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Visible light induced radical cyclization of *o*-iodophenylacrylamides: A concise synthesis of indolin-2-ones

Wuheng Dong,[a] Yan Liu,[b] Bei Hu,[b] Kai Ren,[b] Yuyuan Li,[b] Xiaomin Xie,[b] Yuexiu Jiang*[a] and Zhaoguo Zhang*[b]

[a]*School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China.*

[b] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China.*

zhaoguo@sjtu.edu.cn

Contents

1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and used without further purification. Anhydrous DMF, CH_3CN, DMSO, DCM were freshly distilled from calcium hydride, Anhydrous PhMe was freshly distilled from Sodium. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. The chemical shifts for ^1H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.00 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Analytical GC was performed on an Agilent 7890A with FID detector. HRMS were performed under ESI ionization technique on a Waters Micromass Q-TOF Premier Mass Spectrometer. Flash column chromatography was performed on silica gel (300-400 mesh).

2. Preparation of substrates

2.1 Representative procedure for the preparation of *o*-iodoacryloylanilide (1a-1o, 1s-1t).[1]

Crotonyl chloride[1a]

A 100 mL round-bottom flask was charged with crotonic acid (51.7 g, 600.0 mmol), and the thionyl chloride (85.7 g, 720.0 mmol) was added dropwise to the crotonic acid over 1 hour. After the addition was complete, the mixture was heated to 80 ^oC until no further gas evolution took place (roughly 2 hours). The product was directly distilled from the reaction flask to obtain 58.4 g (93%) crotonyl chloride.

***N*-(2-iodophenyl)but-2-enamide**[1b]

To a solution of 2-iodoaniline (9.86 g, 45.0 mmol) and pyridine (4.27 g, 54.0 mmol) in anhydrous DCM (130 mL) was added crotonyl chloride (5.18 g, 49.5 mmol) at 0 ^oC over 30 min. After the addition was complete, the reaction mixture was stirred at room temperature for 2 hours. After completion, the mixture was washed with H_2O (3×30 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The

resulting residue containing the corresponding to *N*-(2-iodophenyl)but-2-enamide was taken on to the next step without additional purification.

***N*-(2-iodophenyl)-*N*-methylbut-2-enamide**[1b]

To a slurry of NaH (1.57 g, 39.19 mmol, 60%) in THF (50 mL) at 0 °C was added *N*-(2-iodophenyl) but-2-enamide (7.5 g, 26 mmol) dissolved in THF (40 mL) over 20 min. The reaction mixture was stirred at room temperature for 20 min then methane iodide (10.53 g, 74.9 mmol) was added dropwise. The reaction mixture was monitored by TLC and quenched with saturated NH_4Cl (30 mL) upon completion then the solvent (THF) was removed under reduced pressure and diethyl ether (150 mL) was added. The organic phase was washed with H_2O (2×30 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by silica-gel column chromatography to give *N*-(2-iodophenyl)-*N*-methylbut-2-enamide as white solid (6.6 g, 76% yield over 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09 (td, *J* = 7.6, 1.6 Hz, 1H), 6.98–6.91 (m, 1H), 5.51–5.46 (m, 1H), 3.22 (s, 3H), 1.72 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 142.5, 140.7, 130.4, 130.4, 130.0, 122.8, 100.4, 36.6, 18.6.

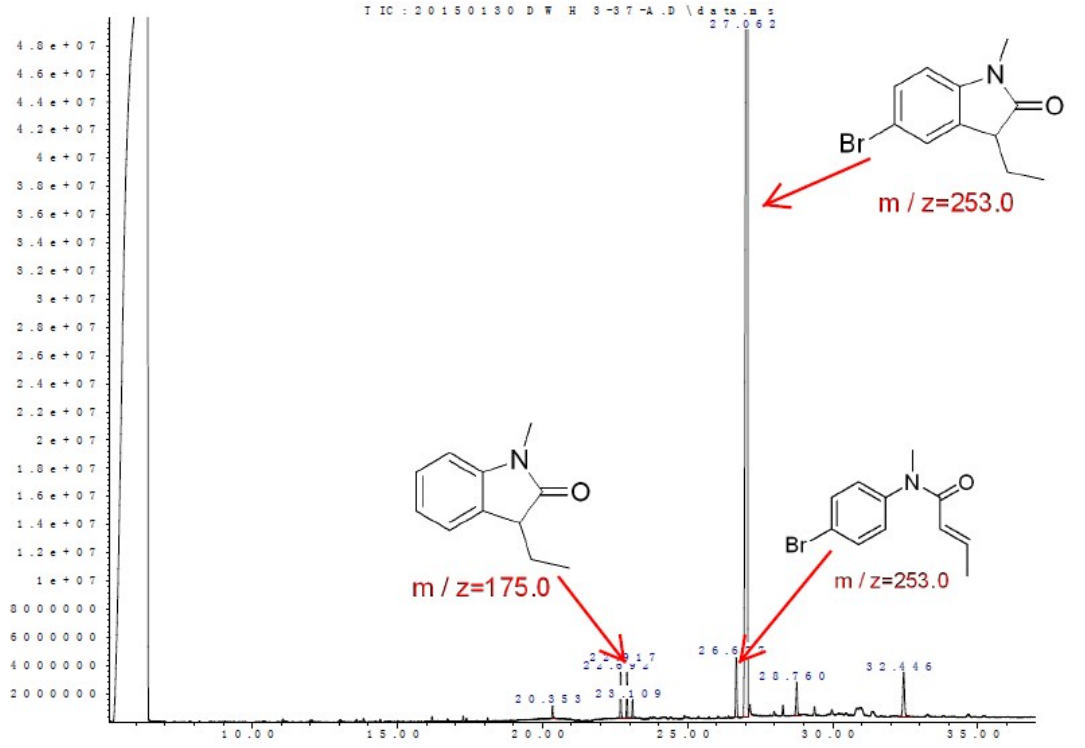
2.2 A General procedure for the preparation of *N*-(2-iodophenyl)-*N*-phenylbut-2-enamide (1p)

To a slurry of NaH (43.37 mg, 1.0 mmol, 60%) in DMF (2 mL) at rt was added 2-iodo-*N*-phenylaniline (320.00 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 20 min then crotonyl chloride (147.4 mg, 1.4 mmol) was added dropwise. The reaction mixture was heated at 65 °C for 4 h and quenched with saturated NH_4Cl (10 mL). The mixture was extracted with EA (2×30 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the crude product was purified by silica-gel column chromatography to give *N*-(2-iodophenyl)-*N*-phenylbut-2-enamide as white solid (200.00 mg, 51% yield). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.40–7.22 (m, 7H), 7.13–7.04 (m, 2H), 6.02–5.61 (m, 1H), 1.81 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 143.7, 140.6, 131.4, 129.8, 129.1, 127.5, 126.0, 123.6, 18.5. M.P.:111.8-114.6 °C. HRMS-ESI (m/z): Calculated for $C_{16}H_{15}NOI$ $(M + H)^+$: 364.0198, Found: 364.0195.

3. A general procedure for $Ir(ppy)_2(dtb\text{-}bpy)PF_6$-catalyzed reaction of *o*-iodoacryloylanilide under visible light

A dried Schlenk tube equipped with a stirrer bar which was evacuated and backfilled with nitrogen was added o-iodoacryloylanilide (0.5 mmol), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (0.005 mmol, 4.50 mg), Et_3N (5.0 mmol, 506.08 mg). Then 5 mL of CH_3CN was added into the reaction tube via a syringe. The reaction mixture was degassed by the freeze-pump-thaw method and then irradiated with a 12 W white LED strip (distance app. 5 cm) for 24 h. After the completion of the reaction, the mixture was concentrated in vacuum and the pure product was obtained by flash column chromatography on silica gel.

4. GC-MS analysis of product 2d and side product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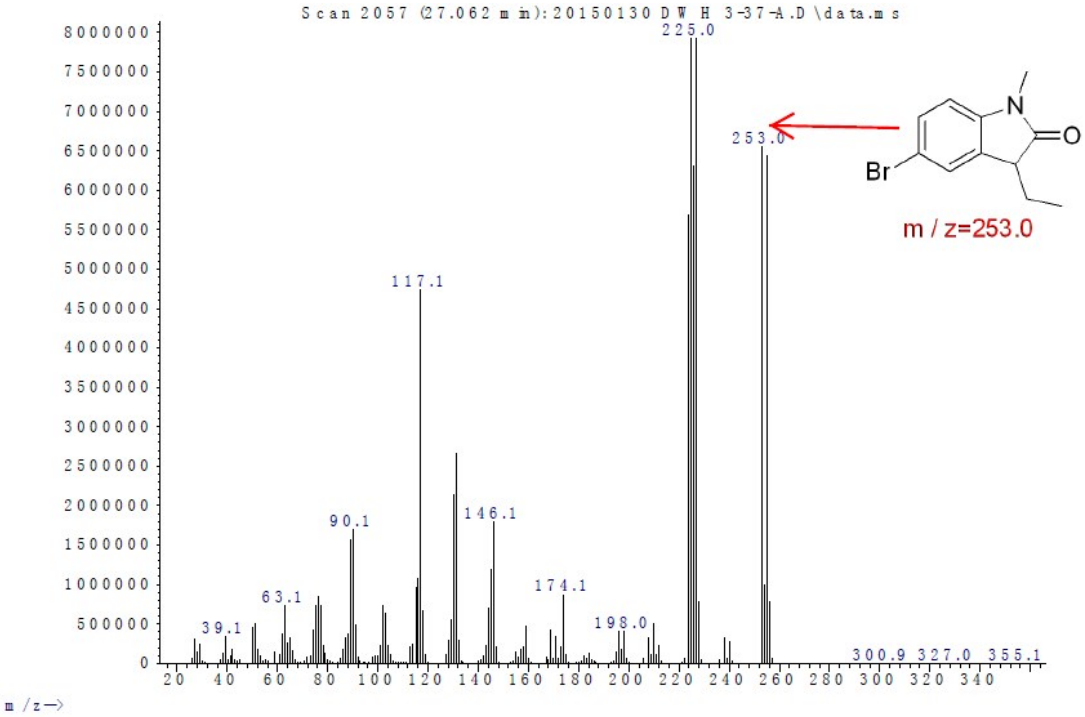
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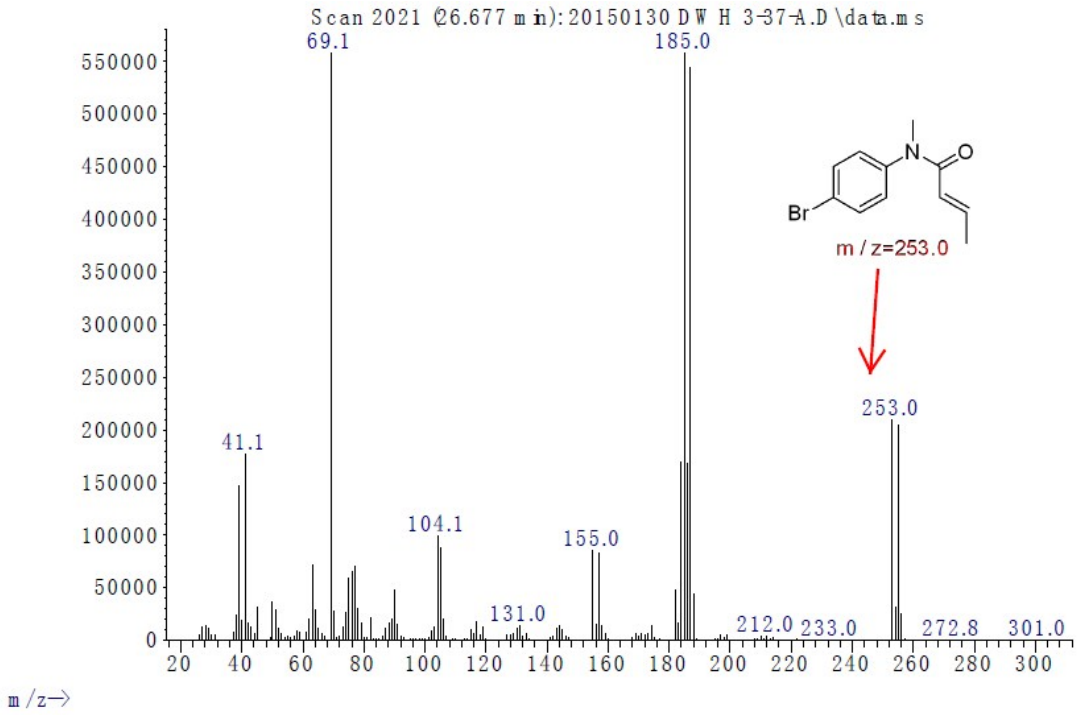
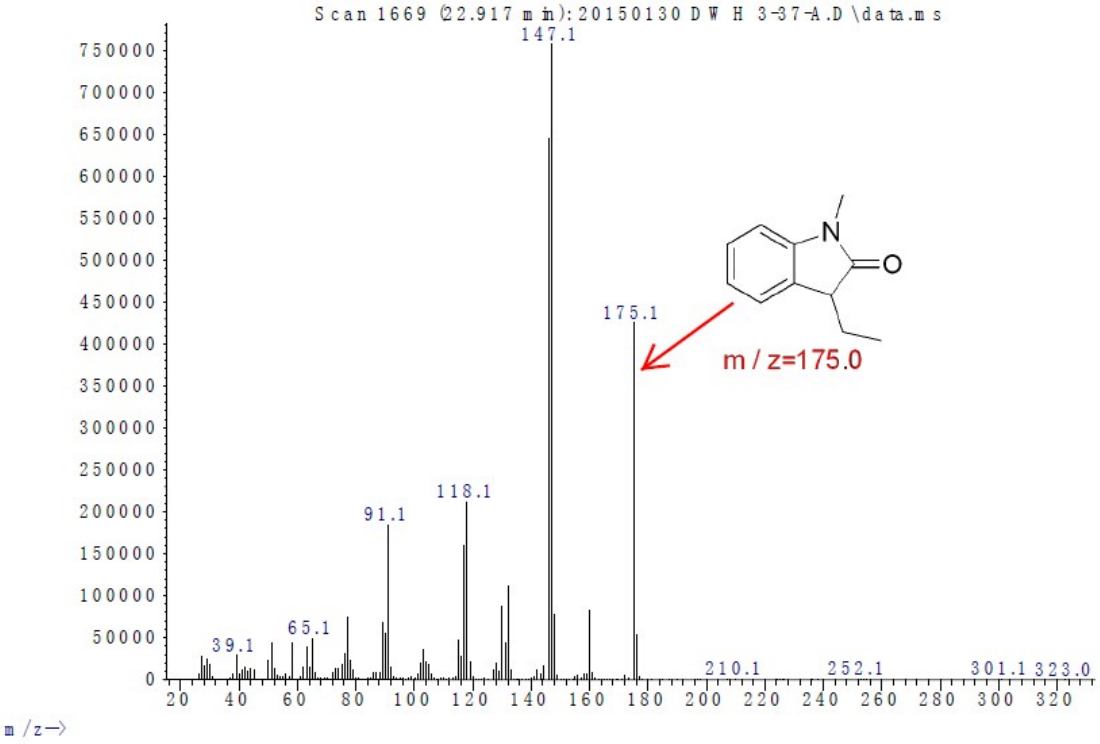
39.1
300.9 327.0 355.1
m / z→

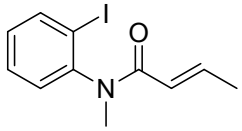




5. Spectral data for substrates and products

5.1. Spectral data for substrates

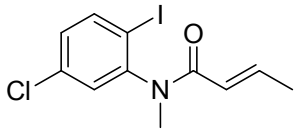
***N*-(2-iodophenyl)-*N*-methylbut-2-enamide**[2]



1a

White solid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09 (td, *J* = 7.6, 1.6 Hz, 1H), 6.98–6.91 (m, 1H), 5.51–5.46 (m, 1H), 3.22 (s, 3H), 1.72 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 142.5, 140.7, 130.4, 130.4, 130.0, 122.8, 100.4, 36.6, 18.6. M.P.:106.3-107.8 ^{o}C.

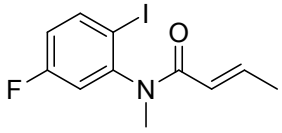
***N*-(5-chloro-2-iodophenyl)-*N*-methylbut-2-enamide**



1b

White solid, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.01–6.92 (m, 1H), 5.51–5.46 (m, 1H), 3.19 (s, 3H), 1.74 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 144.8, 142.8, 139.6, 134.7, 130.2, 130.1, 12.1, 100.4, 36.3, 18.3. M.P.:88.3-89.5 ^{o}C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^{+}$: 335.9652, Found: 335.9662.

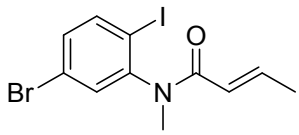
***N*-(5-fluoro-2-iodophenyl)-*N*-methylbut-2-enamide**



1c

Yellow solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.21 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.16–7.11 (m, 1H), 7.00–6.91 (m, 1H), 5.50–5.46 (m, 1H), 3.19 (s, 3H), 1.73 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 162.6, 160.1, 142.6, 130.3, 130.2, 122.1, 117.1, 116.9, 100.0, 99.9, 36.3, 18.3. M.P.:86.7-88.2 ^{o}C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^{+}$: 319.9948, Found: 319.9949.

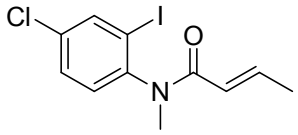
***N*-(5-bromo-2-iodophenyl)-*N*-methylbut-2-enamide**



1d

Yellow solid, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.96–6.87 (m, 1H), 5.44 (d, *J* = 14.8 Hz, 1H), 3.14 (s, 3H), 1.69 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.8, 142.3, 133.2, 130.6, 122.6, 122.1, 100.9, 36.2, 18.3. M.P.:76.9-78.8 °C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^+$: 379.9147, Found: 379.9155.

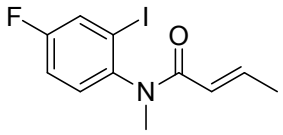
***N*-(4-chloro-2-iodophenyl)-*N*-methylbut-2-enamide**



1e

White solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.01–6.93 (m, 1H), 5.50–5.45 (m, 1H), 3.19 (s, 3H), 1.74 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 147.2, 143.0, 141.0, 135.7, 130.3, 129.9, 122.0, 97.5, 36.2, 18.3. M.P.:131.4-132.8 °C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^+$: 335.9652, Found: 335.9664.

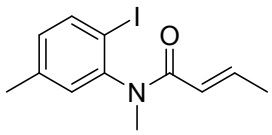
***N*-(4-fluoro-2-iodophenyl)-*N*-methylbut-2-enamide**



1f

White solid, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.01–6.85 (m, 3H), 5.49–5.44 (m, 1H), 3.18 (s, 3H), 1.72 (dd, *J* = 7.2, 2.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.7, 162.2, 142.8, 141.0, 141.0, 122.0, 117.6, 117.4, 117.2, 93.4, 93.3, 36.1, 18.3. M.P.:124.7-126.3. °C HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^+$: 319.9948, Found: 319.9951.

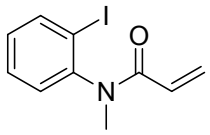
***N*-(2-iodo-5-methylphenyl)-*N*-methylbut-2-enamide**



1g

White solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.20 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.98–6.89 (m, 1H), 5.54–5.49 (m, 1H), 3.19 (s, 3H), 2.36 (s, 3H), 1.71 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 143.4, 141.9, 140.6, 140.3, 130.8, 129.0, 122.5, 99.7, 36.3, 20.8, 18.2. M.P.:73.8-75.3 ^{o}C HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^{+}$: 316.0198, Found: 316.0197.

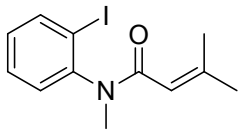
***N*-(2-iodophenyl)-*N*-methylacrylamide**[3]



1h

Yellow liquid, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45–7.40 (m, 1H), 7.27–7.25 (m, 1H), 7.11–7.07 (m, 1H), 6.40 (dd, *J* = 16.8, 2.0 Hz, 1H), 5.84 (dd, *J* = 16.8, 10.4 Hz, 1H), 5.52 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 145.7, 140.4, 130.1, 129.6, 128.4, 128.2, 99.9, 36.4.

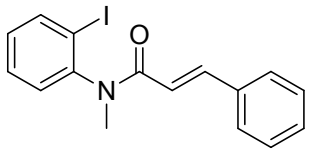
***N*-(2-iodophenyl)-*N*,3-dimethylbut-2-enamide**[4]



1i

White solid, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.39 (td, *J* = 7.2, 1.2 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.06–7.02 (m, 1H), 5.24 (dd, *J* = 2.4, 1.2 Hz, 1H), 3.18 (s, 3H), 2.14 (d, *J* = 1.2 Hz, 3H), 1.65 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 151.7, 146.5, 140.2, 130.0, 129.6, 129.5, 117.3, 100.2, 35.9, 27.5, 20.5. M.P.:79.1-81.1 ^{o}C.

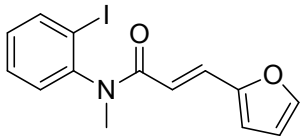
***N*-(2-iodophenyl)-*N*-methylcinnamamide**[5]



1j

White solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51–7.44 (m, 3H), 7.18–7.14 (m, 1H), 6.01 (d, *J* = 15.6 Hz, 1H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 141.9, 130.9, 130.9, 130.5, 130.4, 129.6, 128.2, 118.9, 101.2, 36.6. M.P.:105.3-106.7 °C.

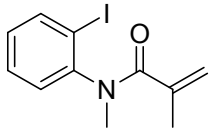
3-(Furan-2-yl)-*N*-(2-iodophenyl)-*N*-methylacrylamide[6]



1k

Pale solid, 88% yield. ^{1}H NMR (400 MHz, DMSO) δ 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.55–7.47 (m, 2H), 7.33 (d, *J* = 15.6 Hz, 1H), 7.22–7.18 (m, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.51 (dd, *J* = 3.6, 2.0 Hz, 1H), 5.82 (d, *J* = 15.2 Hz, 1H), 3.13 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 164.9, 151.3, 145.8, 140.4, 131.0, 130.9, 130.4, 129.0, 115.8, 113.1, 101.2, 36.6. M.P.:110.7-112.8 °C.

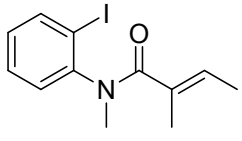
***N*-(2-iodophenyl)-*N*-methylmethacrylamide**[2]



1l

Yellow solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.03–6.99 (m, 1H), 5.02 (d, *J* = 28.4 Hz, 1H), 3.24 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 147.1, 140.4, 129.5, 119.2, 99.3, 37.1, 20.8. M.P.:70.2-71.2 °C.

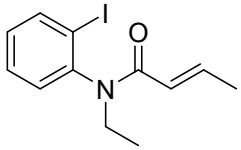
***N*-(2-iodophenyl)-*N*,2-dimethylbut-2-enamide**[7]



1m

Yellow solid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.97 (td, *J* = 7.6, 1.6 Hz, 1H), 5.78 (s, 1H), 3.22 (s, 3H), 1.62 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 147.3, 140.3, 132.3, 130.4, 129.5, 129.1, 99.2, 37.3, 14.3, 13.6. M.P.:82.4-83.7 °C.

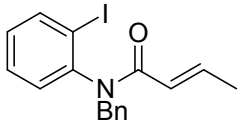
***N*-ethyl-*N*-(2-iodophenyl)but-2-enamide**



1n

Yellow solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.99–6.90 (m, 1H), 5.44 (d, *J* = 15.2 Hz, 1H), 4.25–4.16 (m, 1H), 3.29–3.20 (m, 1H), 1.71 (d, *J* = 7.6 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 144.2, 142.0, 140.4, 131.0, 129.9, 129.5, 122.8, 101.1, 43.4, 18.2, 13.1. M.P.:103.7-104.4 °C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^+$: 316.0198, Found: 316.0194.

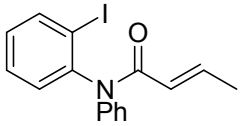
***N*-benzyl-*N*-(2-iodophenyl)but-2-enamide**



1o

White solid, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.26–7.19 (m, 6H), 7.08–6.99 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.70 (d, *J* = 14.0 Hz, 1H), 5.50–5.45 (m, 1H), 4.01 (d, *J* = 14.0 Hz, 1H), 1.73 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.9, 140.3, 130.0, 129.7, 129.3, 128.6, 127.7, 122.5, 100.9, 51.9, 18.3. M.P.:115.0-115.7 °C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^+$: 378.0355, Found: 378.0354.

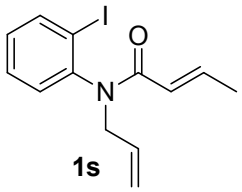
***N*-(2-iodophenyl)-*N*-phenylbut-2-enamide**



1p

White solid, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.40–7.22 (m, 7H), 7.13–7.04 (m, 2H), 6.02–5.61 (m, 1H), 1.81 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 143.7, 140.6, 131.4, 129.8, 129.1, 127.5, 126.0, 123.6, 18.5. M.P.: 111.8-114.6 °C. HRMS-ESI (m/z): Calculated for $C_{16}H_{15}NOI$ $(M + H)^+$: 364.0198, Found: 364.0195.

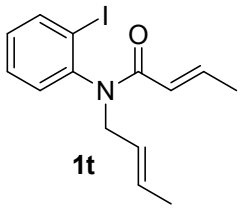
***N*-allyl-*N*-(2-iodophenyl)but-2-enamide**[8]



1s

White solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38–7.34 (m, 1H), 7.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.06 (td, *J* = 7.6, 1.6 Hz, 1H), 6.99–6.90 (m, 1H), 5.94–5.84 (m, 1H), 5.46–5.41 (m, 1H), 5.08–5.00 (m, 2H), 4.84 (dd, *J* = 14.4, 5.2 Hz, 1H), 3.62 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.68 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 142.6, 140.3, 132.9, 131.2, 130.0, 129.5, 122.5, 118.7, 101.1, 51.5, 18.3. M.P.:104.3-105.7 °C.

***N*-(but-2-en-1-yl)-*N*-(2-iodophenyl)but-2-enamide**

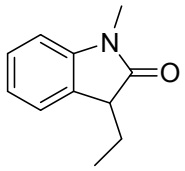


1t

Yellow liquid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.16–7.05 (m, 2H), 7.00–6.91 (m, 1H), 5.60–5.42 (m, 3H), 4.85–4.74 (m, 1H), 3.61 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.71 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.64–1.61 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 142.2, 140.2, 131.3, 130.1, 129.9, 129.4, 125.6, 122.8, 101.2, 50.6, 44.6, 18.3, 18.0. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^+$: 342.0355, Found: 342.0363.

5.2. Spectral data for products

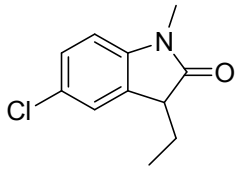
3-Ethyl-1-methylindolin-2-one[2]



2a

Yellow liquid, 92% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.07–7.03 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.41 (t, *J* = 6.0 Hz, 1H), 3.20 (s, 3H), 2.07–1.95 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 144.7, 129.1, 128.0, 124.0, 122.4, 108.1, 46.8, 26.3, 23.9, 10.3.

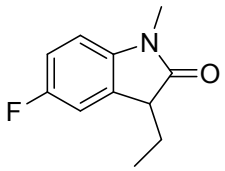
5-Chloro-3-ethyl-1-methylindolin-2-one



2b

White solid, 48% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.22 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 3.41 (t, *J* = 5.6 Hz, 1H), 3.19 (s, 3H), 2.04–1.95 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 143.3, 127.9, 124.5, 108.9, 46.9, 26.4, 23.8, 10.2. M.P.:79.1-79.3 ^{o}C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^{+}$: 210.0686, Found: 210.0680.

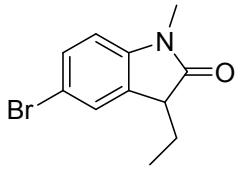
3-Ethyl-5-fluoro-1-methylindolin-2-one



2c

Yellow liquid, 71% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00–6.94 (m, 2H), 6.74–6.71 (m, 2H), 3.40 (t, *J* = 5.6 Hz, 1H), 3.18 (s, 3H), 2.03–1.96 (m, 2H), 0.87 (t, *J* = 7.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 160.5, 158.1, 140.7, 130.8, 130.7, 114.2, 114.0, 112.3, 108.4, 108.3, 47.2, 26.4, 23.8, 10.2. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}FNO$ $(M + H)^{+}$: 194.0981, Found: 194.0979.

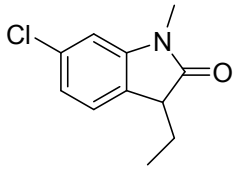
5-Bromo-3-ethyl-1-methylindolin-2-one



2d

White solid, 47% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.39 (m, 1H), 7.36–7.35 (m, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 3.42 (t, *J* = 5.6 Hz, 1H), 3.18 (s, 3H), 2.03–1.96 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 143.8, 130.9, 127.2, 115.2, 109.5, 46.8, 26.4, 23.8, 10.2. M.P.:79.1-79.8 °C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOBr$ $(M + H)^+$: 254.0181, Found: 254.0186.

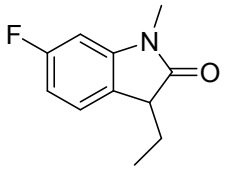
6-Chloro-3-ethyl-1-methylindolin-2-one



2e

White solid, 74% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.14 (m, 1H), 7.04–7.01 (m, 1H), 6.82 (d, *J* = 1.6 Hz, 1H), 3.39 (t, *J* = 5.6 Hz, 1H), 3.18 (s, 3H), 2.03–1.95 (m, 2H), 0.87 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 146.0, 133.8, 124.8, 122.2, 108.8, 46.5, 26.4, 23.9, 10.2. M.P.:62.3-62.9 °C. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}NOCl$ $(M + H)^+$: 210.0686, Found: 210.0678.

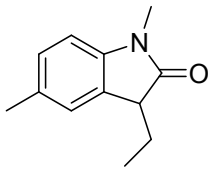
3-Ethyl-6-fluoro-1-methylindolin-2-one



2f

Yellow liquid, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.14 (m, 1H), 6.75–6.70 (m, 1H), 6.58–6.55 (m, 1H), 3.38 (t, *J* = 5.6 Hz, 1H), 3.18 (s, 3H), 2.03–1.93 (m, 1H), 0.87 (t, *J* = 7.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 164.3, 161.9, 146.2, 146.1, 124.8, 124.7, 124.3, 108.4, 108.2, 97.1, 96.8, 46.3, 26.4, 23.9, 10.2. HRMS-ESI (m/z): Calculated for $C_{11}H_{13}FNO$ $(M + H)^+$: 194.0981, Found: 194.0982.

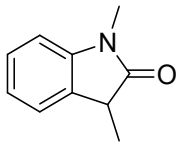
3-Ethyl-1,5-dimethylindolin-2-one



2g

Yellow liquid, 92% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.05 (m, 2H), 6.72–6.70 (m, 1H), 3.38 (t, *J* = 5.6 Hz, 1H), 3.18 (s, 3H), 3.34 (s, 3H), 2.05–1.93 (m, 2H), 0.88 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 142.3, 131.9, 129.2, 128.2, 124.9, 107.8, 46.9, 26.3, 23.9, 21.3, 10.3. HRMS-ESI (m/z): Calculated for $C_{12}H_{16}NO$ $(M + H)^+$: 190.1232, Found: 190.1223.

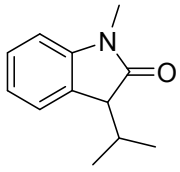
1,3-Dimethylindolin-2-one[9]



2h

Yellow liquid, 52% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.43 (q, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 1.48 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 144.2, 128.1, 123.7, 122.6, 108.2, 40.8, 26.4, 15.6.

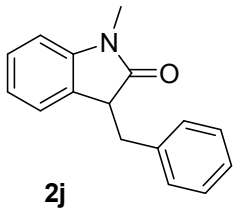
3-Isopropyl-1-methylindolin-2-one[10]



2i

Yellow liquid, 53% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.05–7.02 (m, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 3.37 (d, *J* = 3.2 Hz, 1H), 3.20 (s, 3H), 2.54–2.47 (m, 1H), 1.09 (d, *J* = 7.2 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 145.0, 128.0, 124.5, 122.3, 108.0, 51.8, 31.0, 26.2, 20.1, 18.1.

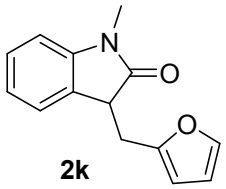
3-Benzyl-1-methylindolin-2-one[10]



2j

Yellow solid, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.16 (m, 6H), 6.59–7.53 (m, 1H), 7.51–7.41 (m, 2H), 3.70 (s, 3H), 3.51–3.44 (m, 1H), 3.14 (qd, *J* = 7.2, 1.6 Hz, 1H), 3.02 (dd, *J* = 17.6, 5.6 Hz, 1H), 1.29–1.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 176.3, 136.5, 133.0, 128.5, 127.9, 51.8, 41.9, 34.8, 17.2. M.P.:65.5-66.3 ^{o}C.

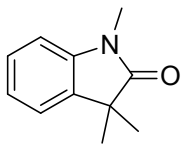
3-(Furan-2-ylmethyl)-1-methylindolin-2-one[11]



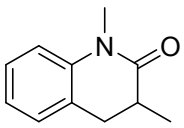
2k

Red liquid, 44% yield, ^{1}H NMR (400 MHz, DMSO) δ 7.48–7.47 (m, 1H), 7.25–7.21 (m, 1H), 6.95–6.91 (m, 2H), 6.87–6.85 (m, 1H), 6.29 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.96 (dd, *J* = 3.2, 0.4 Hz, 1H), 3.79 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.31 (dd, *J* = 14.8, 5.2 Hz, 1H), 3.09 (s, 3H), 2.95 (dd, *J* = 15.2, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 176.5, 152.6, 144.8, 142.4, 128.6, 124.4, 122.4, 111.1, 108.9, 107.5, 44.4, 28.8, 26.6.

1,3,3-Trimethylindolin-2-one[12]



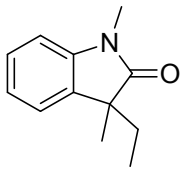
2l



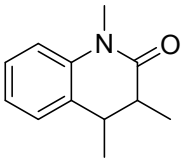
2l'

Yellow liquid, 66% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.16 (m, 3H), 7.10–6.97 (m, 1.8H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.37 (s, 0.8H), 3.23 (s, 3H), 2.94 (dd, *J* = 14.4, 4.8 Hz, 0.4H), 2.74–2.61 (m, 0.8H), 1.38 (s, 6.2H), 1.27 (d, *J* = 6.8 Hz, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6, 173.4, 142.8, 140.6, 136.0, 128.1, 127.9, 127.6, 125.9, 122.9, 122.7, 122.5, 114.7, 108.2, 44.4, 35.7, 33.5, 30.0, 26.4, 24.6, 15.9.

3-Ethyl-1,3-dimethylindolin-2-one[13]



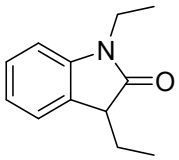
2m



2m'

Colorless liquid, 86% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.22 (m, 1.8H), 7.17–7.14 (m, 1.6H), 7.08–6.96 (m, 2.3H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.36 (s, 1.8H), 3.21 (s, 3H), 2.99–2.92 (m, 0.7H), 2.78–2.71 (m, 0.7H), 1.97–1.86 (m, 1.3H), 1.81–1.72 (m, 1.2H), 1.34 (s, 3.1H), 1.17 (d, *J* = 7.2 Hz, 2H), 1.11 (d, *J* = 7.2 Hz, 2H), 0.58 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 172.9, 143.7, 139.7, 134.1, 132.0, 127.8, 127.5, 126.9, 123.1, 122.7, 122.6, 114.9, 108.0, 49.2, 40.2, 36.2, 31.7, 29.9, 29.8, 26.3, 23.5, 14.8, 12.1, 9.1.

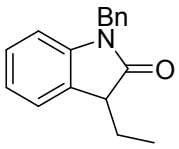
1,3-Diethylindolin-2-one



2n

Yellow liquid, 90% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.90–3.75 (m, 2H), 3.47 (t, *J* = 5.6 Hz, 1H), 2.11–2.04 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 143.8, 129.4, 127.9, 124.1, 122.2, 108.2, 46.8, 34.7, 23.9, 12.9, 10.0. HRMS-ESI (m/z): Calculated for $C_{12}H_{15}NO$ $(M + H)^+$: 190.1232, Found: 190.1224.

1-Benzyl-3-ethylindolin-2-one[14]

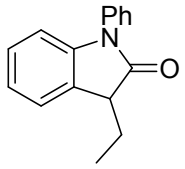


2o

Yellow liquid, 77% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.22 (m, 6H), 7.18–7.14 (m, 1H), 7.04–7.00 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 15.6 Hz, 1H), 3.53 (t, *J* = 5.6 Hz, 1H), 2.12–2.05 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 143.9, 136.3, 129.1, 129.0, 128.0, 127.8, 127.5, 124.1, 122.6, 109.2,

46.8, 43.9, 24.1, 10.4.

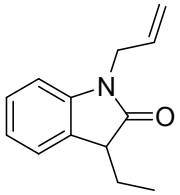
3-Ethyl-1-phenylindolin-2-one



2p

Colorless liquid, 77% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 3.62 (t, *J* = 5.6 Hz, 1H), 2.17–2.05 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 144.7, 134.9, 129.8, 129.0, 128.2, 128.0, 126.9, 124.3, 123.0, 109.4, 47.0, 24.4, 10.2. HRMS-ESI (m/z): Calculated for $C_{16}H_{16}NO$ $(M + H)^+$: 238.1232, Found: 238.1234.

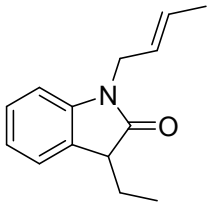
1-Allyl-3-ethylindolin-2-one[15]



2s

Yellow liquid, 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.87–5.78 (m, 1H), 5.21–5.17 (m, 2H), 4.43–4.26 (m, 2H), 3.46 (t, *J* = 5.6 Hz, 1H), 2.07–2.00 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 143.9, 131.7, 129.1, 127.9, 124.0, 122.4, 117.5, 109.0, 46.7, 42.4, 24.0, 10.2.

1-(But-2-en-1-yl)-3-ethylindolin-2-one



2t

Colorless liquid, 77% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.33 (m, 2H), 7.15 (t, *J* = 7.2

Hz, 1H), 6.92 (dd, J = 12.8, 8.0 Hz, 1H), 5.84–5.76 (m, 1H), 5.60–5.48 (m, 1H), 4.51–4.31 (m, 2H), 3.54 (t, J = 5.6 Hz, 1H), 2.17–2.10 (m, 2H), 1.79–1.76 (m, 3H), 1.02–0.97 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 144.1, 129.1, 128.5, 127.9, 124.7, 124.0, 122.0, 109.0, 108.7, 46.8, 41.8, 24.0, 17.9, 10.3. HRMS-ESI (m/z): Calculated for $C_{14}H_{17}NO$ $(M + H)^+$: 216.1388, Found: 216.1386.

6. Reference

1 (a) P. V. Ramachandran, D. Nicponski and B. Kim, *Org. Lett*., 2013, **15**, 1398; (b) T. C. T. Ho and K. Jones, *Tetrahedron*, 1997, **53**, 8287.

2 M. Ishikura, N. Takahashi, K. Yamada and R. Yanada, *Tetrahedron*, 2006, **62**, 11580.

3 T. C. T. Ho and K. Jones, *Tetrahedron*, 1997, **53**, 8287.

4 R. R. Goehring, Y. P. Sachdeva, J. S. Pisipati, M. C. Sleevi and J. F. Wolfe, *J. Am. Chem. Soc*., 1985, **107**, 435.

5 R. Munusamy, K. S. Dhathathreyan, K. K. Balasubramanian and C. S. Venkatachalam, *J. Chem. Soc., Perkin Trans*. **2**, 2001, 1154.

6 W. R. Bowman, H. Heaney and B. M. Jordan, *Tetrahedron Lett*., 1988, **29**, 6657.

7 M. C. McDermott, G. R. Stephenson, D. L. Hughes and A. J. Walkington, *Org. Lett*., 2006, **8**, 2917.

8 D. P. Curran, C. H. T. Chen, S. J. Geib and A. B. Lapierre, *Tetrahedron*, 2004, **60**, 4413.

9 B. M. Trost, J. Xie and J. D. Sieber, *J. Am. Chem. Soc*., 2011, **133**, 20611.

10 B. M. Trost and Y. Zhang, *Chem. —Eur. J*., 2011, **17**, 2916.

11 R. Grigg, S. Whitney, V. Sridharan, A. Keep and A. Derrick, *Tetrahedron*, 2009, **65**, 4375.

12 T. Nishio, H. Asai and T. Miyazaki, *Helv. Chim. Acta*, 2000, **83**, 1475.

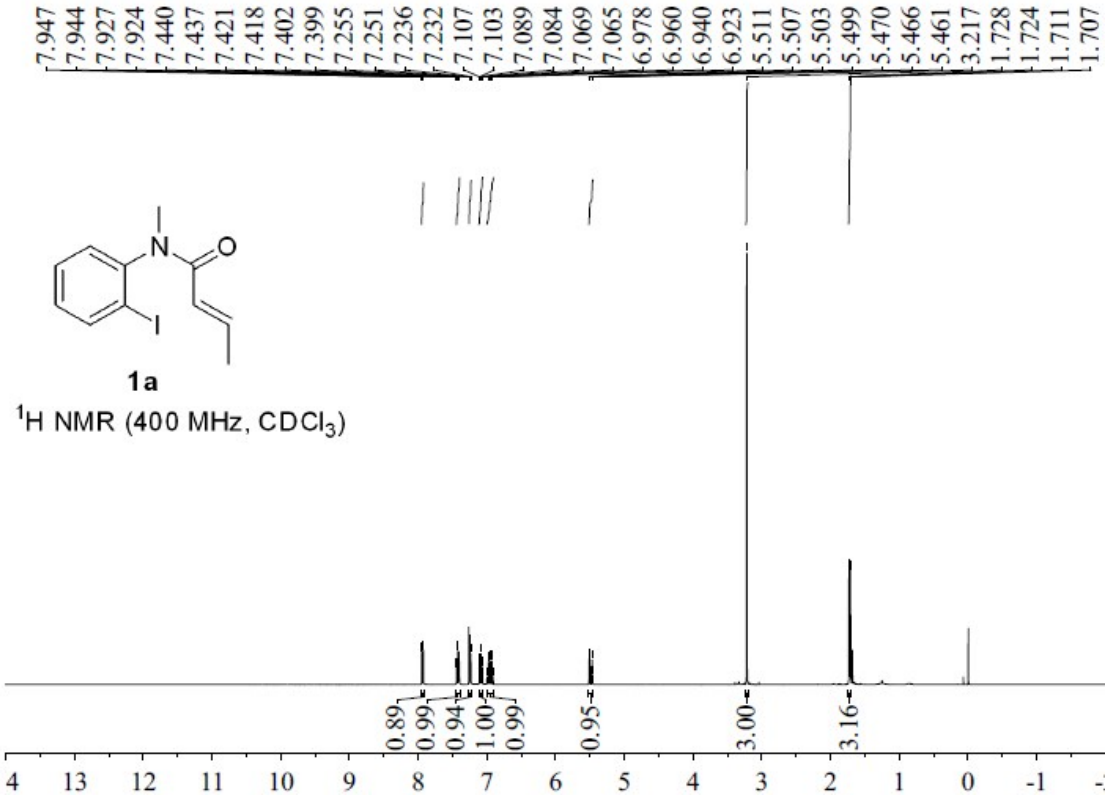
13 A. J. Clark and K. Jones, *Tetrahedron*, 1992, **48**, 6875.

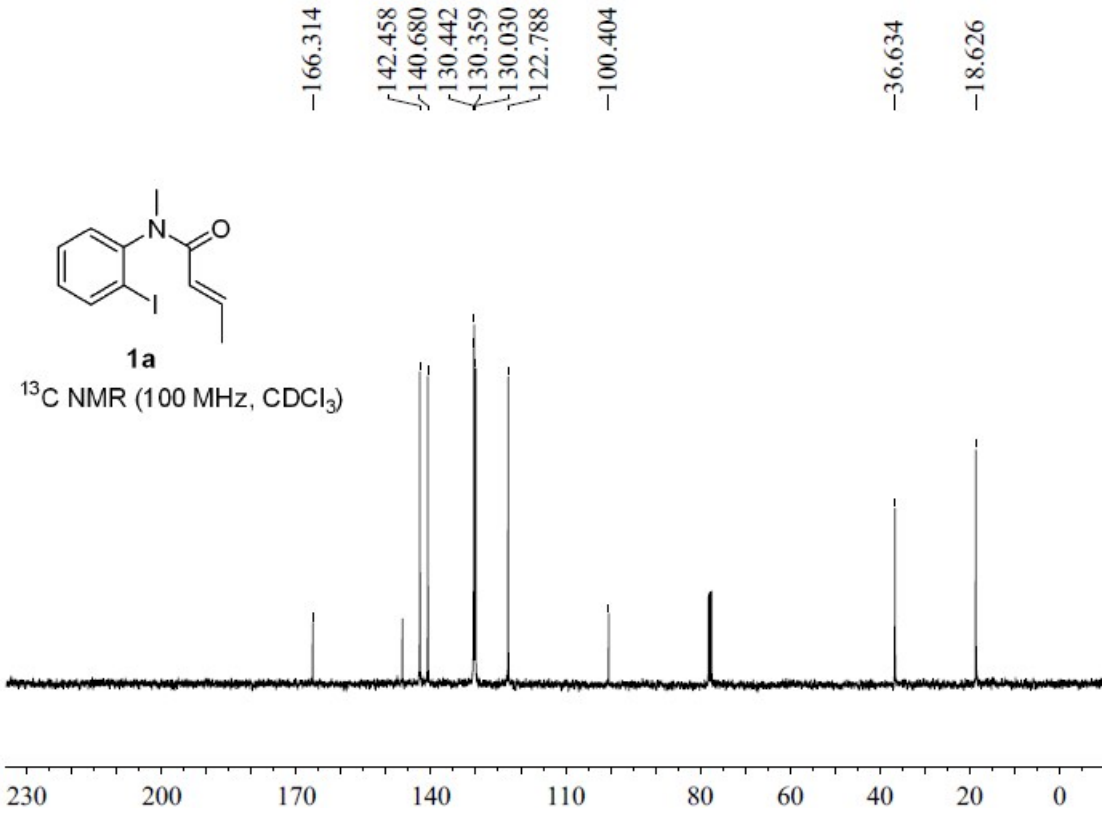
14 Y. Liu, D. Yao, K. Li, F. Tian, F. Xie and W. Zhang, *Tetrahedron*, 2011, **67**, 8445-8450.

15 K. Jones and J. M. D. Storey, *J. Chem. Soc., Chem. Commun*., 1992, 1766.

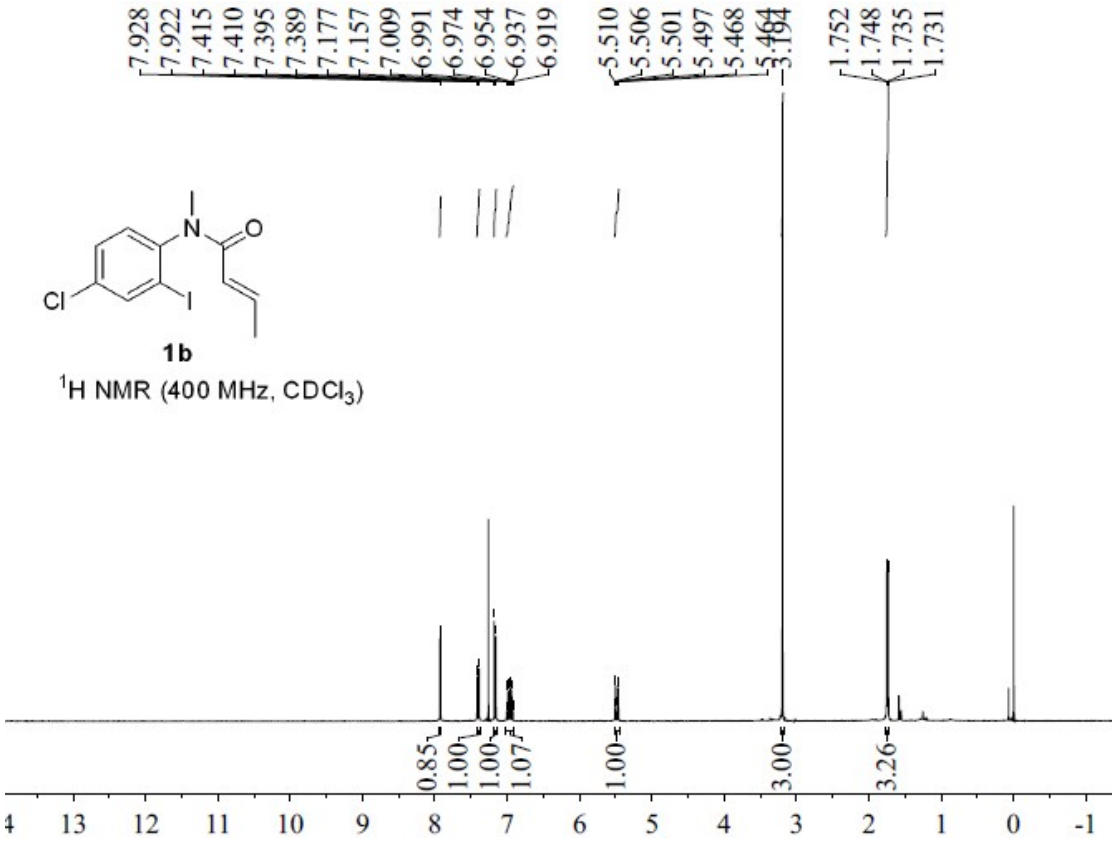
7. NMR spectra of the products

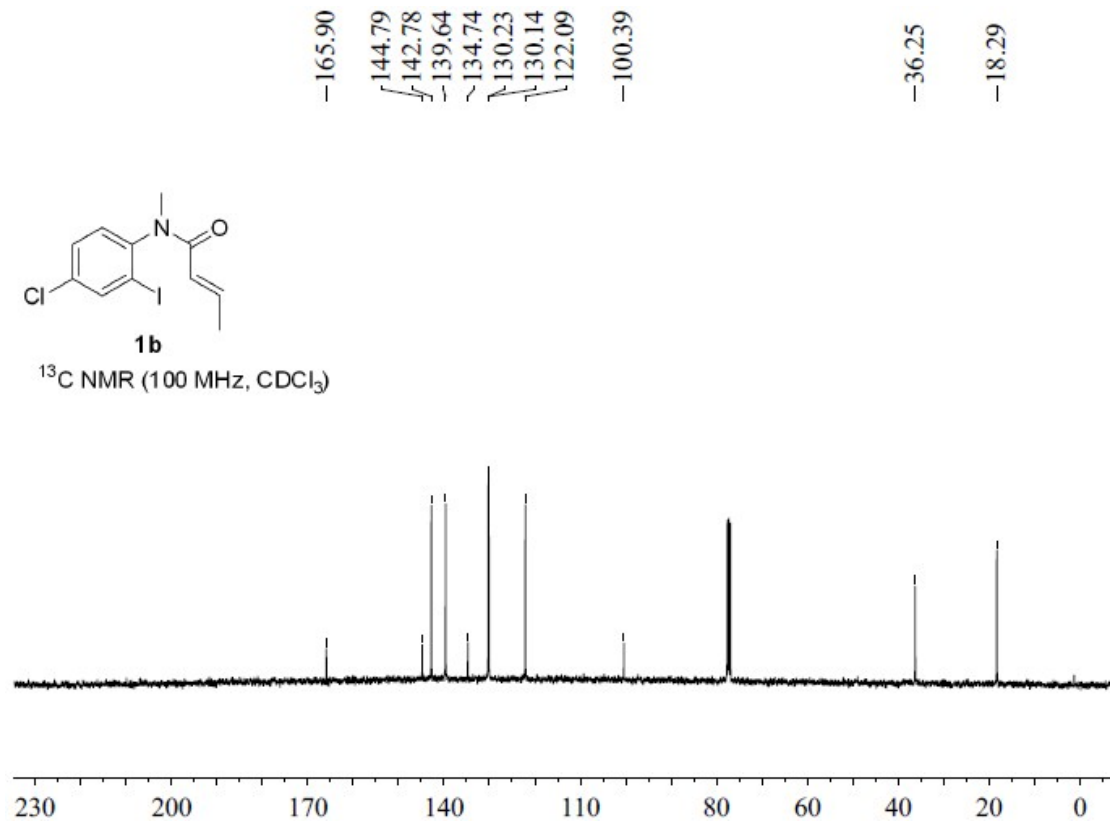
N-(2-iodophenyl)-*N*-methylbut-2-enamide (1a)



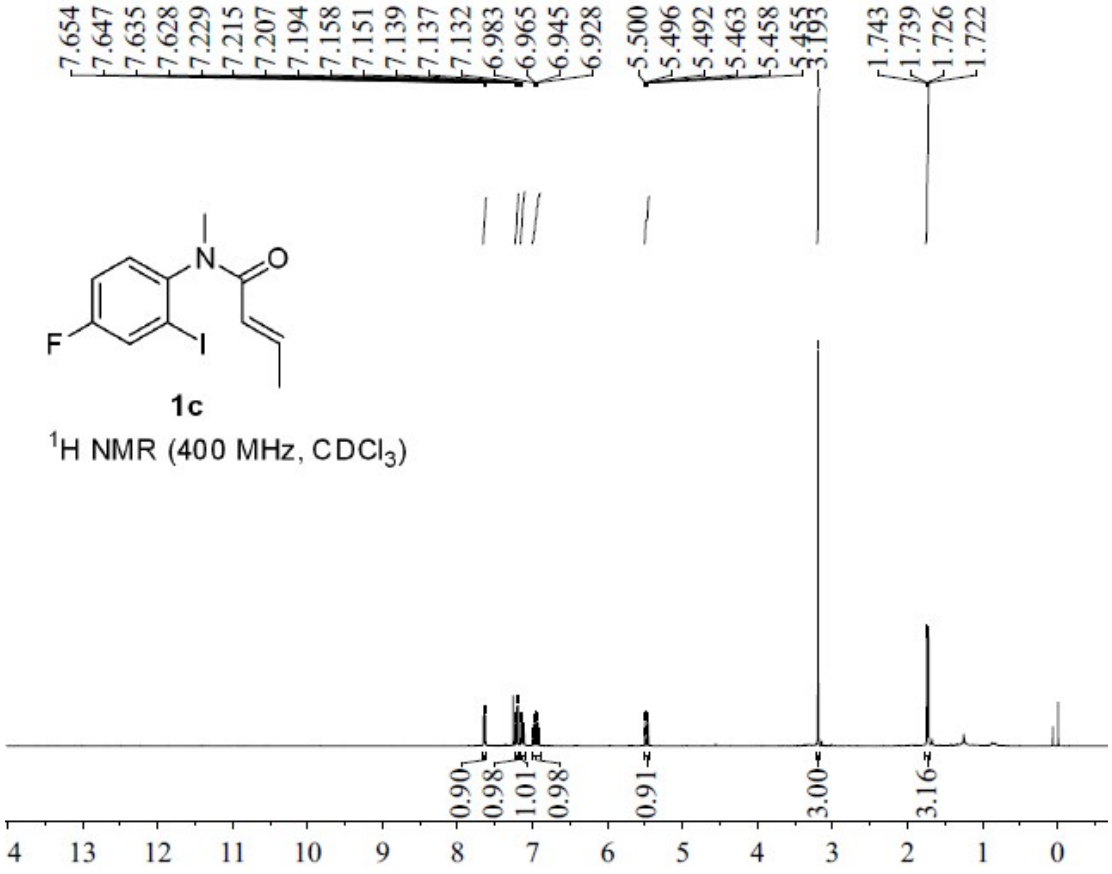


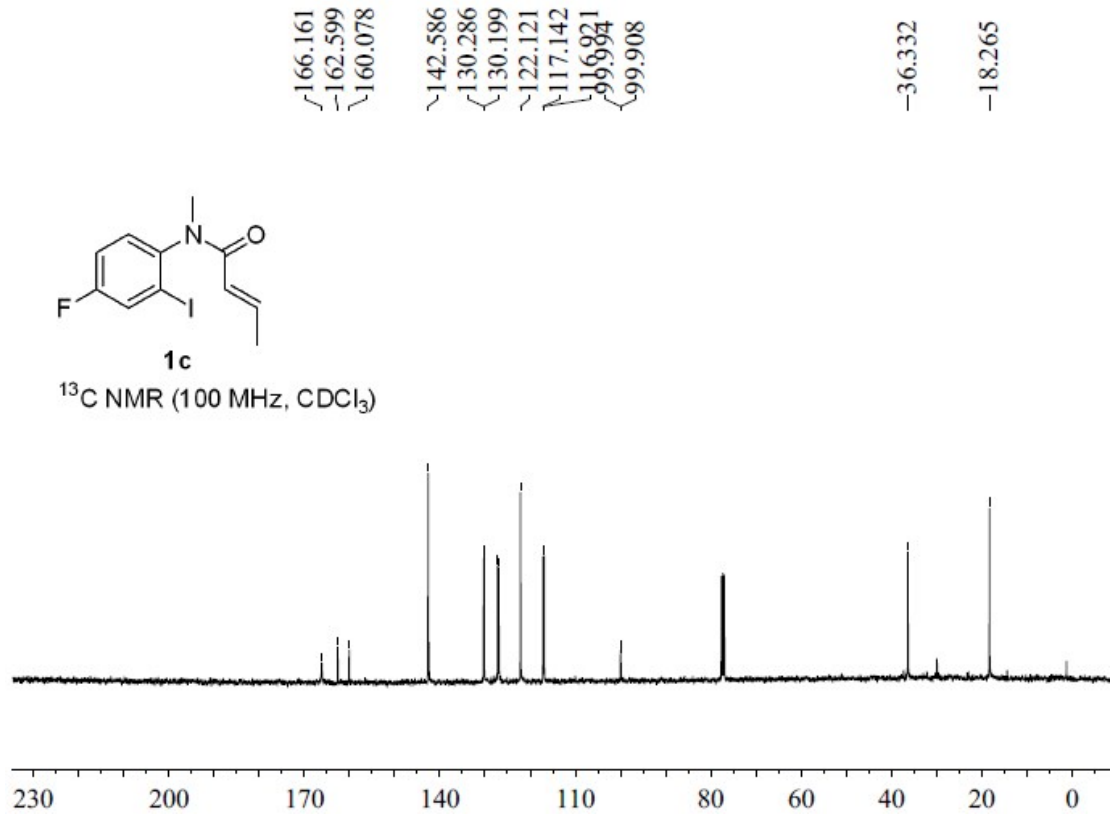
***N*-(5-chloro-2-iodophenyl)-*N*-methylbut-2-enamide (1b)**



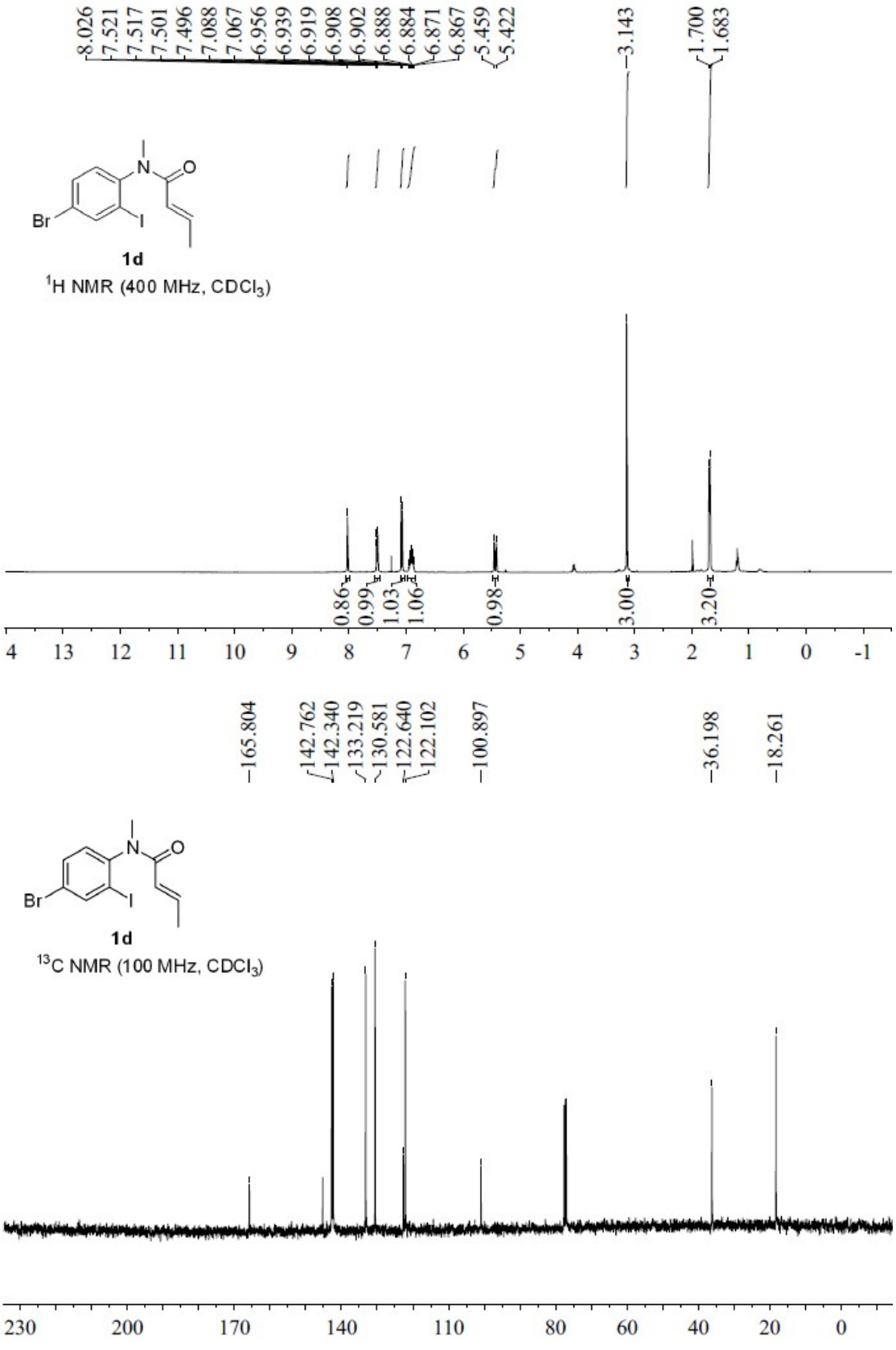


***N*-(5-fluoro-2-iodophenyl)-*N*-methylbut-2-enamide (1c)**

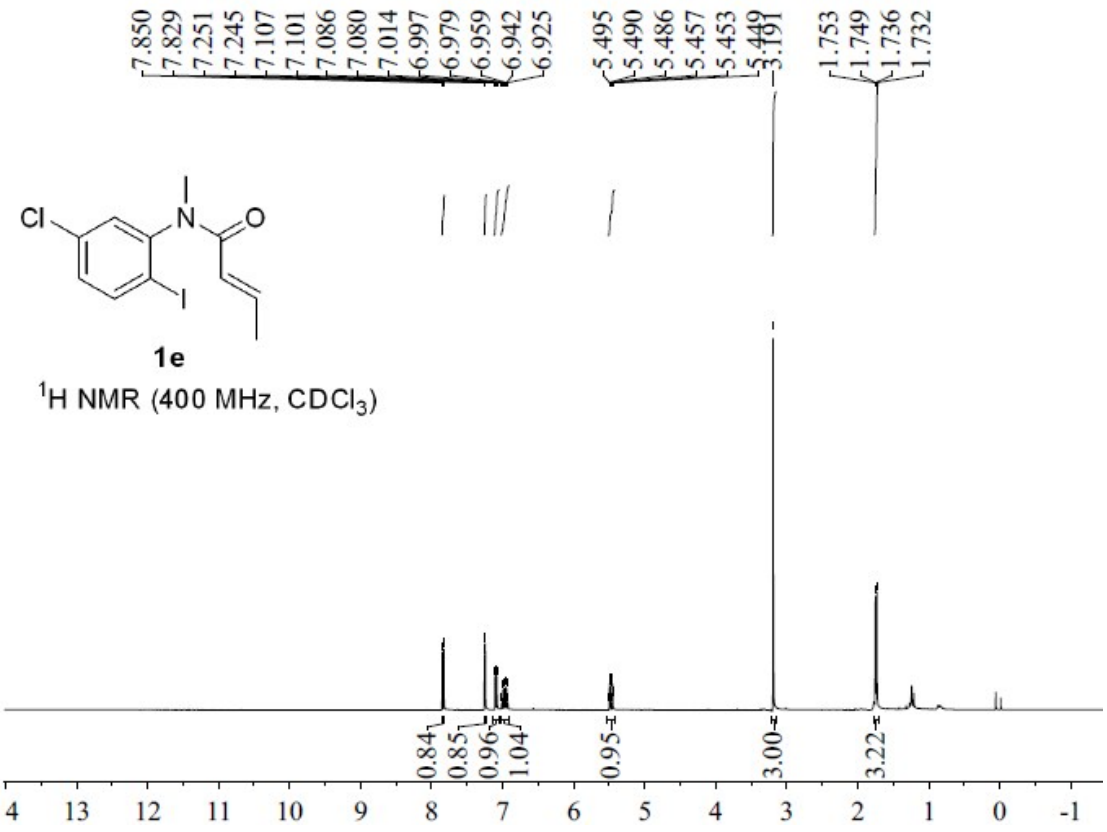




***N*-(5-bromo-2-iodophenyl)-*N*-methylbut-2-enamide (1d)**

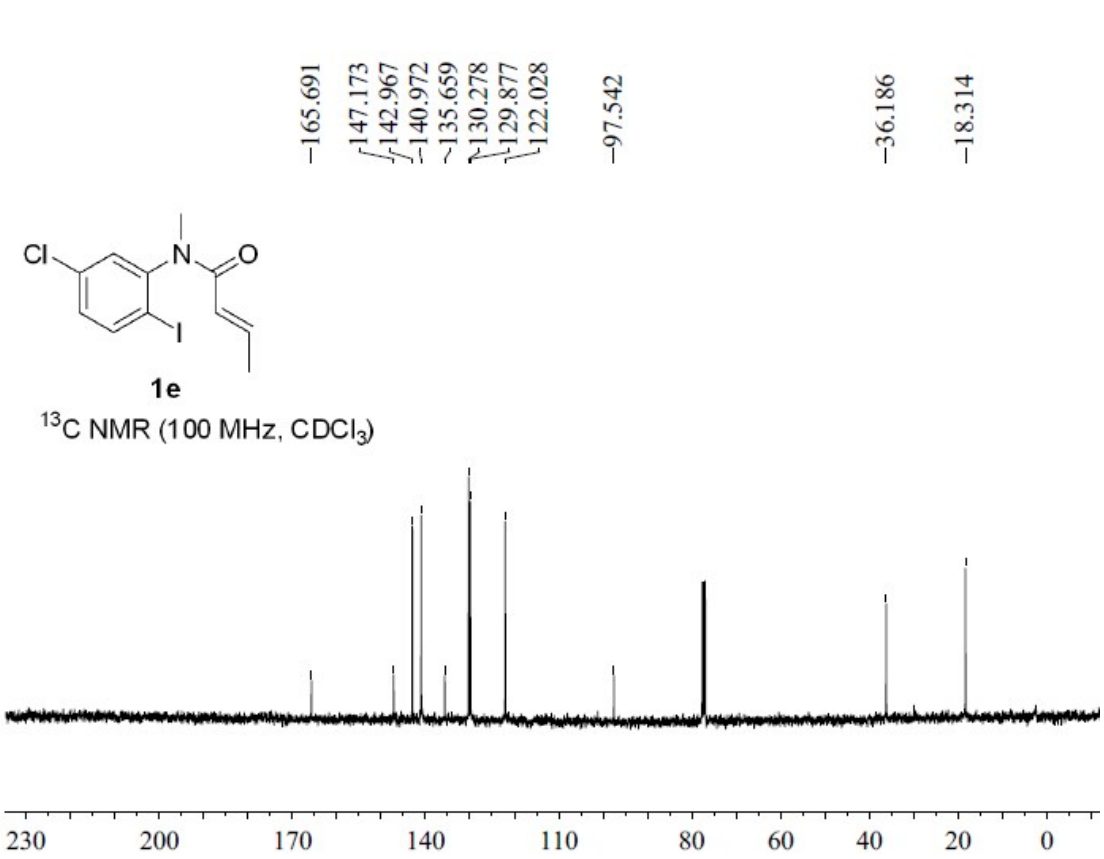


***N*-(4-chloro-2-iodophenyl)-*N*-methylbut-2-enamide (1e)**



1e

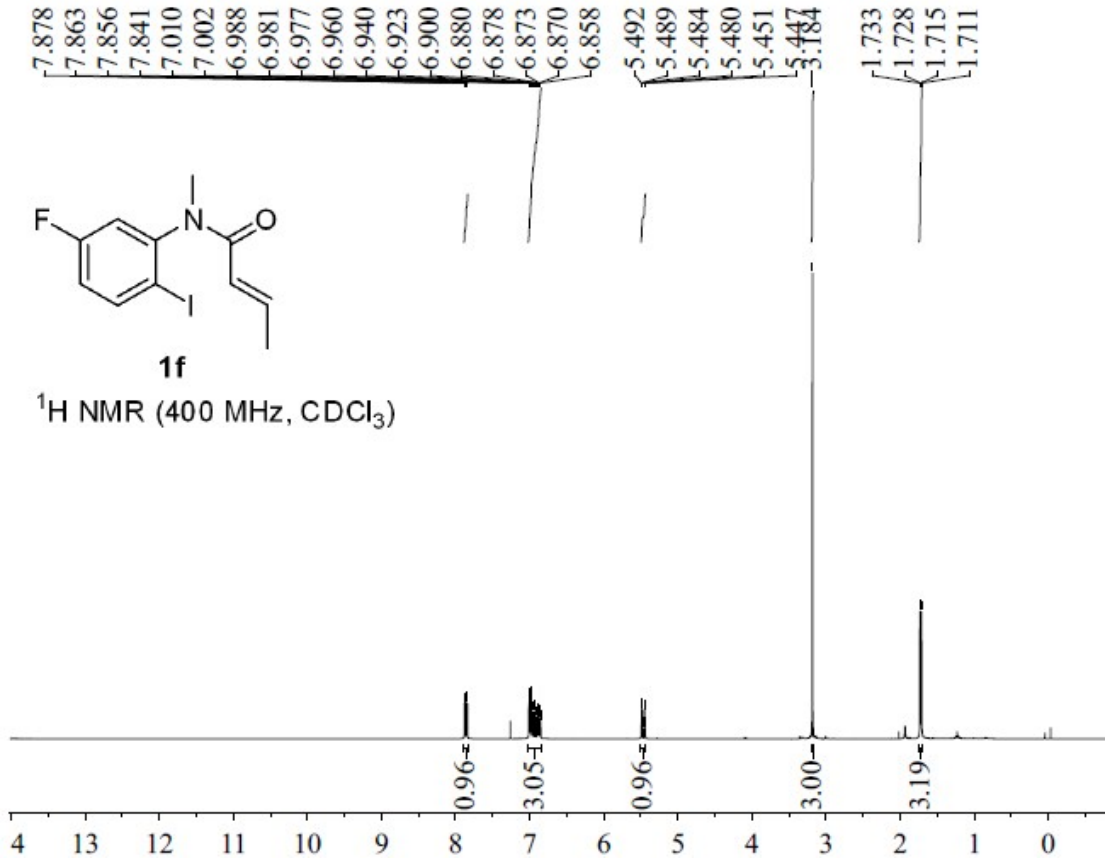
^{1}H NMR (400 MHz, $CDCl_3$)

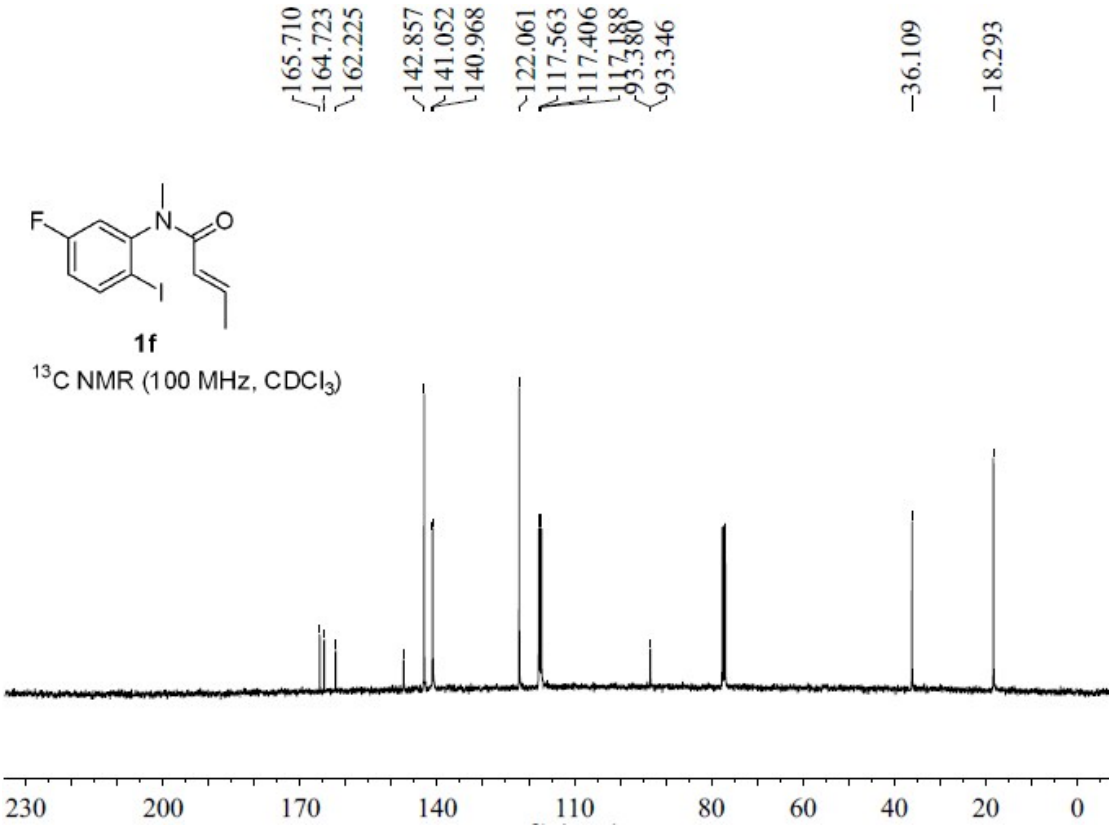


1e

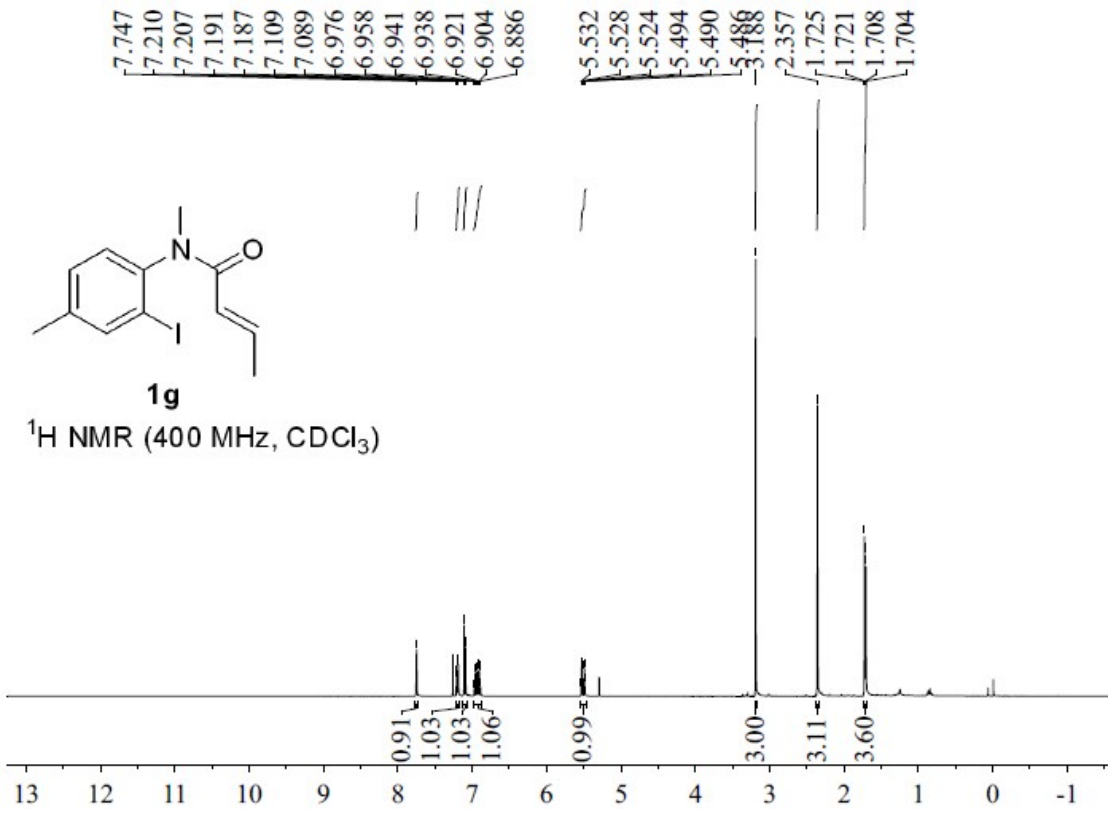
^{13}C NMR (100 MHz, $CDCl_3$)

***N*-(4-fluoro-2-iodophenyl)-*N*-methylbut-2-enamide (1f)**



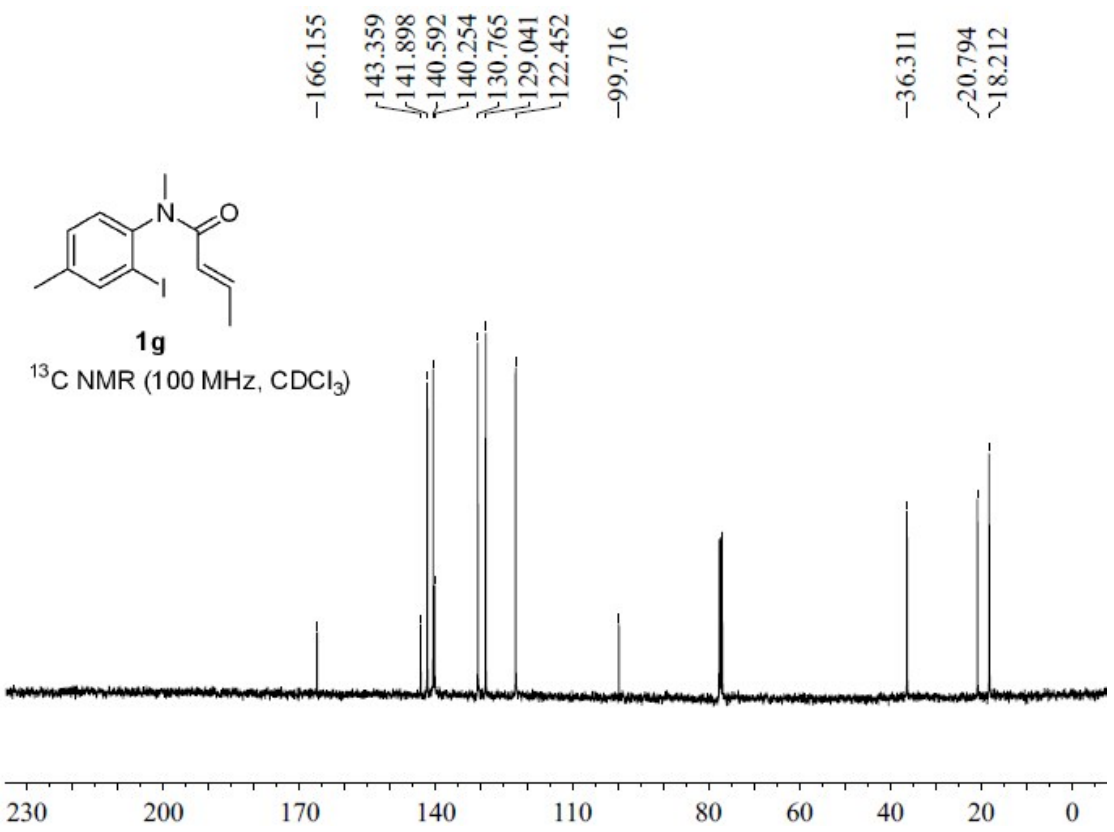


***N*-(2-iodo-5-methylphenyl)-*N*-methylbut-2-enamide (1g)**



1g

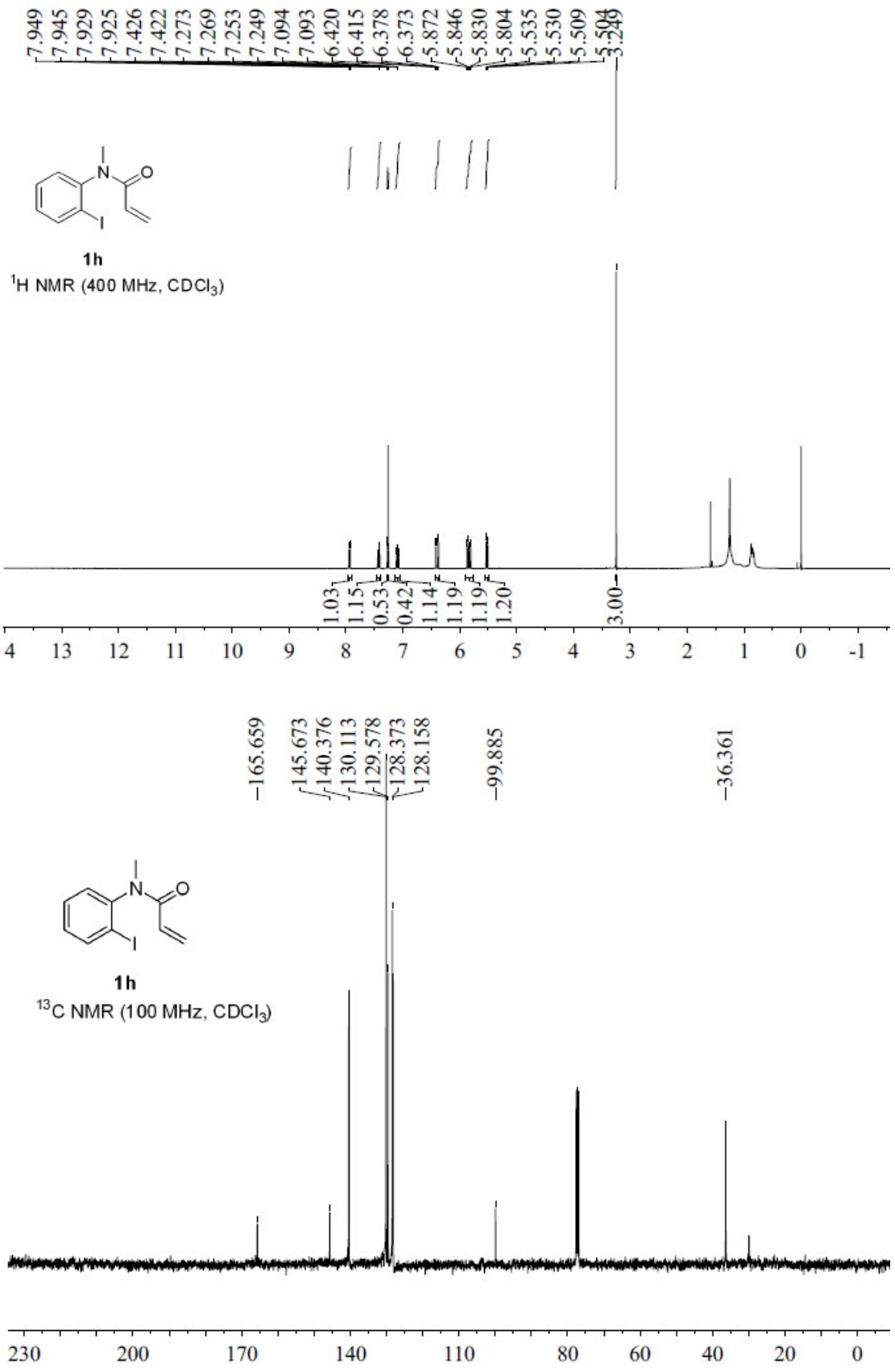
^{1}H NMR (400 MHz, $CDCl_3$)



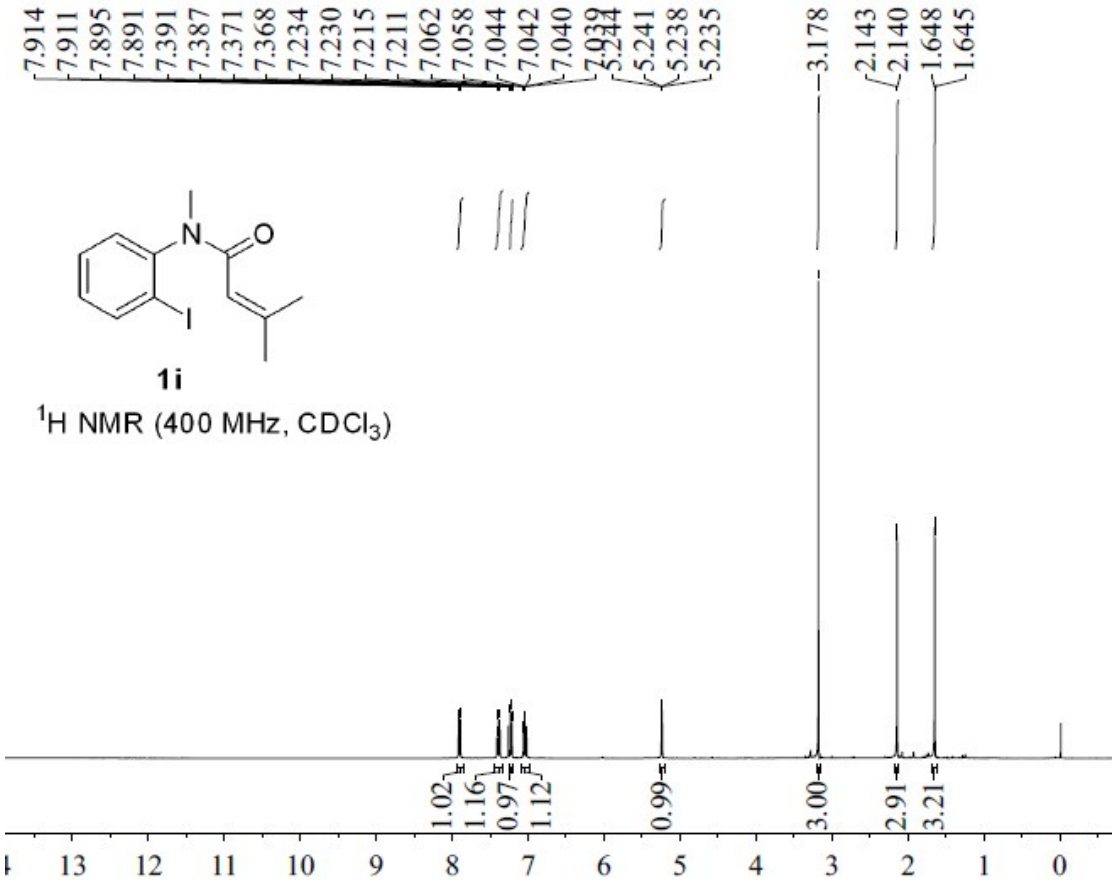
1g

^{13}C NMR (100 MHz, $CDCl_3$)

***N*-(2-iodophenyl)-*N*-methylacrylamide (1h)**

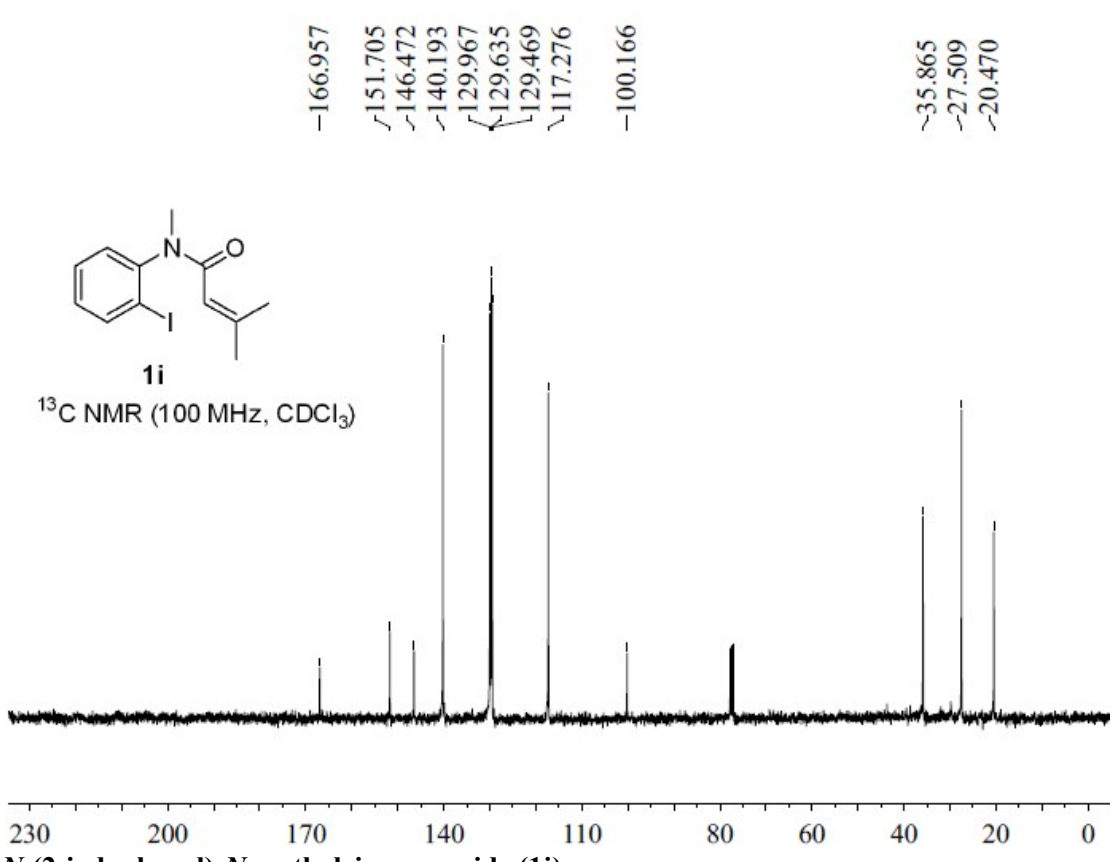


***N*-(2-iodophenyl)-*N*,3-dimethylbut-2-enamide (1i)**



1i

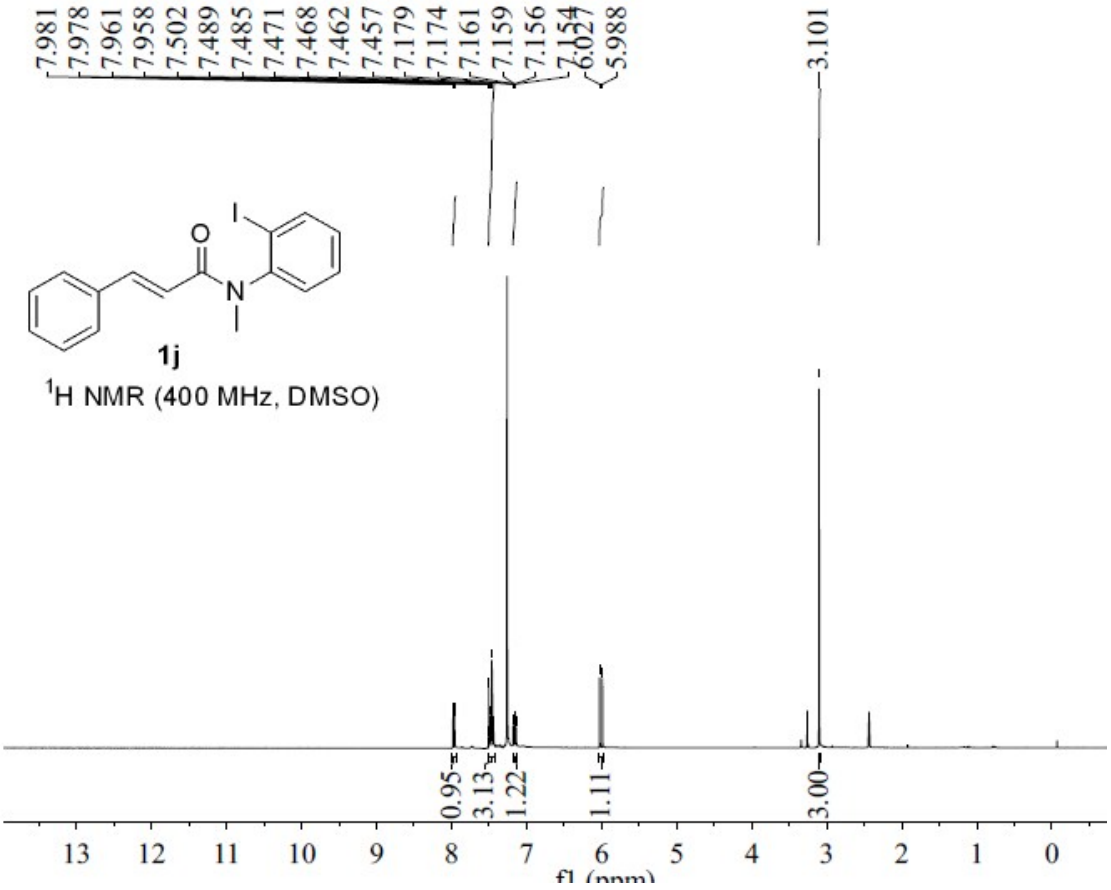
^{1}H NMR (400 MHz, $CDCl_3$)



1i

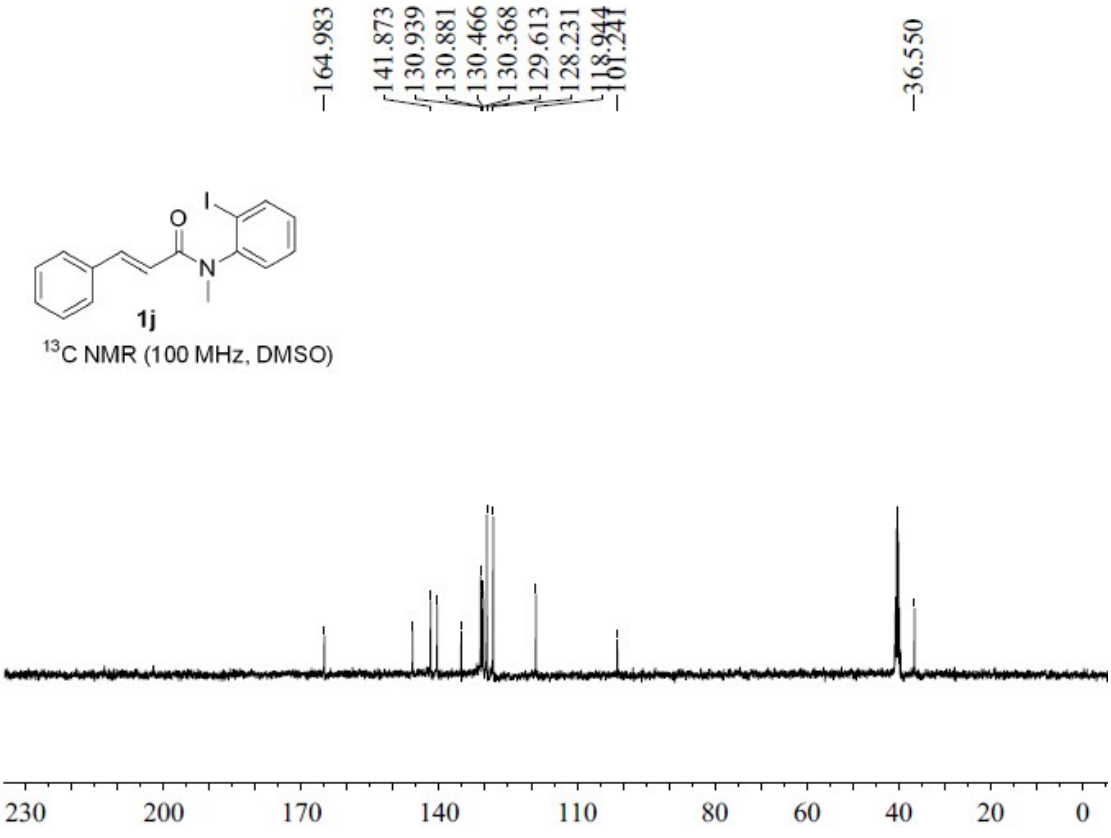
^{13}C NMR (100 MHz, $CDCl_3$)

***N*-(2-iodophenyl)-*N*-methylcinnamamide (1j)**



1j

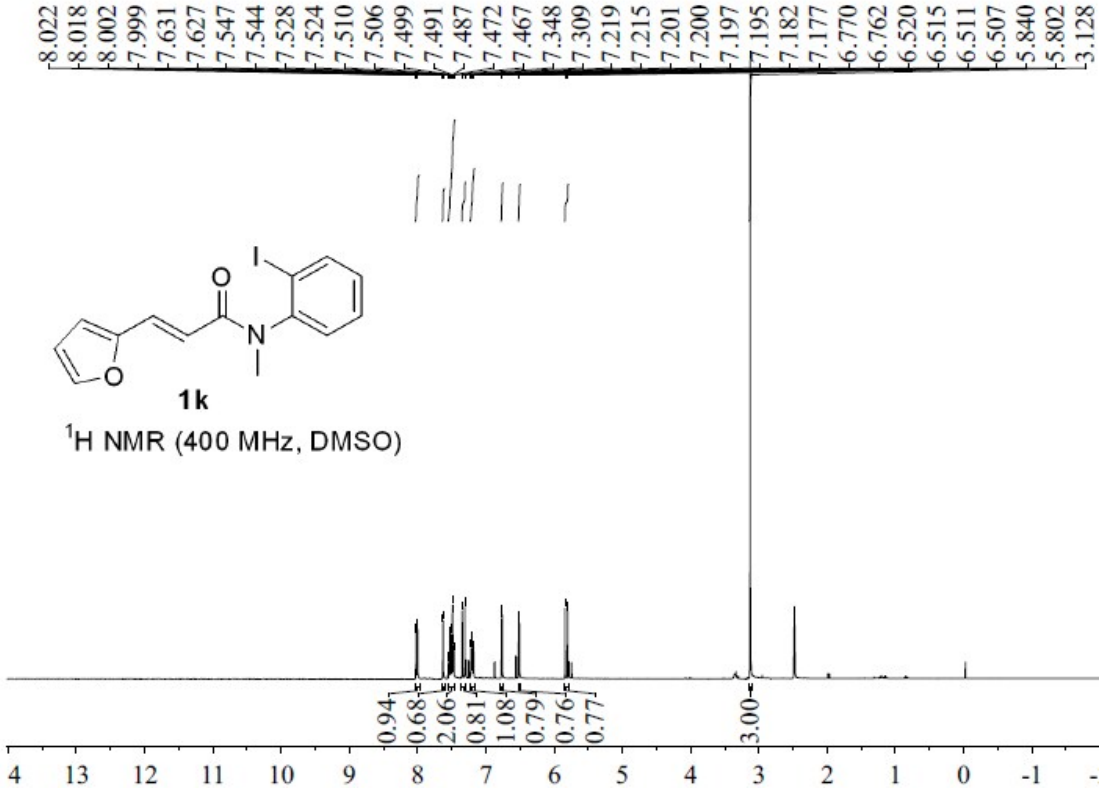
^{1}H NMR (400 MHz, DMSO)



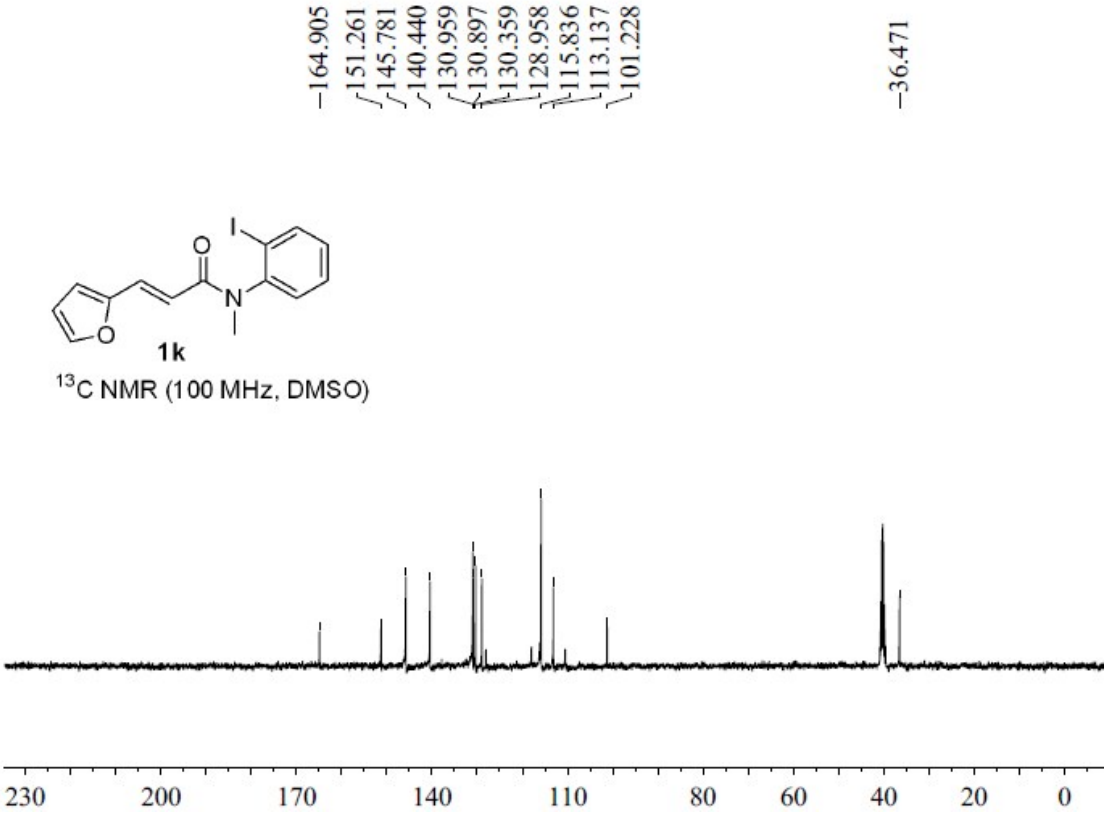
1j

^{13}C NMR (100 MHz, DMSO)

3-(Furan-2-yl)-*N*-(2-iodophenyl)-*N*-methylacrylamide (1k)

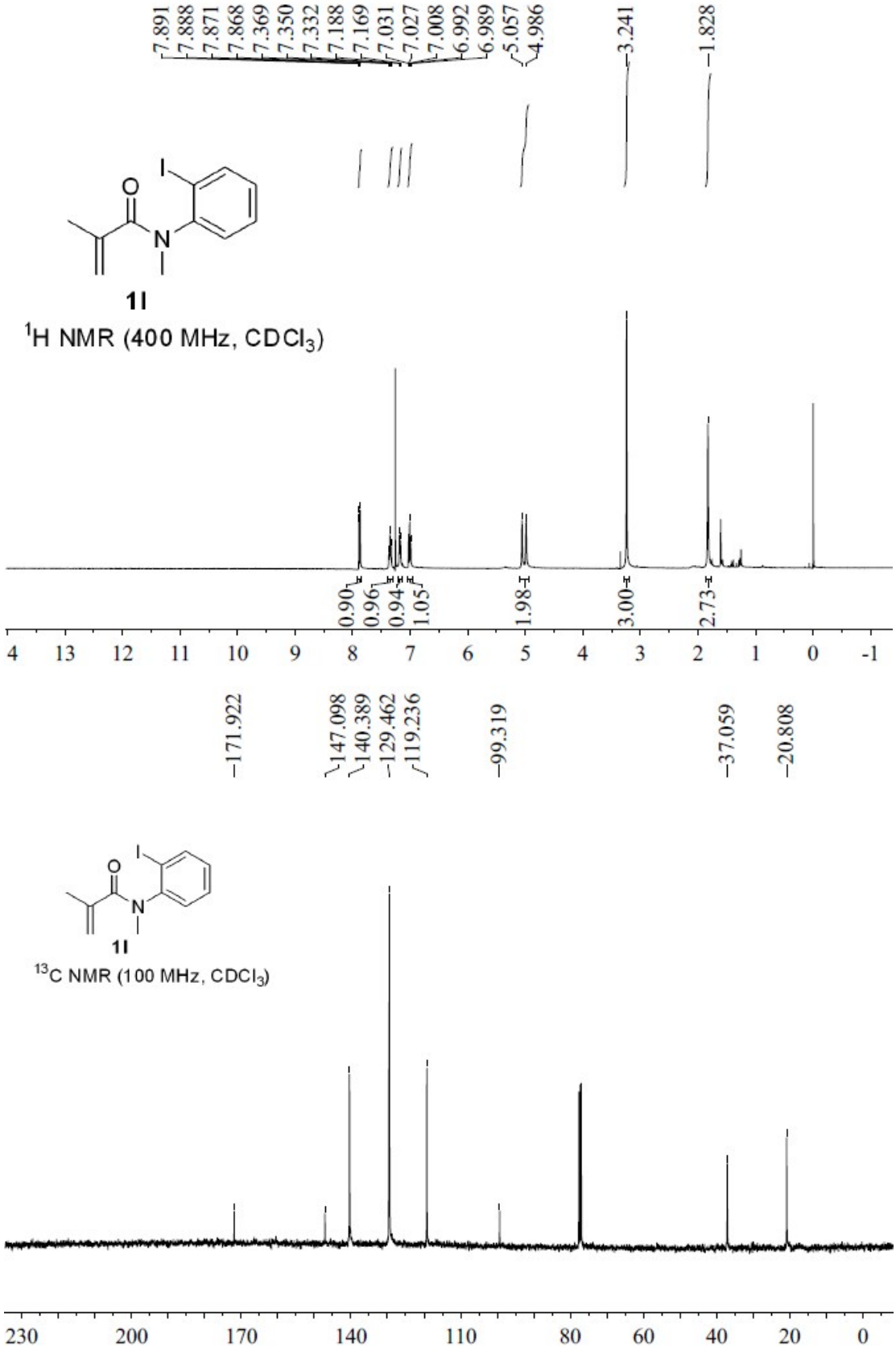


^{1}H NMR (400 MHz, DMSO)

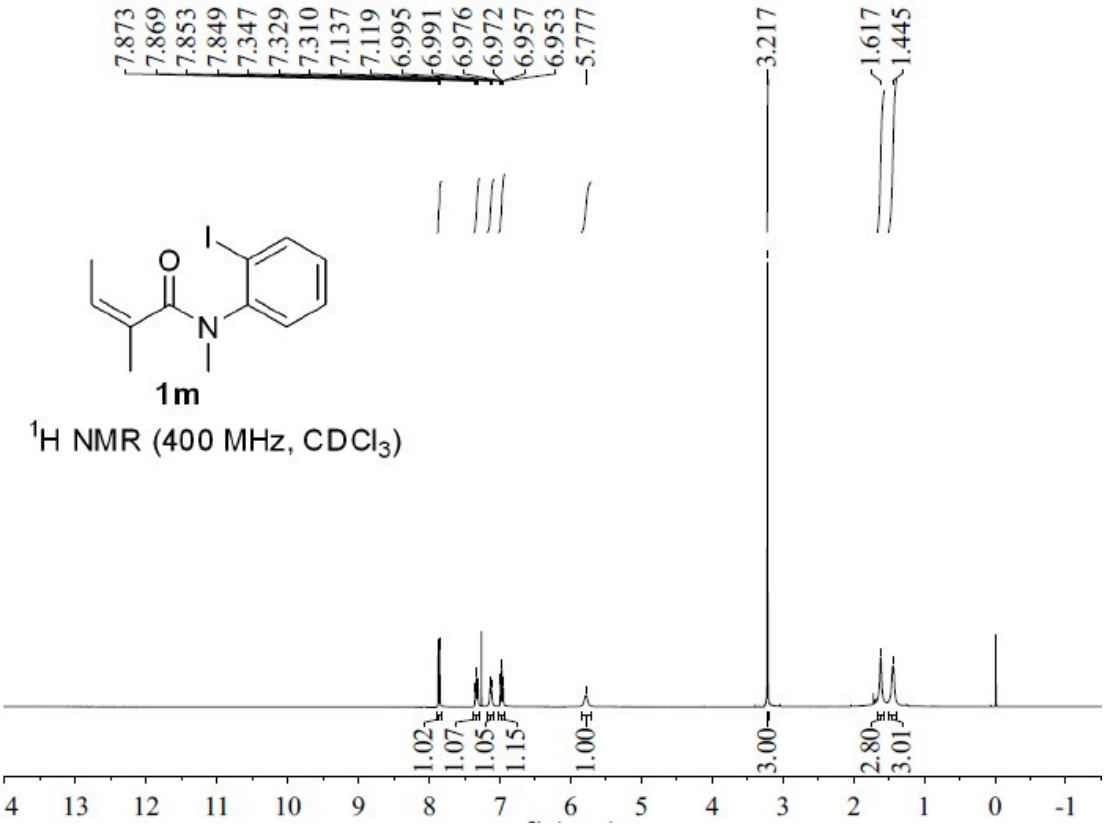


^{13}C NMR (100 MHz, DMSO)

***N*-(2-iodophenyl)-*N*-methylmethacrylamide (1l)**

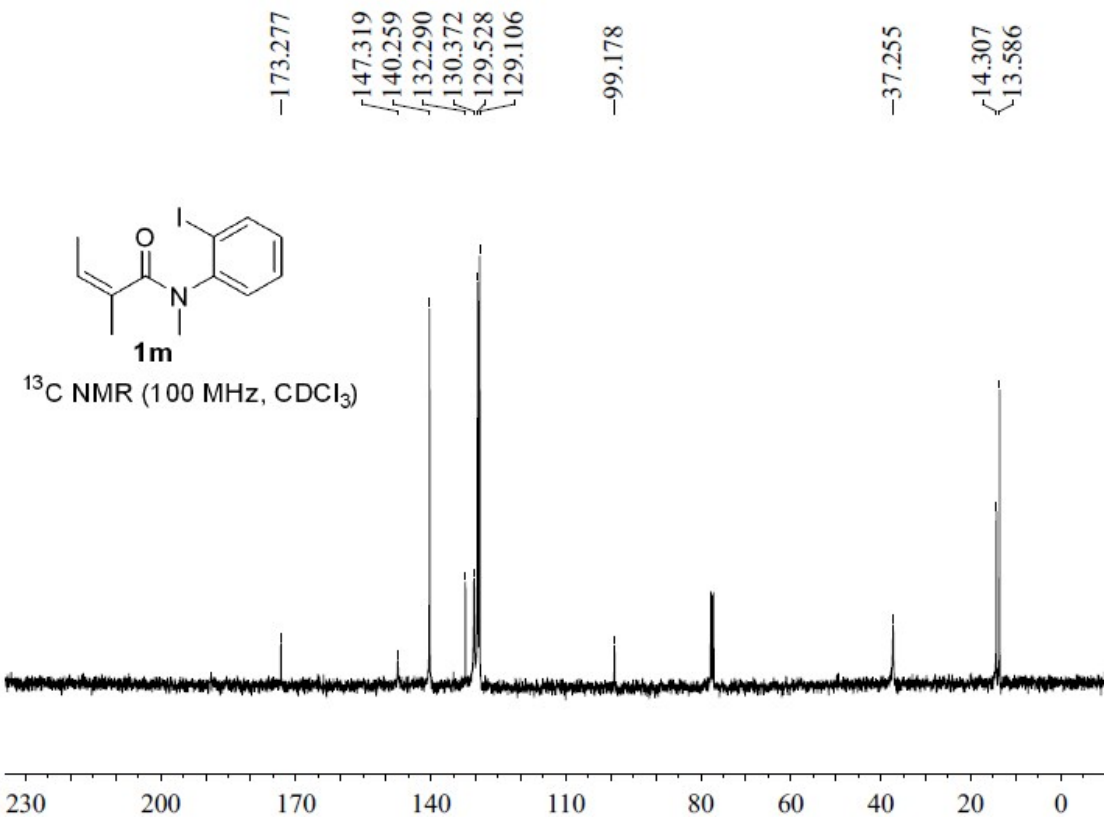


***N*-(2-iodophenyl)-*N*,2-dimethylbut-2-enamide (1m)**



1m

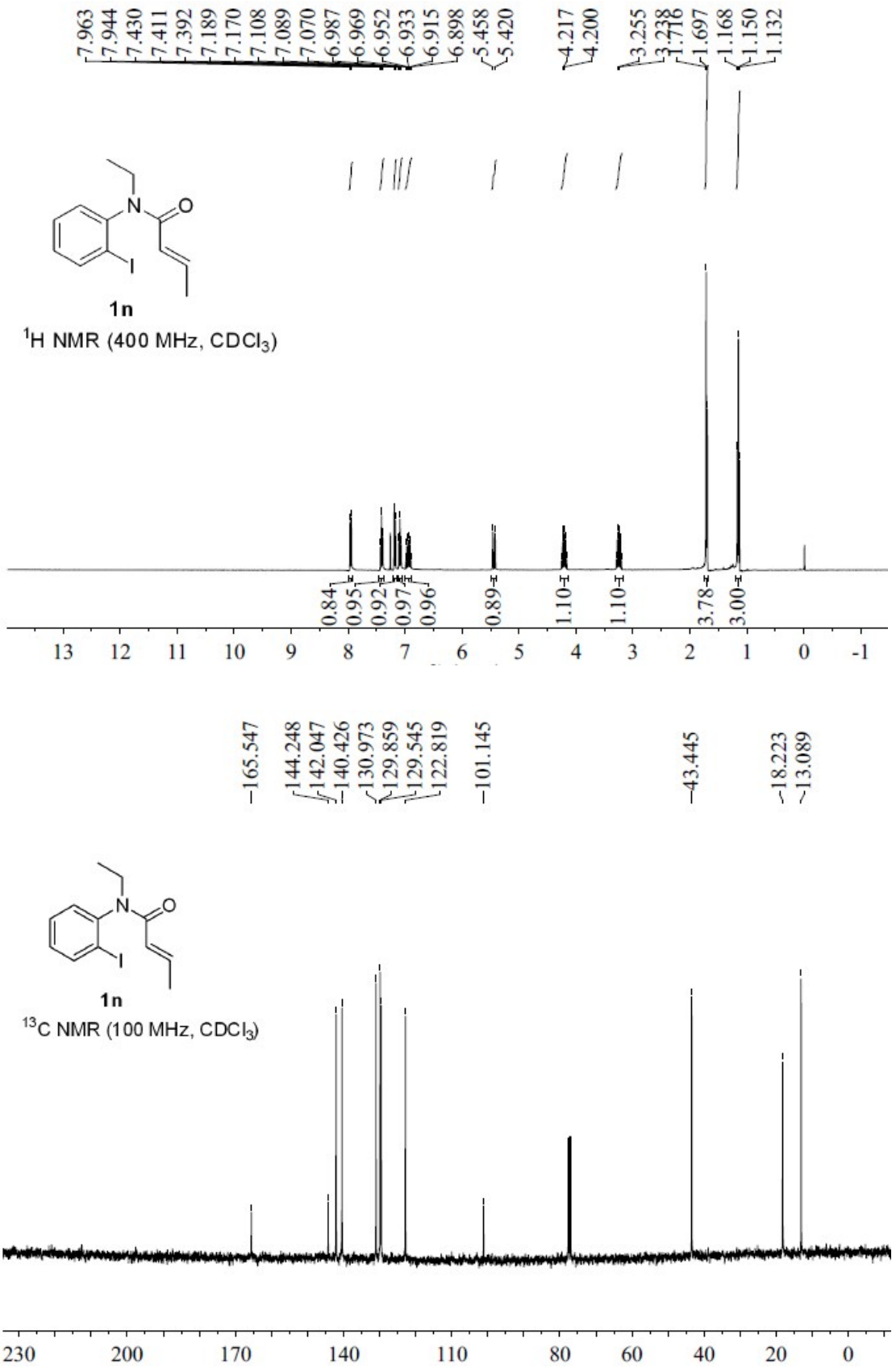
^{1}H NMR (400 MHz, $CDCl_3$)



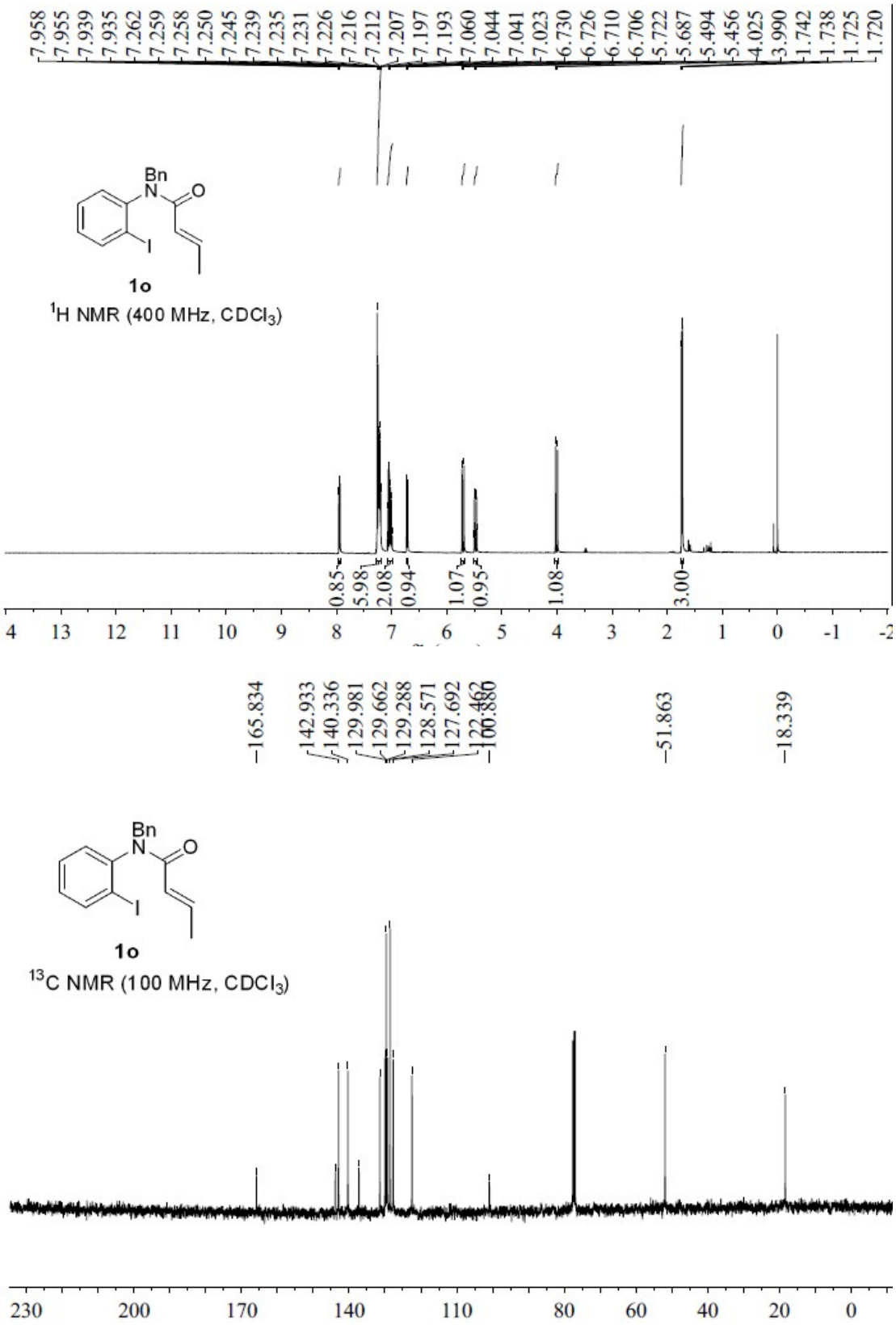
1m

^{13}C NMR (100 MHz, $CDCl_3$)

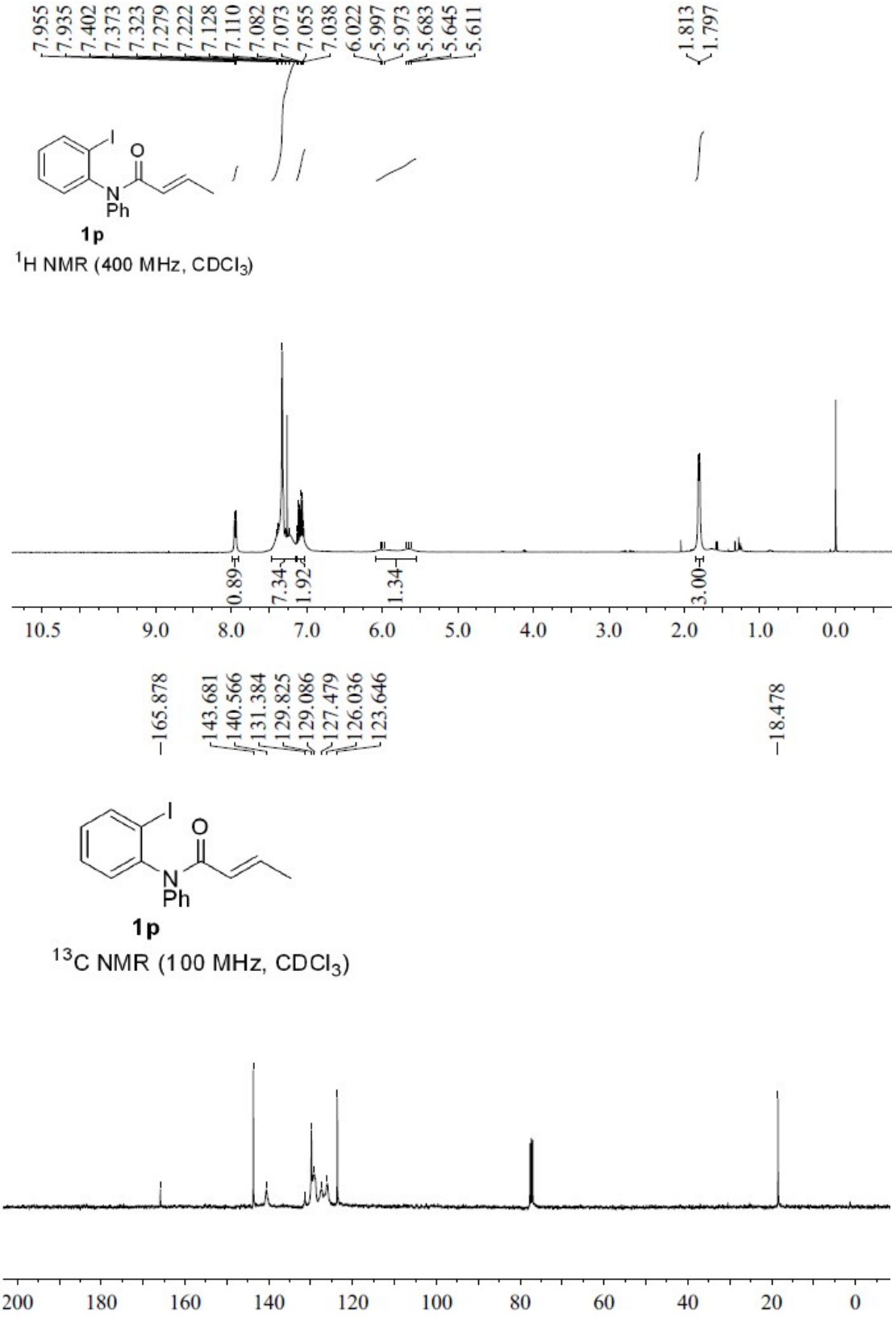
***N*-ethyl-*N*-(2-iodophenyl)but-2-enamide (1n)**



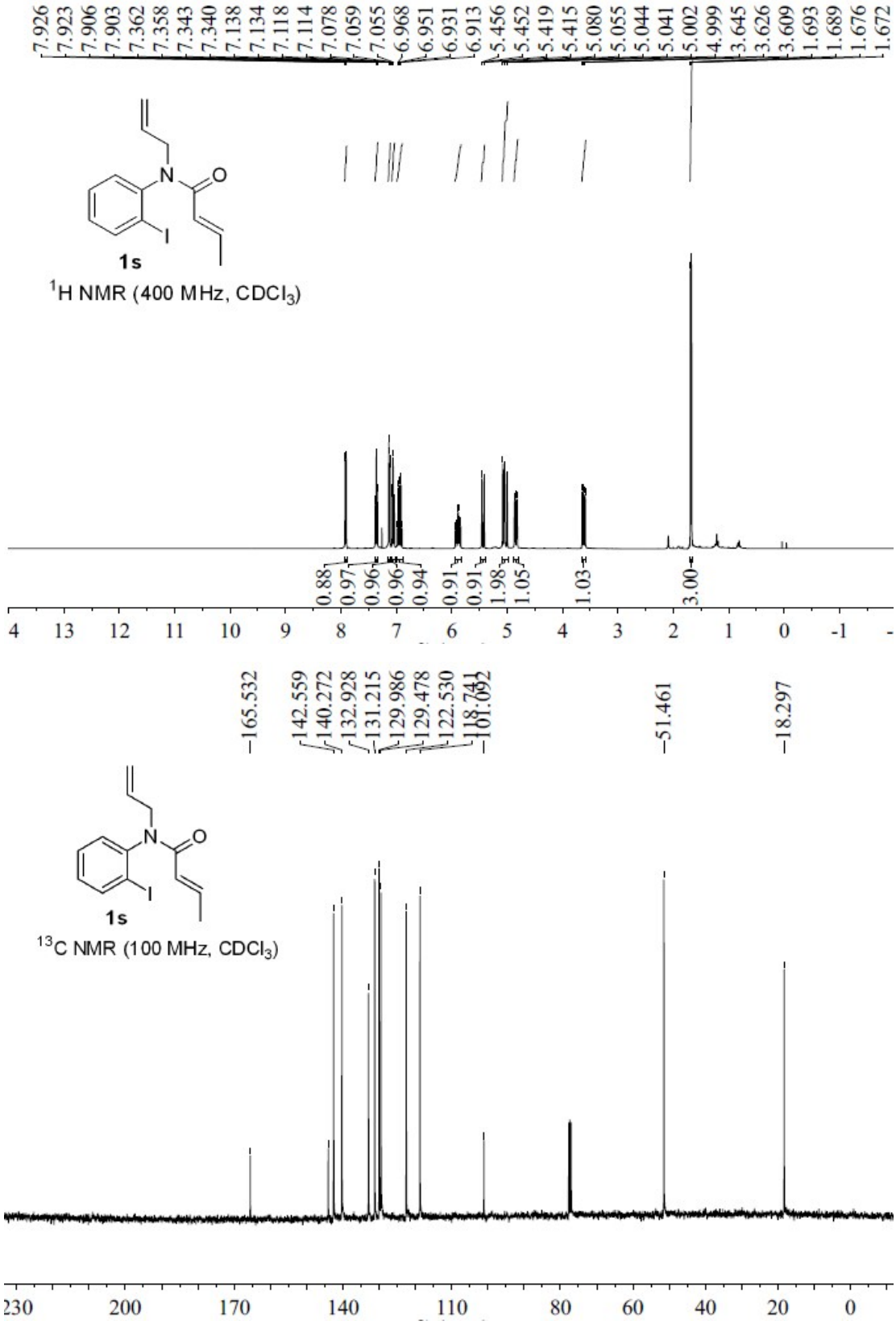
***N*-benzyl-*N*-(2-iodophenyl)but-2-enamide (1o)**



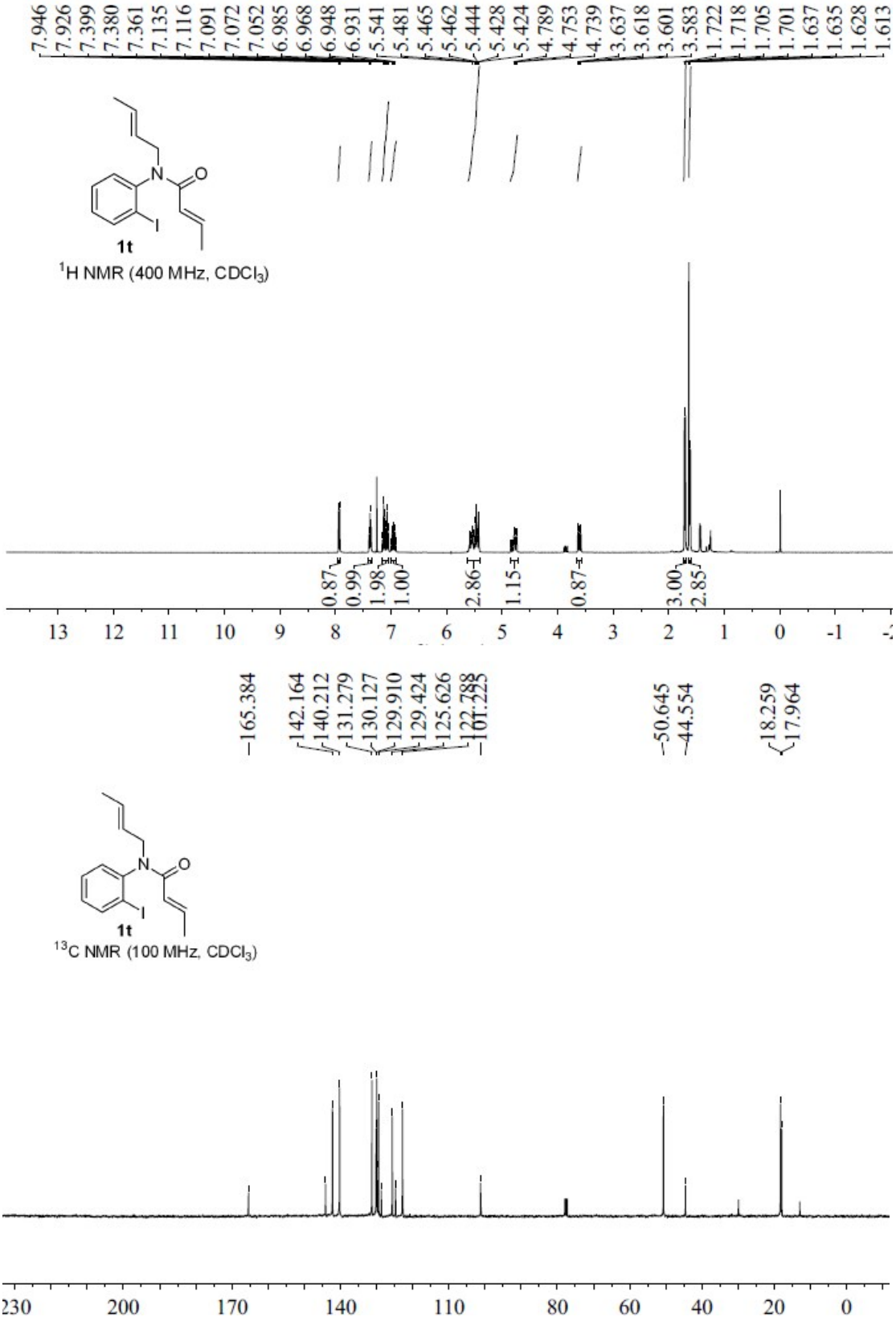
***N*-(2-iodophenyl)-*N*-phenylbut-2-enamide (1p)**



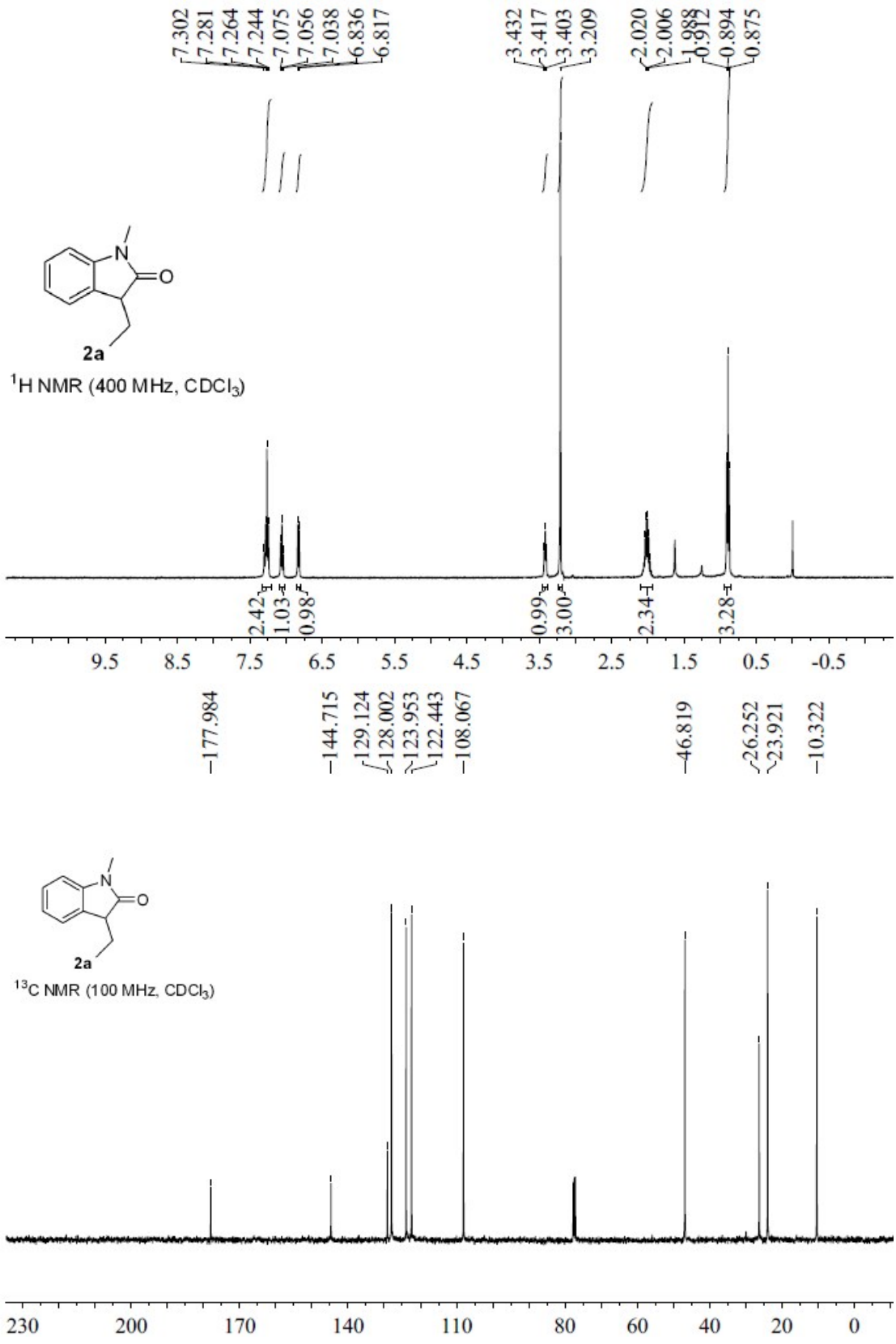
***N*-allyl-*N*-(2-iodophenyl)but-2-enamide (1s)**



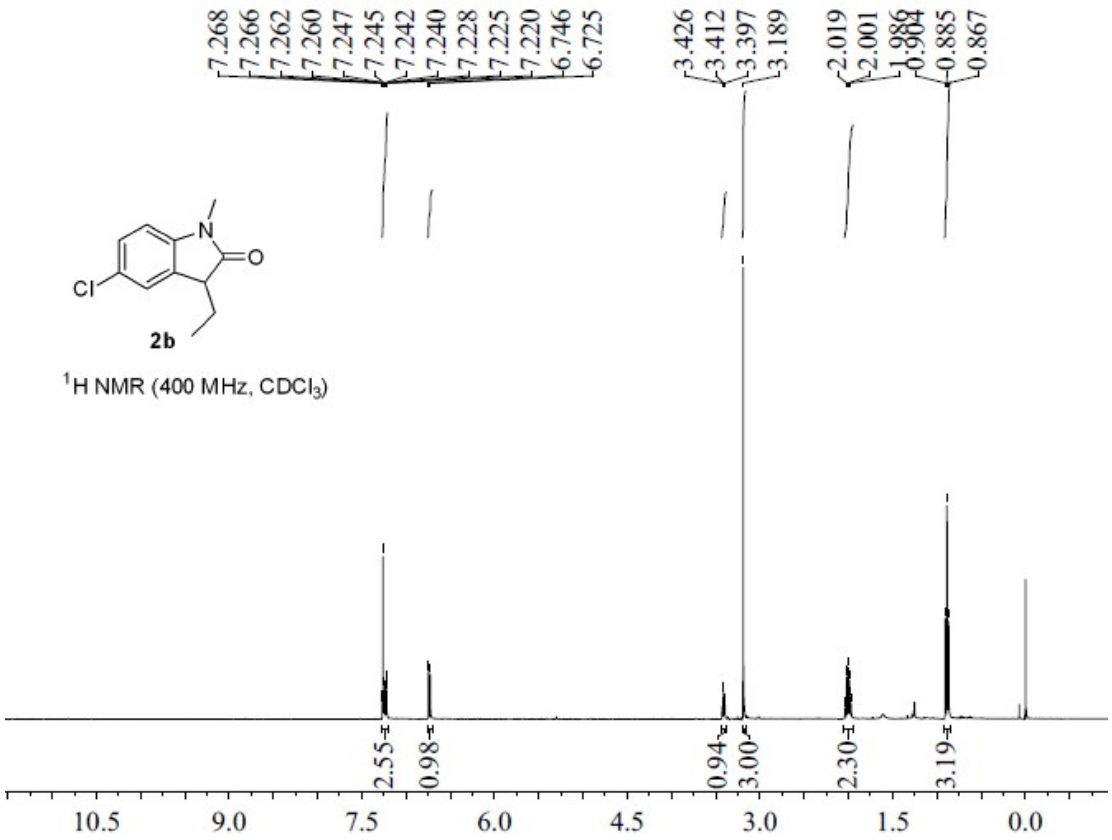
***N*-(but-2-en-1-yl)-*N*-(2-iodophenyl)but-2-enamide (1t)**

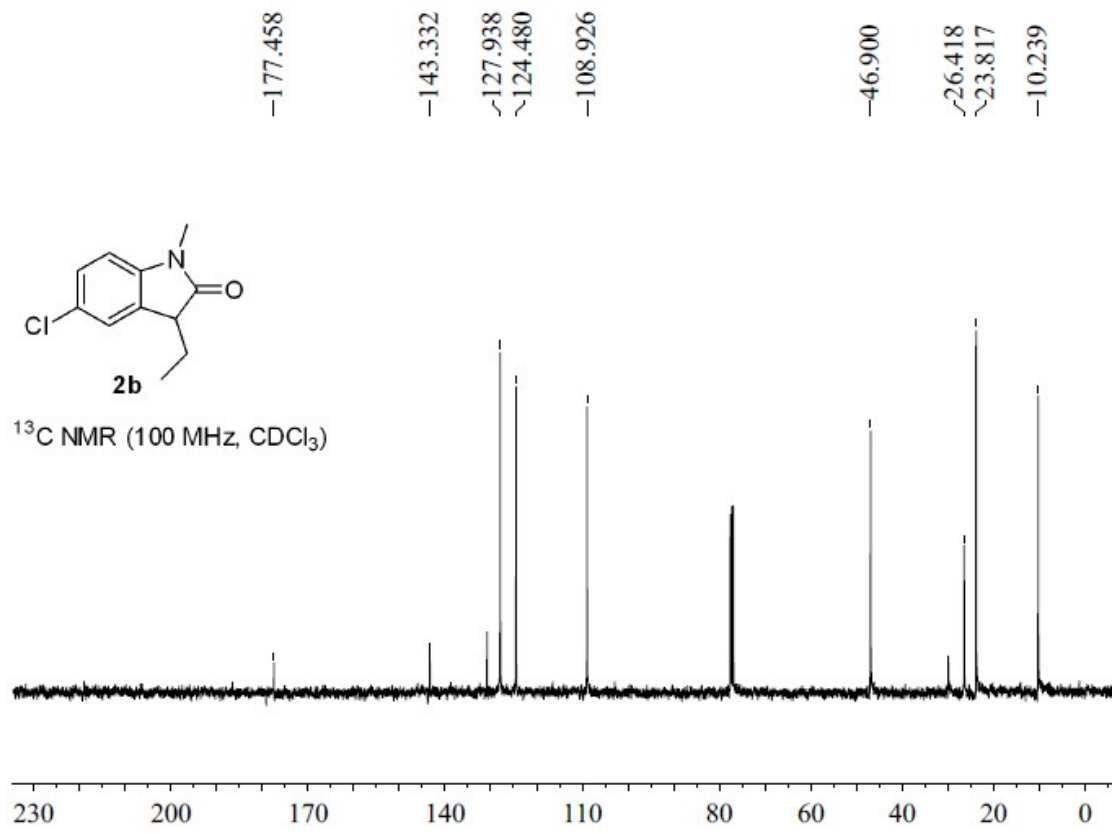


3-Ethyl-1-methylindolin-2-one (2a)

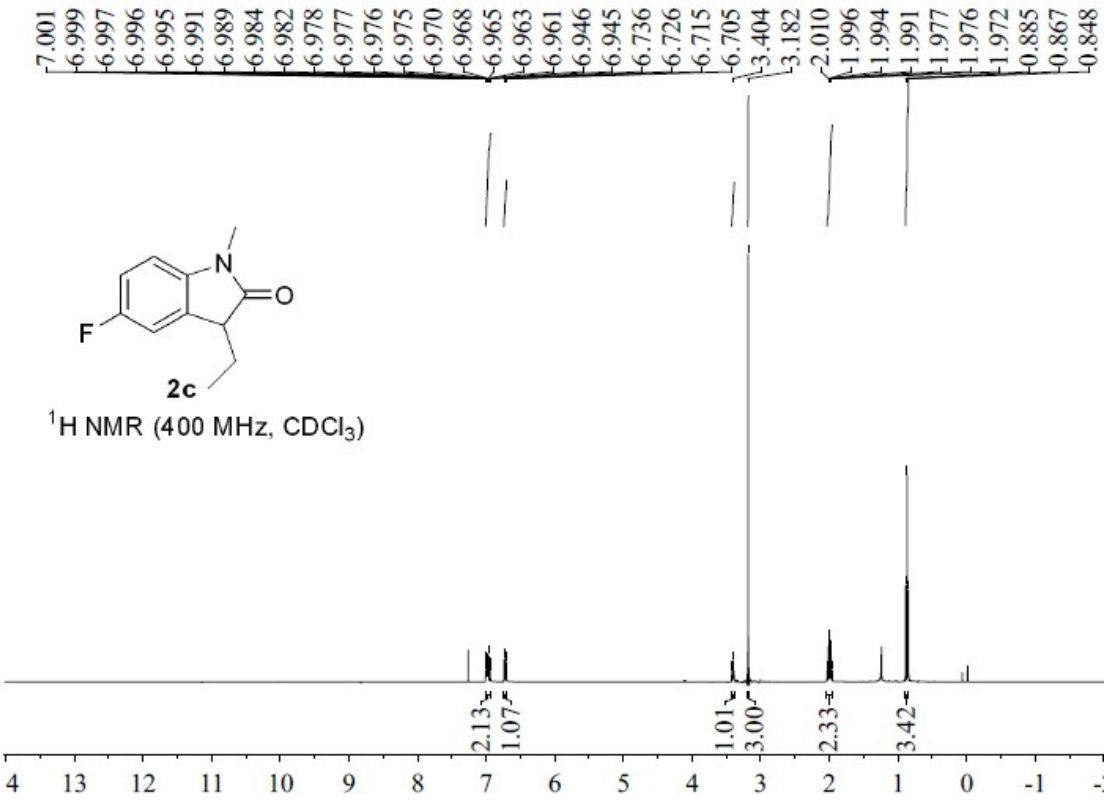


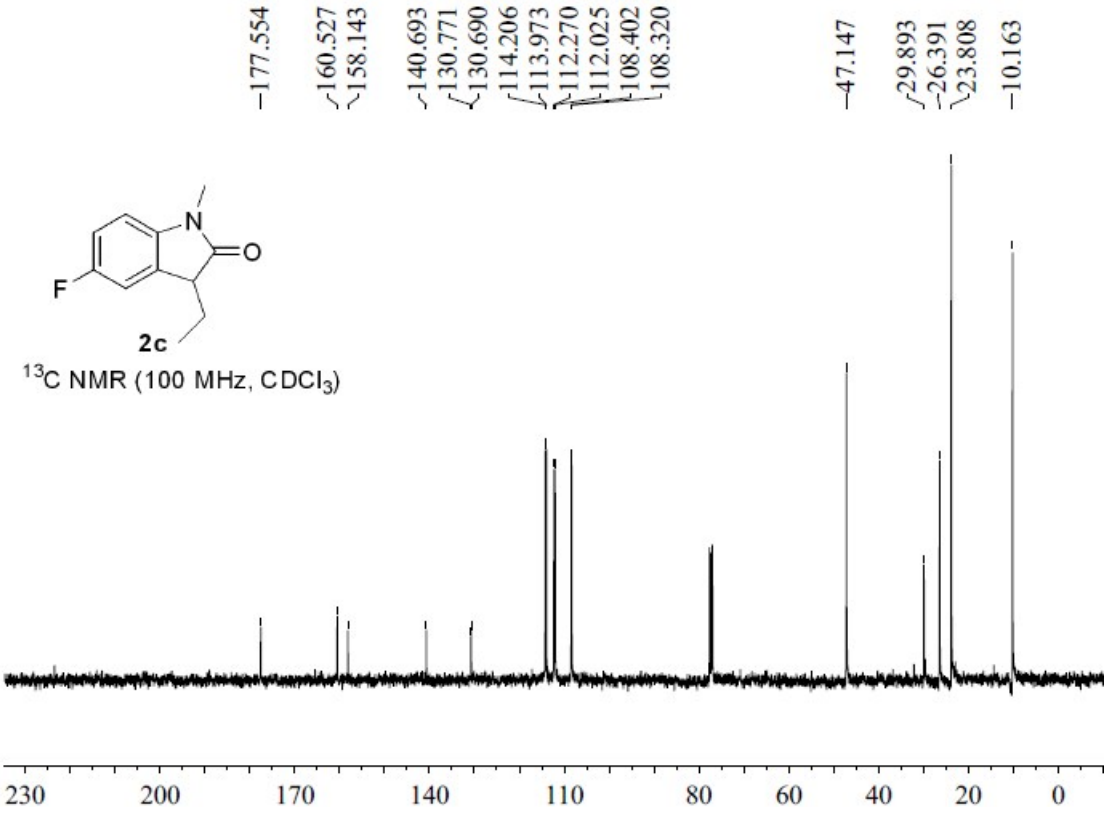
5-Chloro-3-ethyl-1-methylindolin-2-one (2b)



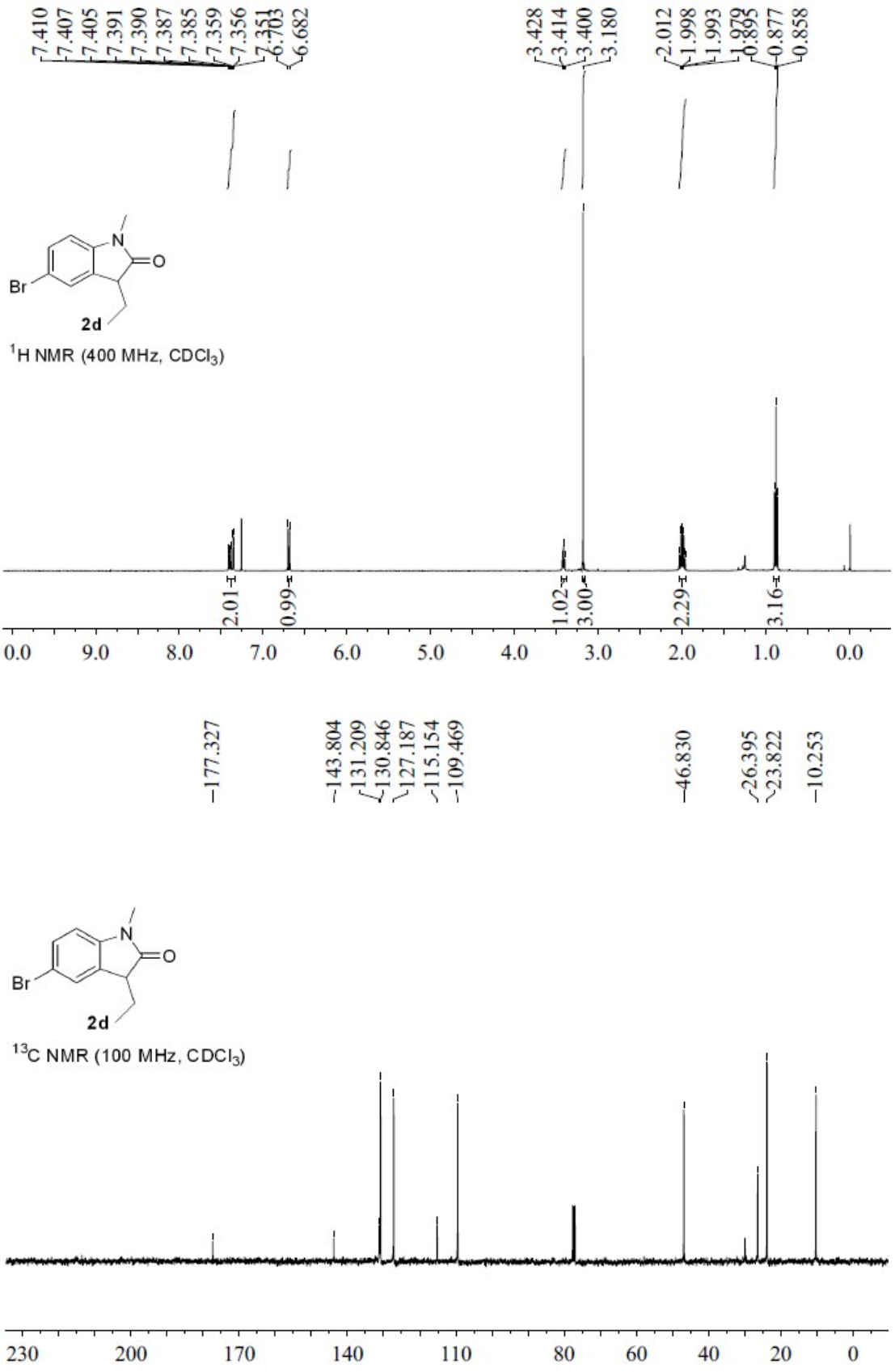


3-Ethyl-5-fluoro-1-methylindolin-2-one (2c)

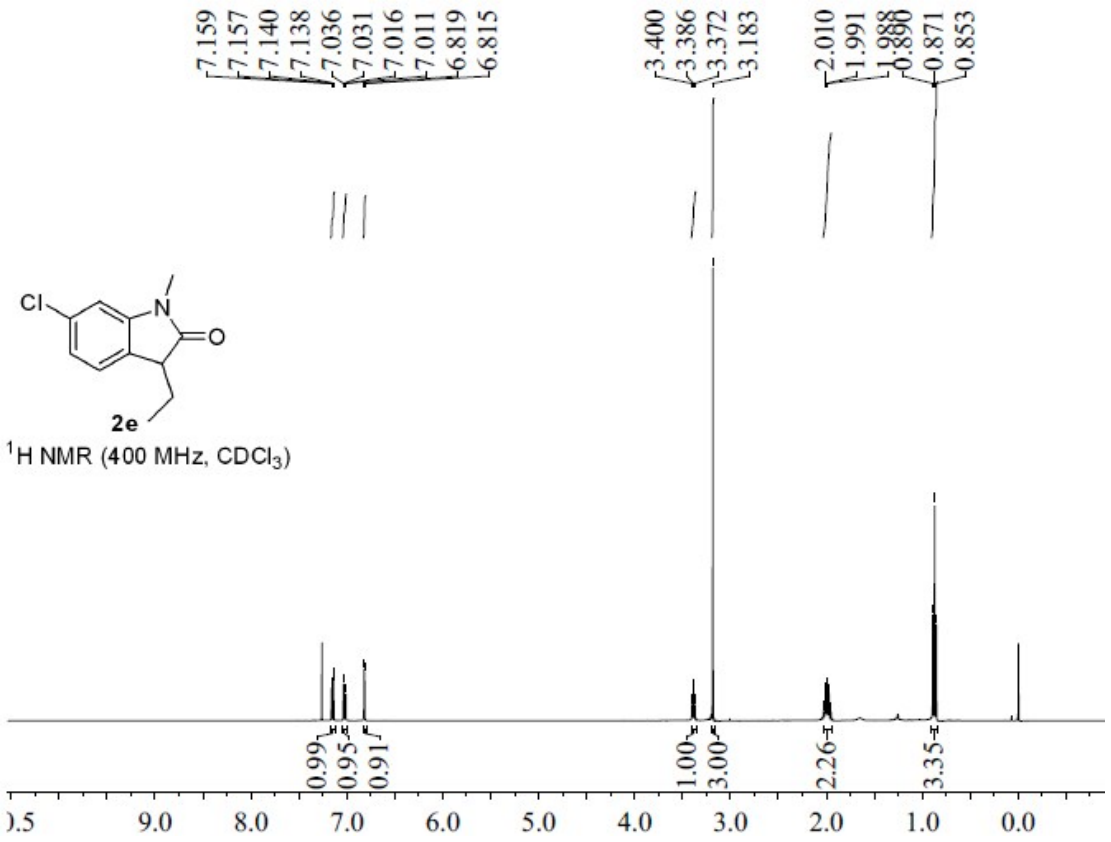


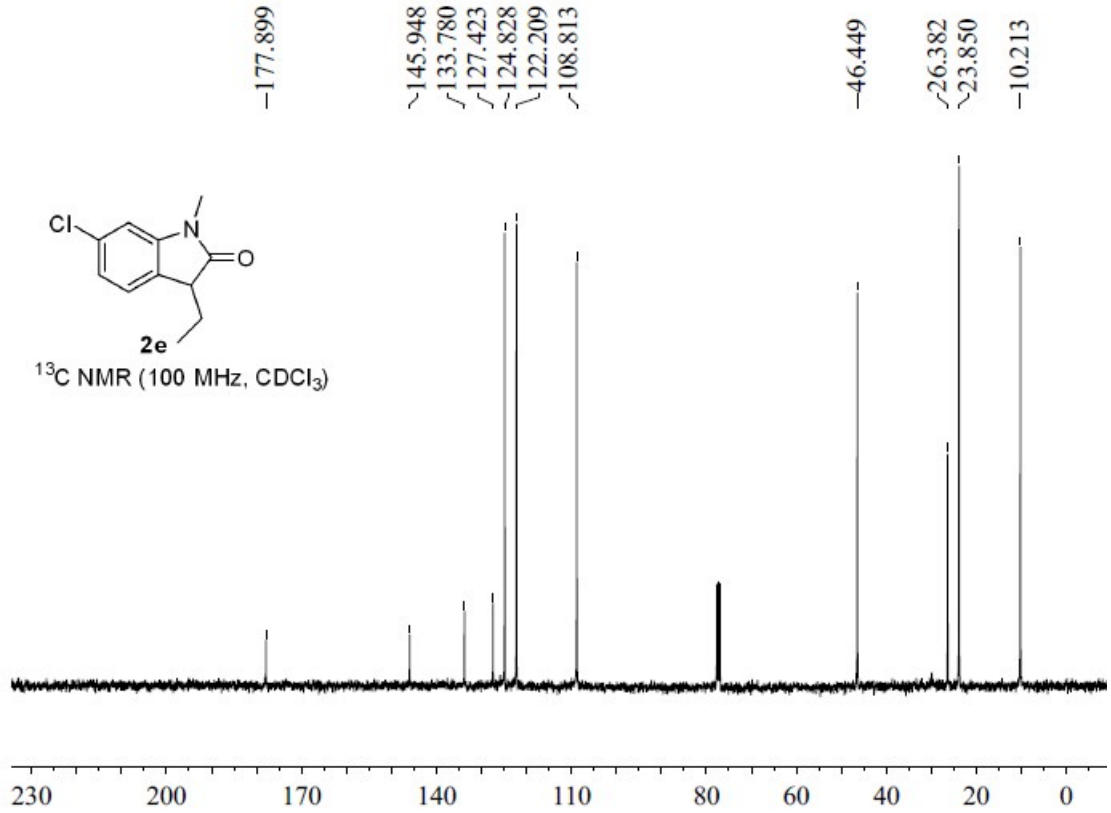


5-Bromo-3-ethyl-1-methylindolin-2-one (2d)

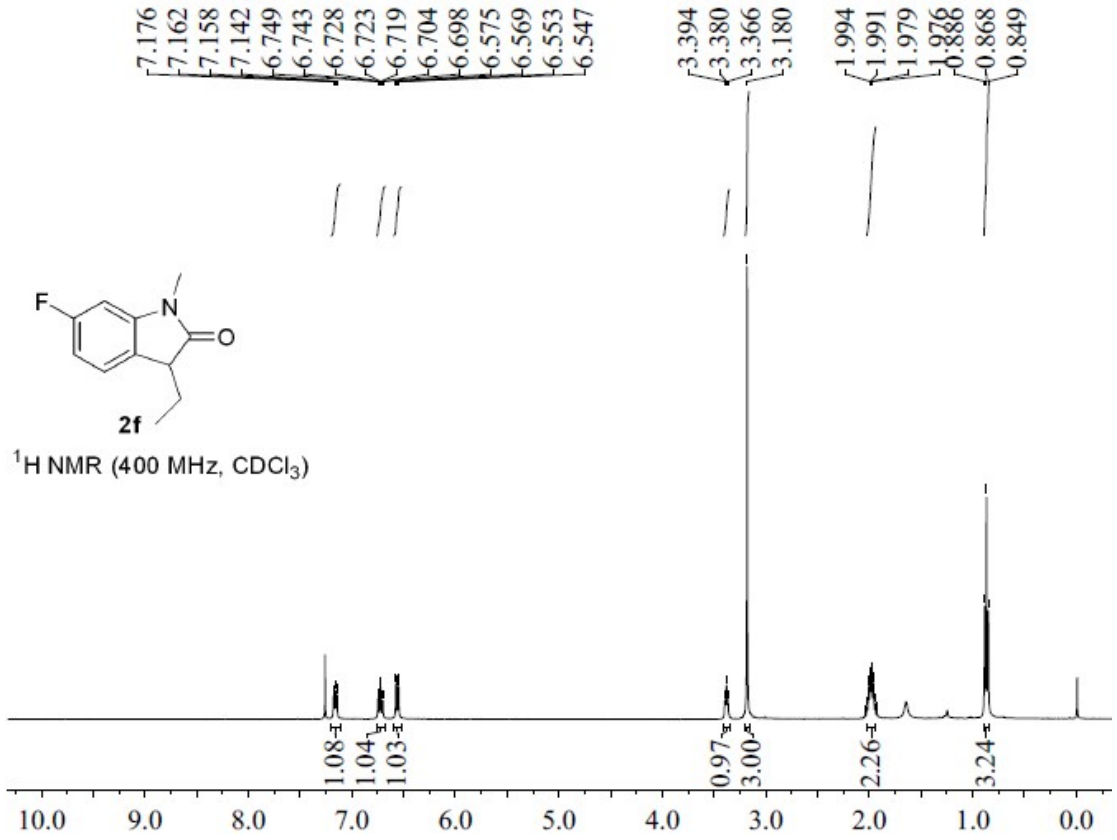


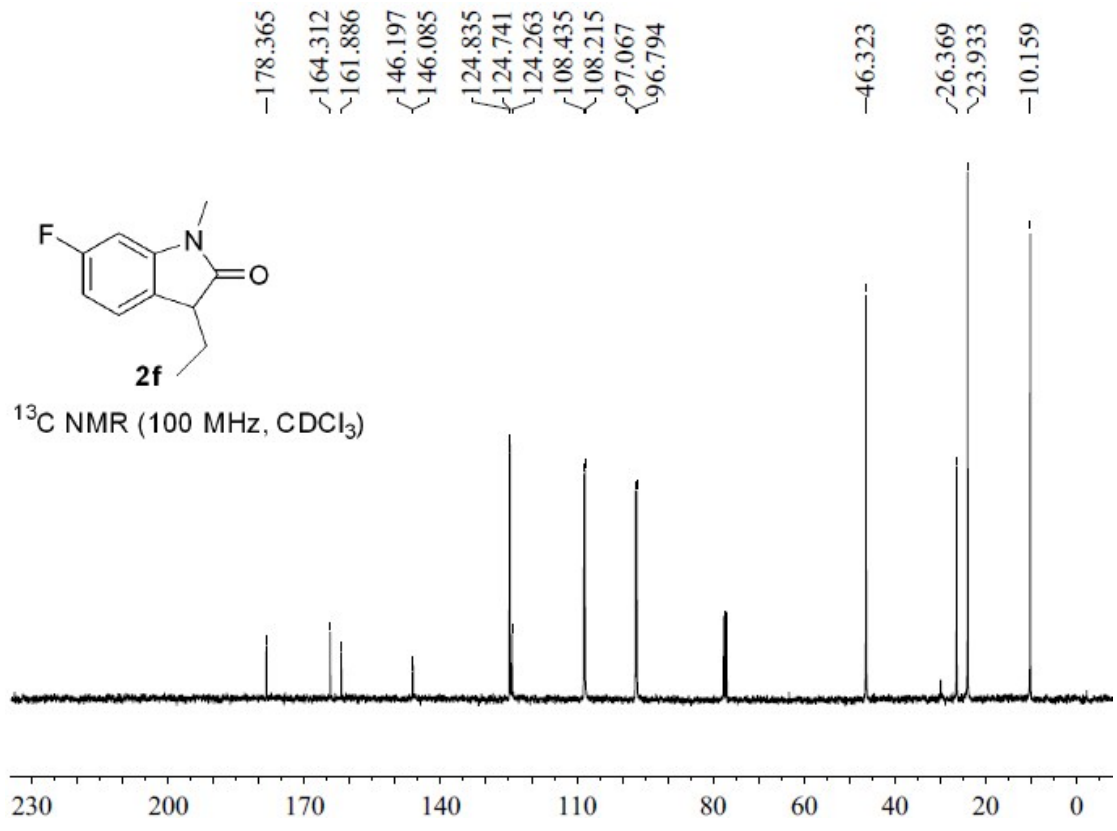
6-Chloro-3-ethyl-1-methylindolin-2-one (2e)



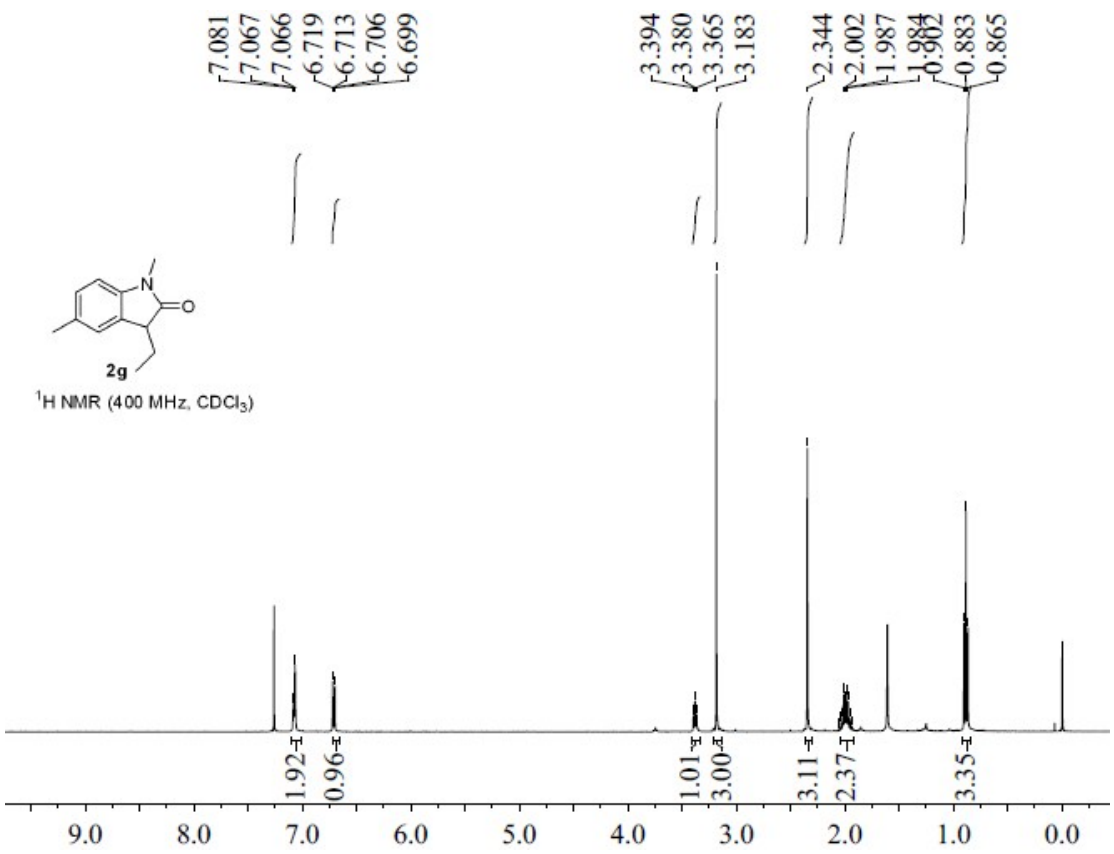


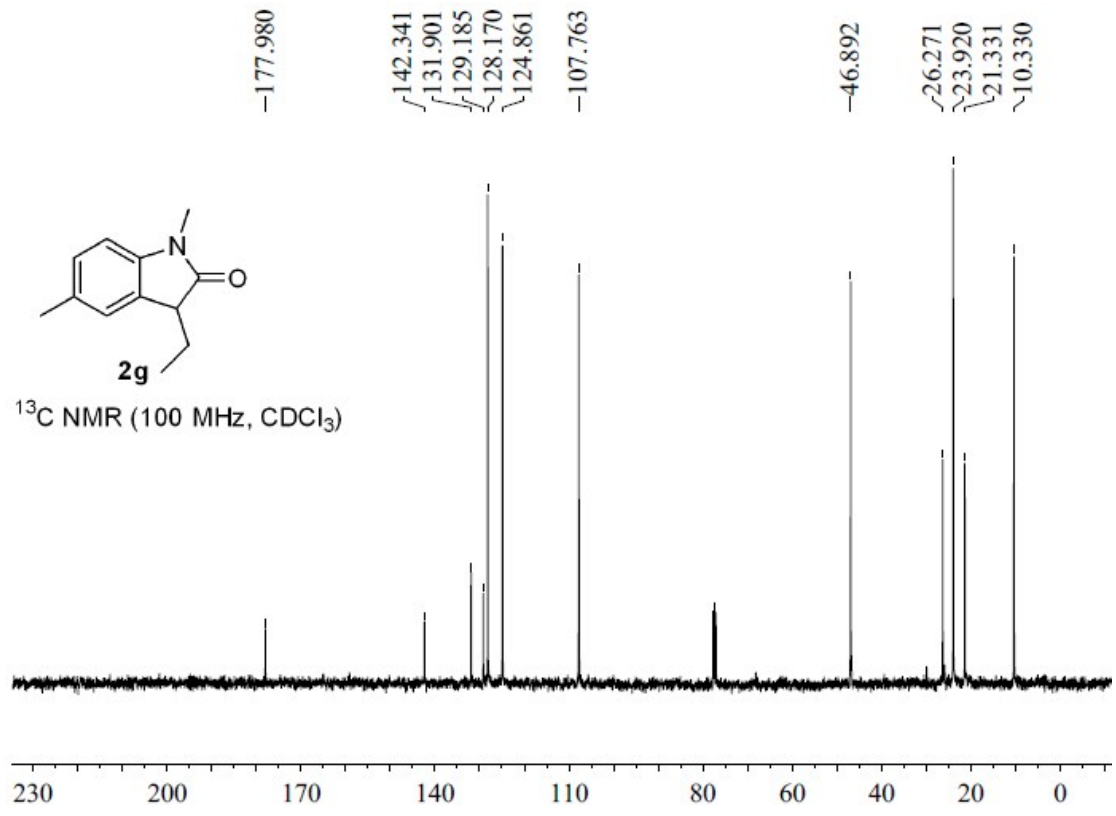
3-Ethyl-6-fluoro-1-methylindolin-2-one (2f)



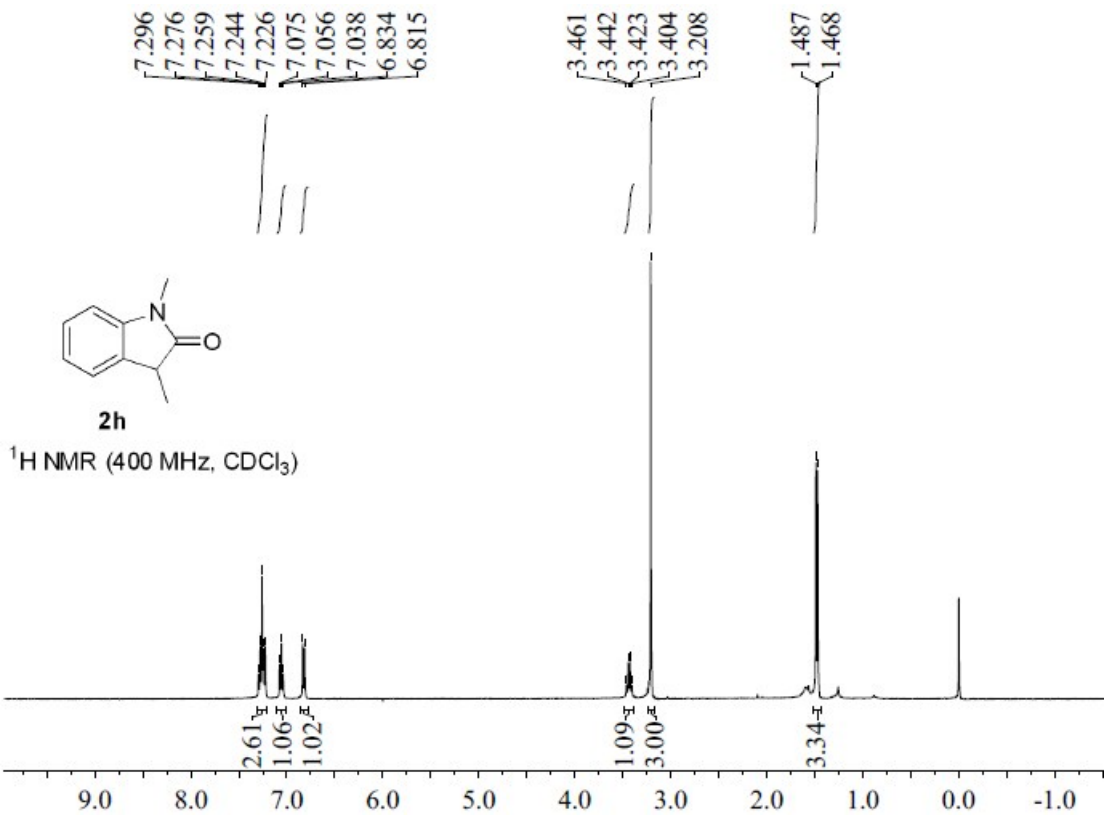


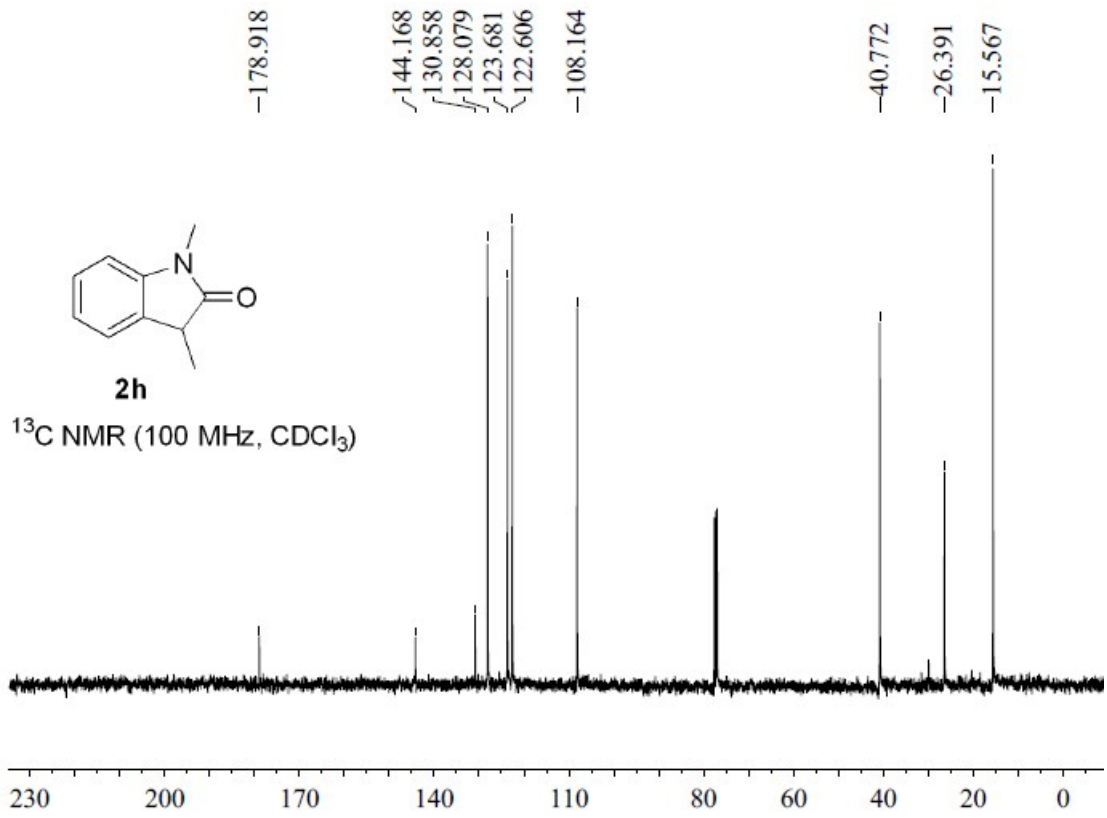
3-Ethyl-1,5-dimethylindolin-2-one (2g)



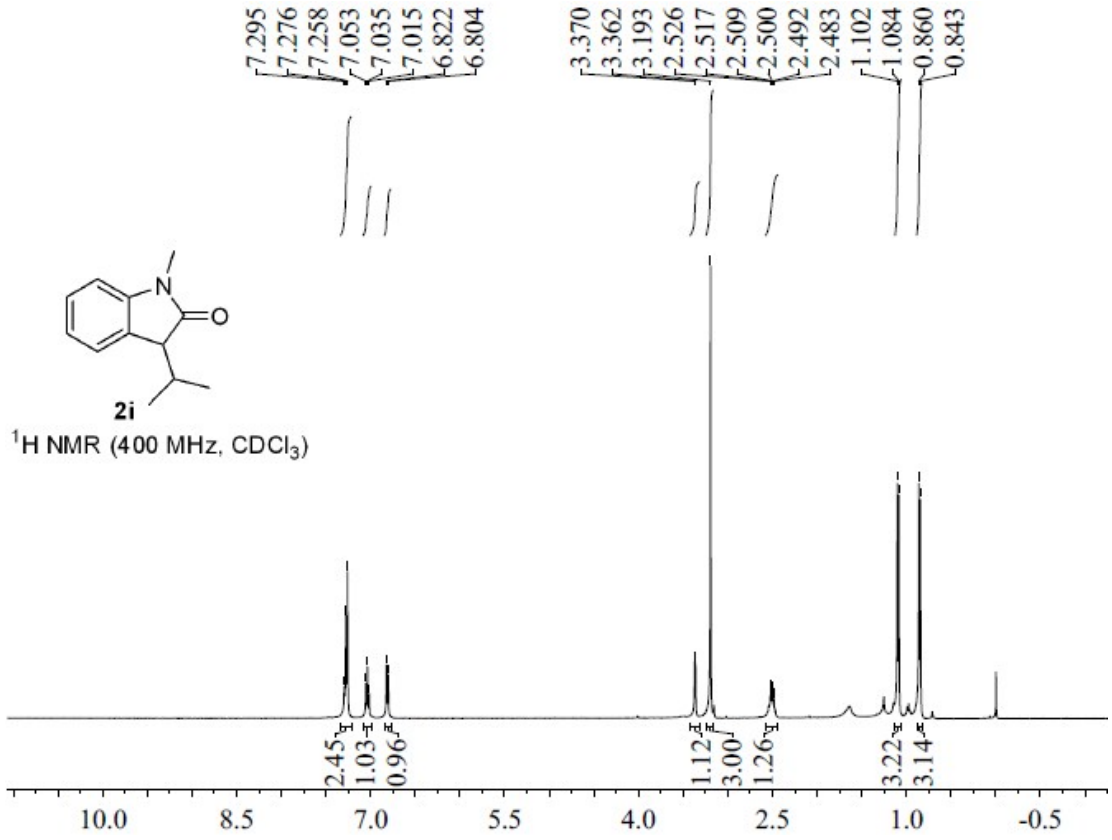


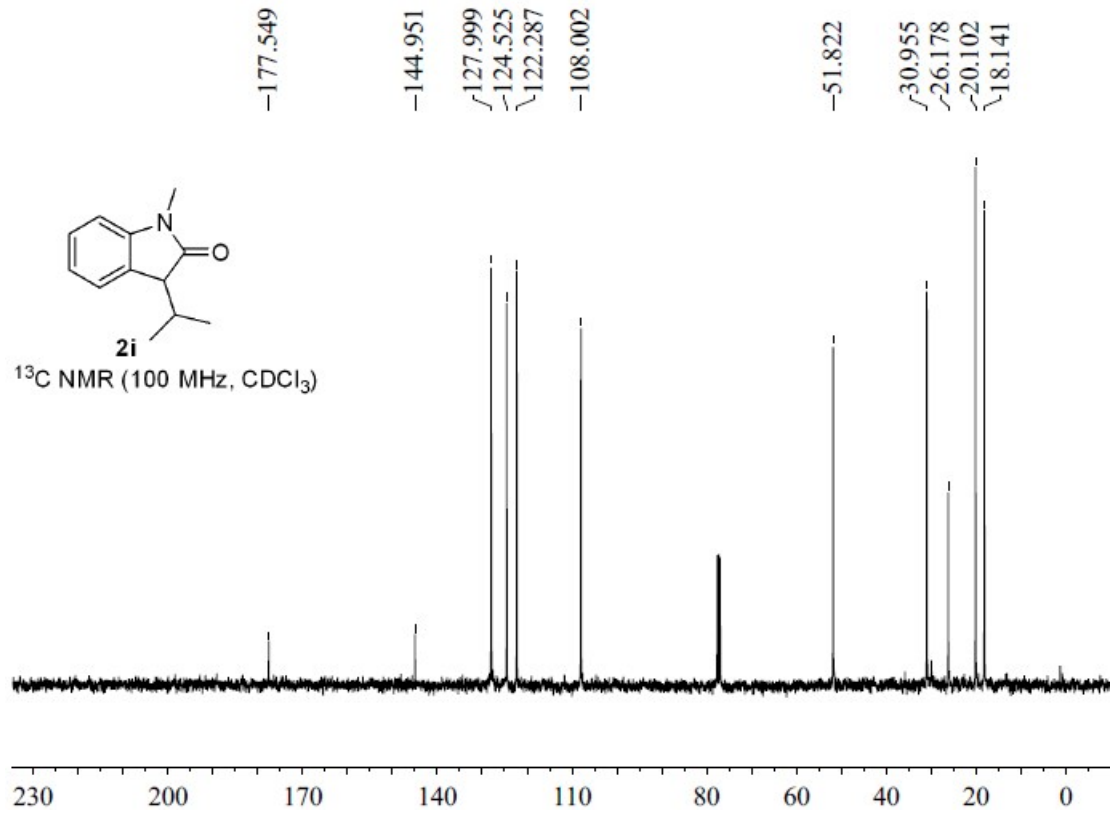
1,3-Dimethylindolin-2-one (2h)



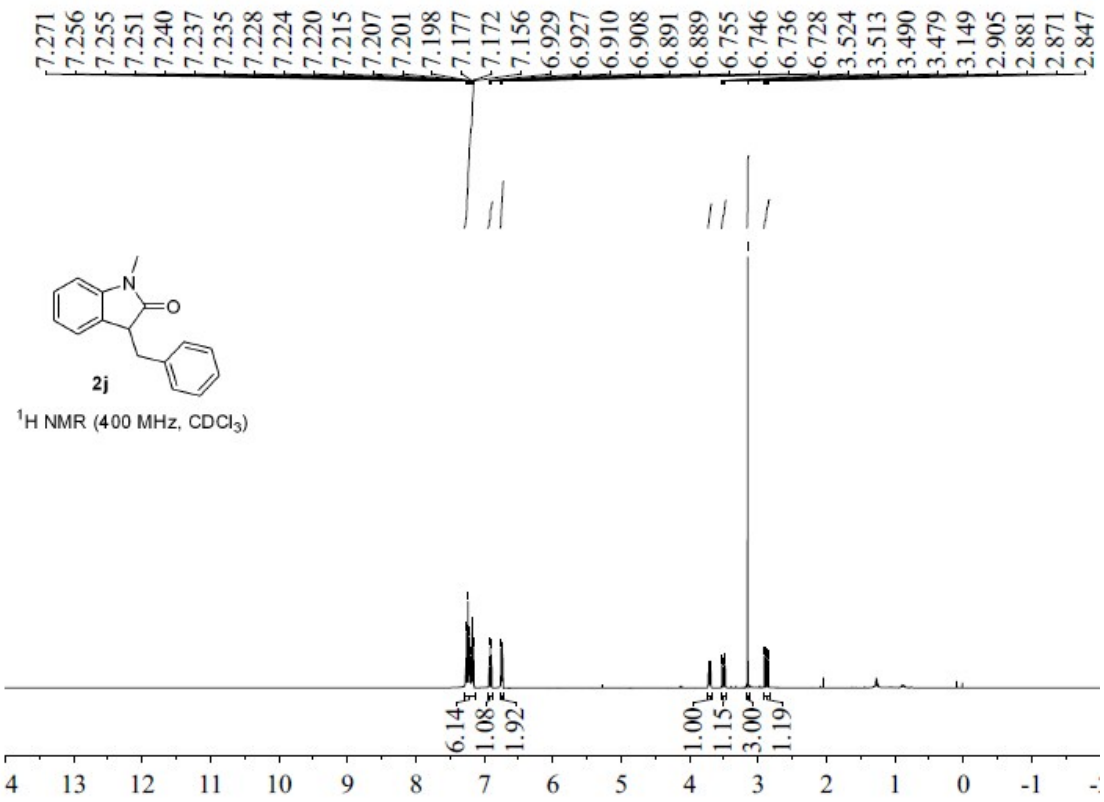


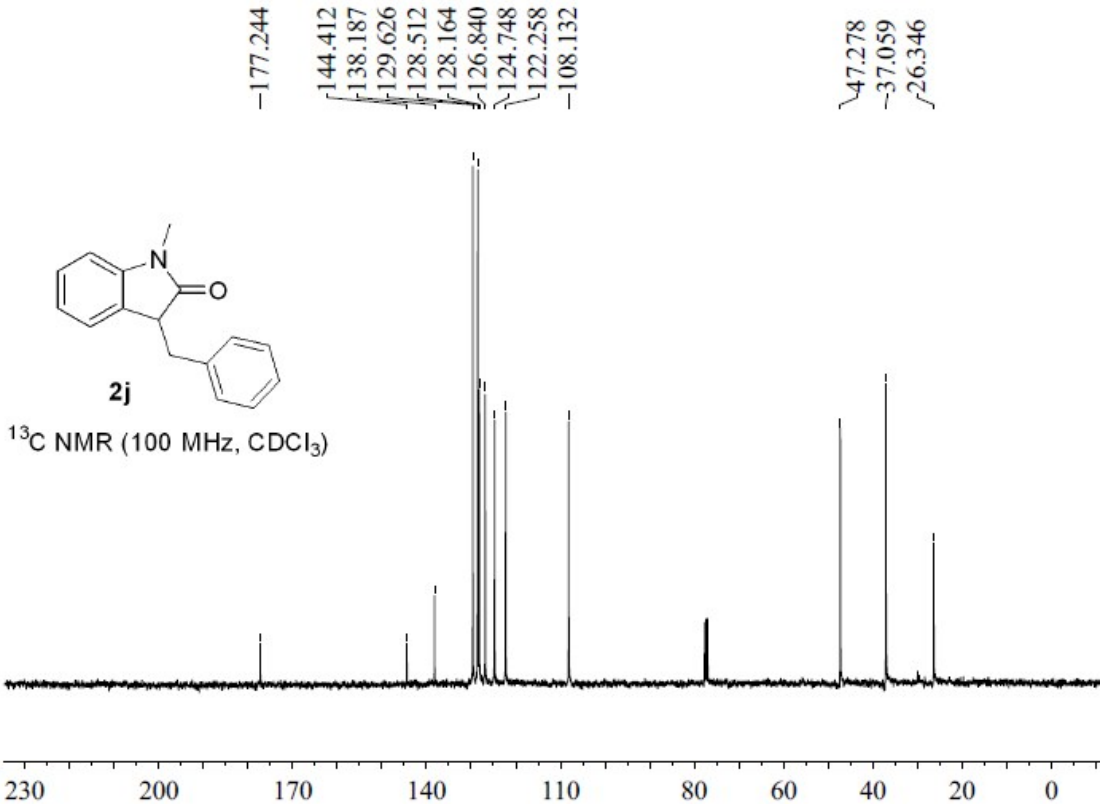
3-Isopropyl-1-methylindolin-2-one (2i)



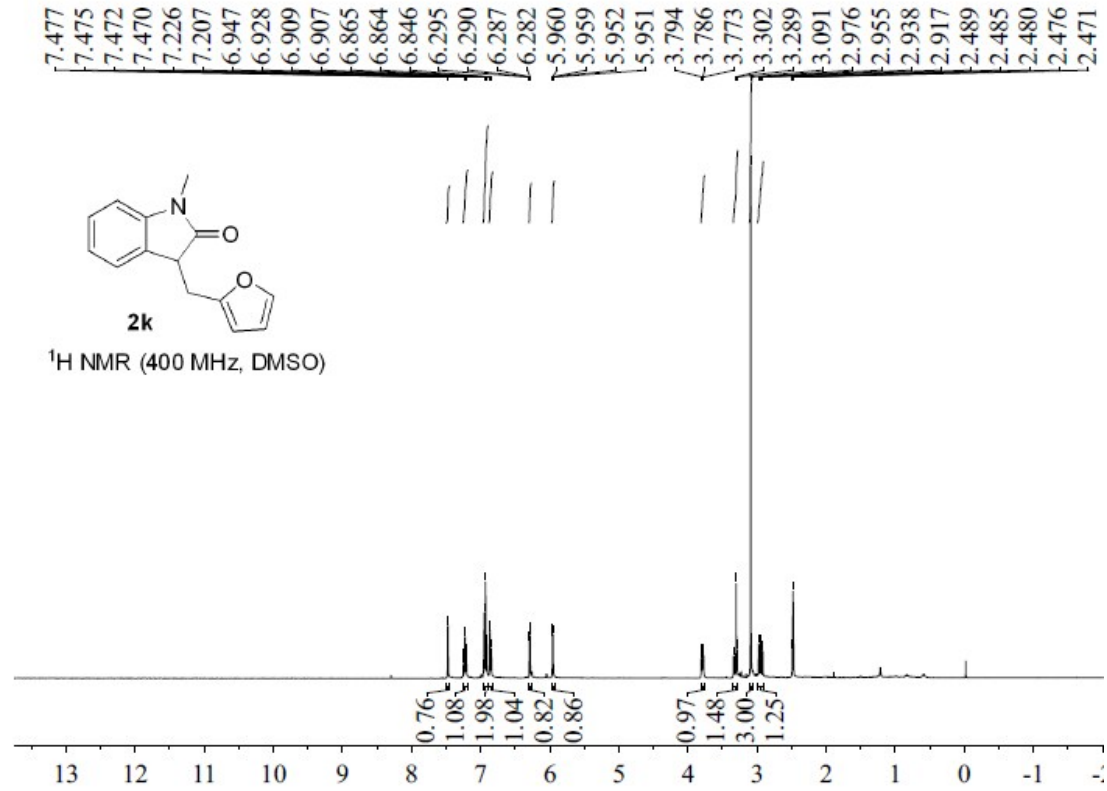


3-Benzyl-1-methylindolin-2-one (2j)



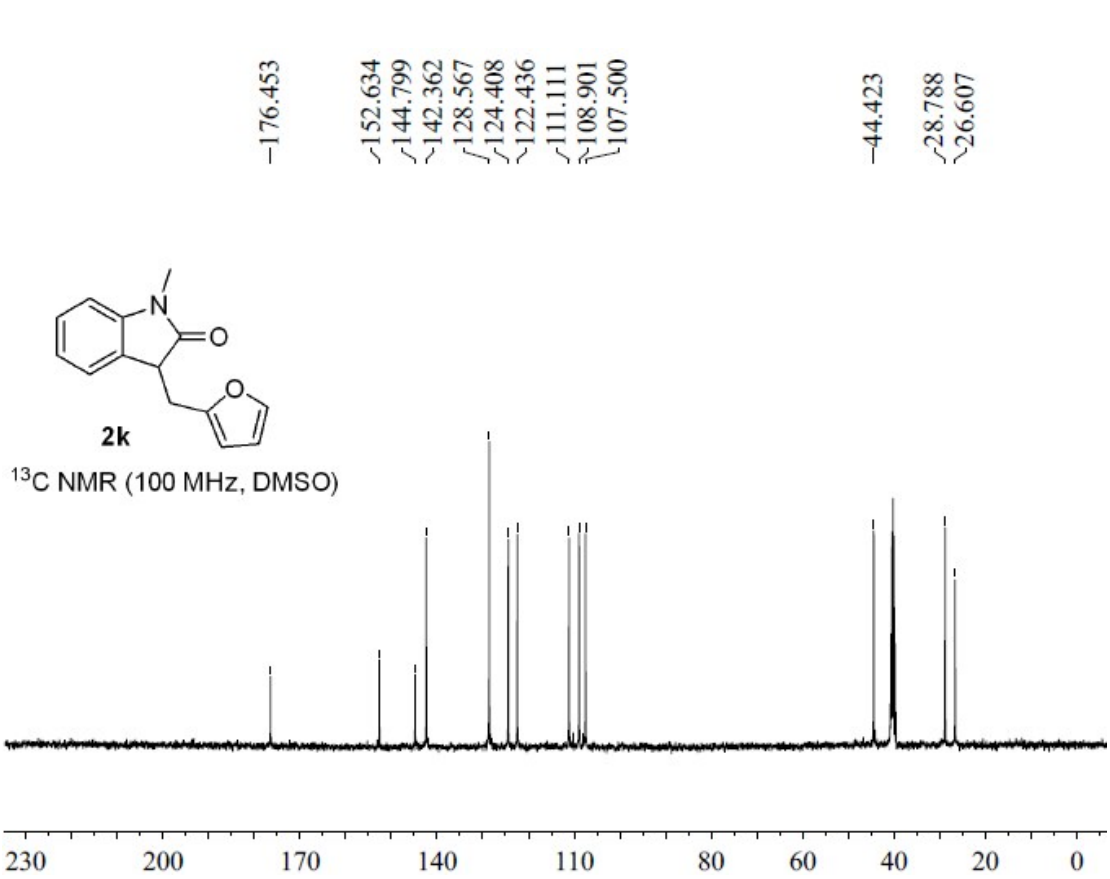


3-(Furan-2-ylmethyl)-1-methylindolin-2-one (2k)



2k

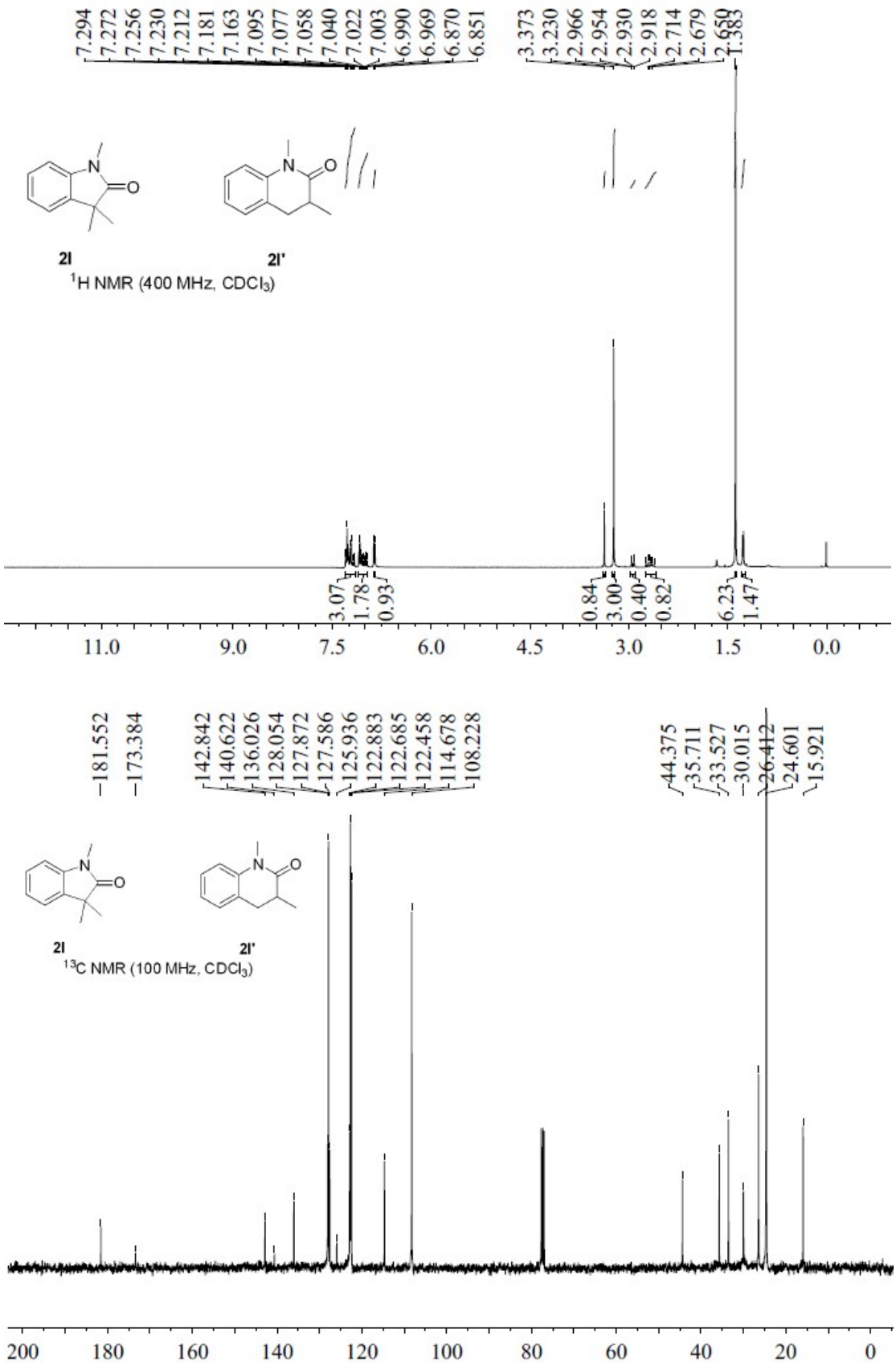
^{1}H NMR (400 MHz, DMSO)



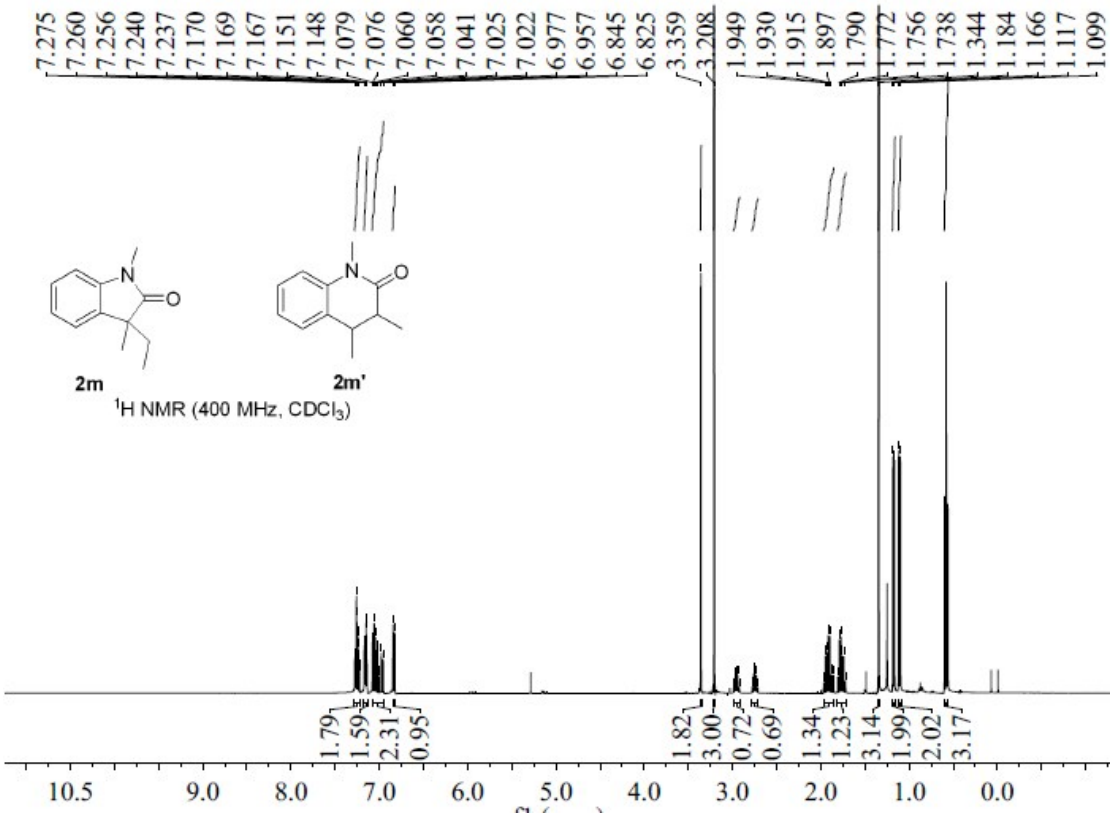
2k

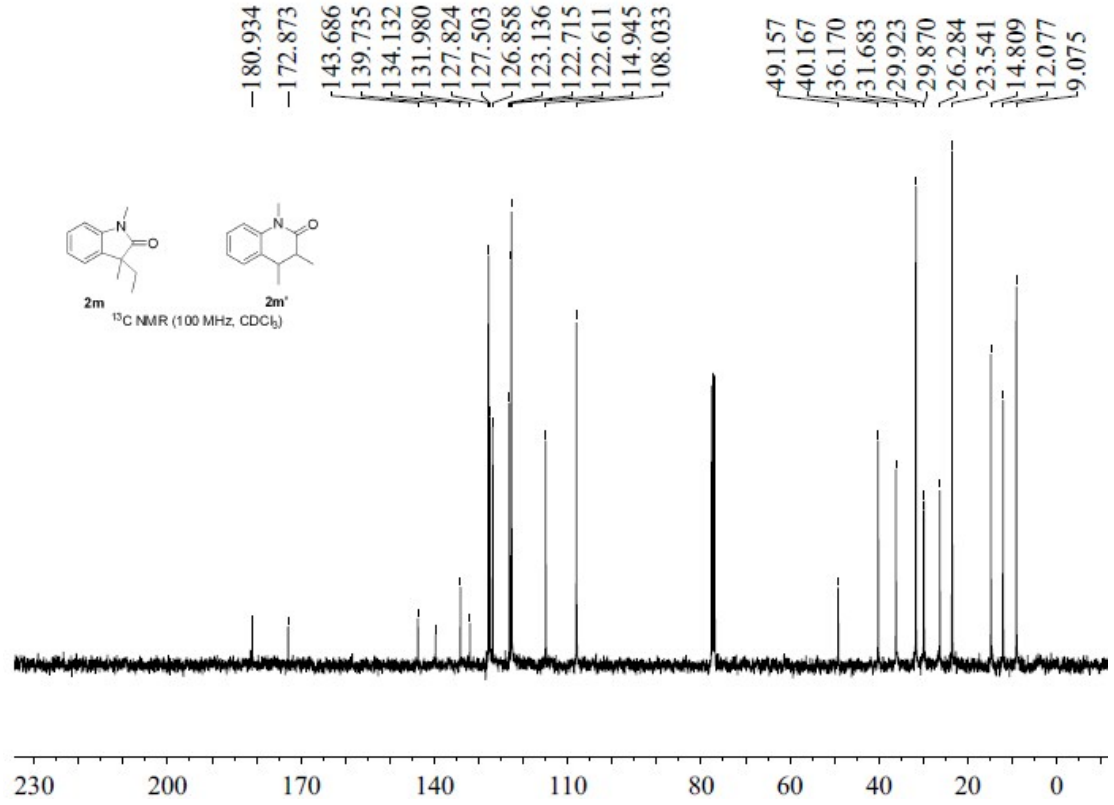
^{13}C NMR (100 MHz, DMSO)

1,3,3-Trimethylindolin-2-one (2l)

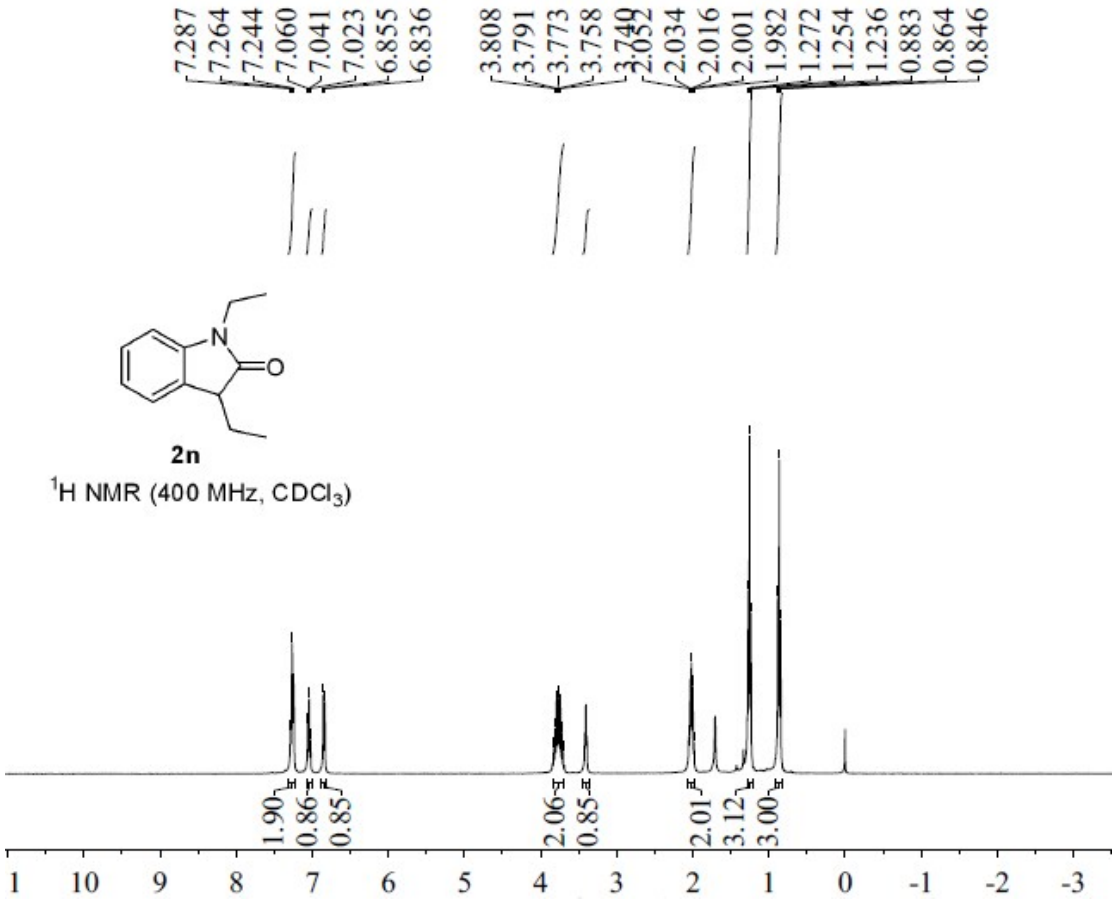


3-Ethyl-1,3-dimethylindolin-2-one (2m)



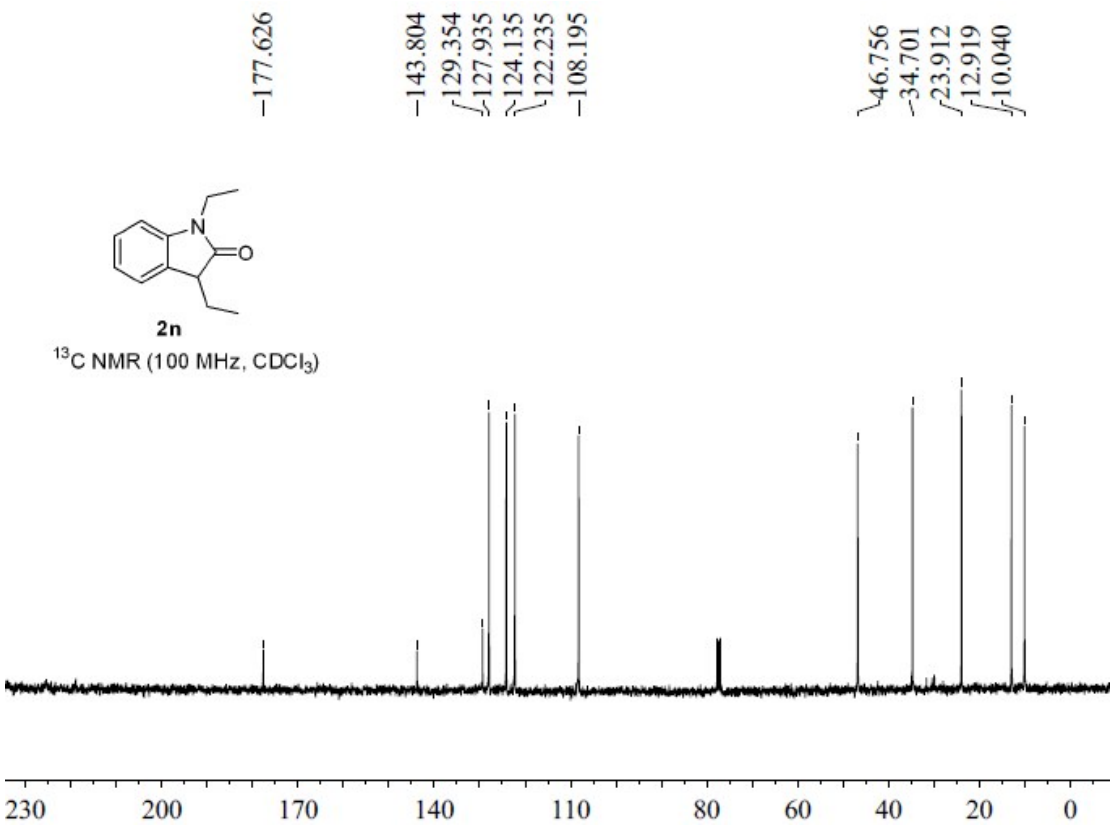


1,3-Diethylindolin-2-one (2n)



2n

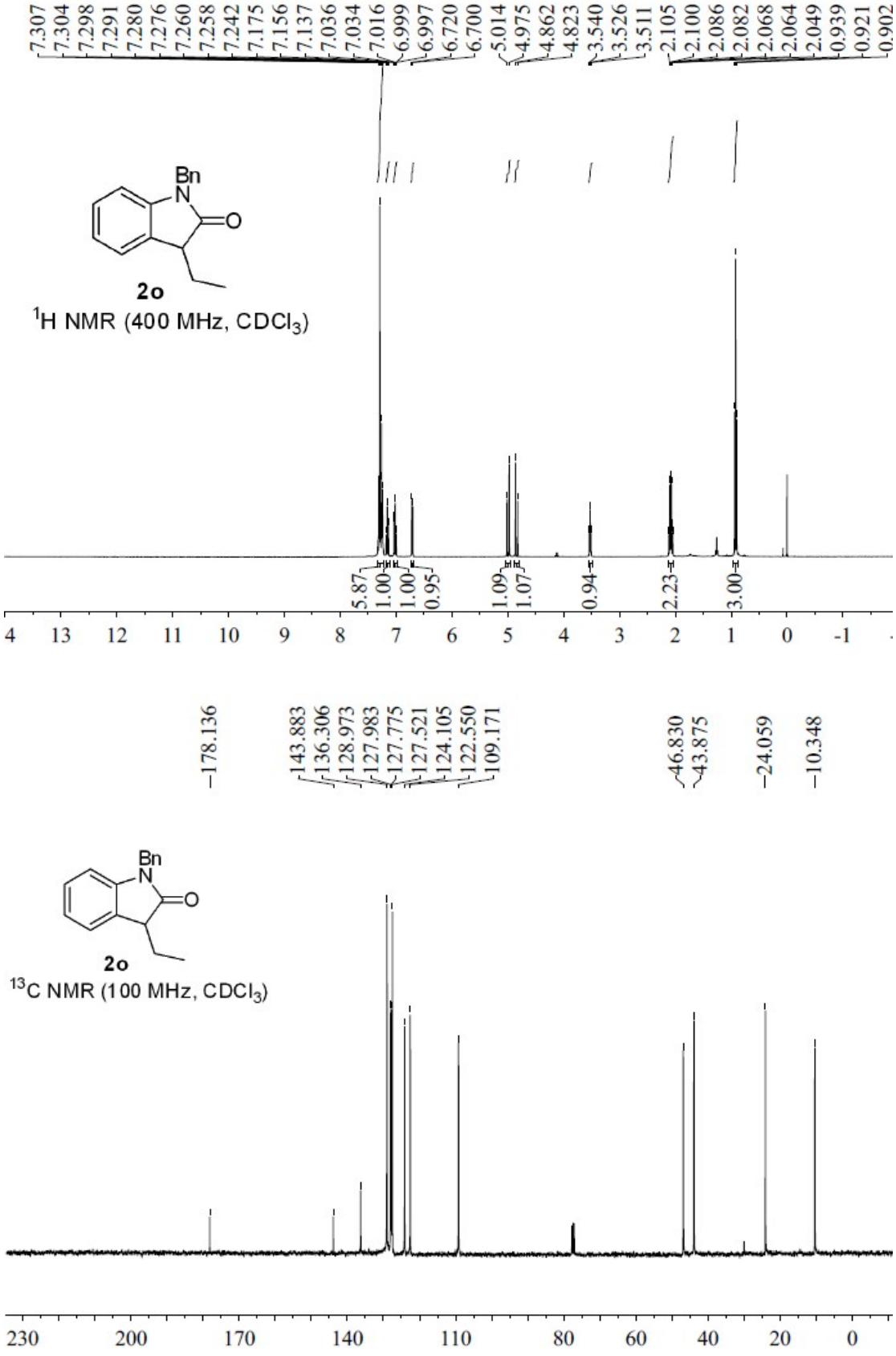
^{1}H NMR (400 MHz, $CDCl_3$)



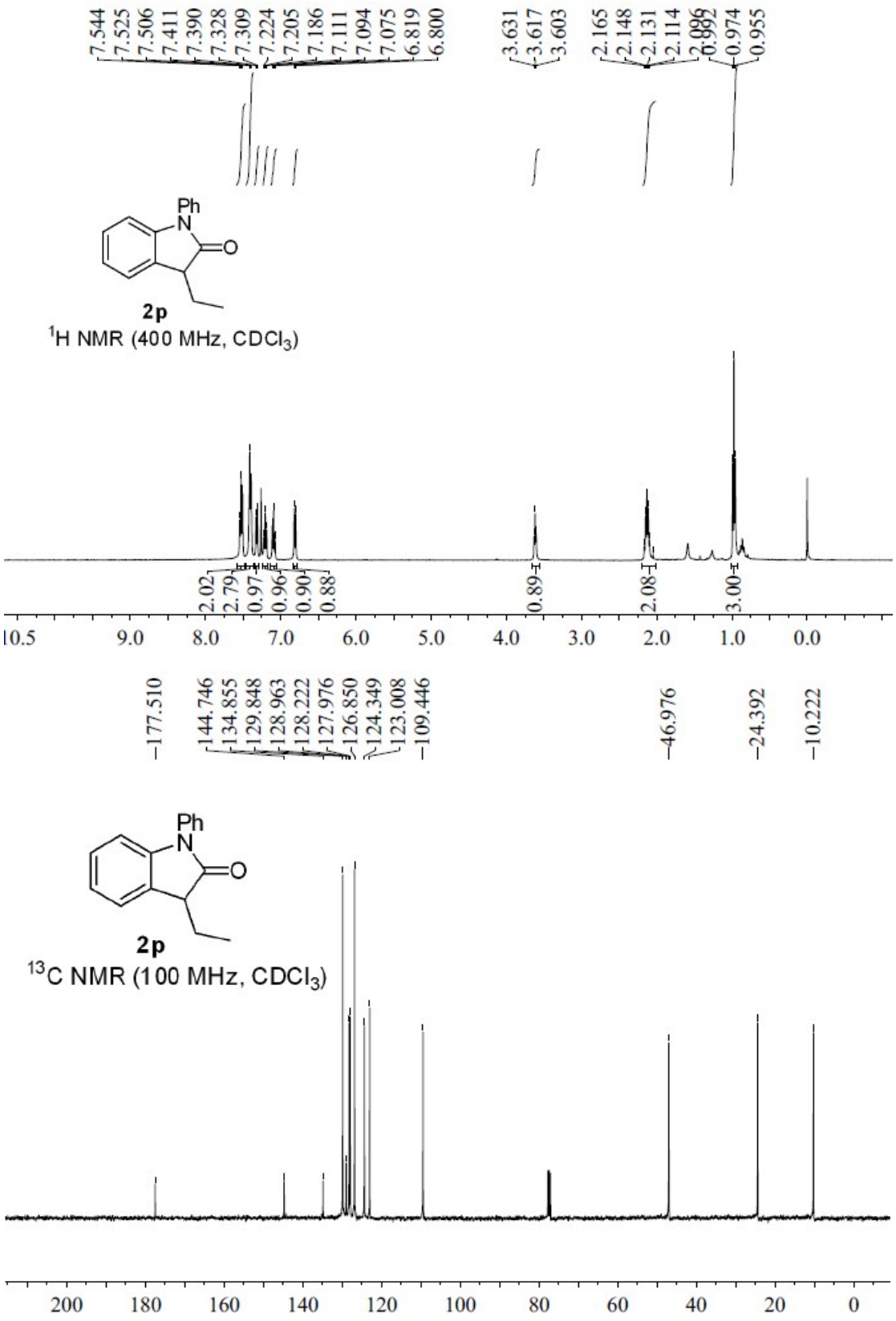
2n

^{13}C NMR (100 MHz, $CDCl_3$)

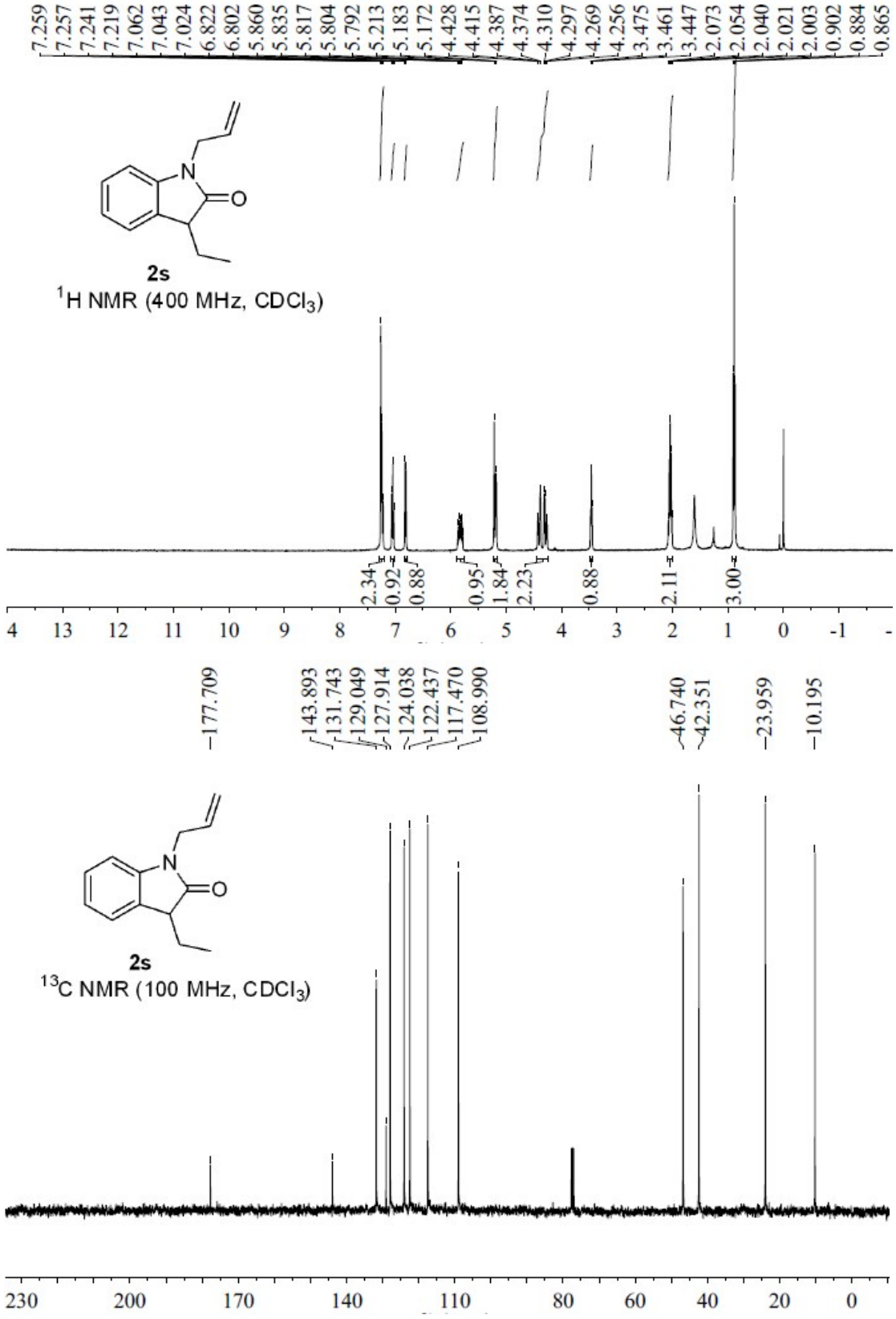
1-Benzyl-3-ethylindolin-2-one (2o)



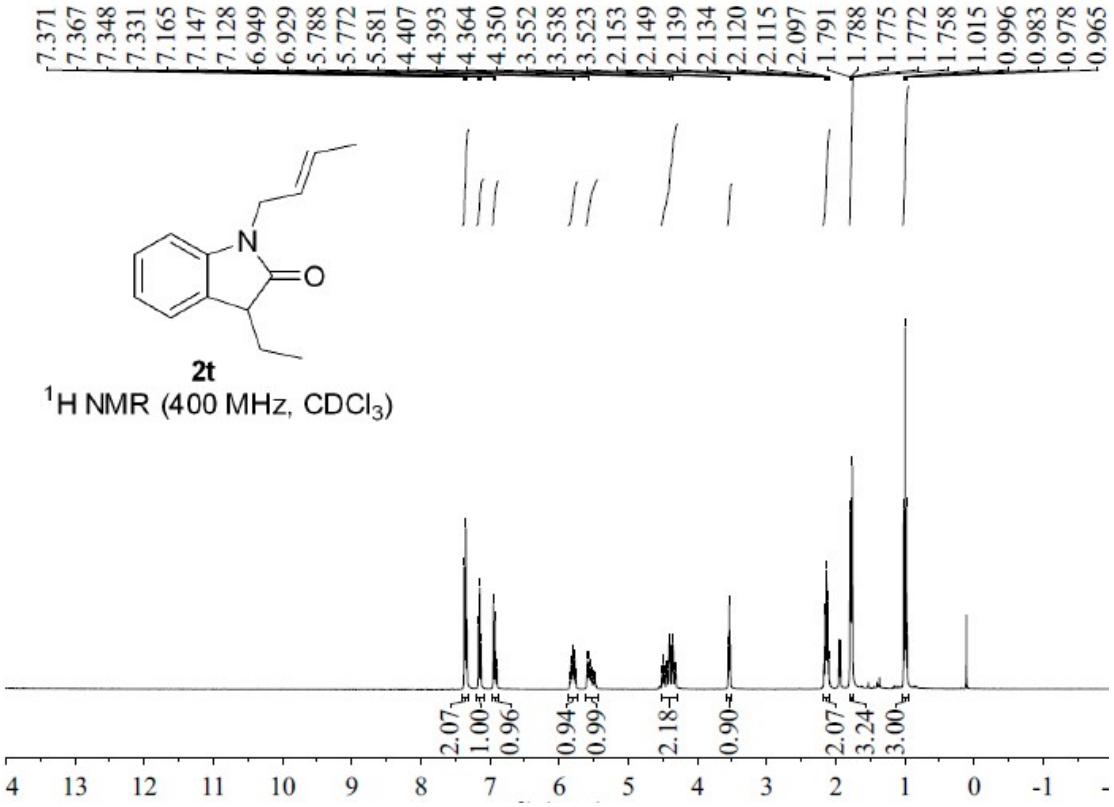
3-Ethyl-1-phenylindolin-2-one (2p)



1-Allyl-3-ethylindolin-2-one (2s)

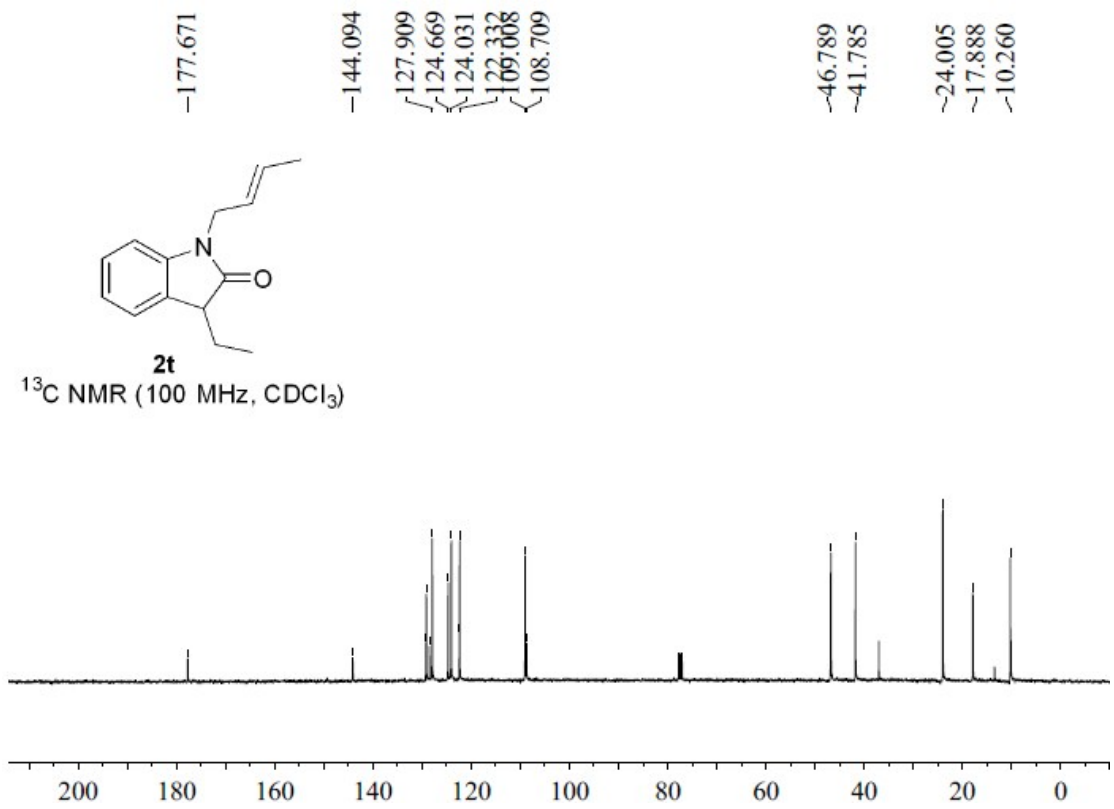


1-(But-2-en-1-yl)-3-ethylindolin-2-one (2t)



2t

^{1}H NMR (400 MHz, $CDCl_3$)



2t

^{13}C NMR (100 MHz, $CDCl_3$)