Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Pd-catalyzed asymmetric hydrogenation of fluorinated aromatic pyrazol-5-ols *via* capture of active tautomers

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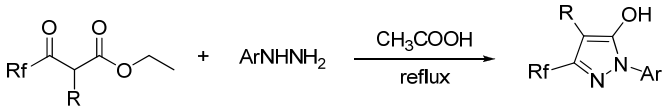
1. General and Materials

General: Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz instrument with tetra-methylsilane (TMS) as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh).

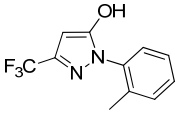
2. General Procedure for Synthesis of Fluorinated Pyrazol-5-ols

All fluorinated pyrazol-5-ols were prepared from the accessible starting materials appropriate fluorinated β-ketoesters and arylhydrazines according to the literature methods.[1] Pyrazol-5-ol **1a** is known and its NMR data matched the literature data.

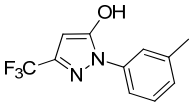


Fluorinated β-ketoesters (5.0 mmol) and arylhydrazines (5.0 mmol) were mixed and refluxed in acetic acid (30 mL) for 6 h. Then the mixture was cooled to room temperature. After filtration, the residue was recrystallized from ethanol to give the pure fluorinated pyrazol-5-ols.

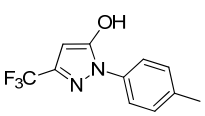
1-(*o*-Tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (1b): Pale yellow solid; mp = 204-205 °C, yield 58%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.03 (br, 1H), 7.45–7.37 (m, 2H), 7.37–7.29 (m, 2H), 5.91 (s, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.4, 140.7 (q, $J_{C\text{-}F}$ = 37 Hz), 136.7, 135.6, 131.2, 129.8, 128.1, 127.0, 121.9 (q, $J_{C\text{-}F}$ = 267 Hz), 84.7, 17.5; ^{19}F NMR (377 MHz, DMSO-d_6) δ -61.6 (s, 3F); IR (film): 2808, 2714, 1558, 1504, 1422, 1259, 1218, 1198, 1157, 1136; HRMS Calculated For $C_{11}H_{10}F_3N_2O$ $[M+H]^+$ 243.0745, found: 243.0740.



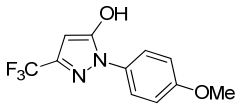
1-(*m*-Tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (1c): Pale yellow solid; mp = 210-211 °C, yield 62%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (br, 1H), 7.57-7.52 (m, 2H), 7.36 (t, J = 7.7 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 5.97 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.1, 140.8 (q, $J_{C\text{-}F}$ = 37 Hz), 139.1, 138.2, 129.2, 128.2, 123.2, 121.4 (q, $J_{C\text{-}F}$ = 266 Hz), 119.8, 86.0, 21.3; ^{19}F NMR (377 MHz, DMSO-d_6) δ -62.0 (s, 3F); IR (film): 2826, 1612, 1565, 1490, 1408, 1333, 1245, 1150, 1116; HRMS Calculated For $C_{11}H_{10}F_3N_2O$ $[M+H]^+$ 243.0745, found: 243.0740.



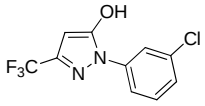
1-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (1d): Pale yellow solid; mp = 226-227 °C, yield 63%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.38 (br, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 5.93 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.0, 140.6 (q, $J_{C\text{-}F}$ = 37 Hz), 137.1, 135.8, 129.9, 122.7, 122.0 (q, $J_{C\text{-}F}$ = 267 Hz), 86.0, 21.0; ^{19}F NMR (377 MHz, DMSO-d_6) δ -61.8 (s, 3F); IR (film): 2883, 1572, 1490, 1415, 1347, 1259, 1415, 1347, 1259, 1218, 1157, 1110; HRMS Calculated For $C_{11}H_{10}F_3N_2O$ $[M+H]^+$ 243.0745, found: 243.0740.



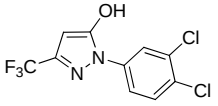
1-(4-Methoxyphenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (1e): Pale yellow solid; mp = 209-210 °C, yield 53%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (br, 1H), 7.58 (d, J = 9.0 Hz, 2H), 7.07–7.04 (m, 2H), 5.91 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.7, 153.8, 140.2 (q, $J_{C\text{-}F}$ = 37 Hz), 131.2, 124.6, 122.4 (q, $J_{C\text{-}F}$ = 267 Hz), 114.6, 85.8, 55.9; ^{19}F NMR (377 MHz, DMSO-d_6) δ -61.7 (s, 3F); IR (film): 2937, 2822, 1613, 1591, 1562, 1499, 1416, 1354, 1306, 1254, 1130, 1096, 1025; HRMS Calculated For $C_{11}H_{10}F_3N_2O_2$ $[M+H]^+$ 259.0694, found 259.0689.



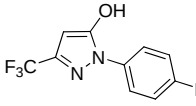
1-(3-Chlorophenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (1f): Pale yellow solid; mp = 220-221 °C, yield 57%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.80 (br, 1H), 7.81 (d, J = 1.7 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.52 (t, J = 8.1 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 5.96 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.6, 141.5 (q, $J_{C\text{-}F}$ = 37 Hz), 139.4, 133.9, 131.2, 127.3, 121.9, 121.5 (q, $J_{C\text{-}F}$ = 267 Hz), 120.7, 86.3; ^{19}F NMR (377 MHz, DMSO-d_6) δ -62.2 (s, 3F); IR (film): 3169, 2802, 1585, 1559, 1505, 1473, 1429, 1401, 1330, 1256, 1139, 1105, 1044; HRMS Calculated For $C_{10}H_7ClF_3N_2O$ $[M+H]^+$ 263.0199, found: 263.0194.



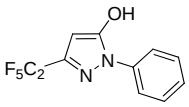
1-(3,4-Dichlorophenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (1g): Pale yellow solid; mp = 213-214 °C, yield 57%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.90 (br, 1H), 7.98 (d, J = 2.2 Hz, 1H), 7.79-7.75 (m, 1H), 7.74–7.68 (m, 1H), 5.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.8, 141.7 (q, $J_{C\text{-}F}$ = 37 Hz), 137.9, 132.0, 131.5, 129.7, 123.4, 121.9, 121.9 (q, $J_{C\text{-}F}$ = 267 Hz), 86.3; ^{19}F NMR (377 MHz, DMSO-d_6) δ -62.3 (s, 3F); IR (film): 3159, 3090, 2914, 1594, 1573, 1557, 1502, 1472, 1385, 1261, 1247, 1202, 1160; HRMS Calculated For $C_{10}H_6Cl_2F_3N_2O$ $[M+H]^+$ 296.9809, found: 296.9804.



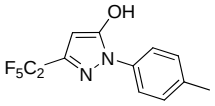
1-(4-Fluorophenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (1h) Pale yellow solid; mp = 216-217 °C, yield 60%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.54 (br, 1H), 7.77–7.70 (m, 2H), 7.35–7.29 (m, 2H), 5.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.2 (d, $J_{C\text{-}F}$ = 245 Hz), 154.1, 140.9 (q, $J_{C\text{-}F}$ = 37 Hz), 134.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 125.0 (d, $J_{C\text{-}F}$ = 8.7 Hz), 122.8 (q, $J_{C\text{-}F}$ = 267 Hz), 116.4 (d, $J_{C\text{-}F}$ = 22.9 Hz), 86.0; ^{19}F NMR (377 MHz, DMSO-d_6) δ -62.0 (s, 3F), -114.8 (s, 1F); IR (film): 3084, 1610, 1571, 1499, 1405, 1331, 1217, 1191, 1135, 1096; HRMS Calculated For $C_{10}H_7F_4N_2O$ $[M+H]^+$ 247.0495, found: 247.0489.



3-(Perfluoroethyl)-1-phenyl-1*H*-pyrazol-5-ol (1i): Pale yellow solid; mp = 190-191 °C, yield 69%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.51 (br, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 5.97 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.4, 139.6 (t, $J_{C\text{-}F}$ = 28 Hz), 138.2, 129.5, 127.6, 122.6, 118.7 (qt, $J_{C\text{-}F}$ = 284 Hz, 39 Hz,), 111.2 (tq, $J_{C\text{-}F}$ = 248 Hz, 38 Hz,), 87.1; ^{19}F NMR (377 MHz, DMSO-d_6) δ -83.8 (s, 3F), -112.7 (s, 2F); IR (film): 2917, 1598, 1569, 1409, 1334, 1185, 1125, 1103; HRMS Calculated For $C_{11}H_8F_5N_2O$ $[M+H]^+$ 279.0557, found: 279.0551.



3-(Perfluoroethyl)-1-(*p*-tolyl)-1*H*-pyrazol-5-ol (1j): Pale yellow solid; mp = 209-210 °C, yield 60%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.41 (br, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.93 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.2, 139.2 (t, $J_{C\text{-}F}$ = 28 Hz), 137.2, 135.8, 129.9, 122.6, 119.4 (qt, $J_{C\text{-}F}$ = 286 Hz, 38 Hz,), 111.2 (tq, $J_{C\text{-}F}$ = 249 Hz, 38 Hz,), 87.0, 20.9; ^{19}F NMR (377 MHz, DMSO-d_6) δ -83.6 (s, 3F), -112.4 (s, 2F); IR (film): 3115, 2955, 1591, 1565, 1523, 1486, 1408,



1336, 1227, 1192, 1138, 1112, 1044; HRMS Calculated For $C_{12}H_{10}F_5N_2O$ $[M+H]^+$ 293.0713, found: 293.0708.

4-Methyl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3a): Pale yellow solid; mp = 148-149 °C, yield 58%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.51 (br, 1H), 7.69 (d, J = 7.3 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.2, 139.4 (q, $J_{C\text{-}F}$ = 36 Hz), 138.4, 129.6, 127.6, 122.9, 122.5 (q, $J_{C\text{-}F}$ = 268 Hz), 96.1, 6.7; ^{19}F NMR (377 MHz, DMSO-d_6) δ -61.4 (s, 3F); IR (film): 2924, 1597, 1579, 1543, 1487, 1455, 1394, 1263, 1151; HRMS Calculated For $C_{11}H_{10}F_3N_2O$ $[M+H]^+$ 243.0745, found: 243.0740.

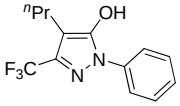
4-Methyl-1-*p*-tolyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3b): Pale yellow solid; mp = 170-171 °C, yield 68%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (br, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 2.35 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.0, 139.0 (q, $J_{C\text{-}F}$ = 36 Hz), 137.1, 136.0, 129.9, 122.9, 122.5 (q, $J_{C\text{-}F}$ = 267 Hz), 96.0, 21.0, 6.7; ^{19}F NMR (377 MHz, DMSO-d_6) δ -61.3 (s, 3F); IR (film): 2922, 1595, 1396, 1280, 1164, 1120, 1052; HRMS Calculated For $C_{12}H_{12}F_3N_2O$ $[M+H]^+$ 257.0902, found: 257.0896.

4-Ethyl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3c): Pale yellow solid; mp = 140-141 °C, yield 48%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.46 (br, 1H), 7.71–7.68 (m, 2H), 7.53–7.49 (m, 2H), 7.40–7.36 (m, 1H), 2.50–2.48 (m, 2H), 1.10 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.8, 138.7 (q, $J_{C\text{-}F}$ = 35 Hz), 138.3, 129.5, 127.7, 123.0, 122.6 (q, $J_{C\text{-}F}$ = 268 Hz), 103.1, 15.7, 15.0; ^{19}F NMR (377 MHz, DMSO-d_6) δ -60.9 (s, 3F); IR (film): 2978, 2872, 1594, 1565, 1477, 1393, 1312, 1266, 1152, 1073; HRMS Calculated For $C_{12}H_{12}F_3N_2O$ $[M+H]^+$ 257.0902, found: 257.0896.

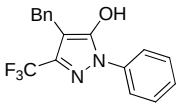
4-Ethyl-1-*p*-tolyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3d): Pale yellow solid; mp = 153-154 °C, yield 68%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (br, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 2.55-2.49 (m, 2H), 2.34 (s, 3H), 1.12 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.7, 138.6 (q, $J_{C\text{-}F}$ = 35 Hz), 137.0, 136.1, 129.8, 122.8, 122.6 (q, $J_{C\text{-}F}$ = 267 Hz), 103.1, 20.9, 15.6, 15.0; ^{19}F NMR (377 MHz, DMSO-d_6) δ -61.0 (s, 3F); IR (film): 2978, 2937, 1593, 1527, 1521, 14901, 1396, 1314, 1287, 1159, 1075; HRMS Calculated For $C_{13}H_{14}F_3N_2O$ $[M+H]^+$ 271.1058, found: 271.1053.

4-Ethyl-1-*m*-tolyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3e): Pale yellow solid; mp = 118-119 °C, yield 63%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (br, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 7.0 Hz, 1H), 2.53 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.8, 139.1, 138.6 (t, $J_{C\text{-}F}$ = 28 Hz), 138.3, 129.3, 128.3, 123.5, 122.3 (q, $J_{C\text{-}F}$ = 268 Hz), 120.1, 103.1, 21.4, 15.7, 15.0; ^{19}F NMR (377 MHz, DMSO-d_6) δ -61.0 (s, 3F); IR (film): 2966, 2917, 1573, 1483, 1390, 1286, 1162, 1112, 1076; HRMS Calculated For $C_{13}H_{14}F_3N_2O$ $[M+H]^+$ 271.1058, found: 271.1053.

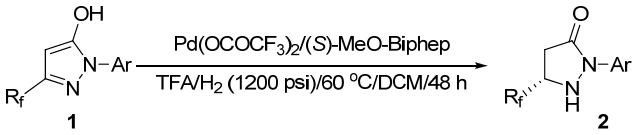
1-Phenyl-4-propyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3f): Pale yellow solid; mp = 123-124 °C, yield 48%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.42 (br, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 2.44 (t, J = 7.6 Hz, 2H), 1.53–1.49 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.1, 139.0 (q, $J_{C\text{-}F}$ = 35 Hz), 138.4, 129.5, 127.6, 122.9, 122.6 (q, $J_{C\text{-}F}$ = 267 Hz), 101.5, 23.8, 23.6, 14.1; ^{19}F NMR (377 MHz, DMSO-d_6) δ -60.7 (s, 3F); IR (film): 3243, 2856, 2414, 1593, 1570, 1481, 1456, 1400, 1270, 1137, 1084; HRMS Calculated For $C_{13}H_{14}F_3N_2O$ $[M+H]^+$ 271.1058, found: 271.1053.



4-Benzyl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3g): Pale yellow solid; mp = 147-148 °C, yield 23%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.78 (br, 1H), 7.76–7.72 (m, 2H), 7.55–7.51 (m, 2H), 7.42–7.38 (m, 1H), 7.31–7.27 (m, 2H), 7.20–7.16 (m, 3H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.7, 140.6, 139.0 (q, $J_{C\text{-}F}$ = 36 Hz), 138.3, 129.6, 128.7, 128.2, 127.8, 126.4, 123.0, 122.4 (q, $J_{C\text{-}F}$ = 268 Hz), 99.9, 27.1; ^{19}F NMR (377 MHz, DMSO-d_6) δ -60.7 (s, 3F); IR (film): 2917, 1595, 1577, 1536, 1457, 1390, 1275, 1132, 1028; HRMS Calculated For $C_{17}H_{14}F_3N_2O$ $[M+H]^+$ 319.1058, found: 319.1053.

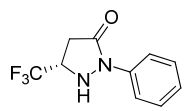


3. General Procedure for Hydrogenation of Disubstituted Fluorinated Pyrazol-5-ols 1a-1h



General procedure: (*S*)-MeO-Biphep (3.8 mg, 0.0066 mmol) and $Pd(OCOCF_3)_2$ (2.0 mg, 0.006 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h, and then solvent was removed under vacuum to give the catalyst. In a glovebox, pyrazol-5-ol **1** (0.30 mmol) and the above catalyst together with dichloromethane (2 mL) were stirred at room temperature for 1 min. Subsequently, trifluoroacetic acid (TFA, 34.2 mg, 22.3 μL, 0.3 mmol) was added to the reaction mixture. The hydrogenation was performed at 60 °C under H_2 (1200 psi) in a stainless steel autoclave for 48 h. After carefully releasing the hydrogen, the resulting mixture was concentrated under vacuum and dissolved in saturated aqueous sodium bicarbonate (5 mL). After stirring for 10 min, the mixture was extracted with dichloromethane and dried over sodium sulfate. After purification by silica gel chromatography using petroleum ether/dichloromethane (1:1) as eluent, the enantiomeric excess of the products were determined by HPLC with chiral column.

(*S*)-2-Phenyl-5-(trifluoromethyl)pyrazolidin-3-one (2a): Pale yellow solid; mp = 104-105 °C, yield 94%, 96% ee, $[\alpha]^{20}_D$ = +20.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 5.15 (d, J = 7.3 Hz, 1H), 4.13–4.02 (m, 1H), 3.18 (dd, J = 17.5, 9.7 Hz, 1H), 2.84 (dd, J = 17.6, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 137.8, 128.9, 125.4 (q, $J_{C\text{-}F}$ = 278 Hz), 125.2, 118.9, 53.9 (q, $J_{C\text{-}F}$ = 32 Hz), 33.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.4 (s, 3F); IR (film): 3257, 2919, 1597, 1494, 1464, 1316, 1188; HRMS Calculated For $C_{10}H_{10}F_3N_2O$ $[M+H]^+$ 231.0745, found: 231.0740; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.2 min (maj), t_2 = 7.5 min.



(+)-2-*o*-Tolyl-5-(trifluoromethyl)pyrazolidin-3-one (2b): Pale yellow solid; mp = 104-105 °C, yield 67%, 82% ee, $[\alpha]^{20}_D$ = +18.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 4H), 5.17 (d, *J* = 7.4 Hz, 1H), 4.15 (d, *J* = 7.1 Hz, 1H), 3.23–3.16 (m, 1H), 2.89–2.83 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 135.4, 135.3, 131.3, 128.7, 126.8, 126.4, 125.8 (q, $J_{C\text{-}F}$ = 277 Hz), 54.4 (q, $J_{C\text{-}F}$ = 32 Hz), 32.3, 18.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.0 (s, 3F); IR (film): 2940, 1698, 1534, 1471, 1350, 1234, 1165; HRMS Calculated For $C_{11}H_{12}F_3N_2O$ $[M+H]^+$ 245.0902, found: 245.0896; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 8.0 min (maj), t_2 = 8.8 min.

(+)-2-*m*-Tolyl-5-(trifluoromethyl)pyrazolidin-3-one (2c): Pale yellow solid; mp = 89-90 °C, yield 93%, 95% ee, $[\alpha]^{20}_D$ = +14.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.50 (m, 2H), 7.26–7.20 (m, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 5.14 (br, 1H), 4.11–4.01 (m, 1H), 3.15 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.82 (dd, *J* = 17.5, 3.1 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 138.9, 137.7, 128.7, 126.1, 125.5 (q, $J_{C\text{-}F}$ = 278 Hz), 119.5, 116.2, 53.8 (q, $J_{C\text{-}F}$ = 33 Hz), 33.8, 21.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.4 (s, 3F); IR (film): 2920, 1707, 1604, 1491, 1353, 1278, 1170, 1126; HRMS Calculated For $C_{11}H_{12}F_3N_2O$ $[M+H]^+$ 245.0902, found: 245.0896; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.3 min (maj), t_2 = 8.4 min.

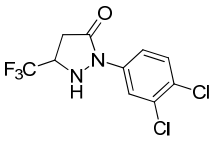
(+)-2-*p*-Tolyl-5-(trifluoromethyl)pyrazolidin-3-one (2d): Pale yellow solid; mp = 140-141 °C, yield 93%, 96% ee, $[\alpha]^{20}_D$ = +15.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.18 (d, *J* = 6.6 Hz, 1H), 4.04 (d, *J* = 6.7 Hz, 1H), 3.13 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.79 (dd, *J* = 17.5, 3.1 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 135.3, 135.1, 129.4, 124.6 (q, $J_{C\text{-}F}$ = 278 Hz), 119.1, 53.9 (q, $J_{C\text{-}F}$ = 33 Hz), 33.7, 20.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.5 (s, 3F); IR (film): 3156, 2937, 1707, 1510, 1138, 1170, 1123, 1041; HRMS Calculated For $C_{11}H_{12}F_3N_2O$ $[M+H]^+$ 245.0902, found: 245.0896; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.7 min (maj), t_2 = 8.4 min.

(+)-2-(4-Methoxyphenyl)-5-(trifluoromethyl)pyrazolidin-3-one (2e): Pale yellow solid; mp = 122-123 °C, yield 94%, 95% ee, $[\alpha]^{20}_D$ = +15.6 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 9.1 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), 5.11 (d, *J* = 7.6 Hz, 1H), 4.13–4.07 (m, 1H), 3.80 (s, 3H), 3.19 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.85 (dd, *J* = 17.5, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 157.2, 131.0, 123.9 (q, $J_{C\text{-}F}$ = 278 Hz), 121.1, 114.1, 55.5, 53.9 (q, $J_{C\text{-}F}$ = 33 Hz), 33.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.4 (s, 3F); IR (film): 2931, 1796, 1551, 1449, 1256, 1211; HRMS Calculated For $C_{11}H_{12}F_3N_2O_2$ $[M+H]^+$ 261.0851, found: 261.0845; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 7.7 min (maj), t_2 = 8.8 min.

(+)-2-(3-Chlorophenyl)-5-(trifluoromethyl)pyrazolidin-3-one (2f): Pale yellow solid; mp = 115-116 °C, yield 89%, 95% ee, $[\alpha]^{20}_D$ = +16.6 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.31-7.26 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 5.16 (d, *J* = 7.4 Hz, 1H), 4.16–4.10 (m, 1H), 3.22 (dd, *J* = 17.5, 9.7 Hz, 1H), 2.87 (dd, *J* = 17.5, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 138.9, 134.7, 129.9, 125.1, 124.5 (q, $J_{C\text{-}F}$ = 278 Hz), 118.7, 116.6, 54.0 (q, $J_{C\text{-}F}$ = 33 Hz), 33.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.4 (s, 3F); IR (film): 3227, 2925, 1726, 1592, 1547, 1482, 1254, 1171, 1125;

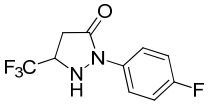
HRMS Calculated For $C_{10}H_9ClF_3N_2O$ $[M+H]^+$ 265.0356, found: 265.0350; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.0 min (maj), t_2 = 7.1 min.

(+)-2-(3,4-Dichlorophenyl)-5-(trifluoromethyl)pyrazolidin-3-one (2g): Pale yellow solid; mp = 122-123 °C, yield 90%, 93% ee, $[\alpha]^{20}_D$ = +5.8 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ



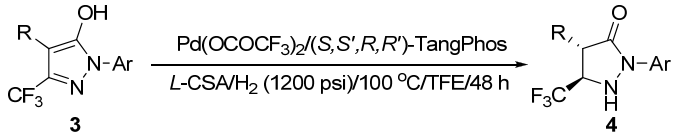
7.93 (d, *J* = 2.5 Hz, 1H), 7.70–7.67 (m, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 5.20 (d, *J* = 7.3 Hz, 1H), 4.17–4.10 (m, 1H), 3.21 (dd, *J* = 17.7, 9.6 Hz, 1H), 2.85 (dd, *J* = 17.7, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 137.2, 132.8, 130.5, 128.3, 124.3 (q, $J_{C\text{-}F}$ = 278 Hz), 120.1, 117.7, 54.0 (q, $J_{C\text{-}F}$ = 33 Hz), 33.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.4 (s, 3F); IR (film): 3235, 2960, 1715, 1556, 1503, 1355, 1259, 1170, 1106; HRMS Calculated For $C_{10}H_8Cl_2F_3N_2O$ $[M+H]^+$ 298.9966, found: 298.9960; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 85/15, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 9.1 min (maj), t_2 = 10.1 min.

(+)-2-(4-Fluorophenyl)-5-(trifluoromethyl)pyrazolidin-3-one (2h): Pale yellow solid; mp = 111-112 °C, yield 93%, 94% ee, $[\alpha]^{20}_D$ = +21.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ



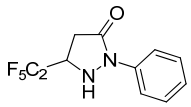
7.77–7.73 (m, 2H), 7.07–7.02 (m, 2H), 5.16 (d, *J* = 7.4 Hz, 1H), 4.15–4.08 (m, 1H), 3.21 (dd, *J* = 17.6, 9.7 Hz, 1H), 2.85 (dd, *J* = 17.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 159.9 (d, $J_{C\text{-}F}$ = 245 Hz), 133.9, 123.6 (q, $J_{C\text{-}F}$ = 275 Hz), 120.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.6 (d, $J_{C\text{-}F}$ = 23 Hz), 53.9 (q, $J_{C\text{-}F}$ = 32 Hz), 33.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.5 (s, 3F), 116.6 (s, 1F); IR (film): 2926, 1721, 1549, 1509, 1353, 1254, 1125, 1006; HRMS Calculated For $C_{10}H_9F_4N_2O$ $[M+H]^+$ 249.0651, found: 249.0646; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.9 min (maj), t_2 = 7.4 min.

4. General Procedure for Hydrogenation of Disubstituted Fluorinated Pyrazol-5-ols 1i, 1j and Trisubstituted Fluorinated Pyrazol-5-ols 3

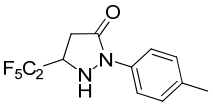


General procedure: (*S,S',R,R'*)-TangPhos (3.0 mg, 0.00104 mmol) and $Pd(OCOCF_3)_2$ (2.7 mg, 0.008 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h, and then solvent was removed under vacuum to give the catalyst. In a glovebox, pyrazol-5-ol **3** (0.2 mmol) and the above catalyst together with trifluoroethanol (TFE, 2 mL) were stirred in 1 mL solvent at room temperature for 1 min. Subsequently, *L*-CSA (46.4 mg, 0.2 mmol) was added to the reaction mixture. The hydrogenation was performed at 100 °C under H_2 (1200 psi) in a stainless steel autoclave for 48 h. After carefully releasing the hydrogen, the resulting mixture was concentrated under vacuum and dissolved in saturated aqueous sodium bicarbonate (5 mL). After stirring for 10 min, the mixture was extracted with dichloromethane and dried over sodium sulfate. After purification by silica gel chromatography using petroleum ether/ dichloromethane (1:1) as eluent, the enantiomeric excess of the products were determined by HPLC with chiral column.

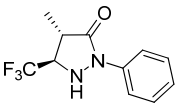
(-)-5-(Perfluoroethyl)-2-phenylpyrazolidin-3-one (2i): Pale yellow solid; mp = 120-121 °C, yield 95%, 94% ee, $[\alpha]^{20}_D$ = -8.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.08 (d, *J* = 7.9 Hz, 1H), 4.27–4.17 (m, 1H), 3.16 (dd, *J* = 17.5, 9.3 Hz, 1H), 2.96 (dd, *J* = 17.4, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 137.80, 128.9, 125.2, 118.7, 52.8 (dd, $J_{C\text{-}F}$ = 29.0, 21.8 Hz), 33.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.7 (s, 3F) -121.6 (d, *J* = 278 Hz), -131.1 (d, *J* = 278 Hz); IR (film): 3243, 2938, 2852, 1684, 1592, 1547, 1496, 1367, 1213, 1127; HRMS Calculated For $C_{11}H_{10}F_5N_2O$ $[M+H]^+$ 281.0713, found: 281.0708; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 5.6 min, t_2 = 7.0 min (maj).



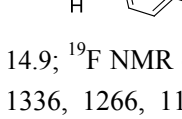
(-)-5-(Perfluoroethyl)-2-(*p*-tolyl)pyrazolidin-3-one (2j): Pale yellow solid; mp = 153-154 °C, yield 92%, 95% ee, $[\alpha]^{20}_D$ = -5.8 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 5.06 (d, *J* = 7.9 Hz, 1H), 4.26–4.13 (m, 1H), 3.14 (dd, *J* = 17.4, 9.4 Hz, 1H), 2.94 (dd, *J* = 17.4, 3.9 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 135.3, 135.0, 129.4, 118.8, 52.8 (dd, *J* = 29.0, 21.8 Hz), 33.2, 20.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.7 (s, 3F), -121.7 (d, *J* = 278 Hz, 1F), -131.0 (d, *J* = 278 Hz, 1F); IR (film): 3259, 2923, 2862, 1695, 1550, 1510, 1348, 1216, 1125; HRMS Calculated For $C_{12}H_{12}F_5N_2O$ $[M+H]^+$ 295.0870, found: 295.0864; HPLC (OG-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 14.8 min, t_2 = 17.1 min (maj).



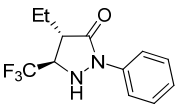
(-)-4-Methyl-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one (4a): Pale yellow solid; mp = 84-85 °C, yield 92%, 89% ee, $[\alpha]^{20}_D$ = -28.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.02 (d, *J* = 8.8 Hz, 1H), 3.77–3.67 (m, 1H), 3.00–2.90 (m, 1H), 1.46 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 137.9, 128.9, 125.1, 124.6 (q, $J_{C\text{-}F}$ = 277 Hz), 118.7, 61.6 (q, $J_{C\text{-}F}$ = 31 Hz), 39.9, 14.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.5 (s, 3F); IR (film): 2985, 2931, 1741, 1544, 1497, 1374, 1245, 1048; HRMS Calculated For $C_{11}H_{12}F_3N_2O$ $[M+H]^+$ 245.0902, found: 245.0896; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 5.5 min, t_2 = 6.2 min (maj).



(+)-4-Methyl-2-(p-tolyl)-5-(trifluoromethyl)pyrazolidin-3-one (4b): Pale yellow oil; yield 97%, 88% ee, $[\alpha]^{20}_D$ = +5.8 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.26–7.15 (m, 2H), 4.96 (d, *J* = 8.8 Hz, 1H), 3.75–3.68 (m, 1H), 3.00-2.92 (m, 1H), 2.33 (s, 3H), 1.45 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 135.4, 134.9, 129.4, 123.7 (q, $J_{C\text{-}F}$ = 278 Hz), 118.8, 61.6 (q, $J_{C\text{-}F}$ = 31 Hz), 39.8, 20.9, 14.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.5 (s, 3F); IR (film): 3243, 2999, 2925, 1677, 1574, 1504, 1336, 1266, 1160; HRMS Calculated For $C_{12}H_{14}F_3N_2O$ $[M+H]^+$ 259.1058, found: 259.1053; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.0 min, t_2 = 6.9 min (maj).

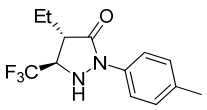


(+)-4-Ethyl-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one (4c): Pale yellow solid; mp = 58-59 °C, yield 93%, 94% ee, $[\alpha]^{20}_D$ = +0.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.18 (d, *J* = 7.5 Hz, 1H), 3.76–3.71 (m, 1H), 2.76–2.73 (m, 1H), 1.96–1.94 (m, 1H), 1.79–1.75 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 137.9, 128.8, 125.1,



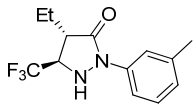
124.7 (q, $J_{C\text{-}F}$ = 278 Hz), 119.0, 58.5 (q, $J_{C\text{-}F}$ = 31 Hz), 46.3, 23.1, 11.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.7 (s, 3F); IR (film): 3241, 2972, 1687, 1593, 1494, 1359, 1281, 1172, 1145; HRMS Calculated For $C_{12}H_{14}F_3N_2O$ $[M+H]^+$ 259.1058, found: 259.1053; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 5.5 min, t_2 = 6.4 min (maj).

(+)-4-Ethyl-2-*p*-tolyl-5-(trifluoromethyl)pyrazolidin-3-one (4d): Pale yellow solid; mp = 90-91 °C, yield 92%, 93% ee, $[\alpha]^{20}_D$ = +2.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d,



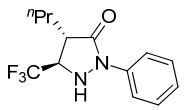
J = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.06 (d, *J* = 7.6 Hz, 1H), 3.76–3.72 (m, 1H), 2.79–2.76 (m, 1H), 2.32 (s, 3H), 2.01–1.90 (m, 1H), 1.84–1.78 (m, 1H), 1.10 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 135.4, 135.0, 129.4, 124.6 (q, $J_{C\text{-}F}$ = 278 Hz), 119.0, 58.5 (q, $J_{C\text{-}F}$ = 32 Hz), 46.2, 23.1, 20.9, 11.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.7 (s, 3F); IR (film): 3230, 2965, 2870, 1675, 1579, 1513, 1359, 1265, 1170, 1149; HRMS Calculated For $C_{13}H_{16}F_3N_2O$ $[M+H]^+$ 273.1215, found: 273.1209; HPLC (OG-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 18.6 min, t_2 = 21.8 min (maj).

(+)-4-Ethyl-2-*m*-tolyl-5-(trifluoromethyl)pyrazolidin-3-one (4e): Pale yellow oil; yield 90%, 92% ee, $[\alpha]^{20}_D$ = +0.4 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.56 (m, 2H),



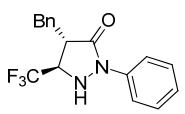
7.26-7.21 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.06 (br, 1H), 3.75 (s, 1H), 2.80-2.75 (m, 1H), 2.36 (s, 3H), 2.00–1.91 (m, 1H), 1.83–1.76 (m, 1H), 1.10 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 138.8, 137.8, 128.7, 126.0, 124.9 (q, $J_{C\text{-}F}$ = 278 Hz), 119.5, 116.1, 58.5 (q, $J_{C\text{-}F}$ = 31 Hz), 46.3, 23.1, 21.5, 11.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.7 (s, 3F); IR (film): 3255, 2969, 1713, 1548, 1490, 1360, 1283, 1184, 1148; HRMS Calculated For $C_{13}H_{16}F_3N_2O$ $[M+H]^+$ 273.1215, found: 273.1209; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 5.4 min, t_2 = 6.9 min (maj).

(+)-2-Phenyl-4-propyl-5-(trifluoromethyl)pyrazolidin-3-one (4f): Pale yellow solid; mp = 96-70 °C, yield 95%, 93% ee, $[\alpha]^{20}_D$ = +2.6 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d,



J = 8.3 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.08 (br, 1H), 3.77–3.73 (m, 1H), 2.86 (d, *J* = 3.1 Hz, 1H), 1.93–1.74 (m, 1H), 1.56–1.54 (m, 1H), 1.55–1.50 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 137.9, 128.8, 126.4 (q, $J_{C\text{-}F}$ = 278 Hz), 125.1, 118.9, 58.9 (q, $J_{C\text{-}F}$ = 32 Hz), 44.7, 31.9, 20.1, 13.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.8 (s, 3F); IR (film): 3237, 2972, 2870, 1714, 1551, 1504, 1354, 1279, 1177, 1157, 1014; HRMS Calculated For $C_{13}H_{16}F_3N_2O$ $[M+H]^+$ 273.1215, found: 273.1209; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 5.6 min, t_2 = 7.2 min (maj).

(4*S*,5*R*)-4-Benzyl-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one (4g): Pale yellow solid; mp = 117-118 °C, yield 94%, 95% ee, $[\alpha]^{20}_D$ = +122.6 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)



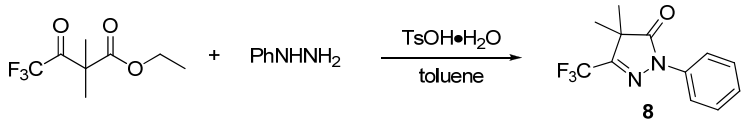
δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.37–7.25 (m, 7H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.19 (s, 1H), 3.76–3.73 (m, 1H), 3.37–3.31 (m, 1H), 3.23–3.19 (m, 1H), 3.13-3.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 137.6, 136.1, 129.1, 129.0, 128.8, 127.7, 125.3, 125.2 (q, $J_{C\text{-}F}$ = 279 Hz), 119.1, 57.7 (q, $J_{C\text{-}F}$ = 32 Hz), 45.7, 35.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.5 (s, 3F); IR (film): 3243, 3055, 2918, 1667, 1592, 1498, 1487, 1457, 1372, 1271, 1201, 1166, 1031; HRMS Calculated For $C_{17}H_{16}F_3N_2O$ $[M+H]^+$ 321.1215, found: 321.1209; HPLC (AD-H,

elute: Hexanes/*i*-PrOH = 70/30, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.5 min (maj), t_2 = 7.1 min.

5. Mechanistic Investigation

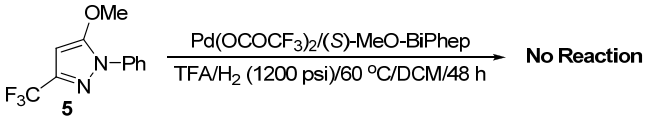
In order to further verify our hypothesis that the hydrogenation carried out *via* capture of the active tautomer, we synthesized three compounds (OH- form type **5**, NH- form type **6** and CH-form type **8**) and exposure them to hydrogenation reaction. 5-Methoxy-1-phenyl-3-(trifluoro-methyl)-1*H*-pyrazole **5** and 1-methyl-2-phenyl-5-(trifluoro-methyl)-1*H*-pyrazol-3(2*H*)- one **6** were prepared according to the literature methods and their NMR data matched the literature data.[2,3] The 4,4-dimethyl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5(4*H*)-one **8** was prepared following the literature report.[4]

Synthesis of 4,4-Dimethyl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5(4*H*)-one 8

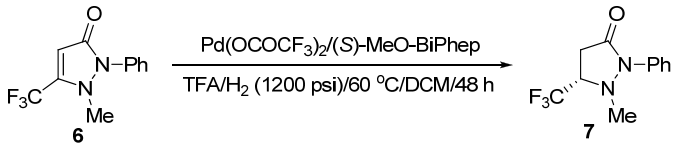


A solution of ethyl 4,4,4-trifluoro-2,2-dimethyl-3-oxobutanoate (0.849 g, 4.0 mmol) and phenylhydrazine (0.433 g, 4 mmol) in toluene (20 ml) was stirred and refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate to remove water with a Dean-Stark apparatus. After 16 h reflux, the reaction mixture was concentrated under vacuum. The residue dissolved in acetic acid (5 ml) was refluxed for 4 h. After evaporation of the solvent, the residue was extracted with diethyl ether. The extract was washed successively with 3% hydrochloric acid, saturated aqueous sodium hydrogen carbonate and brine, and dried over sodium sulfate. The residue was purified by silica gel column chromatography (petroleum ester/CH_2Cl_2 = 1/1) to afford a yellow oil: 0.261 g, 26% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.85 (m, 2H), 7.46–7.40 (m, 2H), 7.28–7.22 (m, 1H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 153.1 (q, $J_{C\text{-}F}$ = 37 Hz), 137.3, 129.1, 126.2, 119.5 (q, $J_{C\text{-}F}$ = 271 Hz), 119.1, 48.8, 21.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -65.1 (s, 3F); IR (film): 2964, 2892, 1650, 1408, 1319, 1251, 1216, 1049; HRMS Calculated For $C_{12}H_{12}F_3N_2O$ $[M+H]^+$ 257.0902, found: 257.0896.

General Procedure for Hydrogenation of Derivatives of Pyrazol-5-ols 5, 6 and 8: (*S*)-MeO-Biphep (6.1 mg, 0.0104 mmol) and $Pd(OCOCF_3)_2$ (2.7 mg, 0.008 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h, and then solvent was removed under vacuum to give the catalyst. In a glovebox, **5**, **6** or **8** (0.2 mmol) and the above catalyst together with dichloromethane (2 mL) were stirred at room temperature for 1 min. Subsequently, trifluoroacetic acid (22.8 mg, 14.8 μL, 0.2 mmol) was added to the reaction mixture. The hydrogenation was performed at 60 ^{o}C under H_2 (1200 psi) in a stainless steel autoclave for 48 h. After carefully releasing the hydrogen, the resulting mixture was concentrated under vacuum and dissolved in saturated aqueous sodium bicarbonate (5 mL). After stirring for 10 min, the mixture was extracted with dichloromethane and dried over sodium sulfate. After purification by silica gel chromatography using petroleum ether/dichloromethane (1:1) as eluent, the enantiomeric excess of the products were determined by HPLC with chiral column.

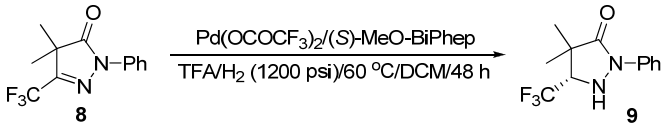


The exposure of the OH- form type substrate **5** with TFA in the presence of $Pd(OCOCF_3)_2$/(*S*)-MeO-BiPhep in dichloromethane failed to reaction.



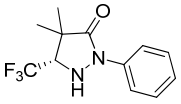
14% yield, 10% ee

The NH-form type substrate **6** only obtained 10% ee with 14% yield. **(+)-1-Methyl-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one (7):** Pale yellow oil; yield 14%, 10% ee, $[\alpha]^{20}_D$ = +2.0 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.68 (m, 2H), 7.41–7.35 (m, 2H), 7.21–7.16 (m, 1H), 3.68–3.60 (m, 1H), 3.40–3.33 (m, 1H), 2.77–2.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 136.2, 129.0, 125.6, 124.0 (q, $J_{C\text{-}F}$ = 278 Hz), 120.5, 61.5 (q, $J_{C\text{-}F}$ = 31 Hz), 45.1, 30.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.7 (s, 3F); IR (film): 3017, 2927, 2851, 1710, 1546, 1496, 1264, 1215, 1112; HRMS Calculated For $C_{11}H_{12}F_3N_2O$ $[M+H]^+$ 245.0902, found: 245.0896; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.8 mL/min), t_1 = 9.2 min (maj), t_2 = 10.1 min.

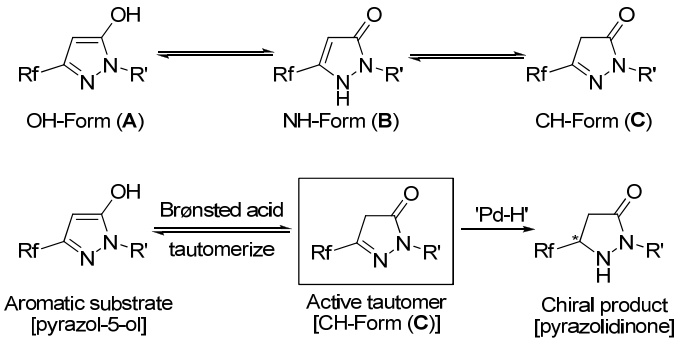


89% yield, 91% ee

When employing the CH-form type **8** as the hydrogenation substrate, 91% ee and 89% yield was obtained. **(+)-4,4-Dimethyl-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one (9):** Yield 89%, Pale yellow oil; 91% ee, $[\alpha]^{20}_D$ = +3.0 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.81 (m, 2H), 7.39–7.34 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.95 (d, *J* = 8.8 Hz, 1H), 3.78–3.69 (m, 1H), 1.42 (s, 3H), 1.36–1.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 138.2, 128.9, 125.4 (q, $J_{C\text{-}F}$ = 279 Hz), 124.9, 118.6, 64.6 (q, $J_{C\text{-}F}$ = 29 Hz), 44.2, 24.3, 18.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.0 (s, 3F); IR (film): 3021, 2987, 2834, 1680, 1533, 1459, 1390, 1120; HRMS Calculated For $C_{12}H_{14}F_3N_2O$ $[M+H]^+$ 259.1058, found: 259.1053; HPLC (OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.8 mL/min), t_1 = 11.2 min (maj), t_2 = 12.4 min.



Based on the experimental results and stereochemistry of the products, we proposed that the reaction experienced the process of Brønsted acid promoted tautomerization of the three tautomeric forms and then Pd-catalyzed asymmetric hydrogenation of the active tautomer **C** to give the optically active pyrazolidinones.



6. The X-ray Crystallographic Analysis of Substrate 3a and Products

The configuration of fluorinated 4-methyl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol **3a** was determined by X-ray diffraction analysis. The CCDC1040656 contains detail supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

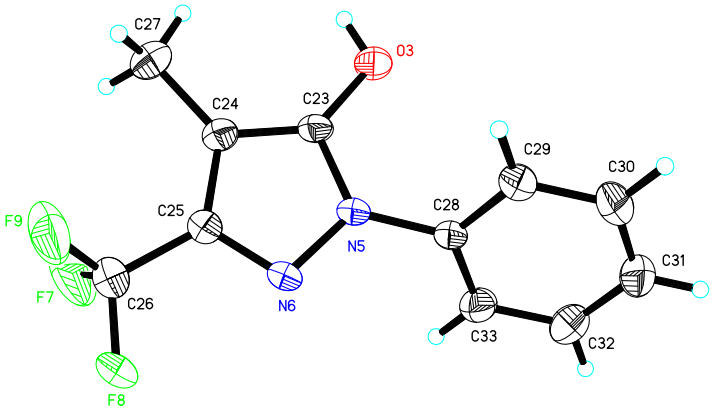


Figure 1. The X-ray structure of 4-methyl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol **3a**.

The absolute configuration of 2,5-disubstituted hydrogenation product **2a** was assigned as (*S*)-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one based on X-ray diffraction analysis after recrystallization from mixture solvent dichloromethane/*n*-hexane to upgrade ee to >99%. The configurations of the other chiral products are assigned by analogy. The CCDC1040657 contains detail supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

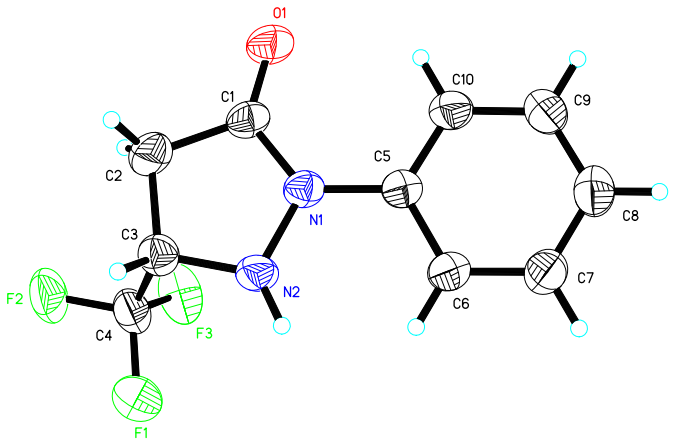


Figure 2. The X-ray structure of (*S*)-2-Phenyl-5-(trifluoromethyl)pyrazolidin-3-one **2a**.

The absolute configuration of 2,4,5-trisubstituted hydrogenation product **4g** was assigned as (4*S*,5*R*)-4-benzyl-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one based on X-ray diffraction analysis after recrystallization from mixture solvent dichloromethane/*n*-hexane to upgrade ee to >99%. The configurations of the other chiral products are assigned by analogy. The CCDC 1040658 contains detail supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

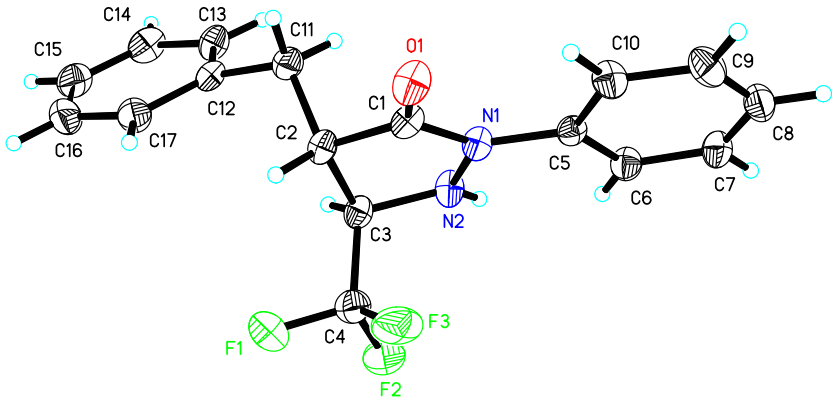


Figure 3. X-ray structure of (4*S*,5*R*)-4-benzyl-2-phenyl-5-(trifluoromethyl)pyrazolidin-3-one **4g**.

7. References

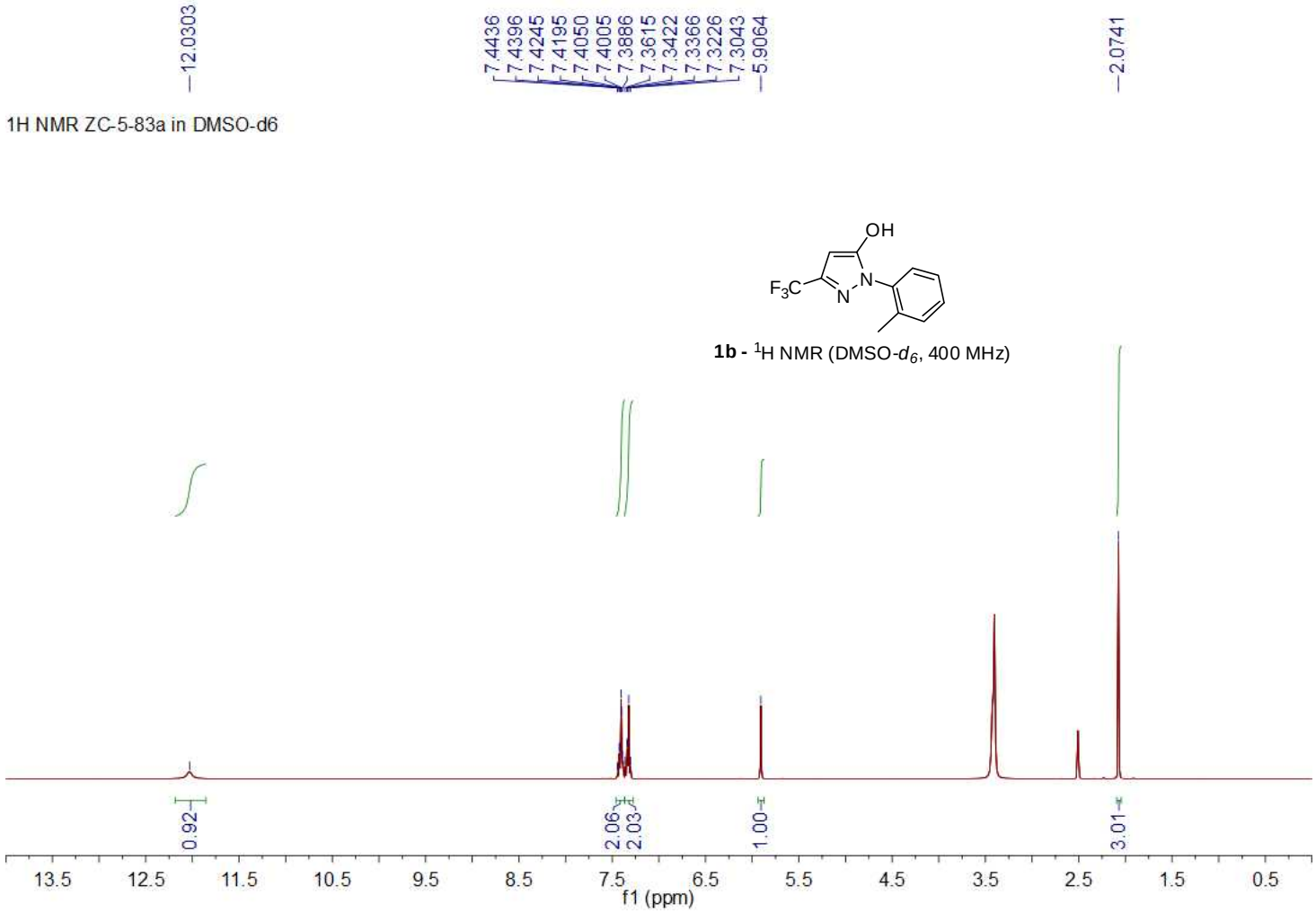
[1] J. Zhang, S. Yang, K. Zhang, J. Chen, H. Deng, M. Shao, H. Zhang, W. Cao, *Tetrahedron* **2012**, *9*, 2121.

[2] S. Bieringer, W. Holzer, *Heterocycles* **2006**, *68*, 1825.

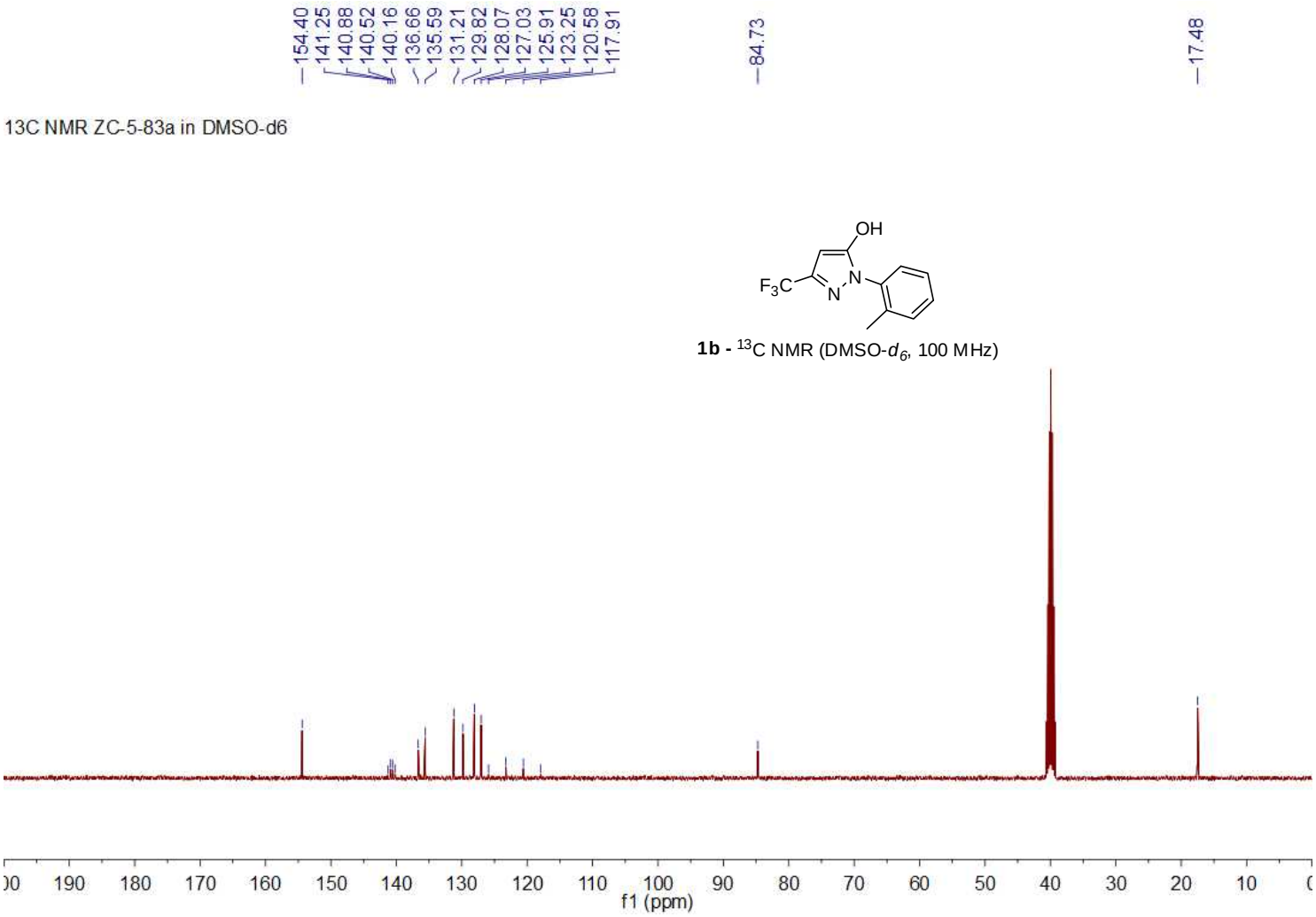
[3] G. Grillot , S. Aftergut, D. Botteron, *J. Org. Chem.* **1958**, *23*, 119.

[4] T. Tada, M. Motoki, N. Takahashi, T. Miyata, T. Takechi, T. Uchida, Y. Takagi, *Pesticide Science* **1996**, *2*, 165.

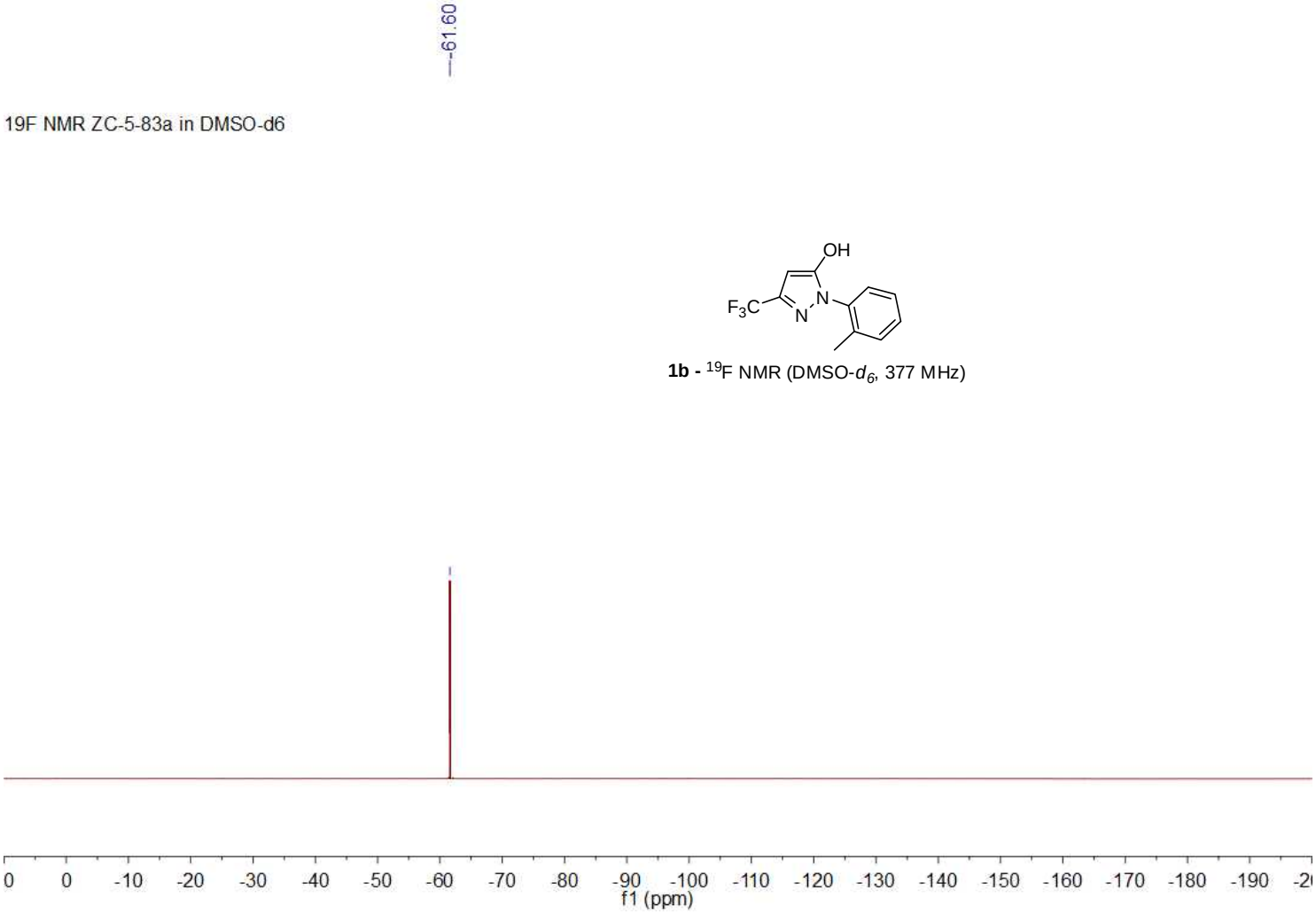
8. Copy of NMR of Substrates and Products



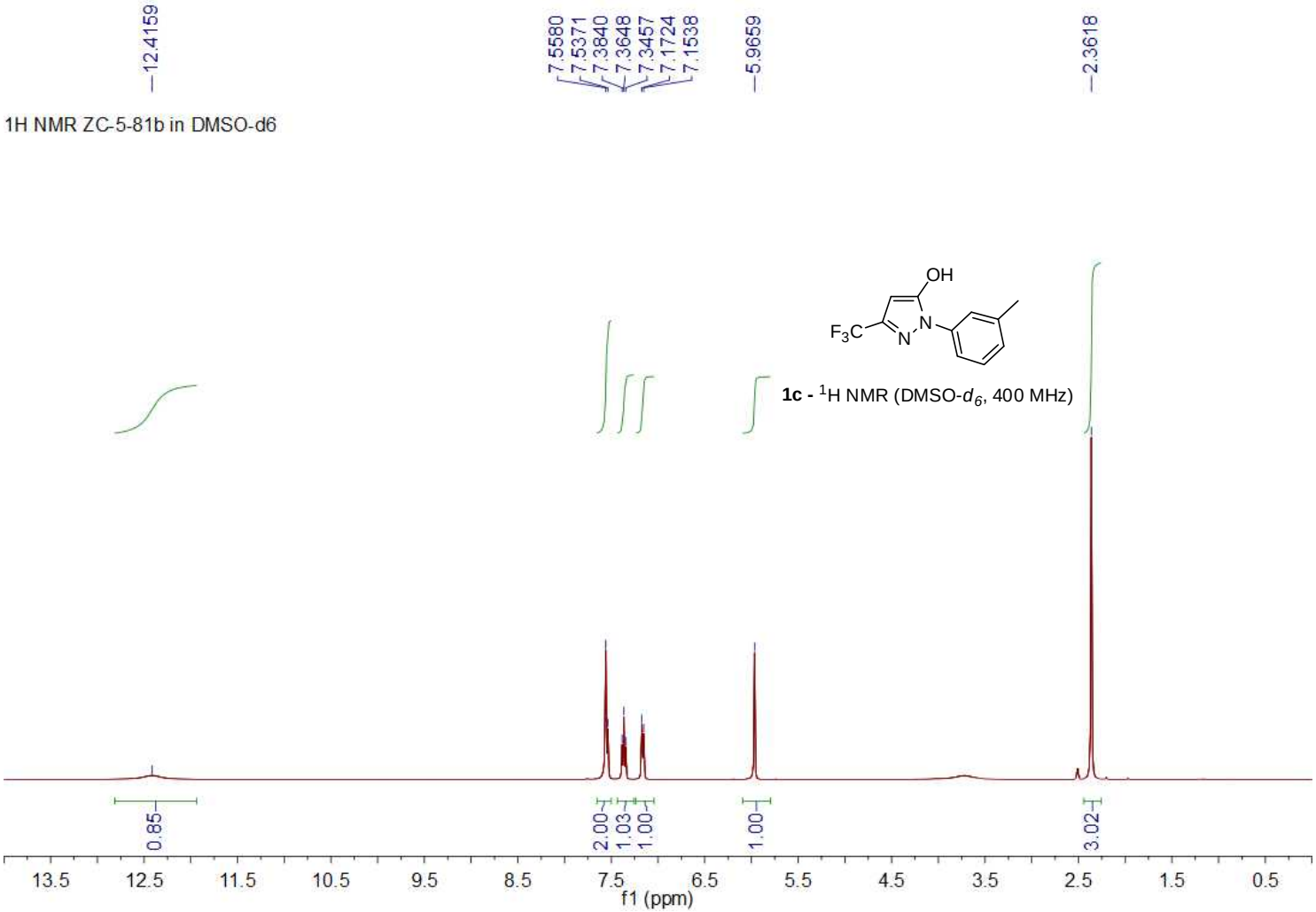
1b - ^{1}H NMR (DMSO-d_6, 400 MHz)



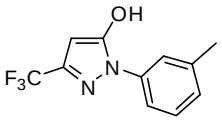
1b - ^{13}C NMR (DMSO-d_6, 100 MHz)



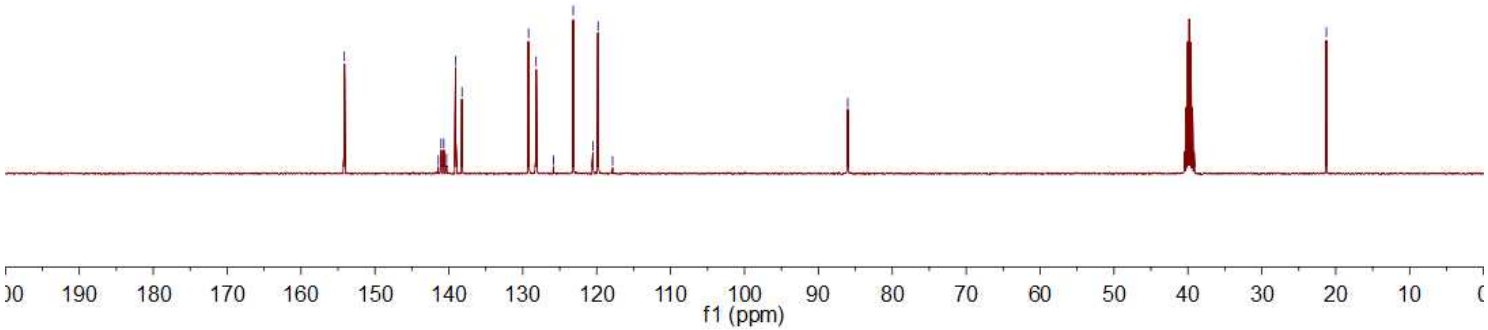
1b - ^{19}F NMR (DMSO-d_6, 377 MHz)

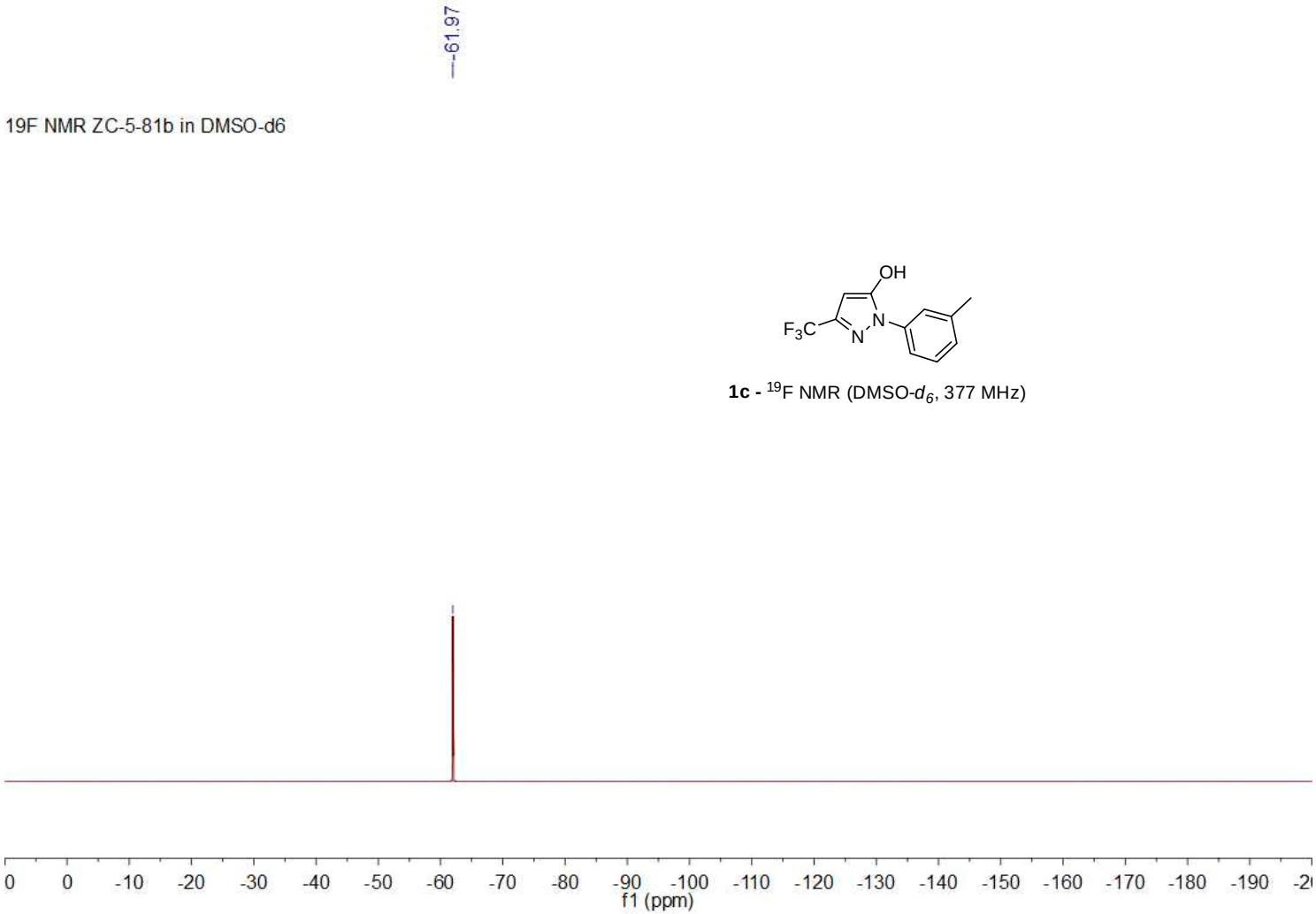

12.4159
7.5580
7.5371
7.3840
7.3648
7.3457
7.1724
7.1538
5.9659
2.3618
1H NMR ZC-5-81b in DMSO-d6
OH
F3C
N
N
1c - 1H NMR (DMSO-d6, 400 MHz)
0.85
2.00
1.03
1.00
1.00
3.02
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

13C NMR ZC-5-81b in DMSO-d6

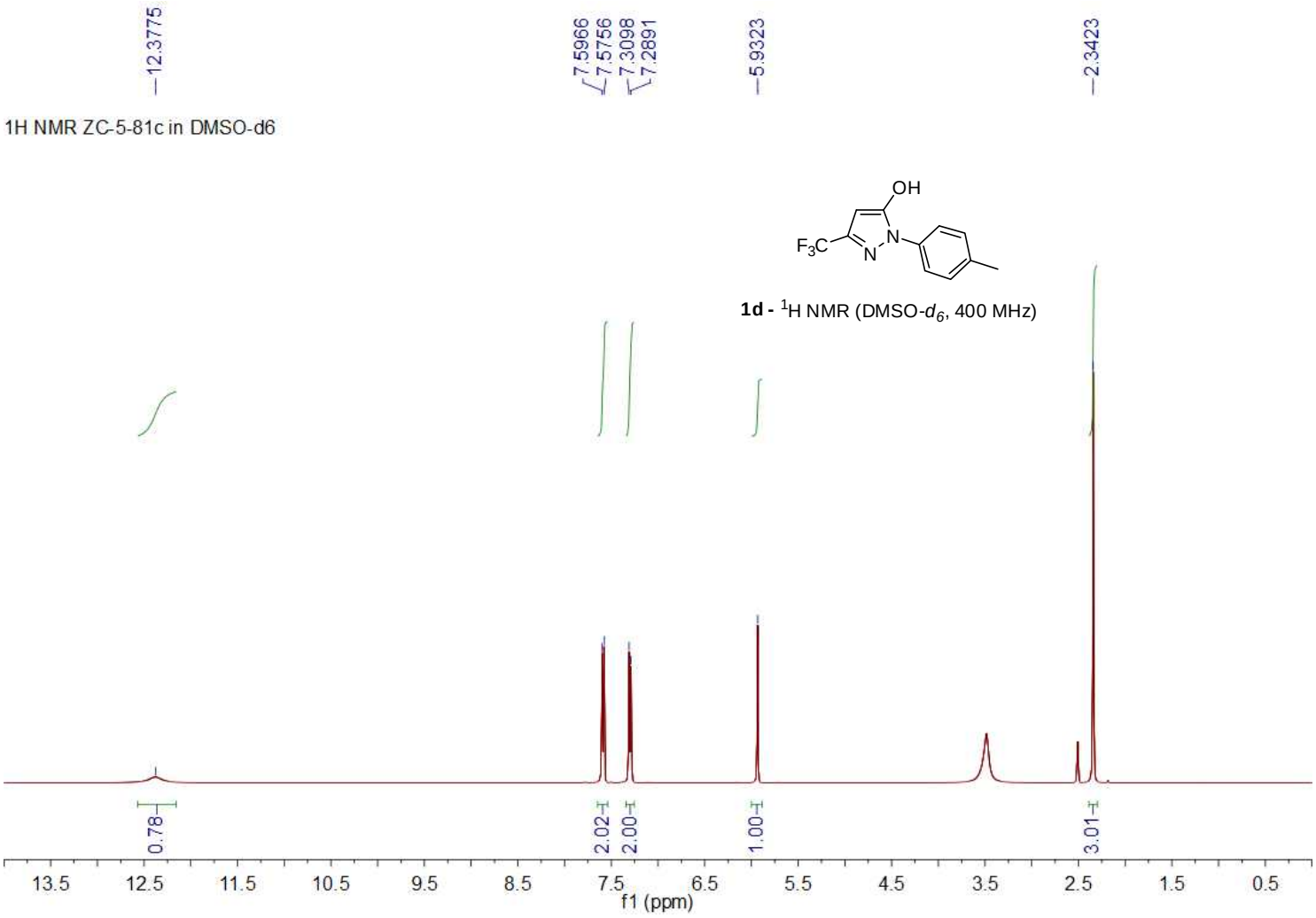


1c - ^{13}C NMR (DMSO-d_6, 100 MHz)

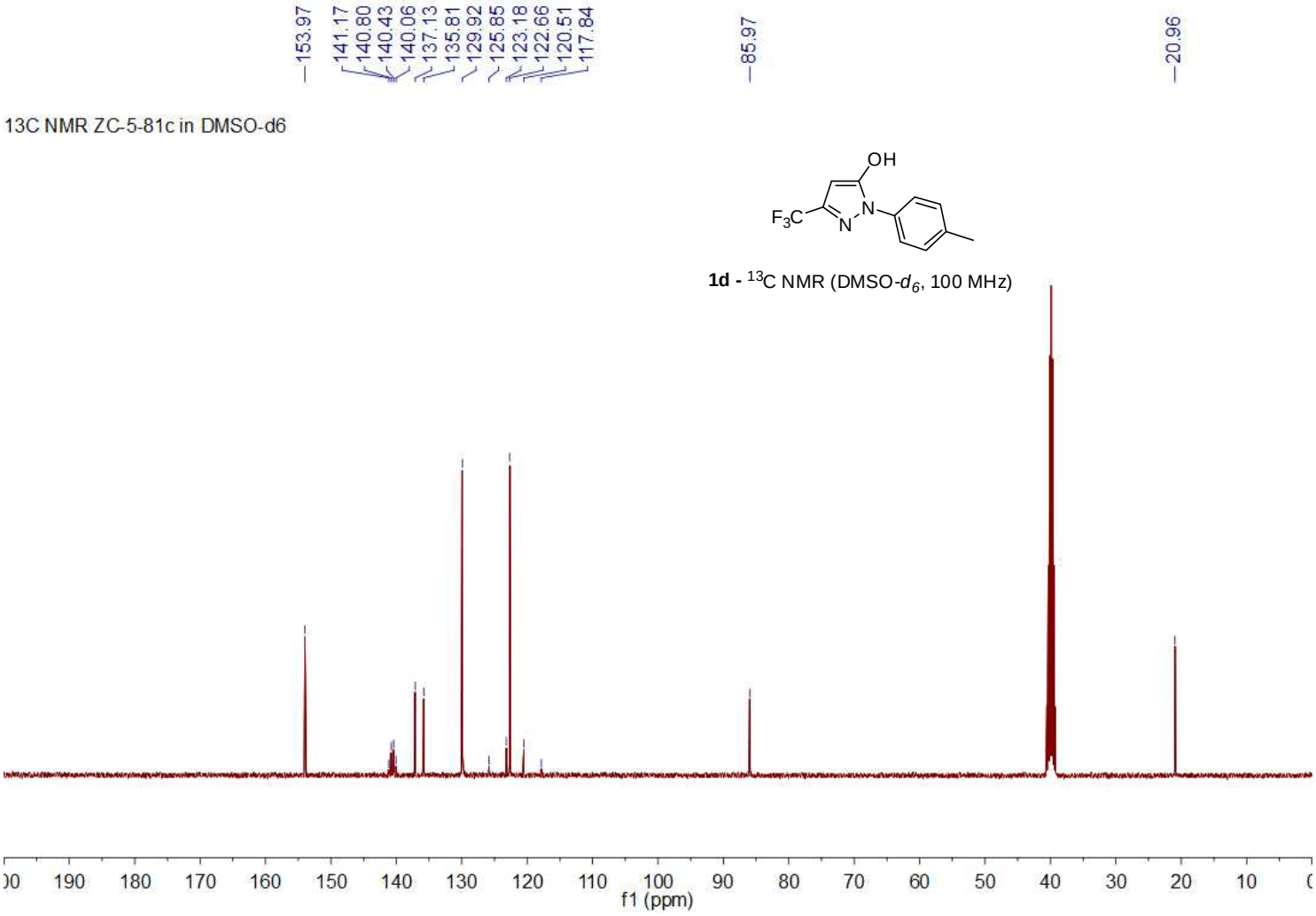




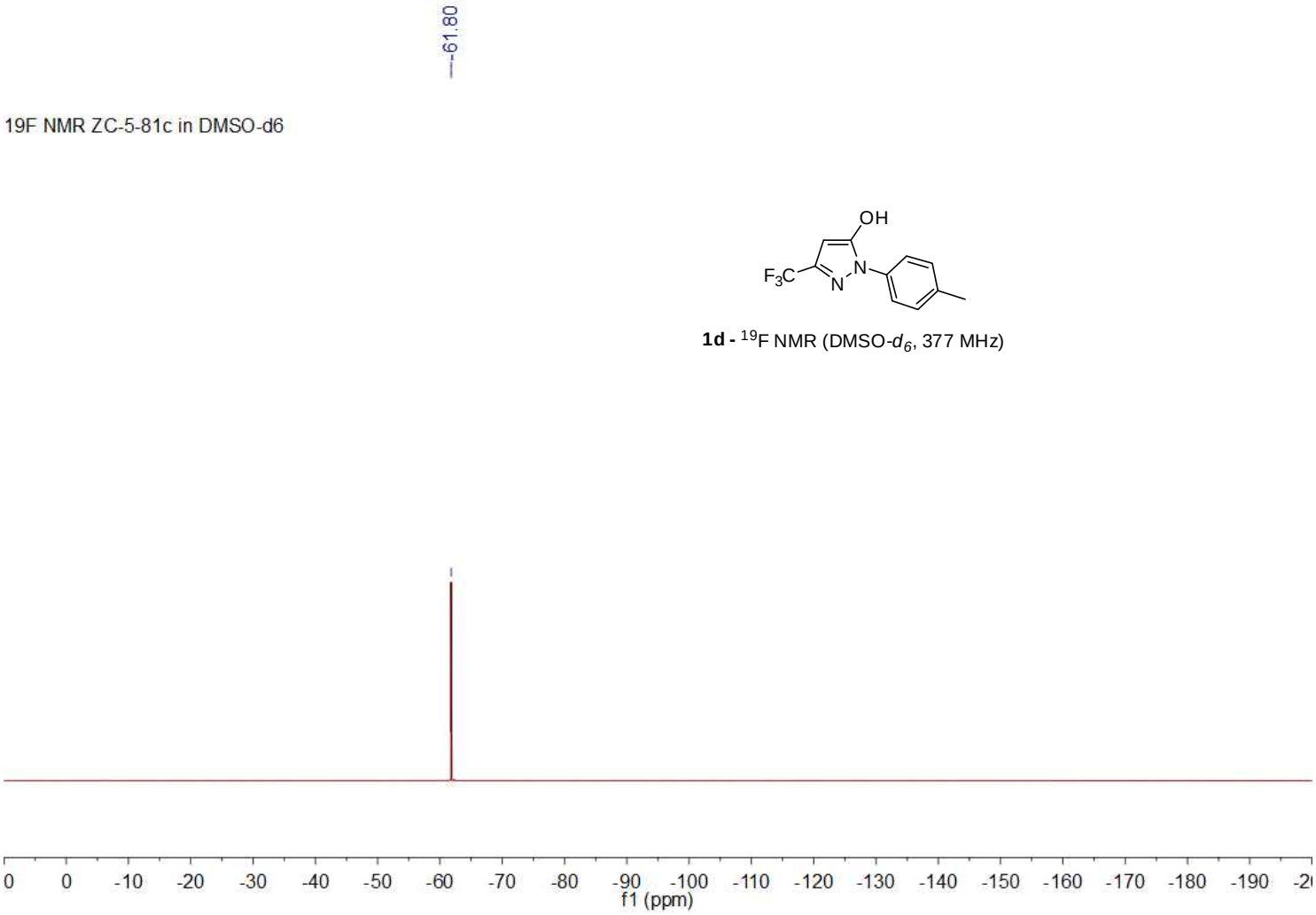
1c - ^{19}F NMR (DMSO-d_6, 377 MHz)



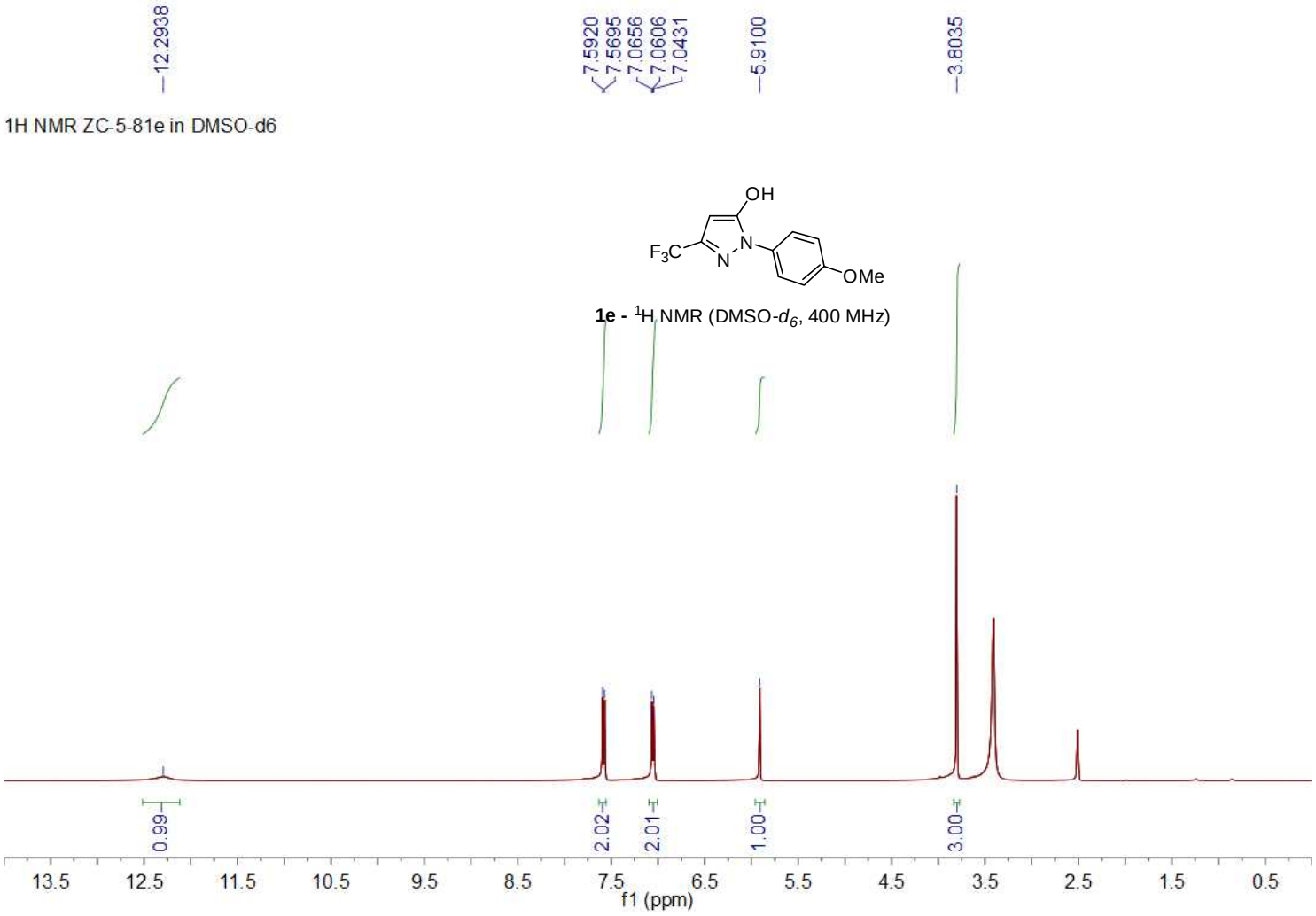
1d - ^{1}H NMR (DMSO-d_6, 400 MHz)



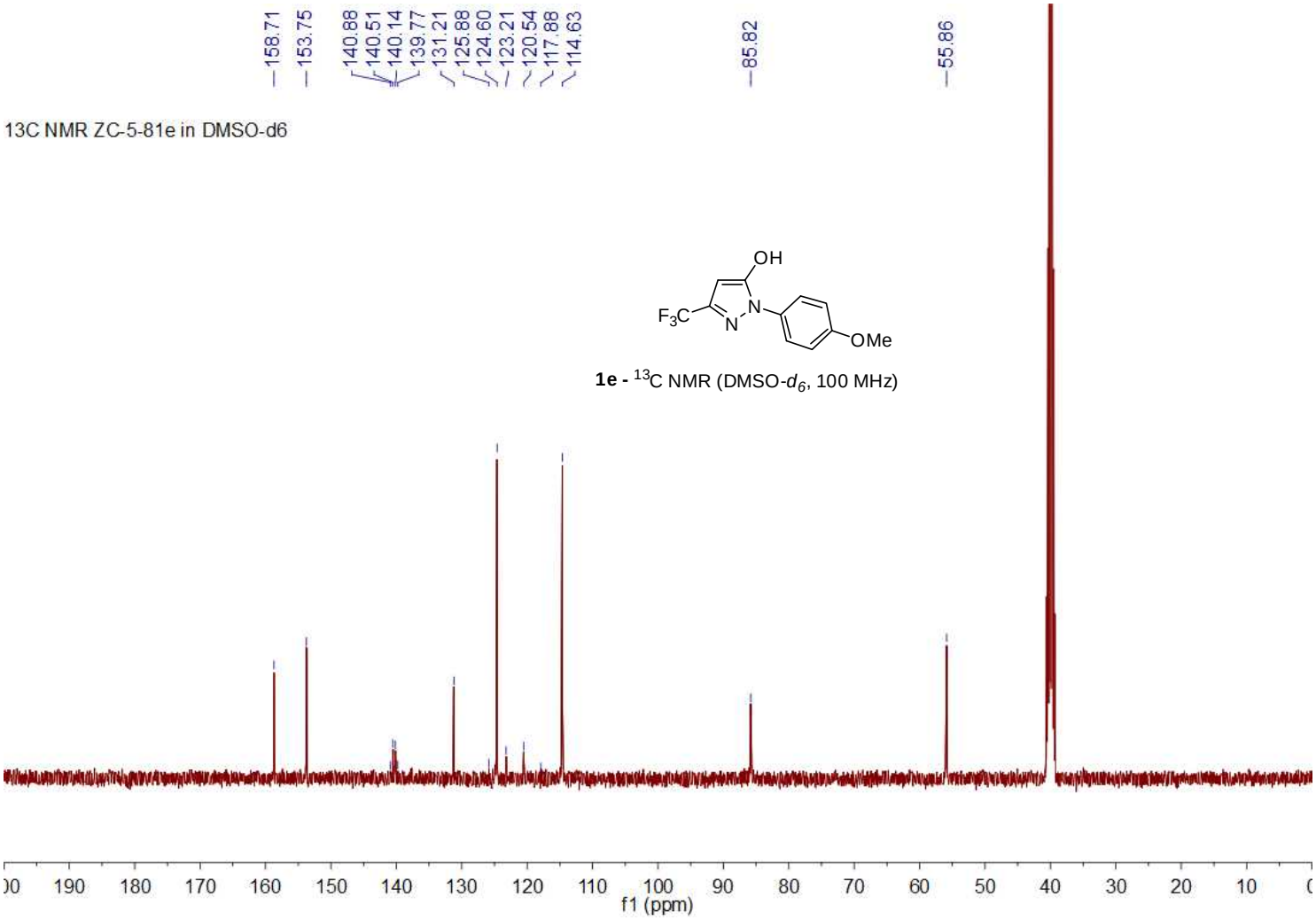
1d - ^{13}C NMR (DMSO-d_6, 100 MHz)



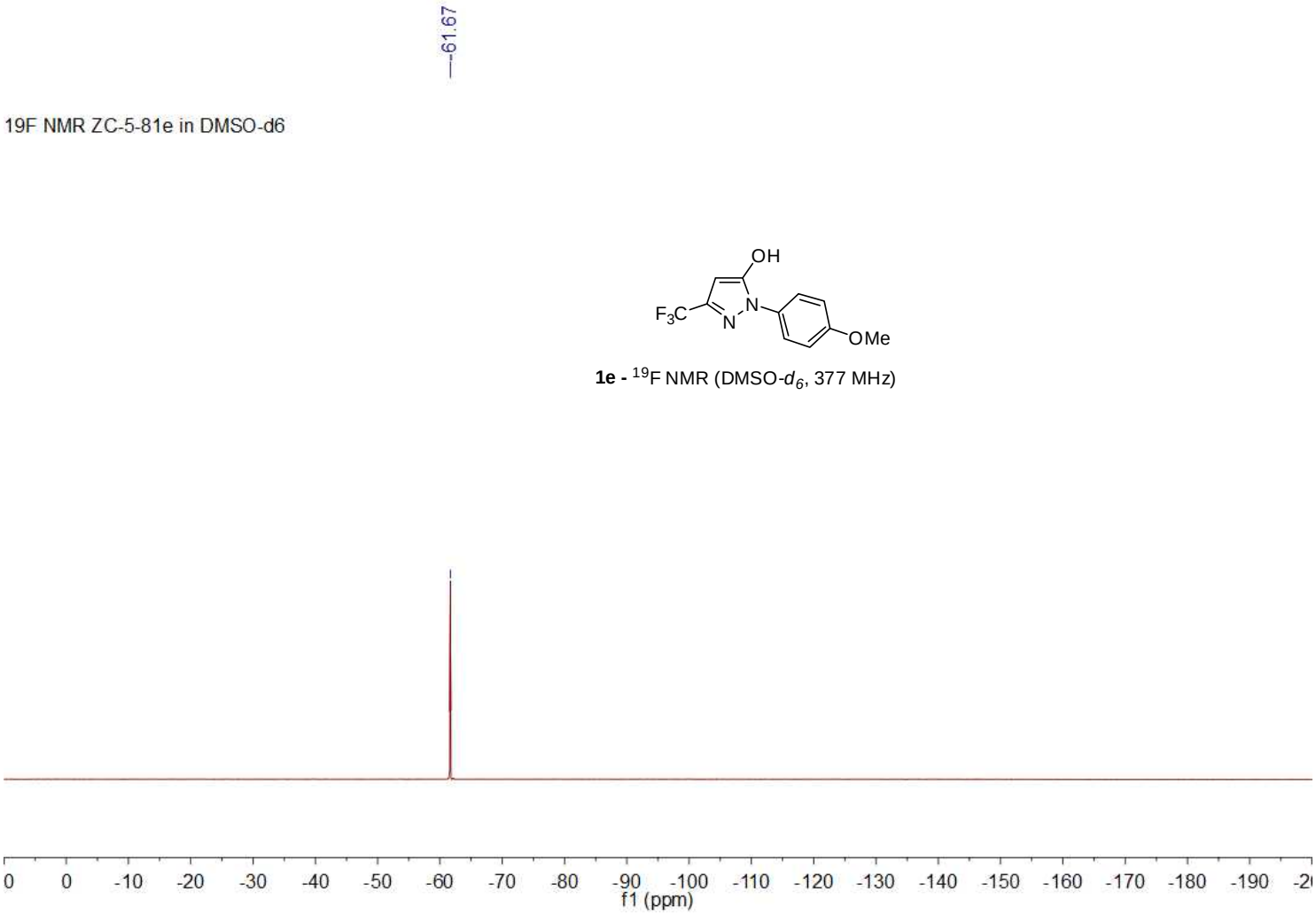
1d - ^{19}F NMR (DMSO-d_6, 377 MHz)



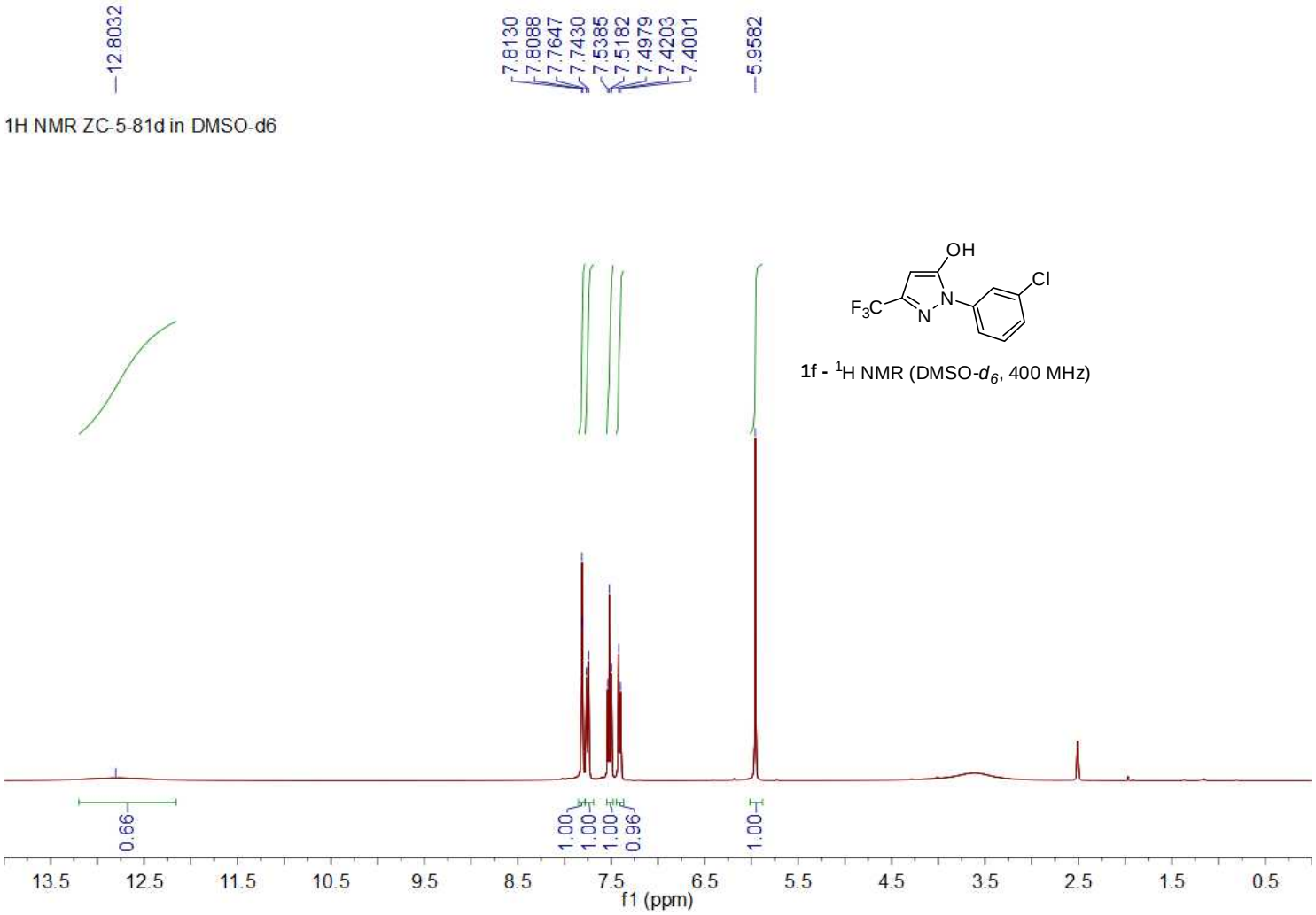
1e - ^{1}H NMR (DMSO-d_6, 400 MHz)



1e - ^{13}C NMR (DMSO-d_6, 100 MHz)

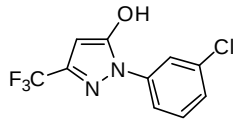


1e - ^{19}F NMR (DMSO-d_6, 377 MHz)

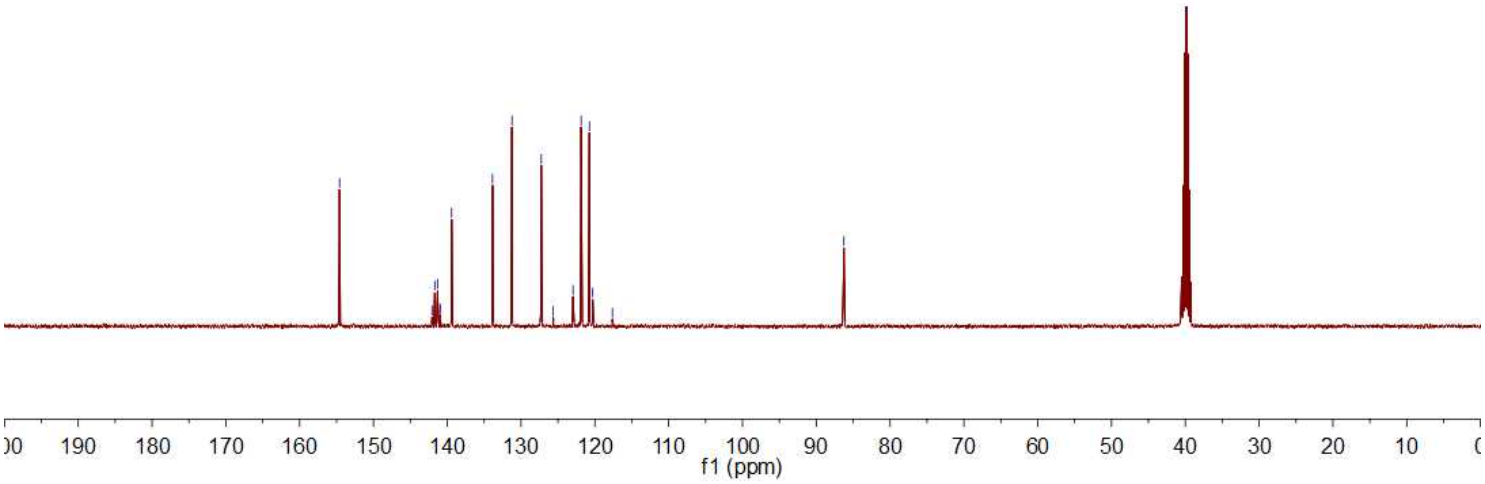


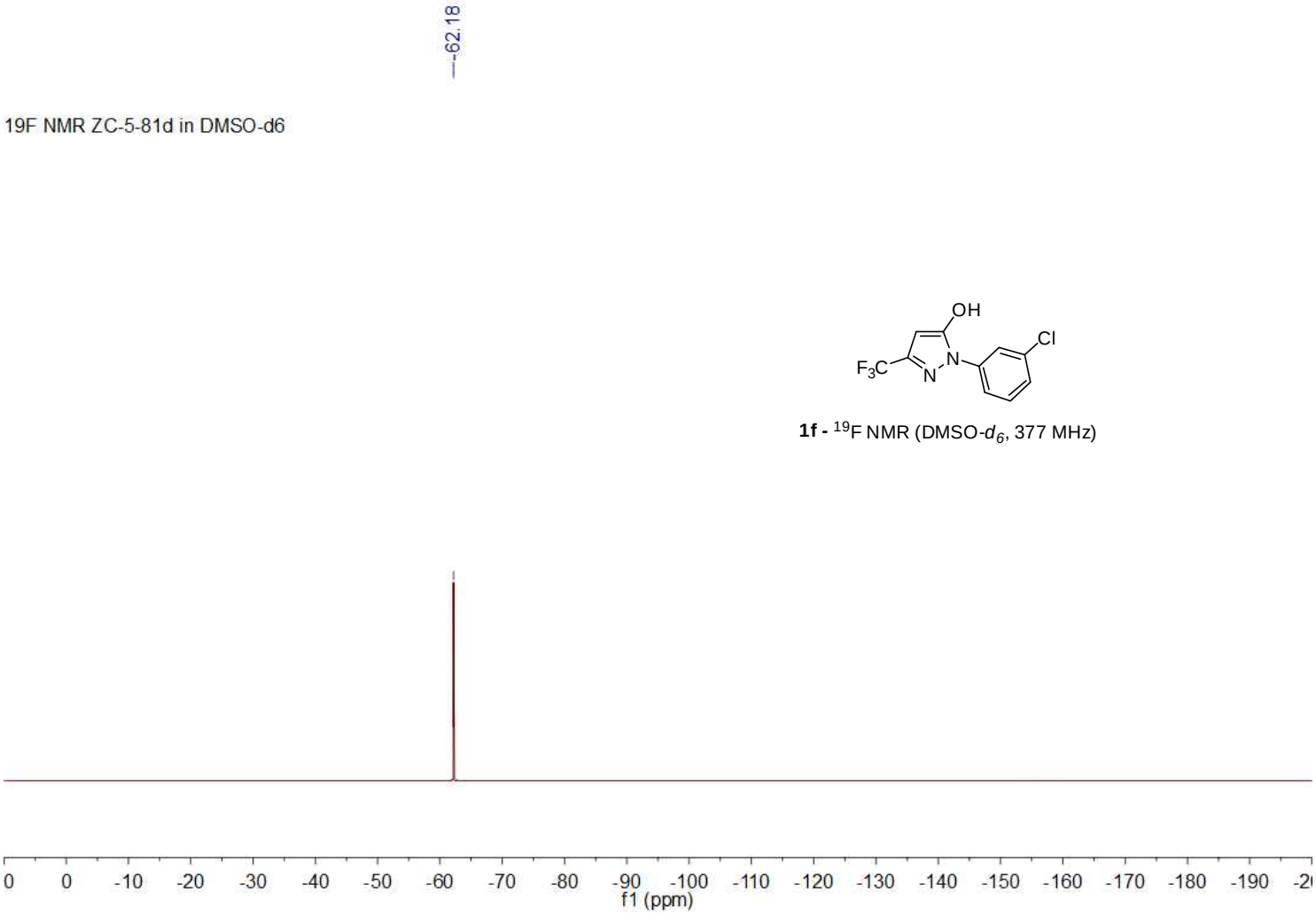
1f - ^{1}H NMR (DMSO-d_6, 400 MHz)

13C NMR ZC-5-81d in DMSO-d6

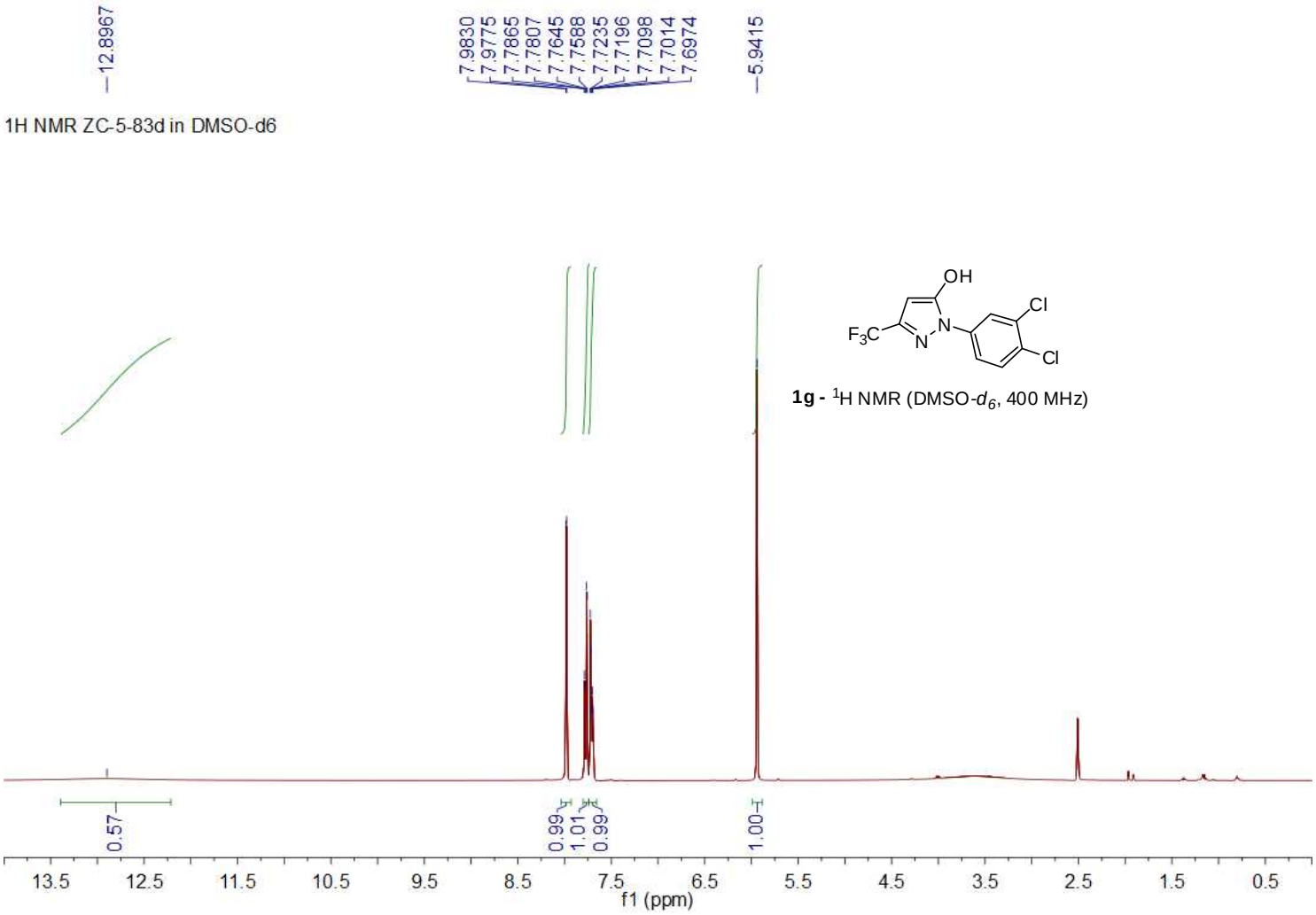


1f - ^{13}C NMR (DMSO-d_6, 100 MHz)

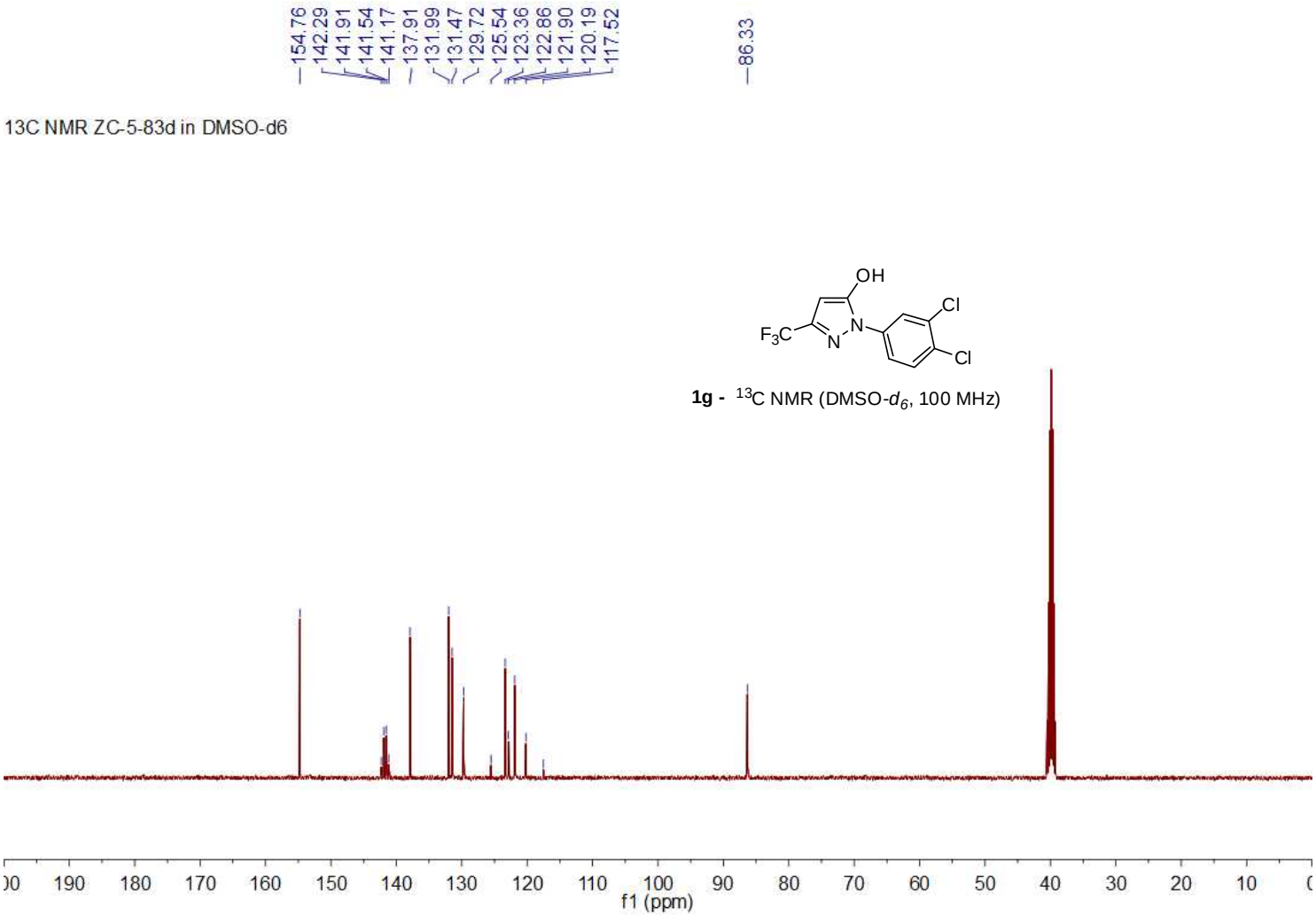




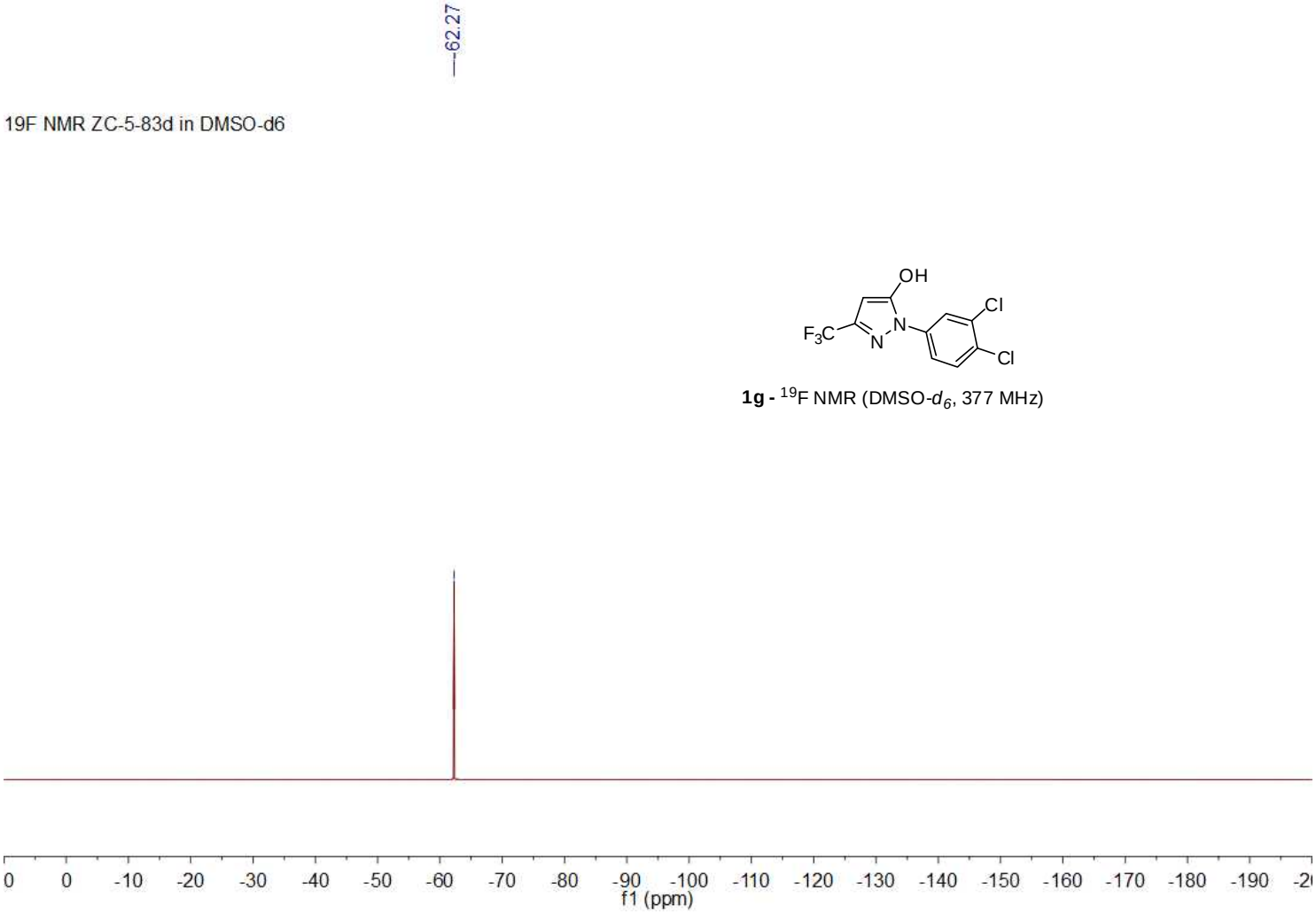
1f - ^{19}F NMR (DMSO-d_6, 377 MHz)



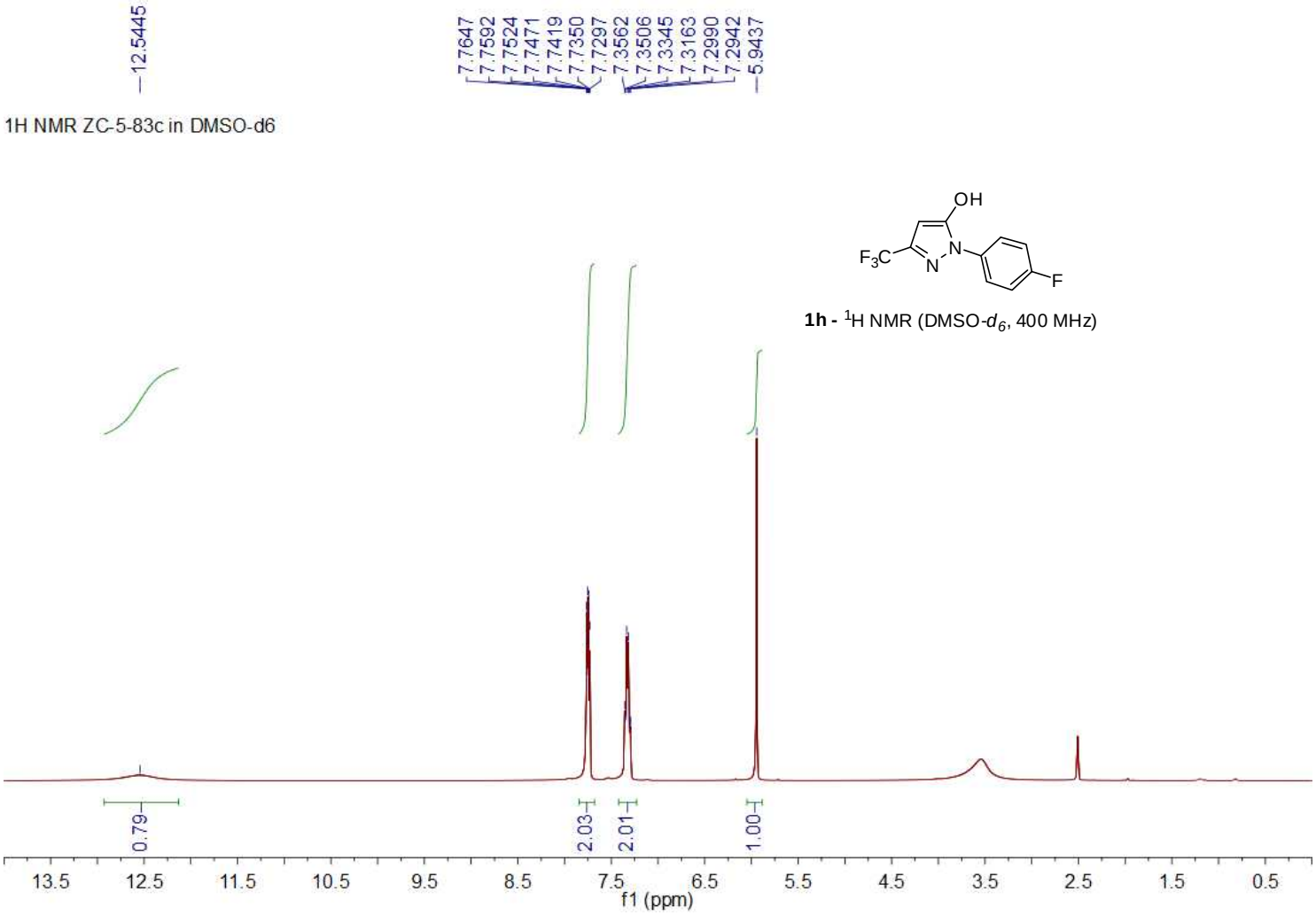
1g - ^{1}H NMR (DMSO-d_6, 400 MHz)



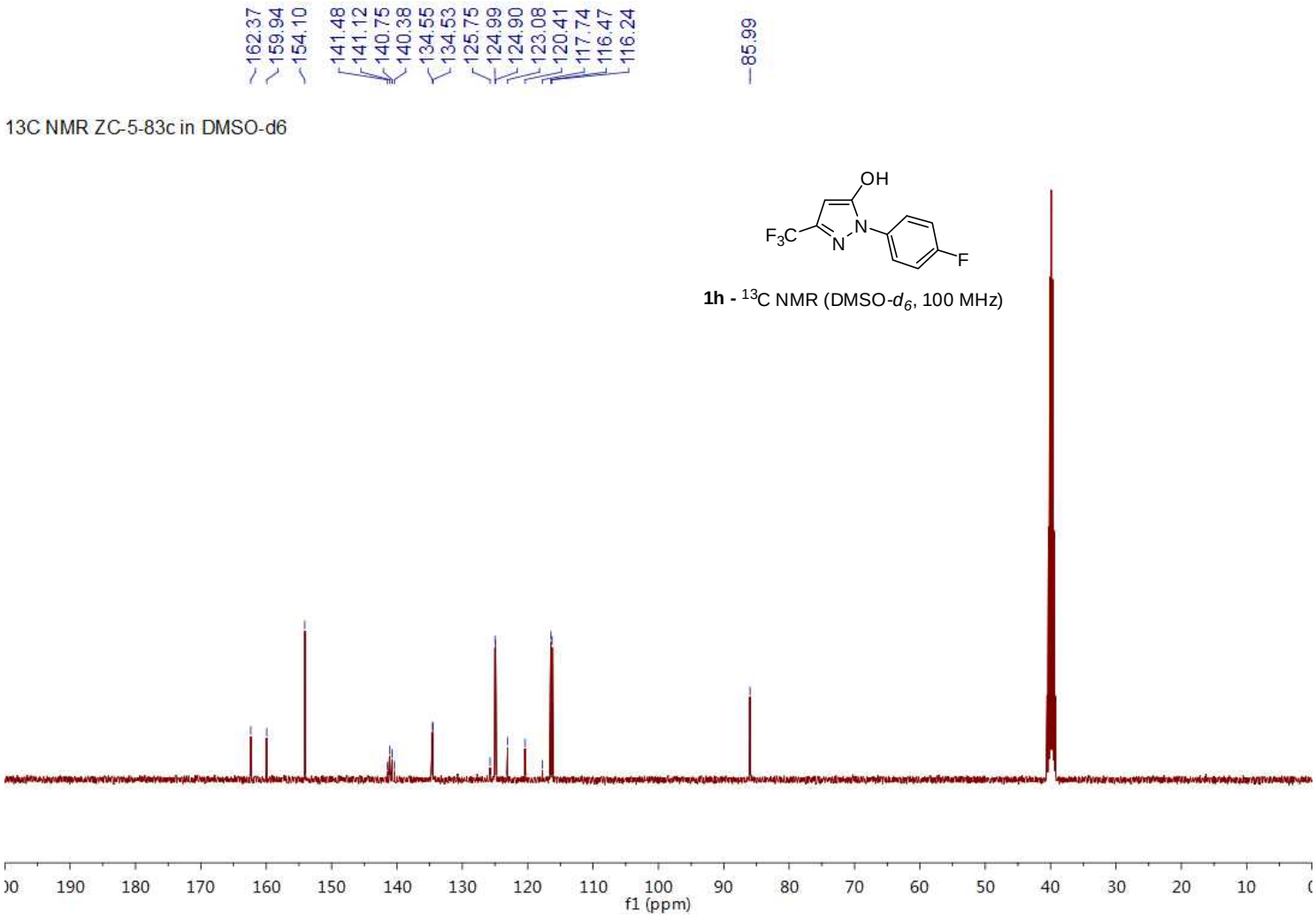
1g - ^{13}C NMR (DMSO-d_6, 100 MHz)



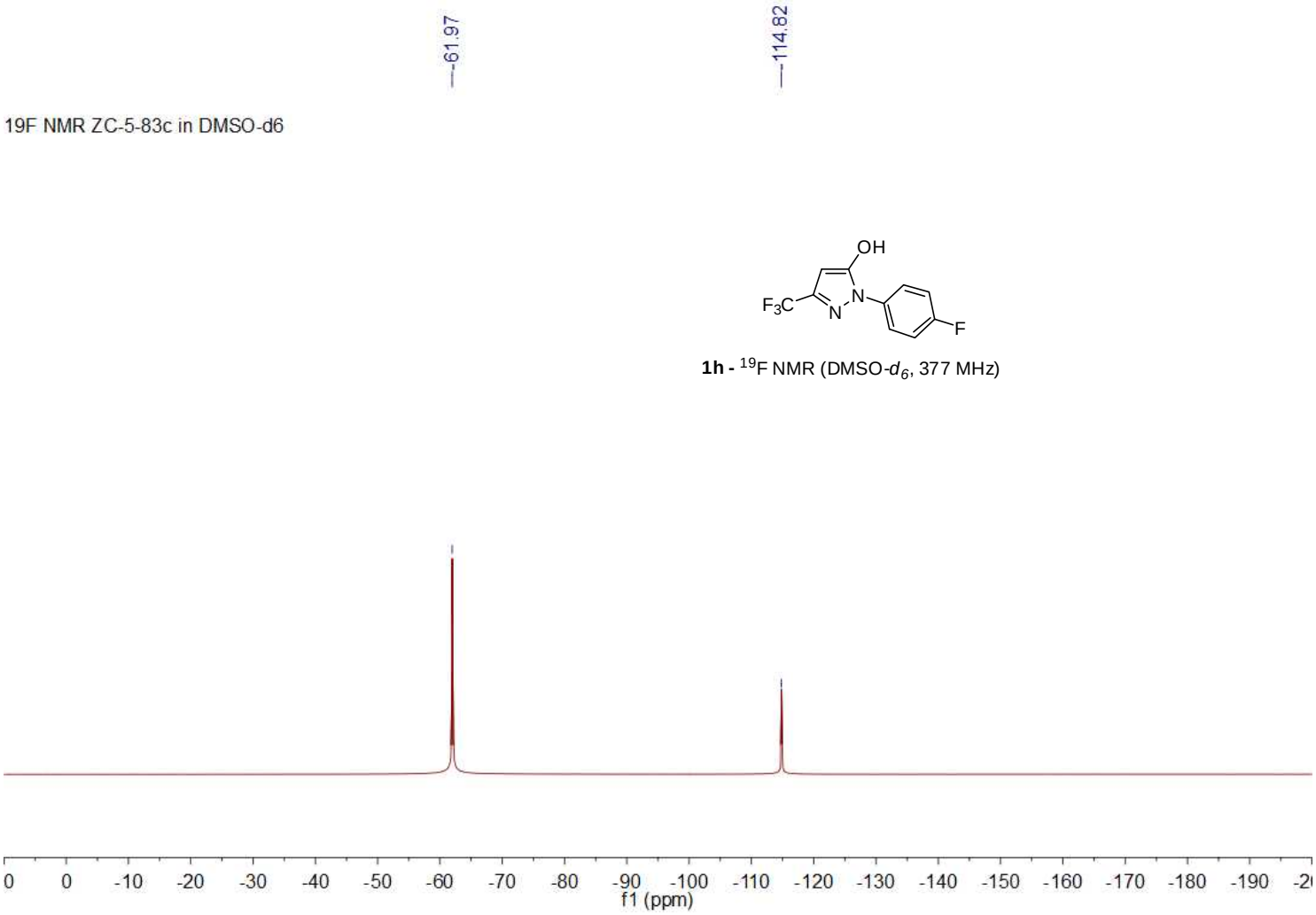
1g - ^{19}F NMR (DMSO-d_6, 377 MHz)



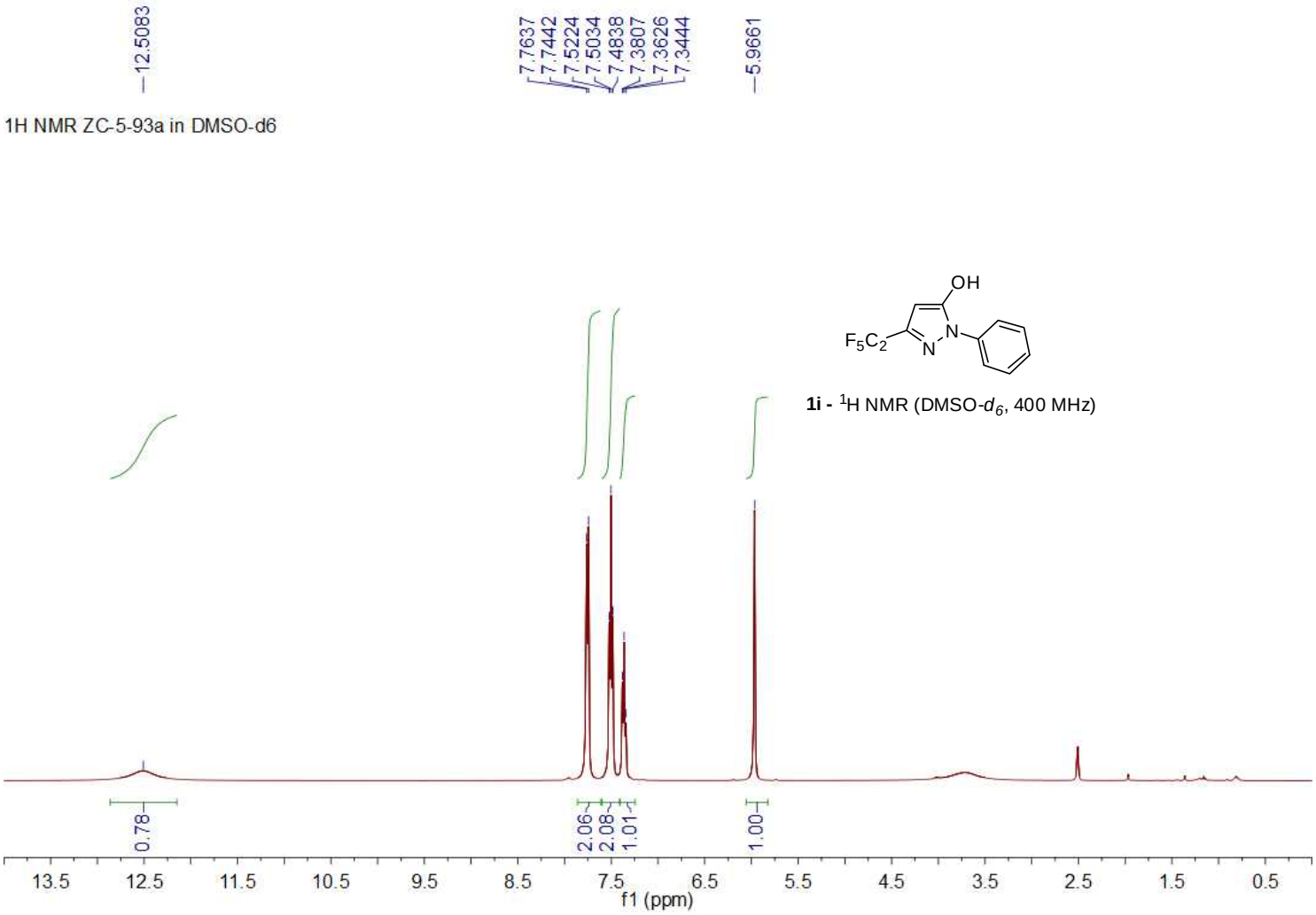
1h - ^{1}H NMR (DMSO-d_6, 400 MHz)



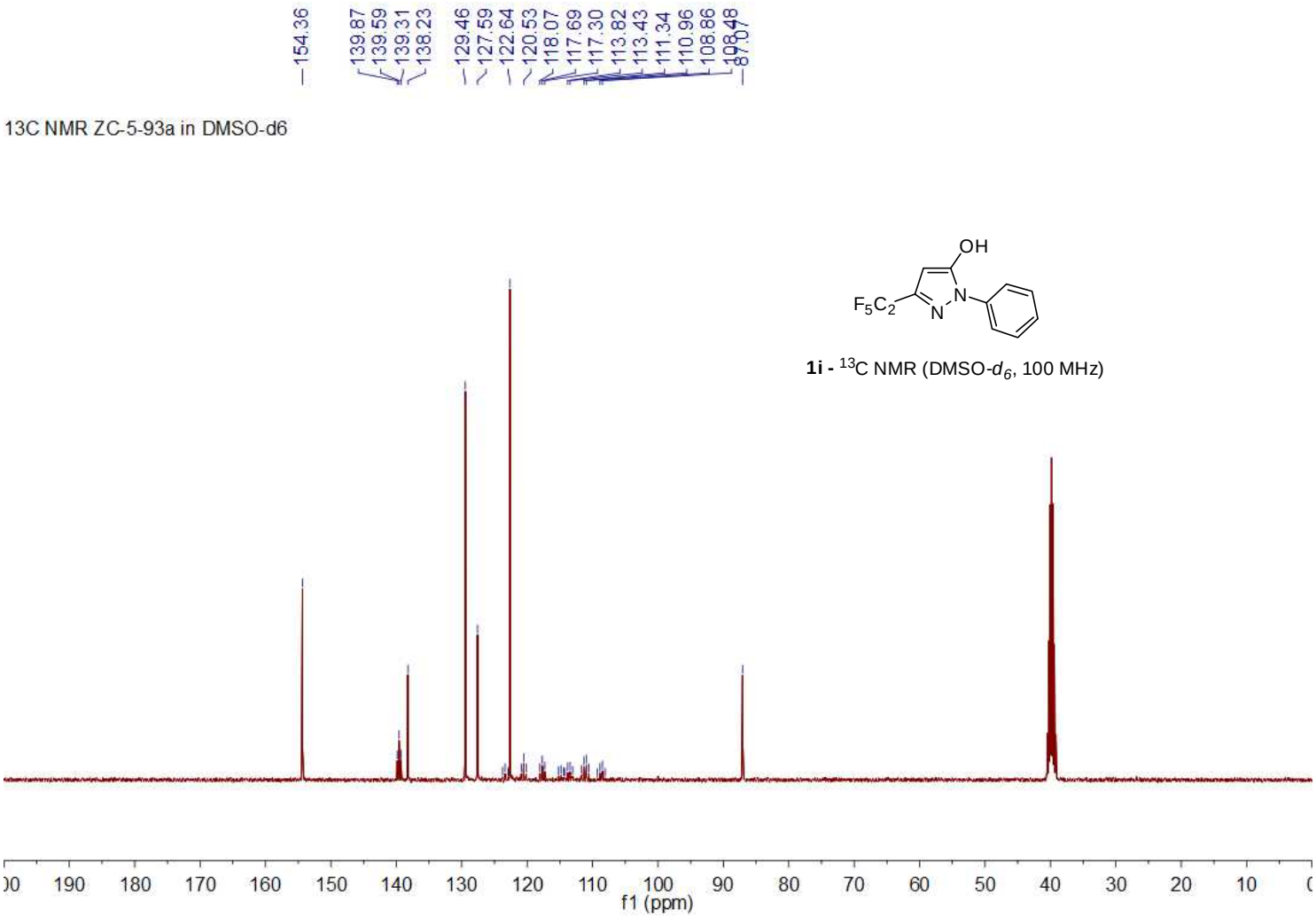
1h - ^{13}C NMR (DMSO-d_6, 100 MHz)



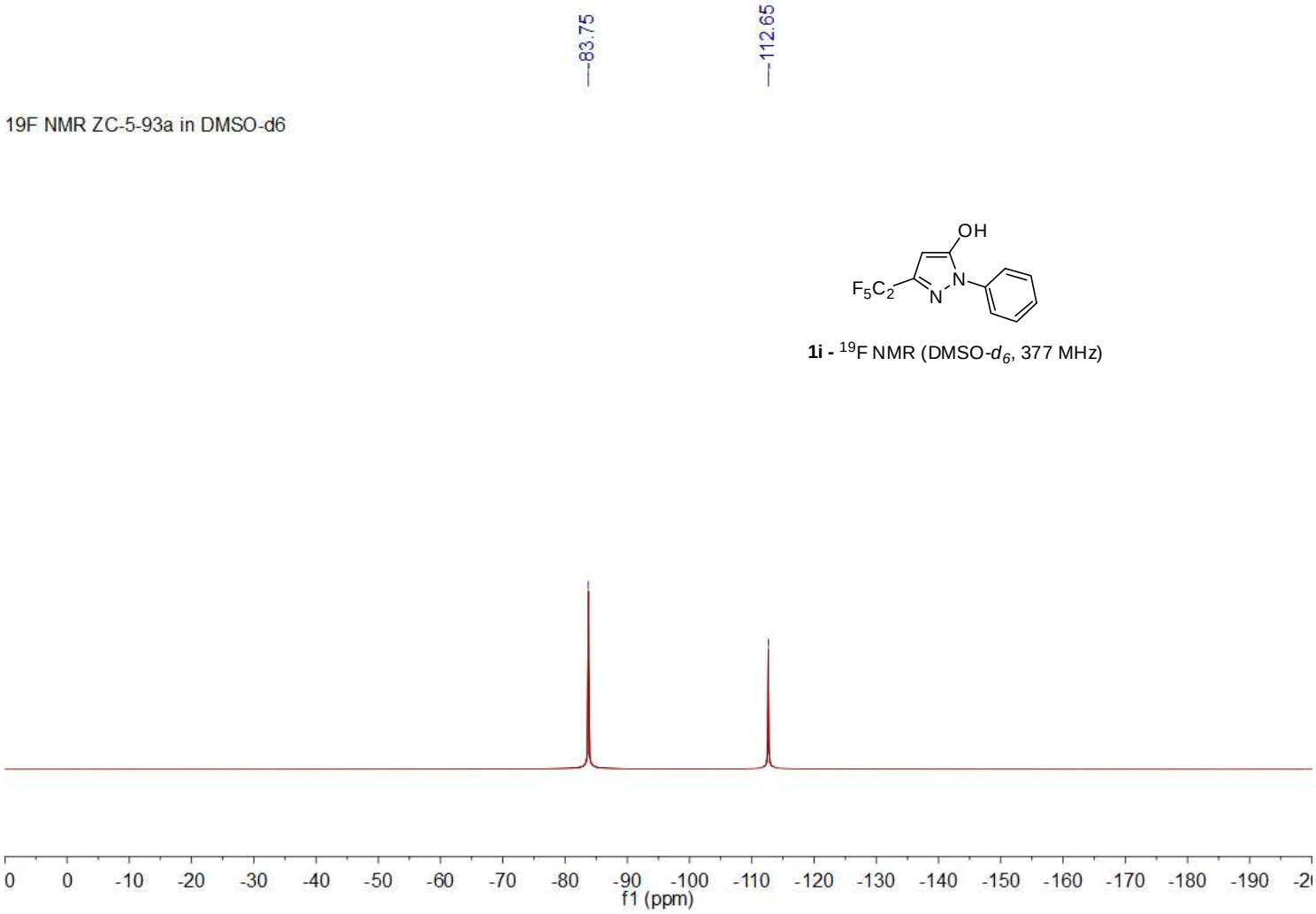
1h - ^{19}F NMR (DMSO-d_6, 377 MHz)



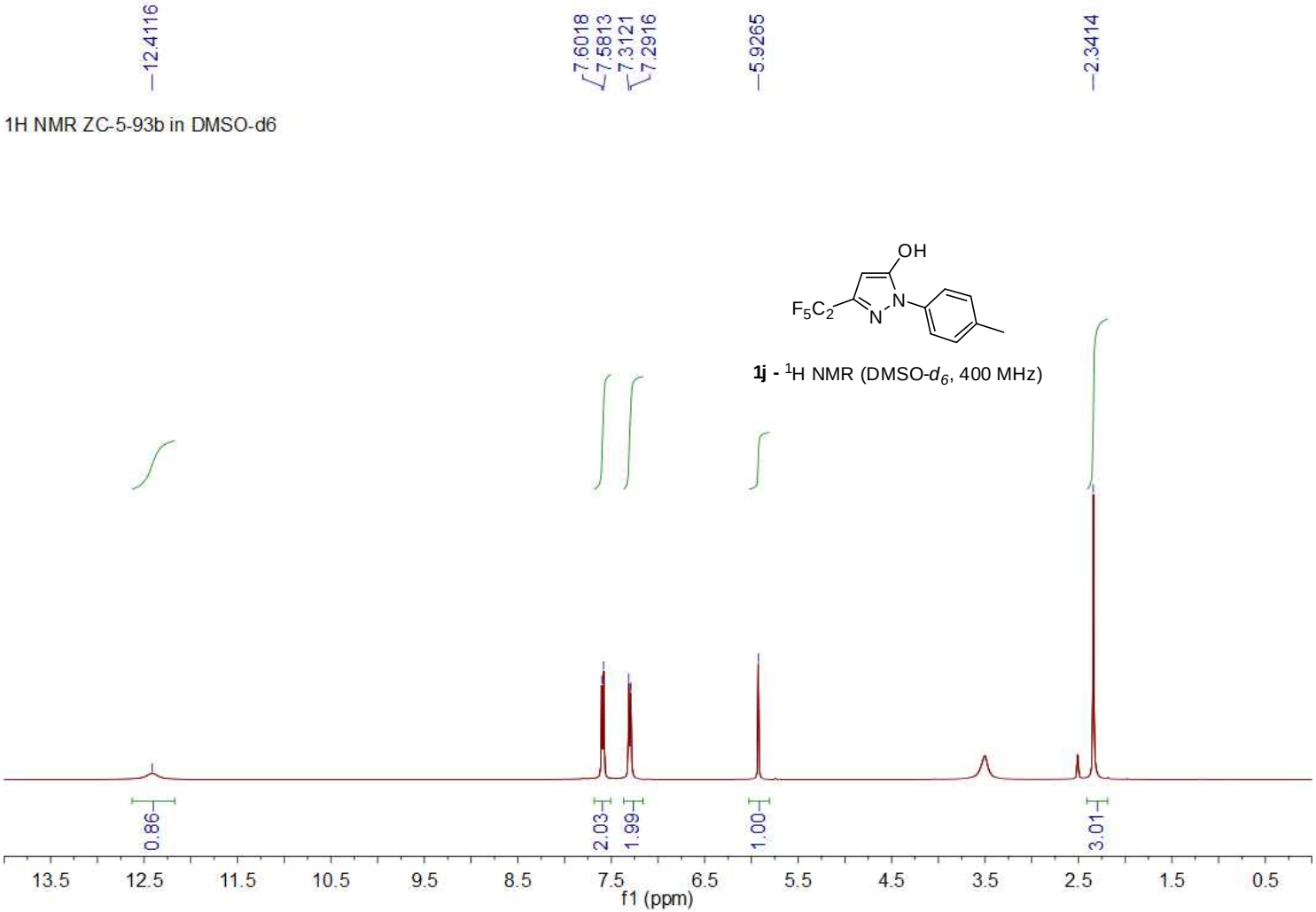
1i - ^{1}H NMR (DMSO-d_6, 400 MHz)

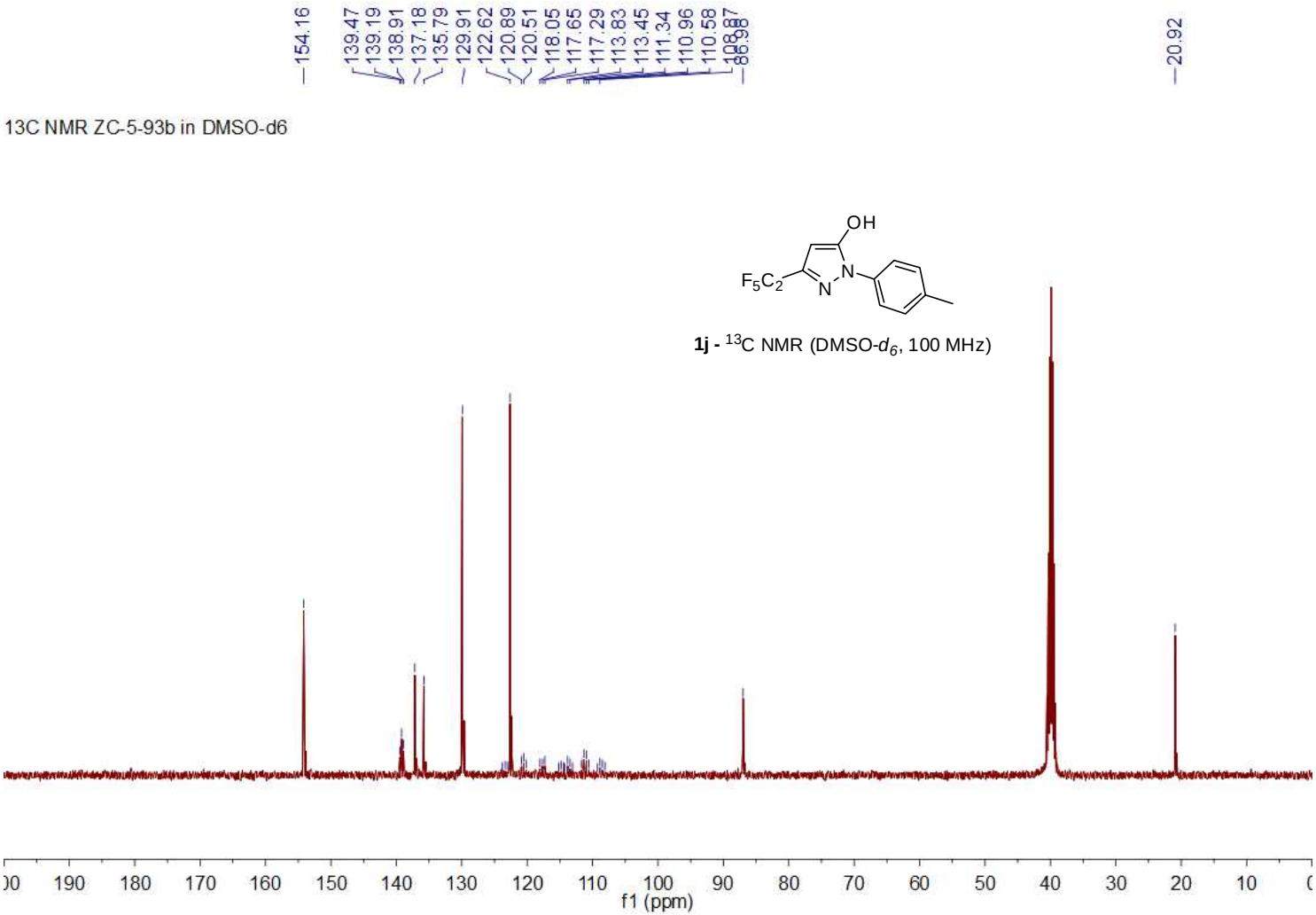


1i - ^{13}C NMR (DMSO-d_6, 100 MHz)

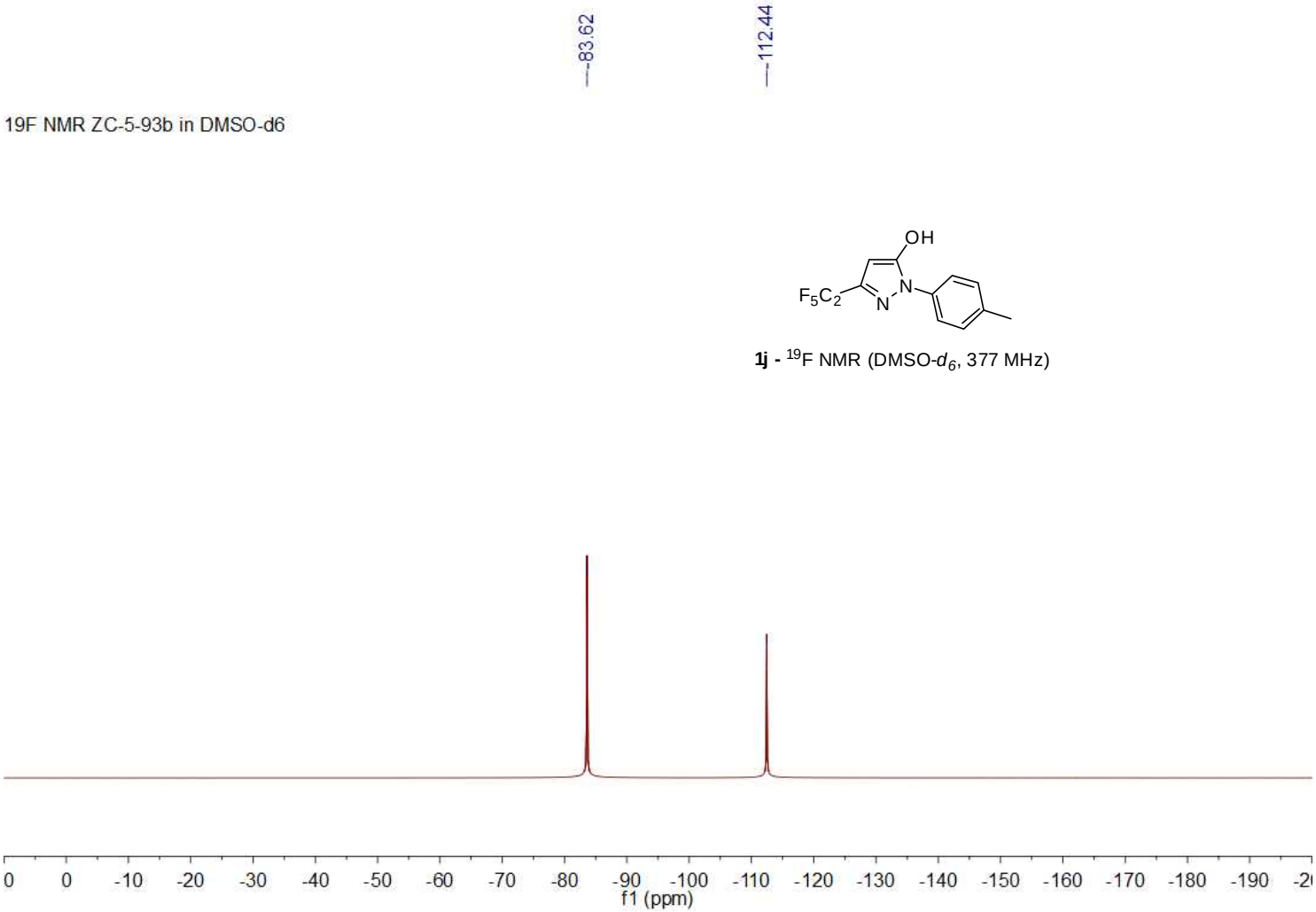


1i - ^{19}F NMR (DMSO-d_6, 377 MHz)

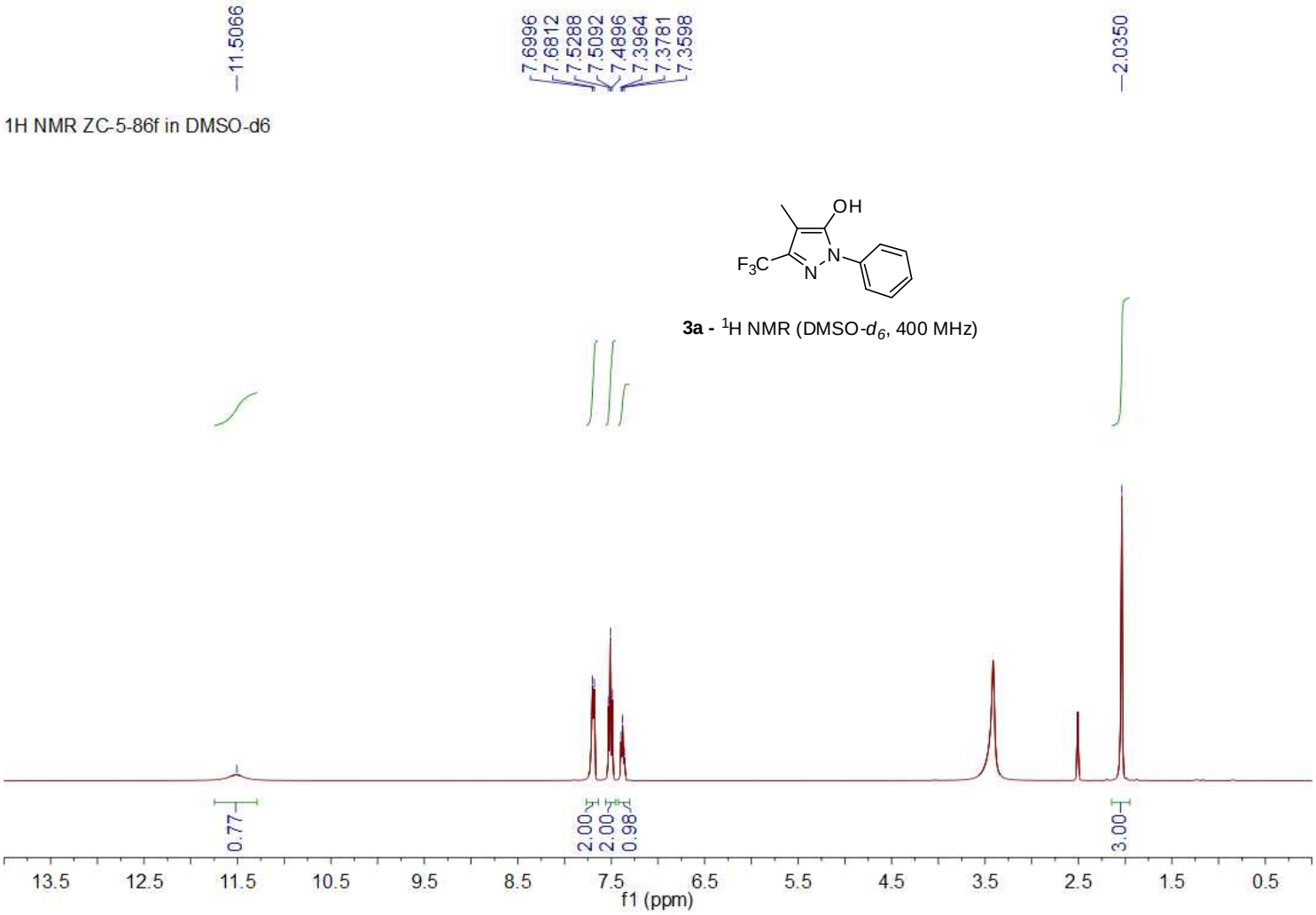

12.4116
7.6018
7.5813
7.3121
7.2916
5.9265
2.3414
1H NMR ZC-5-93b in DMSO-d6
OH
F5C2
N
N
1j - 1H NMR (DMSO-d6, 400 MHz)
0.86
2.03
1.99
1.00
3.01
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



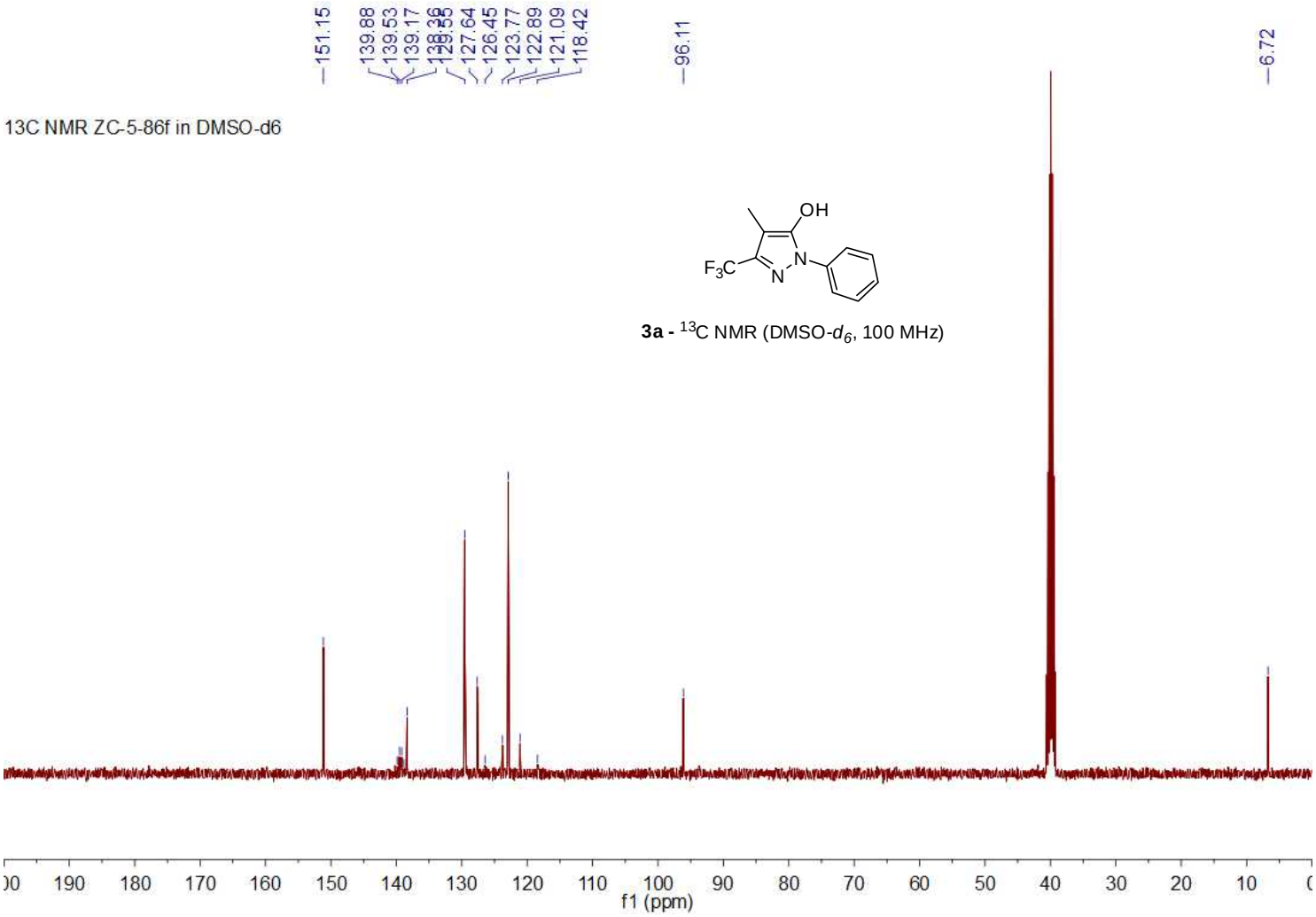
1j - ^{13}C NMR (DMSO-d_6, 100 MHz)



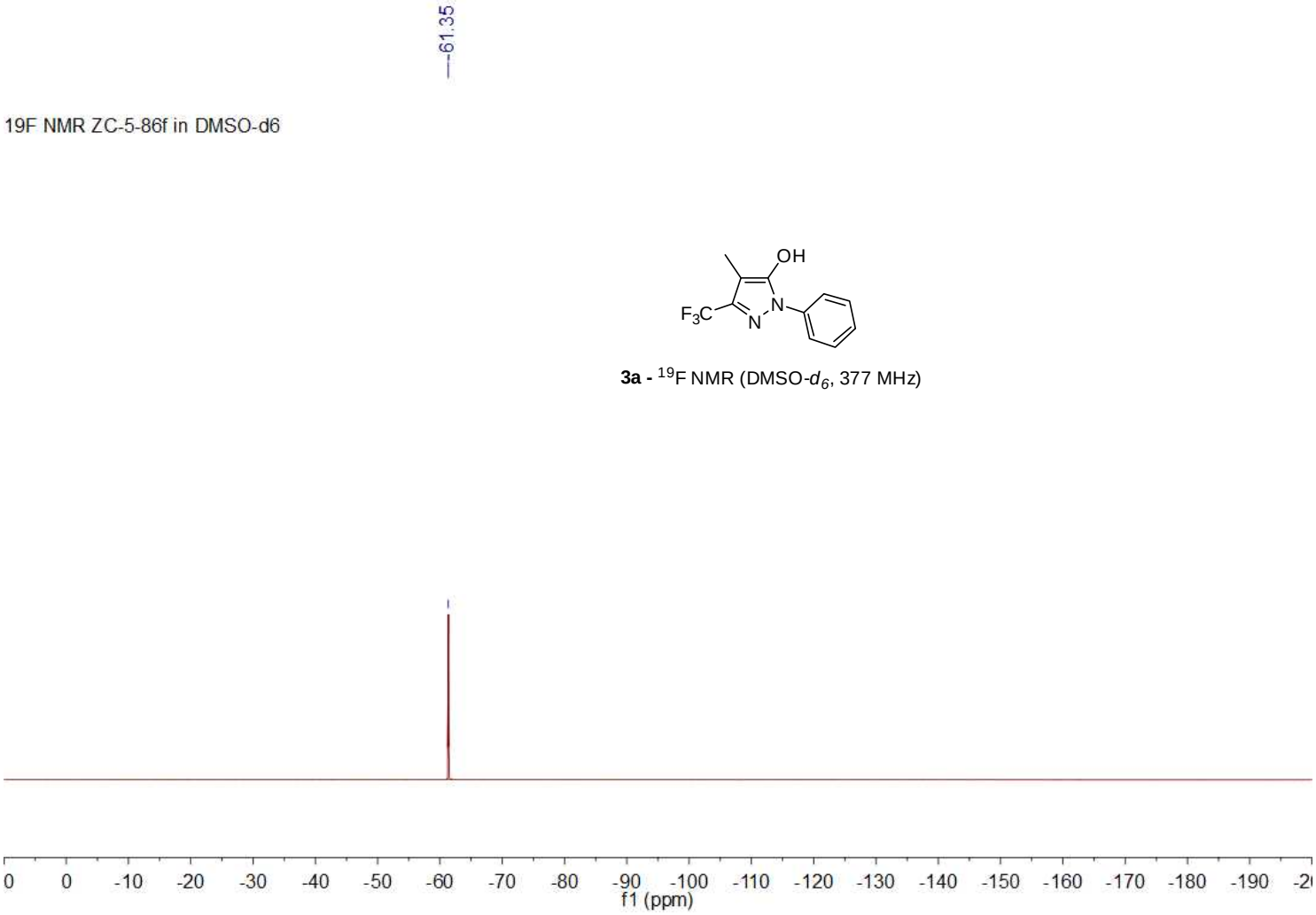
1j - ^{19}F NMR (DMSO-d_6, 377 MHz)



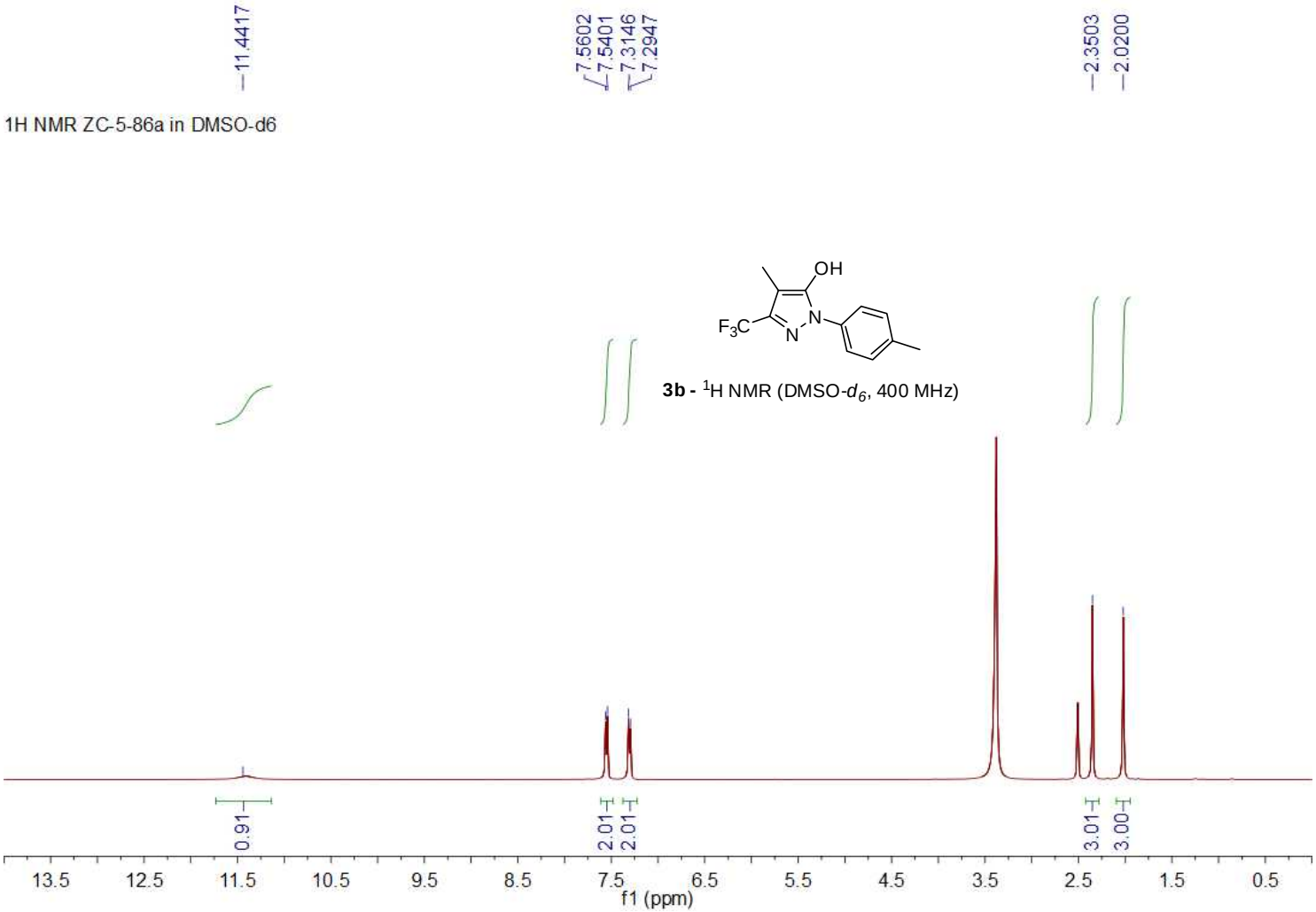
3a - ^{1}H NMR (DMSO-d_6, 400 MHz)



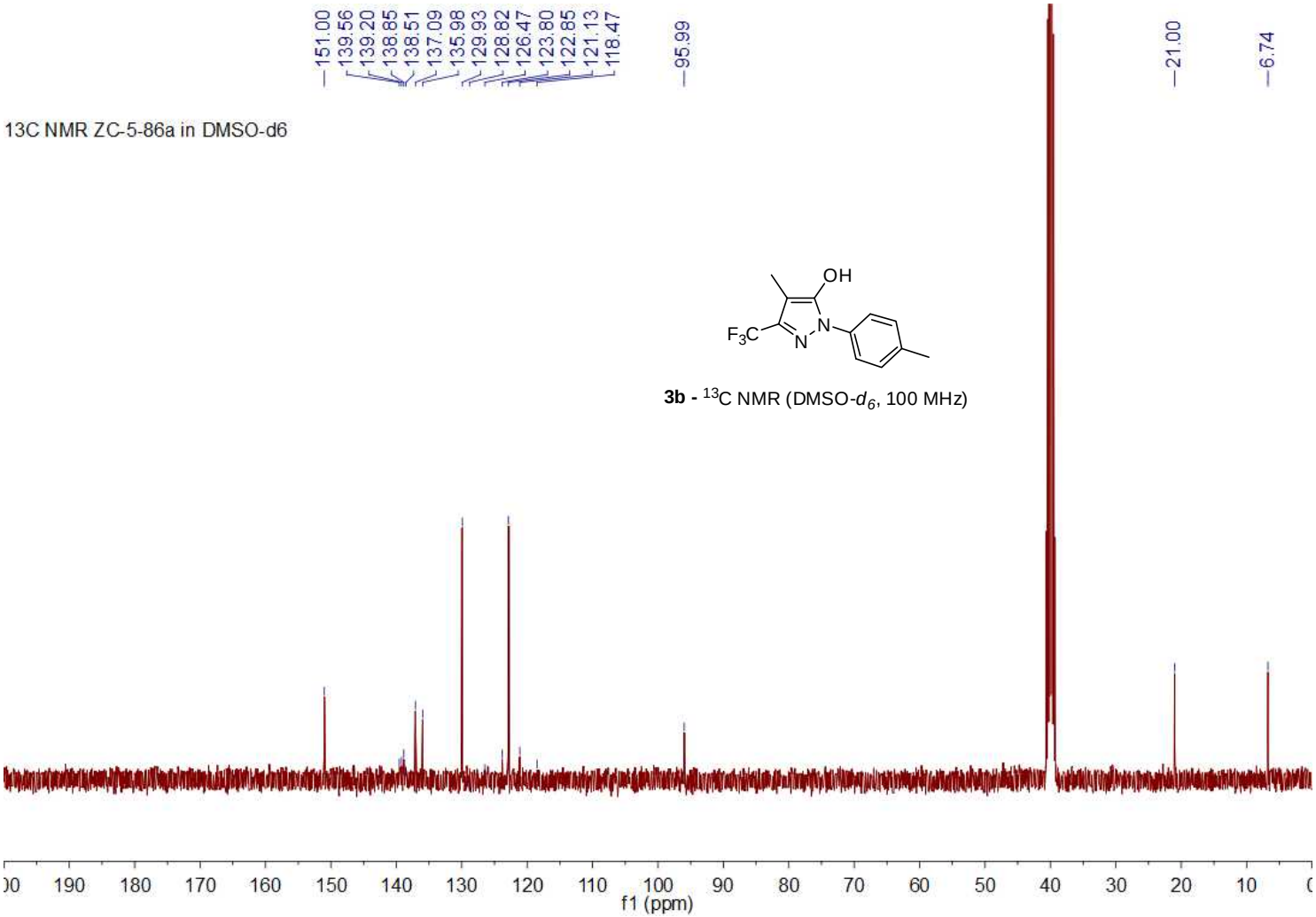
3a - ^{13}C NMR (DMSO-d_6, 100 MHz)



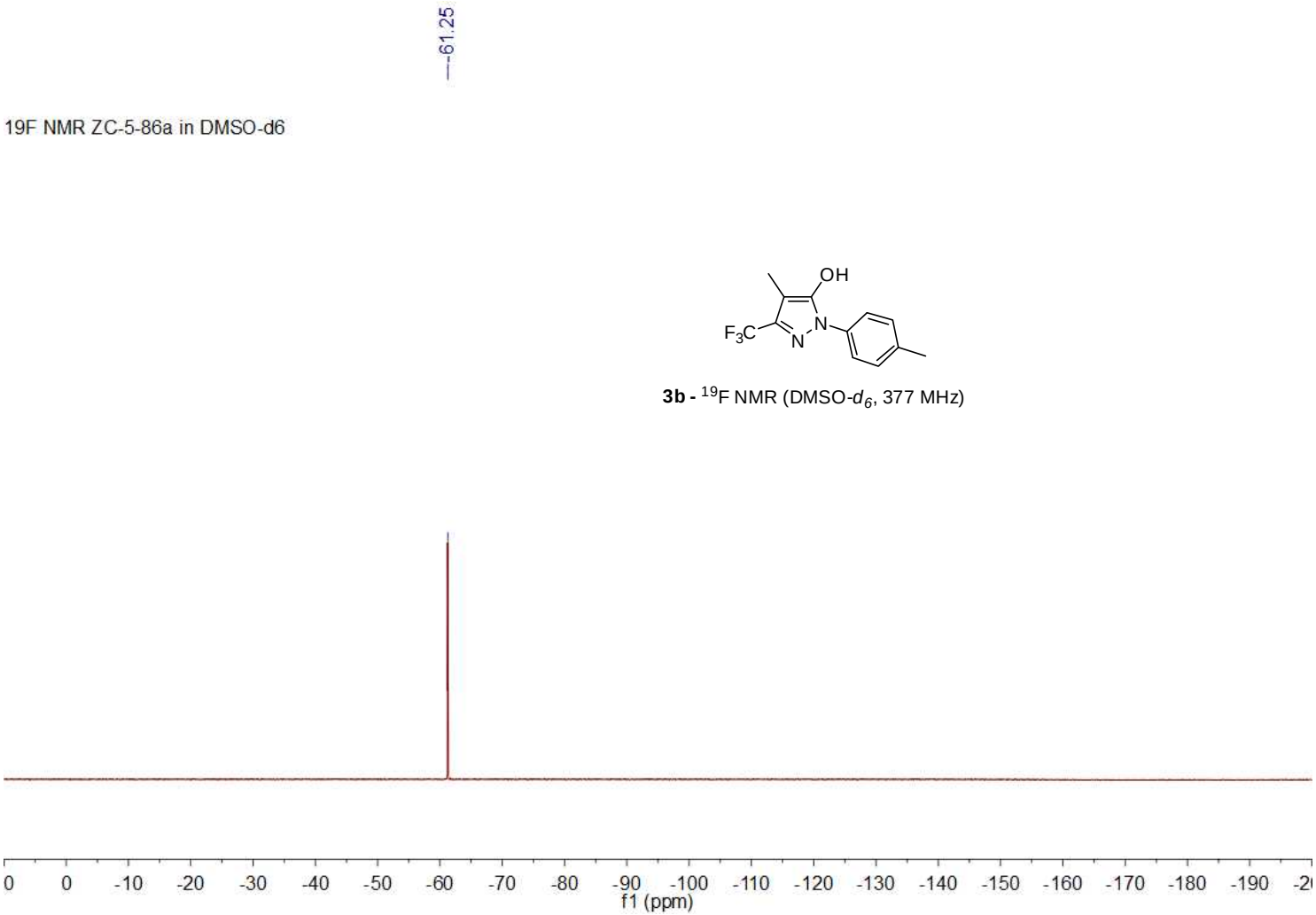
3a - ^{19}F NMR (DMSO-d_6, 377 MHz)



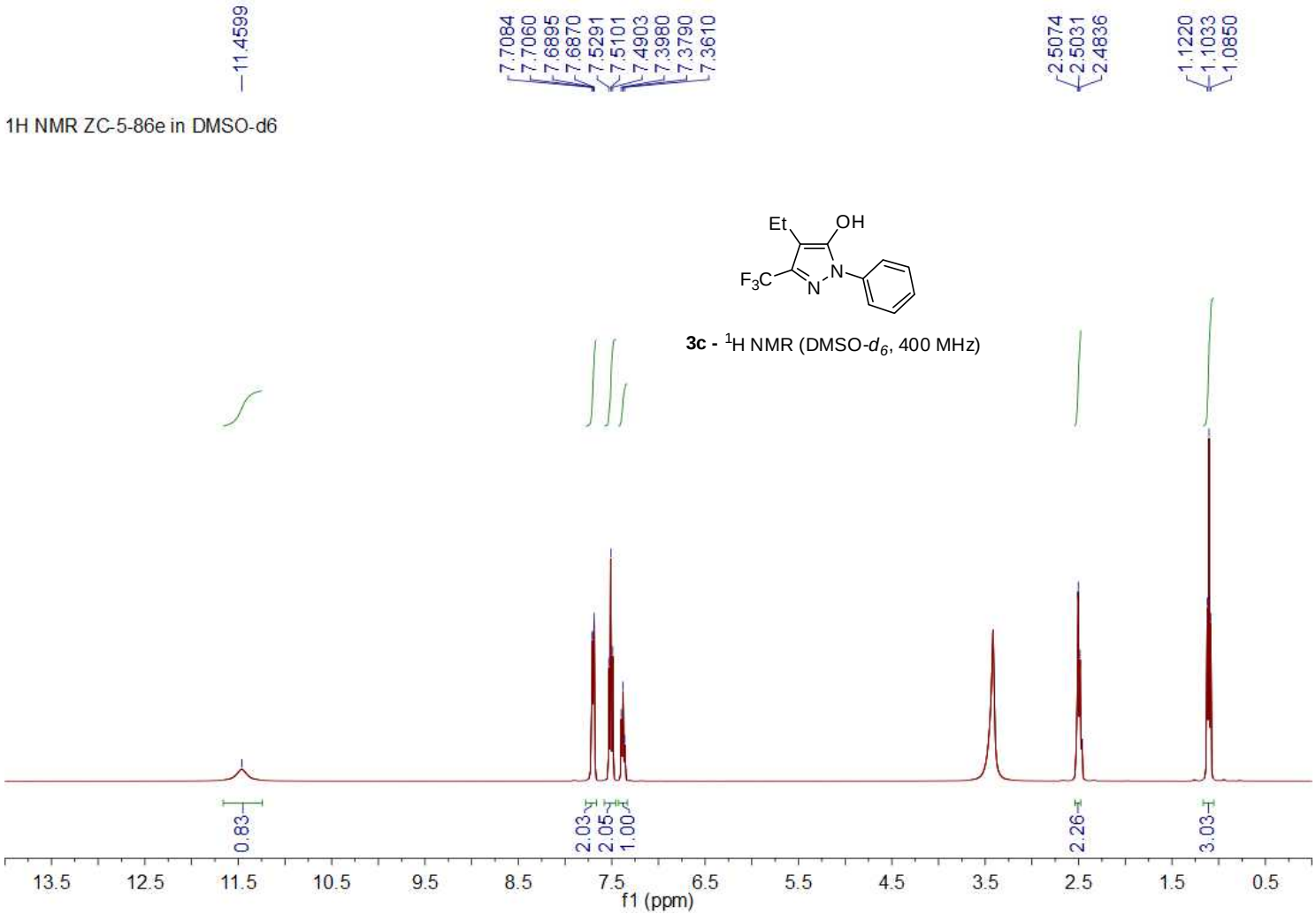
3b - ^{1}H NMR (DMSO-d_6, 400 MHz)



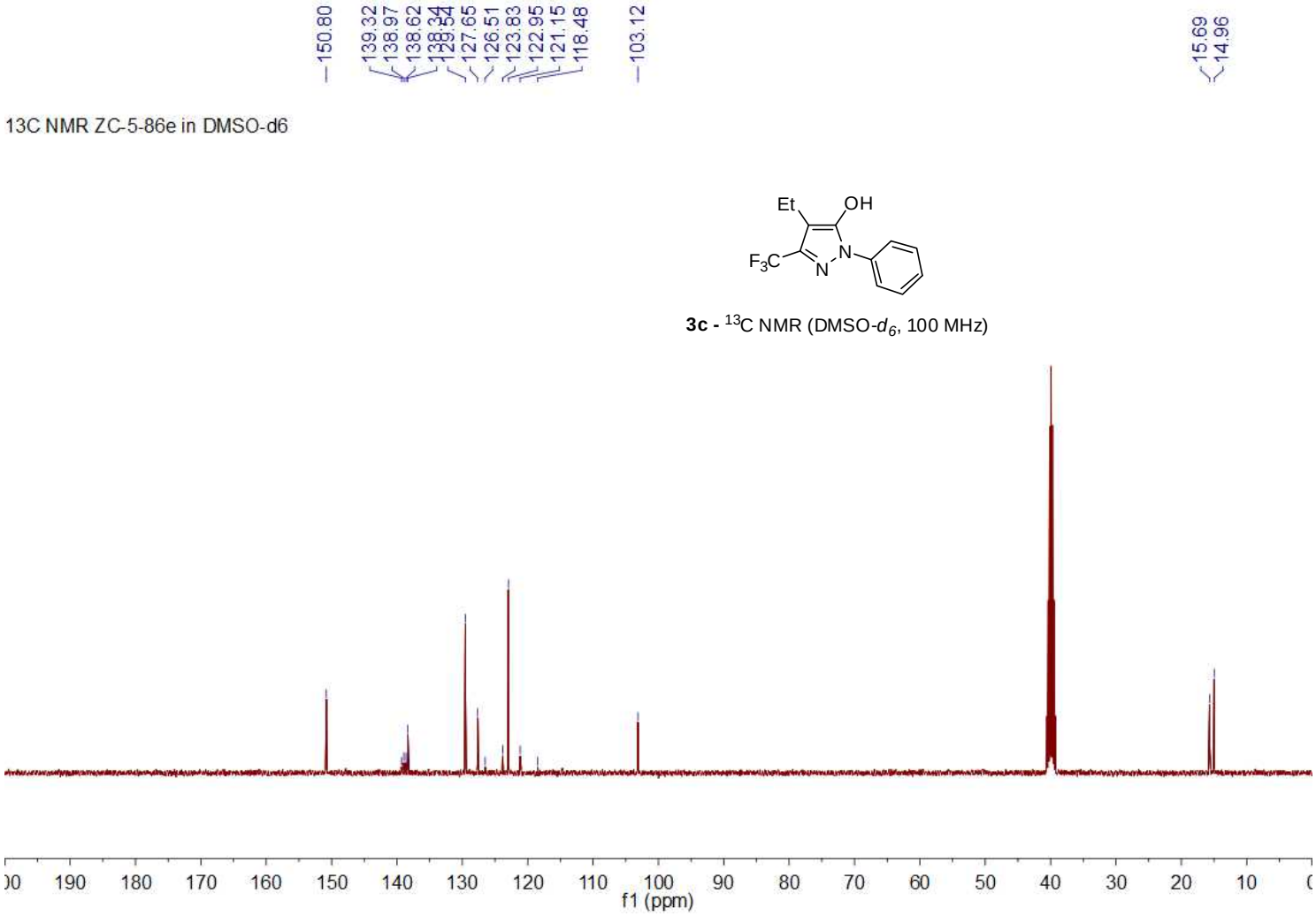
3b - ^{13}C NMR (DMSO-d_6, 100 MHz)



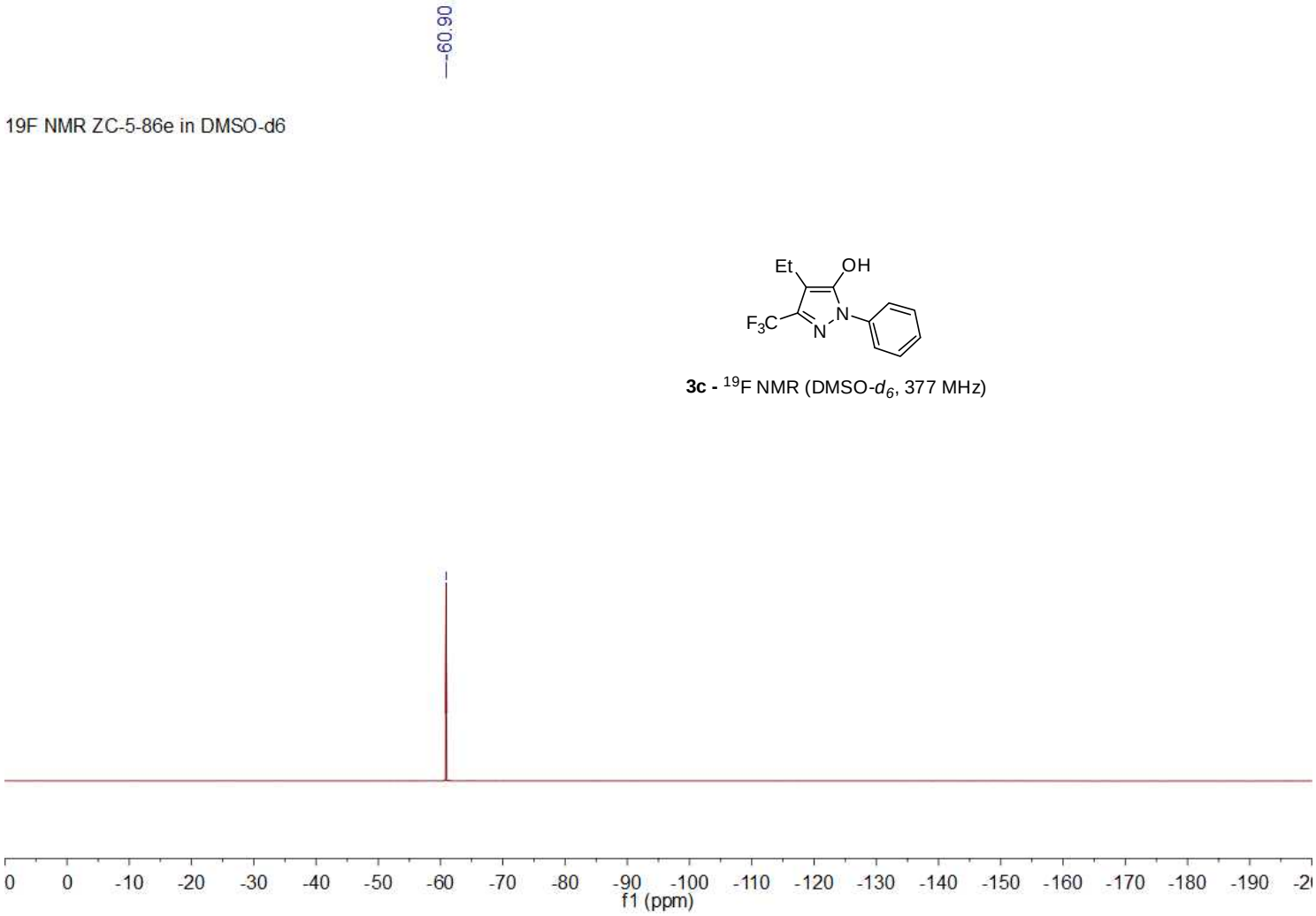
3b - ^{19}F NMR (DMSO-d_6, 377 MHz)



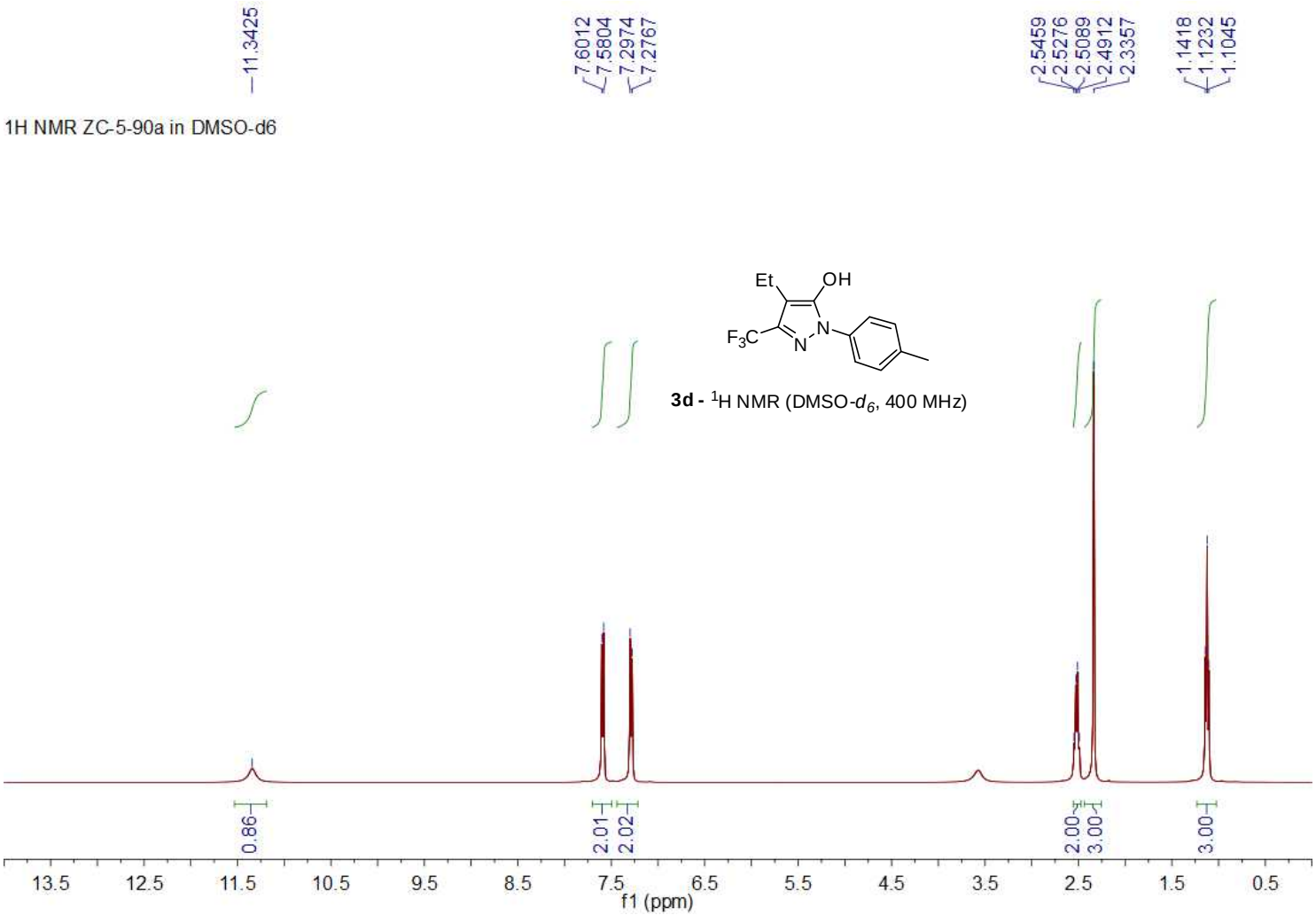
3c - ^{1}H NMR (DMSO-d_6, 400 MHz)



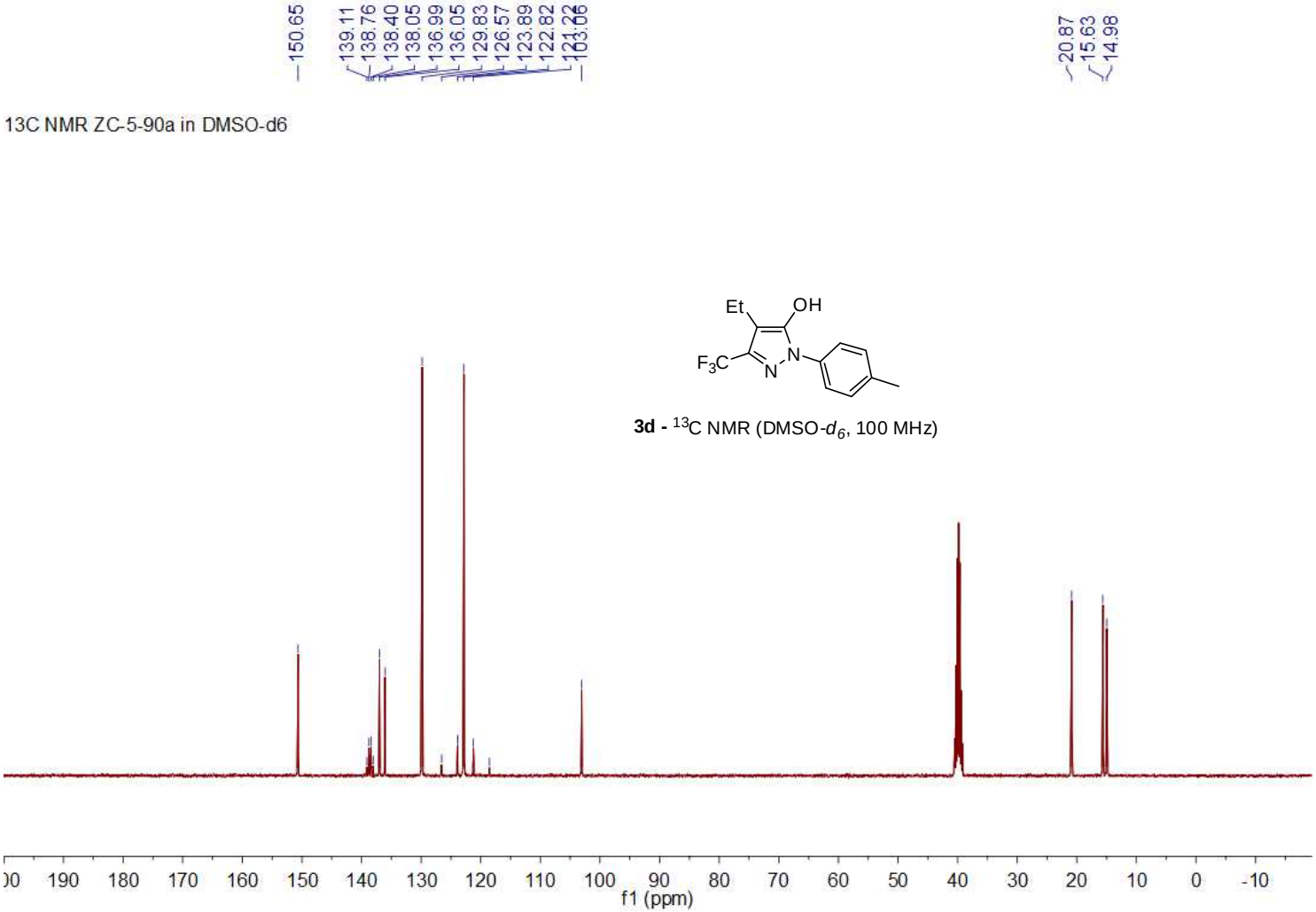
3c - ^{13}C NMR (DMSO-d_6, 100 MHz)



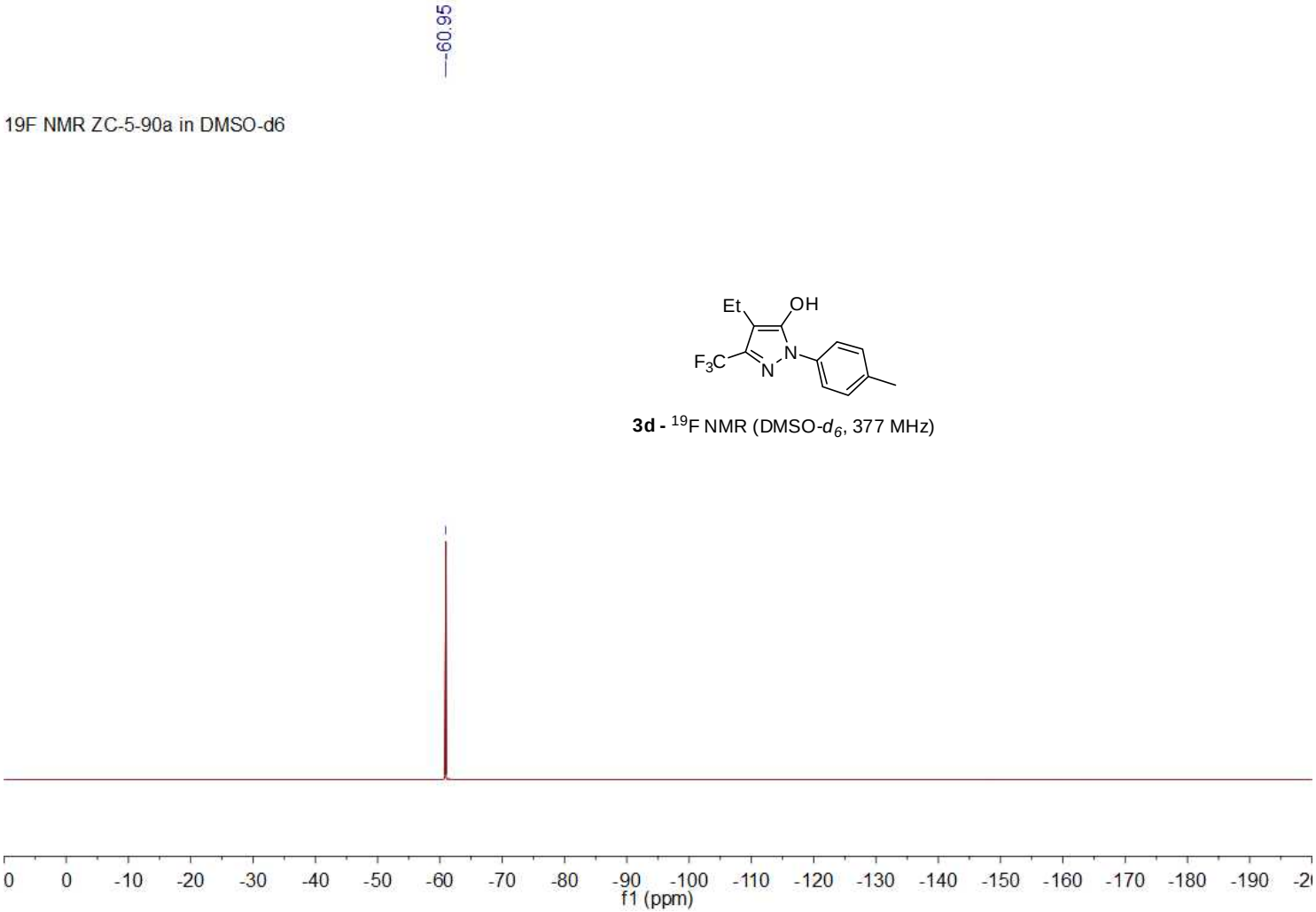
3c - ^{19}F NMR (DMSO-d_6, 377 MHz)



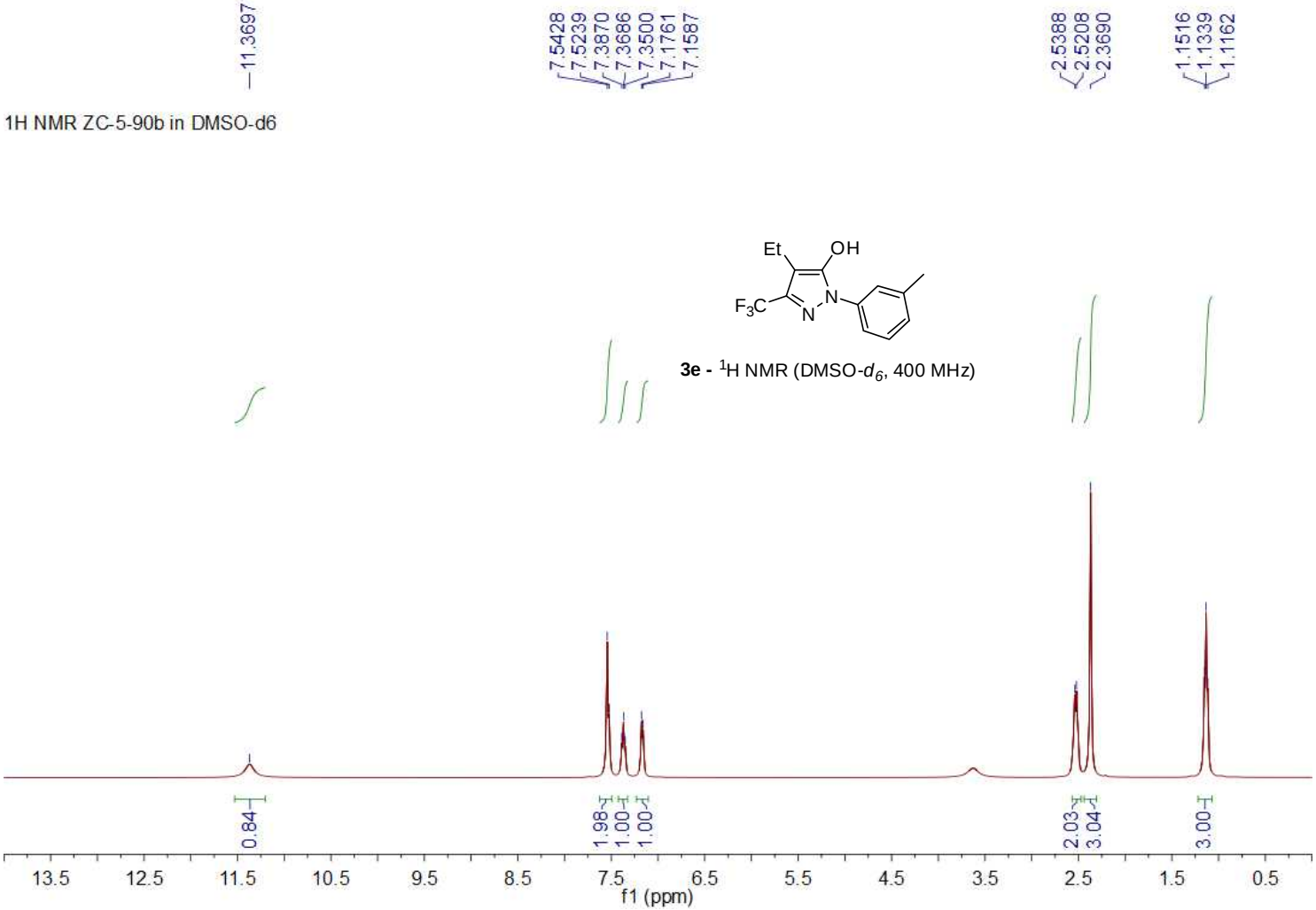
3d - ^{1}H NMR (DMSO-d_6, 400 MHz)



3d - ^{13}C NMR (DMSO-d_6, 100 MHz)

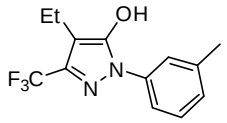


3d - ^{19}F NMR (DMSO-d_6, 377 MHz)

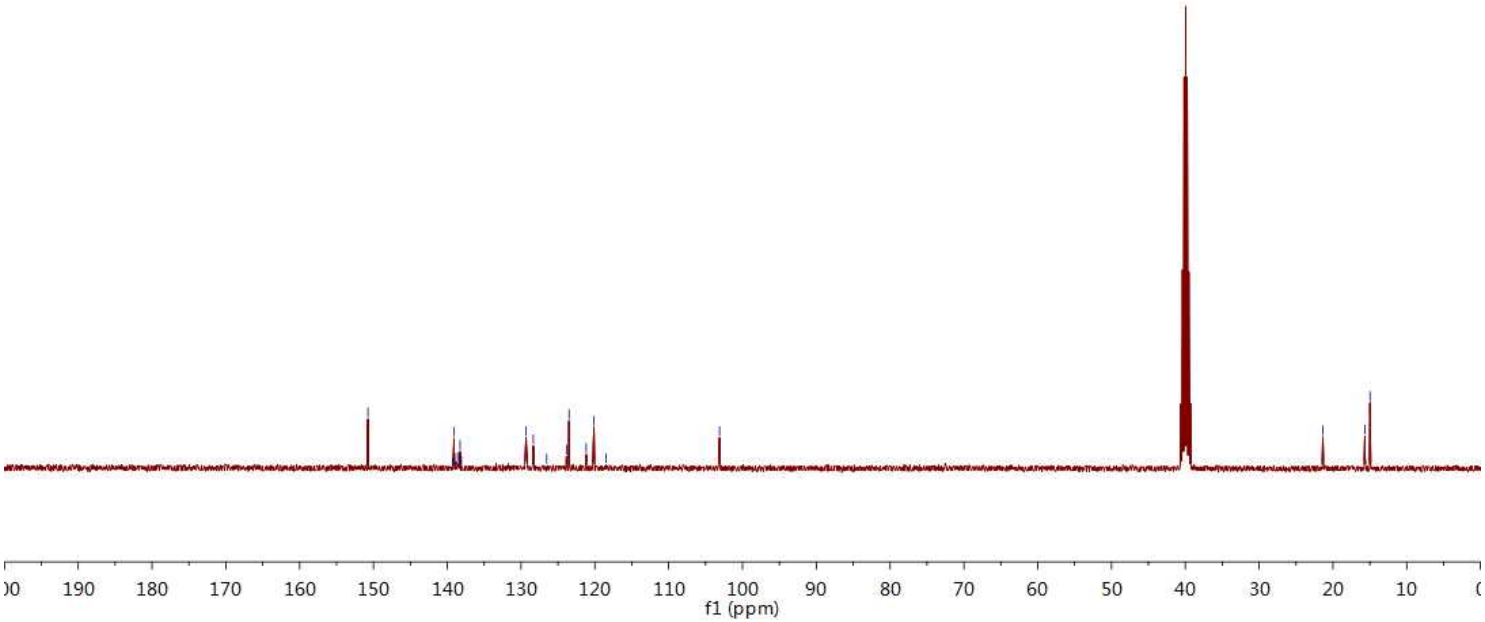


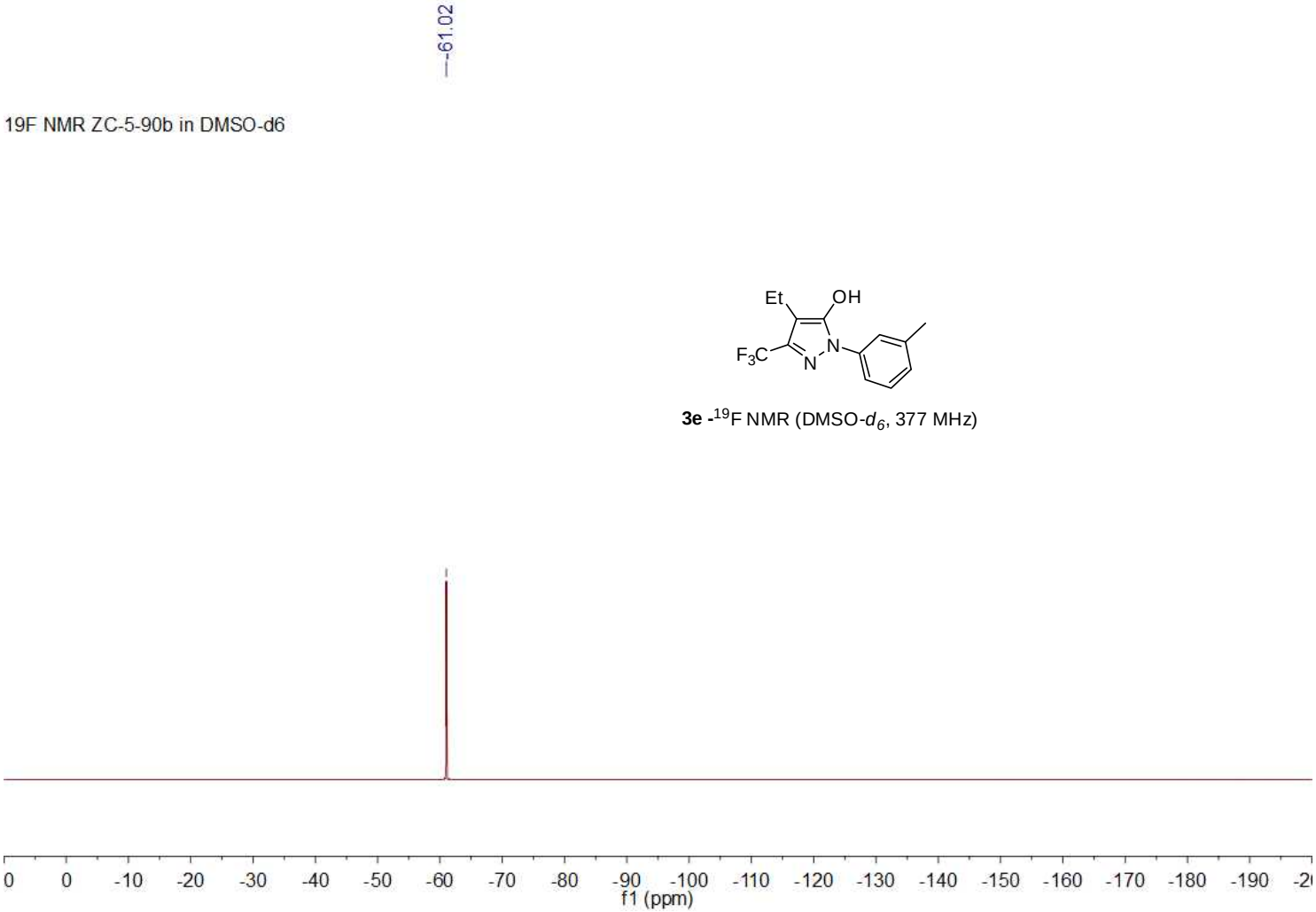
3e - ^{1}H NMR (DMSO-d_6, 400 MHz)

13C NMR ZC-5-90b in DMSO-d6

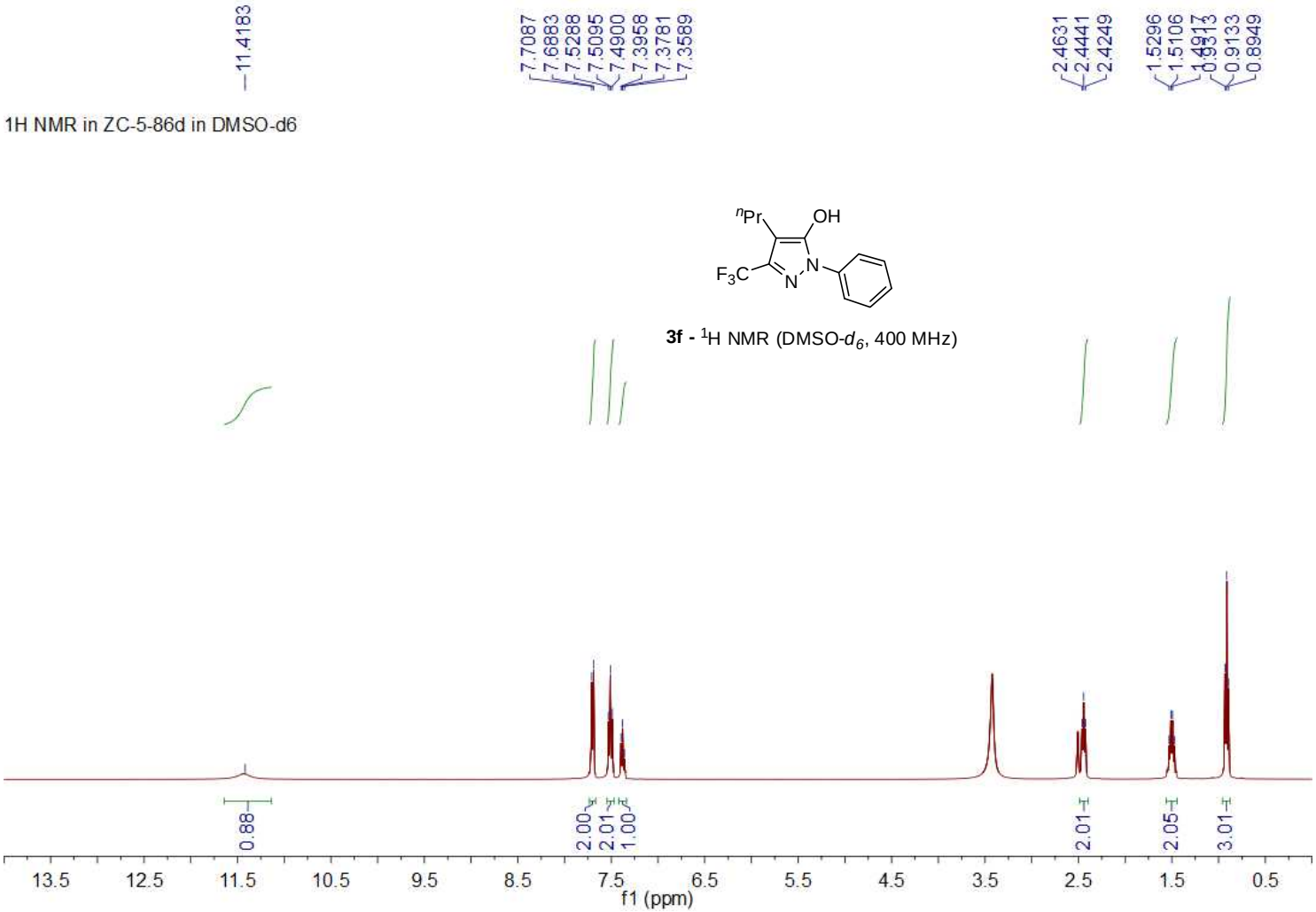


3e - ^{13}C NMR (DMSO-d_6, 100 MHz)

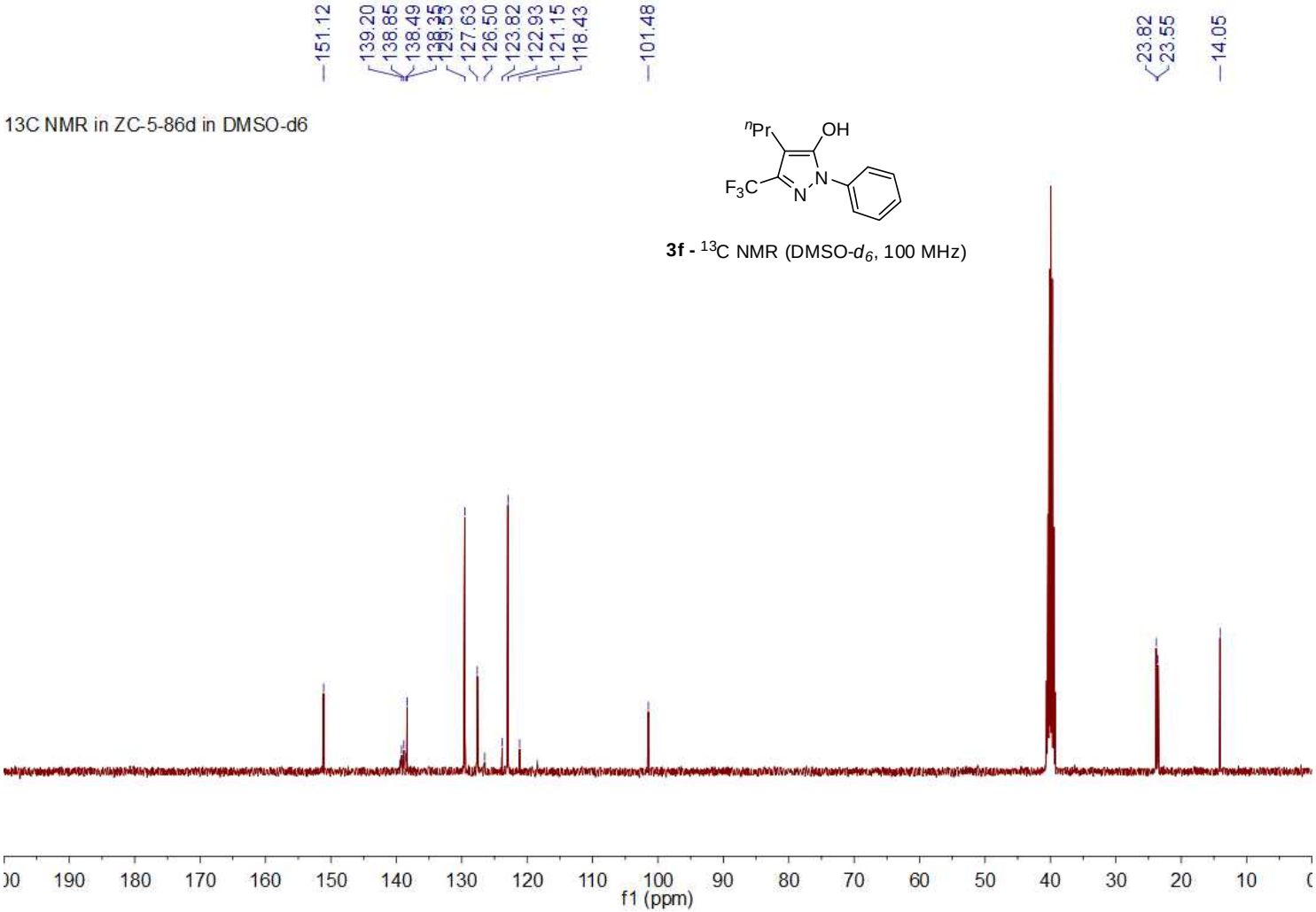




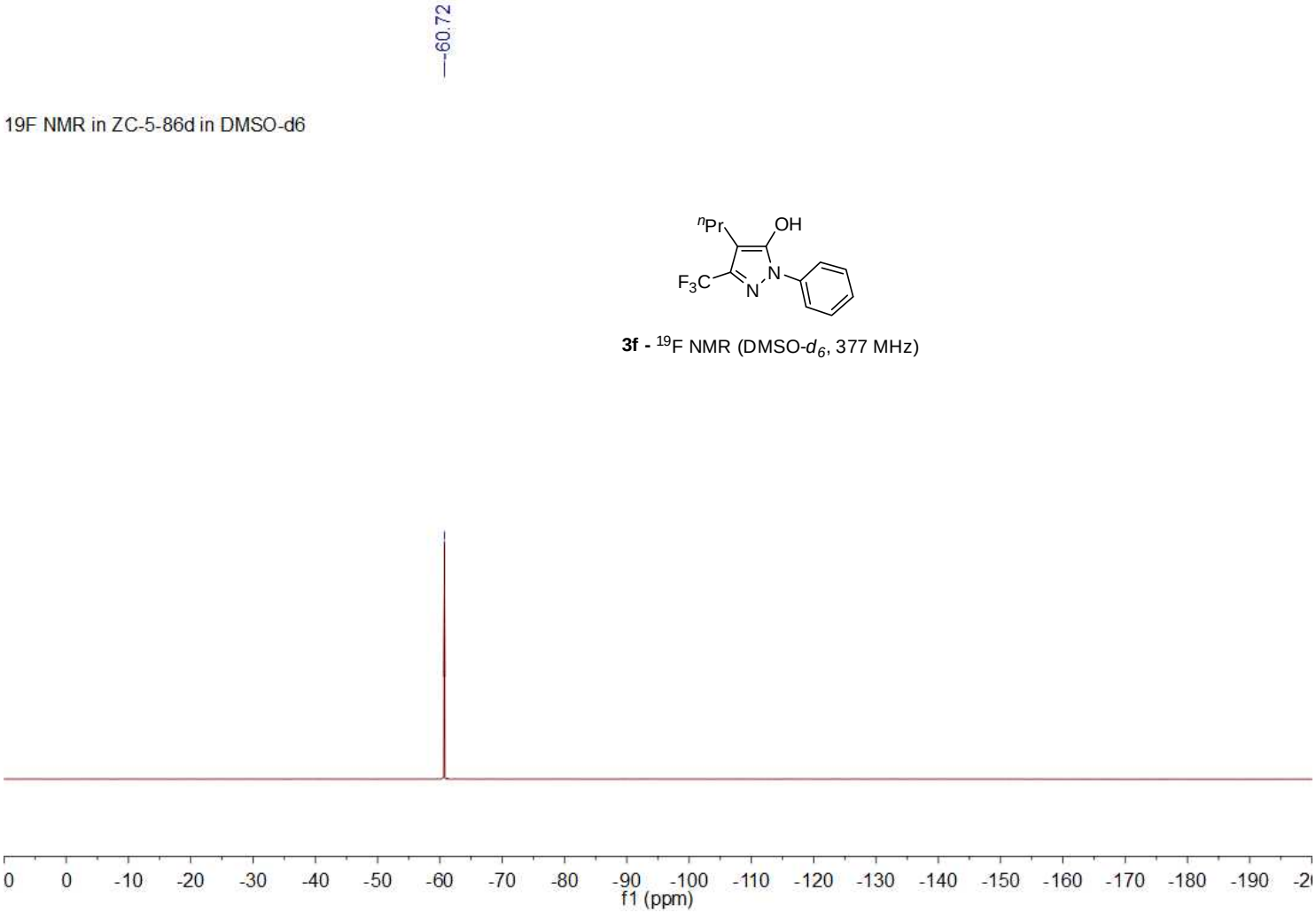
3e - ^{19}F NMR (DMSO-d_6, 377 MHz)



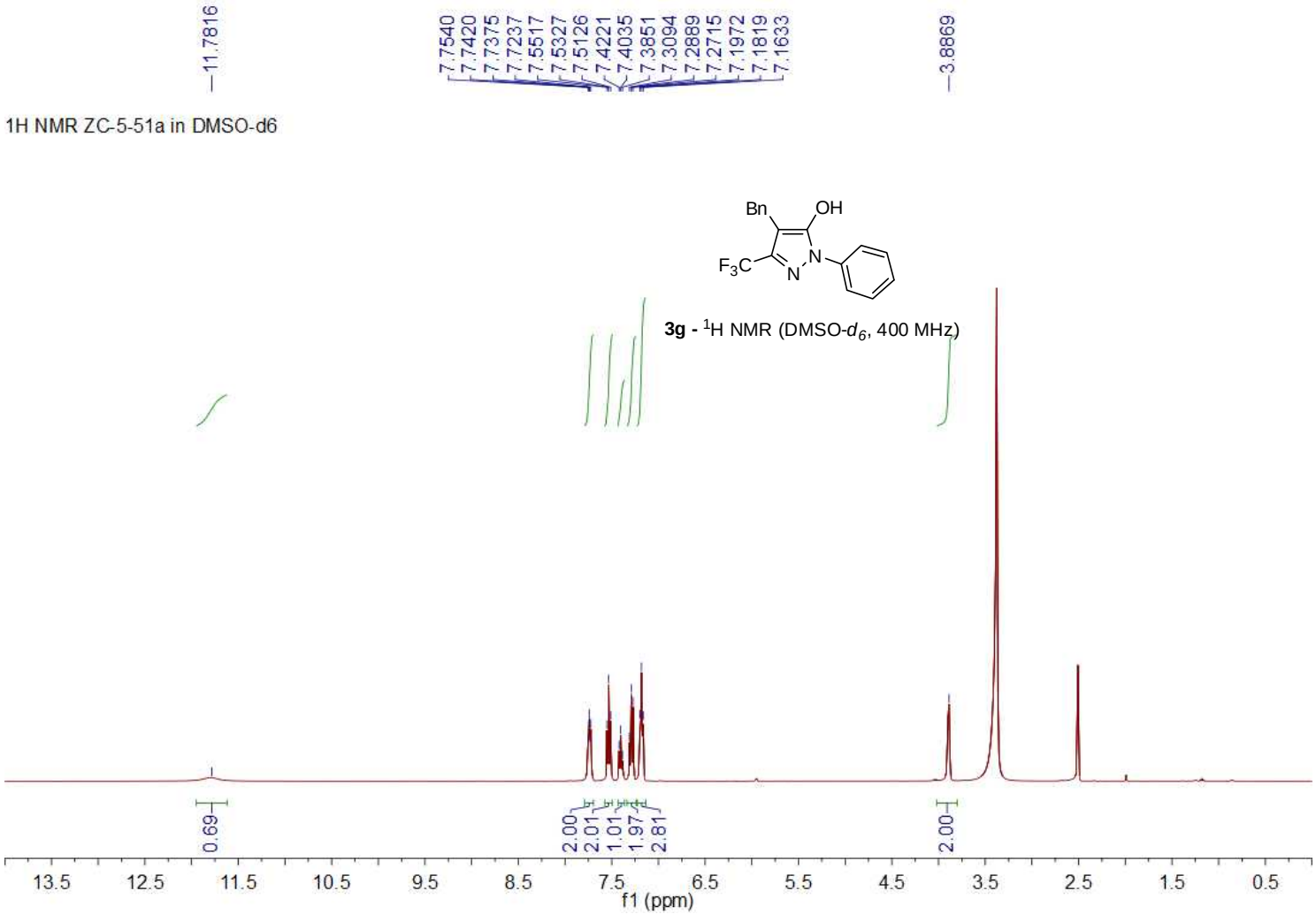
3f - ^{1}H NMR (DMSO-d_6, 400 MHz)

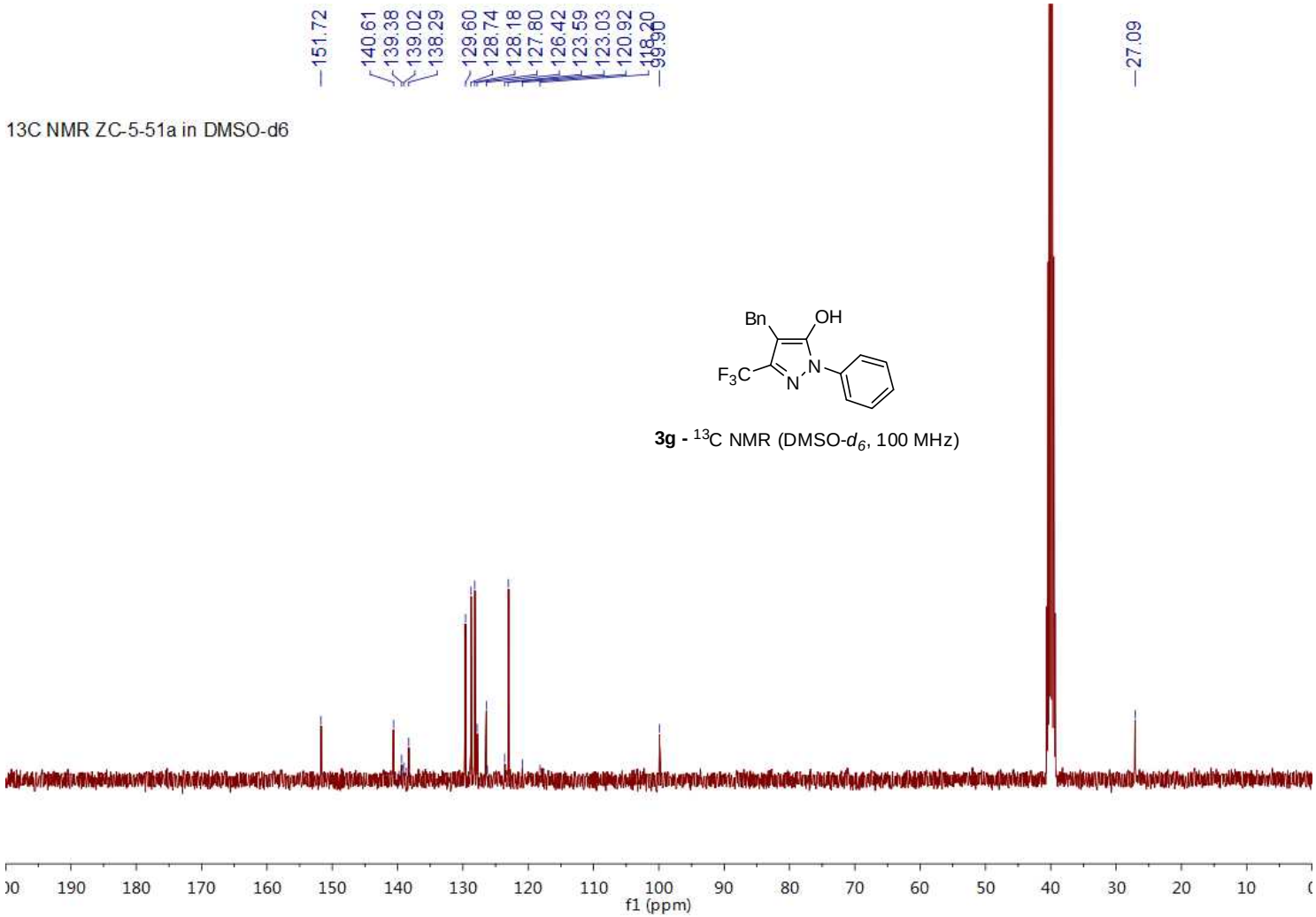


3f - ^{13}C NMR (DMSO-d_6, 100 MHz)

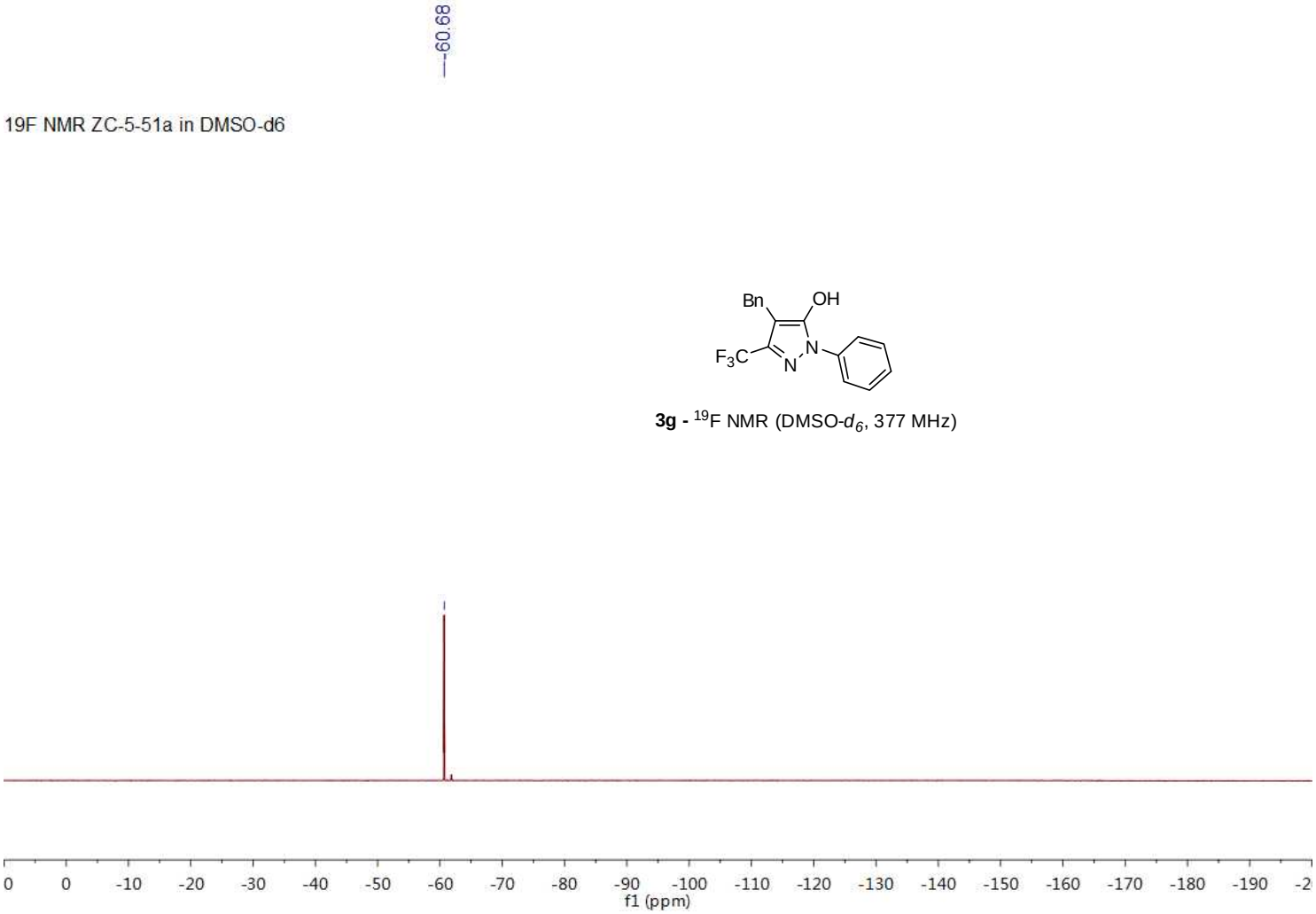


3f - ^{19}F NMR (DMSO-d_6, 377 MHz)

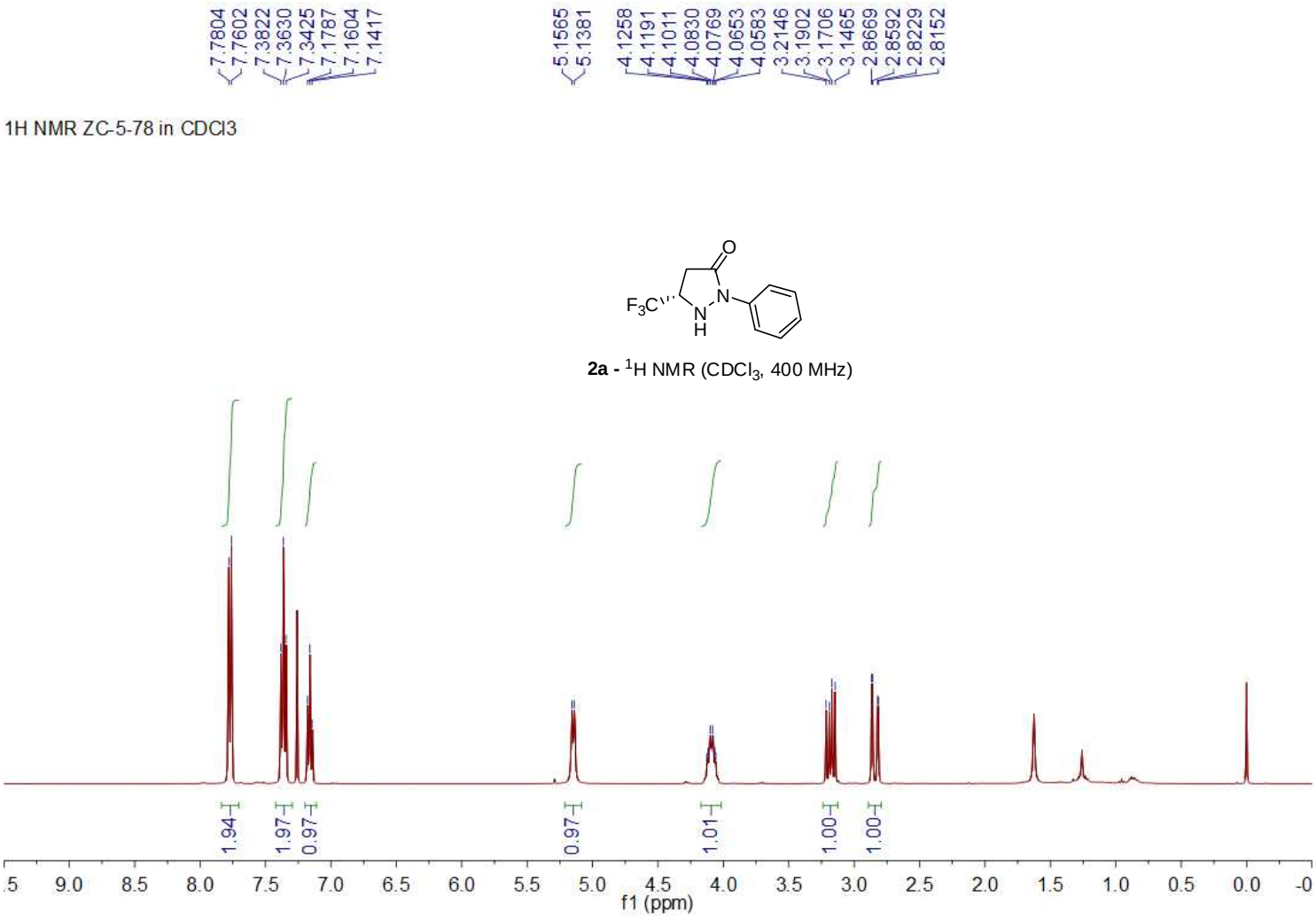

11.7816
7.7540
7.7420
7.7375
7.7237
7.5517
7.5327
7.5126
7.4221
7.4035
7.3851
7.3094
7.2889
7.2715
7.1972
7.1819
7.1633
3.8869
1H NMR ZC-5-51a in DMSO-d6
Bn
OH
F3C
N
N
3g - 1H NMR (DMSO-d6, 400 MHz)
0.69
2.00
2.01
1.01
1.97
2.81
2.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



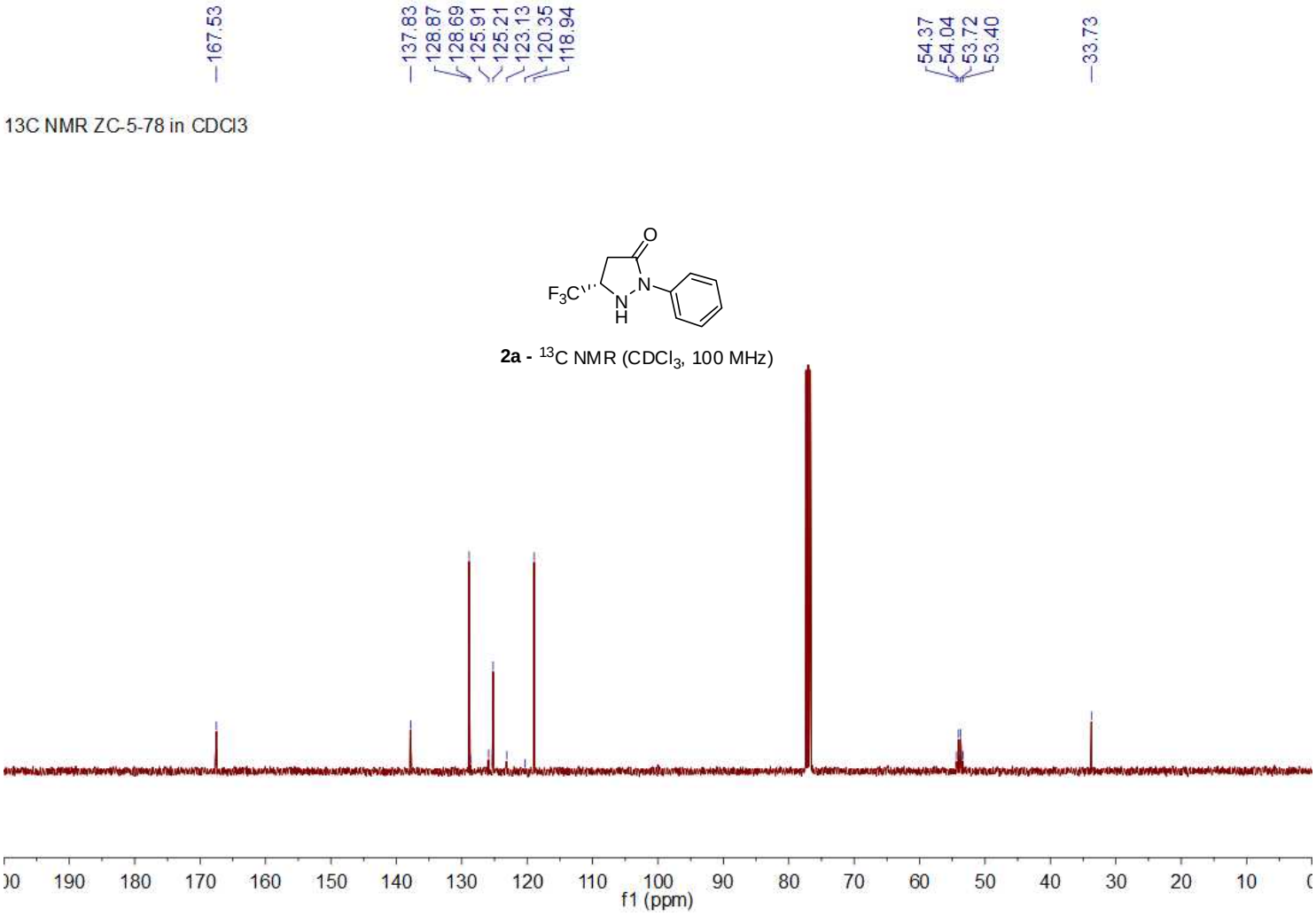
3g - ^{13}C NMR (DMSO-d_6, 100 MHz)



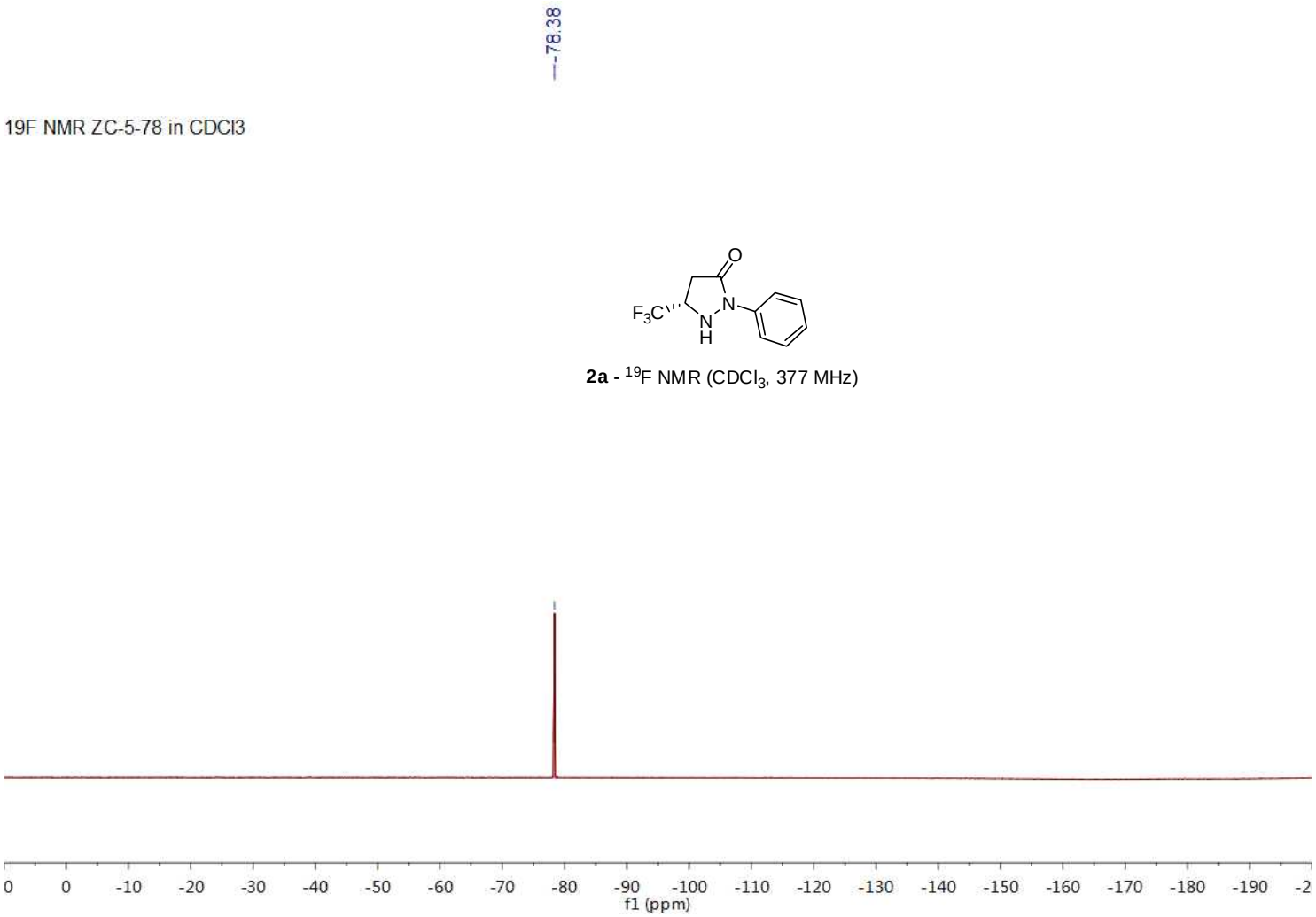
3g - ^{19}F NMR (DMSO-d_6, 377 MHz)



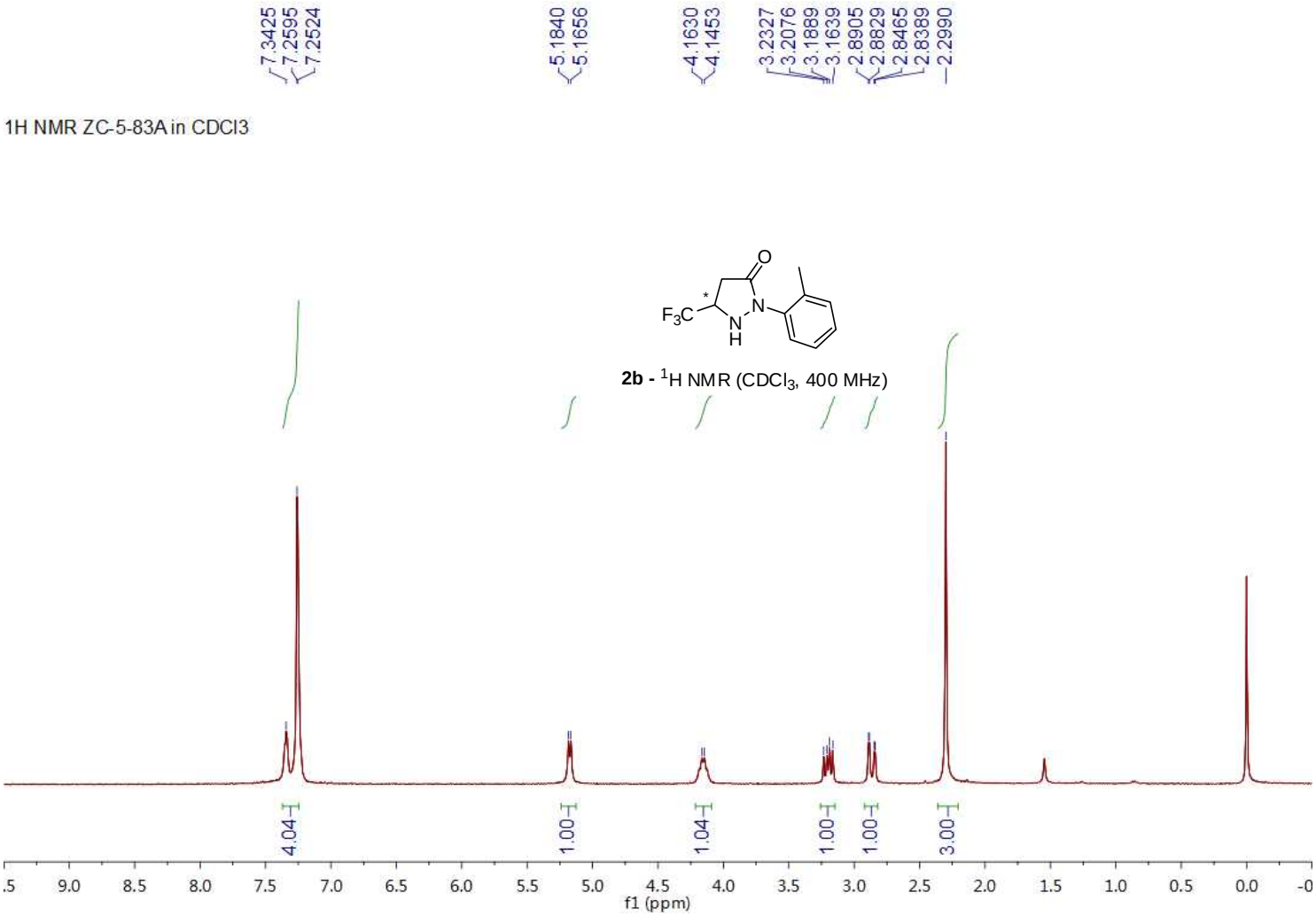
2a - ^{1}H NMR ($CDCl_3$, 400 MHz)



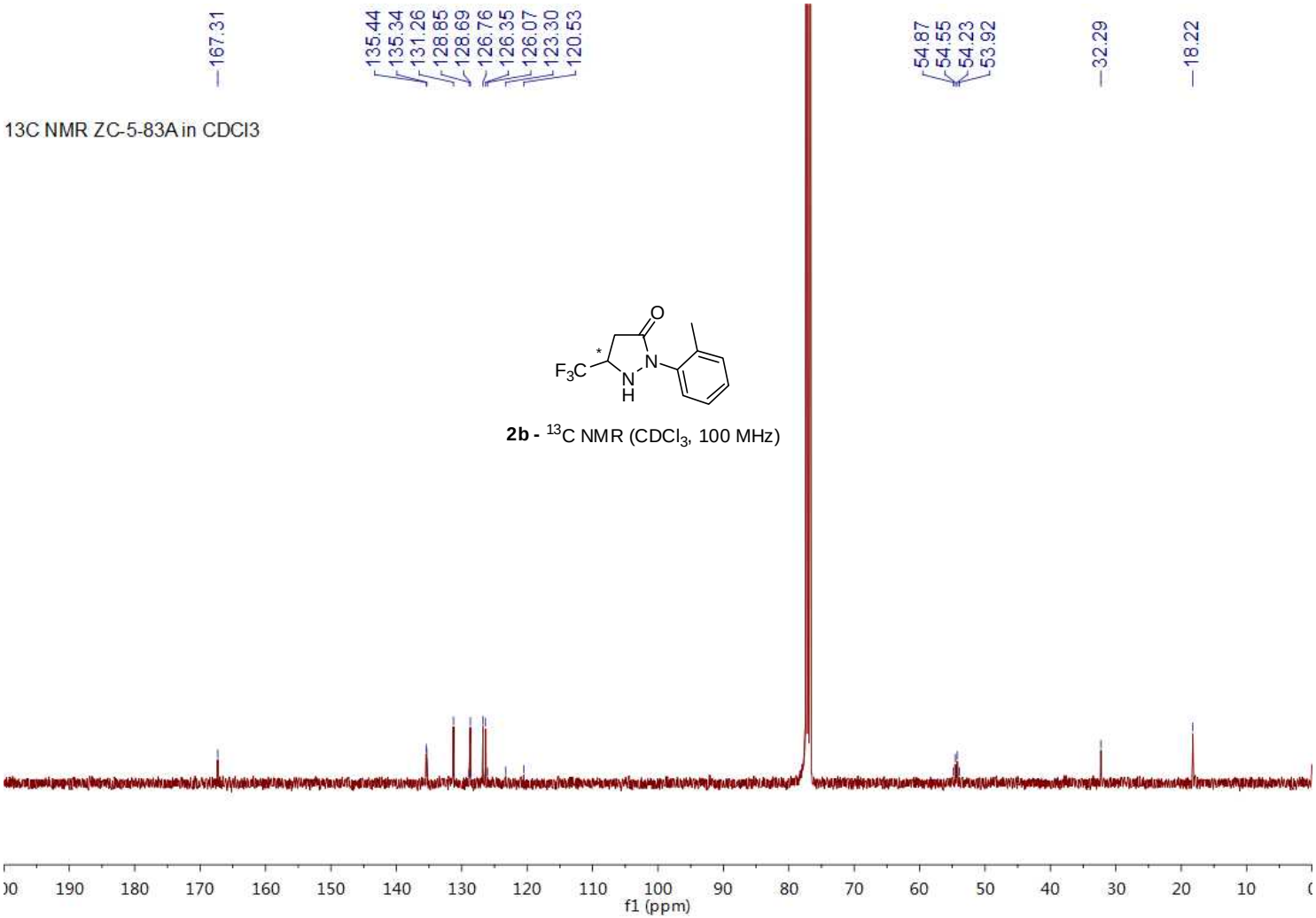
2a - ^{13}C NMR ($CDCl_3$, 100 MHz)



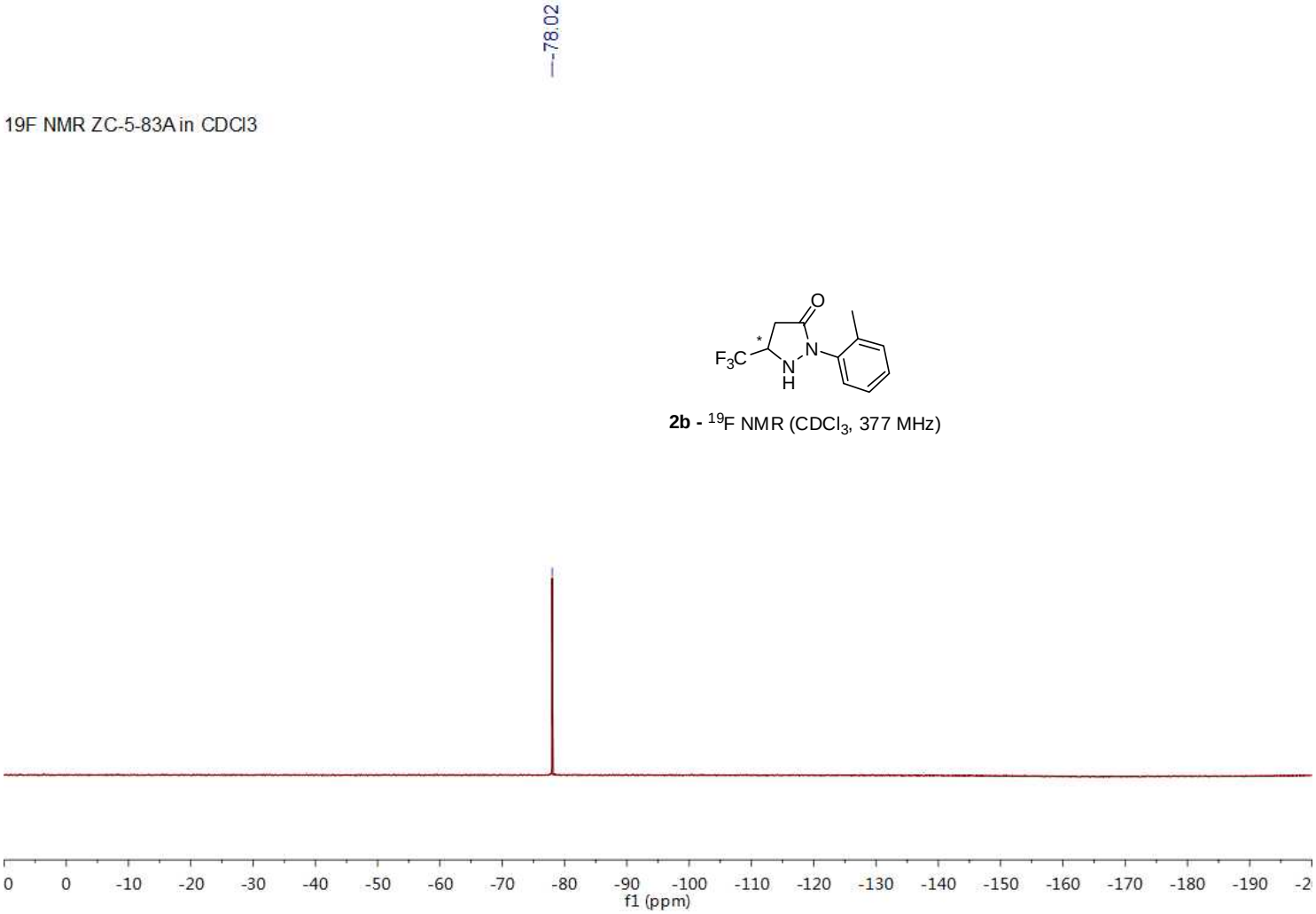
2a - ^{19}F NMR ($CDCl_3$, 377 MHz)



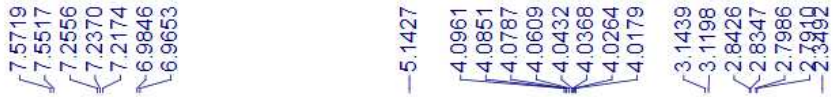
2b - ^{1}H NMR ($CDCl_3$, 400 MHz)



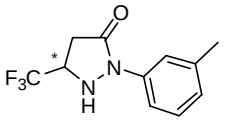
2b - ^{13}C NMR ($CDCl_3$, 100 MHz)



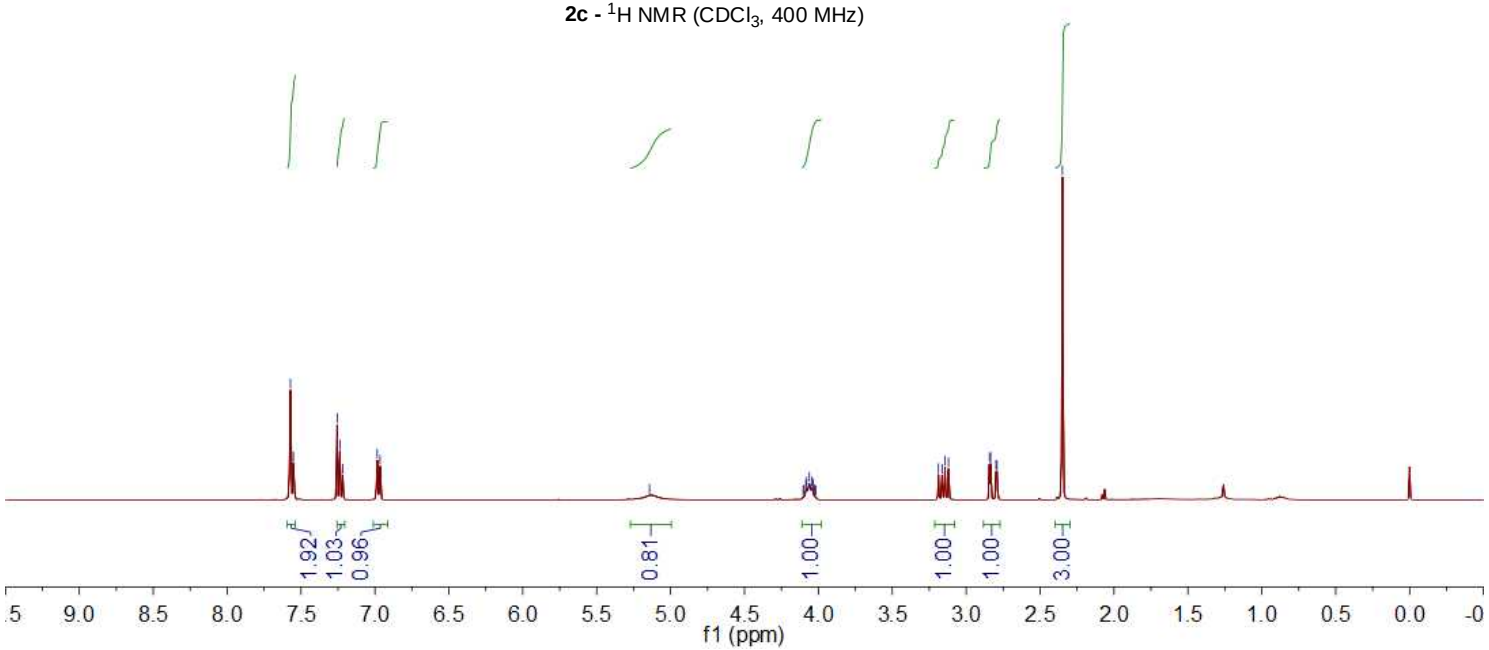
2b - ^{19}F NMR ($CDCl_3$, 377 MHz)

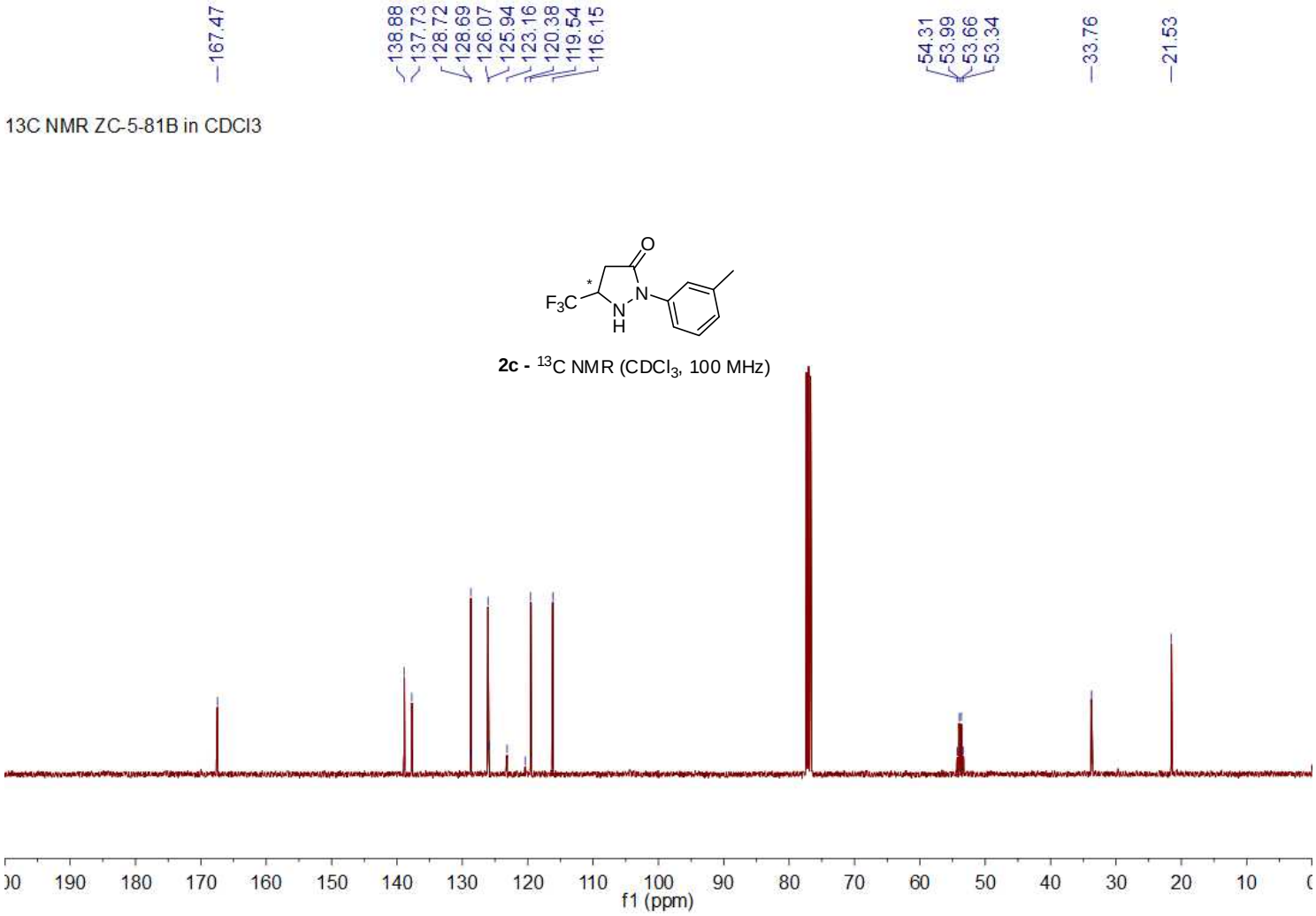


1H NMR ZC-5-81B in CDCl3

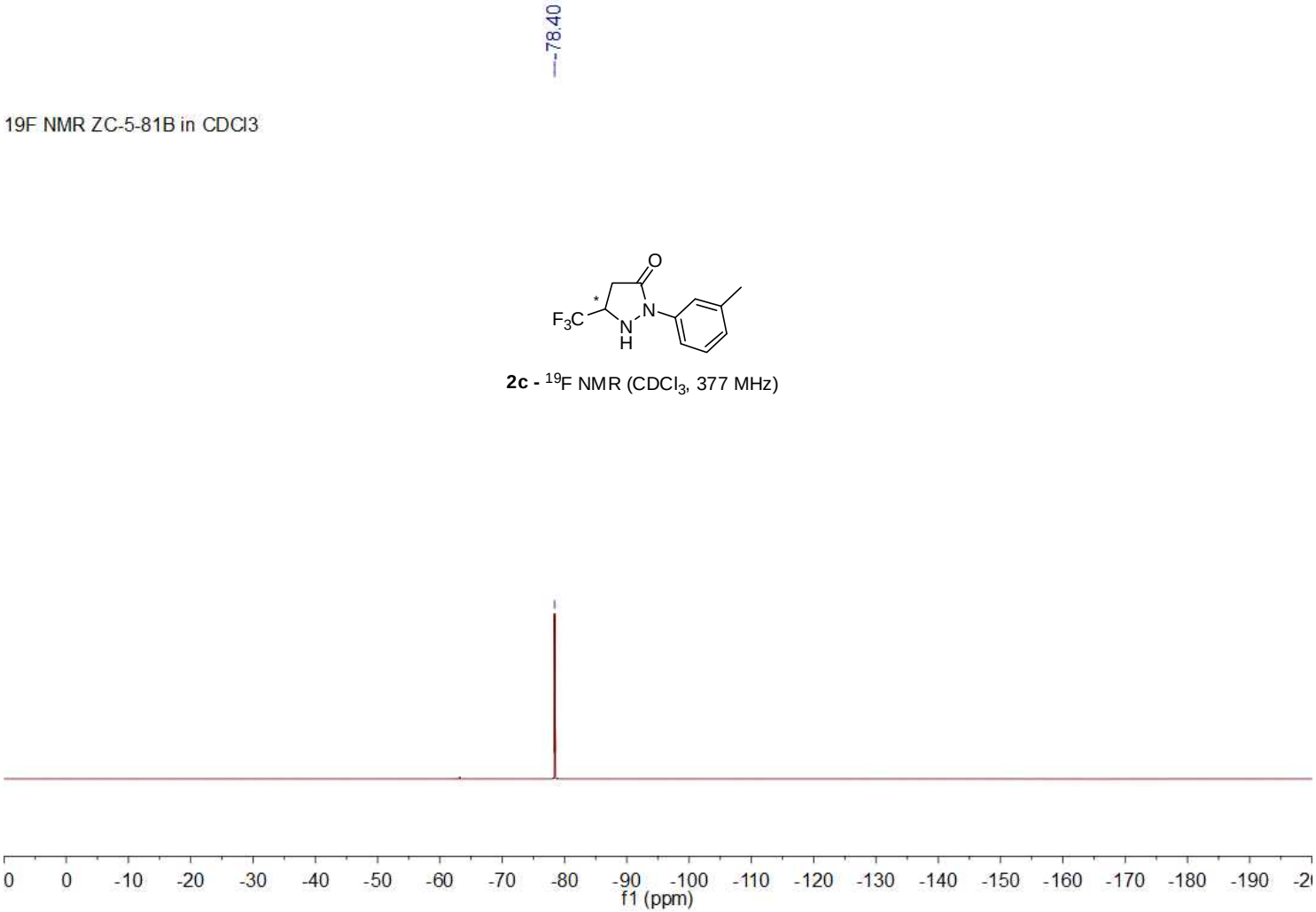


2c - ^{1}H NMR ($CDCl_3$, 400 MHz)

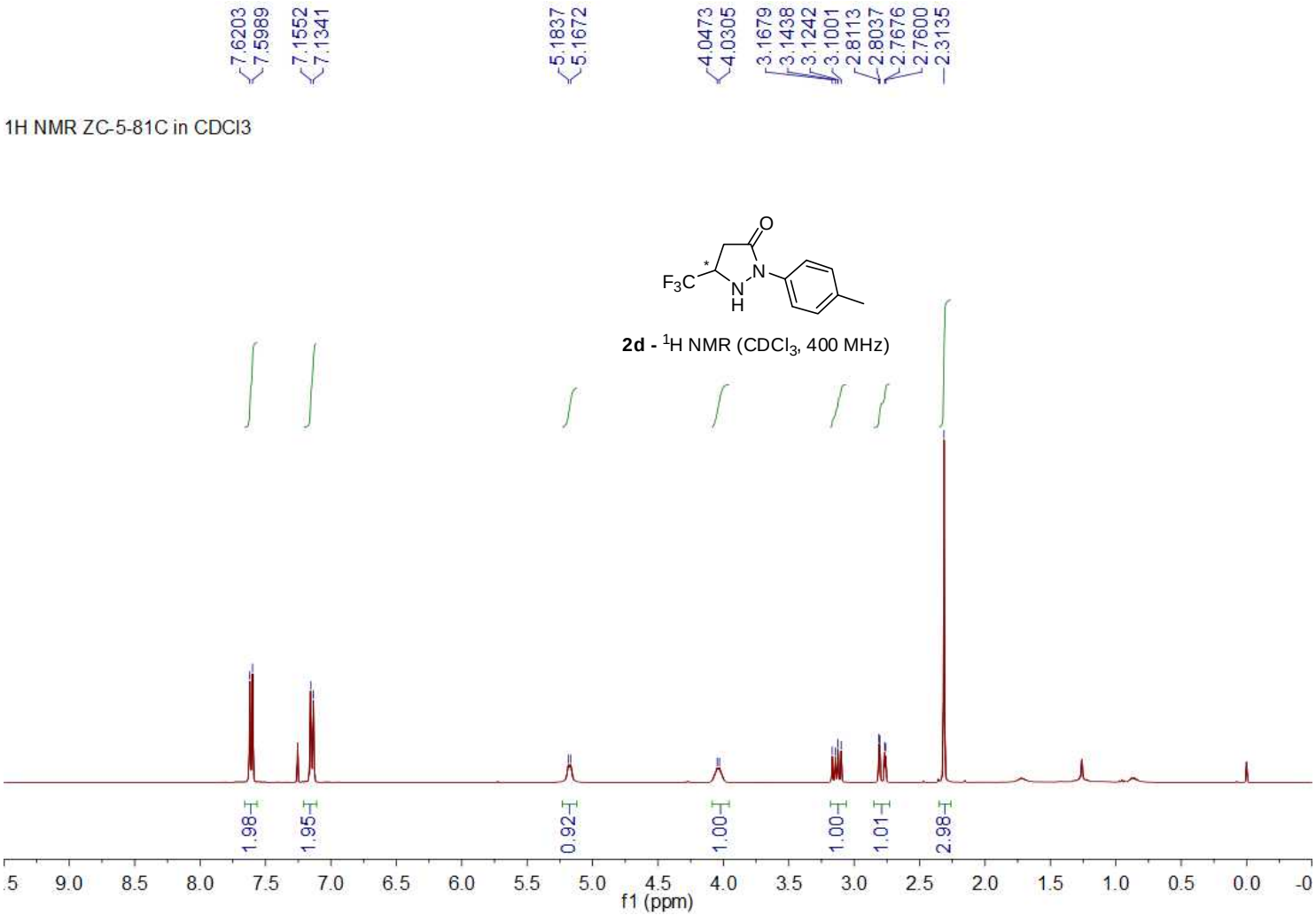




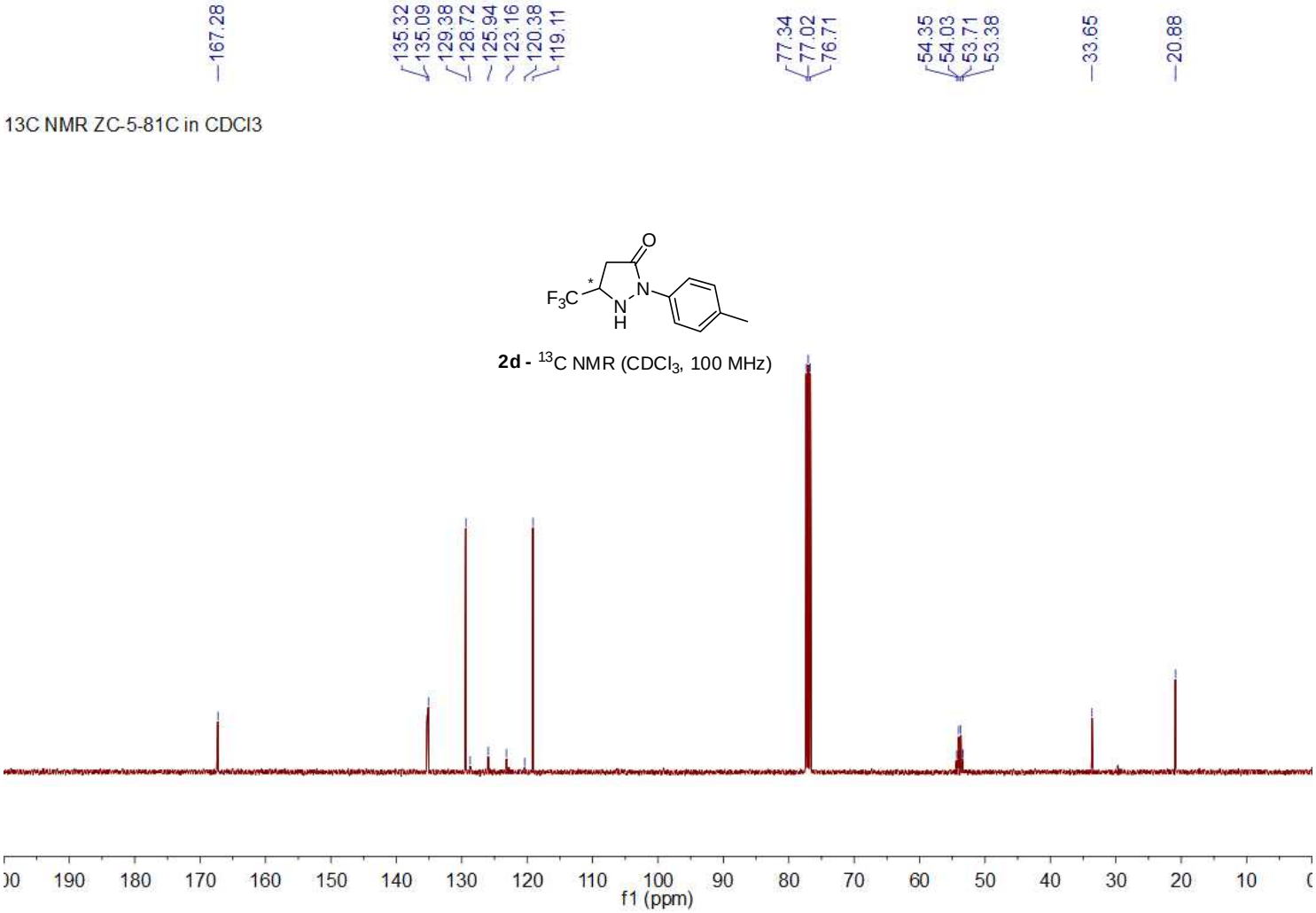
2c - ^{13}C NMR ($CDCl_3$, 100 MHz)



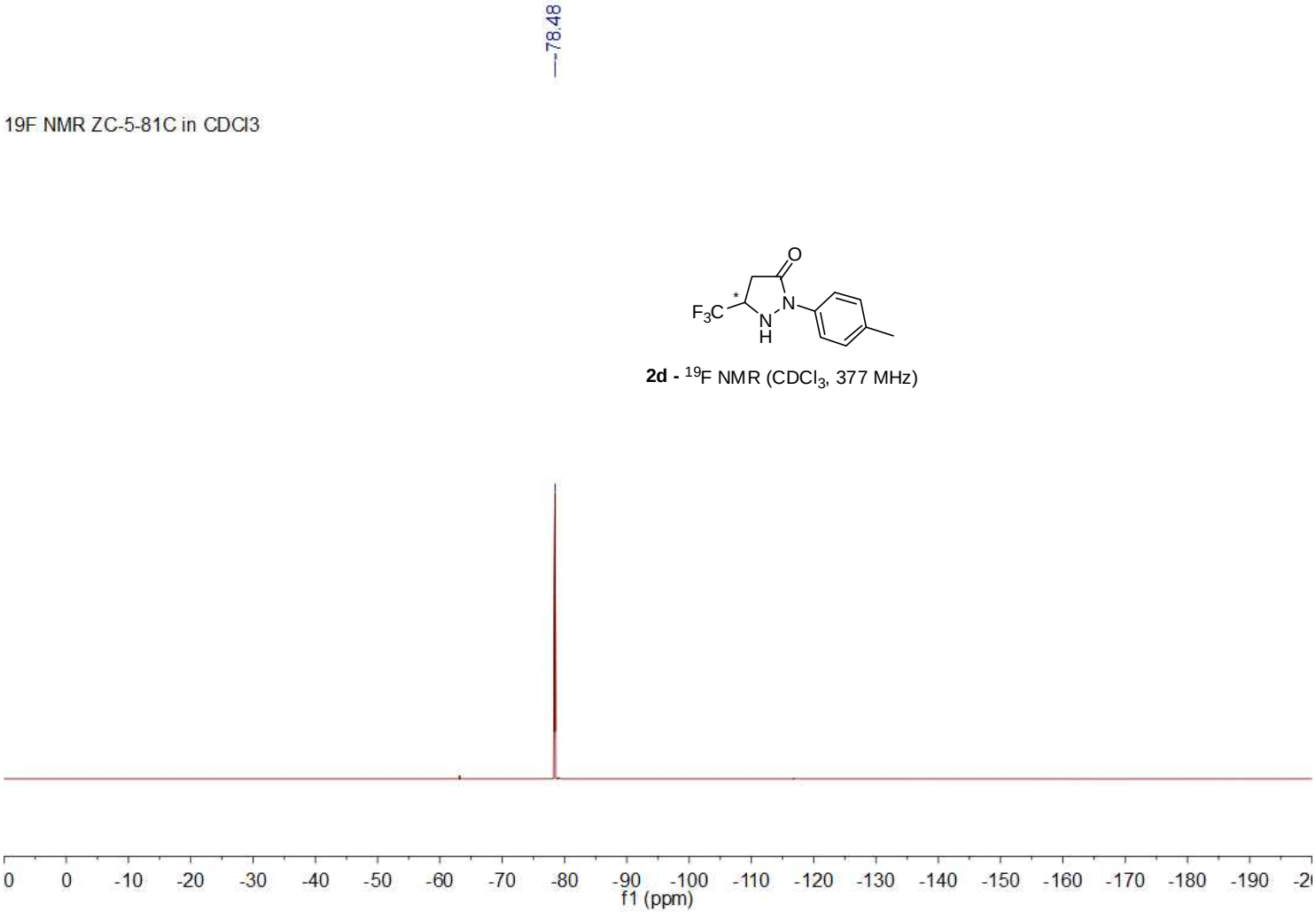
2c - ^{19}F NMR ($CDCl_3$, 377 MHz)



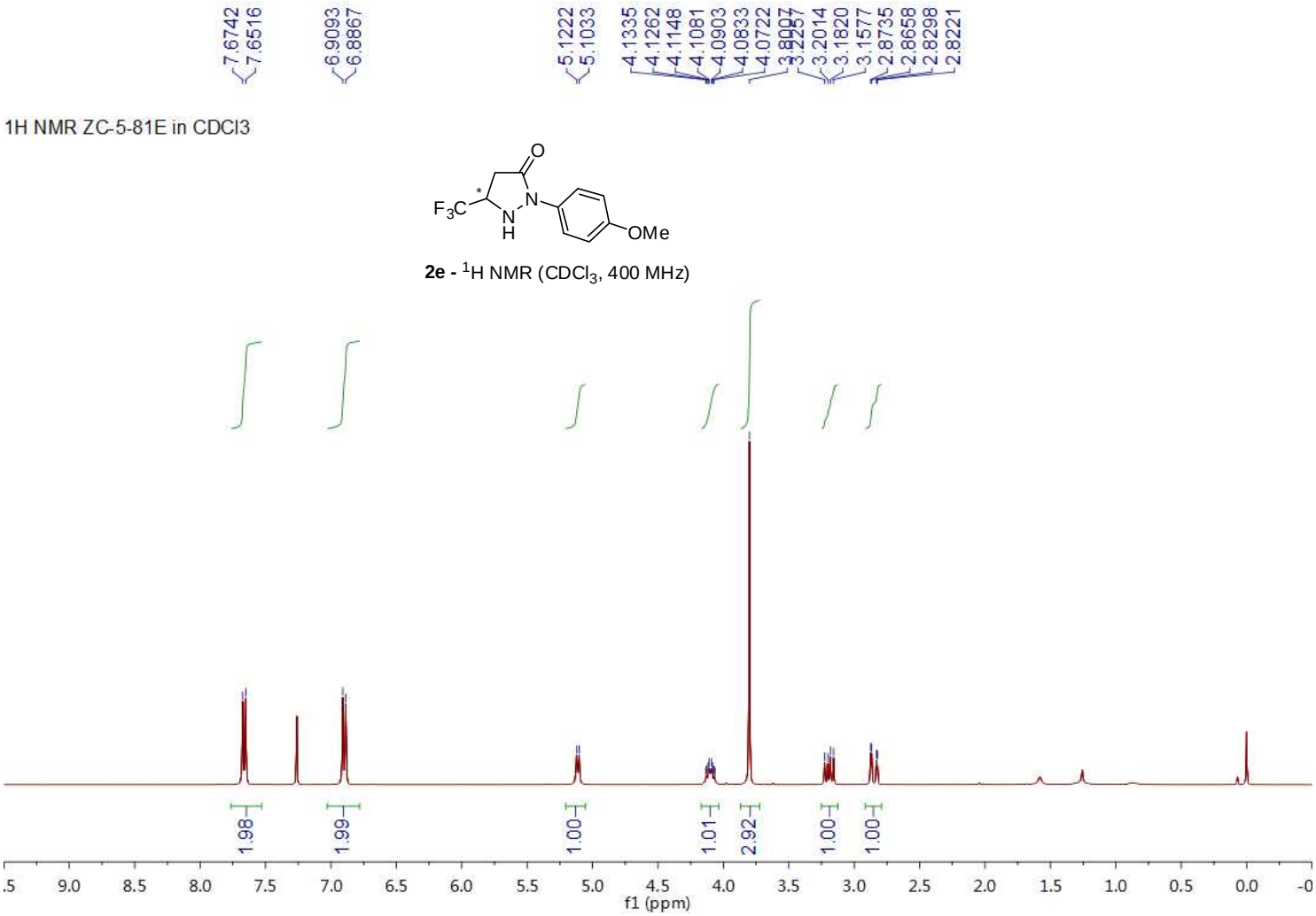
2d - ^{1}H NMR ($CDCl_3$, 400 MHz)



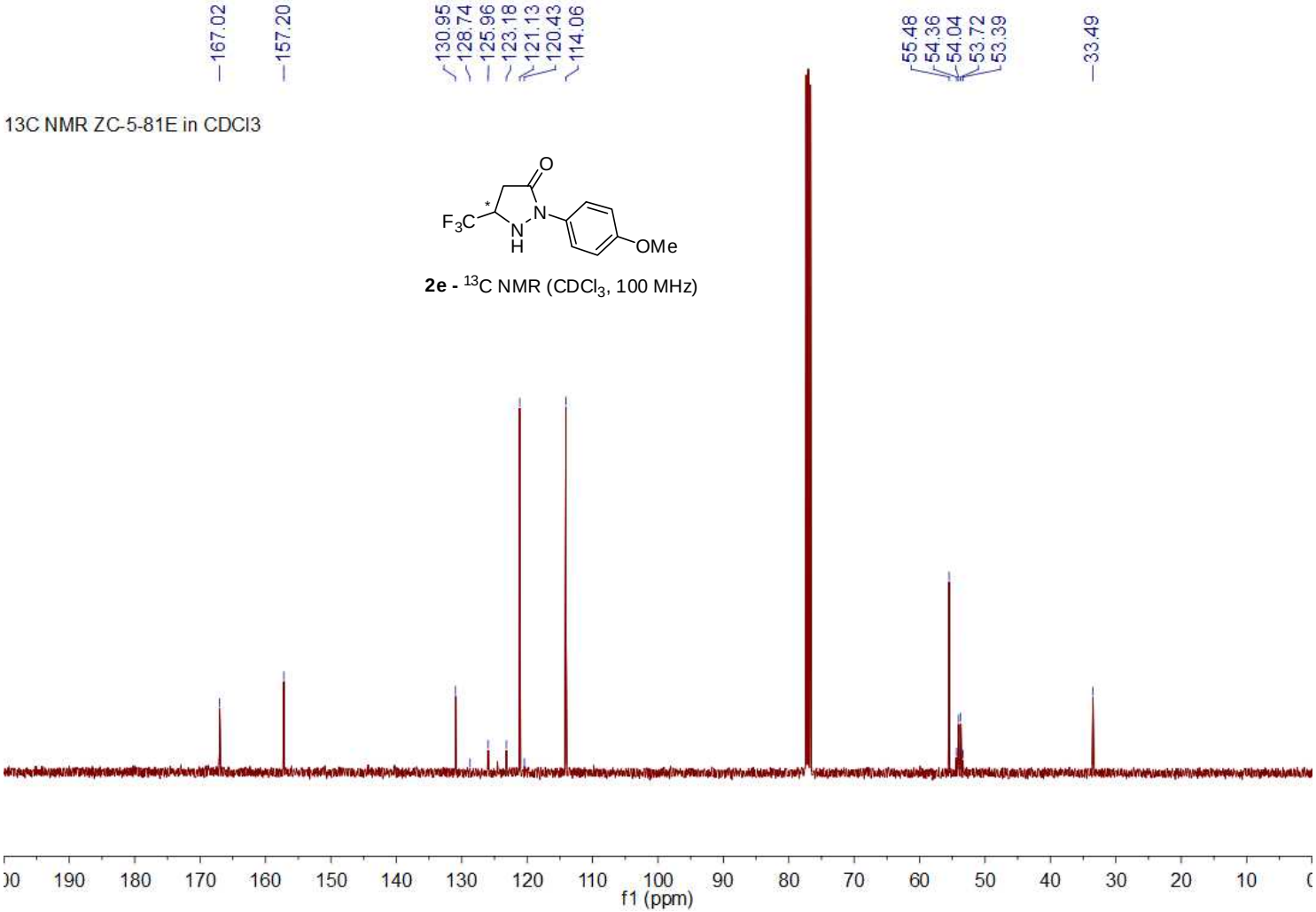
2d - ^{13}C NMR ($CDCl_3$, 100 MHz)



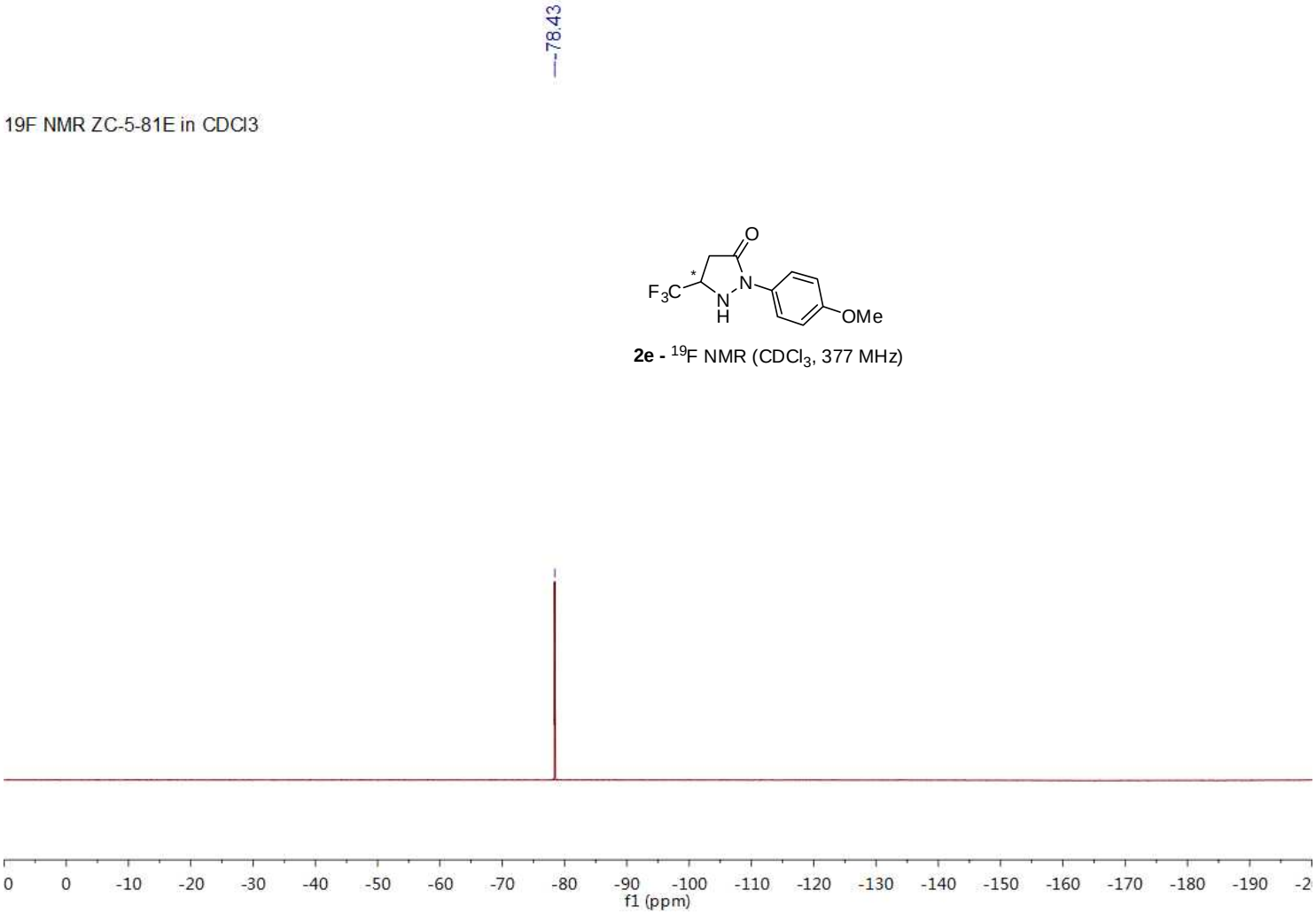
2d - ^{19}F NMR ($CDCl_3$, 377 MHz)



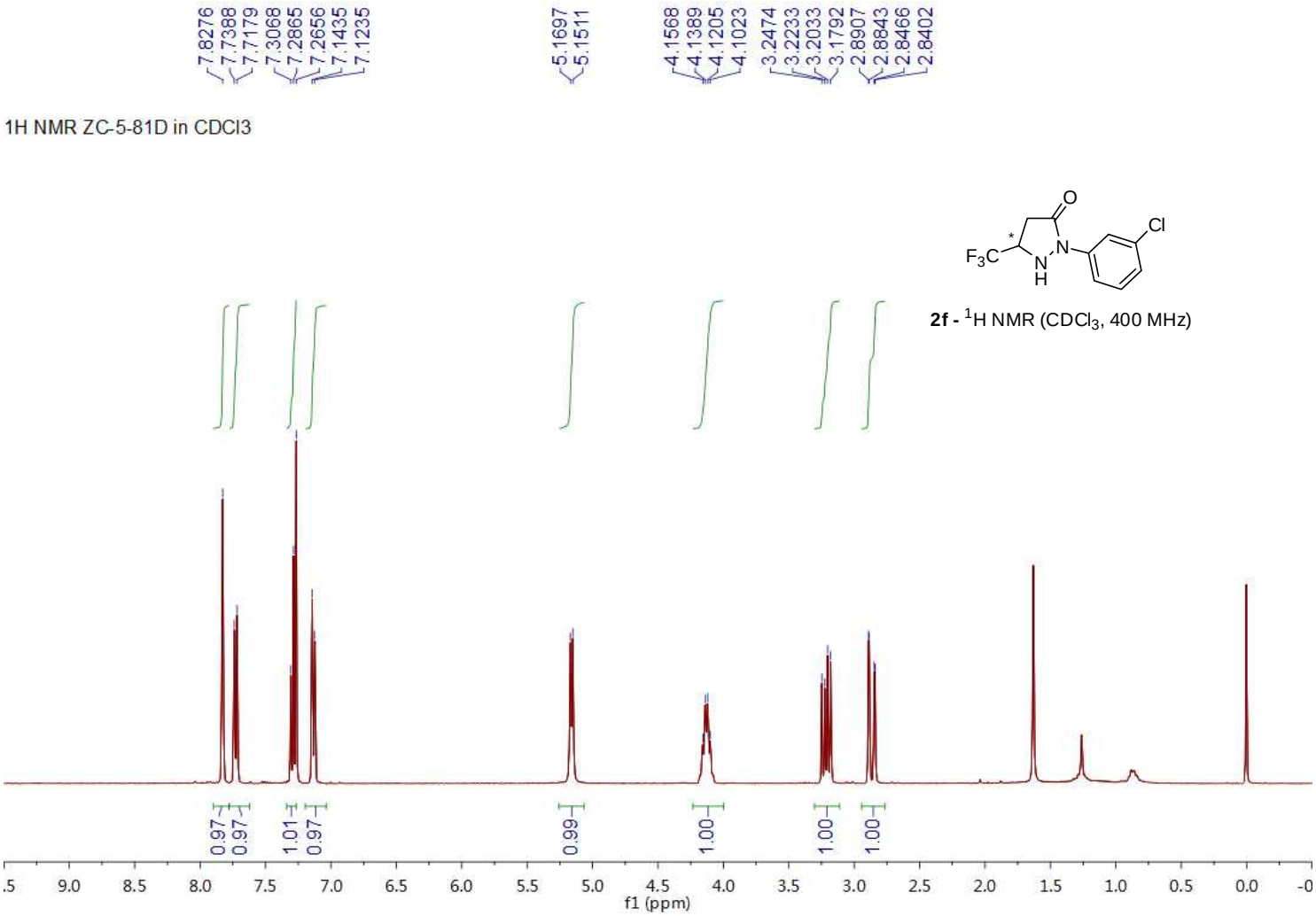
2e - ^{1}H NMR ($CDCl_3$, 400 MHz)



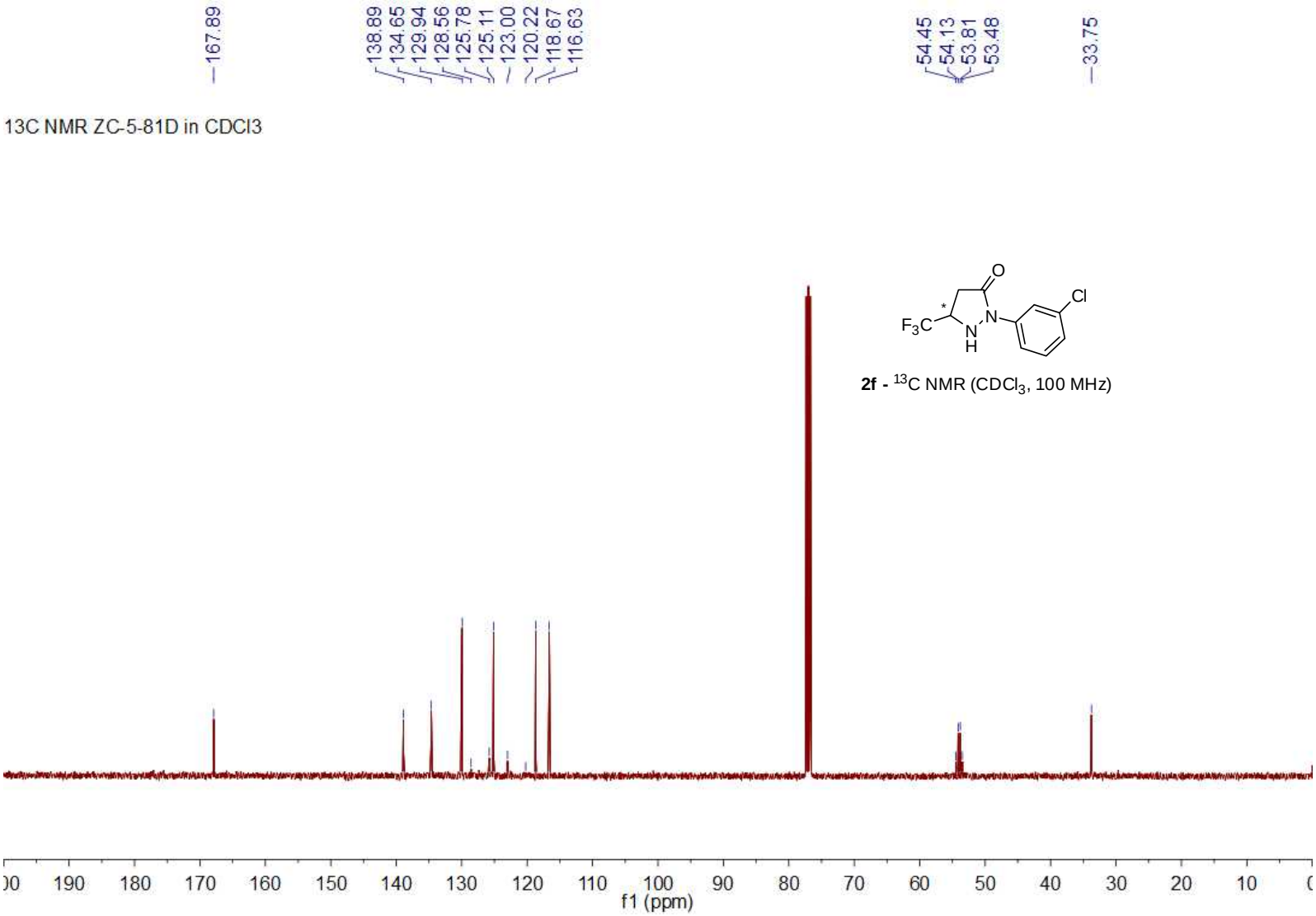
2e - ^{13}C NMR ($CDCl_3$, 100 MHz)



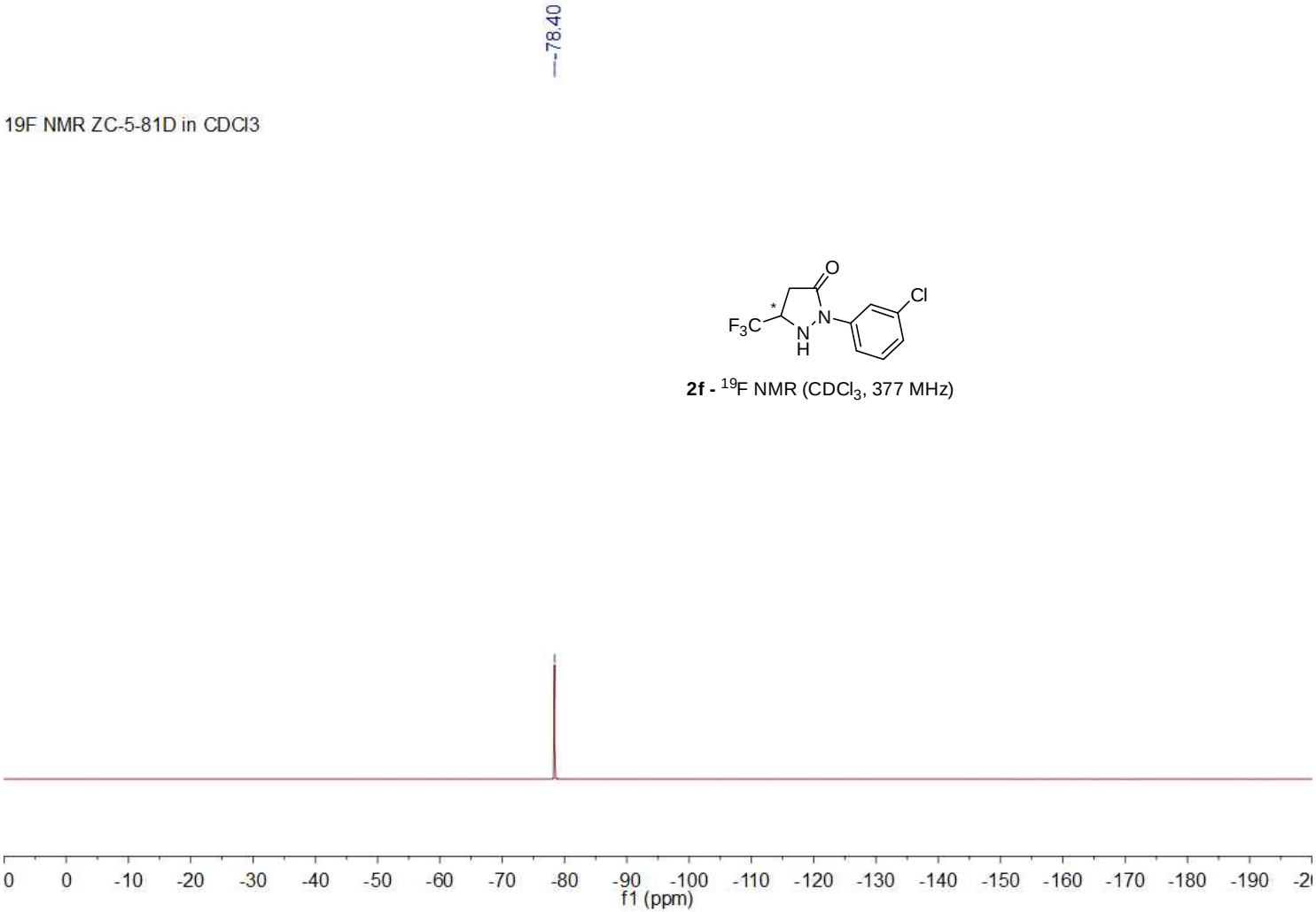
2e - ^{19}F NMR ($CDCl_3$, 377 MHz)



2f - ^{1}H NMR ($CDCl_3$, 400 MHz)

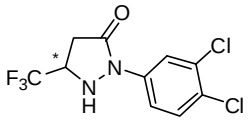


2f - ^{13}C NMR ($CDCl_3$, 100 MHz)

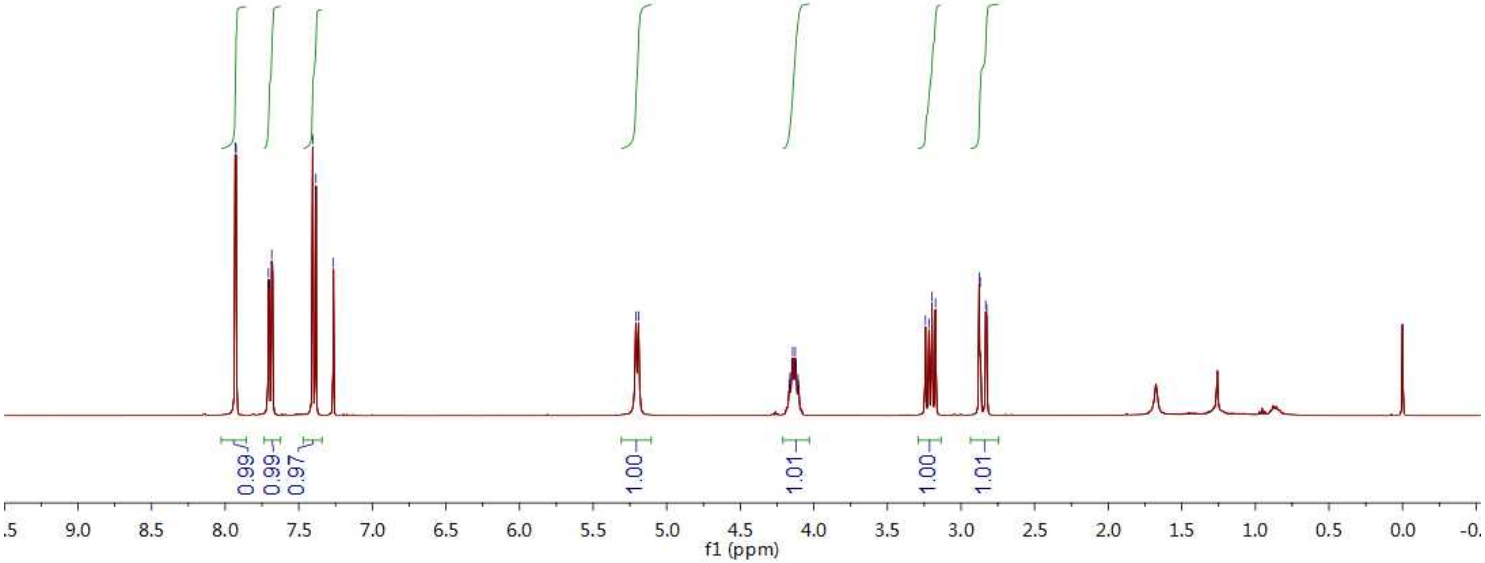


2f - ^{19}F NMR ($CDCl_3$, 377 MHz)

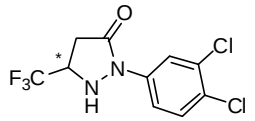
1H NMR ZC-5-83D in CDCl3



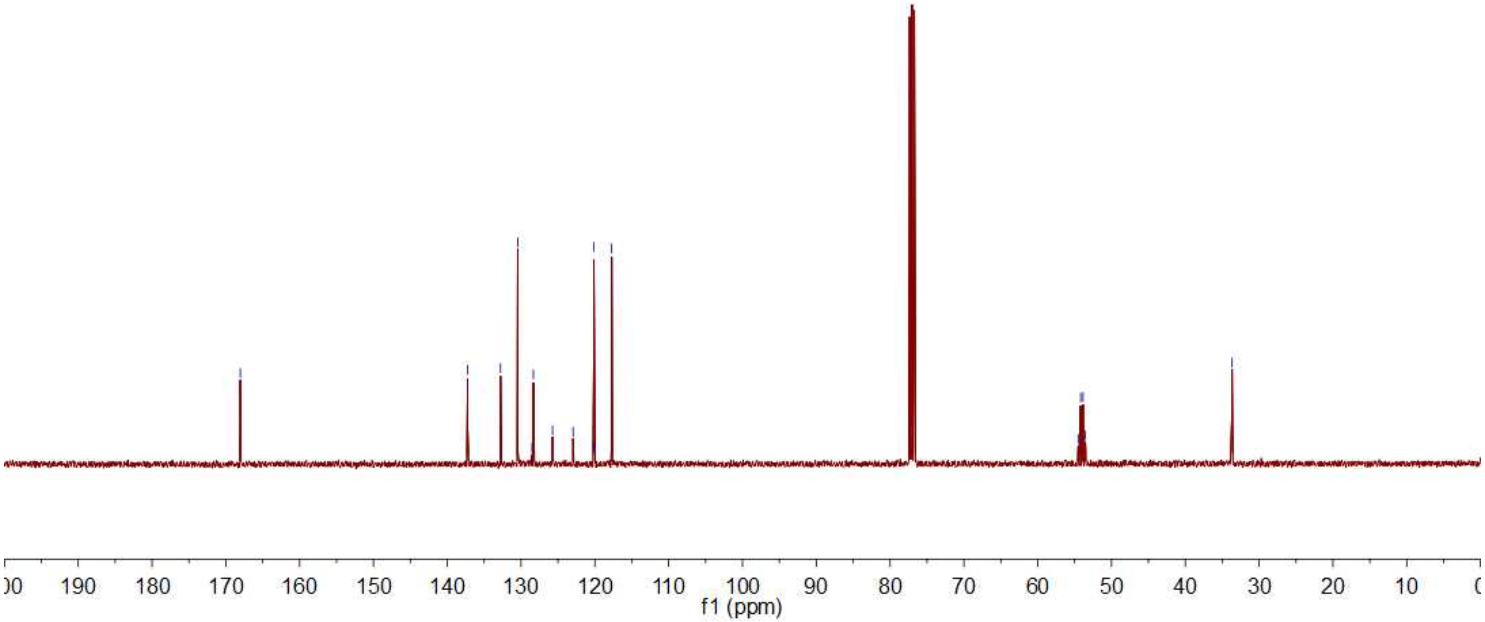
2g - ^{1}H NMR ($CDCl_3$, 400 MHz)

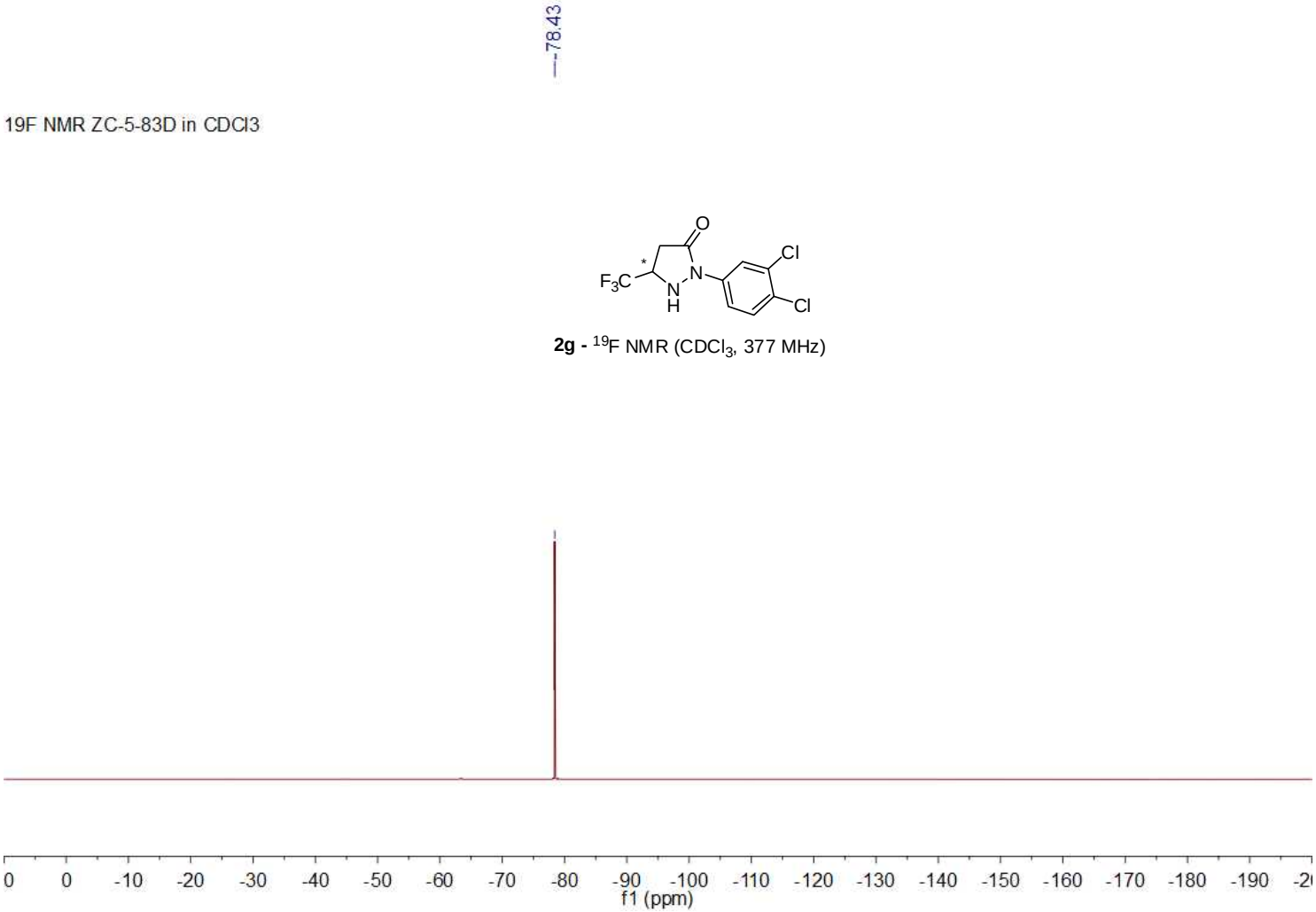


13C NMR ZC-5-83D in DMSO-d6

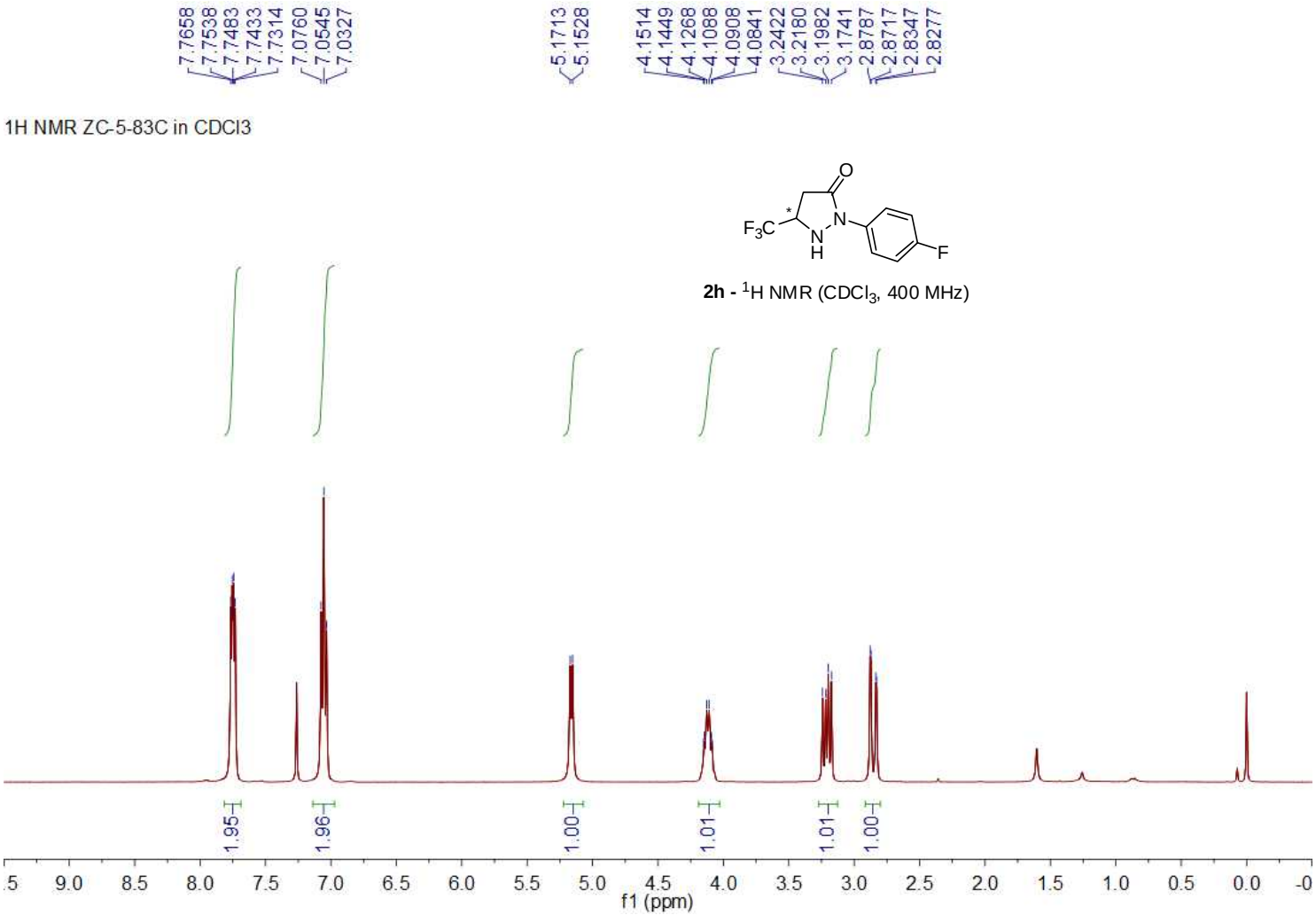


2g - ^{13}C NMR ($CDCl_3$, 100 MHz)

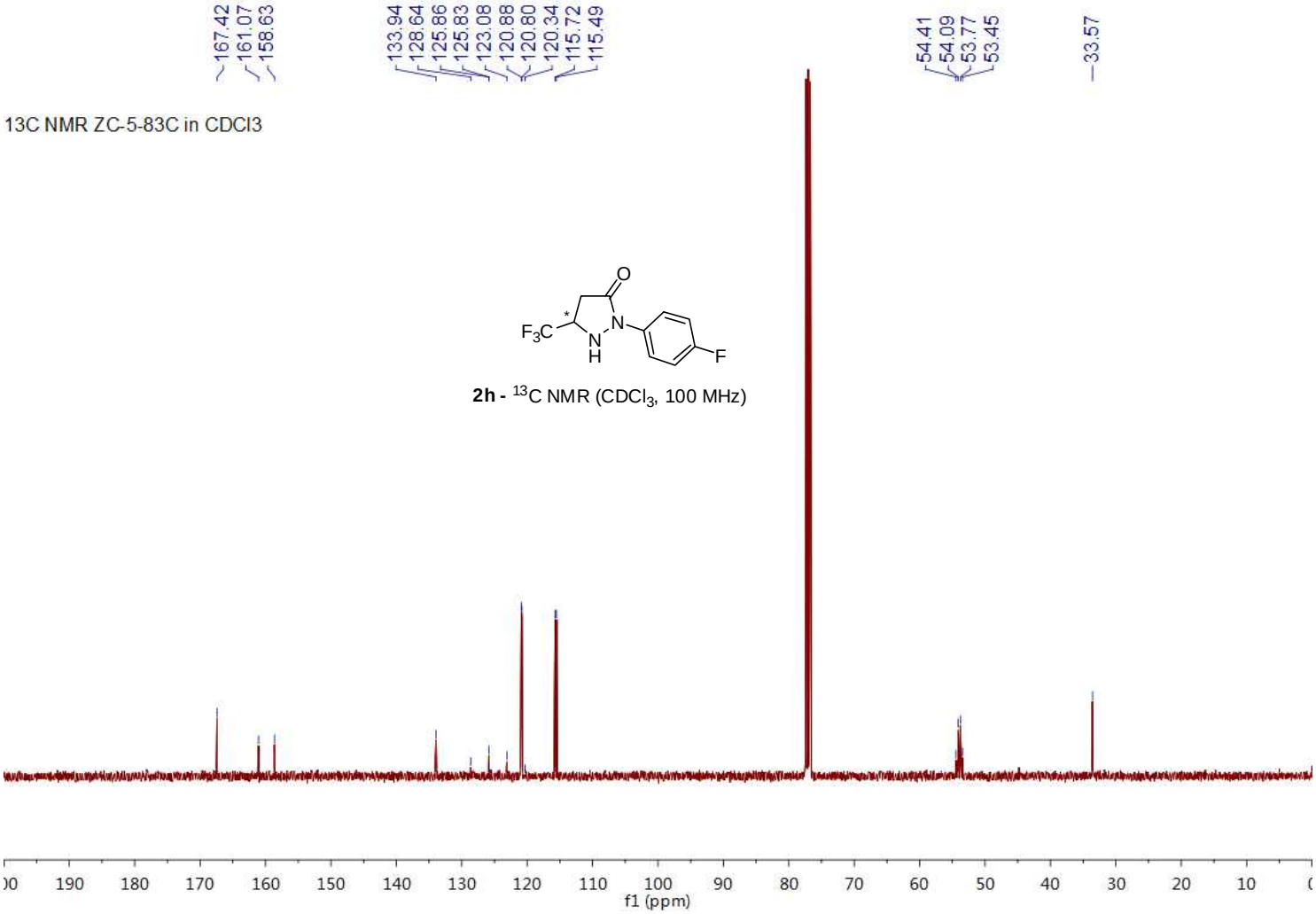




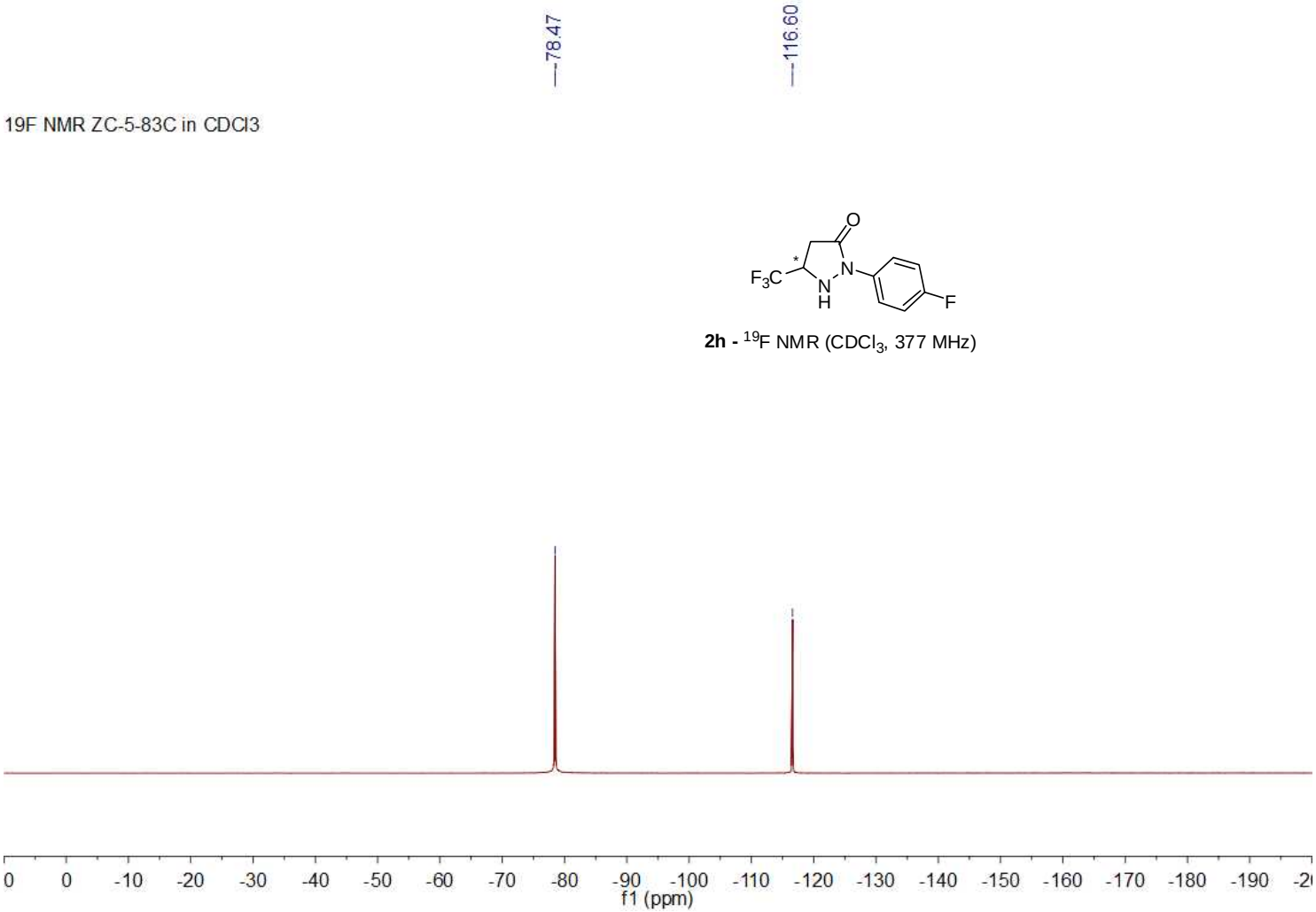
2g - ^{19}F NMR ($CDCl_3$, 377 MHz)



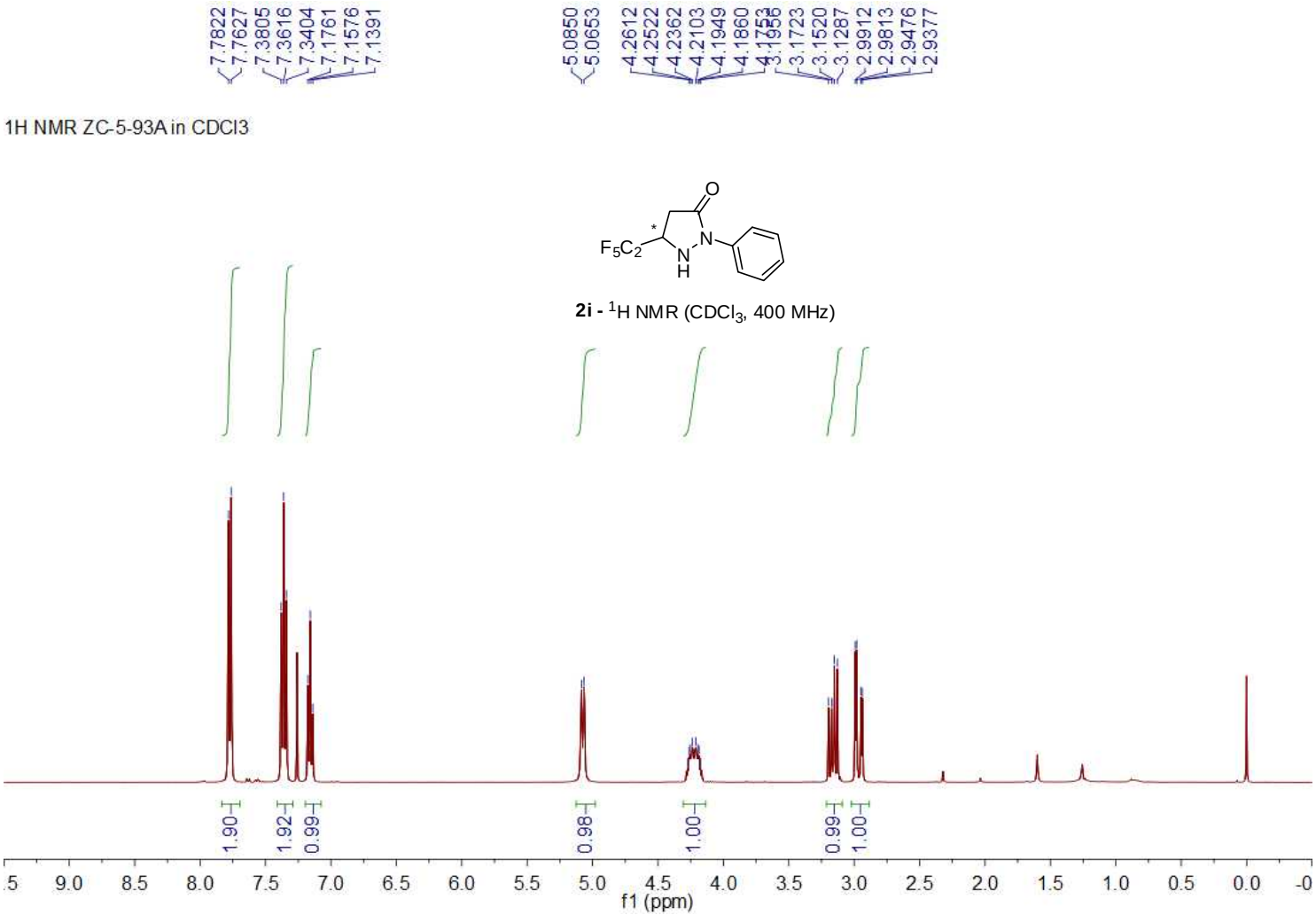
2h - ^{1}H NMR ($CDCl_3$, 400 MHz)



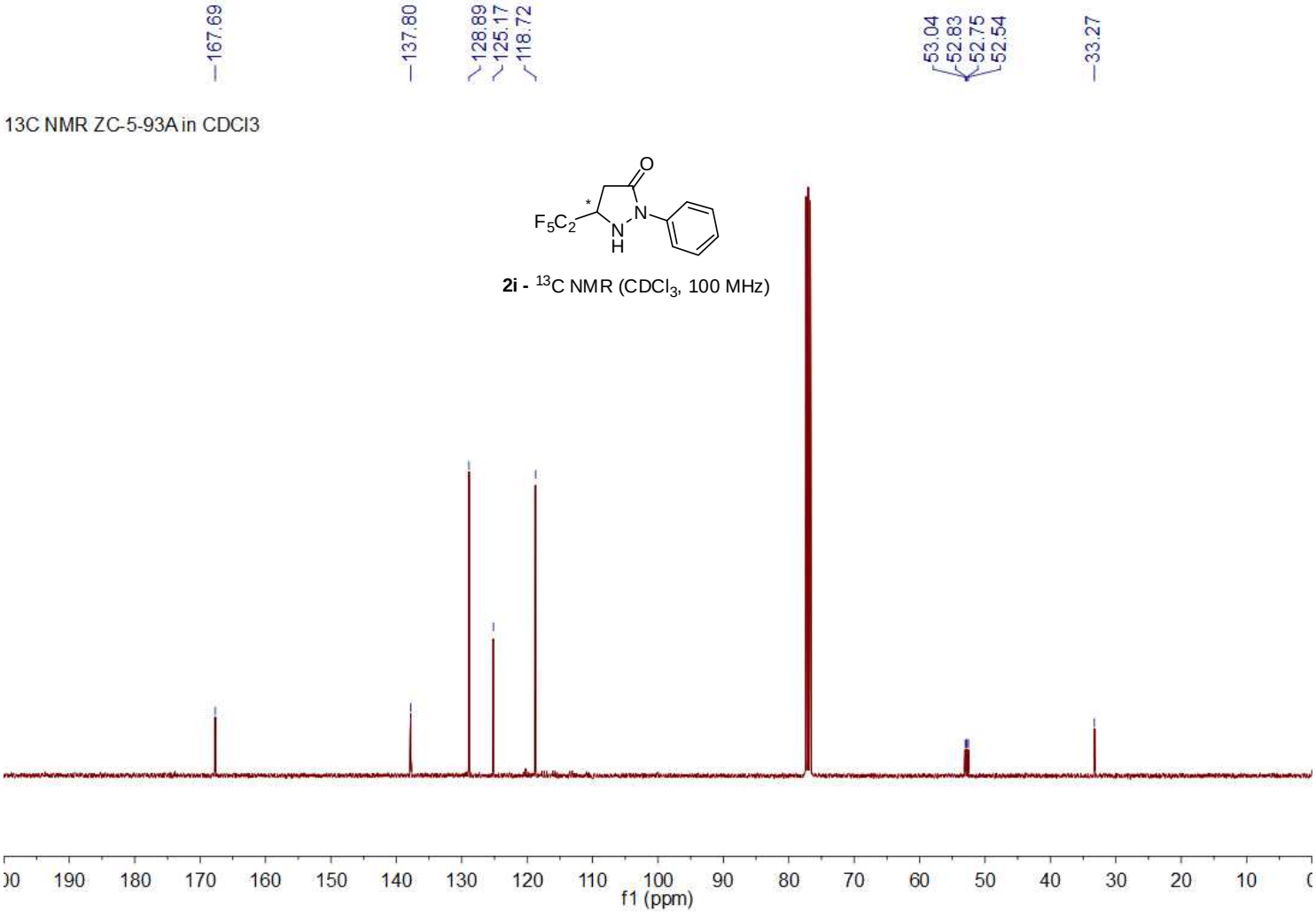
2h - ^{13}C NMR ($CDCl_3$, 100 MHz)



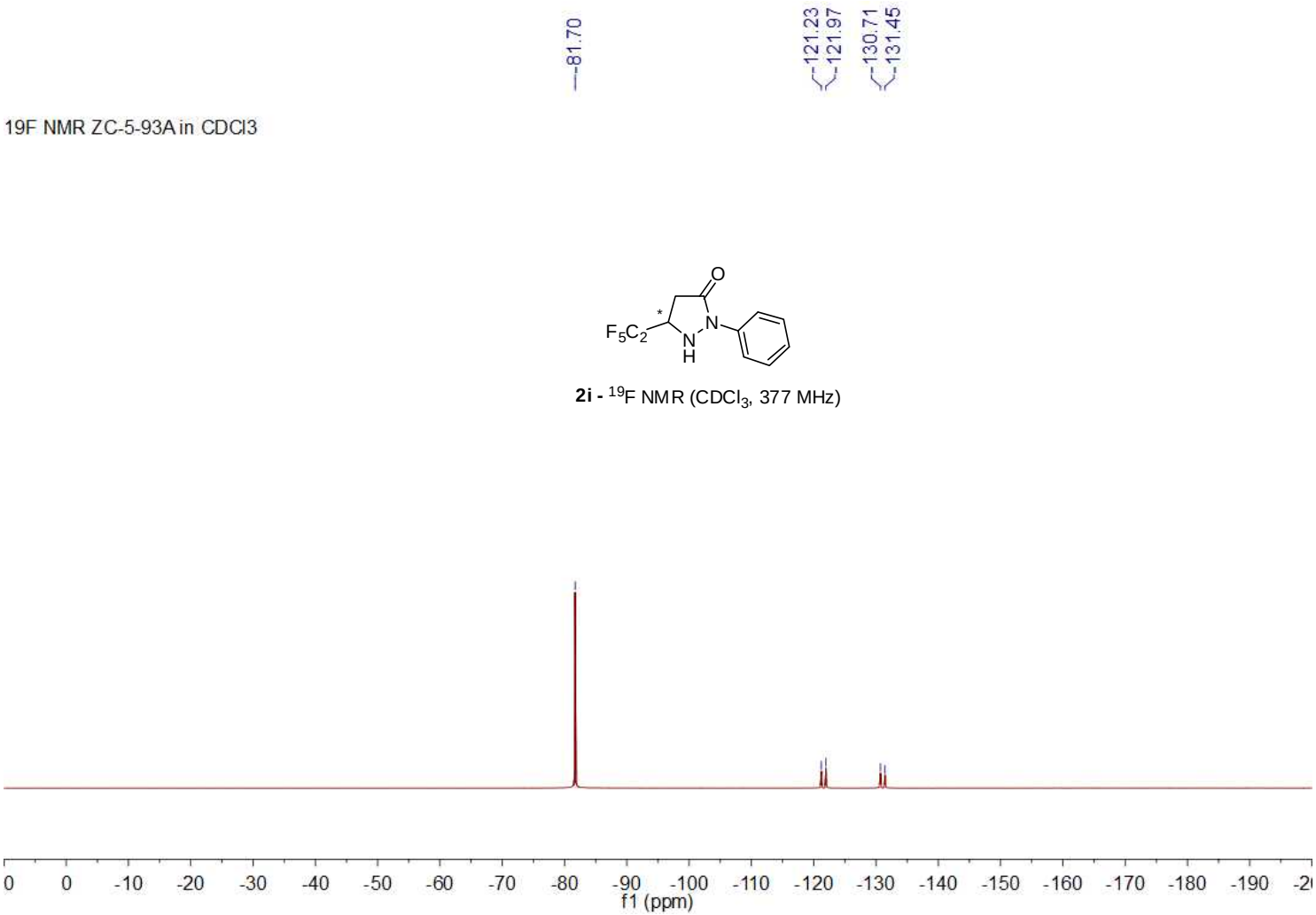
2h - ^{19}F NMR ($CDCl_3$, 377 MHz)



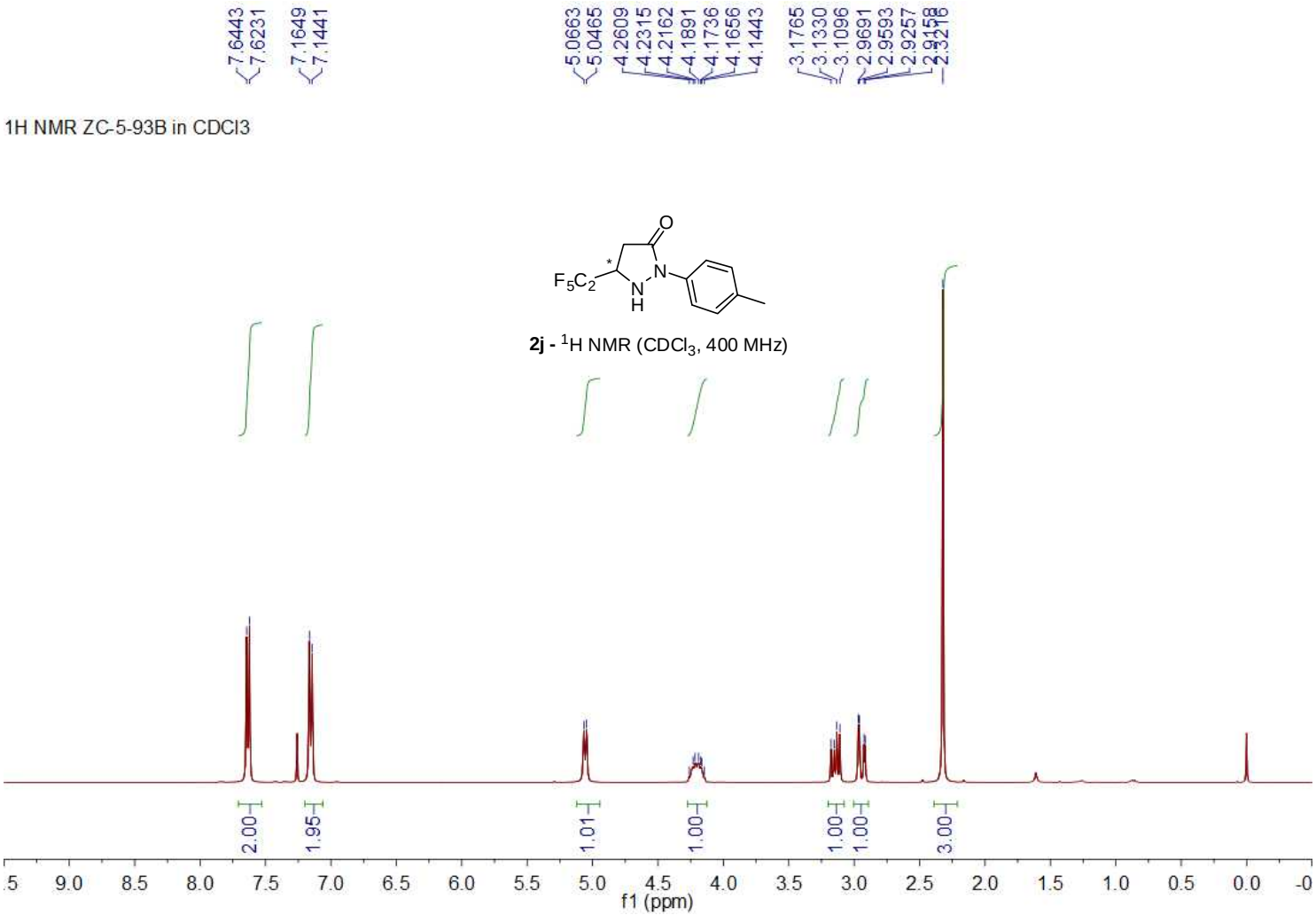
2i - ^{1}H NMR ($CDCl_3$, 400 MHz)



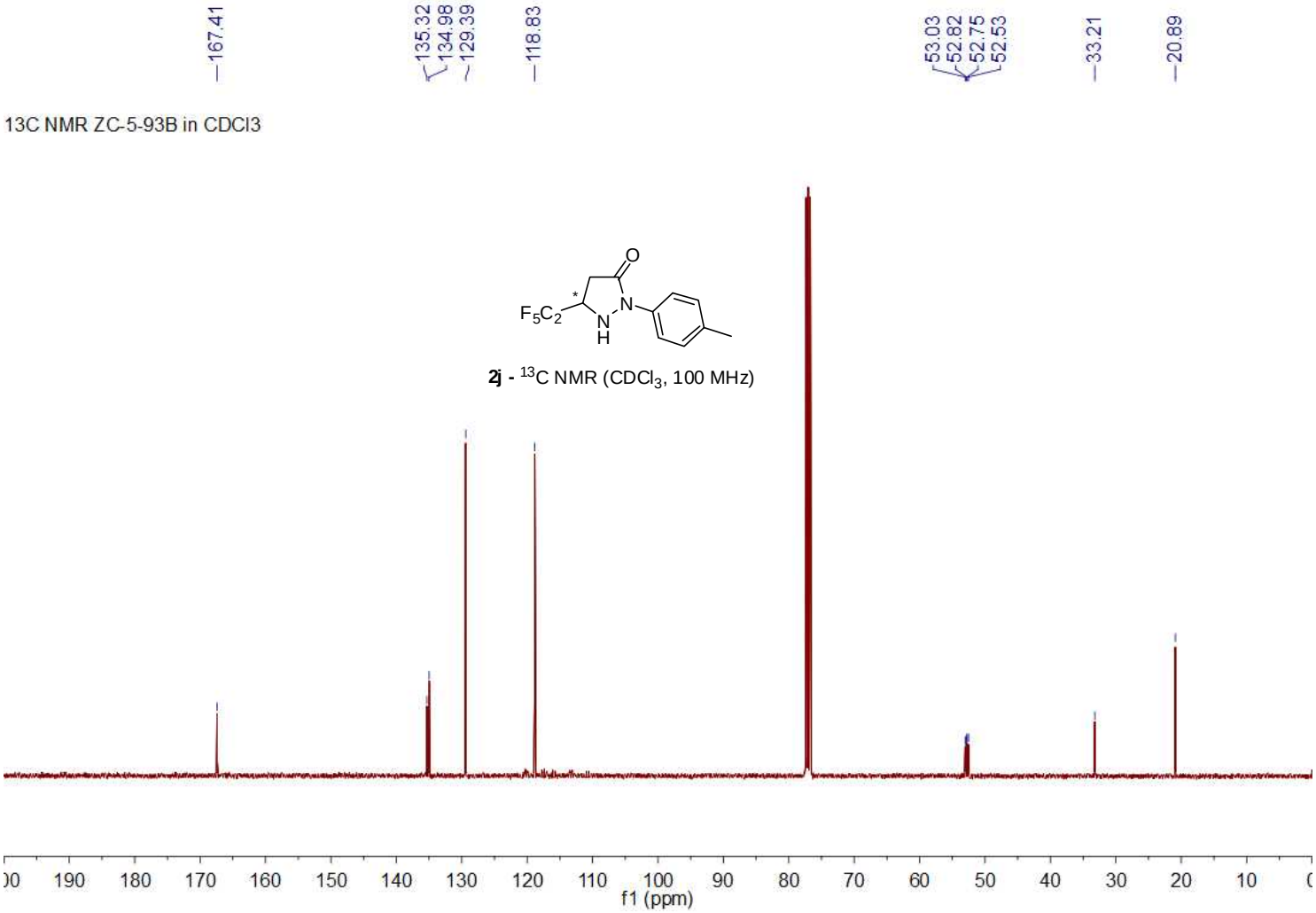
2i - ^{13}C NMR ($CDCl_3$, 100 MHz)



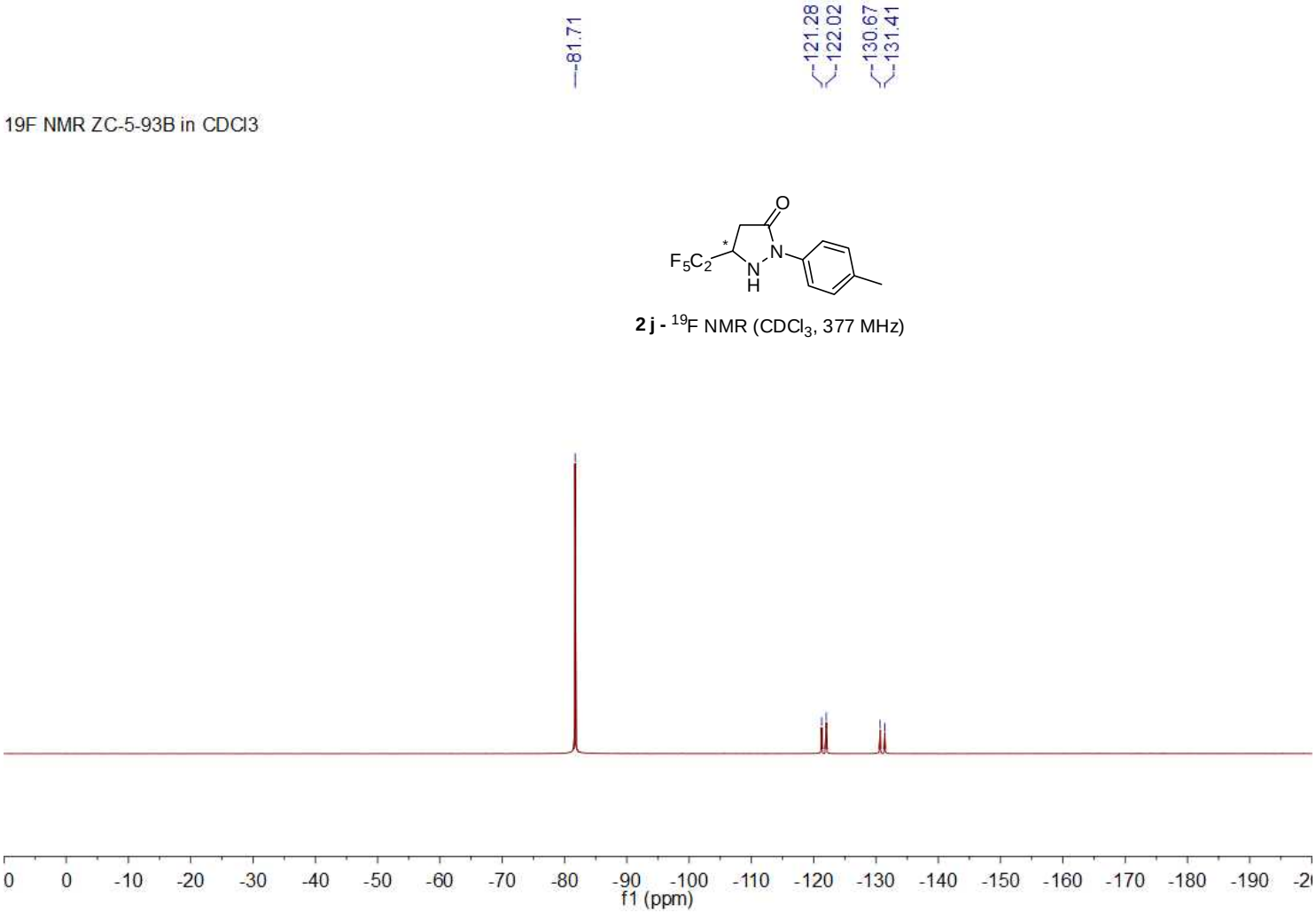
2i - ^{19}F NMR ($CDCl_3$, 377 MHz)



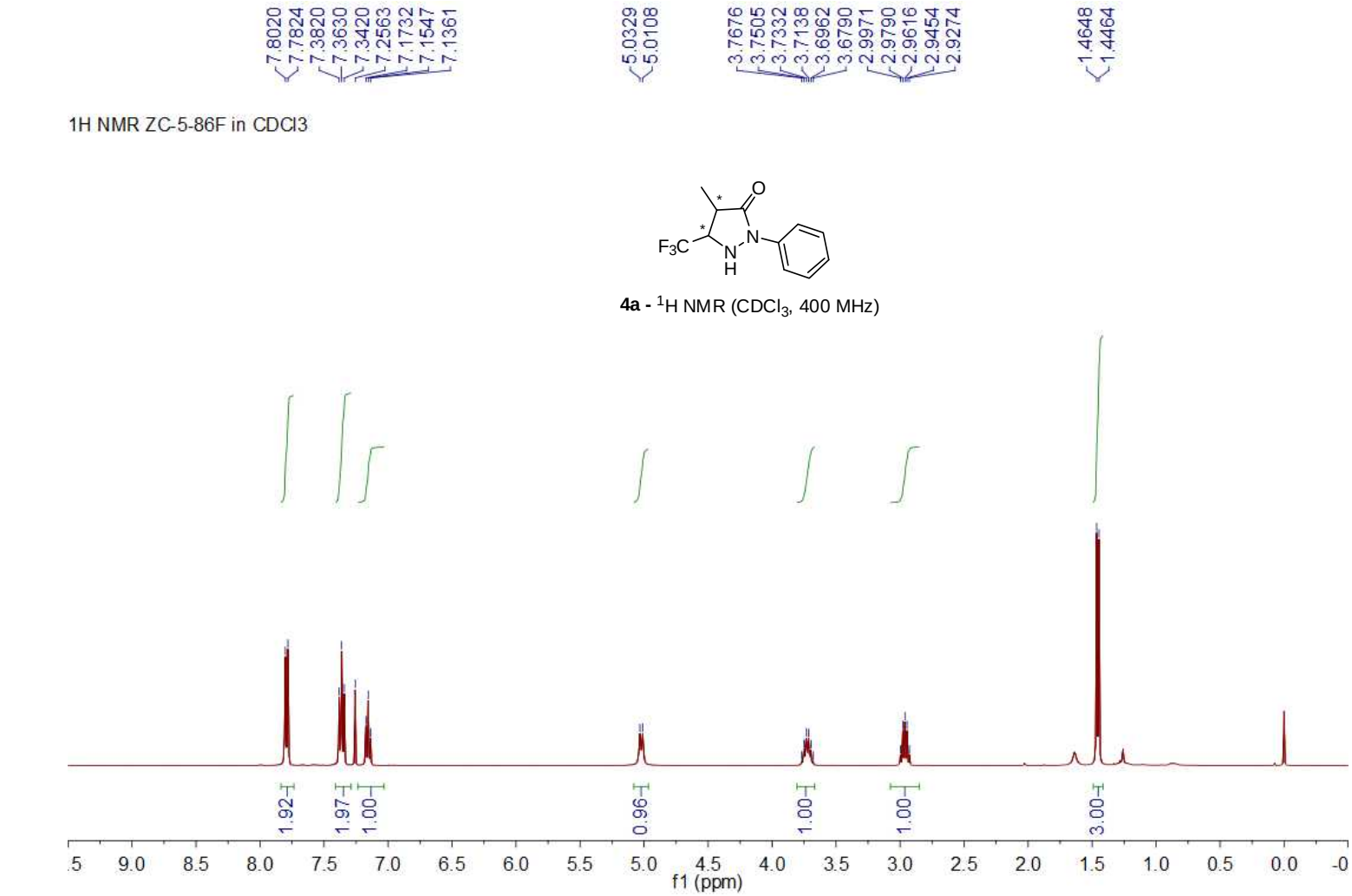
2j - ^{1}H NMR ($CDCl_3$, 400 MHz)



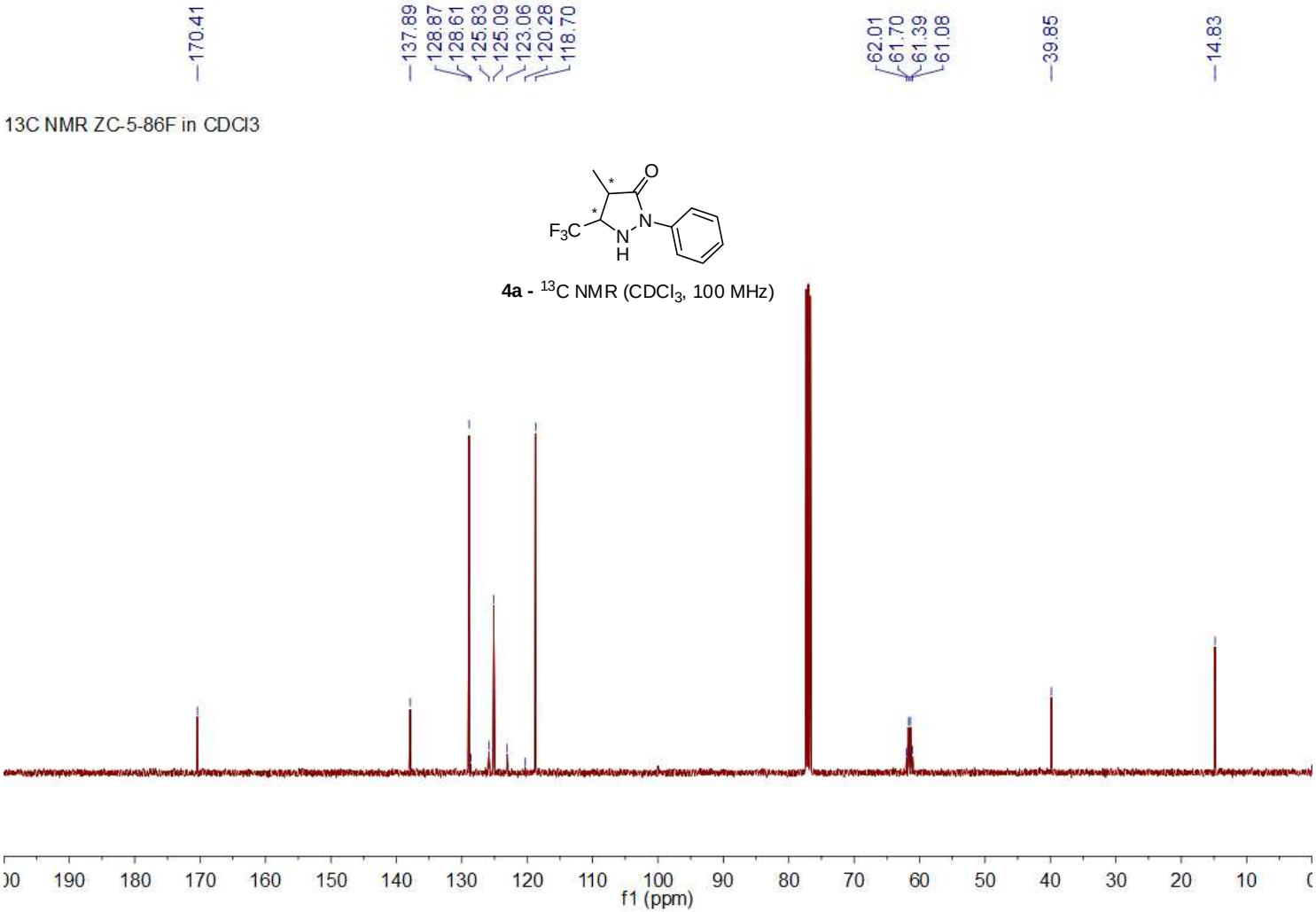
2j - ^{13}C NMR ($CDCl_3$, 100 MHz)



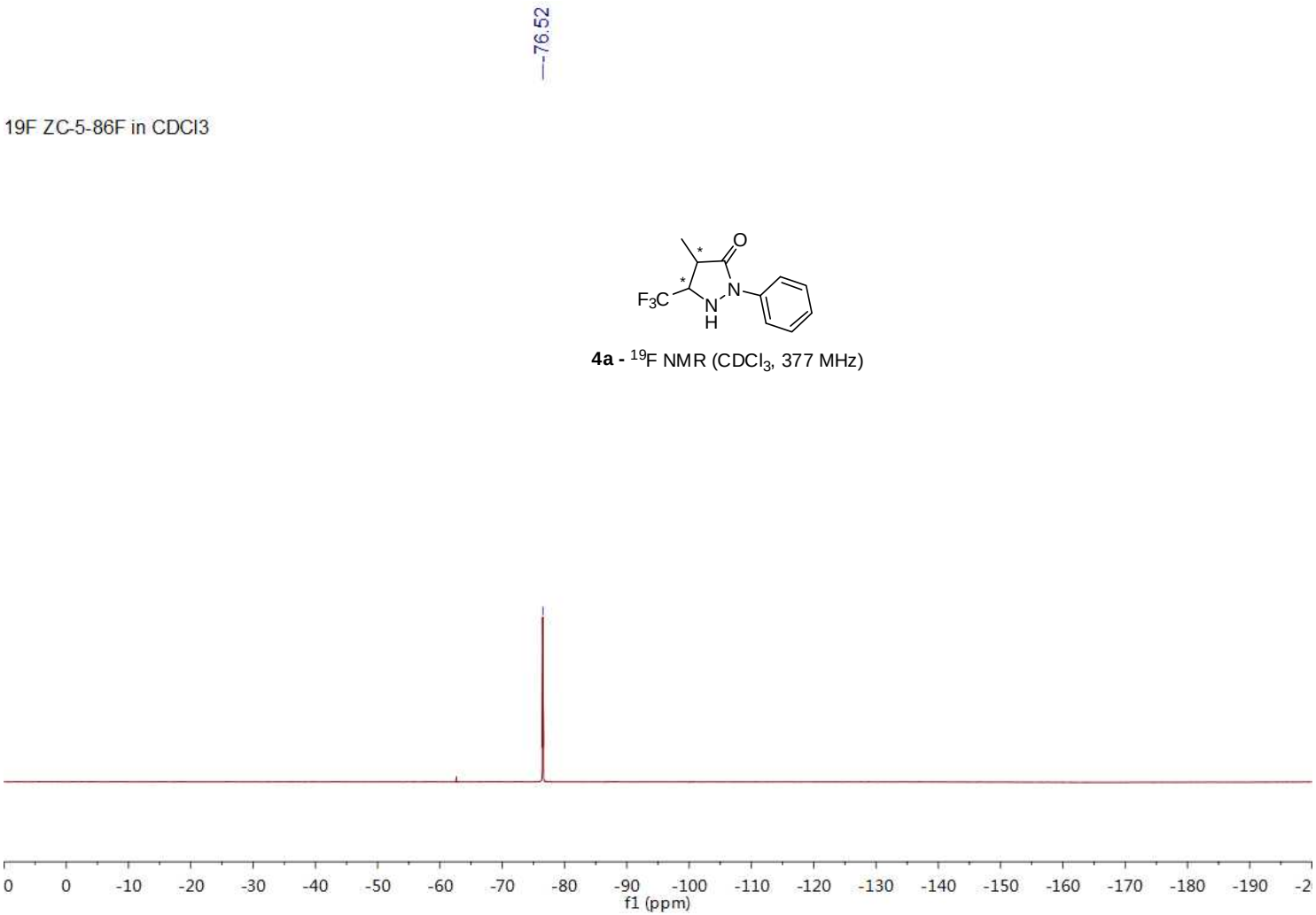
2 j - ^{19}F NMR ($CDCl_3$, 377 MHz)



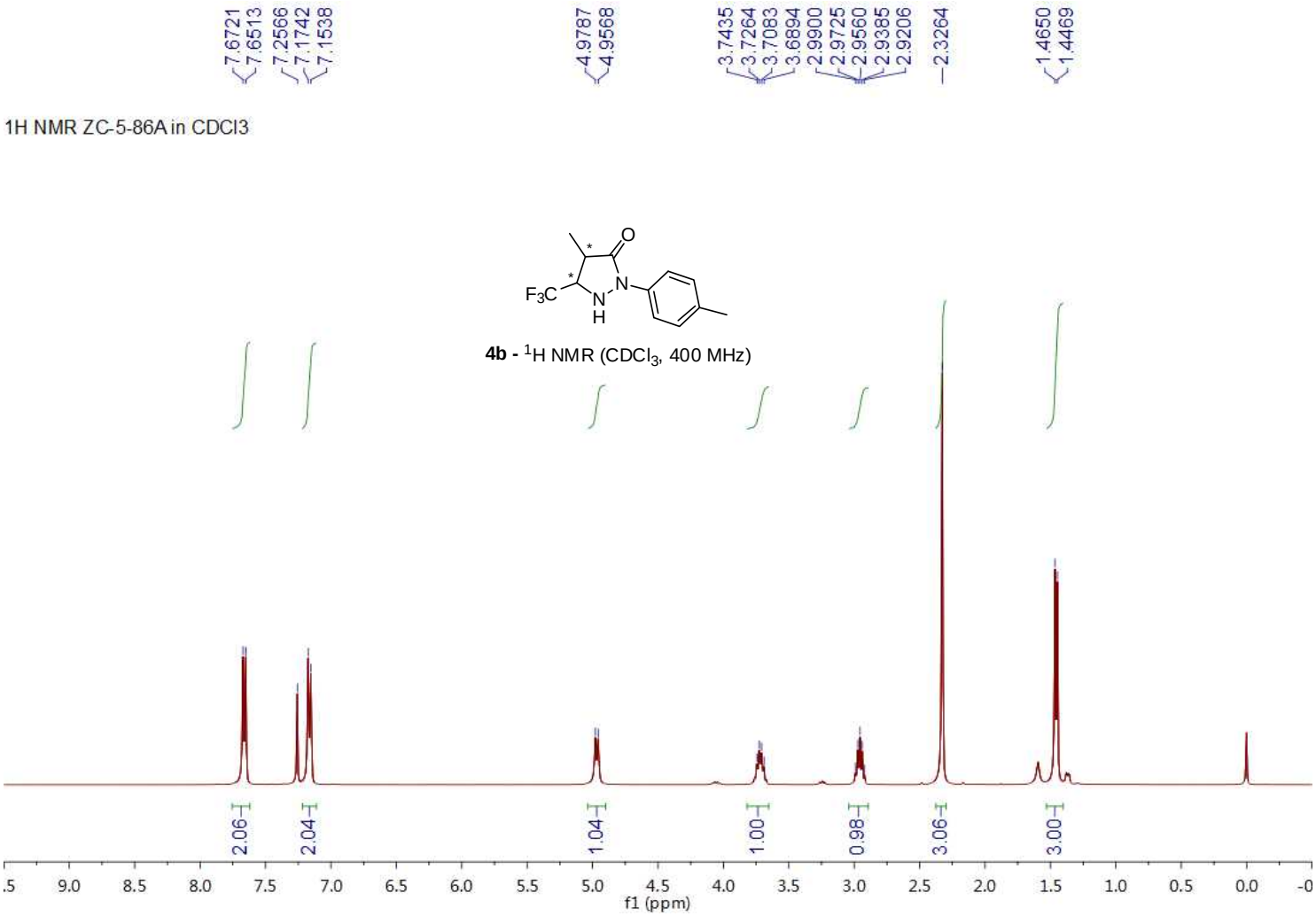
4a - ^{1}H NMR ($CDCl_3$, 400 MHz)



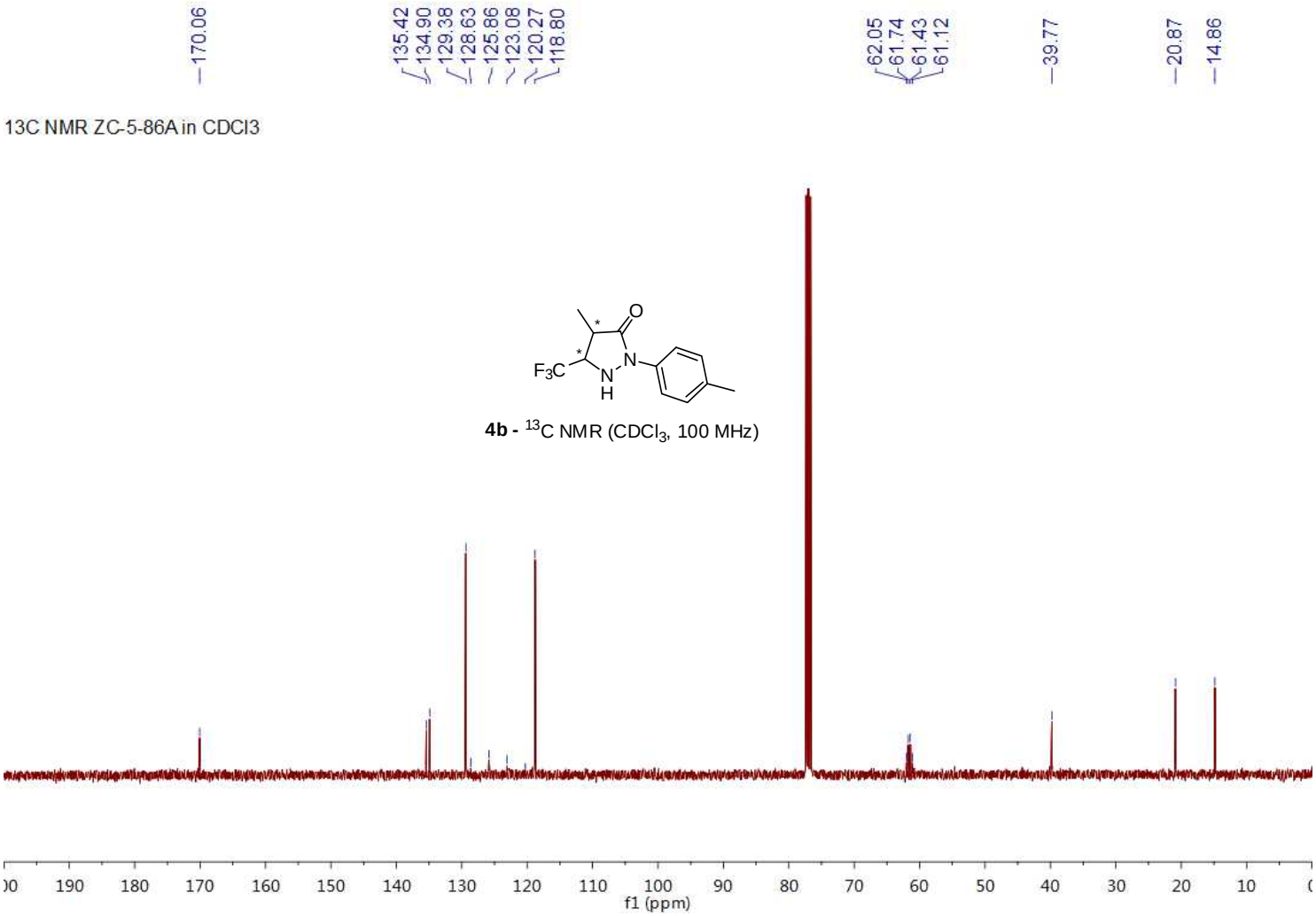
4a - ^{13}C NMR ($CDCl_3$, 100 MHz)



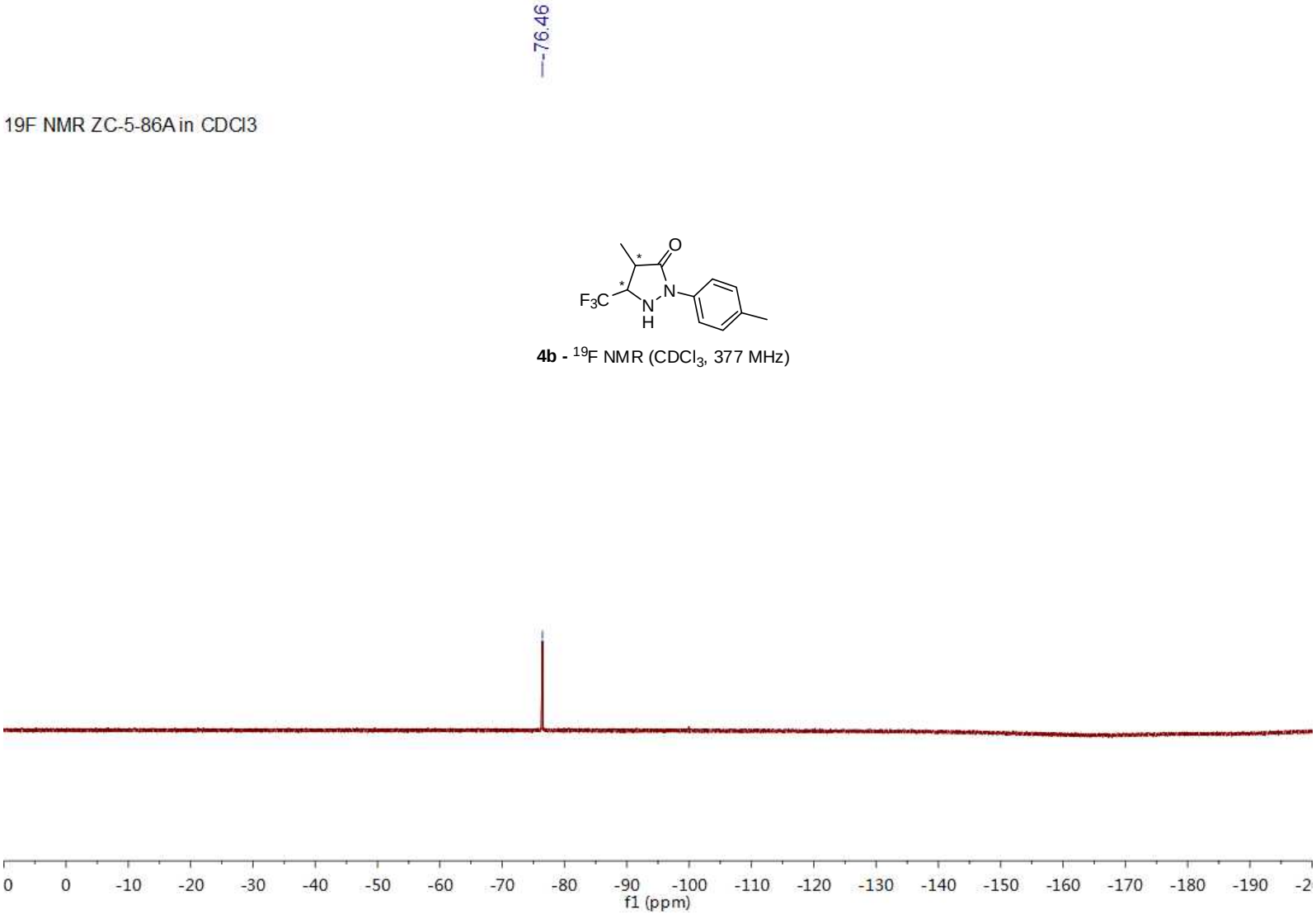
4a - ^{19}F NMR ($CDCl_3$, 377 MHz)



4b - ^{1}H NMR ($CDCl_3$, 400 MHz)

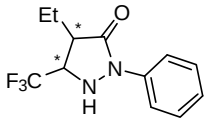


4b - ^{13}C NMR ($CDCl_3$, 100 MHz)

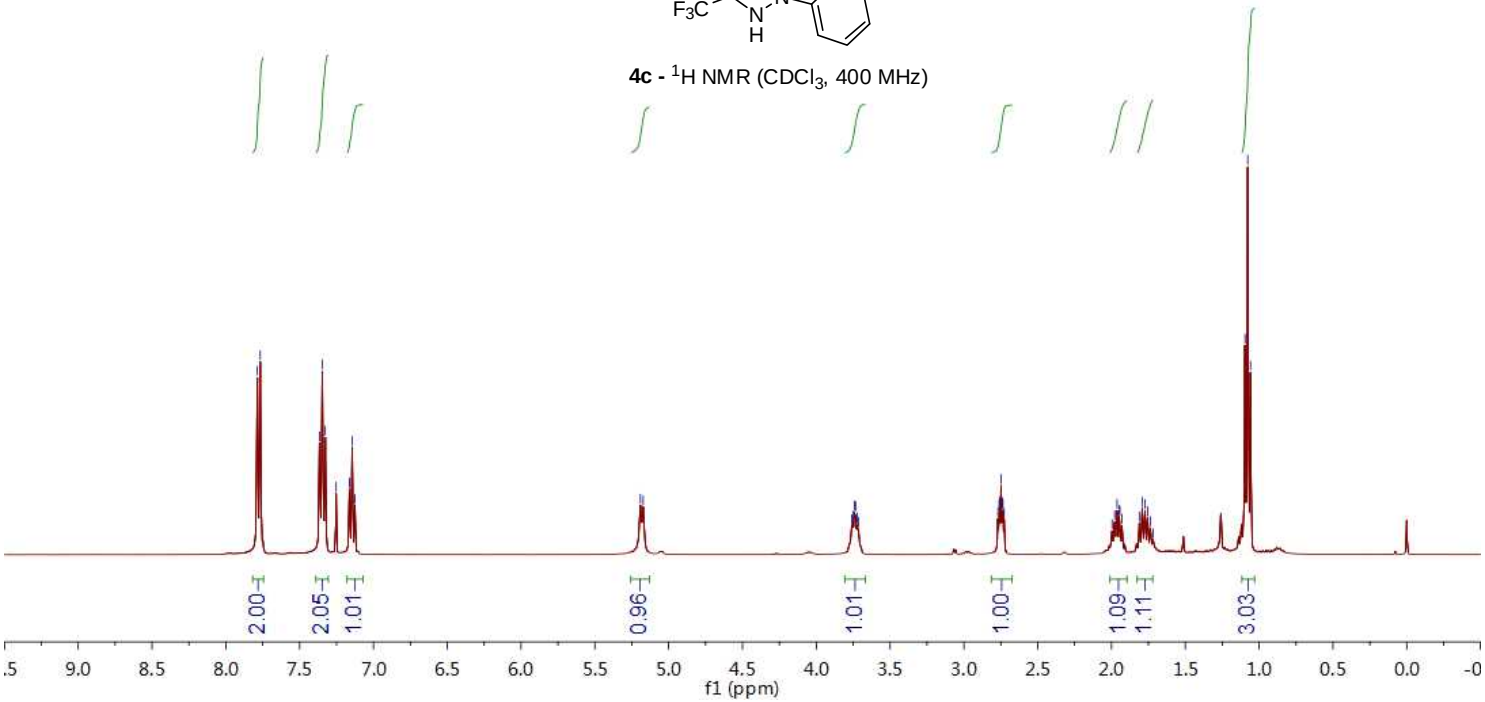


4b - ^{19}F NMR ($CDCl_3$, 377 MHz)

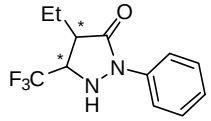
1H NMR ZC-5-86E in CDCl3



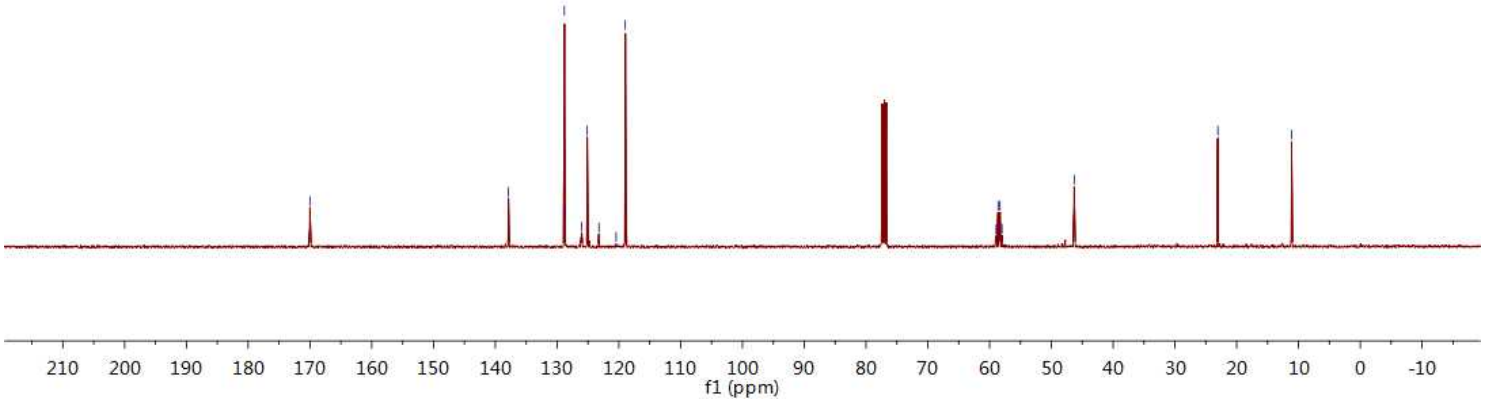
4c - ^{1}H NMR ($CDCl_3$, 400 MHz)

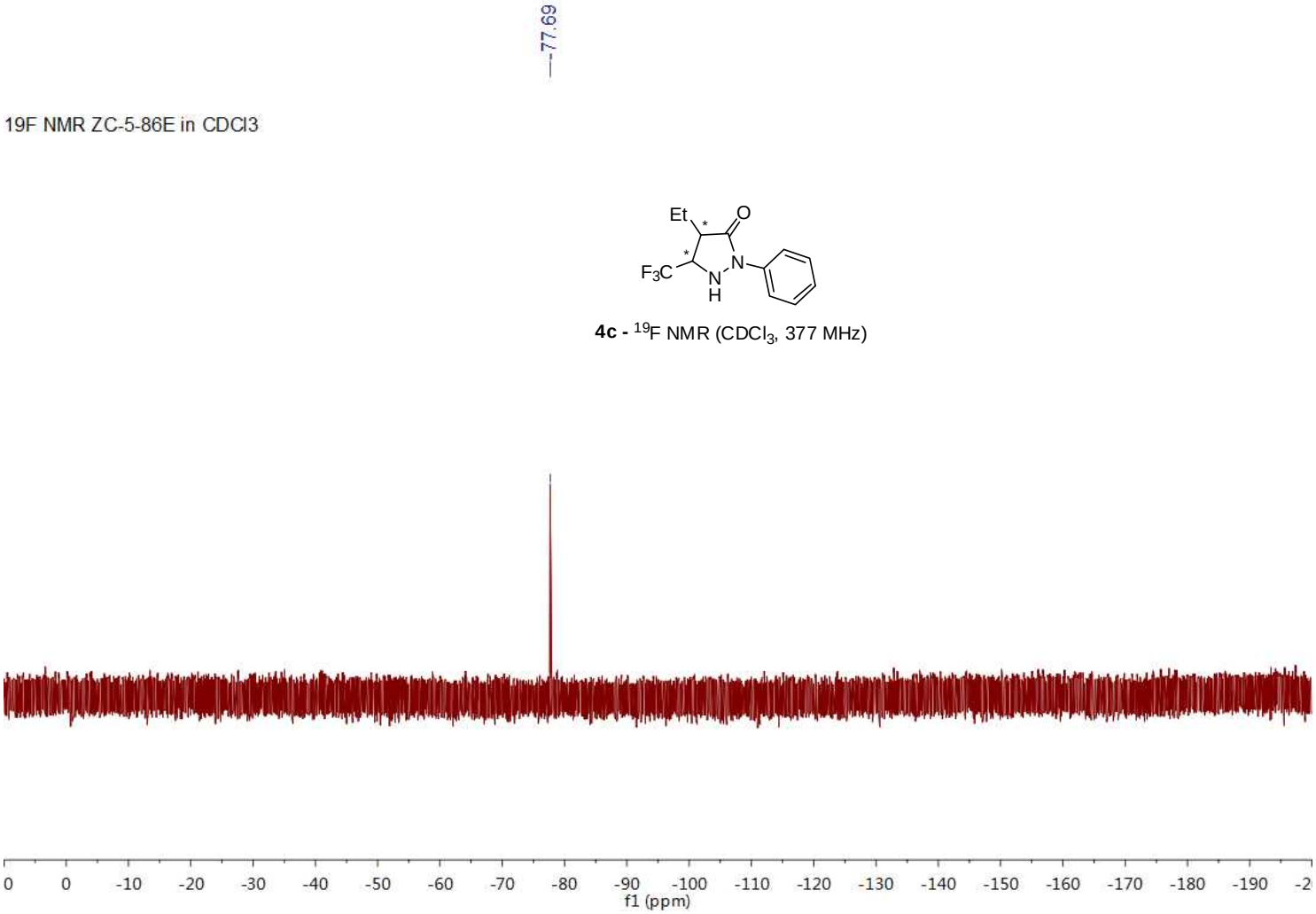


13C NMR ZC-5-86E in CDCl3

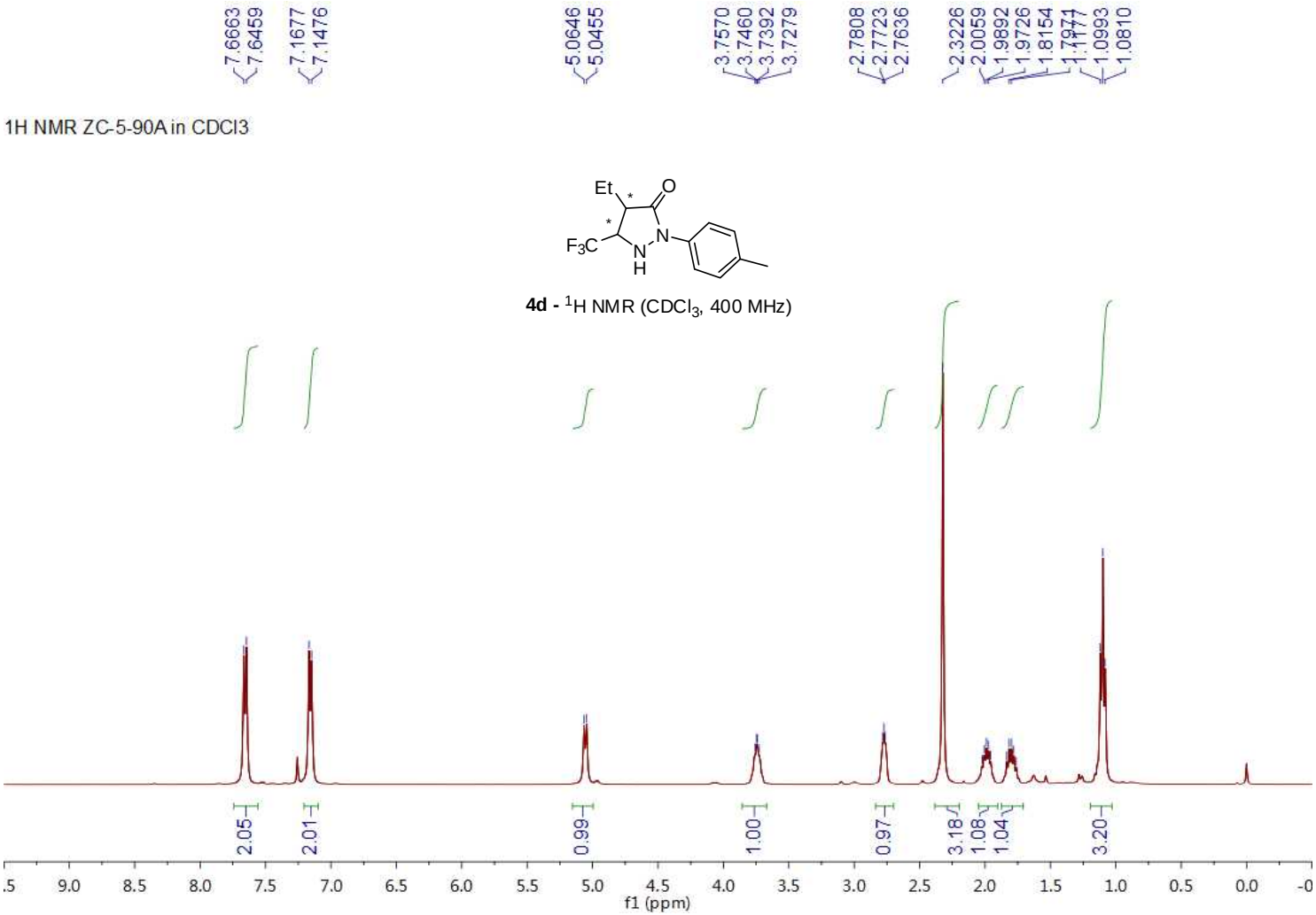


4c - ^{13}C NMR ($CDCl_3$, 100 MHz)

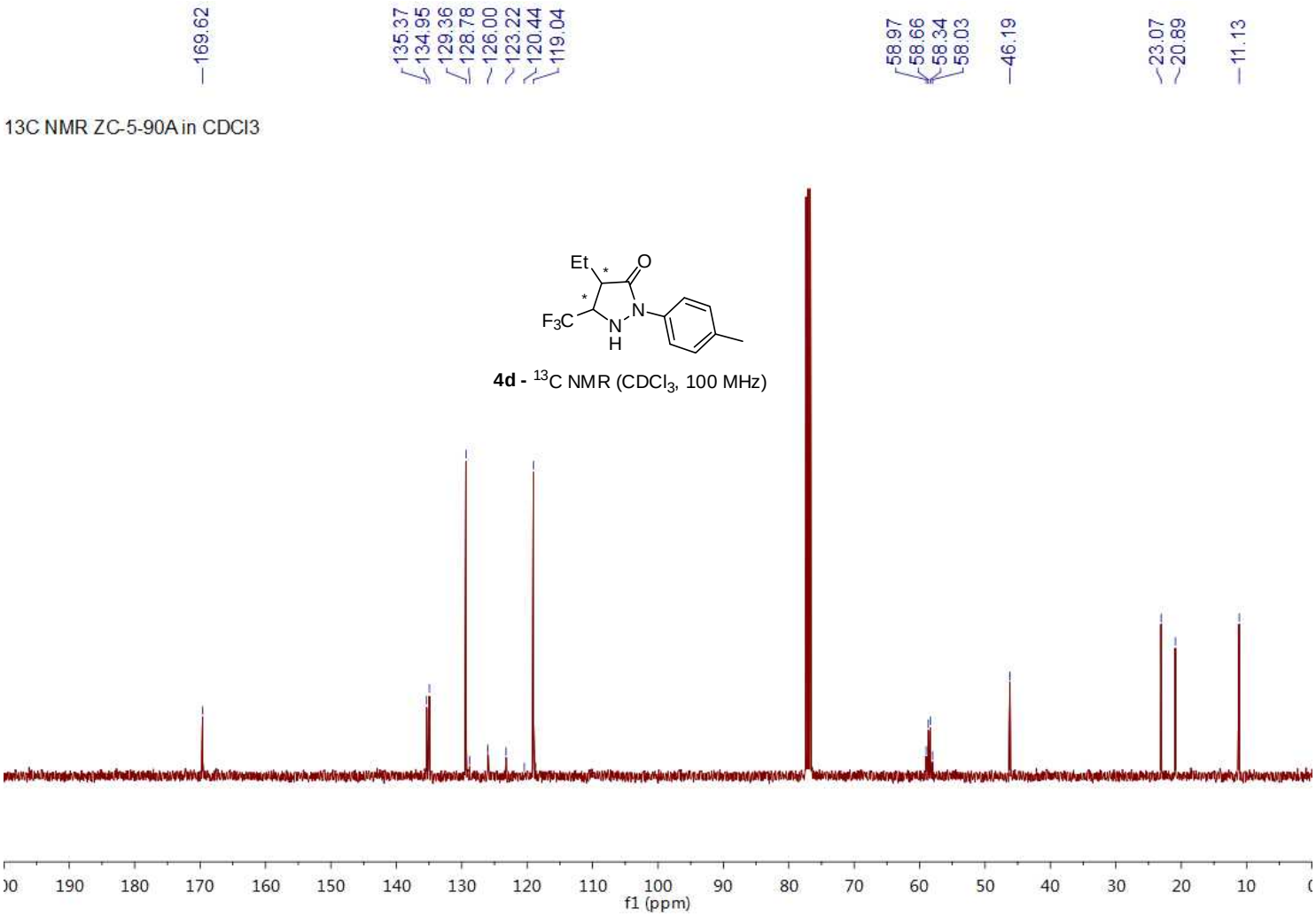




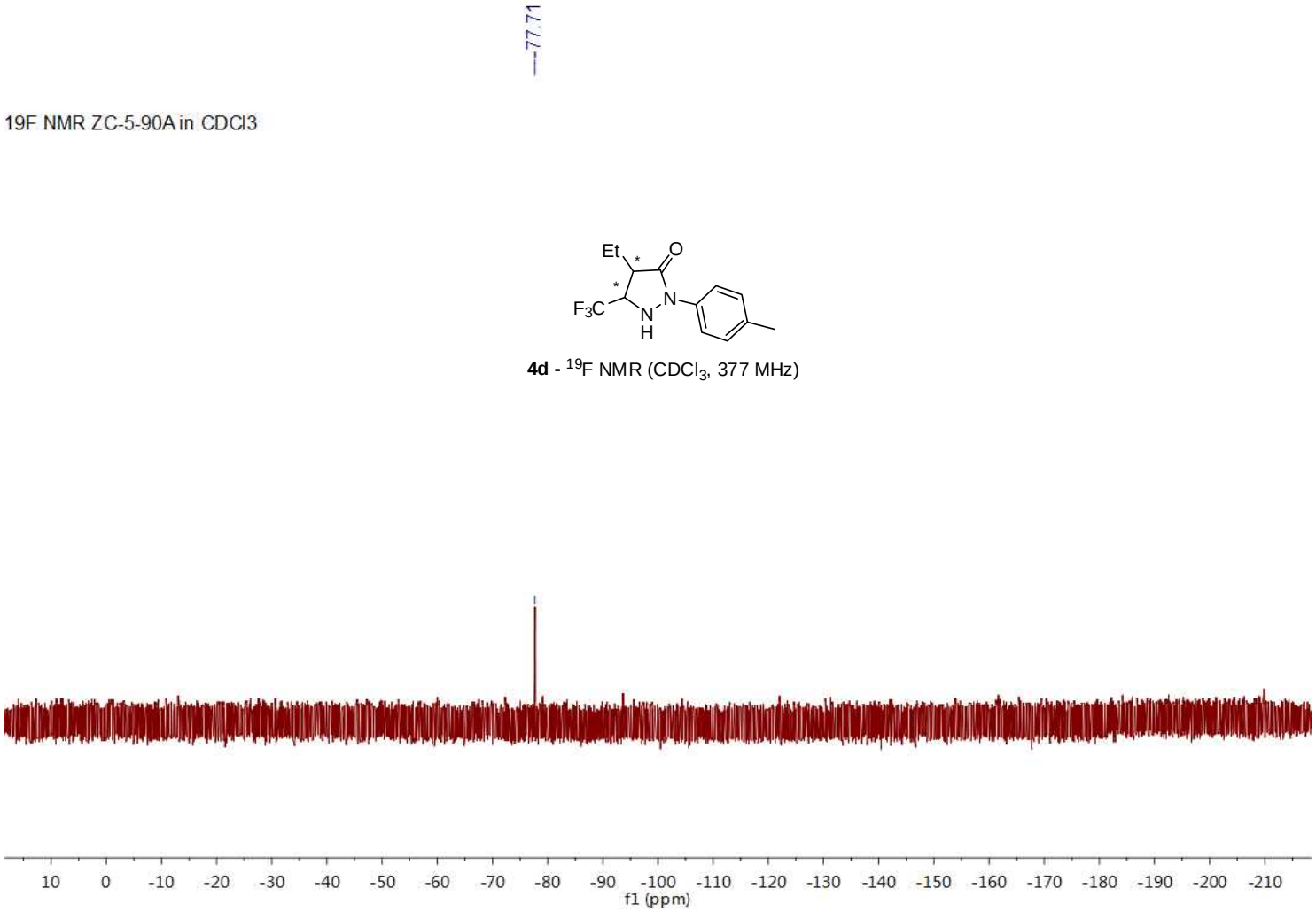
4c - ^{19}F NMR ($CDCl_3$, 377 MHz)



4d - ^{1}H NMR ($CDCl_3$, 400 MHz)

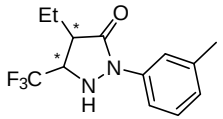


4d - ^{13}C NMR ($CDCl_3$, 100 MHz)

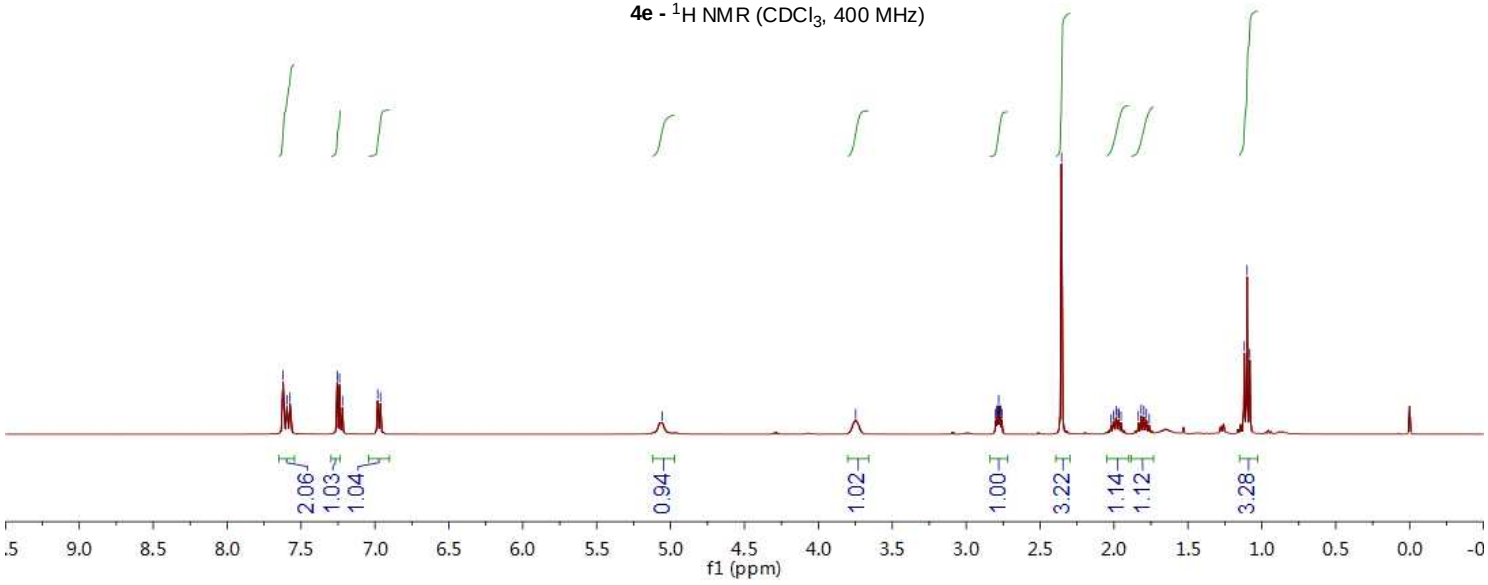


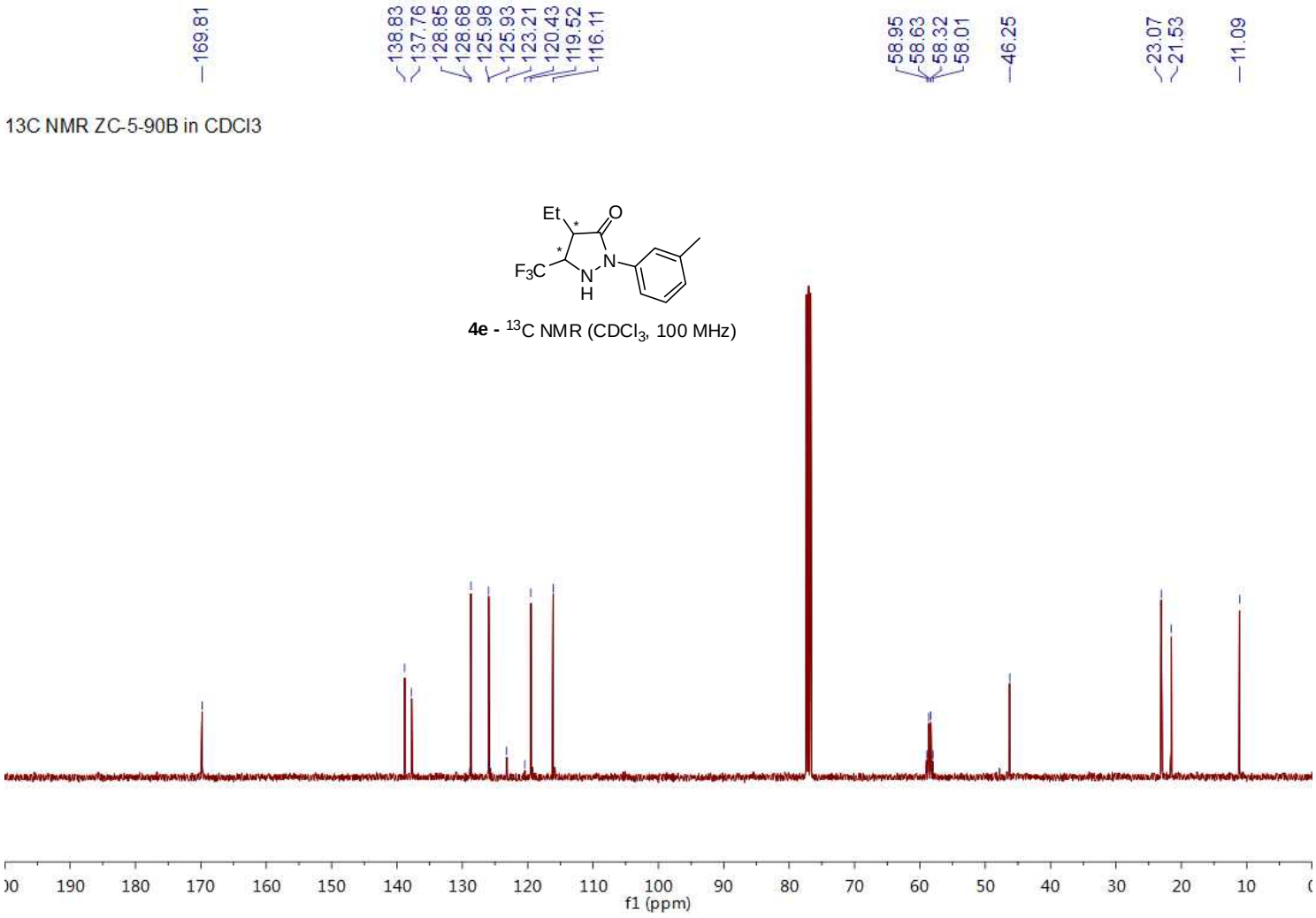
4d - ^{19}F NMR ($CDCl_3$, 377 MHz)

1H NMR ZC-5-90B in CDCl3

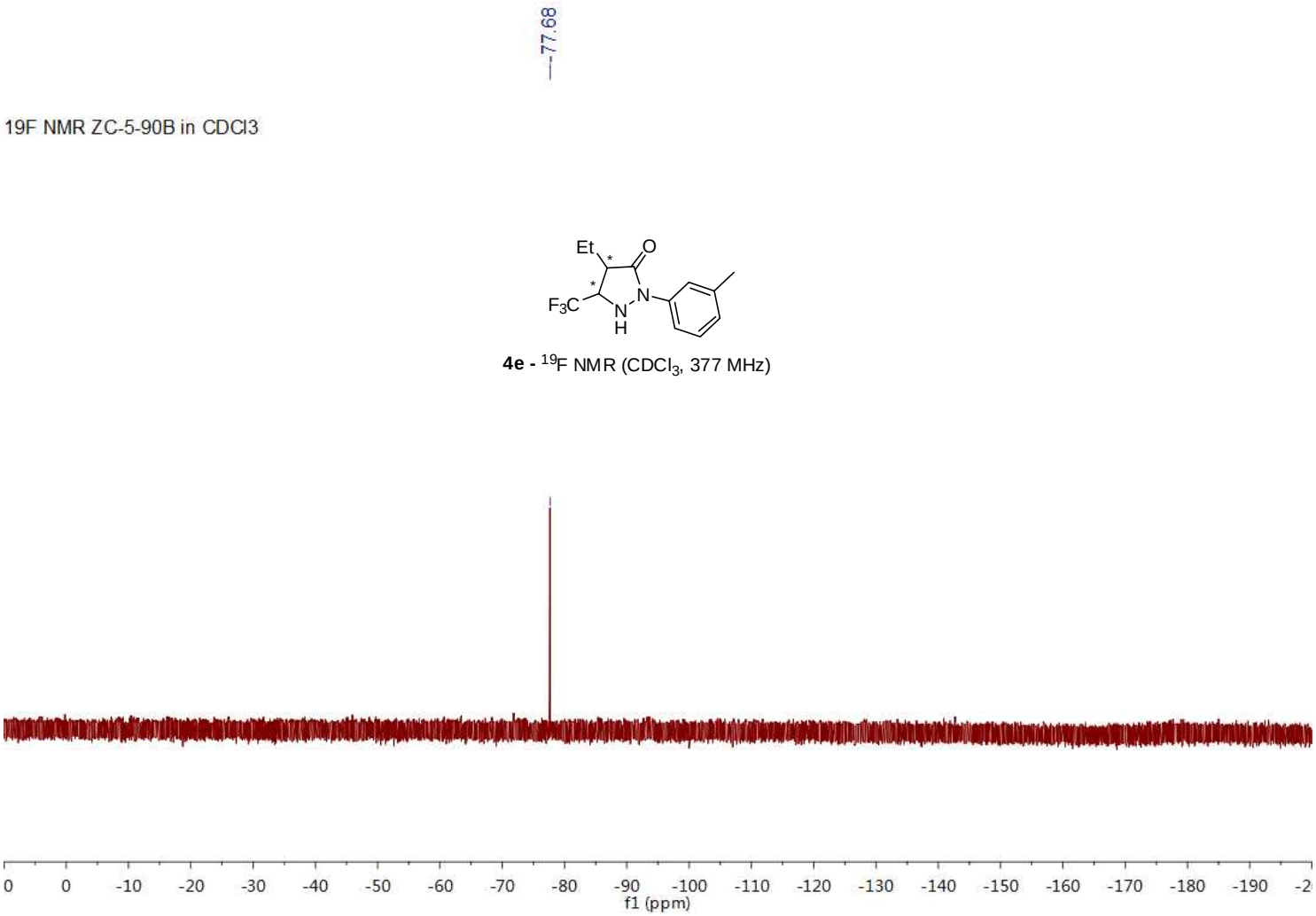


4e - ^{1}H NMR ($CDCl_3$, 400 MHz)

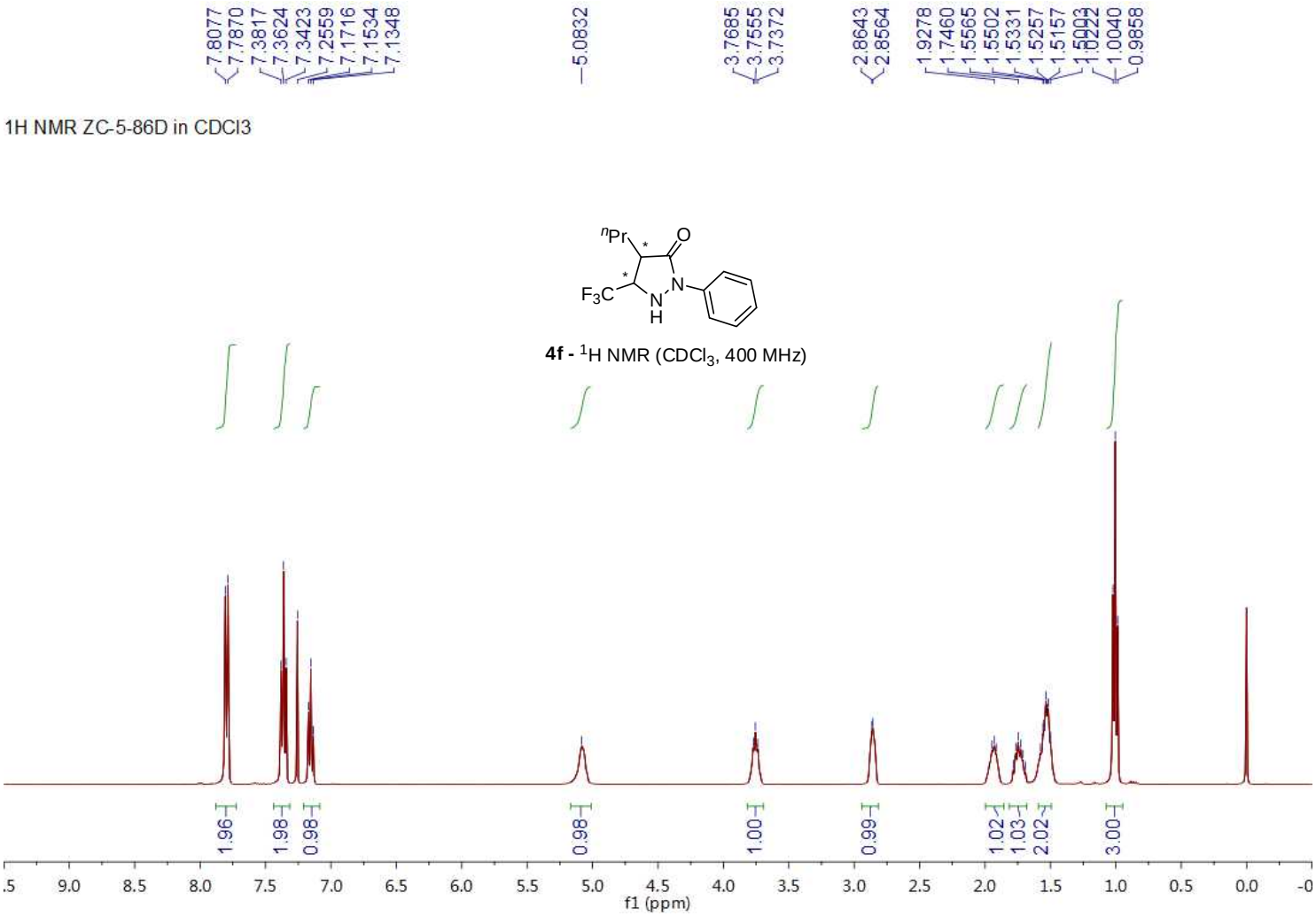




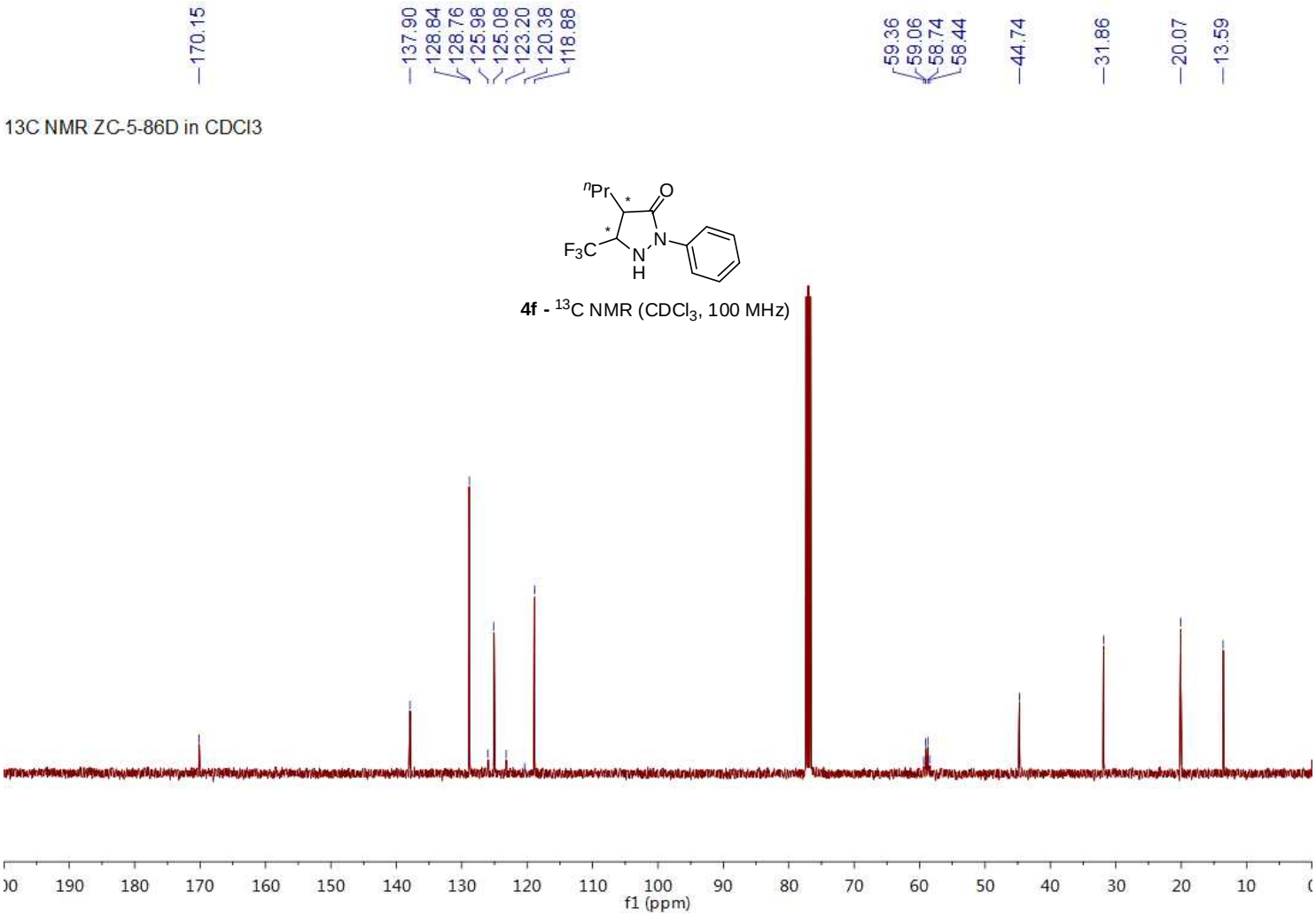
4e - ^{13}C NMR ($CDCl_3$, 100 MHz)



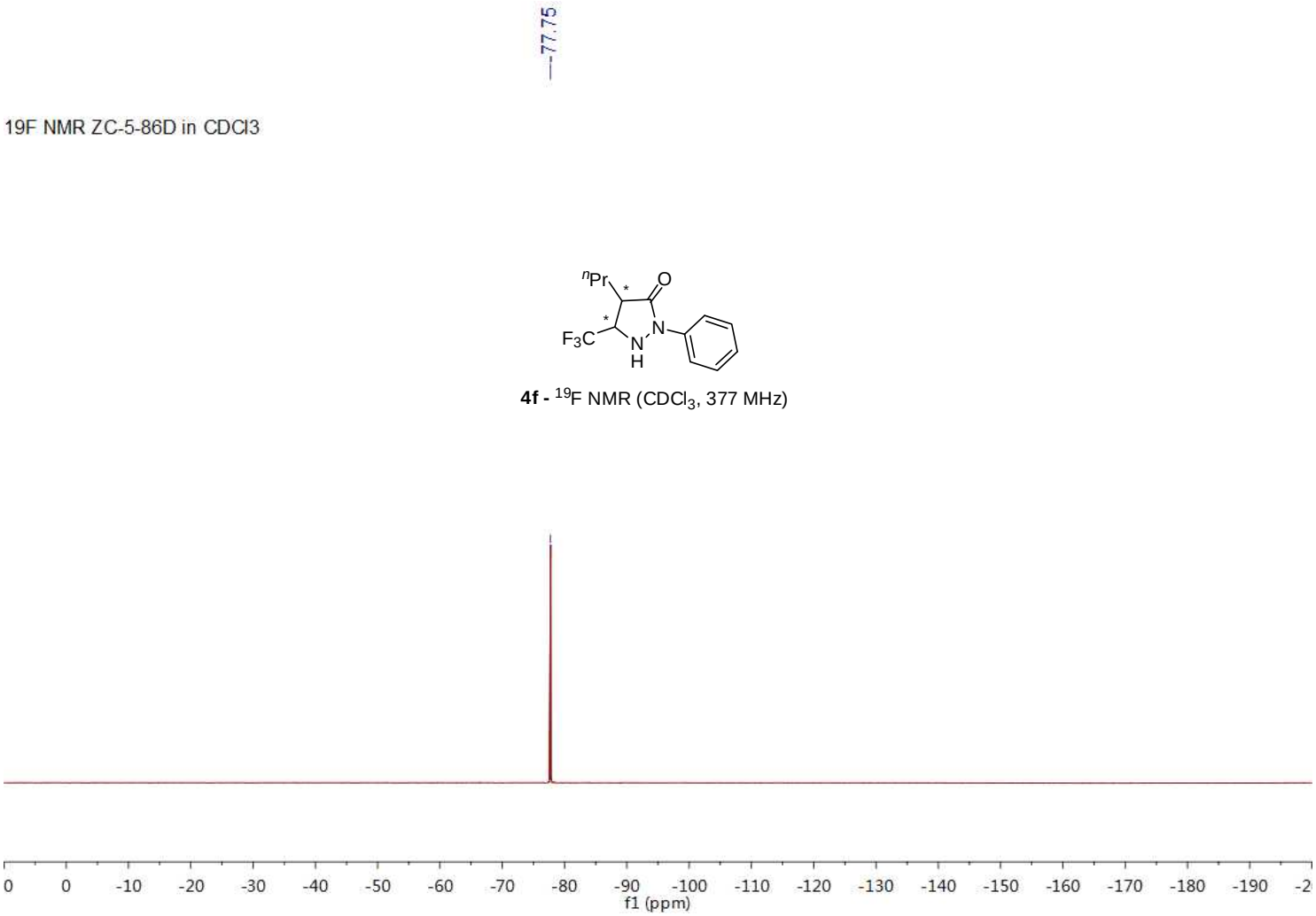
4e - ^{19}F NMR ($CDCl_3$, 377 MHz)



4f - ^{1}H NMR ($CDCl_3$, 400 MHz)

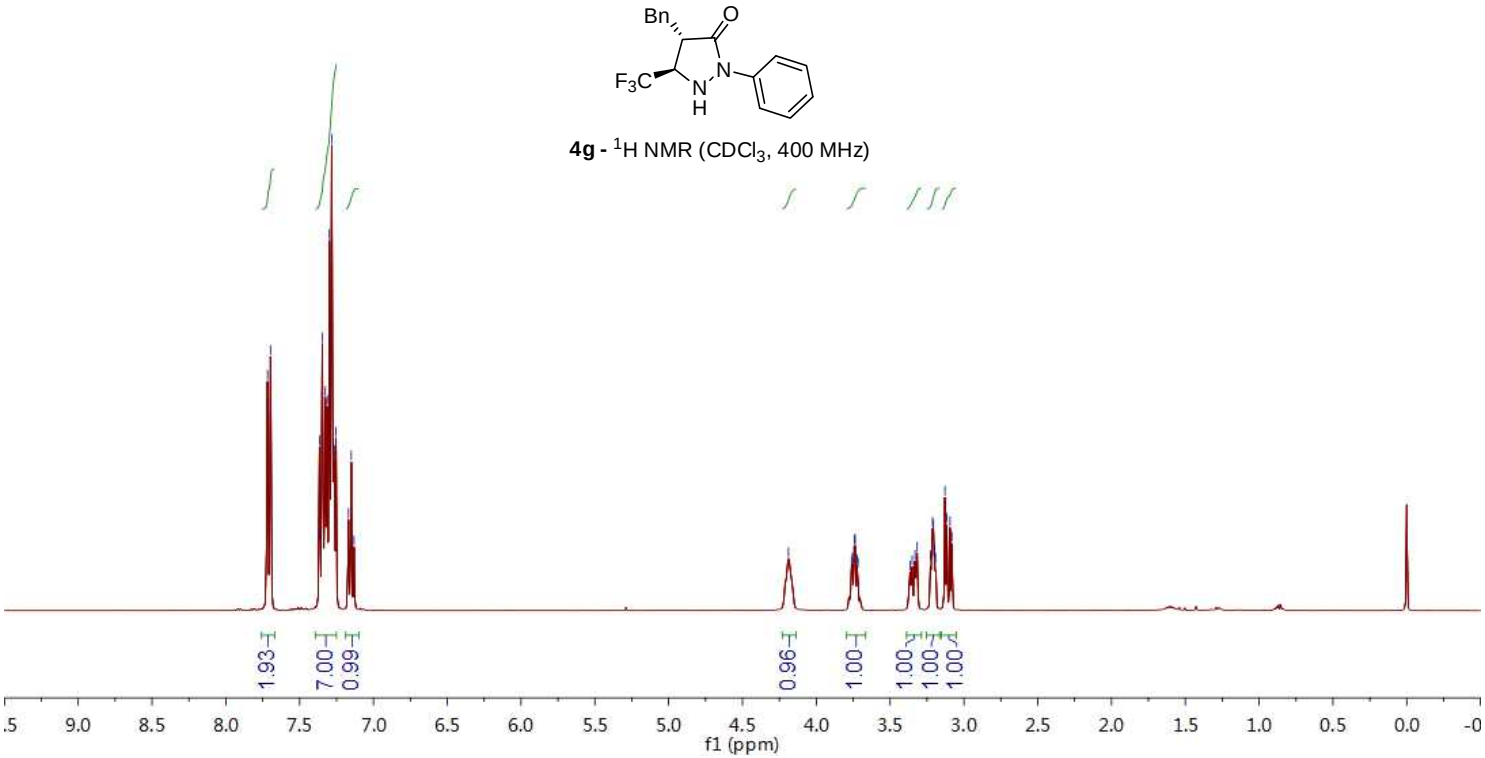


4f - ^{13}C NMR ($CDCl_3$, 100 MHz)



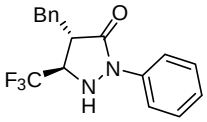
4f - ^{19}F NMR ($CDCl_3$, 377 MHz)

1H NMR ZC-5-51B in CDCl3

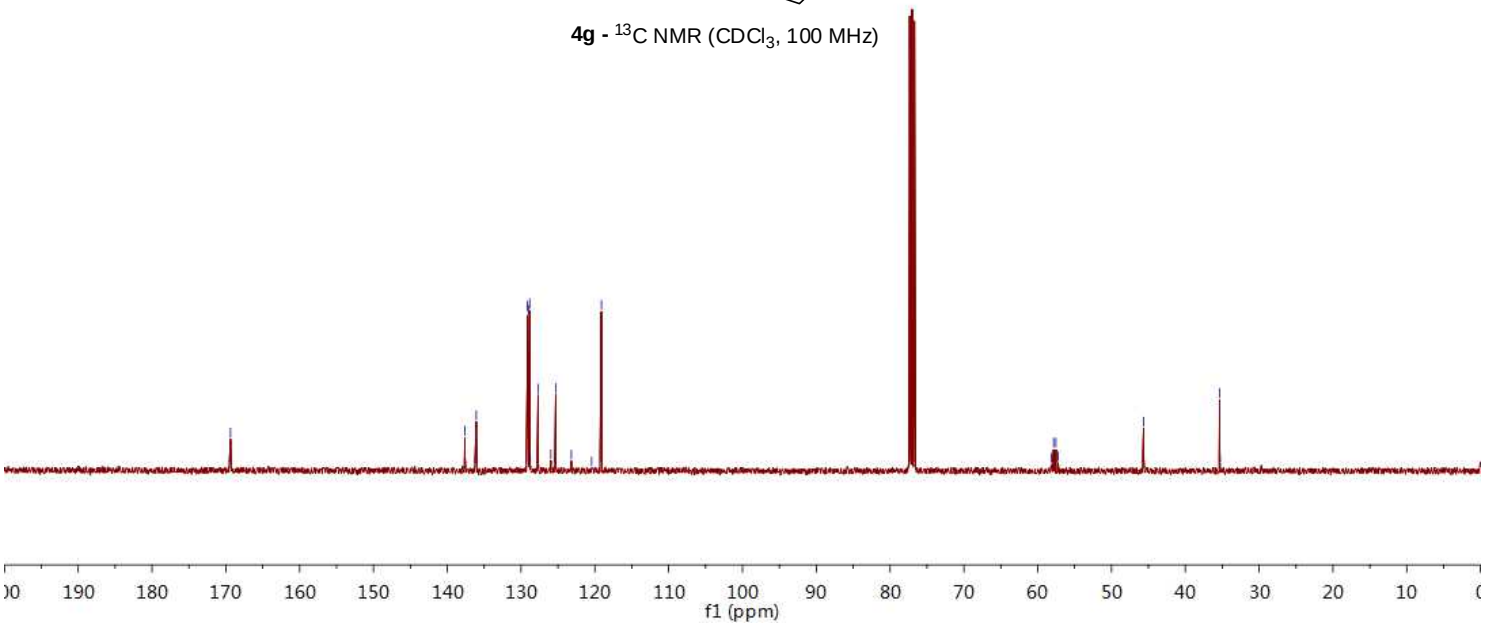


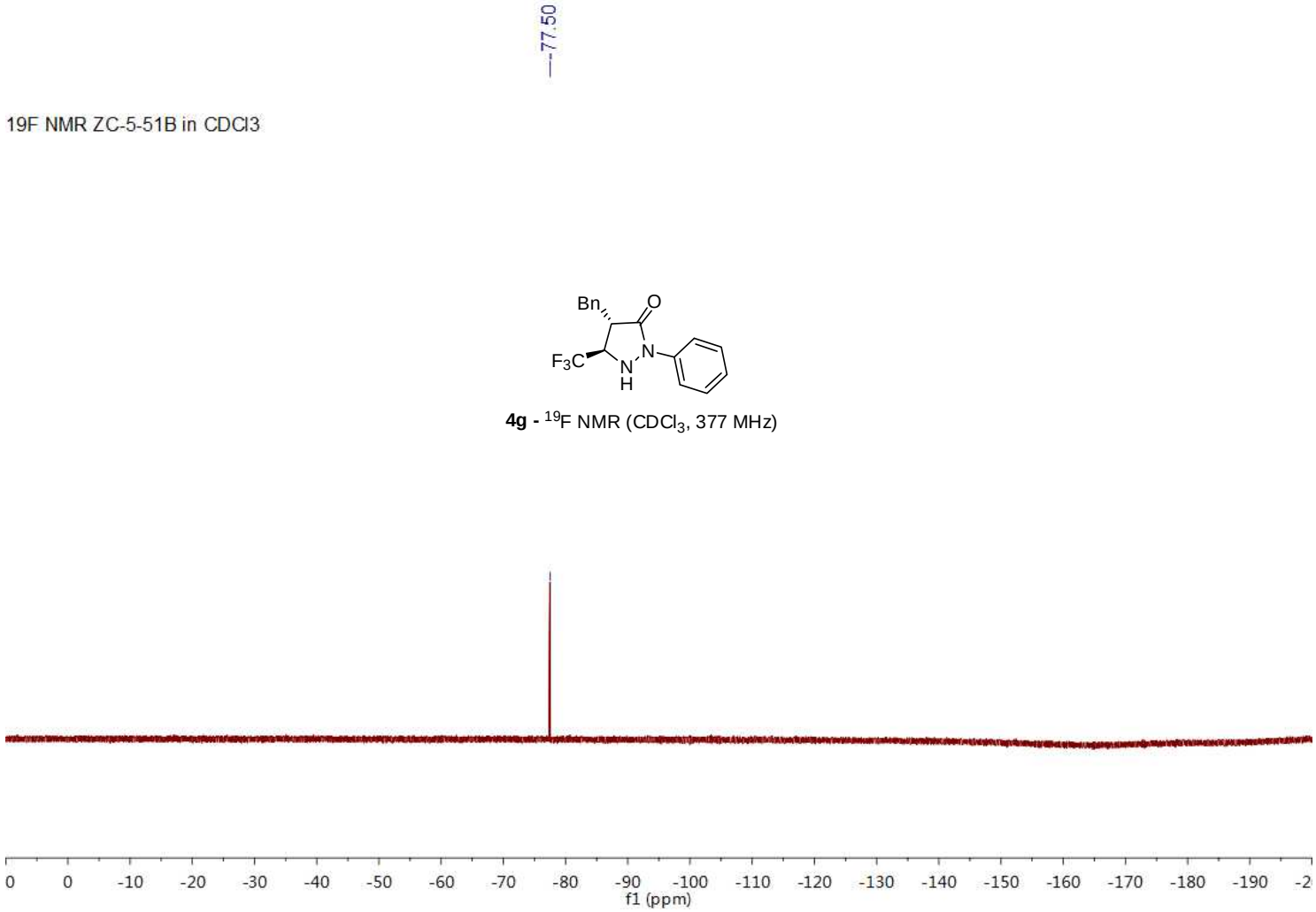
4g - ^{1}H NMR ($CDCl_3$, 400 MHz)

13C NMR ZC-5-51B in CDCl3

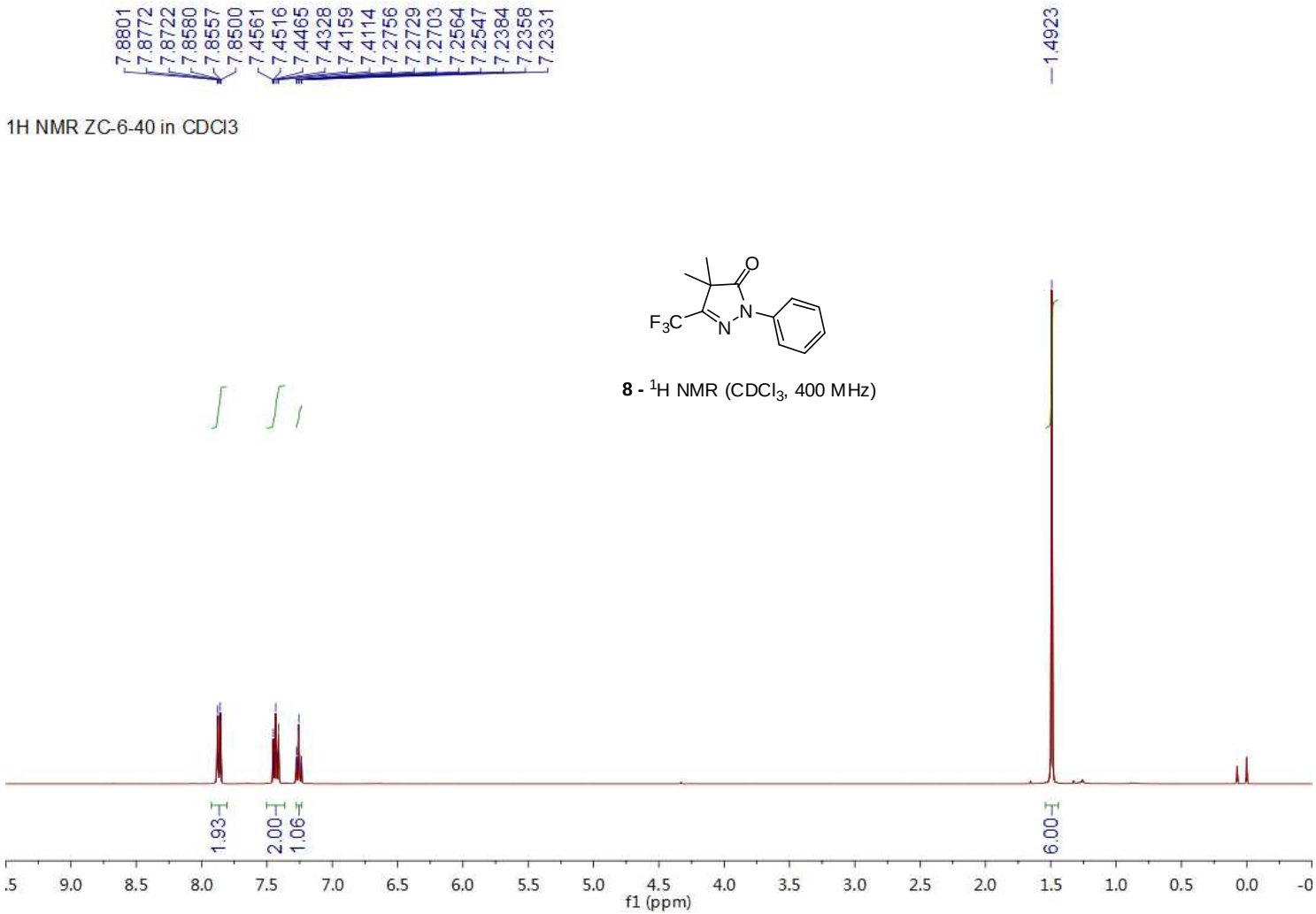


4g - ^{13}C NMR ($CDCl_3$, 100 MHz)

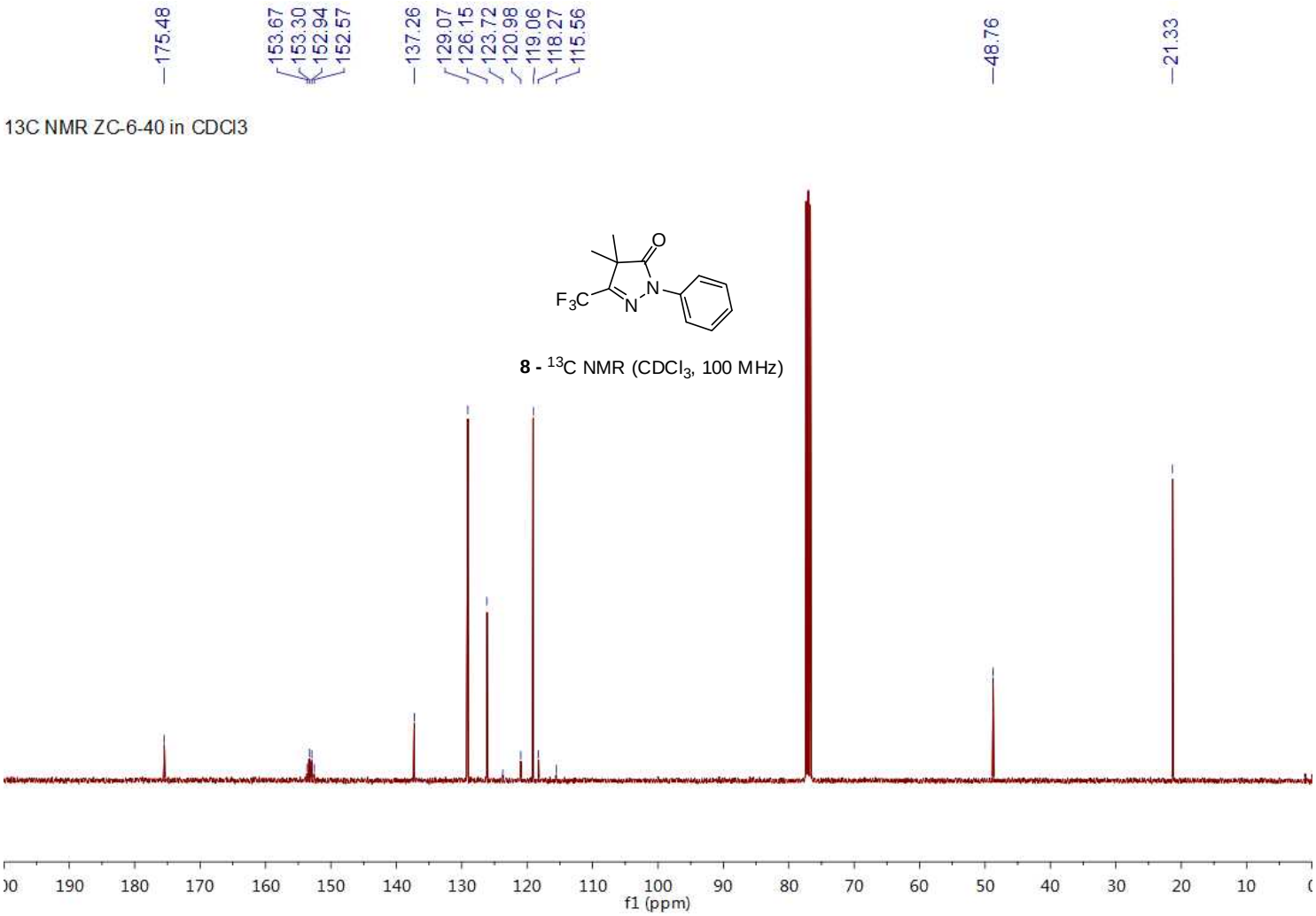




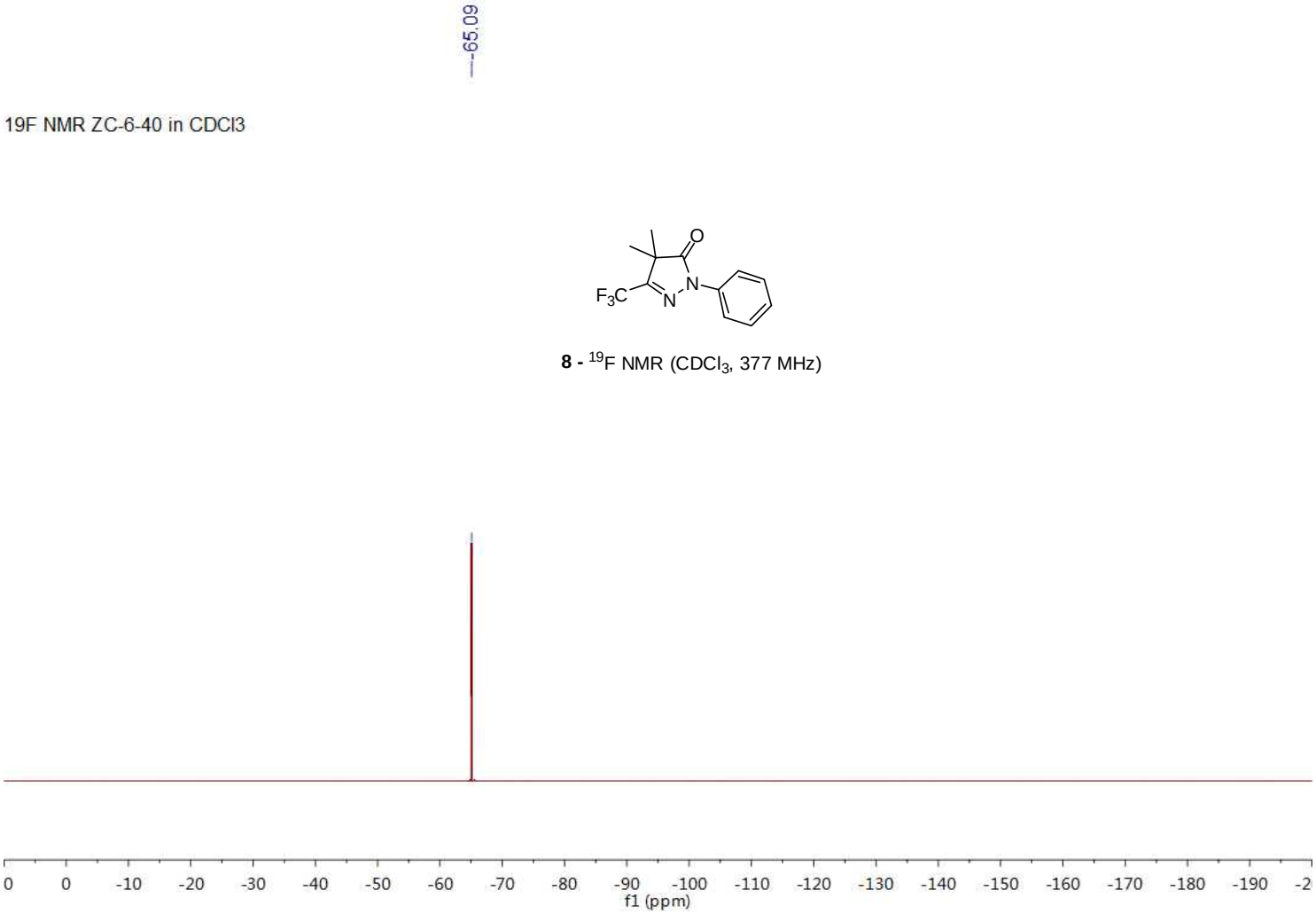
4g - ^{19}F NMR ($CDCl_3$, 377 MHz)



8 - ^{1}H NMR ($CDCl_3$, 400 MHz)

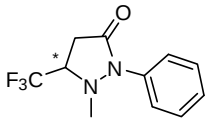


8 - ^{13}C NMR ($CDCl_3$, 100 MHz)

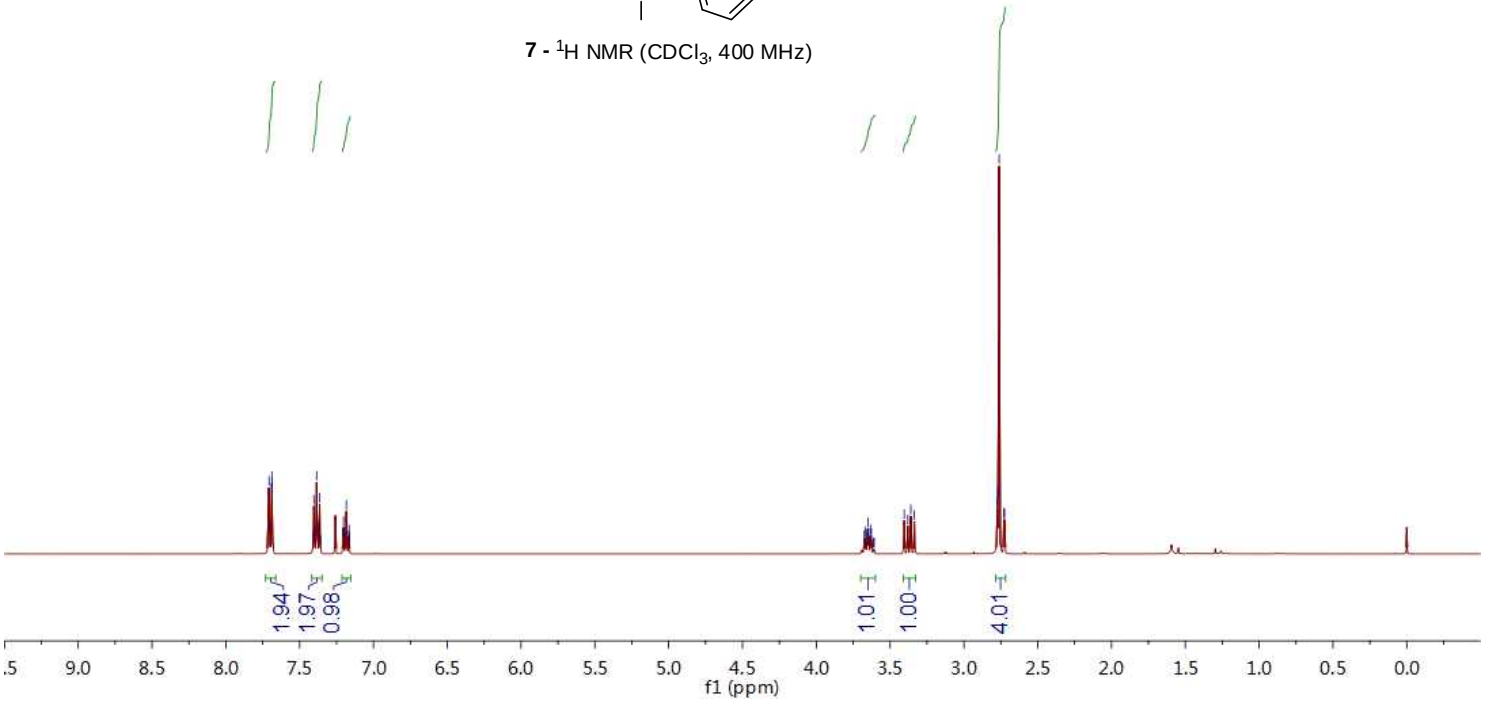


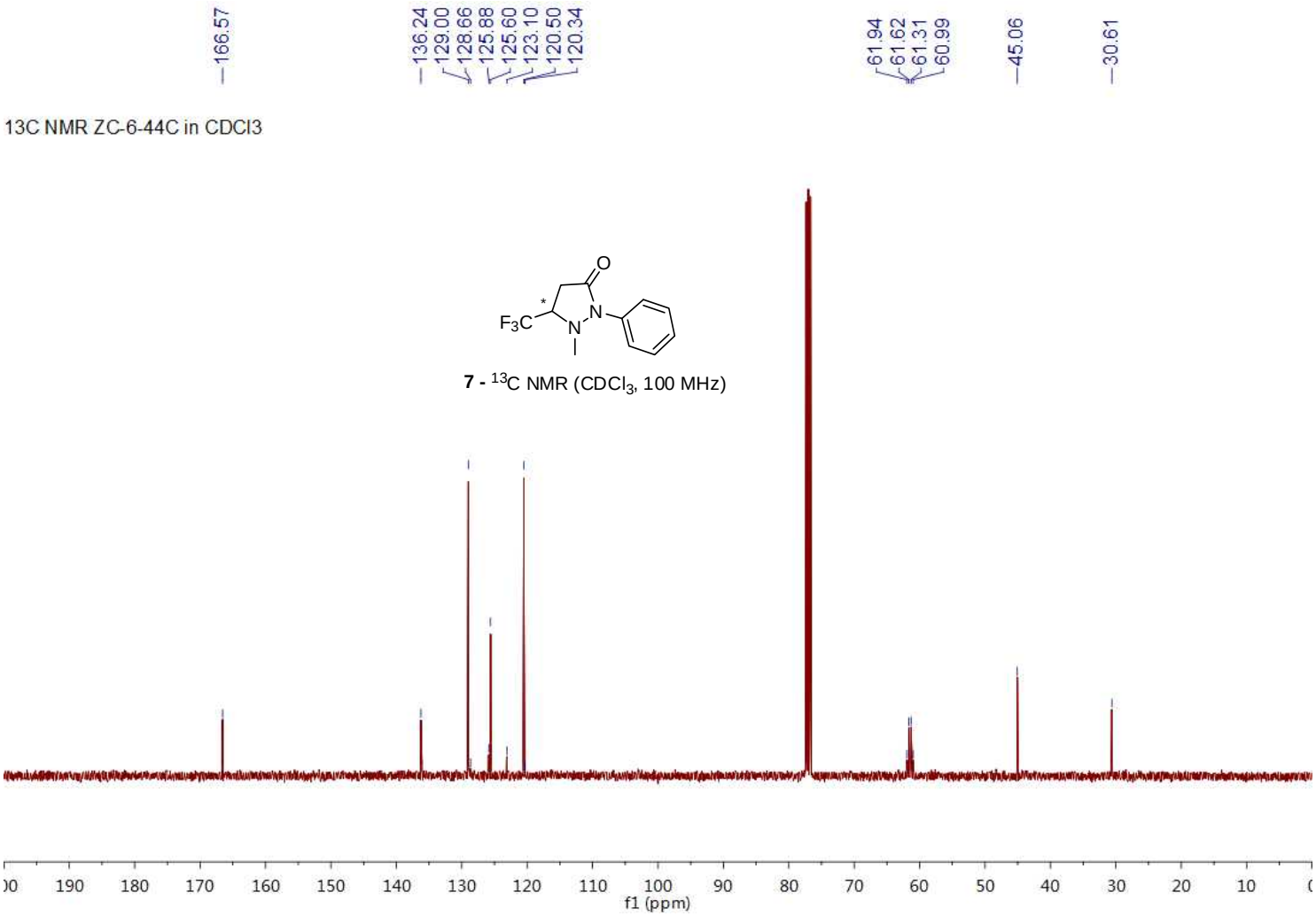
8 - ^{19}F NMR ($CDCl_3$, 377 MHz)

1H NMR ZC-6-44C in CDCl3

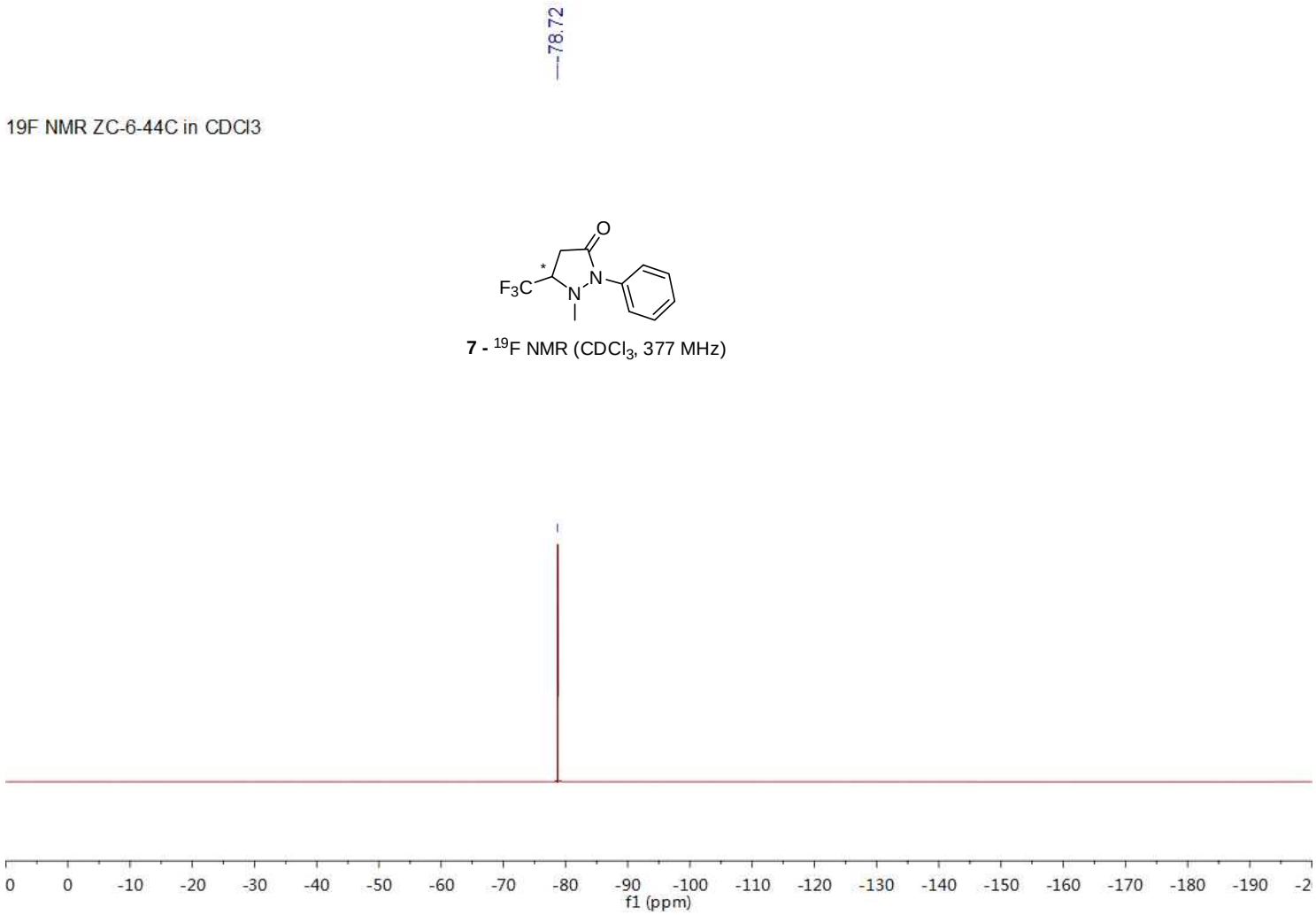


7 - ^{1}H NMR ($CDCl_3$, 400 MHz)

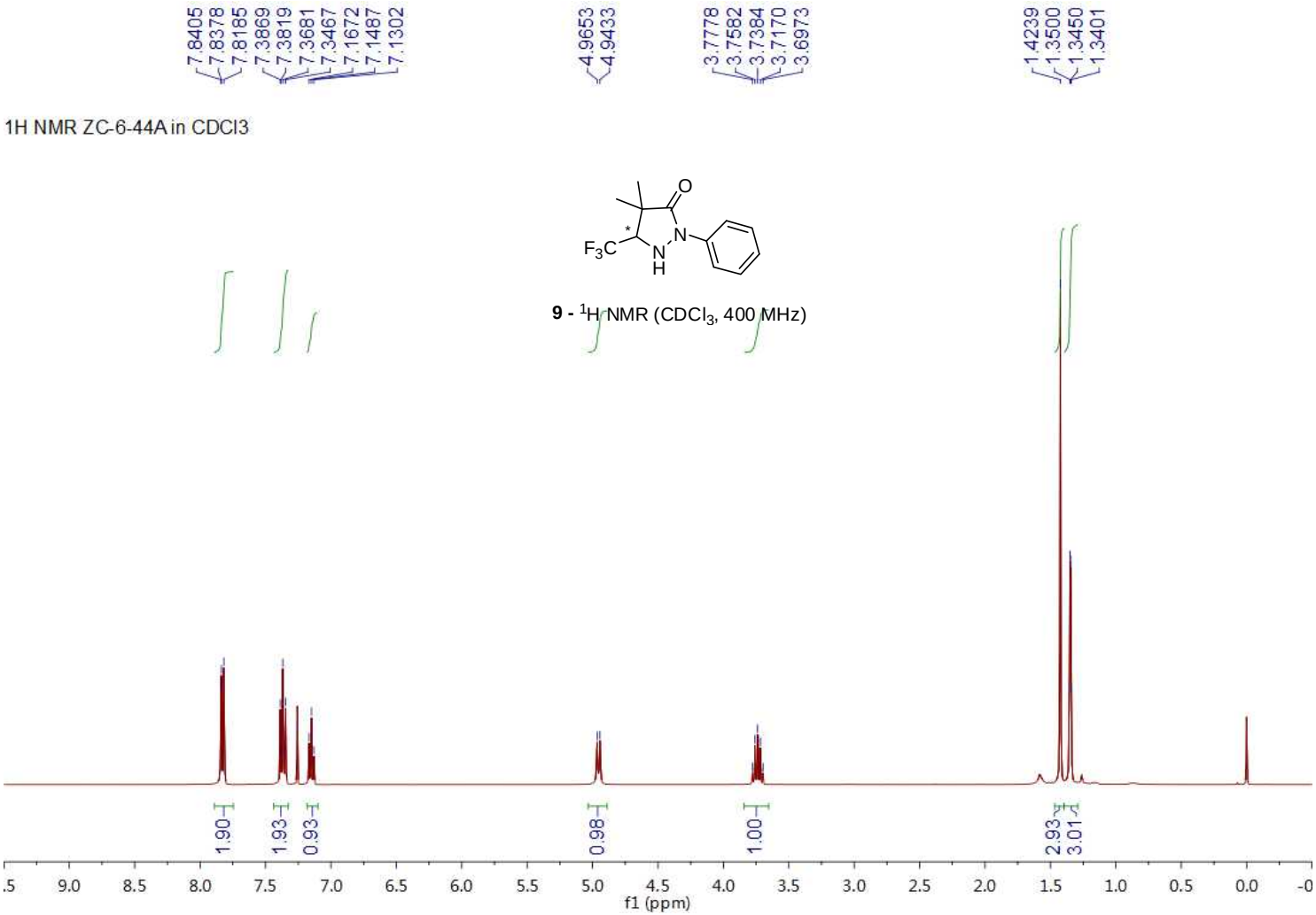




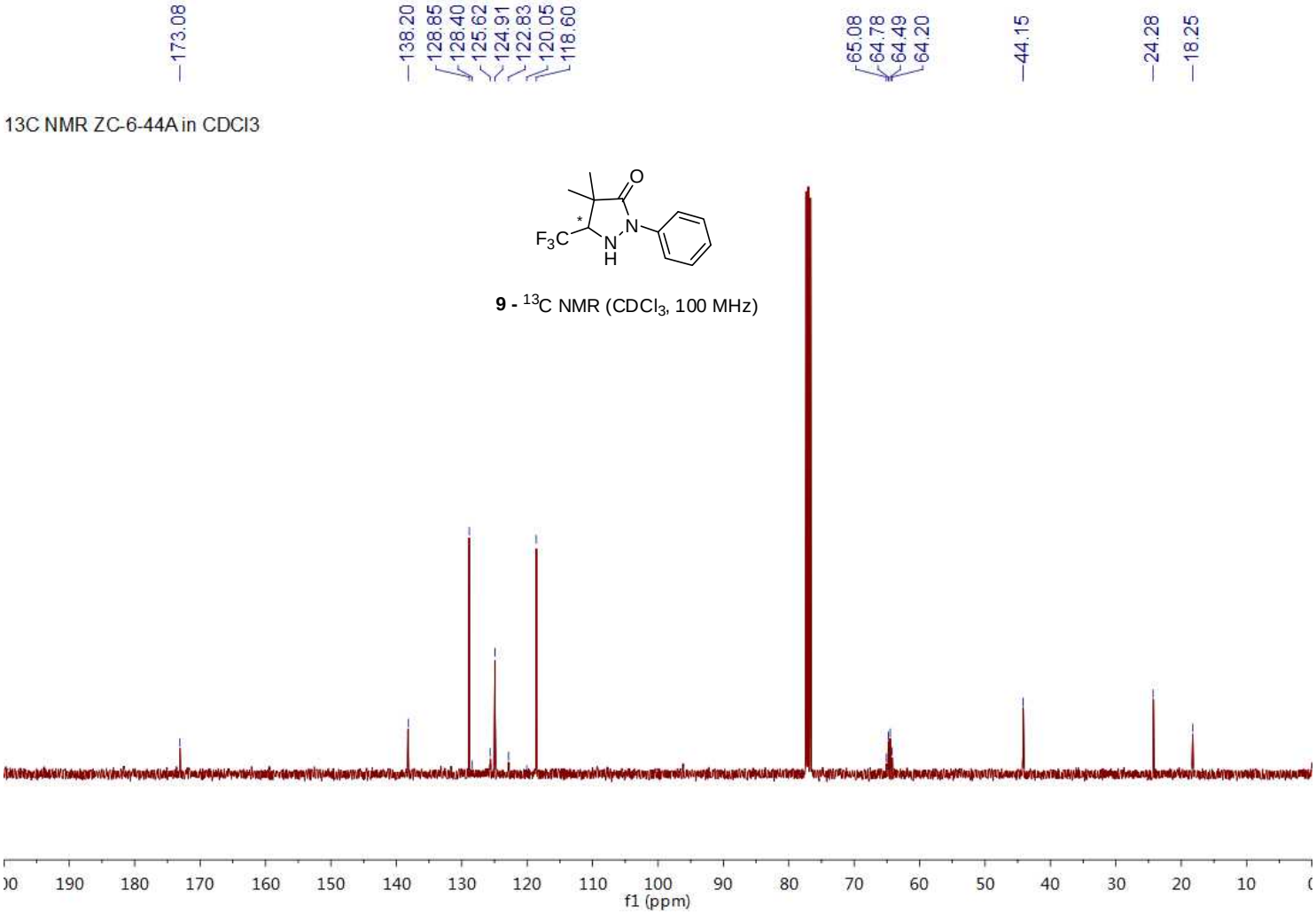
7 - ^{13}C NMR ($CDCl_3$, 100 MHz)



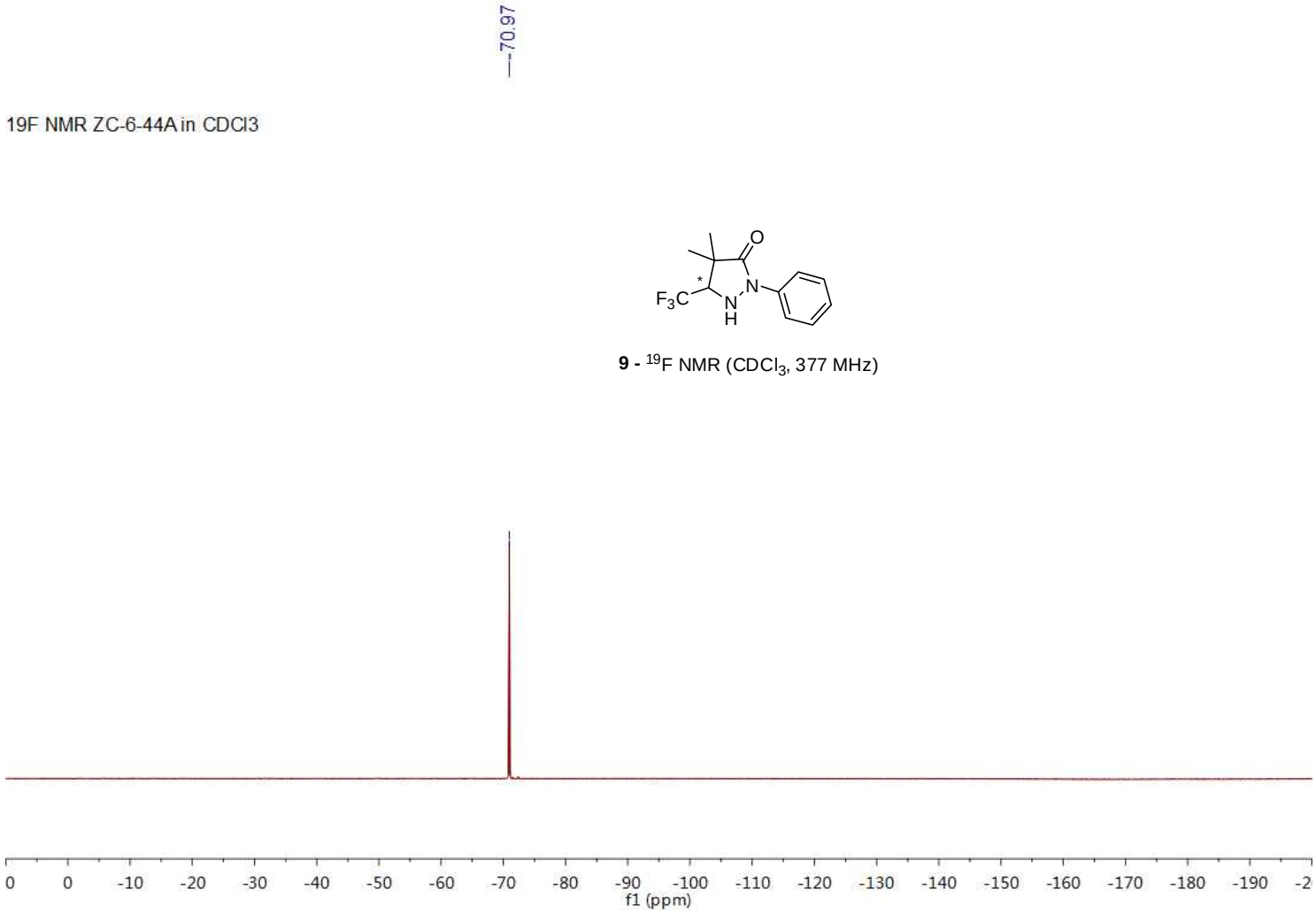
7 - ^{19}F NMR ($CDCl_3$, 377 MHz)



9 - ^{1}H NMR ($CDCl_3$, 400 MHz)



9 - ^{13}C NMR ($CDCl_3$, 100 MHz)

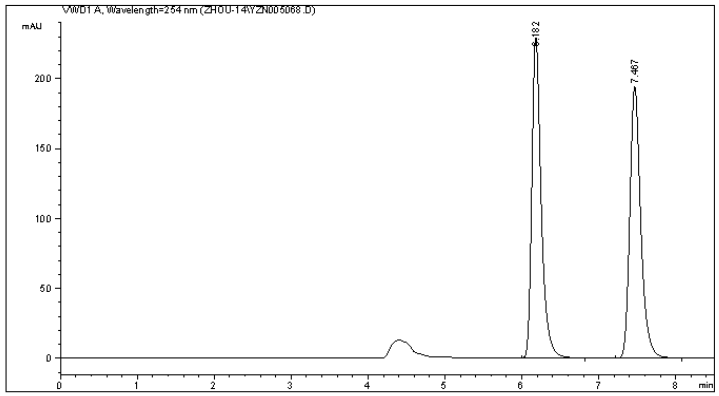


9 - ^{19}F NMR ($CDCl_3$, 377 MHz)

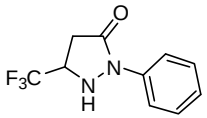
9. Copy of HPLC for Racemic and Chiral Products

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005068.D
Sample Name: ZC-M-20A+-

```
==================================================================
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 5/16/2014 3:37:35 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 5/16/2014 2:57:52 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 5/26/2014 2:25:21 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



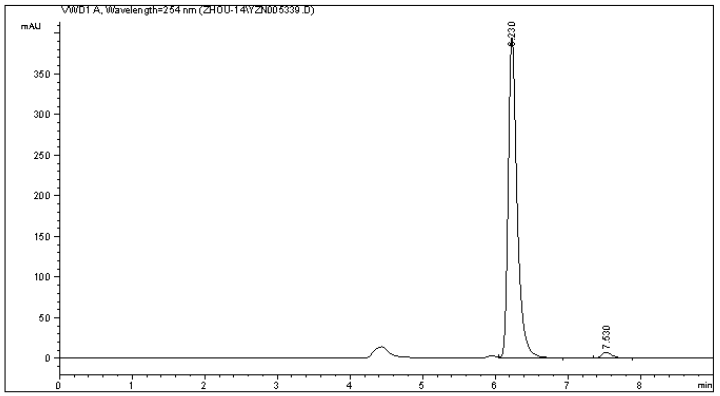

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1   6.182 BB    0.1276 1936.70898  229.33224  50.3419
   2   7.467 BB    0.1496 1910.39893  194.30939  49.6581

Totals :                  3847.10791  423.64163

==================================================================
                      *** End of Report ***
```



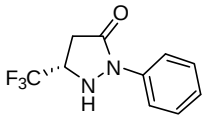
(+/-) - **2a**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005339.D
Sample Name: ZC-5-59A

```
==================================================================
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/20/2014 9:37:41 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 6/20/2014 8:58:39 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 8:57:12 AM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



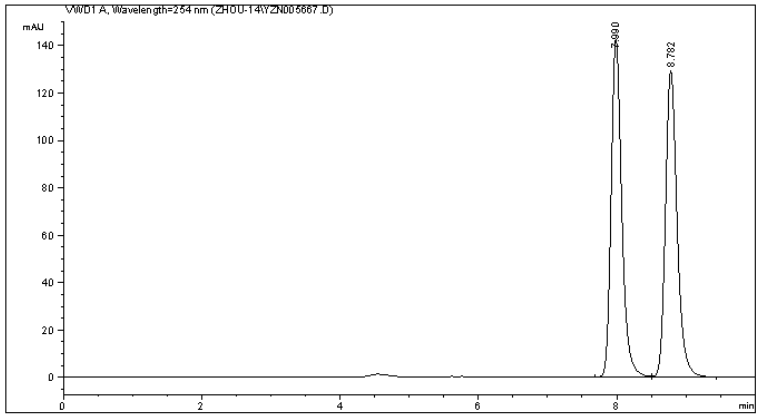

```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1   6.230 VB    0.1287 3367.25513  394.48074  97.9239
   2   7.530 BB    0.1472   71.39044    7.32410   2.0761

Totals :                  3438.64557  401.80484

==================================================================
                      *** End of Report ***
```



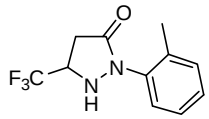
(+) - **2a**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005667.D
Sample Name: ZC-5-83A+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/24/2014 2:36:06 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/24/2014 2:34:41 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 80/20, 0.70 mL/min, 30 oC, 254 nm
```



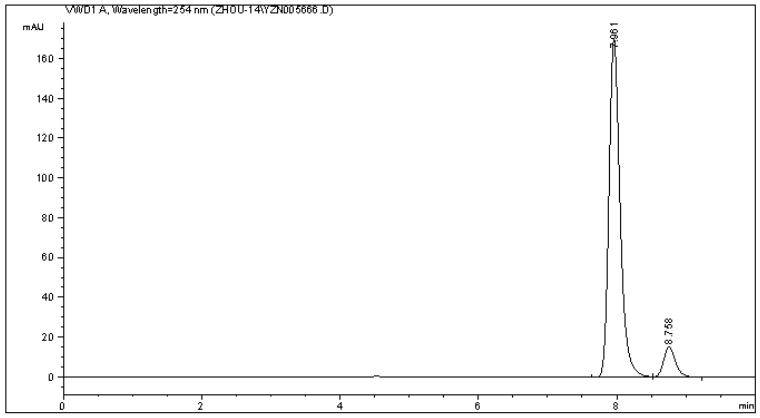

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.990 BV    0.1639 1524.40454  142.75763  50.1431
   2   8.782 VB    0.1789 1515.70349  129.41541  49.8569

Totals :                  3040.10803  272.17303

                          *** End of Report ***
```



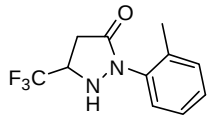
(+/-) - **2b**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005666.D
Sample Name: ZC-5-83A

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/24/2014 2:20:43 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/24/2014 2:18:12 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 80/20, 0.70 mL/min, 30 oC, 254 nm
```



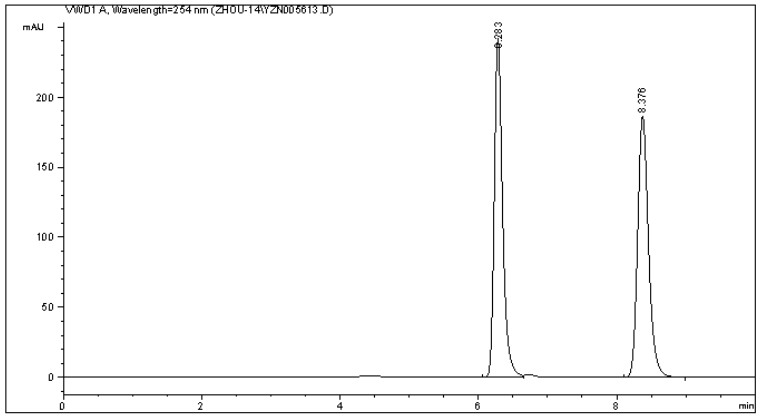

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.961 BV    0.1701 1908.54773  170.18611  91.0756
   2   8.758 VB    0.1866  187.01726   15.27134   8.9244

Totals :                  2095.56499  185.45745

                          *** End of Report ***
```



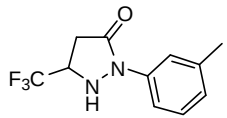
(+) - **2b**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005613.D
Sample Name: ZC-5-81B+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 4:25:12 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 4:24:42 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



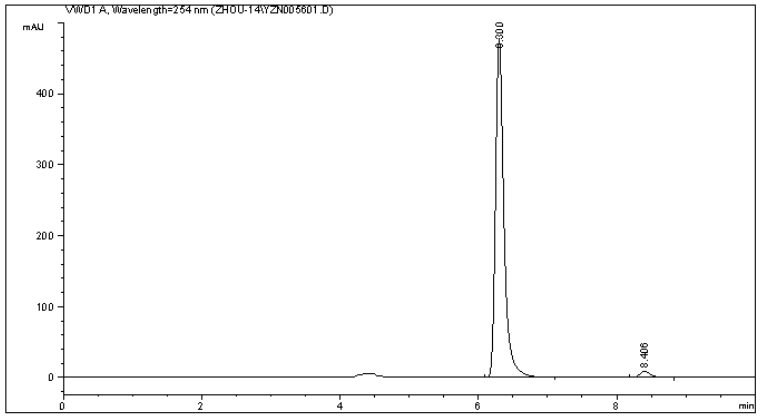

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.283 VV    0.1266 2018.98083  241.69243  49.8280
   2   8.376 BB    0.1665 2032.91565  186.51620  50.1720

Totals :                  4051.89648  428.20863

                          *** End of Report ***
```



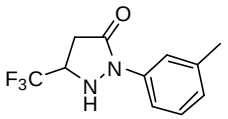
(+/-) - **2c**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005601.D
Sample Name: ZC-5-81B

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 11:03:23 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 11:01:34 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



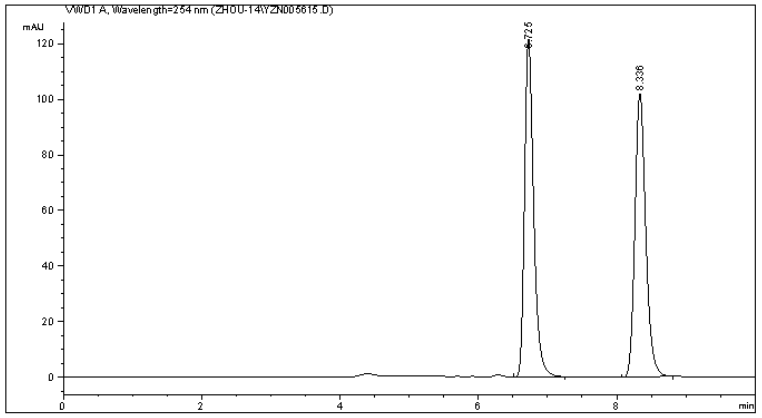

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.300 BB    0.1267 4052.55566  477.21707  97.6812
   2   8.406 BB    0.1666   96.20064    8.81815   2.3188

Totals :                  4148.75630  486.03522

                          *** End of Report ***
```



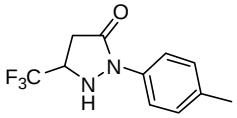
(+) - **2c**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005615.D
Sample Name: ZC-5-81C+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 4:51:12 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 4:50:42 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.725 VB    0.1389 1113.86377  121.64944  50.1462
   2   8.336 BB    0.1676 1107.36755  101.84657  49.8538

Totals :                  2221.23132  223.49602

                          *** End of Report ***
```

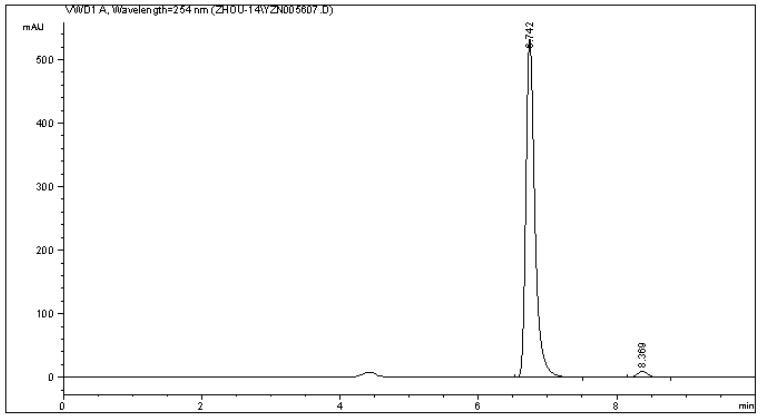


(+/-) - **2d**

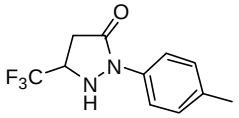
Instrument 1 12/8/2014 9:03:37 AM Z Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005607.D
Sample Name: ZC-5-81C

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 2:46:54 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 2:46:29 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.742 VB    0.1359 4811.26807  532.89709  97.8408
   2   8.369 BB    0.1648  106.17783    9.87357   2.1592

Totals :                  4917.44589  542.77066

                          *** End of Report ***
```

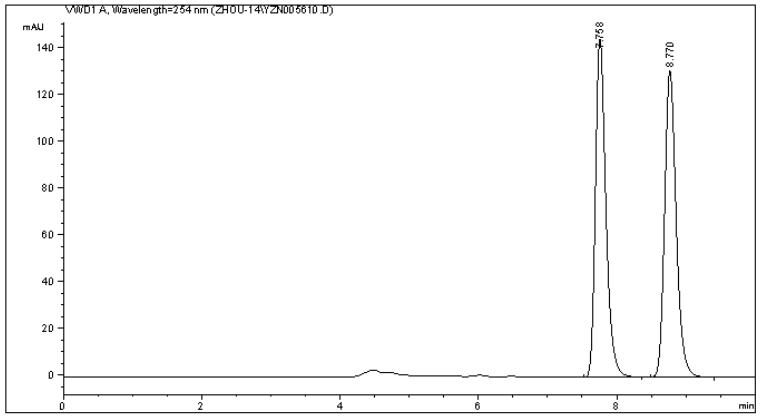


(+) - **2d**

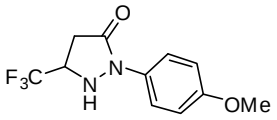
Instrument 1 12/8/2014 9:04:05 AM Z Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005610.D
Sample Name: ZC-5-81E+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 3:43:30 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 3:27:19 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



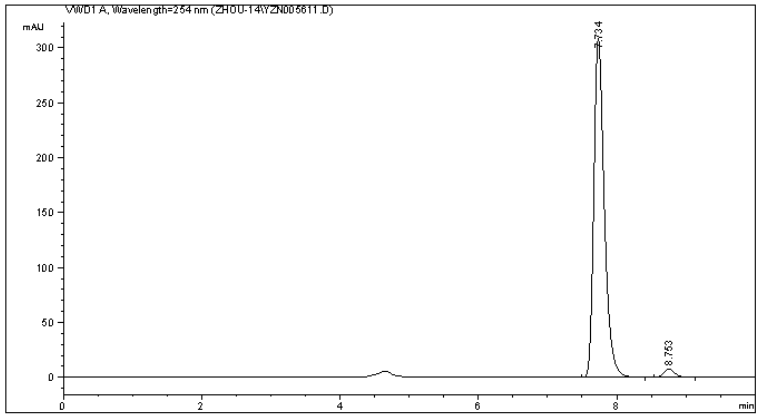

```
Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.758 BB    0.1603 1518.44153  144.70284  49.9998
   2   8.770 BB    0.1773 1518.45313  131.11829  50.0002

Totals :                  3036.89465  275.82112

*** End of Report ***
```



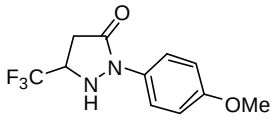
(+/-) - **2e**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005611.D
Sample Name: ZC-5-81E

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 3:56:37 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 3:56:12 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



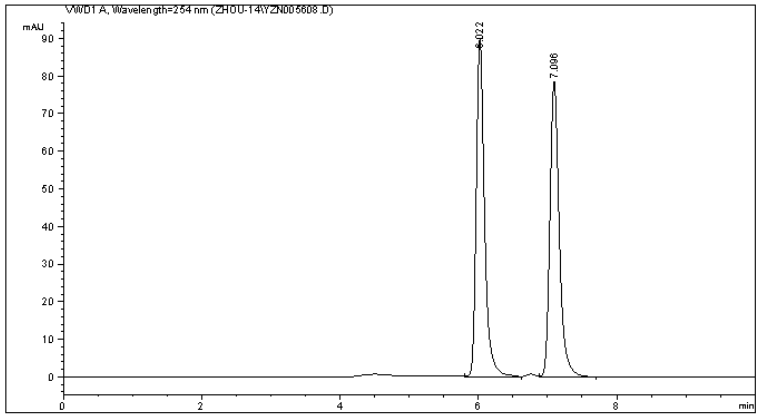

```
Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.734 BB    0.1609 3253.38062  308.39325  97.3675
   2   8.753 BB    0.1762   87.96004    7.66204   2.6325

Totals :                  3341.34066  316.05529

*** End of Report ***
```



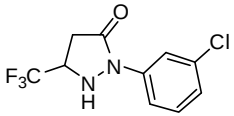
(+) - **2e**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005608.D
Sample Name: ZC-5-81D+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 2:59:21 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 2:57:35 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



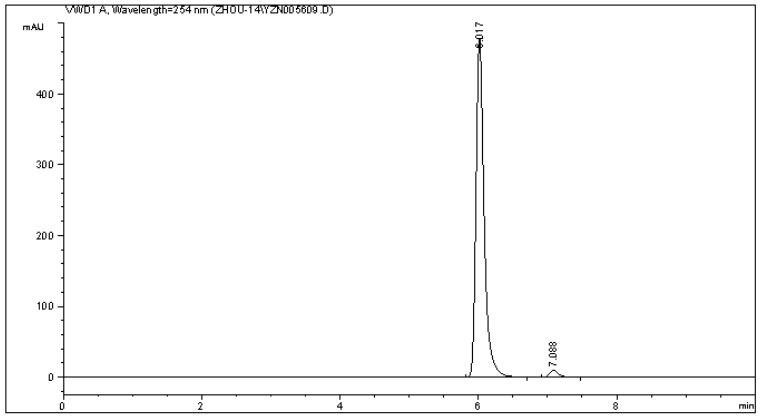

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.022 VB    0.1267  753.17029   90.01208  50.3189
   2   7.096 VB    0.1438  743.62482   78.66964  49.6811

Totals :                  1496.79510  168.68172

                          *** End of Report ***
```



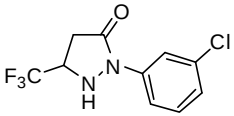
(+/-) - **2f**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005609.D
Sample Name: ZC-5-81D

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2014 3:15:15 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/21/2014 3:13:39 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:00:48 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



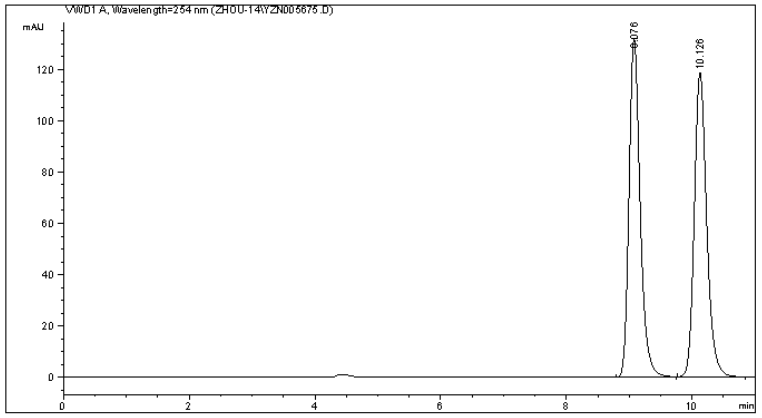

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.017 BB    0.1230 3910.24976  478.38824  97.6016
   2   7.088 BB    0.1410   96.08696   10.42237   2.3984

Totals :                  4006.33672  488.81061

                          *** End of Report ***
```



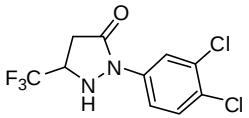
(+) - **2f**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005675.D
Sample Name: ZC-5-83D+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/24/2014 4:27:01 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/24/2014 4:26:00 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:08:01 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 85/15, 0.70 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.076 BB    0.1892 1627.82117  131.78853  50.0202
   2  10.126 BB    0.2096 1626.50952  118.56556  49.9798

Totals :                  3254.33069  250.35409
```

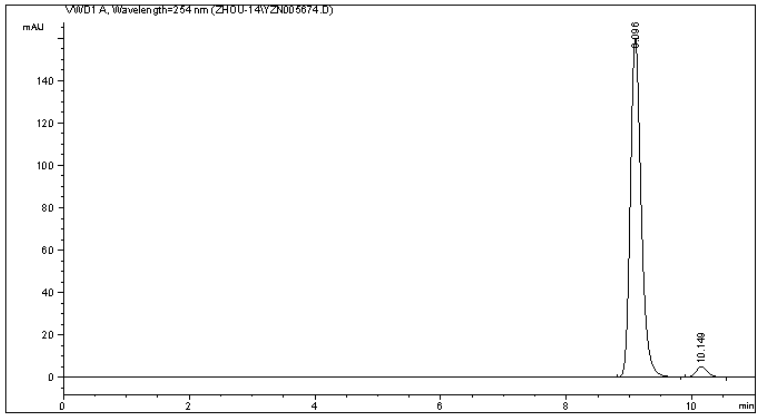


(+/-) - **2g**

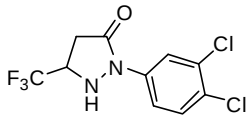
```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005674.D
Sample Name: ZC-5-83D

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/24/2014 4:14:39 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/24/2014 4:13:02 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:08:01 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 85/15, 0.70 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.096 BB    0.1820 1912.09912  159.59459  96.6600
   2  10.149 BB    0.2020   66.07129    5.00566   3.3400

Totals :                  1978.17041  164.60025
```

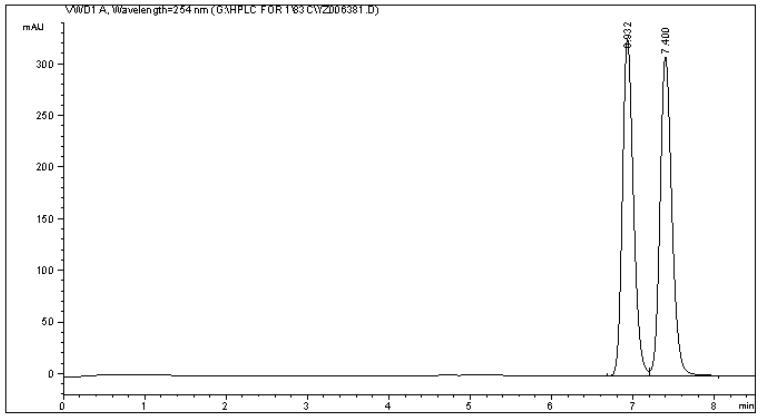


(+) - **2g**

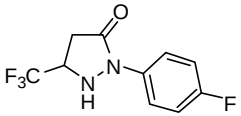
```
                          *** End of Report ***
```

Data File G:\HPLC FOR 1\83C\YZ006381.D
Sample Name: ZC-5-83C+-

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/25/2014 7:27:38 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 7/25/2014 7:22:20 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:17:59 AM by Z
                  (modified after loading)
Sample Info     : OJ, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.932 VV    0.1443 3059.86548  326.39697  49.7621
   2   7.400 VB    0.1530 3089.12012  309.18073  50.2379

Totals :                  6148.98560  635.57770
```

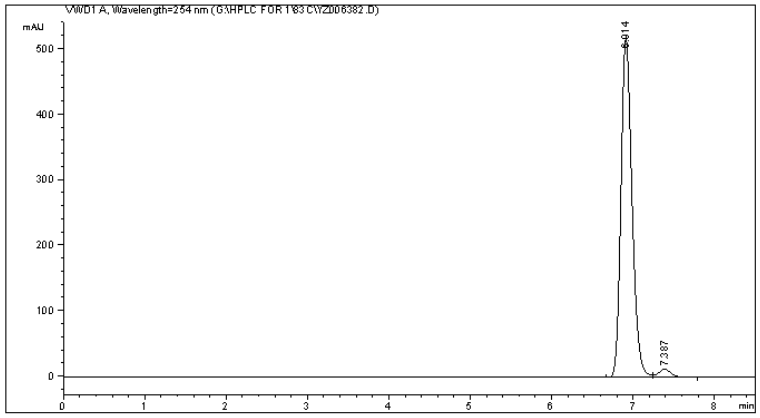


(+/-) - **2h**

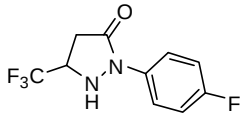
```
                          *** End of Report ***
```


Data File G:\HPLC FOR 1\83C\YZ006382.D
Sample Name: ZC-5-83C

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/25/2014 7:37:01 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 7/25/2014 7:36:48 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:17:59 AM by Z
                  (modified after loading)
Sample Info     : OJ, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.914 BV    0.1454 4895.64893  517.16840  97.3574
   2   7.387 VB    0.1619  132.88655   12.34933   2.6426

Totals :                  5028.53548  529.51773
```

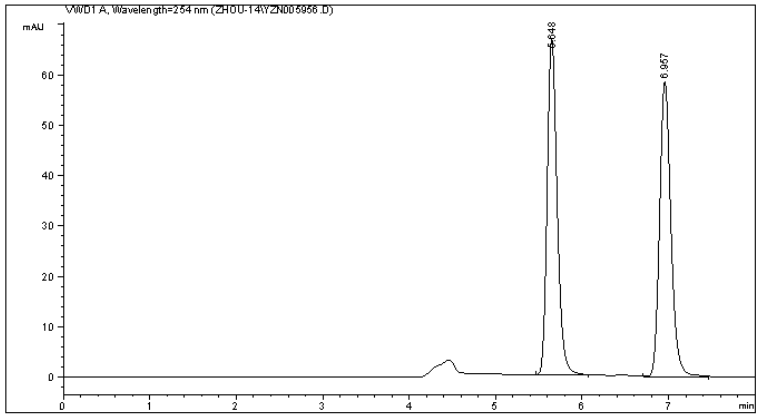


(+) - **2h**

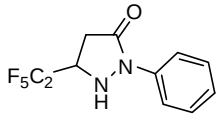
```
                          *** End of Report ***
```

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005956.D
Sample Name: ZC-5-93A+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 9/1/2014 7:51:04 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 9/1/2014 7:44:40 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:10:17 AM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254nm
```



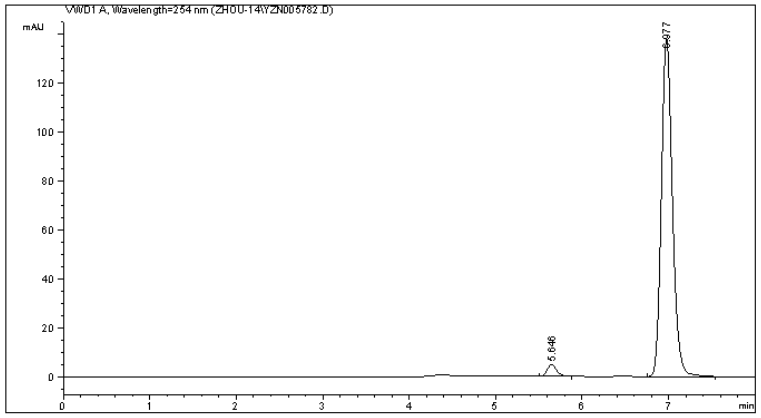

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.648 BB    0.1229  535.93317   66.69895  50.2407
   2   6.957 VB    0.1393  530.79865   58.55206  49.7593

Totals :                  1066.73181  125.25101

                          *** End of Report ***
```



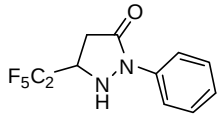
(+/-) - **2i**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005782.D
Sample Name: ZC-5-88A

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/31/2014 10:07:18 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/31/2014 10:06:36 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:10:17 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



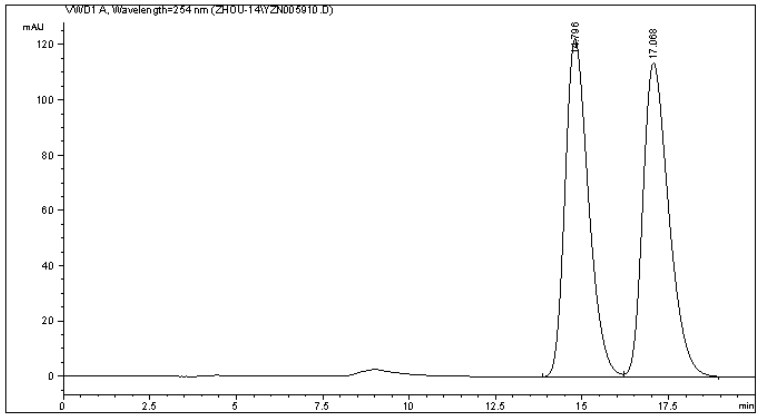

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.646 BB    0.1148   36.22553    4.84819   2.8665
   2   6.977 BB    0.1358 1227.51172  137.97807  97.1335

Totals :                  1263.73725  142.82626

                          *** End of Report ***
```



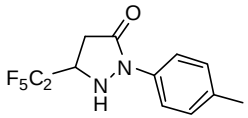
(-) - **2i**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005910.D
Sample Name: ZC-5-93B+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 8/26/2014 2:48:41 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 8/26/2014 2:47:22 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:12:05 AM by Z
                  (modified after loading)
Sample Info     : OG-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 254nm
```



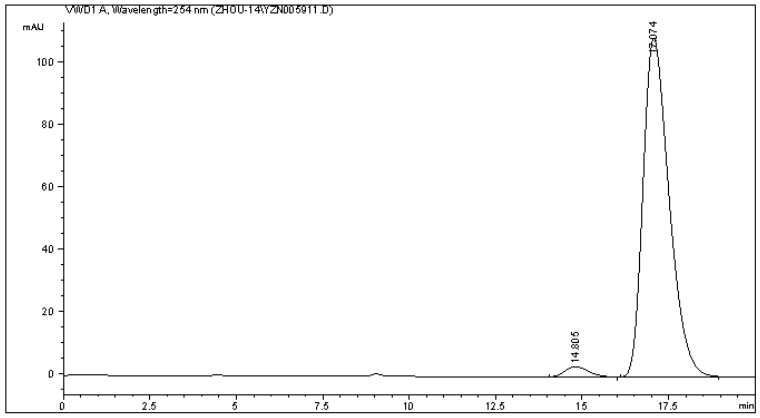

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.796 BB    0.7202 5749.26123  122.31118  49.3583
   2  17.068 BB    0.7968 5898.76172  113.55722  50.6417

Totals :                  1.16480e4   235.86840

                          *** End of Report ***
```



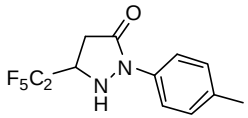
(+/-) - **2j**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005911.D
Sample Name: ZC-5-93B

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 8/26/2014 3:09:53 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 8/26/2014 3:09:15 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/8/2014 9:12:05 AM by Z
                  (modified after loading)
Sample Info     : OG-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 254nm
```



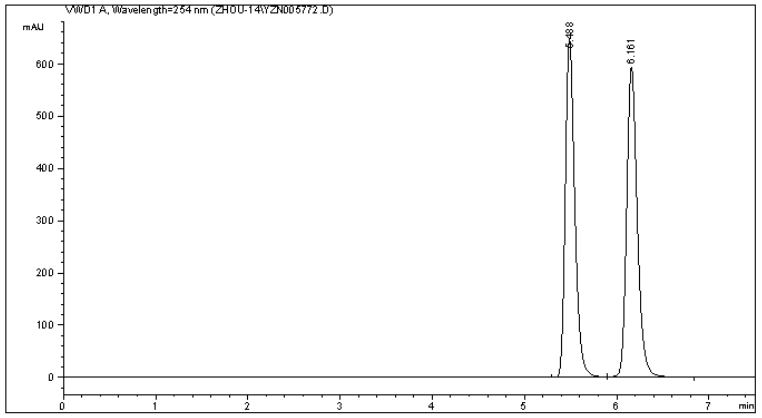

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.805 BB    0.6674  156.58360    3.36045   2.6821
   2  17.074 BB    0.8038 5681.59717  108.37350  97.3179

Totals :                  5838.18077  111.73394

                          *** End of Report ***
```



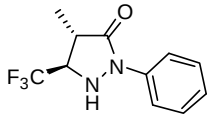
(-) - **2j**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005772.D
Sample Name: ZC-5-86F+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/30/2014 10:01:31 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/30/2014 9:59:11 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:39:58 PM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30 0.7 mL/min, 30 oC, 254 nm
```



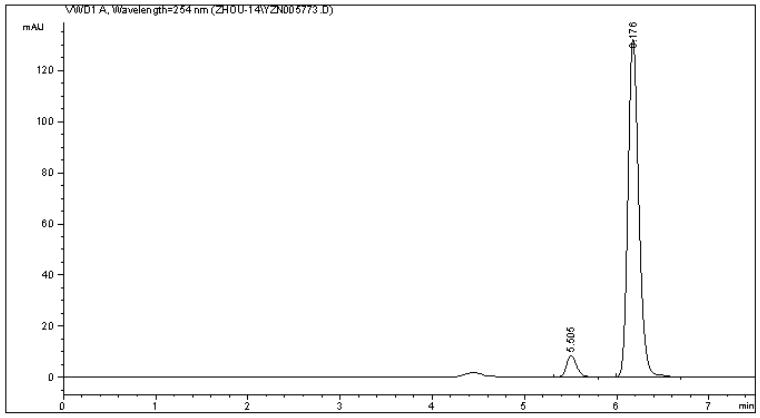

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.488 BV    0.1095 4623.56934  647.60217  49.2684
   2   6.161 VB    0.1228 4760.87842  593.07776  50.7316

Totals :                  9384.44775 1240.67993

                          *** End of Report ***
```



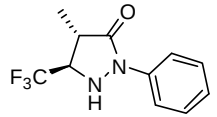
(+/-) - **4a**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005773.D
Sample Name: ZC-5-86F

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/30/2014 10:16:46 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/30/2014 10:15:44 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:39:58 PM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30 0.7 mL/min, 30 oC, 254 nm
```



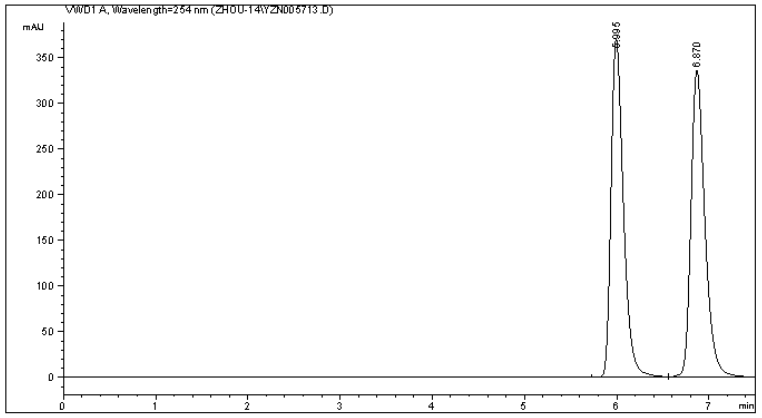

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.505 BB    0.1176   63.91172    8.43166   5.6200
   2   6.176 BB    0.1238 1073.29895  132.26836  94.3800

Totals :                  1137.21067  140.70002

                          *** End of Report ***
```



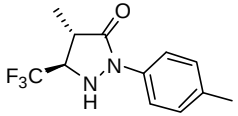
(-) - **4a**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005713.D
Sample Name: ZC-5-86A+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/26/2014 10:30:10 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/26/2014 10:10:25 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:34:10 PM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.995 VV    0.1421 3450.47607  370.58310  49.4396
   2   6.870 VB    0.1604 3528.69922  335.83157  50.5604

Totals :                  6979.17529  706.41467
```

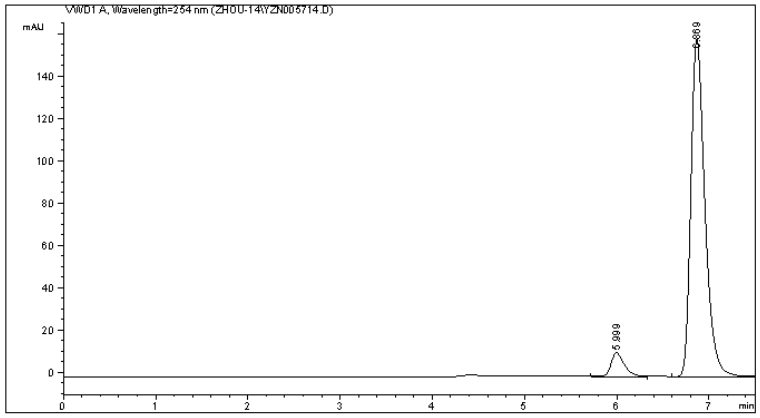


(+/-) -**4b**

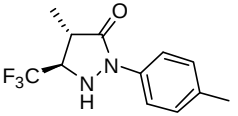
```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005714.D
Sample Name: ZC-5-86A

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/26/2014 10:42:42 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/26/2014 10:40:52 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:34:10 PM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.999 VV    0.1505  112.12787   11.18441   6.2387
   2   6.869 VB    0.1610 1685.17603  159.63228  93.7613

Totals :                  1797.30389  170.81669
```

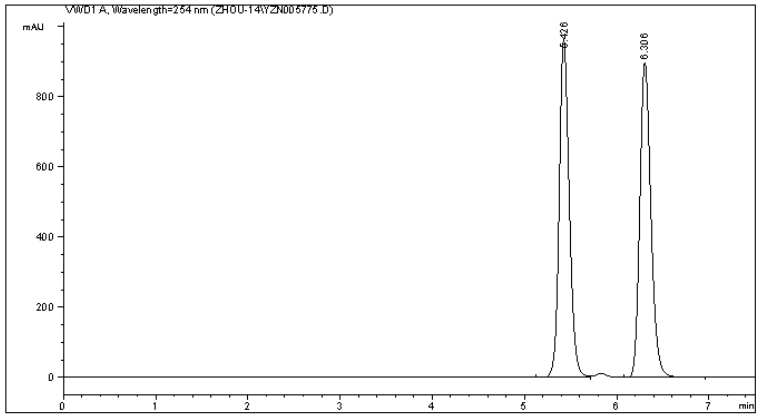


(-) -**4b**

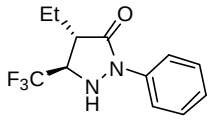
```
                          *** End of Report ***
```

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005775.D
Sample Name: ZC-5-86E+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/30/2014 11:12:11 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/30/2014 10:47:53 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:39:58 PM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30 0.7 mL/min, 30 oC, 254 nm
```



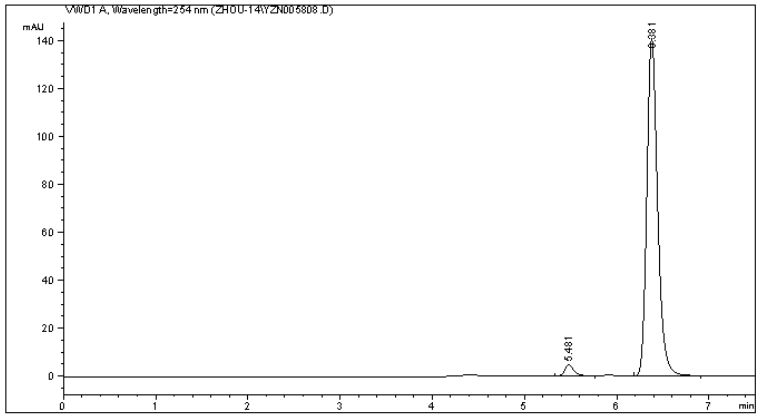

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.426 VV    0.1156 7279.71191  965.33405  49.1759
   2   6.306 VB    0.1297 7523.69189  898.46832  50.8241

Totals :                  1.48034e4  1863.80237

                          *** End of Report ***
```



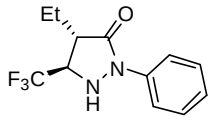
(+/-) -**4c**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005808.D
Sample Name: ZC-5-87E

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 8/14/2014 1:45:06 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 8/14/2014 1:26:59 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:39:58 PM by Z
                  (modified after loading)
Sample Info     : AD, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



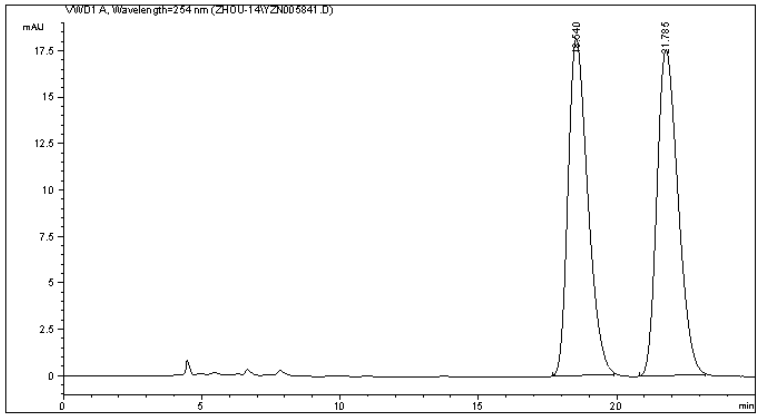

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.481 BB    0.1068   33.74635    4.71308   2.8550
   2   6.381 BB    0.1243 1148.25696  140.71727  97.1450

Totals :                  1182.00331  145.43035

                          *** End of Report ***
```



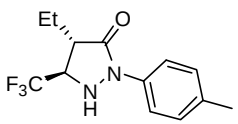
(-) -**4c**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005841.D
Sample Name: ZC-5-90A+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 8/15/2014 9:08:59 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 8/15/2014 9:06:53 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/20/2014 10:57:17 AM by Z
                  (modified after loading)
Sample Info     : OG-H, H/i-PrOH = 95/5, 0.7 mL/min, 30 oC, 254 nm
```



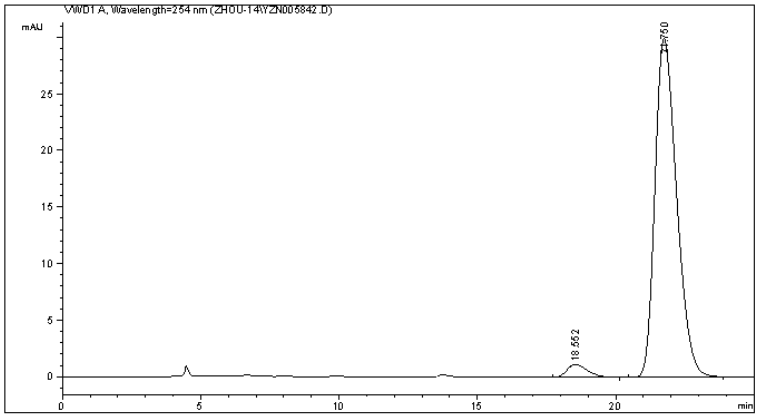

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #  [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.540 BB    0.7551  897.38940   18.13141  49.1149
   2  21.785 BB    0.8105  929.73413   17.54202  50.8851

Totals :                  1827.12354   35.67343

                          *** End of Report ***
```



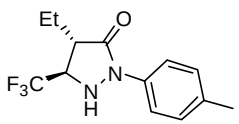
(+/-) -**4d**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005842.D
Sample Name: ZC-5-90A

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 8/15/2014 9:49:35 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 8/15/2014 9:36:53 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/20/2014 10:58:16 AM by Z
                  (modified after loading)
Sample Info     : OG-H, H/i-PrOH = 95/5, 0.7 mL/min, 30 oC, 254 nm
```



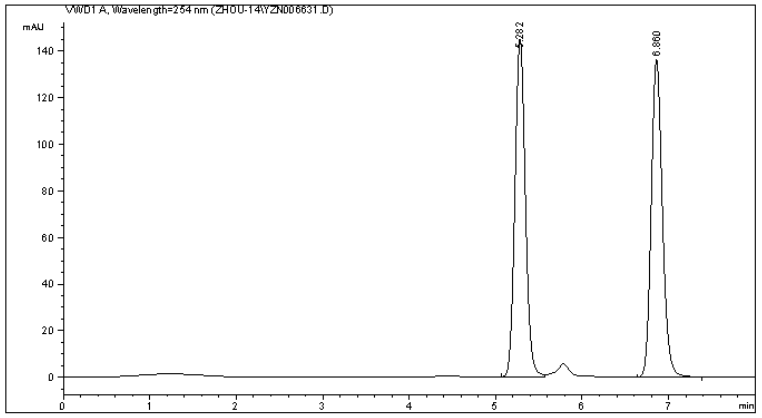

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #  [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.552 BB    0.7550   60.09979    1.16728   3.5548
   2  21.750 BB    0.8428 1630.55042   29.90775  96.4452

Totals :                  1690.65020   31.07504

                          *** End of Report ***
```



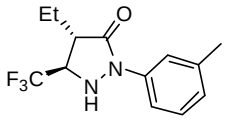
(+) -**4d**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN006631.D
Sample Name: ZC-5-90B+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 12/13/2014 2:15:40 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/13/2014 1:45:53 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/20/2014 10:55:06 AM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



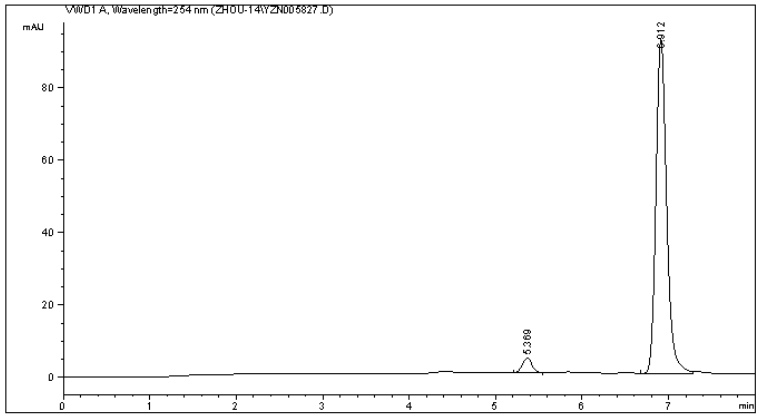

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.282 BV    0.1296 1212.78735  144.99921  49.8640
   2   6.860 BB    0.1380 1219.40527  136.18169  50.1360

Totals :                  2432.19263  281.18089

                          *** End of Report ***
```



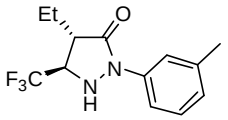
(+/-) -**4e**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005827.D
Sample Name: ZC-5-90B

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 8/14/2014 9:16:36 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 8/14/2014 9:12:39 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:44:22 PM by Z
                  (modified after loading)
Sample Info     : AD, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



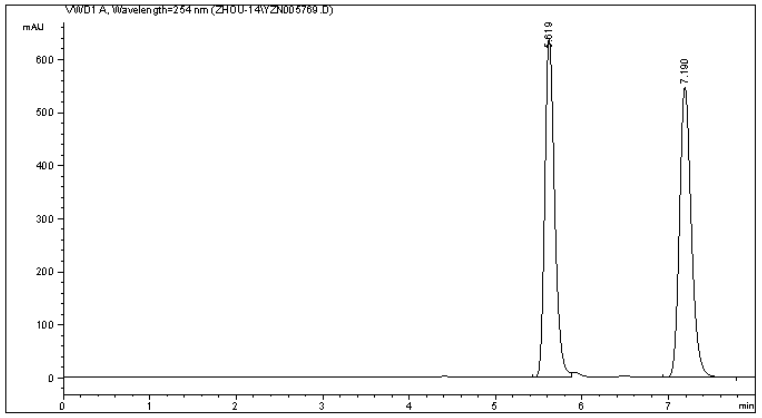

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.369 BV    0.1261   32.52824    4.09973   3.9345
   2   6.912 VV    0.1308  794.20612   92.47683  96.0655

Totals :                  826.73436   96.57656

                          *** End of Report ***
```



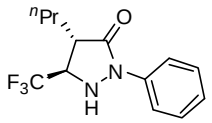
(+) -**4e**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005769.D
Sample Name: ZC-5-86D+-

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/30/2014 9:12:32 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/30/2014 9:11:39 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:37:43 PM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30 0.7 mL/min, 30 oC, 254 nm
```



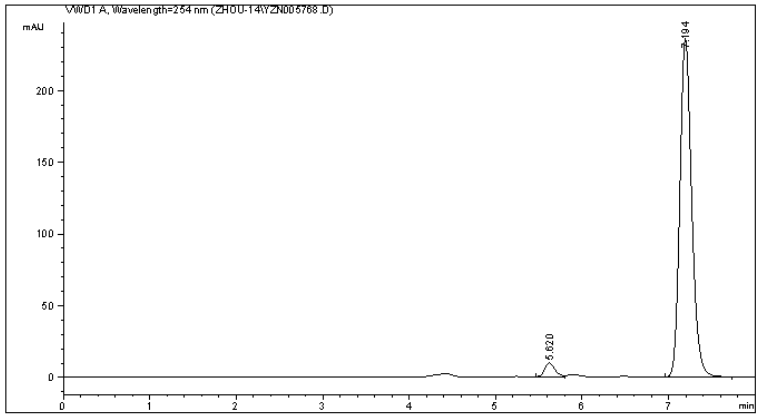

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.619 VV    0.1213 5038.87988  637.91187  49.2415
   2   7.190 BB    0.1457 5194.11768  547.28534  50.7585

Totals :                  1.02330e4  1185.19720

                          *** End of Report ***
```



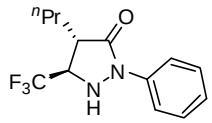
(+/-) **-4f**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005768.D
Sample Name: ZC-5-86D

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/30/2014 8:48:37 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/30/2014 8:16:45 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/4/2014 9:37:43 PM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30 0.7 mL/min, 30 oC, 254 nm
```



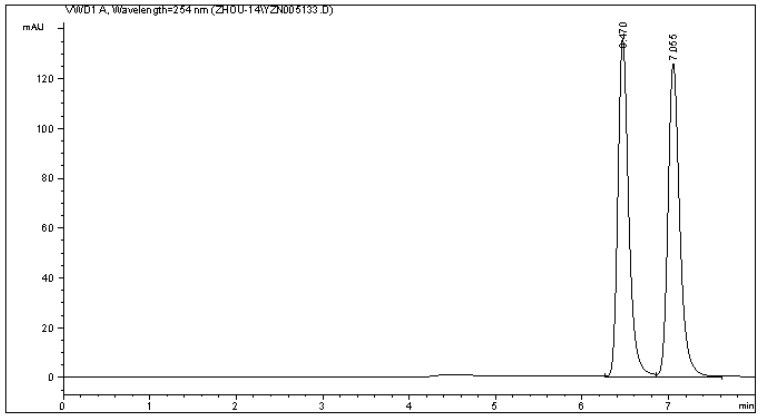

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.620 BV    0.1283   79.75753    9.52649   3.4421
   2   7.194 BB    0.1457 2237.34302  235.64395  96.5579

Totals :                  2317.10055  245.17044

                          *** End of Report ***
```



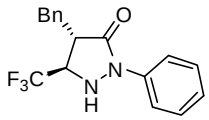
(-) **-4f**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005133.D
Sample Name: ZC-5-42

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 5/27/2014 2:58:09 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 5/27/2014 2:35:10 PM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/5/2014 10:35:55 AM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



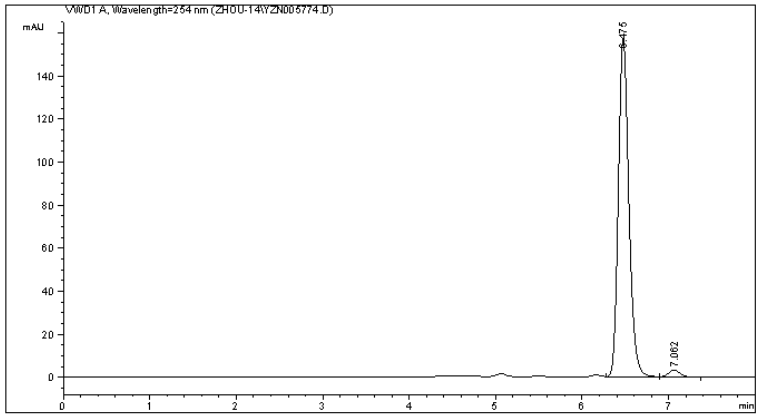

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.470 VV    0.1320 1179.32263  135.60698  49.8211
   2   7.055 VB    0.1436 1187.79102  125.86638  50.1789

Totals :                  2367.11365  261.47336

                          *** End of Report ***
```



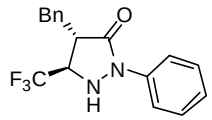
(+/-) -**4g**

Data File C:\CHEM32\1\DATA\ZHOU-14\YZN005774.D
Sample Name: ZC-5-85

```
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/30/2014 10:32:04 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 7/30/2014 10:30:12 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/5/2014 10:35:55 AM by Z
                  (modified after loading)
Sample Info     : AD-H , H/i-PrOH = 70/30 0.7 mL/min, 30 oC, 254 nm
```



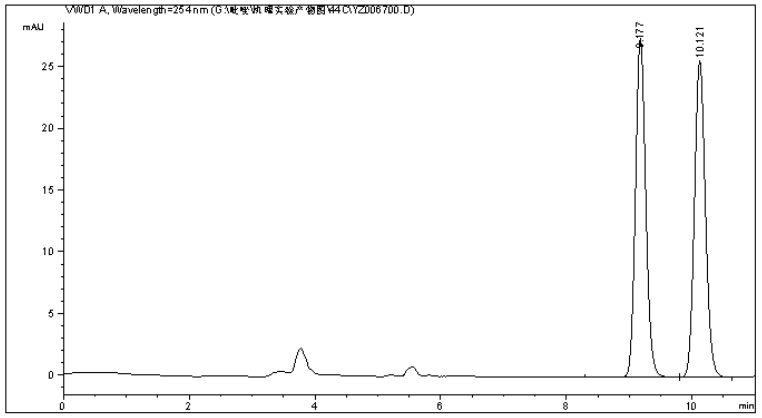

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.475 VV    0.1295 1330.98718  157.02785  97.7393
   2   7.062 VB    0.1438   30.78589    3.25714   2.2607

Totals :                  1361.77308  160.28499

                          *** End of Report ***
```



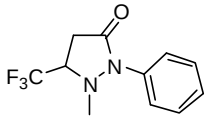
(+) -**4g**

Data File G:\吡唑\机理实验产物图\44C\YZ006700.D
Sample Name: ZC-6-44C+-

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/18/2014 12:24:36 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 11/18/2014 12:21:56 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/20/2014 11:20:25 AM by Z
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.8 mL/min, 30 oC, 254 nm
```



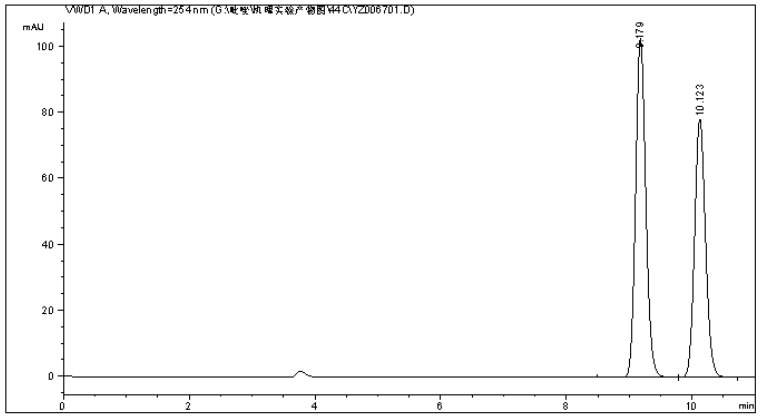

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.177 VV    0.1770  313.46347   27.42233  50.1650
   2  10.121 VV    0.1884  311.40149   25.62359  49.8350

Totals :                  624.86496   53.04592

                          *** End of Report ***
```



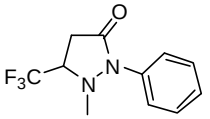
(+/-) - **7**

Data File G:\吡唑\机理实验产物图\44C\YZ006701.D
Sample Name: ZC-6-44C

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/18/2014 12:37:24 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 11/18/2014 12:36:11 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/20/2014 11:19:38 AM by Z
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.8 mL/min, 30 oC, 254 nm
```



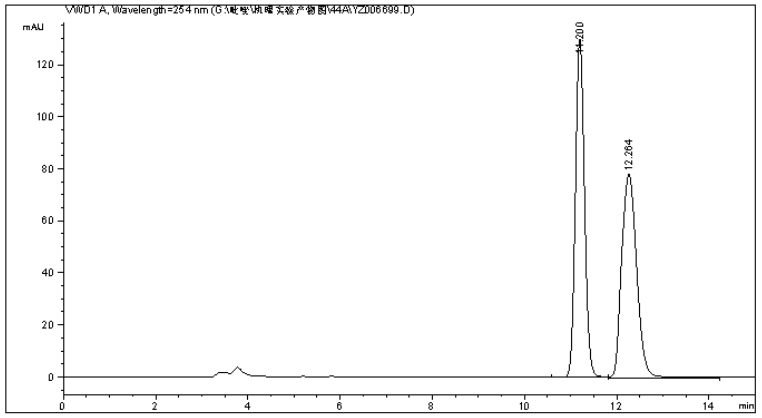

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.179 VV    0.1756 1159.77759  102.57599  54.9986
   2  10.123 VV    0.1881  948.96246   78.25777  45.0014

Totals :                 2108.74005  180.83376

                          *** End of Report ***
```



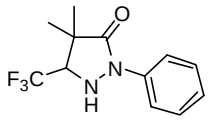
(+) - **7**

Data File G:\吡唑\机理实验产物图\44A\YZ006699.D
Sample Name: ZC-6-44A+-

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/18/2014 12:06:12 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 11/18/2014 11:57:14 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/20/2014 11:18:08 AM by Z
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.8 mL/min, 30 oC, 254 nm
```



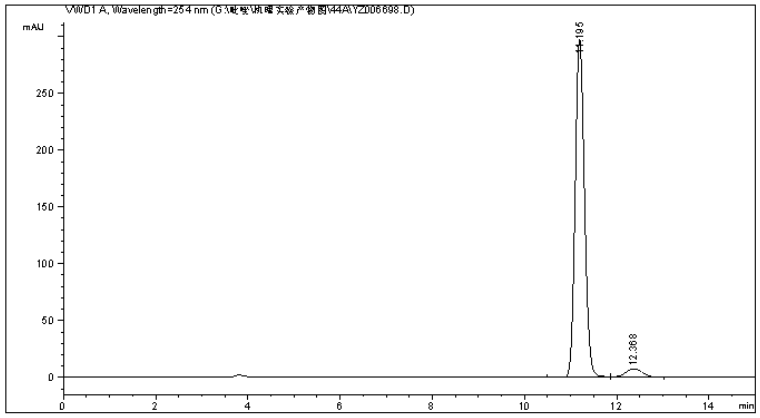

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.200 VV    0.2124 1784.32935  130.15268  50.3100
   2  12.264 VB    0.3680 1762.34241   78.13858  49.6900

Totals :                  3546.67175  208.29126

==========================================================================
                        *** End of Report ***
```



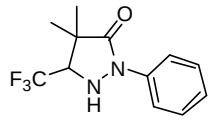
(+/-) -**9**

Data File G:\吡唑\机理实验产物图\44A\YZ006698.D
Sample Name: ZC-6-44A

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/18/2014 11:40:02 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 11/18/2014 11:21:46 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 12/20/2014 11:18:08 AM by Z
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH = 90/10, 0.8 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.195 BV    0.2188 4178.64844  298.17264  95.2759
   2  12.368 VV    0.4133  207.19157    7.69088   4.7241

Totals :                  4385.84001  305.86351

==========================================================================
                        *** End of Report ***
```



(+) - **9**