Electronic Supplementary Information

Microwave-assisted DABCO-promoted regioselective [3+3] tandem cyclization: synthesis of pyrrolo[3,4-*b*]pyridine-4-ones from trifluoromethyl-alkynyl ester and α-aminomaleimide

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1. General information

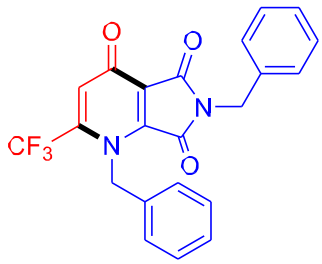
NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Agilent LC/MS TOF mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. All the solvents were used directly without any purification.

2. Experimental

Unless otherwise stated, all reagents and solvents were purchased from Adamas-beta® and used without further purification. NMR spectra were recorded on BRUKER AVANCETM III 400, ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained as solution in $CDCl_3$ or $(CD_3)_2SO$. Chemical shifts were reported in parts per million (ppm, δ) and referenced to TMS (trimethylsilane).

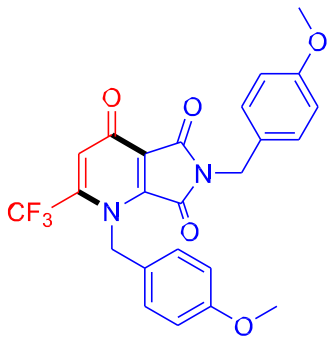
General procedure for the synthesis of 3a:

To a mixture of α-aminomaleimide derivatives (**1a**, 0.1 mmol) and substituted ethyl 2-butynoate (**2a**, 0.12 mmol) in toluene (1. 0 mL), DABCO (2.5 equiv) was added, and the reaction mixture was stirred for microwave radiation 0.5 hours at 110 °C. The progress of the reaction mixture was monitored by TLC. After completion of the reaction, the mixture was extracted with ethyl acetate and concentrated under vacuum. The crude product was purified by silica gel column (200–300 mesh) with petroleum ether/ethyl acetate (10/1~6/1) as eluent to afford the corresponding product. Finally, the pure product can be obtained after vacuum drying and oil pump to remove the remaining solvent.



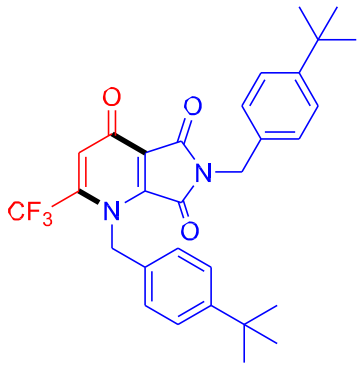
1,6-Dibenzyl-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, DMSO) δ 7.42–7.31 (m, 10H), 7.21 (s, 1H), 5.65 (s, 2H), 4.76 (s, 2H); ^{13}C NMR (100 MHz, DMSO) δ 162.7, 162.3, 161.1, 144.6, 136.1, 135.4, 128.5, 128.3, 127.6, 127.6, 127.5, 121.2 (q, J_{C-F} = 5.7 Hz), 105.7, 46.5, 41.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8; HRMS (ESI-TOF) : *m/z* calcd for $C_{22}H_{15}F_3N_2O_3$ $[(M+H)^+]$, 412.1042; found, 412.1035.



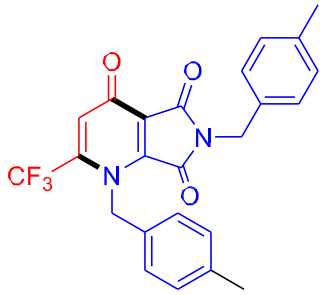
1,6-Bis(4-methoxybenzyl)-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.14 (m, 6H,), 7.13-7.07 (m, 2H), 6.57 (s, 1H), 5.72 (s, 2H), 4.76 (s, 2H), 2.47 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 160.8, 160.3, 142.4, 135.2, 134.6, 132.2, 131.5, 129.6, 127.8, 127., 126.6, 125.3, 122.7, 121.5 (q, $J_{C\text{-}F}$ = 6.0 Hz), 105.9, 98.3, 43.7, 38.6, 18.4, 18.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7; HRMS (ESI-TOF) : *m/z* calcd for $C_{24}H_{19}F_3N_2O_5$ [$(M+H)^+$], 472.1251; found, 472.1246.



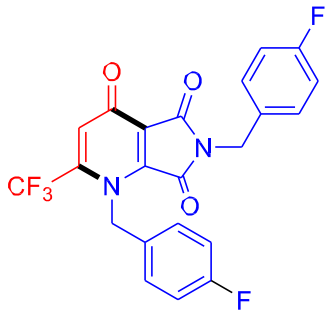
1,6-Bis(4-(tert-butyl)benzyl)-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.38–7.31 (m, 6H), 7.03 (s, 1H), 5.71 (s, 2H), 4.75 (s, 2H), 1.30 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 161.1, 160.6, 150.5, 150.3, 142.1, 131.2, 127.7, 124.7, 121.5 (q, $J_{C\text{-}F}$ = 6.0 Hz), 105.8, 57.4, 45.2, 40.8, 33.5, 30.2, 17.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8; HRMS (ESI-TOF) : *m/z* calcd for $C_{30}H_{31}F_3N_2O_3$ [$(M+H)^+$], 524.2293; found, 524.2287.



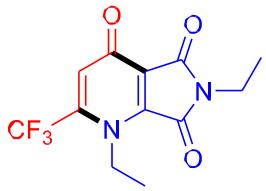
1,6-Bis(4-methylbenzyl)-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.40 (m, 2H), 7.39–7.34 (m, 2H), 7.00 (s, 1H), 6.86–6.81 (m, 4H), 5.65 (s, 2H), 4.71 (s, 2H), 3.78 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 161.1, 160.5, 158.6, 158.5, 141.9, 129.6, 129.4, 126.4 126.3, 121.4 (q, $J_{C\text{-}F}$ = 5.6 Hz), 113.1, 112.9, 105.8, 54.3, 54.2, 45.1, 40.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8; HRMS (ESI-TOF) : *m/z* calcd for $C_{24}H_{19}F_3N_2O_3$ [$(M+H)^+$], 440.1356 ; found, 440.1348.



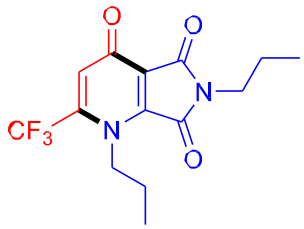
1,6-bis(4-fluorobenzyl)-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 1H), 7.43–7.37 (m, 1H), 7.06–6.97 (m, 2H), 5.68 (s, 1H), 4.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, $^{1}J_{C–F}$ = 246.0 Hz), 161.1, 160.5, 141.8, 130.2 (d, $^{3}J_{C–F}$ = 8.0 Hz), 129.9 (d, $^{3}J_{C–F}$ = 8.0 Hz), 129.8, 121.7 (q, J_{C-F} = 5.7 Hz), 120.6, 114.9 (d, $^{2}J_{C–F}$ = 14.0 Hz), 114.7 (d, $^{2}J_{C–F}$ = 14.0 Hz), 114.6 (d, $^{2}J_{C–F}$ = 14.0 Hz), 114.5(d, $^{2}J_{C–F}$ = 14.0 Hz), 105.9, 44.9, 40.4; ^{19}F NMR (376 MHz, CDCl3) δ -64.8, 112.8, 113.2; HRMS (ESI-TOF) : *m/z* calcd for $C_{22}H_{13}F_5N_2O_3$ [(M+H)$^+$], 448.0859; found, 448.0846.



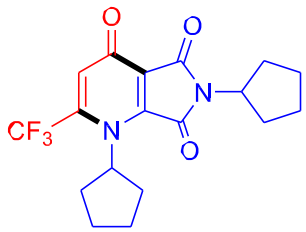
1,6-Diethyl-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 4.58 (q, *J* = 7.1 Hz, 2H), 3.69 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 160.9, 160.2, 142.1, 133.7, 120.9 (q, J_{C-F} = 6.0 Hz), 118.1, 105.7, 38.6, 32.5, 13.1, 12.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8; HRMS (ESI-TOF): *m/z* calcd for $C_{12}H_{11}F_3N_2O_3$ [(M+H)$^+$], 288.0734; found, 288.0722.



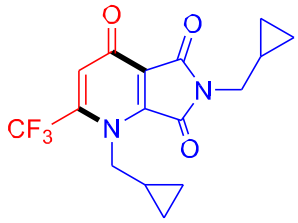
1,6-Dipropyl-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H,), 4.48 (t, *J* = 7.6 Hz, 2H), 3.60 (t, *J* = 7.4 Hz 2H), 1.75 (q, *J* = 7.6 Hz, 2H), 1.68 (q, *J* = 7.4 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 161.2, 160.4, 142.1, 133.5, 120.9 (q, J_{C-F} = 6.0 Hz), 118.1, 115.6, 105.5 44.5, 39.1, 21.4, 20.7, 10.2, 10.1); ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8; HRMS (ESI-TOF) : m/z calcd for $C_{14}H_{15}F_3N_2O_3$ [(M+H)$^+$], 316.1044; found, 316.1035.



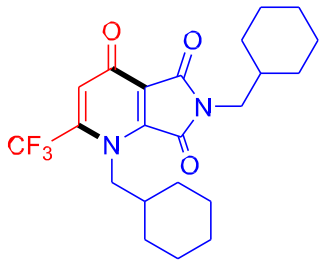
1,6-Dicyclopentyl-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.16–6.07 (q, *J* = 8.5 Hz, 1H), 4.57 (q, *J* = 8.5 Hz, 1H), 2.30–2.21(m, 2H), 2.12–1.87 (m, 8H), 1.73–1.55 (m, 4H), 1.28-1.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 161.4, 160.6, 142.6, 133.2, 132.8, 122.2, 122.1 (q, $J_{C\text{-}F}$ = 6.0 Hz), 105.8, 56.9, 50.4, 28.4, 27.6, 25.1, 24.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7; HRMS (ESI-TOF): *m/z* calcd for $C_{18}H_{19}F_3N_2O_3$ [$(M+H)^+$], 368.1352; found, 368.1348.



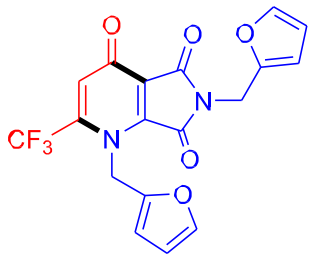
1,6-Bis(cyclopropylmethyl)-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 4.45 (d, *J* = 7.3 Hz, 2H), 3.48 (d, *J* = 7.3 Hz, 2H), 1.40–1.29 (m, 1H), 1.19–1.07 (m, 1H), 0.55–0.49 (m, 6H), 0.35 (q, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 161.5, 160.8, 142.3, 133.5, 121.1 (q, $J_{C\text{-}F}$ = 6.0 Hz), 120.9, 118.2, 105.6, 47.2, 42.3, 9.8, 9.2, 2.9, 2.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7; HRMS (ESI-TOF): *m/z* calcd for $C_{16}H_{15}F_3N_2O_3$ [$(M+H)^+$], 340.1041; found, 340.1035.



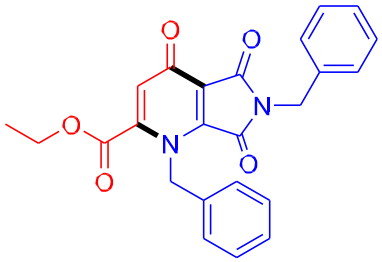
1,6-Bis(cyclohexylmethyl)-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)t-rione

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 4.41 (d, *J* = 7.3 Hz, 2H), 3.45 (d, *J* = 7.1 Hz, 2H), 1.74–1.58 (m, 12H), 1.23–1.08 (m, 8H), 1.02–0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 161.6, 160.7, 142.4, 133.5, 133.1, 120.9 (q, $J_{C\text{-}F}$ = 6.0 Hz), 105.2, 48.3, 43.7, 36.6, 35.9, 29.7, 29.3, 25.2, 25.1, 24.7, 24.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7; HRMS (ESI-TOF) : *m/z* calcd for $C_{22}H_{27}F_3N_2O_3$ [$(M+H)^+$], 424.1981; found, 424.1974.



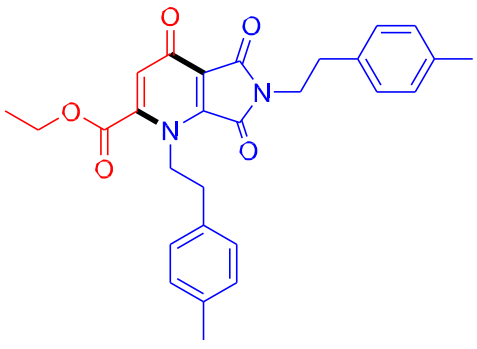
1,6-bis(furan-2-ylmethyl)-2-(trifluoromethyl)-1H-pyrrolo[3,4-b]pyridine-4,5,7(6H)-trione (3k).

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.34 (m, 1H), 7.34–7.32 (m, 1H), 6.97 (s, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.33–6.29 (m, 2H), 5.74 (s, 2H), 4.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 161.4, 160.7, 160.4, 147.3, 146.9, 142.1, 141.7, 140.7, 136.3, 123.7 (q, $J_{C\text{-}F}$ = 6.0 Hz), 109.8, 109.6, 109.5, 108.4, 107.5 52.3, 38.3, 33.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7; HRMS (ESI-TOF) : *m/z* calcd for $C_{18}H_{11}F_3N_2O_5$ $[(M+H)^+]$, 392.0633; found, 392.0620.



Ethyl 1,6-dibenzyl-4,5,7-trioxo-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b] pyridine-2-carboxylate

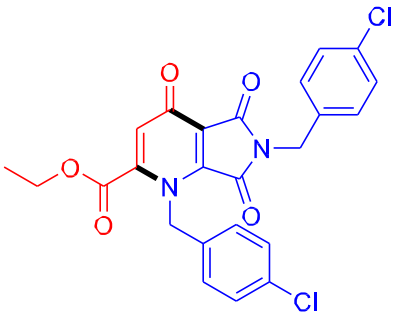
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.38 (dt, *J* = 3.7, 2.1 Hz, 2H), 7.35–7.27 (m, 6H), 6.96 (s, 1H), 5.72 (s, 2H), 4.75 (s, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 161.9, 161.3, 161.1, 140.1, 136.7, 134.4, 134.3, 127.8, 127.7, 127.6, 127.5, 127.2, 127.1, 123.3, 107.7, 61.5, 45.4, 40.9, 12.9; HRMS (ESI-TOF) : *m/z* calcd for $C_{24}H_{20}N_2O_5$ $[(M+H)^+]$, 416.1381; found, 416.1372



Ethyl 1,6-bis(4-methylphenethyl)-4,5,7-trioxo-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b]pyridine-2-carboxylate

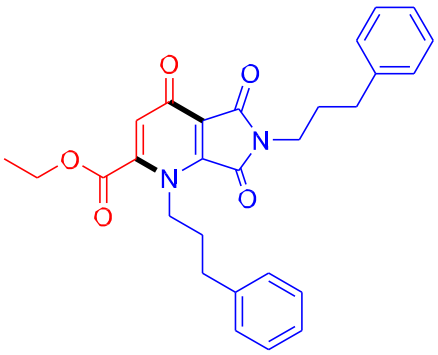
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.01 (m, 8H), 6.88 (s, 1H), 4.61 (t, *J* = 7.6 Hz 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.70 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.23 (s, 3H), 2.21 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 162.1, 161.1,

160.8, 141.1, 136.6, 135.5, 135.4, 133.4, 132.8, 128.3, 128.2, 128.1, 127.6, 122.8, 107.2, 61.7, 44.1, 38.7, 33.4, 33.1, 20.1, 20.0, 12.9; HRMS (ESI-TOF) : *m/z* calcd for $C_{28}H_{28}N_2O_5$ [(M+H)$^+$], 472.2011; found, 472.1998.



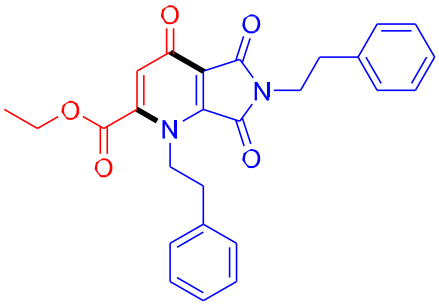
Ethyl 1,6-bis(4-chlorobenzyl)-4,5,7-trioxo-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b] pyridine-2-carboxylate

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.39 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.34–7.28 (m, 4H), 6.96 (s, 1H), 5.72 (s, 2H), 4.75 (s, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 161.9, 161.3, 161.1, 140.9, 136.7, 134.4, 134.3,127.8, 127.7, 127.6, 127.5, 127.2, 127.1, 123.3, 107.7, 61.7, 45.4, 41.1, 12.9; HRMS (ESI-TOF) : *m/z* calcd for $C_{24}H_{18}Cl_2N_2O_5$ [(M+H)$^+$], 484.0601; found, 484.0593.



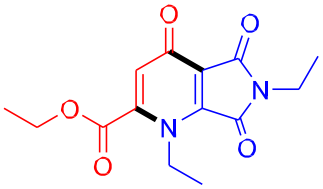
Ethyl 4,5,7-trioxo-1,6-bis(3-phenylpropyl)-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b]pyridine-2-carboxylate:

Yellow oil; ^{1}H NMR (400 MHz, DMSO) δ 7.28–7.17 (m, 10H), 6.80 (s, 1H), 4.38 (d, *J* = 5.9 Hz, 2H), 4.33 (q, *J* = 7.1 Hz 2H), 3.52 (t, *J* = 6.9 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.97 (d, *J* =7.7 Hz, 2H), 1.87 (d, *J* = 7.3 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).); ^{13}C NMR (100 MHz, DMSO) δ 163.8, 163.4, 162.4, 161.3, 143.2, 141.1, 140.8, 137.3, 128.3, 128.2, 128.1, 128.0, 125.8, 125.7, 120.6, 106.9, 62.1, 43.1, 37.4, 32.4, 32.3, 29.3, 29.2, 13.7; HRMS (ESI-TOF) : *m/z* calcd for $C_{28}H_{28}N_2O_5$ [(M+H)$^+$], 472.2012; found, 472.1998.



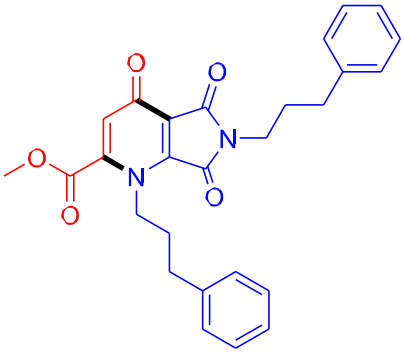
Ethyl4,5,7-trioxo-1,6-diphenethyl-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b]pyridine-2-carboxylate:

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.18 (m, 10H), 6.95 (s, 1H), 4.68 (t, *J* = 8.6 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.79 (t, *J* = 8.6 Hz, 2H), 2.90 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 161.9, 161.3, 161.1, 140.9, 136.6, 134.4, 134.3 128.1, 127.7, 127.7, 125.9, 125.8, 122.8, 107.7, 61.7, 43.9, 38.5, 33.8, 33.5, 12.9; HRMS (ESI-TOF) : *m/z* calcd for $C_{26}H_{24}N_2O_5$ [$(M+H)^+$], 444.1691; found, 444.1685.



Ethyl 1,6-diethyl-4,5,7-trioxo-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b]pyridinee-2-carboxylate:

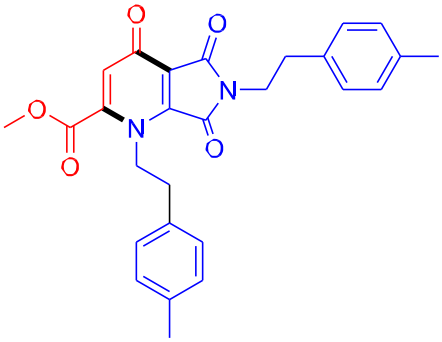
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.67 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 162.2, 161.2, 160.8, 141.1, 136.6, 122.7, 107.4, 61.7, 38.4, 32.3, 13.2, 12.9, 12.8; HRMS (ESI-TOF) : *m/z* calcd for $C_{14}H_{16}N_2O_5$ [$(M+H)^+$], 292.1072; found, 292.1059.



Methyl 1,6-bis(4-(tert-butyl)benzyl)-4,5,7-trioxo-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b]pyridine-2-carboxylate (3r).

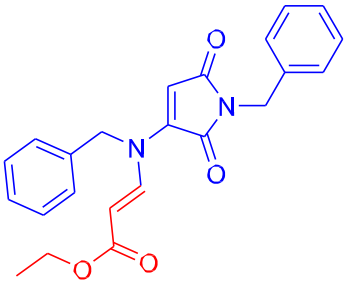
Yellow oil; ^{1}H NMR (400 MHz, DMSO) δ 7.36–7.32 (m, 4H), 7.27–7.23 (m, 4H), 6.91 (s, 1H), 5.53 (s, 2H), 4.63 (s, 2H), 3.87 (s, 3H), 1.25 (s, 9H), 1.24 (s, 9H); ^{1}H NMR (400 MHz, DMSO) δ 163.8, 163.6, 162.5, 161.4, 149.9, 149.8, 143.7, 137.2, 133.2, 132.7, 127.4, 127.3, 125.2, 125.1, 121.6, 107.2, 53.1, 45.9, 40.7, 34.2, 34.1, 31.2, 31.1; HRMS (ESI-TOF) : *m/z* calcd for $C_{31}H_{34}N_2O_5$ [$(M+H)^+$],

514.2477; found, 514.2468.



Methyl 1,6-bis(4-methylphenethyl)-4,5,7-trioxo-4,5,6,7-tetrahydro-1H-pyrrolo[3,4-b]pyridine-2-carboxylate (3s).

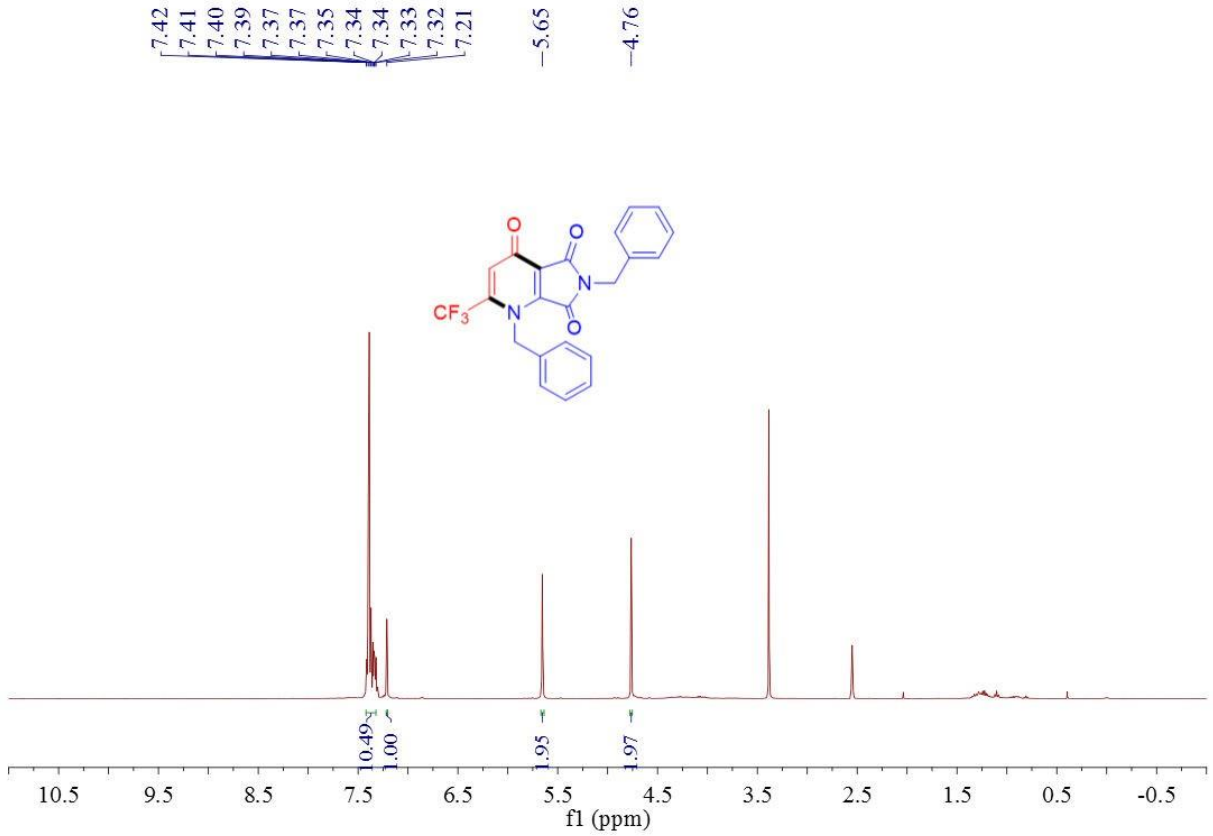
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) 7.16 – 7.09(m, 8H), 6.97 (s, 1H), 6.97 (s, 1H), 4.70 – 4.65 (m, 2H), 3.99 (s, 3H), 3.79 – 3.74 (m, 2H), 2.92 – 2.87 (m, 2H), 2.83 (m, 2H), 2.30 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 162.1, 160.9, 160.8, 141.1, 136.1, 135.5, 135.4, 133.4, 132.8, 128.3, 128.2, 127.6, 123.1, 107.1, 52.2, 44.1, 38.7, 33.4, 33.1, 20.1, 20.0; HRMS (ESI-TOF) : *m/z* calcd for $C_{31}H_{34}N_2O_5$ $[(M+H)^+]$, 458.1855; found, 458.1842.



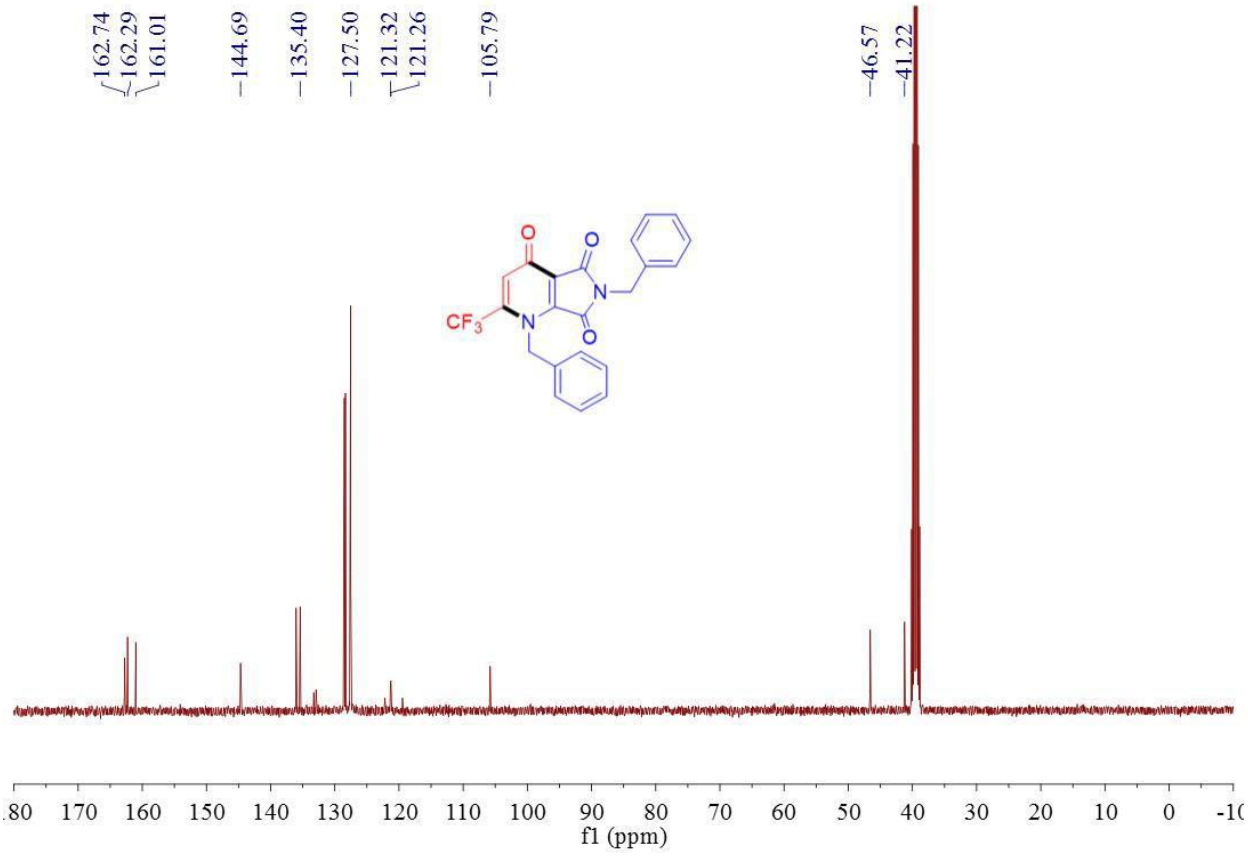
Ethyl (E)-3-(benzyl(1-benzyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)amino)acrylate

Yellow oil; ^{1}H NMR (400 MHz, DMSO) δ 9.04 (d, *J* = 13.7 Hz, 1H), 7.39 – 7.26 (m, 10H), 5.93 (s, 1H), 5.35 (d, *J* = 13.7 Hz, 1H), 4.98 (s, 2H), 4.61 (s, 2H), 4.07 (q, *J* = 13.7 Hz, 2H), 1.17 (t, *J* = 13.7 Hz 3H); ^{13}C NMR (100 MHz, DMSO) δ 169.4, 166.7, 166.3, 145.9, 143.7, 136.7, 134.5, 128.5, 128.4, 127.4, 127.3, 126.4, 99.7, 98.4, 59.3, 51.2, 40.5, 14.2; HRMS (ESI-TOF) : *m/z* calcd for $C_{23}H_{22}N_2O_4$ $[(M+H)^+]$, 390.1591; found, 390.1580.

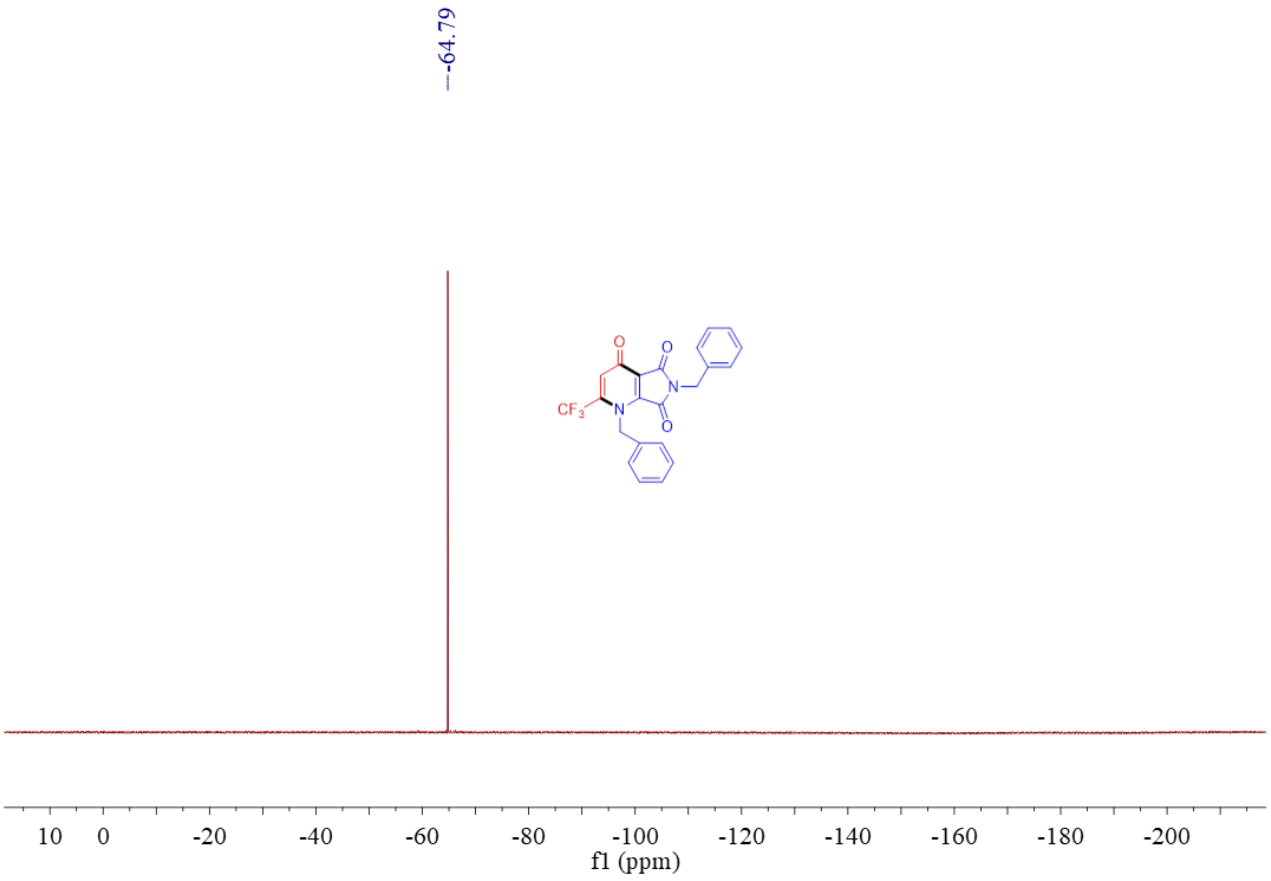
3. NMR spectra of compound 3a-3aa:



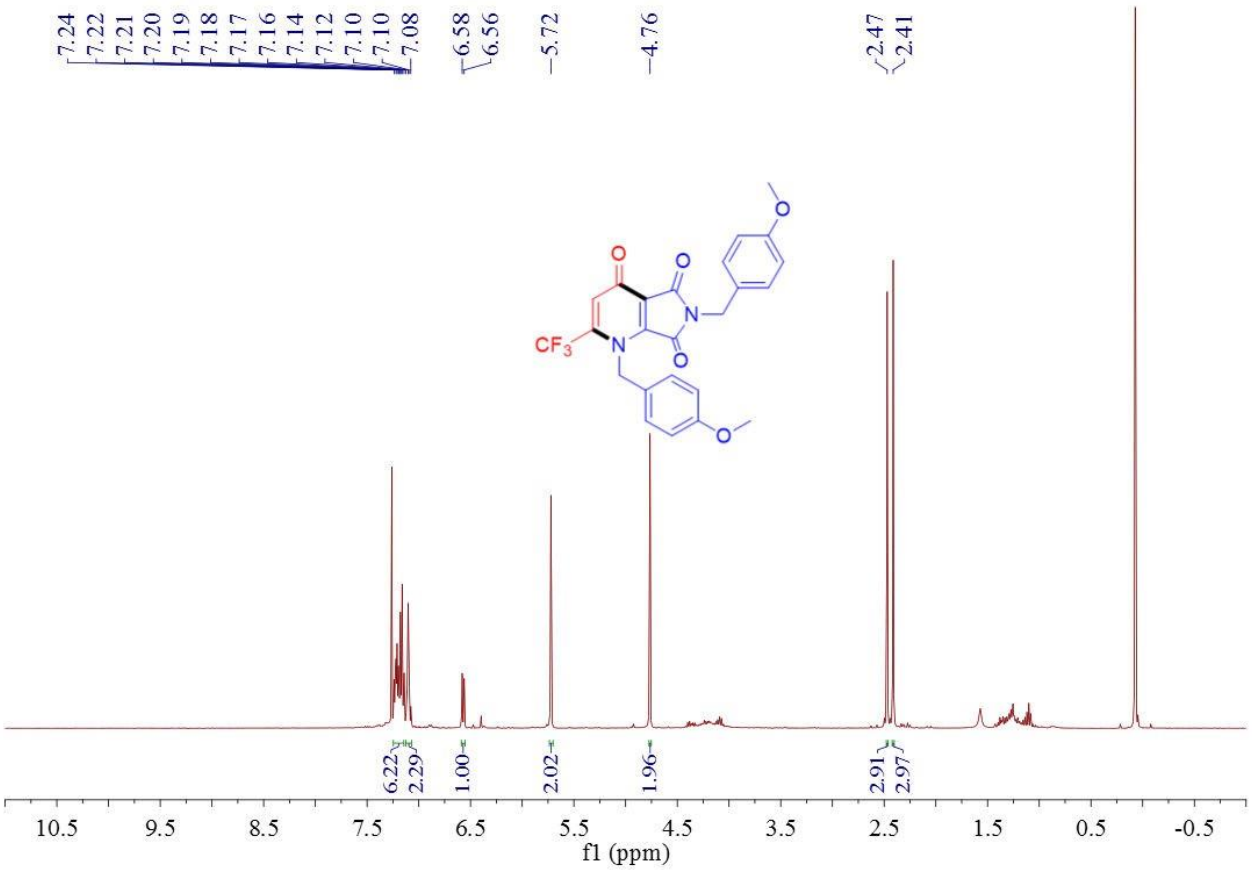
^{1}H NMR of product **3a** in DMSO (400 MHz)



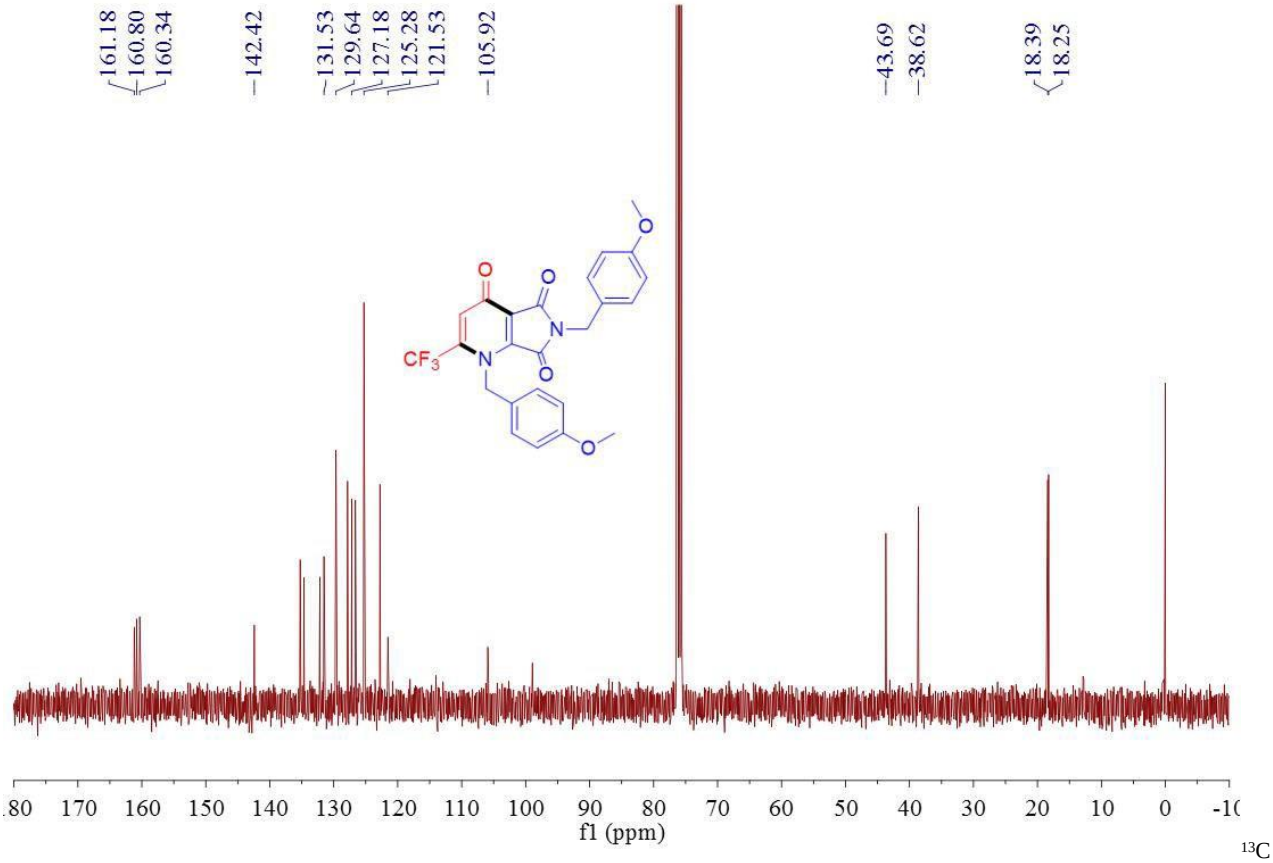
^{13}C NMR of product **3a** in DMSO (100 MHz)



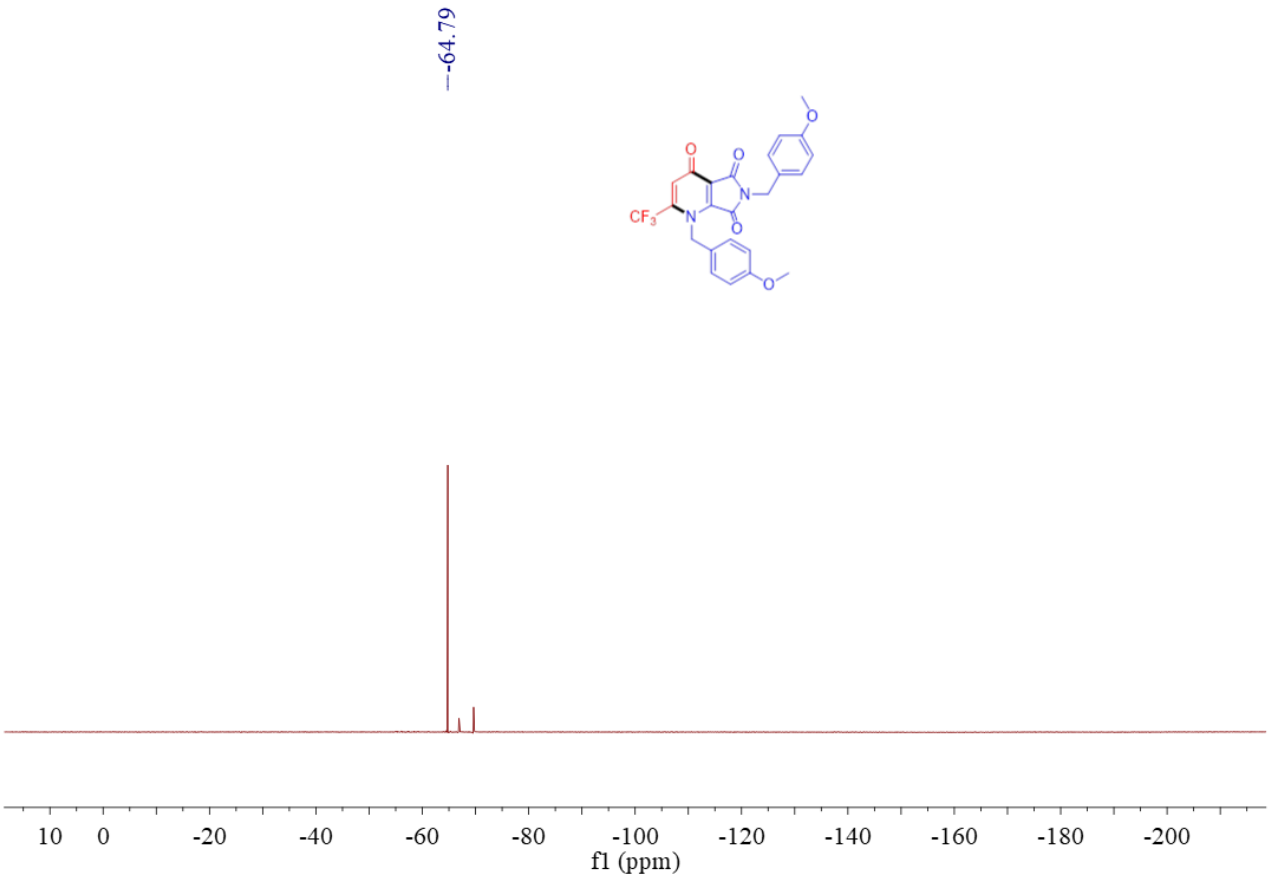
^{19}F NMR of product **3a** in $CDCl_3$ (376 MHz)



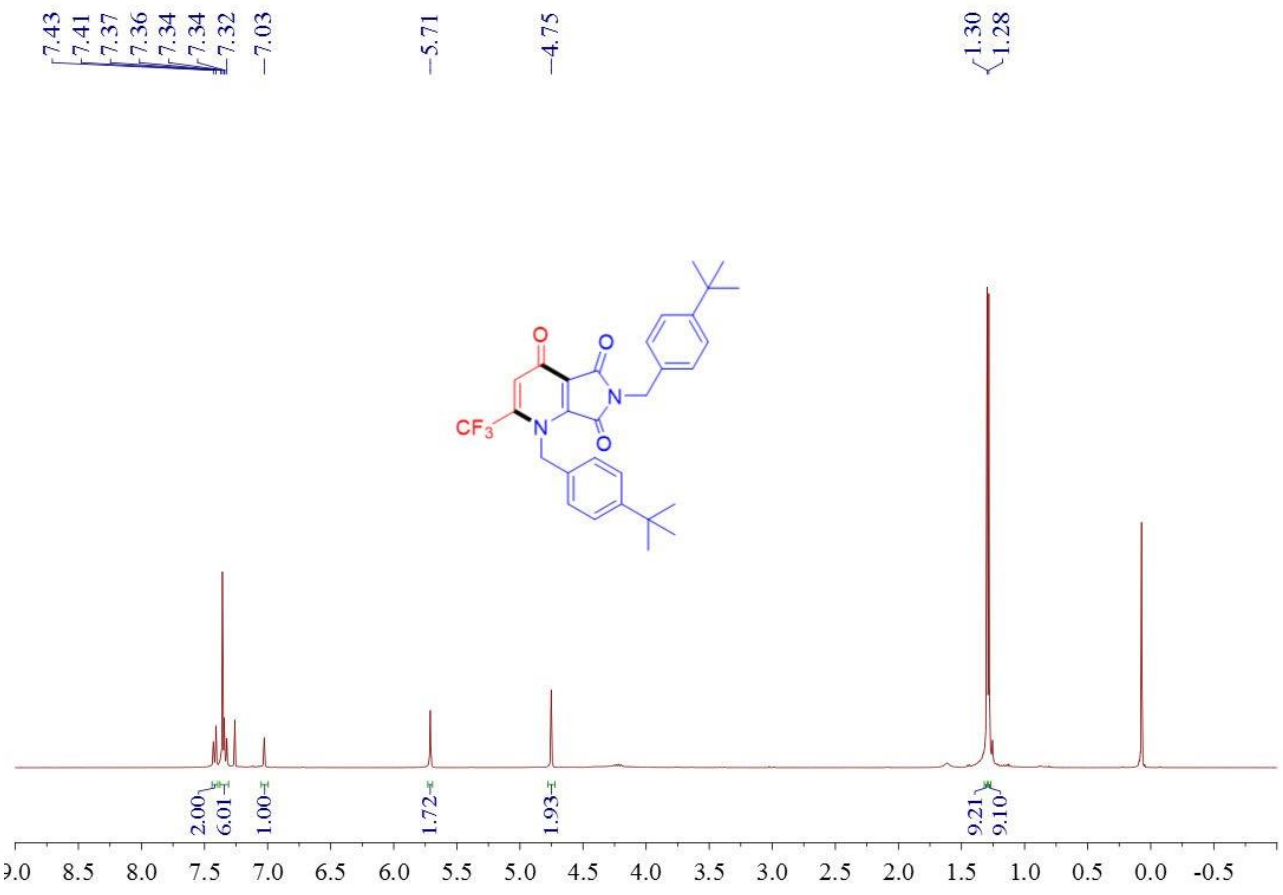
^{1}H NMR of product **3b** in $CDCl_3$ (400 MHz)



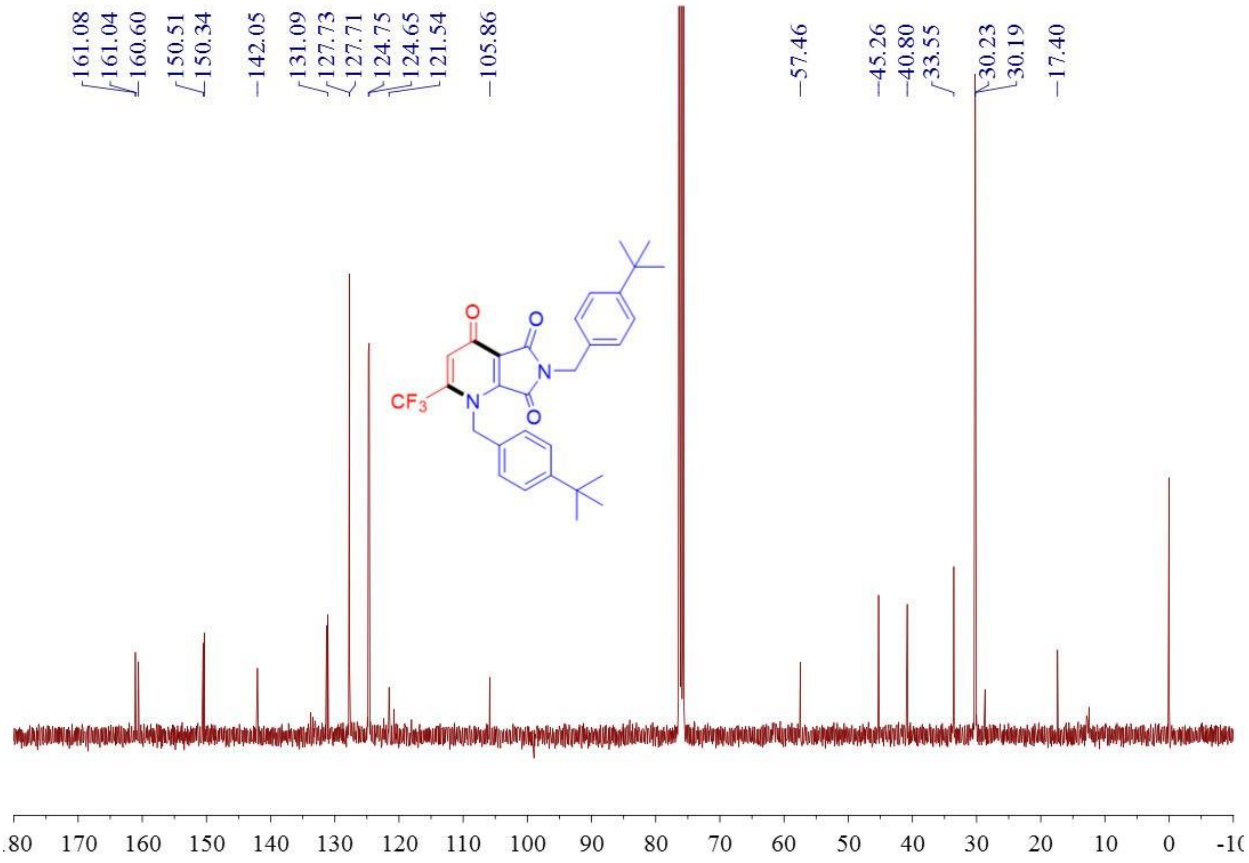
^{13}C NMR of product **3b** in $CDCl_3$ (100 MHz)



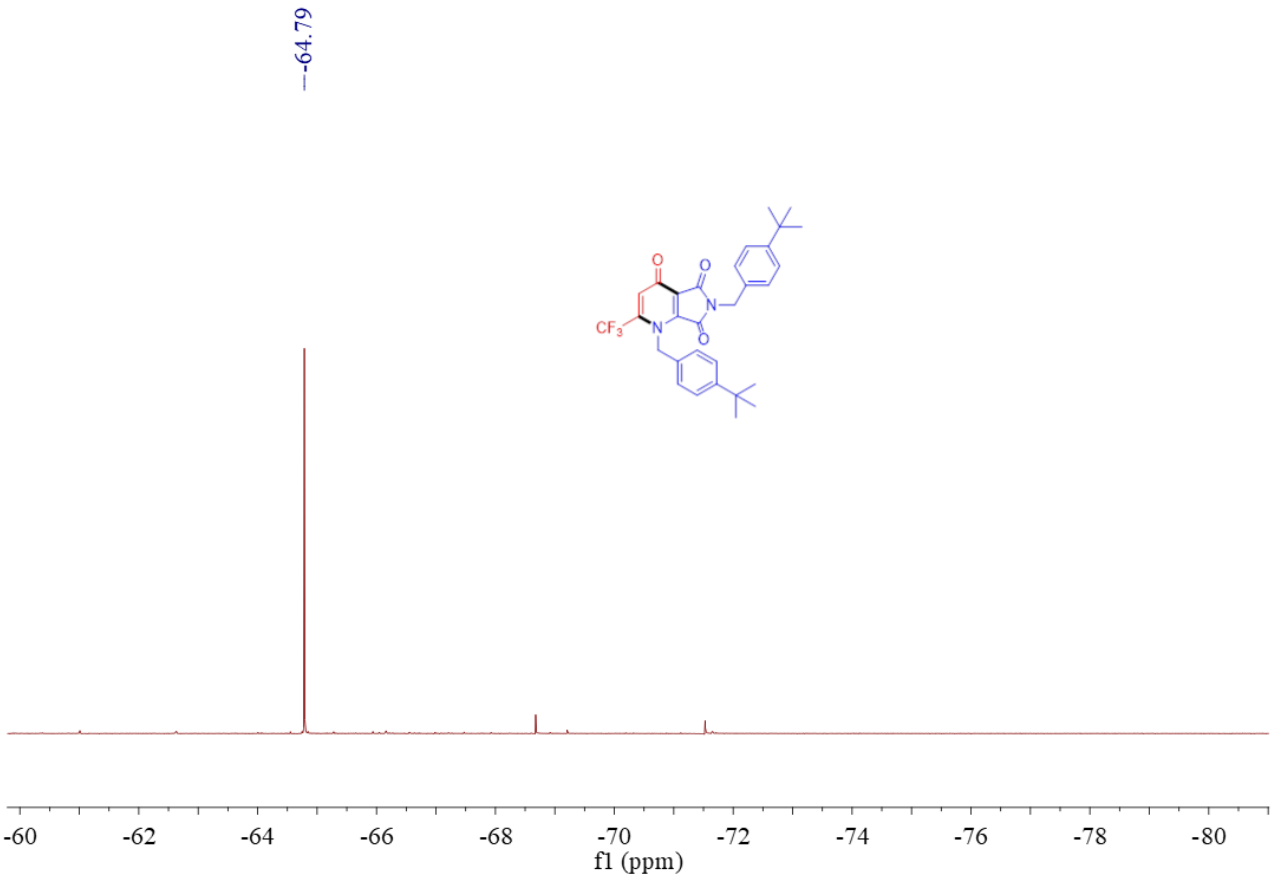
^{19}F NMR of product **3b** in $CDCl_3$ (376 MHz)



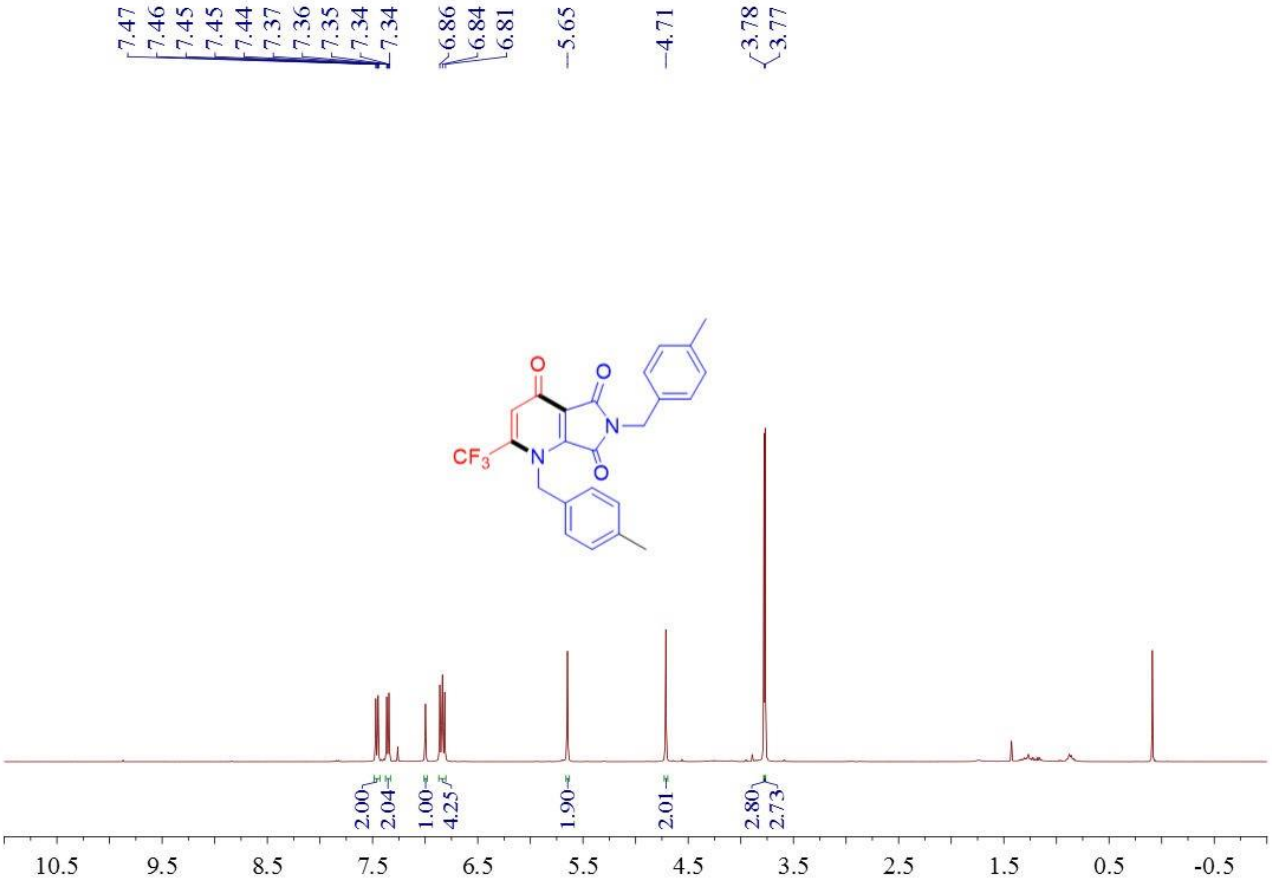
^{1}H NMR of product **3c** in $CDCl_3$ (400 MHz)



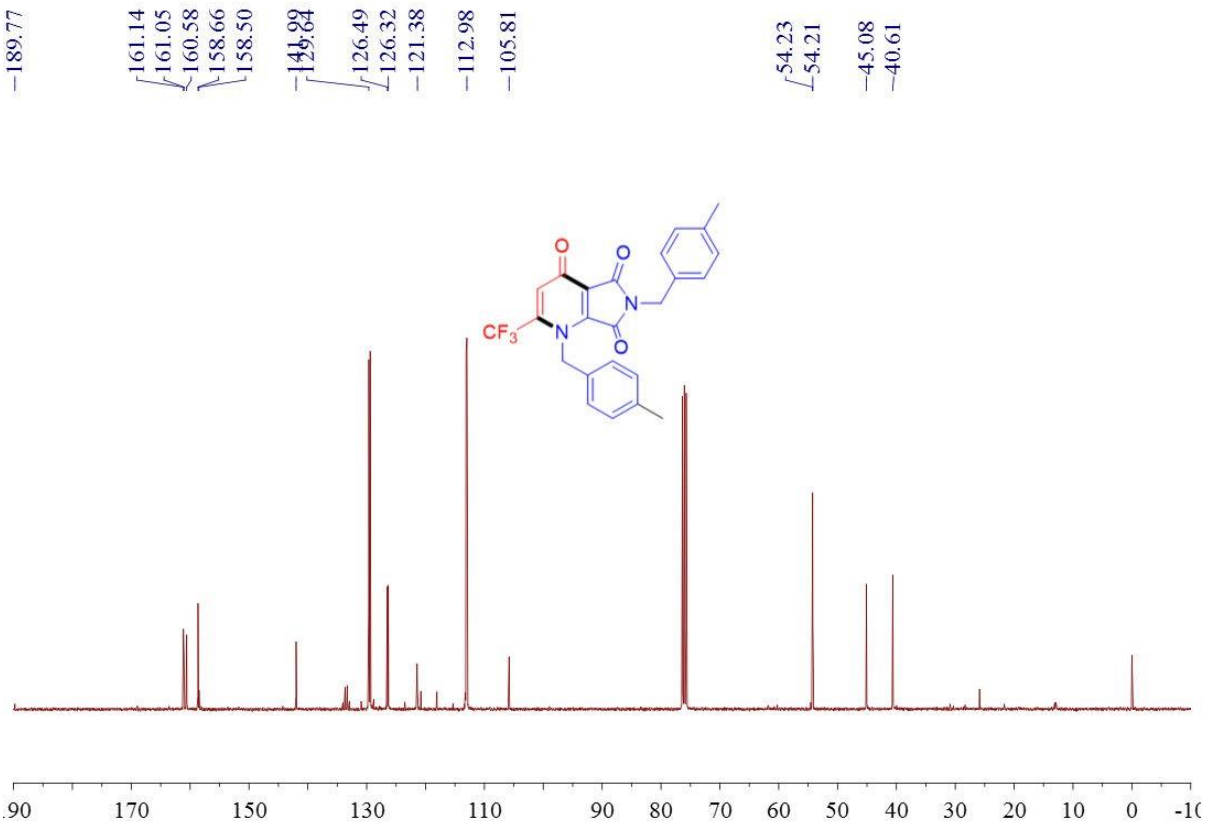
^{13}C NMR of product **3c** in $CDCl_3$ (100 MHz)



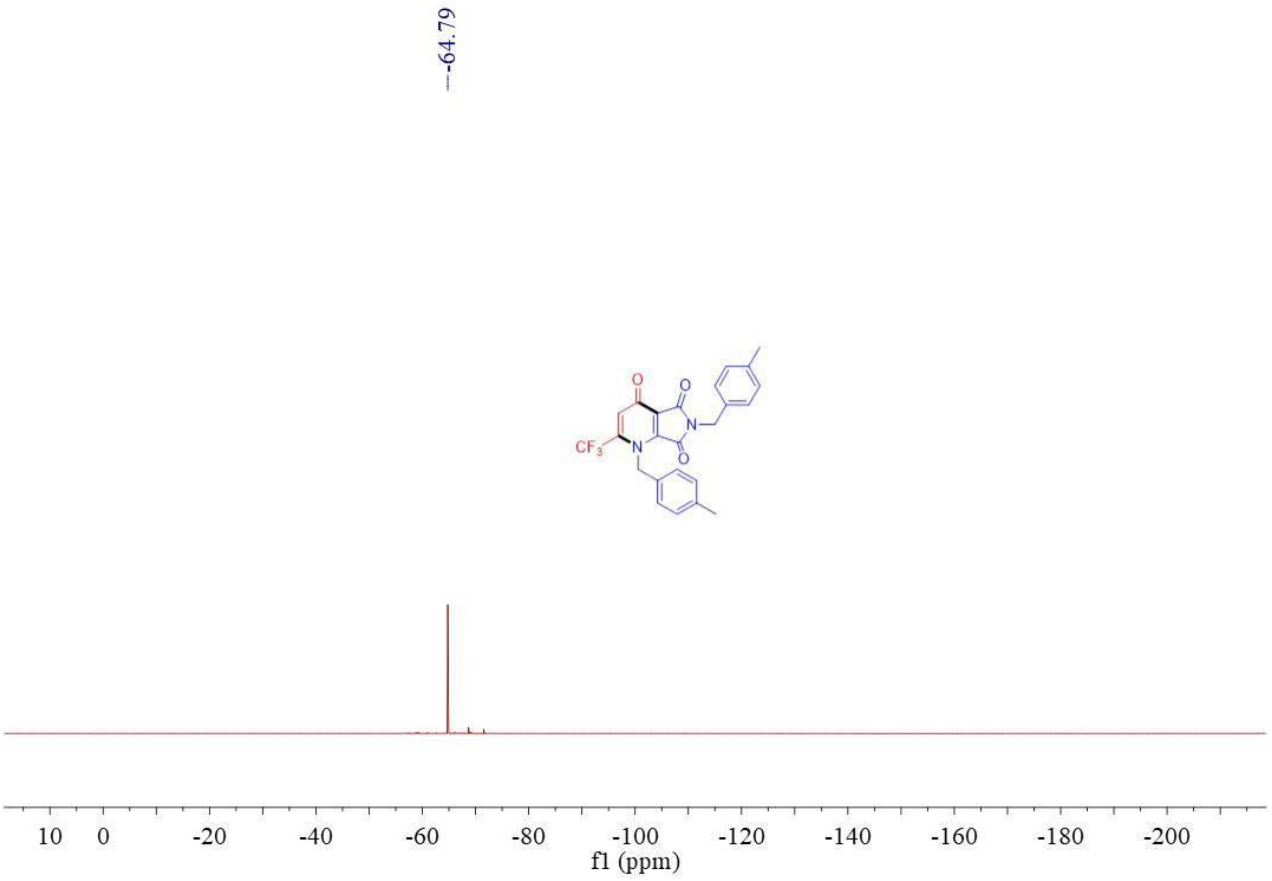
^{19}F NMR of product **3c** in $CDCl_3$ (376 MHz)



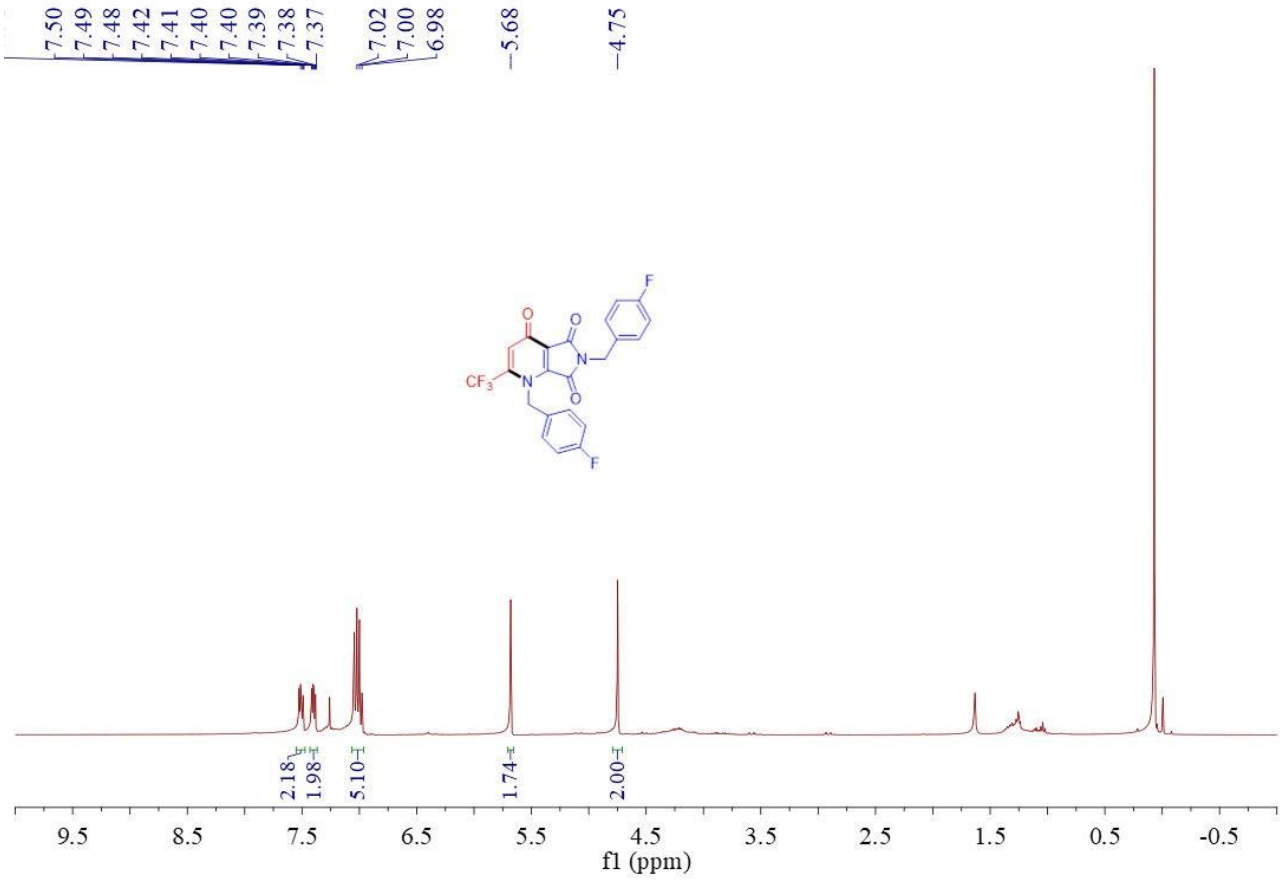
^{1}H NMR of product **3d** in $CDCl_3$ (400 MHz)



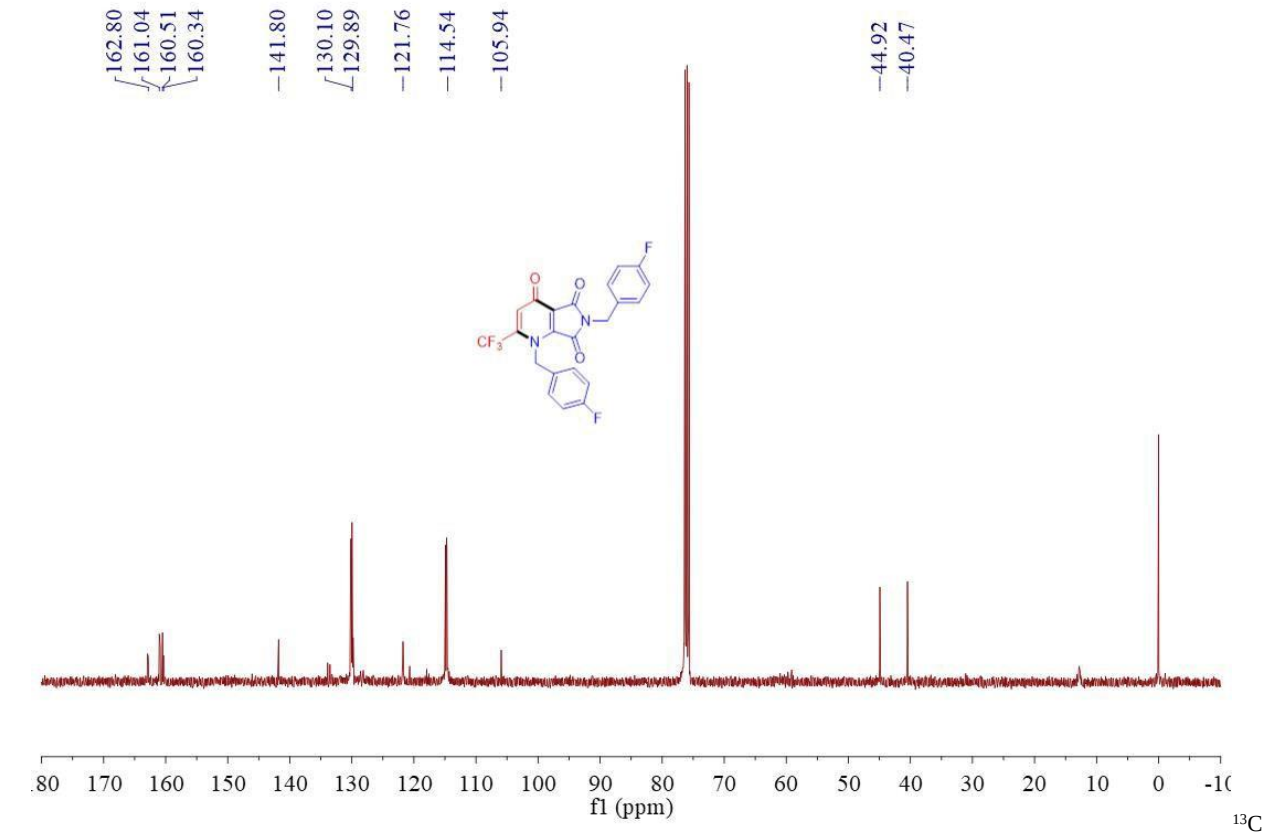
^{13}C NMR of product **3d** in $CDCl_3$ (100 MHz)



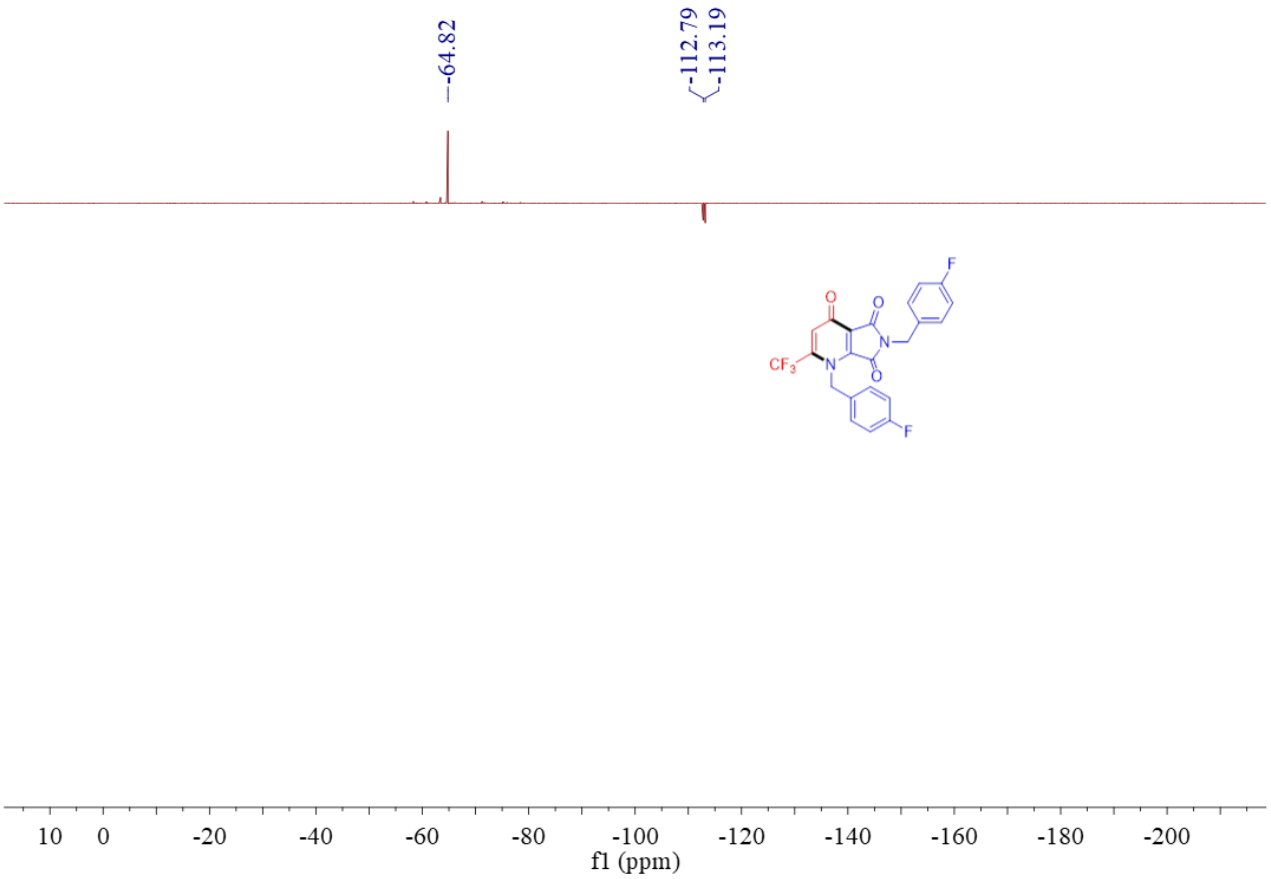
^{19}F NMR of product **3d** in $CDCl_3$ (376 MHz)



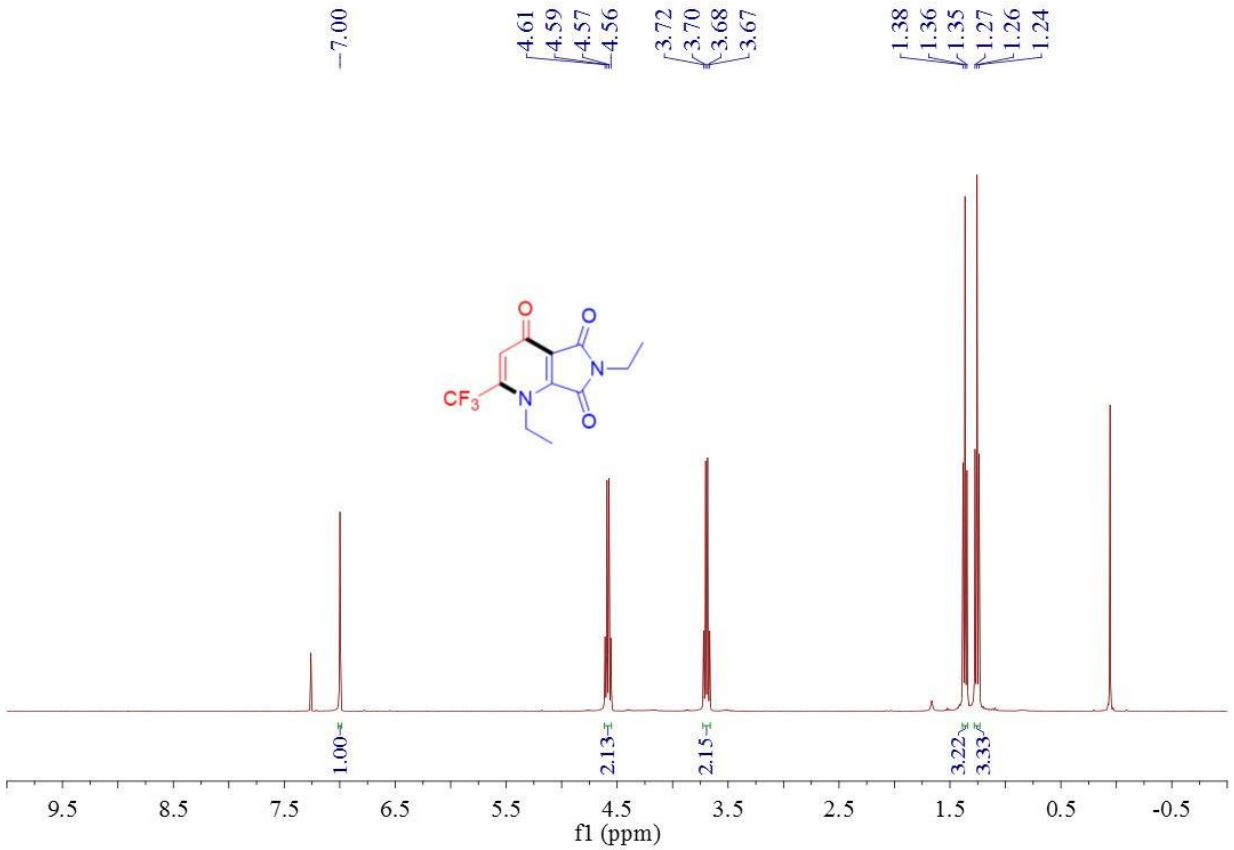
^{1}H NMR of product **3e** in $CDCl_3$ (400 MHz)



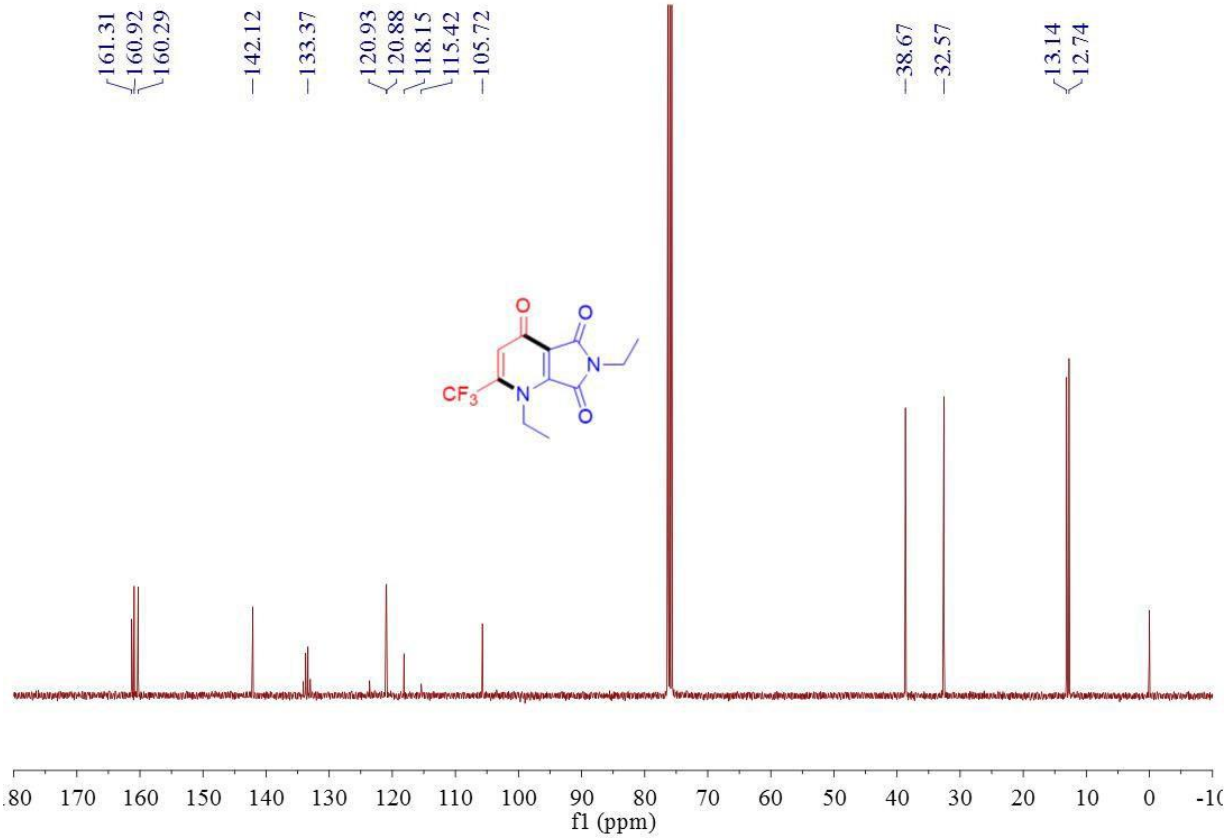
^{13}C NMR of product **3e** in $CDCl_3$ (100 MHz)



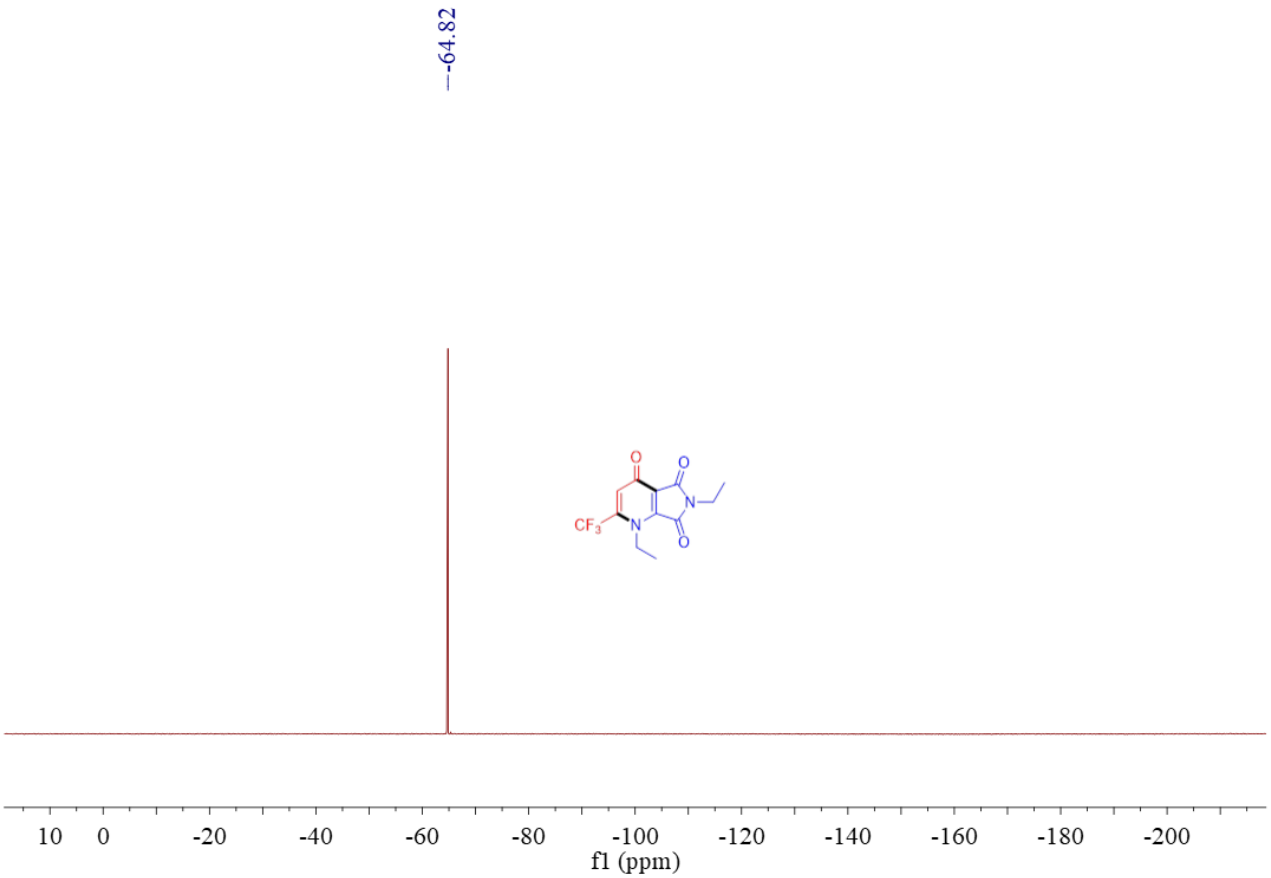
^{19}F NMR of product **3e** in $CDCl_3$ (376 MHz)



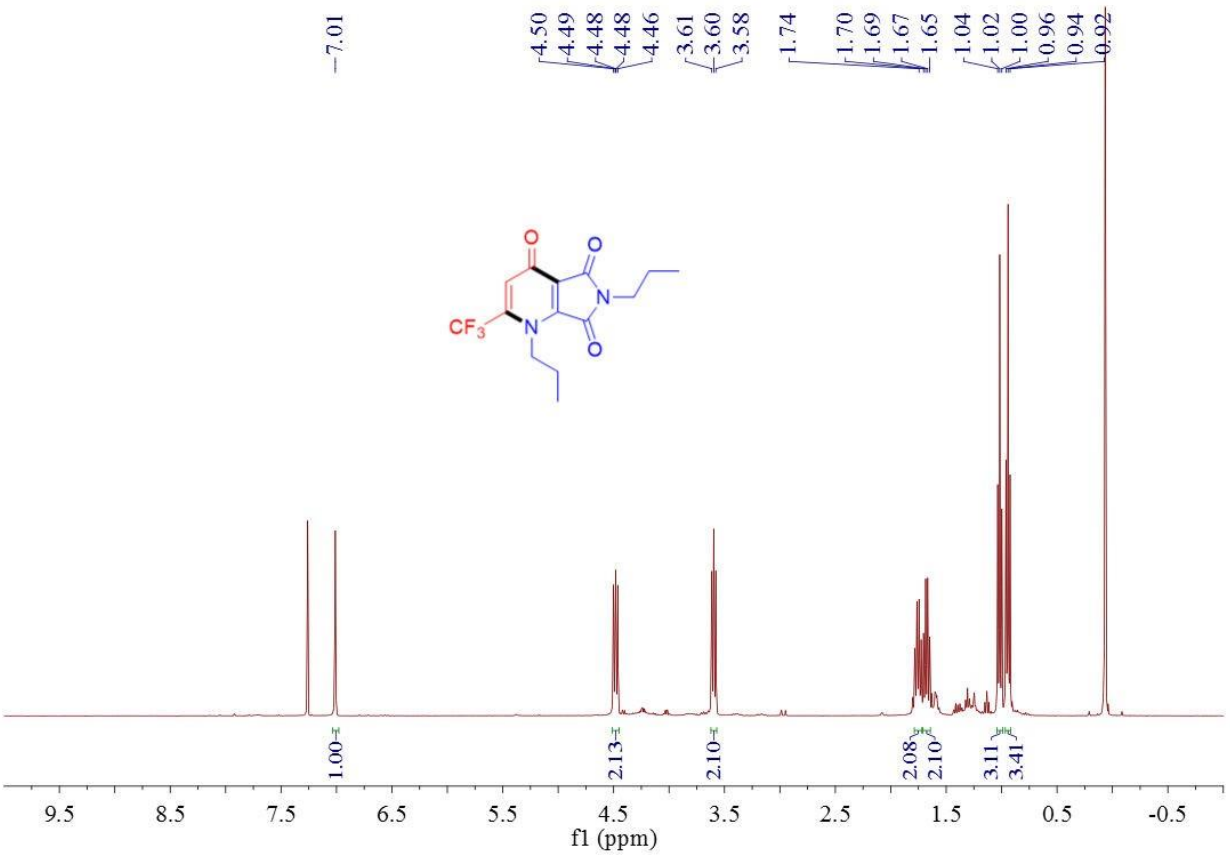
^{1}H NMR of product **3f** in $CDCl_3$ (400 MHz)



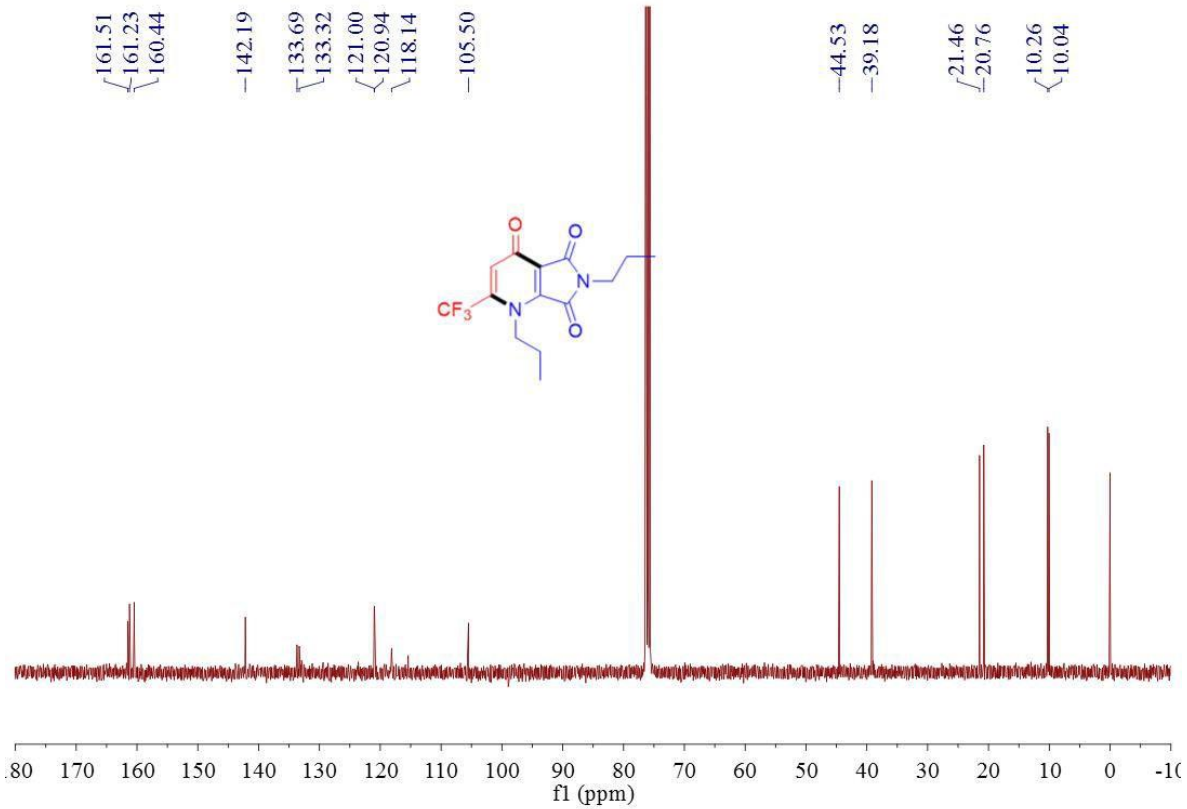
^{13}C NMR of product **3f** in $CDCl_3$ (100 MHz)



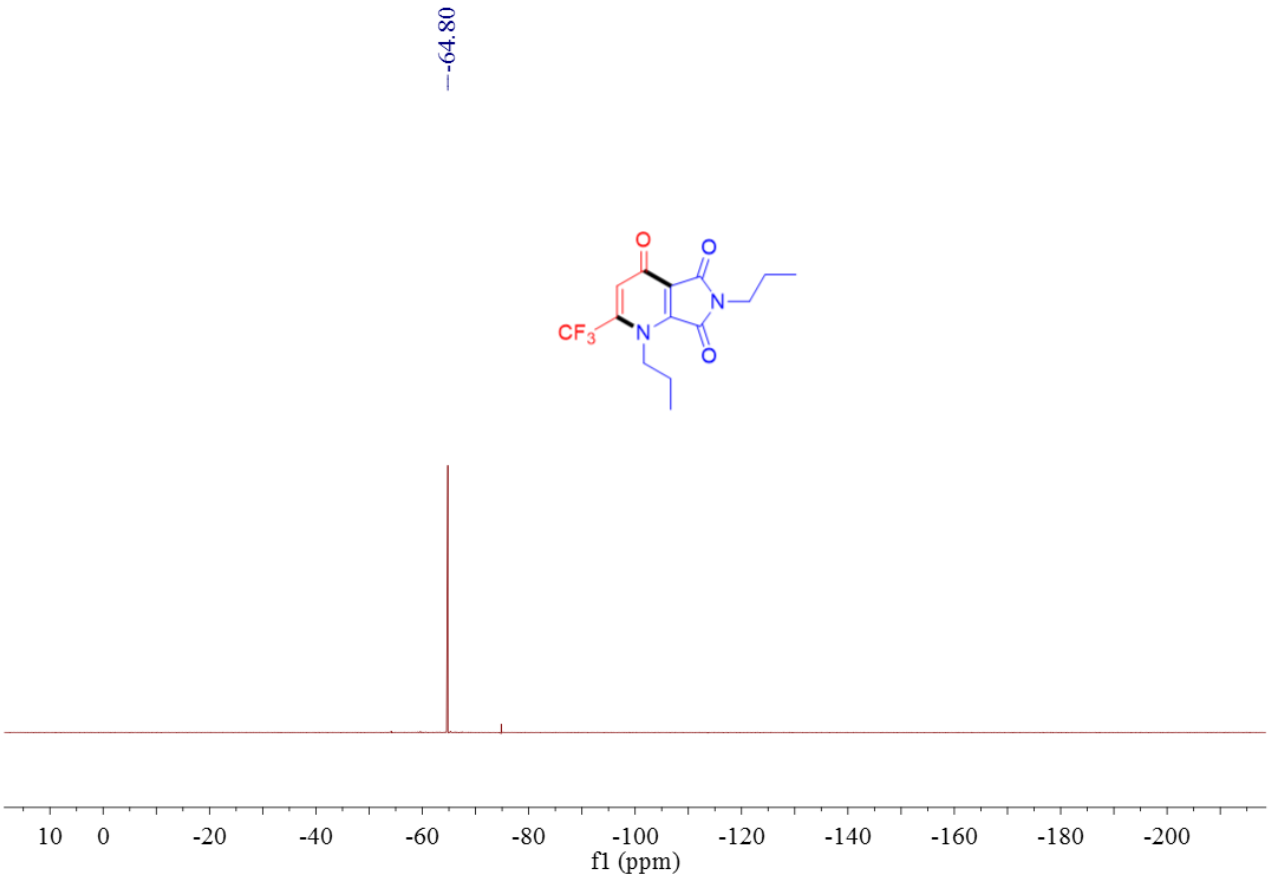
^{19}F NMR of product **3f** in $CDCl_3$ (376 MHz)



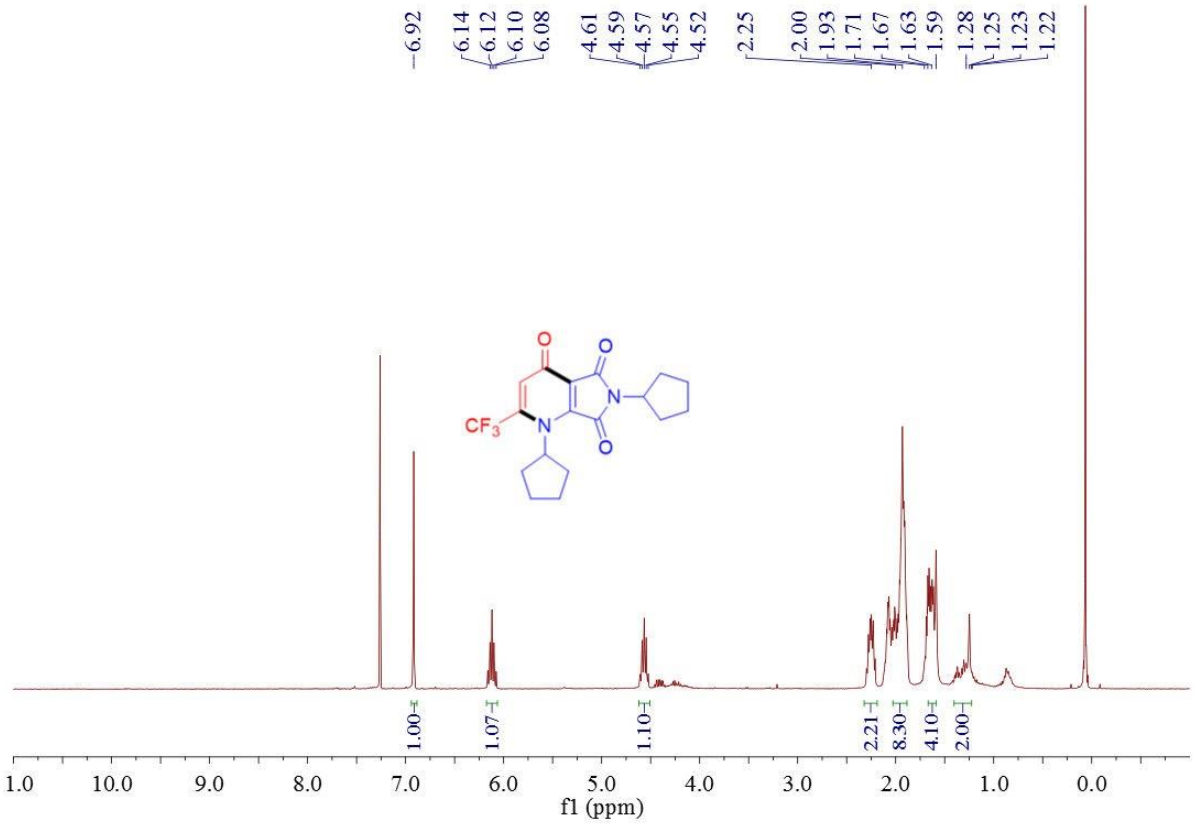
^{1}H NMR of product **3g** in $CDCl_3$ (400 MHz)



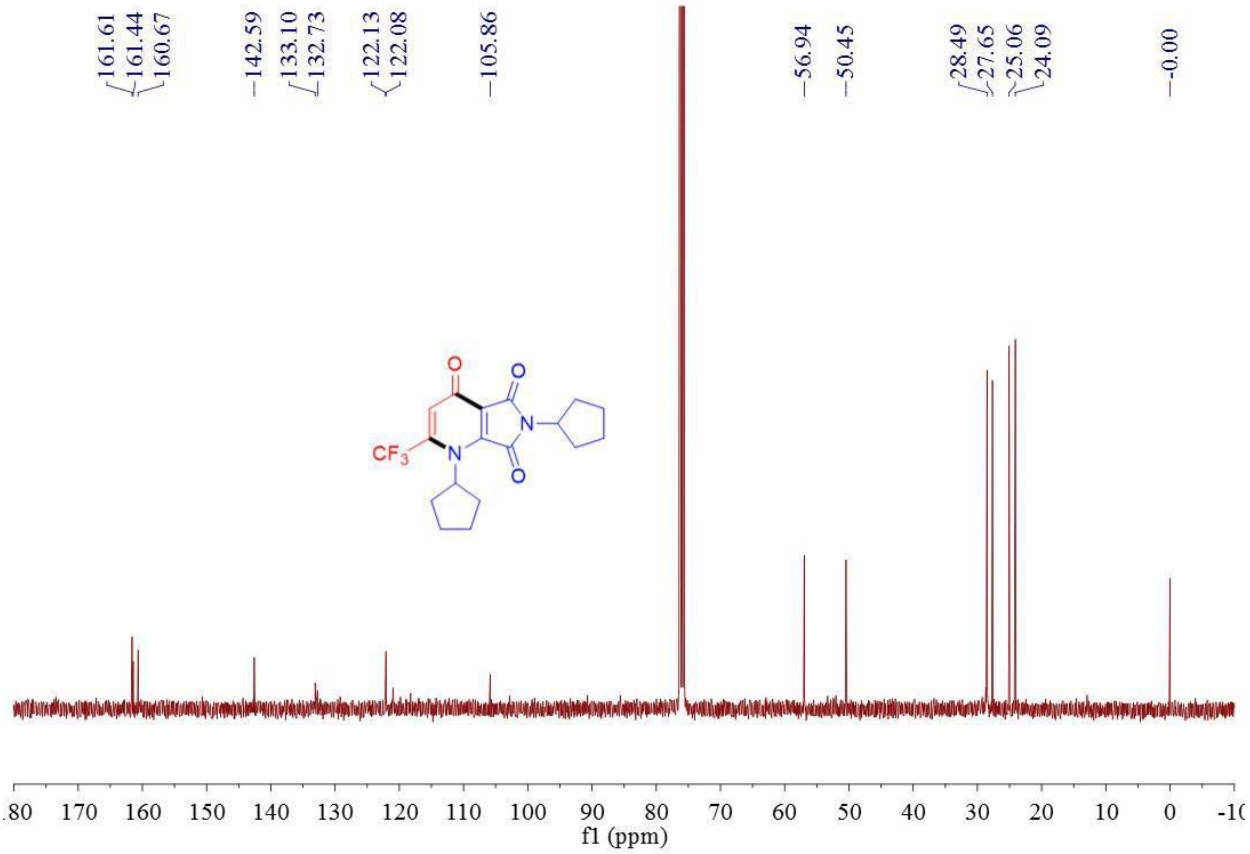
^{13}C NMR of product **3g** in $CDCl_3$ (100 MHz)



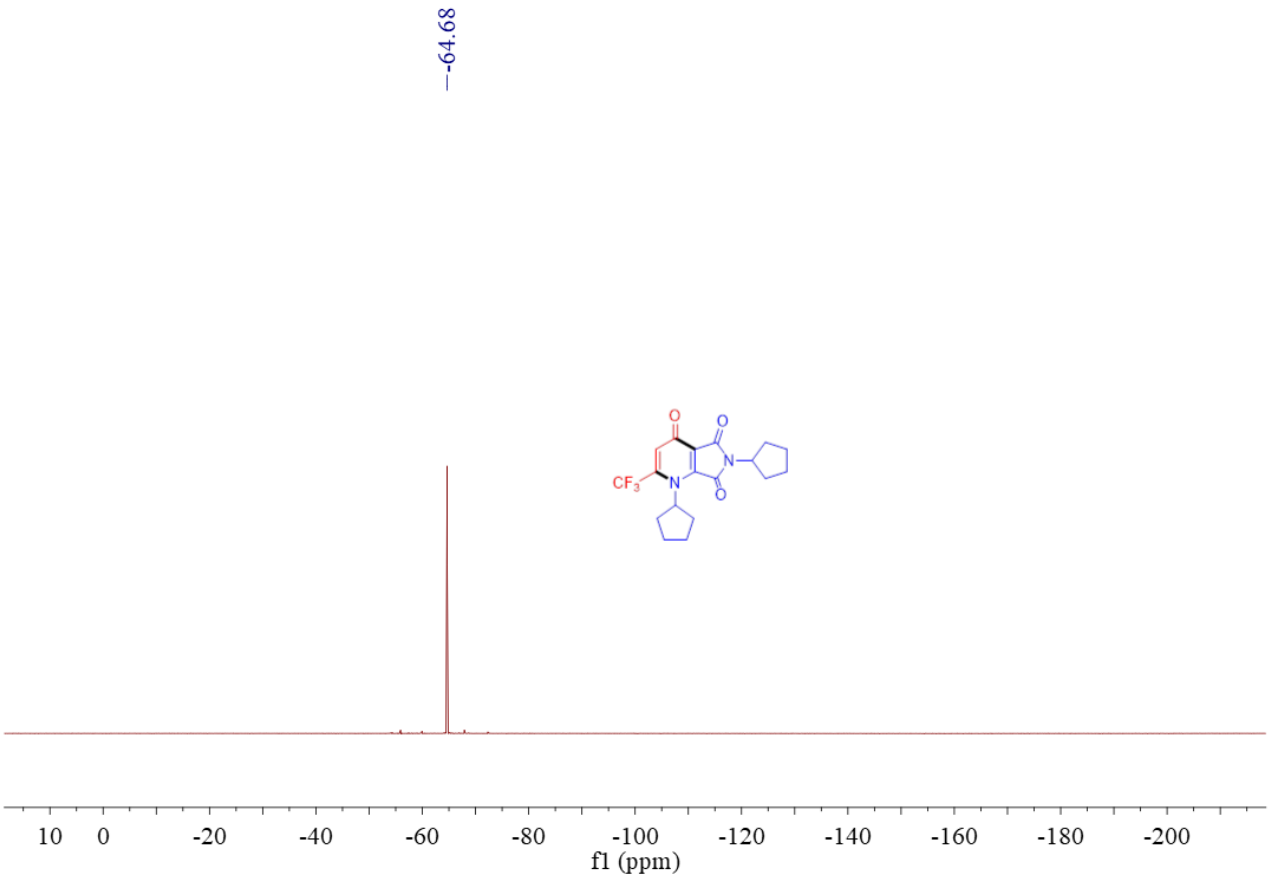
^{19}F NMR of product **3g** in $CDCl_3$ (376 MHz)



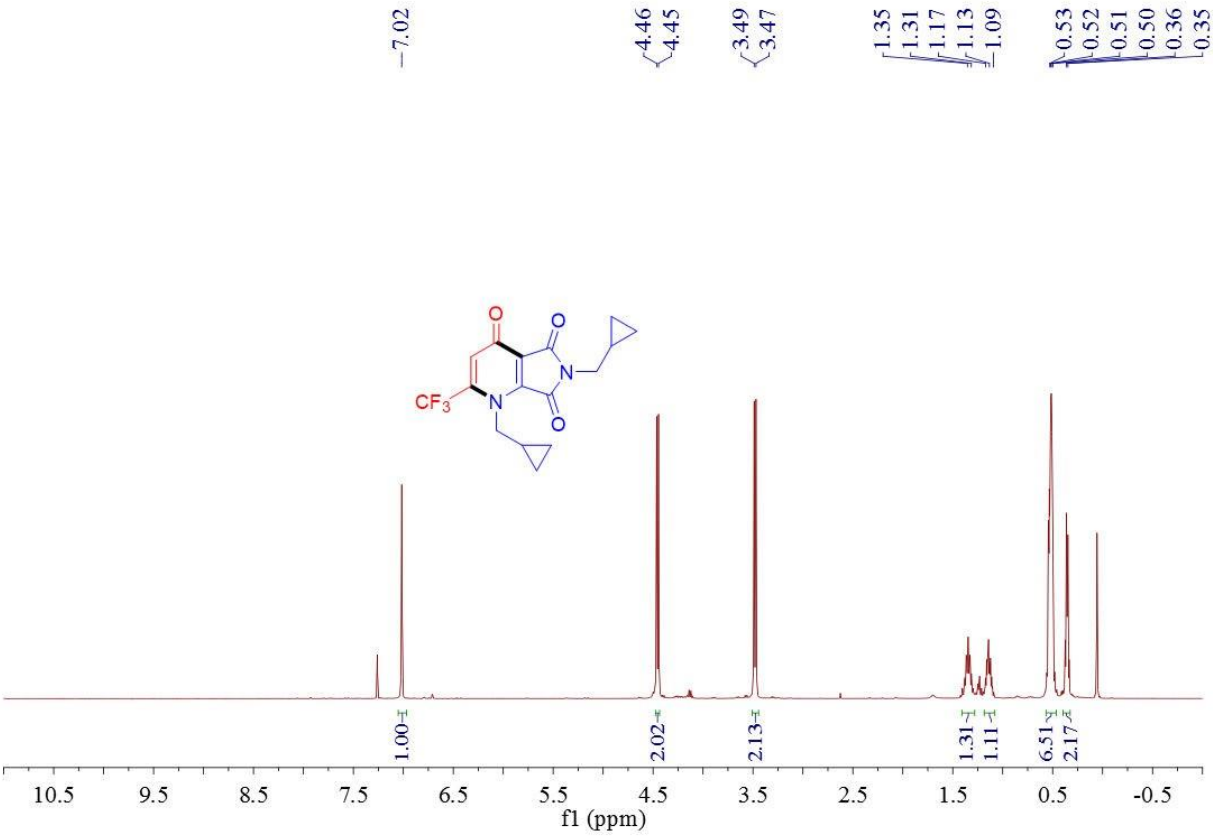
^{1}H NMR of product **3h** in $CDCl_3$ (400 MHz)



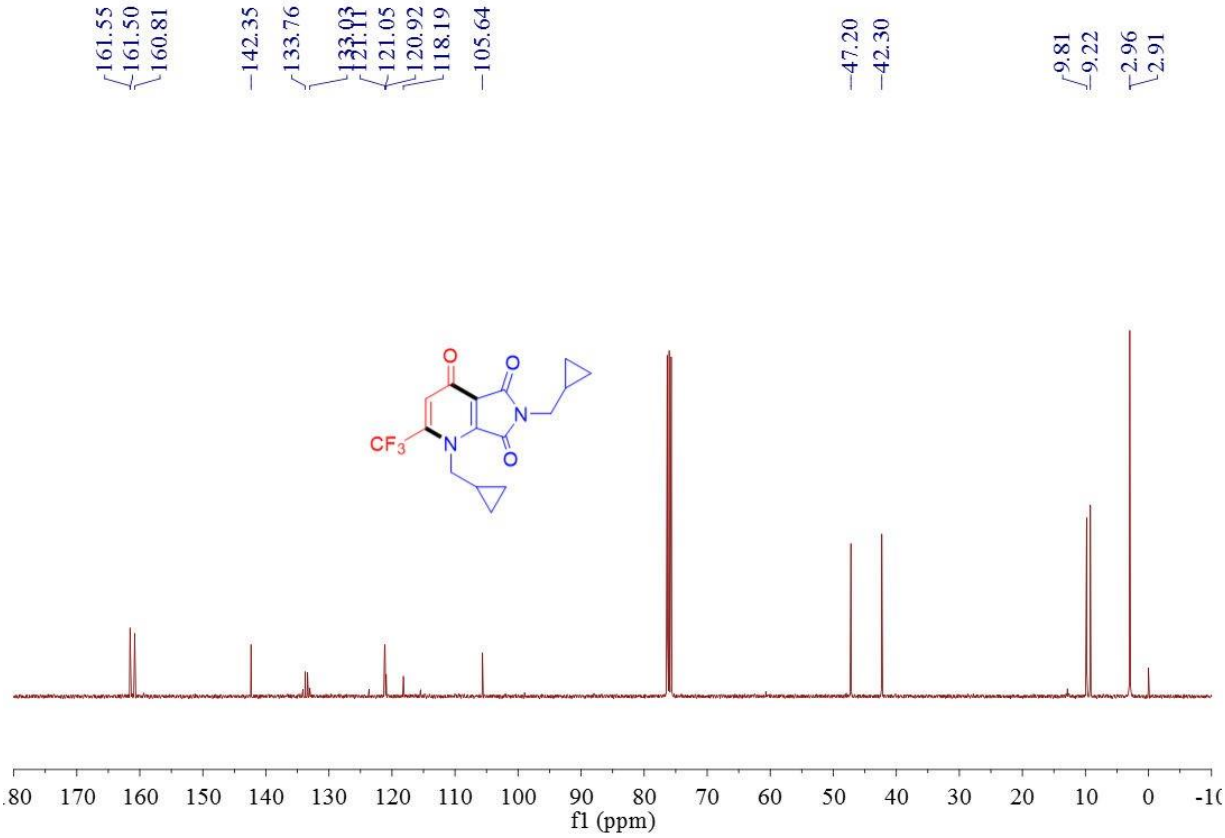
^{13}C NMR of product **3h** in $CDCl_3$ (100 MHz)



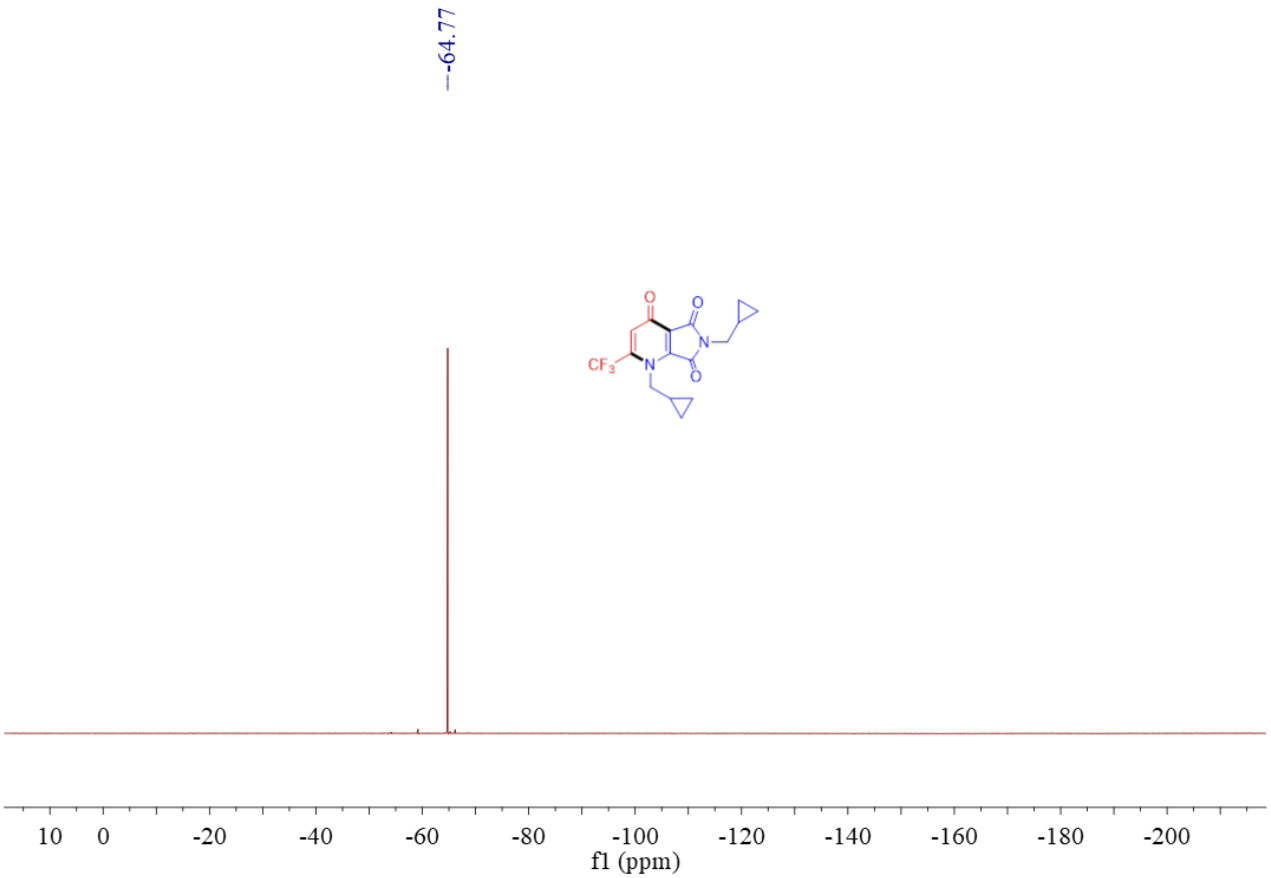
^{19}F NMR of product **3h** in $CDCl_3$ (376 MHz)



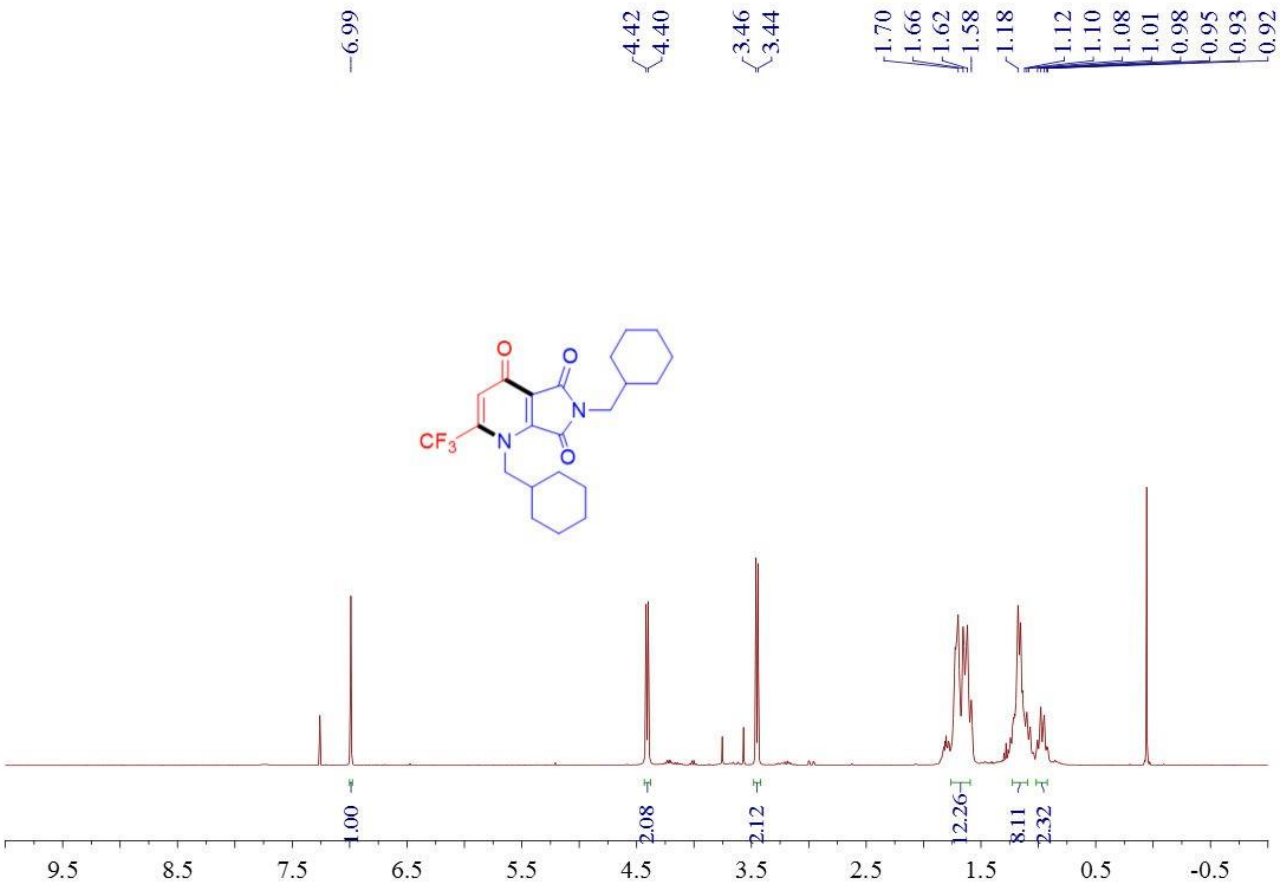
^{1}H NMR of product **3i** in $CDCl_3$ (400 MHz)



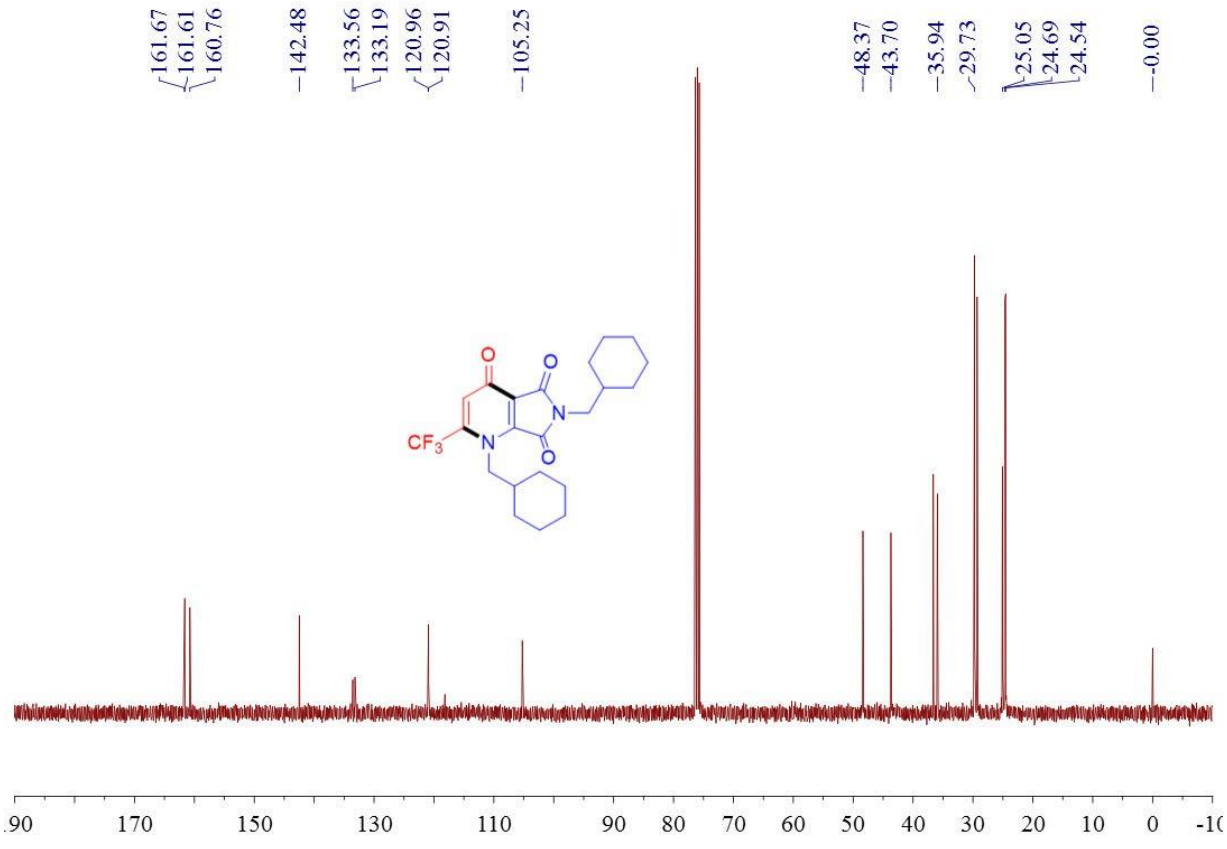
^{13}C NMR of product **3i** in $CDCl_3$ (100 MHz)



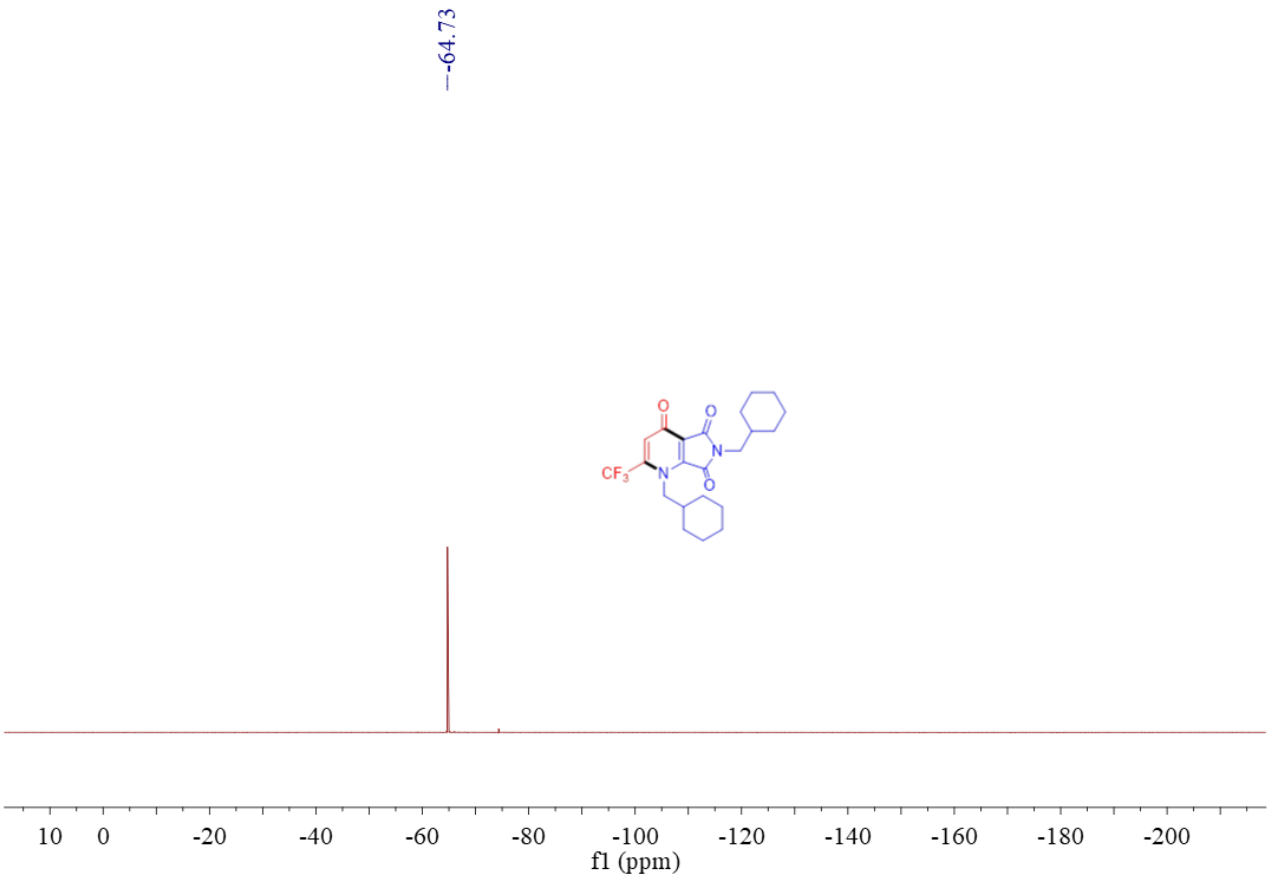
^{19}F NMR of product **3i** in $CDCl_3$ (376 MHz)



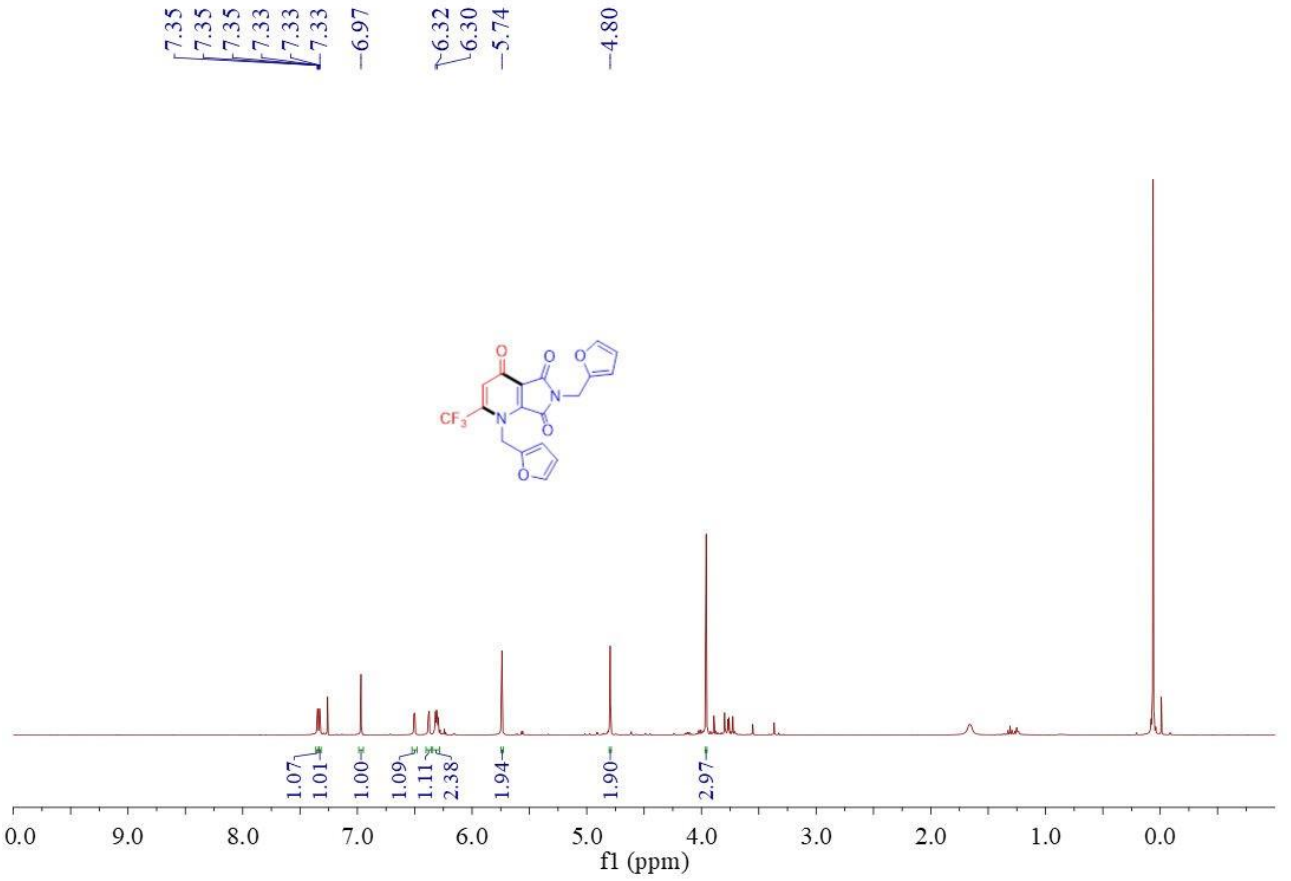
^{1}H NMR of product **3j** in $CDCl_3$ (400 MHz)



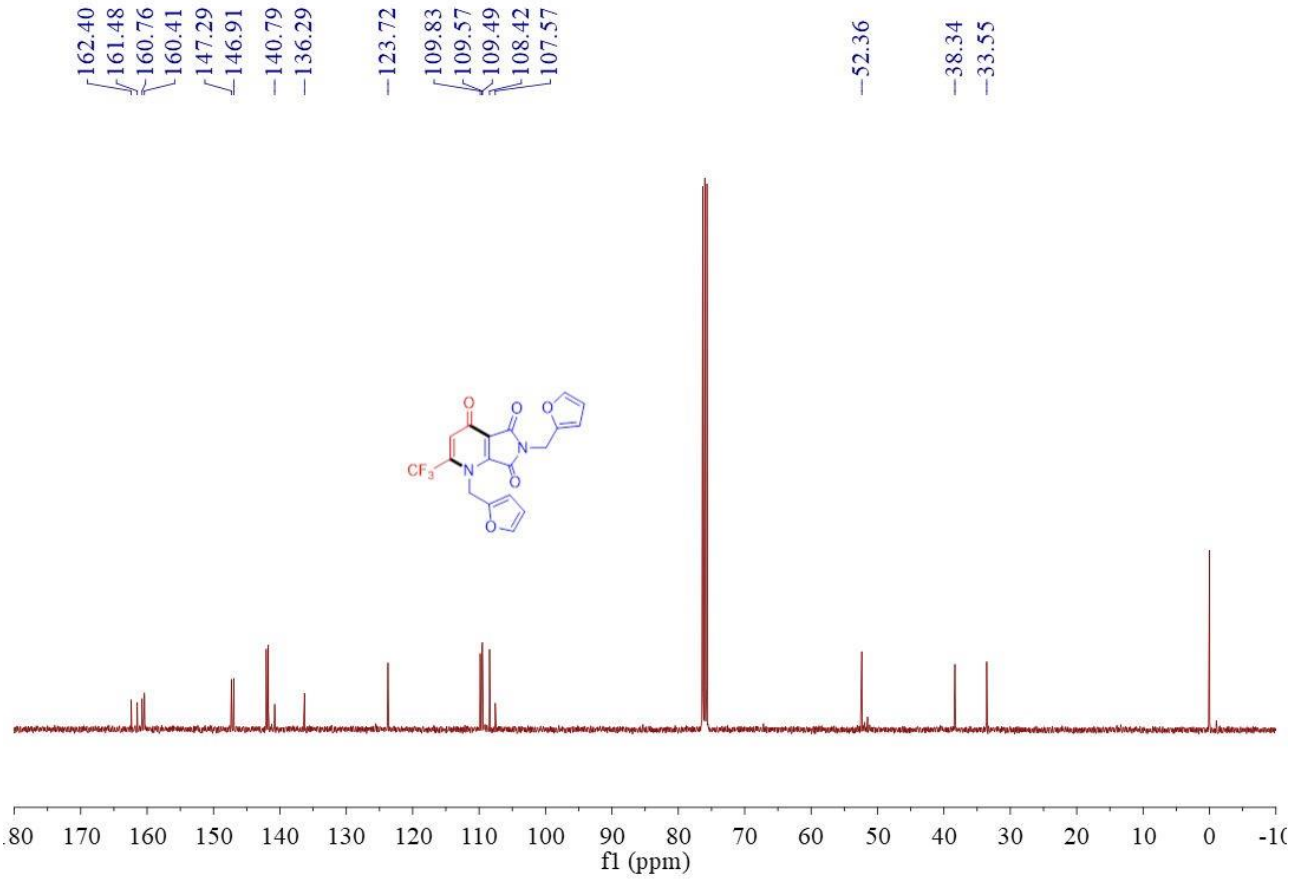
^{13}C NMR of product **3j** in $CDCl_3$ (100 MHz)



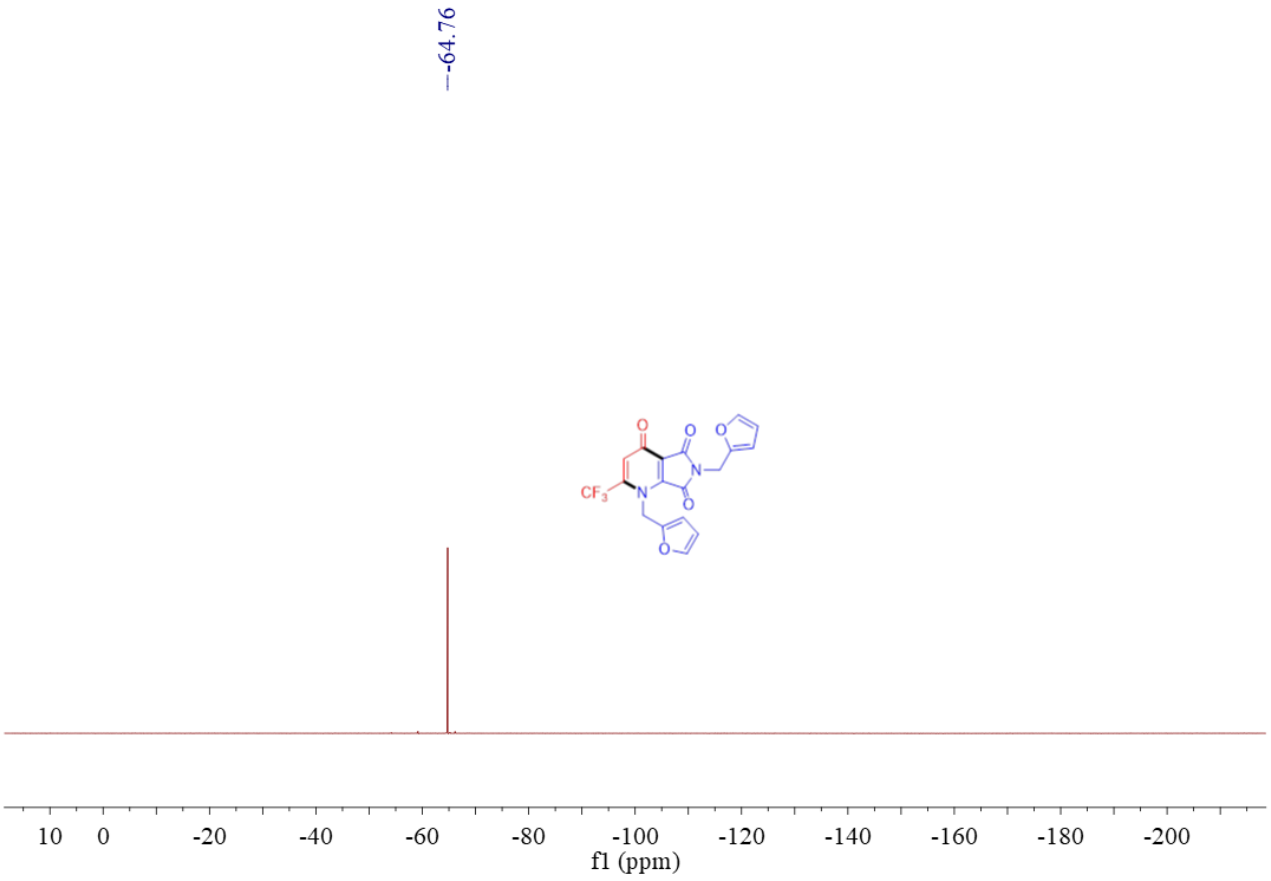
^{19}F NMR of product **3j** in $CDCl_3$ (376 MHz)



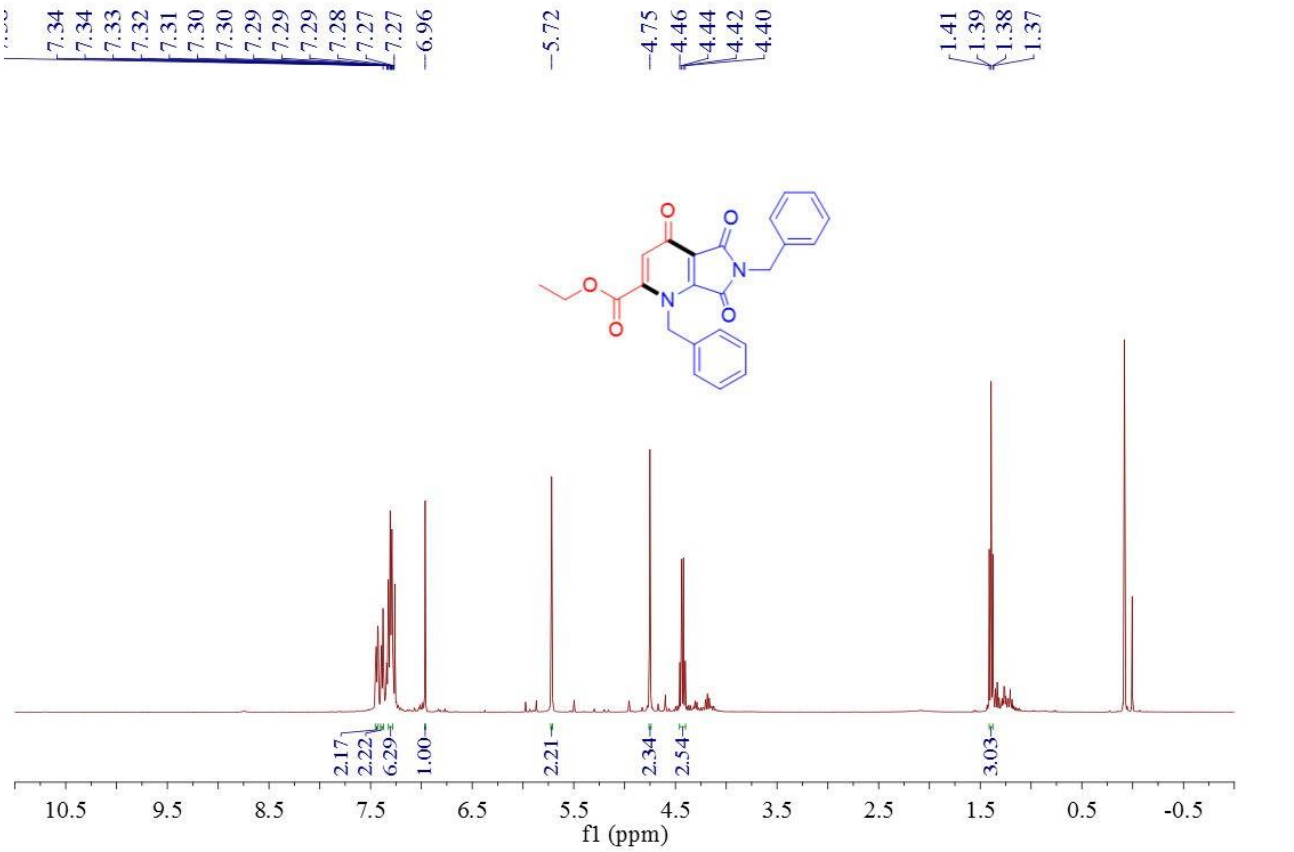
^{1}H NMR of product **3k** in $CDCl_3$ (400 MHz)



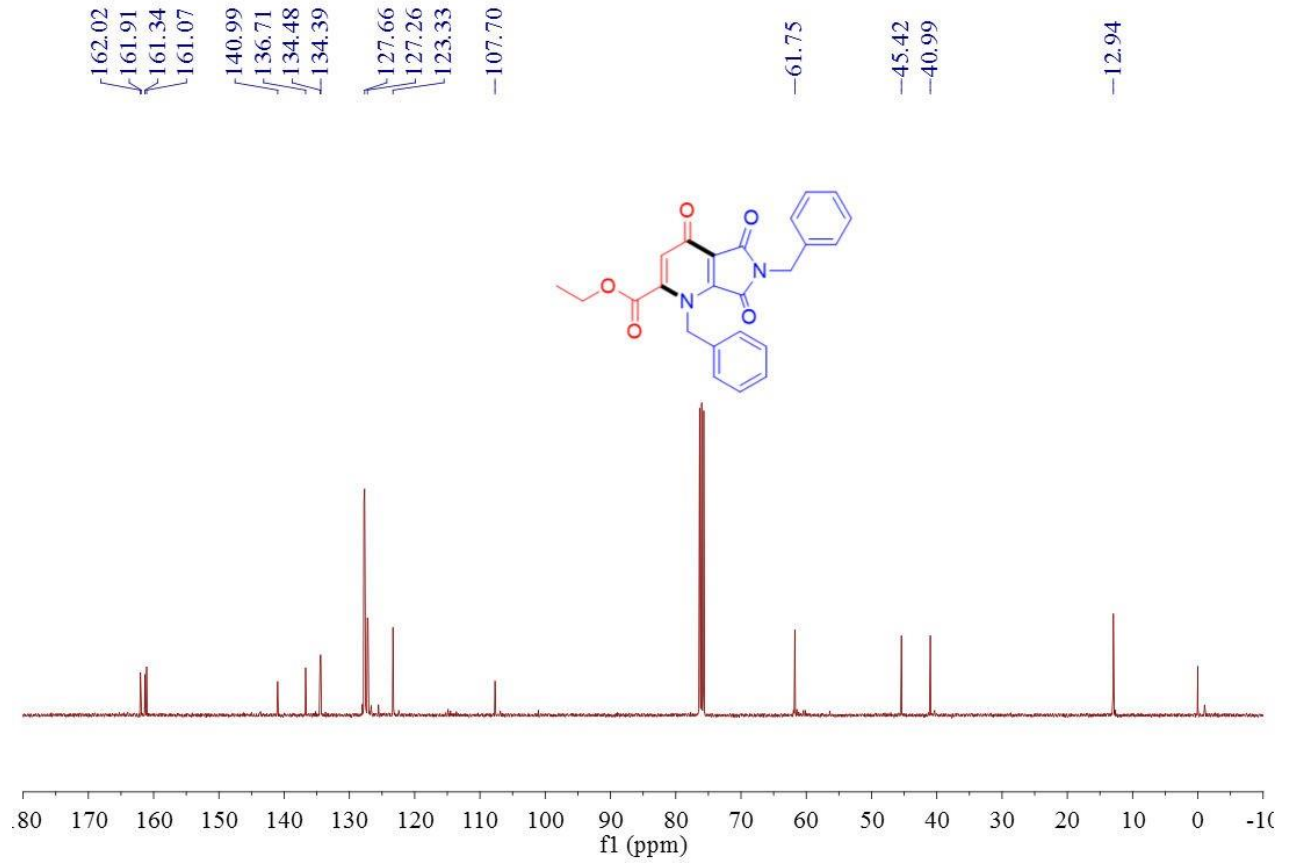
^{13}C NMR of product **3k** in $CDCl_3$ (100 MHz)



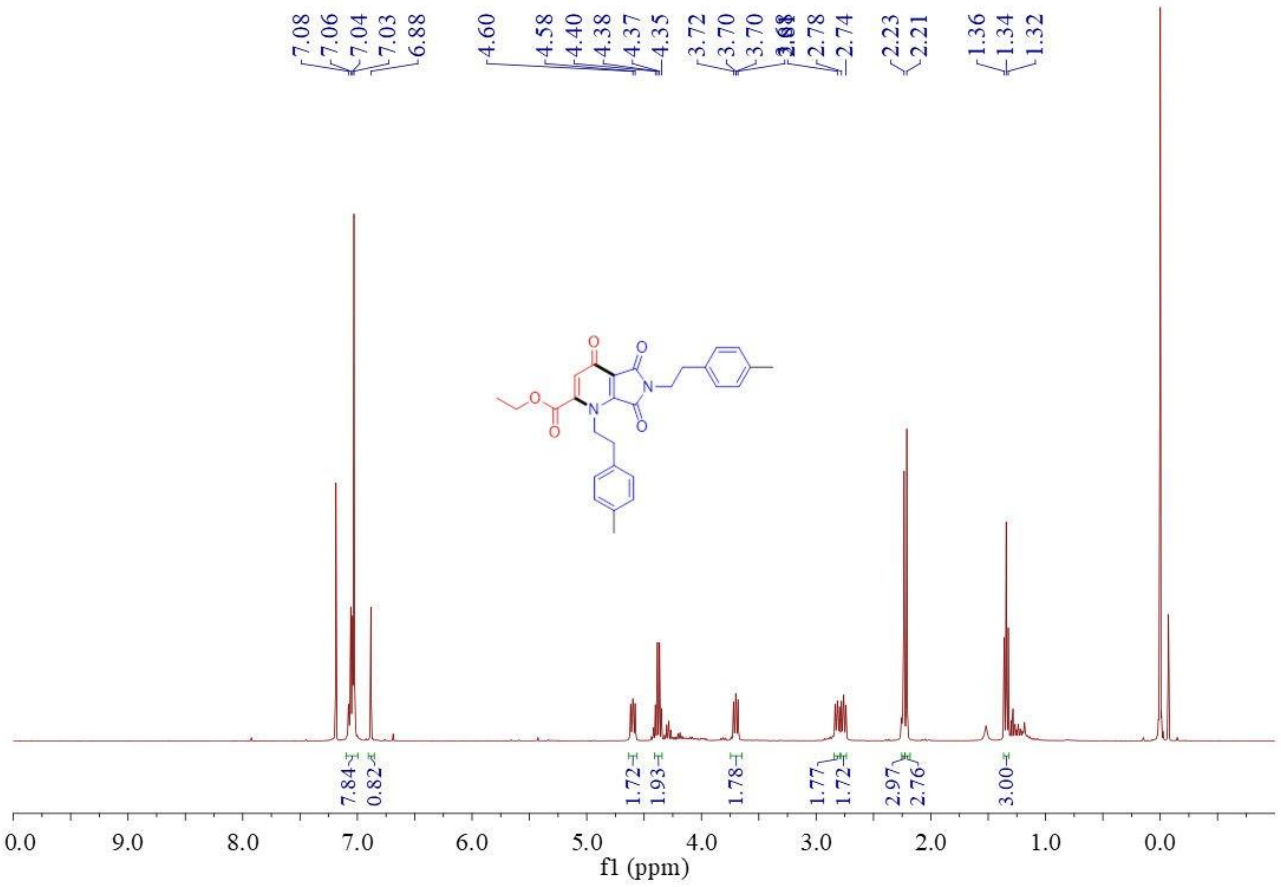
^{19}F NMR of product **3k** in $CDCl_3$ (376 MHz)



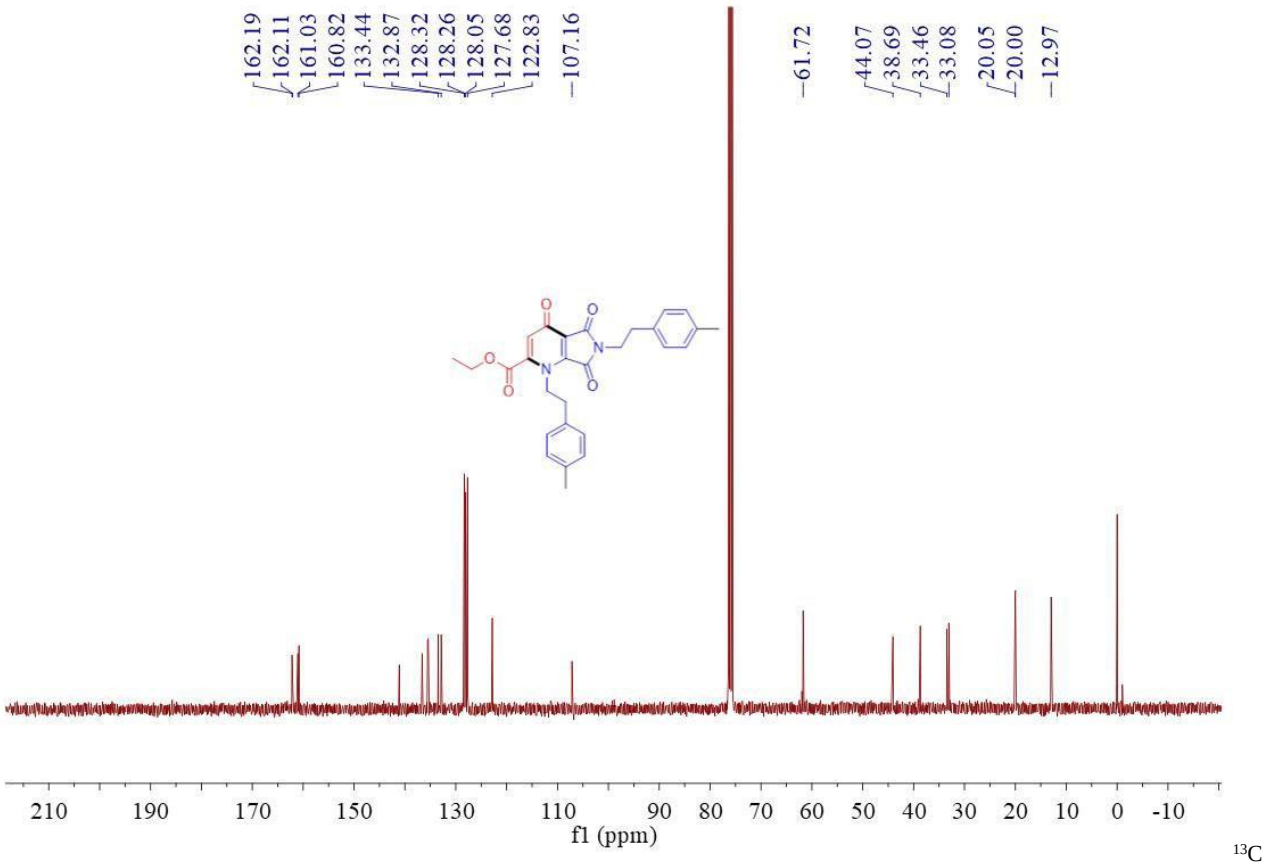
^{1}H NMR of product **3l** in $CDCl_3$ (400 MHz)



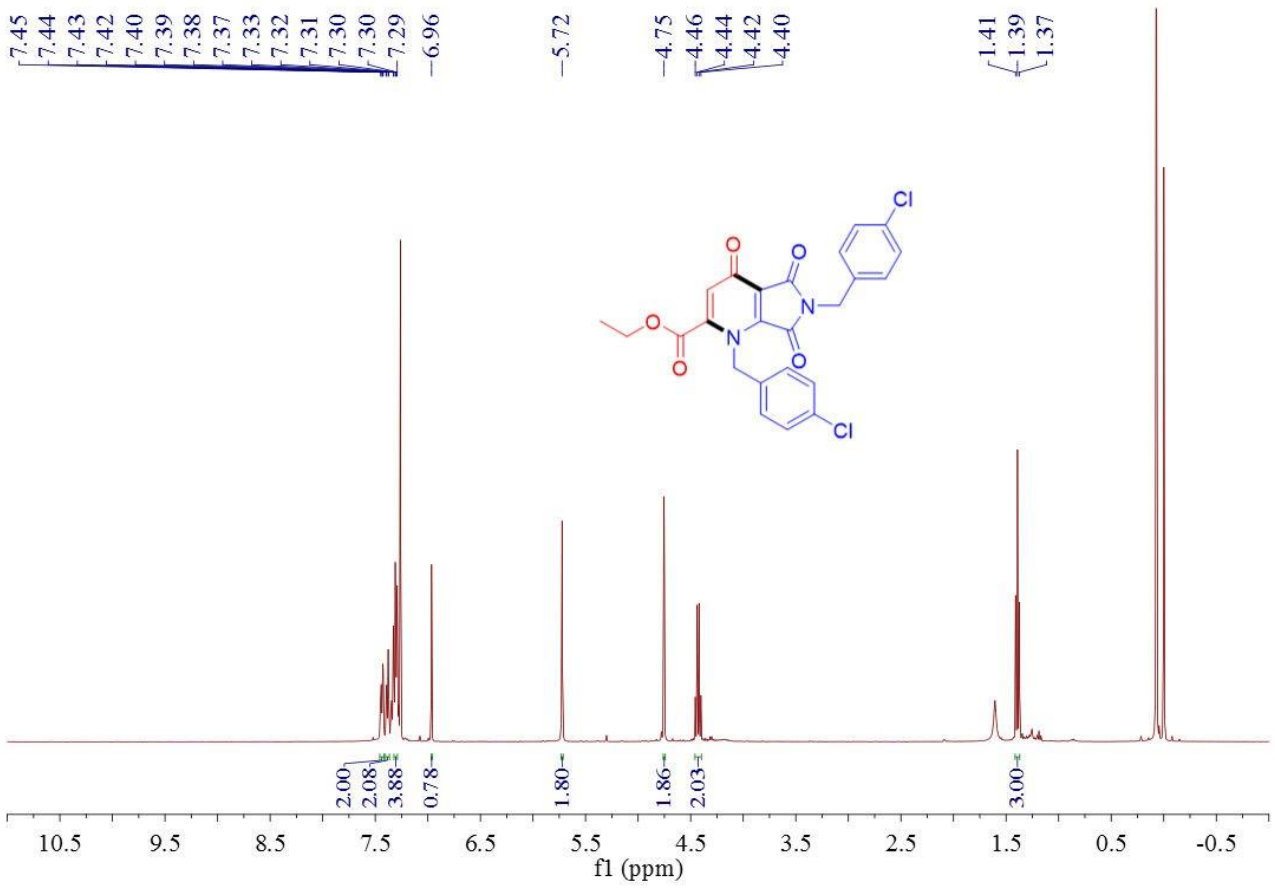
^{13}C NMR of product **3l** in $CDCl_3$ (100 MHz)



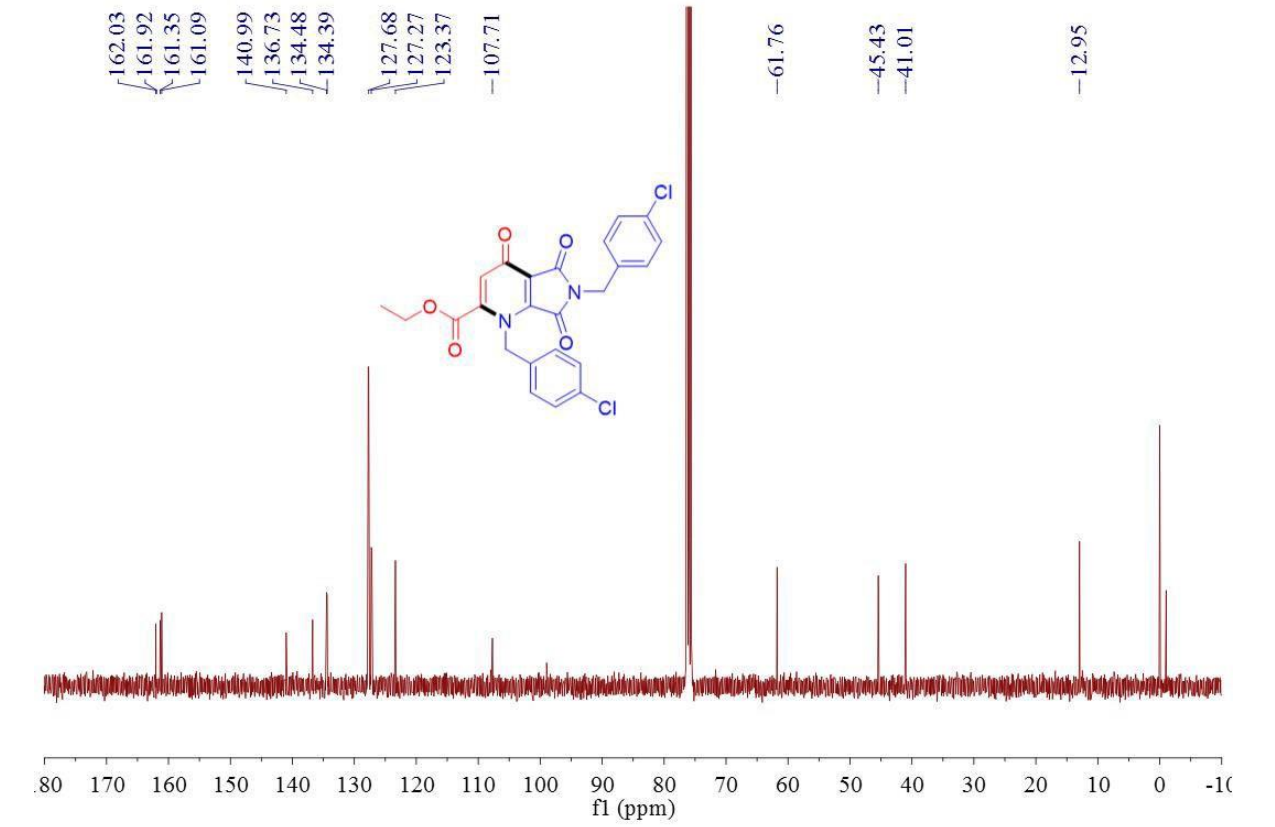
^{1}H NMR of product **3m** in $CDCl_3$ (400 MHz)



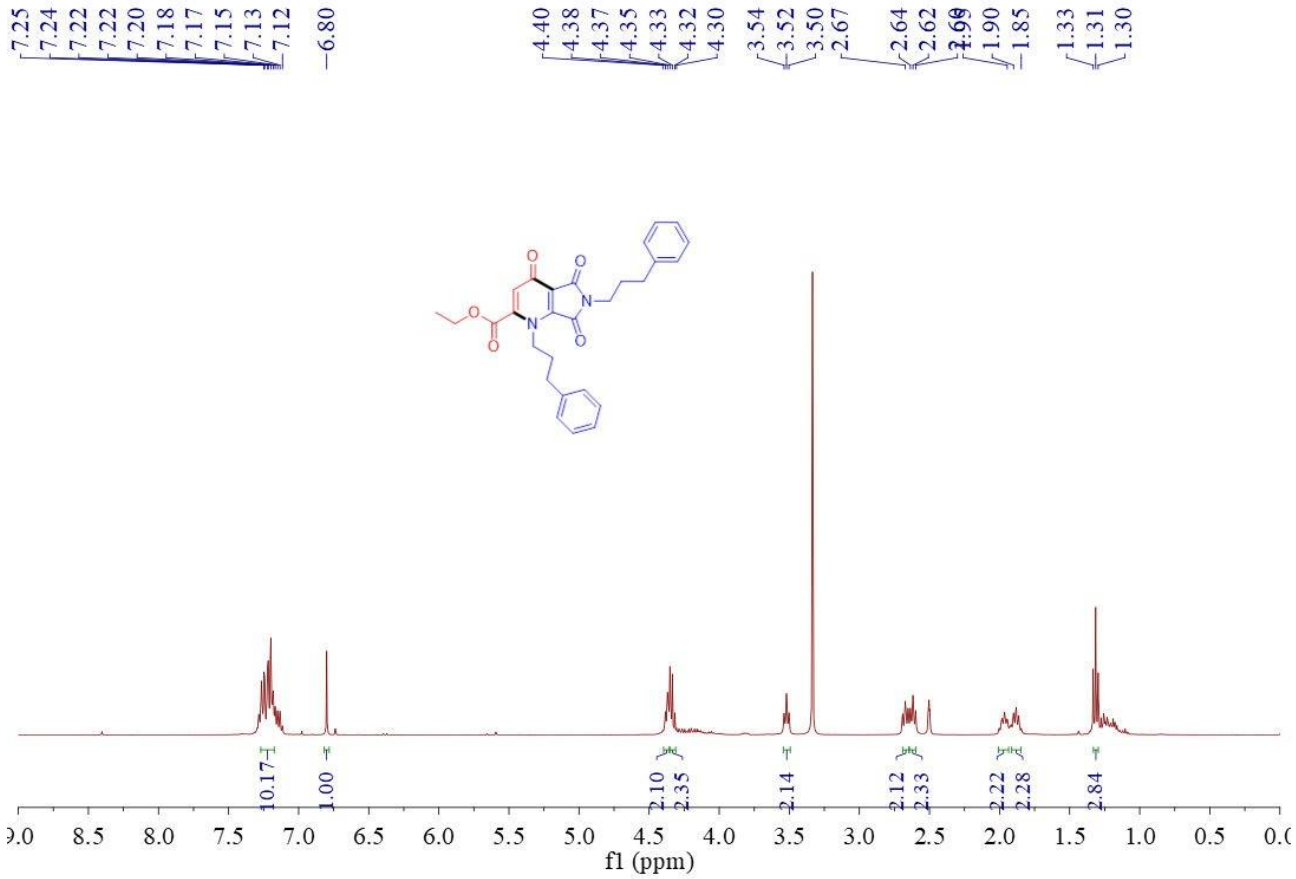
^{13}C NMR of product **3m** in $CDCl_3$ (100 MHz)



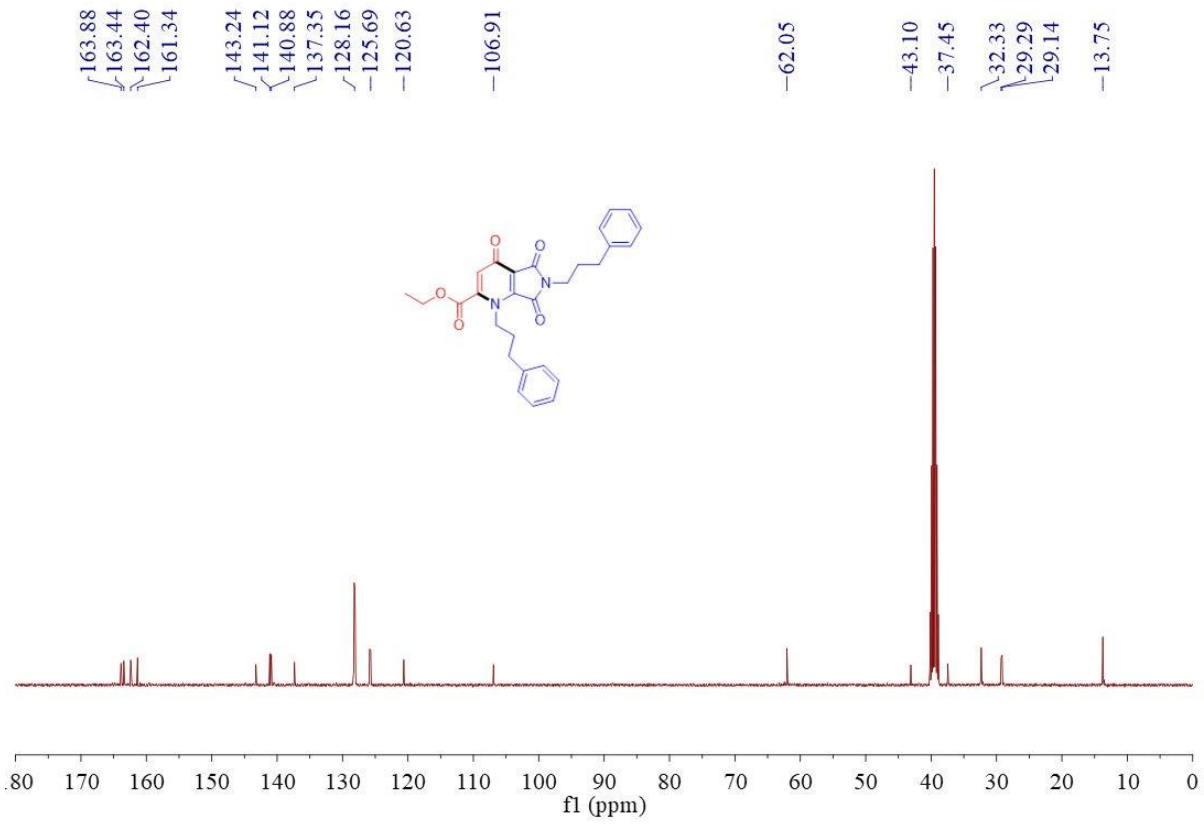
^{1}H NMR of product **3n** in $CDCl_3$ (400 MHz)



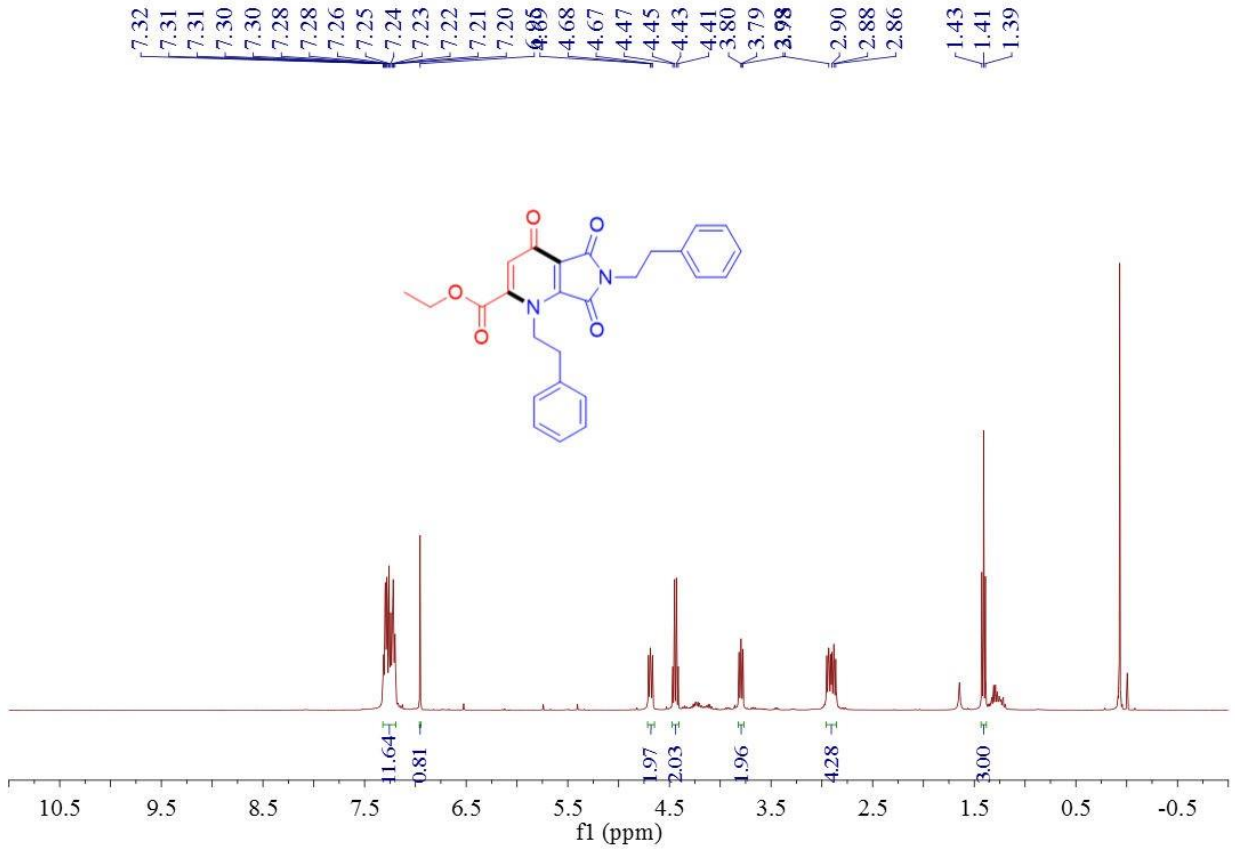
^{13}C NMR of product **3n** in $CDCl_3$ (100 MHz)



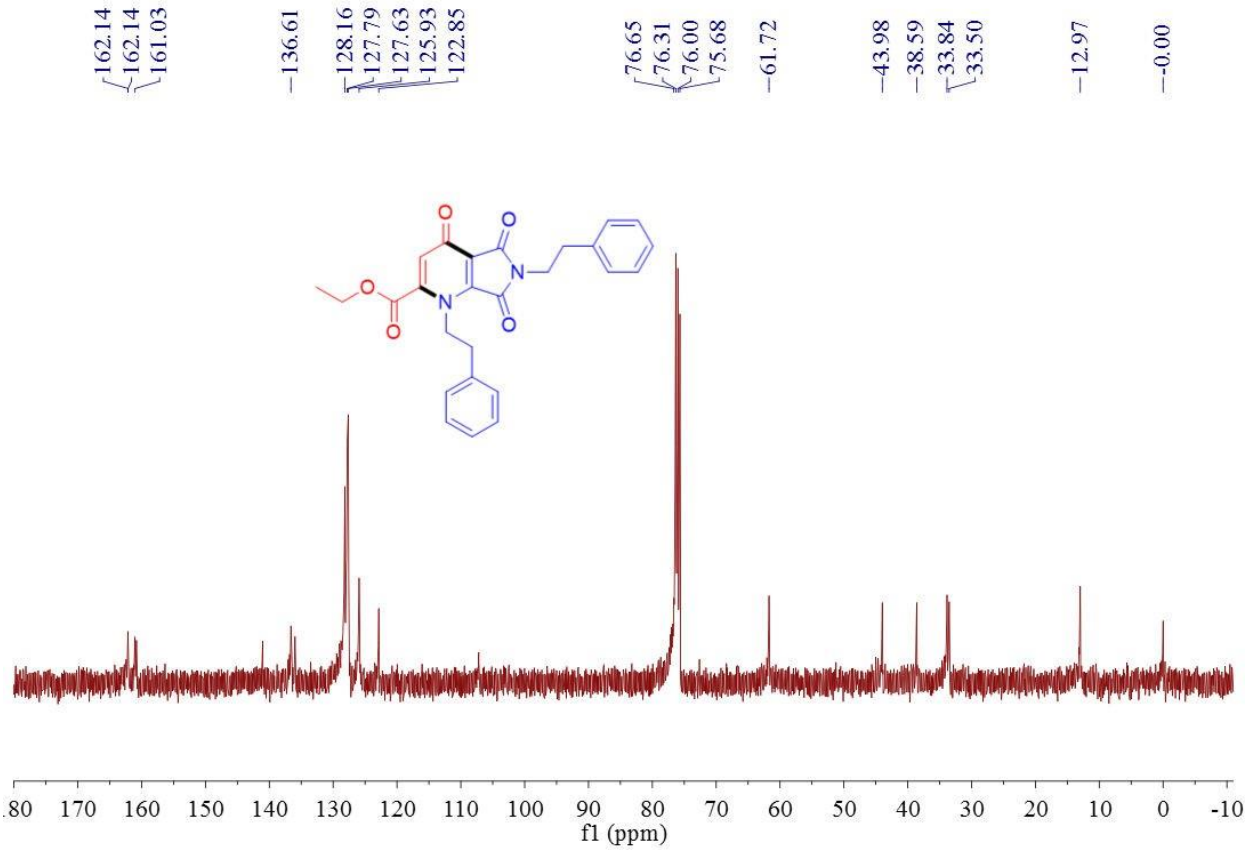
^{1}H NMR of product **3o** in DMSO (400 MHz)



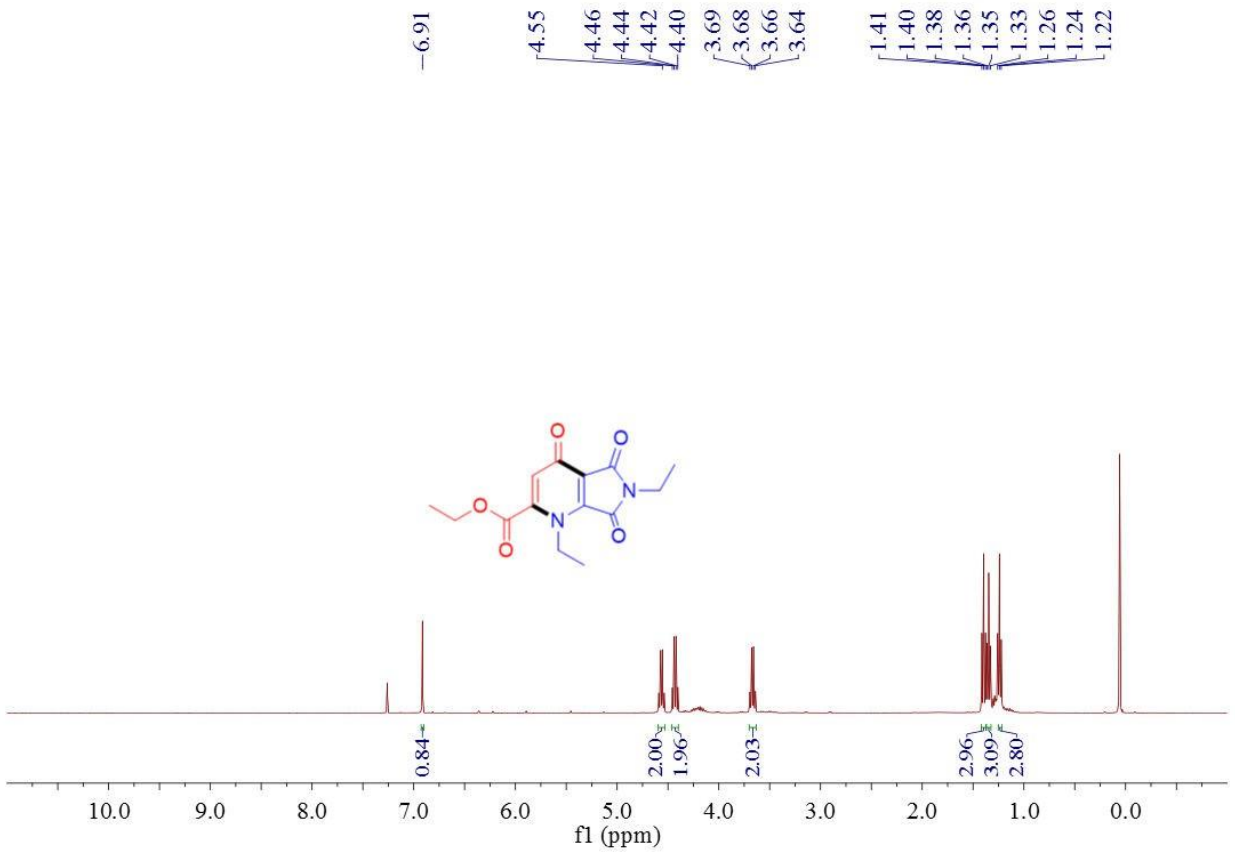
^{13}C NMR of product **3o** in DMSO (100 MHz)



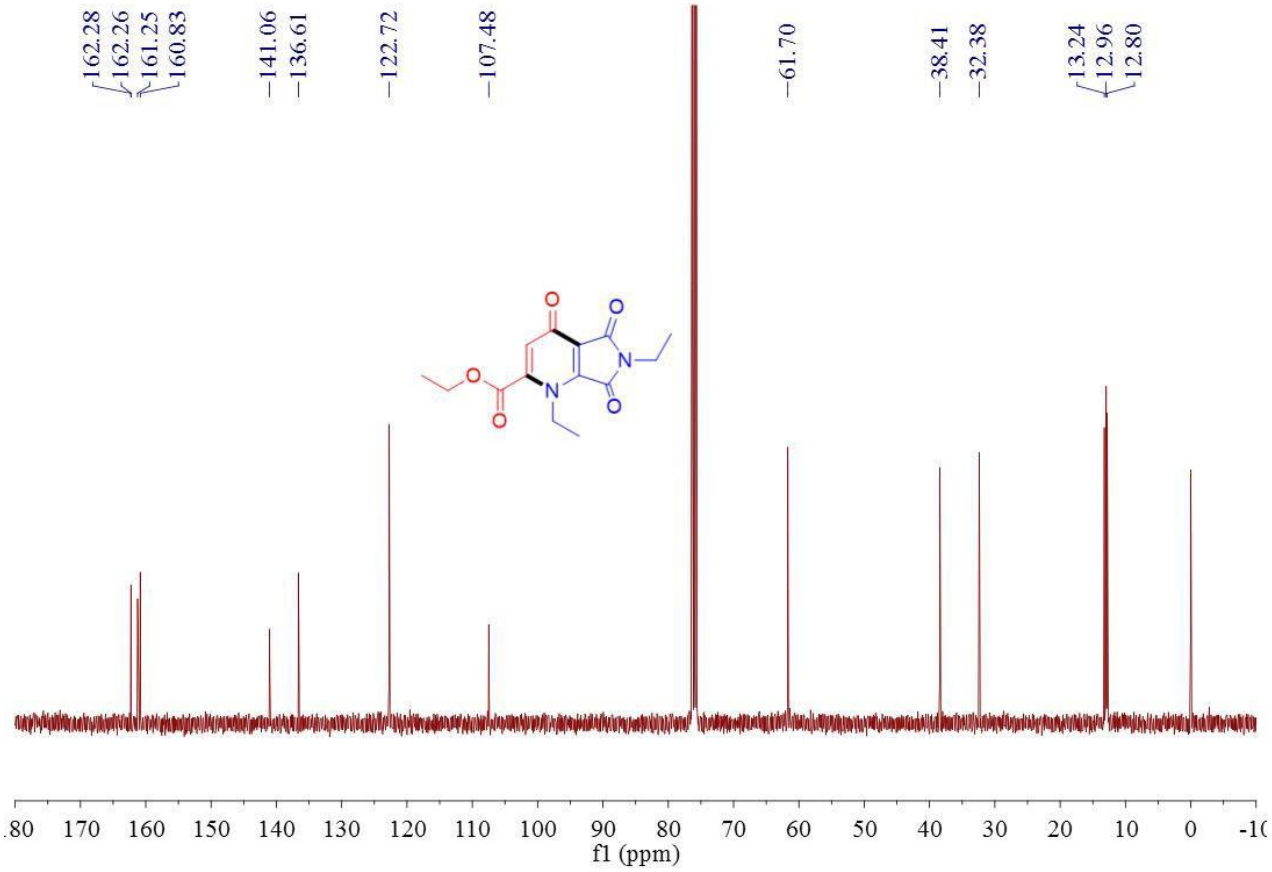
^{1}H NMR of product **3p** in $CDCl_3$ (400 MHz)



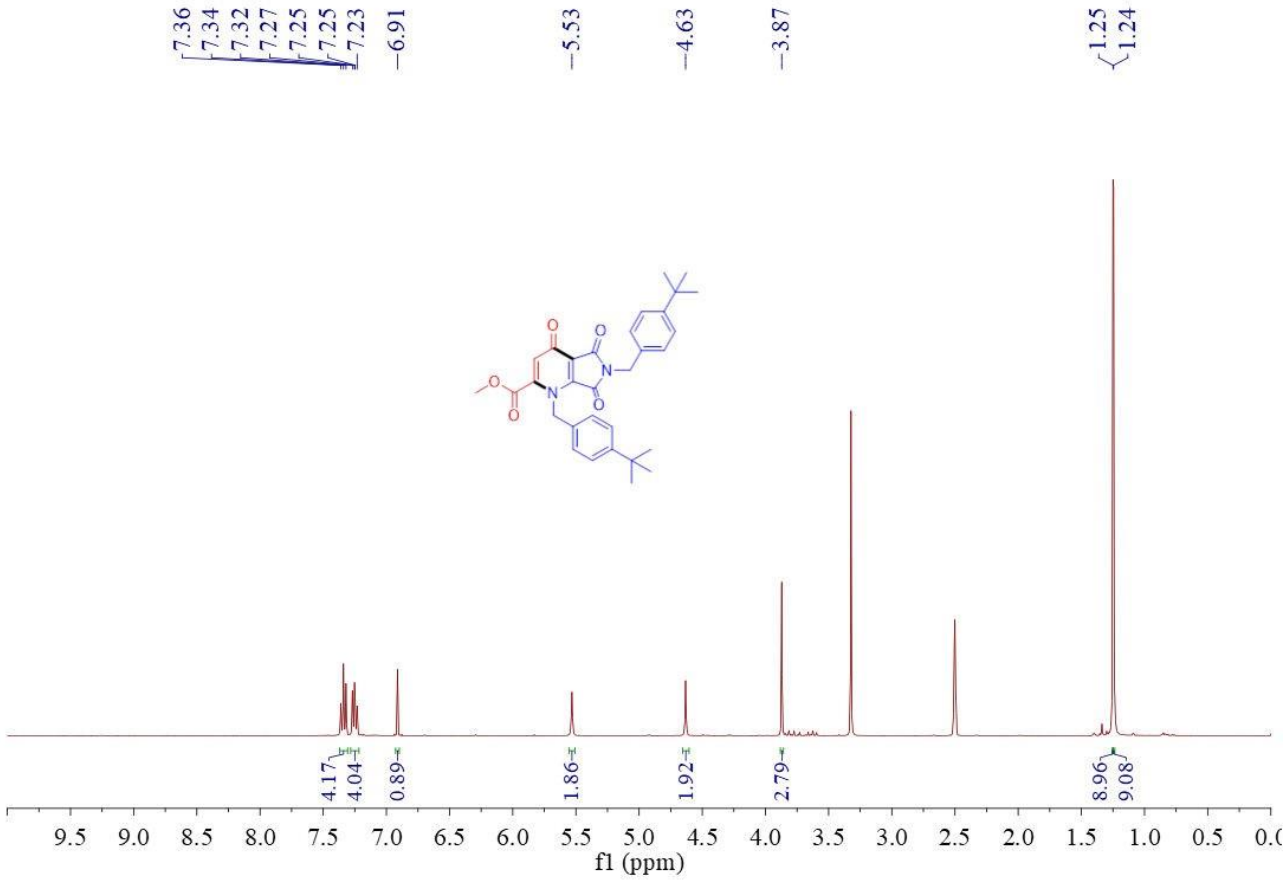
^{13}C NMR of product **3p** in $CDCl_3$ (100 MHz)



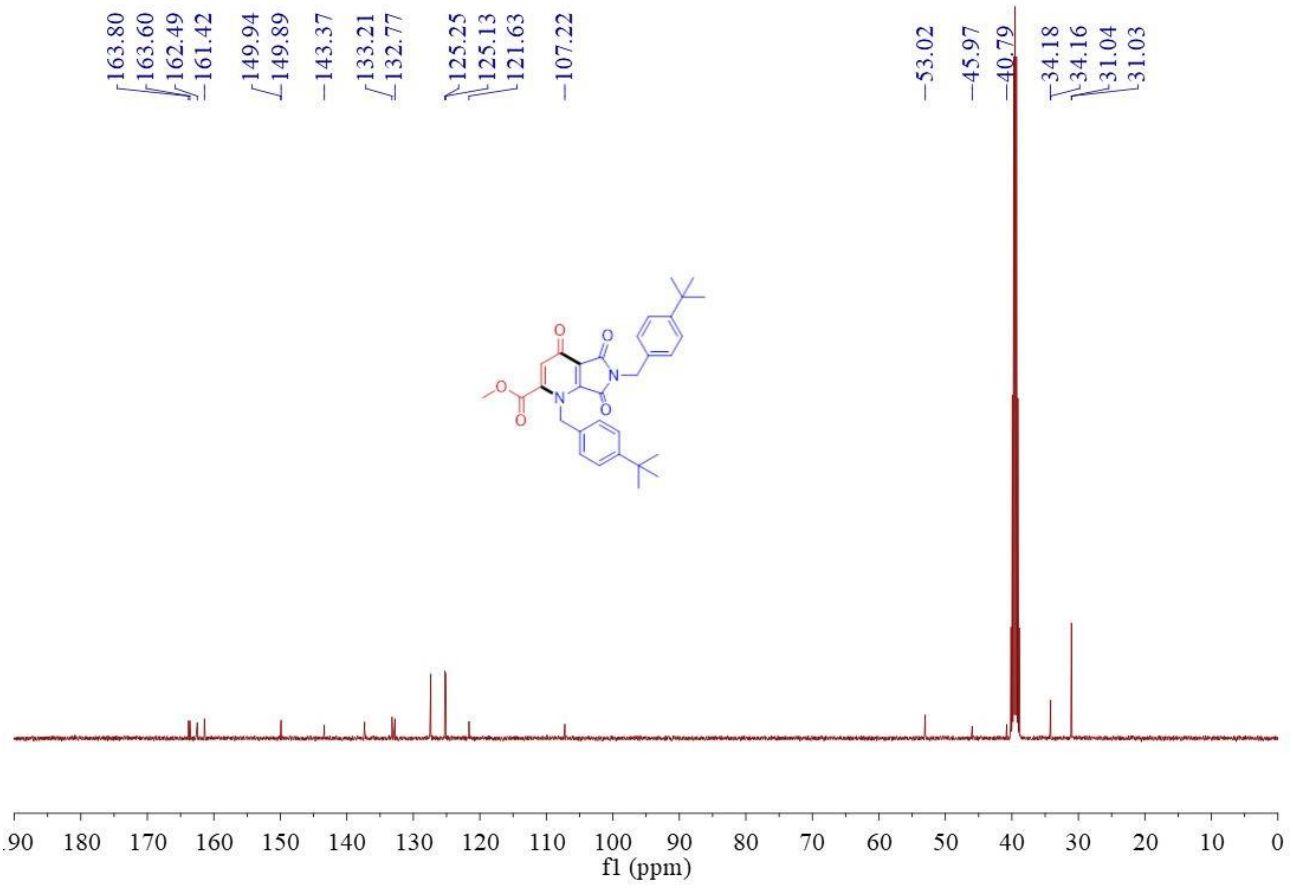
^{1}H NMR of product **3q** in $CDCl_3$ (400 MHz)



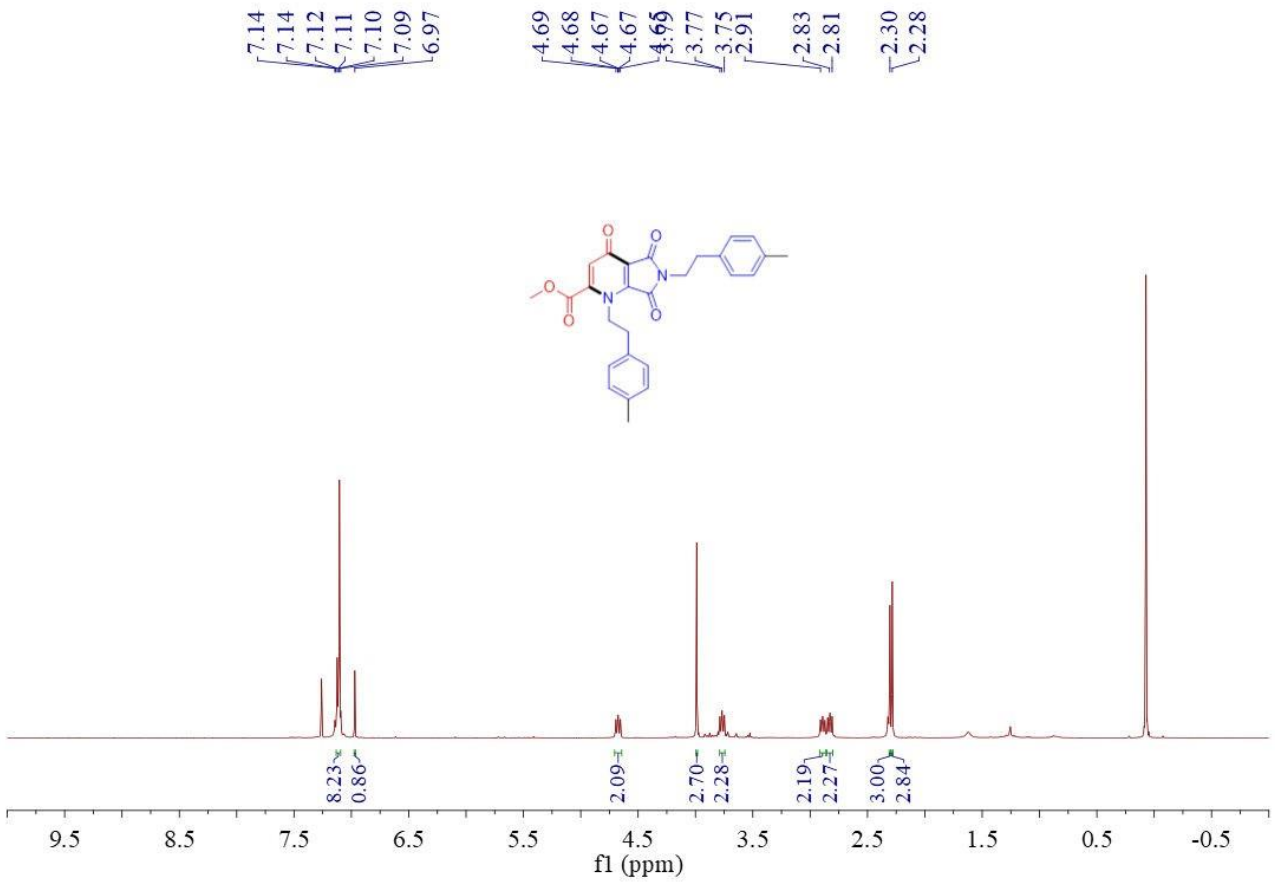
^{13}C NMR of product **3q** in $CDCl_3$ (100 MHz)



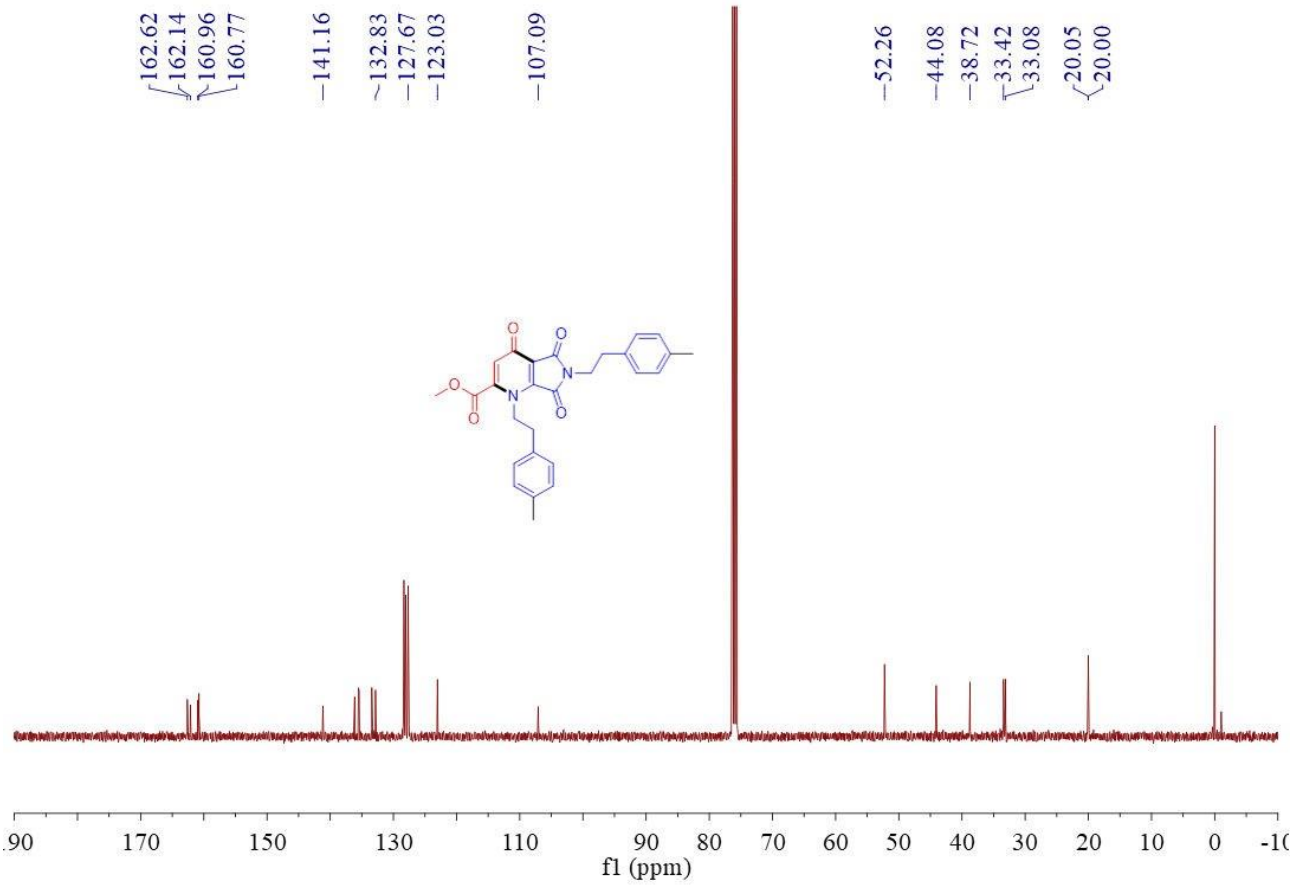
^{1}H NMR of product **3r** in DMSO (400 MHz)



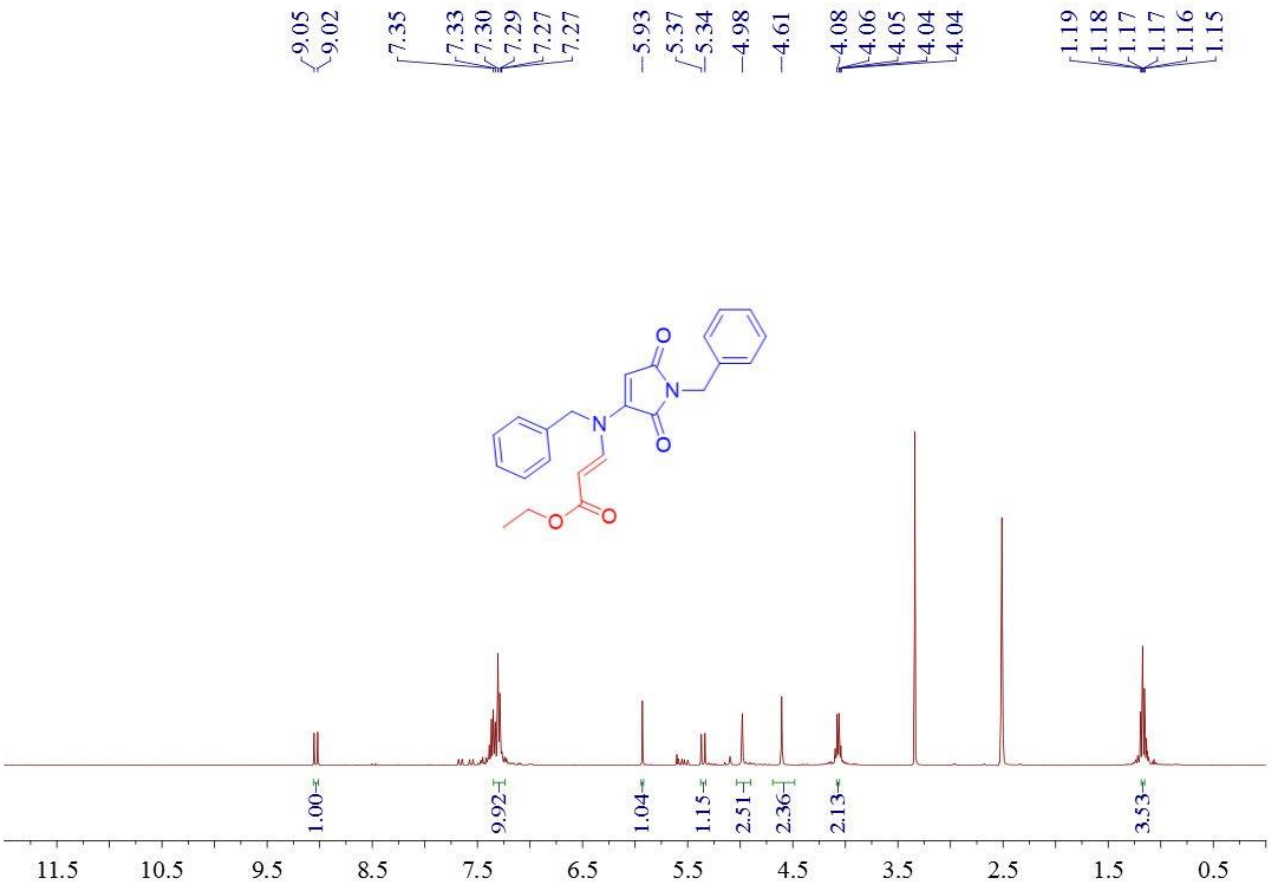
^{13}C NMR of product **3r** in DMSO (100 MHz)



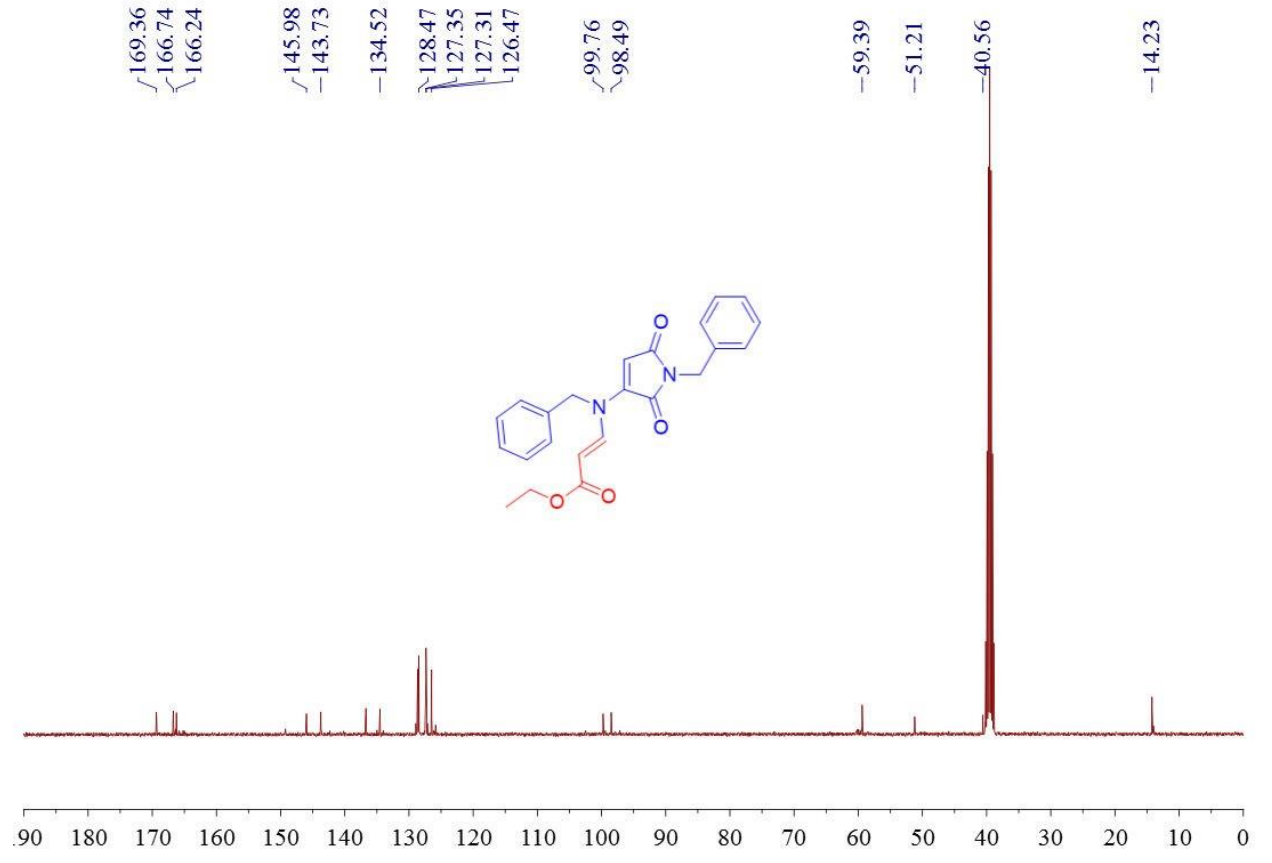
^{1}H NMR of product **3s** in $CDCl_3$ (400 MHz)



^{13}C NMR of product **3s** in $CDCl_3$ (100 MHz)



^{1}H NMR of product **3aa** in DMSO(400 MHz)



^{13}C NMR of product **3aa** in DMSO(100 MHz)