Supplementary Information (SI) for ChemComm.

Metal-Free Halogen Atom Transfer for Carbocyclization of *N*-Arylacrylamides Enabled by Visible Light-Excited Ligated Boryl Radical

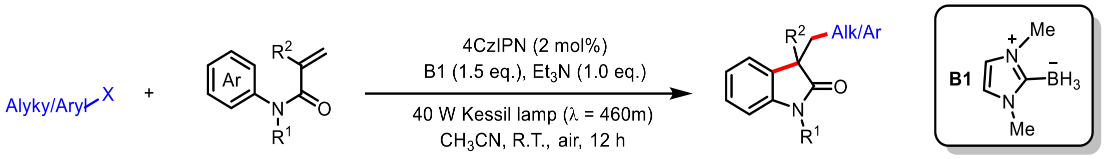
Content

1. General Information

Chemicals were purchased from commercial suppliers and used as delivered. aniline, methacryloyl chloride, triethylamine, MeCN and various photocatalyst are bought from Adamas, TCI and Sigma-Aldrich. Propargyl alcohol derivatives were prepared according to related literatures1-7. Deuterated solvents were bought from Adamas. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the following spectrometers: Bruker Avance-III-500. Chemical shifts are given in ppm and coupling constants in Hz. The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet) and m (multiplet) as well as combinations of them. When combinations of multiplicities are given the first character noted refers to the biggest coupling constant. All ^{13}C NMR spectra were measured with 1H-decoupling. Mass spectra (MS and HRMS) were measured on an Agilent 6546 TOF LC-MS spectrometer. Infrared X-ray crystal structure analyses were measured on a Bruker D8 Quest instrument using Mo-Kα-radiation. Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS based on the Laue symmetry of reciprocal space. Heavy atom diffractions were solved by direct methods and refined against F2 with full matrix least square algorithm. Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined using the SHELXTL software package. Melting Points were measured in open glass capillaries in a Büchi melting point apparatus. Flash Column Chromatography was accomplished using Silica gel 60 (0.04 - 0.063 mm / 230 - 400 mesh ASTM) purchased from Santai Science Inc. or Aluminium oxide (neutral or basic) purchased from Santai Science Inc. As eluents, mixtures of petroleum ether (PE), ethyl acetate (EA), dichloromethane (DCM) and methanol (MeOH) were used. Analytical Thin Layer Chromatography (TLC) was carried out on precoated Yantai POLYGRAM® SIL G/UV254 or POLYGRAM® ALOX N/UV254 plastic sheets. Detection was accomplished using UV-light (254 nm), KMnO4 (in 1.5M Na2CO3 (aq.)), molybdatophosphoric acid (5 % in ethanol), vanillin/H2SO4 (in ethanol) or anisaldehyde/HOAc (in ethanol). IUPAC names of the compounds described in the experimental section were determined with the program ACDLabs 12.0®.
Attention: The reaction temperature could reach and stabilize at 60°C measured by an infrared thermometer under prolonged 40W LED irradiation. The LED was positioned 4 cm from the reaction tube. By employing a fan for cooling, the reaction temperature can be maintained at around 25°C, which is our controlled room temperature.

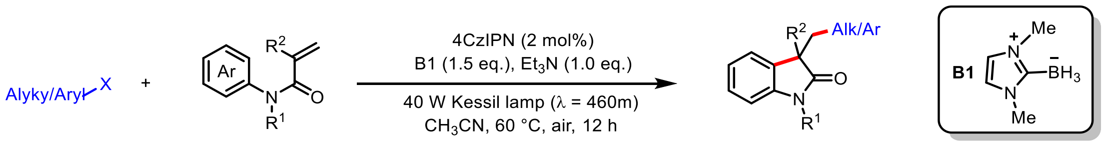
2. Experimental Procedures

General procedure for the cyclization at room temperature – GP1



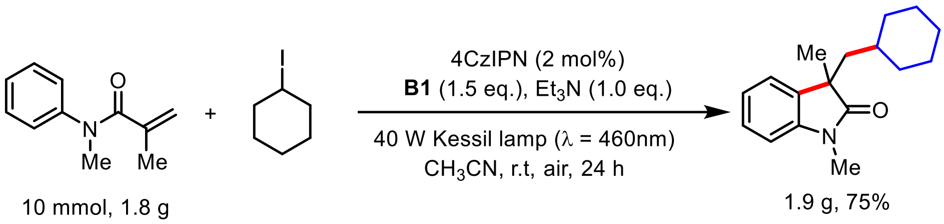
To a 10 mL pre-dried Schlenk tube equipped with a magnetic stirring bar were added *N*-Arylacrylamides (0.2 mmol, 10. equiv), 4CzIPN (2 mol%) and NHC-BH_3 (0.3 mmol, 1.5 equiv) were dissolved in MeCN (2.0 mL). Then, the alkyl or aryl halides (0.3 mmol, 1.5 equiv) and Et_3N (0.2 mmol, 1.0 equiv) were added. The reaction was placed approximately 4 cm from 40 W Kessil light (460 nm) temperature for 12 h. The LEDs were switched on and the mixture was stirred under irradiation at room temperature for 12 h with a fan. The reaction was monitored by TLC. After the reaction completed, the reaction mixture was concentrated in vacuo. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with CH_2Cl_2 (3 x 10 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product.

General procedure for the cyclization at 60 ºC – GP2



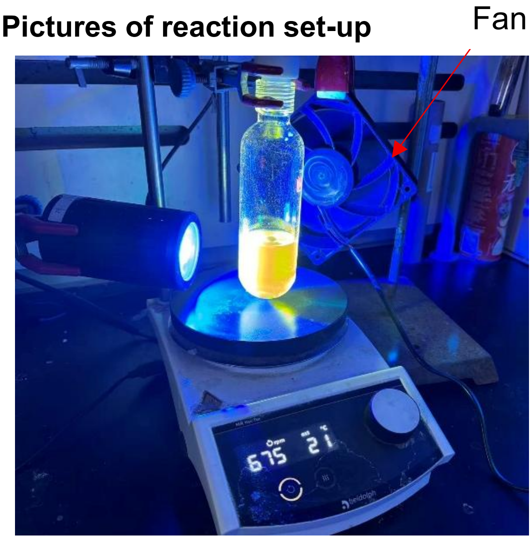
To a 10 mL pre-dried Schlenk tube equipped with a magnetic stirring bar were added *N*-Arylacrylamides (0.2 mmol, 10. equiv), 4CzIPN (2 mol%) and NHC-BH_3 (0.3 mmol, 1.5 equiv) were dissolved in MeCN (2.0 mL). Then, the alkyl or aryl halides (0.3 mmol, 1.5 equiv) and Et_3N (0.2 mmol, 1.0 equiv) were added. The reaction was placed approximately 4 cm from 40 W Kessil light (460 nm) temperature for 12 h. The LEDs were switched on and the mixture was stirred under irradiation, reaching a constant temperature of 60ºC. The reaction was monitored by TLC, After the reaction completed, the tube was allowed to cool down to room temperature and the reaction mixture was concentrated in vacuo. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with CH_2Cl_2 (3 x 10 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product.

Representative procedure for the scale-up reaction



To a 100 mL pre-dried Schlenk tube equipped with a magnetic stirring bar were added *N*-Arylacrylamides (10 mmol, 1.0 equiv), 4CzIPN (2 mol%) and NHC-BH_3 (15 mmol, 1.5 equiv) were dissolved in MeCN (50.0 mL). Then, the aryl halides (15 mmol, 1.5 equiv) and Et_3N (10 mmol, 1.0 equiv) were added. The reaction was placed approximately 4 cm from 40 W Kessil light (460 nm) temperature for 24 h. The LEDs were switched on and the mixture was stirred under irradiation at room temperature for 24 h with a fan. The reaction was monitored by TLC. After the reaction completed, the reaction mixture was concentrated in vacuo. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with CH_2Cl_2 (3 x 10 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product.

Pictures of reaction set-up



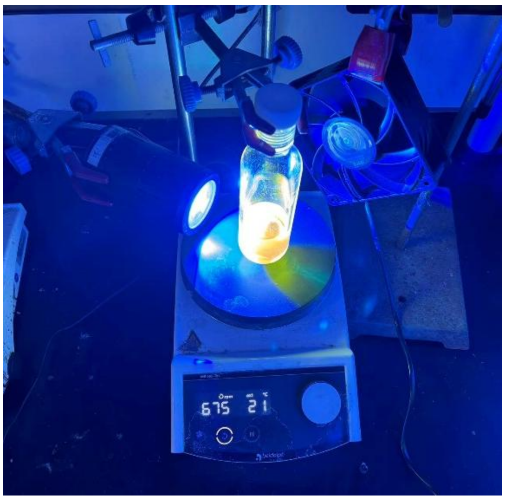
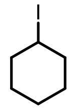


Figure S1. Set up for photochemical reactions under 460 nm with a 40 W Kessil light.

Starting materials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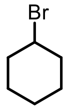
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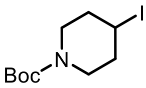
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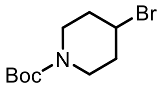
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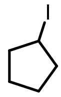
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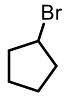
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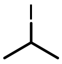
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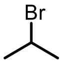
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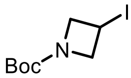
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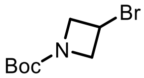
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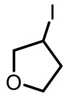
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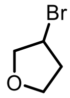
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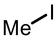
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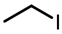
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1o


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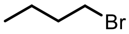
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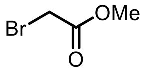
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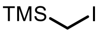
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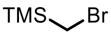
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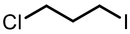
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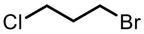
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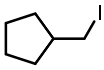
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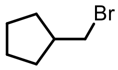
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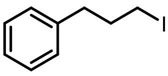
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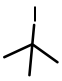
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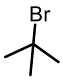
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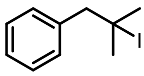
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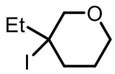
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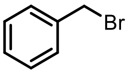
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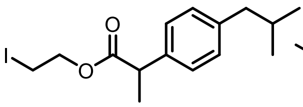
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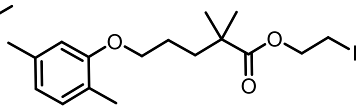
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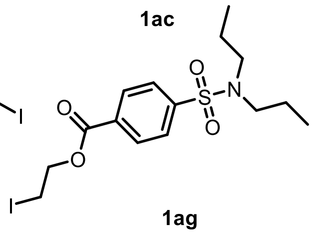
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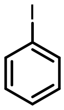
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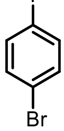
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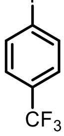
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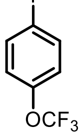
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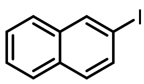
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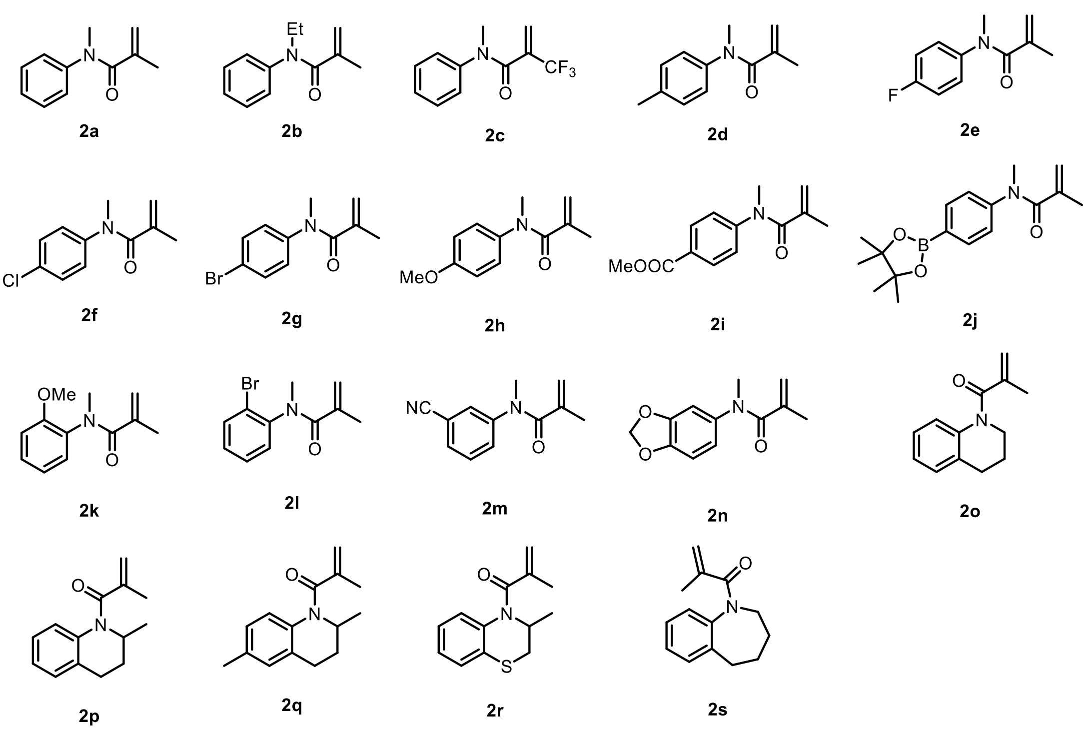
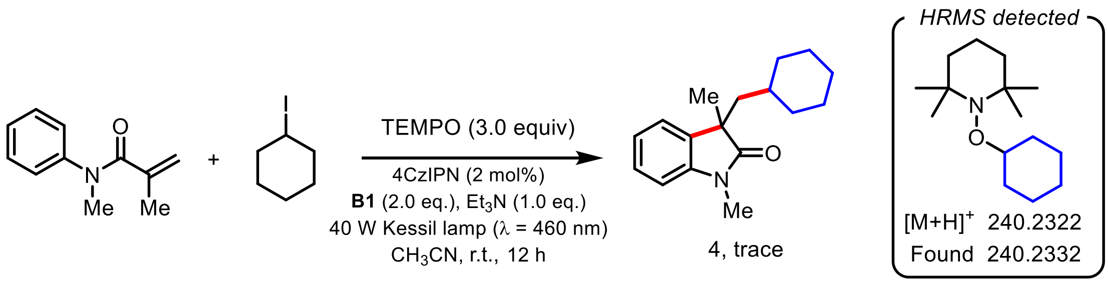
Alkyl/aryl halides employed for the substrate scope.

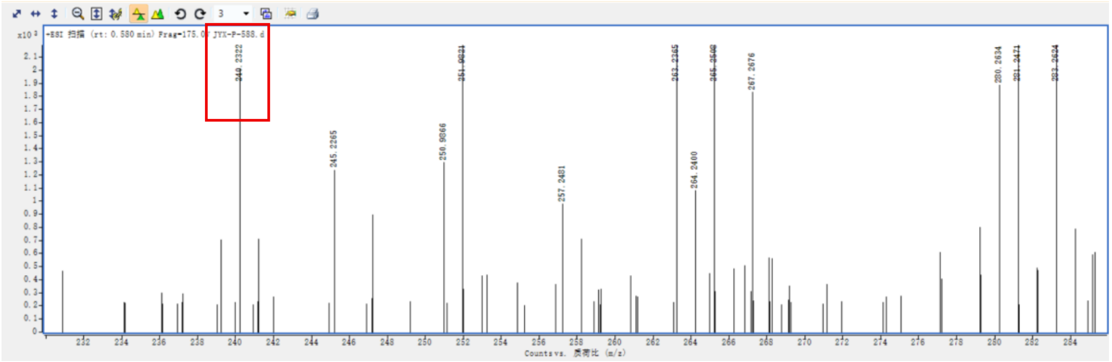


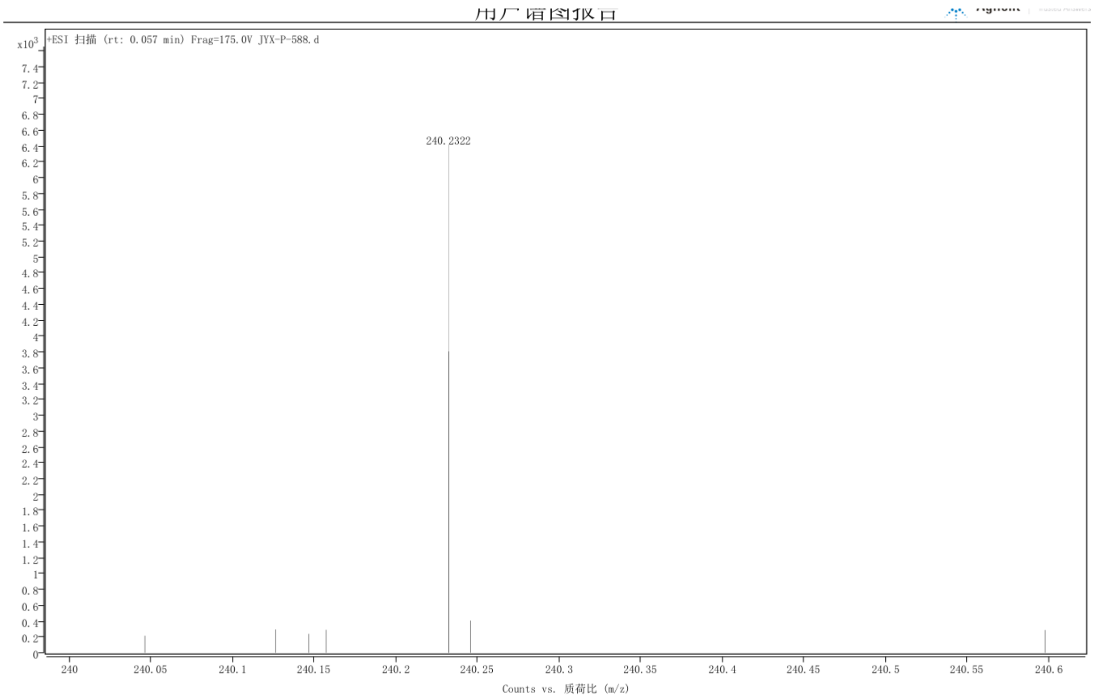
***N*-Arylacrylamides employed for the substrate scope.**

3. Mechanistic Experiments

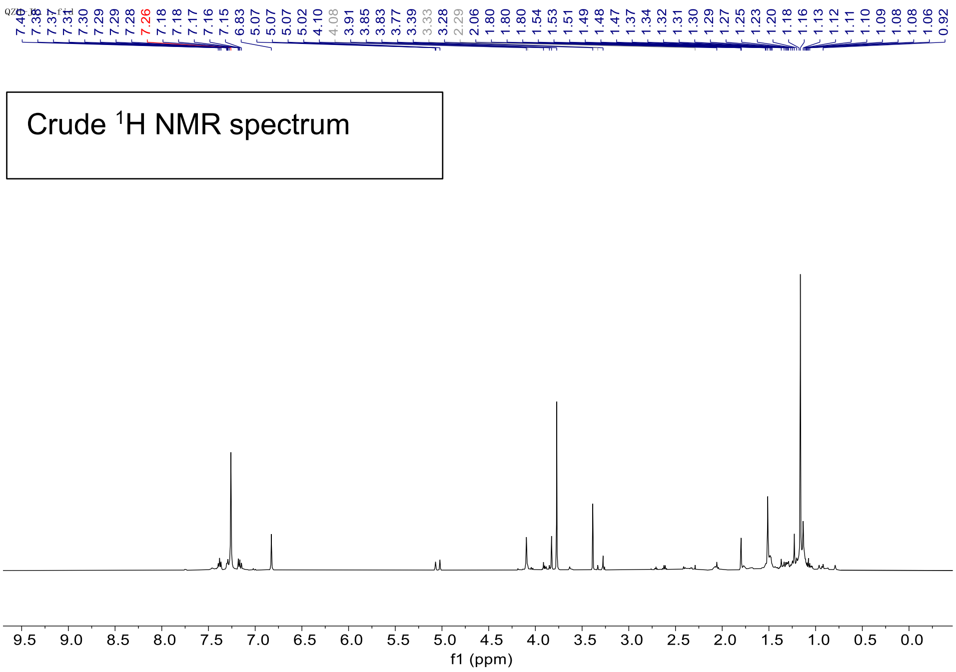


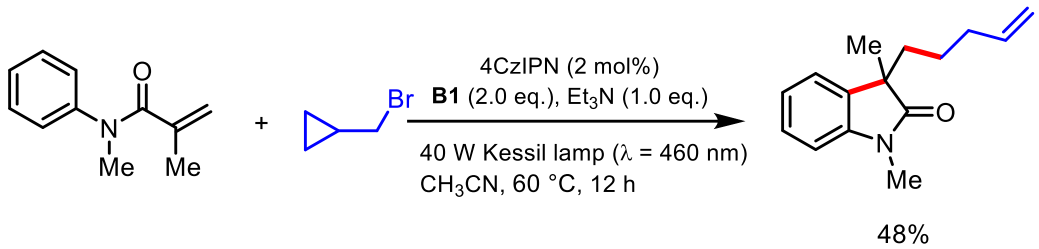
To a 10 mL pre-dried Schlenk tube equipped with a magnetic stirring bar were added *N*-Arylacrylamides (0.2 mmol, 10. equiv), 4CzIPN (2 mol%), NHC-BH_3 (0.3 mmol, 1.5 equiv) and TEMPO (0.6 mmol) were dissolved in MeCN (2.0 mL). Then, the Iodocyclohexane (0.3 mmol, 1.5 equiv) and Et_3N (0.2 mmol, 1.0 equiv) were added. The reaction was placed approximately 4 cm from 40 W Kessil light (456 nm) temperature for 12 h. The LEDs were switched on and the mixture was stirred under irradiation at room temperature for 12 h with a fan. The reaction was monitored by TLC. After the reaction completed, the reaction mixture was concentrated in vacuo. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with CH_2Cl_2 (3 x 10 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. The crude product was dissolved in MeOH to test HRMS. The reaction was inhibited and no target product was observed.





Crude ^{1}H NMR spectrum



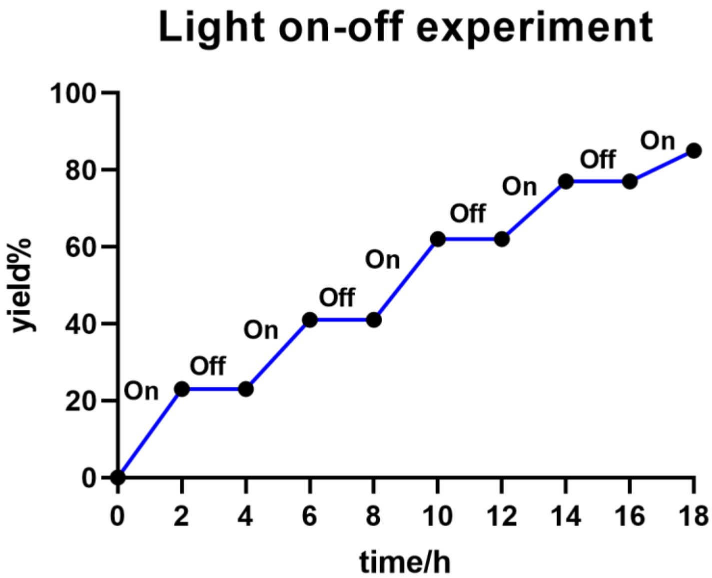


To a 10 mL pre-dried Schlenk tube equipped with a magnetic stirring bar were added *N*-Arylacrylamides (0.2 mmol, 10. equiv), 4CzIPN (2 mol%) and NHC-BH_3 (0.3 mmol, 1.5 equiv) were dissolved in MeCN (2.0 mL). Then, (Bromomethyl)cyclopropane (0.3 mmol, 1.5 equiv) and Et_3N (0.2 mmol, 1.0 equiv) were added. The reaction was placed approximately 4 cm from 40 W Kessil light (456 nm) temperature for 12 h. The LEDs were switched on and the mixture was stirred under irradiation, reaching a constant temperature of 60ºC. The reaction was monitored by TLC, After the reaction completed, the tube was allowed to cool down to room temperature and the reaction mixture was concentrated in vacuo. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with CH_2Cl_2 (3 x 10 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product.

Light on-off experiment

To a 10 mL pre-dried Schlenk tube equipped with a magnetic stirring bar were added N-Arylacrylamides (0.2 mmol, 10. equiv), 4CzIPN (2 mol%), NHC-BH_3 (0.3 mmol, 1.5 equiv) were dissolved in MeCN (2.0 mL). Then, the Iodocyclohexane (0.3 mmol, 1.5 equiv) and Et_3N (0.2 mmol, 1.0 equiv) were added. The vial was wrapped in tin foil and a 20 μL sample of the reaction mixture was taken with a syringe and measured by ^1H NMR. After being stirred for 2 hours in dark, a 20 μL sample of the reaction mixture was taken with a syringe and measured by ^1H NMR. The reaction mixture was then irradiated with blue LEDs and stirred for2 hours. Repeating this process four times.

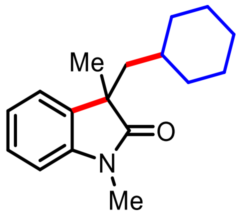
These resulted in a total interruption of the reaction progress in the absence of light and recuperation of reactivity on further illumination. The results demonstrated that light was a necessary component of the reaction. Even though we could not definitively rule out a radical-chain process, the data shown that any chain-propagation process must be short-lived.



Light on-off experiment
yield%
time/h
On
Off
On
Off
On
Off
On
Off
On
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
18

4. Characterizations

<u>3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one</u> (4)



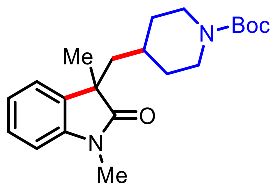
Following **GP1** using **1a** and **2a** gave **4** (44 mg, 85%, Colorless oil). Following **GP2** using **1b** and **2a** gave **4** (33 mg, 64%, Colorless oil).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 7.16 (d, *J* = 7.3, 1H), 7.08 – 7.03 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 1.96 – 1.90 (m, 1H), 1.72 (m, 1H), 1.52 – 1.43 (m, 3H), 1.31 (s, 3H), 1.28 – 1.16 (m, 2H), 0.95 (m, 4H), 0.86 – 0.72 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.2, 143.1, 134.4, 127.5, 122.7, 122.4, 107.9, 47.9, 45.4, 34.8, 34.5, 33.5, 26.2, 26.2, 26.12, 26.1, 26.0.

The spectral data obtained were identical with those reported in literature[1]

<u>tert-butyl -1,3-dimethyl-2-oxoindolin-3-yl)methyl)piperidine-1-carboxylate</u> (**5**).

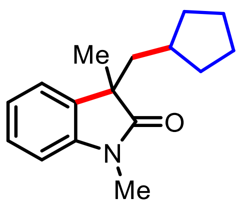


Following **GP1** using **1c** and **2a** gave **5** (45 mg, 87%, Colorless oil). Following **GP2** using **1d** and **2a** gave **5** (39 mg, 60%, Colorless oil)**.**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 6.7 Hz, 1H), 7.12 (s, 1H), 7.03 (s, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.85 (m, 2H), 3.19 (s, 3H), 2.43 – 2.29 (m, 2H), 1.96 – 1.90 (m, 1H), 1.76 – 1.62 (m, 2H), 1.41 (m, 1H), 1.36 (s, 9H), 1.29 (s, 3H), 1.08 – 0.97 (m, 3H), 0.84 (m, 1H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.8, 154.7, 143.0, 134.0, 127.8, 122.7, 122.6, 108.2, 79.2, 47.7, 44.4, 33.2, 33.0, 32.5, 28.5, 28.4, 26.3, 26.2.

The spectral data obtained were identical with those reported in literature[1]

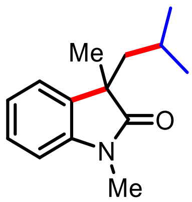
<u>3-(cyclopentylmethyl)-1,3-dimethylindolin-2-one</u> (6).



Following **GP1** using **1e** and **2a** gave **6** (39 mg, 80%, Colorless oil). Following **GP2** using **1f** and **2a** gave **6** (26 mg, 55%, Colorless oil).

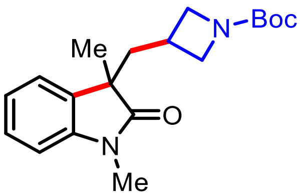
^{1}**H NMR (400 MHz, Chloroform-d)** δ 7.3 (d, J = 7.4 Hz, 1H), 7.2 (d, J = 7.3 Hz, 1H), 7.1 (t, J = 7.3 Hz, 1H), 6.8 (d, J = 7.7 Hz, 1H), 3.2 (s, 3H), 2.1 (m, 1H), 1.9 (dd, J = 13.7, 6.0 Hz, 1H), 1.4 (m, 3H), 1.3 (s, 3H), 1.3 – 1.1 (m, 4H), 1.0 – 1.0 (m, 1H), 0.8 (m, 1H). ^{13}**C NMR (100 MHz, Chloroform-*d*)** δ 181.1, 143.3, 134.4, 127.6, 122.9, 122.3, 107.9, 48.5, 44.5, 37.2, 33.8, 32.7, 26.2, 25.3, 24.9, 24.9.

<u>3-isobutyl-1,3-dimethylindolin-2-one</u> (7)



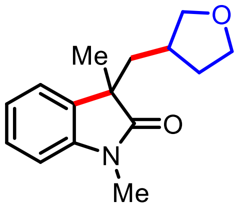
Following **GP1** using **1g** and **2a** gave **7** (32 mg, 74%, Colorless oil). Following **GP2** using **1h** and **2a** gave **7** (22 mg, 50%, Colorless oil)
^{1}**H NMR (400 MHz, Chloroform-d)** δ 7.3 – 7.2 (m, 1H), 7.2 (d, J = 7.8 Hz, 1H), 7.1 (t, J = 7.6 Hz, 1H), 6.8 (d, J = 7.8 Hz, 1H), 3.2 (s, 3H), 2.0 – 1.9 (m, 1H), 1.8 (dd, J = 14.0, 5.3 Hz, 1H), 1.3 (s, 3H), 1.3 – 1.2 (m, 2H), 0.6 (dd, J = 17.4, 6.6 Hz, 6H). ^{13}**C NMR (100 MHz, Chloroform-*d*)** δ 181.1, 143.2, 134.2, 127.6, 122.8, 122.3, 108.0, 48.1, 46.7, 26.2, 26.2, 25.6, 24.1, 22.8.
The spectral data obtained were identical with those reported in literature[1]

<u>tert-butyl 3-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)azetidine-1-carboxylate.</u> (8)



Following **GP1** using **1g** and **2a** gave **8** (32 mg, 74%, Colorless oil). Following **GP2** using **1h** and **2a** gave **8** (22 mg, 50%, Colorless oil)
^{1}**H NMR (400 MHz, Chloroform-*d*)** δ 7.2 – 7.2 (m, 1H), 7.1 (d, *J* = 7.3 Hz, 1H), 7.0 (t, *J* = 7.5 Hz, 1H), 6.8 (d, *J* = 7.7 Hz, 1H), 3.7 (t, *J* = 8.2 Hz, 1H), 3.5 – 3.3 (m, 2H), 3.2 – 3.2 (m, 1H), 3.1 (s, 3H), 2.1 (q, *J* = 5.8 Hz, 2H), 2.0 – 1.9 (m, 1H), 1.3 (s, 9H), 1.3 (s, 3H). ^{13}**C NMR (100 MHz, Chloroform-*d*)** δ 180.0, 156.1, 143.0, 133.0, 128.2, 122.8, 122.6, 108.1, 79.2, 47.7, 42.7, 28.4, 26.2, 25.7, 23.5.
The spectral data obtained were identical with those reported in literature[1]

<u>1,3-dimethyl-3-((tetrahydrofuran-3-yl)methyl)indolin-2-one</u> (9)

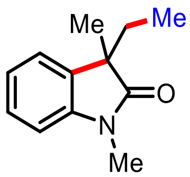


Following **GP1** using **1k** and **2a** gave **9** (44 mg, 90%, Colorless oil). Following **GP2** using **1l** and **2a** gave **9** (34mg, 70%, Colorless oil)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 1H), 7.2 (dd, *J* = 13.3, 7.2 Hz, 1H), 7.1 (td, *J* = 7.5, 4.1 Hz, 1H), 6.9 (d, *J* = 7.7 Hz, 1H), 3.7 – 3.6 (m, 2H), 3.6 – 3.5 (m, 1H), 3.2 (s, 3H), 3.2 (m, 1H), 2.2 – 2.1 (m, 1H), 2.0 – 1.7 (m, 3H), 1.5 – 1.4 (m, 1H), 1.4 (s, 3H), 1.3 – 1.2 (m, 1H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.5, 180.4, 143.2, 143.2, 133.7, 133.5, 128.1, 128.0, 122.8, 122.8, 122.6, 122.5, 108.1, 73.4, 73.1, 67.6, 67.4, 48.2, 48.2, 41.5, 41.3, 36.4, 36.2, 33.3, 32.9, 26.3, 26.2, 24.8, 24.7.

The spectral data obtained were identical with those reported in literature[1]

3-ethyl-1,3-dimethylindolin-2-one (10)

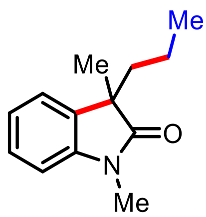


Following **GP1** using **1m** and **2a** gave **10** (44 mg, 90%, Colorless oil).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 1H), 7.1 (d, *J* = 7.4, 1H), 7.0 (d, *J* = 7.4, 1H), 6.8 (d, *J* = 7.7, 1H), 3.1 (s, 3H), 1.9 (m, 1H), 1.7 (m, 1H), 1.3 (s, 3H), 0.5 – 0.5 (m, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.8, 143.5, 134.0, 129.2, 127.6, 122.5, 122.4, 107.8, 49.0, 31.5, 26.1, 23.3, 8.8.

The spectral data obtained were identical with those reported in literature [2]

1,3-dimethyl-3-propylindolin-2-one (11)

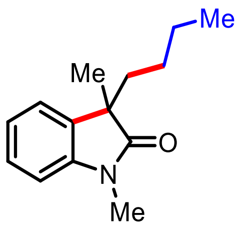


Following **GP1** using **1n** and **2a** gave **11** (25 mg, 62%, Colorless oil). Following **GP2** using **1o** and **2a** gave **11** (14 mg, 35%, Colorless oil).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (s, 1H), 7.2 (d, *J* = 7.9 Hz, 1H), 7.1 (d, *J* = 7.5 Hz, 1H), 6.8 (d, *J* = 7.8 Hz, 1H), 3.2 (s, 3H), 1.9 – 1.8 (m, 1H), 1.7 (m, 1H), 1.3 (s, 3H), 1.0 – 1.0 (m, 1H), 0.9 (m, 1H), 0.8 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 180.9, 143.3, 134.3, 127.6, 122.5, 122.4, 107.8, 48.5, 40.8, 23.7, 17.9, 14.2.

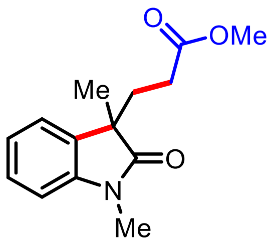
The spectral data obtained were identical with those reported in literature[3]

3-butyl-1,3-dimethylindolin-2-one (12)



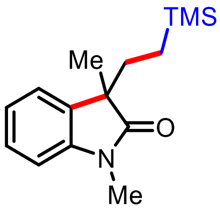
Following **GP1** using **1p** and **2a** gave **12** (30 mg, 70%, Colorless oil). Following **GP2** using **1q** and **2a** gave **12** (16 mg, 35%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 2H), 7.2 (d, *J* = 7.3 Hz, 1H), 7.1 (t, *J* = 7.5 Hz, 1H), 6.8 (d, *J* = 7.8 Hz, 1H), 3.2 (s, 3H), 1.9 – 1.8 (m, 1H), 1.8 – 1.7 (m, 1H), 1.3 (s, 3H), 1.2 (m, 4H), 1.0 – 0.8 (m, 2H), 0.8 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 48.5, 38.5, 31.9, 26.1, 24.1, 23.8, 22.3, 14.0.
The spectral data obtained were identical with those reported in literature[4]

<u>methyl 3-(1,3-dimethyl-2-oxoindolin-3-yl)propanoate</u> (**13**)



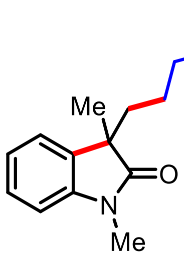
Following **GP1** using **1r** and **2a** gave **13** (28 mg, 51%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-d) δ 7.3 – 7.2 (m, 1H), 7.2 (m, , 1H), 7.1 (dd, J = 7.5, 1.0 Hz, 1H), 6.8 (m, 1H), 3.5 (s, 3H), 3.2 (s, 3H), 2.3 – 2.2 (m, 1H), 2.1 (dd, J = 10.7, 4.9 Hz, 1H), 2.0 (dd, J = 10.7, 5.1 Hz, 1H), 1.9 – 1.8 (m, 1H), 1.4 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 179.9, 173.2, 143.3, 132.9, 128.1, 122.7, 122.7, 108.1, 51.6, 47.6, 33.0, 29.4, 26.2, 23.6.
The spectral data obtained were identical with those reported in literature[5]

<u>1,3-dimethyl-3-(3-(trimethylsilyl)propyl)indolin-2-one</u> (**14**)



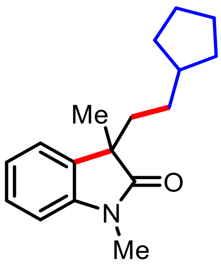
Following **GP1** using **1s** and **2a** gave **14** (40 mg, 73%, Colorless oil). Following **GP2** using **1t** and **2a** gave **14** (20 mg, 45%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.4 (d, *J* = 7.8, 1H), 7.3 – 7.2 (m, 1H), 7.2 (t, *J* = 7.4 Hz, 1H), 6.9 (d, *J* = 7.7 Hz, 1H), 3.3 (d, *J* = 1.3 Hz, 3H), 2.0 (m, 1H), 1.8 – 1.7 (m, 1H), 1.4 (s, 3H), 0.3 – 0.2 (m, 1H), 0.1 – 0.1 (m, 1H), -0.0 (d, *J* = 1.3 Hz, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 182.8, 145.6, 136.2, 129.5, 124.4, 124.4, 109.8, 51.9, 35.0, 31.7, 28.1, 25.1, 12.7, 3.0.
The spectral data obtained were identical with those reported in literature[1]

<u>3-(4-chlorobutyl)-1,3-dimethylindolin-2-one</u> (**15**)



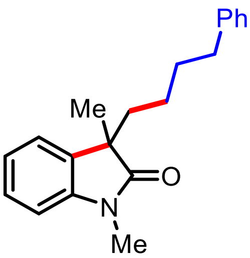
Following **GP1** using **1u** and **2a** gave **15** (35 mg, 70%, Colorless oil). Following **GP2** using **1v** and **2a** gave **15** (20 mg, 45%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 1H), 7.2 (d, J = 7.3 Hz, 1H), 7.1 (d, J = 7.5 Hz, 1H), 6.8 (d, J = 7.8 Hz, 1H), 3.4 (td, J = 6.8, 1.5 Hz, 2H), 3.2 (s, 3H), 1.9 (m, 1H), 1.8 (m, 1H), 1.6 (m, 2H), 1.3 (s, 3H), 1.0 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.6, 143.3, 133.8, 127.8, 122.6, 122.5, 108.0, 48.3, 44.5, 37.6, 32.6, 26.2, 23.8, 22.0.
The spectral data obtained were identical with those reported in literature[6]

<u>3-(2-cyclopentylethyl)-1,3-dimethylindolin-2-one</u> (**16**)



Following **GP1** using **1w** and **2a** gave **16** (41 mg, 75%, Colorless oil). Following **GP2** using **1x** and **2a** gave **16** (27 mg, 50%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (s, 1H), 7.2 (d, J = 7.3 Hz, 1H), 7.1 (d, J = 7.5 Hz, 1H), 6.8 (d, J = 7.8 Hz, 1H), 3.2 (s, 3H), 1.9 (m, 1H), 1.7 (m, 1H), 1.7 – 1.6 (m, 4H), 1.5 – 1.4 (m, 2H), 1.3 (s, 3H), 1.0 – 0.8 (m, 5H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 179.8, 142.3, 133.3, 128.5, 126.5, 121.4, 121.4, 106.8, 47.4, 39.1, 36.7, 31.5, 31.4, 29.6, 28.7, 25.1, 24.1, 23.9, 22.8.
The spectral data obtained were identical with those reported in literature[1]

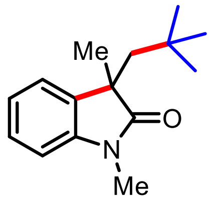
<u>1,3-dimethyl-3-(4-phenylbutyl)indolin-2-one</u> (17)



Following **GP1** using **1y** and **2a** gave **17** (36 mg,62%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.2 – 7.1 (m, 3H), 7.1 – 7.0 (m, 2H), 7.0 (d, J = 7.4 Hz, 3H), 6.7 (d, J = 7.7 Hz, 1H), 3.1 (s, 3H), 2.5 – 2.3 (m, 2H), 1.9 – 1.9 (m, 1H), 1.8 – 1.7 (m, 1H), 1.3 (s, 3H), 1.2 – 1.0 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ

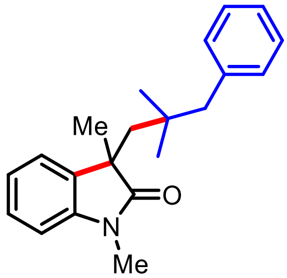
180.7, 143.3, 141.9, 134.0, 128.4, 128.3, 127.7, 125.8, 122.5, 122.5, 108.0, 48.4, 38.2, 36.0, 26.4, 26.2, 23.9.
The spectral data obtained were identical with those reported in literature[1]

1,3-dimethyl-3-neopentylindolin-2-one (18)



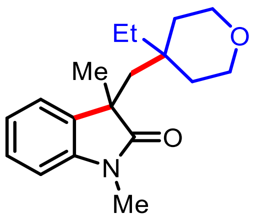
Following **GP1** using **1z** and **2a** gave **18** (31 mg, 68%, Colorless oil). Following **GP2** using **1aa** and **2a** gave **18**(18 mg, 40%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (s, 1H), 7.2 (d, *J* = 7.4 Hz, 1H), 7.0 (d, *J* = 7.5 Hz, 1H), 6.8 (d, *J* = 7.7 Hz, 1H), 3.2 (s, 3H), 2.2 (d, *J* = 14.3 Hz, 1H), 1.9 (d, *J* = 14.4 Hz, 1H), 1.3 (s, 3H), 0.6 (d, *J* = 1.3 Hz, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 181.1, 142.9, 134.2, 127.5, 123.9, 122.0, 108.0, 50.8, 47.4, 31.8, 30.8, 28.3, 26.3.
The spectral data obtained were identical with those reported in literature[1]

3-(2,2-dimethyl-3-phenylpropyl)-1,3-dimethylindolin-2-one (19)



Following **GP1** using **1ab** and **2a** gave **19** (43 mg, 68%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 2H), 7.2 – 7.2 (m, 3H), 7.0 – 7.0 (m, 3H), 6.9 (d, *J* = 7.7 Hz, 1H), 3.2 (d, *J* = 1.4 Hz, 3H), 2.4 (d, *J* = 12.9 Hz, 1H), 2.3 – 2.2 (m, 2H), 1.9 (d, *J* = 14.3 Hz, 1H), 1.3 (s, 3H), 0.6 (s, 3H), 0.4 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 181.1, 142.8, 138.8, 134.2, 130.7, 127.6, 127.6, 125.8, 124.0, 122.1, 108.1, 50.6, 50.1, 47.3, 35.4, 28.6, 27.4, 27.0, 26.3.
HRMS (ESI) (m/z): Calcd for: $C_{20}H_{24}NO$ $[M + H]^+$: 308.2009 found: 2308.2006.

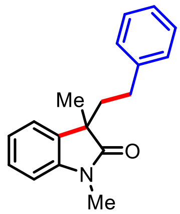
3-((4-ethyltetrahydro-2H-pyran-4-yl)methyl)-1,3-dimethylindolin-2-one (20)



Following **GP1** using **1ac** and **2a** gave **20** (29 mg, 68%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 2H), 7.0 (td, *J* = 7.5, 1.0 Hz, 1H), 6.8 (d, *J* = 7.8 Hz, 1H), 3.6 – 3.4 (m, 4H), 3.2 (s, 3H), 2.2 (d, *J* = 14.8 Hz, 1H), 2.0 (s, 1H), 1.3 (s, 3H), 1.2 – 1.1 (m, 3H), 1.1 – 0.9 (m, 3H), 0.7 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR**

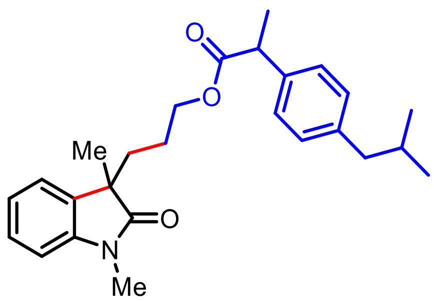
(100 MHz, Chloroform-*d*) δ 180.7, 142.6, 134.1, 127.8, 123.4, 122.0, 108.2, 63.4, 63.3, 46.7, 44.8, 35.9, 35.6, 34.6, 28.7, 27.0, 26.3, 7.4.
HRMS (ESI) (m/z): Calcd for: $C_{18}H_{26}NO_2$ [M + H]$^+$: 288.1958 found: 288.1956.

1,3-dimethyl-3-phenethylindolin-2-one (21)



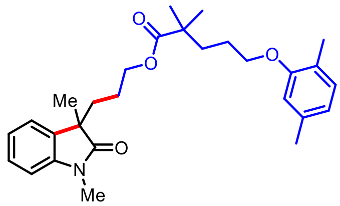
Following **GP2** using **1ad** and **2a** gave **21** (30 mg, 56%, Colorless oil).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.3 – 7.3 (m, 1H), 7.2 – 7.2 (m, 3H), 7.1 – 7.1 (m, 2H), 7.0 – 7.0 (m, 2H), 6.9 (d, *J* = 7.8 Hz, 1H), 3.2 (s, 3H), 2.3 – 2.3 (m, 2H), 2.0 (s, 2H), 1.4 (s, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 180.4, 143.5, 141.4, 133.8, 128.3, 128.3, 127.9, 125.9, 122.6, 122.5, 108.0, 48.4, 40.3, 31.0, 26.2, 24.0.
The spectral data obtained were identical with those reported in literature[7]

3-(1,3-dimethyl-2-oxoindolin-3-yl)propyl 2-(4-isobutylphenyl)propanoate (**22**)



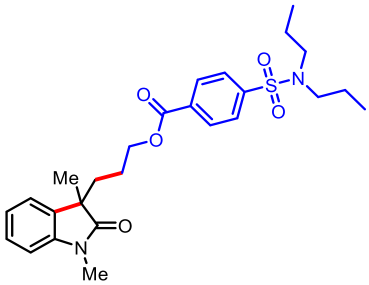
Following **GP1** using **1ae** and **2a** gave **22** (64 mg, 64%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.2 (s, 1H), 7.2 (d, *J* = 8.1 Hz, 2H), 7.1 (d, *J* = 7.8 Hz, 2H), 7.0 (d, *J* = 9.2 Hz, 2H), 6.8 (d, *J* = 7.7 Hz, 1H), 3.9 (q, *J* = 6.0 Hz, 2H), 3.7 – 3.6 (m, 1H), 3.2 (s, 3H), 2.5 (d, *J* = 7.2 Hz, 2H), 1.8 (m, 2H), 1.4 (d, *J* = 7.2, 3H), 1.3 (s, 3H), 1.3 (m, 1H), 1.1 (m, 1H), 0.9 (d, *J* = 6.6 Hz, 7H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.3, 180.3, 174.6, 143.2, 143.2, 140.5, 137.9, 137.8, 133.6, 133.6, 129.3, 129.3, 127.9, 127.2, 127.2, 126.5, 122.6, 122.4, 108.0, 108.0, 64.3, 64.2, 47.9, 47.9, 45.2, 45.1, 45.0, 34.5, 30.2, 26.2, 23.9, 23.8, 22.4, 18.6, 18.3.
HRMS (ESI) (m/z): Calcd for: $C_{25}H_{32}NO_3$ [M + H]$^+$: 408.2533 found: 408.2539.

3-(1,3-dimethyl-2-oxoindolin-3-yl) propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (23)



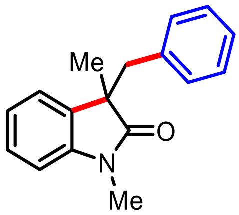
Following **GP1** using **1af** and **2a** gave **23** (61 mg, 68%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (d, *J* = 2.1 Hz, 1H), 7.2 (d, *J* = 7.1 Hz, 1H), 7.1 (d, *J* = 7.5 Hz, 1H), 7.0 (d, *J* = 7.5 Hz, 1H), 6.8 (d, *J* = 7.8 Hz, 1H), 6.7 (d, *J* = 7.5 Hz, 1H), 6.6 (s, 1H), 3.9 (q, *J* = 5.3 Hz, 4H), 3.2 (s, 3H), 2.3 (s, 3H), 2.2 (s, 3H), 2.0 (m, 1H), 1.8 – 1.8 (m, 1H), 1.7 (d, *J* = 2.9 Hz, 4H), 1.4 (s, 4H), 1.2 (s, 7H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.3, 177.7, 157.0, 143.3, 136.5, 133.7, 130.3, 127.9, 123.6, 122.6, 122.4, 120.7, 112.0, 108.0, 68.0, 64.1, 48.0, 42.1, 37.0, 34.8, 26.1, 25.2, 25.2, 24.0, 23.8, 21.4, 15.8.
HRMS (ESI) (m/z): Calcd for: $C_{28}H_{38}NO_4$ $[M + H]^+$: 452.2795 found: 452.2785.

3-<u>(1,3-dimethyl-2-oxoindolin-3-yl)propyl 4-(N-butyl-N-propylsulfamoyl)benzoate</u> (24)



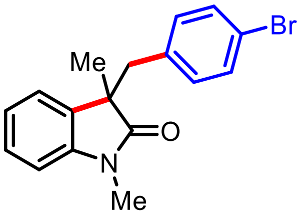
Following **GP1** using **1ag** and **2a** gave **24** (80 mg, 80%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.0 (d, *J* = 8.1 Hz, 2H), 7.8 (d, *J* = 8.2 Hz, 2H), 7.2 (d, *J* = 7.5 Hz, 1H), 7.1 (d, *J* = 7.3 Hz, 1H), 7.0 (d, *J* = 7.5 Hz, 1H), 6.8 (d, *J* = 7.8 Hz, 1H), 4.1 (d, *J* = 6.5 Hz, 2H), 3.2 (s, 3H), 3.0 – 3.0 (m, 4H), 2.0 (m, 1H), 1.8 (m, 1H), 1.5 (q, *J* = 7.6 Hz, 6H), 1.3 (s, 3H), 0.8 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.2, 165.1, 144.2, 143.3, 133.5, 130.2, 128.0, 127.0, 122.7, 122.5, 108.2, 65.3, 49.9, 48.0, 34.7, 26.2, 24.0, 23.8, 21.9, 11.2.
HRMS (ESI) (m/z): Calcd for: $C_{26}H_{35}N_2O_5$ $[M + H]^+$: 487.2261 found: 487.2270.

<u>3-benzyl-1,3-dimethylindolin-2-one</u> (**25**)



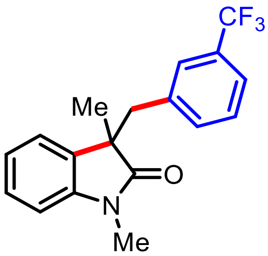
Following **GP1** using **1ah** and **2a** gave **25** (26 mg, 52%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.1 (m, 1H), 7.1 (m, 1H), 7.0 – 7.0 (m, 4H), 6.8 – 6.8 (m, 2H), 6.6 (d, *J* = 7.8 Hz, 1H), 3.1 – 3.0 (m, 2H), 2.9 (s, 3H), 1.4 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.0, 143.1, 136.2, 133.0, 129.8, 127.8, 127.5, 126.4, 123.3, 122.1, 107.8, 49.9, 44.6, 25.9, 22.7.
The spectral data obtained were identical with those reported in literature[8]

<u>3-(4-bromobenzyl)-1,3-dimethylindolin-2-one</u> (26)



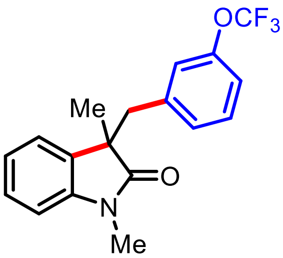
Following **GP1** using **1ai** and **2a** gave **26** (26 mg, 42%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.2 (s, 1H), 7.2 – 7.1 (m, 4H), 7.0 (m,1H), 6.7 (d, *J* = 2.0 Hz, 1H), 6.6 (d, *J* = 7.7 Hz, 1H), 3.1 (d, *J* = 13.0 Hz, 1H), 3.0 (s, 3H), 2.9 (d, *J* = 13.0 Hz, 1H), 1.5 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 179.6, 143.1, 135.2, 132.6, 131.5, 130.6, 128.0, 123.1, 122.2, 120.5, 108.0, 49.8, 43.8, 25.9, 22.9.
HRMS (ESI) (m/z): Calcd for: $C_{16}H_{15}BrNO$ $[M + H]^+$: 316.0332 found: 316.0339.

<u>1,3-dimethyl-3-(4-(trifluoromethyl)benzyl)indolin-2-one</u> (27)



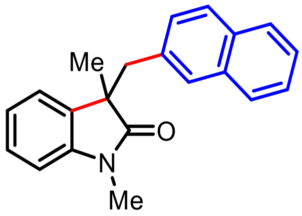
Following **GP1** using **1aj** and **2a** gave **27** (26 mg, 48%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.2 (d, *J* = 16.4, 2H), 7.1 (t, *J* = 7.7 Hz, 2H), 6.9 (d, *J* = 10.9 Hz, 1H), 6.8 (d, *J* = 7.2 Hz, 1H), 6.7 – 6.6 (m, 2H), 3.2 (d, *J* = 13.0 Hz, 1H), 3.0 (d, *J* = 13.3 Hz, 1H), 3.0 (s, 3H), 1.5 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 179.5, 143.1, 138.5, 132.4, 128.7 (q, *J* = 32.2 Hz), 128.3, 128.1,126.3 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 274.2 Hz), 123.1(q, *J* = 3.8 Hz), 123.2, 122.4, 119.2, 107.9, 49.9, 44.2, 25.8, 22.8.
The spectral data obtained were identical with those reported in literature[9]

<u>1,3-dimethyl-3-(4-(trifluoromethoxy)benzyl)indolin-2-one</u> (28)



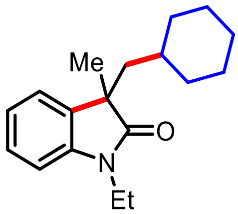
Following **GP1** using **1ak** and **2a** gave **28** (26 mg, 40%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (d, *J* = 7.8 Hz, 1H), 7.2 – 7.1 (m, 3H), 7.1 – 7.0 (m, 3H), 6.6 (d, *J* = 7.5 Hz, 1H), 3.2 (d, *J* = 12.9 Hz, 1H), 3.0 (d, *J* = 12.9 Hz,1H), 2.9 (s, 3H), 1.5 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.4, 143.0, 137.1, 133.2, 132.3, 129.5, 128.1, 127.8, 126.4 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 278 Hz), 123.2(q, *J* = 3.8 Hz), 123.1, 122.3, 108.0, 9.9, 44.4, 25.8, 22.5
HRMS (ESI) (m/z): Calcd for: $C_{18}H_{17}F_3NO_2$ $[M + H]^+$: 336.1206 found: 336.1206.

1,3-dimethyl-3-(naphthalen-2-ylmethyl)indolin-2-one (**29**)



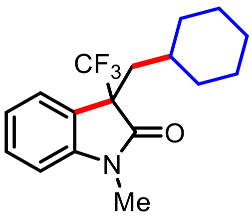
Following **GP1** using **1al** and **2a** gave **29** (30 mg, 51%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.9 (d, J = 9.8 Hz, 1H), 7.7 – 7.7 (m, 1H), 7.7 (s, 1H), 7.4 – 7.3 (m, 2H), 7.3 – 7.2 (m, 1H), 7.1 – 7.1 (m, 2H), 6.8 – 6.8 (m, 2H), 6.6 (d, J = 7.7 Hz, 1H), 3.6 – 3.5 (m, 2H), 3.0 (s, 3H), 1.5 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.6, 143.0, 133.6, 133.1, 132.8, 132.6, 128.6, 128.3, 127.7, 127.4, 125.2, 124.8, 124.7, 124.2, 121.8, 107.7, 49.6, 39.6, 26.1, 22.7.
The spectral data obtained were identical with those reported in literature[(10)]

3-(cyclohexylmethyl)-1-ethyl-3-methylindolin-2-one (**30**)



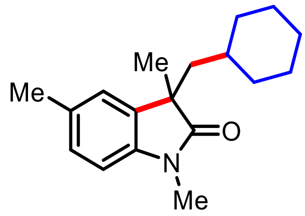
Following **GP1** using **1a** and **2b** gave **30** (38 mg, 71%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 1H), 7.2 (d, J = 7.3 Hz, 1H), 7.0 (t, J = 7.5 Hz, 1H), 6.9 (d, J = 7.8 Hz, 1H), 3.9 (dd, J = 14.2, 7.1 Hz, 1H), 3.7 (m, 1H), 1.9 – 1.9 (m, 1H), 1.7 (m, 1H), 1.5 – 1.4 (m, 4H), 1.3 (s, 3H), 1.3 (d, J = 7.1 Hz, 3H), 1.2 – 1.1 (m, 1H), 1.0 – 0.9 (m, 4H), 0.8 – 0.6 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.0, 138.9, 133.0, 126.3, 121.8, 120.6, 120.0, 49.2, 45.3, 38.8, 34.8, 34.5, 33.6, 26.1, 26.0, 25.8, 24.7, 21.4.
The spectral data obtained were identical with those reported in literature[7]

3-(cyclohexylmethyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (**31**)



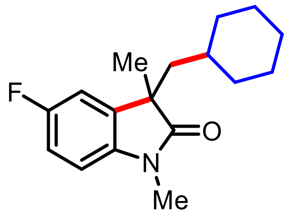
Following **GP1** using **1a** and **2c** gave **31** (41 mg, 67%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.4 (m, 1H), 7.3 (m, 1H), 7.1 (m, 1H), 6.9 (d, J = 7.8 Hz, 1H), 3.2 (s, 3H), 2.3 (dd, J = 13.9, 7.0 Hz, 1H), 2.0 (dd, J = 13.9, 4.9 Hz, 1H), 1.6 – 1.4 (m, 3H), 1.3 – 1.2 (m, 2H), 1.0 – 0.8 (m, 6H). **^{13}C NMR (100MHz, Chloroform-*d*)** δ 172.2, 144.4, 129.9, 125.2, 125.0 (q, J = 281.3 Hz), 124.4, 123.0, 108.5, 56.3 (q, J = 26.3 Hz), 37.3, 34.3, 33.6, 33.2, 26.6, 25.9, 25.8, 25.8.
The spectral data obtained were identical with those reported in literature[6]

3-(cyclohexylmethyl)-1,3,5-trimethylindolin-2-one (**32**)



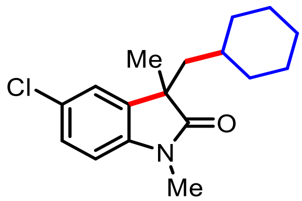
Following **GP1** using **1a** and **2d** gave **32** (45mg, 83%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-d) δ 7.0 (d, J = 8.6 Hz, 1H), 7.0 (s, 1H), 6.7 (d, J = 7.8 Hz, 1H), 3.2 (s, 3H), 2.3 (s, 3H), 1.9 (dd, J = 14.0, 7.1 Hz, 1H), 1.7 (dd, J = 14.0, 5.2 Hz, 1H), 1.5 (m, , 3H), 1.4 – 1.3 (m, 1H), 1.3 (s, 3H), 1.2 – 1.2 (m, 1H), 1.0 – 0.9 (m, 4H), 0.9 – 0.7 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 181.1, 140.7, 134.5, 131.8, 127.7, 123.6, 107.6, 47.9, 45.4, 34.7, 34.5, 33.5, 26.3, 26.2, 26.1, 26.0, 21.2.
The spectral data obtained were identical with those reported in literature[(7)]

3-(cyclohexylmethyl)-5-fluoro-1,3-dimethylindolin-2-one (**33**)



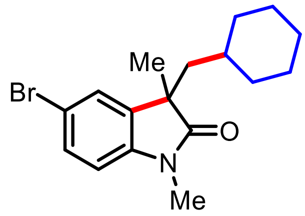
Following **GP1** using **1a** and **2e** gave **33** (38 mg, 70%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.9 – 6.9 (m, 1H), 6.8 (dd, *J* = 8.0, 2.6 Hz, 1H), 6.7 (dd, *J* = 8.4, 4.1 Hz, 1H), 3.1 (s, 3H), 1.9 (m, 1H), 1.6 (dd, *J* = 14.1, 5.2 Hz, 1H), 1.5 – 1.4 (m, 3H), 1.3 – 1.2 (m, 1H), 1.2 (s, 3H), 1.1 (m, , 1H), 1.0 – 0.8 (m, 4H), 0.8 – 0.6 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.8, 160.5 (d, *J* = 237.8 Hz), 139.0 (d, *J* = 1.6 Hz) 136.2 (d, *J* = 7.8 Hz), 113.3 (d, *J* = 23.3 Hz), 111.0 (d, *J* = 24.3 Hz), 108.3 (d, *J* = 8.2 Hz), 48.4, 45.3, 34.7, 34.4, 33.4, 26.3, 26.1, 26.1, 26.0, 26.0.
The spectral data obtained were identical with those reported in literature[12]

5-chloro-3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one (**34**)



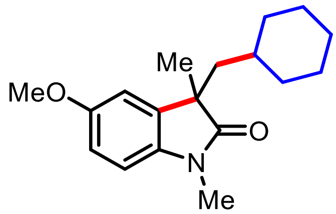
Following **GP1** using **1a** and **2f** gave **34** (44 mg, 76%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.2 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.1 (d, *J* = 2.1 Hz, 1H), 6.7 (d, *J* = 8.2 Hz, 1H), 3.1 (s, 3H), 1.9 (m, 1H), 1.6 (m, 1H), 1.5 – 1.4 (m, 3H), 1.3 – 1.2 (m, 1H), 1.2 (s, 3H), 1.2 – 1.1 (m, 1H), 1.0 – 0.8 (m, 4H), 0.8 – 0.6 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.6, 141.7, 136.2, 127.8, 127.5, 123.2, 108.9, 48.1, 45.3, 34.7, 34.4, 33.4, 26.3, 26.2, 26.1, 26.0, 26.0.
The spectral data obtained were identical with those reported in literature[13]

5-bromo-3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one (**35**)



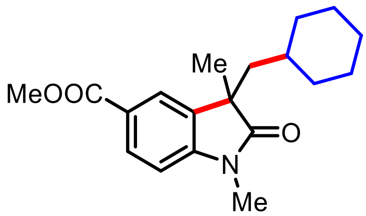
Following **GP1** using **1a** and **2g** gave **35** (47 mg, 70%, Colorless oil). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.4 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.3 (d, *J* = 2.0 Hz, 1H), 6.7 (d, *J* = 8.2 Hz, 1H), 3.2 (s, 3H), 1.9 (dd, *J* = 14.1, 7.1 Hz, 1H), 1.7 (s, 1H), 1.5 – 1.4 (m, 3H), 1.3 – 1.3 (m, 1H), 1.3 (s, 3H), 1.2 – 1.2 (m, 1H), 1.0 – 0.8 (m, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 180.5, 142.2, 136.6, 130.4, 126.0, 115.1, 109.4, 48.1, 45.3, 34.7, 34.4, 33.4, 26.3, 26.2, 26.1, 26.0, 26.0.
The spectral data obtained were identical with those reported in literature[14]

3-(cyclohexylmethyl)-5-methoxy-1,3-dimethylindolin-2-one (**36**)



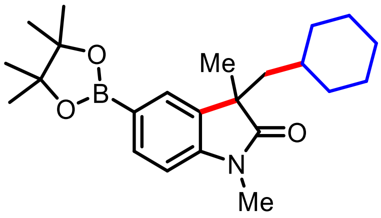
Following **GP1** using **1a** and **2h** gave **36** (46 mg, 81%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.7 – 6.7 (m, 2H), 6.7 (d, *J* = 9.2 Hz, 1H), 3.7 (s, 3H), 3.1 (s, 3H), 1.8 (m, 1H), 1.6 (m, 1H), 1.5 – 1.4 (m, 3H), 1.3 – 1.2 (m, 1H), 1.2 (s, 3H), 1.2 – 1.1 (m, 1H), 1.0 – 0.8 (m, 4H), 0.8 – 0.6 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.8, 155.9, 136.7, 135.9, 111.4, 110.5, 108.1, 55.8, 48.3, 45.4, 34.7, 34.4, 33.5, 26.3, 26.1, 26.0.
The spectral data obtained were identical with those reported in literature[7]

3-(cyclohexylmethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (**37**)



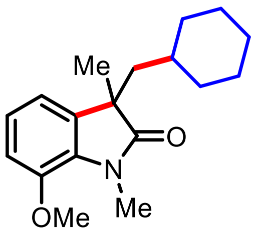
Following **GP1** using **1a** and **2i** gave **37** (36 mg, 67%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.0 – 7.9 (m, 1H), 7.8 – 7.7 (m, 1H), 6.8 (d, *J* = 8.2 Hz, 1H), 3.8 (s, 3H), 3.2 (s, 3H), 1.9 (dd, *J* = 14.1, 7.0 Hz, 1H), 1.7 (dd, *J* = 14.1, 5.1 Hz, 1H), 1.5 – 1.4 (m, 3H), 1.3 (s, 3H), 1.2 – 1.1 (m, 2H), 0.9 – 0.8 (m, 4H), 0.7 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 181.4, 167.1, 147.3, 134.4, 130.4, 124.3, 124.0, 107.5, 52.0, 47.7, 45.3, 34.8, 34.4, 33.4, 26.4, 26.1, 26.0, 26.0, 26.0.
The spectral data obtained were identical with those reported in literature[12]

3-(cyclohexylmethyl)-1,3-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-2-one (**38**)



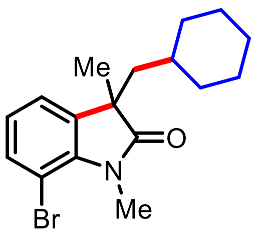
Following **GP1** using **1a** and **2j** gave **38** (37 mg, 74%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.8 (m, 1H), 7.6 (s, 1H), 6.8 (d, *J* = 7.8 Hz, 1H), 3.2 (s, 3H), 1.9 (m, 1H), 1.8 (m, 1H), 1.6 – 1.4 (m, 4H), 1.4 (s, 12H), 1.3 (s, 3H), 1.3 – 1.2 (m, 1H), 1.0 – 0.9 (m, 4H), 0.9 – 0.7 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 181.6, 145.9, 135.1, 133.7, 128.6, 107.4, 83.7, 47.6, 45.4, 34.7, 34.4, 33.4, 26.3, 26.2, 26.1, 26.1, 26.0, 24.9.
HRMS (ESI) (m/z): Calcd for: $C_{23}H_{24}BNO_3$ $[M + H]^+$: 384.2705 found: 384.2712

3-(cyclohexylmethyl)-7-methoxy-1,3-dimethylindolin-2-one (**39**)



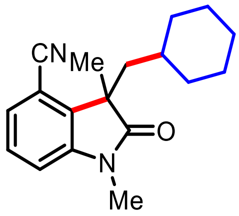
Following **GP1** using **1a** and **2k** gave **39** (29 mg, 51%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.0 – 7.0 (m, 1H), 6.8 (d, *J* = 8.3 Hz, 1H), 6.8 (d, *J* = 7.6, 1H), 3.9 (s, 3H), 3.5 (s, 3H), 1.9 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.7 (dd, *J* = 14.0, 5.1 Hz, 2H), 1.5 – 1.4 (m, 3H), 1.3 (s, 3H), 1.2 (m, 2H), 1.0 – 1.0 (m, 3H), 0.8 – 0.7 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 145.3, 136.2, 130.9, 122.8, 115.5, 111.3, 55.9, 47.9, 45.5, 34.7, 34.5, 33.5, 29.5, 26.5, 26.1, 26.0.
The spectral data obtained were identical with those reported in literature[7]

7-bromo-3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one (**40**)



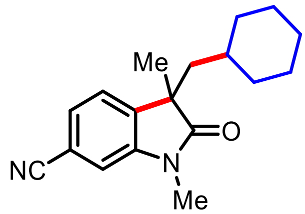
Following **GP1** using **1a** and **2l** gave **40** (44 mg, 66%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (d, *J* = 9.4 Hz, 1H), 7.0 (d, *J* = 7.2, 1H), 6.8 – 6.8 (m, 1H), 3.5 (s, 3H), 1.9 (m, 1H), 1.6 (m, 1H), 1.5 – 1.4 (m, 3H), 1.3 – 1.2 (m, 1H), 1.2 (s, 3H), 1.2 – 1.1 (m, 1H), 0.9 – 0.7 (m, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 181.5, 140.4, 137.6, 133.2, 123.5, 121.8, 102.4, 47.6, 45.6, 34.6, 34.5, 33.5, 29.8, 26.6, 26.1, 26.0.
The spectral data obtained were identical with those reported in literature[13]

3-(cyclohexylmethyl)-1,3-dimethyl-2-oxoindoline-6-carbonitrile (**41**)



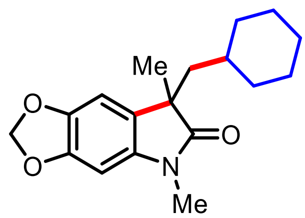
Following **GP1** using **1a** and **2m** gave **41** (27 mg, 48%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.4 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.2 (d, *J* = 7.5 Hz, 1H), 7.1 (d, *J* = 1.3 Hz, 1H), 3.2 (s, 3H), 1.9 (s, 1H), 1.7 (dd, *J* = 14.2, 5.1 Hz, 1H), 1.5 – 1.4 (m, 3H), 1.3 (s, 3H), 1.3 – 1.2 (m, 1H), 1.2 – 1.1 (m, 1H), 1.0 – 0.9 (m, 3H), 0.9 – 0.7 (m, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.2, 143.9, 139.9, 127.0, 123.4, 118.9, 111.4, 110.5, 48.1, 45.2, 34.8, 34.4, 33.5, 26.4, 26.0, 26.0, 25.9.
HRMS (ESI) (m/z): Calcd for: $C_{18}H_{23}N_2O$ [M + H]$^+$: 283.1805 found: 283.1805.

3-(cyclohexylmethyl)-1,3-dimethyl-2-oxoindoline-4-carbonitrile (**41'**)



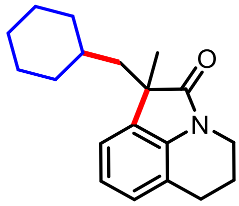
Following **GP1** using **1a** and **2m** gave **41'** (13 mg, 24%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.4 (t, *J* = 7.8 Hz, 1H), 7.3 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.0 (dd, *J* = 7.8, 1.0 Hz, 1H), 3.2 (s, 3H), 2.2 (dd, *J* = 14.2, 4.5 Hz, 1H), 2.0 – 2.0 (m, 1H), 1.5 – 1.5 (m, 2H), 1.5 (s, 3H), 1.5 – 1.4 (m, 1H), 1.2 (s, 2H), 1.0 – 0.8 (m, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.0, 144.2, 137.5, 128.5, 125.8, 116.7, 111.8, 107.8, 48.7, 43.4, 35.1, 33.9, 33.3, 26.5, 26.0, 26.0, 26.0, 24.4.
HRMS (ESI) (m/z): Calcd for: $C_{18}H_{23}N_2O$ [M + H]$^+$: 283.1805 found: 283.1805.

7-(cyclohexylmethyl)-5,7-dimethyl-5,7-dihydro-6H-[1,3]dioxolo[4,5-f]indol-6-one (**42**)



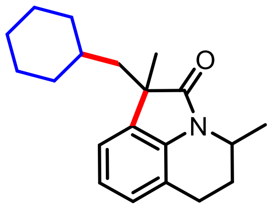
Following **GP1** using **1a** and **2n** gave **42** (36 mg, 60%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.6 (d, *J* = 8.0 Hz, 1H), 6.2 (d, *J* = 8.0 Hz, 1H), 5.9 m, 2H), 3.1 (s, 3H), 1.8 (d, *J* = 6.1 Hz, 2H), 1.5 – 1.4 (m, 3H), 1.3 (s, 3H), 1.3 – 1.2 (m, 2H), 0.9 (m, 4H), 0.8 (m, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.1, 144.2, 143.1, 138.4, 115.2, 106.2, 101.4, 99.6, 47.4, 43.9, 35.1, 34.1, 33.6, 29.7, 26.6, 26.1, 26.0, 24.2.
HRMS (ESI) (m/z): Calcd for: $C_{18}H_{24}NO_3$ [M + H]$^+$: 302.1751 found: 302.1755.

1-(cyclohexylmethyl)-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (**43**)



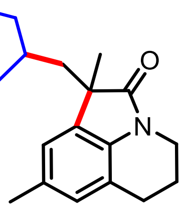
Following **GP1** using **1a** and **2o** gave **43** (39 mg, 70%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.9 (d, *J* = 6.1 Hz, 2H), 6.9 – 6.8 (m, 1H), 3.6 (t, *J* = 5.8 Hz, 2H), 2.7 – 2.7 (m, 2H), 2.0 – 1.9 (m, 2H), 1.8 (m, 1H), 1.7 – 1.6 (m, 1H), 1.5 – 1.4 (m, 3H), 1.3 – 1.3 (m, 1H), 1.3 (s, 3H), 1.2 – 1.1 (m, 1H), 1.0 – 0.9 (m, 4H), 0.8 – 0.7 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.6, 142.2, 134.8, 127.4, 122.9, 122.1, 108.1, 47.7, 45.5, 34.8, 34.4, 34.4, 33.7, 26.2, 26.1, 26.0, 12.5.
The spectral data obtained were identical with those reported in literature[6]

1-(cyclohexylmethyl)-1,4-dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (**44**)



Following **GP1** using **1a** and **2p** gave **44** (41 mg, 73%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.0 (d, *J* = 7.5 Hz, 1H), 7.0 – 6.9 (m, 2H), 4.5 (m, 1H), 2.9 (m, 1H), 2.7 – 2.7 (m, 1H), 1.9 (m , 3H), 1.7 – 1.7 (m, 2H), 1.5 – 1.4 (m, 4H), 1.3 (s, 3H), 1.3 – 1.2 (m, 3H), 1.2 – 1.2 (m, 1H), 1.0 – 0.9 (m, 4H), 0.9 – 0.7 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.7, 138.4, 133.1, 126.2, 121.5, 120.5, 119.5, 49.1, 45.1, 43.9, 34.9, 34.5, 33.5, 27.2, 26.2, 26.1, 26.1, 25.8, 20.6, 18.0.
HRMS (ESI) (m/z): Calcd for: $C_{20}H_{28}NO$ [M + H]$^+$: 298.2165 found: 302.1755.

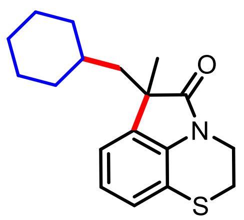
1-(cyclohexylmethyl)-1,8-dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (**45**)



Following **GP1** using **1a** and **2q** gave **45** (37 mg, 63%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.8 (d, *J* = 6.9 Hz, 2H), 3.7 (t, *J* = 5.9 Hz, 2H), 2.7 (t, *J* = 6.2 Hz, 2H), 2.3 (s, 3H), 2.0 (q, *J* = 6.4 Hz, 2H), 1.9 – 1.8 (m, 1H), 1.7 (dd, *J* = 14.0, 4.9 Hz, 1H), 1.5 – 1.5 (m, 3H), 1.4 (d, *J* = 13.1 Hz, 1H), 1.3 (s, 3H), 1.3 (s, 1H), 1.0 (m, 4H), 0.8 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.0, 136.5, 133.0,

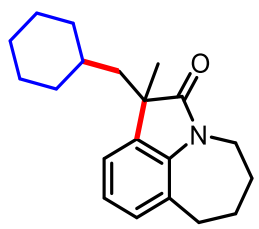
131.2, 126.7, 121.3, 119.6, 49.3, 45.3, 38.8, 34.8, 34.5, 33.5, 26.2, 26.0, 25.9, 24.6, 21.5, 21.5.
HRMS (ESI) (m/z): Calcd for: $C_{20}H_{28}NO$ [M + H]$^+$: 298.2165 found: 302.1763.

<u>6-(cyclohexylmethyl)-6-methyl-2,3-dihydro-[1,4]thiazino[2,3,4-hi]indol-5(6H)-one</u> (**46**)



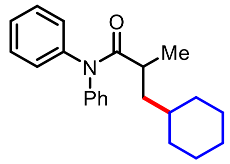
Following **GP1** using **1a** and **2r** gave **46** (40 mg, 67%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.0 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.9 – 6.8 (m, 2H), 4.0 (t, *J* = 5.2 Hz, 2H), 3.0 – 2.9 (m, 2H), 1.8 (dd, *J* = 14.0, 7.1 Hz, 1H), 1.7 (dd, *J* = 14.1, 5.2 Hz, 1H), 1.5 – 1.4 (m, 3H), 1.3 (q, *J* = 1.7 Hz, 1H), 1.3 (s, 3H), 1.2 – 1.2 (m, 1H), 1.0 – 0.9 (m, 4H), 0.8 – 0.7 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.2, 135.8, 133.9, 125.3, 122.5, 119.6, 115.4, 48.6, 45.3, 40.4, 34.8, 34.5, 33.6, 26.1, 26.1, 26.0, 25.9, 25.6.
HRMS (ESI) (m/z): Calcd for: $C_{18}H_{24}NOS$ [M + H]$^+$: 302.1537 found: 302.1531

<u>7-(cyclohexylmethyl)-7-methyl-1,2,3,4,6,7-hexahydroazepino[3,2,1-hi]indole</u> (**47**)



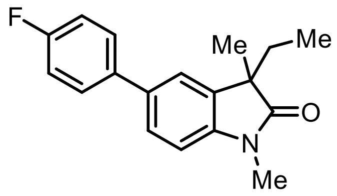
Following **GP1** using **1a** and **2s** gave **47** (39 mg, 66%, Colorless oil).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.9 (m, 3H), 3.9 – 3.8 (m, 2H), 3.0 – 2.8 (m, 2H), 2.0 – 1.9 (m, 4H), 1.9 – 1.8 (m, 1H), 1.6 – 1.6 (m, 2H), 1.5 – 1.4 (m, 3H), 1.3 – 1.3 (m, 1H), 1.2 (d, *J* = 2.1 Hz, 3H), 1.2 – 1.1 (m, 2H), 1.0 – 0.8 (m, 4H), 0.8 – 0.6 (m, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 141.9, 134.7, 128.8, 125.1, 122.1, 120.6, 47.9, 45.8, 40.5, 34.8, 34.4, 33.6, 30.6, 26.5, 26.3, 26.2, 26.2, 26.1, 26.1.
HRMS (ESI) (m/z): Calcd for: $C_{20}H_{30}N$ [M + H]$^+$: 284.2373 found: 284.2379.

<u>3-cyclohexyl-2-methyl-N,N-diphenylpropanamide (48)</u>



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.5 – 7.3 (m, 5H), 7.3 (d, *J* = 7.6 Hz, 5H), 2.7 (m, 1H), 1.8 (m, 1H), 1.7 (m, 3H), 1.6 – 1.5 (m, 2H), 1.3 – 1.2 (m, 4H), 1.1 (m, 3H), 1.1 – 1.0 (m, 1H), 0.8 – 0.7 (m, 2H).

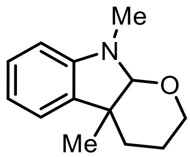
3-ethyl-5-(4-fluorophenyl)-1,3-dimethylindolin-2-one (49)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.5 – 7.5 (m, 2H), 7.4 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.3 (d, *J* = 1.9 Hz, 1H), 7.1 (d, *J* = 8.7 Hz, 2H), 6.9 (d, *J* = 8.1 Hz, 1H), 3.2 (s, 3H), 2.0 (dd, *J* = 13.7, 7.3 Hz, 1H), 1.9 – 1.8 (m, 1H), 1.4 (s, 3H), 0.6 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.8, 162.1 (d, *J* = 245.1 Hz), 142.9, 137.3 (d, *J* = 3.2 Hz), 135.0, 134.7, 128.4 (d, *J* = 7.8 Hz), 126.4, 121.3, 115.7 (d, *J* = 21.3 Hz Hz), 108.1, 49.2, 31.5, 26.2, 23.4, 8.9.

The spectral data obtained were identical with those reported in literature[7]

9-dimethyl-2,3,4,4a,9,9a-hexahydropyrano[2,3-b]indole (50)

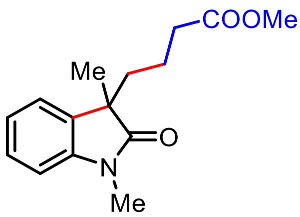


Colorless oil, 67% yield (27 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.1 (m, 1H), 7.0 (m,1H), 6.7 (m, 1H), 6.5 (dt, *J* = 7.8, 0.7 Hz, 1H), 4.5 (s, 1H), 3.7 (m, z, 1H), 3.6 – 3.5 (m, 1H), 2.8 (s, 3H), 1.9 – 1.9 (m, 1H), 1.7 – 1.6 (m, 1H), 1.6 – 1.6 (m, 1H), 1.5 – 1.4 (m, 1H), 1.3 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 149.6, 136.3, 127.7, 121.3, 118.2, 107.1, 100.2, 61.1, 40.9, 31.8, 31.7, 24.4, 21.1.

The spectral data obtained were identical with those reported in literature[14]

methyl 4-(1,3-dimethyl-2-oxoindolin-3-yl)butanoate (51)

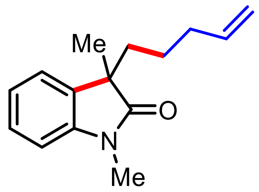


Following **GP1**, Colorless oil, 53% yield (29 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (m, 1H), 7.2 (m, 1H), 7.1 (m, 1H), 6.8 (m, 1H), 3.6 (s, 3H), 3.2 (s, 3H), 2.2 – 2.2 (m, 2H), 1.9 – 1.9 (m, 1H), 1.8 (m, , 1H), 1.4 (s, 3H), 1.3 – 1.2 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 149.6, 136.3, 127.7, 121.3, 118.2, 107.1, 100.2, 61.1, 40.9, 31.8, 31.7, 24.4, 21.1. **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.4, 173.6, 143.3, 133.7, 127.8, 122.6, 122.6, 108.0, 51.5, 48.2, 37.7, 33.9, 26.2, 23.8, 20.0.

The spectral data obtained were identical with those reported in literature[15]

1,3-dimethyl-3-(pent-4-en-1-yl)indolin-2-one (**52**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.2 (m, 1H), 7.2 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.1 (td, *J* = 7.5, 1.0 Hz, 1H), 6.8 (d, *J* = 7.7 Hz, 1H), 5.7 – 5.6 (m, 1H), 4.9 – 4.8 (m, 2H), 3.2 (s, 3H), 2.0 – 1.9 (m, 3H), 1.7 (td, *J* = 13.0, 4.4 Hz, 1H), 1.3 (s, 3H), 1.1 – 1.0 (m, 1H), 1.0 – 0.9 (m, 1H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 180.7, 143.3, 138.2, 134.2, 127.7, 122.5, 122.5, 114.7, 107.9, 48.4, 38.0, 33.8, 26.1, 23.8. The spectral data obtained were identical with those reported in literature[1]

5. Reference

1. Muralirajan, K.; Kancherla, R.; Gimnkhan, A.; Rueping, M. Unactivated Alkyl Chloride Reactivity in Excited-State Palladium Catalysis. *Org. Lett.* **2021**, *23*, 6905–6910.
2 Liu, Z.; Zhong, S.; Ji, X.; Deng, G.-J.; Huang, H. Hydroarylation of Activated Alkenes Enabled by Proton-Coupled Electron Transfer. *ACS Catal.* **2021**, *11*, 4422–4429.
3 Ren, Y.-Z.; Fang, C.-Z.; Zhang, B.-B.; He, L.; Tu, Y.-L.; Chen, X.-Y. Photocatalytic Charge-Transfer Complex Enables Hydroarylation of Alkenes for Heterocycle Synthesis. *Org. Lett.* **2023**, *25* (19), 3585–3589.
4 Zhang, L.; Wang, Y.; Yang, Y.; Zhang, P.; Wang, C. Rhenium-Catalyzed Alkylarylation of Alkenes with $PhI(O_2\ CR)_2$ *via* Decarboxylation to Access Indolinones and Dihydroquinolinones. *Org. Chem. Front.* **2020**, *7* , 3234–3241.
5 Zhang, C.-S.; Fang, C.-Z.; Yi, L.; Zhu, C.; Wang, Z.-X.; Chen, X.-Y.; Rueping, M. N-Heterocyclic Nitrenium Charge Transfer Catalysis *via* Inner-Sphere Electron Transfer in Concert with Halogen-Atom Dissociation. *Org. Chem. Front.* **2024**, *11*, 673–683.
6 Liu, Y.-L.; Shi, L.-S.; He, X.-C.; Gao, J.; Li, K.-R.; Xiang, H.-Y.; Chen, K.; Yang, H. Photoredox Nickel-Catalyzed Radical Cyclization of *N* -Arylacrylamides with Alkyl Bromides. *Org. Biomol. Chem.* **2025**, *23* (13), 3126–3130.
7 Li, Z.; Zhang, Y.; Zhang, L.; Liu, Z.-Q. Free-Radical Cascade Alkylarylation of Alkenes with Simple Alkanes: Highly Efficient Access to Oxindoles via Selective (Sp^3)C–H and (Sp^2)C–H Bond Functionalization. *Org. Lett.* **2014**, *16*, 382–385.
8 Liu, Z.; Zhong, S.; Ji, X.; Deng, G.-J.; Huang, H. Hydroarylation of Activated Alkenes Enabled by Proton-Coupled Electron Transfer. *ACS Catal.* **2021**, *11*, 4422–4429.
9 Sarró, P.; Gallego-Gamo, A.; Pleixats, R.; Vallribera, A.; Gimbert-Suriñach, C.; Granados, A. Access to Benzyl Oxindoles via Electron Donor-Acceptor Complex Photoactivation Using Thianthrenium Salts and Potassium Carbonate. *Adv Synth Catal* **2024**, *366*, 2587–2595.

10 Li, Y.; Wang, K.; Ping, Y.; Wang, Y.; Kong, W. Nickel-Catalyzed Domino Heck Cyclization/Suzuki Coupling for the Synthesis of 3,3-Disubstituted Oxindoles. *Org. Lett.* **2018**, *20*, 921–924.

11 Yu, W.-Q.; Fan, J.-H.; Chen, P.; Xiong, B.-Q.; Xie, J.; Tang, K.-W.; Liu, Y. Transition-Metal-Free Alkylation Strategy: Facile Access to Alkylated Oxindoles *via* Alkyl Transfer. *Org. Biomol. Chem.* **2022**, *20*, 1958–1968.

12 Du, J.; Wang, X.; Wang, H.; Wei, J.; Huang, X.; Song, J.; Zhang, J. Photoinduced Palladium-Catalyzed Intermolecular Radical Cascade Cyclization of *N* -Arylacrylamides with Unactivated Alkyl Bromides. *Org. Lett.* **2021**, *23*, 5631–5635.

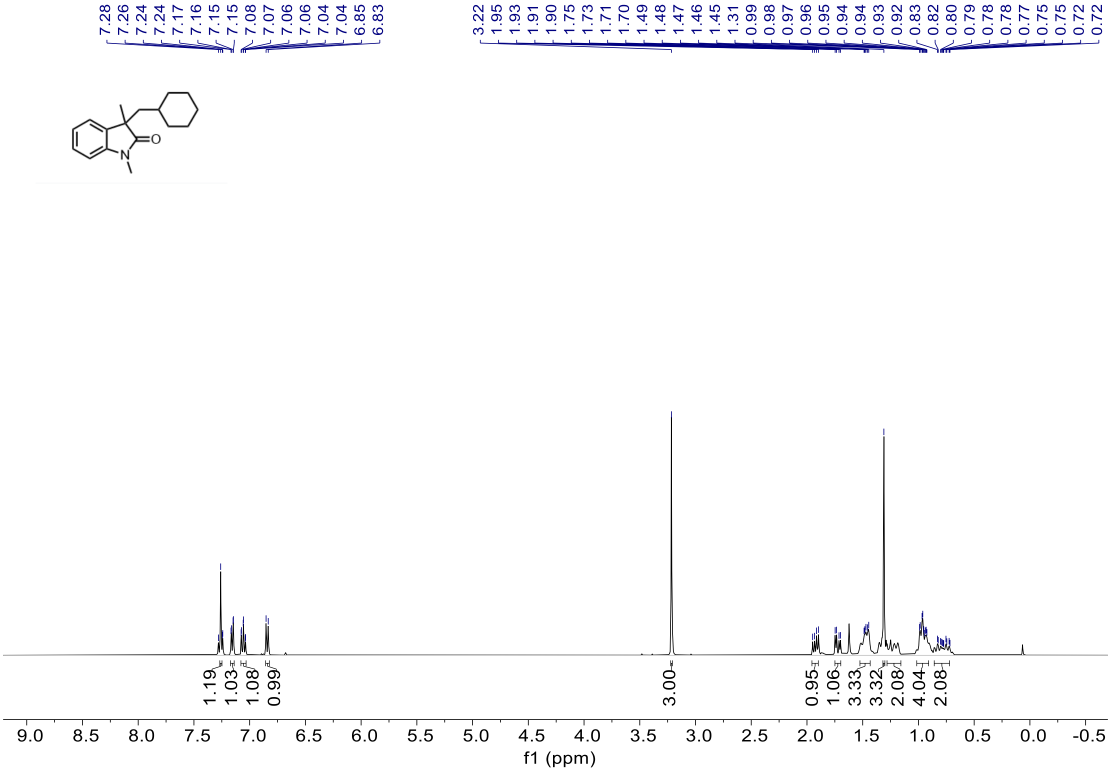
13 Li, X.; Han, M.-Y.; Wang, B.; Wang, L.; Wang, M. Visible-Light-Induced Deboronative Alkylarylation of Acrylamides with Organoboronic Acids. *Org. Biomol. Chem.* **2019**, *17* (27), 6612–6619.

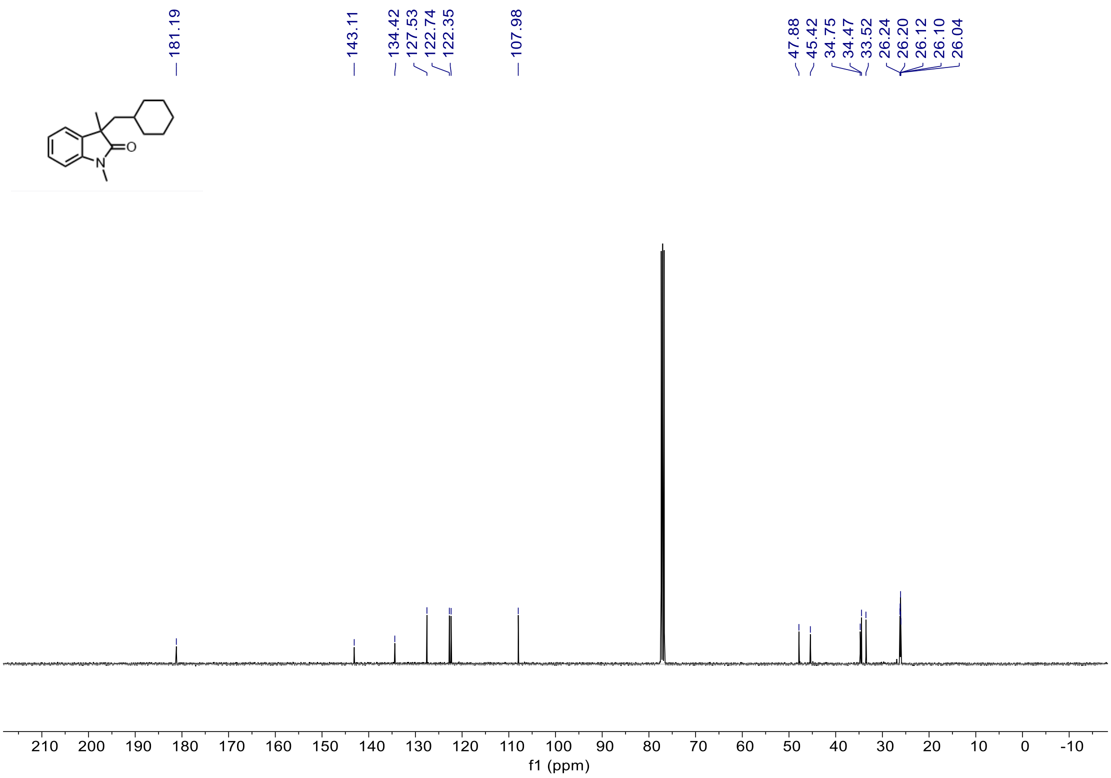
14 Fang, S.-C.; Cai, S.-Q.; Li, P.-P.; Yang, Z.; Zhao, J.-F.; Xiao, H.-X.; Zhou, Y.-T.; Sun, X.-R.; He, S.-Y.; Liu, F.; Liang, W.; Pan, B.; Du, F. The Cascade Reaction Chemistry of Diazo Compounds with Intentionally Designed Alkene to Access Esterified Heterocycles. *Org. Lett.* **2025**, *27*, 559–564.

15 Ding, S.; Ren, H.; Zhu, M.; Ma, Q.; Miao, Z.; Li, P. Silver(I)-Mediated Oxidation/Cyclization of Acrylamides with Alkyl Trifluoroborates. *Synthetic Communications* **2021**, *51*, 593–600.

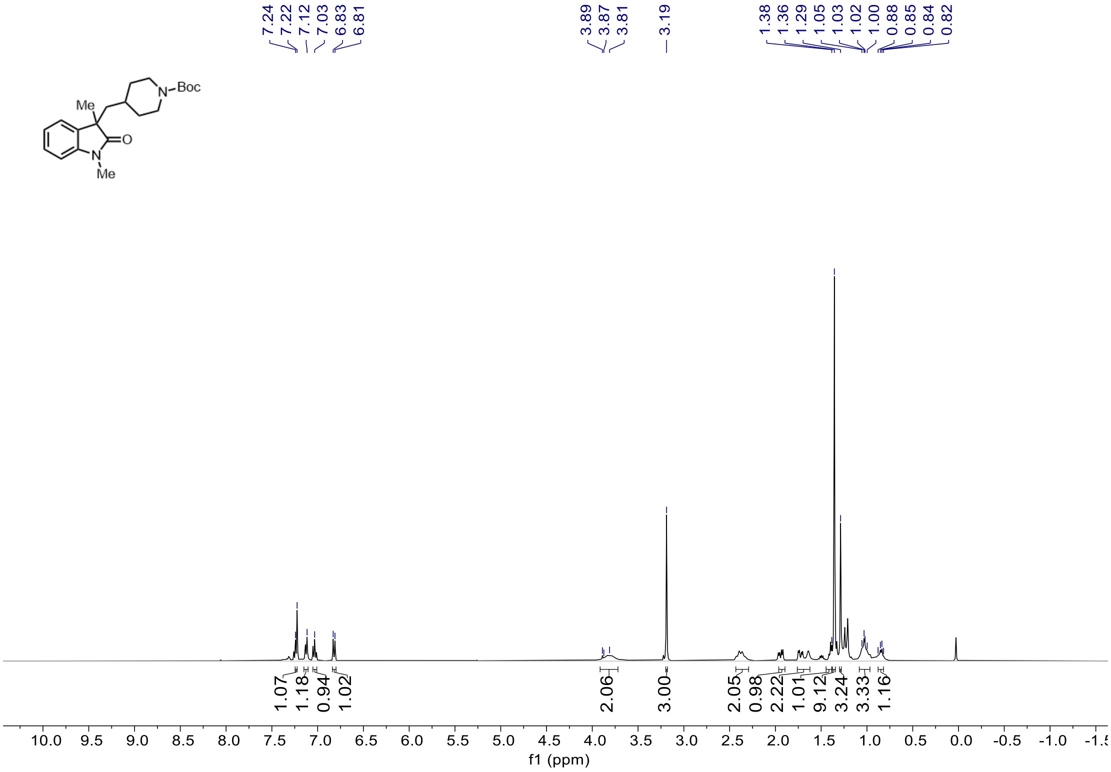
6. NMR Spectra

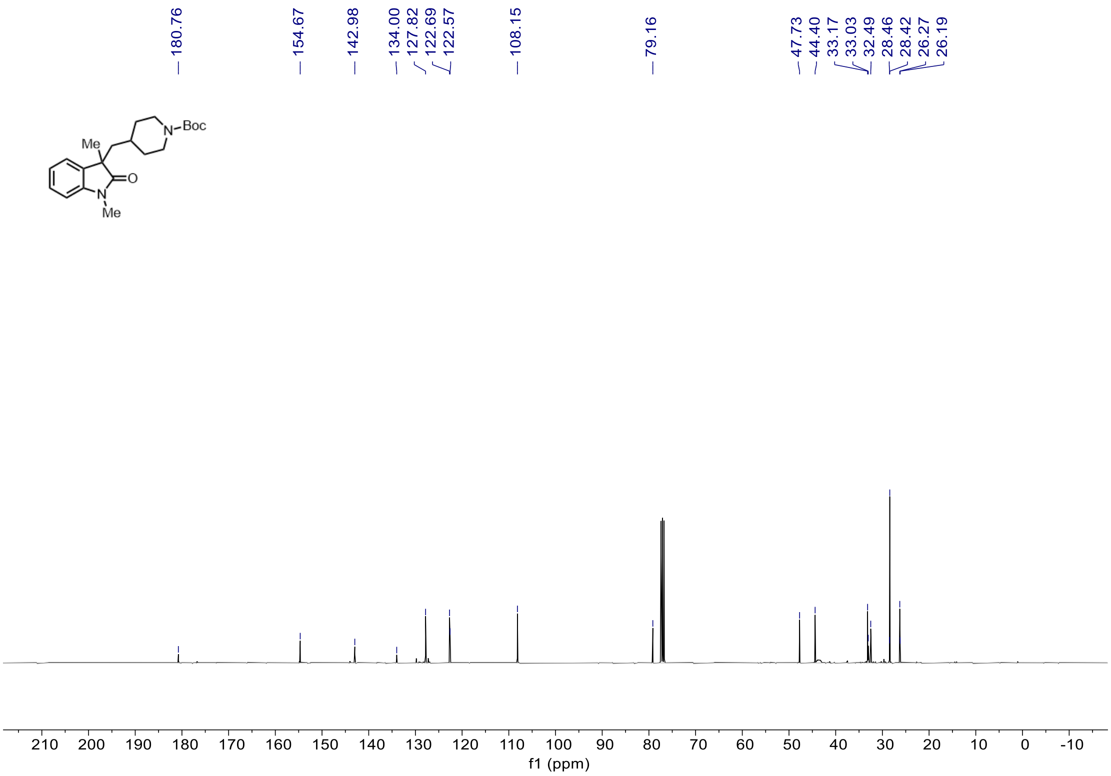
^{1}H and ^{13}C spectra for compound **4**



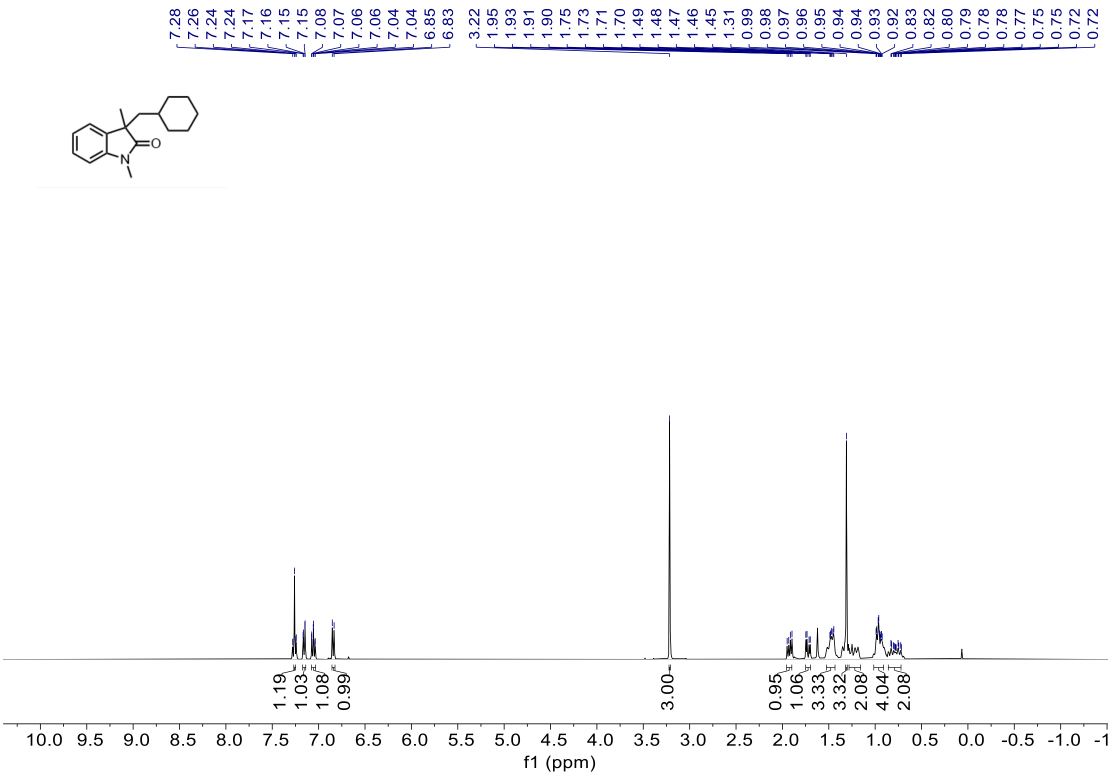


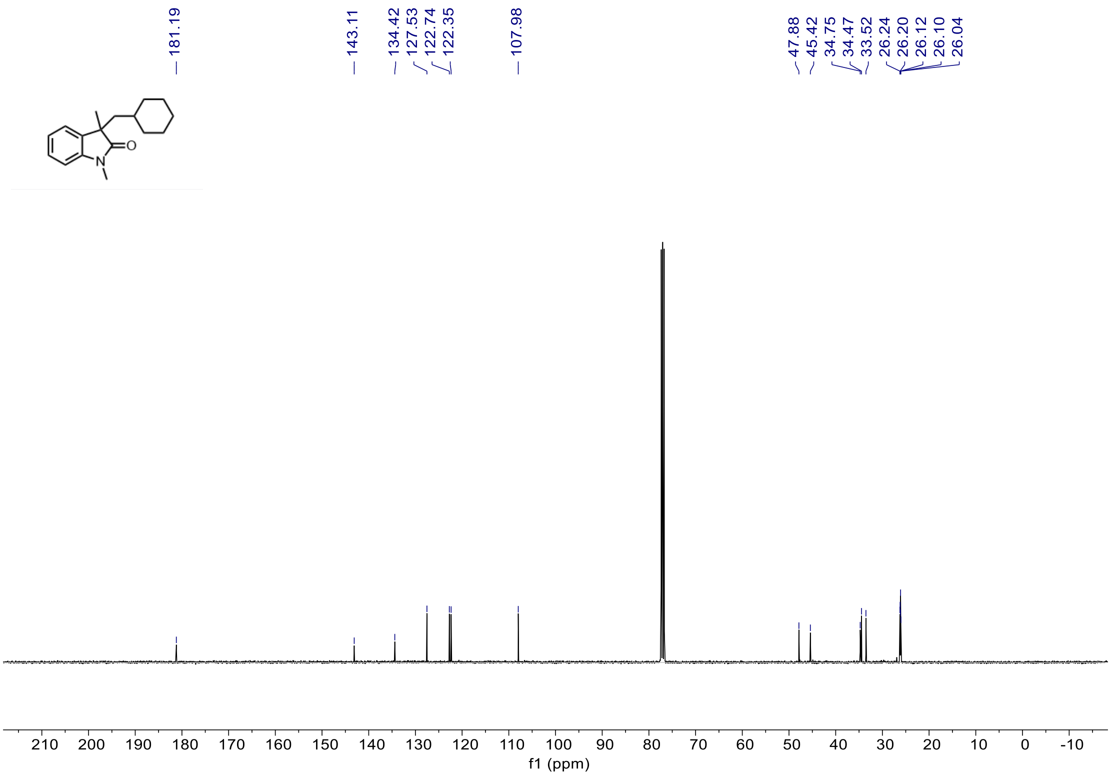
[1]H and [13]C spectra for compound **5**



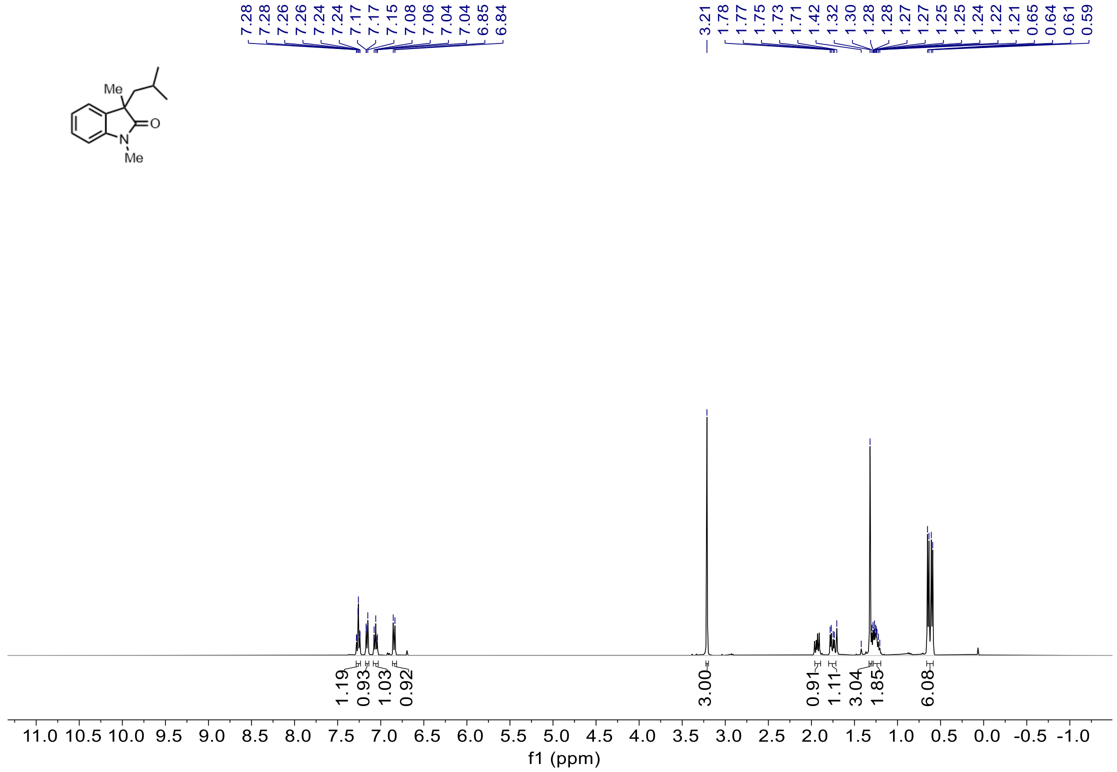


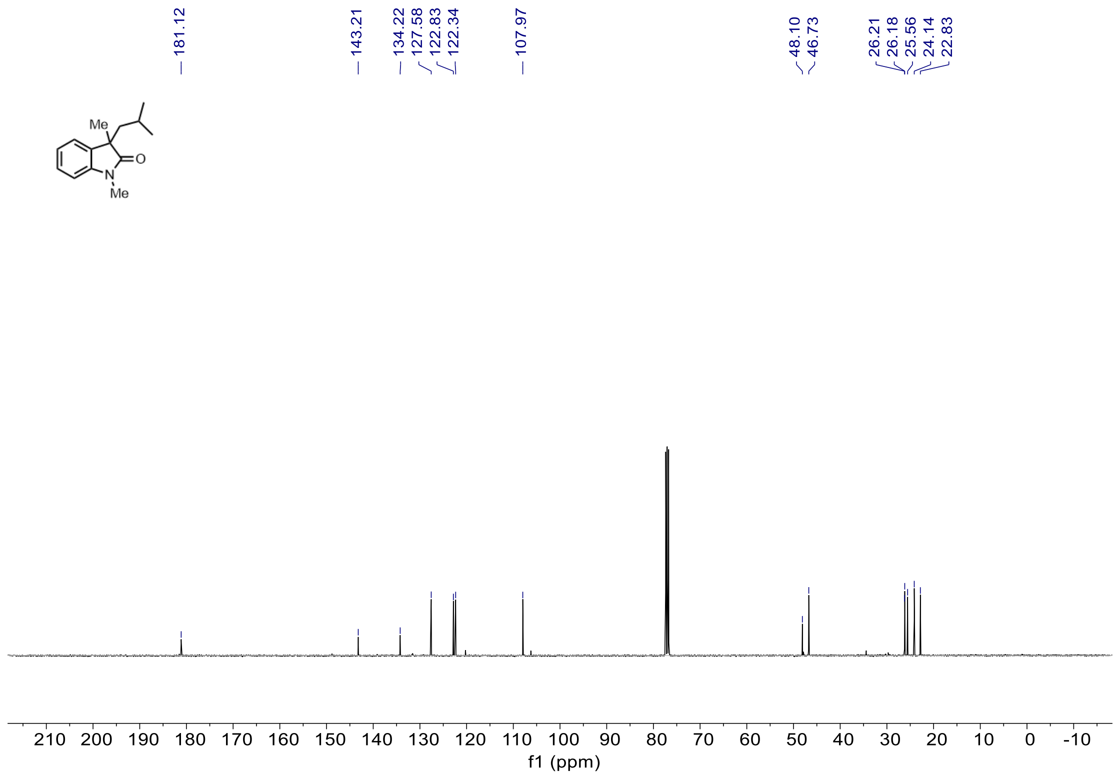
^{1}H and ^{13}C spectra for compound **6**



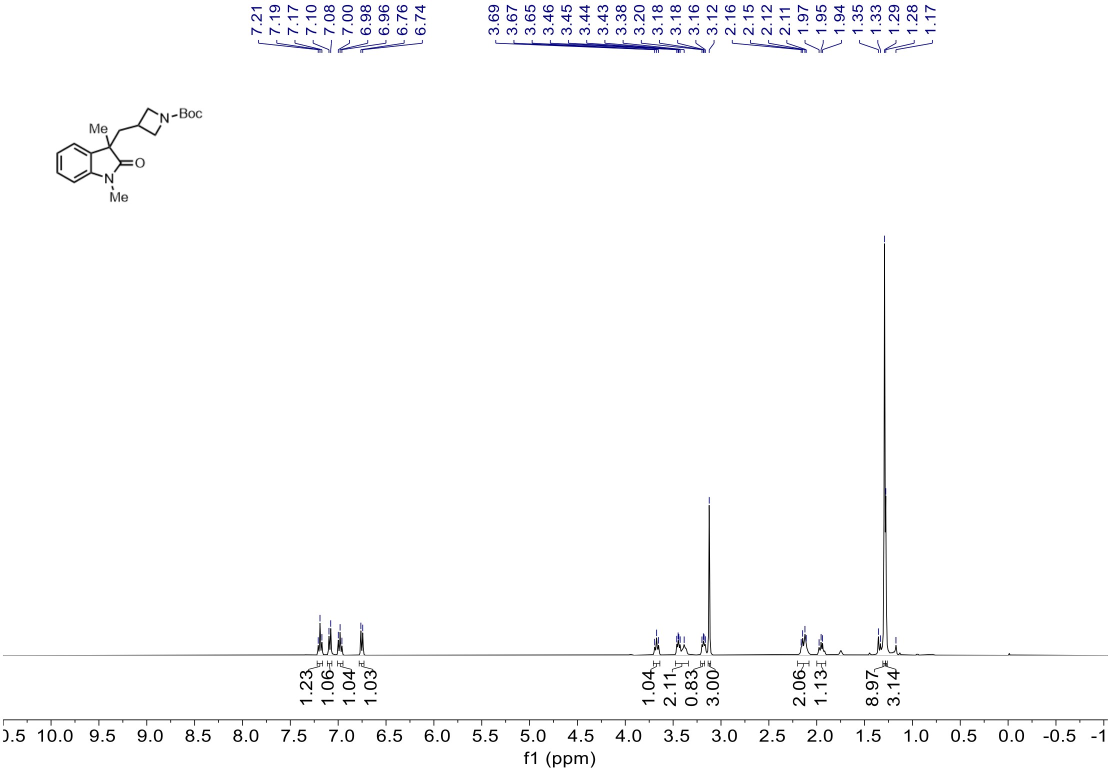


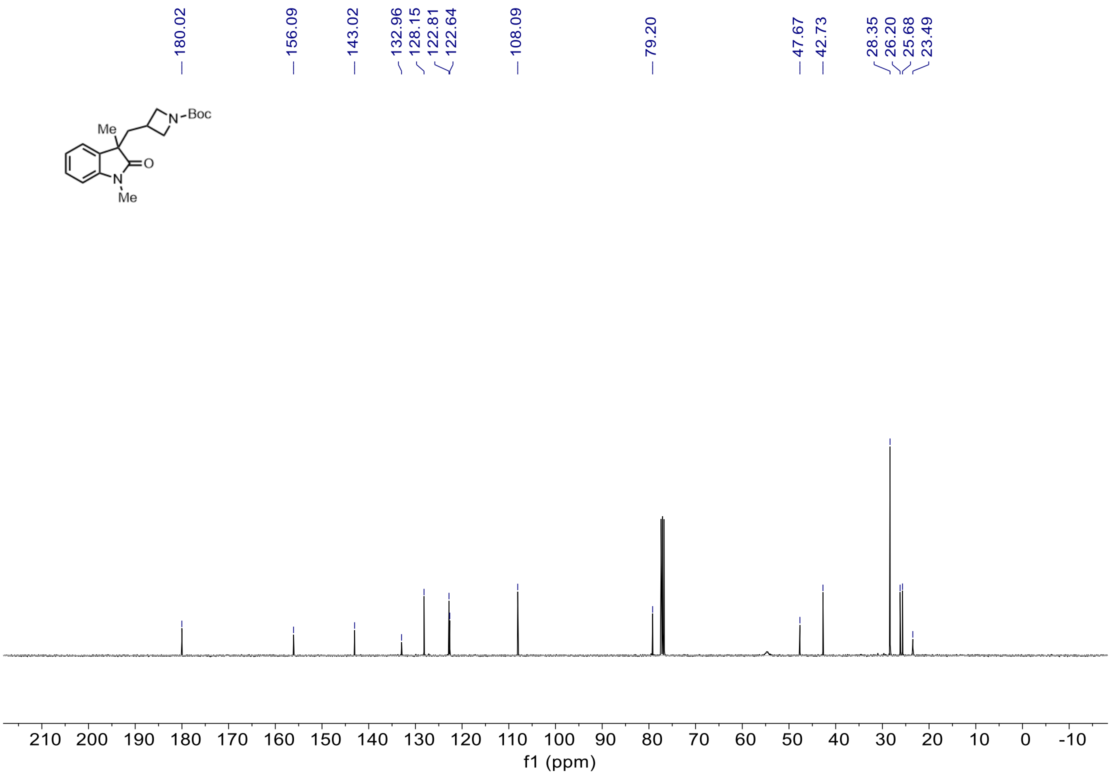
[1]H and [13]C spectra for compound **7**



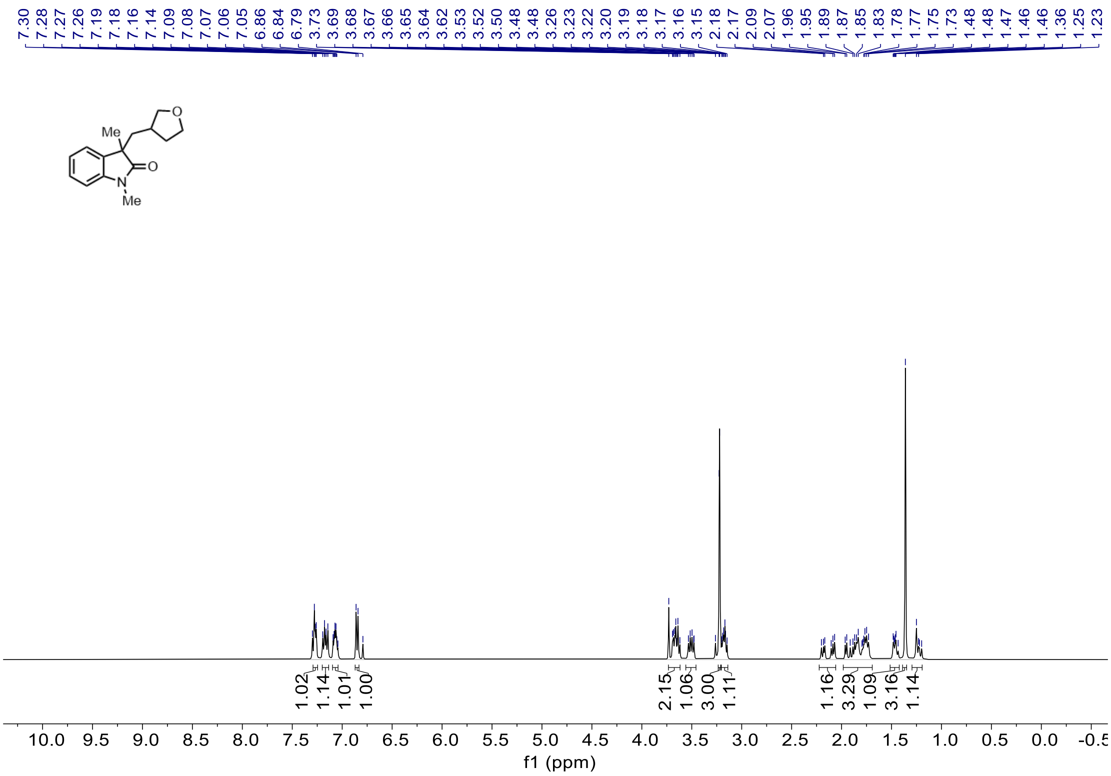


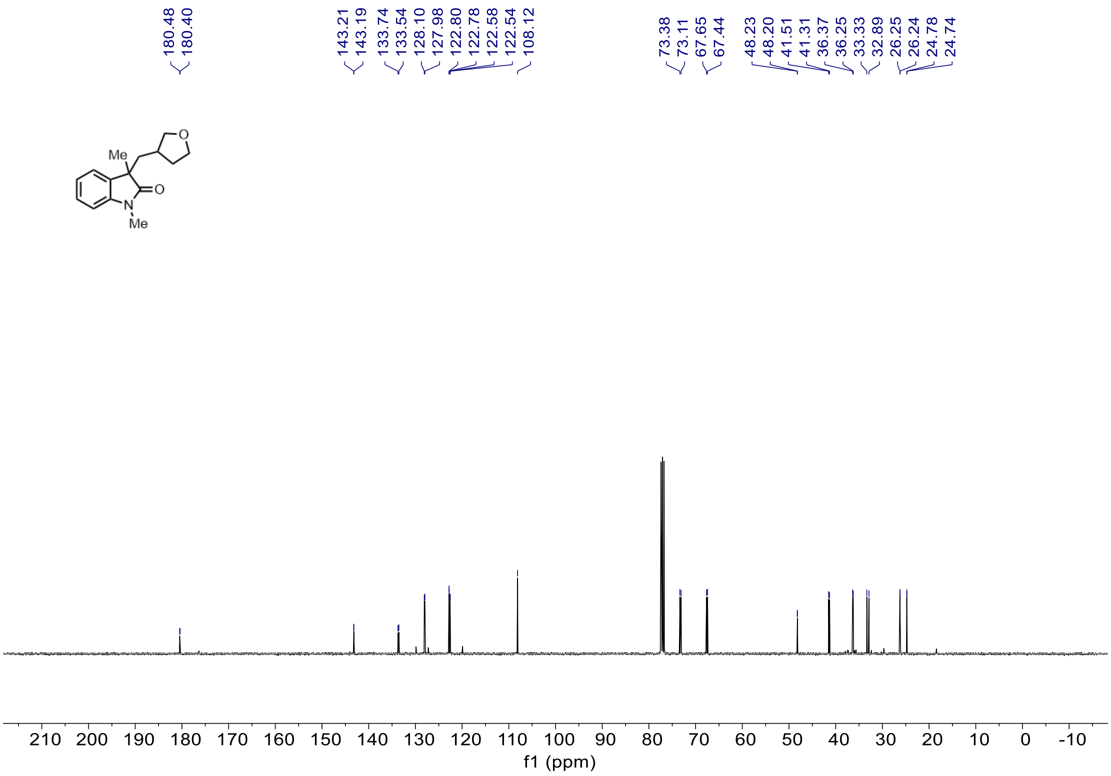
^{1}H and ^{13}C spectra for compound **8**



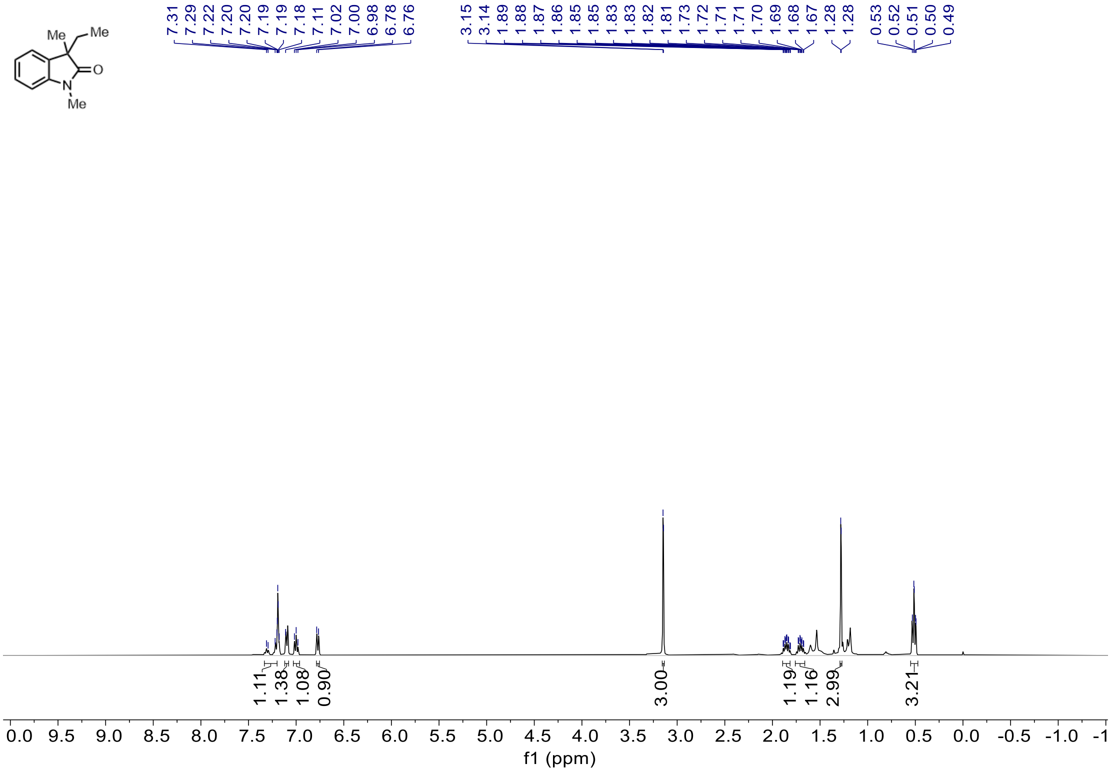


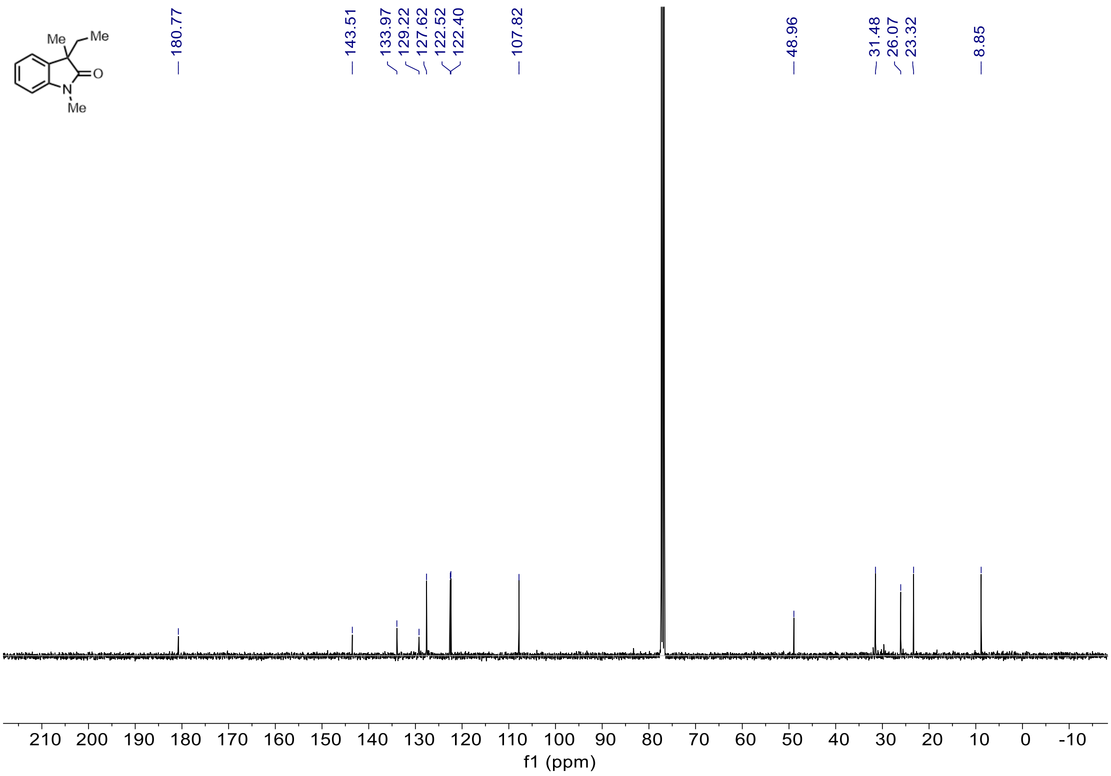
^{1}H and ^{13}C spectra for compound **9**



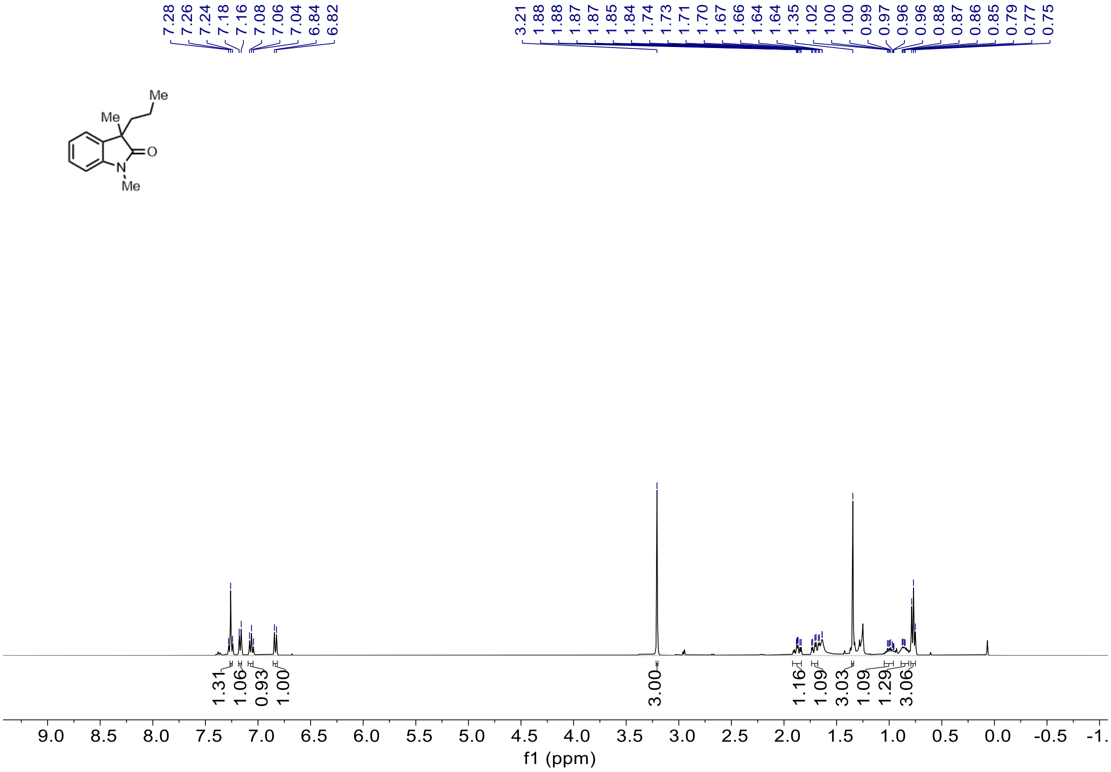


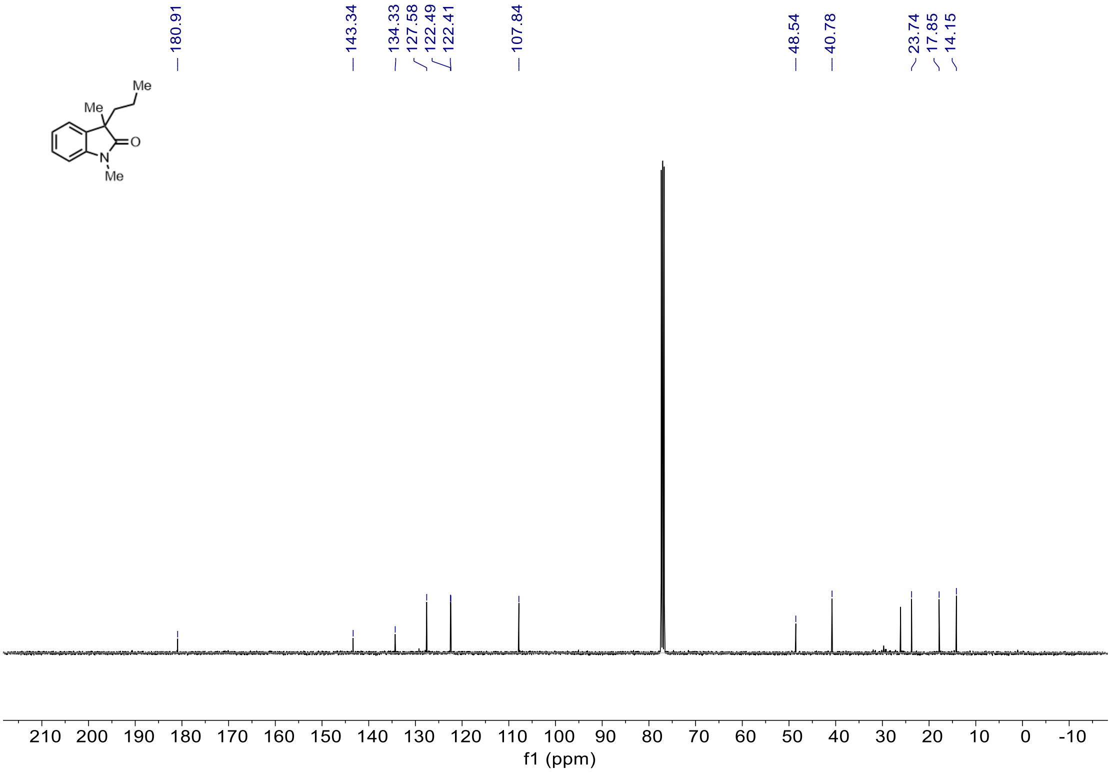
[1]H and [13]C spectra for compound **10**



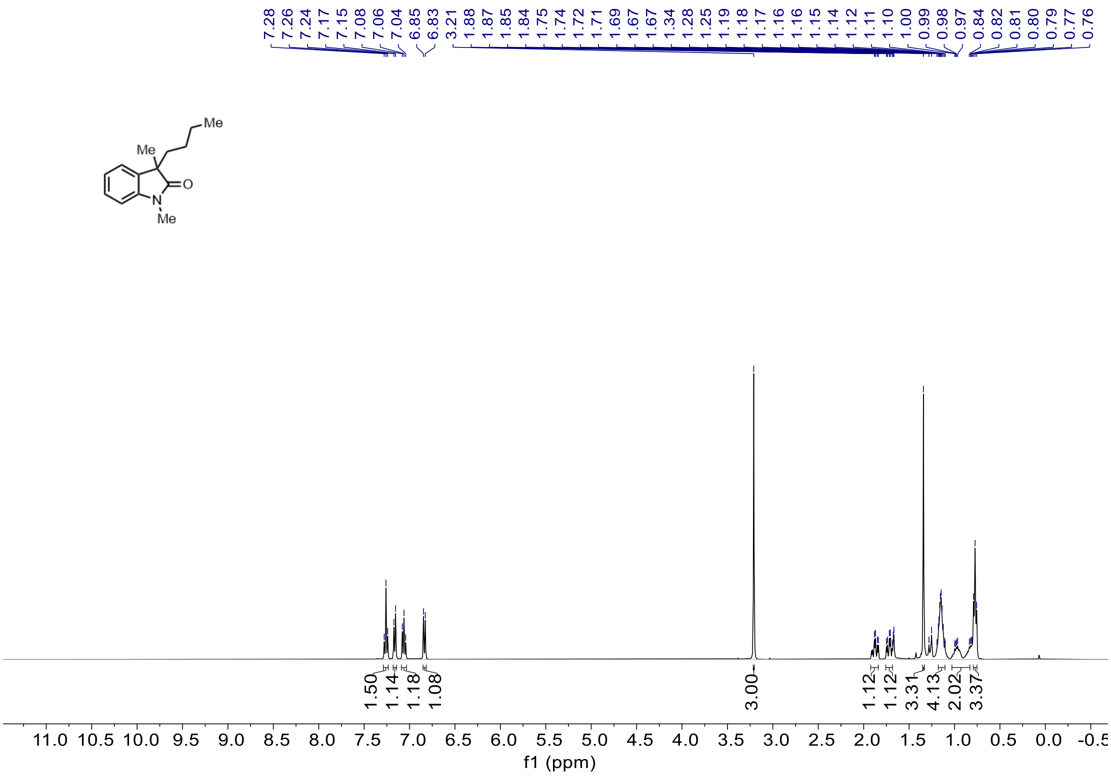


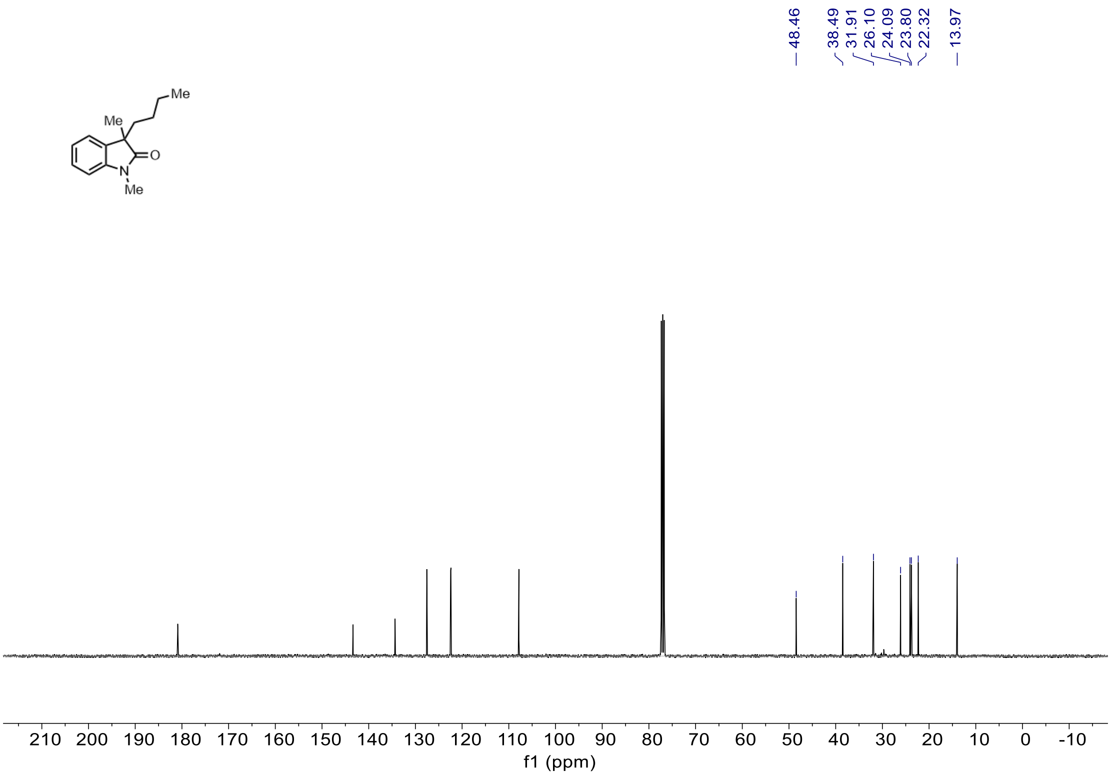
^{1}H and ^{13}C spectra for compound **11**



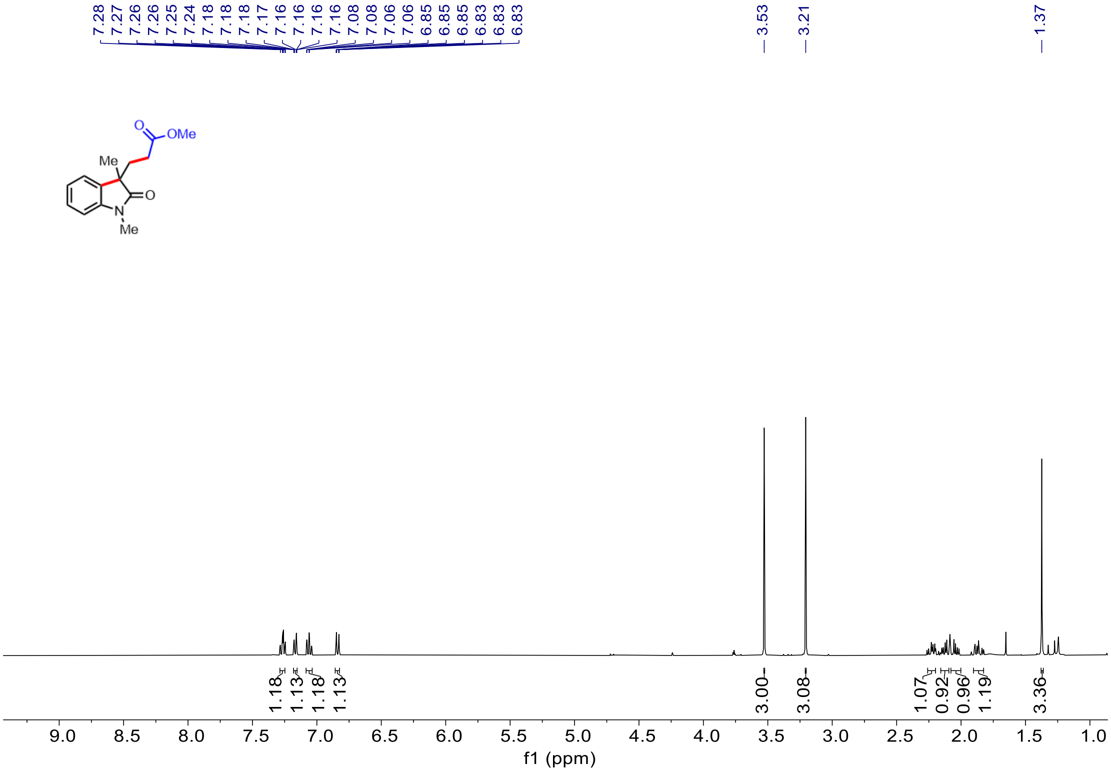


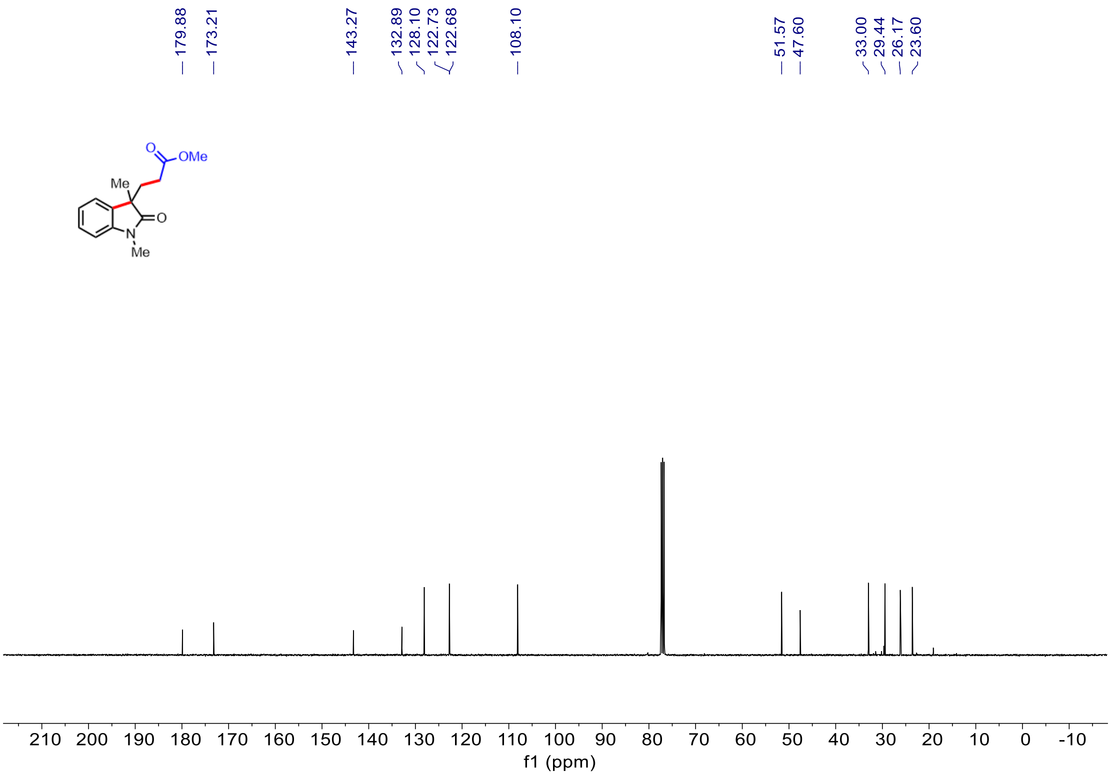
^{1}H and ^{13}C spectra for compound **12**



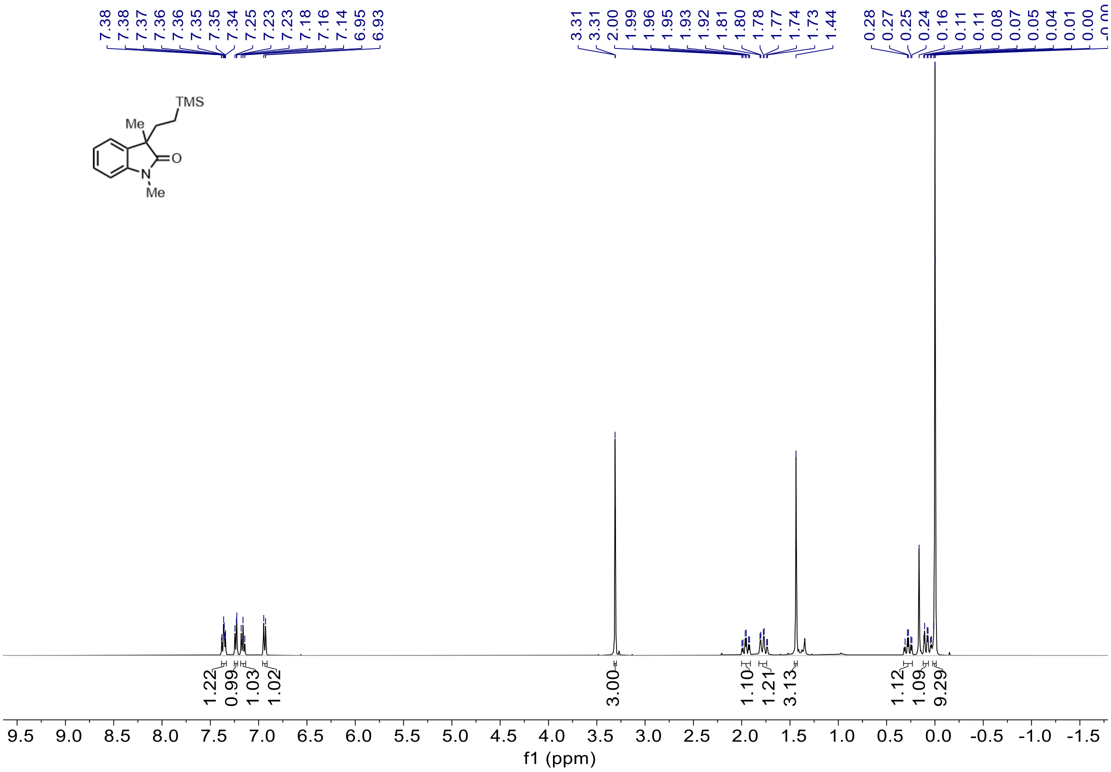


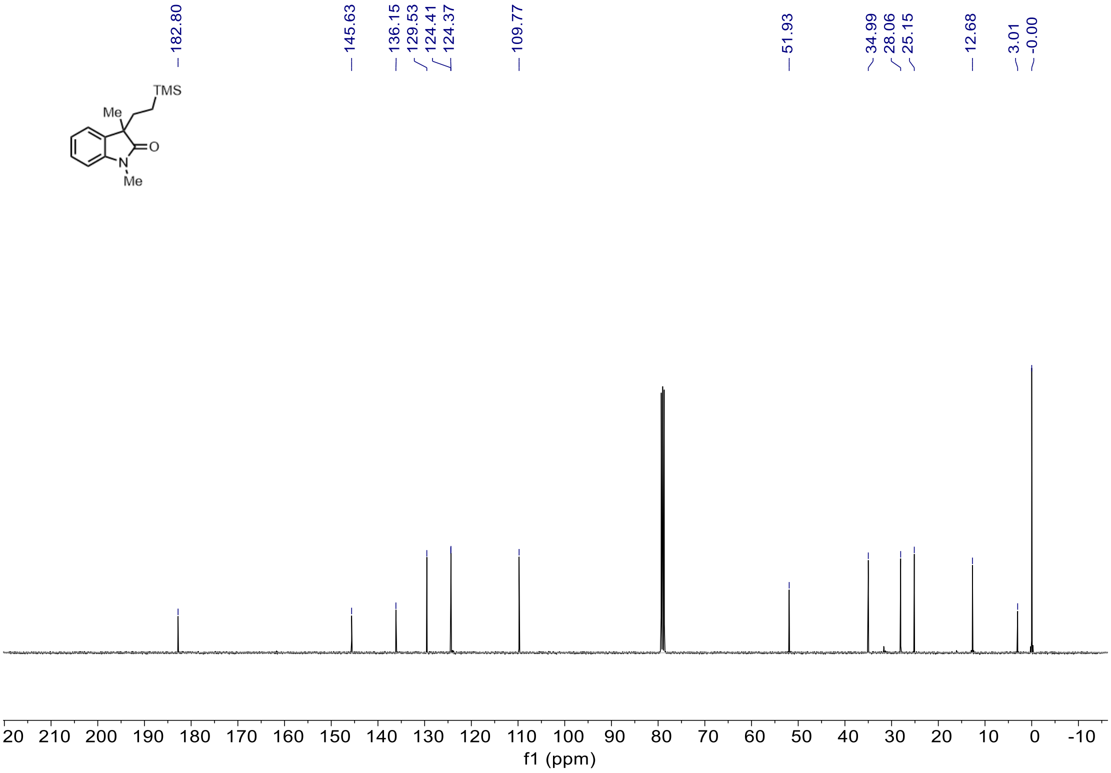
^{1}H and ^{13}C spectra for compound **13**



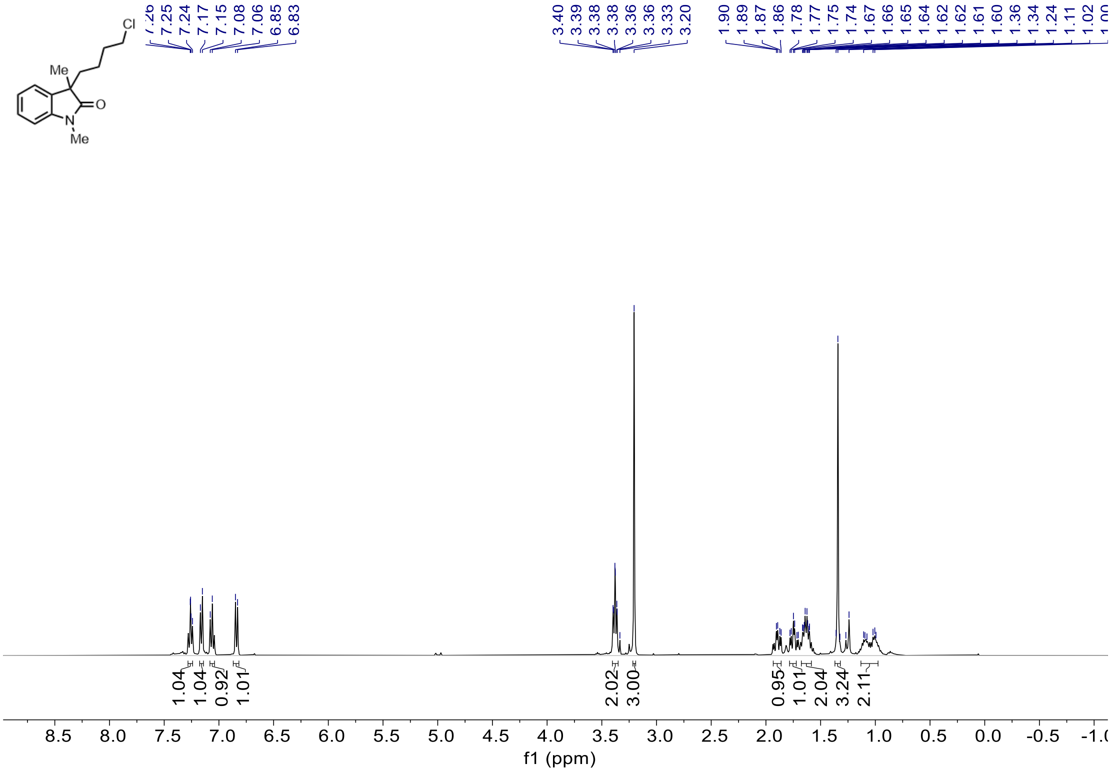


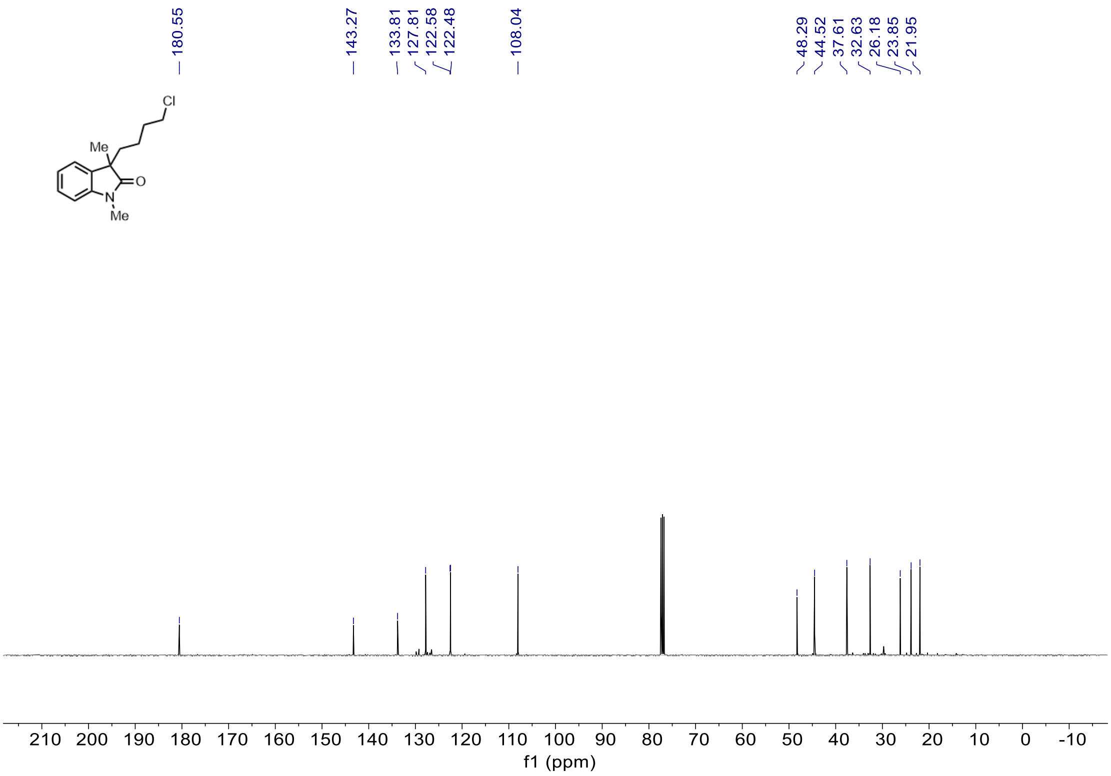
[1]H and [13]C spectra for compound **14**



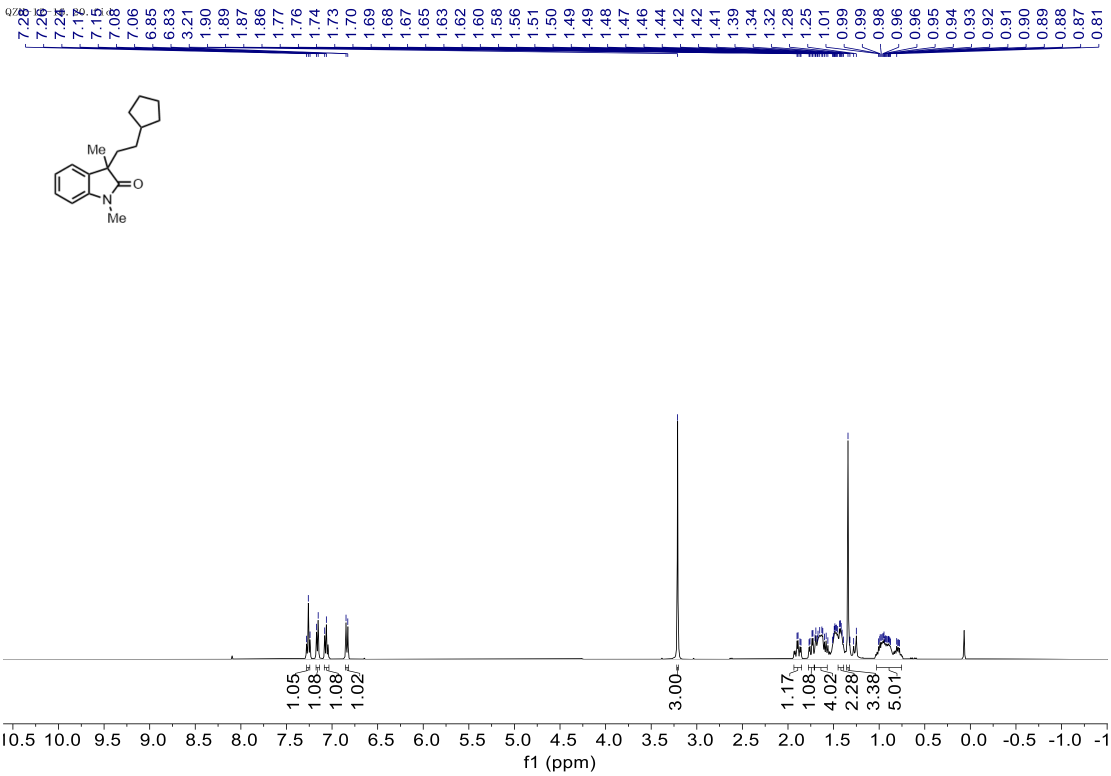


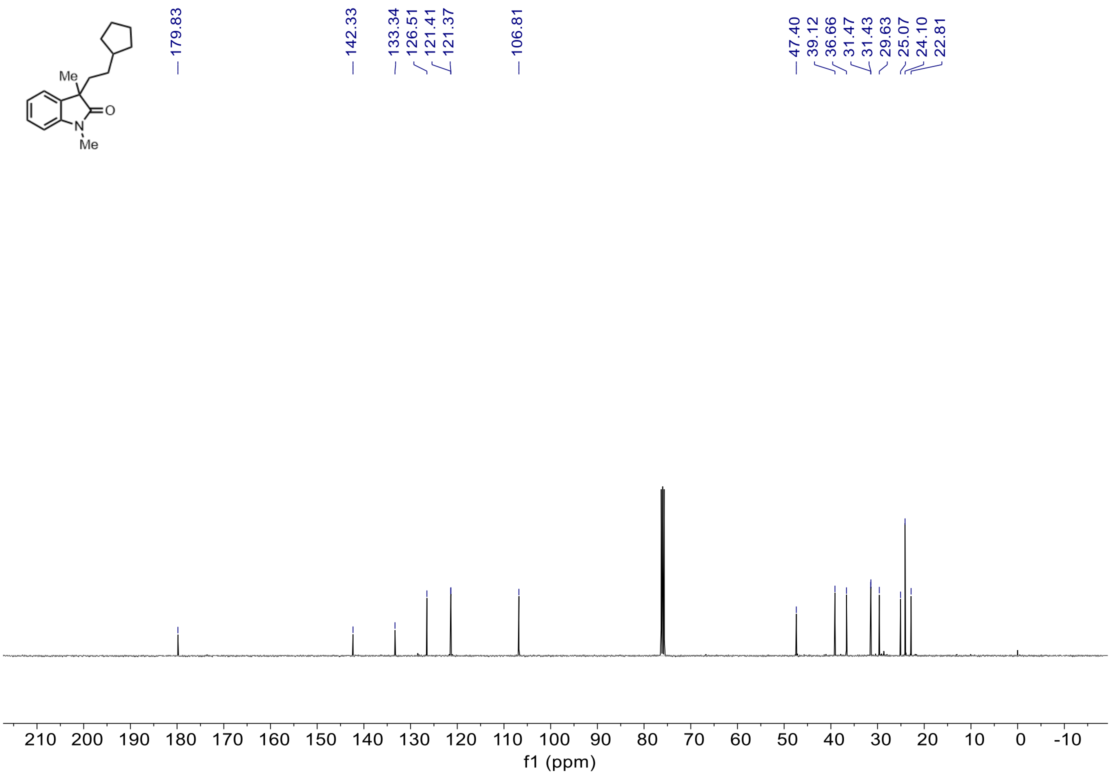
[1]H and [13]C spectra for compound **15**



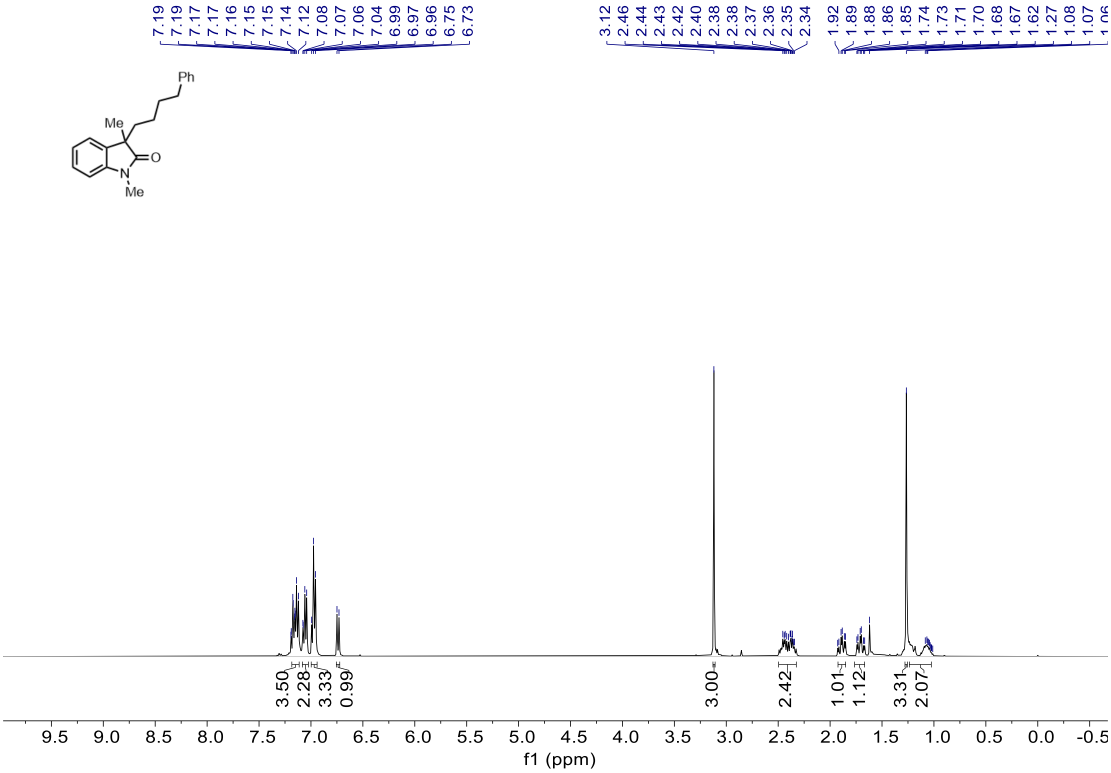


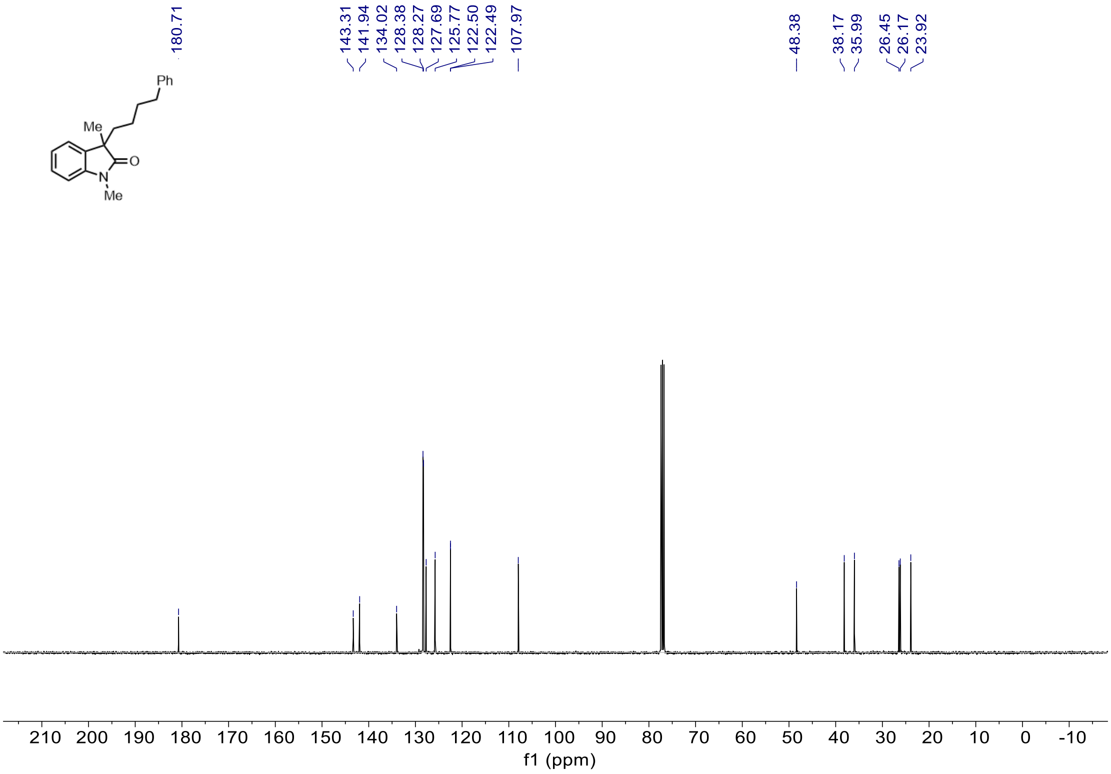
^{1}H and ^{13}C spectra for compound **16**



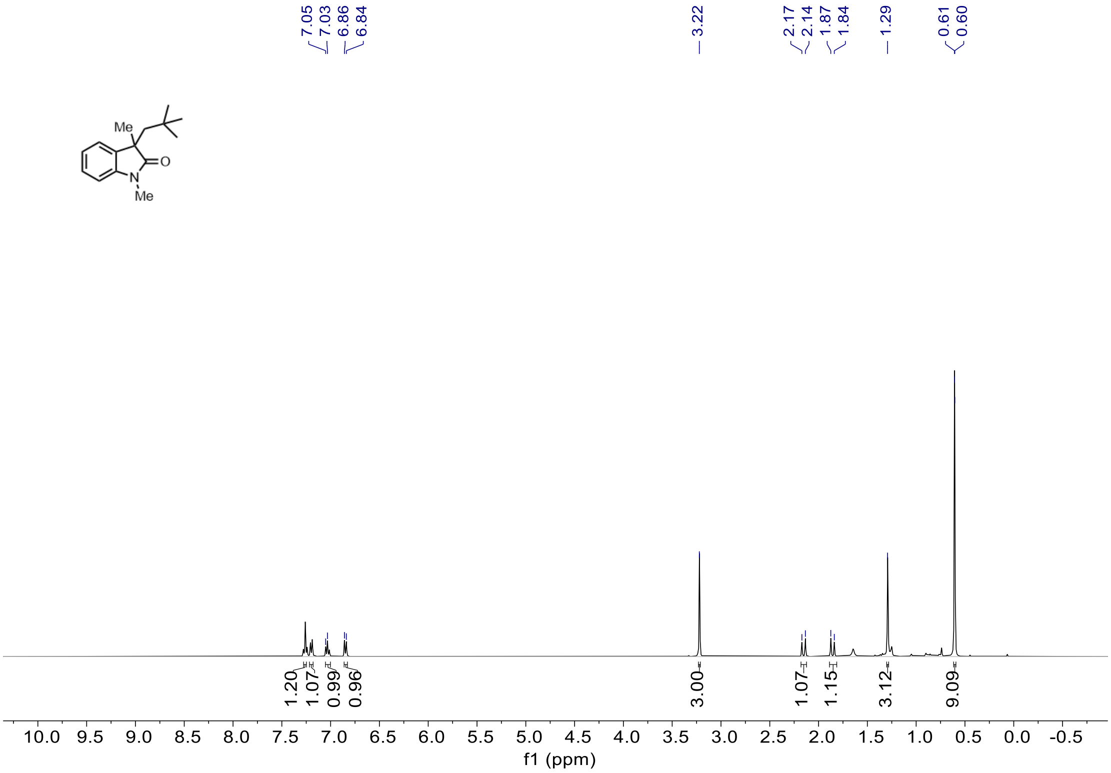


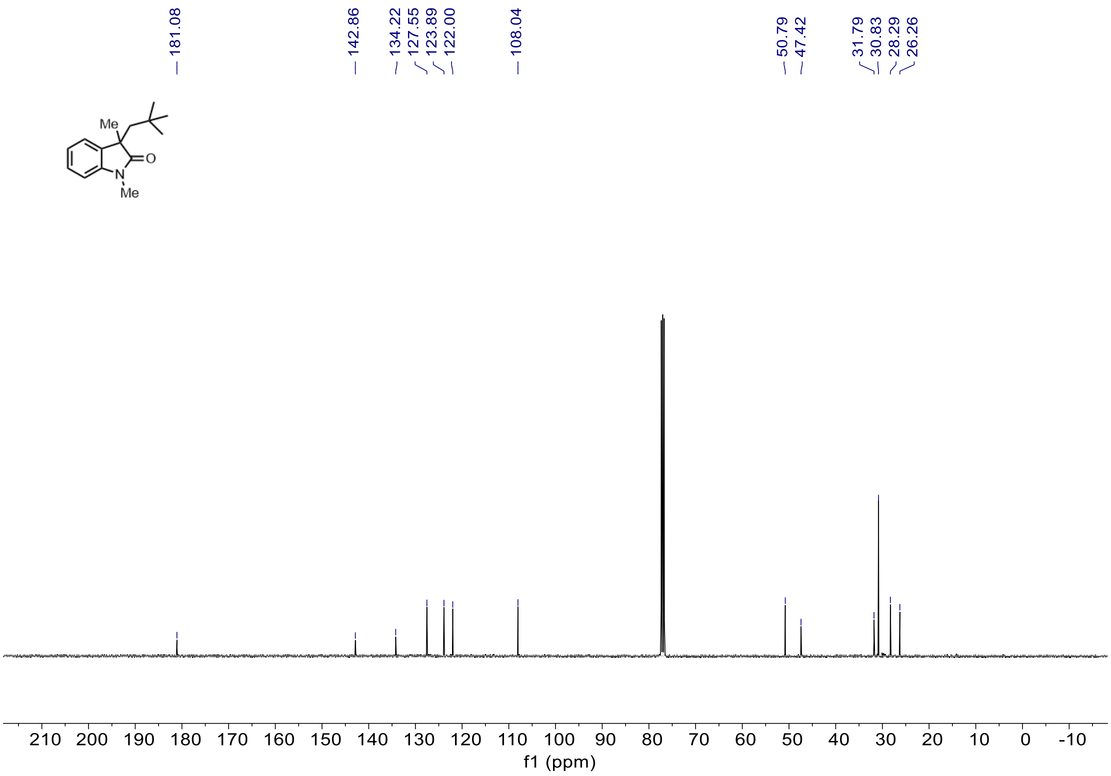
[1]H and [13]C spectra for compound **17**



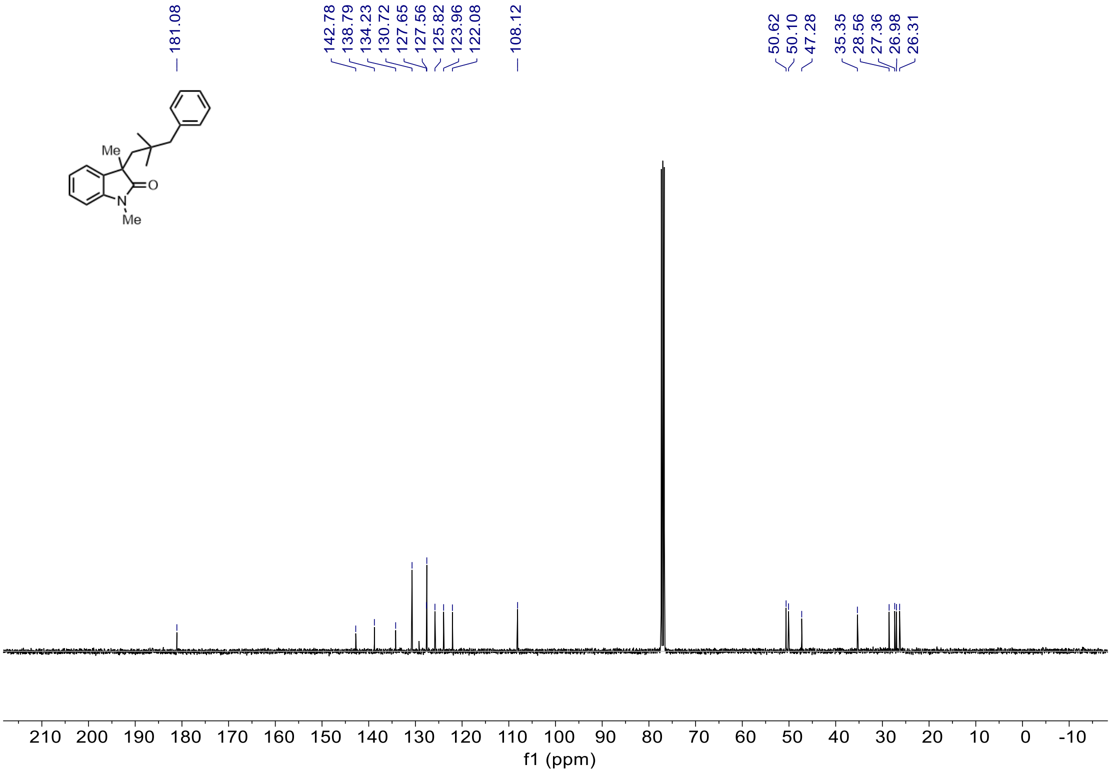


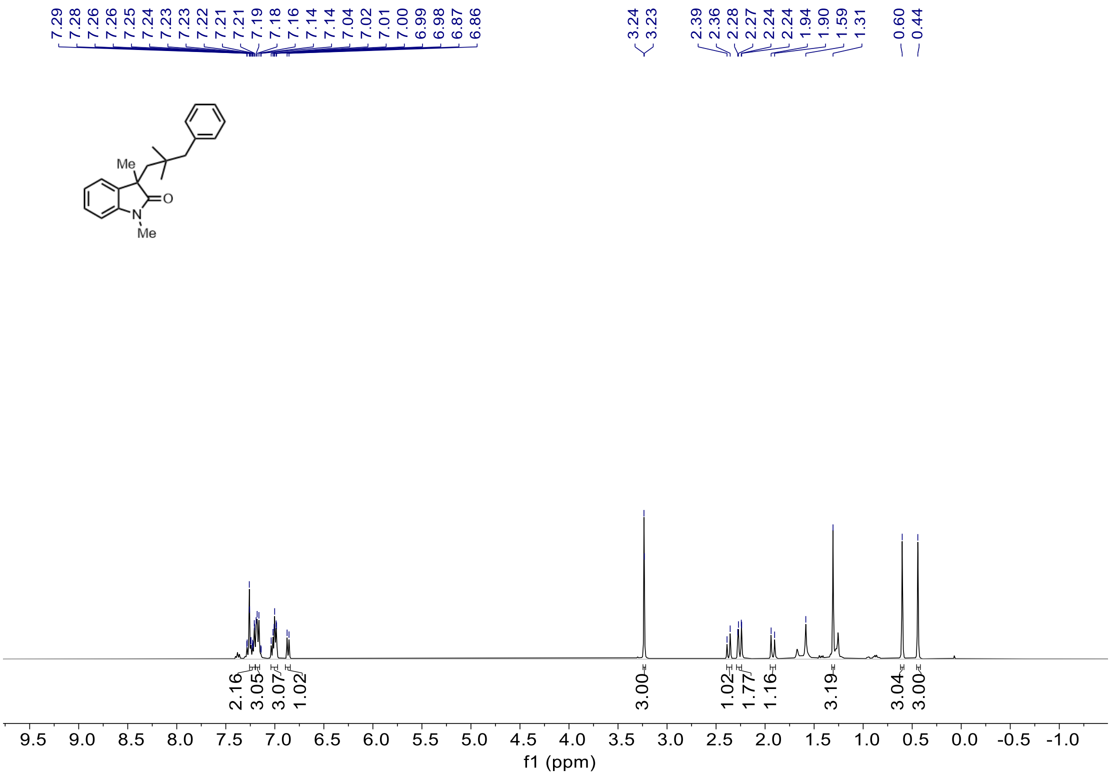
^{1}H and ^{13}C spectra for compound **18**



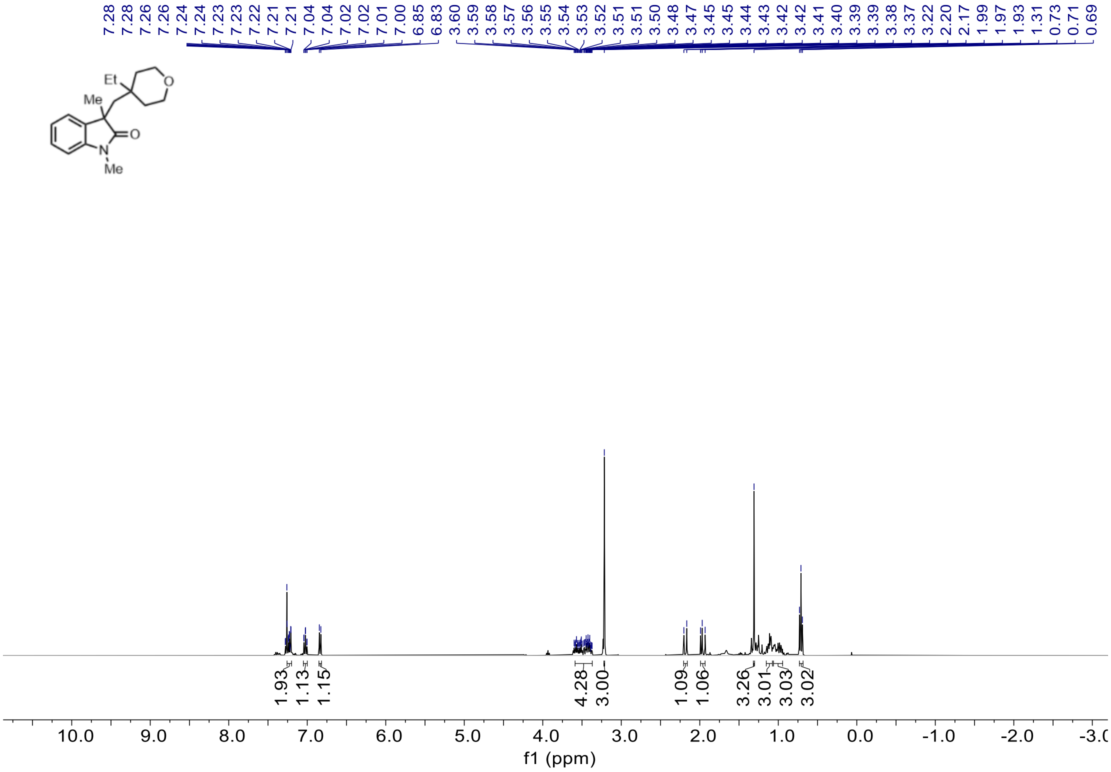


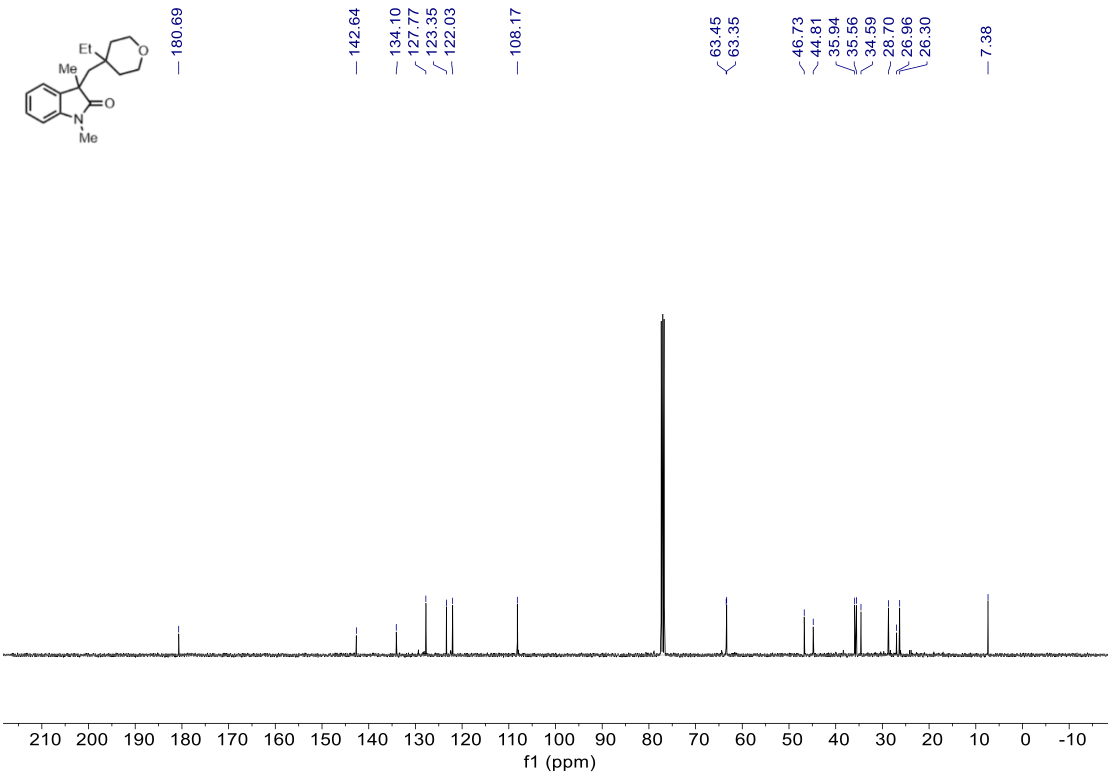
^{1}H and ^{13}C spectra for compound **19**



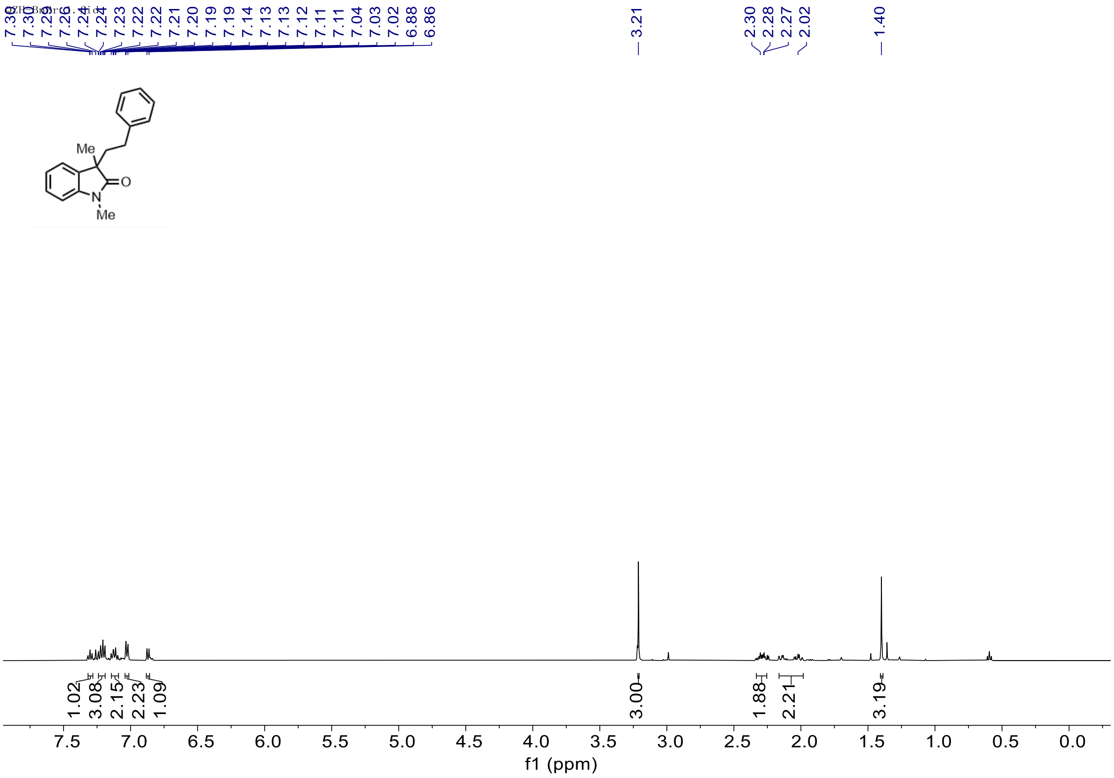


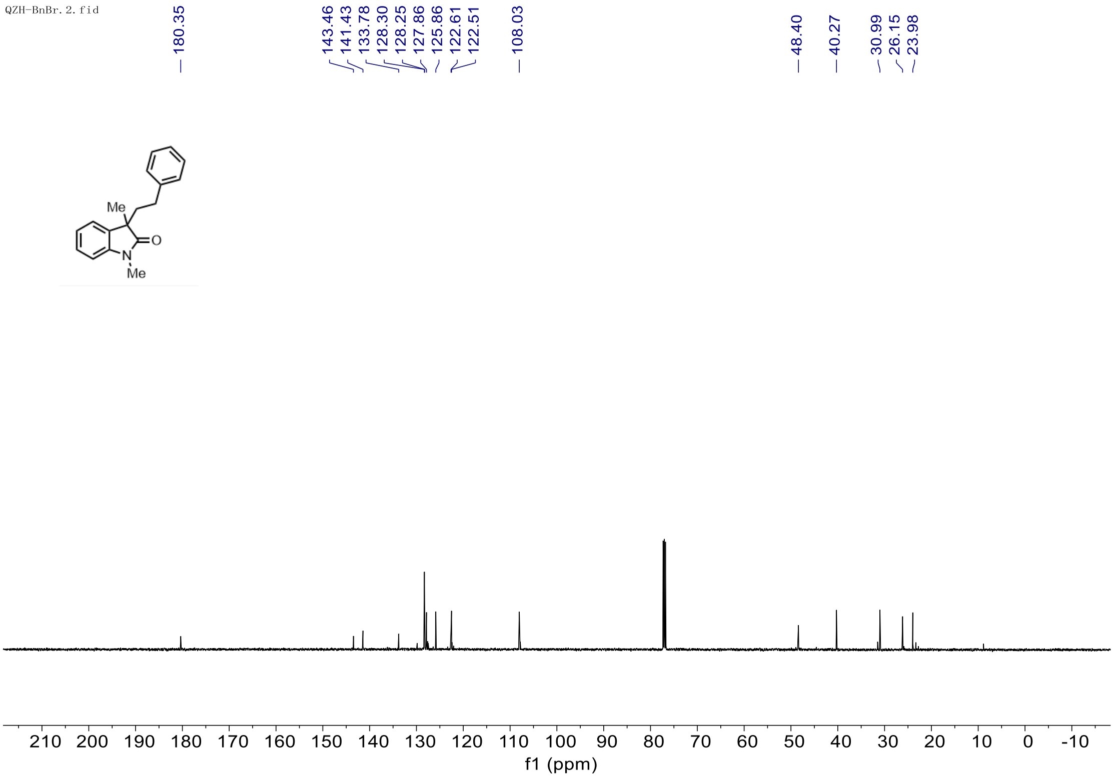
^{1}H and ^{13}C spectra for compound **20**



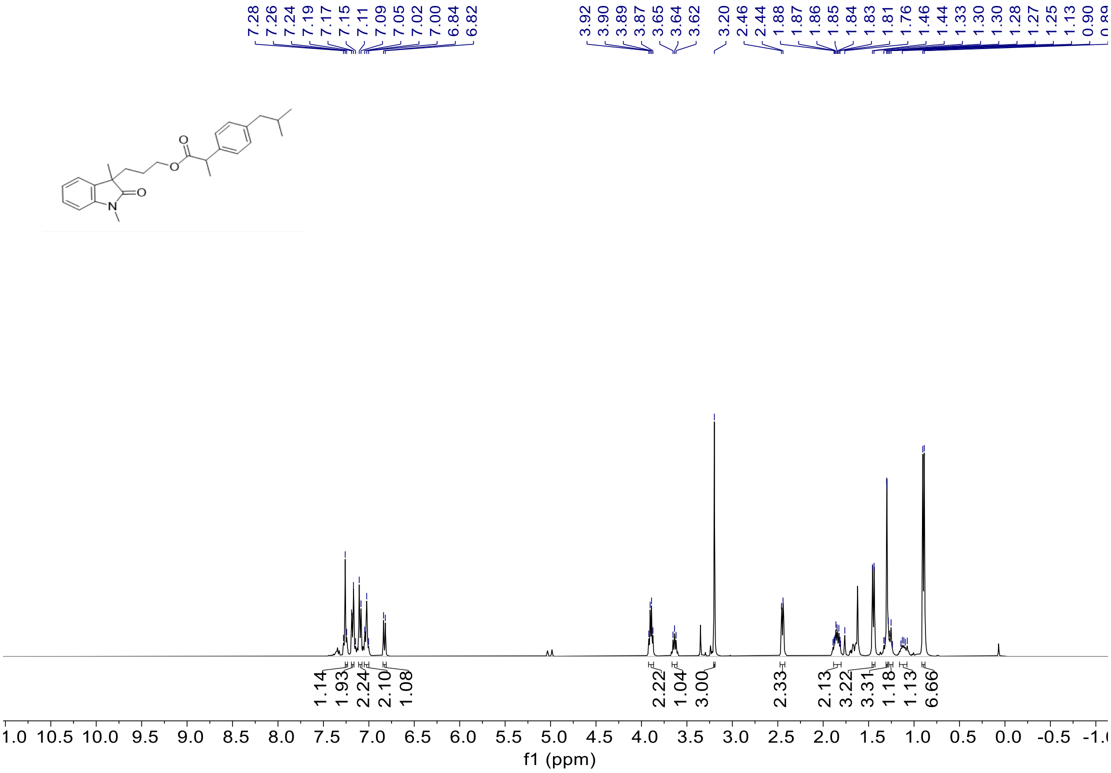


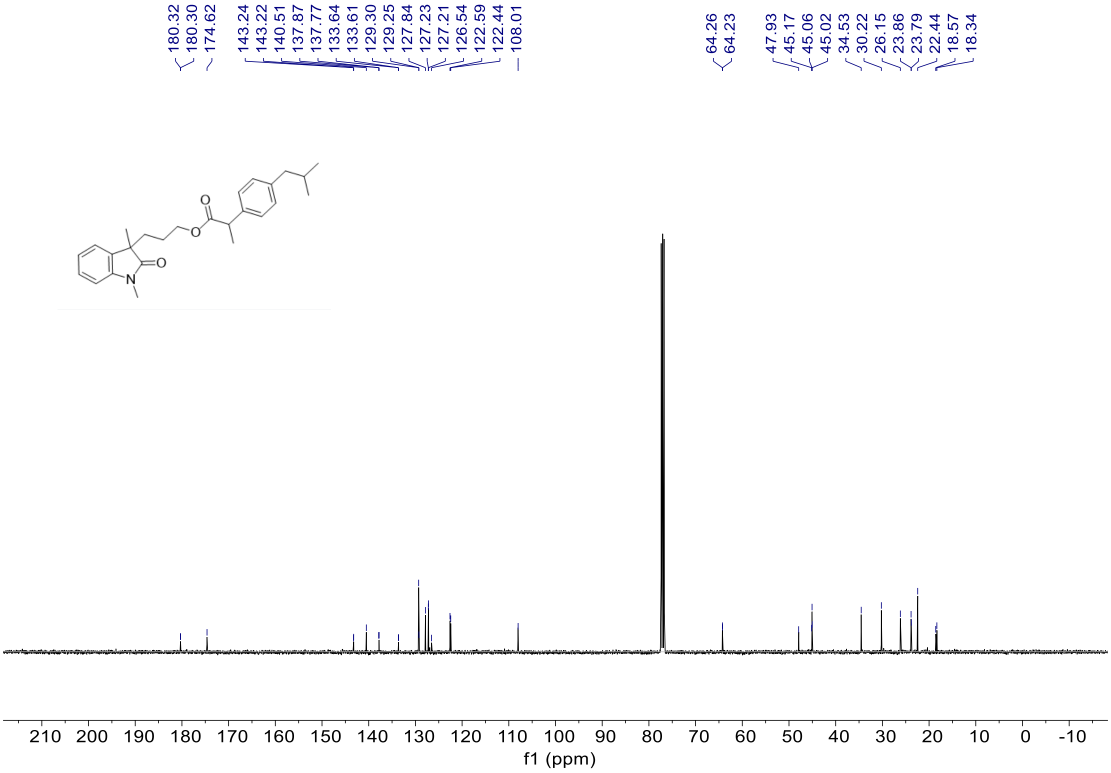
^{1}H and ^{13}C spectra for compound **21**



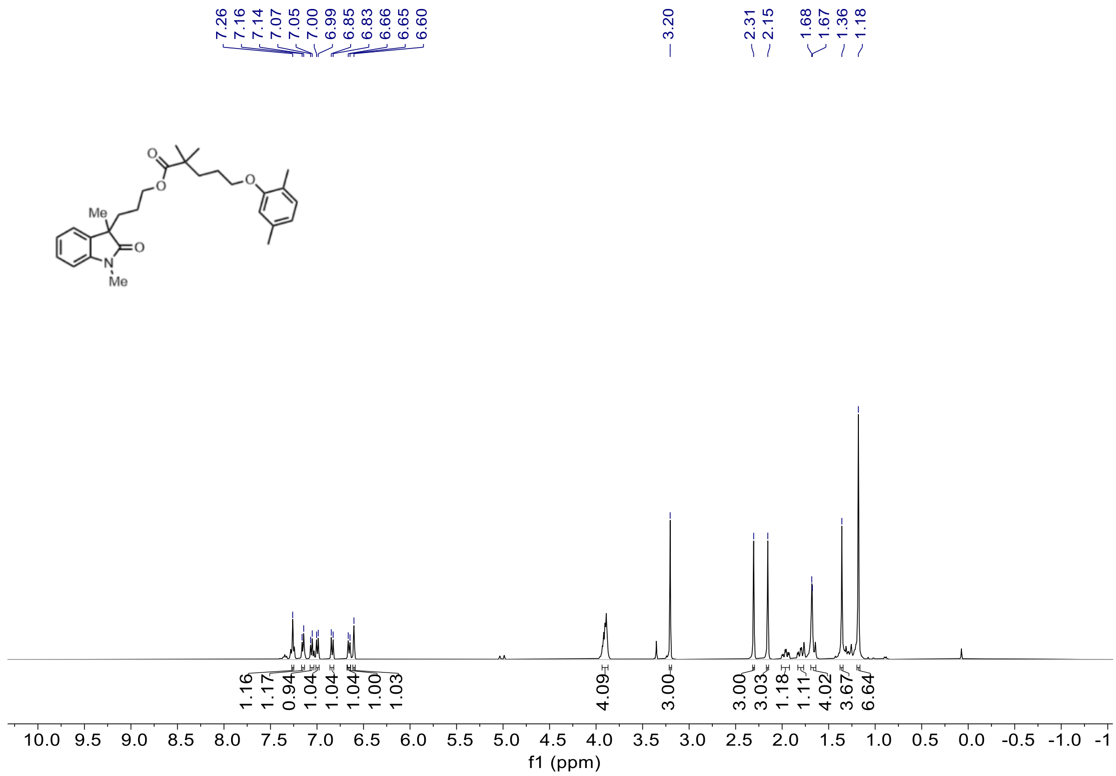


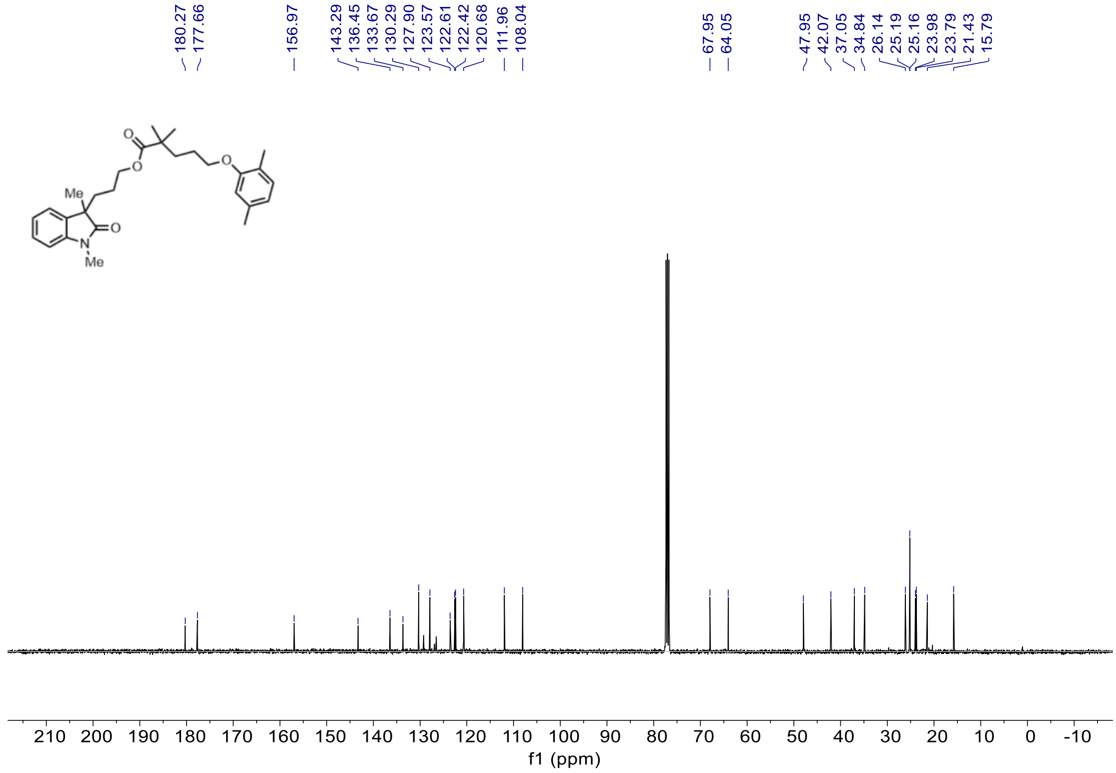
^1H and ^{13}C spectra for compound **22**



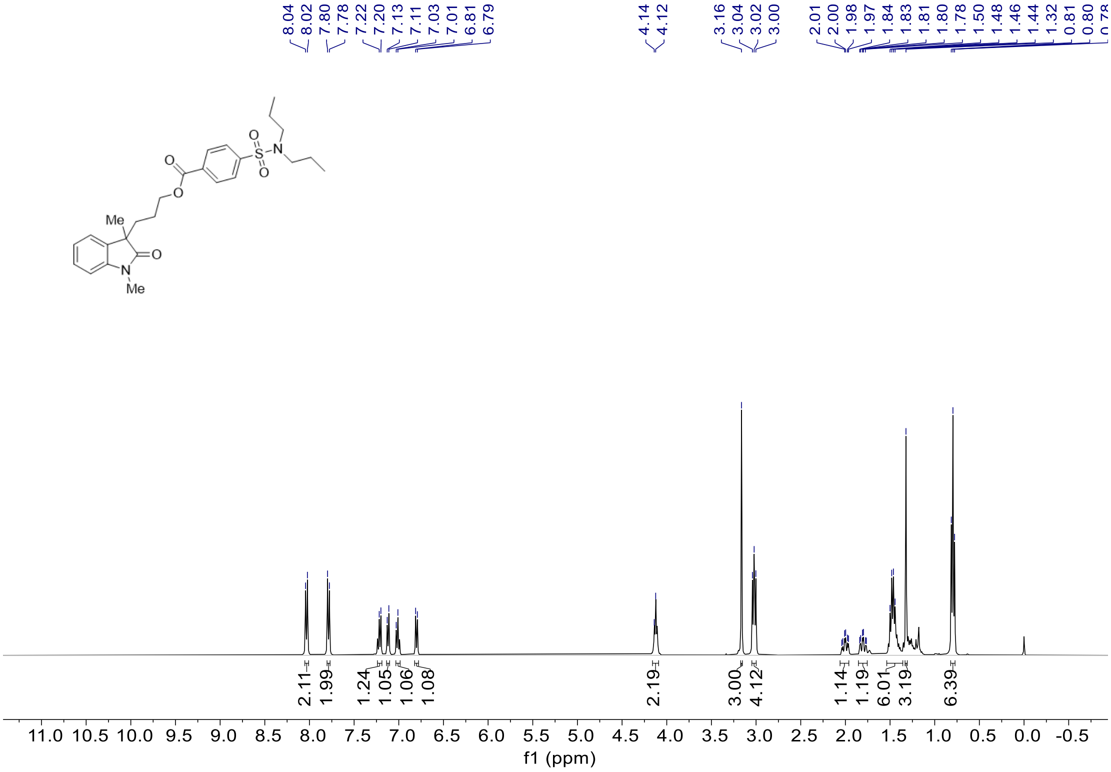


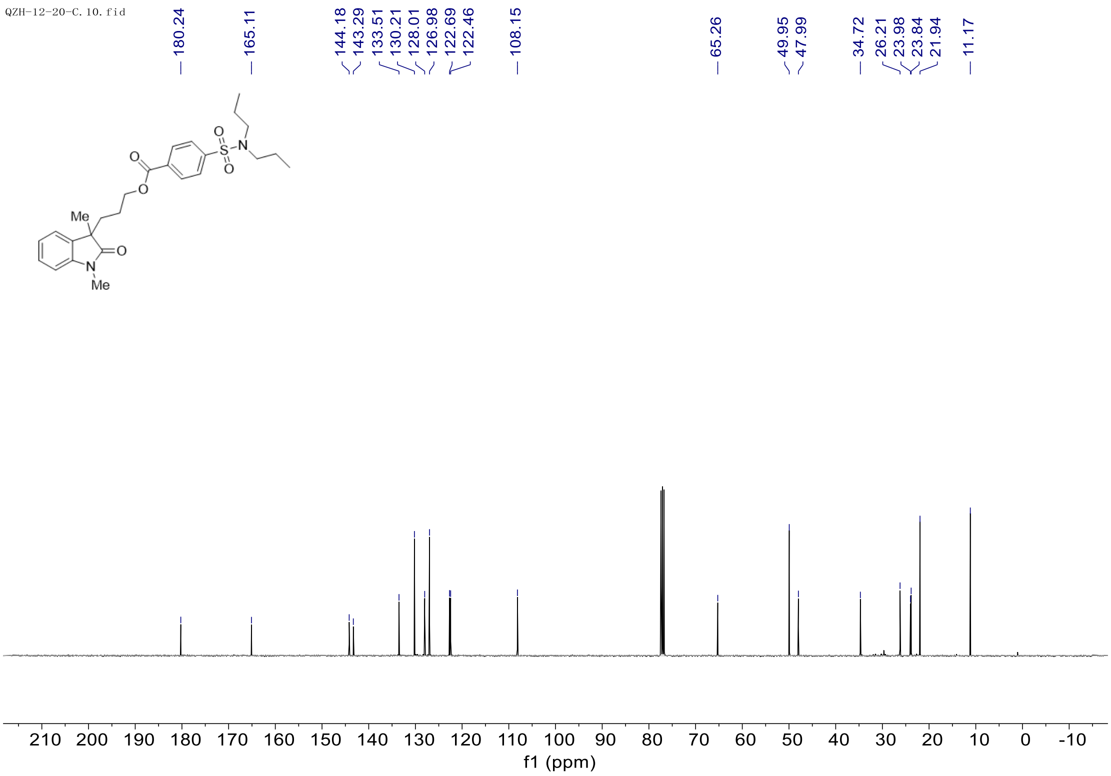
[1]H and [13]C spectra for compound **23**



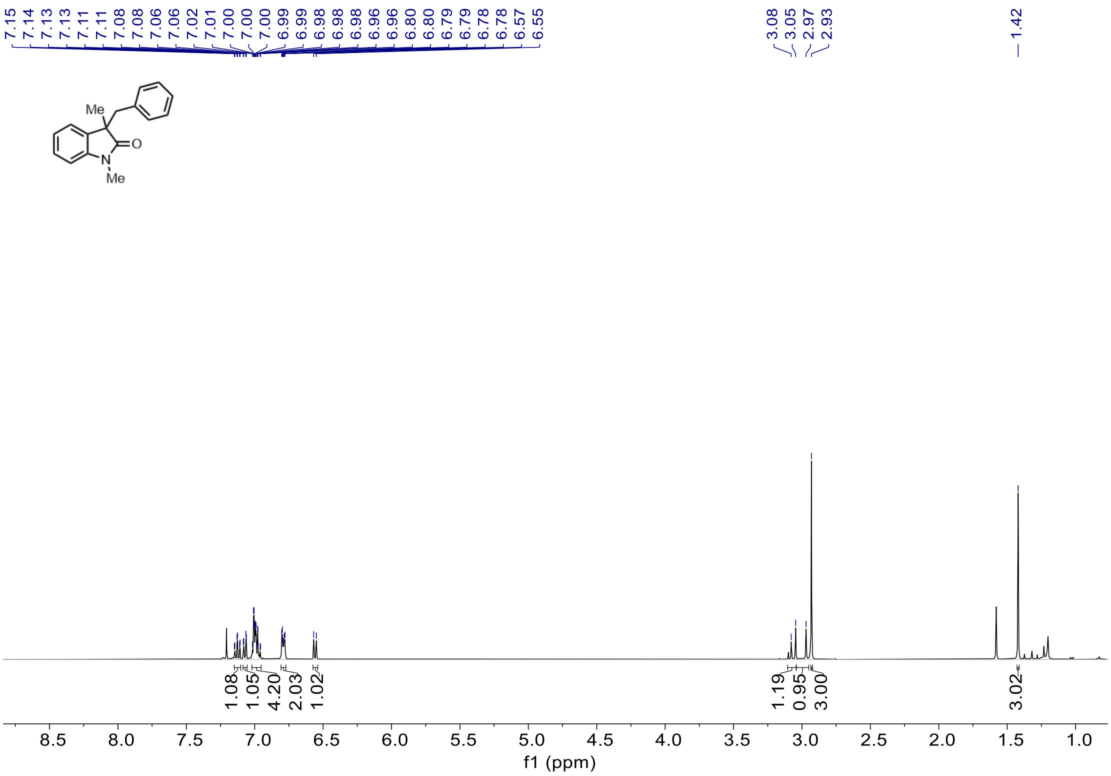


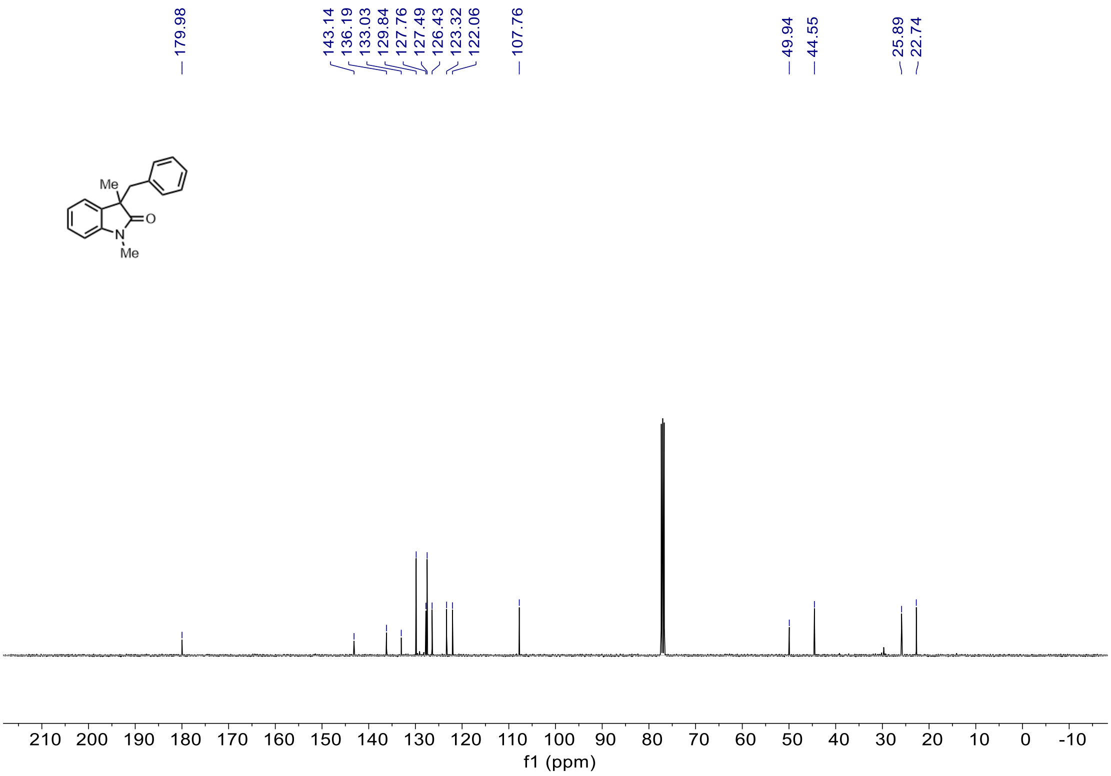
[1]H and [13]C spectra for compound **24**



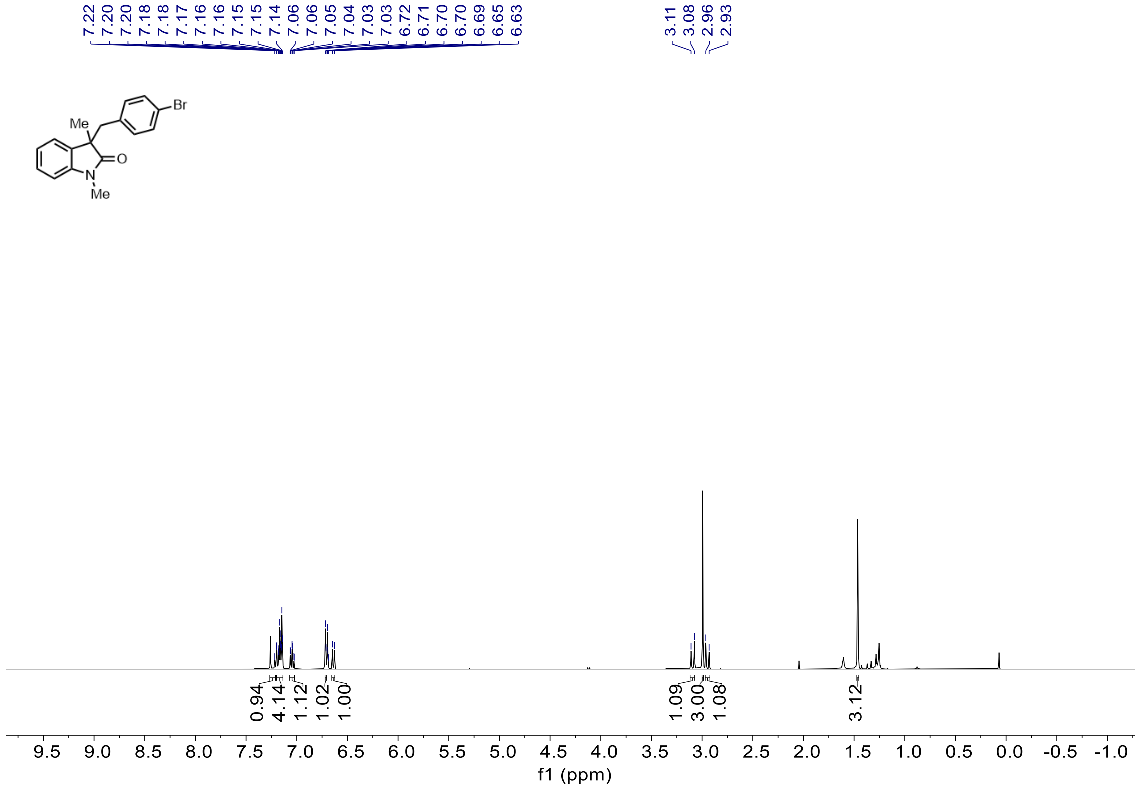


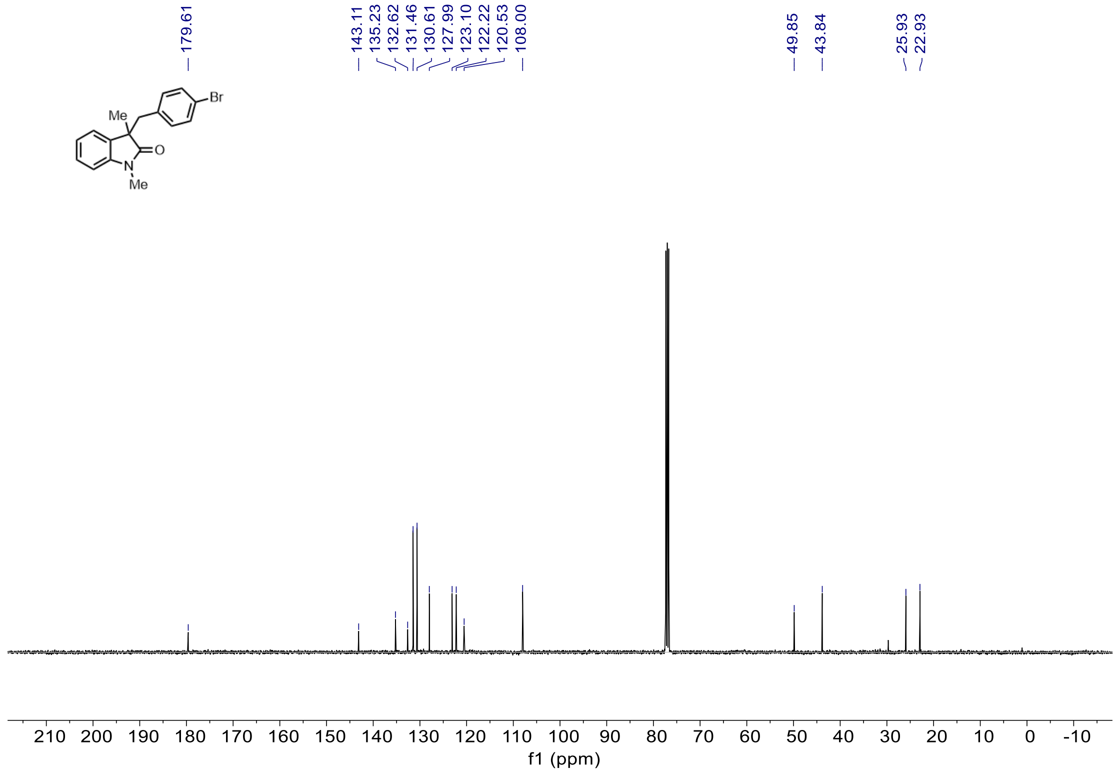
^{1}H and ^{13}C spectra for compound **25**



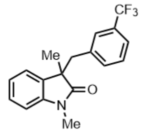


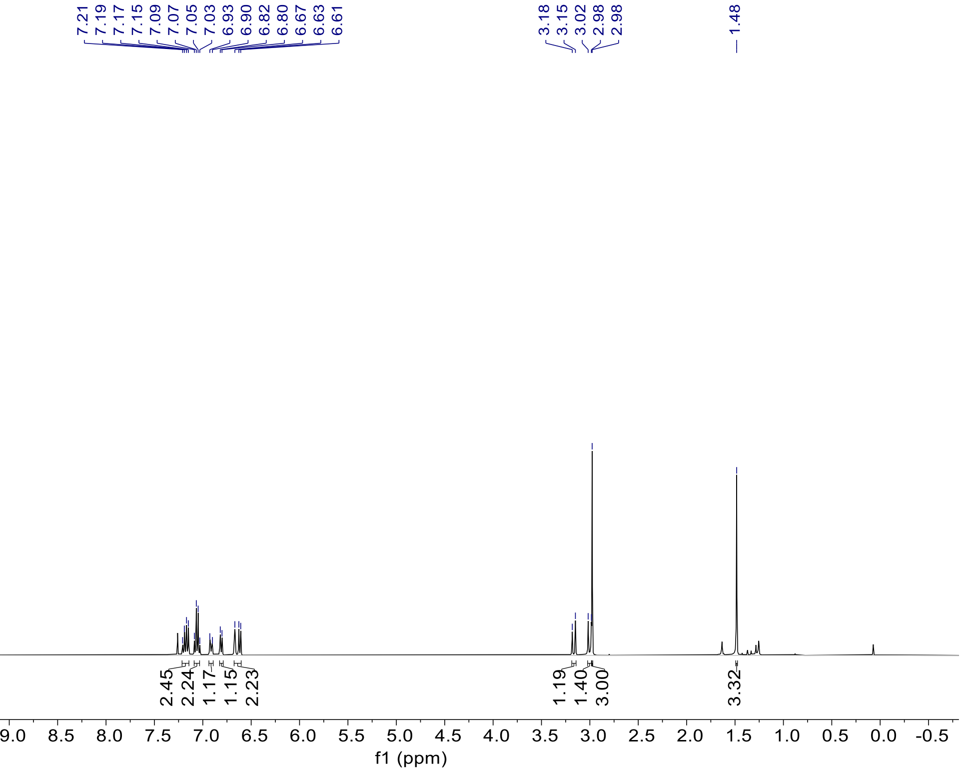
^{1}H and ^{13}C spectra for compound **26**

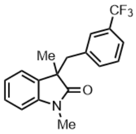


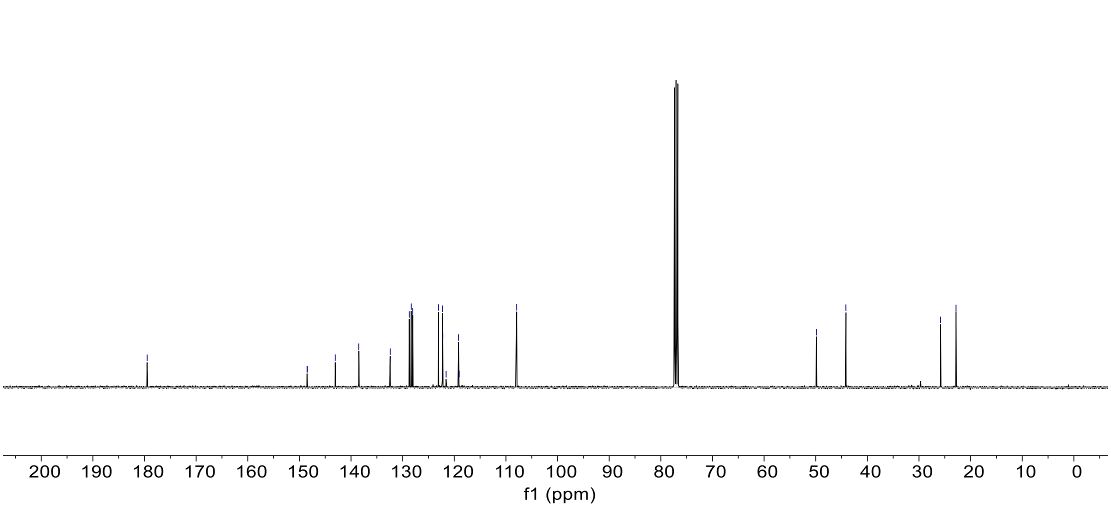


^{1}H and ^{13}C spectra for compound **27**

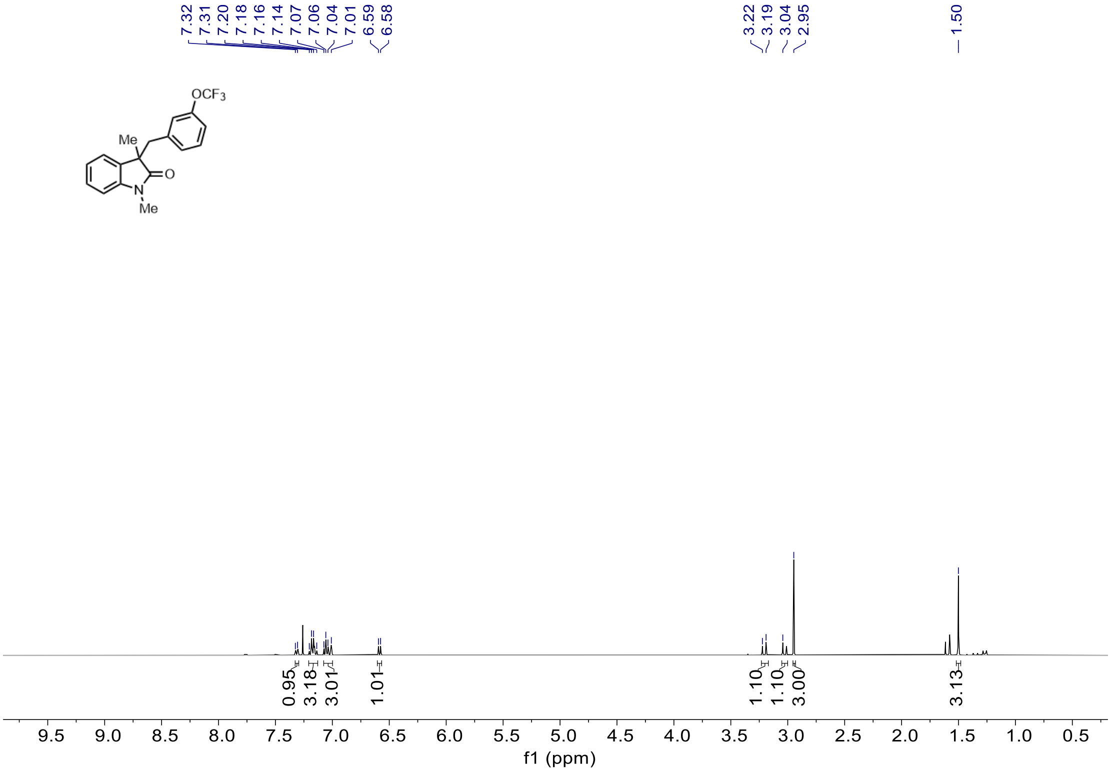


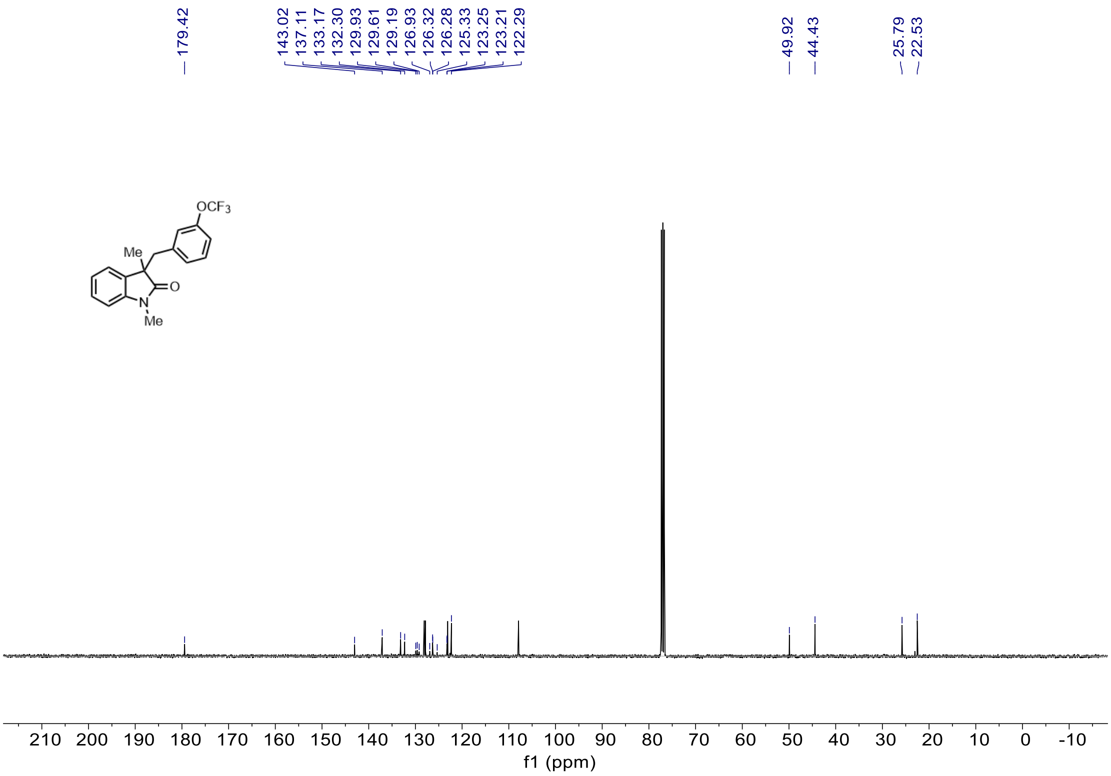




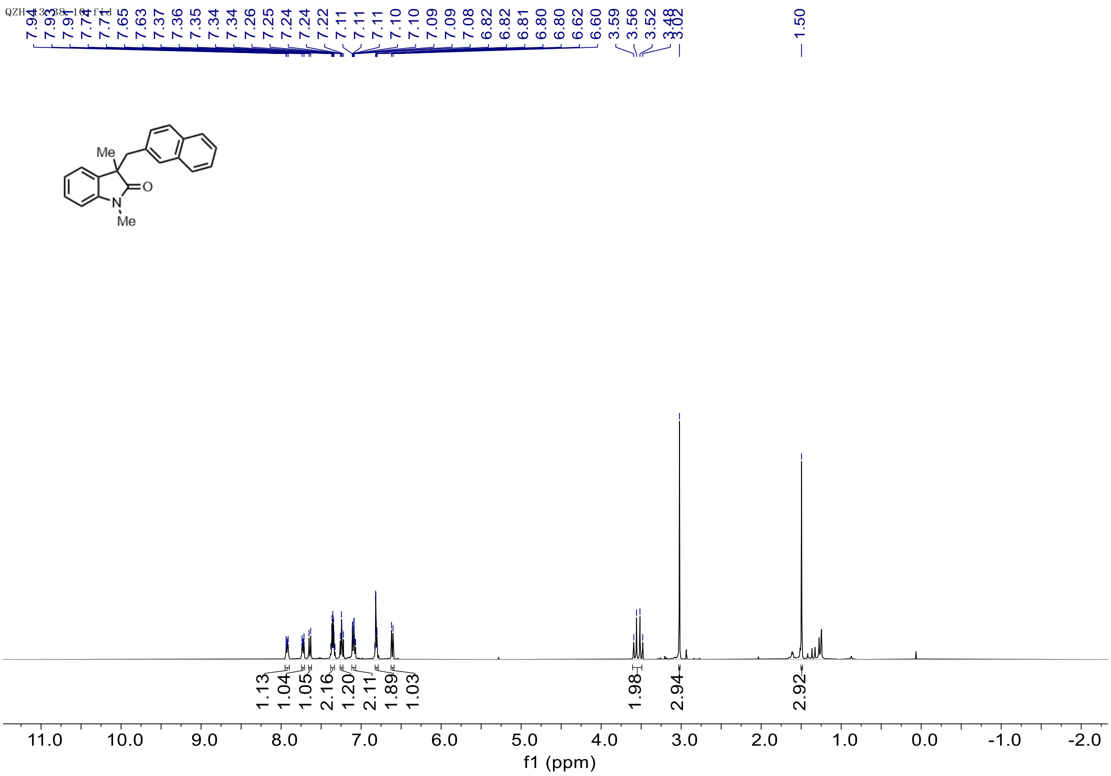


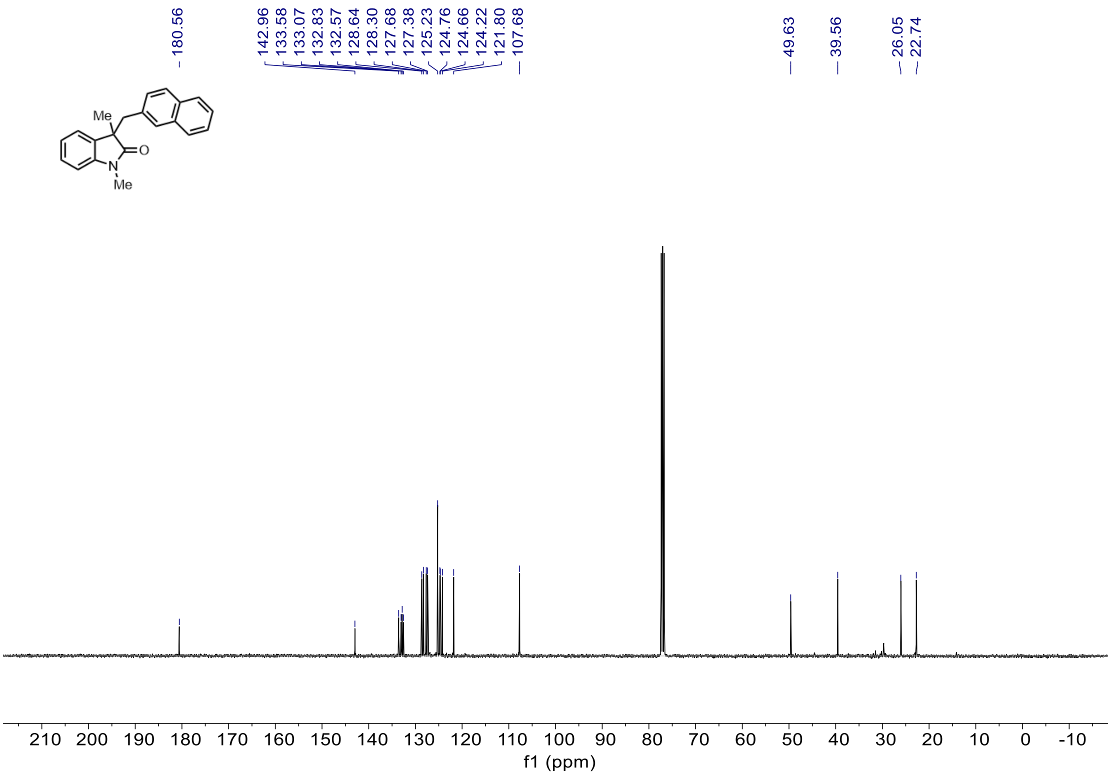
^{1}H and ^{13}C spectra for compound **28**



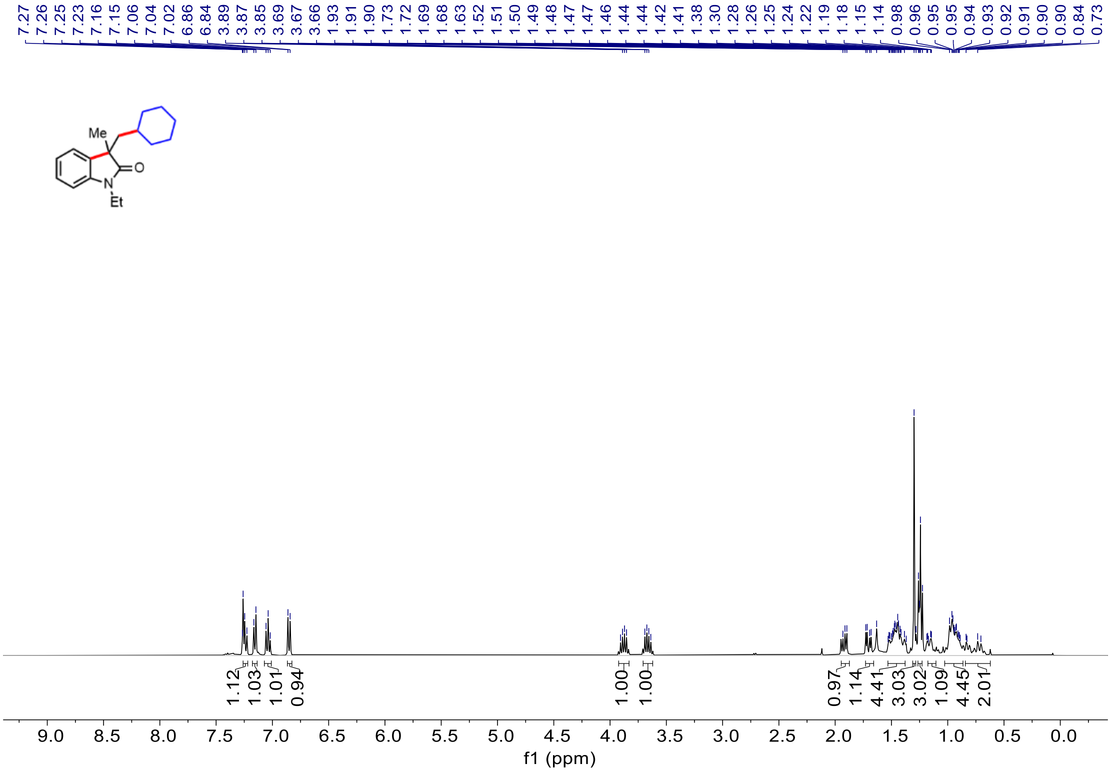


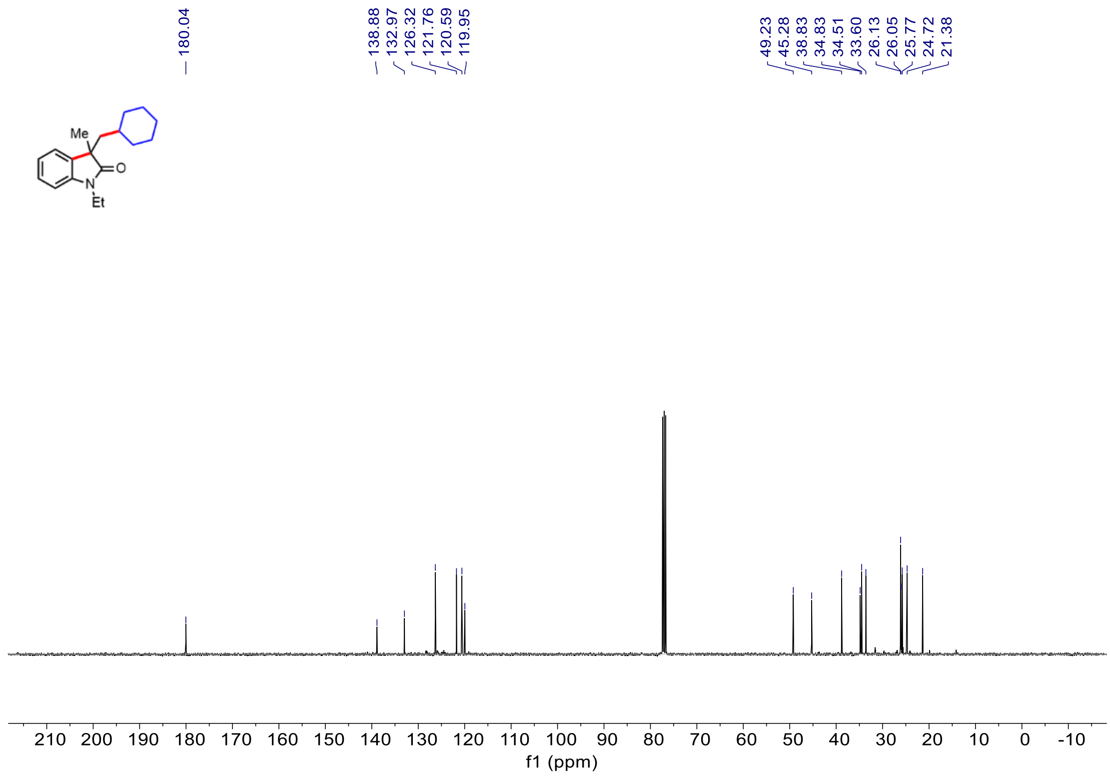
^{1}H and ^{13}C spectra for compound **29**



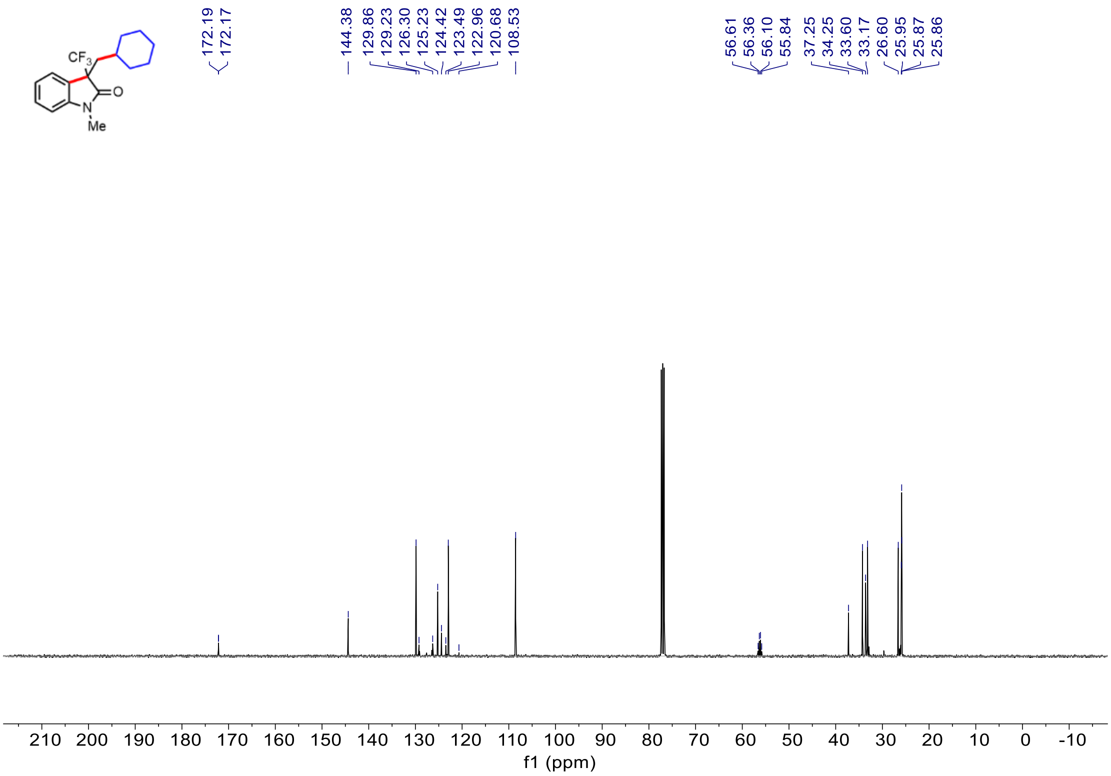


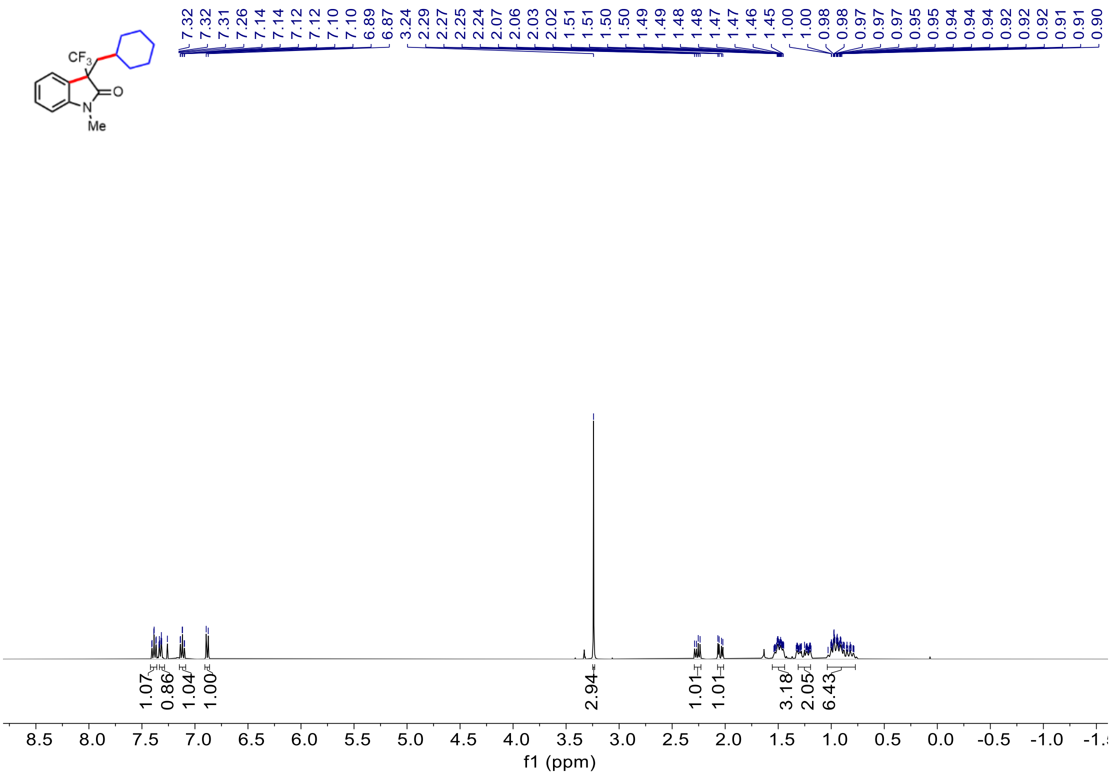
^{1}H and ^{13}C spectra for compound **30**



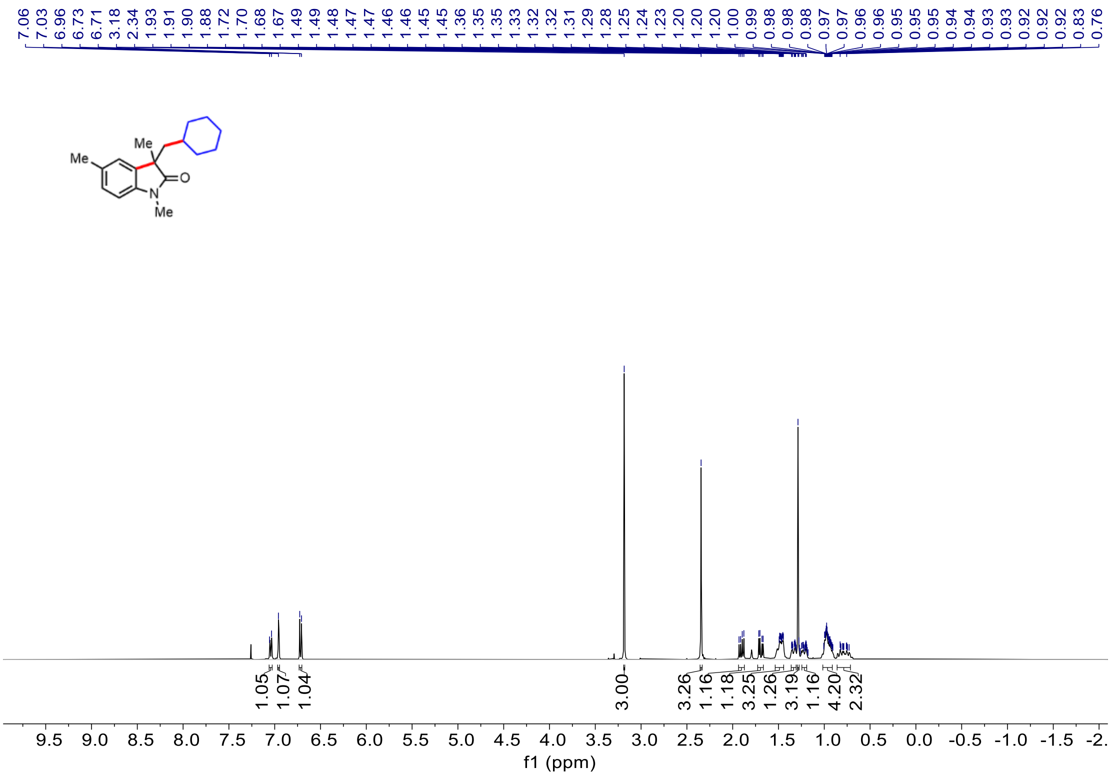


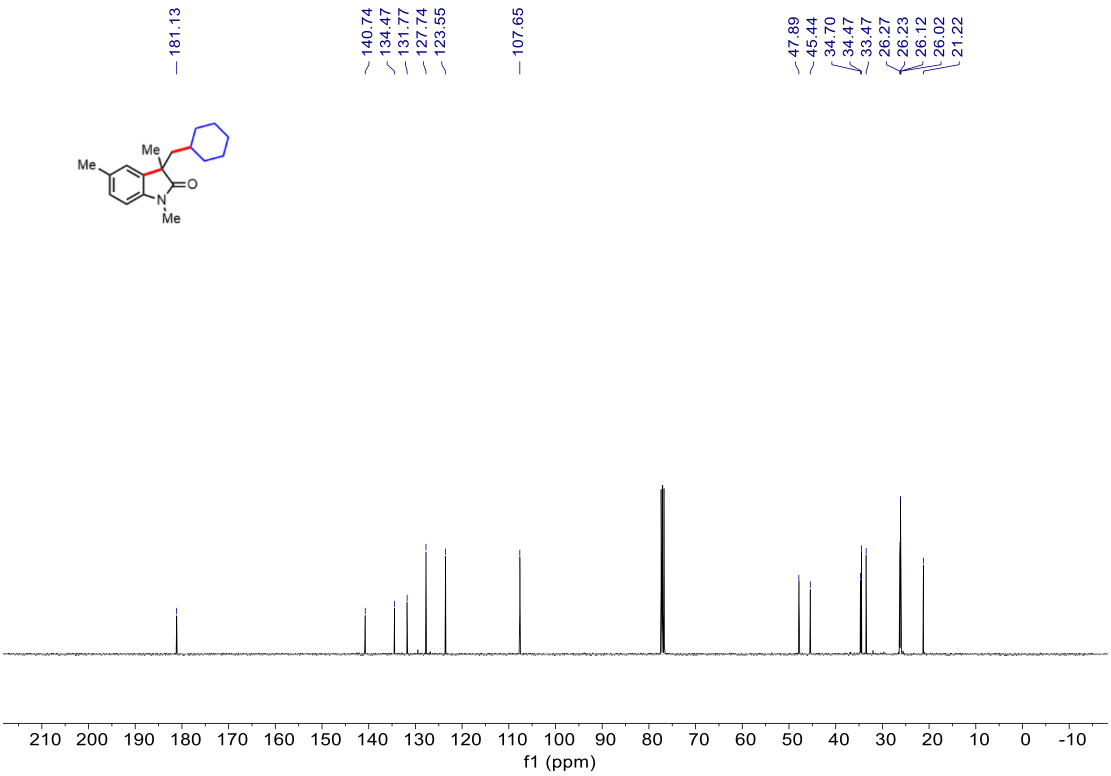
^{1}H and ^{13}C spectra for compound **31**



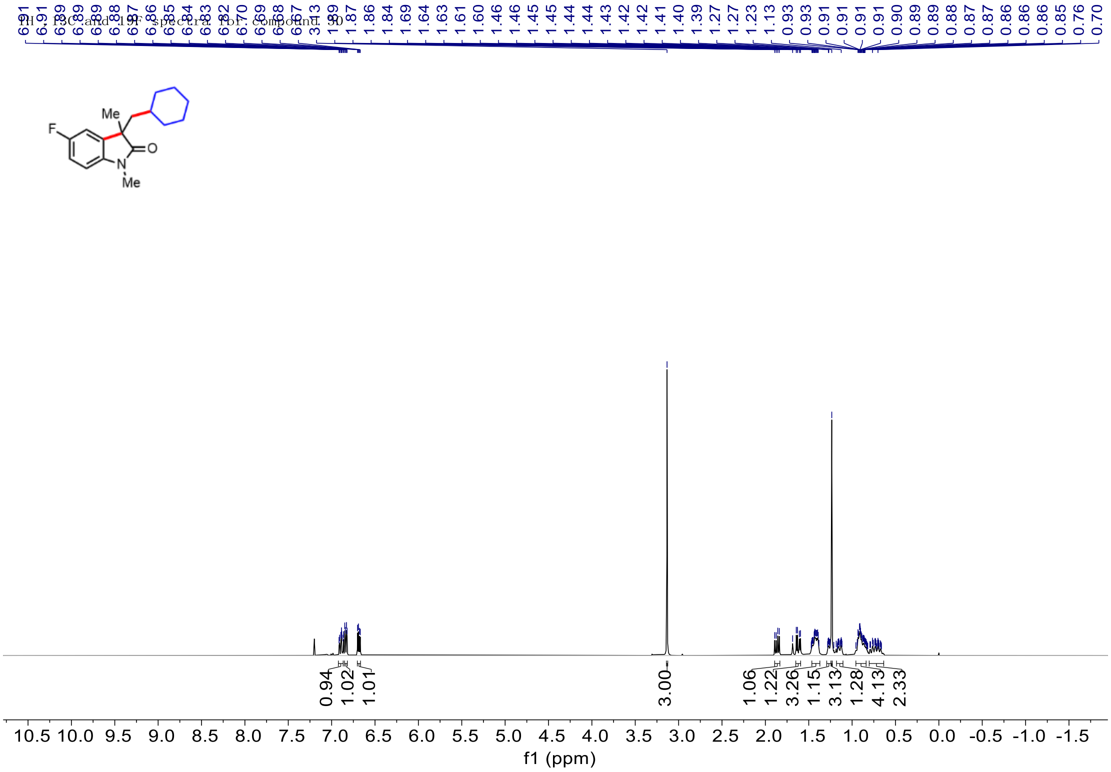


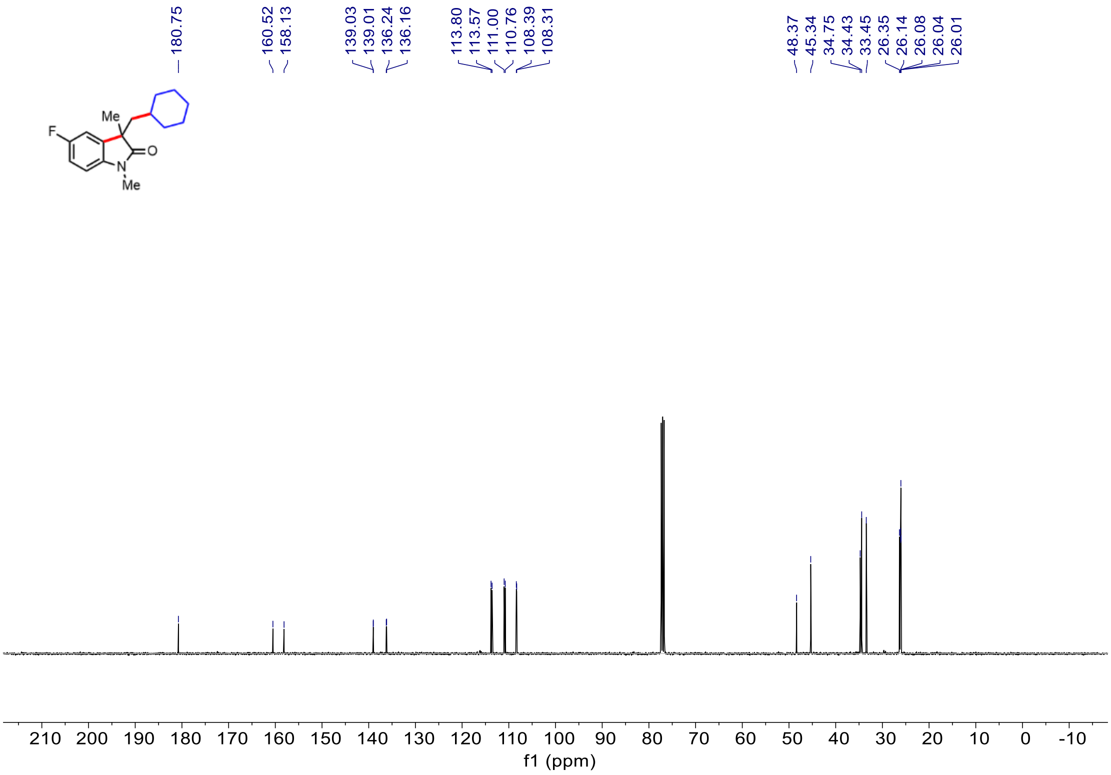
^1H and ^{13}C spectra for compound **32**



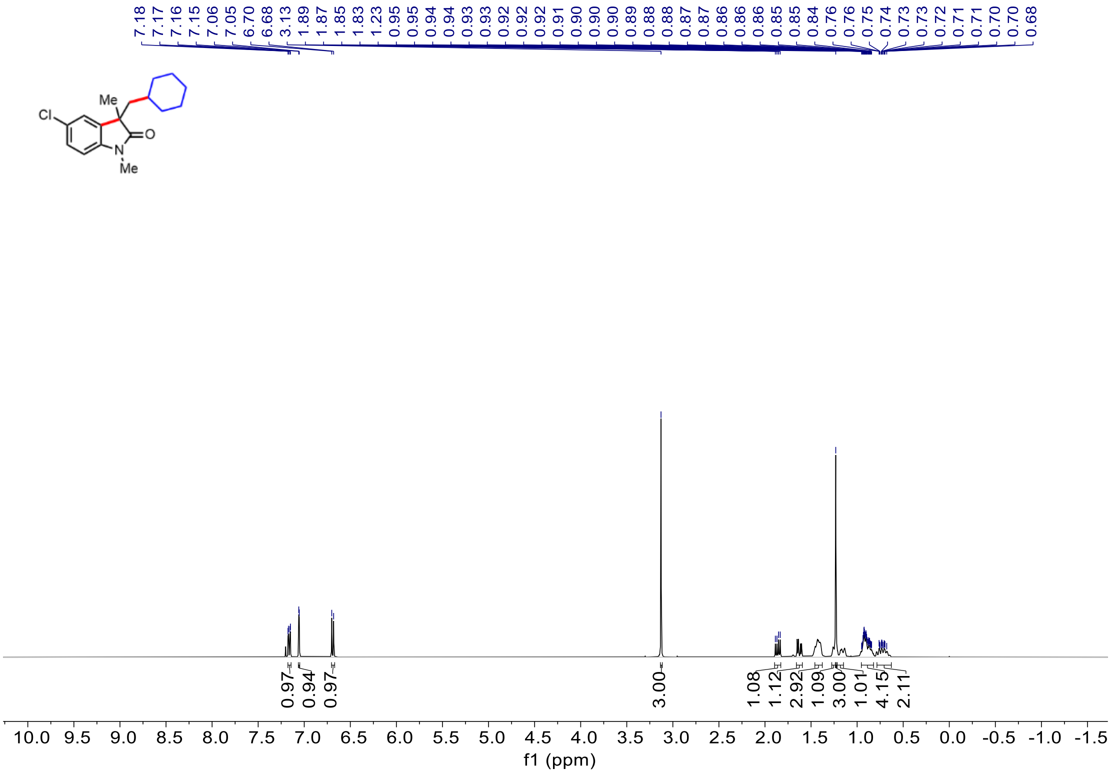


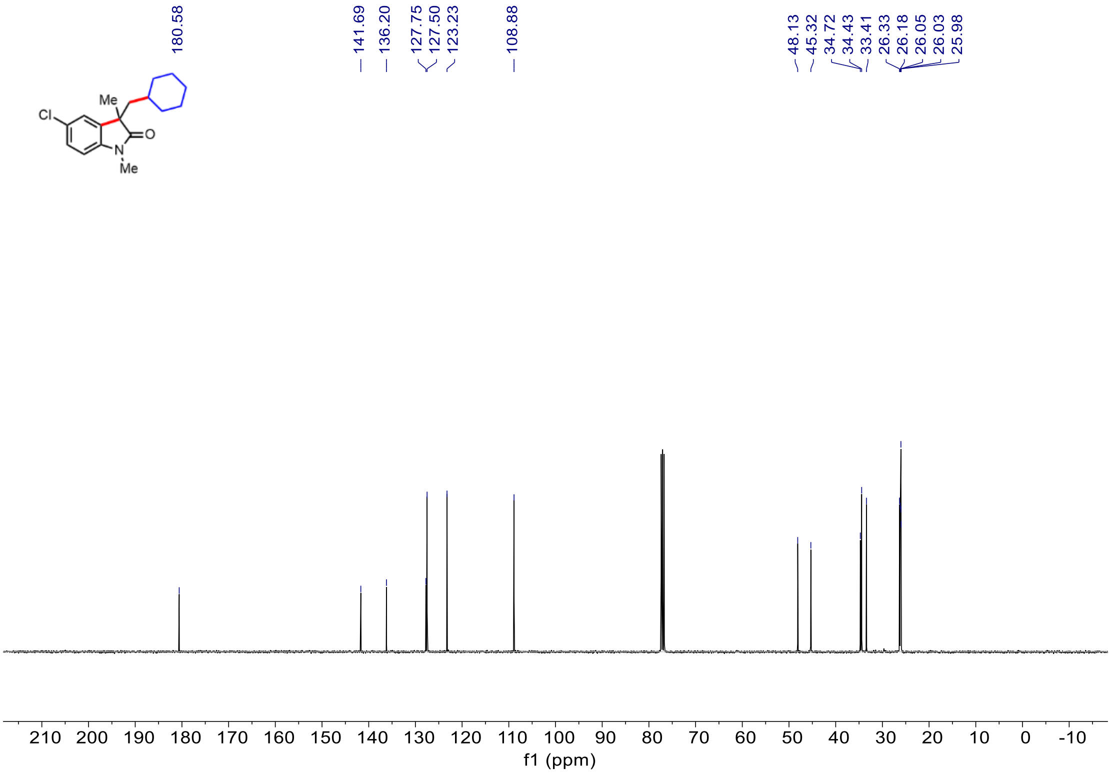
^{1}H and ^{13}C spectra for compound **33**



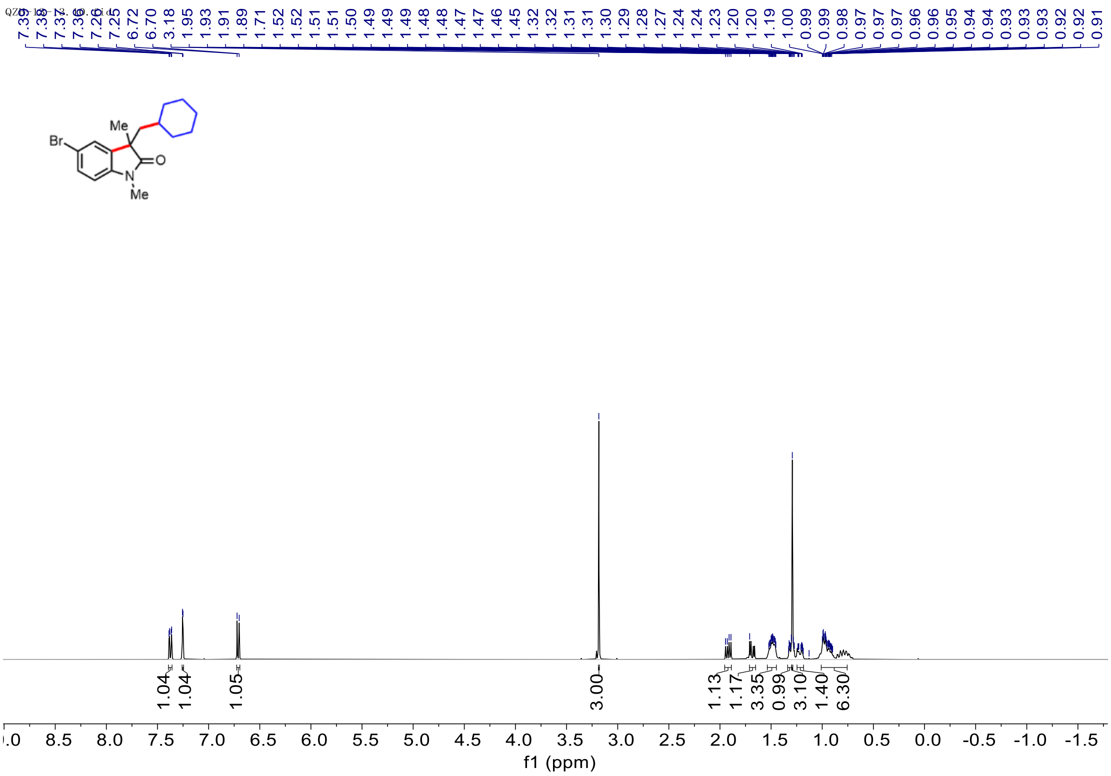


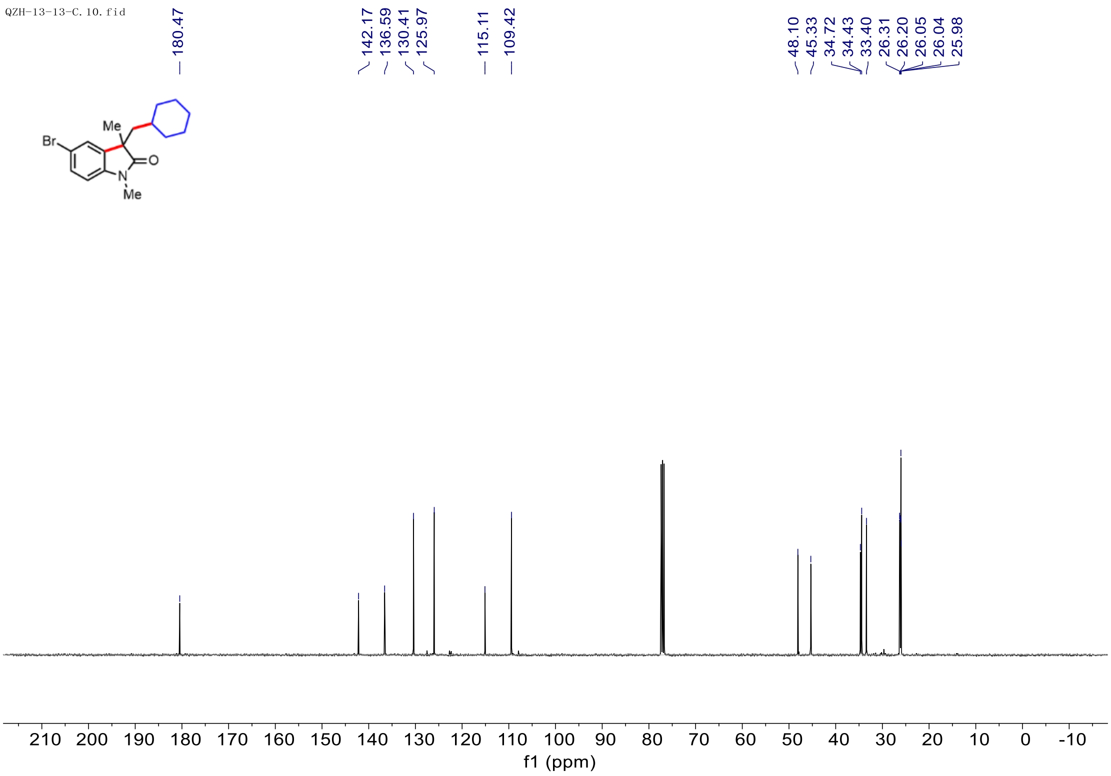
^{1}H and ^{13}C spectra for compound **34**



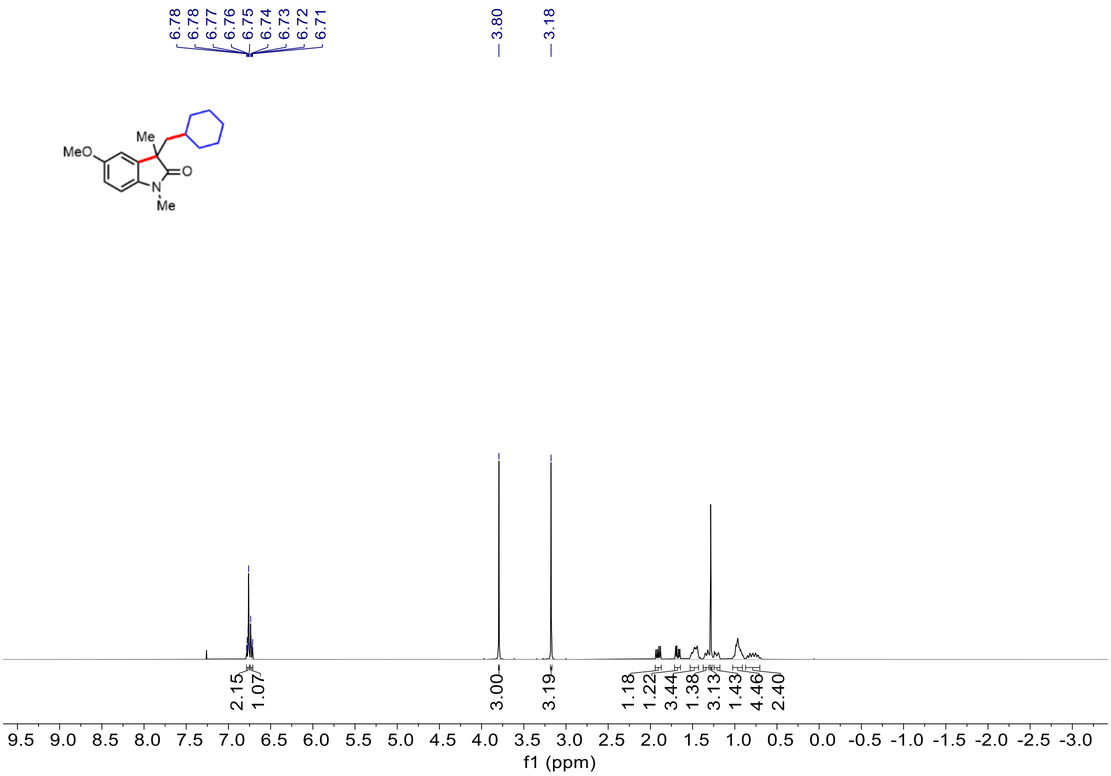


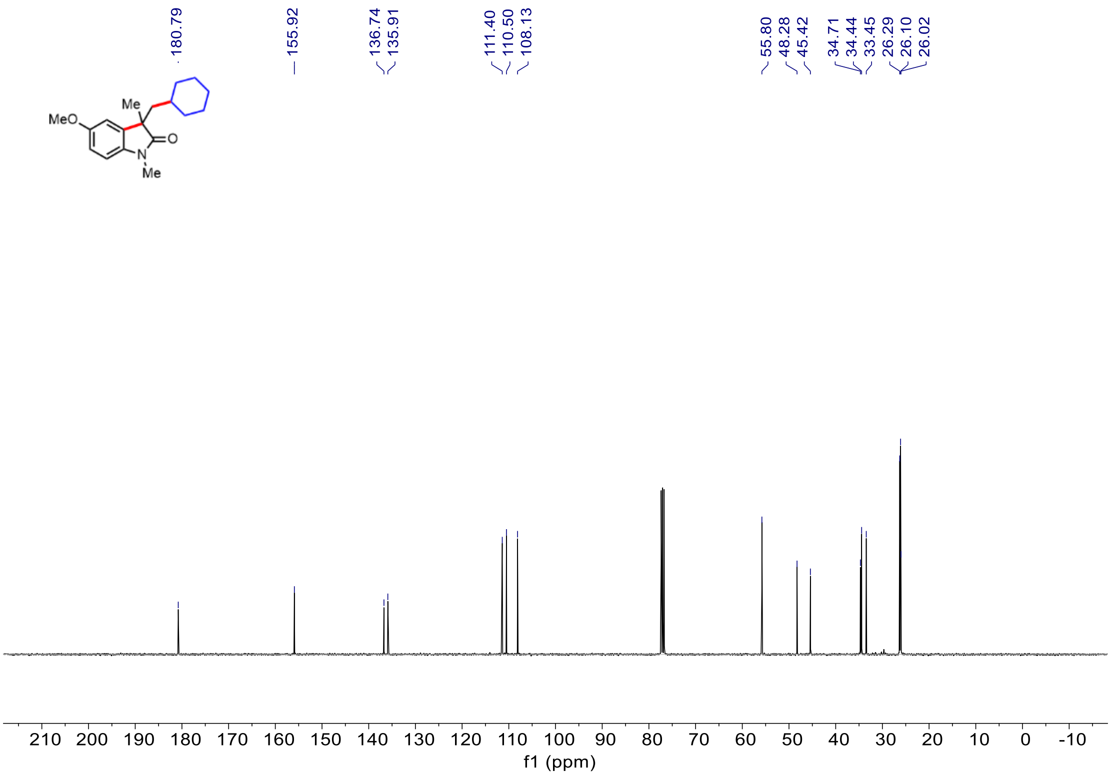
¹H and ¹³C spectra for compound **35**



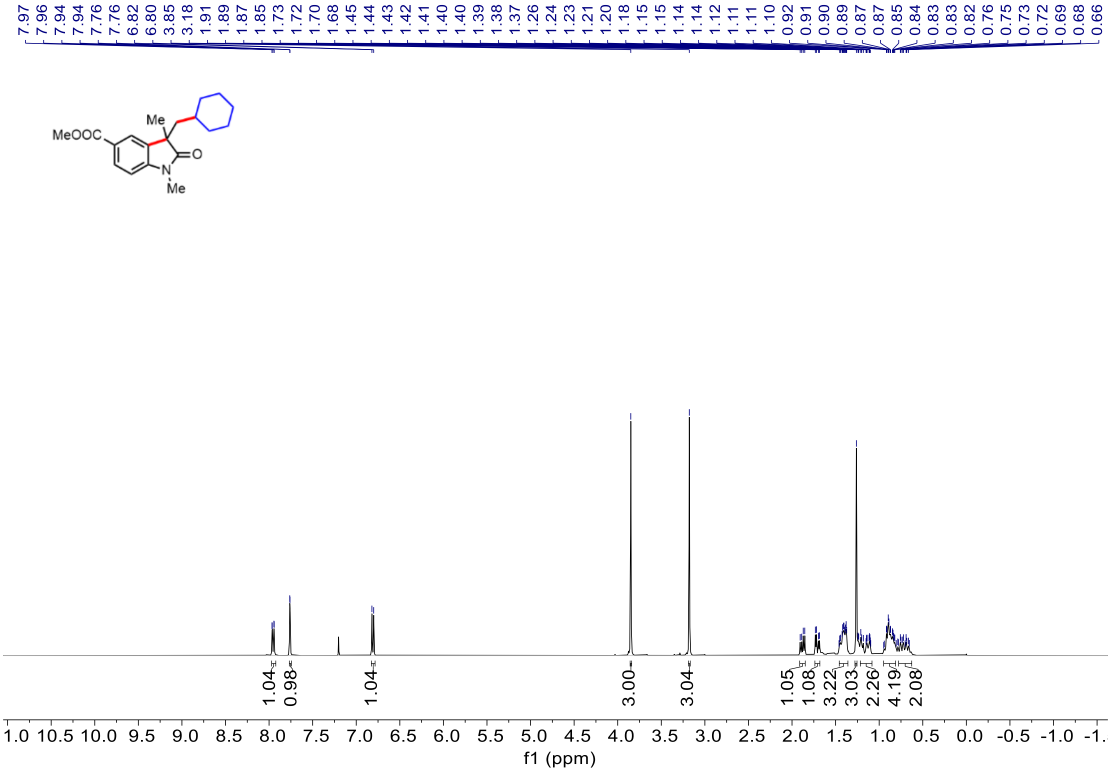


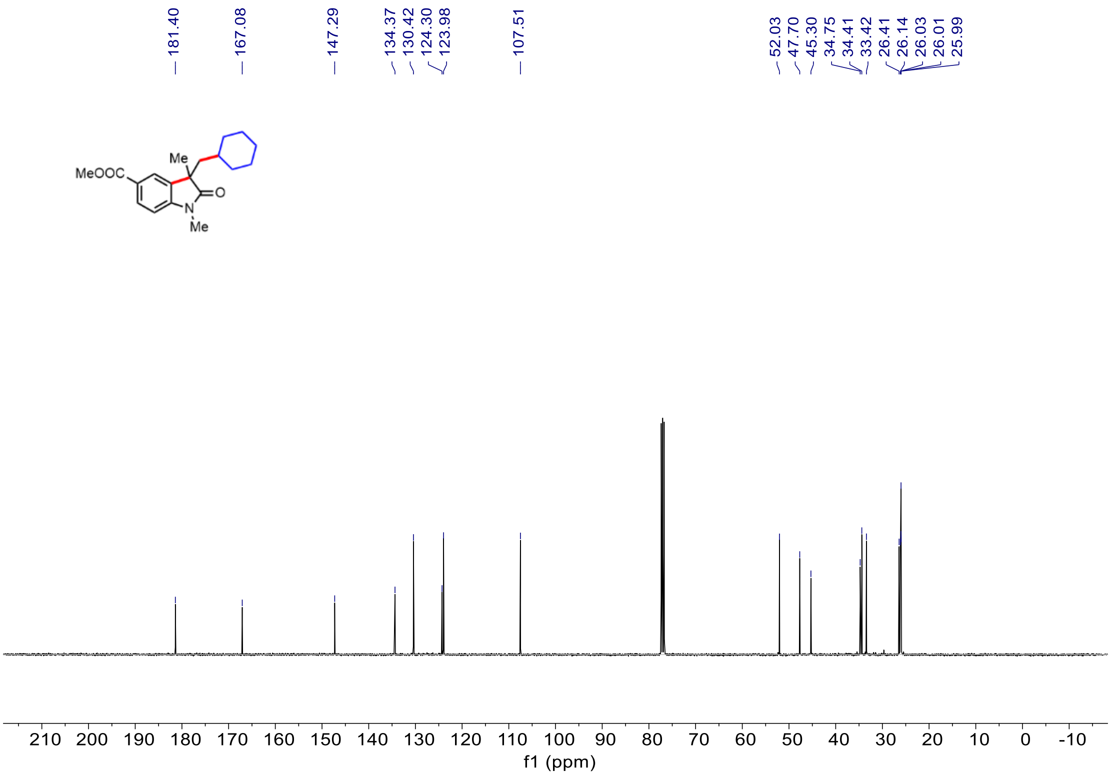
^{1}H and ^{13}C spectra for compound **36**



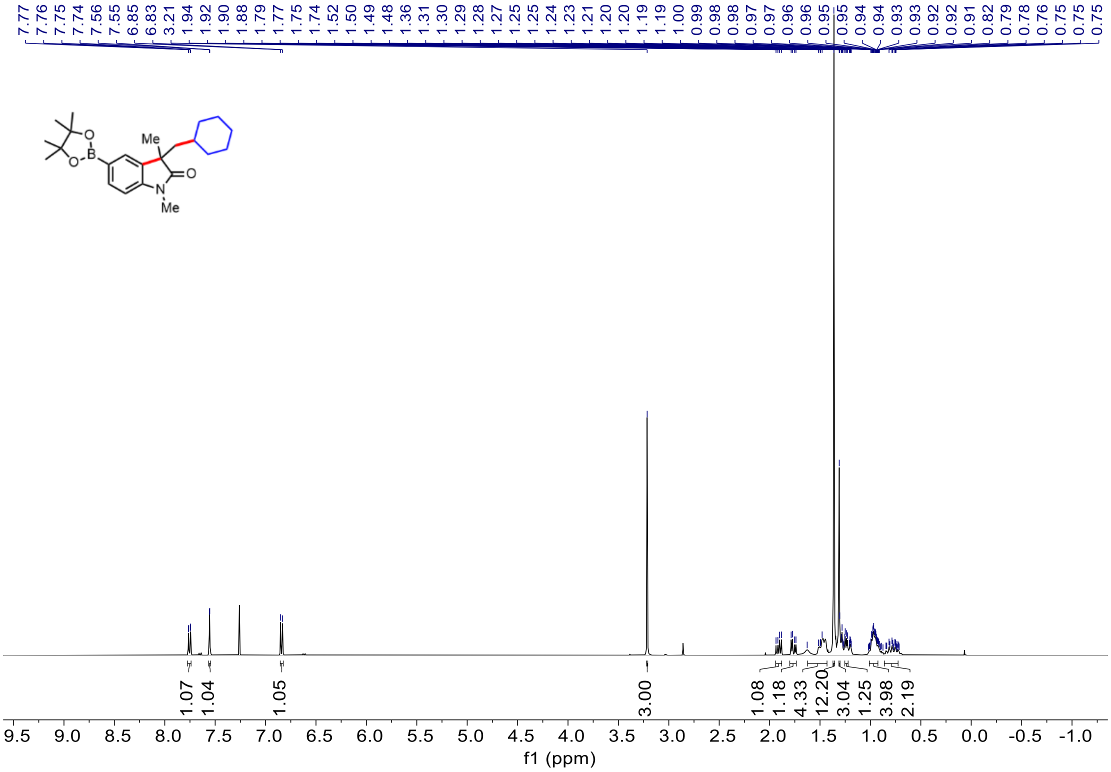


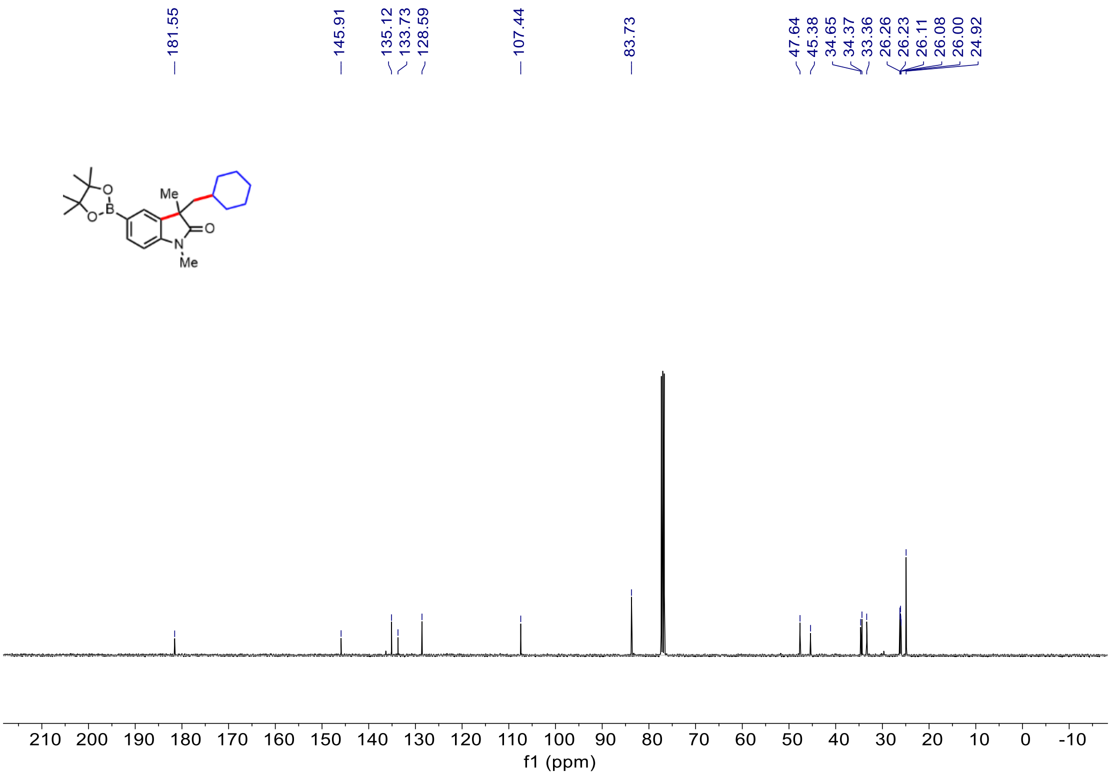
^{1}H and ^{13}C spectra for compound **37**



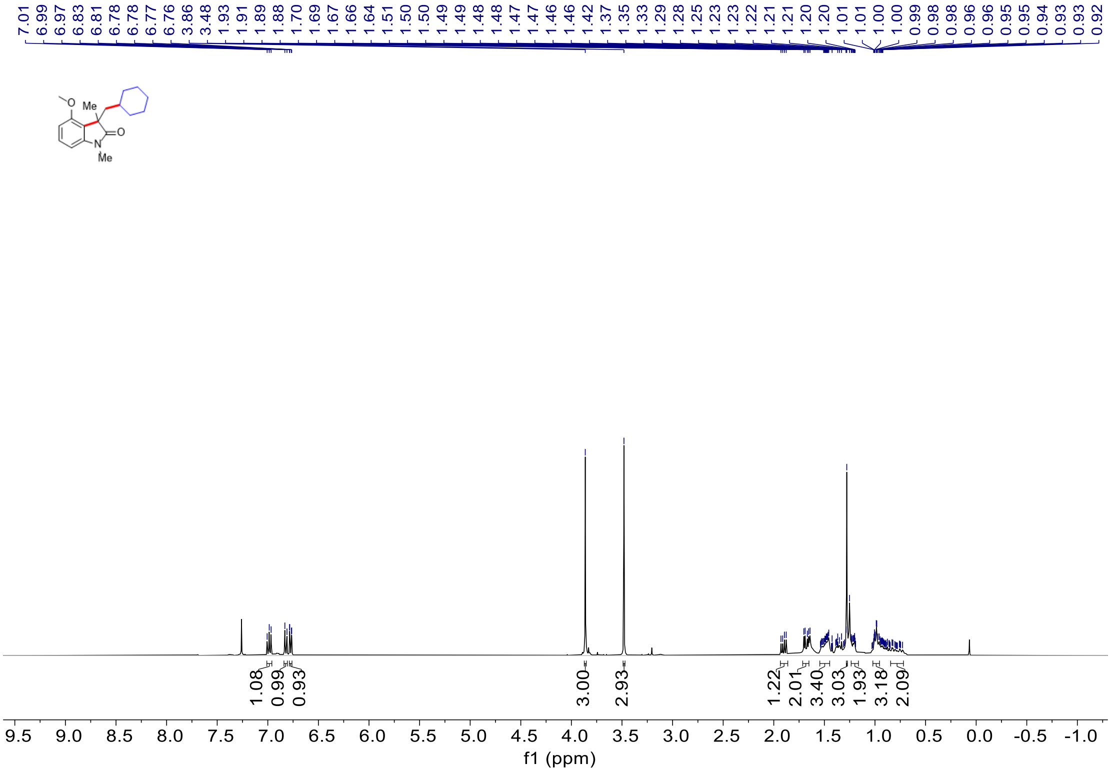


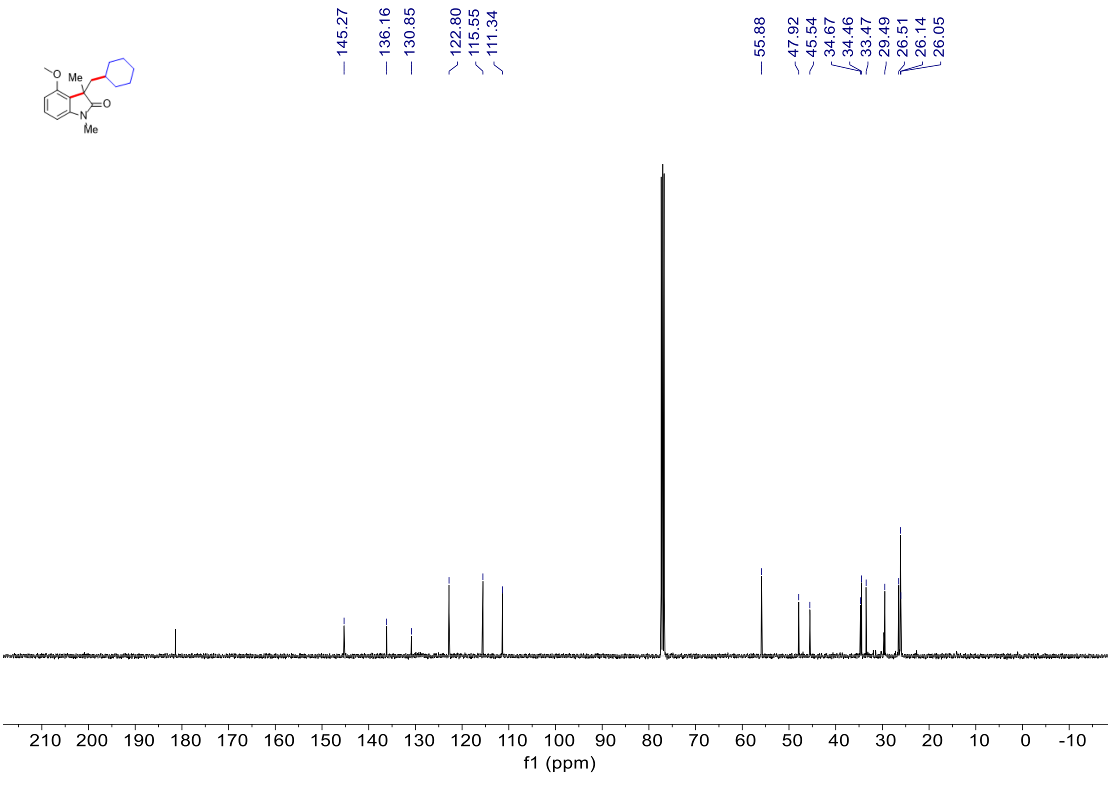
^{1}H and ^{13}C spectra for compound **38**



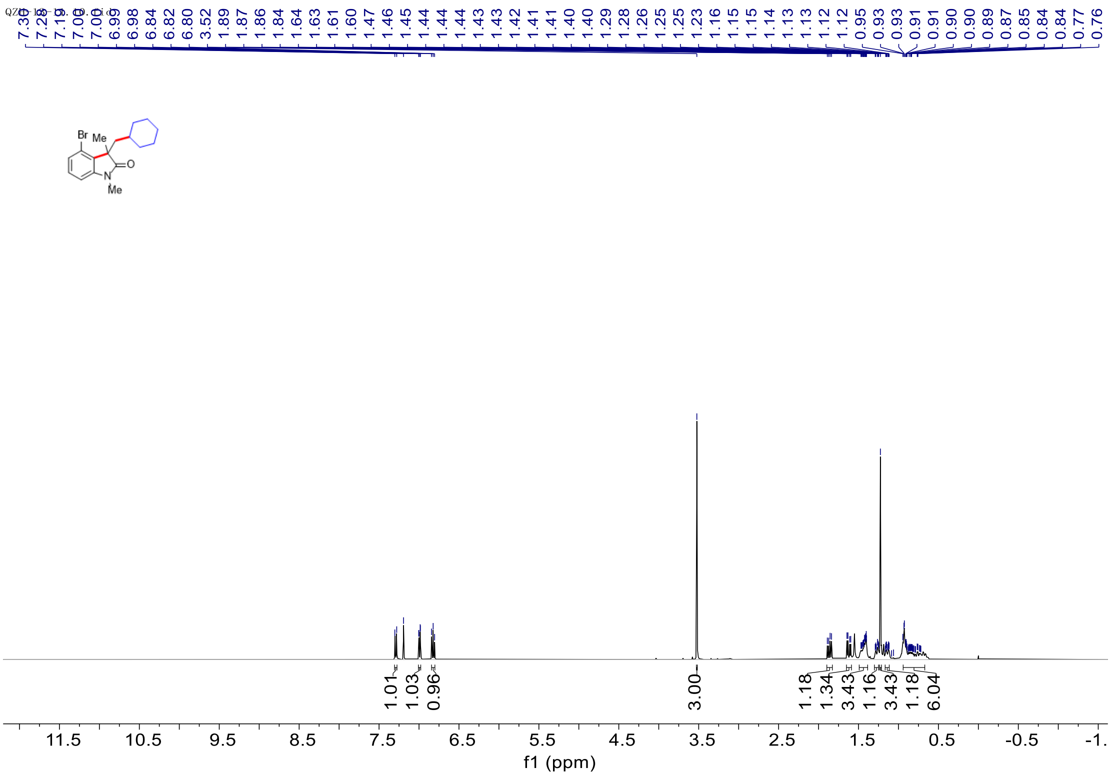


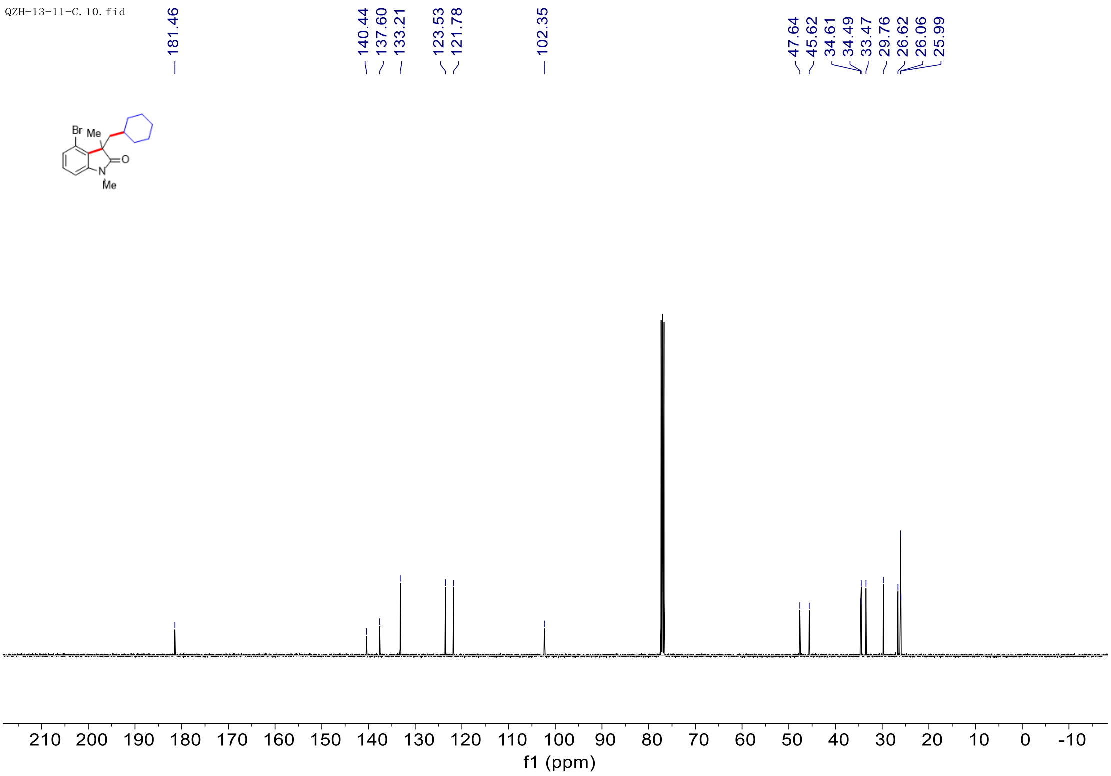
^{1}H and ^{13}C spectra for compound **39**



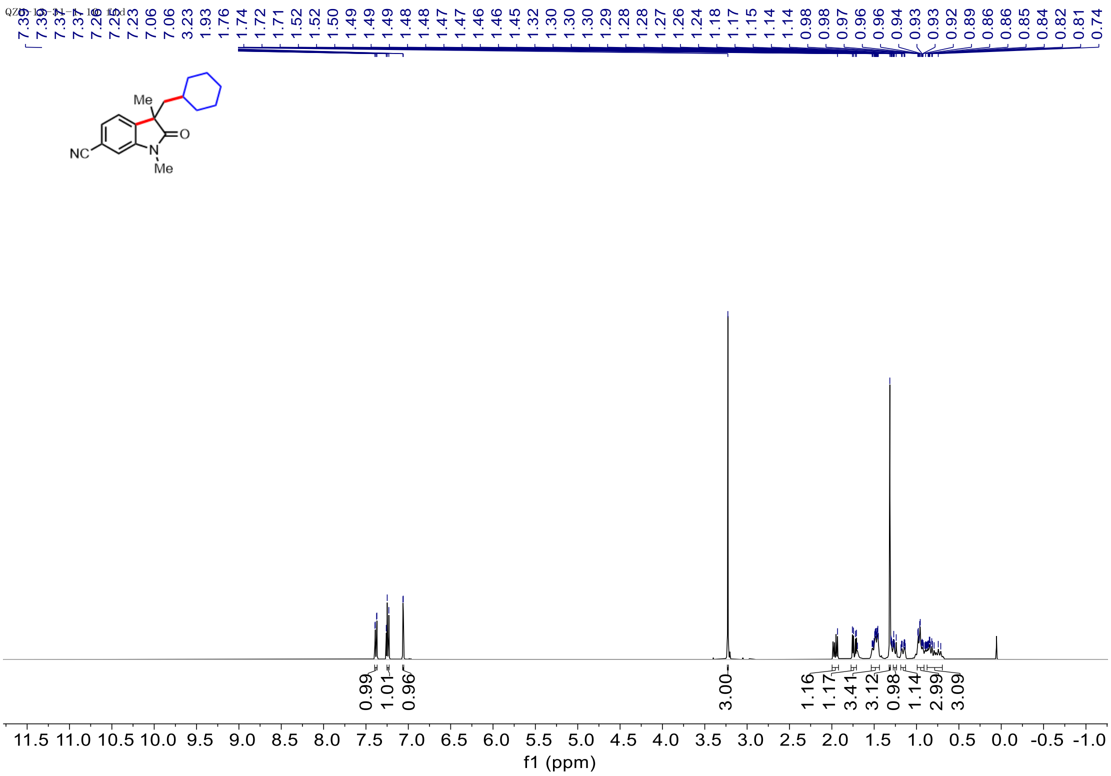


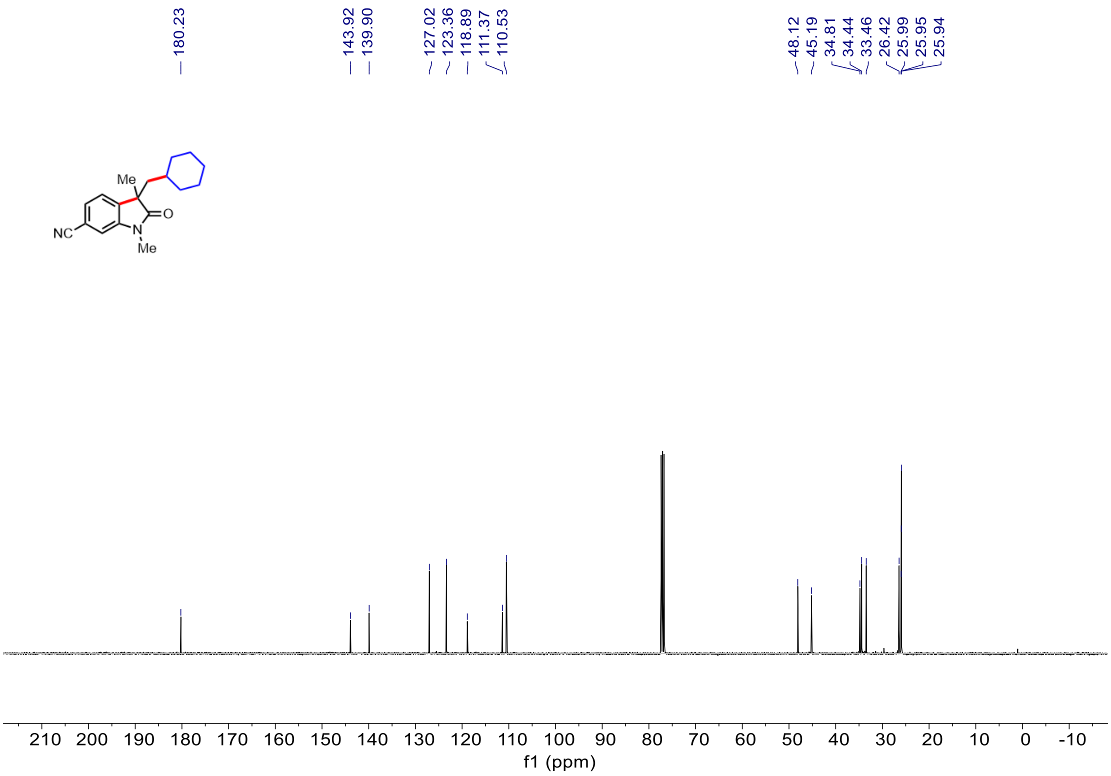
^{1}H and ^{13}C spectra for compound **40**



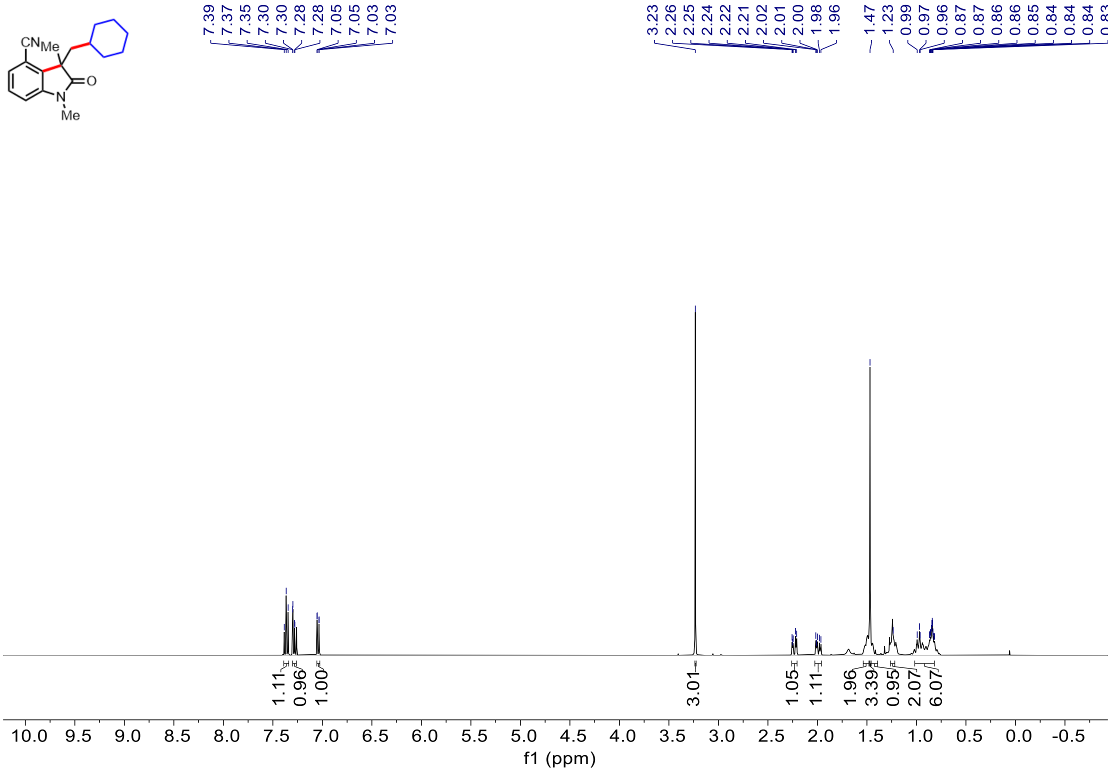


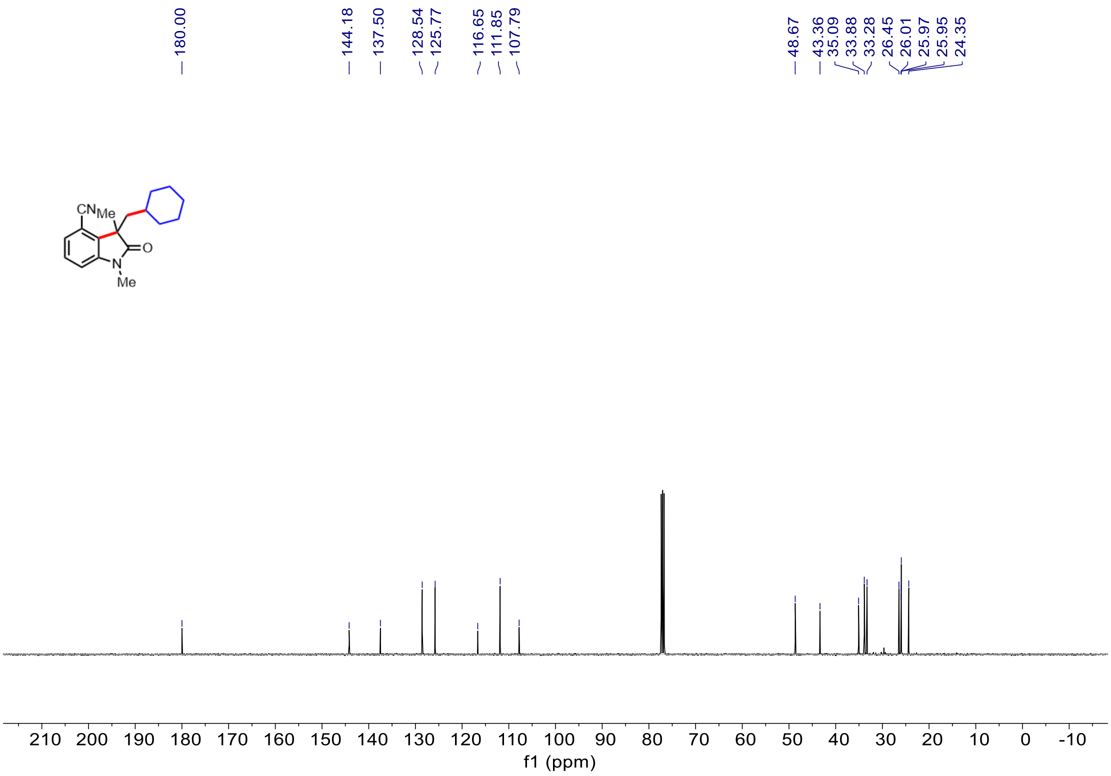
[1]H and [13]C spectra for compound **41**



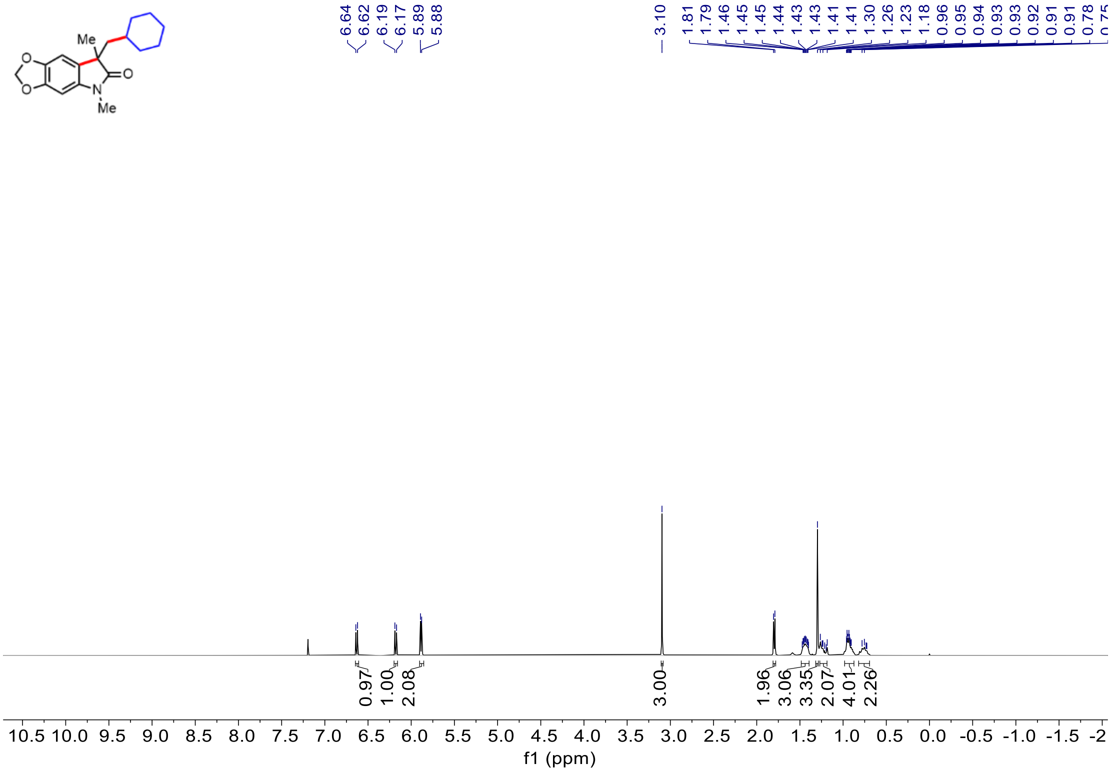


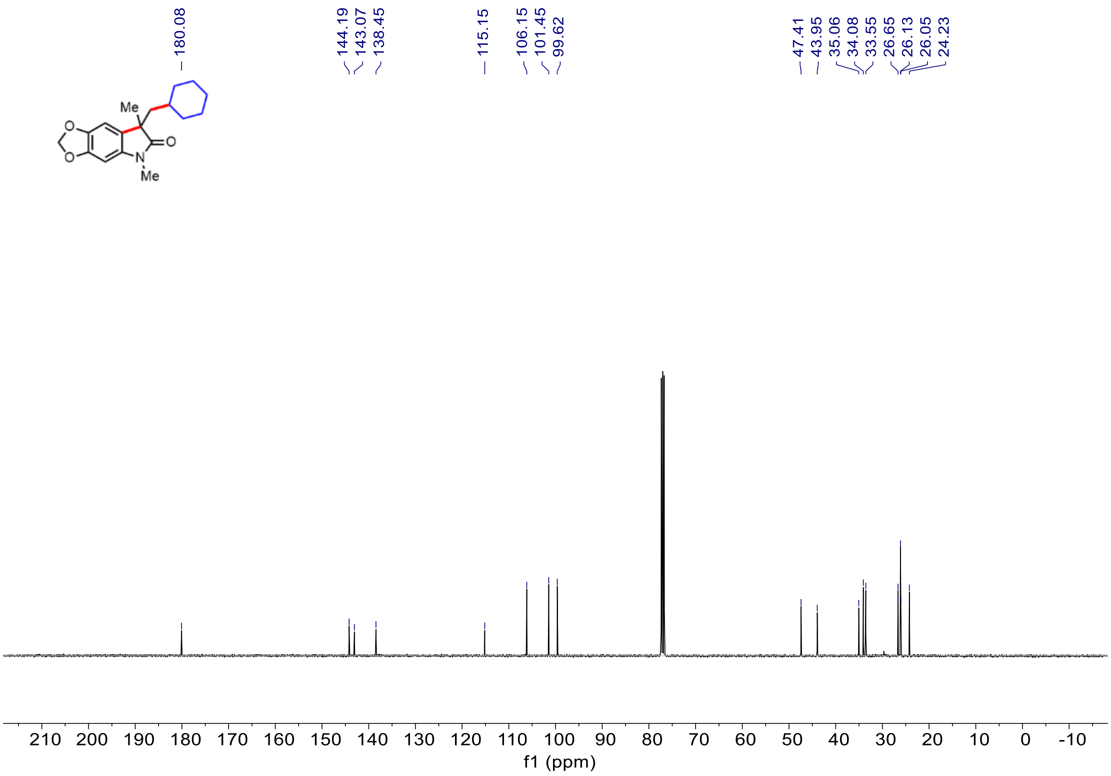
[1]H and [13]C spectra for compound **41’**



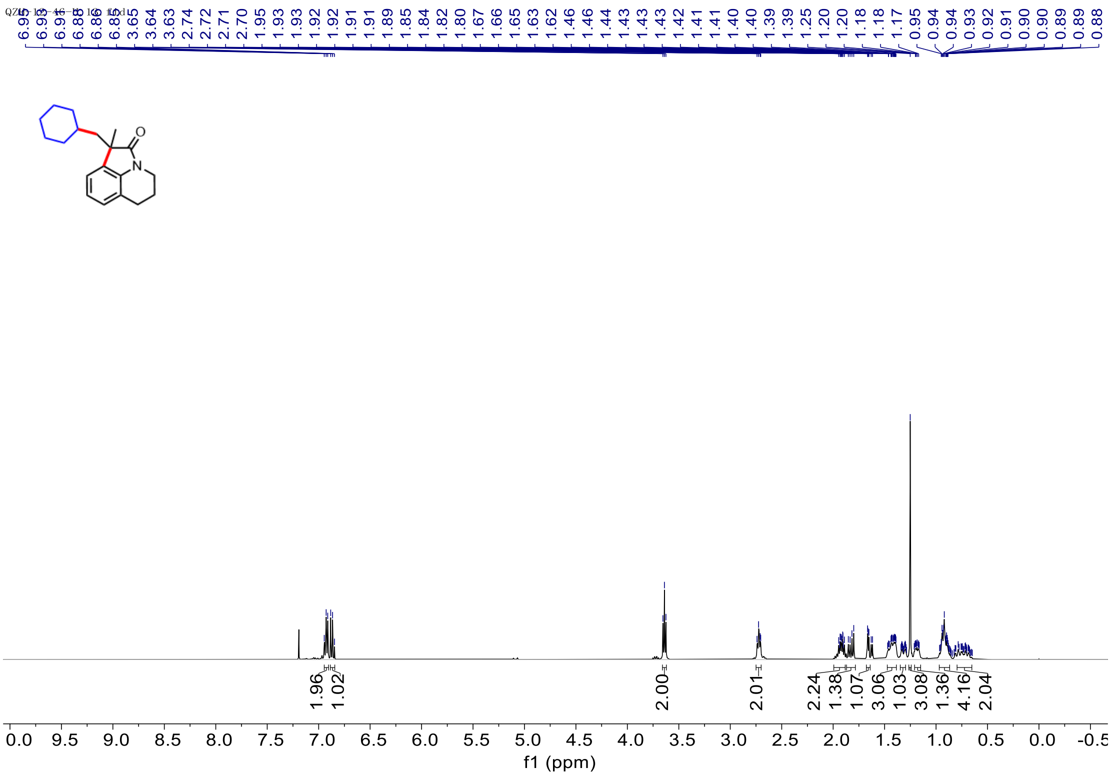


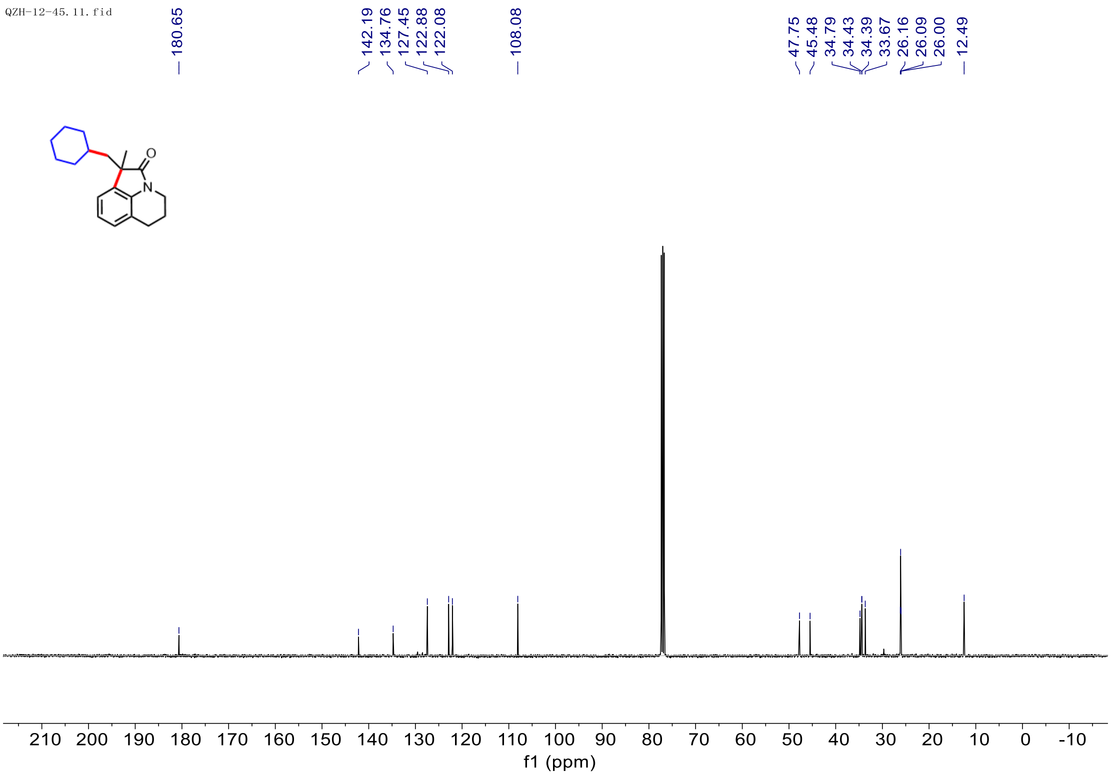
[1]H and [13]C spectra for compound **42**



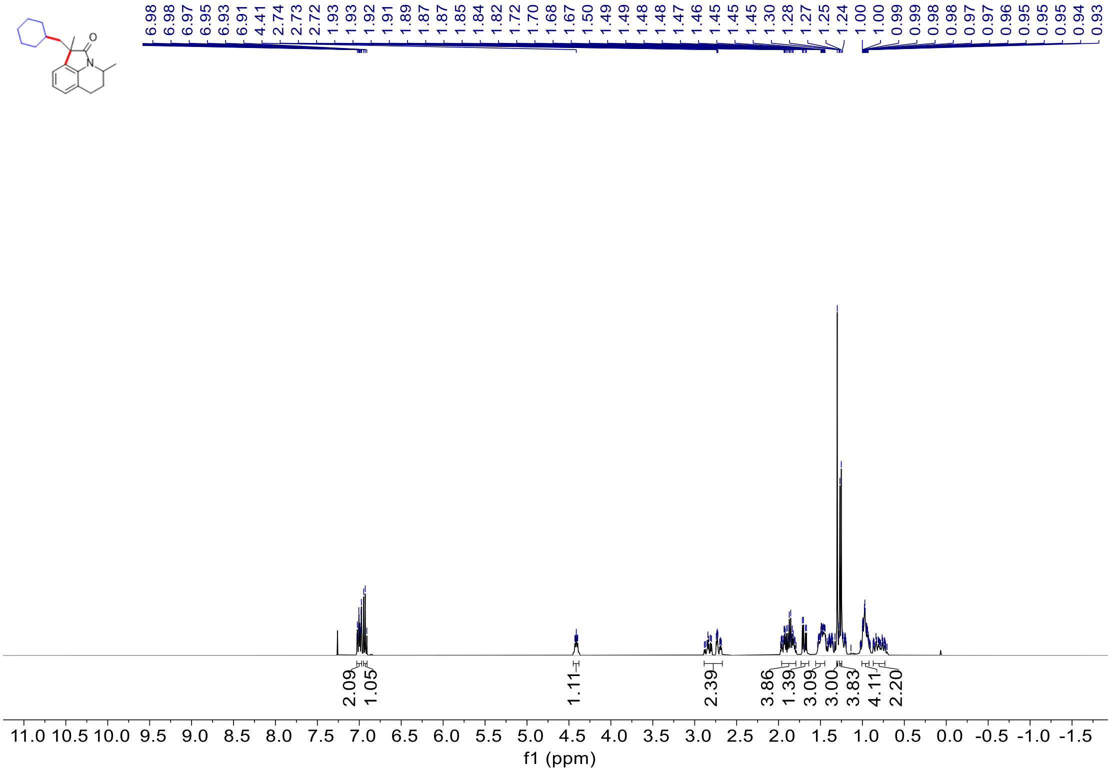


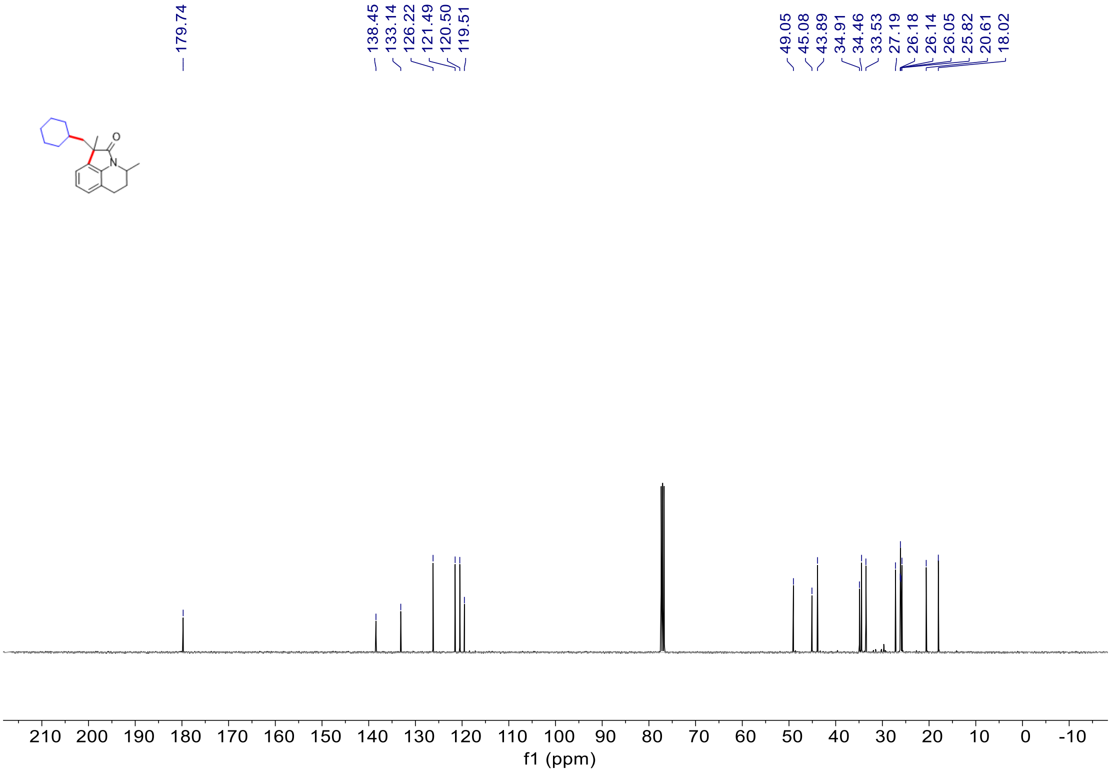
^{1}H and ^{13}C spectra for compound **43**



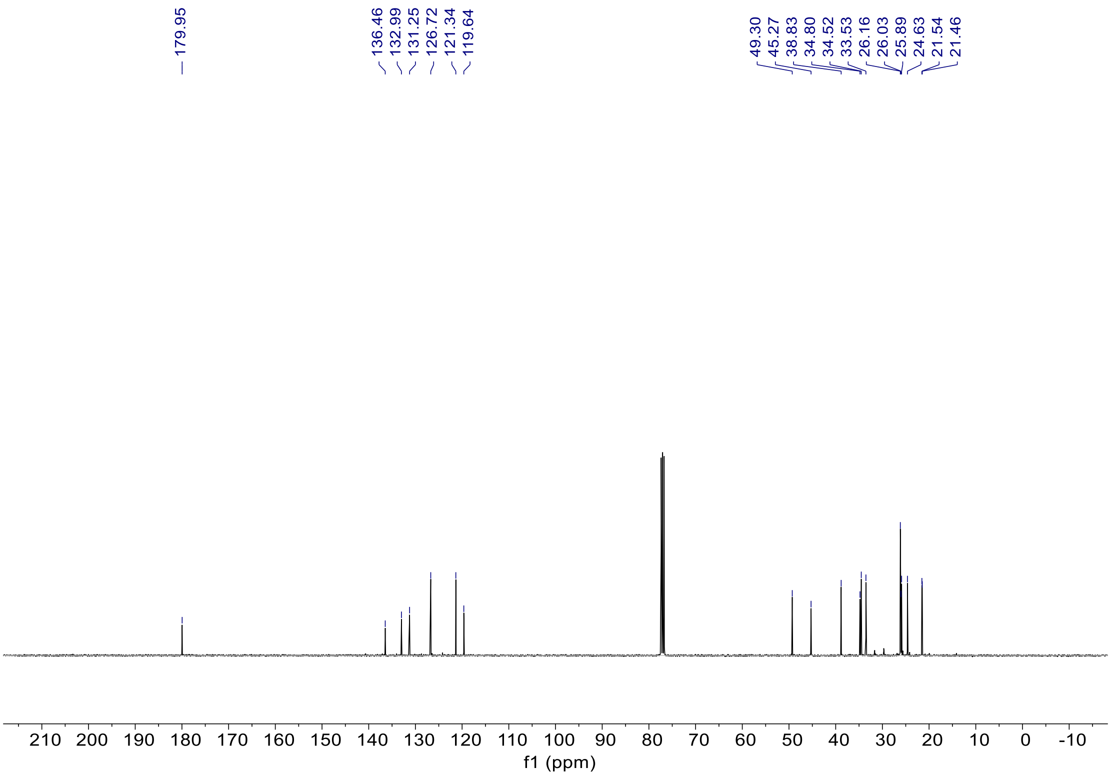


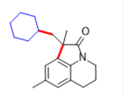
^{1}H and ^{13}C spectra for compound **44**

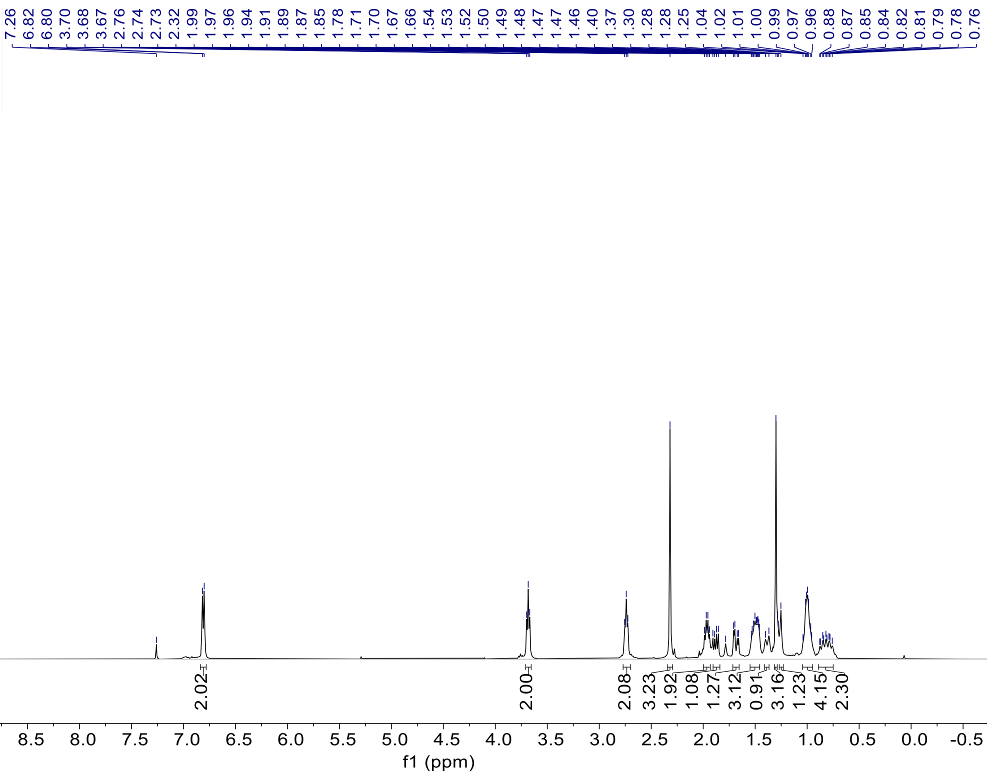




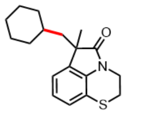
^{1}H and ^{13}C spectra for compound **45**

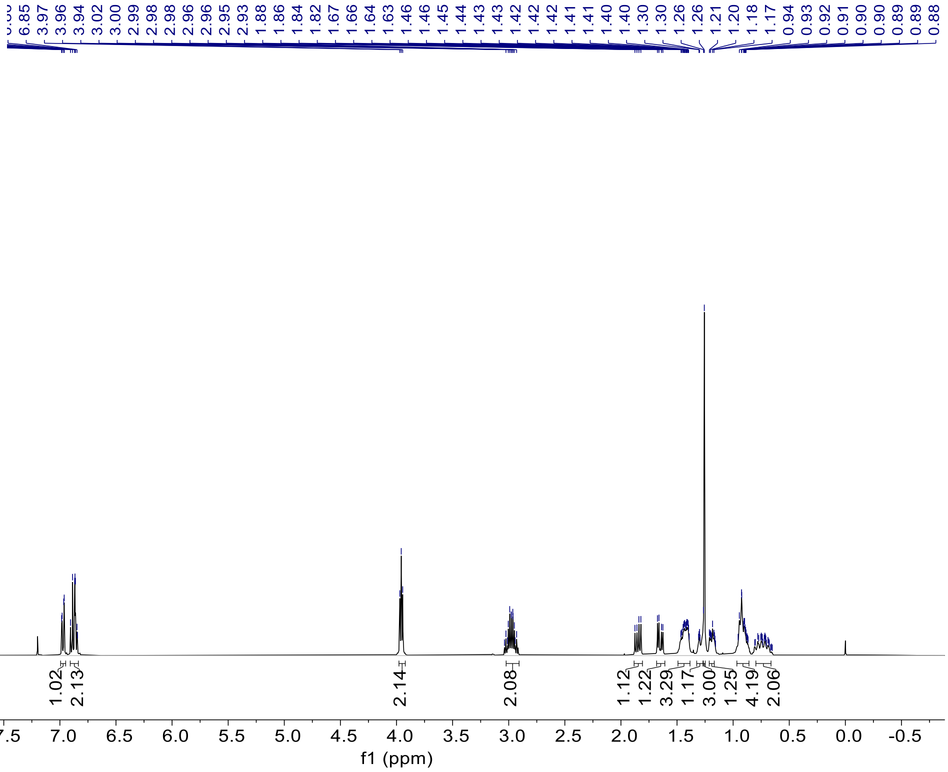


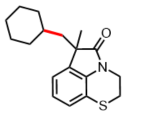


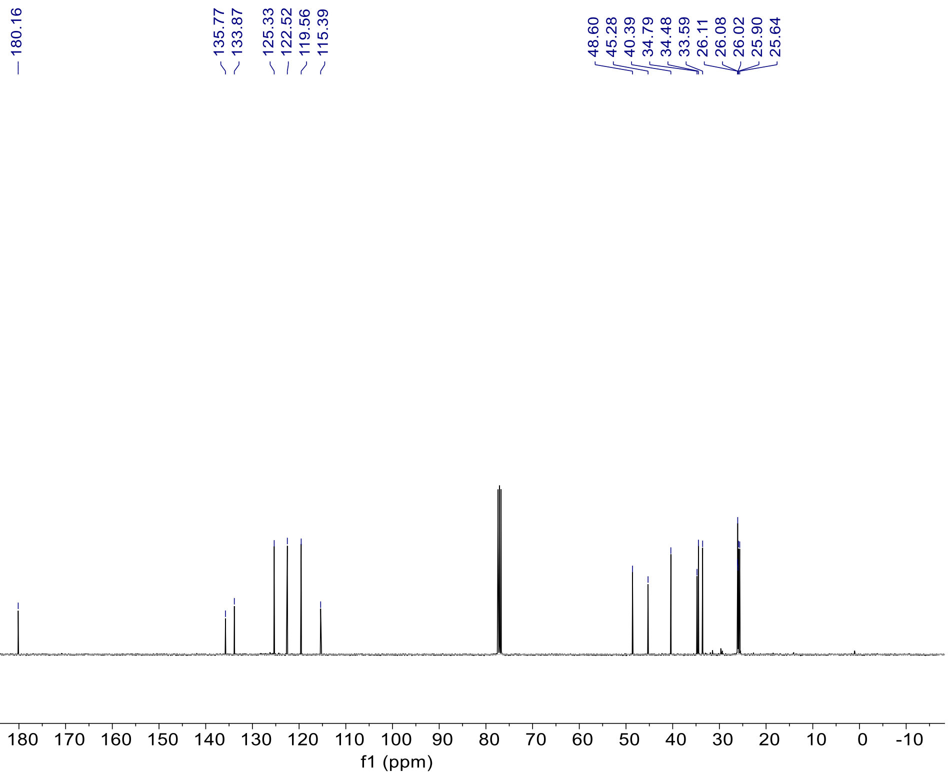


^{1}H and ^{13}C spectra for compound **46**

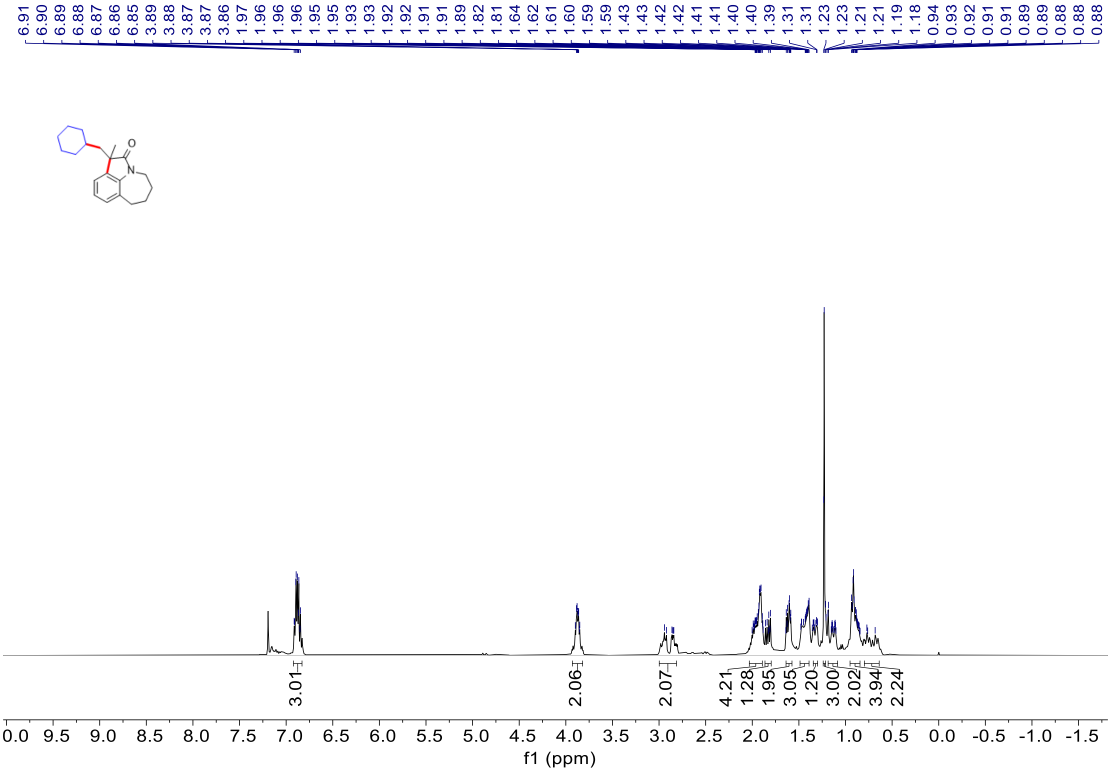


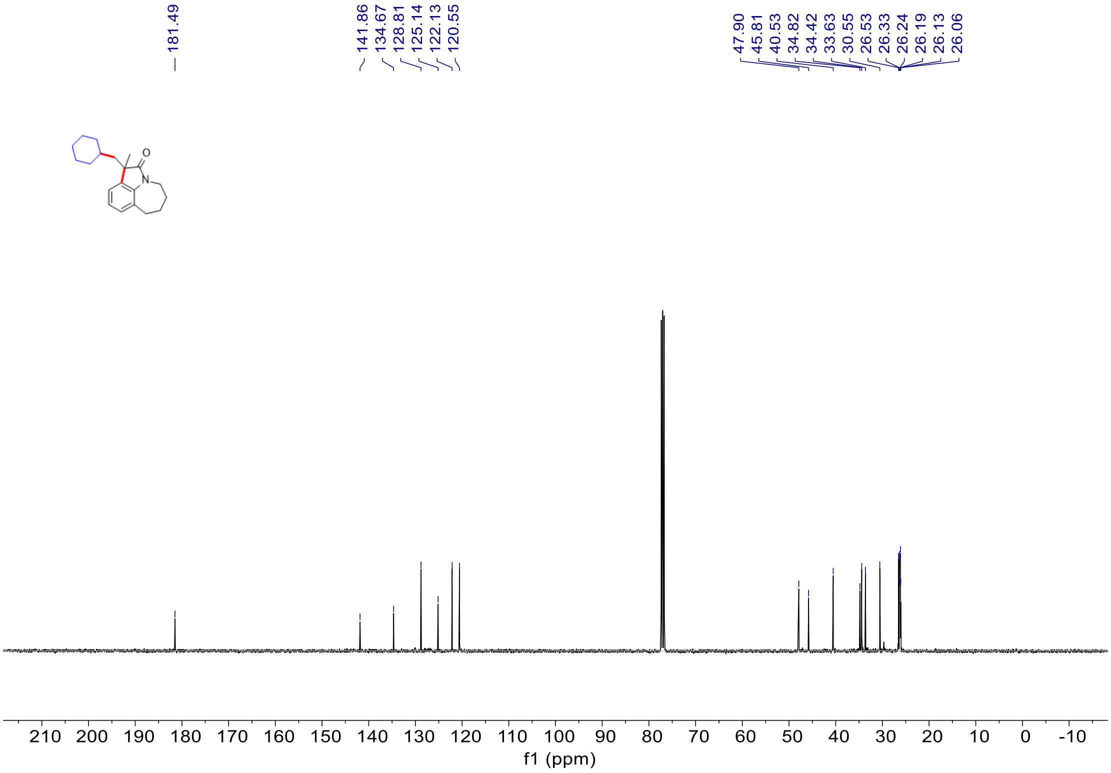




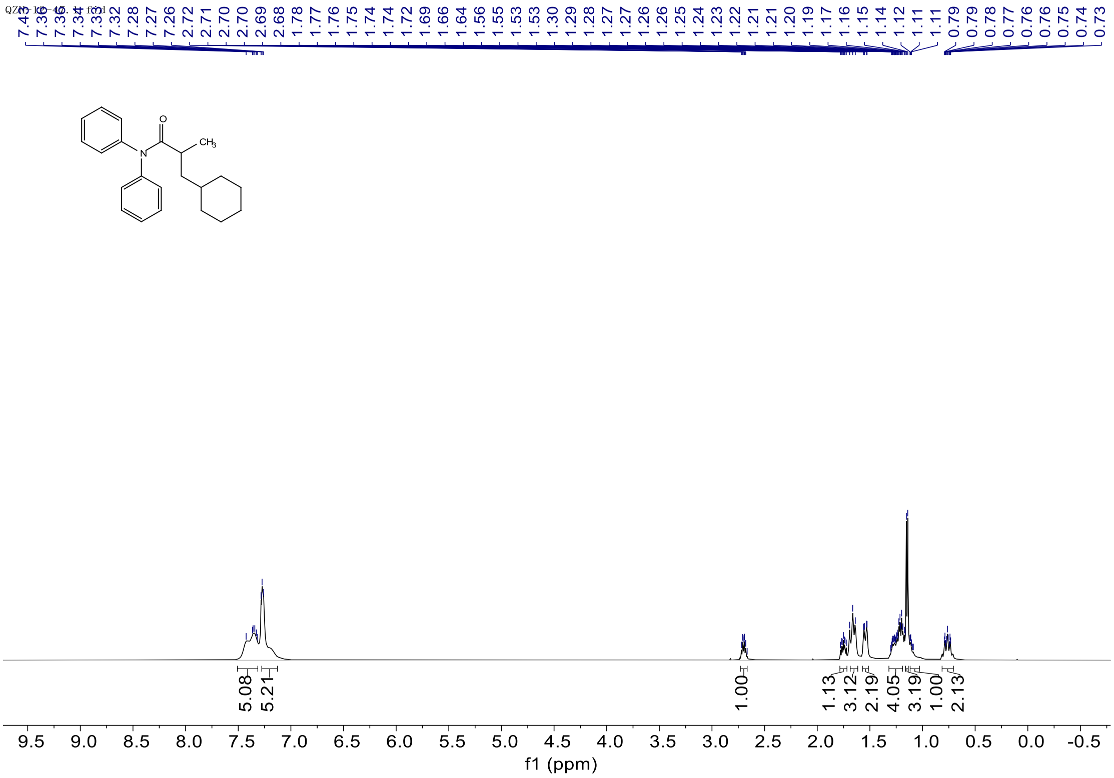


[1]H and [13]C spectra for compound **47**

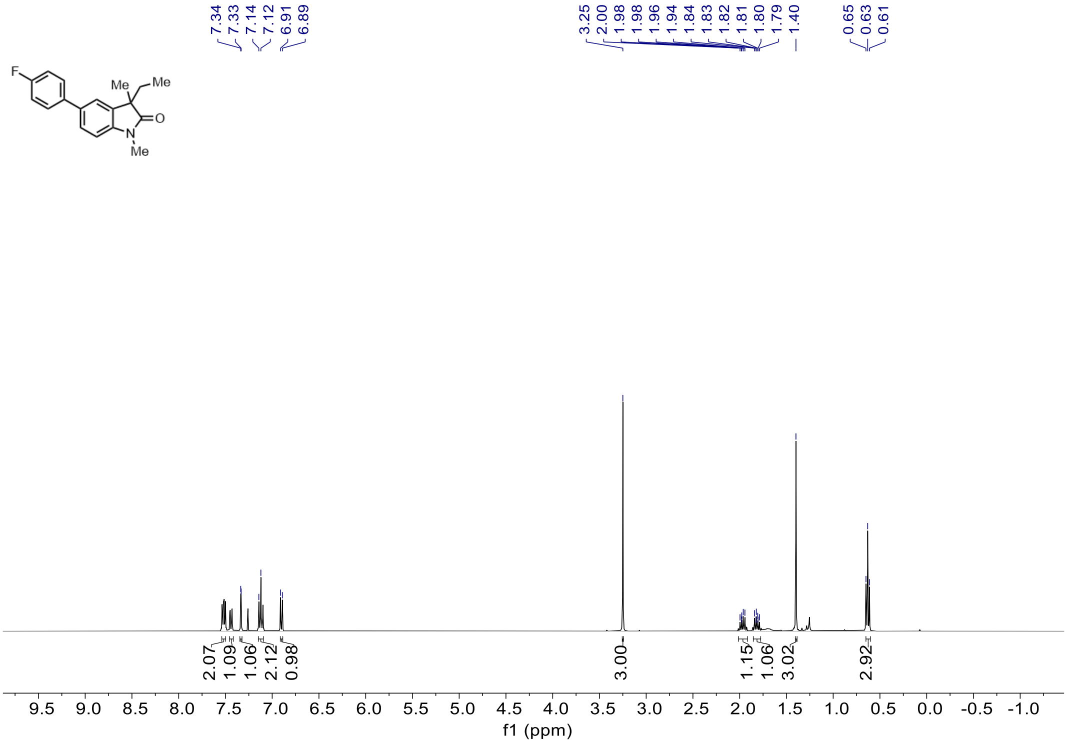


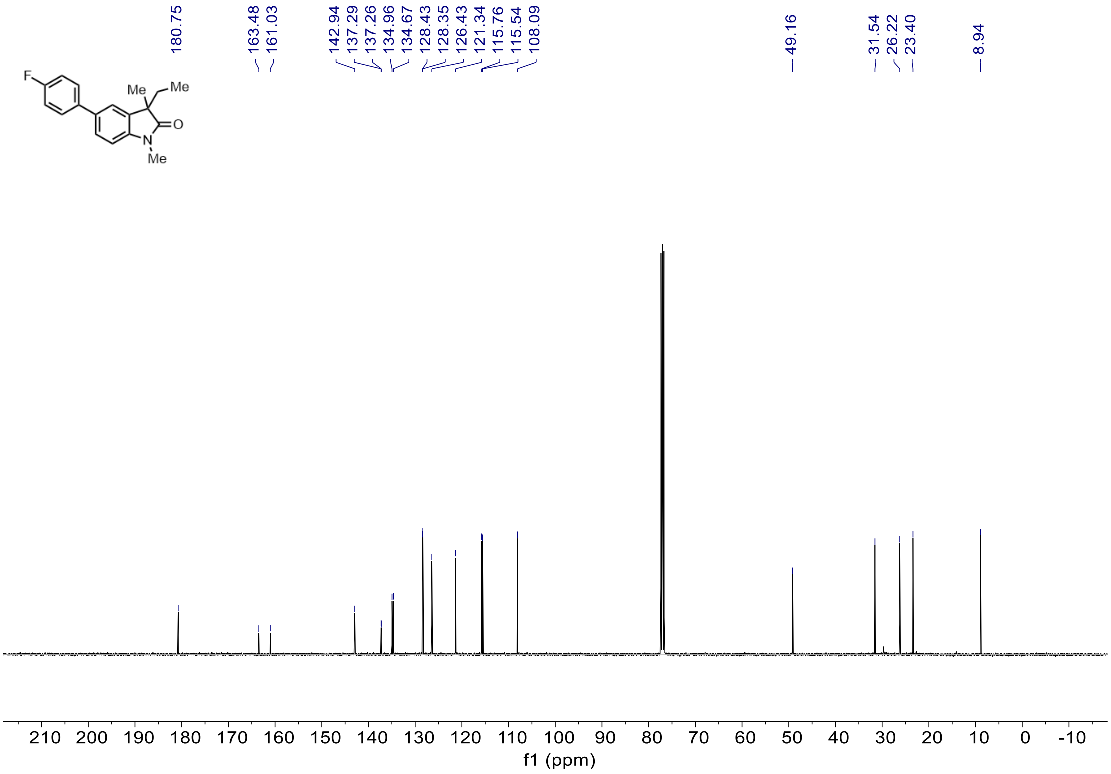


^{1}H spectra for compound **48**

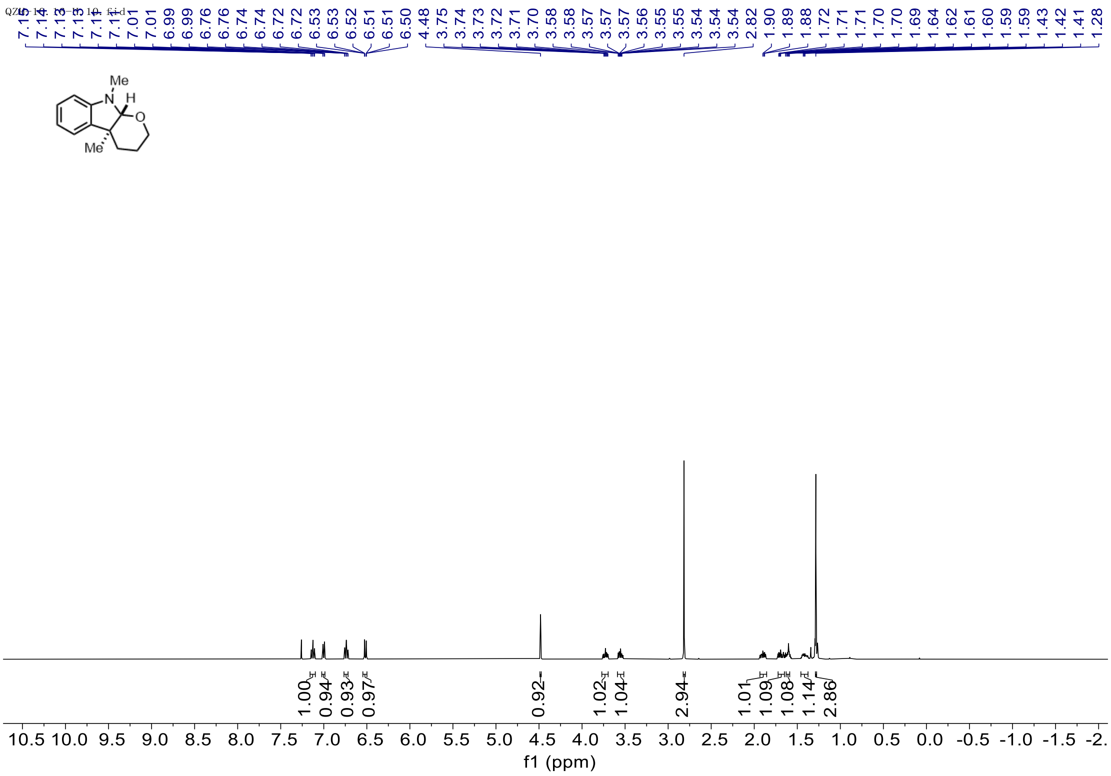


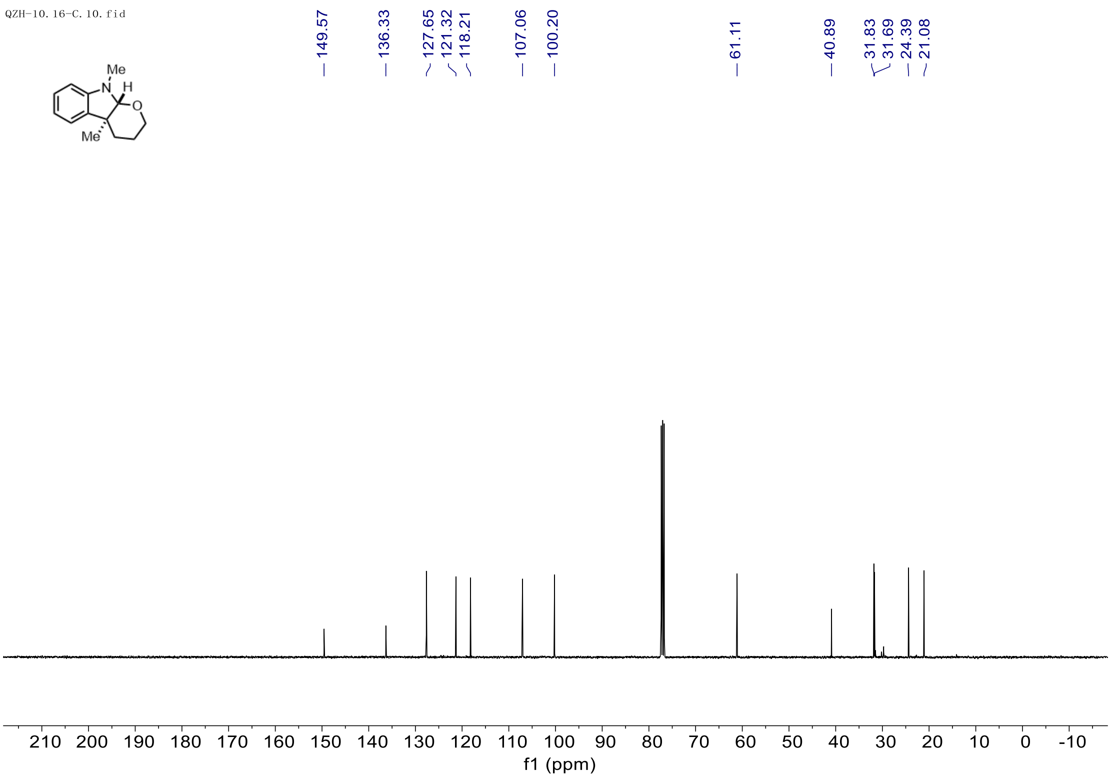
^{1}H and ^{13}C spectra for compound **49**



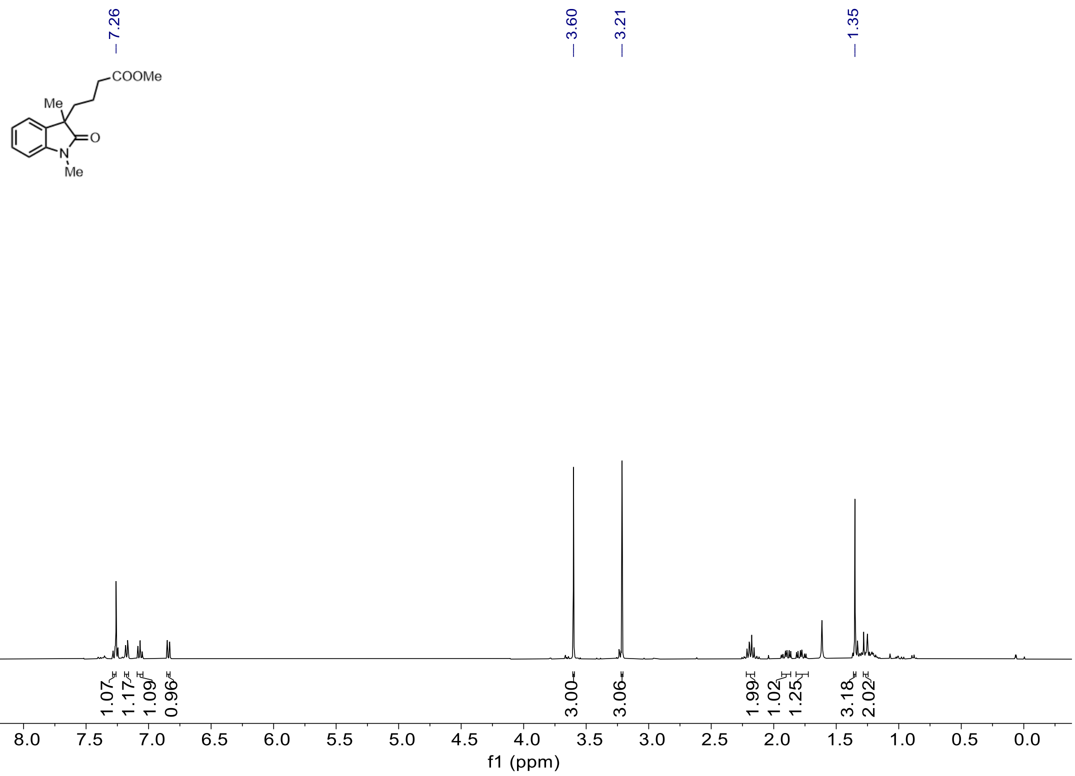


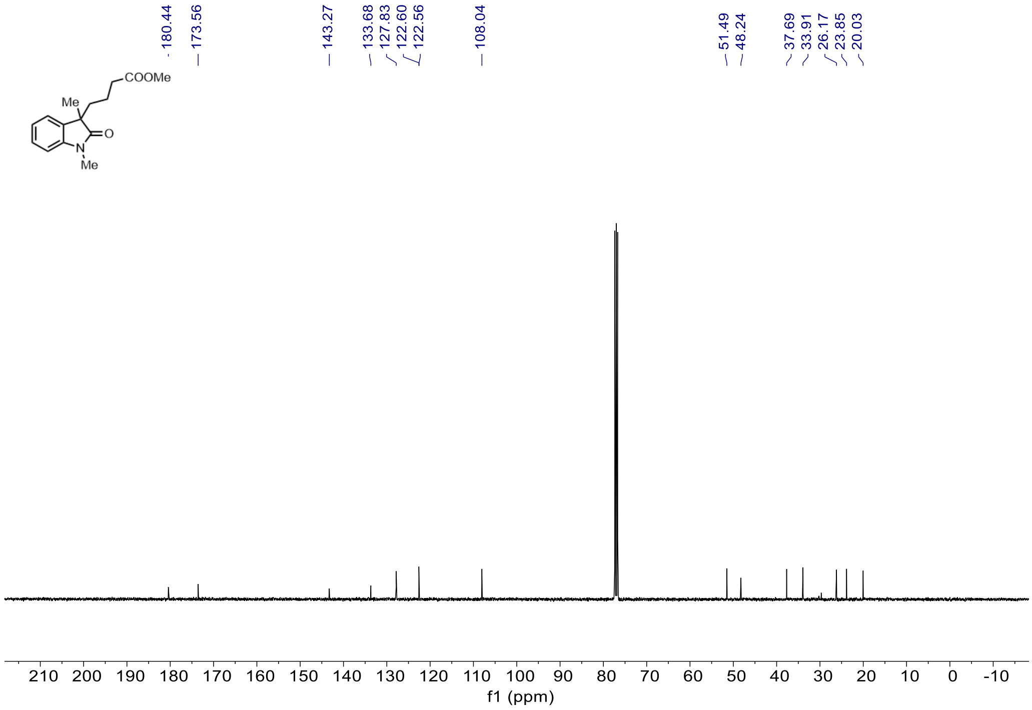
^{1}H and ^{13}C spectra for compound **50**



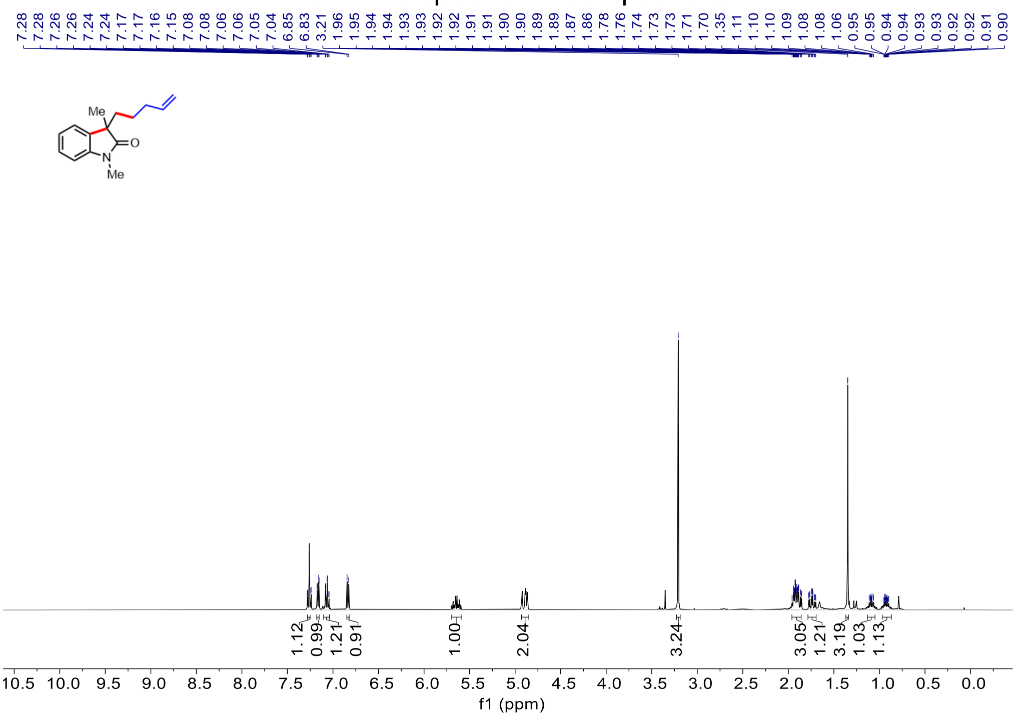


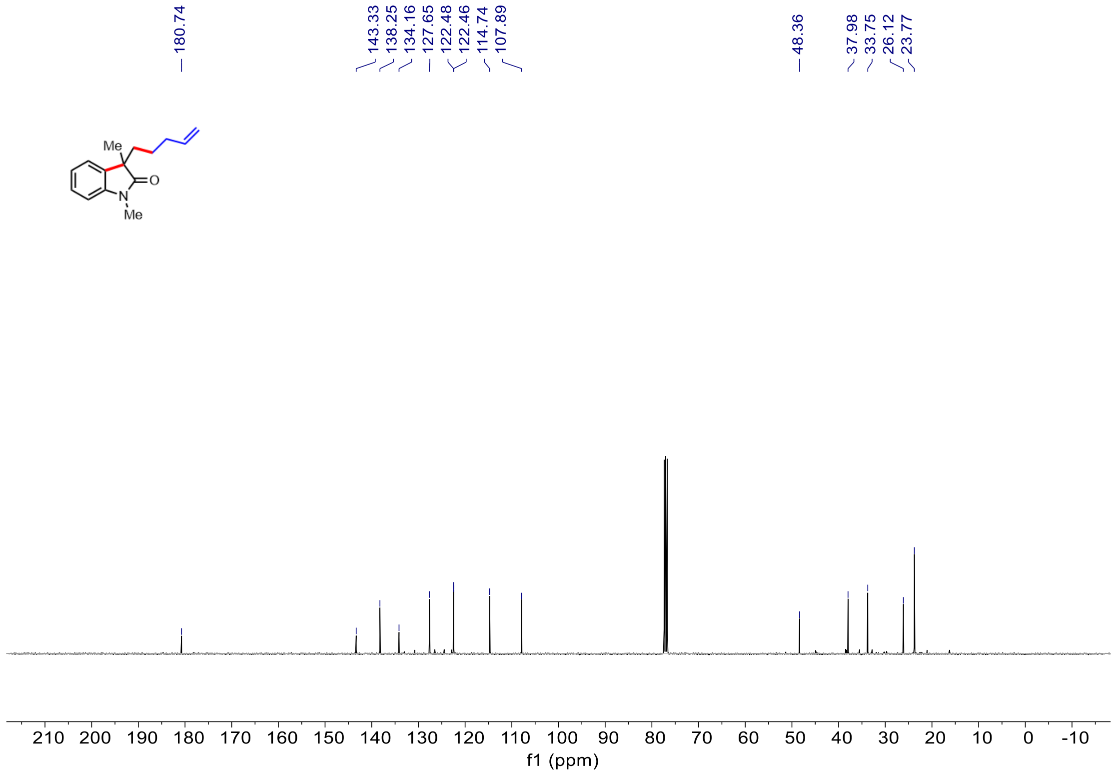
^{1}H and ^{13}C spectra for compound **51**





^{1}H and ^{13}C spectra for compound **52**




180.74
143.33
138.25
134.16
127.65
122.48
122.46
114.74
107.89
48.36
37.98
33.75
26.12
23.77
Me
N
Me
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)