

Supporting Information

Iodine and Ammonium Persulfate Mediated Activation of DMSO: Approach to N-Formylation of Amides and Synthesis of Isatins.

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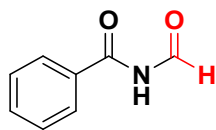
1. General information

All the necessary reagents and solvents were purchased from Sigma Aldrich, TCI, and Sdfine respectively. Solvents were purified using standard protocols. All the reactions were carried out in oven-dried glassware. UV lamp (254 nm) was used to analyze developed chromatograms. All the products were purified using silica gel (mesh size 100-200) column chromatography. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 and DMSO-d_6 as per requirement using 400 MHz spectrometer. Chemical shifts of ^1H and ^{13}C NMR were expressed in parts per million (ppm). The representation of the signals includes the following: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet, q = quartet, dq = doublet of quartet, m = multiplet, br = broad. Solvent peaks: CDCl_3 , ^1H δ 7.26 (s), ^{13}C δ 77.2 (t). DMSO-d_6 , ^1H δ 2.5 (m) & δ 3.4 (s) corresponding to moisture, ^{13}C δ 39.5 (m).

2. General procedure for the synthesis of *N*-Formyl amides (2a-2u) (Scheme A) & 8.

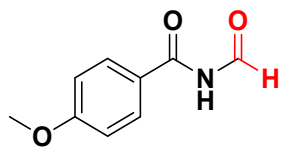
A reaction mixture containing amide (1 equiv., 0.83 mmoles) and molecular iodine (1.5 equiv., 1.24 mmoles) in DMSO (3 mL) were heated in the round bottom flask at 120°C . After 5 minutes, ammonium persulfate (2 equiv., 1.66 mmoles) was added slowly and the reaction mixture was stirred for 10 minutes. The progress of the reaction was monitored by TLC. After the reaction was complete, an ice-cooled aqueous solution of sodium thiosulfate was added to the reaction mixture and was extracted with EtOAc ($20\text{ mL} \times 3$). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethyl acetate and hexane as eluents to obtain the desired product.

N-formylbenzamide (2a)¹



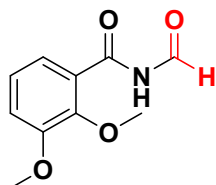
White solid, eluent (8% ethyl acetate/hexane); yield (77 %, 104 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 11.75 (s, 1H), 9.27 (s, 1H), 8.06 – 8.00 (m, 2H), 7.71–7.64 (m, 1H), 7.60–7.52 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.98 (s), 164.96 (s), 133.96 (s), 131.98 (s), 129.18 (s), 128.88 (s). HRMS (ESI) for $\text{C}_8\text{H}_7\text{NO}_2$ [M-H]⁻ : Calculated 148.0387 Found: 148.0393

N-formyl-4-methoxybenzamide (**2b**)²



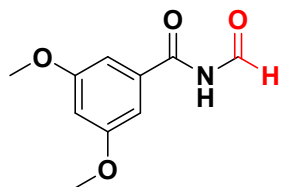
White solid, eluent (13% ethyl acetate/hexane), yield (76%, 113 mg); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.62 (s, 1H), 9.25 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.07 (s), 165.00 (s), 163.88 (s), 131.14 (s), 123.92 (s), 114.50 (s), 56.08 (s)

N-formyl-2,3-dimethoxybenzamide (**2c**)²



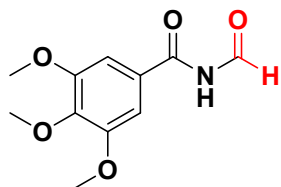
White solid, eluent (16% ethyl acetate/hexane), yield (71%, 123 mg); ¹H NMR (400 MHz, CDCl₃) δ 10.37 (s, 1H), 9.42 (d, *J* = 9.9 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.18 (m, 1H), 4.01 (s, 3H), 3.93 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.48 (s), 158.27 (s), 147.97 (s), 144.00 (s), 120.06 (s), 118.98 (s), 118.16 (s), 112.99 (s), 57.14 (s), 51.46 (s). HRMS (ESI) for C₁₀H₁₁NO₄ [M-H]⁻: calculated 208.0595 Found: 208.0610

N-formyl-3,5-dimethoxybenzamide (**2d**)



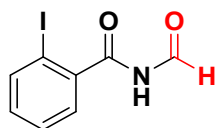
White solid, eluent (16% ethyl acetate/hexane), yield (73%, 126.7mg); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.70 (s, 1H), 9.26 (d, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 2.3 Hz, 2H), 6.76 (d, *J* = 2.0 Hz, 1H), 3.80 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.46 (s), 164.98 (s), 160.95 (s), 133.82 (s), 106.48 (s), 106.10 (s), 56.00 (s). HRMS (ESI) for C₁₀H₁₁NO₄ [M-H]⁻: calculated 208.0593 Found: 208.0607

N-formyl-3,4,5-trimethoxybenzamide (2e)



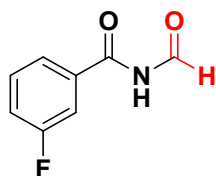
White solid, eluent (24% ethyl acetate/hexane), yield (69%, 198.5 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.65 (s, 1H), 9.40 (d, $J = 9.5$ Hz, 1H), 7.34 (d, $J = 2.3$ Hz, 2H), 3.96 (s, 6H), 3.94 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.24 (s), 165.61 (s), 153.38 (s), 142.98 (s), 125.65 (s), 105.62 (s), 61.01 (s), 56.40 (s). HRMS (ESI) for $\text{C}_{11}\text{H}_{13}\text{NO}_5$ $[\text{M}-\text{H}]^-$: Calculated 238.1862 Found: 238.1868

N-formyl-2-iodobenzamide (2f)



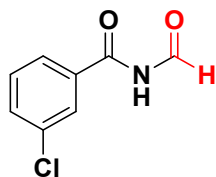
White solid, eluent (12% ethyl acetate/hexane), yield (74%, 168.9 mg); $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 11.68 (d, $J = 7.4$ Hz, 1H), 9.11 (s, 1H), 7.97 (d, $J = 7.9$ Hz, 1H), 7.53 (m, 2H), 7.28 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO}-d_6$) δ 170.60 (s), 164.26 (s), 140.05 (s), 139.94 (s), 132.68 (s), 129.09 (s), 128.66 (s), 93.58 (s). HRMS (ESI) for $\text{C}_8\text{H}_6\text{INO}_2$ $[\text{M}-\text{H}]^-$: Calculated 273.9364 Found: 273.9365

3-fluoro-*N*-formylbenzamide (2g)



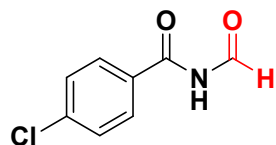
White solid, eluent (13% ethyl acetate/hexane), yield (82%, 113.7 mg); $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 11.79 (s, 1H), 9.26 (s, 1H), 7.92 – 7.77 (m, 2H), 7.61 (m, 1H), 7.54 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO}-d_6$) δ 166.78 (d, $J = 2.8$ Hz), 164.86 (s), 162.40 (d, $J = 245.0$ Hz), 134.28 (d, $J = 7.0$ Hz), 131.38 (d, $J = 7.8$ Hz), 125.10 (d, $J = 2.7$ Hz), 120.85 (d, $J = 21.1$ Hz), 115.62 (d, $J = 23.2$ Hz). $^{19}\text{F NMR}$ (377 MHz, $\text{DMSO}-d_6$) δ -110.43 – -115.18 (m). HRMS (ESI) for $\text{C}_8\text{H}_6\text{FNO}_2$ $[\text{M}-\text{H}]^-$: Calculated 166.0304 Found: 166.0288

3-chloro-*N*-formylbenzamide (2h) ³



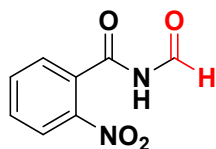
White solid, eluent (12% ethyl acetate/hexane), yield (80%, 121.9 mg); ¹H NMR (400 MHz, CDCl₃) δ 9.90 (s, 1H), 9.39 (d, *J* = 9.6 Hz, 1H), 8.00 (t, *J* = 1.8 Hz, 1H), 7.85 (m, 1H), 7.63 (m, 1H), 7.50 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 165.41 (s), 164.37 (s), 135.54 (s), 134.00 (s), 132.80 (s), 130.42 (s), 128.48 (s), 125.90 (s). HRMS (ESI) for C₈H₆ClNO₂ [M-H]⁻ : Calculated 182.0012 Found: 182.0009

4-chloro-*N*-formylbenzamide (2i) ¹



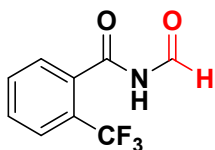
White solid, eluent (11% ethyl acetate/hexane), yield (81%, 123.4 mg); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.81 (s, 1H), 9.25 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.68 – 7.56 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.12 (s), 164.90 (s), 138.89 (s), 130.80 (s), 129.31 (s). HRMS (ESI) for C₈H₆ClNO₂ [M-H]⁻ : Calculated 182.0012 Found: 182.0009

N-formyl-2-nitrobenzamide (2j)



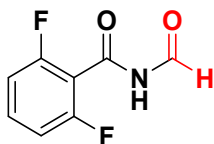
White solid, eluent (15% ethyl acetate/hexane), yield (82%, 132 mg); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.87 (s, 1H), 9.16 (s, 1H), 8.31 – 8.15 (m, 1H), 7.92 (td, *J* = 7.5, 1.0 Hz, 1H), 7.81 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.09 (s), 163.78 (s), 146.31 (s), 135.08 (s), 132.46 (s), 130.64 (s), 129.66 (s), 124.95 (s). HRMS (ESI) for C₈H₆N₂O₄ [M-H]⁻ : calculated 193.0238 Found: 193.0249

N-formyl-2-(trifluoromethyl)benzamide (2k)



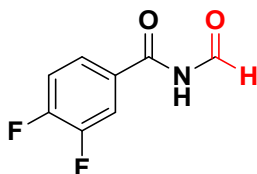
White solid, eluent (12% ethyl acetate/hexane), yield (81%, 146 mg); **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.84 (d, *J* = 7.6 Hz, 1H), 9.14 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.2 Hz, 2H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 169.07 (s), 163.93 (s), 133.54 (s), 133.17 (s), 131.72 (s), 129.11 (s), 127.06 (d, *J* = 4.7 Hz), 125.61 – 125.59 (m), 125.21 (dd, *J* = 248.4 Hz). **¹⁹F NMR (377 MHz, DMSO-*d*₆)** δ -57.97 (s). HRMS (ESI) for C₉H₆F₃NO₂ [M-H]⁻ : calculated 216.0269 Found: 216.0272

2,6-difluoro-*N*-formylbenzamide (2l)³



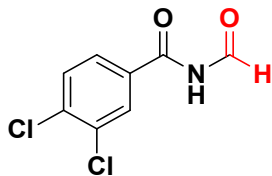
White solid, eluent (14% ethyl acetate/hexane), yield (83%, 127 mg); **¹H NMR (400 MHz, CDCl₃)** δ 9.19 (s, 1H), 8.68 (s, 1H), 7.47 (m, 1H), 7.05 – 6.94 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 161.89 (s), 161.79 (s), 159.81 (d, *J* = 105.5 Hz), 134.39 (d, *J* = 21.7 Hz), 112.84 (d, *J* = 3.1 Hz), 112.62 (d, *J* = 3.1 Hz). **¹⁹F NMR (377 MHz, DMSO)** δ -114.13 (dd, *J* = 9.1, 4.7 Hz). HRMS (ESI) for C₈H₅F₂NO₂ [M-H]⁻ : calculated 184.0198 Found: 184.0210

3,4-difluoro-*N*-formylbenzamide (2m)



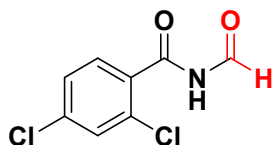
White solid, eluent (13% ethyl acetate/hexane), yield (87 %, 133 mg); **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.81 (s, 1H), 9.24 (s, 1H), 8.09 (m, 1H), 7.93 (m, 1H), 7.64 (m, 1H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 165.92 (d, *J* = 1.8 Hz), 164.87 (s), 153.15 (d, *J* = 241.2 Hz), 150.11 (d, *J* = 118.3 Hz), 129.39 (d, *J* = 3.6 Hz), 126.75 (d, *J* = 3.6 Hz), 118.53 (d, *J* = 17.8 Hz), 118.40 (d, *J* = 18.0 Hz). **¹⁹F NMR (377 MHz, DMSO-*d*₆)** δ -134.69 – -134.97 (m), -138.02 – -138.29 (m). HRMS (ESI) for C₈H₅F₂NO₂ [M-H]⁻ : calculated 184.0198 Found: 184.0210

3,4-dichloro-*N*-formylbenzamide (2n)⁹



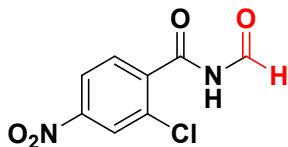
White solid, eluent (12% ethyl acetate/hexane), yield (79%, 142.9 mg); $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.85 (s, 1H), 9.25 (s, 1H), 8.26 (d, $J = 2.1$ Hz, 1H), 7.98 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 166.07(s), 164.77 (s), 136.77 (s), 132.45 (s), 132.15 (s), 131.53 (s), 130.81 (s), 129.05(s). HRMS (ESI) for $\text{C}_8\text{H}_5\text{Cl}_2\text{NO}_2$ $[\text{M-H}]^-$: Calculated 215.9619 Found: 216.9604

2,4-dichloro-N-formylbenzamide (2o)



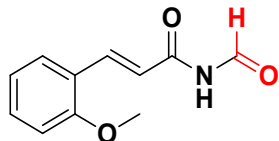
White solid, eluent (12% ethyl acetate/hexane), yield (81%, 146.5 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.26 (d, $J = 9.3$ Hz, 1H), 8.98 (s, 1H), 7.75 (m, 1H), 7.52 (m, 1H), 7.42 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 167.52 (s), 164.03 (s), 136.74 (s), 132.99 (s), 131.85 (s), 131.28 (s), 130.05 (s), 128.09 (s). HRMS (ESI) for $\text{C}_8\text{H}_5\text{Cl}_2\text{NO}_2$ $[\text{M-H}]^-$: Calculated 215.9619 Found: 216.9604

2-chloro-N-formyl-4-nitrobenzamide (2p)



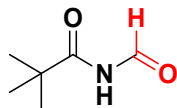
White solid, eluent (13% ethyl acetate/hexane), yield (82%, 155.5 mg); $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.96 (s, 1H), 9.14 (s, 1H), 8.44 (d, $J = 2.1$ Hz, 1H), 8.32 (m, 1H), 7.94 (t, $J = 6.9$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 167.16 (s), 163.87 (s), 149.47 (s), 139.79 (s), 131.53 (s), 130.89 (s), 125.30 (s), 123.05 (s). HRMS (ESI) for $\text{C}_8\text{H}_5\text{ClN}_2\text{O}_4$ $[\text{M-H}]^-$: $[\text{M-H}]$ Calculated 226.9935 Found: 226.9942

(E)-N-formyl-3-(2-methoxyphenyl)acrylamide (2q)



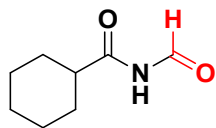
White solid, eluent (11% ethyl acetate/hexane), yield (76%, 129.4 mg); $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.32 (d, $J = 9.4$ Hz, 1H), 9.14 (d, $J = 9.5$ Hz, 1H), 7.96 (d, $J = 16.0$ Hz, 1H), 7.58 (dd $J = 7.7, 1.6$ Hz, 1H), 7.43 (m $J = 8.9, 7.4, 1.7$ Hz, 1H), 7.10 (d, $J = 7.9$ Hz, 1H), 7.05 – 6.98 (m, 1H), 6.84 (d, $J = 15.9$ Hz, 1H), 3.88 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 166.73 (s), 164.17 (s), 158.73 (s), 139.72 (s), 132.78 (s), 129.51 (s), 122.73 (s), 121.25 (s), 120.24 (s), 56.08 (s). HRMS (ESI) for $\text{C}_{11}\text{H}_{11}\text{NO}_3$ $[\text{M-H}]^-$: calculated 204.0643 Found: 204.0661

N-formylpivalamide (2r) ¹



White solid, eluent (15 % ethyl acetate/hexane), yield (68%, 72 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.86 (s, 1H), 9.20 – 9.00 (m, 1H), 1.20 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 179.22 (s), 165.02 (s), 39.57 (s), 26.26 (s).

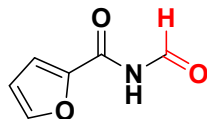
N-formylcyclohexanecarboxamide (2s) ³



White solid, eluent (20% ethyl acetate/hexane), yield (66%, 85 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.23 (s, 1H), 9.16 (d, $J = 9.9$ Hz, 1H), 2.29 (tt, $J = 11.5, 3.5$ Hz, 1H), 1.92 (dd, $J = 13.3, 2.4$ Hz, 2H), 1.88 – 1.80 (m, 2H), 1.76 – 1.67 (m, 1H), 1.49 (qd, $J = 12.2, 3.0$ Hz, 2H), 1.41

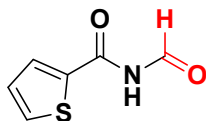
– 1.21 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.42 (s), 163.91 (s), 45.24 (s), 28.54 (s), 25.27 (s).

N-formylfuran-2-carboxamide (2t) ¹



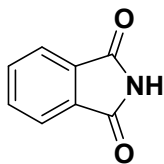
White solid, eluent (11% ethyl acetate/hexane), yield (71%, 82 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 11.65 (s, 1H), 9.18 (s, 1H), 8.05 (d, $J = 1.1$ Hz, 1H), 7.66 (dd, $J = 3.6, 0.6$ Hz, 1H), 6.74 (dd, $J = 3.6, 1.7$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.08 (s), 158.03 (s), 148.86 (s), 145.39 (s), 118.99 (s), 113.00 (s).

N-formylthiophene-2-carboxamide (2u) ¹



White solid, eluent (11% ethyl acetate/hexane), yield (69%, 88 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 11.80 (s, 1H), 9.20 (d, $J = 4.5$ Hz, 1H), 8.20 – 8.14 (m, 1H), 8.04 (d, $J = 4.9$ Hz, 1H), 7.29 – 7.22 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.44 (s), 162.28 (s), 137.21 (s), 135.70 (s), 132.95 (s), 129.19 (s). HRMS (ESI) for $[\text{M-H}]^-$ Calculated 153.9946 Found: 153.9963

Isoindoline-1,3-dione (8) ⁴

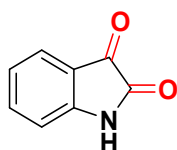


White solid, eluent (18% ethyl acetate/hexane), yield (84%,102 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 1H), 7.82 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.73 (s), 134.79 (s), 133.04 (s), 123.39 (s).

3. General procedure for the synthesis of Isatins (4a-4f) (Scheme B)

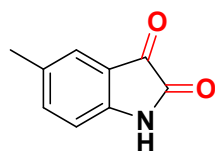
A reaction mixture containing simple or substituted indoline (1 equiv., 0.83 mmoles) and molecular iodine (1.5equiv. 1.24 mmoles) in DMSO (3 mL) were heated in the round bottom flask at 120 °C. After 5 minutes, Ammonium persulfate (2 equiv., 1.66 mmoles) was added slowly and the reaction mixture was stirred for 10 minutes. After the reaction was complete, an ice-cooled aqueous solution of sodium thiosulfate was added to the reaction mixture and was extracted with EtOAc (20mL × 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure and purified by using silica gel column chromatography (mesh size 100-200) and ethylacetate and hexane as eluents to obtained the desired product.

indoline-2,3-dione (4a)⁵



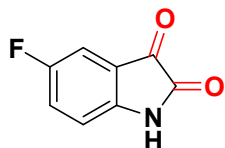
Red solid, eluent (20% ethyl acetate/hexane), yield (74%, 91 mg); ¹H NMR (400 MHz, DMSO-d₆) δ 11.05 (s, 1H), 7.59 (m, 1H), 7.53 – 7.47 (m, 1H), 7.07 (td, *J* = 7.5, 0.8 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H). ¹³C NMR (101 MHz, DMSO-d₆) δ 184.86 (s), 159.84 (s), 151.18 (s), 138.83 (s), 125.16 (s), 123.22 (s), 118.29 (s), 112.66 (s).

5-methylindoline-2,3-dione (4b)⁵



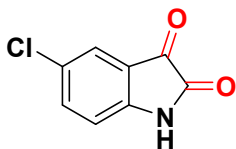
Red solid eluent (17% ethyl acetate/hexane), yield (76%, 102 mg); ¹H NMR (400 MHz, DMSO-d₆) δ 10.96 (s, 1H), 7.42 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.40 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.34 – 7.32 (m, 1H), 2.26 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 185.13 – 184.97 (m), 160.00 – 159.84 (m), 149.01 – 148.98 (m), 139.24 (s), 132.46 – 132.45 (m), 125.28 (s), 118.27 – 118.24 (m), 112.47 (s), 20.56 (s).

5-fluoroindoline-2,3-dione (4c)⁵



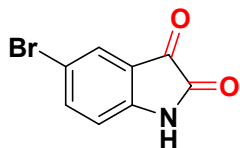
Red solid, eluent (21% ethyl acetate/hexane), yield (81%, 112 mg); $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.04 (s, 1H), 7.58 – 7.34 (m, 2H), 6.91 (dd, $J = 8.6, 3.9$ Hz, 1H). $^{13}\text{CNMR}$ (101 MHz, DMSO-d_6) δ 184.36 (d, $J = 2.1$ Hz), 159.85 (d, $J = 21.9$ Hz), 157.35 (s), 147.42 (s), 124.96 (d, $J = 24.2$ Hz), 118.96 (d, $J = 7.1$ Hz), 113.92 (d, $J = 7.2$ Hz), 111.85 (d, $J = 24.0$ Hz). $^{19}\text{F NMR}$ (377 MHz, DMSO-d_6) δ -120.60 – -120.70 (m).

5-chloroindoline-2,3-dione (4d)⁵



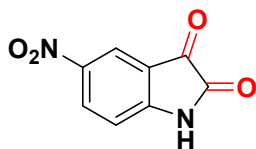
Orange solid, eluent (20% ethyl acetate/hexane), yield (79%, 120 mg); $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.15 (s, 1H), 7.65 – 7.58 (m, 1H), 7.54 (s, 1H), 6.92 (d, $J = 8.4$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 183.81 (s), 159.63 (s), 149.66 (s), 137.70 (s), 127.26 (s), 124.59 (s), 119.60 (s), 114.29 (s).

5-bromoindoline-2,3-dione (4e)⁵



Brown solid, eluent (17% ethyl acetate/hexane), yield 71%, 189 mg); $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.15 (s, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.64 (s, 1H), 6.87 (d, $J = 8.1$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 183.65 (s), 159.45 (s), 150.00 (s), 140.48 (s), 127.35 (s), 120.02 (s), 114.75 (s), 114.72 (s).

5-nitroindoline-2,3-dione (4f)^[5]

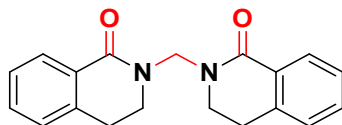


Yellow solid, eluent (18% ethyl acetate/hexane), yield (68%,110 mg); $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.67 (s, 1H), 8.48 – 8.41 (m, 1H), 8.22 (s, 1H), 7.09 (d, $J = 8.7$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 182.83 (s), 160.39 (s), 155.65 (s), 143.04 (s), 133.53 (s), 120.04 (s), 118.64 (s), 112.95 (s).

4. Procedure for the synthesis of 6

A reaction mixture containing simple or substituted 1,2,3,4-tetrahydroisoquinoline **5** (1 equiv., 0.83 mmol) and molecular iodine (1.5 equiv., 1.24 mmol) in DMSO (3 mL) were heated in the round bottom flask at 120 °C. After 5 minutes, Ammonium persulphate (2 eq, 1.66 mmol) was added slowly and the reaction mixture was stirred for 10 minutes. After the reaction was complete, an ice-cooled aqueous solution of sodium thiosulphate was added to the reaction mixture and was extracted with EtOAc (20 mL \times 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100) and ethyl acetate and hexane as eluents to obtain the desired product.

2,2'-methylenebis(3,4-dihydroisoquinolin-1(2H)-one) (**6**);



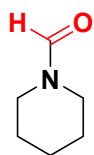
Red viscous liquid, eluent (20% ethyl acetate/hexane), yield (68%,86 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (dd, $J = 7.7, 1.1$ Hz, 2H), 7.44 (m, 2H), 7.35 (m, 2H), 7.19 (d, $J = 7.4$ Hz, 2H), 5.42 (s, 2H), 3.79 (t, $J = 6.6$ Hz, 4H), 2.98 (t, $J = 6.6$ Hz, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.72 (s), 138.66 (s), 132.17 (s), 128.90 (s), 128.39 (s), 127.14 (s), 127.12 (s), 57.10 (s), 45.67 (s), 28.19 (s). HRMS (ESI) for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$: 254.1186 Found: 254.1181

5. Procedure for the synthesis of piperidine-1-carbaldehyde (**9**)

To a solution of the *N*-formyl benzamide (**2a**) (1.00 equiv.) in H_2O (0.1 M) was added *p*-toluenesulfonic acid monohydrate (0.20 equiv.) and piperidine (2.00-5.00 equiv.). Then the resulting reaction mixture was stirred at 35 °C for 1-2 hours under a nitrogen atmosphere. After the reaction was completed, the mixture was extracted with ethyl acetate three times and the

combined organic phase was washed with brine, dried over MgSO₄, filtered, and concentrated. The crude products were purified by flash column chromatography to afford the desired product.

Piperidine-1-carbaldehyde (9)⁶

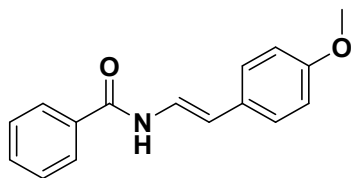


Clear liquid, eluent (5% ethyl acetate/hexane), yield (56%); ¹H NMR (400 MHz, DMSO-d₆) δ 7.93 (s, 1H), 3.29 (m, 4H), 1.59 (m 2H), 1.49 – 1.42 (m, 2H), 1.39 (m, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 165.72 (s), 138.66 (s), 132.17 (s), 128.90 (s), 128.39 (s), 127.14 (s), 127.12 (s), 57.10 (s), 45.67 (s), 28.19 (s).

6. Procedure for the synthesis of 10.

The compound was synthesized by subjecting 2a to the reaction procedure already reported in the literature⁷.

(E)-N-(4-methoxystyryl)benzamide (10)⁷



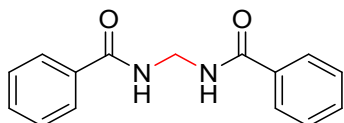
Brown solid, eluent (20% ethyl acetate/hexane), yield (47%); ¹H NMR (400 MHz, DMSO-d₆) δ 9.96 (d, *J* = 9.0 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 6.98 (t, *J* = 5.8 Hz, 2H), 6.85 (t, *J* = 9.4 Hz, 1H), 5.82 (d, *J* = 9.7 Hz, 1H), 3.78 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 165.72 (s), 158.43 (s), 134.01 (s), 132.23 (s), 130.19 (s), 128.83 (s), 128.73 (s), 128.30 (s), 121.74 (s), 114.47 (s), 113.25 (s), 55.56 (s). HRMS (ESI) for C₁₆H₁₅NO₂ [M + H]⁺ : Calculated 329.1260 Found: 329.12

Procedure for Control experiments

Control Experiment 1. Benzamide (1a) (1 equiv., 0.83 mmoles) in DMSO (3 ml) was heated in a round bottom flask at 120 °C. After 5 minutes Ammonium persulfate (2 equiv., 1.66 mmoles)

were added to the reaction mixture slowly. The progress of the reaction was monitored by TLC. It was observed that most of the reactant gets consumed within 30 minutes.. After the reaction was complete, ice crystals were added to the reaction mixture and were extracted with EtOAc (20mL × 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethylacetate and hexane as eluents to obtain the desired product.

***N,N'*-methylenedibenzamide (11) ⁸**

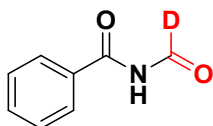


¹H NMR (400 MHz, DMSO-*d*₆) δ 9.05 (t, *J* = 5.5 Hz, 1H), 7.91 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.58 – 7.50 (m, 1H), 7.46 (dd, *J* = 10.2, 4.6 Hz, 2H), 4.87 (t, *J* = 5.6 Hz, 1H).

Control Experiment 2: Benzamide (**1a**) (1 equiv., 0.83 mmoles) and molecular iodine (1.5 equiv., 1.24 mmoles) in DMSO (3 ml) were heated in a round bottom flask at 120 °C. All of the reactant remained unconsumed during the reaction and no product was detected .The reaction was monitored for 2 hours.

Control Experiment 3: A reaction mixture containing benzamide (**1a**) (1 equiv., 0.83 mmoles) and molecular iodine(1.5 equiv., 1.24 mmoles) in DMSO-*d*₆ (3 mL) were heated in the round bottom flask at 120 °C. After 5 minutes, ammonium persulphate (2 equiv., 1.66 mmoles) was added slowly and the reaction mixture was stirred for 10 minutes.The progress of the reaction was monitored by TLC. After the reaction was complete, an ice-cooled aqueous solution of sodium thiosulphate was added to the reaction mixture and was extracted with EtOAc (20mL × 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethyl acetate and hexane as eluents to obtain the desired product.

***N*-(formyl-*d*)benzamide (2a')**



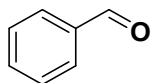
White solid, melting point 120- 124 °C , eluent (11% ethyl acetate/hexane), yield (76%,129.4 mg); ¹H NMR (400 MHz, CDCl₃) δ 10.22 (s, 1H), 8.02 (m, 2H), 7.70 – 7.61 (m, 1H), 7.59 – 7.51 (m, 2H).¹³C NMR (101 MHz, CDCl₃) δ 166.75 (s), 166.67 (s), 134.00 (s), 131.06 (s), 129.12 (s), 128.14 (s), 128.09 (s). HRMS (ESI) for C₈H₆DNO₂: [M - H]⁻ : Calculated 149.0356 Found: 149.0369

Control Experiment 4; To a heating mixture of benzamide (**2a**) (1 equiv., 0.83 mmoles) and molecular iodine (1.5 equiv., 1.24 mmoles) in 3 ml of DMSO taken in round bottom flask at 120 °C was added Ammonium persulfate (2 equiv., 1.66 mmoles) followed by TEMPO (2 equiv.,1.66 mmoles).The reaction was carried out for 3 hours. A continuous observation of reaction was carried out by using the mass spectrometry of reaction mixture aliquots at regular intervals of time. No intermediate was identified. The desired compound **2a** was formed in trace quantity probably due to the fast kinetics.

Control Experiment 5: A reaction mixture containing *N*-methylbenzamide (**12**) (1 equiv., 0.83 mmoles) and molecular iodine(1.5 equiv., 1.24 mmoles) in DMSO (3mL) were heated in the round bottom flask at 120 °C. After 5 minutes, ammonium persulfate (2 equiv., 1.66 mmoles) was added slowly and the reaction mixture was stirred for 10 minutes. No *N*-formylated product was formed during the reaction.

Control Experiment 6: A mixture of benzylamine (**13**) (1 equiv., 0.83 mmoles), and molecular iodine (1.5 equiv., 1.24 mmoles) in DMSO (3mL) were heated in the round bottom flask at 120 °C. After 5 minutes, ammonium persulfate (2 eq, 1.66 mmoles) was added slowly and the reaction mixture was stirred for 10 minutes. The progress of the reaction was monitored by TLC. After the reaction was complete, an ice-cooled aqueous solution of sodium thiosulfate was added to the reaction mixture and was extracted with EtOAc (20mL × 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethyl acetate and hexane as eluents to obtain the desired product.

Benzaldehyde (**14**)¹⁰

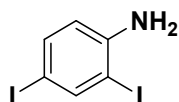


$^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 7.92 – 7.88 (m, 2H), 7.71 – 7.65 (m, 1H), 7.56 (dd, $J = 10.6, 4.6$ Hz,

Some Additional Control Experiments.

Control Experiment A: A mixture of Aniline (**15**) (1 equiv., 0.83 mmoles), and molecular iodine (1.5 equiv., 1.24 mmoles) in DMSO (3 mL) were heated in the round bottom flask at 120 °C. After 5 minutes, ammonium persulfate (2 eq, 1.66 mmoles) was added slowly and the reaction mixture was stirred for 40 minutes. The progress of the reaction was monitored by TLC. After the reaction was complete, an ice-cooled aqueous solution of sodium thiosulfate was added to the reaction mixture and was extracted with EtOAc (20mL \times 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethyl acetate and hexane as eluents to obtain the desired product.

2,4-diiodoaniline (**16**)⁹

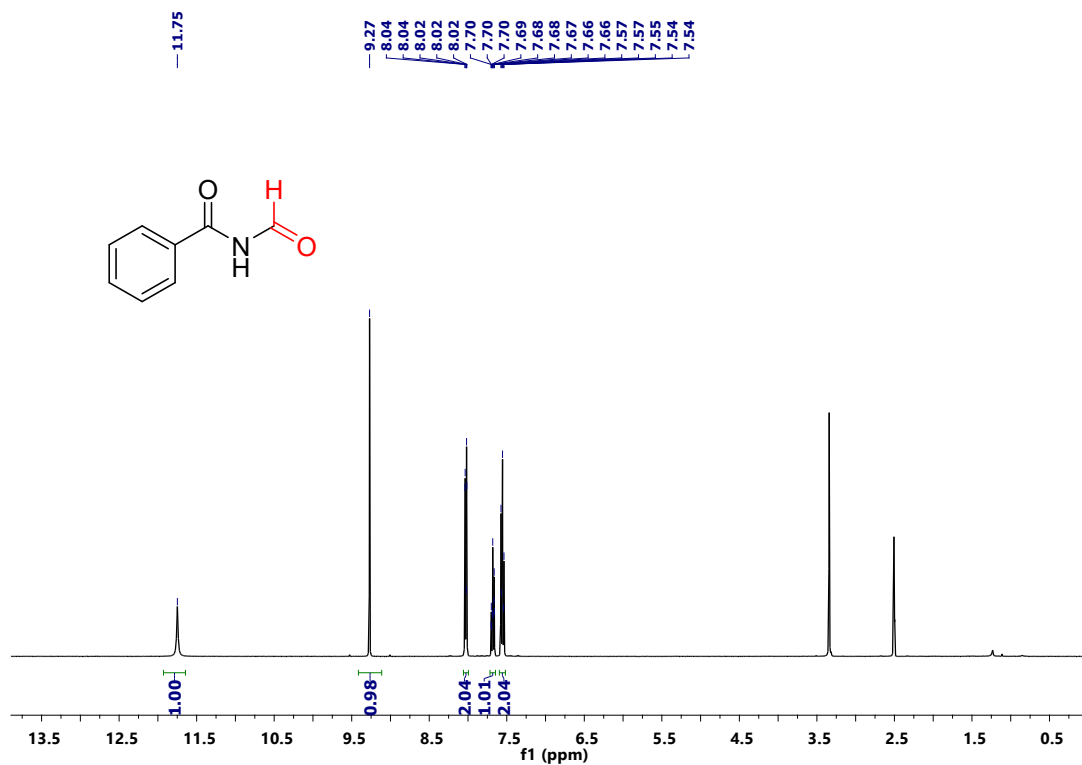


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (d, $J = 2.0$ Hz, 1H), 7.37 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.51 (d, $J = 8.4$ Hz, 1H), 4.13 (s, 2H).

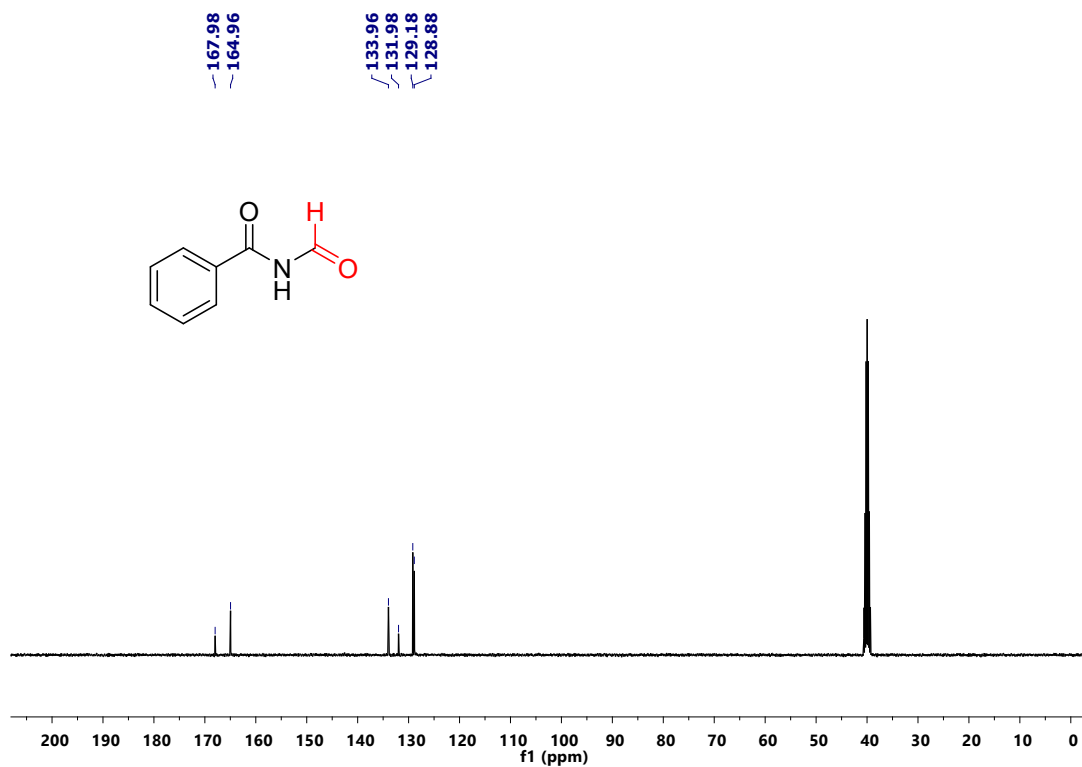
Control Experiment B: A reaction mixture containing *N*-methylaniline (**17**) (1 equiv., 0.83 mmoles) and molecular iodine (1.5 equiv., 1.24 mmoles) in DMSO (3 mL) were heated in the round bottom flask at 120 °C. After 5 minutes, ammonium persulfate (2 equiv., 1.66 mmoles) was added slowly and the reaction mixture was stirred for 10 minutes. No *N*-formylated product was formed during the reaction.

Control Experiment C: A reaction mixture containing piperidine (**18**) (1 equiv., 0.83 mmoles) and molecular iodine (1.5 equiv., 1.24 mmoles) in DMSO (3 mL) were heated in the round bottom flask at 120 °C. After 5 minutes, ammonium persulfate (2 equiv., 1.66 mmoles) was added slowly and the reaction mixture was stirred for 10 minutes. No *N*-formylated product was formed during the reaction.

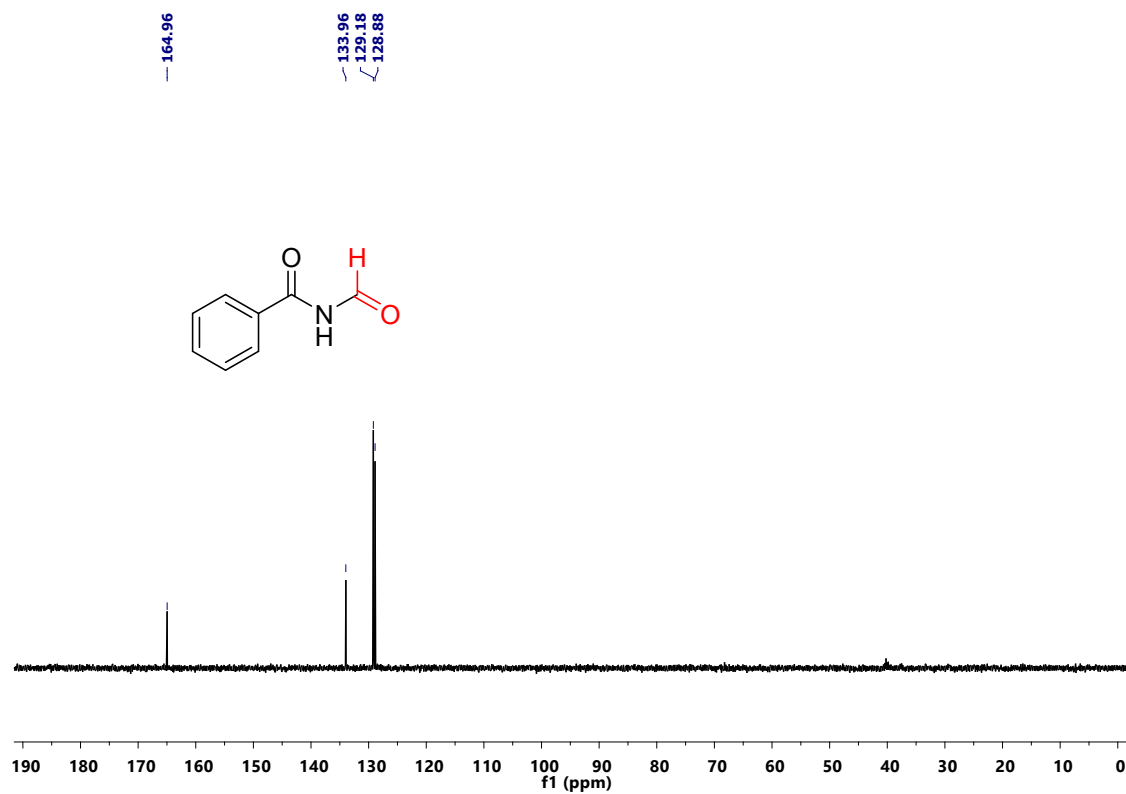
^1H NMR (400 MHz, DMSO-d_6) of **2a**



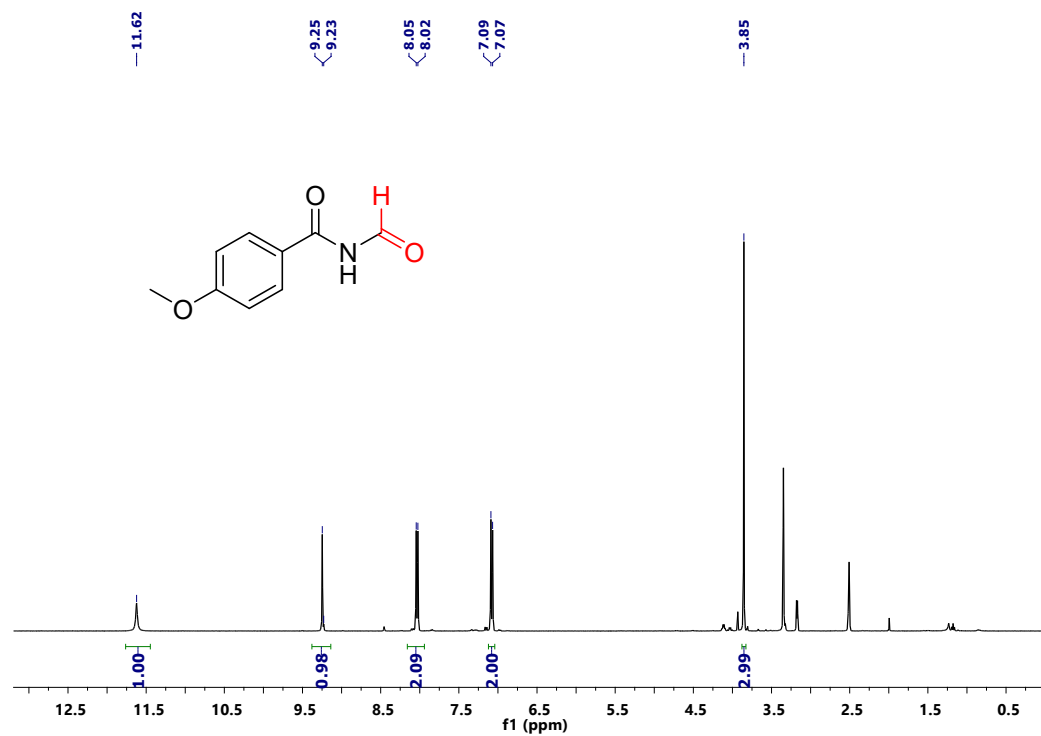
^{13}C NMR (101 MHz, DMSO-d_6) of **2a**



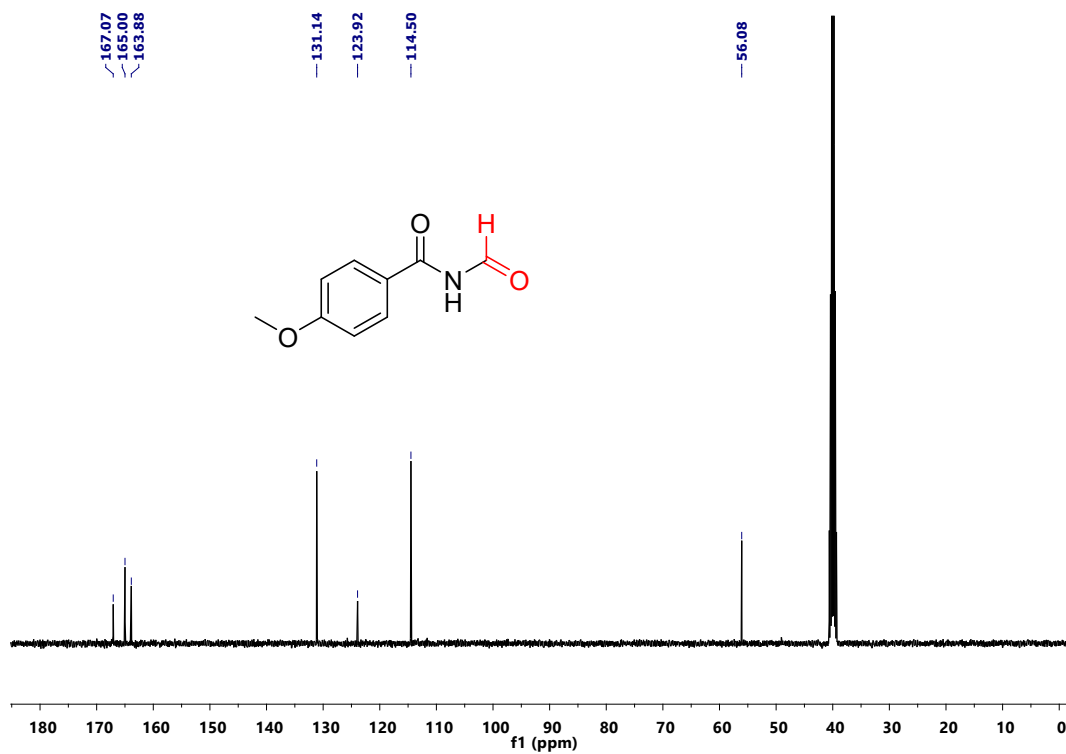
DEPT-135 NMR (101 MHz, DMSO- d₆) of **2a**



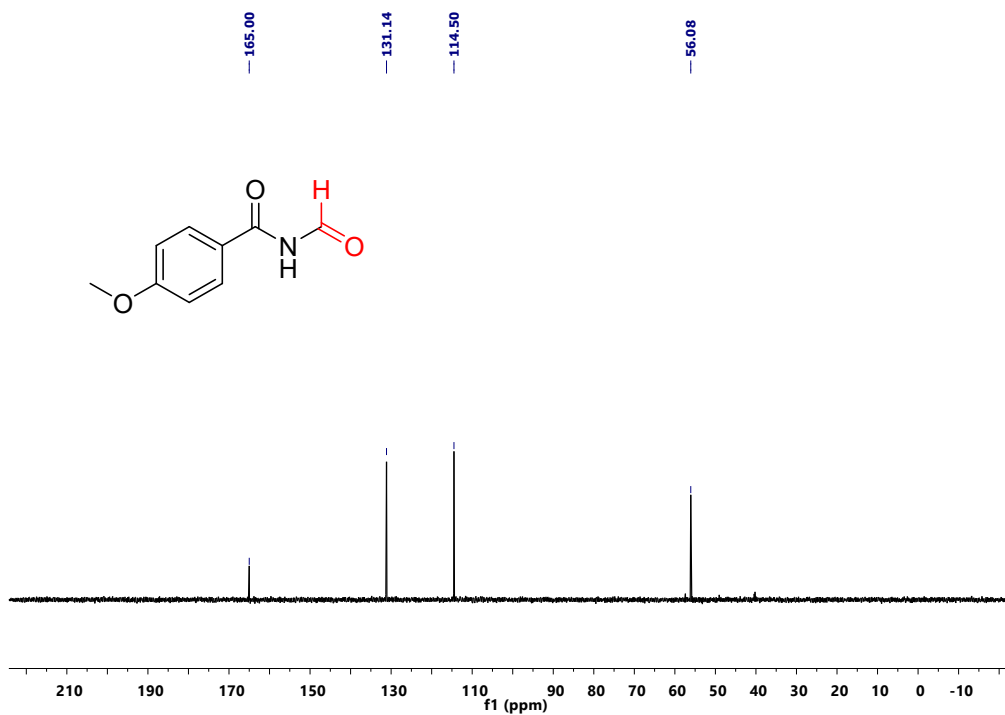
¹H NMR (400 MHz, DMSO- d₆) of **2b**



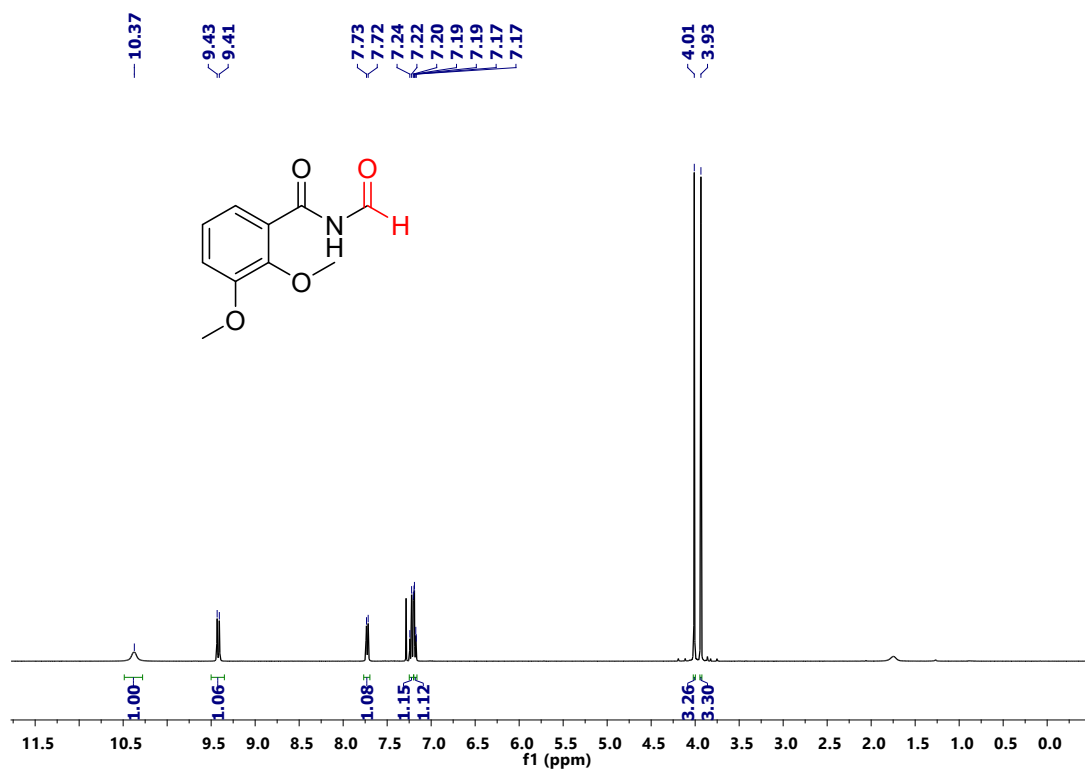
^{13}C NMR (101 MHz, DMSO- d_6) of **2b**



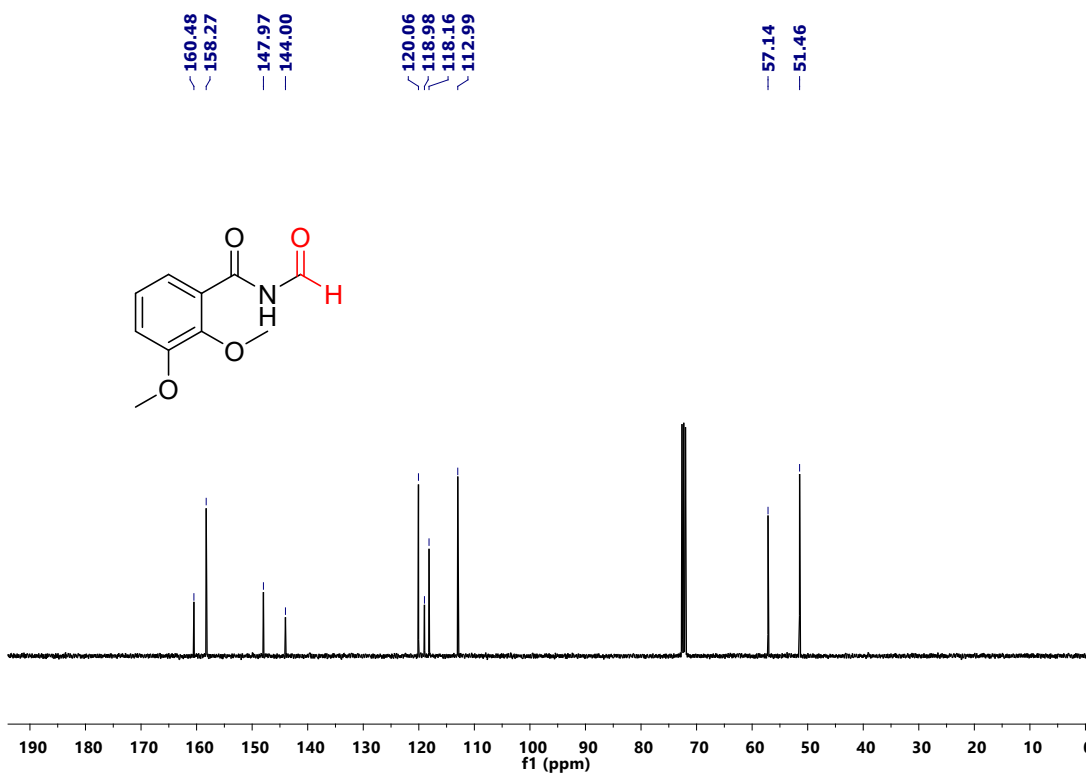
DEPT-135 NMR (101 MHz, DMSO- d_6) of **2b**



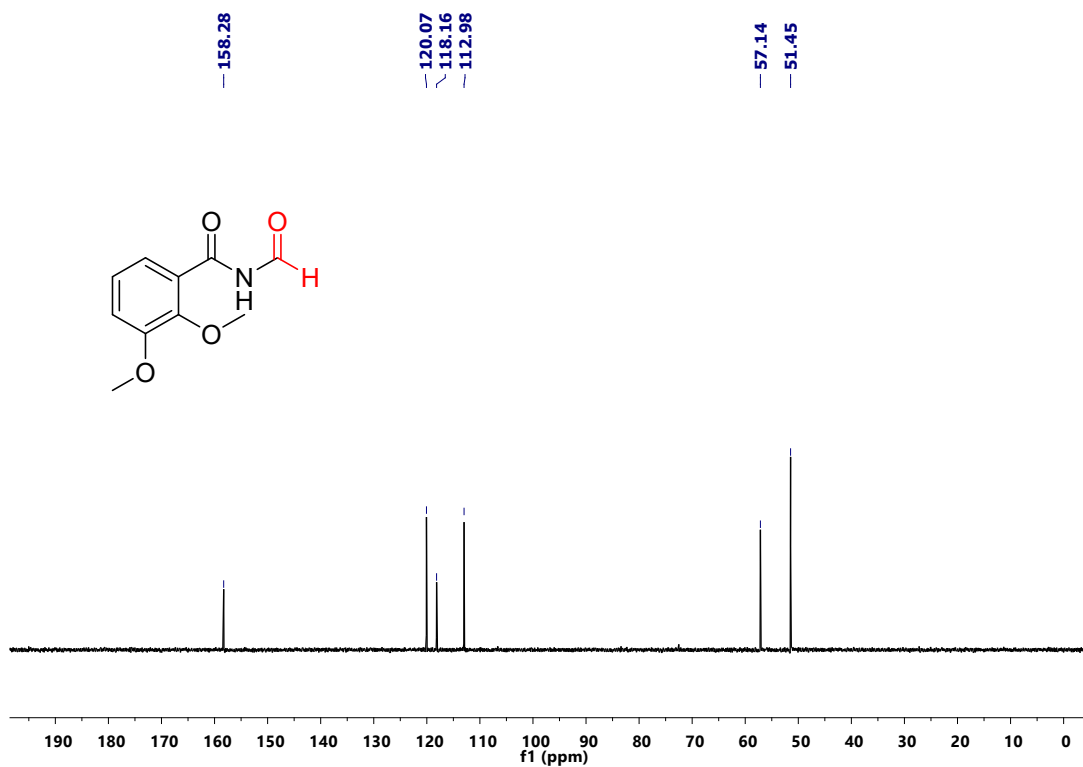
^1H NMR (400 MHz, CDCl_3) of **2c**



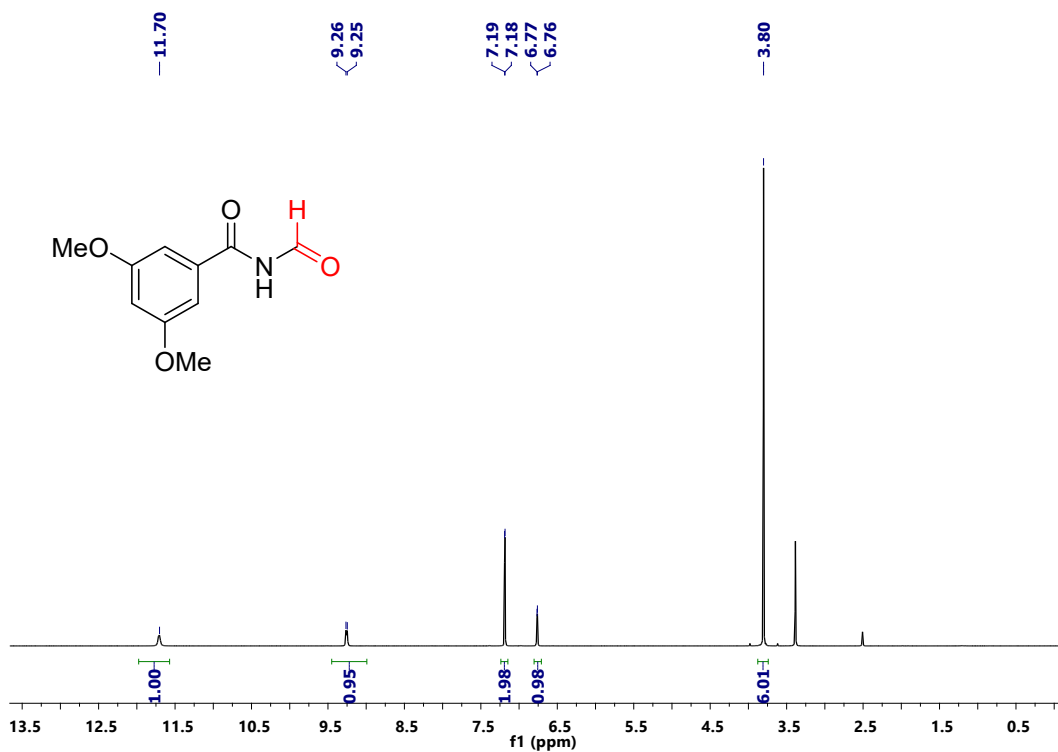
^{13}C NMR (101 MHz, CDCl_3) of **2c**



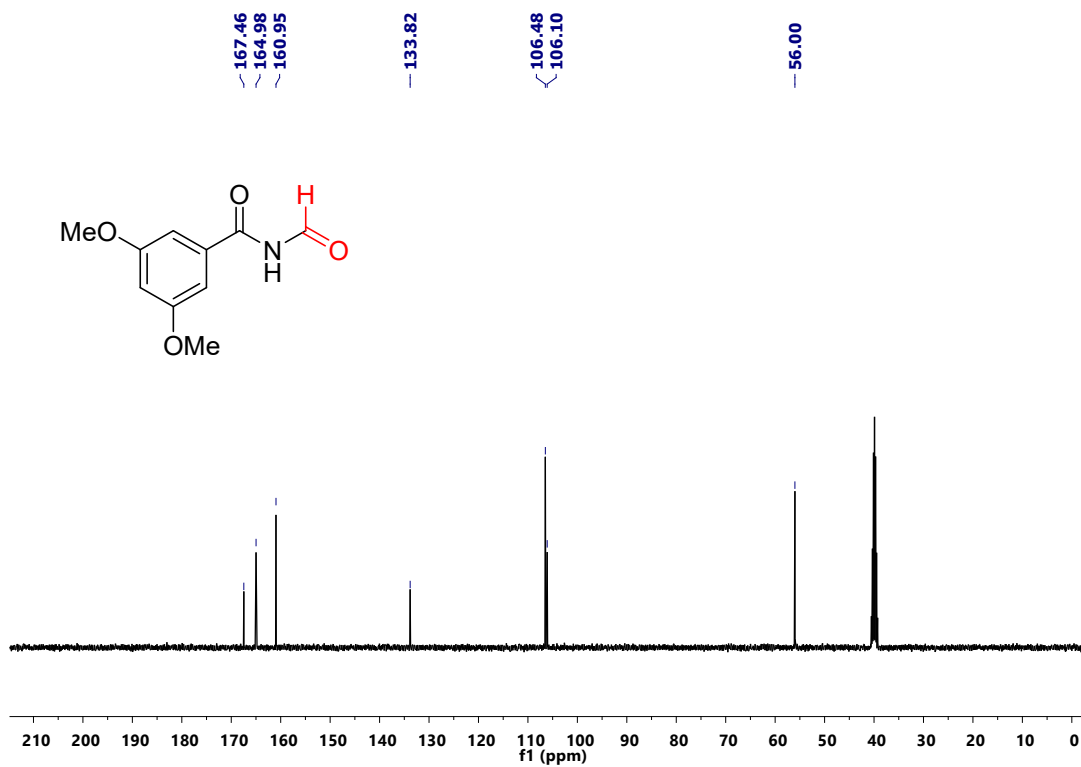
DEPT-135 NMR (101 MHz, CDCl₃) of **2c**



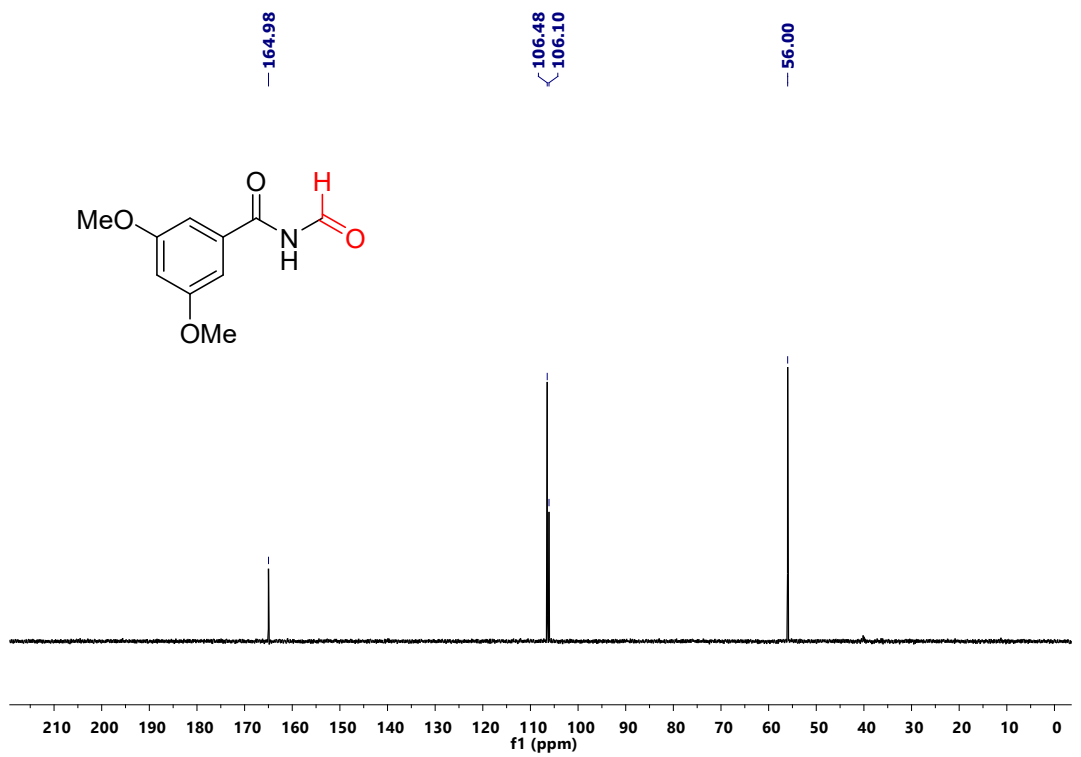
¹H NMR (400 MHz, DMSO- d₆) of **2d**



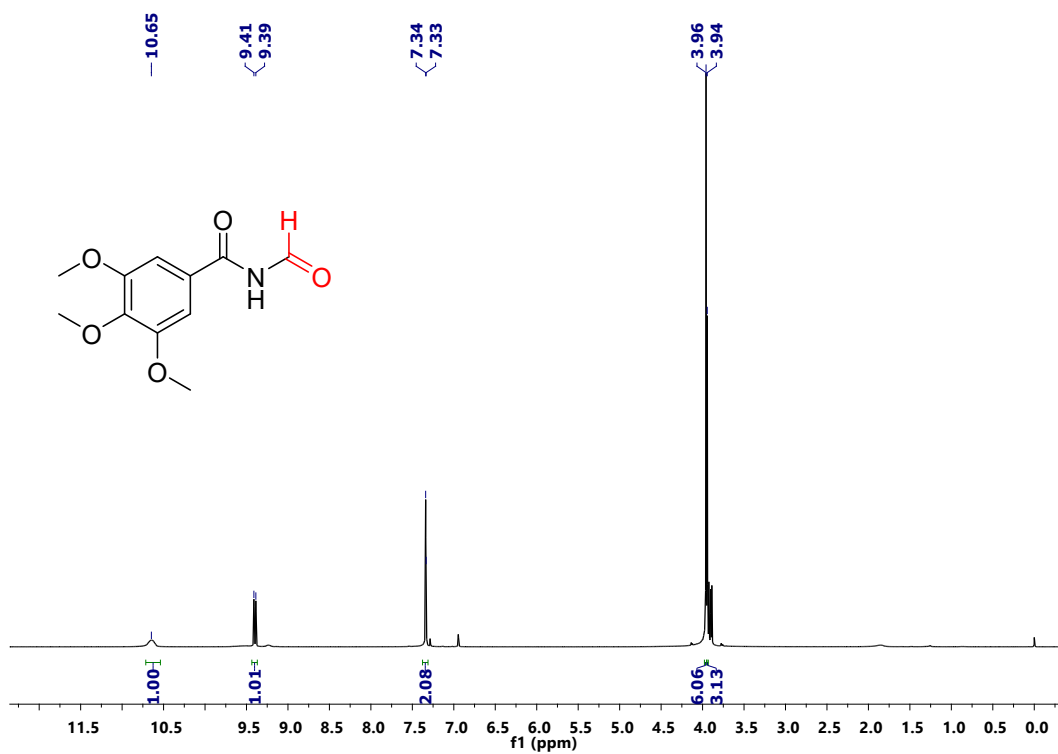
^{13}C NMR (101 MHz, DMSO- d_6) of **2d**



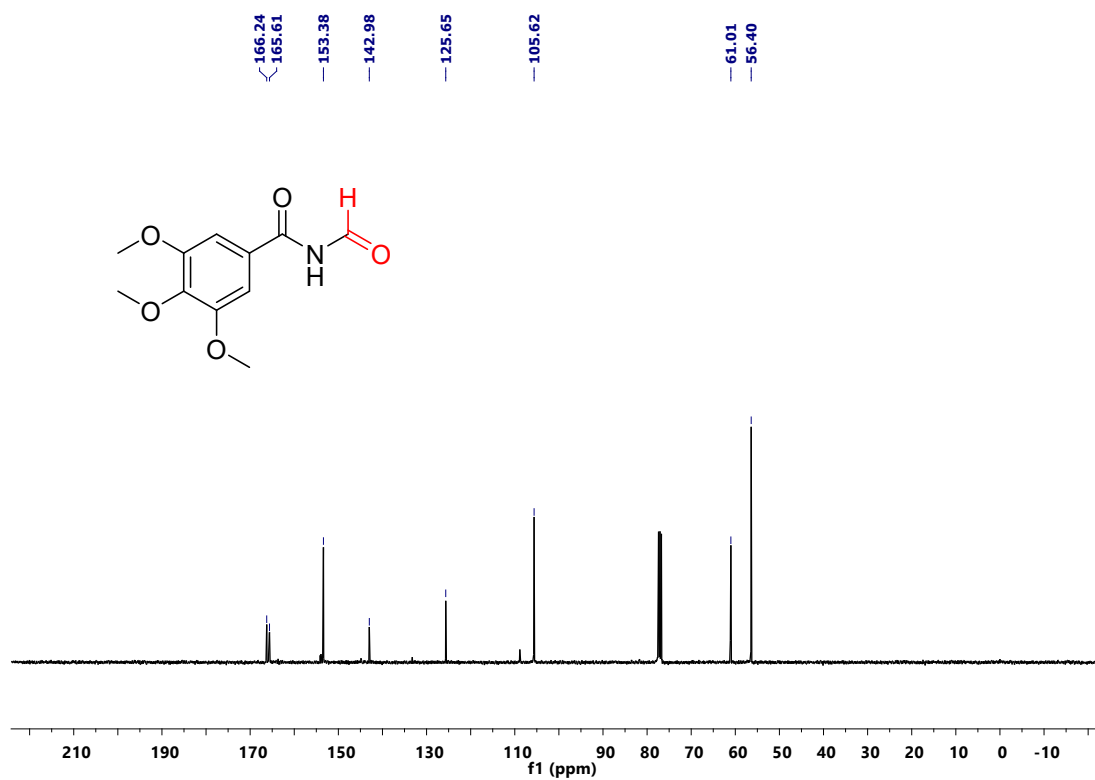
DEPT-135 NMR (101 MHz, DMSO- d_6) of **2d**



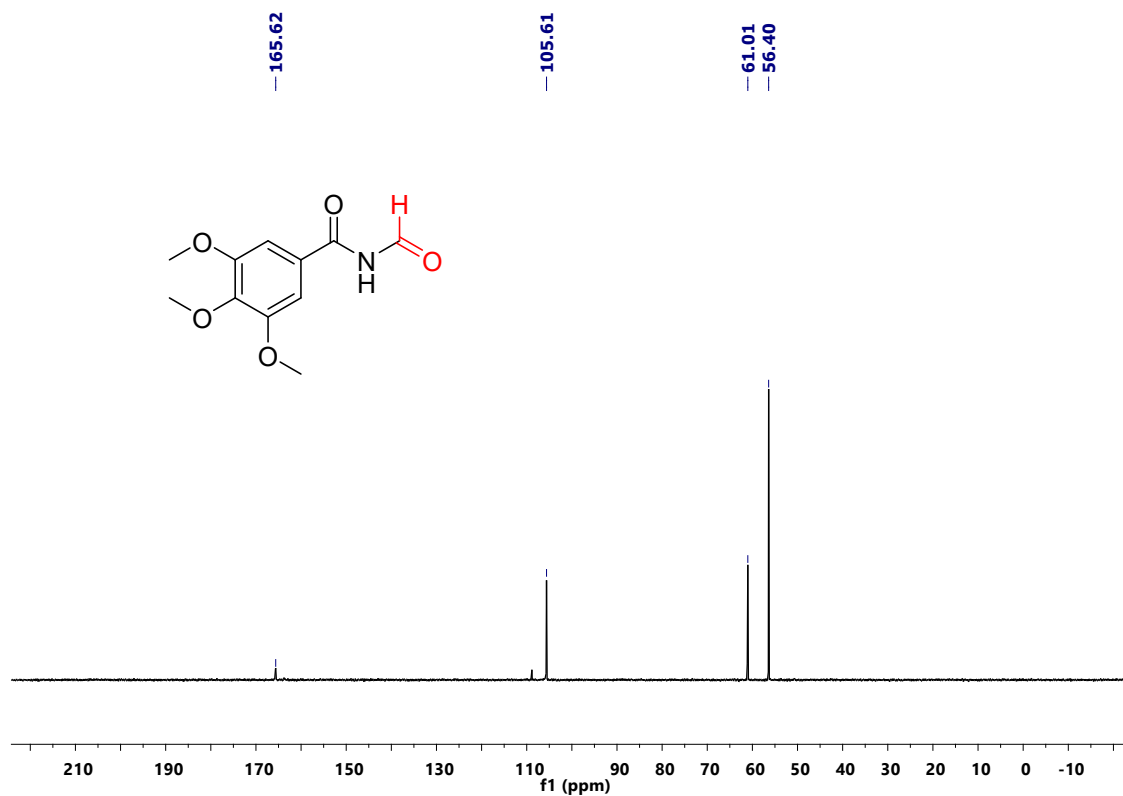
^1H NMR (400 MHz, CDCl_3) of **2e**



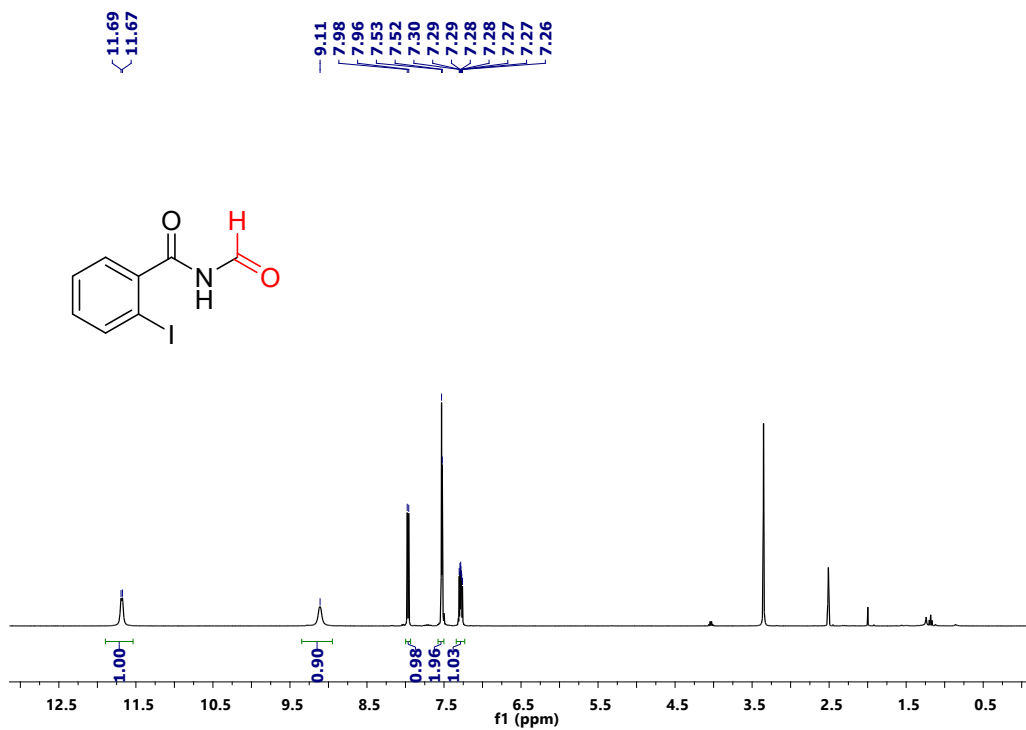
^{13}C NMR (101 MHz, CDCl_3) of **2e**



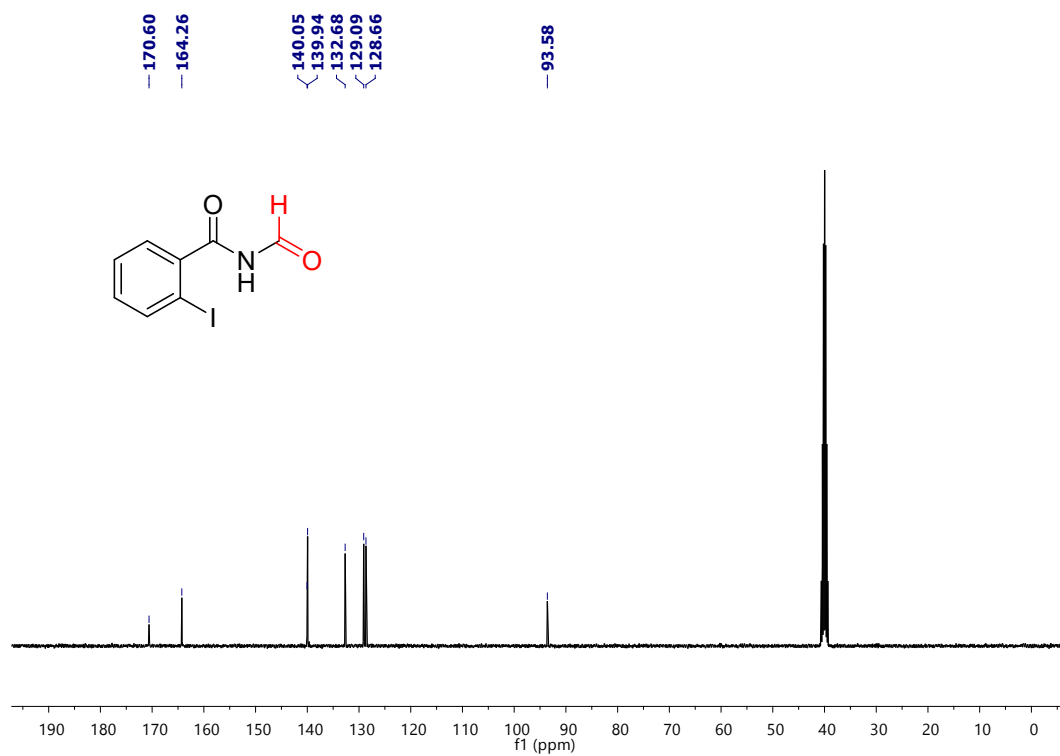
DEPT-135 NMR (101 MHz, DMSO- d_6) of **2e**



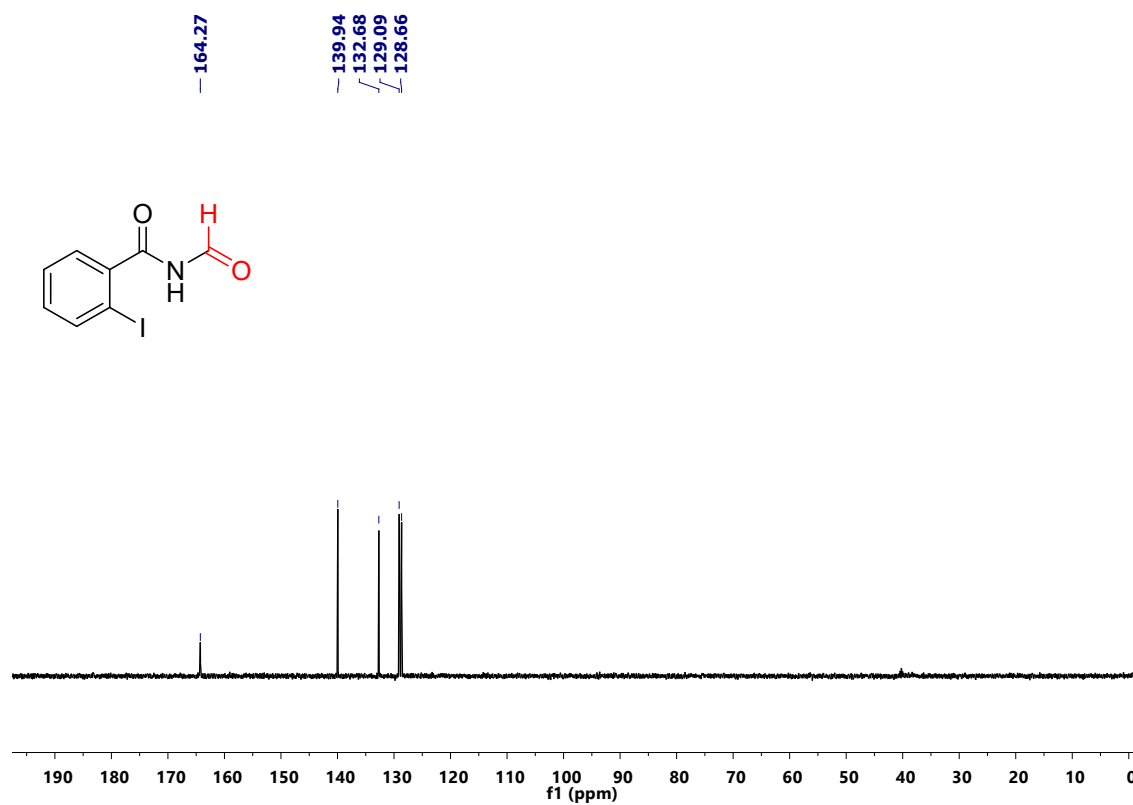
^1H NMR (400 MHz, DMSO- d_6) of **2f**



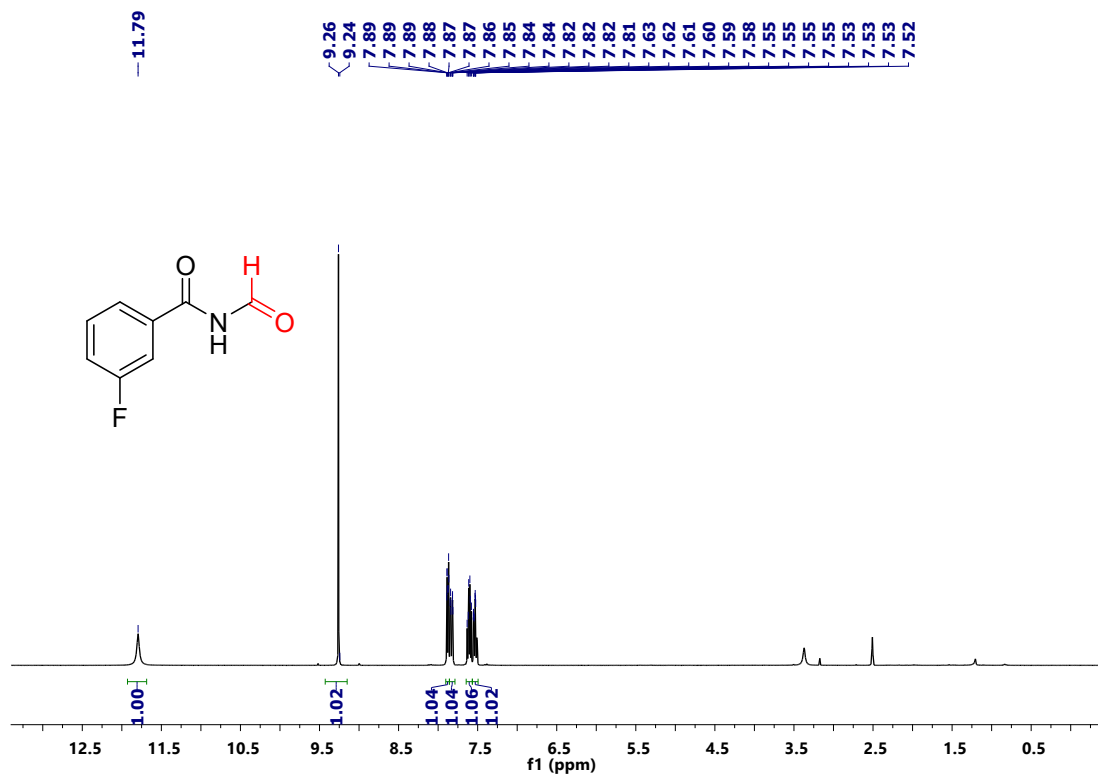
^{13}C NMR (101 MHz, DMSO- d_6) of **2f**



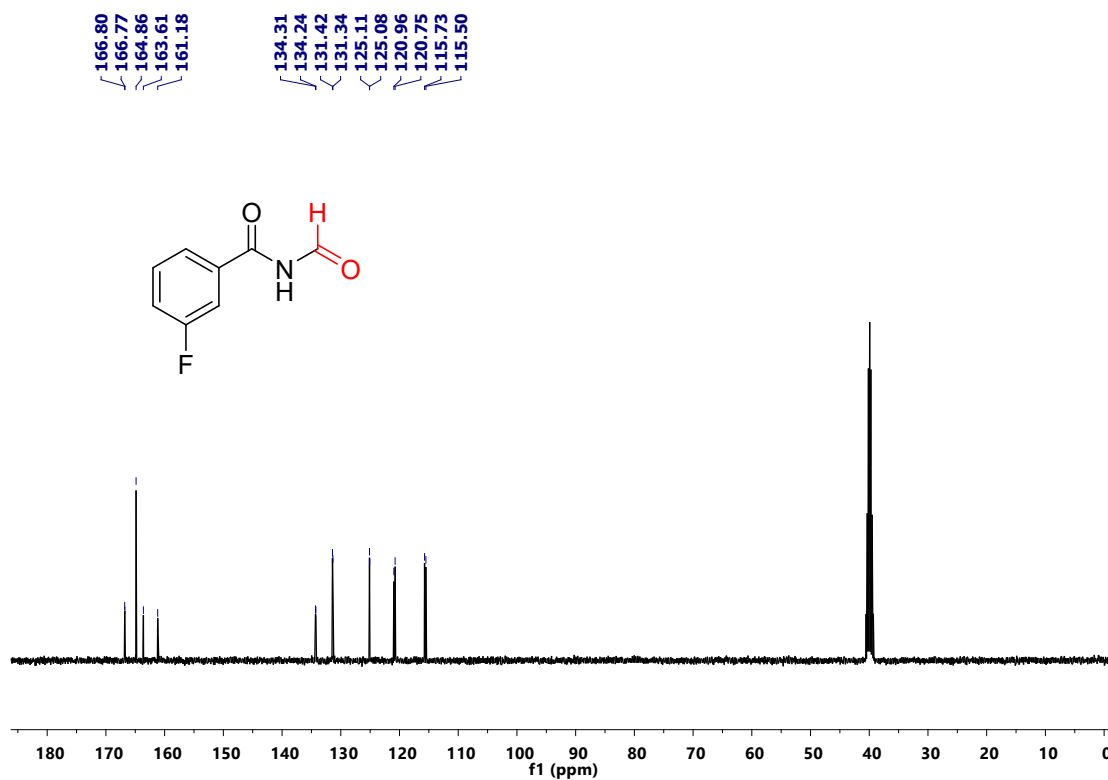
DEPT-135 NMR (101 MHz, DMSO- d_6) of **2f**



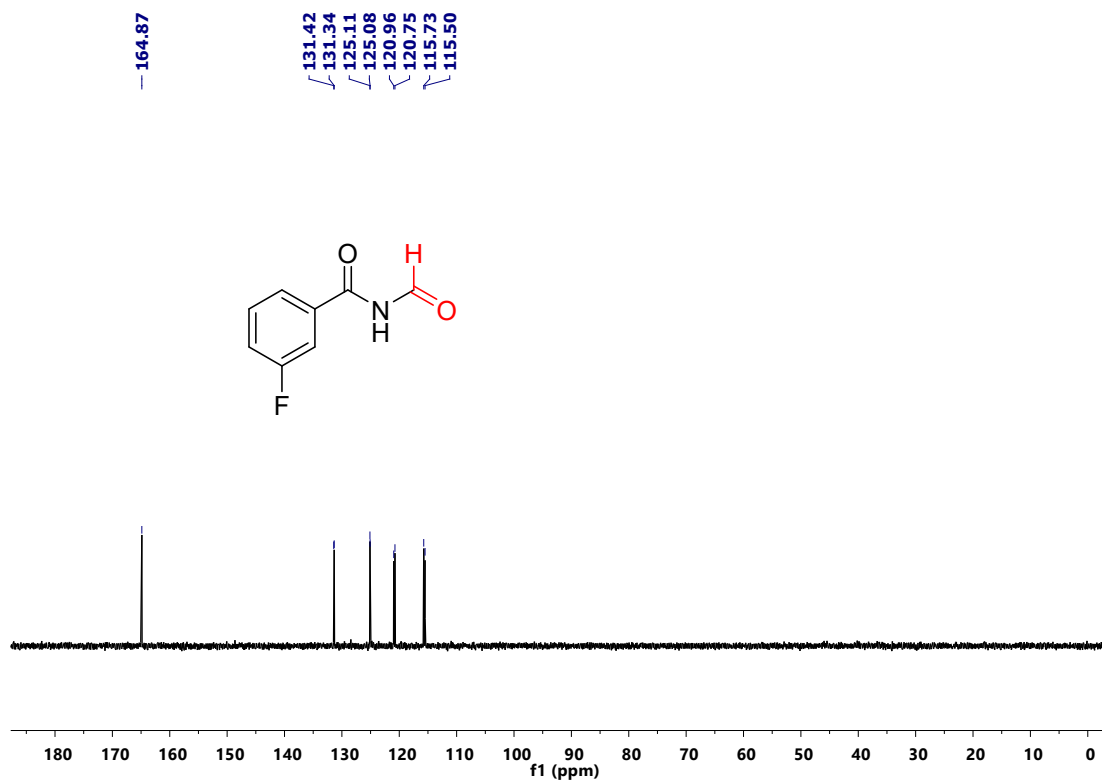
^1H NMR (400 MHz, DMSO- d_6) of **2g**



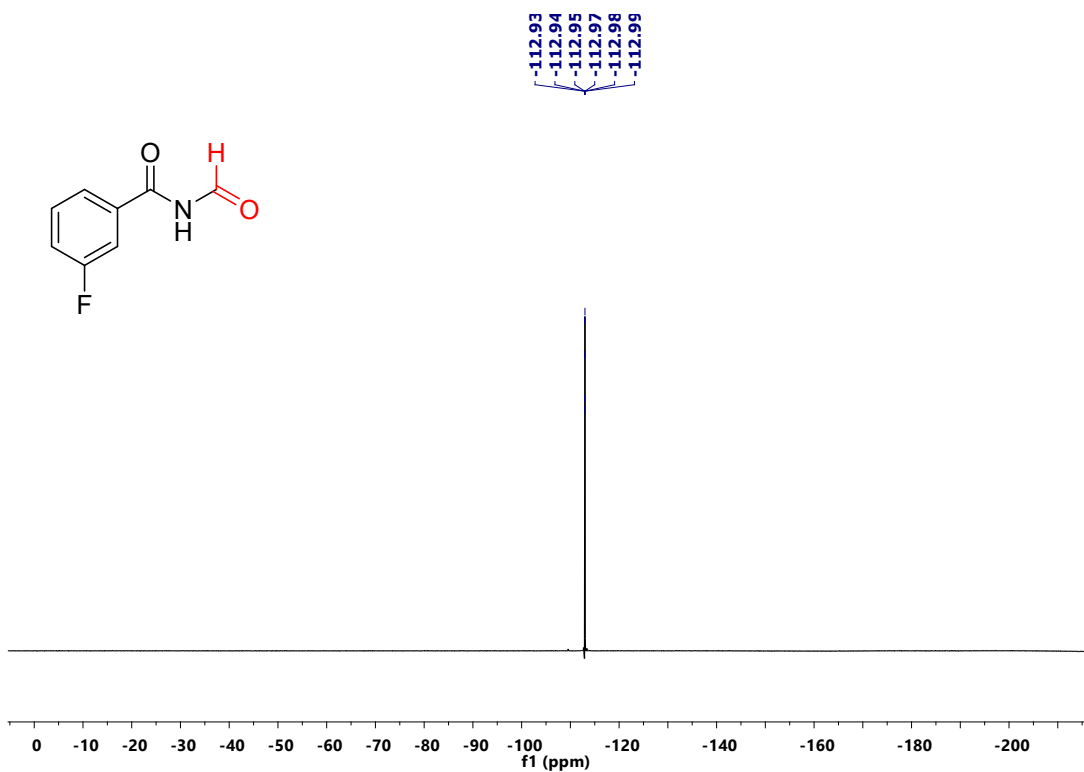
^{13}C NMR (101 MHz, DMSO- d_6) of **2g**



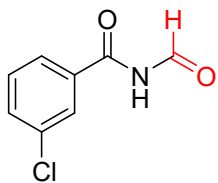
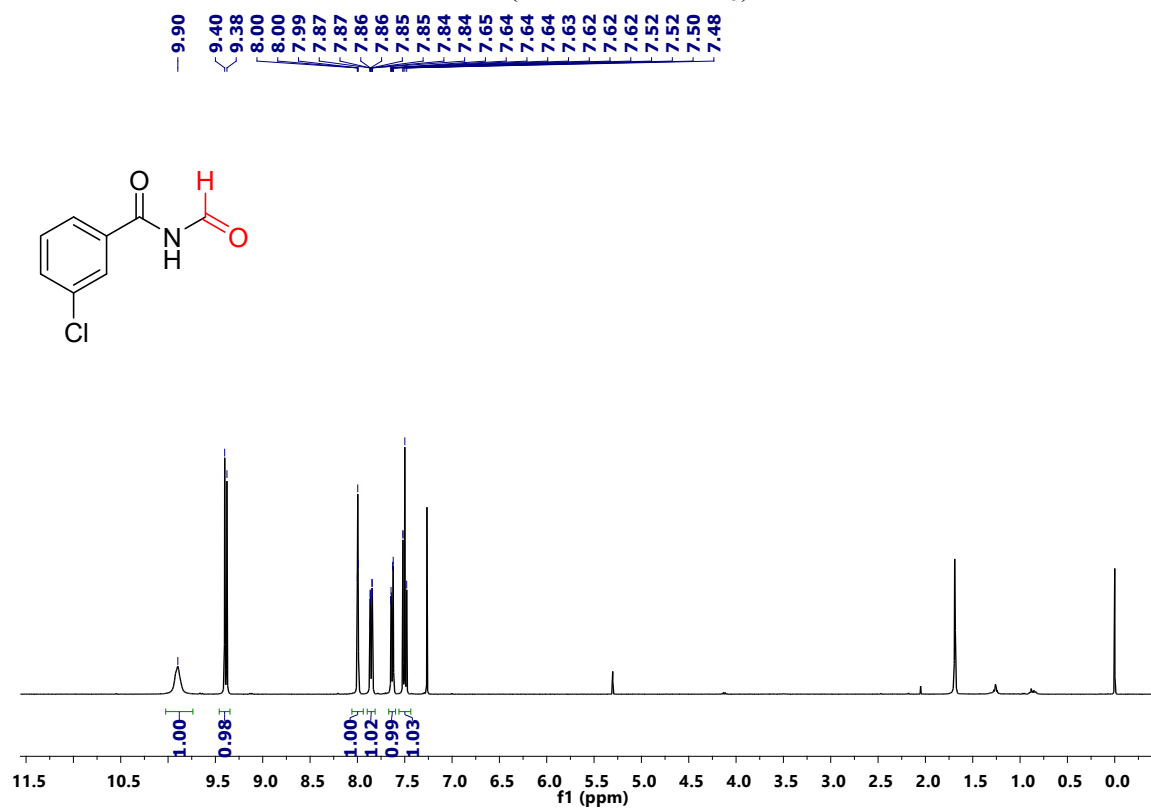
DEPT-135 NMR (101 MHz, DMSO- d₆) of **2g**



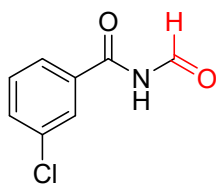
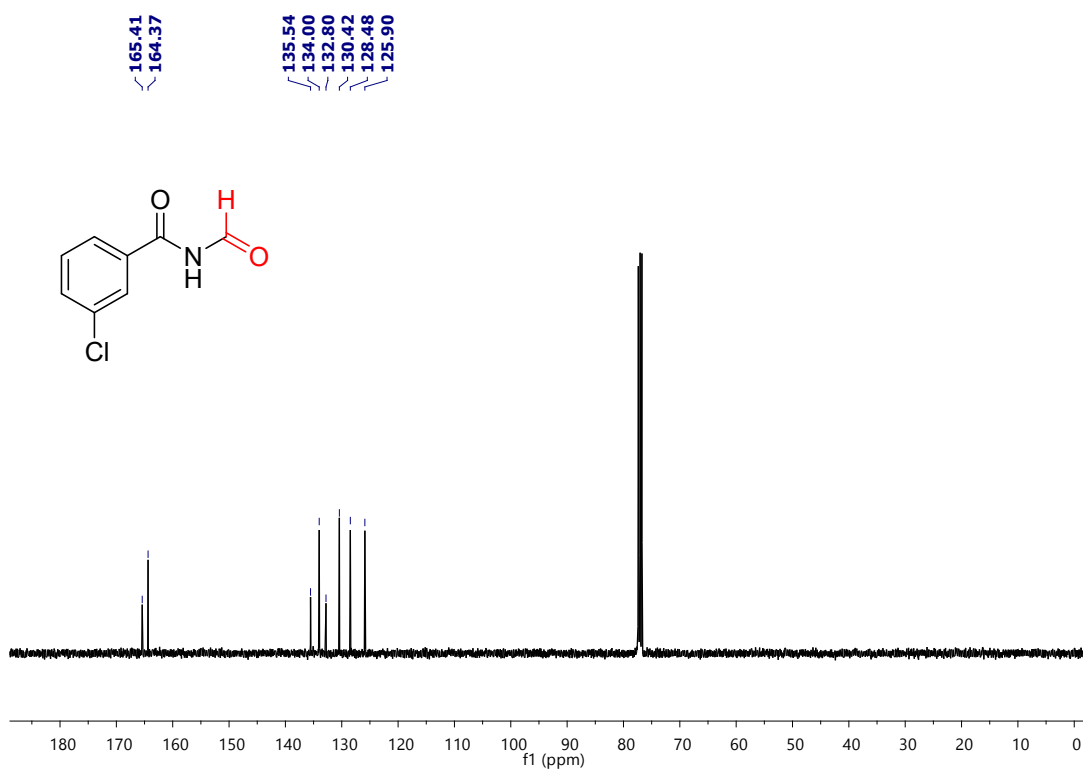
¹⁹F NMR (377 MHz, DMSO-d₆) of **2g**



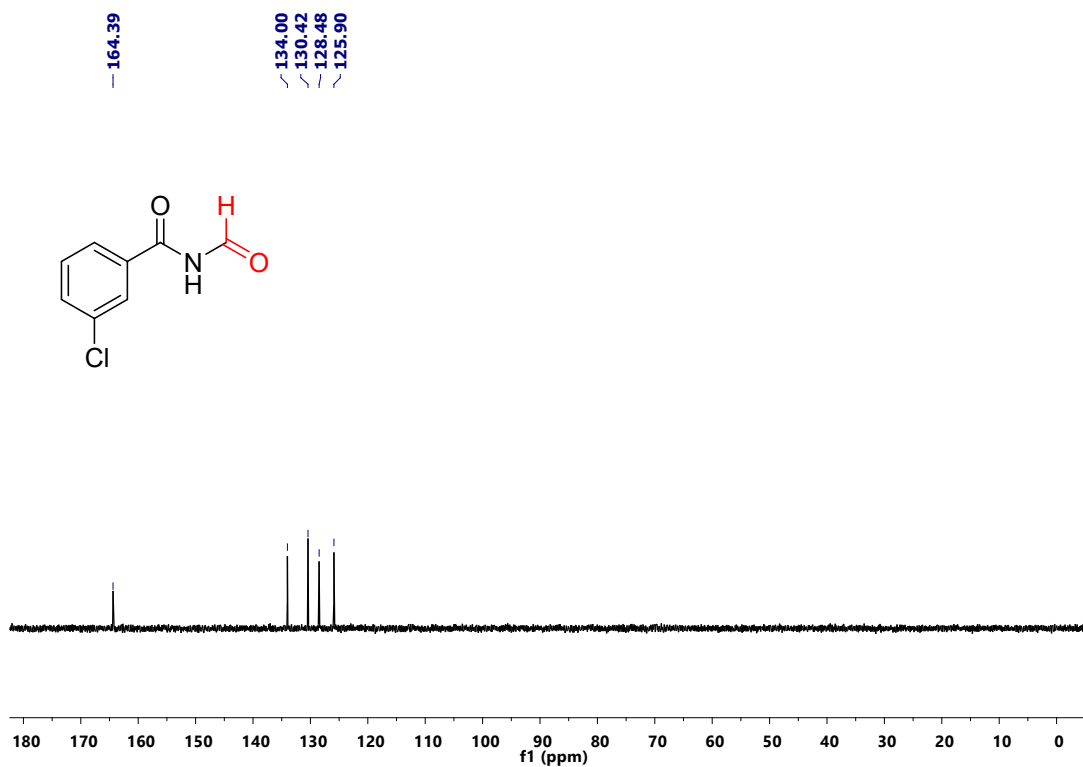
¹H NMR (400 MHz, CDCl₃) of **2h**



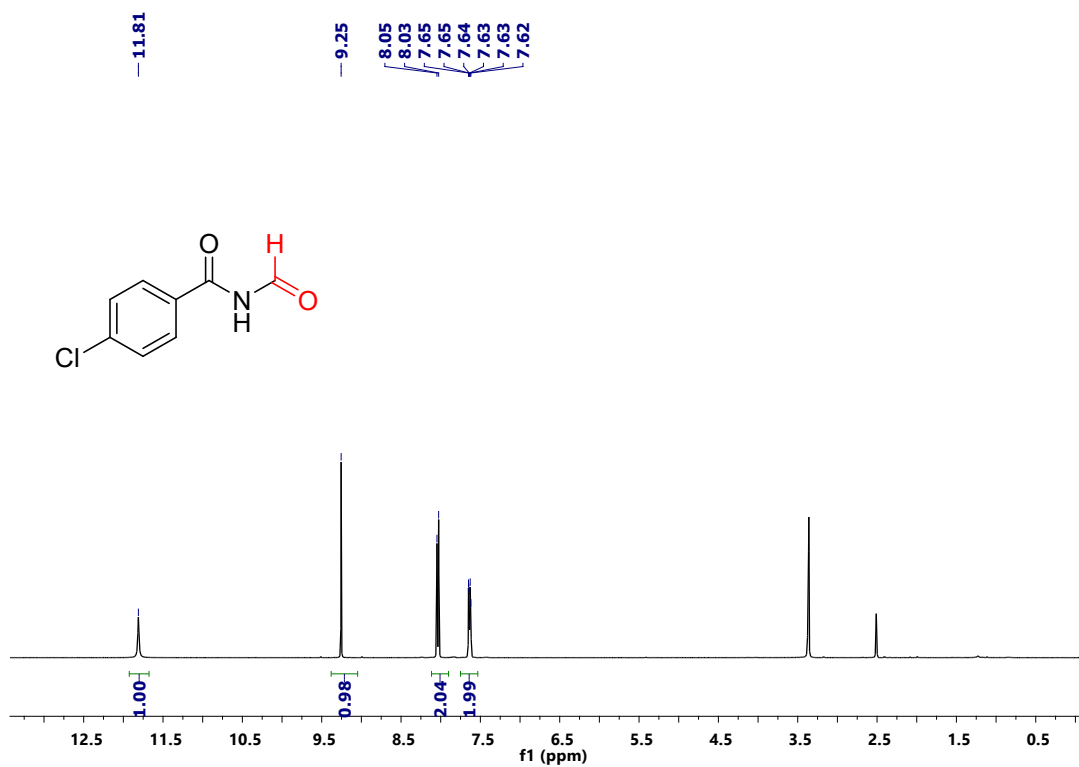
¹³C NMR (101 MHz, CDCl₃) of **2h**



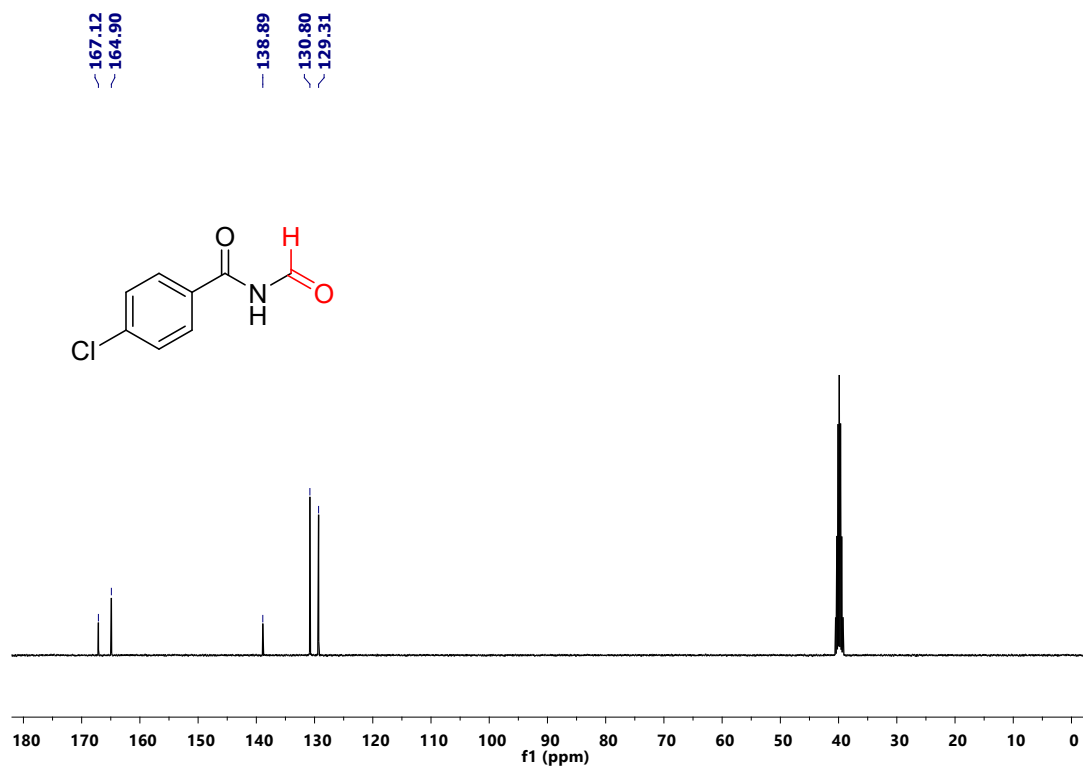
DEPT-135 NMR (101 MHz, CDCl₃) of **2h**



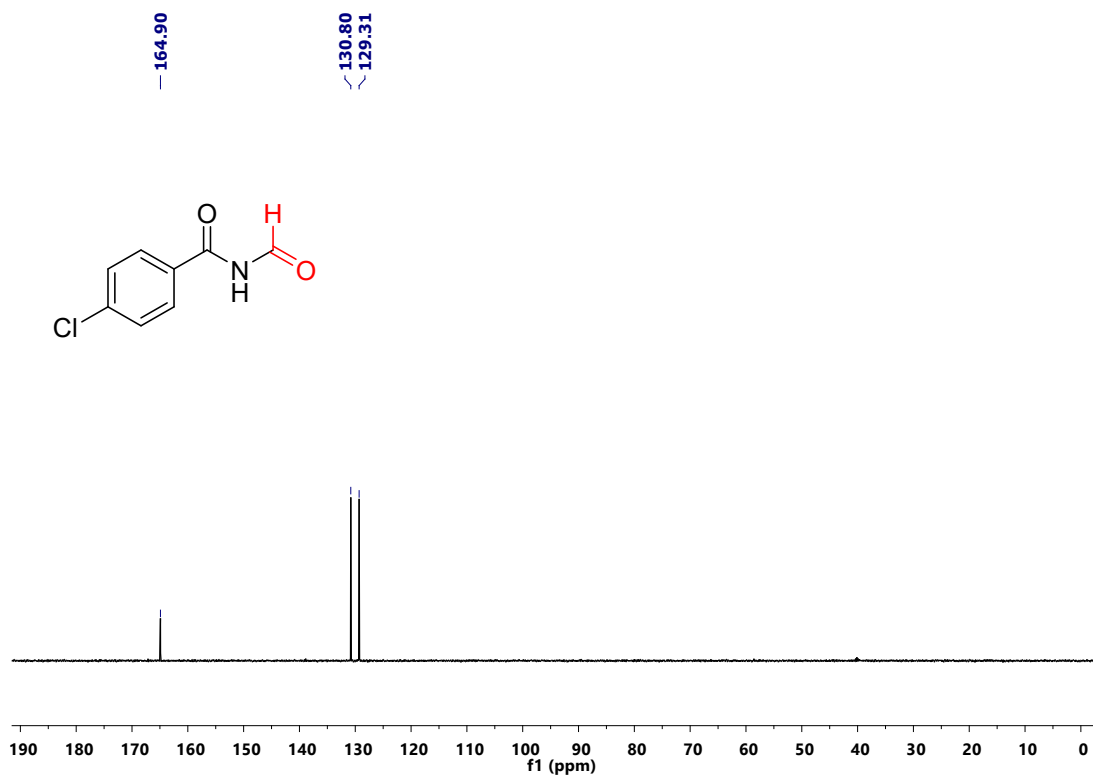
¹H NMR (400 MHz, DMSO-*d*₆) of **2i**



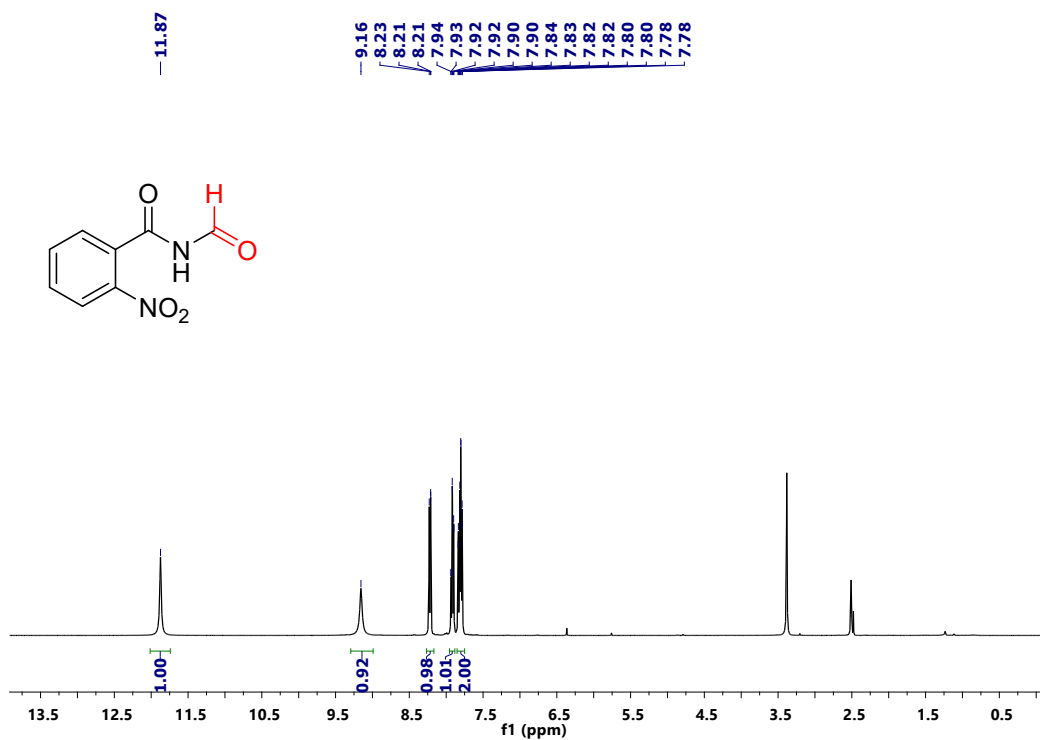
^{13}C NMR (101 MHz, DMSO- d_6) of **2i**



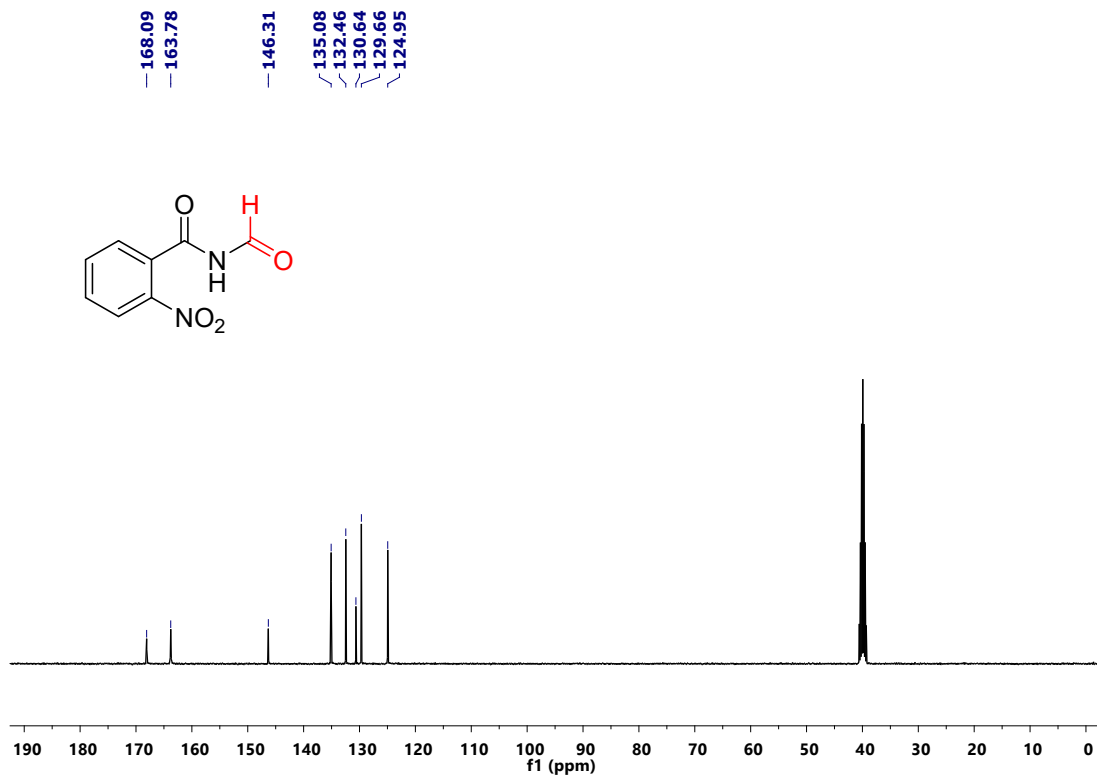
DEPT-135 NMR (101 MHz, DMSO- d_6) of **2i**



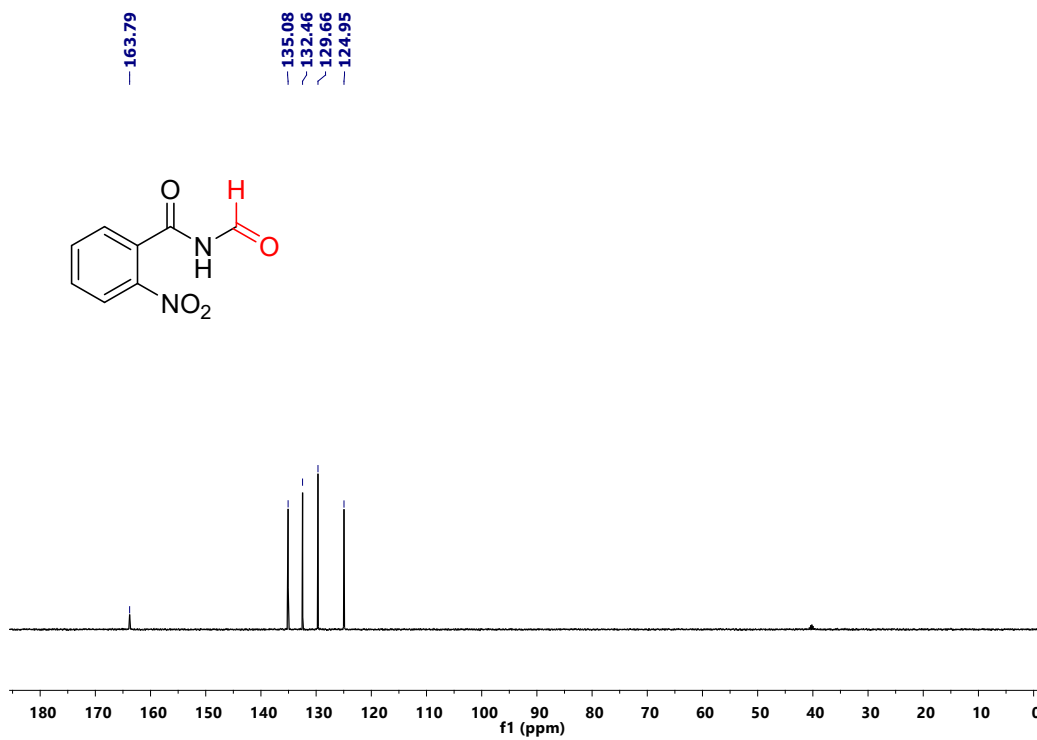
¹H NMR (400 MHz, DMSO- d₆) of **2j**



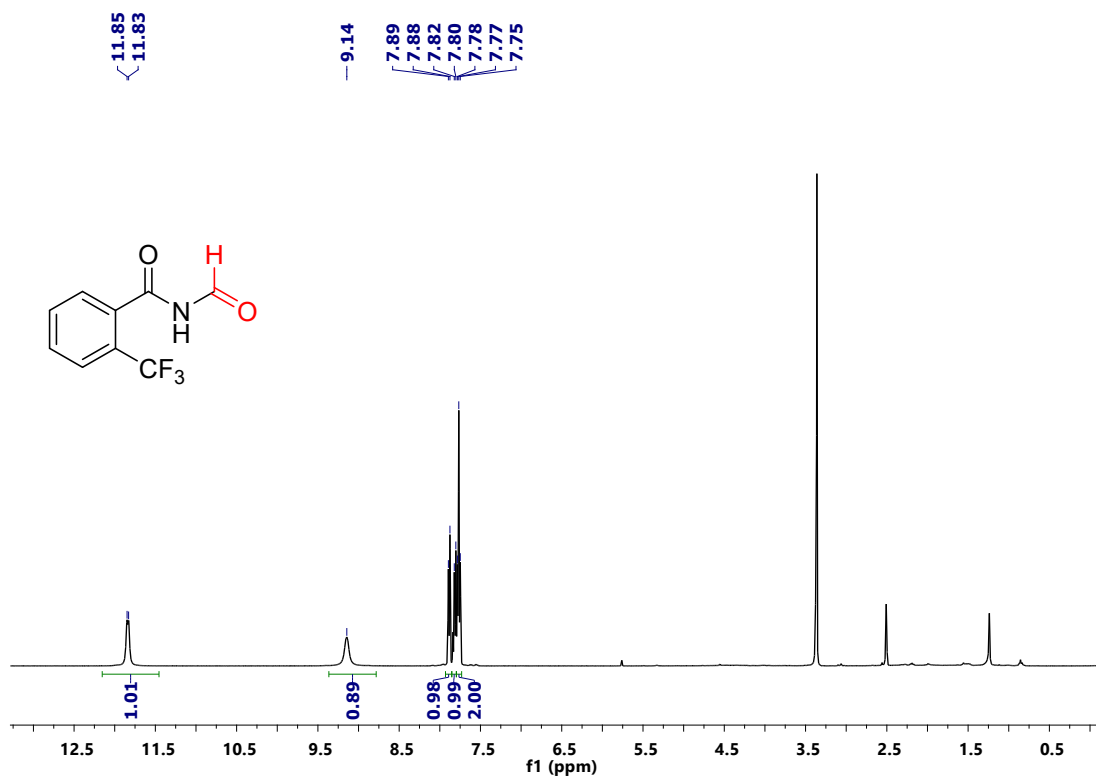
¹³C NMR (101 MHz, DMSO- d₆) of **2j**



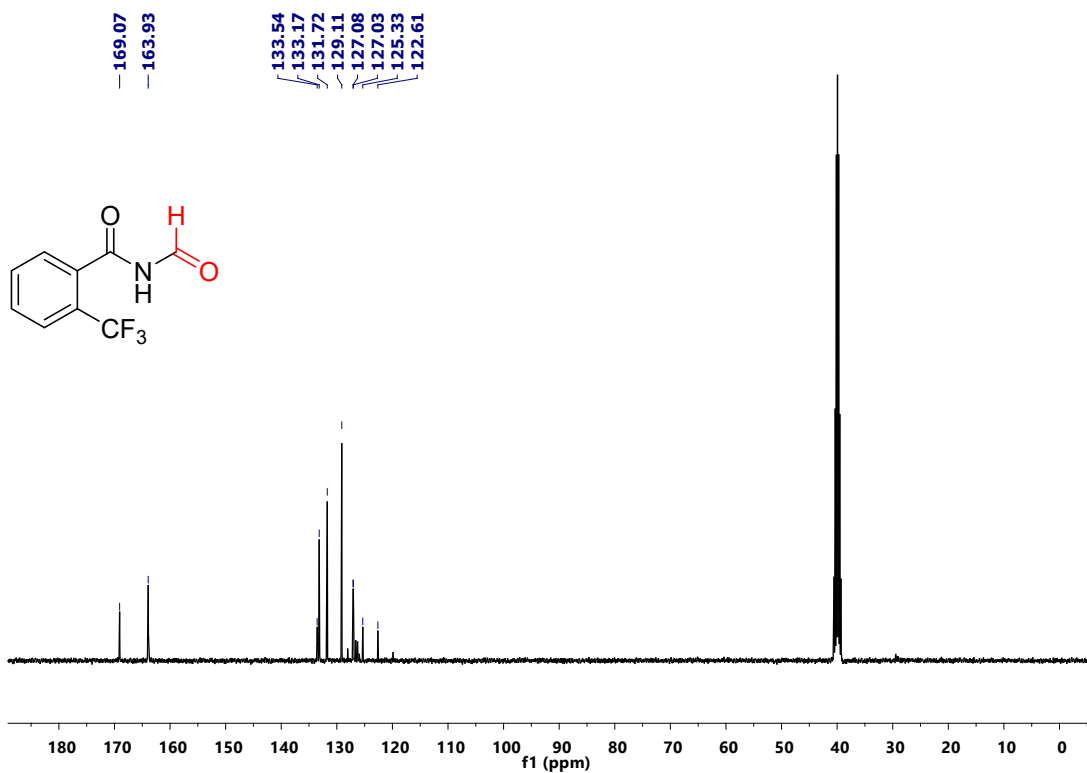
DEPT-135 NMR (101 MHz, DMSO- d₆) of **2j**



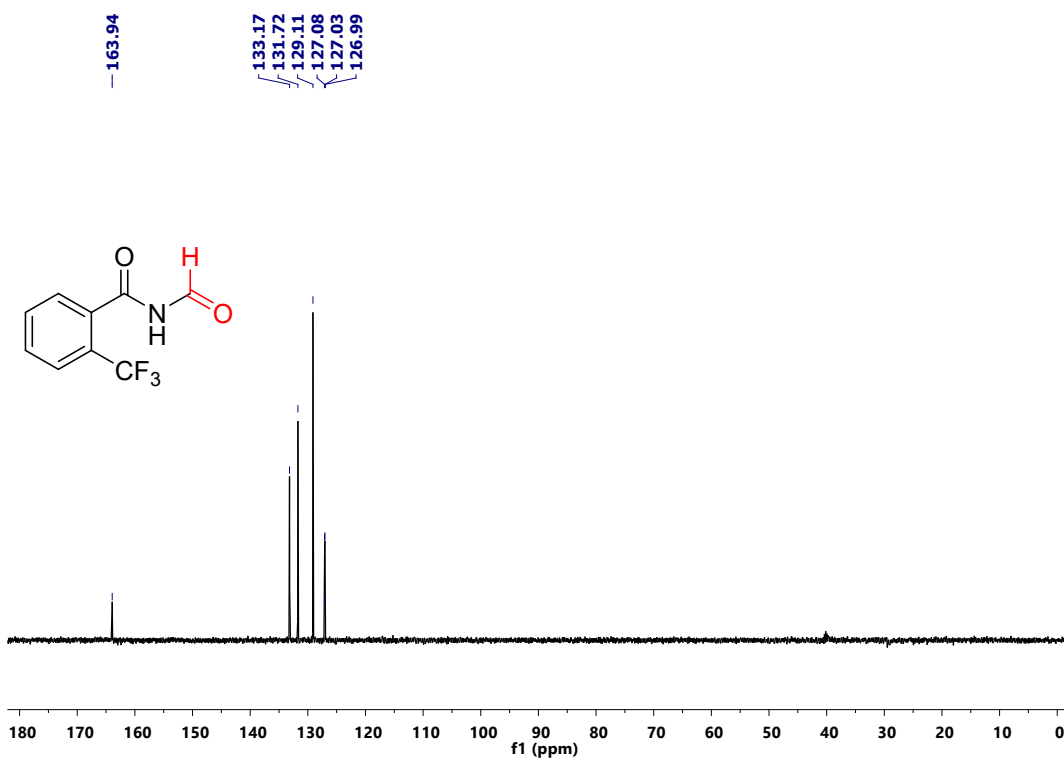
¹H NMR (400 MHz, DMSO- d₆) of **2k**



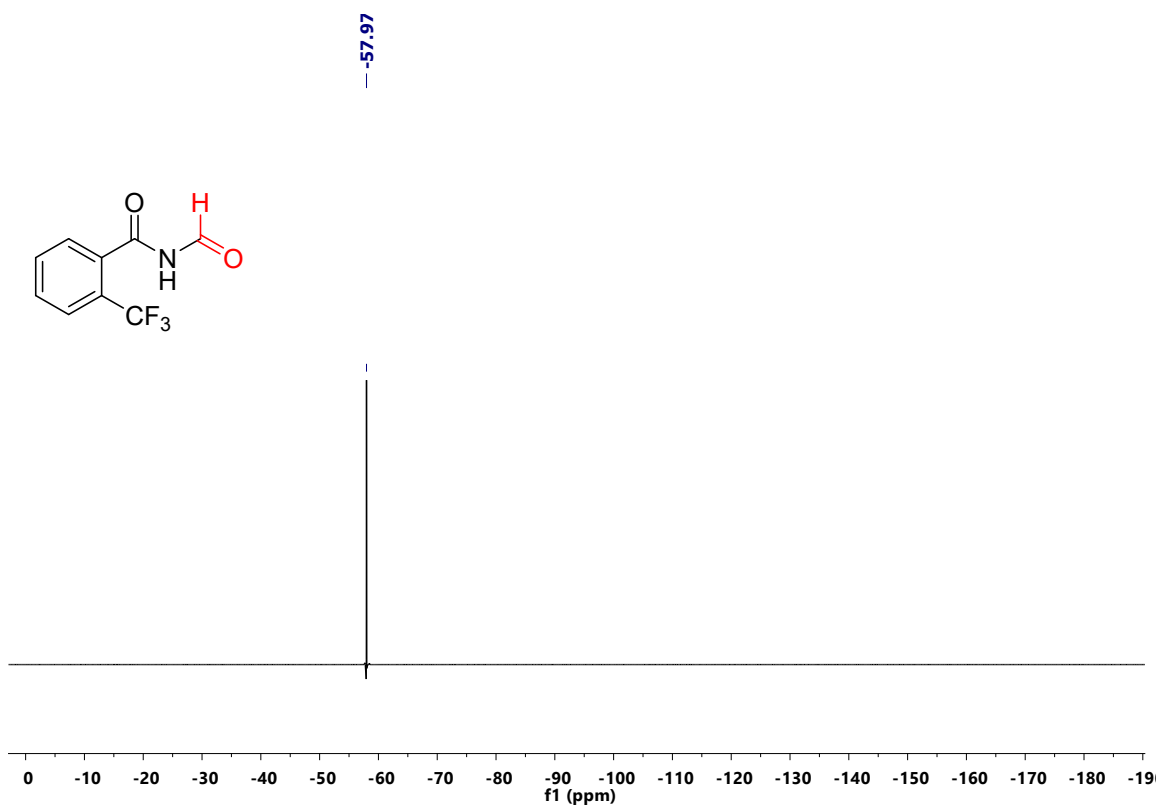
^{13}C NMR (101 MHz, DMSO- d_6) of **2k**



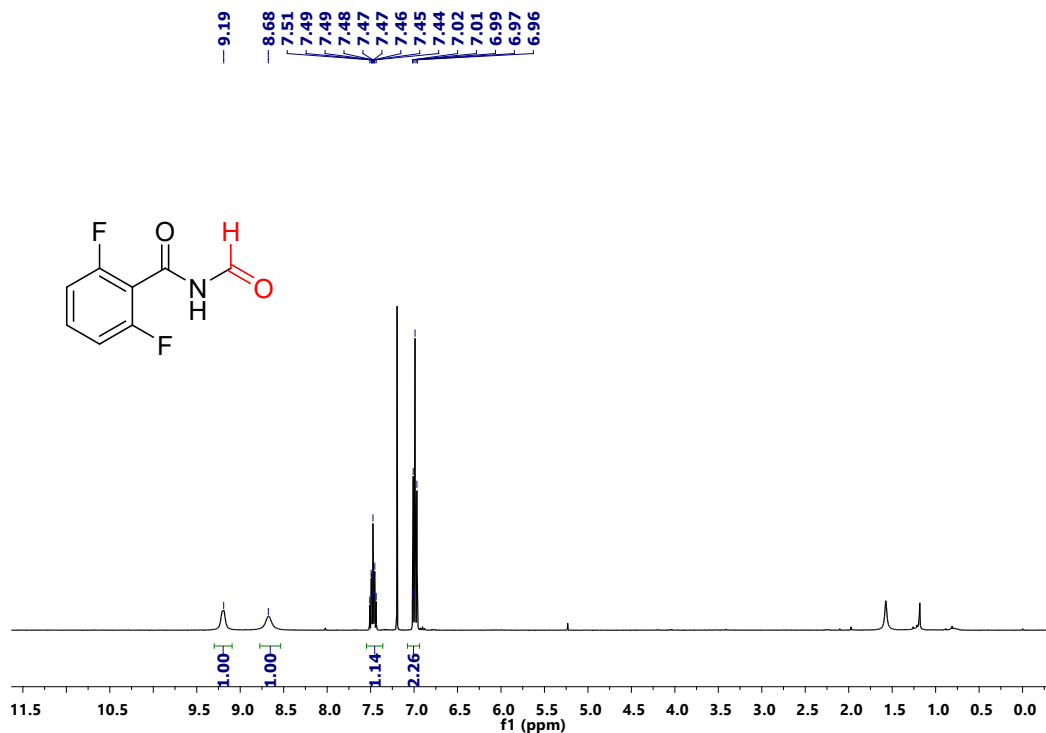
DEPT-135 NMR (101 MHz, DMSO- d_6) of **2k**



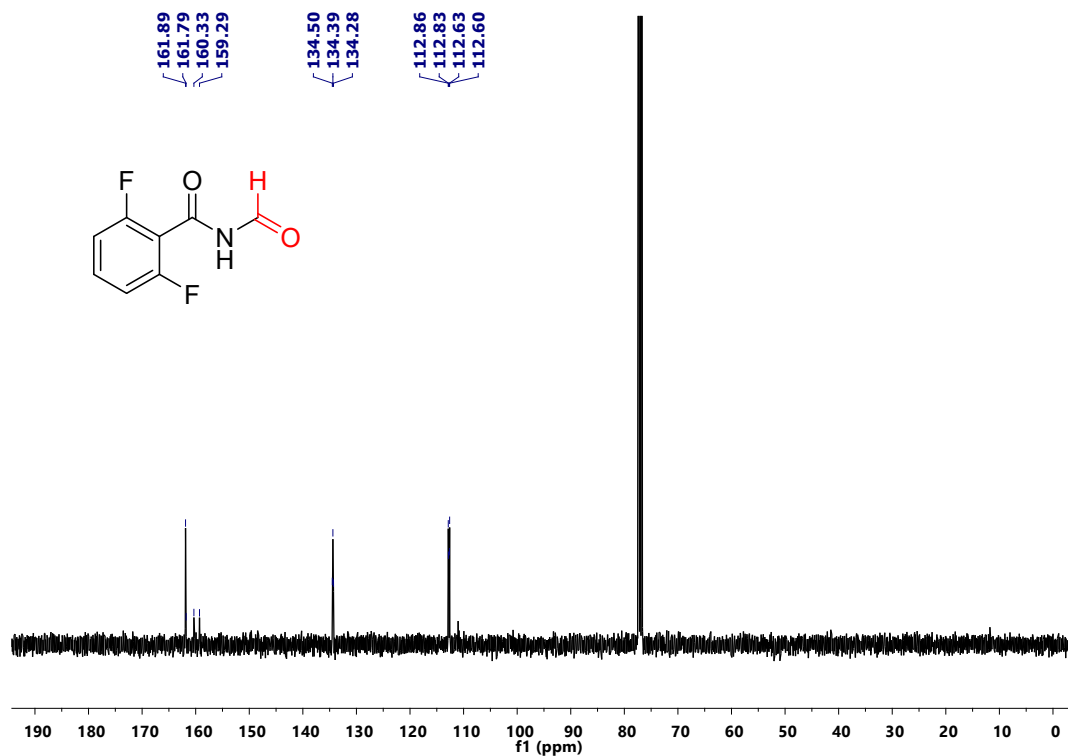
^{19}F NMR (377 MHz, DMSO- d_6) of **2k**



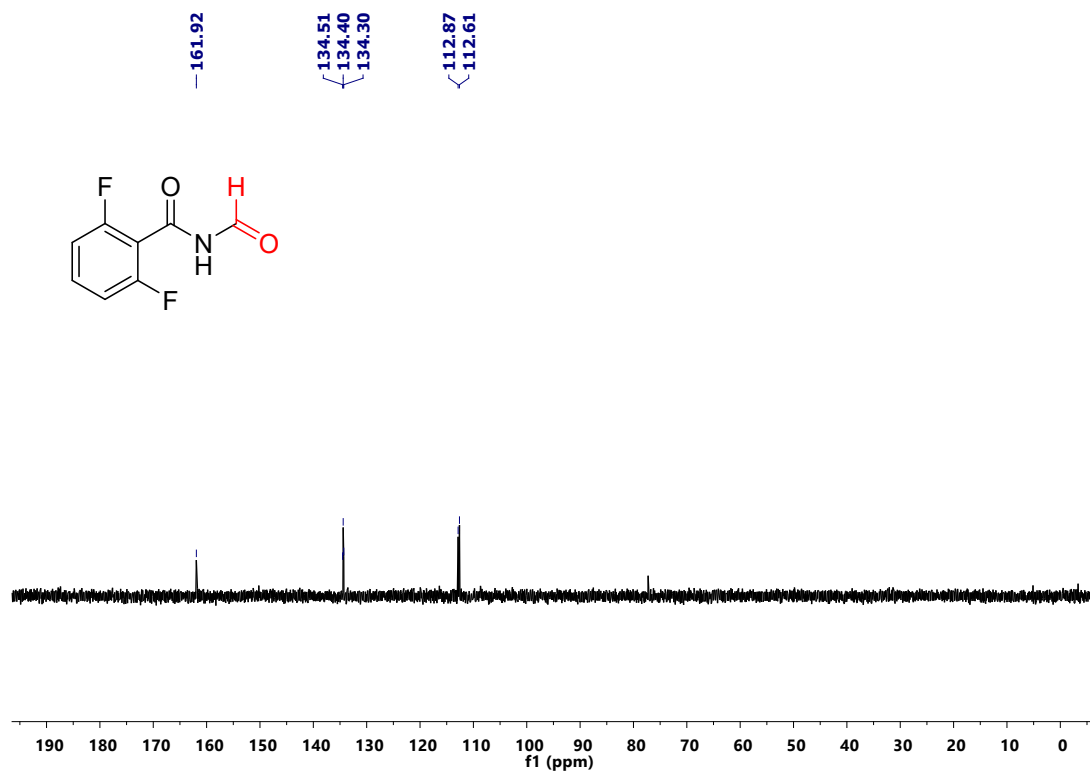
^1H NMR (400 MHz, CDCl_3) of **2l**



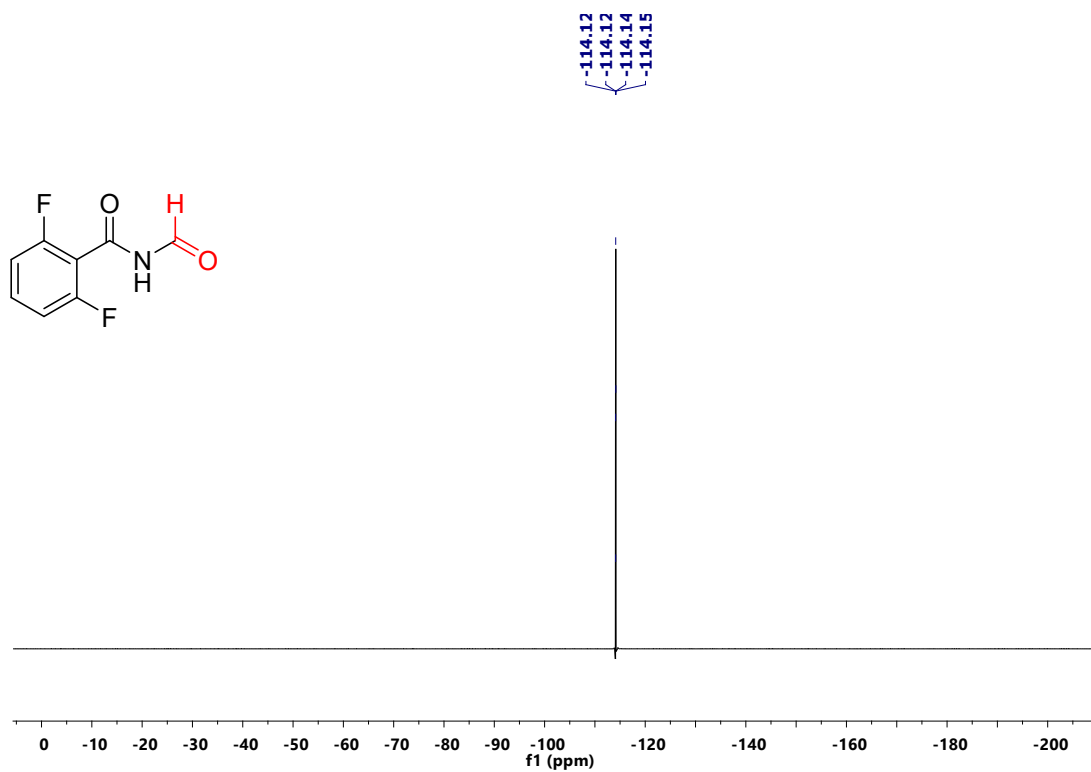
^{13}C NMR (101 MHz CDCl_3 ,) of **21**



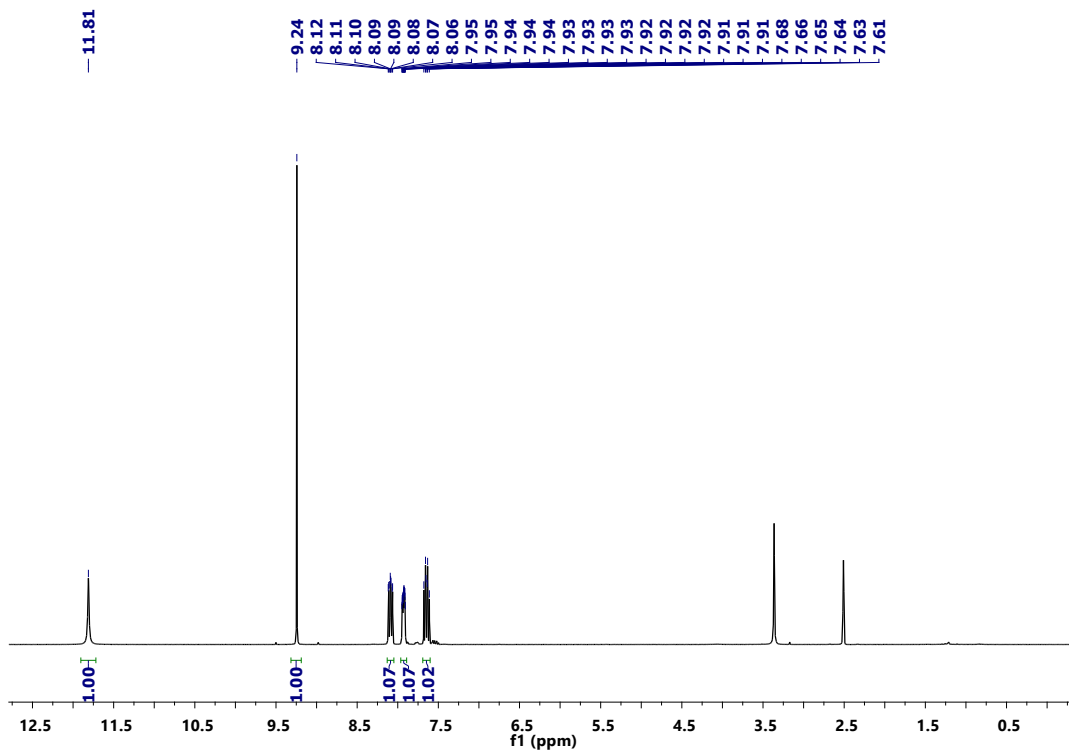
DEPT-135 NMR (101 MHz, CDCl_3) of **21**



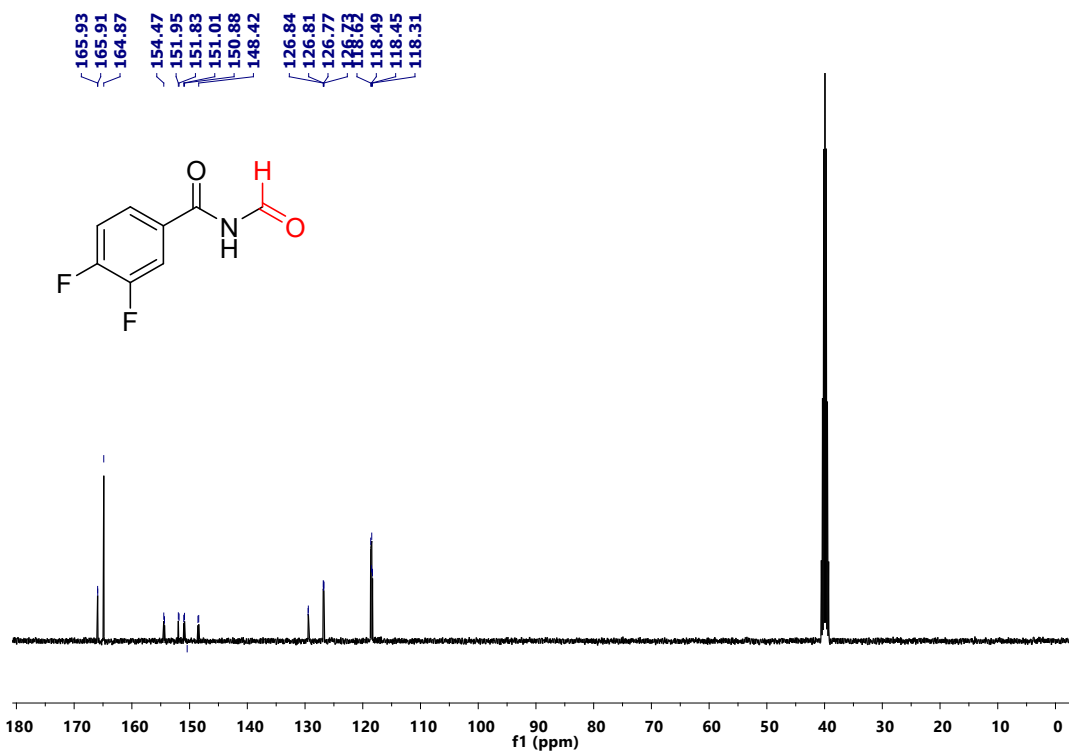
^{19}F NMR (377 MHz, DMSO-d_6) of **2l**



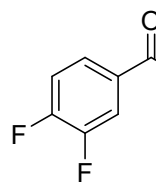
^1H NMR (400 MHz, DMSO-d_6) of **2m**

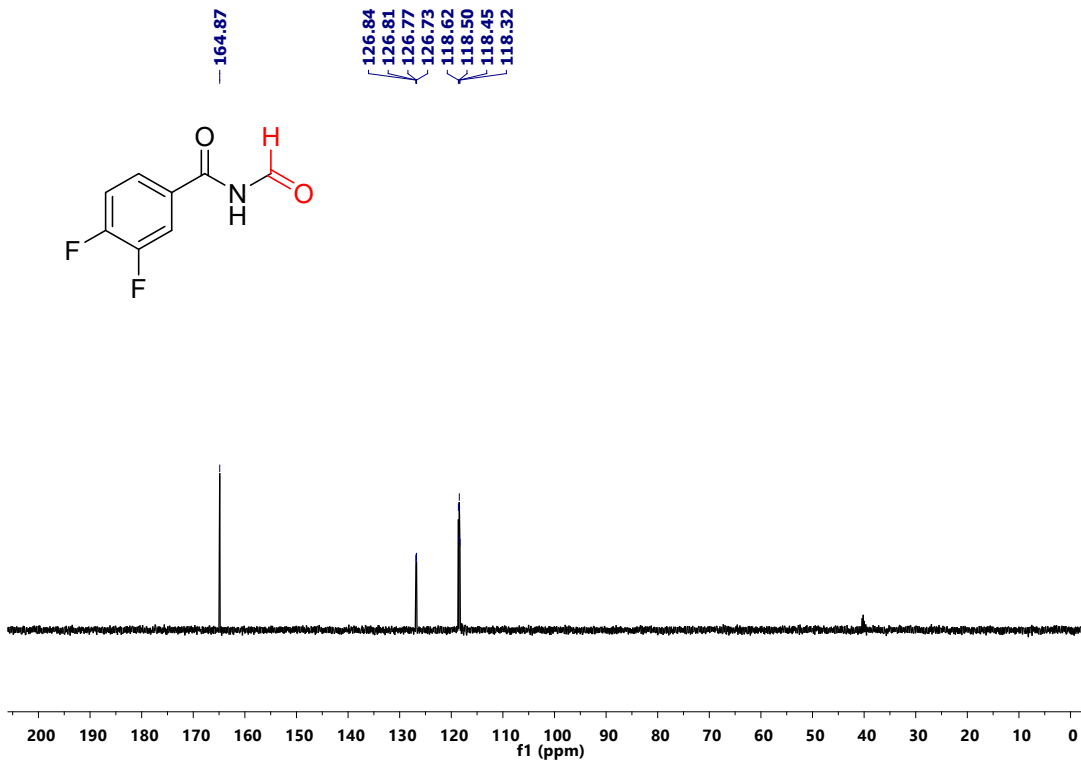


^{13}C NMR (101 MHz, DMSO- d_6) of **2m**

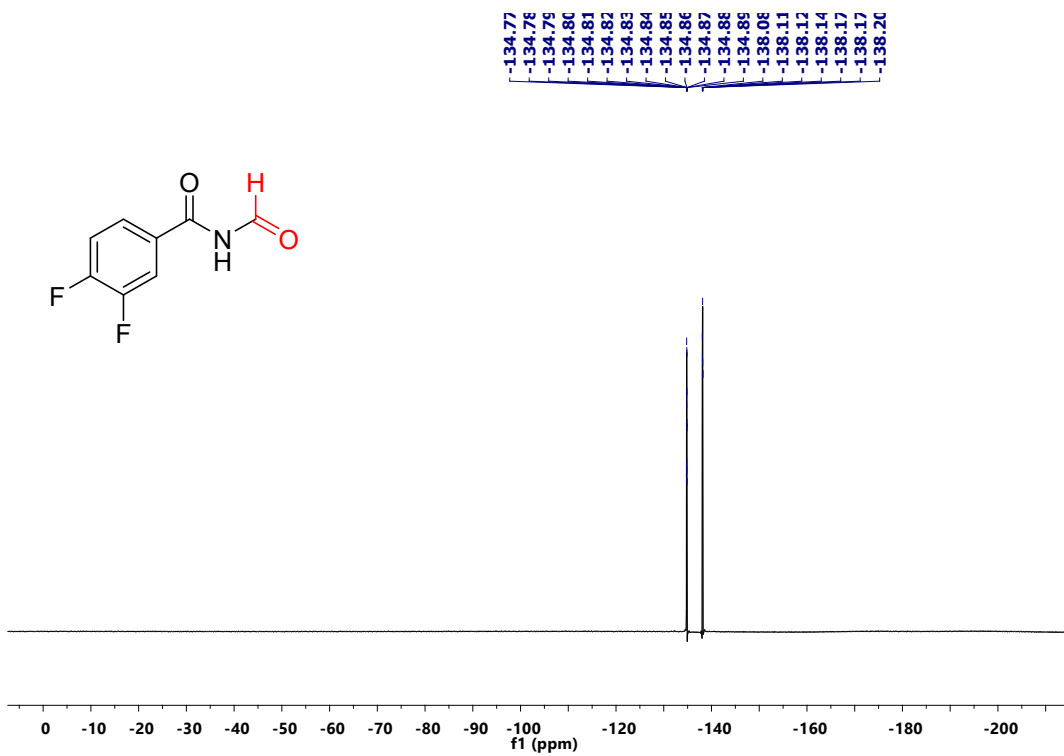


DEPT-135 NMR (101 MHz, DMSO- d_6) of **2m**

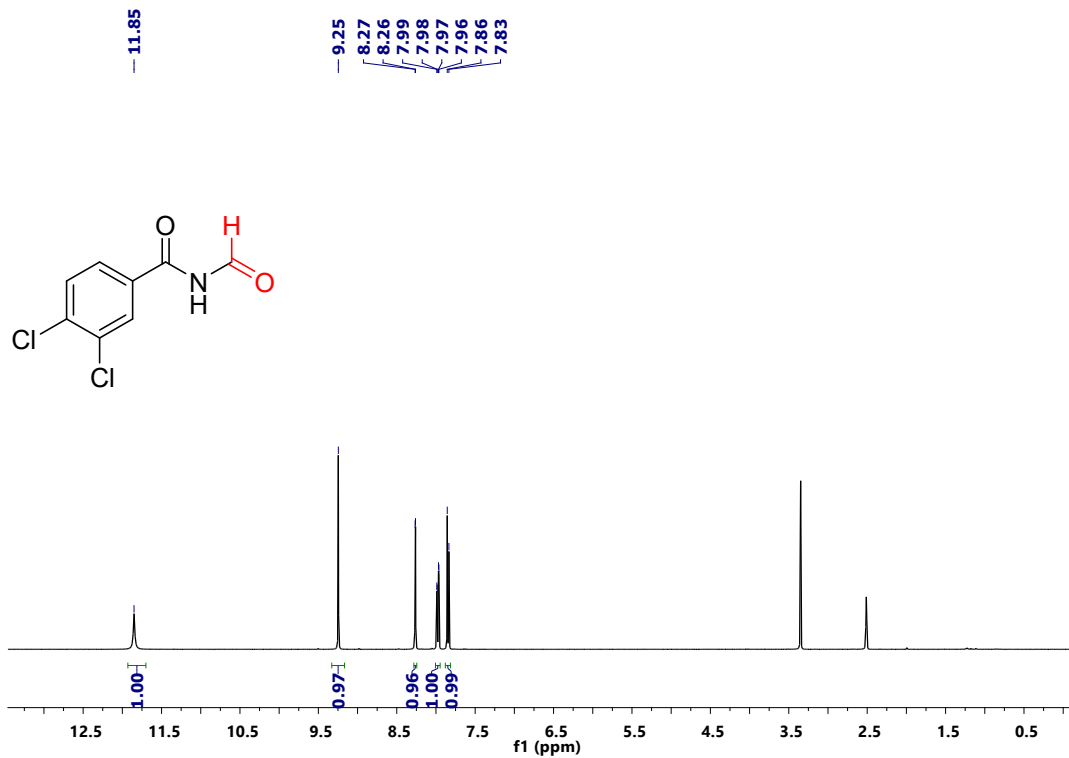




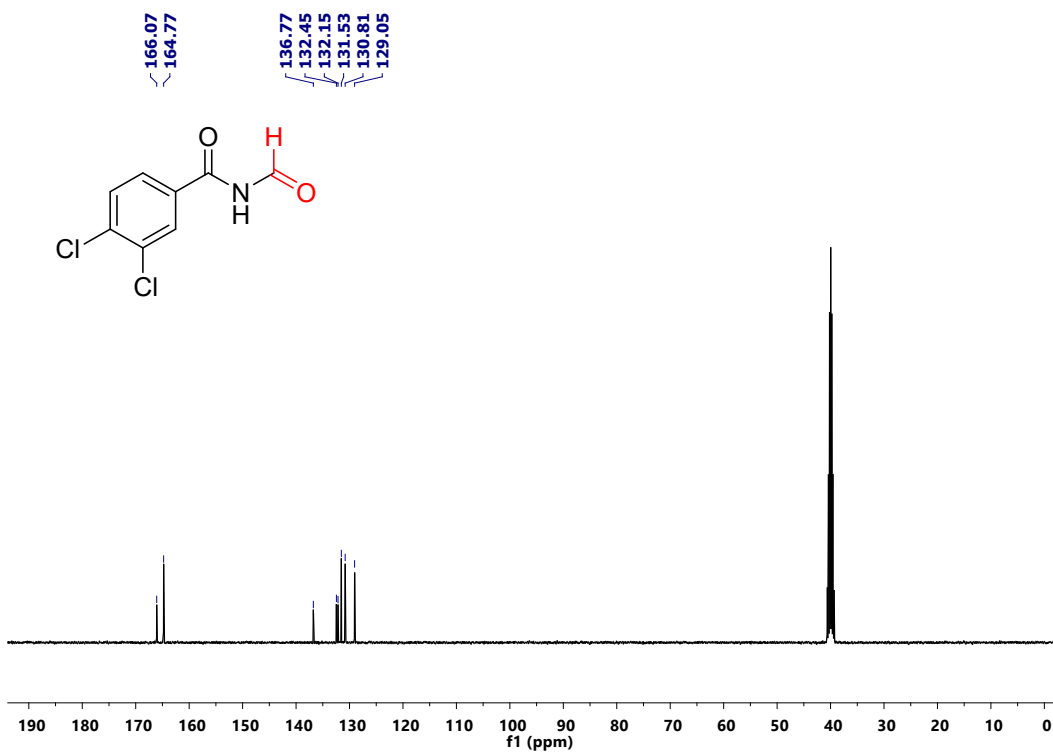
^{19}F NMR (377 MHz, DMSO- d_6) of 2m



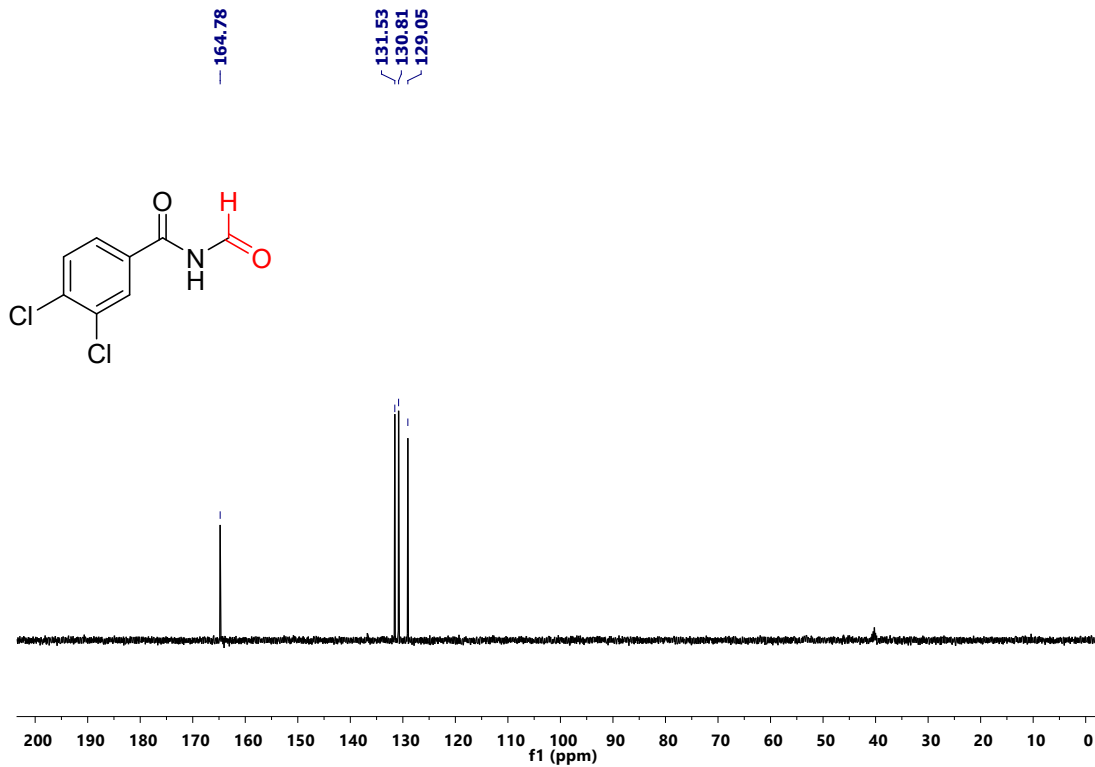
^1H NMR (400 MHz, DMSO- d_6) of 2n



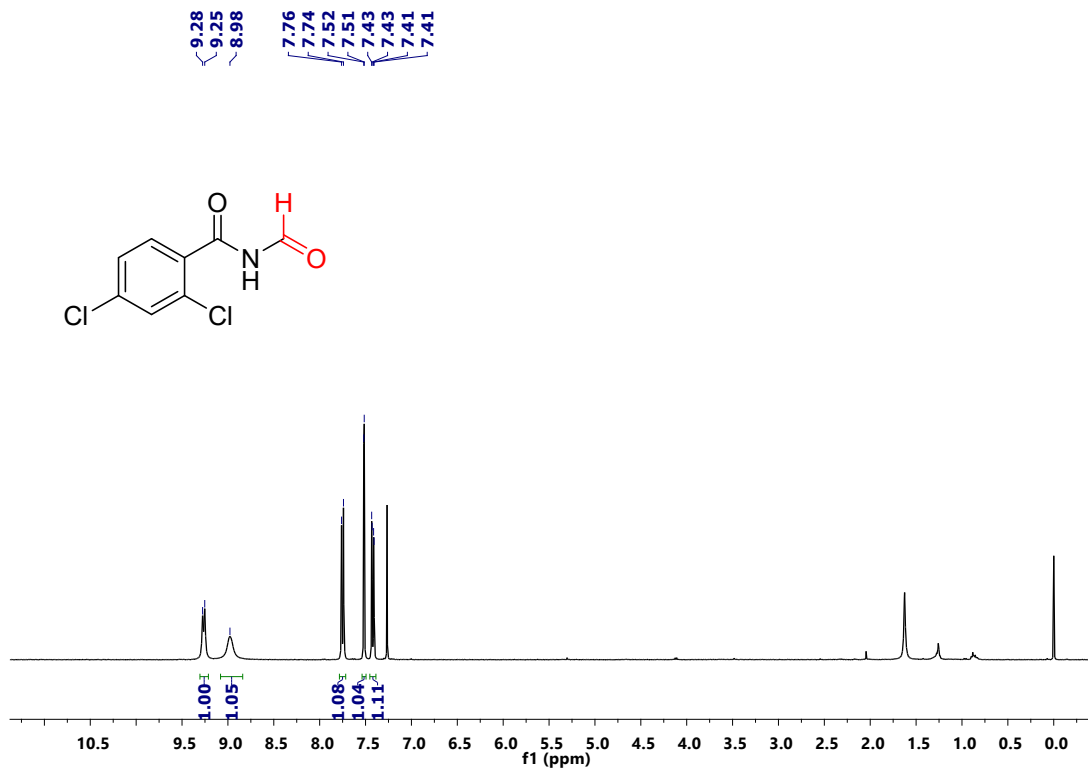
¹³C NMR (101 MHz, DMSO-*d*₆) of **2n**



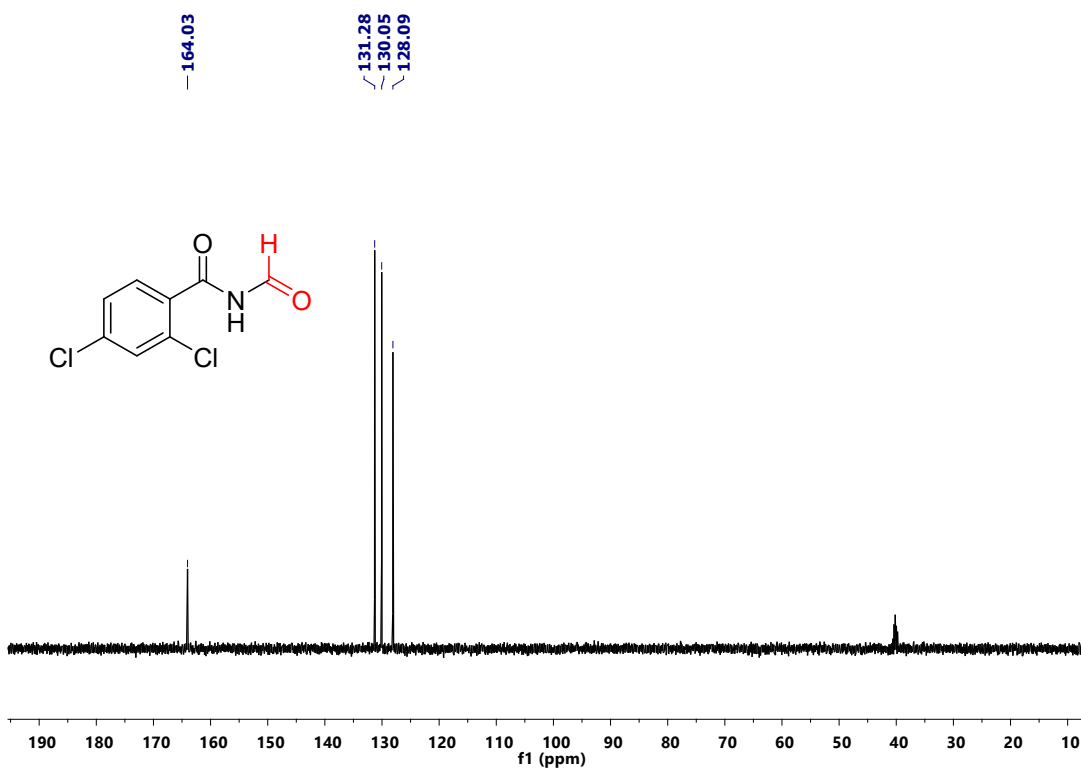
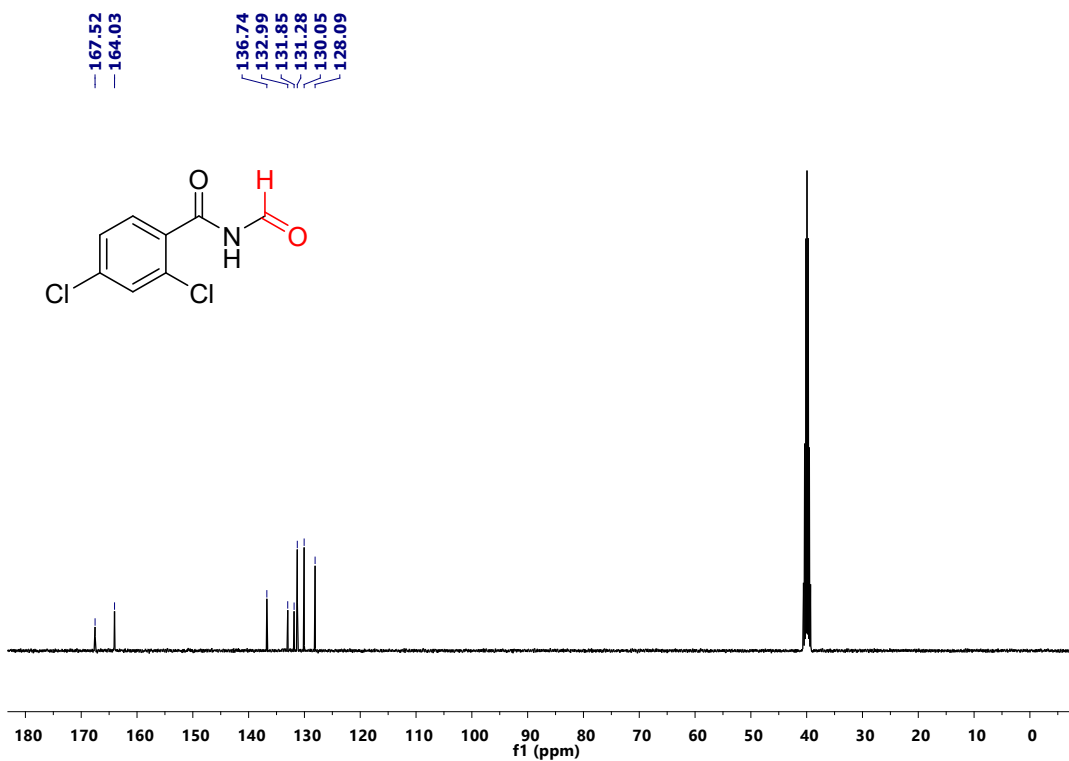
DEPT-135 NMR (101 MHz, DMSO-*d*₆) of **2n**

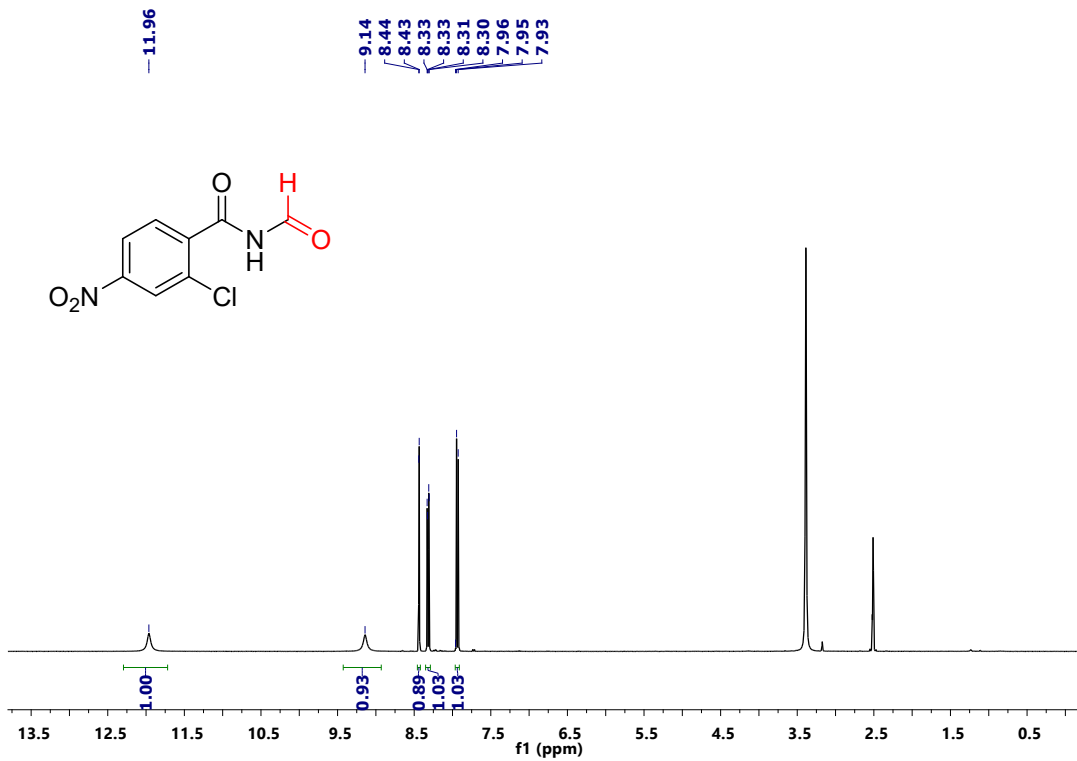


^1H NMR (400 MHz, CDCl_3) of 2o

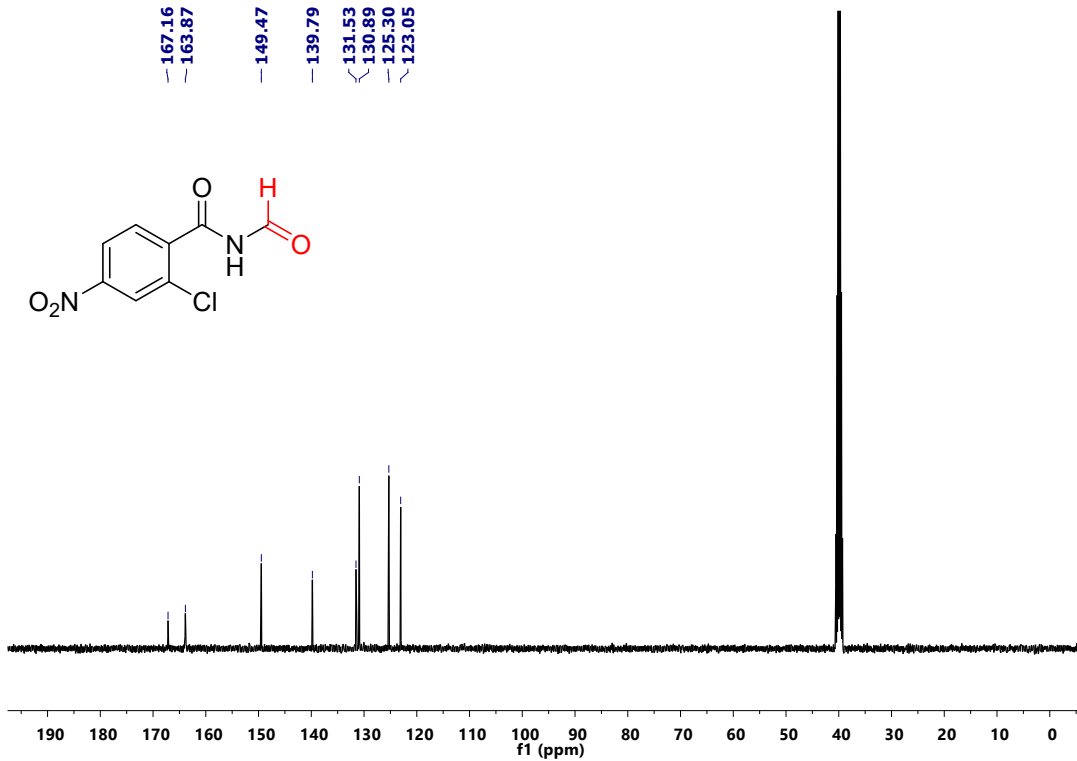


^{13}C NMR (101 MHz, CDCl_3) of 2o

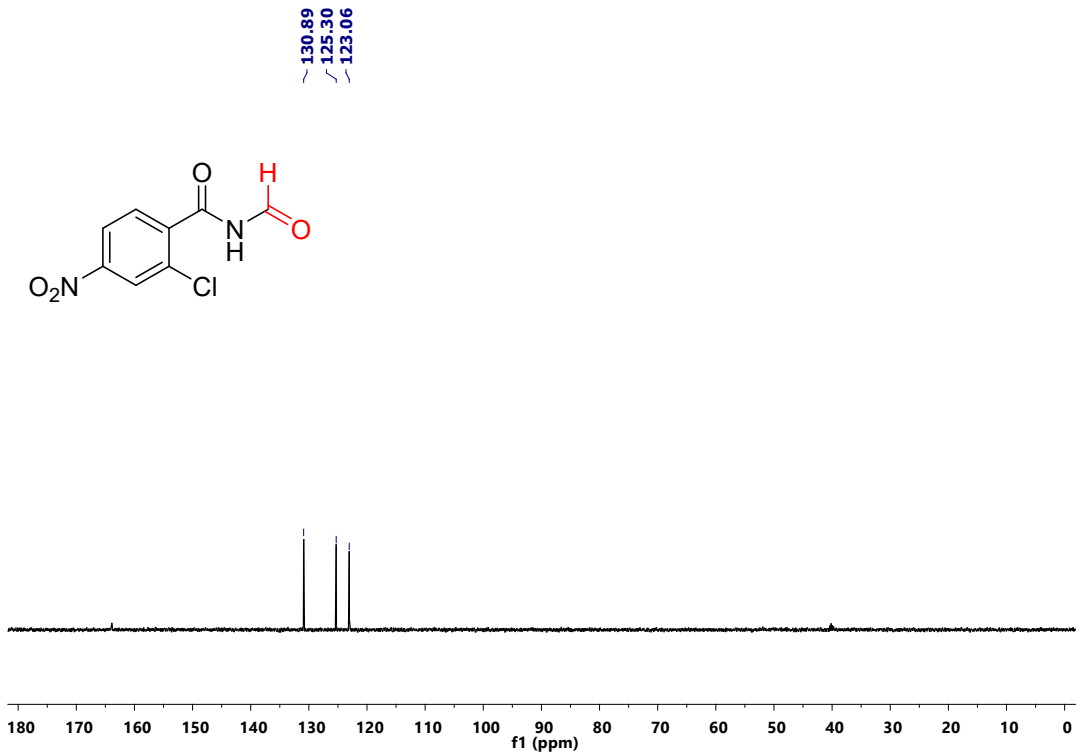




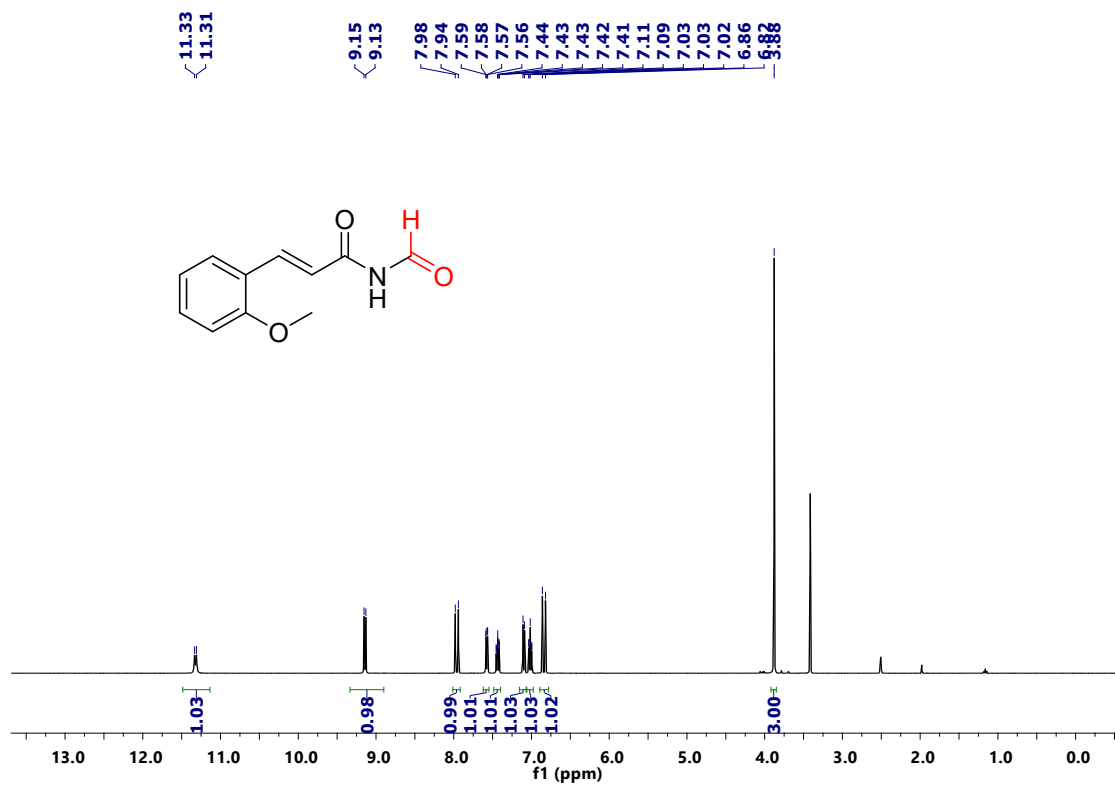
¹³C NMR (101 MHz, DMSO-*d*₆) of **2p**



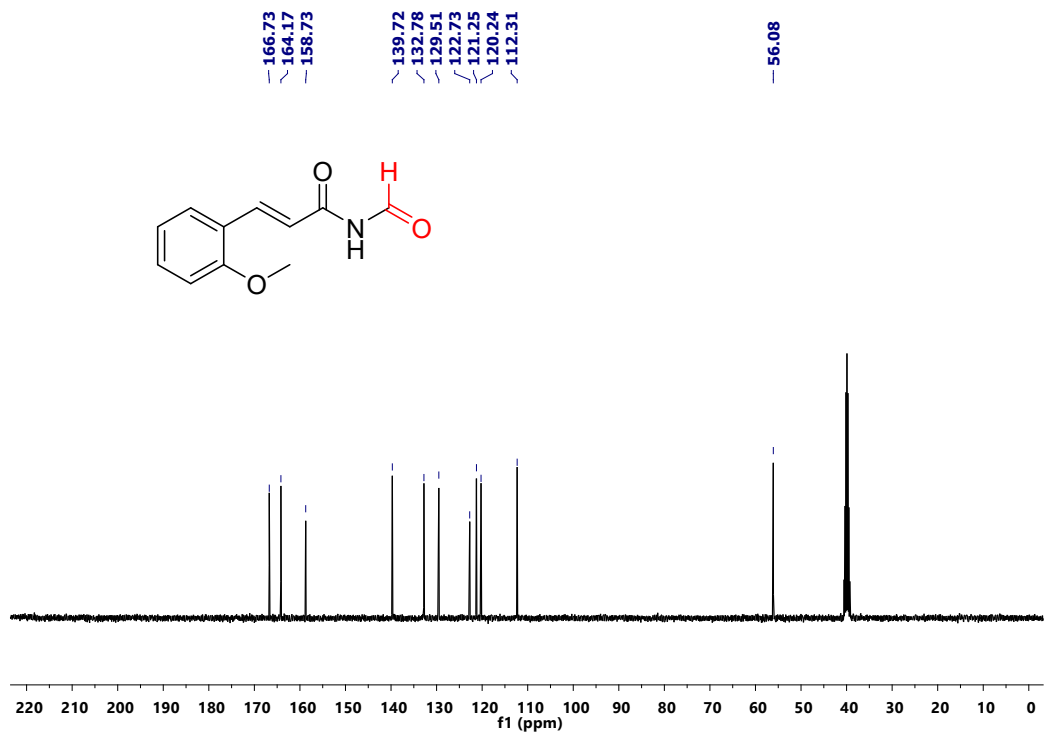
DEPT-135 NMR (101 MHz, DMSO-*d*₆) of **2p**



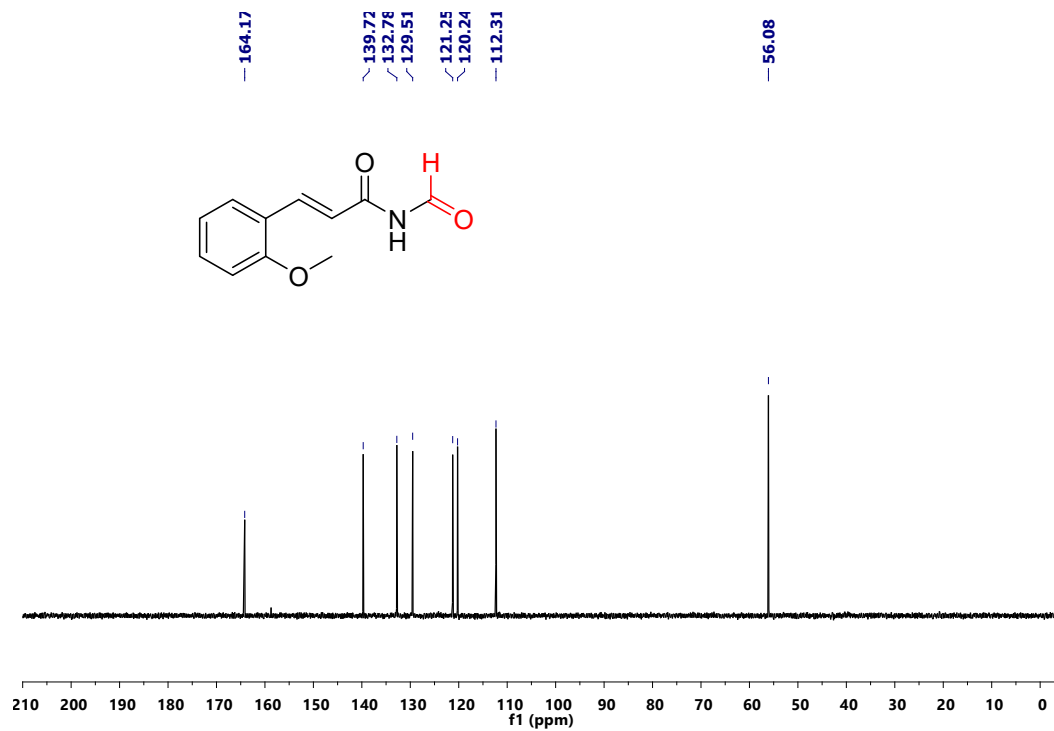
^1H NMR (400 MHz, DMSO- d_6) of 2q



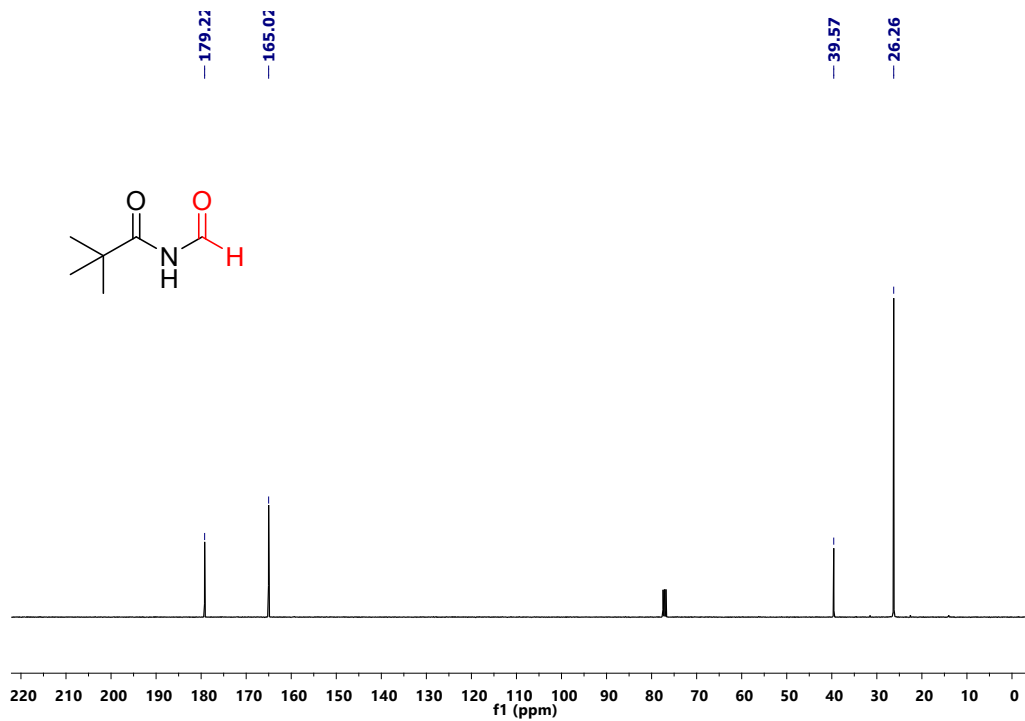
^{13}C NMR (101 MHz, DMSO- d_6) of 2q



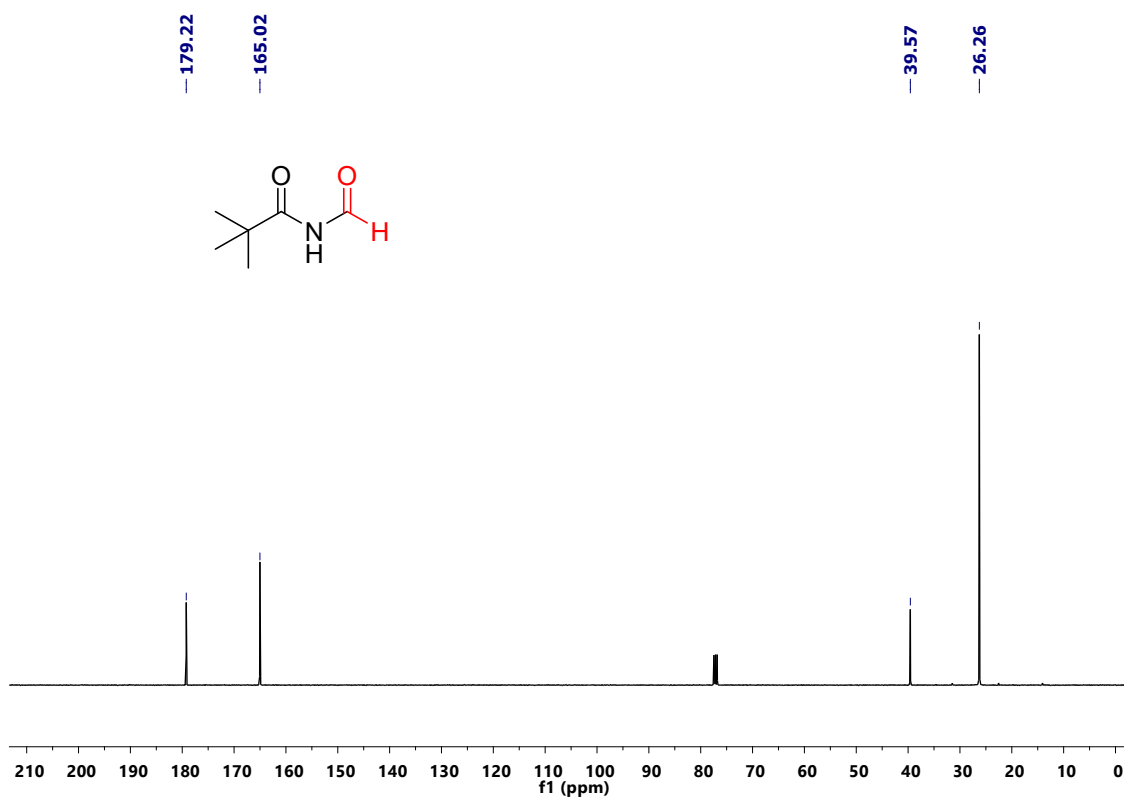
DEPT-135 NMR (101 MHz, DMSO- d_6) of **2q**



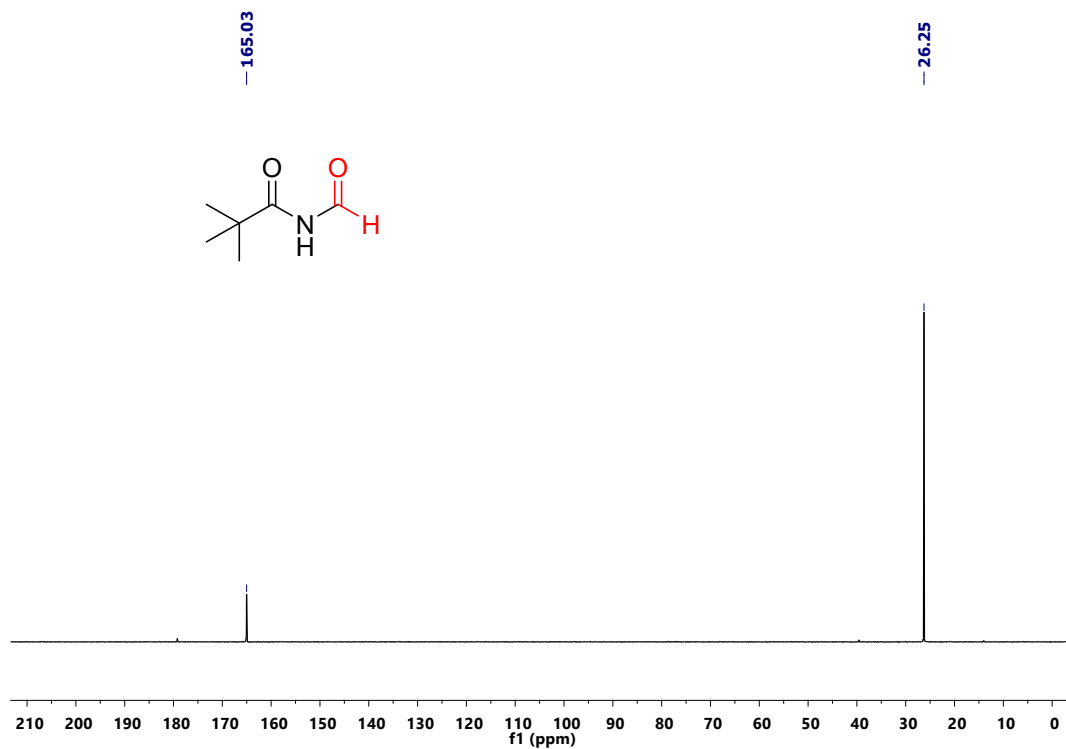
^1H NMR (400 MHz, CDCl_3) of **2r**



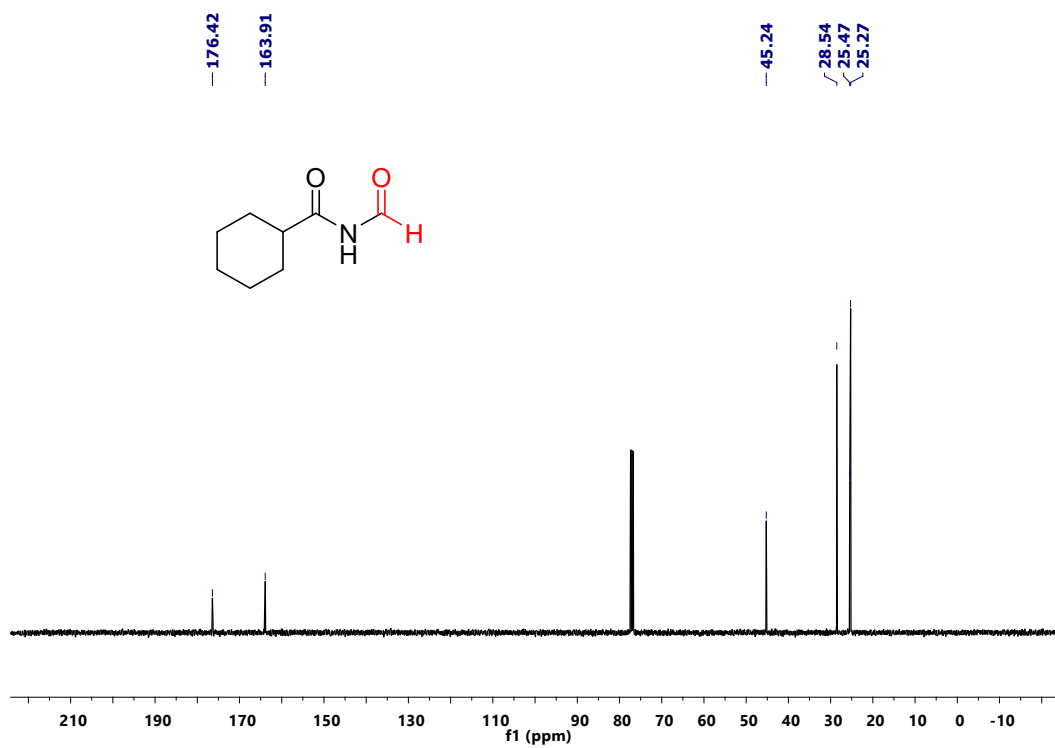
^{13}C NMR (101 MHz, CDCl_3) of **2r**



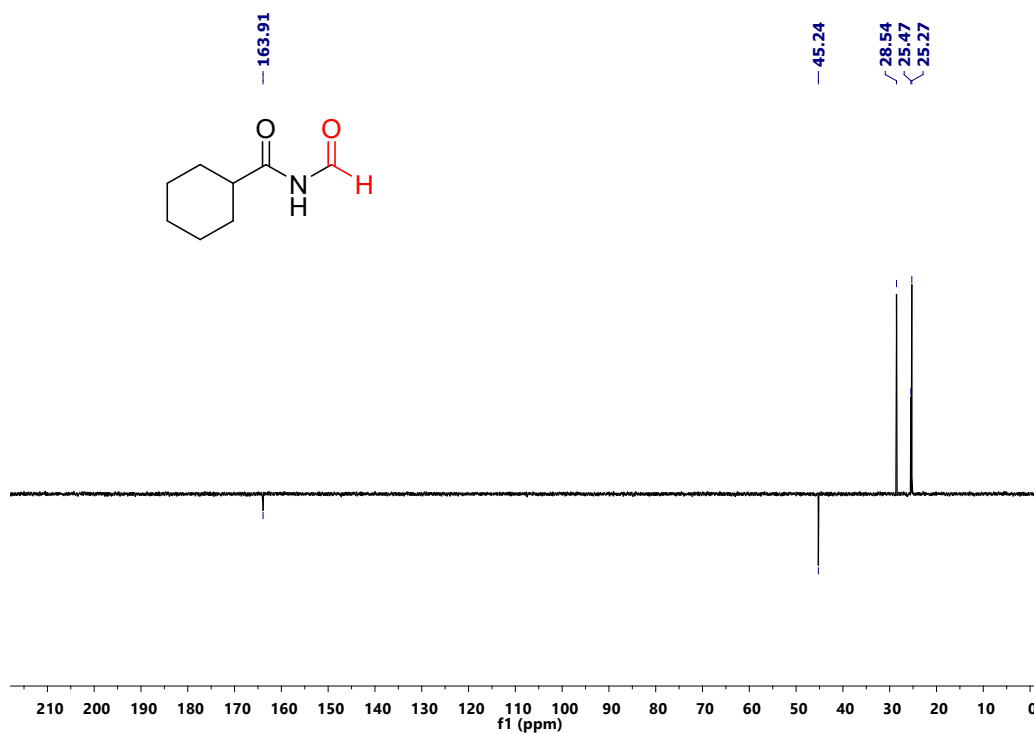
DEPT-135 NMR (101 MHz, CDCl_3) of **2r**



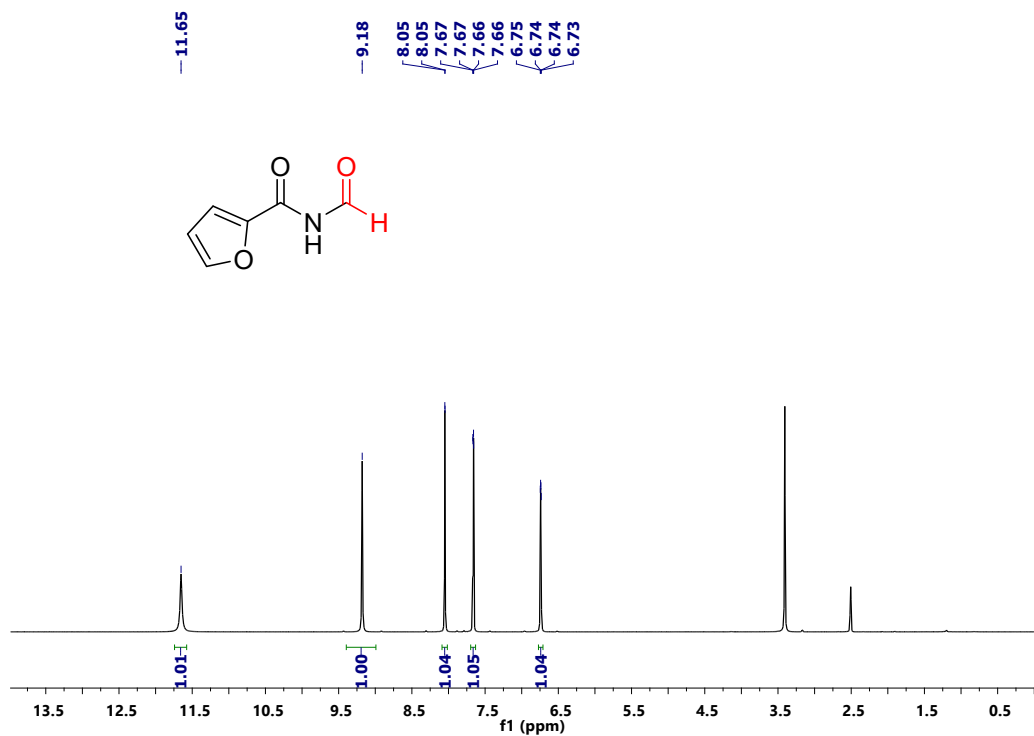
^{13}C NMR (101 MHz, CDCl_3) of 2s



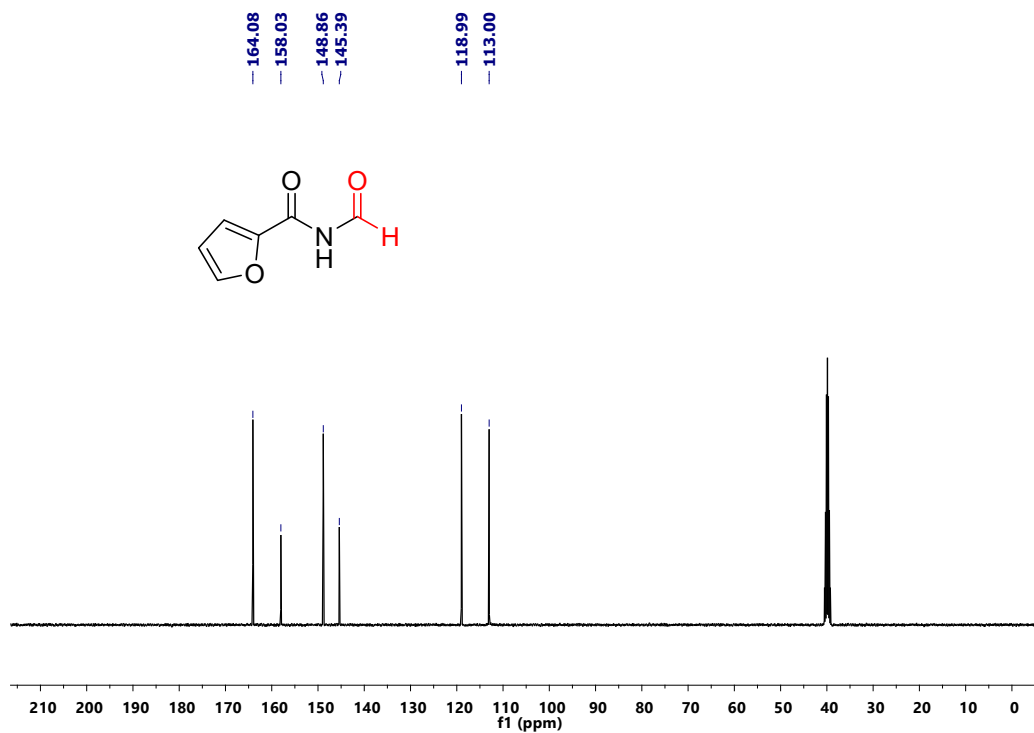
DEPT-135 NMR (101 MHz, CDCl₃) of **2s**



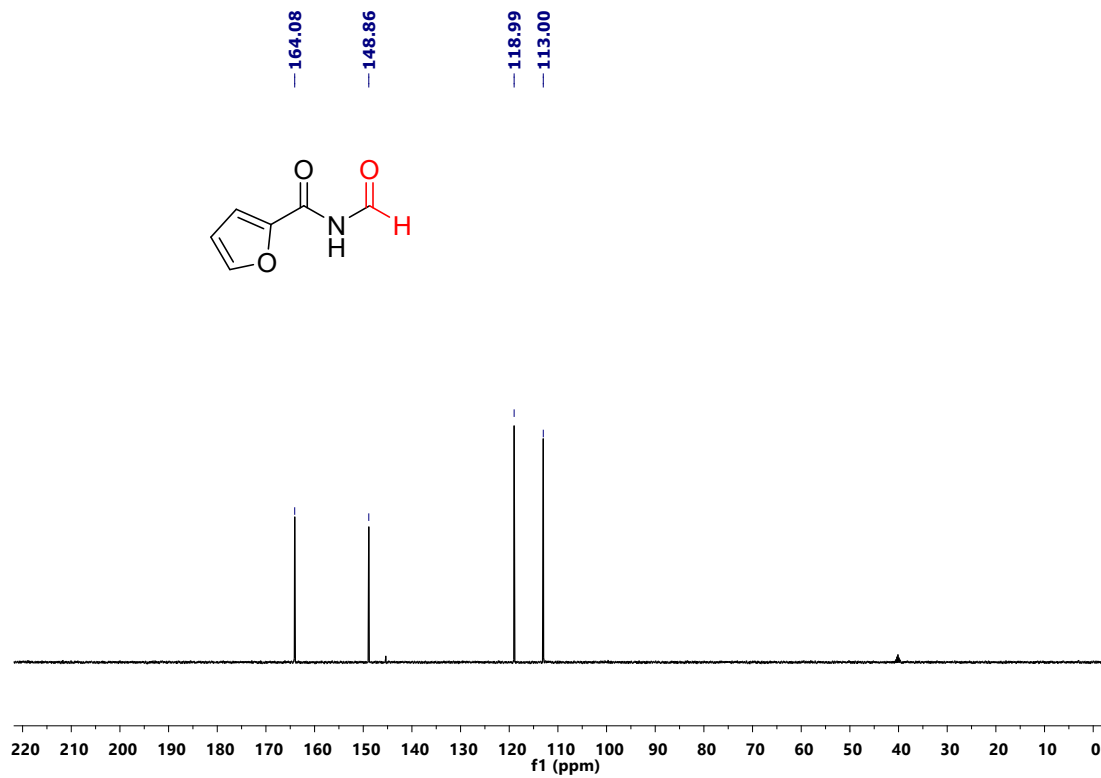
¹H NMR (400 MHz, DMSO-*d*₆) of **2t**



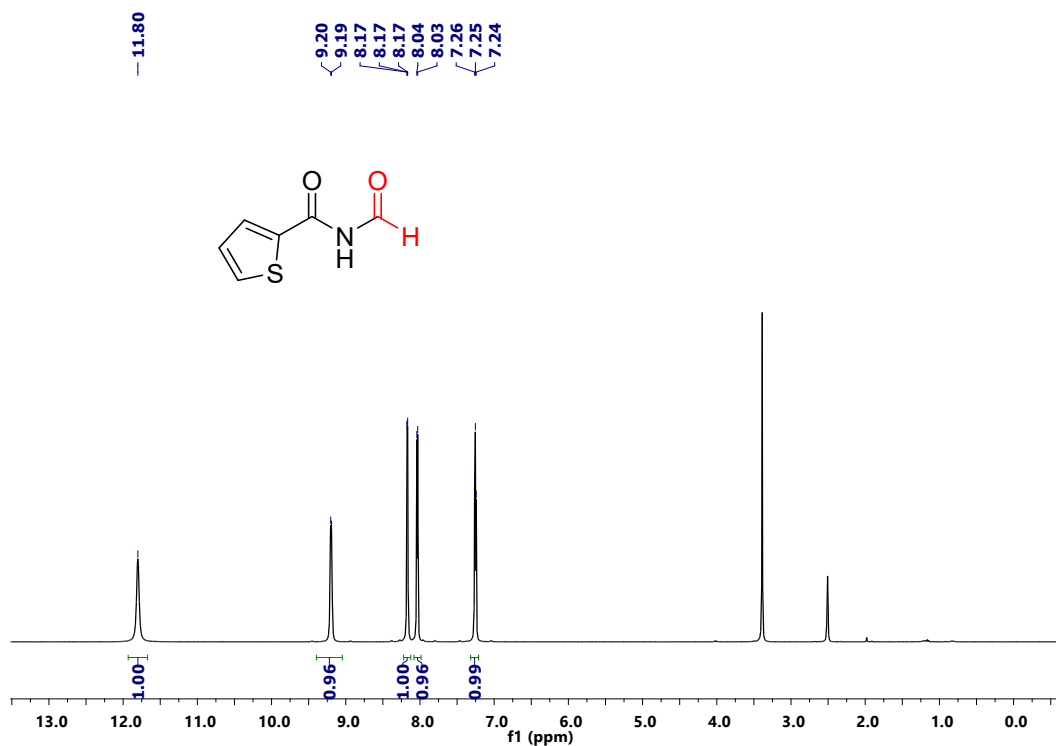
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) of **2t**



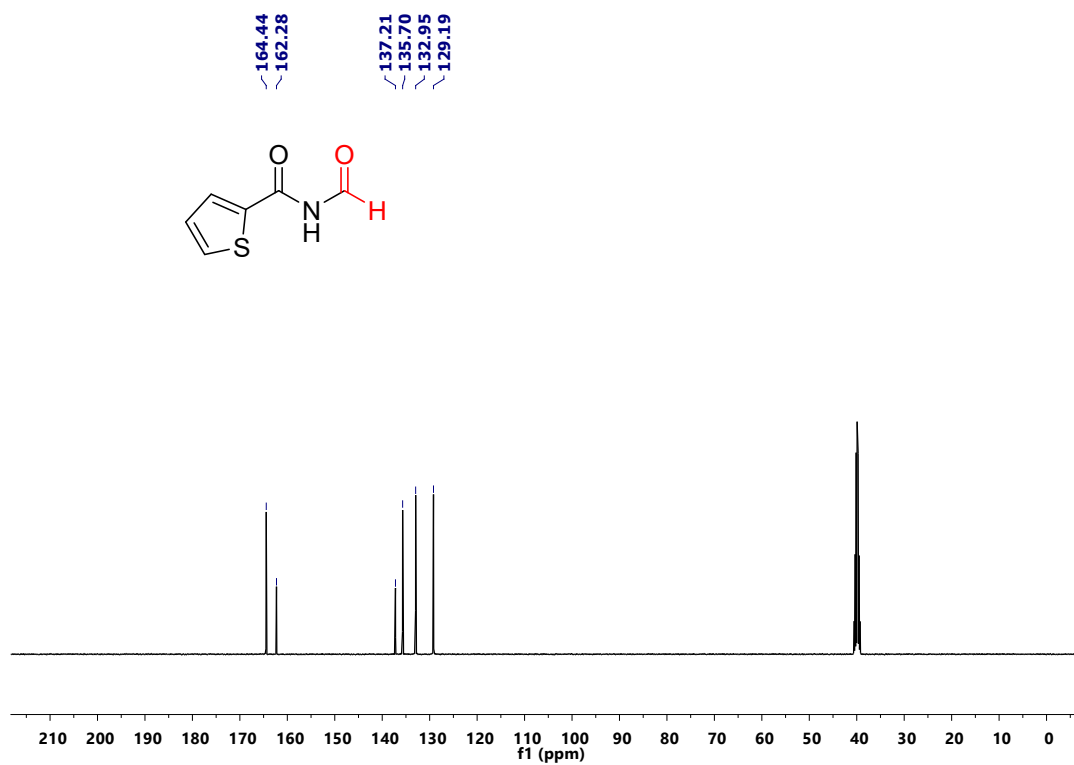
DEPT-135 NMR (101 MHz, $\text{DMSO-}d_6$) of **2t**



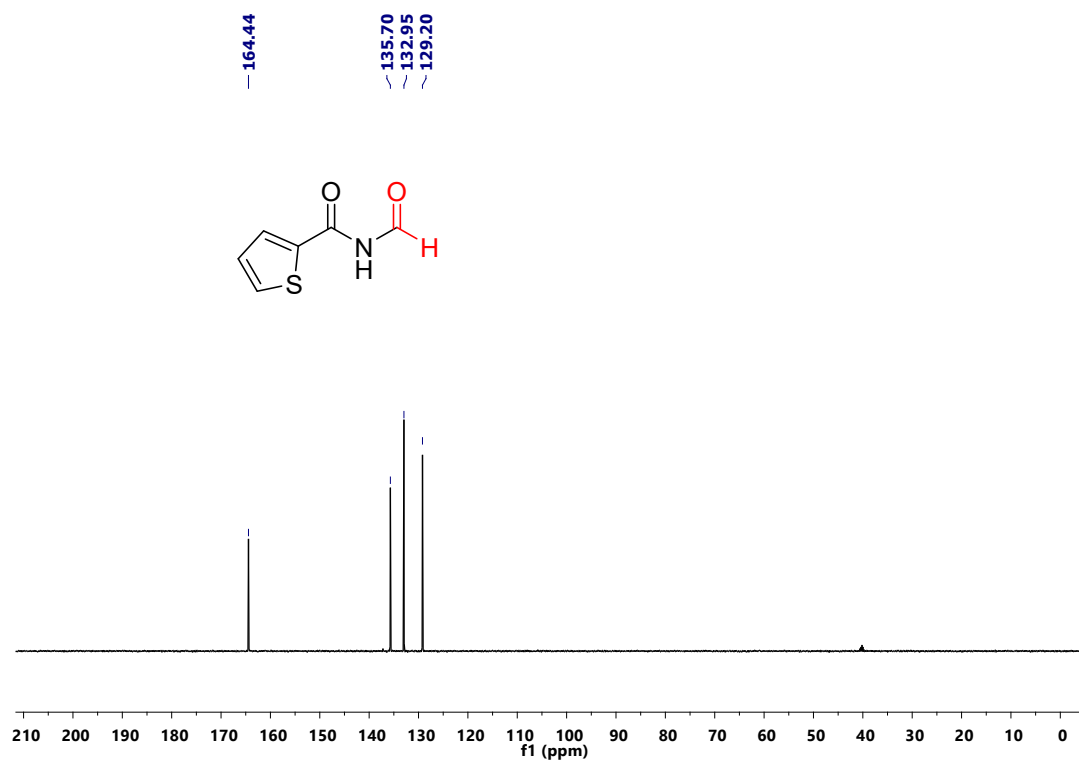
^1H NMR (400 MHz, $\text{DMSO-}d_6$) of **2u**



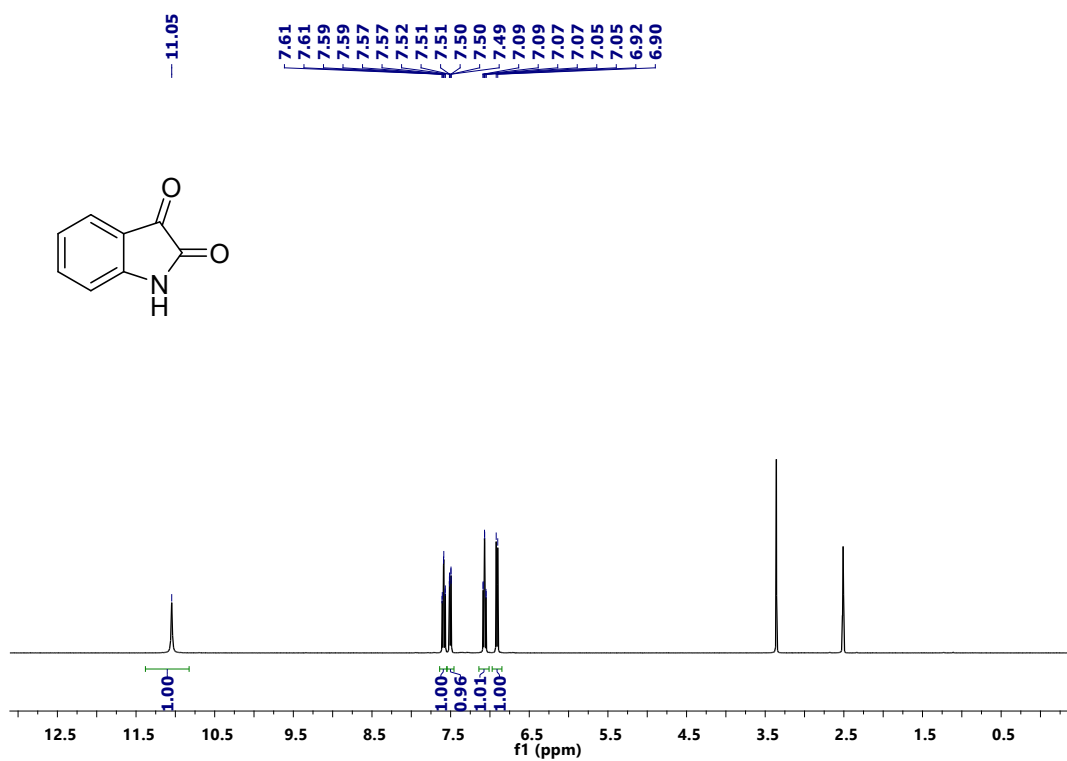
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) of **2u**



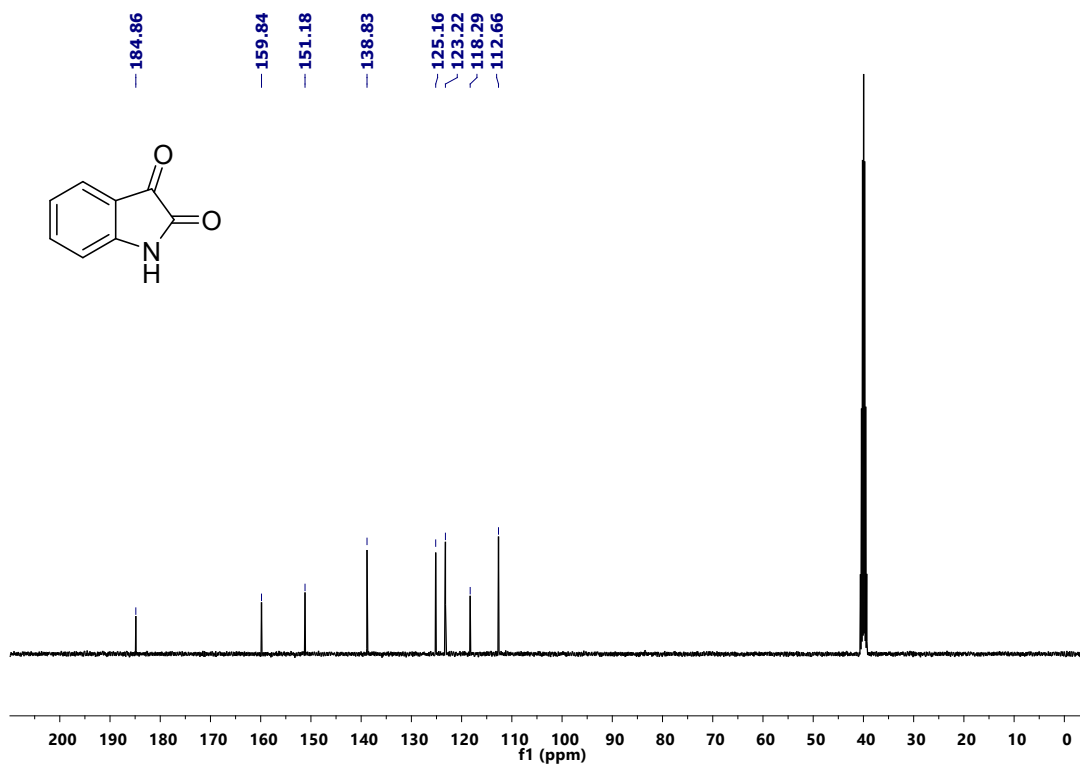
DEPT-135 NMR (101 MHz, DMSO- d₆) of **2u**



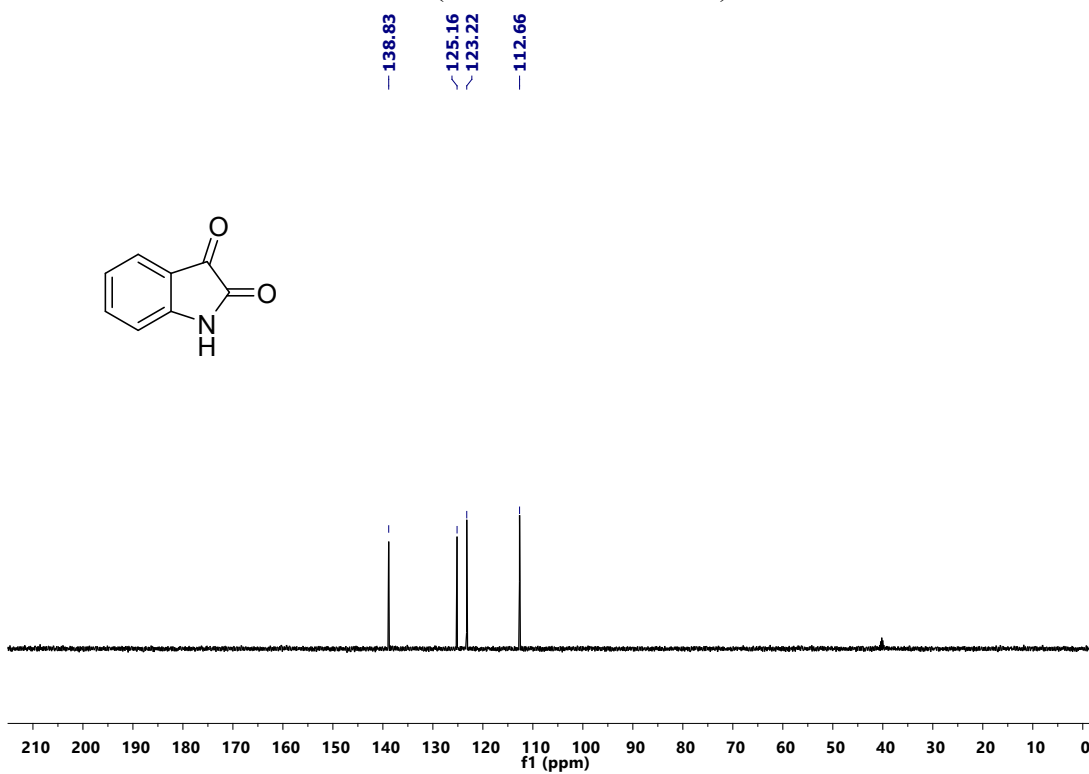
¹H NMR (400 MHz, DMSO- d₆) of **4a**



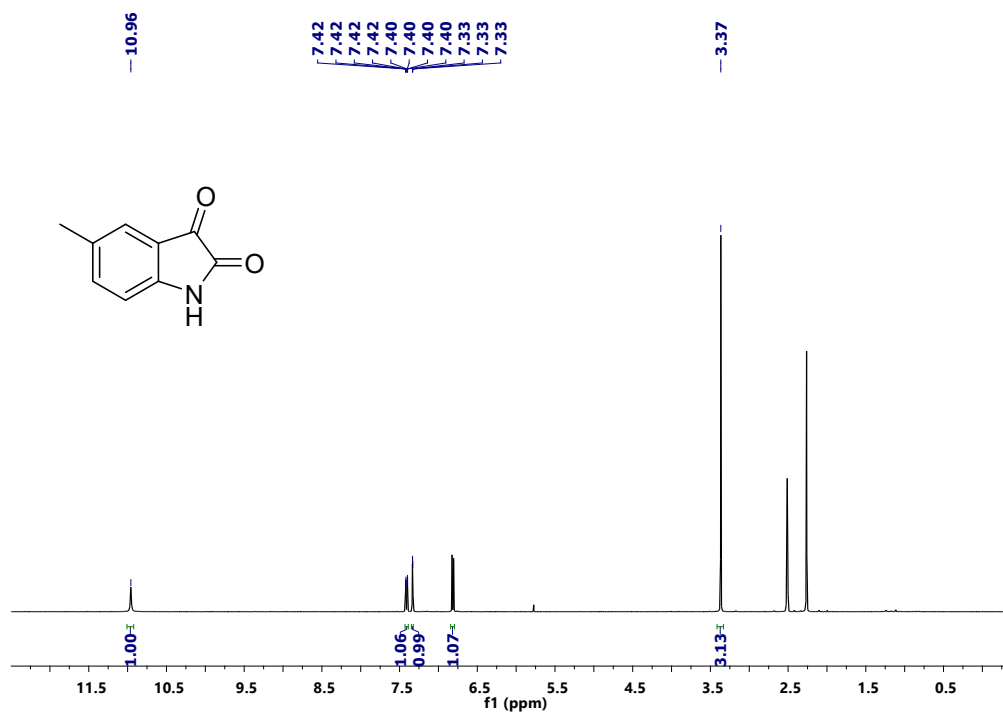
^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) of **4a**



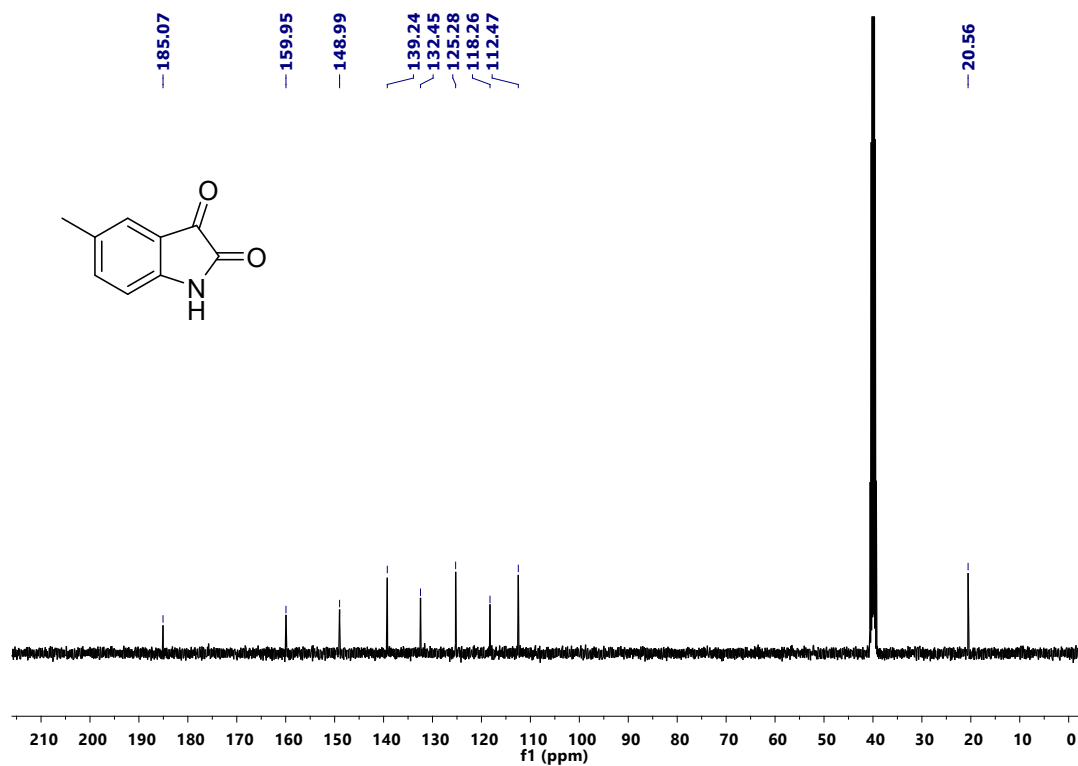
DEPT-135 NMR (101 MHz, $\text{DMSO-}d_6$) of **4a**



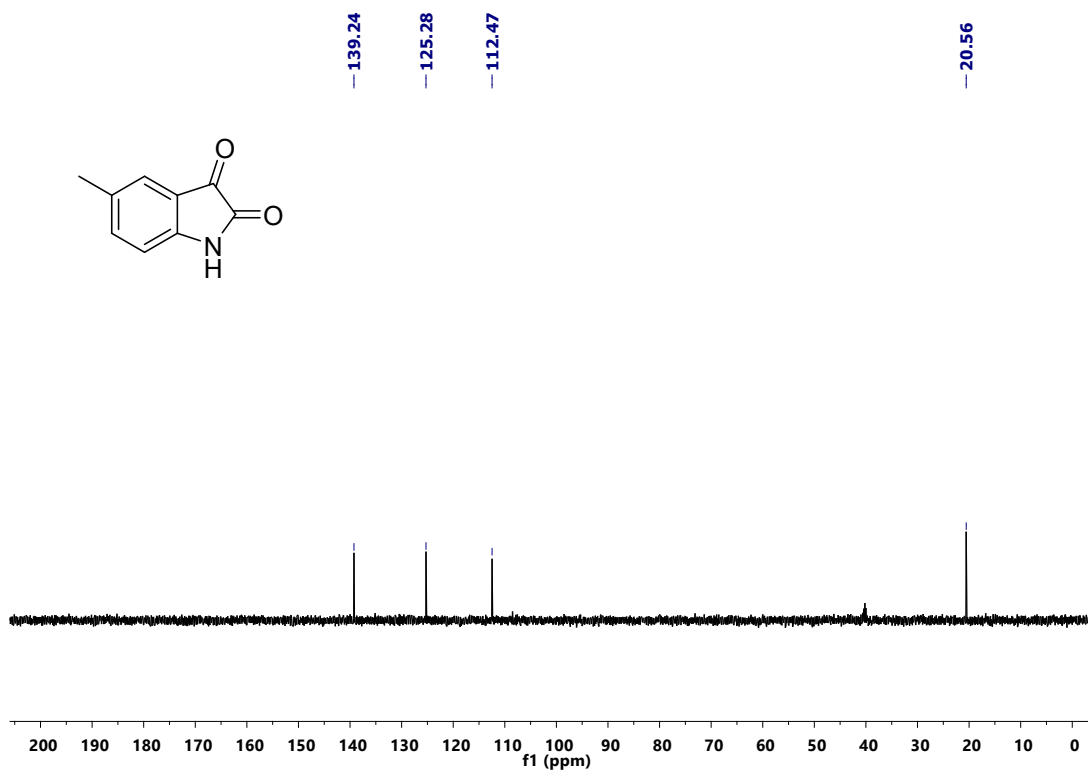
^1H NMR (400 MHz, $\text{DMSO-}d_6$) of **4b**



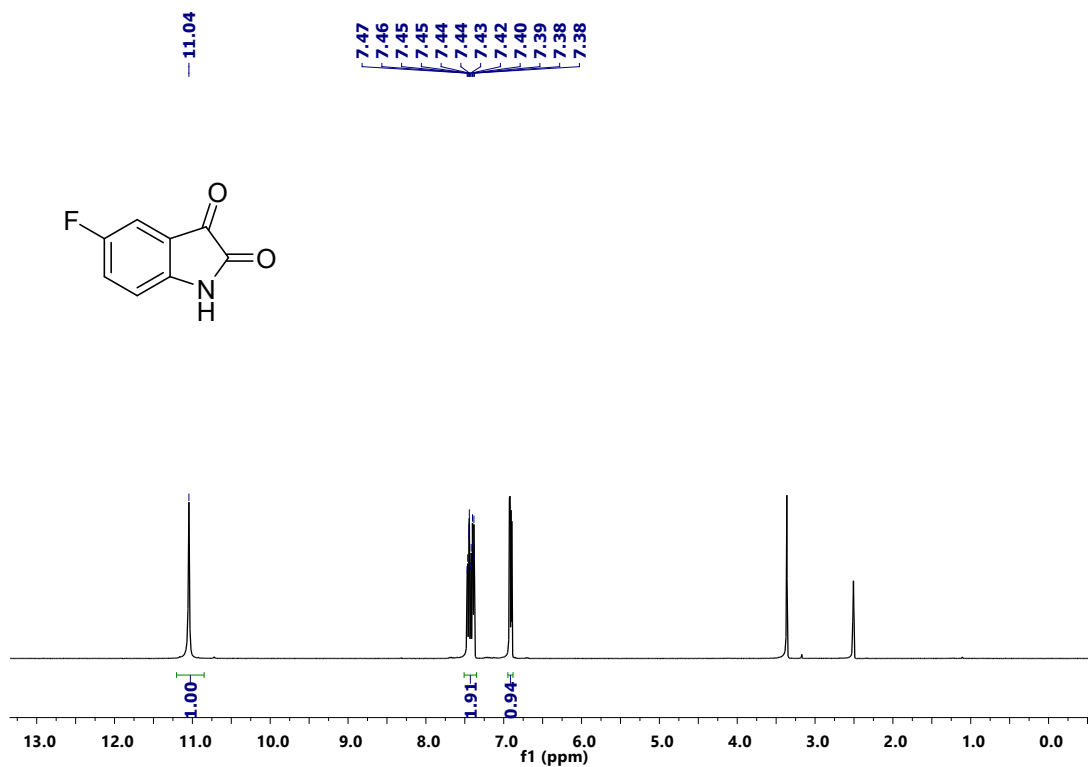
^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) of **4b**



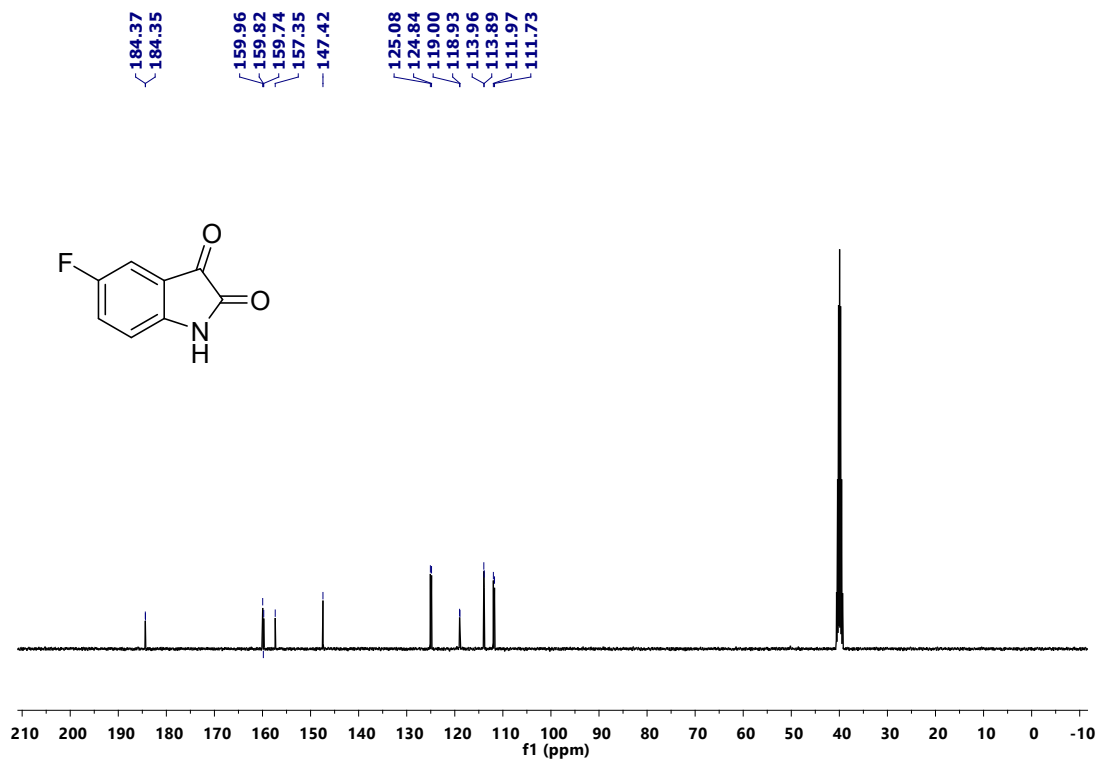
DEPT-135 NMR (101 MHz, DMSO- d₆) of **4b**



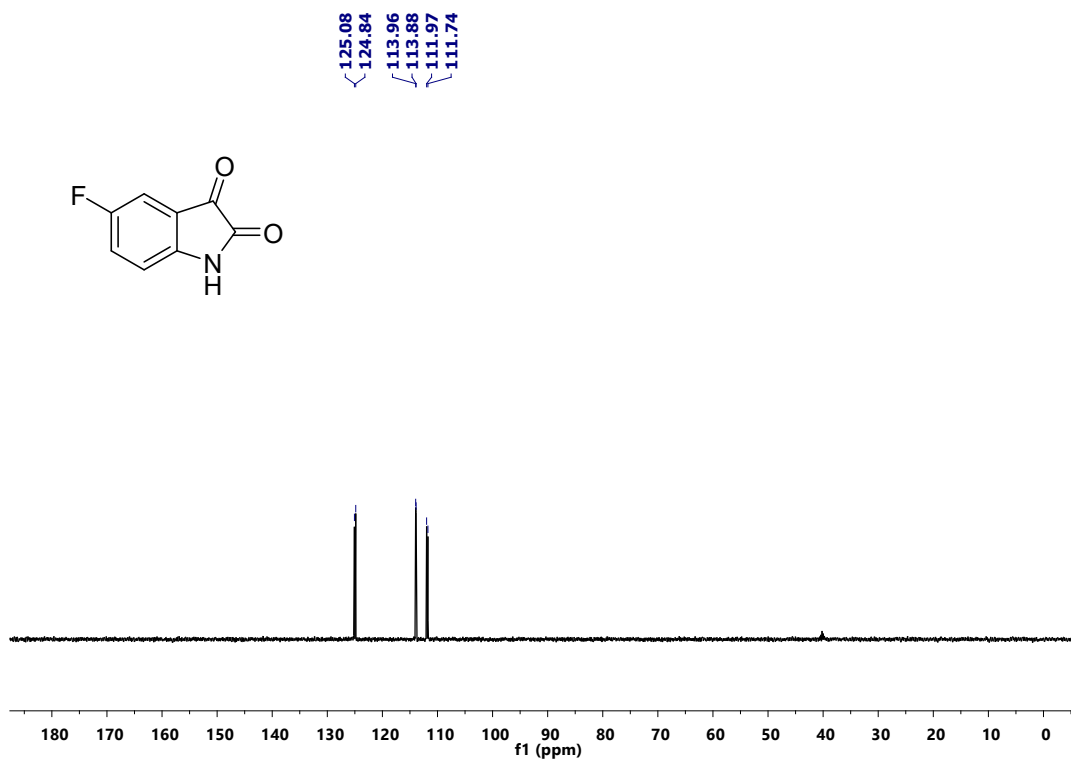
¹H NMR (400 MHz, DMSO- d₆) of **4c**



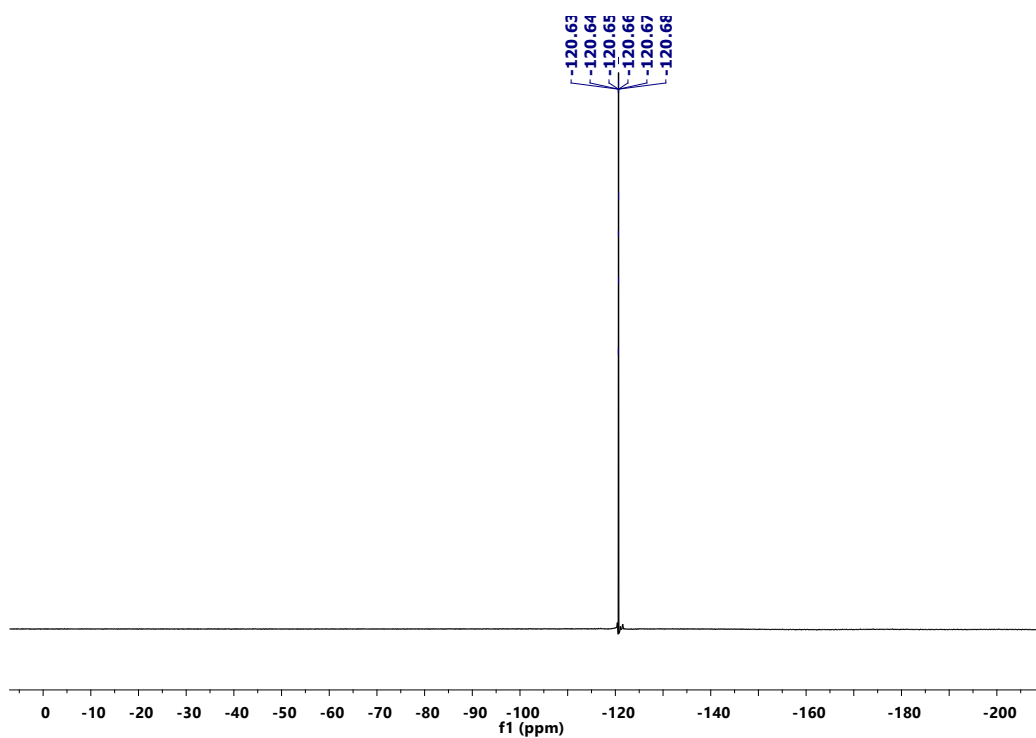
^{13}C NMR (400 MHz, DMSO- d_6) of **4c**



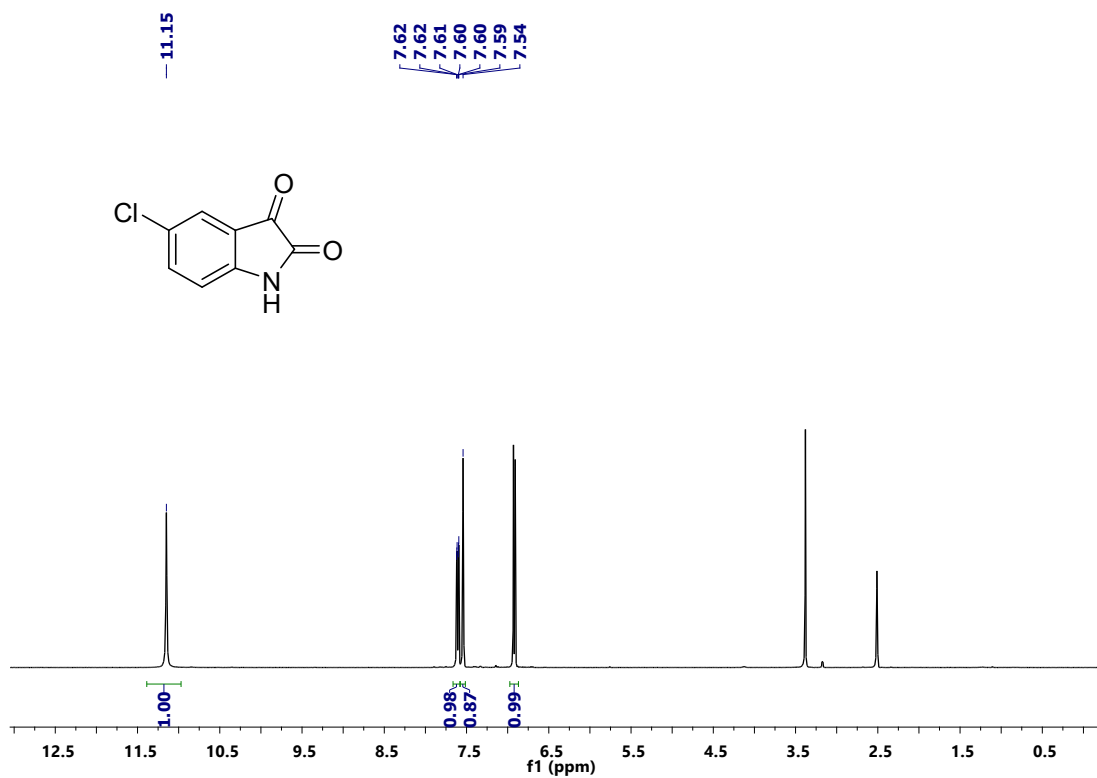
DEPT-135 NMR (101 MHz, DMSO- d_6) of **4c**



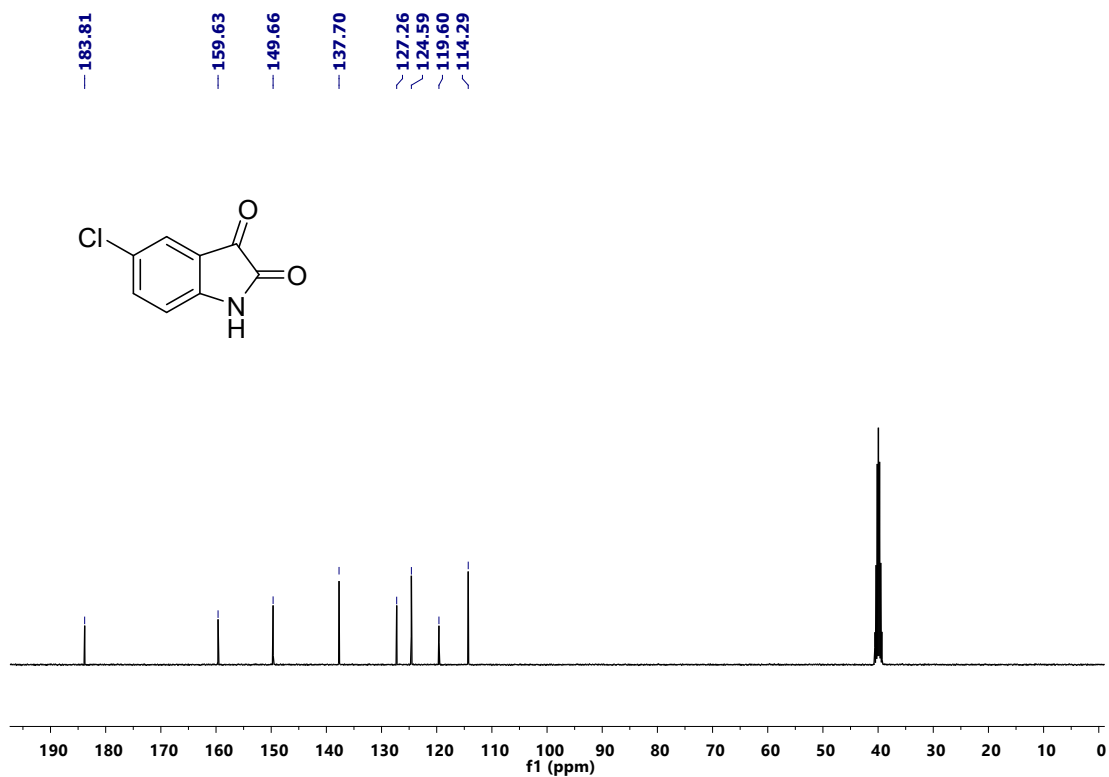
^{19}F NMR (377 MHz, DMSO-d_6) of **4c**



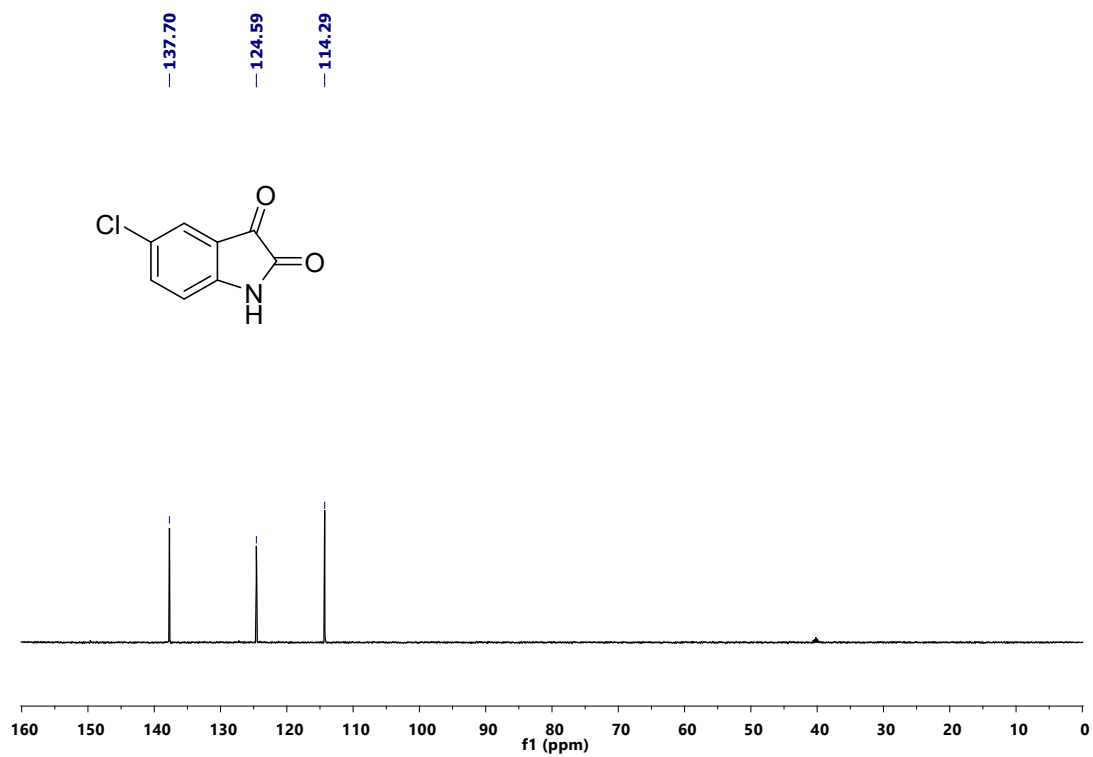
^1H NMR (400 MHz, DMSO-d_6) of **4d**



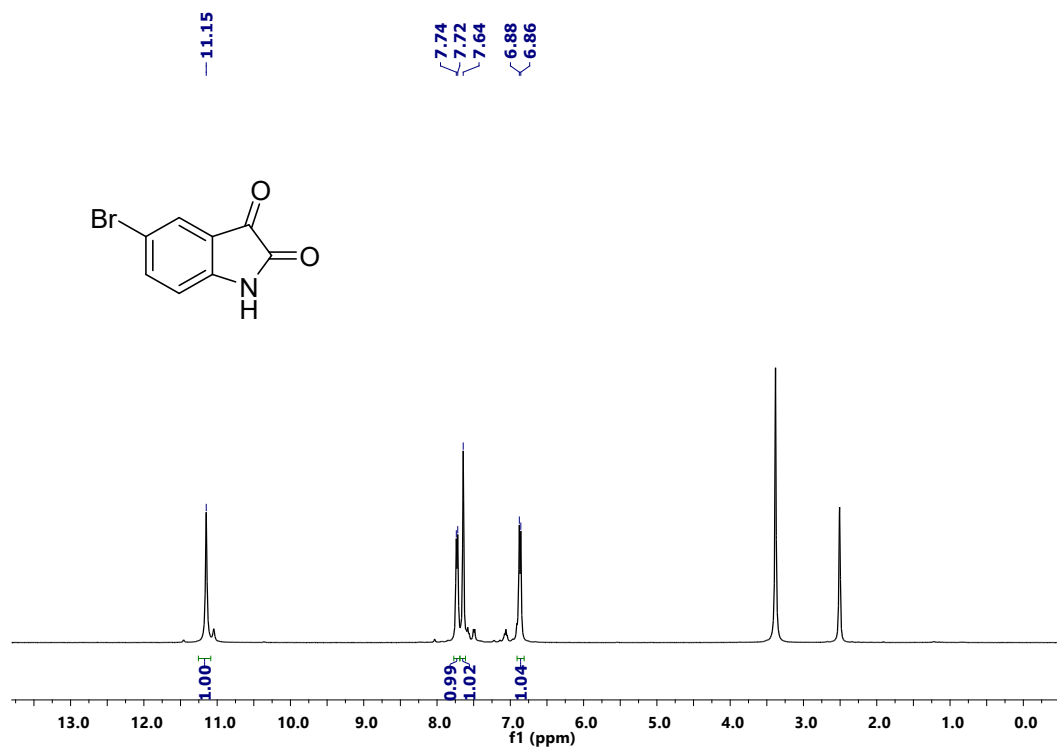
^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) of **4d**



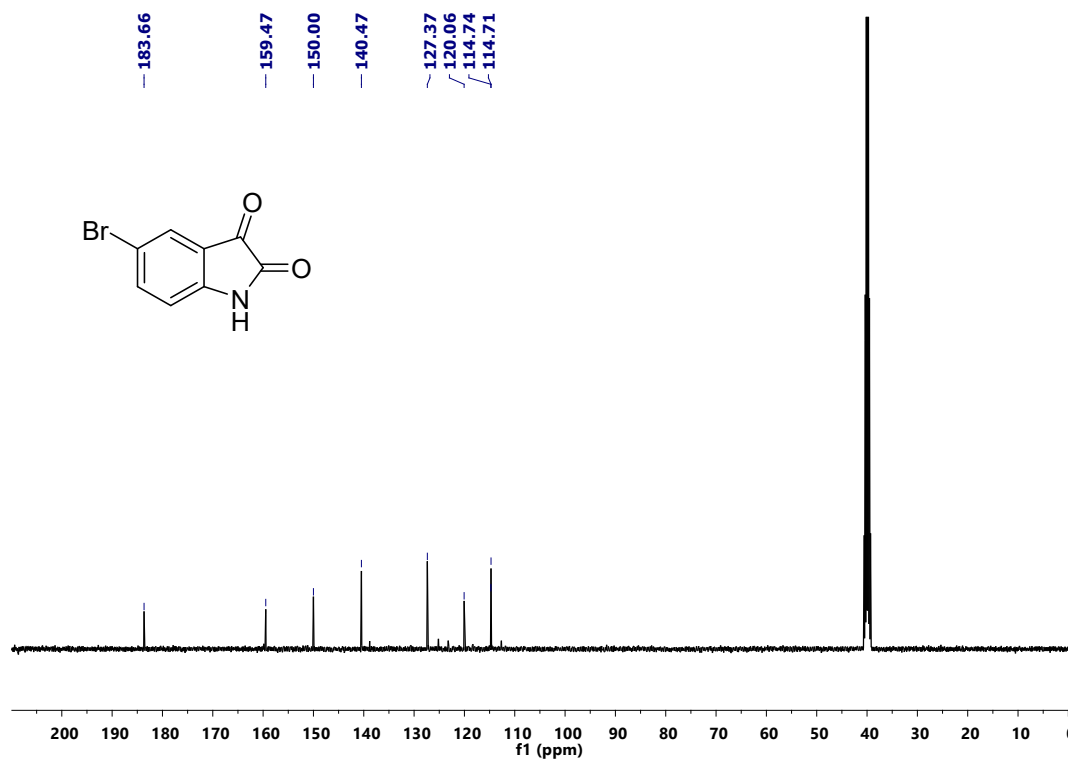
DEPT-135 NMR (101 MHz, $\text{DMSO-}d_6$) of **4d**



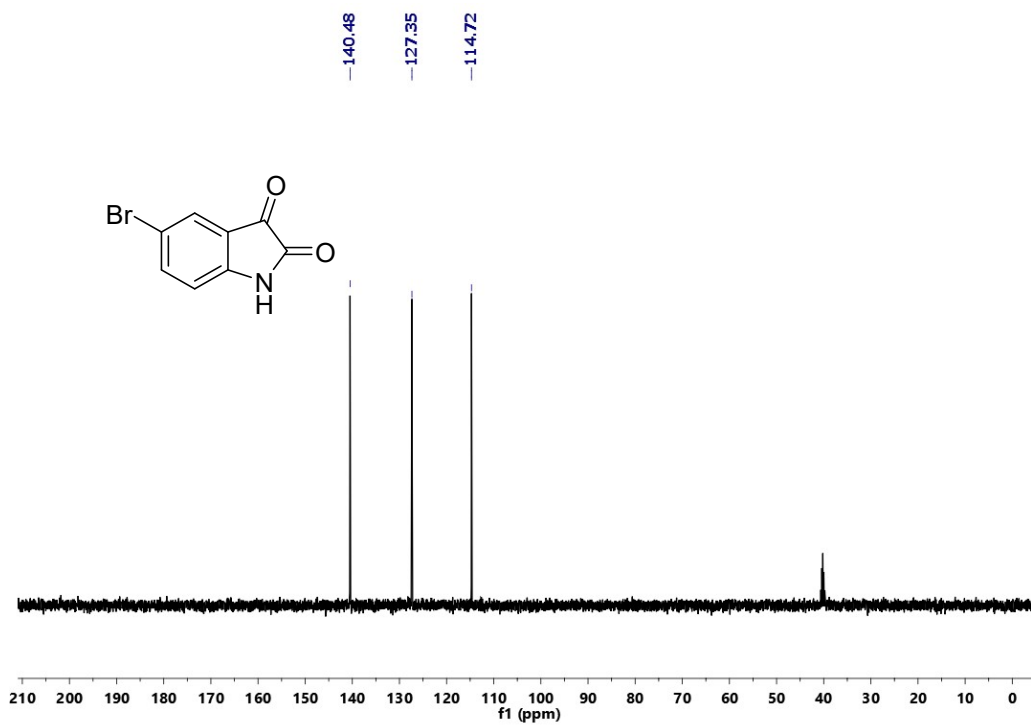
^1H NMR (400 MHz, DMSO- d_6) of **4e**



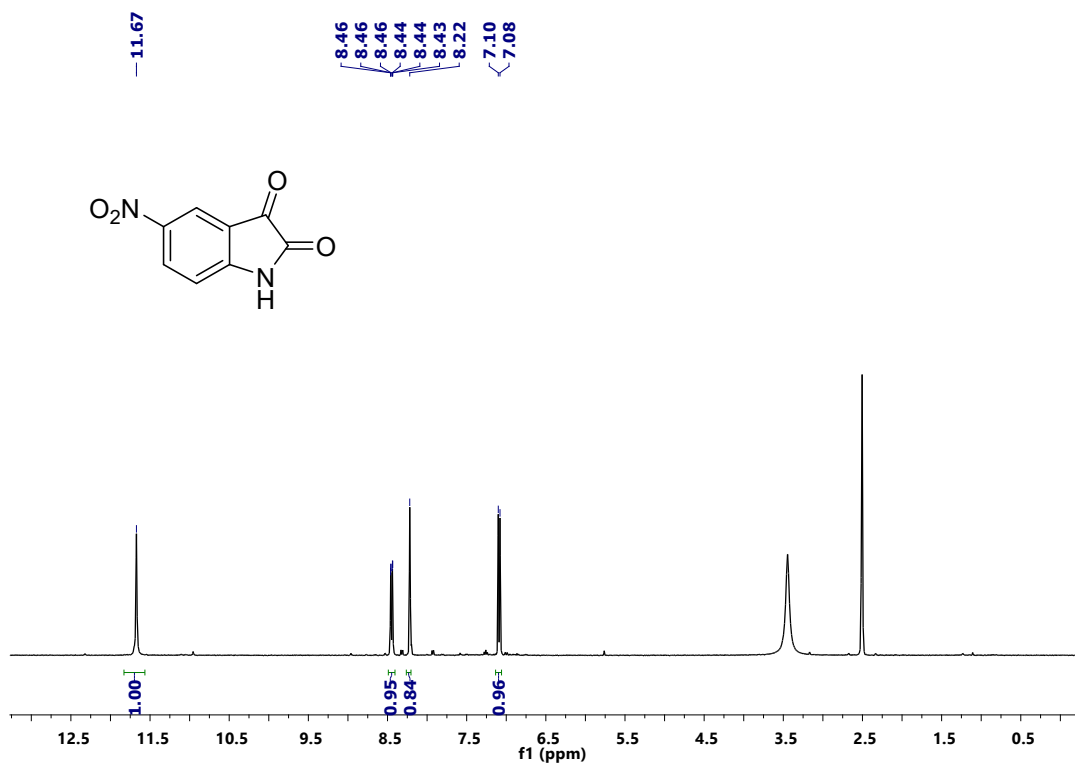
^{13}C NMR (400 MHz, DMSO- d_6) of **4e**



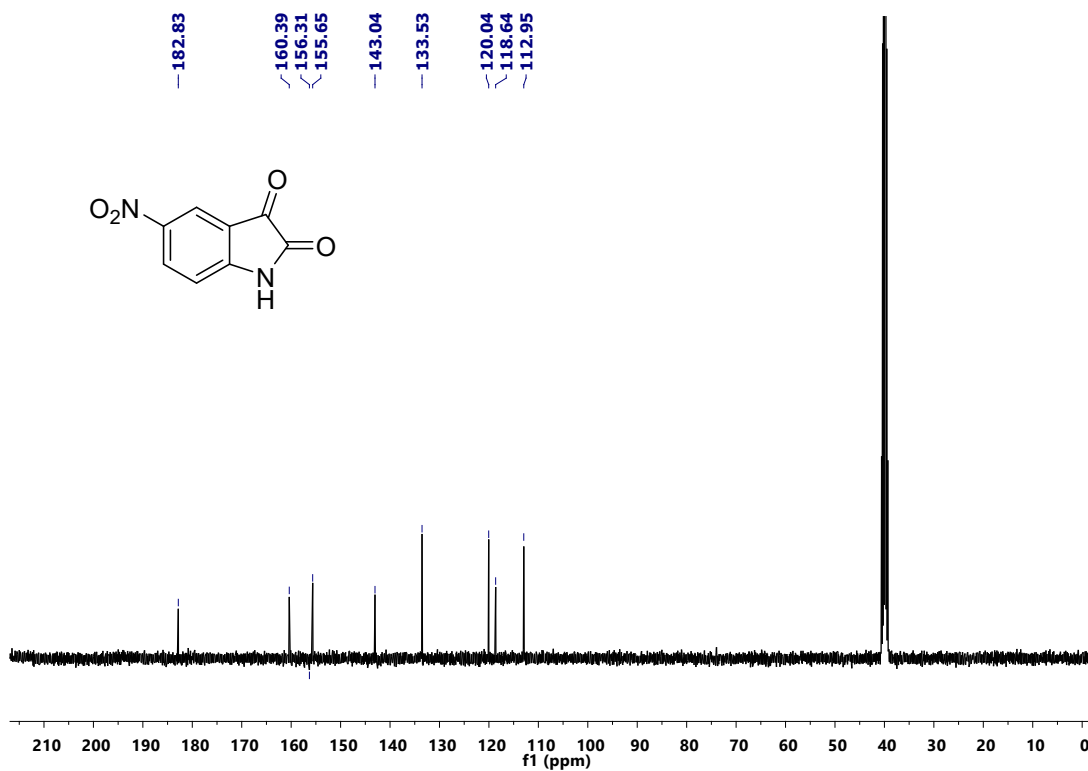
DEPT-135 NMR (101 MHz, DMSO- d₆) of **4e**



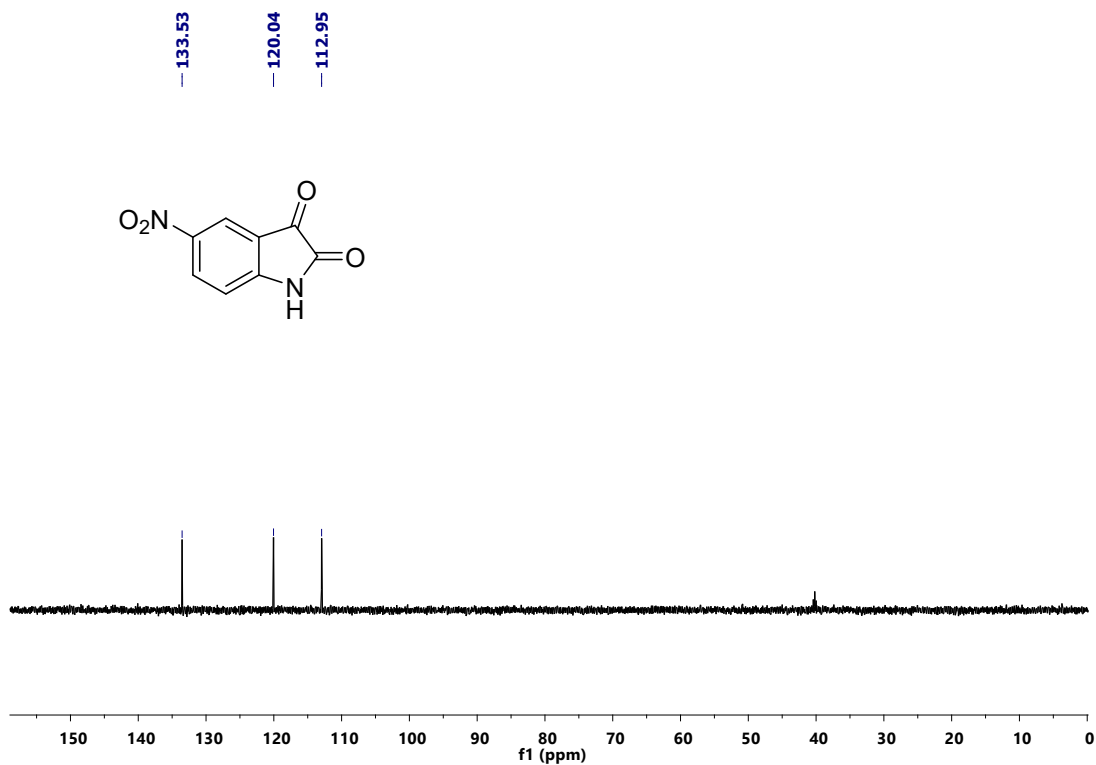
¹H NMR (400 MHz, DMSO- d₆) of **4f**



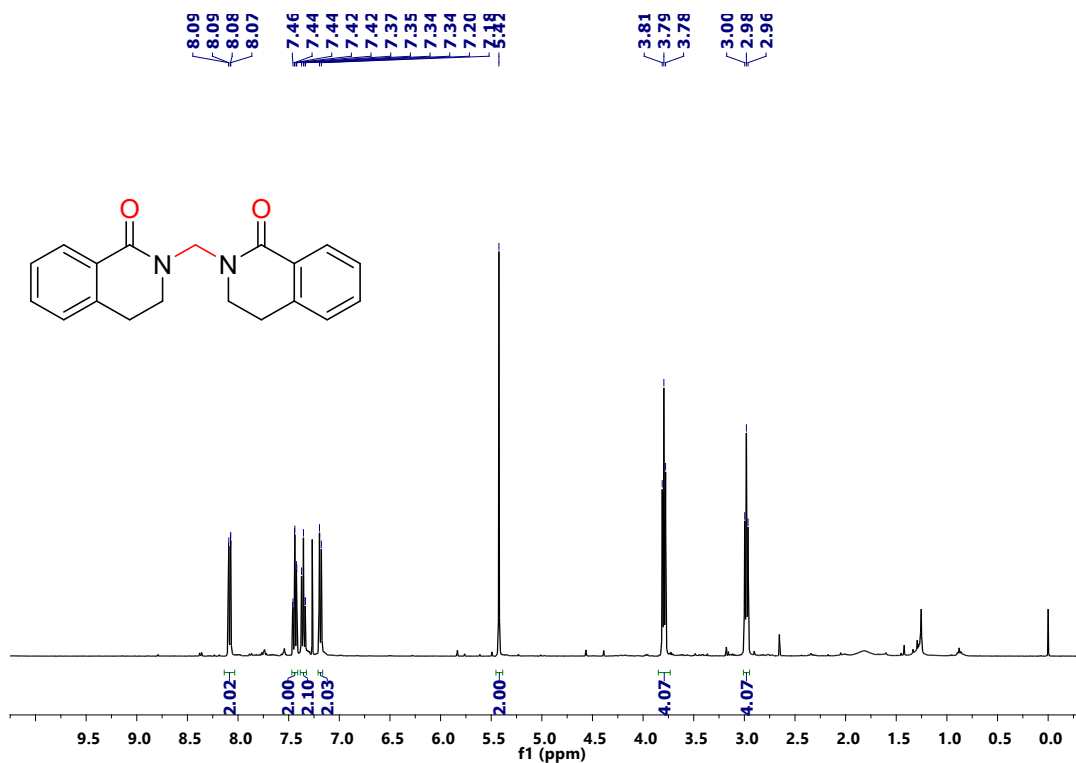
^{13}C NMR (400 MHz, DMSO- d_6) of **4f**



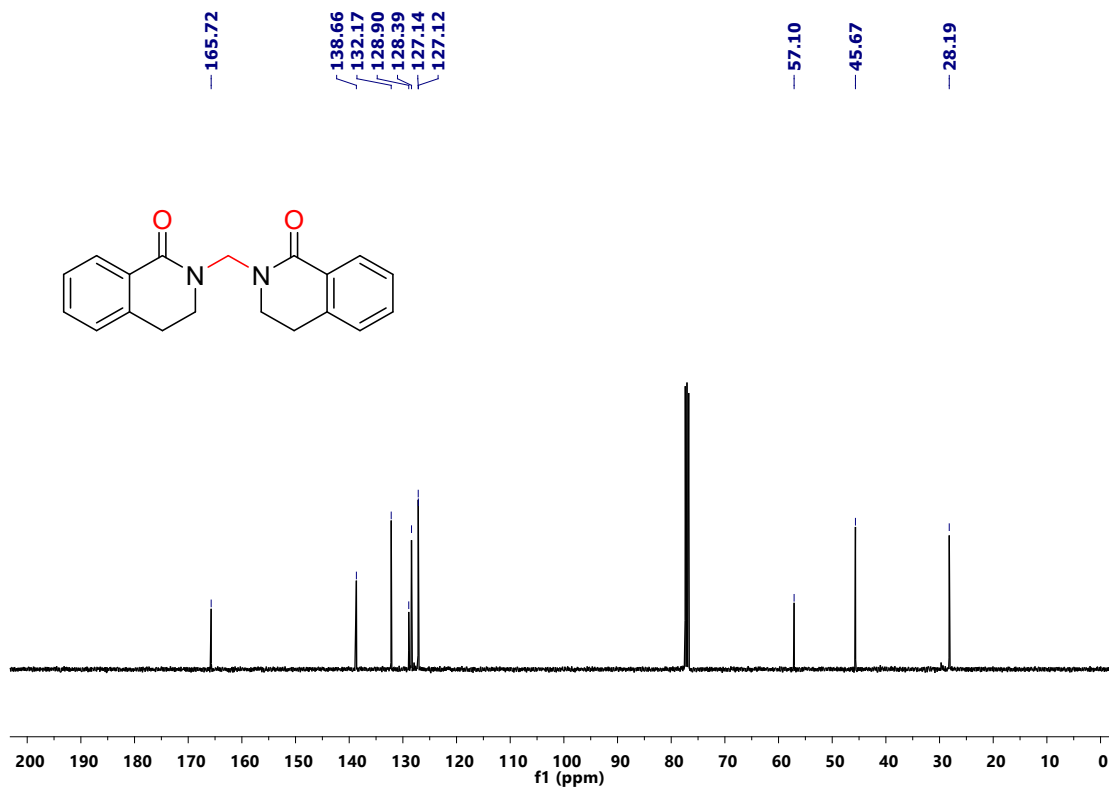
DEPT-135 NMR (101 MHz, DMSO- d_6) of **4f**



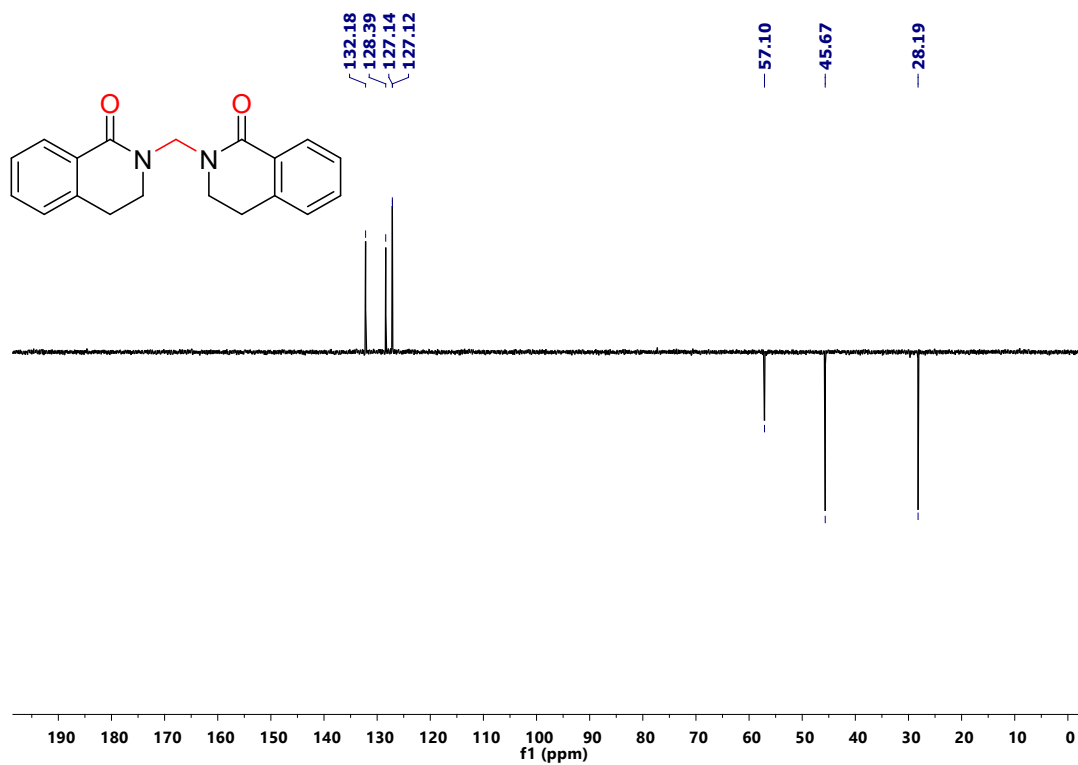
¹H NMR (400 MHz, CDCl₃) of 6



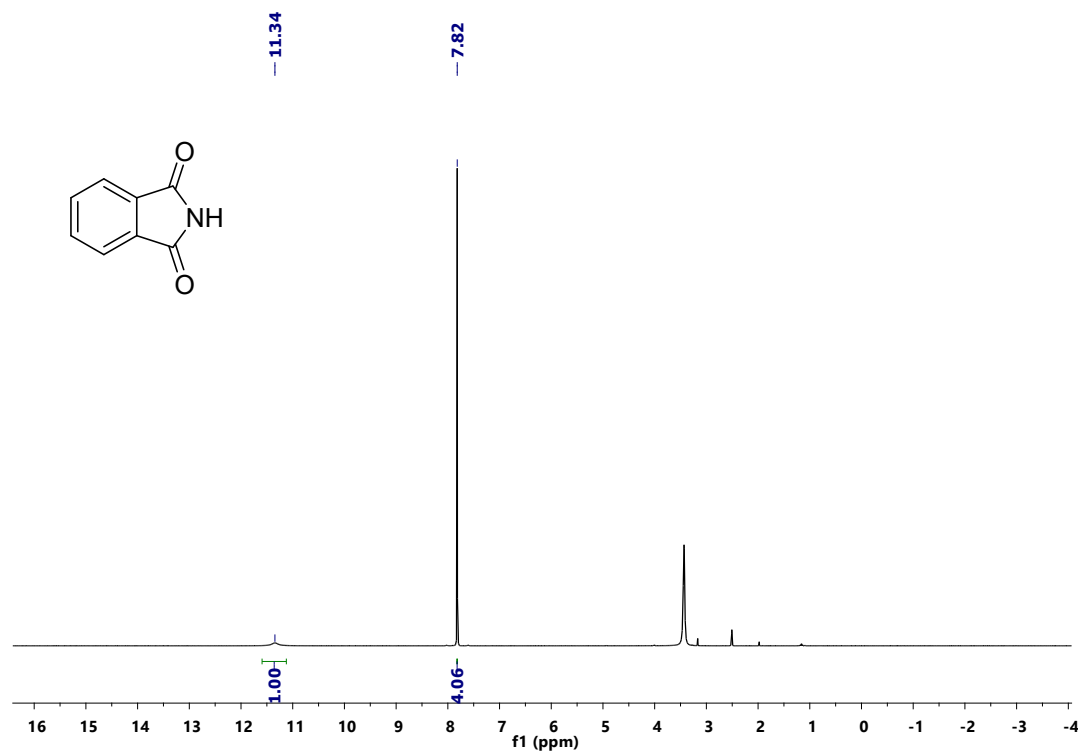
¹³C NMR (400 MHz, CDCl₃) of 6



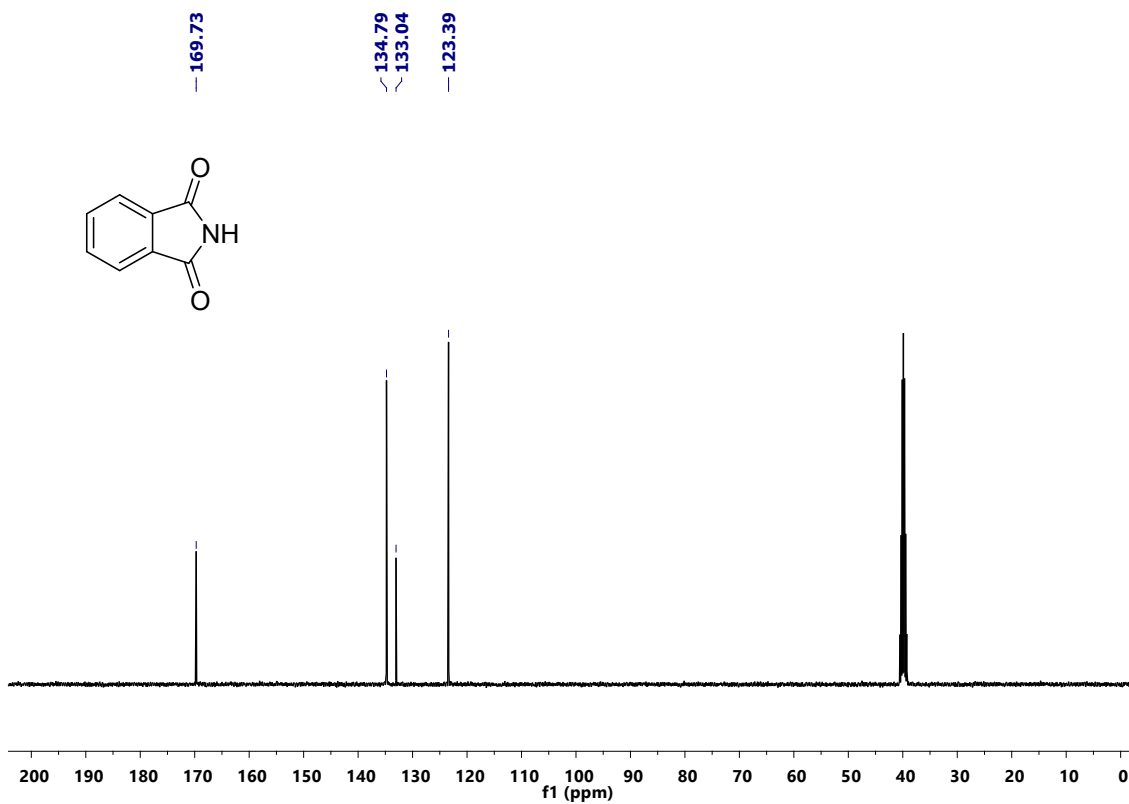
DEPT-135 NMR (101 MHz, CDCl₃) of **6**



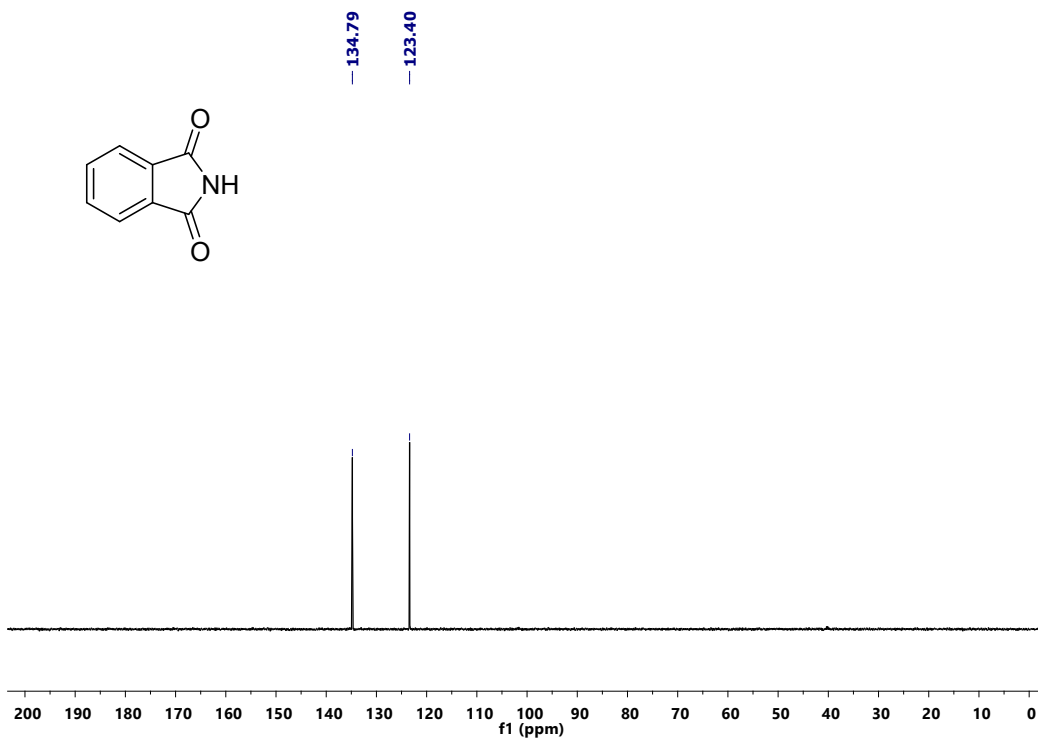
¹H NMR (400 MHz, DMSO- d₆) of **8**



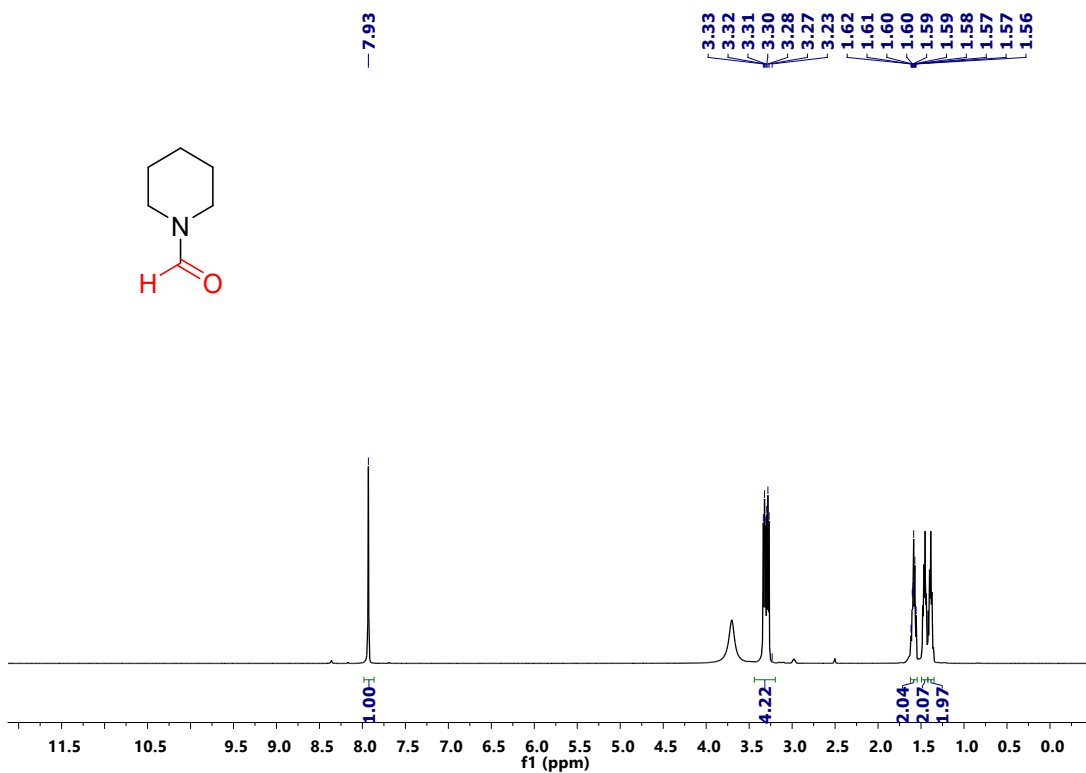
^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) of **8**



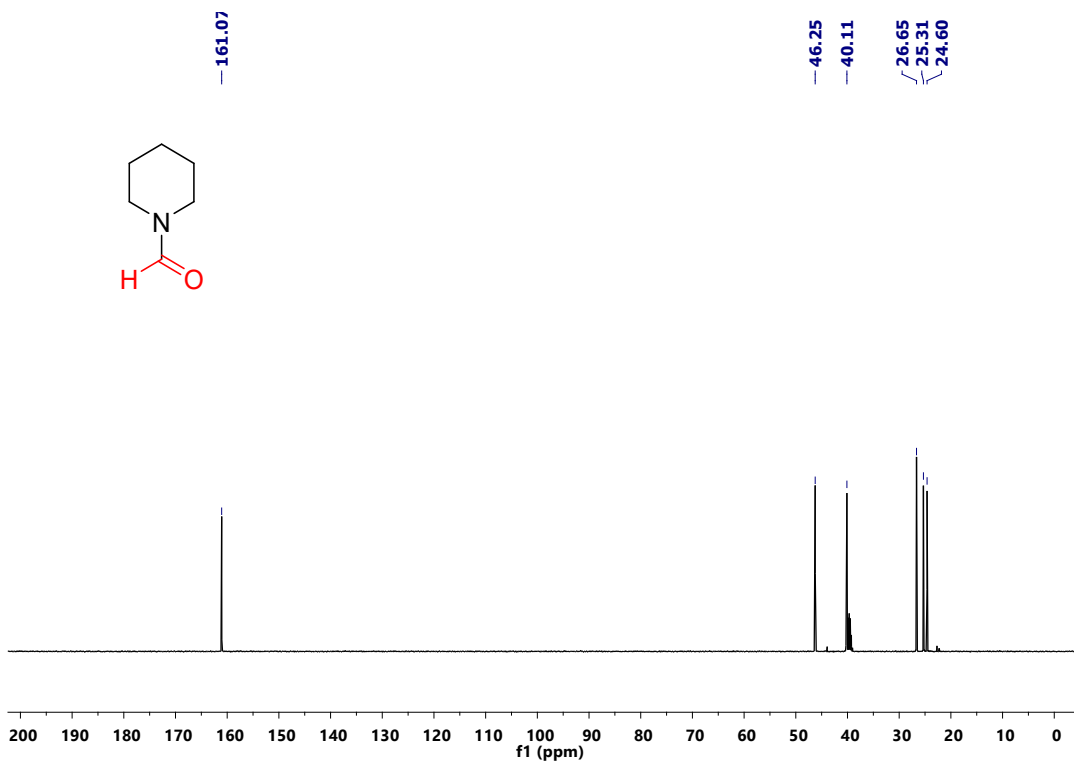
DEPT-135 NMR (101 MHz, $\text{DMSO-}d_6$) of **8**



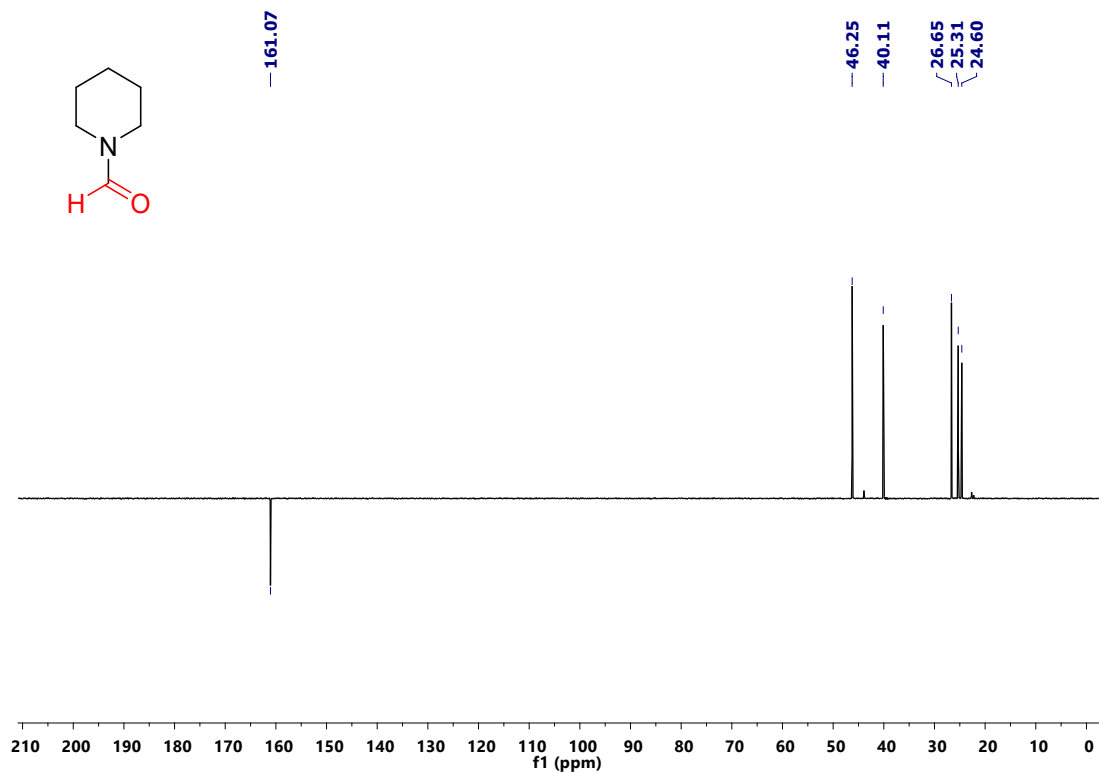
¹H NMR (400 MHz, DMSO- d₆) of **9**



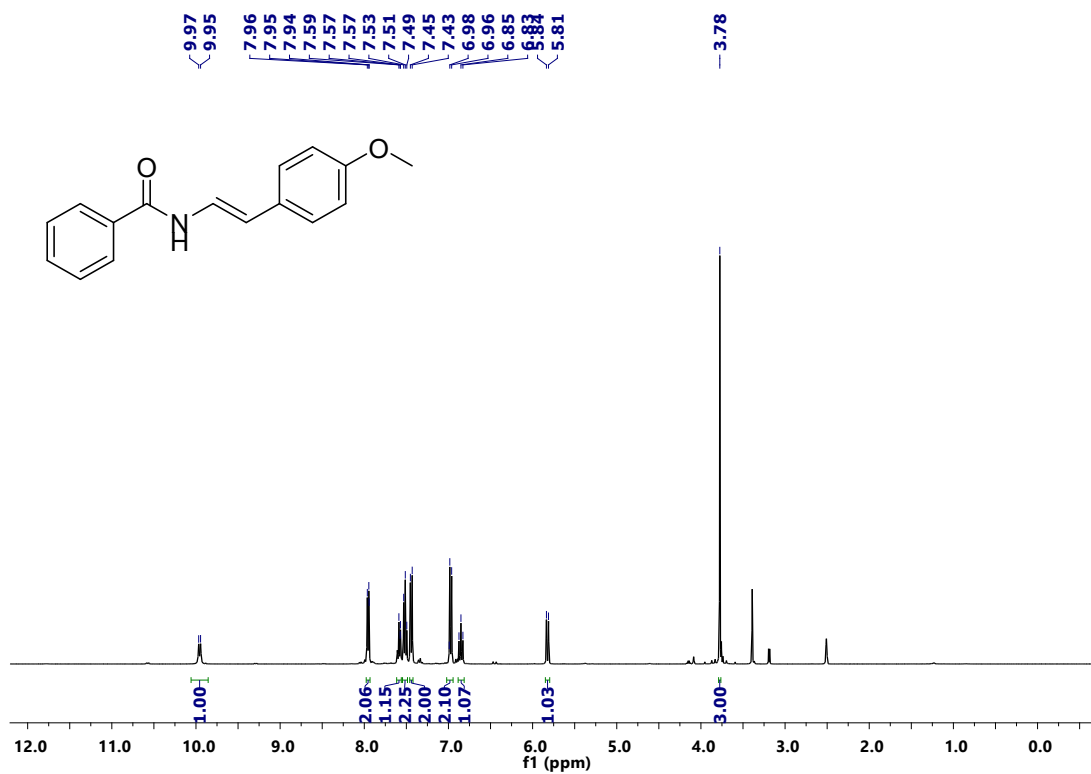
¹³C NMR (400 MHz, DMSO- d₆) of **9**



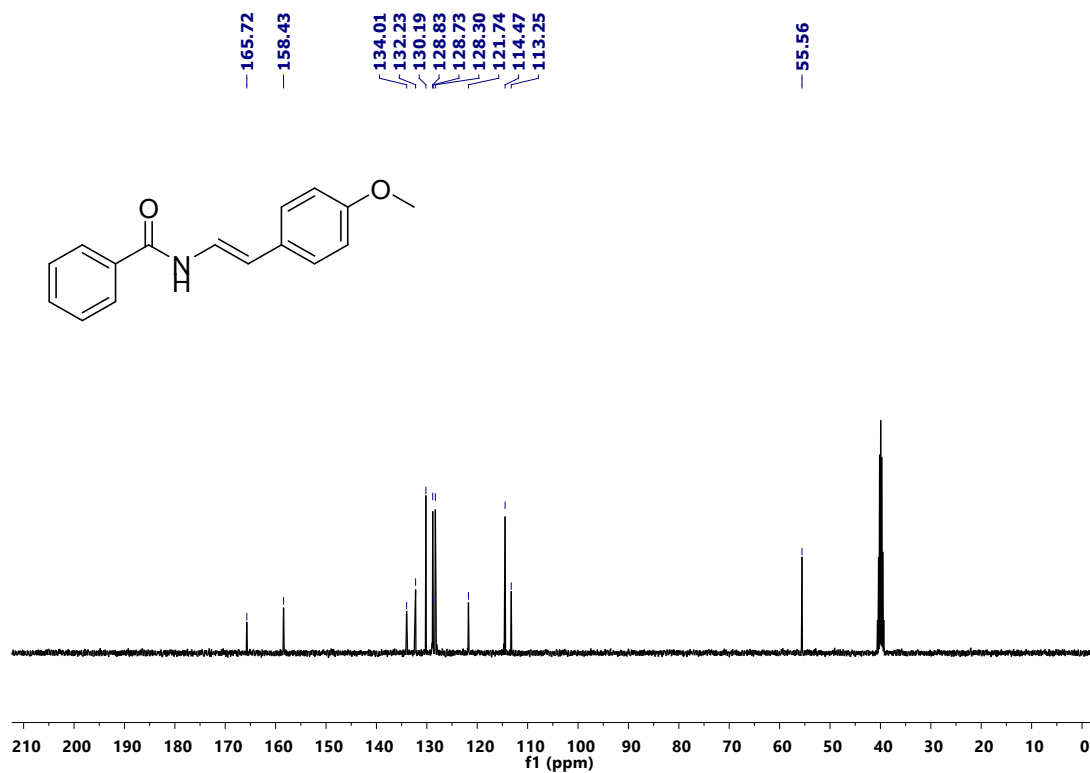
DEPT-135 NMR (101 MHz, DMSO- d₆) of **9**



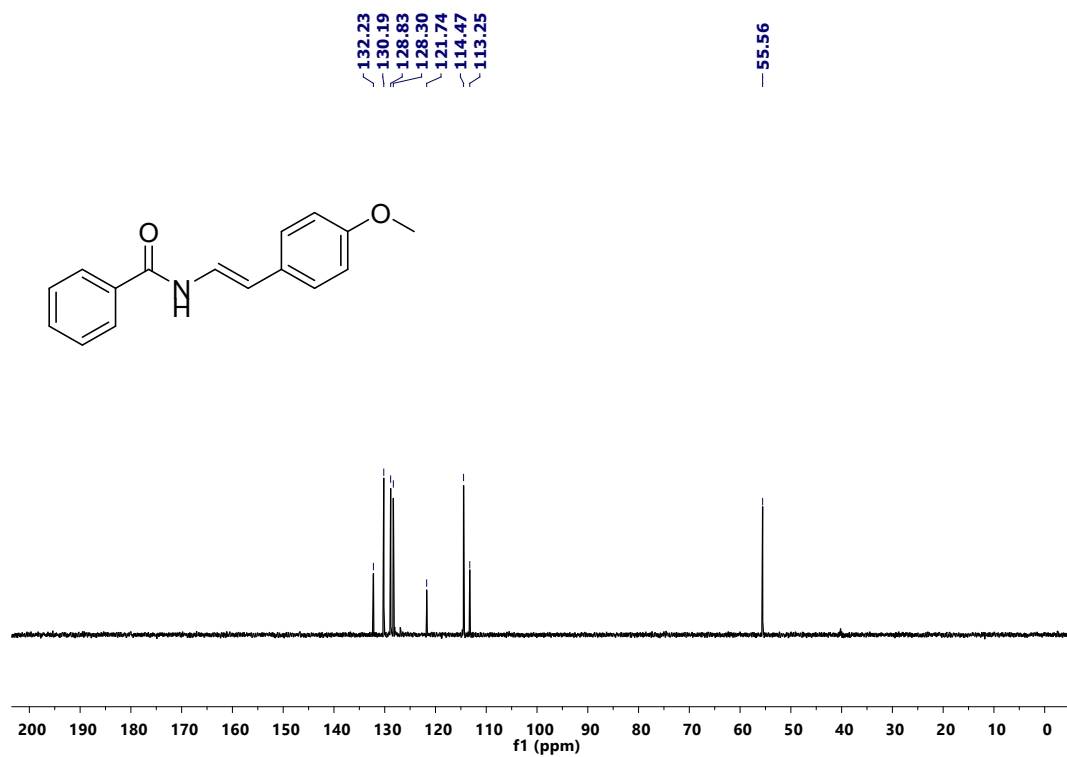
¹H NMR (400 MHz, DMSO- d₆) of **10**



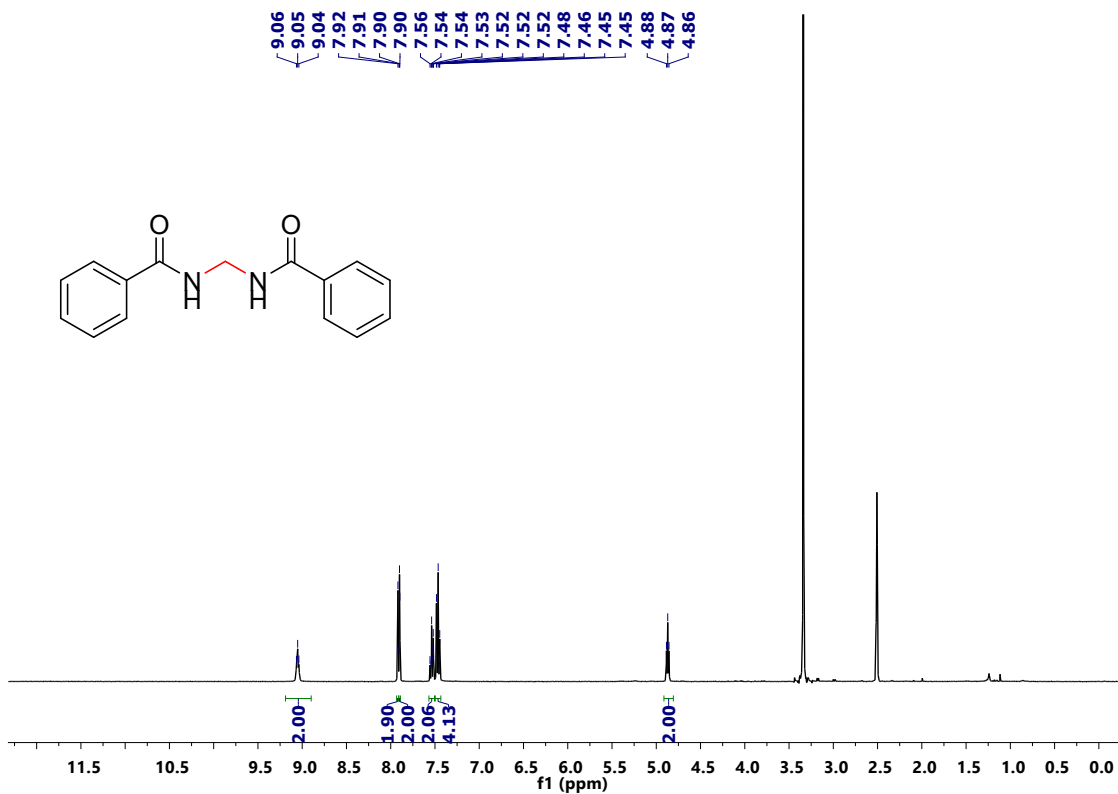
^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) of **10**



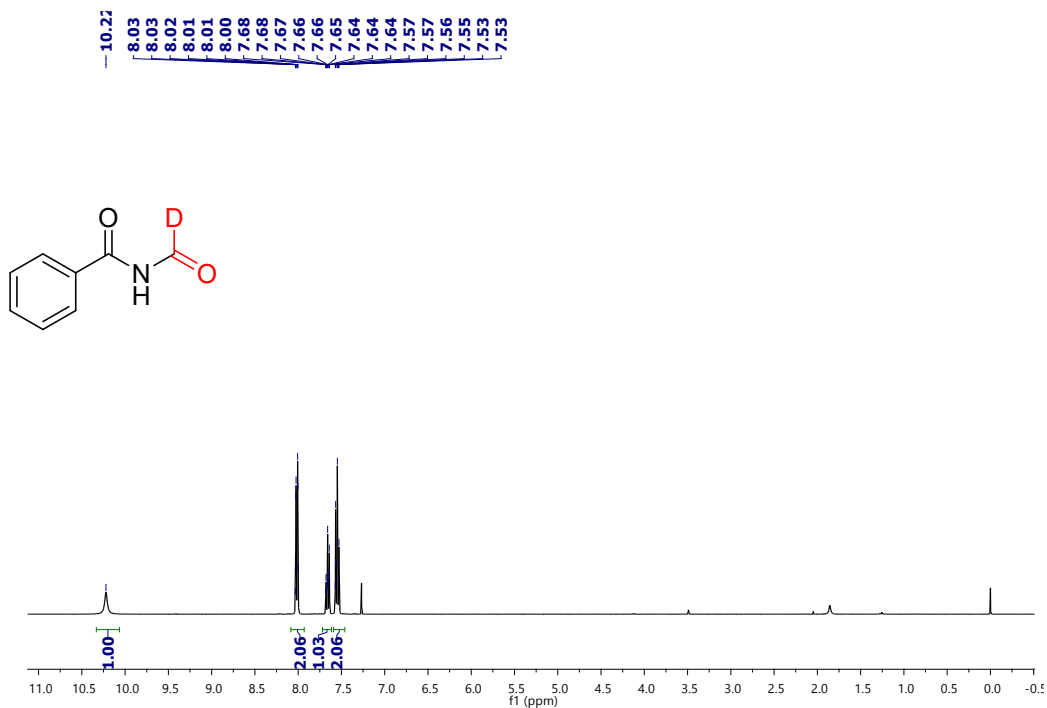
DEPT-135 NMR (101 MHz, $\text{DMSO-}d_6$) of **10**



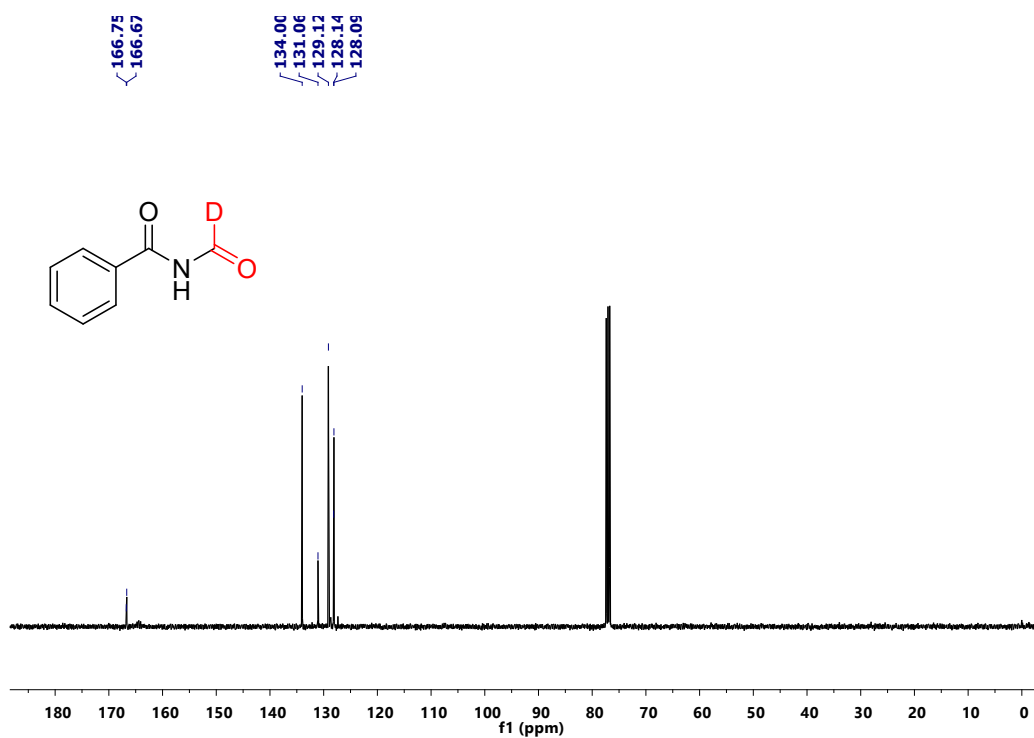
^1H NMR (400 MHz, $\text{DMSO-}d_6$) of **11**



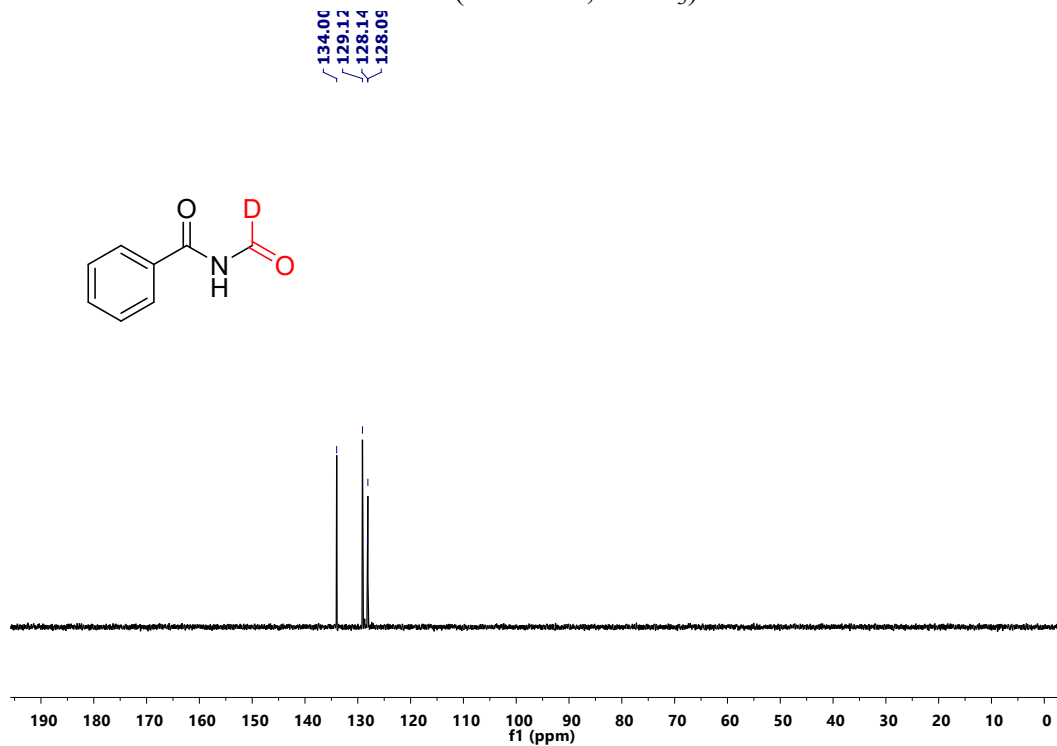
^1H NMR (400 MHz, CDCl_3) of **2a'**



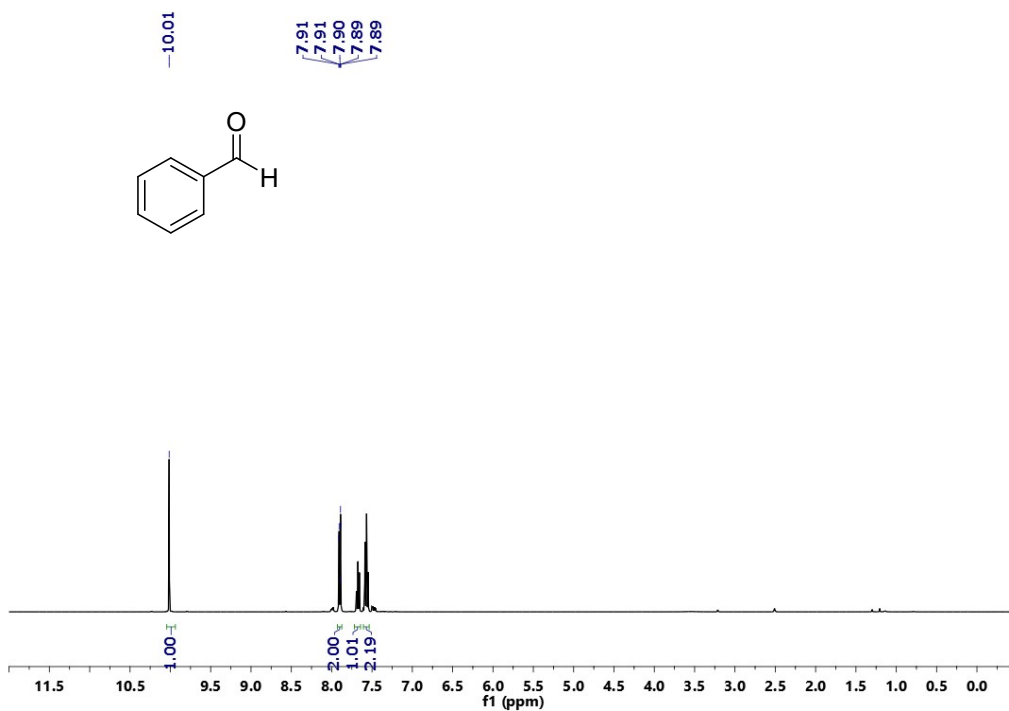
^{13}C NMR (400 MHz, CDCl_3) of **2a'**



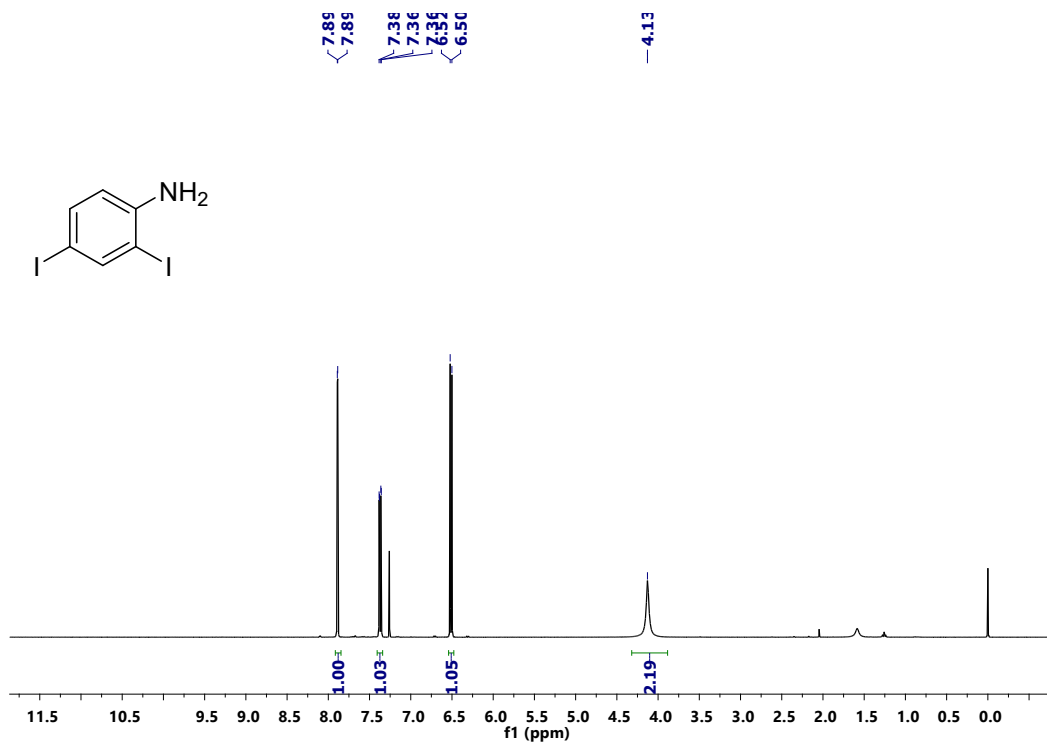
DEPT-135 NMR (101 MHz, CDCl_3) of **2a'**



^1H NMR (400 MHz, CDCl_3) of **14**



¹H NMR (400 MHz, CDCl₃) of 16



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