Supporting Information

A Practical and Sustainable Two-Component Minisci Alkylation *via* Photo-Induced EDA-Complex Activation

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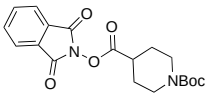
1. General Considerations

1.1 General: All chemical transformations requiring inert atmospheric conditions were carried out using Schlenk line techniques with a 4- or 5-port dual-bank manifold. For irradiation, a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) were placed 1.5 inches away from the reaction vials. NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K using 400, 500 and 600 MHz spectrometers. ^{1}H NMR spectra were referenced to residual, $CHCl_3$ (δ 7.26) in $CDCl_3$. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.2). Reactions were monitored by ^{1}H NMR, GCMS, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using phosphomolybdic stain, and/or UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GC/MS and leucine enkephalin for ESI-LC/MS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on an FT-IR using either neat oil or solid products. Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected. UV/vis studies were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific.

1.2 Chemicals: Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Solvents were obtained from commercial suppliers and used as purchased. DMF (dimethylformamide) 99.5% extra pure over molecular sieves was purchased from Acros Organics and used as received. All other reagents were purchased commercially and used as received. Photoredox-catalyzed reactions were performed using 8 mL Chemglass vials (2-dram, 17 x 60 mm, 15-425 Green Open Top Cap, TFE Septa).

2. List of *N*-(Acyloxy)phthalimides or Redox Active Esters

The redox-active esters (**2a**-**q**) shown in Figure 1 were prepared according to previously described methods in the literature.[1,2,3,4]



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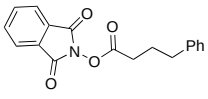

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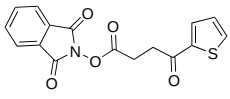

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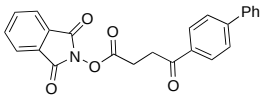

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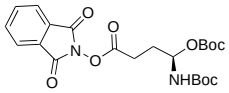

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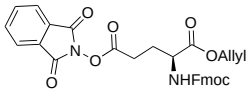

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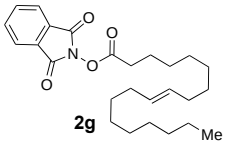

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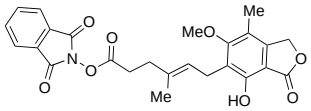

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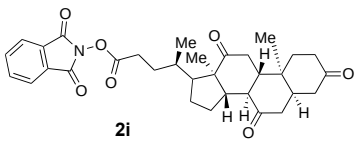

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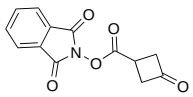

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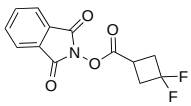

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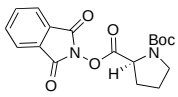

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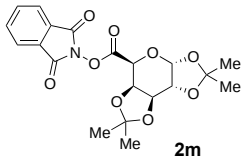

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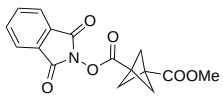

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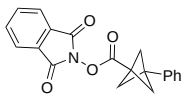

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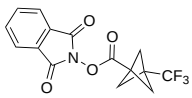

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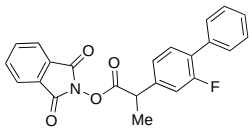


2q

[1] Mills, L. Reginald; Zhou, Cuihan; Fung, Emily; Rousseaux, Sophie A. L. Ni-Catalyzed β-Alkylation of Cyclopropanol-Derived Homoenolates. *Org. Lett.* **2019**, *21*, 8805-8809.

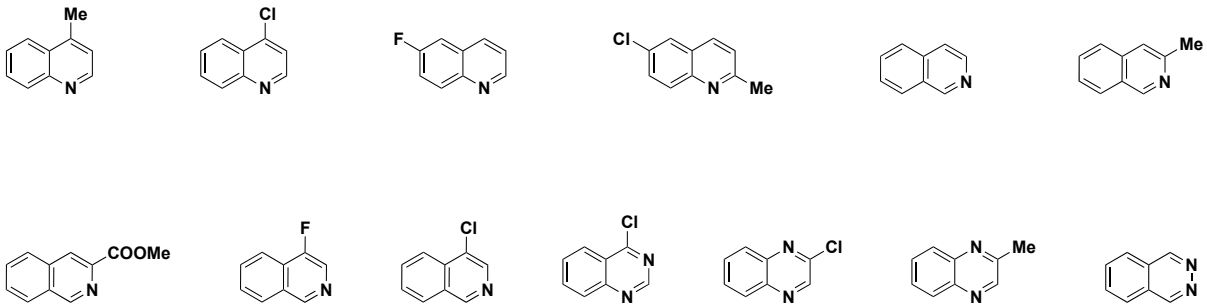
[2] Polites, V. C.; Badir, S. O.; Keess, S.; Jolit, A.; Molander, G. A. Nickel-Catalyzed Decarboxylative Cross-Coupling of Bicyclo[1.1.1]pentyl Radicals Enabled by Electron Donor–Acceptor Complex Photoactivation. *Org. Lett.* **2021**, *23*, 4828– 4833.

[3] Kammer, L. M.; Badir, S. O.; Hu, R.-M.; Molander, G. A. Photoactive electron donor–acceptor complex platform for Ni-mediated C(sp3)–C(sp2) bond formation. *Chem. Sci.* **2021**, *12*, 5450– 5457.

[4] Cabrera-Afonso, M. J.; Sookezian, A.; Badir, S. O.; Khatib, M. E.; Molander, G. A. Photoinduced 1,2-dicarbofunctionalization of alkenes with organotrifluoroborate nucleophiles via radical/polar crossover. *Chem. Sci.* **2021**, *12*, 9189– 9195.

3. List of Heterocycles

All the heterocycles utilized in our synthetic experiments (shown below) are commercially available.



4. General Procedure for Two-Component Minisci Alkylation and Reaction Workflow

4A. Reaction Workflow:

All photoredox reactions were performed with two Kessil PR160-Purple LED lamps (30 W High Luminous DEX 2100 LED, 390 nm). The lamps were placed 1.5 inches away from the reaction vials within a ventilated fume hood. A typical reaction setup is shown below.

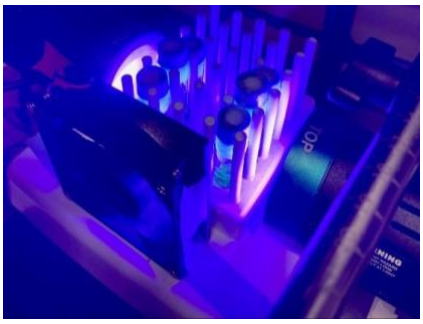
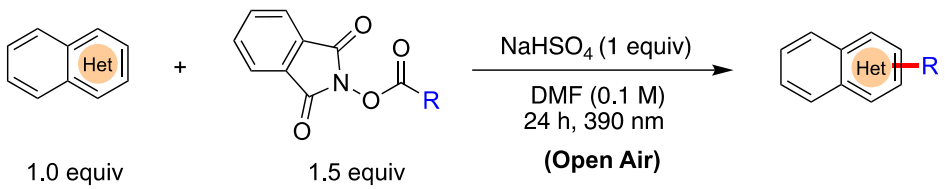


Figure S1. *Reaction setup for the photoinduced two-component Minisci alkylation reaction*

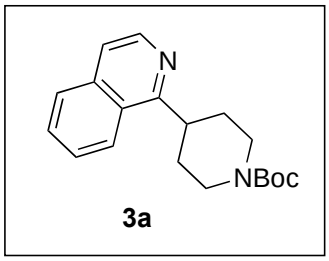
4B. General Procedure:



To an 8 mL vial equipped with a magnetic stir bar and a rubber septum was added the heterocyclic compound (0.3 mmol, 1.0 equiv), redox active ester (0.45 mmol, 1.5 equiv), $NaHSO_4$ (36 mg, 0.3 mmol, 1.0 equiv) and DMF (3 mL, c = 0.1 M) under an open-air conditions. The reaction system was closed,

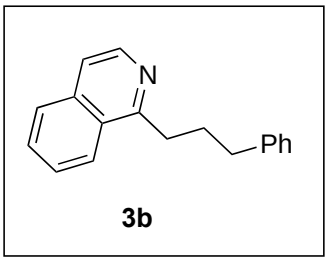
and the reaction mixture was irradiated for 24 h with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) as described in the "Workflow" section. The temperature of the reaction was maintained at approximately 24 °C via a fan. When the reaction was over, it was poured into a separatory funnel containing a satd. NaCl soln and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with more satd. NaCl soln (20 mL), dried (Na_2SO_4), and then the solvents were removed under reduced pressure. The crude mixture was subjected to automated flash column chromatography to obtain the pure product.

4C. Characterization Data:



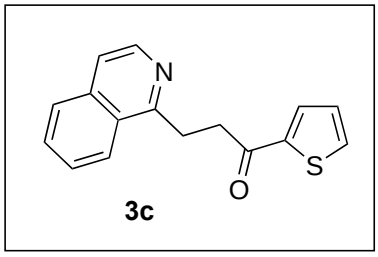
3a

***tert*-Butyl 4-(Isoquinolin-1-yl)piperidine-1-carboxylate, 3a** (54 mg, 58%) was prepared according to the *General Procedure*. The desired compound was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.45 (d, *J* = 5.7 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.65 – 7.63 (m, 1H), 7.59 – 7.56 (m, 1H), 7.48 (dd, *J* = 5.7, 0.9 Hz, 1H), 4.30 (br, 2H), 3.70 – 3.65 (m, 1H), 2.95 (s, 2H), 2.14 – 1.95 (m, 2H), 1.95 – 1.84 (m, 2H), 1.47 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 163.5, 154.8, 14, 136.5, 129. 8, 127.8, 127.2, 126.2, 124.3, 119.4, 79.4, 44.7, 43.8, 39.8, 31.5, 29.8, 28.6 (3C). **FT-IR** (cm^{-1}, neat, ATR) 1683, 1448, 1162, 867, 768. **HRMS** (ESI) calcd for $C_{19}H_{25}N_2O_2$ [M + H^+]: 313.1916, found: 313.1915.

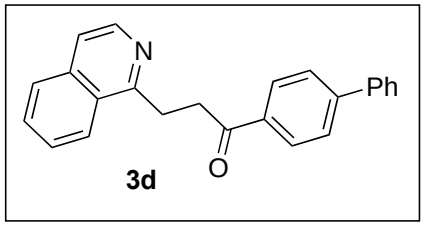


3b

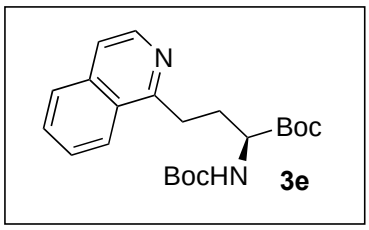
1-(3-Phenylpropyl)isoquinoline, 3b (45 mg, 61%) was prepared according to the *General Procedure.* The desired compound was obtained as a dense, yellow oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.44 (d, *J* = 5.7 Hz, 1H), 8.06 – 8.04 (m, 1H), 7.82 – 7.80 (m, 1H), 7.67 – 7.64 (m, 1H), 7.57 – 7.54 (m, 1H), 7.53 – 7.48 (m, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 7.21 – 7.17 (m, 1H), 3.37 – 3.31 (m, 2H), 2.81 (t, *J* = 7.7 Hz, 2H), 2.26 – 2.18 (m, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 162.0, 142.2, 142.1, 136.4, 129.9, 128.7 (2C), 128.5 (2C), 127.5, 127.1, 127.1, 126.0, 125.4, 119.4, 36.1, 35.0, 31.3. **FT-IR** (cm^{-1}, neat, ATR) 1724, 1586, 823, 743, 699. **HRMS** (ESI) calcd for $C_{18}H_{18}N$ [M + H^+]: 248.1439, found: 248.1445.



3-(Isoquinolin-1-yl)-1-(thiophen-2-yl)propan-1-one, 3c (45 mg, 56%) was prepared according to the *General Procedure*. The desired compound was obtained as a yellow solid. **mp** = 101 – 102 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.41 (d, *J* = 5.7 Hz, 1H), 8.28 – 8.23 (m, 1H), 7.85 – 7.80 (m, 2H), 7.69 – 7.67 (m, 1H), 7.65 – 7.59 (m, 2H), 7.52 (d, *J* = 5.7 Hz, 1H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1H), 3.77 (t, *J* = 7.4 Hz, 2H), 3.62 (dd, *J* = 8.3, 6.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 192.7, 159.9, 144.5, 141.8, 136.2, 133.5, 132.1, 130.1, 128.2, 127.5, 127.4, 127.2, 125.1, 119.6, 37.4, 28.8. **FT-IR** (cm^{-1}, neat, ATR) 1659, 1415, 1250, 822, 721. **HRMS** (ESI) calcd for $C_{16}H_{14}NOS$ [M + H^+]: 268.0796, found: 268.0789.

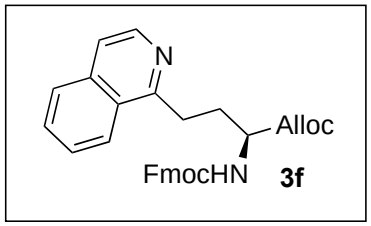


1-([1,1'-Biphenyl]-4-yl)-3-(isoquinolin-1-yl)propan-1-one, 3d (57 mg, 56%) was prepared according to the *General Procedure*. The desired compound was obtained as a white crystalline solid. **mp** = 149 – 150 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.42 (d, *J* = 5.7 Hz, 1H), 8.29 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.17 – 8.12 (m, 2H), 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.71 – 7.67 (m, 3H), 7.65 – 7.61 (m, 3H), 7.52 (d, *J* = 5.7 Hz, 1H), 7.47 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.42 – 7.38 (m, 1H), 3.83 – 3.79 (m, 2H), 3.72 (dd, *J* = 7.8, 6.0 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 99.4, 160.1, 145.8, 141.9, 140.1, 136.2, 136.0, 130.0, 129.1 (2C), 128.9 (2C), 128.3, 127.5, 127.4 (2C), 127.4, 127.3 (2C), 127.3, 125.1, 119.5, 36.7, 28.7. **FT-IR** (cm^{-1}, neat, ATR) 1682, 1565, 1368, 825, 750. **HRMS** (ESI) calcd for $C_{24}H_{20}NO$ [M + H^+]: 338.1543, found: 338.1531.

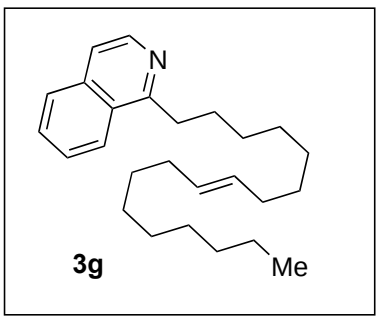


***tert*-Butyl (*R*)-(1-((*tert*-Butoxycarbonyl)oxy)-3-(isoquinolin-1-yl)propyl)carbamate, 3e** (59 mg, 51%) was prepared according to the *General Procedure*. The desired compound was obtained as dense, light-yellowish oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.41 (d, *J* = 5.7 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.60 – 7.57 (m, 1H), 7.51 (d, *J* = 5.7 Hz, 1H), 5.43 (d, *J* = 8.3 Hz, 1H), 4.39 – 4.35 (m, 1H), 3.44 – 3.38 (m, 1H), 3.37 – 3.31 (m, 1H), 2.42 – 2.36 (m, 1H), 2.28 – 2.18 (m, 1H), 1.46 (s, 9H), 1.44 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 171.8, 160.7, 155.7, 141.8, 136.3, 130.1, 127.6, 127.3, 127.0, 125.1, 119.7,

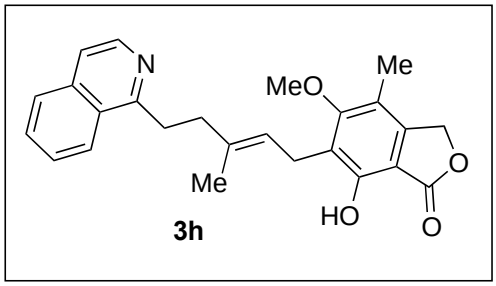
82.0, 79.7, 54.3, 32.0, 31.1, 28.4 (3C), 28.1 (3C). **FT-IR** (cm^{-1}, neat, ATR) 2978, 1709, 1391, 1150, 731. **HRMS** (ESI) calcd for $C_{22}H_{31}N_2O_4$ [M + H^+]: 387.2284, found: 387.2285.



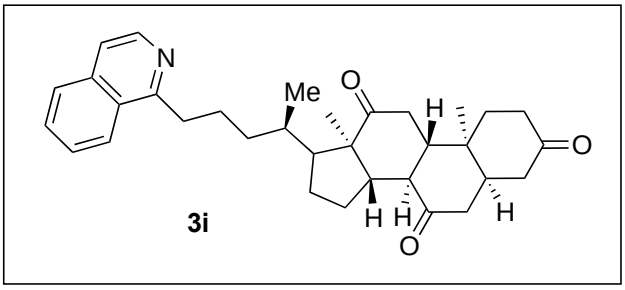
Allyl (*S*)-2-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)amino)-4-(isoquinolin-1-yl)butanoate, 3f (80 mg, 54%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 101 – 102 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.45 (d, *J* = 5.7 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 7.8, 5.3 Hz, 2H), 7.68 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.62 – 7.58 (m, 3H), 7.55 (d, *J* = 5.8 Hz, 1H), 7.38 (q, *J* = 7.2 Hz, 2H), 7.30 – 7.26 (m, 2H), 6.31 (d, *J* = 7.9 Hz, 1H), 5.94 – 5.84 (m, 1H), 5.33 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.24 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.67 – 4.57 (m, 3H), 4.47 – 4.33 (m, 2H), 4.23 (t, *J* = 7.3 Hz, 1H), 3.56 – 3.33 (m, 2H), 2.59 – 2.34 (m, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 172.1, 160.2, 156.3, 144.1, 143.9, 141.6, 141.4, 141.4, 136.3, 131.7, 130.2, 127.8, 127.6, 127.5, 127.2 (2C), 127.1, 125.3, 125.3, 124.9, 120.1 (2C), 119.8, 119.0, 77.4, 67.1, 66.2, 54.4, 47.3, 30.8, 30.6. **FT-IR** (cm^{-1}, neat, ATR) 1717, 1264, 1047, 732, 702. **HRMS** (ESI) calcd for $C_{31}H_{29}N_2O_4$ [M + H^+]: 493.2127, found: 493.2119.



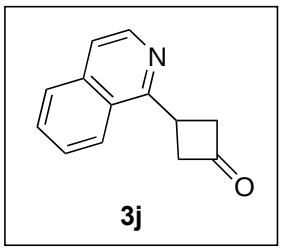
***(E)*-1-(Heptadec-8-en-1-yl)isoquinoline, 3g** (64 mg, 59%) was prepared according to the *General Procedure*. The desired compound was obtained as a dense, yellow oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.43 (d, *J* = 5.7 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.59 – 7.56 (m, 1H), 7.49 (d, *J* = 5.7 Hz, 1H), 5.41 – 5.35 (m, 2H), 3.30 – 3.27 (m, 2H), 1.97 – 1.94 (m, 4H), 1.88 – 1.83 (m, 2H), 1.49 – 1.45 (m, 2H), 1.39 – 1.24 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 162.6, 142.0, 136.4, 130.5, 130.4, 129.8, 127.5, 127.0(5), 127.0(2), 125.5, 119.2, 35.7, 32.7, 32.7, 32.0, 30.0, 29.9, 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2, 22.8, 14.2. **FT-IR** (cm^{-1}, neat, ATR) 2922, 2852, 1464, 821, 723. **HRMS** (ESI) calcd for $C_{26}H_{40}N$ [M + H^+]: 366.3161, found: 366.3168.



***(E)*-7-Hydroxy-6-(5-(isoquinolin-1-yl)-3-methylpent-2-en-1-yl)-5-methoxy-4-methylisobenzofuran-1(3*H*)-one, 3h** (42 mg, 35%) was prepared according to the *General Procedure*. The desired compound was obtained as a light-yellow solid. **mp** = 121 – 122 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.39 (d, *J* = 5.7 Hz, 1H), 8.13 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.65 – 7.63 (m, 1H), 7.58 – 7.55 (m, 1H), 7.46 (d, *J* = 5.7 Hz, 1H), 5.31 – 5.28 (m, 1H), 5.20 (s, 2H), 3.73 (s, 3H), 3.45 – 3.32 (m, 4H), 2.59 – 2.49 (m, 2H), 2.14 (s, 3H), 1.93 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 173.1, 163.8, 162.0, 153.8, 144.0, 142.0, 136.4, 135.6, 129.9, 127.5, 127.1, 127.1, 125.4, 122.6, 122.5, 119.3, 116.8, 106.5, 70.2, 61.2, 39.6, 34.4, 22.8, 16.6, 11.7. **FT-IR** (cm^{-1}, neat, ATR) 2932, 1729, 1165, 824, 733. **HRMS** (ESI) calcd for $C_{25}H_{26}NO_4$ [M + H^+]: 404.1862, found: 404.1892.

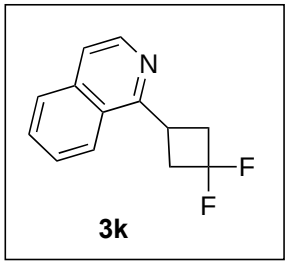


(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*)-17-((*R*)-4-(Isoquinolin-1-yl)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione, 3i (114 mg, 78%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 160 – 161 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.39 (d, *J* = 5.8 Hz, 1H), 8.14 – 8.09 (m, 1H), 7.78 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.58 – 7.54 (m, 1H), 7.47 (d, *J* = 5.7 Hz, 1H), 3.47 – 3.39 (m, 1H), 3.16 – 3.08 (m, 1H), 2.92 – 2.83 (m, 3H), 2.35 – 2.20 (m, 6H), 2.18 – 2.08 (m, 4H), 2.02 – 1.91 (m, 5H), 1.87 – 1.79 (m, 1H), 1.71 – 1.50 (m, 3H), 1.37 (s, 3H), 1.09 – 1.04 (m, 6H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 212.1, 2092, 208.8, 162.7, 141.9, 136.3, 129.9, 127.5, 127.1, 126.9, 125.3, 119.2, 57.0, 51.8, 49.1, 46.9, 45.8, 45.6, 45.0, 42.8, 38.7, 36.6, 36.5, 36.1, 35.6, 35.3, 32.9, 27.8, 25.2, 22.0, 19.2, 11.9. **FT-IR** (cm^{-1}, neat, ATR) 2925, 1707, 1385, 729, 673. **HRMS** (ESI) calcd for $C_{32}H_{40}NO_3$ [M + H^+]: 486.3008, found: 486.2993.



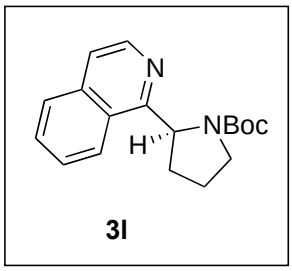
3j

3-(Isoquinolin-1-yl)cyclobutan-1-one, 3j (23 mg, 38%) was prepared according to the *General Procedure*. The desired compound was obtained as a dense brownish oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.49 (d, *J* = 5.7 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 5.7 Hz, 1H), 4.47 – 4.41 (m, 1H), 3.88 – 3.75 (m, 2H), 3.61 – 3.46 (m, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 206.9, 160.4, 141.8, 136.5, 130.2, 127.8, 127.6, 126.8, 124.7, 120.1, 52.9 (2C), 27.2. **FT-IR** (cm^{-1}, neat, ATR) 1783, 1377, 1106, 825, 749. **HRMS** (ESI) calcd for $C_{13}H_{12}NO$ [M + H^+]: 198.0919, found: 198.0911.



3k

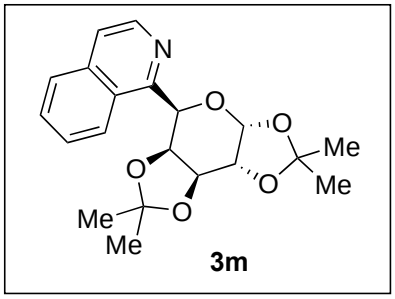
1-(3,3-Difluorocyclobutyl)isoquinoline, 3k (36 mg, 55%) was prepared according to the *General Procedure*. The desired compound was obtained as a dense, yellowish oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.49 (d, *J* = 5.7 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.56 (d, *J* = 5.7 Hz, 1H), 4.18 – 4.12 (m, 1H), 3.27 – 3.18 (m, 2H), 3.10 – 3.03 (m, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 159.9 (t, J_{C-F} = 2.3 Hz), 141.8, 136.4, 130.2, 127.7, 127.5, 126.6, 124.5, 120.0, 120.0 (t, J_{C-F} = 276.3 Hz), 40.4 (t, J_{C-F} = 22.6 Hz), 27.0 (dd, J_{C-F} = 4.5, 3.0 Hz), **^{19}F NMR** (376 MHz, $CDCl_3$) δ –81.63, –98.78. **FT-IR** (cm^{-1}, neat, ATR) 1290, 1231, 1164, 881, 746. **HRMS** (ESI) calcd for $C_{13}H_{12}F_2N$ [M + H^+]: 220.0938, found: 220.0938.



3l

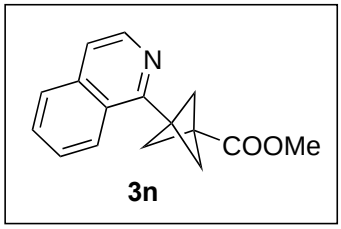
***tert*-Butyl (*S*)-2-(Isoquinolin-1-yl)pyrrolidine-1-carboxylate, 3l** (37 mg, 41%) was prepared according to the *General Procedure*. The desired compound was obtained as an orange solid and a mixture of rotamers (ratio 0.35: 0.65). **mp** = 70 – 71 °C . **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.45 (d, *J* = 10.4, 5.6 Hz, 1H), 8.19 (d, *J* = 19.8, 8.5 Hz, 1H), 7.81 (d, *J* = 23.1, 8.2 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.59 – 7.55 (m, 1H), 7.52 – 7.49 (m, 1H), 5.85 – 5.83 (m, 0.35H), 5.64 – 5.61 (m, 0.65H), 3.88 – 3.82 (m, 1H), 3.75 – 3.59 (m, 1H), 2.52 – 2.43 (m, 1H), 2.15 – 1.92 (m, 3H), 1.44 (s, 3.5H), 0.91 (s, 6.5H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 162.28, 161.20, 154.79, 154.48, 141.95, 136.59, 136.37, 129.77, 129.74, 127.63, 127.57, 127.05, 125.80, 125.74, 124.43, 124.18,

119.85, 119.64, 79.29, 78.85, 59.62, 58.76, 47.46, 47.20, 34.04, 33.03, 28.65, 28.05, 24.19, 23.90. **FT-IR** (cm^{-1}, neat, ATR) 2973, 1687, 1389, 1157, 868. **HRMS** (ESI) calcd for $C_{18}H_{23}N_2O_2$ [M + H^+]: 298.1760, found: 298.1765.



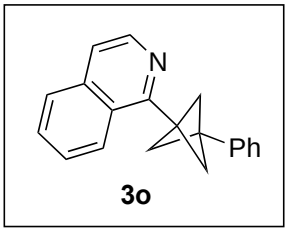
3m

1-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)isoquinoline, 3m (64 mg, 60%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 64 – 65 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.64 (d, *J* = 8.6 Hz, 1H), 8.50 (d, *J* = 5.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.51 (m, 2H), 5.88 (d, *J* = 5.0 Hz, 1H), 5.65 (d, *J* = 1.8 Hz, 1H), 4.80 – 4.75 (m, 2H), 4.49 (dd, *J* = 5.1, 2.2 Hz, 1H), 1.64 (s, 3H), 1.50 (s, 3H), 1.40 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 156.1, 141.4, 137.0, 129.7, 127.2, 127.1, 127.1, 126.5, 120.8, 109.6, 108.9, 97.1, 73.8, 72.8, 71.3, 70.9, 26.4, 25.9, 25.1, 24.0. **FT-IR** (cm^{-1}, neat, ATR) 1382, 1209, 1065, 902, 775. **HRMS** (ESI) calcd for $C_{20}H_{24}NO_5$ [M + H^+]: 358.1654, found: 358.1643.



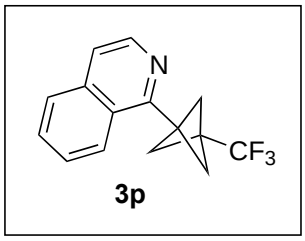
3n

Methyl 3-(Isoquinolin-1-yl)bicyclo[1.1.1]pentane-1-carboxylate, 3n (32 mg, 42%) was prepared according to a slightly modified *General Procedure* by using TFA (34.2 mg, 0.3 mmol, 1 equiv) instead of $NaHSO_4$. The desired compound was obtained as a dense, colorless oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.47 (d, *J* = 5.7 Hz, 1H), 8.38 – 8.35 (m, 1H), 7.84 – 7.81 (m, 1H), 7.69 – 7.65 (m, 1H), 7.61 – 7.58 (m, 1H), 7.57 – 7.55 (m, 1H), 3.75 (s, 3H), 2.73 (s, 6H).**^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 170.7, 157.36, 142.0, 136.5, 130.0, 127.6, 127.2, 125.7, 123.6, 120.5, 54.9 (3C), 51.9, 43.7, 38.8. **FT-IR** (cm^{-1}, neat, ATR) 2989, 1723, 1203, 971, 799. **HRMS** (ESI) calcd for $C_{16}H_{16}NO_2$ [M + H^+]: 254.1181, found: 254.1194.



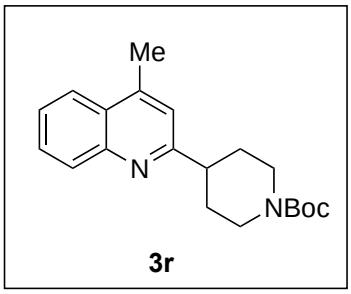
3o

1-(3-Phenylbicyclo[1.1.1]pentan-1-yl)isoquinoline, 3o (38 mg, 47%) was prepared according to a slightly modified *General Procedure* by using TFA (34.2 mg, 0.3 mmol, 1 equiv) instead of $NaHSO_4$. The desired compound was obtained as an orange solid. **mp** = 74 – 75 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.55 – 8.53 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.38 – 7.34 (m, 4H), 7.31 – 7.27 (m, *J* = 5.2, 2.2 Hz, 1H), 2.78 (s, 6H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 158.3, 141.1, 140.5, 136.7, 130.5, 128.4, 127.6, 127.5, 127.3, 126.9, 126.3, 126.3, 120.5, 55.8, 42.9, 42.6. **FT-IR** (cm^{-1}, neat, ATR) 2970, 1724, 825, 743, 670. **HRMS** (ESI) calcd for $C_{20}H_{18}N$ [M + H^+]: 272.1439, found: 272.1445.



3p

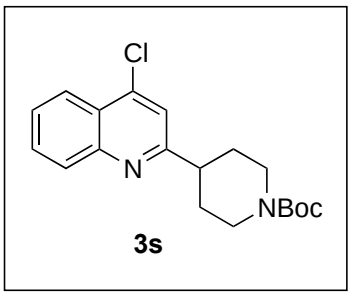
1-(3-(Trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)isoquinoline, 3p (41 mg, 52%) was prepared according to a slightly modified *General Procedure* by using TFA (34.2 mg, 0.3 mmol, 1 equiv) instead of $NaHSO_4$. The desired compound was obtained as a white solid. **mp** = 79 – 80 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.49 (d, *J* = 5.8 Hz, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.65 – 7.61 (m, 2H), 2.66 (s, 6H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 156.2, 141.4, 136.7, 130.5, 127.8, 127.6, 127.3, 125.6, 123.1 (q, J_{C-F} = 275.8 Hz), 121.0, 52.1 (q, J_{C-F} = 2.5 Hz), 43.0, 38.6, 38.2 (q, J_{C-F} = 38.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –76.15. **FT-IR** (cm^{-1}, neat, ATR) 1378, 1171, 1127, 826, 729. **HRMS** (ESI) calcd for $C_{15}H_{13}F_3N$ [M + H^+]: 264.1000, found: 264.0979.



3r

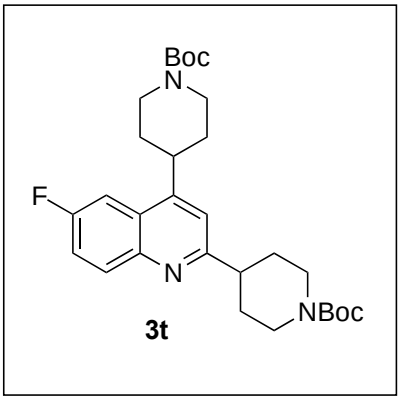
***tert*-Butyl 4-(4-Methylquinolin-2-yl)piperidine-1-carboxylate, 3r** (64 mg, 65%) was prepared according to the *General Procedure*. The desired compound was obtained as a dense, yellowish oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.02 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.93 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.51 – 7.48 (m, 1H), 7.13 (d, *J* = 1.2 Hz, 1H), 4.28 (br, 2H), 3.03 – 2.98 (m, 1H), 2.87 (br, 2H), 2.67 (s, 3H), 1.99 – 1.91 (m, 2H), 1.85 – 1.79 (m, 2H), 1.48 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 164.4, 154.9, 147.7, 144.8, 129.6, 129.3,

127.2, 125.8, 123.7, 120.1, 79.5, 45.5, 44.5, 43.8, 31.7, 29.8, 28.6 (3C), 18.9. **FT-IR** (cm^{-1}, neat, ATR) 1683, 1447, 1165, 758, 729. **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_2$ [M + H^+]: 327.2073, found: 327.2085.



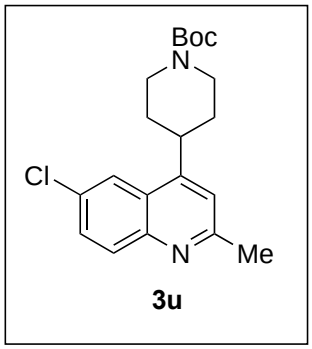
3s

***tert*-Butyl 4-(4-Chloroquinolin-2-yl)piperidine-1-carboxylate, 3s** (26 mg, 25%) was prepared according to the *General Procedure*. The desired compound was obtained as a dense, yellowish oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.19 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.41 (s, 1H), 4.29 (br, 2H), 3.03 (t, *J* = 12.5 Hz, 1H), 2.89 (br, 2H), 2.04 – 1.98 (m, 2H), 1.88 – 1.79 (m, 2H), 1.49 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 164.6, 154.9 (2C), 130.7, 129.3, 127.2, 125.4, 124.1, 122.1, 119.8, 79.7 (2C), 45.2, 44.7, 44.2, 31.6, 28.6 (3C). **FT-IR** (cm^{-1}, neat, ATR) 1688, 1477, 1164, 936, 761. **HRMS** (ESI) calcd for $C_{19}H_{24}ClN_2O_2$ [M + H^+]: 347.1526, found: 347.1523.



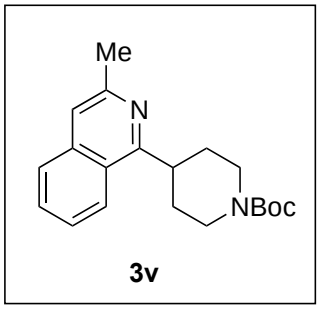
3t

Di-*tert*-butyl 4,4'-(6-Fluoroquinoline-2,4-diyl)bis(piperidine-1-carboxylate), 3t (102 mg, 66%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 84 – 85 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 8.03 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.59 (dd, *J* = 10.4, 2.8 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.26 (s, 1H), 4.30 (br, 4H), 3.30 – 3.25 (m, 1H), 3.01 – 2.95 (m, 1H), 2.93 (br, 2H), 2.86 (br, 2H), 1.94 (d, *J* = 4.8 Hz, 2H), 1.92 (d, *J* = 5.5 Hz, 2H), 1.86 – 1.77 (m, 2H), 1,74 – 1.67 (m, 2H), 1.48 (s, 9H), 1.47 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 163.9 (2C), 160.4 (d, J_{C-F} = 246.6 Hz), 159.6, 154.9, 154.8, 151.0, 145.3, 132.6, 132.6, 126.2, 126.2, 119.2, 119.0, 116.6, 106.4, 106.2, 79.8, 79.5, 45.5, 44.2, 37.6, 32.3, 31.7, 28.6 (3C), 28.6 (3C). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.78. **FT-IR** (cm^{-1}, neat, ATR) 1688, 1340, 1275, 1168, 961. **HRMS** (ESI) calcd for $C_{29}H_{41}FN_3O_4$ [M + H^+]: 514.3081, found: 514.3091.



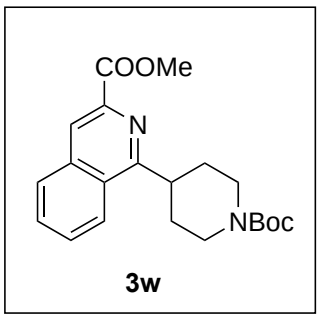
3u

***tert*-Butyl 4-(6-Chloro-2-methylquinolin-4-yl)piperidine-1-carboxylate, 3u** (41 mg, 38%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 78 – 79 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 4.33 (s, 2H), 3.45 – 3.37 (m, 1H), 2.94 (t, *J* = 13.1 Hz, 2H), 2.78 (s, 3H), 1.94 (d, *J* = 13.0 Hz, 2H), 1.77 – 1.67 (m, 2H), 1.49 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 160.0, 154.8, 151.5, 144.6, 134.0, 129.3, 126.4, 125.4, 121.7, 119.4, 79.9, 77.4, 44.6, 37.5, 32.5, 29.8, 28.6 (3C), 26.0. **FT-IR** (cm^{-1}, neat, ATR) 1686, 1423, 1289, 1161, 756. **HRMS** (ESI) calcd for $C_{20}H_{26}ClN_2O_2$ [M + H^+]: 361.1683, found: 361.1672.



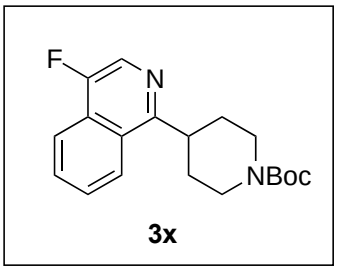
3v

***tert*-Butyl 4-(3-Methylisoquinolin-1-yl)piperidine-1-carboxylate, 3v** (46 mg, 47%) was prepared according to the *General Procedure*. The desired compound was obtained as a dense, colorless oil. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 8.15 – 8.13 (m, 1H), 7.75 – 7.71 (m, 1H), 7.61 – 7.58 (m, 1H), 7.51 – 7.49 (m, 1H), 7.32 (s, 1H), 4.31 (br, 2H), 3.66 (tt, *J* = 11.5, 3.7 Hz, 1H), 2.96 (br, 2H), 2.64 (s, 3H), 2.06 (br, 2H), 1.90 (br, 2H), 1.49 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 162.9, 155.0, 150.8, 137.3, 129.6, 127.2, 126.1, 124.4, 124.3, 117.2, 79.5, 44.6(7), 44.6(6), 43.9, 39.8, 31.5(2), 31.5(1), 28.7 (3C), 24.5. **FT-IR** (cm^{-1}, neat, ATR) 1683, 1423, 1276, 1167, 749. **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_2$ [M + H^+]: 327.2073, found: 327.2084.



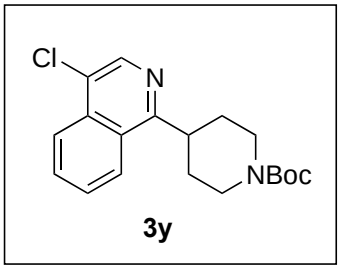
3w

Methyl 1-(1-(*tert*-Butoxycarbonyl)piperidin-4-yl)isoquinoline-3-carboxylate, 3w (37 mg, 33%) was prepared according to the *General Procedure*. The desired compound was obtained as a dense, gummy liquid. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 8.43 (s, 1H), 8.28 – 8.24 (m, 1H), 8.00 – 7.95 (m, 1H), 7.74 (dd, *J* = 7.8, 4.8 Hz, 2H), 4.33 (s, 2H), 4.03 (s, 3H), 3.74 – 3.69 (m, 1H), 2.99 (s, 2H), 2.24 – 2.07 (m, 2H), 1.97 (s, 2H), 1.49 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 166.8, 164.1, 154.9, 140.8, 136.3, 130.5, 129.5, 129.4, 127.8, 124.6, 122.9, 79.6, 52.8, 44.5, 43.7, 40.2, 31.2, 29.8, 28.7 (3C). **FT-IR** (cm^{-1}, neat, ATR) 2923, 1738, 1425, 1243, 1167, 783. **HRMS** (ESI) calcd for $C_{21}H_{27}N_2O_4$ [M + H^+]: 371.1971, found: 371.1969.



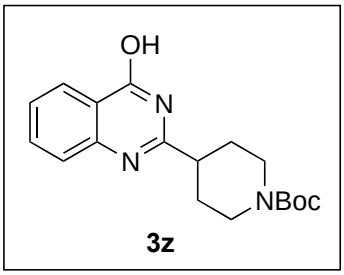
3x

***tert*-Butyl 4-(4-Fluoroisoquinolin-1-yl)piperidine-1-carboxylate, 3x** (59 mg, 56%) was prepared according to the *General Procedure*. The desired compound was obtained as a yellow solid. **mp** = 92 – 93 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm 8.33 (d, *J* = 1.8 Hz, 1H), 8.23 – 8.21 (m, 1H), 8.14 – 8.13 (m, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.73 – 7.67 (m, 1H), 4.32 (br, 2H), 3.68 – 3.63 (m, 1H), 2.95 (br, 2H), 2.16 – 1.89 (m, 4H), 1.48 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 159.5, 159.5, 154.9, 154.3 (d, $J_{C\text{-}F}$ = 258.2 Hz), 130.6, 128.3, 127.3 (d, $J_{C\text{-}F}$ = 1.5 Hz), 126.3, 124.5, 120.7 (d, $J_{C\text{-}F}$ = 4.5 Hz), 79.6 (2C), 44.6, 43.8, 39.8, 31.5, 28.6 (3C). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –143.29. **FT-IR** (cm^{-1}, neat, ATR) 1684, 1415, 1276, 1163, 763. **HRMS** (ESI) calcd for $C_{19}H_{24}FN_2O_2$ [M + H^+]: 331.1822, found: 331.1814.



3y

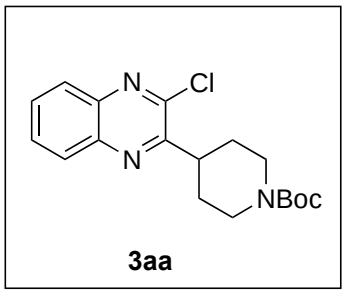
***tert*-Butyl 4-(4-Chloroisoquinolin-1-yl)piperidine-1-carboxylate, 3y** (36 mg, 35%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 82 – 83 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 8.51 (s, 1H), 8.26 – 8.24 (m, 1H), 8.23 – 8.20 (m, 1H), 7.81 – 7.78 (m, 1H), 7.69 – 7.66 (m, 1H), 4.32 (br, 2H), 3.69 – 3.63 (m, 1H), 2.96 (br, 2H), 2.00 (br, 2H), 1.91 (br, 2H), 1.48 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 162.6, 154.9, 140.9, 134.0, 130.8, 128.0, 127.2, 126.8, 124.7, 124.5, 79.6, 44.6, 43.7, 39.8, 31.5, 28.6 (3C), 28.6. **FT-IR** (cm^{-1}, neat, ATR) 1685, 1448, 1164, 986, 760. **HRMS** (ESI) calcd for $C_{19}H_{24}N_2O_2Cl$ [M + H^+]: 347.1526, found: 347.1526.



3z

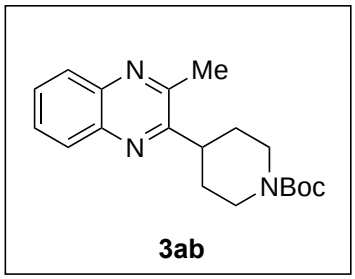
***tert*-Butyl 4-(4-Hydroxyquinazolin-2-yl)piperidine-1-carboxylate, 3z** (52 mg, 53%) was prepared according to the *General Procedure* from the 4-chloroquinazoline precursor. The desired compound was obtained as a white solid. **mp** = 222 – 223 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 12.16 (s, 1H), 8.30 – 8.25 (m, 1H), 7.80 – 7.74 (m, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 4.30 (br, 2H), 3.01 – 2.84 (m, 3H), 2.08 – 1.92 (m, 4H), 1.49 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 164.6, 158.4, 154.8, 149.5, 135.0, 127.6, 126.7, 126.4,

120.8, 79.7, 44.0, 43.1, 42.7, 29.8, 29.6, 28.6 (3C). **FT-IR** (cm^{-1}, neat, ATR) 1672, 1611, 1283, 977, 778. **HRMS** (ESI) calcd for $C_{18}H_{24}N_3O_3$ [M + H^+]: 330.1818, found: 330.1819.



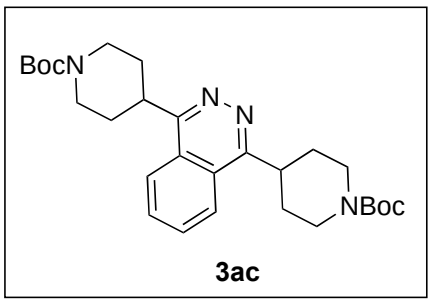
3aa

***tert*-Butyl 4-(3-Chloroquinoxalin-2-yl)piperidine-1-carboxylate, 3aa** (57 mg, 55%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 146 – 147 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 8.06 – 8.02 (m, 1H), 8.00 – 7.95 (m, 1H), 7.76 – 7.71 (m, 2H), 4.30 (br, 2H), 3.51 – 3.46 (m, 1H), 2.93 (br, 2H), 2.03 – 1.86 (m, 4H), 1.49 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 157.2, 154.9, 147.2, 141.2, 140.9, 130.4, 130.2, 129.0, 128.2, 79.7, 44.1, 43.6, 40.9, 30.3 (2C), 28.6 (3C). **FT-IR** (cm^{-1}, neat, ATR) 1687, 1422, 1163, 1054, 726. **HRMS** (ESI) calcd for $C_{18}H_{23}ClN_3O_2$ [M + H^+]: 348.1479, found: 348.1460.



3ab

***tert*-Butyl 4-(3-Methylquinoxalin-2-yl)piperidine-1-carboxylate, 3ab** (43 mg, 44%) was prepared according to the *General Procedure*. The desired compound was obtained as a white solid. **mp** = 128 – 129 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 8.02 – 7.93 (m, 2H), 7.69 – 7.62 (m, 2H), 4.32 (s, 2H), 3.21 – 3.16 (m, 1H), 2.91 (br, 2H), 2.80 (s, 3H), 2.07 – 1.93 (m, 2H), 1.86 (br, 2H), 1.49 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 158.4, 154.9, 152.4, 141.4, 140.9, 129.2, 128.9 (2C), 128.4, 79.6, 44.4, 43.7, 40.8, 30.7 (2C), 28.6 (3C), 22.8. **FT-IR** (cm^{-1}, neat, ATR) 1688, 1449, 1230, 1020, 762. **HRMS** (ESI) calcd for $C_{19}H_{26}N_3O_2$ [M + H^+]: 328.2025, found: 328.2023.



3ac

Di-*tert*-butyl 4,4'-(Phthalazine-1,4-diyl)bis(piperidine-1-carboxylate), 3ac (106 mg, 71%) was prepared according to the *General Procedure*. The desired compound was obtained as a light-yellow solid. **mp** = 171 – 172 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ ppm δ 8.17 – 8.12 (m, 2H), 7.89 – 7.86 (m, 2H), 4.28 (br, 4H), 3.64 –

3.56 (m, 2H), 2.99 – 2.92 (m, 4H), 2.27 – 1.87 (m, 8H), 1.44 (s, 18H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ ppm 160.5 (2C), 154.9 (2C), 131.8 (2C), 124.9 (2C), 124.0 (2C), 79.5 (2C), 44.5 (2C), 43.9 (2C), 38.7 (2C), 31.2 (2C), 30.8 (2C), 28.5 (6C). **FT-IR** (cm^{-1}, neat, ATR) 1681, 1423, 1226, 1122, 732. **HRMS** (ESI) calcd for $C_{28}H_{41}N_4O_4$ [M + H^+]: 497.3128, found: 497.3143.

5. Mechanistic Investigations

5A. UV-Absorption Spectral Studies

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific. Absorption spectra of individual reaction components and mixtures thereof were recorded. A bathochromic shift was observed for a mixture of isoquinoline **1a**, *N*-Boc-piperidine redox active ester **2a**, and $NaHSO_4$ in DMF (0.1 M). This indicates the formation of an electron donor-acceptor (EDA) complex (*Figure S2*, red band).

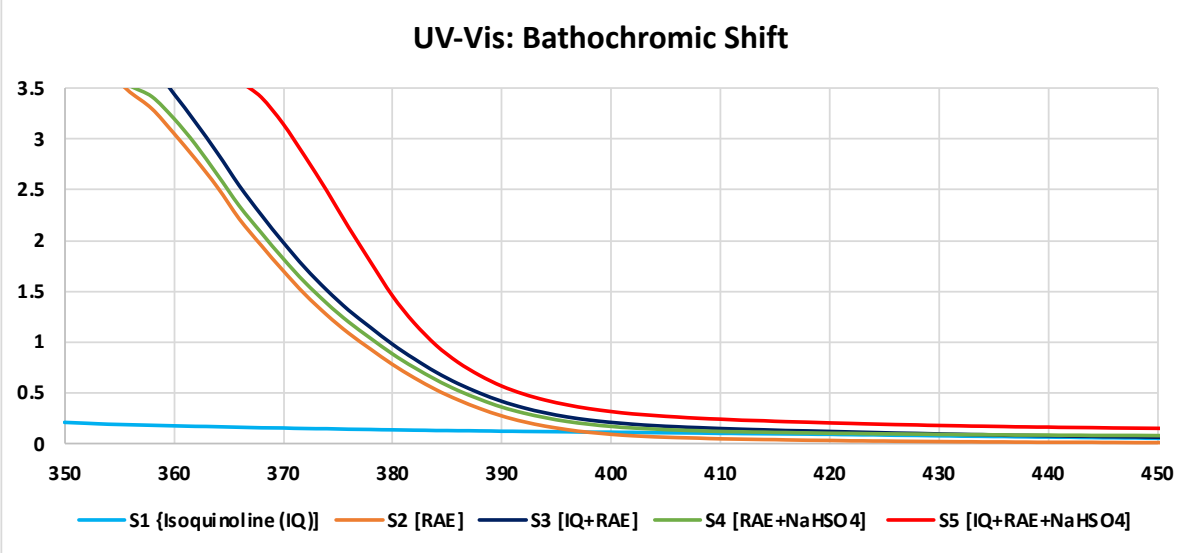
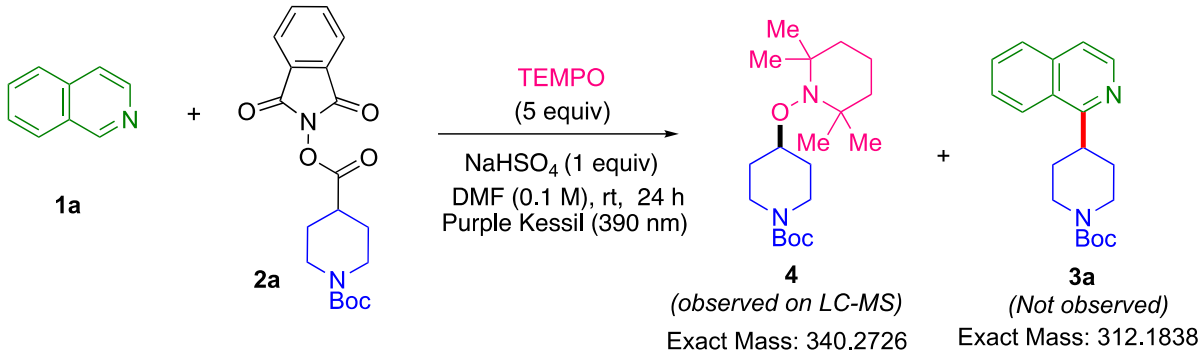
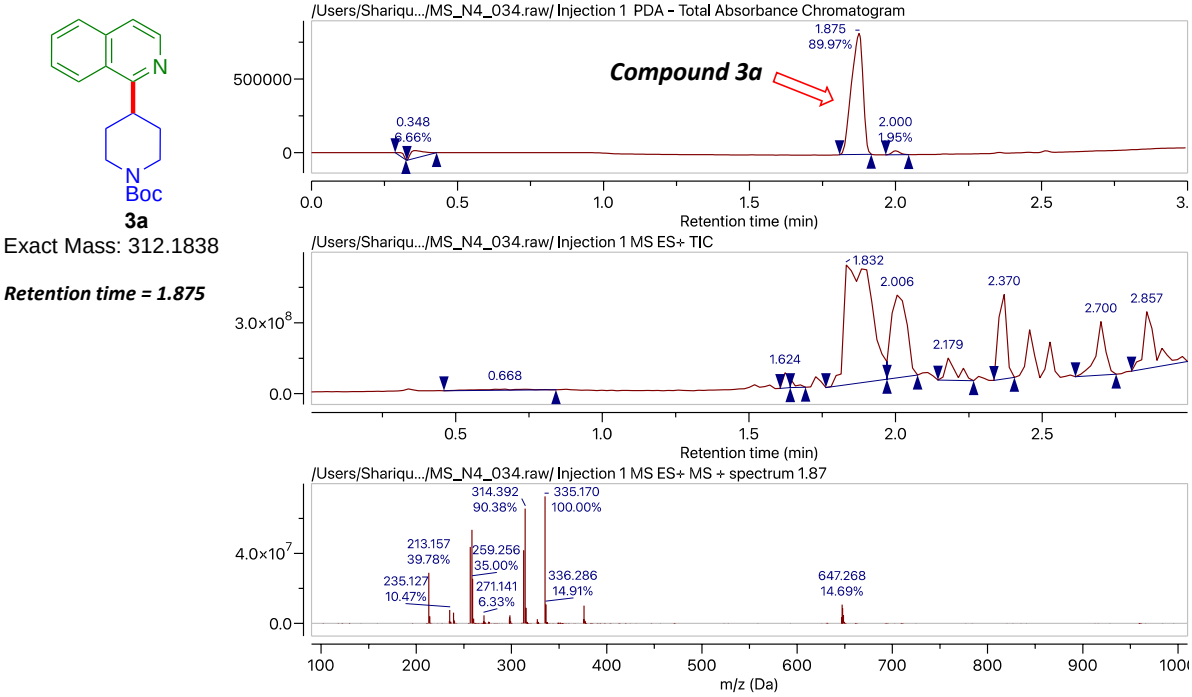


Figure S2. *UV-Vis spectra of individual reaction components and mixtures*

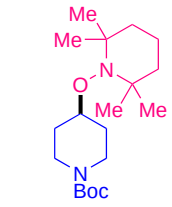
5B. Radical trapping experiments



LC-MS trace of compound 3a



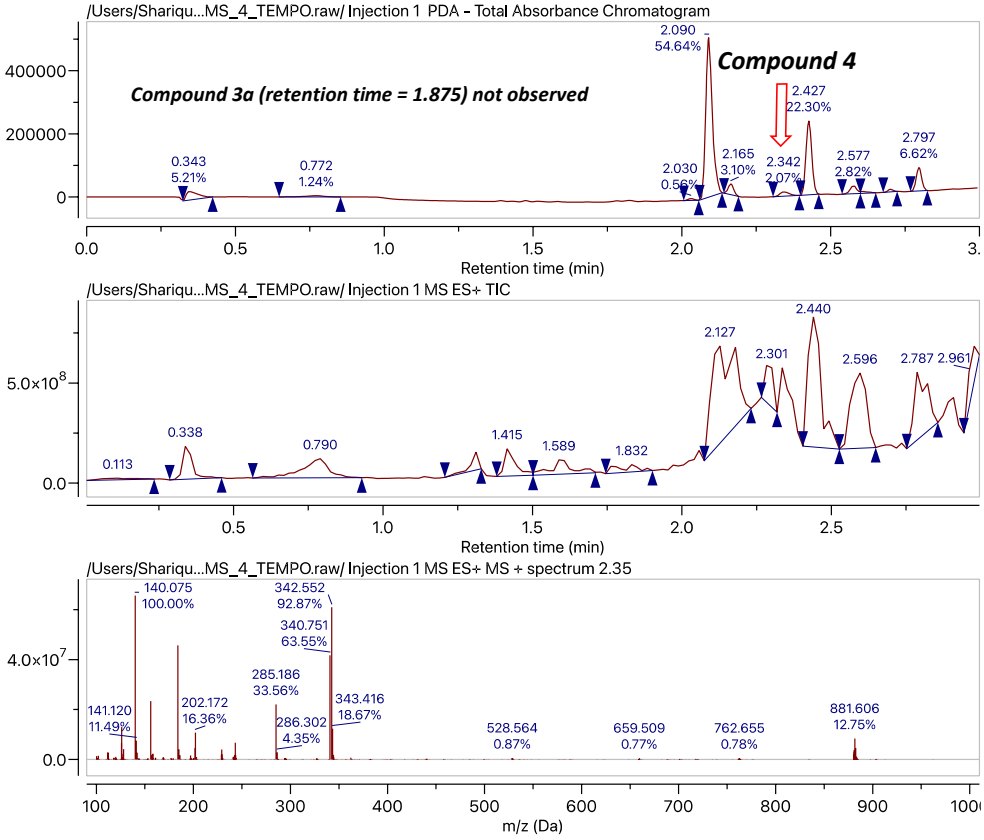
LC-MS trace of TEMPO experiment



4

Exact Mass: 340.2726

Retention time = 2.342



6. Measurement of Quantum Yield

6A. Determination of the light intensity

The photon flux of the LEDs (λ_{max} = 390 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (1.84 g) in 25 mL H_2SO_4 (0.05 M). A buffered solution of 1,10-phenanthroline was prepared by dissolving sodium acetate (11.2 g) and phenanthroline (50 mg) in 50 mL H_2SO_4 (0.5 M) at the same time. Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (1.0 mL) was placed in a cuvette and irradiated for 30 seconds at λ_{max} = 390 nm. After irradiation, the phenanthroline solution (1 mL), and water (4 mL) were added to the vial and the mixture was stirred in the dark for 1 hour to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

$$\text{mol } Fe^{2+} = V \times \Delta A/1 \times \varepsilon \quad (1)$$

$$= 0.006 \text{ L} \times 2.76/ 1 \text{ cm} \times 11100 \text{ L mol}^{-1}\text{cm}^{-1} = 1.5 \times 10^{-6} \text{ mol}$$

ΔA is the difference in absorbance between the irradiated and non-irradiated solutions at 510 nm; 1 is the path length (1.000 cm); V is the total volume (0.006 L) of the solution; and ε is the molar absorptivity at 510 nm (11,100 L $mol^{-1}cm^{-1}$). The photon flux can be calculated according to eq 2.

$$\text{Photon flux} = \text{mol } Fe^{2+}/\Phi * t * f \quad (2)$$

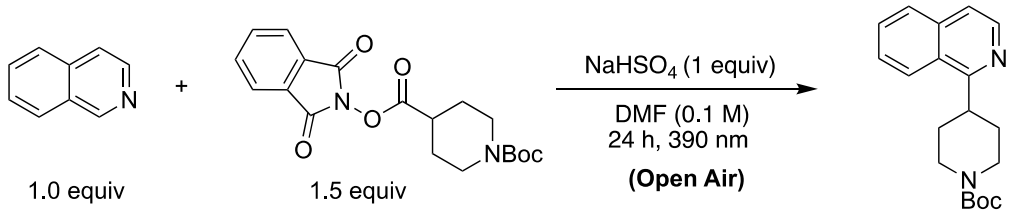
$$= 1.5 \times 10^{-6} \text{ mol}/1.1 \times 30 \text{ s} \times 0.75 = 6 \times 10^{-8} \text{ einsteins } s^{-1}.$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.1 for a 0.15 M solution at λ = 390 nm), t is the time (30.0 s), and f is the fraction of light absorbed at λ = 390 nm (eq 3). The absorbance of the above ferrioxalate solution at 390 nm was measured to be 0.6 indicating the fraction of light absorbed is >0.999. The fraction of light absorbed (f) by this solution was calculated using eq 3, where A is the measured absorbance at 420 nm.

$$f = 1 - 10^{-A} \quad (3)$$

According to the above formula, the photon flux was calculated to be 6 x 10^{-8} einsteins s^{-1}.

6B. Determination of quantum yield:



To an 8 mL vial equipped with a magnetic stir bar and a rubber septum was added the isoquinoline (52 mg, 0.4 mmol, 1.0 equiv), redox active ester (225 mg, 0.6 mmol, 1.5 equiv), $NaHSO_4$ (48 mg, 0.4 mmol, 1.0 equiv) and DMF (4 mL, c = 0.1 M) under an open-air condition. The reaction system was closed, and the reaction mixture was irradiated for 60 min with a

Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390. After irradiation, the yield of product was determined by ^{1}H NMR analysis to be 25%.

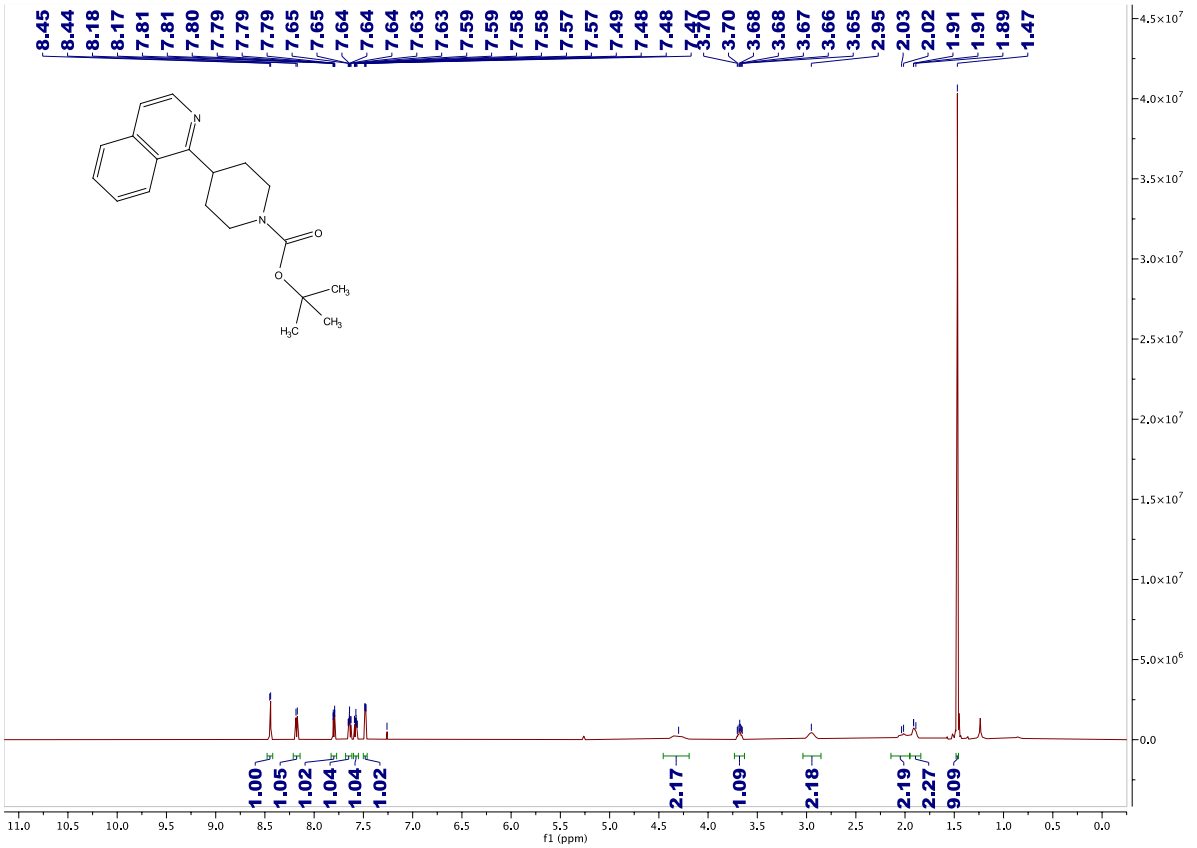
The quantum yield was determined using eq 4.

$$\Phi = \text{moles of product formed/ Photon flux x t x f} \qquad (4)$$

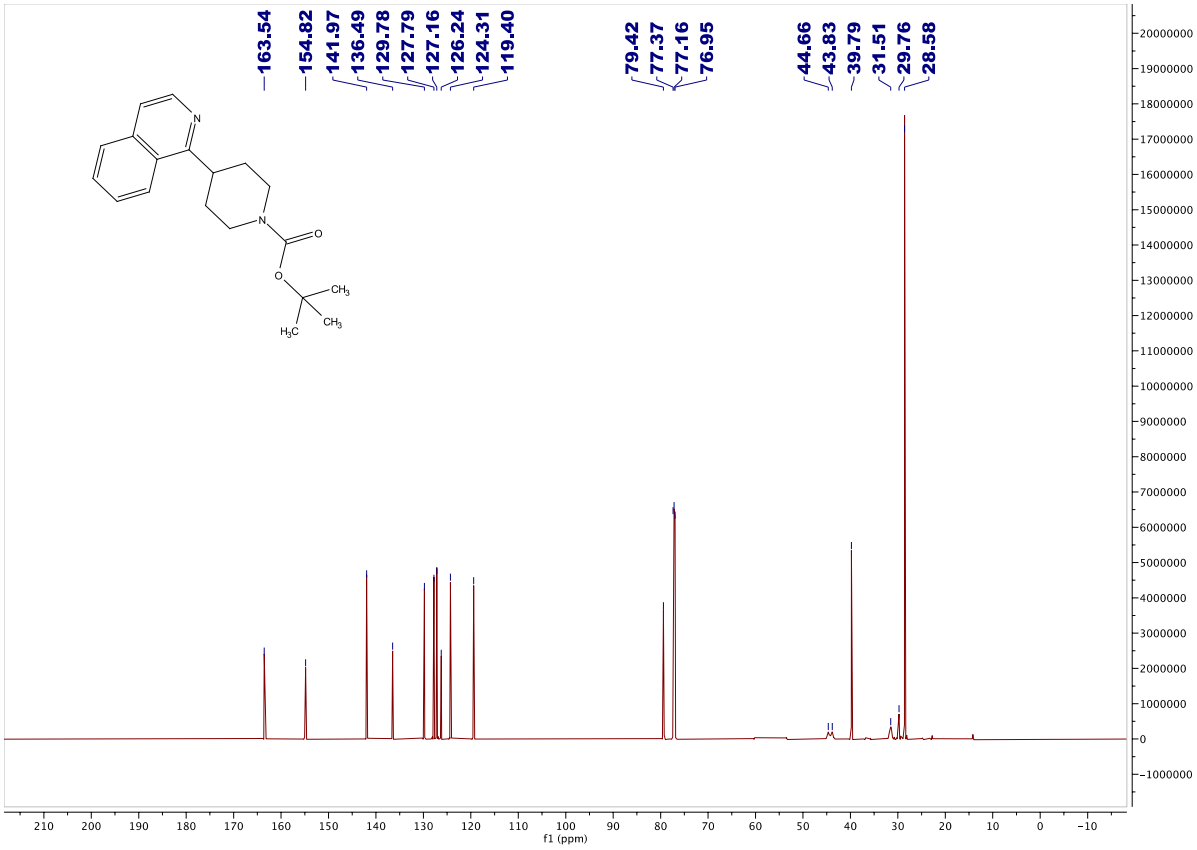
$$= 0.4 \times 0.25 \times 10^{-3} / 6 \times 10^{-8} \times 3600 \times 0.75 = 0.62$$

The quantum yield Φ for the reaction was calculated to be 0.62.

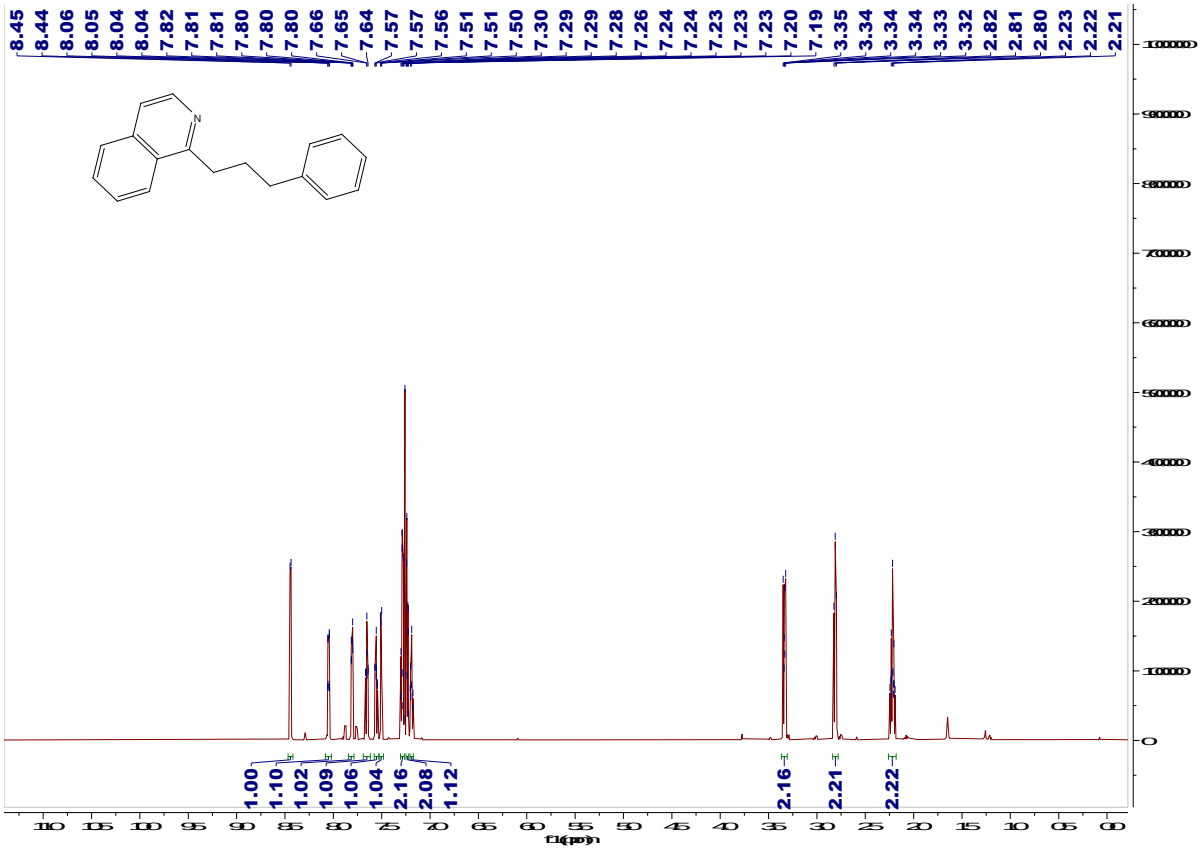
7. NMR Spectra



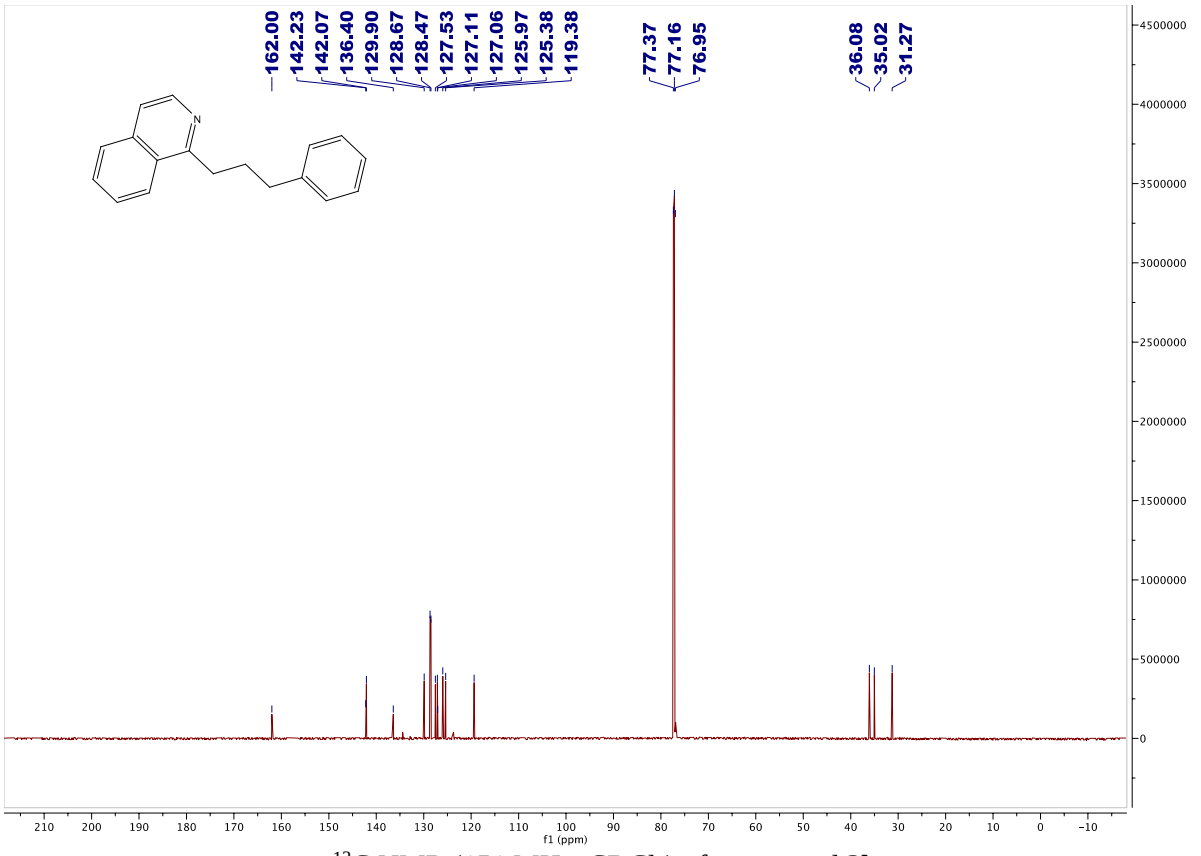
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3a**



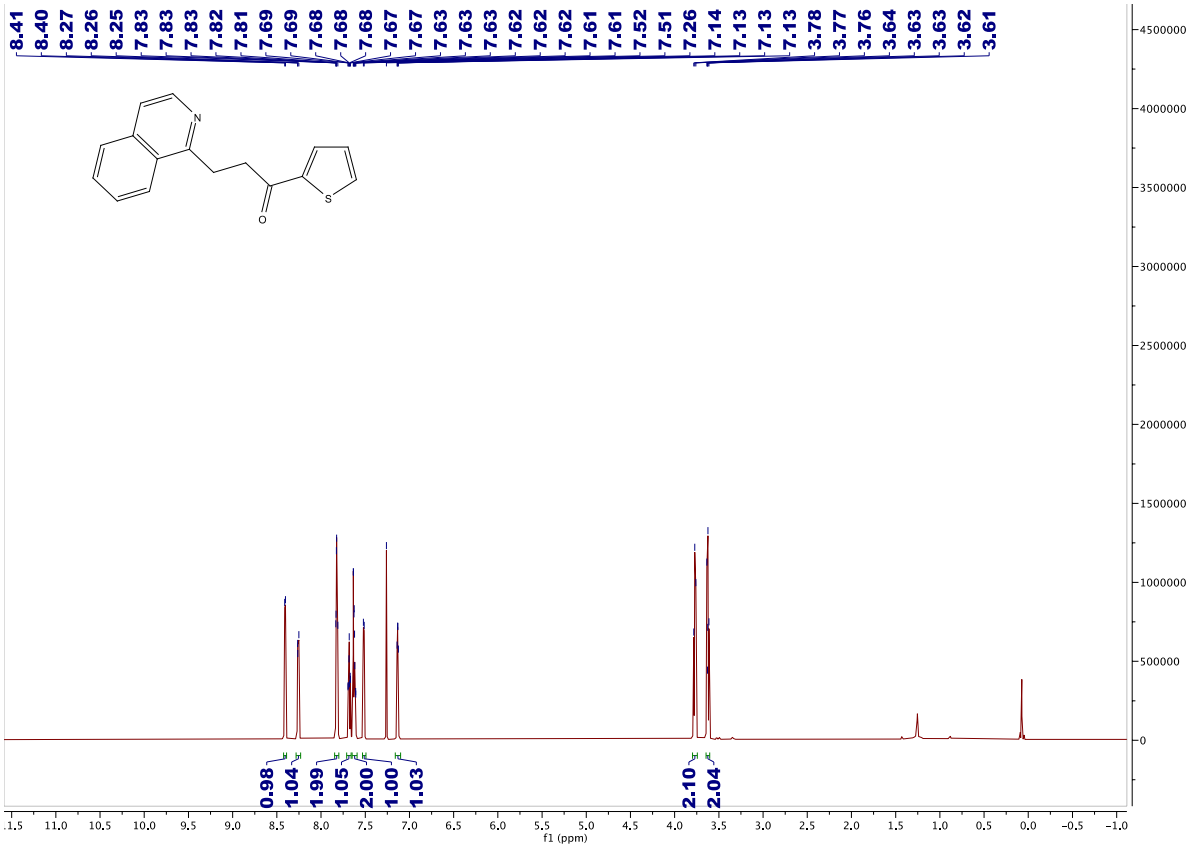
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3a**



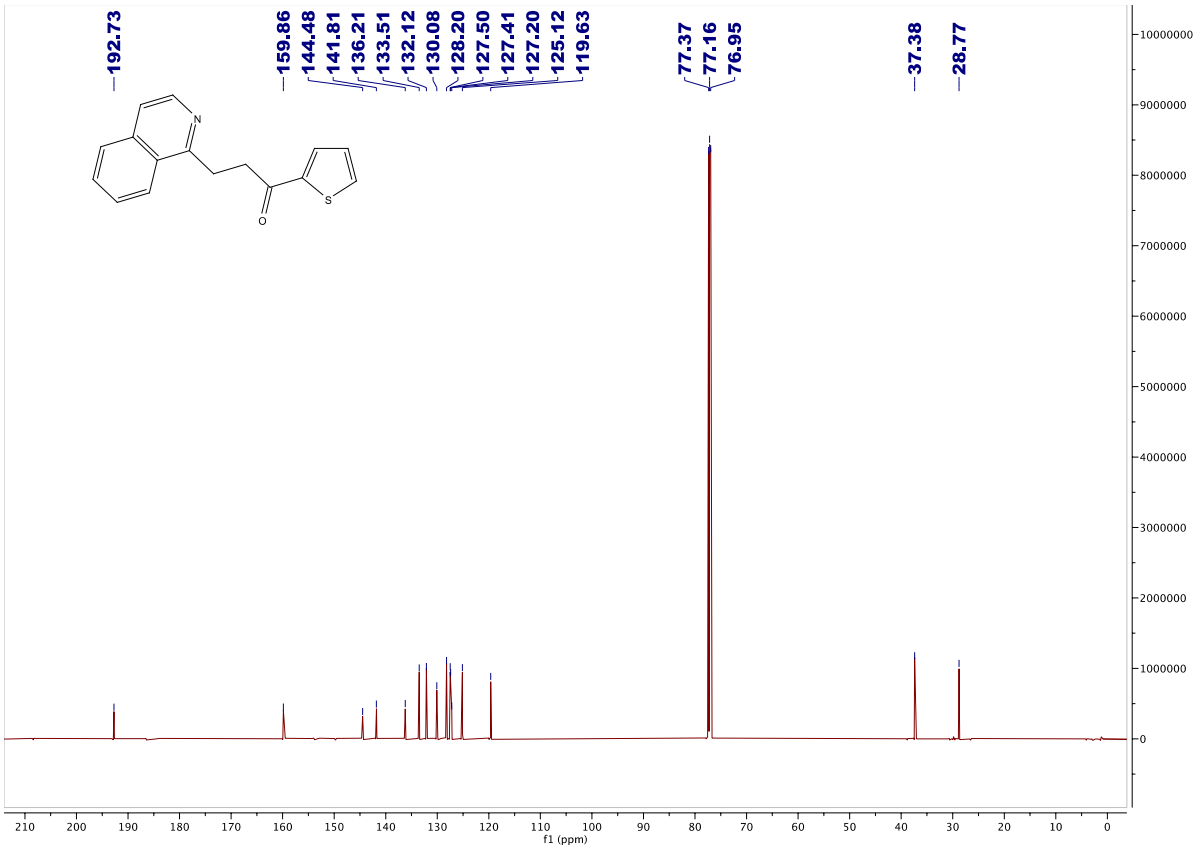
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3b**



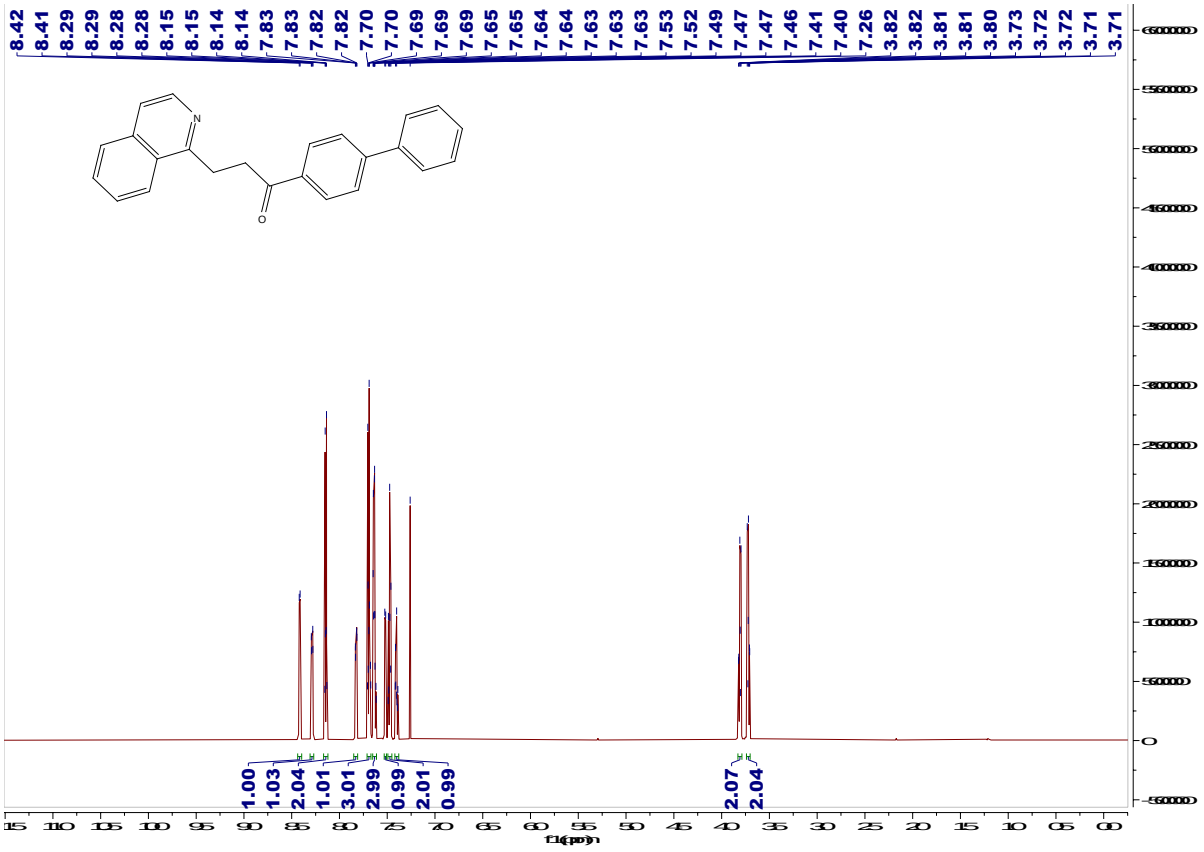
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3b**



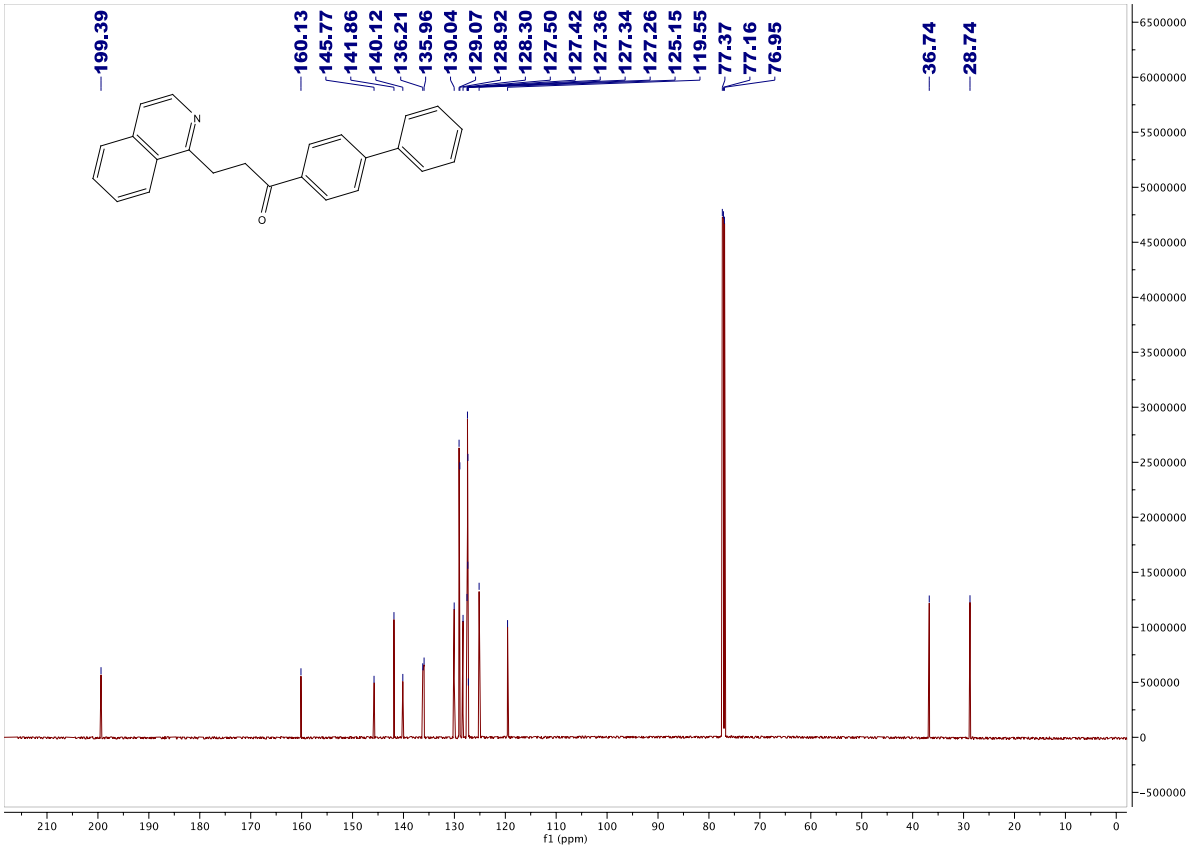
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3c**



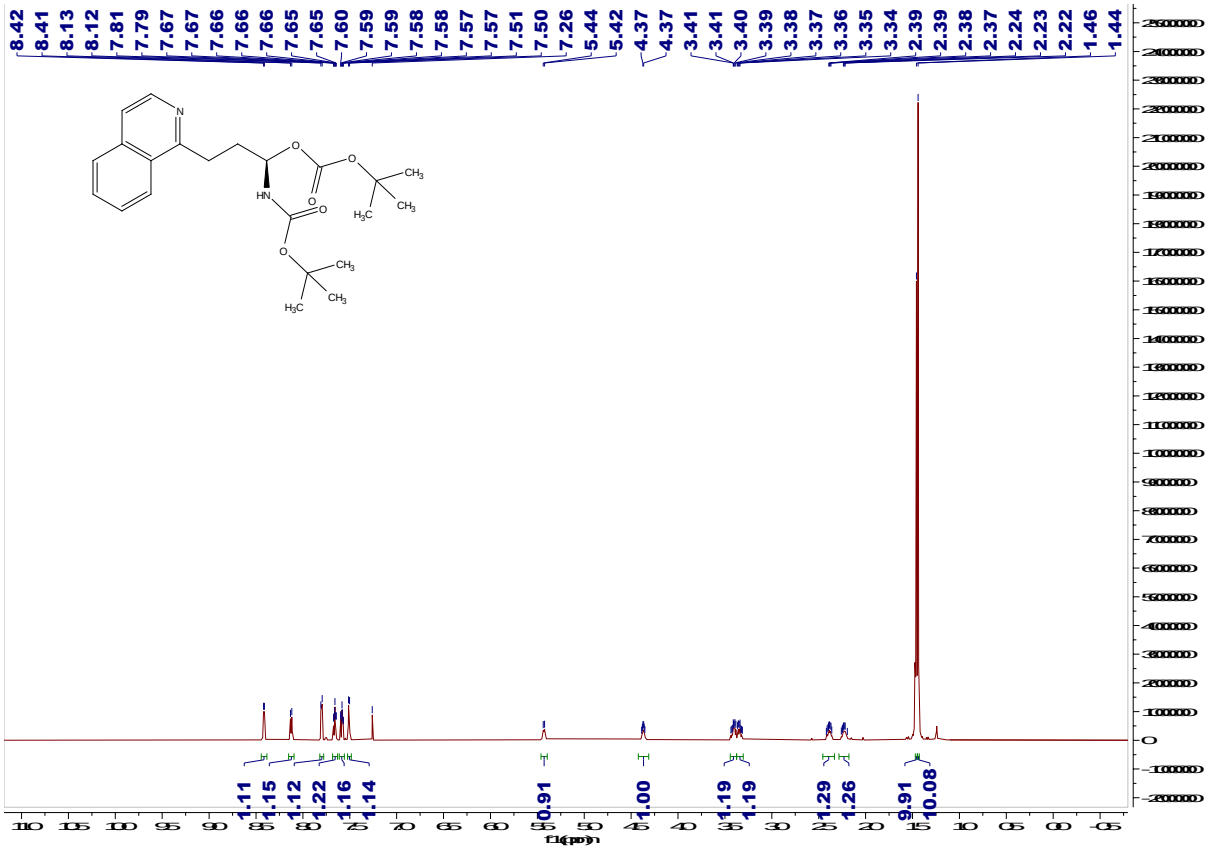
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3c**



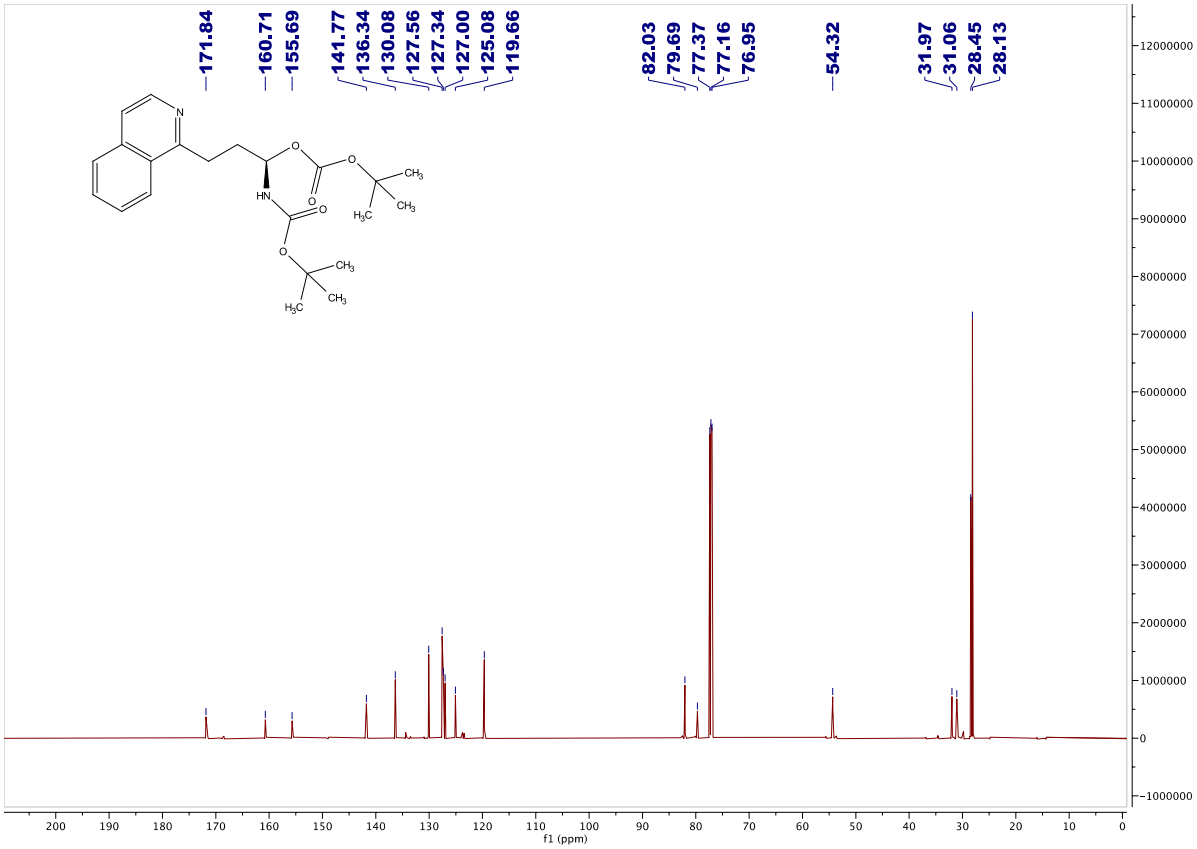
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3d**



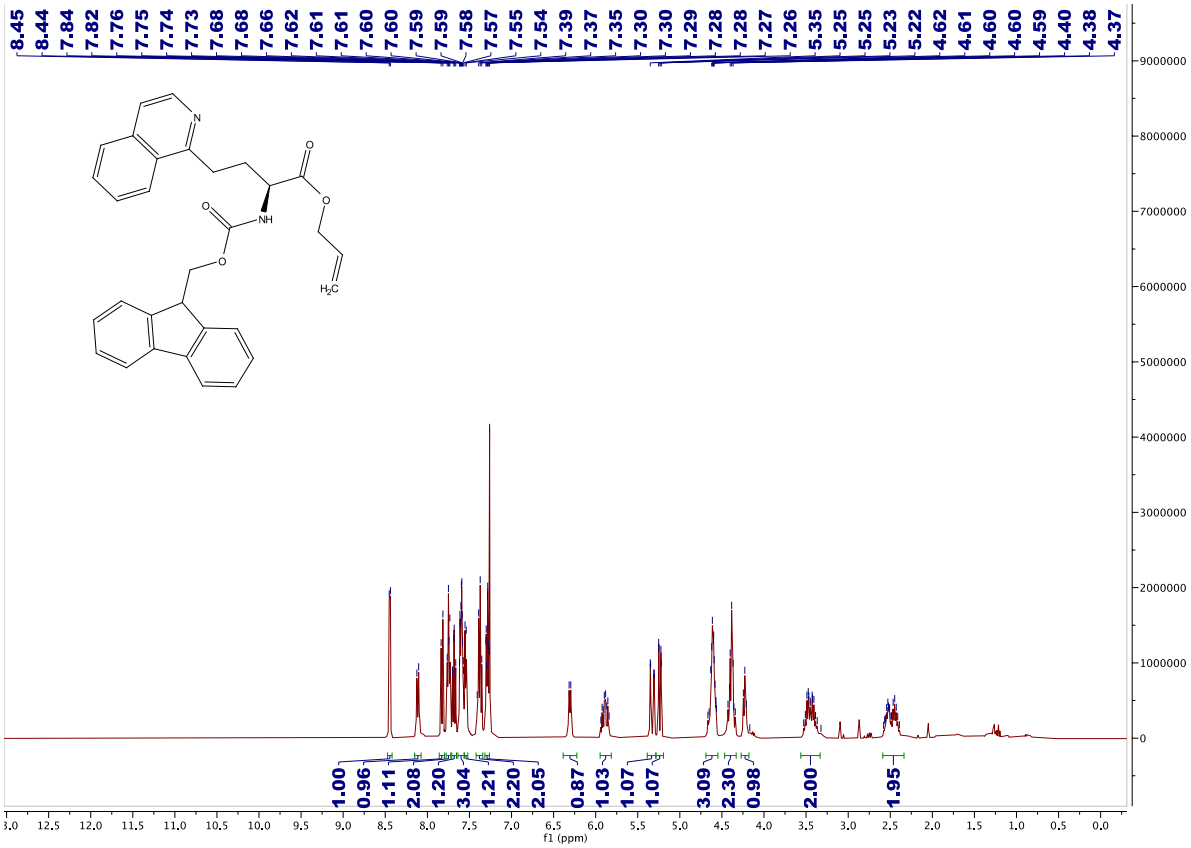
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3d**



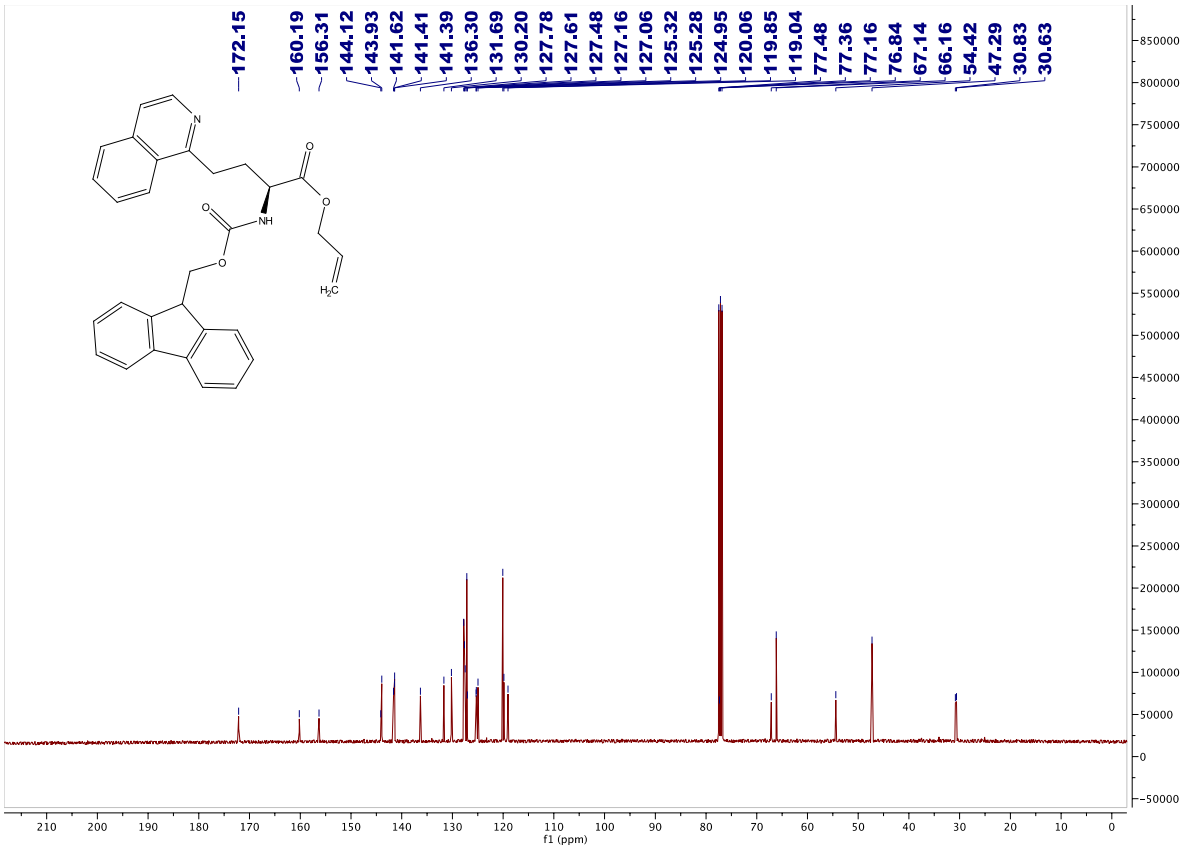
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3e**



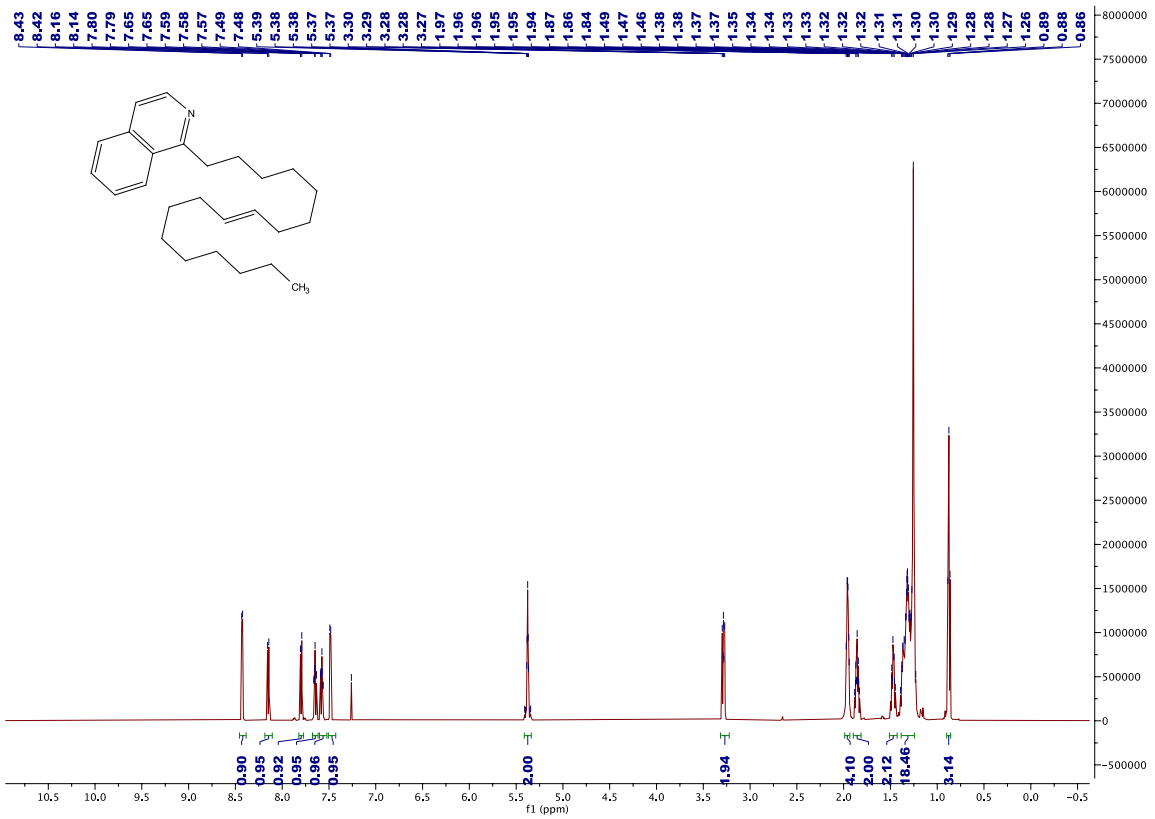
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3e**



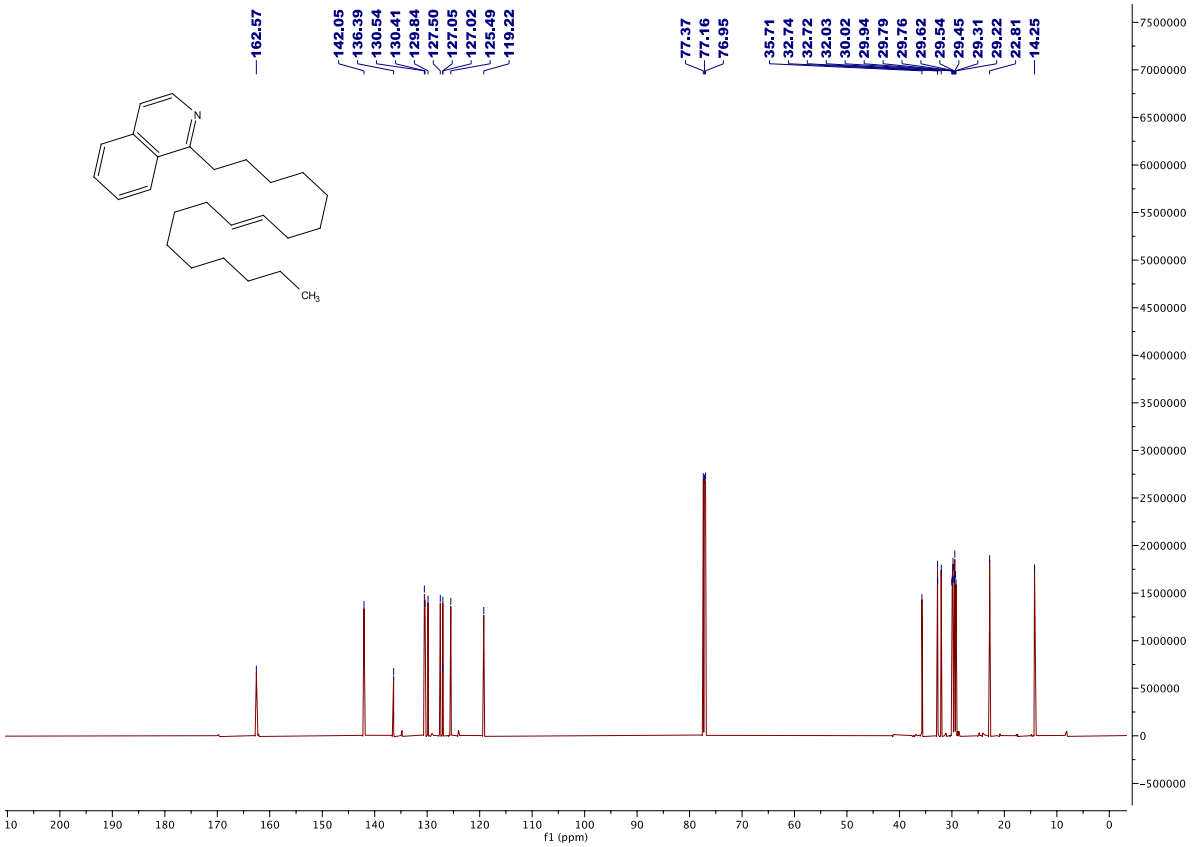
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3f**



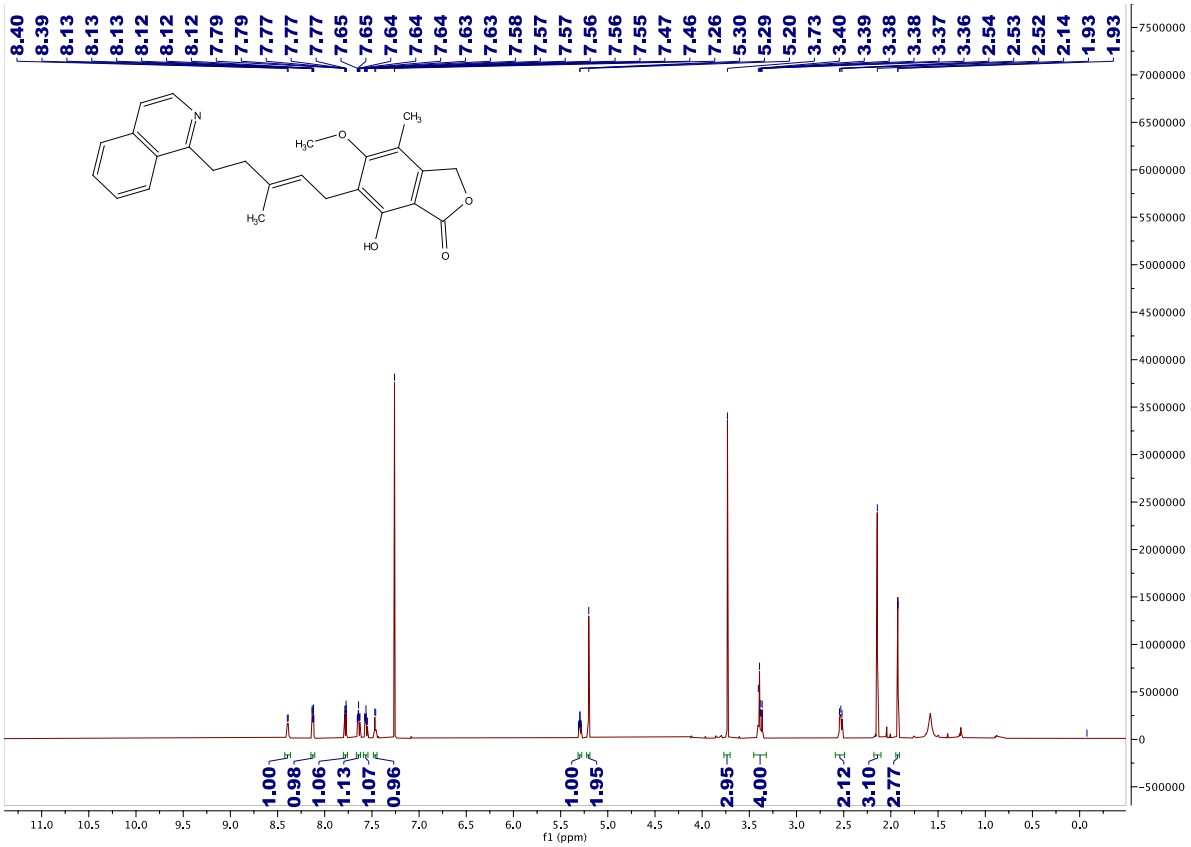
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3f**



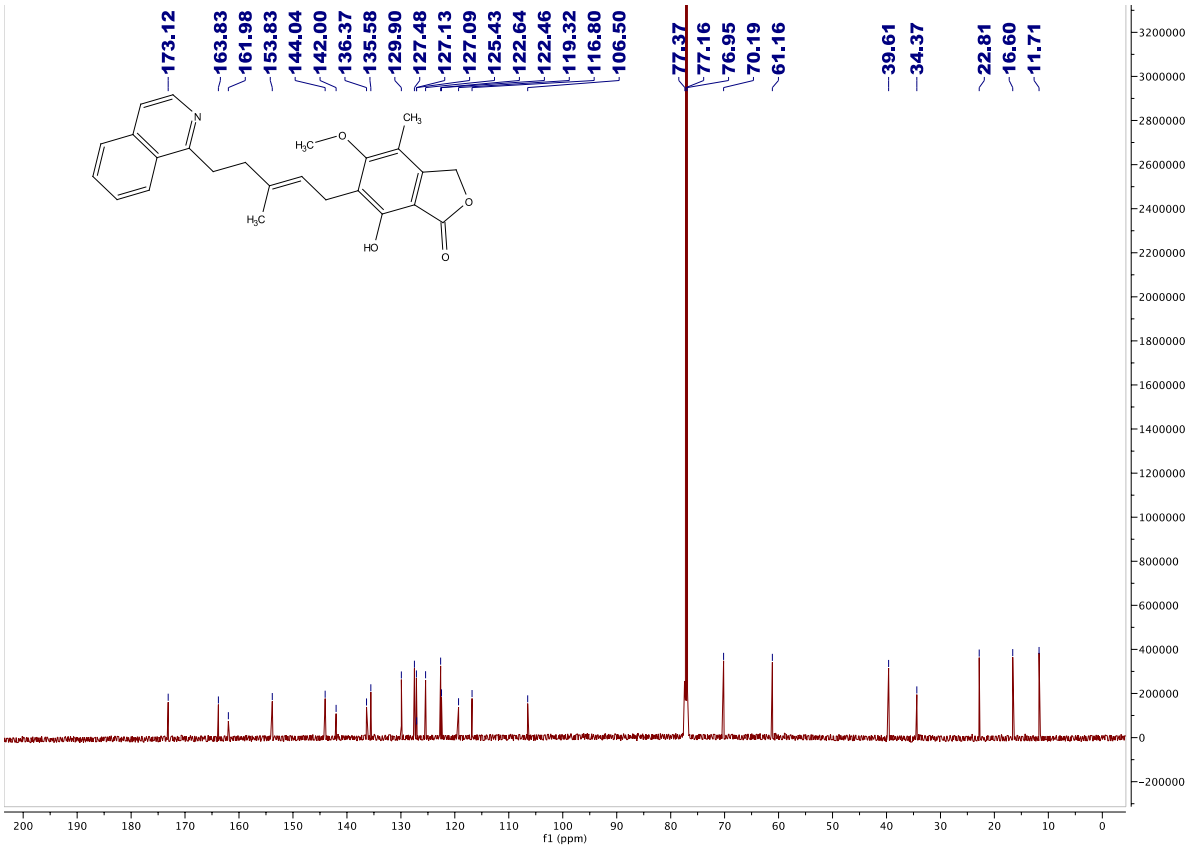
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3g**



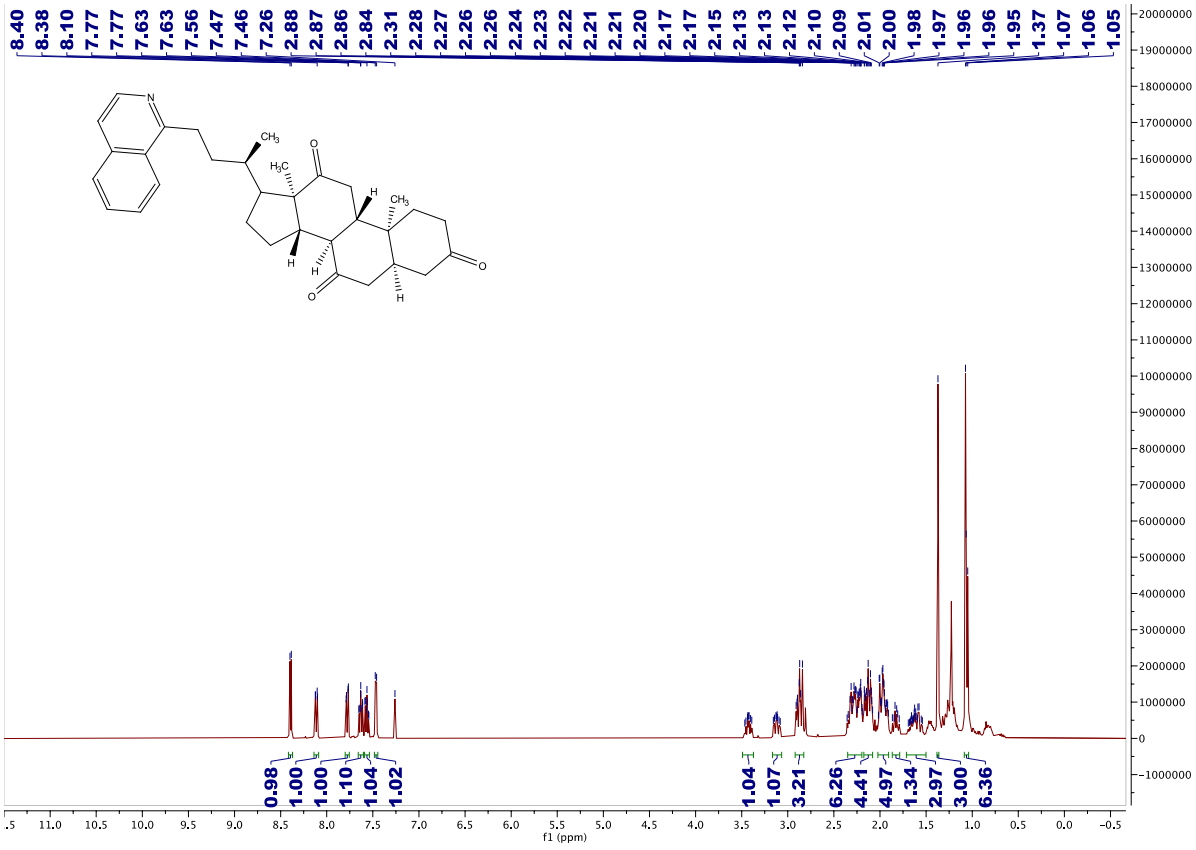
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3g**



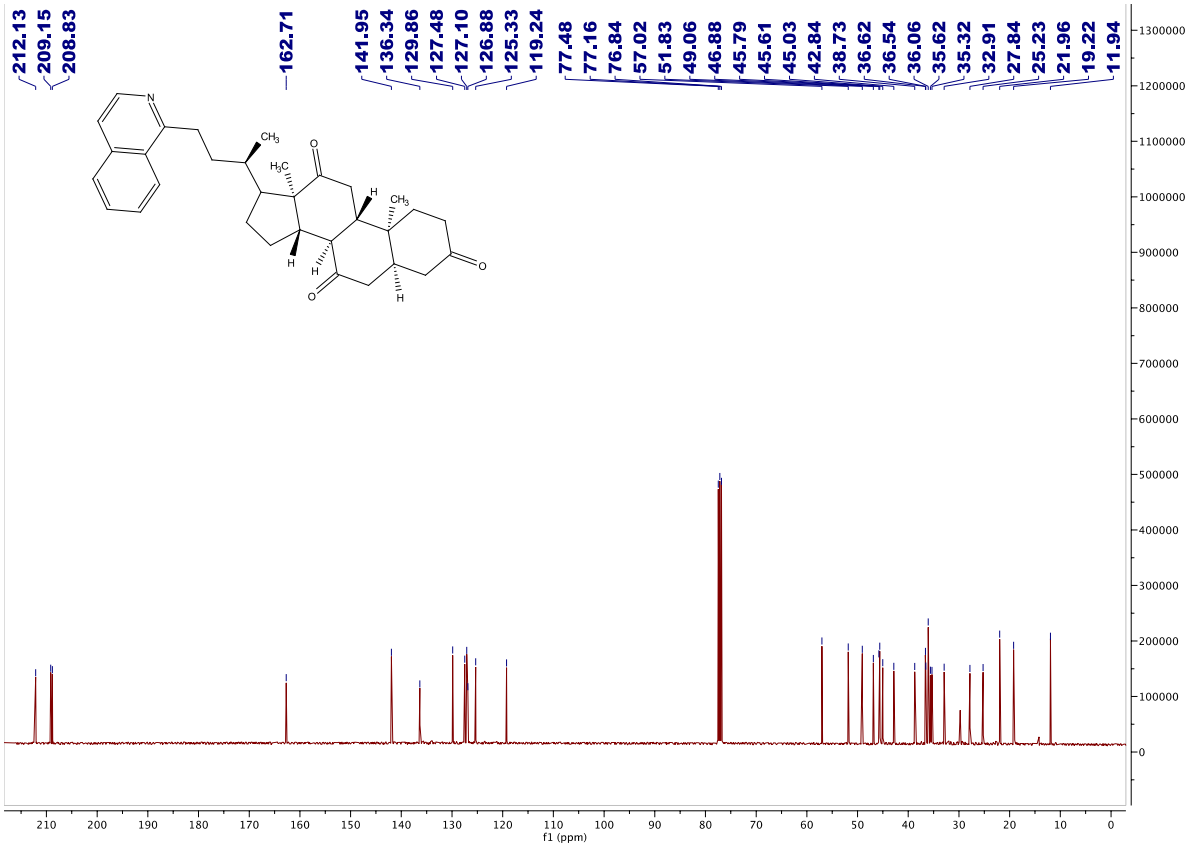
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3h**



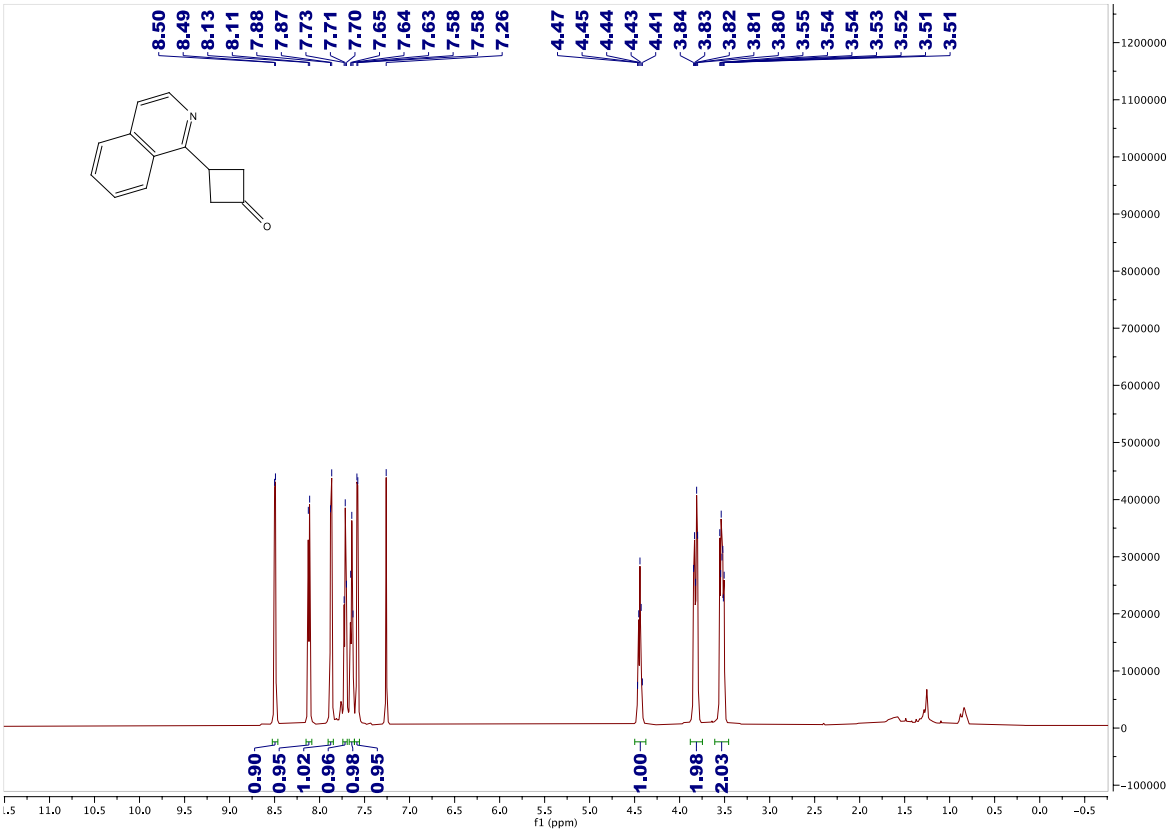
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3h**



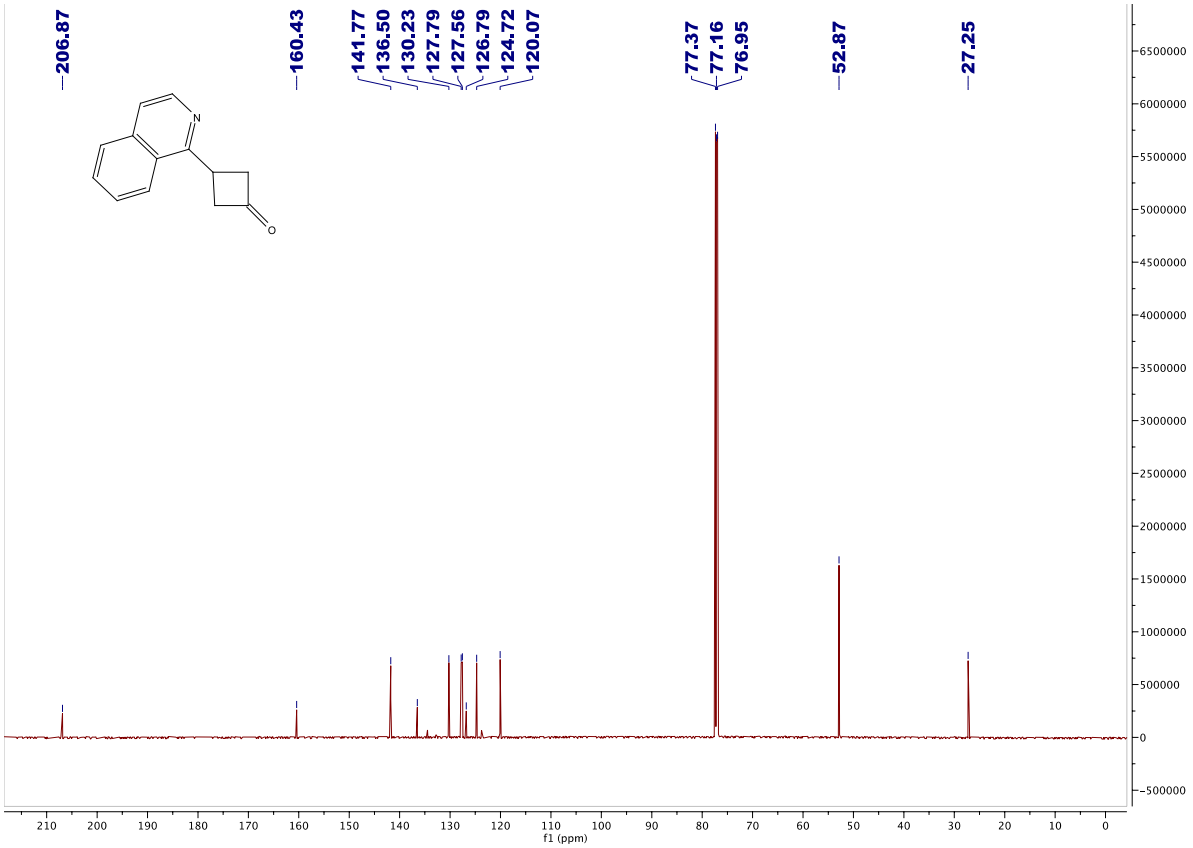
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3i**



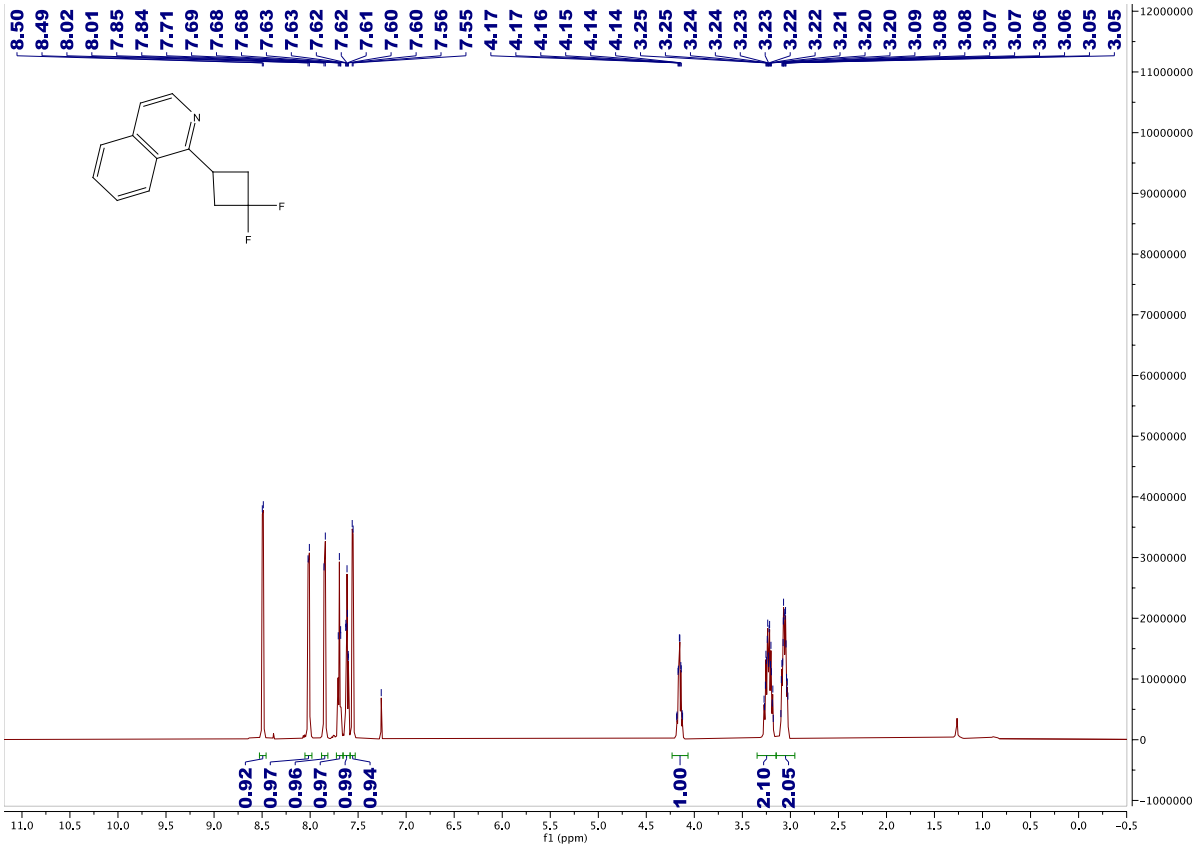
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3i**



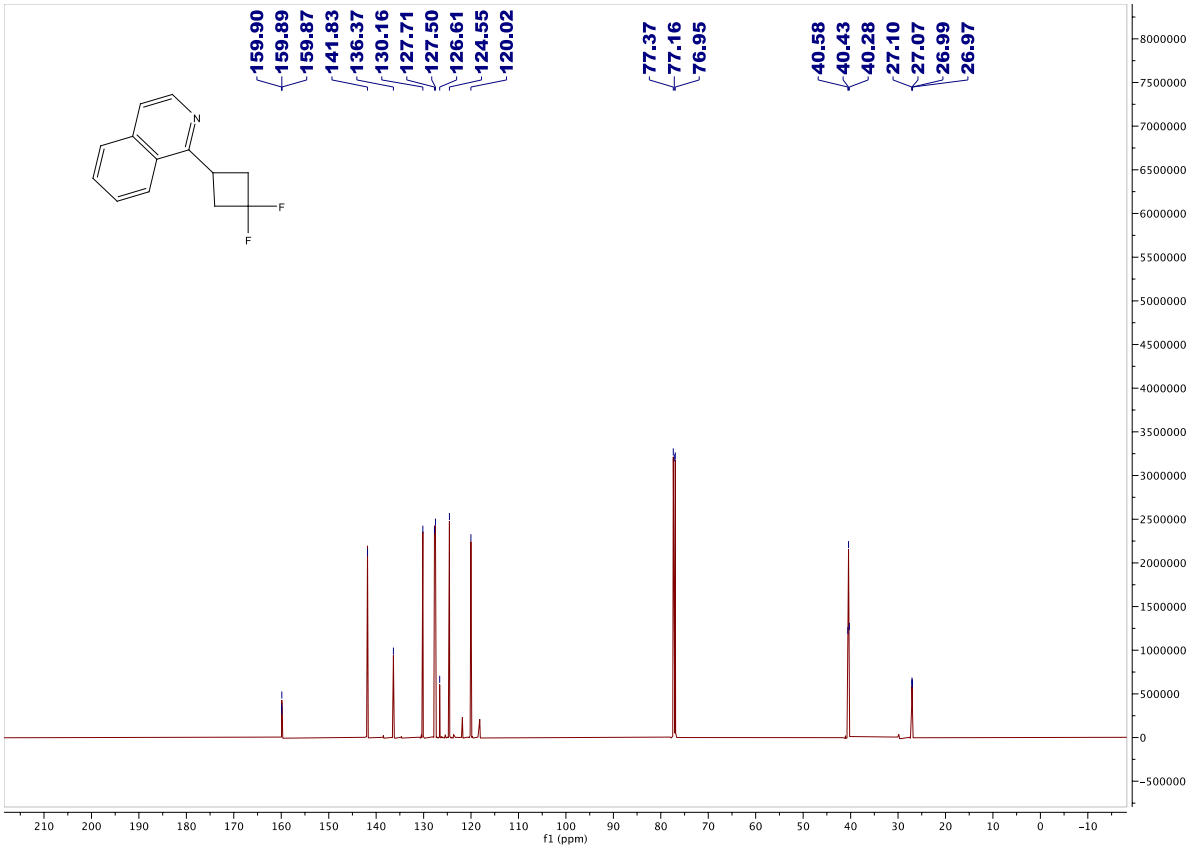
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3j**



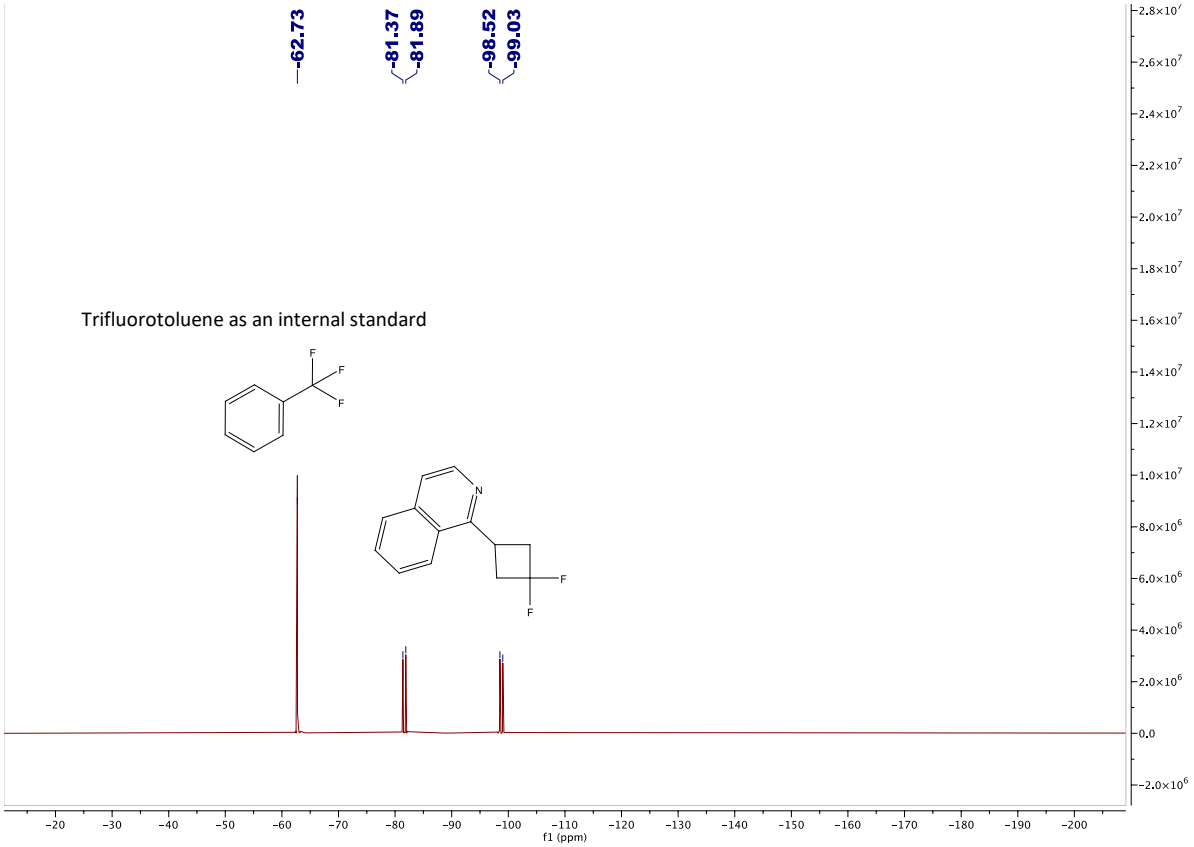
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3j**



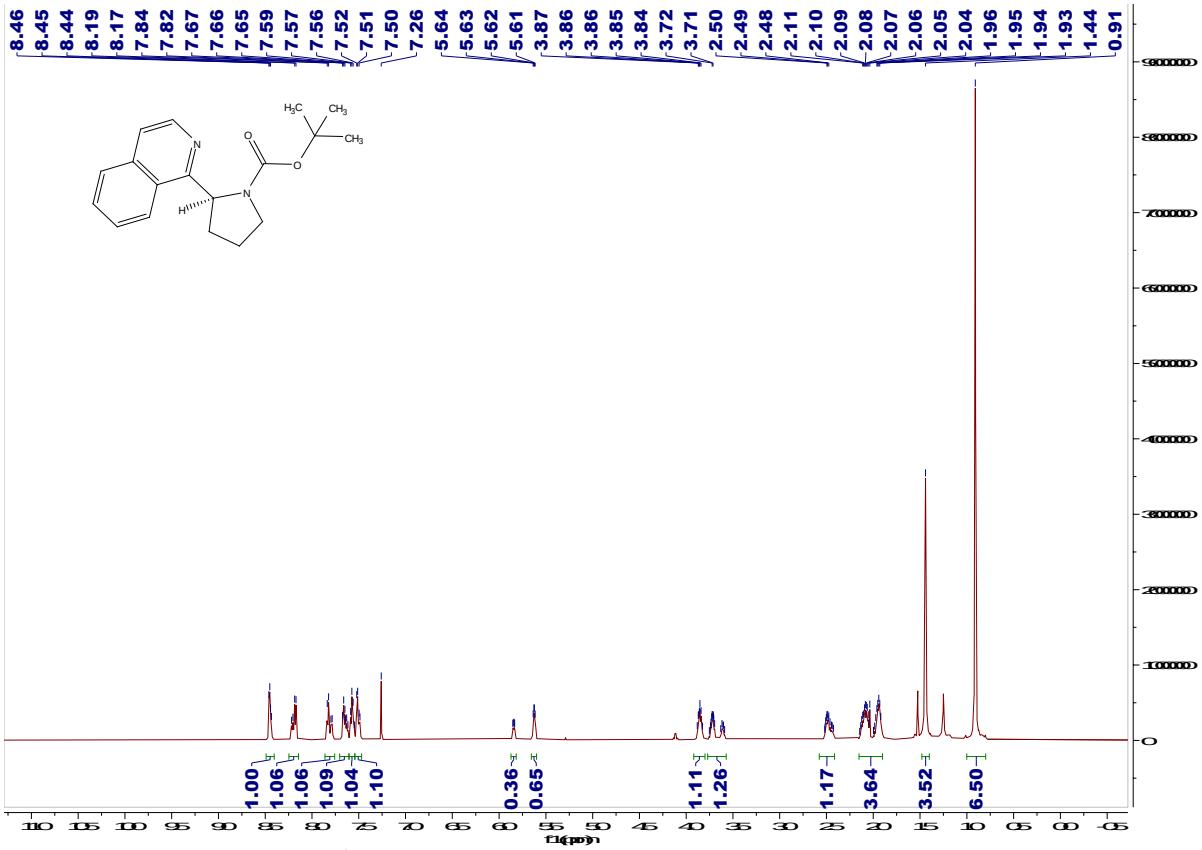
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3k**



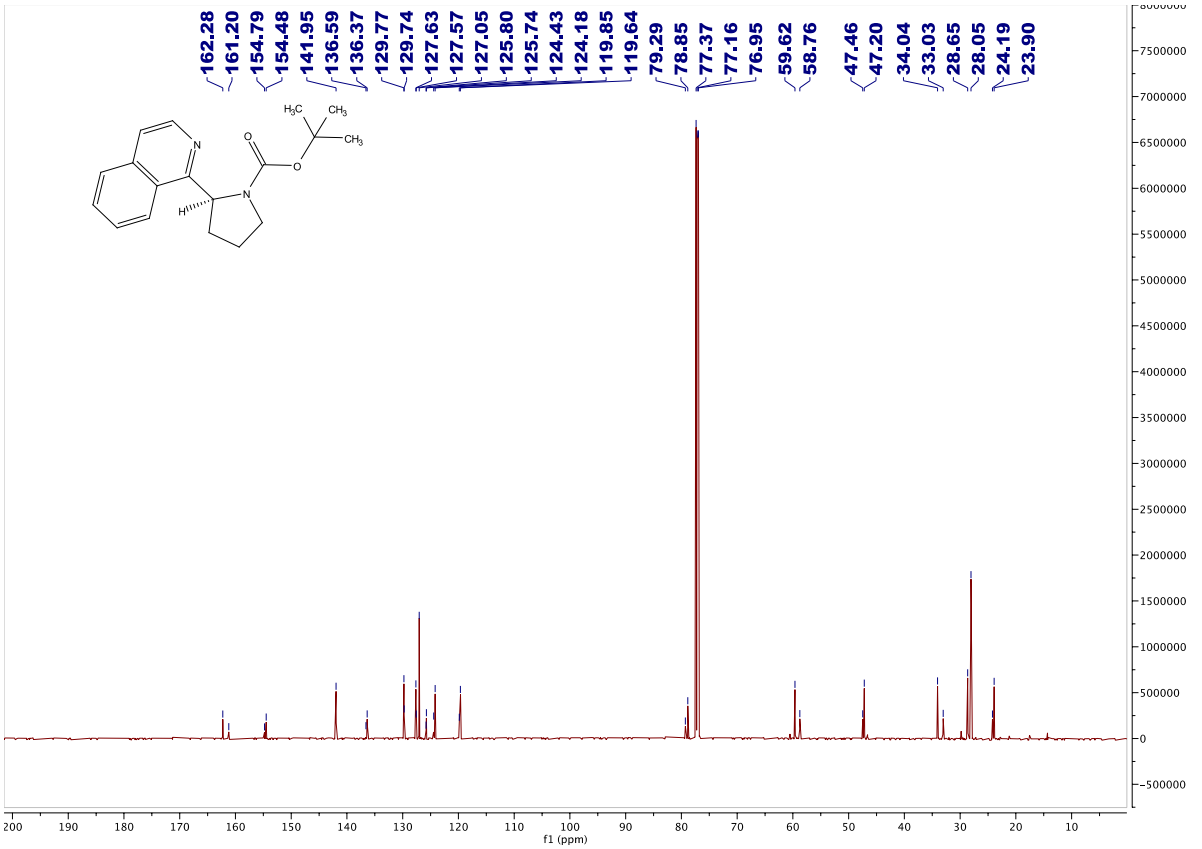
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3k**



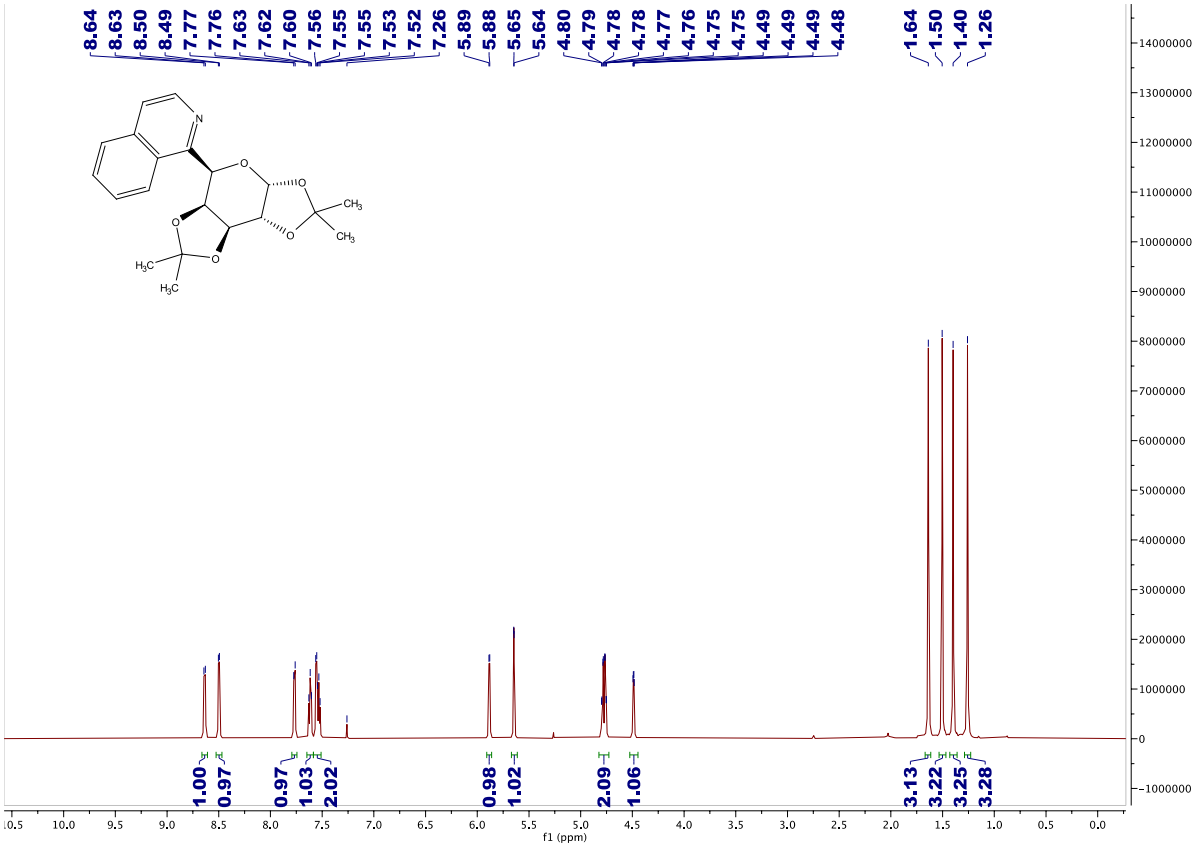
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3k**



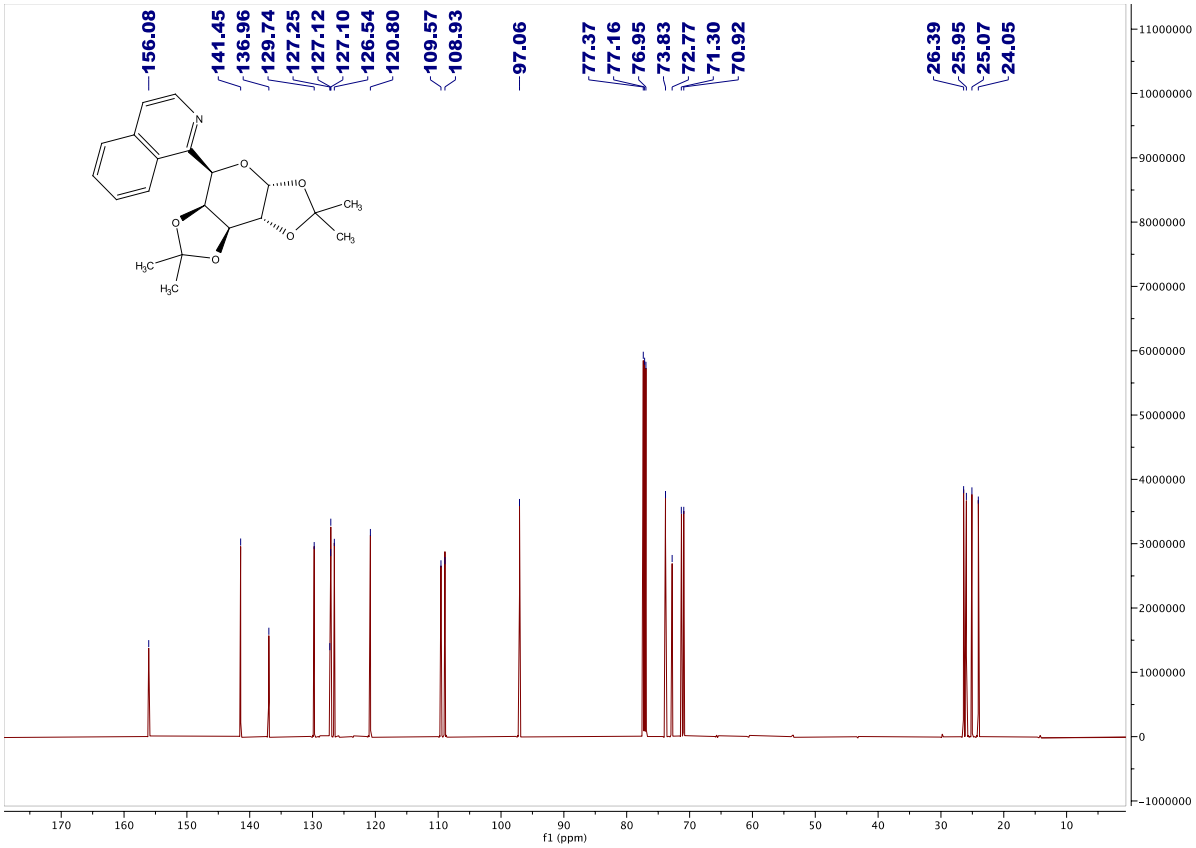
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3l**



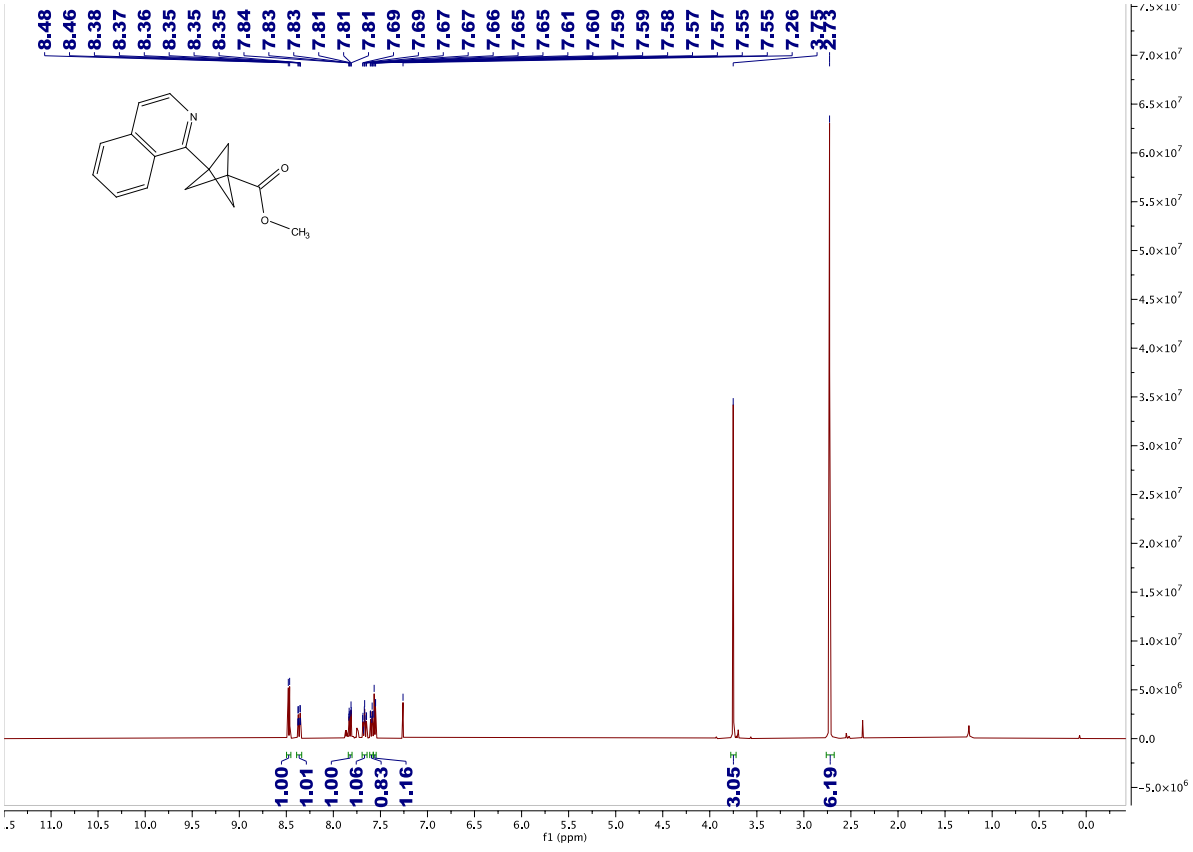
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3l**



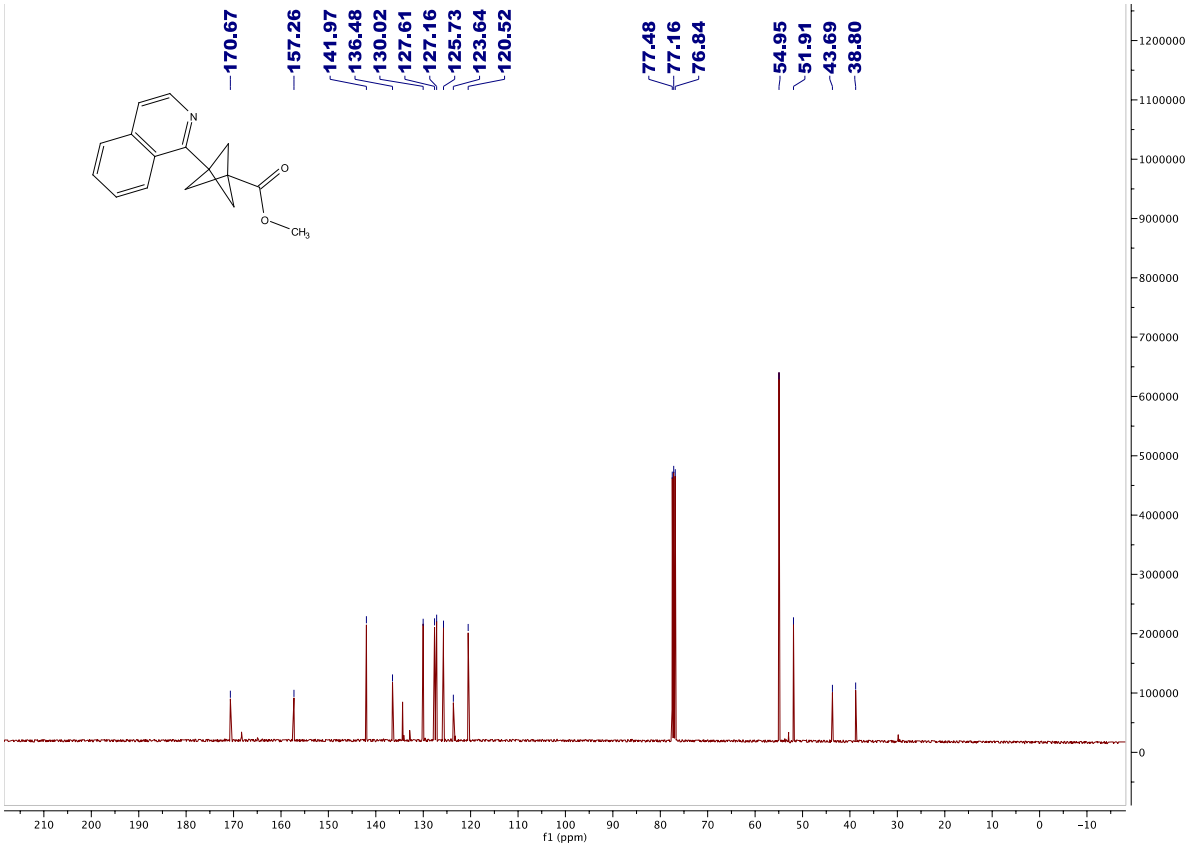
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3m**



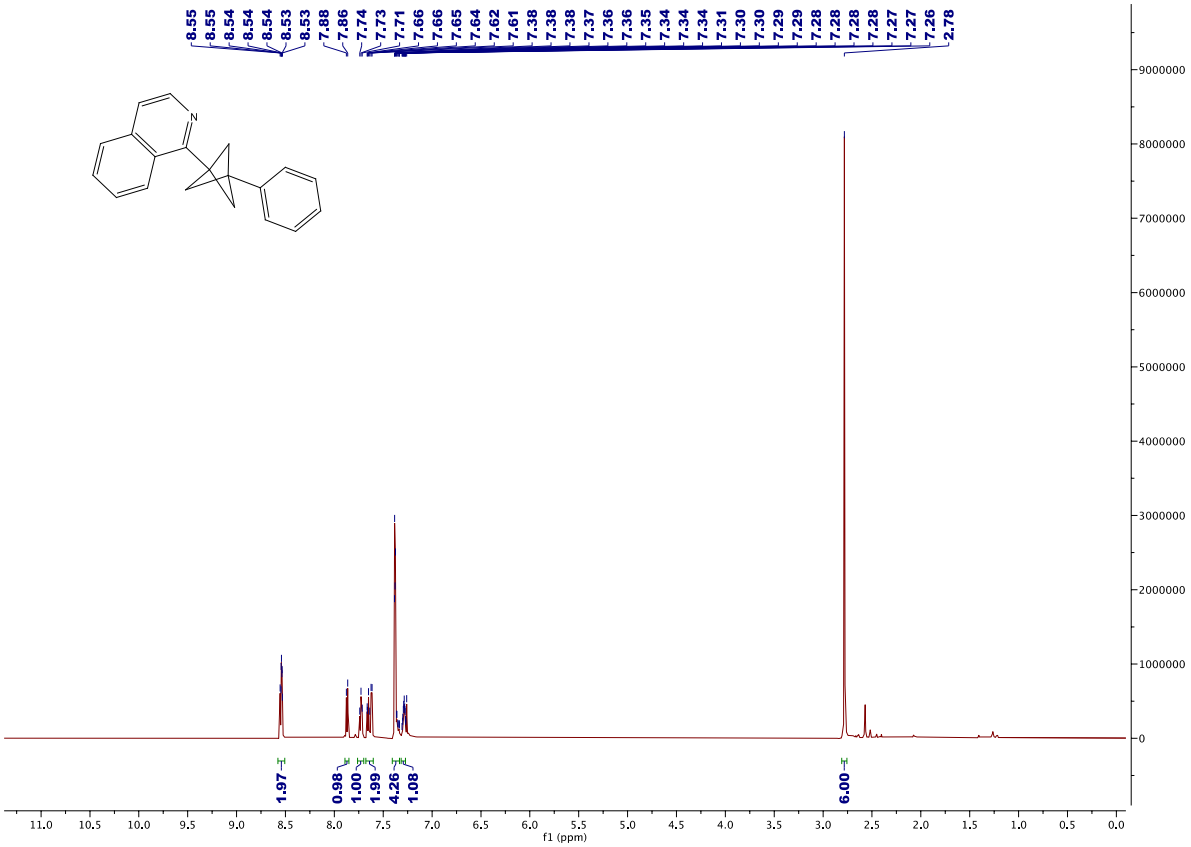
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3m**



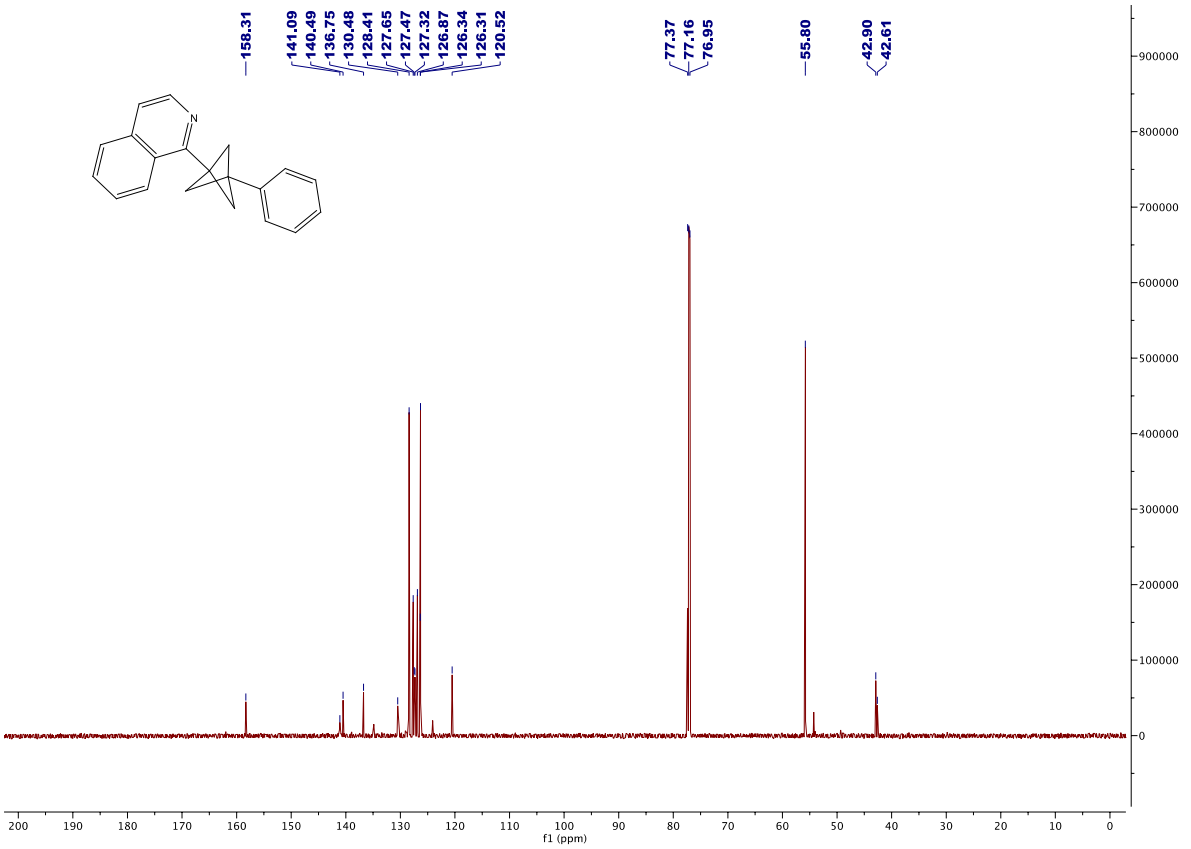
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3n**



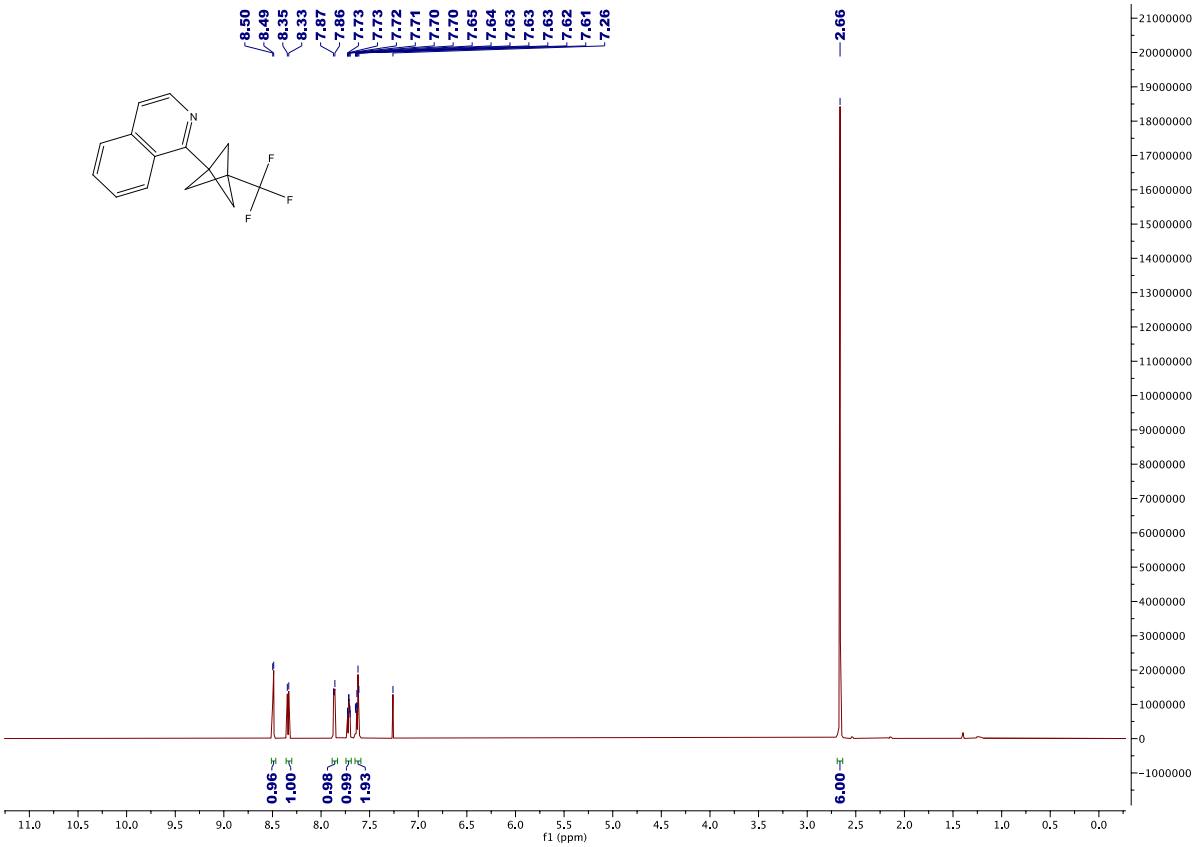
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3n**



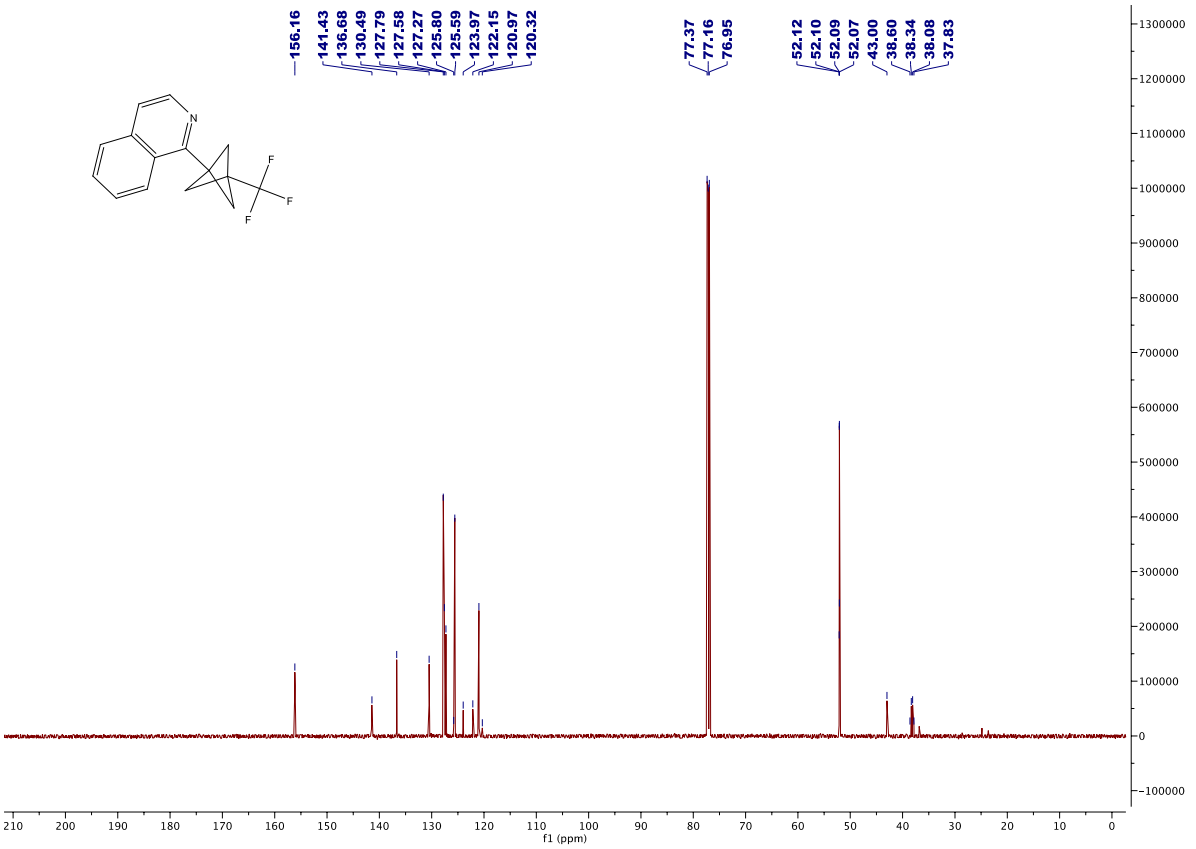
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3o**



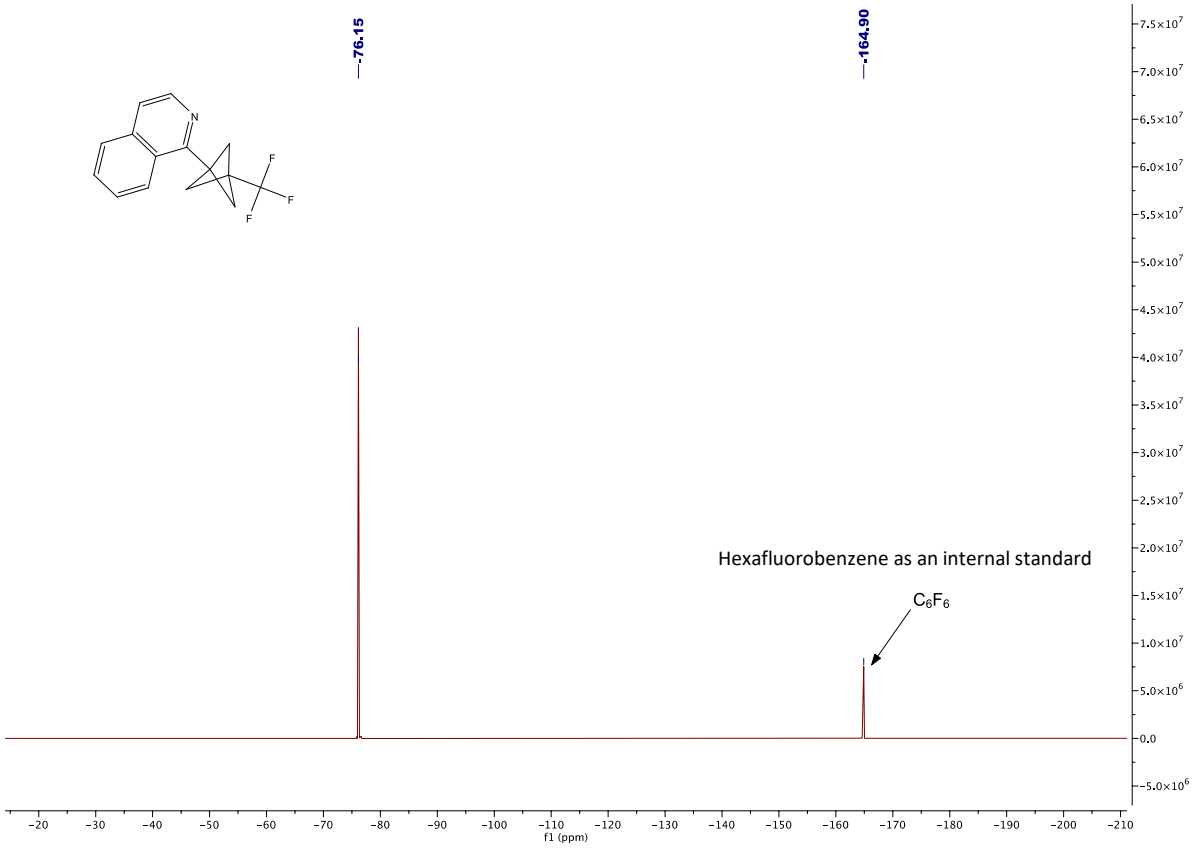
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3o**



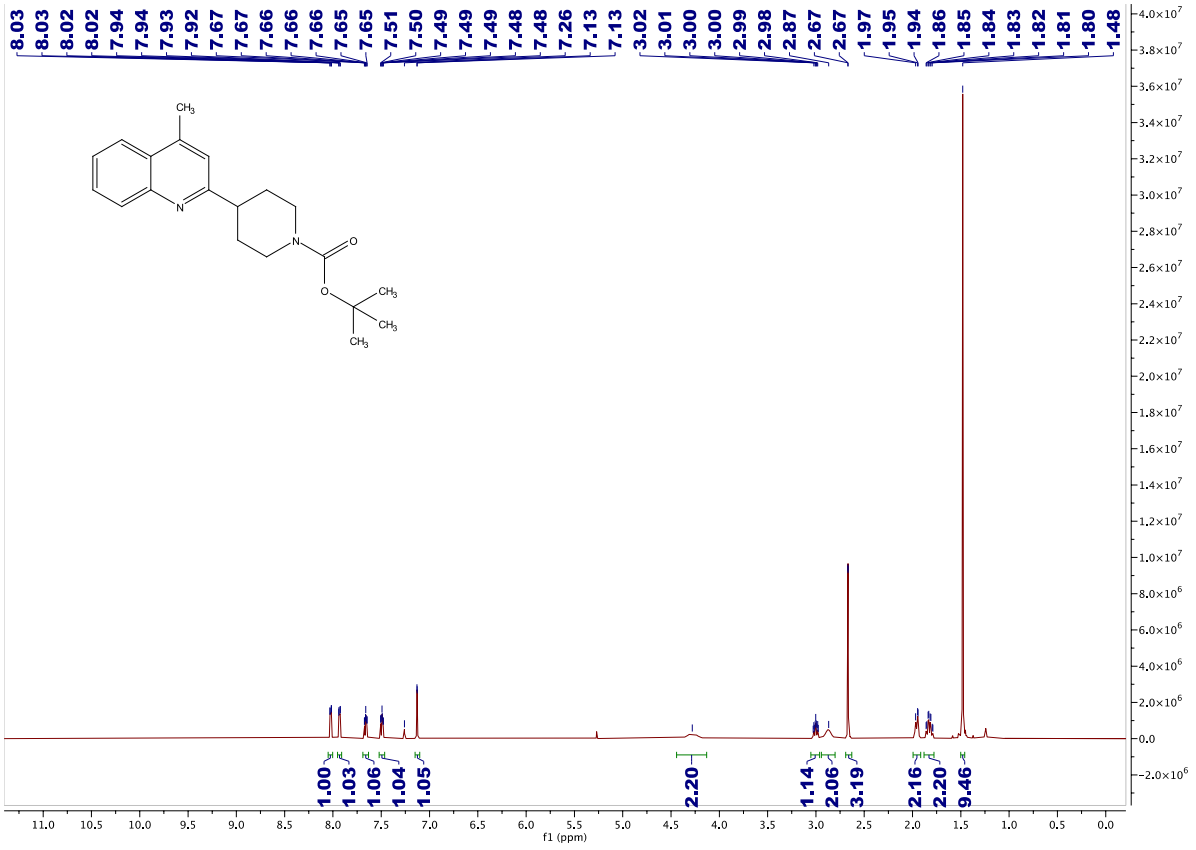
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3p**



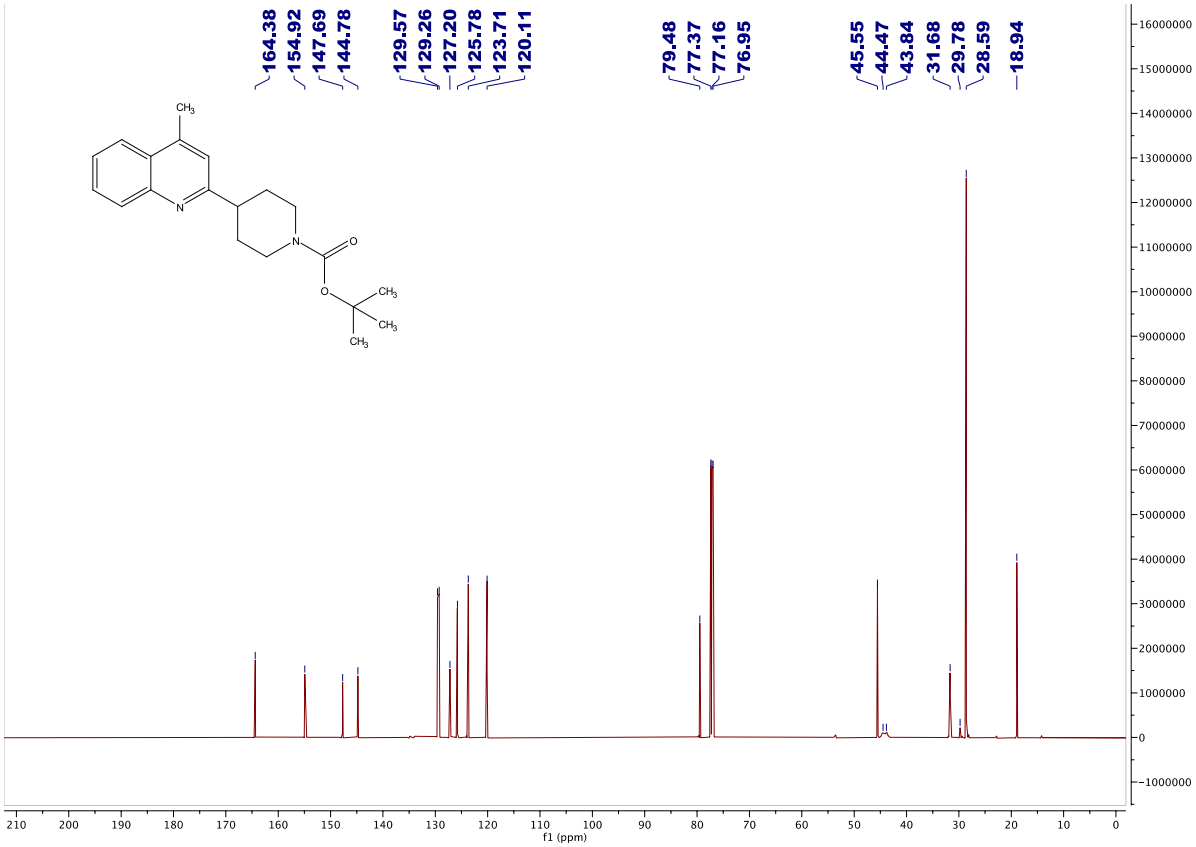
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3p**



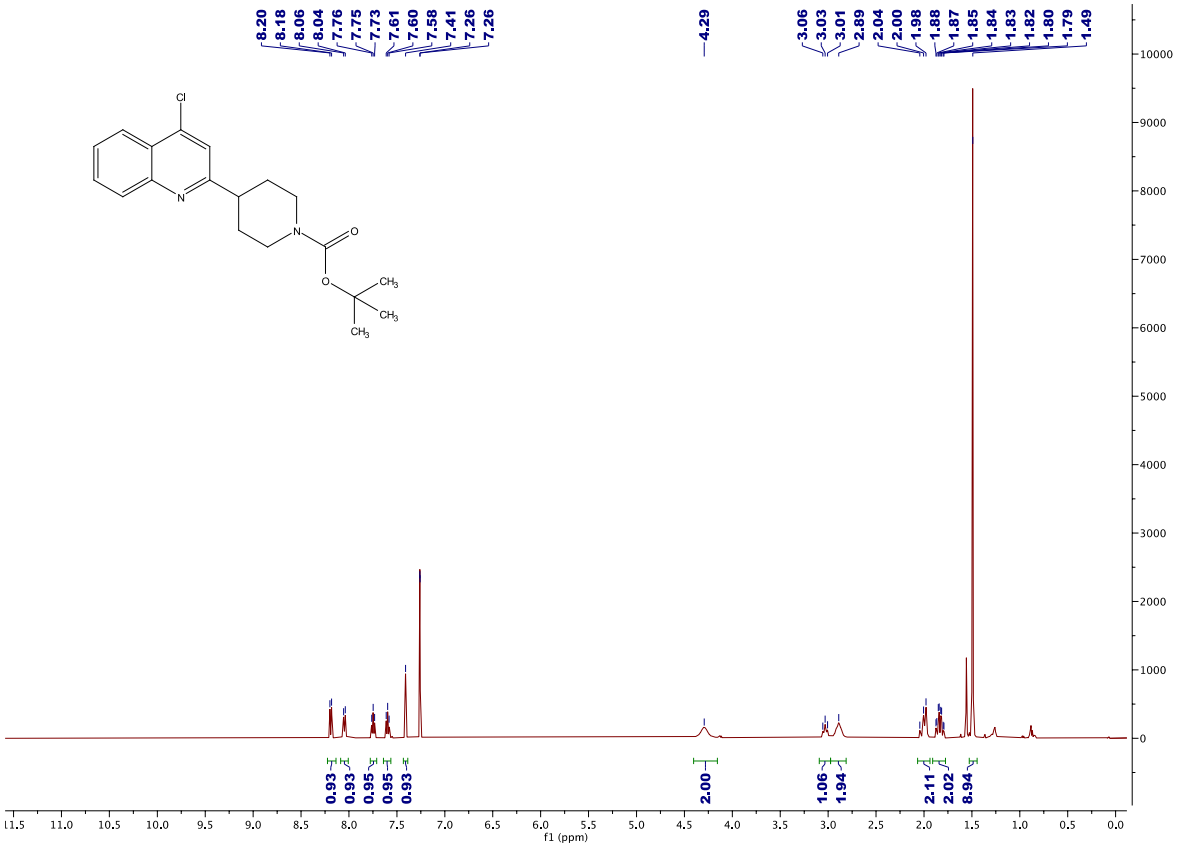
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3p**



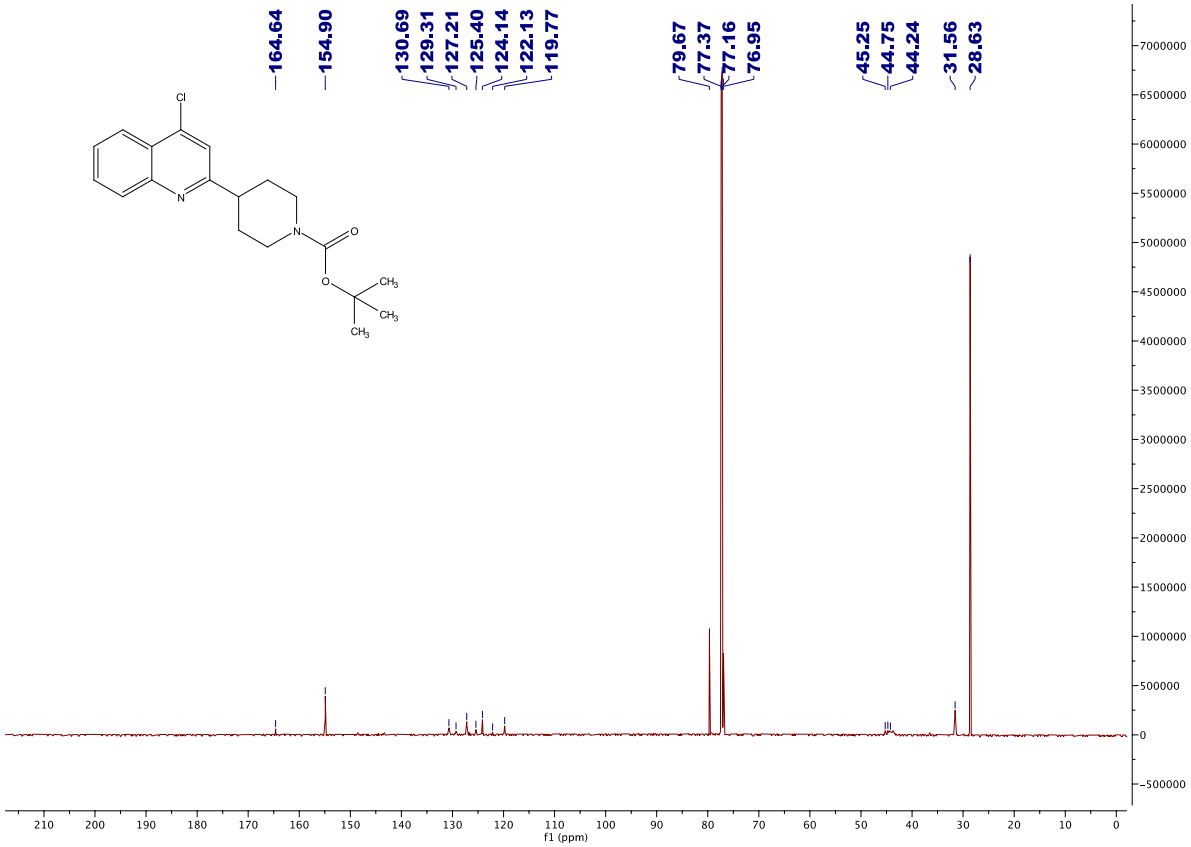
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3r**



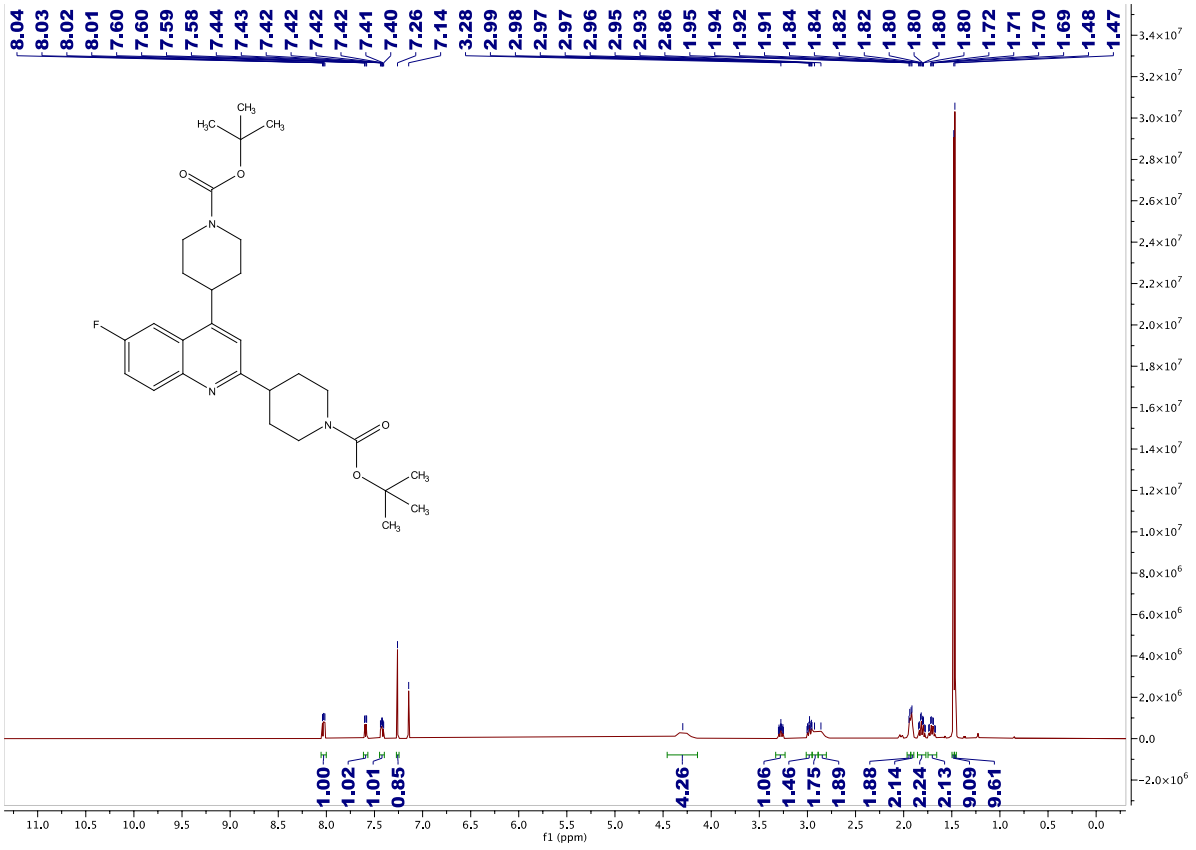
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3r**



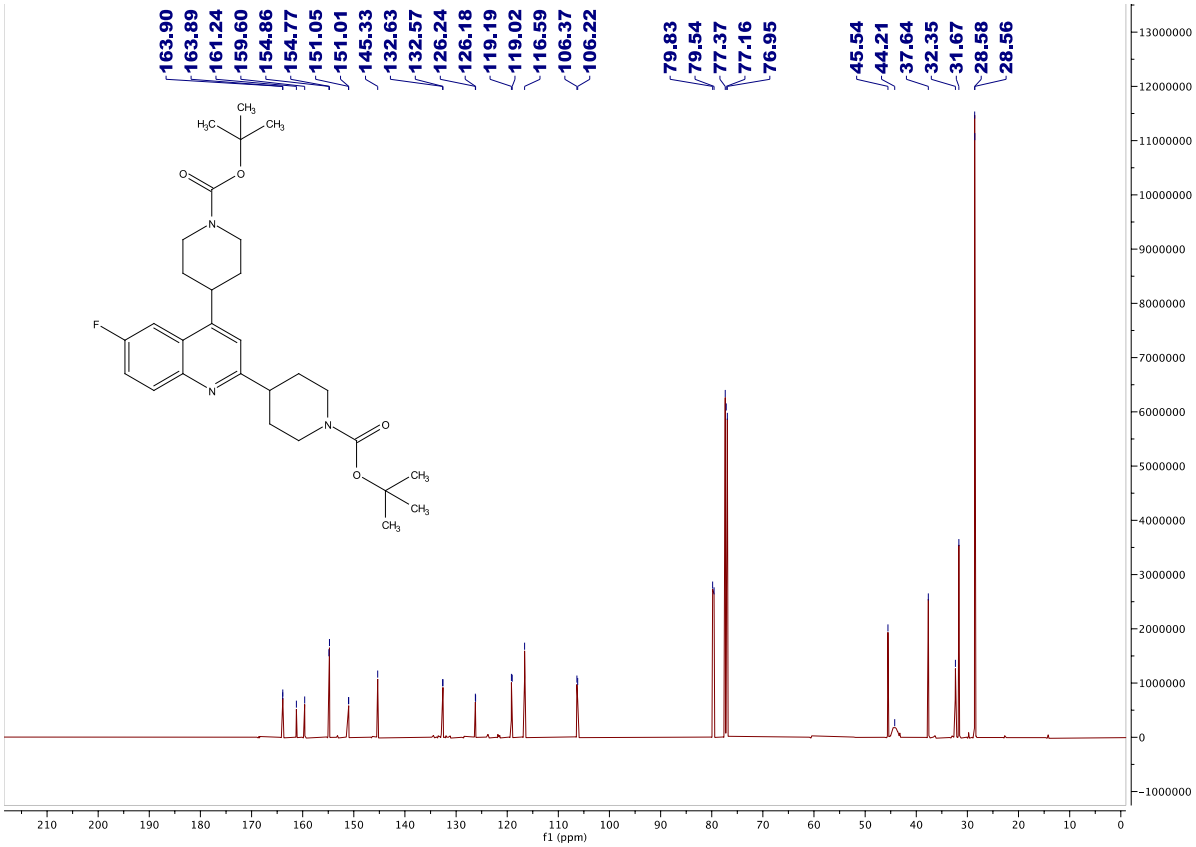
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3s**



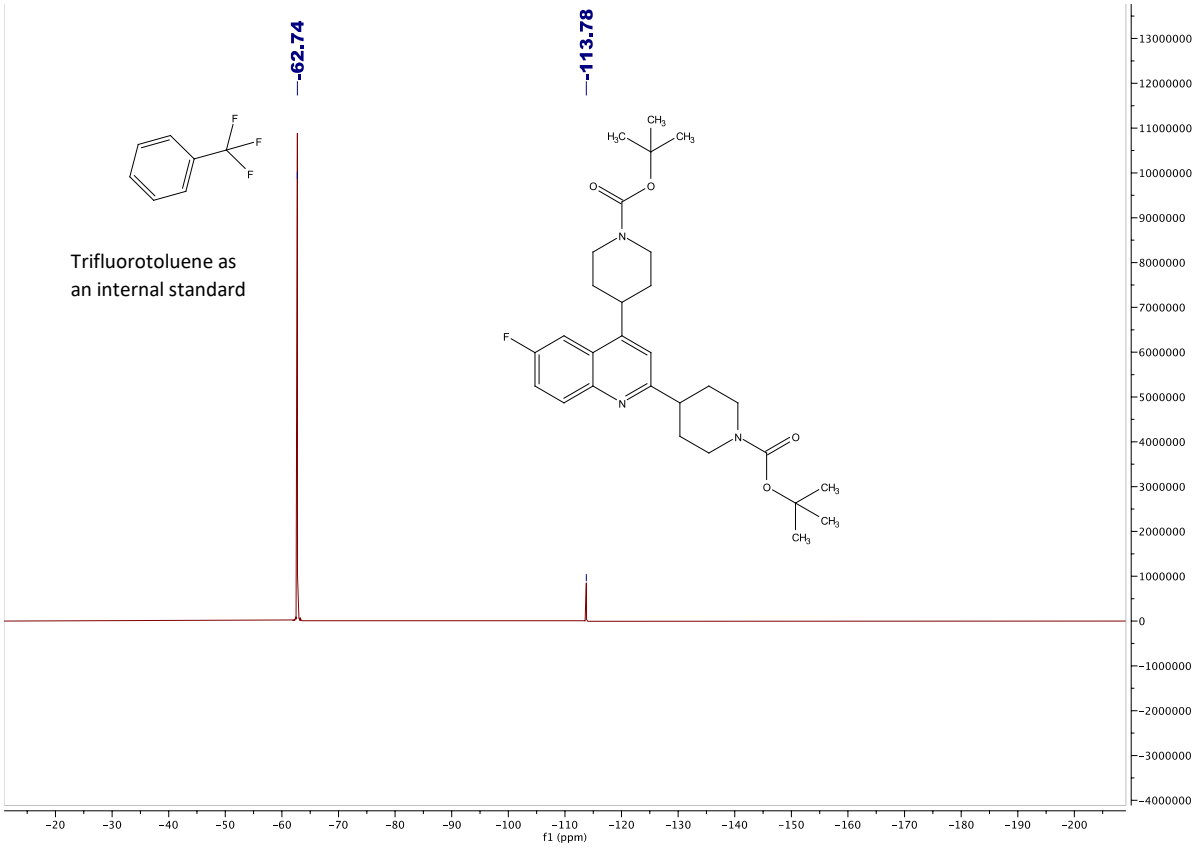
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3s**



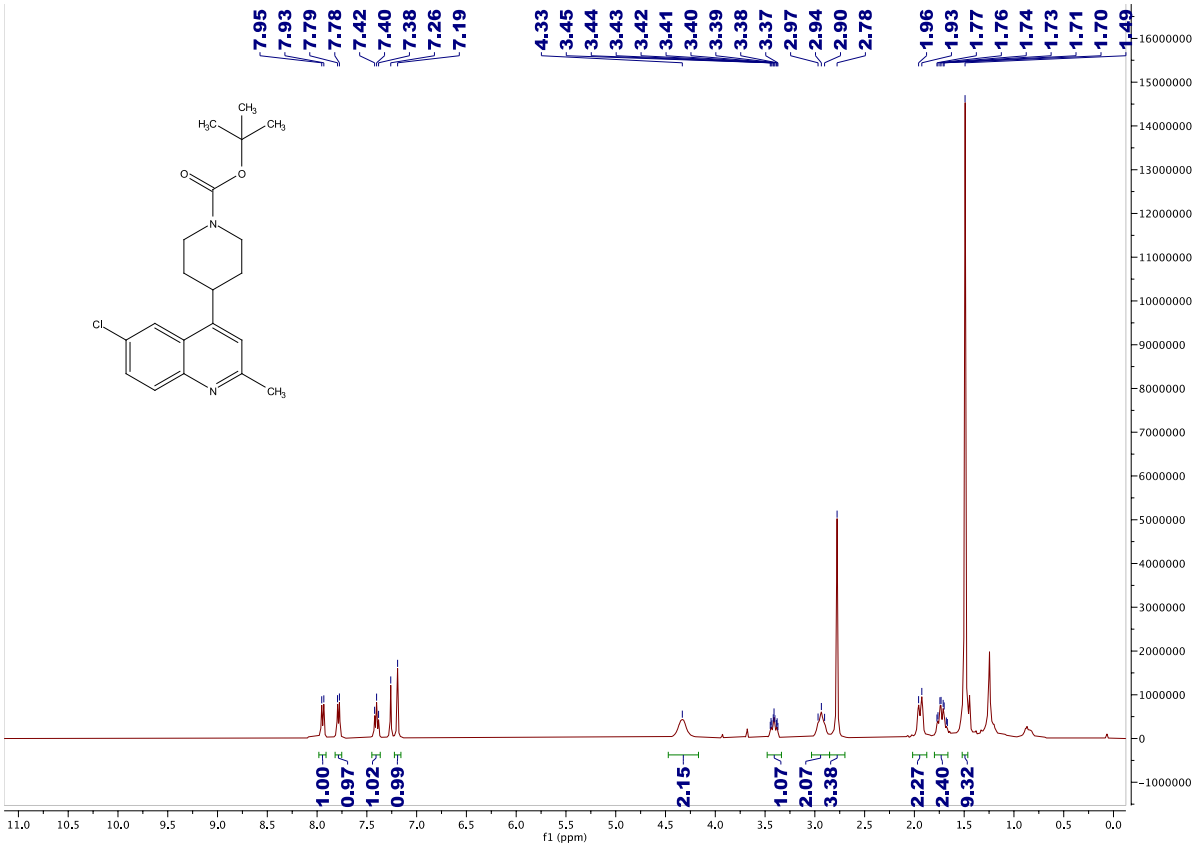
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3t**



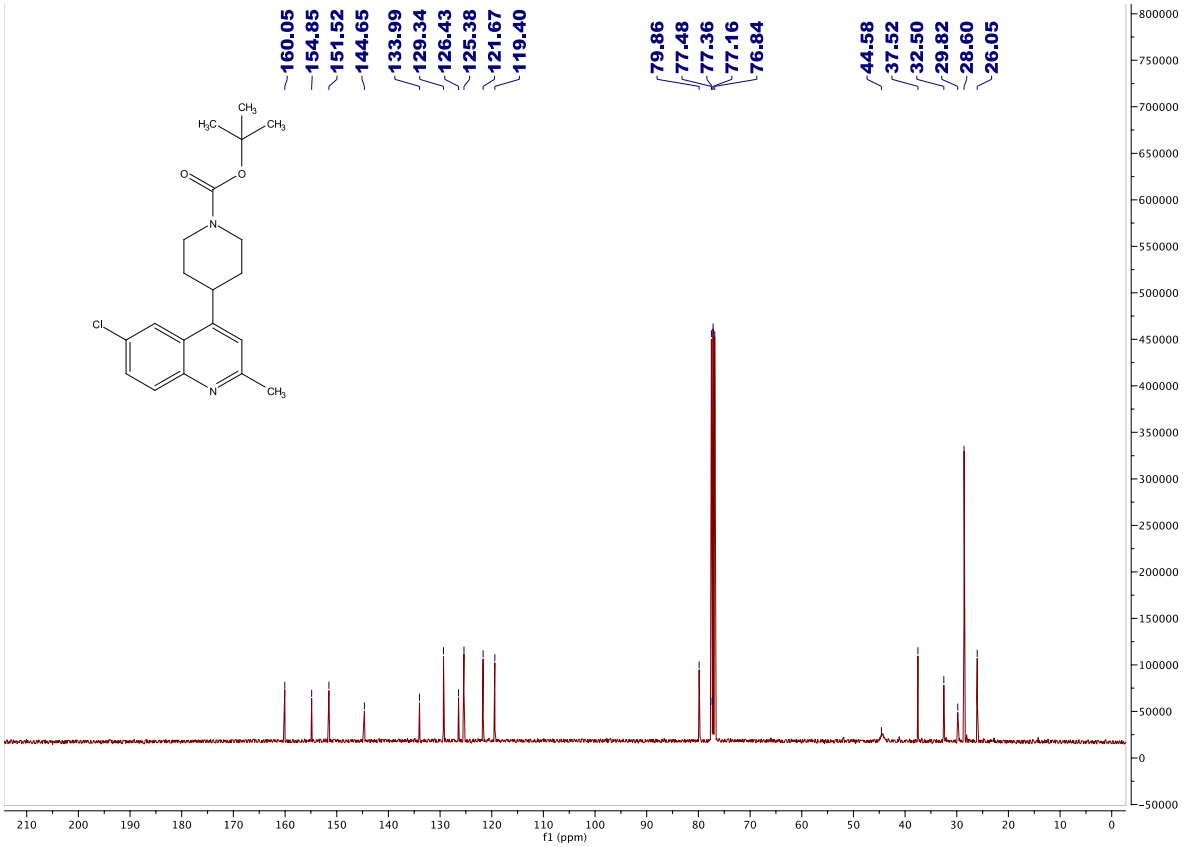
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3t**



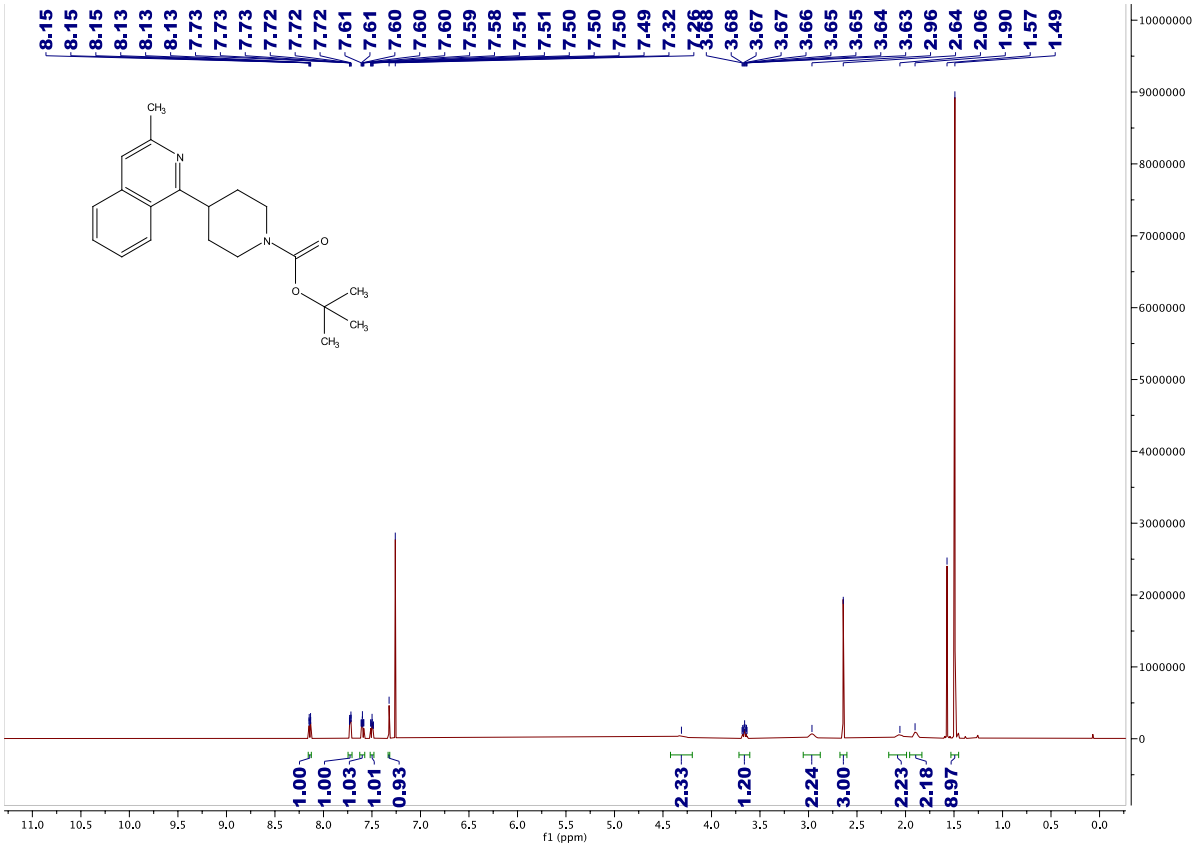
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3t**



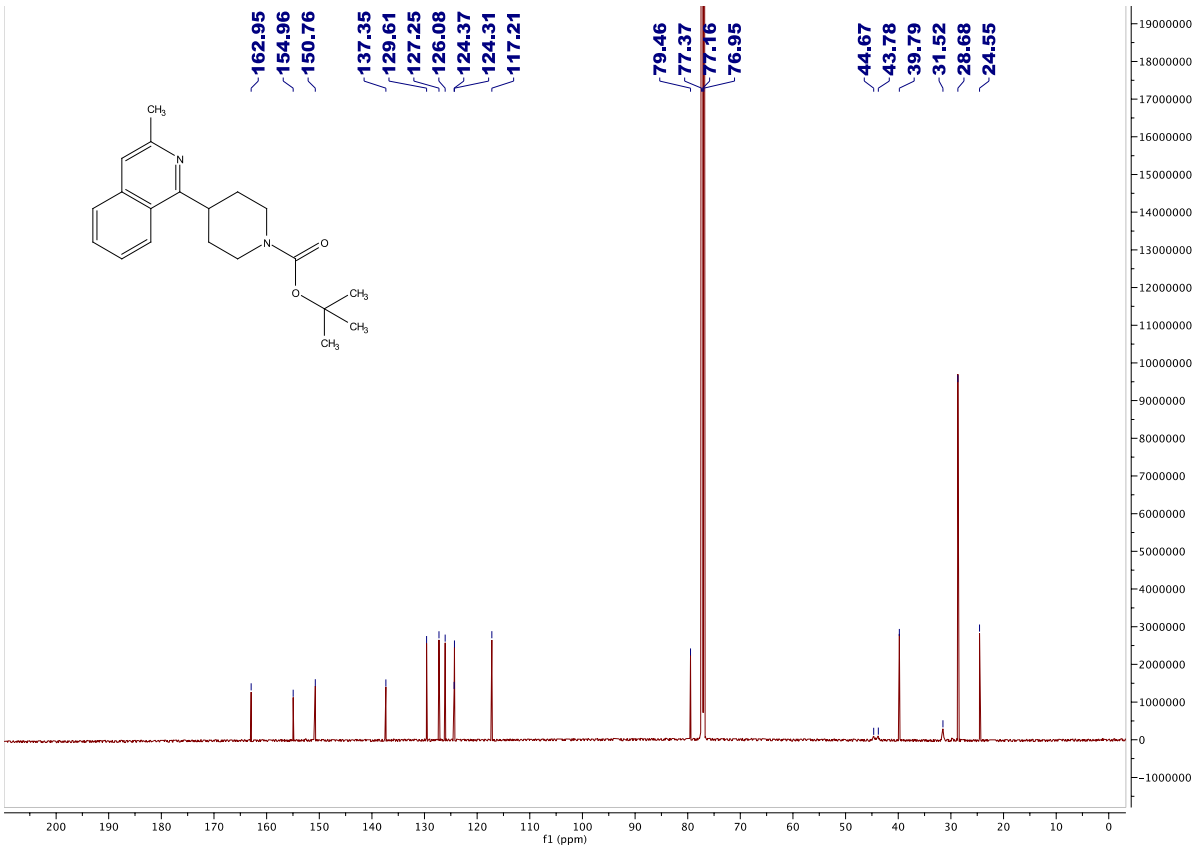
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3u**



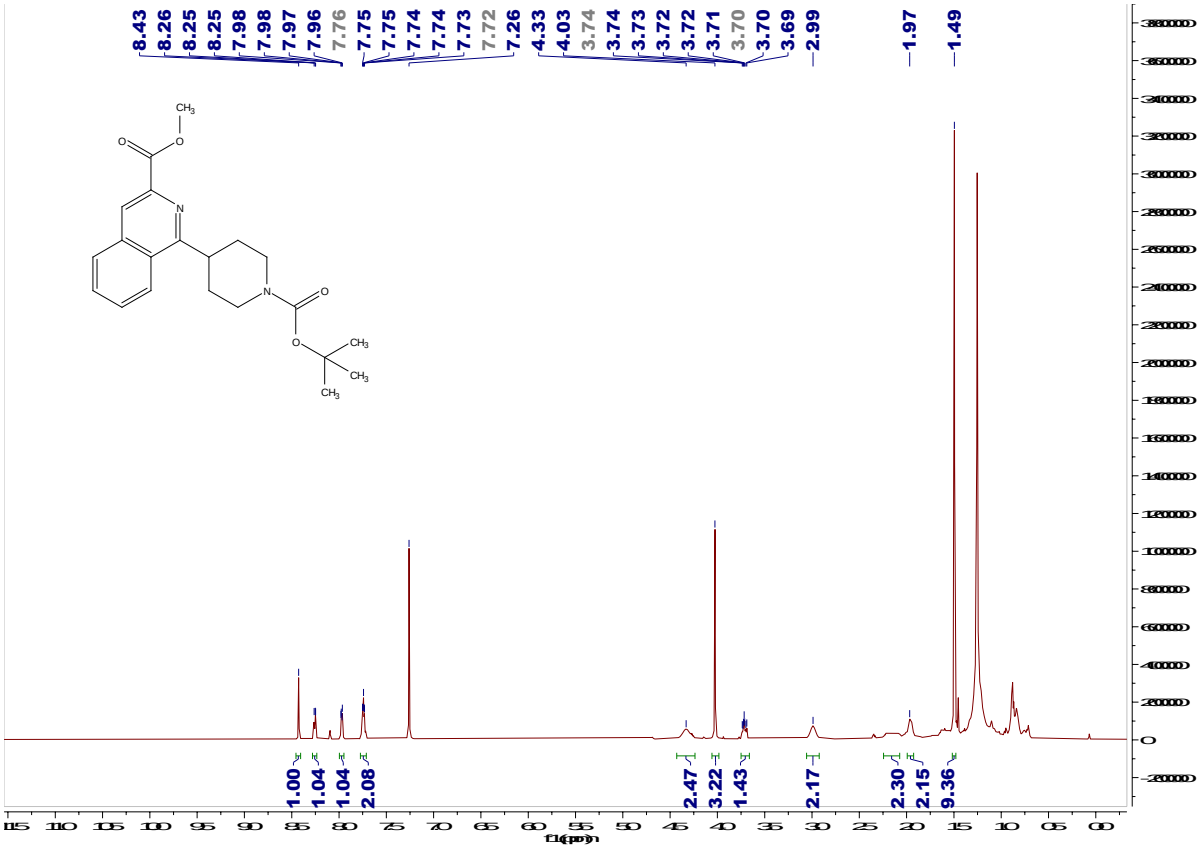
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3u**



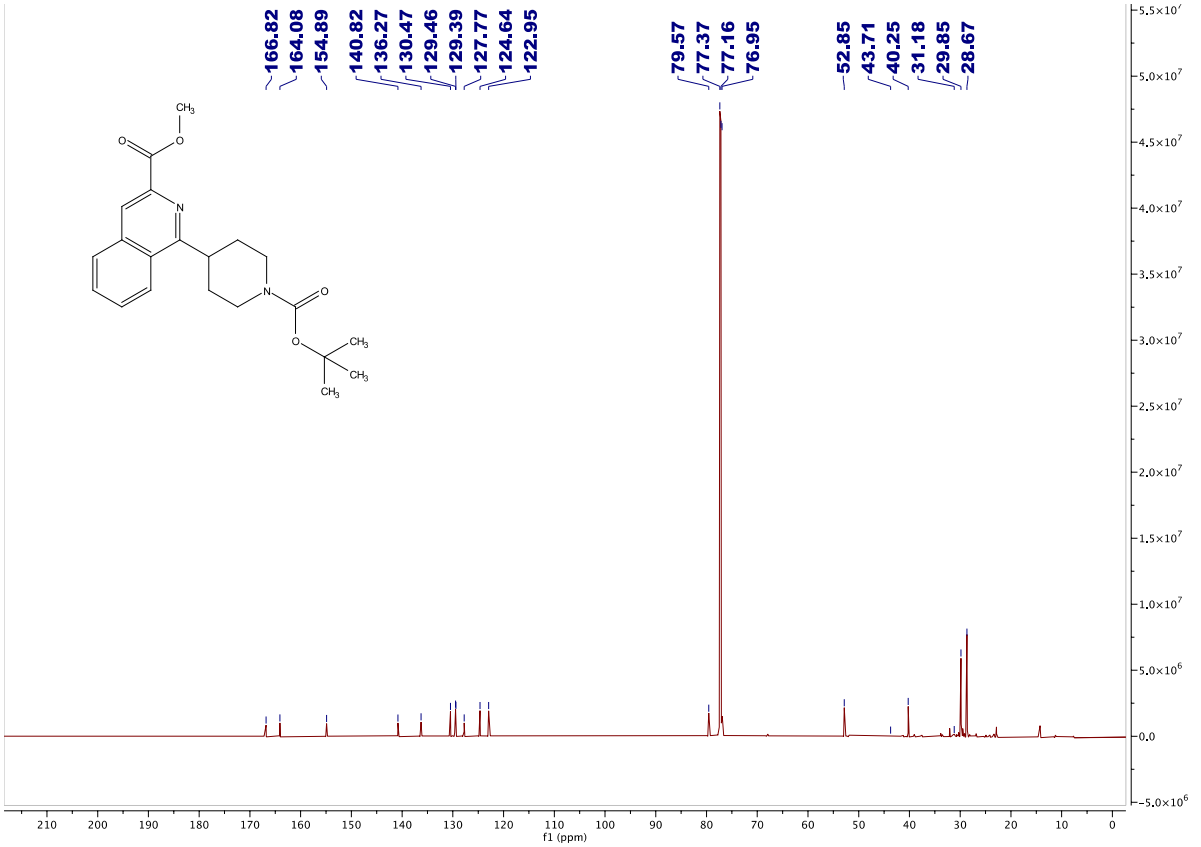
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3v**



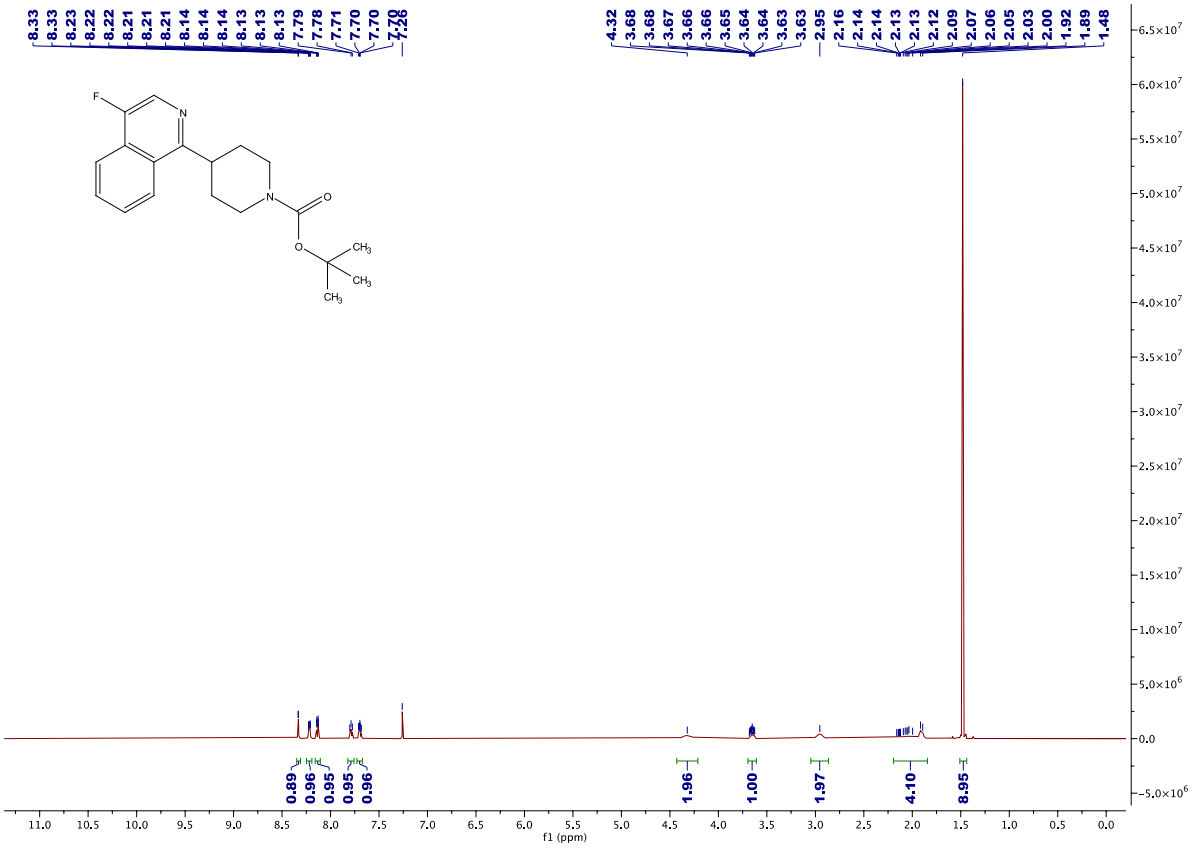
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3v**



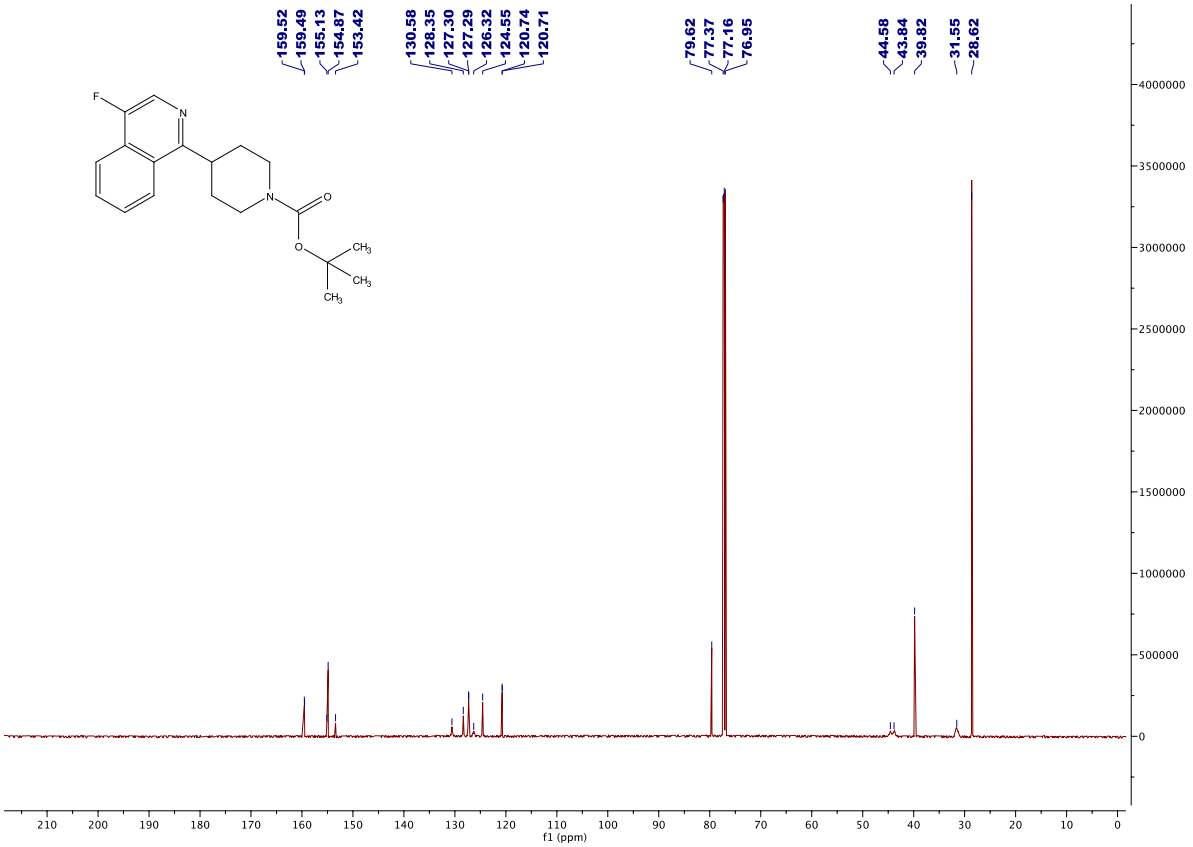
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3w**



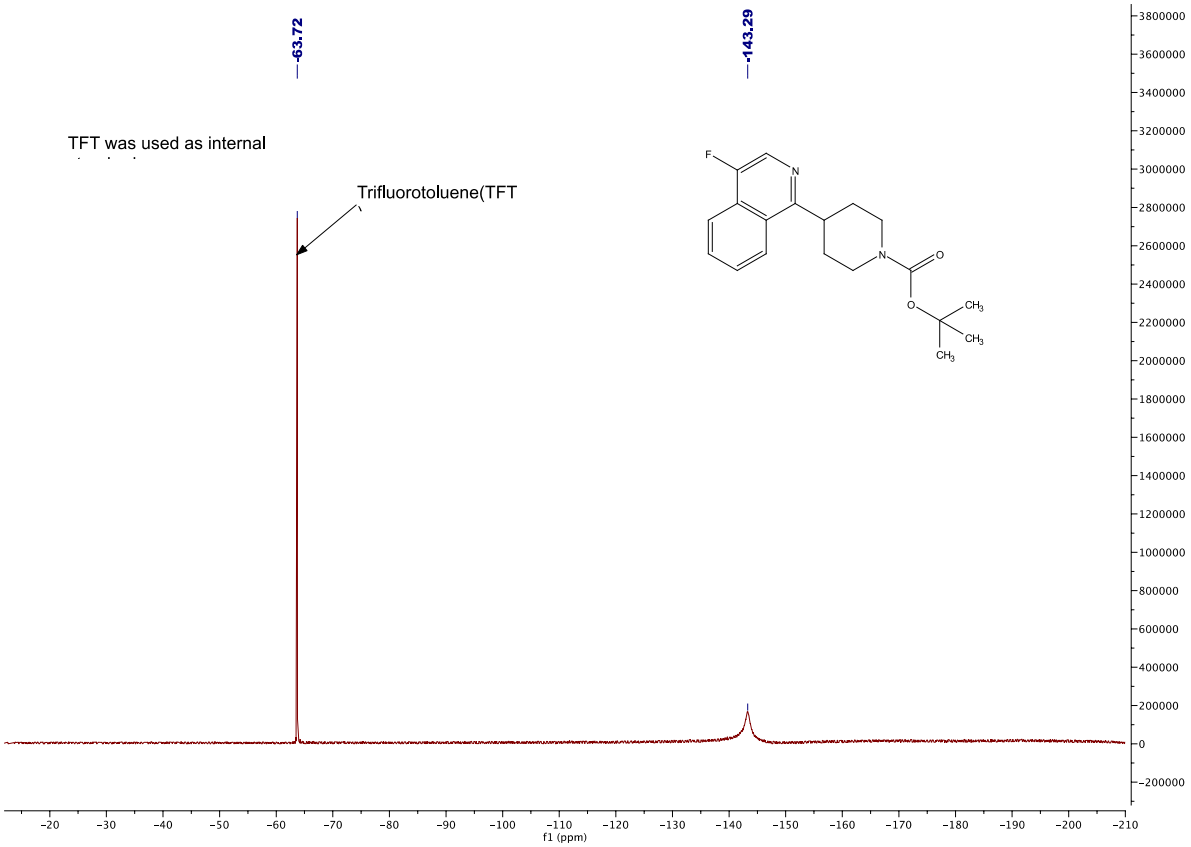
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3w**



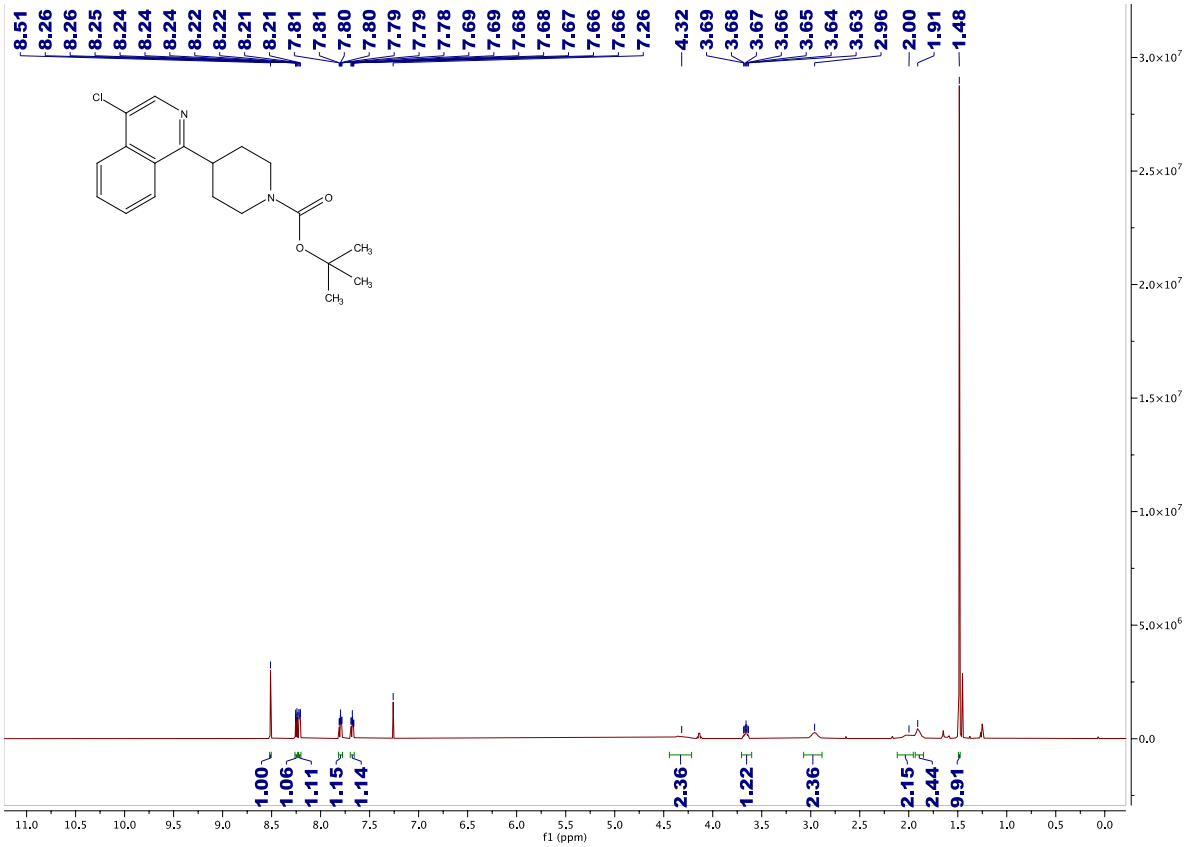
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3x**



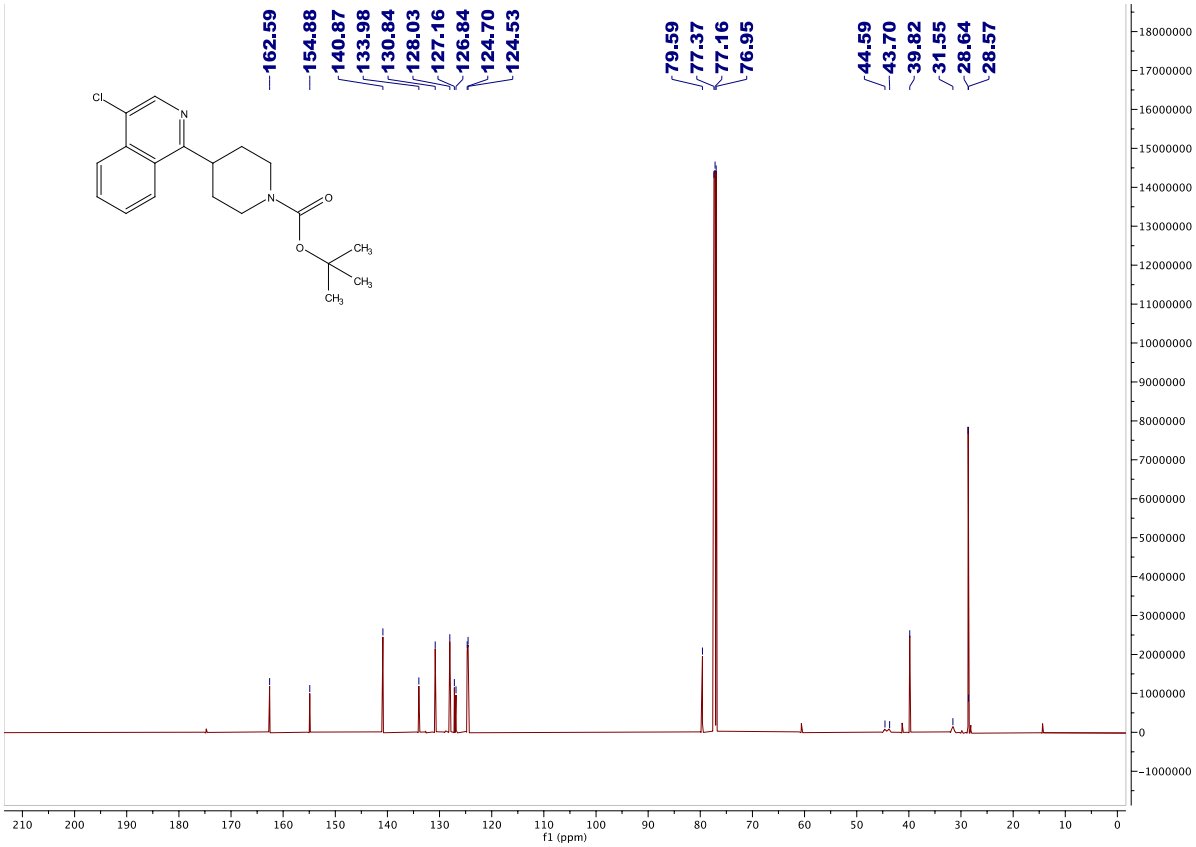
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3x**



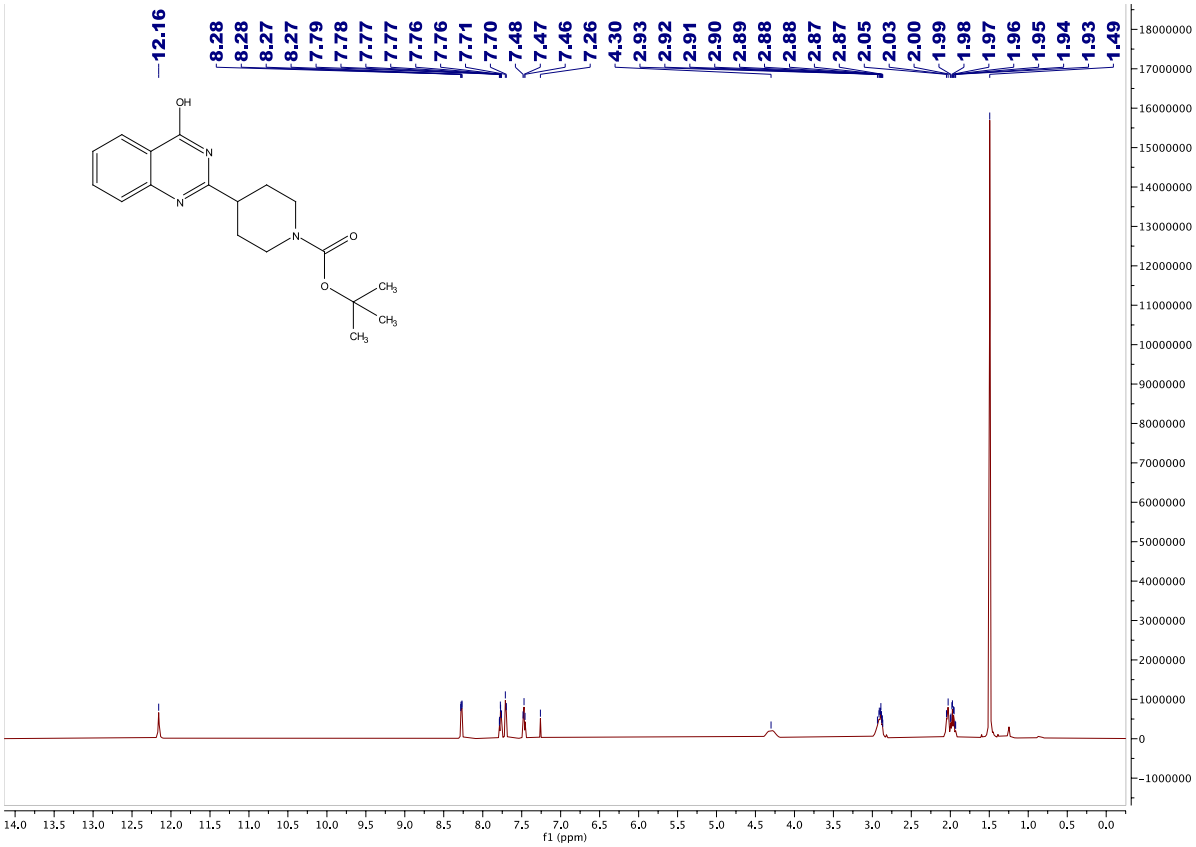
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3x**



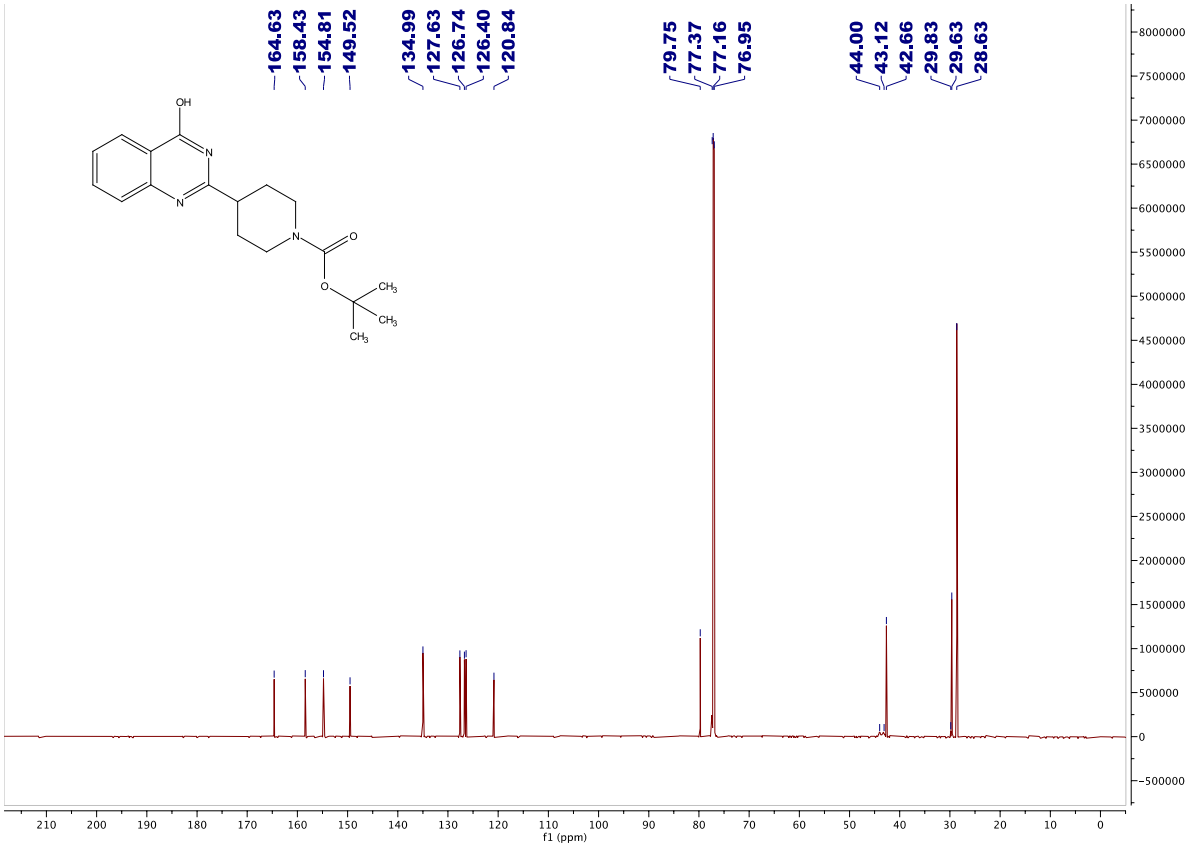
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3y**



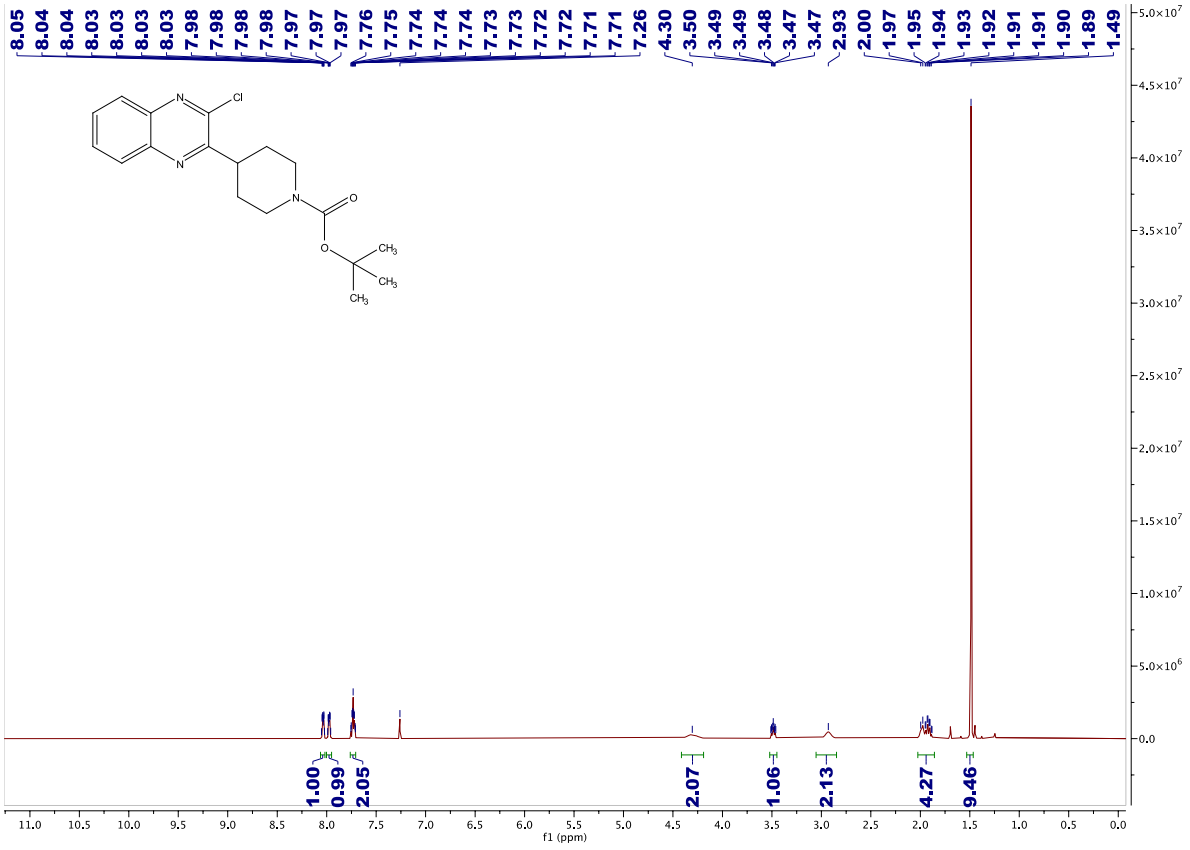
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3y**



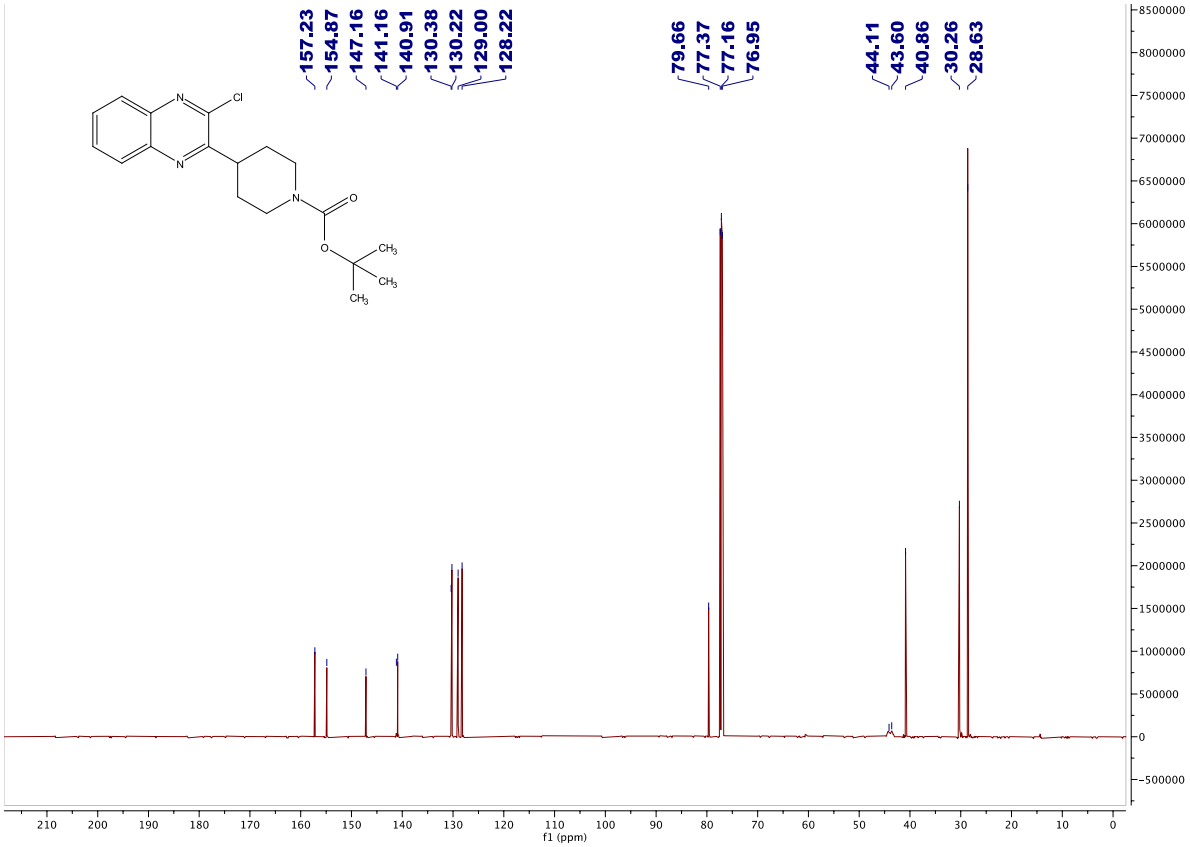
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3z**



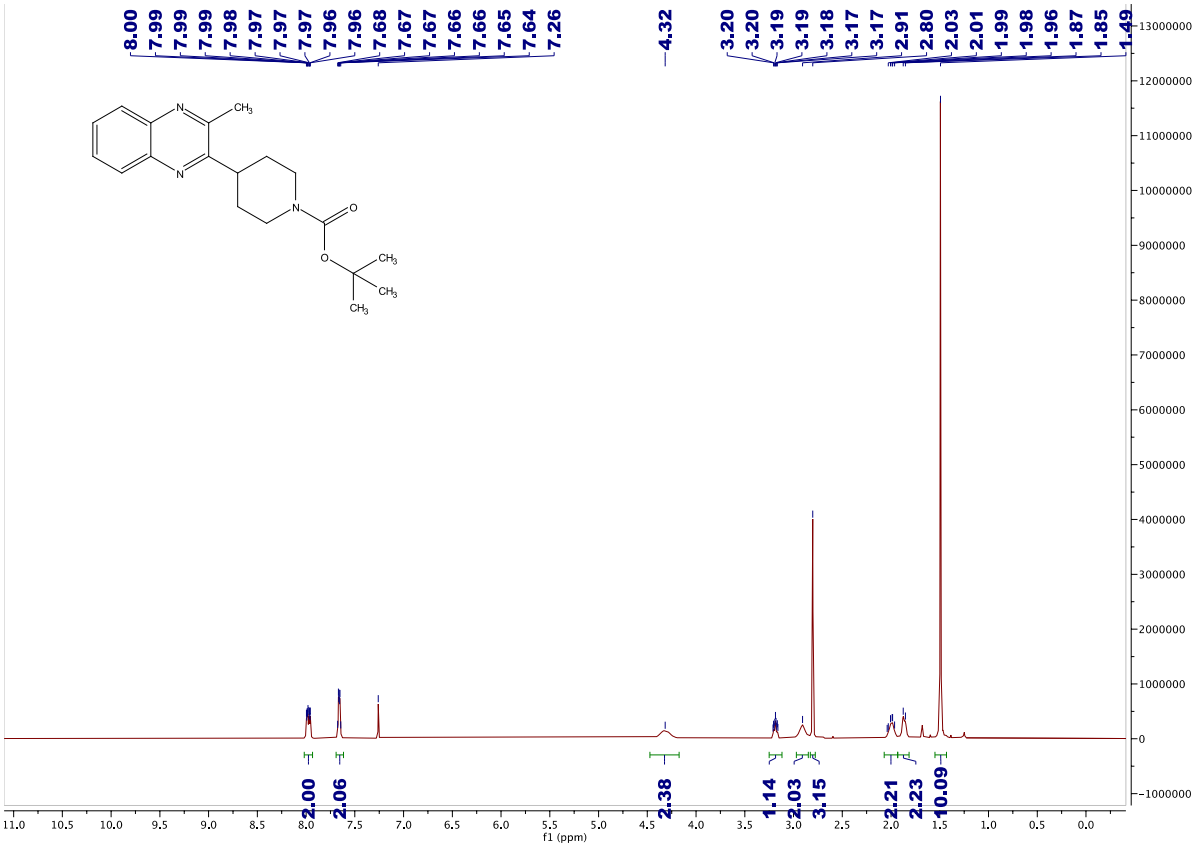
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3z**



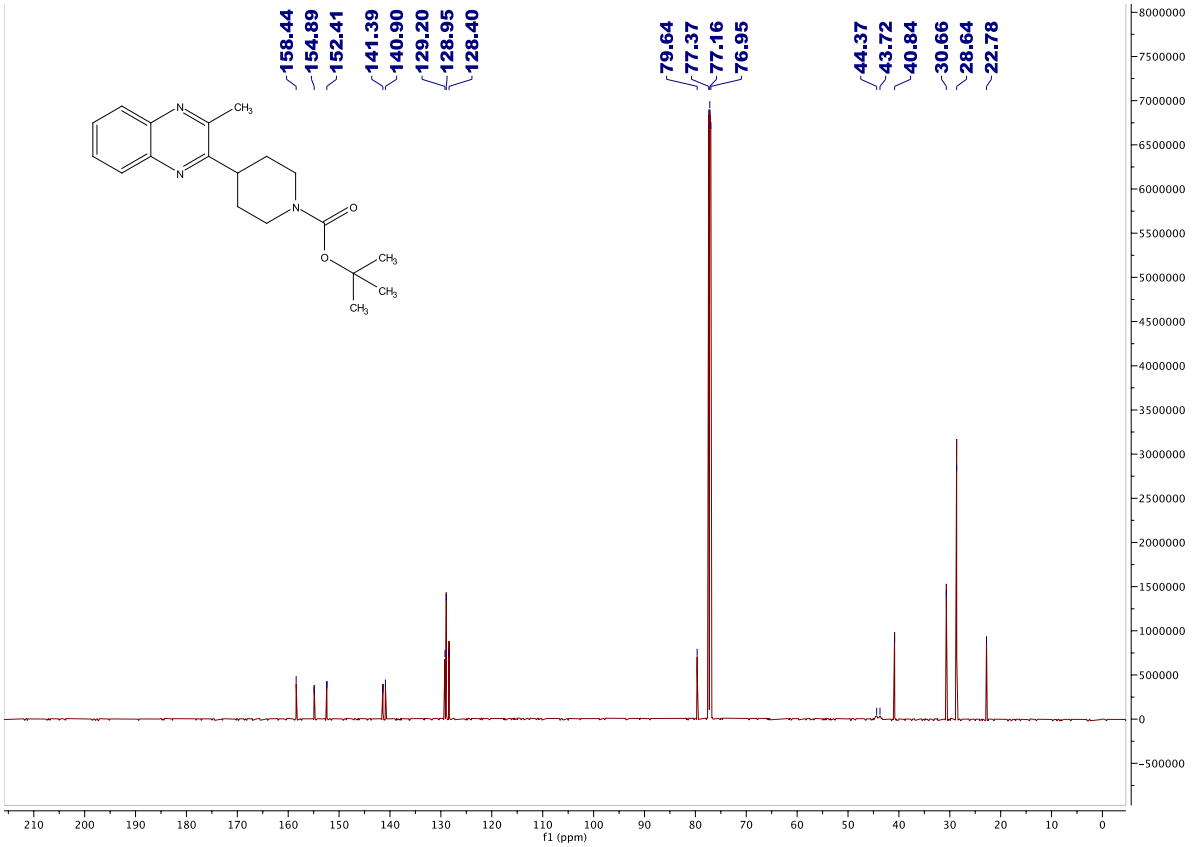
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3aa**



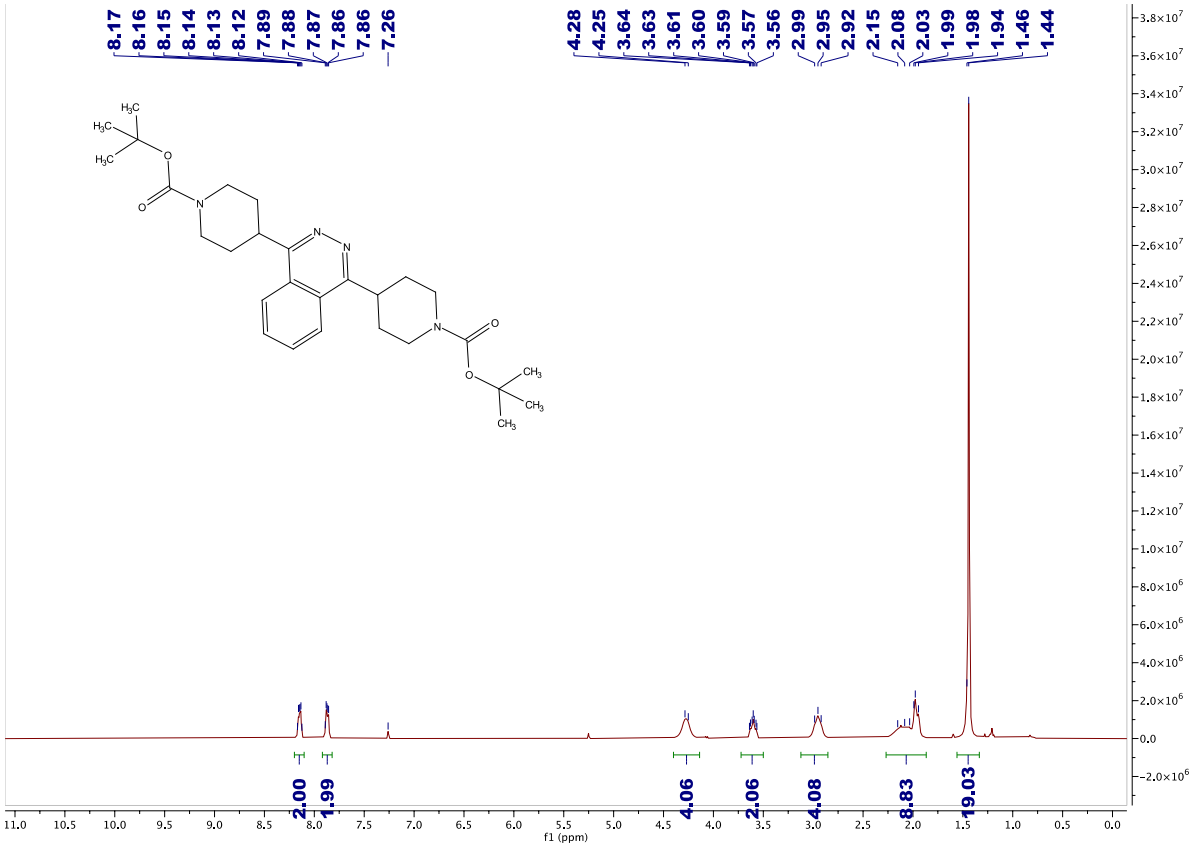
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3aa**



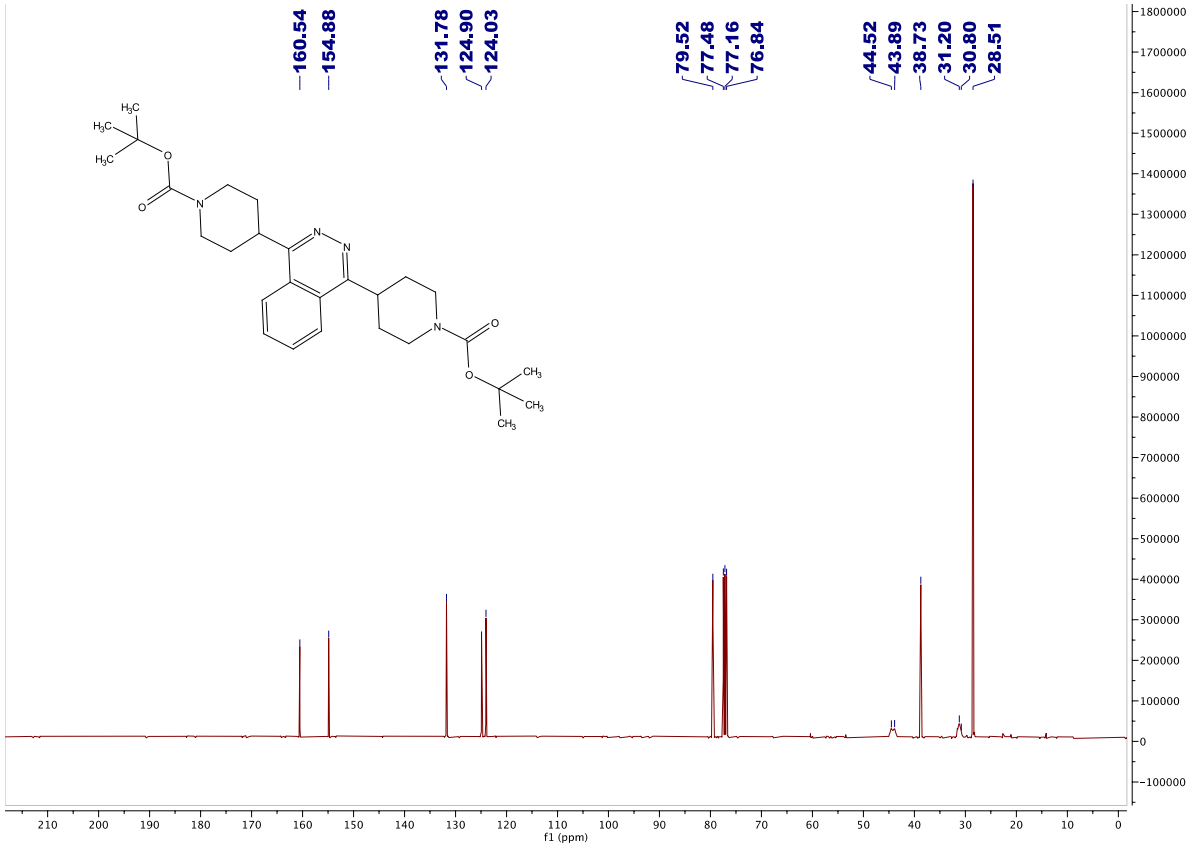
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3ab**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **3ab**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **3ac**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **3ac**