Supporting Information

Electrochemical thiocyanation/cyclization cascade towards thiocyanato-containing benzoxazines

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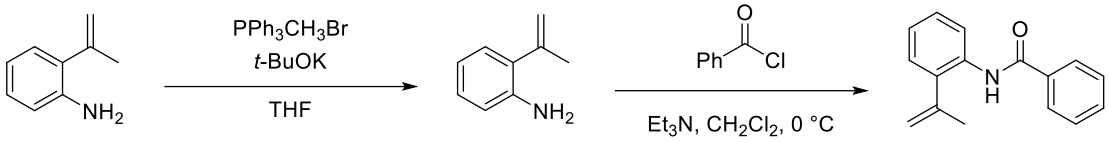
General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). The anodic electrode was graphite rod (ϕ 6 mm) and cathodic electrode was platinum plate (15 mm×15 mm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum (boiling point was between 60-90 ºC). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratios. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. The NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 377 MHz (^{19}F NMR). The chemical shifts (δ) were reported relative to tetramethylsilane (TMS, 0 ppm for ^{1}H NMR), $CDCl_3$ (77.00 ppm for ^{13}C NMR). And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). GC-MS spectra were recorded on a Shimadzu GC-MS QP2010 Ultra. High resolution mass spectra (HRMS) were measured with a Thermo Orbitrap Elite instrument were reported for the molecular ion+ Hydrogen [M+H]+.

Experimental procedure

General procedure for the preparation of 1a-1w:[1]



1-1 **1-2** **1a**

A round-bottom flask was charged with methyltriphenylphosphonium bromide (5.36 g, 15.00 mmol) and dry THF (20.00 mL) under N_2 atmosphere, followed by the addition of potassiumtert-butoxide (1.68 g, 15.00 mmol) at 0 ℃. The reaction mixture was allowed to warm to ambient temperature and stir for 0.50 h. Next, 2-aminoacetophenone (**1-1**) (1.35 g, 10.00 mmol) was added. The reaction mixture was stirred at room temperature overnight. After completion, the reaction was quenched with saturated $NaHCO_3$ solution, and extracted with EtOAc (100.00 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The reaction mixture was purified via column chromatography to give **1-2**.

To a solution of **1-2** (0.99 g, 7.40 mmol) and Et_3N (1.53 g, 11.10 mmol) in CH_2Cl_2 (15.00 mL) was added the solution of benzoylchloride (1.00 mL, 8.90 mmol) in dichloromethane (5.00 mL) dropwise at 0 ℃. After completion, the reaction mixture was purified via column chromatography to give **1a**.

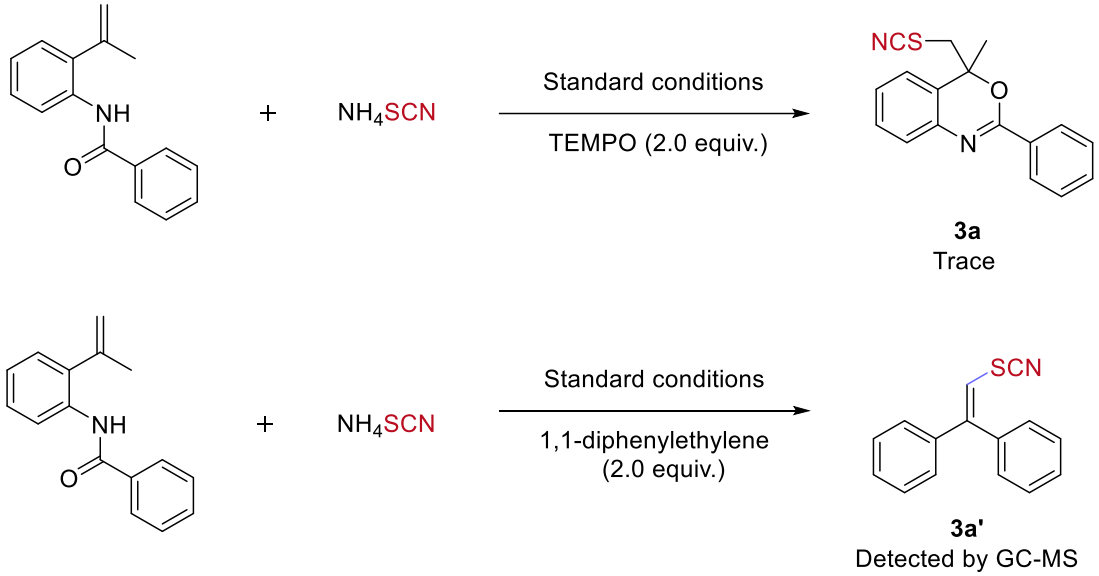
Analogues **1a ~ 1w** were synthesized by using similar procedures.

General procedure for the preparation of 3a-3w：

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, N-(2-(prop-1-en-2-yl)phenyl)benzamide **1a** (0.30 mmol), ammonium thiocyanate **2** (0.90 mmol) was added to the mixture of acetonitrile (6 mL) and sulfuric acid (0.30 mmol). The bottle was equipped with graphite rod (ϕ 6 mm, about 15 mm immersion depth in solution) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA under air atmosphere at at room temperature for 3 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel.

Mechanistic Study

To investigate the possible mechanism of this transformation, a series of control experiments were carried out. No desired product was obtained when 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) or butylated hydroxytoluene (BHT) was added, and the yield of **3a** was trace. The **3a'** adduct was detected by LC-MS in the reaction system. These results indicated this reaction probably underwent a radical pathway, and Thiocyanate radical might be involved in the transformation.



CV experiments:

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under air at room temperature. The working electrode was a glassy carbon electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 6 mL of CH_3CN containing 0.03 M H_2SO_4 were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 2.5 V. The peak potentials *vs*. Ag/AgCl for used. When no acid is added, the oxidation peak of **1a** is not observed, but after adding acid, the oxidation peak potential of **1a** is detected at 2.27 V under the reaction solvent system. However, the oxidation peak potential of **2** appears at 1.48 V. After added acid continuously, the solution has white precipitates. At the same time, two oxidation peaks are observed on the CV, which may promote the hydrogen evolution of the cathode due to the addition of acid, so that thiocyanate has a secondary oxidation similar to the halogen property {SCN^--$(SCN)_3^-$-$(SCN)_2^-$}. This result shows that the acid plays an important role in the reaction.

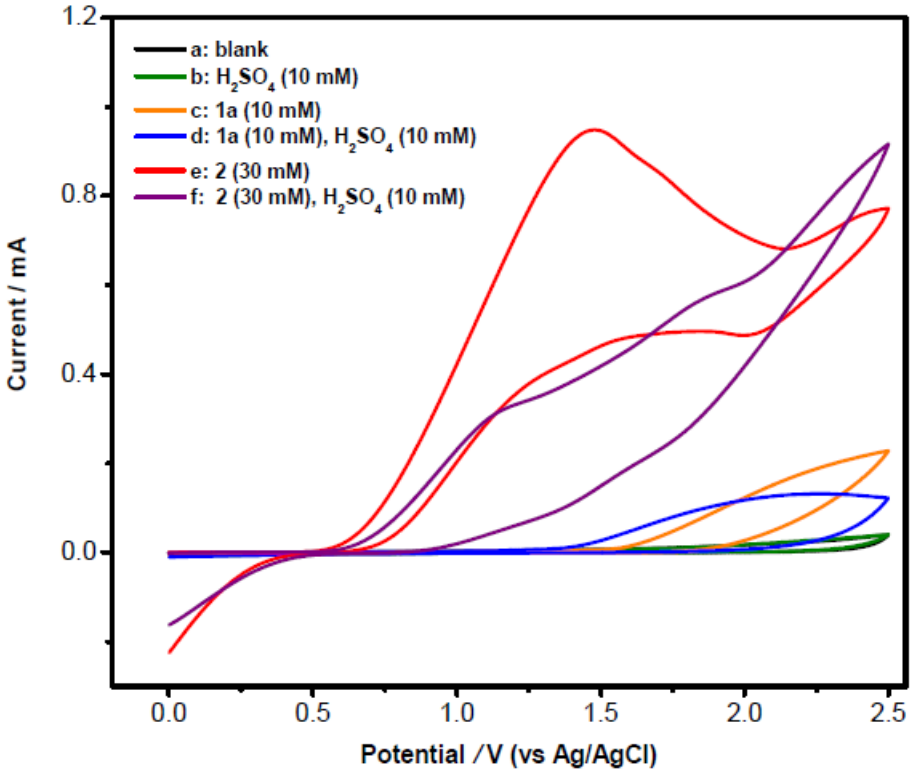
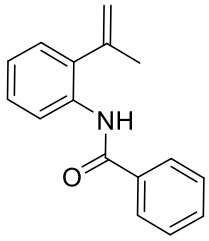


Figure S1 Cyclic voltammogram

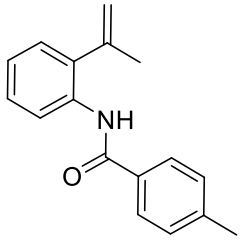
Detail descriptions for products



N-(2-(prop-1-en-2-yl)phenyl)benzamide (1a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.35 (m, 2H), 7.85 – 7.79 (m, 2H), 7.60 – 7.43 (m, 3H), 7.29 – 7.35 (m, 1H), 7.22 – 7.07 (m, 2H), 5.53 – 5.42 (m, 1H), 5.11 (s, 1H), 2.11 (s, 3H).

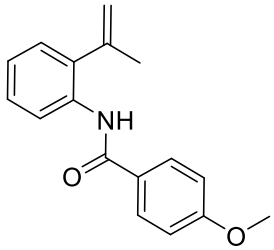
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 143.3, 135.1, 134.0, 133.5, 131.7, 128.8, 128.0, 127.6, 126.9, 123.9, 120.7, 116.8, 24.6.



4-methyl-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.40 (m, 2H), 7.77 – 7.66 (m, 2H), 7.32 – 7.24 (m, 3H), 7.19 – 7.14 (m, 1H), 7.11 – 7.06 (m, 1H), 5.45 – 5.42 (m, 1H), 5.09 (s, 1H), 2.39 (s, 3H), 2.09 (s, 3H).

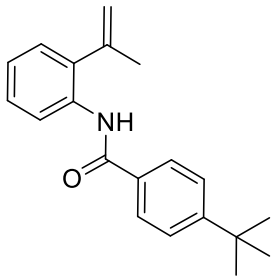
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 143.2, 142.2, 134.0, 133.4, 132.1, 129.4, 127.9, 127.5, 126.8, 123.7, 120.7, 116.7, 24.5, 21.3.



4-methoxy-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.39 (s, 1H), 7.83 – 7.74 (m, 2H), 7.35 – 7.27 (m, 1H), 7.20 – 7.15 (m, 1H), 7.13 – 7.07 (m, 1H), 7.01 – 6.95 (m, 2H), 5.50 – 5.44 (m, 1H), 5.11 (s, 1H), 3.86 (s, 3H), 2.11 (s, 3H).

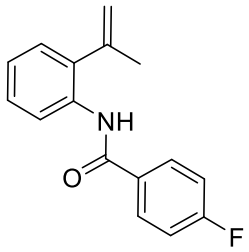
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 162.4, 143.4, 134.2, 133.4, 128.7, 128.0, 127.6, 127.3, 123.6, 120.6, 116.7, 114.0, 55.4, 24.6.



4-(tert-butyl)-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.44 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.20 – 7.06 (m, 2H), 5.47 (s, 1H), 5.11 (s, 1H), 2.11 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 155.3, 143.3, 134.1, 133.4, 132.2, 128.0, 127.6, 126.8, 125.8, 123.7, 120.6, 116.8, 34.9, 31.1, 24.6.

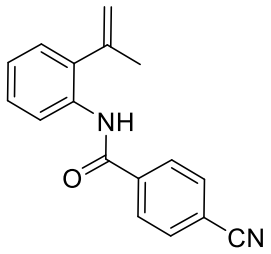


4-fluoro-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.38 (m, 2H), 7.88 – 7.79 (m, 2H), 7.36 – 7.29 (m, 1H), 7.23 – 7.08 (m, 4H), 5.48 (t, *J* = 1.7 Hz, 1H), 5.11 (dd, *J* = 2.0, 1.1 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 164.0, 163.6, 143.3, 133.8, 133.5, 131.17, 131.14, 129.3, 129.2, 128.0, 127.6, 124.0, 120.7, 116.8, 116.0, 115.8, 24.7.

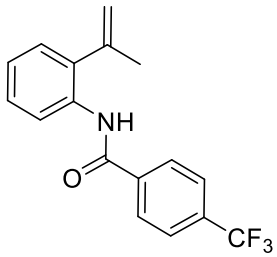
^{19}F NMR (376 MHz, $CDCl_3$) δ -107.46.



4-cyano-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.82 – 7.73 (m, 2H), 7.33 (ddd, *J* = 8.5, 7.3, 1.7 Hz, 1H), 7.22 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 5.50 – 5.45 (m, 1H), 5.11 (s, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 143.2, 138.9, 133.7, 133.3, 132.7, 128.1, 127.7, 127.6, 124.6, 120.8, 117.9, 116.9, 115.3, 24.6.

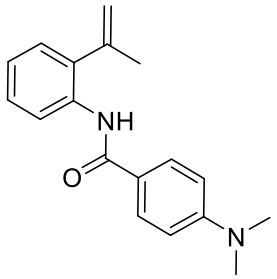


N-(2-(prop-1-en-2-yl)phenyl)-4-(trifluoromethyl)benzamide (1g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.34 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.29 (m, 1H), 7.25 – 7.08 (m, 2H), 5.49 (p, *J* = 1.6 Hz, 1H), 5.12 (dd, *J* = 2.1, 1.1 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 143.3, 138.4, 133.7, 133.6, 133.6, 133.3, 128.2, 127.8, 127.5, 126.1, 126.0, 125.97, 125.93, 125.0, 124.4, 122.3, 120.8, 117.0, 24.8.

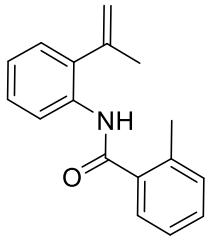
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99.



4-(dimethylamino)-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.35 (s, 1H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.79 – 7.66 (m, 2H), 7.34 – 7.25 (m, 1H), 7.07 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.75 – 6.67 (m, 2H), 5.46 (t, *J* = 1.7 Hz, 1H), 5.11 (s, 1H), 3.02 (s, 6H).

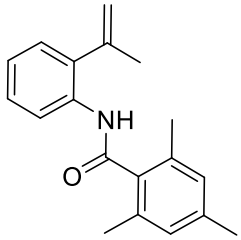
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 163.3, 154.0, 152.5, 143.4, 134.6, 133.1, 132.5, 128.4, 127.9, 127.5, 123.1, 121.5, 120.5, 116.6, 115.5, 111.2, 110.7, 40.0, 39.9, 24.6.



2-methyl-N-(2-(prop-1-en-2-yl)phenyl)benzamide (3i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.3 Hz, 1H), 7.95 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.27 – 7.21 (m, 2H), 7.16 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.10 (td, *J* = 7.5, 1.2 Hz, 1H), 5.33 (q, *J* = 1.8 Hz, 1H), 5.02 (d, *J* = 2.0 Hz, 1H), 2.51 (s, 3H), 2.05 (s, 3H).

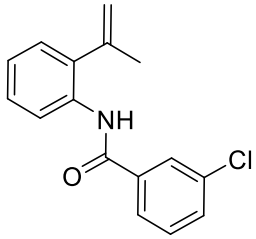
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 142.8, 136.4, 134.0, 133.7, 131.3, 130.1, 127.8, 127.7, 126.4, 125.9, 124.0, 120.9, 116.8, 24.4, 19.8.



2,4,6-trimethyl-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.64 (s, 1H), 7.32 (ddd, *J* = 8.5, 7.4, 1.8 Hz, 1H), 7.14 (ddd, *J* = 21.2, 7.5, 1.5 Hz, 2H), 6.88 (s, 2H), 5.27 (t, *J* = 1.7 Hz, 1H), 4.97 (s, 1H), 2.34 (s, 6H), 2.30 (s, 3H), 2.03 (s, 3H).

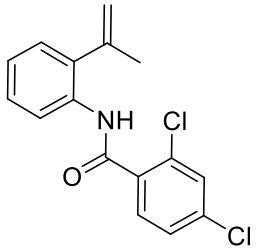
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 142.5, 138.7, 135.1, 134.2, 133.8, 133.7, 128.3, 127.9, 127.8, 124.1, 121.1, 117.1, 24.6, 21.0, 19.1.



3-chloro-N-(2-(prop-1-en-2-yl)phenyl)benzamide (3k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.32 (m, 2H), 7.83 (t, *J* = 1.9 Hz, 1H), 7.64 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.49 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.30 (td, *J* = 7.8, 1.7 Hz, 1H), 7.22 – 7.09 (m, 2H), 5.47 (p, *J* = 1.7 Hz, 1H), 5.13 – 5.07 (m, 1H), 2.11 (s, 3H).

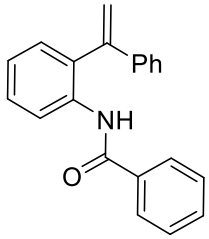
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 143.1, 136.8, 135.0, 133.7, 133.6, 131.7, 130.0, 128.0, 127.7, 127.5, 124.6, 124.2, 120.9, 116.8, 24.5.



2,4-dichloro-N-(2-(prop-1-en-2-yl)phenyl)benzamide (3l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.2 Hz, 1H), 8.32 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.16 (qd, *J* = 7.4, 1.5 Hz, 2H), 5.36 (q, *J* = 1.7 Hz, 1H), 5.03 (d, *J* = 1.9 Hz, 1H), 2.07 (s, 3H).

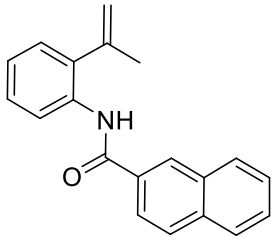
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 142.6, 137.1, 134.0, 133.8, 133.6, 131.5, 131.3, 130.2, 128.0, 127.8, 127.7, 124.4, 121.0, 117.3, 24.7.



N-(2-(1-phenylvinyl)phenyl)benzamide (3m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.8 Hz, 1H), 7.94 (s, 1H), 7.56 – 7.43 (m, 3H), 7.42 – 7.33 (m, 3H), 7.26 (q, *J* = 3.4 Hz, 2H), 7.21 – 7.02 (m, 3H), 5.99 (d, *J* = 1.2 Hz, 1H), 5.66 (d, *J* = 1.2 Hz, 1H).

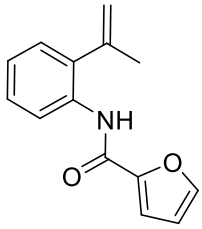
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 161.3, 158.8, 139.8, 134.4, 133.7, 131.9, 130.3, 130.21, 130.17, 130.14, 129.5, 129.3, 128.7, 128.6, 126.9, 126.8, 126.7, 124.67, 124.63, 123.2, 123.1, 122.6, 116.5, 116.3.



N-(2-(prop-1-en-2-yl)phenyl)-2-naphthamide (3n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.53 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.34 (d, *J* = 1.8 Hz, 1H), 7.97 – 7.83 (m, 4H), 7.62 – 7.49 (m, 2H), 7.34 (ddd, *J* = 8.5, 7.4, 1.8 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 5.50 (t, *J* = 1.7 Hz, 1H), 5.16 (dd, *J* = 2.1, 1.0 Hz, 1H), 2.13 (d, *J* = 1.3 Hz, 3H).

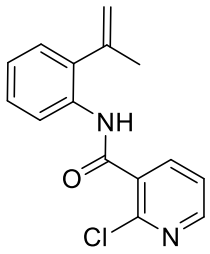
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 143.4, 134.9, 134.2, 133.7, 132.7, 132.4, 129.1, 128.9, 128.2, 127.96, 127.83, 127.76, 127.73, 127.0, 124.1, 123.3, 120.9, 116.9, 24.7.



N-(2-(prop-1-en-2-yl)phenyl)furan-2-carboxamide (3o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.45 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.29 (td, *J* = 8.3, 7.8, 1.6 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.47 (p, *J* = 1.6 Hz, 1H), 5.13 – 5.08 (m, 1H), 2.11 (d, *J* = 1.3 Hz, 3H).

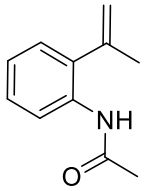
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 148.0, 144.2, 142.5, 133.5, 133.4, 127.9, 127.7, 123.8, 120.5, 117.0, 114.9, 112.4, 24.3.



2-chloro-N-(2-(prop-1-en-2-yl)phenyl)nicotinamide (3p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.51 (dd, *J* = 4.7, 2.0 Hz, 1H), 8.45 (d, *J* = 8.1 Hz, 1H), 8.20 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.46 – 7.29 (m, 2H), 7.23 – 7.08 (m, 2H), 5.40 (p, *J* = 1.7 Hz, 1H), 5.10 – 5.03 (m, 1H), 2.09 (s, 3H).

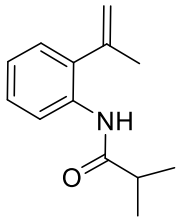
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 151.3, 146.8, 142.5, 140.2, 134.2, 133.5, 131.6, 128.0, 127.9, 124.7, 123.0, 121.1, 117.5, 24.8, 24.8.



N-(2-(prop-1-en-2-yl)phenyl)acetamide (3q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.13 (m, 1H), 7.57 (s, 1H), 7.26 (td, *J* = 8.2, 7.7, 1.8 Hz, 1H), 7.18 – 7.01 (m, 2H), 5.43 – 5.34 (m, 1H), 5.02 (d, *J* = 1.9 Hz, 1H), 2.16 (s, 3H), 2.07 (s, 3H).

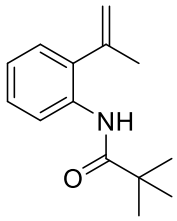
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 142.9, 133.8, 133.3, 127.9, 127.6, 123.8, 121.0, 116.7, 24.8, 24.5.



N-(2-(prop-1-en-2-yl)phenyl)isobutyramide (3r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.68 (s, 1H), 7.26 (ddd, *J* = 8.5, 7.3, 1.7 Hz, 1H), 7.17 – 7.02 (m, 2H), 5.41 (p, *J* = 1.7 Hz, 1H), 5.03 (dd, *J* = 2.0, 1.1 Hz, 1H), 2.51 (p, *J* = 6.9 Hz, 1H), 2.07 (d, *J* = 1.2 Hz, 3H), 1.24 (d, *J* = 6.9 Hz, 6H).

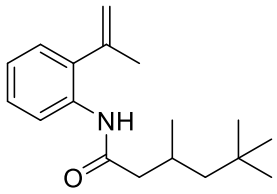
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 143.0, 133.9, 133.2, 127.8, 127.5, 123.5, 120.7, 116.7, 36.8, 24.4, 19.5.



N-(2-(prop-1-en-2-yl)phenyl)pivalamide (3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.99 (s, 1H), 7.26 (ddd, *J* = 10.1, 6.8, 1.7 Hz, 1H), 7.19 – 6.95 (m, 2H), 5.43 (p, *J* = 1.6 Hz, 1H), 5.08 – 4.98 (m, 1H), 2.08 (t, *J* = 1.3 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 9H).

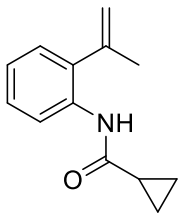
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 143.2, 134.1, 133.1, 127.9, 127.5, 123.4, 120.3, 116.6, 39.9, 27.5, 26.4, 24.5.



3,5,5-trimethyl-N-(2-(prop-1-en-2-yl)phenyl)hexanamide (3t)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.57 (s, 1H), 7.25 (ddd, *J* = 8.4, 5.5, 1.7 Hz, 1H), 7.17 – 6.94 (m, 2H), 5.42 – 5.35 (m, 1H), 5.05 – 4.97 (m, 1H), 2.35 (dt, *J* = 11.6, 5.8 Hz, 1H), 2.15 – 2.04 (m, 5H), 1.28 (ddd, *J* = 11.5, 9.6, 2.8 Hz, 2H), 1.19 – 1.13 (m, 1H), 1.03 (d, *J* = 6.2 Hz, 3H), 0.92 (d, *J* = 5.4 Hz, 9H).

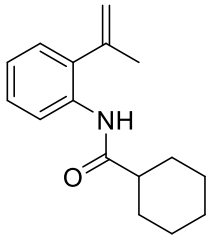
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 143.0, 133.9, 133.2, 127.8, 127.5, 123.6, 120.9, 116.6, 50.6, 50.5, 47.9, 43.7, 31.0, 29.91, 29.86, 27.6, 26.8, 24.5, 22.6.



N-(2-(prop-1-en-2-yl)phenyl)cyclopropanecarboxamide (3u)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.81 (s, 1H), 7.25 – 7.17 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 5.39 (s, 1H), 5.05 (s, 1H), 2.08 (t, *J* = 1.2 Hz, 3H), 1.47 (dt, *J* = 8.2, 3.9 Hz, 1H), 1.05 (dt, *J* = 6.8, 3.5 Hz, 2H), 0.81 (dq, *J* = 7.2, 4.0 Hz, 2H).

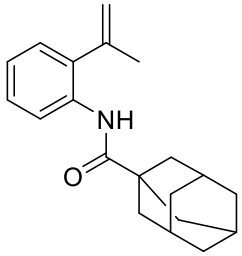
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 143.0, 134.1, 133.0, 127.7, 127.5, 123.4, 120.8, 116.7, 24.4, 15.8, 7.7.



N-(2-(prop-1-en-2-yl)phenyl)cyclohexanecarboxamide (3v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.64 (s, 1H), 7.25 (ddd, *J* = 8.5, 5.6, 1.8 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.05 (td, *J* = 7.5, 1.2 Hz, 1H), 5.41 (p, *J* = 1.6 Hz, 1H), 5.08 – 4.97 (m, 1H), 2.22 (ddd, *J* = 11.6, 8.1, 3.5 Hz, 1H), 2.07 (t, *J* = 1.3 Hz, 3H), 2.01 – 1.90 (m, 2H), 1.83 (dq, *J* = 11.6, 3.3 Hz, 2H), 1.75 – 1.65 (m, 1H), 1.48 (qd, *J* = 12.1, 3.3 Hz, 2H), 1.39 – 1.21 (m, 3H).

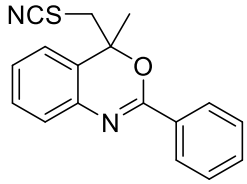
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 143.1, 134.0, 133.3, 127.9, 127.6, 123.5, 120.8, 116.7, 46.6, 29.6, 25.7, 25.7, 24.4.



N-(2-(prop-1-en-2-yl)phenyl)adamantane-1-carboxamide (3w)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.2 Hz, 1H), 7.92 (s, 1H), 7.25 (td, *J* = 8.2, 7.7, 2.0 Hz, 1H), 7.12 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 5.44 (t, *J* = 1.9 Hz, 1H), 5.03 (d, *J* = 2.0 Hz, 1H), 2.09 (d, *J* = 5.2 Hz, 6H), 1.99 – 1.57 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 143.2, 134.1, 133.3, 127.8, 127.5, 123.4, 120.6, 116.6, 41.8, 39.2, 36.4, 28.1, 24.4.



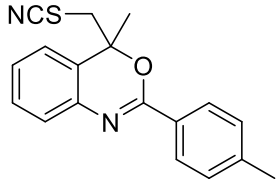
4-methyl-2-phenyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3a).[2]

White solid was obtained in 91% isolated yield, 79.9 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.58–7.42 (m, 3H), 7.41–7.33 (m, 2H), 7.29–7.22 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 3.58 (d, *J* = 13.8 Hz, 1H), 3.45 (d, *J* = 13.9 Hz, 1H), 1.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 138.6, 131.78, 131.76, 129.9, 128.3, 127.9, 127.2, 126.3, 125.9, 122.8, 112.2, 78.9, 44.4, 25.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2OS^+$ 295.0899; Found 295.09245.



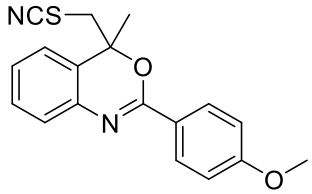
4-methyl-4-(thiocyanatomethyl)-2-(p-tolyl)-4*H*-benzo[*d*][1,3]oxazine (3b) .[2]

Colorless oil was obtained in 74% isolated yield, 68.1 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–7.96 (m, 2H), 7.40–7.30 (m, 2H), 7.28–7.19 (m, 3H), 7.11 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.54 (d, *J* = 13.8 Hz, 1H), 3.41 (d, *J* = 13.8 Hz, 1H), 2.40 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 142.3, 138.7, 129.8, 129.0, 128.9, 127.9, 126.9, 126.2, 125.7, 122.8, 112.2, 78.6, 44.2, 25.6, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2OS^+$ 309.1056; Found 309.1062.



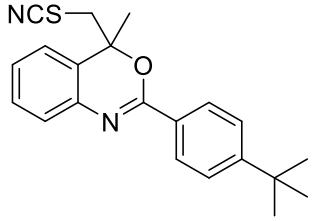
2-(4-methoxyphenyl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3c).[2]

Colorless oil was obtained in 86% isolated yield, 83.8 mg, 0.3 mmol scale, R_f = 0.32 (petroleum ether/ethyl acetate =10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.07 (m, 2H), 7.38–7.29 (m, 2H), 7.21 (td, *J* = 7.3, 1.7 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.97–6.91 (m, 2H), 3.84 (s, 3H), 3.55 (d, *J* = 13.8 Hz, 1H), 3.40 (d, *J* = 13.8 Hz, 1H), 1.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 155.1, 138.8, 129.72, 129.69, 126.6, 126.1, 125.4, 124.0, 122.7, 113.6, 112.2, 78.5, 55.3, 44.1, 25.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_2S^+$ 325.1005; Found 325.1013.



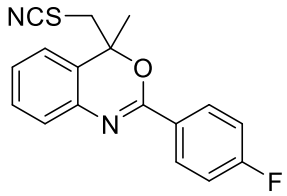
2-(4-(tert-butyl)phenyl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazin e (3d).

White solid was obtained in 76% isolated yield, 79.8 mg, 0.3 mmol scale, R_f = 0.39 (petroleum ether/ ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.05 (m, 2H), 7.53–7.45 (m, 2H), 7.41–7.33 (m, 2H), 7.29–7.21 (m, 1H), 7.14 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.59 (d, *J* = 13.7 Hz, 1H), 3.45 (d, *J* = 13.8 Hz, 1H), 1.91 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 138.8, 129.9, 129.0, 127.8, 127.0, 126.4, 125.83, 125.79, 125.4, 122.8, 112.3, 78.7, 44.3, 34.9, 31.1, 25.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2OS^+$ 351.1525; Found 351.1547.



2-(4-fluorophenyl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3e).

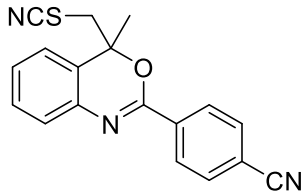
White solid was obtained in 79% isolated yield, 73.7 mg, 0.3 mmol scale, R_f = 0.30 (petroleum ether/ ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.12 (m, 2H), 7.40–7.30 (m, 2H), 7.24 (td, *J* = 7.4, 1.7 Hz, 1H), 7.17–7.08 (m, 3H), 3.56 (d, *J* = 13.9 Hz, 1H), 3.42 (d, *J* = 14.0 Hz, 1H), 1.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 163.7, 154.3, 138.4, 130.2, 130.1, 129.9, 127.89, 127.86, 127.2, 126.1, 125.8, 122.8, 115.5, 115.3, 112.1, 79.0, 44.3, 25.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.52.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}FN_2OS^+$ 313.0803; Found 313.0805.



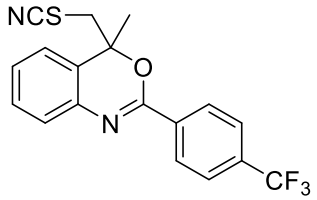
4-(4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzonitrile (3f).[4]

White solid was obtained in 84% isolated yield, 79.7 mg, 0.3 mmol scale, R_f = 0.20 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.23 (m, 2H), 7.77–7.69 (m, 2H), 7.45–7.34 (m, 2H), 7.34–7.25 (m, 1H), 7.14 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.58 (d, *J* = 14.1 Hz, 1H), 3.46 (d, *J* = 14.1 Hz, 1H), 1.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 137.8, 135.8, 131.9, 130.0, 128.2, 128.0, 126.2, 126.0, 122.8, 118.3, 114.6, 111.8, 79.6, 44.4, 26.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}FN_3OS^+$ 320.0852; Found 320.0863.



4-methyl-4-(thiocyanatomethyl)-2-(4-(trifluoromethyl)phenyl)-4*H*-benzo[*d*][1,3]oxazine (3g).

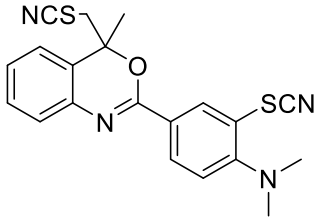
White solid was obtained in 75% isolated yield, 81.3 mg, 0.3 mmol scale, R_f = 0.21 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.43–7.34 (m, 2H), 7.32–7.25 (m, 1H), 7.13 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.57 (d, *J* = 14.0 Hz, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 1.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 138.1, 135.2 (d, *J* = 1.5 Hz), 133.0 (q, *J* = 32.7 Hz), 130.0, 128.2, 127.8, 126.1 (d, *J* = 1.8 Hz), 125.2 (q, *J* = 3.8 Hz),125.1, 123.8 (q, *J* = 273.7 Hz) 122.9, 112.0, 79.4, 44.4, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}F_3N_2OS^+$ 363.0772; Found 363.0773.



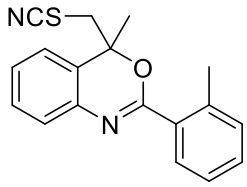
4-(4-(isothiocyanatomethyl)-4-methyl-4*H*-benzo[*d*][1,3]oxazin-2-yl)-N,N-dimethyl-2-thiocyanatoaniline (3h).

White solid was obtained in 31% isolated yield, 31.3 mg, 0.3 mmol scale, R_f = 0.39 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 2.0 Hz, 1H), 8.11 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.28 – 7.22 (m, 2H), 7.13 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.58 (d, *J* = 13.9 Hz, 1H), 3.45 (d, *J* = 13.9 Hz, 1H), 2.78 (s, 6H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 153.8, 138.4, 130.0, 129.1, 128.9, 128.0, 127.4, 126.2, 126.0, 122.9, 122.8, 120.6, 112.1, 111.1, 78.8, 44.4, 44.3, 25.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}N_3OS^+$ 395.0095; Found 395.1007.



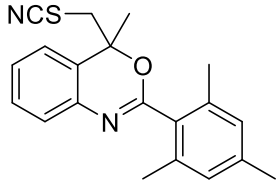
4-methyl-4-(thiocyanatomethyl)-2-(o-tolyl)-4*H*-benzo[*d*][1,3]oxazine (3i).[2]

Colorless oil was obtained in 77% isolated yield, 70.5 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 1H), 7.41–7.30 (m, 3H), 7.30–7.22 (m, 3H), 7.12 (dd, *J* = 7.7, 1.4 Hz, 1H), 3.60 (d, *J* = 13.7 Hz, 1H), 3.47 (d, *J* = 13.7 Hz, 1H), 2.65 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 138.4, 138.3, 131.6, 131.5, 130.6, 129.8, 129.5, 127.3, 125.8, 125.7, 125.4, 122.8, 112.0, 79.2, 44.4, 26.4, 21.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2OS^+$ 309.1056; Found 309.1071.



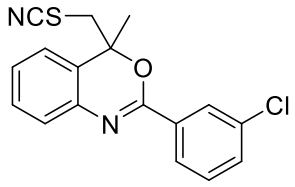
2-mesityl-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3j).[4]

White solid was obtained in 86% isolated yield, 86.3 mg, 0.3 mmol scale, R_f = 0.36 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 1H), 7.31–7.25 (m, 2H), 7.11 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.89 (s, 2H), 3.69 (d, *J* = 13.7 Hz, 1H), 3.48 (d, *J* = 13.6 Hz, 1H), 2.36 (s, 6H), 2.28 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 139.1, 137.8, 135.7, 130.5, 129.9, 128.3, 127.5, 125.9, 124.6, 123.0, 111.9, 79.8, 45.2, 28.4, 21.1, 19.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2OS^+$ 337.1369; Found 337.1380.



2-(3-chlorophenyl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3k).[2]

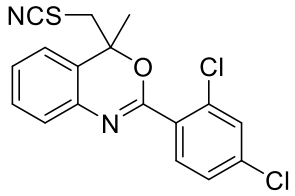
White solid was obtained in 62% isolated yield, 60.7 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, *J* = 1.9 Hz, 1H), 7.99–7.94 (m, 1H), 7.43–7.37

(m, 1H), 7.34–7.24 (m, 3H), 7.22–7.16 (m, 1H), 7.05 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.48 (d, *J* = 13.9 Hz, 1H), 3.36 (d, *J* = 13.9 Hz, 1H), 1.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 138.2, 134.4, 133.6, 131.7, 129.9, 129.6, 127.8, 127.6, 126.1, 126.0, 125.8, 122.8, 111.9, 79.3, 44.4, 26.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}ClN_2OS^+$ 329.0510; Found 329.0519.



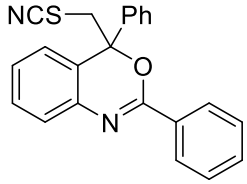
2-(2,4-dichlorophenyl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3l).

White solid was obtained in 82% isolated yield, 88.4 mg, 0.3 mmol scale, R_f = 0.29 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.31 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.27–7.19 (m, 3H), 7.04 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.54 (d, *J* = 13.9 Hz, 1H), 3.43 (d, *J* = 13.9 Hz, 1H), 1.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 137.9, 137.0, 133.9, 132.2, 130.5, 130.3, 130.0, 128.0, 127.1, 126.0, 125.3, 123.0, 111.9, 80.5, 44.6, 26.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2Cl_2OS^+$ 363.0120; Found 363.0129.



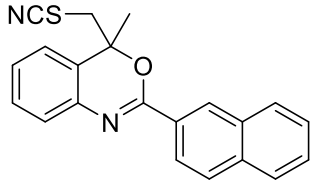
2,4-diphenyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3m).[2]

Colorless oil was obtained in 64% isolated yield, 68.4 mg, 0.3 mmol scale, R_f = 0.27 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.21 (m, 2H), 7.54–7.43 (m, 3H), 7.42 – 7.37 (m, 2H), 7.36–7.24 (m, 6H), 7.20–7.14 (m, 1H), 4.05–3.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 140.0, 139.5, 131.8, 131.6, 130.1, 129.0, 128.8, 128.4, 127.9, 126.9, 126.1, 125.6, 124.7, 124.0, 112.1, 82.3, 43.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}N_2OS^+$ 357.1056; Found 357.1084.



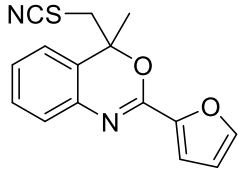
4-methyl-2-(naphthalen-2-yl)-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3n).[4]

Colorless oil was obtained in 88% isolated yield, 90.3 mg, 0.3 mmol scale, R_f = 0.31 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.7 Hz, 1H), 8.26 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.98–7.94 (m, 1H), 7.90–7.81 (m, 2H), 7.58–7.47 (m, 2H), 7.42–7.34 (m, 2H), 7.27–7.19 (m, 1H), 7.12–7.07 (m, 1H), 3.55 (d, *J* = 13.9 Hz, 1H), 3.42 (d, *J* = 13.9 Hz, 1H), 1.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 138.6, 134.9, 132.6, 129.8, 129.04, 129.02, 128.6, 128.0, 127.7, 127.2, 126.5, 126.3, 125.8, 124.3, 122.8, 112.2, 78.9, 44.2, 25.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_2OS^+$ 345.1056; Found 345.1060.



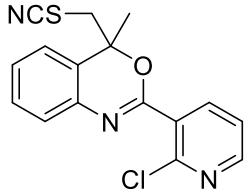
2-(furan-2-yl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3o).[2]

Yellow oil was obtained in 76% isolated yield, 64.8 mg, 0.3 mmol scale, R_f = 0.22 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.42–7.33 (m, 2H), 7.27–7.21 (m, 1H), 7.15 (dd, *J* = 3.5, 0.8 Hz, 1H), 7.14–7.09 (m, 1H), 6.54 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.58 (d, *J* = 14.0 Hz, 1H), 3.39 (d, *J* = 13.9 Hz, 1H), 1.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 145.9, 145.7, 137.9, 129.9, 127.2, 126.2, 125.8, 122.8, 115.5, 112.0, 111.9, 78.8, 43.9, 25.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O_2S^+$ 285.0692; Found 285.0721.



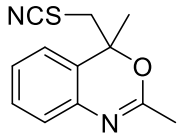
2-(2-chloropyridin-3-yl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3p).

White solid was obtained in 84% isolated yield, 82.9 mg, 0.3 mmol scale, R_f = 0.21 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.17 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.45–7.30 (m, 4H), 7.14 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.65 (d, *J* = 14.0 Hz, 1H), 3.55 (d, *J* = 14.0 Hz, 1H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 150.8, 149.3, 140.0, 137.7, 130.0, 128.8, 128.2, 126.0, 125.2, 123.1, 122.2, 111.8, 80.8, 44.7, 27.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_3ClOS^+$ 330.0462; Found 330.0471.



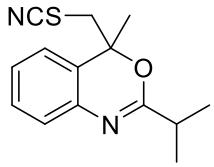
2,4-dimethyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3q).

Colorless oil was obtained in 46% isolated yield, 32.1 mg, 0.3 mmol scale, R_f = 0.32 (petroleum ether/ethyl acetate =5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 7.6, 1.5 Hz, 1H), 7.25–7.13 (m, 2H), 7.03 (dd, *J* = 7.7, 1.4 Hz, 1H), 3.48 (d, *J* = 13.9 Hz, 1H), 3.27 (d, *J* = 14.0 Hz, 1H), 2.19 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 138.0, 129.8, 127.0, 125.3, 125.0, 122.8, 112.2, 78.7, 45.0, 26.5, 21.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}N_2OS^+$ 233.0743; Found 233.0743.



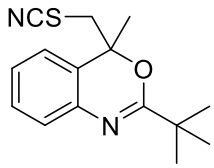
2-isopropyl-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3r).

Colorless oil was obtained in 66% isolated yield, 51.5 mg, 0.3 mmol scale, R_f = 0.33 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (td, *J* = 7.6, 1.5 Hz, 1H), 7.32–7.24 (m, 2H), 7.06 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.63–3.42 (m, 2H), 1.86 (s, 6H), 1.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 137.0, 130.0, 128.2, 126.2, 125.4, 122.9, 111.8, 111.6, 80.6, 55.5, 44.2, 26.7, 26.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}N_2OS^+$ 260.1055; Found 260.1056.



2-(tert-butyl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3s).[2]

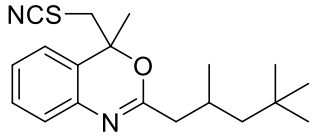
Colorless oil was obtained in 50% isolated yield, 41.2 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ethyl acetate =10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.04

(d, J = 8.1 Hz, 1H), 3.53 (d, J = 13.6 Hz, 1H), 3.42 (d, J = 13.7 Hz, 1H), 1.74 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 138.3, 129.6, 126.8, 125.6, 125.5, 122.5, 112.3, 78.0, 44.1, 37.2, 27.4, 26.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}N_2OS^+$ 275.1212; Found 275.1213.



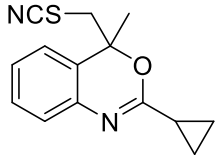
4-methyl-4-(thiocyanatomethyl)-2-(2,4,4-trimethylpentyl)-4*H*-benzo[*d*][1,3]oxazine (3t).

Colorless oil was obtained in 45% isolated yield, 44.6 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 1H), 7.23–7.17 (m, 2H), 7.06–7.01 (m, 1H), 3.52 (dd, *J* = 13.8, 8.3 Hz, 1H), 3.34 (t, *J* = 14.1 Hz, 1H), 2.52–2.34 (m, 1H), 2.30–2.16 (m, 1H), 2.15–2.06 (m, 1H), 1.79 (d, *J* = 6.5 Hz, 3H), 1.39–1.28 (m, 1H), 1.20–1.09 (m, 1H), 1.04 (dd, *J* = 6.6, 3.4 Hz, 3H), 0.92 (d, *J* = 4.8 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (d, *J* = 5.8 Hz), 138.0 (d, *J* = 5.3 Hz), 129.8 (d, *J* = 4.0 Hz), 126.8 (d, *J* = 3.6 Hz), 125.5 (d, *J* = 6.3 Hz), 125.2, 122.7 (d, *J* = 10.6 Hz), 112.1 (d, *J* = 1.8 Hz), 78.4 (d, *J* = 3.9 Hz), 50.5 (d, *J* = 25.3 Hz), 44.7 (dd, *J* = 39.5, 19.6 Hz), 31.0 (d, *J* = 2.9 Hz), 30.0, 27.5 (d, *J* = 10.3 Hz), 26.8, 26.5, 22.5 (d, *J* = 19.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{27}N_2OS^+$ 331.1839; Found 331.1843.



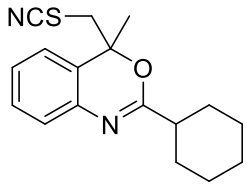
2-cyclopropyl-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3u).[2]

Colorless oil was obtained in 73% isolated yield, 56.6 mg, 0.3 mmol scale, R_f = 0.22 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (td, *J* = 7.6, 1.4 Hz, 1H), 7.21–7.12 (m, 2H), 7.02 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.48 (d, *J* = 13.8 Hz, 1H), 3.32 (d, *J* = 13.9 Hz, 1H), 1.80–1.67 (m, 4H), 1.16–1.04 (m, 2H), 0.97–0.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 138.4, 129.7, 126.3, 125.6, 124.6, 122.6, 112.1, 78.4, 44.2, 25.8, 14.4, 7.4, 6.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}N_2OS^+$ 259.0900; Found 259.0906.



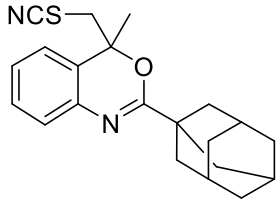
2-cyclohexyl-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3v).[4]

White solid was obtained in 51% isolated yield, 45.5 mg by ^{1}H NMR, 0.3 mmol scale, R_f = 0.39 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 1H), 7.23–7.17 (m, 2H), 7.07–7.02 (m, 1H), 3.51 (d, *J* = 13.7 Hz, 1H), 3.36 (d, *J* = 13.7 Hz, 1H), 2.42–2.29 (m, 1H), 2.00–1.91 (m, 2H), 1.87–1.78 (m, 2H), 1.76 (s, 3H), 1.74–1.65 (m, 1H), 1.57–1.45 (m, 2H), 1.38–1.19 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 138.2, 129.8, 126.8, 125.7, 125.2, 122.7, 112.2, 78.1, 44.5, 43.6, 26.1, 25.7, 25.7, 25.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2OS^+$ 301.1369; Found 301.1379.



2-(adamantan-1-yl)-4-methyl-4-(thiocyanatomethyl)-4*H*-benzo[*d*][1,3]oxazine (3w).

Colorless oil was obtained in 53% isolated yield, 46.7 mg, 0.3 mmol scale, R_f = 0.44 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 1H), 7.23–7.17 (m, 2H), 7.04 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 2.11–2.02 (m, 3H), 1.95 (d, *J* = 2.9 Hz, 6H), 1.74 (d, *J* = 2.7 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 138.5, 129.6, 126.7, 125.9, 125.5, 122.6, 112.4, 77.8, 44.2, 39.03, 38.98, 36.5, 28.0, 25.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}N_2OS^+$ 353.1682; Found 3531694.

References

(1) J. Guo, Y. Hao, G. Li, Z. Wang, Y. Liu, Y. Li and Q. Wang, *Org. Biomol. Chem.*, **2020**, *18*, 1994-2001.

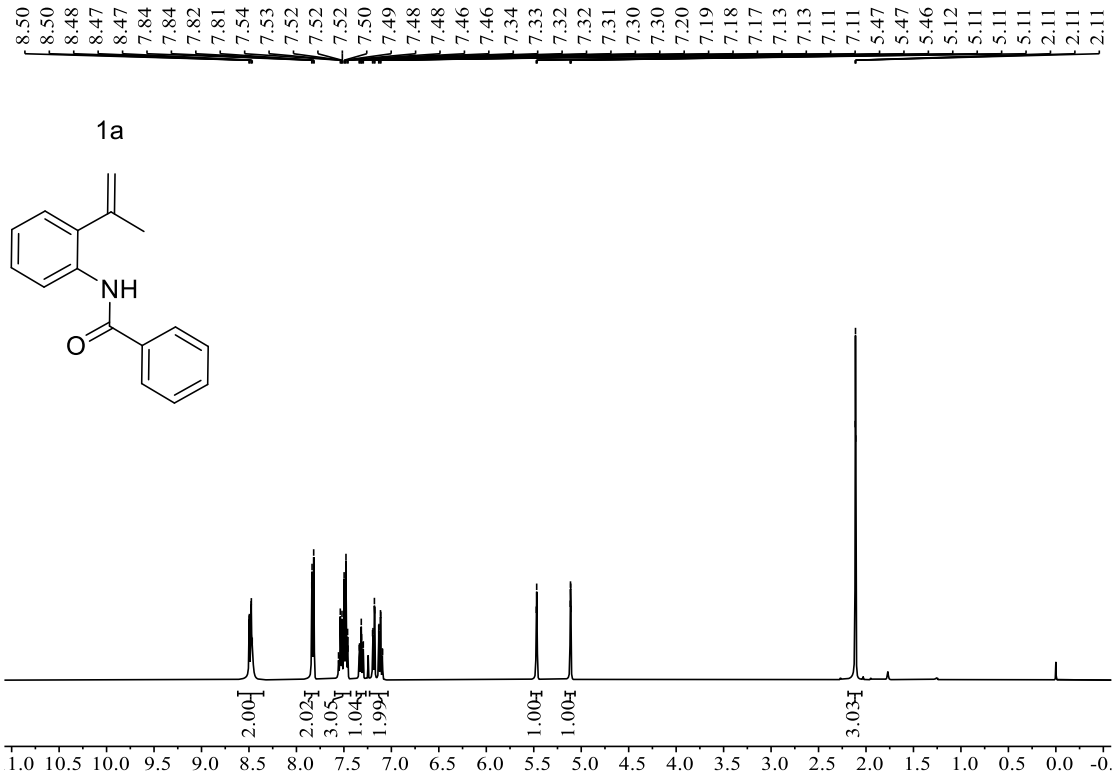
(2) H. Yang, X. H. Duan, J. F. Zhao, and L. N. Guo, *Org. Lett.*, **2015**, *17*, 1998-2001.

(3) Qumruddeen, A. Yadav, R. Kant, and C. B. Tripathi, *J. Org. Chem.*, **2020**, *85*, 2814-2822.

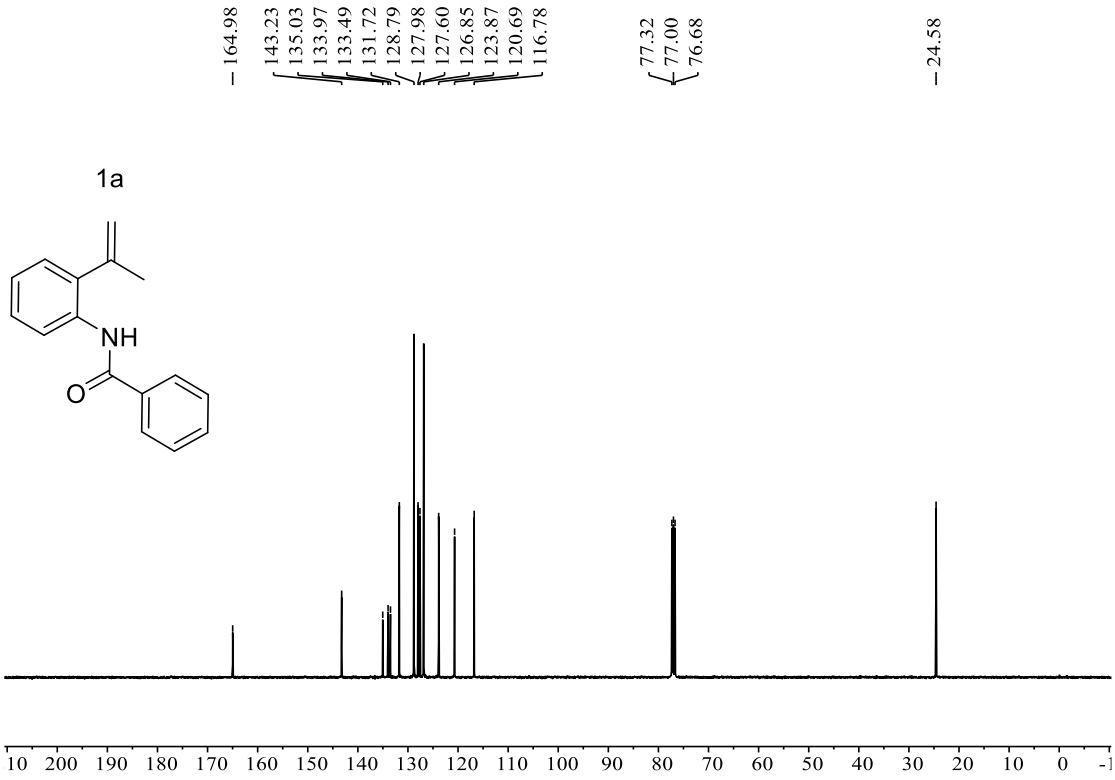
(4) S. C. Qian, P. C. Xu, Y. Zheng, S. L. Huang, *Tetrahedron Lett.*, **2023**, doi: org/10.1016/j. Tetlet.2023.154341.

Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

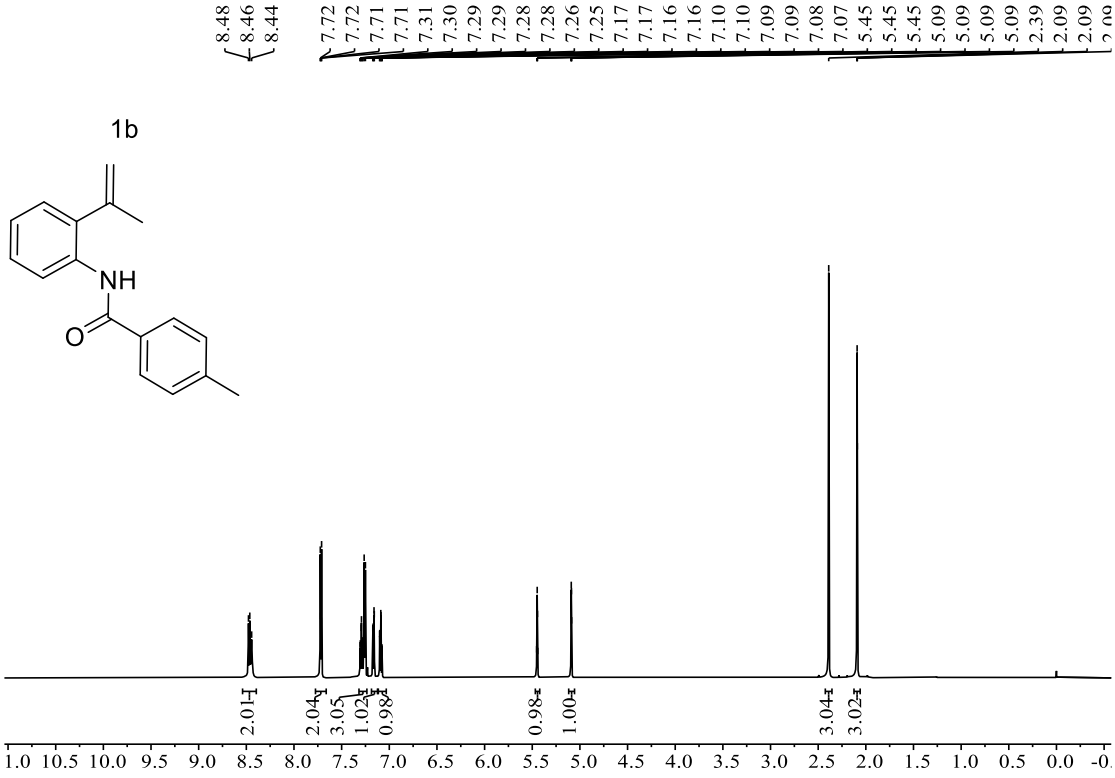
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1a**



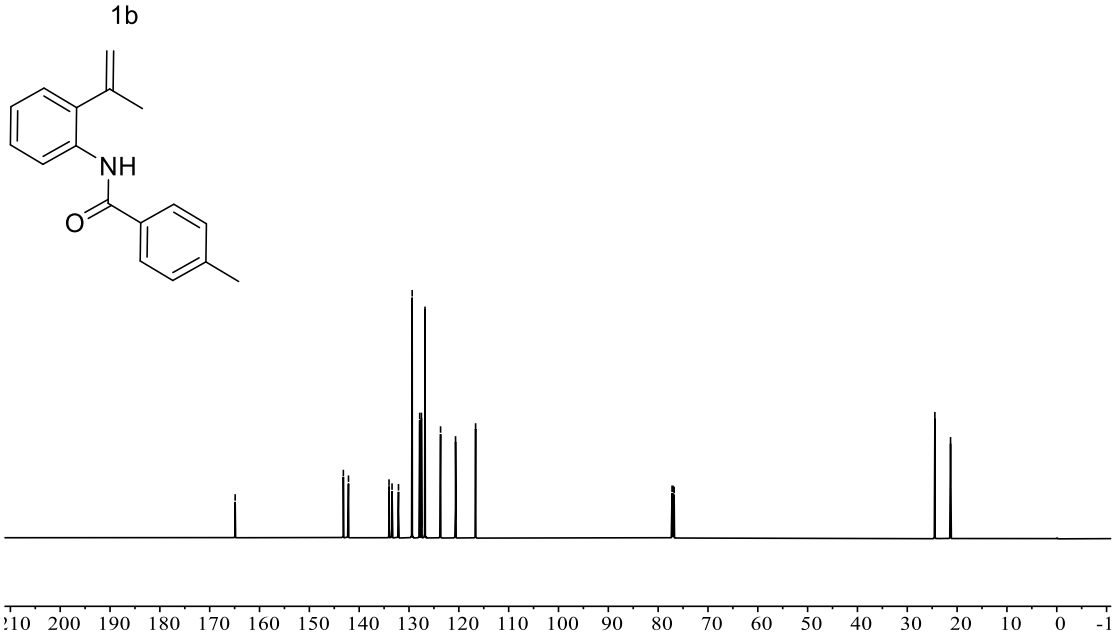
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1a**



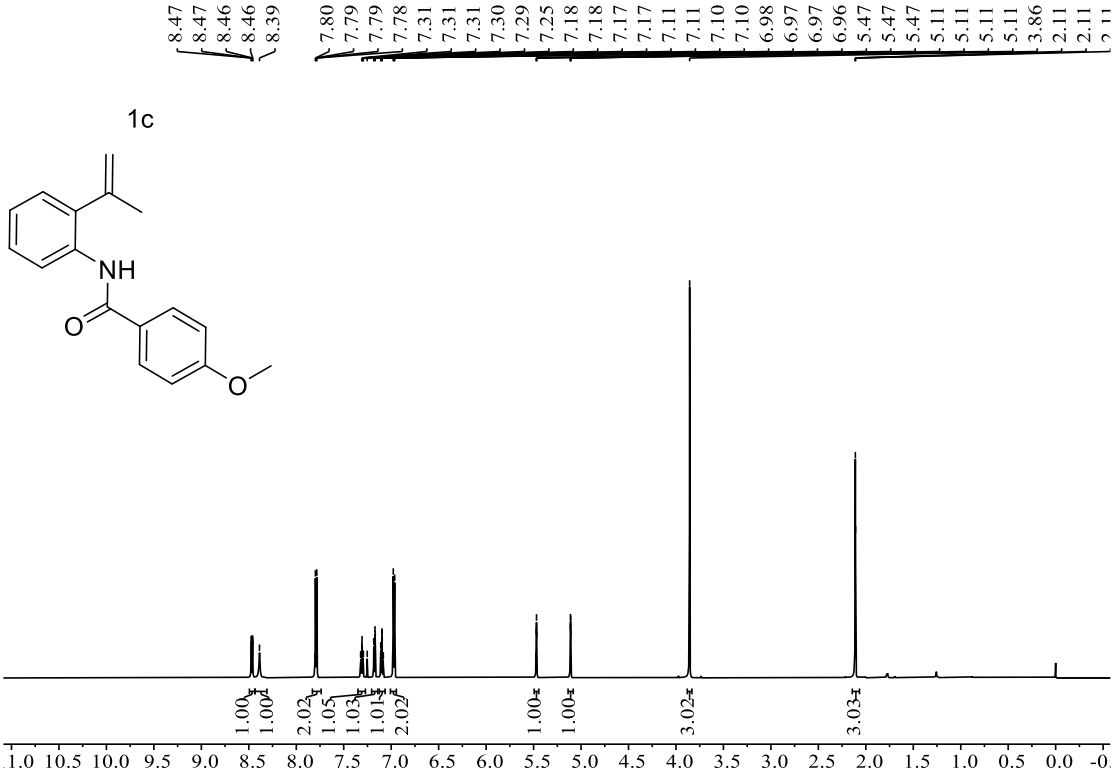
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1b**



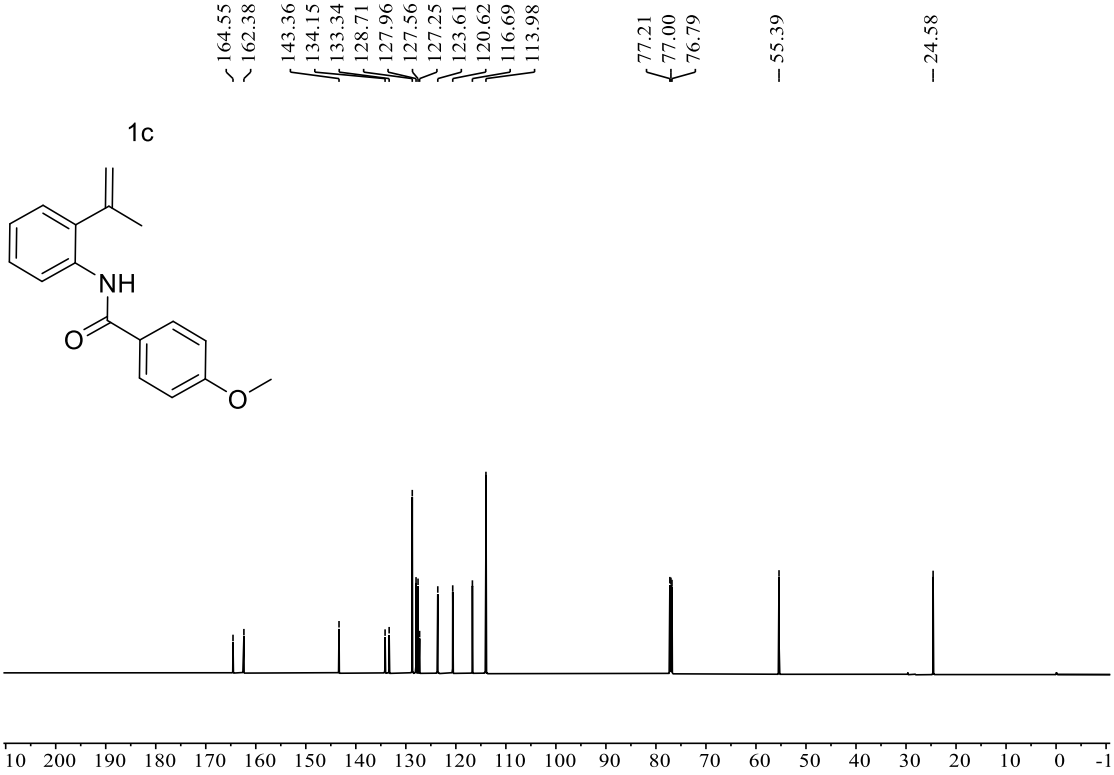
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1b**



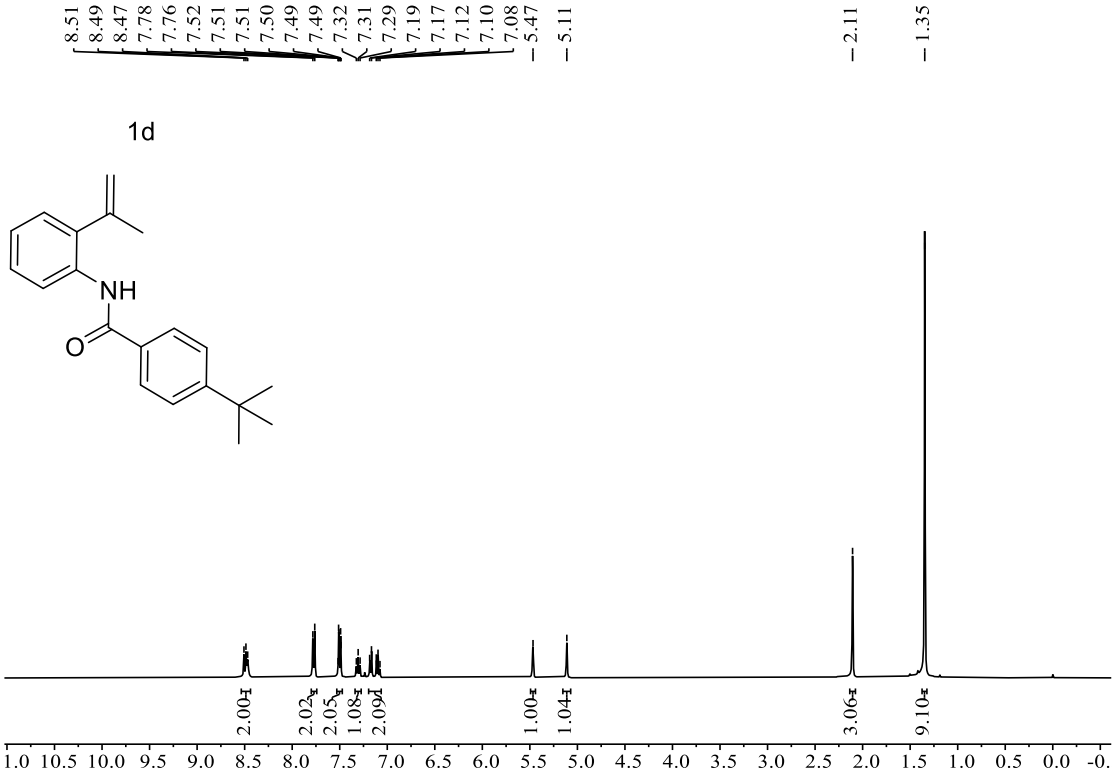
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1c**



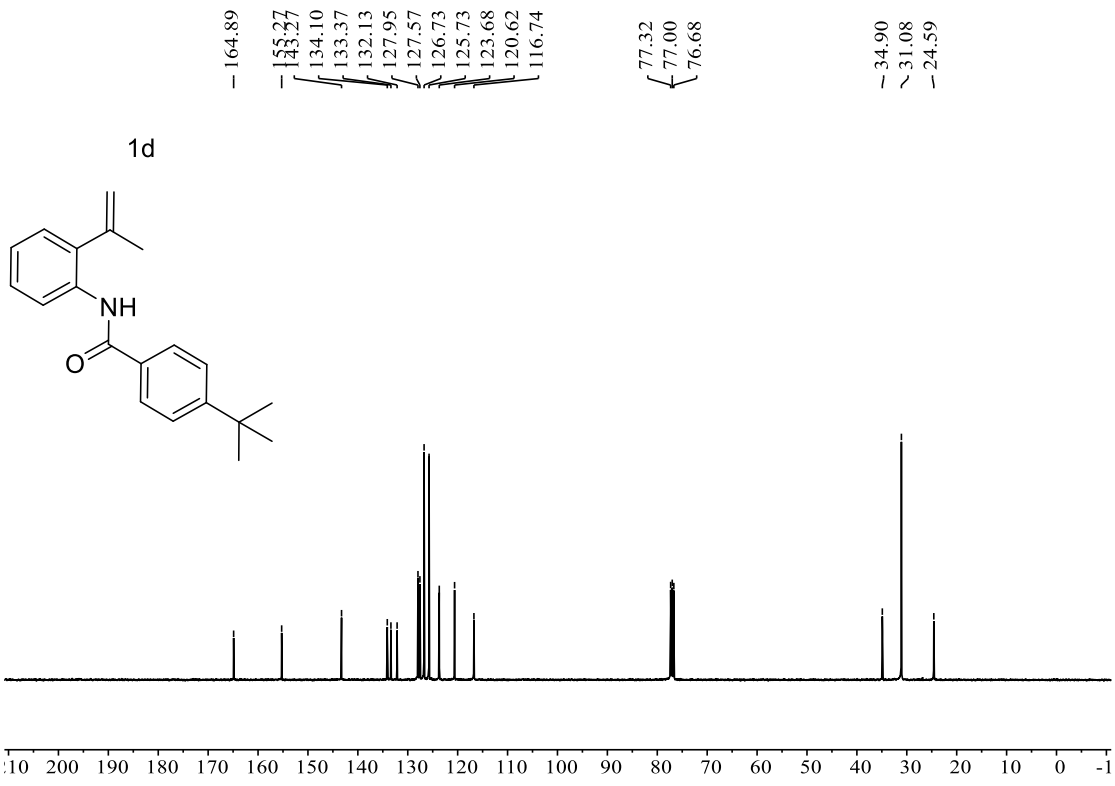
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1c**



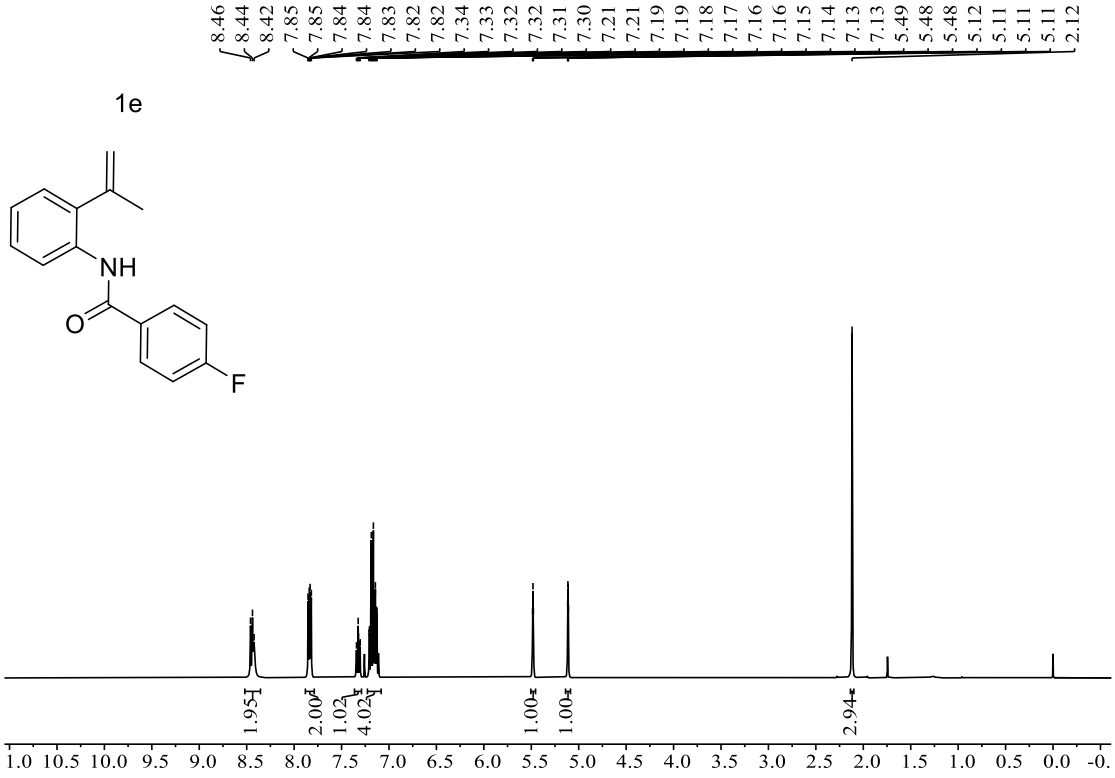
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1d**



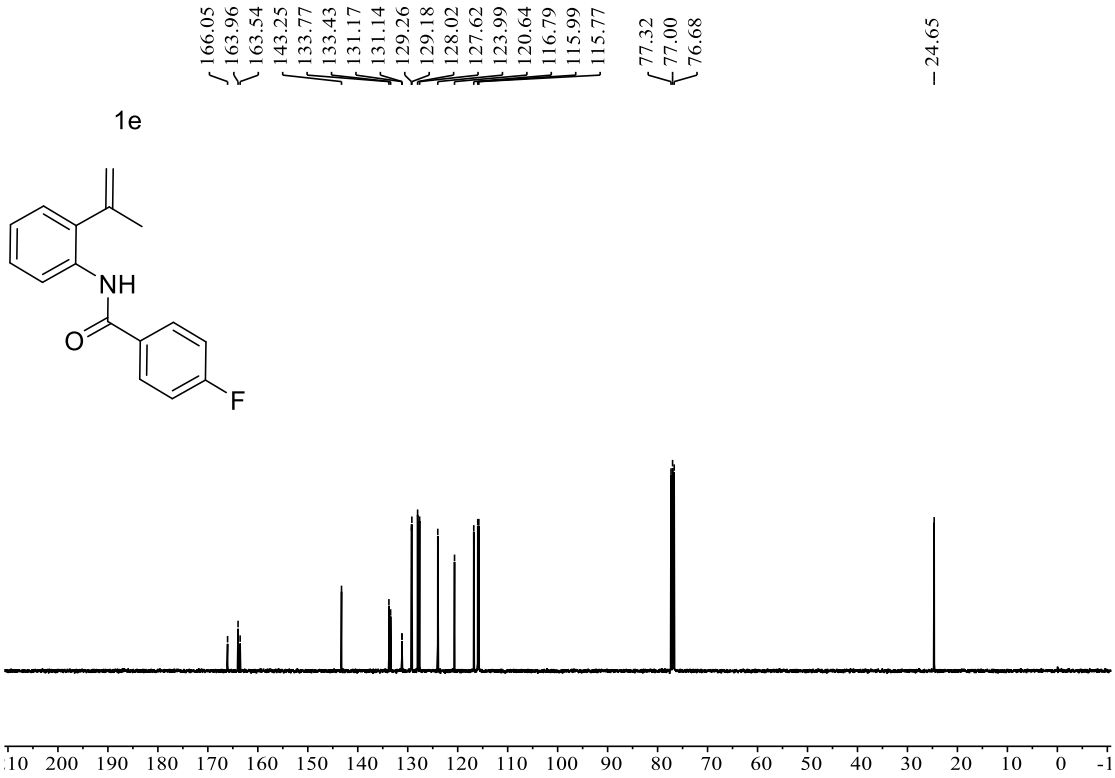
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1d**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1e**



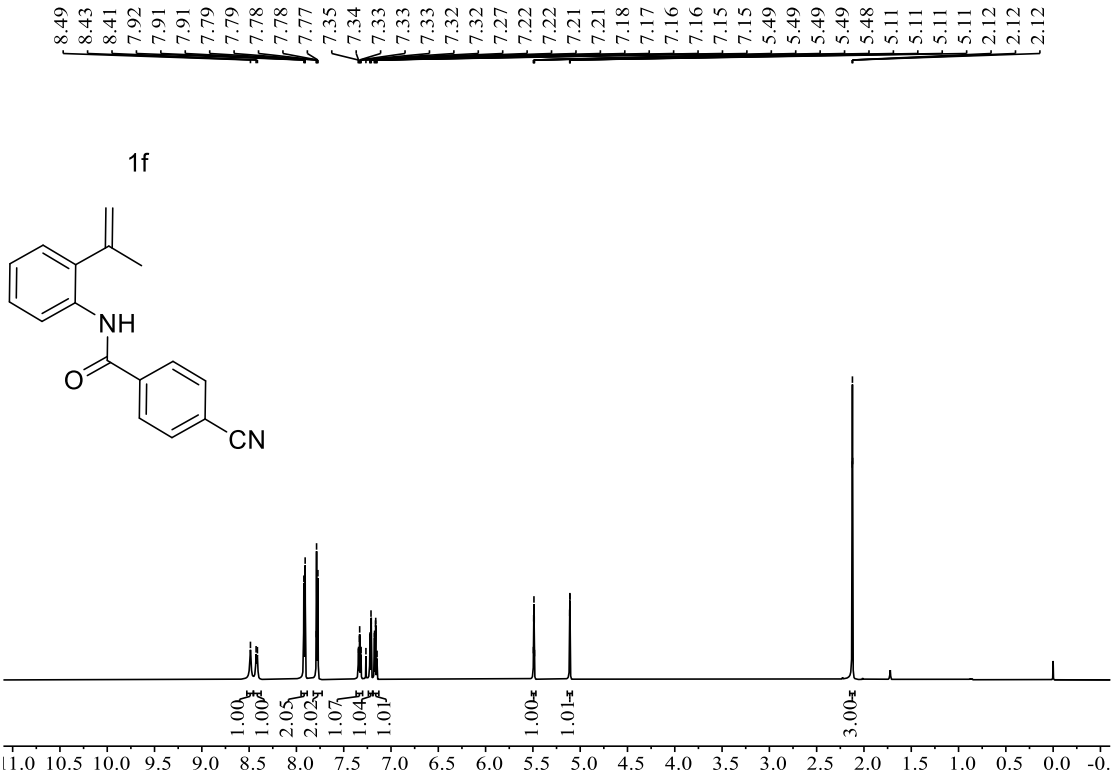
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1e**



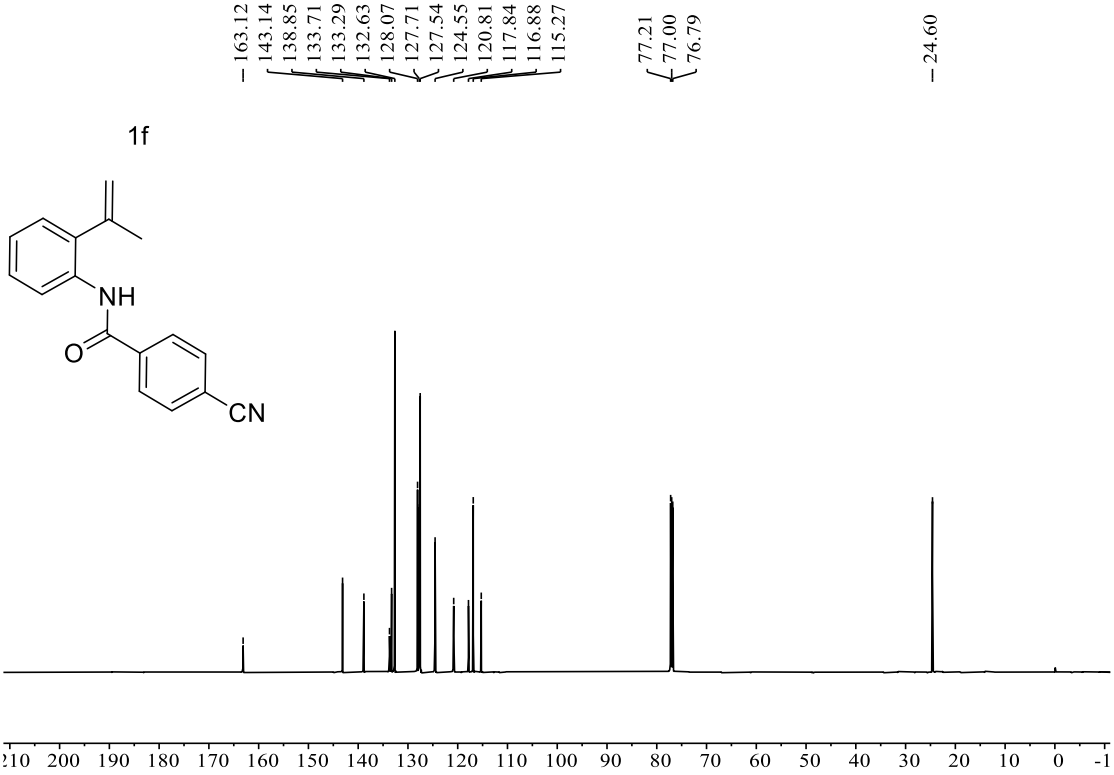
^{19}F NMR (377 MHz, $CDCl_3$) of compound **1e**


1e
-107.46
NH
O
F
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180

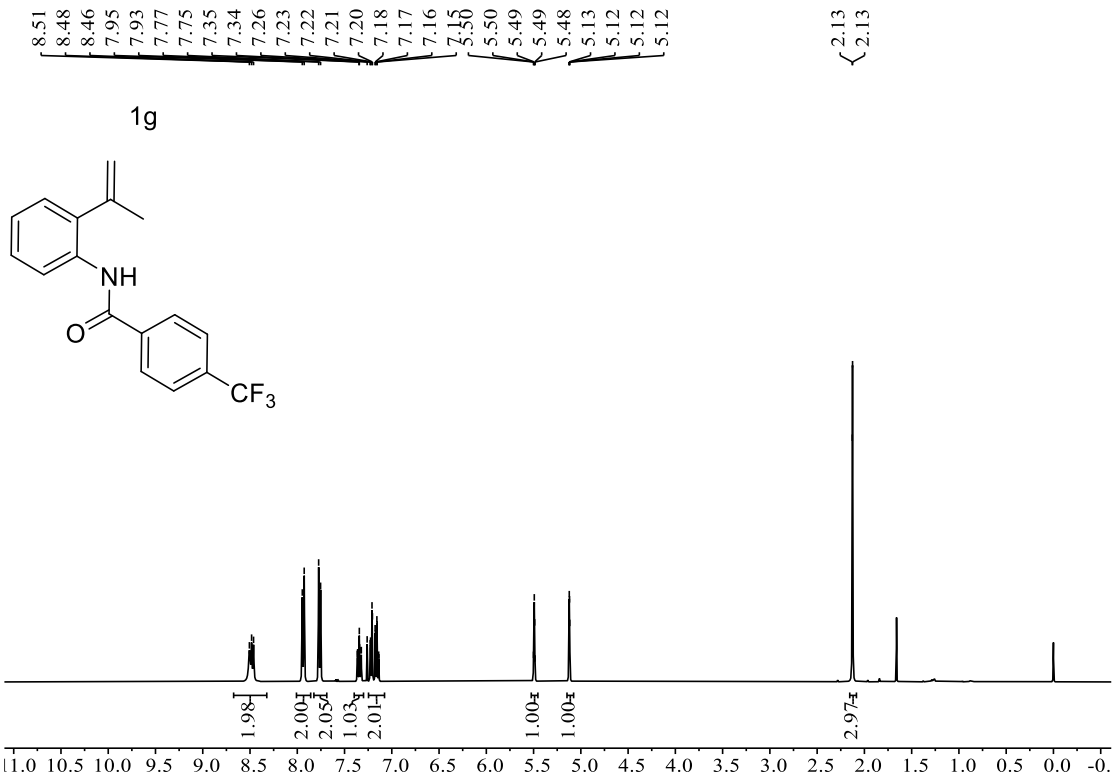
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1f**



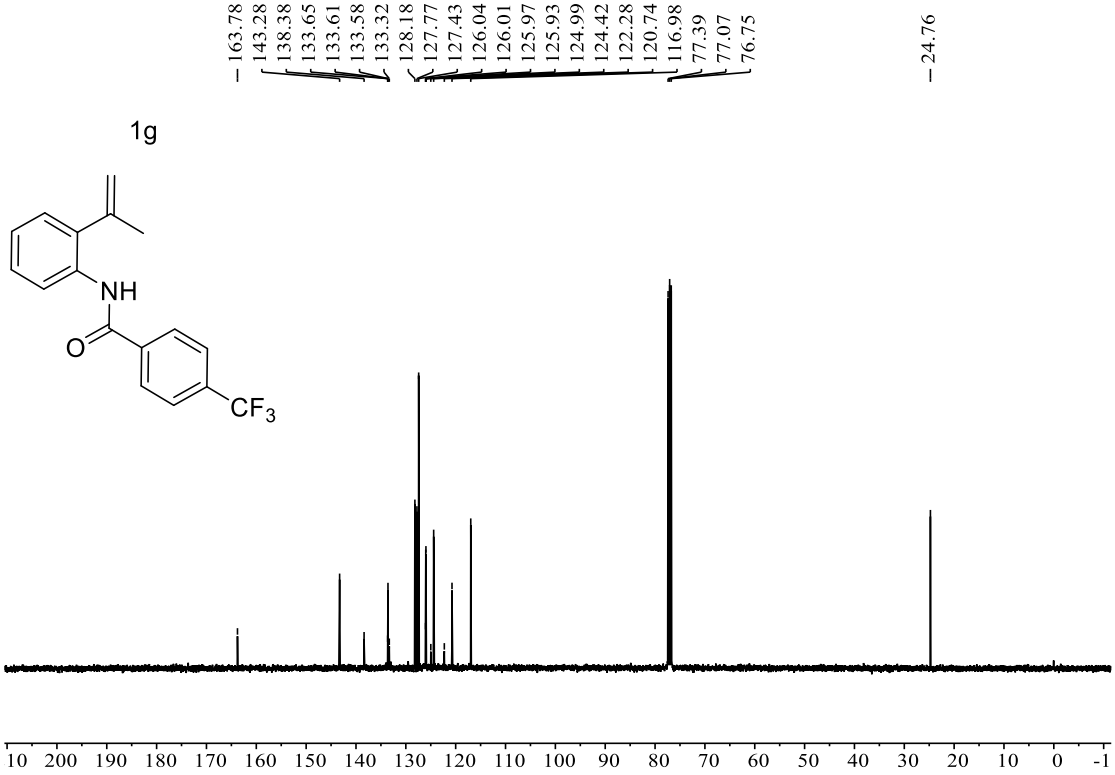
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1f**



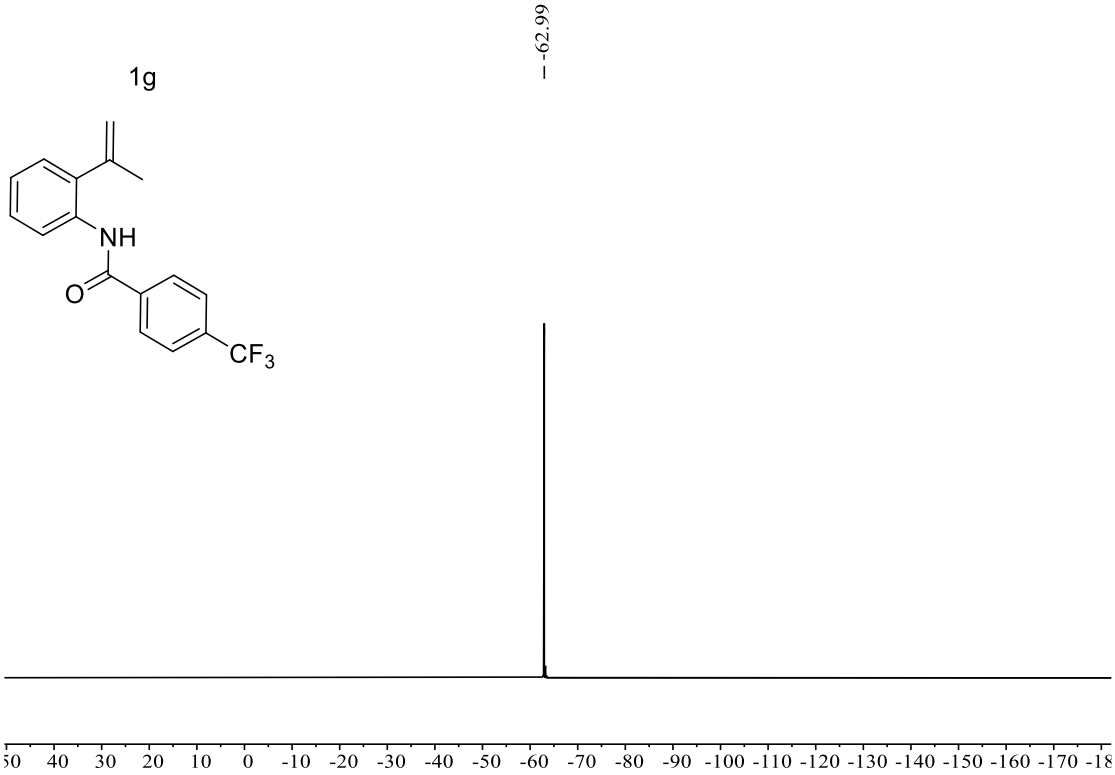
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1g**



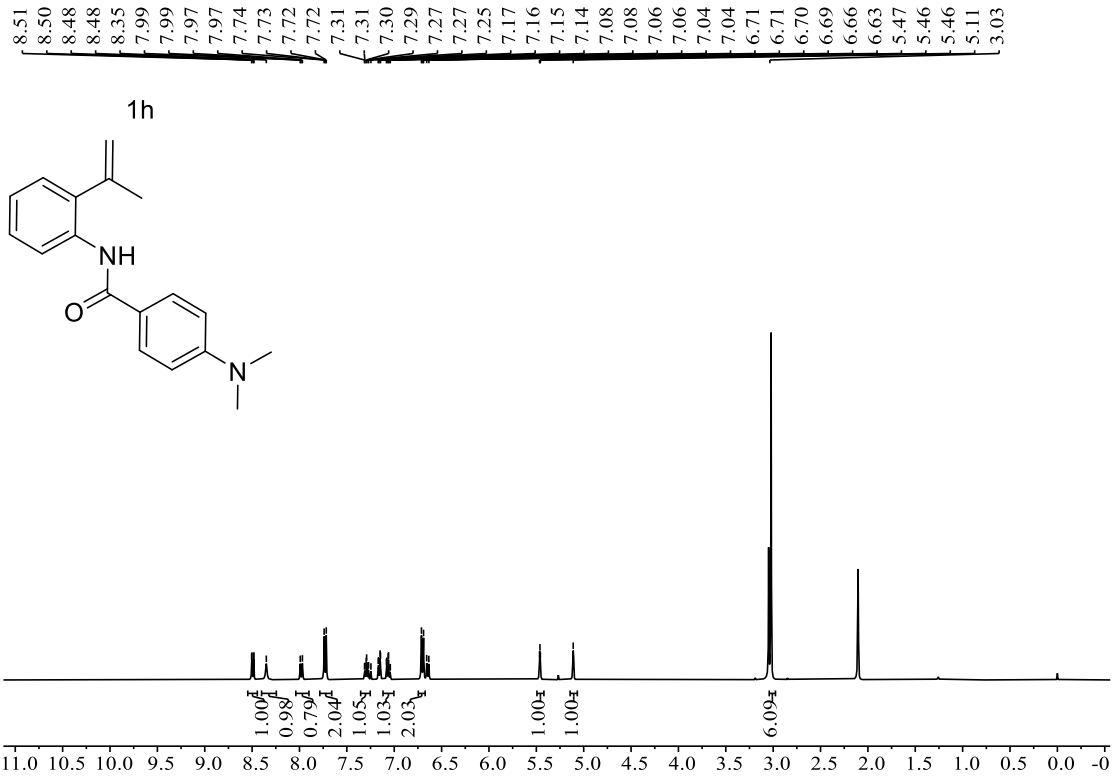
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1g**



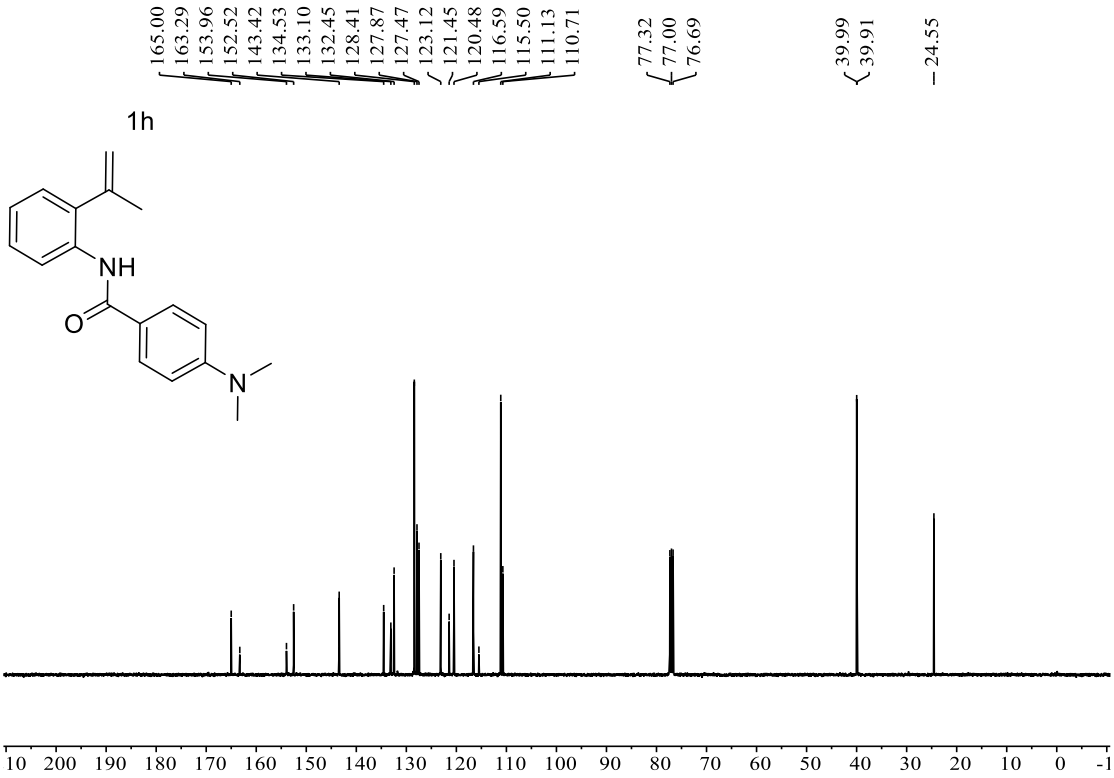
^{19}F NMR (377 MHz, $CDCl_3$) of compound **1g**



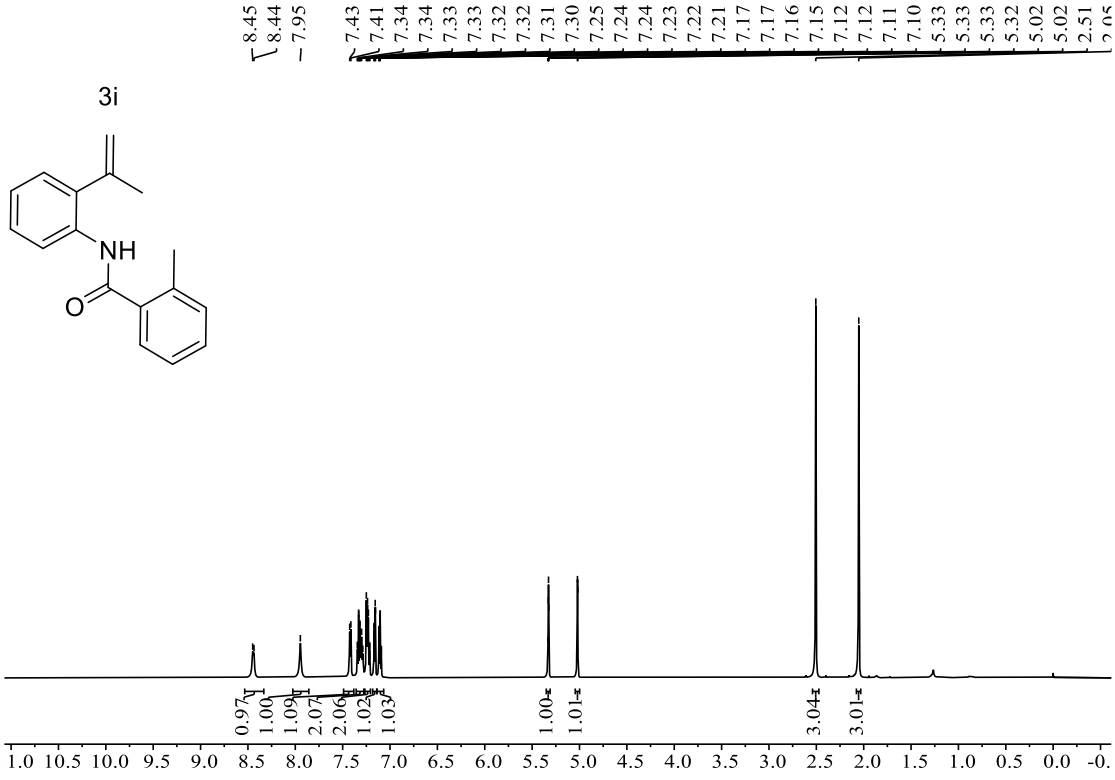
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1h**



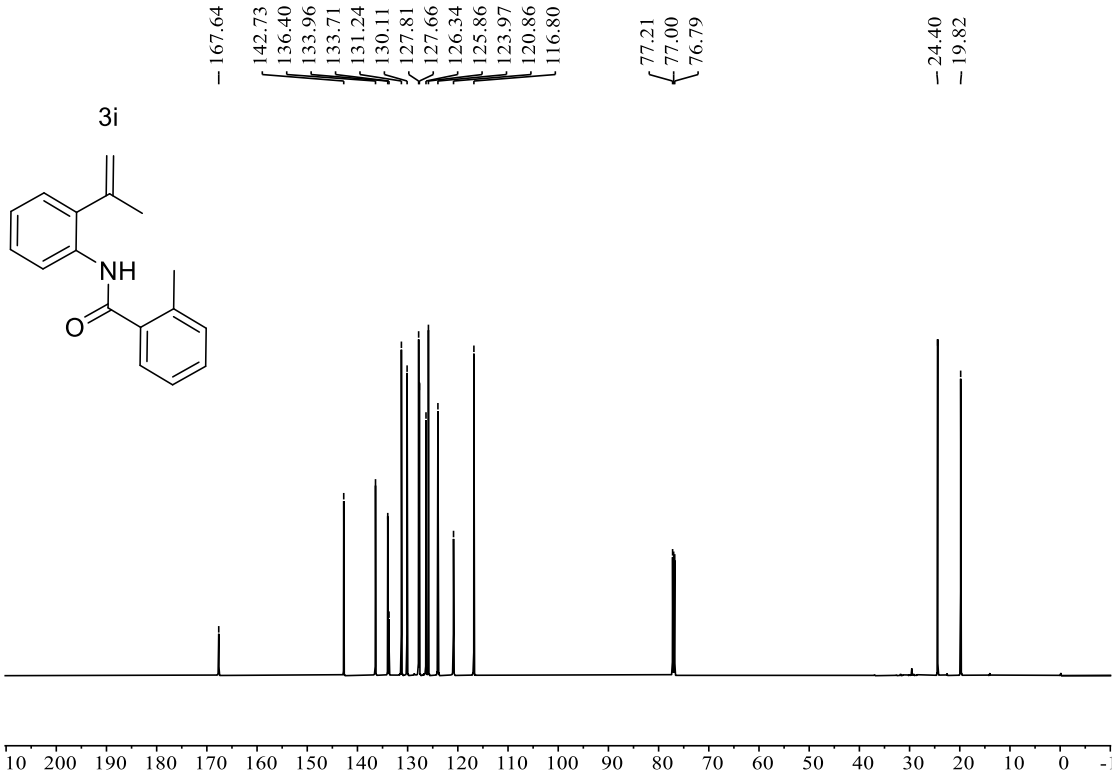
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1h**



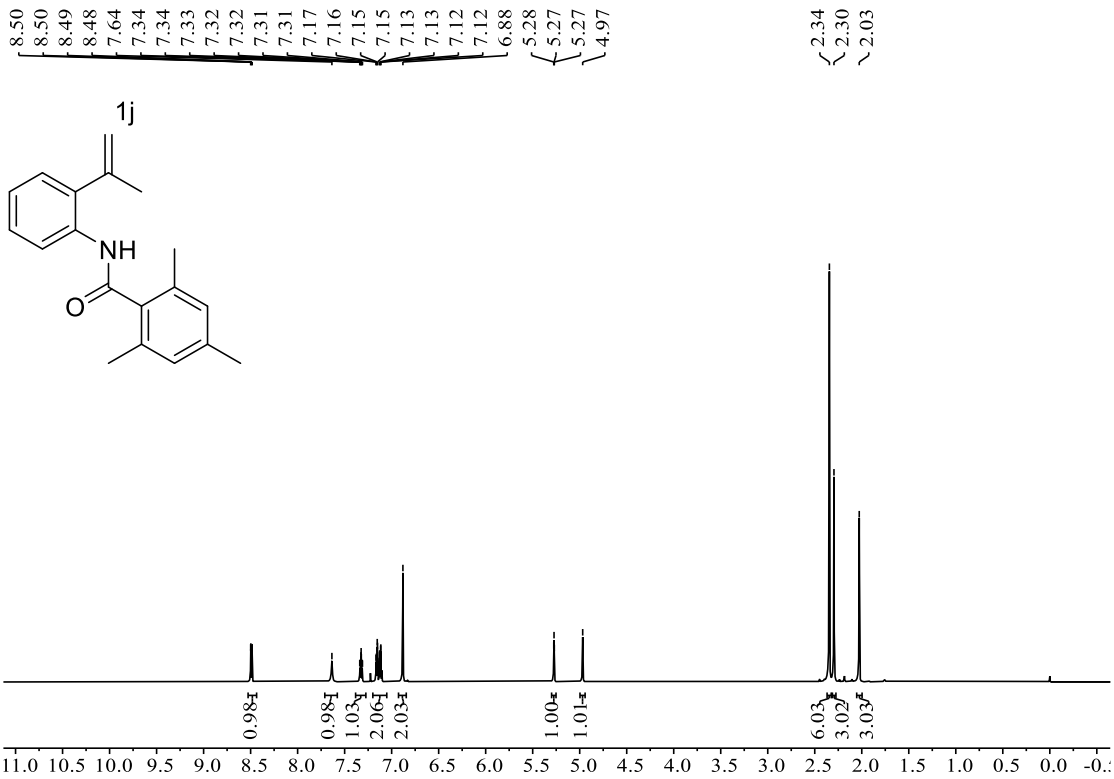
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1i**



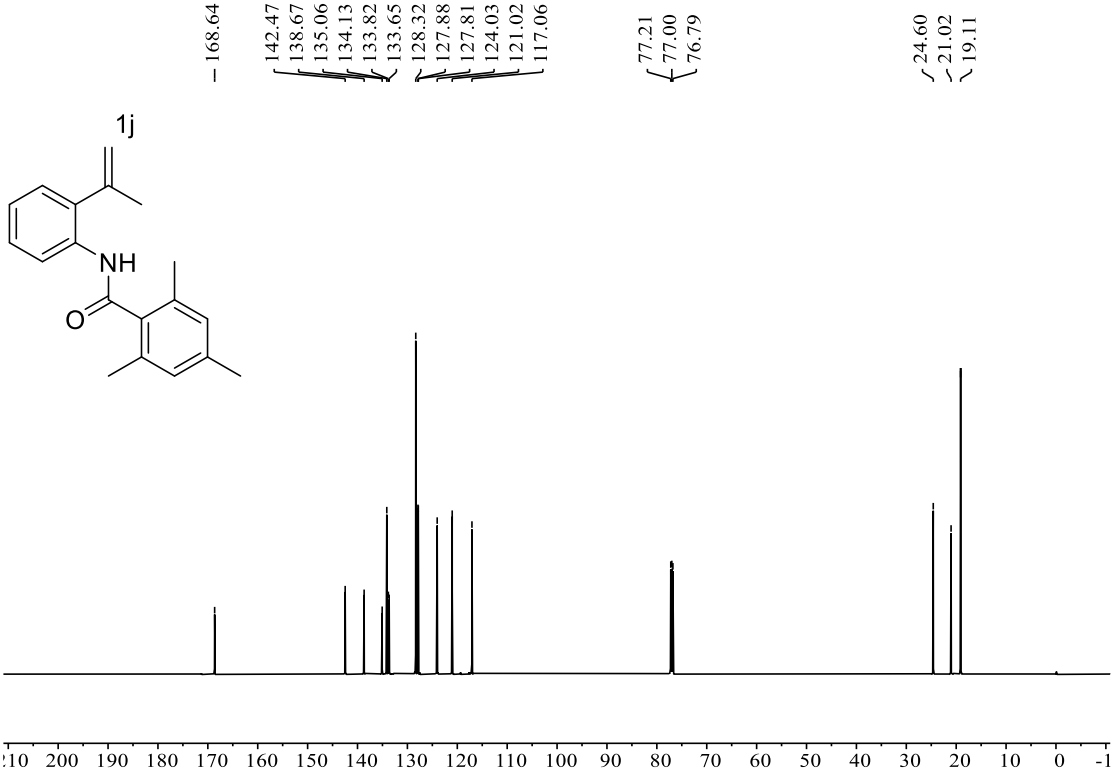
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1i**



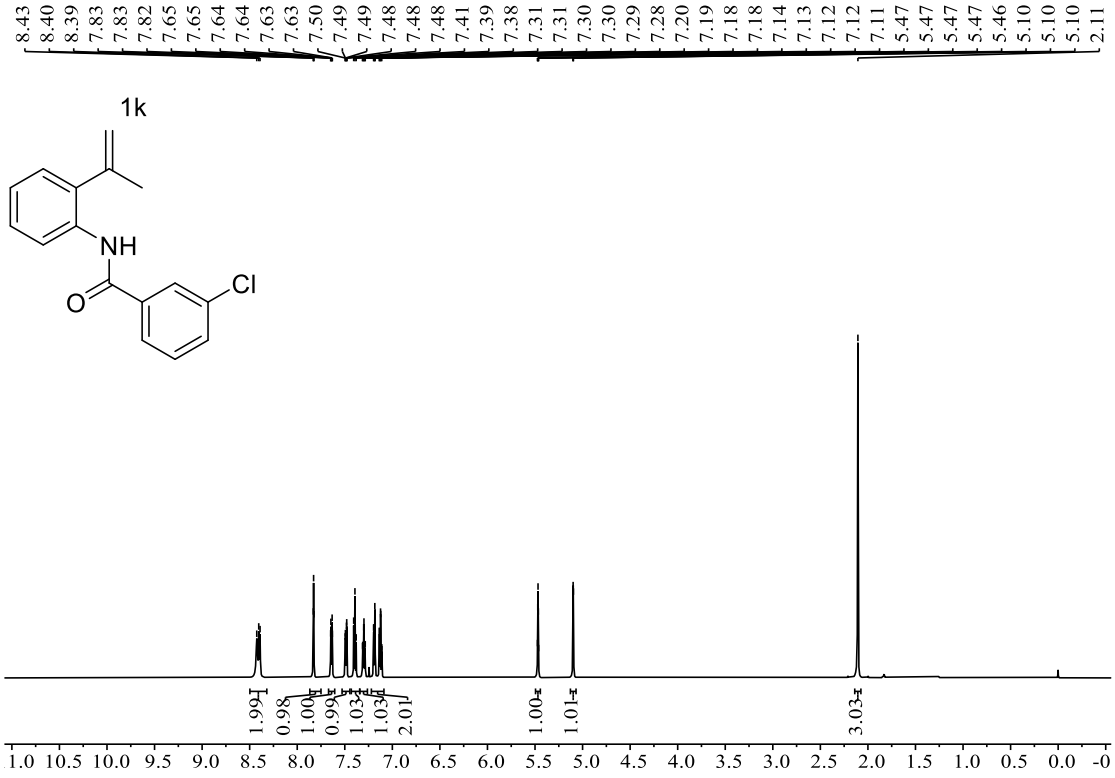
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1j**



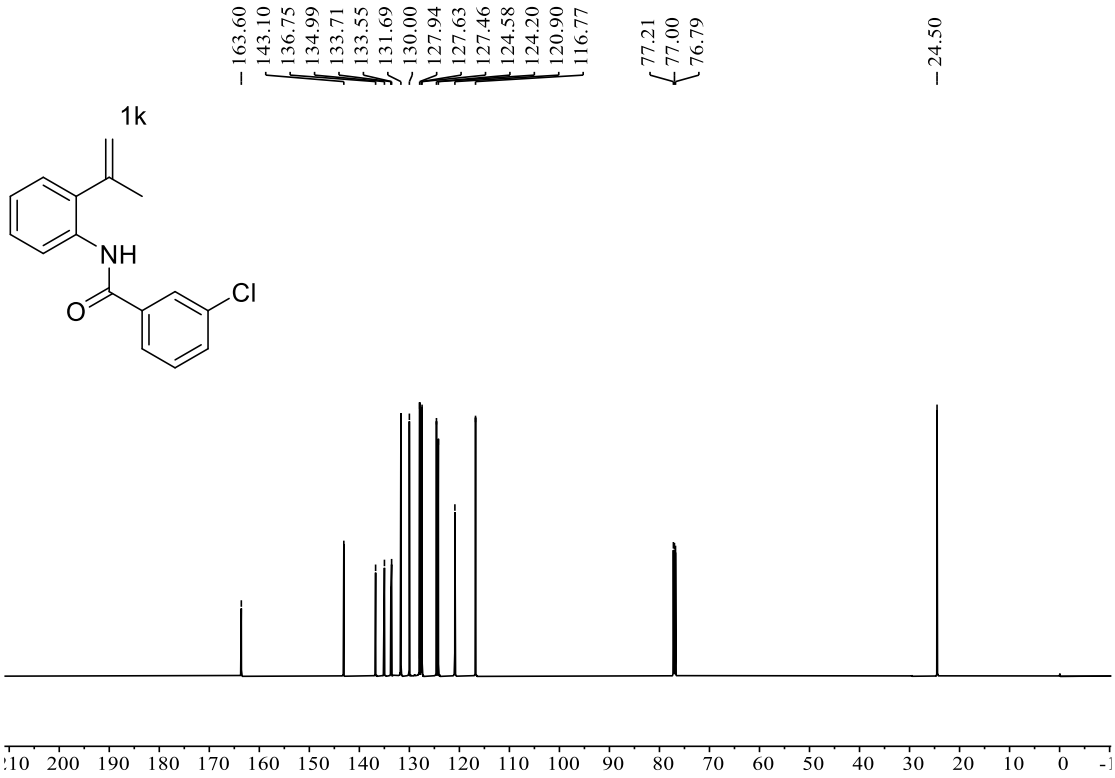
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1j**



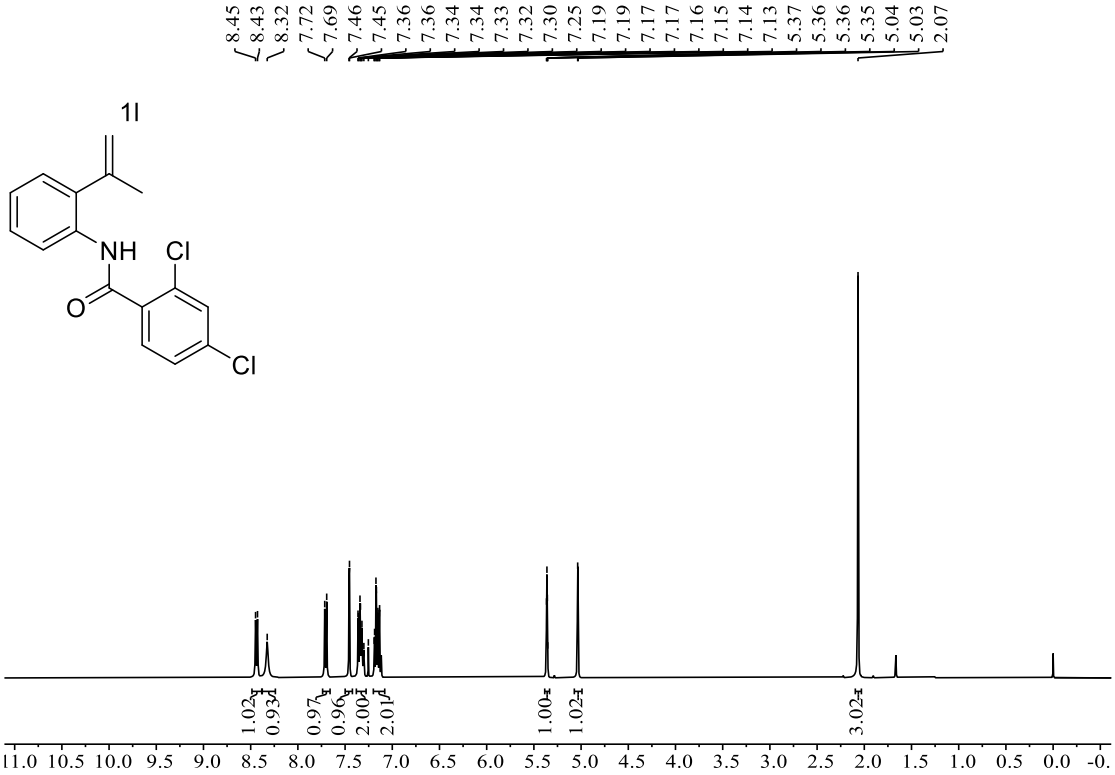
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1k**



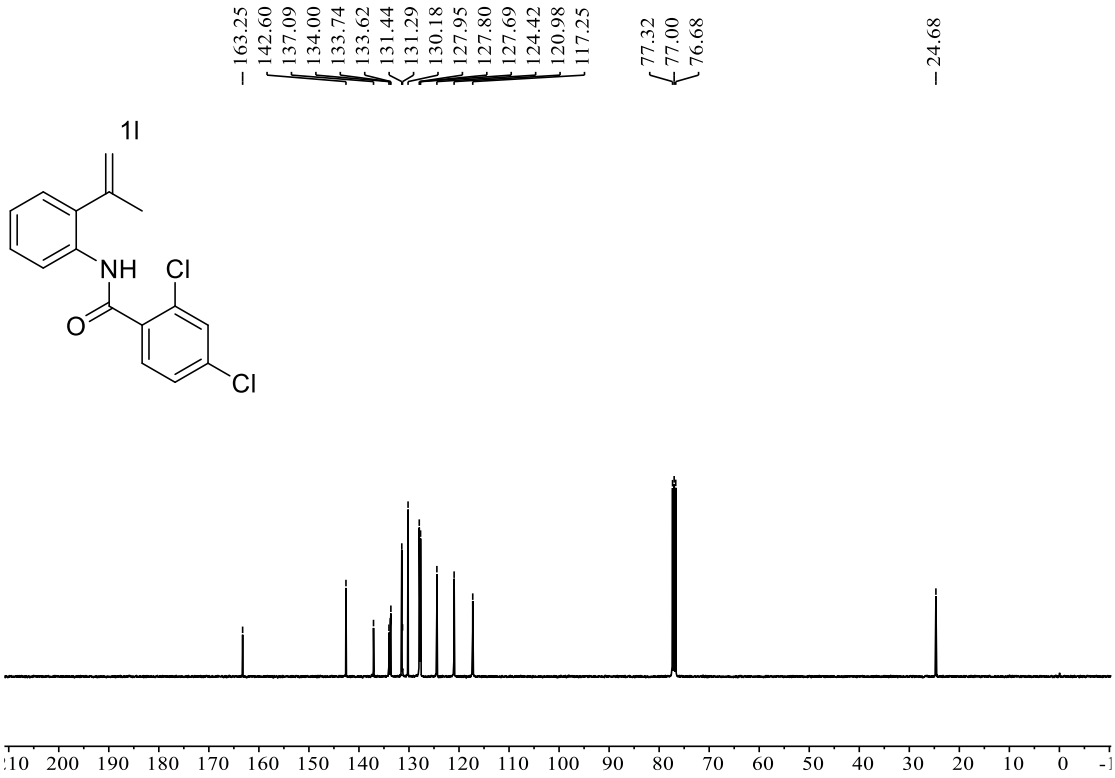
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1k**



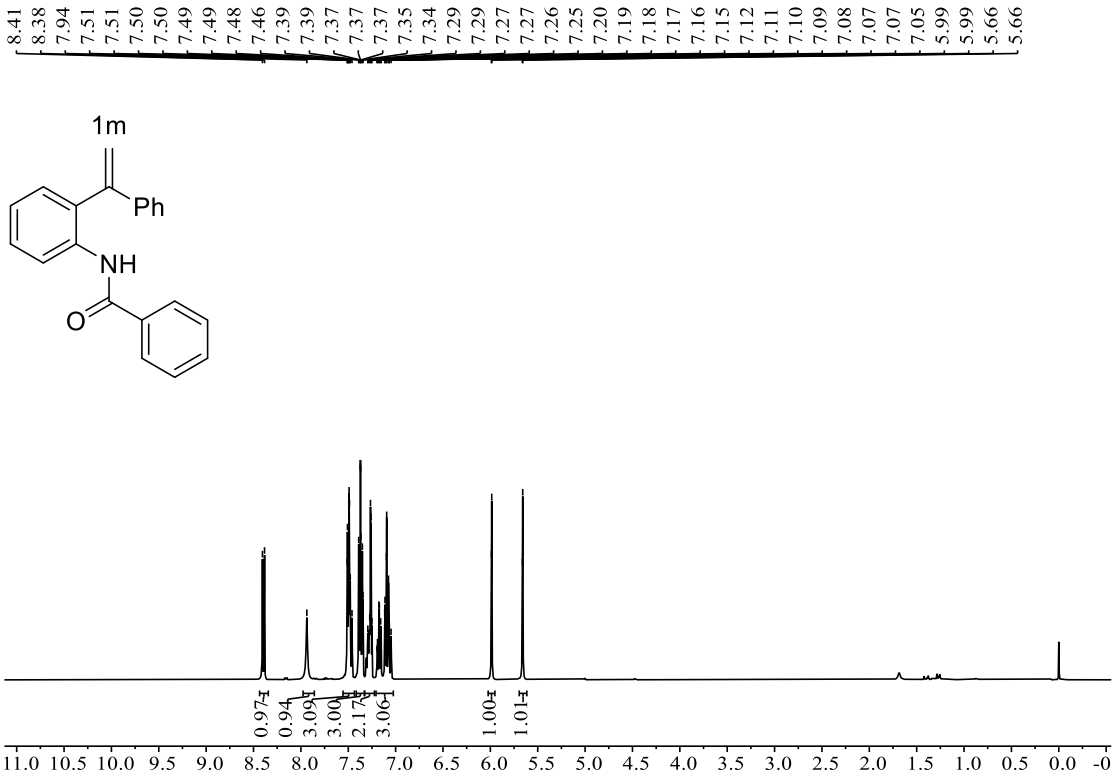
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1l**



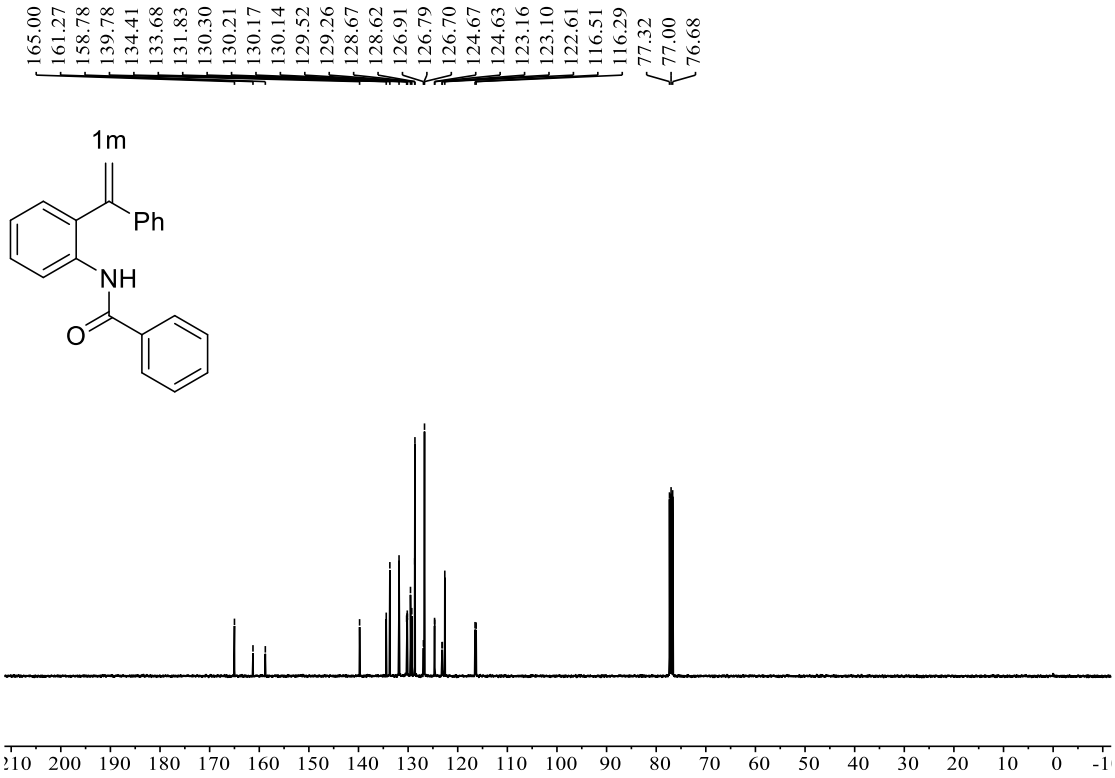
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1l**



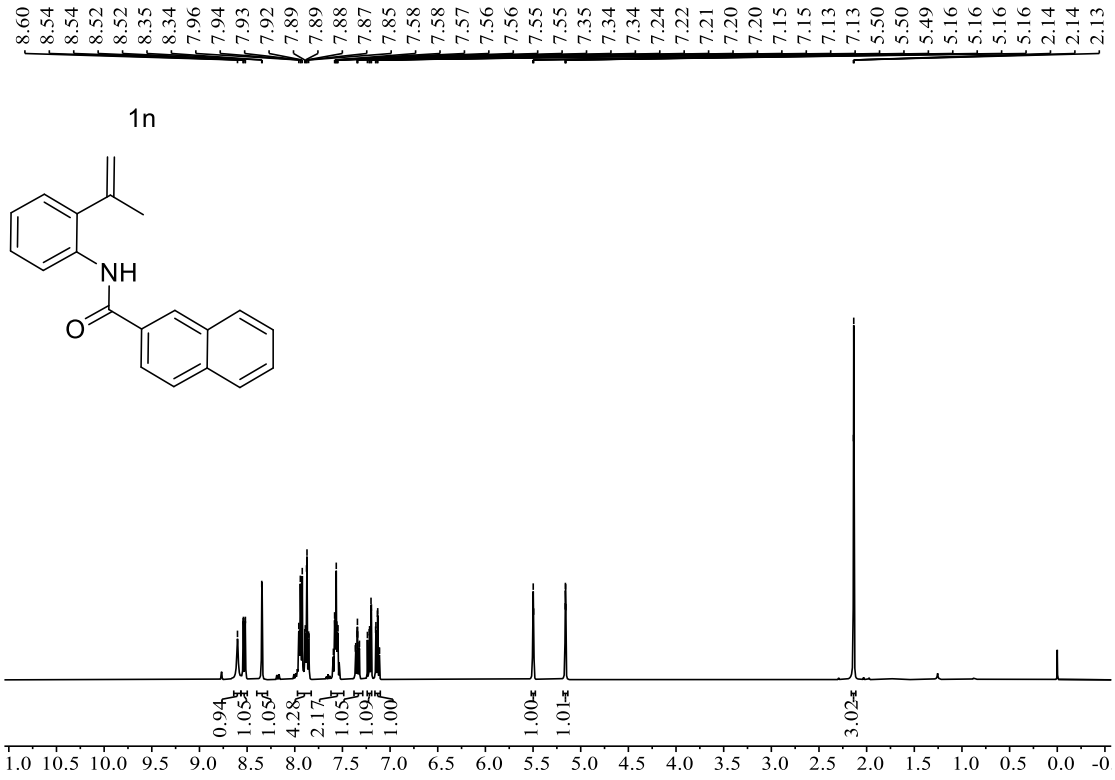
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1m**



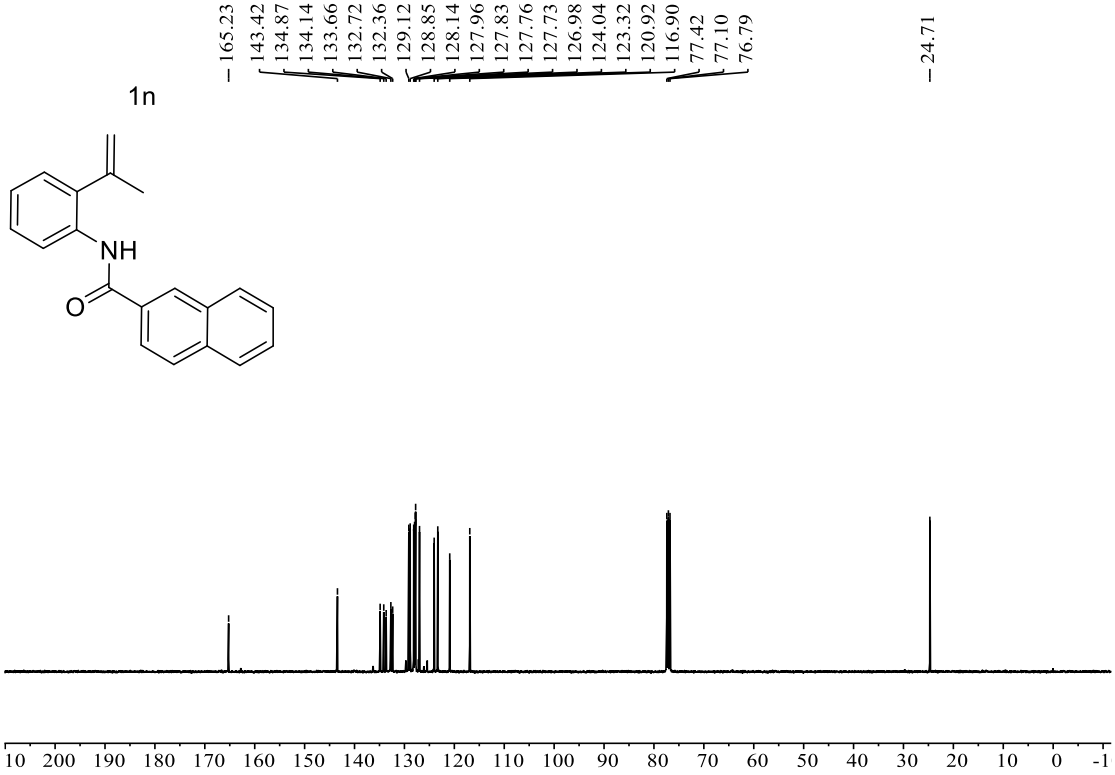
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1m**



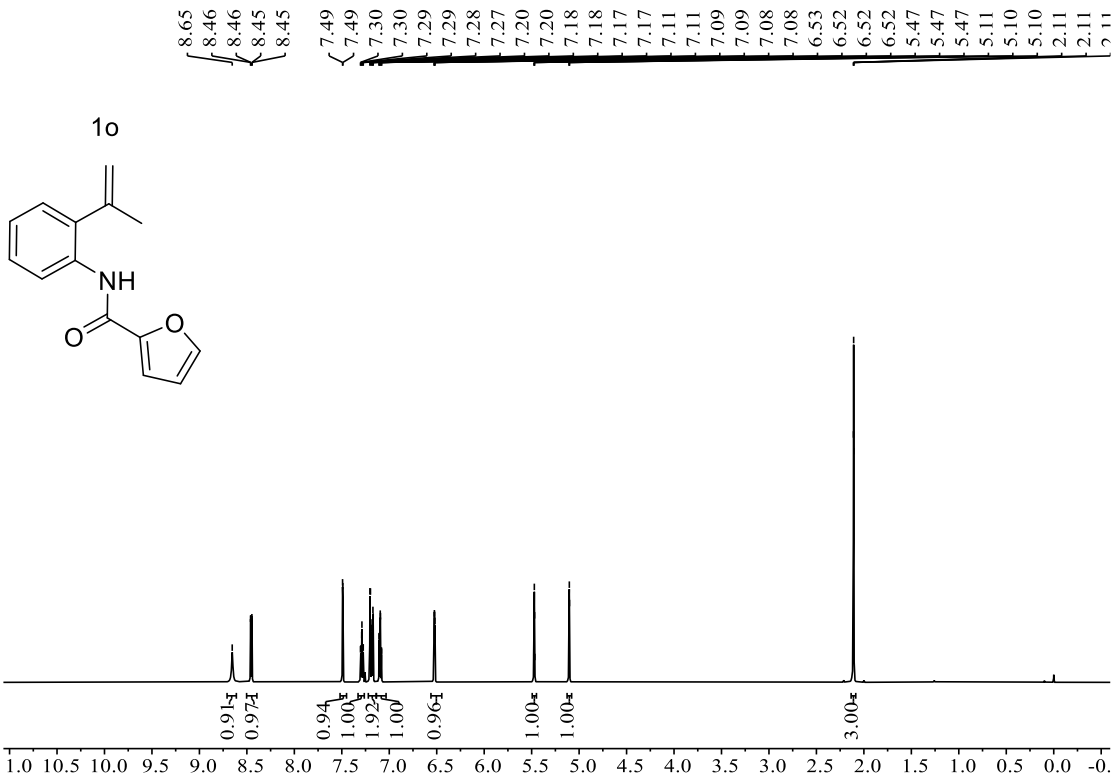
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1n**



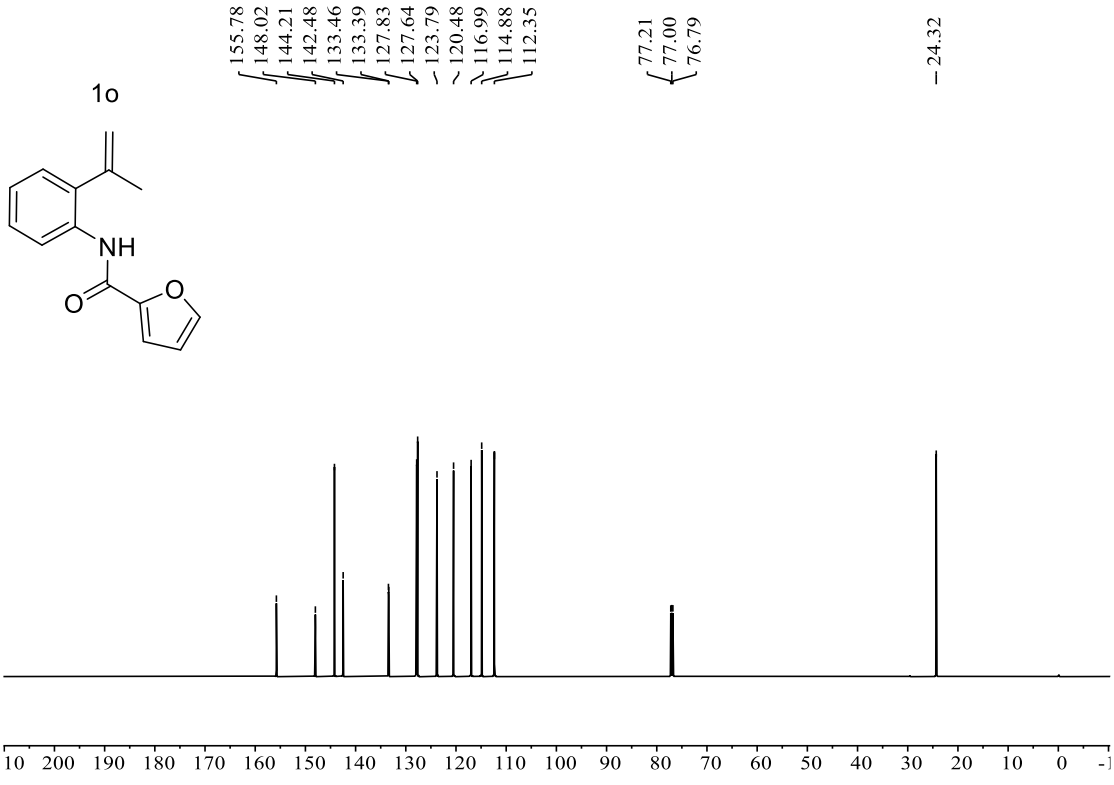
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1n**



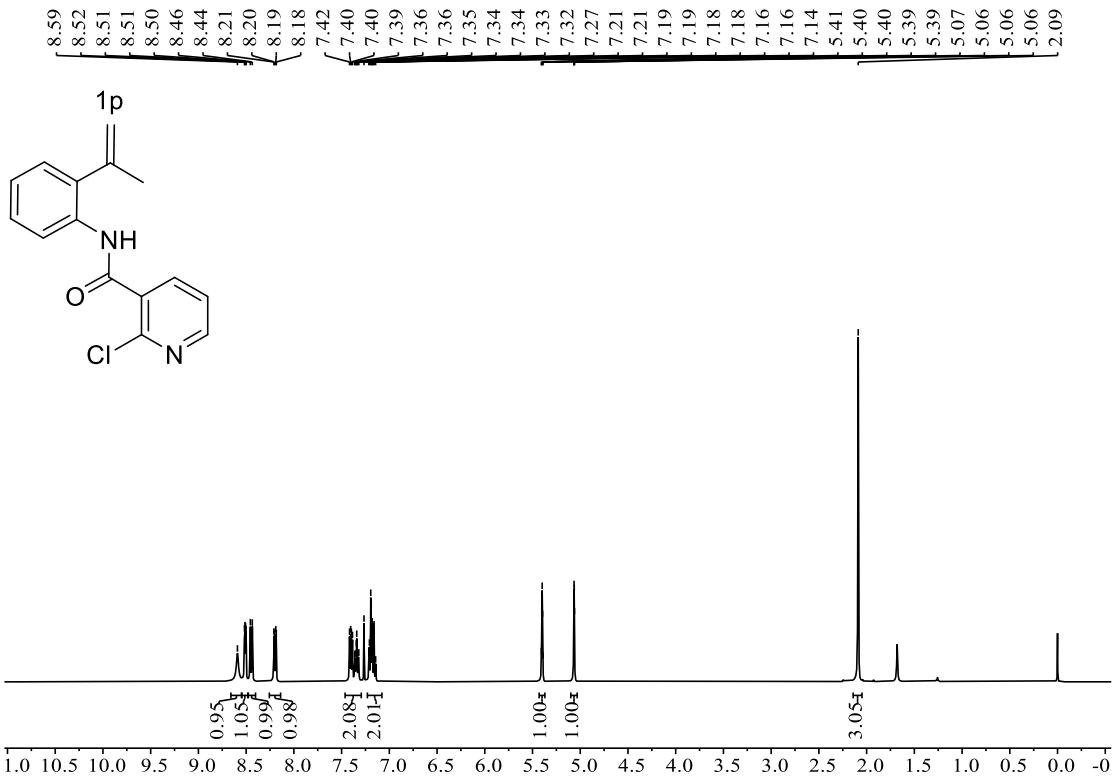
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1o**



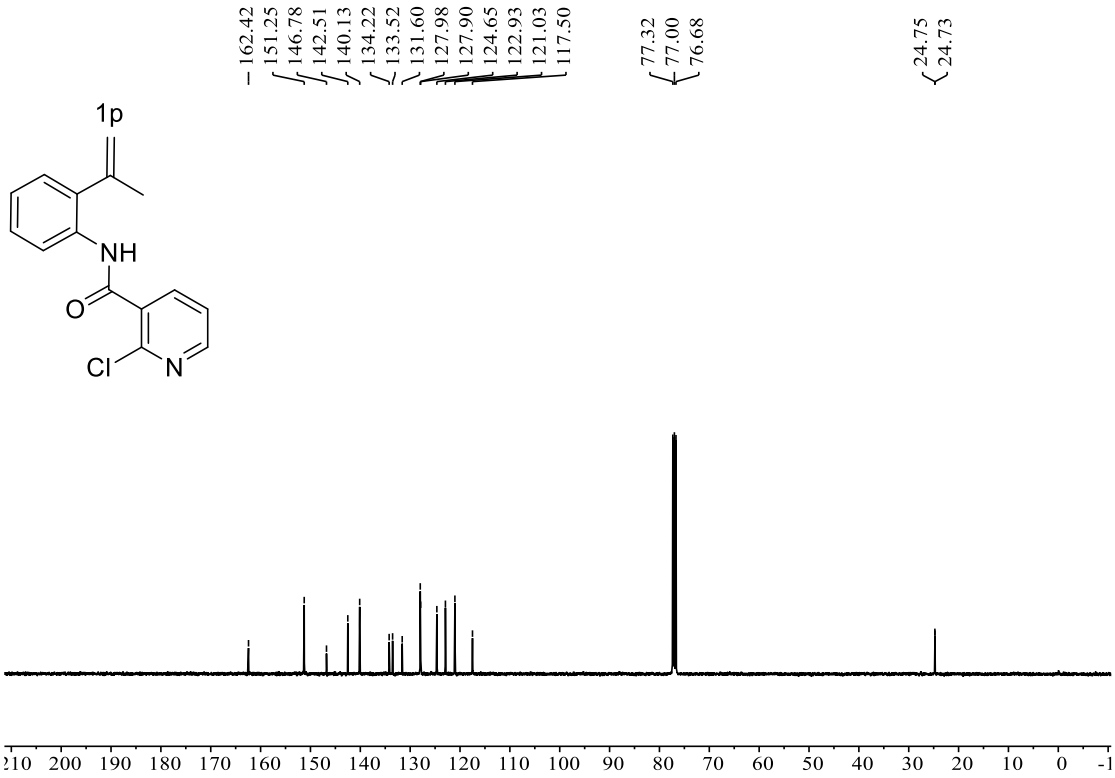
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1o**



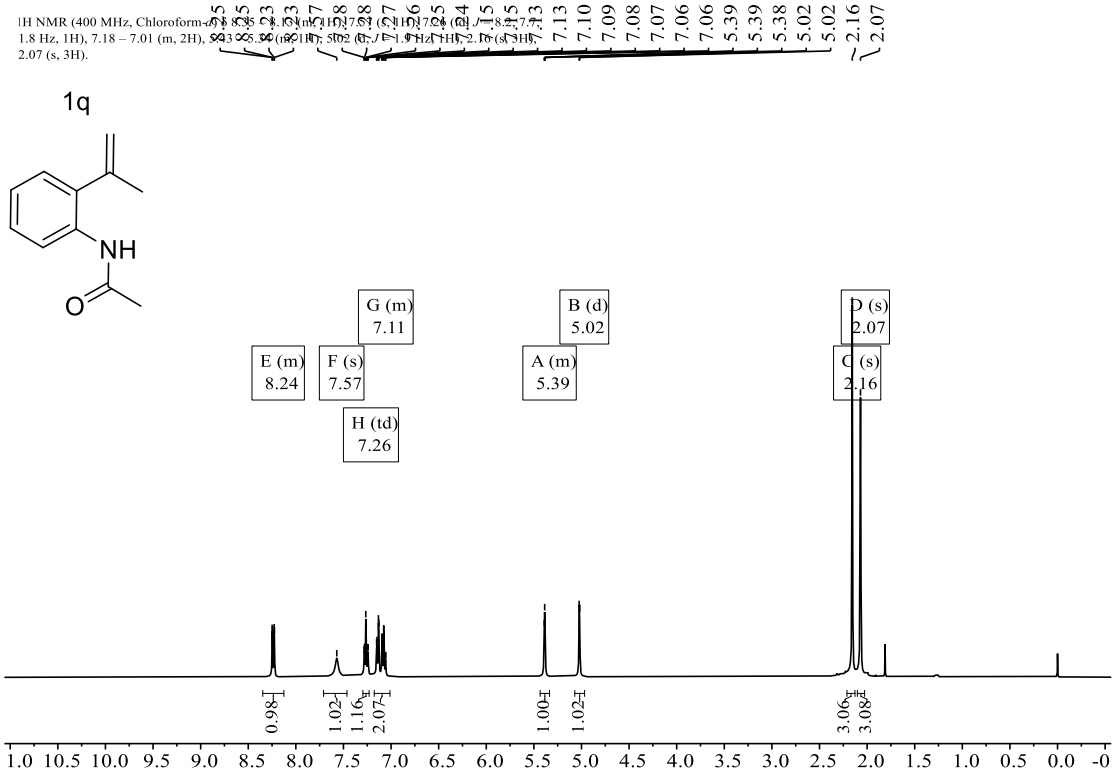
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1p**



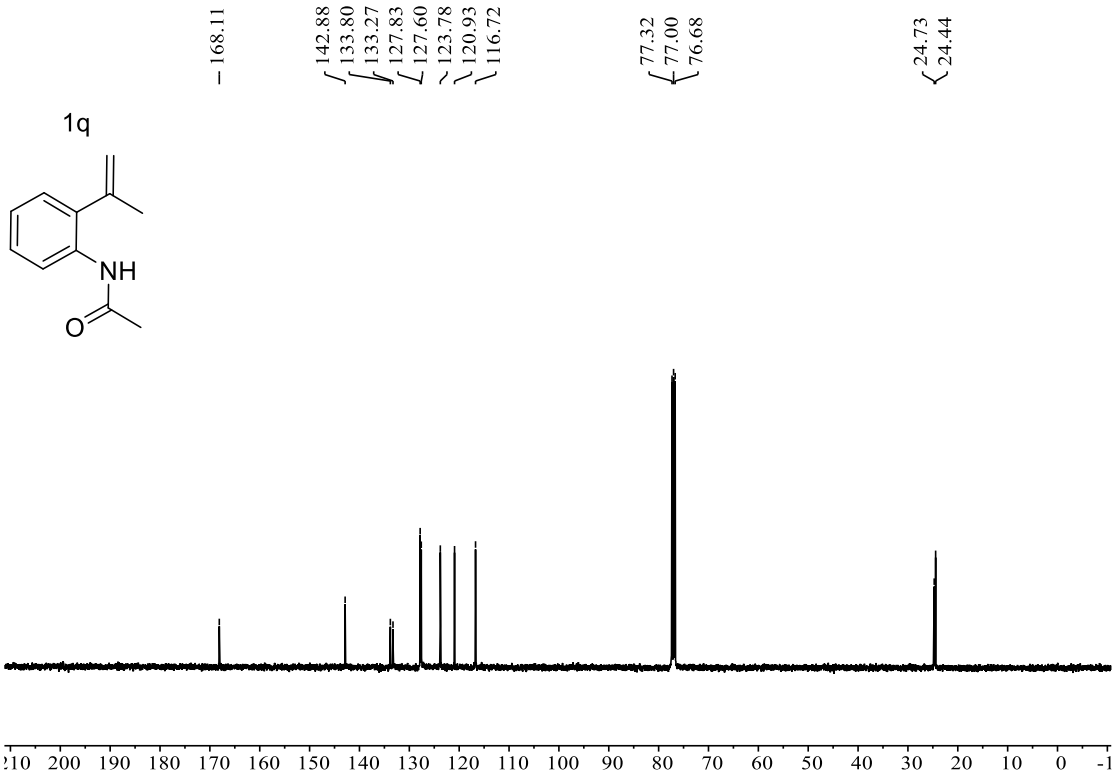
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1p**



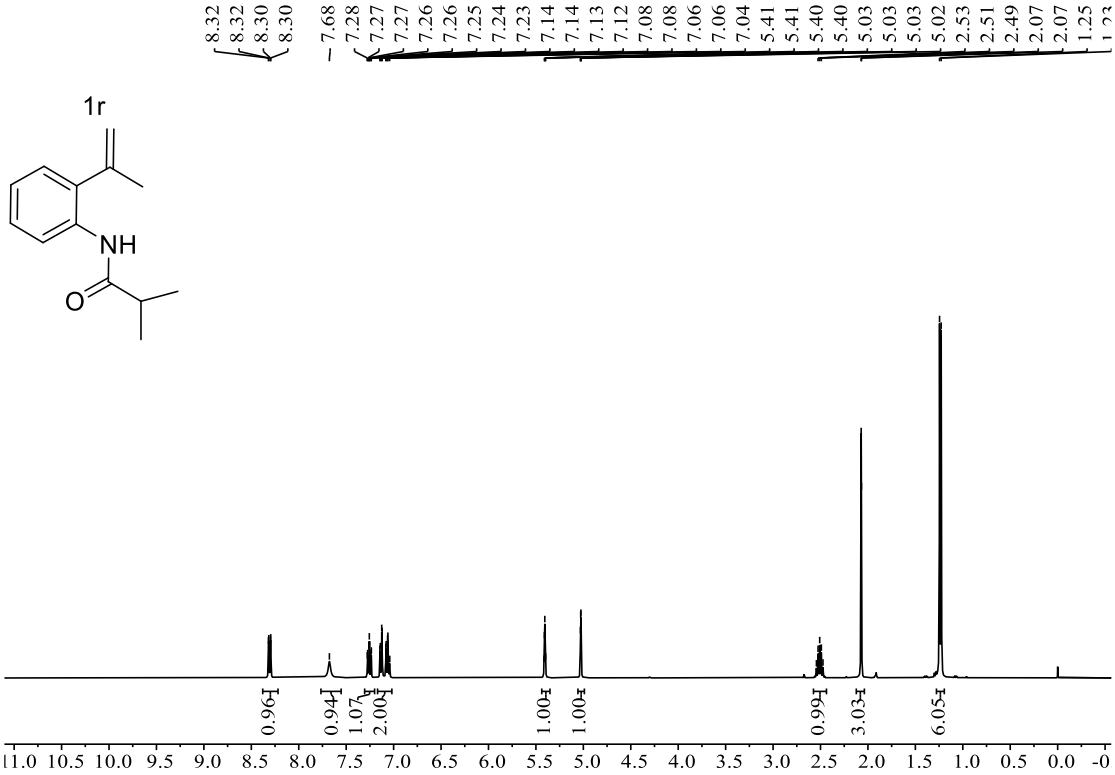
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1q**



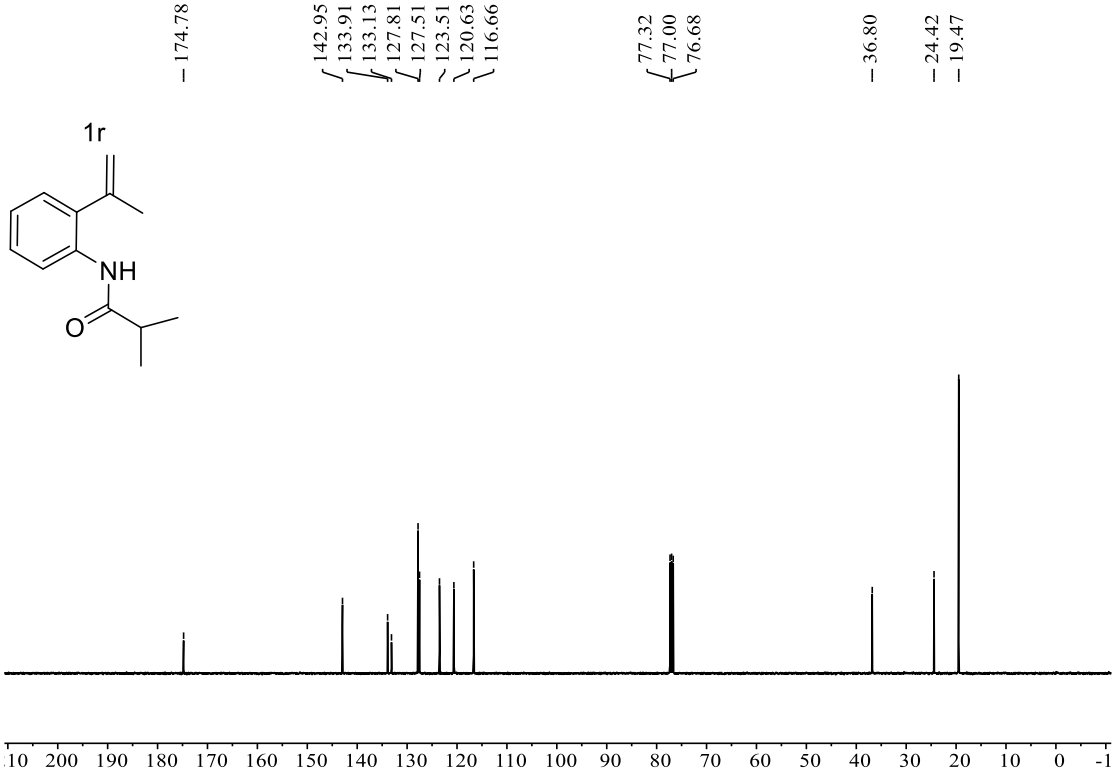
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1q**



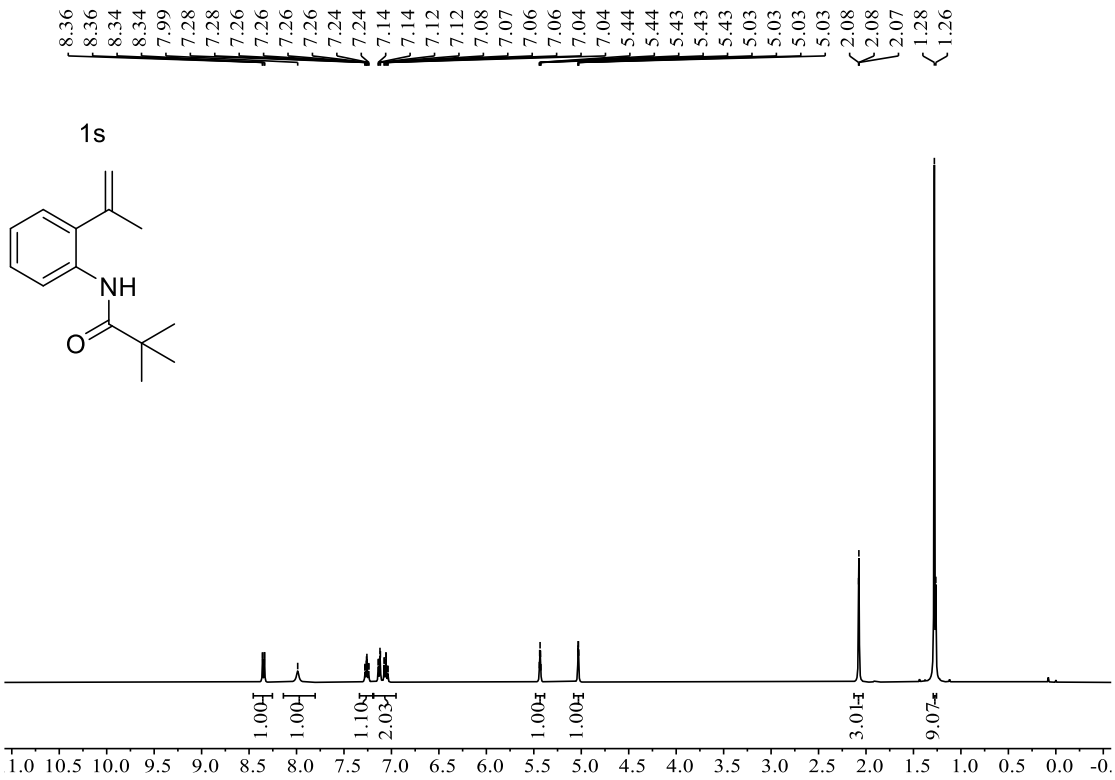
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1r**



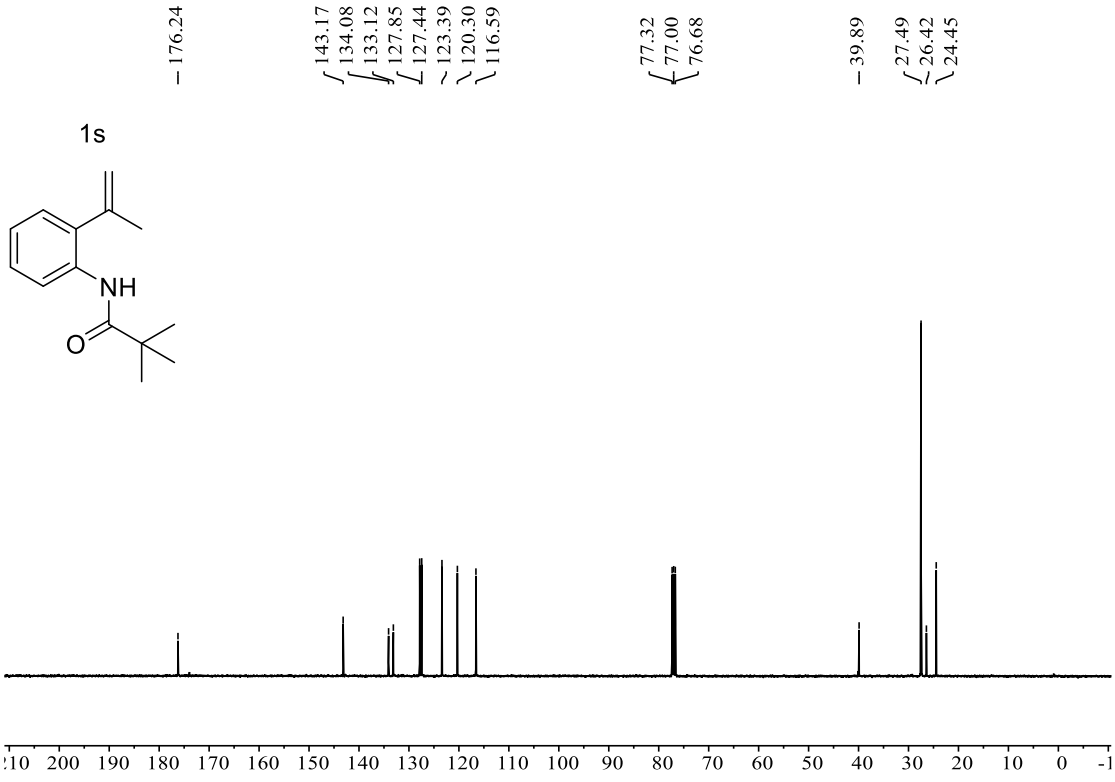
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1r**



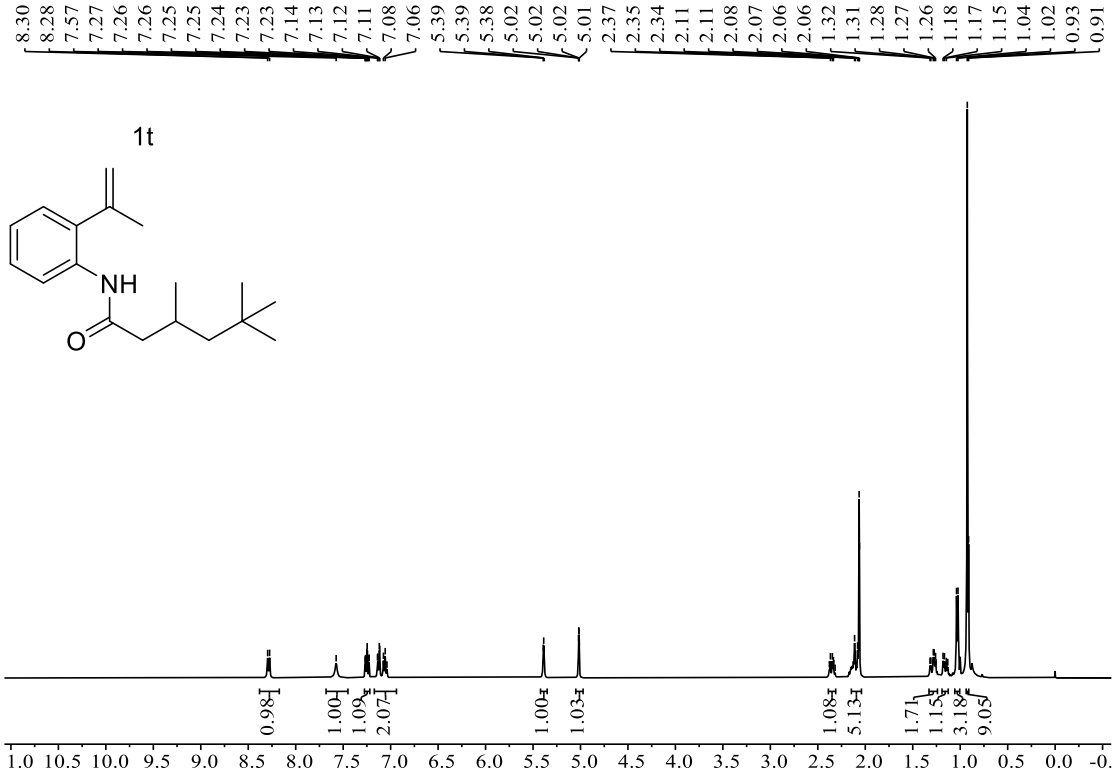
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1s**



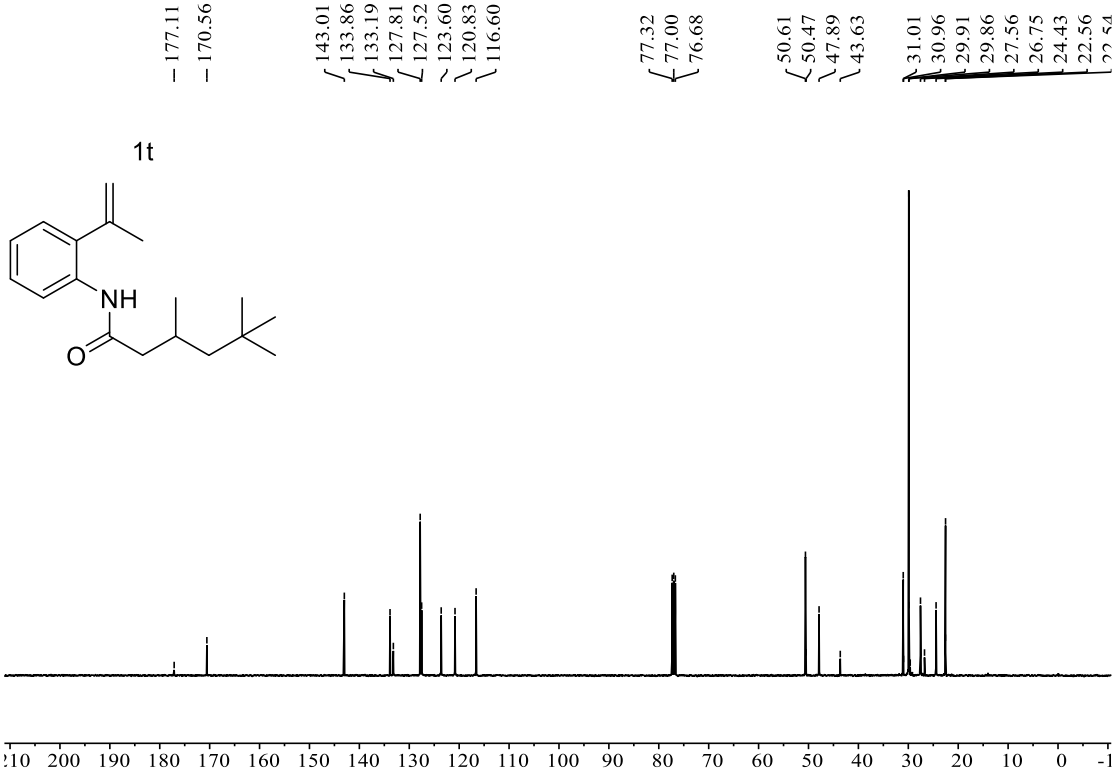
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1s**



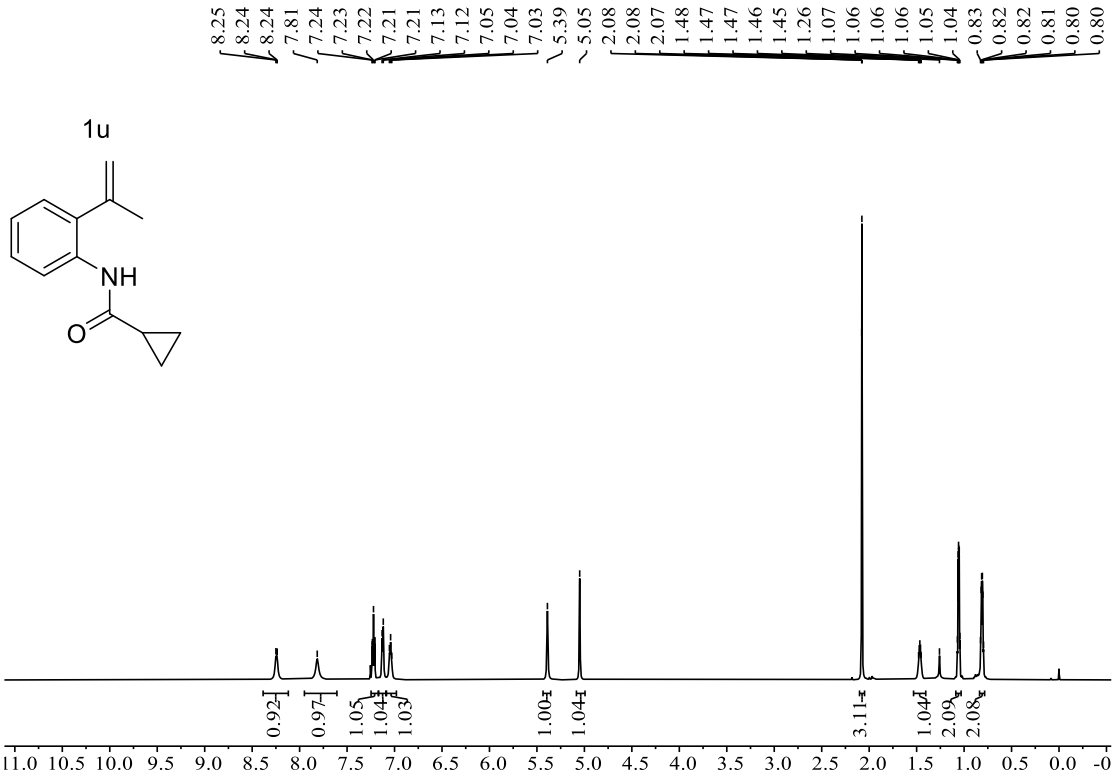
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1t**



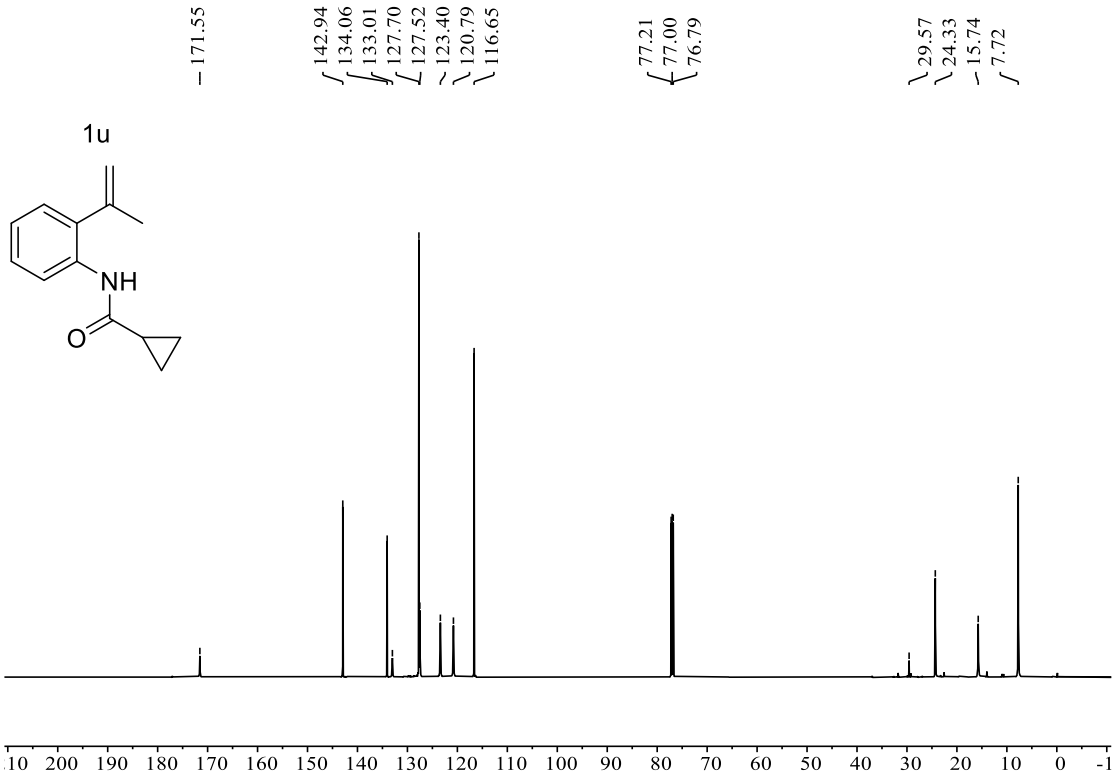
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1t**



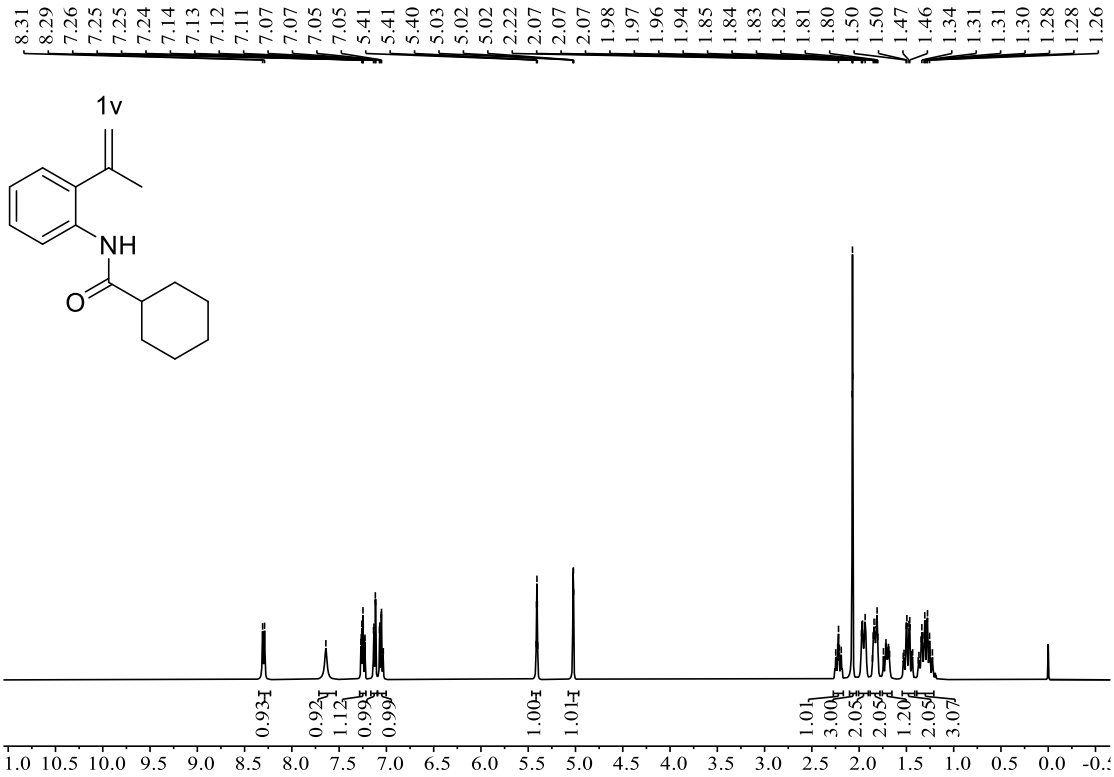
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1u**



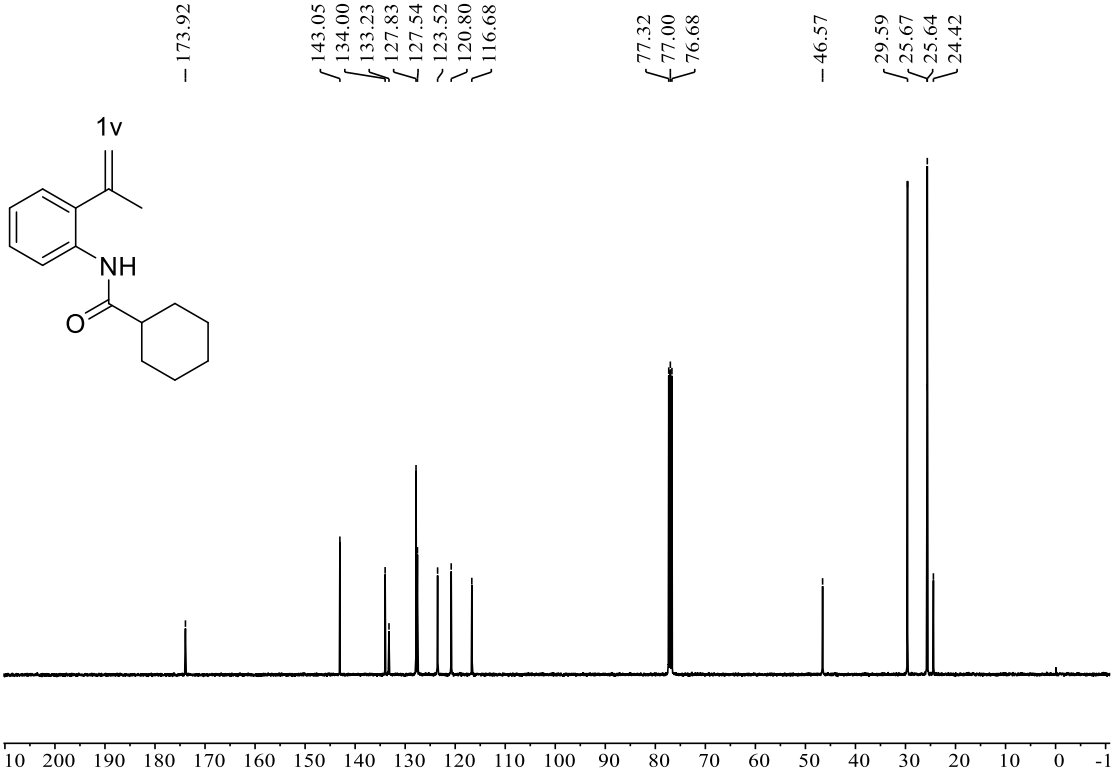
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1u**



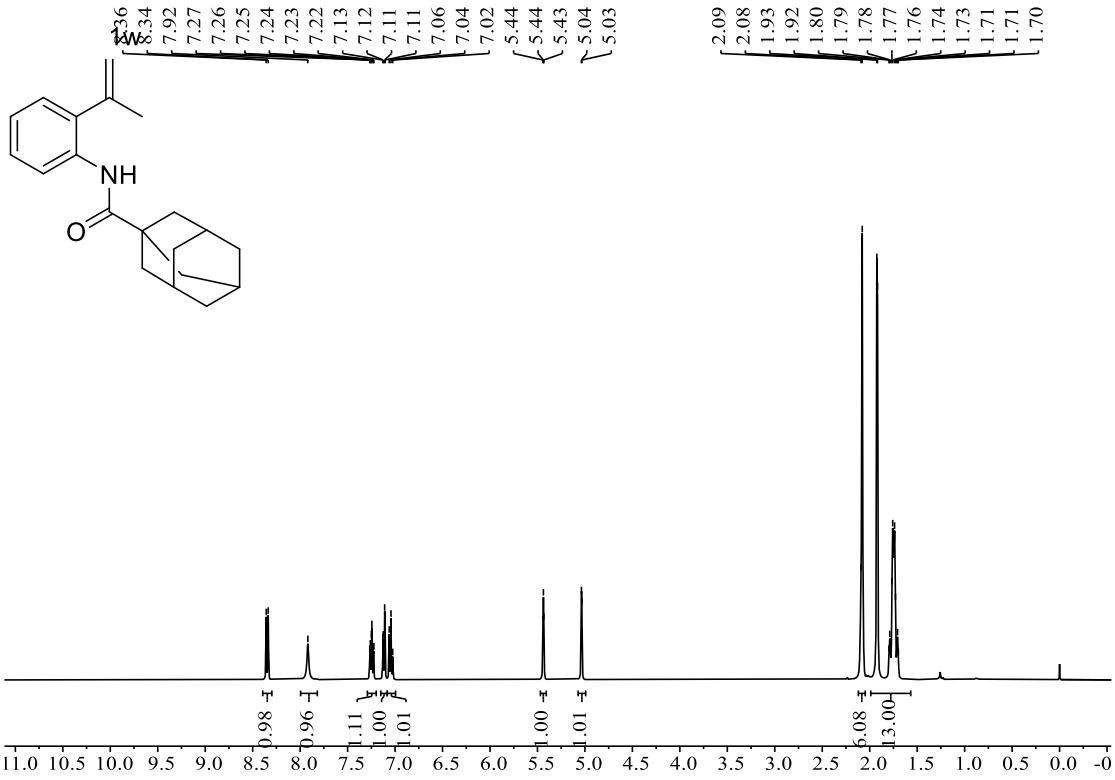
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1v**



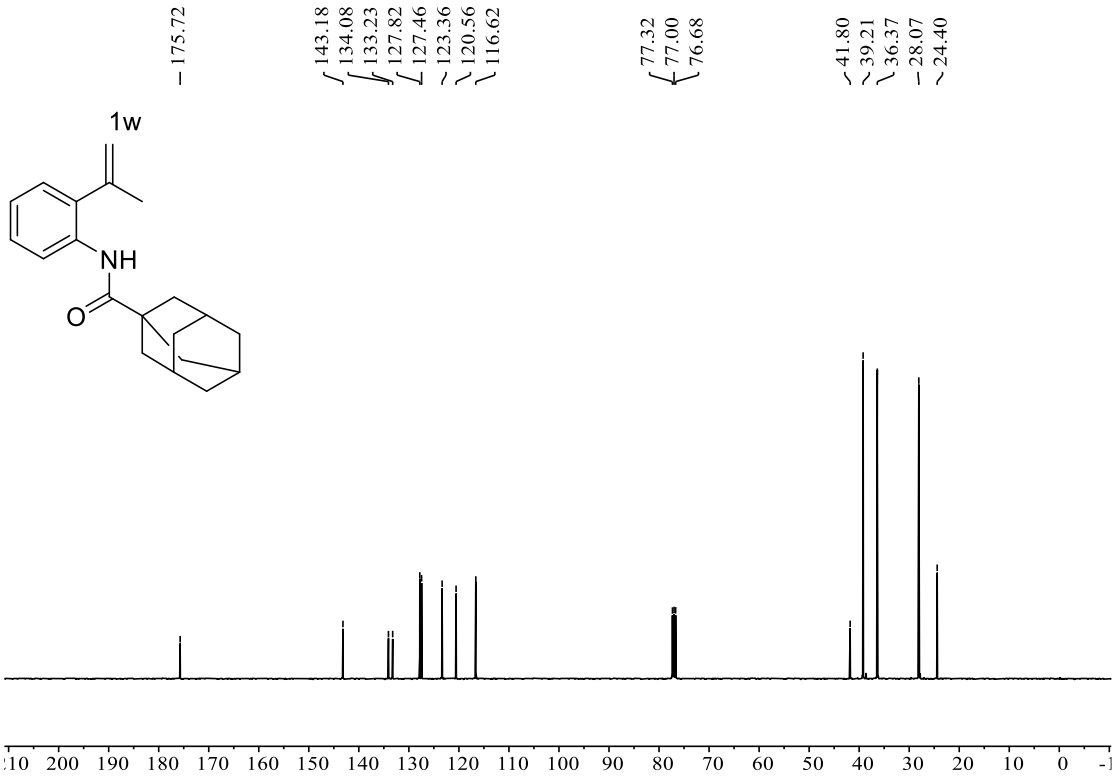
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1v**



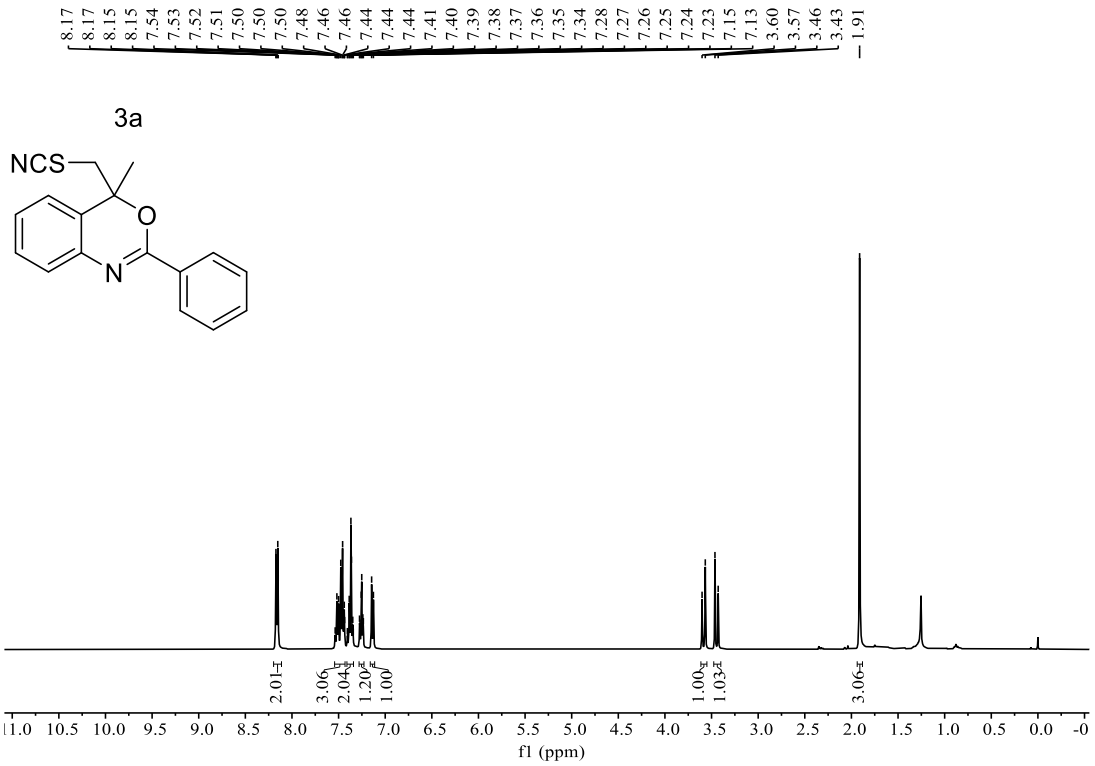
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1w**



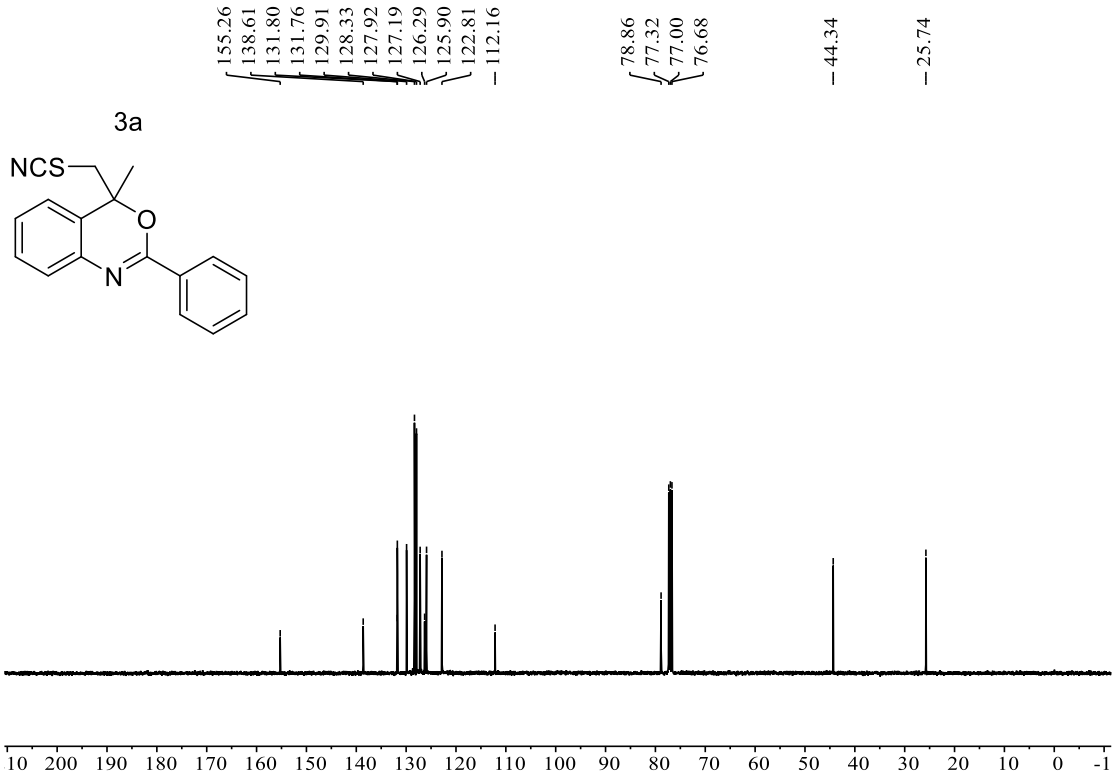
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1w**



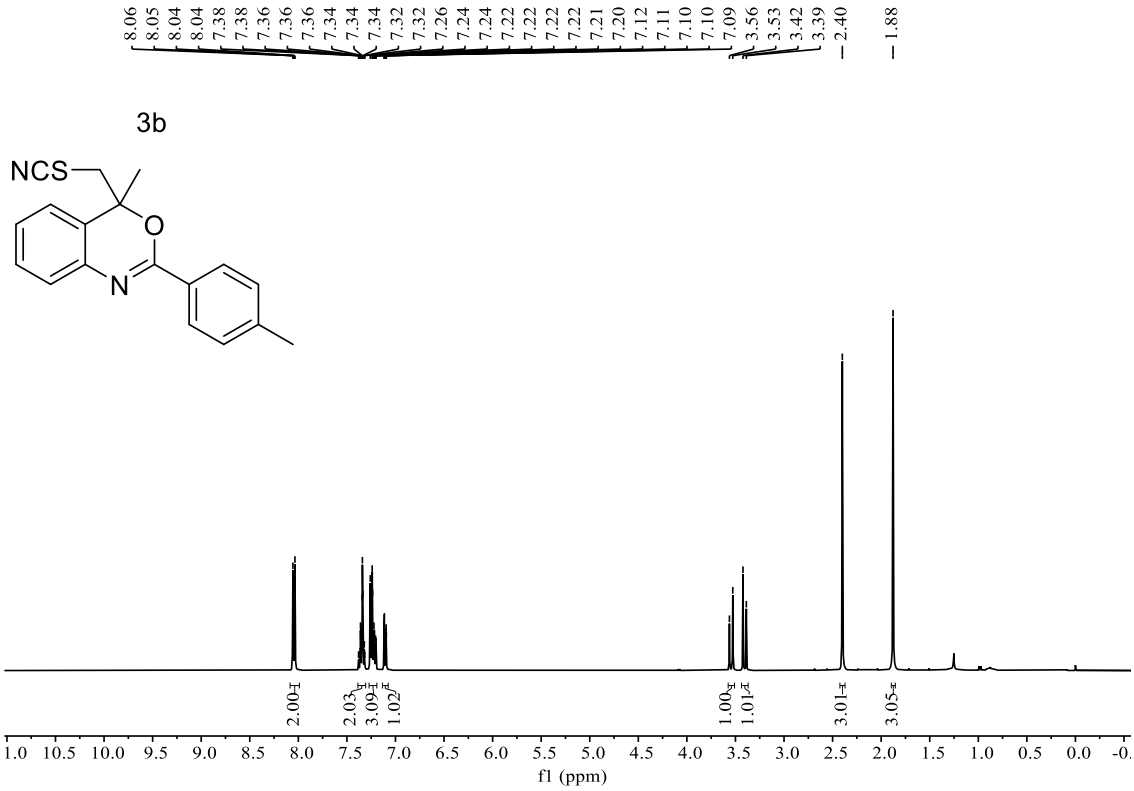
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



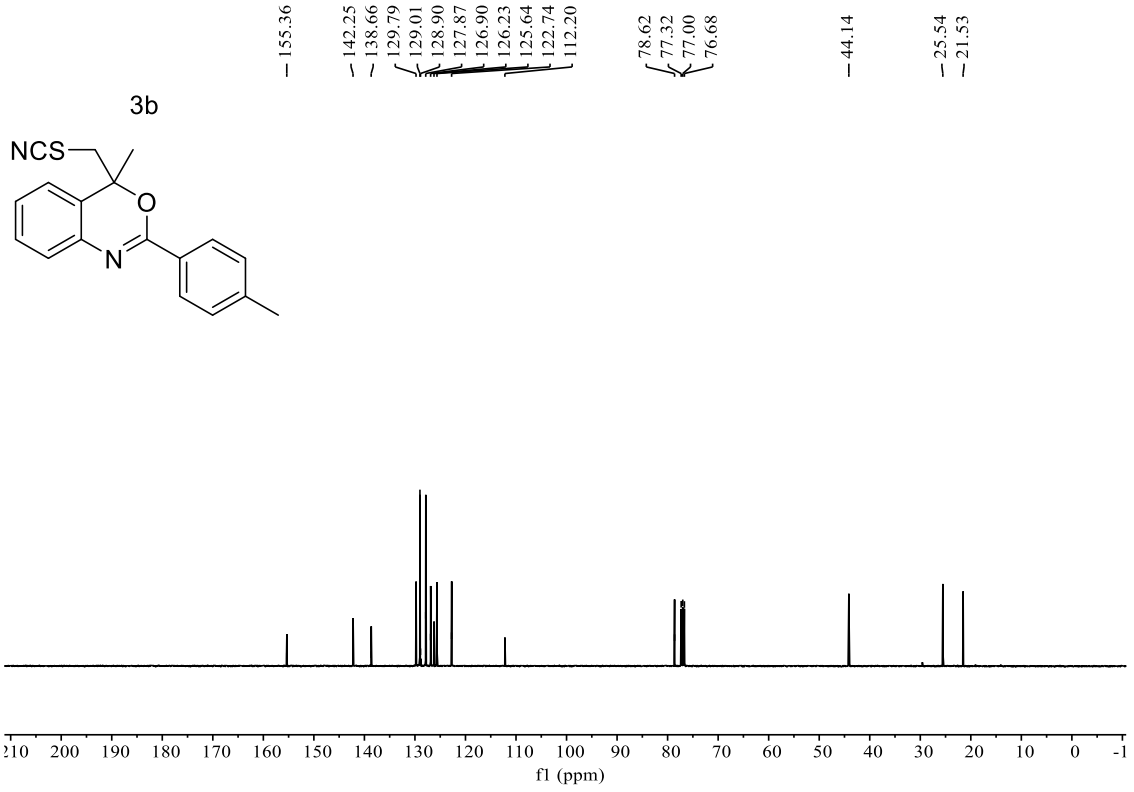
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3a**



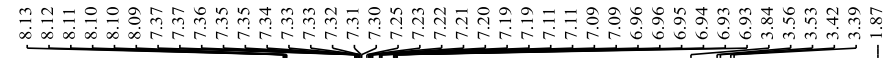
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**

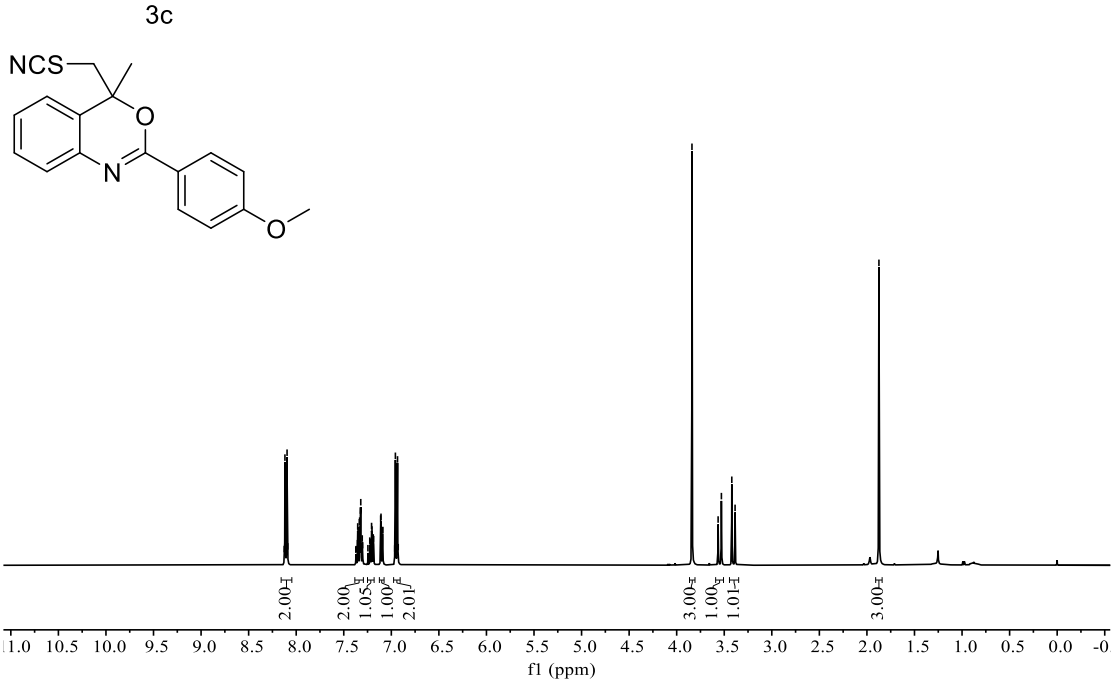


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3b**

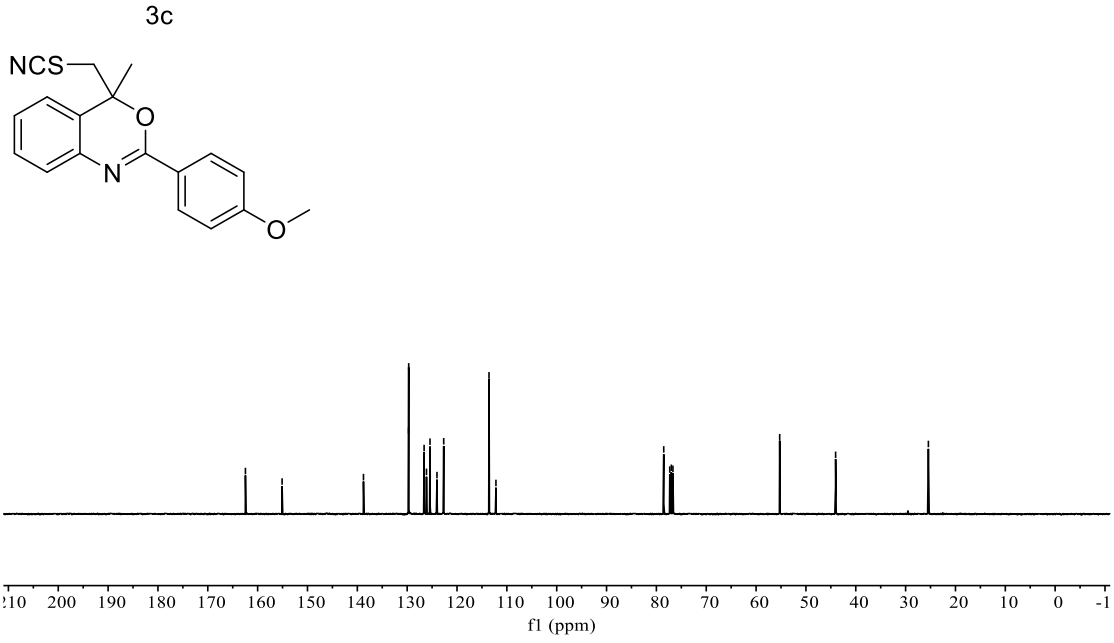


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**

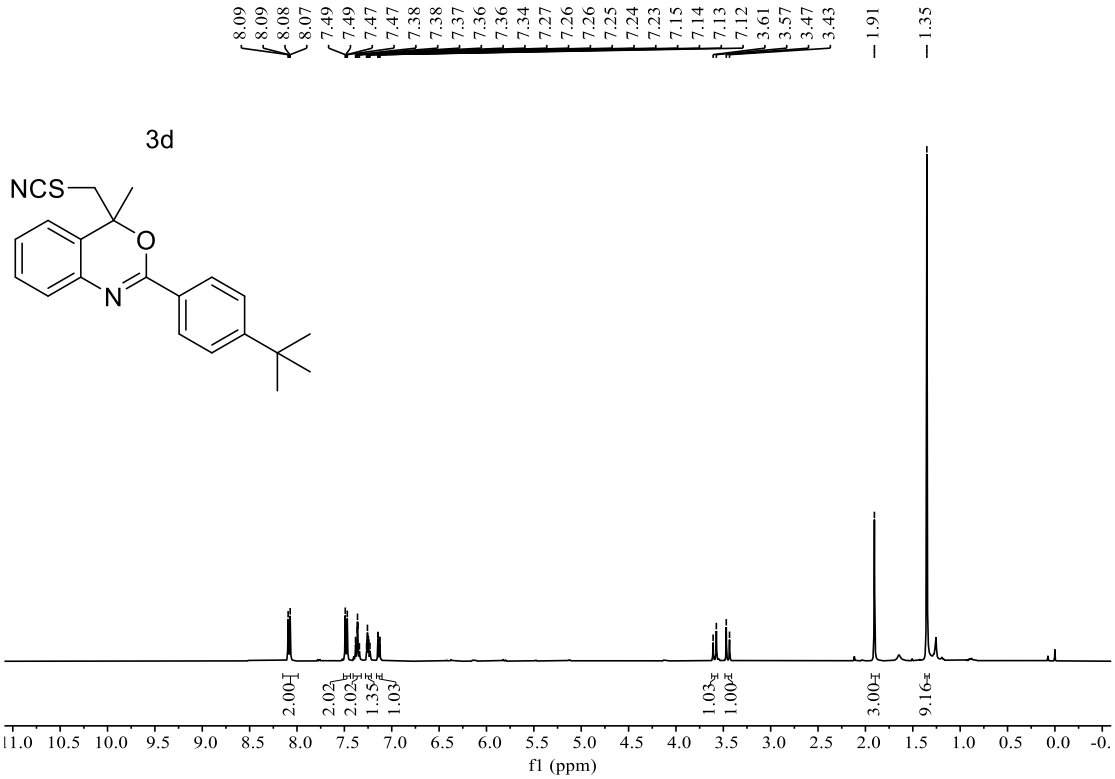




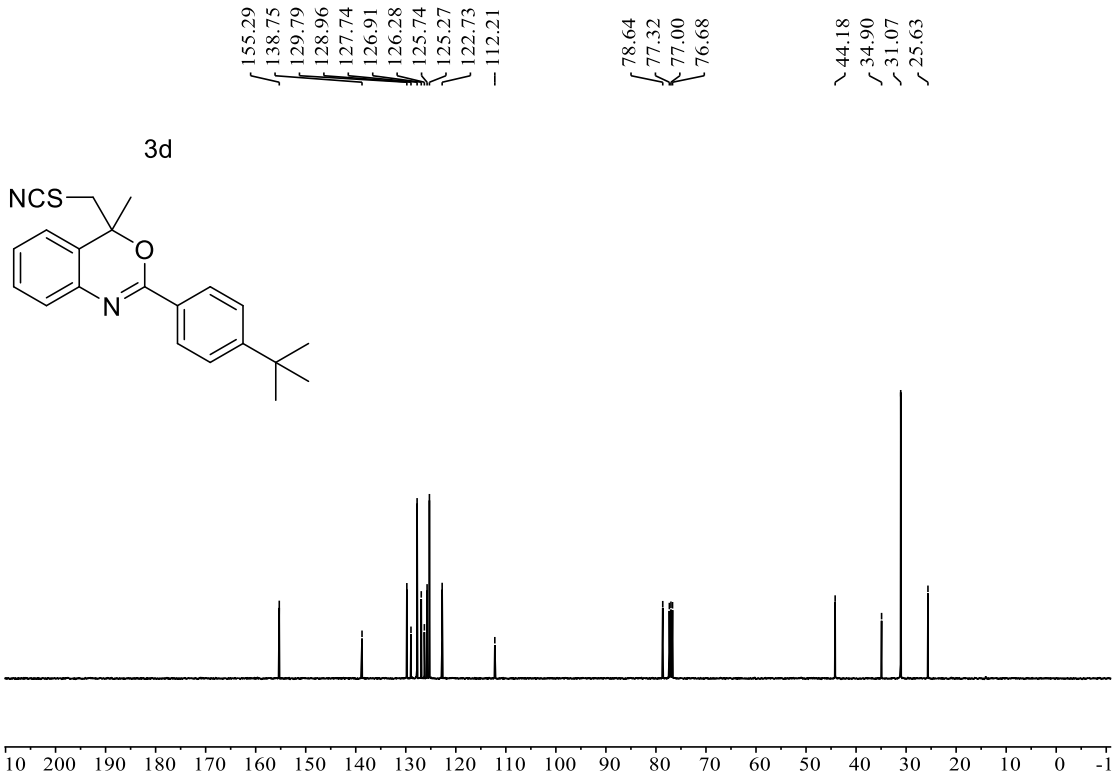
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3c**



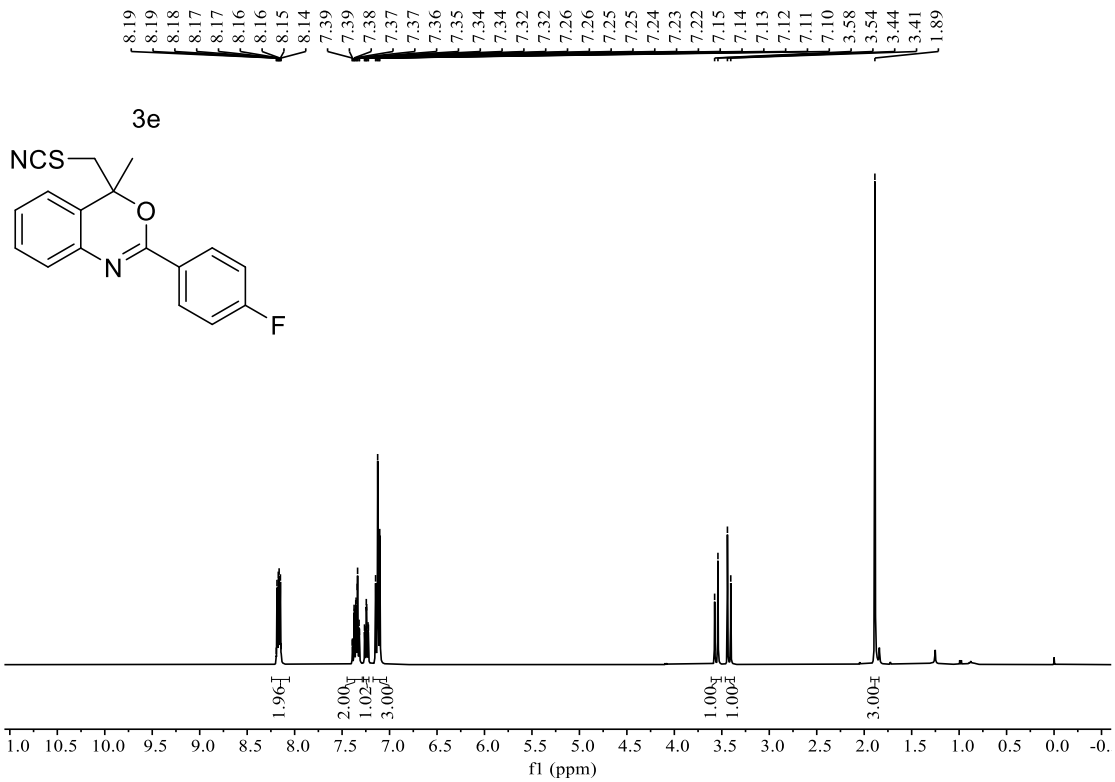
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



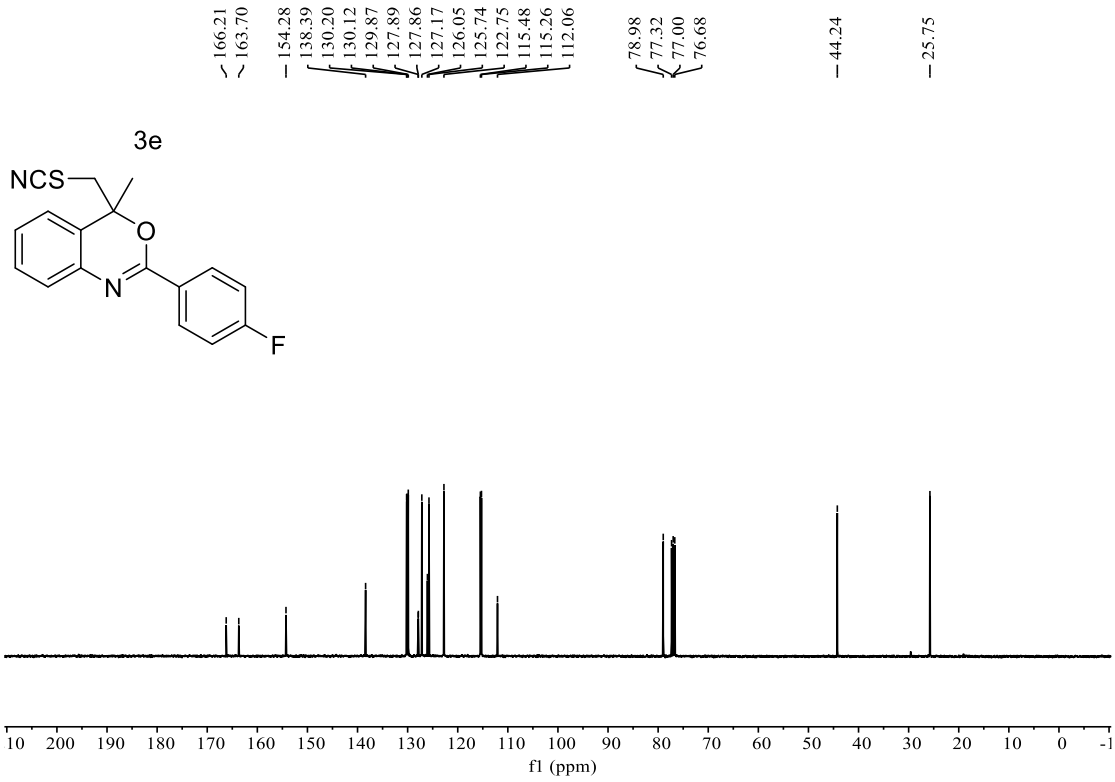
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3d**



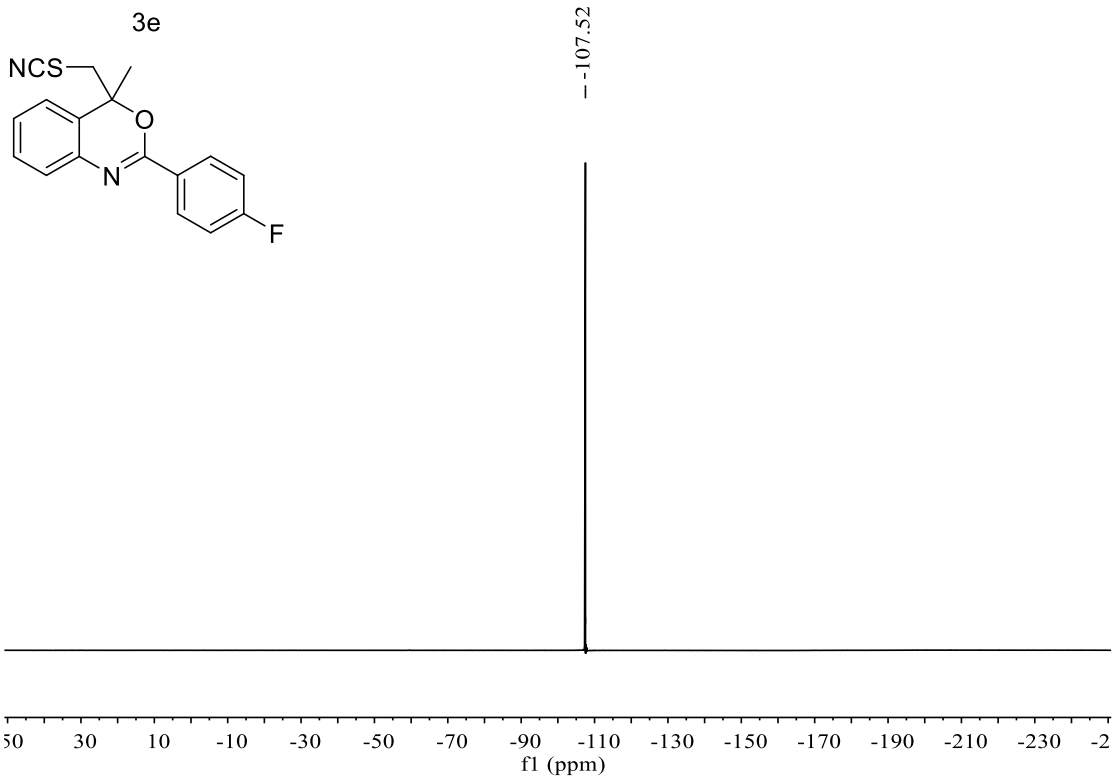
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



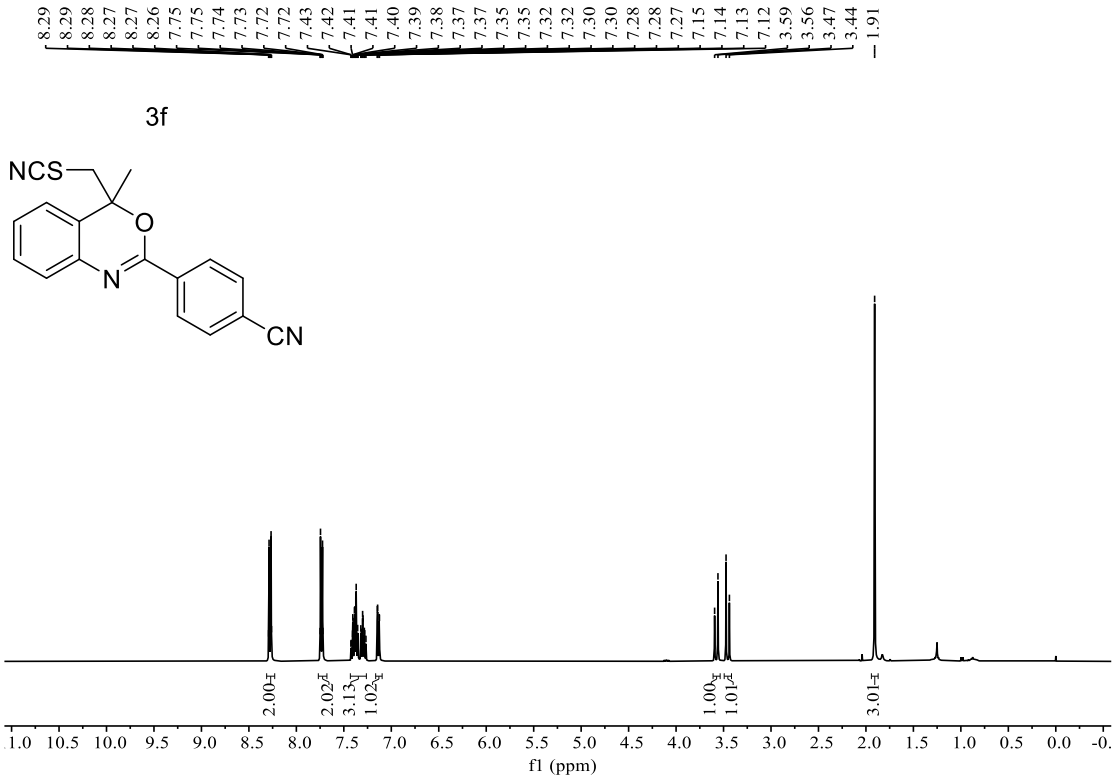
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3e**



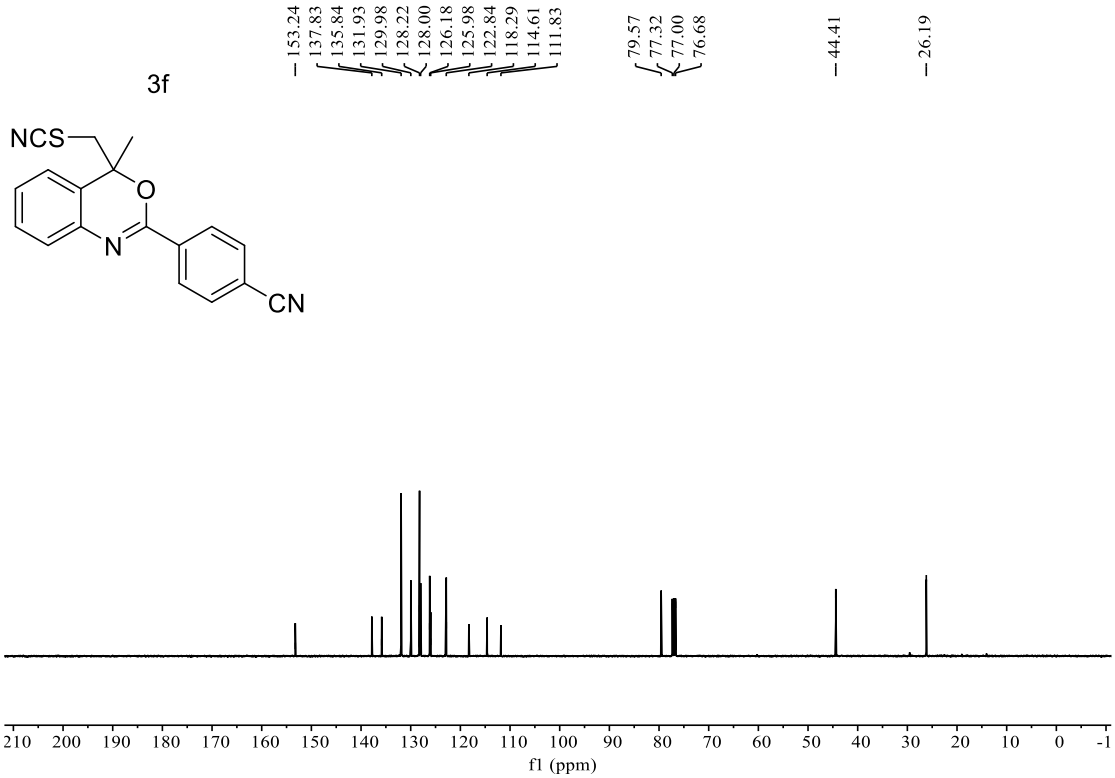
^{19}F NMR (377 MHz, $CDCl_3$) of compound **3e**



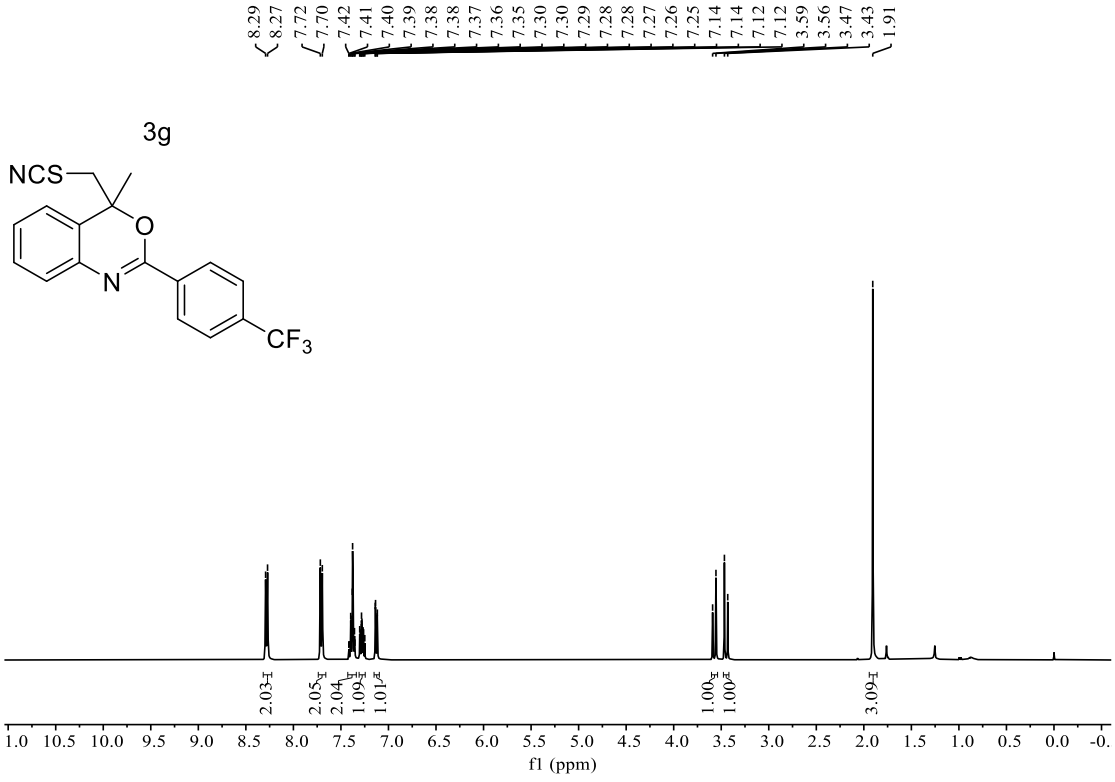
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**



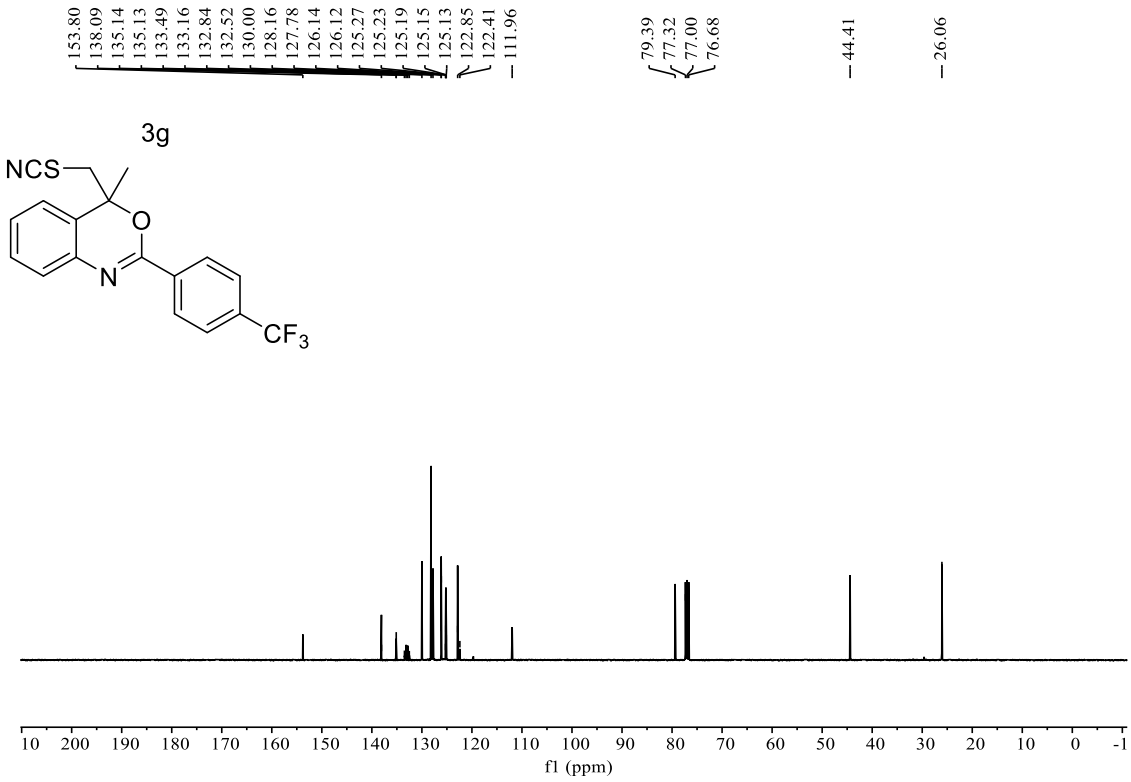
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3f**



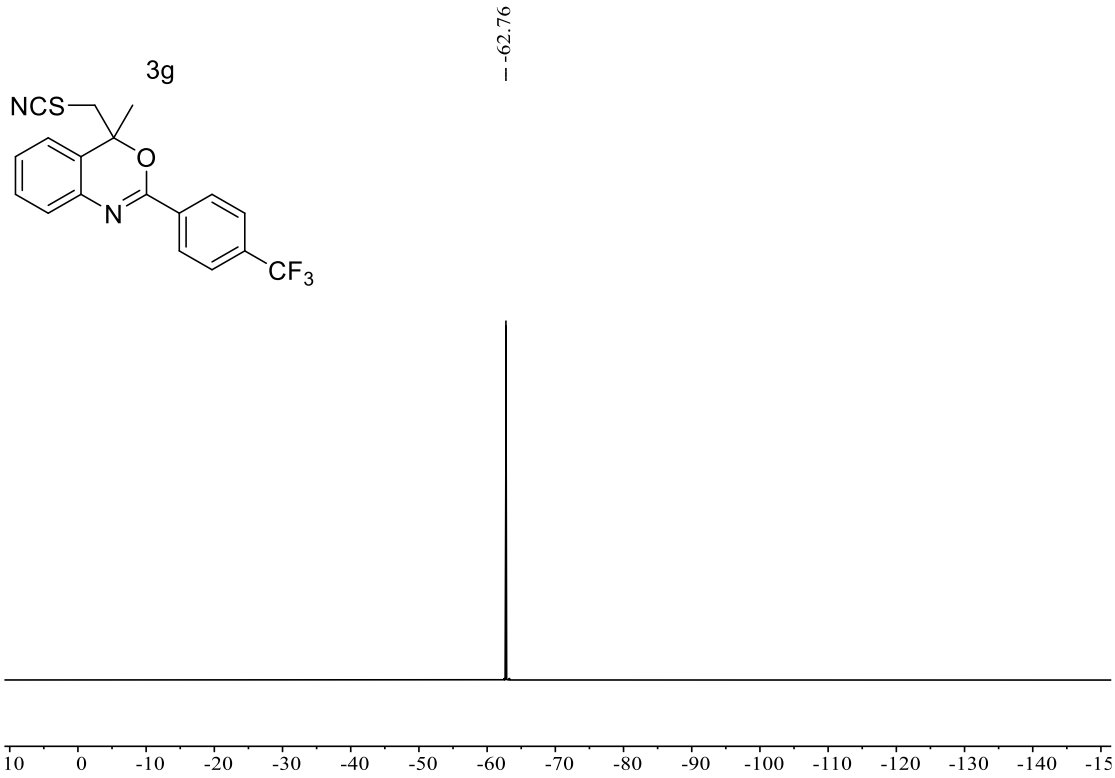
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**



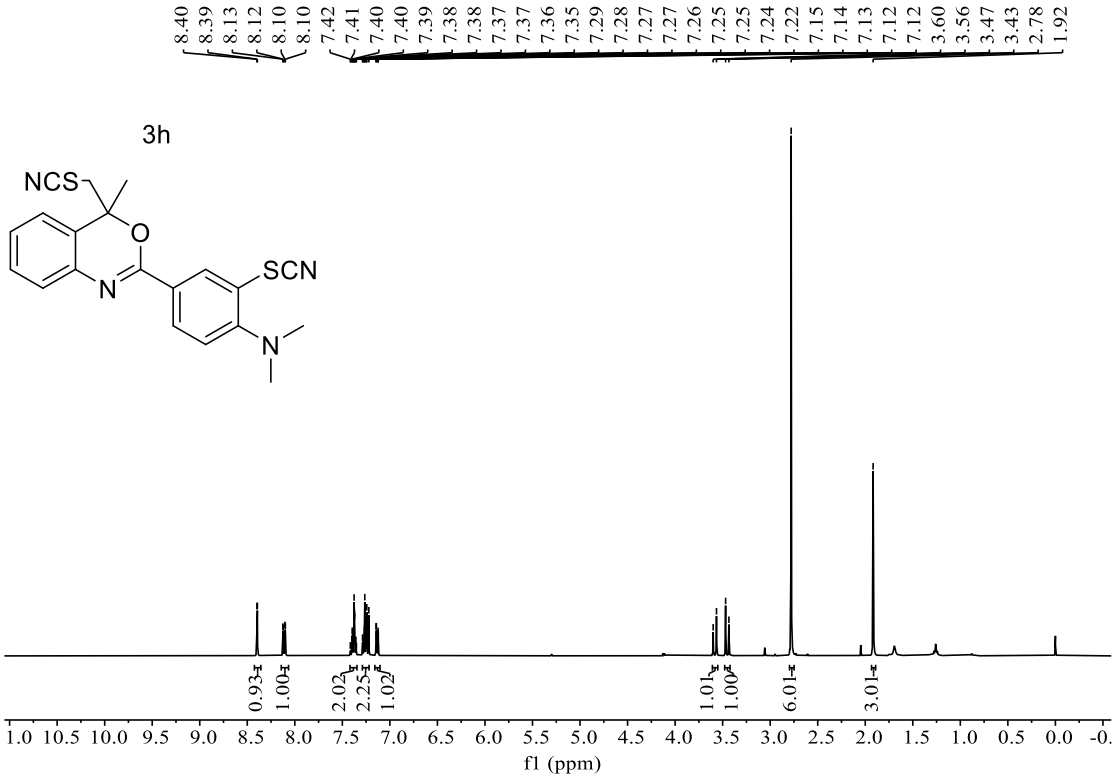
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3g**



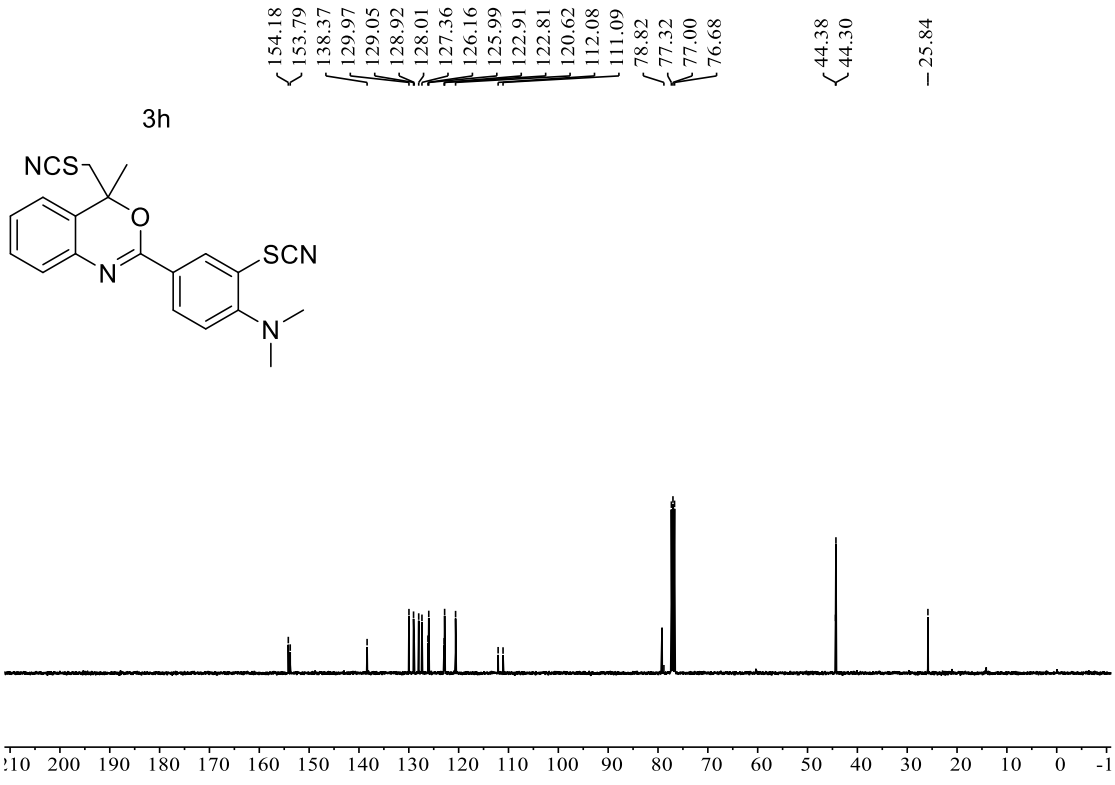
^{19}F NMR (377 MHz, $CDCl_3$) of compound **3g**



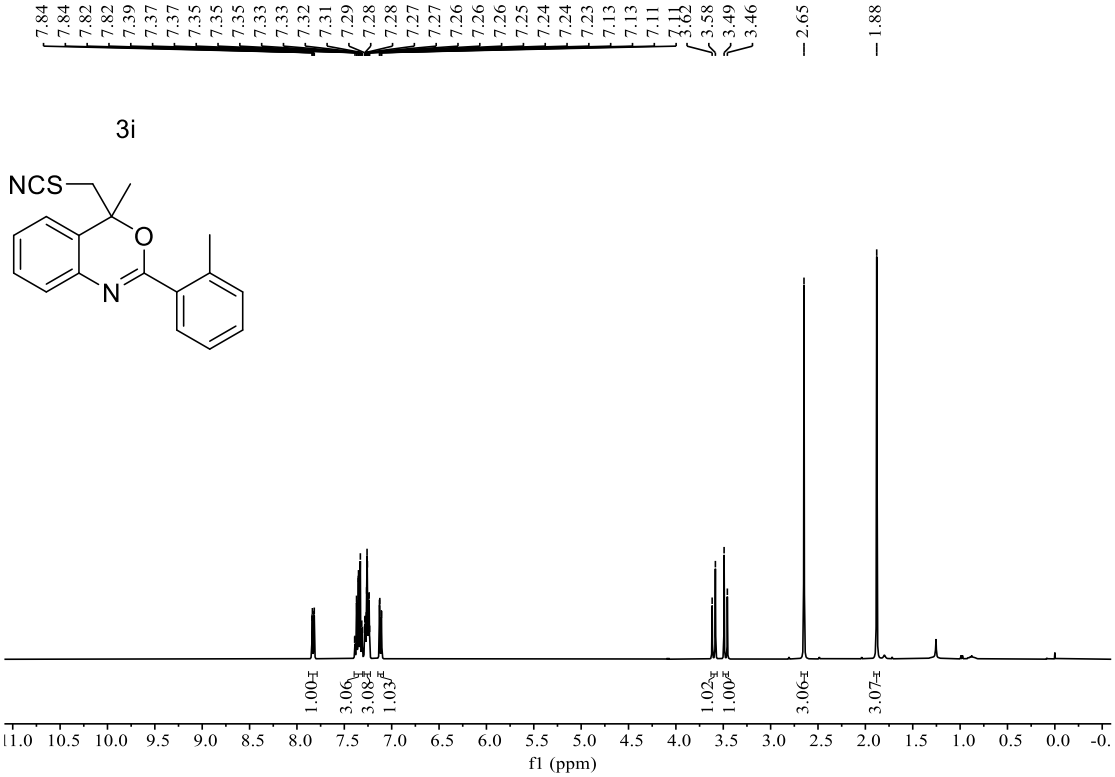
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



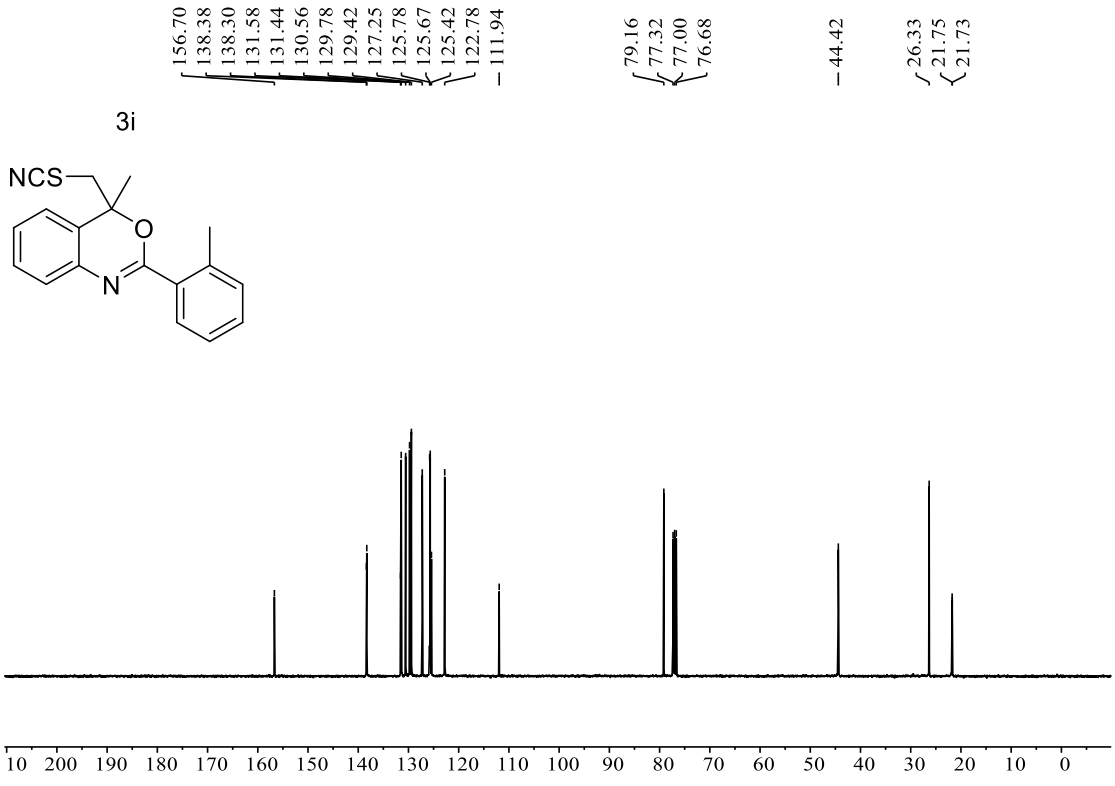
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3h**



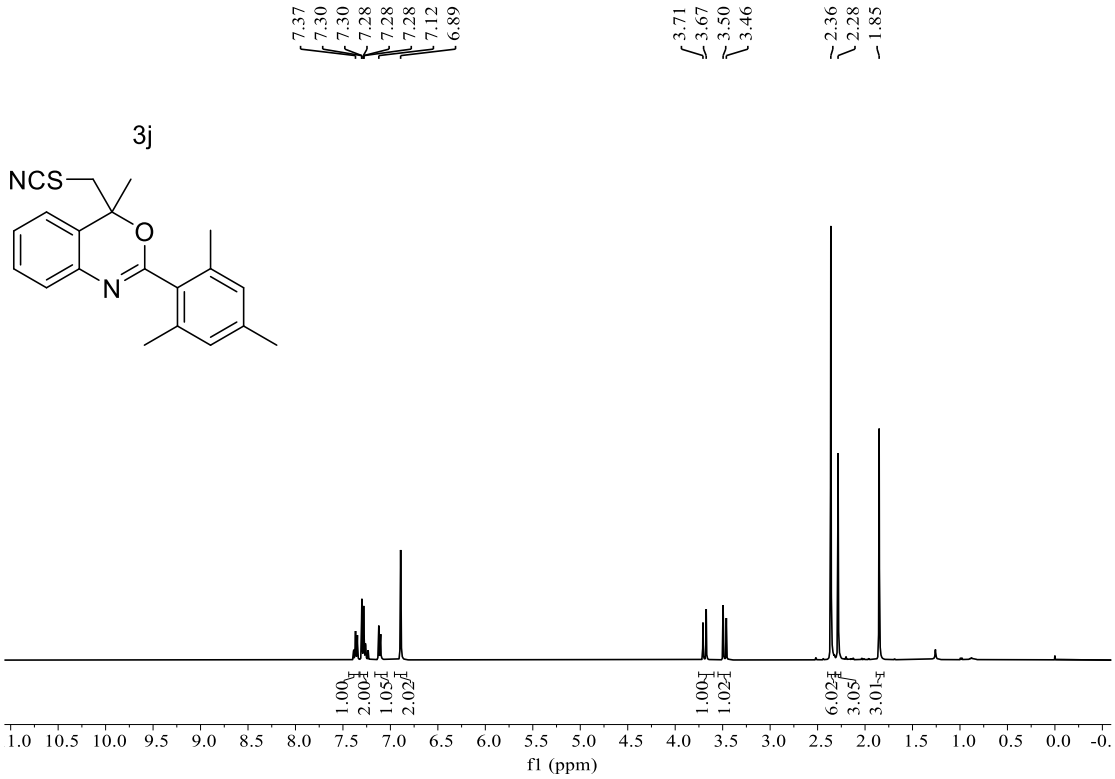
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**



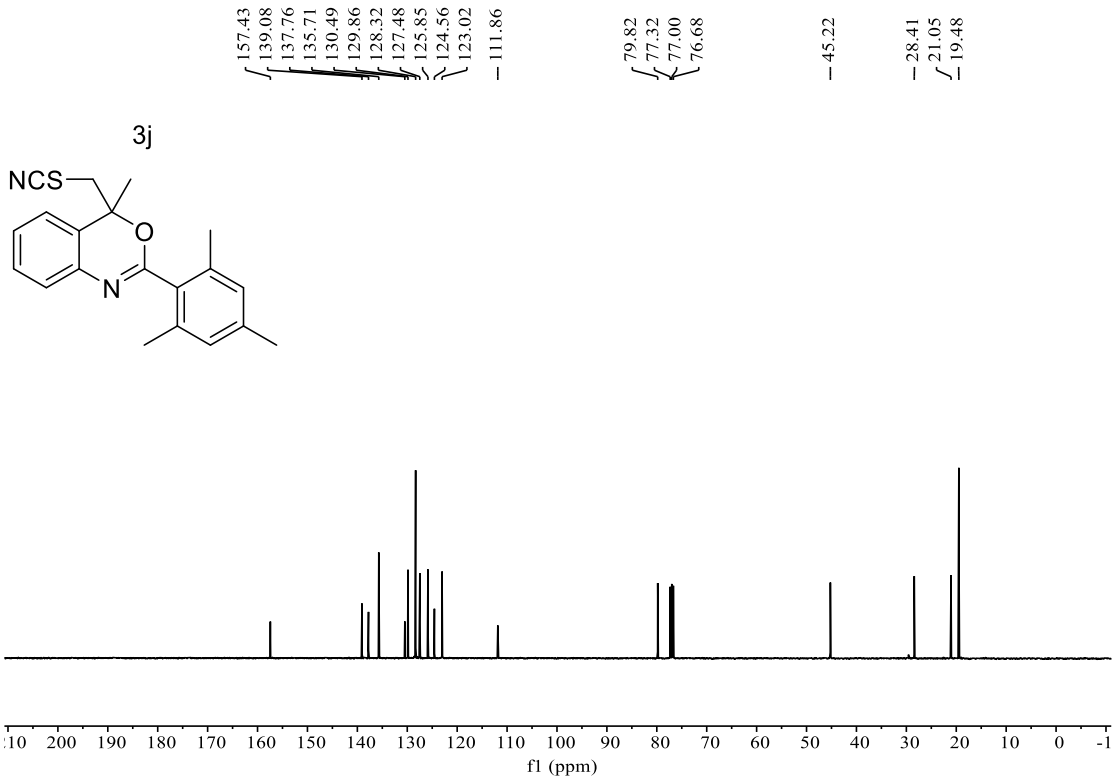
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3i**



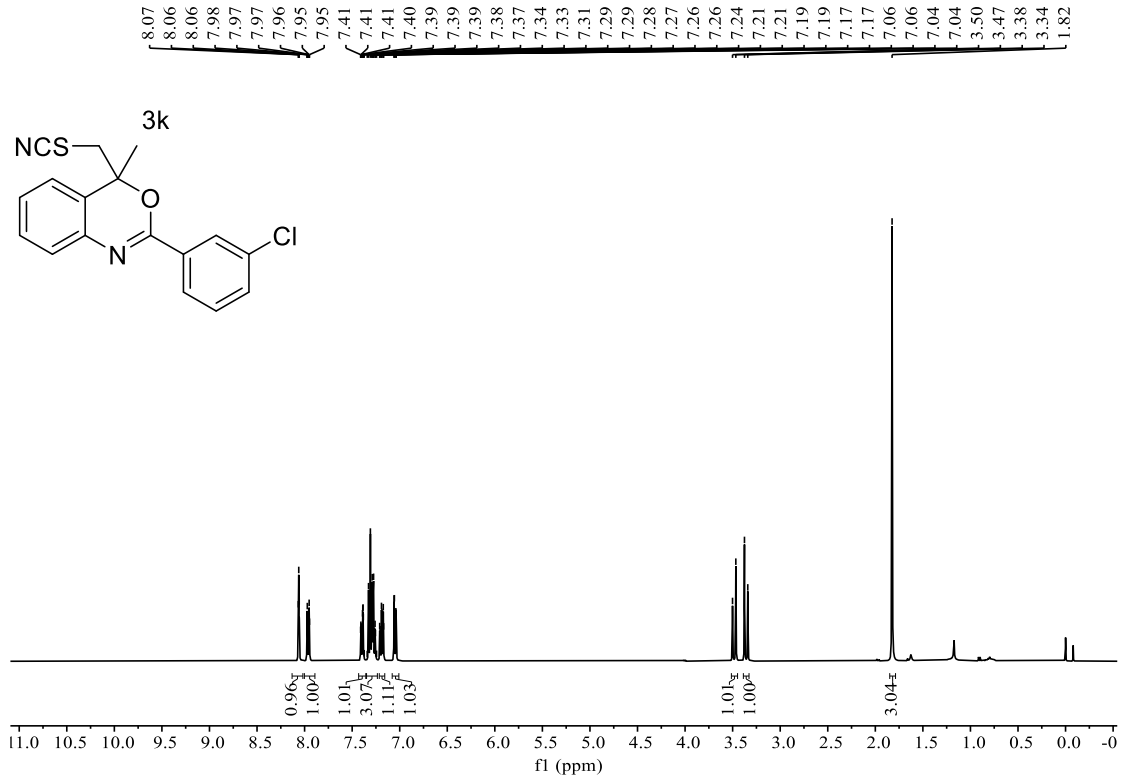
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**



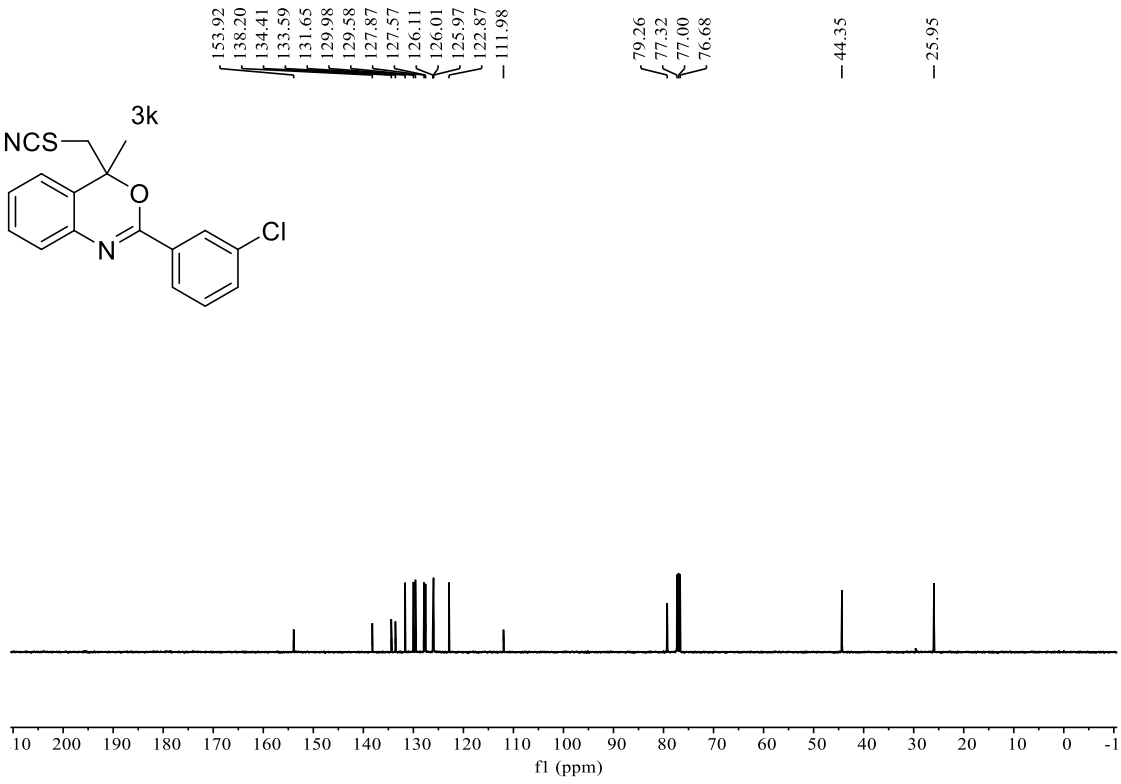
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3j**



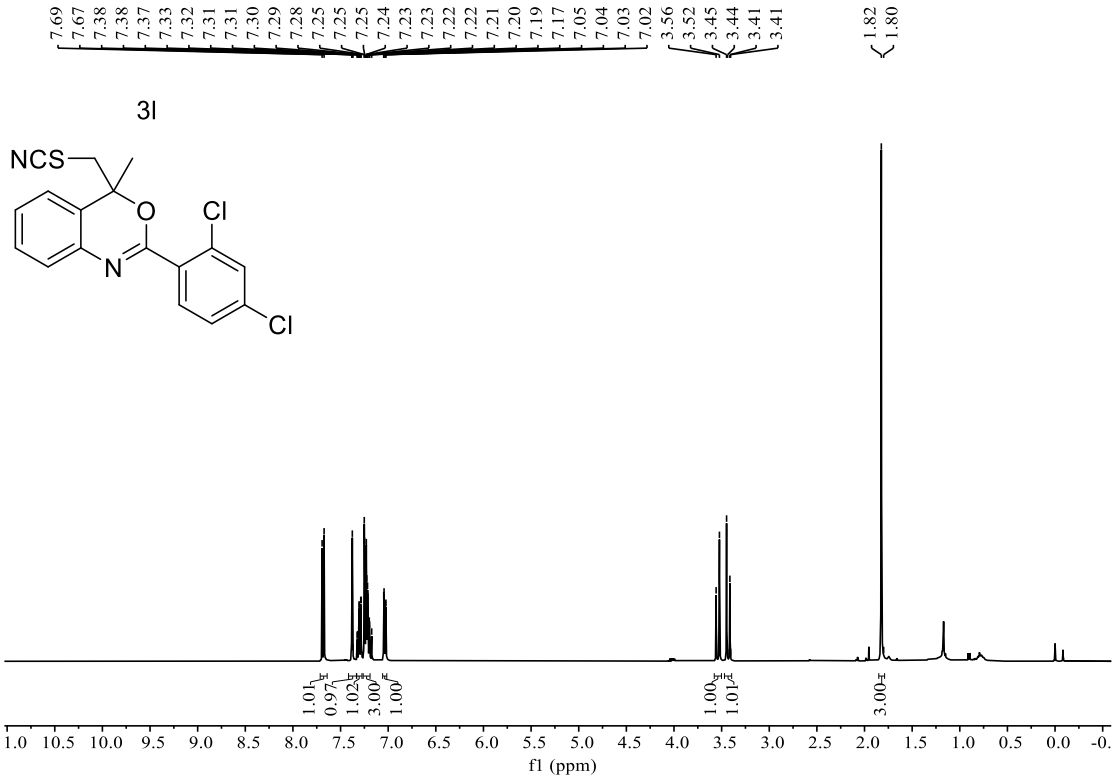
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**



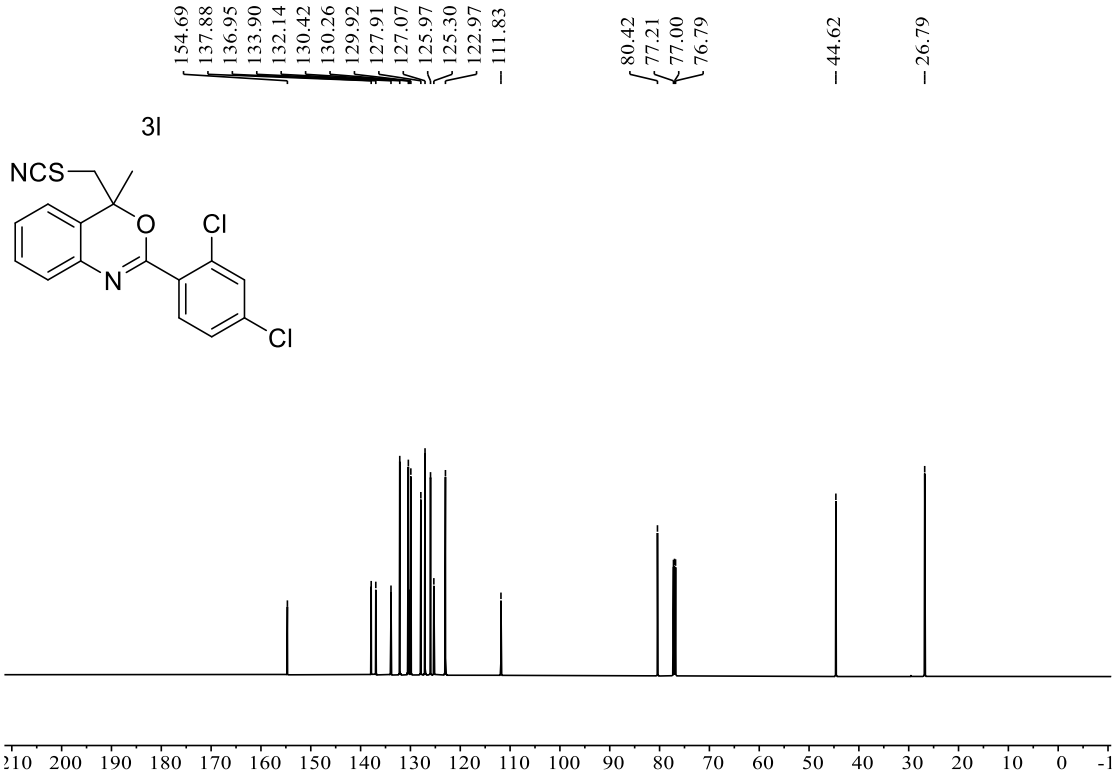
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3k**



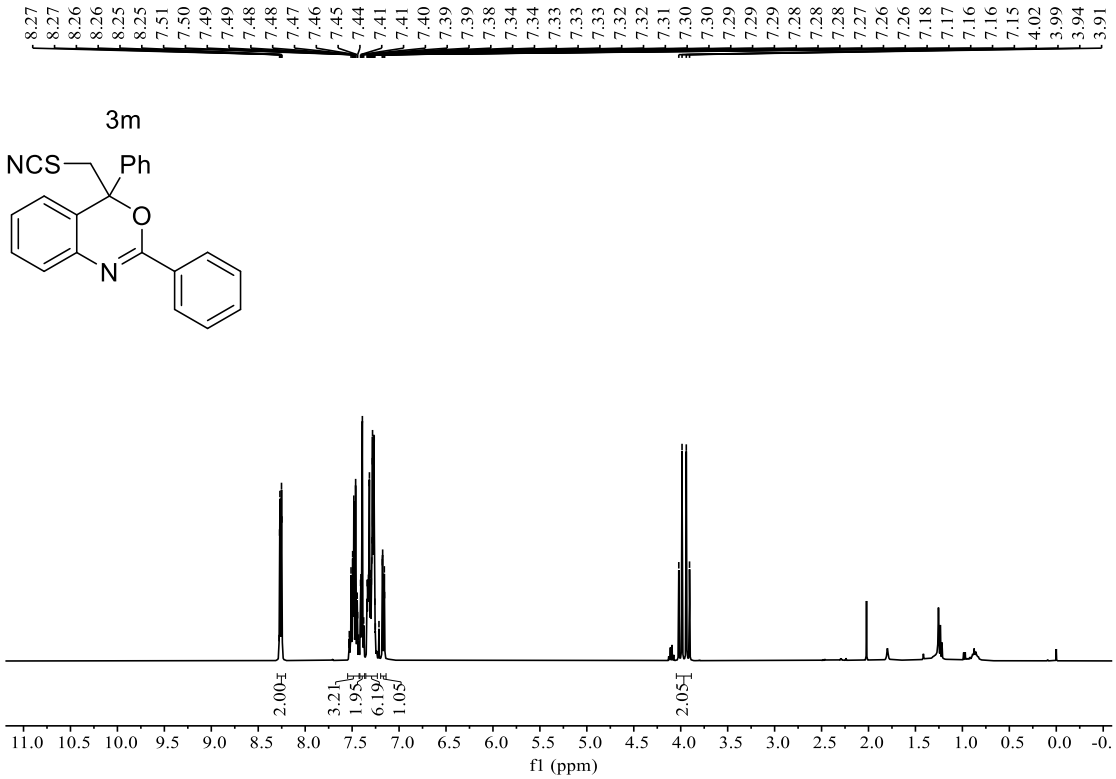
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**



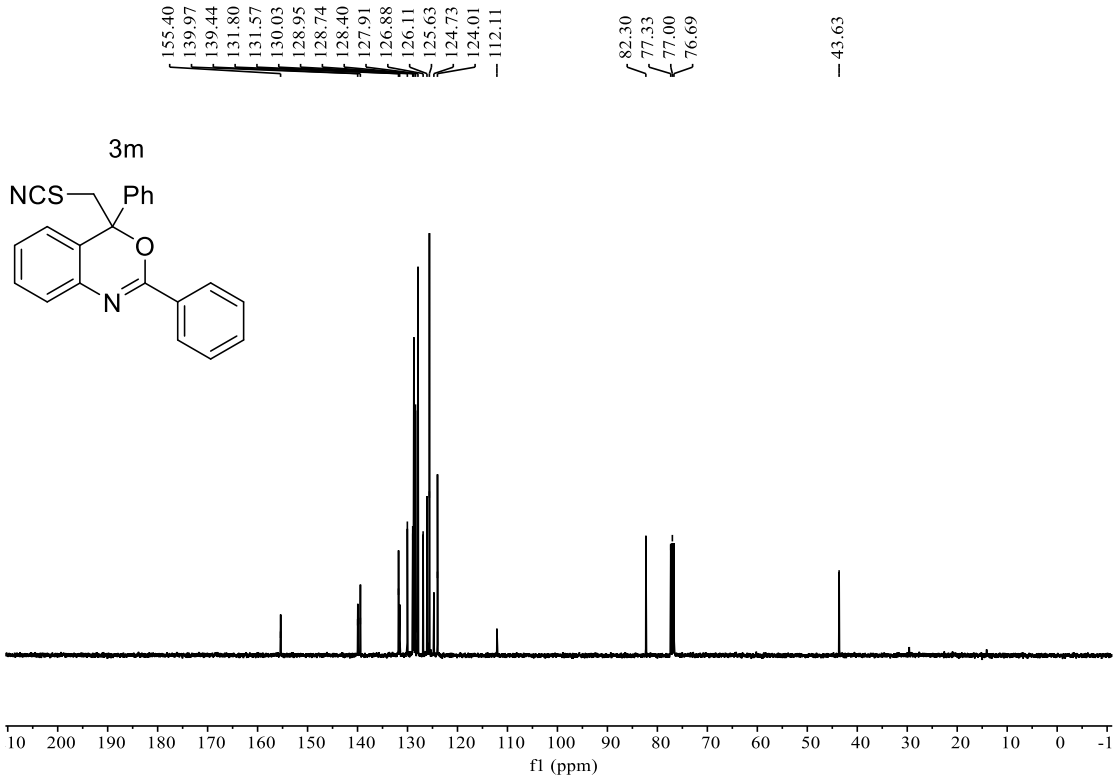
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3l**



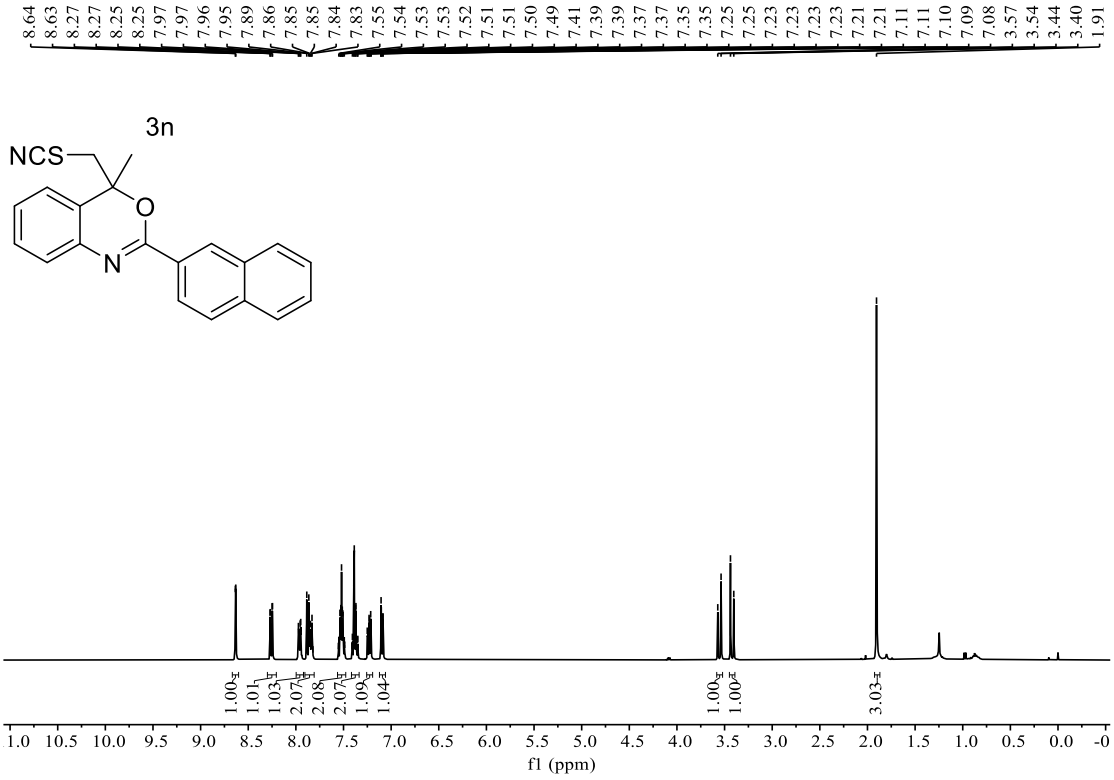
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**



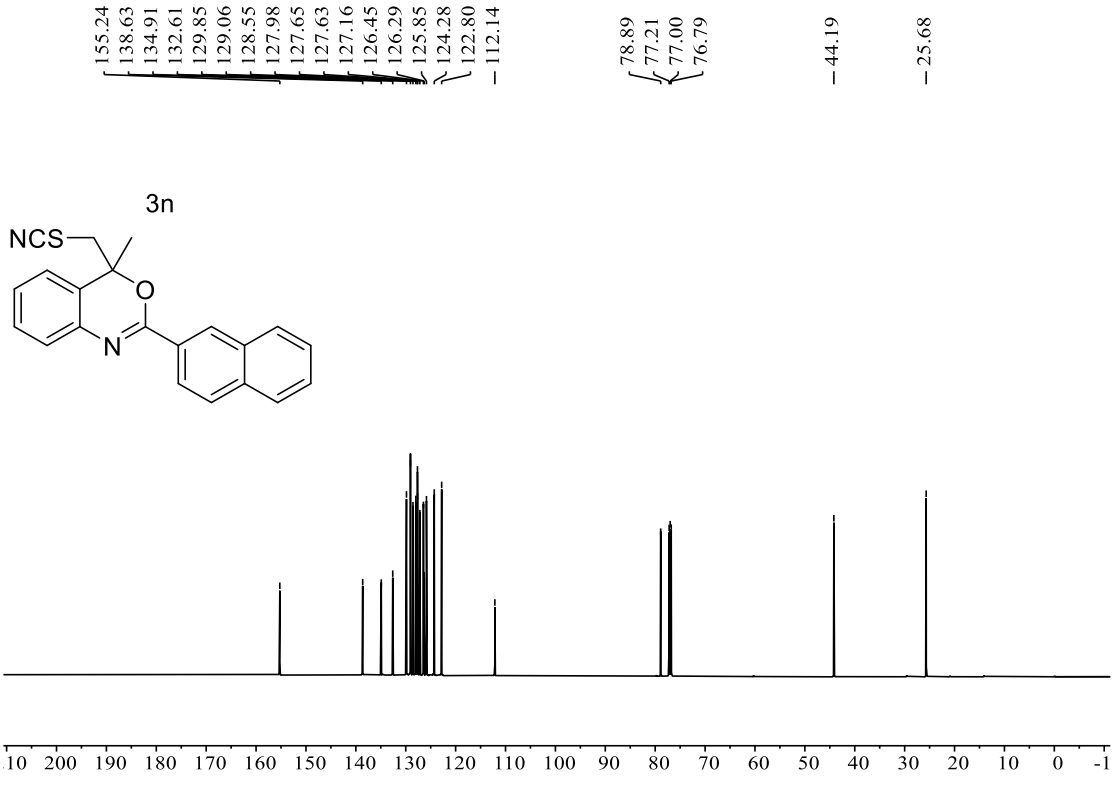
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3m**



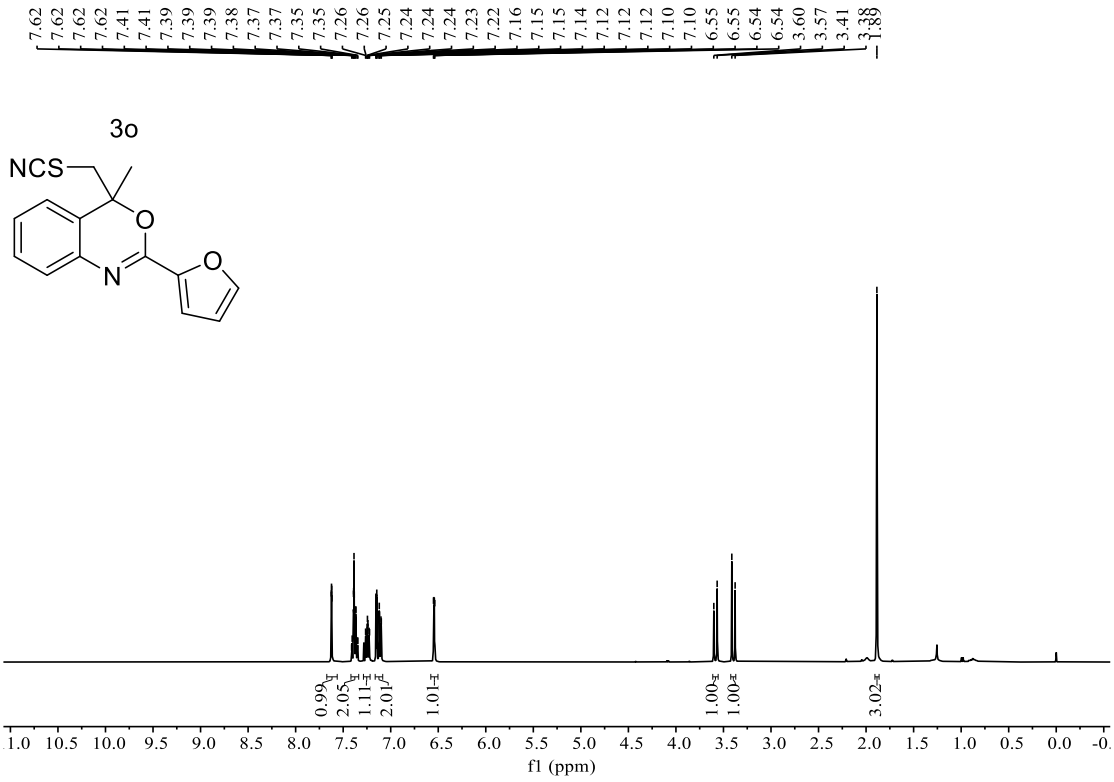
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**



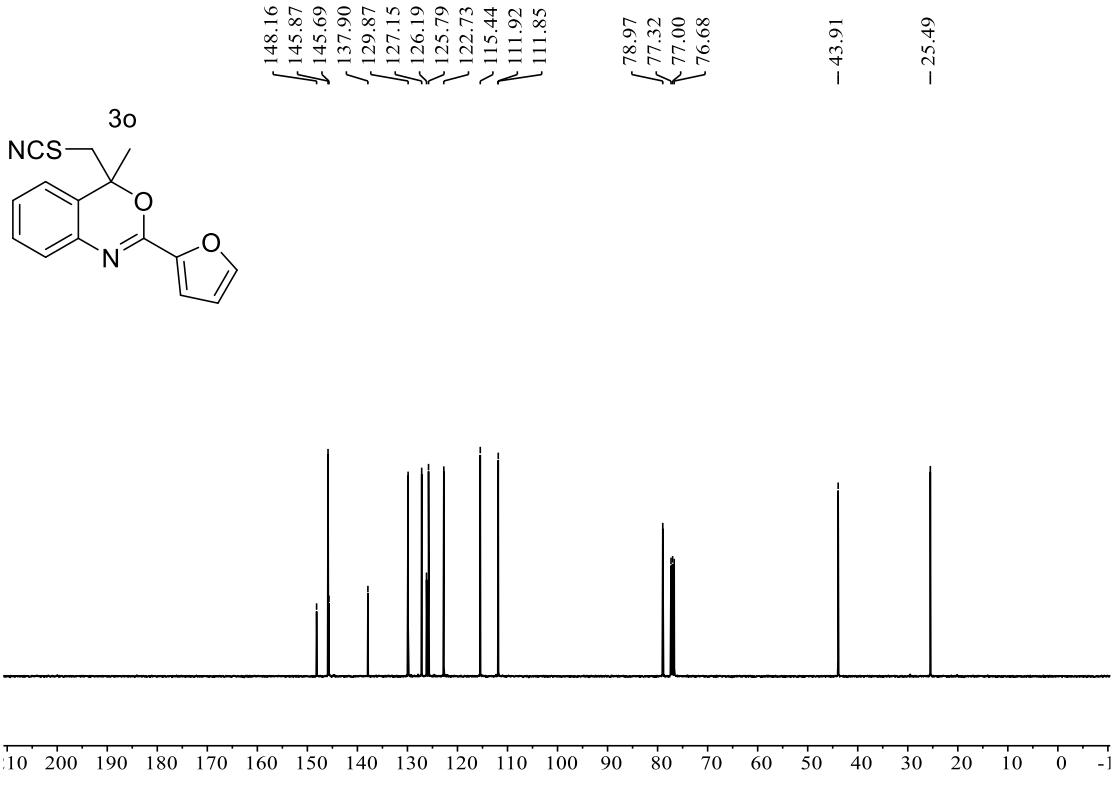
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3n**



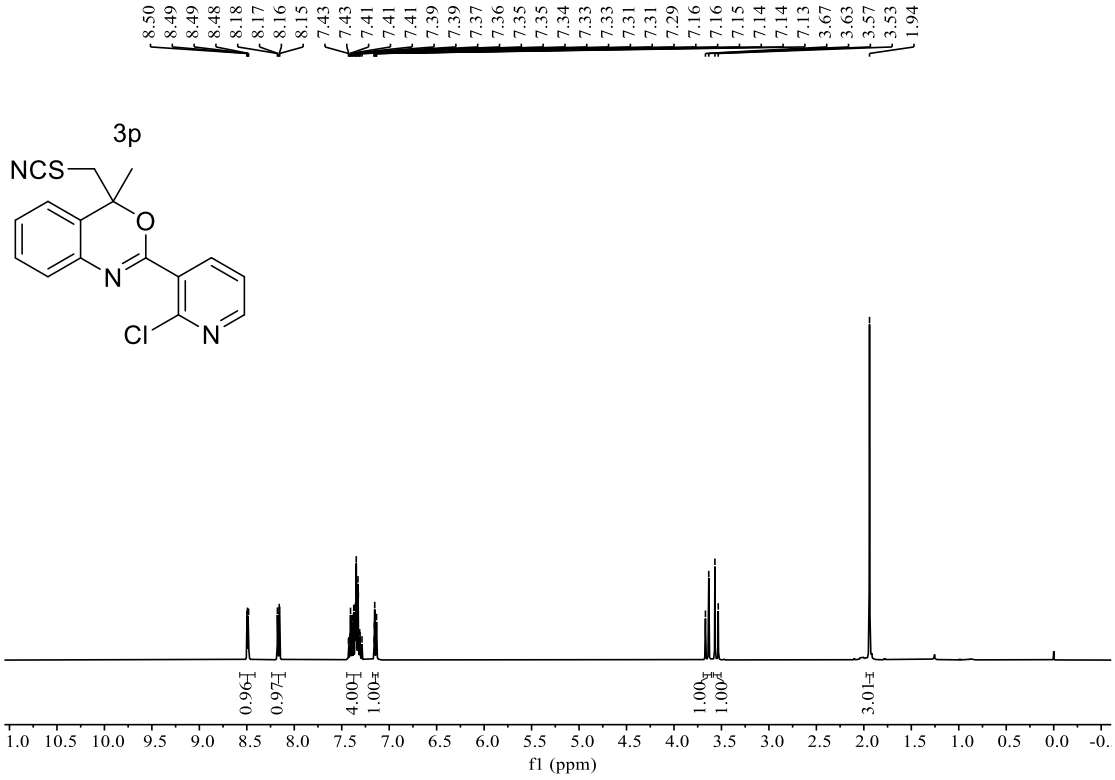
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



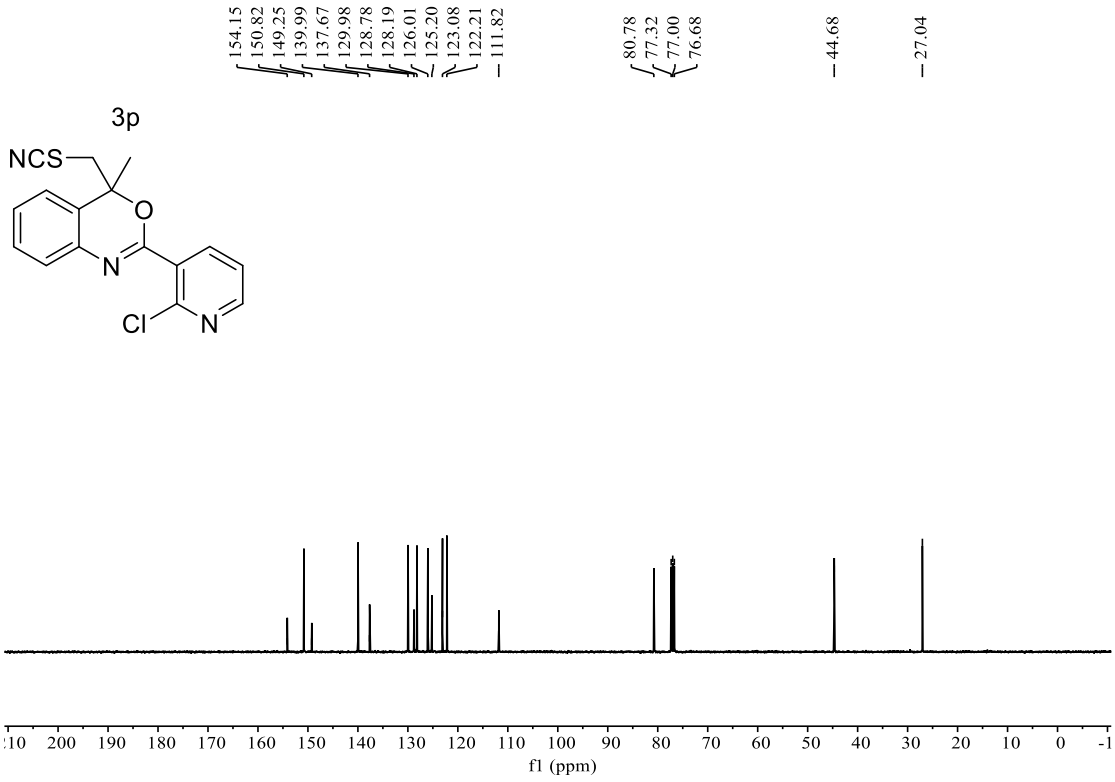
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3o**



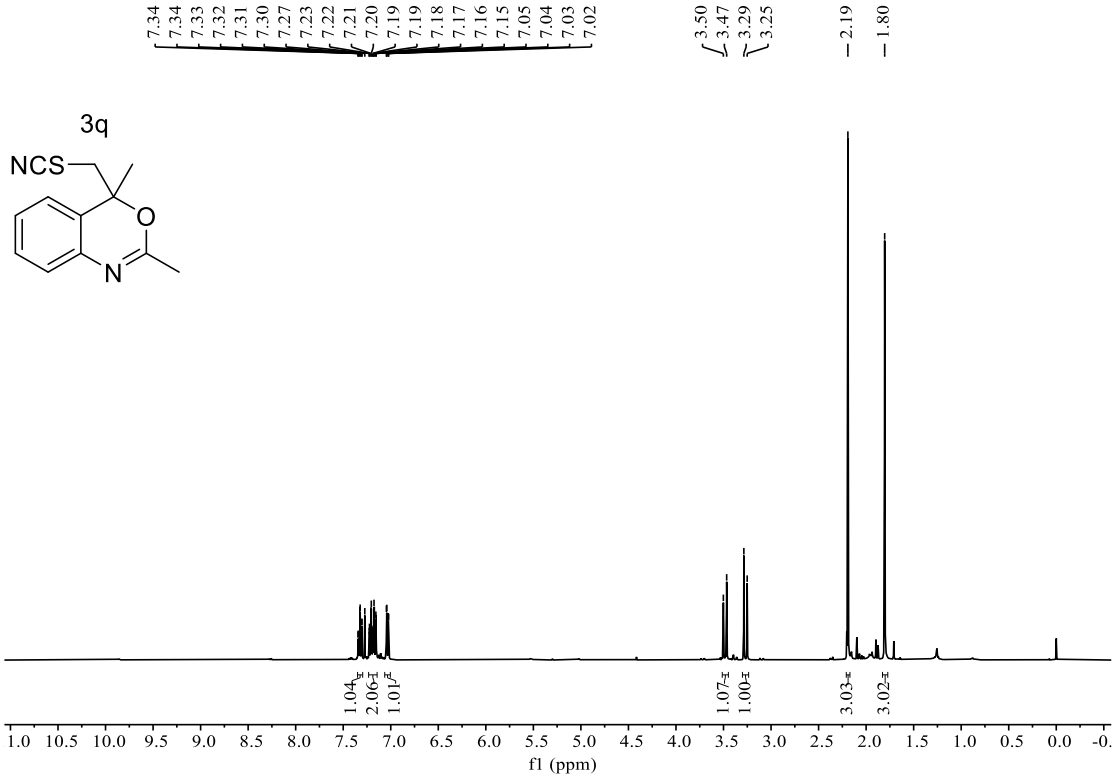
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**



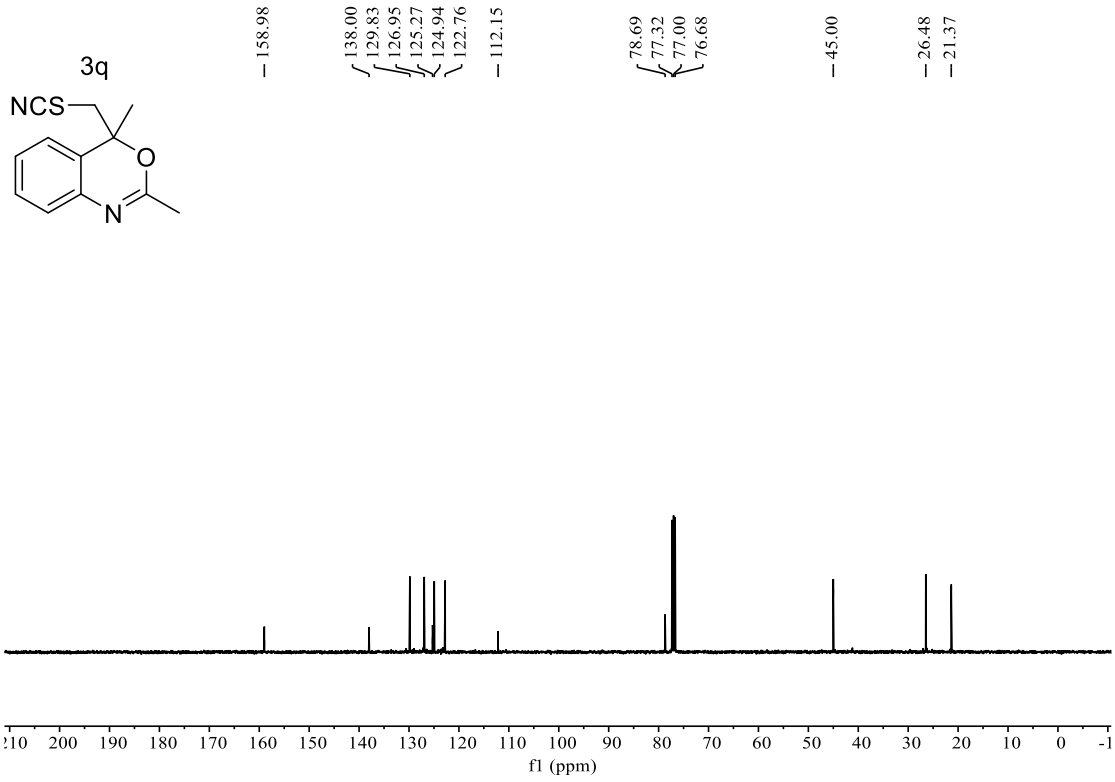
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3p**



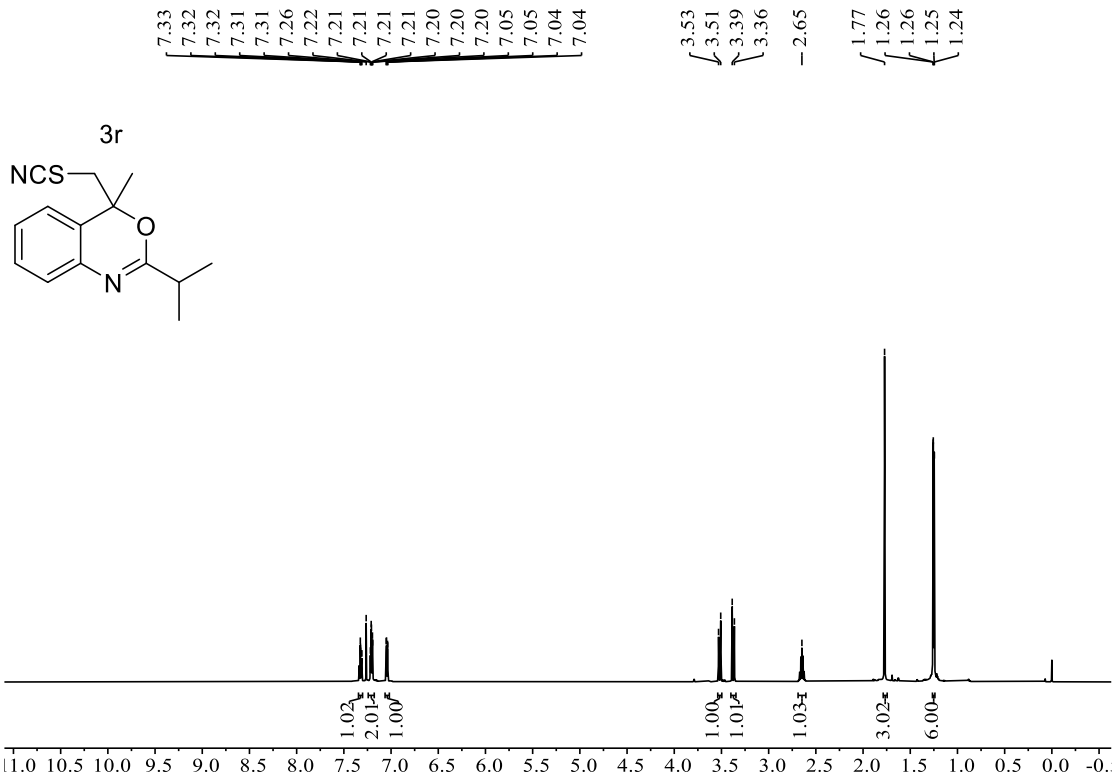
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**



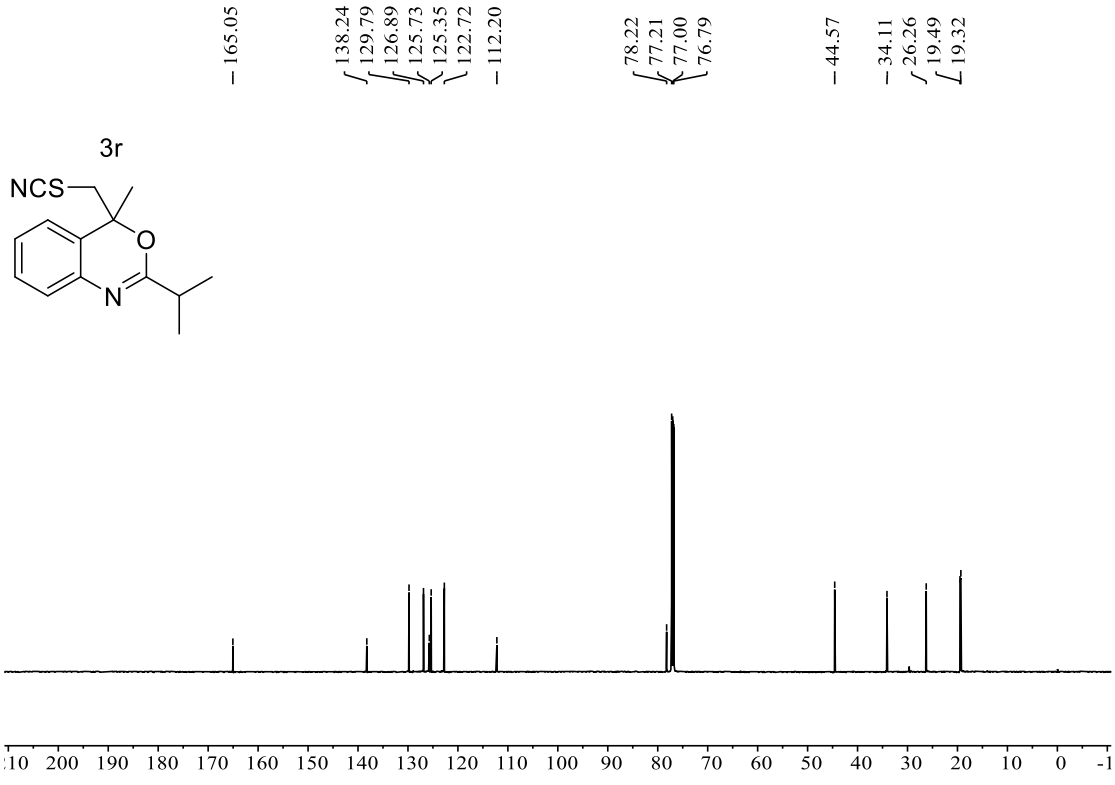
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3q**



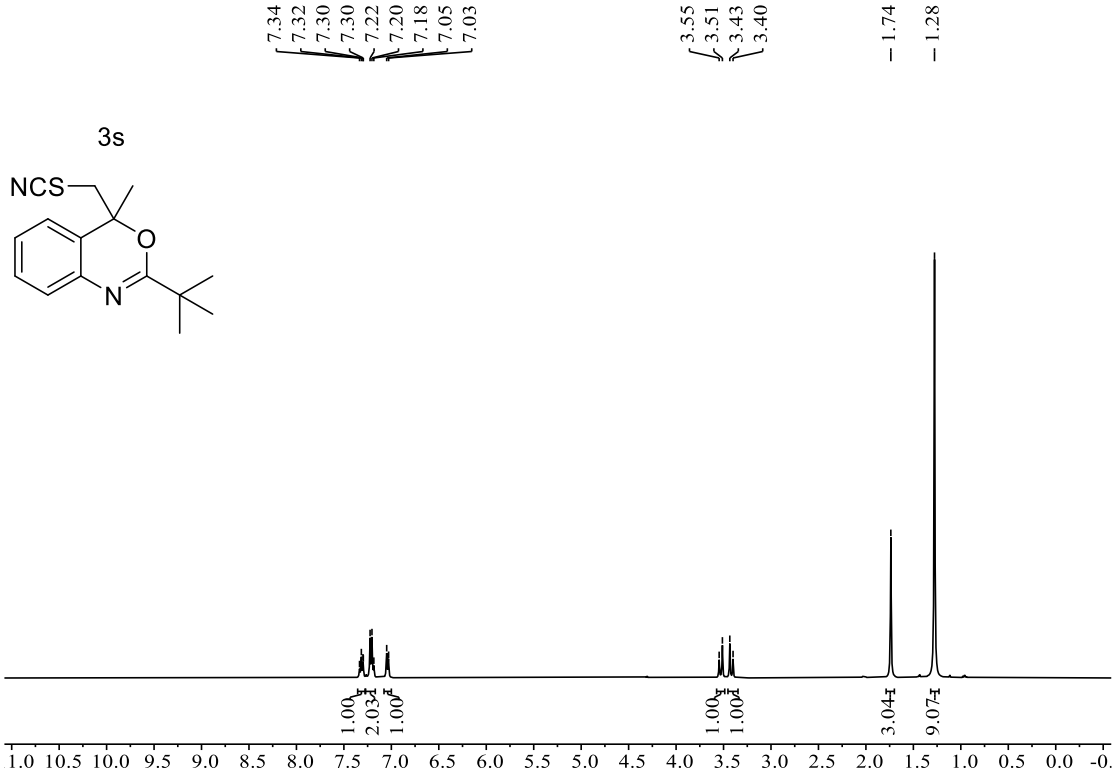
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**



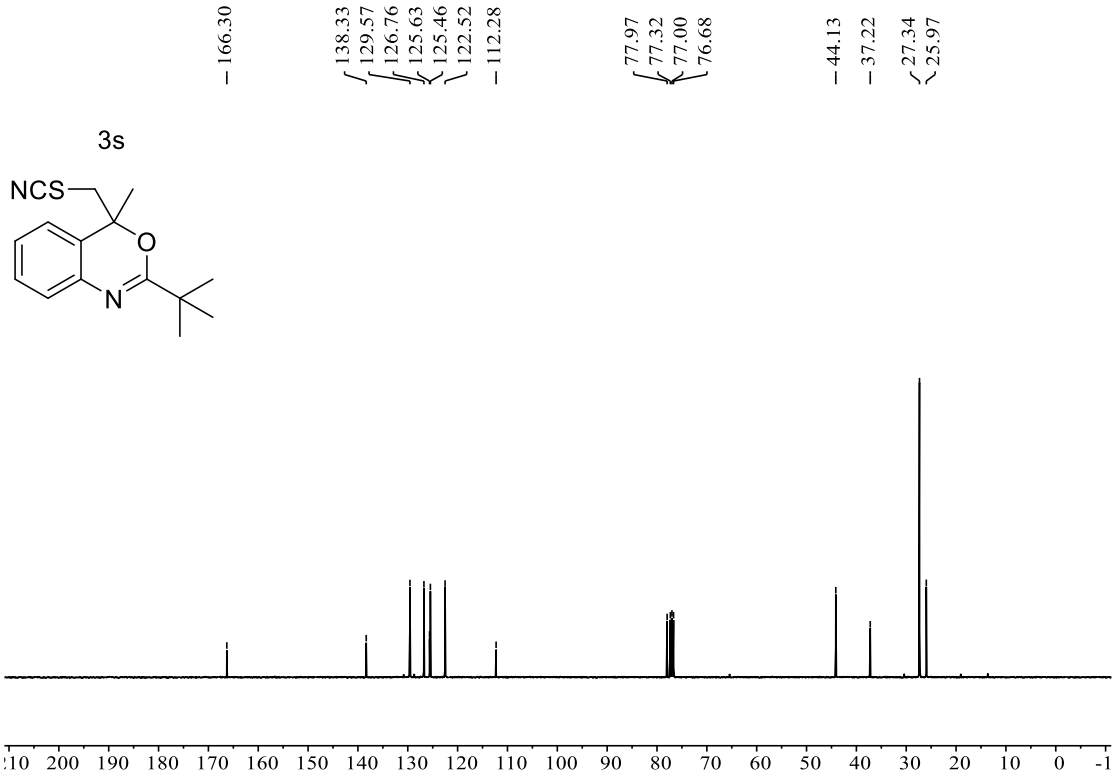
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3r**



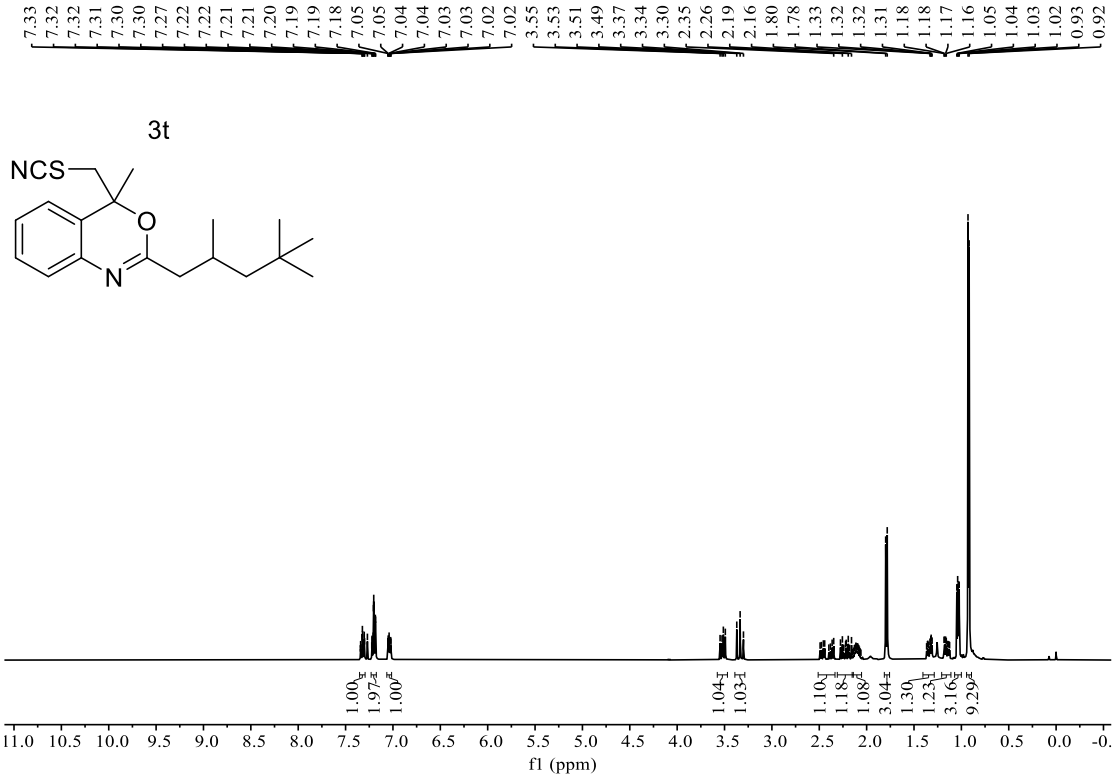
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3s**



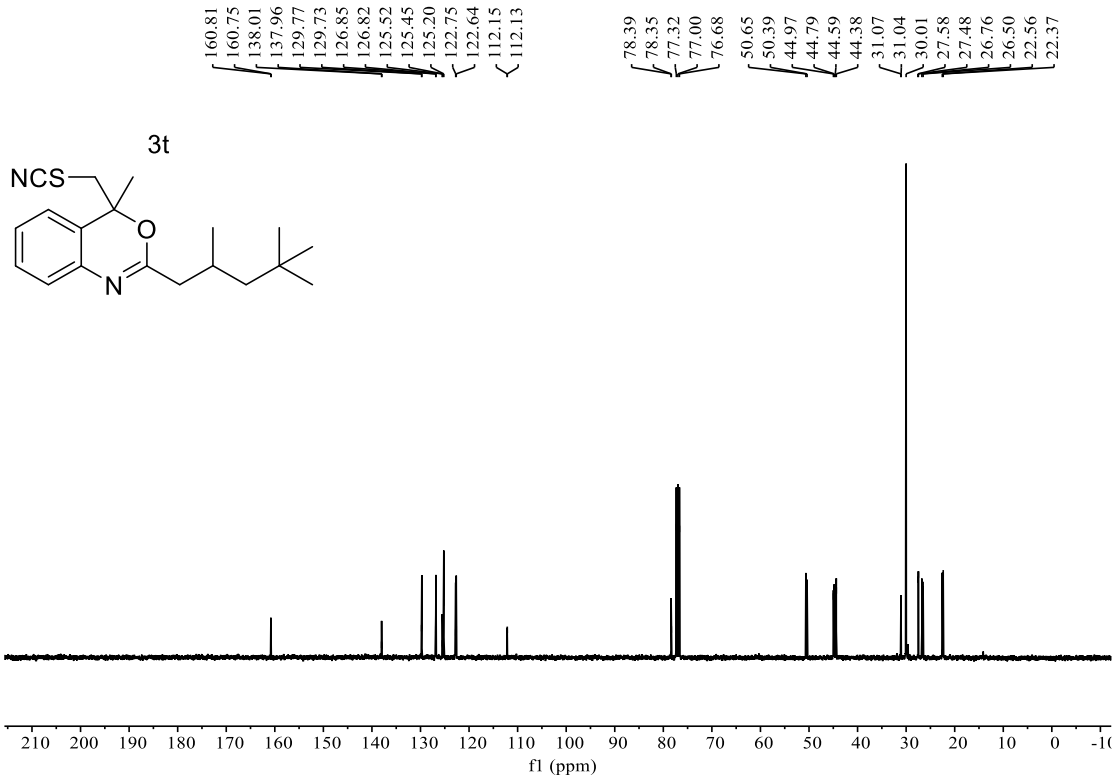
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3s**



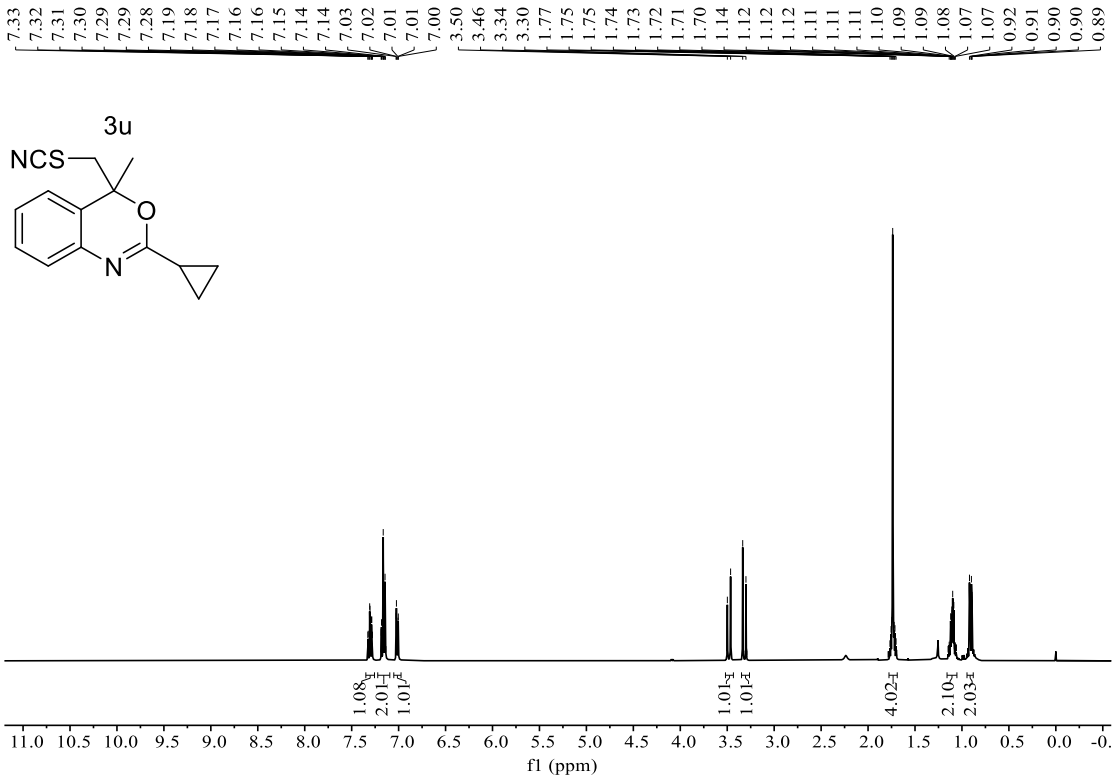
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3t**



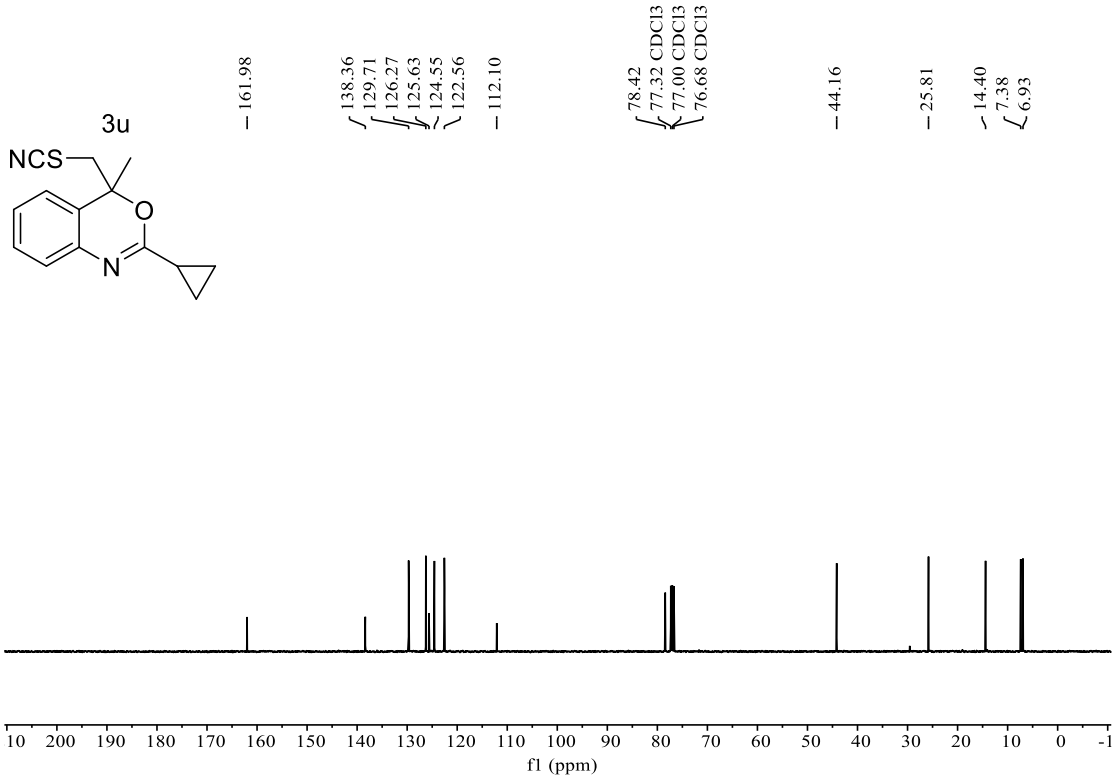
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3t**



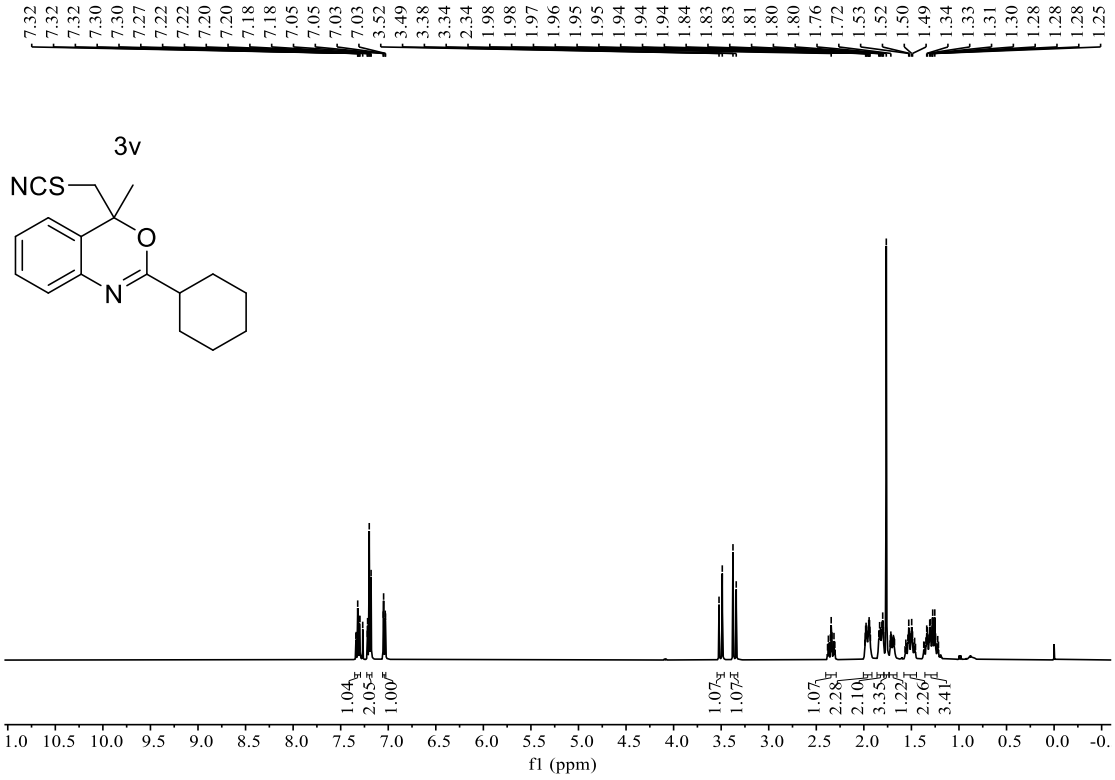
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3u**



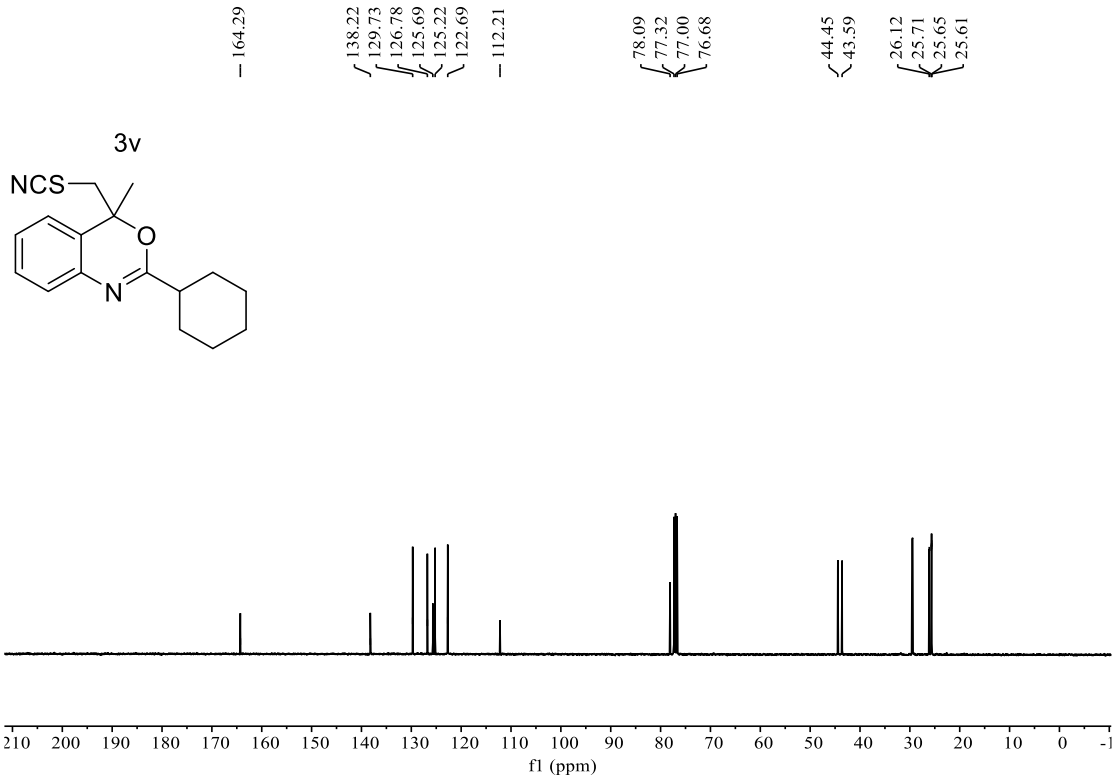
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3u**



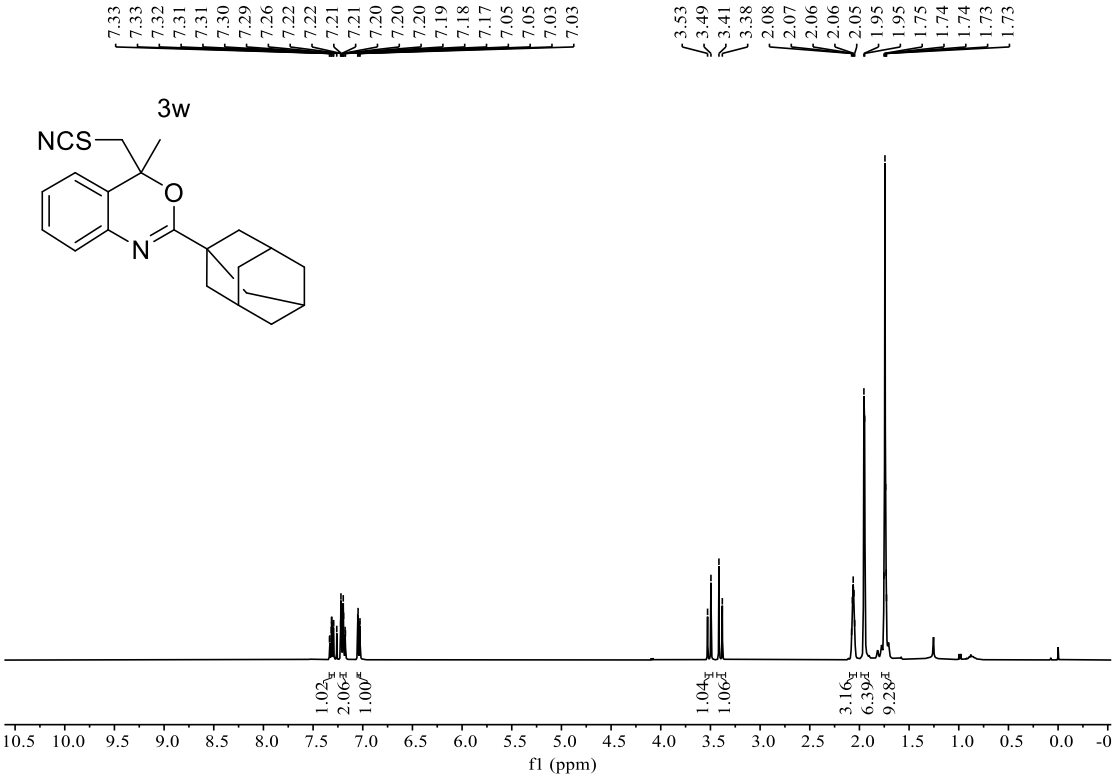
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3v**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3v**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3w**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3w**