-
1h, R^1 = H, R^2 = Ph
1i, R^1 = H, R^2 = 4-MeO-C_6H_4-
1j, R^1 = H, R^2 = 2-Br-C_6H_4-



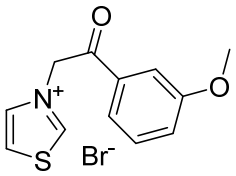
1k



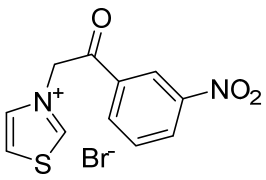
1l



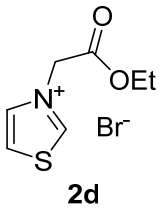
2a



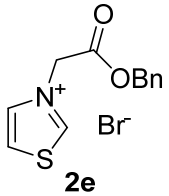
2b



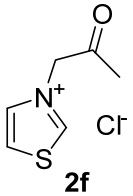
2c



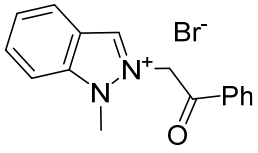
2d



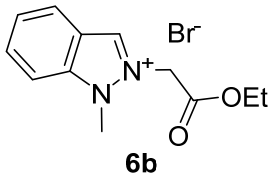
2e



2f



6a



6b

Synthesis of thiazolium salts **2a-2c**:

To the solution of thiazole (255 mg, 3 mmol) in EtOAc (3 ml) corresponding bromoacetophenone (3 mmol) was added and the mixture was stirred at r.t. for 3 days. Precipitated product **2** was filtered, washed with EtOAc and dried under air.

3-(2-Oxo-2-phenylethyl)-1,3-thiazol-3-ium bromide 2a

White solid, yield 0.79 g (93%). mp = 232-235°C (dec.) (EtOAc) (lit. 223-223.5°C (dec.))[s8] NMR matches previously reported data.[s9]

3-[2-(3-Methoxyphenyl)-2-oxoethyl]-1,3-thiazol-3-ium bromide 2b

White amorphous solid, yield 0.84 g (89%).

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.83 (s, 3H, OMe), 6.45 (s, 2H, CH_2), 7.30-7.37 (m, 1H, CH_{Ar}), 7.48-7.66 (m, 3H, CH_{Ar}), 8.39 (s, *J* = 2.1 Hz, 1H, CH(thiazole)), 8.51 (d, *J* = 2.1 Hz, 1H, CH(thiazole)), 10.22 (s, 1H, H2(thiazole)).

^{13}C NMR (75 MHz, DMSO-d_6, DEPT-135): δ 56.1 (OMe), 61.1 (CH_2), 113.3 (CH_{Ar}), 121.0 (CH_{Ar}), 121.1 (CH_{Ar}), 126.5 (CH(thiazole)), 130.9 (CH_{Ar}), 135.2 (C_{Ar}), 138.8 (CH(thiazole)), 160.0 (**C_{Ar}**-OMe), 161.9 (CH(thiazole)), 191.0 (C=O).

HRMS (ESI): *m/z* calcd. for $[C_{12}H_{12}BrNO_2S - Br]^+$: 234.0583, found: 234.0586.

3-[2-(3-Nitrophenyl)-2-oxoethyl]-1,3-thiazol-3-ium bromide 2c

White solid, yield 0.90 g (91%). mp = 234-236°C (dec.) (EtOAc)

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.48 (s, 2H, CH_2, proton exchange with water), 7.96 (app t, *J* = 8.1 Hz, 1H, CH_{Ar}), 8.40 (dd, *J* = 3.6, 2.5 Hz, 1H, CH_{Ar}), 8.44 (br s, 1H, CH(thiazole)), 8.46-8.50 (m, 2H, CH), 8.59 (dd, *J* = 8.1, 1.7 Hz, 1H, CH_{Ar}), 8.72 (app t, *J* = 1.7 Hz, 1H, CH_{Ar}), 10.18 (s, 1H, H2(thiazole)).

^{13}C NMR (75 MHz, DMSO-d_6, DEPT-135): δ 123.0 (CH_{Ar}), 126.6 (CH(thiazole)), 129.1 (CH_{Ar}), 131.5 (CH_{Ar}), 134.8 (CH_{Ar}), 135.3 (C_{Ar}), 138.7 (CH(thiazole)), 148.5 (C_{Ar}-NO_2), 162.1 (CH(thiazole)), 190.0 (C=O).

HRMS (ESI): *m/z* calcd. for [$C_{11}H_9BrN_2O_3S$-Br]$^+$: 249.0328, found: 249.0339

3-(2-Ethoxy-2-oxoethyl)-1,3-thiazol-3-ium bromide 2d

Solution of thiazole (425 mg, 5 mmol) and ethyl bromoacetate (835 mg, 5 mmol) in toluene (5 ml) was heated at 100°C for 36 hours, then cooled to r. t. Mother liquor was removed and the precipitated slightly yellow oil was triturated with PhMe and dried in vacuo to give 1.04 g (82%) of **2d** as a slightly yellow semisolid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.21 (t, *J* = 7.1 Hz, 3H, CH_3), 4.19 (q, *J* = 7.1 Hz, 2H, O**CH_2**CH_3), 5.68 (s, 2H, N^+-CH_2), 8.39 (m, 1H, CH(thiazole)), 8.58 (d, *J* = 3.4 Hz, 1H, CH(thiazole)), 10.32 (s, 1H, H2(thiazole)).

^{13}C NMR (75 MHz, DMSO-d_6, DEPT-135): δ 14.4 (CH_3), 55.0 (N-CH_2), 62.3 (O**CH_2**CH_3), 126.8 (CH), 138.5 (CH), 162.1 (CH), 166.6 (**C**O_2Et).

HRMS (ESI): *m/z* calcd. for [$C_7H_{10}BrNO_2S$-Br]$^+$: 172.0427, found: 172.0424

3-[2-(Benzyloxy)-2-oxoethyl]-1,3-thiazol-3-ium bromide 2e

Solution of thiazole (255 mg, 3 mmol) and benzyl bromoacetate (687 mg, 3 mmol) in EtOAc (3 ml) was refluxed for 24 hours, then cooled to r. t. Precipitated solid was filtered and dried under air to give 735 mg (78%) of **2e** as a white solid.

mp = 109-112°C (EtOAc)

^{1}H NMR (300 MHz, DMSO-d_6): δ 5.23 (s, 2H, O-CH_2), 5.74 (s, 2H, N^+–CH_2), 7.30-7.42 (m, 5H, CH_{Ph}), 8.38 (s, *J* = 2.4 Hz, 1H, CH(thiazole)), 8.58 (d, *J* = 2.4 Hz, 1H, CH(thiazole)), 10.31 (s, 1H, H2(thiazole)).

^{13}C NMR (75 MHz, DMSO-d_6, DEPT-135): δ 55.0 (N-CH_2), 67.9 (O**CH_2**Ph), 126.8 (CH(thiazole)), 128.7 128.9 (CH_{Ph}), 129.0 (CH_{Ph}), 135.4 (C_{Ph}), 138.6 (CH(thiazole)), 162.3 (CH(thiazole)), 166.6 (**C**O_2Et).

HRMS (ESI): *m/z* calcd. for [$C_{12}H_{12}BrNO_2$ S-Br]$^+$: 234.0583, found: 234.0577

3-(2-Oxopropyl)-1,3-thiazol-3-ium chloride 2f

Solution of thiazole (255 mg, 3 mmol) and chloroacetone (278 mg, 3 mmol) in toluene (3 ml) was heated at 100°C for 24 hours, then maintained at r. t. for 8 hours. Precipitated material was filtered, washed with PhMe and dried under air to give 325 mg (61%) of **2f** as a brown solid.

mp = 132-133°C (dec.) (PhMe)

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.26 (s, 3H, Me), 5.80 (s, 2H, CH_2, proton exchange with water), 8.35 (br s, 1H, CH(thiazole)), 8.43 (br s, 1H, CH(thiazole)), 10.18 (s, 1H, H2(thiazole)).

^{13}C NMR (75 MHz, DMSO-d_6, DEPT-135): δ 27.5 (CH_3), 62.9 (N^+-CH_2), 126.4 (CH), 138.5 (CH), 161.5 (CH), 199.9 (C=O).

HRMS (ESI): *m/z* calcd. for $[C_6H_8ClNOS\text{-}Cl]^+$: 142.0321, found: 142.0331

Synthesis of indazolium salts **6a-6b**:

1-Methyl-2-(2-oxo-2-phenylethyl)-1*H*-indazol-2-ium bromide 6a

A solution of 1-methyl-1H-indazole (264 mg, 2 mmol) and 2-bromoacetophenone (398 mg, 2 mmol) in toluene (2 ml) was heated at 100°C for 2 days. The mixture was cooled down and the precipitated white solid **6a** (549 mg, 83%) was filtered, washed with toluene and dried under air.

mp = 189-192°C (EtOAc)

^{1}H NMR (300 MHz, DMSO-d_6): δ 4.27 (s, 3H, Me), 6.94 (s, 2H, CH_2, proton exchange with water), 7.57 (app t, *J* = 6.9 Hz, 1H, CH_{Ar}), 7.63-7.74 (m, 2H, CH_{Ar}), 7.82 (app t, *J* = 6.9 Hz, 1H, CH_{Ar}), 7.90-7.97 (m, 1H, CH_{Ar}), 8.05-8.23 (m, 4H, CH_{Ar}), 9.35 (s, 1H, H3(indazole)).

^{13}C NMR (75 MHz, DMSO-d_6, DEPT-135): δ 34.1 (N-Me), 58.1 (CH_2), 111.9 (CH), 119.4 (C_q), 123.7 (CH), 125.7 (CH), 129.1 (CH), 129.6 (CH), 133.8 (C_q), 133.9 (CH), 134.8 (CH), 135.4 (CH), 140.8 (C_q), 191.1 (C=O).

HRMS (ESI): *m/z* calcd. for $[C_{16}H_{15}N_2O]^+$: 251.1179, found: 251.1183

2-(2-Ethoxy-2-oxoethyl)-1-methyl-1*H*-indazol-2-ium bromide 6b

A solution of 1-methyl-1H-indazole (264 mg, 2 mmol) and ethyl bromoacetate (0.28 ml, 418 mg, 2.5 mmol) in toluene (2 ml) was heated at 100°C for 4 days. The mixture was cooled down and the precipitated white solid **6b** (281 mg, 47%) was filtered, washed with toluene and dried under air.

mp = 154-156°C (PhMe)

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.27 (s, 3H, -CH_2-**C**H_3), 4.29 (br s, 5H, N-Me + OCH_2-), 6.04 (s, 2H, N^+-CH_2), 7.56 (br s, 1H, CH_{Ar}), 7.89-7.97 (m, 1H, CH_{Ar}), 8.00-8.08 (m, 1H, CH_{Ar}), 8.18 (d, *J* = 7.7 Hz, 1H, CH_{Ar}), 9.36 (s, 1H, H3(indazole)).

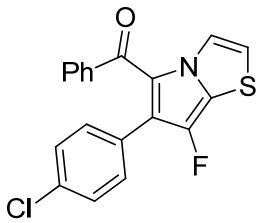
^{13}C NMR (75 MHz, DMSO-d_6, DEPT-135): δ 14.4 (-CH_2-**C**H_3), 34.1 (N-Me), 51.9 (N^+-CH_2-), 63.1 (**C**H_2CH_3), 111.9 (CH), 119.3 (C_q), 123.8 (CH), 125.9 (CH), 134.3 (CH), 135.0 (CH), 140.9 (C_q), 165.9 (**C**O_2Et).

HRMS (ESI): *m/z* calcd. for $[C_{12}H_{15}N_2O_2]^+$: 219.1128, found: 219.1125

General procedure 1 for the synthesis of 7-fluoropyrrolo[2,1-b]thiazoles **3**.

To the solution of thiazolium salt **2** (0.5 mmol, 2.5 equiv.) in dry DMSO (1 ml) powdered 4Å molecular sieves (100 mg) and 2,6-lutidine (107 mg, 1 mmol, 5 equiv.) were added, followed by addition of nitroalkene **1** (0.2 mmol, 1.0 equiv.) and $Cu(OCOCF_3)_2 \cdot H_2O$ (123 mg, 0.4 mmol, 2.0 equiv.) The mixture was stirred at r. t. for 1 h – 3 d. After the reaction was complete (TLC monitoring), it was quenched with EtOAc/1% aqueous Na_2EDTA solution (30/30 ml). Aqueous layer was extracted with 3*30 ml EtOAc. Combined organic layer was dried over anhydrous Na_2SO_4 and evaporated after addition of silica gel. Crude product was purified by column chromatography using PE/EtOAc as an eluent to give pyrrolo[2,1-b]thiazoles **3**.

[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-b][1,3]thiazol-5-yl](phenyl)methanone 3a



Pyrrolo[2,1-b]thiazole **3a** was obtained from α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 5 h). Column chromatography (eluent: 15:1 PE/EtOAc) afforded **3a** (44 mg, 62%) as a yellow solid.

R_f = 0.36 (PE/EtOAc, 3:1) (UV) mp = 128-129°C ($CHCl_3$)

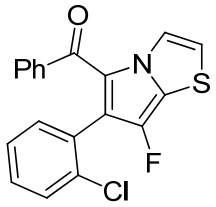
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (d, *J* = 4.2 Hz, 1H, H2), 6.97-7.03 (m, 4H, CH_{Ar}), 7.06 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.24 (m, 1H, CH_{Ar}), 7.33 – 7.39 (m, 2H, CH_{Ar}), 8.78 (dd, *J* = 4.2, 1.9 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 113.1 (C2-H), 117.2 (C5), 122.8 (d, $^2J_{CF}$ = 9.1 Hz, C6), 123.9 (C3-H), 124.1 (d, $^2J_{CF}$ = 27.0 Hz, C7a), 127.5 (CH_{Ar}), 127.9 (CH_{Ar}), 129.1 (CH_{Ar}), 129.3 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 131.0 (CH_{Ar}), 131.7 (d, $^4J_{CF}$ = 1.0 Hz, CH_{Ar}), 133.2 (C_{Ar}-Cl), 138.4 (C_{Ar}), 141.2 (d, $^1J_{CF}$ = 242.5 Hz, C7-F), 184.9 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -170.7 (d, *J* = 1.9 Hz).

HRMS (ESI): m/z calcd. for $[C_{19}H_{11}ClFNOS + H^+]$: 356.0307, found: 356.0302

[6-(2-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone 3b



Pyrrolo[2,1-b]thiazole **3b** was obtained from α-fluoronitroalkene **1b** (60.3 mg, 0.25 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 8 h). Column chromatography (eluent: 7:1 PE/EtOAc) afforded **3b** (76 mg, 71%) as a yellow solid.

R_f = 0.37 (PE/EtOAc, 3:1) (UV), mp = 167-168°C ($CHCl_3$)

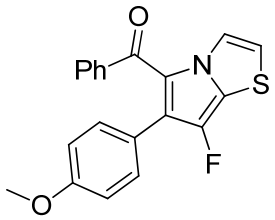
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.83-6.94 (m, 2H, CH_{Ar}), 6.96 (d, J = 4.1 Hz, 1H, H2), 6.98-7.05 (m, 3H, CH_{Ar}), 7.11-7.17 (m, 1H, CH_{Ar}), 7.21 (dd, J = 8.0, 0.7 Hz, 1H, CH_{Ar}), 7.36-7.43 (m, 2H, CH_{Ar}), 8.81 (dd, J = 4.1, 1.8 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 113.3 (C2-H), 117.6 (C5), 120.8 (d, $^2J_{CF}$ = 10.5 Hz, C6), 123.9 (d, $^2J_{CF}$ = 28.2 Hz, C7a), 124.0 (C3-H), 126.0 (CH_{Ar}), 127.2 (CH_{Ar}), 128.6 (CH_{Ar}), 129.0 (CH_{Ar}), 129.1 (CH_{Ar}), 130.4 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 130.7 (CH_{Ar}), 133.2 (CH_{Ar}), 134.2 (C_{Ar}-Cl), 138.6 (C_{Ar}), 141.5 (d, $^1J_{CF}$ = 243.2 Hz, C7-F), 185.0 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -166.1 (d, J = 1.8 Hz).

HRMS (ESI): m/z calcd. for [$C_{19}H_{11}ClFNOS + H^+$]: 356.0307, found: 356.0304.

[7-Fluoro-6-(4-methoxyphenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone 3c



Pyrrolo[2,1-b]thiazole **3c** was obtained from α-fluoronitroalkene **1c** (39.4 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 2 days). Column chromatography (eluent: 7:1 to 3:1 PE/EtOAc) afforded **3c** (47.5 mg, 53%) as a yellow solid.

R_f = 0.34 (PE/EtOAc, 3:1) (UV), mp = 126-129°C ($CHCl_3$)

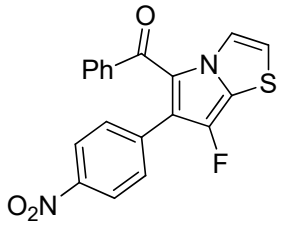
^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 3.71 (s, 3H, OMe), 6.55-6.61 (m, 2H, CH_{Ar}), 6.90 (d, J = 4.1 Hz, 1H, H2), 6.93-7.07 (m, 4H, CH_{Ar}), 7.16-7.22 (m, 1H, CH_{Ar}), 7.36-7.42 (m, 2H, CH_{Ar}), 8.77 (dd, J = 4.1, 1.9 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135, HSQC, HMBC): δ 55.2 (OMe), 112.5 (C2-H), 113.3 (CH_{Ar}), 117.3 (C5), 123.1 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 124.0 (C3-H), 124.0 (d, $^2J_{CF}$ = 9.1 Hz, C6), 124.1 (d, $^2J_{CF}$ = 28.3 Hz, C7a), 127.4 (CH_{Ar}), 129.2 (CH_{Ar}), 130.7 (CH_{Ar}), 131.7 (d, $^4J_{CF}$ = 0.9 Hz, CH_{Ar}), 138.6 (C_{Ar}), 141.4 (d, $^1J_{CF}$ = 241.0 Hz, C7-F), 158.7 (**C_{Ar}**-OMe), 185.1 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -171.1 (s).

HRMS (ESI): m/z calcd. for [$C_{20}H_{14}FNO_2S + H^+$]: 352.0802, found: 352.0803.

[7-Fluoro-6-(4-nitrophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone 3d



Pyrrolo[2,1-b]thiazole **3d** was obtained from α-fluoronitroalkene **1d** (42.4 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 3 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3d** (26 mg, 34%) as a bright yellow solid.

R_f = 0.30 (PE/EtOAc, 3:1) (UV), mp = 163-164°C ($CHCl_3$)

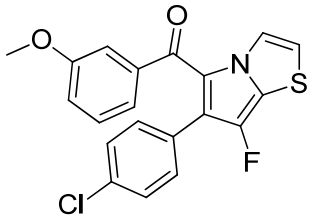
^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.01 (d, *J* = 4.2 Hz, 1H, H2), 7.04 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.17-7.24 (m, 3H, CH_{Ar}), 7.33-7.39 (m, 2H, CH_{Ar}), 7.91 (d, *J* = 8.8 Hz, 2H, CH_{Ar}), 8.79 (dd, *J* = 4.2, 1.9 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1 (C2-H), 117.1 (C5), 121.3 (d, $^2J_{CF}$ = 8.7 Hz, C6), 122.7 (CH_{Ar}), 123.8 (C3-H), 124.2 (d, $^2J_{CF}$ = 28.0 Hz, C7a), 127.7 (CH_{Ar}), 129.1 (CH_{Ar}), 131.2 (d, $^4J_{CF}$ = 1.0 Hz, CH_{Ar}), 131.4 (CH_{Ar}), 137.8 (d, $^3J_{CF}$ = 2.6 Hz, C_{Ar}), 138.3 (C_{Ar}), 141.2 (d, $^1J_{CF}$ = 244.5 Hz, C7-F), 146.4 (C_{Ar}-NO_2), 184.7 (d, $^4J_{CF}$ = 2.7 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -170.1 (m).

HRMS (ESI): m/z calcd. for [$C_{19}H_{11}FN_2O_3S + H^+$]: 367.0547, found: 367.0550.

[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](3-methoxyphenyl)methanone 3e



Pyrrolo[2,1-b]thiazole **3e** was obtained from α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2b** (2.5 equiv.) following the general procedure 1 (reaction time 3 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3e** (50 mg, 65%) as an amorphous yellow solid.

R_f = 0.31 (PE/EtOAc, 3:1) (UV)

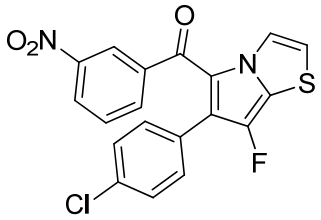
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H, OMe), 6.79 (m, 1H, CH_{Ar}), 6.88 (br s, 1H, CH_{Ar}), 6.94 (d, *J* = 4.1 Hz, 1H, H2), 6.96-7.07 (m, 6H, CH_{Ar}), 8.77 (dd, *J* = 4.1, 1.8 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2 (OMe), 113.2 (CH_{Ar}), 114.1 (C2-H), 117.2 (C5, overlapped signal), 117.2 (CH_{Ar}), 121.8 (CH_{Ar}), 122.7 (d, $^2J_{CF}$ = 9.0 Hz, C6), 124.0 (C3-H), 124.2 (d, $^2J_{CF}$ = 28.4 Hz, C7a), 127.8 (CH_{Ar}), 128.7 (CH_{Ar}), 129.4 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 131.5 (d, $^4J_{CF}$ = 0.9 Hz, CH_{Ar}), 133.2 (C_{Ar}-Cl), 139.7 (C_{Ar}), 141.2 (d, $^1J_{CF}$ = 242.5 Hz, C7-F), 158.9 (**C**$_{Ar}$-OMe), 184.6 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -170.6 (s).

HRMS (ESI): m/z calcd. for [$C_{20}H_{13}ClFNO_2S + H^+$]: 386.0412, found: 386.0411.

[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](3-nitrophenyl)methanone 3f



Pyrrolo[2,1-b]thiazole **3f** was obtained from α-fluoronitroalkene **1a** (50.4 mg, 0.25 mmol) and thiazolium salt **2c** (2.5 equiv.) following the general procedure 1 (reaction time 1 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3f** (41 mg, 41%) as a bright yellow solid.

R_f = 0.20 (PE/EtOAc, 3:1) (UV) mp = 213-215°C ($CHCl_3$)

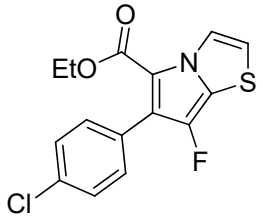
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94-7.02 (m, 4H, CH_{Ar}), 7.04 (d, *J* = 4.1 Hz, 1H, H2), 7.32 (dd, *J* = 8.7, 7.7 Hz, 1H, CH_{Ar}), 7.75 (d, *J* = 7.7 Hz, 1H, CH_{Ar}), 8.05-8.14 (m, 2H, CH_{Ar}), 8.82 (dd, *J* = 4.1, 1.8 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1 (C2-H), 116.7 (C5), 123.1 (d, $^2J_{CF}$ = 9.6 Hz, C6), 124.0 (C3-H), 124.5 (CH_{Ar}), 125.1 (CH_{Ar}), 125.9 (d, $^2J_{CF}$ = 28.0 Hz, C7a), 128.1 (CH_{Ar}), 128.6 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 128.9 (CH_{Ar}), 131.8 (br s, CH_{Ar}), 133.9 (C_{Ar}-Cl), 134.4 (CH_{Ar}), 139.9 (C_{Ar}), 141.4 (d, $^1J_{CF}$ = 243.8 Hz, C7-F), 147.0 (C_{Ar}-NO_2), 181.5 (d, $^4J_{CF}$ = 3.0 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -169.5 (s).

HRMS (ESI): m/z calcd. for [$C_{19}H_{10}ClFN_2O_3S + H^+$]: 401.0157, found: 401.0149.

Ethyl 6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazole-5-carboxylate 3g



Pyrrolo[2,1-b]thiazole **3g** was obtained from α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2d** (3.0 equiv.) following the general procedure 1 (reaction time 2 days). Column chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **3g** (36 mg, 57%) as a white solid.

R_f = 0.47 (PE/EtOAc, 3:1) (UV), mp = 102-103°C ($CHCl_3$)

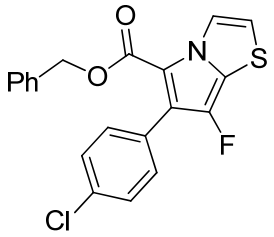
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.1 Hz, 3H, CH_3), 4.22 (q, *J* = 7.1 Hz, 2H, CH_2), 6.84 (d, *J* = 4.2 Hz, 1H, H2), 7.36-7.45 (m, 4H, CH_{Ar}), 8.43 (dd, *J* = 4.2, 1.9 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 (CH_3), 60.1 (CH_2), 108.0 (d, $^{3}J_{CF}$ = 1.5 Hz, C5), 112.3 (C2-H), 121.1 (d, $^{2}J_{CF}$ = 28.1 Hz, C7a), 121.8 (d, $^{2}J_{CF}$ = 10.0 Hz, C6), 123.3 (C3-H), 127.8 (CH_{Ar}), 129.4 (d, $^{3}J_{CF}$ = 2.4 Hz, C_{Ar}), 131.9 (d, $^{4}J_{CF}$ = 1.0 Hz, CH_{Ar}), 133.6 (C_{Ar}-Cl), 141.2 (d, $^{1}J_{CF}$ = 240.3 Hz, C7-F), 160.7 (d, $^{4}J_{CF}$ = 2.7 Hz, **C**O_2Et).

^{19}F NMR (282 MHz, $CDCl_3$): δ -171.1 (br s).

HRMS (ESI): m/z calcd. for [$C_{15}H_{11}ClFNO_2S + Na^+$]: 346.0075, found: 346.0069.

Benzyl 6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazole-5-carboxylate 3h



Pyrrolo[2,1-b]thiazole **3h** was obtained from α-fluoronitroalkene **1a** (30.3 mg, 0.15 mmol) and thiazolium salt **2e** (3.5 equiv.) following the general procedure 1 (reaction time 3 days). Column chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **3h** (28.5 mg, 50%) as a white solid.

R_f = 0.65 (PE/EtOAc, 3:1) (UV), mp = 101-103°C ($CHCl_3$)

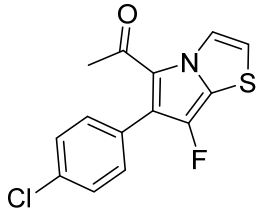
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.18 (s, 2H, CH_2), 6.84 (d, *J* = 4.2 Hz, 1H, H2), 7.08 (dd, *J* = 6.5, 2.9 Hz, 2H, CH_{Ar}), 7.26-7.32 (m, 5H, CH_{Ar}), 7.36 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 8.44 (dd, *J* = 4.2, 1.9 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 65.9 (CH_2), 107.8 (d, $^{3}J_{CF}$ = 1.7 Hz, C5), 112.5 (C2-H), 121.6 (d, $^{2}J_{CF}$ = 28.1 Hz, C7a), 122.1 (d, $^{2}J_{CF}$ = 10.6 Hz, C6), 123.3 (C3-H), 127.9 (CH_{Ar}), 128.0 (CH_{Ar}), 128.1 (CH_{Ar}), 128.4 (CH_{Ar}), 129.3 (d, $^{3}J_{CF}$ = 2.2 Hz, C_{Ar}), 131.9 (d, $^{4}J_{CF}$ = 0.9 Hz, CH_{Ar}), 133.7 (C_{Ar}-Cl), 135.5 (C_{Ar}), 141.2 (d, $^{1}J_{CF}$ = 240.4 Hz, C7-F), 160.5 (d, $^{4}J_{CF}$ = 2.9 Hz, **C**O_2Et).

^{19}F NMR (282 MHz, $CDCl_3$): δ -171.4 (br s).

HRMS (ESI): m/z calcd. for [$C_{20}H_{13}ClFNO_2S + H^+$]: 386.0412, found: 386.0418.

1-[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl]ethan-1-one 3i



Pyrrolo[2,1-b]thiazole **3i** was obtained from α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2f** (3.0 equiv.) following the general procedure 1 (reaction time 48 h). Column

chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **3i** (26.5 mg, 44%) as a colorless oil, which solidifies upon storage in a refrigerator.

R_f = 0.35 (PE/EtOAc, 3:1) (UV)

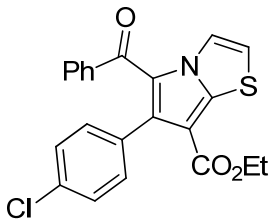
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 3H, Me), 6.89 (d, *J* = 4.1 Hz, 1H, H2), 7.36-7.39 (m, 2H, CH_{Ar}), 7.45-7.48 (m, 2H, CH_{Ar}), 8.82 (dd, *J* = 4.1, 1.8 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3 (Me), 112.9 (C2-H), 118.3 (C5), 122.0 (d, $^2J_{CF}$ = 10.3 Hz, C6), 123.3 (d, $^2J_{CF}$ = 28.1 Hz, C7a), 124.3 (C3-H), 128.8 (CH_{Ar}), 129.8 (d, $^3J_{CF}$ = 1.9 Hz, C_{Ar}), 131.8 (br s, CH_{Ar}), 134.7 (C_{Ar}-Cl), 141.5 (d, $^1J_{CF}$ = 241.0 Hz, C7-F), 186.2 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -171.0 (d, *J* = 1.8 Hz).

HRMS (ESI): m/z calcd. for [$C_{14}H_9ClFNOS + H^+$]: 293.0072, found: 293.0068.

Ethyl 5-benzoyl-6-(4-chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate 4a



Pyrrolo[2,1-b]thiazole **4a** was obtained from nitroalkene **1e** (37 mg, 0.145 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 10 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3k** (39 mg, 66%) as a slightly yellow solid.

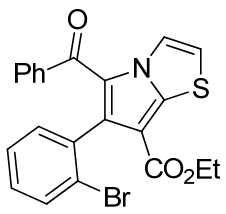
R_f = 0.33 (PE/EtOAc, 3:1) (UV), mp = 158-161°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.1 Hz, 3H, CH_3), 4.24 (q, *J* = 7.1 Hz, 2H, CH_2), 6.92-6.98 (m, 2H, CH_{Ar}), 6.99-7.07 (m, 4H, CH_{Ar}), 7.13 (d, *J* = 4.2 Hz, 1H, H2), 7.20-7.32 (m, 3H, CH_{Ar}), 8.74 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (CH_3), 60.3 (CH_2), 105.3 (C7), 115.4 (C2-H), 123.9 (C_q), 124.3 (C3-H), 127.0 (CH_{Ar}), 127.5 (CH_{Ar}), 128.8 (CH_{Ar}), 130.9 (CH_{Ar}), 131.4 (C_q), 132.5 (CH_{Ar}), 133.5 (C_q), 138.0 (C_q), 138.1 (C_q), 144.7 (C_q), 162.9 (**C**O_2Et), 186.8 (**C**OPh).

HRMS (ESI): m/z calcd. for [$C_{22}H_{16}ClNO_3S + H^+$]: 410.0612, found: 410.0604.

Ethyl 5-benzoyl-6-(2-bromophenyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate 4b



Pyrrolo[2,1-b]thiazole **4b** was obtained from α-fluoronitroalkene **1f** (60 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 5 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **4b** (72 mg, 79%) as a slightly yellow solid.

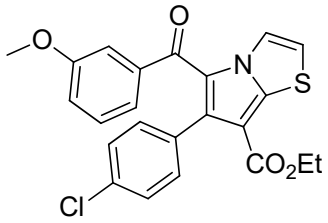
R_f = 0.35 (PE/EtOAc, 3:1) (UV), mp = 123-126°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (t, *J* = 7.1 Hz, 3H, CH_3), 4.06-4.28 (m, 2H, CH_2), 6.89-6.91 (m, 3H, CH_{Ar}), 7.03 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 4.2 Hz, 1H, H2), 7.12-7.18 (m, 1H, CH_{Ar}), 7.32-7.36 (m, 1H, CH_{Ar}), 7.40-7.44 (m, 2H, CH_{Ar}), 8.77 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0 (CH_3), 60.2 (CH_2), 106.3 (C7), 115.3 (C2-H), 123.7 (C_q), 124.4 (C3-H), 125.1 (C_{Ar}-Br), 126.0 (CH_{Ar}), 127.2 (CH_{Ar}), 128.2 (CH_{Ar}), 128.8 (CH_{Ar}), 130.8 (CH_{Ar}), 131.7 (CH_{Ar}), 132.4 (CH_{Ar}), 134.9 (C_q), 137.1 (C_q), 138.5 (C_q), 144.3 (C_q), 162.9 (**C**O_2Et), 186.6 (**C**OPh).

HRMS (ESI): m/z calcd. for [$C_{22}H_{16}BrNO_3S$ + H^+]: 454.0107, found: 454.0098.

Ethyl 6-(4-chlorophenyl)-5-(3-methoxybenzoyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate 4c



Pyrrolo[2,1-b]thiazole **4c** was obtained from α-fluoronitroalkene **1e** (35 mg, 0.137 mmol) and thiazolium salt **2b** (2.5 equiv.) following the general procedure 1 (reaction time 4 h). Column chromatography (eluent: 4:1 PE/EtOAc) afforded **4c** (41 mg, 68%) as an amorphous slightly yellow solid.

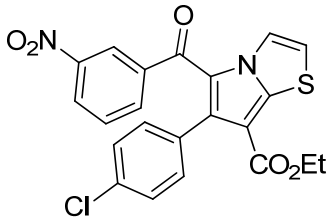
R_f = 0.26 (PE/EtOAc, 3:1) (UV).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.1 Hz, 3H, CH_3), 3.69 (s, 3H, OMe), 4.23 (q, *J* = 7.1 Hz, 2H, CH_2), 6.74-6.80 (m, 1H, CH_{Ar}), 6.89 (dt, *J* = 7.5, 1.2 Hz, 1H, CH_{Ar}), 6.93-7.06 (m, 5H, CH_{Ar}), 7.12 (d, *J* = 4.2 Hz, 1H, H2), 8.73 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3), 55.2 (OMe), 60.3 (CH_2), 105.3 (C7), 114.0 (CH_{Ar}), 115.4 (C2-H), 116.7 (CH_{Ar}), 121.3 (CH_{Ar}), 123.8 (C_q), 124.3 (C3-H), 127.0 (CH_{Ar}), 128.8 (CH_{Ar}), 131.5 (C_q), 132.2 (CH_{Ar}), 133.4 (C_q), 138.1 (C_q), 139.5 (C_q), 144.7 (C_q), 158.6 (**C$_{Ar}$**-OMe), 162.9 (**C**O_2Et), 186.4 (**C**OPh).

HRMS (ESI): m/z calcd. for [$C_{23}H_{18}ClNO_4S$ + H^+]: 410.0612, found: 410.0604.

Ethyl 6-(4-chlorophenyl)-5-(3-nitrobenzoyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate 4d



Pyrrolo[2,1-b]thiazole **4d** was obtained from α-fluoronitroalkene **1e** (44 mg, 0.172 mmol) and thiazolium salt **2c** (2.5 equiv.) following the general procedure 1 (reaction time 2 h). Column chromatography (eluent: 4:1 PE/EtOAc) afforded **4d** (36.5 mg, 51%) as a dark yellow solid.

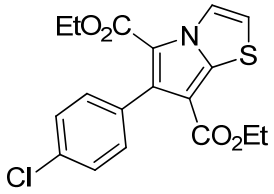
R_f = 0.19 (PE/EtOAc, 3:1) (UV), mp = 172-175°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, *J* = 7.1 Hz, 3H, CH_3), 4.23 (q, *J* = 7.1 Hz, 2H, CH_2), 6.94 (d, *J* = 8.4 Hz, 2H, CH_{Ar}), 7.00-7.06 (m, 2H, CH_{Ar}), 7.20 (d, *J* = 4.2 Hz, 1H, H2), 7.32 (t, *J* = 7.9 Hz, 1H, CH_{Ar}), 7.70 (app dt, *J* = 7.7, 1.3 Hz, 1H, CH_{Ar}), 7.99 (t, *J* = 1.8 Hz, 1H, CH_{Ar}), 8.09 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H, CH_{Ar}), 8.78 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3), 60.5 (CH_2), 106.1 (C7), 116.1 (C2-H), 123.3 (C_q), 124.1 (CH), 124.3 (CH), 125.0 (CH), 127.2 (CH_{Ar}), 128.9 (CH_{Ar}), 131.1 (C_q), 132.4 (CH_{Ar}), 133.9 (C_q), 134.0 (CH_{Ar}), 138.7 (C_q), 139.7 (C_q), 145.5 (C_q), 146.9 (C_{Ar}-NO_2), 162.6 (**C**O_2Et), 183.5 (**C**OPh).

HRMS (ESI): m/z calcd. for [$C_{22}H_{15}ClN_2O_5S + H^+$]: 455.0463, found: 455.0454.

Diethyl 6-(4-chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazole-5,7-dicarboxylate 4e



Pyrrolo[2,1-b]thiazole **4e** was obtained from nitroalkene **1e** (51.6 mg, 0.2 mmol) and thiazolium salt **2d** (3.0 equiv.) following the general procedure 1 (reaction time 2 days). Column chromatography (eluent: 19:1 to 5:1 PE/EtOAc) afforded **4e** (37.5 mg, 47%) as a white solid.

R_f = 0.38 (PE/EtOAc, 3:1) (UV), mp = 114-115°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (t, *J* = 7.1 Hz, 3H, CH_3), 1.20 (t, *J* = 7.1 Hz, 3H, CH_3), 4.13 (q, *J* = 7.1 Hz, 2H, CH_2), 4.19 (q, *J* = 7.1 Hz, 2H, CH_2), 7.05 (d, *J* = 4.2 Hz, 1H, H2), 7.27-7.38 (m, 4H, CH_{Ar}), 8.48 (d, *J* = 4.2 Hz, 1H, H3).

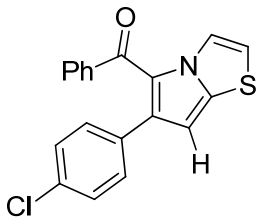
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8 (CH_3), 14.2 (CH_3), 60.1 (CH_2), 60.3 (CH_2), 105.7 (C7), 114.9 (C2-H), 115.0 (C_q), 123.6 (C3-H), 127.1 (CH_{Ar}), 131.4 (CH_{Ar}), 132.7 (C_q), 133.3 (C_q), 137.0 (C_q), 142.6 (C_q), 160.7 (**C**O_2Et), 163.0 (**C**O_2Et).

HRMS (ESI): m/z calcd. for [$C_{18}H_{16}ClNO_4S + H^+$]: 378.0561, found: 378.0560.

General procedure 2 for the synthesis of 7-unsubstituted pyrrolo[2,1-b]thiazoles **5**

To the solution of thiazolium salt **2** (0.5 mmol, 2.5 equiv.) in dry MeCN (1 ml) powdered 4Å molecular sieves (100 mg) and 2,6-lutidine (107 mg, 1 mmol, 5 equiv.) were added, followed by addition of nitroalkene **1** (0.2 mmol, 1.0 equiv.) and $Cu(OCOCF_3)_2 \cdot H_2O$ (92 mg, 0.3 mmol, 1.5 equiv.) The mixture was stirred at r. t. for 5-24 hours. After the reaction was complete (TLC monitoring), it was evaporated after addition of silica gel. Crude product was purified by column chromatography using PE/EtOAc as an eluent to give pyrrolo[2,1-b]thiazoles **5**.

[6-(4-Chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone 5a



Pyrrolo[2,1-b]thiazole **5a** was obtained from nitroalkene **1g** (37 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 2 (reaction time 5 h). Column chromatography (eluent: 15:1 to 5:1 PE/EtOAc) afforded **5a** (32 mg, 53%) as a slightly yellow solid.

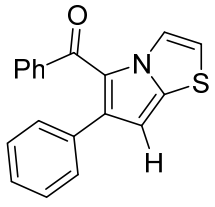
R_f = 0.41 (PE/EtOAc, 3:1) (UV), mp = 141-142°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 6.42 (s, 1H, H7), 6.93-6.98 (m, 5H, CH_{Ar}, H2), 7.02-7.08 (m, 2H, CH_{Ar}), 7.20-7.27 (m, 1H, CH_{Ar}), 7.37-7.41 (m, 2H, CH_{Ar}), 8.75 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ 101.7 (C7-H), 113.1 (C2-H), 121.4 (C6), 124.0 (C3-H), 127.5 (CH_{Ar}), 127.7 (CH_{Ar}), 129.2 (CH_{Ar}), 130.8 (CH_{Ar}), 130.9 (CH_{Ar}), 132.7 (C_{Ar}-Cl), 134.2 (C_{Ar}), 138.9 (C_q), 139.0 (C_q), 139.1 (C_q), 185.1 (C=O).

HRMS (ESI): m/z calcd. for [$C_{19}H_{12}ClNOS + H^+$]: 338.0401, found: 338.0396.

Phenyl(6-phenylpyrrolo[2,1-*b*][1,3]thiazol-5-yl)methanone 5b



Pyrrolo[2,1-b]thiazole **5b** was obtained from nitroalkene **1h** (37 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 2 (reaction time 5 h). Column chromatography (eluent: 15:1 to 7:1 PE/EtOAc) afforded **5b** (44 mg, 58%) as a slightly yellow solid.

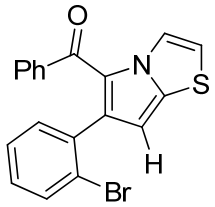
R_f = 0.46 (PE/EtOAc, 3:1) (UV) mp = 106-109°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 1H, H7), 6.93 (d, *J* = 4.2 Hz, 1H, H2), 6.98-7.07 (m, 7H, CH_{Ar}), 7.12-7.20 (m, 1H, CH_{Ar}), 7.38-7.44 (m, 2H, CH_{Ar}), 8.77 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ 101.8 (C7-H), 112.8 (C2-H), 121.4 (C6), 124.0 (C3-H), 126.6 (CH_{Ar}), 127.3 (CH_{Ar}), 127.5 (CH_{Ar}), 129.3 (CH_{Ar}), 129.8 (CH_{Ar}), 130.6 (CH_{Ar}), 135.6 (C_{Ar}), 139.0 (C_q), 139.1 (C_q), 140.4 (C_q), 185.3 (C=O).

HRMS (ESI): m/z calcd. for [$C_{19}H_{13}NOS + H^+$]: 304.0791, found: 304.0802.

[6-(2-Bromophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone 5c



Pyrrolo[2,1-b]thiazole **5c** was obtained from nitroalkene **1j** (45.6 mg, 0.2 mmol) and thiazolium salt **2b** (2.5 equiv.) following the general procedure 2 (reaction time 6 h). Column chromatography (eluent: 15:1 to 7:1 PE/EtOAc) afforded **5c** (49 mg, 64%) as a slightly yellow oil, which solidifies upon storage in a refrigerator.

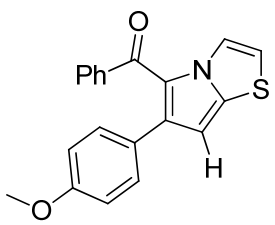
R_f = 0.38 (PE/EtOAc, 3:1) (UV)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.44 (s, 1H, H7), 6.86-7.04 (m, 6H, CH_{Ar}), 7.10-7.16 (m, 1H, CH_{Ar}), 7.34 (dd, *J* = 6.9, 1.7 Hz, CH_{Ar}), 7.42 (d, *J* = 7.3 Hz, 2H), 8.79 (d, *J* = 4.1 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 103.0 (C7-H), 113.2 (C2-H), 122.0 (C6), 123.8 (C_{Ar}-Br), 124.0 (C3-H), 126.3 (CH_{Ar}), 127.1 (CH_{Ar}), 128.5 (CH_{Ar}), 128.7 (CH_{Ar}), 130.4 (CH_{Ar}), 132.3 (CH_{Ar}), 132.8 (CH_{Ar}), 136.7 (C_{Ar}), 137.9 (C_q), 138.9 (C_q), 139.0 (C_q), 185.0 (C=O).

HRMS (ESI): m/z calcd. for [$C_{19}H_{12}BrNOS + H^+$]: 381.9896, found: 381.9894.

[6-(4-Methoxyphenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone 5d



Pyrrolo[2,1-b]thiazole **5d** was obtained from nitroalkene **1i** (35 mg, 0.2 mmol) and thiazolium salt **2a** (3.0 equiv.) following the general procedure 2 (reaction time 24 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **5d** (31 mg, 47%) as an amorphous yellow solid.

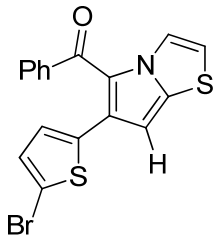
R_f = 0.34 (PE/EtOAc, 3:1) (UV)

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 3H, OMe), 6.41 (s, 1H, H7), 6.55 (d, *J* = 8.8 Hz, 2H, CH_{Ar}), 6.91 (d, *J* = 4.2 Hz, 1H, H2), 6.96 (d, *J* = 8.8 Hz, 2H, CH_{Ar}), 7.03 (t, *J* = 7.6 Hz, 2H), 7.15-7.21 (m, 1H, CH_{Ar}), 7.38-7.43 (m, 2H, CH_{Ar}), 8.75 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2 (OMe), 101.7 (C7-H), 112.5 (C2-H), 113.1 (CH_{Ar}), 121.4 (C6), 124.0 (C3-H), 127.3 (CH_{Ar}), 128.1 (C_{Ar}), 129.3 (CH_{Ar}), 130.5 (CH_{Ar}), 130.9 (CH_{Ar}), 139.0 (C_q), 139.1 (C_q), 140.2 (C_q), 158.5 (**C_{Ar}**-OMe), 185.2 (C=O).

HRMS (ESI): m/z calcd. for [$C_{20}H_{15}NO_2S$ + H^+]: 334.0896, found: 334.0900.

[6-(5-Bromothiophen-2-yl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone 5e



Pyrrolo[2,1-b]thiazole **5e** was obtained from nitroalkene **1k** (46.8 mg, 0.2 mmol) and thiazolium salt **2a** (3.0 equiv.) following the general procedure 2 (reaction time 24h). Column chromatography (eluent: 9:1 PE/EtOAc) afforded **5e** (43 mg, 56%) as a slightly yellow solid.

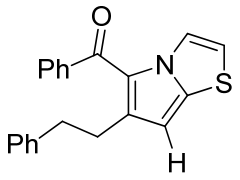
R_f = 0.44 (PE/EtOAc, 3:1) (UV), mp = 119-123°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 6.21 (d, *J* = 3.8 Hz, 1H, thiophene), 6.44 (s, 1H, H7), 6.57 (d, *J* = 3.8 Hz, 1H, thiophene), 6.95 (d, *J* = 4.2 Hz, 1H, H2), 7.19 (t, *J* = 7.6 Hz, 2H, CH_{Ar}), 7.30-7.37 (m, 1H, CH_{Ar}), 7.50-7.55 (m, 2H, CH_{Ar}), 8.68 (d, *J* = 4.2 Hz, 1H, H3).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC): δ 102.3 (C7-H), 112.1 (C(thiophene)-Br), 113.5 (C2-H), 121.5 (C6), 123.8 (C3-H), 127.8 (CH_{Ph}), 128.2 (CH(thiophene)), 128.9 (CH_{Ph}), 129.5 (CH(thiophene), 130.6 (C_q(thiophene)), 131.1 (CH_{Ph}), 138.5 (C_q), 139.0 (C_q), 139.1 (C_q), 185.0 (C=O).

HRMS (ESI): m/z calcd. for [$C_{17}H_{10}BrNOS_2$ + H^+]: 387.9460, found: 387.9468.

Phenyl[6-(2-phenylethyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl]methanone 5f



Pyrrolo[2,1-b]thiazole **5f** was obtained from α-fluoronitroalkene **1l** (35.4 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 2 (reaction time 24 h). Column

chromatography (eluent: 9:1 PE/EtOAc) afforded **5f** (30.5 mg, 45%) as a slightly yellow oil, which solidifies upon storage in a refrigerator.

R_f = 0.34 (PE/EtOAc, 3:1) (UV)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54-2.73 (m, 4H, 2*CH_2), 6.27 (s, 1H, H7), 6.82 (d, *J* = 6.4 Hz, 2H, CH_{Ar}), 6.85 (d, *J* = 4.3 Hz, 1H, H2), 7.09-7.21 (m, 3H, CH_{Ar}), 7.42-7.55 (m, 3H, CH_{Ar}), 7.61-7.66 (m, 2H, CH_{Ar}), 8.59 (d, *J* = 4.2 Hz, 1H, H3).

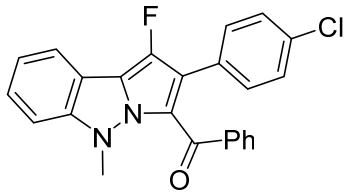
^{13}C NMR (75 MHz, $CDCl_3$): δ 30.6 (CH_2), 37.9 (CH_2), 101.7 (C7-H), 112.1 (C2-H), 122.5 (C6), 124.1 (C3-H), 125.8 (CH_{Ar}), 128.0 (CH_{Ar}), 128.2 (CH_{Ar}), 128.4 (CH_{Ar}), 130.7 (CH_{Ar}), 139.6 (C_q), 140.1 (2*C_q), 141.1 (C_q), 141.2 (C_q), 184.9 (C=O).

HRMS (ESI): m/z calcd. for [$C_{21}H_{17}NOS + H^+$]: 332.1104, found: 332.1102.

General procedure 3 for the synthesis of pyrrolo[1,2-b]indazoles **7**.

To the solution of indazolium salt **6** (0.25 mmol, 2.5 equiv.) in dry DMSO (0.5 ml) powdered 4Å molecular sieves (100 mg) and 2,6-lutidine (54 mg, 0.5 mmol, 5 equiv.) were added, followed by addition of nitroalkene **1** (0.1 mmol, 1.0 equiv.) and $Cu(OCOCF_3)_2 \cdot H_2O$ (62 mg, 0.2 mmol, 2.0 equiv.) The mixture was stirred at r. t. for 24 hours (for **7c** and **7f** – 3 days). After the reaction was complete (TLC monitoring), it was quenched with EtOAc/1% aqueous Na_2EDTA solution (20+20 ml). Aqueous layer was extracted by EtOAc (3*20 ml). Combined organic layer was dried over anhydrous Na_2SO_4 and evaporated after addition of silica gel. Crude product was purified by column chromatography using PE/EtOAc as an eluent to give pyrrolo[1,2-b]indazoles **7**.

[2-(4-Chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone 7a



Pyrrolo[1,2-b]indazole **7a** was obtained from α-fluoronitroalkene **1a** (20 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3. Column chromatography (eluent: 19:1 to 7:1 PE/EtOAc) afforded **7a** (28 mg, 70%) as a bright yellow solid.

R_f = 0.53 (PE/EtOAc, 3:1) (UV), mp = 178-179°C ($CHCl_3$)

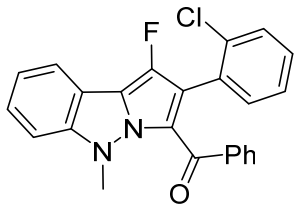
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 3H, N-Me), 7.02 (s, 4H, CH_{Ar}), 7.10 (t, *J* = 7.7 Hz, 2H), 7.26-7.35 (m, 3H, CH_{Ar}), 7.44-7.50 (m, 1H, CH_{Ar}), 7.51-7.56 (m, 2H, CH_{Ar}), 7.84 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 41.8 (N-Me), 111.5 (CH), 115.6 (C3), 116.8 (d, $^3J_{CF}$ = 2.9 Hz, C9a), 119.3 (d, $^2J_{CF}$ = 9.4 Hz, C2), 120.4 (C9-H), 121.2 (d, $^2J_{CF}$ = 28.5 Hz, C9b), 123.4 (CH), 127.6 (CH), 127.7 (CH_{Ar}), 127.8 (CH_{Ar}), 129.6 (CH_{Ar}), 129.7 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 131.6 (CH_{Ar}), 131.9 (d, $^4J_{CF}$ = 0.7 Hz, CH_{Ar}), 132.8 (C_{Ar}-Cl), 137.5 (d, $^1J_{CF}$ = 242.8 Hz, C1-F), 138.8 (C_{Ph}), 149.0 (C5a), 183.8 (d, $^4J_{CF}$ = 2.4 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -172.4 (s).

HRMS (ESI): m/z calcd. for [$C_{24}H_{16}ClFN_2O + H^+$]: 403.1008, found: 403.0998.

[2-(2-Chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone 7b



Pyrrolo[1,2-b]indazole **7b** was obtained from α-fluoronitroalkene **1b** (20 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3. Column chromatography (eluent: 19:1 to 7:1 PE/EtOAc) afforded **7b** (33 mg, 82%) as a bright yellow solid

R_f = 0.40 (PE/EtOAc, 3:1) (UV), mp = 176-177°C ($CHCl_3$)

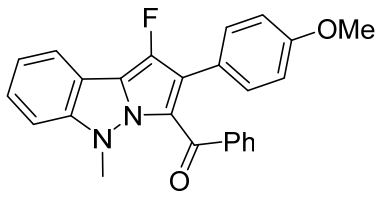
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, N-Me), 6.85-6.92 (m, 1H, CH_{Ar}), 6.96-7.11 (m, 4H, CH_{Ar}), 7.15-7.22 (m, 2H, CH_{Ar}), 7.29-7.33 (m, 1H, CH_{Ar}), 7.35 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.48 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H, CH_{Ar}), 7.53-7.56 (m, 2H, CH_{Ar}), 7.85 (d, *J* = 7.7 Hz, 1H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ 41.3 (N-Me), 111.2 (CH), 115.7 (d, $^3J_{CF}$ = 0.9 Hz, C3), 116.8 (d, $^3J_{CF}$ = 2.9 Hz, C9a), 117.3 (d, $^2J_{CF}$ = 10.8 Hz, C2), 120.4 (C9-H), 121.1 (d, $^2J_{CF}$ = 28.6 Hz, C9b), 123.3 (CH), 125.8 (CH), 127.3 (CH), 127.6 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 130.8 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 131.3 (CH), 133.5 (CH), 134.5 (C_{Ar}-Cl), 137.8 (d, $^1J_{CF}$ = 243.5 Hz, C1-F), 139.0 (C_{Ph}), 148.7 (C5a), 183.7 (d, $^4J_{CF}$ = 2.5 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -167.9 (s).

HRMS (ESI): m/z calcd. for [$C_{24}H_{16}ClFN_2O + H^+$]: 403.1008, found: 403.1006.

[1-Fluoro-2-(4-methoxyphenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone 7c



Pyrrolo[1,2-b]indazole **7c** was obtained from α-fluoronitroalkene **1c** (20 mg, 0.1 mmol) and indazolium salt **6a** (3.0 equiv.) following the general procedure 3 (reaction time 3 days). Column chromatography (eluent: 19:1 to 5:1 PE/EtOAc) afforded **7c** (26.5 mg, 67%) as a bright yellow solid.

R_f = 0.29 (PE/EtOAc, 3:1) (UV), mp = 173-176°C ($CHCl_3$)

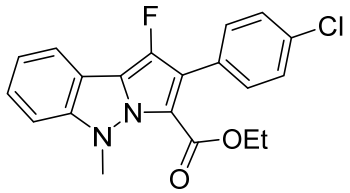
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 3H, OMe), 3.75 (s, 3H, N-Me), 6.60 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.01 (d, *J* = 8.4 Hz, 2H, CH_{Ar}), 7.08 (t, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.20-7.35 (m, 3H, CH_{Ar}), 7.42-7.49 (m, 1H, CH_{Ar}), 7.54 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.83 (d, *J* = 7.7 Hz, 1H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ 41.9 (N-Me), 55.1 (OMe), 111.5 (CH), 113.2 (CH_{Ar}), 115.7 (C3), 117.1 (d, $^3J_{CF}$ = 3.0 Hz, C9a), 120.3 (d, $^4J_{CF}$ = 0.7 Hz, C9-H), 120.5 (d, $^2J_{CF}$ = 9.6 Hz, C2), 121.2 (d, $^2J_{CF}$ = 28.8 Hz, C9b), 123.3 (CH), 123.5 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 127.4 (CH), 127.5 (CH_{Ar}), 129.6 (CH_{Ar}), 131.3 (CH_{Ar}), 131.8 (br s, CH_{Ar}), 137.7 (d, $^1J_{CF}$ = 241.4 Hz, C1-F), 138.9 (C_{Ph}), 149.2 (C5a), 158.4 (**C$_{Ar}$**-OMe), 184.0 (d, $^4J_{CF}$ = 2.4 Hz, **C**=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ -172.4 (s).

HRMS (ESI): m/z calcd. for [$C_{25}H_{19}FN_2O_3$ + H^+]: 399.1503, found: 399.1494.

Ethyl 2-(4-chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazole-3-carboxylate 7d



Pyrrolo[1,2-b]indazole **7d** was obtained from α-fluoronitroalkene **1a** (20 mg, 0.1 mmol) and indazolium salt **6b** (3.0 equiv.) following the general procedure 3 (reaction time 3 days). Column chromatography (eluent: 19:1 to 7:1 PE/EtOAc) afforded **7b** (22 mg, 59%) as a white solid

R_f = 0.50 (PE/EtOAc, 3:1) (UV), mp = 108-110°C ($CHCl_3$)

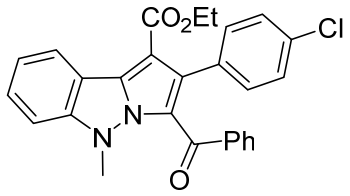
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.1 Hz, 3H, CH_3), 3.76 (s, 3H, N-Me), 4.18 (q, *J* = 7.1 Hz, 1H, CH_2),7.26-7.33 (m, 2H, CH_{Ar}), 7.36-7.45 (m, 5H, CH_{Ar}), 7.76 (d, *J* = 7.7 Hz, 1H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9 (CH_3), 43.6 (N-Me), 60.2 (CH_2), 107.6 (d, $^3J_{CF}$ = 1.3 Hz, C3), 112.3 (CH), 117.8 (d, $^4J_{CF}$ = 2.9 Hz, C9a), 119.1 (d, $^2J_{CF}$ = 9.9 Hz, C2), 120.1 (d, $^4J_{CF}$ = 1.1 Hz, C9-H), 120.6 (d, $^2J_{CF}$ = 28.1 Hz, C9b), 123.7 (CH), 127.1 (CH), 127.7 (CH_{Ar}), 130.1 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 132.1 (d, $^4J_{CF}$ = 1.0 Hz, CH_{Ar}), 133.2 (C_{Ar}-Cl), 137.6 (d, $^1J_{CF}$ = 241.4 Hz, C1-F), 150.3 (**C**5a-NMe), 159.9 (d, $^4J_{CF}$ = 2.3 Hz, **C**O_2Et).

^{19}F NMR (282 MHz, $CDCl_3$): δ -173.0 (s).

HRMS (ESI): m/z calcd. for [$C_{20}H_{16}ClFN_2O_2$ + H^+]: 371.0957, found: 371.0951.

Ethyl 3-benzoyl-2-(4-chlorophenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazole-1-carboxylate 7e



Pyrrolo[1,2-b]indazole **7e** was obtained from α-fluoronitroalkene **1e** (25.5 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3. Column chromatography (eluent: 19:1 to 5:1 PE/EtOAc) afforded **7e** (28.5 mg, 62%) as a slightly yellow solid.

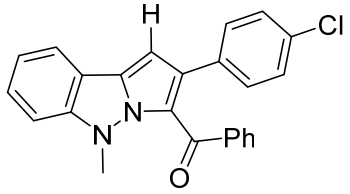
R_f = 0.39 (PE/EtOAc, 3:1) (UV), mp = 189-191°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (t, *J* = 7.1 Hz, 3H, CH_3), 3.73 (s, 3H, N-Me), 4.26 (q, *J* = 7.1 Hz, 2H, CH_2), 6.97 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 7.04 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 7.11 (t, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.27-7.42 (m, 3H, CH_{Ar}), 7.48-7.52 (m, 2H, CH_{Ar}), 7.53-7.60 (m, 1H, CH_{Ar}), 8.57 (d, *J* = 7.9 Hz, 1H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (CH_3), 40.3 (N-Me), 59.9 (CH_2), 102.0 (C1), 110.6 (CH), 117.2 (C_q), 122.9 (CH), 123.9 (CH), 126.9 (CH_{Ar}), 127.7 (CH_{Ar}), 128.6 (CH), 128.7 (C_q), 129.4 (CH_{Ar}), 131.8 (CH_{Ar}), 132.5 (CH_{Ar}), 132.7 (C_q), 132.9 (C_q), 135.2 (C_q), 135.6 (C_q), 138.5 (C_{Ph}), 148.9 (C5a), 164.1 (**C**O_2Et), 185.6 (C=O).

HRMS (ESI): m/z calcd. for [$C_{27}H_{21}ClN_2O_3$ + H^+]: 457.1313, found: 457.1312.

[2-(4-Chlorophenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone 7f



Pyrrolo[1,2-b]indazole **7f** was obtained from nitroalkene **1g** (18.4 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3 using MeCN as a solvent. Column

chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **7f** (13.5 mg, 35%) as a slightly yellow solid

R_f = 0.43 (PE/EtOAc, 3:1) (UV), mp = 168-170°C ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 3.79 (s, 3H, N-Me), 6.50 (s, 1H, C1-H), 6.98-7.05 (m, 4H, CH_{Ar}), 7.13 (t, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.27-7.34 (m, 2H, CH_{Ar}), 7.39 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.49 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H, CH_{Ar}), 7.58 (dd, *J* = 8.2, 1.2 Hz, 2H, CH_{Ar}), 7.81 (d, *J* = 7.7 Hz, 1H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$, HSQC): δ 41.5 (N-Me), 97.2 (C1-H), 111.7 (CH), 118.1 (C_q), 120.1 (C9-H), 123.0 (CH), 127.5 (CH), 127.59 (CH_{Ar}), 127.63 (CH_{Ar}), 129.7 (CH_{Ar}), 131.1 (CH_{Ar}), 131.5 (CH_{Ar}), 132.3 (C_{Ar}-Cl), 134.0 (C_q), 135.1 (C_q), 135.7 (C_q), 139.3 (C_{Ph}), 149.7 (C5a), 184.4 (**C**=O).

HRMS (ESI): m/z calcd. for [$C_{24}H_{17}ClN_2O + H^+$]: 385.1102, found: 385.1092.

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s4 A. A. Fadeeva, S. L. Ioffe, A. A. Tabolin, *Synthesis*, 2020, **52**, 2679.

s5 Ji, X.; Tong, H.; Yuan, Y. *Synth. Commun.,* 2011, **47**, 372-379.

s6 Kolarovic, A.; Kaslin, A.; Wennemers, H. *Org. Lett*., 2014, **16**, 4236-4239.

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s8 T. Ukai, R. Tanaka, T. Dokawa, *Yakugaki Zasshi*, 1943, **63**, 296. [*Chem. Abstr*. 1951, **45**, 5148].

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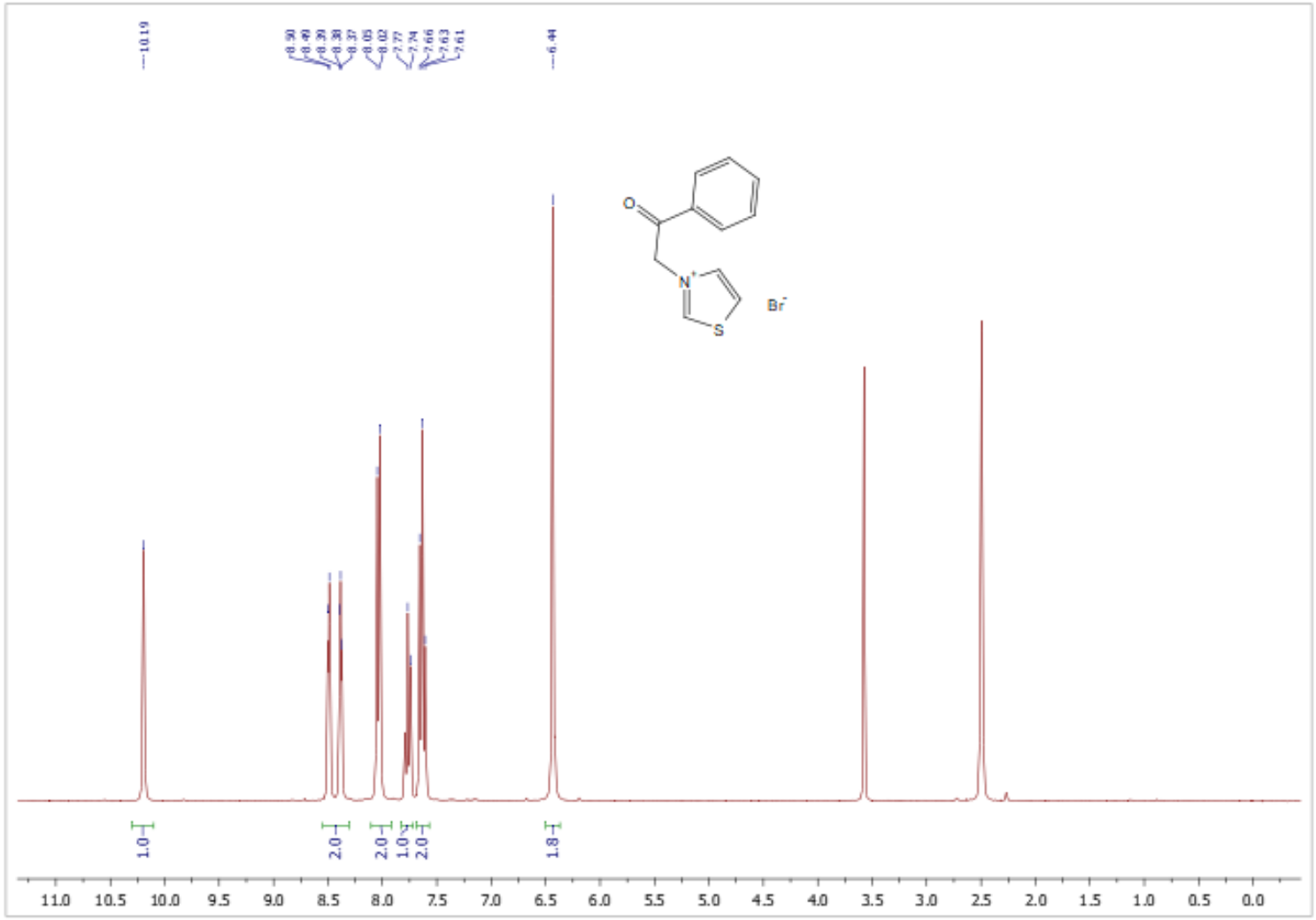
Copies of NMR spectra

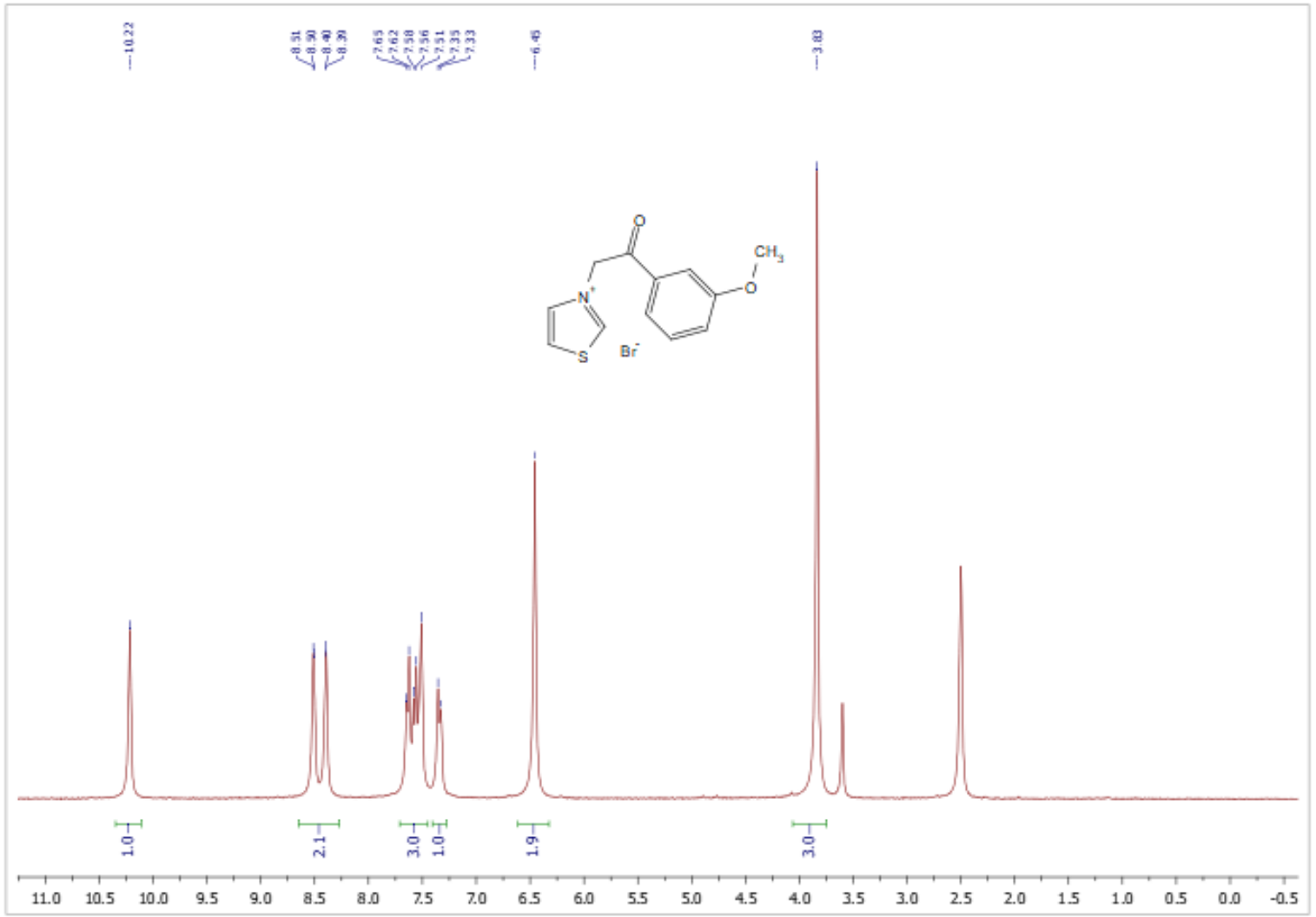
3-(2-oxo-2-phenylethyl)-1,3-thiazol-3-ium bromide **2a**

^{1}H NMR

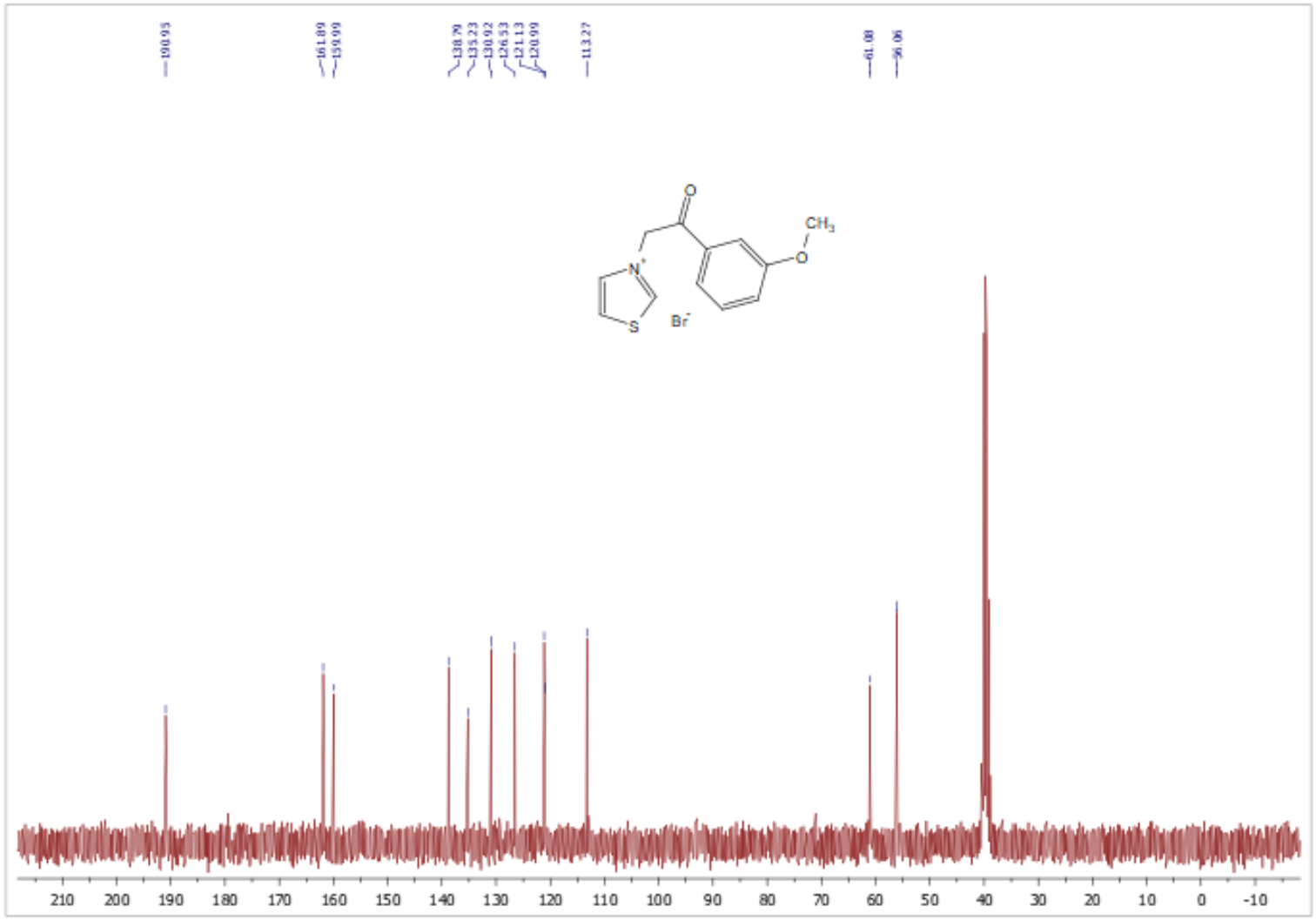


3-[2-(3-methoxyphenyl)-2-oxoethyl]-1,3-thiazol-3-ium bromide **2b**

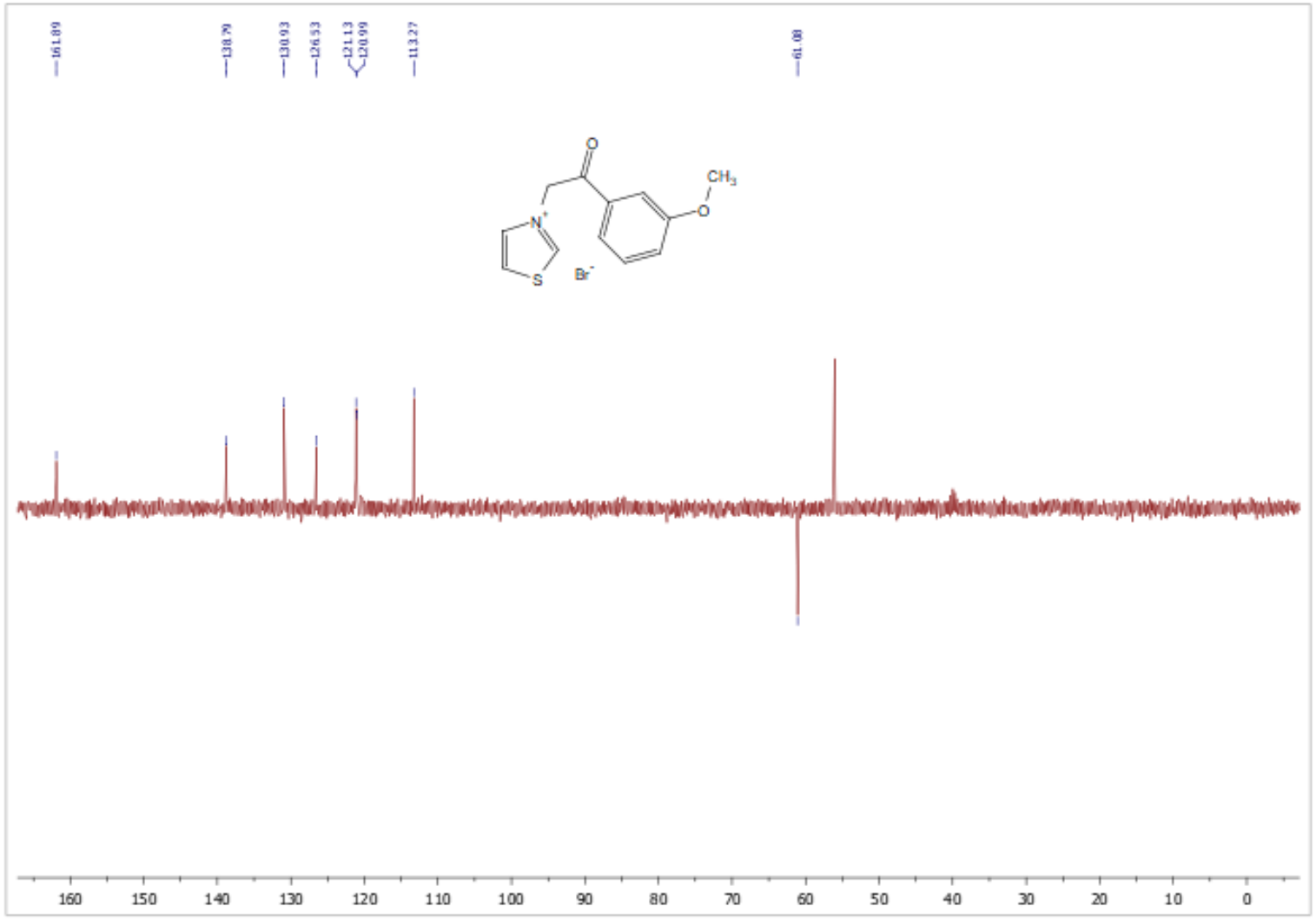
^{1}H NMR



^{13}C NMR

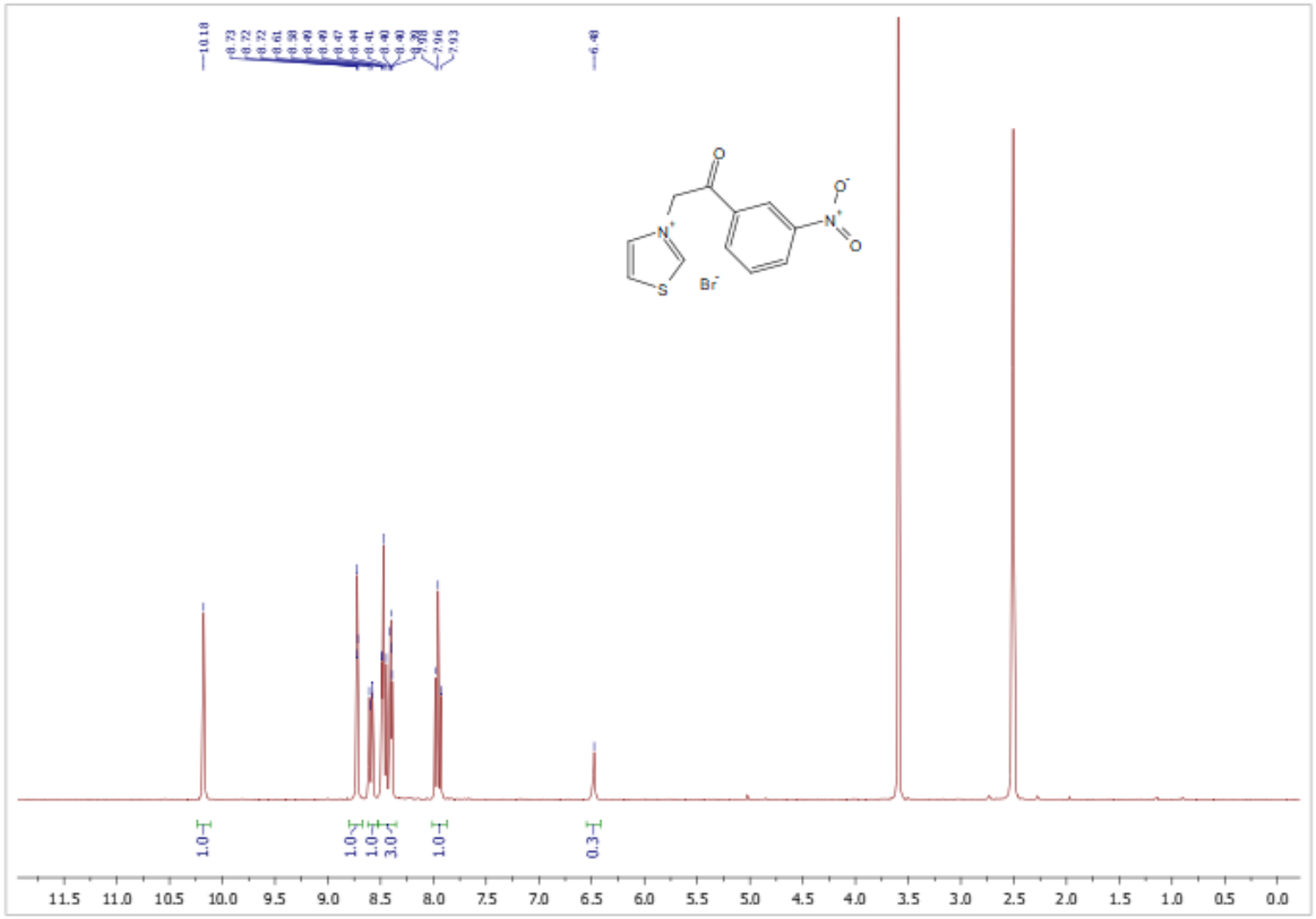

190.95
161.89
159.99
138.79
135.23
130.92
126.53
121.13
120.99
113.27
61.08
56.06
O
CH3
O
N+
S
Br-
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

DEPT-135 ^{13}C NMR

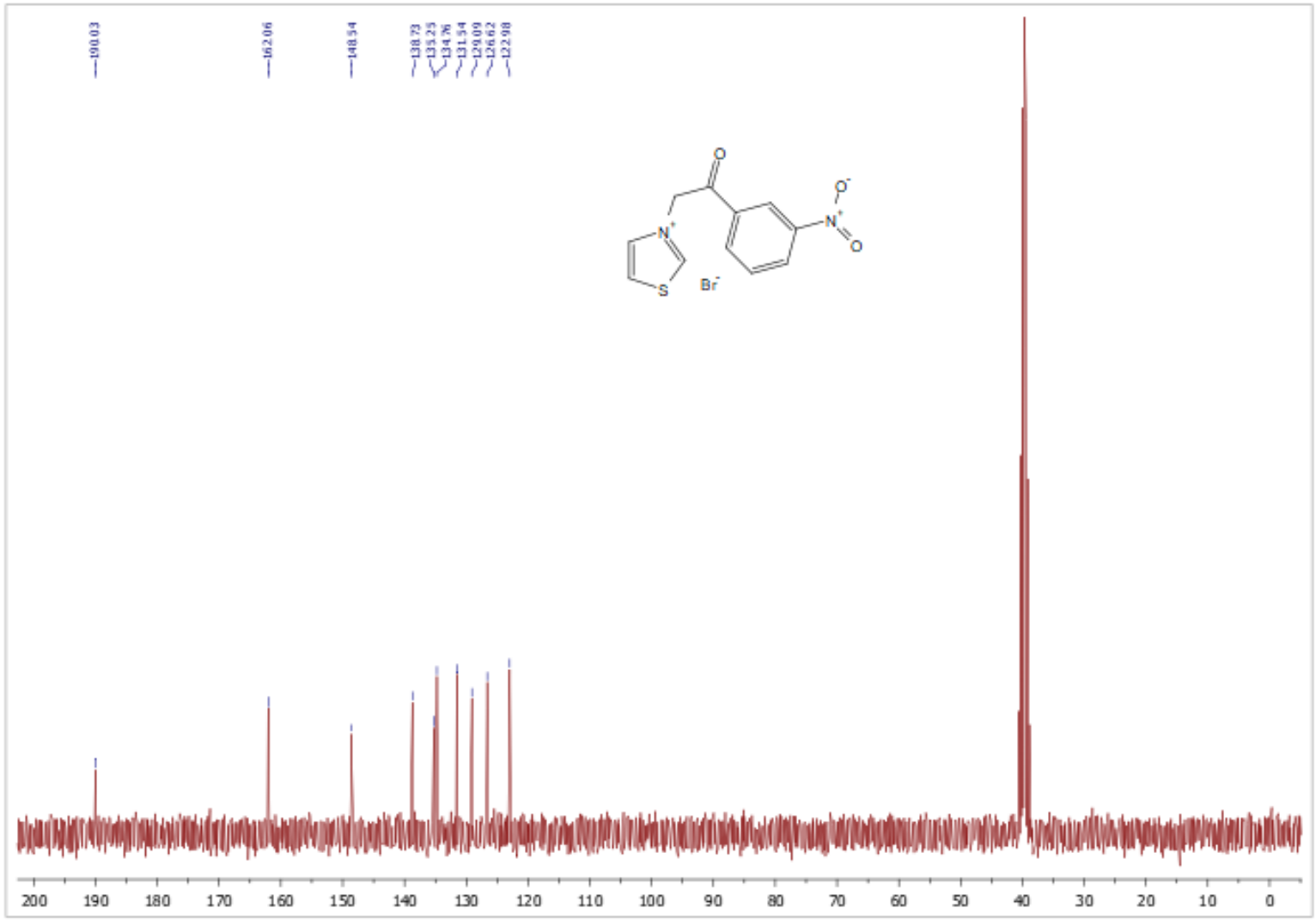


3-[2-(3-nitrophenyl)-2-oxoethyl]-1,3-thiazol-3-ium bromide **2c**

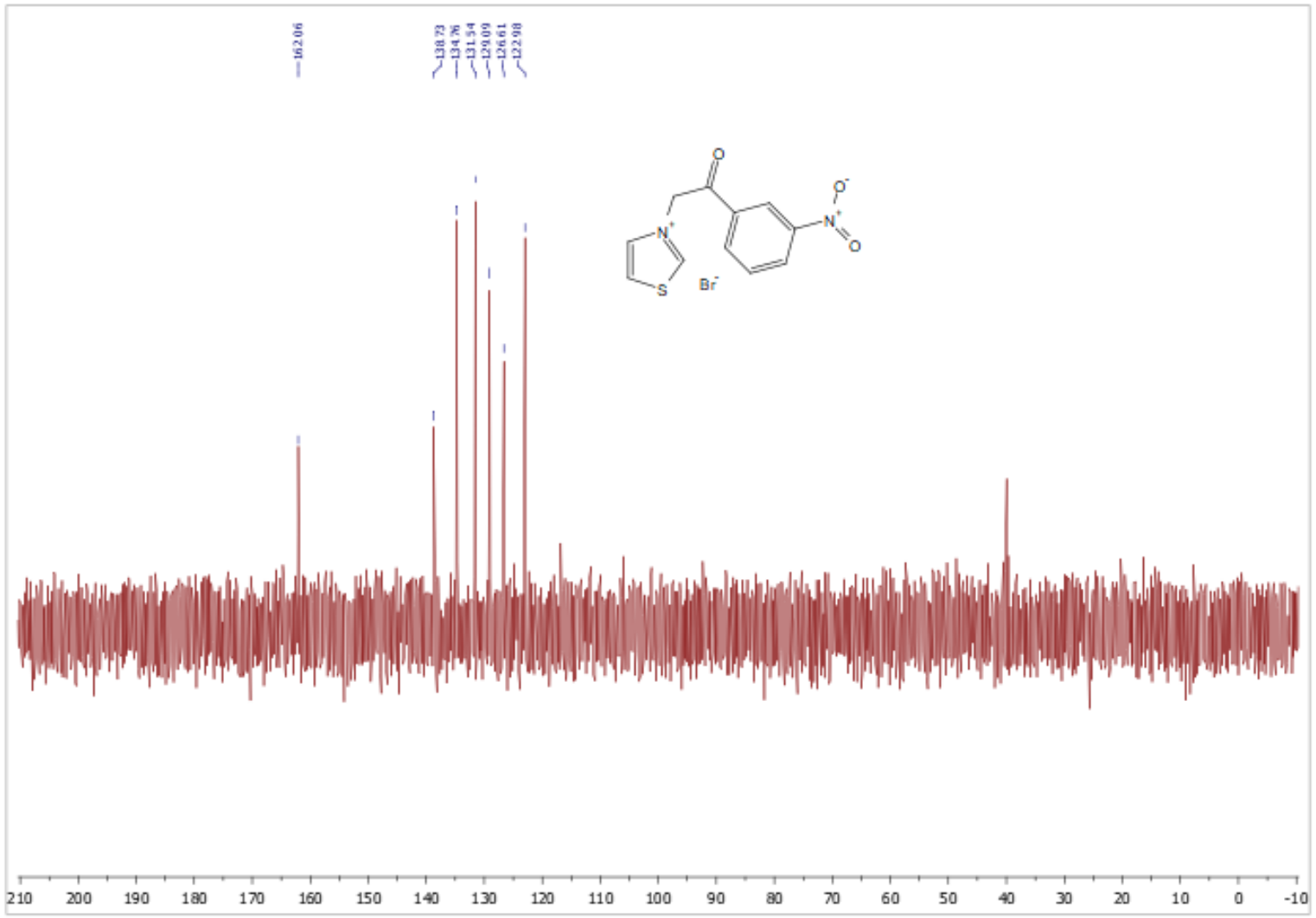
^{1}H NMR



^{13}C NMR

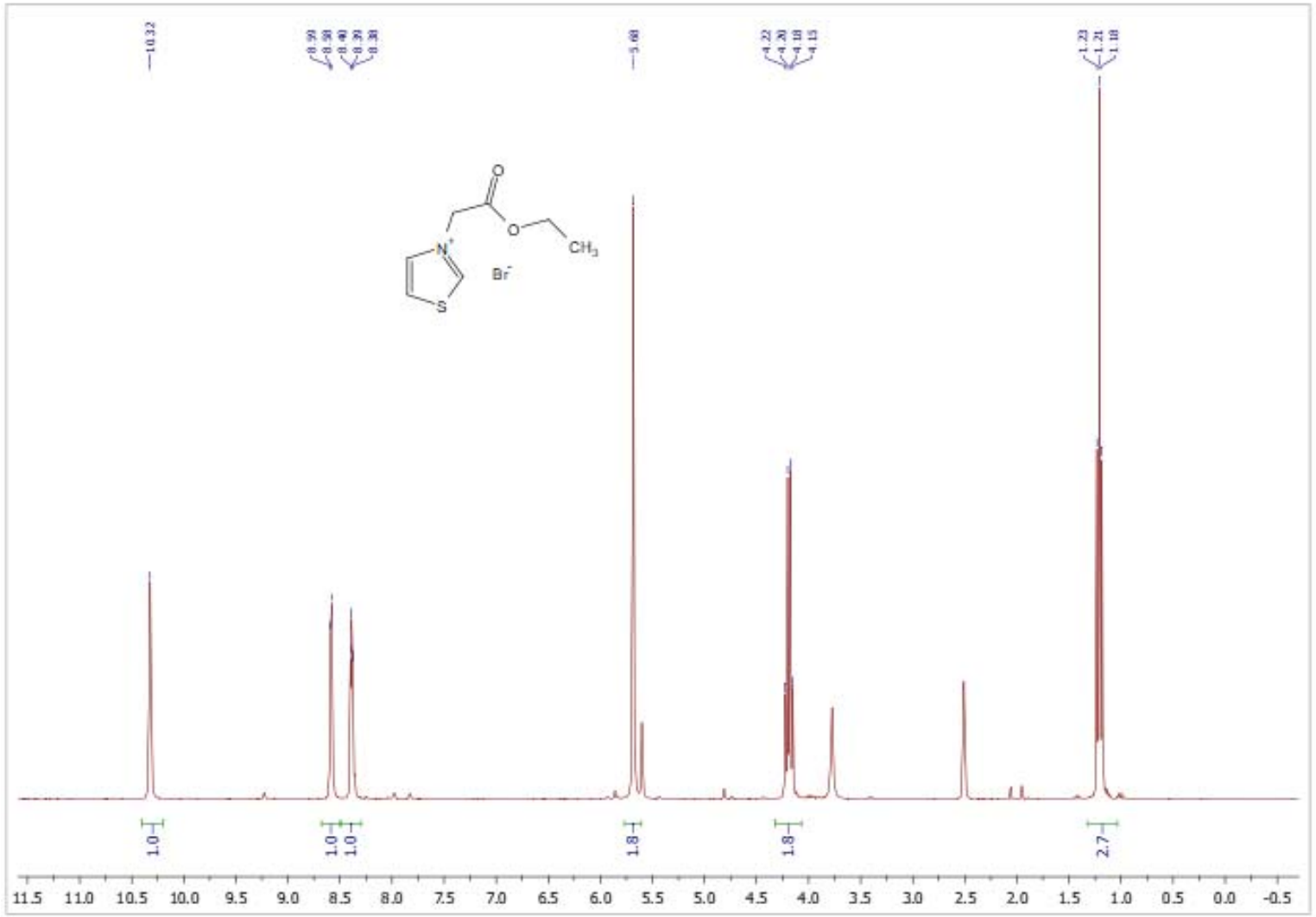

190.03
162.06
148.54
138.73
135.25
134.76
131.54
129.09
126.62
122.98
O
O-
N+
O
N+
S
Br-
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DEPT-135 ^{13}C NMR

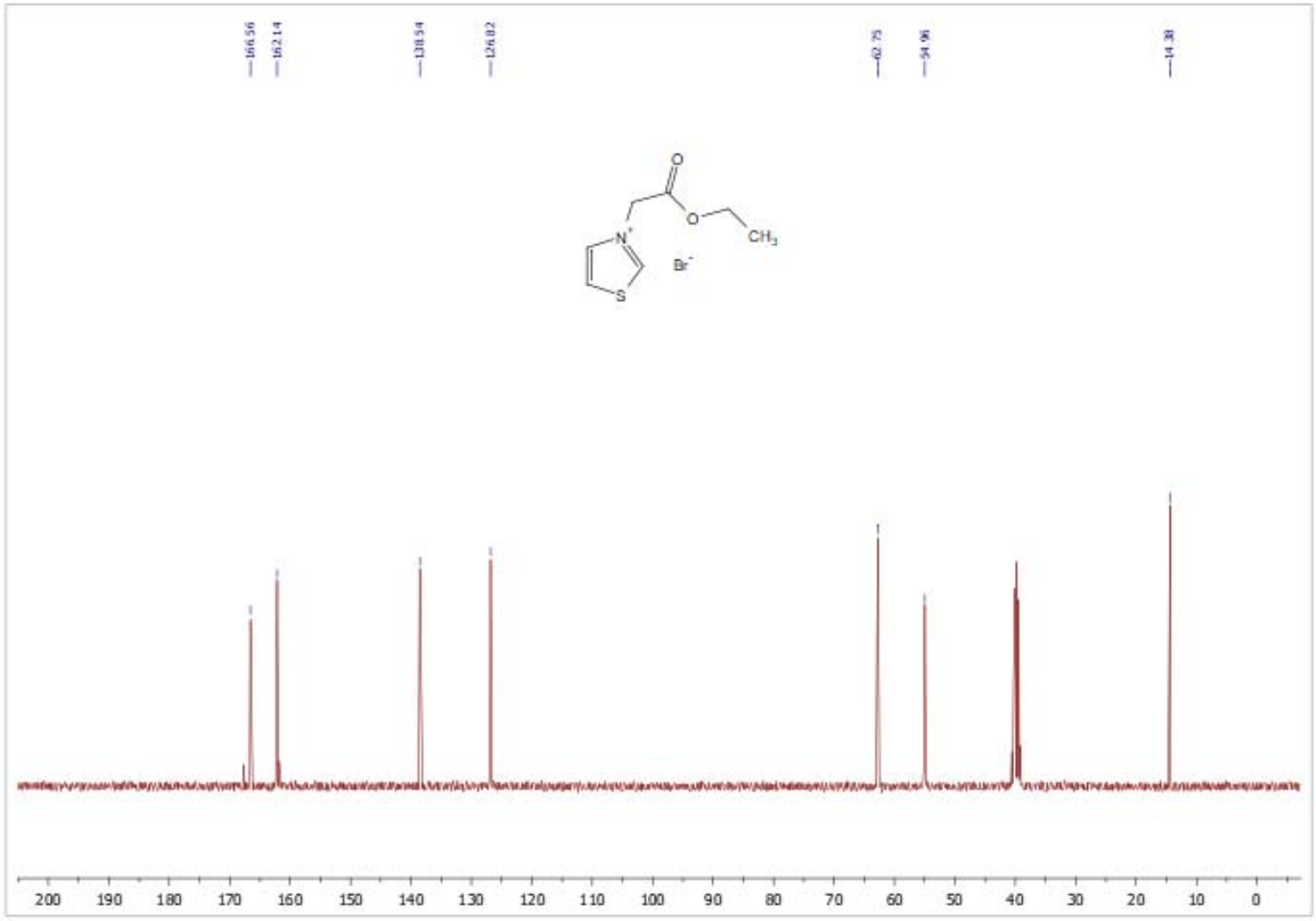


3-(2-ethoxy-2-oxoethyl)-1,3-thiazol-3-ium bromide **2d**

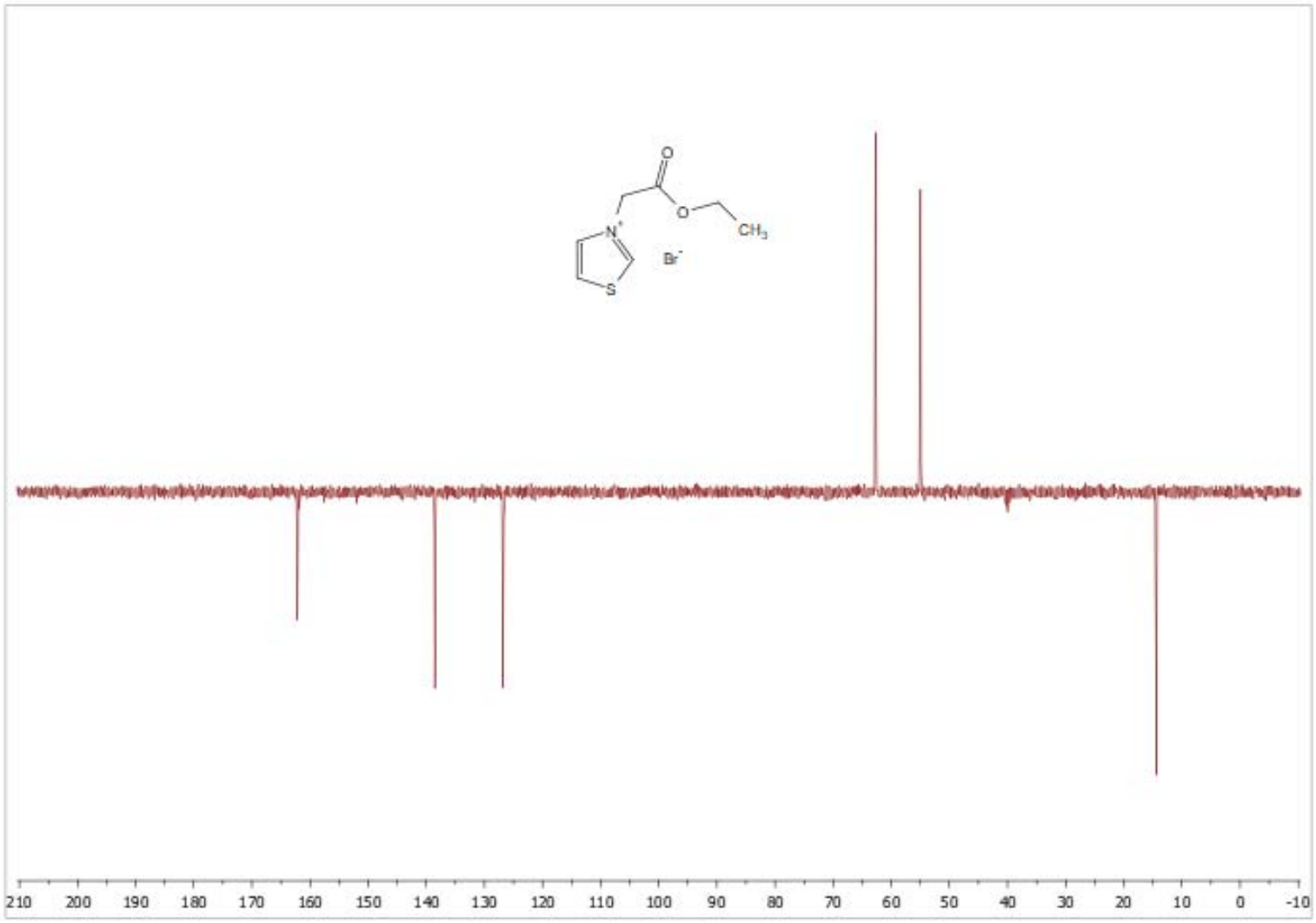
^{1}H NMR



^{13}C NMR

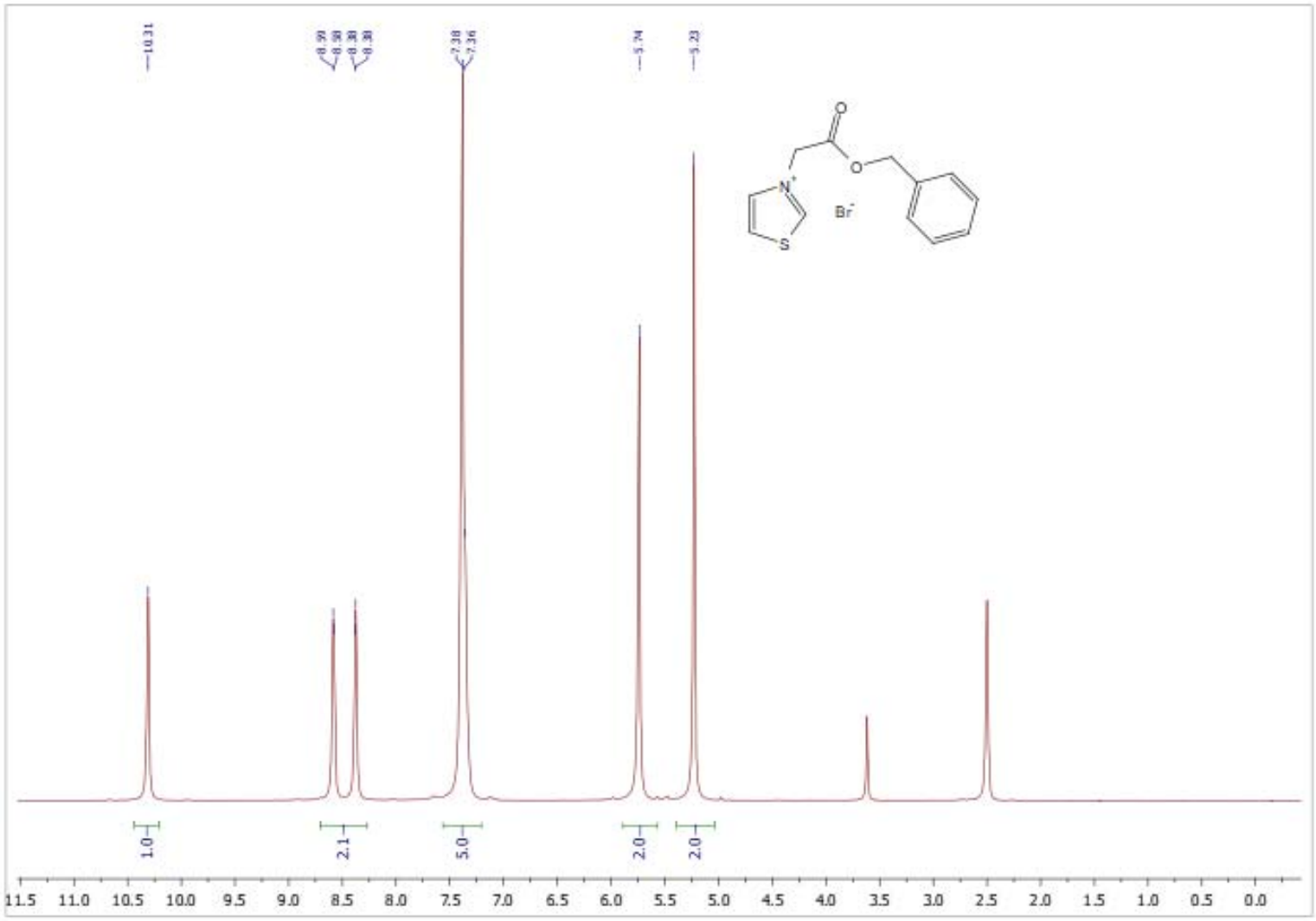

166.56
162.14
138.54
126.82
62.73
54.96
14.38
O
O
CH3
N+
Br-
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DEPT-135 ^{13}C NMR

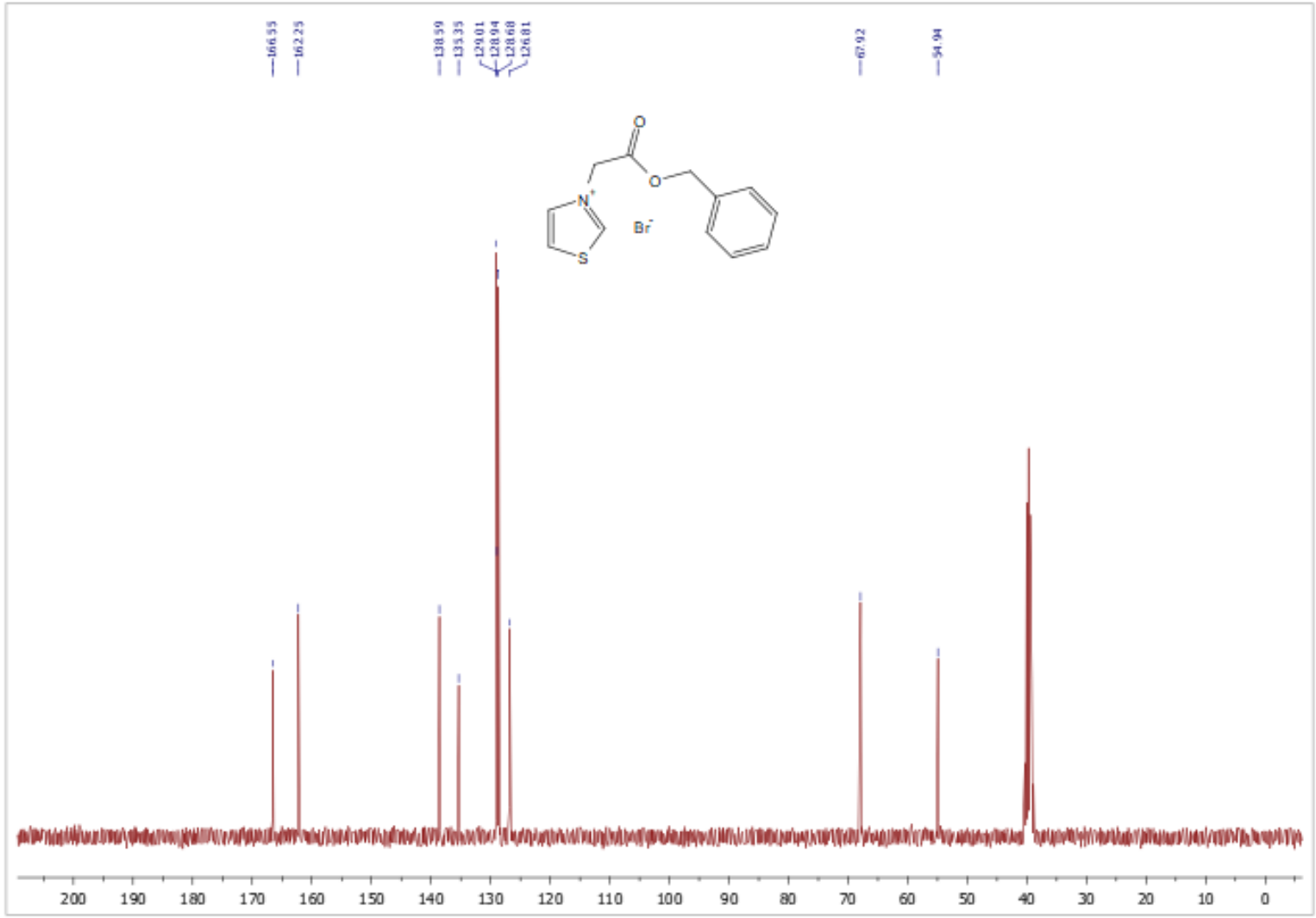


3-[2-(benzyloxy)-2-oxoethyl]-1,3-thiazol-3-ium bromide **2e**

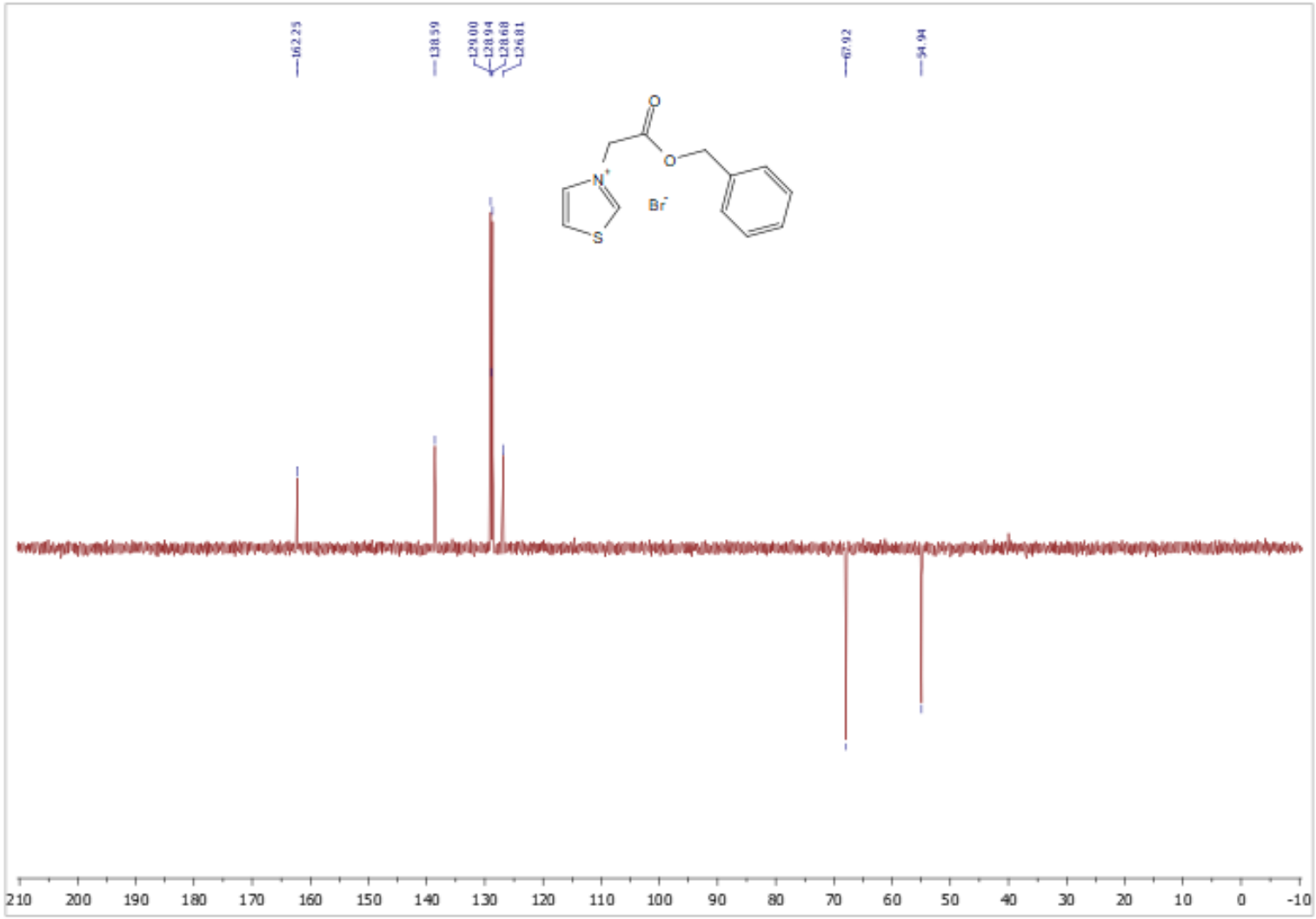
^{1}H NMR



^{13}C NMR

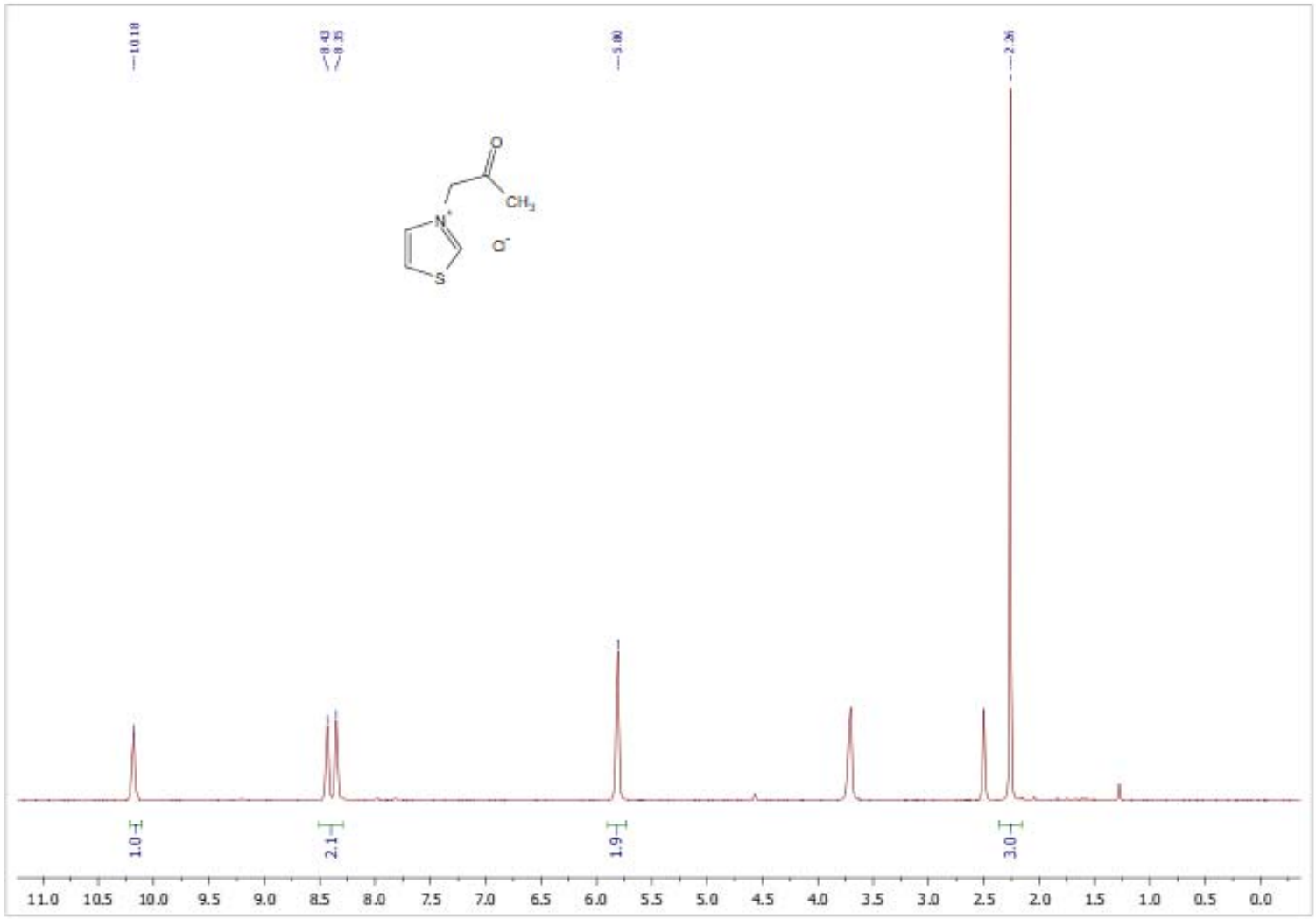

166.55
162.25
138.59
135.35
129.01
128.94
128.68
126.81
67.92
34.94
O
O
N
S
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DEPT-135 ^{13}C NMR

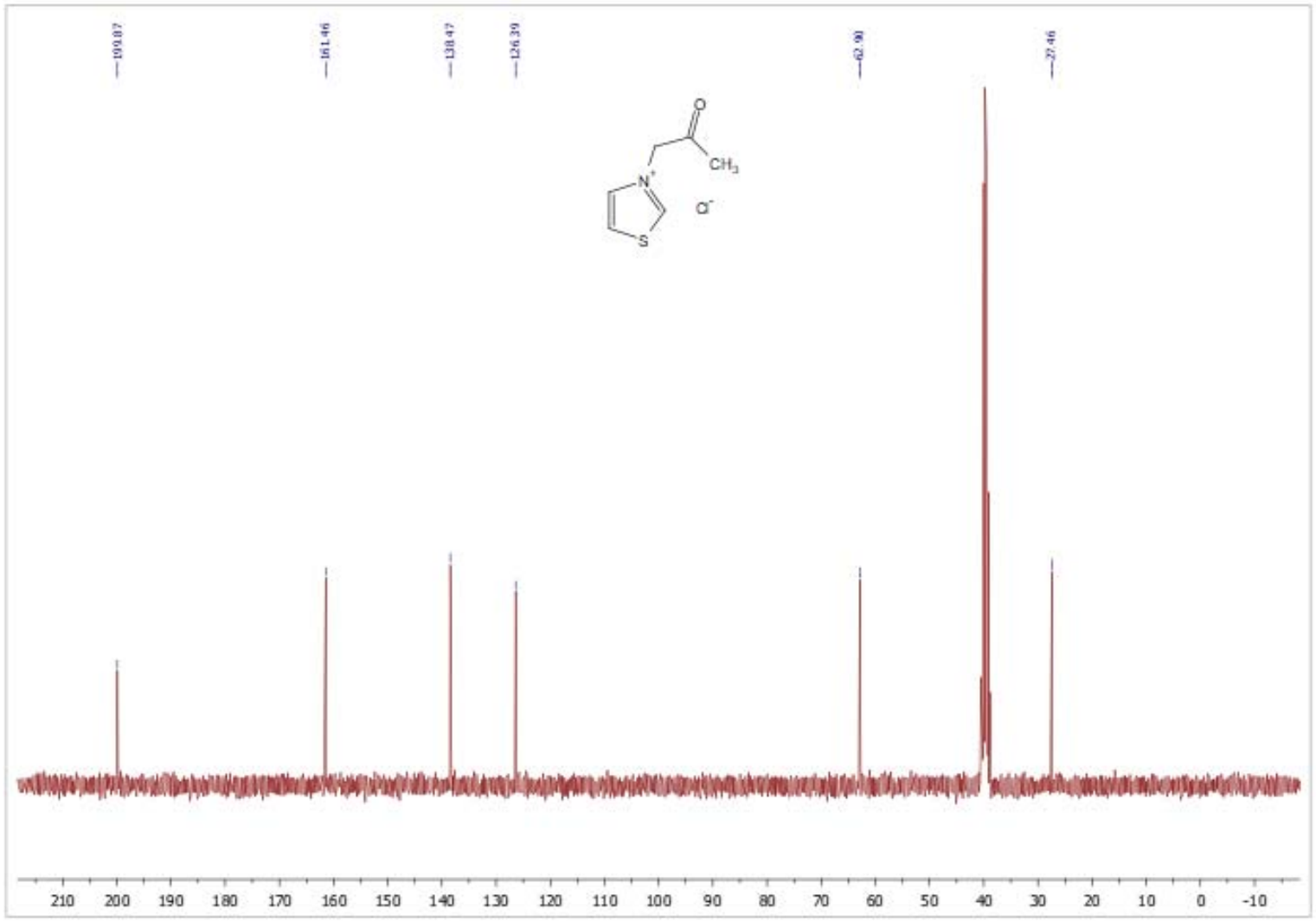


3-(2-oxopropyl)-1,3-thiazol-3-ium chloride **2f**

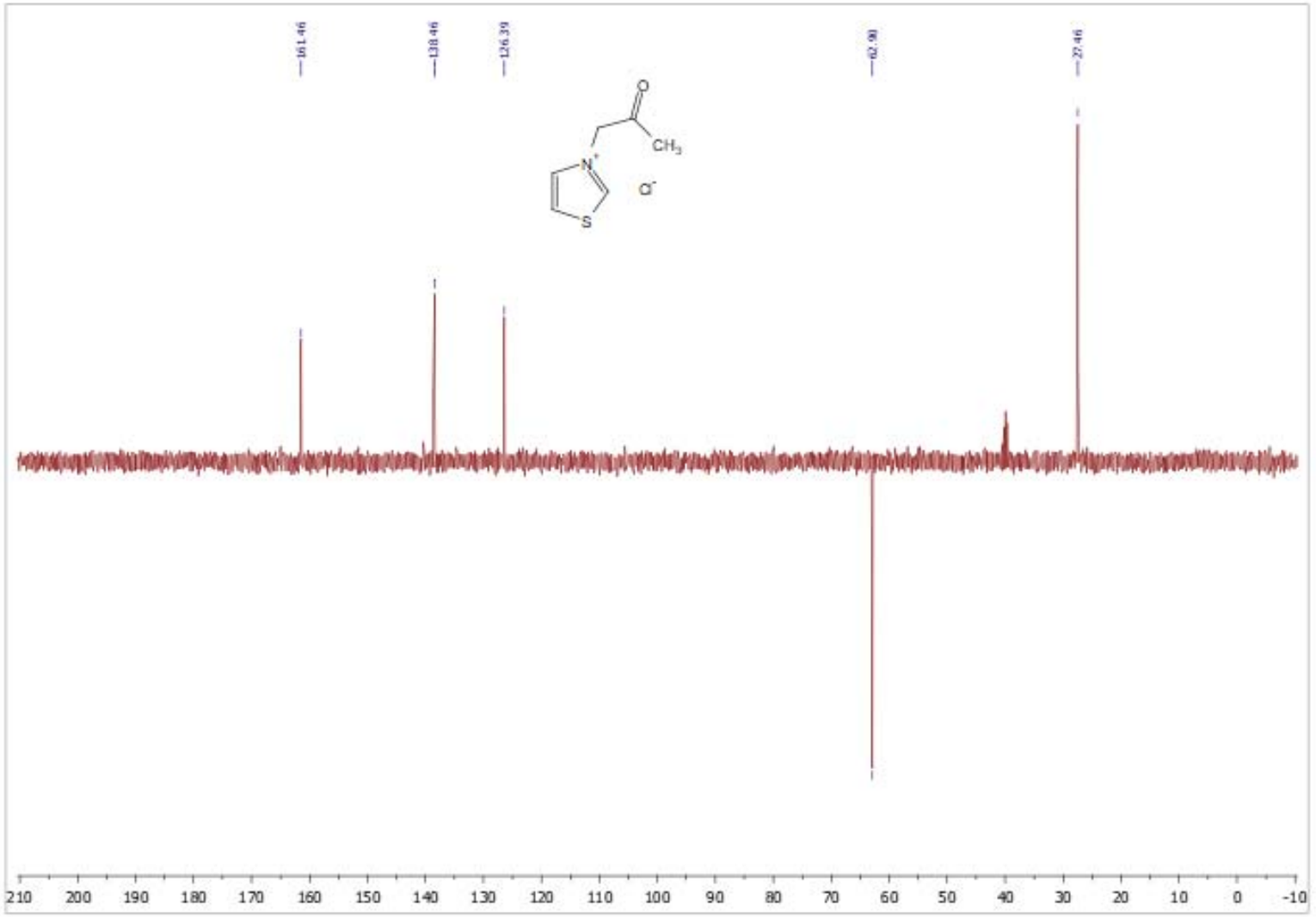
^{1}H NMR



^{13}C NMR

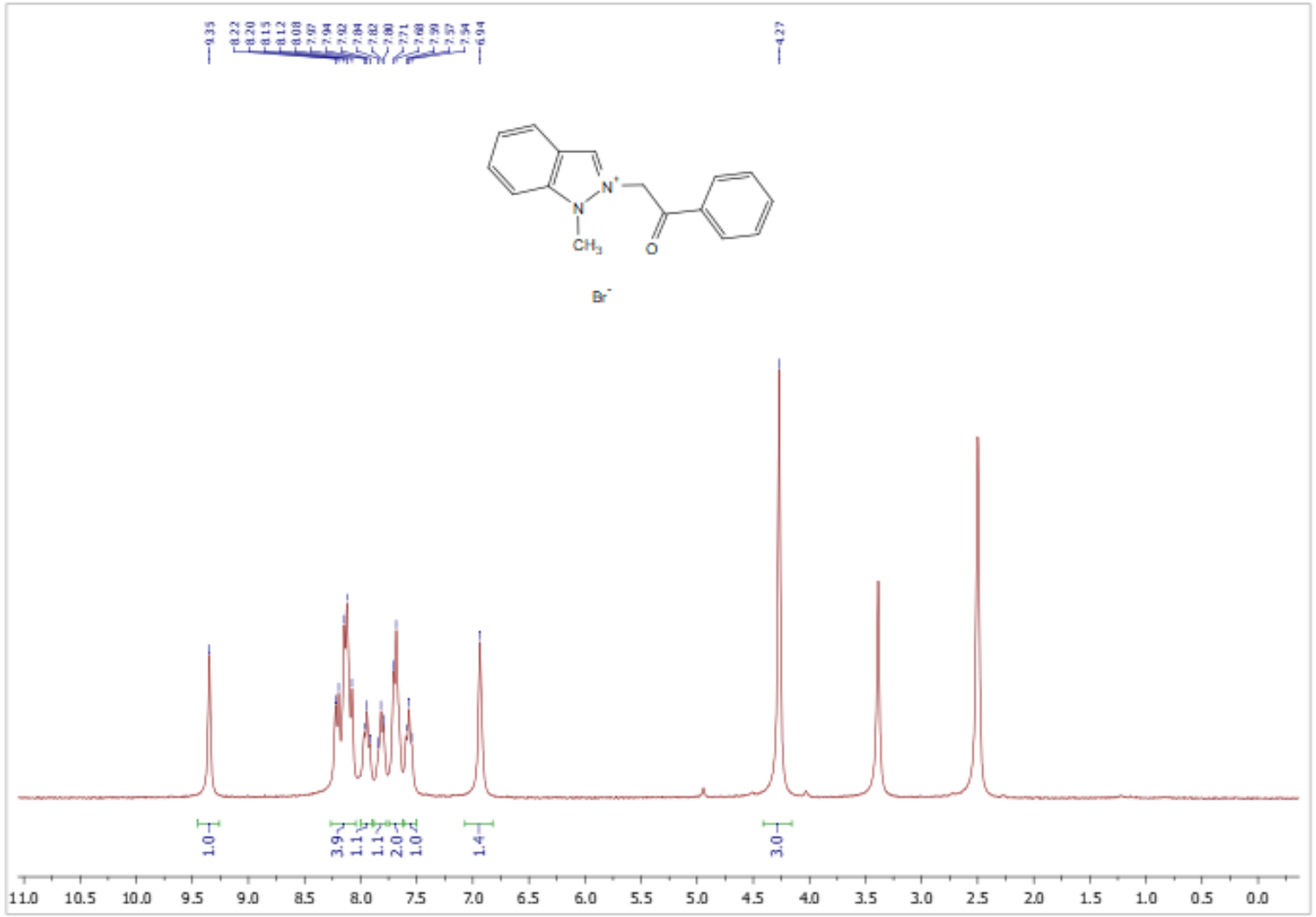

199.87
161.46
138.47
126.39
62.90
27.46
O
CH3
N+
Cl-
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

DEPT-135 ^{13}C NMR

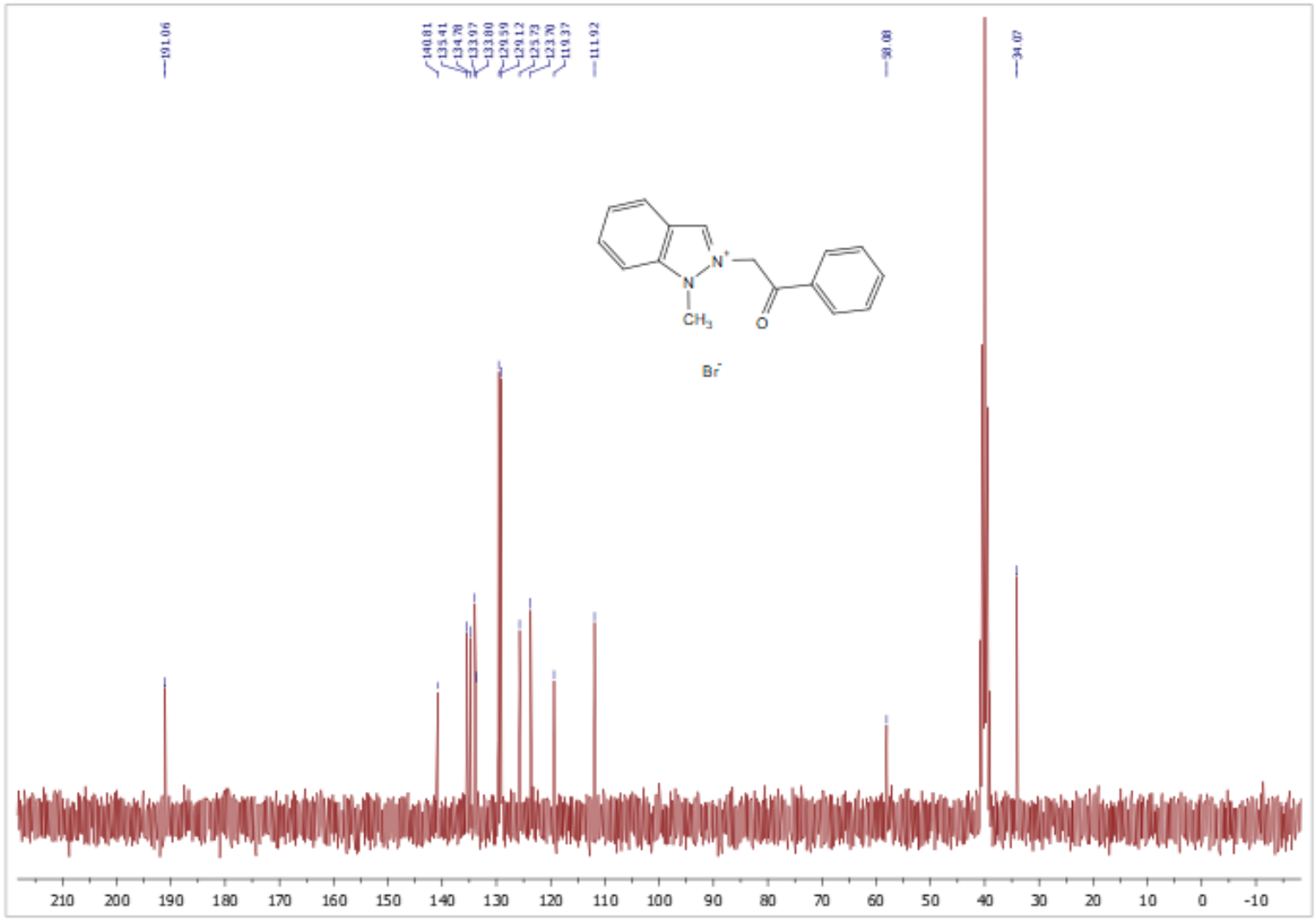


1-methyl-2-(2-oxo-2-phenylethyl)-1*H*-indazol-2-ium bromide **6a**

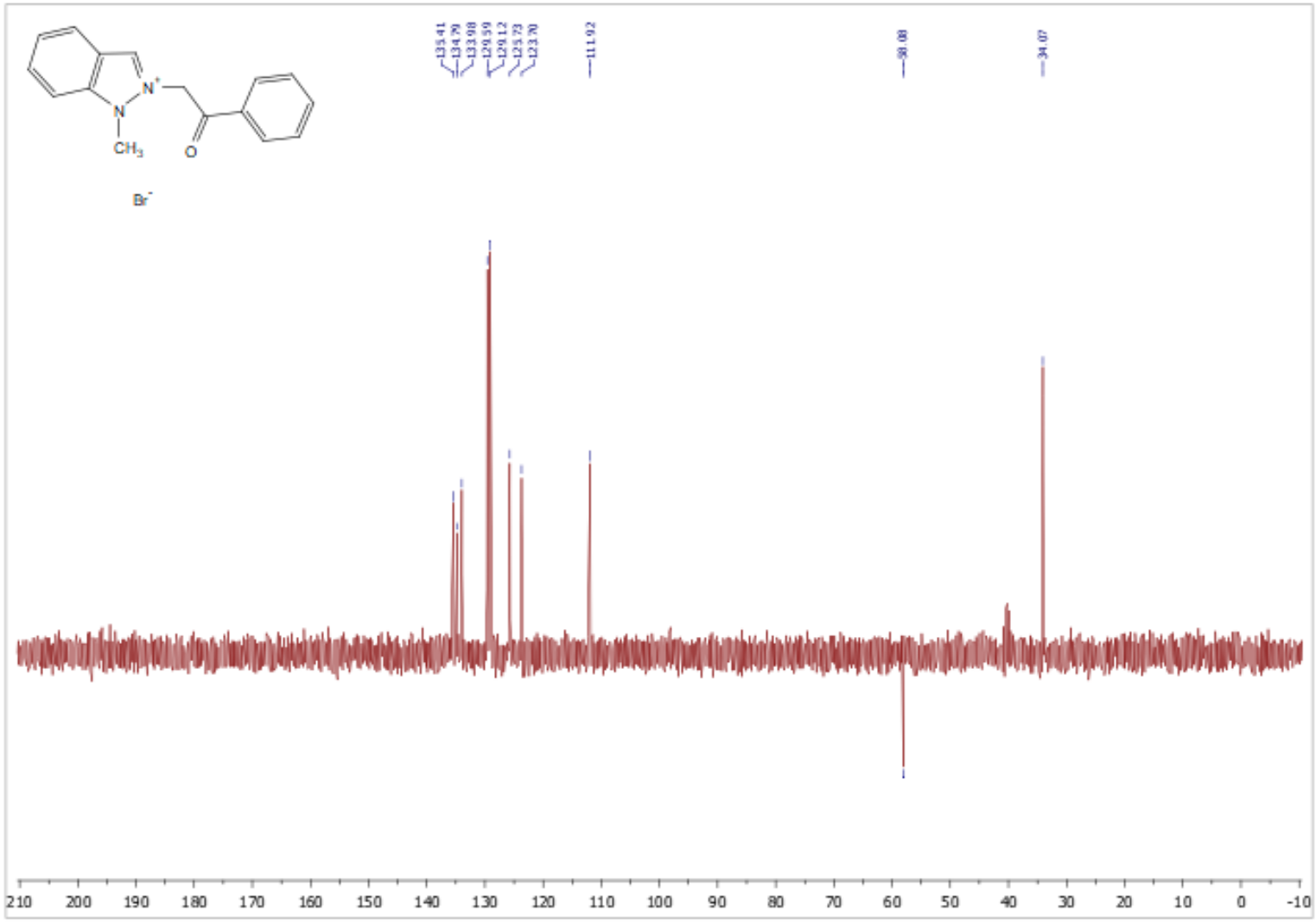
^{1}H NMR



^{13}C NMR

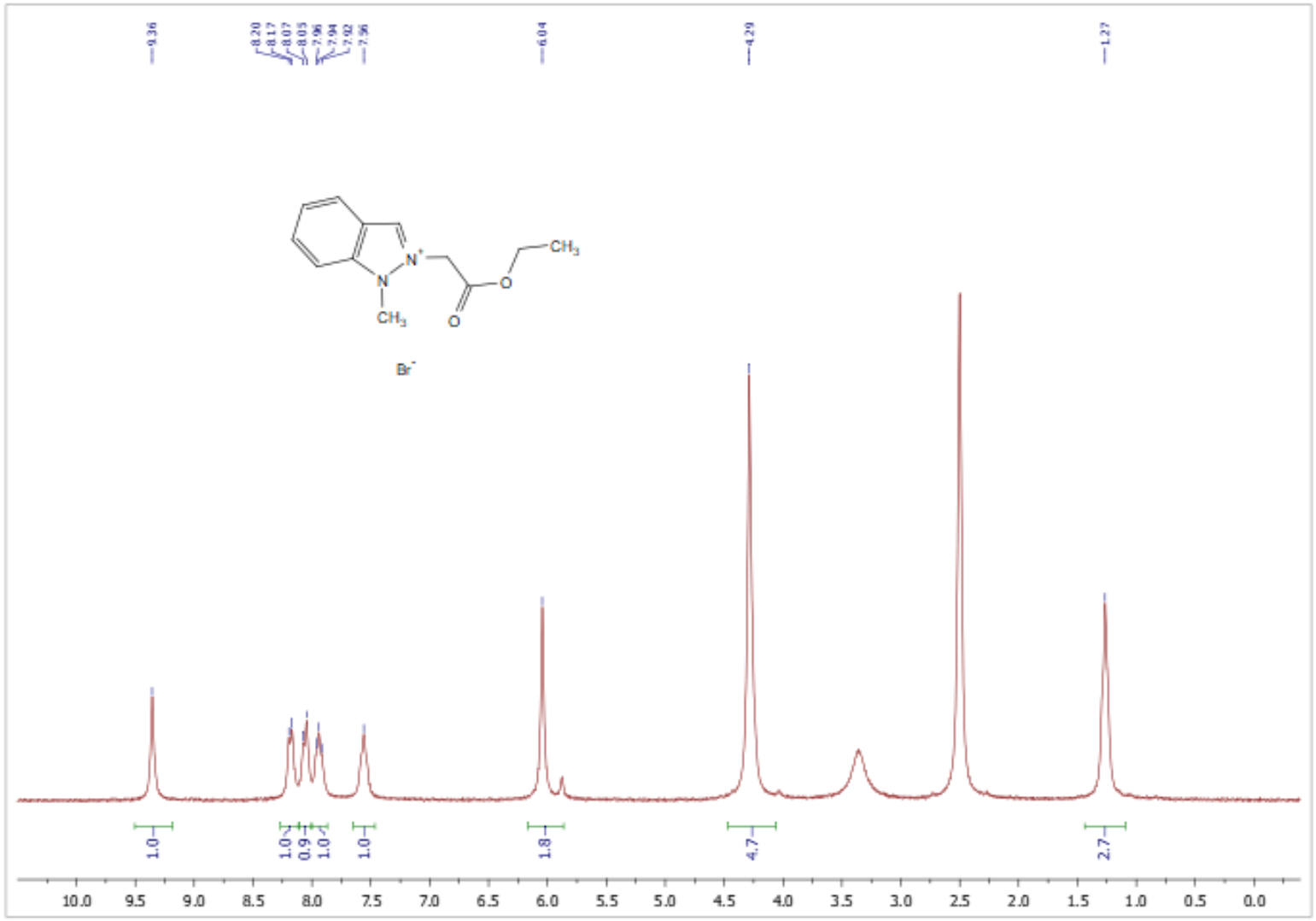

191.06
140.81
135.41
134.78
133.97
133.80
129.59
129.12
125.73
123.70
119.37
111.92
38.08
34.07
N+
N
CH3
O
Br-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

DEPT-135 ^{13}C NMR

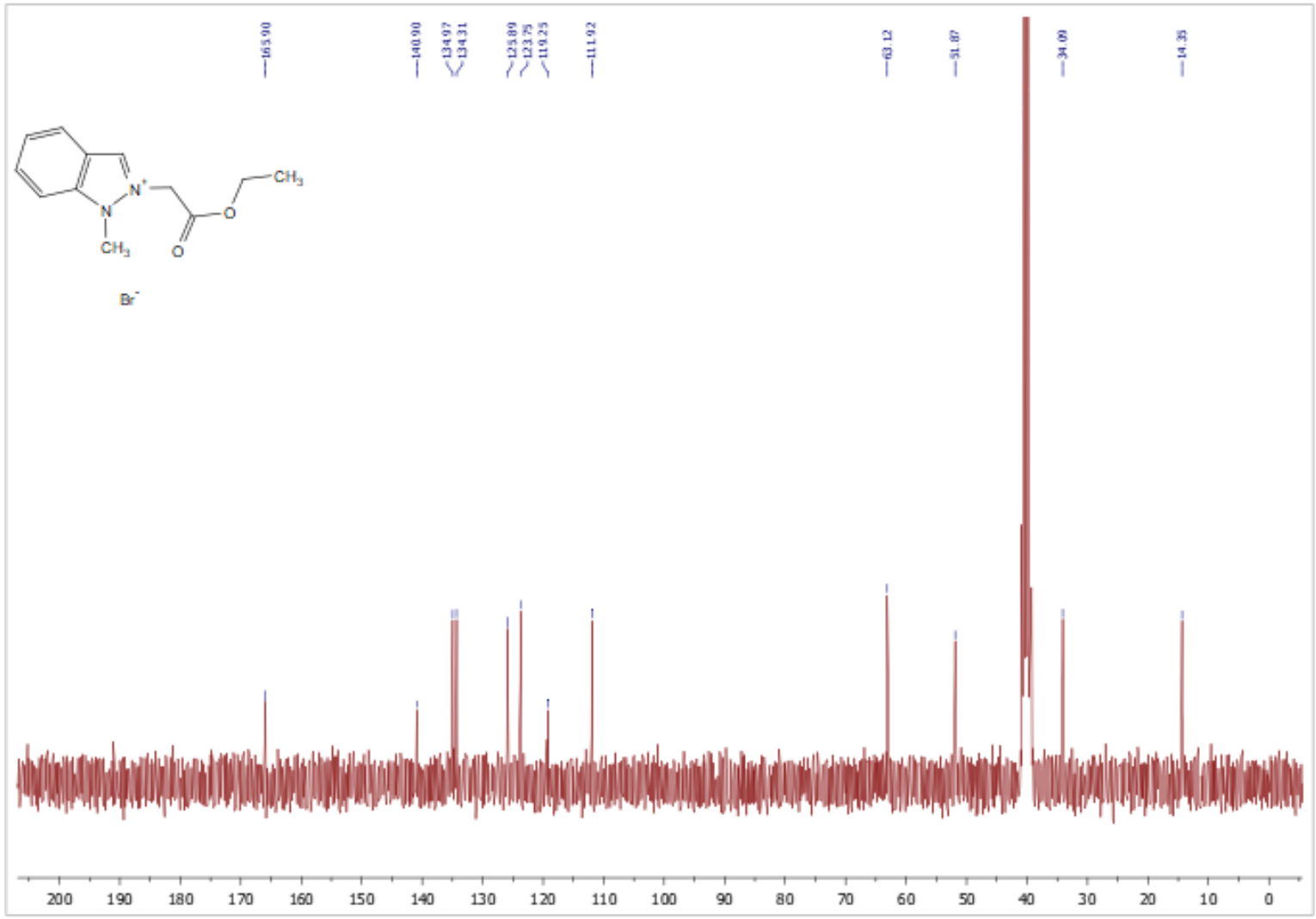


2-(2-ethoxy-2-oxoethyl)-1-methyl-1*H*-indazol-2-ium bromide **6b**

^{1}H NMR



^{13}C NMR


165.90
140.90
134.97
134.31
125.89
123.75
119.25
111.92
63.12
51.87
34.09
14.35
N+
N
CH3
O
O
CH3
Br-
200
190
180
170
160
150
140
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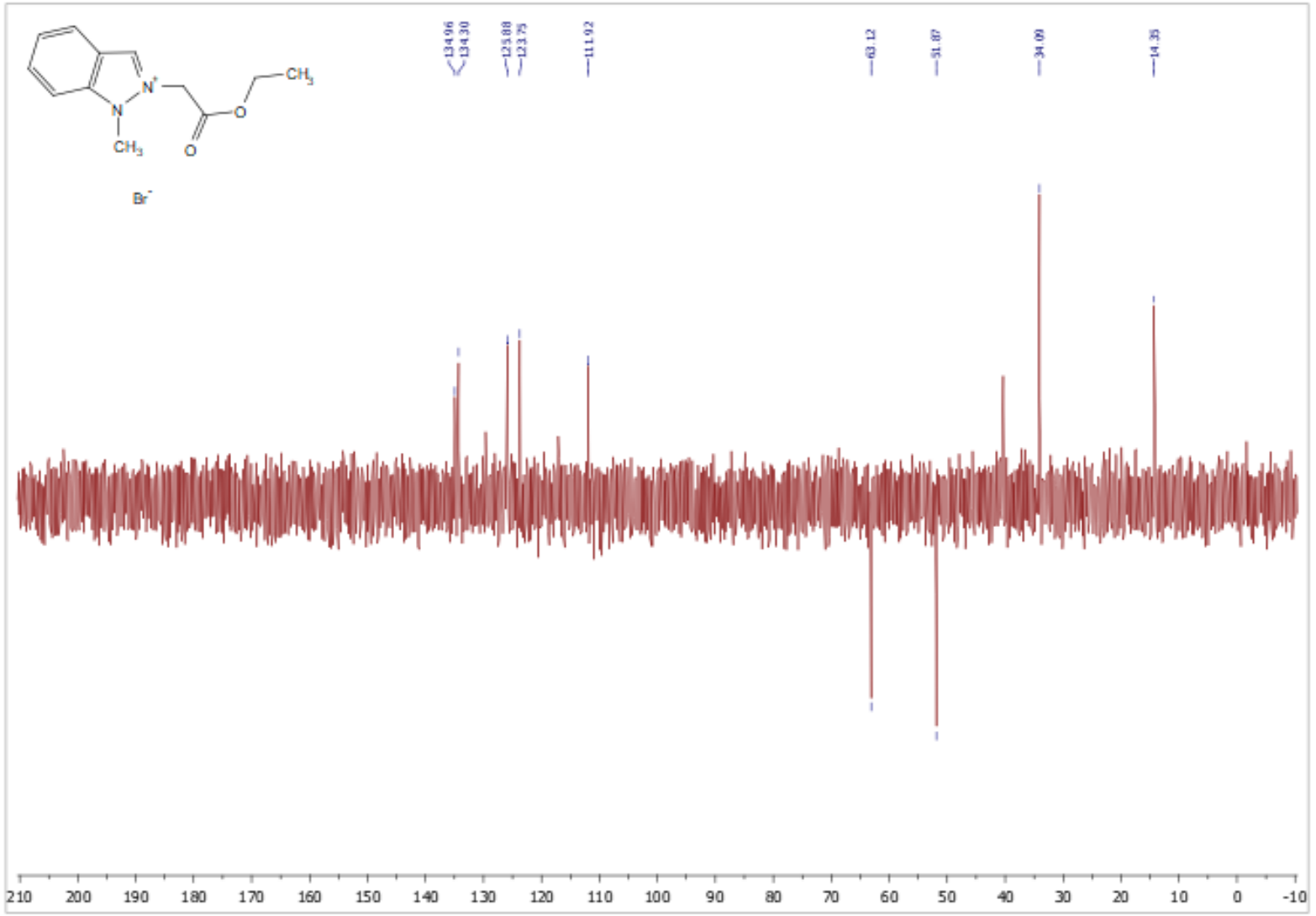
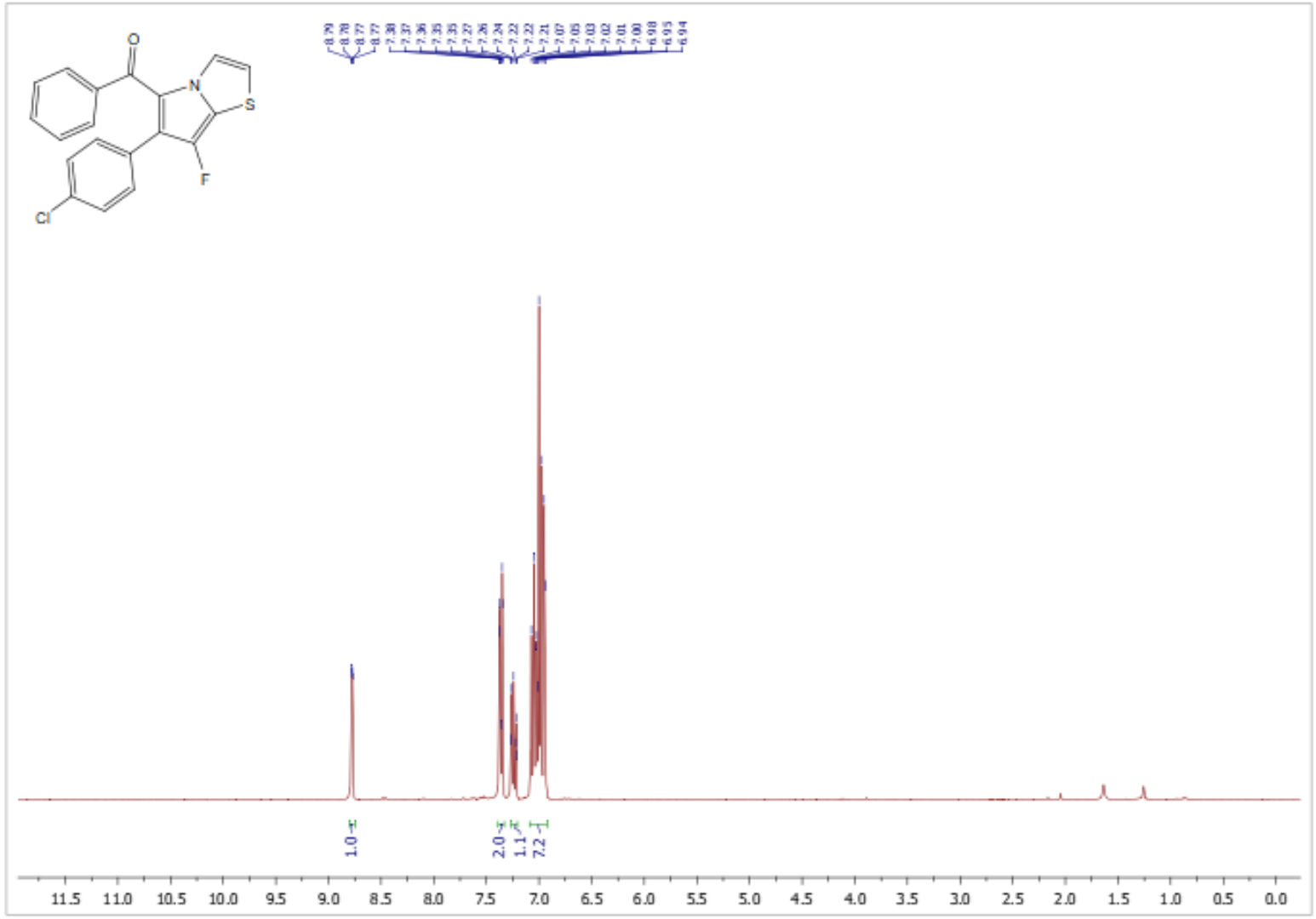
120
110
100
90
80
70
60
50
40
30
20
10
0

DEPT-135 ^{13}C NMR

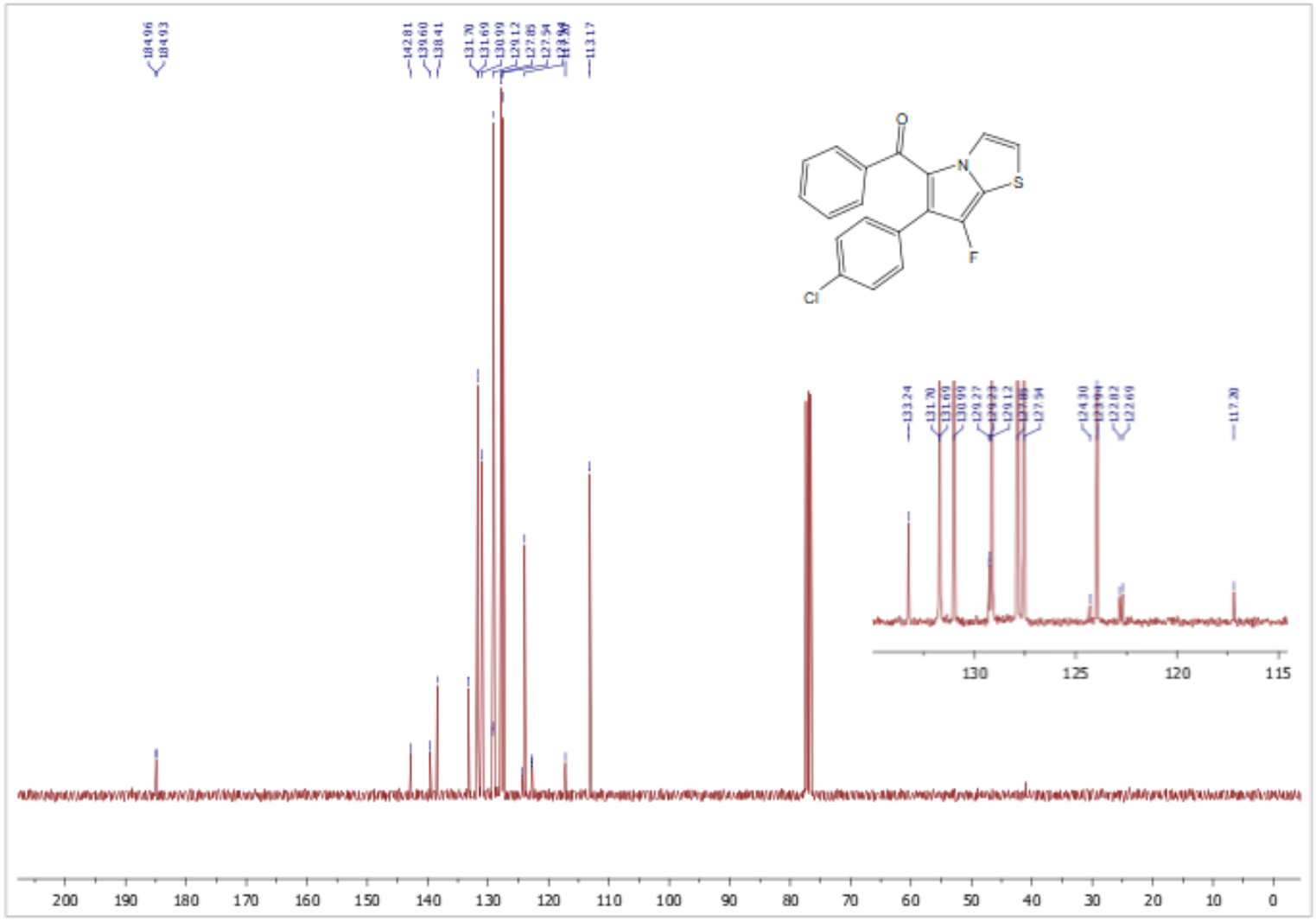


[6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-b][1,3]thiazol-5-yl](phenyl)methanone **3a**

^{1}H NMR



^{13}C NMR


184.96
184.93
142.81
139.60
138.41
131.70
131.69
130.99
129.12
127.85
127.54
113.17
O
N
S
F
Cl
133.24
131.70
131.69
130.99
129.27
129.12
127.94
124.30
123.82
122.69
117.30
130
125
120
115
200
190
180
170
160
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90
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50
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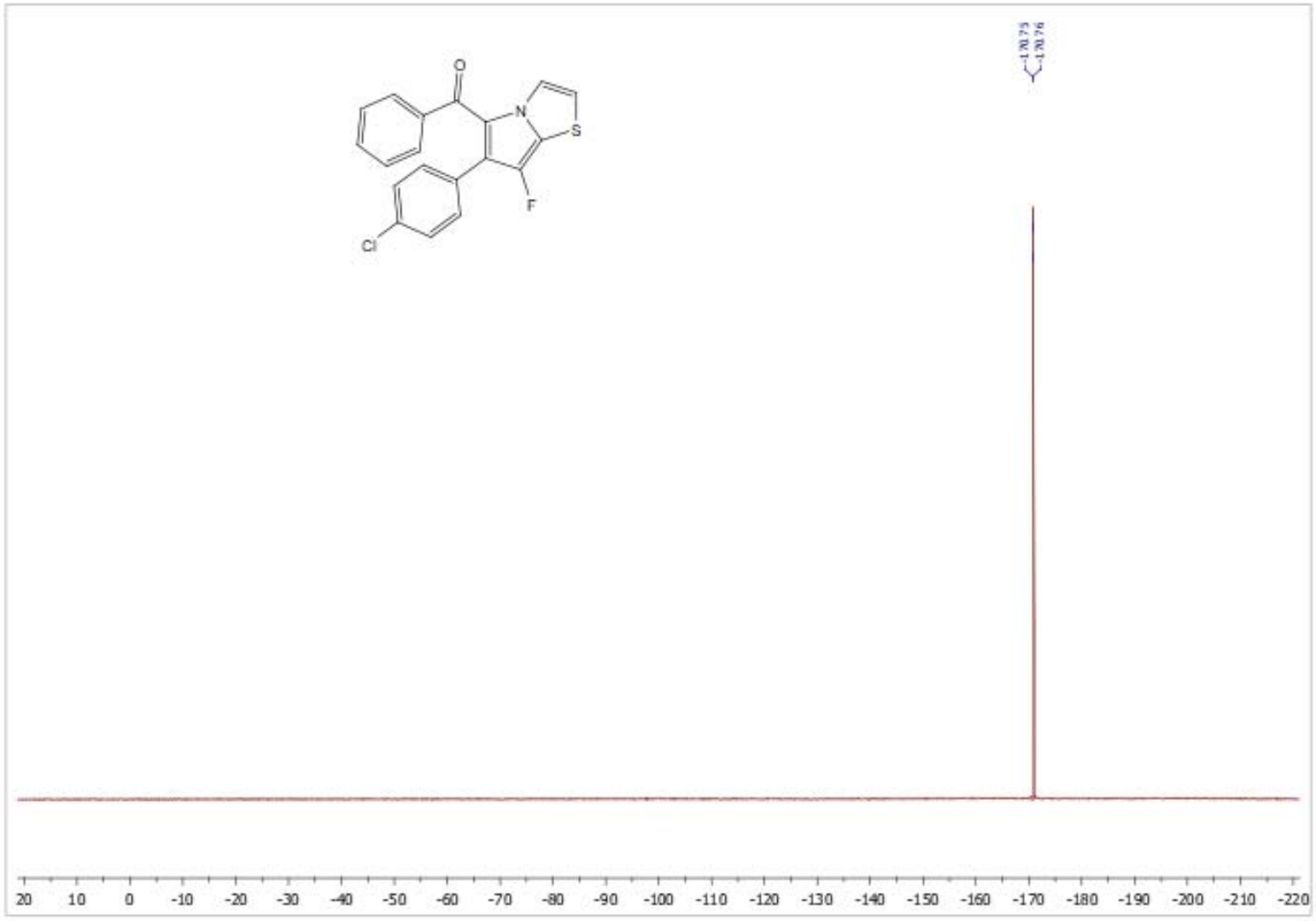
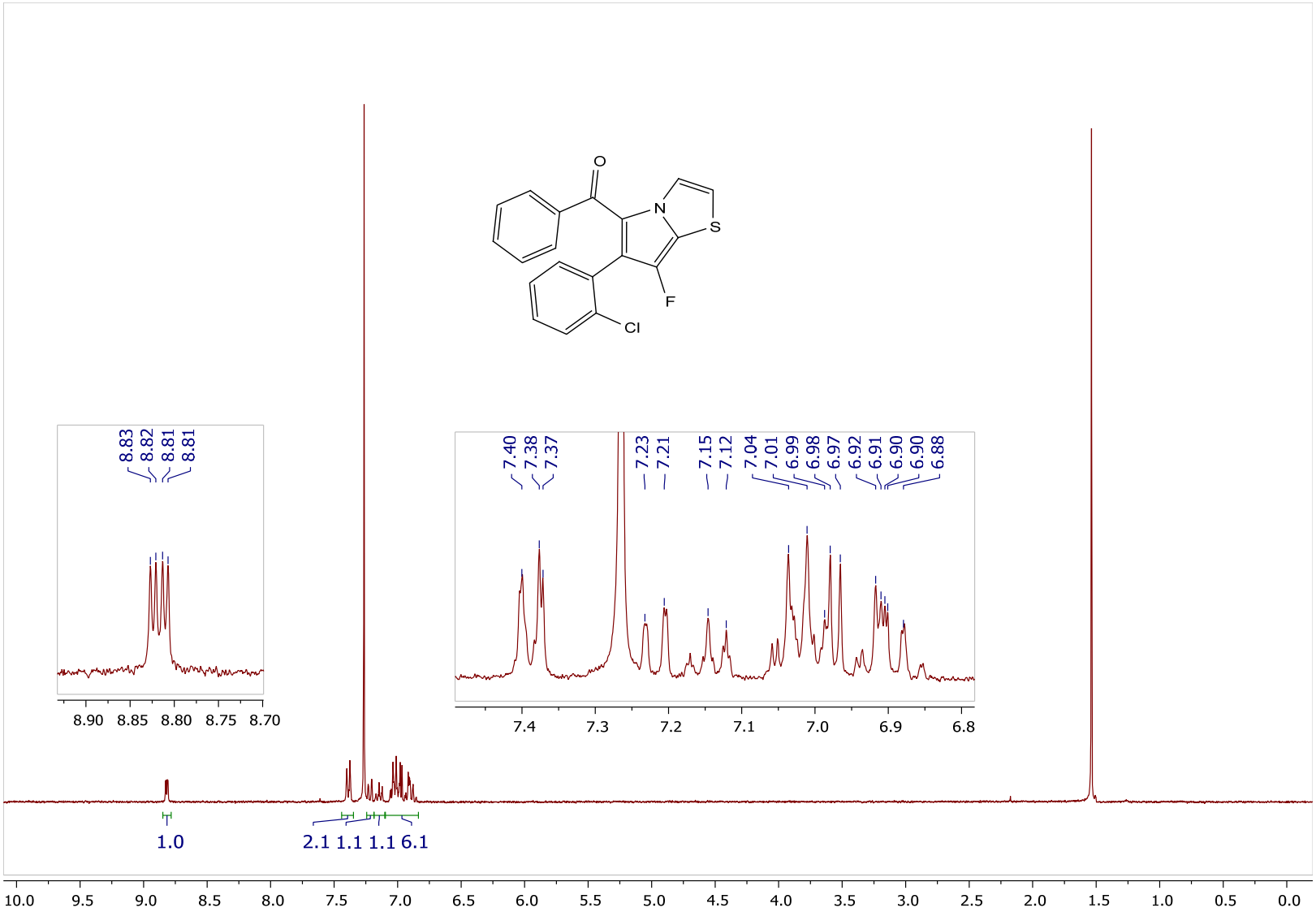
30
20
10
0

^{19}F NMR

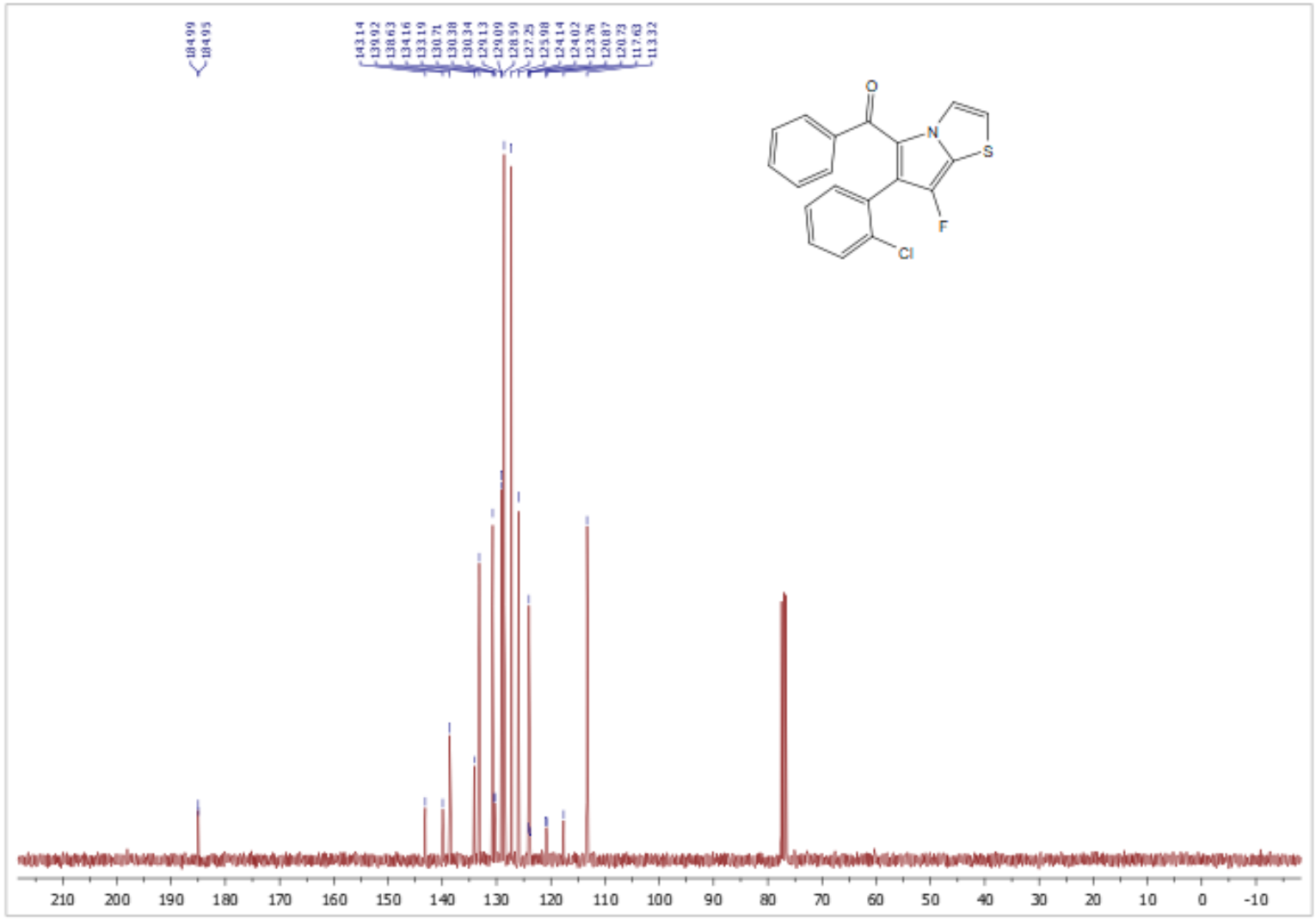

O
N
S
F
Cl
-170.73
-170.76
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

[6-(2-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone **3b**

^{1}H NMR



^{13}C NMR


184.99
184.95
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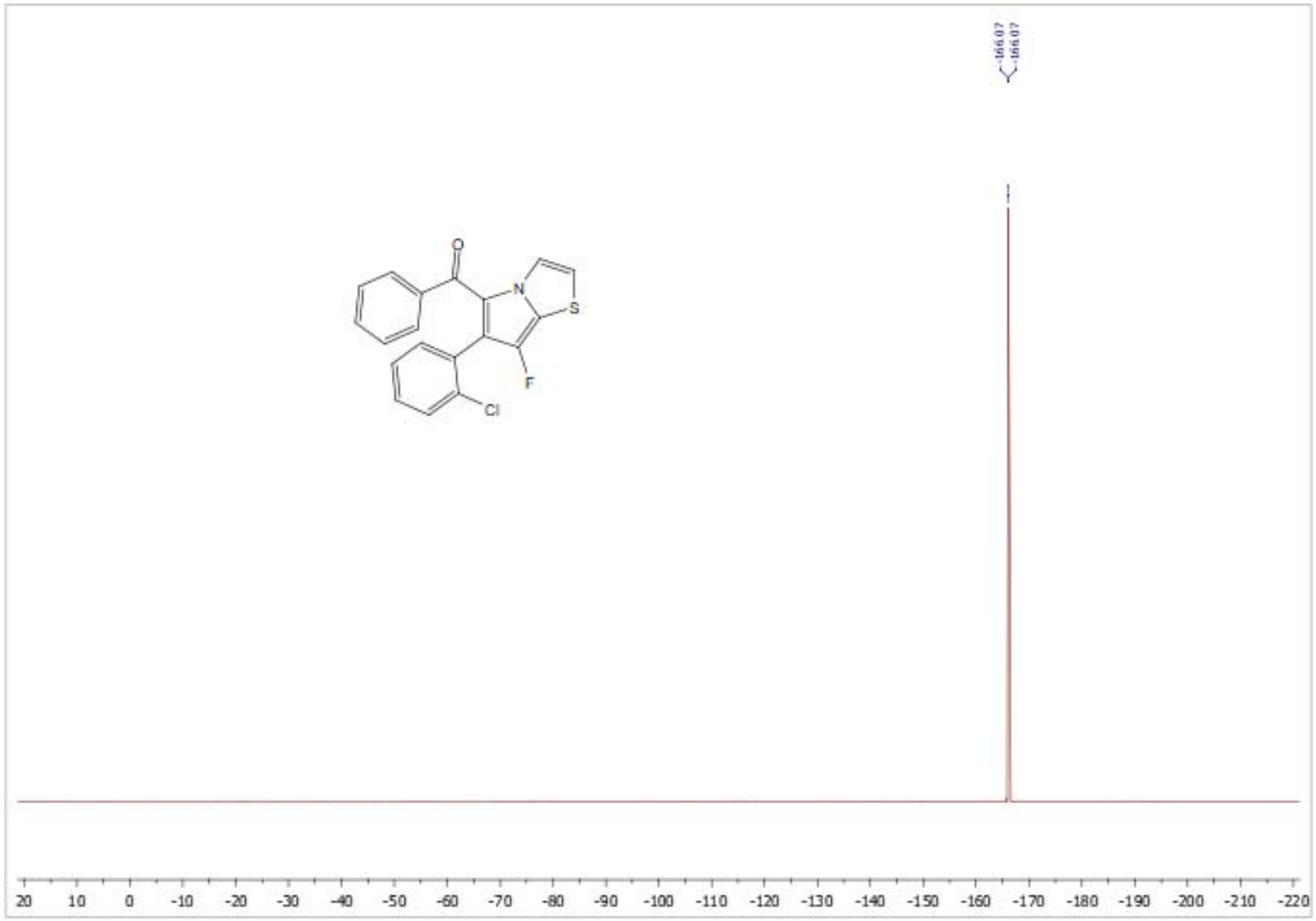
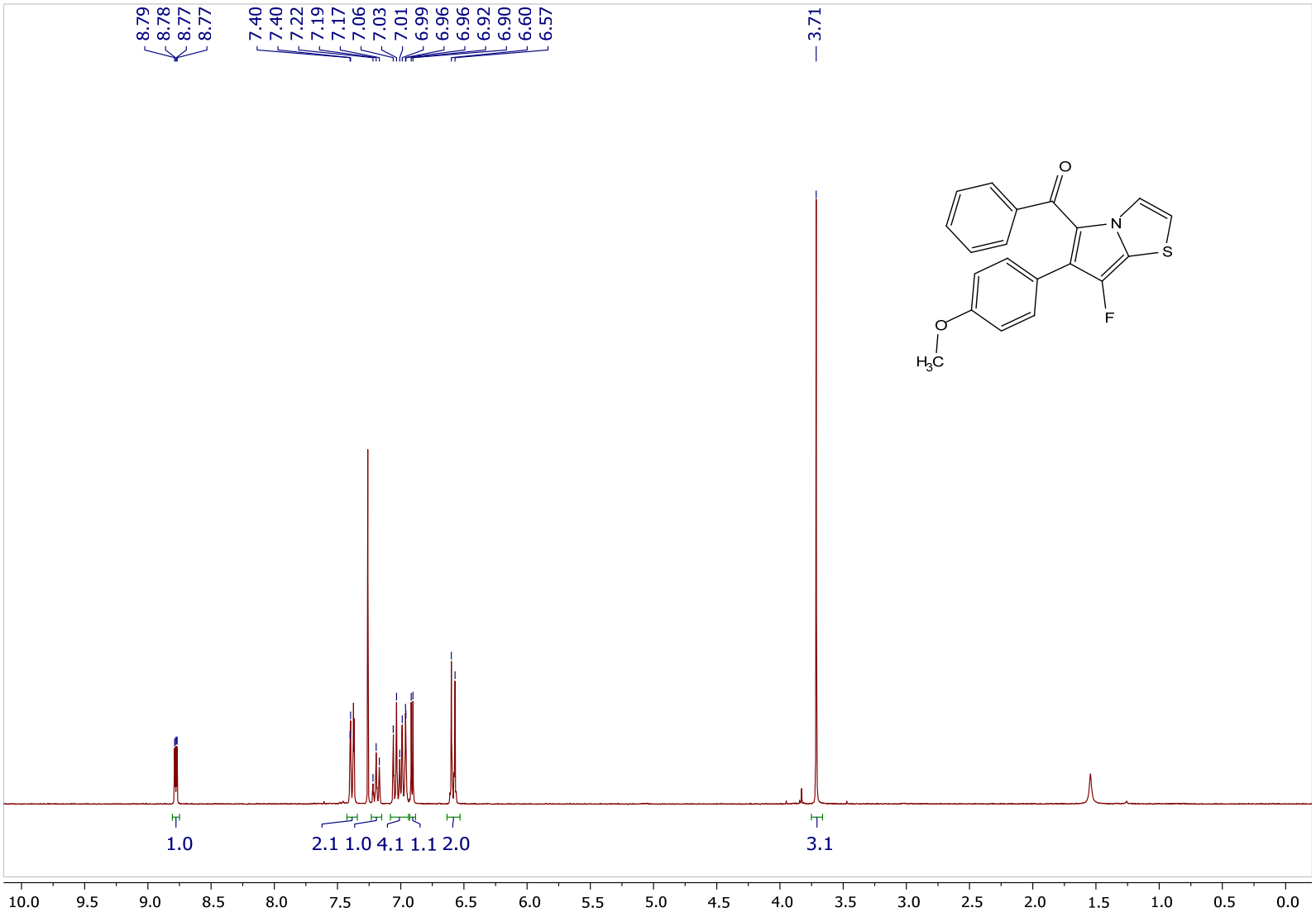
139.92
138.63
134.16
133.19
130.71
130.38
130.34
129.13
129.09
128.99
127.25
125.98
124.14
124.02
123.76
120.87
120.73
117.63
113.32
O
N
S
F
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

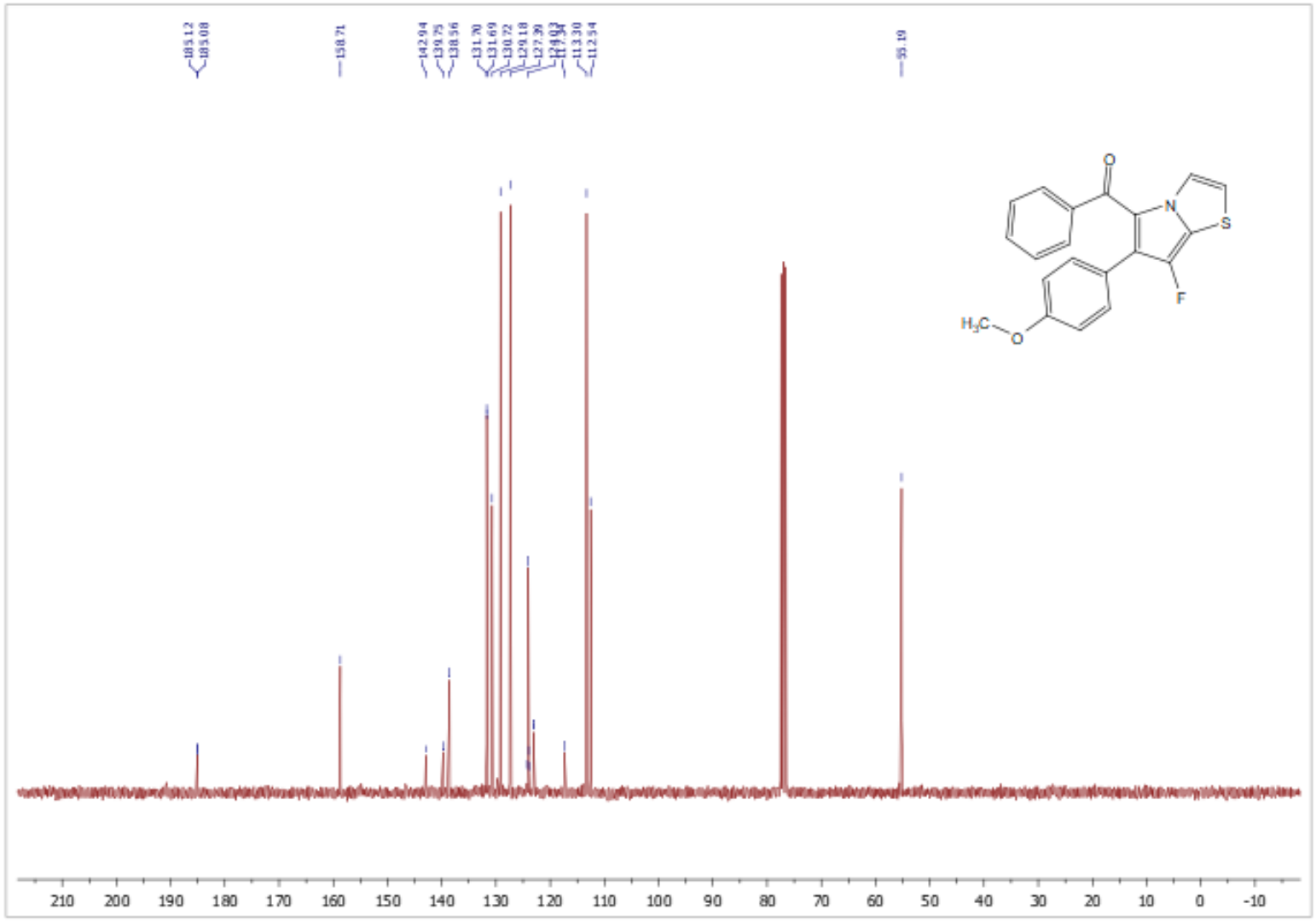

-166.07
-166.07
O
N
S
F
Cl
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220

[7-fluoro-6-(4-methoxyphenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone **3c**

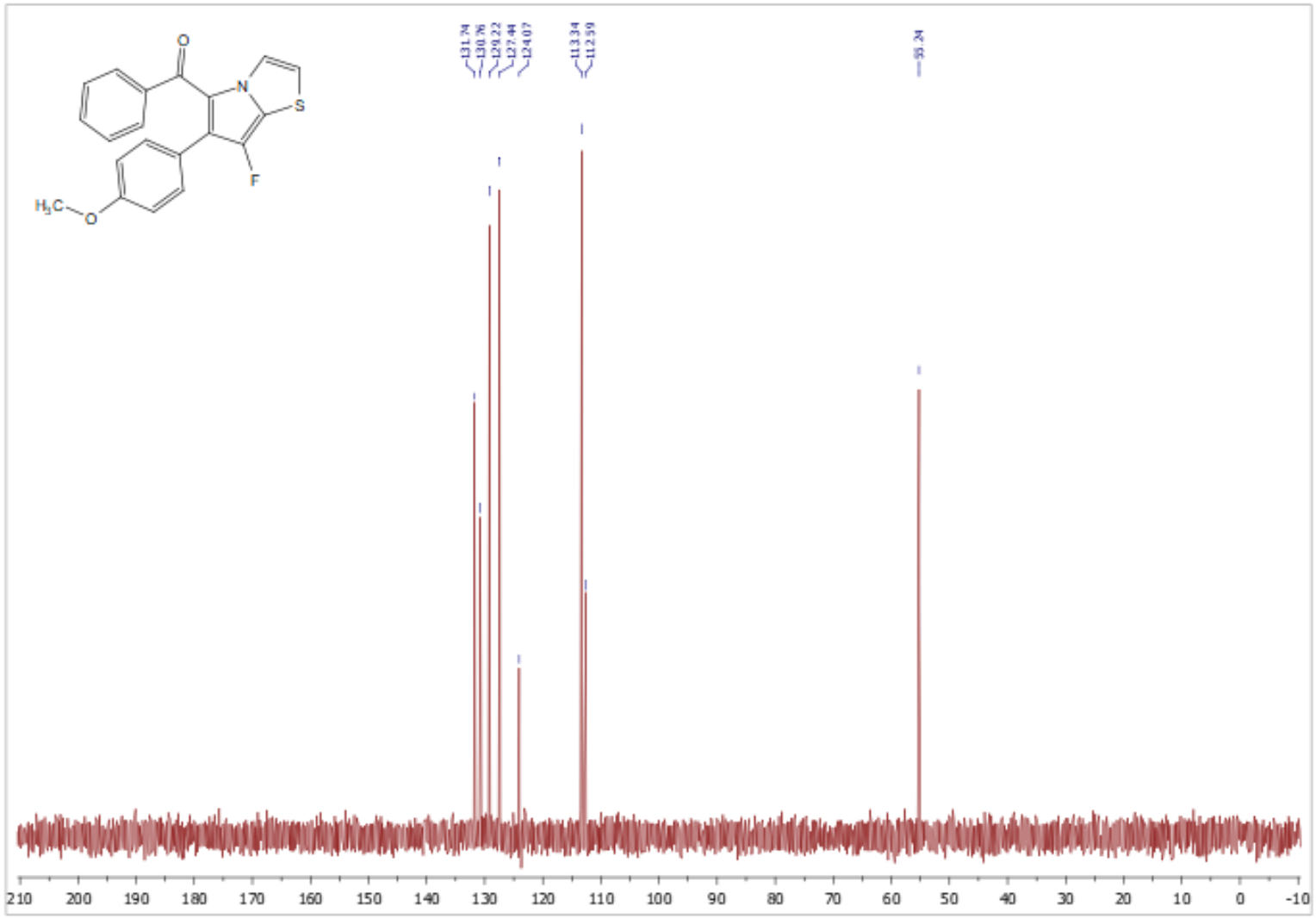
^{1}H NMR



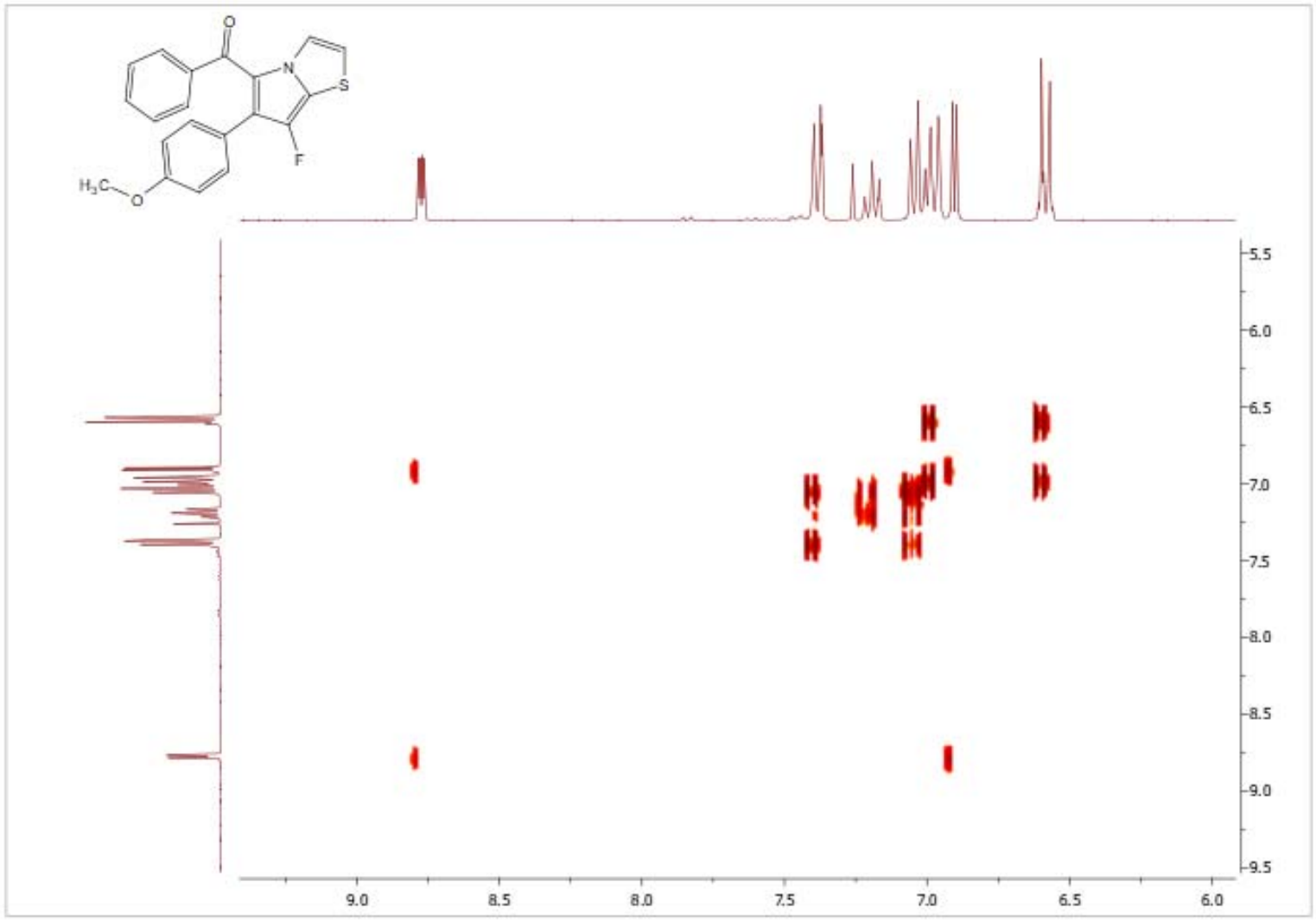
^{13}C NMR


183.12
183.08
158.71
142.94
139.75
138.56
131.70
131.69
130.72
129.18
127.39
113.30
112.54
55.19
O
N
S
F
H3C
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

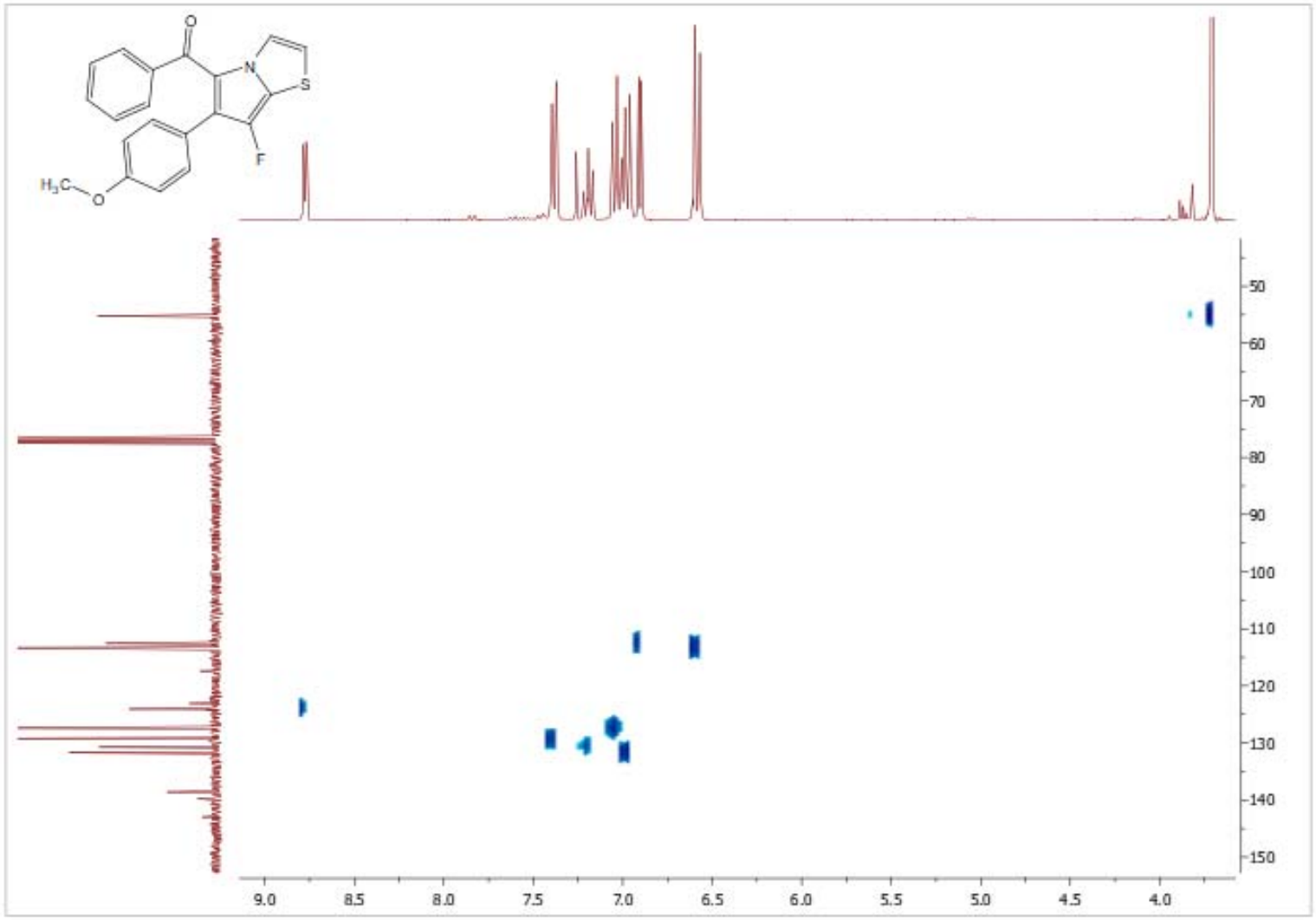
DEPT-135 ^{13}C NMR



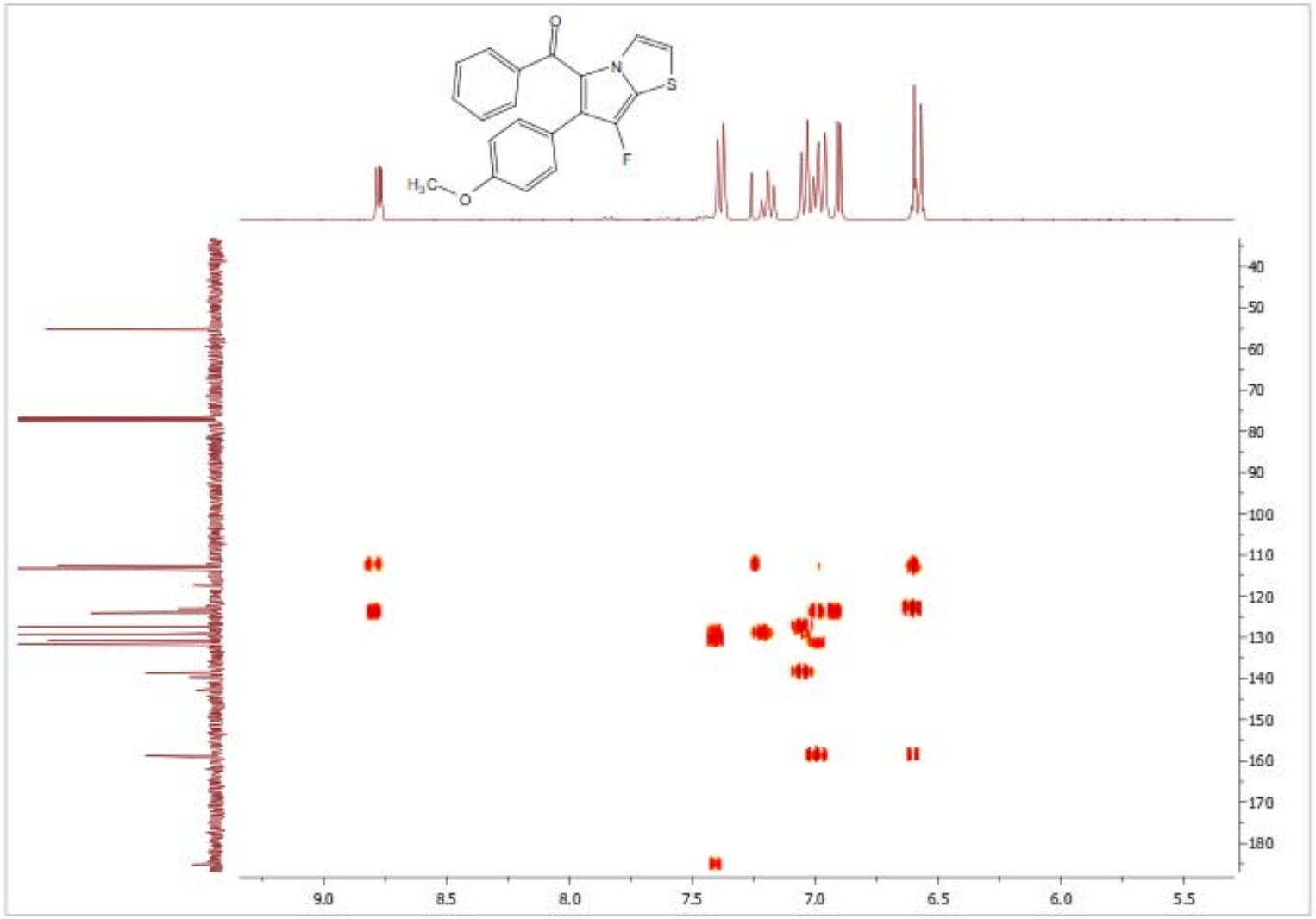
^{1}H-^{1}H COSY NMR



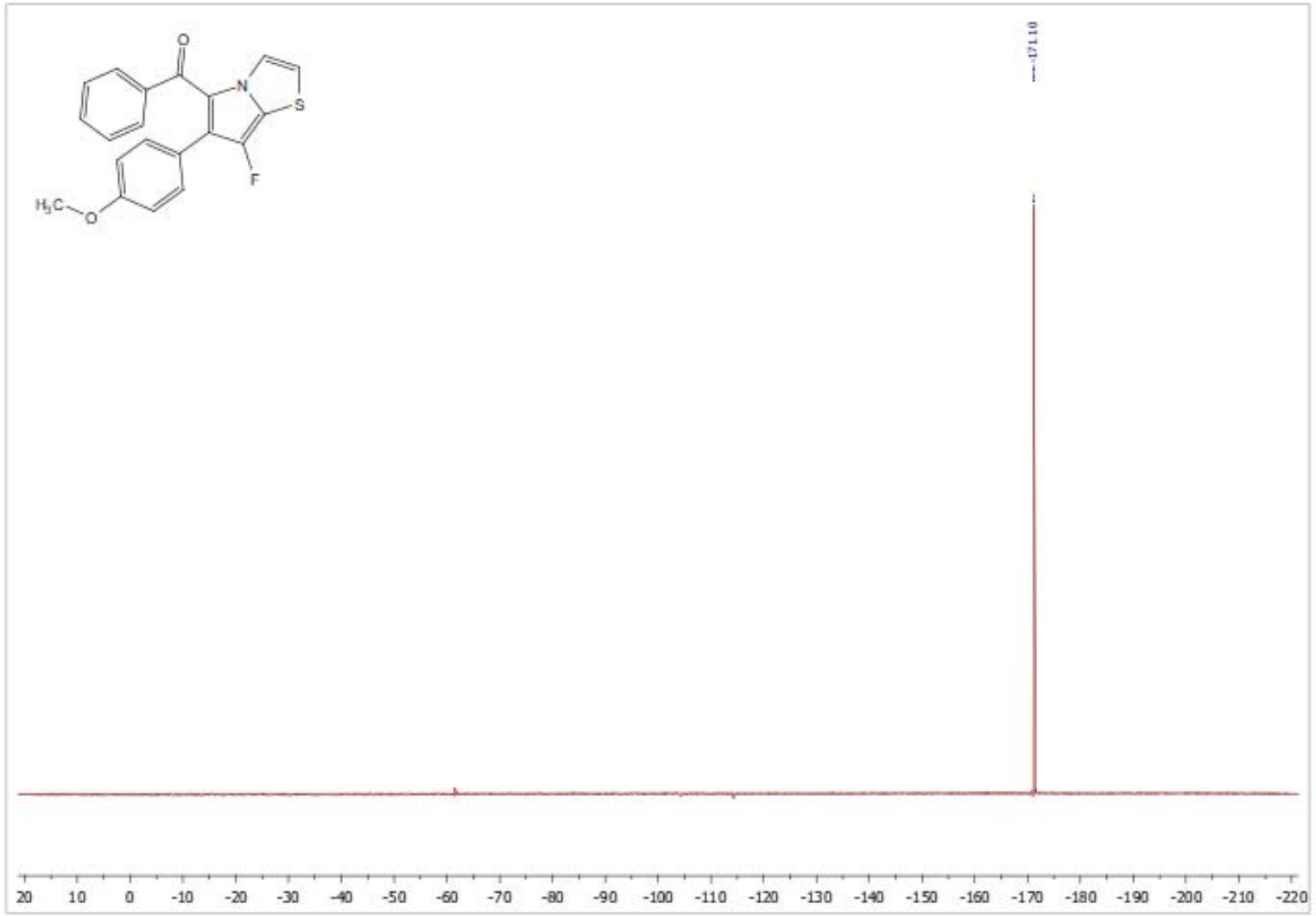
^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR

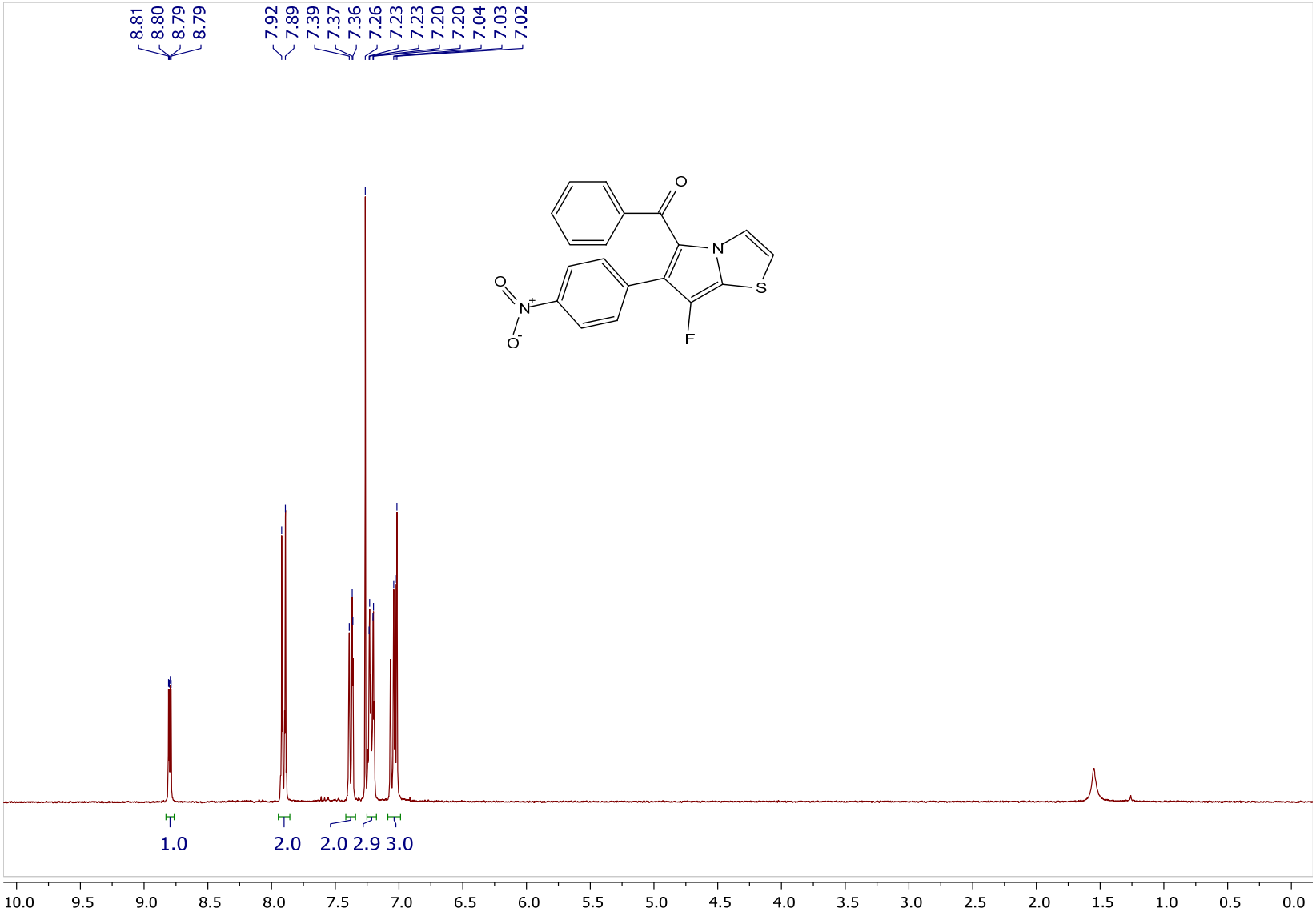


^{19}F NMR

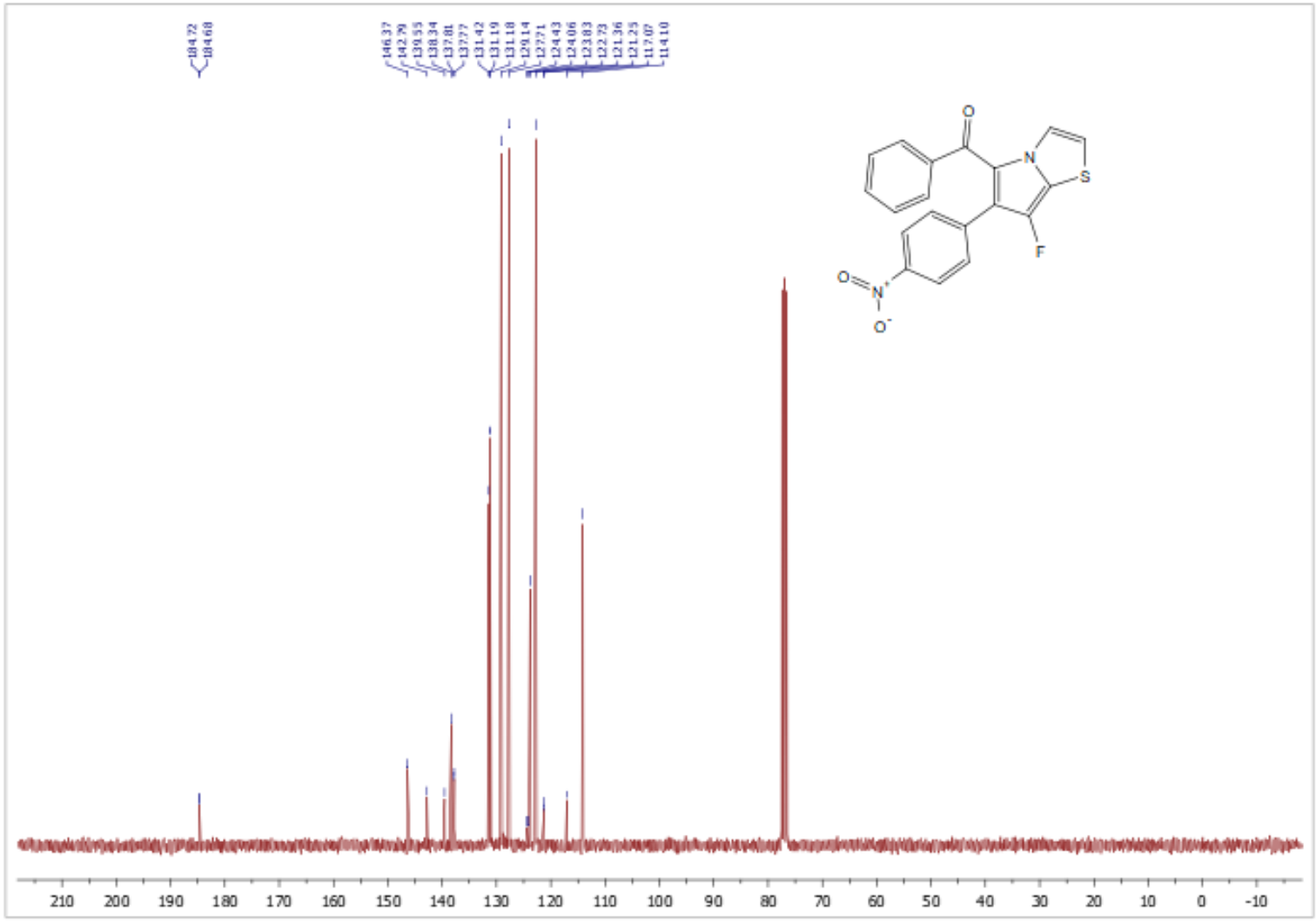

O
N
S
F
H3C
O
-171.10
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220

[7-fluoro-6-(4-nitrophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone **3d**

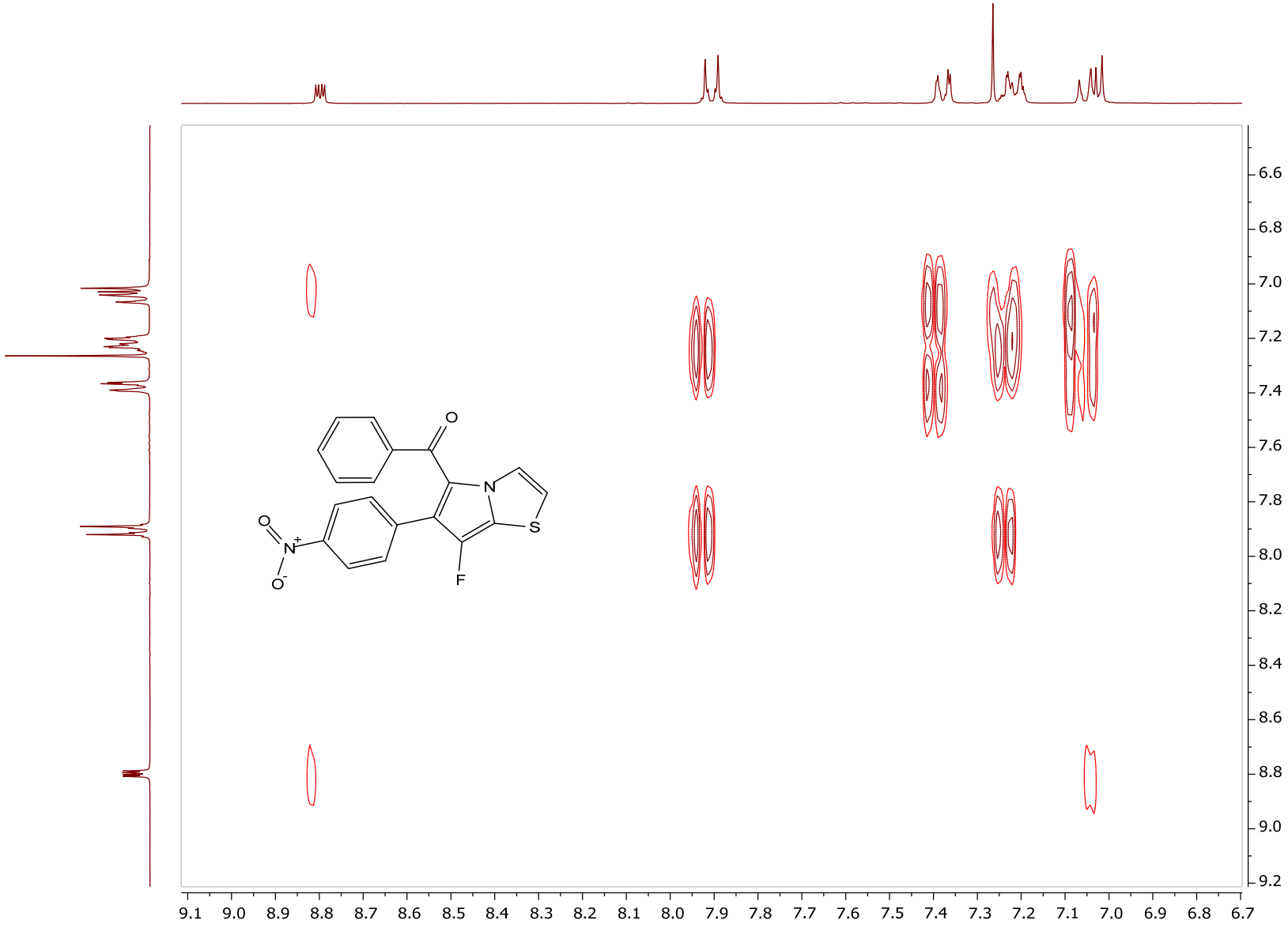
^{1}H NMR



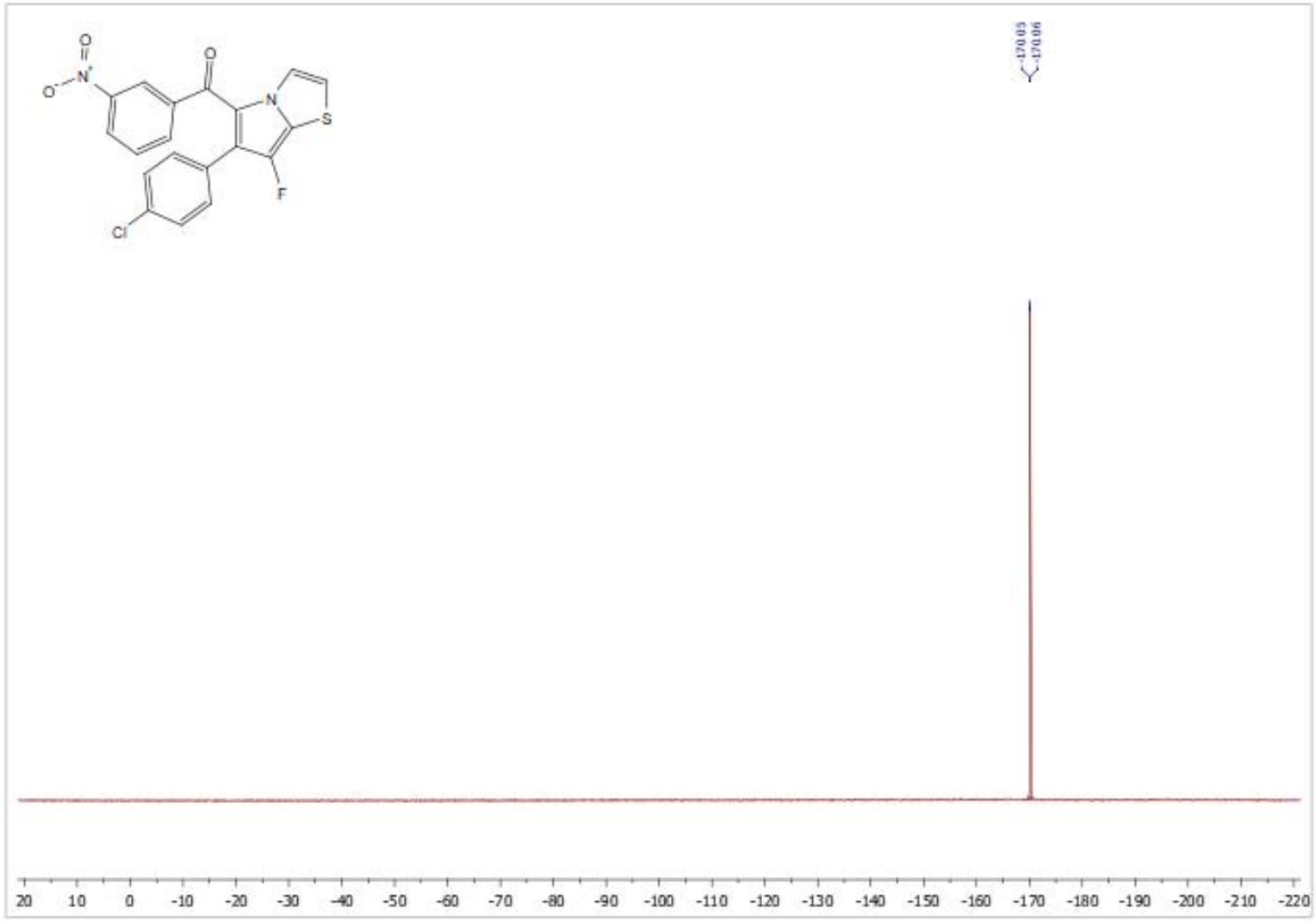
^{13}C NMR


184.72
184.68
146.37
142.79
139.55
138.34
137.81
137.77
131.42
131.19
131.18
129.14
127.71
124.43
124.06
123.83
122.73
121.36
121.25
117.07
114.10
O
N
S
F
O
N+
O-
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{1}H-^{1}H COSY

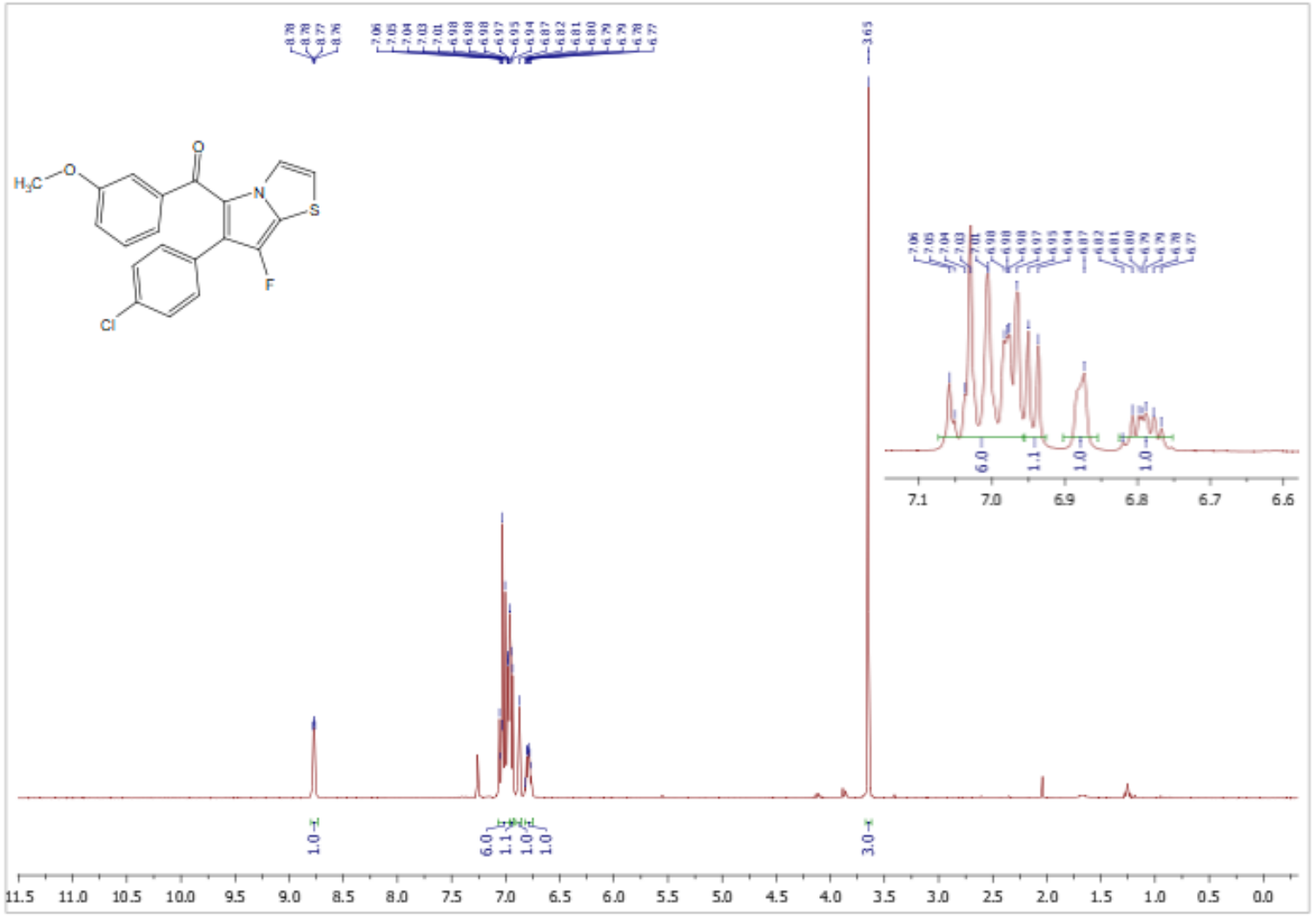

O
N
S
F
O
N+
O-
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7

^{19}F NMR

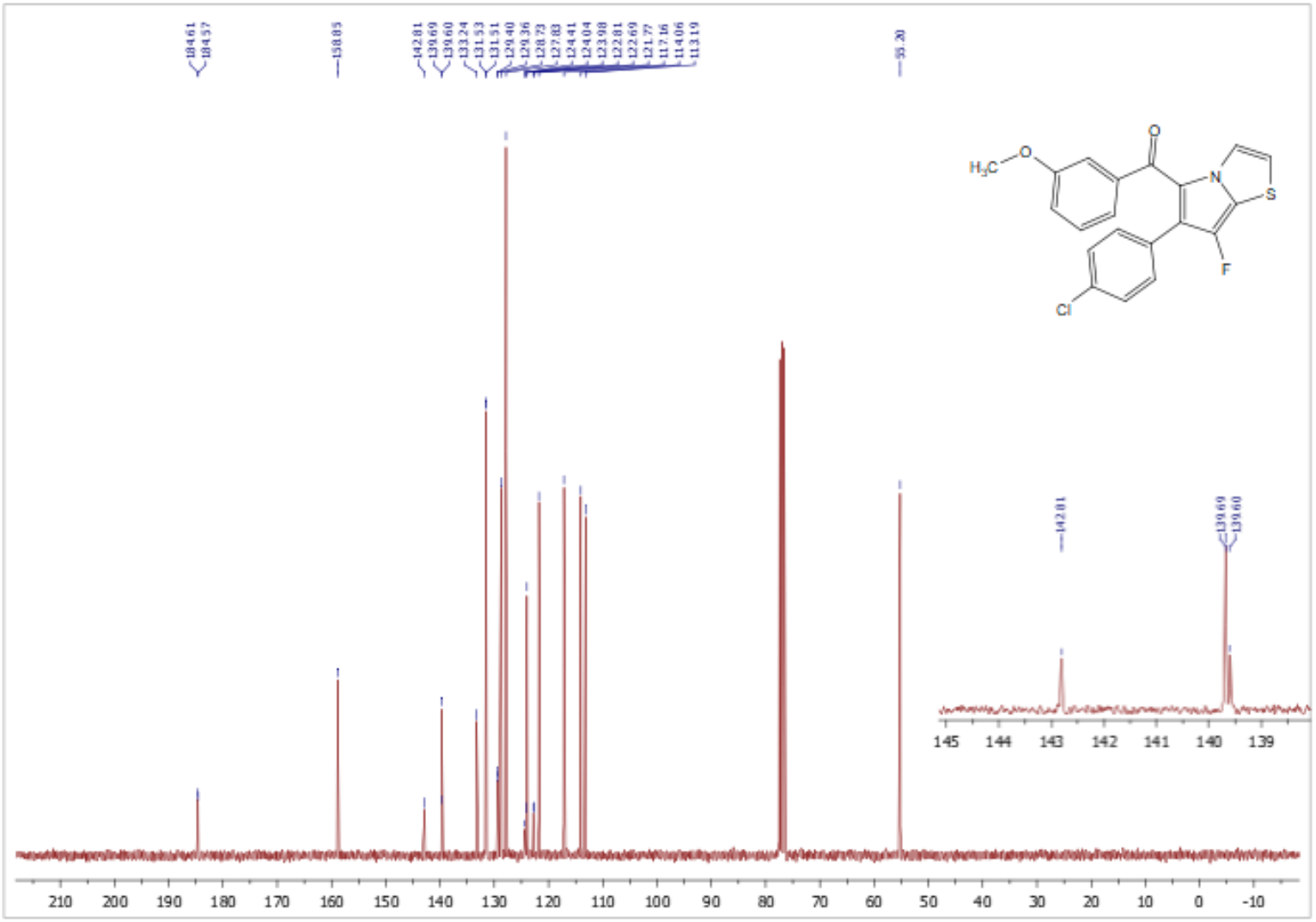

-170.03
-170.06
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

[6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](3-methoxyphenyl)methanone **3e**

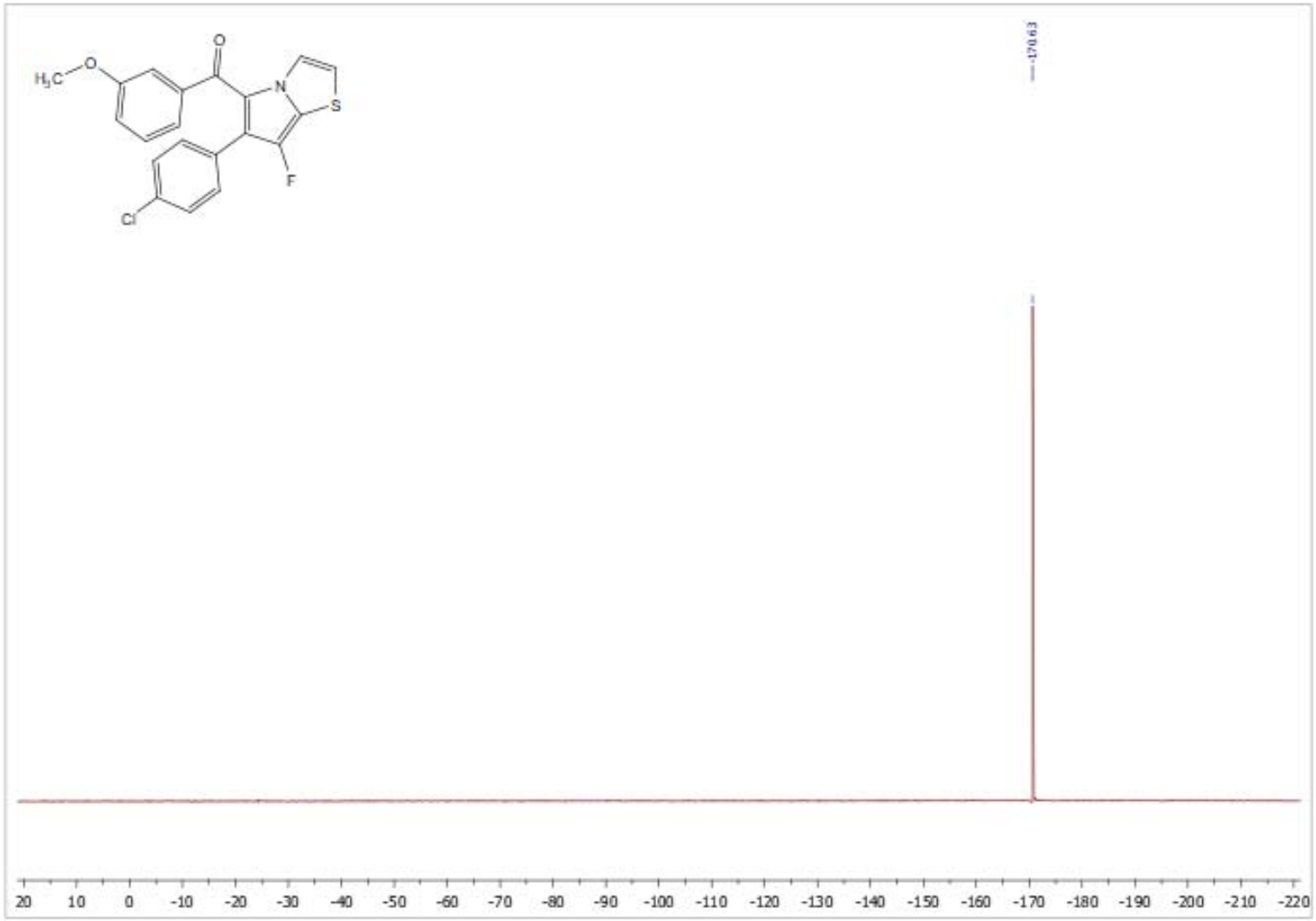
^{1}H NMR



^{13}C NMR

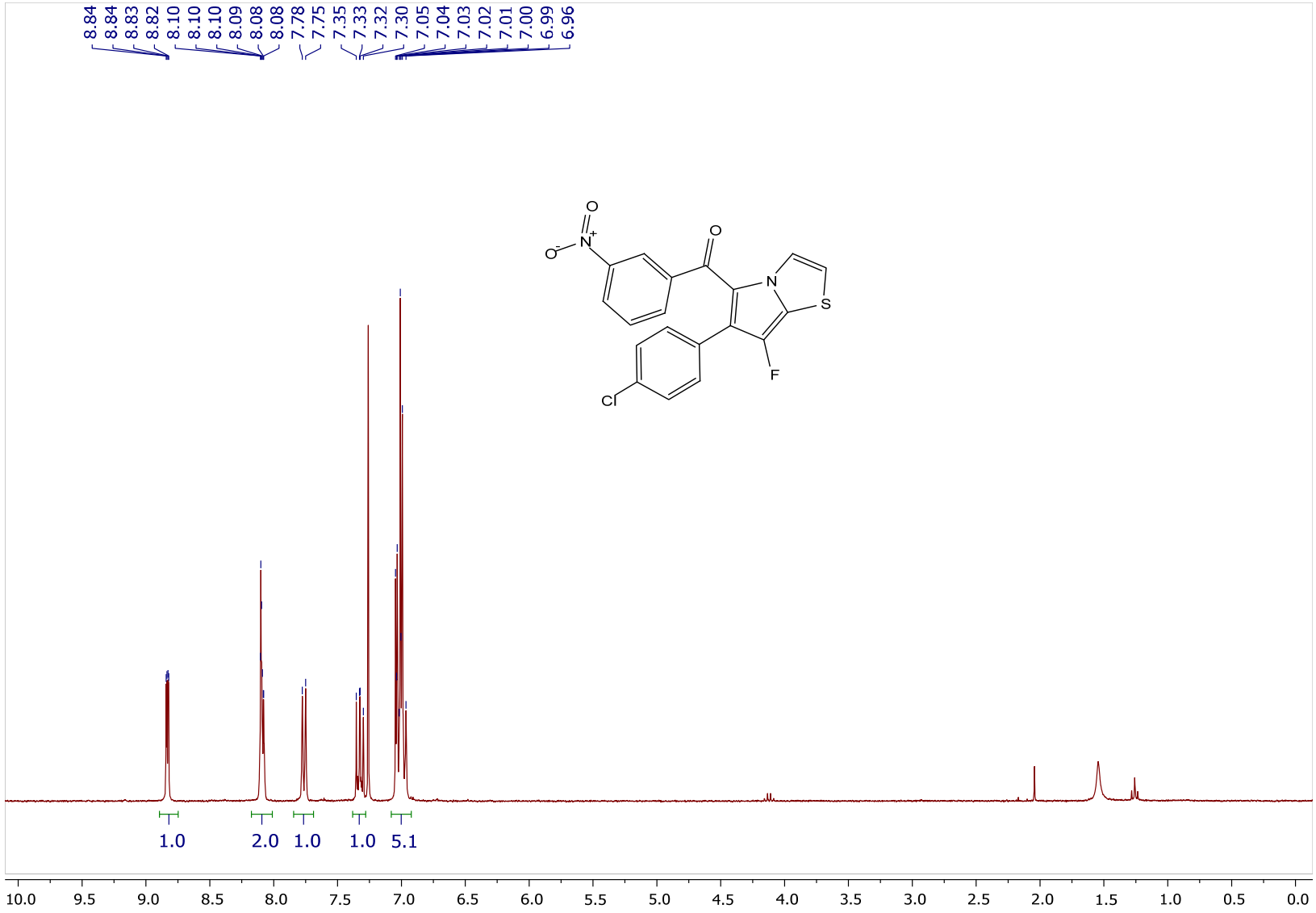

184.61
184.37
158.85
142.81
139.69
139.60
133.24
131.53
131.51
129.40
129.36
128.73
127.83
124.41
124.04
123.98
122.81
122.69
121.77
117.16
114.06
113.19
55.20
O
H3C
O
N
S
F
Cl
142.81
139.69
139.60
145
144
143
142
141
140
139
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

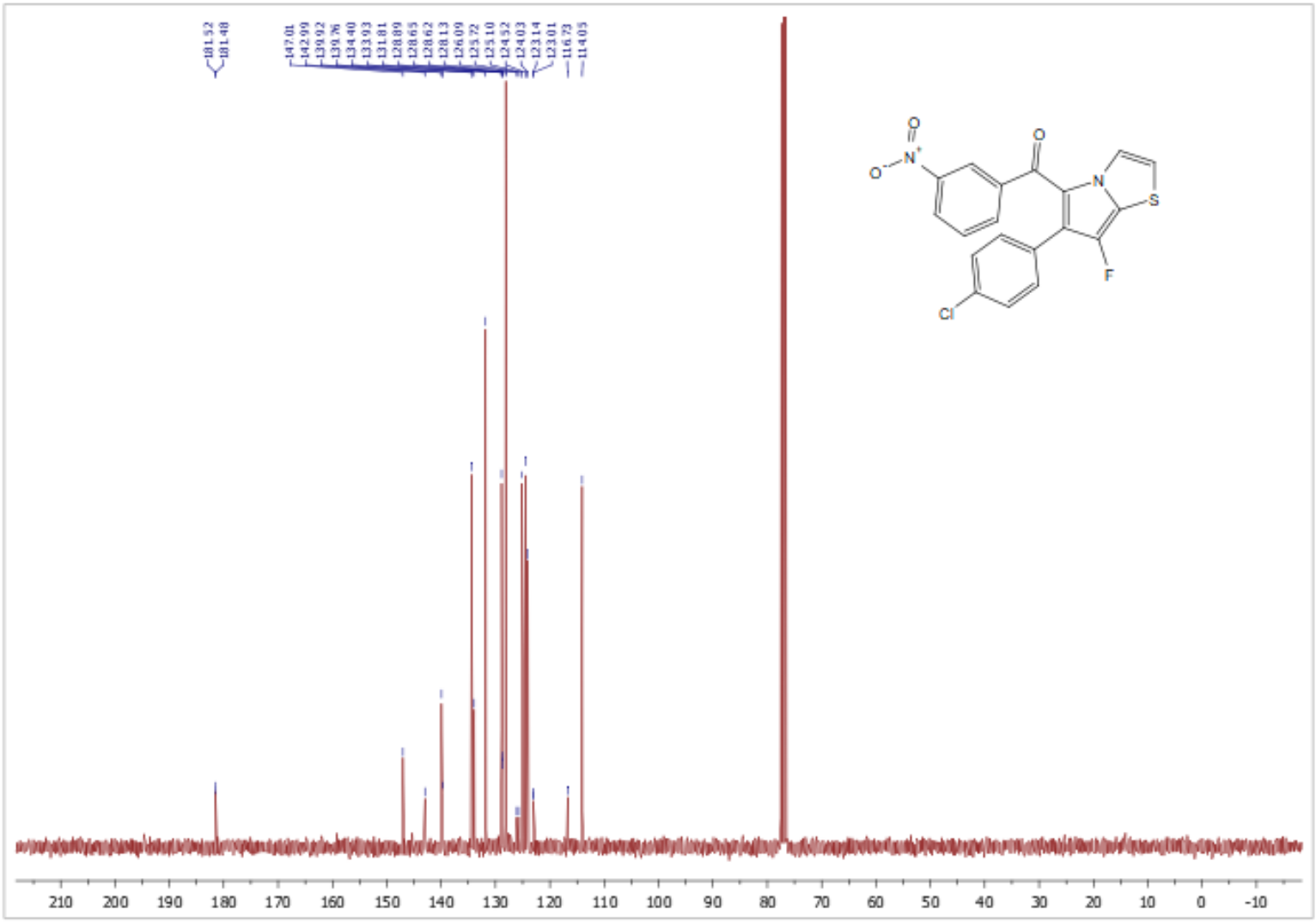

O
H3C
O
N
S
F
Cl
-170.63
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

[6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](3-nitrophenyl)methanone **3f**

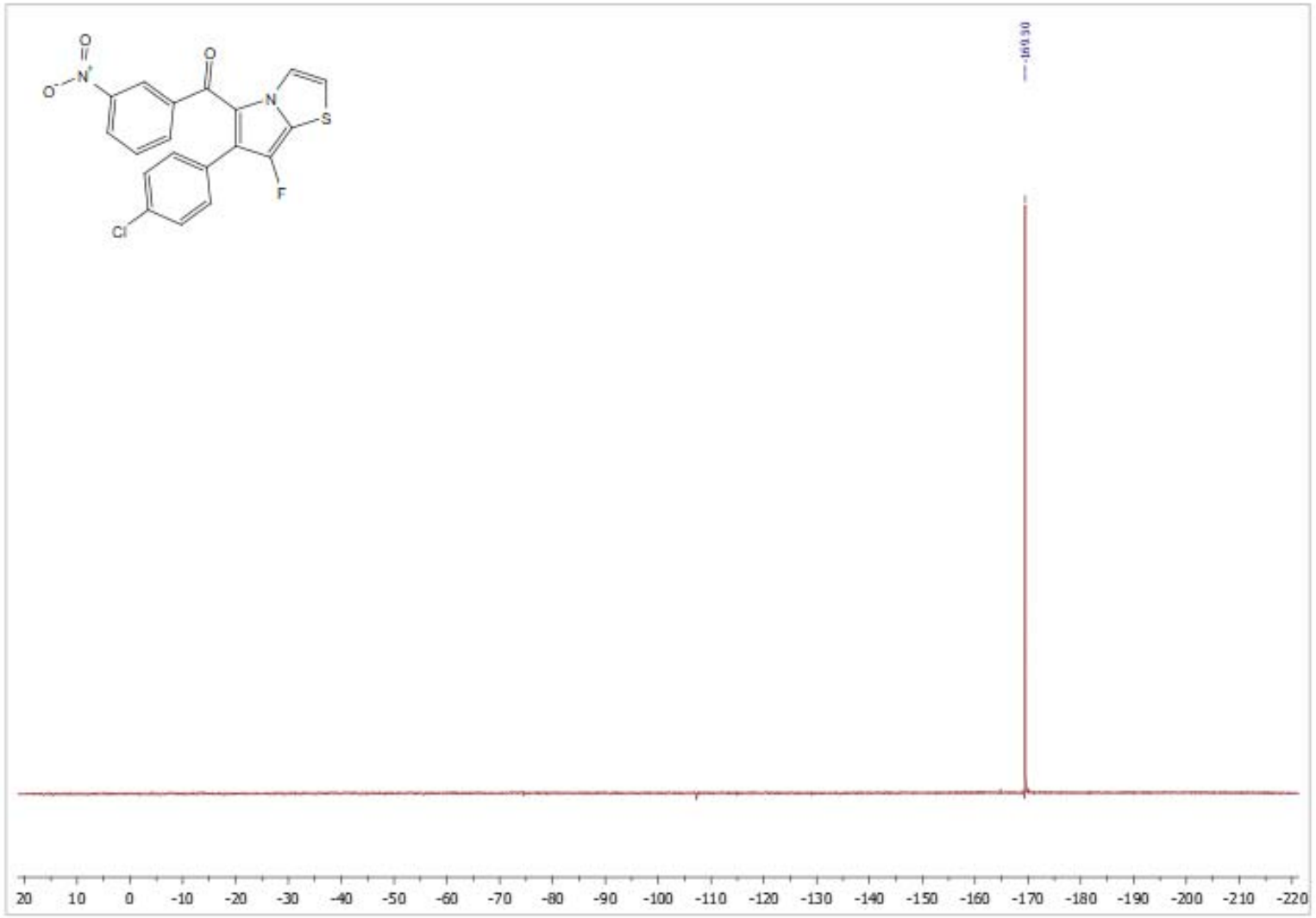
^{1}H NMR



^{13}C NMR

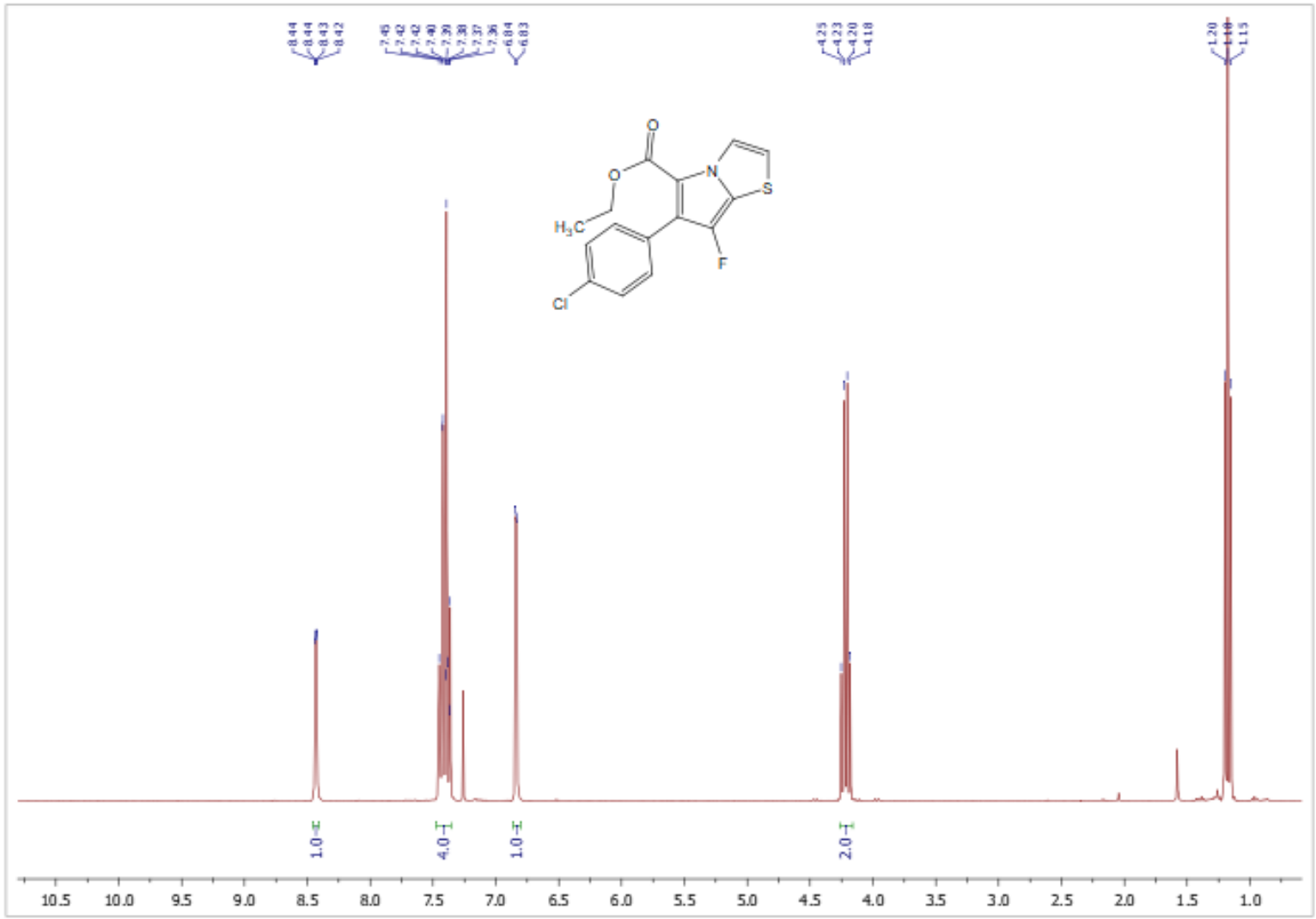

181.52
181.48
147.01
142.99
139.92
139.76
134.40
133.93
131.81
128.89
128.65
128.62
128.13
126.09
125.72
125.10
124.52
124.03
123.14
123.01
116.73
114.05
O
O
N+
O-
N
S
F
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

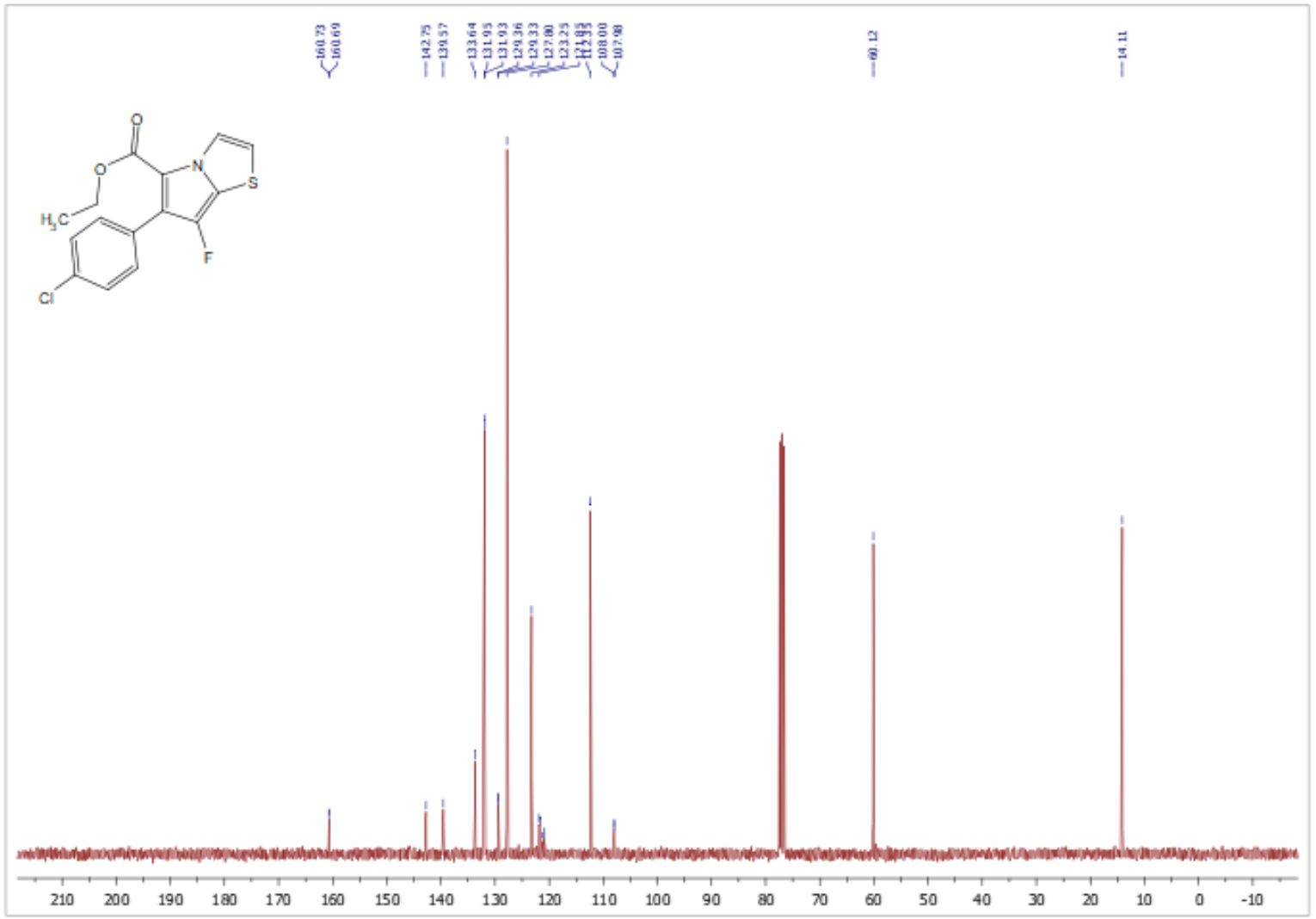

O
O
N
O
N
S
F
Cl
-169.50
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

ethyl 6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazole-5-carboxylate **3g**

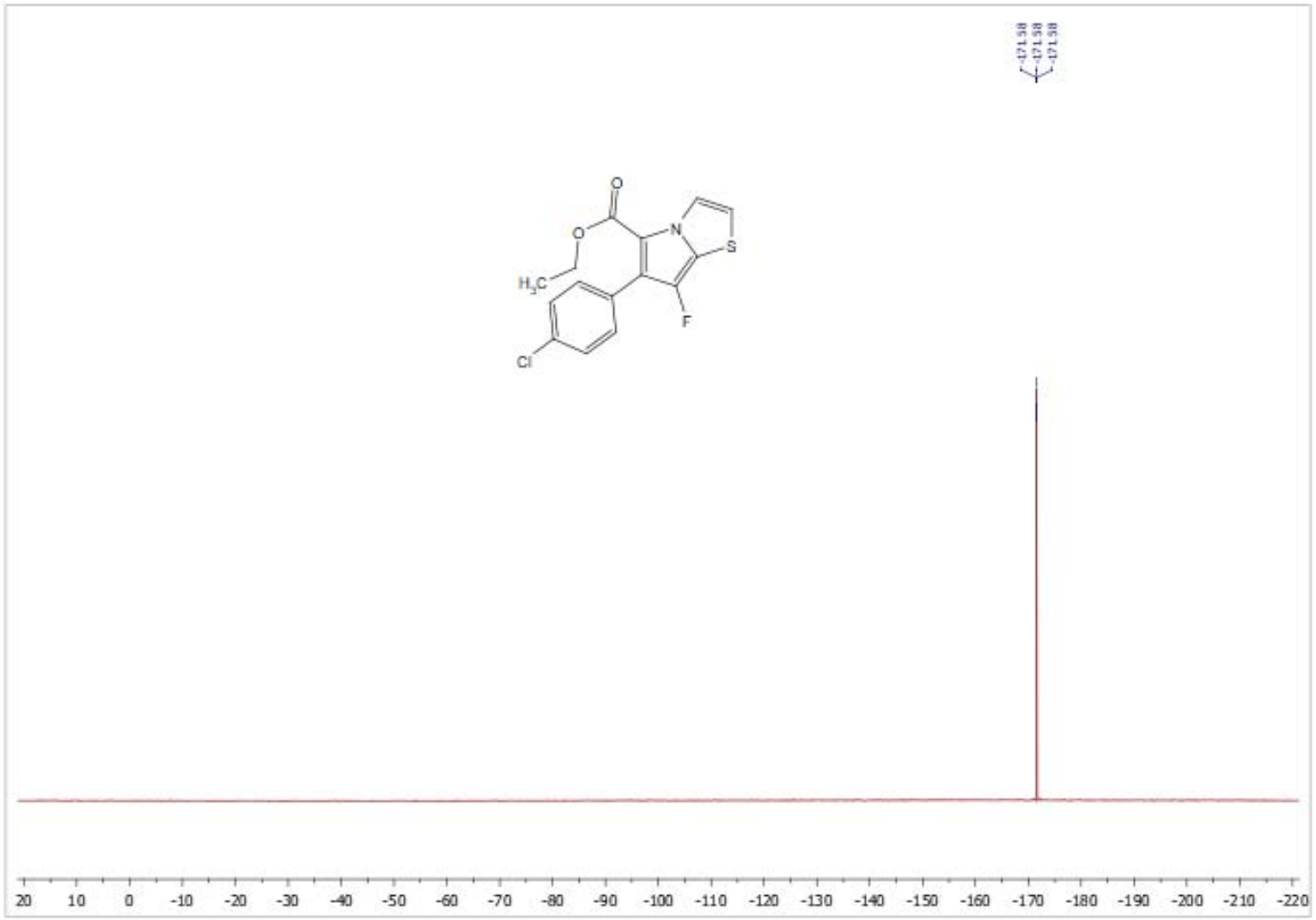
^{1}H NMR



^{13}C NMR

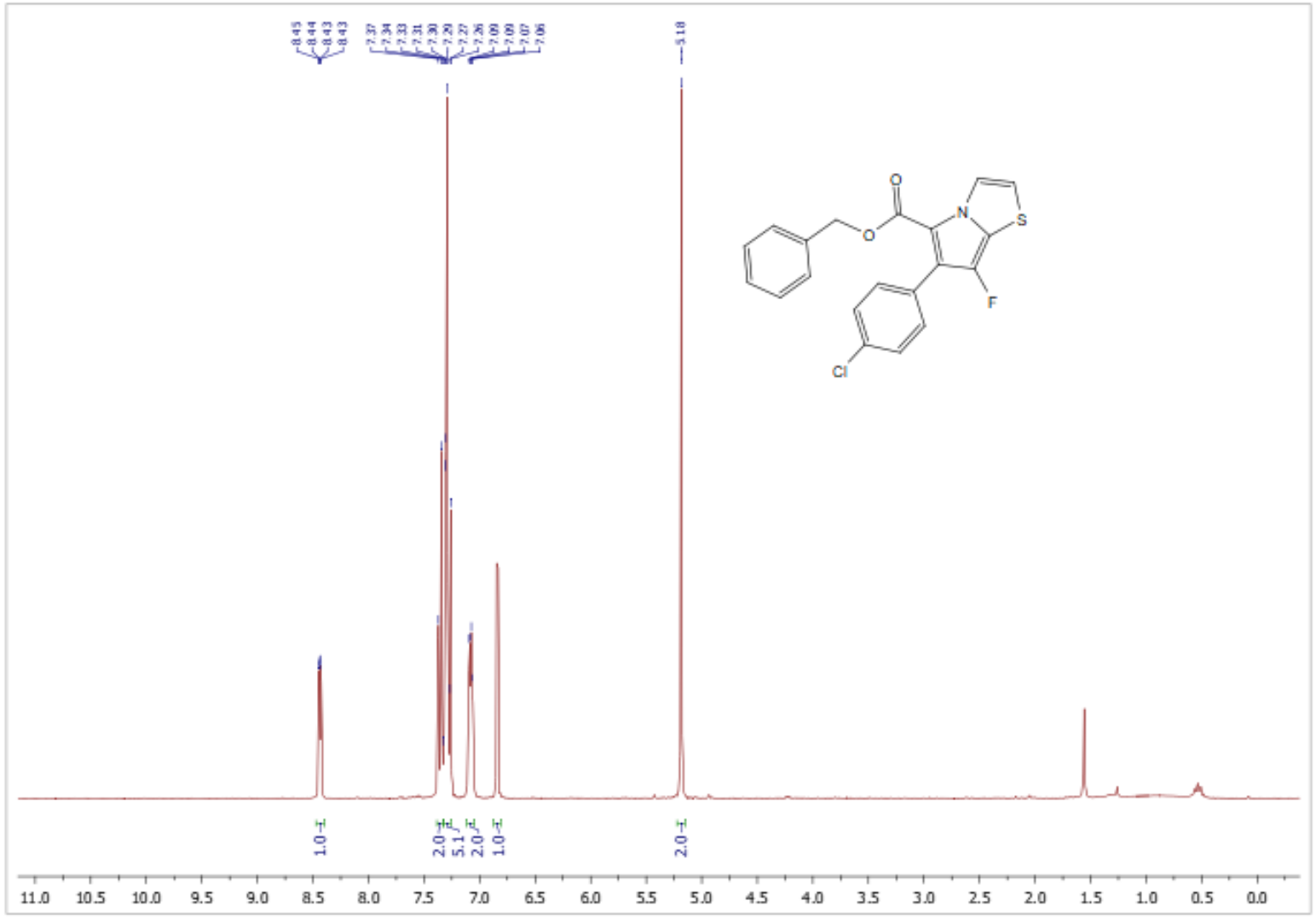

160.73
160.69
142.75
139.57
133.64
131.95
131.93
129.36
129.33
127.80
123.25
60.12
14.11
108.00
107.98
O
O
N
S
H3C
F
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

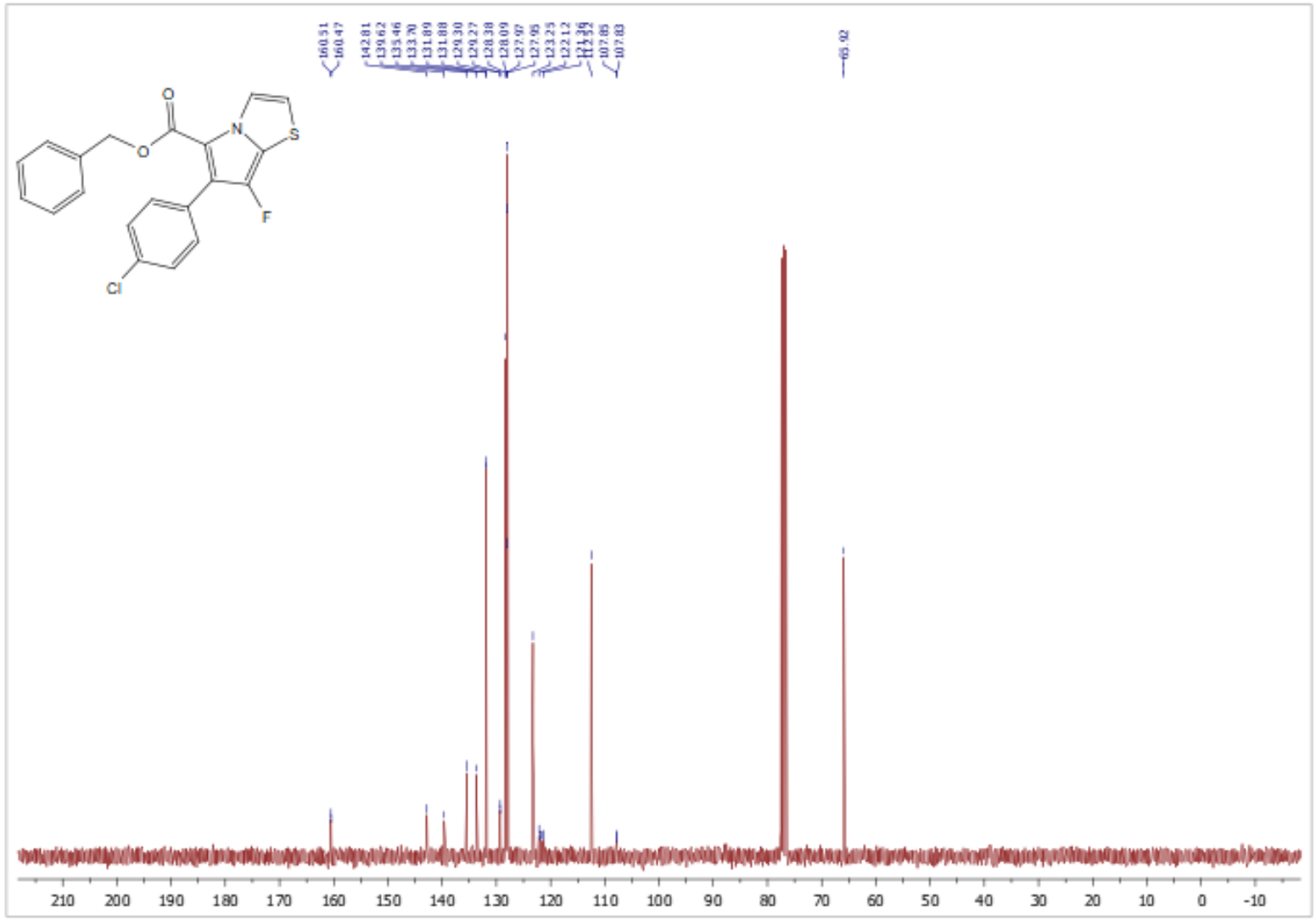

-171.38
-171.38
-171.38
O
O
N
S
H3C
F
Cl
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220

benzyl 6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazole-5-carboxylate **3h**

^{1}H NMR



^{13}C NMR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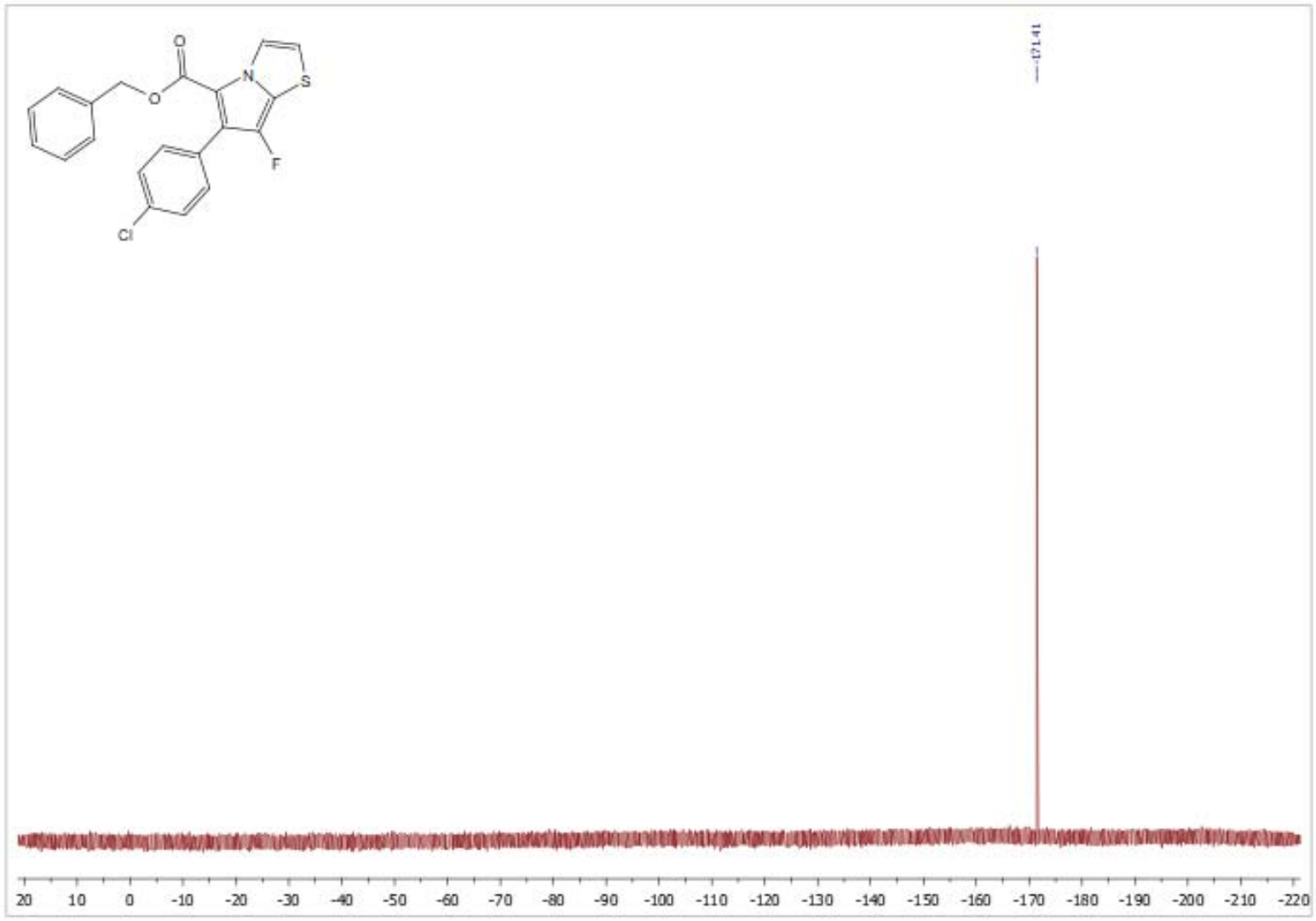
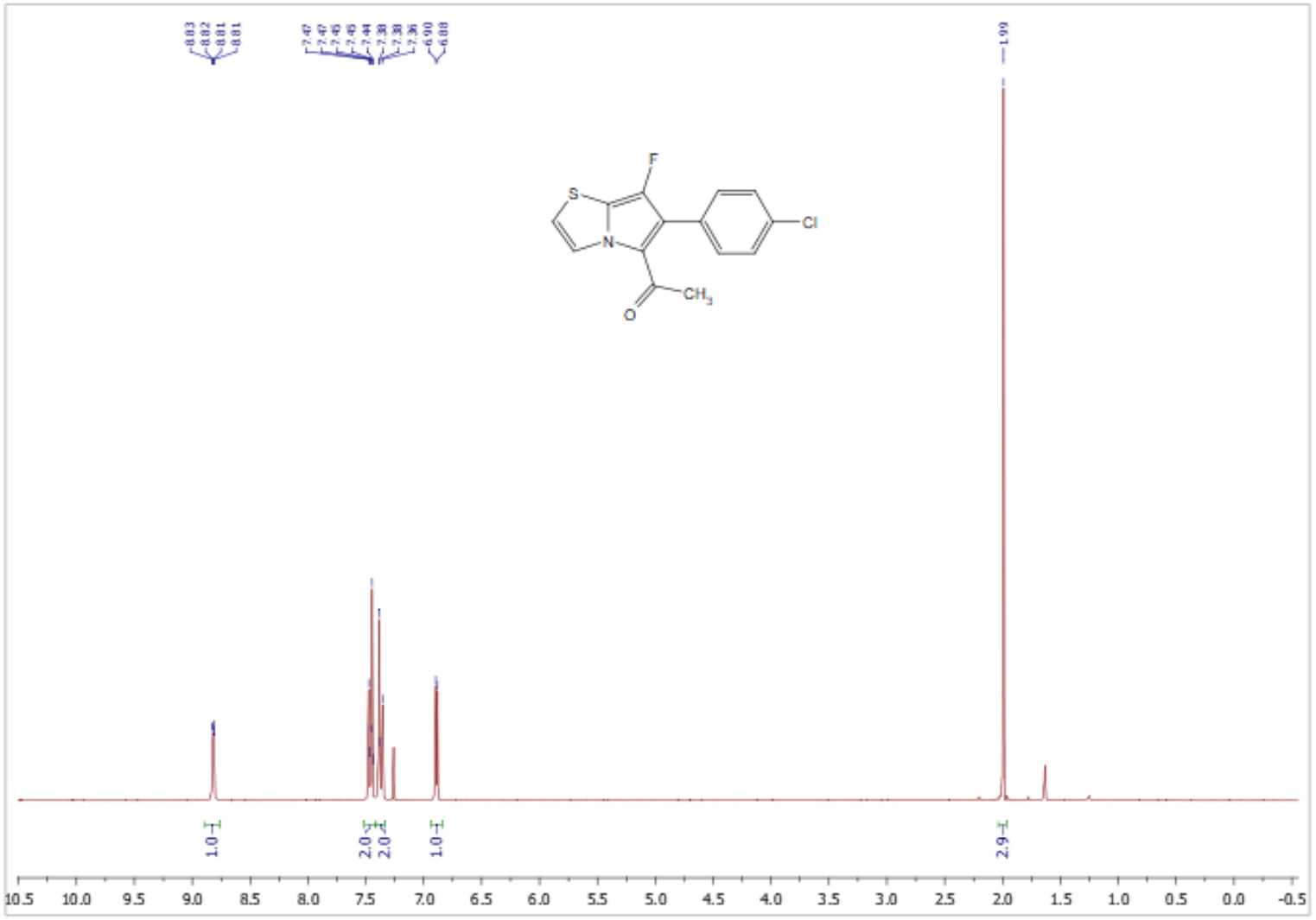
160.47
142.81
139.62
133.46
133.70
131.89
131.88
129.30
129.27
128.38
128.09
127.97
127.95
123.25
122.12
111.36
111.32
107.85
107.83
65.92
O
O
N
S
F
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

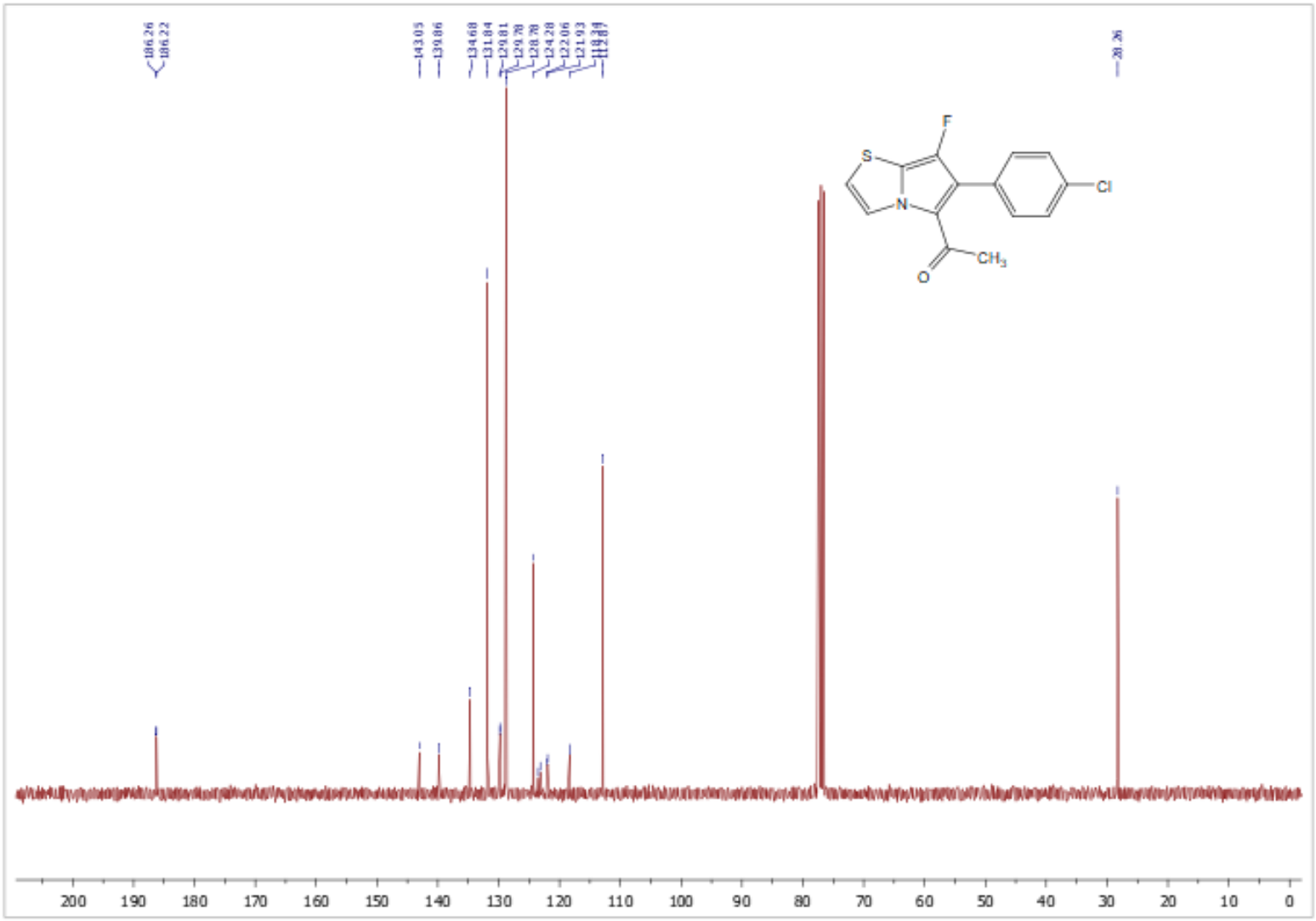

O
O
N
S
F
Cl
-117.141
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

1-[6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl]ethan-1-one **3i**

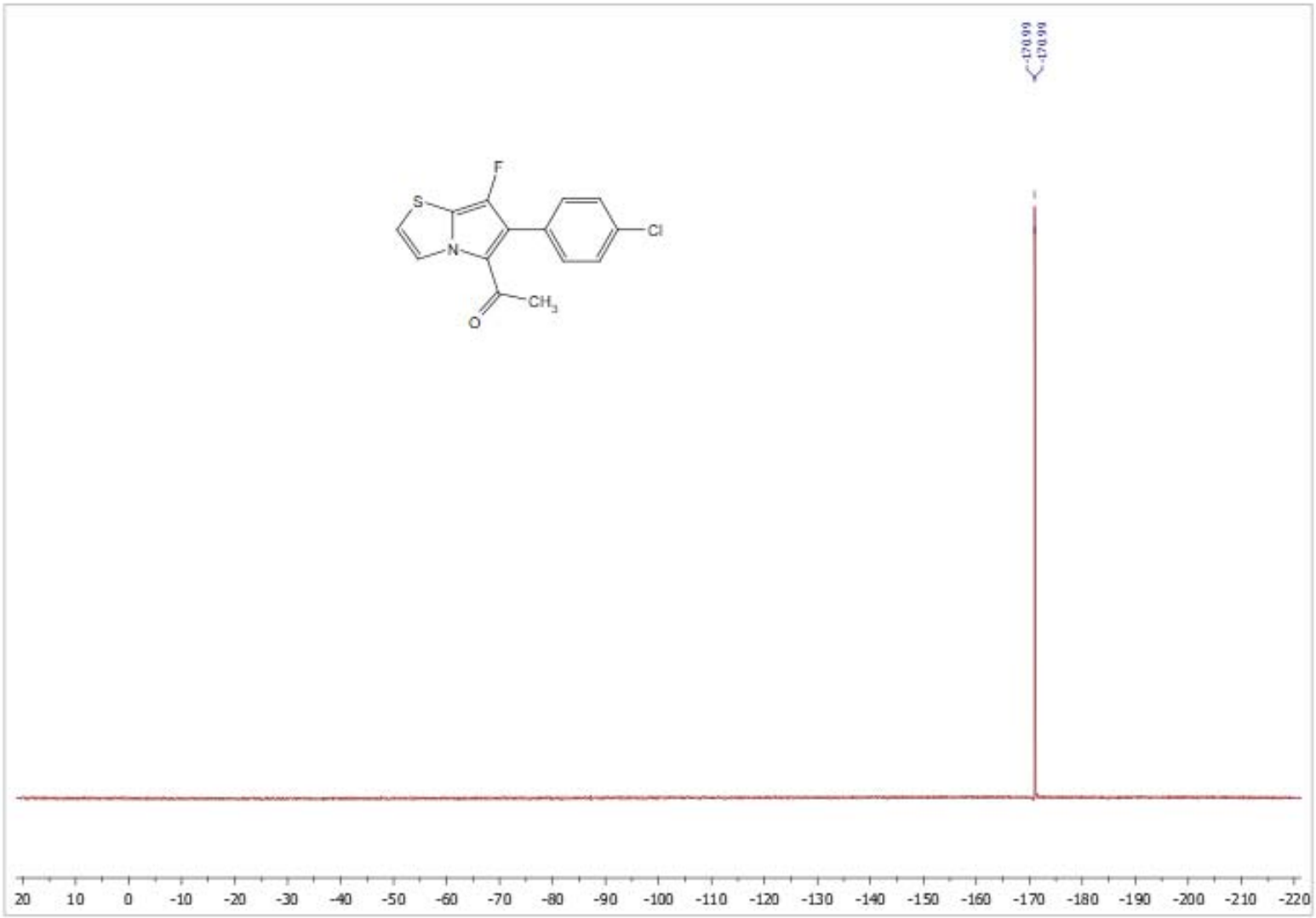
^{1}H NMR



^{13}C NMR

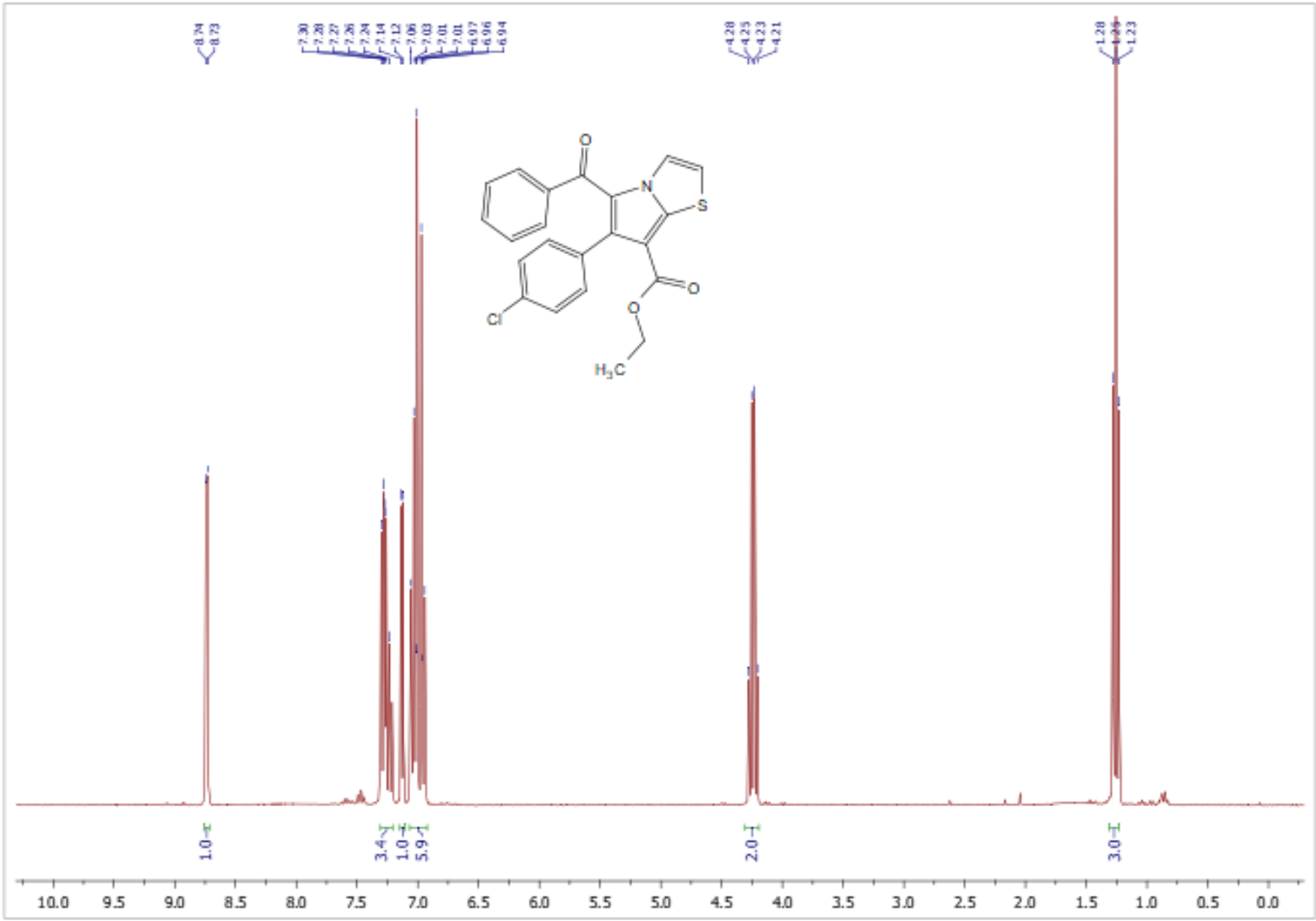

186.26
186.22
143.05
139.86
134.68
131.84
129.81
129.78
128.78
124.28
122.06
121.93
28.26
F
S
N
Cl
CH3
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{19}F NMR

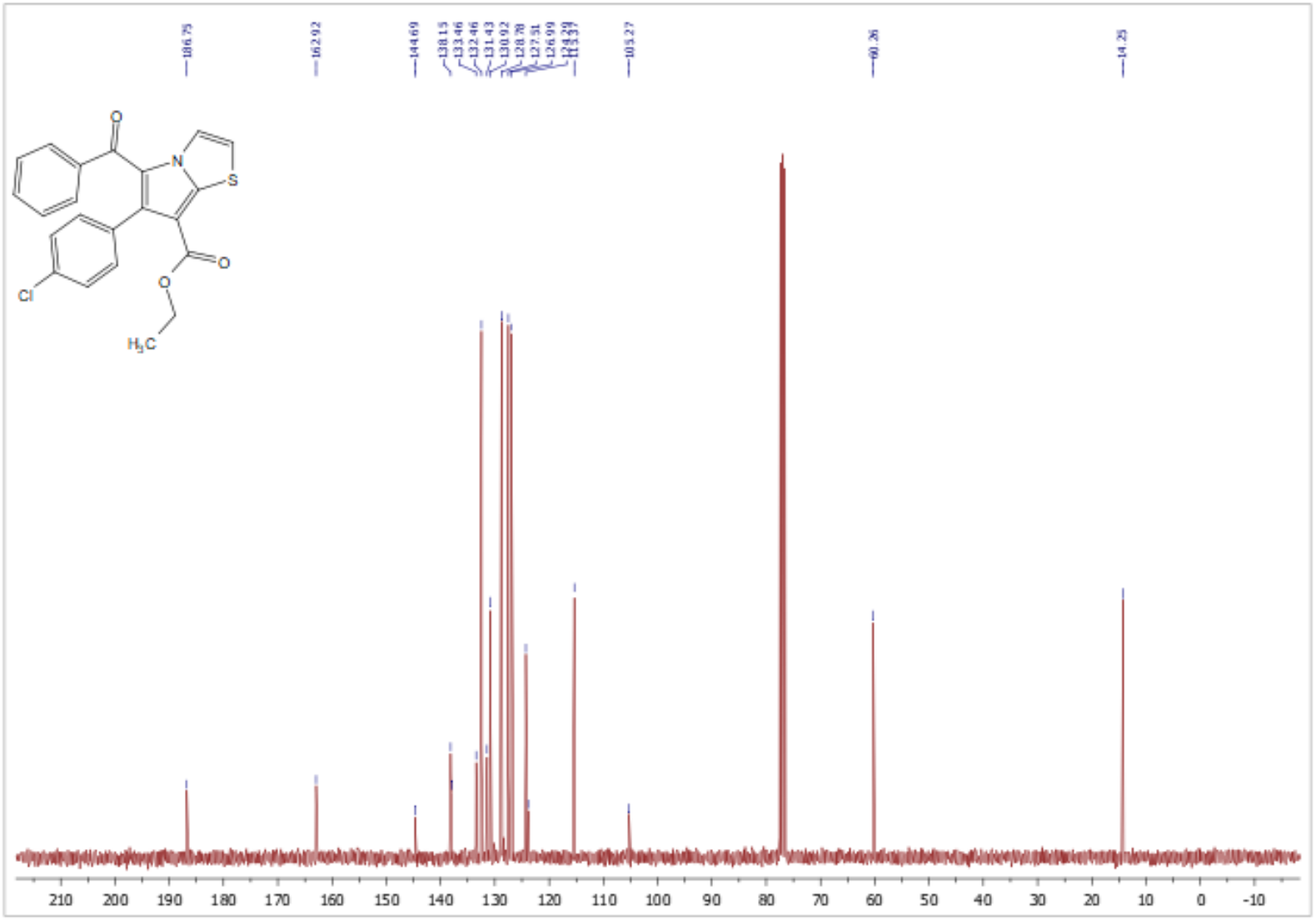

-170.99
-170.99
F
S
N
Cl
CH3
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

ethyl 5-benzoyl-6-(4-chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate **4a**

^{1}H NMR

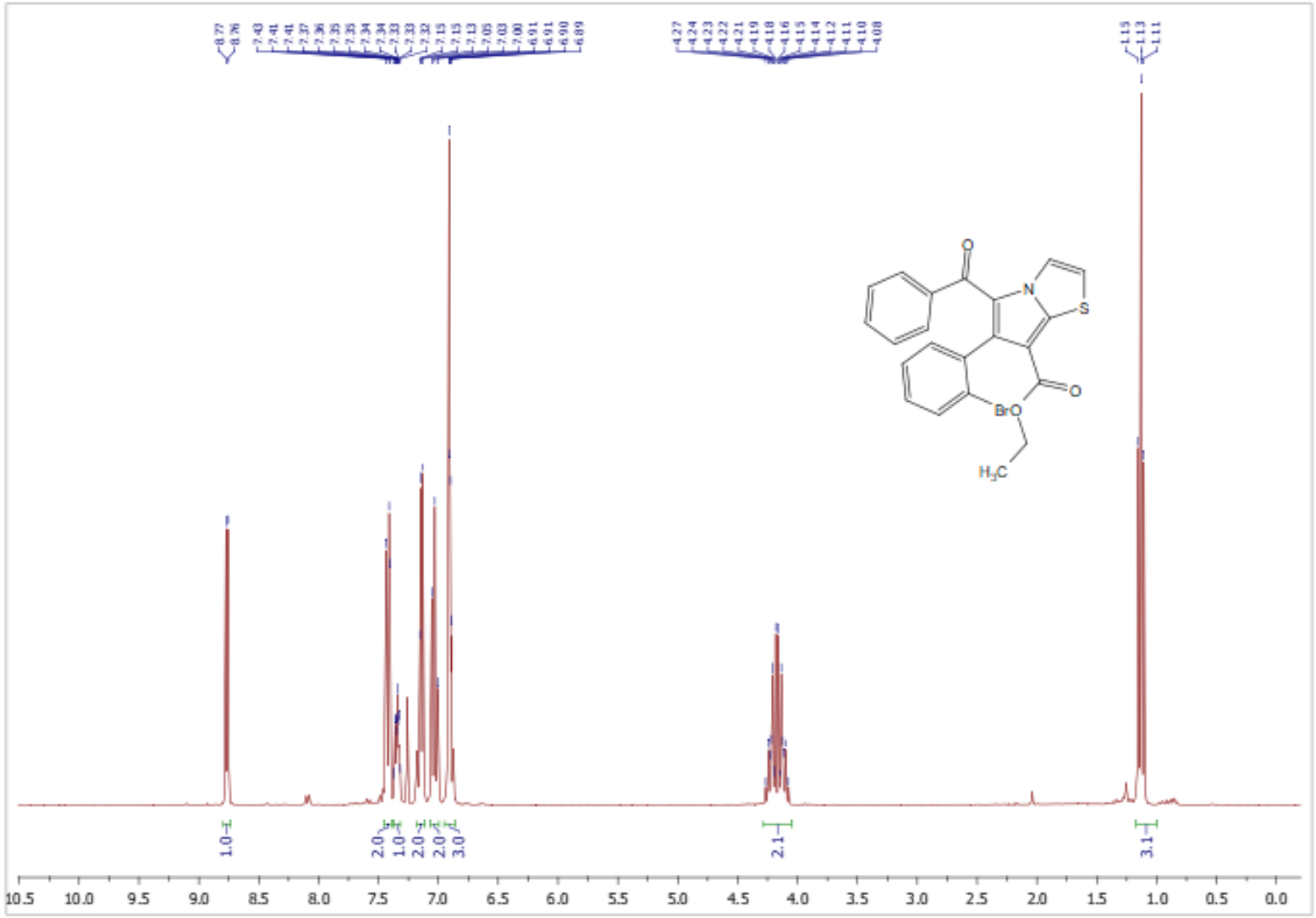


^{13}C NMR

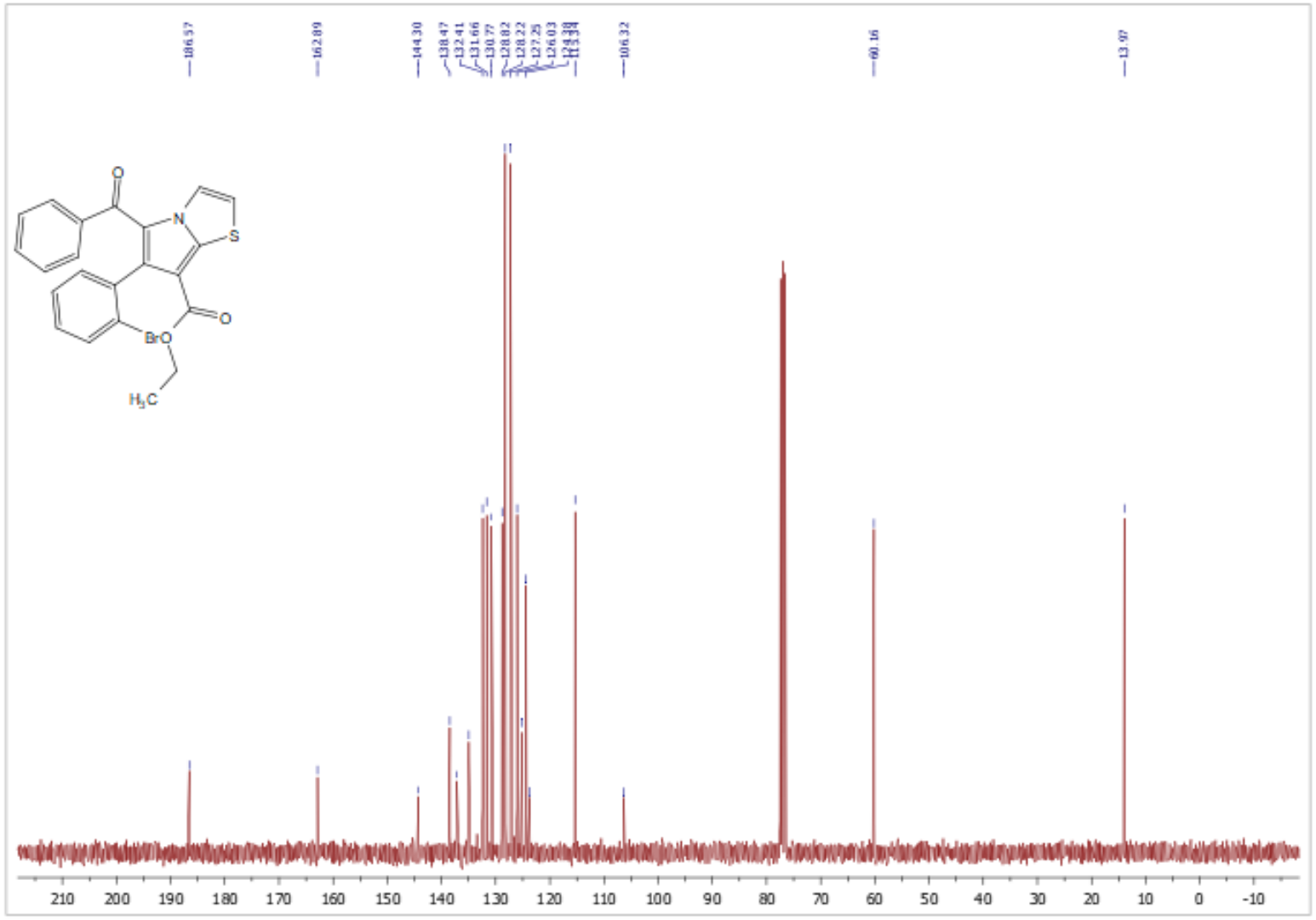

186.75
162.92
144.69
138.15
133.46
132.46
131.43
130.92
128.78
127.51
126.99
105.27
60.26
14.25
O
N
S
O
O
Cl
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

ethyl 5-benzoyl-6-(2-bromophenyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate **4b**

^{1}H NMR

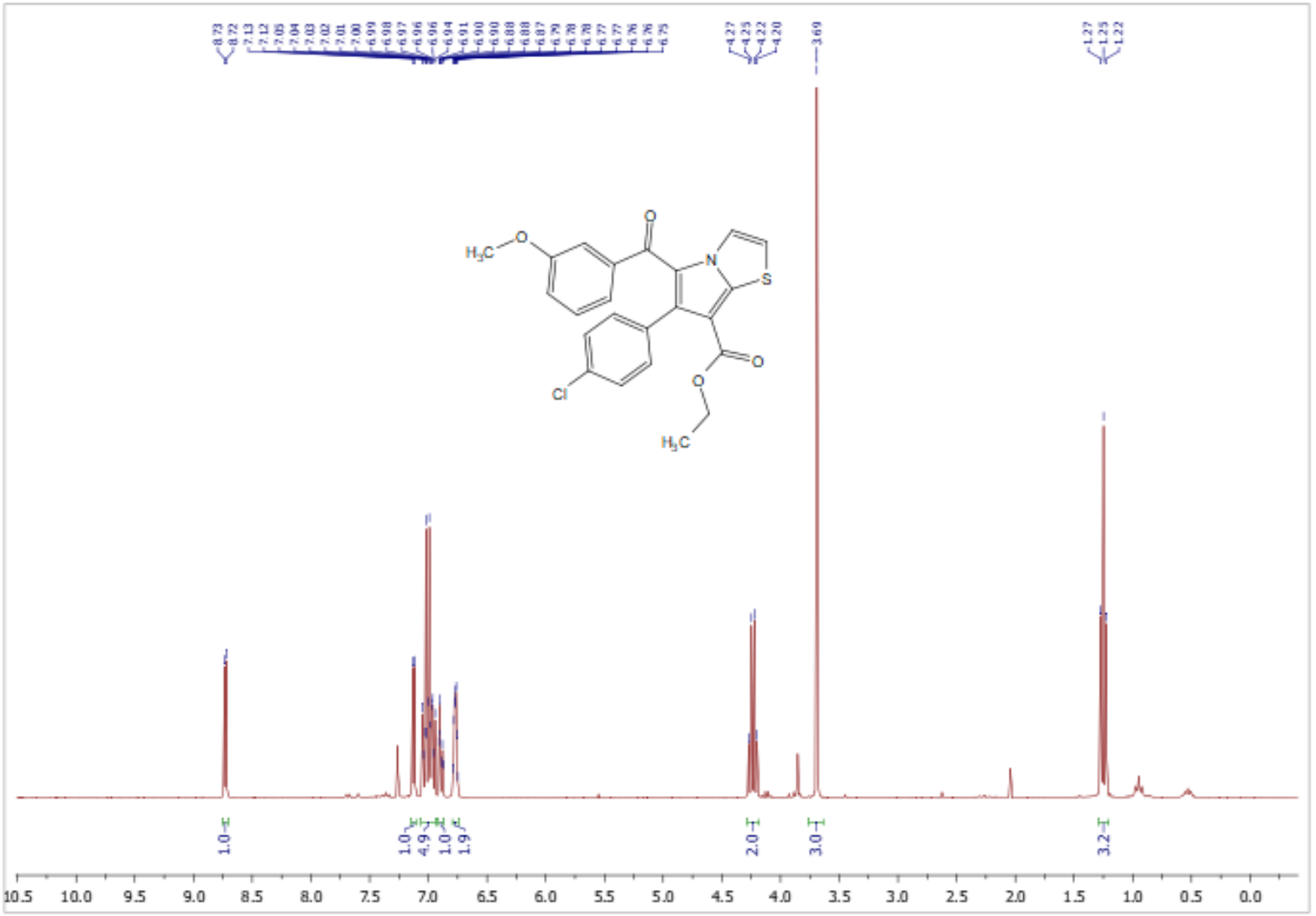


^{13}C NMR

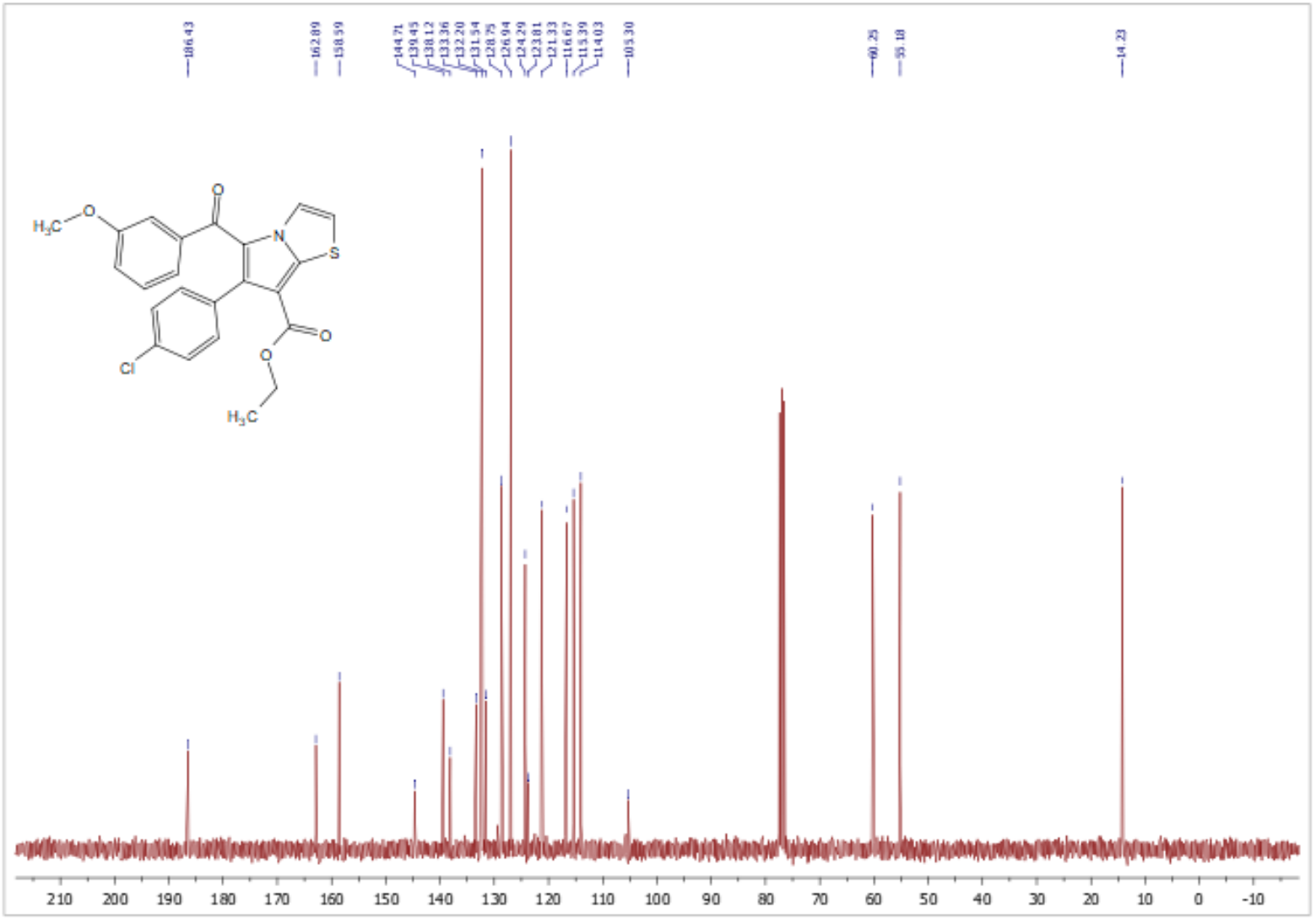

186.57
162.89
144.30
138.47
132.41
131.66
130.77
128.82
128.22
127.25
126.03
106.32
60.16
13.97
O
N
S
O
BrO
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

ethyl 6-(4-chlorophenyl)-5-(3-methoxybenzoyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate **4c**

^{1}H NMR



^{13}C NMR


186.43
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138.12
133.36
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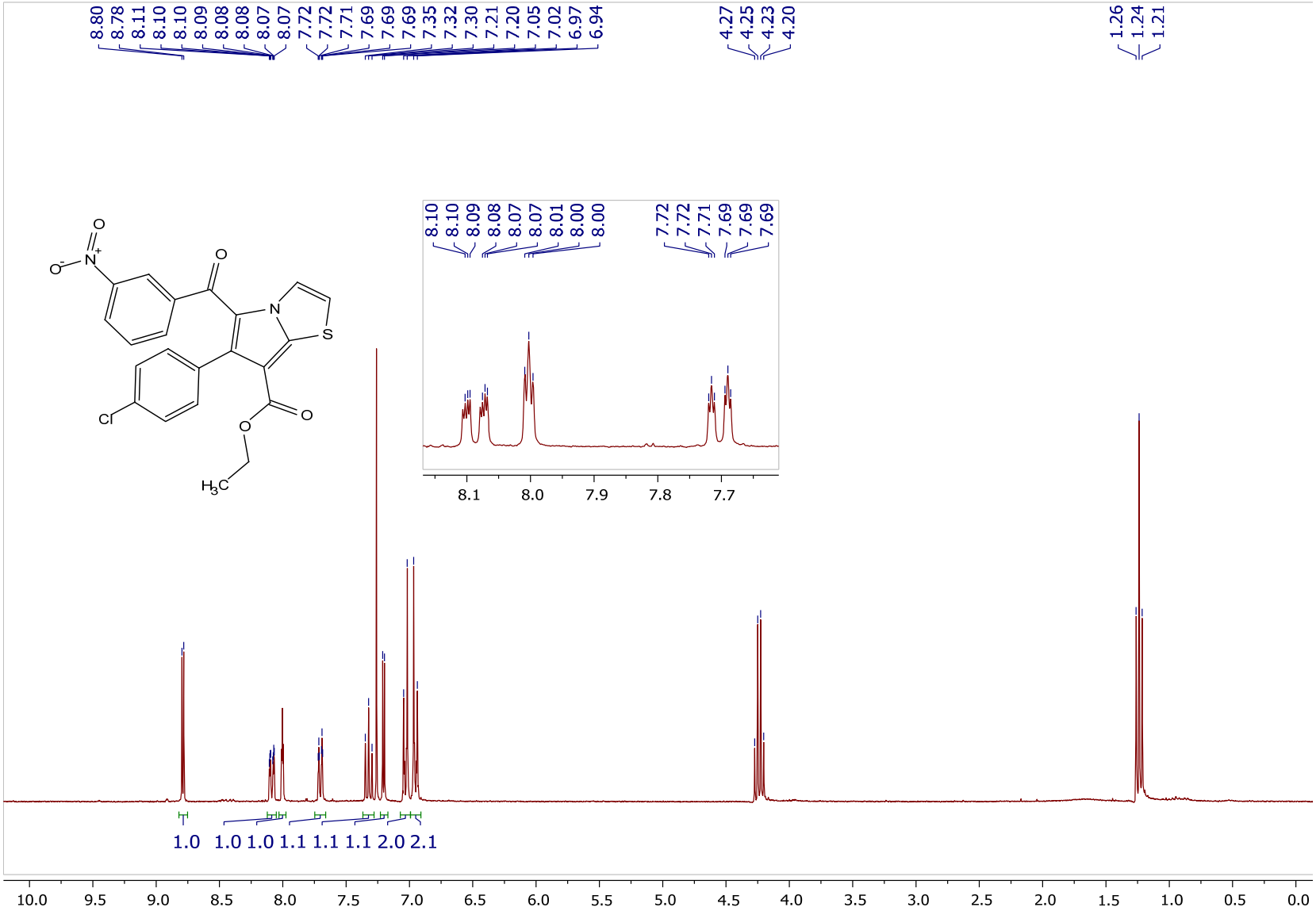
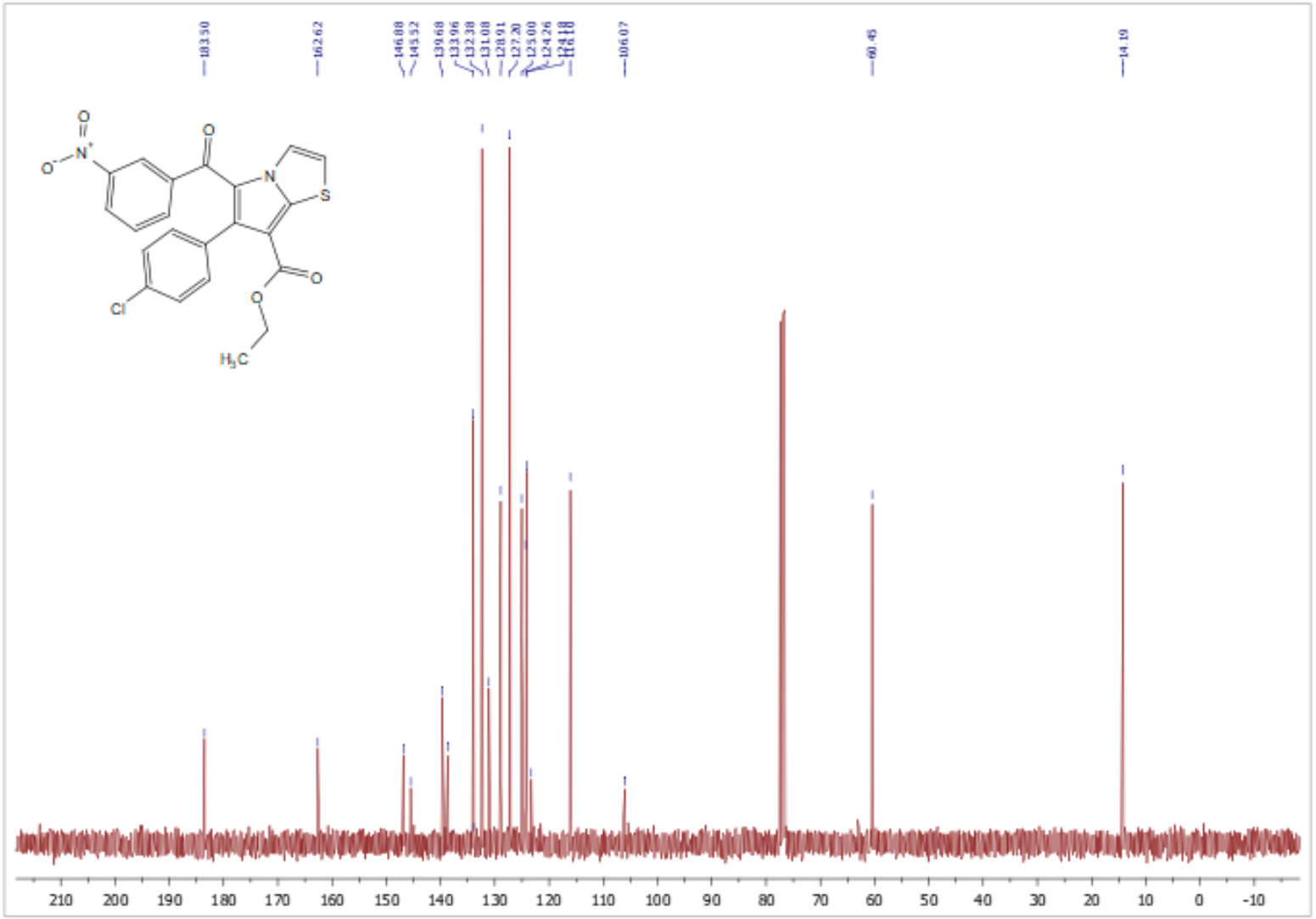
131.54
128.75
126.94
124.29
123.81
121.33
116.67
115.39
114.03
105.30
60.25
55.18
14.23
O
H3C
O
N
S
O
O
Cl
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

ethyl 6-(4-chlorophenyl)-5-(3-nitrobenzoyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate **4d**

^{1}H NMR



^{13}C NMR


183.50
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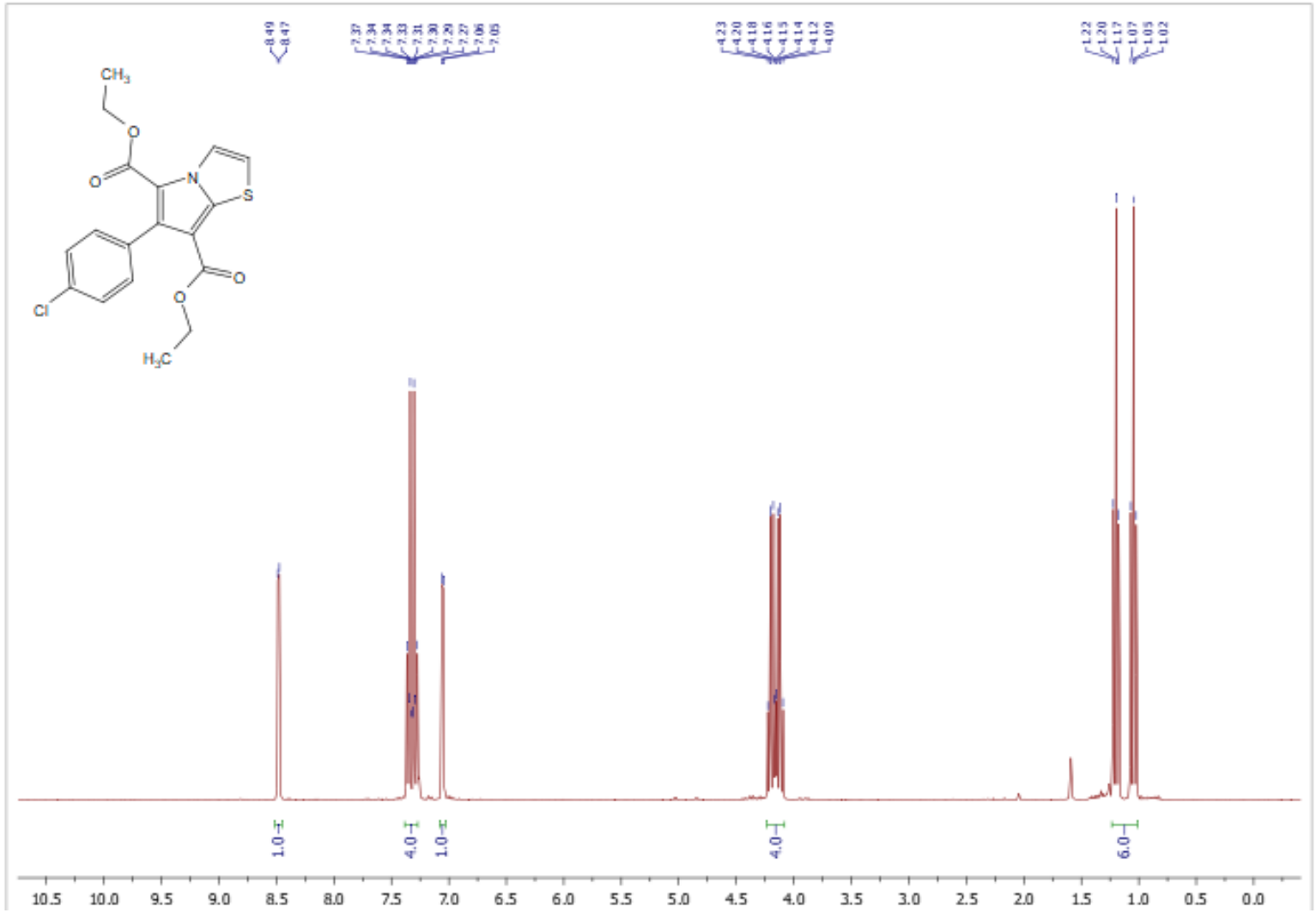
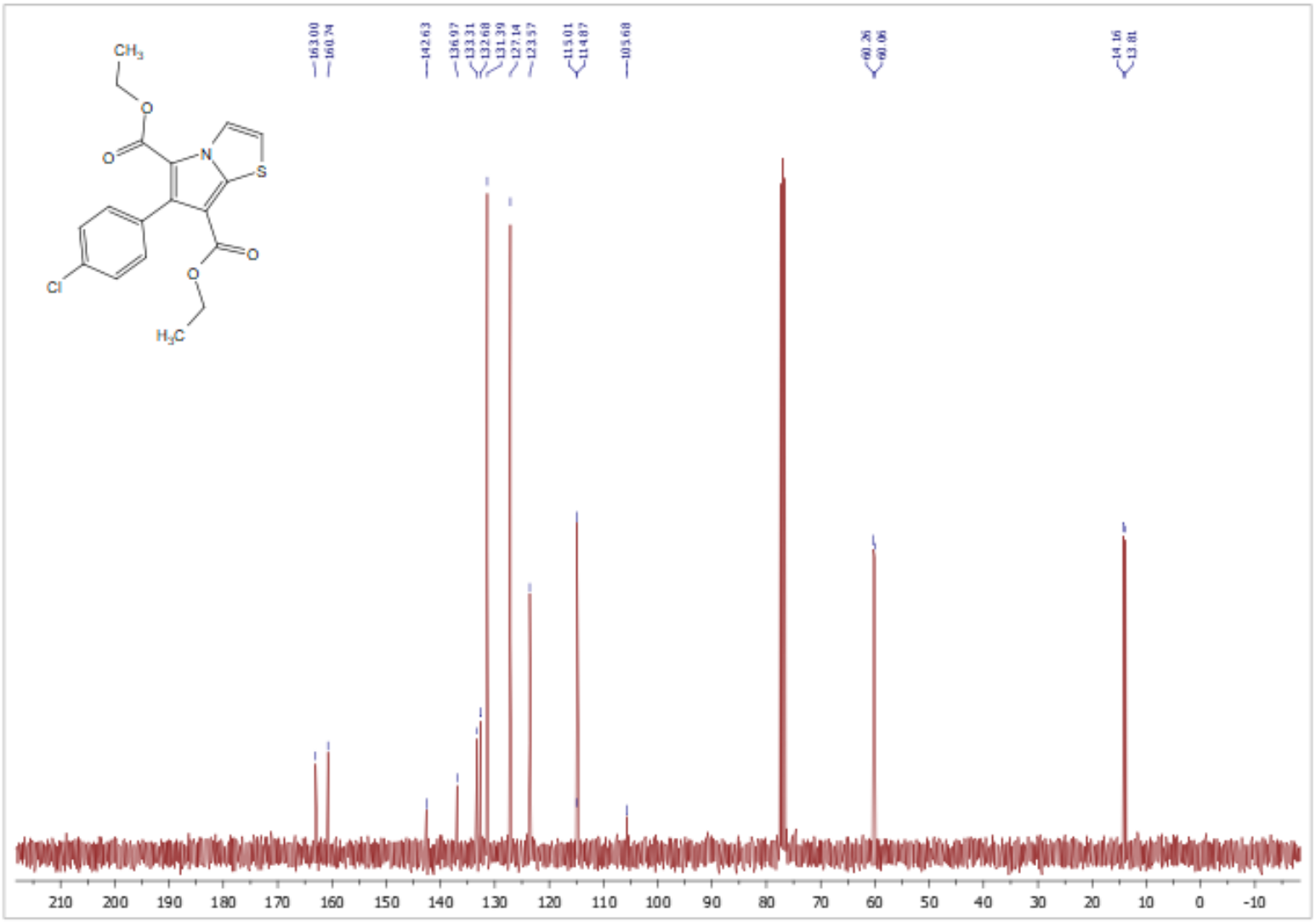
145.52
139.68
133.96
132.38
131.08
128.91
127.20
125.00
124.26
106.07
60.45
14.19
O
O
N+
O-
N
S
O
O
Cl
O
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

diethyl 6-(4-chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazole-5,7-dicarboxylate **4e**

^{1}H NMR

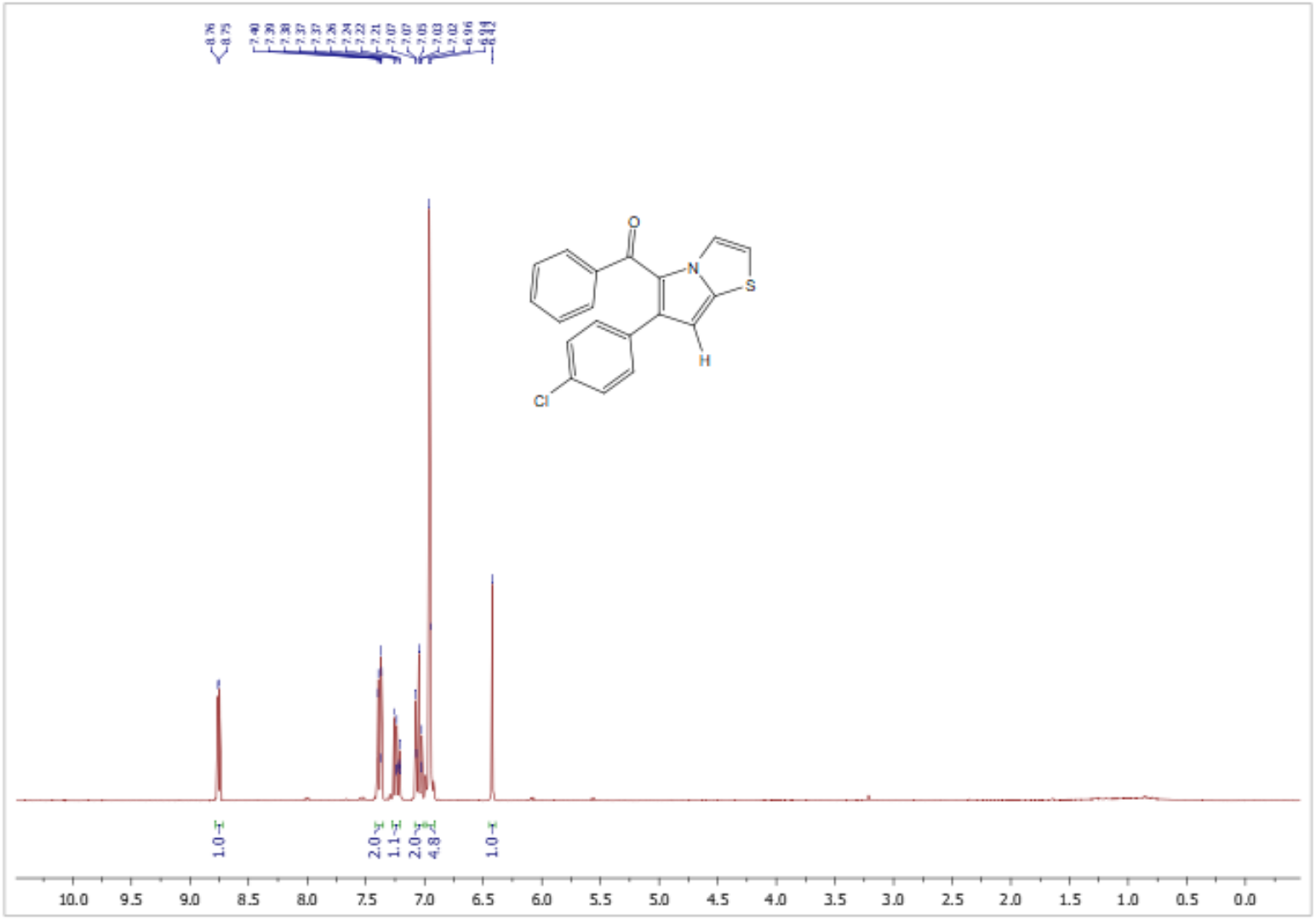


^{13}C NMR

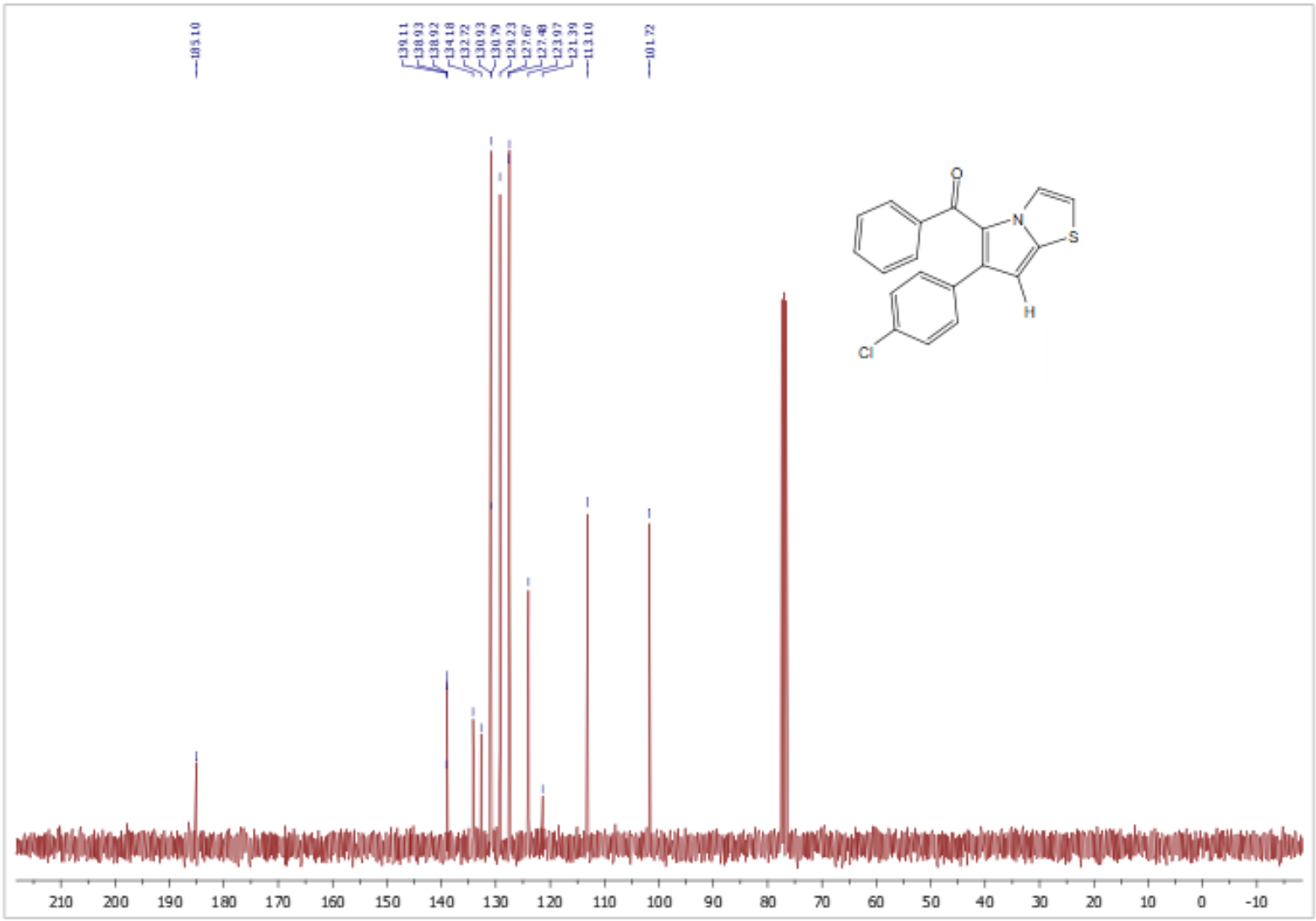

CH3
O
O
N
S
Cl
O
O
H3C
163.00
160.74
142.63
136.97
133.31
132.60
131.39
127.14
123.57
115.01
114.87
105.68
60.26
60.06
14.16
13.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

[6-(4-chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone **5a**

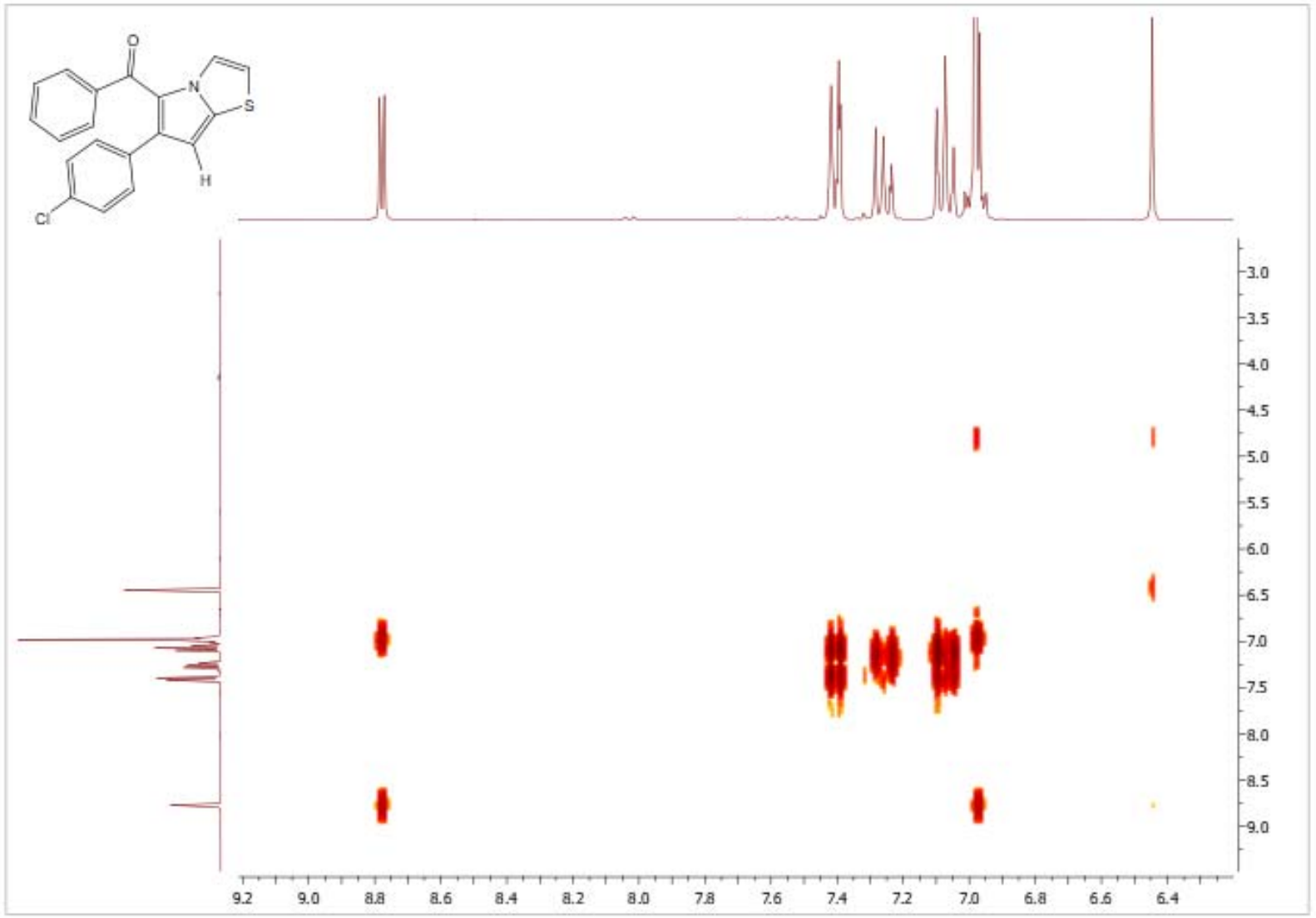
^{1}H NMR



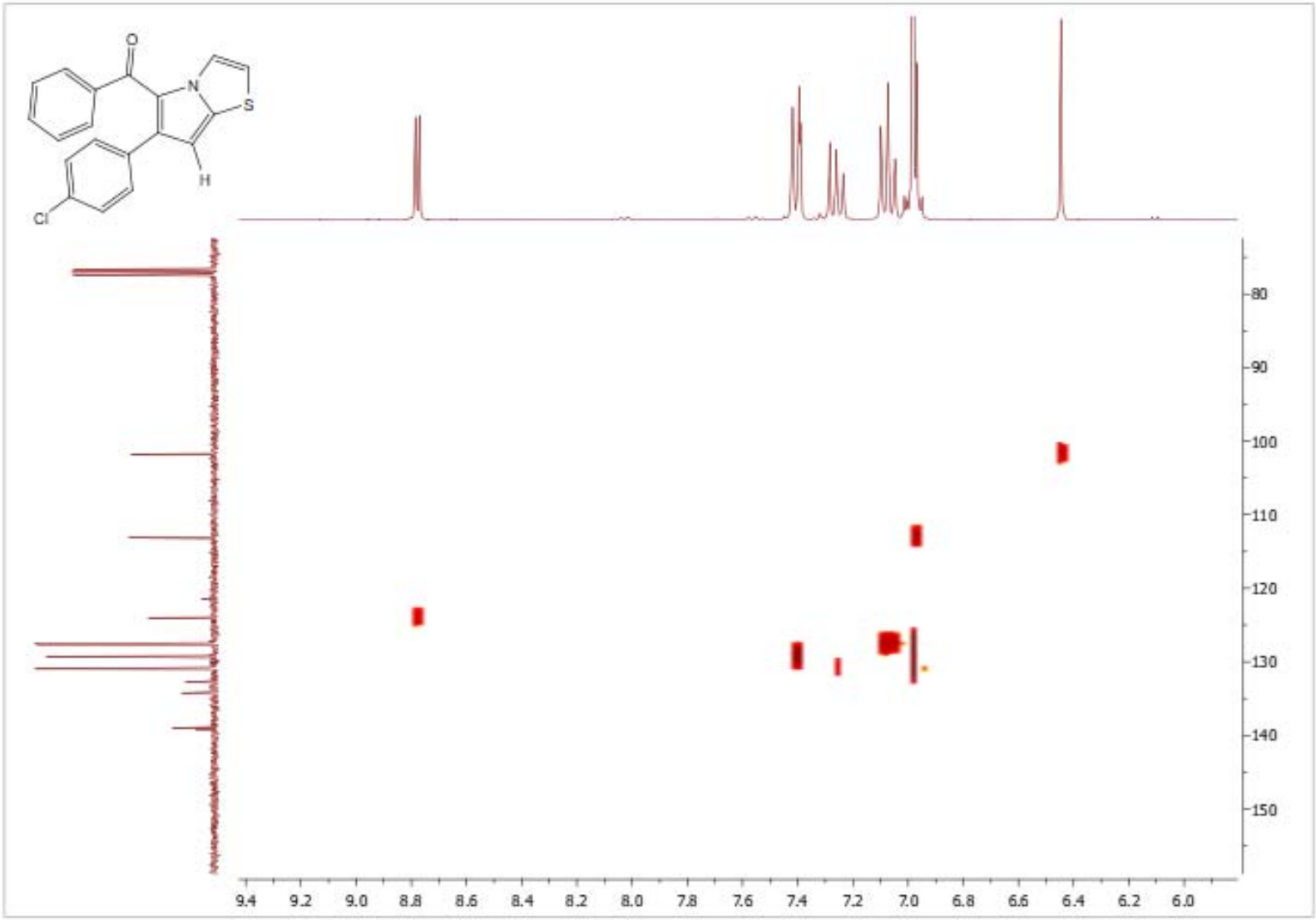
^{13}C NMR


185.10
139.11
138.93
138.92
134.18
132.72
130.93
130.79
129.23
127.67
127.48
123.97
121.39
113.10
101.72
O
N
S
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

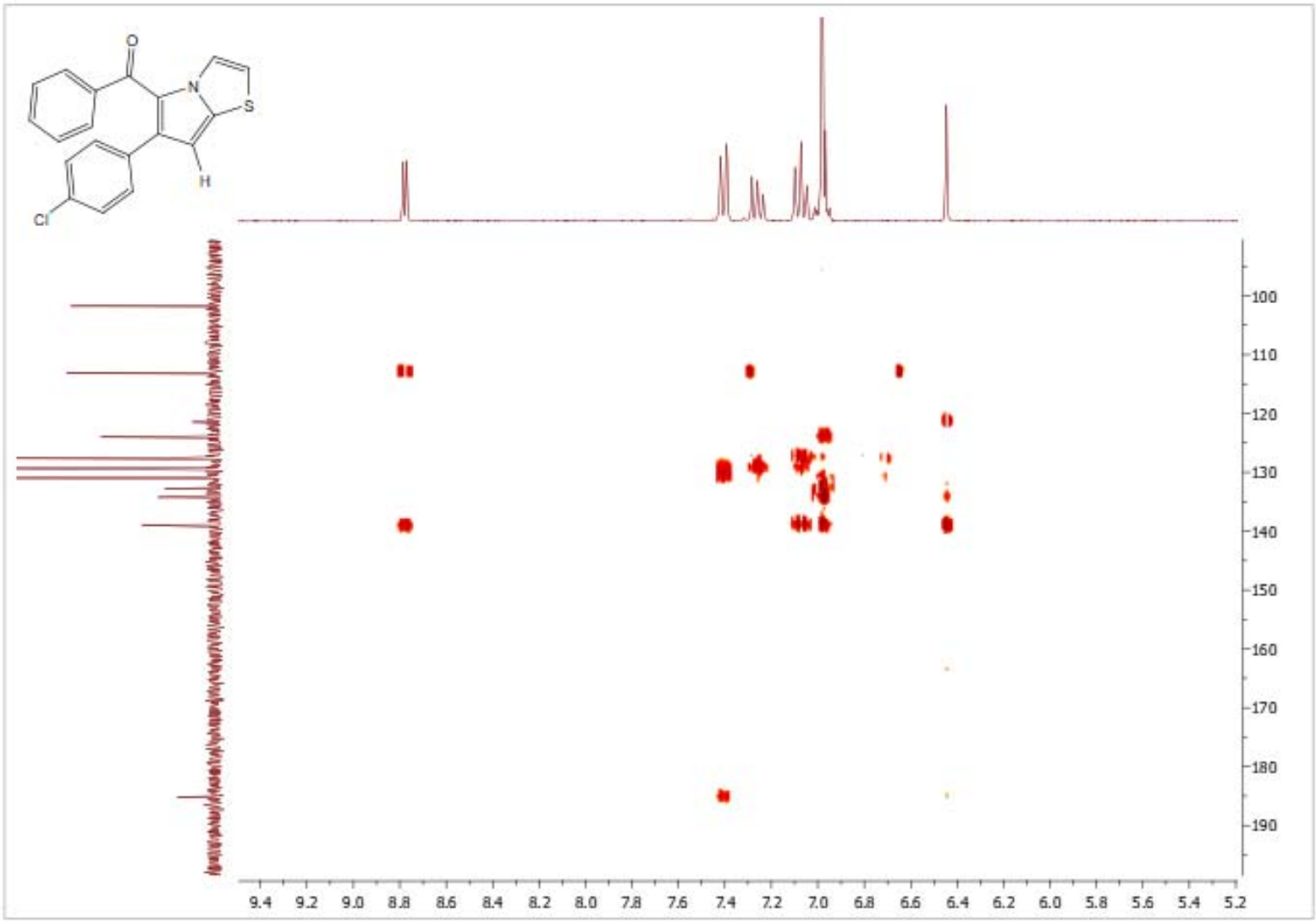
^{1}H-^{1}H COSY NMR



^{1}H-^{13}C HSQC NMR

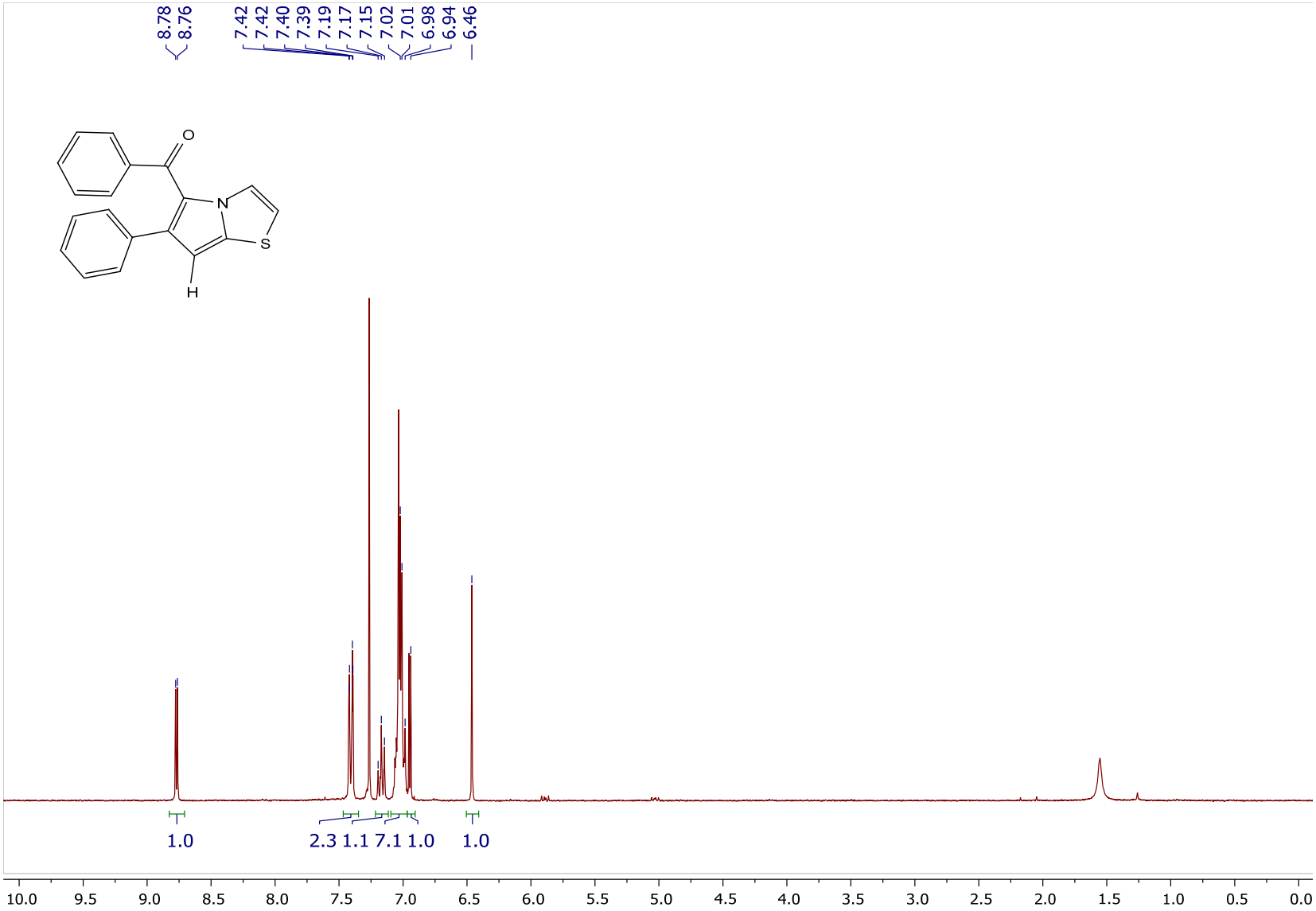


^{1}H-^{13}C HMBC NMR

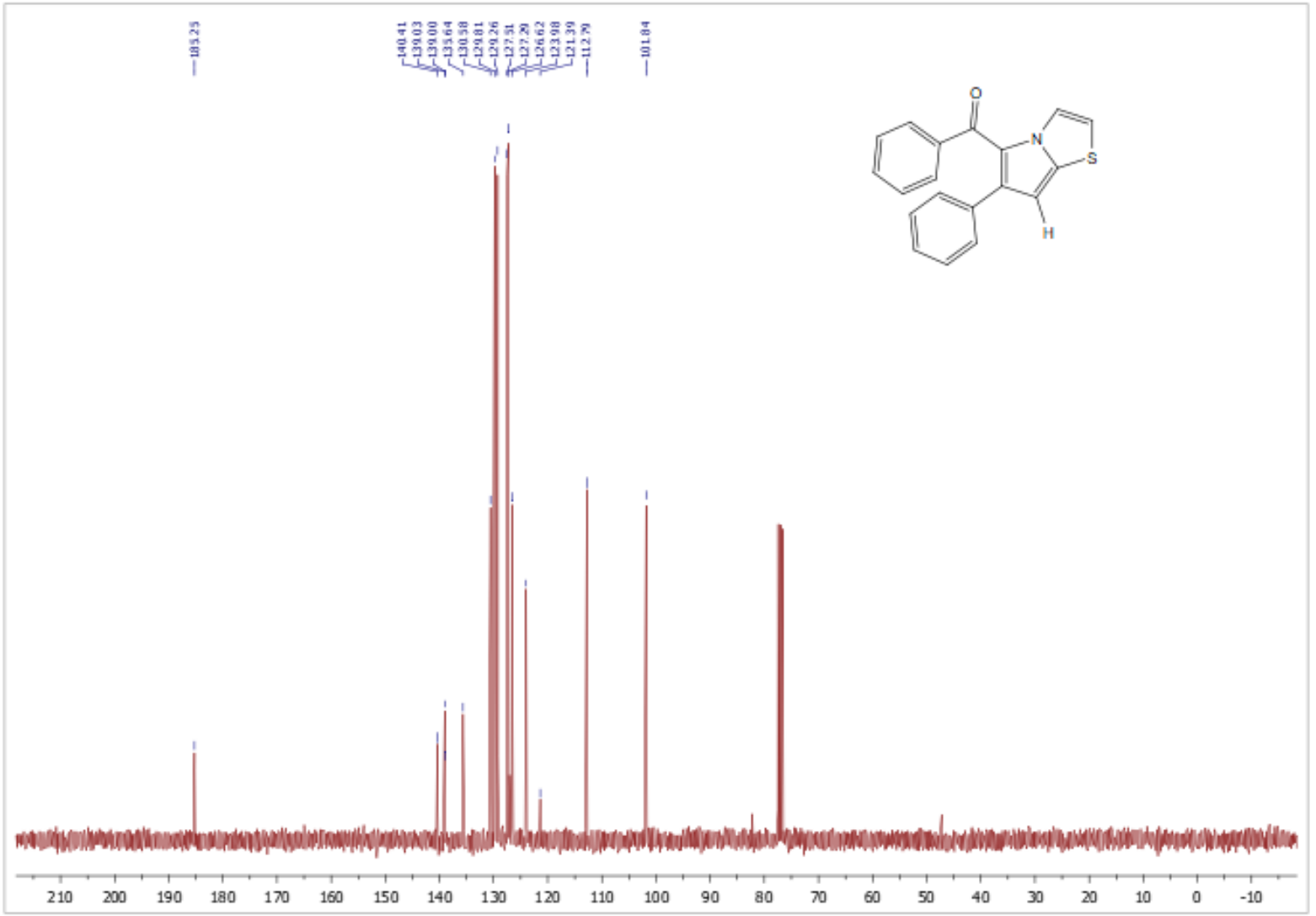


phenyl(6-phenylpyrrolo[2,1-*b*][1,3]thiazol-5-yl)methanone **5b**

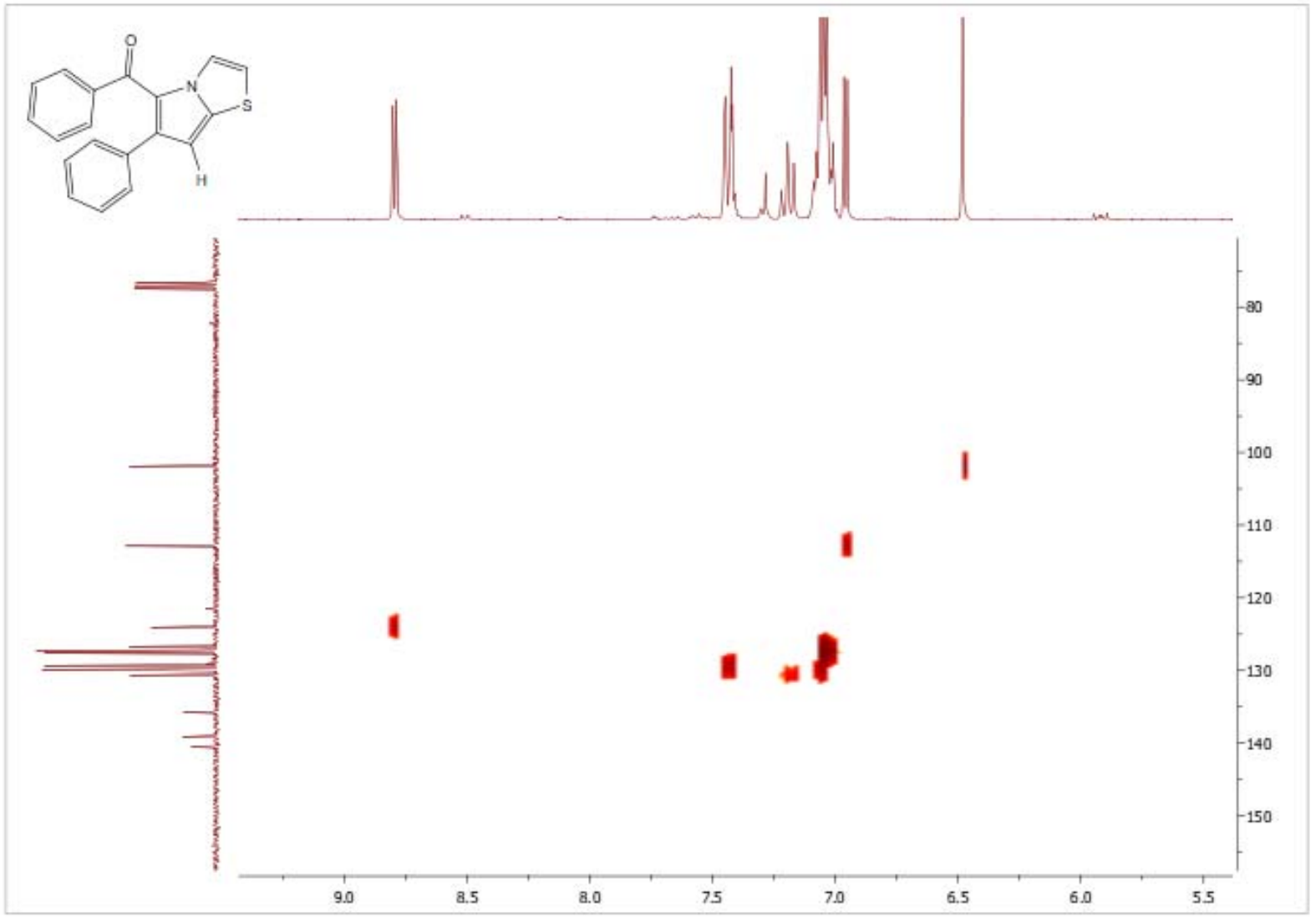
^{1}H NMR



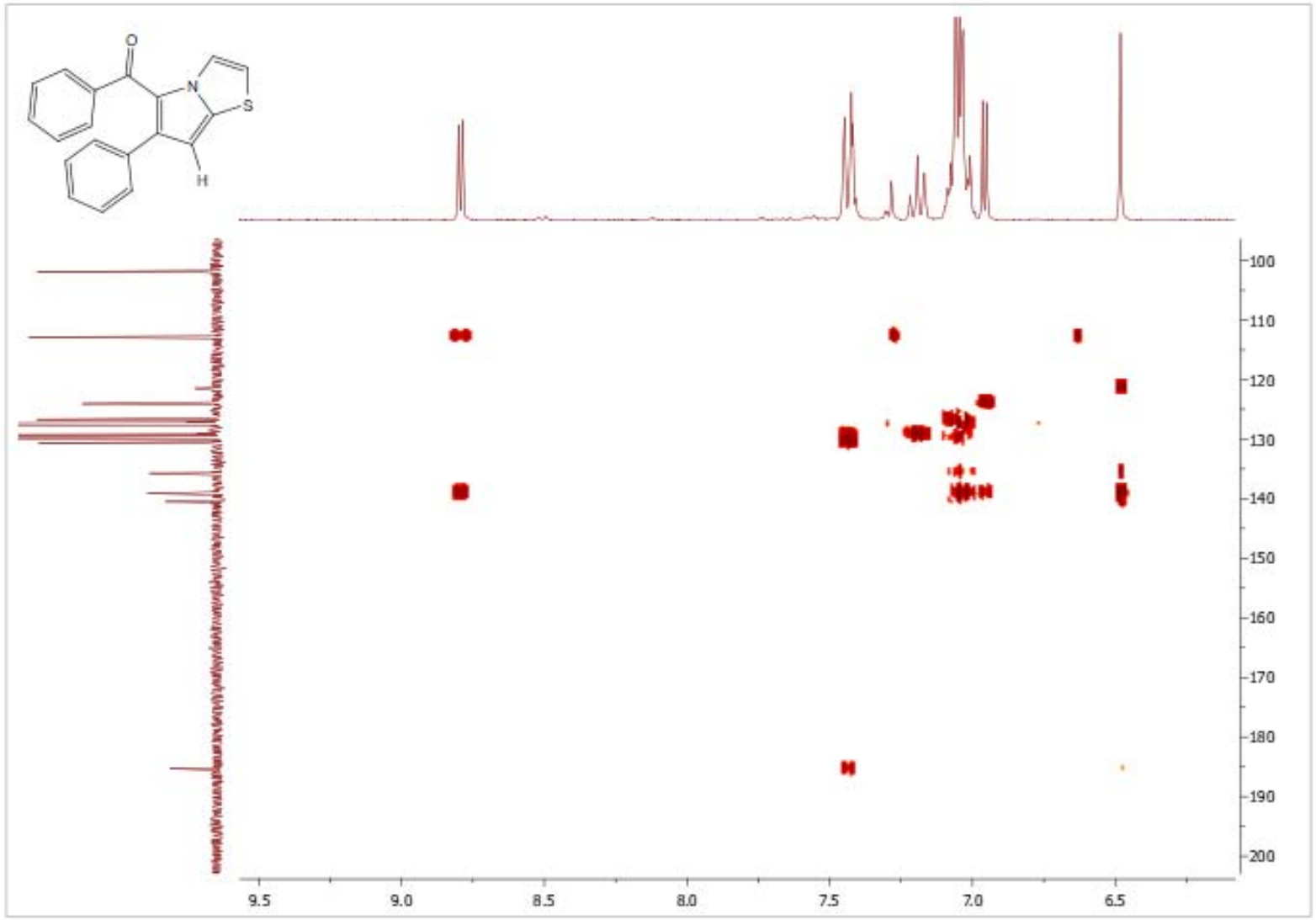
^{13}C NMR


185.25
140.41
139.03
139.00
135.64
130.58
129.81
129.26
127.51
127.20
126.62
123.98
121.39
112.79
101.84
O
N
S
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{1}H-^{13}C HSQC NMR

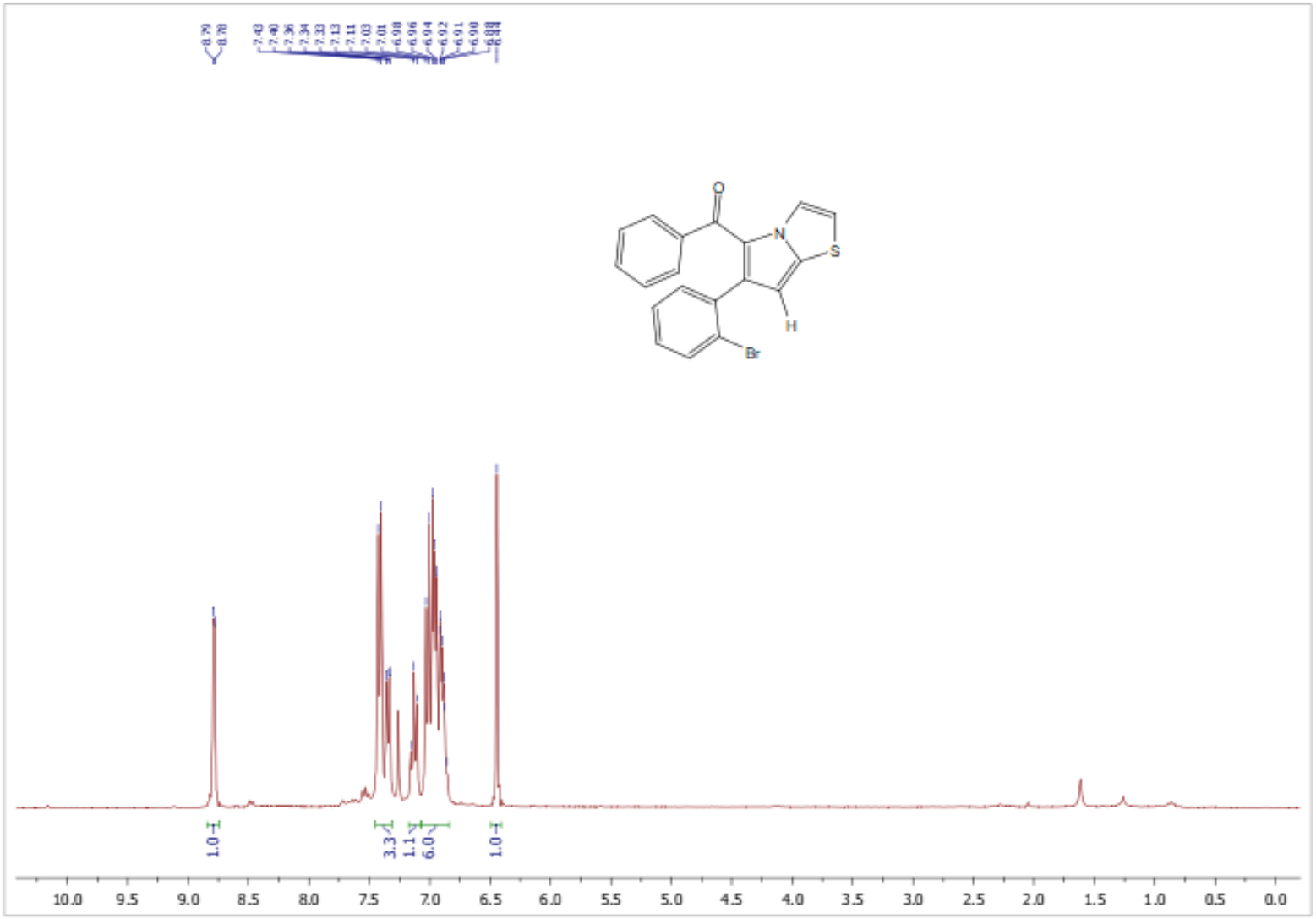


^{1}H-^{13}C HMBC NMR

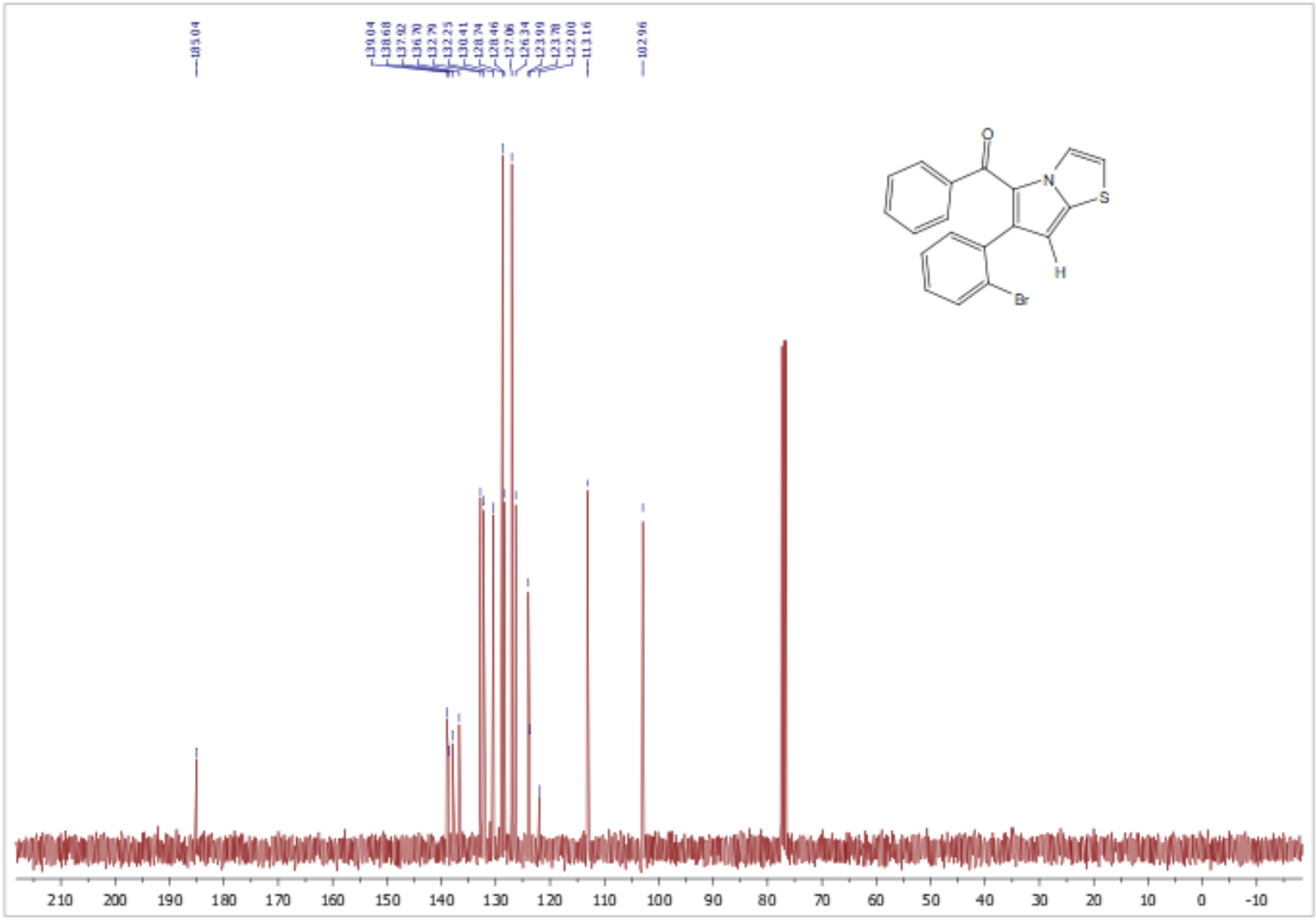


[6-(2-bromophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone **5c**

^{1}H NMR

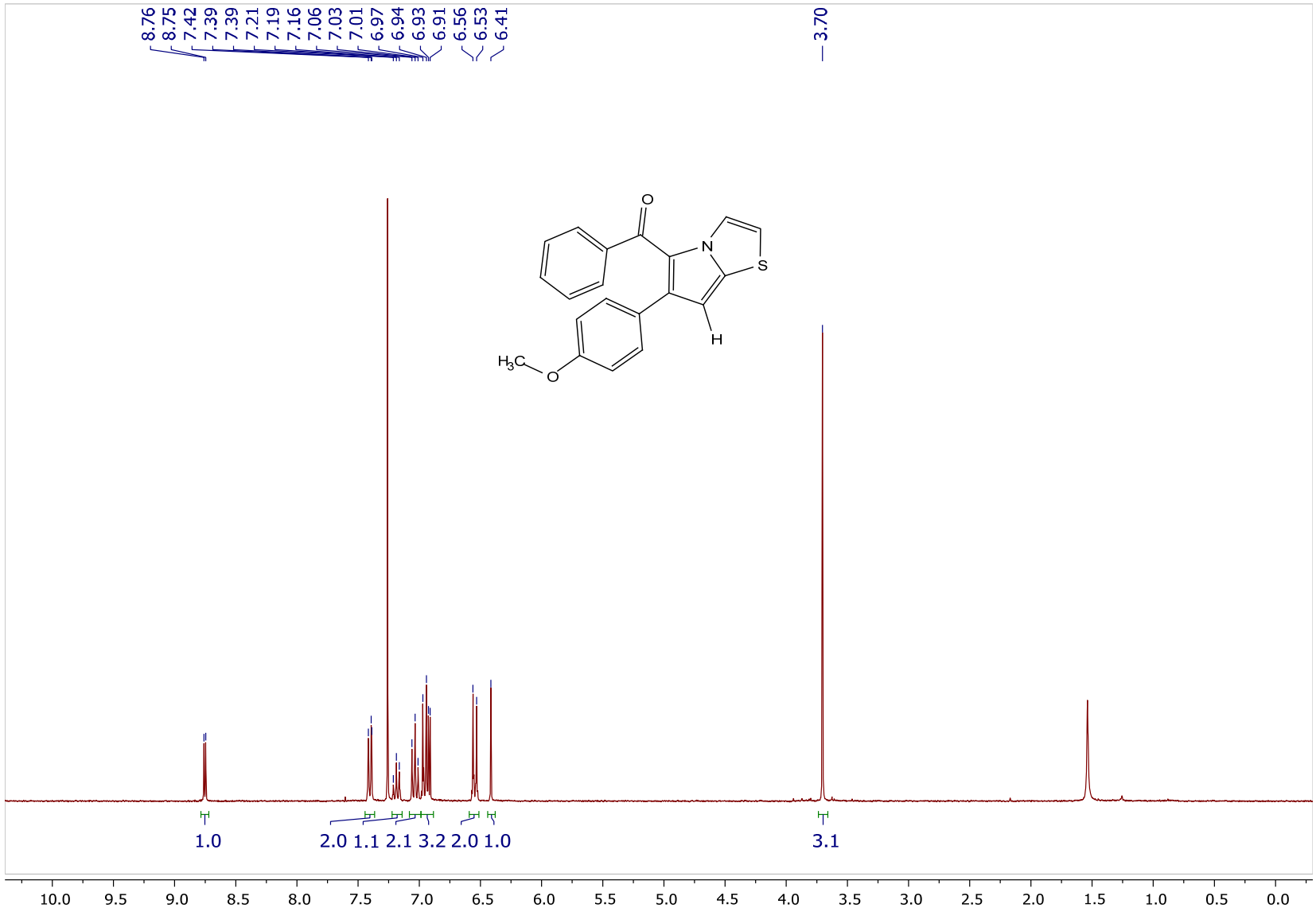


^{13}C NMR

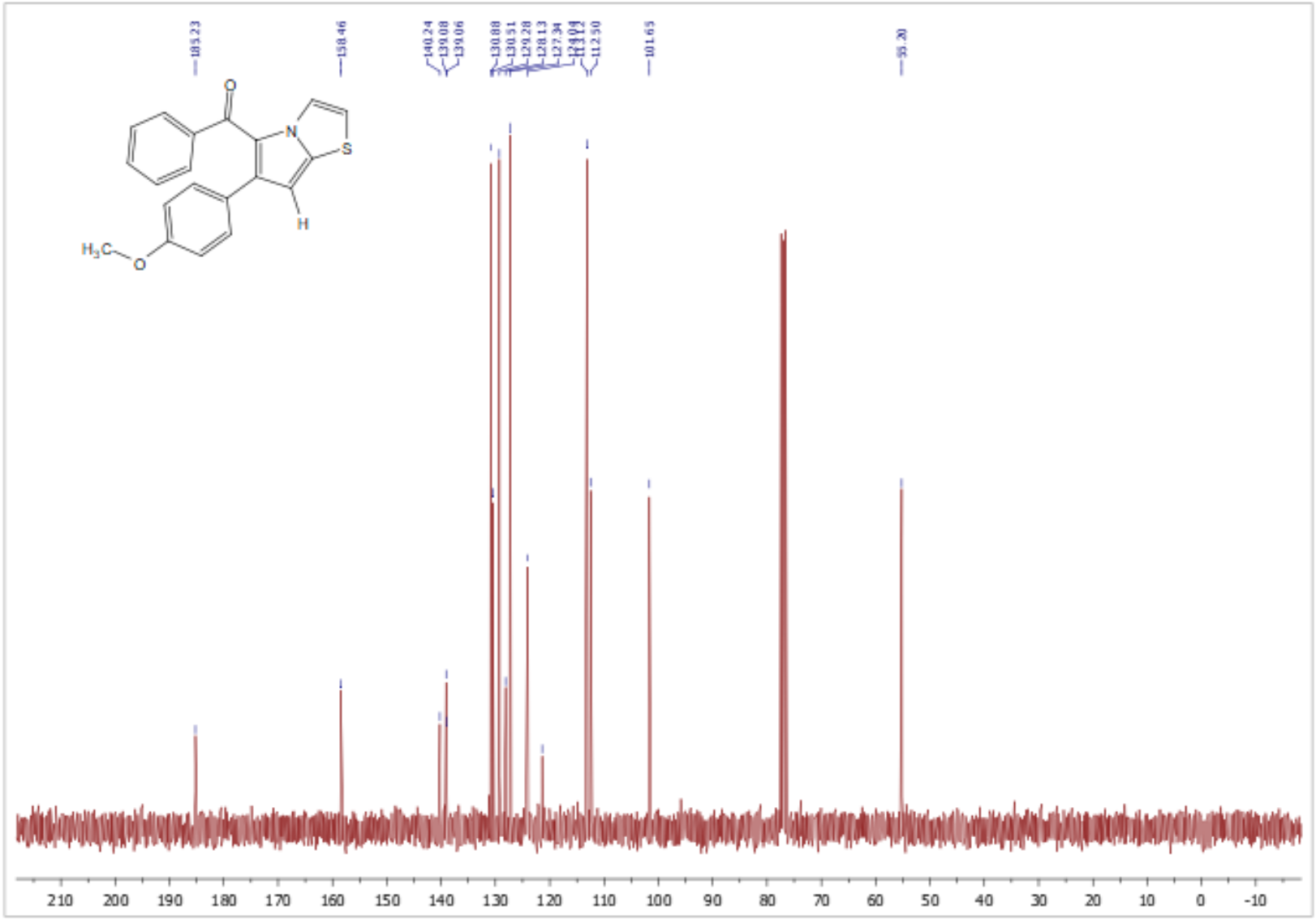

185.04
139.04
138.68
137.92
136.70
132.79
132.25
130.41
128.74
128.46
127.06
126.34
123.99
123.78
122.00
113.16
102.96
O
N
S
H
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

[6-(4-methoxyphenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone **5d**

^{1}H NMR

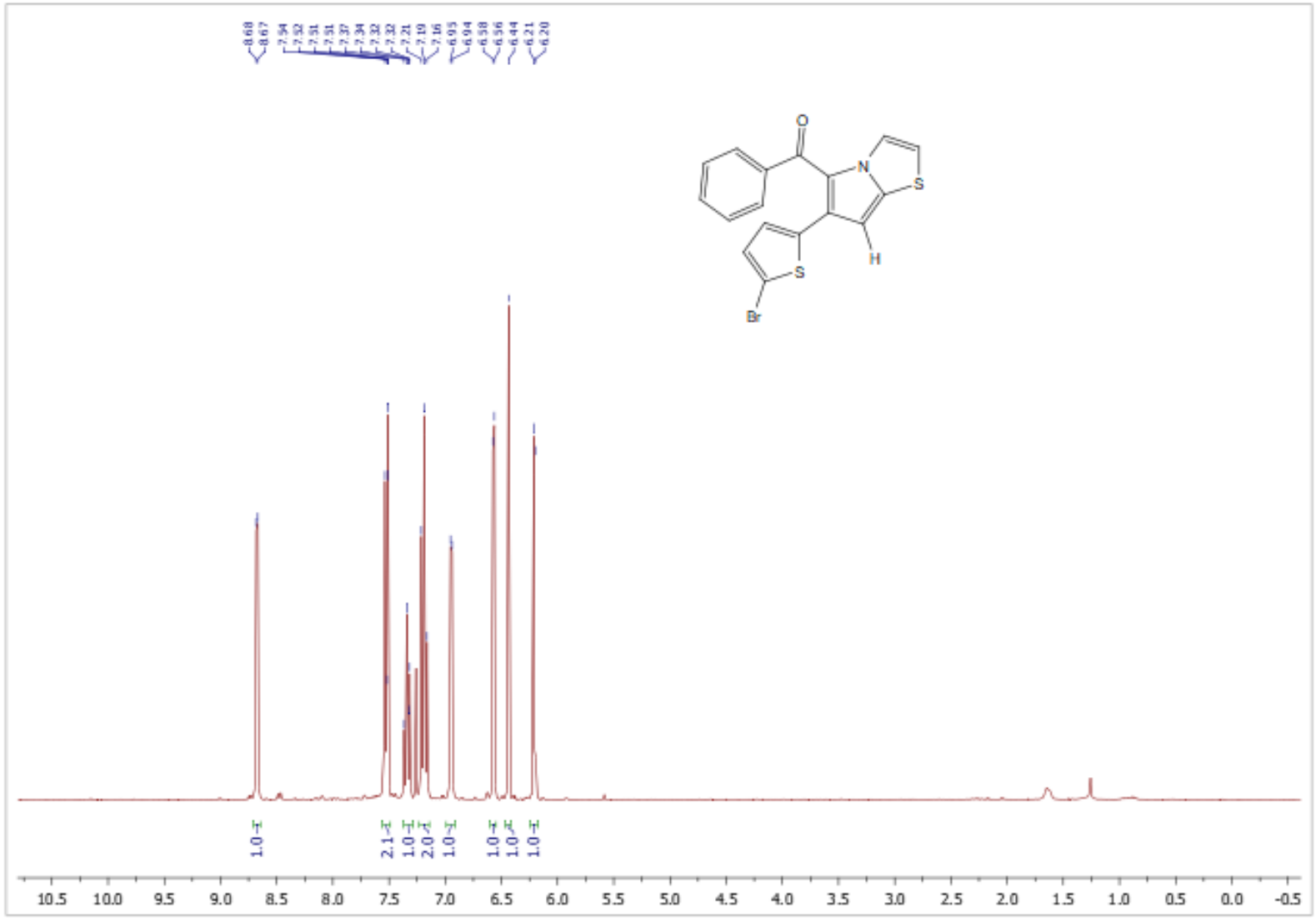


^{13}C NMR

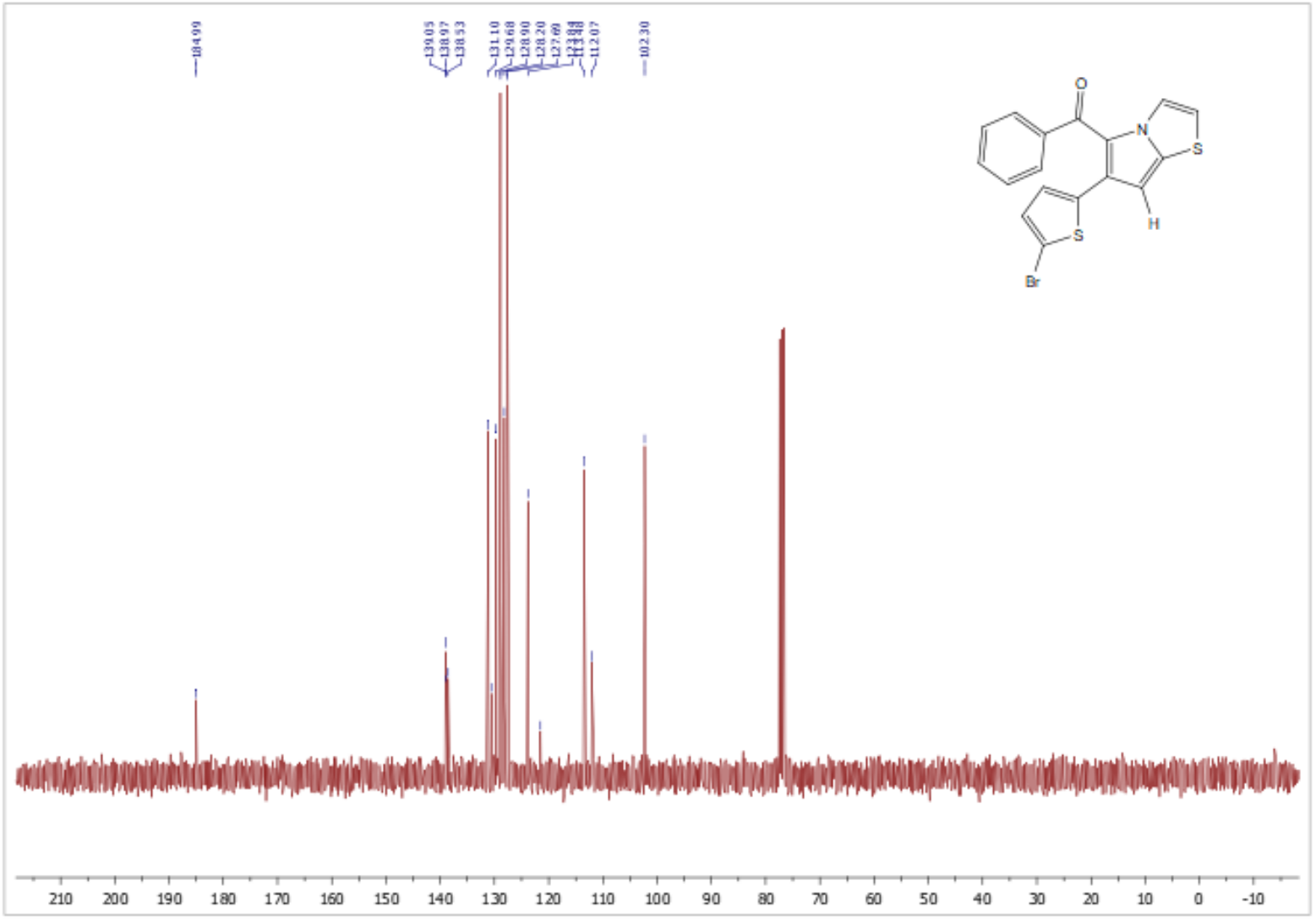

185.23
158.46
140.24
139.08
139.06
130.88
130.51
129.28
128.13
127.34
112.50
101.65
55.20
O
N
S
H
H3C
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

[6-(5-bromothiophen-2-yl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone **5e**

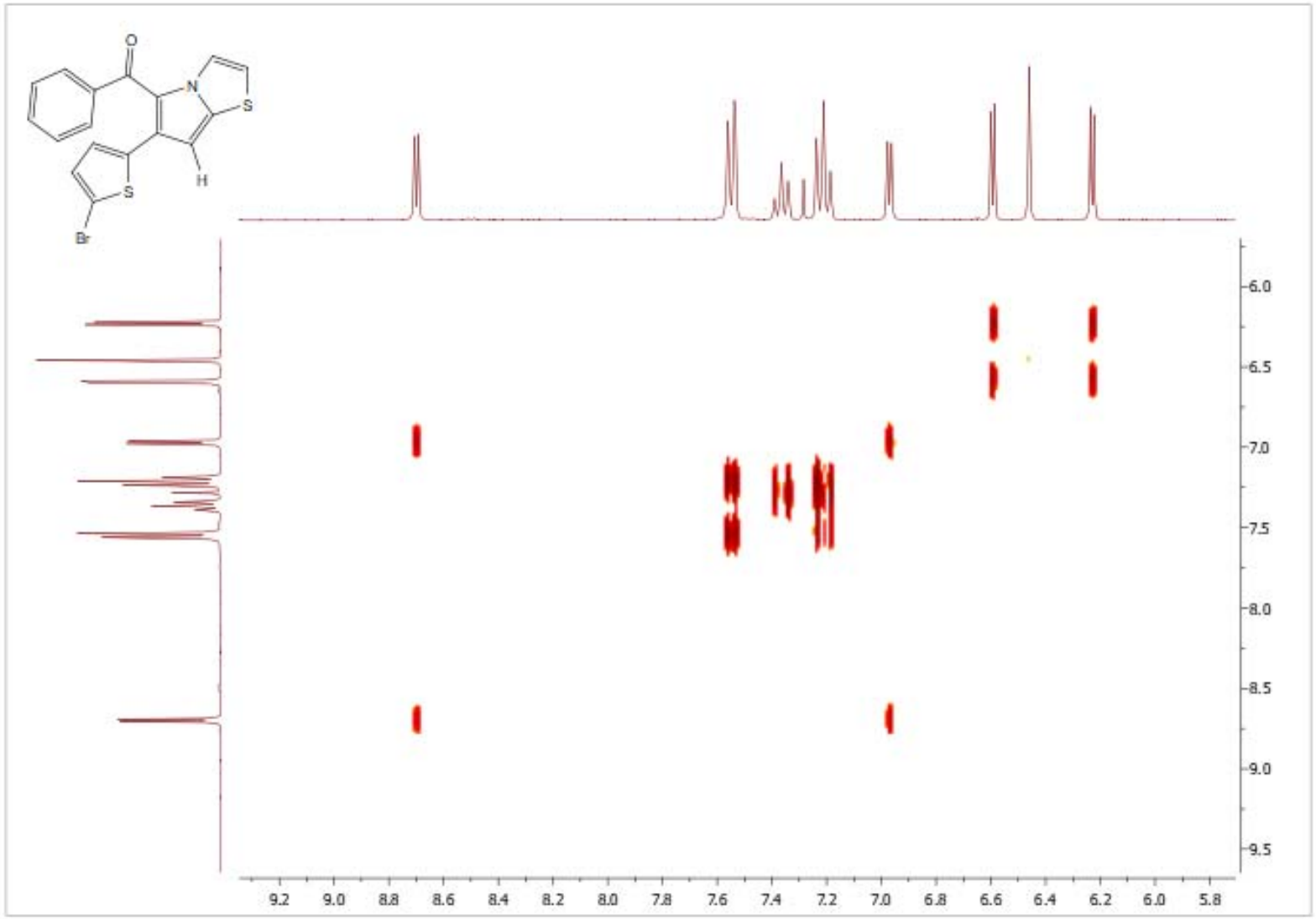
^{1}H NMR



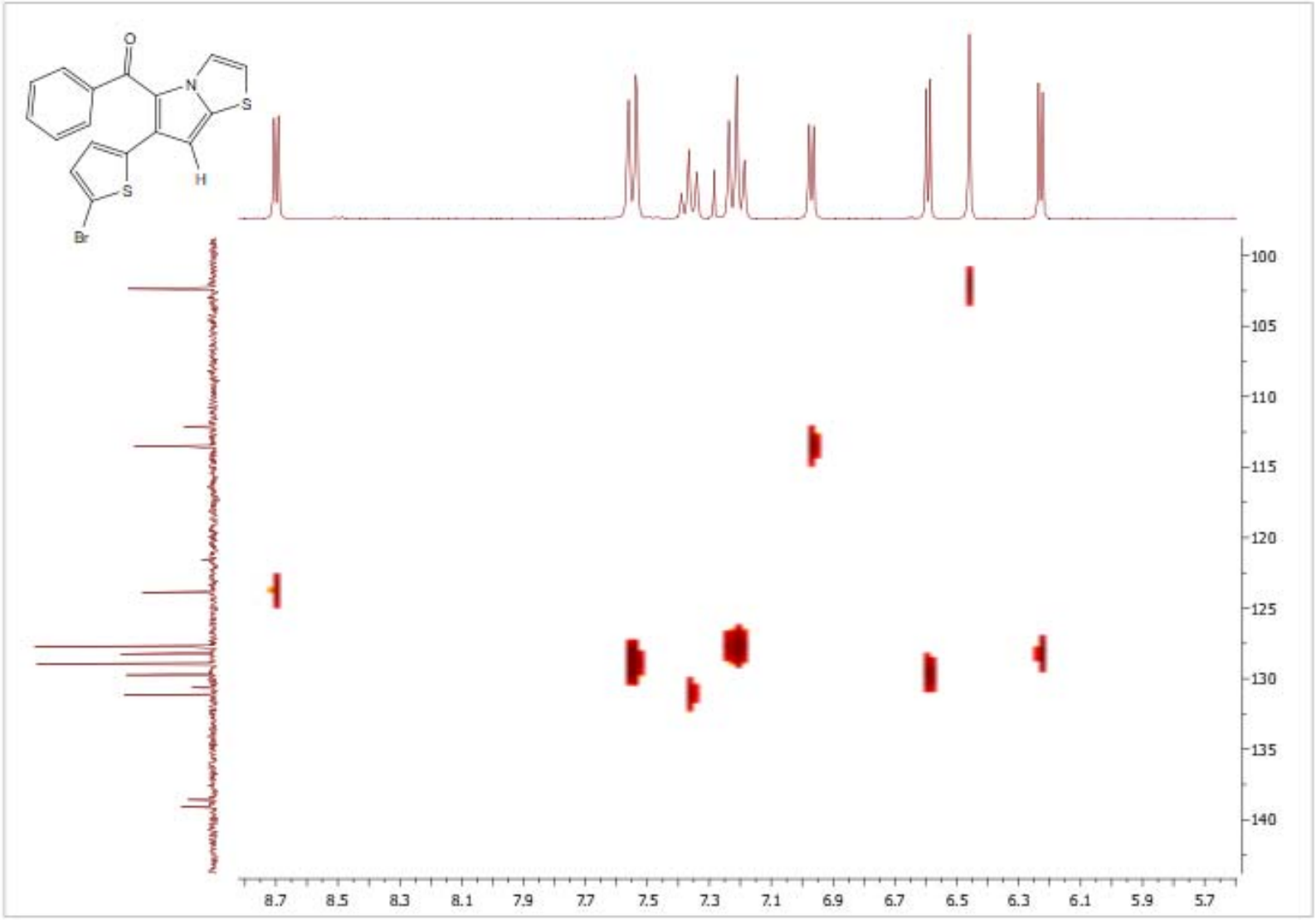
^{13}C NMR


184.99
139.05
138.97
138.53
131.10
129.68
128.90
128.20
127.69
112.07
102.30
O
N
S
S
H
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{1}H-^{1}H COSY NMR

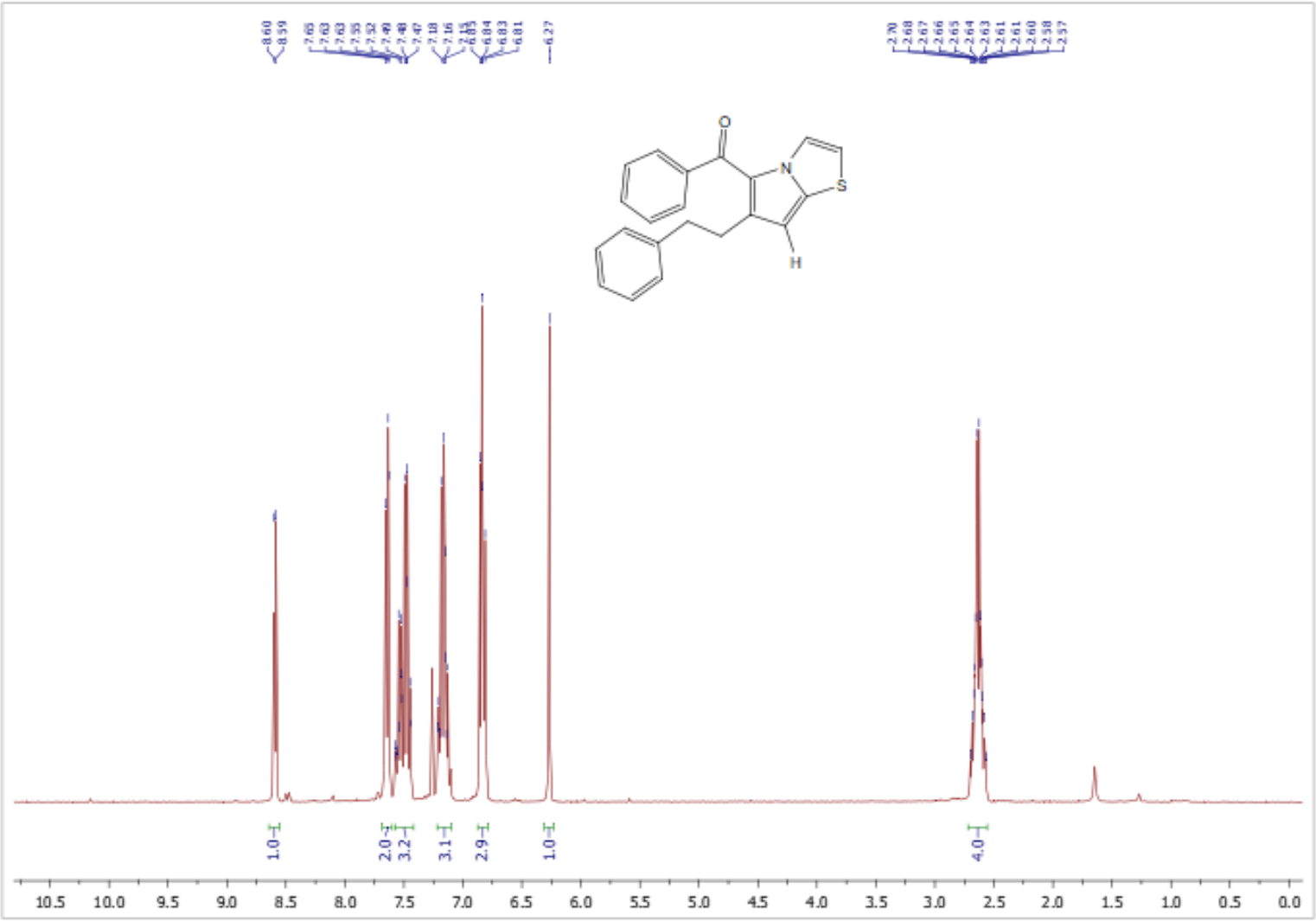


^{1}H-^{13}C HSQC NMR

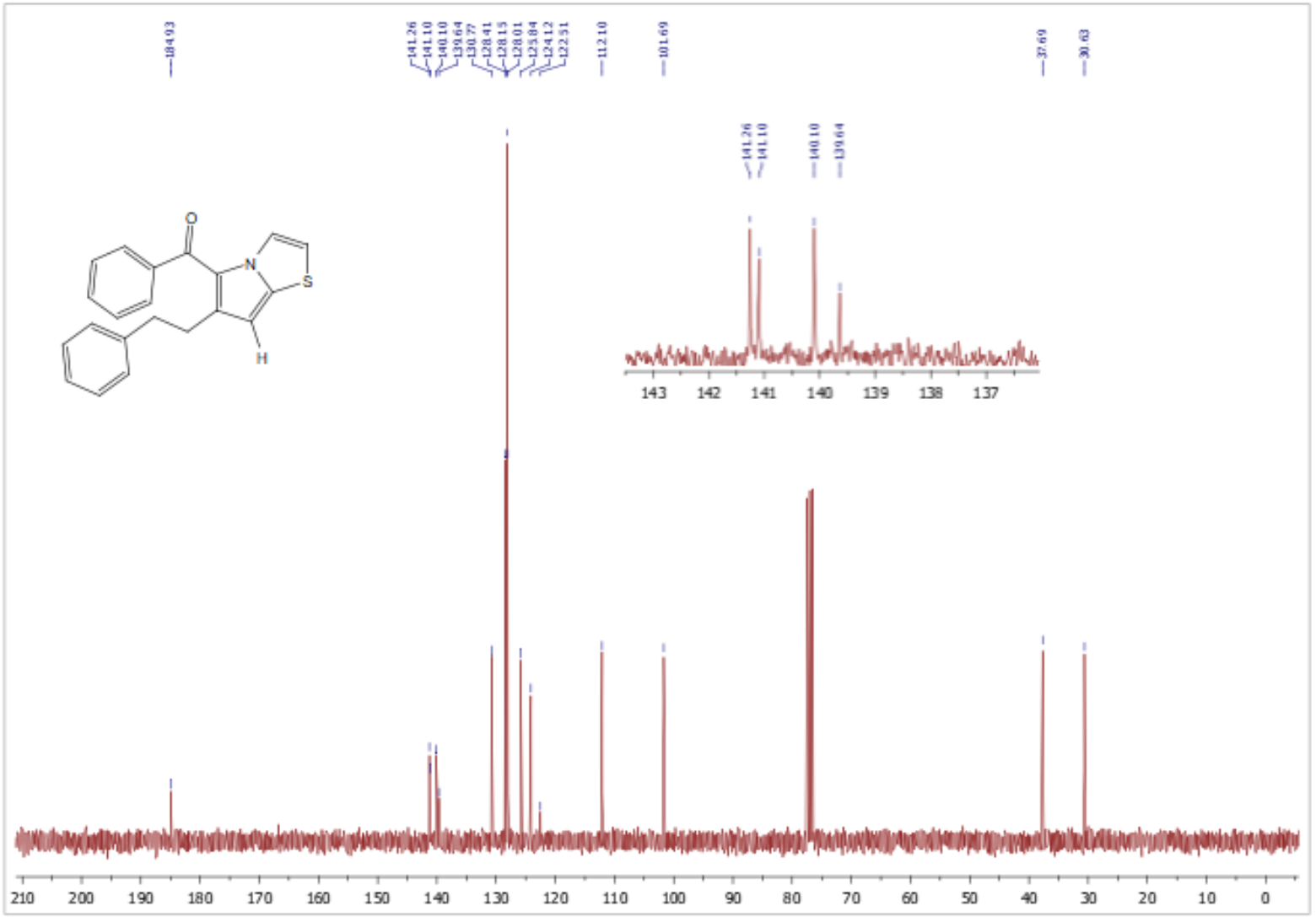


phenyl[6-(2-phenylethyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl]methanone **5f**

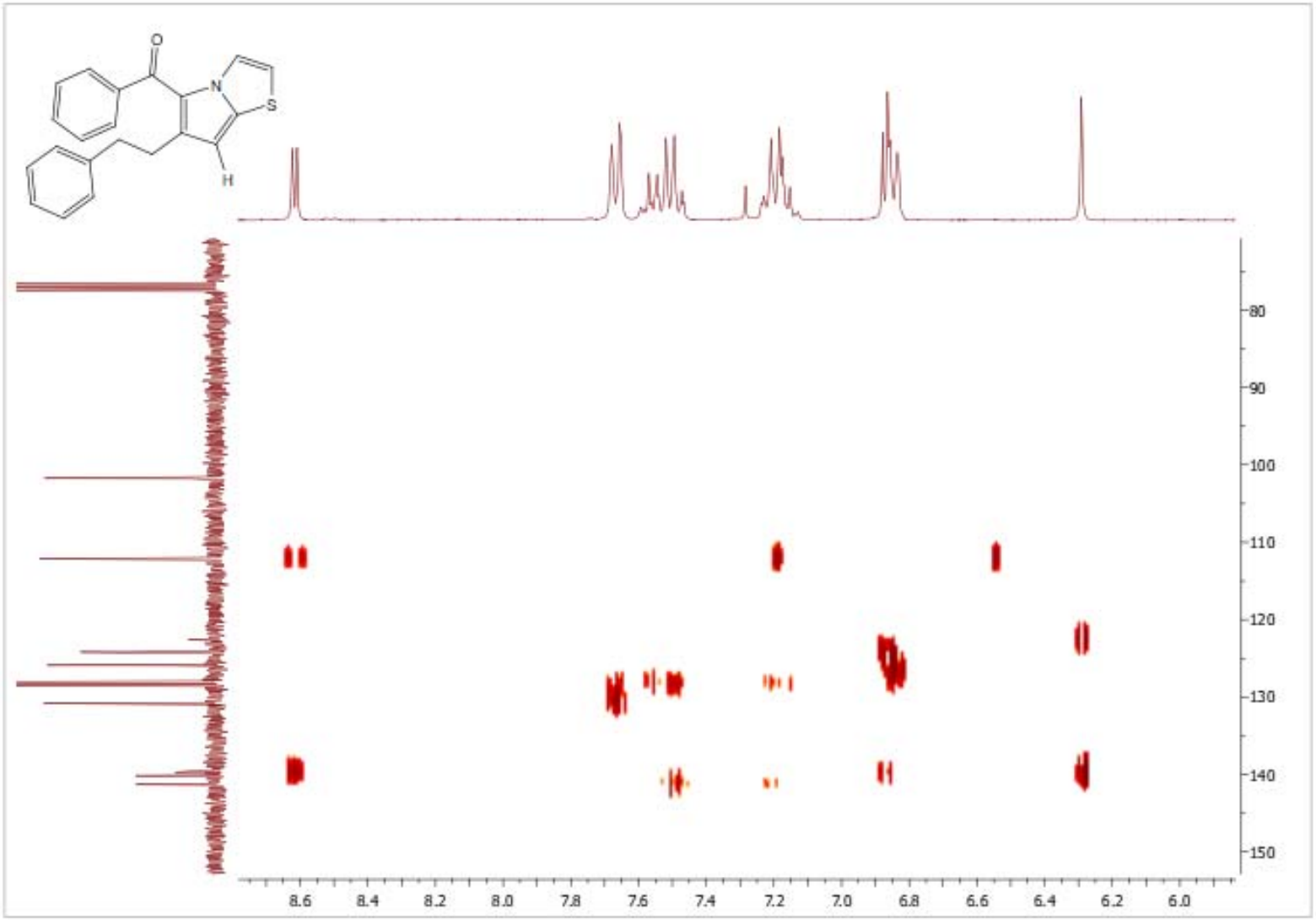
^{1}H NMR



^{13}C NMR

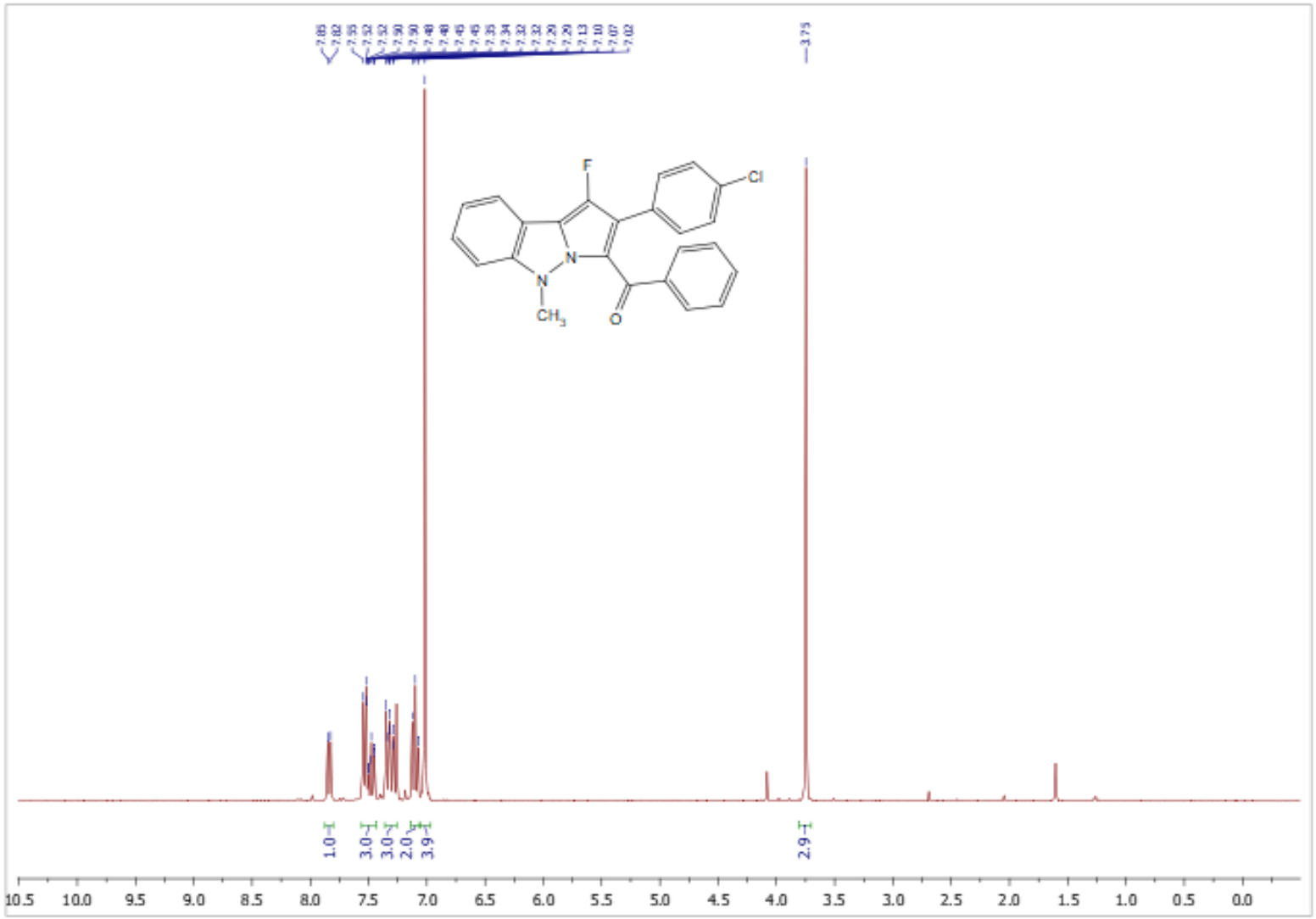

184.93
141.26
141.10
140.10
139.64
130.77
128.41
128.15
128.01
125.84
124.12
122.51
112.10
101.69
37.69
30.63
O
N
S
H
143
142
141
140
139
138
137
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H-^{13}C HMBC NMR

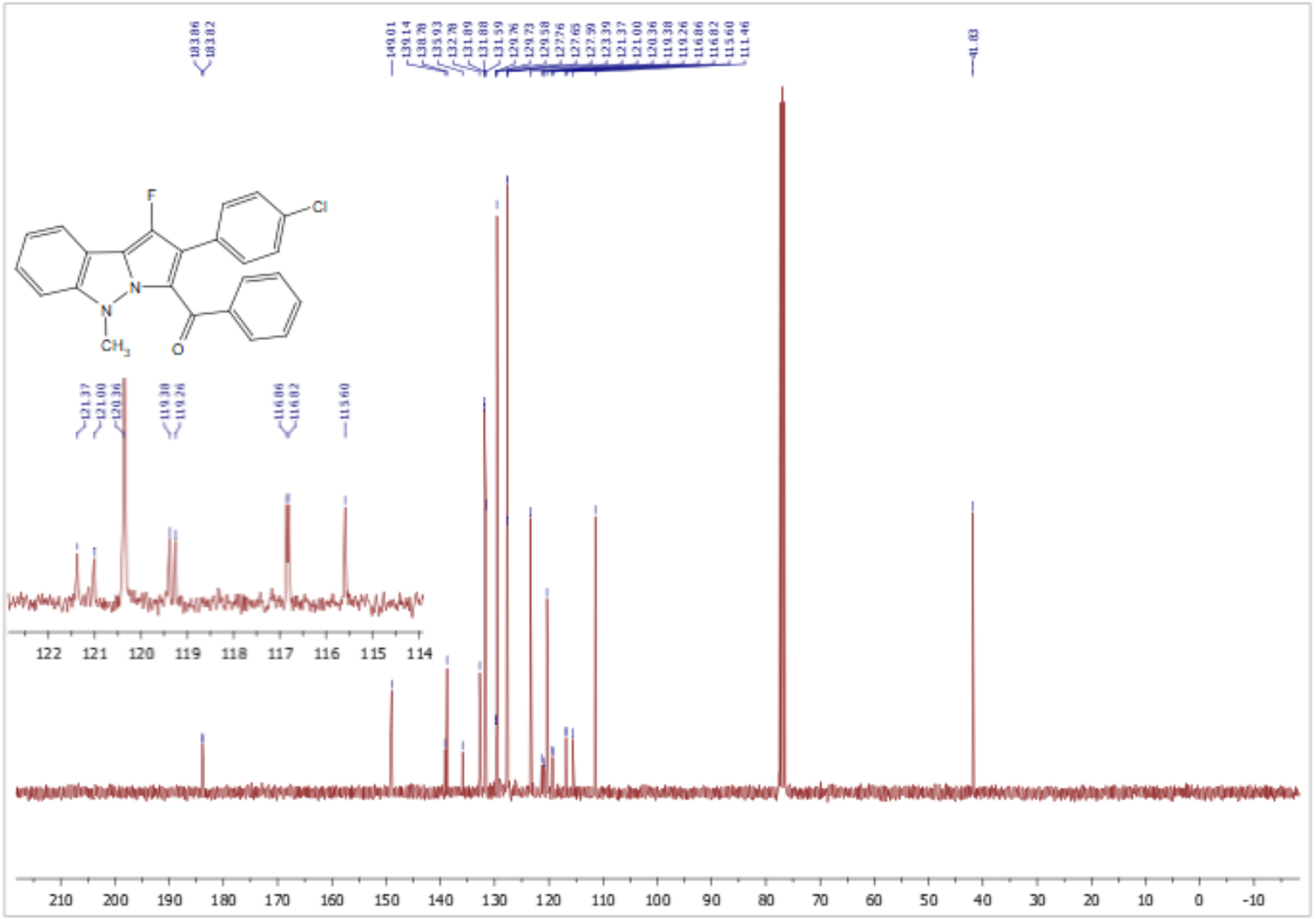


[2-(4-chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone **7a**

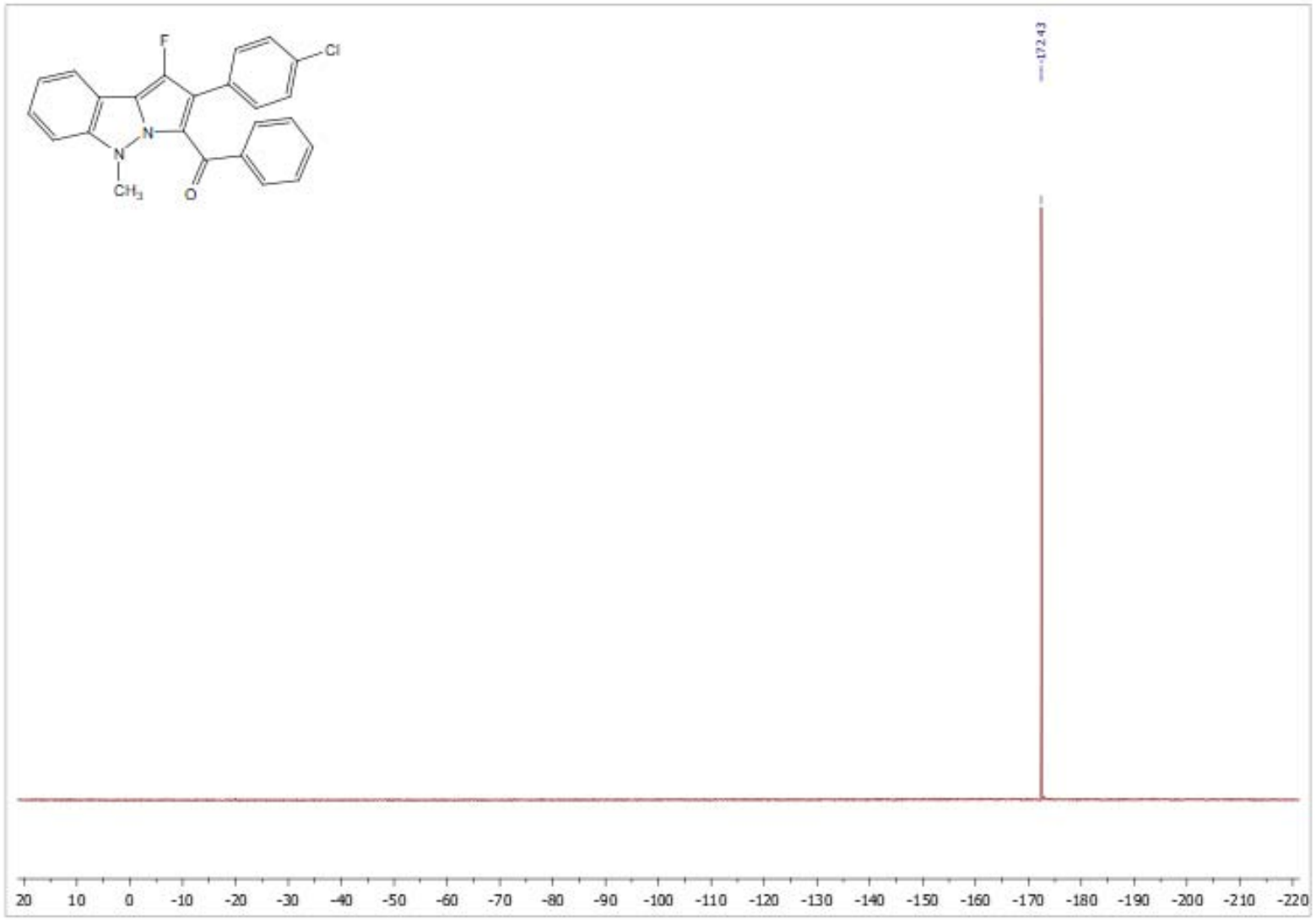
^{1}H NMR



^{13}C NMR

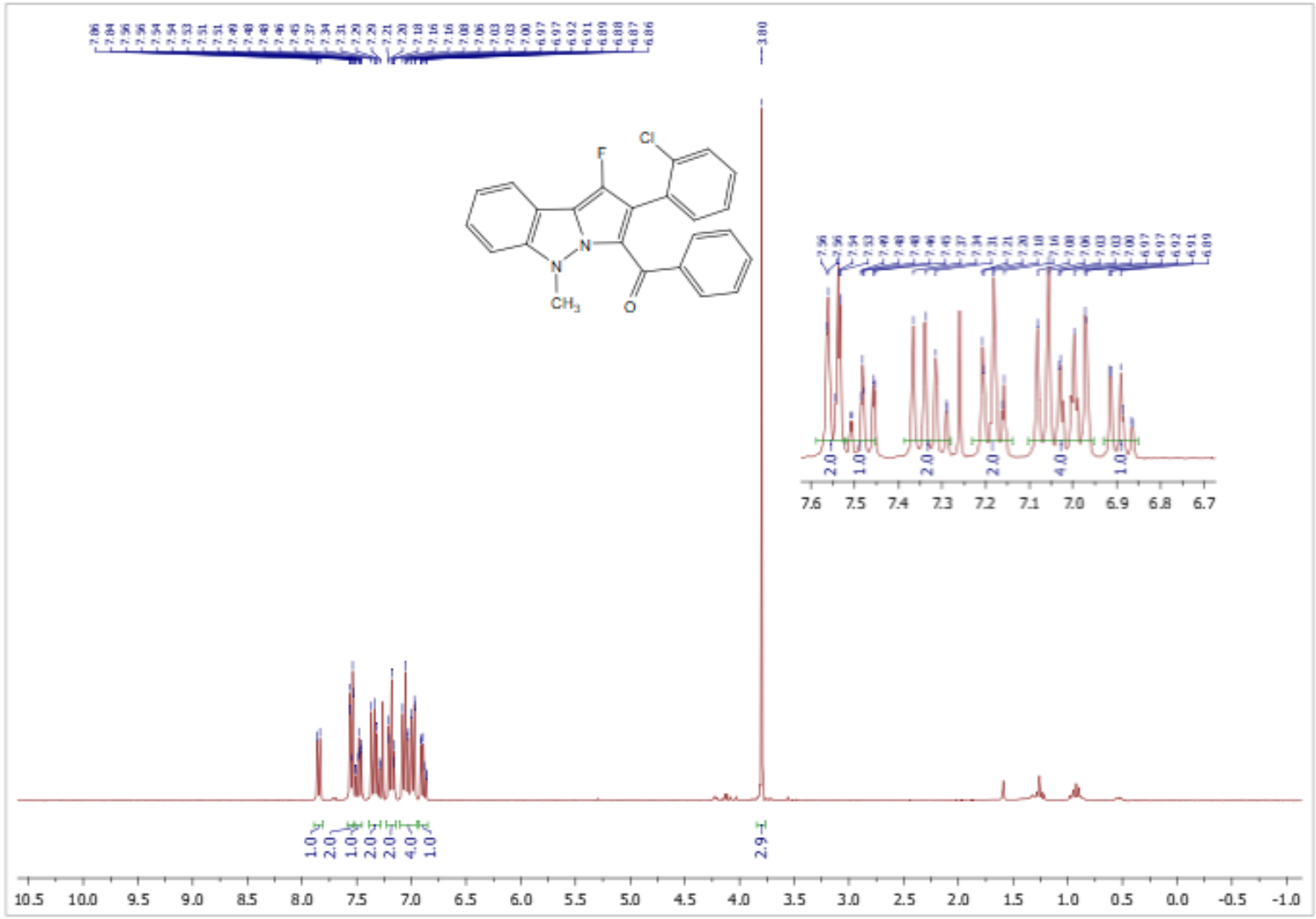

183.86
183.82
149.01
139.14
138.78
135.93
132.78
131.89
131.88
131.59
129.76
129.73
129.58
127.76
127.65
127.59
123.39
121.37
121.00
120.36
119.38
119.26
116.86
116.82
115.60
111.46
41.83
F
Cl
N
N
CH3
O
121.37
121.00
120.36
119.38
119.26
116.86
116.82
115.60
122 121 120 119 118 117 116 115 114
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{19}F NMR

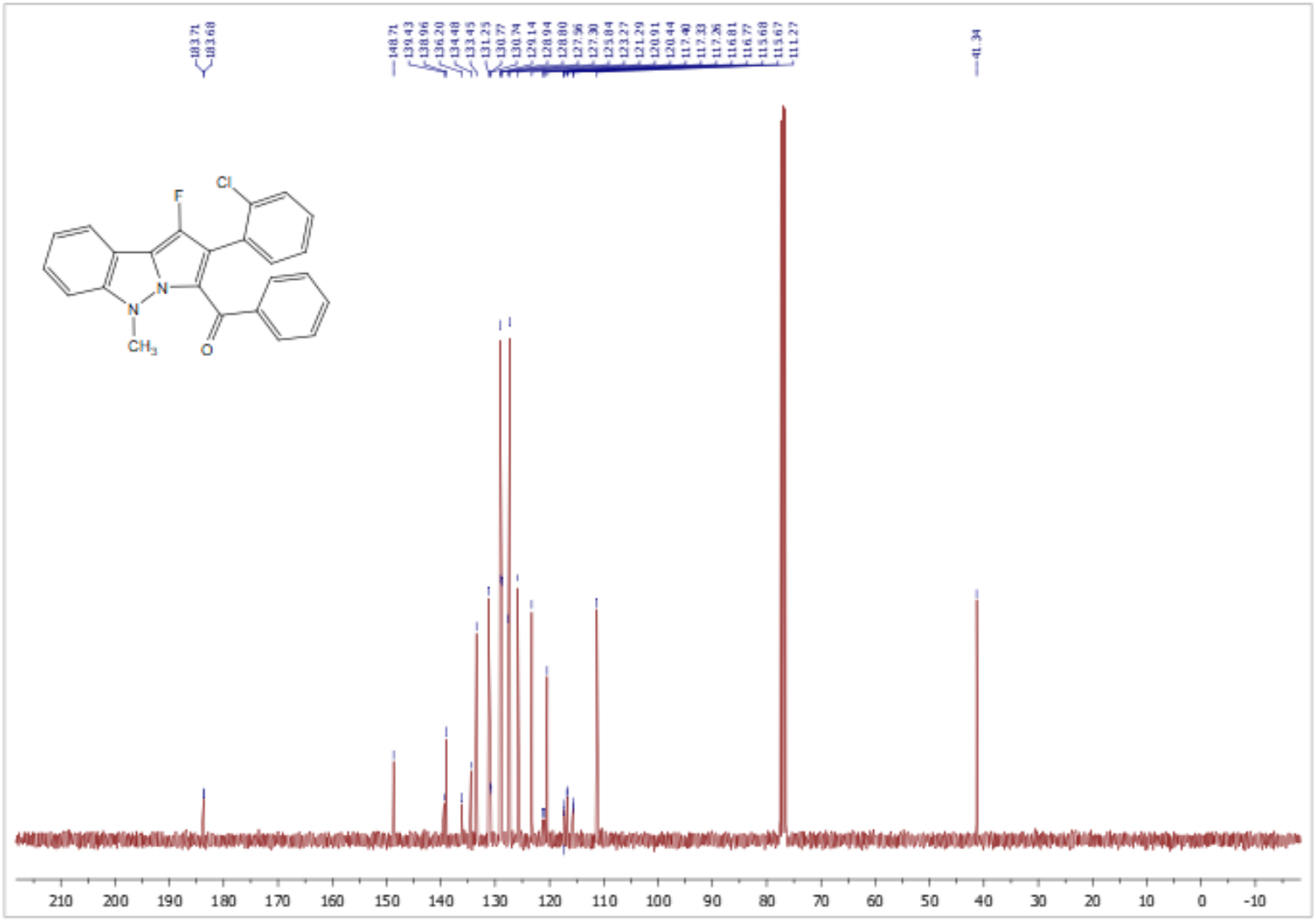

F
Cl
N
N
CH3
O
-117.43
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220

[2-(2-chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone **7b**

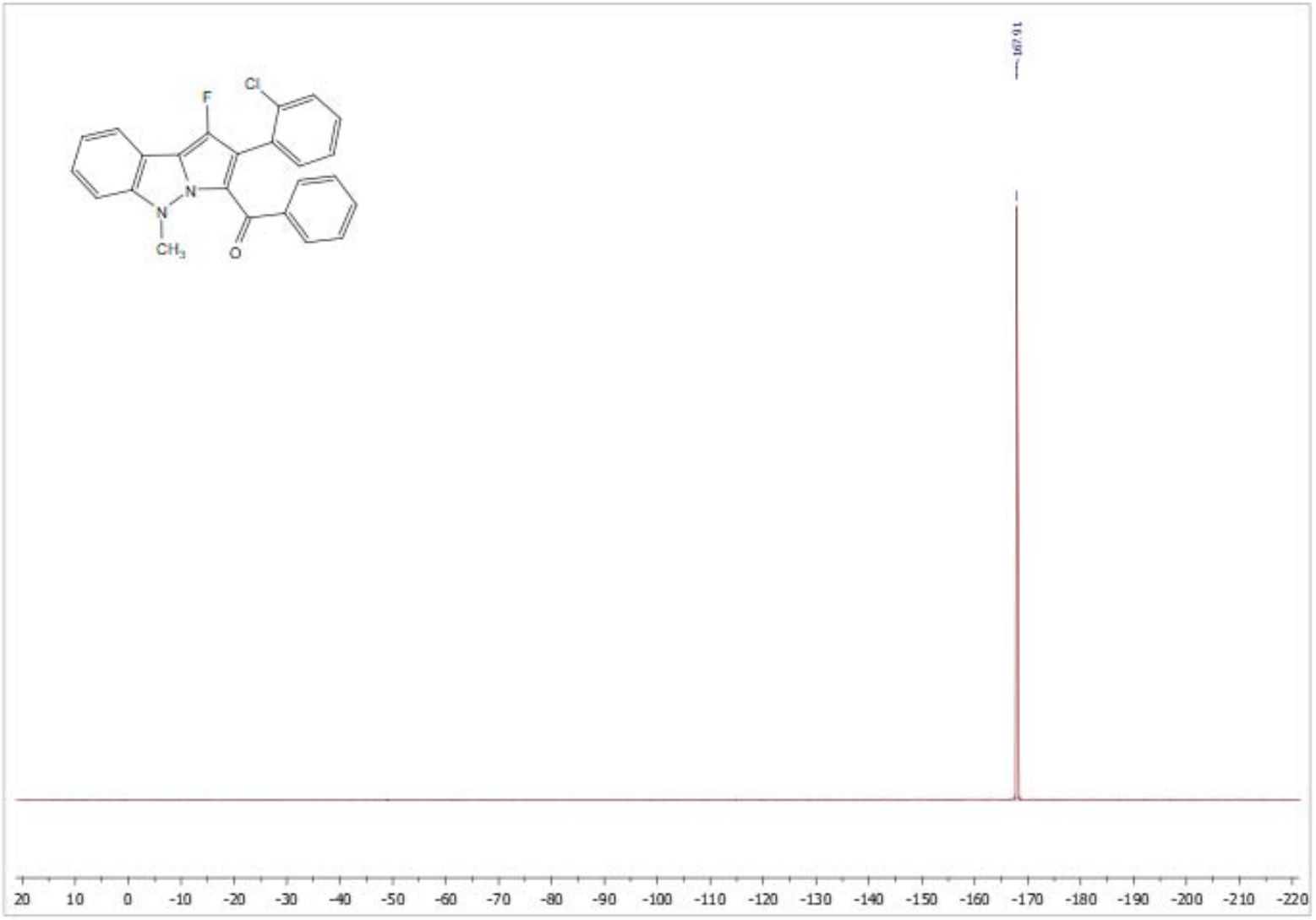
^{1}H NMR



^{13}C NMR


183.71
183.68
148.71
139.43
138.96
136.20
134.48
133.45
131.25
130.77
130.74
129.14
128.94
128.80
127.96
127.30
125.84
123.27
121.29
120.91
120.44
117.40
117.33
117.26
116.81
116.77
115.68
115.67
111.27
41.34
F
Cl
N
N
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR


F
Cl
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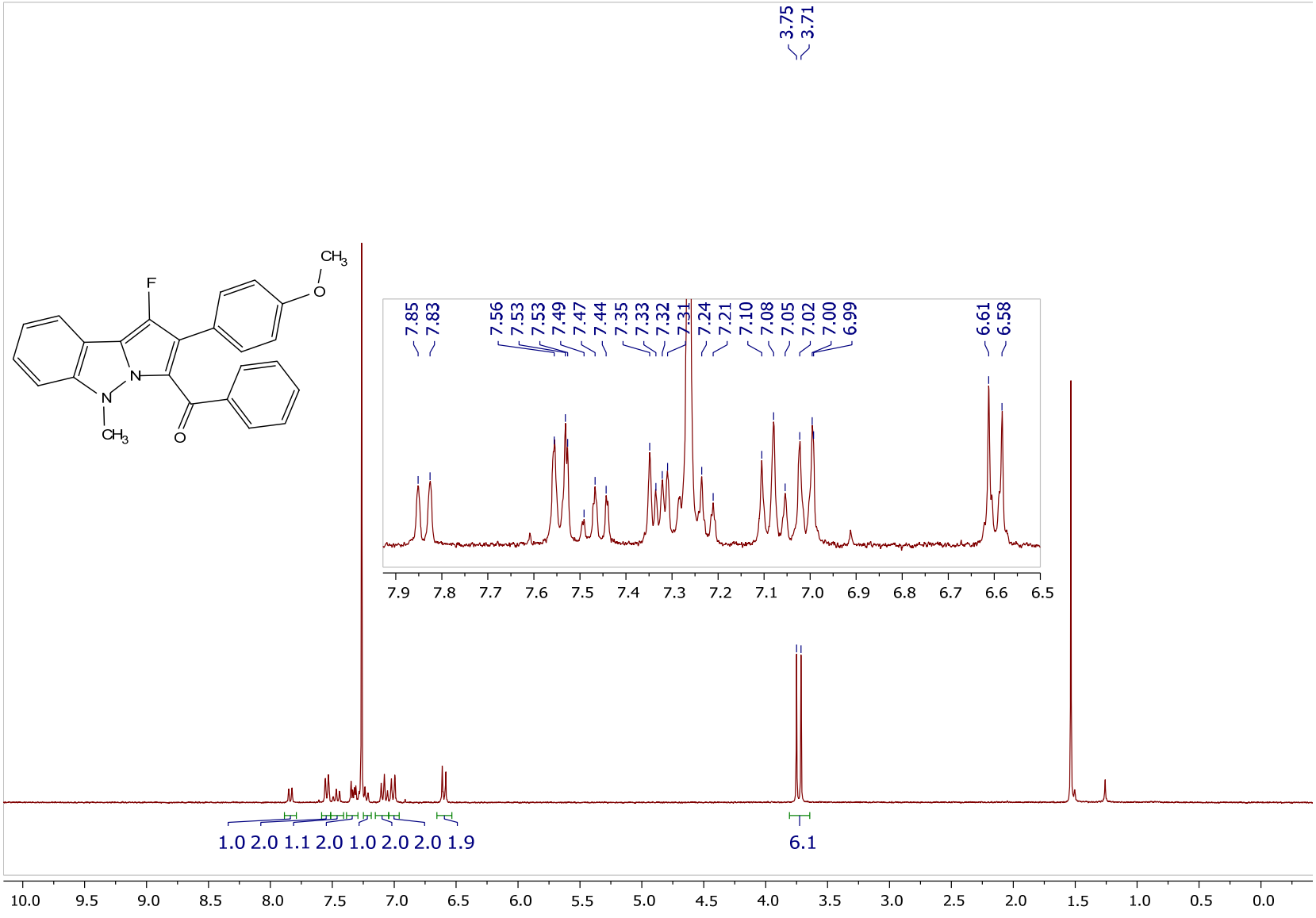
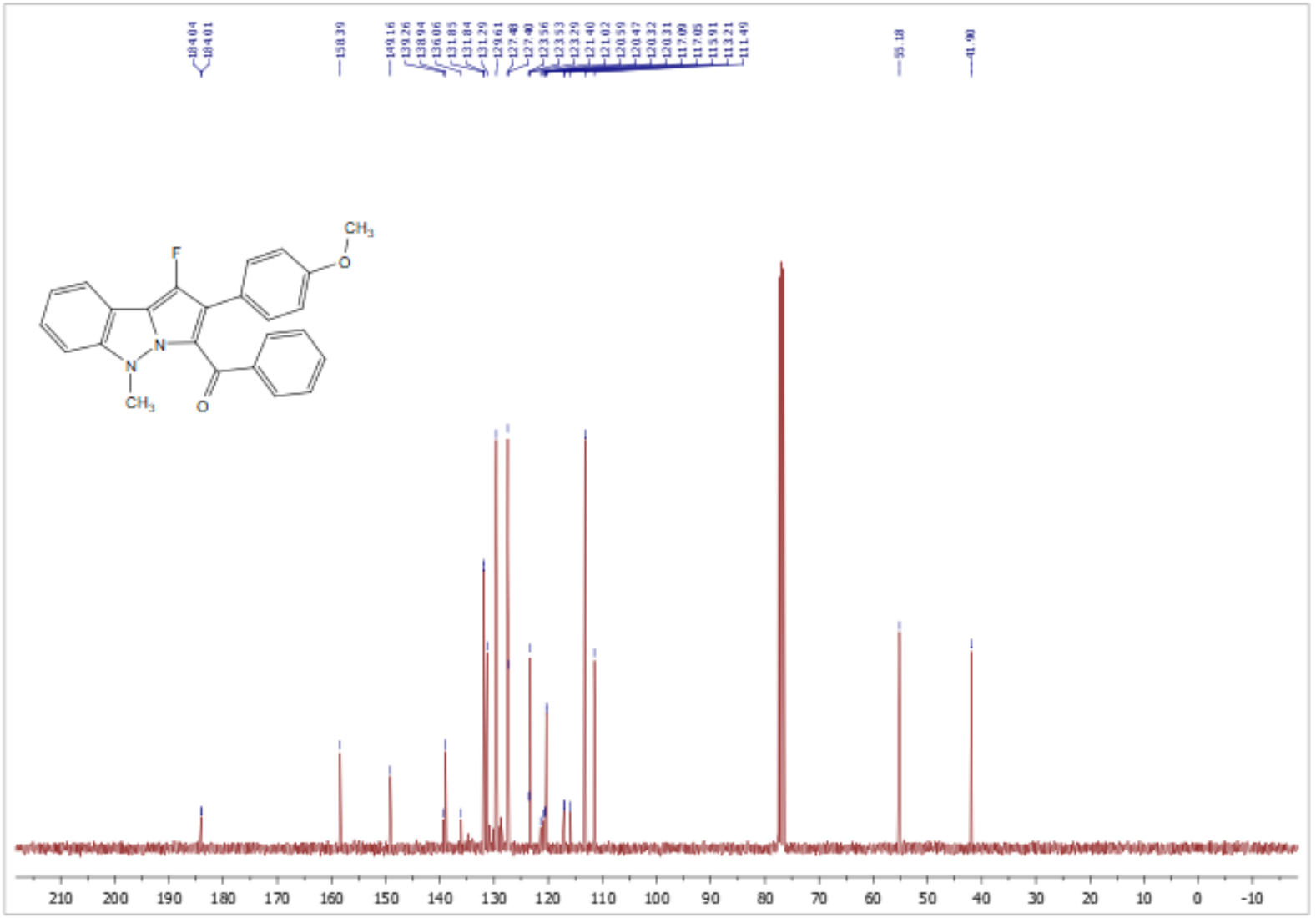
N
CH3
O
-168.91
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220

[1-fluoro-2-(4-methoxyphenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone **7c**

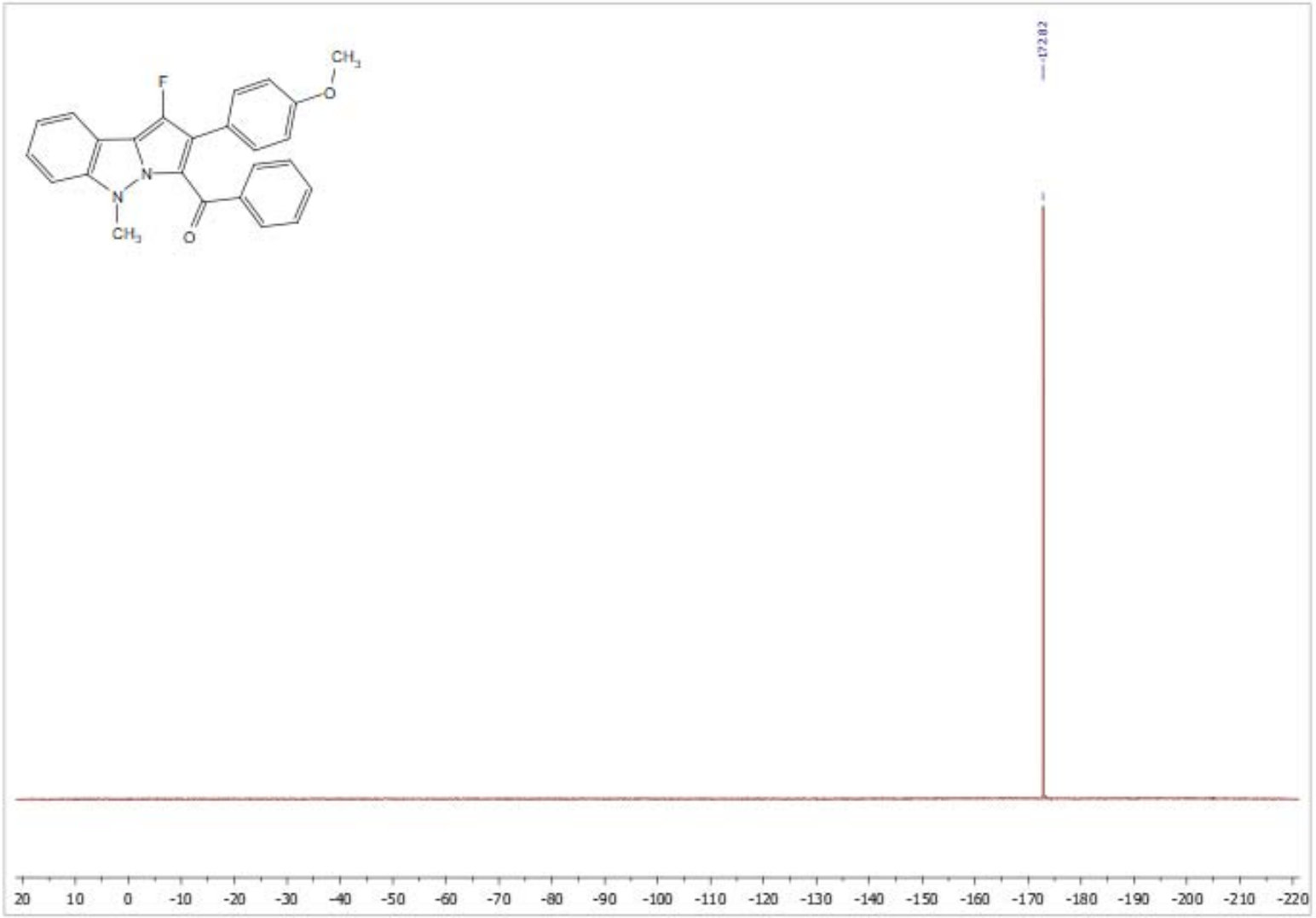
^{1}H NMR



^{13}C NMR

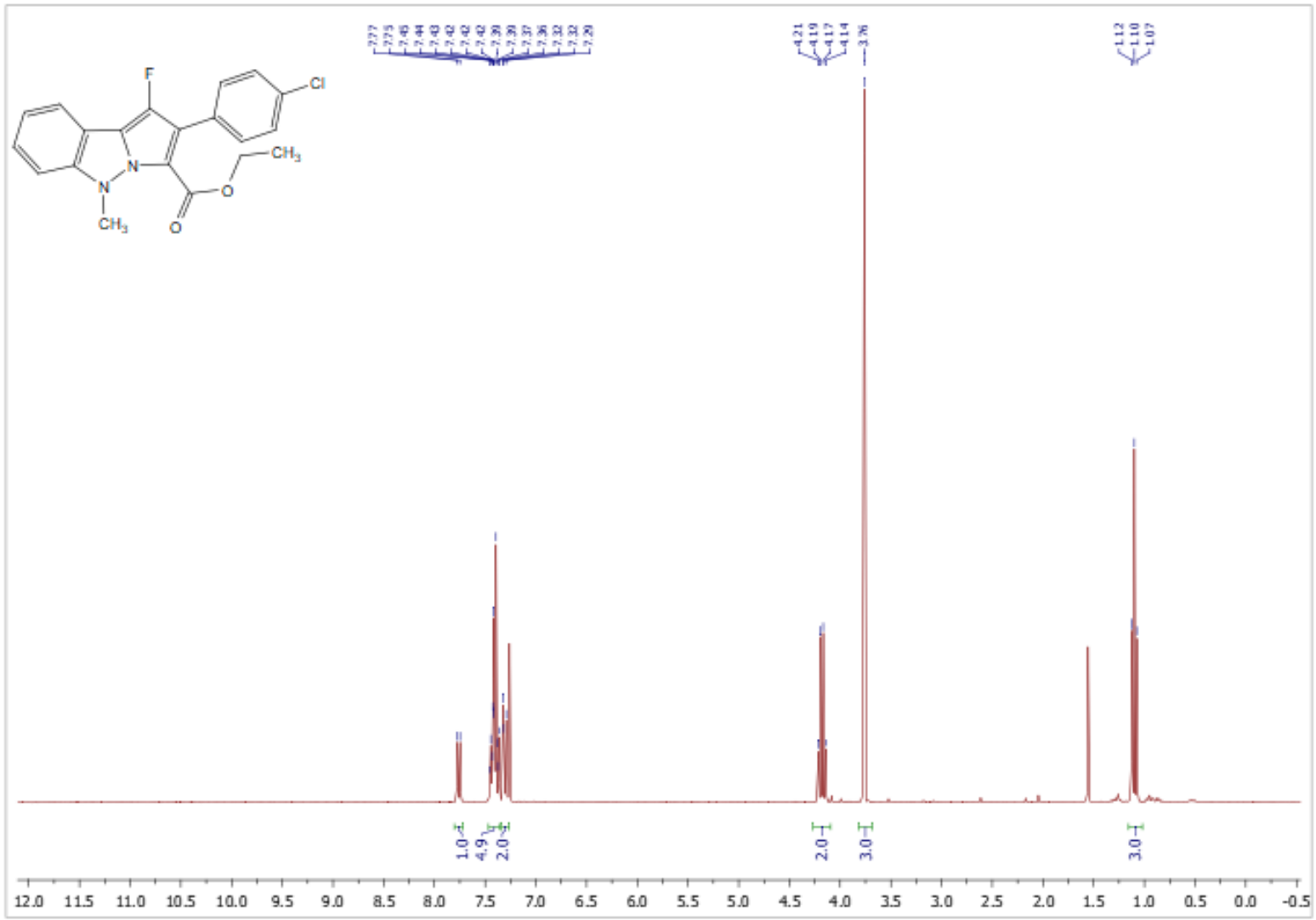

184.04
184.01
158.39
149.16
139.26
138.94
136.06
131.85
131.84
131.29
129.61
127.48
127.40
123.56
123.53
123.29
121.40
121.02
120.59
120.47
120.32
120.31
117.09
117.05
115.91
113.21
111.49
55.18
41.90
F
O
CH3
N
N
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

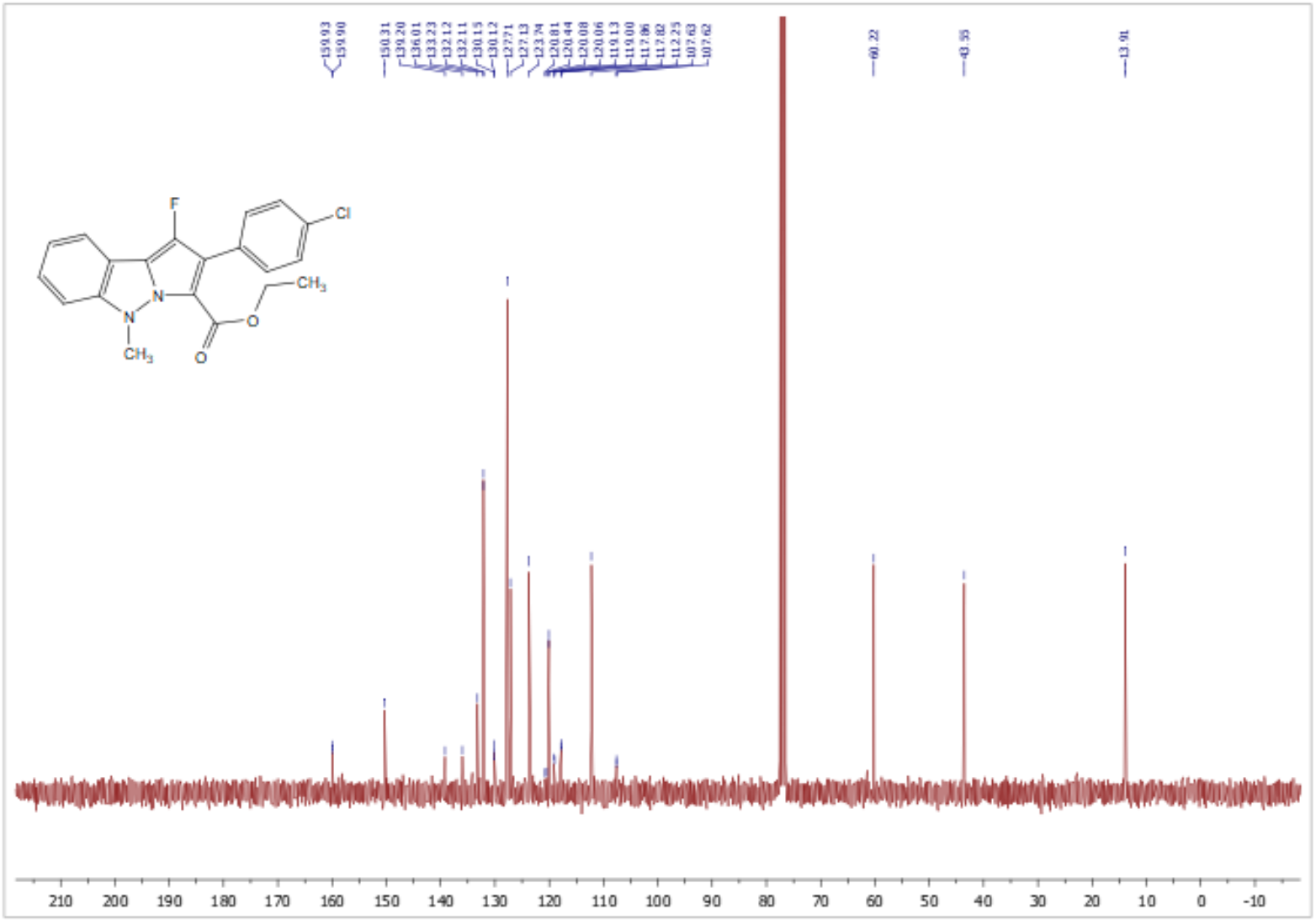

F
CH3
O
N
N
CH3
O
-17282
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

ethyl 2-(4-chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazole-3-carboxylate **7d**

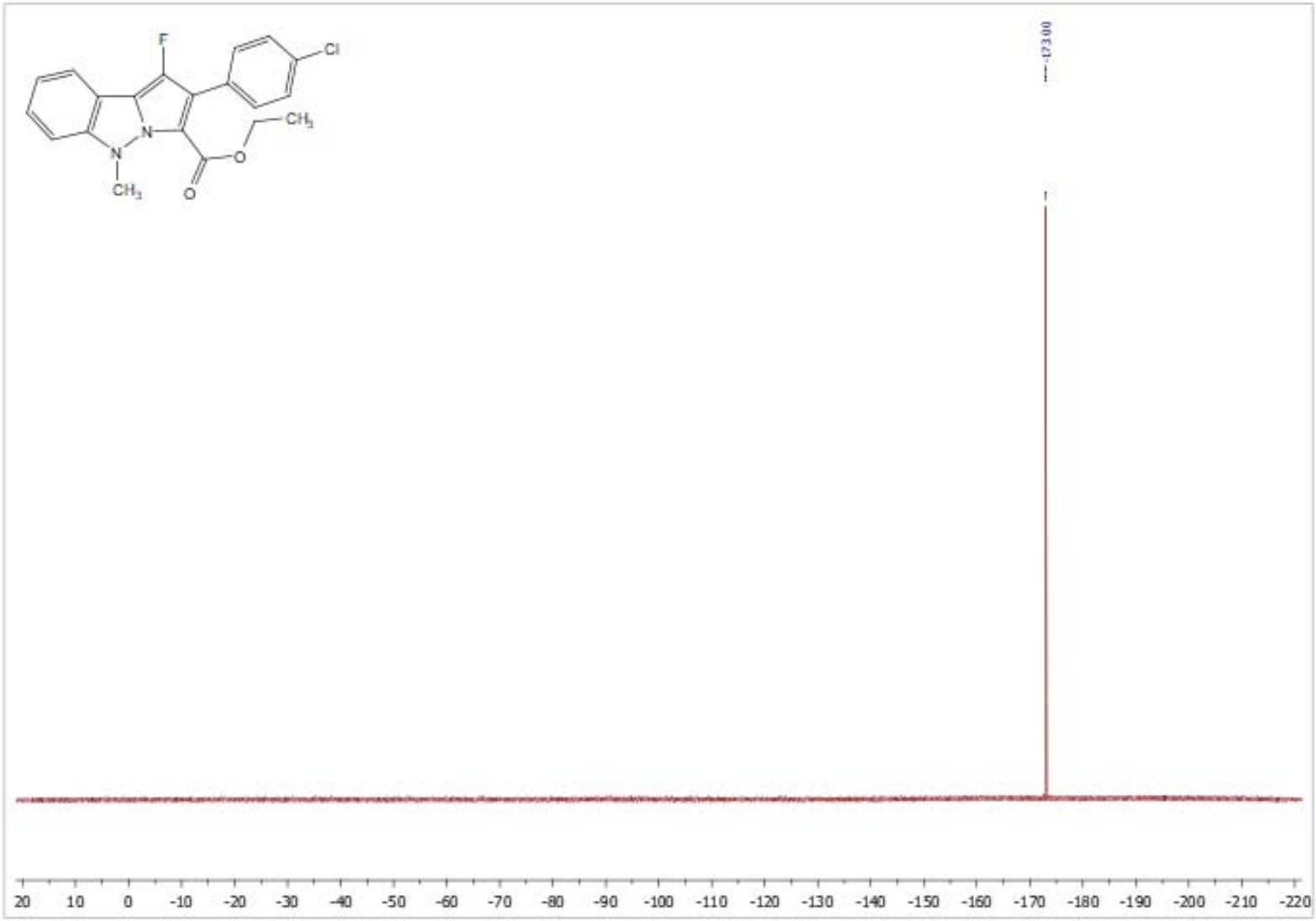
^{1}H NMR



^{13}C NMR

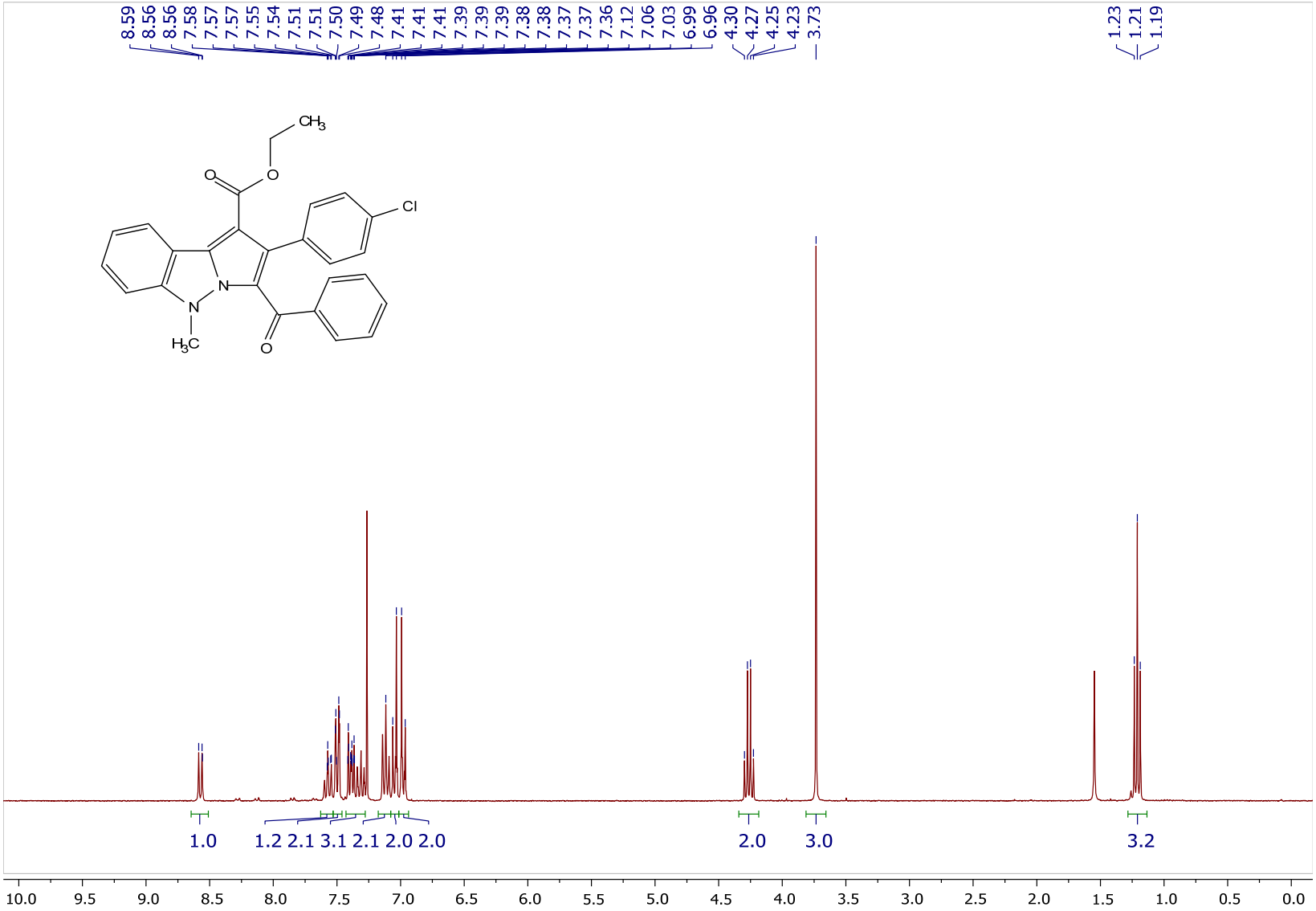

159.93
159.90
150.31
139.20
136.01
133.23
132.12
132.11
130.15
130.12
127.71
127.13
123.74
120.81
120.44
120.08
120.06
119.13
119.00
117.86
117.82
112.25
107.63
107.62
60.22
43.35
13.91
F
Cl
N
N
CH3
CH3
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{19}F NMR

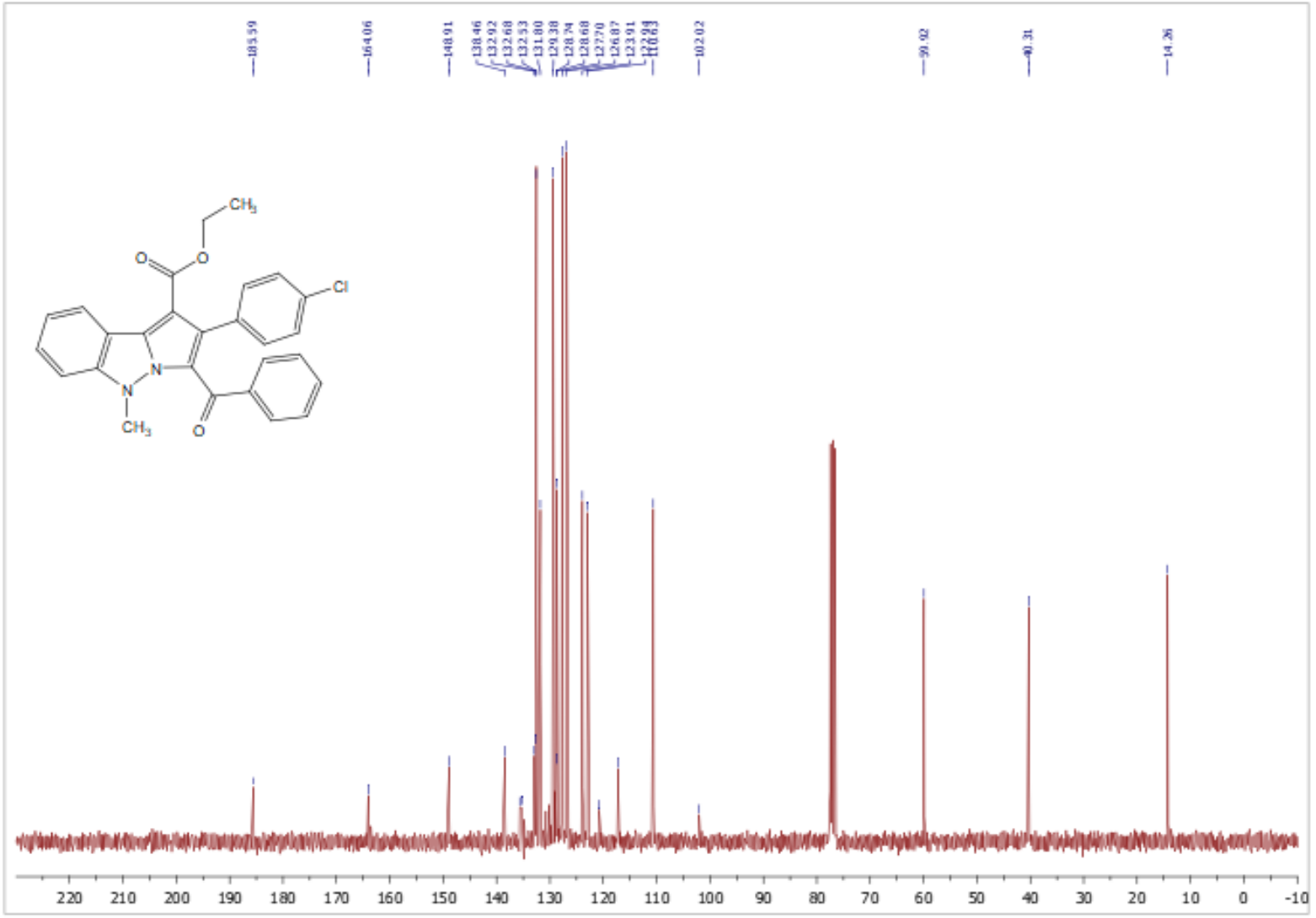

F
Cl
CH3
N
N
O
CH3
O
-172.300
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

ethyl 3-benzoyl-2-(4-chlorophenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazole-1-carboxylate **7e**

^{1}H NMR

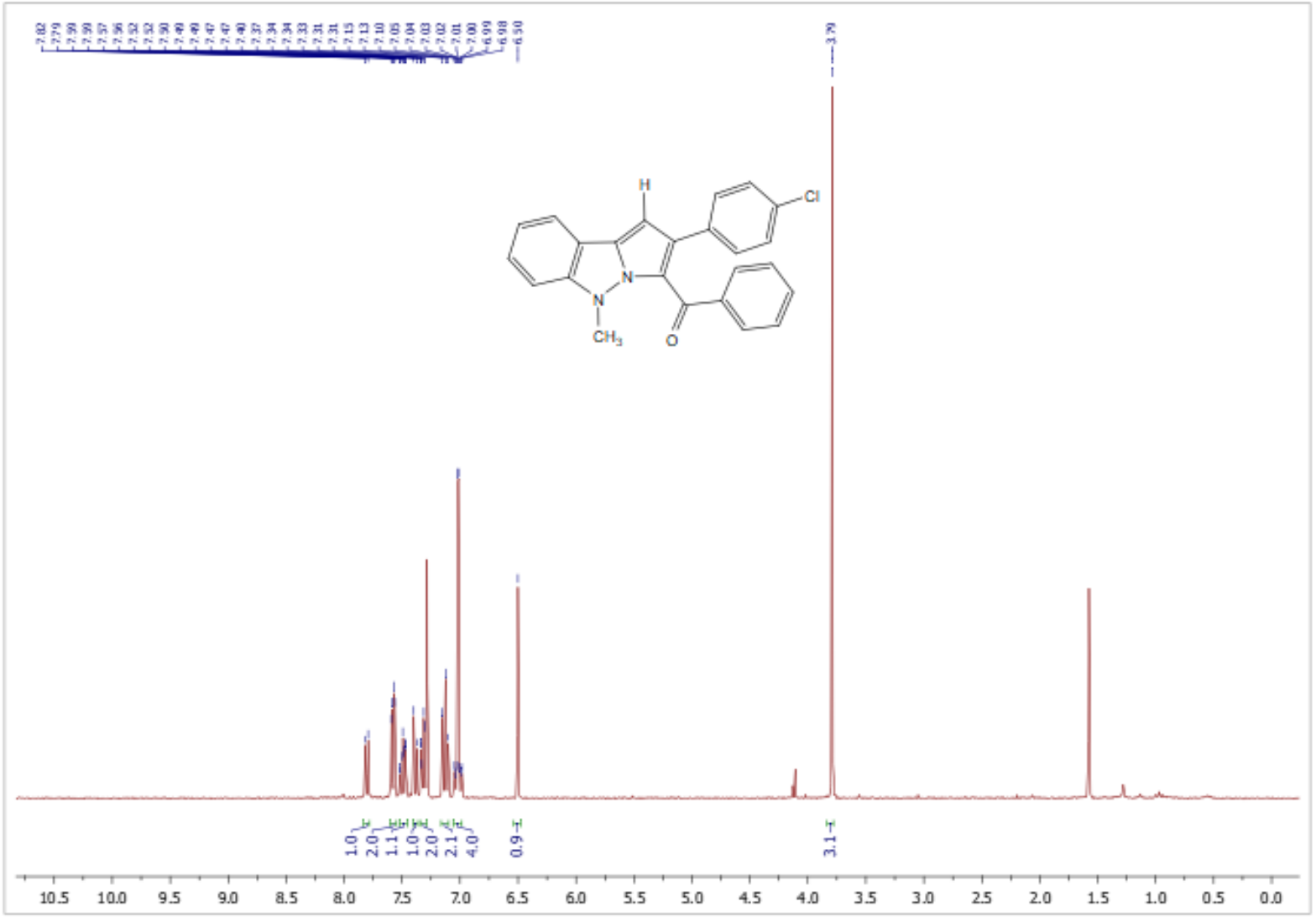


^{13}C NMR

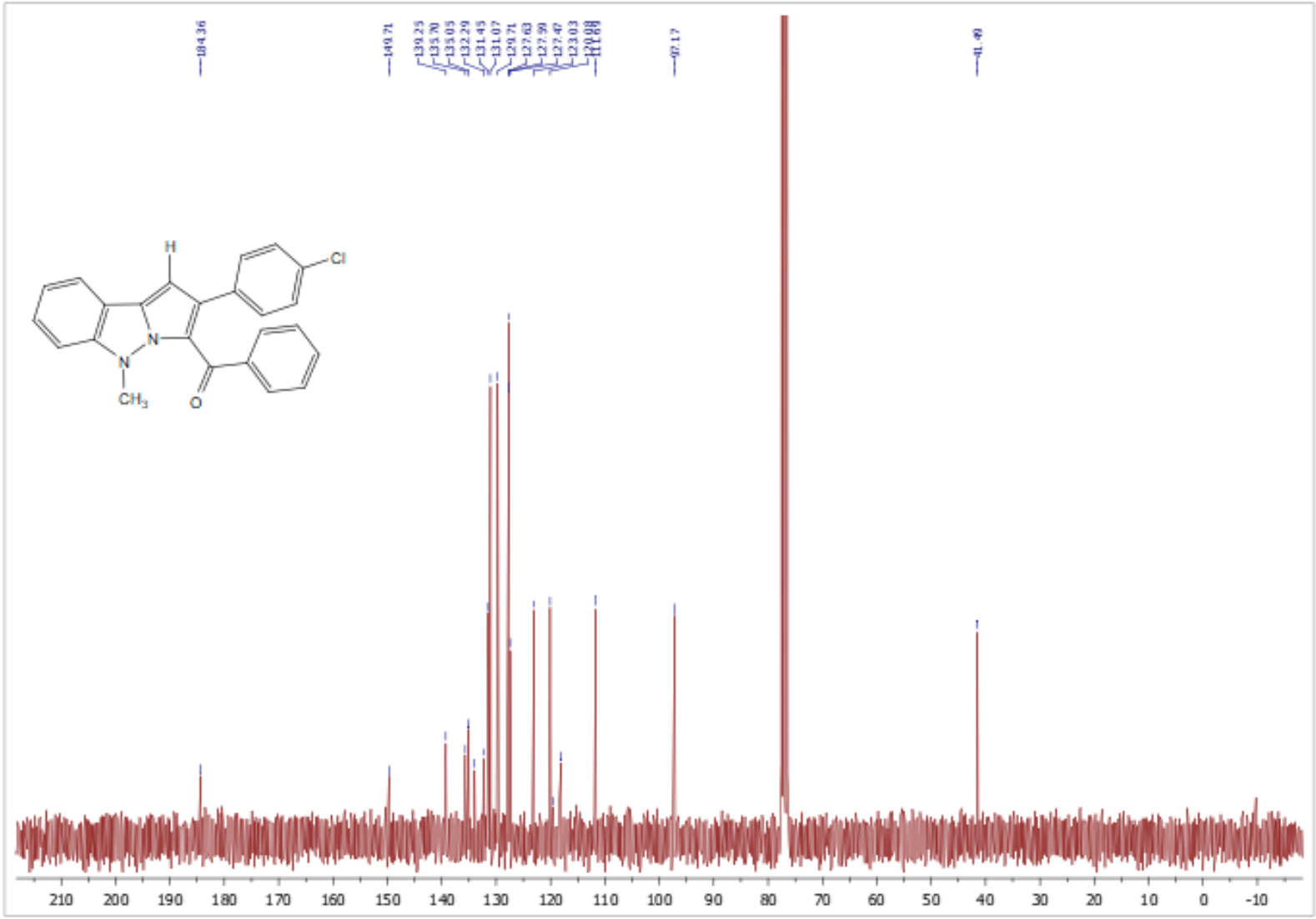

185.59
164.06
148.91
138.46
132.92
132.68
132.53
131.80
129.38
128.74
128.68
127.70
126.87
123.91
102.02
99.92
40.31
14.26
CH3
O
O
Cl
N
N
CH3
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

[2-(4-chlorophenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone **7f**

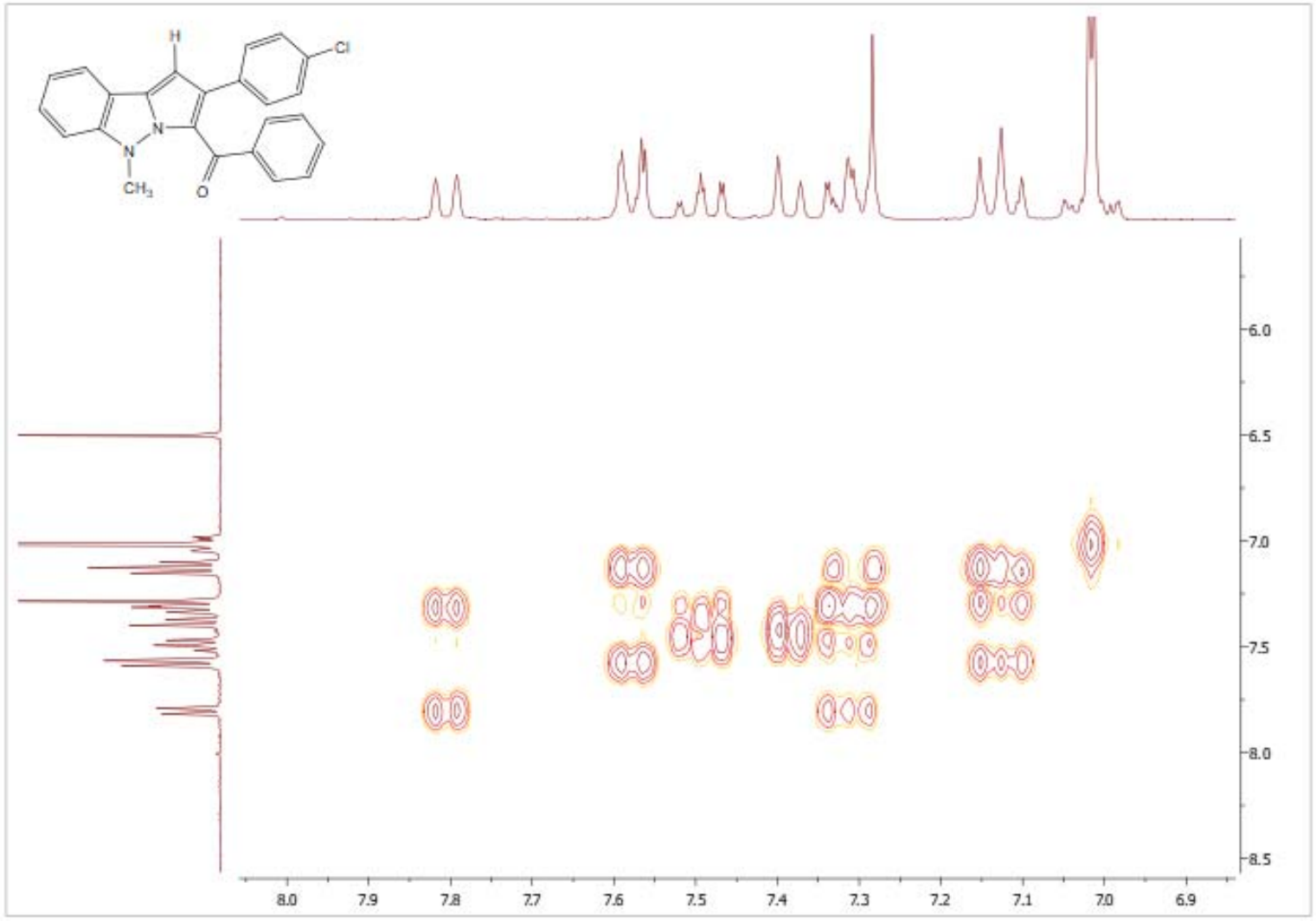
^{1}H NMR



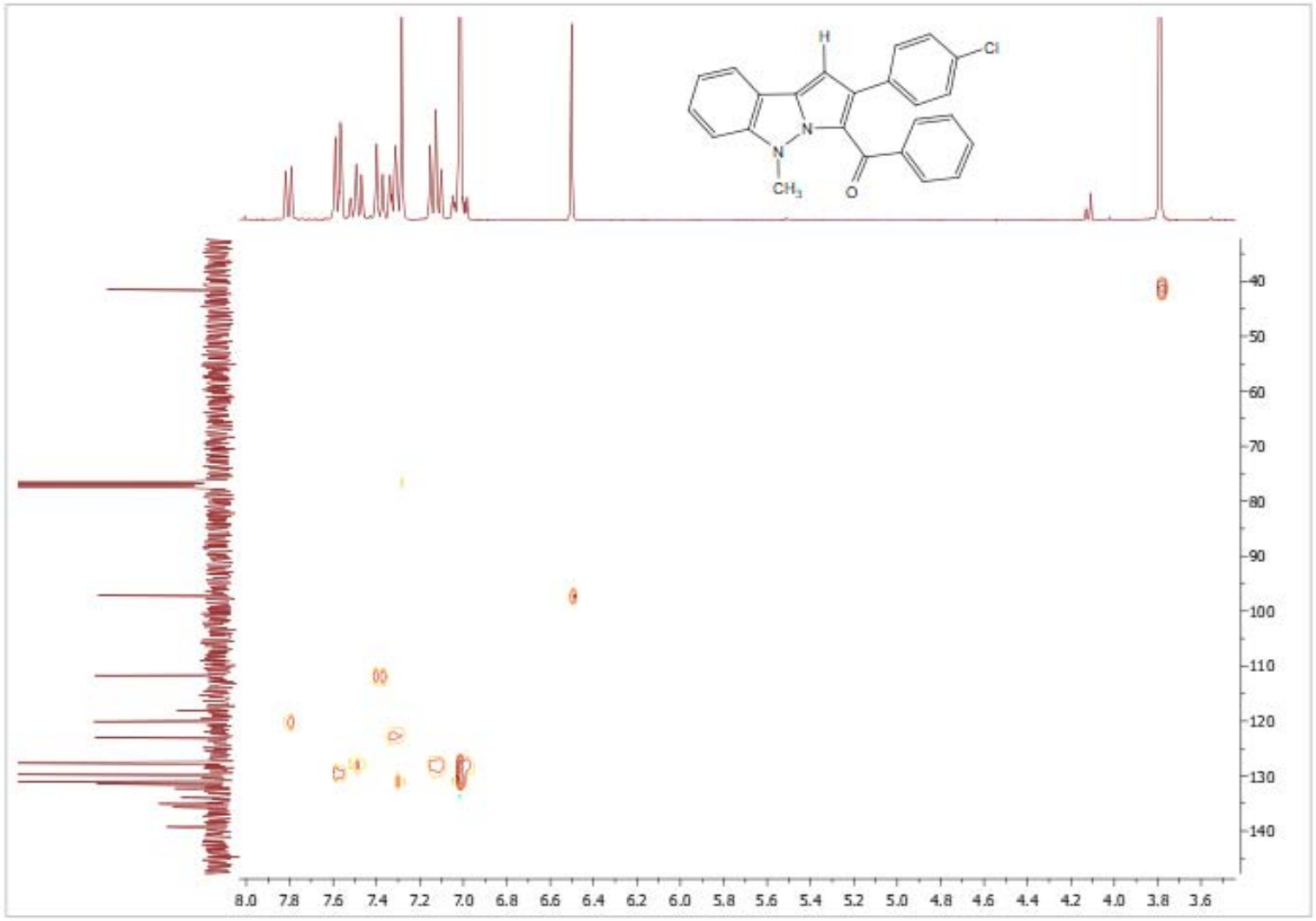
^{13}C NMR


184.36
149.71
130.25
135.70
133.05
132.29
131.45
131.07
129.71
127.63
127.39
127.47
123.03
97.17
41.49
H
Cl
N
N
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

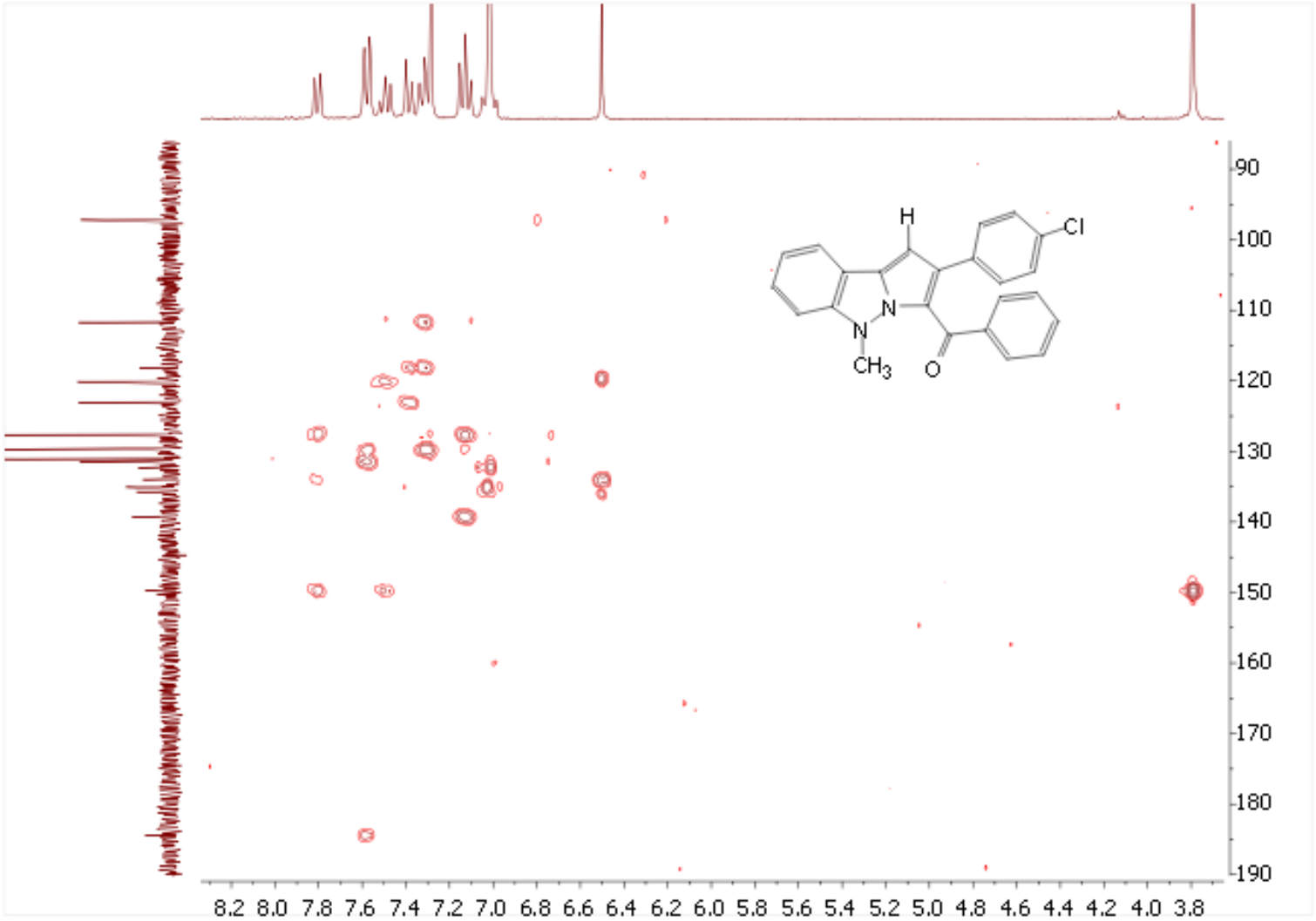
^{1}H-^{1}H COSY NMR



^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR



^{19}F NMR of reaction mixture containing primary cycloadduct **8**