Supplementary Information (SI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2026

Supplementary Information

A Divergent Electrochemical Platform for Diazene Radical Generation and C–N Coupling Reactions

Roopam Pandey,[§,1] Suchismita Rath,[§,1] Yashika Tyagi,[1] Shivani Jadon,[1] Tejas Prabakar,[1] Shreemad Patel,[1] Debajit Maiti, and Subhabrata Sen*

[1]Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence Deemed to be University, Chithera, Dadri, Gautam Buddha Nagar, UP 201314, India.

Email: subhabrata.sen@snu.edu.in

Table of Contents

1. General information **S2**

2. Starting materials **S3**

3. General procedure for substituted 2-alkoxy-2-oxo-1-phenylethylidene hydrazine-1-carboxylate or substituted (2-isonicotinoylhydrazono)acetate **S4**

3.1 Characterization data S4-S15

3.2 XRD analysis S16-S17

4. General procedure for 2,5-dioxo-1-arylpyrrolidin-3-yl hydrazine-1-carboxylate **S18**

4.1 Characterization data S18-S21

5. Mechanistic investigation **S21-S24**

5.1 Divided cell experiment S21-S22

5.2 Radical trapping experiment S22-S23

5.3 Cyclic voltammetry experiment S24

6. NMR spectral data. **S25-S60**

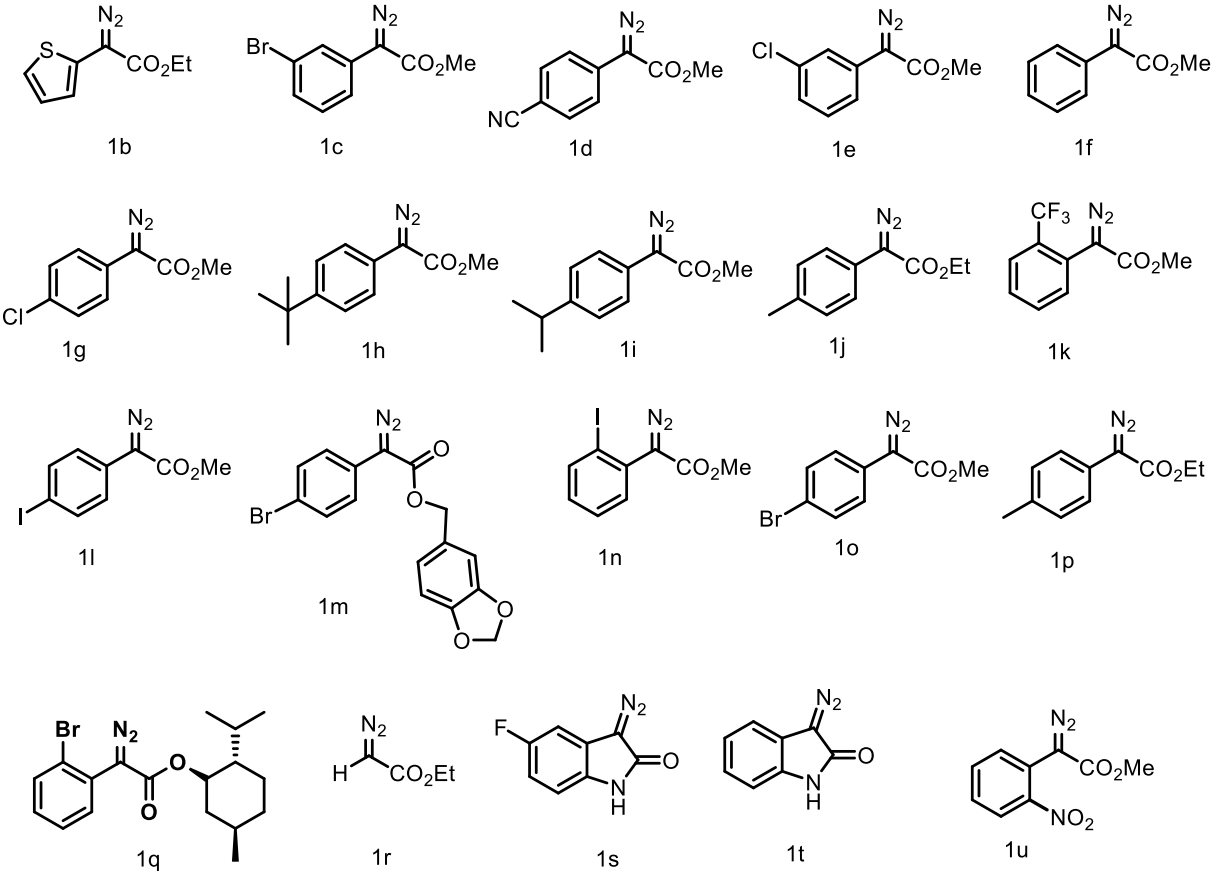
7. References **S61**

1. General experimental information

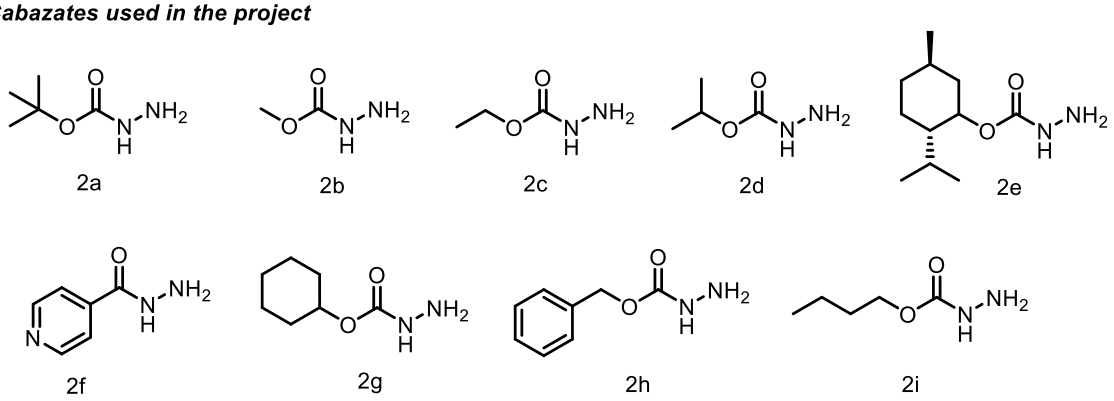
All electrochemical, electro-photochemical reactions and CV experiments were carried out using potentiostat Kanopy using volt-amperometric techniques and in IKA Electrasyn 2.0 and Orgel 1.0. 34W watt blue LED Kessil lamp were used as light source (wavelength was in range of 440-456 nm). Reactions were monitored through TLC by visualizing in UV detector. All purifications were done in silica gel (100-200 mesh size) column chromatography. All ^{1}H and ^{13}C NMR spectra were recorded taking tetramethylsilane (TMS) as an internal standard at ambient temperature unless otherwise indicated with Bruker 400 MHz instruments at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR spectroscopy. Splitting patterns are designated as singlet (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), quintet (quin), doublet of doublets (dd) and triplet of doublets (td). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Ultra-performance liquid chromatography (UPLC) was carried out using an Agilent 6540 accurate–mass Q-TOF LC/MS (Agilent Technologies, U.S.A.). MS analyses were performed under the following operation parameters: dry gas temperature 350°C, dry gas (N_2) flow rate 10 L/min, nebulizer pressure 30 psi, Vcap 4000 and fragmentor voltage 100 V. Mass spectra were acquired in the positive ion mode by scanning from 100 to 1500 in the mass to charge ratio (m/z). The mobile phase composition used for UHPLC–QTOF MS comprised of H_2O (A) and ACN (B), with optimized linear gradient elution. The injection volume was 5 µL. The flow rate was set at 0.3 mL/min. Accurate mass analysis calibration was carried out by ESI-low concentration tuning mix solution provided by Agilent technologies, U.S.A. All the chemicals required were purchased from Sigma-Aldrich, TCI; solvents from Finar, Rankem. Electrodes used were purchased from IKA and Amazon online shopping (10 mm diameter and 100 mm length which were cut into pieces for desired sizes). For CV reference electrode (non-aqueous reference electrode Ag/Ag^{+}), glassy carbon and platinum wire electrodes were purchased from CH Instruments, Inc.

2. Starting materials

Diazo compounds used in the project



Cabazates used in the project



Scheme 1. All aryl diazo compounds and carbazates used in this project

3. General procedure for substituted (2-alkoxy-2-oxo-1-phenylethylidene hydrazine-1-carboxylate) or substituted (2-isonicotinoylhydrazono)acetate

In an oven-dried electrochemical cell equipped with a magnetic stir bar, **carbazate/Isoniazid** (1 equiv, 100 mg), **aryl diazoacetate** (3 equiv), and **n-tetrabutylammonium hexafluorophosphate** (0.1 M) were dissolved in DMSO (6–8 mL). The cell was equipped with a platinum anode (+) and a carbon cathode (–) connected to an Orgel 1.0 instrument. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under an argon atmosphere at 50-55 °C with simultaneous irradiation using blue LEDs (456 nm) for 6–8 h. Upon completion, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on silica gel (100–200 mesh) using ethyl acetate/hexane as the eluent.

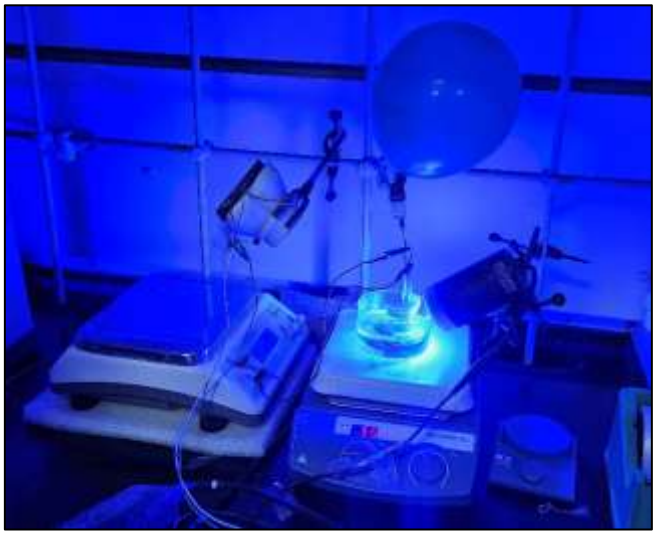
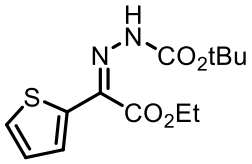
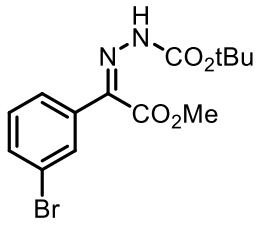


Figure 1. Direct current Electro-photochemical setup used in the experiments

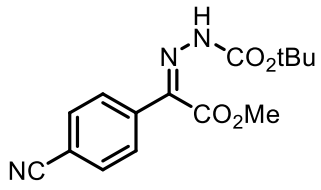
2.1 Characterization data



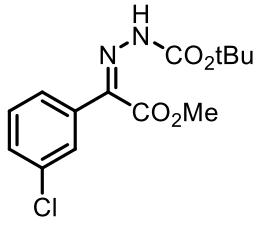
tert-butyl 1-2-(2-ethoxy-2-oxo-1-(thiophen-2-yl)ethylidene)hydrazine-1-carboxylate,3b : By following the above general procedure, the desired compound **3b** was synthesized from **2a** (0.76 mmol, 100 mg) and **1b** (2.27 mmol, 445.4 mg) in 178.34 mg , 79% yield as viscous pale solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.56 (s, 1H), 7.85 – 7.69 (m, 1H), 7.56 (d, *J* = 5.1 Hz, 1H), 7.24 (d, *J* = 3.0 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.54 (s, 9H), 1.43 (t, *J* = 7.0 Hz, 3H). **13C NMR** (100 MHz, CDCl3) δ 152.69, 136.07, 127.84, 125.73, 124.77, 123.00, 82.08, 62.13, 50.23, 29.71, 28.19, 14.09. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{13}H_{18}N_2O_4S$ 321.0879; found 321.0868.



tert-butyl (Z)-2-(1-(3-bromophenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3c : By following the above general procedure, the desired compound **3c** was synthesized from **2a** (0.76 mmol, 100 mg) and **1c** (2.27 mmol, 579 mg) in 191.89 mg , 71% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.55 (s, 1H), 7.77 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 1.55 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.70, 152.09, 132.07, 131.73, 129.64, 127.54, 122.25, 100.13, 82.64, 77.16, 52.78. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}BrN_2O_4$ 356.0372; found 379.0270.

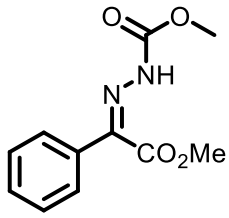


tert-butyl (Z)-2-(1-(4-cyanophenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3d : By following the above general procedure, the desired compound **3d** was synthesized from **2a** (0.76 mmol, 100 mg) and **1d** (2.27 mmol, 456.7 mg) in 183.60 mg , 80% yield as viscous pale solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.65 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 3.91 (s, 3H), 1.55 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.36, 151.84, 139.31, 131.92, 129.46, 118.73, 112.49, 82.96, 77.16, 52.85, 28.24. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{15}H_{17}N_3O_4$ 326.1111; found 326.1103.

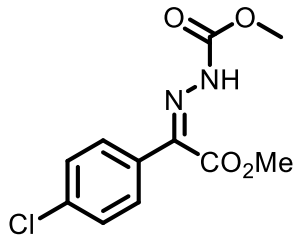


tert-butyl (Z)-2-(1-(3-chlorophenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3e : By following the above general procedure, the desired compound **3e** was synthesized from **2a** (0.76 mmol, 100 mg) and **1e** (2.27 mmol, 478.1 mg) in 172.75 mg , 73% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H**

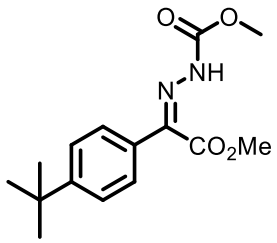
NMR (400 MHz, Chloroform-*d*) δ 11.55 (s, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 3.90 (s, 3H), 1.55 (s, 8H). **13C NMR** (100 MHz, $CDCl_3$) δ 162.40, 151.76, 136.38, 133.85, 129.07, 128.84, 128.58, 126.74, 82.30, 77.16, 52.42, 27.99, 27.89. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}ClN_2O_4$ 335.0769; found 335.0750.



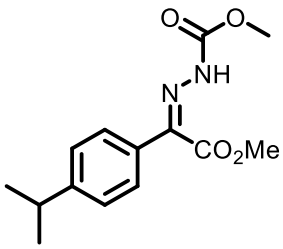
Methyl (Z)-2-(2-methoxy-2-oxo-1-phenylethylidene)hydrazine-1-carboxylate,3a : By following the above general procedure, the desired compound **3a** was synthesized from **2b** (1.11 mmol, 100 mg) and **1a** (3.33 mmol, 586.7 mg) in 212.38 mg , 81% yield as white oil from the crude via column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.14 (s, 1H), 7.56 – 7.49 (m, 3H), 7.29 – 7.27 (m, 2H), 3.88 (d, J = 8.0 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 165.7, 159.7, 157.2, 129.5, 129.5, 128.7, 128.6, 124.7, 124.7, 115.8, 115.6, 113.9, 113.8, 52.7, 52.2 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{11}H_{13}N_2O_4$ 237.0870; found 237.0846.



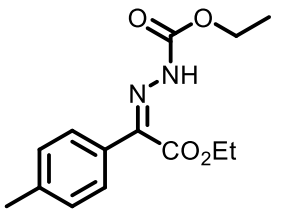
methyl (Z)-2-(1-(4-chlorophenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3f : By following the above general procedure, the desired compound **3f** was synthesized from **2b** (1.11 mmol, 100 mg) and **1f** (3.33 mmol, 701.4 mg) in 240.34 mg, 80% yield as white oil from the crude via column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.09 (s, 1H), 7.52 (d, J = 8 Hz, 2H), 7.23 (d, J = 8 Hz, 2H), 3.88 (d, J = 4.0 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 165.4, 160.2, 147.1, 146.7, 145.6, 131.6, 129.2, 127.6, 125.2, 124.2, 53.5, 52.2 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}ClN_2O_4$ 271.0480; found 271.0455.



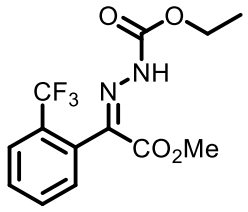
methyl (Z)-2-(1-(4-(tert-butyl)phenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3g : By following the above general procedure, the desired compound **3g** was synthesized from **2b** (1.11 mmol, 100 mg) and **1g** (3.33 mmol, 773.57 mg) in 256.34 mg, 79% yield as white oil from the crude via column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.54 (d, J = 8 Hz, 2H), 7.21 (d, J = 8 Hz, 2H), 3.88 (d, J = 8 Hz, 6H), 1.35 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 165.9, 150.0, 149.1, 131.0, 128.9, 126.0, 125.6, 124.1, 122.2, 52.7, 52.0, 34.5, 31.4 ppm**. HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}N_2O_4$ 293.1496; found 271.1479.



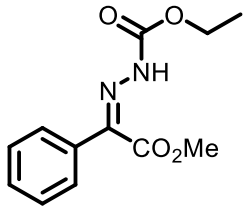
methyl (Z)-2-(1-(4-isopropylphenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3h : By following the above general procedure, the desired compound **3h** was synthesized from **2b** (1.11 mmol, 100 mg) and **1h** (3.33 mmol, 726.85 mg) in 262.57 mg, 85% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.38 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 3.88 (d, J = 8 Hz, 6H), 2.30-1.93 (m, 1H), 1.29 (d, J = 4 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 147.2, 146.6, 135.9, 130.7, 129.5, 128.0, 127.9, 127.5, 127.0, 124.7, 122.8, 53.0, 52.3, 34.1, 24.3 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}N_2O_4$ 279.1339; found 279.1304.



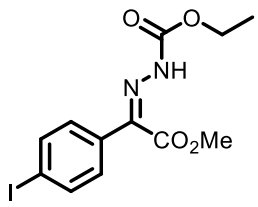
ethyl (Z)-2-(2-ethoxy-2-oxo-1-(p-tolyl)ethylidene)hydrazine-1-carboxylate, 3i : By following the above general procedure, the desired compound **3i** was synthesized from **2c** (0.96 mmol, 100 mg) and **1j** (2.88 mmol, 588.53 mg) in 224.50 mg, 80% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.33 (d, J = 8 Hz, 3H), 7.17 (d, J = 8 Hz, 2H), 4.38-4.27 (m, 4H), 2.42 (s, 3H), 1.37-1.30 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 135.7, 129.7, 129.3, 129.2, 124.2, 122.4,61.7, 61.0, 21.1, 14.7, 14.6 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}N_2O_4$ 279.1339; found 279.1308.



ethyl(Z)-2-(2-methoxy-2-oxo-1-(2-(trifluoromethyl)phenyl)ethylidene)hydrazine-1-carboxylate, 3j : By following the above general procedure, the desired compound **3j** was synthesized from **2c** (0.96 mmol, 100 mg) and **1i** (2.88 mmol, 703.65 mg) in 244.41 mg, 70% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.7, 1.4 Hz, 1H), 7.75 – 7.64 (m, 3H), 7.27 (d, J = 8 Hz, 1H), 4.31 (q, J = 6.7 Hz, 2H), 3.86 (s, 3H), 1.33 (t, J = 6 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 163.4, 133.2, 130.9, 130.1, 127.5, 127.4, 124.6, 121.9, 63.3, 53.1, 14.4 ppm. **^{19}F NMR** (376.5MHz, CDCl3) δ 62.75. δ -62.75 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3N_2O_4$ 319.0900; found 319.0904.

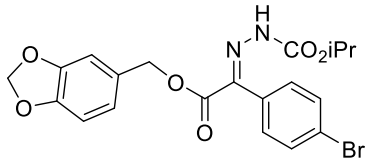


ethyl (Z)-2-(2-methoxy-2-oxo-1-phenylethylidene)hydrazine-1-carboxylate,3k : By following the above general procedure, the desired compound **3k** was synthesized from **2c** (0.96 mmol, 100 mg) and **1a** (2.88 mmol, 507.69 mg) in 177.77 mg, 74% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.57 – 7.51 (m, 3H), 7.28 (dd, J = 7.8, 2.0 Hz, 2H), 4.31 (q, J = 8Hz, 2H), 3.88 (s, 3H), 1.33 (t, J = 6Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 129.3, 129.0, 128.6, 127.1, 125.9, 125.5, 124.0, 61.6, 52.0, 14.6 ppm. **HRMS (ESI-TOF)** m/z: [M+H]+ Calcd for $C_{12}H_{15}N_2O_4$ 251.1026; found 251.0994.

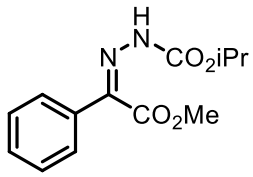


ethyl (Z)-2-(1-(4-iodophenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3l: By following the above general procedure, the desired compound **3l** was synthesized from **2c** (0.96 mmol, 100 mg) and **1k** (2.88 mmol, 870.51 mg) in 252.77 mg, 70% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR**

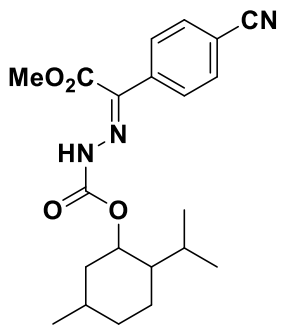
(400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.90(d, J = 8 Hz, 2H), 7.03 (d, J = 8 Hz, 2H), 4.31 (q, J = 6.7 Hz, 2H), 3.88 (s, 3H), 1.32 (t, J = 6Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 161.9, 139.0, 130.0, 128.0, 97.1,63.2, 53.2, 14.5 ppm. **HRMS (ESI-TOF)** m/z: [M+H]+ Calcd for $C_{12}H_{14}IN_2O_4$ 376.9993; found 376.9998.



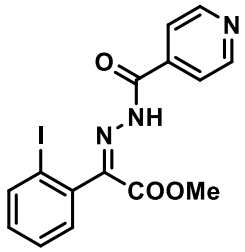
isopropylI-2-(2-(benzo[d][1,3]dioxol-5-ylmethoxy)-1-(4-bromophenyl)-2-oxoethylidene)hydrazine-1-carboxylate, 3m : By following the above general procedure, the desired compound **3m** was synthesized from **2d** (0.85 mmol, 100 mg) and **1m** (2.54 mmol, 952.8 mg) in 270.60 mg , 69% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.57 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.90 – 6.75 (m, 3H), 5.98 (s, 2H), 5.22 (s, 2H), 5.17 – 5.02 (m, 1H), 1.33 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.06, 152.99, 148.33, 148.14, 135.28, 133.24, 130.23, 128.40, 128.14, 123.01, 109.37, 108.57, 101.50, 77.16, 70.56, 67.89, 22.09. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}BrN_2O_6$ 463.0499; found 463.0487.



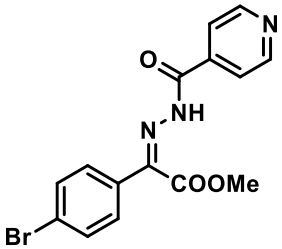
Isopropyl (Z)-2-(2-methoxy-2-oxo-1-phenylethylidene)hydrazine-1-carboxylate,3n : By following the above general procedure, the desired compound **3n** was synthesized from **2d** (0.85 mmol, 100 mg) and **1a** (2.54 mmol, 447.4 mg) in 170.02 mg , 76% yield as viscous pale solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.57 (s, 1H), 7.62 – 7.60 (m, 2H), 7.38 – 7.36 (m, 3H), 5.14 – 5.08 (m, 1H), 3.89 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.04, 153.10, 134.80, 132.25, 129.22, 128.96, 128.87, 128.35, 128.18, 128.14, 77.16, 70.38, 52.66, 22.09. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2O_4$ 265.1183; found 265.1175.



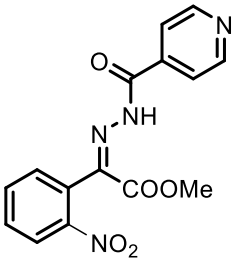
2-isopropyl-5-methylcyclohexyl(Z)-2-(1-(4-cyanophenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3o : By following the above general procedure, the desired compound **3o** was synthesized from **2e** (0.47 mmol, 100 mg) and **1d** (1.40 mmol, 281.6 mg) in 124.11 mg , 69% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.77 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 4.78 (td, *J* = 10.9, 4.4 Hz, 1H), 3.92 (s, 3H), 3.71 (s, 1H), 2.11 (dd, *J* = 12.2, 4.5 Hz, 1H), 2.01 – 1.85 (m, 1H), 1.76 – 1.64 (m, 2H), 1.44 (t, *J* = 12.2 Hz, 2H), 1.16 – 0.97 (m, 2H), 0.92 (dd, *J* = 6.9, 2.9 Hz, 6H), 0.81 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.88, 162.36, 152.91, 139.37, 139.21, 132.49, 131.96, 130.31, 129.57, 118.80, 118.71, 112.63, 111.38, 77.16, 52.94, 52.49, 47.29, 41.21, 41.09, 34.27, 31.53, 26.50, 23.66, 22.13, 20.84, 16.61. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{28}N_3O_4$ 386.2074; found 386.2072.



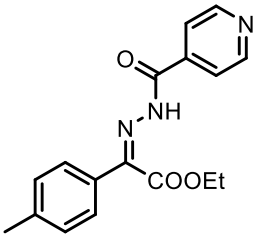
Methyl (Z)-2-(2-iodophenyl)-2-(2-isonicotinoylhydrazono)acetate,3p : By following the above general procedure, the desired compound **3p** was synthesized from **2f** (0.72 mmol, 100 mg) and **1l** (2.18 mmol, 660.79 mg) in 247.84 mg, 84% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane.**^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 13.68 (s, 1H), 8.85 (s, 2H), 7.86 – 7.81 (m, 3H), 7.45 (d, J = 4 Hz, 2H), 7.16 – 7.11 (m, 1H), 3.87 (s, 3H) ppm. **^{13}CNMR** (100 MHz, $CDCl_3$) *δ* 162.6, 161.5, 152.0, 151.1, 139.5, 139.3, 138.8, 131.1, 130.8, 128.5, 121.3, 98.0, 53.3 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}IN_3O_3$ 409.9996; found 409.9941.



Methyl (Z)-2-(4-bromophenyl)-2-(2-isonicotinoylhydrazono)acetate,3q : By following the above general procedure, the desired compound **3q** was synthesized from **2f** (0.72 mmol, 100 mg) and **1n** (2.18 mmol, 557.82 mg) in 224.26 mg, 86% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.43 (s, 1H), 8.84 (s, 2H), 8.04 – 7.40 (m, 6H), 3.97 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 151.0, 150.7, 139.6, 139.5, 133.2, 132.9, 132.4, 132.3, 131.5, 130.7, 129.1, 128.5, 124.5, 121.2, 121.0, 53.3 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}BrN_3O_3$ 362.0135; found 362.0091.

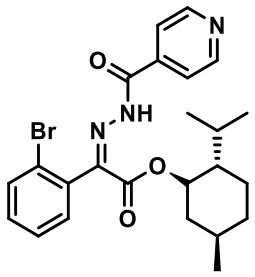


Methyl (Z)-2-(2-isonicotinoylhydrazono)-2-(2-(nitrophenyl)acetate,3r : By following the above general procedure, the desired compound **3r** was synthesized from **2f** (0.72 mmol, 100 mg) and **1u** (2.18 mmol, 525.13 mg) in 190.4 mg, 79% yield as dark yellow oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79-8.78 (m, 2H), 7.91 - 7.90 (t, $J_1 = J_2 = 4$Hz, 1H), 7.68 - 7.61 (m, 4H), 7.57 - 7.55 (m, 1H), 5.66 (s, 1H), 3.81 (s, 3H) ppm. **^{19}F NMR (376.5 MHz, $CDCl_3$)** δ -62.68 ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.07, 169.52, 150.07, 140.25, 134.47, 133.41, 131.62, 128.87, 125.53, 123.70, 119.23, 54.52 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}N_4O_5$ 328.0941; found 328.0902.

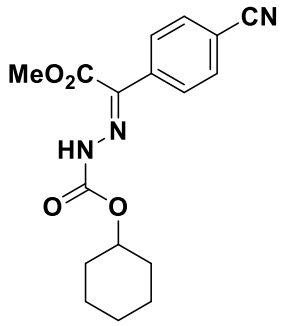


Methyl (Z)-2-(4-tolyl)-2-(2-isonicotinoylhydrazono)acetate, 3s : By following the above general procedure, the desired compound **3s** was synthesized from **2f** (0.72 mmol, 100 mg) and **1p** (2.18 mmol, 401.20 mg) in 162.68 mg, 83% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.31 (s, 1H),

8.84 (s, 2H), 7.78 - 7.61 (m, 4H), 7.26-7.20 (m, 2H), 4.47 – 4.42 (q, *J* = 8Hz, 2H), 2.39 (s, 3H), 1.41 – 1.38 (t, *J* = 4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) 185.17, 181.37, 151.27, 150.92, 148.93, 144.51, 140.09, 137.52, 131.21, 128.96, 121.15, 62.74, 21.39, 14.03 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}N_3O_3$ 311.3465; found 311.3461.

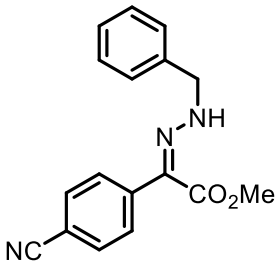


((1S,2S,5R)-2-isopropyl-5-methylcyclohexyl(Z)-2-(2-bromophenyl)-2-(2-isonicotinoylhydrazono)acetate,3t : By following the above general procedure, the desired compound **3t** was synthesized from **2f** (0.72 mmol, 100 mg) and **1q** (2.18 mmol, 829.71 mg) in 245.15 mg, 70% yield as white oil from the crude *via* column chromatography in silica gel (100-200 mesh) in 20-30% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.43 (s, 1H), 8.84 (s, 2H), 7.76 – 7.48 (m, 6H), 5.05-6.98 (m, 1H), 2.12 (d, J = 12 Hz, 1H), 1.78 – 1.71 (m, 3H), 1.59 (s, 2H), 1.49 – 1.41 (m, 1H), 1.17 – 1.06 (m, 2H), 0.96 (d, J = 4 Hz, 3H), 0.88 (d, J = 8 Hz, 3H), 0.78 (d, J = 8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 161.6, 159.2, 132.1, 130.4, 127.7, 126.2, 126.1, 125.4, 125.1, 119.2, 116.6, 116.4,75.4, 71.7, 50.3, 47.2, 45.2, 41.4, 34.6, 34.3, 31.7, 31.6, 26.6, 26.0, 23.8, 23.3, 22.3, 22.1, 21.1, 20.8, 16.7, 16.2 ppm. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}BrN_3O_3$ 486.1387; found 486.1390.

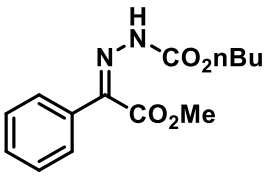


cyclohexyl (Z)-2-(1-(4-cyanophenyl)-2-methoxy-2-oxoethylidene)hydrazine-1-carboxylate,3u : By following the above general procedure, the desired compound **3u** was synthesized from **2g** (0.63 mmol, 100 mg) and **1d** (1.9 mmol, 381.5 mg) in 164.46 mg , 79% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.76 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 4.86 (tt, *J* = 9.0, 4.0 Hz, 1H), 3.92 (s, 3H), 1.98 – 1.91 (m, 2H), 1.81 – 1.71 (m, 2H), 1.53 – 1.48 (m, 2H), 1.47 – 1.33 (m, 2H), 1.31 – 1.23 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.34, 152.73, 139.21, 131.98, 129.57, 118.72,

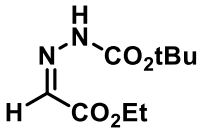
112.63, 100.13, 77.16, 75.66, 52.95, 31.81, 25.40, 23.82. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}N_3O_4$ 330.1448; found 330.1441.



methyl (Z)-2-(2-benzylhydrazono)-2-(4-cyanophenyl)acetate,3v : By following the above general procedure, the desired compound **3v** was synthesized from **2h** (0.6 mmol, 100 mg) and **1d** (1.81 mmol, 363.2 mg) in 104.13 mg , 59% yield as viscous pale solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.63 (q, *J* = 8.3 Hz, 5H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 2H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.24, 134.01, 133.05, 133.02, 132.21, 132.11, 130.95, 130.58, 129.13, 129.09, 129.06, 128.92, 128.88, 128.57, 128.51, 127.79, 77.16, 71.11, 68.01, 53.71, 53.59, 52.11, 30.15. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}N_3O_2$ 294.1237; found 294.1232.

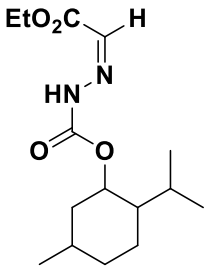


butyl (Z)-2-(2-methoxy-2-oxo-1-phenylethylidene)hydrazine-1-carboxylate,3w : By following the above general procedure, the desired compound **3w** was synthesized from **2i** (0.76 mmol, 100 mg) and **1a** (2.27 mmol, 445.4 mg) in 178.34 mg , 79% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.63 (s, 1H), 7.60 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.42 – 7.33 (m, 3H), 4.27 (t, *J* = 6.7 Hz, 2H), 3.89 (s, 3H), 1.74 – 1.65 (m, 2H), 1.43 (q, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.03, 153.68, 134.75, 129.26, 128.89, 128.21, 77.16, 66.40, 52.71, 30.95, 19.13, 13.84. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}N_2O_4$ 279.1339; found 279.1325.

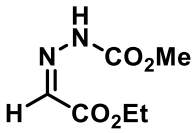


tert-butyl (Z)-2-(2-ethoxy-2-oxoethylidene)hydrazine-1-carboxylate,4a : By following the above general procedure, the desired compound **4a** was synthesized from **2a** (0.76 mmol, 100 mg) and **1s** (3.33 mmol, 380 mg) in 109.62 mg , 67% yield as viscous pale solid from the crude via column

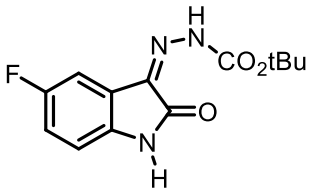
chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.79 (s, 1H), 6.81 (s, 1H), 4.24 (q, *J* = 7.3 Hz, 2H), 1.50 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.19, 152.07, 126.31, 82.47, 77.16, 61.47, 28.20, 28.19, 14.07. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_9H_{16}N_2O_4$ 239.1002; found 239.9997.



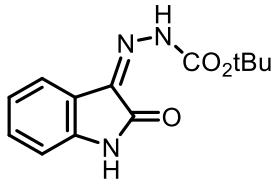
2-isopropyl-5-methylcyclohexyl (Z)-2-(2-ethoxy-2-oxoethylidene)hydrazine-1-carboxylate,4b : By following the above general procedure, the desired compound **4b** was synthesized from **2e** (0.47 mmol, 100 mg) and **1s** (1.40 mmol, 159.7 mg) in 101.64 mg , 73% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.92 (s, 1H), 6.87 (s, 1H), 4.77 (td, *J* = 10.9, 4.4 Hz, 1H), 4.31 – 4.18 (m, 2H), 2.22 – 2.04 (m, 1H), 2.01 – 1.83 (m, 1H), 1.73 – 1.65 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 7.0 Hz, 1H), 1.26 – 1.23 (m, 2H), 1.12 – 1.01 (m, 2H), 0.91 (d, *J* = 5.4 Hz, 6H), 0.79 (d, *J* = 6.6 Hz, 3H). **13C NMR** (100 MHz, CDCl3) δ 161.89, 152.85, 126.62, 77.16, 61.45, 61.31, 46.92, 40.76, 33.96, 31.21, 29.53, 26.10, 26.02, 23.22, 21.81, 20.57, 16.16, 14.00, 13.82. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{15}H_{27}N_2O_4$ 299.1965; found 299.1960.



methyl (Z)-2-(2-ethoxy-2-oxoethylidene)hydrazine-1-carboxylate,4c : By following the above general procedure, the desired compound **4c** was synthesized from **2b** (1.11 mmol, 100 mg) and **1s** (3.33 mmol, 380 mg) in 135.33 mg , 70% yield as viscous pale solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.99 (s, 1H), 6.87 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.88, 163.41, 161.85, 149.35, 125.38, 92.92, 77.16, 62.38, 61.72, 61.44, 60.61, 14.10. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_9H_{17}N_2O_4$ 216.1110; found 217.1183.



tert-butyl (Z)-2-(5-fluoro-2-oxoindolin-3-ylidene)hydrazine-1-carboxylate,5a : By following the above general procedure, the desired compound **5a** was synthesized from **2a** (0.76 mmol, 100 mg) and **1r** (2.27 mmol, 402.1 mg) in 162.71 mg , 77% yield as viscous pale solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.16 (s, 1H), 7.83 (s, 1H), 7.45 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.10 – 6.94 (m, 1H), 6.82 (dd, *J* = 8.6, 4.0 Hz, 1H), 1.57 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.69, 152.00, 135.93, 117.36, 117.12, 111.32, 111.24, 109.01, 108.76, 83.05, 28.13. **^{19}F NMR** (376.5MHz, CDCl3) δ 110.51. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{13}H_{14}FN_3O_3$ 302.0911; found 302.0899.



tert-butyl (Z)-2-(2-oxoindolin-3-ylidene)hydrazine-1-carboxylate,5b : By following the above general procedure, the desired compound **5b** was synthesized from **2a** (0.76 mmol, 100 mg) and **1t** (2.27 mmol, 361 mg) in 158.16 mg , 80% yield as viscous pale solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.19 (s, 1H), 8.77 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.20 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 1.57 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.16, 152.48, 140.50, 130.87, 123.38, 121.59, 120.76, 110.87, 82.90, 77.16, 29.82, 28.28. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{13}H_{15}N_3O_3$ 284.1006; found 284.1001.

2.2 XRD analysis

Single crystal data collections and corrections with D8 Venture Bruker AXS single-crystal Xray diffractometer equipped with CMOS PHOTON 100 detector having monochromatized microfocus sources (Mo-Kα = 0.71073 Å). Single crystals of **3p** (CCDC 2346164) and **3r** (CCDC 2346164) suitable for X-ray diffraction study were obtained from the slow evaporation process. The structure solution and refinement were performed by using the SHELX program implemented in APEX3.[1-2] The non-H atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. All the hydrogen atoms were placed at the hybridized positions and refined using a riding model with appropriate HFIX commands. The molecular structures were drawn by ORTEP.[3]

Table S1: Crystallographic data of 3q

Sample Code	**3q**
CCDC	2346164
Lattice	monoclinic
Formula	C15 H12 Br N3 O3
Formula Weight	362.19
Space Group	P 21/c
a/ A°	11.6044(2)
b/ A°	5.91410(10)
c/A°	21.8474(4)
α/ °	90
β/ °	102.5510(10)
γ/ °	90
V/ (A°)^3	1463.55
Z	4
Radiation (λ)/A°	0.71073
ρ/ (g cm-3)	1.644
μ (Mo Kα) mm-1	2.825
θmax/deg	26.367
Collected reflections	2519
Unique reflections	2988
No of parameters	200
R1 [I> 2σI]	0.0391
wR2 [I> 2σI]	0.0663
R1 [all data]	0.0288
wR2 [all data]	0.0756
Rint [all data]	0.0346
GOF	1.087

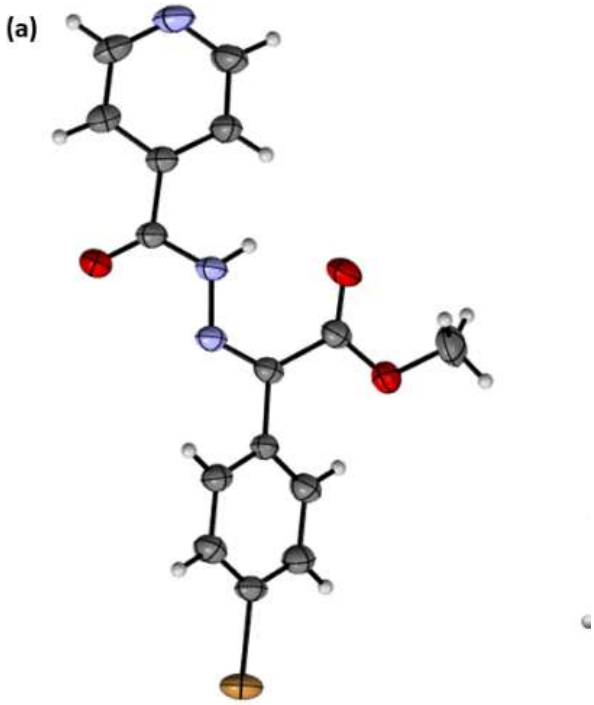


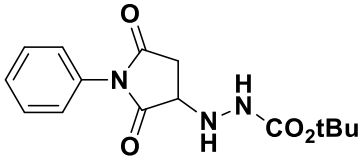
Figure 2. ORTEP diagrams of 3q

4. General procedure for 2,5-dioxo-1-arylpyrrolidin-3-yl hydrazine-1-carboxylate.

In an oven-dried 10 mL reaction vial equipped with a magnetic stir bar, **N-aryl maleimide** (1 equiv, 100 mg), **carbazate** (3 equiv), and **n-tetrabutylammonium hexafluorophosphate** (0.1 M) were dissolved in DMSO (6–8 mL). The vial was capped with an IKA ElectraSyn vial head equipped with a platinum electrode (anode) and a carbon electrode (cathode). The reaction mixture was sparged with argon and electrolyzed using an IKA ElectraSyn 2.0 instrument under rapid alternating polarity (rAP) conditions at a constant current of 20 mA (10Hz frequency) for 5–6 h at room temperature. Upon completion, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (100–200 mesh) using ethyl acetate/hexane as the eluent.

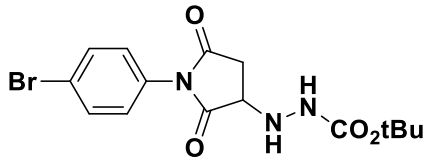
Figure 3. rAP Electrochemical setup used in the experiments

3.1 Characterization data

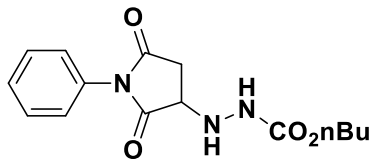


tert-butyl 2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)hydrazine-1-carboxylate,7a : By following the above general procedure, the desired compound **7a** was synthesized from **4a** (0.58 mmol, 100 mg) and **2a** (1.73 mmol, 229 mg) in 134.00 mg , 76% yield as white solid from the crude via column chromatography in silica gel (100-200 mesh) in 25-30% ethyl acetate in hexane. ^{1}H NMR (400 MHz,

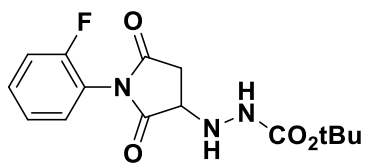
Chloroform-*d*) δ 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 6.23 (s, 1H), 4.68 (s, 1H), 4.44 – 4.22 (m, 1H), 3.09 (dd, *J* = 18.3, 8.7 Hz, 1H), 2.84 (dd, *J* = 18.2, 5.1 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.31, 174.04, 131.57, 129.35, 128.93, 126.45, 81.76, 77.16, 57.96, 34.30, 28.41. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{15}H_{19}N_3O_4$ 328.1268; found 328.1252.



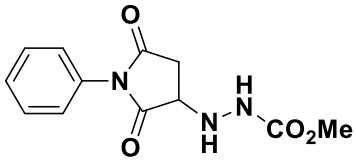
tert-butyl 2-(1-(4-bromophenyl)-2,5-dioxopyrrolidin-3-yl)hydrazine-1-carboxylate,7b : By following the above general procedure, the desired compound **7b** was synthesized from *para*-bromo phenyl maleimide (0.4 mmol, 100 mg) and **2a** (1.19 mmol, 157.3 mg) in 118.9 mg , 78% yield as white solid from the crude via column chromatography in silica gel (100-200 mesh) in 25-30% ethyl acetate in hexane. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.18 (s, 1H), 4.63 – 4.04 (m, 1H), 3.09 (dd, *J* = 18.3, 8.6 Hz, 1H), 2.83 (dd, *J* = 18.3, 5.0 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.67, 173.67, 157.96, 132.53, 130.55, 127.92, 122.78, 122.78, 81.88, 77.16, 57.89, 29.85, 28.40. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{15}H_{18}BrN_3O_4$ 406.0373; found 406.0366.



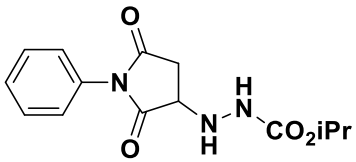
butyl 2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)hydrazine-1-carboxylate,7c : By following the above general procedure, the desired compound **7c** was synthesized from **4a** (0.58 mmol, 100 mg) and **2i** (1.73 mmol, 229 mg) in 153.39 mg , 87% yield as white solid from the crude via column chromatography in silica gel (100-200 mesh) in 25-30% ethyl acetate in hexane. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.51 (s, 1H), 4.30 (dd, *J* = 8.7, 5.2 Hz, 1H), 4.13 (t, *J* = 6.2 Hz, 2H), 3.08 (dd, *J* = 18.3, 8.6 Hz, 1H), 2.84 (dd, *J* = 18.3, 5.1 Hz, 1H), 1.68 – 1.55 (m, 2H), 1.46 – 1.28 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.38, 173.95, 157.83, 131.49, 129.33, 128.94, 126.41, 77.16, 66.03, 57.95, 34.14, 30.99, 19.09, 13.81. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_3O_4$ 306.1448; found 306.1440.



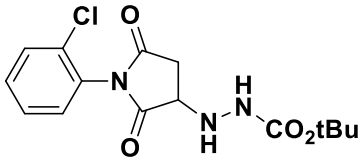
tert-butyl 2-(1-(2-fluorophenyl)-2,5-dioxopyrrolidin-3-yl)hydrazine-1-carboxylate,7d: By following the above general procedure, the desired compound **7d** was synthesized from *o*-fluorophenyl substituted maleimide (0.52 mmol, 100 mg) and **2a** (1.57 mmol, 207.4 mg) in 143.76 mg , 85% yield as white solid from the crude via column chromatography in silica gel (100-200 mesh) in 25-30% ethyl acetate in hexane. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dt, *J* = 9.0, 4.6 Hz, 1H), 7.31 (dd, *J* = 12.4, 7.3 Hz, 3H), 6.45 (s, 1H), 4.47 – 4.38 (m, 1H), 3.18 (dd, *J* = 18.4, 8.6 Hz, 1H), 3.03 – 2.80 (m, 1H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.68, 173.26, 156.91, 131.28, 129.27, 124.83, 119.43, 116.76, 81.66, 77.16, 58.24, 34.32, 29.80, 28.36. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{15}H_{18}FN_3O_4$ 346.1174; found 346.1168.



methyl 2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)hydrazine-1-carboxylate,7e : By following the above general procedure, the desired compound **7e** was synthesized from **4a** (0.58 mmol, 100 mg) and **2b** (1.73 mmol, 156.1 mg) in 120.09 mg , 79% yield as white solid from the crude *via* column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.51 (s, 1H), 4.67 – 4.10 (m, 1H), 3.76 (s, 3H), 3.11 (dd, *J* = 18.3, 8.7 Hz, 1H), 2.85 (dd, *J* = 18.3, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.35, 173.87, 158.07, 131.44, 129.38, 129.01, 126.42, 77.16, 57.93, 53.10, 34.12. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}N_3O_4$ 264.0979; found 264.0971.



isopropyl 2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)hydrazine-1-carboxylate,7f : By following the above general procedure, the desired compound **7f** was synthesized from **4a** (0.58 mmol, 100 mg) and **2d** (1.73 mmol, 204.6 mg) in 144.66 mg , 86% yield as white solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.35 (s, 1H), 4.97 (p, *J* = 6.3 Hz, 1H), 4.51 – 4.26 (m, 1H), 3.10 (dd, *J* = 18.3, 8.7 Hz, 1H), 2.85 (dd, *J* = 18.3, 5.2 Hz, 1H), 1.27 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.31, 173.95, 157.35, 131.50, 129.36, 128.97, 126.43, 77.16, 70.03, 57.98, 34.20, 29.83, 22.20, 22.15. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_3O_4$ 292.1292; found 292.1288.



tert-butyl 2-(1-(2-chlorophenyl)-2,5-dioxopyrrolidin-3-yl)hydrazine-1-carboxylate,7g : By following the above general procedure, the desired compound **7g** was synthesized from *o*-chloro phenyl substituted maleimide (0.48 mmol, 100 mg) and **2a** (1.45 mmol, 191 mg) in 121.10 mg , 74% yield as white solid from the crude via column chromatography in silica gel (100-200 mesh) in 15-20% ethyl acetate in hexane. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 7.1 Hz, 1H), 7.44 – 7.34 (m, 2H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.34 (s, 1H), 4.52 – 4.30 (m, 1H), 3.11 (dd, *J* = 10.8, 8.5 Hz, 1H), 2.87 (dd, *J* = 18.3, 5.1 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.64, 173.44, 173.24, 156.91, 132.40, 132.13, 131.11, 131.01, 130.59, 130.53, 129.99, 129.82, 129.65, 129.54, 128.03, 127.93, 81.77, 81.56, 77.16, 58.61, 58.18, 34.39, 29.82, 28.39, 28.38. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calcd for $C_{15}H_{18}ClN_3O_4$ 362.0878; found 362.0866.

5. Mechanistic studies:

5.1 Divided cell experiment:

Divided cell experiments were conducted in a standard H-cell separated by a Nafion membrane using an Orgel 1.0 instrument.

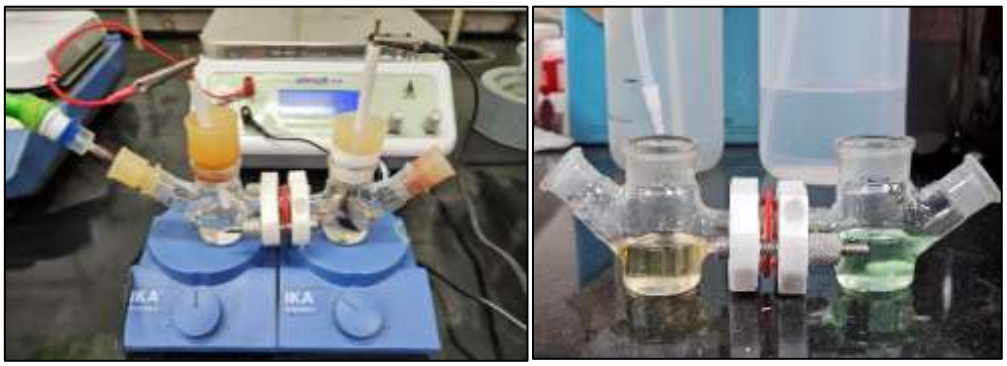


Figure 4. Divided cell experiment setup (left), after reaction with sacrificial electrode (copper wire) (right)

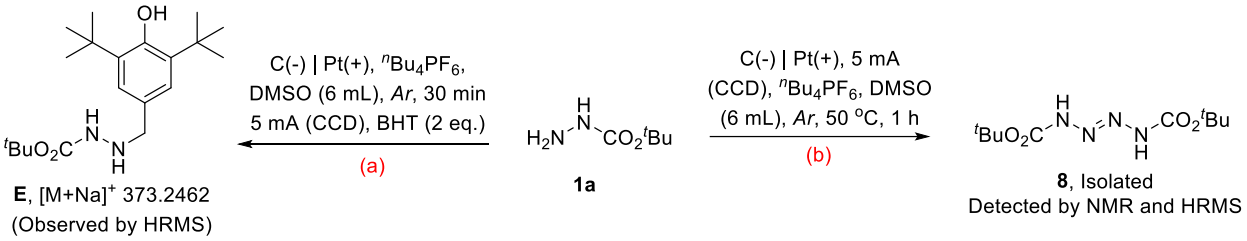
Experiment 1 (Anodic Reaction): The **anodic chamber** was charged with **carbazate** (1 equiv, 100 mg), **aryldiazoacetate** (3 equiv), and n-tetrabutylammonium hexafluorophosphate (0.1 M) in DMSO (6–8 mL), equipped with a **platinum anode**. The **cathodic chamber** (counter chamber) was charged with a solution of n-Bu_4NPF_6 (0.1 M) in DMSO containing **methanol** (added as a proton source) and equipped with a **carbon cathode**. The cell was sparged with argon, irradiated with blue LEDs (456

nm), and electrolyzed at a constant current of 5 mA for 6 h. Upon completion, the anodic solution was purified by column chromatography to determine the yield.

Experiment 2 (Cathodic Reaction): The **cathodic chamber** was charged with **carbazate** (1 equiv, 100 mg), **aryldiazoacetate** (3 equiv), and n-Bu_4NPF_6 (0.1 M) in DMSO (6–8 mL), equipped with a **carbon cathode**. The **anodic chamber** (counter chamber) was charged with a solution of n-Bu_4NPF_6 (0.1 M) in DMSO and equipped with a **sacrificial copper wire anode** to facilitate charge balance. The cell was sparged with argon, irradiated with blue LEDs (456 nm), and electrolyzed at a constant current of 5 mA for 6 h under identical conditions.

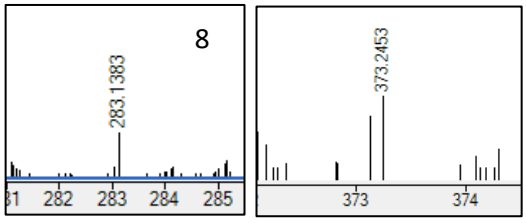
This result suggests that the reaction is primarily driven by an oxidative pathway. Mechanistically, we propose that the **carbazate** undergoes direct anodic oxidation at the platinum anode to generate the corresponding reactive nitrogen-centered radical or diazenium intermediate. Concurrently, the **aryl diazoacetate** undergoes photolysis under blue LED irradiation (456 nm) to generate the key carbene intermediate. It is important to note that while carbene formation is less efficient, the blue light irradiation is sufficient to promote this transformation in the bulk solution, independent of the electrode surface. Consequently, the successful formation of the product in the anodic chamber is attributed to the synergistic coupling of the anodically generated nitrogen species and the photo-generated carbene.

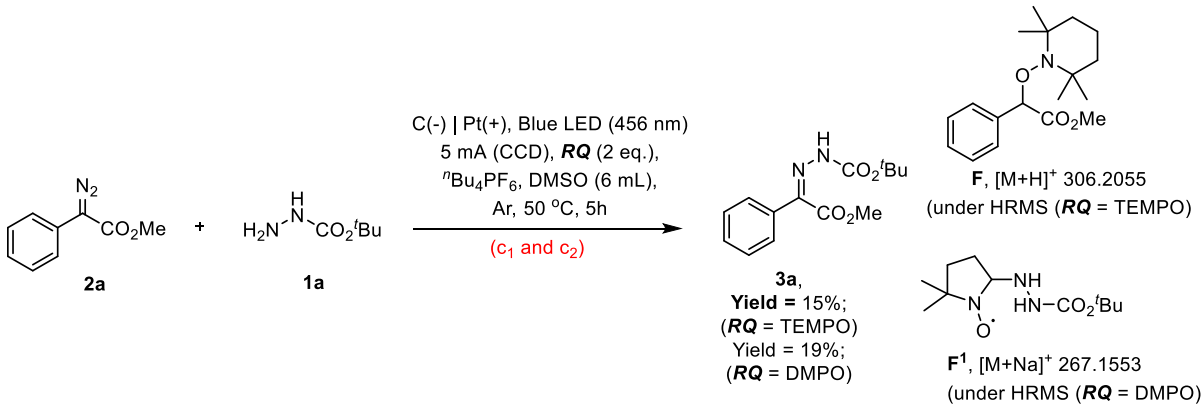
5.2 Radical trapping Experiment:



Scheme 1. (a) Hydrazinyl trapping by BHT, (b) Dimerization of carbazate

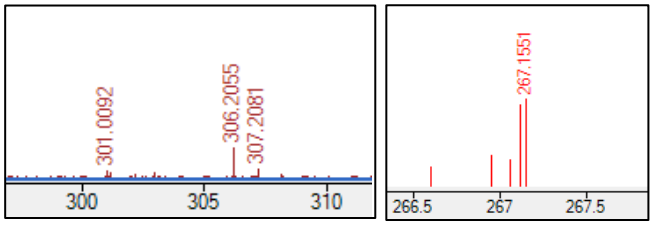
To investigate the reaction mechanism, a control experiment was conducted using **1a** (1.0 equiv) under standard conditions in the presence of TEMPO (2.0 equiv) (Scheme 1. (a)). After 30 minutes, an aliquot was collected and analyzed by ESI-MS. In a parallel experiment under identical conditions, **1a** was reacted without additives for 1 hour. (Scheme 2. (b)) The mixture was subsequently extracted with ethyl acetate and water, and the isolated product was characterized by NMR and LC-MS.

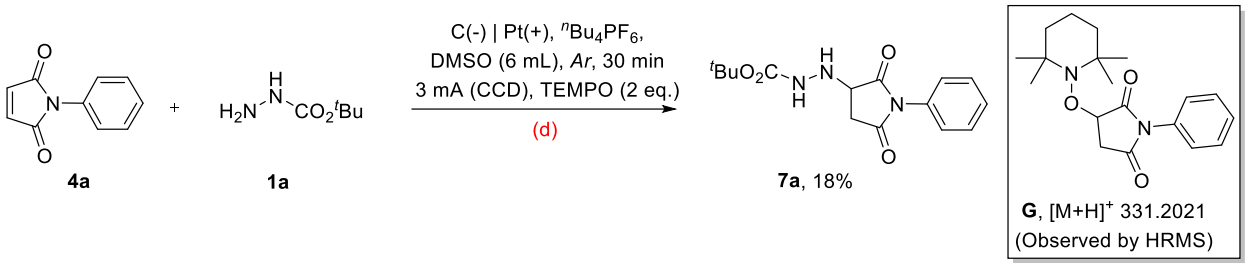




Scheme 2. Radical trapping experiment of N-acyl hydrazone reaction by TEMPO and DMPO

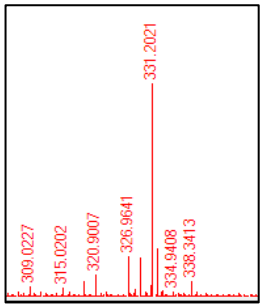
In a standard reaction of **1a** (1 equivalent) and **2a** (3 equivalent) (Scheme 2.) 2 equivalent of TEMPO was added in the reaction mixture. After 30 minutes after adding an aliquot was collected and ESI-Mass spectrometry was recorded. Similarly reaction was carried out for DMPO.





Scheme 3. Radical trapping experiment of succinimide linked hydrazines reaction by TEMPO

In a standard reaction of **4a** (1 equivalent) and **1a** (3 equivalent) (Scheme 3.) 2 equivalent of TEMPO was added in the reaction mixture. After 30 minutes after adding an aliquot was collected and ESI-Mass spectrometry was recorded.



5.3 CV experiments:

All CVs were recorded using 3 electrode systems: Ag/Ag^{+} non-aqueous reference electrode, glassy carbon working electrode and platinum wire as counter electrode. 0.1 M TBAPF6 in DMSO was used as medium to dissolve every samples of 0.001 M concentration to record CV. Reference electrode solution was 0.01 M $AgNO_3$ in 0.1 M TBAPF6 solution in DMSO. Before recording every CV, electrodes were cleaned properly using standard procedure and solutions were purged with nitrogen gas for at least 2 minutes.

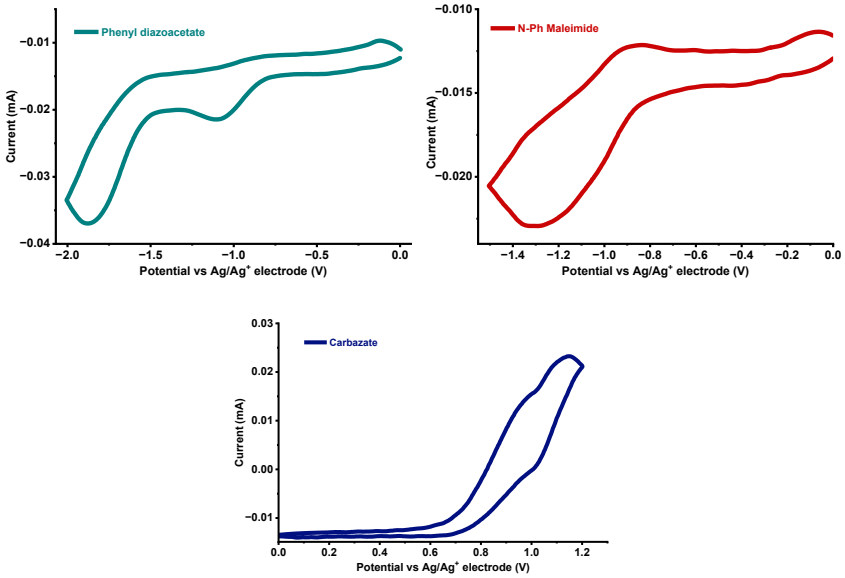
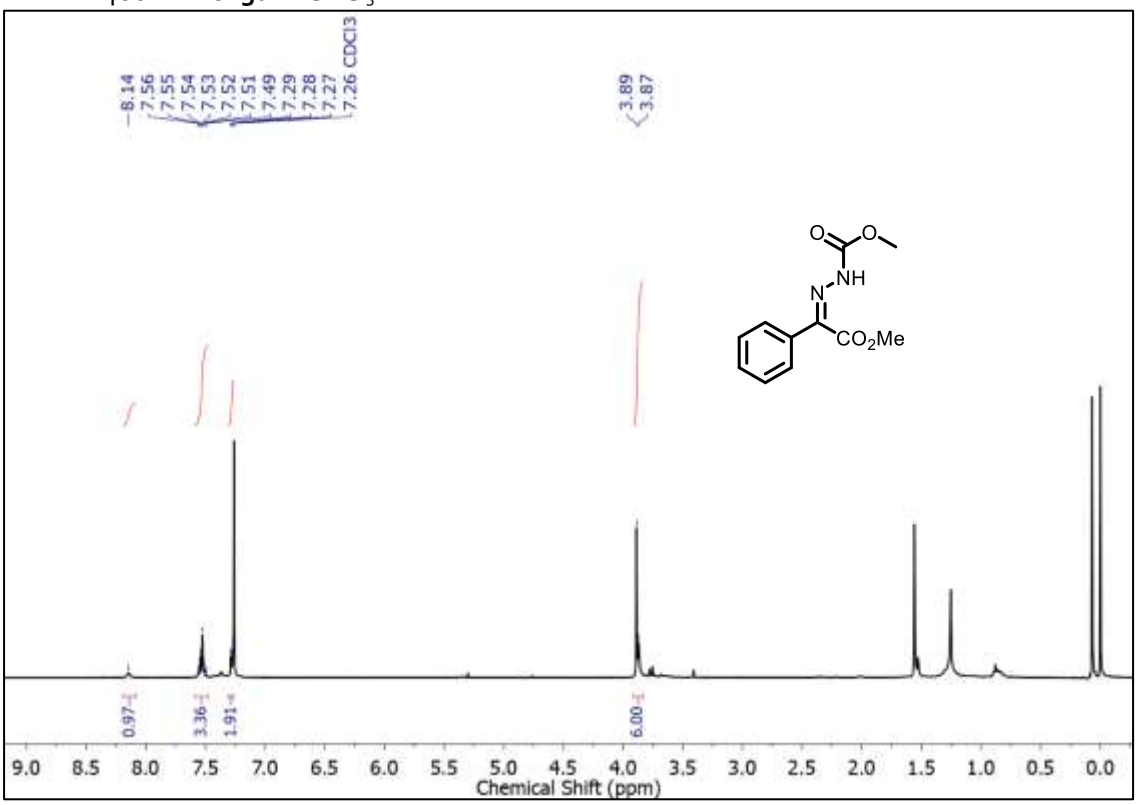


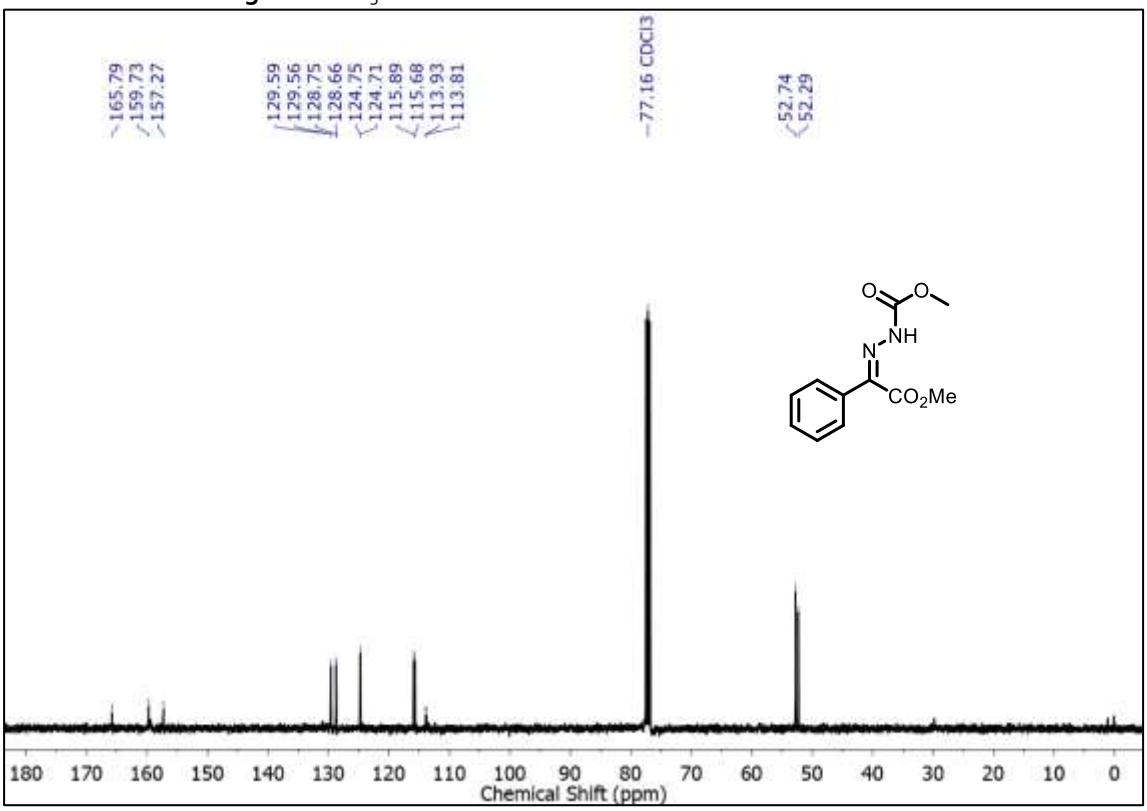
Figure 4. CV for phenyl diazoacetate, N-Ph Maleimide and Carbazate

6. NMR Spectral data

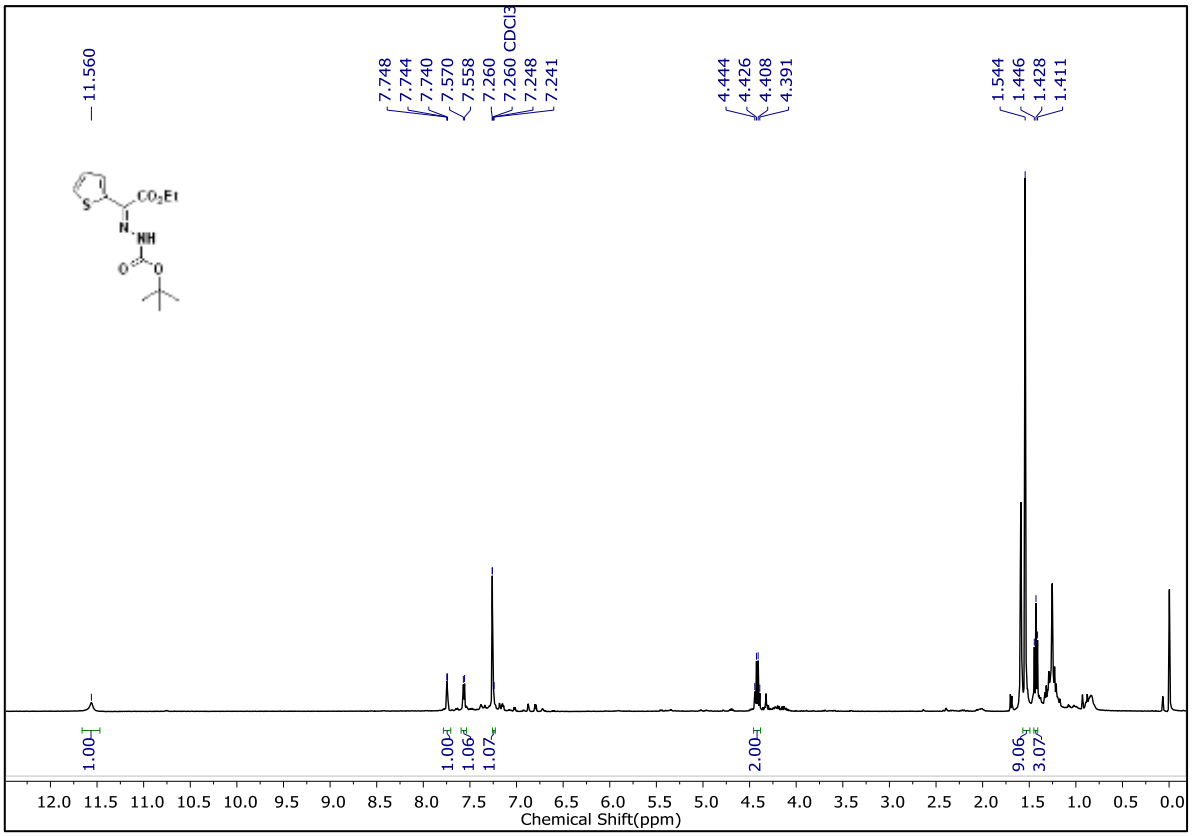
^{1}H NMR 400MHz of **3a** in $CDCl_3$



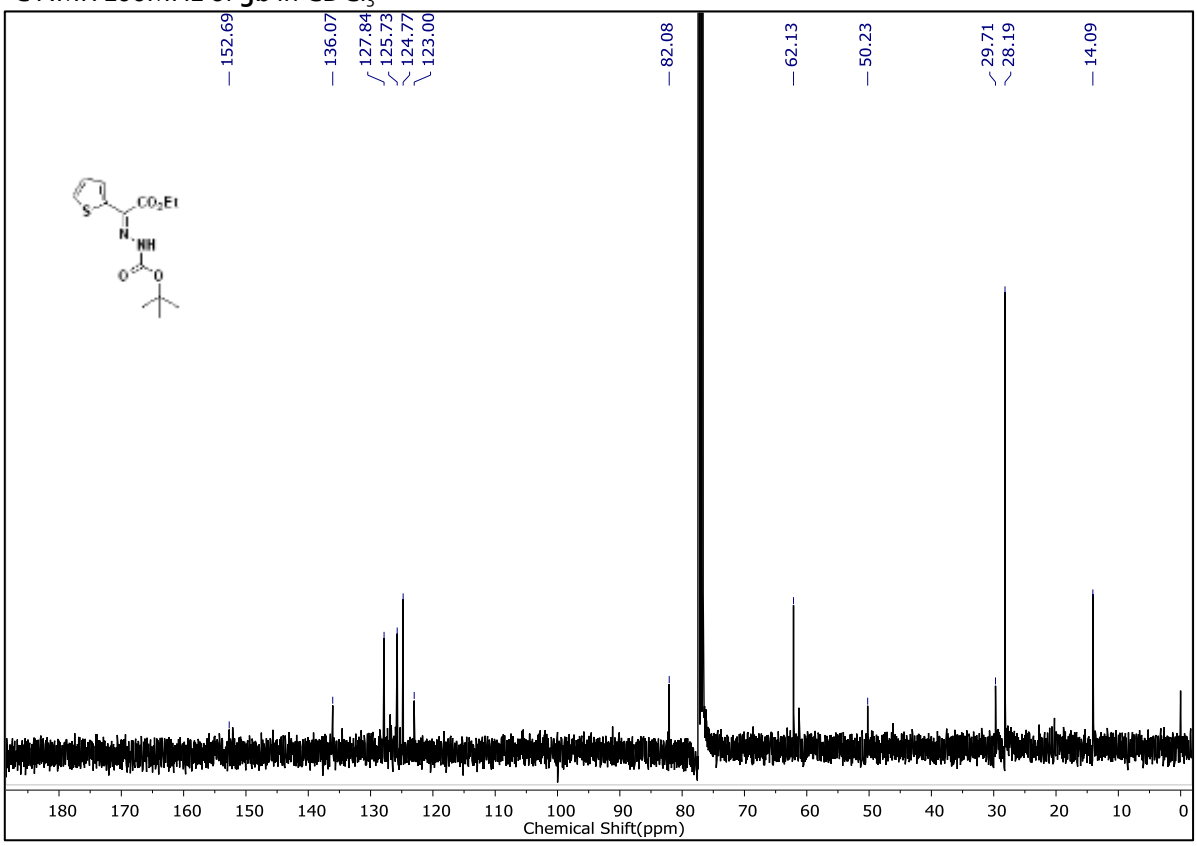
^{13}C NMR 100MHz of **3a** in $CDCl_3$



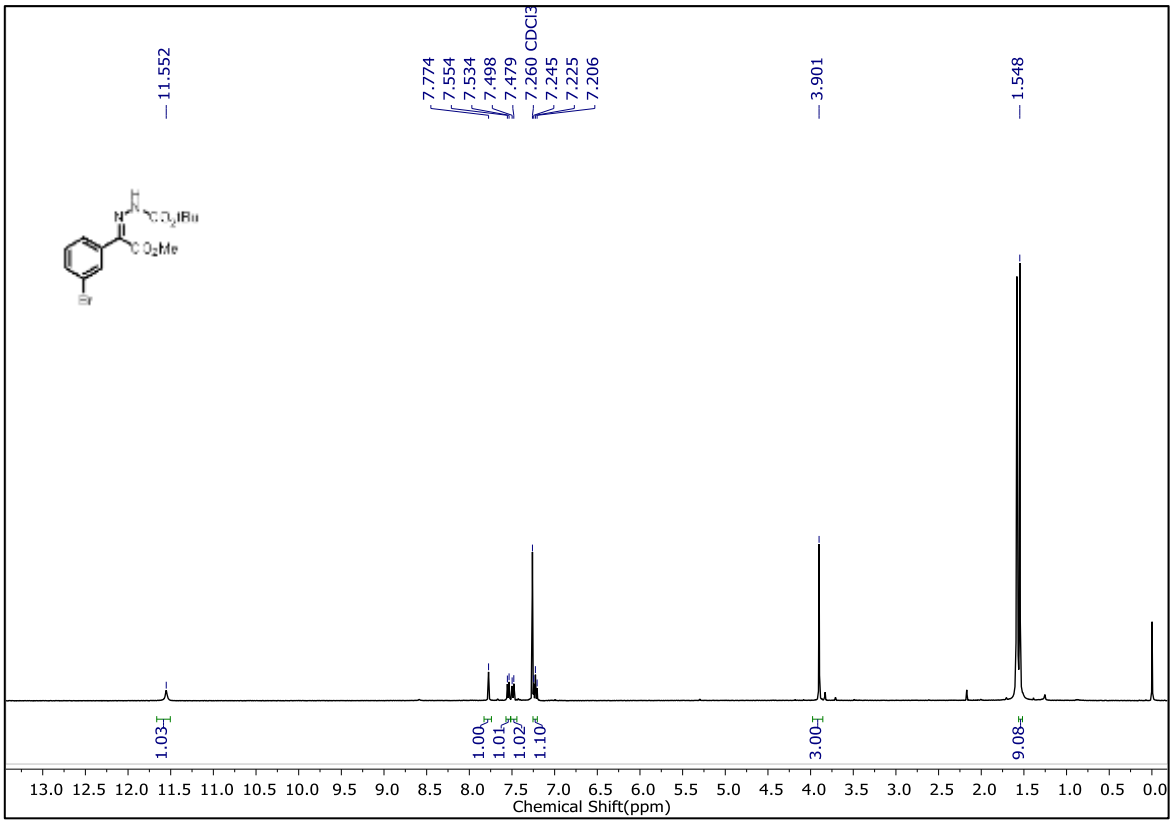
^{1}H NMR 400MHz of **3b** in $CDCl_3$



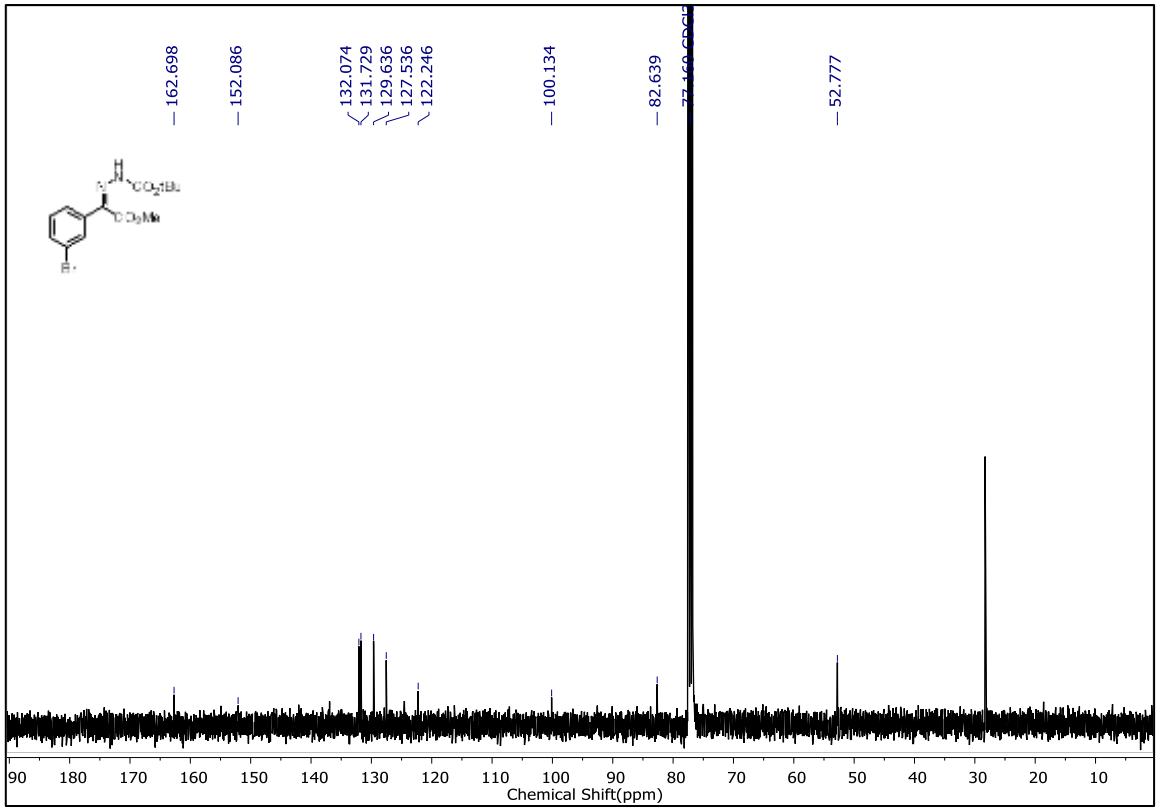
^{13}C NMR 100MHz of **3b** in $CDCl_3$



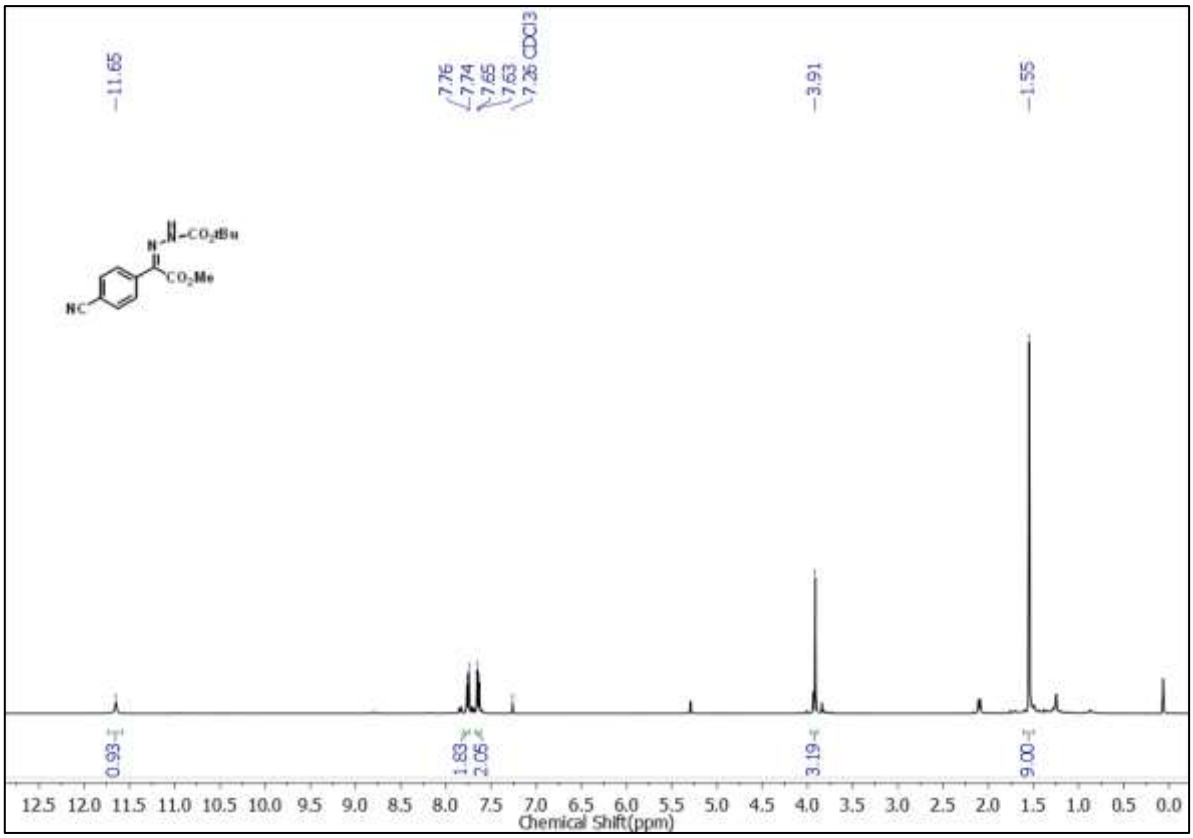
^{1}H NMR 400MHz of **3c** in $CDCl_3$



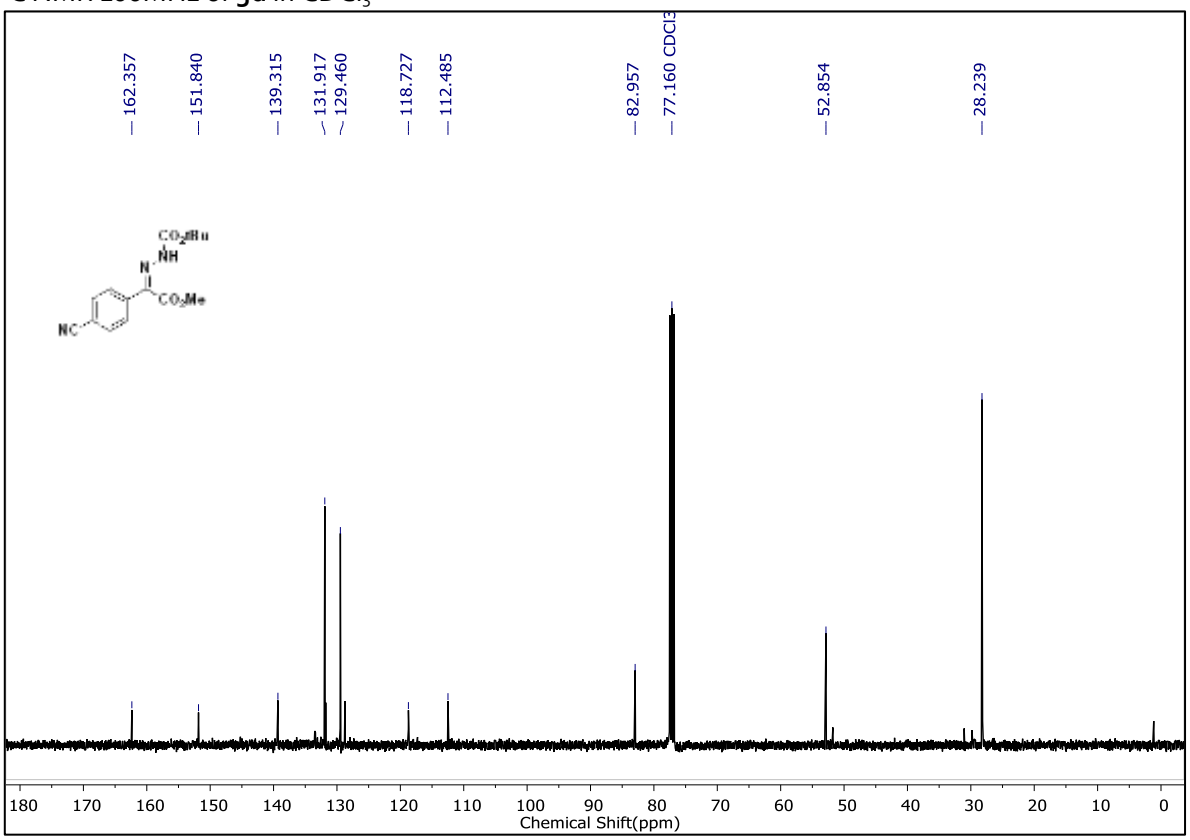
^{13}C NMR 100MHz of **3c** in $CDCl_3$



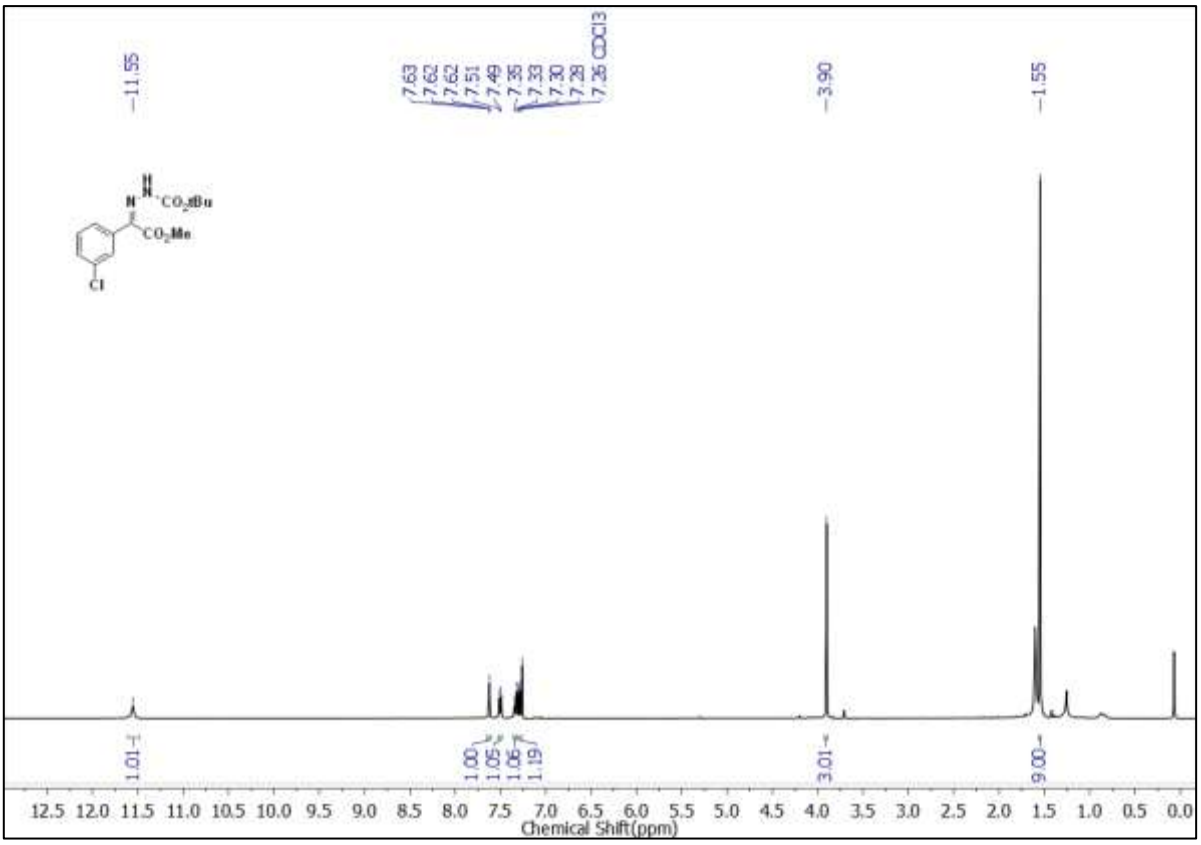
^{1}H NMR 400MHz of **3d** in $CDCl_3$



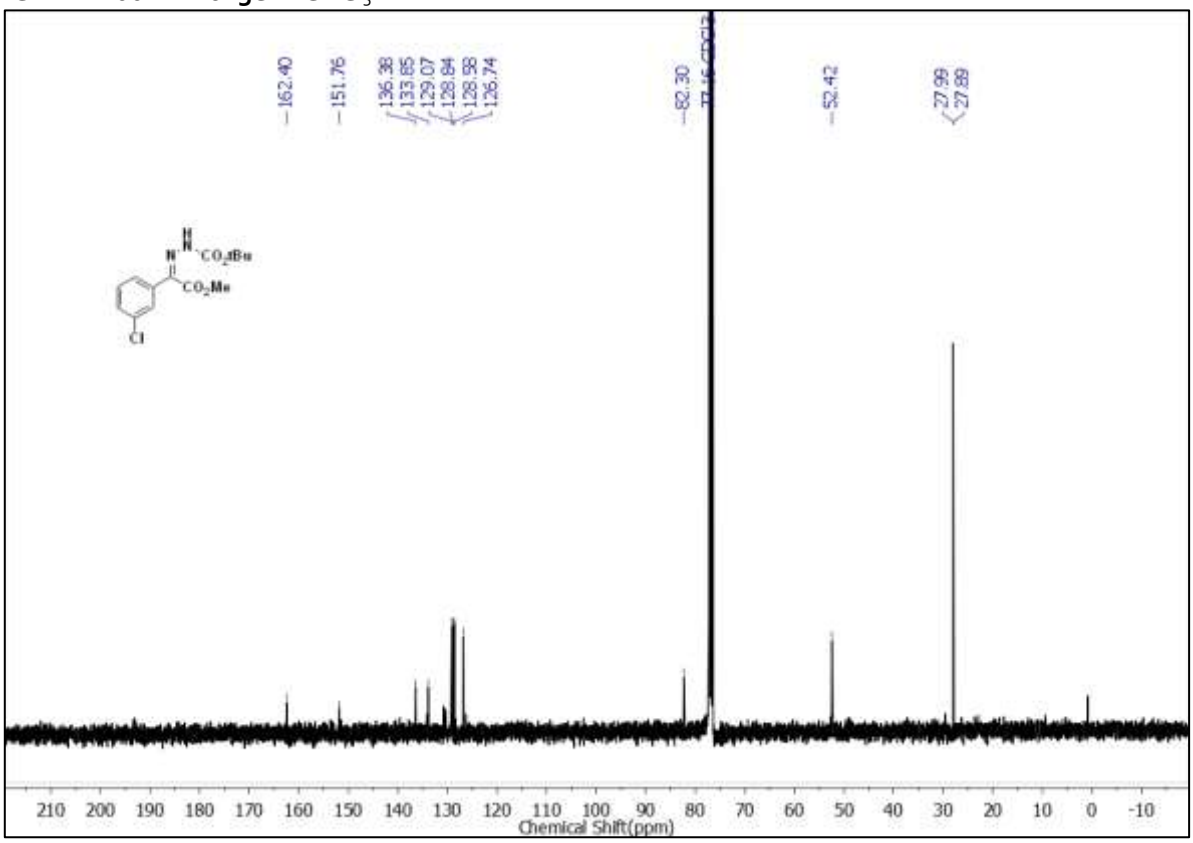
^{13}C NMR 100MHz of **3d** in $CDCl_3$



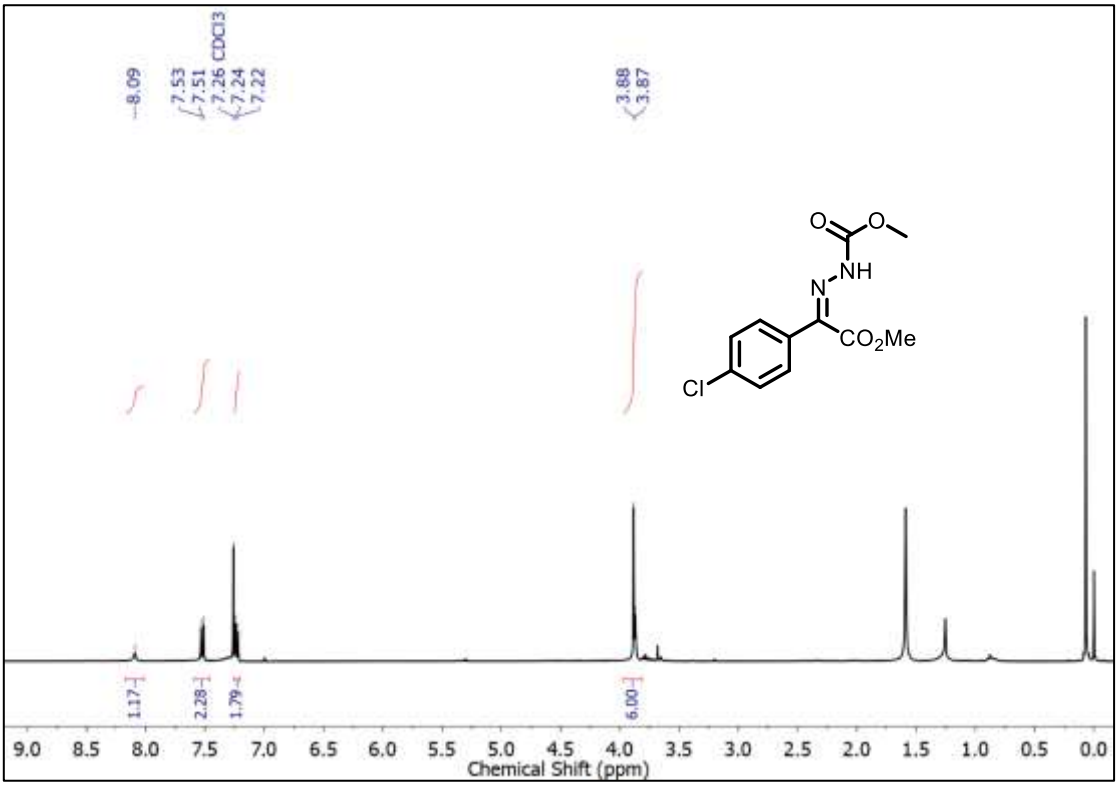
^{1}H NMR 400MHz of **3e** in $CDCl_3$



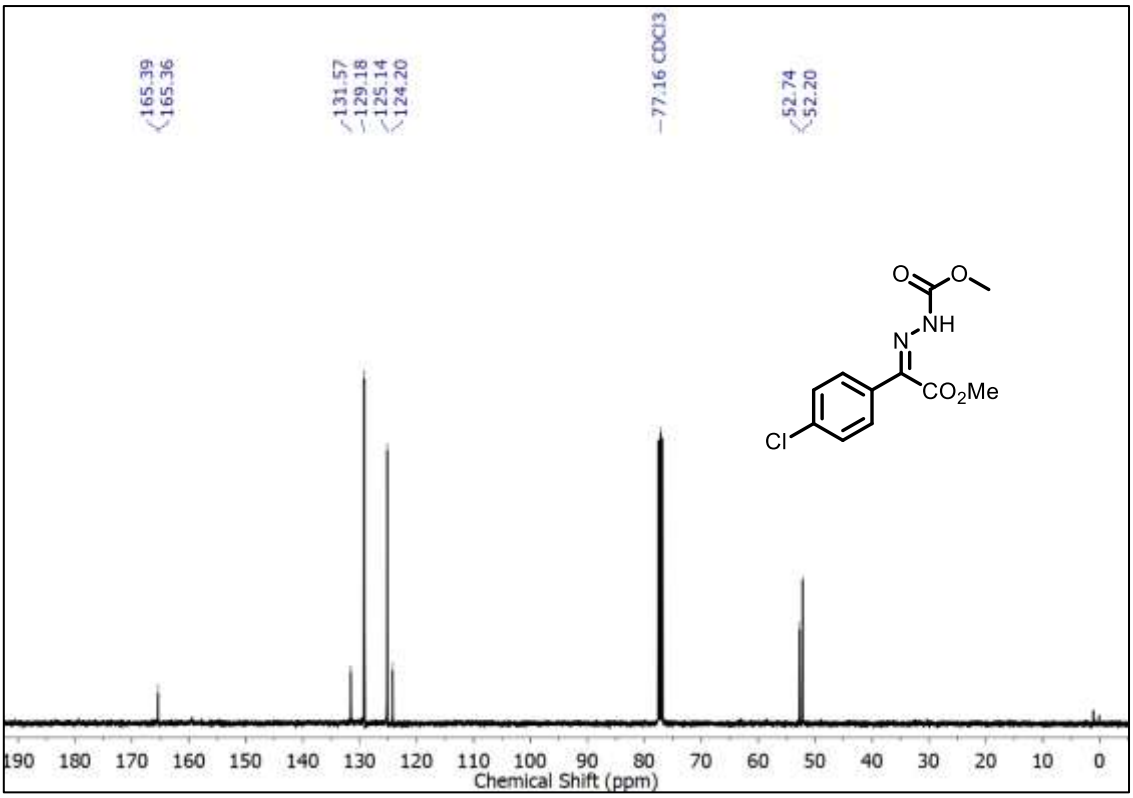
^{13}C NMR 100MHz of **3e** in $CDCl_3$



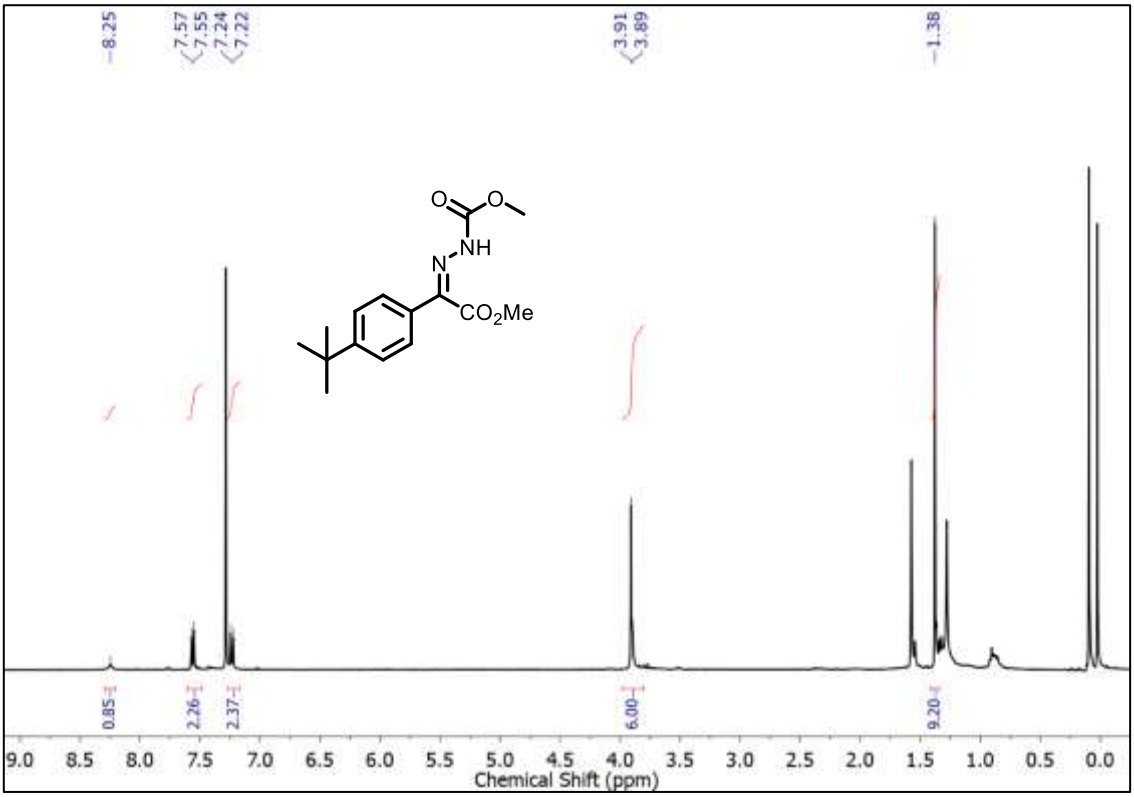
^{1}H NMR 400MHz of **3f** in $CDCl_3$



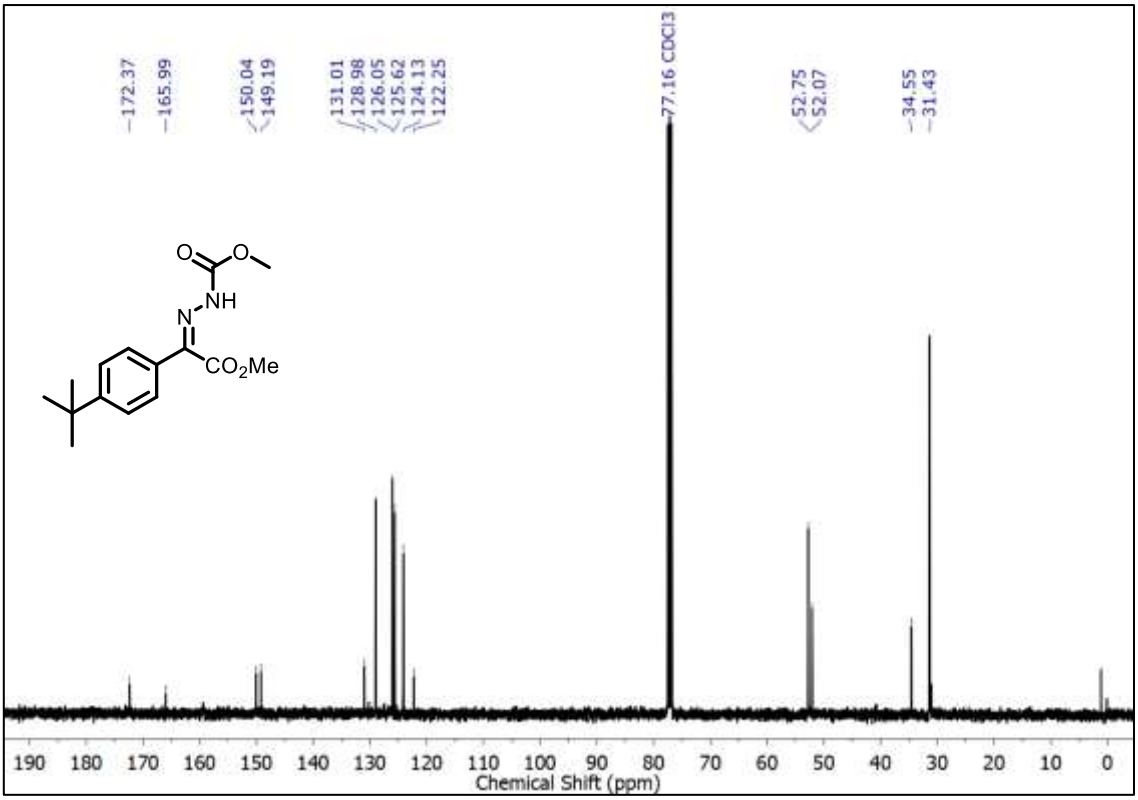
^{13}C NMR 100MHz of **3f** in $CDCl_3$



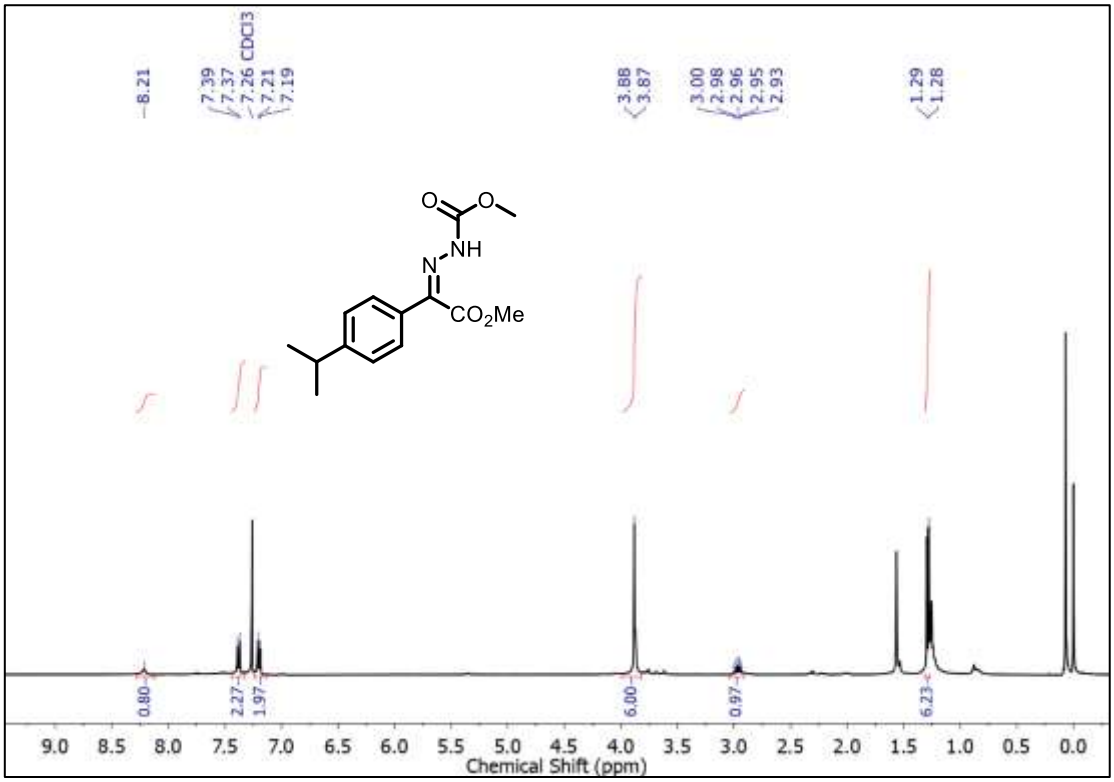
^{1}H NMR 400MHz of **3g** in $CDCl_3$



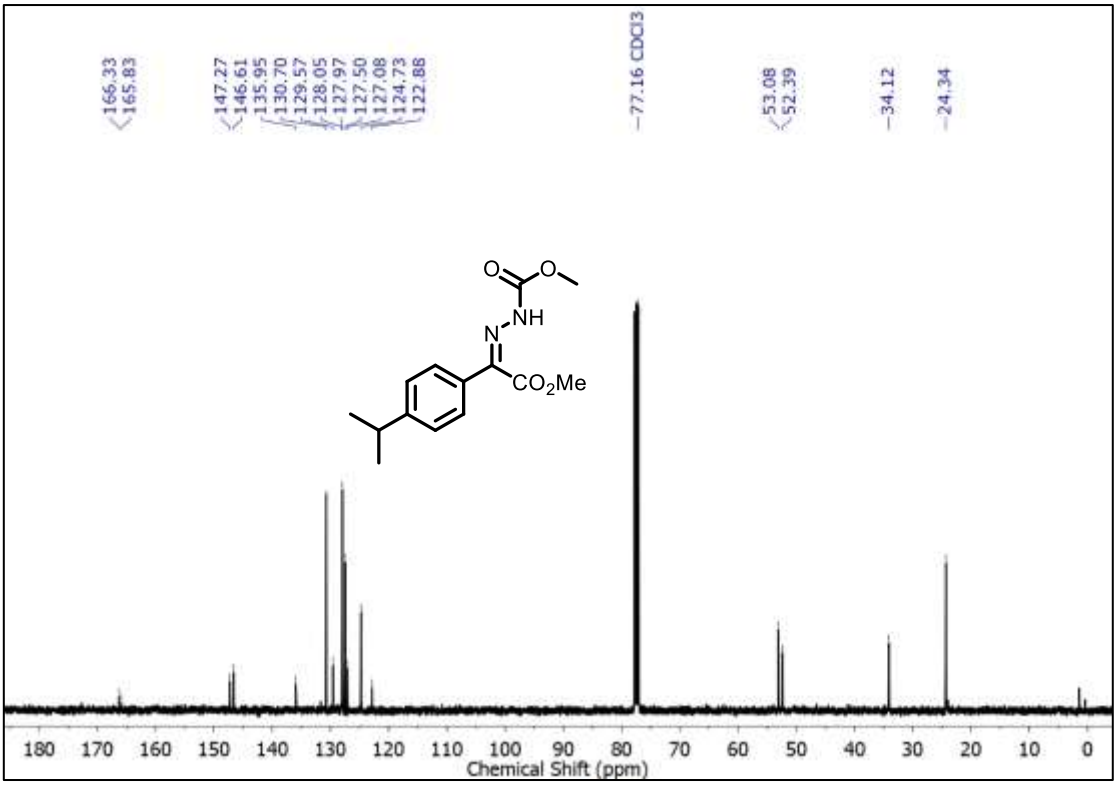
^{13}C NMR 100MHz of **3g** in $CDCl_3$



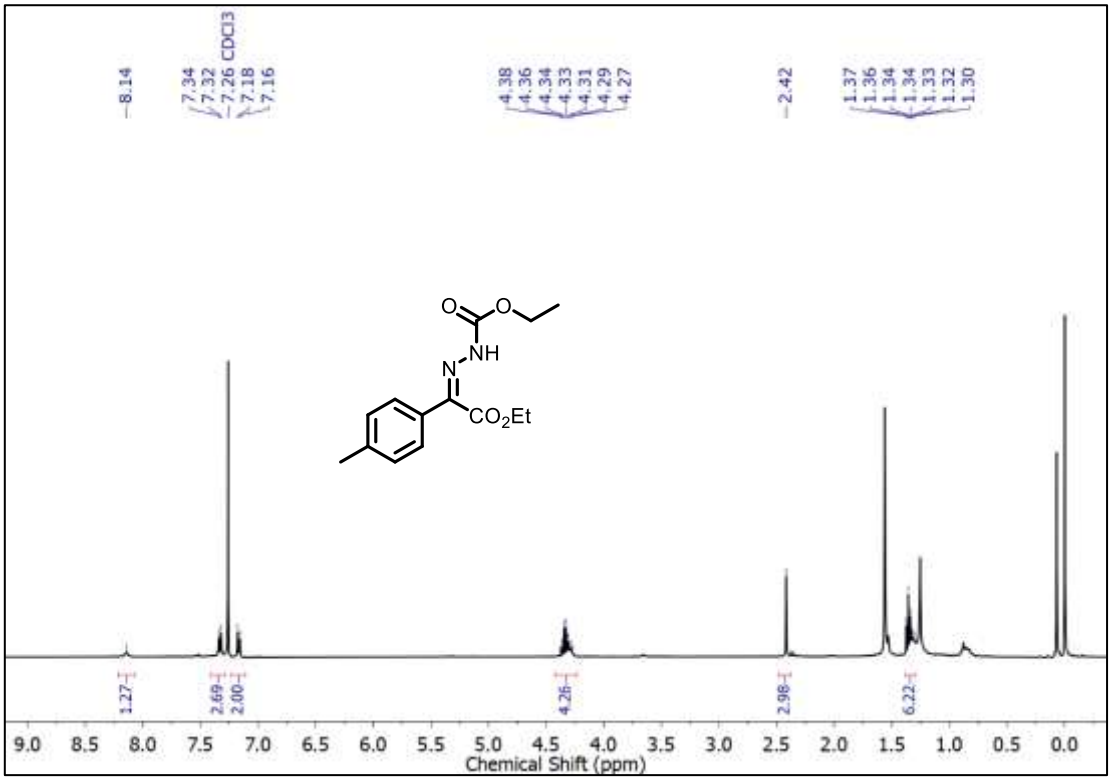
^{1}H NMR 400MHz of **3h** in $CDCl_3$



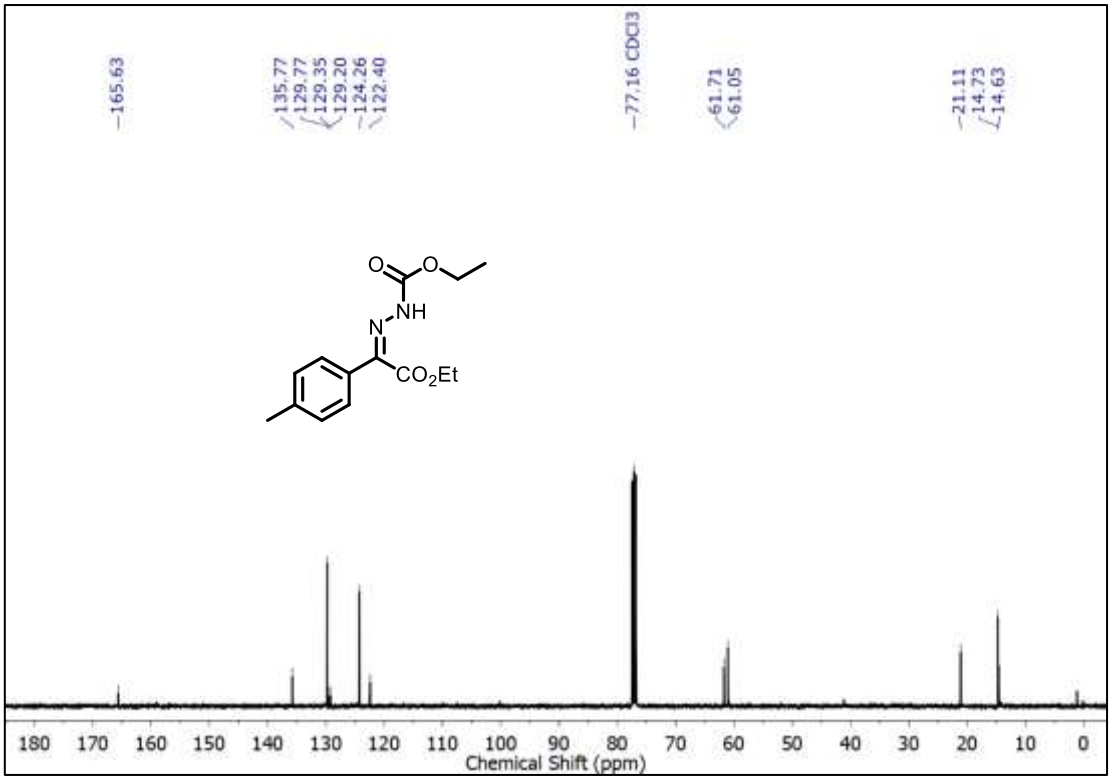
^{13}C NMR 100MHz of 3h in $CDCl_3$



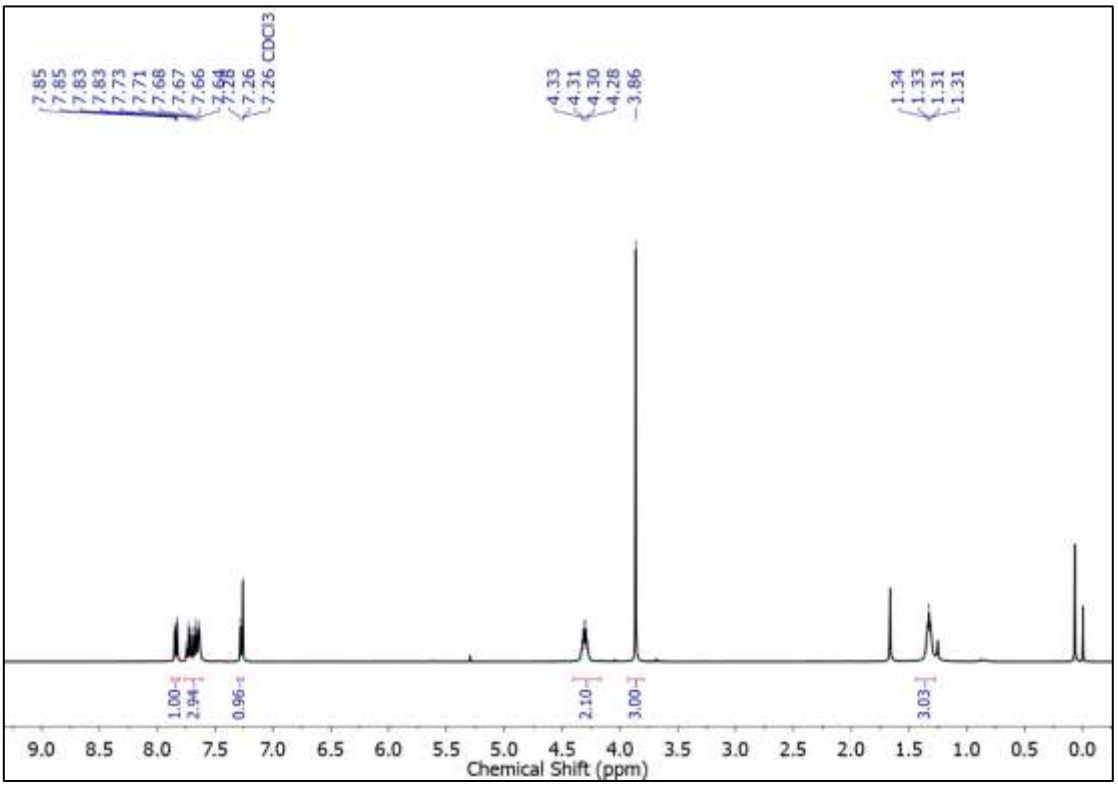
^{1}H NMR 400MHz of **3i** in $CDCl_3$



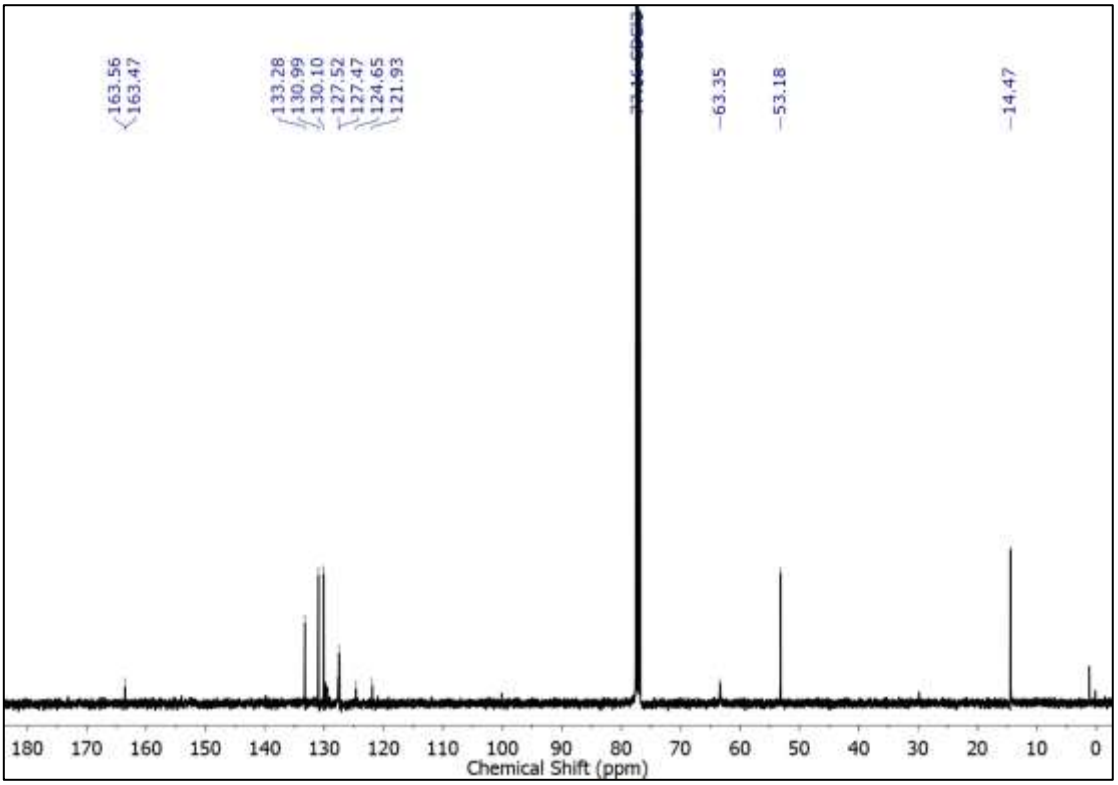
^{13}C NMR 100MHz of **3i** in $CDCl_3$



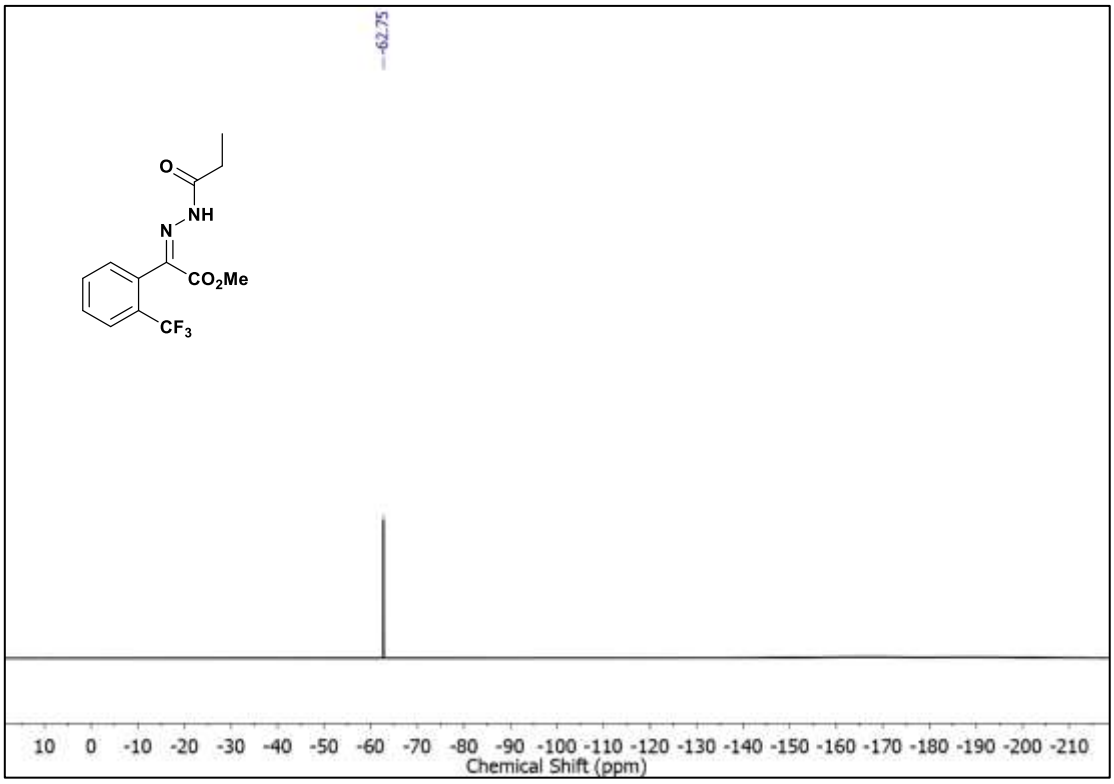
^{1}H NMR 400MHz of **3j** in $CDCl_3$



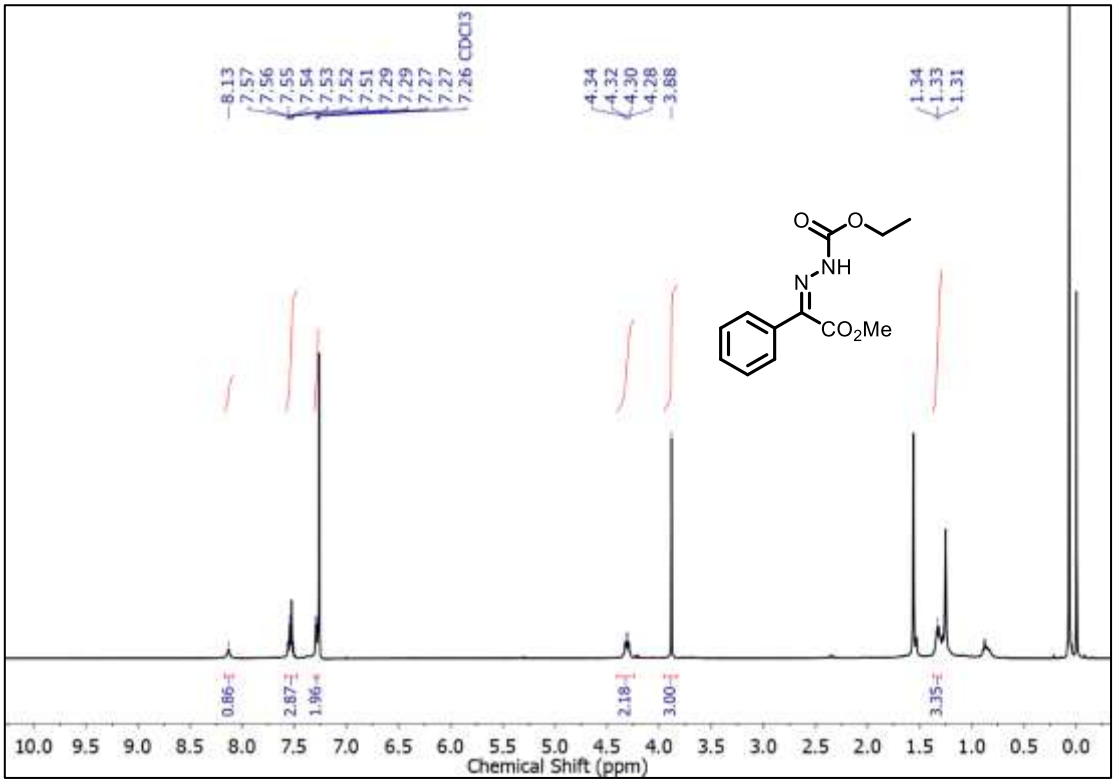
^{13}C NMR 100MHz of **3j** in $CDCl_3$



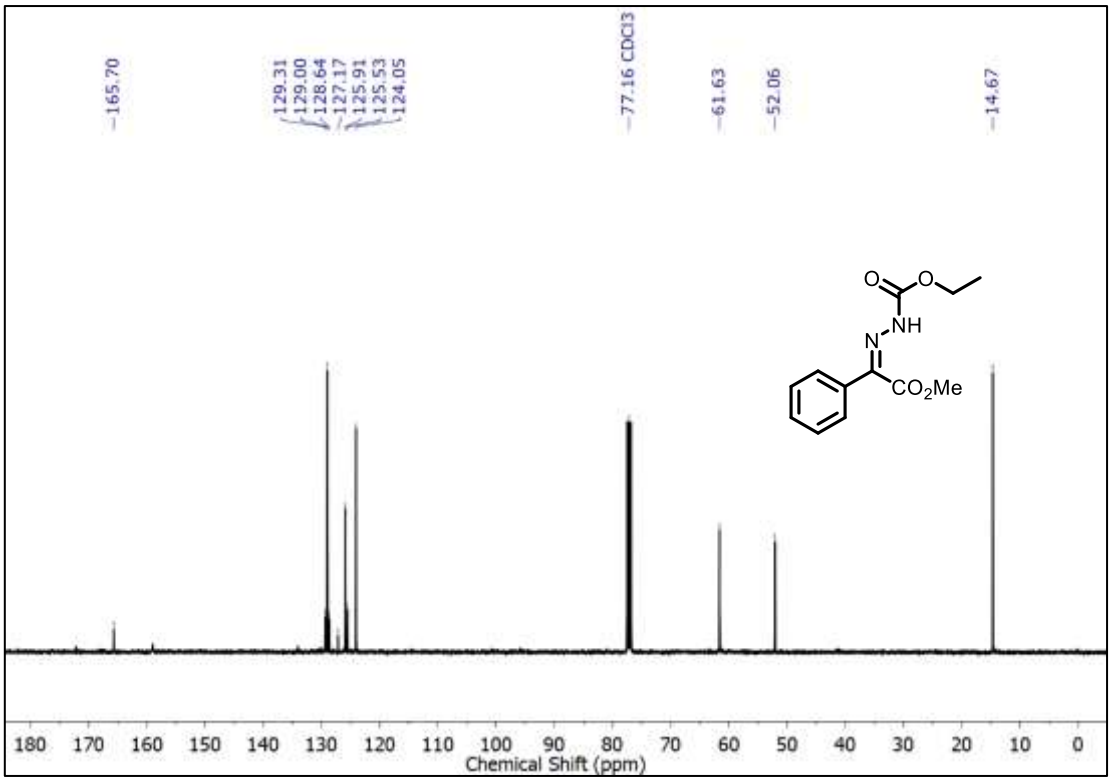
^{19}F NMR 376 MHz of **3j** in $CDCl_3$



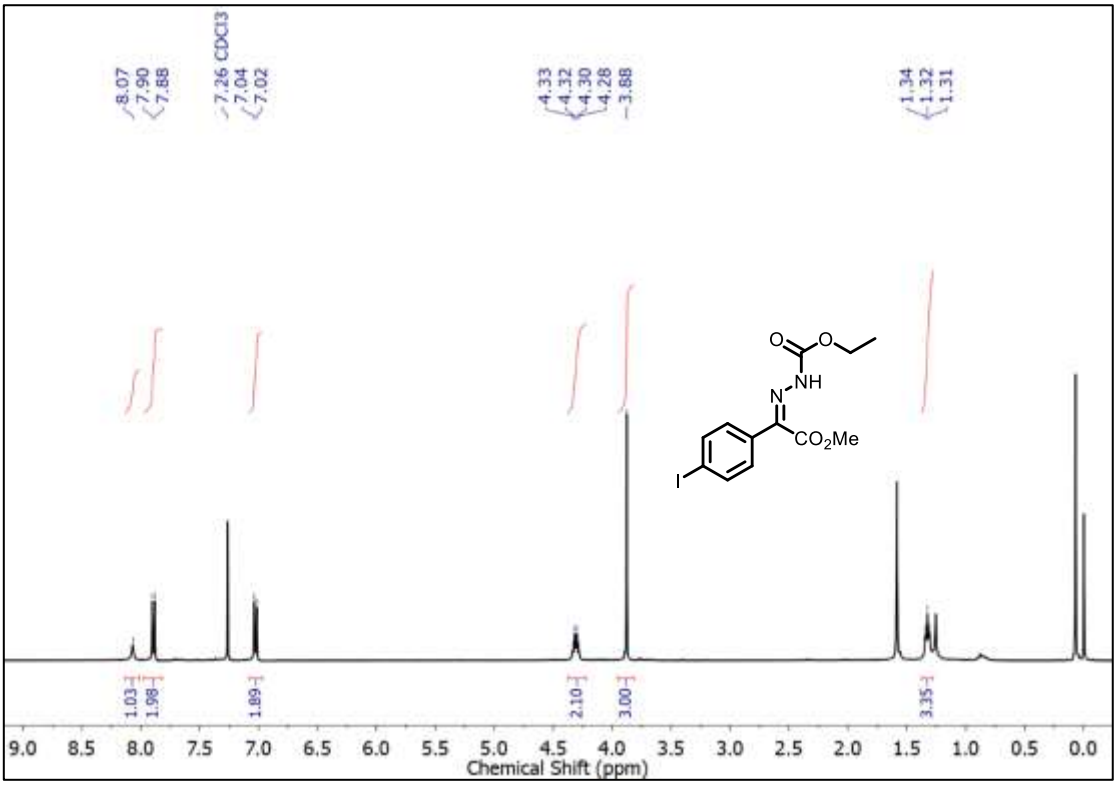
^{1}H NMR 400MHz of **3k** in $CDCl_3$



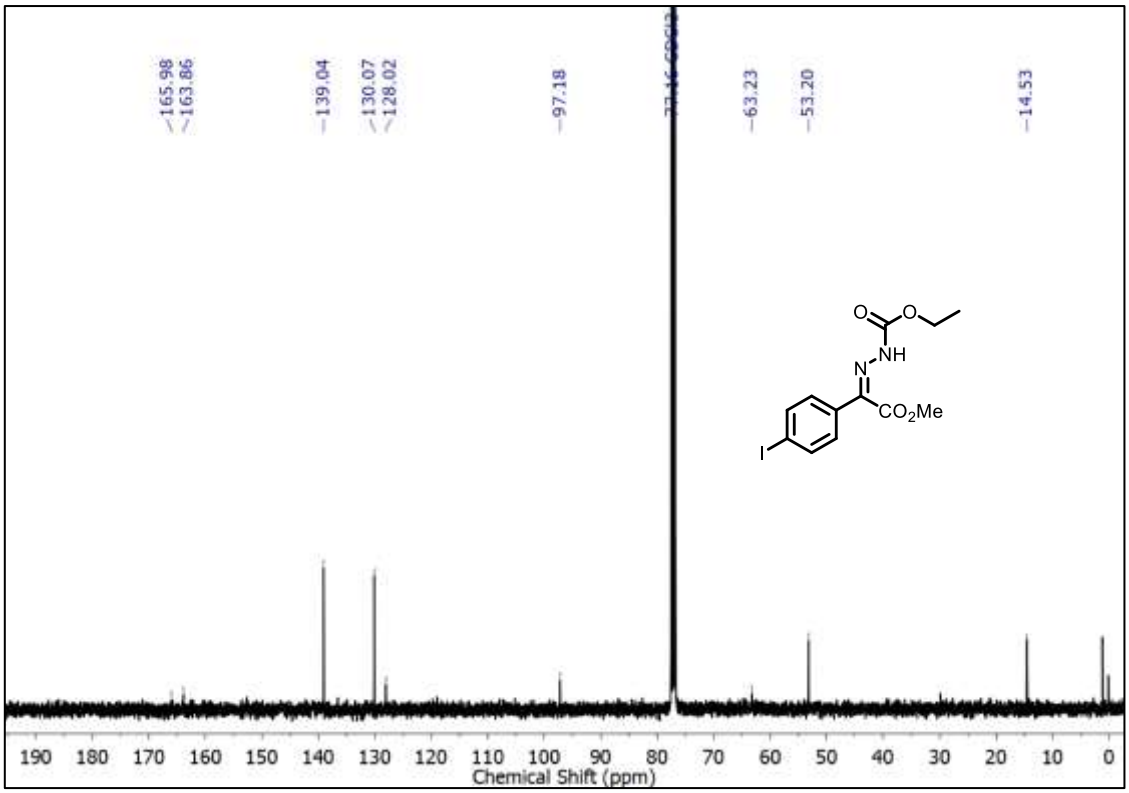
^{13}C NMR 100MHz of **3k** in $CDCl_3$



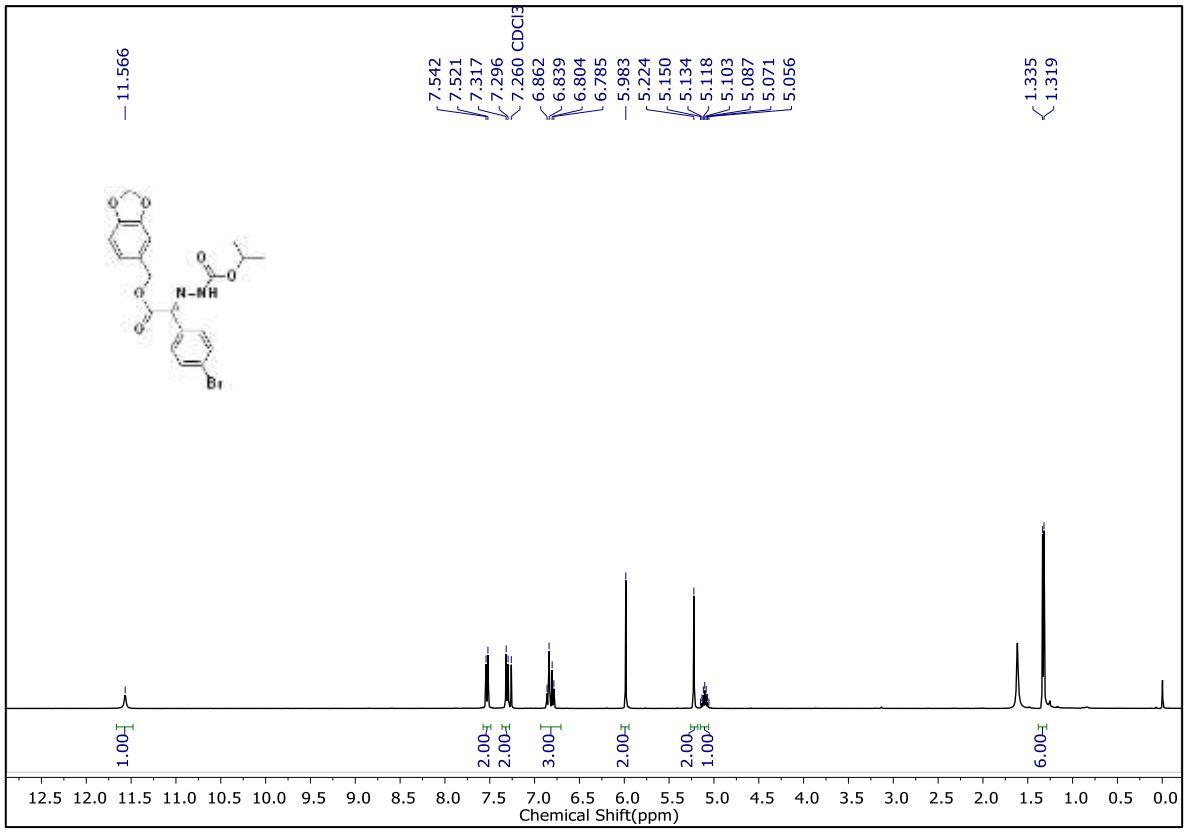
^{1}H NMR 400MHz of **3l** in $CDCl_3$



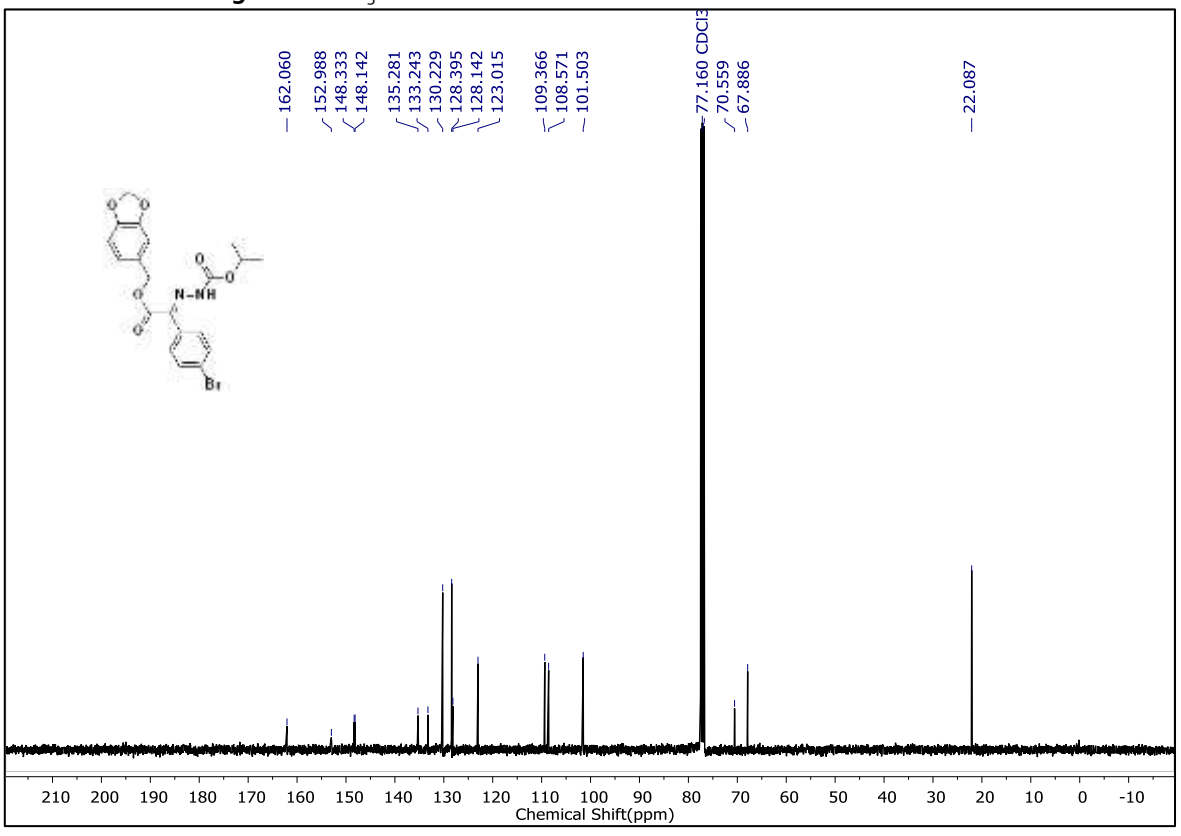
^{13}C NMR 100MHz of **3l** in $CDCl_3$



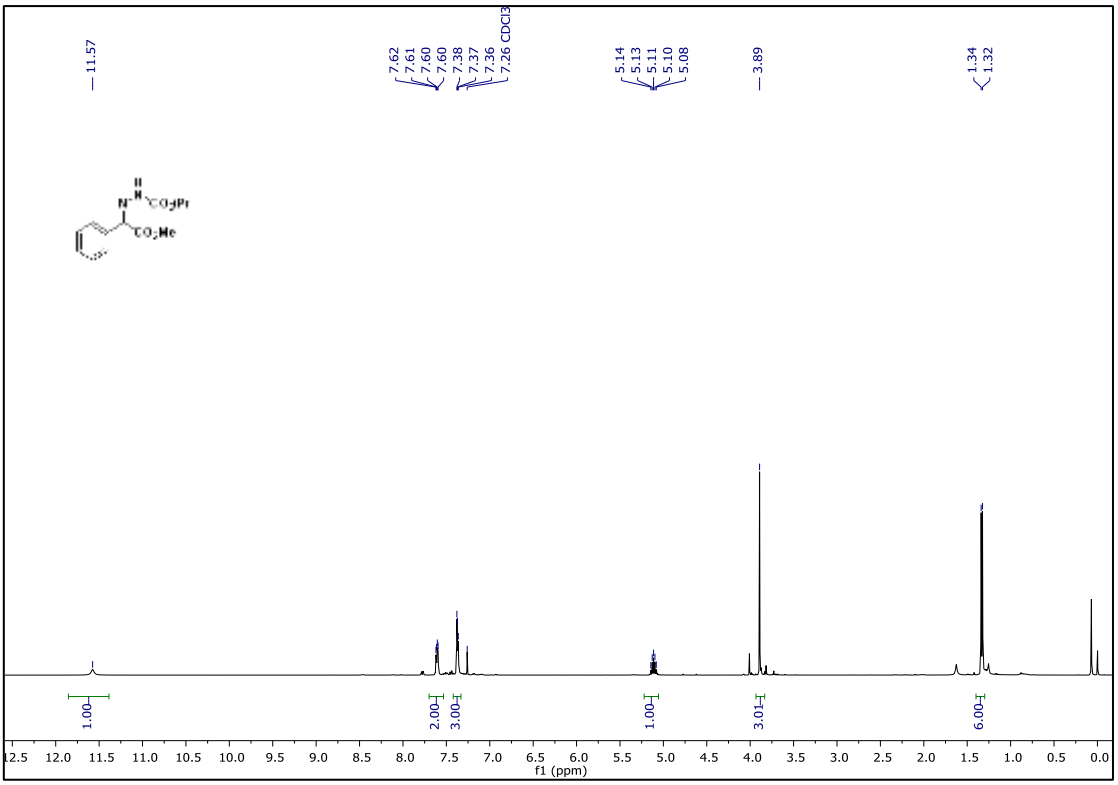
^{1}H NMR 400MHz of **3m** in $CDCl_3$



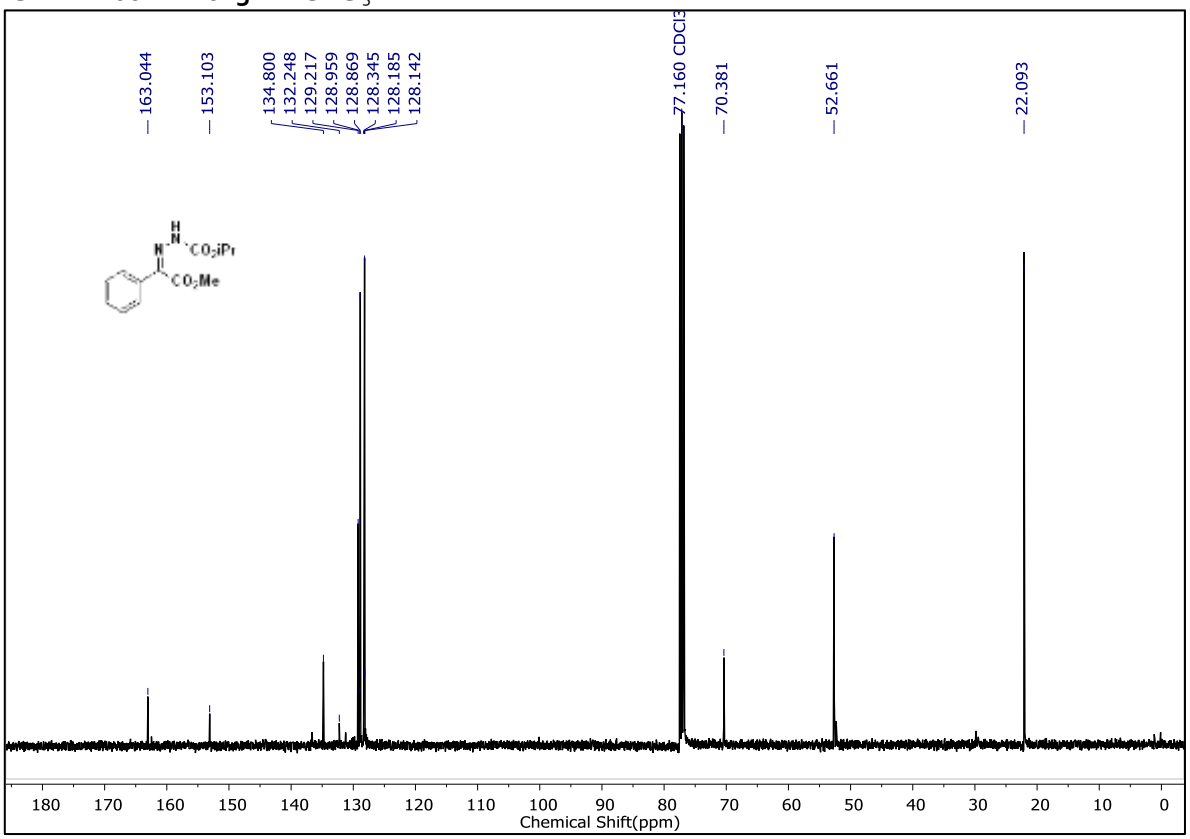
^{13}C NMR 100MHz of **3m** in $CDCl_3$



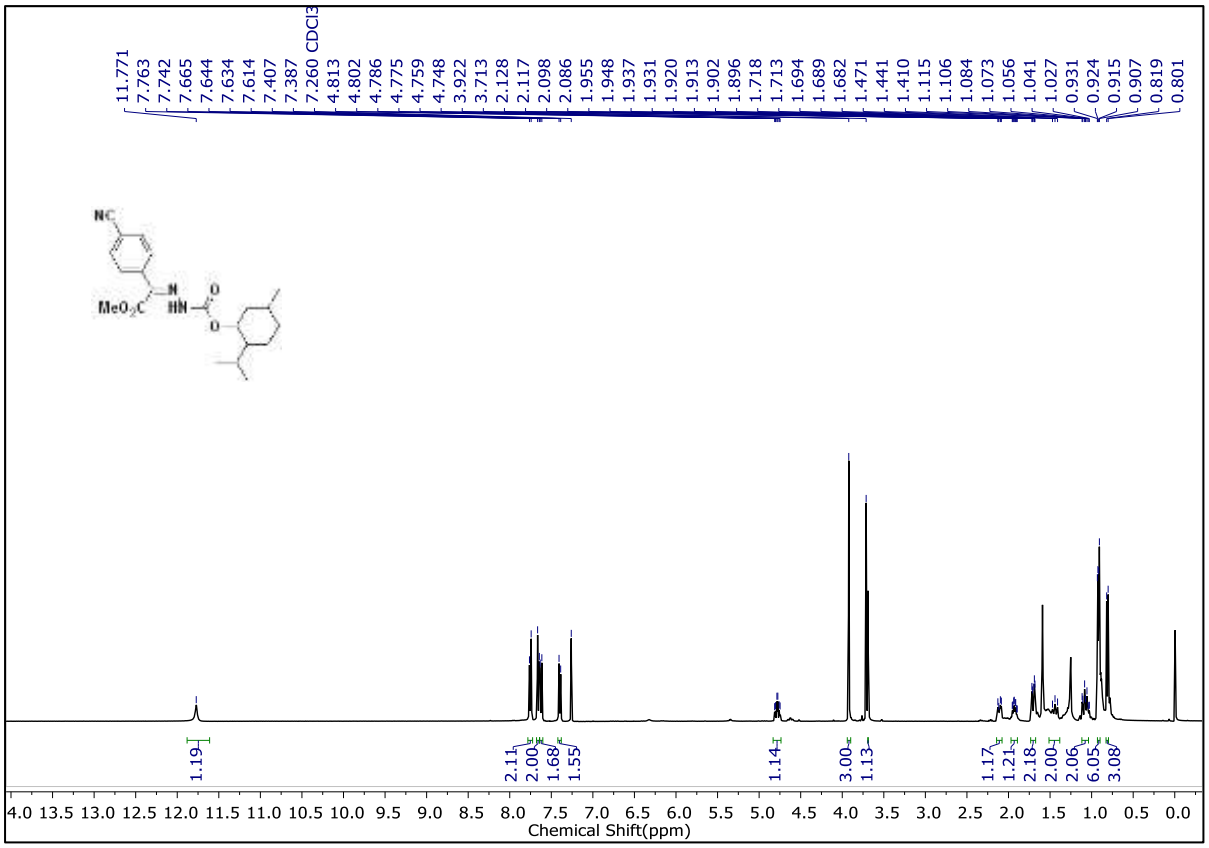
^{1}H NMR 400MHz of **3n** in $CDCl_3$



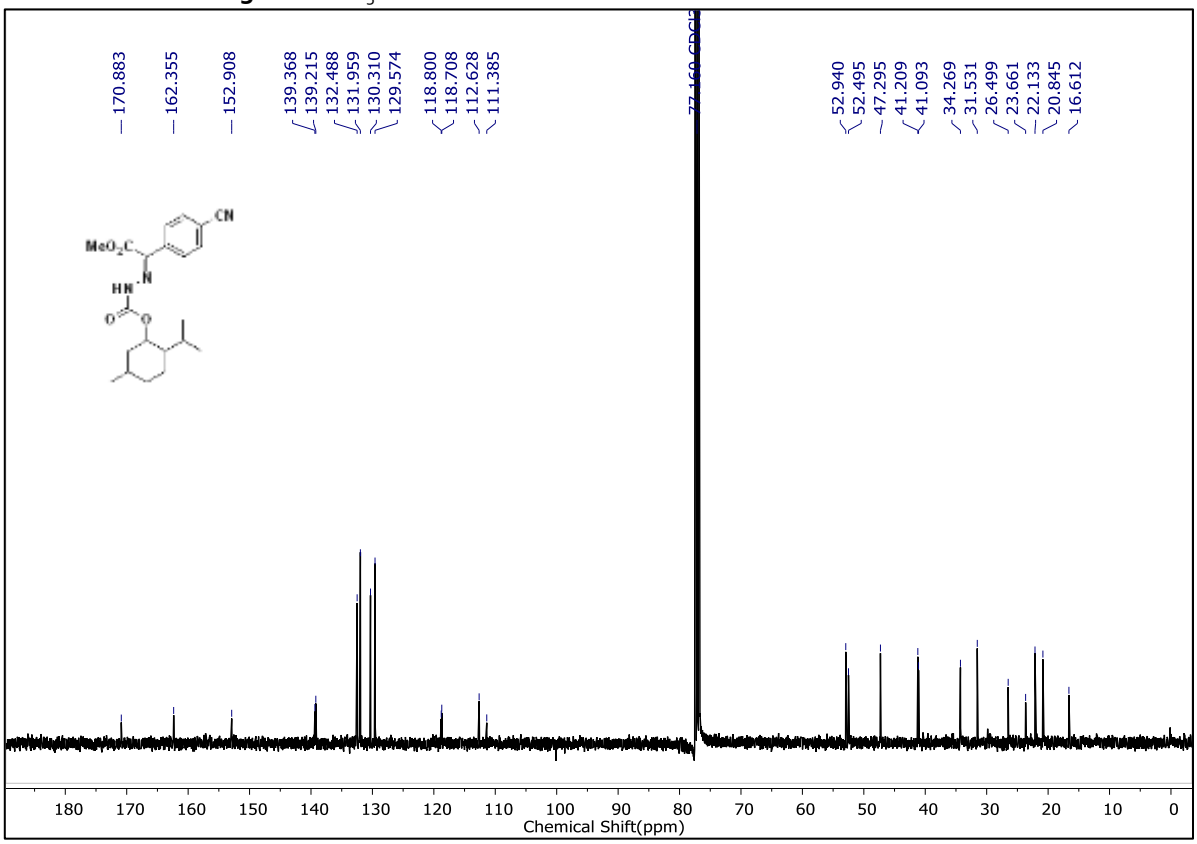
^{13}C NMR 100MHz of **3n** in $CDCl_3$



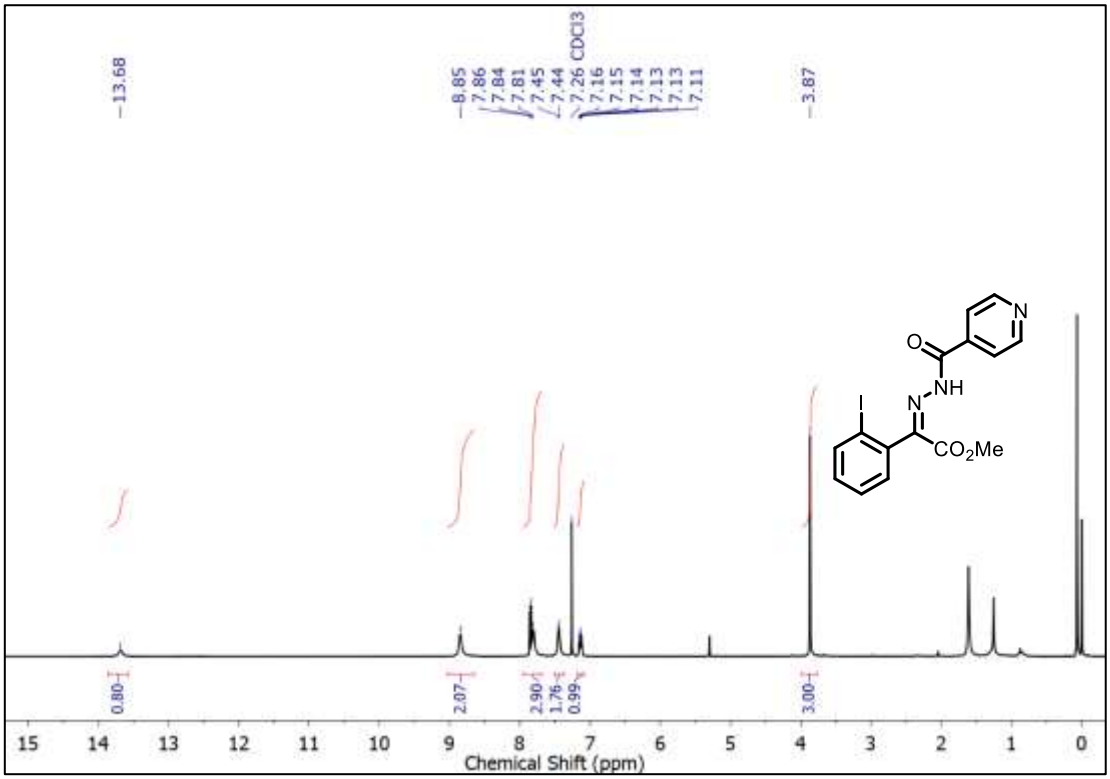
^{1}H NMR 400MHz of **30** in $CDCl_3$



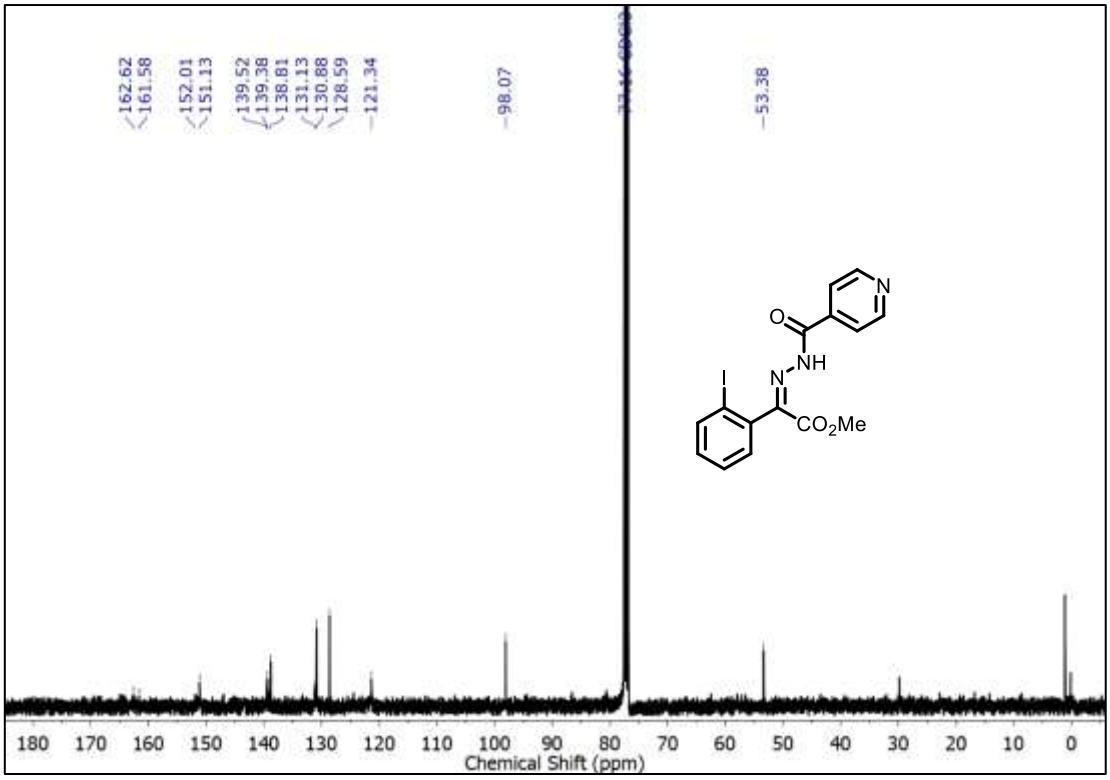
^{13}C NMR 100MHz of **30** in $CDCl_3$



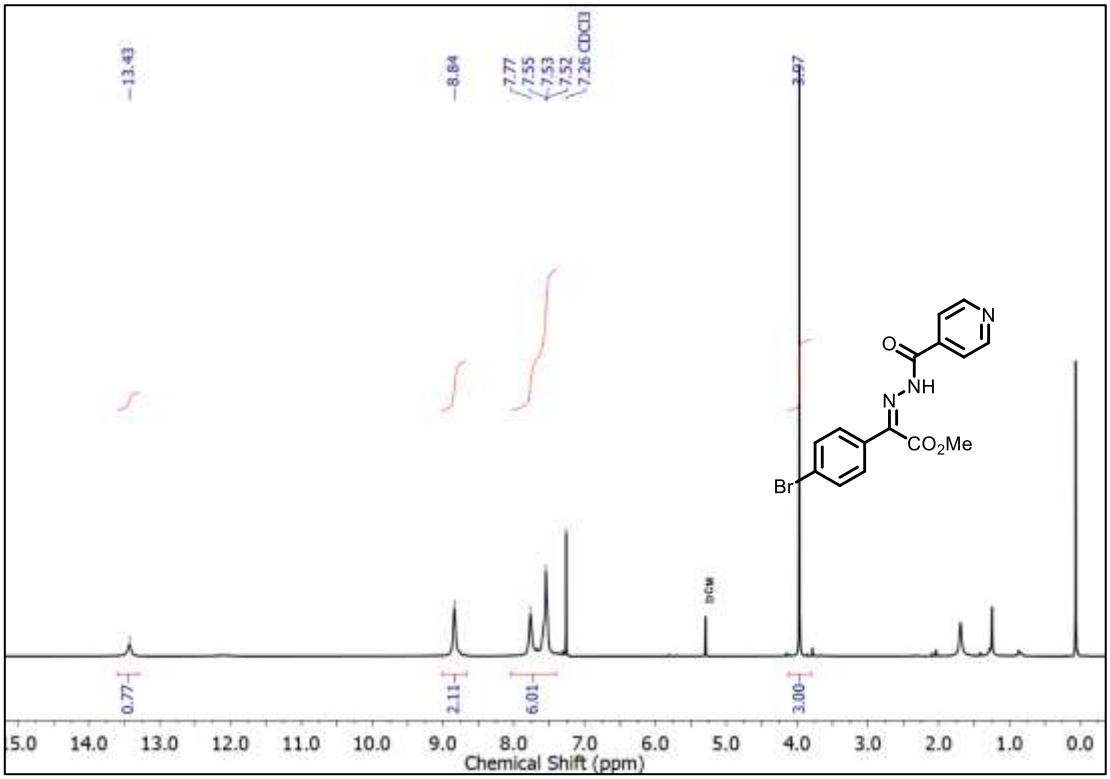
^{1}H NMR 400MHz of **3p** in $CDCl_3$



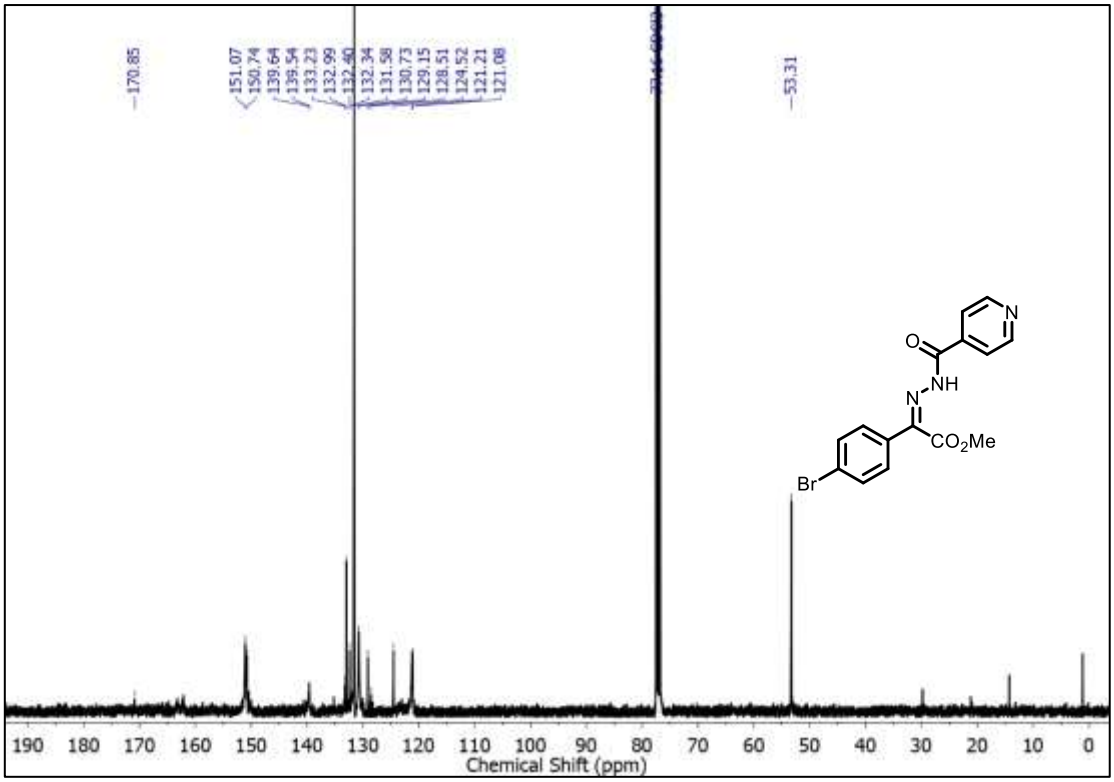
^{13}C NMR 100MHz of **3p** in $CDCl_3$



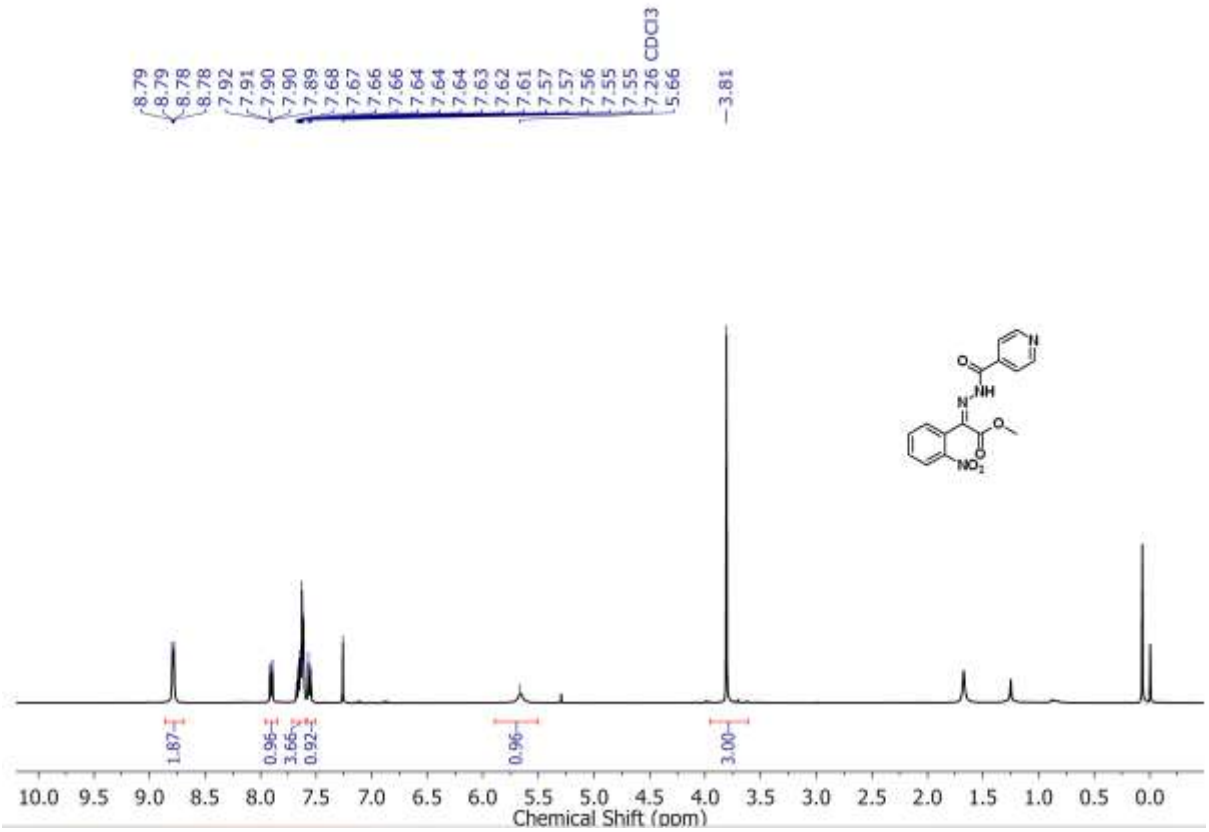
^{1}H NMR 400MHz of **3q** in $CDCl_3$



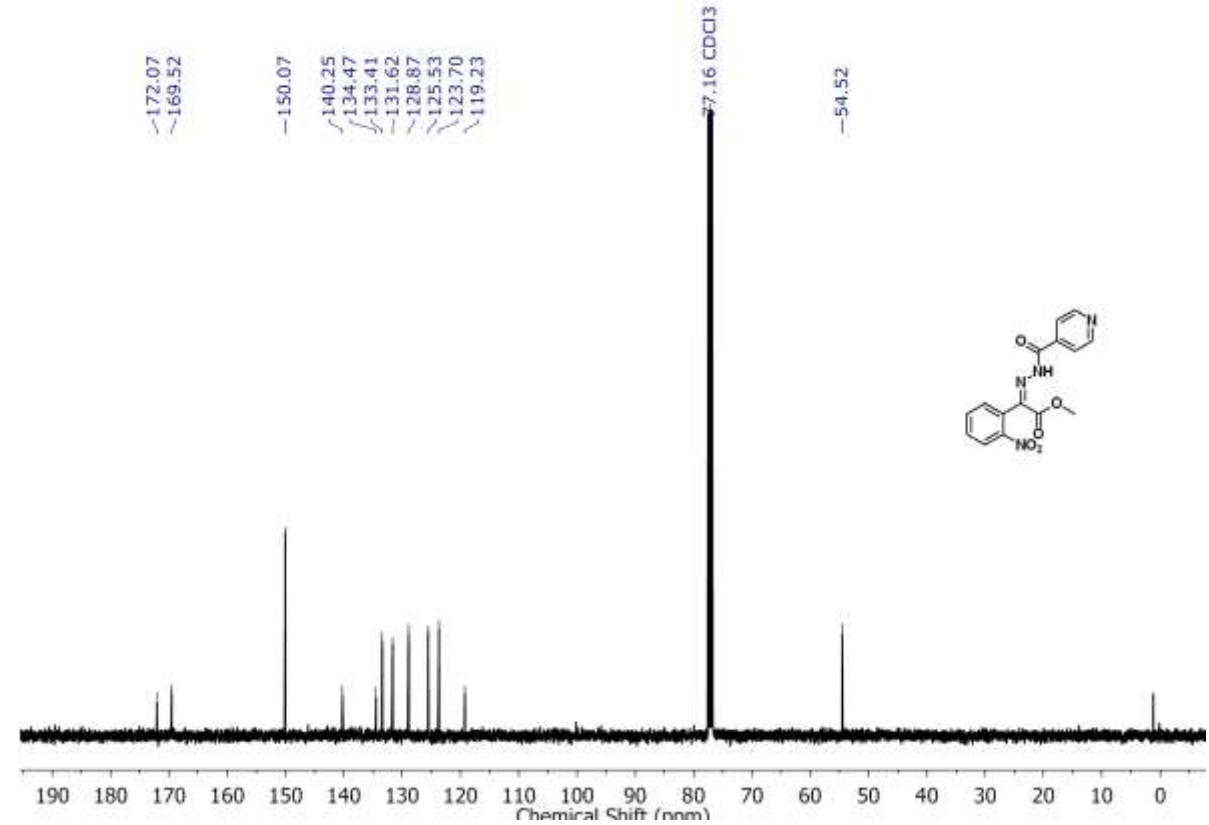
^{13}C NMR 100MHz of **3q** in $CDCl_3$



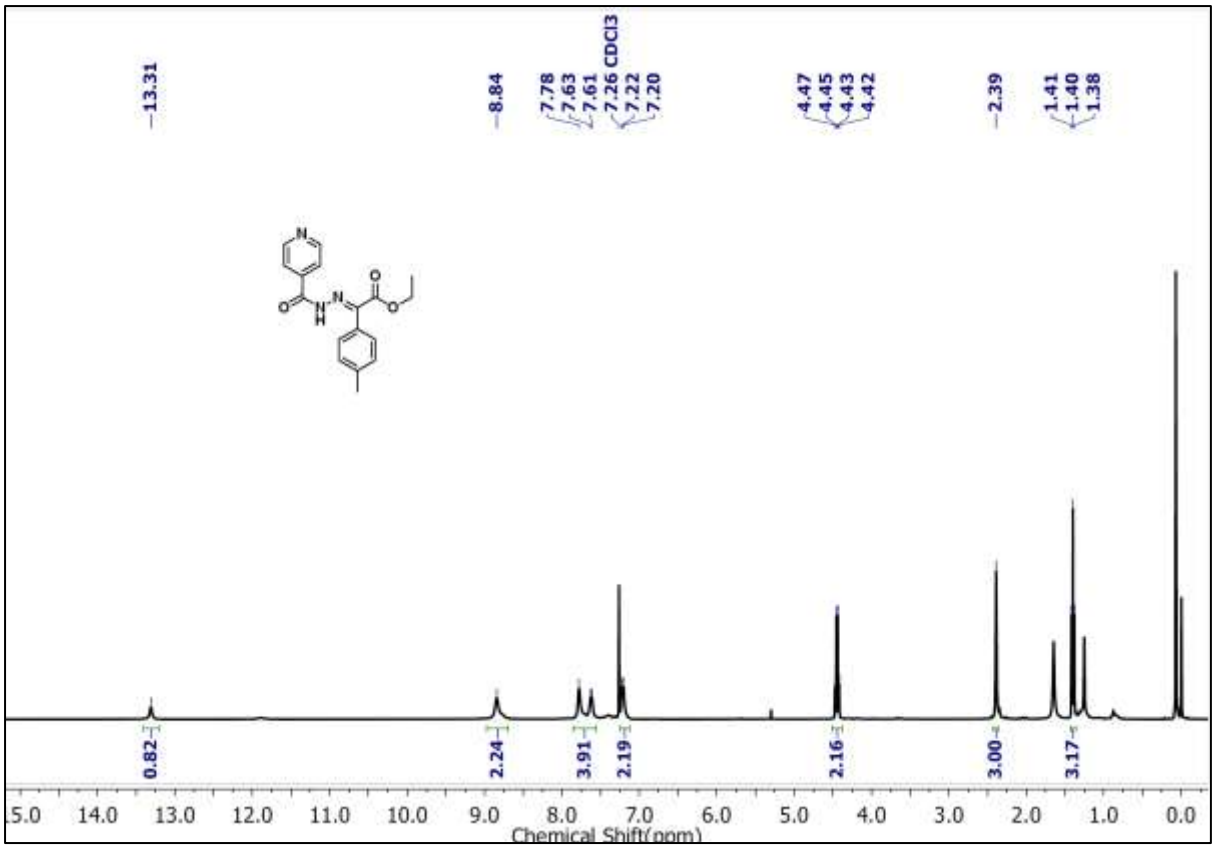
^{1}H NMR 400MHz of **3r** in $CDCl_3$



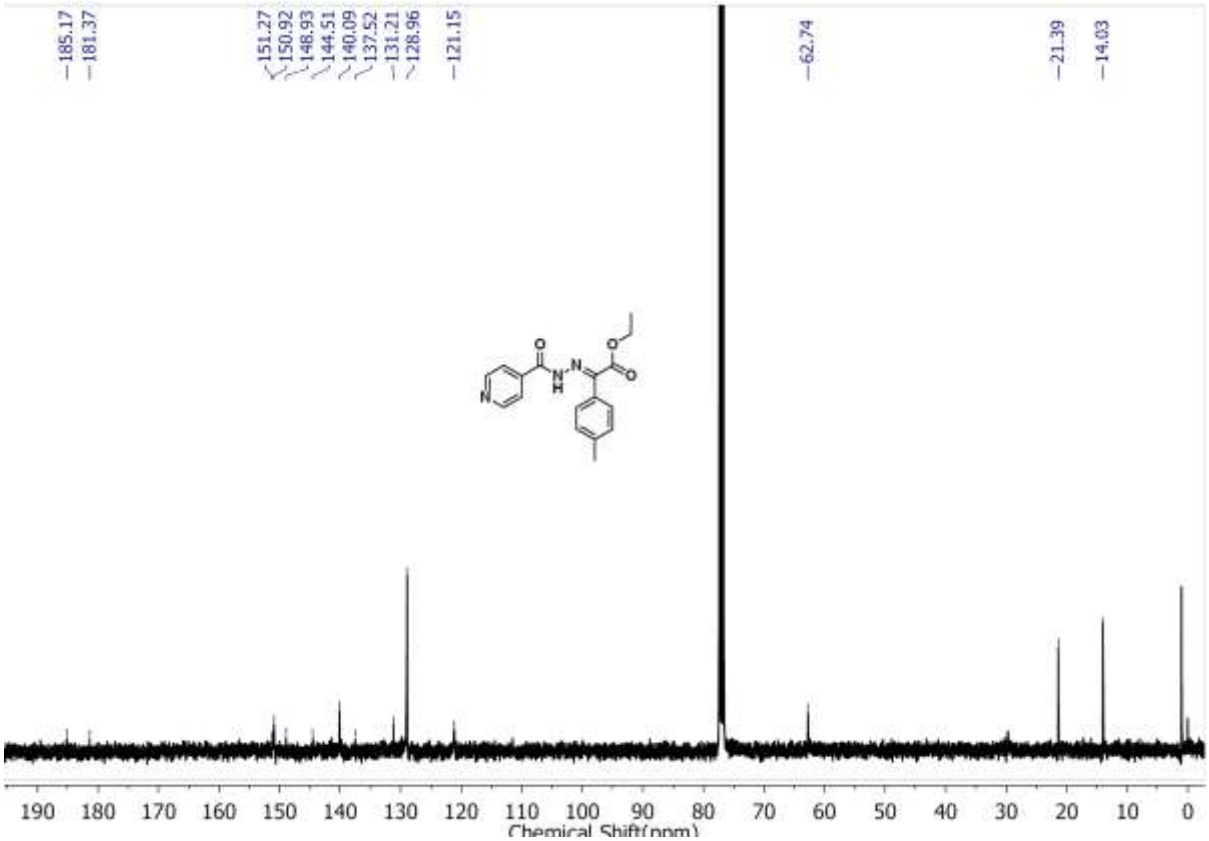
^{13}C NMR 100MHz of **3r** in $CDCl_3$



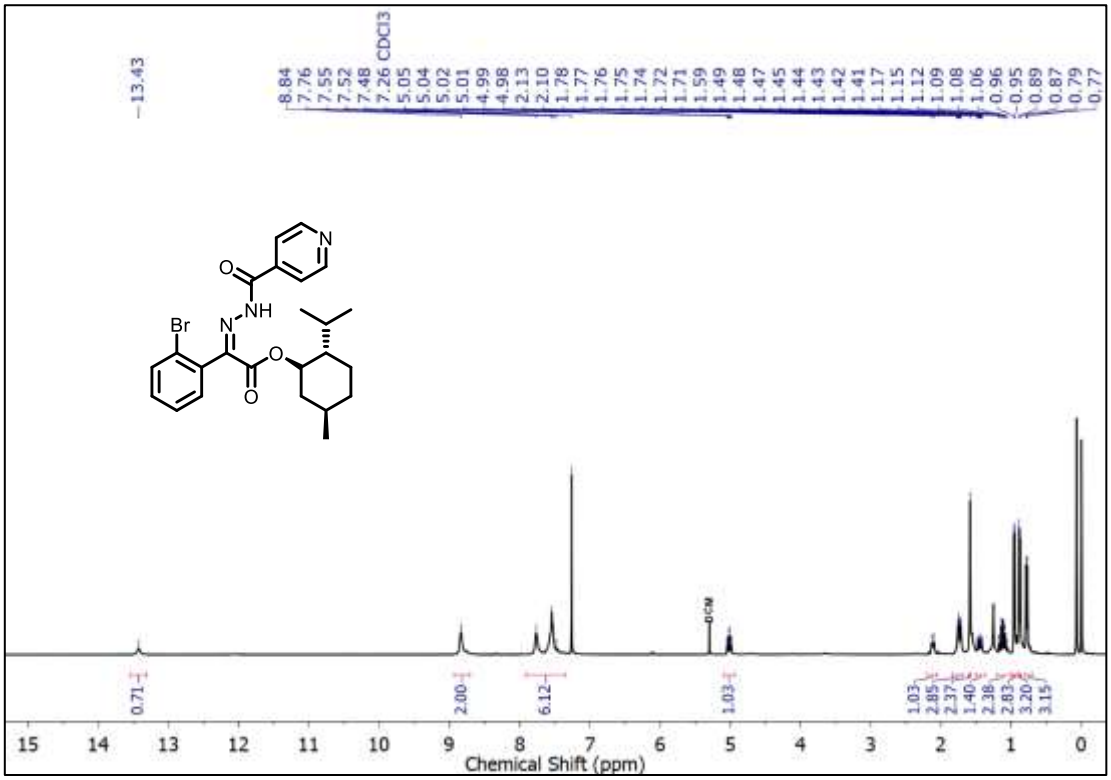
^{1}H NMR 400MHz of **3s** in $CDCl_3$



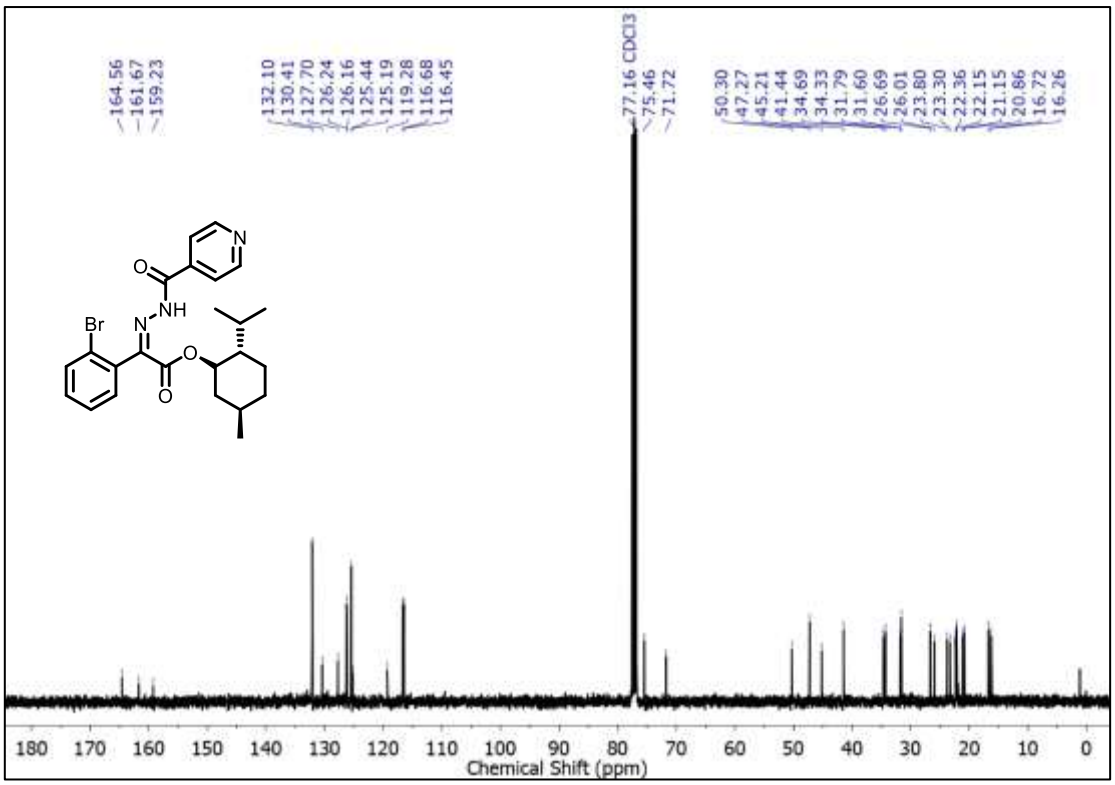
^{13}C NMR 100MHz of **3s** in $CDCl_3$



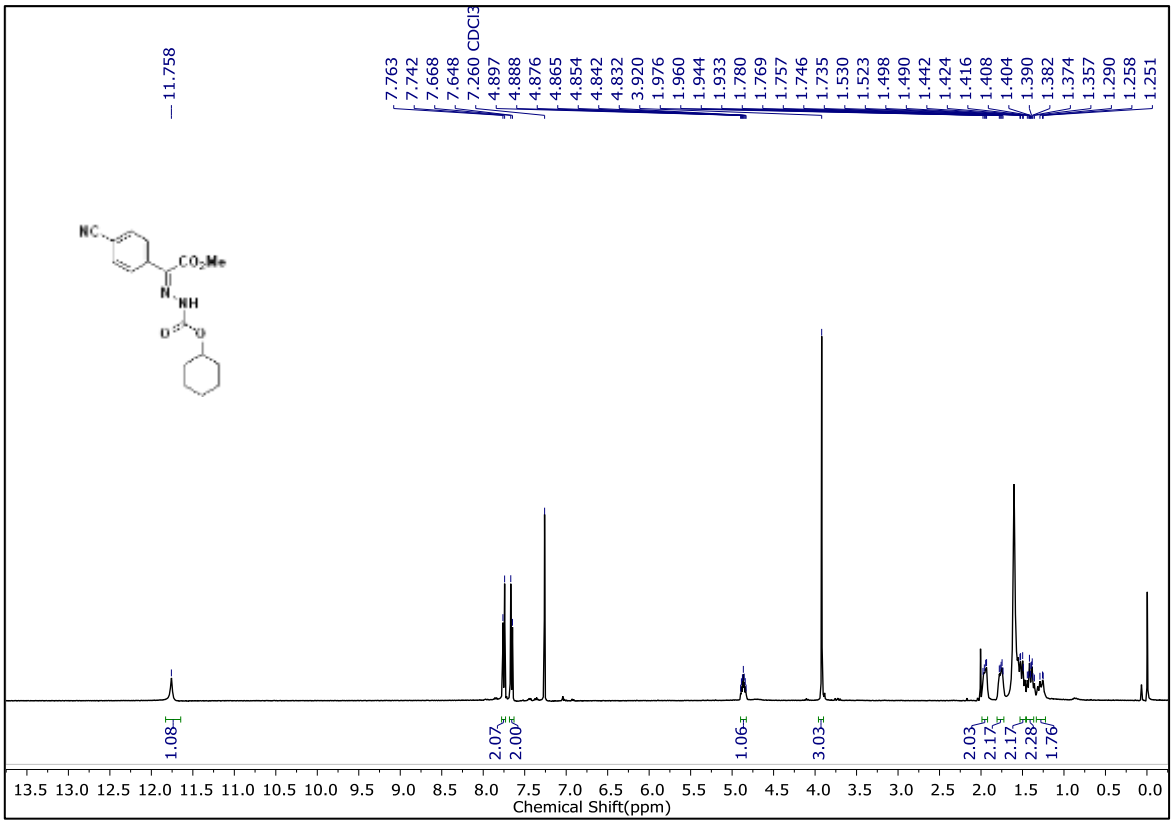
^{1}H NMR 400MHz of **3t** in $CDCl_3$



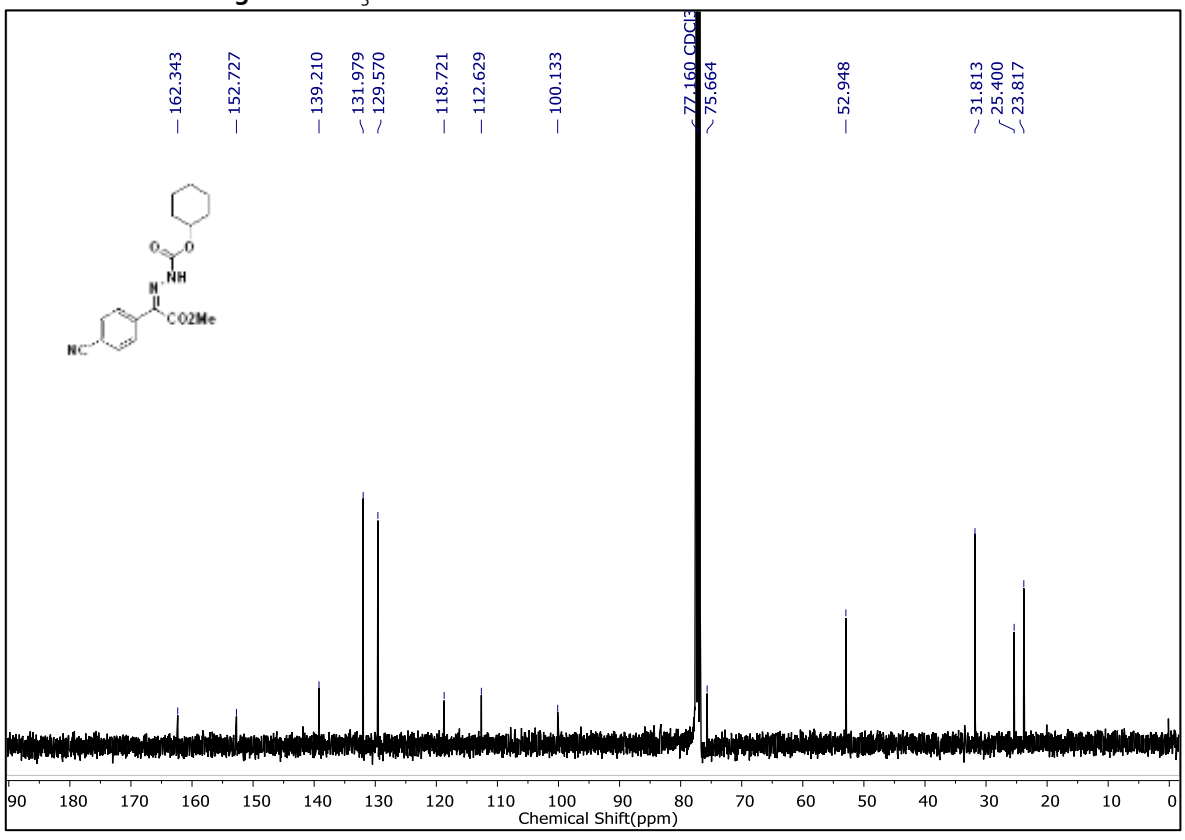
^{13}C NMR 100MHz of **3t** in $CDCl_3$



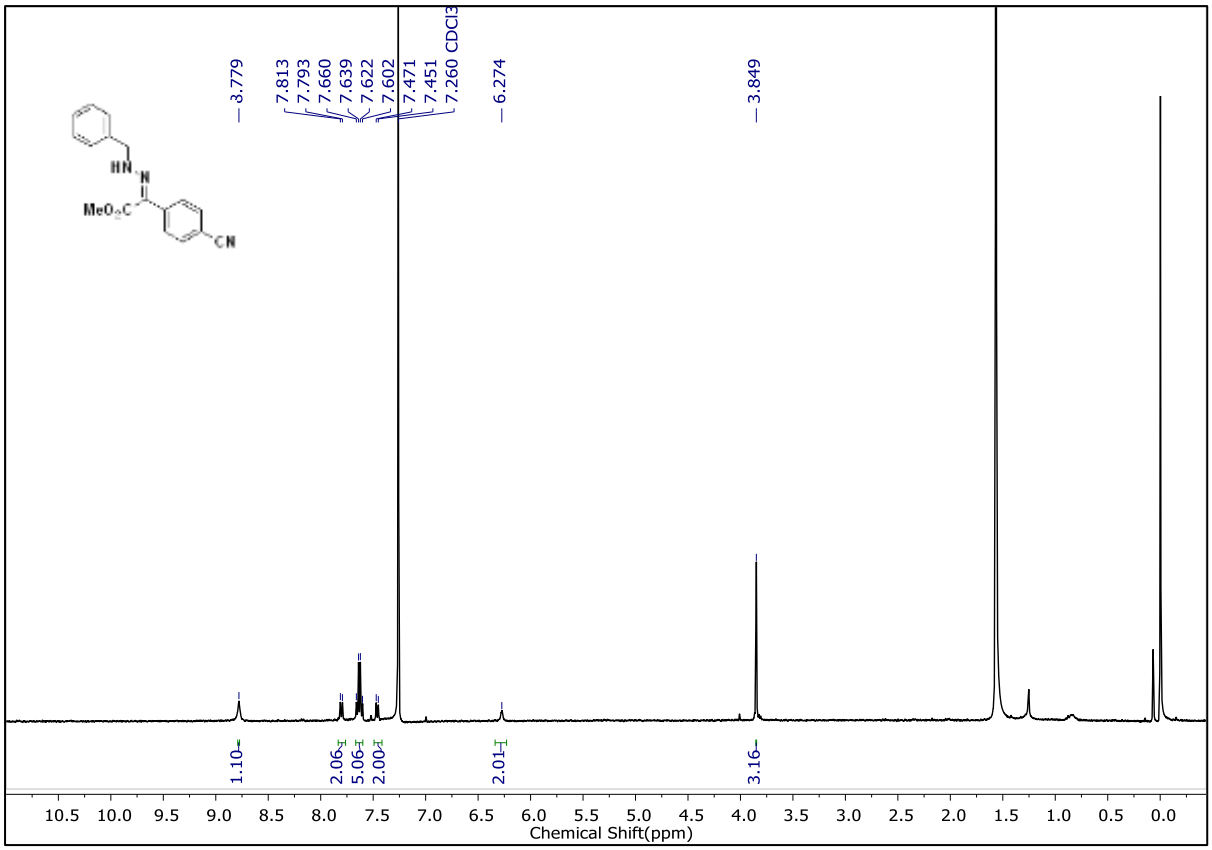
^{1}H NMR 400MHz of **3u** in $CDCl_3$



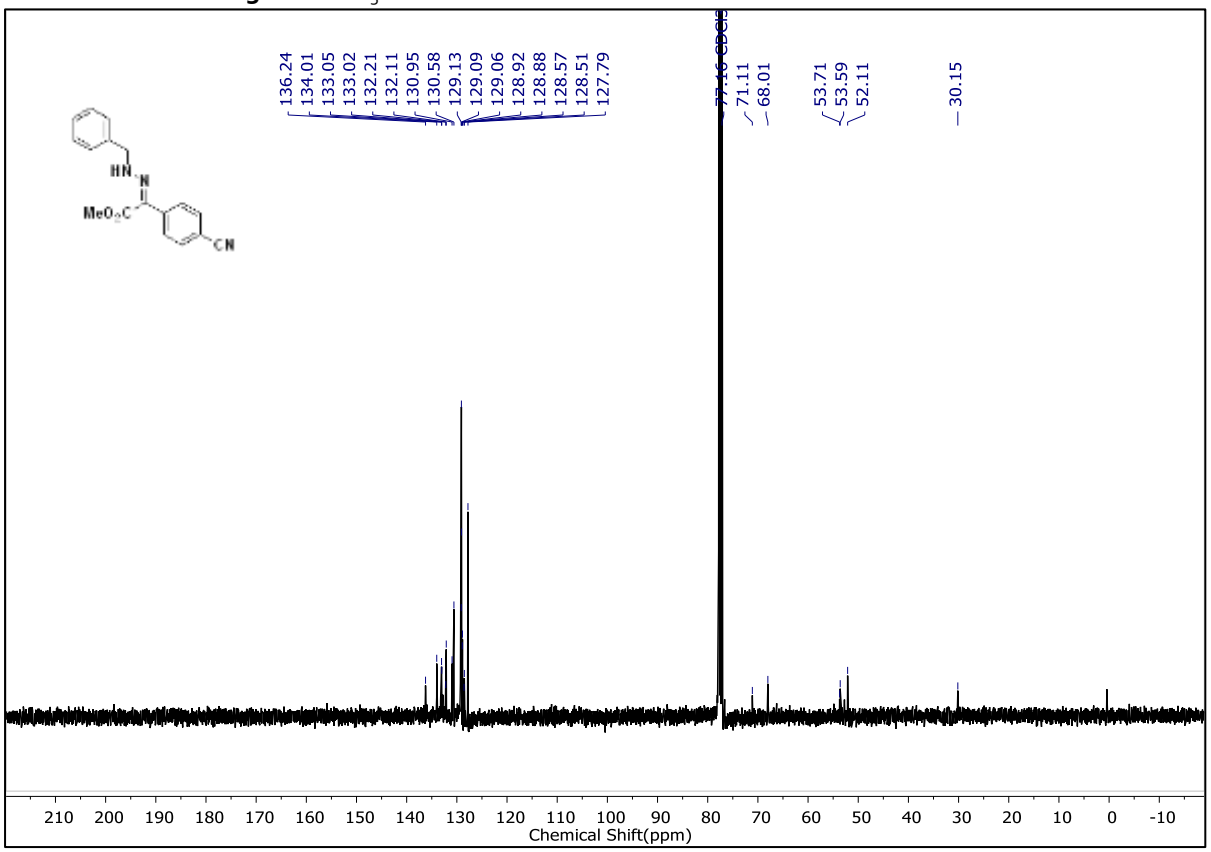
^{13}C NMR 100MHz of **3u** in $CDCl_3$



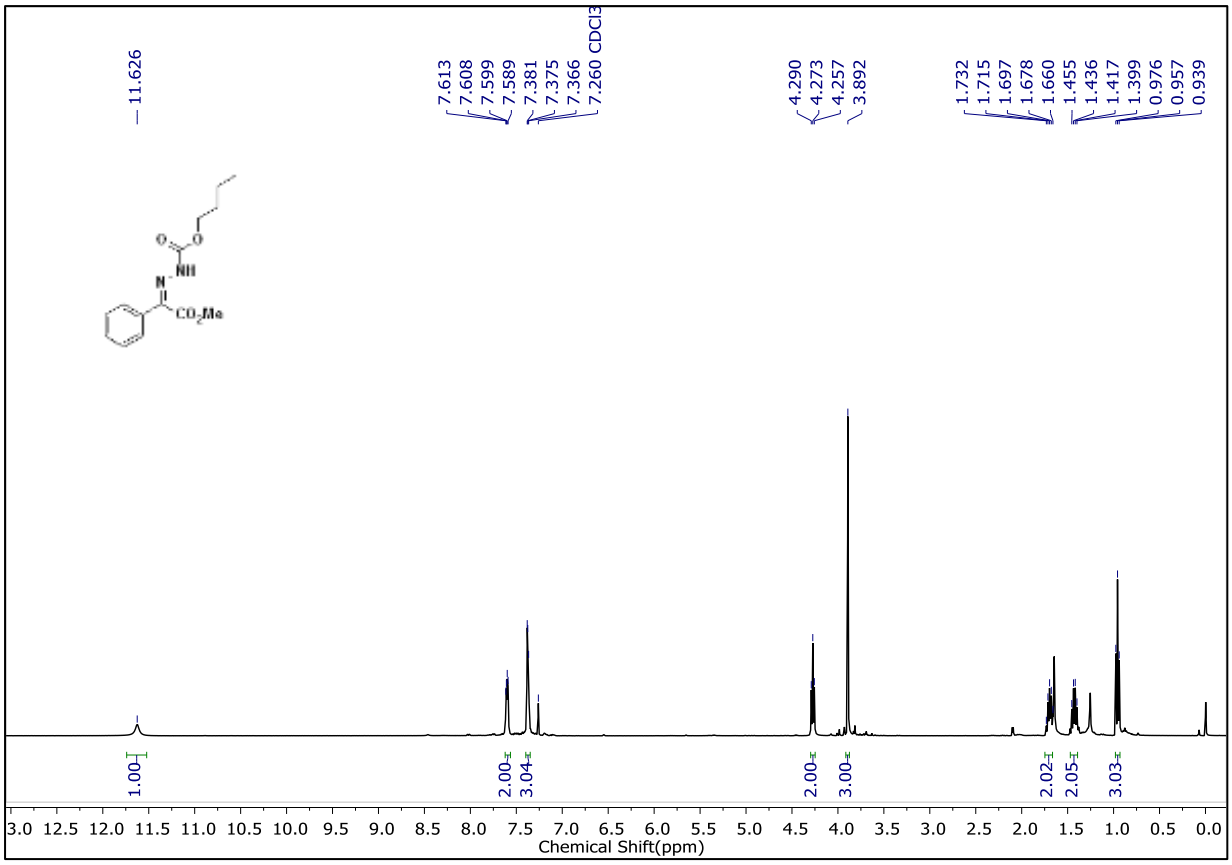
^{1}H NMR 400MHz of **3v** in $CDCl_3$



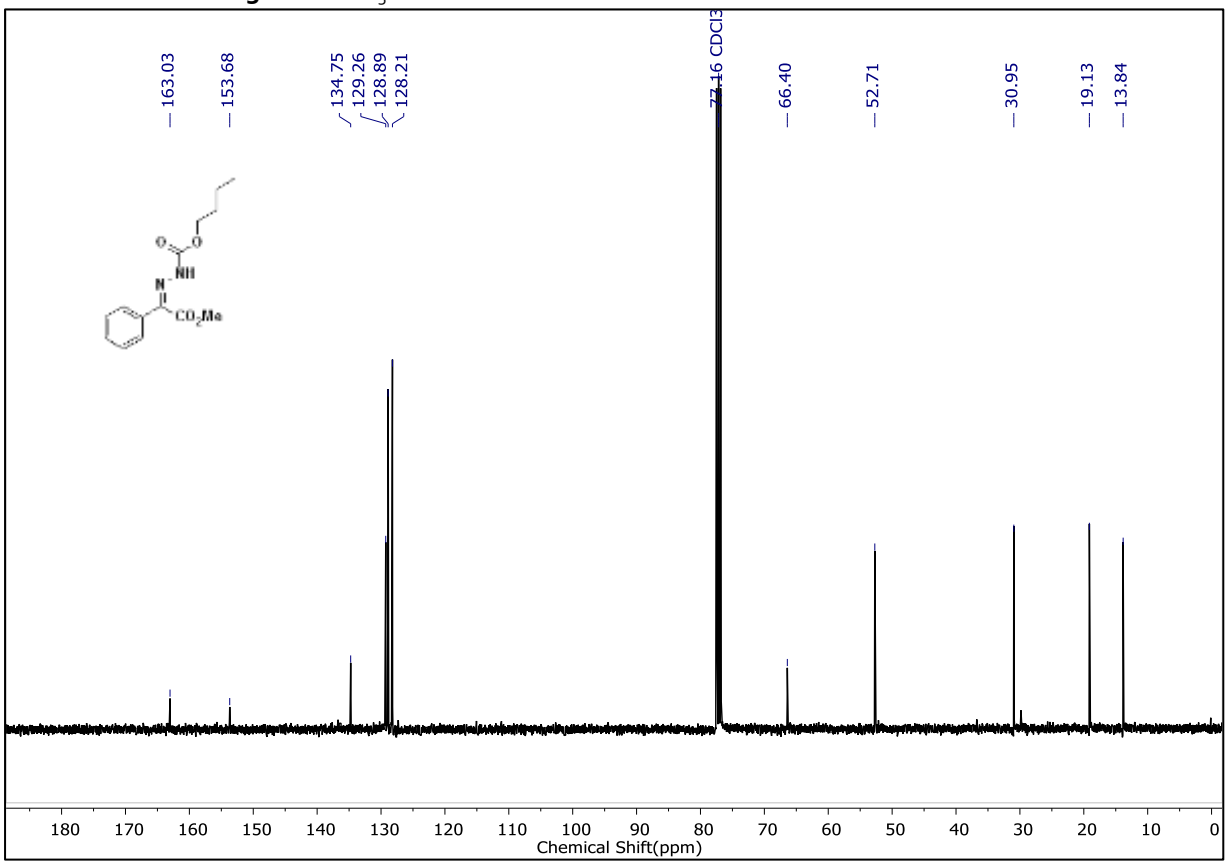
^{13}C NMR 100MHz of **3v** in $CDCl_3$



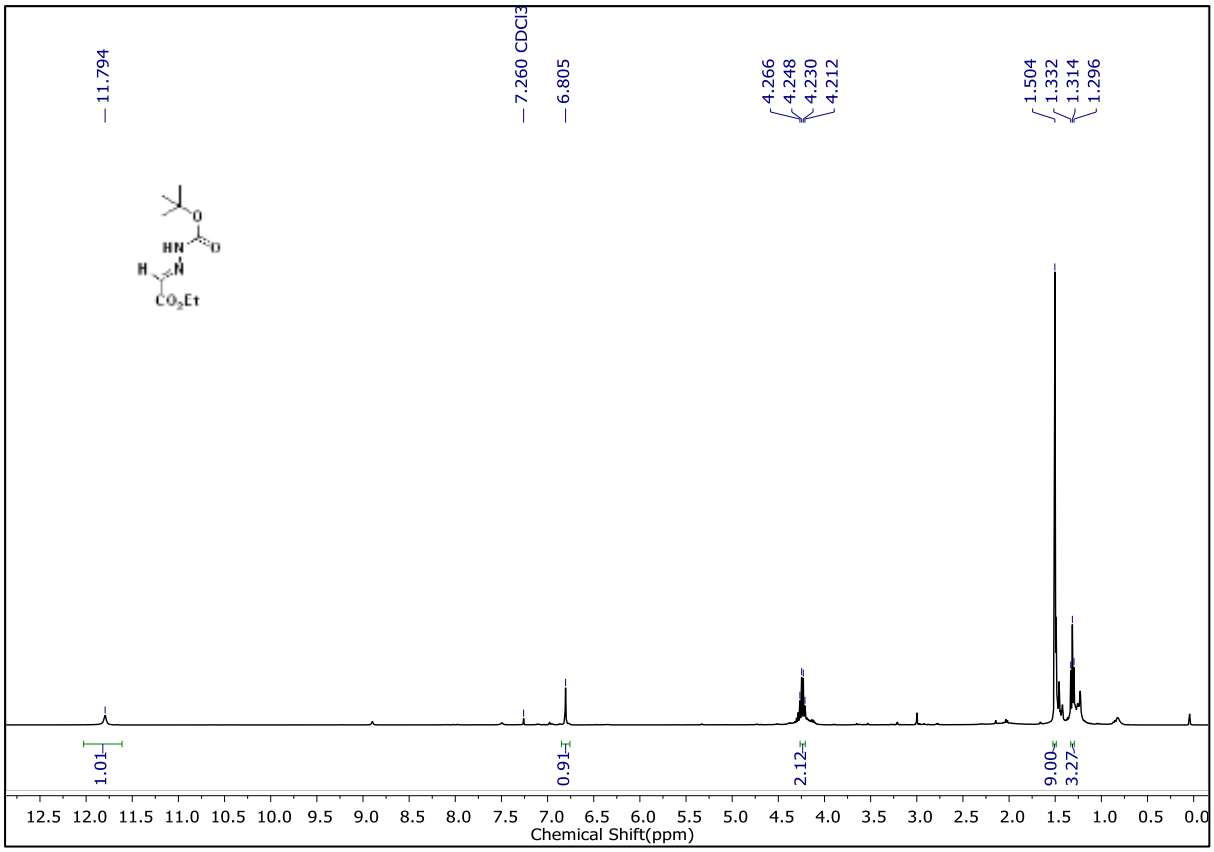
^{1}H NMR 400MHz of **3w** in $CDCl_3$



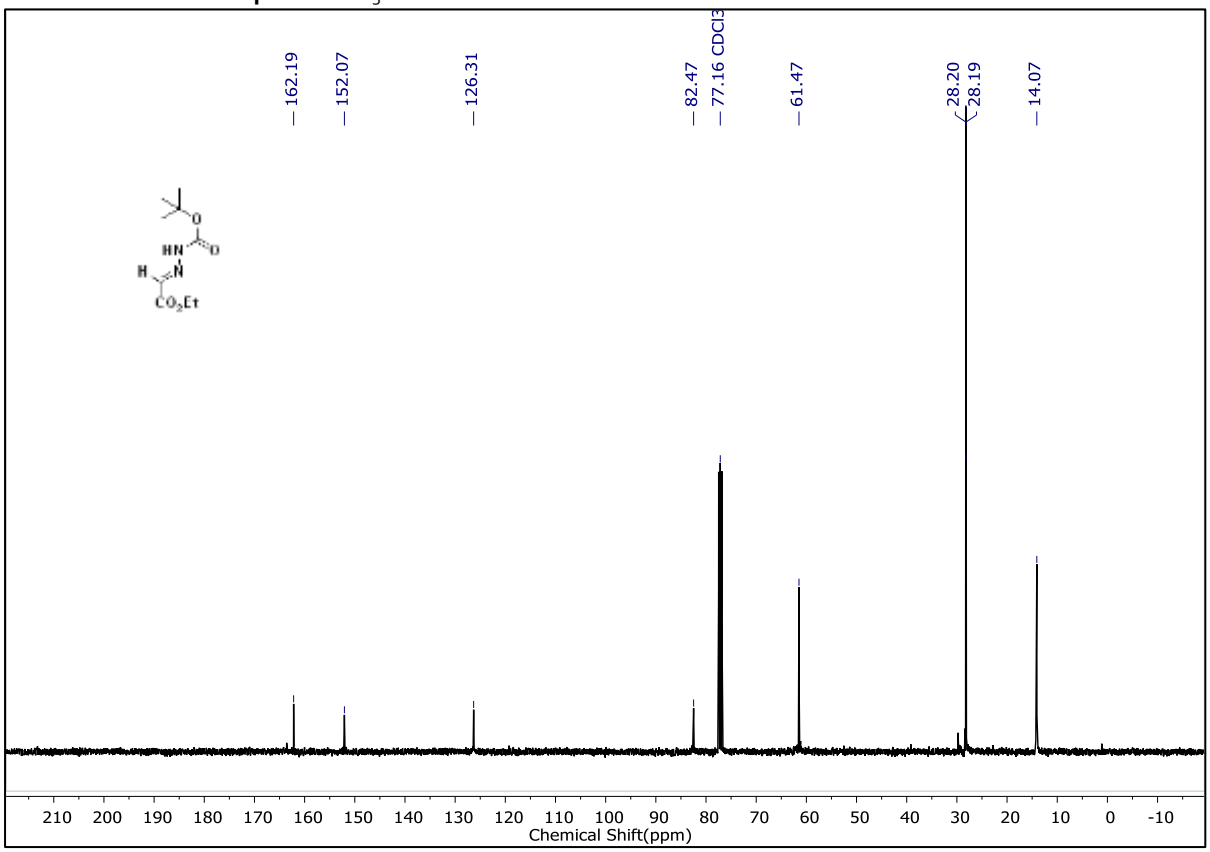
^{13}C NMR 100MHz of **3w** in $CDCl_3$



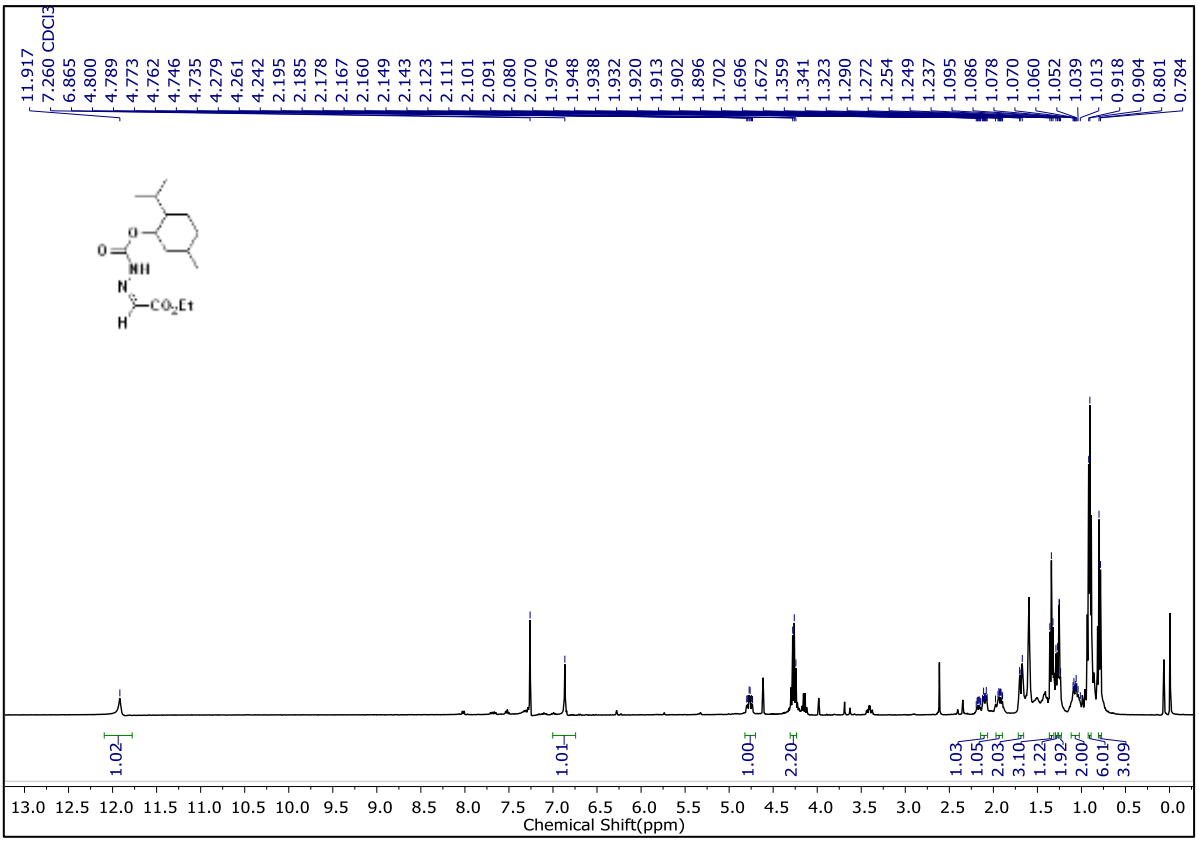
^{1}H NMR 400MHz of **4a** in $CDCl_3$



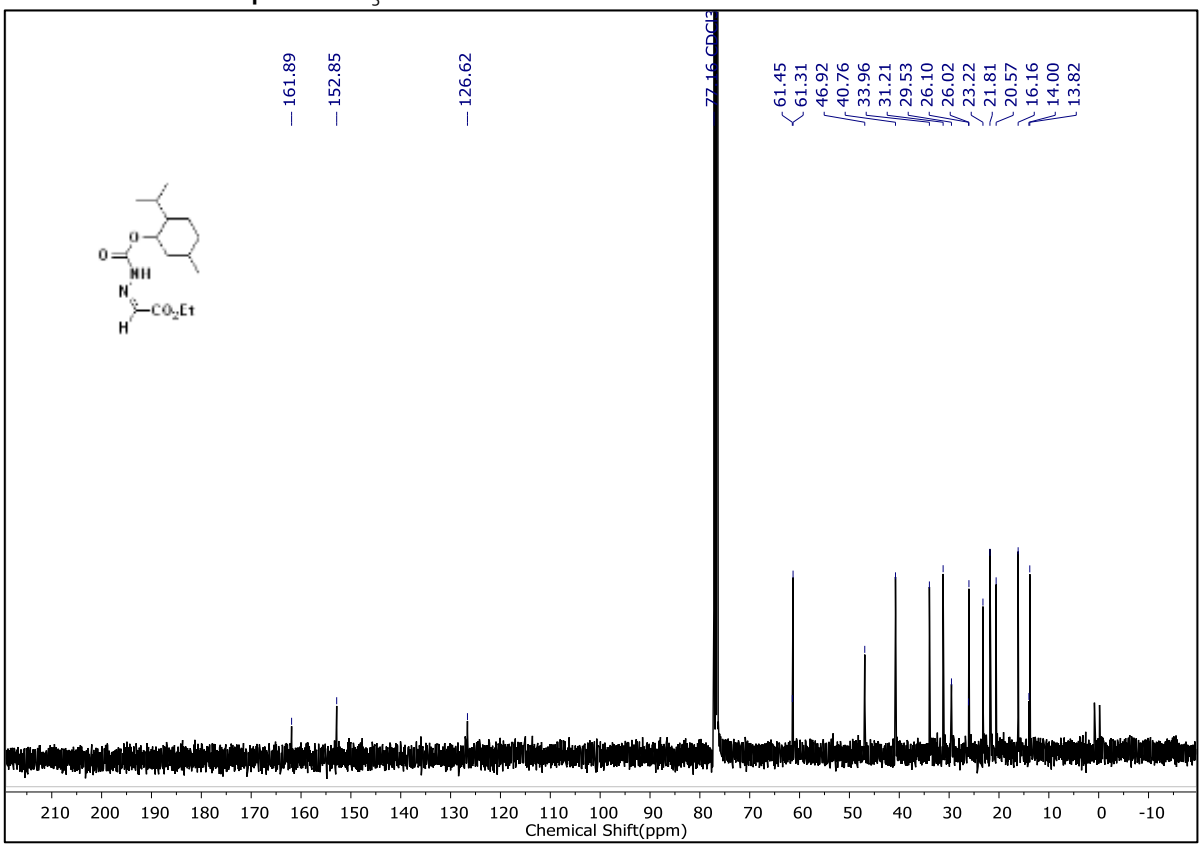
^{13}C NMR 100MHz of **4a** in $CDCl_3$



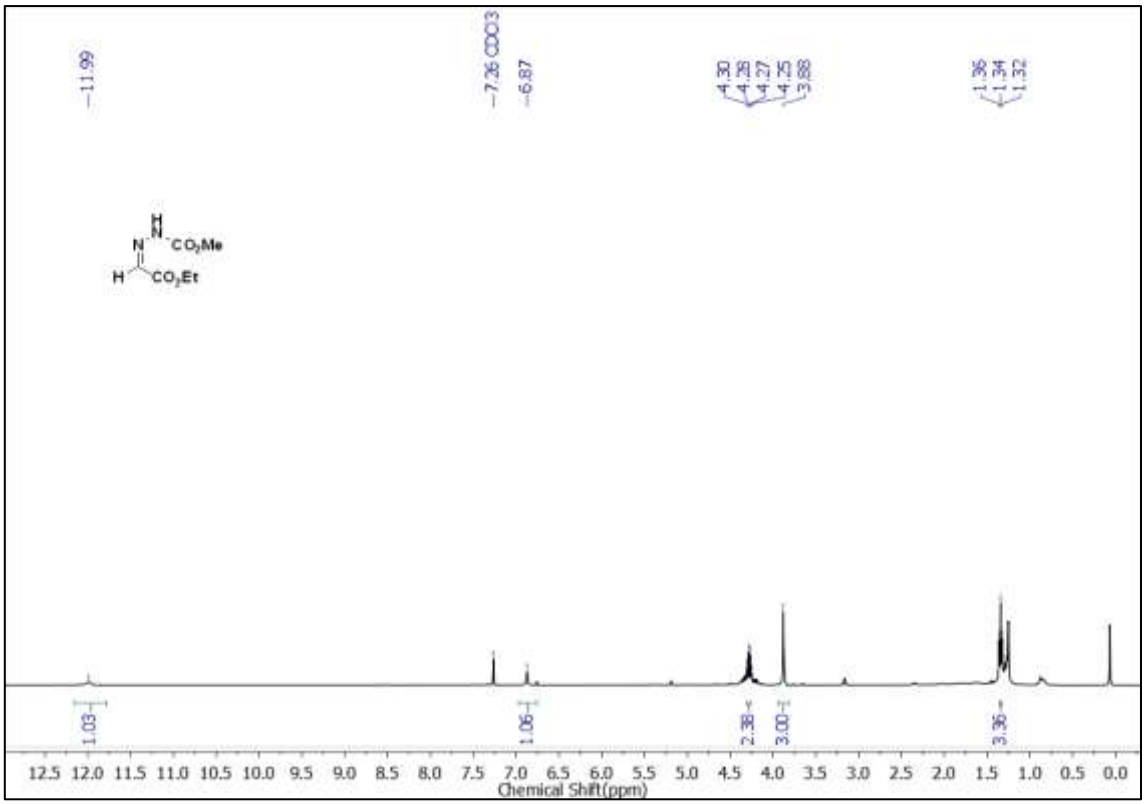
^{1}H NMR 400MHz of **4b** in $CDCl_3$



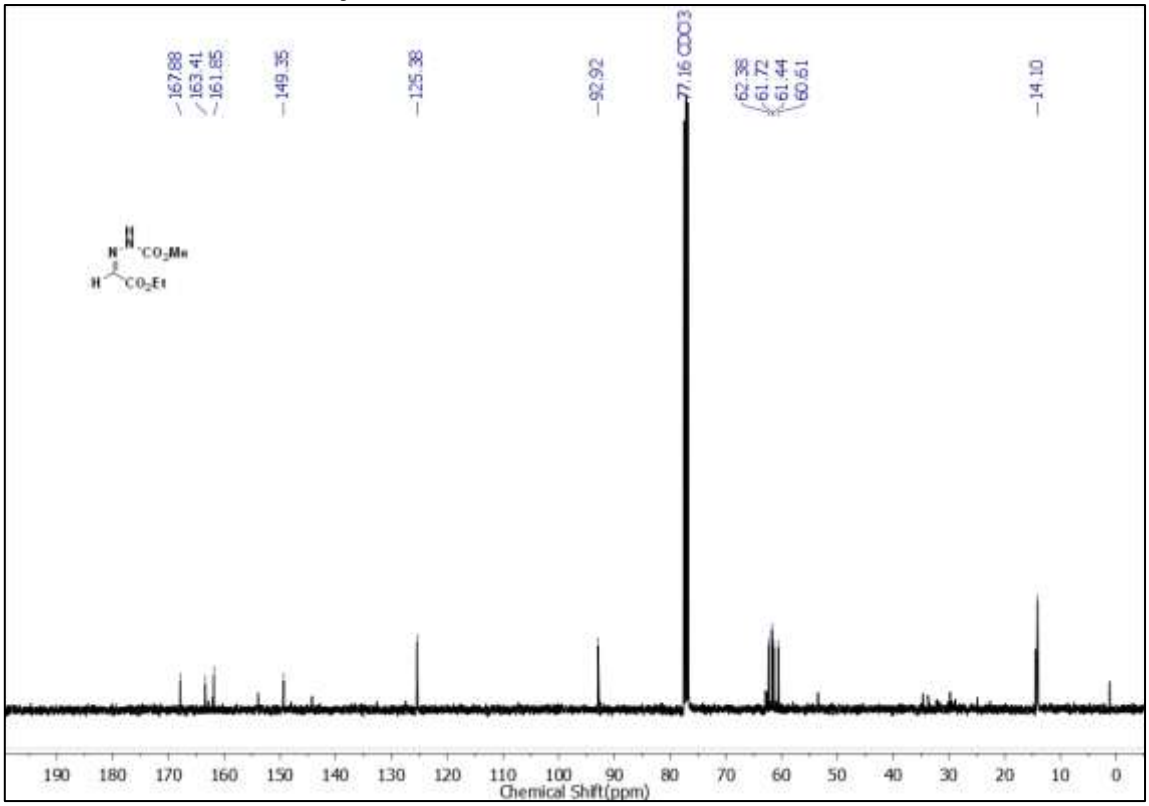
^{13}C NMR 100MHz of **4b** in $CDCl_3$



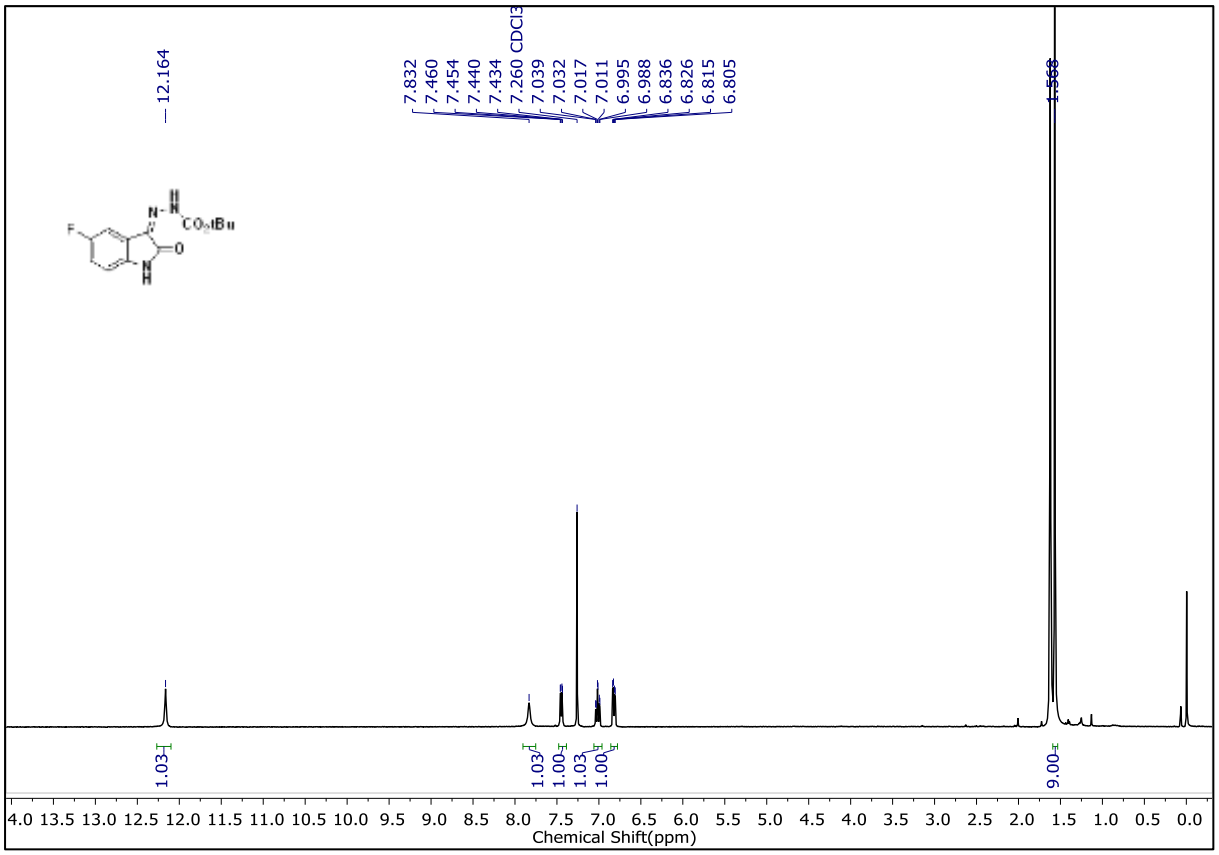
^{1}H NMR 400MHz of **4c** in $CDCl_3$



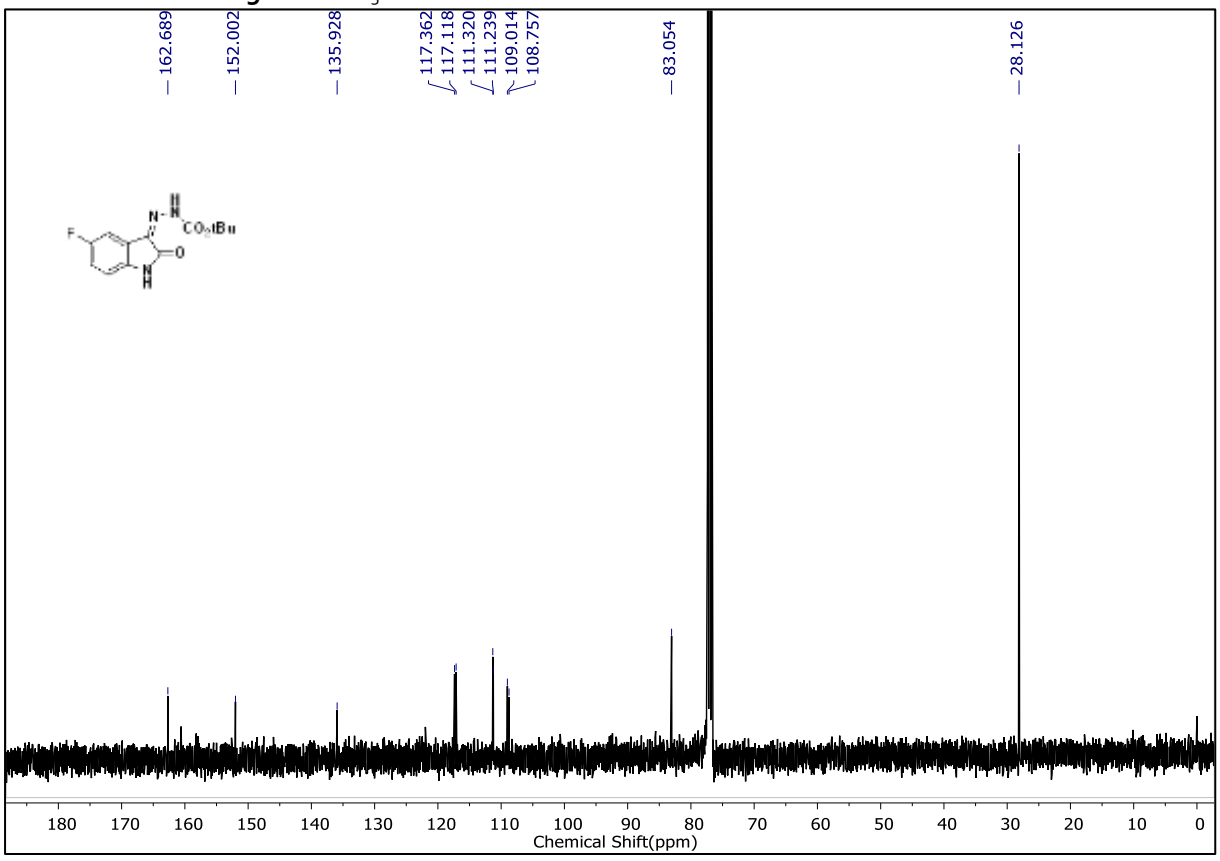
^{13}C NMR 100MHz of **4c** in $CDCl_3$



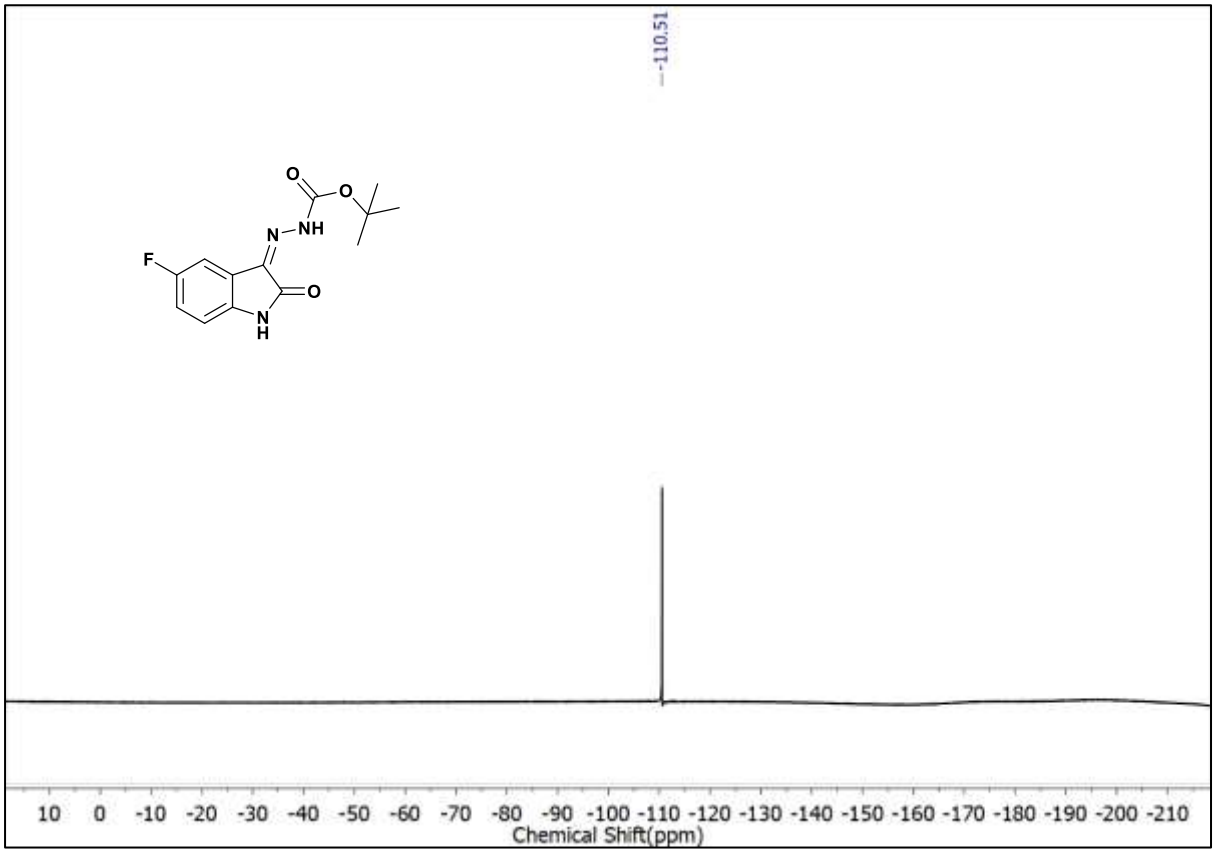
^{1}H NMR 400MHz of **5a** in $CDCl_3$



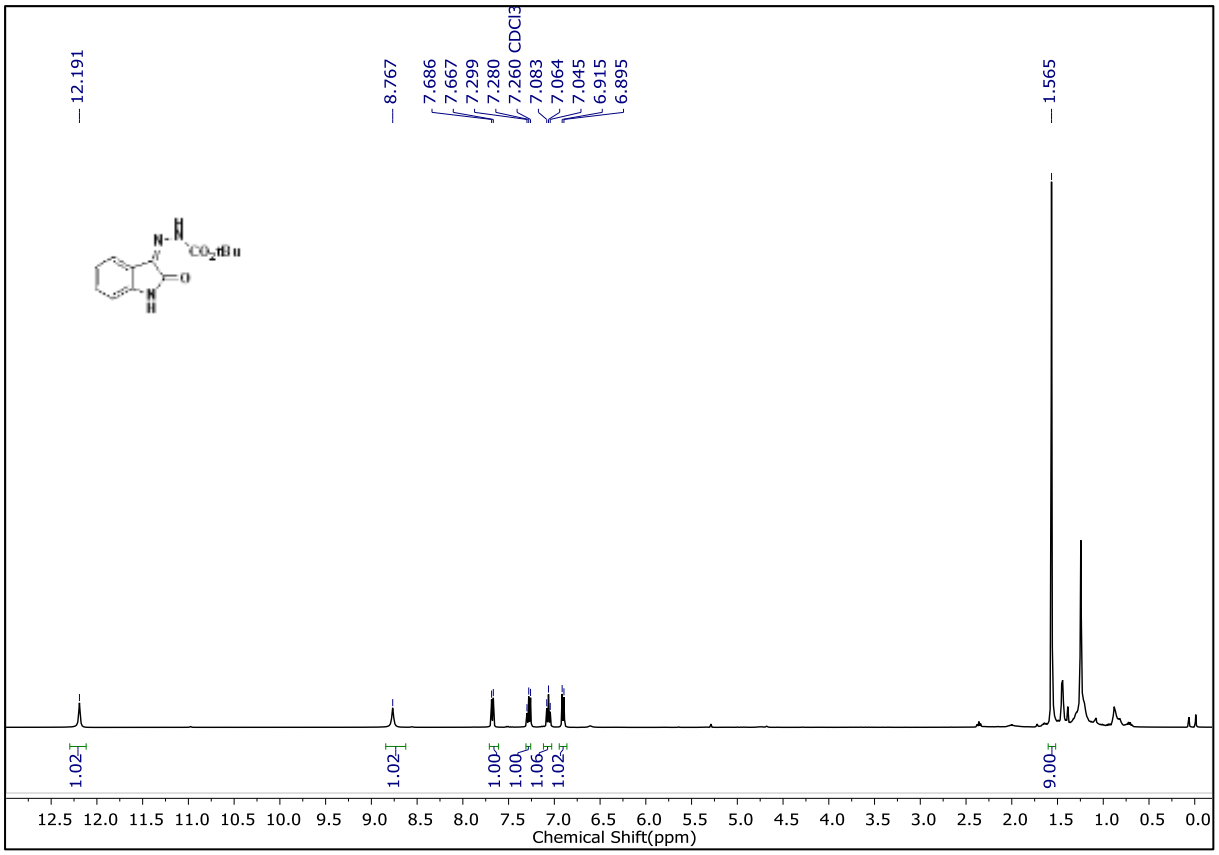
^{13}C NMR 100MHz of **5a** in $CDCl_3$



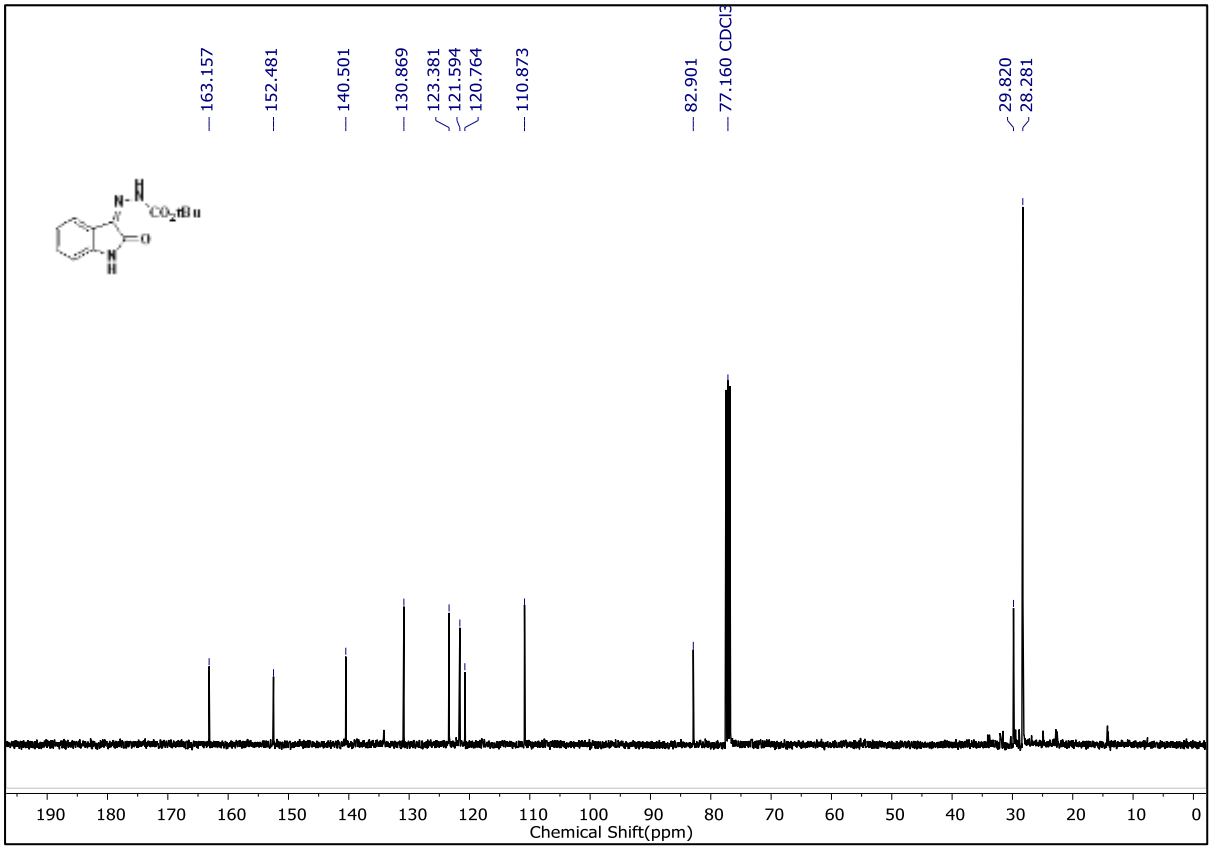
^{19}F NMR 376 MHz of **5a** in $CDCl_3$



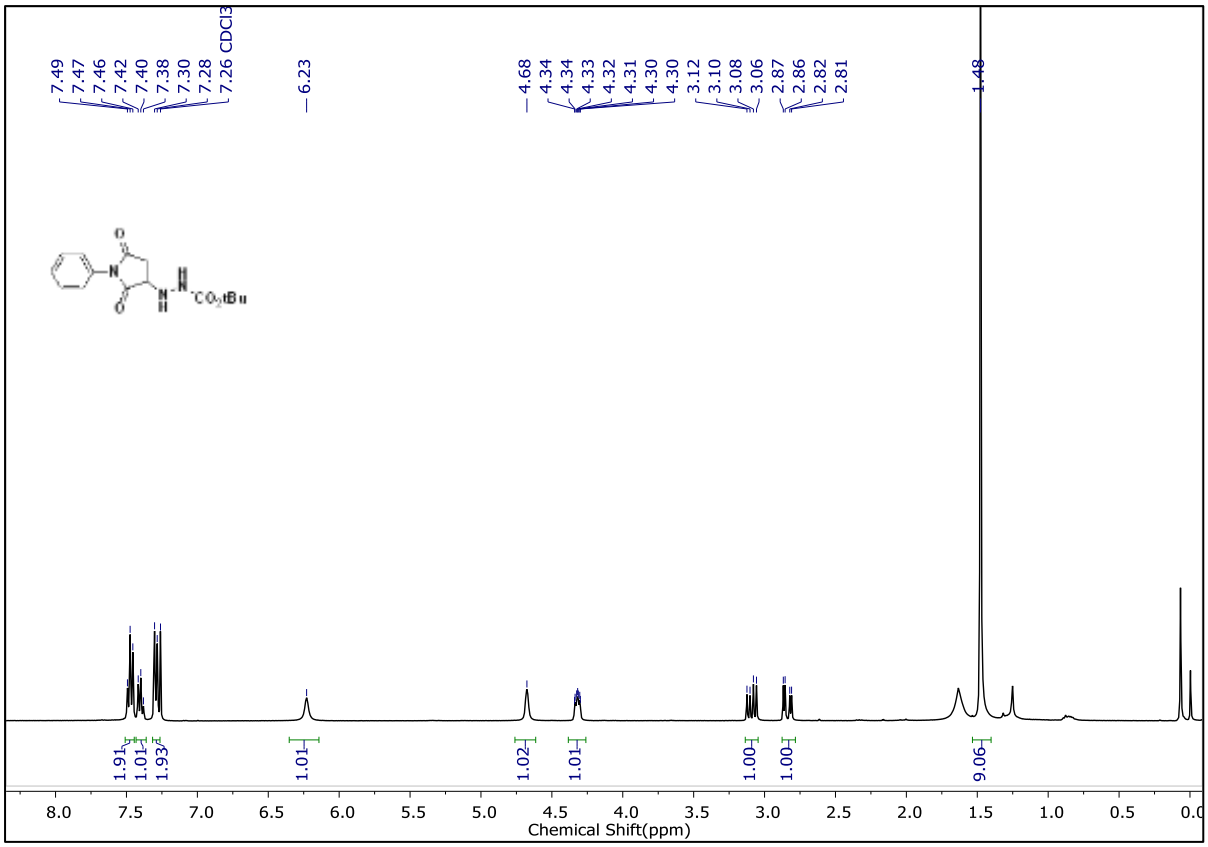
^{1}H NMR 400MHz of **5b** in $CDCl_3$



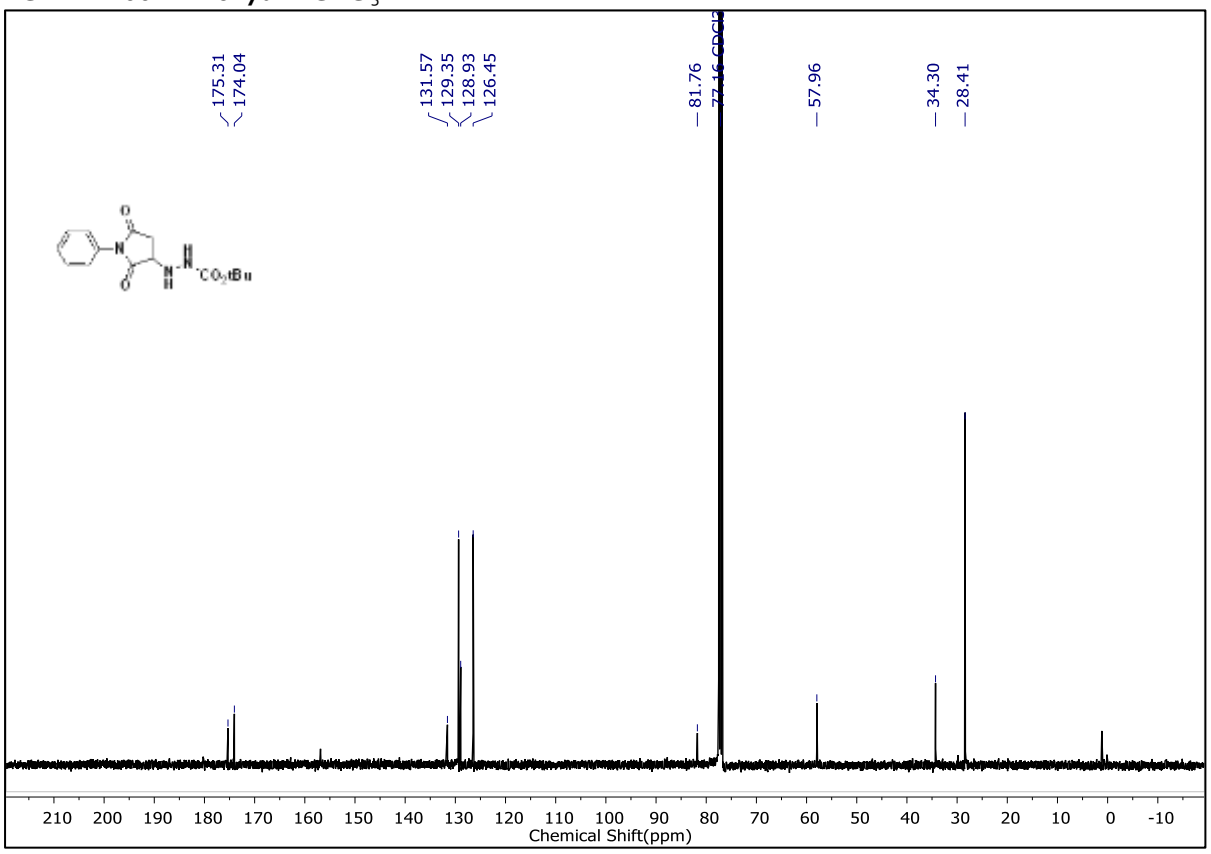
^{13}C NMR 100MHz of **5b** in $CDCl_3$



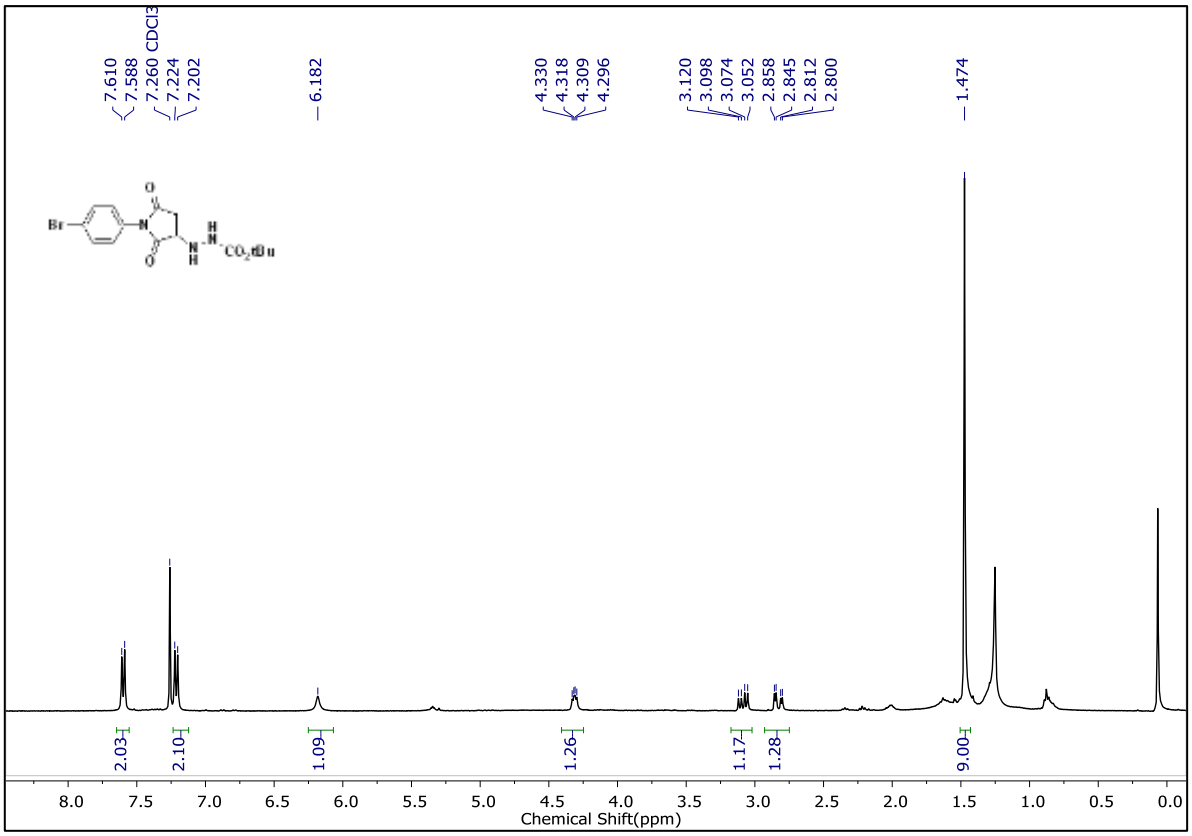
^{1}H NMR 400MHz of **7a** in $CDCl_3$



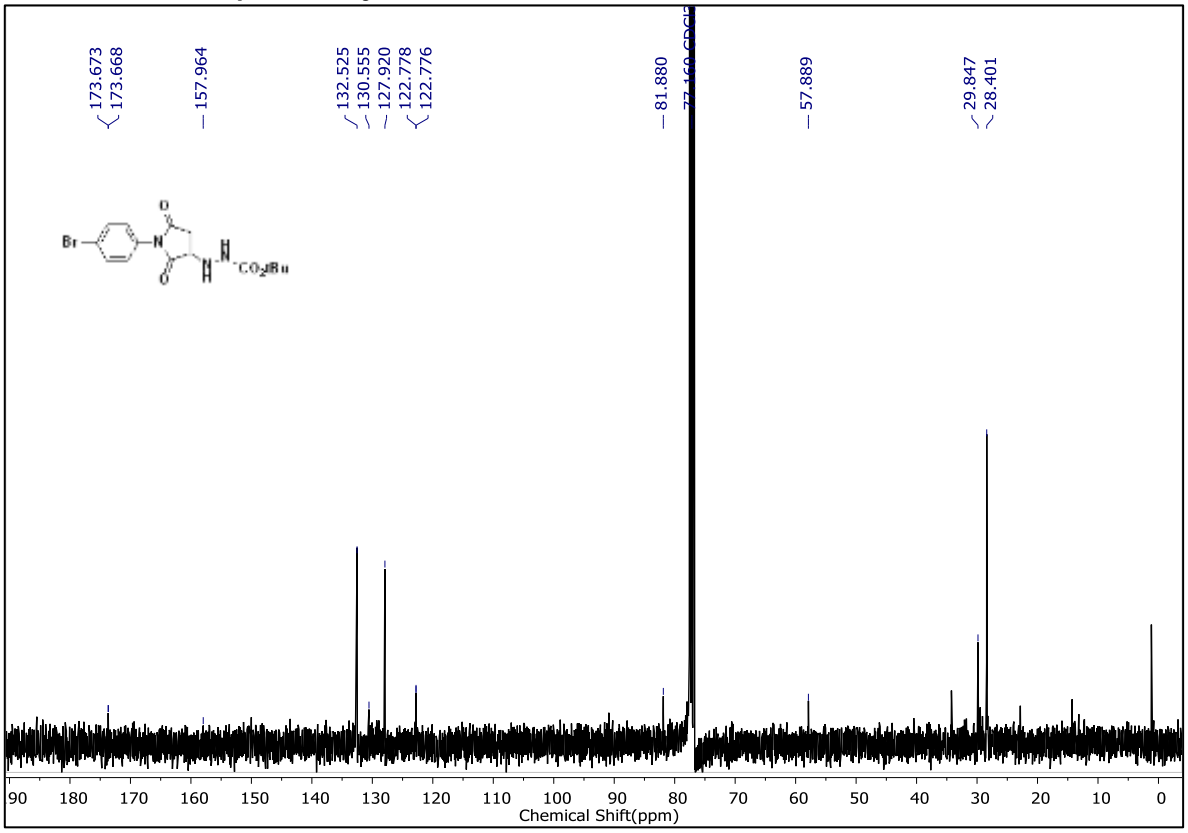
^{13}C NMR 100MHz of **7a** in $CDCl_3$



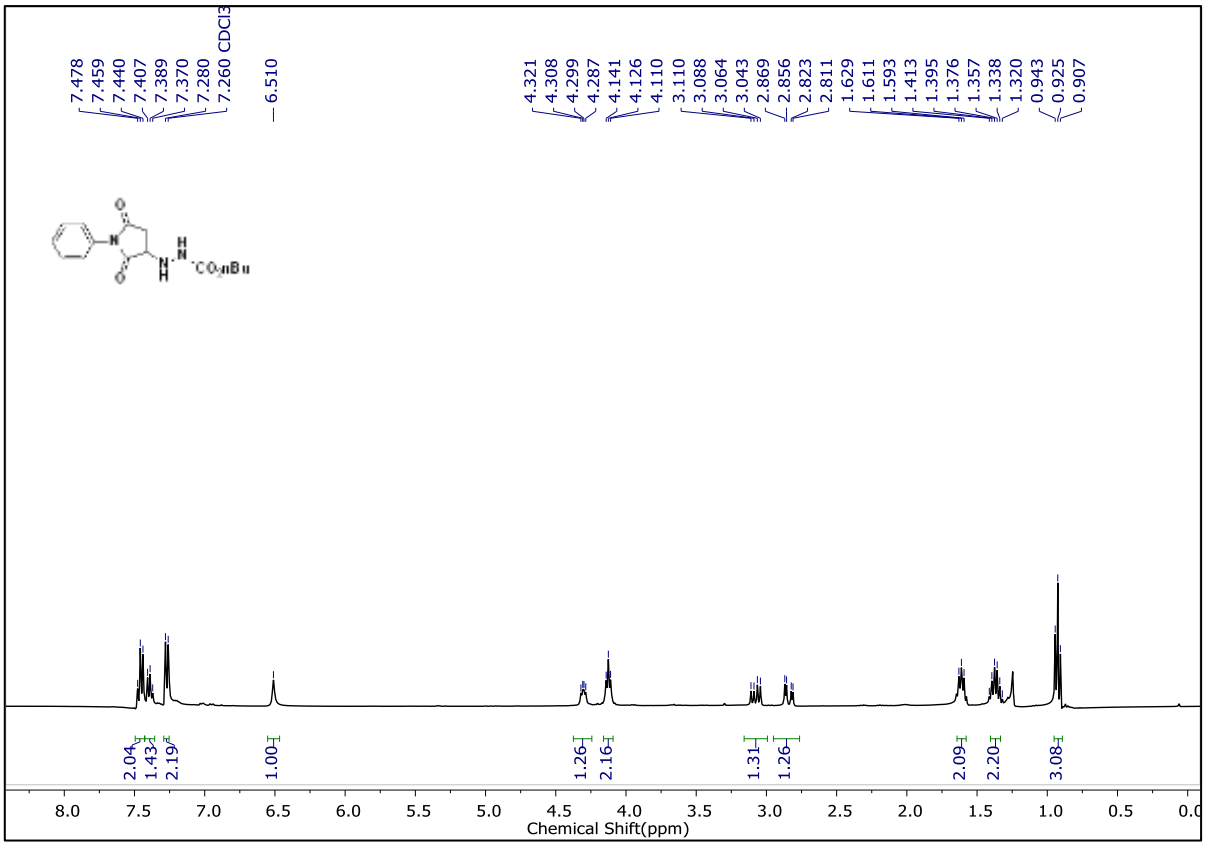
^{1}H NMR 400MHz of **7b** in $CDCl_3$



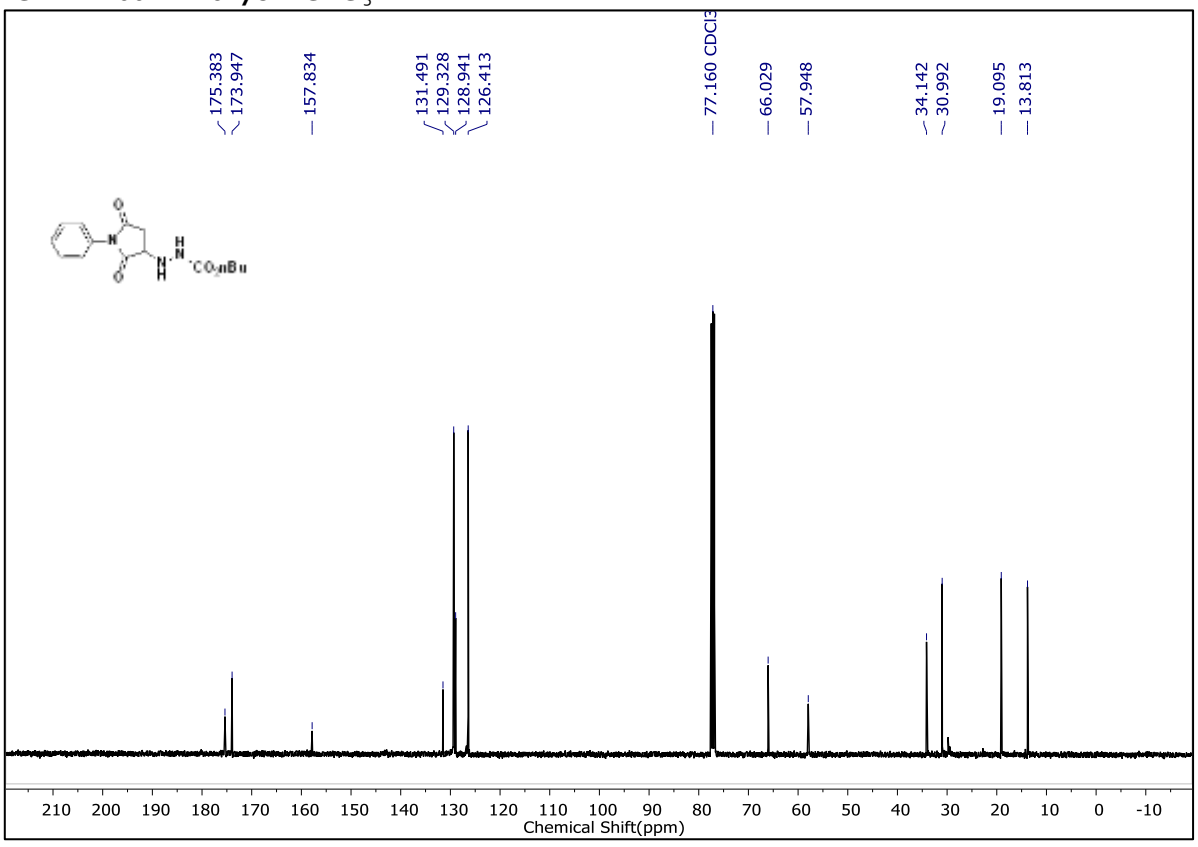
^{13}C NMR 100MHz of **7b** in $CDCl_3$



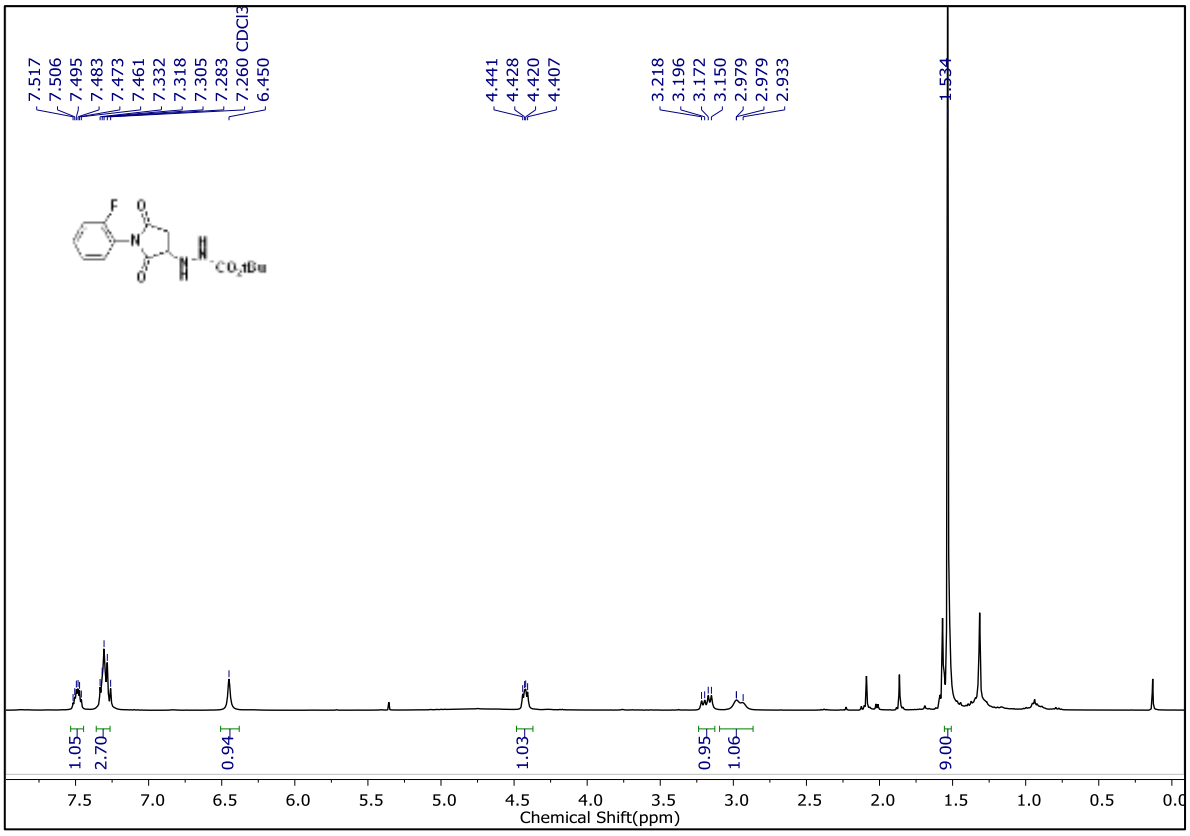
^{1}H NMR 400MHz of **7c** in $CDCl_3$



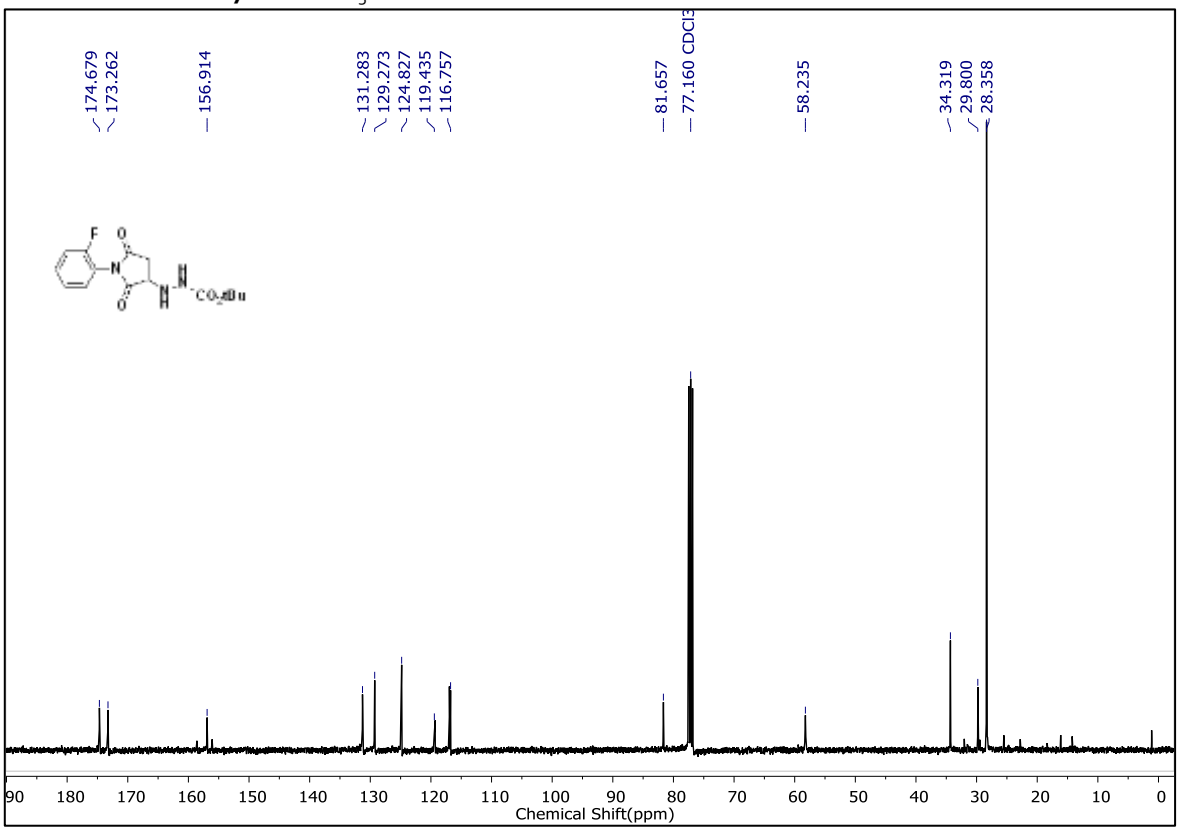
^{13}C NMR 100MHz of **7c** in $CDCl_3$



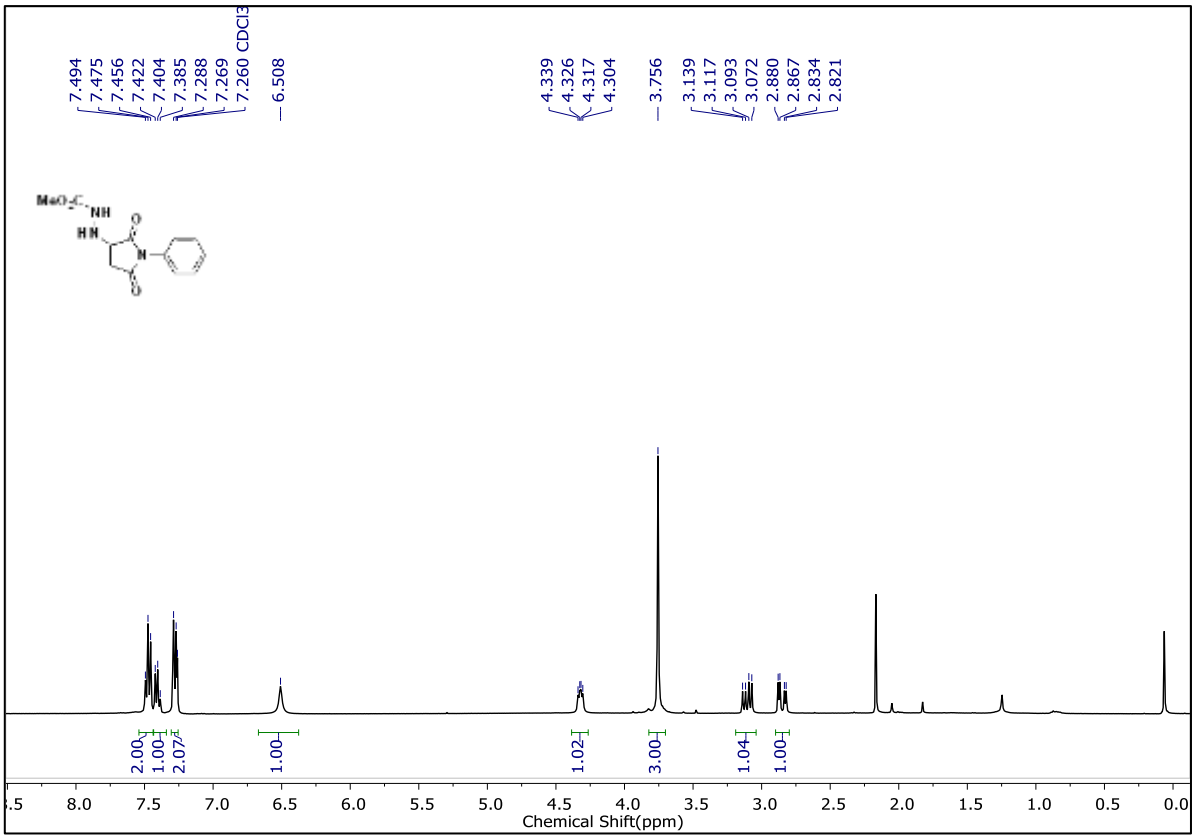
^{1}H NMR 400MHz of **7d** in $CDCl_3$



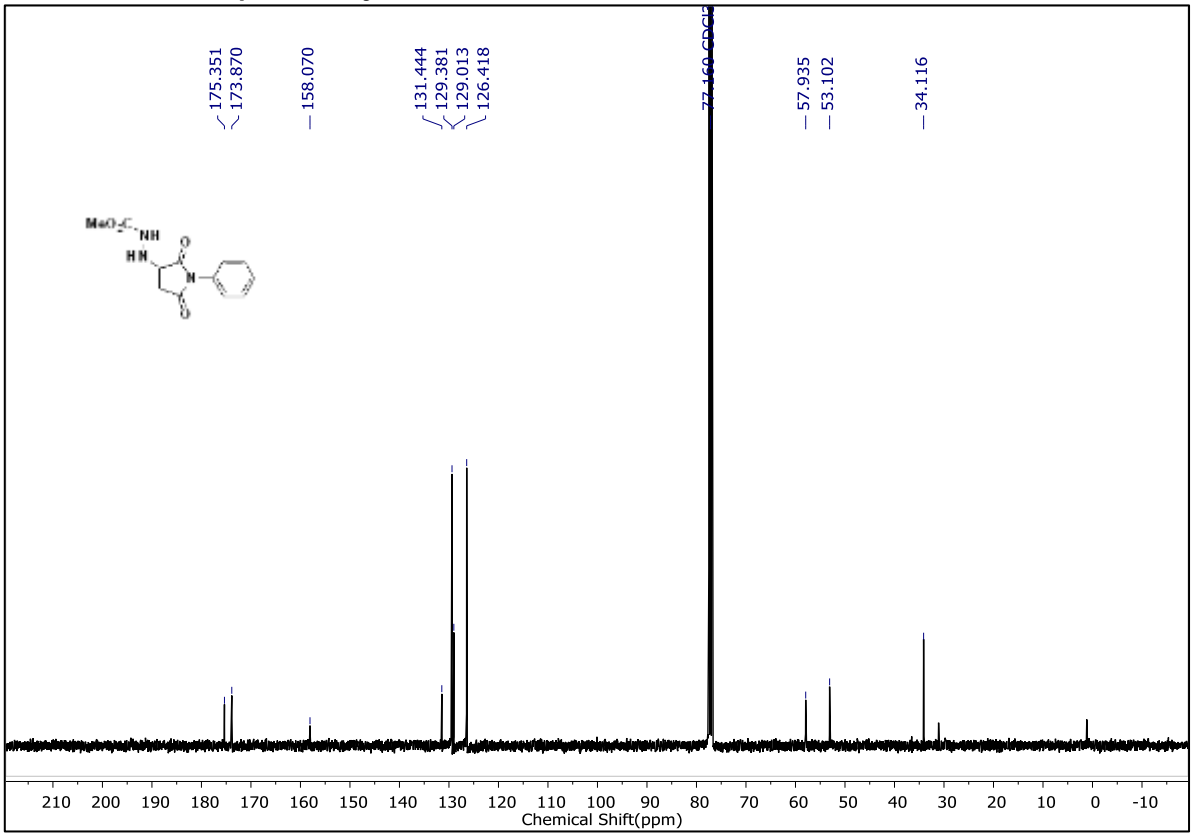
^{13}C NMR 100MHz of **7d** in $CDCl_3$



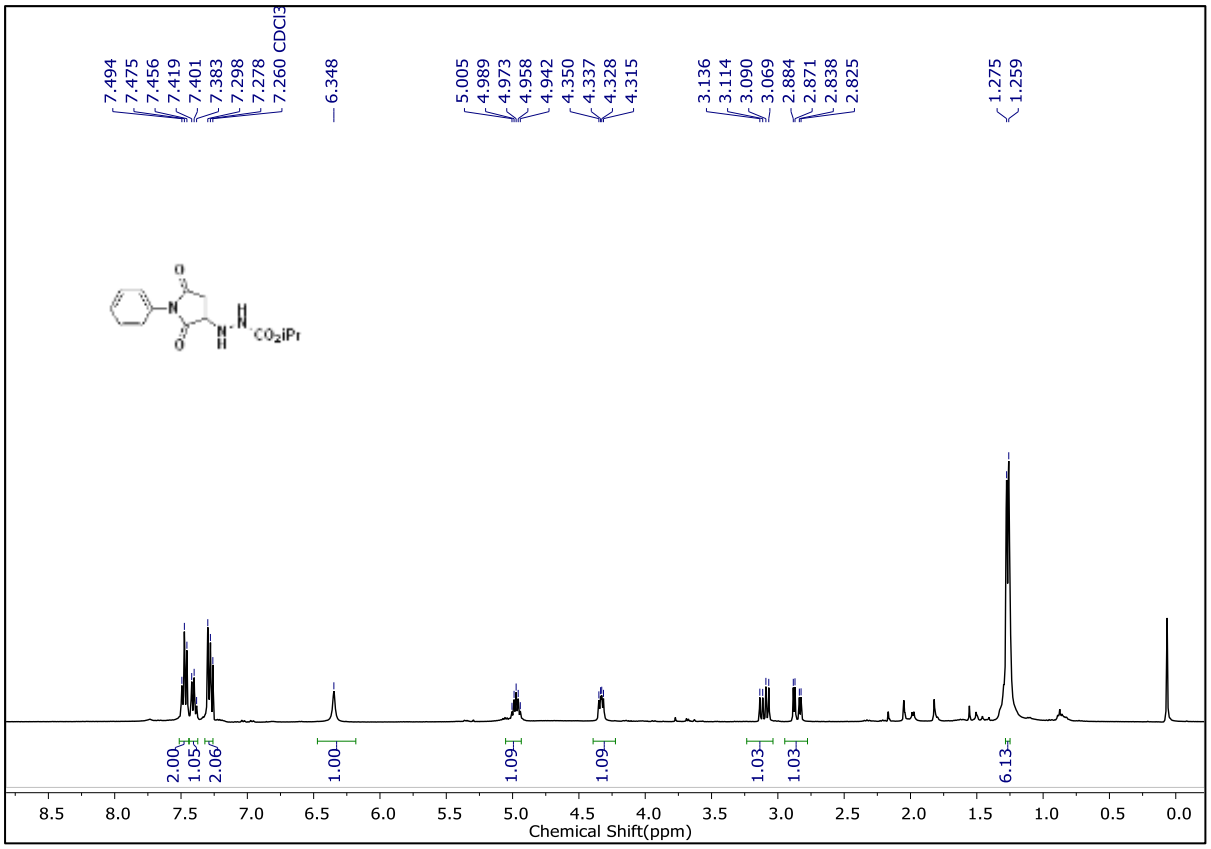
^{1}H NMR 400MHz of **7e** in $CDCl_3$



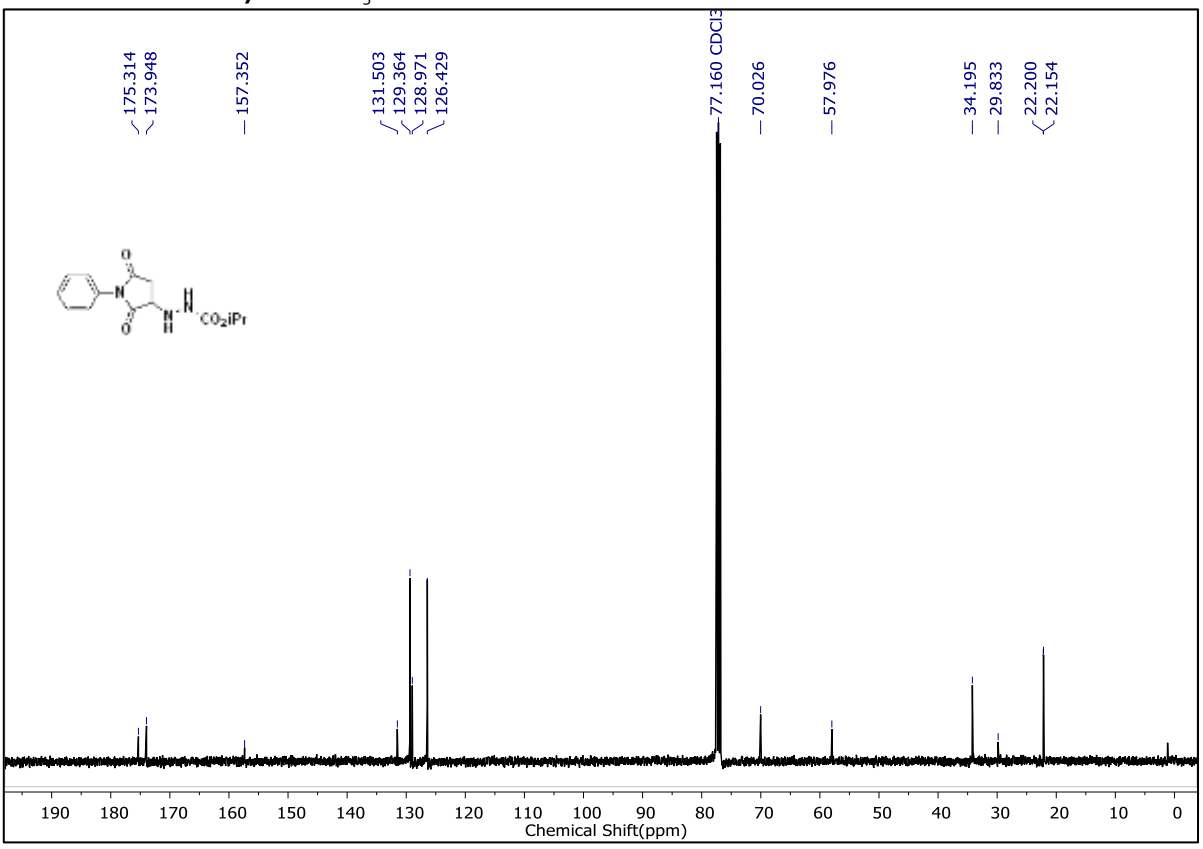
^{13}C NMR 100MHz of **7e** in $CDCl_3$



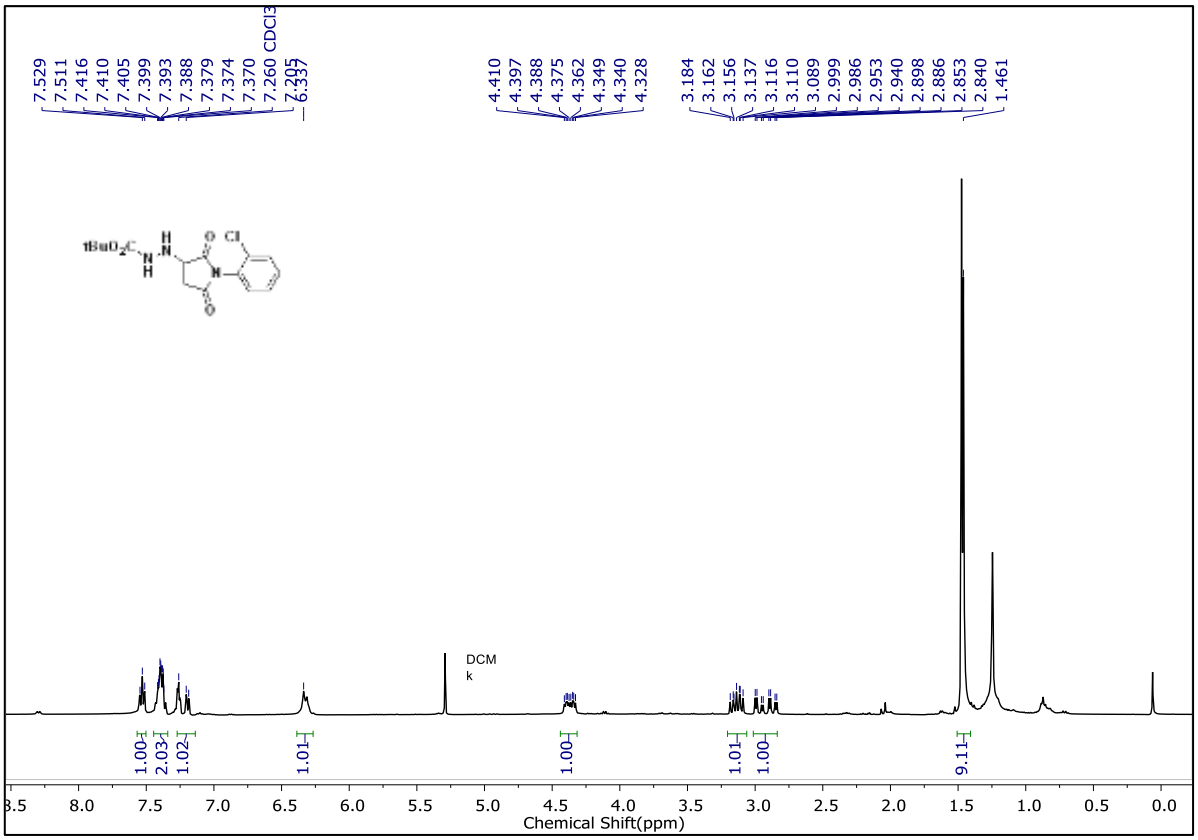
^{1}H NMR 400MHz of **7f** in $CDCl_3$



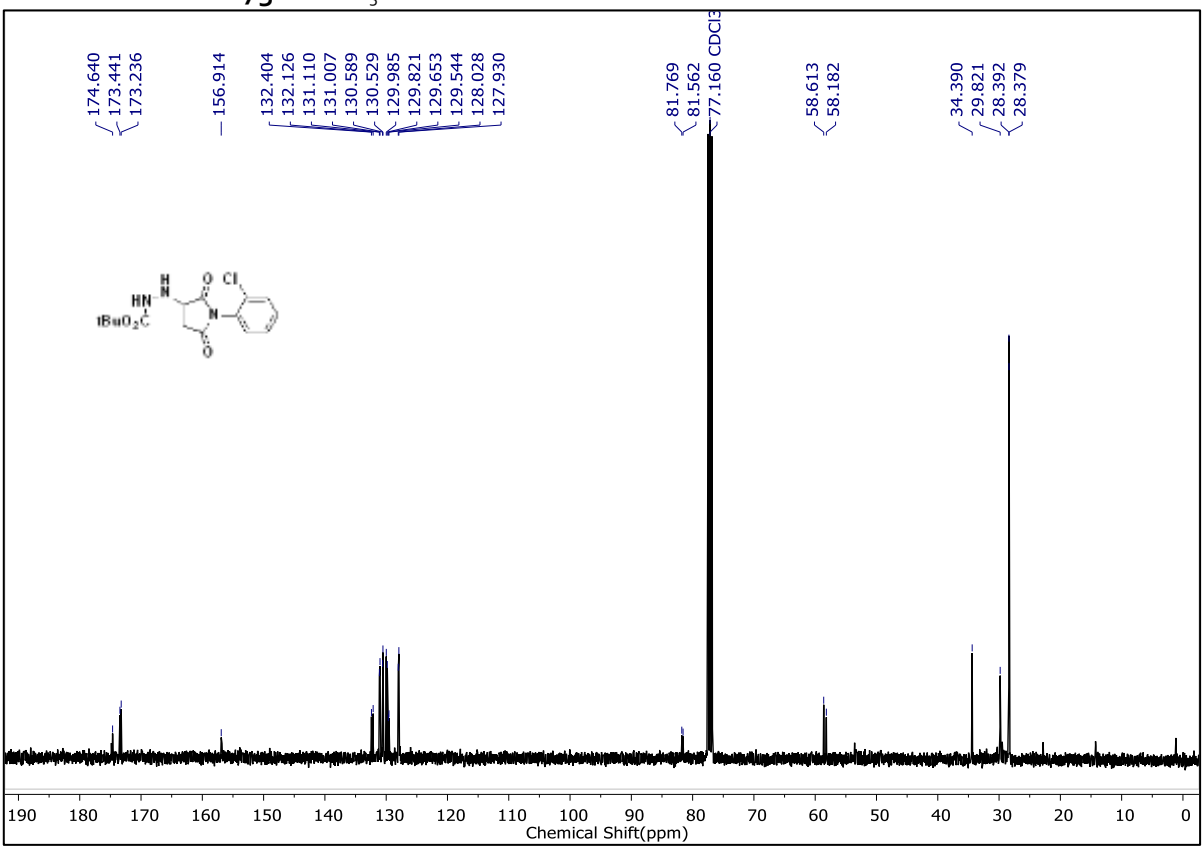
^{13}C NMR 100MHz of **7f** in $CDCl_3$



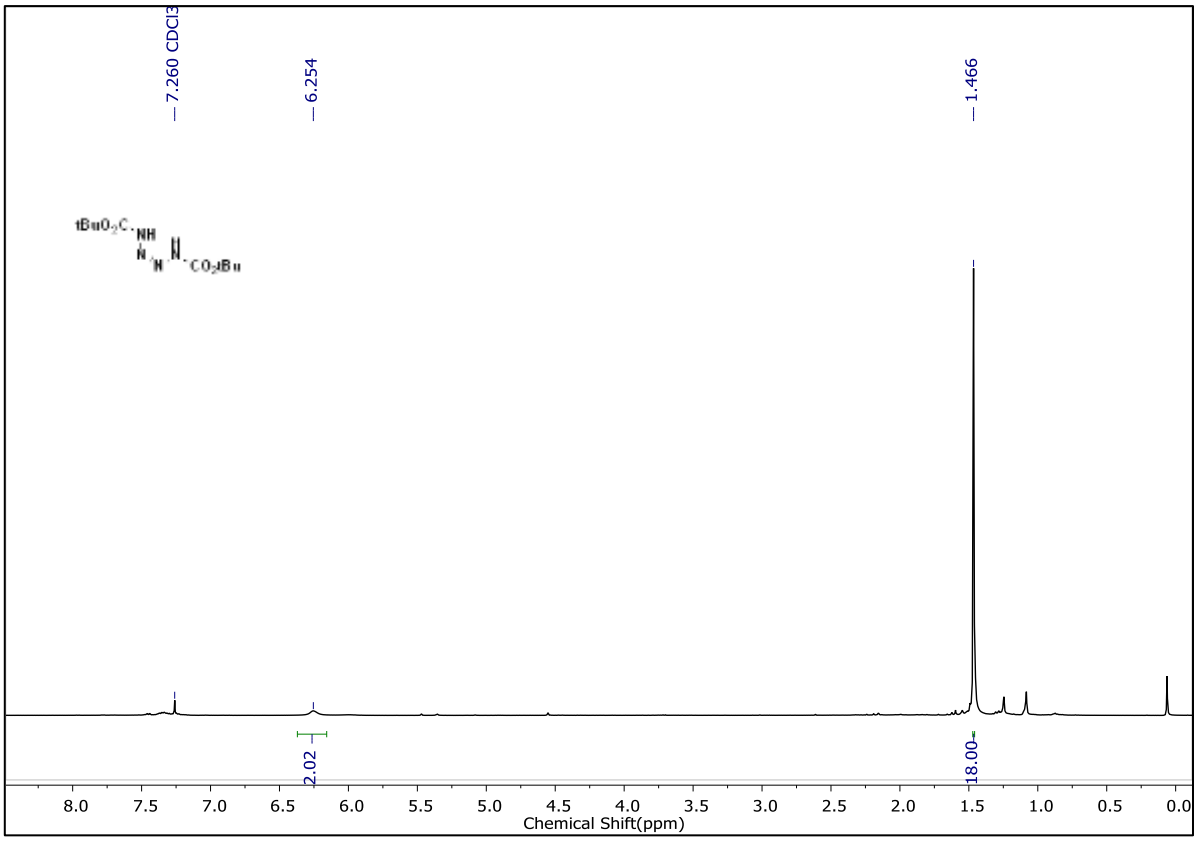
^{1}H NMR 400MHz of **7g** in $CDCl_3$



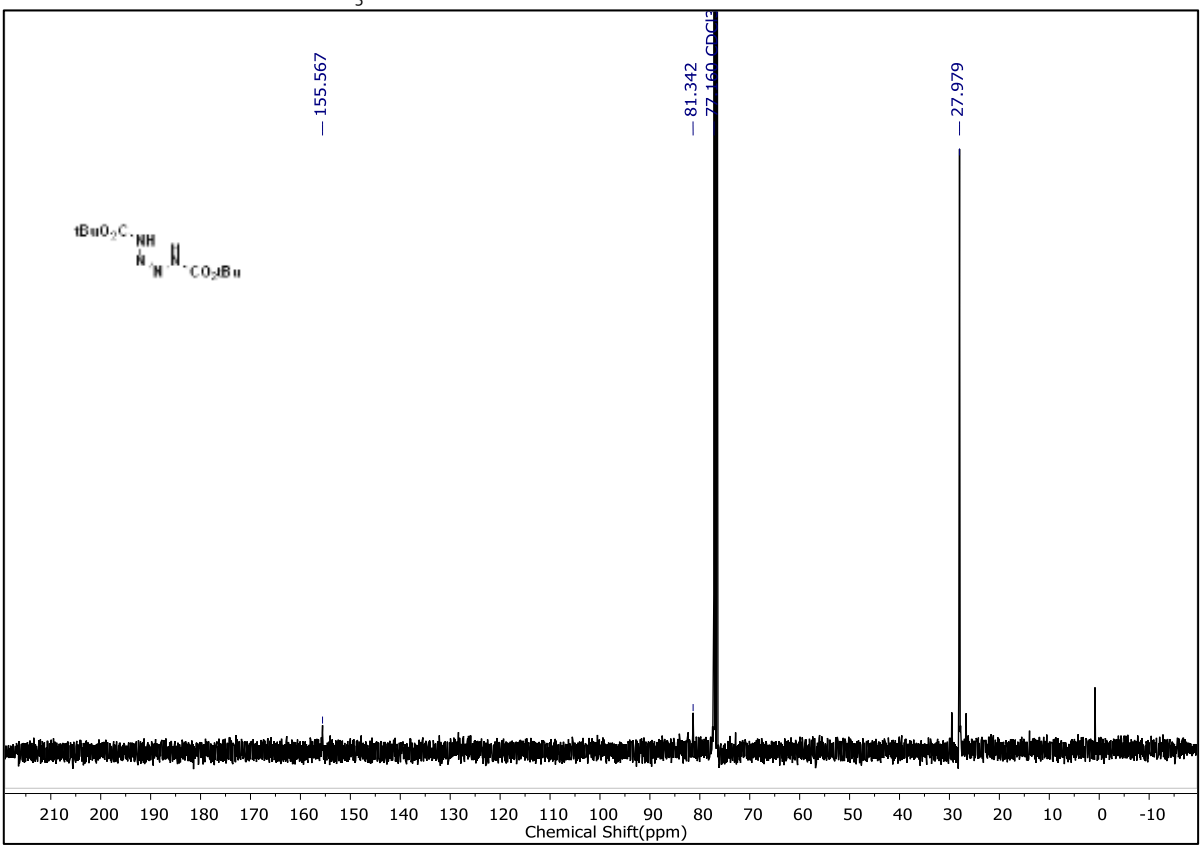
^{13}C NMR 100MHz of **7g** in $CDCl_3$



^{1}H NMR 400MHz of **8** in $CDCl_3$



^{13}C NMR 100MHz of **8** in $CDCl_3$



7. References:

1. Sheldrick, G. M. SHELXTL Version 2014/7: Programs for the determination of small and macromolecular crystal structures by single crystal X-ray and neutron diffraction; University of Göttingen, Göttingen, Germany, 2014; http://shelx.uniac.gwdg.de/SHELX/ index.php.
2. Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, **64**, 112–122.
3. Farrugia, L. J. ORTEP-3 for Windows-a version of ORTEP-III with a Graphical User Interface (GUI). J. Appl. Crystallogr. 1997, **30**, 565.