

Supporting Information

Synthesis of Pyrazolo[1,5-*c*]quinazoline Derivatives through Copper-Catalyzed Domino Reaction of *o*-Alkenyl Aromatic Isocyanides with Diazo Compounds

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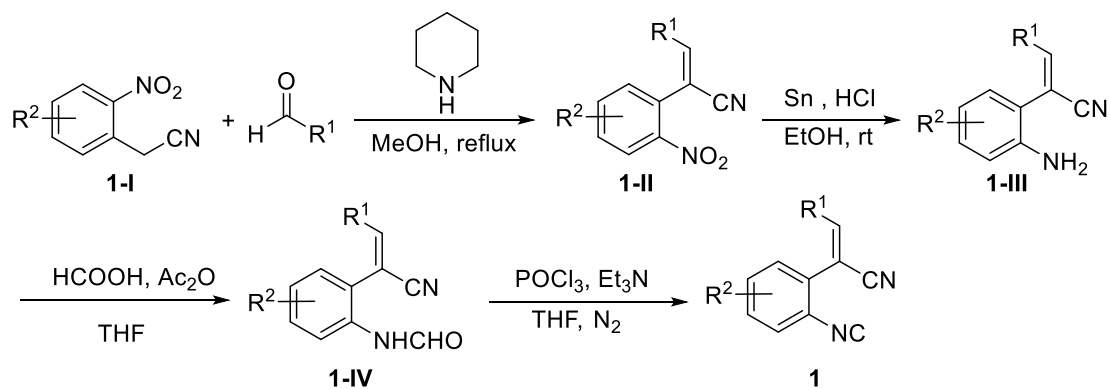
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1. General Information

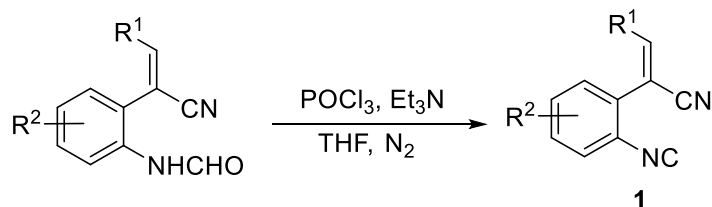
All chemicals were obtained from commercial sources and used as received unless otherwise noted. Unless noted, the ^1H NMR spectra were recorded at 400 MHz in CDCl_3 or $\text{DMSO-}d_6$ and the ^{13}C NMR spectra were recorded at 100 or 125 MHz in CDCl_3 or $\text{DMSO-}d_6$ with TMS as internal standard. All coupling constants (J values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained on an Agilent Q-TOF 6224 spectrometer. The intensity data were recorded on a Bruker D8 QUEST with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structure was solved by means of direct methods and refined by employing full-matrix least squares on F2 (SHELXTL-2014). Column chromatography was performed on silica gel (300-400 mesh) with ethyl acetate (EA)/petroleum ether (PE). The diazo compounds were prepared according to the previous method reported.¹

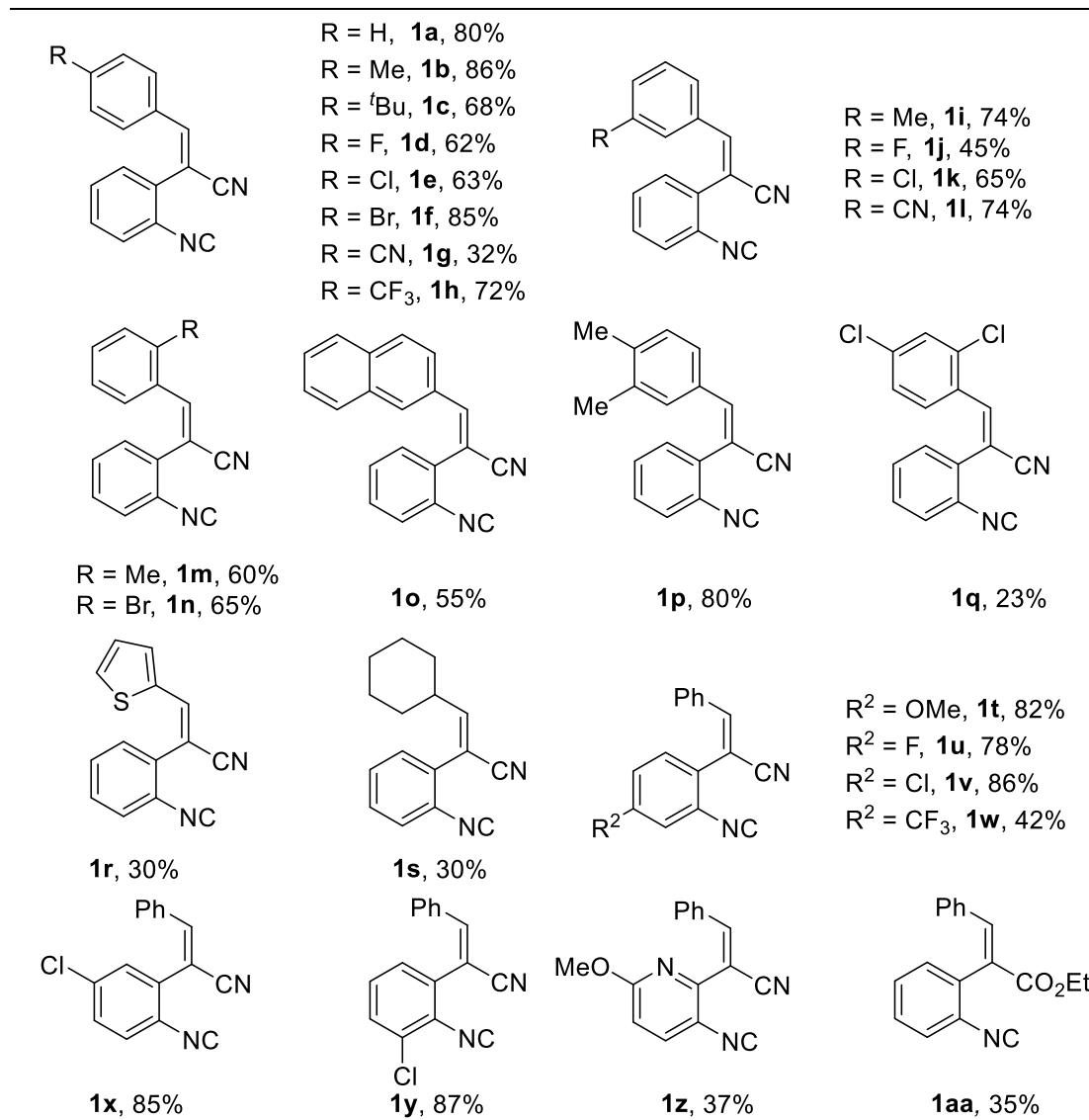
2. Preparation of Substrates and analytical data of compounds 1

Substrates **1** were prepared by following the procedures in references 2, 3.

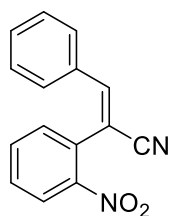


Scheme S1. Synthesis of *o*-vinyl aromatic isocyanides **1**.



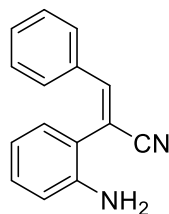


Typical synthetic procedure (with **1a** as an example)

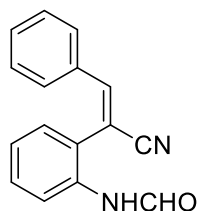


Synthesis of (E)-2-(2-Nitrophenyl)-3-phenylacrylonitrile: To a solution of 2-nitrophenylacetonitrile (1.621 g, 10 mmol, 1.0 equiv) in 40 mL of methanol was added 1.167 g of benzaldehyde (11 mmol, 1.1 equiv) and 0.426 g of piperidine (5 mmol, 0.5 equiv). The reaction mixture was heated to reflux at 70°C. After 4 h, the

reaction mixture was cooled to room temperature and the yellow precipitate was collected. Recrystallization of the precipitate from methanol provided the product (*E*)-2-(2-nitrophenyl)-3-phenylacrylonitrile as yellow solid (2.127 g, 85%).

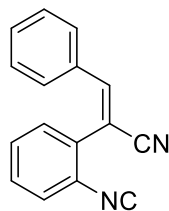


Synthesis of (*E*)-2-(2-Aminophenyl)-3-phenylacrylonitrile: To a round bottom flask (50 mL) were added (*E*)-2-(2-nitrophenyl)-3-phenylacrylonitrile (2.002 g, 8 mmol, 1.0 equiv), Sn powder (9.497 g, 80 mmol, 10 equiv) and EtOH (15 mL). The mixture was kept stirring at ambient temperature. HCl (12 M, 12 mL) was slowly injected to the solution mixture at 0°C. After complete the injection, the solution was kept stirring at ambient temperature for another 2 h. The mixture was quenched by saturated aqueous solution of NaHCO₃. The reaction mixture was extracted with CH₂Cl₂ (100 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to yield the (*E*)-2-(2-aminophenyl)-3-phenylacrylonitrile as a light yellow solid (1.057 g, 60%).



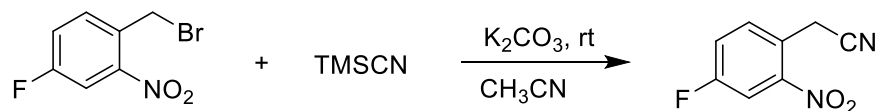
Synthesis of (*E*)-*N*-(2-(1-Cyano-2-phenylvinyl)phenyl)formamide: To an oven-dried three necked flask equipped with a dropping funnel, (*E*)-2-(2-aminophenyl)-3-phenylacrylonitrile (0.661 g, 3 mmol) and THF (10 mL) were added under N₂ atmosphere and cooled to 0 °C. Acetic formic anhydride, which was prepared from the reaction of acetic anhydride (2.400 mL) with formic acid (1.200 mL) at 55 °C for 2 h, was transferred to the dropping funnel and dropped to the solution of (*E*)-2-(2-aminophenyl)-3-phenylacrylonitrile at 0 °C. After the addition was complete, the mixture was warmed to room temperature and stirred for 2 h. Then, the mixture was quenched by saturated aqueous solution of NaHCO₃ and extracted with CH₂Cl₂ three times. The extract was dried over Na₂SO₄ and concentrated under

reduced pressure to give formamide (*E*)-*N*-(2-(1-cyano-2-phenylvinyl)phenyl)formamide as a pale white solid (0.596 g, 80%).



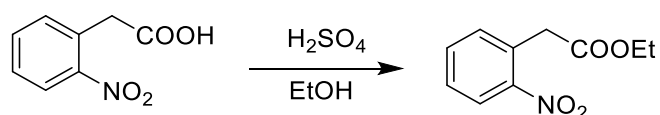
Synthesis of (*E*)-2-(2-Isocyanophenyl)-3-phenylacrylonitrile 1a: To an oven-dried three necked flask equipped with a dropping funnel, THF (3 mL), NEt₃ (0.698 ml, 5 mmol, 5.0 equiv) and the (*E*)-*N*-(2-(1-cyano-2-phenylvinyl)phenyl)formamide (0.248 g, 1mmol,) were added under N₂ atmosphere and cooled to 0 °C. POCl₃ (0.230 g, 1.5 mmol, 1.5 equiv) was added dropwise, and the mixture was stirred for 2 h at 0 °C after the addition was complete. Then, the mixture was quenched by saturated aqueous solution of Na₂CO₃ and stirred for 1 h. The reaction mixture was extracted with CH₂Cl₂ (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to yield the (*E*)-2-(2-isocyanophenyl)-3-phenylacrylonitrile (0.184 g, 80%).

Synthesis of 2-(4-Fluoro-2-nitrophenyl)acetonitrile⁴:



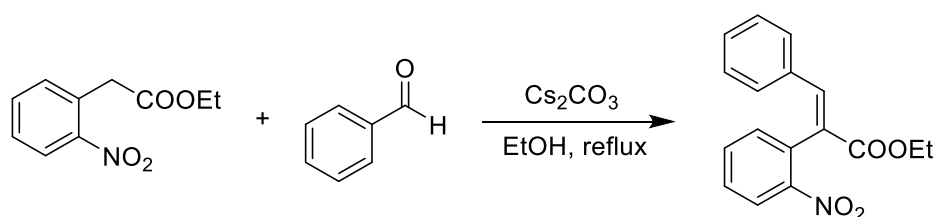
A solution of 1-(bromomethyl)-4-fluoro-2-nitrobenzene (4.680 g, 20 mmol, 1.0equiv), K₂CO₃ (3.317 g, 24 mmol, 1.2 equiv) in CH₃CN (50 mL) was under air atmosphere and cooled to 0 °C. TMSCN (2.381 g, 24 mmol, 1.2 equiv) was added dropwise. After the addition was complete, the mixture was warmed to room temperature and stirred for 8 h. The crude reaction mixture was diluted with CH₂Cl₂, extracted by aqueous NaHCO₃. The combined organic layer was collected, dried over the Na₂SO₄ and concentrated in vacuo. The residue was purified through flash column chromatography by using hexane and ethyl acetate as eluent to give 2-(4-fluoro-2-nitrophenyl)acetonitrile (1.801 g, 50%).

Synthesis of ethyl 2-(2-Nitrophenyl)acetate⁵:

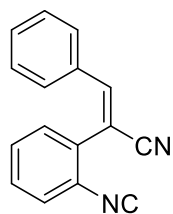


H₂SO₄ (98%; 0.300 g, 3 mmol, 0.1 equiv) was added to a stirred solution of 2-(2-nitrophenyl)acetic acid (5.434 g, 30 mmol, 1.0 equiv) in EtOH (60 mL). The solution was heated at 60 °C for 24 h, then it was cooled and diluted with H₂O (100 mL), and extracted with CH₂Cl₂. The organic extract was washed with NaHCO₃ (saturated aq.), the combined organic extracts were dried, and the solvents were evaporated to give ethyl 2-(2-nitrophenyl)acetate (6.025 g, 96%).

Synthesis of ethyl (*E*)-2-(2-nitrophenyl)-3-phenylacrylate:

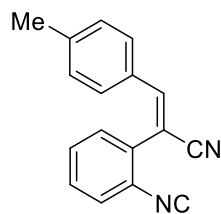


To a solution of ethyl 2-(2-nitrophenyl)acetate (5.230 g, 25 mmol, 1.0 equiv.) in 50 mL of ethanol was added 2.918 g of benzaldehyde (27.5 mmol, 1.1 equiv.) and 4.073 g of cesium carbonate (12.5 mmol, 0.5 equiv.). The reaction mixture was heated to reflux at 85°C. After 4 h, the reaction mixture was cooled to room temperature. The mixture was extracted with CH₂Cl₂ three times, dried over the anhydrous NaSO₄ and concentrated in vacuo. The compound was purified by column to give ethyl (*E*)-2-(2-nitrophenyl)-3-phenylacrylate white solid (2.230 g, 30%).



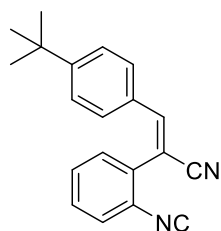
(*E*)-2-(2-Isocyanophenyl)-3-phenylacrylonitrile (**1a**)

White solid; m.p. 86-87 °C; yield: 184.2 mg (80%); ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.91 (m, 2H), 7.58-7.56 (m, 1H), 7.52-7.42 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 149.0, 132.9, 132.2, 131.5, 130.0, 129.9, 129.5, 129.1, 128.4, 124.5, 117.1, 106.6. HRMS (ESI): calcd for C₁₆H₁₀N₂ ([M+H]⁺) 231.0917, found. 231.0921.



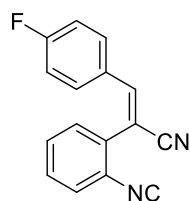
(E)-2-(2-Isocyanophenyl)-3-(*p*-tolyl)acrylonitrile (**1b**)

White solid; m.p. 102-103 °C; yield: 210.1 mg (86%); ¹H NMR (400 MHz, CDCl₃) δ 7.83, (d, *J* = 8.0 Hz, 2H), 7.57-7.55 (m, 1H), 7.50- 7.41 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 149.0, 142.3, 132.4, 130.3, 130.0, 129.9, 129.8, 129.6, 128.4, 124.5, 117.3, 105.2, 21.7. HRMS (ESI): calcd for C₁₇H₁₂N₂ ([M+H]⁺) 245.1073, found. 245.1075.



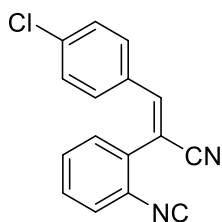
(E)-3-(4-(*Tert*-butyl)phenyl)-2-(2-isocyanophenyl)acrylonitrile (**1c**)

White solid; m.p. 105-106 °C; yield: 194.7 mg (68%); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.58-7.41 (m, 7H), 1.36 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 155.3, 148.9, 132.4, 130.2, 130.0, 129.8, 129.5, 128.4, 126.1, 124.5, 117.3, 105.3, 35.1, 31.1. HRMS (ESI): calcd for C₂₀H₁₈N₂ ([M+H]⁺) 287.1543, found .287.1549.



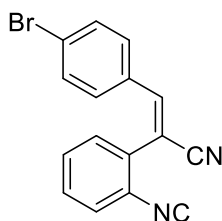
(E)-3-(4-Fluorophenyl)-2-(2-isocyanophenyl)acrylonitrile (**1d**)

Yellow solid; m.p. 127-128 °C; yield: 153.9 mg (62%); ¹H NMR (400 MHz, CDCl₃) δ 7.96-7.93 (m, 2H), 7.58-7.56 (m, 1H), 7.53-7.43 (m, 4H), 7.20-7.16 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 164.3 (d, *J* = 252.6 Hz), 147.6, 131.9, 131.8 (d, *J* = 8.7 Hz), 130.1, 130.0, 129.9, 129.2 (d, *J* = 3.3 Hz), 128.4, 124.5, 117.0, 116.4 (d, *J* = 21.9 Hz), 106.2 (d, *J* = 1.7 Hz). HRMS (ESI): calcd for C₁₆H₉FN₂ ([M+H]⁺) 249.0823, found. 249.0826.



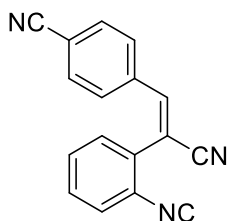
(E)-3-(4-Chlorophenyl)-2-(2-isocyanophenyl)acrylonitrile (**1e**)

Yellow solid; m.p. 130-131 °C; yield: 166.8 mg (63%); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.58-7.56 (m, 1H), 7.53-7.43 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 147.4, 137.5, 131.8, 131.3, 130.7, 130.2, 130.1, 129.9, 129.4, 128.5, 124.5, 116.8, 107.1. HRMS (ESI): calcd for C₁₆H₉ClN₂ ([M+H]⁺) 265.0527, found. 265.0526.



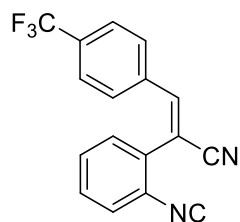
(E)-3-(4-Bromophenyl)-2-(2-isocyanophenyl)acrylonitrile (**1f**)

White solid; m.p. 118-119 °C; yield: 262.8 mg (85%); ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.58-7.56 (m, 1H), 7.53-7.44 (m, 3H), 7.42 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 147.5, 132.4, 131.8, 131.7, 130.8, 130.2, 130.1, 129.9, 128.5, 126.0, 124.4, 116.8, 107.3. HRMS (ESI): calcd for C₁₆H₉BrN₂ ([M+H]⁺) 309.0022, found. 309.0027.



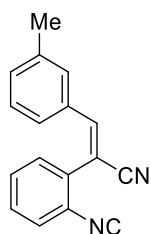
(E)-4-(2-Cyano-2-(2-isocyanophenyl)vinyl)benzonitrile (**1g**)

White solid; m.p. 136-137 °C; yield: 81.7 mg (32%); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.62-7.59 (m, 1H), 7.57-7.49 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 146.4, 136.9, 132.8, 131.1, 130.7, 130.2, 129.9, 129.8, 128.6, 124.4, 118.0, 116.2, 114.5, 110.4. HRMS (ESI): calcd for C₁₇H₉N₃ ([M+H]⁺) 256.0869, found. 256.0878.



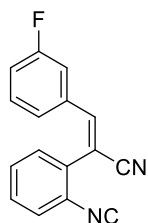
(E)-2-(2-Isocyanophenyl)-3-(4-(trifluoromethyl)phenyl)acrylonitrile (**1h**)

White solid; m.p. 97-98 °C; yield: 214.8 mg (72%); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.61-7.59 (m, 1H), 7.55-7.47 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.0, 147.1, 136.1, 132.7 (q, *J* = 32.5 Hz), 131.4, 130.5, 130.1, 129.9, 129.6, 128.5, 126.1 (q, *J* = 3.8 Hz), 124.5, 123.6 (q, *J* = 270.8 Hz), 116.4, 109.5. HRMS (ESI): calcd for C₁₇H₉F₃N₂ ([M+H]⁺) 299.0791, found. 299.0791.



(E)-2-(2-Isocyanophenyl)-3-(*m*-tolyl)acrylonitrile (**1i**)

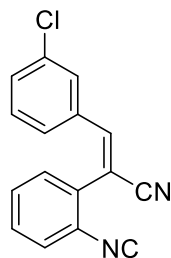
White solid; m.p. 70-71 °C; yield: 180.8 mg (74%); ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.71 (s, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.49 (t, *J* = 6.8 Hz, 2H), 7.46-7.41 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 149.2, 138.9, 132.9, 132.3, 132.2, 130.2, 130.0, 129.9, 129.0, 128.4, 126.6, 124.5, 117.1, 106.2, 21.4. HRMS (ESI): calcd for C₁₇H₁₂N₂ ([M+H]⁺) 245.1073, found. 245.1075.



(E)-3-(3-Fluorophenyl)-2-(2-isocyanophenyl)acrylonitrile (**1j**)

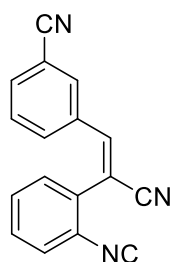
Yellow solid; m.p. 109-110 °C; yield: 111.7 mg (45%); ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.63 (m, 2H), 7.59-7.57 (m, 1H), 7.54-7.44 (m, 5H), 7.20 (td, *J* = 8.4, 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 162.8 (d, *J* = 246.3 Hz), 147.4 (d, *J* = 2.7

Hz), 134.8 (d, $J = 7.9$ Hz), 131.7, 130.7 (d, $J = 8.2$ Hz), 130.3, 130.1, 129.9, 128.5, 125.5 (d, $J = 2.9$ Hz), 124.5. 118.4 (d, $J = 21.1$ Hz), 116.6, 115.9 (d, $J = 22.7$ Hz), 108.1. ^{19}F NMR (377 MHz, CDCl_3) δ -111.2. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_9\text{FN}_2$ ($[\text{M}+\text{H}]^+$) 249.0823, found. 249.0827.



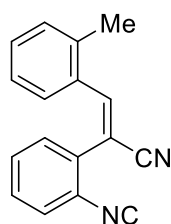
(E)-3-(3-Chlorophenyl)-2-(2-isocyanophenyl)acrylonitrile (1k)

Yellow solid; m.p. 101-102 °C; yield: 172.1 mg (65%); ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.83 (m, 2H), 7.59-7.55 (m, 1H), 7.53-7.41 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 147.2, 135.1, 134.5, 131.6, 131.3, 130.4, 130.3, 130.1, 129.9, 129.5, 128.5, 127.3, 124.5, 116.6, 108.2. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_9\text{ClN}_2$ ($[\text{M}+\text{H}]^+$) 265.0527, found. 265.0537.



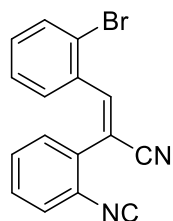
(E)-3-(2-Cyano-2-(2-isocyanophenyl)vinyl)benzonitrile (1l)

Yellow solid; m.p. 114-115 °C; yield: 188.9 mg (74%); ^1H NMR (400 MHz, CDCl_3) δ 8.24-8.21 (m, 1H), 8.09-8.08 (m, 1H), 7.79-7.76 (m, 1H), 7.65 (t, $J = 8.0$ Hz, 1H), 7.61-7.59 (m, 1H), 7.57-7.51 (m, 3H). 7.49 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 146.0, 134.2, 134.1, 132.9, 132.8, 131.1, 130.7, 130.2, 130.1, 129.9, 128.5, 124.5, 117.8, 116.2, 113.6, 109.8. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_9\text{N}_3$ ($[\text{M}+\text{H}]^+$) 256.0869, found. 256.0872.



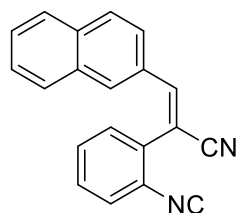
(E)-2-(2-Isocyanophenyl)-3-(*o*-tolyl)acrylonitrile (**1m**)

White solid; m.p. 99-100°C; yield: 146.6 mg (60%); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 6.8 Hz, 1H), 7.74 (s, 1H), 7.59-7.26 (m, 7H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 148.0, 138.1, 132.4, 131.9, 131.1, 130.8, 130.1, 130.0, 128.5, 128.1, 126.5, 124.4, 117.0, 108.6, 20.2. HRMS (ESI): calcd for C₁₇H₁₂N₂ ([M+H]⁺) 245.1073, found. 245.1078.



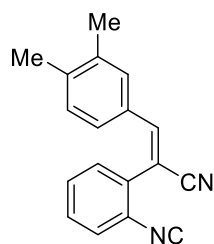
(E)-3-(2-Bromophenyl)-2-(2-isocyanophenyl)acrylonitrile (**1n**)

White solid; m.p. 116-117 °C; yield: 201.0 mg (65%); ¹H NMR (400 MHz, CDCl₃) δ 8.14 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.79 (s, 1H), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62-7.59 (m, 1H), 7.55-7.45 (m, 4H), 7.34 (td, *J* = 8.0, 1.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 148.1, 133.3, 133.2, 132.2, 131.4, 130.4, 130.1, 130.0, 129.8, 128.5, 128.0, 125.1, 124.6, 116.2, 110.2. HRMS (ESI): calcd for C₁₆H₉BrN₂ ([M+H]⁺) 309.0022, found. 309.0027.



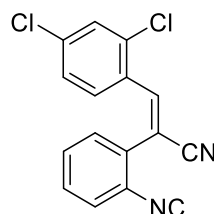
(E)-2-(2-Isocyanophenyl)-3-(naphthalen-2-yl)acrylonitrile (**1o**)

White solid; m.p. 126-127 °C; yield: 154.2 mg (55%); ¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 1H), 8.13 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.94-7.91 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.62-7.42 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 149.0, 134.6, 133.0, 132.3, 131.3, 130.5, 130.1, 130.0, 129.9, 129.0, 128.9, 128.5, 128.2, 127.8, 127.0, 124.9, 124.5, 117.3, 106.4. HRMS (ESI): calcd for C₂₀H₁₂N₂ ([M+H]⁺) 281.1073, found. 281.1076.



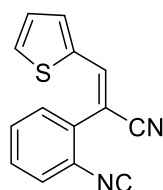
(E)-3-(3,4-Dimethylphenyl)-2-(2-isocyanophenyl)acrylonitrile (**1p**)

White solid; m.p. 97-98 °C; yield: 206.7 mg (80%); ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.70 (m, 1H), 7.68 (s, 1H), 7.57-7.54 (m, 1H), 7.50-7.46 (m, 2H), 7.44-7.42 (m, 1H), 7.40 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 149.2, 141.1, 137.5, 132.5, 130.8, 130.7, 130.4, 129.9, 129.7, 128.4, 127.1, 124.5, 117.4, 104.9, 20.0, 19.8. HRMS (ESI): calcd for C₁₈H₁₄N₂ ([M+H]⁺) 259.1230, found. 259.1321



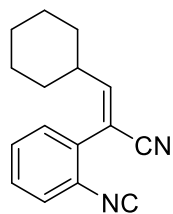
(E)-3-(2,4-Dichlorophenyl)-2-(2-isocyanophenyl)acrylonitrile (**1q**)

White solid; m.p. 110-111 °C; yield: 68.8 mg (23%); ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 1H), 7.61-7.58 (m, 1H), 7.55-7.47 (m, 4H), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 144.2, 137.6, 135.8, 131.2, 130.5, 130.1 (2C), 130.0 (2C), 129.9, 128.6, 127.8, 124.5, 116.1, 110.4. HRMS (ESI): calcd for C₁₆H₈Cl₂N₂ ([M+H]⁺) 299.0137, found. 299.0139.



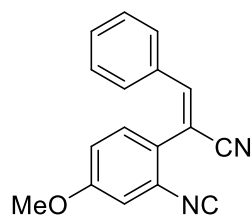
(E)-2-(2-Isocyanophenyl)-3-(thiophen-2-yl)acrylonitrile (**1r**)

White solid; m.p. 118-119 °C; yield: 70.9 mg (30%); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 3.6 Hz, 1H), 7.63 (s, 2H), 7.57-7.55 (m, 1H), 7.51-7.46 (m, 2H), 7.44-7.40 (m, 1H), 7.19-7.17 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 140.9, 137.0, 133.9, 131.6, 131.5, 130.0, 129.9, 129.8, 128.5, 128.0, 124.4, 117.3, 102.9. HRMS (ESI): calcd for C₁₄H₈N₂S ([M+H]⁺) 237.0481, found. 237.0483.



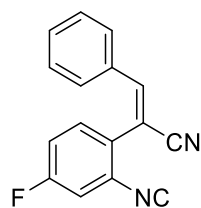
(E)-3-Cyclohexyl-2-(2-isocyanophenyl)acrylonitrile (**1s**)

Yellow liquid; yield: 70.9 mg (30%); ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.38 (m, 4H), 6.70 (d, $J = 10.4$ Hz, 1H), 2.86-2.76 (m, 1H), 1.90-1.66 (m, 5H), 1.47-1.19 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 159.9, 130.8, 129.8, 129.7, 129.6, 128.2, 124.4, 115.8, 108.8, 41.8, 31.8, 25.5, 25.1 HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2$ ($[\text{M}+\text{H}]^+$) 237.1386, found. 237.1387.



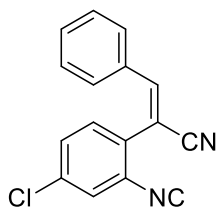
(E)-2-(2-Isocyano-4-methoxyphenyl)-3-phenylacrylonitrile (**1t**)

White solid; m.p. 97-98 °C; yield: 214.3 mg (82%); ^1H NMR (400 MHz, CDCl_3) δ 7.91-7.89 (m, 2H), 7.50-7.46 (m, 4H), 7.41 (s, 1H), 7.03-6.99 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 160.3, 147.9, 133.1, 131.2, 131.0, 129.3, 129.0, 124.5, 117.3, 116.3, 113.4, 106.4, 100.0, 55.9. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$) 261.1022, found. 261.1025.



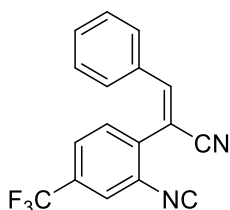
(E)-2-(4-Fluoro-2-isocyanophenyl)-3-phenylacrylonitrile (**1u**)

White solid; m.p. 108-109 °C; yield: 193.6 mg (78%); ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.90 (m, 2H), 7.58-7.55 (m, 1H), 7.52-7.49 (m, 3H), 7.43 (s, 1H), 7.26-7.21 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 162.3 (d, $J = 251.8$ Hz), 149.2, 132.7, 131.7 (d, $J = 9.1$ Hz), 131.6, 129.5, 129.2, 128.6 (d, $J = 4.0$ Hz), 125.6, 117.7 (d, $J = 21.4$ Hz), 116.9, 116.8 (d, $J = 25.6$ Hz), 105.6. ^{19}F NMR (377 MHz, CDCl_3) δ -108.4. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_9\text{FN}_2$ ($[\text{M}+\text{H}]^+$) 249.0823, found. 249.0825.



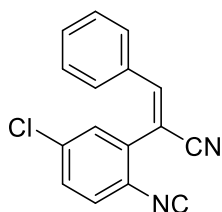
(*E*)-2-(4-Chloro-2-isocyanophenyl)-3-phenylacrylonitrile (**1v**)

White solid; m.p. 106-107 °C; yield: 226.3 mg (86%); ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.90 (m, 2H), 7.53-7.46 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 149.3, 135.7, 132.7, 131.7, 131.0, 130.7, 130.4, 129.6, 129.2, 128.3, 125.2, 116.7, 105.5. HRMS (ESI): calcd for C₁₆H₉ClN₂ ([M+H]⁺) 265.0527, found. 265.0531.



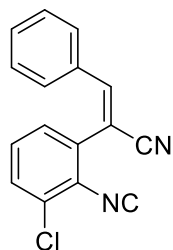
(*E*)-2-(2-Isocyano-4-(trifluoromethyl)phenyl)-3-phenylacrylonitrile (**1w**)

Yellow solid; m.p. 104-105 °C; yield: 125.2 mg (42%); ¹H NMR (400 MHz, CDCl₃) δ 7.85-7.83 (m, 2H), 7.67-7.62 (m, 3H), 7.44-7.38 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 172.2, 150.2, 135.5, 132.5, 132.3 (q, *J* = 34.0 Hz), 132.0, 130.8, 129.7, 129.2, 126.7 (q, *J* = 3.7 Hz), 125.5 (q, *J* = 3.8 Hz), 125.0, 122.6 (q, *J* = 271.2 Hz), 116.4, 105.3. HRMS (ESI): calcd for C₁₇H₉F₃N₂ ([M+H]⁺) 299.0791, found. 299.0793.



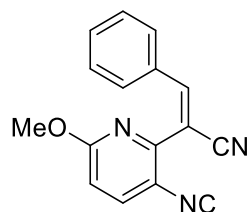
(*E*)-2-(5-Chloro-2-isocyanophenyl)-3-phenylacrylonitrile (**1x**)

White solid; m.p. 99-100 °C; yield: 223.1 mg (85%); ¹H NMR (400 MHz, CDCl₃) δ 7.94-7.91 (m, 2H), 7.57-7.40 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 149.8, 136.0, 133.6, 132.6, 131.9, 130.1, 130.0, 129.6, 129.5, 129.2, 123.0, 116.5, 105.4. HRMS (ESI): calcd for C₁₆H₉ClN₂ ([M+H]⁺) 265.0527, found. 265.0524.



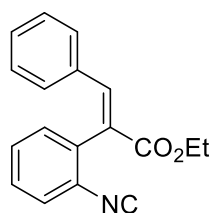
(E)-2-(3-Chloro-2-isocyanophenyl)-3-phenylacrylonitrile (**1y**)

White solid; m.p. 128-129 °C; yield: 230.5 mg (87%); ¹H NMR (400 MHz, CDCl₃) δ 7.94-7.91 (m, 2H), 7.58-7.41 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 149.6, 134.2, 132.8, 132.6, 131.8, 130.5, 130.1, 129.6, 129.2, 128.1, 127.1, 116.7, 106.0. HRMS (ESI): calcd for C₁₆H₉ClN₂ ([M+H]⁺) 265.0527, found. 265.0529.



(E)-2-(3-Isocyano-6-methoxypyridin-2-yl)-3-phenylacrylonitrile (**1z**)

Yellow solid; m.p. 96-97 °C; yield: 96.3 mg (37%); ¹H NMR (400 MHz, CDCl₃) δ 8.01-7.98 (m, 3H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.53-7.51 (m, 3H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.04 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 162.5, 150.1, 138.9, 132.7, 131.9, 130.1, 129.1, 128.8, 116.3, 114.9, 112.1, 107.7, 54.5. HRMS (ESI): calcd for C₁₆H₁₁N₃O ([M+H]⁺) 262.0975, found. 262.0978.



Ethyl *(E)*-2-(2-isocyanophenyl)-3-phenylacrylate (**1aa**)

White solid; m.p. 68-69 °C; yield: 97.1 mg (35%); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 7.47-7.42 (m, 1H), 7.41-7.36 (m, 2H), 7.27-7.23 (m, 2H), 7.20-7.17 (m, 2H), 7.02-6.99 (m, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 143.0, 134.1, 134.0, 131.2, 130.2, 129.7, 129.6, 129.0, 128.5, 128.1, 127.2, 61.6, 14.3. HRMS (ESI): calcd for C₁₈H₁₅NO₂ ([M+H]⁺) 278.1176, found. 278.1178.

3. Experimental Section and Characterization Data of compound 3

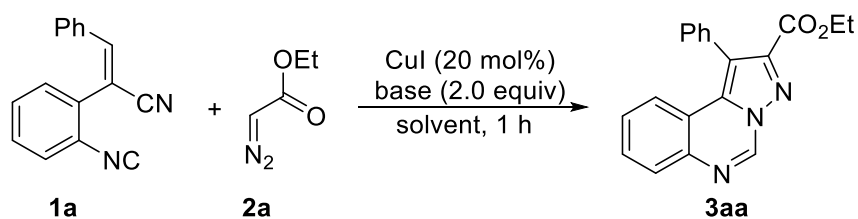
(3aa as Example):

Table S1. Optimization of the reaction conditions^{a,b}

1a + **2a** $\xrightarrow[\text{DMAc, 1 h}]{\text{catalyst (x mol\%) base (n equiv.)}}$ **3aa**

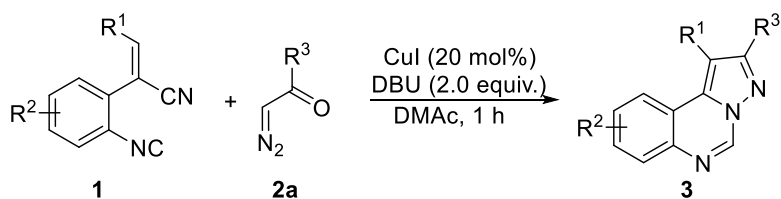
Entry	Catalyst (x mol%)	Base (n equiv.)	Yield (%) ^b
1	CuI (20)	DBU (0.5)	16%
2	CuI (20)	DBU (1.5)	50%
3	CuI (20)	DBU (2.0)	78%
4	CuI (20)	DBU (3.0)	67%
5 ^c	CuI (20)	DBU (2.0)	66%
6 ^d	CuI (20)	DBU (2.0)	78%
7 ^e	CuI (20)	DBU (2.0)	59%
8	CuI (10)	DBU (2.0)	68%
9	CuBr (20)	DBU (2.0)	57%
10	CuCl (20)	DBU (2.0)	72 %
11	Cu ₂ O (20)	DBU (2.0)	63%
12	CuCN (20)	DBU (2.0)	56%
13	CuCl ₂ (20)	DBU (2.0)	68%
14	Cu(OAc) ₂ (20)	DBU (2.0)	62%
15	Ag ₂ CO ₃ (20)	DBU (2.0)	43%
16	AgOAc (20)	DBU (2.0)	68%

^a Reactions were carried out using **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (20 mol%), base (0.4 mmol) and in a DMAc (1 mL) at room temperature for 1 h under air. ^b Isolated yield. ^c under N₂ atmosphere. ^d **2a** (0.4 mmol). ^e Reaction was performed at 40 °C.

Table S2. Optimization of Reaction Conditions^{a,b}

entry	solvent	base (2.0 equiv)	yield [%]
1	DMAc	NaOH	37%
2	DMAc	K ₂ CO ₃	40%
3	DMAc	Et ₃ N	0
4	DMAc	pyridine	0
5	DMAc	^t BuOK	0
6	DMAc	DABCO	0
7	DMAc	Na ₂ HPO ₄	0
8	CH ₃ CN	DBU	71%
9	DMF	DBU	72%
10	THF	DBU	11%
11	DMSO	DBU	69%
12	toluene	DBU	12%
13	1,4-dioxane	DBU	44%
14	EtOH	DBU	18%
15	HFIP	DBU	0
16	TFE	DBU	0

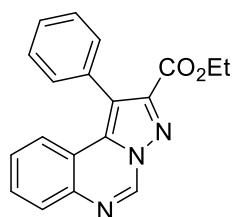
^a Reactions were carried out using **1a** (0.2 mmol), **2a** (0.3 mmol), CuI (20 mol%), base (0.4 mmol) and in a solvent (1 mL) at room temperature for 1 h under air. ^b Isolated yield.



A solution of **1a** (0.2 mmol, 46.1 mg), **2a** (0.3 mmol, 0.037 mL), CuI (20 mol %), and DBU (0.4 mmol, 0.062 mL) in DMAc (1.0 mL) was stirred at room temperature for 1 h. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:15, V/V) to afford pure product **3aa** (49.5mg, 78%) as a yellow solid.

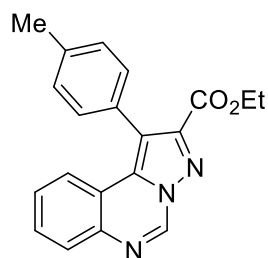
A gram-scale synthesis of compound **3aa**:

A solution of **1a** (5 mmol, 1.15g), **2a** (7.5 mmol, 0.928 mL), CuI (20 mol %), and DBU (10 mmol, 1.551 mL) in DMAc (25 mL) was stirred at room temperature for 1 h. After the reaction was complete (monitored by TLC), the reaction mixture was poured into water (100 mL) and extracted with CH₂Cl₂ (30 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to yield the corresponding crude product. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:15, V/V) to afford pure product **3aa** (1.13 g, 71%) as a yellow solid.



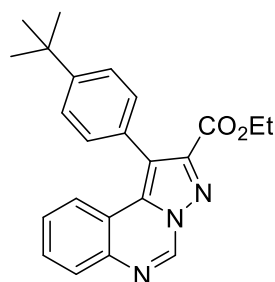
Ethyl 1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3aa**)

Yellow solid; m.p. 110-111 °C; yield: 49.5 mg (78%); ¹H NMR (400 MHz, CDCl₃) δ 9.19 (s, 1H), 7.96-7.94 (m, 1H), 7.63-7.59 (m, 1H), 7.55-7.51 (m, 4H), 7.18-7.45 (m, 2H), 7.37-7.33 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 144.8, 139.8, 139.2, 136.1, 131.7, 130.4, 130.1, 129.1, 128.7, 128.5, 128.4, 123.0, 120.5, 118.6, 61.5, 14.0. HRMS (ESI): calcd for C₁₉H₁₅N₃O₂ ([M+H]⁺) 318.1237, found 318.1242.



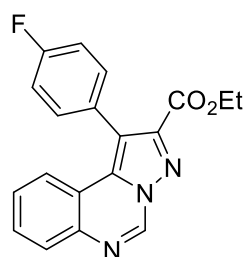
Ethyl 1-(*p*-tolyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ba**)

Yellow solid; m.p. 125-126 °C; yield: 35.1 mg (53%); ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.63-7.58 (m, 2H), 7.39-7.33 (m, 5H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 144.8, 139.8, 139.3, 138.2, 136.1, 130.2, 130.0, 129.4, 129.0, 128.5, 128.4, 123.1, 120.6, 118.8, 61.5, 21.5, 14.1. HRMS (ESI): calcd for C₂₀H₁₇N₃O₂ ([M+H]⁺) 332.1394, found 332.1396.



Ethyl 1-(4-(*tert*-butyl)phenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ca**)

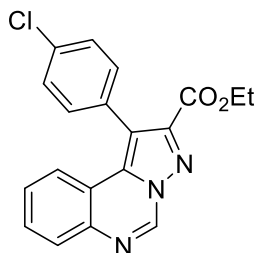
Yellow solid; m.p. 151-153 °C; yield: 34.3 mg (46%); ¹H NMR (400 MHz, CDCl₃) δ 9.19 (s, 1H), 7.96-7.94 (m, 1H), 7.62-7.59 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.40-7.37 (m, 3H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.43 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 151.3, 144.9, 139.8, 139.3, 136.1, 130.0, 129.5, 129.0, 128.5, 126.1, 125.5, 123.1, 120.6, 118.7, 61.5, 34.8, 31.4, 13.9. HRMS (ESI): calcd for C₂₃H₂₃N₃O₂ ([M+H]⁺) 374.1863, found 374.1867.



Ethyl 1-(4-fluorophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3da**)

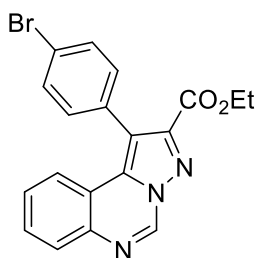
Yellow solid; m.p. 134-135 °C; yield: 41.6 mg (62%); ¹H NMR (400 MHz, CDCl₃) δ

9.19 (s, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.66-7.62 (m, 1H), 7.52 (dd, $J = 1.2, 8.0$ Hz, 1H), 7.48-7.43 (m, 2H), 7.41-7.37 (m, 1H), 7.27-7.21 (m, 2H), 4.36 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9 (d, $J = 246.3$ Hz), 161.8, 144.7, 139.8, 139.2, 136.3, 132.2 (d, $J = 8.1$ Hz), 130.2, 129.2, 128.6, 127.4 (d, $J = 3.6$ Hz), 122.8, 120.3, 117.5, 115.8 (d, $J = 21.4$ Hz), 61.6, 14.1. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{14}\text{FN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 336.1143, found 336.1147.



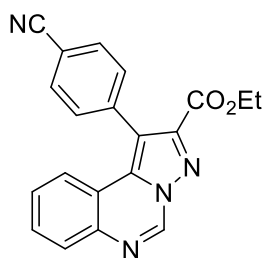
Ethyl 1-(4-chlorophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ea**)

Yellow solid; m.p. 148-149 °C; yield: 44.2 mg (63%); ^1H NMR (400 MHz, CDCl_3) δ 9.18 (s, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.66-7.62 (m, 1H), 7.55-7.50 (m, 3H), 7.44-7.38 (m, 3H), 4.36, (q, $J = 7.2$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.8, 144.6, 139.9, 139.1, 136.2, 134.6, 131.9, 130.3, 130.2, 129.2, 129.0, 128.6, 122.9, 120.2, 117.3, 61.7, 14.1. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 352.0847, found 352.0853.



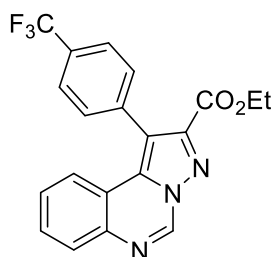
Ethyl 1-(4-bromophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3fa**)

Yellow solid; m.p. 156-157 °C; yield: 51.4 mg (65%); ^1H NMR (400 MHz, CDCl_3) δ 9.18 (s, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.69-7.62 (m, 3H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 4.36 (q, $J = 7.2$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.8, 144.5, 139.9, 139.1, 136.1, 132.2, 131.9, 130.7, 130.3, 129.2, 128.6, 122.9, 122.8, 120.2, 117.3, 61.7, 14.1. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{14}\text{BrN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) , 396.0342, found 396.0347.



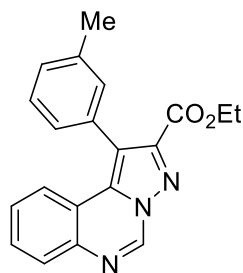
Ethyl 1-(4-cyanophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ga**)

Yellow solid; m.p. 214-215 °C; yield: 41.1 mg (60%); ¹H NMR (400 MHz, CDCl₃) δ 9.21 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.70-7.65 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.45-7.39 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 144.3, 140.0, 139.1, 137.1, 136.2, 132.4, 131.5, 130.6, 129.5, 128.8, 122.7, 119.9, 118.6, 116.6, 112.5, 61.9, 14.1. HRMS (ESI): calcd for C₂₀H₁₄N₄O₂ ([M+H]⁺) 343.1190, found 343.1191.



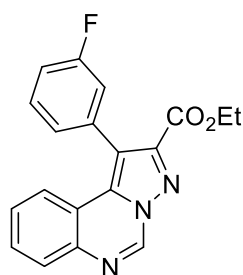
Ethyl 1-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ha**)

Yellow solid; m.p. 179-180 °C; yield: 53.1 mg (69%); ¹H NMR (400 MHz, CDCl₃) δ 9.21 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.68-7.61 (m, 3H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 144.5, 139.9, 139.1, 136.2, 135.8 (q, *J* = 1.1 Hz), 131.0, 130.6 (q, *J* = 32.6 Hz), 130.4, 129.3, 128.7, 125.6 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.5 Hz), 122.8, 120.0, 117.0, 61.7, 14.0. HRMS (ESI): calcd for C₂₀H₁₄F₃N₃O₂ ([M+H]⁺) 386.1111, found 386.1116.



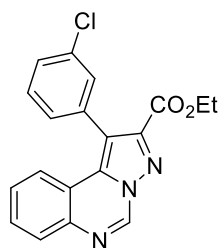
Ethyl 1-(*m*-tolyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ia**)

Yellow solid; m.p. 90-91 °C; yield: 33.1 mg (50%); ¹H NMR (400 MHz, CDCl₃) δ 9.19 (s, 1H), 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64-7.59 (m, 1H), 7.57-7.54 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.36-7.34 (m, 1H), 7.34-7.31 (m, 1H), 7.28-7.25 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 144.8, 139.8, 139.2, 138.2, 136.1, 131.6, 131.0, 130.0, 129.2, 129.1, 128.5, 128.4, 127.4, 123.1, 120.5, 118.9, 61.5, 21.5, 14.0. HRMS (ESI): calcd for C₂₀H₁₇N₃O₂ ([M+H]⁺) 332.1394, found 332.1398.



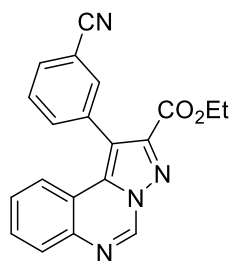
Ethyl 1-(3-fluorophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ja**)

Yellow solid; m.p. 125-127°C; yield: 40.9 mg (61%); ¹H NMR (400 MHz, CDCl₃) δ 9.19 (s, 1H), 7.97 (d, *J* = 8.4, 1H), 7.66-7.62 (m, 1H), 7.54-7.48 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.26-7.18 (m, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.8 (d, *J* = 245.6 Hz), 161.7, 144.6, 139.9, 139.1, 136.2, 134.0 (d, *J* = 8.3 Hz), 130.3, 130.2 (d, *J* = 8.4 Hz), 129.2, 128.6, 126.3 (d, *J* = 2.9 Hz), 122.9, 120.2, 117.6 (d, *J* = 21.6 Hz), 117.2 (d, *J* = 2.3 Hz), 115.5 (d, *J* = 20.8 Hz), 61.6, 14.0. HRMS (ESI): calcd for C₁₉H₁₄FN₃O₂ ([M+H]⁺) 336.1143, found 336.1146.



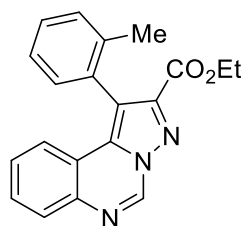
Ethyl 1-(3-chlorophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ka**)

Yellow solid; m.p. 114-116 °C; yield: 47.0 mg (67%); ¹H NMR (400 MHz, CDCl₃) δ 9.20, (s, 1H), 7.98 (d, *J* = 8.0, 1H), 7.68-7.63 (m, 1H), 7.56-7.46 (m, 4H), 7.43-7.35 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 144.7, 139.9, 139.1, 136.2, 134.5, 133.7, 130.6, 130.3, 129.9, 129.3, 128.7, 128.7, 128.6, 122.9, 120.1, 117.0, 61.6, 14.0. HRMS (ESI): calcd for C₁₉H₁₄ClN₃O₂ ([M+H]⁺) 352.0847, found 352.0852.



Ethyl 1-(3-cyanophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3la**)

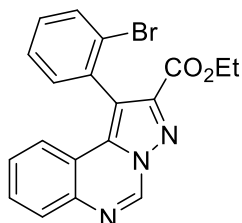
Yellow solid; m.p. 179-180 °C; yield: 39.0 mg (57%); ¹H NMR (400 MHz, CDCl₃) δ 9.22 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.80 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.72-7.66 (m, 2H), 7.42-7.40 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 144.5, 140.0, 139.1, 136.4, 135.1, 134.1, 133.5, 132.1, 130.6, 129.6, 129.5, 128.8, 122.6, 119.9, 118.4, 116.0, 113.0, 61.8, 14.1. HRMS (ESI): calcd for C₂₀H₁₄N₄O₂ ([M+H]⁺) 343.1190, found 343.1191.



Ethyl 1-(*o*-tolyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ma**)

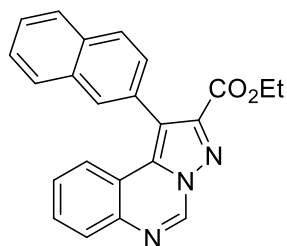
Yellow solid; m.p. 101-103 °C; yield: 39.8 mg (60%); ¹H NMR (400 MHz, CDCl₃) δ

9.22 (s, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.64-7.60 (m, 1H), 7.46-7.29 (m, 6H), 4.33 (q, $J = 7.2$ Hz, 2H), 2.10 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.8, 144.8, 139.7, 139.3, 137.5, 136.0, 131.3, 130.4, 130.2, 130.1, 129.0, 128.8, 128.7, 126.2, 122.7, 120.6, 117.6, 61.5, 20.1, 14.0. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 332.1394, found 332.1398.



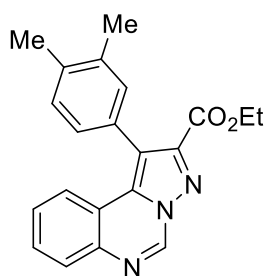
Ethyl 1-(2-bromophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3na**)

Yellow solid; m.p. 110-111 °C; yield: 41.1 mg (52%); ^1H NMR (400 MHz, CDCl_3) δ 9.22 (s, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.65 (t, $J = 7.2$ Hz, 1H), 7.51-7.34 (m, 5H), 4.37-4.30 (m, 2H) 1.23 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.6, 144.9, 139.9, 139.2, 136.3, 133.3, 133.0, 132.0, 130.3, 130.2, 129.1, 128.8, 127.7, 125.3, 122.9, 120.3, 117.2, 61.6, 13.9. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{14}\text{BrN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 396.0342, found 396.0347.



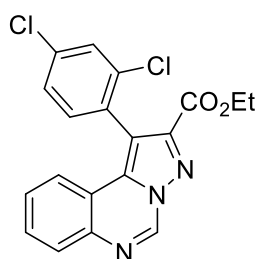
Ethyl 1-(naphthalen-2-yl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3oa**)

Yellow solid; m.p. 158-159 °C; yield: 41.1 mg (56%); ^1H NMR (400 MHz, CDCl_3) δ 9.22 (s, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 8.00-7.95 (m, 3H), 7.89-7.86 (m, 1H), 7.61-7.52 (m, 5H), 7.28-7.24 (m, 1H), 4.31 (q, $J = 7.2$ Hz, 2H), 1.19 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.9, 144.9, 139.9, 139.3, 136.3, 133.4, 133.1, 130.1, 129.6, 129.2, 129.1, 128.6, 128.4, 128.3, 128.2, 127.9, 126.6, 126.4, 123.1, 120.5, 118.6, 61.6, 14.0. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 368.1394, found 368.1397.



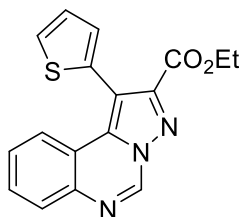
Ethyl 1-(3,4-dimethylphenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3pa**)

Yellow solid; m.p. 117-118 °C; yield: 26.2 mg (38%); ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 1H), 7.95 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.63-7.59 (m, 2H), 7.39-7.35 (m, 1H), 7.28 (q, *J* = 8.0 Hz, 1H), 7.22 (m, 1H), 7.18 (dd, *J* = 2.0, 7.6 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.34 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 144.8, 139.8, 139.3, 136.8, 136.8, 136.1, 131.4, 130.0, 129.9, 129.0, 128.8, 128.4, 127.7, 123.1, 120.6, 119.0, 61.5, 19.9, 19.8, 14.1. HRMS (ESI): calcd for C₂₁H₁₉N₃O₂ ([M+H]⁺) 346.1550, found 346.1554.



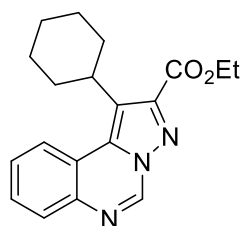
Ethyl 1-(2,4-dichlorophenyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3qa**)

Yellow solid; m.p. 90-91 °C; yield: 27.0 mg (35%); ¹H NMR (400 MHz, CDCl₃) δ 9.22 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.70-7.64 (m, 2H), 7.47-7.38 (m, 4H), 4.41-4.33 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 144.8, 139.9, 139.1, 136.6, 135.8, 135.4, 132.9, 130.5, 129.8, 129.7, 129.2, 128.9, 127.5, 122.7, 120.1, 114.0, 61.7, 14.0. HRMS (ESI): calcd for C₁₉H₁₃Cl₂N₃O₂ ([M+H]⁺) 386.0458, found 386.0462.



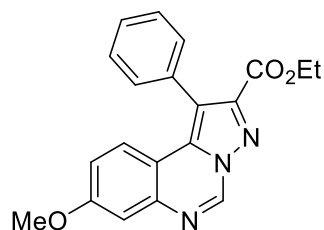
Ethyl 1-(thiophen-2-yl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ra**)

Yellow solid; m.p. 138-140 °C; yield: 37.5 mg (58%); ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.68-7.64 (m, 2H), 7.58 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.18 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 145.8, 140.0, 139.0, 137.5, 131.5, 130.5, 129.1, 129.0, 128.7, 127.6, 127.5, 123.2, 120.1, 110.4, 61.6, 14.0. HRMS (ESI): calcd for C₁₇H₁₃N₃O₂S ([M+H]⁺) 324.0801, found 324.0805.



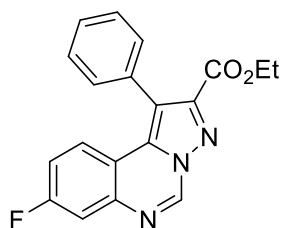
Ethyl 1-cyclohexylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3sa**)

Yellow solid; m.p. 103-104 °C; yield: 24.6 mg (38%); ¹H NMR (400 MHz, CDCl₃) δ 9.08 (s, 1H), 8.35-8.33 (m, 1H), 7.99-7.97 (m, 1H), 7.70-7.65 (m, 2H), 4.52 (q, *J* = 7.2 Hz, 2H), 3.63-3.57 (m, 1H), 2.22-2.12 (m, 2H), 1.96-1.82 (m, 5H), 1.53-1.45 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 145.6, 140.1, 139.6, 134.9, 129.4, 128.4, 123.7, 123.2, 121.2, 61.9, 35.5, 30.6, 27.1, 25.8, 14.3. HRMS (ESI): calcd for C₁₉H₂₁N₃O₂ ([M+H]⁺) 324.1707, found 324.1710.



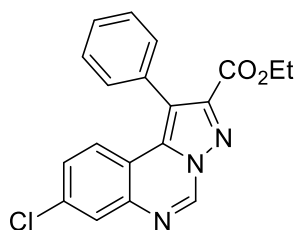
Ethyl 8-methoxy-1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ta**)

Yellow solid; m.p. 184-185 °C; yield: 42.4 mg (61%); ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 7.52-7.37 (m, 7H), 6.97-6.94 (m, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 161.0, 144.9, 141.7, 139.6, 136.4, 131.9, 130.5, 128.6, 128.3, 124.1, 118.1, 117.1, 114.0, 110.4, 61.4, 55.6, 14.0. HRMS (ESI): calcd for C₂₀H₁₇N₃O₃ ([M+H]⁺) 348.1343, found. 348.1345.



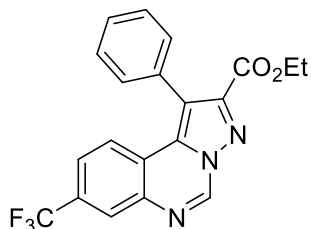
Ethyl 8-fluoro-1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ua**)

Yellow solid; m.p. 159-160 °C; yield: 40.4 mg (60%); ¹H NMR (400 MHz, CDCl₃) δ 9.20 (s, 1H), 7.62 (dd, *J* = 2.8, 9.2 Hz, 1H), 7.56-7.50 (m, 4H), 7.47-7.44 (m, 2H), 7.13-7.08 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.1 (d, *J* = 249.7 Hz), 161.8, 145.1, 141.6 (d, *J* = 11.8 Hz), 140.2, 135.8, 131.5, 130.3, 128.8, 128.6, 124.9 (d, *J* = 9.3 Hz), 118.2, 117.2 (d, *J* = 2.6 Hz), 117.1 (d, *J* = 23.3 Hz), 114.7 (d, *J* = 21.9 Hz), 61.6, 14.0. HRMS (ESI): calcd for C₁₉H₁₄FN₃O₂ ([M+H]⁺) 336.1143, found 336.1149.



Ethyl 8-chloro-1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3va**)

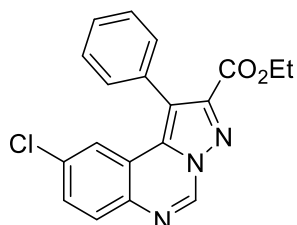
Yellow solid; m.p. 158-159 °C; yield: 42.8 mg (61%); ¹H NMR (400 MHz, CDCl₃) δ 9.17 (s, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.55-7.51 (m, 3H), 7.46-7.43 (m, 3H), 7.30 (dd, *J* = 2.0, 8.8 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 145.1, 140.7, 140.1, 135.8, 135.6, 131.4, 130.3, 128.9, 128.7, 128.6, 128.5, 124.0, 118.9, 118.7, 61.6, 14.0. HRMS (ESI): calcd for C₁₉H₁₄ClN₃O₂ ([M+H]⁺) 352.0847, found. 352.0846.



Ethyl 1-phenyl-8-(trifluoromethyl)pyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3wa**)

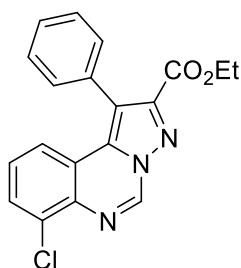
Yellow solid; m.p. 130-131 °C; yield: 32.8 mg (43%); ¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 1H), 8.23 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.59-7.53 (m, 4H), 7.47-7.44 (m,

2H), 4.35 (q, $J = 7.2$ Hz, 2H), 1.25 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.6, 145.2, 140.3, 139.6, 135.3, 131.5 (q, $J = 33.2$ Hz), 131.1, 130.2, 128.8, 128.7, 126.4 (q, $J = 4.1$ Hz), 124.7 (q, $J = 3.4$ Hz), 123.8, 123.4 (q, $J = 271.0$ Hz), 123.0, 119.8, 61.7, 14.0. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{N}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 386.1111, found. 386.1113.



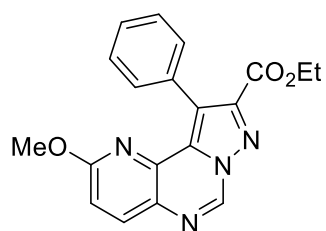
Ethyl 9-chloro-1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3xa**)

Yellow solid; m.p. 129-130 °C; yield: 35.2 mg (50%); ^1H NMR (400 MHz, CDCl_3) δ 9.16 (s, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.57-7.53 (m, 4H), 7.46-7.44 (m, 3H), 4.34 (q, $J = 7.2$ Hz, 2H), 1.25 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.7, 145.0, 139.3, 138.3, 135.0, 134.3, 131.0, 130.5, 130.2, 128.8, 128.7, 122.5, 121.5, 119.2, 61.6, 14.0. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 352.0847, found. 352.0844.



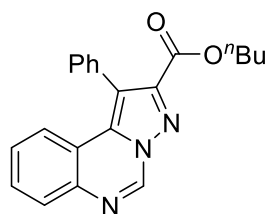
Ethyl 7-chloro-1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ya**)

Yellow solid; m.p. 153-154 °C; yield: 40.7 mg (58%); ^1H NMR (400 MHz, CDCl_3) δ 9.30 (s, 1H), 7.70 (dd, $J = 1.2, 8.0$ Hz, 1H), 7.55-7.52 (m, 3H), 7.46-7.44 (m, 3H), 7.29-7.25 (m, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 1.25 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.6, 145.4, 139.7, 136.5, 135.5, 133.6, 131.3, 130.6, 130.3, 128.8, 128.7, 128.6, 122.2, 121.7, 119.3, 61.6, 14.0. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 352.0847, found. 352.0850.



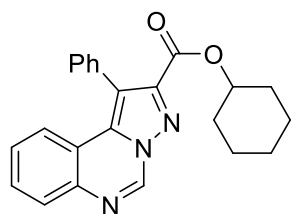
Ethyl 2-methoxy-10-phenylpyrazolo[1,5-*c*]pyrido[2,3-*e*]pyrimidine-9-carboxylate (**3za**)

Yellow solid; m.p. 167-168 °C; yield: 43.2 mg (62%); ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 8.07 (d, *J* = 9.2 Hz, 1H), 7.56-7.53 (m, 2H), 7.45-7.36 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.50 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.0, 162.0, 144.8, 138.8, 137.6, 136.4, 136.2, 131.7, 131.3, 131.2, 127.5, 127.2, 119.5, 114.4, 61.6, 54.2, 14.0. HRMS (ESI): calcd for C₁₉H₁₆N₄O₃ ([M+H]⁺) 349.1295, found. 342.1293.



Prop-2-yn-1-yl 1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ab**)

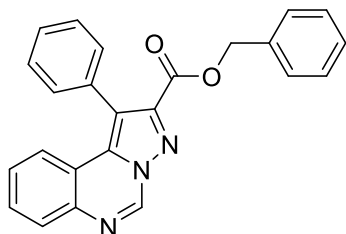
Yellow solid; m.p. 96-97 °C; yield: 57.3 mg (83%); ¹H NMR (400 MHz, CDCl₃) δ 9.19 (s, 1H), 7.95 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.63-7.58 (m, 1H), 7.55-7.45 (m, 6H), 7.36-7.32 (m, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 1.58-1.51 (m, 2H), 1.25-1.16 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 144.9, 139.8, 139.2, 136.1, 131.9, 130.4, 130.0, 129.1, 128.7, 128.5, 128.4, 123.0, 120.5, 118.4, 65.4, 30.4, 19.0, 13.7. HRMS (ESI): calcd for C₂₁H₁₉N₃O₂ ([M+H]⁺) 346.1550, found 346.1554.



Cyclohexyl 1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ac**)

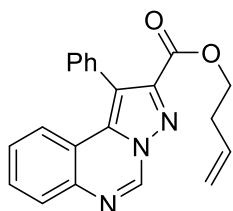
Yellow solid; m.p. 143-144 °C; yield: 49.7 mg (67%); ¹H NMR (400 MHz, CDCl₃) δ 9.20 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.63-7.59 (m, 1H), 7.54-7.44 (m, 6H), 7.34 (t, *J*

= 7.6 Hz, 1H), 5.01-4.95 (m, 1H), 1.84-1.79 (m, 2H), 1.57-1.46 (m, 3H), 1.38-1.26 (m, 4H), 1.21-1.14 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 145.4, 139.8, 139.3, 136.1, 132.1, 130.4, 130.0, 129.1, 128.7, 128.4, 128.3, 123.0, 120.5, 118.3, 74.2, 31.3, 25.2, 23.5. HRMS (ESI): calcd for C₂₃H₂₁N₃O₂ ([M+H]⁺) 372.1707, found 372.1711.



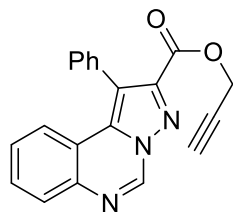
Benzyl 1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (3ad)

Yellow solid; m.p. 115-116 °C; yield: 56.9 mg (75%); ¹H NMR (400 MHz, CDCl₃) δ 9.18 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.63-7.59 (m, 1H), 7.51-7.47 (m, 4H), 7.46-7.42 (m, 2H), 7.36-7.32 (m, 1H), 7.30-7.27 (m, 3H), 7.18-7.15 (m, 2H), 5.31 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 144.5, 139.8, 139.2, 136.2, 135.1, 131.7, 130.4, 130.1, 129.1, 128.9, 128.8, 128.5, 128.4, 128.2, 123.0, 120.5, 118.6, 67.1. HRMS (ESI): calcd for C₂₄H₁₇N₃O₂ ([M+H]⁺) 380.1394, found 380.1398.



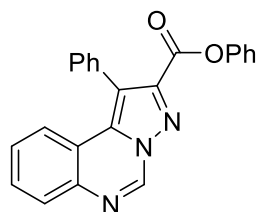
But-3-en-1-yl 1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (3ae)

Yellow solid; m.p. 111-112 °C; yield: 50.1 mg (73%); ¹H NMR (400 MHz, CDCl₃) δ 9.19 (s, 1H), 7.95 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.63-7.59 (m, 1H), 7.55-7.50 (m, 4H), 7.49-7.44 (m, 2H), 7.37-7.33 (m, 1H), 5.69-5.58 (m, 1H), 5.08-5.00 (m, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 2.37-2.32 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 144.7, 139.8, 139.2, 136.2, 133.6, 131.8, 130.4, 130.1, 129.1, 128.7, 128.5, 128.4, 123.0, 120.5, 118.5, 117.4, 64.6, 32.8. HRMS (ESI): calcd for C₂₁H₁₇N₃O₂ ([M+H]⁺) 344.1394, found 344.1391.



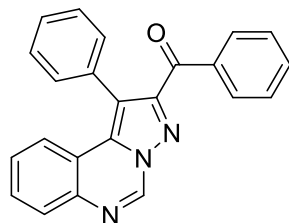
Prop-2-yn-1-yl 1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3af**)

Yellow solid; m.p. 128-129 °C; yield: 39.9 mg (61%); ¹H NMR (400 MHz, CDCl₃) δ 9.10 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.48-7.43 (m, 4H), 7.41-7.37 (m, 2H), 7.29-7.25 (m, 1H), 4.80 (d, *J* = 2.4 Hz, 2H), 2.39 (d, *J* = 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 143.7, 139.8, 139.1, 136.2, 131.2, 130.4, 130.2, 129.1, 128.8, 128.6, 128.5, 123.0, 120.4, 119.1, 75.6, 52.8. HRMS (ESI): calcd for C₂₀H₁₃N₃O₂ ([M+H]⁺) 328.1081, found 328.1084.



Phenyl 1-phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylate (**3ag**)

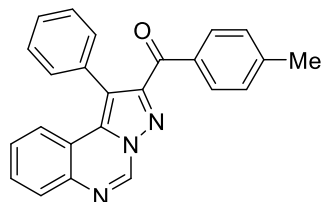
Yellow solid; m.p. 100-102 °C; yield: 19.7 mg (27%); ¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.48 (m, 5H), 7.40-7.33 (m, 3H), 7.24-7.20 (m, 1H), 7.14-7.12 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 150.3, 144.0, 139.8, 139.2, 136.4, 131.4, 130.4, 130.3, 129.4, 129.2, 128.8, 128.7, 128.6, 126.1, 123.1, 121.5, 120.4, 119.3. HRMS (ESI): calcd for C₂₃H₁₅N₃O₂ ([M+H]⁺) 366.1237, found 366.1242.



Phenyl(1-phenylpyrazolo[1,5-*c*]quinazolin-2-yl)methanone (**3ah**)

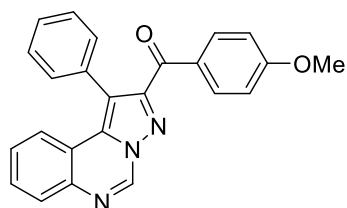
Yellow solid; m.p. 130-131 °C; yield: 44.7 mg (64%); ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 8.14-8.11 (m, 2H), 7.97 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.70 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.65-7.57 (m, 2H), 7.51-7.45 (m, 7H), 7.39-7.35 (m, 1H). ¹³C NMR (100

MHz, CDCl₃) δ 189.2, 151.0, 140.0, 139.4, 137.0, 135.6, 133.5, 131.5, 130.7, 130.4, 130.1, 129.1, 128.8, 128.4, 128.3 (2C), 123.1, 120.6, 118.5, HRMS (ESI): calcd for C₂₃H₁₅N₃O ([M+H]⁺) 350.1288, found 350.1294.



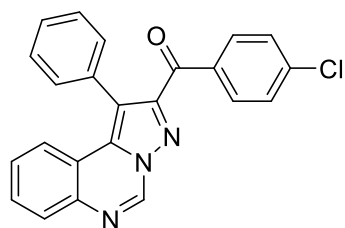
Phenylpyrazolo[1,5-*c*]quinazolin-2-yl(*p*-tolyl)methanone (**3ai**)

Yellow solid; m.p. 153-154 °C; yield: 45.8 mg (63%); ¹H NMR (400 MHz, CDCl₃) δ 9.15 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.96 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.70 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.52-7.44 (m, 6H), 7.39-7.34 (m, 1H), 7.28-7.27 (m, 1H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 188.9, 151.3, 144.5, 140.0, 139.5, 135.5, 134.5, 131.6, 130.8, 130.4, 130.1, 129.1, 129.0, 128.8, 128.4, 128.3, 123.1, 120.6, 118.3, 21.8. HRMS (ESI): calcd for C₂₄H₁₇N₃O ([M+H]⁺) 364.1444, found 364.1448.



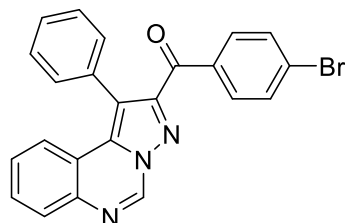
(4-Methoxyphenyl)(1-phenylpyrazolo[1,5-*c*]quinazolin-2-yl)methanone (**3aj**)

Yellow solid; m.p. 191-192 °C; yield: 46.3 mg (61%); ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64-7.60 (m, 1H), 7.51-7.49 (m, 5H), 7.39-7.35 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 187.6, 164.0, 151.5, 140.0, 139.4, 135.5, 133.1, 131.6, 130.4, 130.1, 129.9, 129.0, 128.8, 128.3, 128.2, 123.1, 120.6, 118.2, 113.7, 55.6. HRMS (ESI): calcd for C₂₄H₁₇N₃O₂ ([M+H]⁺) 380.1394, found 380.1397.



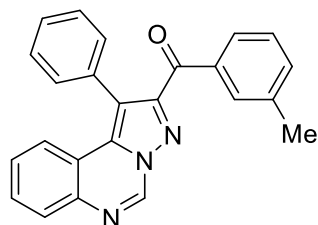
(4-Chlorophenyl)(1-phenylpyrazolo[1,5-*c*]quinazolin-2-yl)methanone (**3ak**)

Yellow solid; m.p. 138-140 °C; yield: 56.7 mg (74%); ¹H NMR (400 MHz, CDCl₃) δ 9.15 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.68-7.61 (m, 2H), 7.50-7.48 (m, 5H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.40-7.36 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 187.7, 150.5, 140.0, 139.9, 139.3, 135.7, 135.3, 132.1, 131.5, 130.4, 130.2, 129.1, 128.9, 128.7, 128.5, 128.4, 123.1, 120.5, 118.6. HRMS (ESI): calcd for C₂₃H₁₄ClN₃O ([M+H]⁺) 384.0898, found 384.0903.



(4-Bromophenyl)(1-phenylpyrazolo[1,5-*c*]quinazolin-2-yl)methanone (**3al**)

Yellow solid; m.p. 133-135 °C; yield: 71.7 mg (84%); ¹H NMR (400 MHz, CDCl₃) δ 9.14 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.68-7.62 (m, 2H), 7.61-7.59 (m, 2H), 7.50-7.48 (m, 5H), 7.39-7.35 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 187.9, 150.4, 140.0, 139.3, 135.7, 135.7, 132.2, 131.7, 131.5, 130.4, 130.2, 129.1, 128.9, 128.8, 128.5, 128.4, 123.1, 120.2, 118.6. HRMS (ESI): calcd for C₂₃H₁₄BrN₃O ([M+H]⁺) 428.0393, found 428.0397.

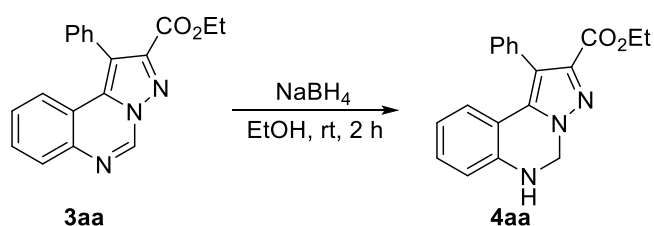


Phenylpyrazolo[1,5-*c*]quinazolin-2-yl(*m*-tolyl)methanone (**3am**)

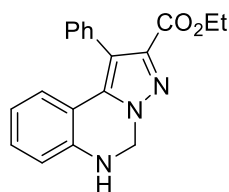
Yellow solid; m.p. 108-109 °C; yield: 58.1 mg (80%); ¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.88 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.50-7.43 (m, 5H), 7.40-7.33 (m, 3H), 2.39 (s,

3H). ^{13}C NMR (100 MHz, CDCl_3) δ 189.5, 151.3, 140.0, 139.5, 138.1, 136.9, 135.5, 134.4, 131.6, 131.0, 130.5, 130.1, 129.1, 128.8, 128.4, 128.3, 128.2, 128.0, 123.1, 120.6, 118.3, 21.4. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{17}\text{N}_3\text{O}$ ($[\text{M}+\text{H}]^+$) 364.1444 found 364.1450.

4. Derivatization of Product

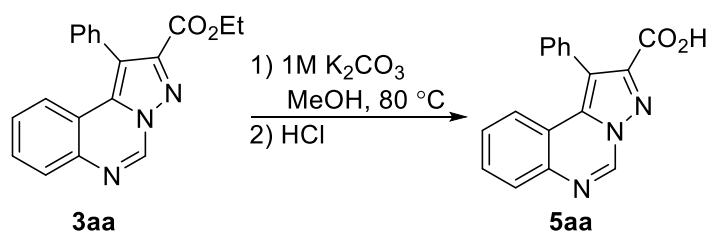


A solution of **3aa** (0.2 mmol, 63.4 mg), NaBH_4 (0.24 mmol, 38.0 mg, 1.2 equiv.) in EtOH (1.0 mL) was stirred at room temperature for 12 h. After the reaction was complete (monitored by TLC). Then the mixture was quenched by water. The reaction mixture was extracted with CH_2Cl_2 (10 mL \times 3). The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure to yield the corresponding product **4aa** (46.0 mg, 72%) as a white solid.

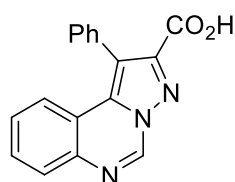


Ethyl 1-phenyl-5,6-dihydropyrazolo[1,5-c]quinazoline-2-carboxylate (**4aa**)

White solid; m.p. 184-185 $^\circ\text{C}$; yield: 46.0 mg (72%); ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.34 (m, 5H), 7.12-7.08 (m, 1H), 6.93 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.80 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.66-6.62 (m, 1H), 5.47 (s, 2H), 4.57 (br, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 1.19 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.3, 141.1, 140.9, 135.0, 132.6, 130.3, 129.5, 128.3, 127.7, 124.6, 120.7, 120.6, 116.4, 115.5, 60.8, 60.5, 14.1. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 320.1394 found 320.1397.



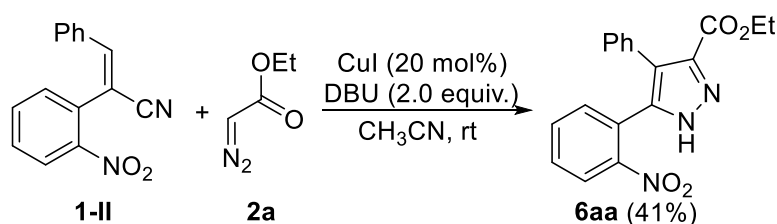
To a solution of **3aa** (0.2 mmol, 63.4 mg) in 0.6 mL of methanol was added K_2CO_3 aq (0.6 mL, 1M). The reaction mixture was heated to reflux at 80°C . After 4 h, the reaction mixture was cooled to room temperature. Then the mixture was quenched by solution of HCl (6.0 M, 1 mL). The reaction mixture was extracted with CH_2Cl_2 (10 mL \times 3). The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure to yield the corresponding product **5aa** (53.8 mg, 93%) as a white solid



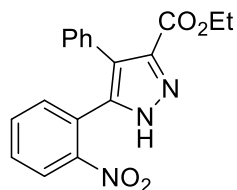
1-Phenylpyrazolo[1,5-*c*]quinazoline-2-carboxylic acid (**5aa**)

White solid; m.p. $254\text{--}255^\circ\text{C}$; yield: 53.8 mg (93%); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 13.31 (br, 1H), 9.48 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.70-7.66 (m, 1H), 7.58-7.52 (m, 3H), 7.51-7.48 (m, 2H), 7.47-7.43 (m, 1H), 7.40 (dd, $J = 8.0, 1.6$ Hz, 1H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 163.4, 145.6, 140.6, 139.8, 135.4, 132.3, 130.8, 130.6, 129.2, 129.0, 128.7, 128.6, 122.5, 120.3, 117.9. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 290.0924 found 290.0929.

5. Control Experiment



A solution of **1-II** (0.2 mmol, 50.0 mg), **2a** (0.3 mmol, 0.037 mL), CuI (20 mol %), and DBU (0.4 mmol, 0.062 mL) in CH₃CN (1.0 mL) was stirred at room temperature for 1 h. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:3, V/V) to afford pure product **6aa** (27.6 mg, 41%) as a yellow solid.



Ethyl 5-(2-nitrophenyl)-4-phenyl-1*H*-pyrazole-3-carboxylate (**6aa**)

Yellow solid; m.p. 177-178 °C; yield: 27.6 mg (41%); ¹H NMR (400 MHz, CDCl₃) δ 11.82 (br, 1H), 7.82-7.80 (m, 1H), 7.51 (td, *J* = 7.6, 1.6 Hz, 1H), 7.44 (td, *J* = 7.6, 1.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26-7.23 (m, 3H), 7.22-7.19 (m, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 149.5, 132.7, 132.5, 130.4, 130.3, 129.2, 127.9, 127.6, 124.3, 124.3, 61.4, 13.9. HRMS (ESI): calcd for C₁₈H₁₅N₃O₄ ([M+H]⁺) 338.1135 found 338.1139.

6. Crystal structure of 3aa

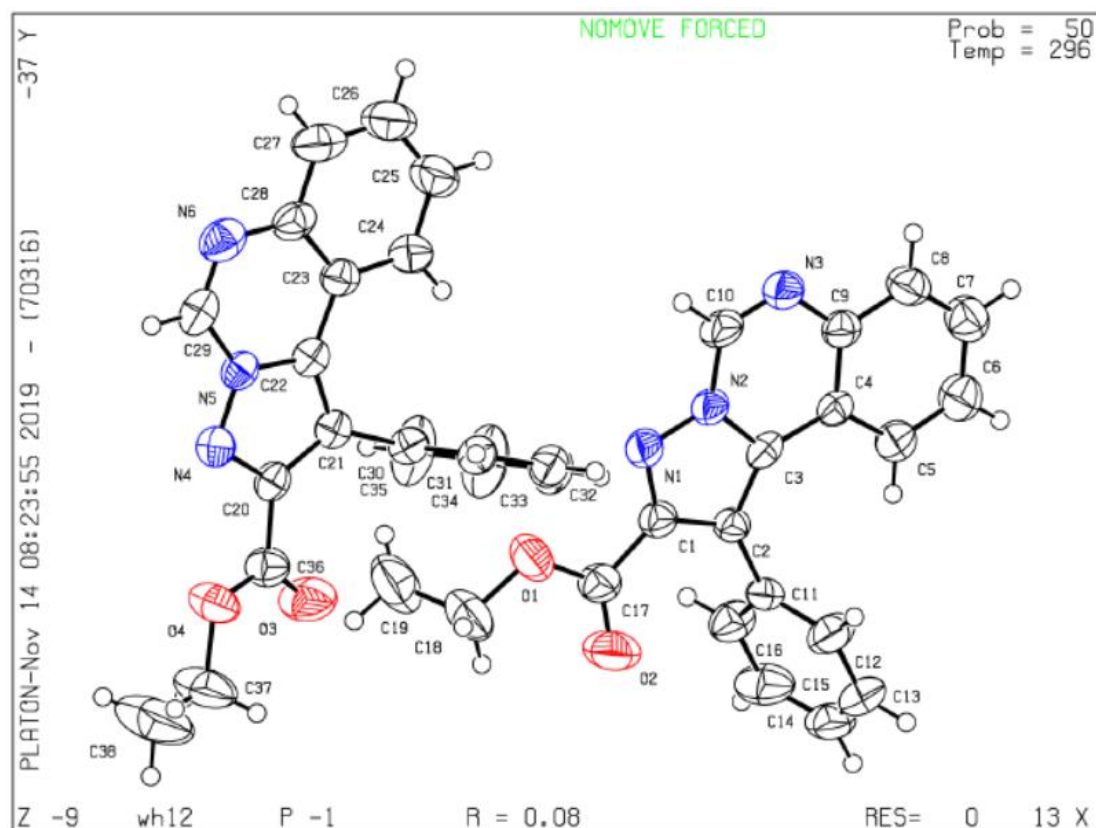


Table 1. Single crystal data for wh12.

Identification code	wh12	
Chemical formula	$C_{38}H_{30}N_6O_4$	
Formula weight	634.68 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.260 x 0.280 x 0.280 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 9.346(2)$ Å	$\alpha = 104.993(9)^\circ$
	$b = 12.963(3)$ Å	$\beta = 99.436(10)^\circ$
	$c = 13.931(4)$ Å	$\gamma = 97.900(9)^\circ$
Volume	$1579.3(7)$ Å ³	
Z	2	
Density (calculated)	1.335 g/cm ³	

Absorption coefficient	0.089 mm ⁻¹
F(000)	664

Table 2. Data collection and structure refinement for wh12.

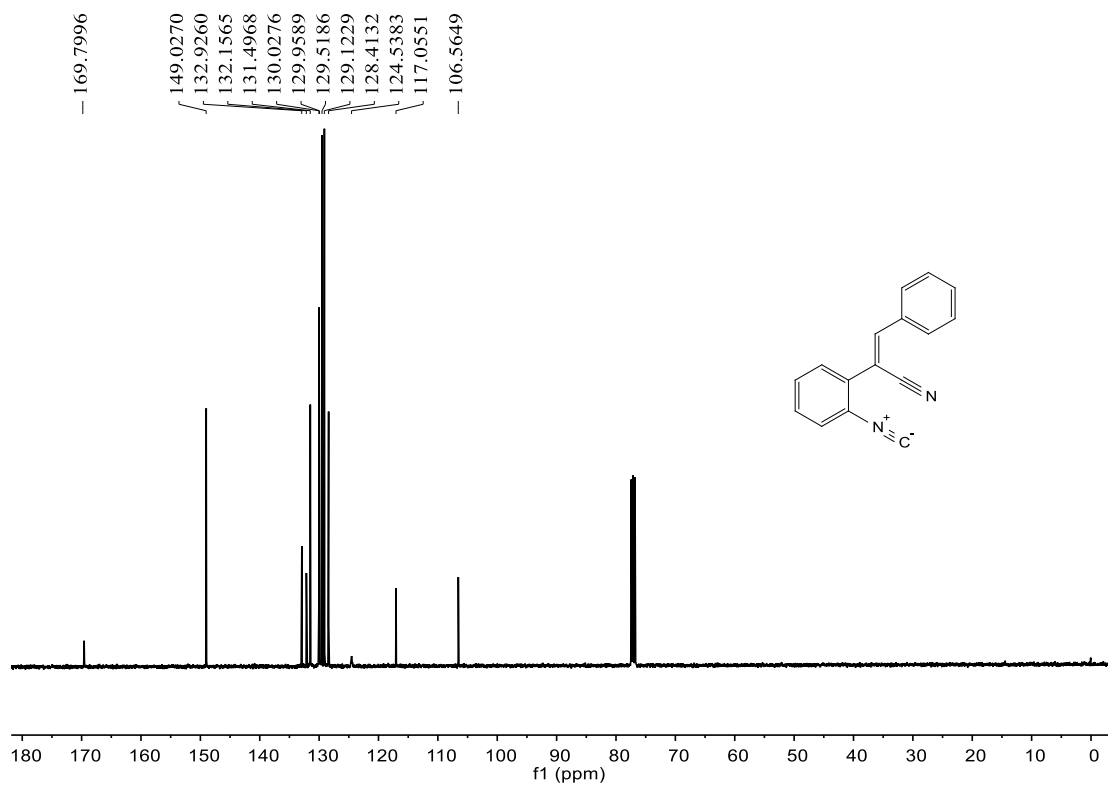
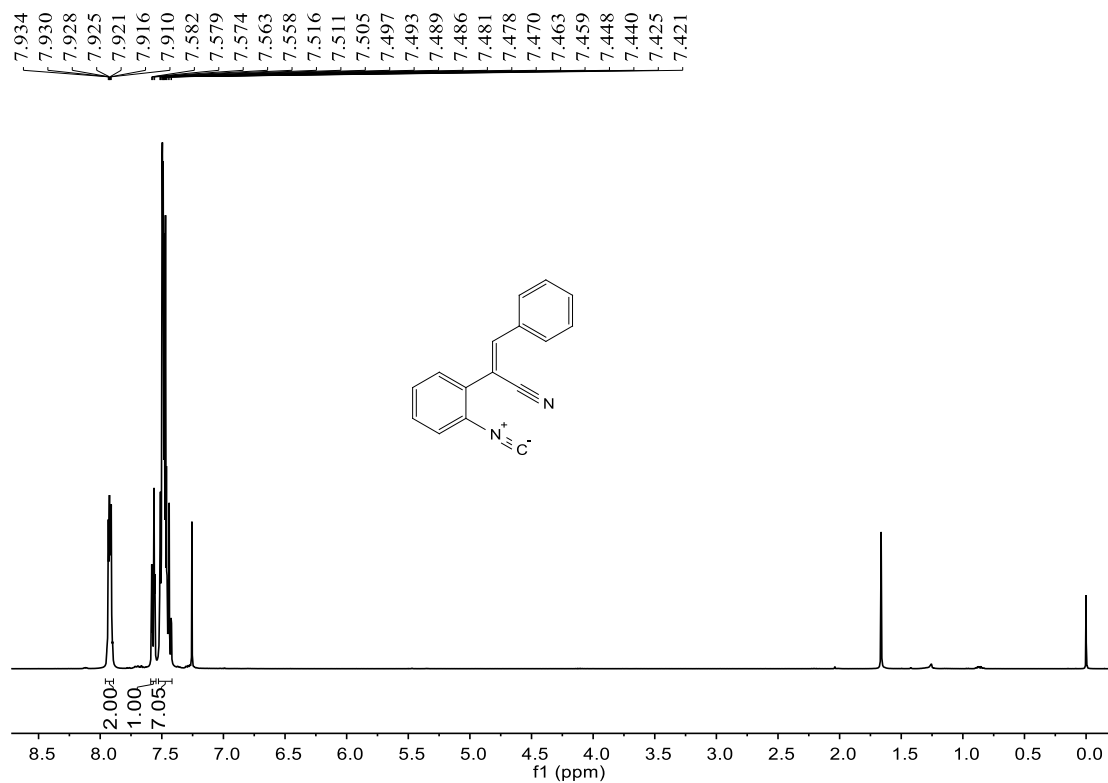
Theta range for data collection	2.25 to 25.19°
Index ranges	-11<=h<=11, -15<=k<=15, -16<=l<=16
Reflections collected	18650
Independent reflections	5598 [R(int) = 0.0911]
Coverage of independent reflections	98.4%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9770 and 0.9750
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5598 / 0 / 435
Goodness-of-fit on F ²	1.037
Final R indices	2968 data; I>2 σ (I) R1 = 0.0818, wR2 = 0.1788 all data R1 = 0.1647, wR2 = 0.2228
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1117P)^2+0.2711P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.426 and -0.551 eÅ ⁻³
R.M.S. deviation from mean	0.179 eÅ ⁻³

References

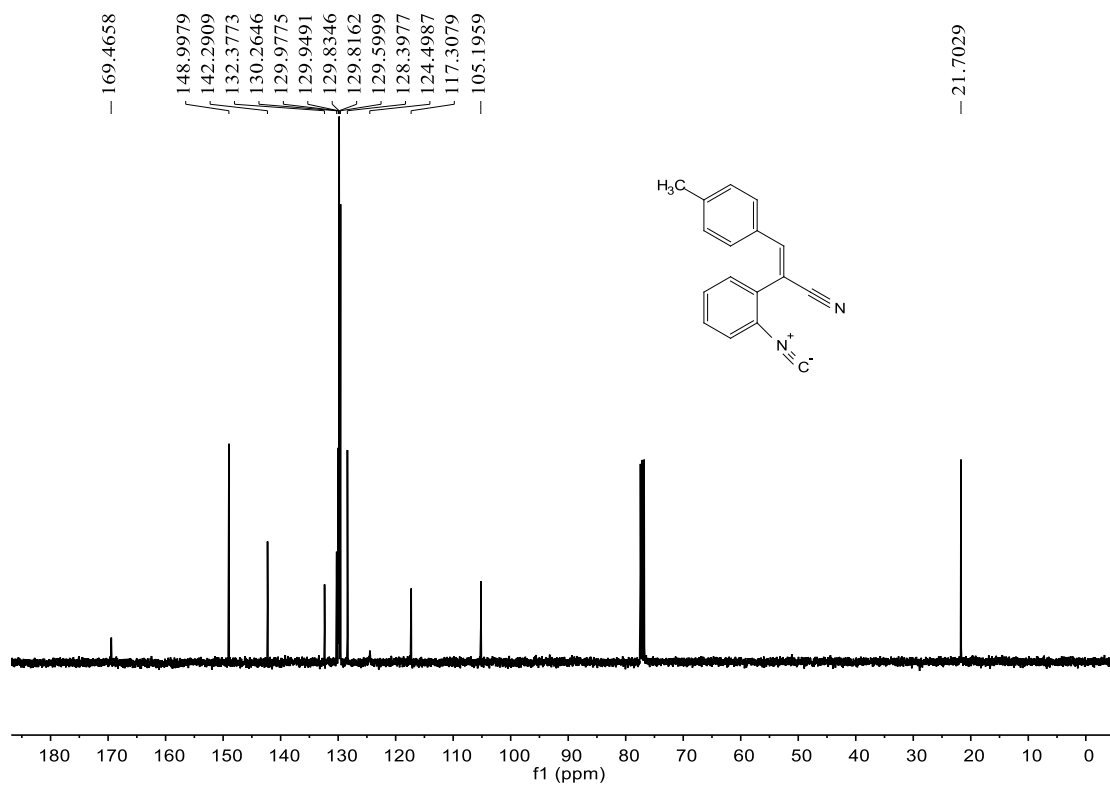
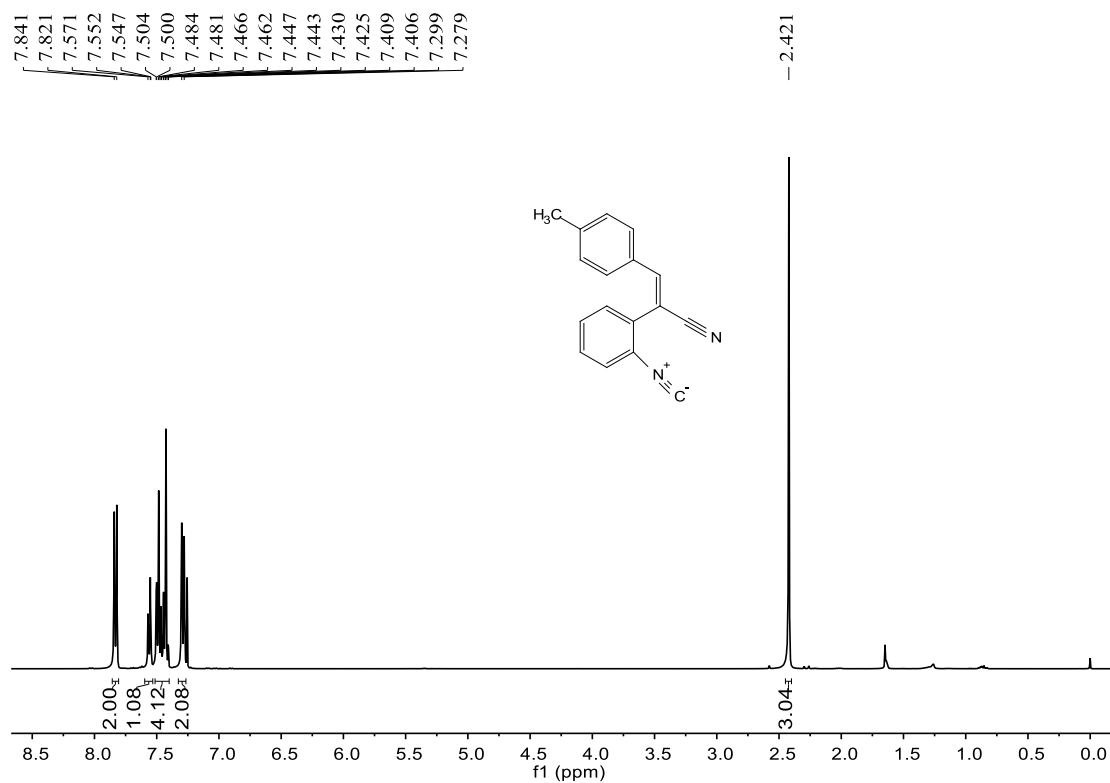
1. T. Toma, J. Shimokawa and T. Fukuyama, *Org. Lett.* 2007, **9**, 3195-3197.
2. L. H. Yeh, H. K. Wang, Y. L. Ciou and J. C. Hsieh, *Org. Lett.* 2019, **21**, 6, 1730-1734.
3. M. Tobisu, H. Fujihara, K. Koh and N. Chatani, *J. Org. Chem.* 2010, **75**, 4841-4847.
4. O. Yabe, H. Mizufune and T. Ikemoto, *Synlett.* 2009, **8**, 1291-1294.
5. . Marco Buccini, S. Y. Jeow, L. Byrne, Brian W. Skelton, T. M. Nguyen, Christina L. L. Chai and Matthew J. Piggott, *Eur. J. Org. Chem.* 2013, **2013**, 3232-3240.

7. NMR Spectra

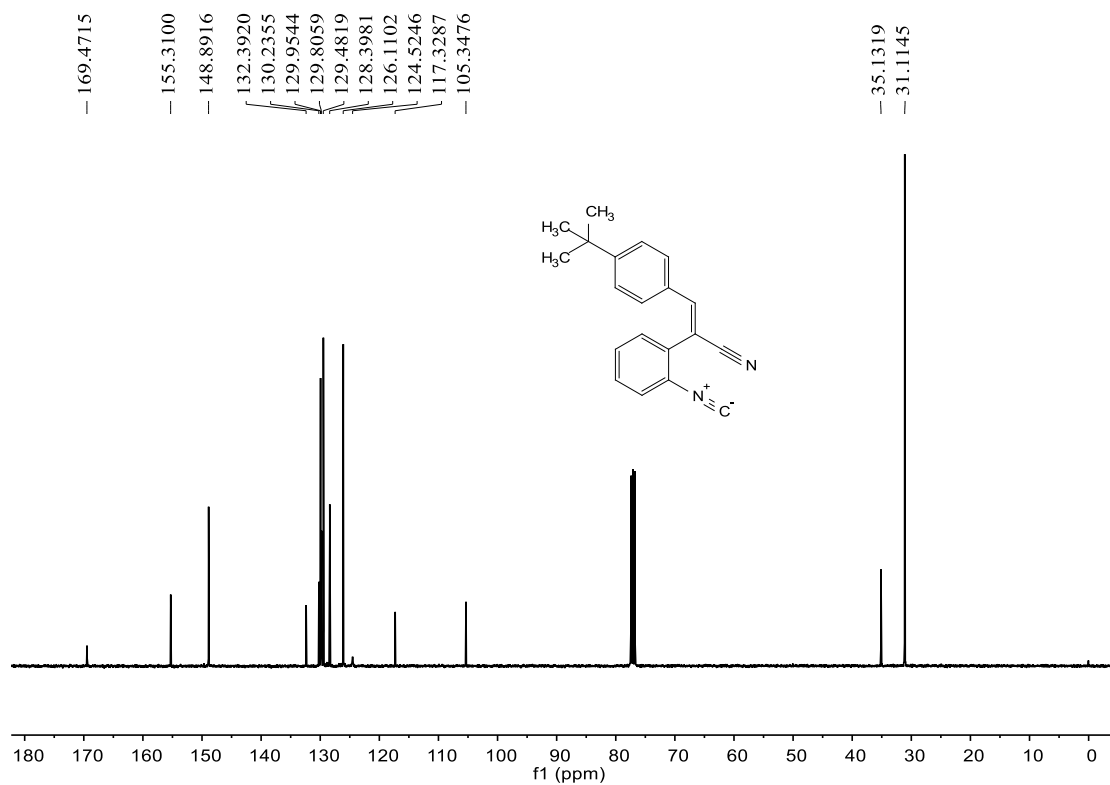
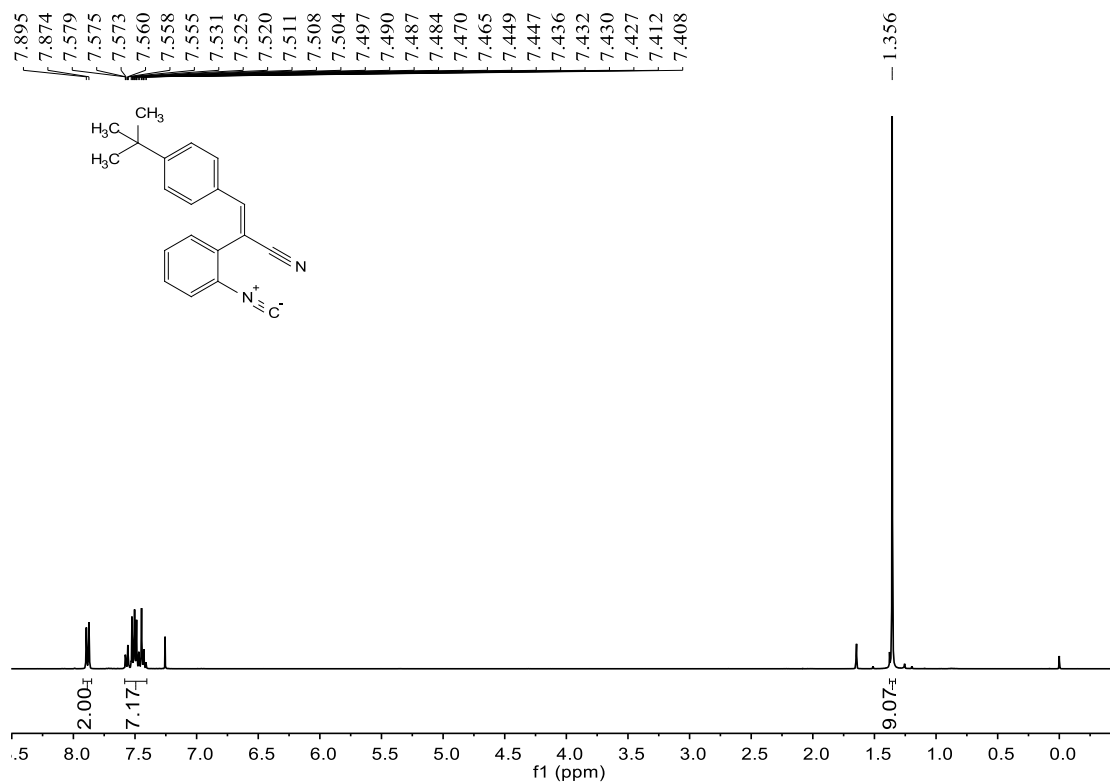
^1H NMR and ^{13}C NMR spectra of compound **1a**



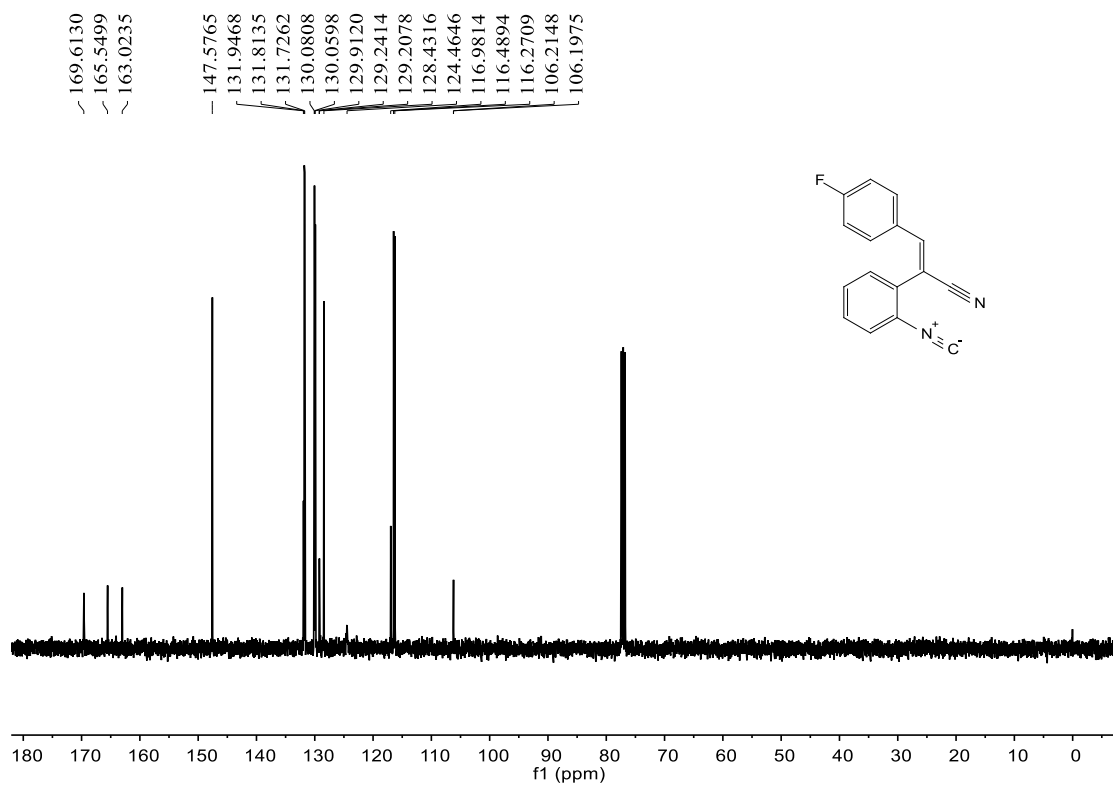
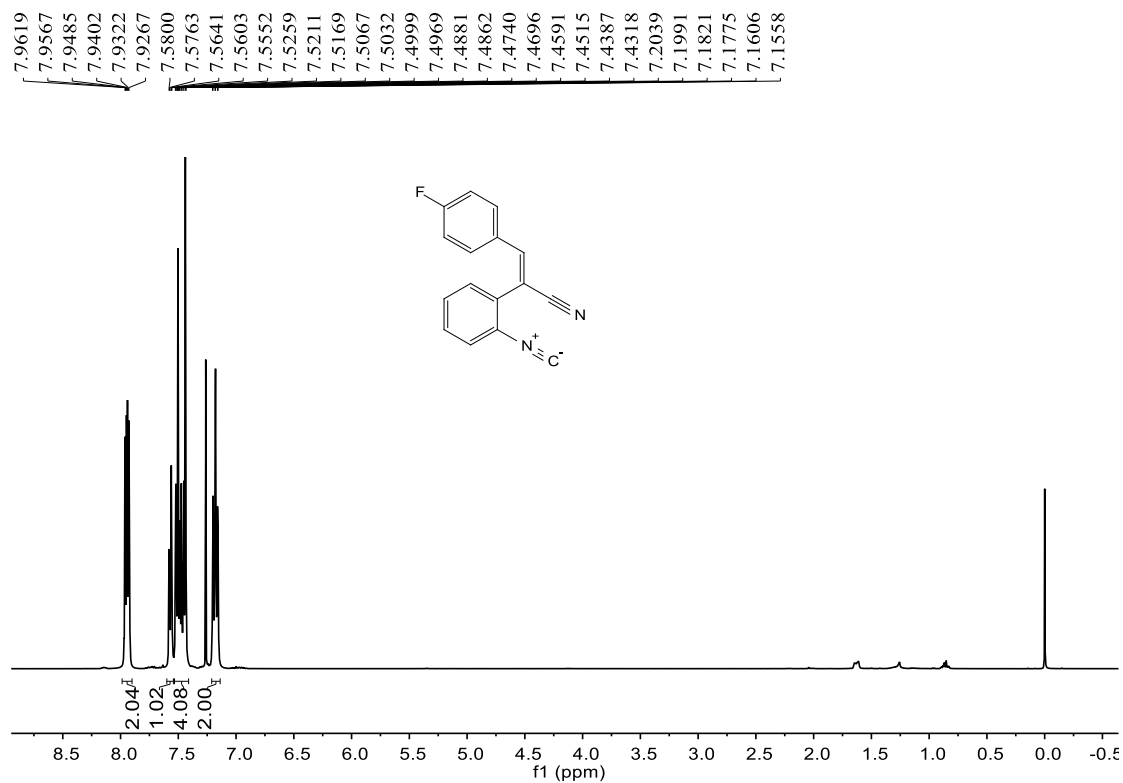
¹H NMR and ¹³C NMR spectra of compound **1b**



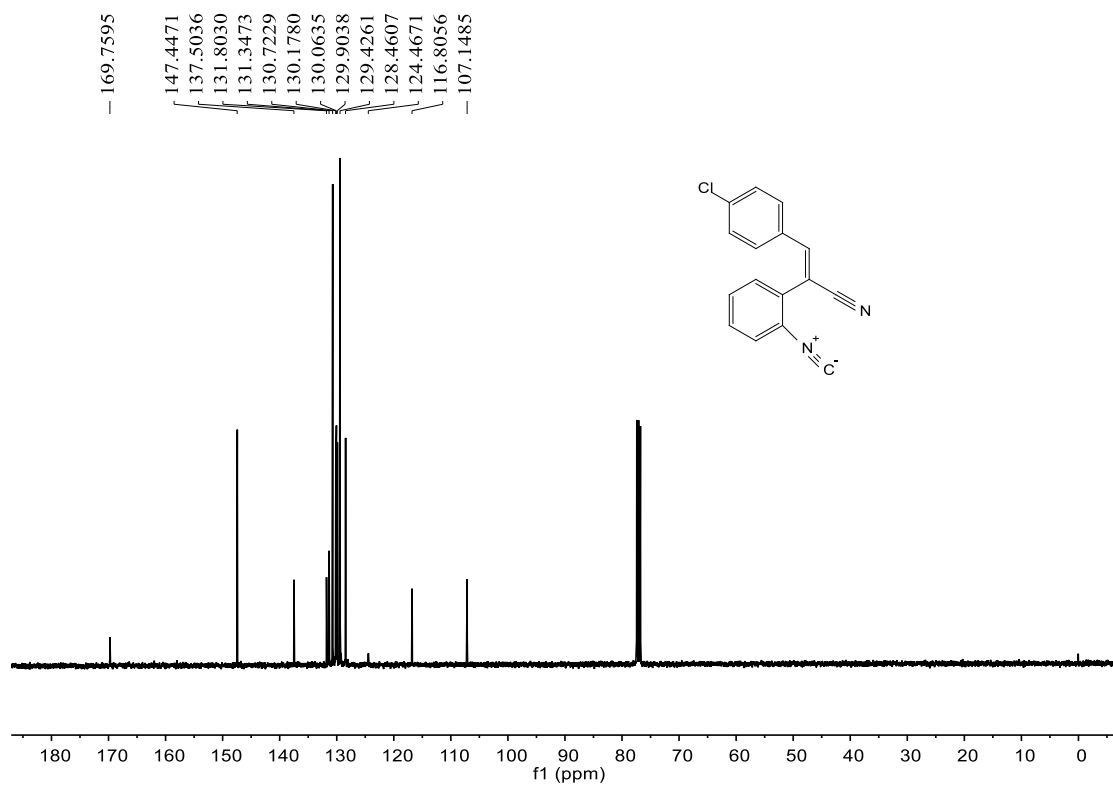
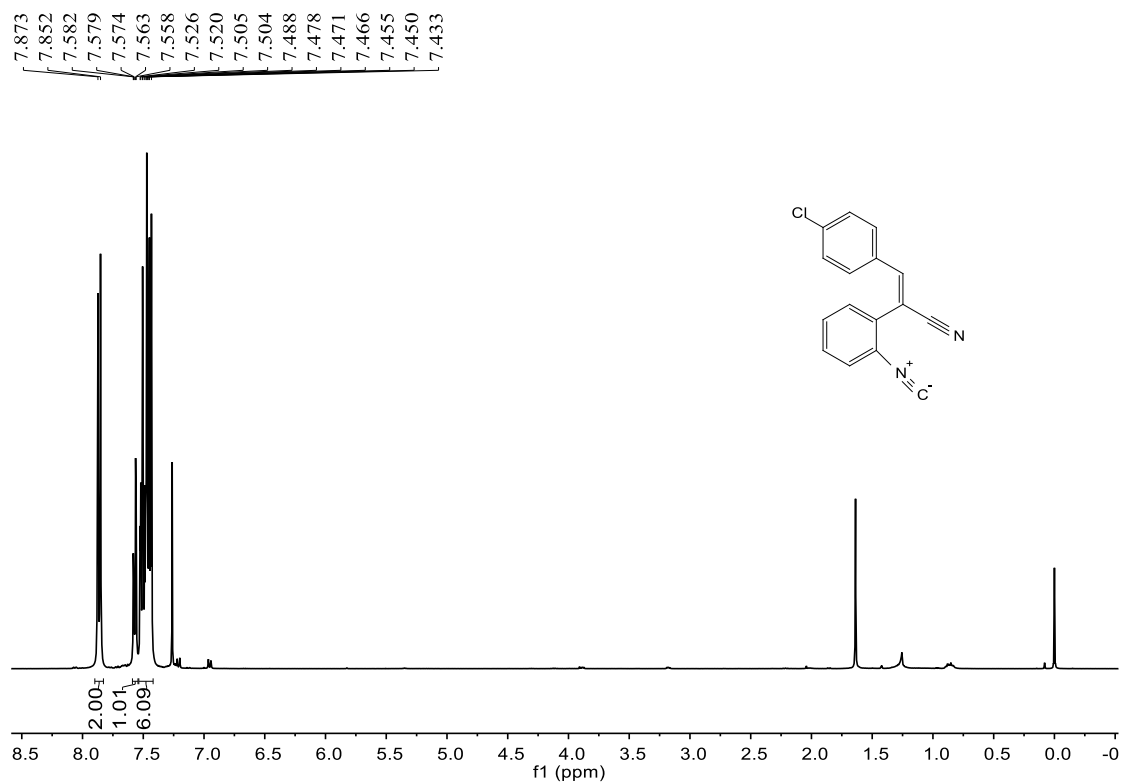
¹H NMR and ¹³C NMR spectra of compound **1c**



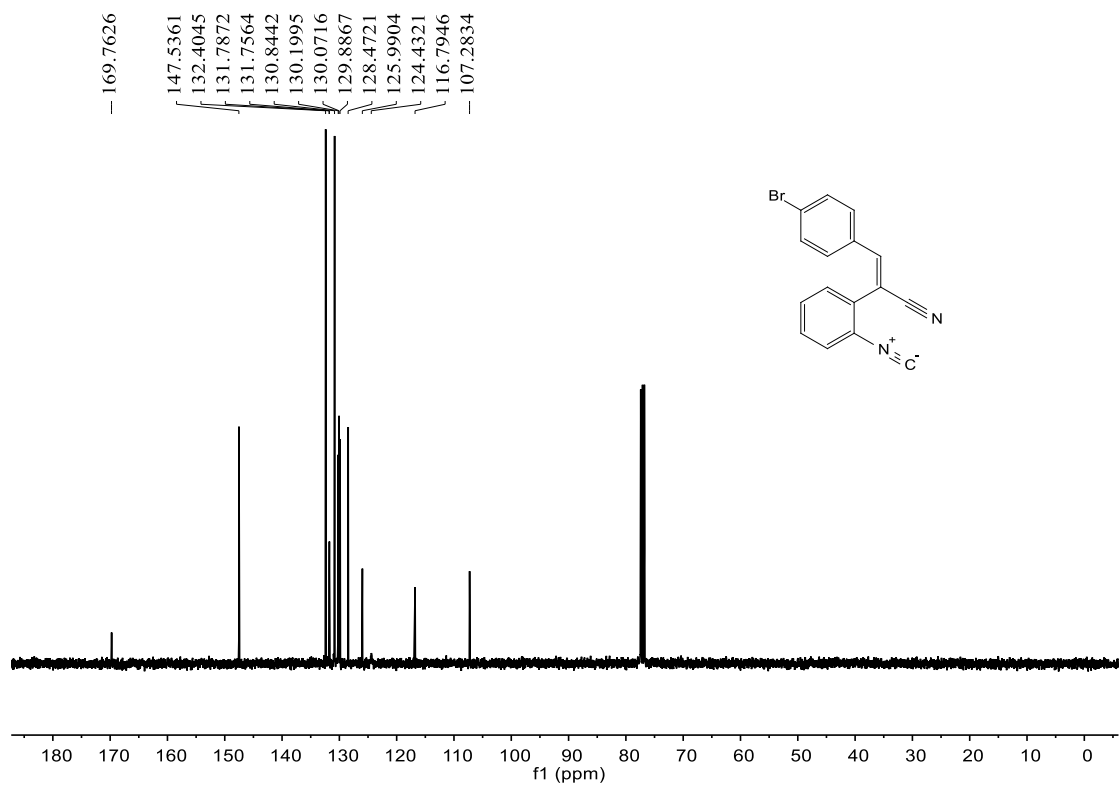
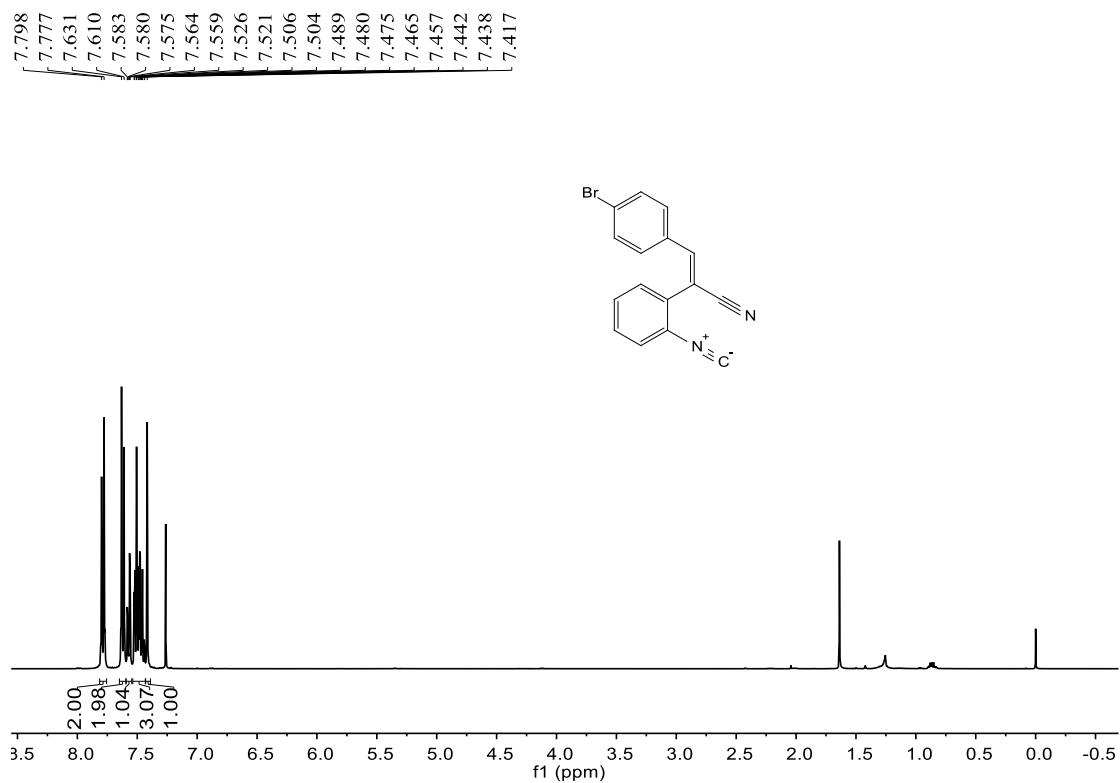
¹H NMR and ¹³C NMR spectra of compound **1d**



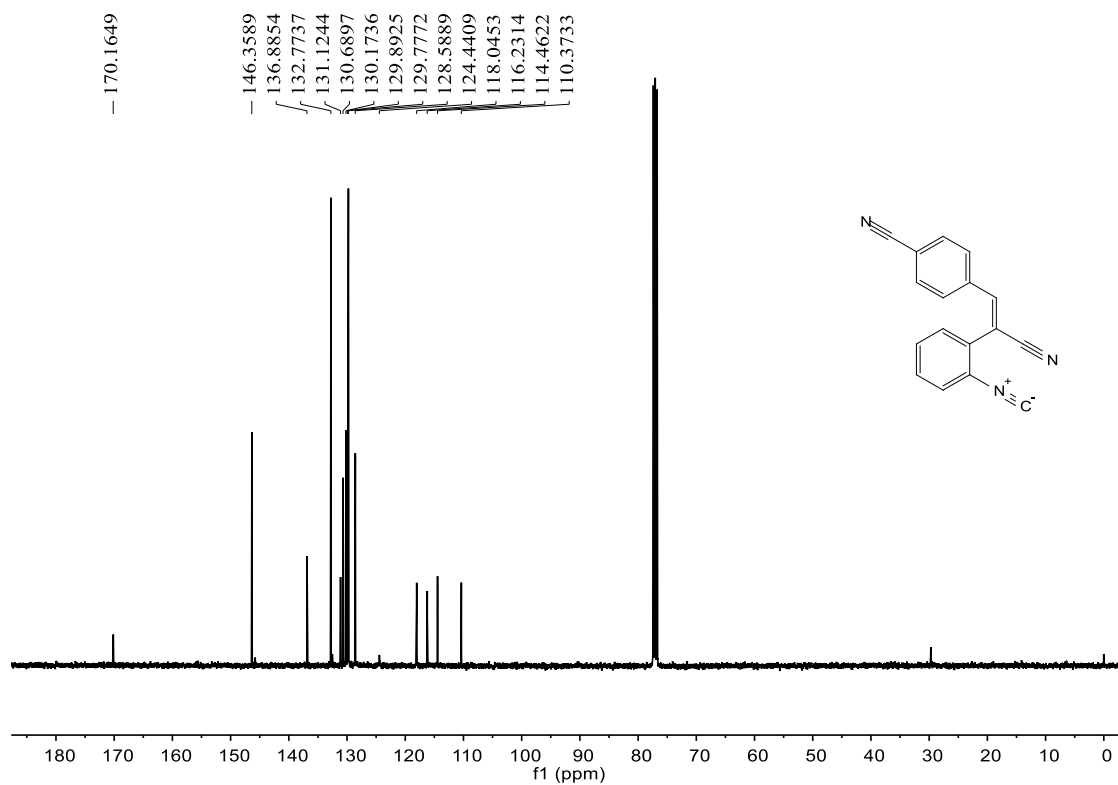
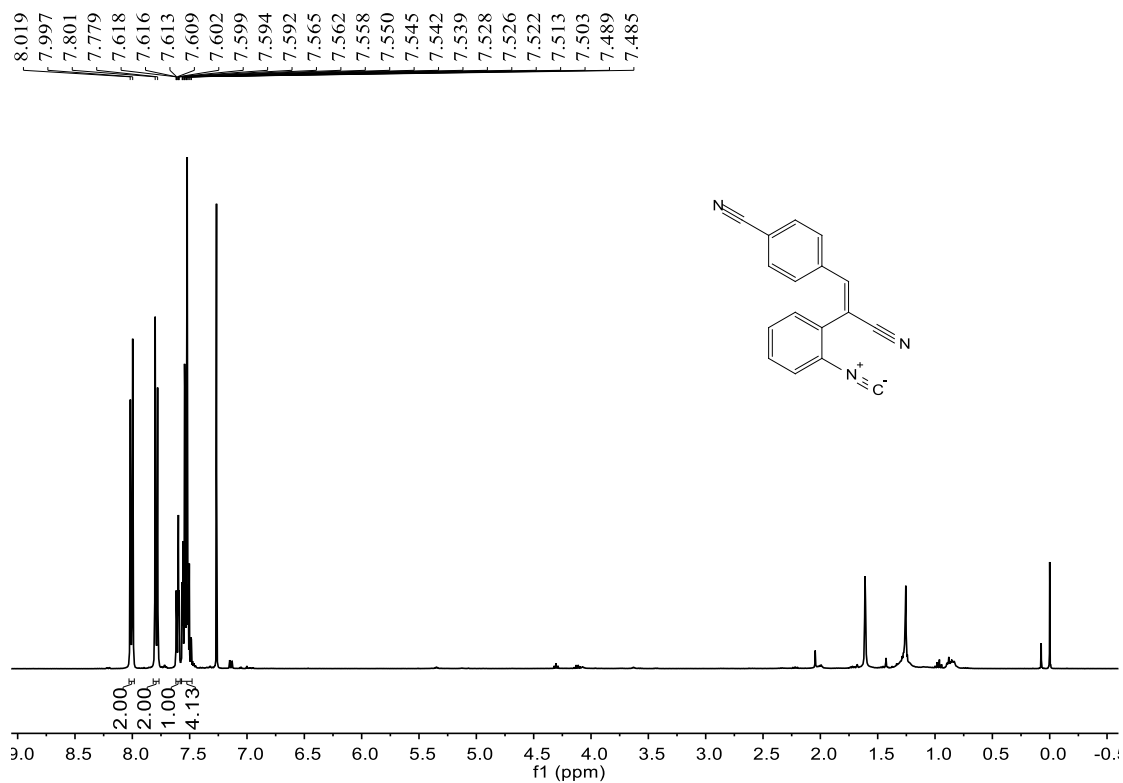
¹H NMR and ¹³C NMR spectra of compound 1e



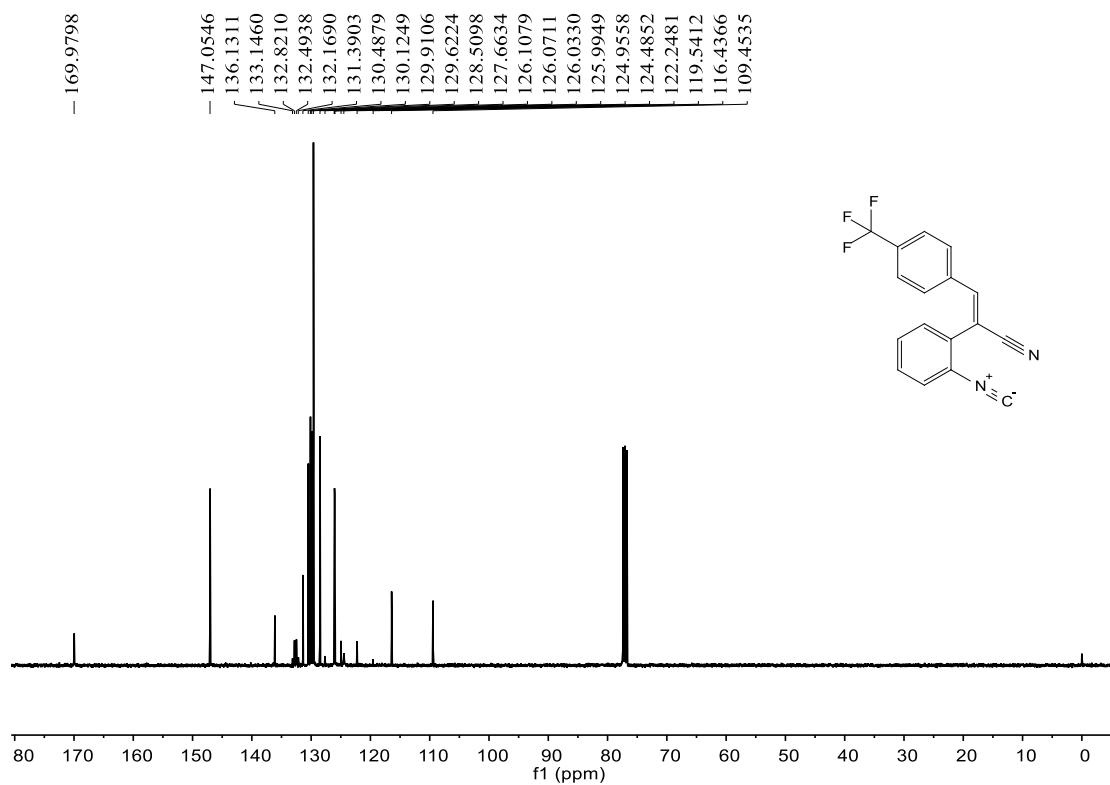
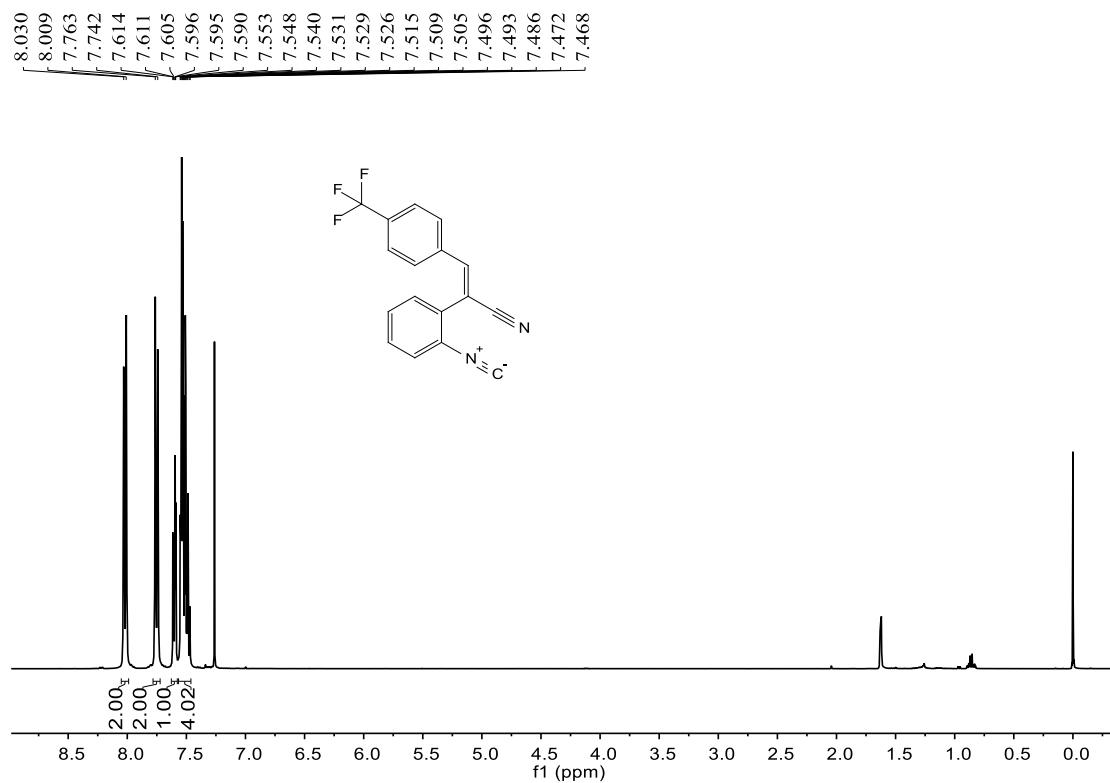
¹H NMR and ¹³C NMR spectra of compound 1f



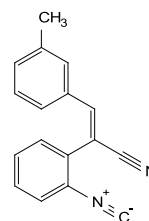
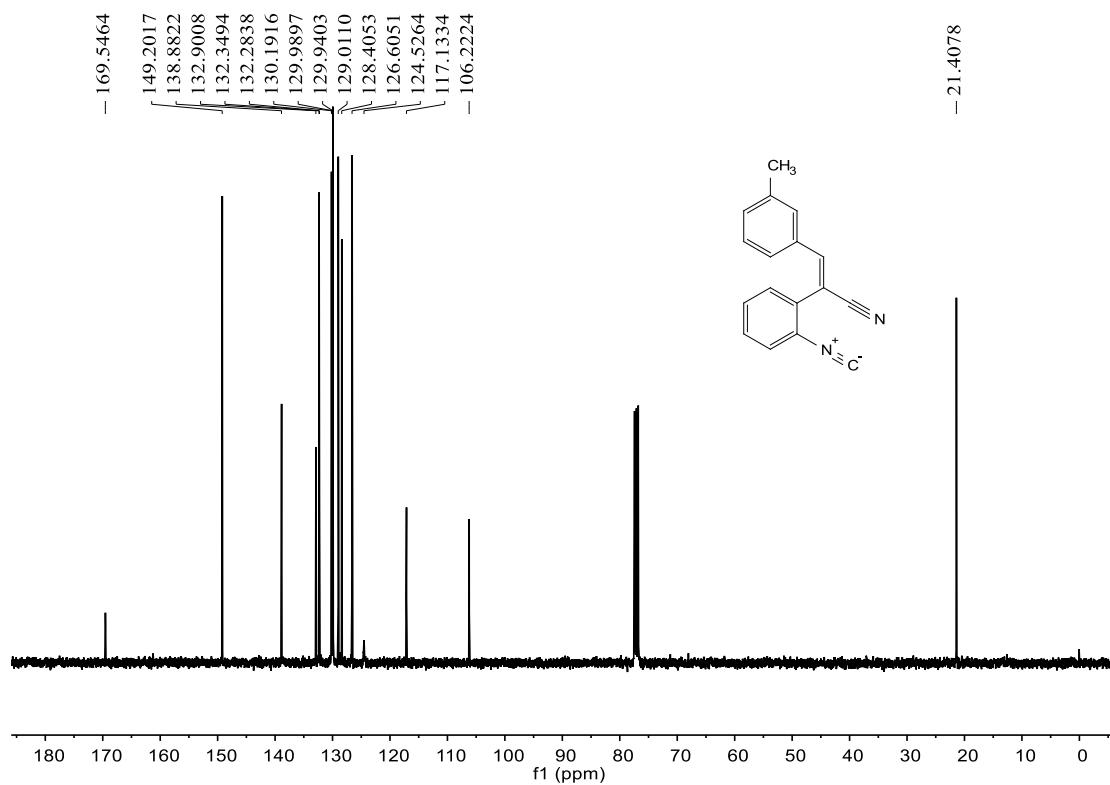
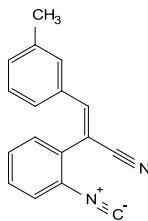
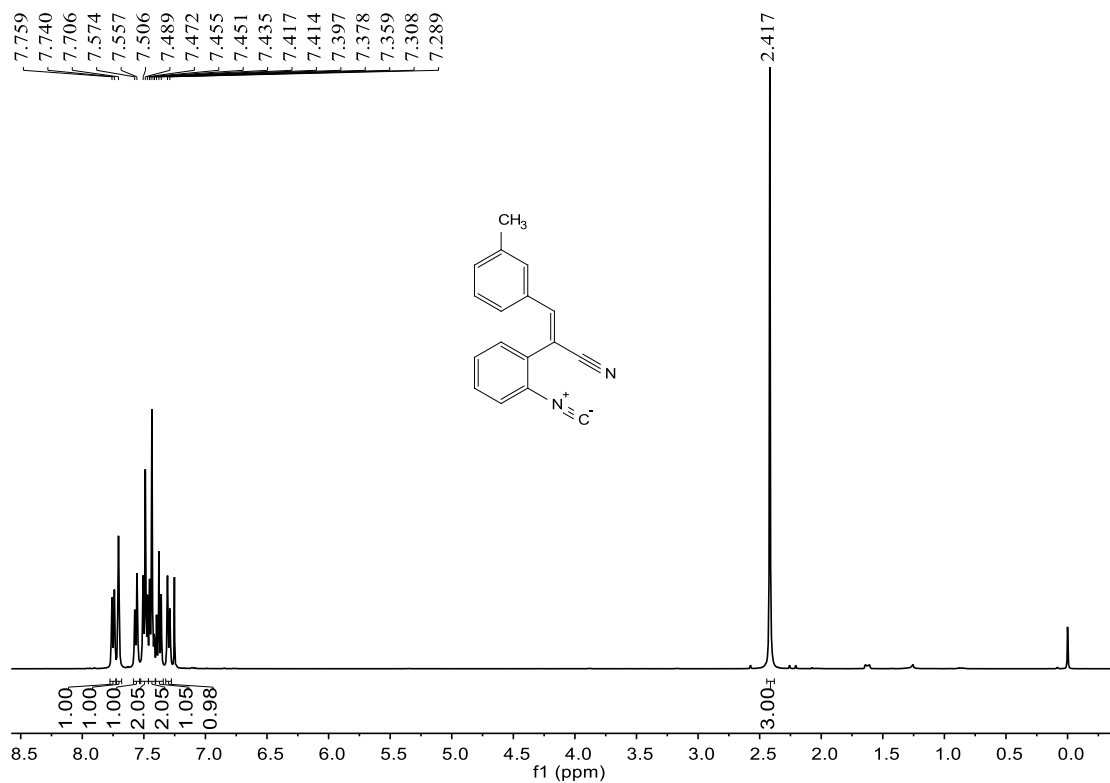
¹H NMR and ¹³C NMR spectra of compound **1g**



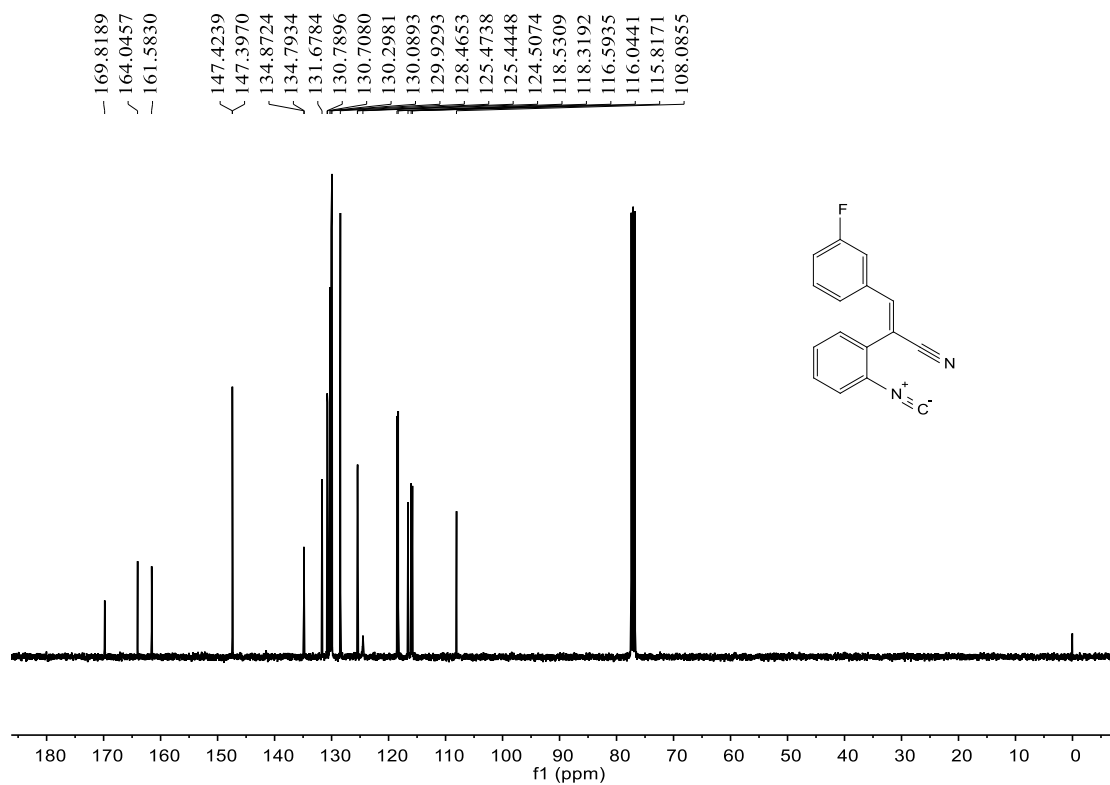
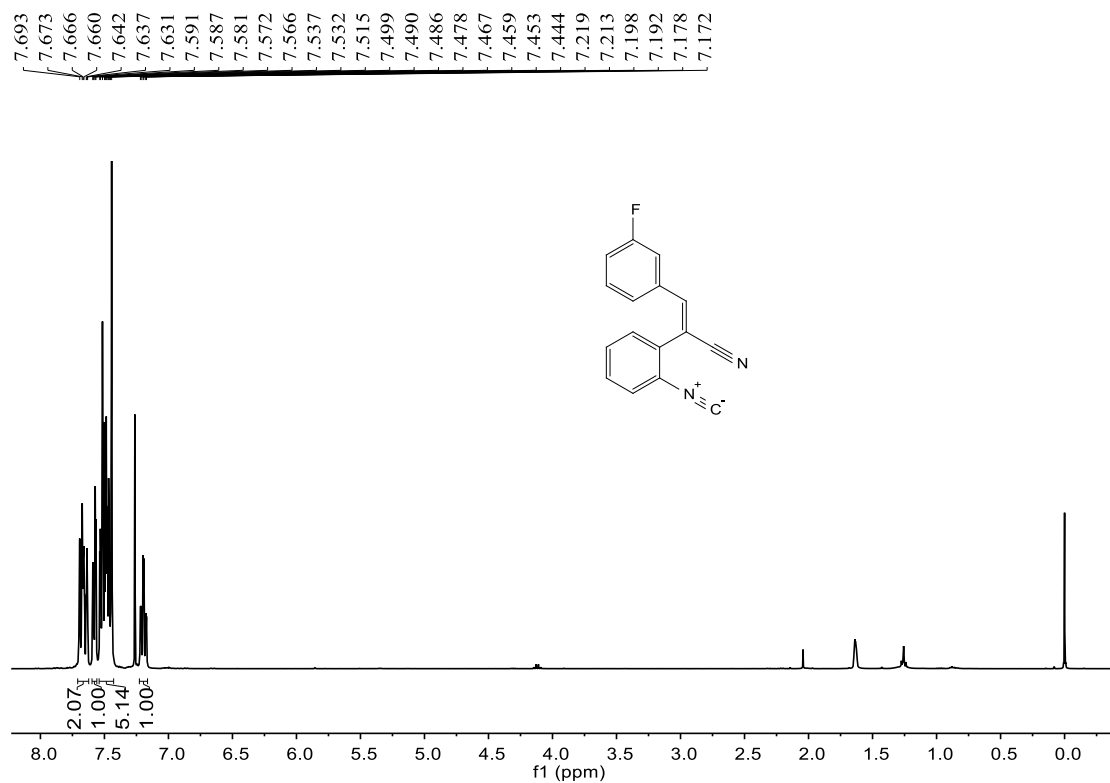
¹H NMR and ¹³C NMR spectra of compound **1h**



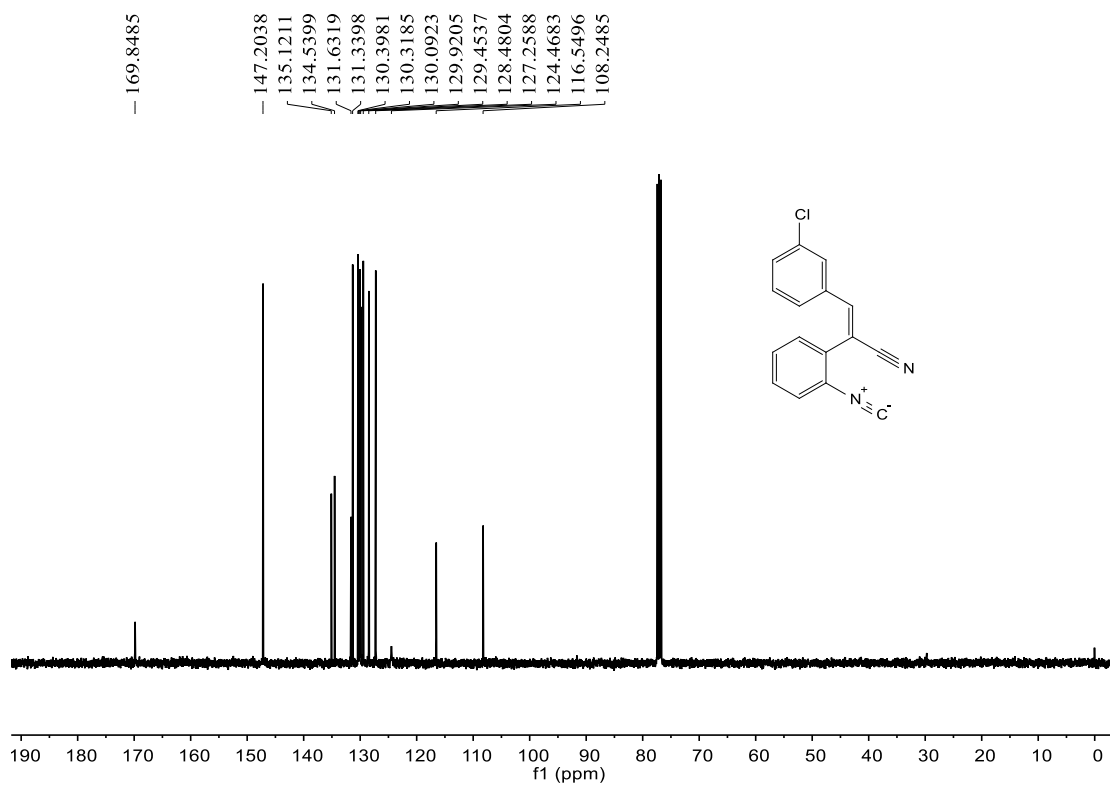
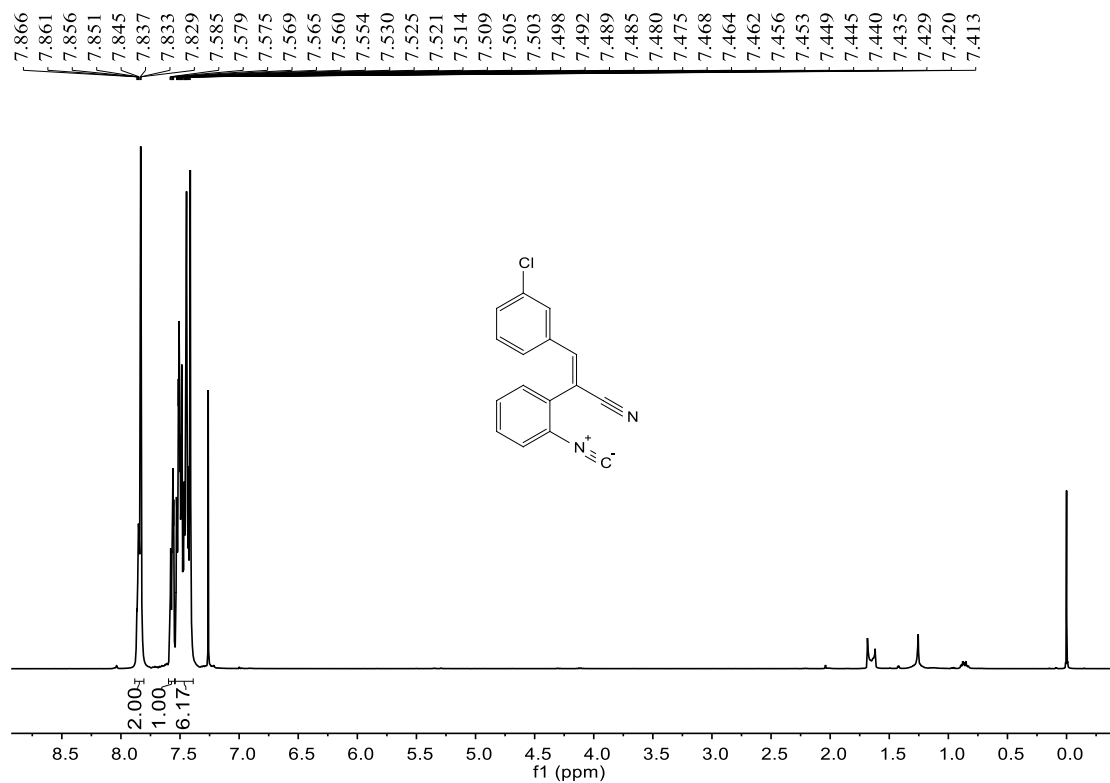
¹H NMR and ¹³C NMR spectra of compound **1i**



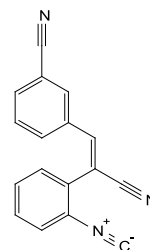
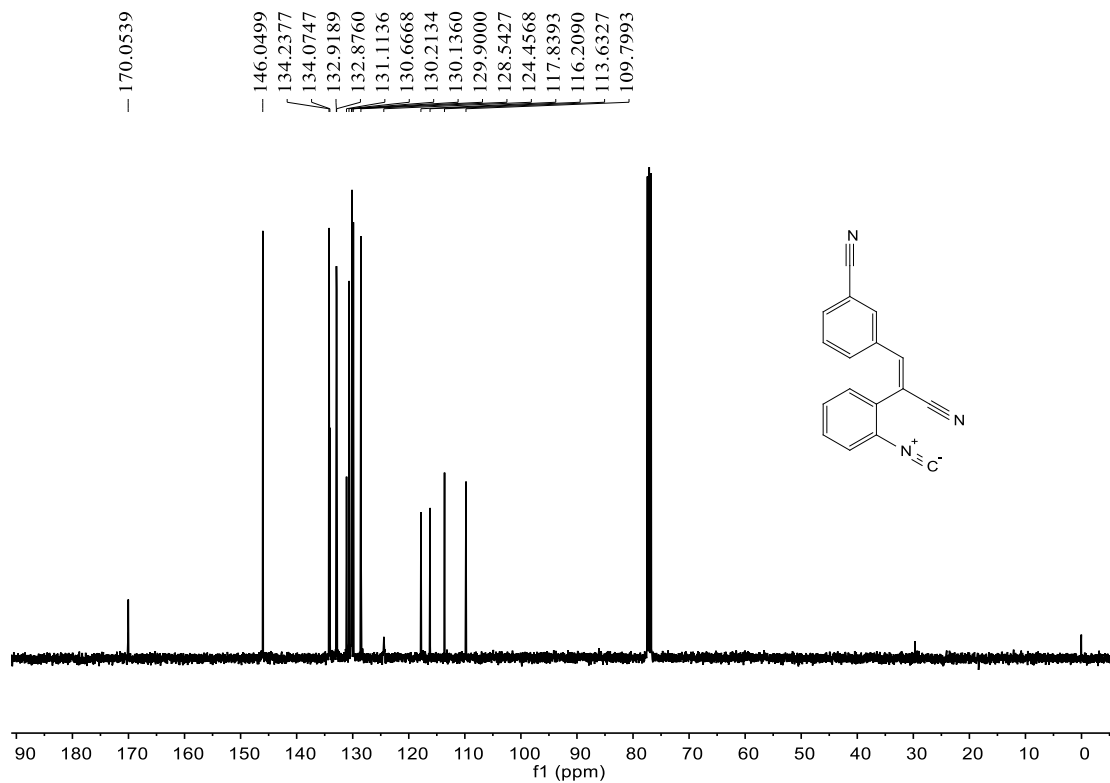
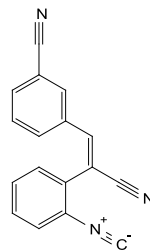
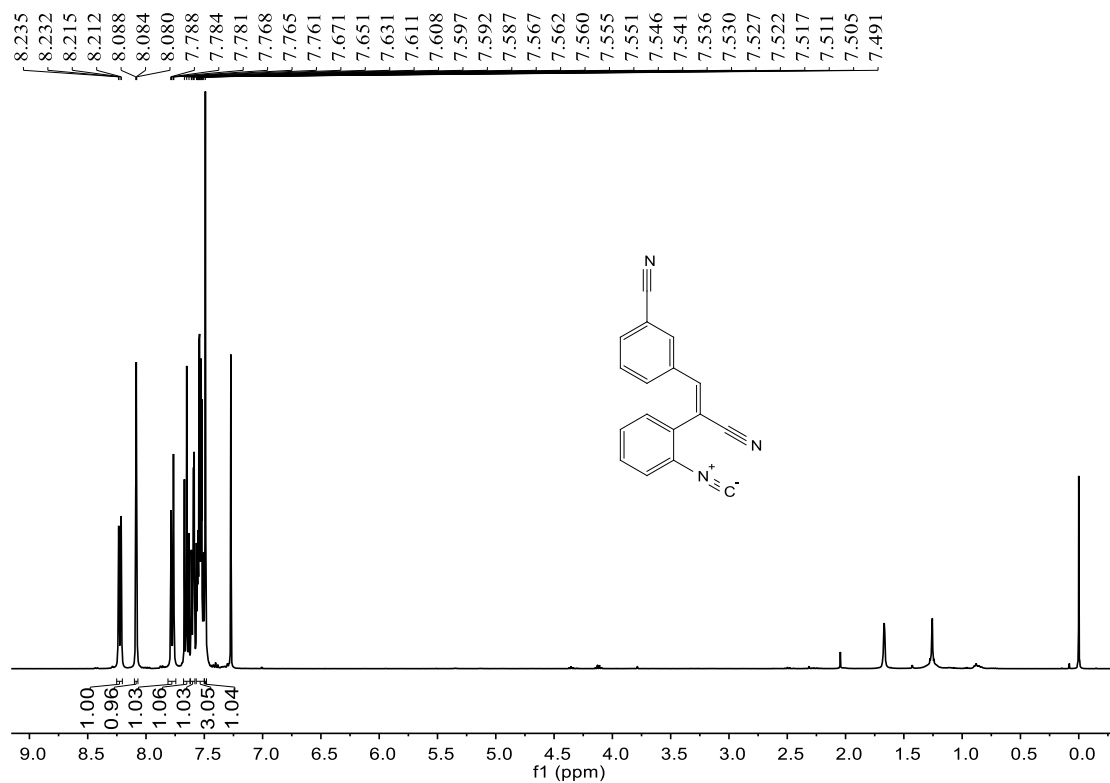
¹H NMR and ¹³C NMR spectra of compound 1j



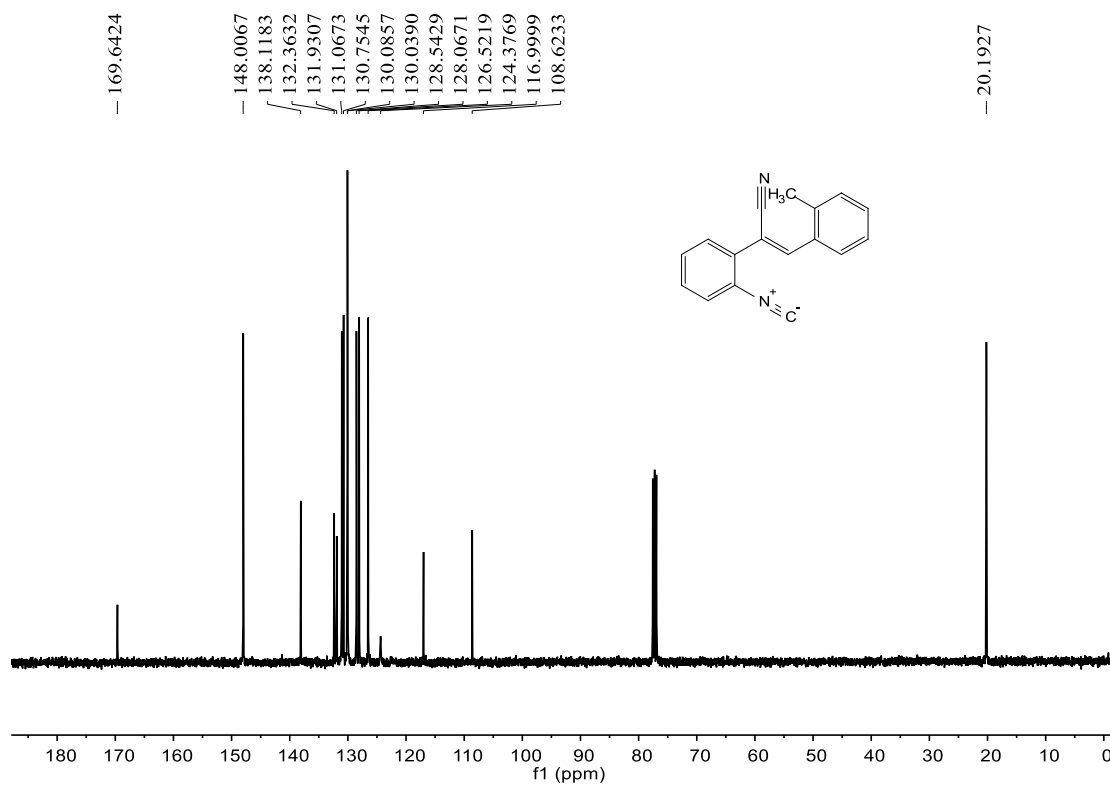
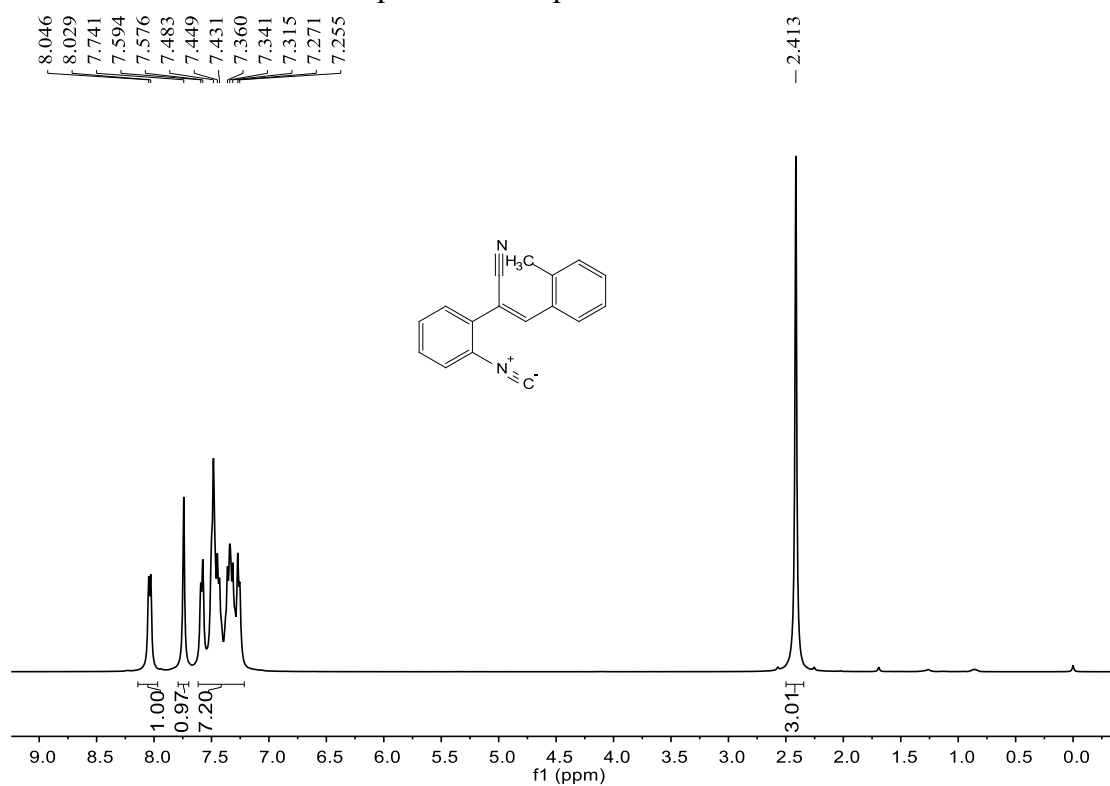
¹H NMR and ¹³C NMR spectra of compound **1k**



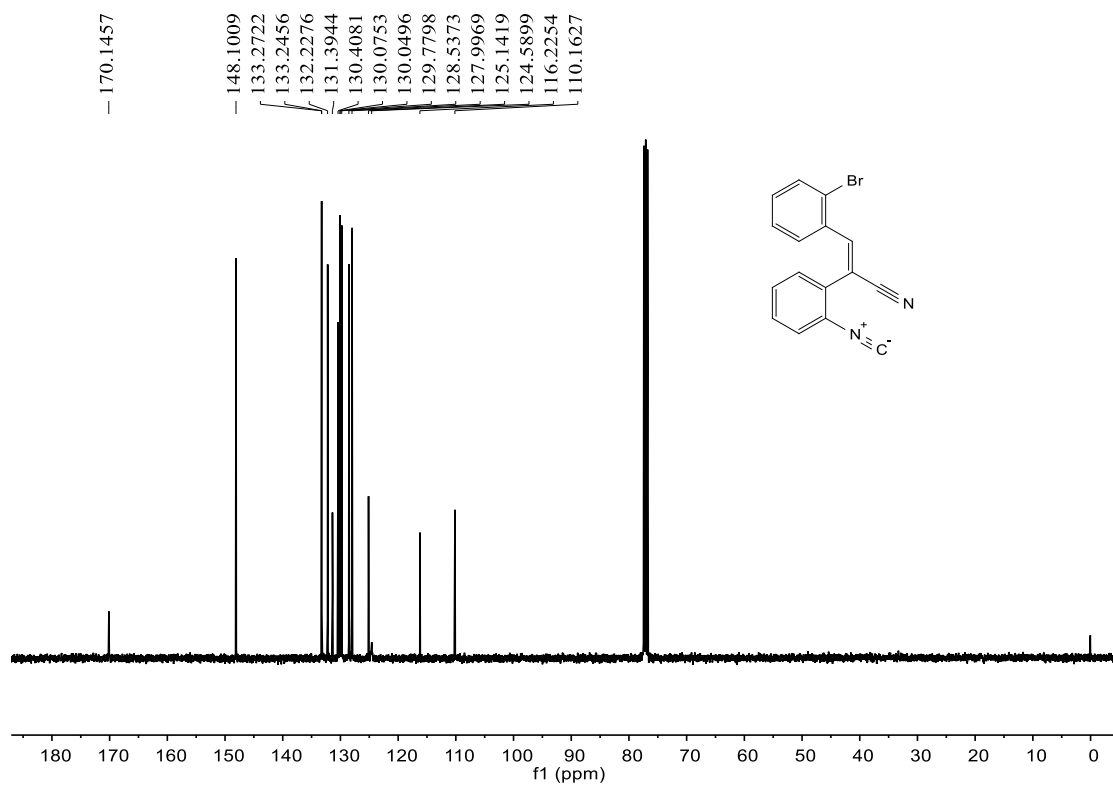
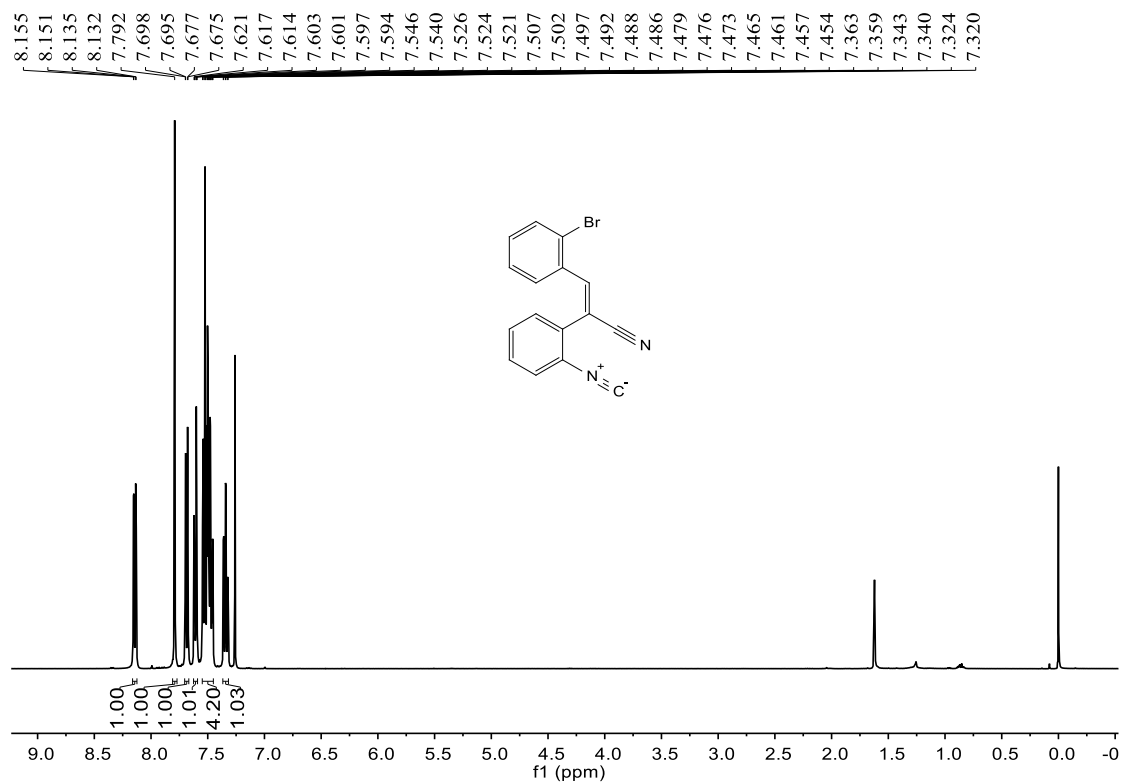
^1H NMR and ^{13}C NMR spectra of compound 11



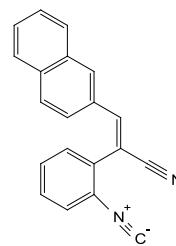
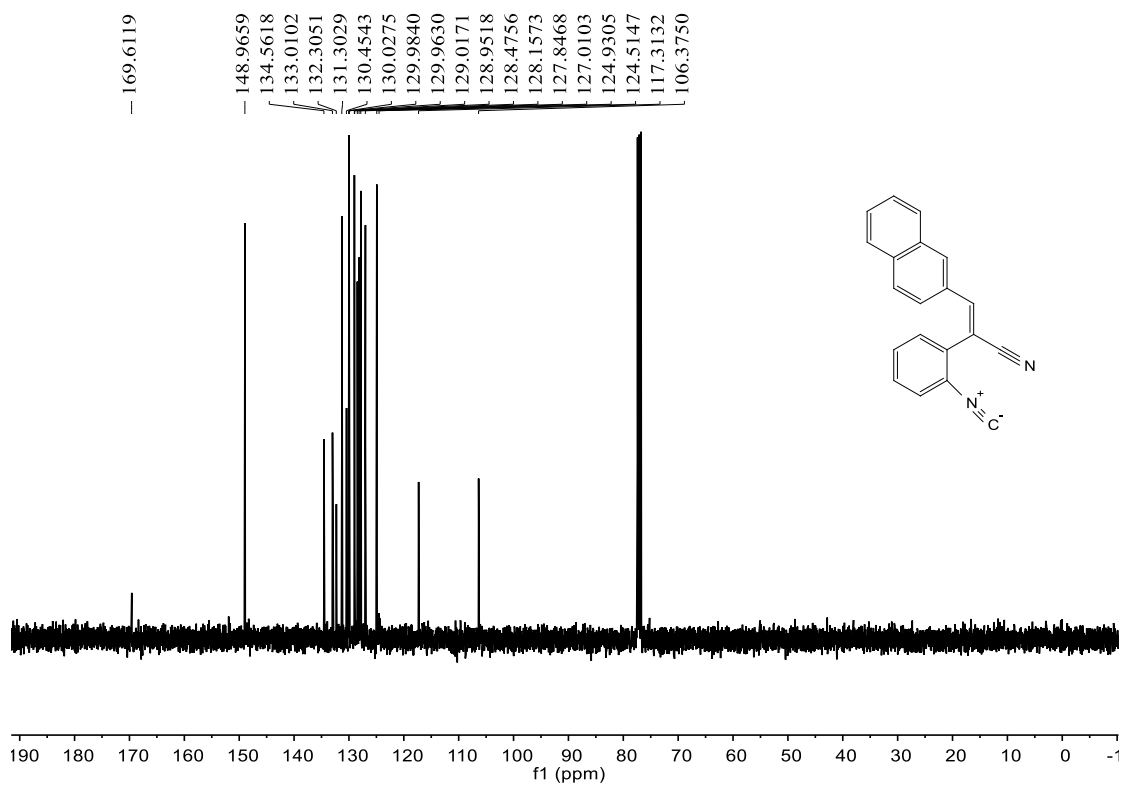
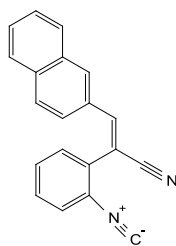
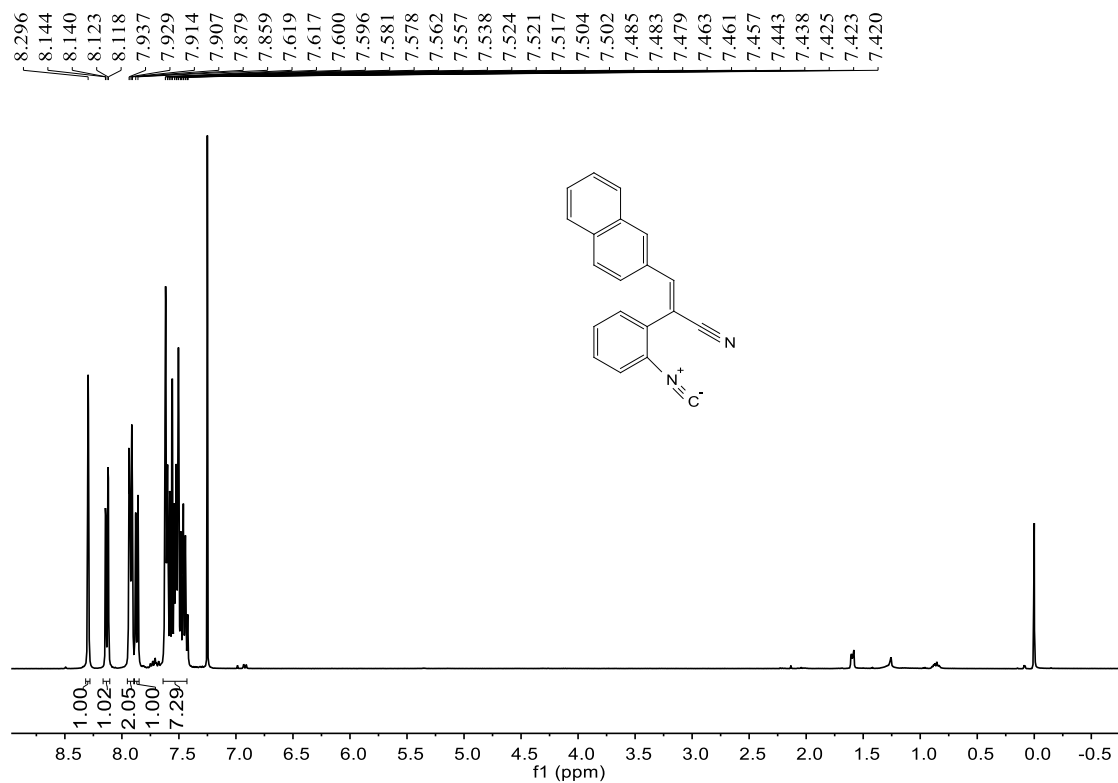
¹H NMR and ¹³C NMR spectra of compound **1m**



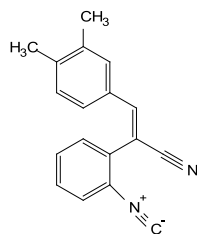
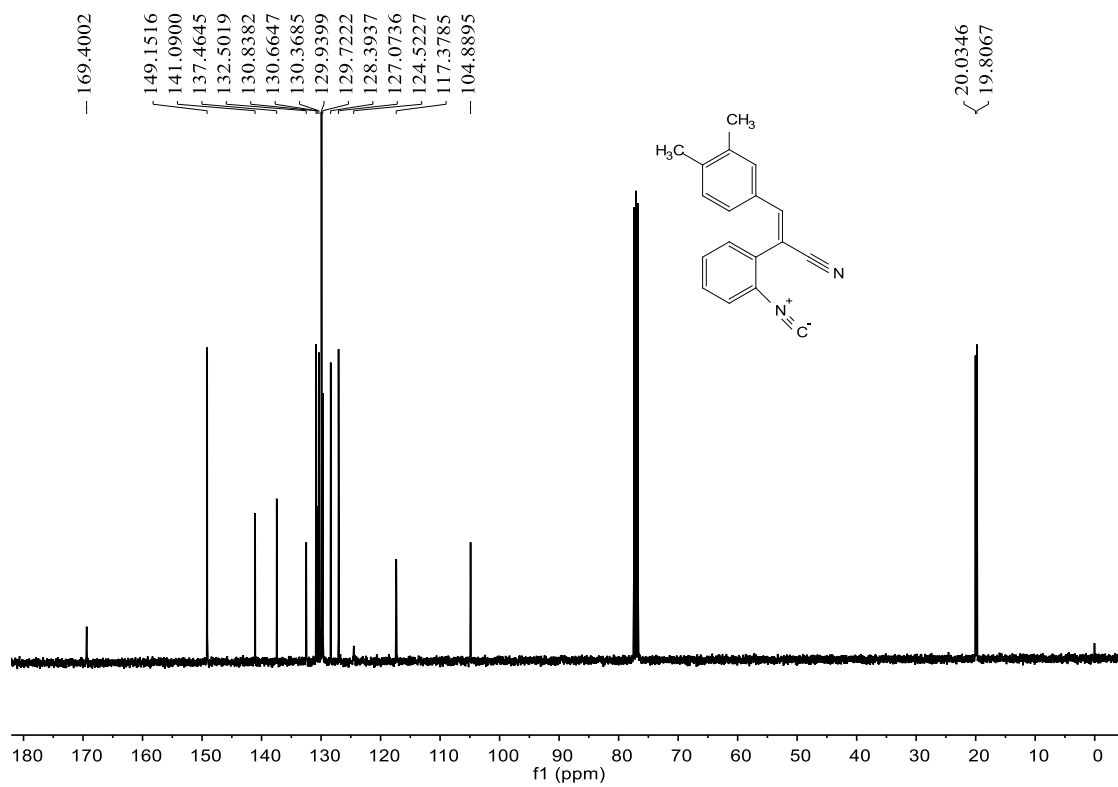
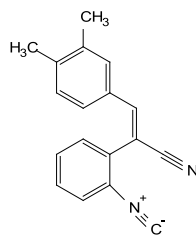
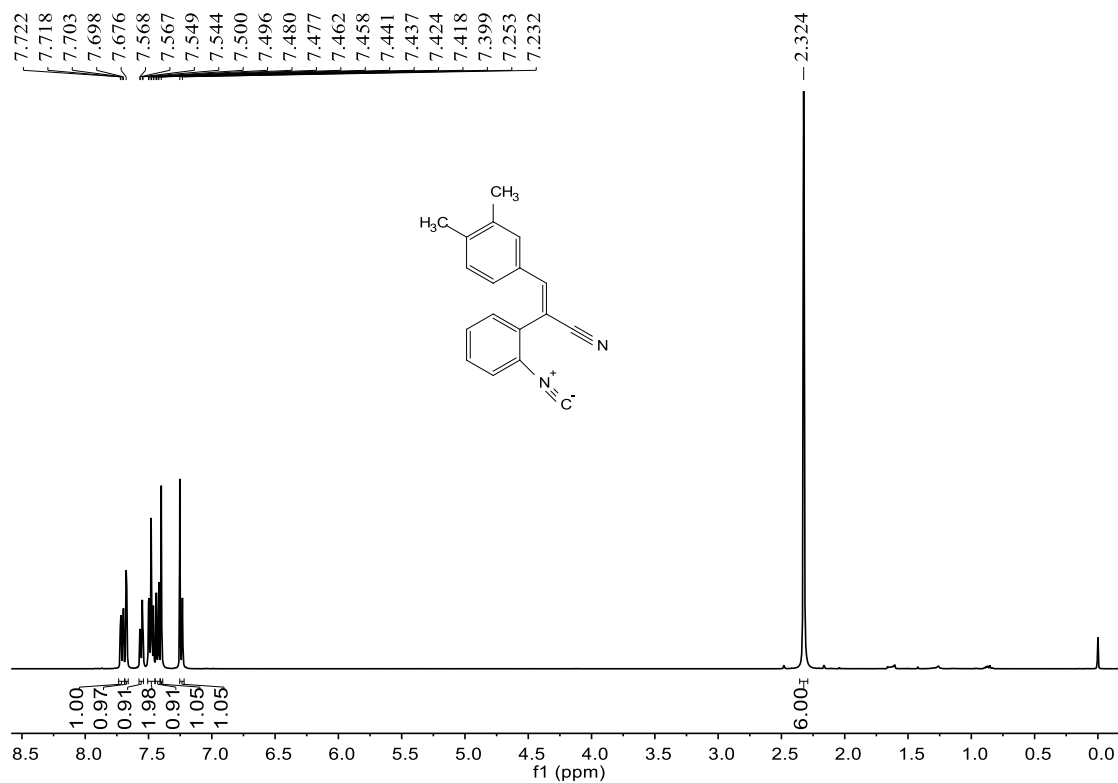
¹H NMR and ¹³C NMR spectra of compound **1n**



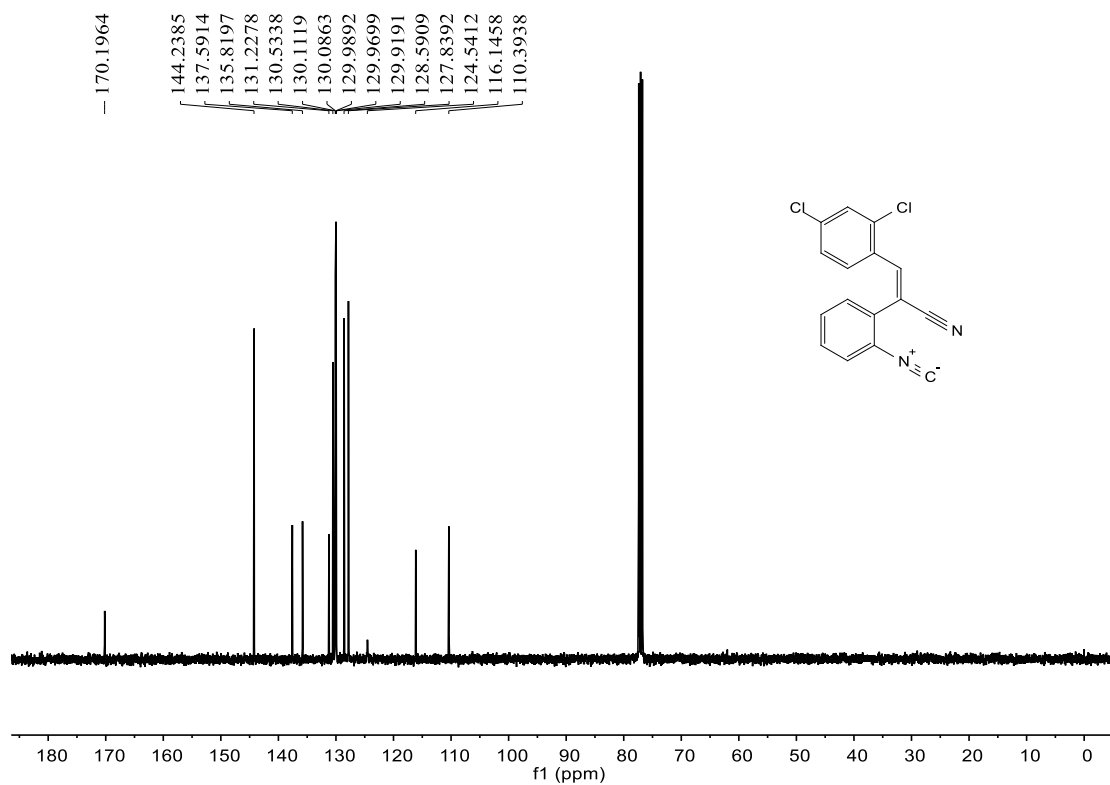
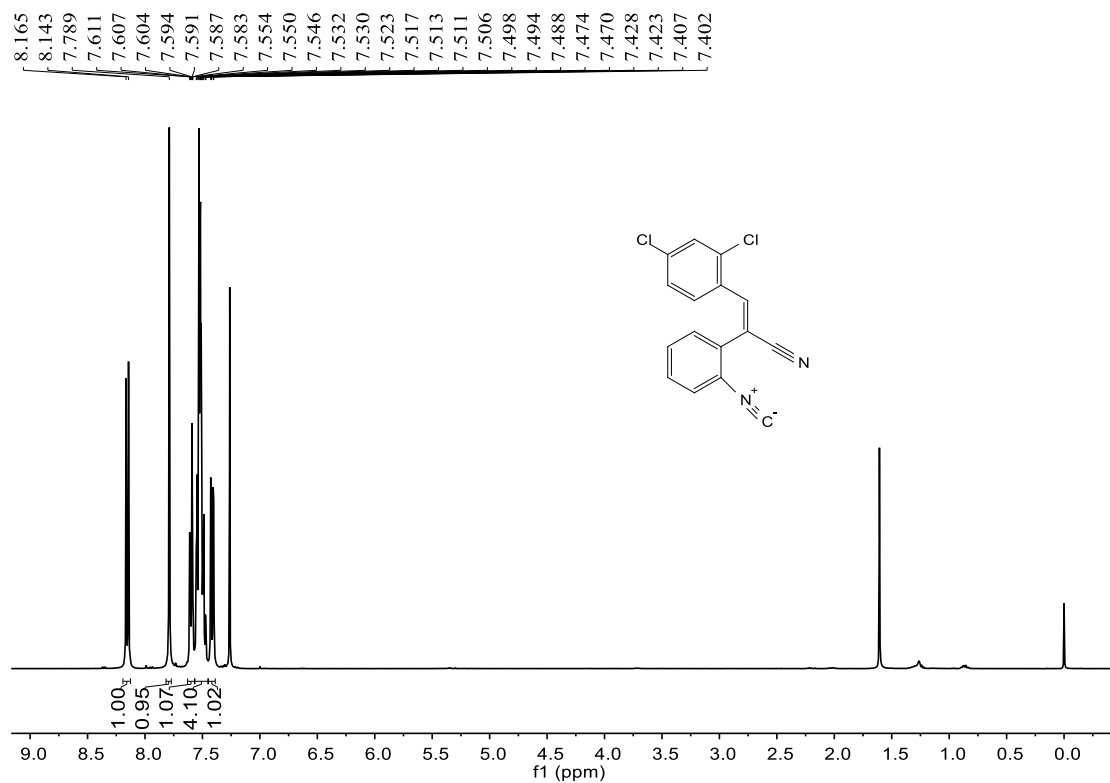
¹H NMR and ¹³C NMR spectra of compound **1o**



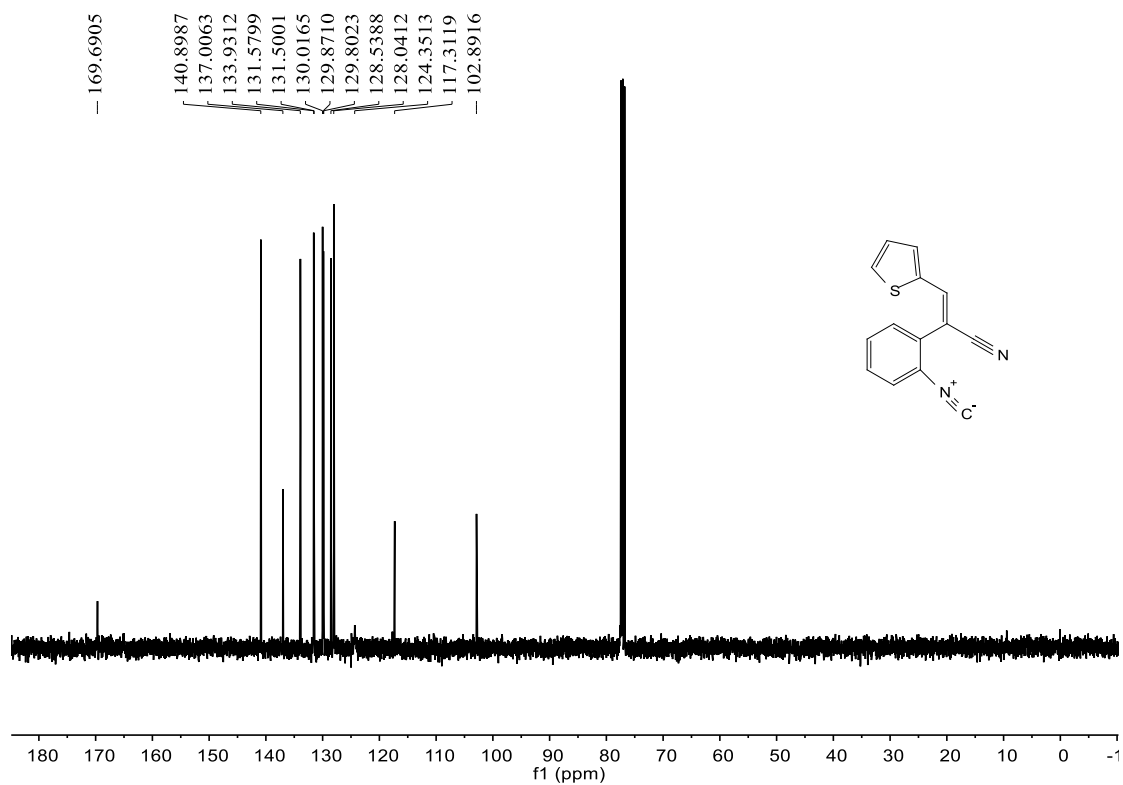
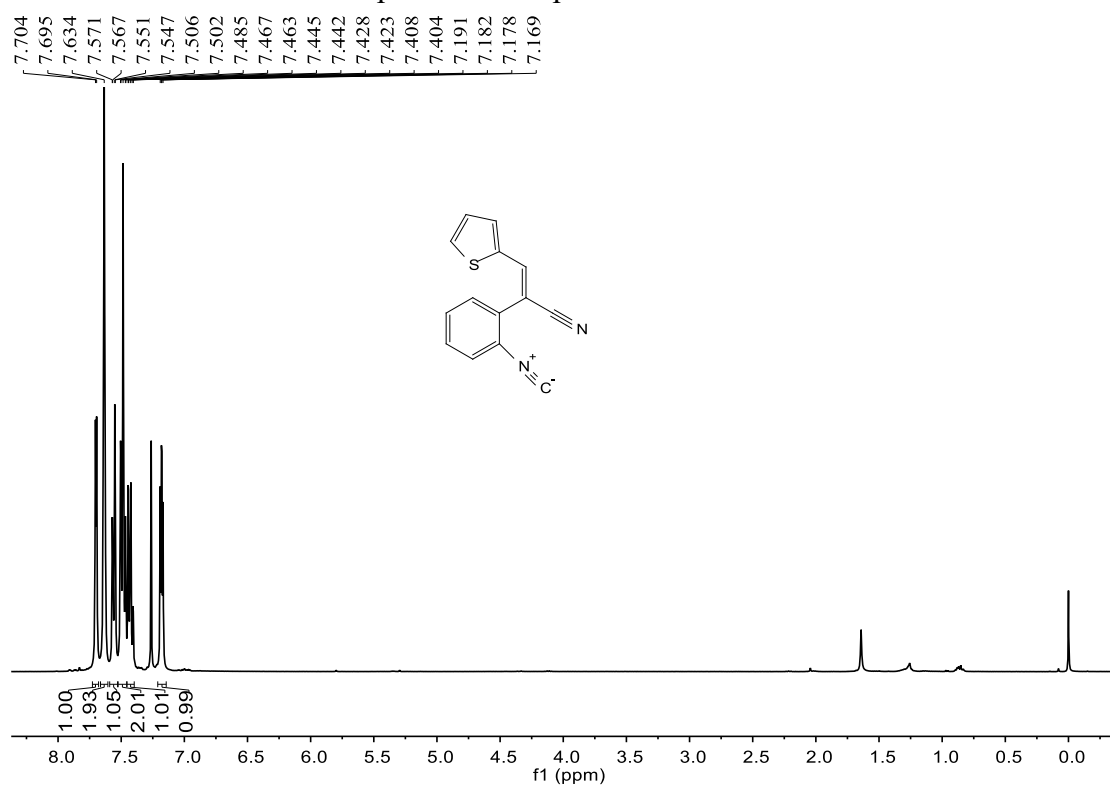
¹H NMR and ¹³C NMR spectra of compound 1p



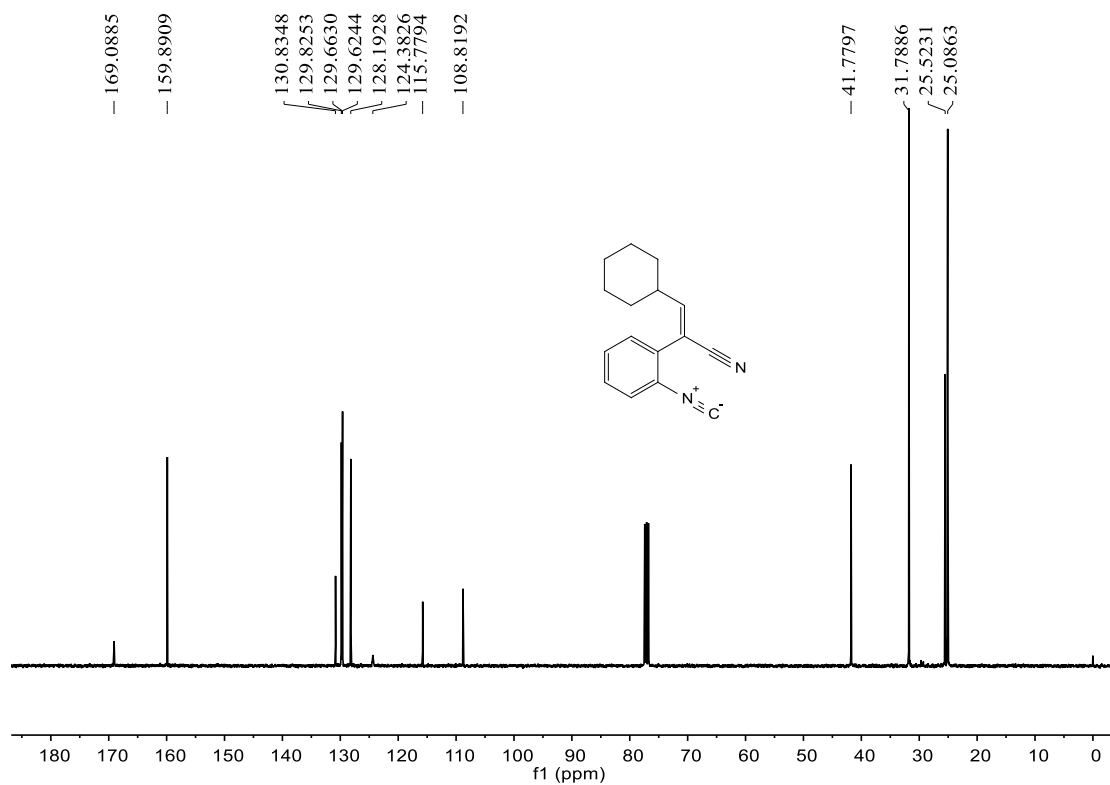
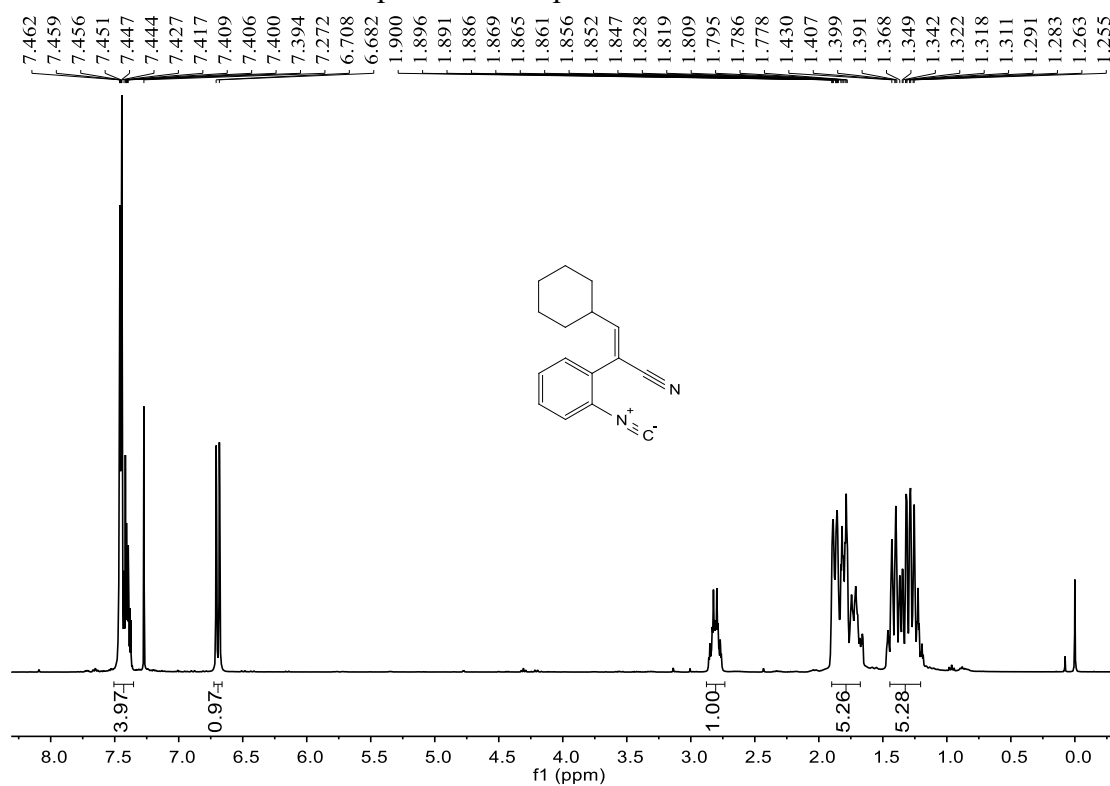
¹H NMR and ¹³C NMR spectra of compound **1q**



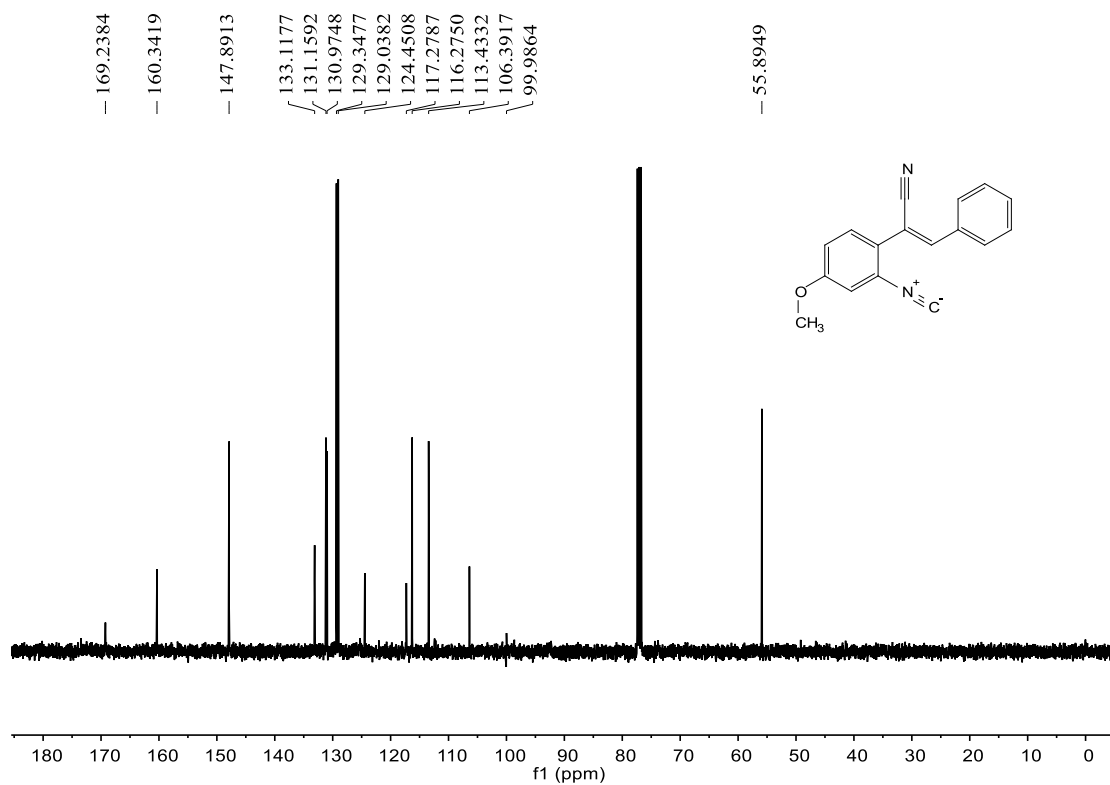
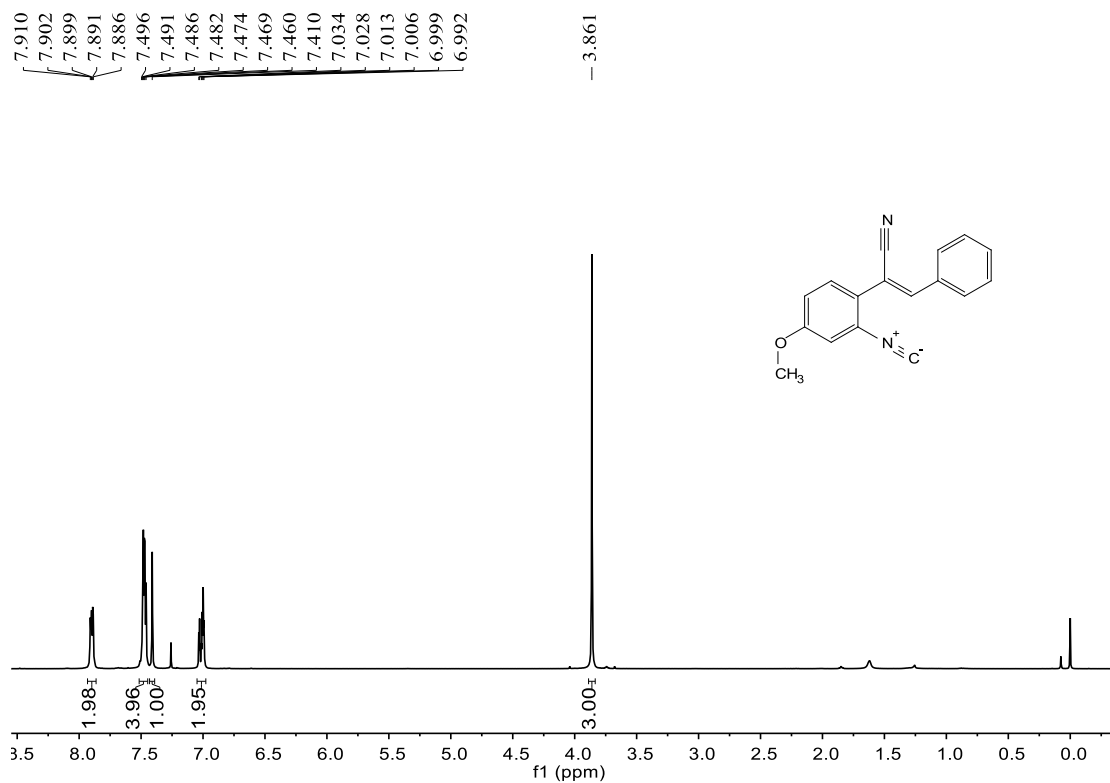
¹H NMR and ¹³C NMR spectra of compound **1r**



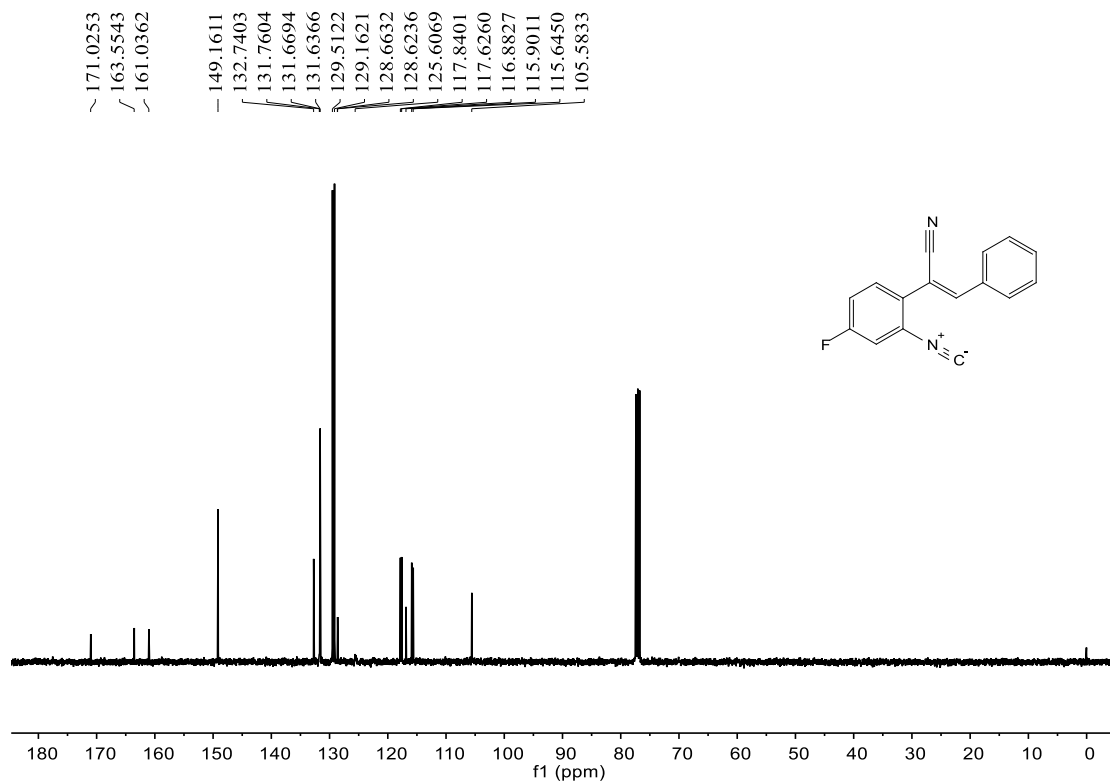
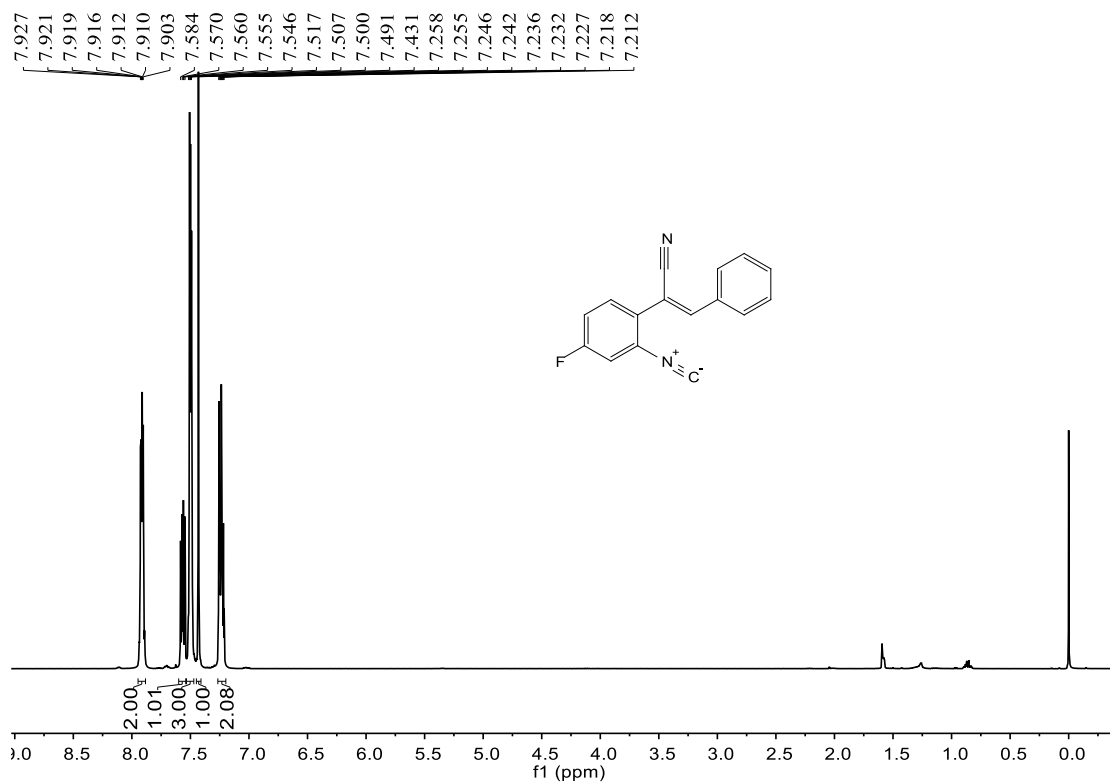
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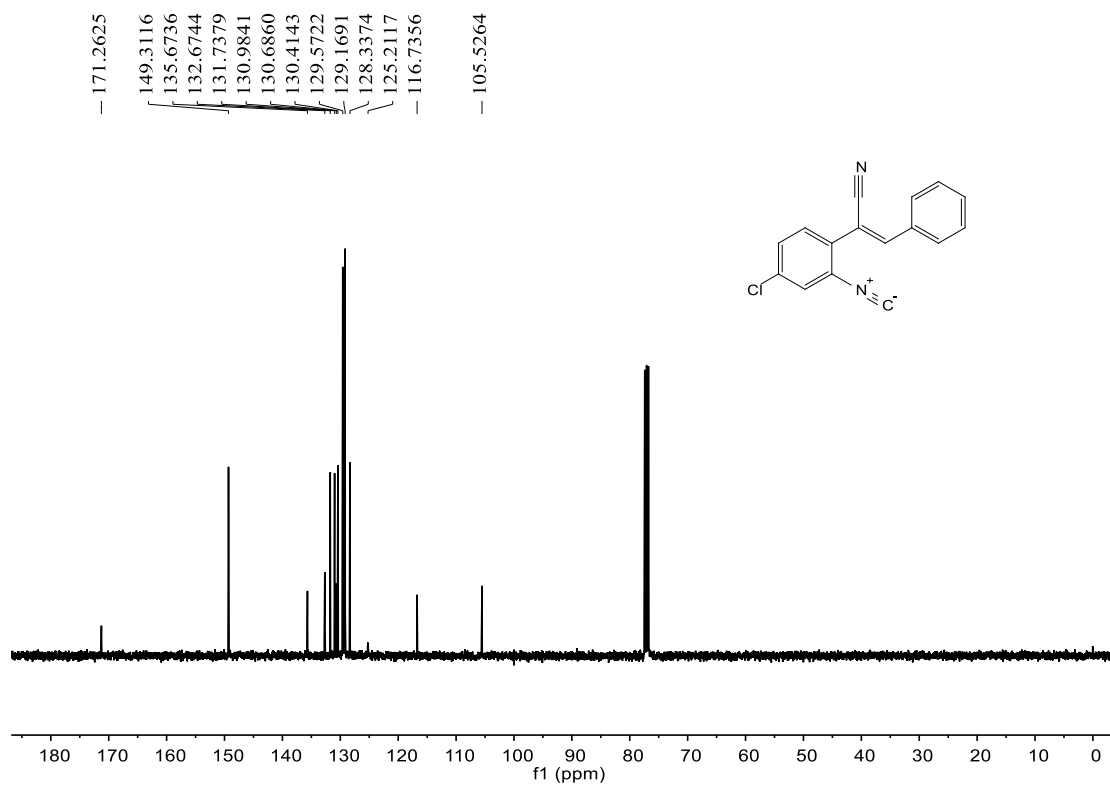
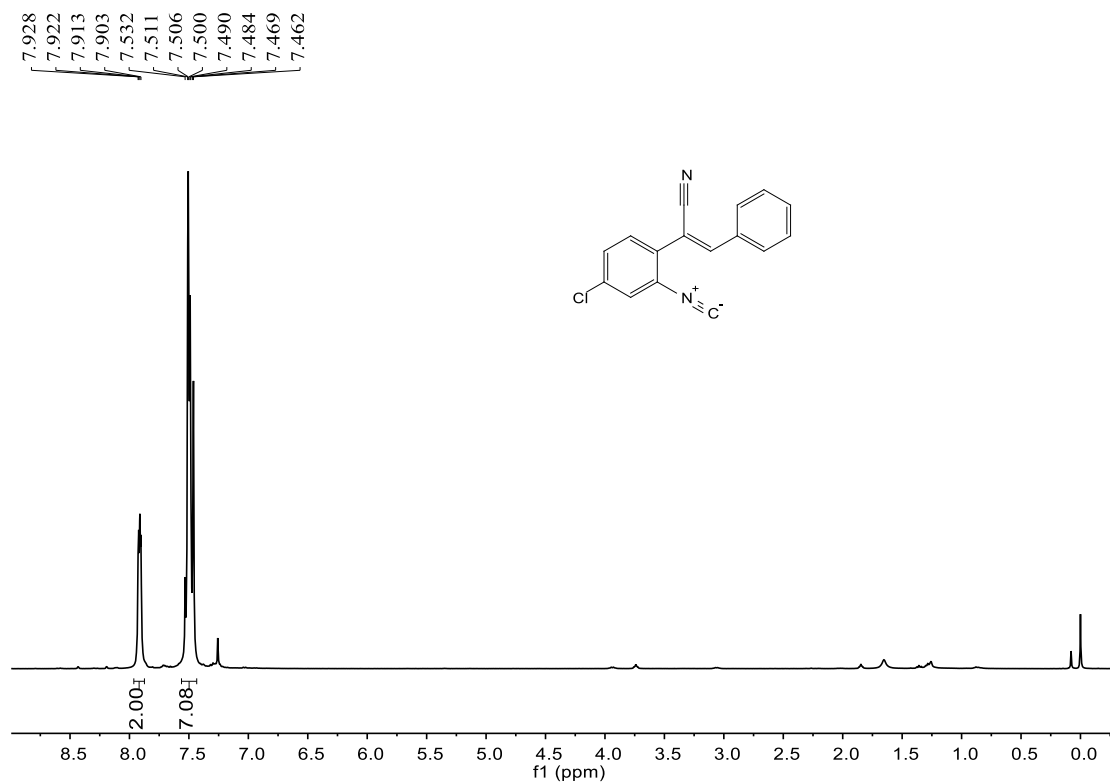
¹H NMR and ¹³C NMR spectra of compound 1t



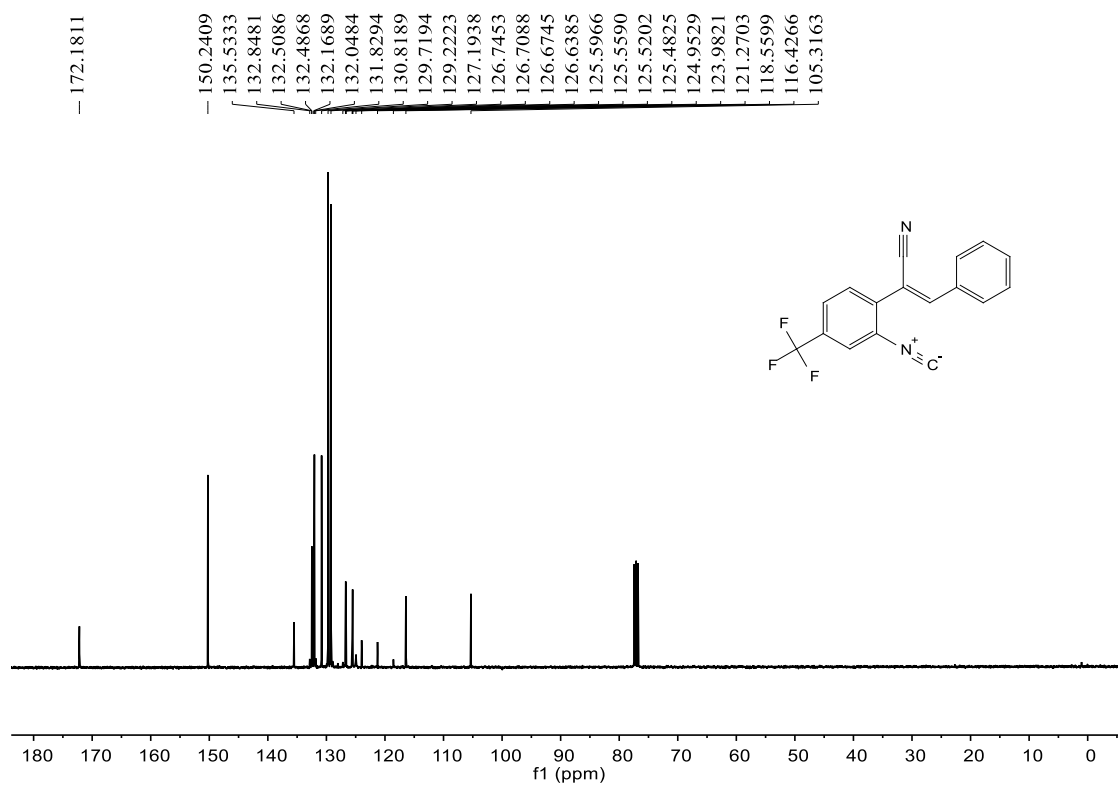
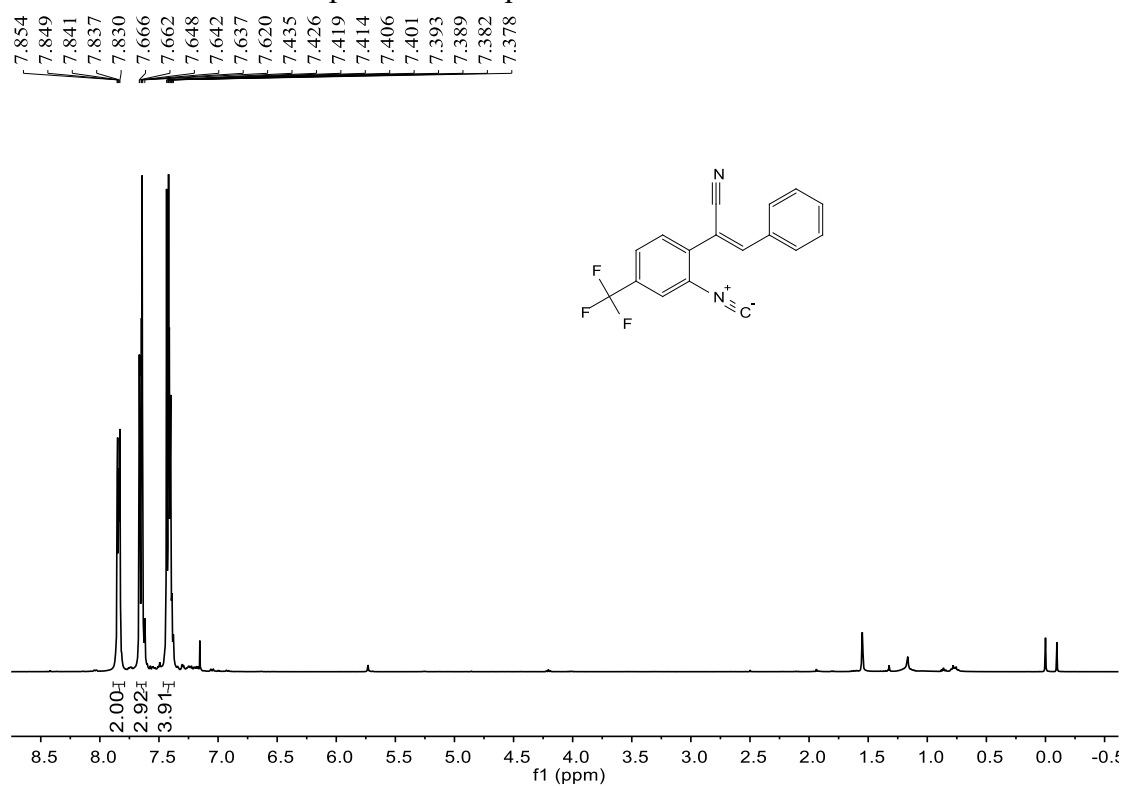
¹H NMR and ¹³C NMR spectra of compound **1u**



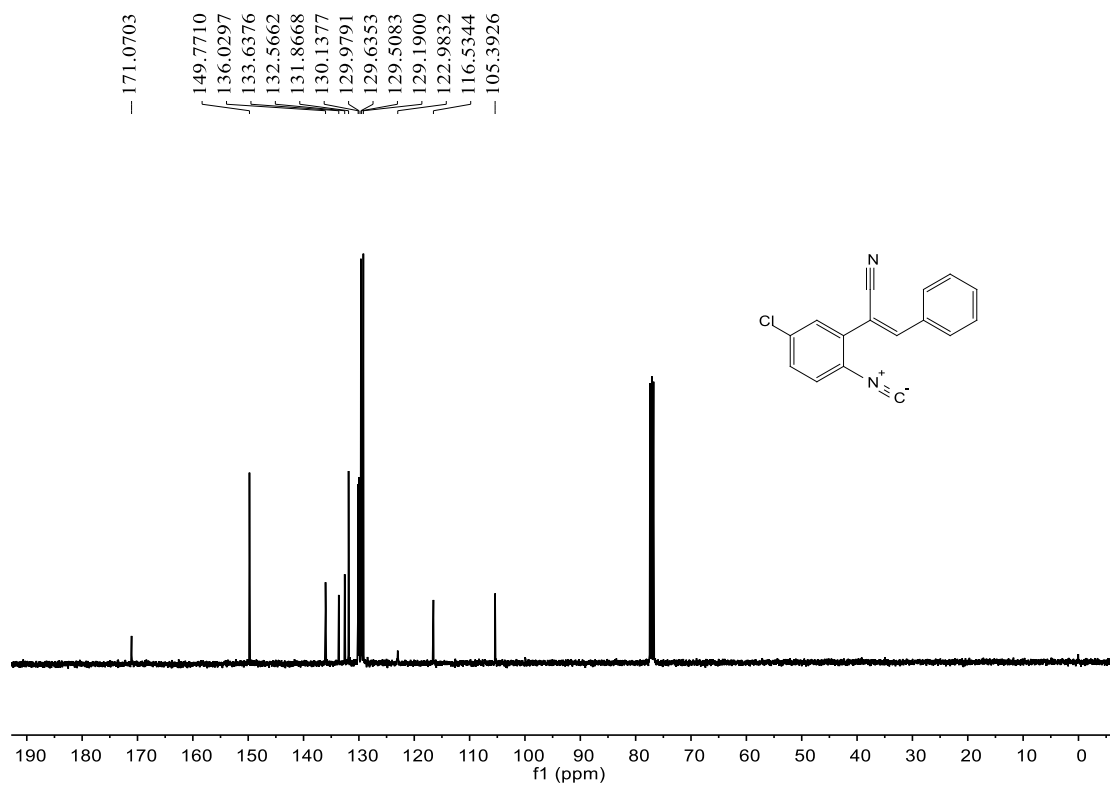
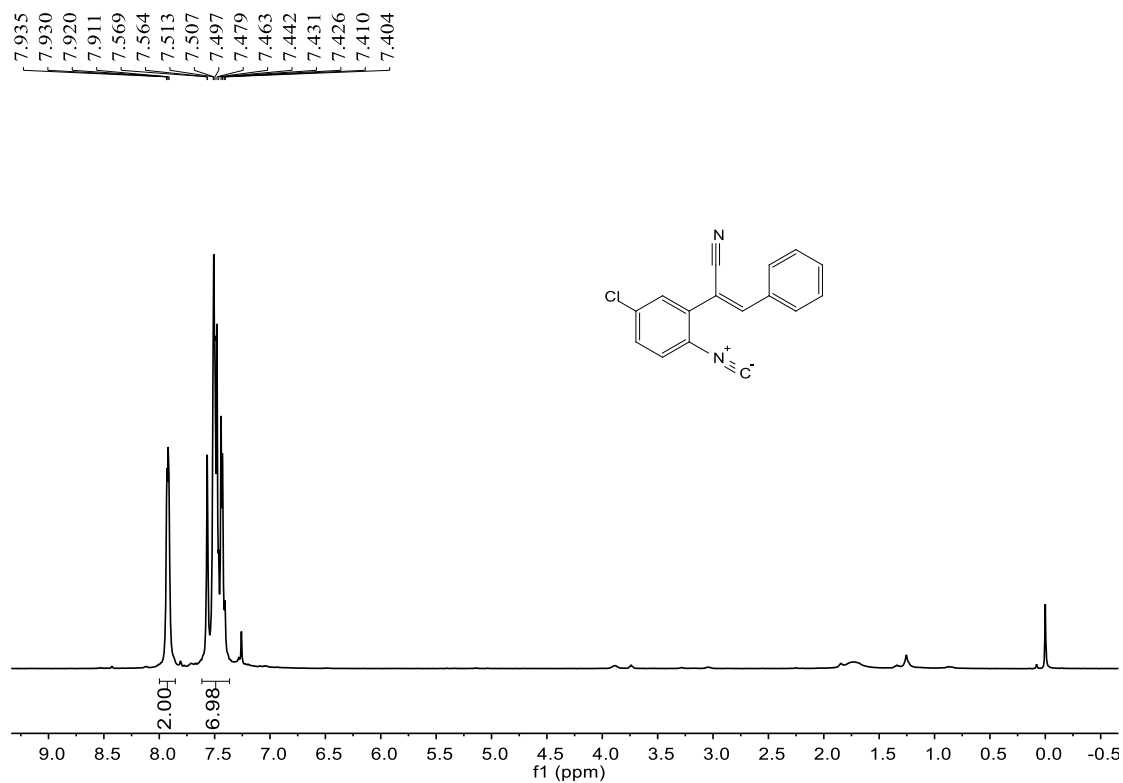
^1H NMR and ^{13}C NMR spectra of compound **1v**



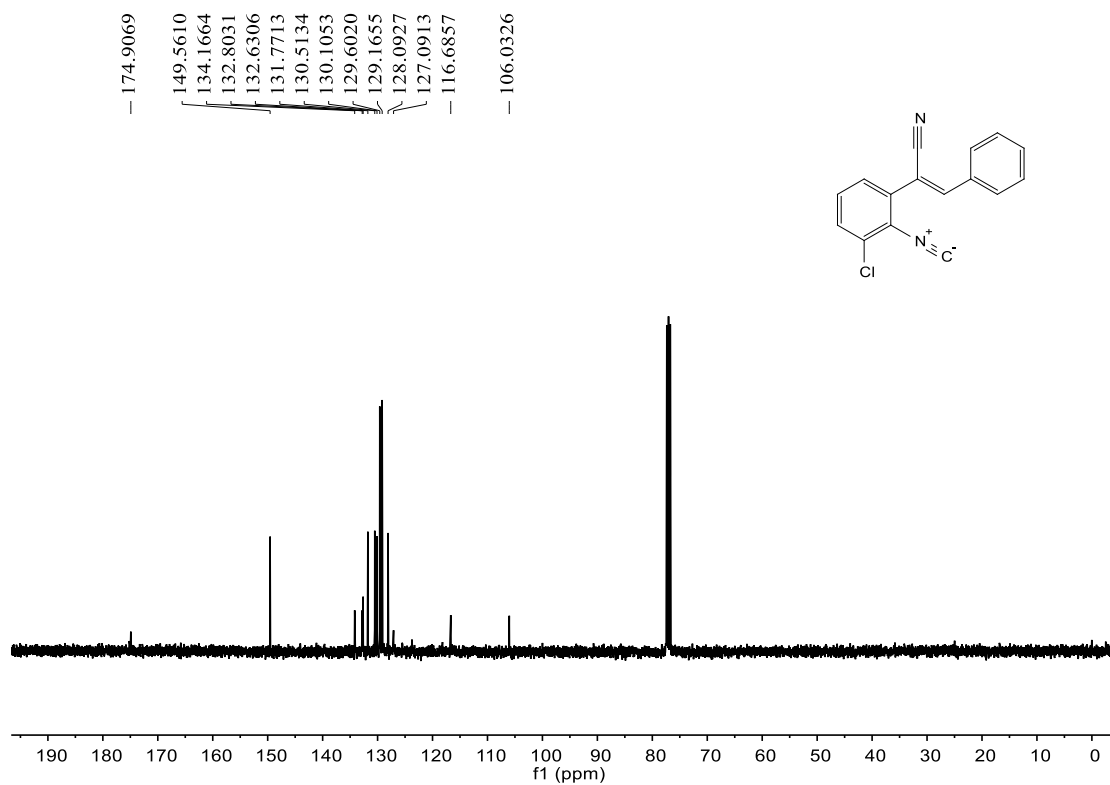
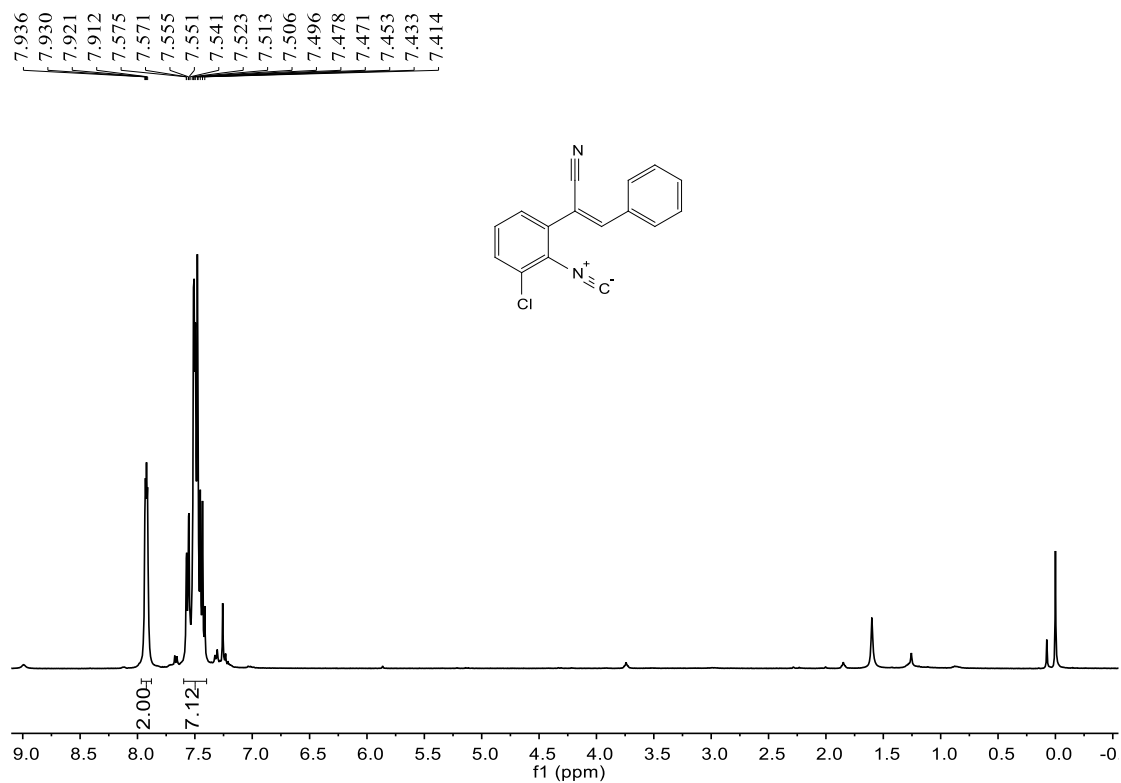
¹H NMR and ¹³C NMR spectra of compound **1w**



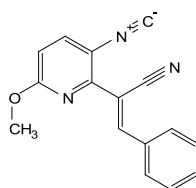
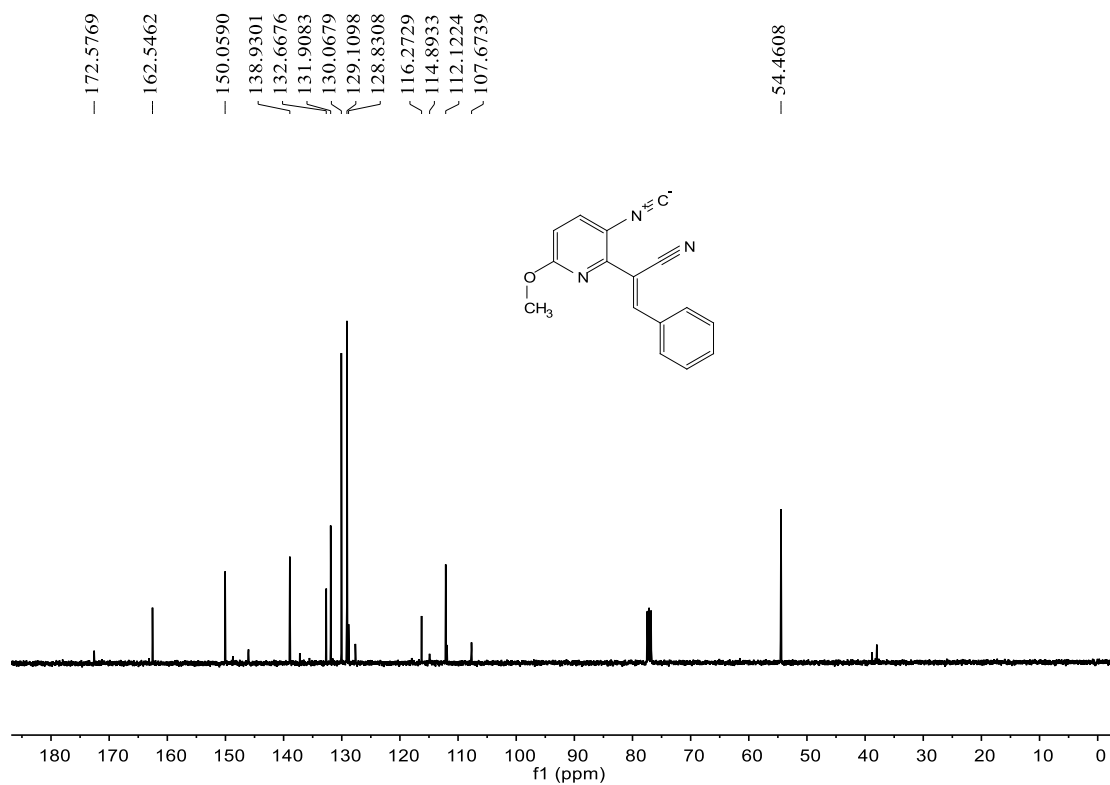
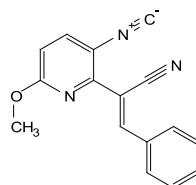
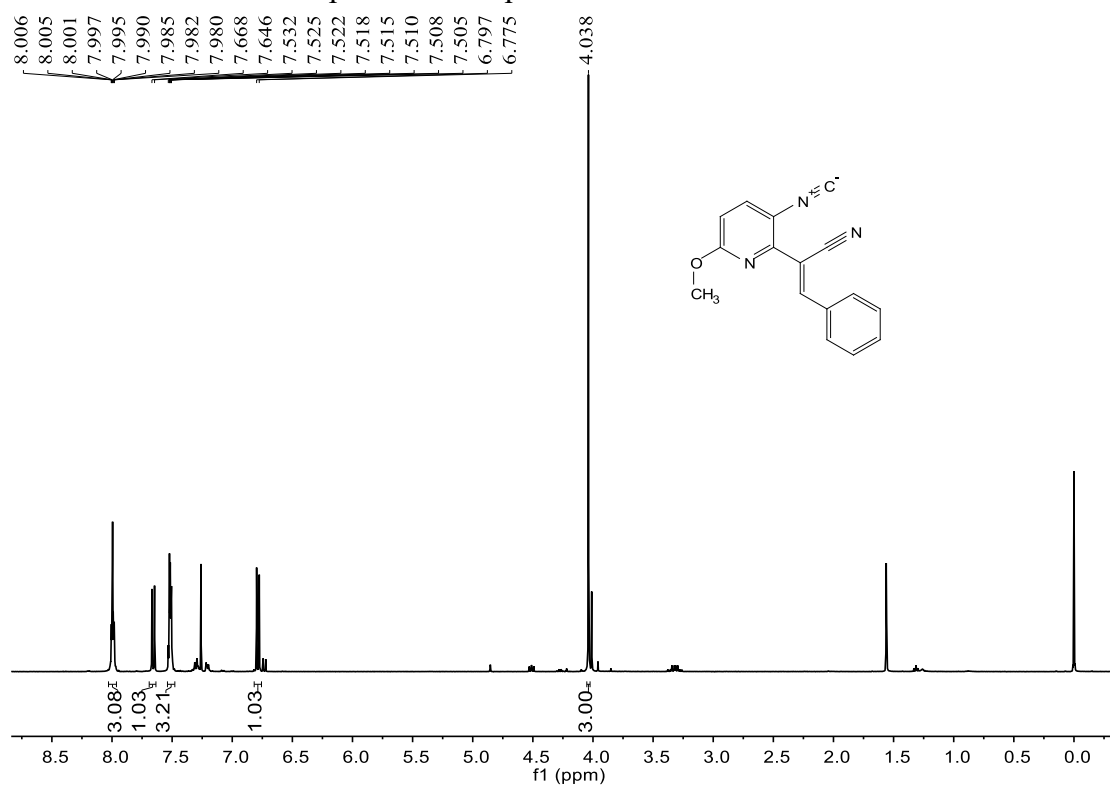
^1H NMR and ^{13}C NMR spectra of compound **1x**



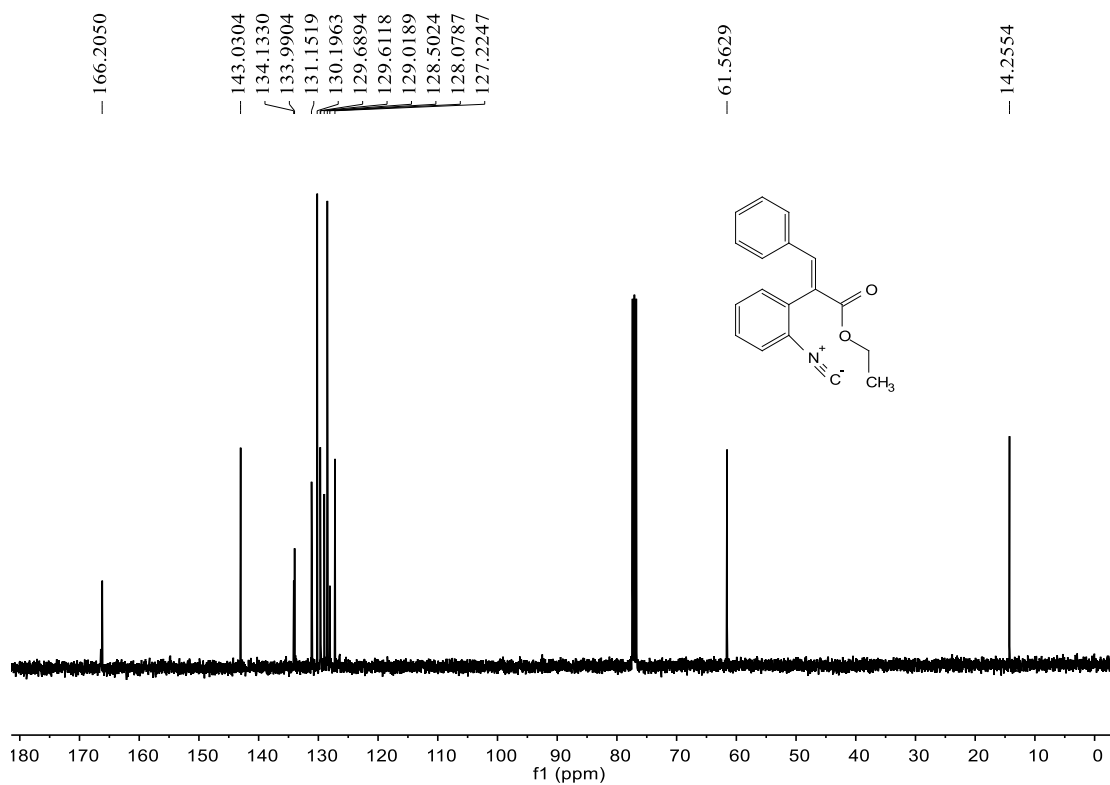
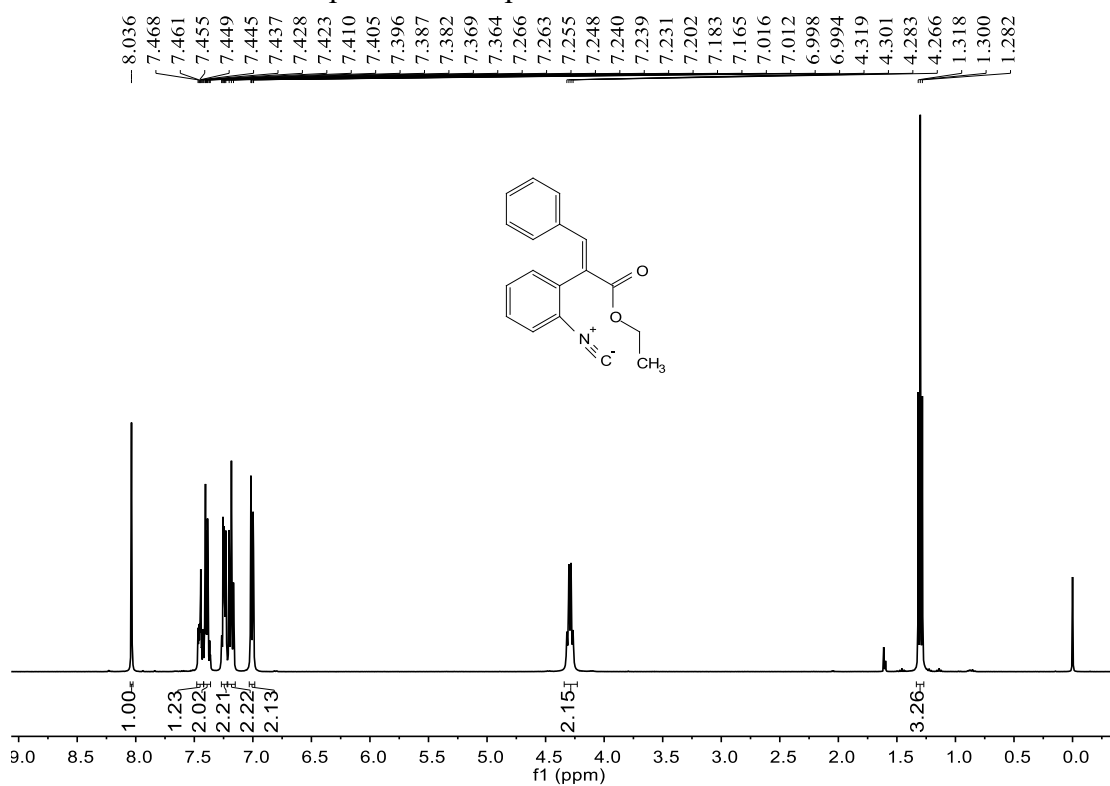
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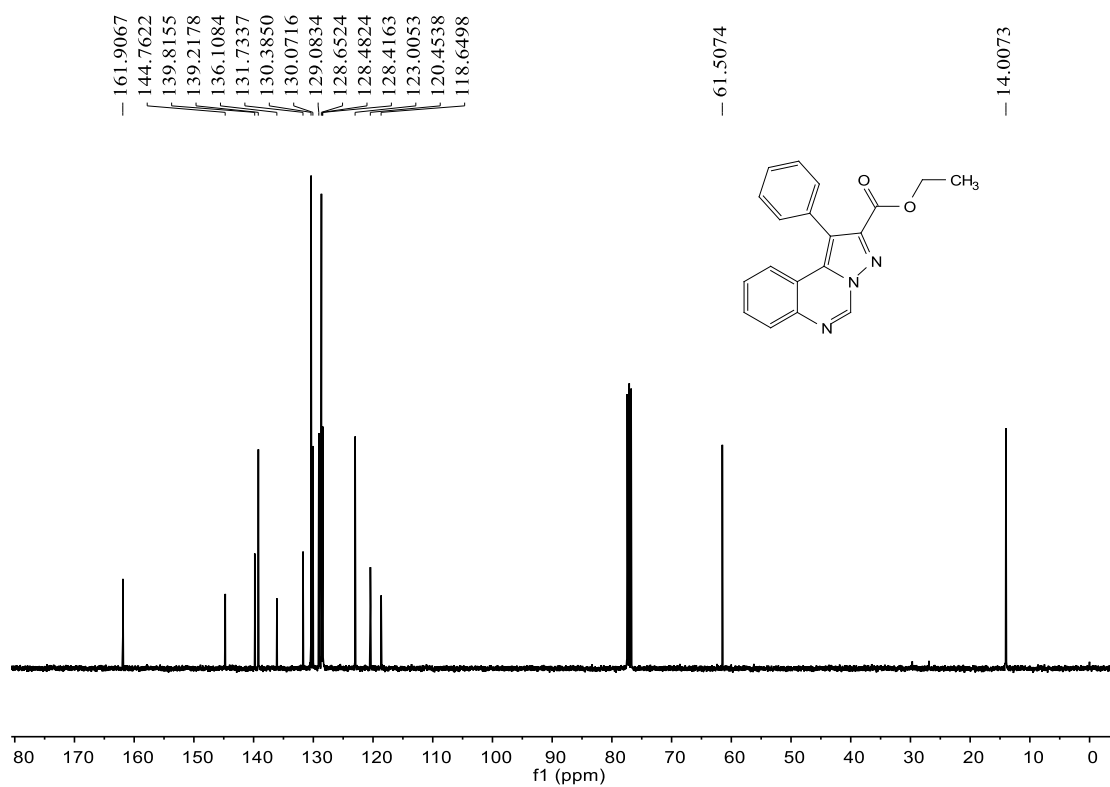
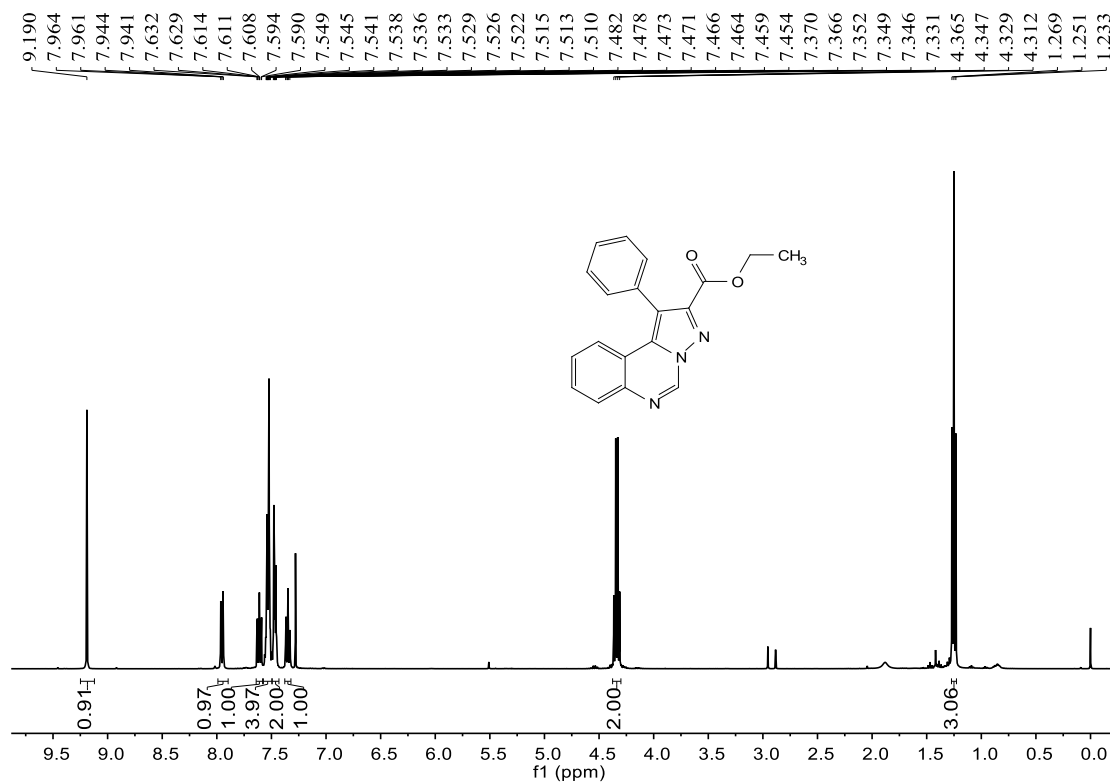
¹H NMR and ¹³C NMR spectra of compound 1z



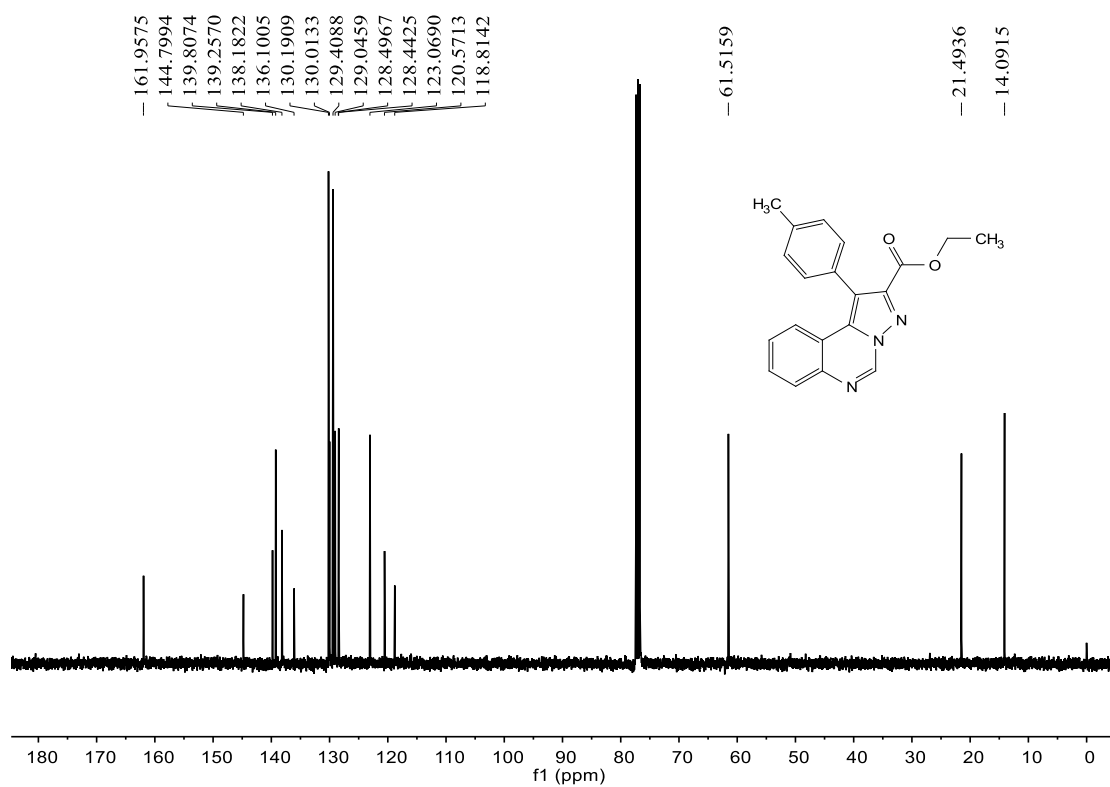
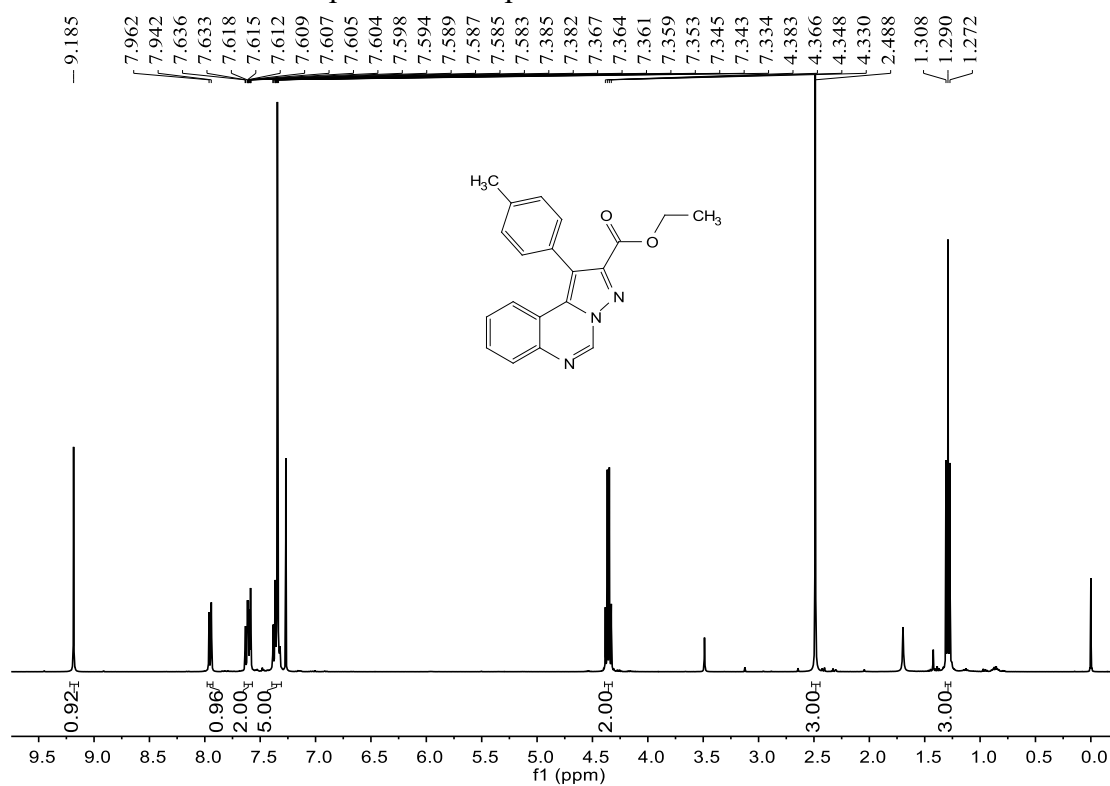
¹H NMR and ¹³C NMR spectra of compound **1aa**



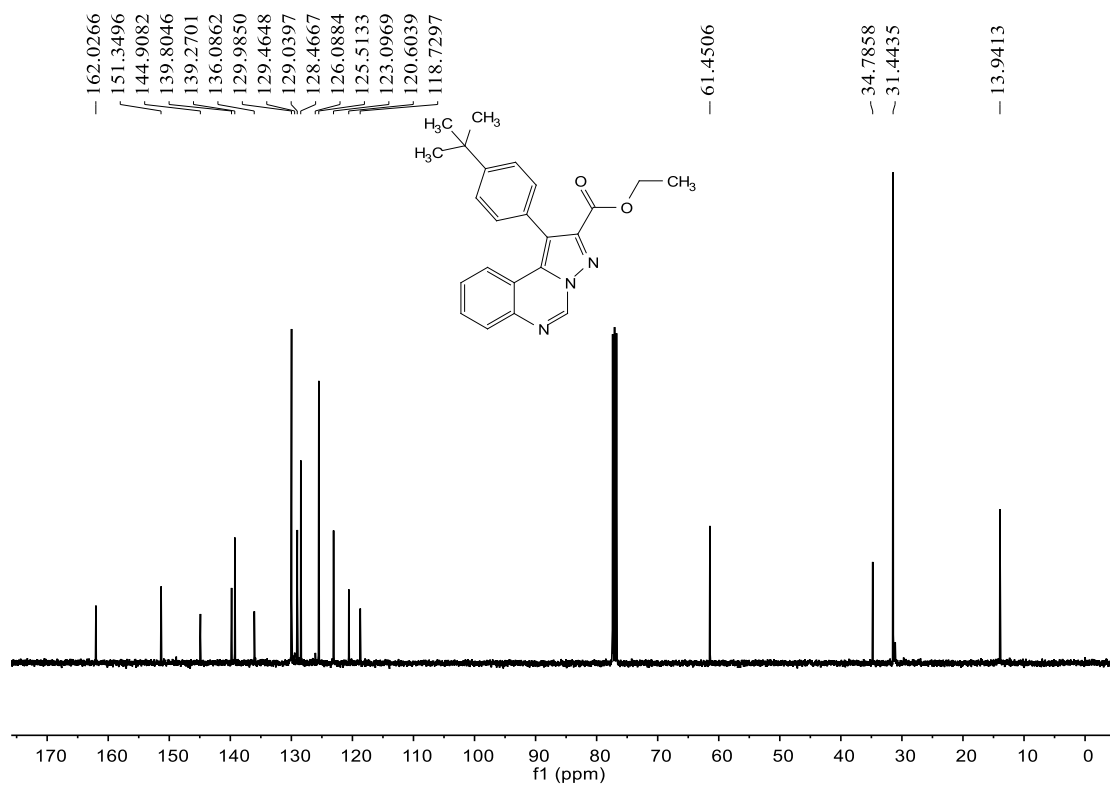
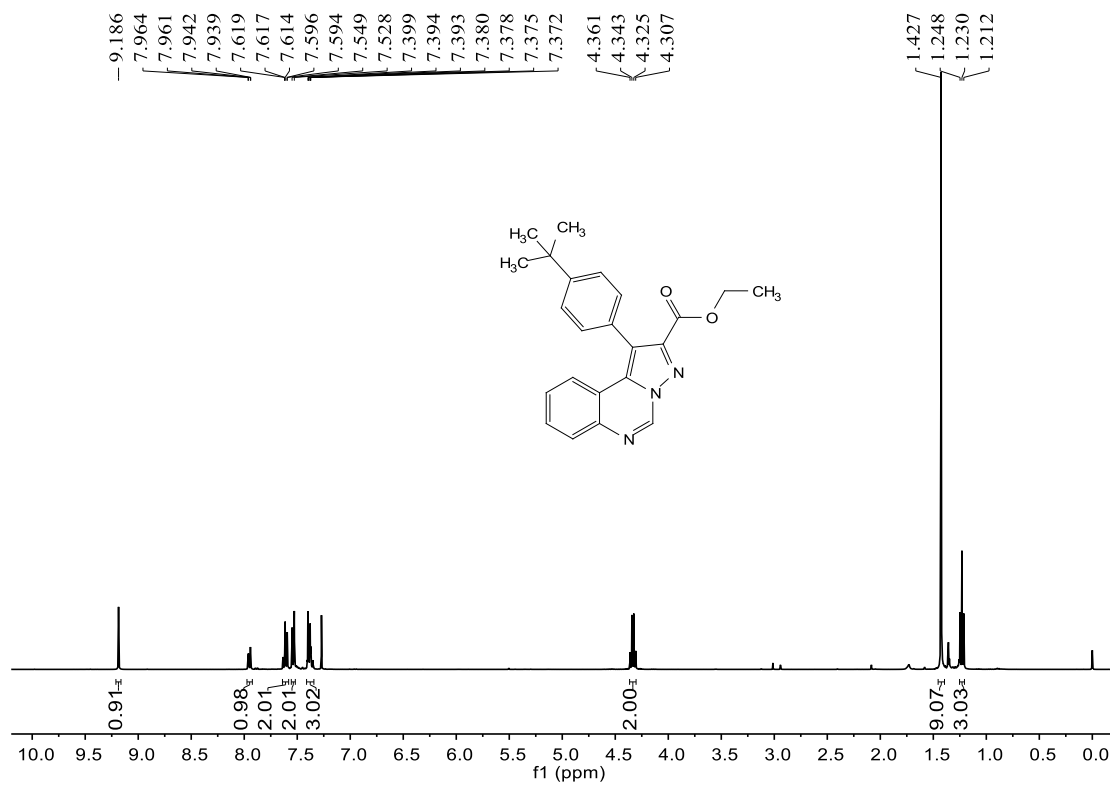
¹H NMR and ¹³C NMR spectra of compound **3aa**



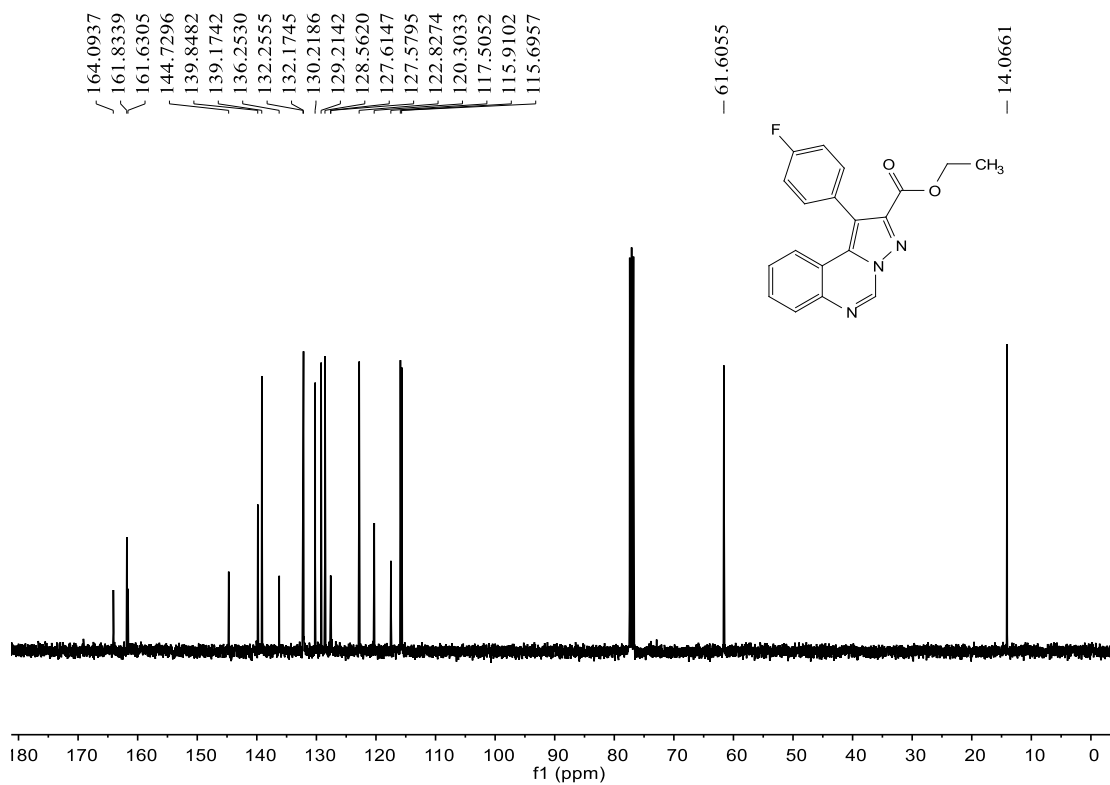
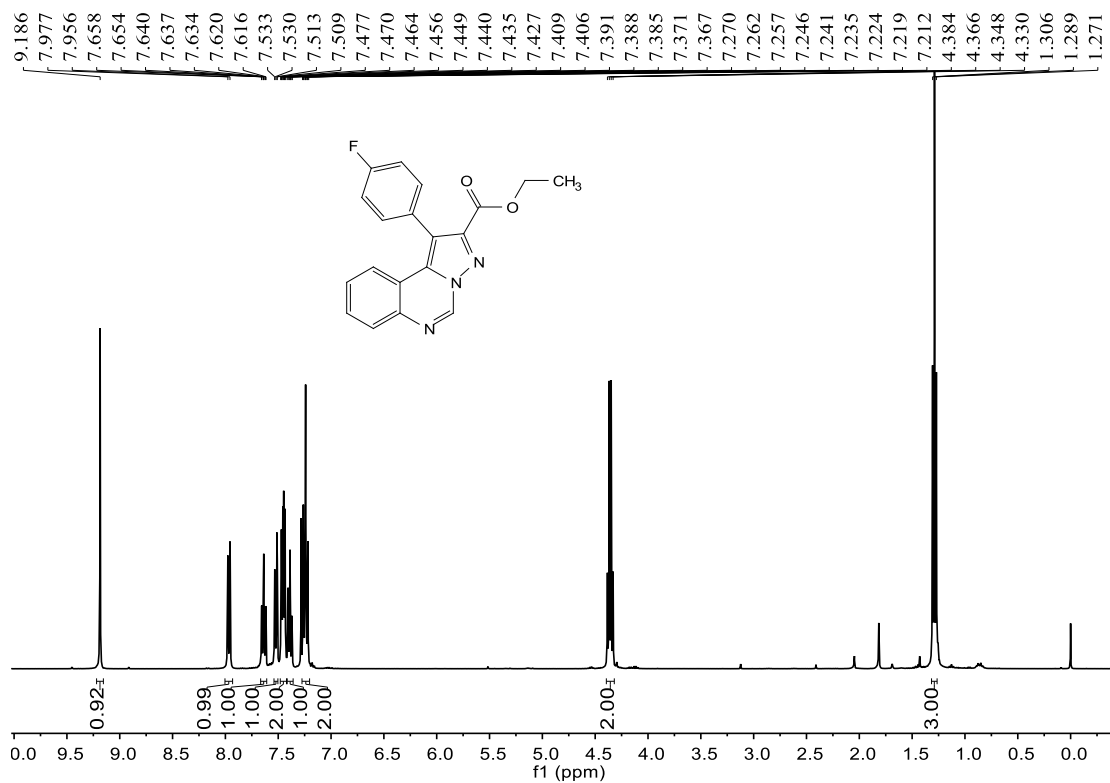
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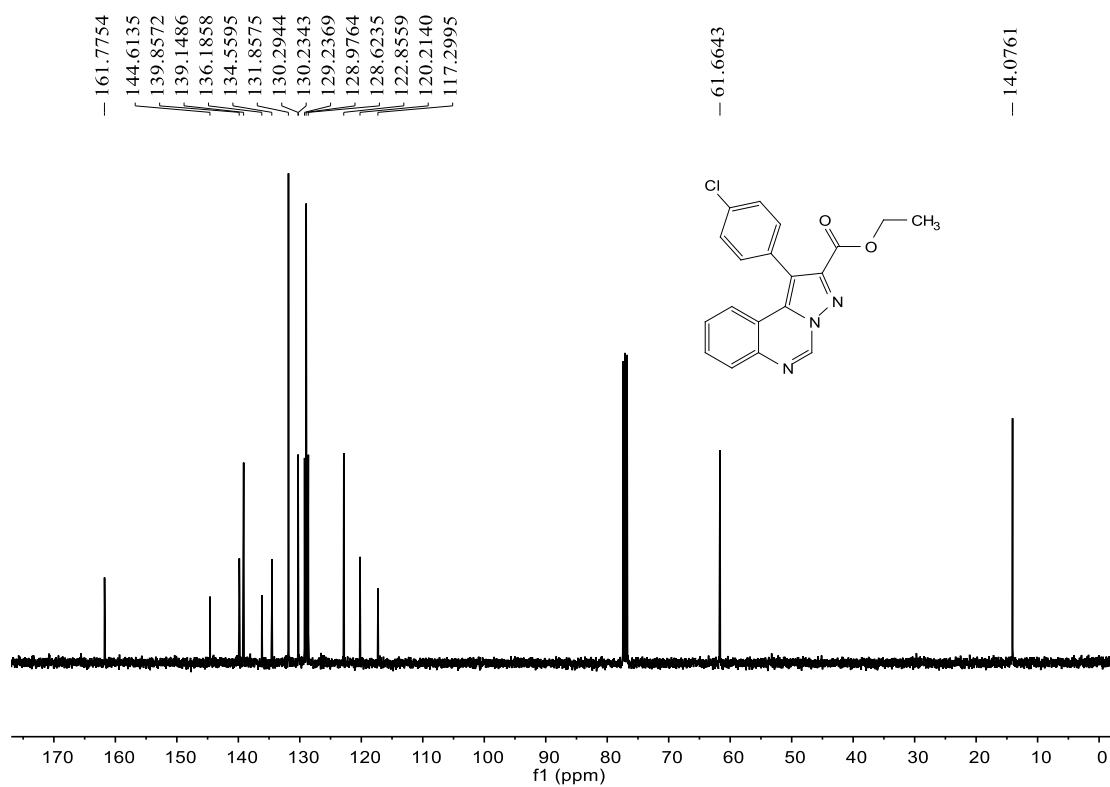
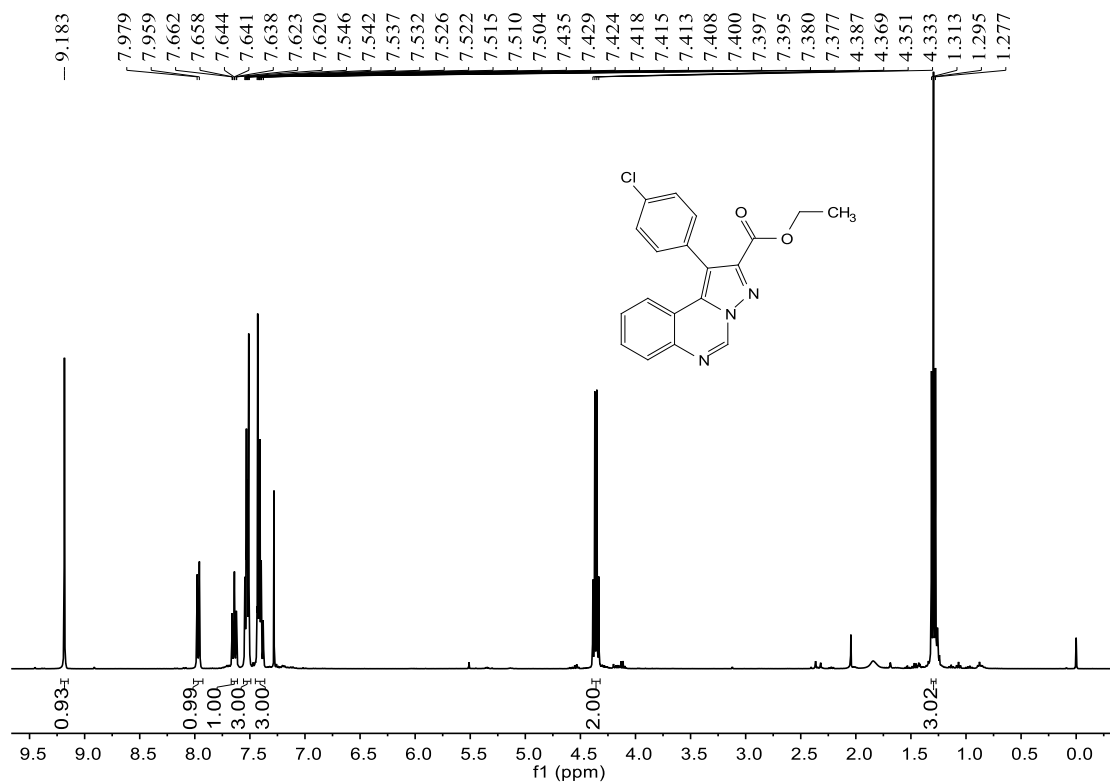
^1H NMR and ^{13}C NMR spectra of compound **3ca**



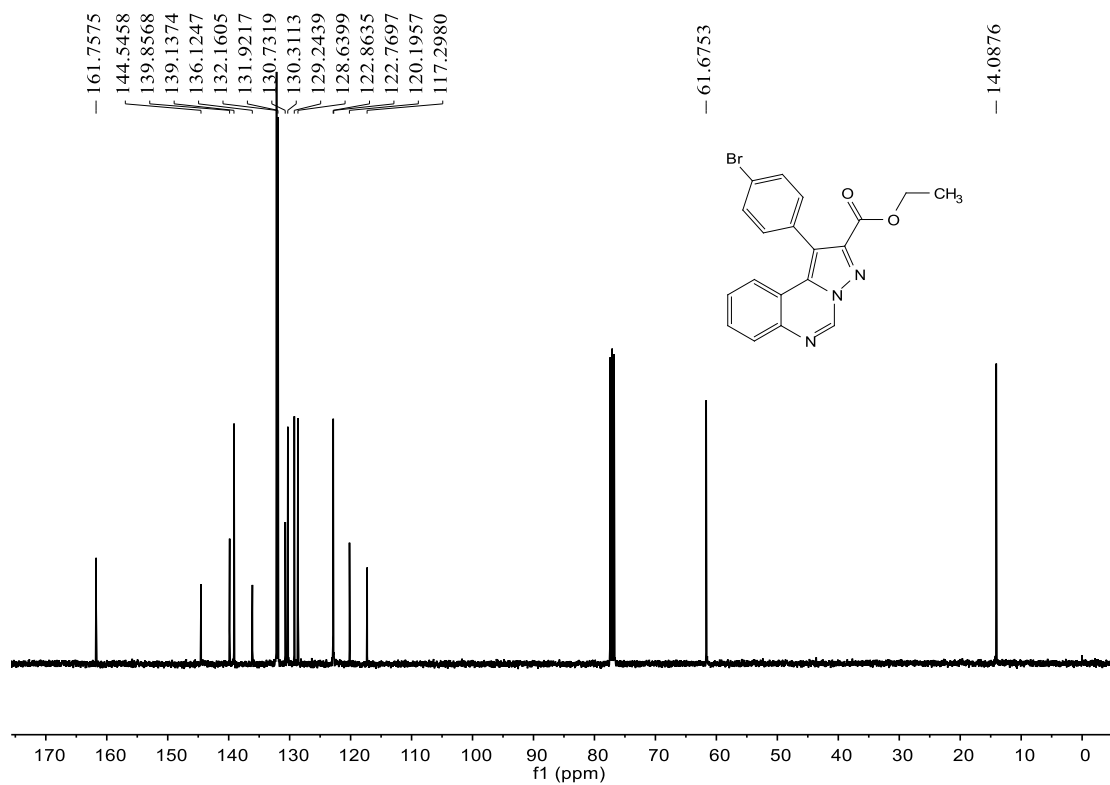
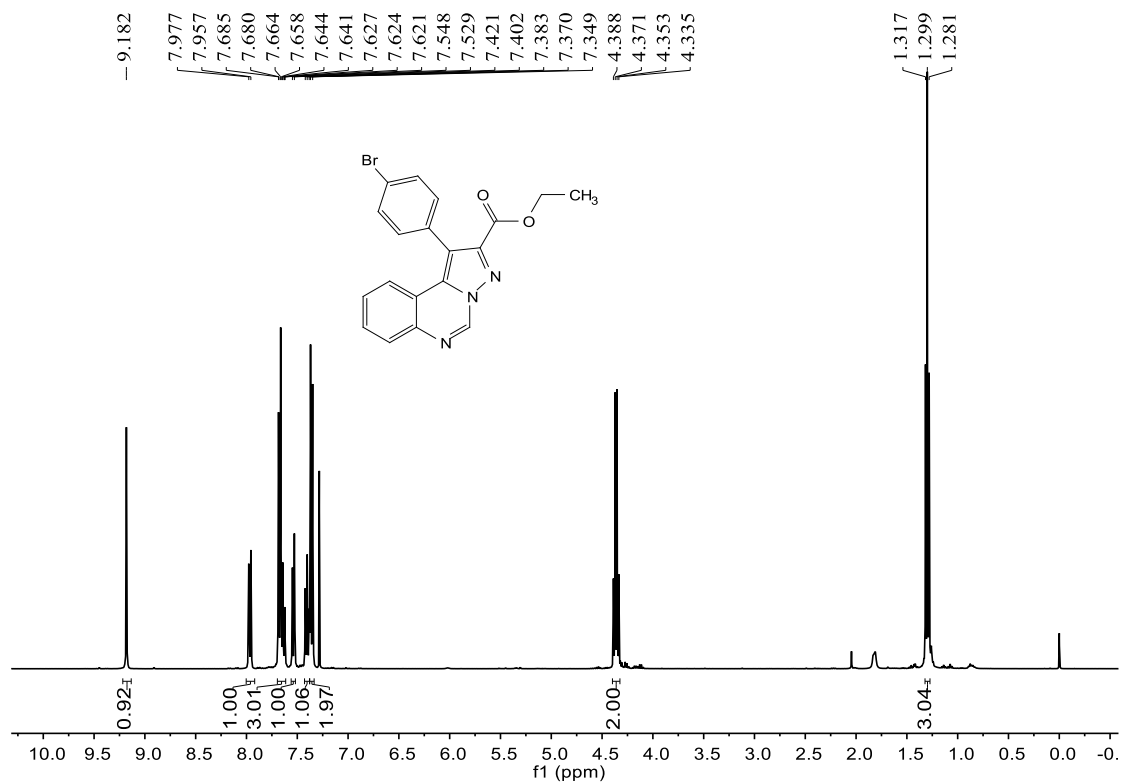
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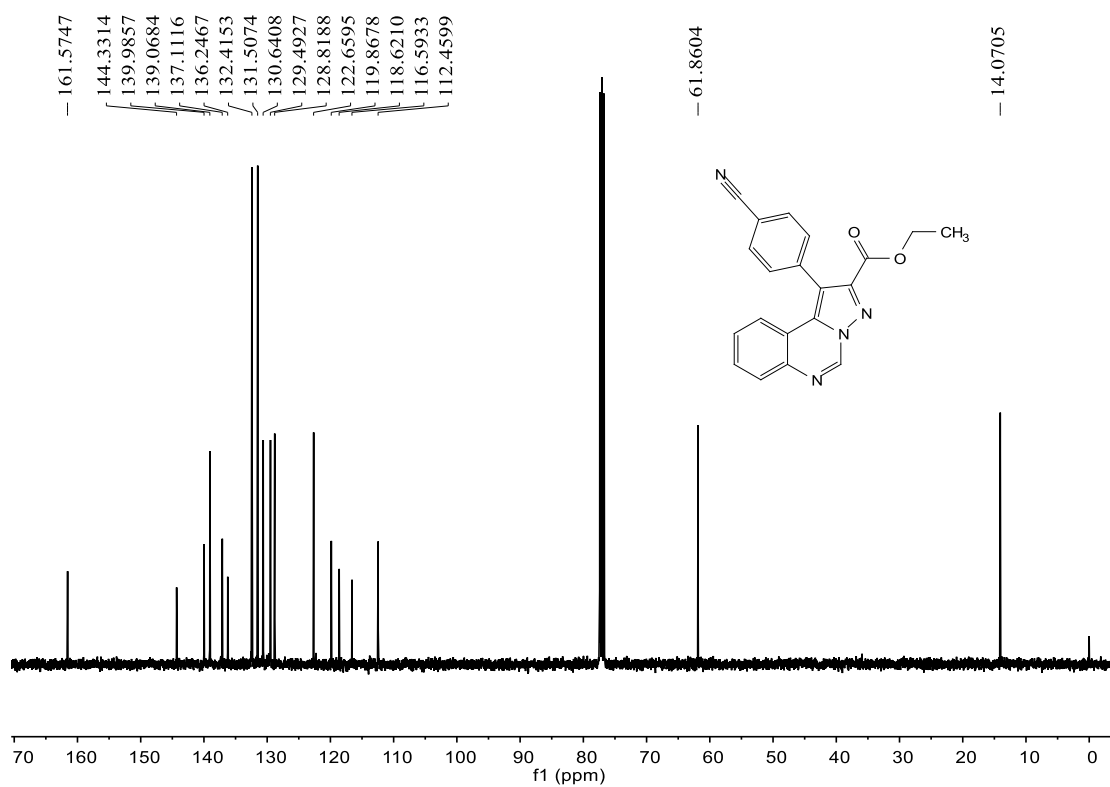
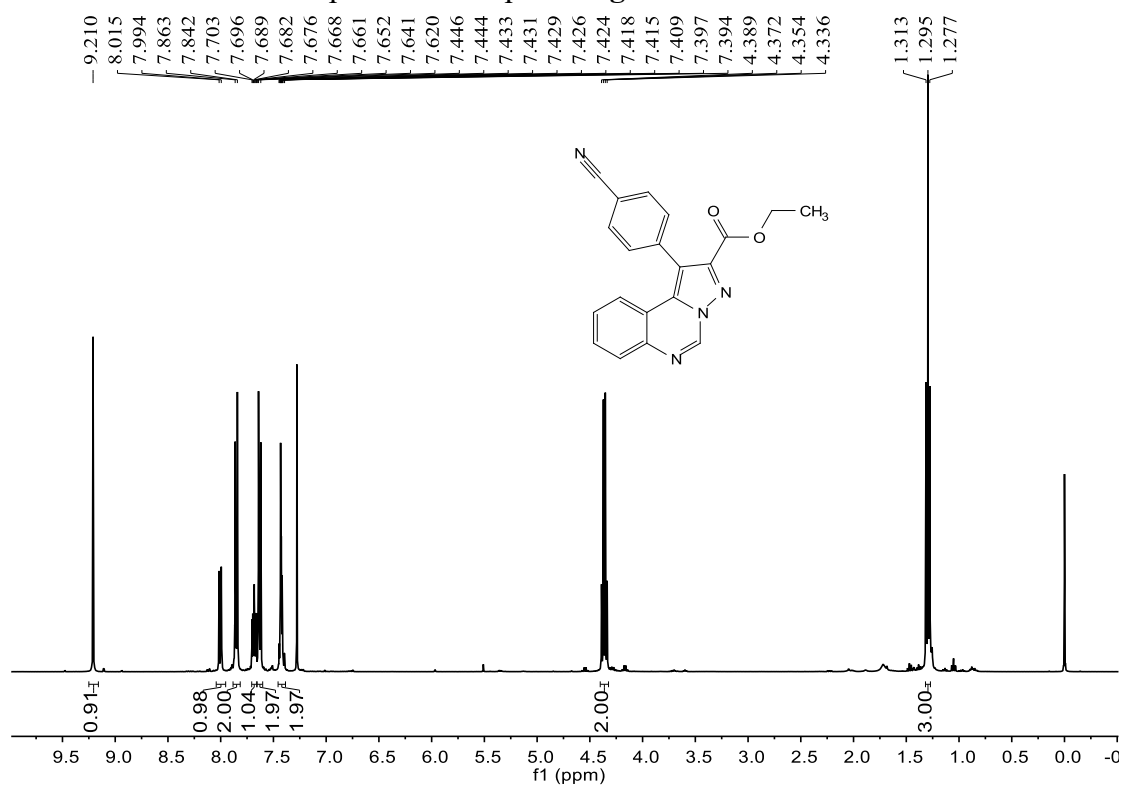
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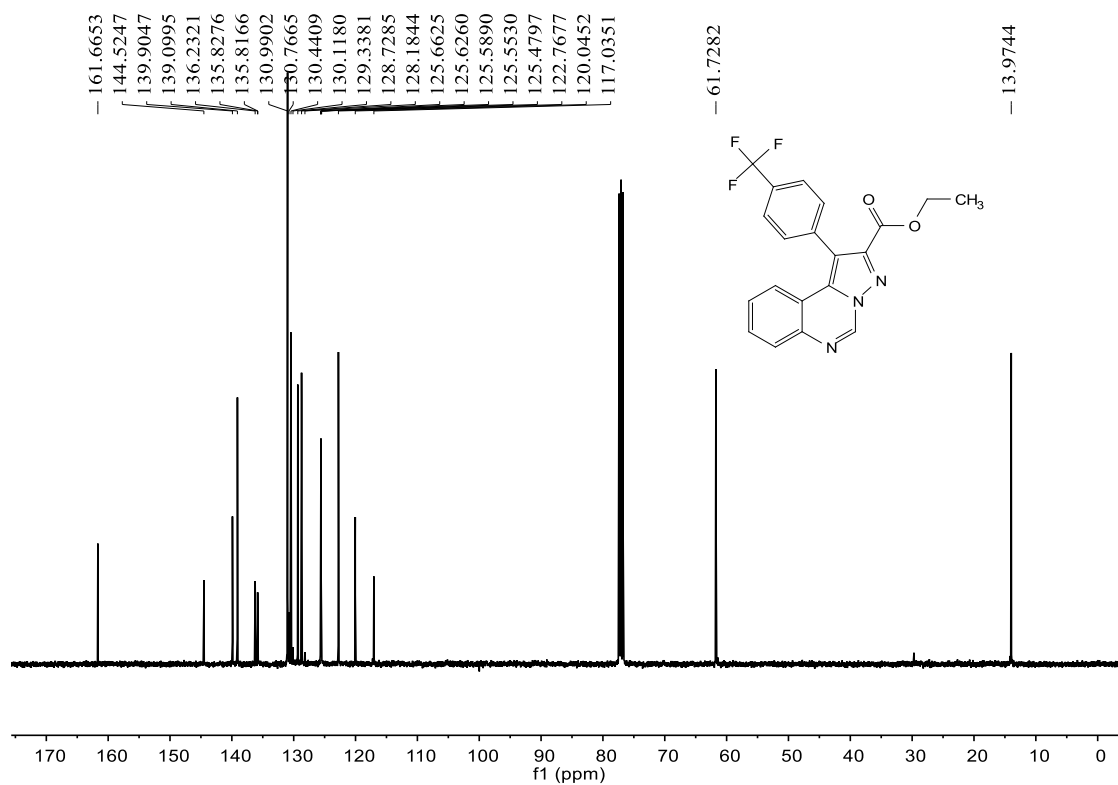
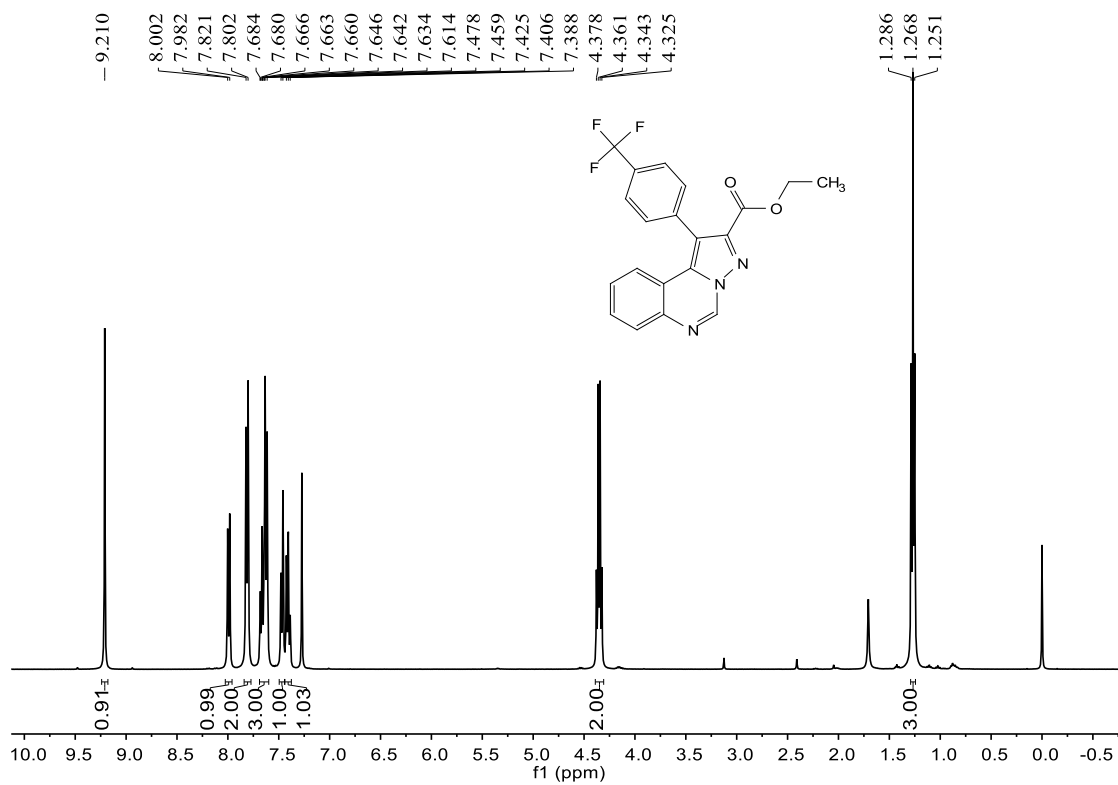
^1H NMR and ^{13}C NMR spectra of compound **3fa**



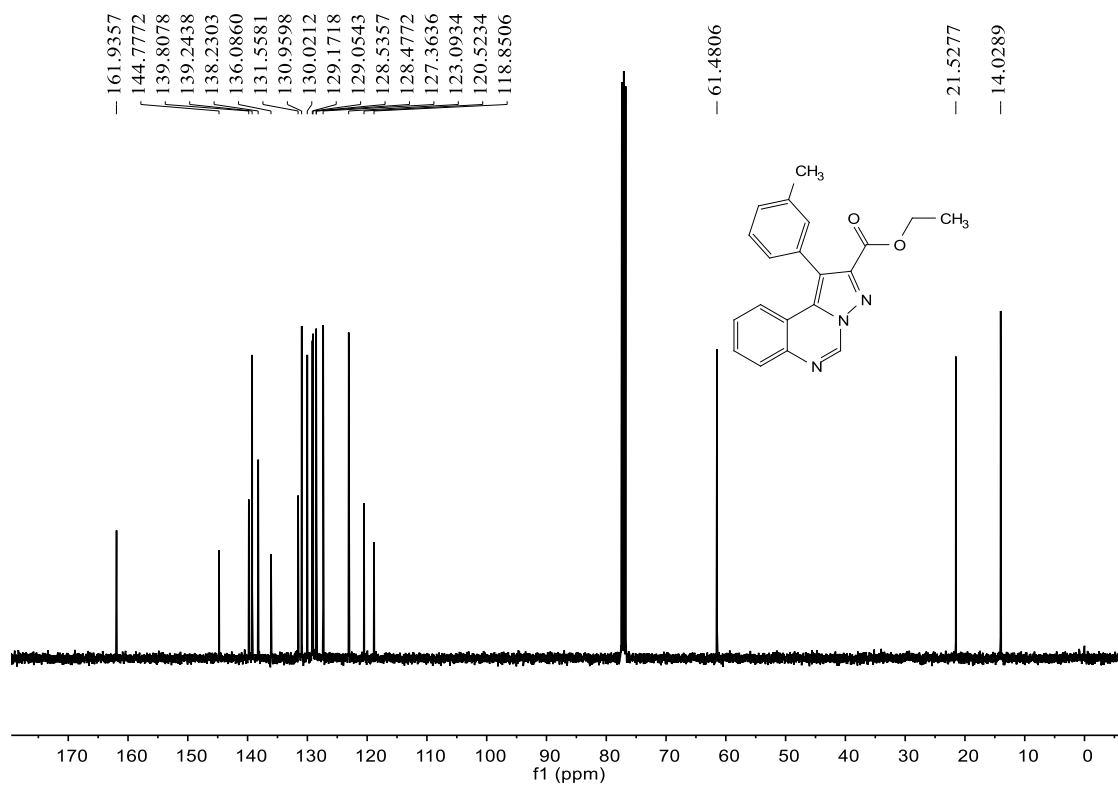
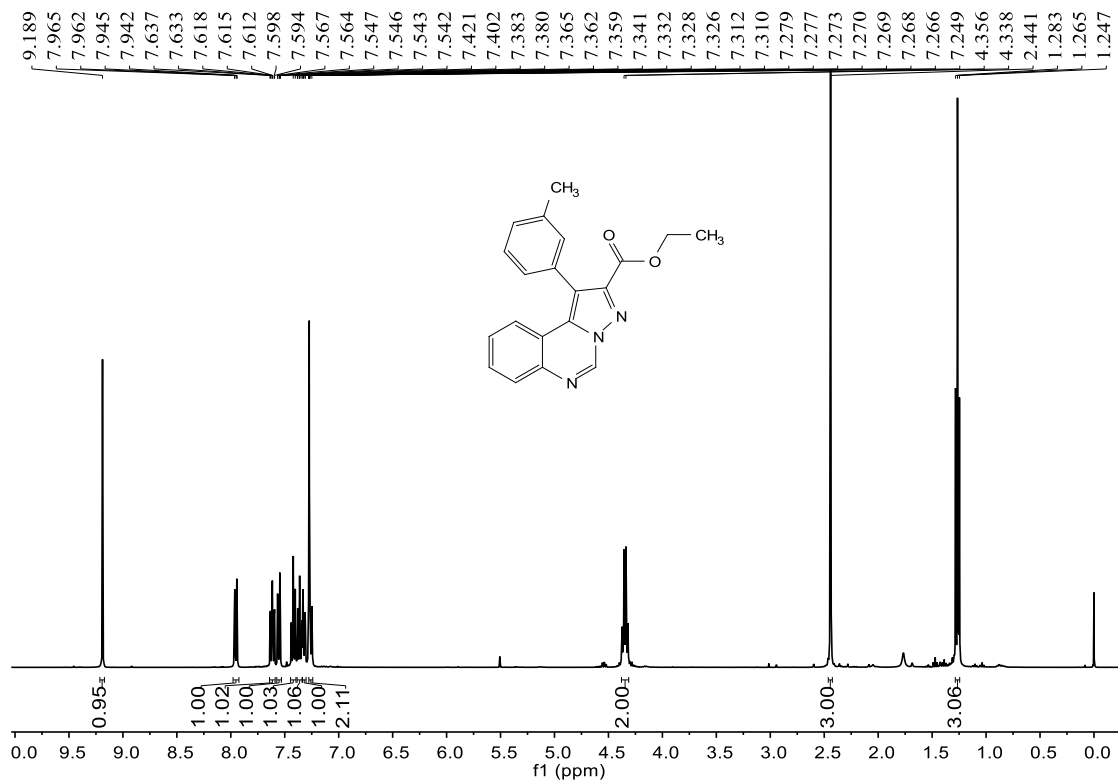
¹H NMR and ¹³C NMR spectra of compound **3ga**



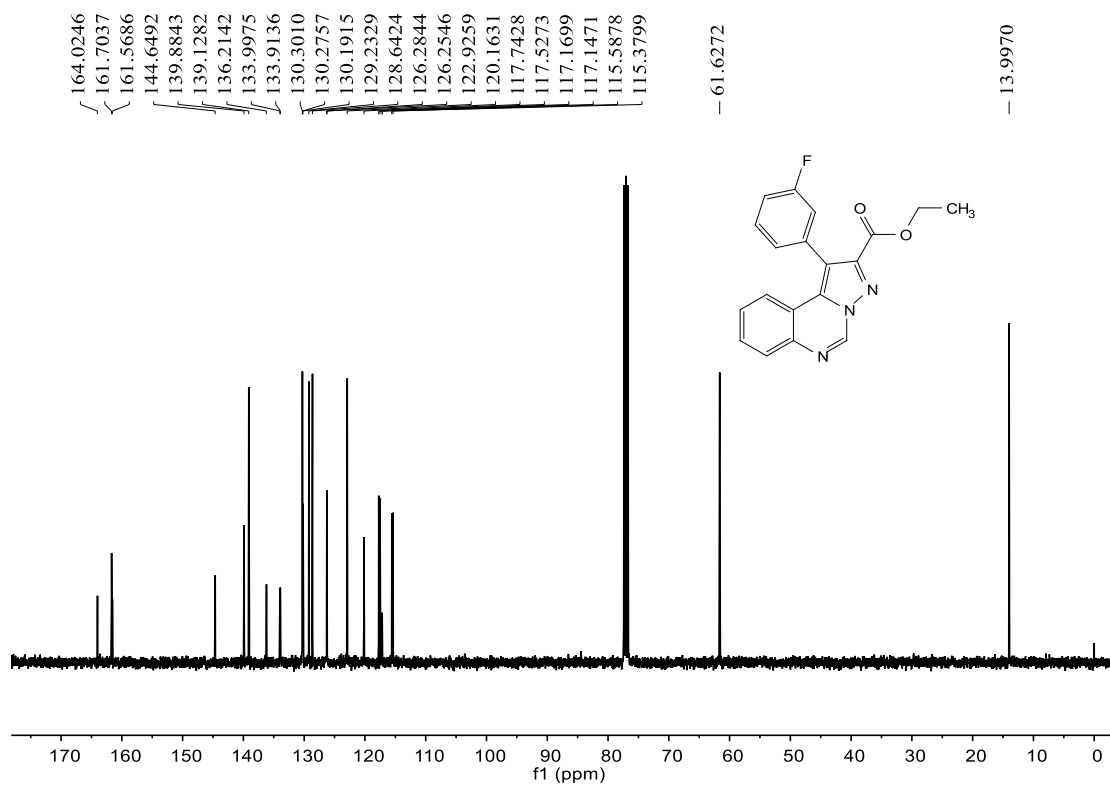
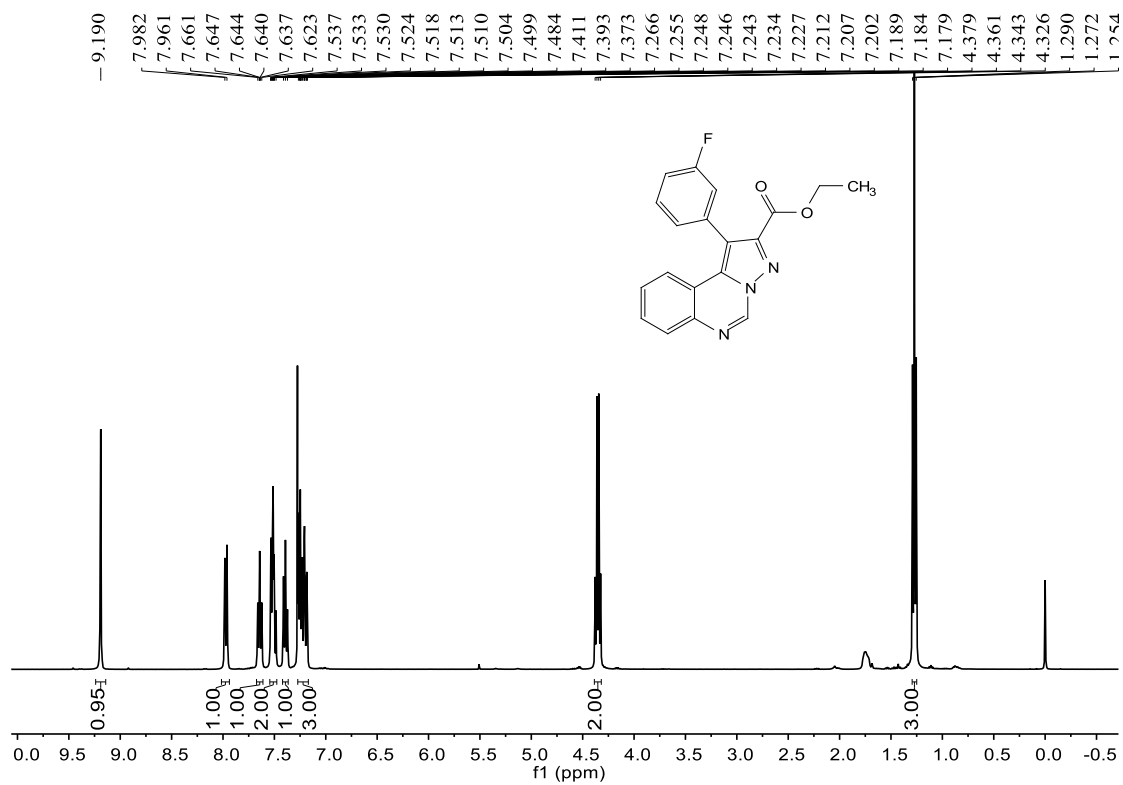
^1H NMR and ^{13}C NMR spectra of compound **3ha**



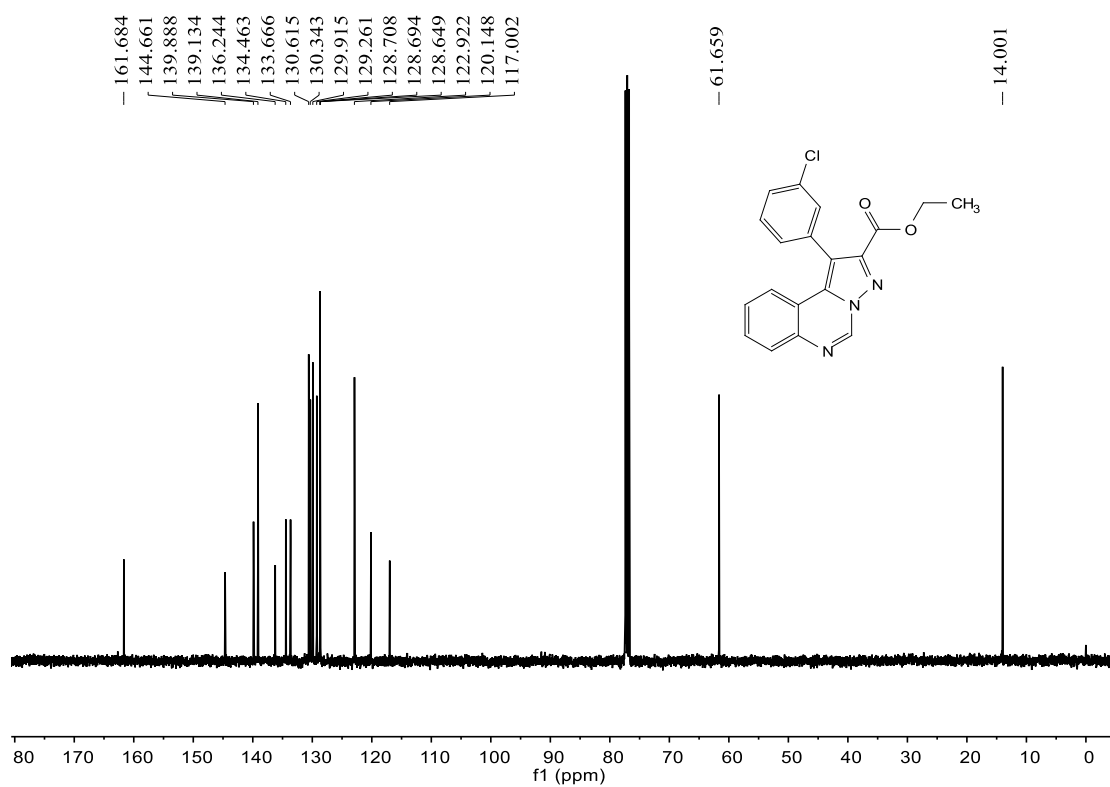
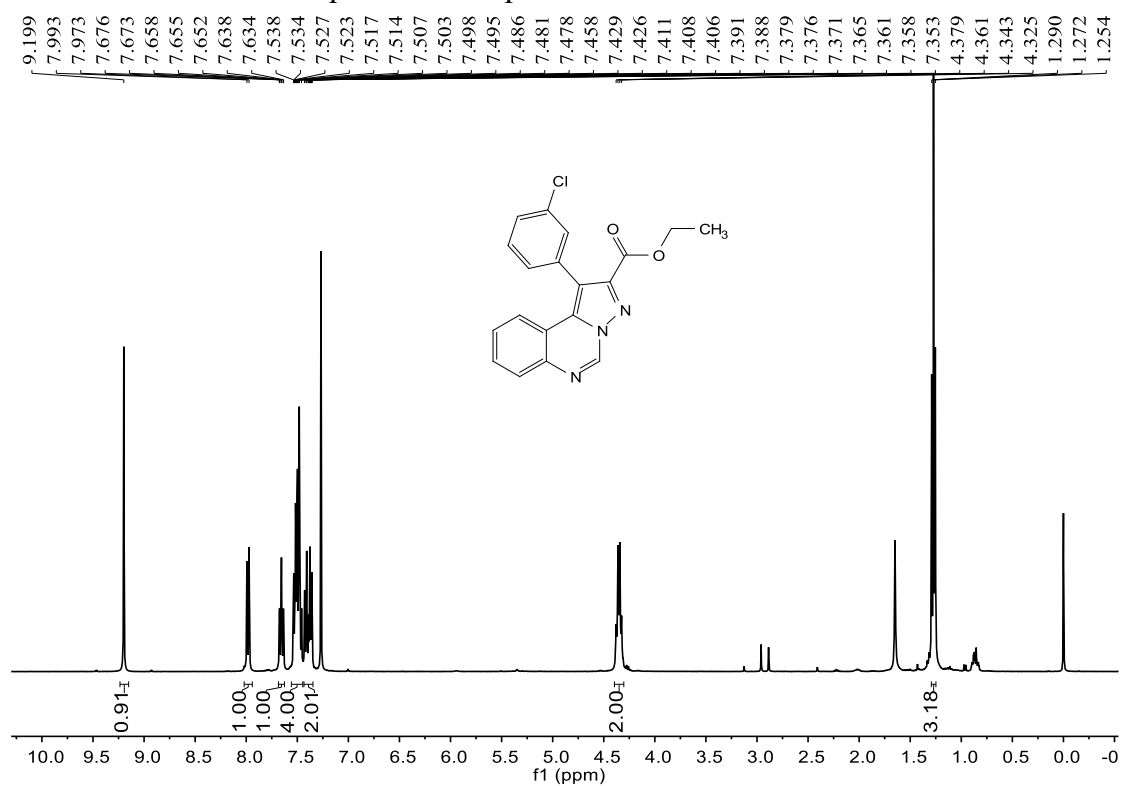
^1H NMR and ^{13}C NMR spectra of compound **3ia**



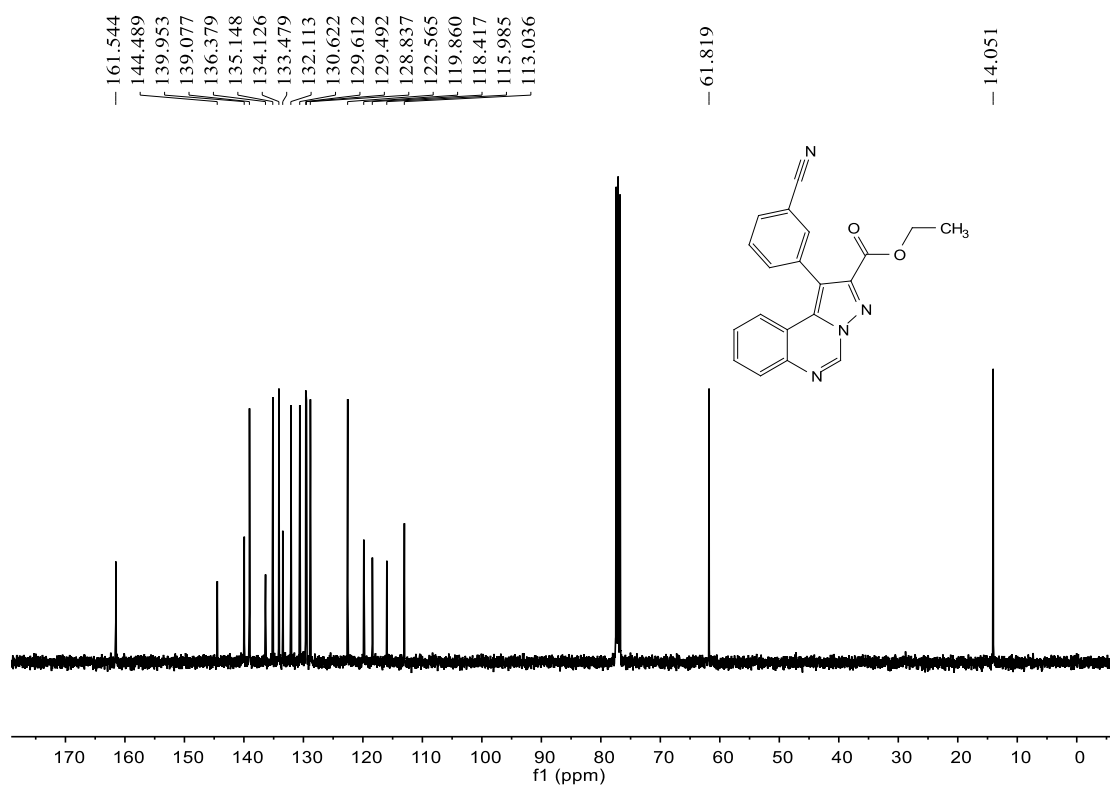
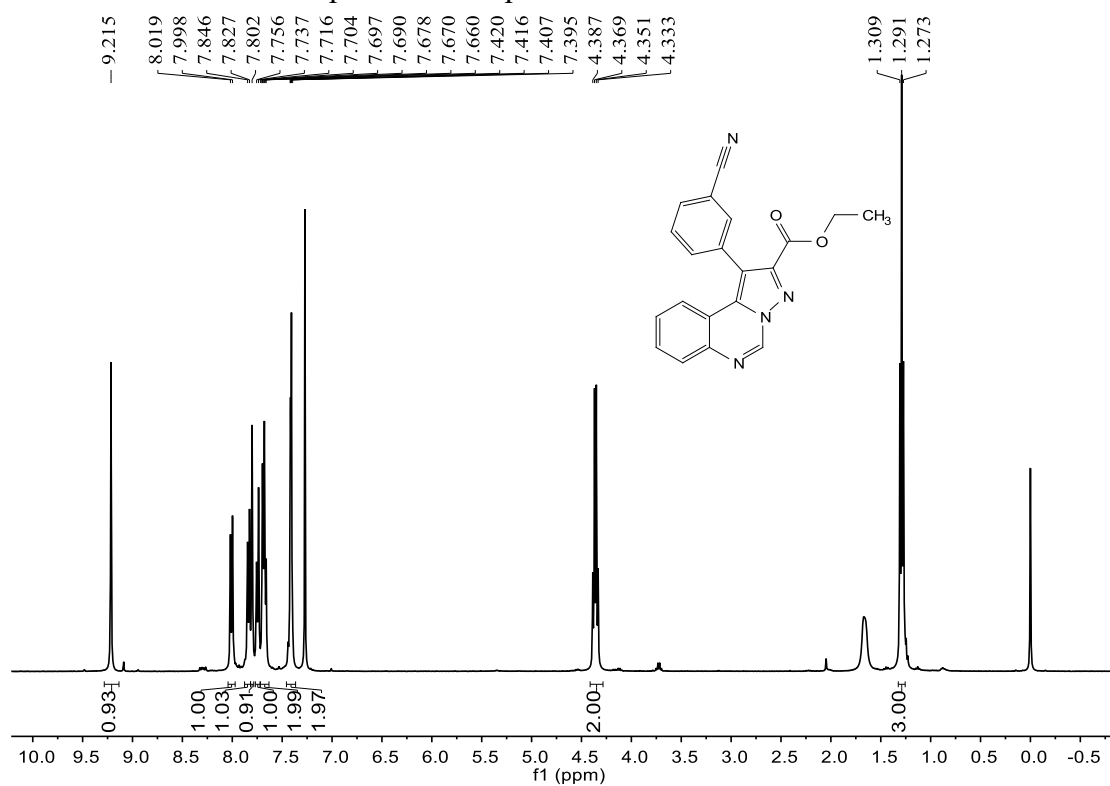
^1H NMR and ^{13}C NMR spectra of compound **3ja**



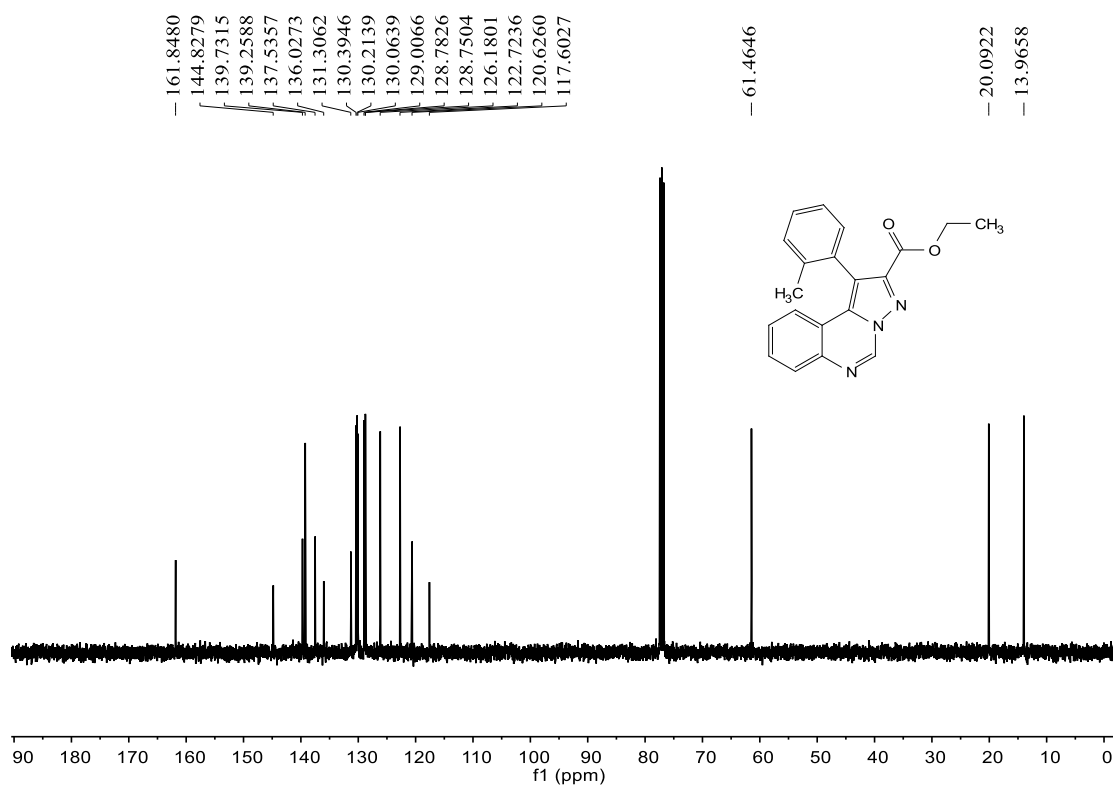
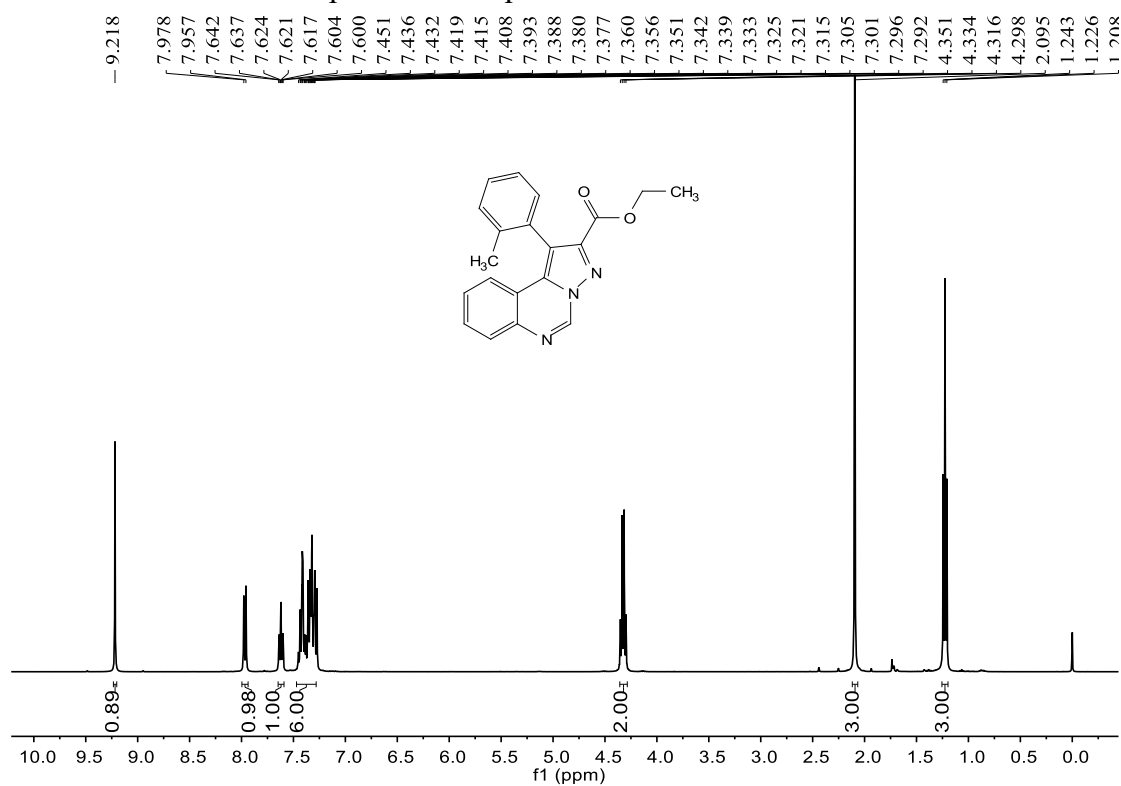
¹H NMR and ¹³C NMR spectra of compound **3ka**



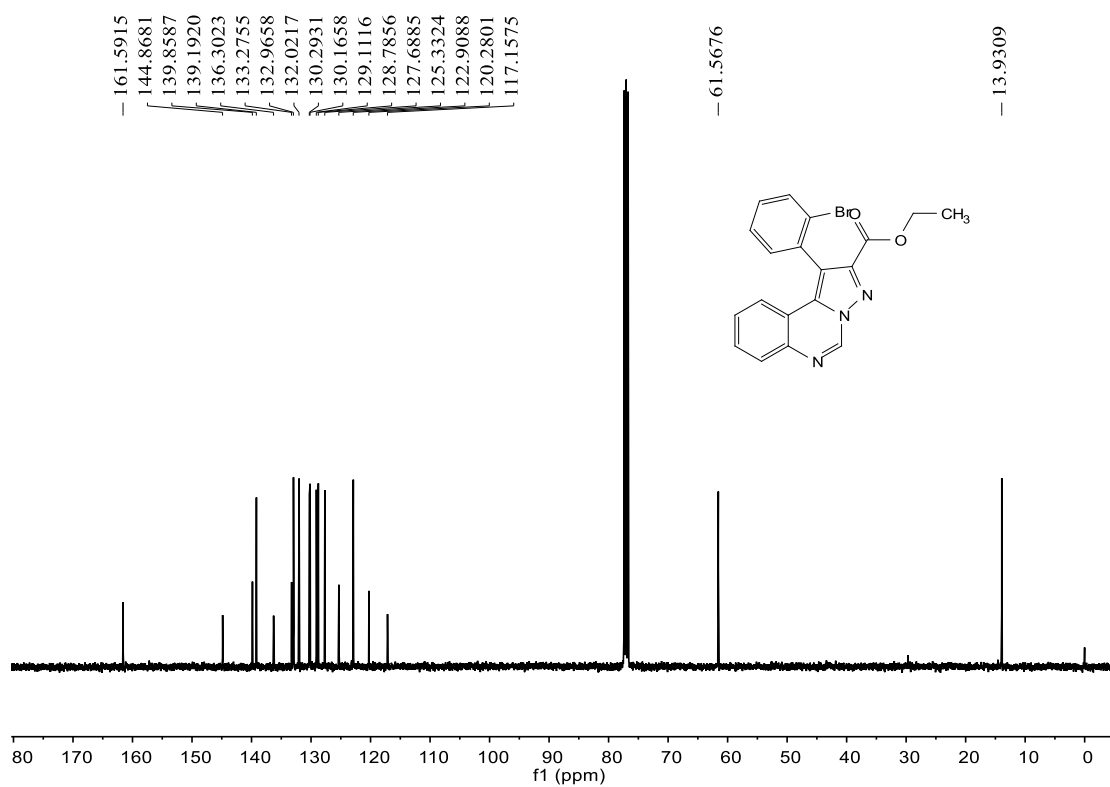
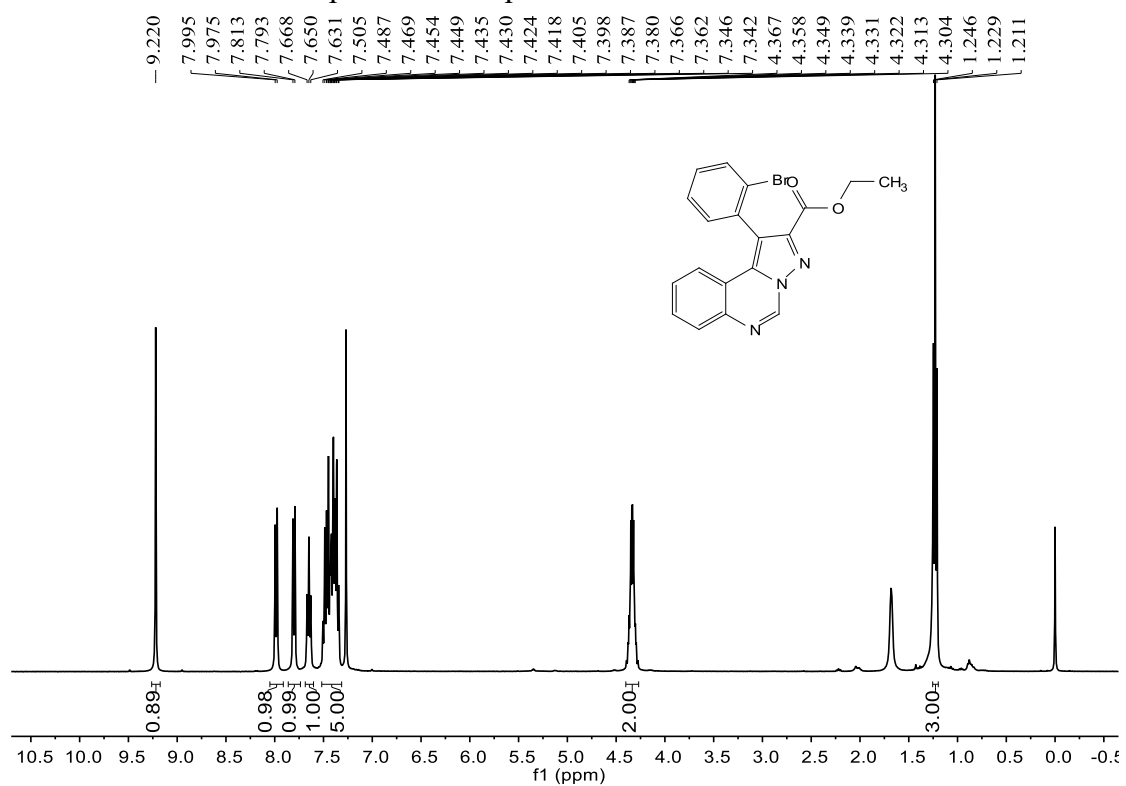
^1H NMR and ^{13}C NMR spectra of compound **3la**



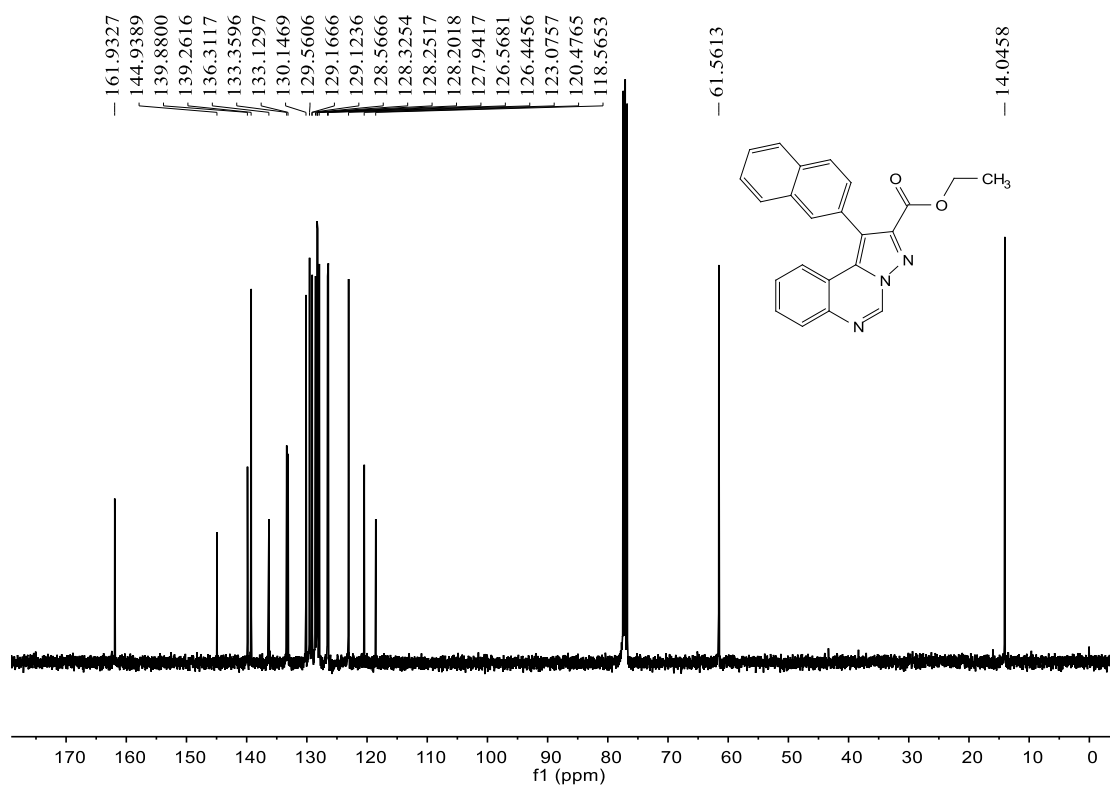
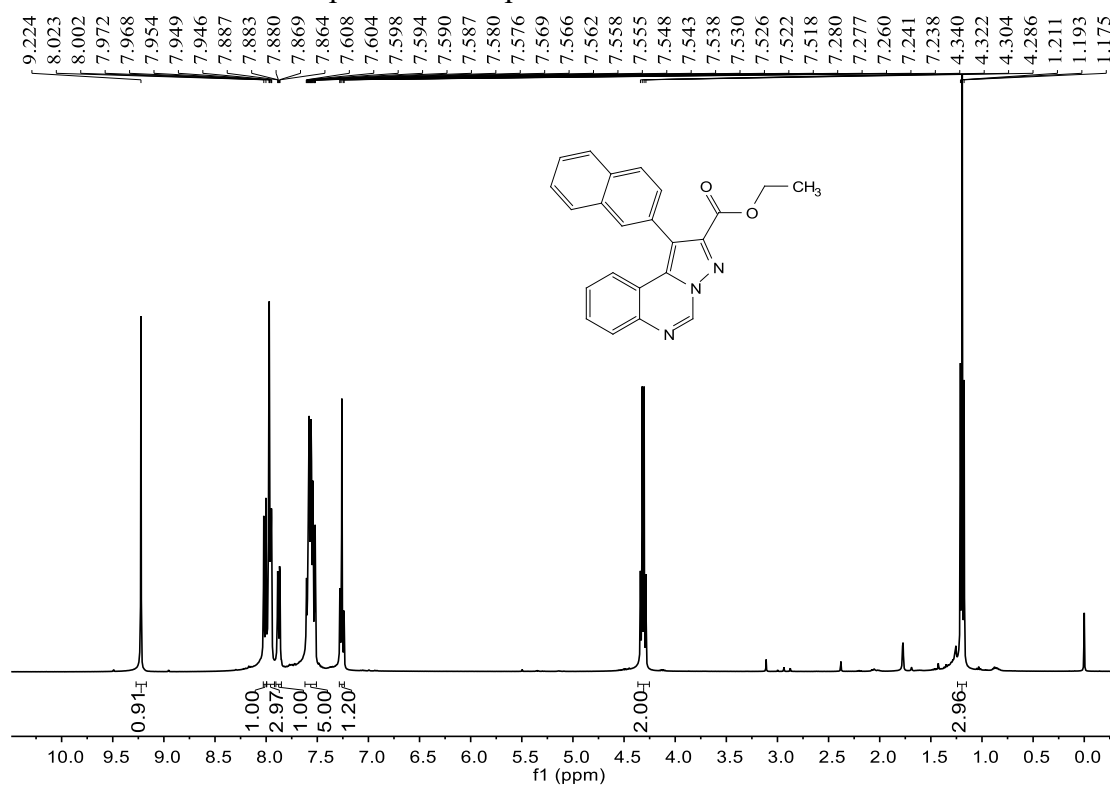
^1H NMR and ^{13}C NMR spectra of compound **3ma**



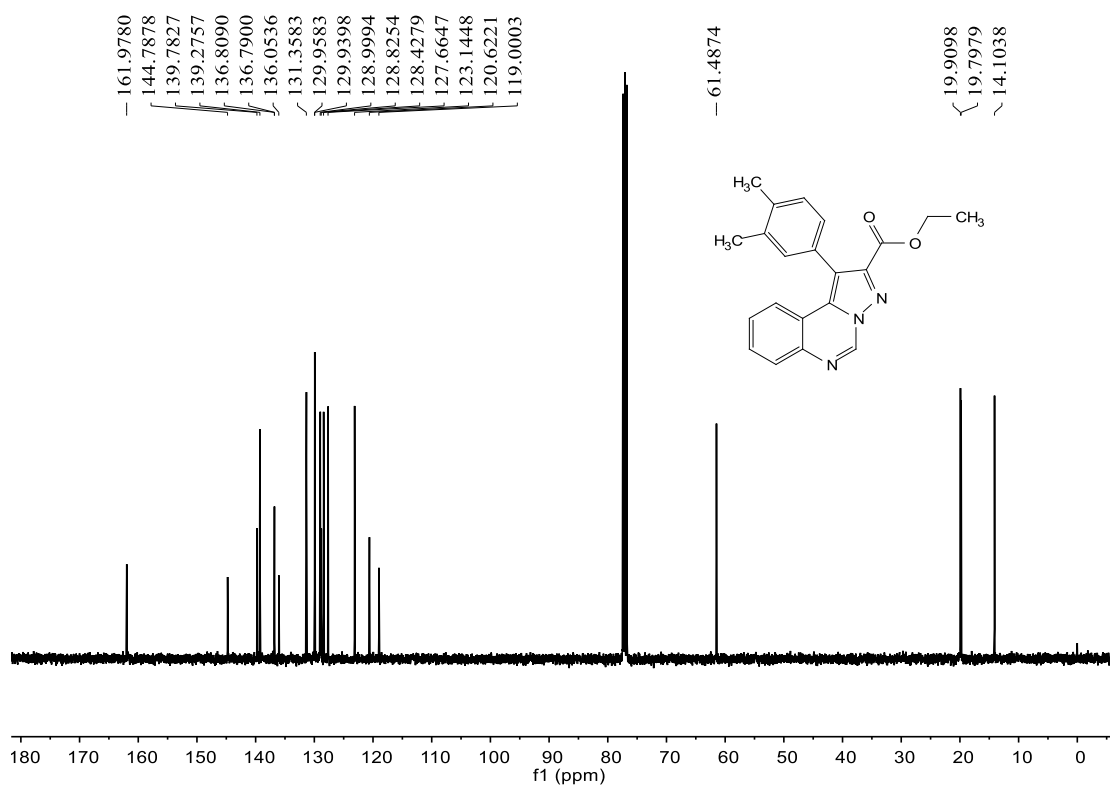
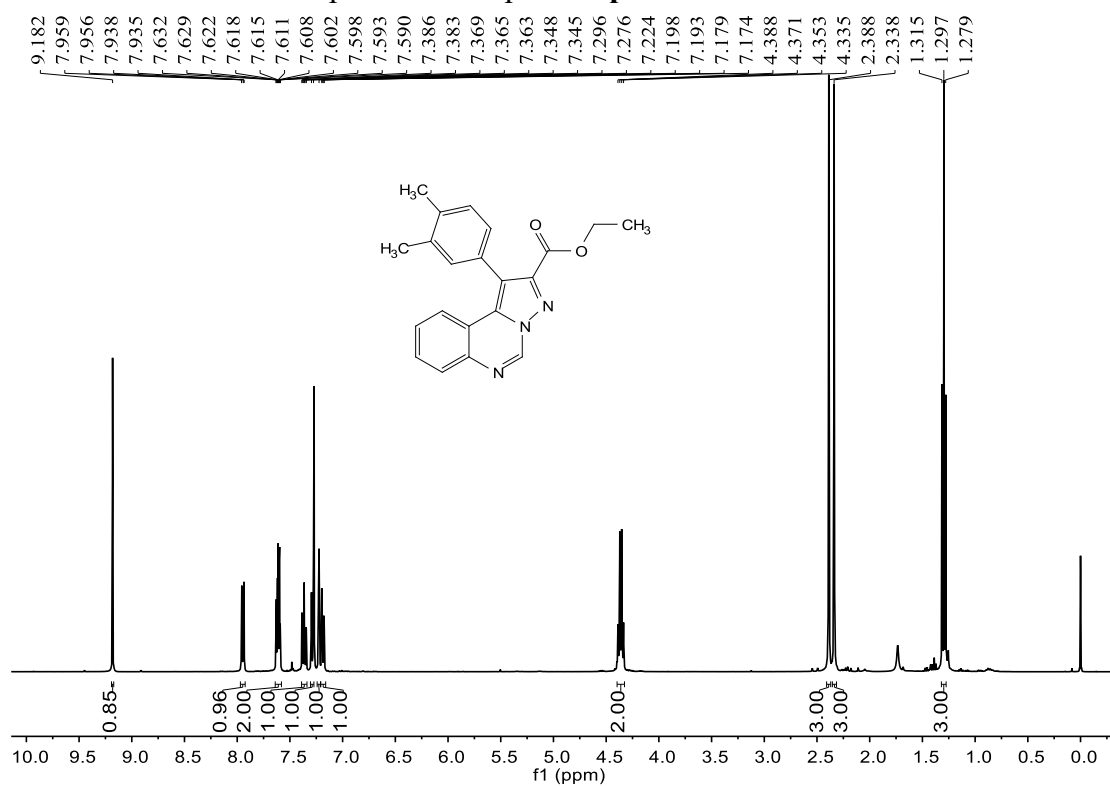
^1H NMR and ^{13}C NMR spectra of compound **3na**



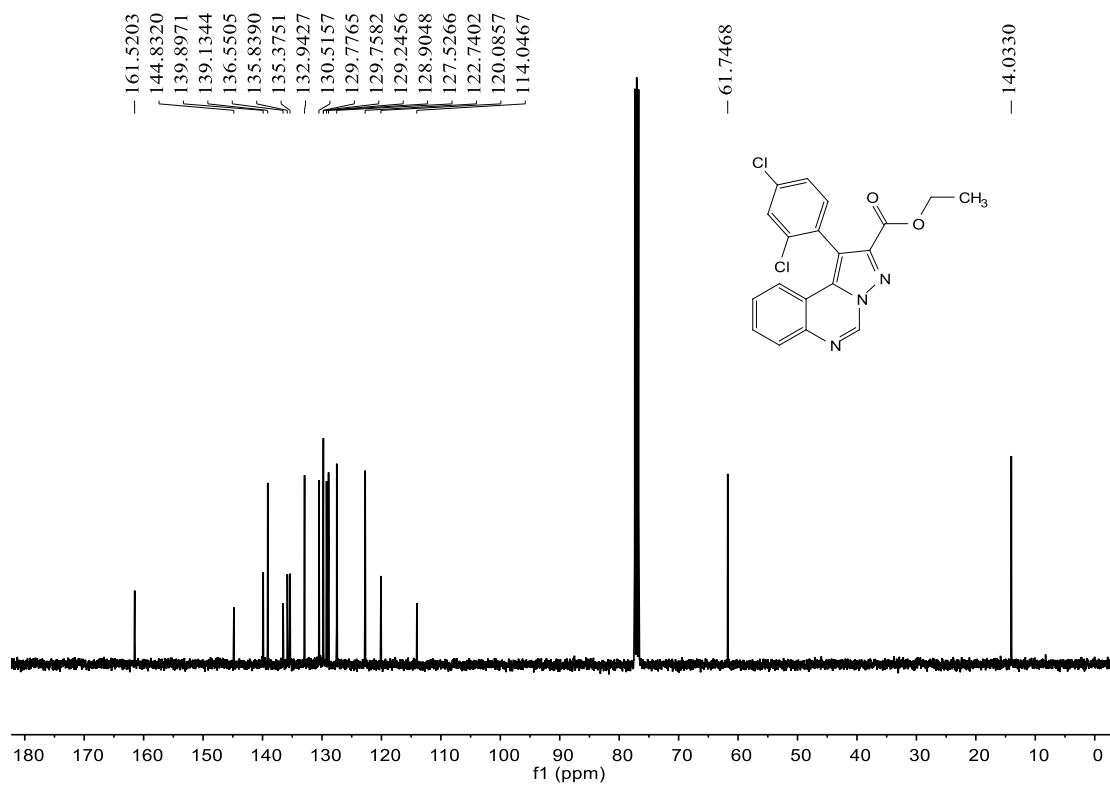
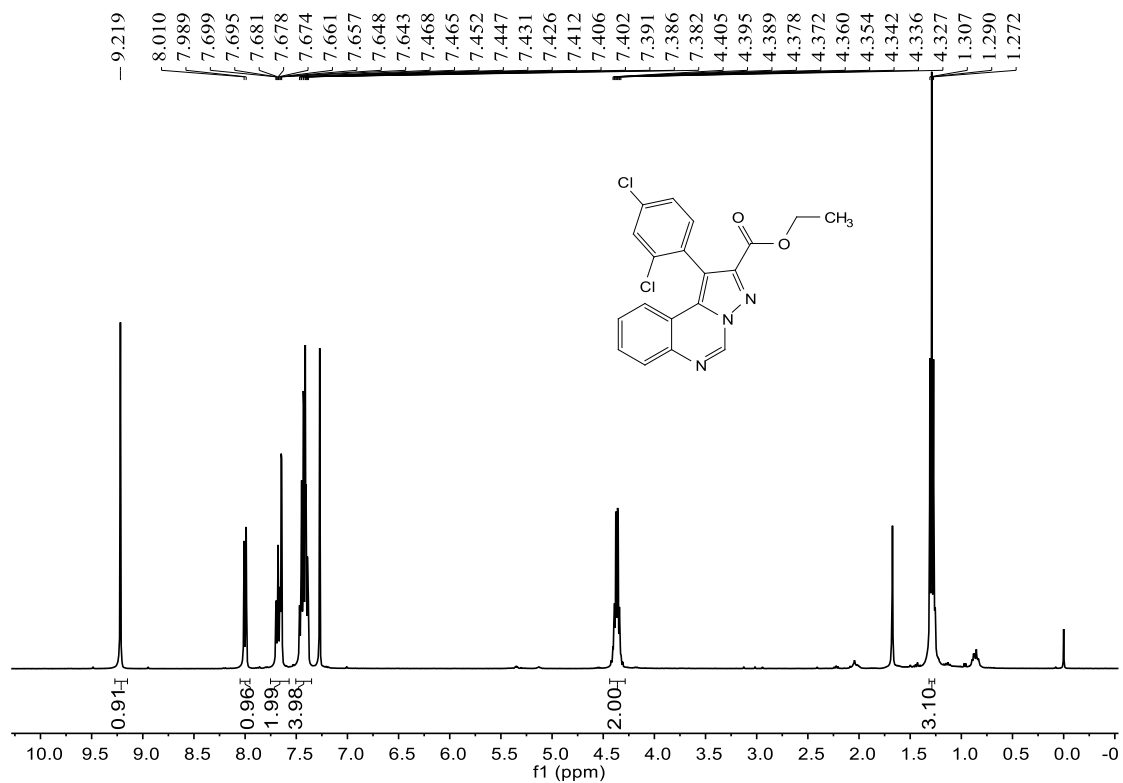
^1H NMR and ^{13}C NMR spectra of compound **30a**



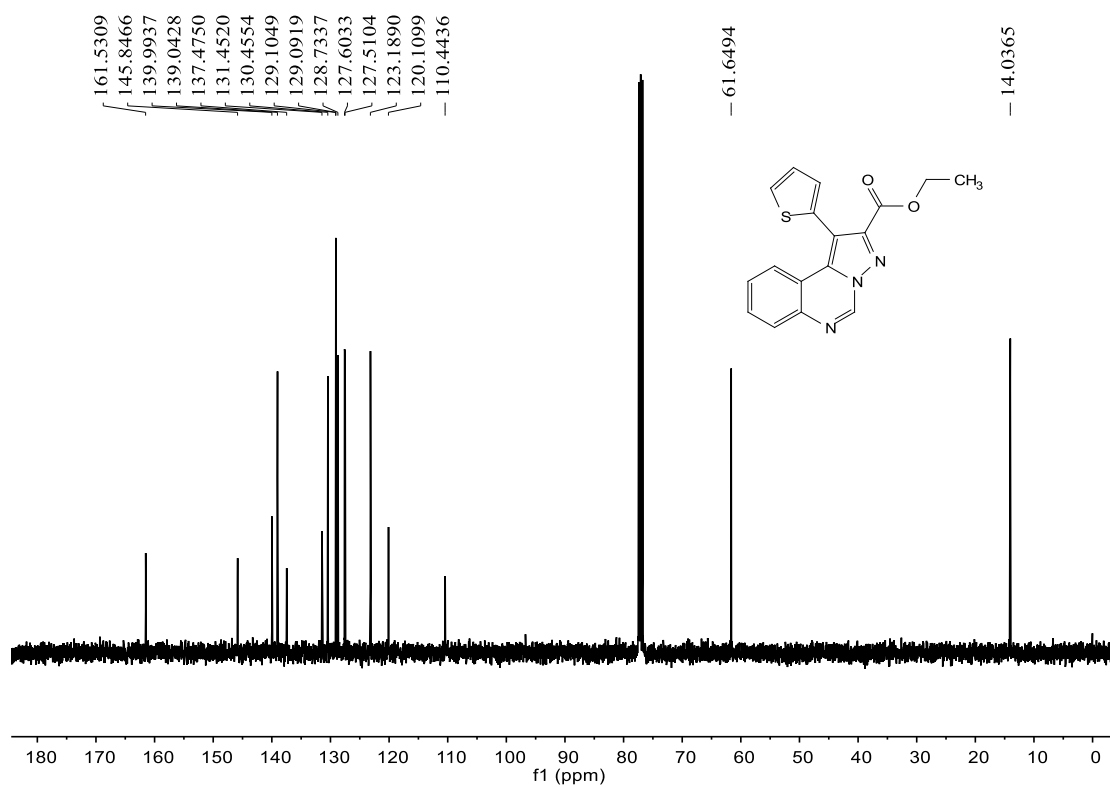
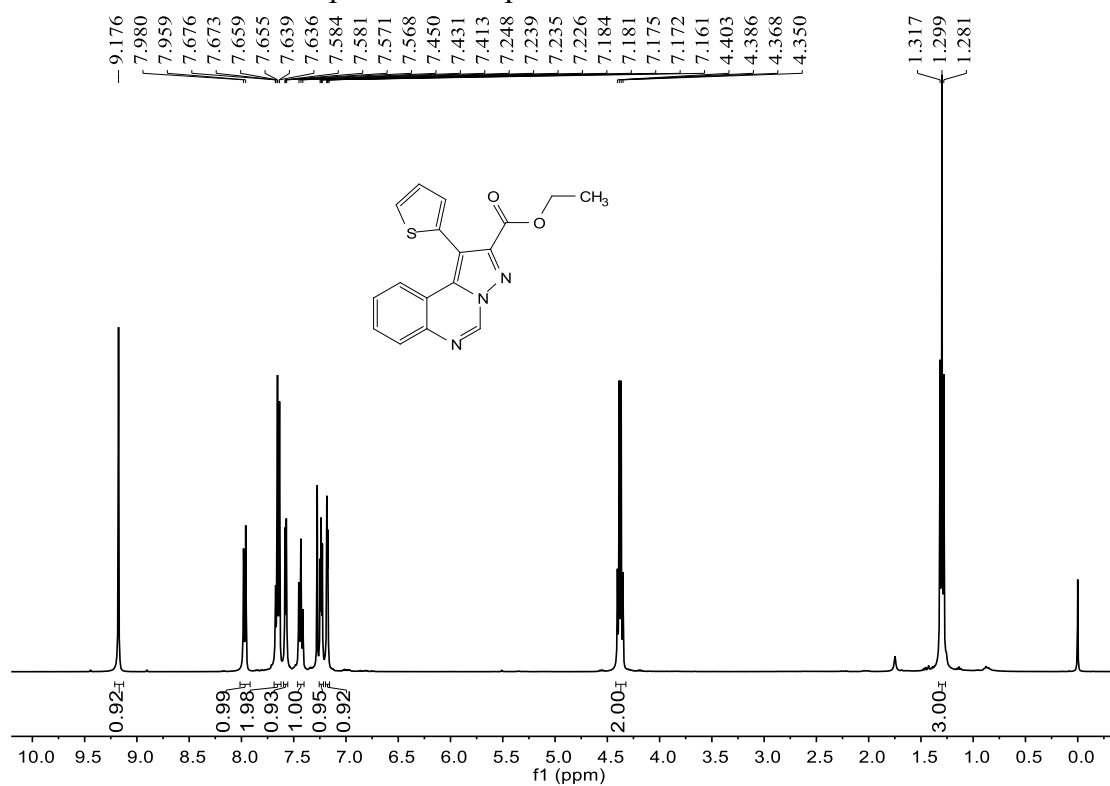
^1H NMR and ^{13}C NMR spectra of compound **3pa**



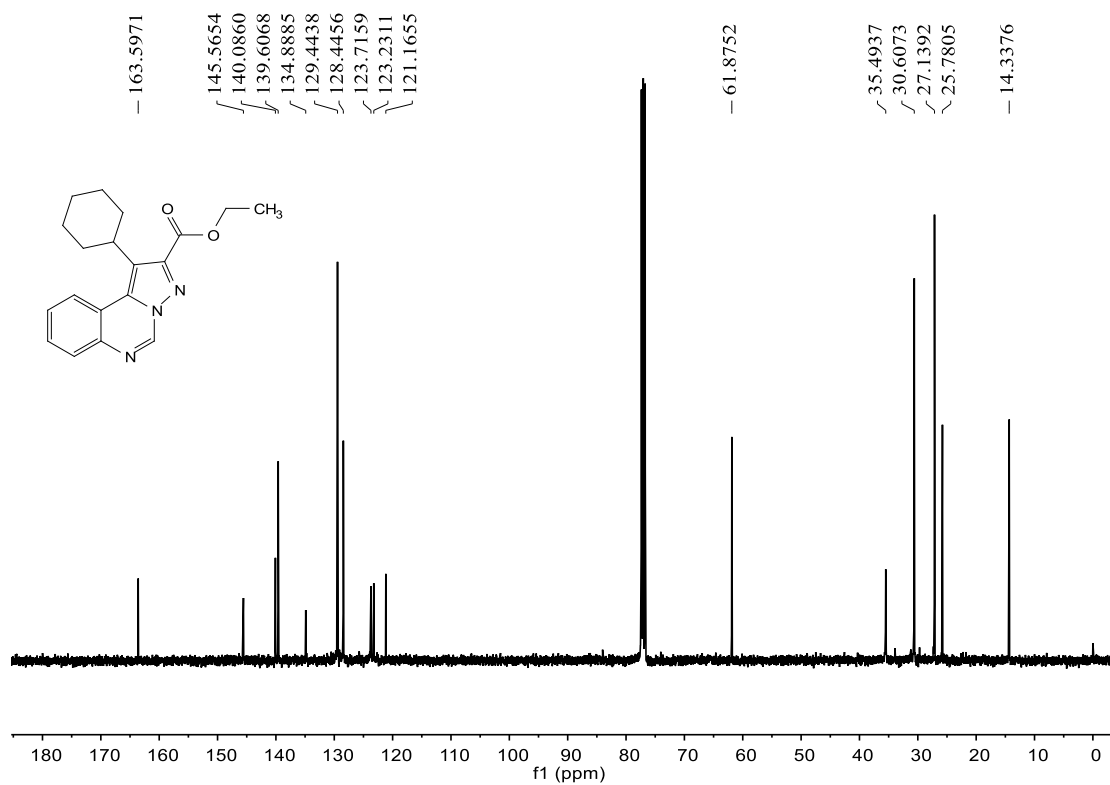
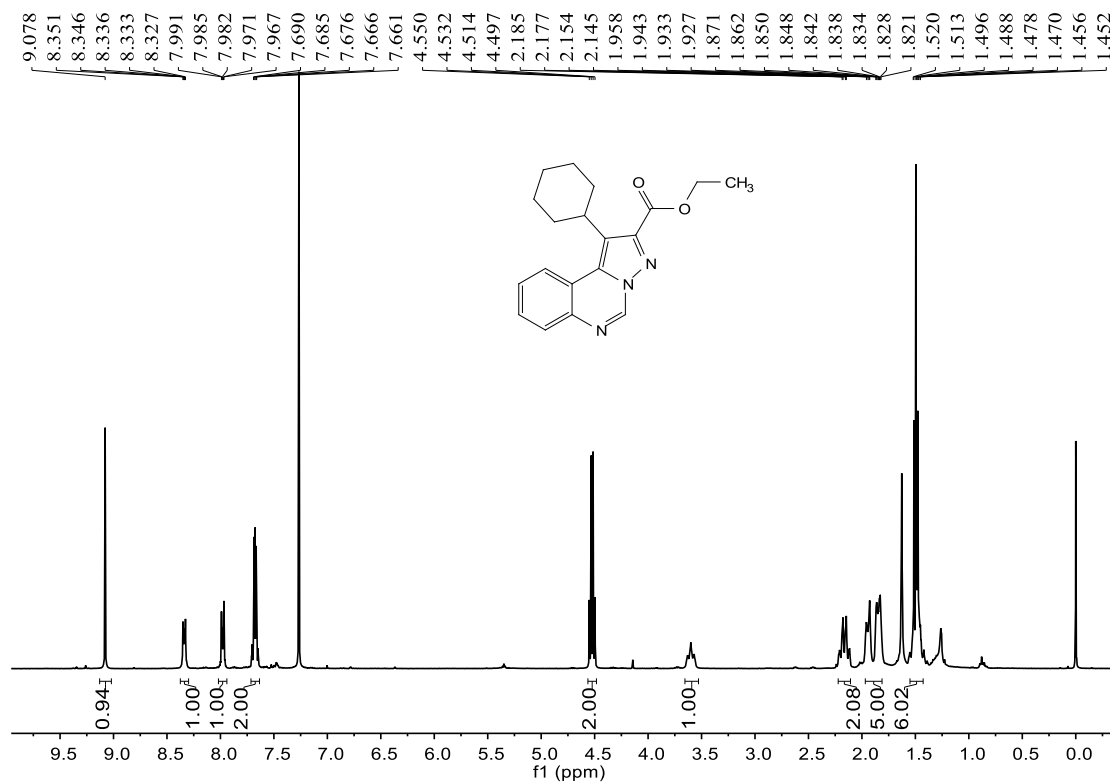
^1H NMR and ^{13}C NMR spectra of compound **3qa**



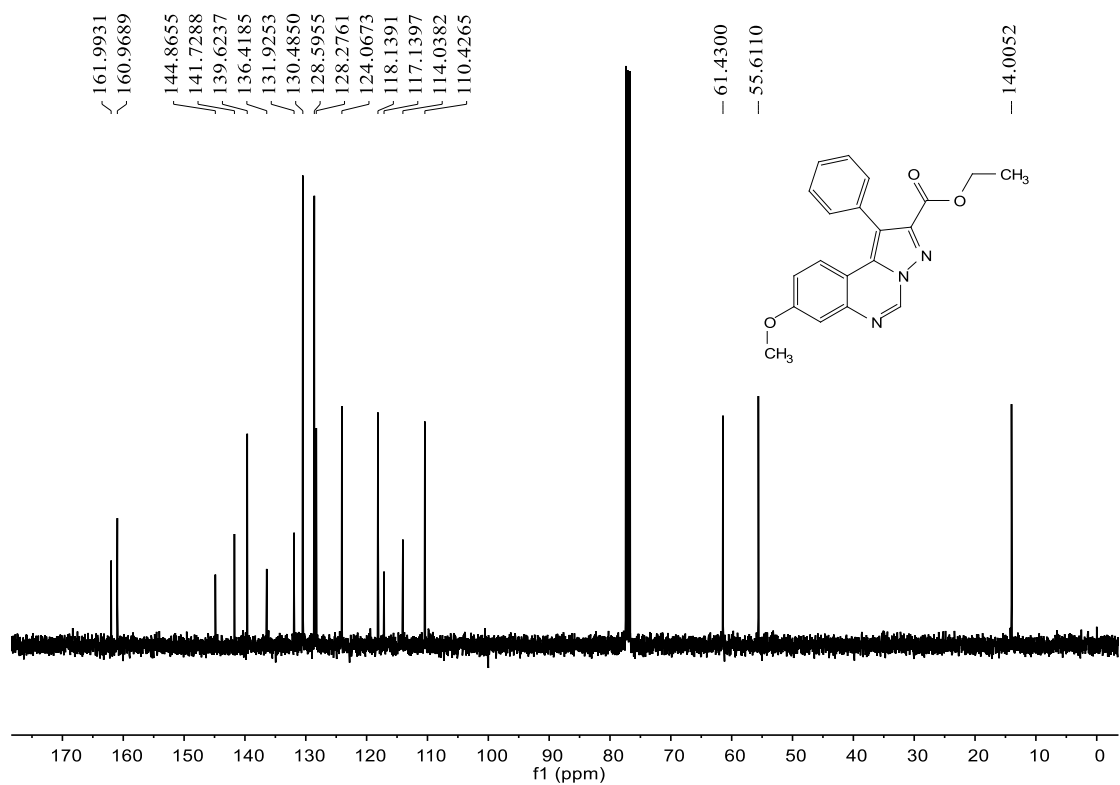
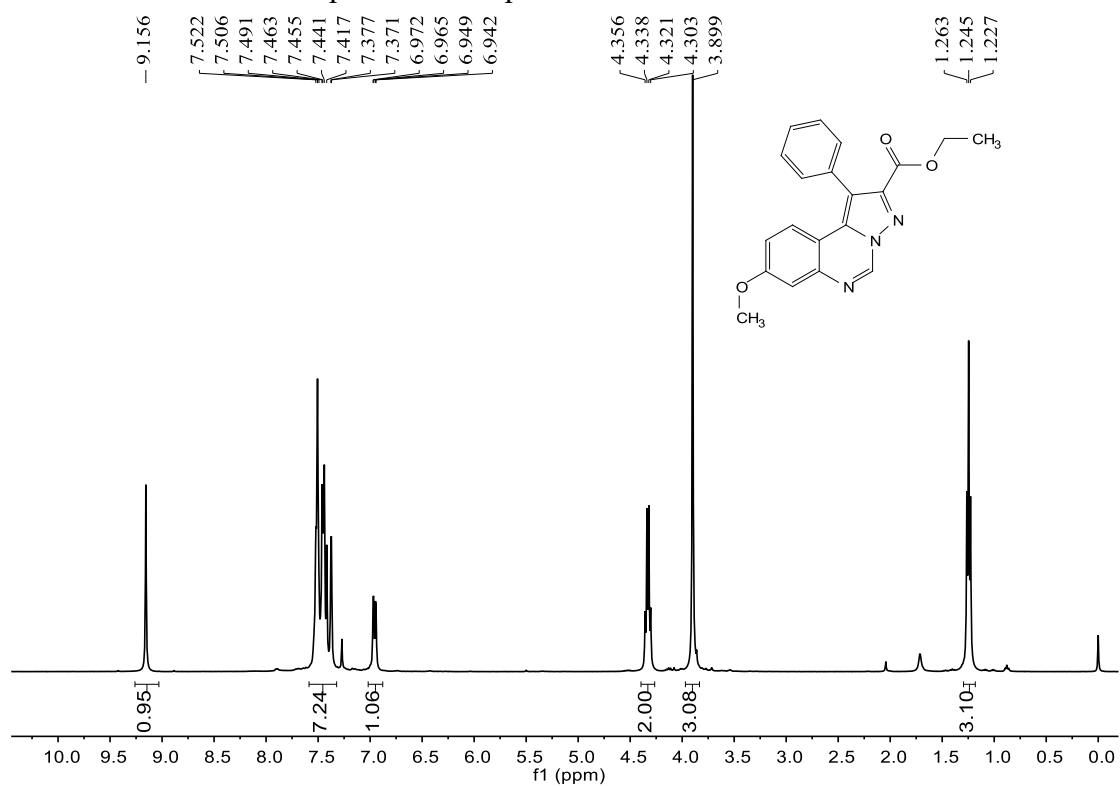
^1H NMR and ^{13}C NMR spectra of compound **3ra**



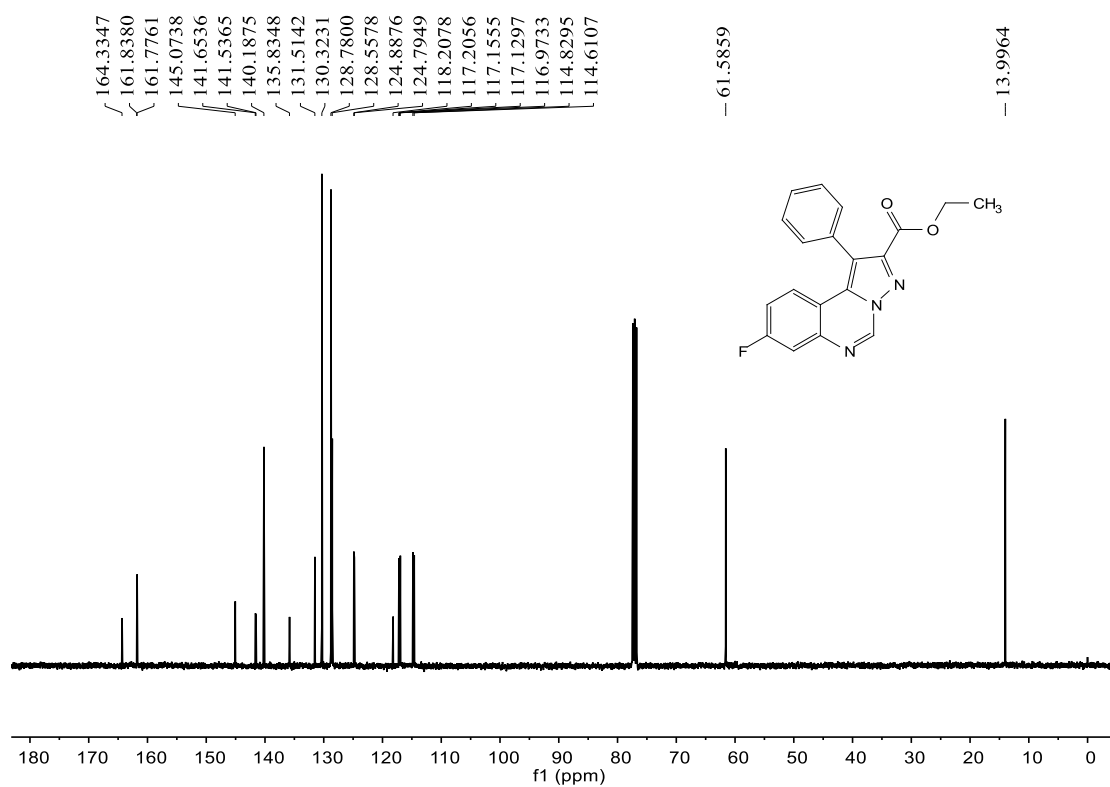
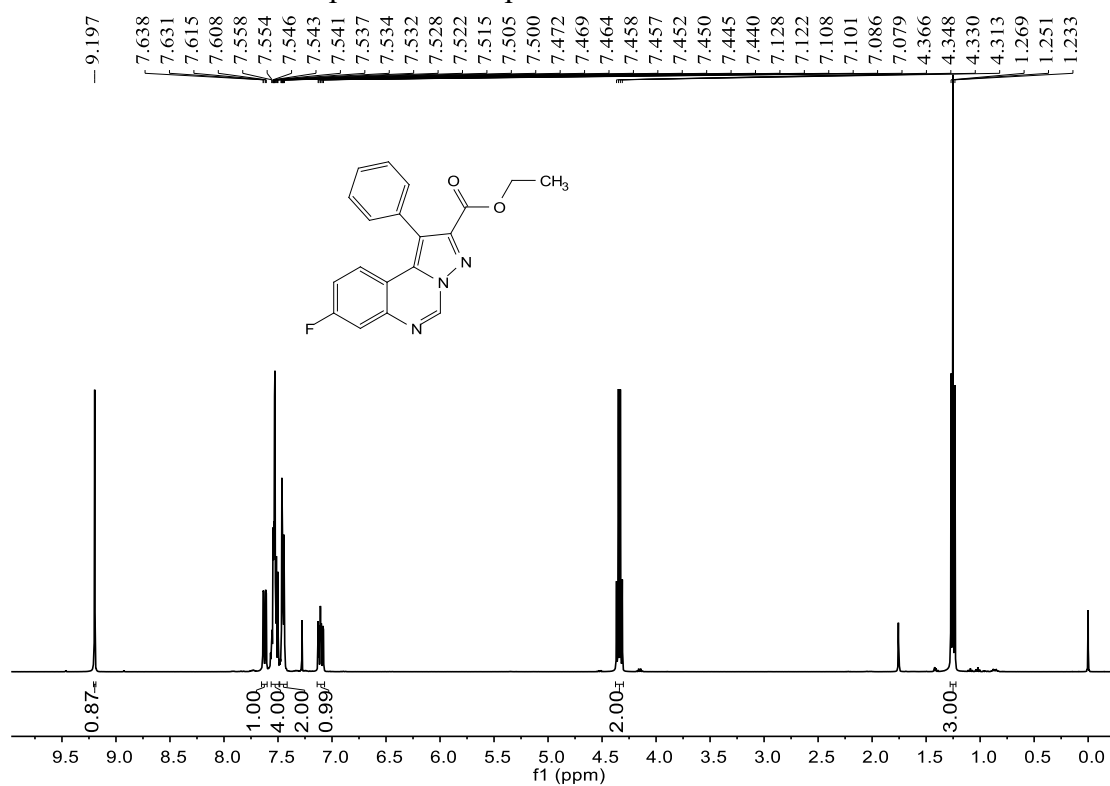
¹H NMR and ¹³C NMR spectra of compound **3sa**



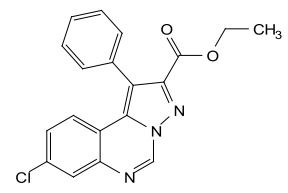
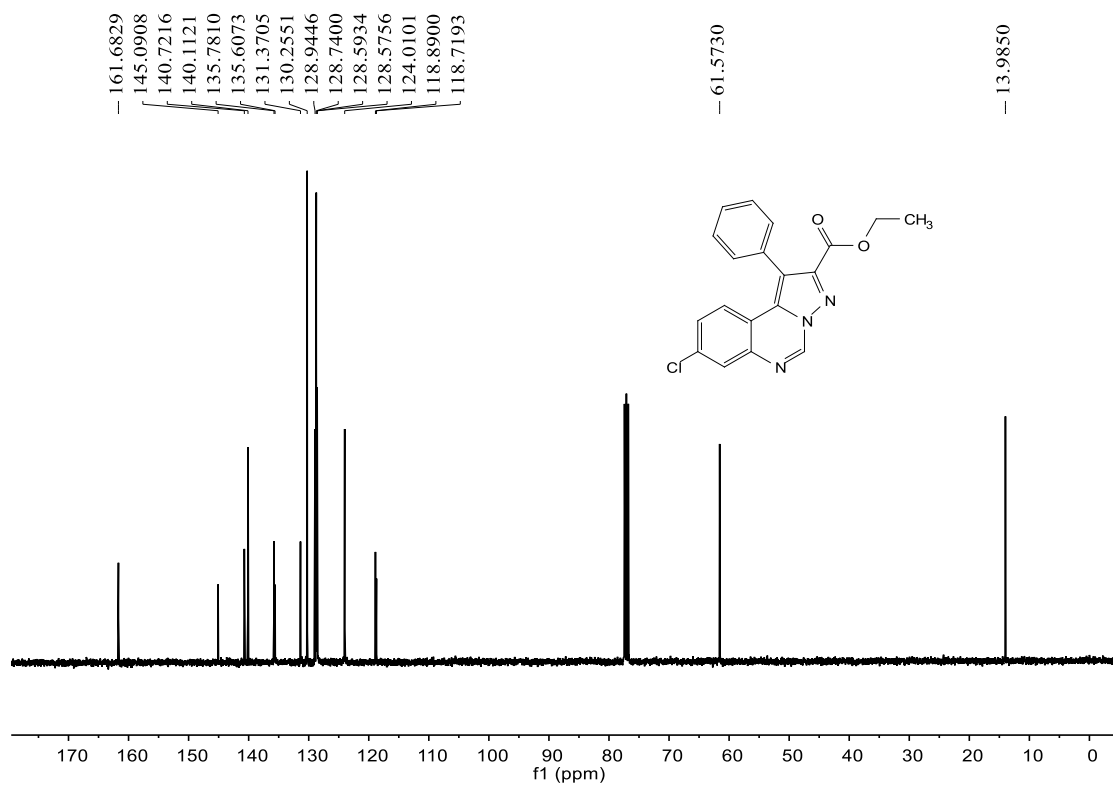
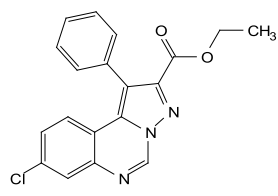
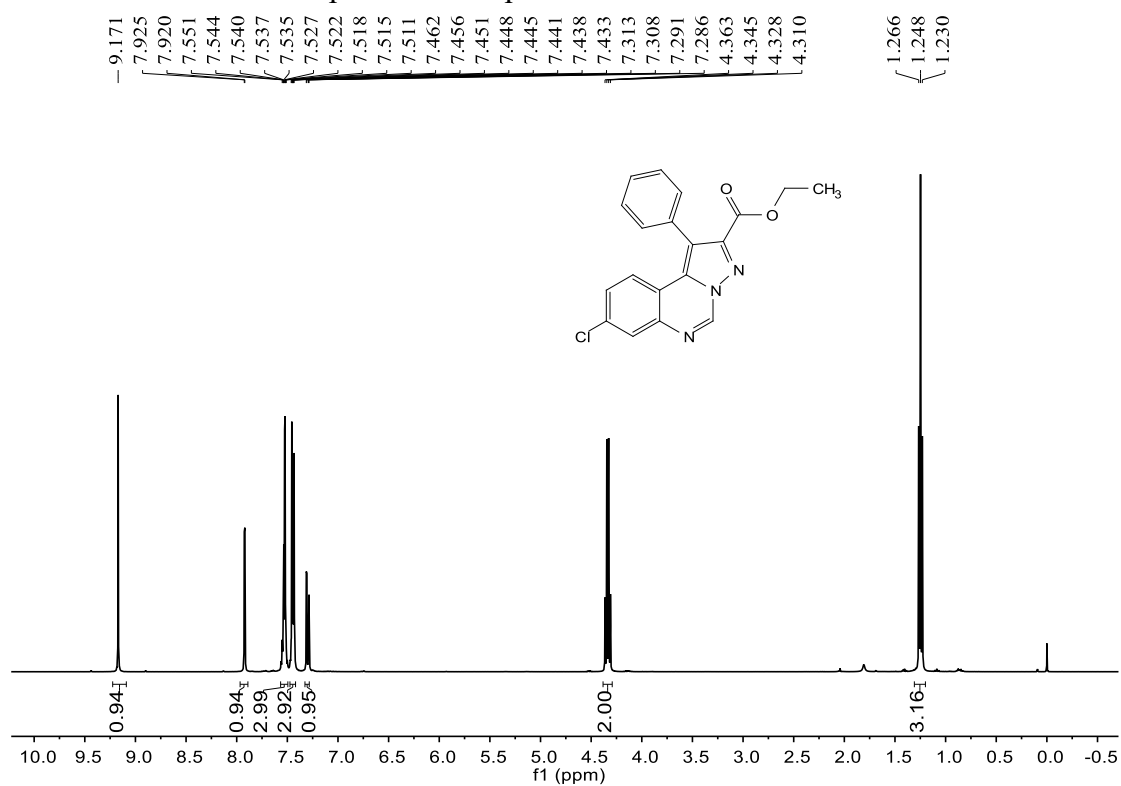
^1H NMR and ^{13}C NMR spectra of compound **3ta**



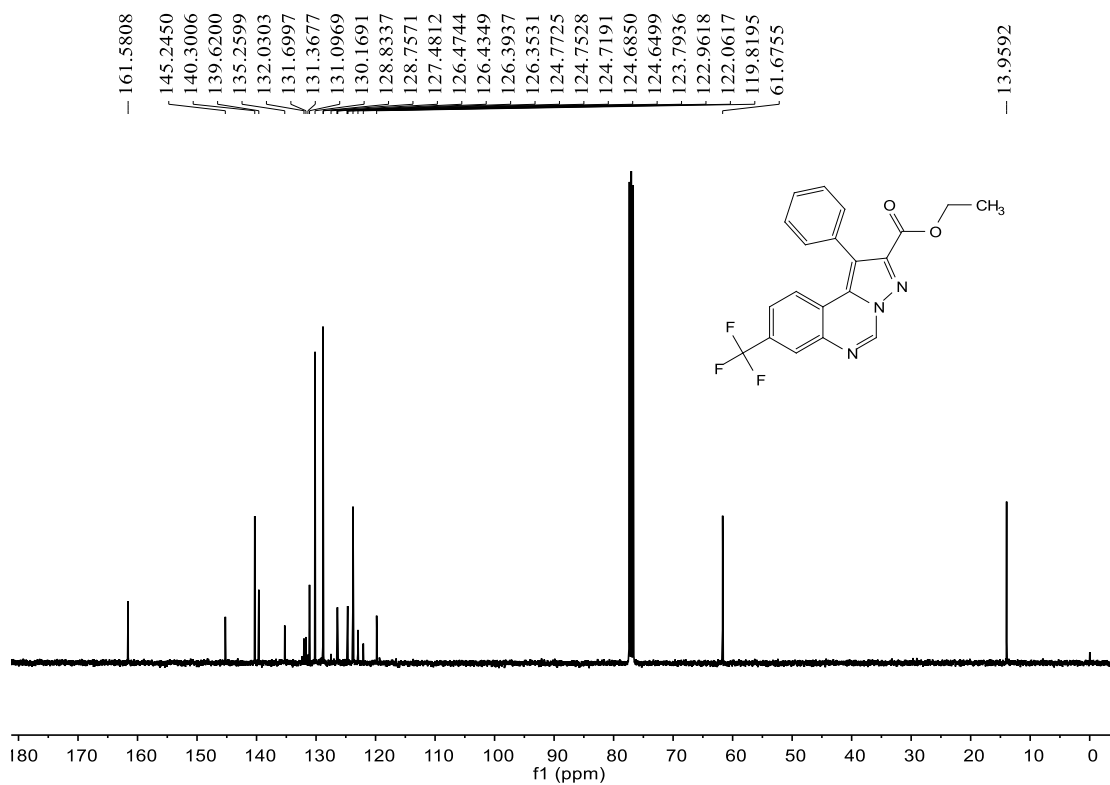
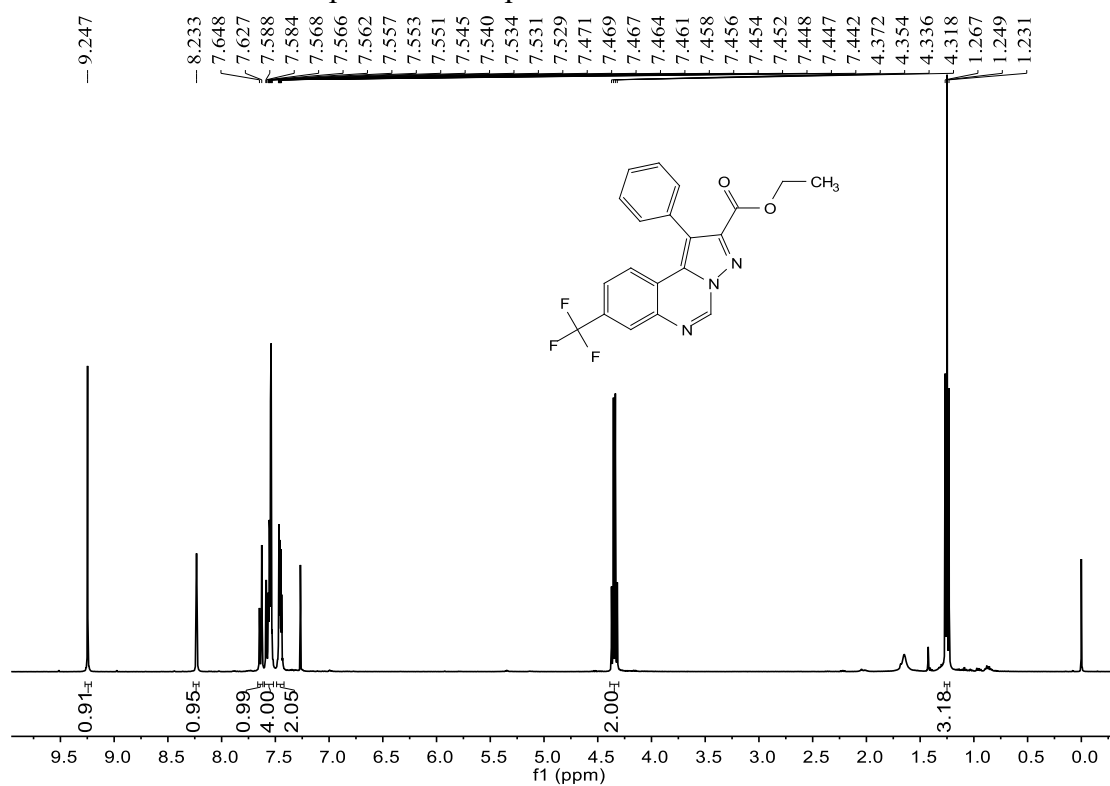
^1H NMR and ^{13}C NMR spectra of compound **3ua**



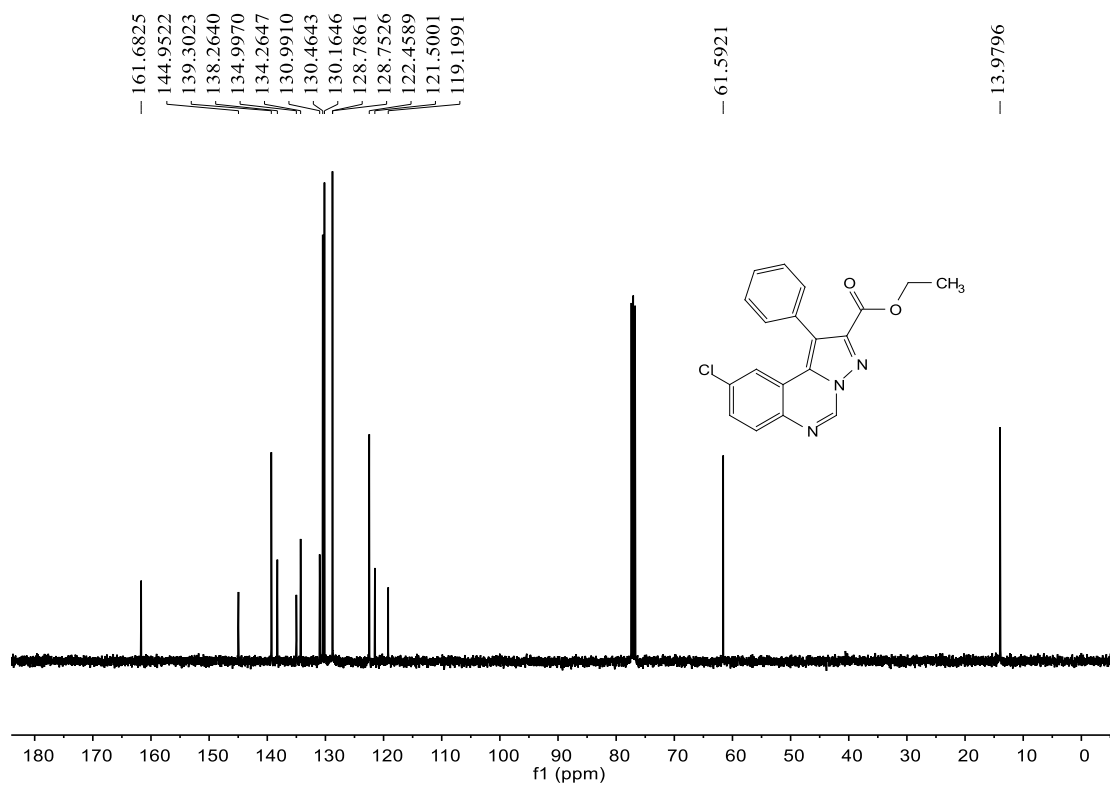
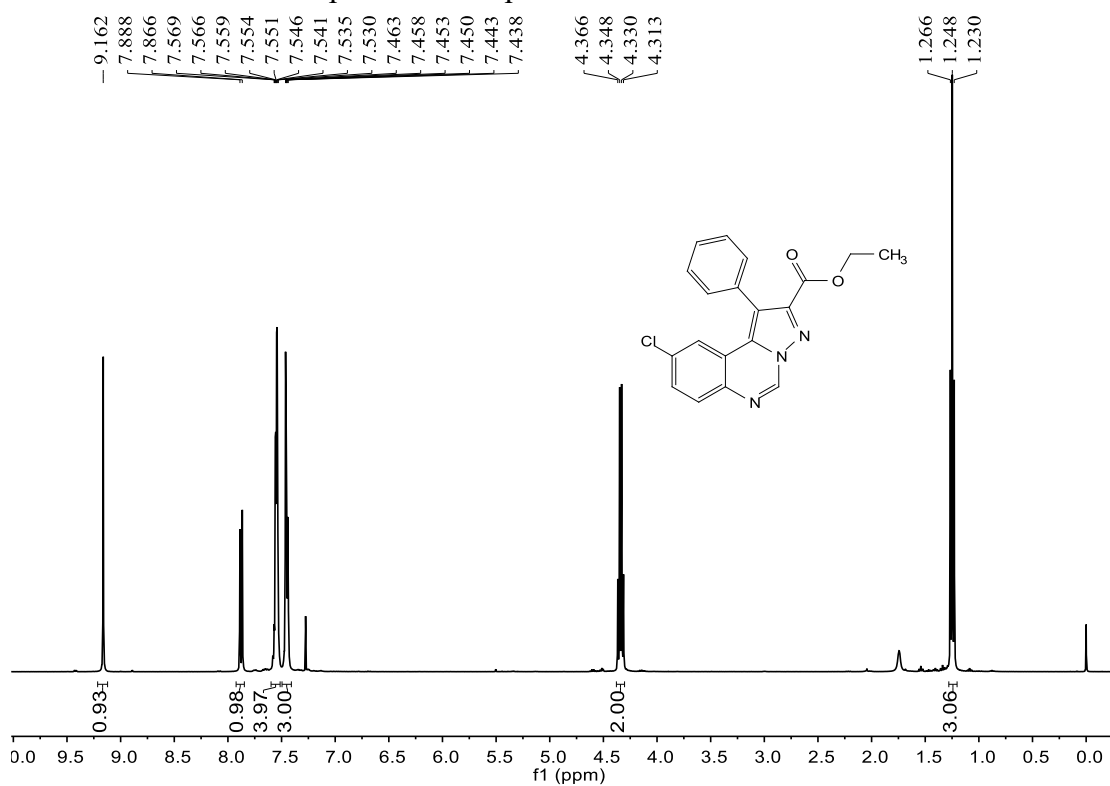
^1H NMR and ^{13}C NMR spectra of compound **3va**



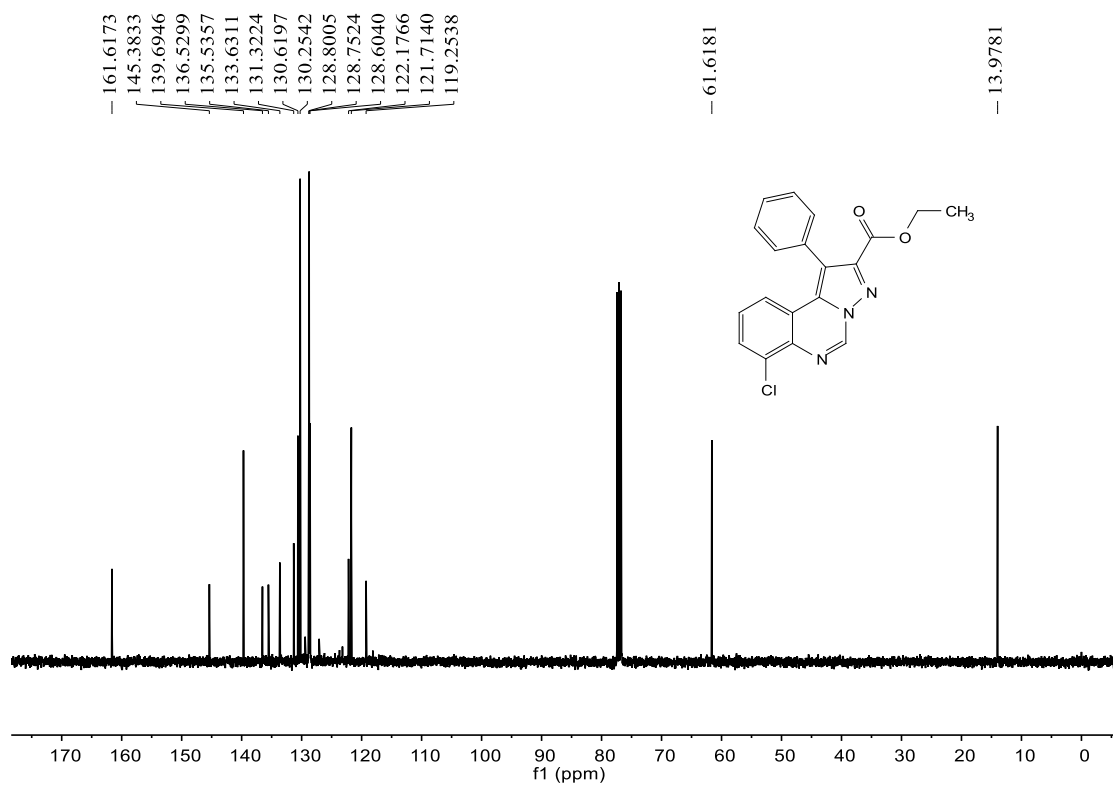
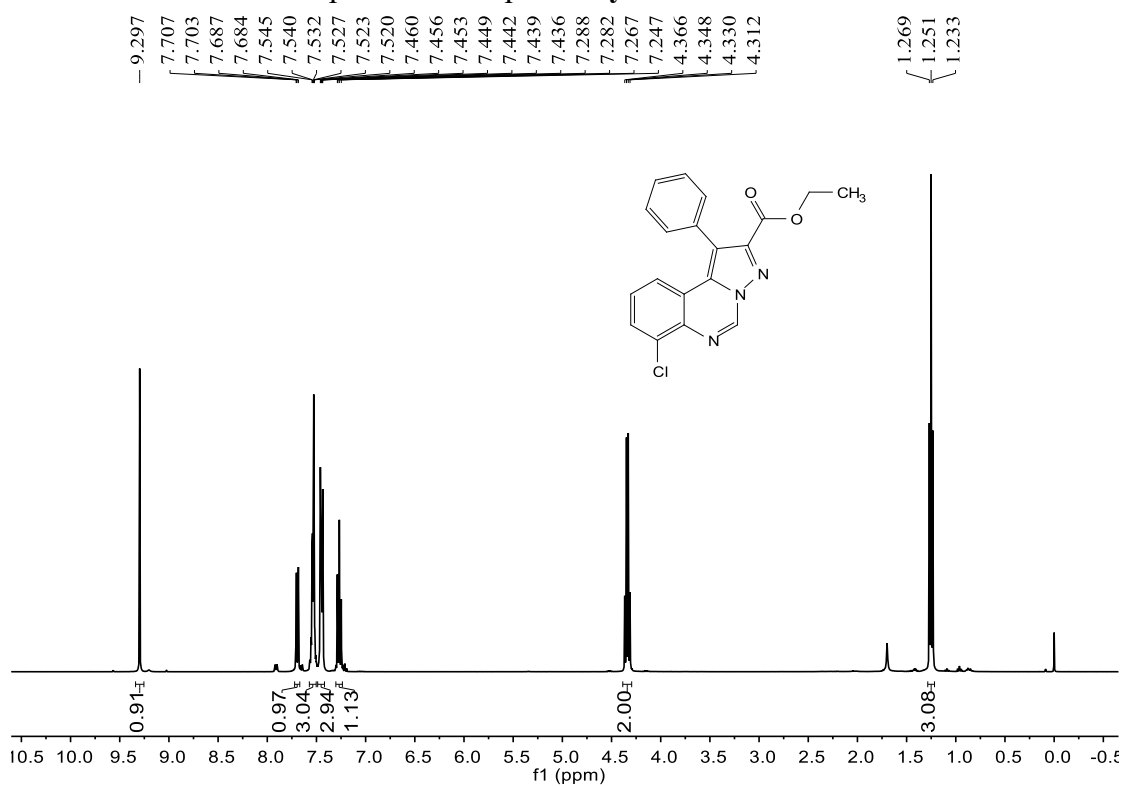
¹H NMR and ¹³C NMR spectra of compound **3wa**



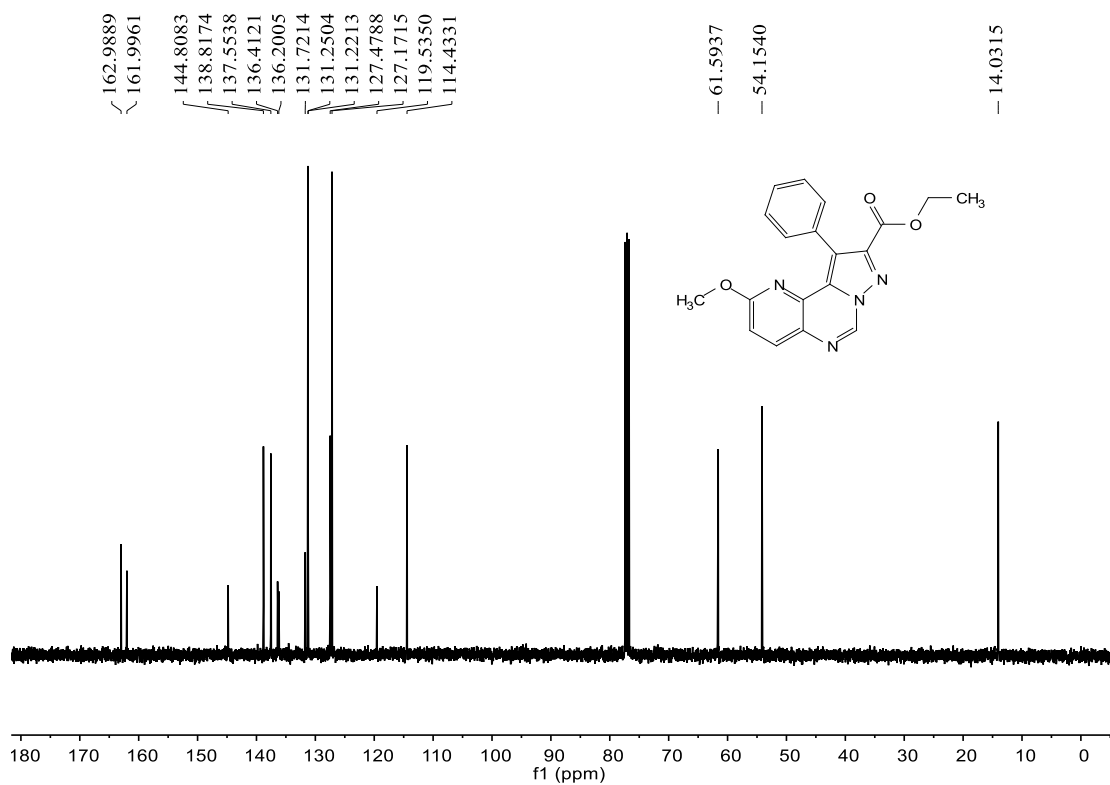
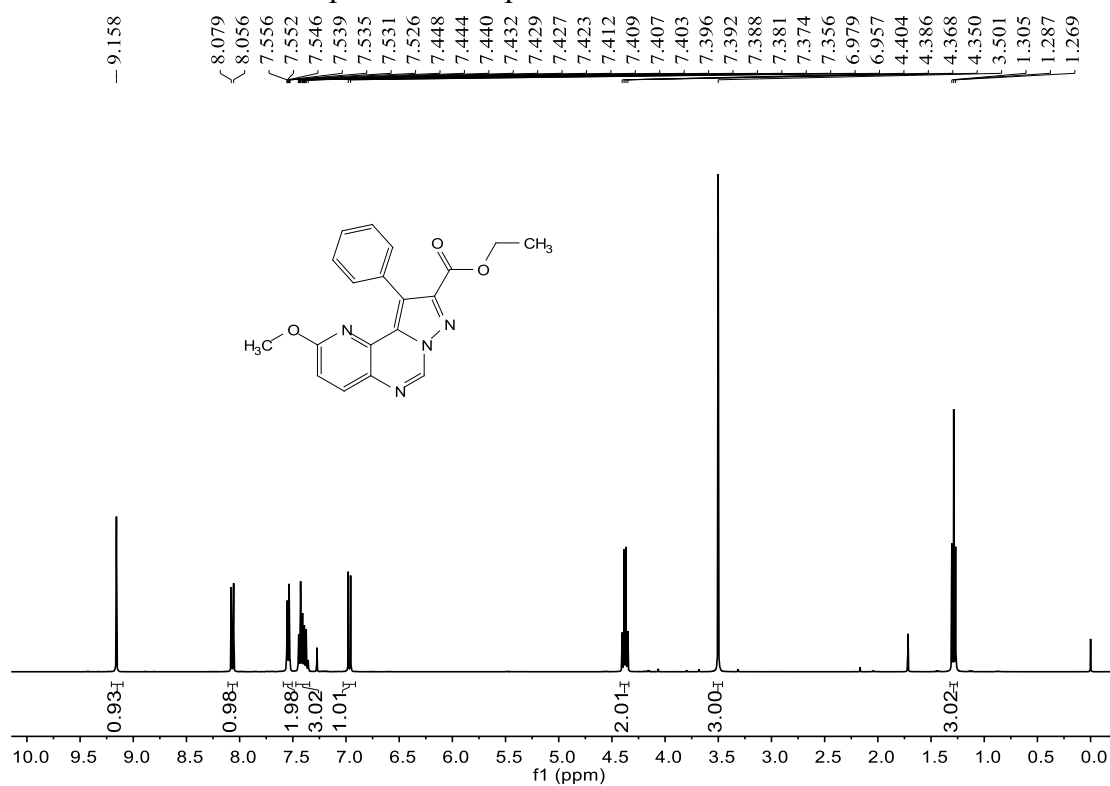
¹H NMR and ¹³C NMR spectra of compound **3xa**



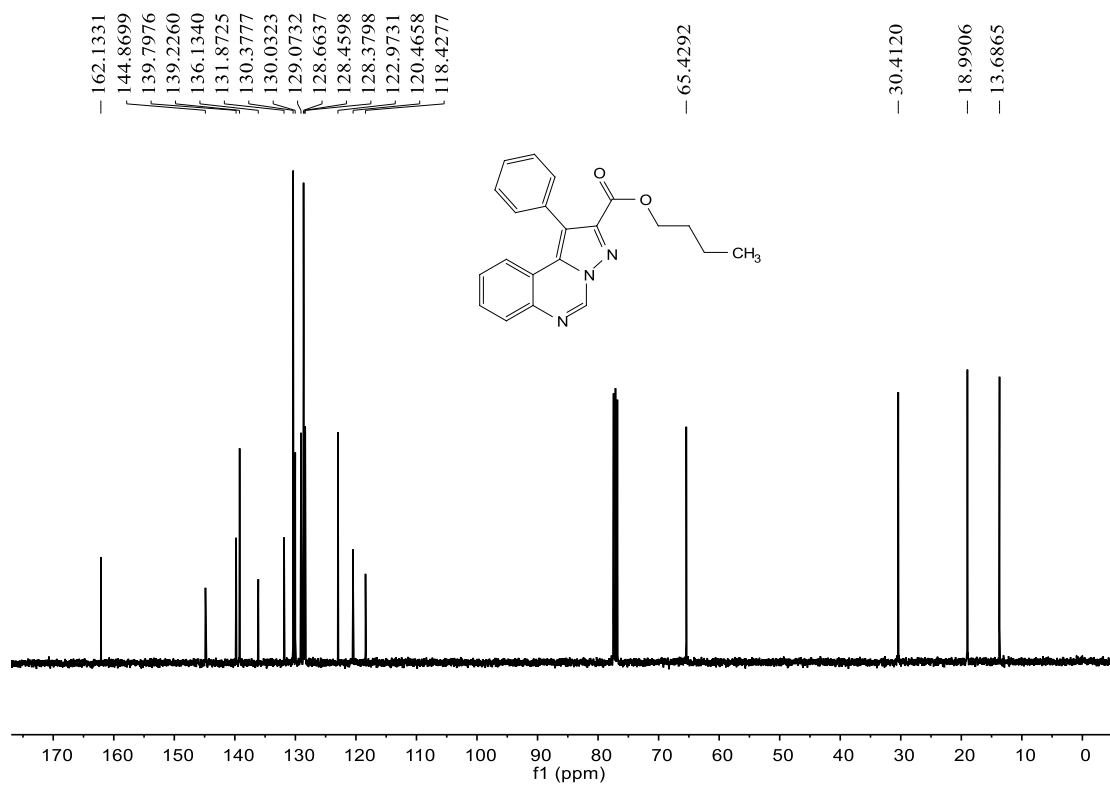
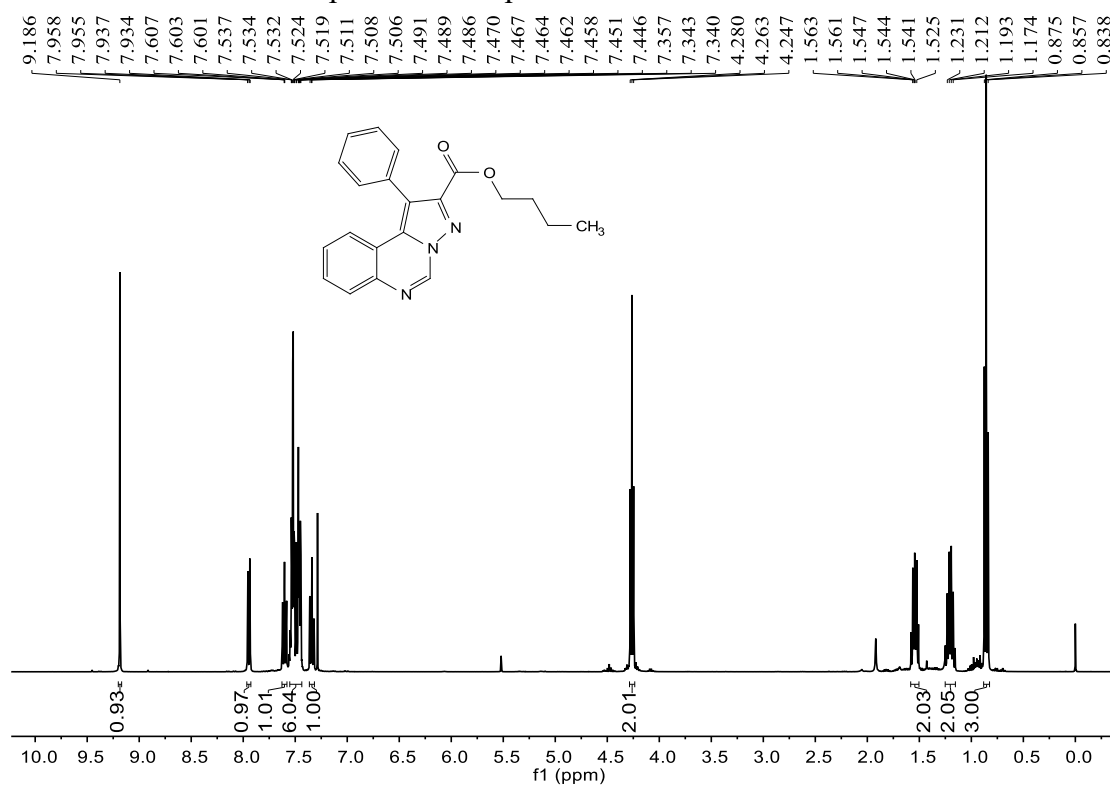
¹H NMR and ¹³C NMR spectra of compound 3ya



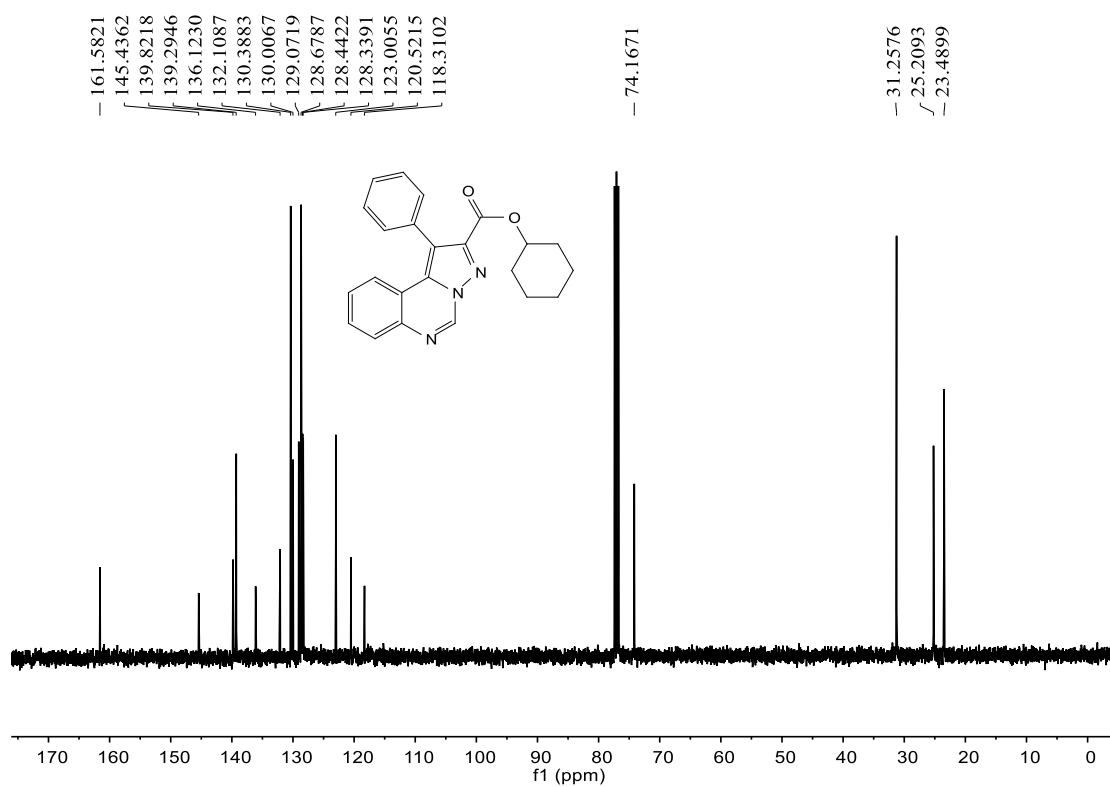
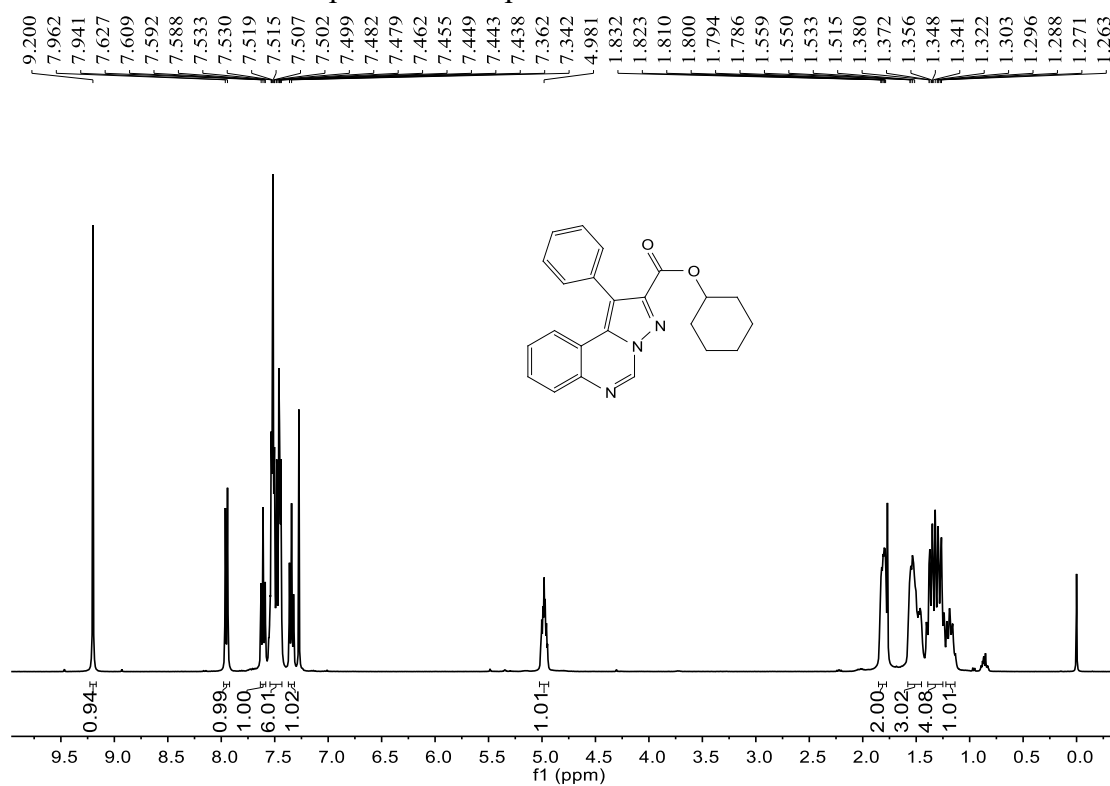
^1H NMR and ^{13}C NMR spectra of compound **3za**



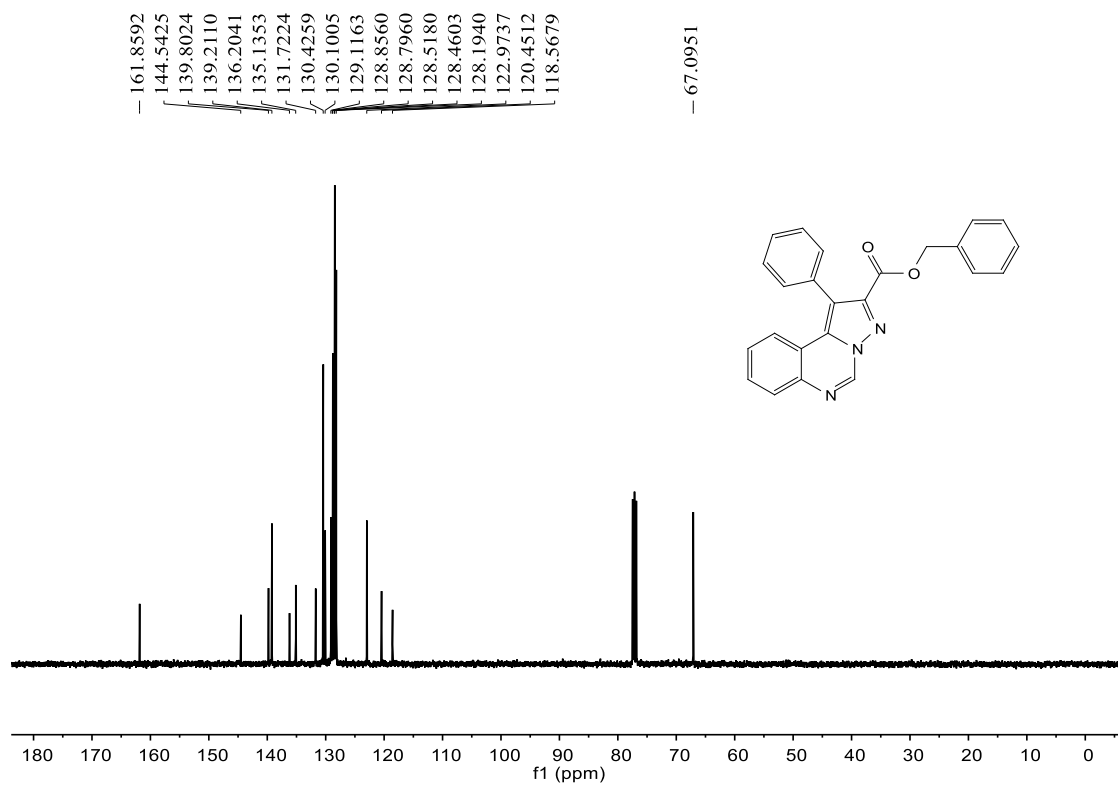
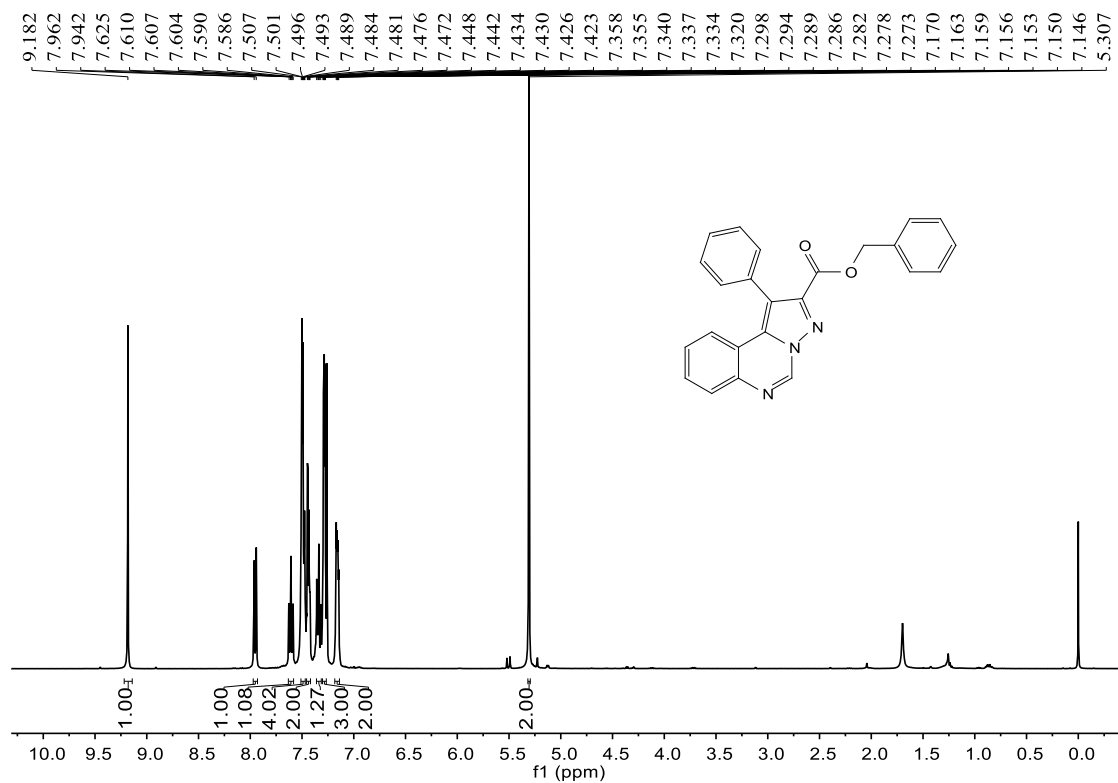
¹H NMR and ¹³C NMR spectra of compound **3ab**



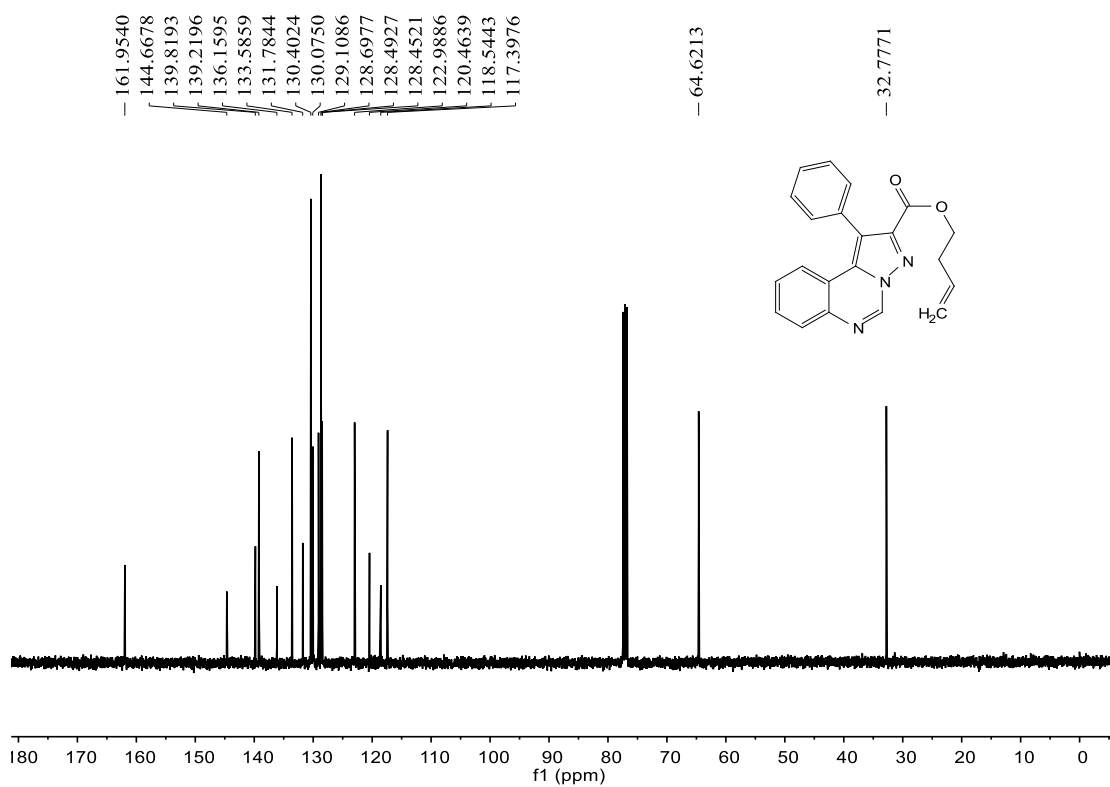
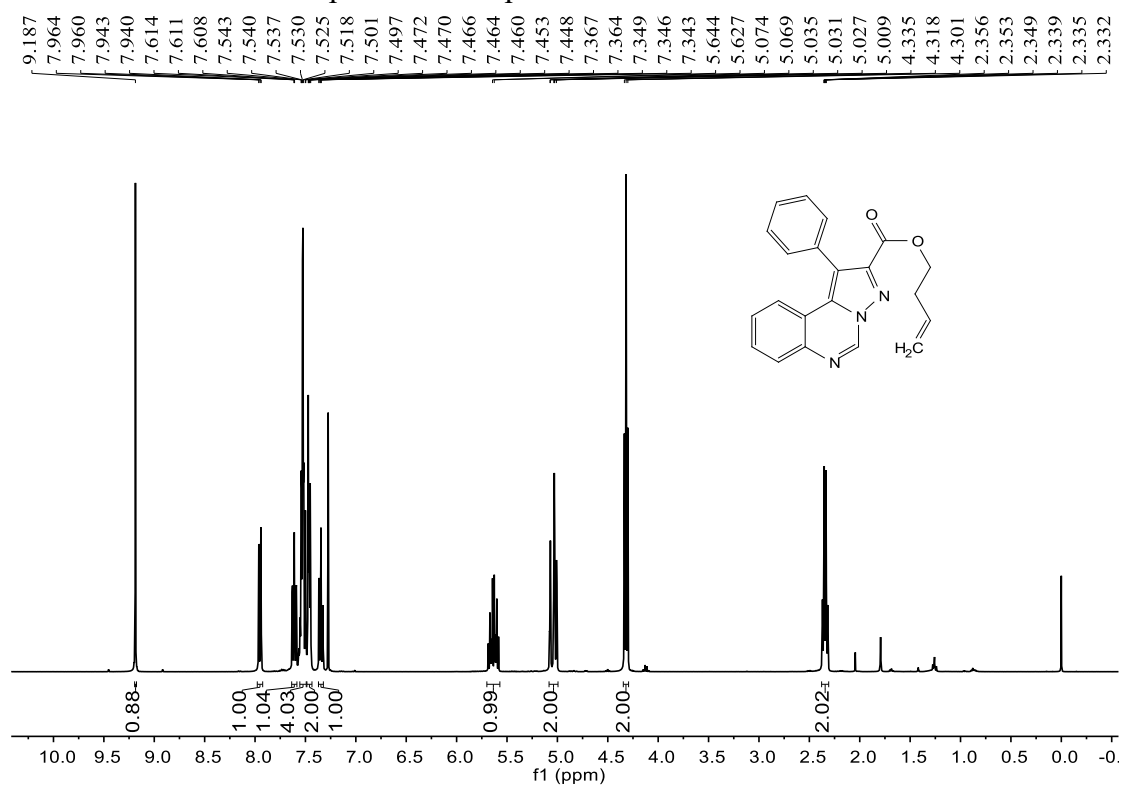
¹H NMR and ¹³C NMR spectra of compound **3ac**



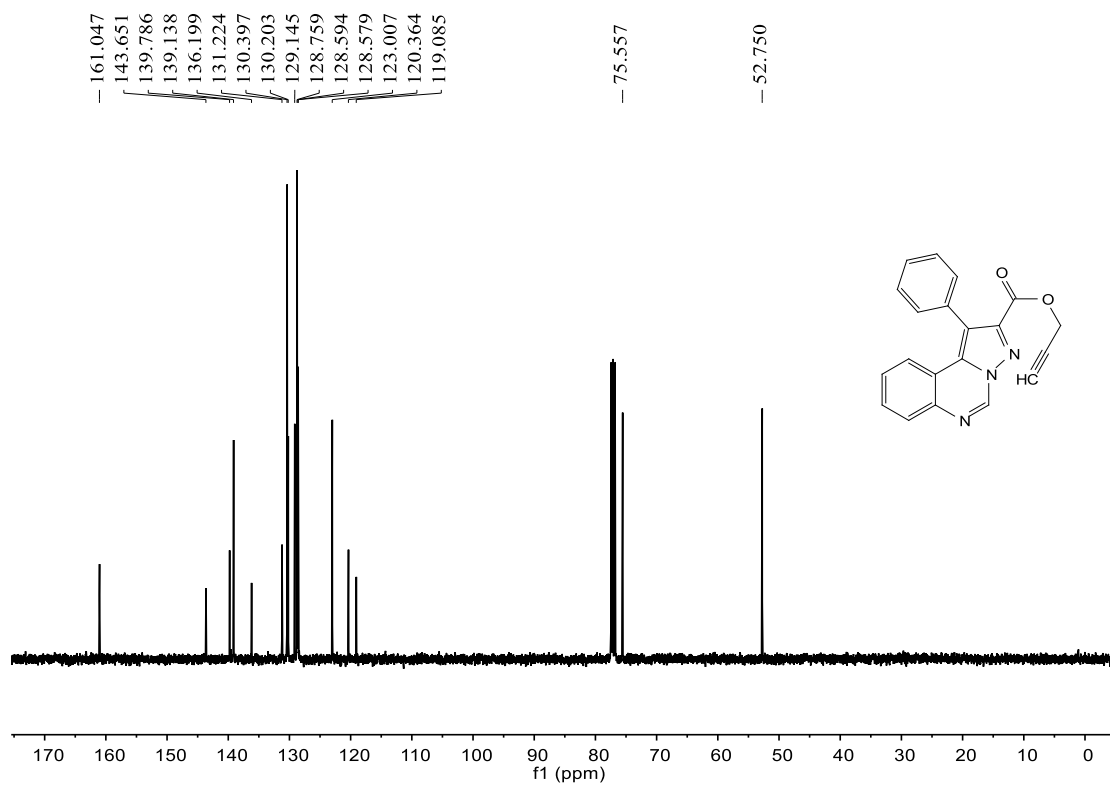
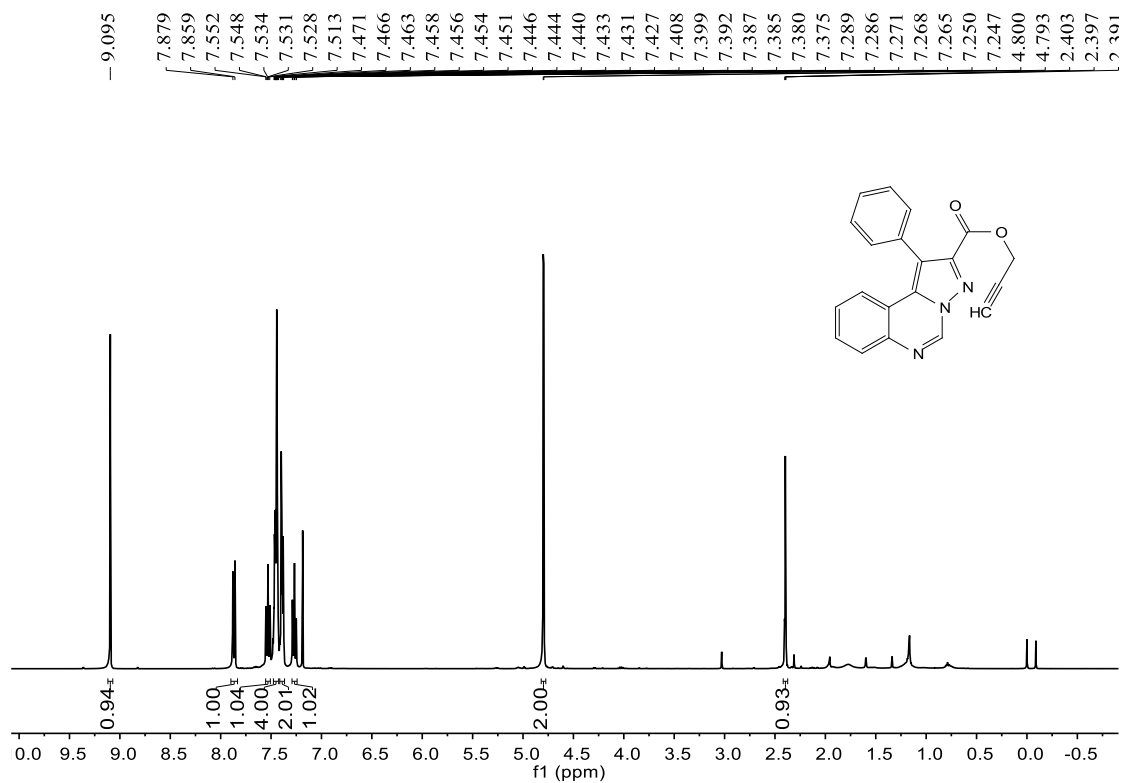
¹H NMR and ¹³C NMR spectra of compound **3ad**



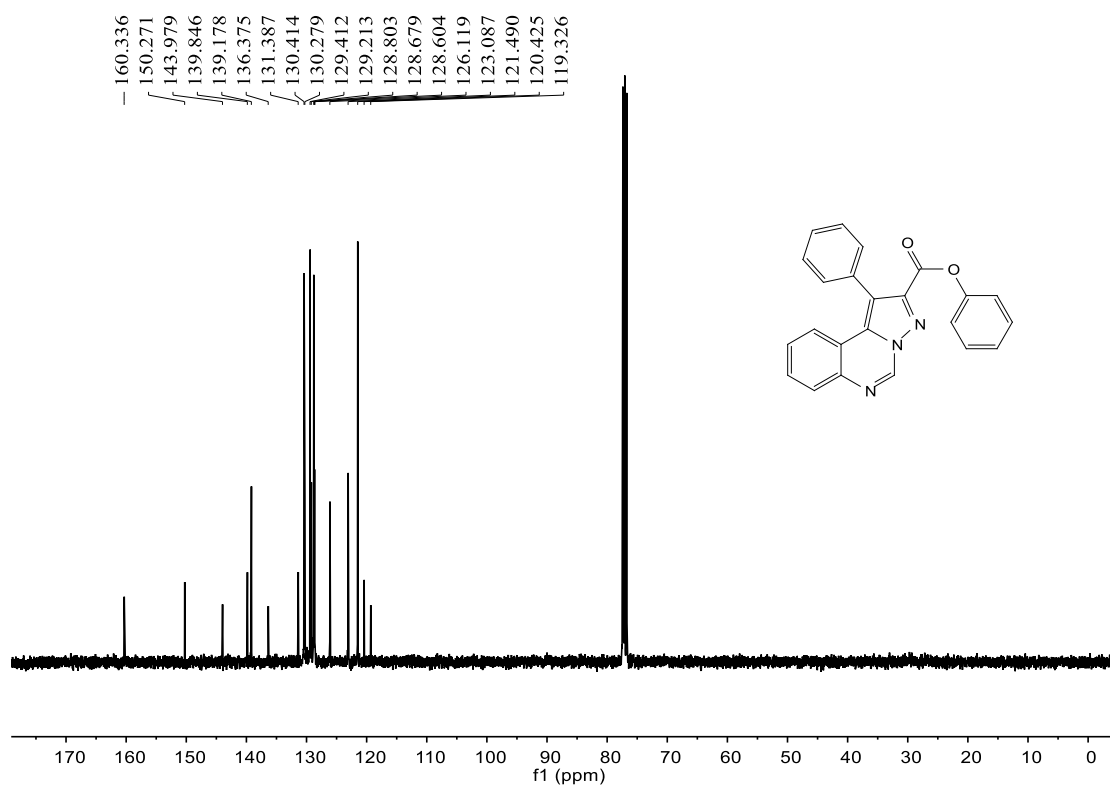
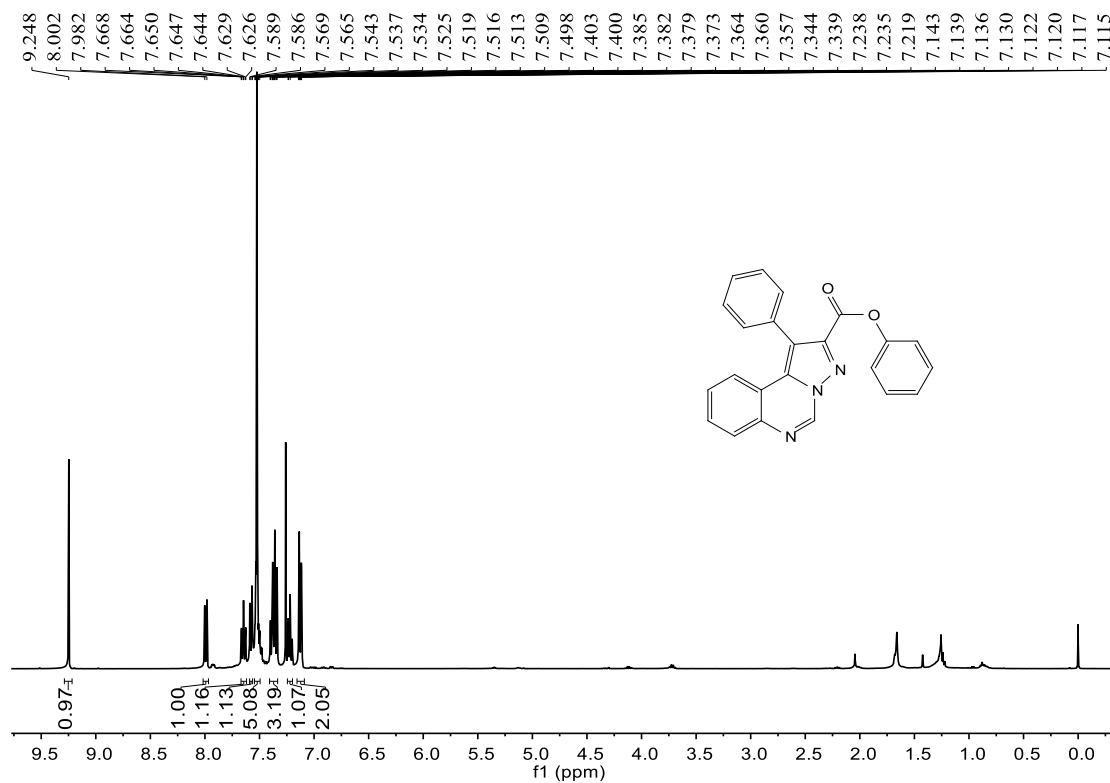
^1H NMR and ^{13}C NMR spectra of compound **3ae**



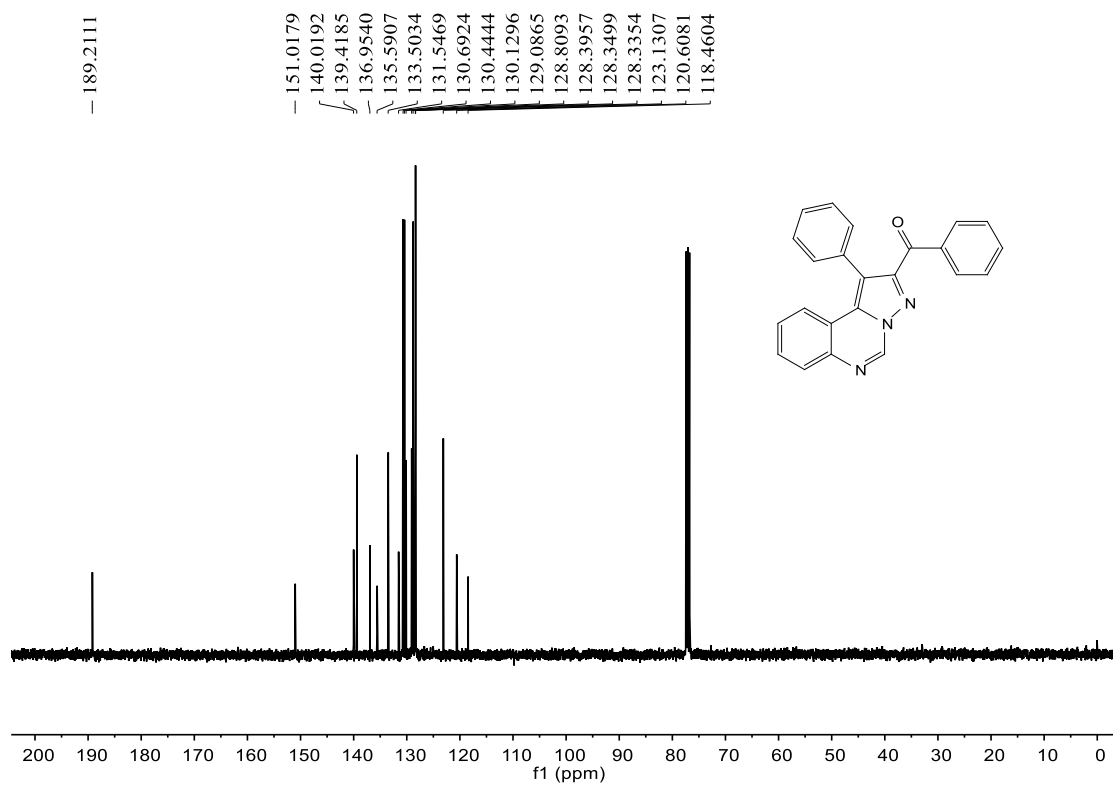
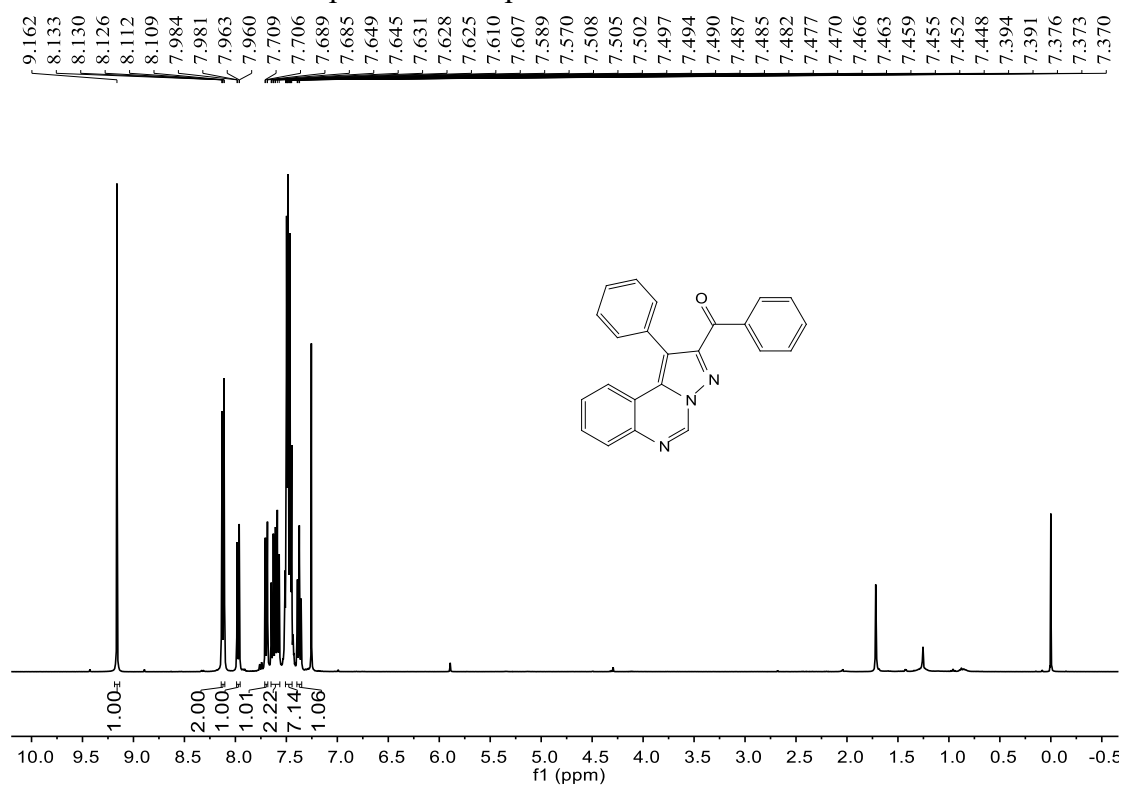
¹H NMR and ¹³C NMR spectra of compound **3af**



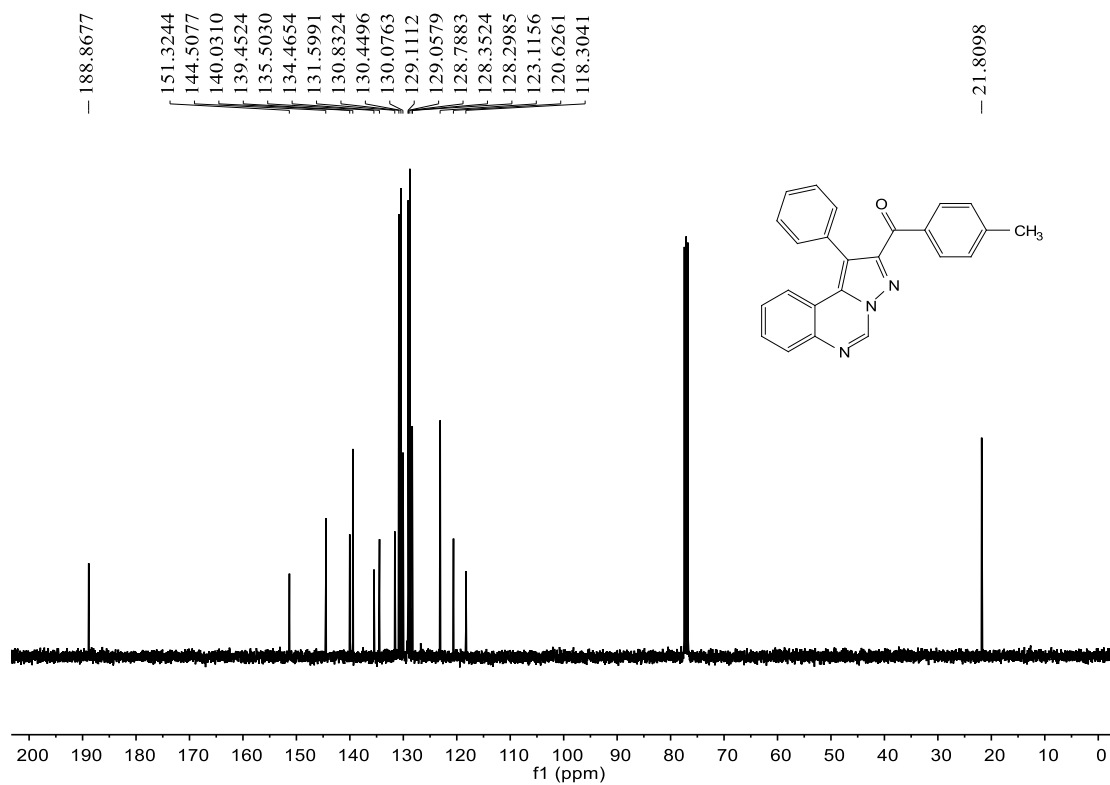
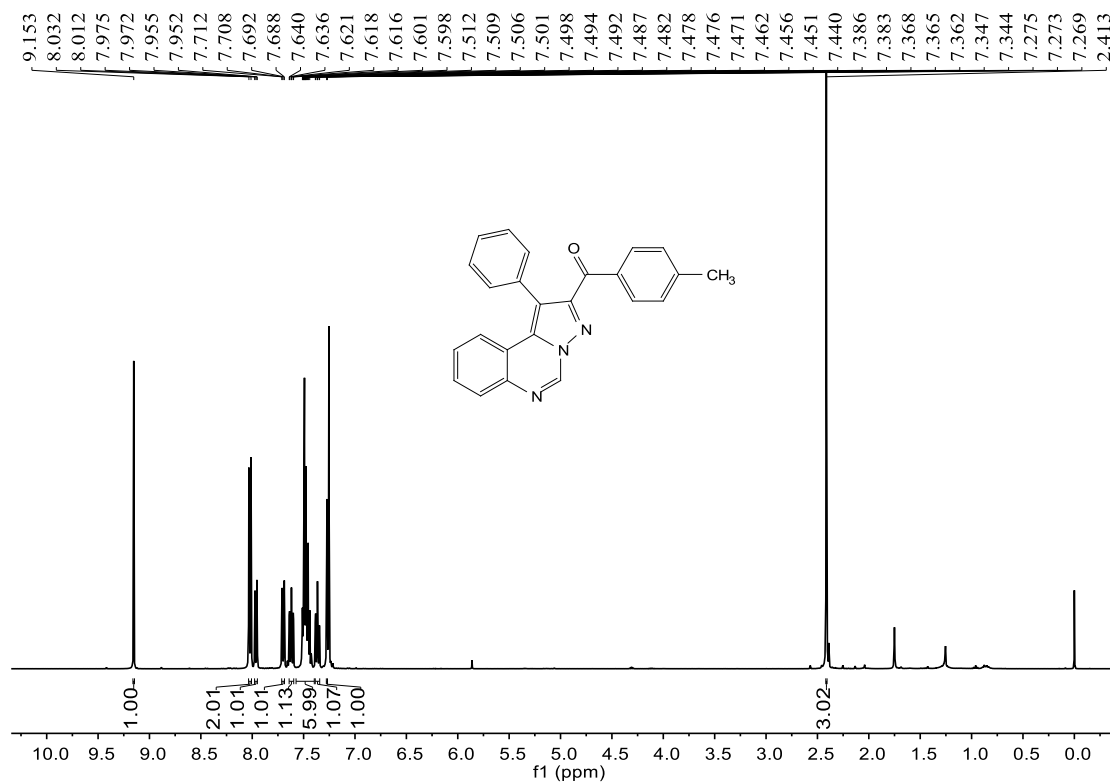
¹H NMR and ¹³C NMR spectra of compound **3ag**



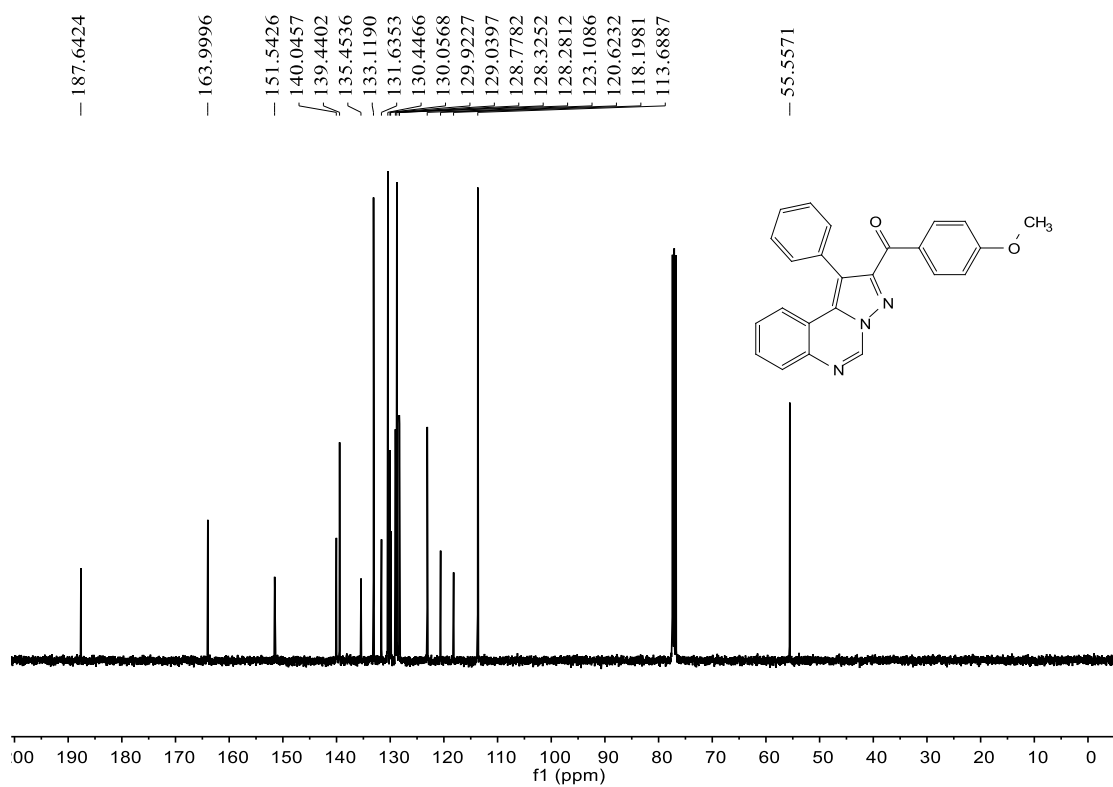
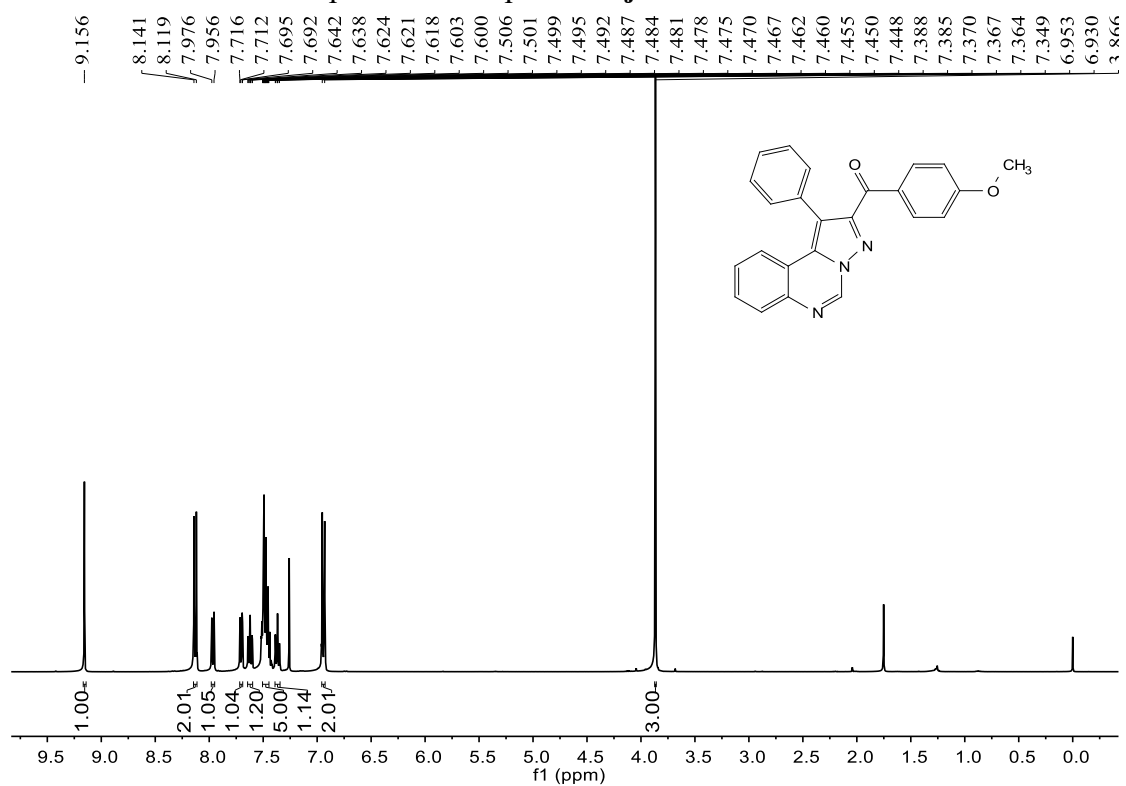
^1H NMR and ^{13}C NMR spectra of compound **3ah**



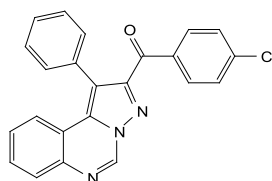
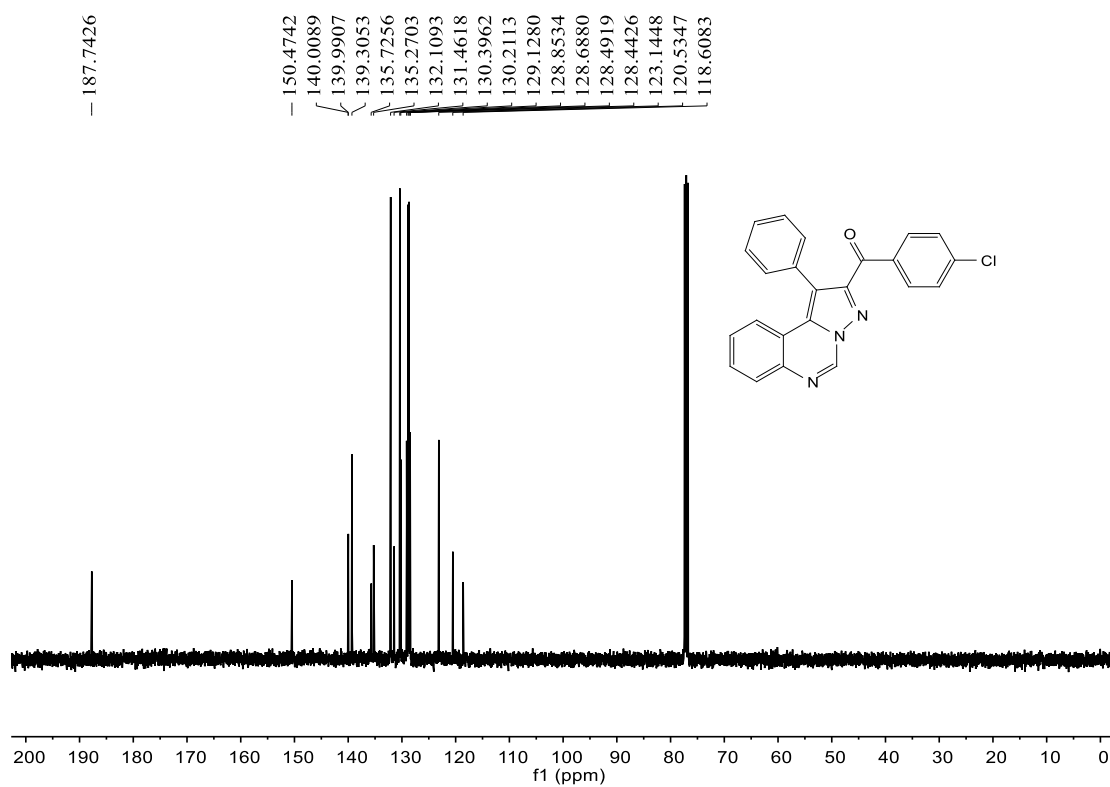
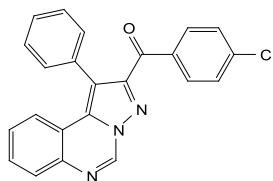
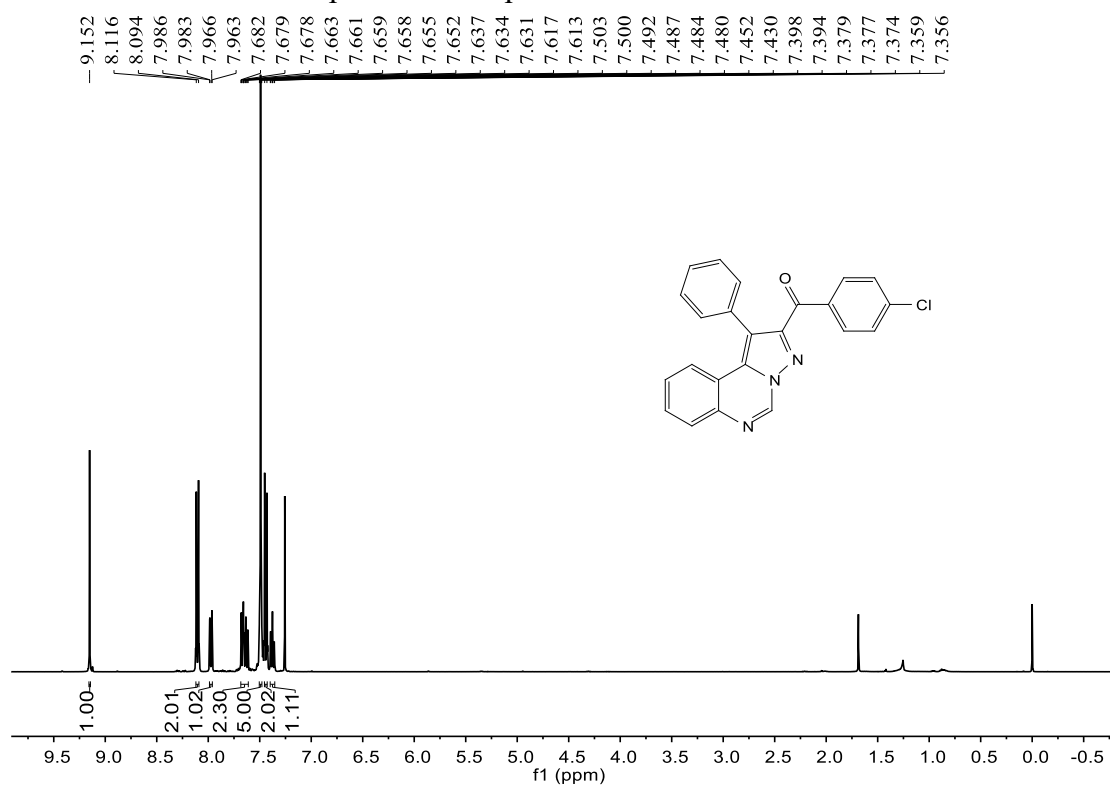
¹H NMR and ¹³C NMR spectra of compound **3ai**



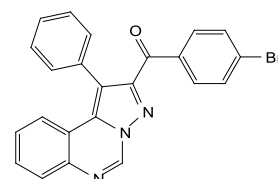
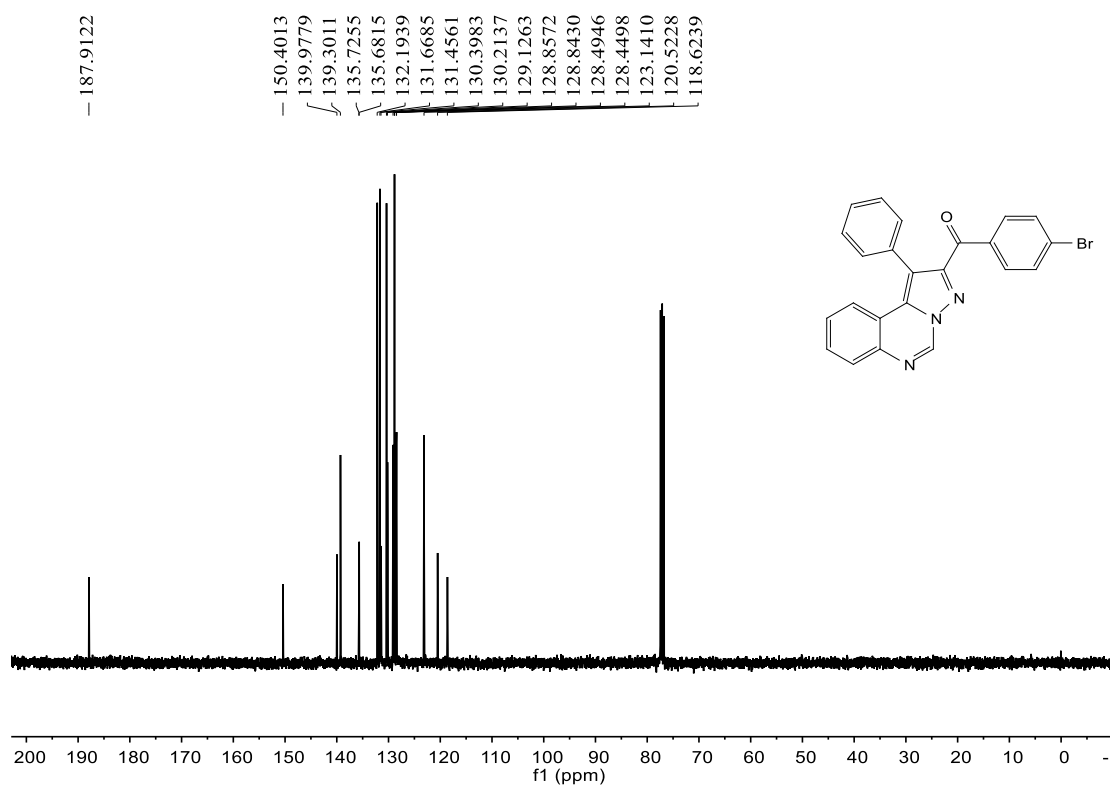
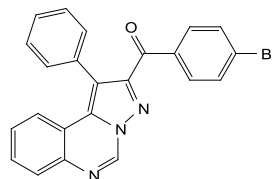
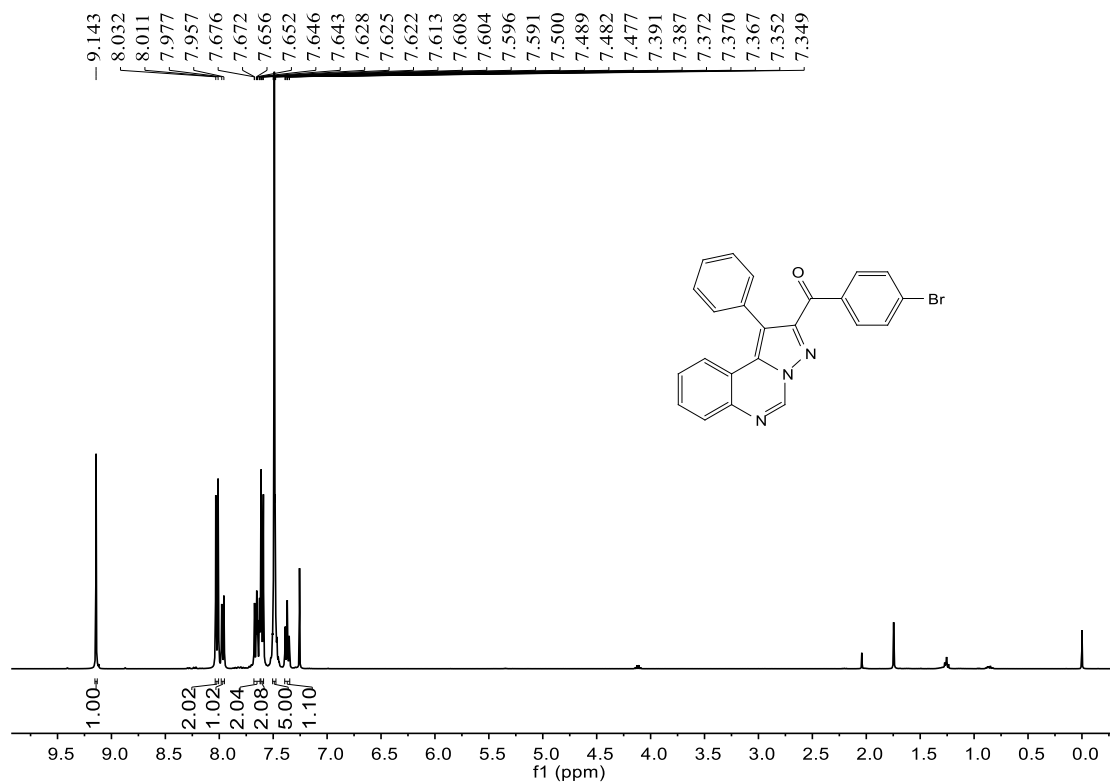
¹H NMR and ¹³C NMR spectra of compound **3aj**



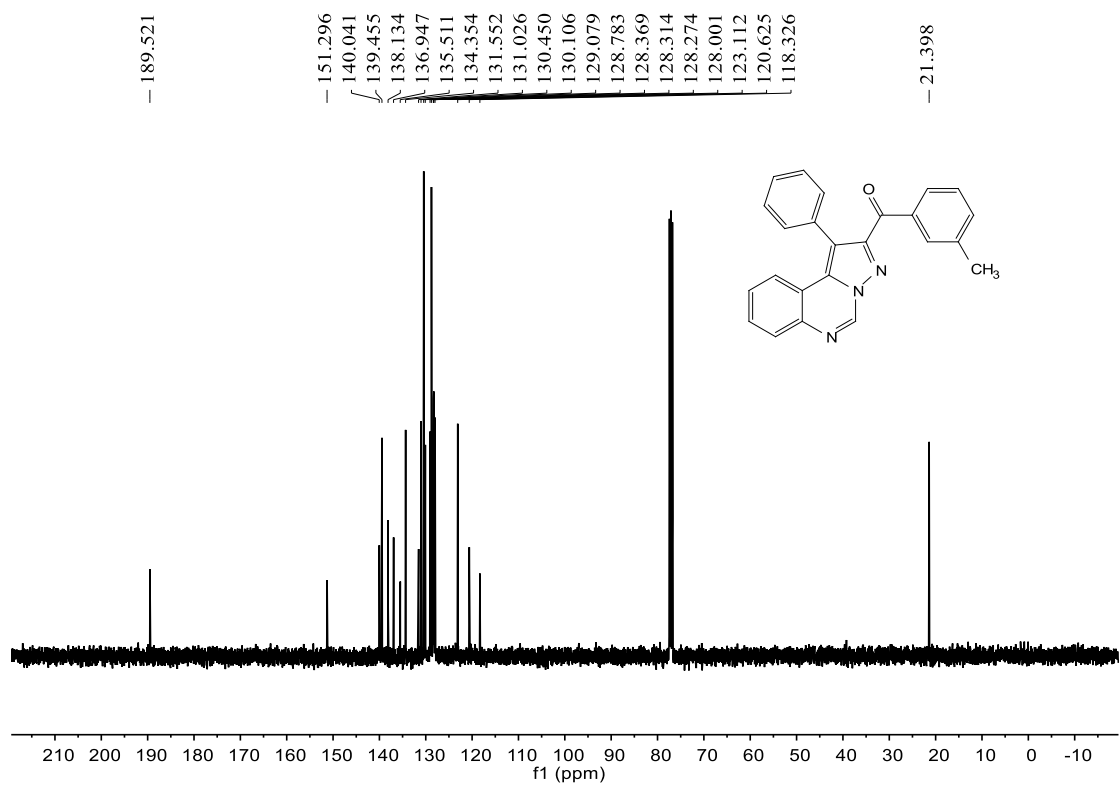
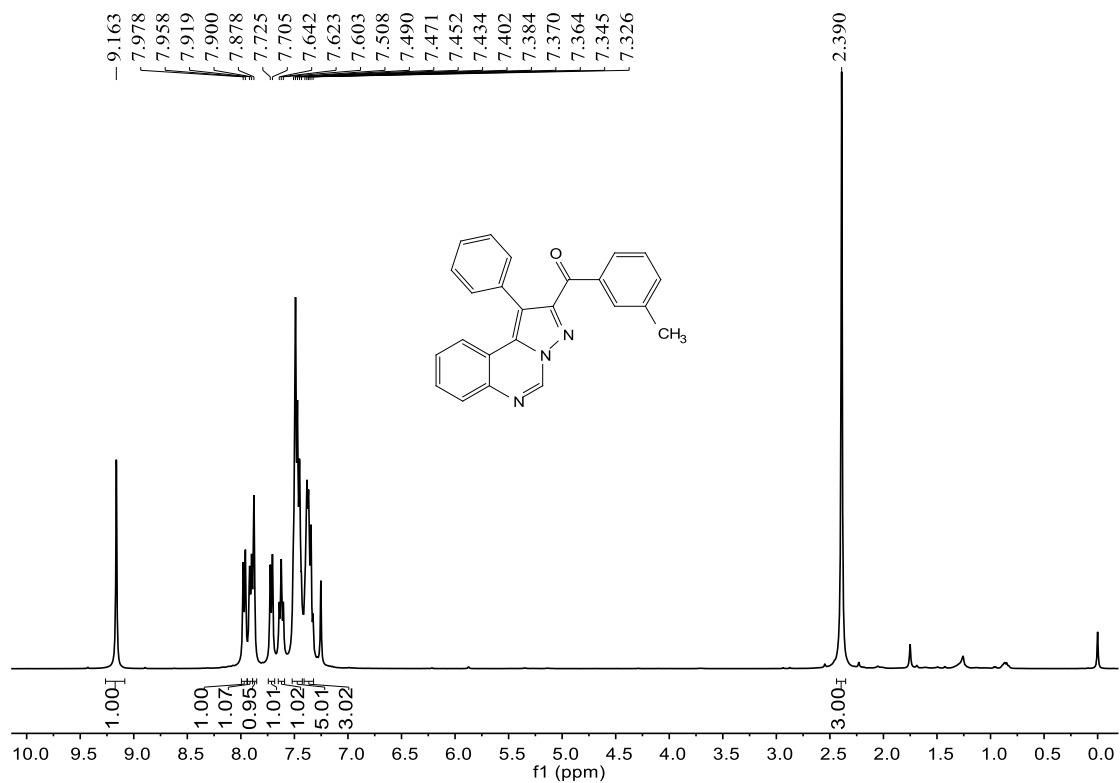
^1H NMR and ^{13}C NMR spectra of compound **3ak**



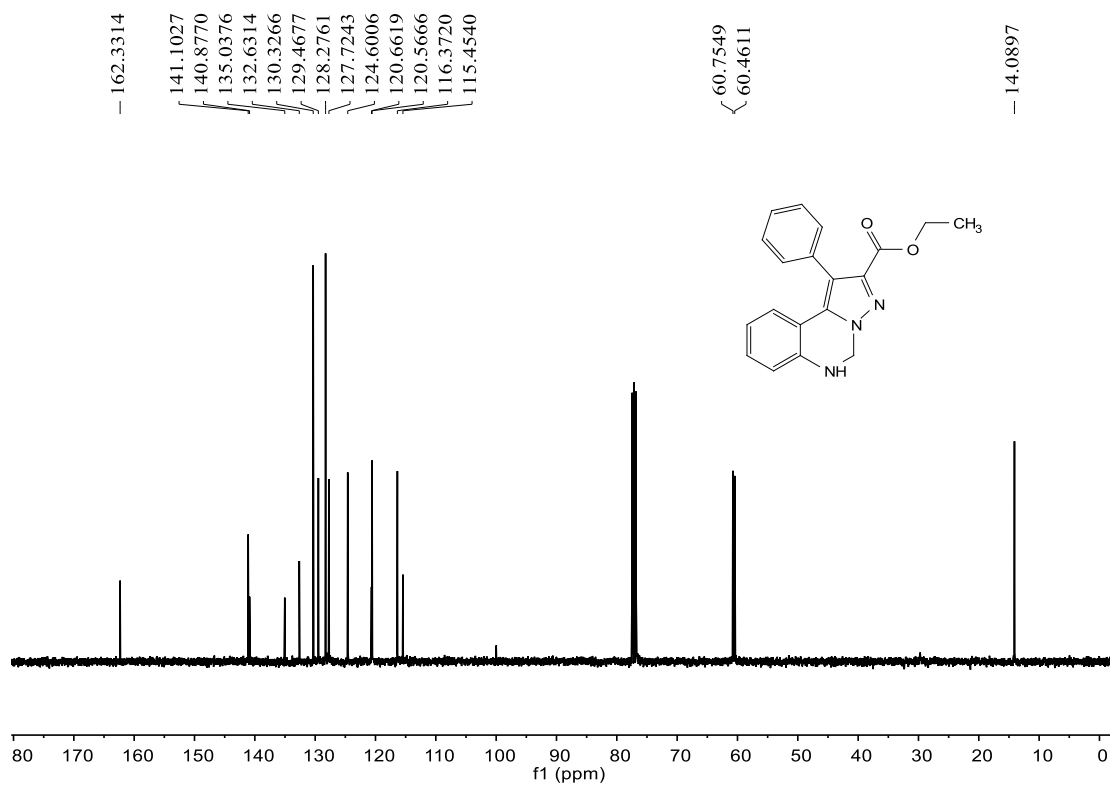
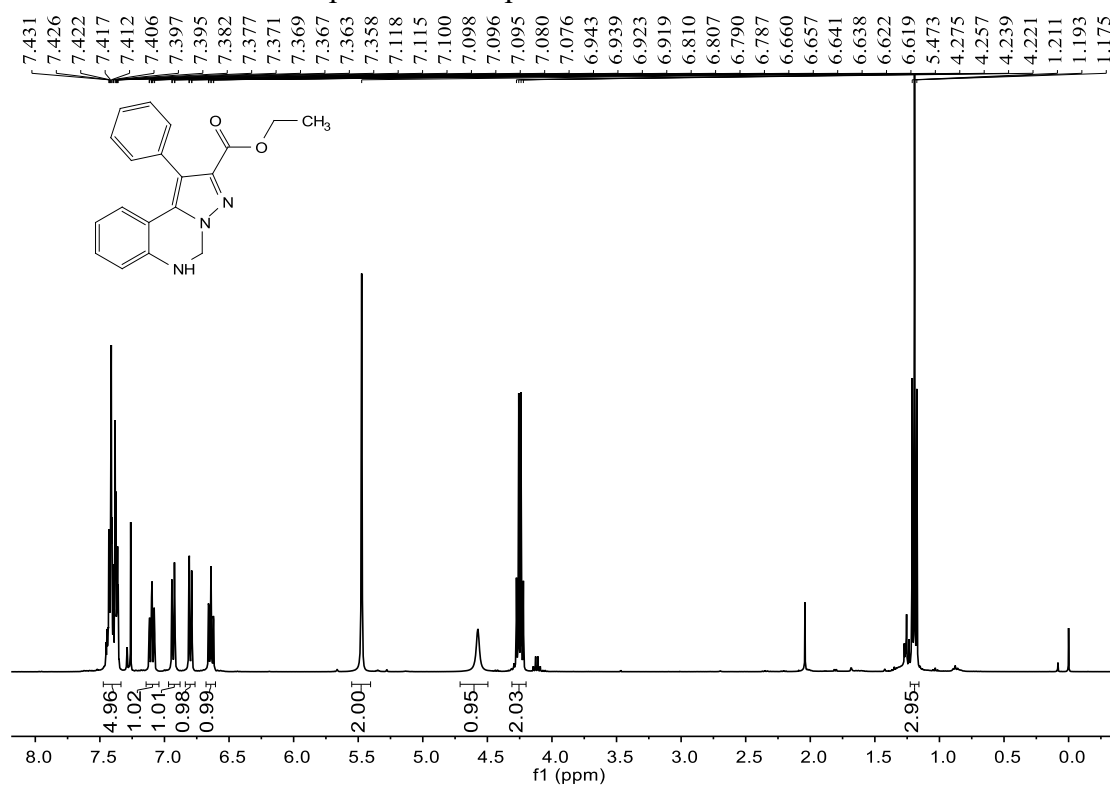
^1H NMR and ^{13}C NMR spectra of compound **3al**



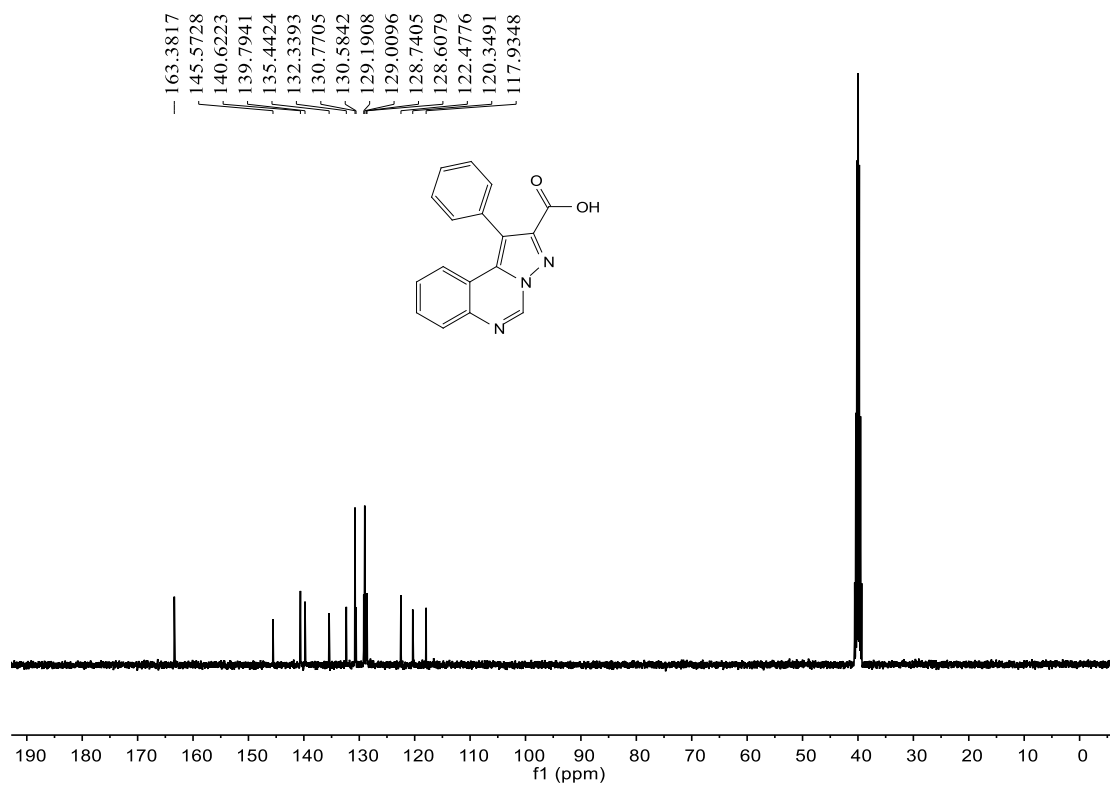
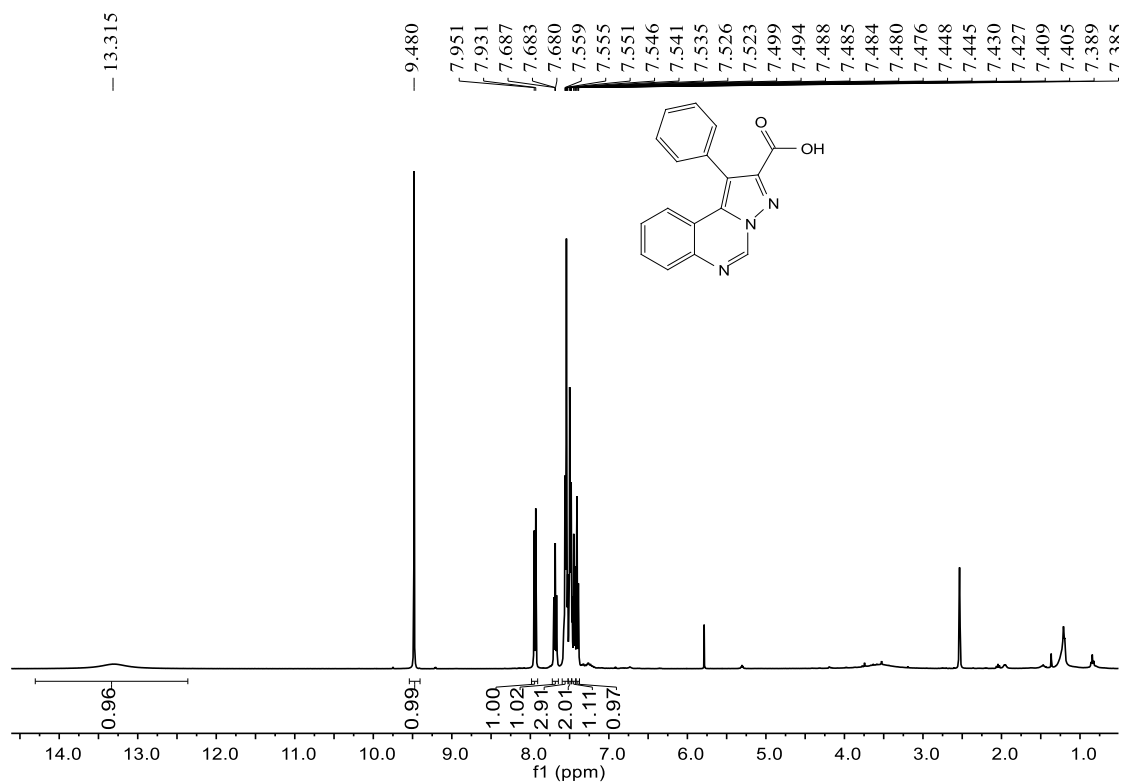
^1H NMR and ^{13}C NMR spectra of compound **3am**



¹H NMR and ¹³C NMR spectra of compound **4aa**



¹H NMR and ¹³C NMR spectra of compound **5aa**



¹H NMR and ¹³C NMR spectra of compound **6aa**

