Electronic Supplementary Information

Room temperature decarboxylation/C-H functionalization cascade by visible-light photoredox catalysis

Jin Xie,[a] Pan Xu,[a] Huamin Li, [a] Qicai Xue, [a] Hongming Jin, [a] Yixiang Cheng[a] and Chengjian Zhu[*a,b]

[a]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China.

[b]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, P. R. China.

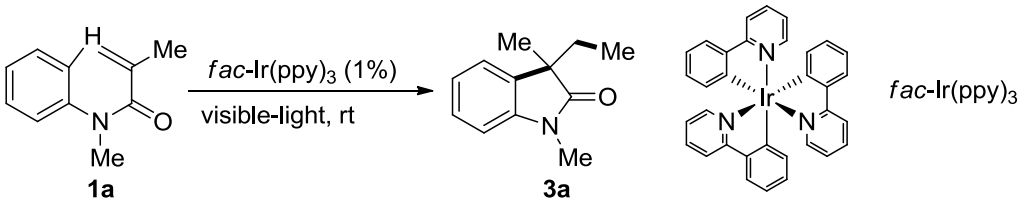
E-mail: cjzhu@nju.edu.cn

Part I. General Information

Unless otherwise stated, all the reactions were performed under argon atmosphere. Solvents and reagents were used as received from suppliers unless otherwise stated. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR data were obtained on Bruker Advance III 400 MHz nuclear resonance spectrometers with $CDCl_3$ as solvents at ambient temperature. Chemical shifts were reported in units (ppm) by assigning chloroform residue in the ^{1}H NMR spectrum as 7.26 ppm. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant (J values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from chloroform using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Flash column chromatography was performed using 200- 300 mesh silica with the indicated solvent system according to standard techniques. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by *UV* absorbance (254 nm). Low resolution mass spectra were obtained using ThermoFisher Scientific LCQ FLEET mass spectrometer or Daojin (Japan) LC-MS 2020 spectrometer. High resolution mass spectra were obtained using an Agilent 6210 Series TOF LC-MS or G6520B Accurate-Mass Q-TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. Melting points (m.p.) were determined with a digital electrothermal apparatus without further correction. The alkene substrates **1** were prepared according to the literature.[1] The 35 W fluorescent light bulb was directly got from the supermarket (daylight, energy saving, 220 V, 50 Hz).

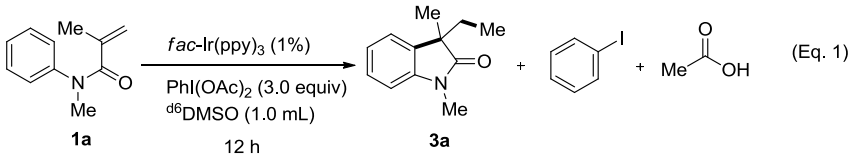
Part II. Optimization of the Tandem Reaction Conditions.

Table 1. Optimization of the Decarboxylation/C-H Functionalization Tandem Reaction[a]

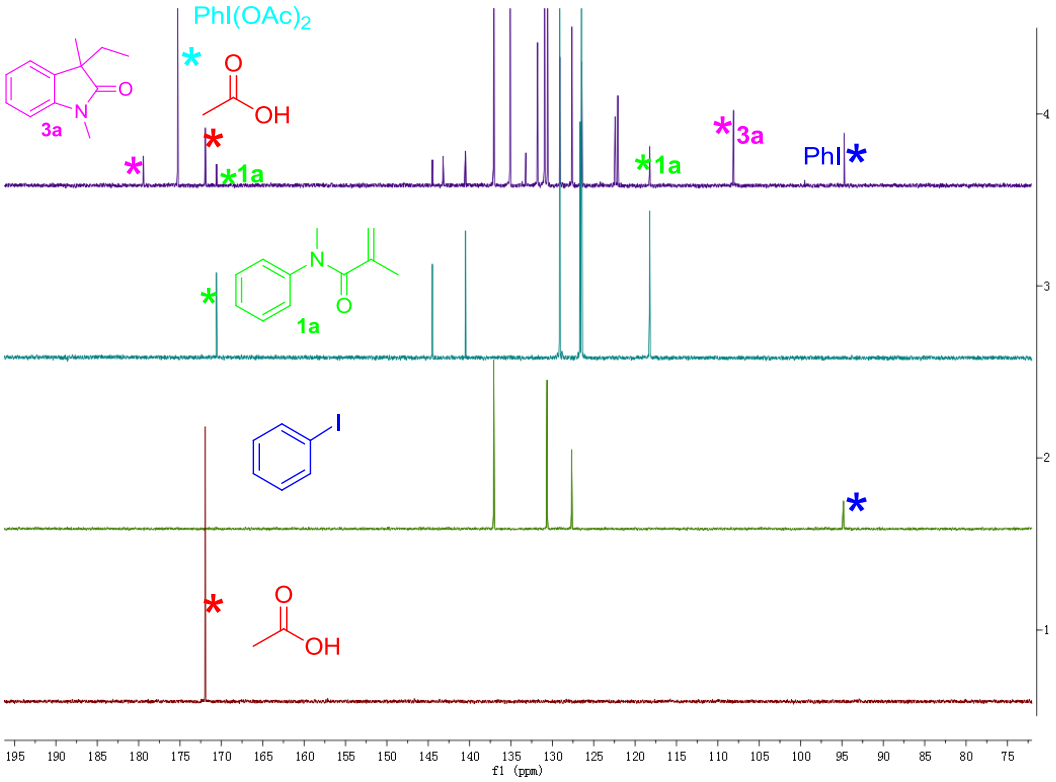


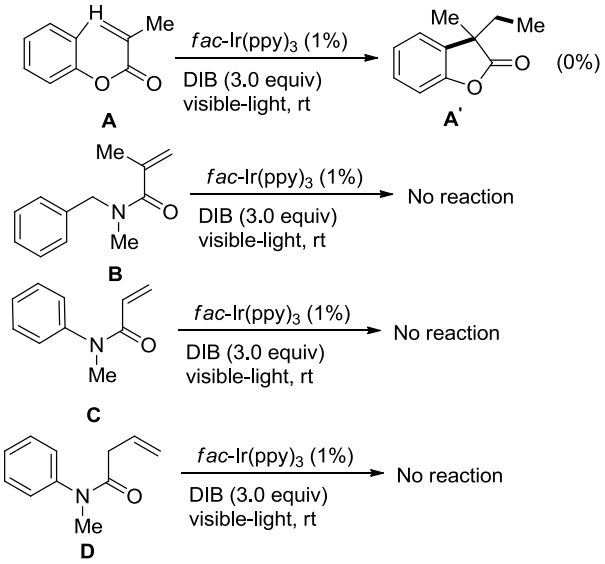
Entry	Catalyst	Solvent	Additives	Time/h	Yield(%)[b]
1	(1%)	MeCN	DIB (3.0 equiv)	20	51
2	(1%)	MeCN	DIB (3.0 equiv)	48	72
3	(1%)	DCM	DIB (3.0 equiv)	36	66
4	(1%)	DMF	DIB (3.0 equiv)	24	83
5	(1%)	DMA	DIB (3.0 equiv)	36	70
6	(1%)	diglyme	DIB (3.0 equiv)	36	75
7	(1%)	DMSO	DIB (3.0 equiv)	36	77
8	(1%)	1,4-dioxane	DIB (3.0 equiv)	48	56
9	(3%)	DMF	DIB (3.0 equiv)	24	79
10	(1%)	DMF	K_2HPO_4 (2.0 equiv) DIB (3.0 equiv)	24	82
11	(1%)	DMF	2,6-lutidine(2.0 equiv) DIB (3.0 equiv)	24	81
12	(1%)	DMF	K_2CO_3 (2.0 equiv) DIB (3.0 equiv)	24	58
13	(1%)	DMF	$NaHCO_3$ (2.0 equiv) DIB (3.0 equiv)	24	67
14	(1%)	DMF	KOBu-*t* (2.0 equiv) DIB (3.0 equiv)	24	trace
15	(1%)	DMF	4 Å MS (50 mg) DIB (3.0 equiv)	24	74
16	(1%)	DMF	DIB (2.0 equiv)	24	79
17	(1%)	DMF	DIB (1.0 equiv)	24	40
18	(1%)	DMF	DIB (4.0 equiv)	24	83
19	-	DMF	DIB (3.0 equiv)	72	NP
20[c]	(1%)	DMF	DIB (3.0 equiv)	72	NP

[a]Reaction conditions: **1a** (1.0 equiv), DIB **2a** (1.0-4.0 equiv), *fac*-Ir(ppy)$_3$ (1-3 mol%), argon atmosphere, room temperature, 35 W fluorescent light bulb. [b]Isolated yields. [c]In the dark.



The ^{13}C NMR (400 MHz, ^{d6}DMSO) of Eq. 1.



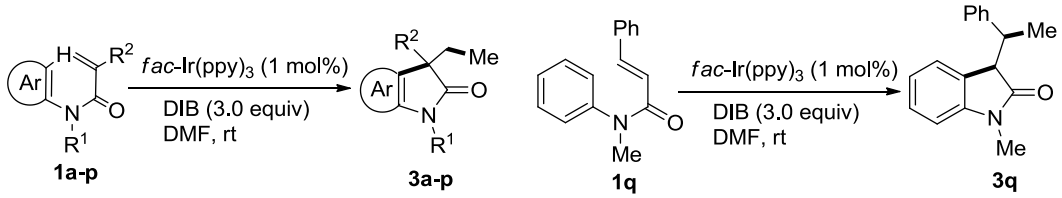


Scheme 1. Screening of another reaction substrates.

Part III. General Experimental Details of the Visible-Light-Mediated Decarboxylation/Radical-C-H Functionzalization Tandem Reactions and Characterization Data for Products

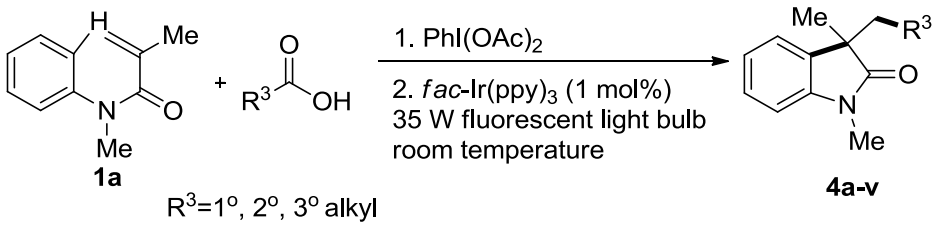
General procedure

Method A:



An oven-dried Schlenk tube (20 mL) was equipped with a magnetic stir bar, **1a-p** (0.3 mmol), *fac*-Ir(ppy)$_3$ (2.0 mg, 0.01 equiv), PhI(OAc)$_2$ (3.0 equiv) and DMF (2.0 mL). The tube was degassed by alternating vacuum evacuation (5 min) and argon backfill three times. The tube was palced at a distance (app. 5 cm) from 35 W fluorescent light bulb, and the resulting yellow solution was stirred at ambient temperature under visible-light irradiation. When the reaction finished, the mixture was diluted with ethyl acetate and added to a separatory funnel containing 15 mL saturated K_2CO_3 solution. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with saturated brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel (petroleum ether 60-90 : EtOAc, 10:1-1:1 v/v)to afford the oxindoles **3a-q**.

Method B:

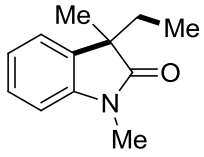


In a 25 mL round flask was equipped with a magnetic stir bar, aliphatic carboxylic acid (3.0 mmol, 2.0 equiv), PhI(OAc)$_2$ (1.5 mmol, 1.0 equiv) and $CHCl_3$ (10 mL). The phenyliodine(III) dicarboxylate can be easily obtained as a white solid or a viscous oil

at 30-40 ^{o}C under reduced pressure to remove the HOAc,[2] and it can be directly used without further purification. Then, an oven-dried Schlenk tube (20 mL) was equipped with a magnetic stir bar, **1a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (2.0 mg, 0.01 equiv), phenyliodine(III) dicarboxylate (3.0 equiv) and DMF (2.0 mL). The tube was degassed by alternating vacuum evacuation (5 min) and argon backfill three times. The tube was palced at a distance (app. 5 cm) from 35 W fluorescent light bulb, and the resulting yellow solution was stirred at ambient temperature under visible-light irradiation. When the reaction finished, the mixture was diluted with ethyl acetate and added to a separatory funnel containing 15 mL saturated K_2CO_3 solution. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with saturated brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography (petroleum ether 60-90 : EtOAc, 10:1-3:1 v/v) to afford the oxindoles **4a-u**.

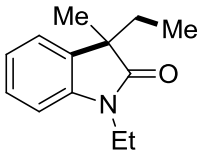
Characterization data

3-ethyl-1,3-dimethylindolin-2-one 3a



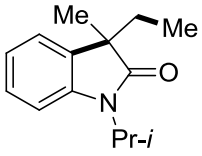
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 24 h, and purified by flash column chromatography in 83% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30-7.24 (m, 1 H), 7.19-7.15 (m, 1 H), 7.09-7.04 (m, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 3.22 (s, 3 H), 1.98-1.86 (m, 1 H), 1.82-1.71 (m, 1 H), 1.35 (s, 3 H), 0.59 (t, *J* = 7.2, 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.8, 143.5, 134.0, 127.6, 122.5, 122.4, 107.8, 49.0, 31.5, 26.1, 23.3, 8.8; MS (ESI) *m/z:* 212.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226; found:190.1225.

1,3-diethyl-3-methylindolin-2-one 3b



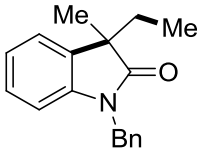
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 80% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.23 (m, 1 H), 7.20-7.15 (m, 1 H), 7.09-7.02 (m, 1 H), 6.89-6.83 (m, 1 H), 3.90-3.66 (m, 2 H), 1.99-1.89 (m, 1 H), 1.82-1.70 (m, 1 H), 1.34 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 0.57 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.3, 142.6, 134.2, 127.5, 122.7, 122.2, 108.0, 48.8, 34.5, 34.6, 23.4, 12.8, 8.8; MS (ESI) *m/z:* 226.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NNaO$ $[M+Na]^+$: 226.1202; found: 226.1201 .

3-ethyl-1-isopropyl-3-methylindolin-2-one 3c



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 88% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.26-7.13 (m, 2 H), 7.07-6.99 (m, 2 H), 4.72- 4.61 (m,1 H), 1.99-1.87 (m, 1 H), 1.80-1.68 (m, 1 H), 1.48 (d, *J* = 3.2 Hz, 3 H), 1.46 (d, *J* = 3.2 Hz, 3 H), 1.33 (s, 3 H), 0.55 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.4, 142.2, 134.5, 127.3, 122.7, 121.8, 109.6, 48.5, 43.5, 31.8, 23.5, 19.6, 19.4, 8.7; MS (ESI) *m/z:* 240.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1539; found:218.1538 .

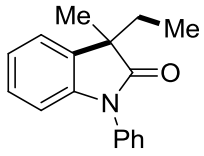
1-benzyl-3-ethyl-3-methylindolin-2-one 3d



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 73% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.49. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.34-7.23 (m, 5 H), 7.20-7.12 (m, 2 H), 7.07-6.99 (m, 1 H), 6.72 (d, *J* = 8.0 Hz, 1 H),

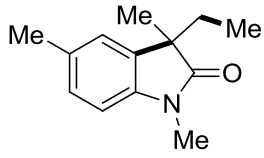
4.99 (d, *J* = 15.6 Hz, 1 H), 4.85 (d, *J* = 15.6 Hz, 1 H), 2.07-1.95 (m, 1 H), 1.89-1.77 (m, 1 H), 1.41 (s, 3 H), 0.64 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.8, 142.6, 136.2, 133.9, 128.7 (2C), 127.5 (2C), 127.3 (2C), 122.6, 122.4, 108.9, 49.0, 43.7, 31.5, 23.8, 9.1; MS(ESI): MS (ESI) *m/z:* 288.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}NNaO$ $[M+Na]^+$: 288.1359; found: 288.1354.

3-ethyl-3-methyl-1-phenylindolin-2-one 3e



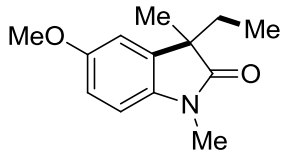
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 24 h, and purified by flash column chromatography in 90% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.56-7.48 (m, 2 H), 7.44-7.37 (m, 3 H), 7.25-7.06 (m, 3 H), 6.86-6.80 (m, 1 H), 2.11-1.97 (m, 1 H), 1.92-1.79 (m, 1 H), 1.47 (s, 3 H), 0.71 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.2, 143.4, 134.7, 133.7, 129.6 (2C), 127.9, 127.5, 126.6 (2C), 122.9, 122.8, 109.2, 49.0, 32.1, 23.6, 8.9; MS (ESI) *m/z:* 274.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{17}H_{17}NNaO$ $[M+Na]^+$: 274.1202; found: 274.1197 .

3-ethyl-1,3,5-trimethylindolin-2-one 3f



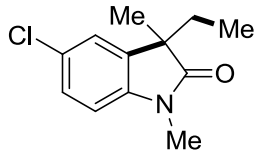
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 80% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.09-7.03 (m, 1 H), 6.98 (s, 1 H), 6.73 (d, *J* = 7.6 Hz, 1 H), 3.19 (s, 3 H), 2.35 (s, 3 H), 1.97-1.86 (m, 1 H), 1.80-1.69 (m, 1 H), 1.34 (s, 3 H), 0.59 (t, *J* = 7.6, 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.7, 141.1, 134.0, 131.9, 127.8, 123.4, 49.0, 31.5, 26.1, 23.4, 21.2, 8.9. MS (ESI) *m/z:* 226.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NNaO$ $[M+Na]^+$: 226.1202; found:226.1201 .

3-ethyl-5-methoxy-1,3-dimethylindolin-2-one 3g



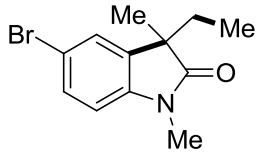
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 76% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.82-6.71 (m, 3 H), 3.01 (s, 3 H), 3.19 (s, 3 H), 1.99-1.88 (m, 1 H), 1.80-1.68 (m, 1 H), 1.34 (s, 3 H), 0.59 (t, *J* = 7.2, 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.4, 156.1, 137.1, 135.4, 111.5, 110.4, 108.0, 55.8, 49.4, 31.5, 26.2, 23.4, 8.9; MS (ESI) *m/z:* 242.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NNaO_2$ $[M+Na]^+$: 242.1151; found:242.1149 .

5-chloro-3-ethyl-1,3-dimethylindolin-2-one 3h



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 85% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.25-7.21 (m, 1 H), 7.17-7.12 (m, 1 H), 6.76 (d, *J* = 8.4 Hz, 1 H), 3.19 (s, 3 H), 1.99-1.87 (m, 1 H), 1.82-1.70 (m, 1 H), 1.34 (s, 3 H), 0.59 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.2, 142.1, 135.7, 127.8, 127.6, 123.1, 108.7, 9.3, 31.4, 26.2, 23.3, 8.8; MS (ESI) *m/z:* 246.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{12}H_{15}ClNO$ $[M+H]^+$: 224.0837; found: 224.0838 .

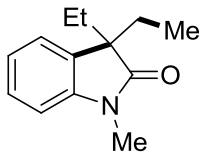
5-bromo-3-ethyl-1,3-dimethylindolin-2-one 3i



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 81% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.42-7.36 (m, 1 H), 7.30-7.25 (m, 1 H), 6.72 (d, *J* =8.0 Hz, 1 H), 3.19 (s, 3 H), 1.98-1.88 (m, 1 H), 1.80-1.69 (m, 1 H), 1.34 (s, 3 H), 0.60 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.1, 142.6, 136.1, 130.5,

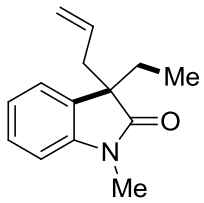
125.9, 115.2, 109.3, 49.3, 31.5, 26.2, 23.3, 8.8; MS (ESI) *m/z:* 290.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{12}H_{15}BrNO$ $[M+H]^+$: 268.0332; found: 268.0337.

3,3-diethyl-1-methylindolin-2-one 3k



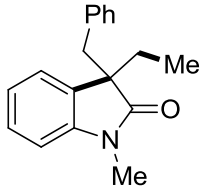
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 82% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.23 (m, 1 H), 7.16-7.03 (m, 2 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 3.21 (s, 3 H), 1.98-1.86 (m, 2 H), 1.84-1.72 (m, 2 H), 0.56 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.1, 144.4, 132.0, 127.6, 122.7, 122.3, 107.6, 54.3, 30.6 (2C), 25.9, 8.7 (2C); MS (ESI) *m/z:* 226.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NNaO$ $[M+Na]^+$: 226.1202; found:226.1200.

3-allyl-3-ethyl-1-methylindolin-2-one 3l



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 24 h, and purified by flash column chromatography in 83% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30-7.23 (m, 1 H), 7.19-7.14 (m, 1 H), 7.09-7.03 (m, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 5.47-5.33 (m, 1 H), 5.00-4.84 (m, 2 H), 3.19 (s, 3 H), 2.59-2.47 (m, 2 H), 2.00-1.75 (m, 2 H), 0.57 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 178.4, 143.0, 131.5, 130.6, 126.7, 122.0, 121.3, 117.4, 106.7, 52.5, 40.8, 29.1, 25.0, 7.6; MS (ESI) *m/z:* 238.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NO$ $[M+H]^+$: 216.1383; found: 216.1381.

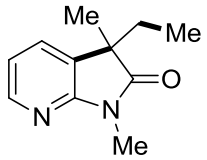
3-benzyl-3-ethyl-1-methylindolin-2-one 3m



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb

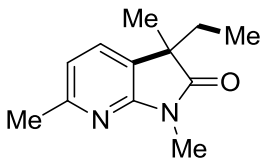
for 36 h, and purified by flash column chromatography in 73% yield. White solid, m.p.71-73 ^{o}C; TLC (PE:EA, 5:1): R*f* = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.20-7.10 (m, 2 H), 7.08-6.99 (m, 4 H), 6.87-6.79 (m, 2 H), 6.58 (d, *J* = 8.0 Hz, 1 H), 3.12 (d, *J* = 12.8 Hz, 1 H), 3.00 (d, *J* = 12.8 Hz, 1 H), 2.96 (s, 3 H), 2.16-2.07 (m, 1 H), 1.96-1.86 (m,1 H), 0.59 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 179.2, 144.1, 136.1, 131.0, 129.9, 127.7, 127.4, 126.3, 123.4, 122.0, 107.6, 55.5, 44.0, 30.1, 25.8, 8.9; MS (ESI) *m/z:* 288.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}NNaO$ $[M+Na]^+$: 288.1359; found:288.1354 .

3-ethyl-1,3-dimethyl-1H-pyrrolo[2,3-b]pyridin-2(3H)-one 3n



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 40 h at 40 ^{o}C with 3.0 equiv K_2HPO_4, and purified by flash column chromatography in 61% yield. Colorless oil, TLC (PE:EA, 3:2): R*f* = 0.49. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.17 (dd, *J* = 1.6, 5.2 Hz, 1 H), 7.39 (dd, *J* = 7.2, 1.6 Hz), 6.96 (dd, *J* = 7.2, 5.2 Hz, 1 H), 3.30 (s, 3 H), 2.00-1.89 (m, 1 H), 1.83-1.73 (m, 1 H), 1.37 (s, 3 H), 0.64 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 179.3, 156.0, 145.6, 128.8, 127.3, 117.0, 47.6, 30.0, 24.2, 21.7, 7.8; MS (ESI) *m/z:* 213.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{11}H_{15}N_2O$ $[M+H]^+$: 191.1179; found:191.1186 .

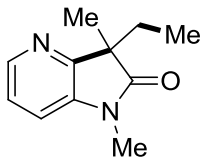
3-ethyl-1,3,6-trimethyl-1H-pyrrolo[2,3-b]pyridin-2(3H)-one 3o



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 40 h at 40 ^{o}C with 3.0 equiv K_2HPO_4, and purified by flash column chromatography in 70% yield. White solid, m.p. 84-86 ^{o}C; TLC (PE:EA, 5:1): R*f* = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.28 (d, *J*=7.2 Hz, 1 H), 6.80 (d, *J*= 7.2 Hz, 1 H), 3.29 (s, 3 H), 2.51 (s, 3 H), 1.97-1.86 (m, 1 H), 1.81-1.71 (m, 1 H), 1.34 (s, 3 H), 0.63 (t, *J*= 7.32 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.8, 156.6, 155.9, 130.1, 124.9, 116.9, 48.4, 31.0, 25.2, 24.2,

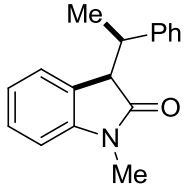
22.8, 8.9; MS (ESI) *m/z:* 227.25 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{12}H_{17}N_2O$ $[M+H]^+$: 205.1335; found:205.1340 .

3-ethyl-1,3-dimethyl-1H-pyrrolo[3,2-b]pyridin-2(3H)-one 3p



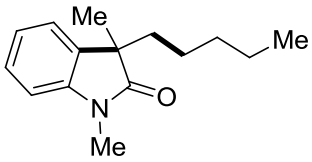
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 40 h at 40 °C with 3.0 equiv K_2HPO_4, and purified by flash column chromatography in 48% yield. Colorless oil, TLC (PE:EA, 3:2): R*f* = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.27-8.20 (m, 1 H), 7.15 (dd, *J* = 5.2, 4.0 Hz, 1 H), 7.05 (dd, *J* = 4.0, 1.2 Hz, 1 H), 3.22 (s, 3 H), 2.05-1.90 (m, 2 H), 1.40 (s, 3 H), 0.58 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 178.3, 154.2, 141.8, 137.6, 121.3, 112.7, 48.3, 29.3, 24.8, 20.6, 7.8; MS (ESI) *m/z:* 213.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{11}H_{15}N_2O$ $[M+H]^+$: 191.1179; found:191.1186 .

1-methyl-3-(1-phenylethyl)indolin-2-one 3q



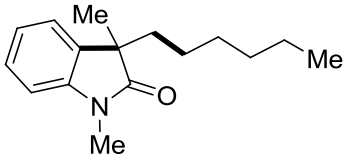
The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 38% yield. Semi-solid, TLC (PE:EA, 5:1): R*f* = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$, 8:1 mixture of diastereoisomers): δ (ppm) = 7.37-7.21 (m, 4 H), 7.19-6.80 (m, 5 H), [4.06 (d, *J* = 6.4 Hz), 3.86 (d, *J* = 9.2 Hz), 1 H], [3.45 (s), 3.41 (s), 3 H], [3.08-3.00 (m), 2.98-2.88 (m), 1 H], 1.15 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, major diastereoisomer): δ (ppm) = 171.2, 140.1, 138.9, 127.8 (2C), 127.7, 127.5, 127.3 (2C), 126.8, 126.1, 121.9, 113.5, 47.9, 41.1, 28.9, 14.5; MS (ESI) *m/z:* 274.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383; found:252.1382 .

1,3-dimethyl-3-pentylindolin-2-one 4a



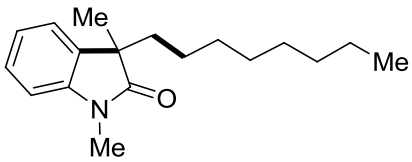
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 82% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.31-7.23 (m, 1 H), 7.19-7.14 (m, 1 H), 7.10-7.02 (m, 1 H), 6.87-6.81 (m, 1 H), 3.21 (s, 3 H), 1.92-1.82 (m, 1 H), 1.77-1.66 (m,1 H), 1.35 (s, 3 H), 1.23-1.07 (m, 4 H), 1.05-0.81 (m, 2 H), 0.78 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.9, 143.4, 134.4, 127.6, 122.5, 122.4, 107.8, 48.5, 38.5, 31.9, 26.1, 24.1, 23.8, 22.3, 14.0; MS (ESI) *m/z:* 254.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{15}H_{22}NO$ $[M+H]^+$: 232.1696; found:232.1700 .

3-hexyl-1,3-dimethylindolin-2-one 4b



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 80% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30-7.23 (m, 1 H), 7.19-7.14 (m, 1 H), 7.10-7.03 (m, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 3.21 (s, 3 H), 1.93-1.83 (m, 1 H), 1.76-1.67 (m, 1 H), 1.34 (s, 3 H), 1.24-0.83 (m, 8 H), 0.81 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.9, 143.4, 134.4, 127.6, 122.5, 122.4, 107.8, 48.5, 38.6, 31.5, 29.4, 26.1, 24.4, 23.8, 22.6, 14.0; MS (ESI) *m/z:* 268.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{16}H_{24}NO$ $[M+H]^+$: 246.1852; found: 246.1847.

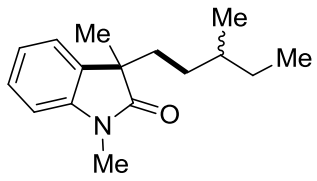
1,3-dimethyl-3-octylindolin-2-one 4c



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 75% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30-7.23 (m, 1 H), 7.19-7.14

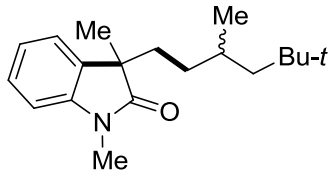
(m, 1 H), 7.10-7.03 (m, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 3.21 (s, 3 H), 1.93-1.83 (m, 1 H), 1.76-1.64 (m, 1 H), 1.34 (s, 3 H), 1.28-1.08 (m, 10 H), 1.04-0.74 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.9, 143.4, 134.4, 127.6, 122.5, 122.4, 107.8, 48.5, 38.6, 31.8, 29.8, 29.3, 29.2, 26.1, 24.5, 23.8, 22.6, 14.1; MS (ESI) *m/z:* 296.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{18}H_{27}NNaO$ $[M+Na]^+$: 296.1985; found:296.1989 .

1,3-dimethyl-3-(3-methylpentyl)indolin-2-one 4d



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 80% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$, 1:1 mixture of diastereoisomers): δ (ppm) = 7.30-7.23 (m, 1 H), 7.19-7.13 (m, 1 H), 7.11-7.04 (m, 1 H), 6.88-6.81 (m, 1 H), 3.22 (s, 3 H), 1.97-1.65 (m, 2 H), 1.35 (m, 3 H), 1.24-0.94 (m, 4 H), 0.88-0.68 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture of diastereoisomers): δ (ppm) = 180.9 (2C), 143.4 (2C), 134.4 (2C), 127.5 (2C), 122.4 (2C), 107.8 (2C), 48.4 (2C), 36.0, 35.9, 34.5 (2C), 30.8 (2C), 29.1 (2C), 28.9 (2C), 26.1 (2C), 23.9 (2C), 19.1, 19.0, 11.3, 11.2; MS (ESI) *m/z:* 268.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{16}H_{24}NO$ $[M+H]^+$: 246.1852; found: 246.1847.

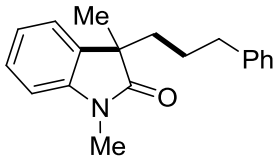
1,3-dimethyl-3-(3,5,5-trimethylhexyl)indolin-2-one 4e



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 84% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$, 1:1 mixture of diastereoisomers): δ (ppm) = 7.30-7.24 (m, 1 H), 7.18-7.14 (m, 1 H), 7.10-7.02 (m, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 3.21 (s, 3 H, 1:1), 1.96-1.82 (m, 1 H), 1.78-1.64 (m, 1 H), 1.37-1.28 (m,4 H), 1.13-0.59 (m, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture

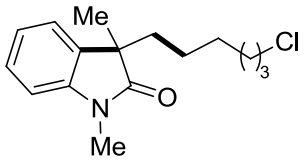
of diastereoisomers): δ (ppm) = 180.8 (2C), 143.4 (2C), 134.3 (2C), 127.5 (2C), 122.5 (2C) , 122.4 (2C), 107.8 (2C), 50.8 (2C), 48.4 (2C), 36.1, 36.0, 33.7, 33.6, 31.0, 30.9, 30.0 (3C), 29.9 (3C), 29.4, 29.3, 26.1 (2C), 23.9 (2C), 22.5, 22.4; MS (ESI) *m/z:* 310.50 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{19}H_{30}NO$ $[M+H]^+$: 288.2322; found:288.2318 .

1,3-dimethyl-3-(3-phenylpropyl)indolin-2-one 4f



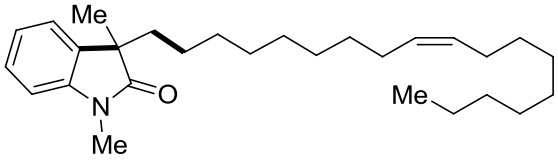
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 72% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.28-7.18 (m, 3 H), 7.19-7.09 (m, 2 H), 7.09-7.00 (m, 3 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 3.19 (s, 3 H), 2.58-2.39 (m, 2 H), 2.02-1.91 (m, 1 H), 1.83-1.72 (m, 1 H), 1.38-1.27 (m, 4 H), 1.22-1.08 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.7, 143.3, 141.9, 134.0, 128.4 (2C), 128.3 (2C), 127.7, 125.8, 122.5, 107.9, 48.4, 38.2, 36.0, 26.4, 26.2, 23.9; MS (ESI) *m/z:* 302.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NNaO$ $[M+Na]^+$: 302.1515; found: 302.1511.

3-(6-chlorohexyl)-1,3-dimethylindolin-2-one 4g



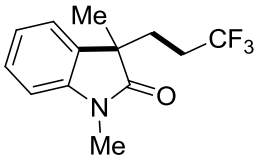
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 68% yield. Colorless oil. TLC (PE:EA, 5:1): R*f* = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.24 (m, 1 H), 7.19-7.14 (m, 1 H), 7.10-7.03 (m, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 3.44 (t, *J* = 6.4 Hz, 2 H), 3.21 (s, 3 H), 1.94-1.85 (m, 1 H), 1.77-1.60 (m, 3 H), 1.34 (s, 3 H), 1.31-1.12 (m, 4 H), 1.05-0.75 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 179.9, 142.3, 133.2, 126.6, 121.4 (2C), 106.9, 47.4, 44.0, 37.3, 31.4, 27.9, 25.5, 25.1, 23.3, 22.8; MS (ESI) *m/z:* 302.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{16}H_{22}ClNNaO$ $[M+Na]^+$: 302.1282; found: 302.1275.

(*Z*)-1,3-dimethyl-3-(octadec-9-en-1-yl)indolin-2-one 4h



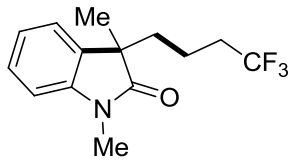
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 65% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.24 (m, 1 H), 7.20-7.14 (m, 1 H), 7.09-7.04 (m, 1 H), 6.83 (d, J = 7.6 Hz, 1 H), 5.38-5.28 (m, 2 H), 3.21 (s, 3 H), 2.06-1.94 (m, 4 H), 1.92-1.82 (m, 1 H), 1.76-1.66 (m, 1 H), 1.34 (s, 3 H), 1.32-1.10 (m, 22 H), 1.04-0.74 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.9, 143.4 (2C) 129.9 (2C), 127.6, 122.5, 122.4, 107.8, 48.5, 38.6, 31.9, 29.8 (2C), 29.7, 29.5 (2C), 29.3 (3C), 29.2, 27.2 (2C), 26.1, 24.5, 23.8, 22.7, 14.1; MS (ESI) *m/z:* 434.83 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{28}H_{46}NO$ $[M+H]^+$: 412.3574; found: 412.3580 .

1,3-dimethyl-3-(3,3,3-trifluoropropyl)indolin-2-one 4i



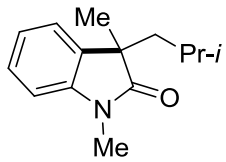
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 72% yield. Colorless oil. TLC (PE:EA, 5:1): R*f* = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.34-7.28 (m, 1 H), 7.21-7.16 (m, 1 H), 7.14-7.08 (m, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 3.23 (s, 3 H), 2.22-2.12 (m, 1 H), 2.00-1.77 (m, 2 H), 1.73-1.60 (m, 1 H), 1.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 179.4, 143.1, 132.6, 128.4, 126.8 (d, *J* = 274.4 Hz), 123.0, 122.5, 108.3, 47.0, 30.2 (q, *J* = 2.7 Hz), 29.3 (q, *J* = 28.7 Hz), 26.3, 23.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) = -66.6. MS (ESI) *m/z:* 280.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}F_3NNaO$ $[M+Na]^+$: 280.0920; found: 280.0931.

1,3-dimethyl-3-(4,4,4-trifluorobutyl)indolin-2-one 4j



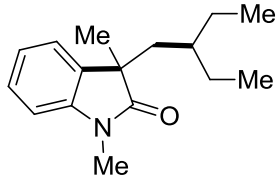
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 80% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.33-7.24 (m, 1 H), 7.20-7.15 (m, 1 H), 7.12-7.05 (m, 1 H), 6.86 (d, *J* = 7.6 Hz, 1 H), 3.22 (s, 3 H), 2.06-1.74 (m, 4 H), 1.37 (s, 3 H), 1.29-1.08 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.2, 143.2, 133.3, 128.0, 126.8 (q, *J* = 127.2 Hz), 122.7, 122.4, 108.2, 48.1, 37.3, 33.7 (q, *J* = 29.0), 26.2, 23.9, 17.3 (q, *J* = 2.8 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) = -66.3. MS (ESI) *m/z:* 294.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{14}H_{17}F_3NO$ $[M+H]^+$: 272.1257; found: 272.1260 .

3-isobutyl-1,3-dimethylindolin-2-one 4l



The title compound was prepared according to the general method A described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 70% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 70.23-7.17 (m, 1 H), 7.12-7.06 (m, 1 H), 7.03-6.94 (m, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 3.14 (s, 3 H), 1.92-1.82 (m, 1 H), 1.73-1.64 (m, 1 H), 1.25 (s, 3 H), 1.20-1.12 (m, 1 H), 0.58 (d, *J* = 6.4 Hz, 3 H), 0.53 (d, J = 6.4 z, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.0, 142.2, 133.2, 126.5, 121.8, 121.3, 106.9, 47.1, 45.7, 25.2, 25.1, 24.5, 23.1, 21.8; MS (ESI) *m/z:* 240.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1539; found: 218.1538.

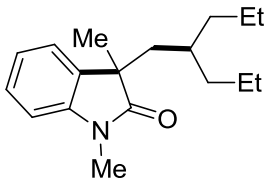
3-(2-ethylbutyl)-1,3-dimethylindolin-2-one 4m



The title compound was prepared according to the general method B described above by irradiation with 35 W

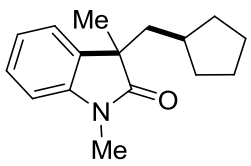
fluorescent light bulb for 36 h, and purified by flash column chromatography in 70% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.22 (m, 1 H), 7.19-7.13 (m, 1 H), 7.09-7.02 (m, 1 H), 6.83 (d, *J* =7.6 Hz, 1 H), 3.21 (s, 3 H), 1.95-1.87 (m, 1 H), 1.79-1.70 (m, 1 H), 1.34 (s, 3 H), 1.16-0.95 (m, 4 H), 0.88-0.78 (m, 1 H), 0.69 (t, *J* = 7.2 Hz, 3 H), 0.64 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 180.0, 142.3, 133.3, 126.5, 121.8, 121.2, 106.8, 47.1, 40.5, 36.1, 25.1, 25.0, 24.6, 24.5, 9.4, 9.3; MS (ESI) *m/z:* 268.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{16}H_{24}NO$ $[M+H]^+$: 246.1851; found:246.1847 .

1,3-dimethyl-3-(2-propylpentyl)indolin-2-one 4n



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 78% yield. Colorless oil. TLC (PE:EA, 5:1): R*f* = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30-7.22 (m, 1 H), 7.20-7.14 (m, 1 H), 7.08-7.00 (m, 1 H), 6.83 (d, J = 8.0 Hz, 1 H), 3.21 (s, 3 H), 1.96-1.88 (m, 1 H), 1.80-1.71 (m, 1 H), 1.33 (s, 3 H), 1.23-0.83 (m, 9 H), 0.71 (t, *J* = 7.2 Hz, 3 H), 0.64 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 181.1, 143.3, 134.3, 127.6, 122.9, 122.2, 107.8, 48.1, 42.5, 36.5, 36.1, 33.9, 26.1, 25.5, 19.1 (2C), 14.3, 14.1; MS (ESI) *m/z:* 296.50 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{18}H_{28}NO$ $[M+H]^+$: 274.2165; found: 274.2168.

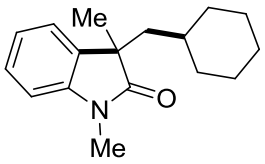
3-(cyclopentylmethyl)-1,3-dimethylindolin-2-one 4o



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 61% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.49. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30-7.24 (m, 1 H), 7.20-7.14 (m, 1 H), 7.09-7.03 (m, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 3.22 (s, 3 H), 2.10-2.03 (m, 1 H), 1.93-1.85 (m, 1 H), 1.52-1.38 (m, 3 H), 1.34 (s, 3 H),1.33-1.19 (m, 4 H), 1.06-0.94 (m, 1 H), 0.88-0.76 (m,

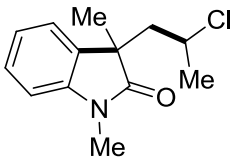
1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 181.1, 143.3, 134.4, 127.6, 122.9, 122.3, 107.9, 48.5, 44.5, 37.2, 33.8, 32.8, 26.2, 25.3, 25.0, 24.9; MS (ESI) *m/z:* 266.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{16}H_{22}NO$ $[M+H]^+$: 244.1696; found:244.1694 .

3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one 4p



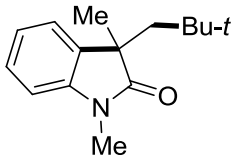
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 66% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.22 (m, 1 H), 7.18-7.11 (m, 1 H), 7.11-7.02 (m, 1 H), 6.84 (d, J = 8.0 Hz, 1 H), 3.21 (s, 3 H), 1.96-1.89 (m, 1 H), 1.76-1.68 (m, 1 H), 1.54-1.40 (m, 3 H), 1.39-1.16 (m, 5 H), 1.03-0.69 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 181.1, 143.1, 134.4, 127.5, 122.7, 122.3, 107.9, 47.8, 45.4, 34.7, 34.5, 33.6, 26.2 (2C), 26.1 (2C), 26.0; MS (ESI) *m/z:* 280.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{17}H_{24}NO$ $[M+H]^+$: 258.1852; found: 258.1850.

3-((S)-2-chloropropyl)-1,3-dimethylindolin-2-one 4q



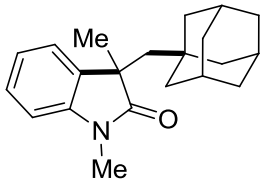
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 24 h, and purified by flash column chromatography in 86% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$, 5:2 mixture of diastereoisomers): δ (ppm) = 7.34-7.02 (m, 3 H), 6.90-6.82 (m, 1 H), 3.76-3.59 (m, 1 H), [3.22 (s), 3.21 (s), 3 H], 2.61-2.10 (m, 2 H), [1.38 (s), 1.37 (s), 3 H], [1.33 (d, *J* = 6.4 Hz), 1.28 (d, *J* = 6.4 Hz), 3 H]; ^{13}C NMR (100 MHz, $CDCl_3$, 5:2 mixture of diastereoisomers): δ (ppm) = 180.2, 179.8, 143.7, 143.0, 132.7, 132.4, 128.2, 128.1, 123.1, 122.7, 122.6, 122.3, 122.1, 108.4, 108.3, 54.6, 54.5, 47.6 (2C), 47.4, 47.2, 26.5, 26.3, 26.2, 25.6, 25.5; MS (ESI) *m/z:* 260.33 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}ClNO$ $[M+H]^+$: 238.0993; found:238.0989 .

1,3-dimethyl-3-neopentylindolin-2-one 4s



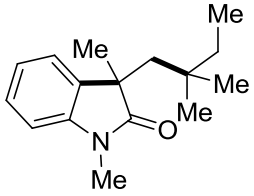
The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 30 h, and purified by flash column chromatography in 87% yield. White solid, m.p. 77-79 ^{o}C; TLC (PE:EA, 5:1): R*f* = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32-7.17 (m, 2 H), 7.06-7.00 (m, 1 H), 6.88-6.83 (m, 1 H), 3.22 (s, 3 H), 2.16 (d, *J* = 14.4 Hz, 1 H), 1.86 (d, *J* = 14.4 Hz, 1 H), 1.30 (s, 3 H), 0.61 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 181.0, 142.9, 134.2, 127.5, 123.9, 122.0, 108.0, 50.8, 47.4, 31.8 (3C), 30.8, 28.3, 26.3. MS (ESI) *m/z:* 254.42 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{15}H_{22}NO$ $[M+H]^+$: 232.1696; found:232.1700 .

3-(-adamantan-1-ylmethyl)-1,3-dimethylindolin-2-one 4t



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 30 h, and purified by flash column chromatography in 88% yield. White solid, m.p. 107-109 ^{o}C. TLC (PE:EA, 5:1): R*f* = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.16 (m, 2 H), 7.07-7.00 (m, 1 H), 6.85 (d, *J* = 7.6 Hz, 1 H), 3.23 (s, 3 H), 2.00 (d, *J* = 14.4 Hz, 1 H), 1.77-1.68 (m, 4 H), 1.55-1.47 (m, 3 H), 1.42-1.34 (m, 3 H), 1.27 (s, 3 H), 1.23-1.12 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 181.2, 142.7, 134.7, 127.5, 123.6, 122.0, 108.0, 52.1, 46.7, 43.4 (3C), 36.7 (3C), 33.9, 28.6 (4C), 26.3; MS (ESI) *m/z:* 332.50 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{21}H_{27}NNaO$ $[M+Na]^+$: 332.1985; found: 332.1986.

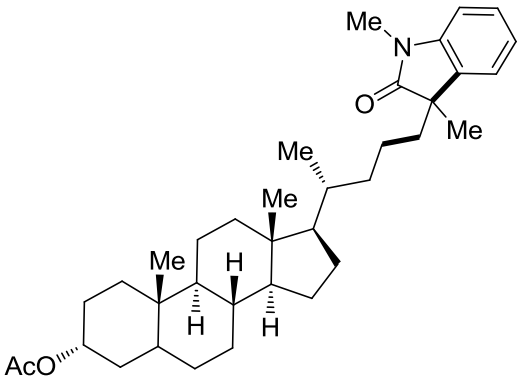
3-(2,2-dimethylbutyl)-1,3-dimethylindolin-2-one 4u



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h, and purified by flash column chromatography in 71% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.49. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.18 (m, 2 H), 7.06-7.01 (m,

1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 3.22 (s, 3 H), 2.12 (d, *J* = 14.4Hz, 1 H), 1.87 (d, *J* = 14.4 Hz, 1 H), 1.29 (s, 3 H), 1.06-0.87 (m, 2 H), 0.72 (t, *J* = 7.2 Hz, 3 H), 0.56 (s, 3 H), 0.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 181.1, 142.8, 134.4, 127.5, 123.7, 121.9, 108.0, 48.5, 47.3, 36.2, 34.2, 28.5, 27.6, 26.9, 26.3, 8.4; MS (ESI) *m/z:* 268.50 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{16}H_{23}NNaO$ $[M+Na]^+$: 268.1672; found:268.1675.

(3R,8R,9S,10S,13R,14S,17R)-17-((2R)-5-(1,3-dimethyl-2-oxoindolin-3-yl)pentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate 4v



The title compound was prepared according to the general method B described above by irradiation with 35 W fluorescent light bulb for 36 h with a mixture solvent (DMF:DCM=2:1), and purified by flash column chromatography in 52% yield. Colorless oil, TLC (PE:EA, 5:1): R*f* = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$, 1:1 mixture of diastereoisomers): δ (ppm) = 7.29-7.23 (m, 1 H), 7.20-7.14 (m, 1 H), 7.10-7.03 (m, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 4.77-4.66 (m, 1 H), 3.22 (s, 3 H), 1.95-0.68 (m, 39 H), 0.58 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture of diastereoisomers): δ (ppm) = 180.9 (2C), 170.6, 143.3, 134.4, 127.6, 122.5, 122.4, 107.8, 74.4, 56.5 (2C), 48.5 (2C), 42.7, 41.9, 40.4, 40.1, 38.8 (2C), 36.0, 35.9, 35.8, 35.5 (2C), 35.0, 34.6, 32.3, 28.2, 27.0, 26.6, 26.3, 26.1, 24.2, 23.9, 23.3, 21.5, 21.2 (2C), 20.8, 18.5 (2C), 12.0; MS (ESI) *m/z:* 570.40 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{36}H_{53}NNaO_3$ $[M+Na]^+$: 570.3918; found: 570.3927.

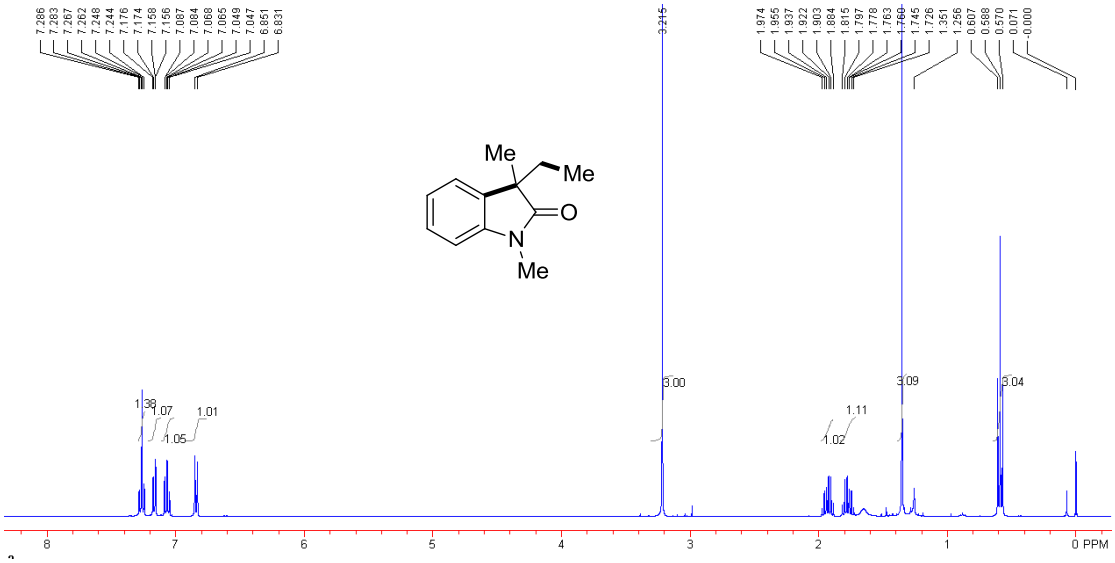
References:

(1). (a) Pinto, A.; Jia, Y.; Neuville, L.; Zhu, J. *Chem.-Eur. J.* **2007**, *13*, 961. (b) Wu, T.; Mu, X.; Liu. G. *Angew. Chem. Int. Ed.* **2011**, *50*, 12578.

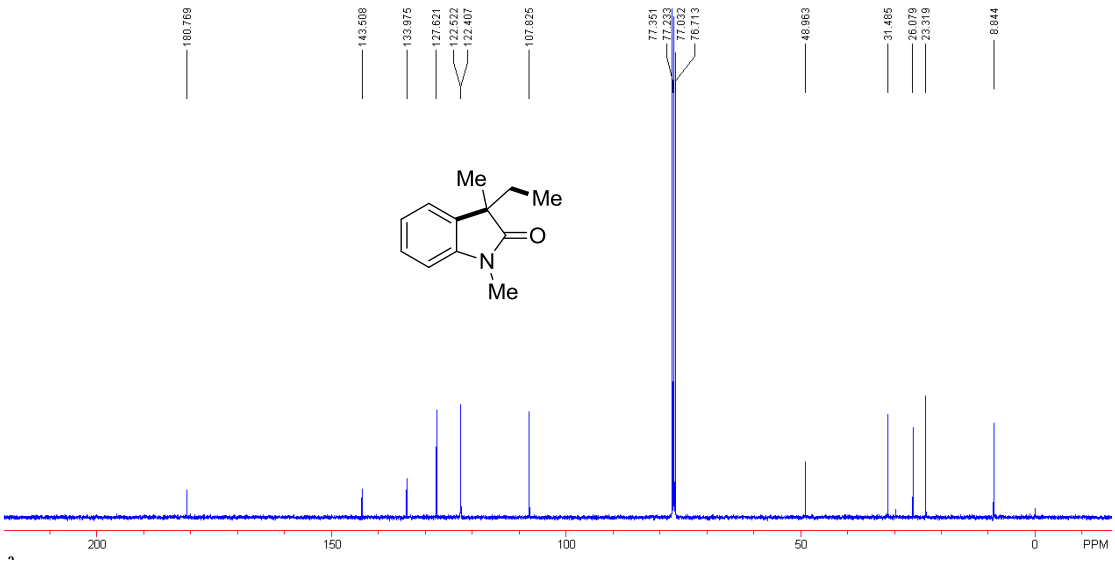
(2) Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.* **1988**, *110*, 3272.

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

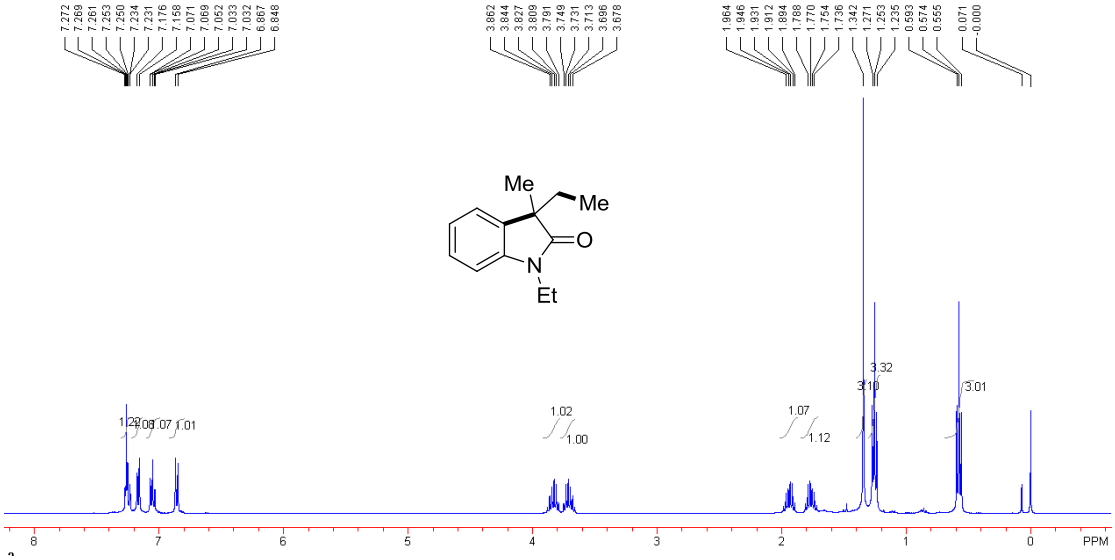
The ^{1}H NMR spectrum of 3a



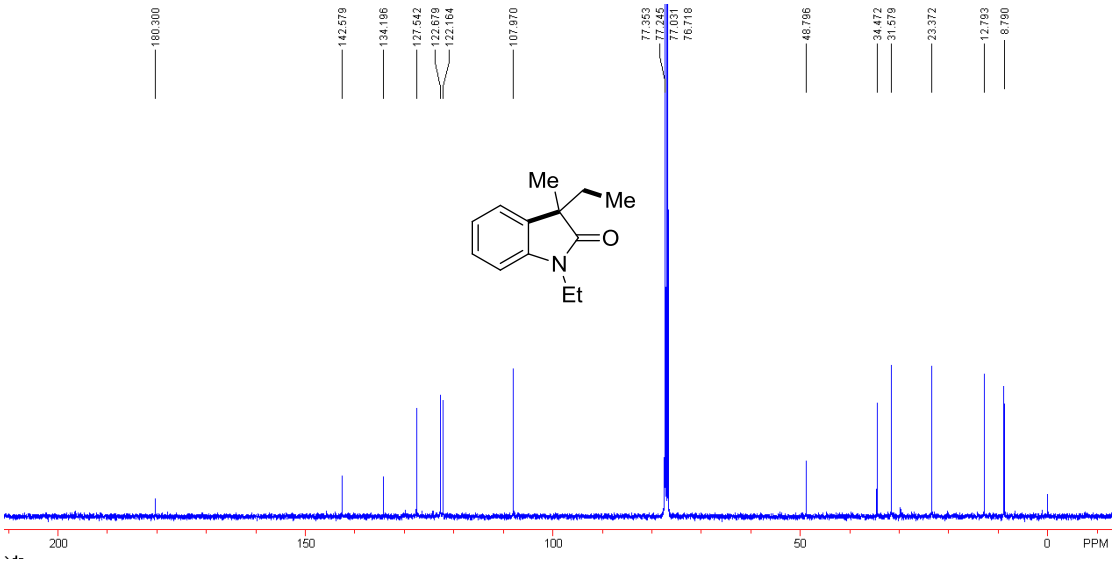
The ^{13}C NMR spectrum of 3a



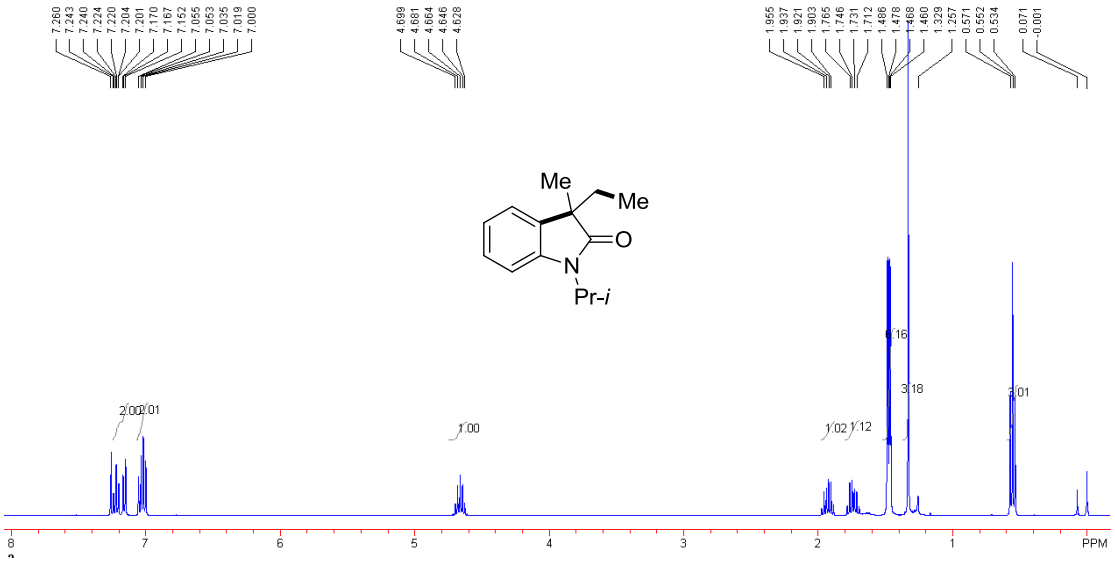
The ^{1}H NMR spectrum of 3b



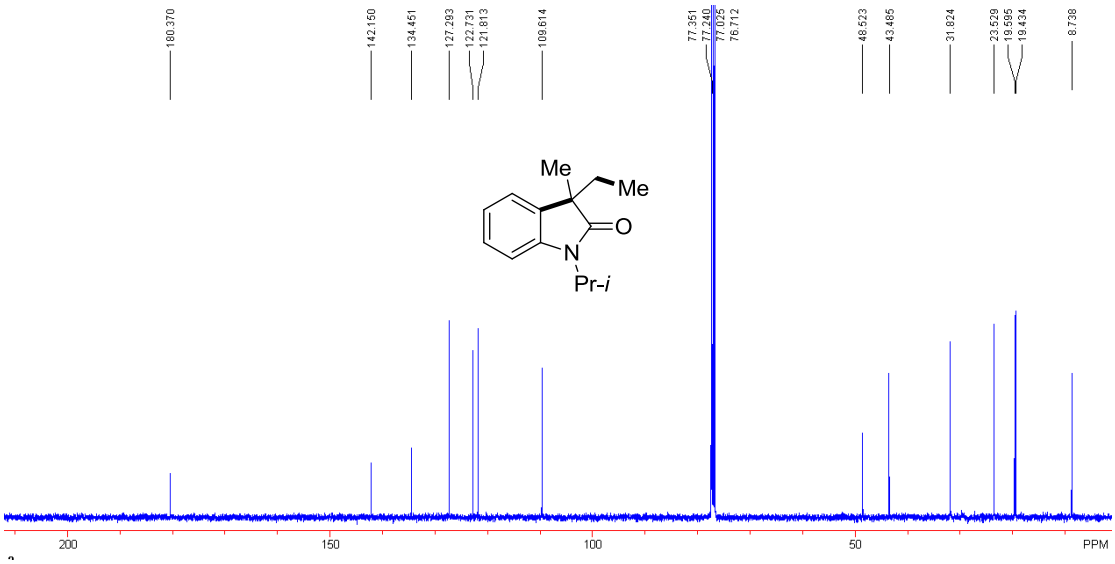
The ^{13}C NMR spectrum of 3b



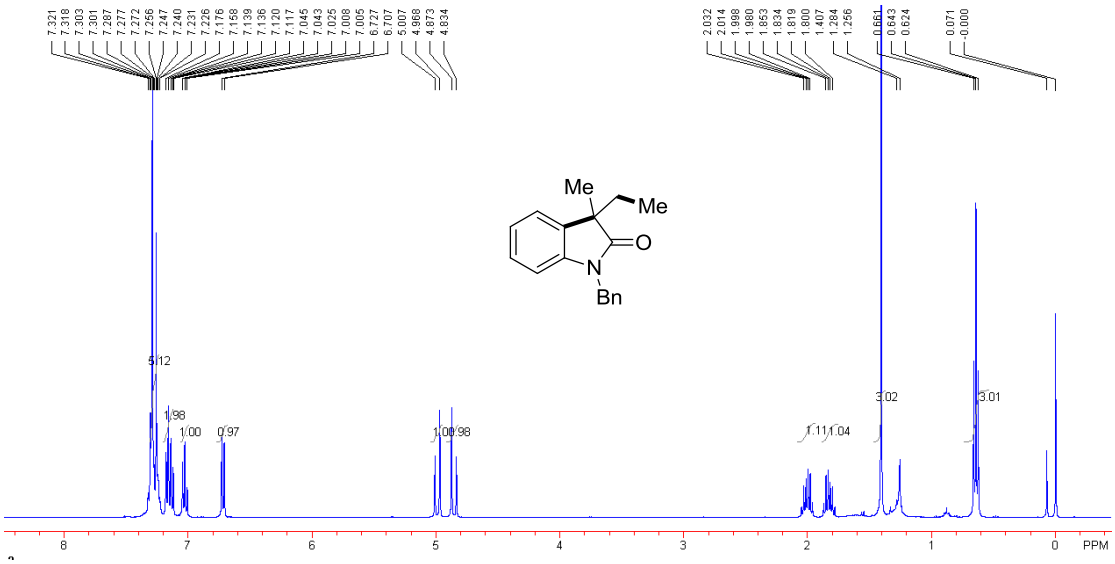
The ^{1}H NMR spectrum of 3c



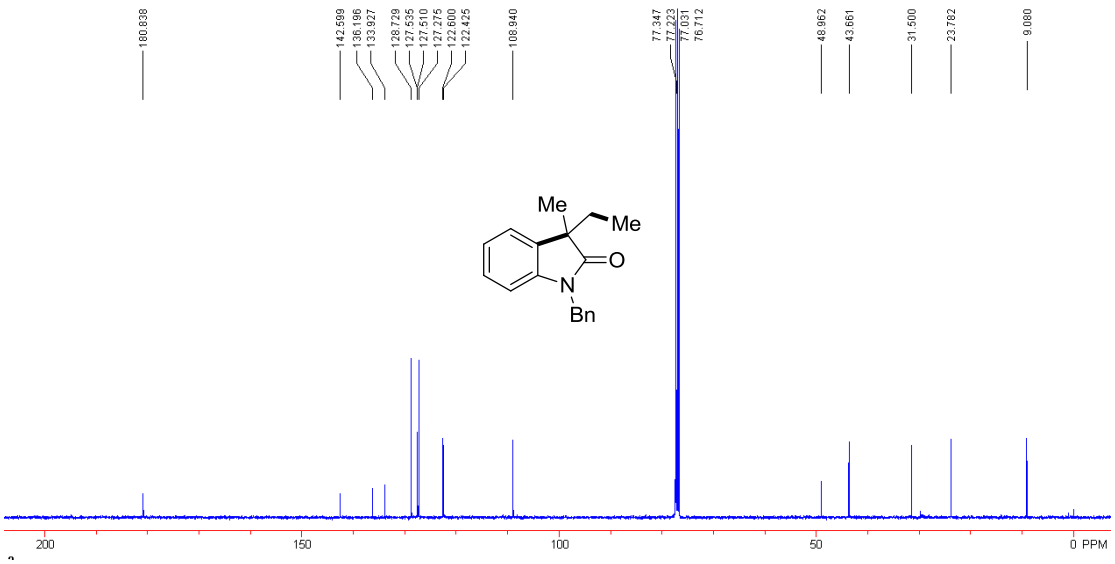
The ^{13}C NMR spectrum of 3c



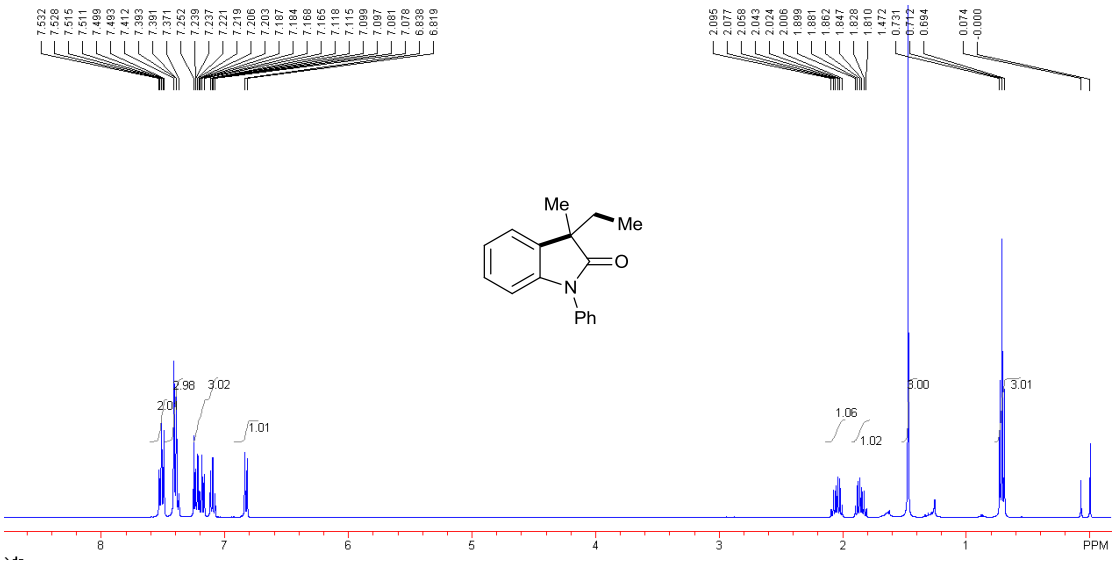
The ^{1}H NMR spectrum of 3d



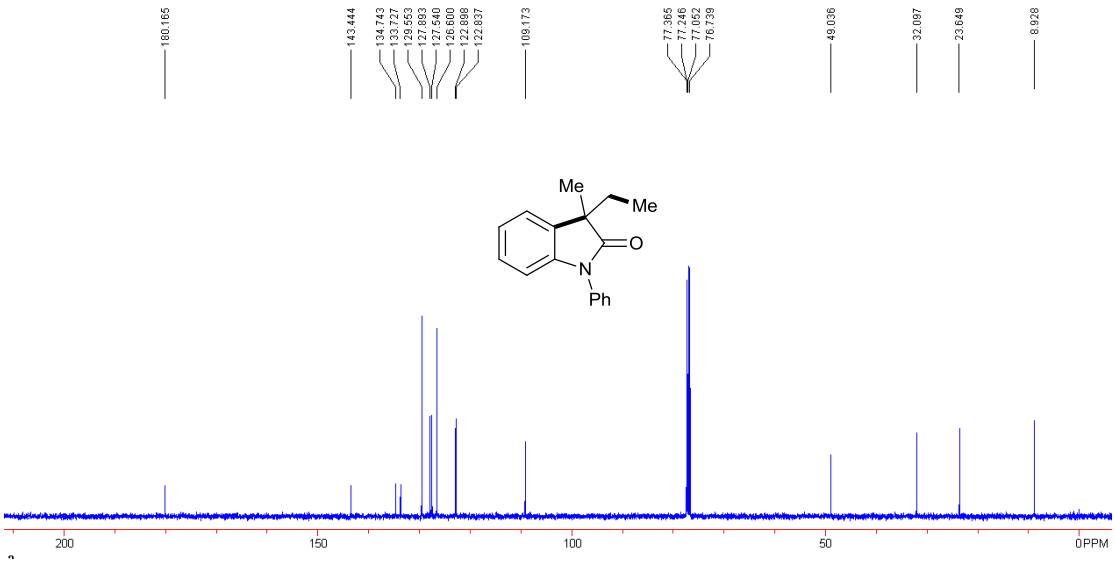
The ^{13}C NMR spectrum of 3d



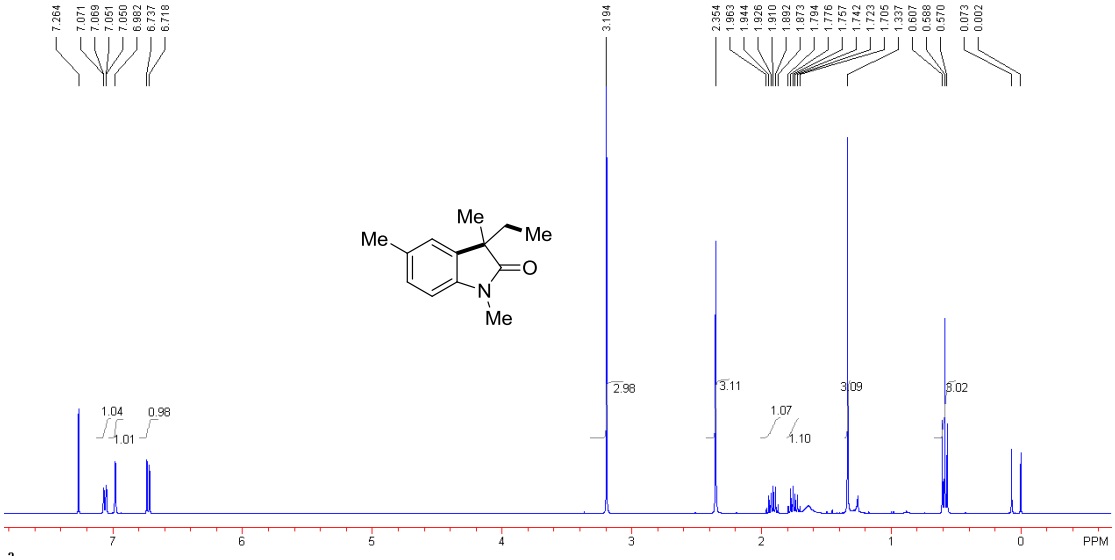
The ^{1}H NMR spectrum of 3e



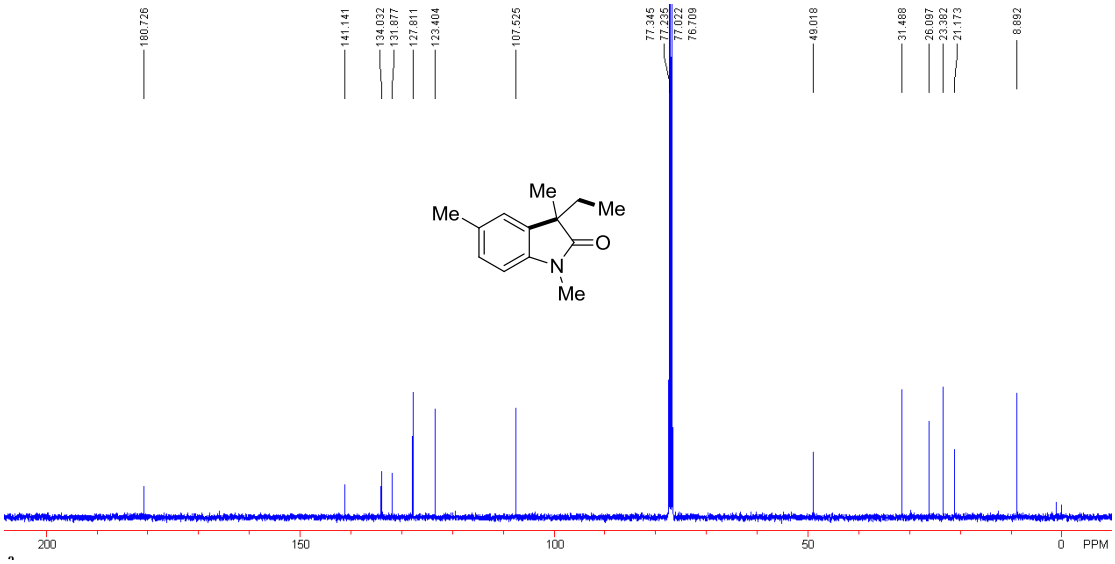
The ^{13}C NMR spectrum of 3e



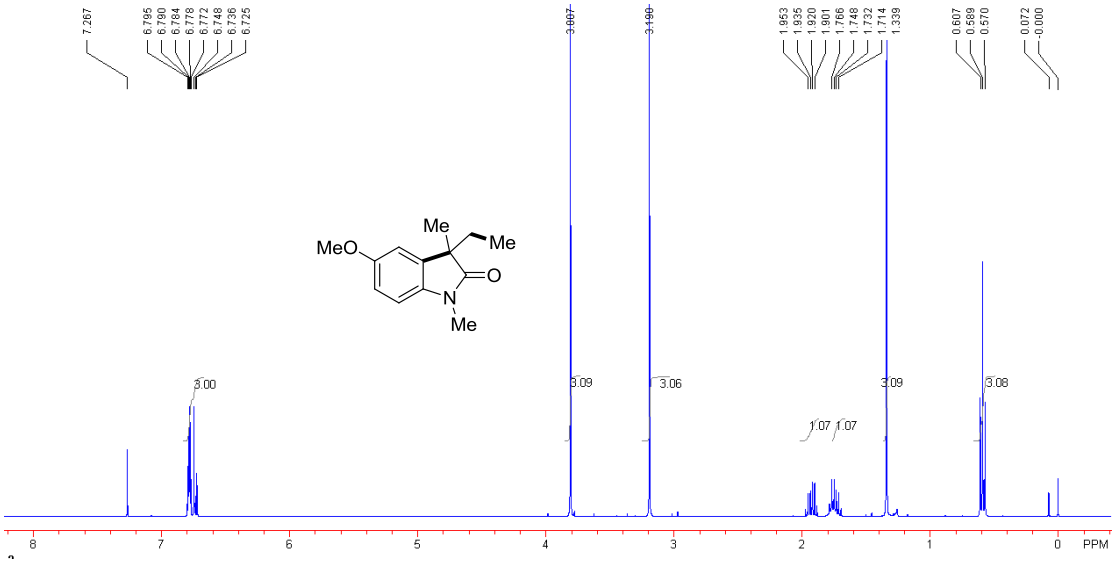
The ^{1}H NMR spectrum of 3f



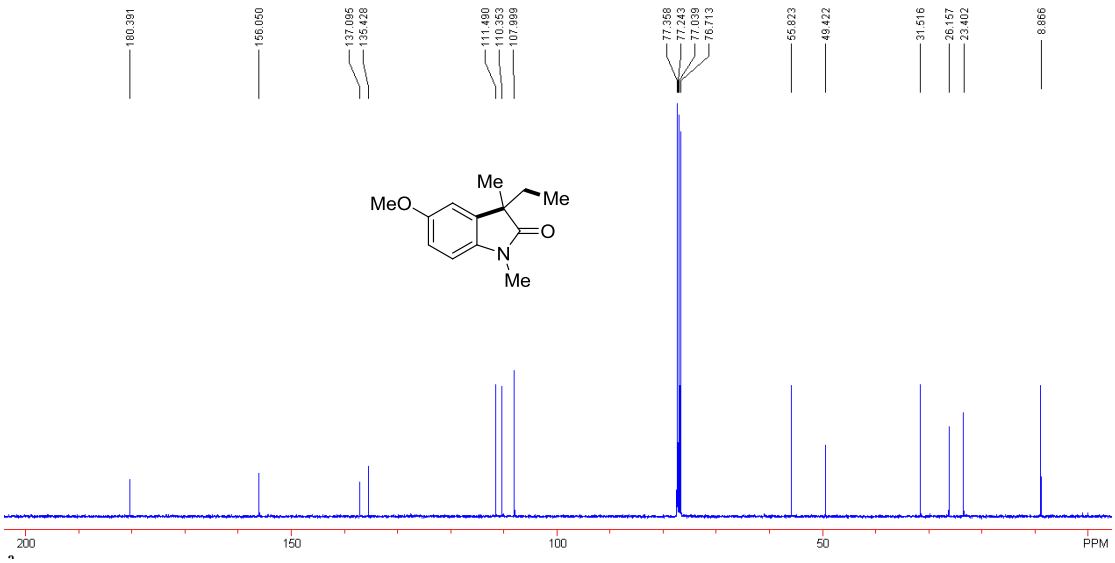
The ^{13}C NMR spectrum of 3f



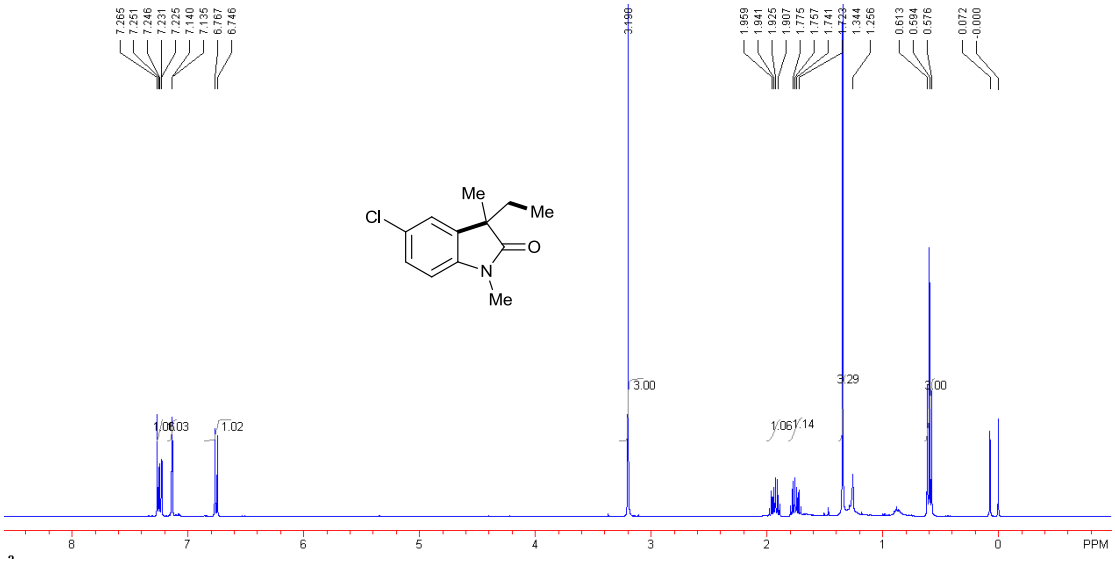
The ^{1}H NMR spectrum of 3g



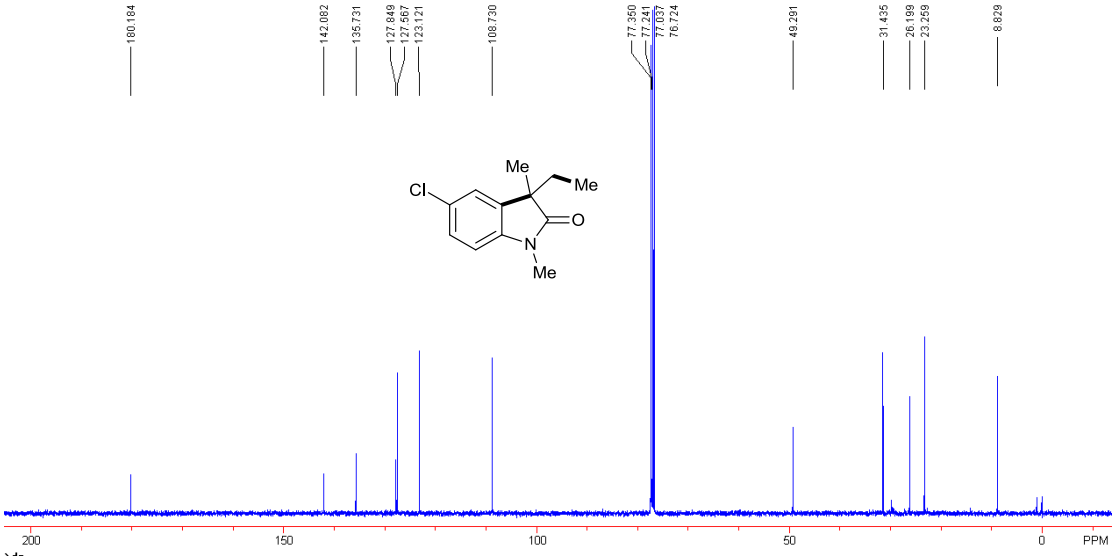
The ^{13}C NMR spectrum of 3g



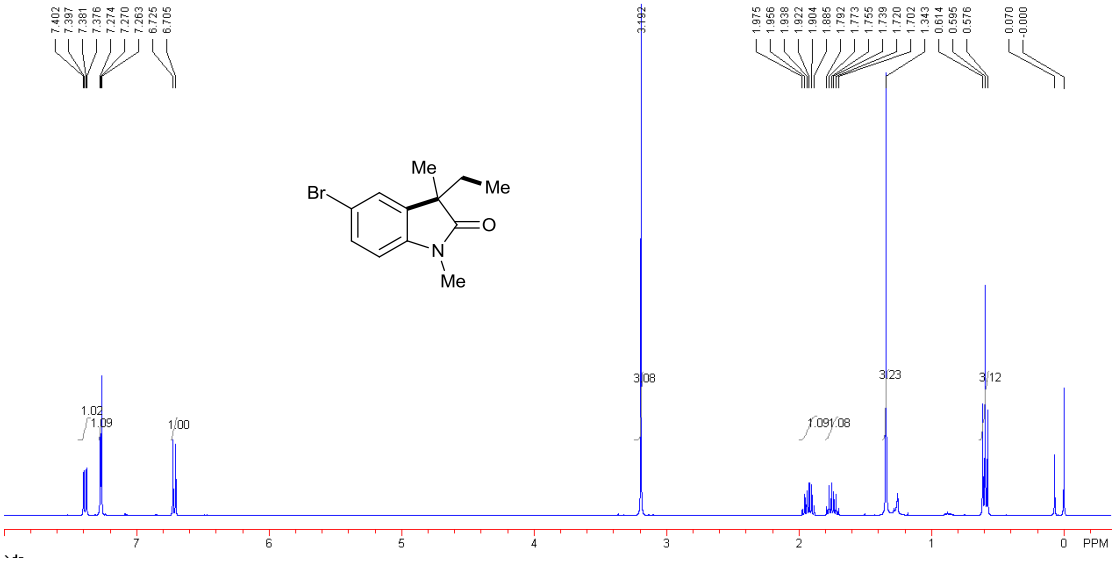
The ^{1}H NMR spectrum of 3h



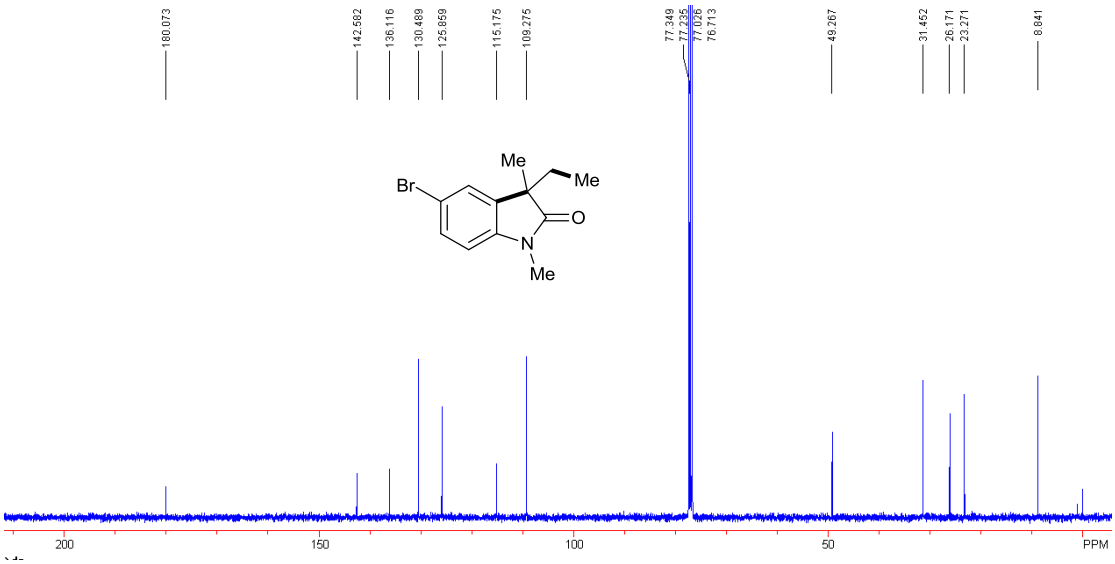
The ^{13}C NMR spectrum of 3h



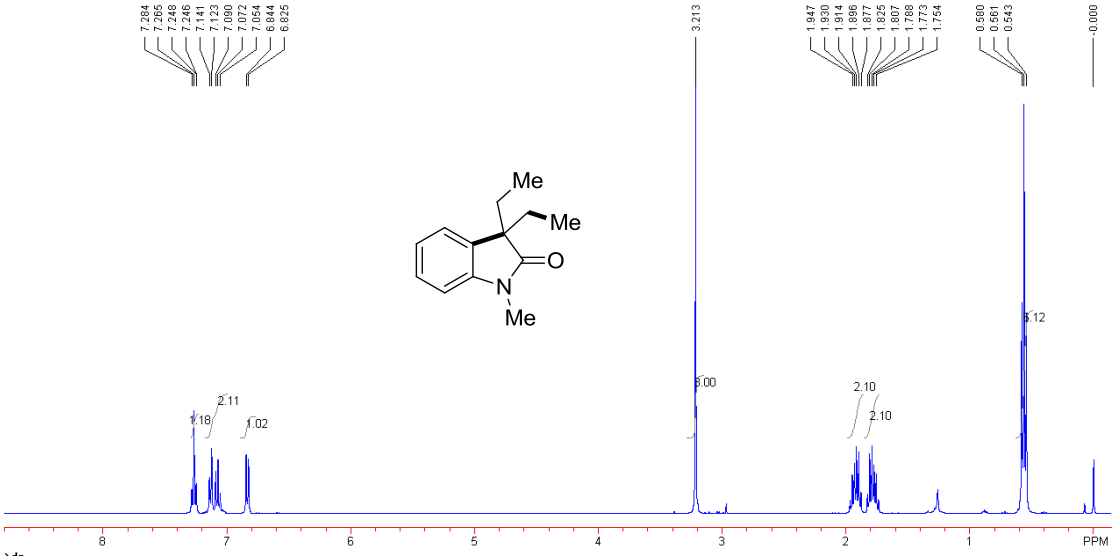
The ^{1}H NMR spectrum of 3i



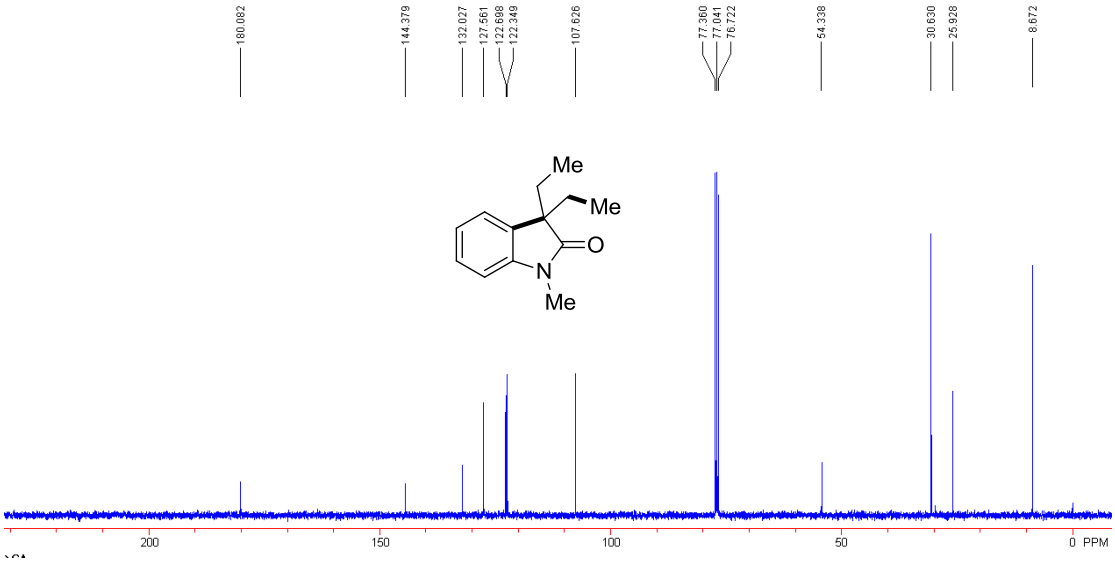
The ^{13}C NMR spectrum of 3i



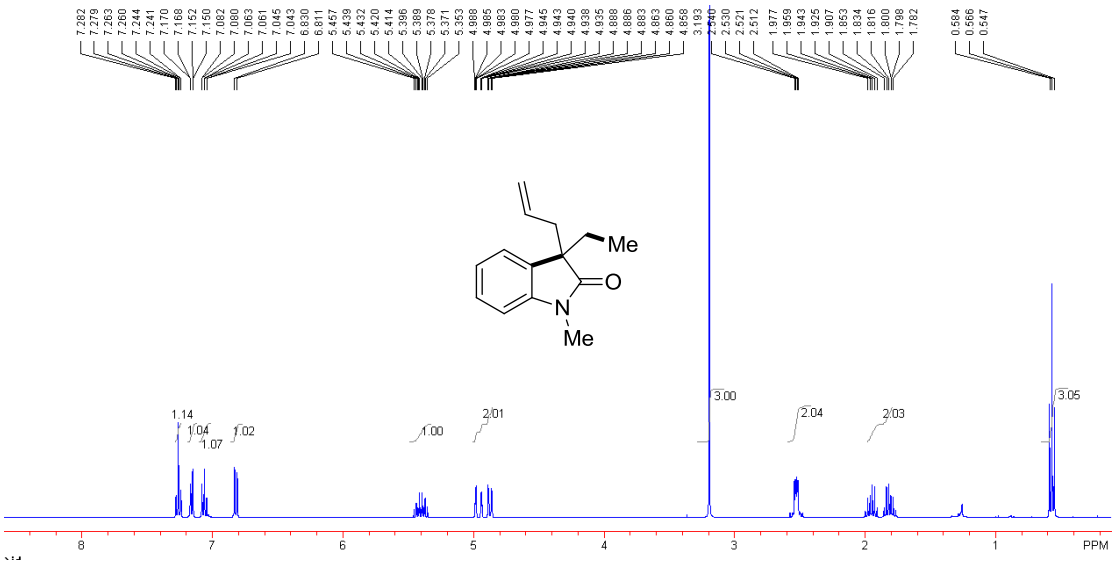
The ^{1}H NMR spectrum of 3k



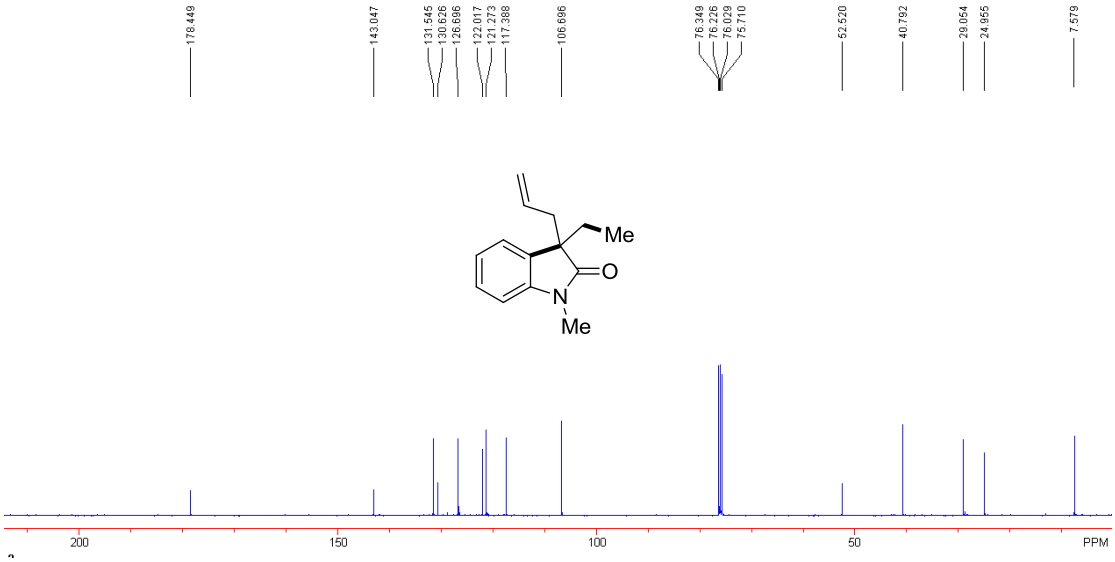
The ^{13}C NMR spectrum of 3k



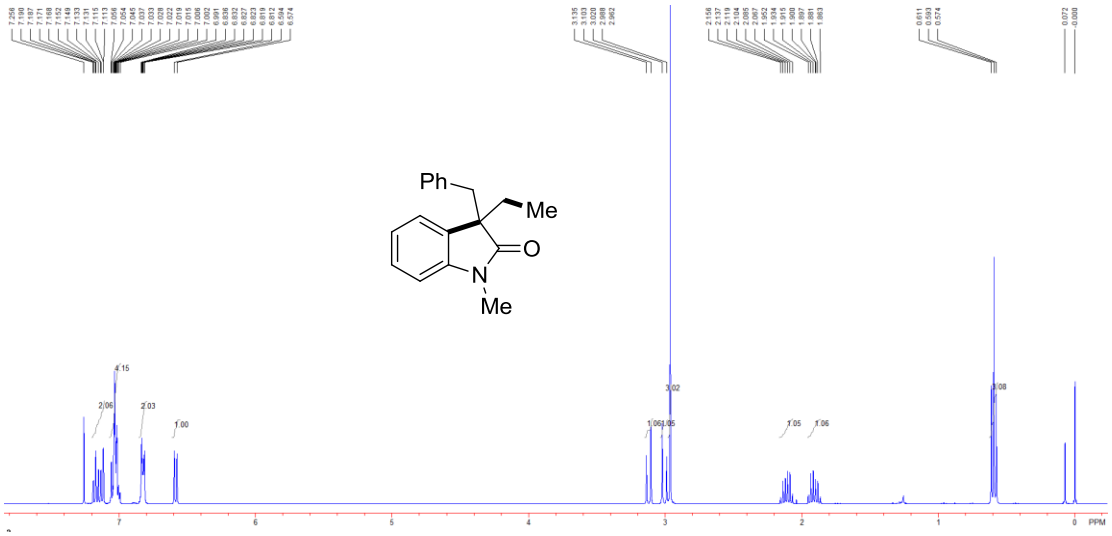
The ^{1}H NMR spectrum of 3l



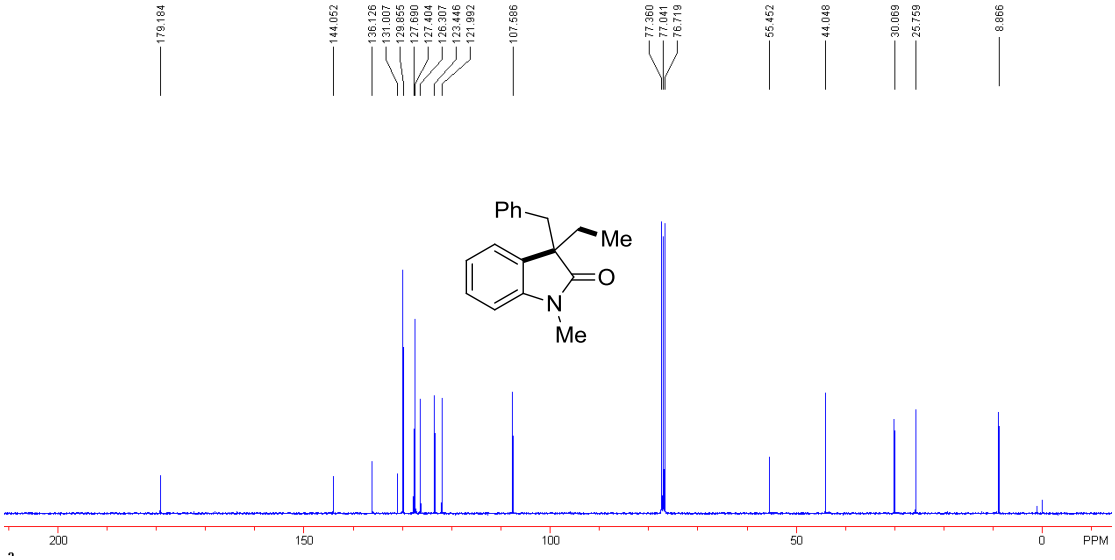
The ^{13}C NMR spectrum of 3l



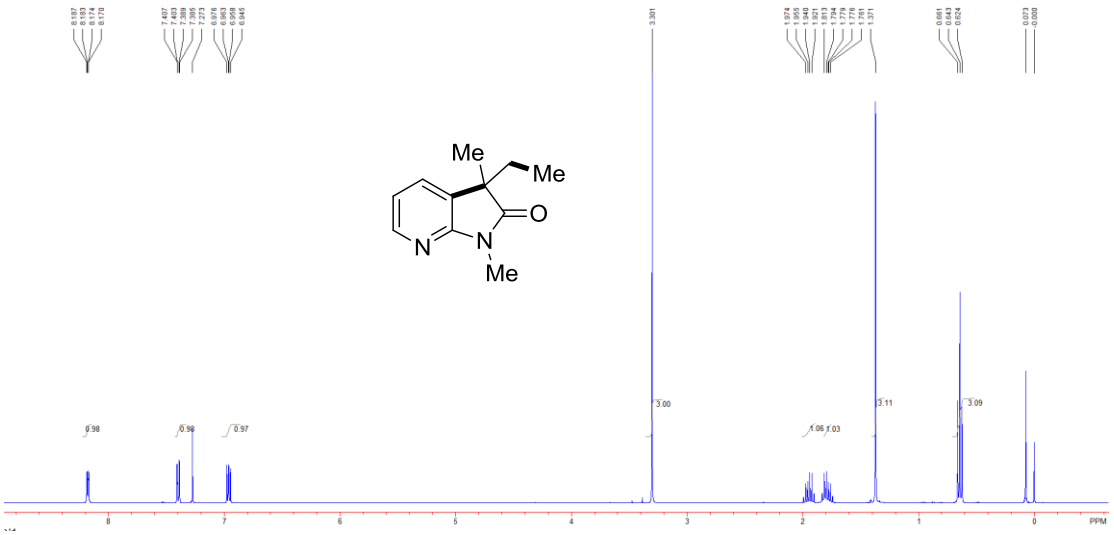
The ^{1}H NMR spectrum of 3m



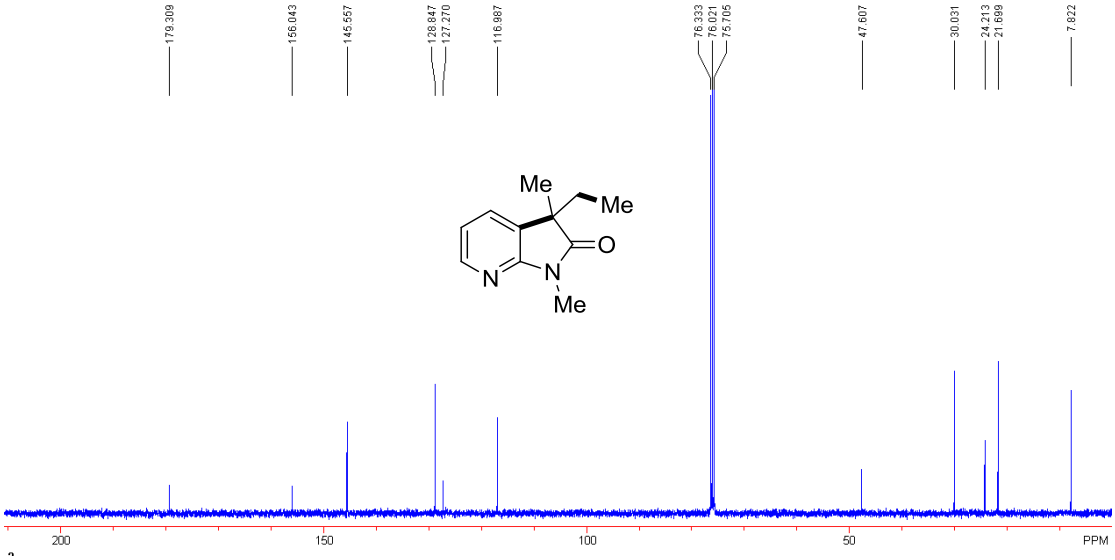
The ^{13}C NMR spectrum of 3m



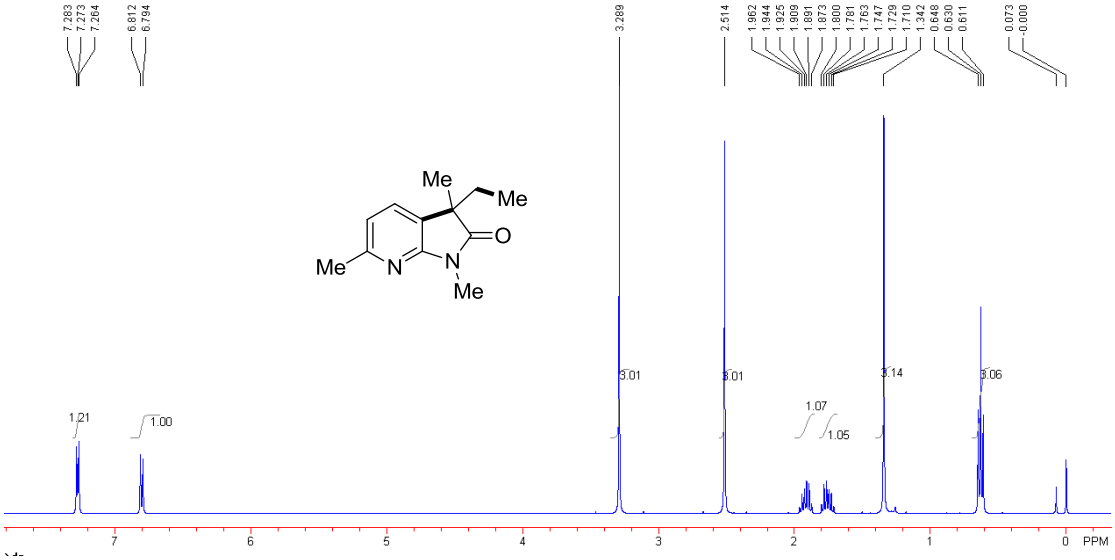
The ^{1}H NMR spectrum of 3n



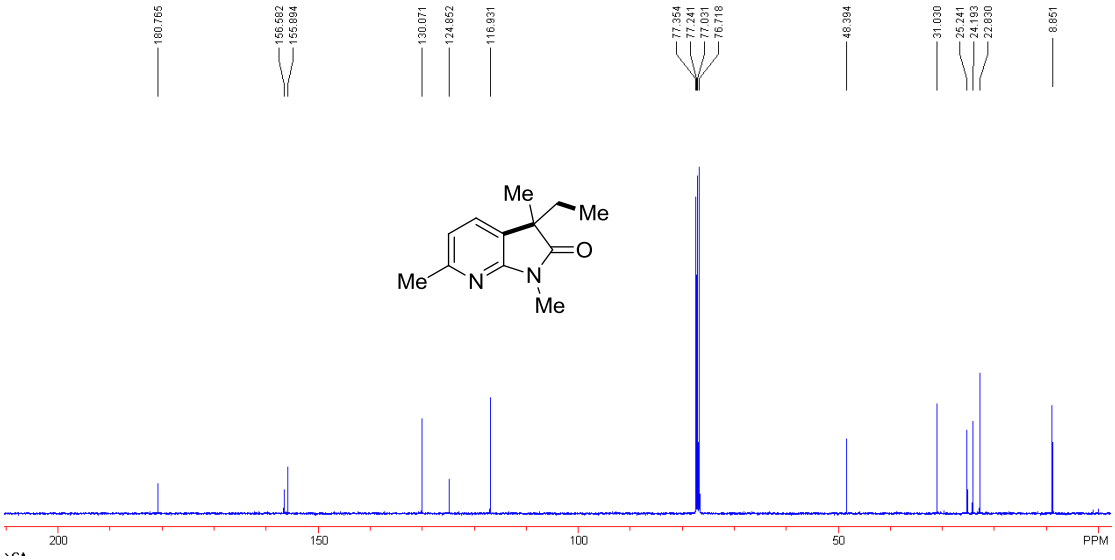
The ^{13}C NMR spectrum of 3n



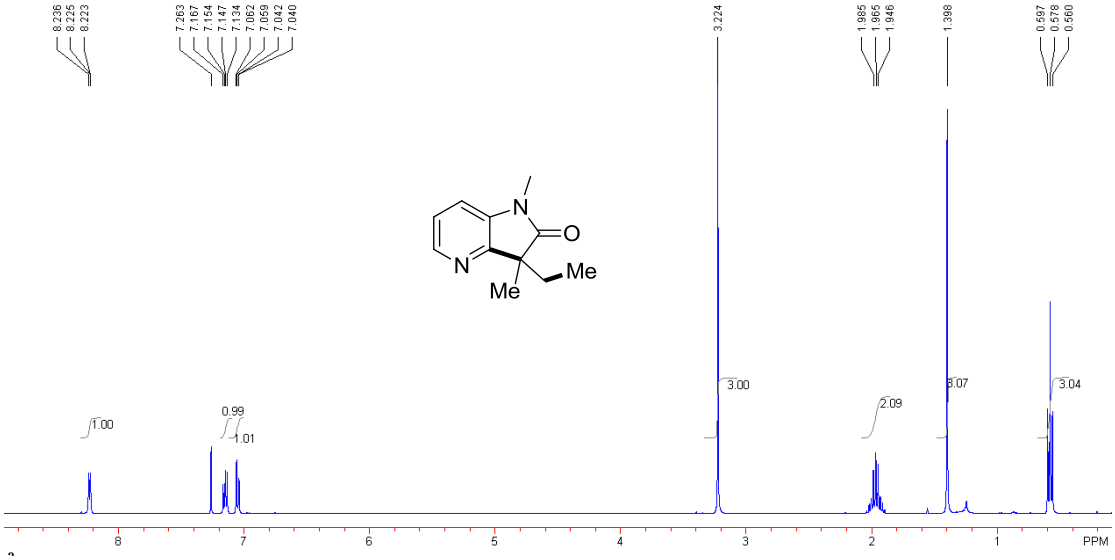
The ^{1}H NMR spectrum of 3o



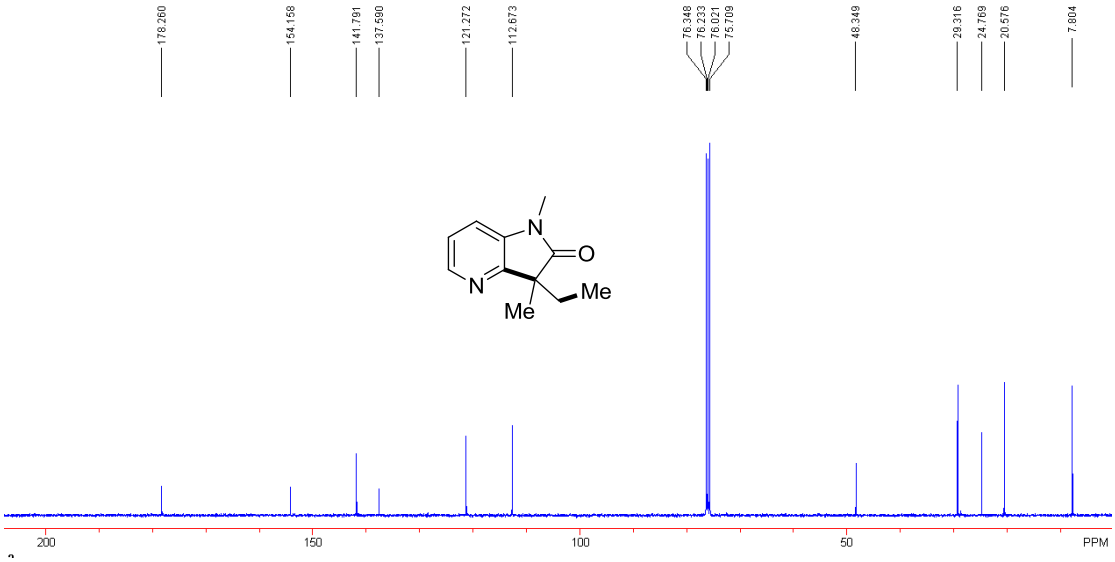
The ^{13}C NMR spectrum of 3o



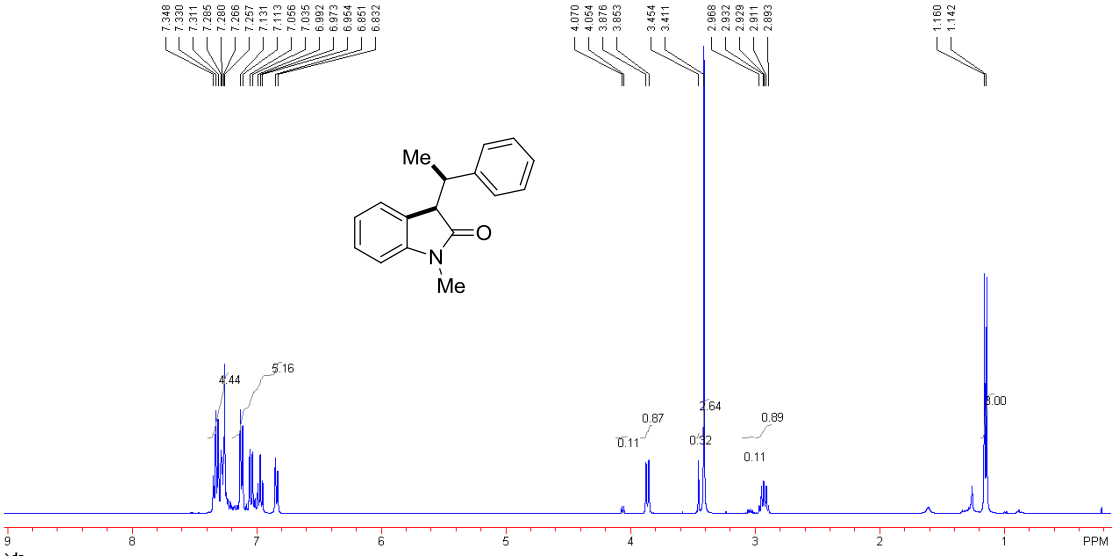
The ^{13}C NMR spectrum of 3p



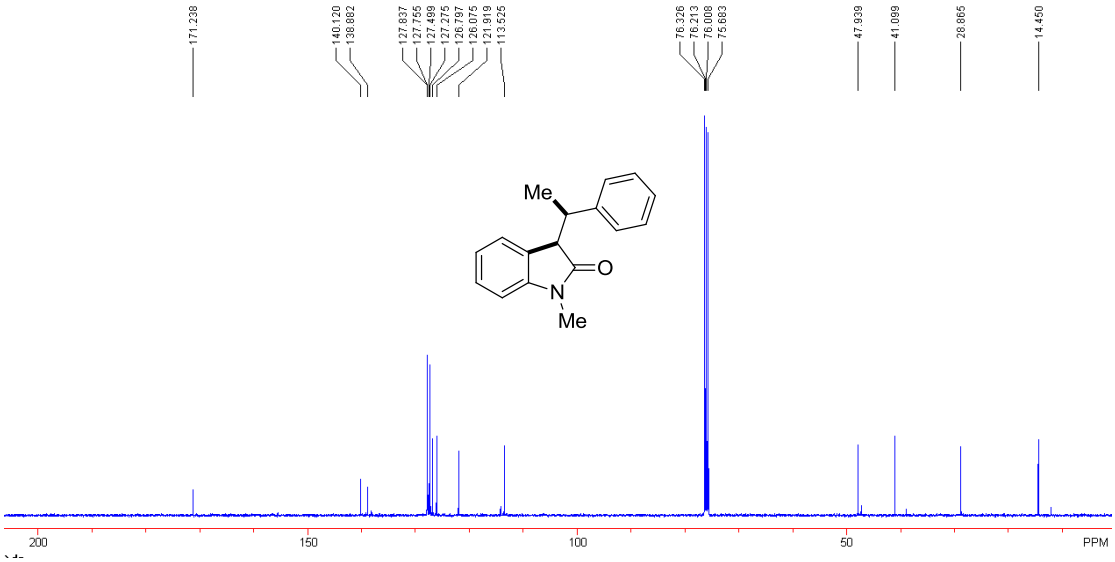
The ^{13}C NMR spectrum of 3p



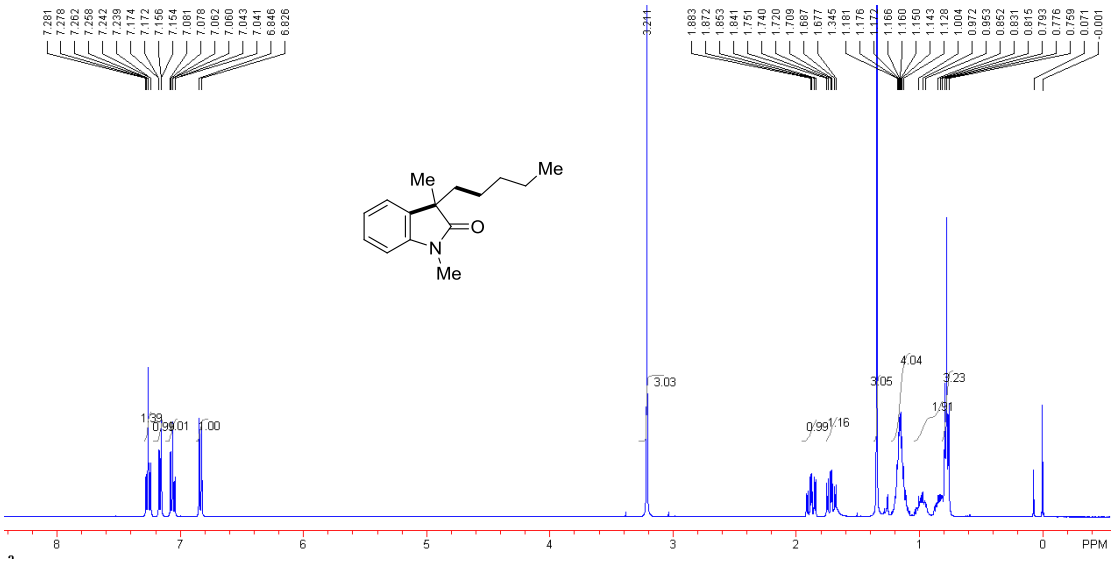
The ^{1}H NMR spectrum of 3q



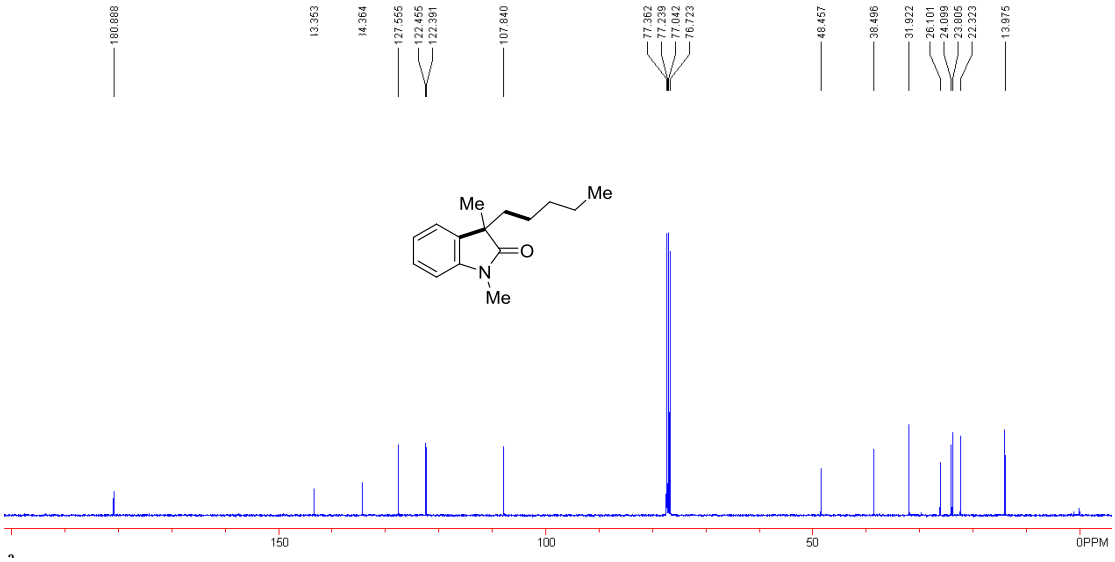
The ^{13}C NMR spectrum of 3q



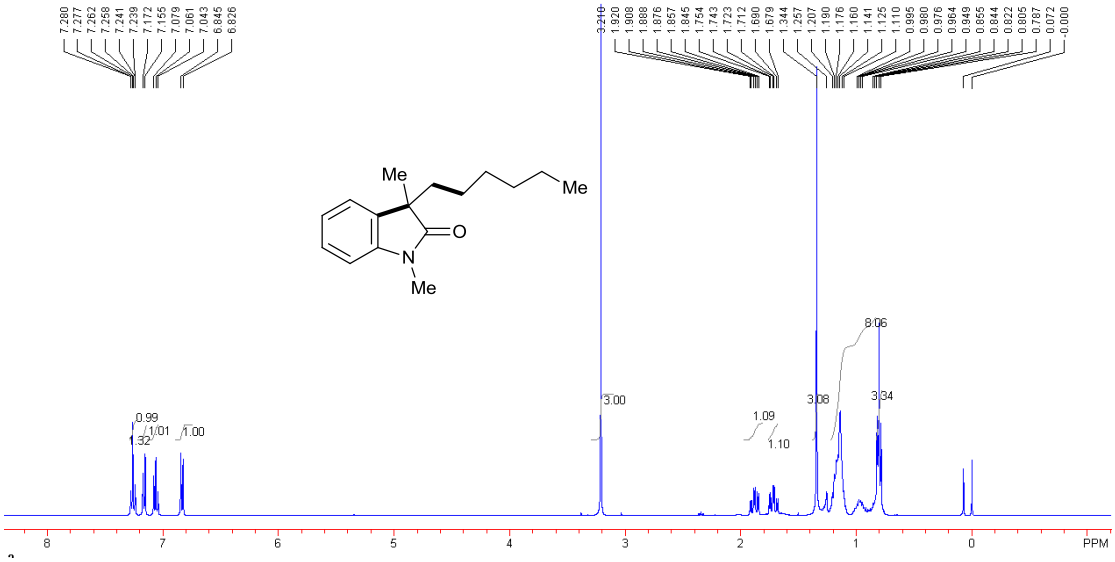
The ^{1}H NMR spectrum of 4a



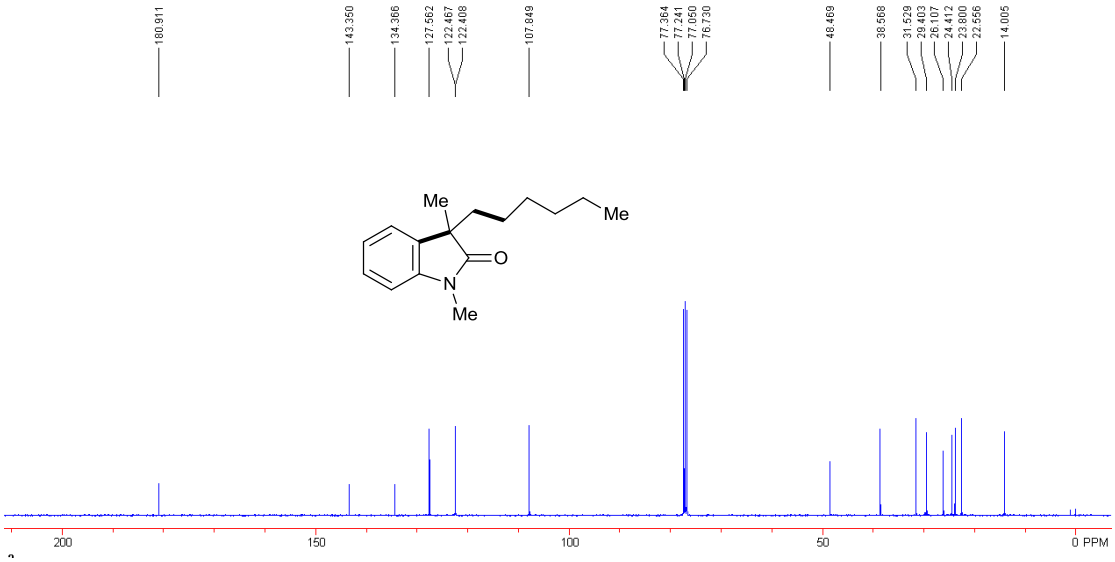
The ^{13}C NMR spectrum of 4a



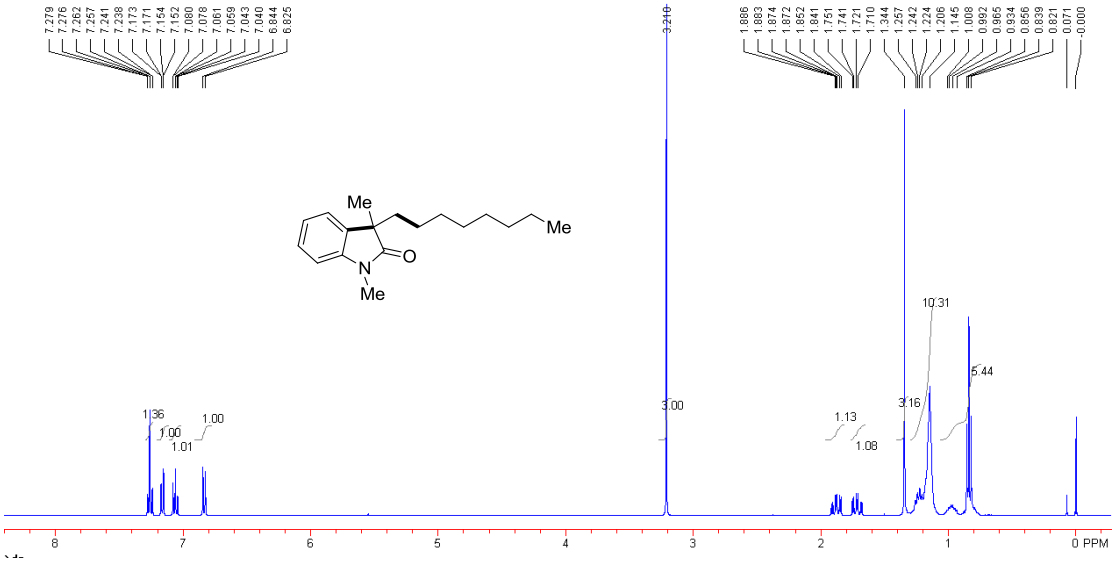
The ^{1}H NMR spectrum of 4b



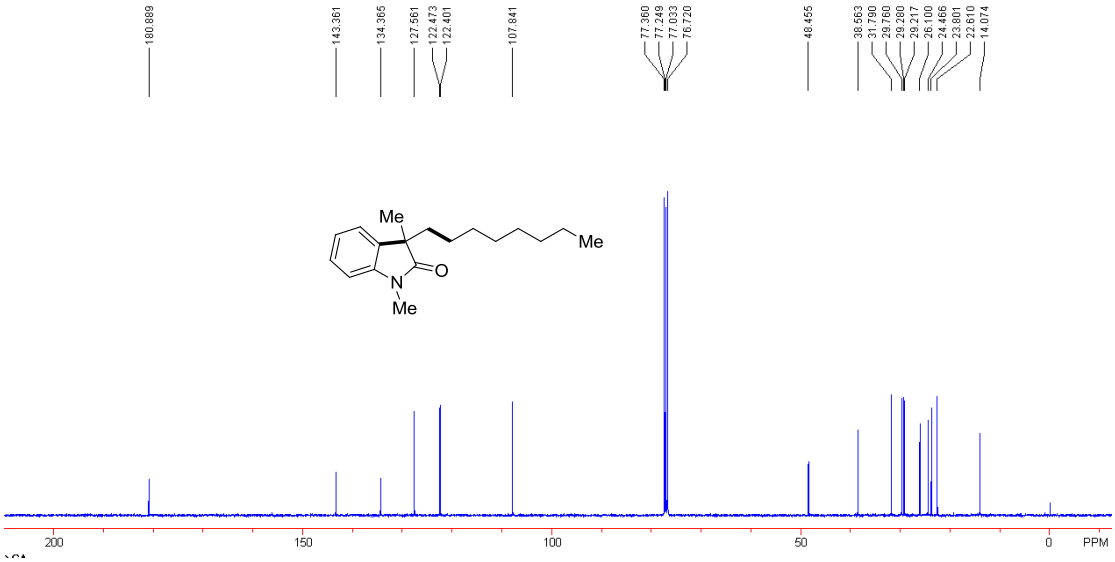
The ^{13}C NMR spectrum of 4b



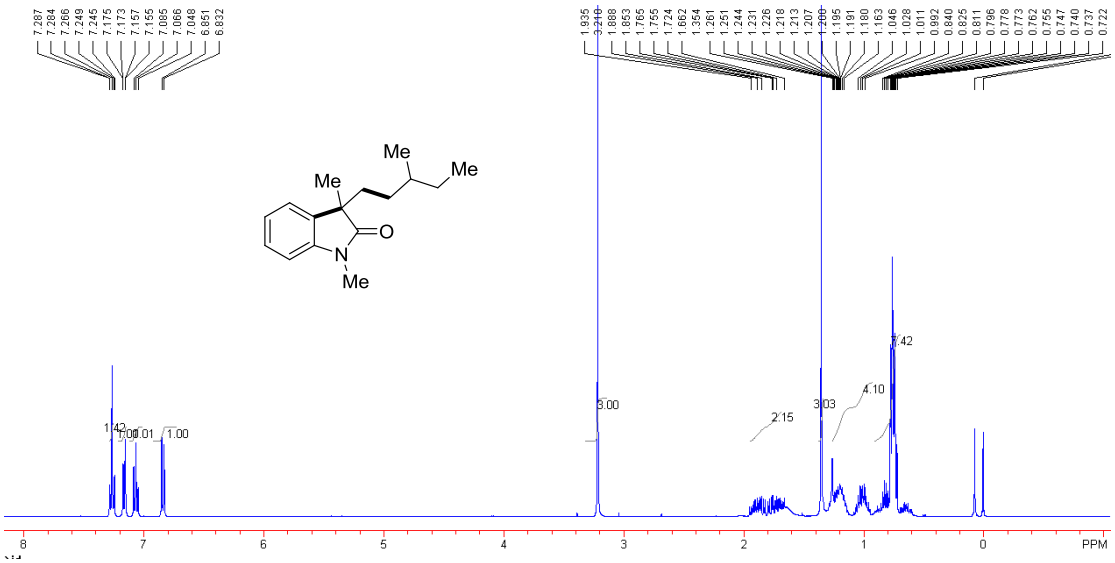
The ^{1}H NMR spectrum of 4c



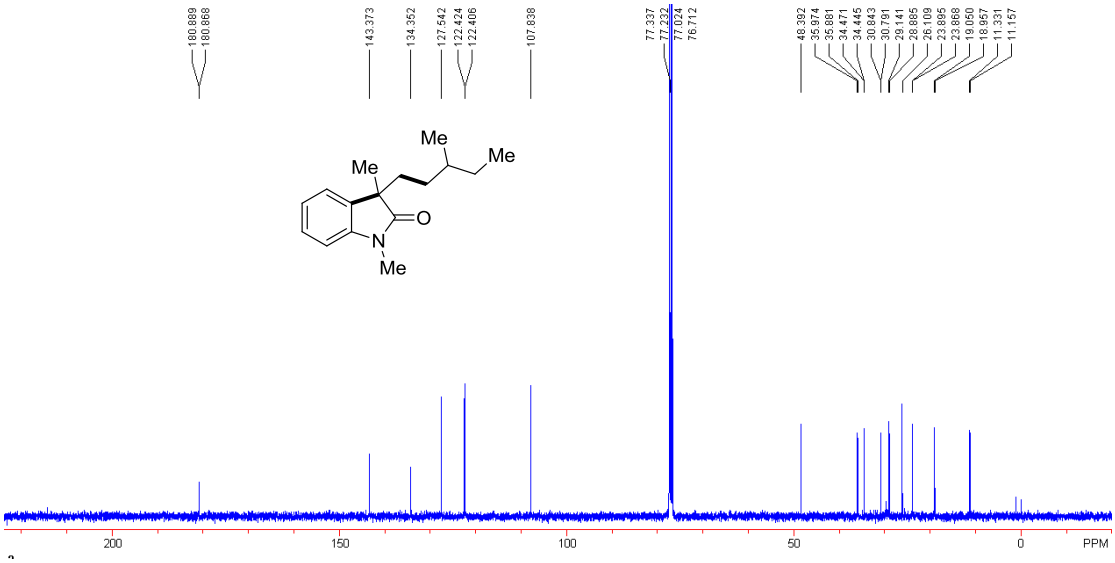
The ^{13}C NMR spectrum of 4c



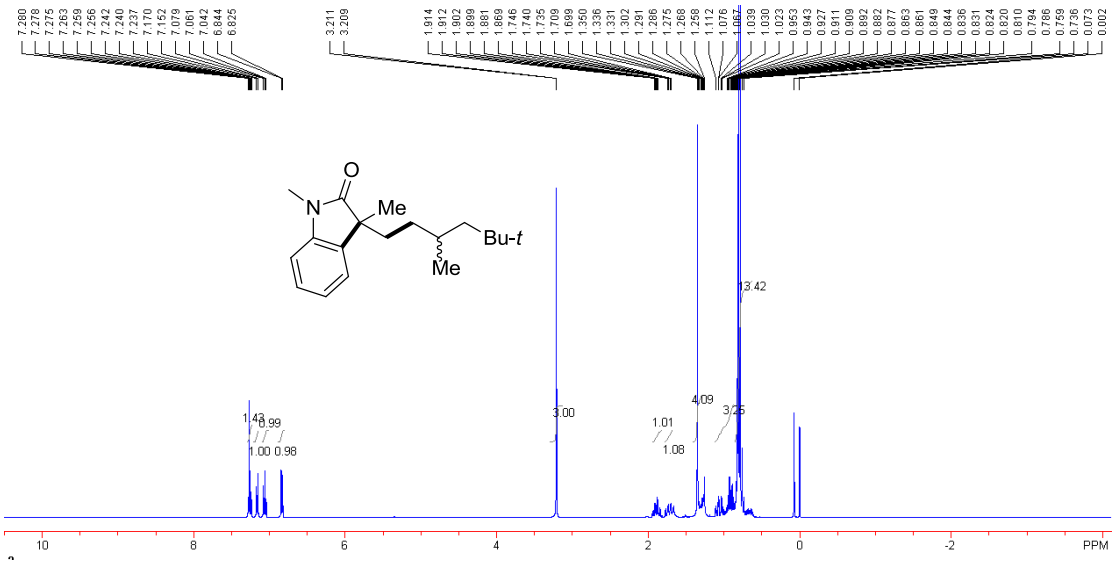
The ^{1}H NMR spectrum of 4d



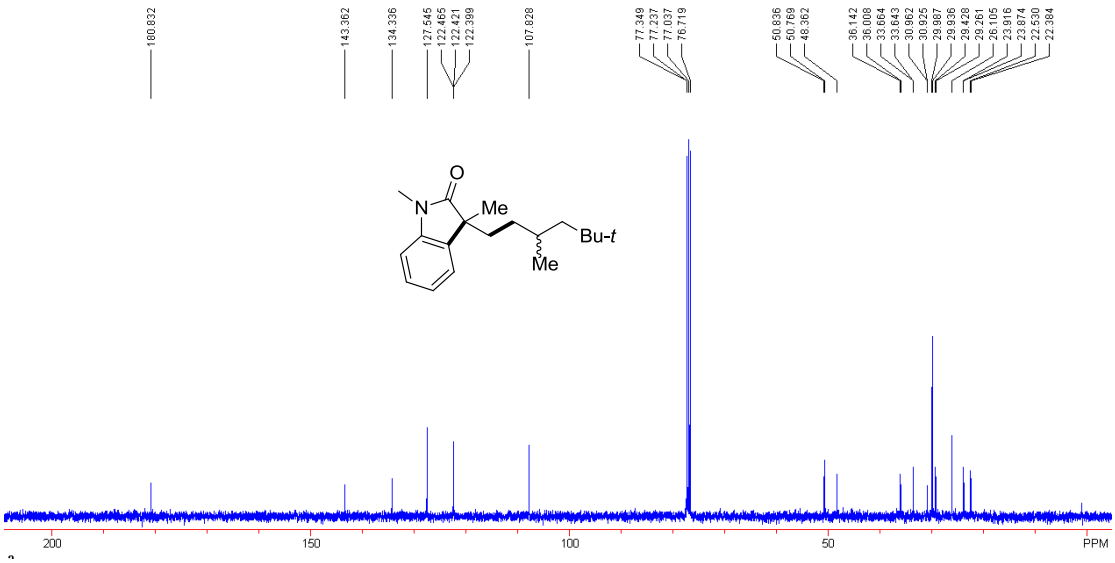
The ^{13}C NMR spectrum of 4d



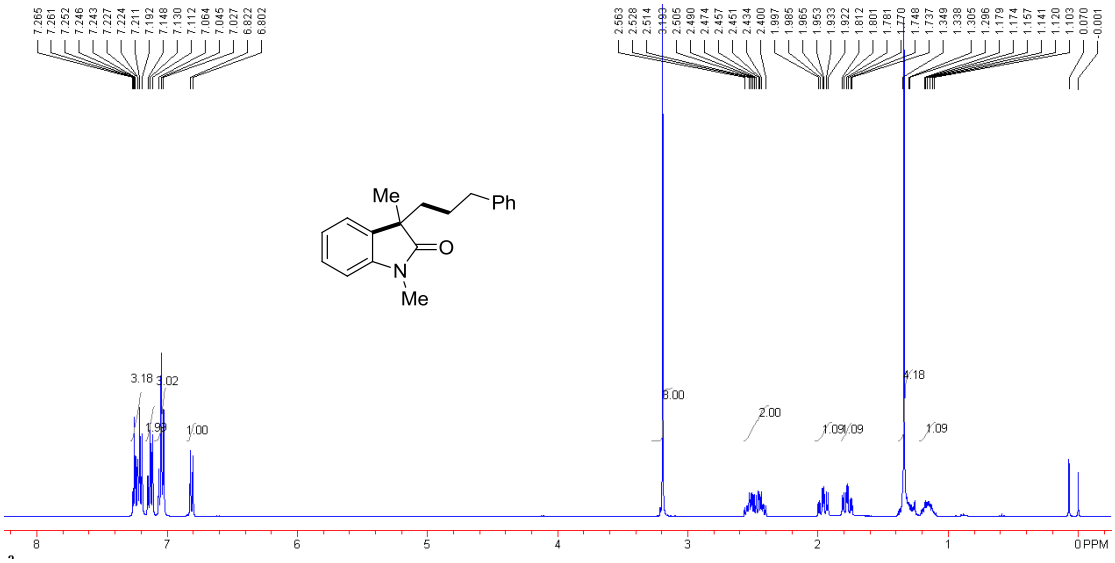
The ^{1}H NMR spectrum of 4e



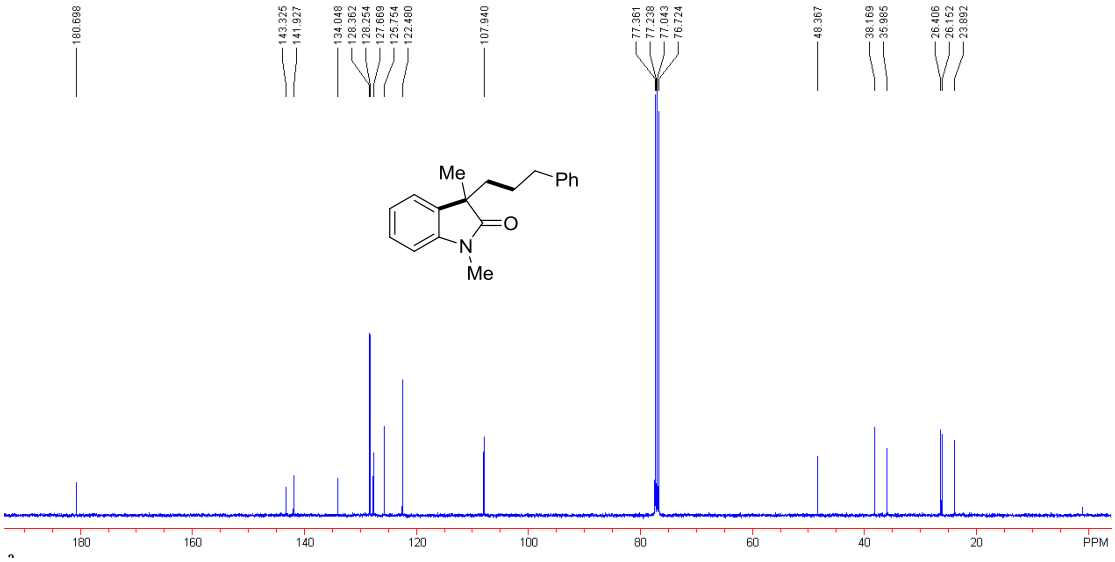
The ^{13}C NMR spectrum of 4e



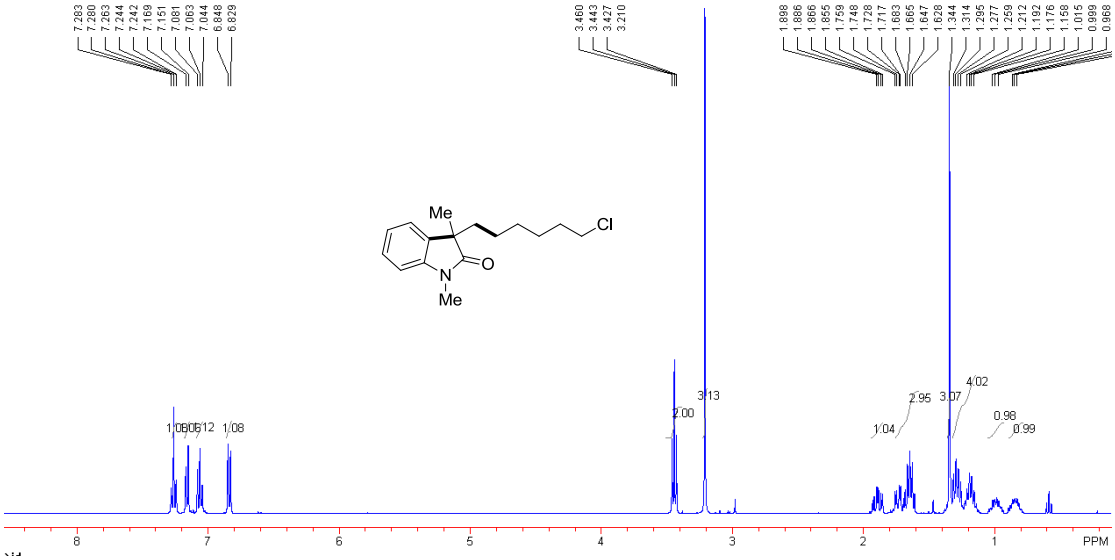
The ^{1}H NMR spectrum of 4f



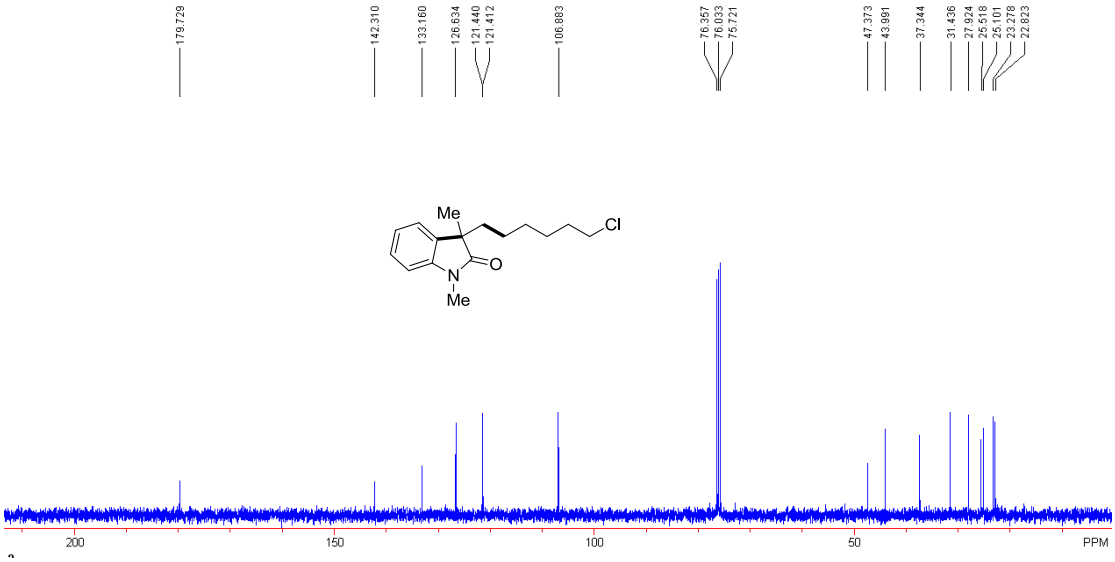
The ^{13}C NMR spectrum of 4f



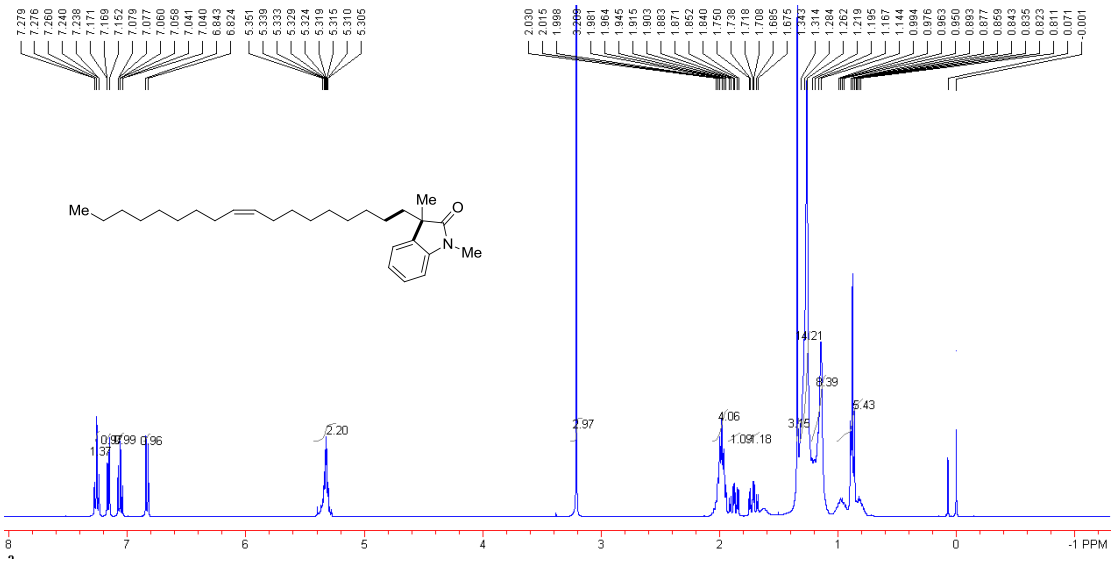
The ^{1}H NMR spectrum of 4g



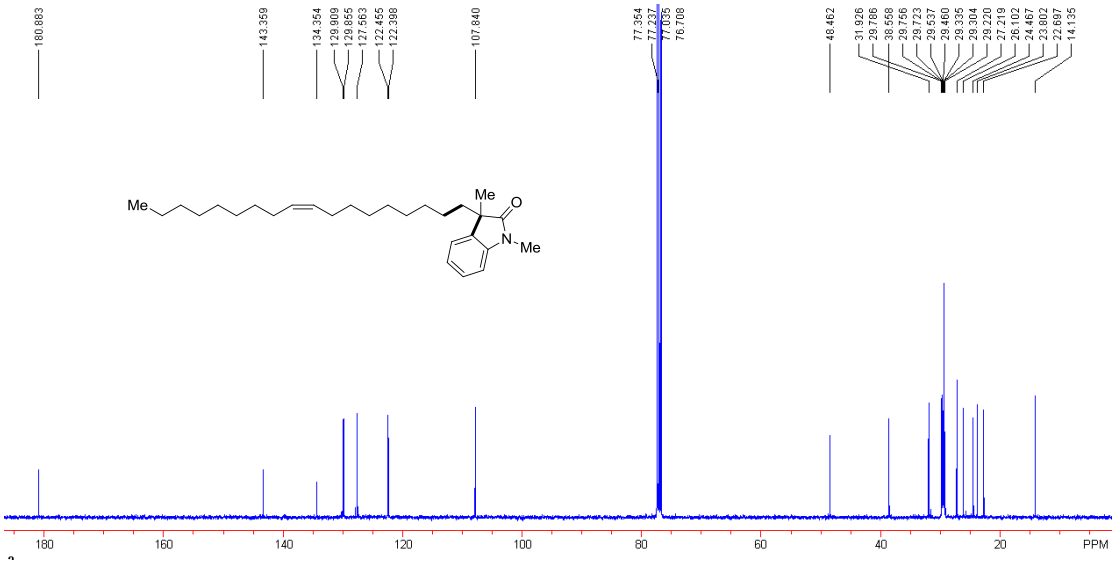
The ^{13}C NMR spectrum of 4g



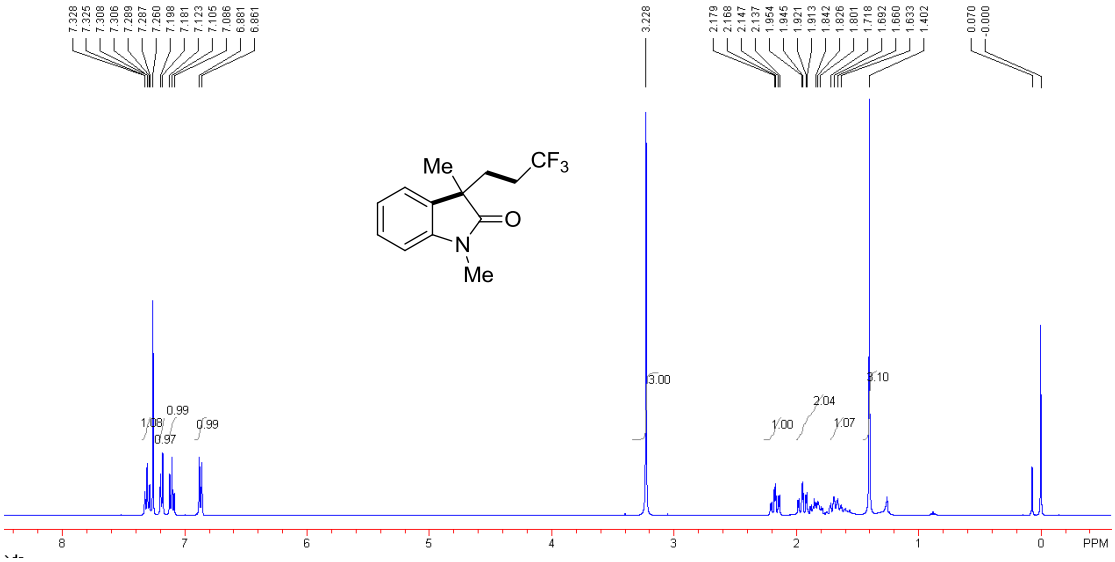
The ^{1}H NMR spectrum of 4h



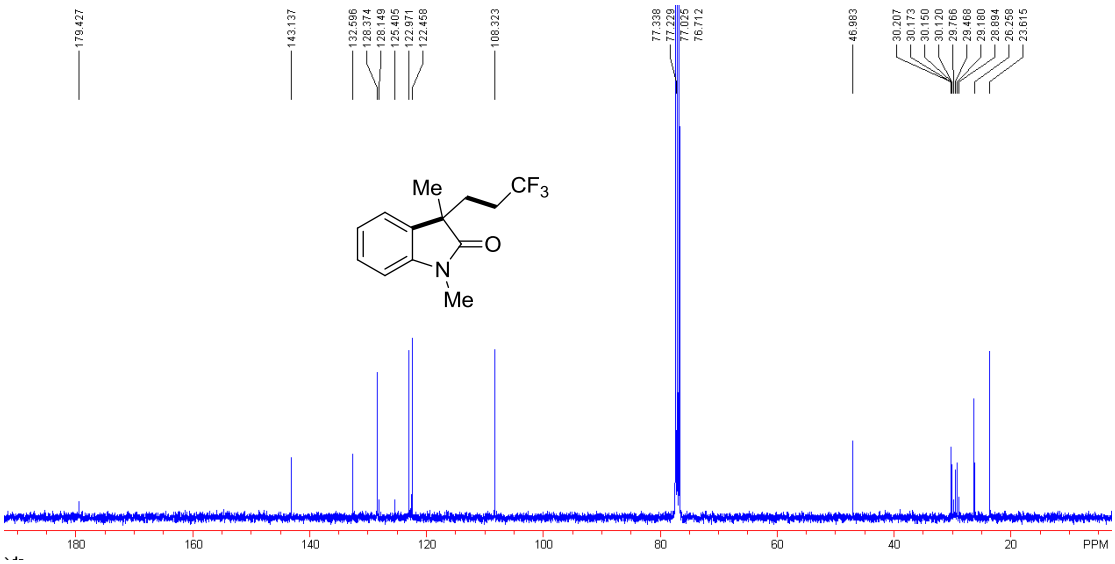
The ^{13}C NMR spectrum of 4h



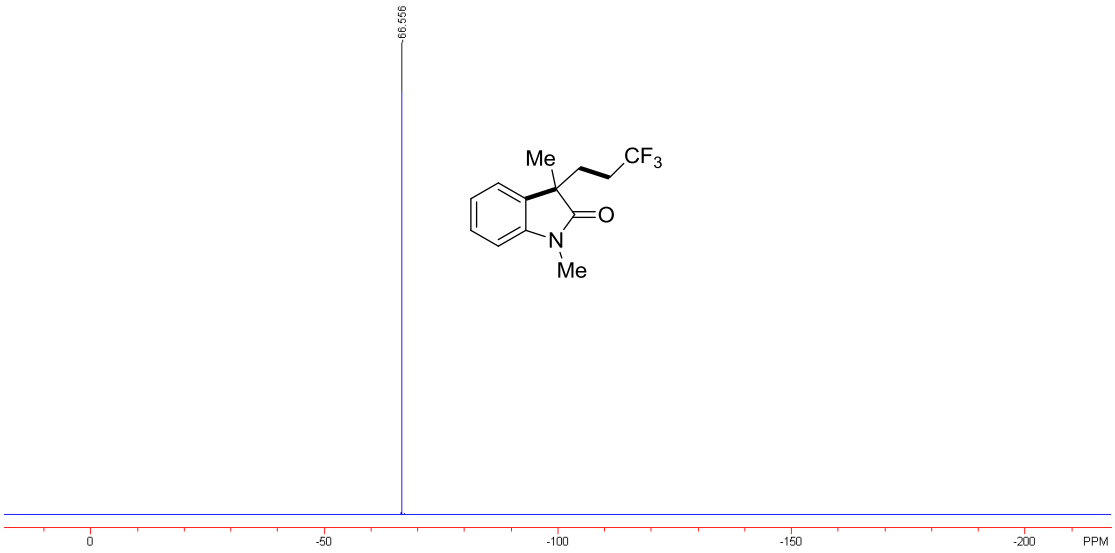
The ^{1}H NMR spectrum of 4i



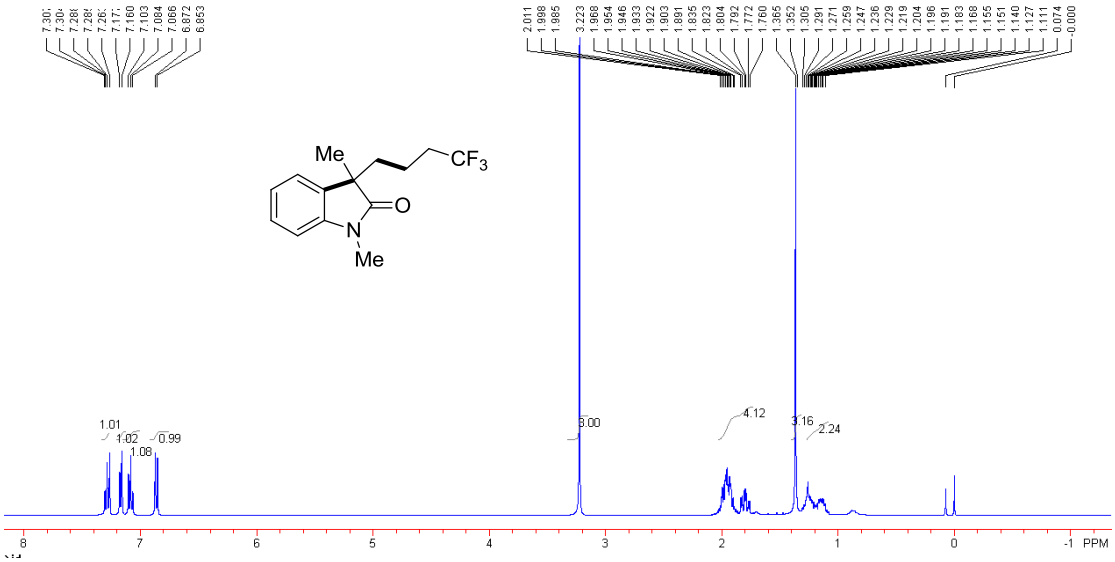
The ^{13}C NMR spectrum of 4i



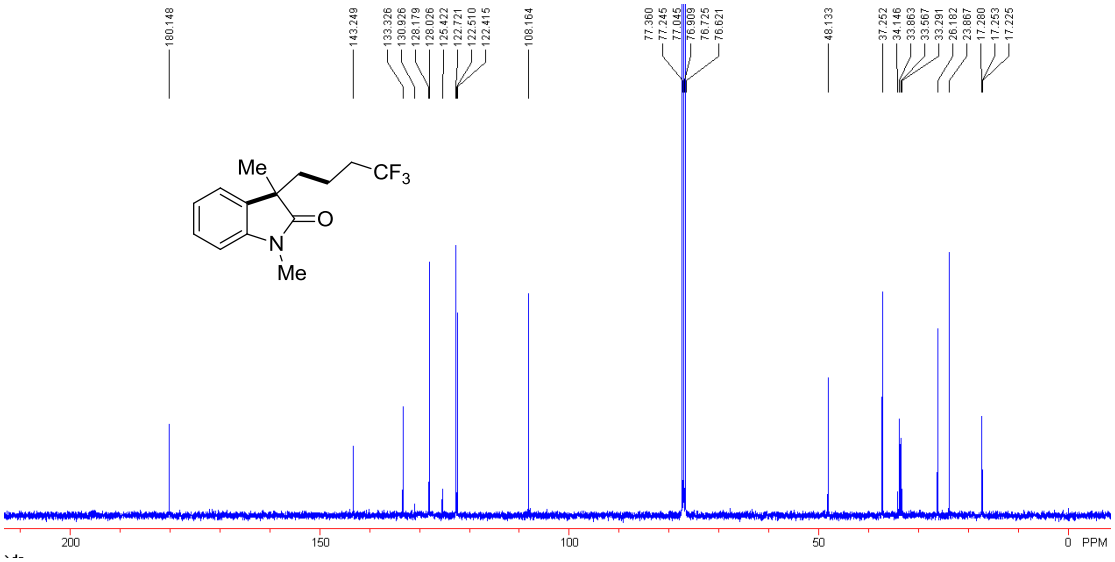
The ^{19}F NMR spectrum of 4i



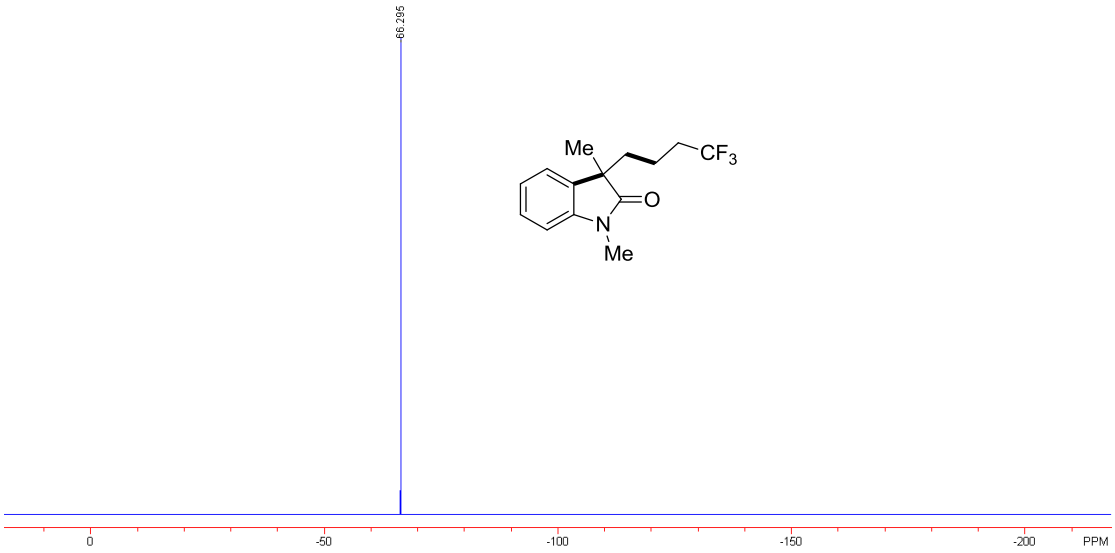
The ^{1}H NMR spectrum of 4j



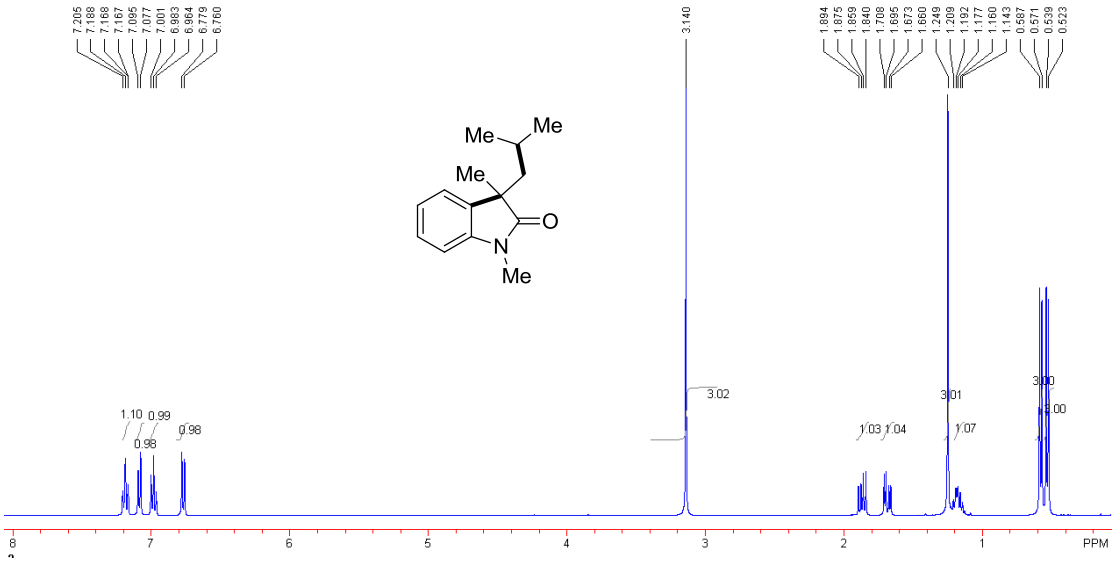
The ^{13}C NMR spectrum of 4j



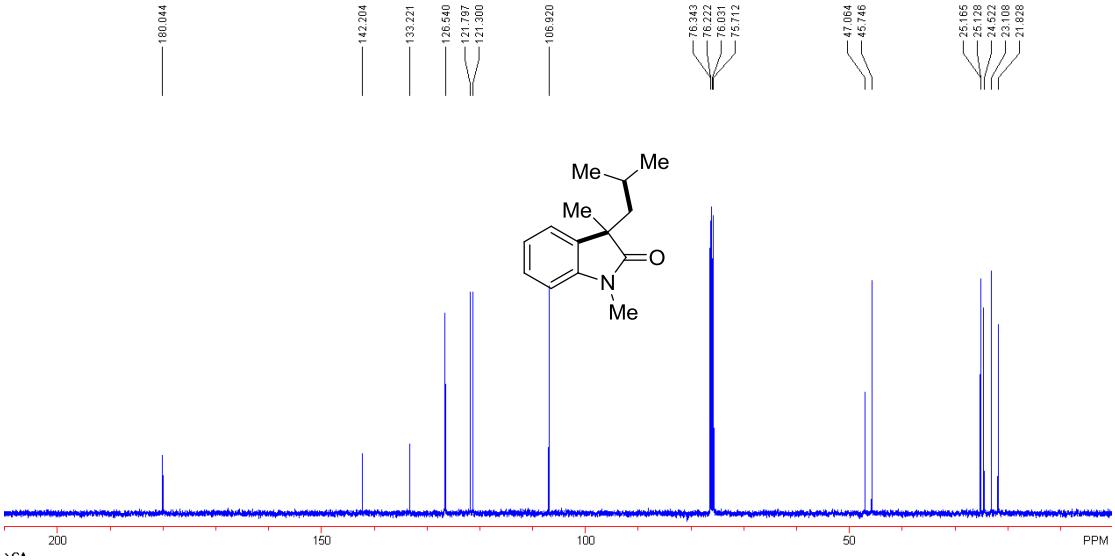
The ^{19}F NMR spectrum of 4j



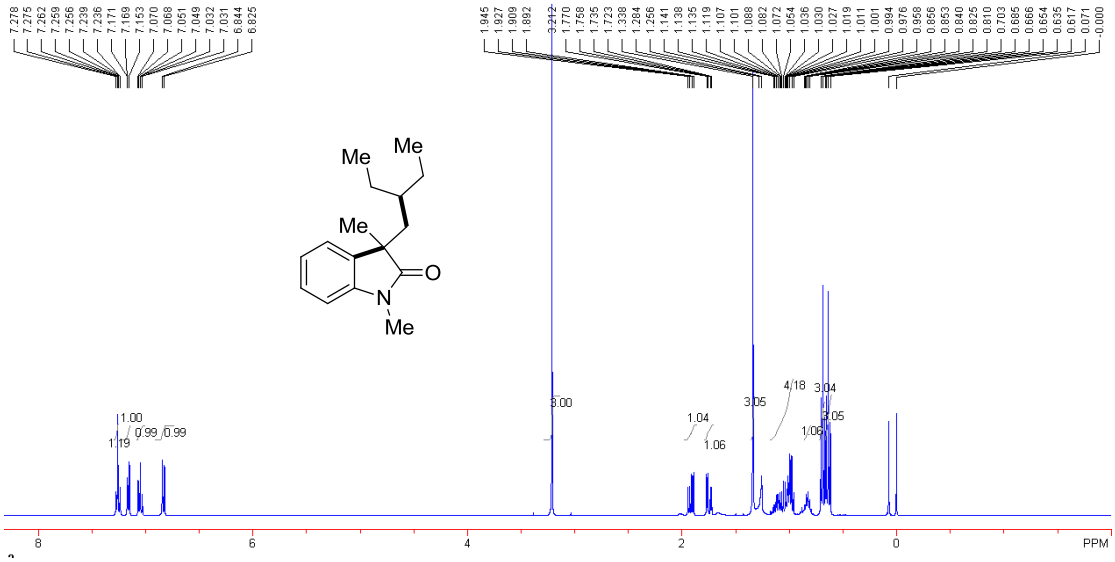
The ^{1}H NMR spectrum of 4l



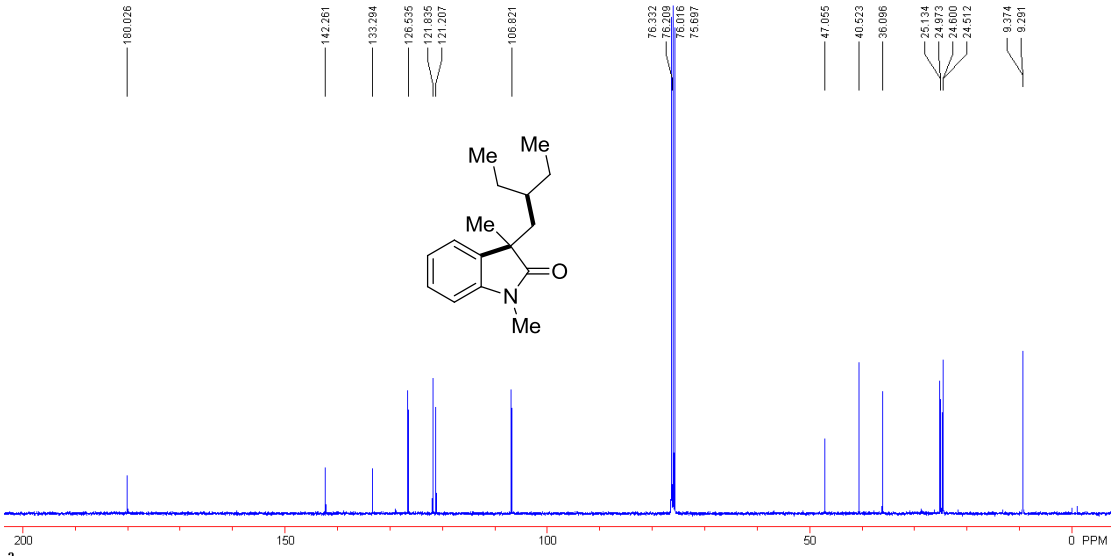
The ^{13}C NMR spectrum of 4l



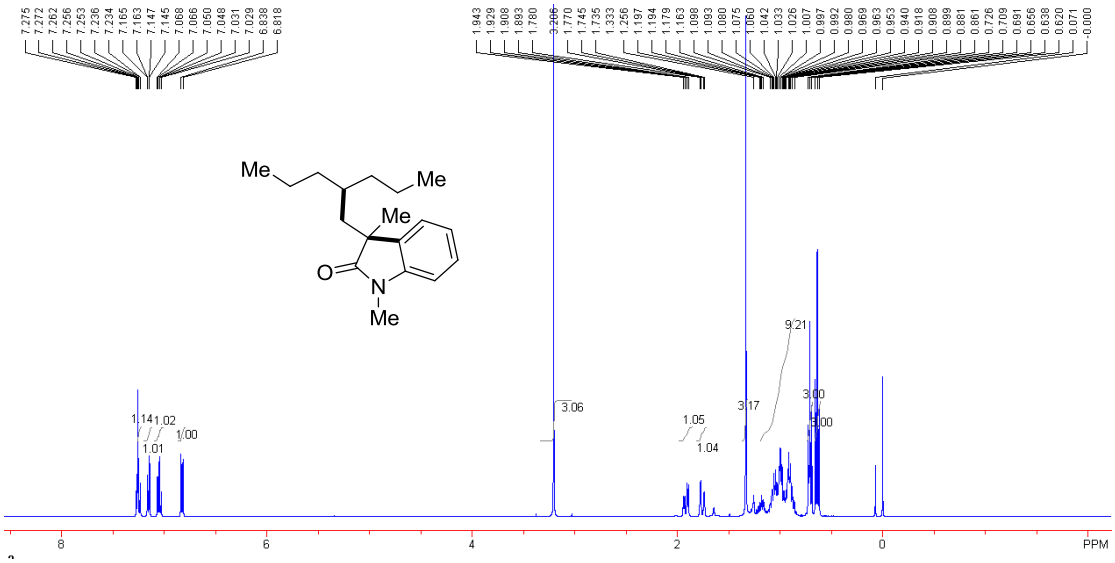
The ^{1}H NMR spectrum of 4m



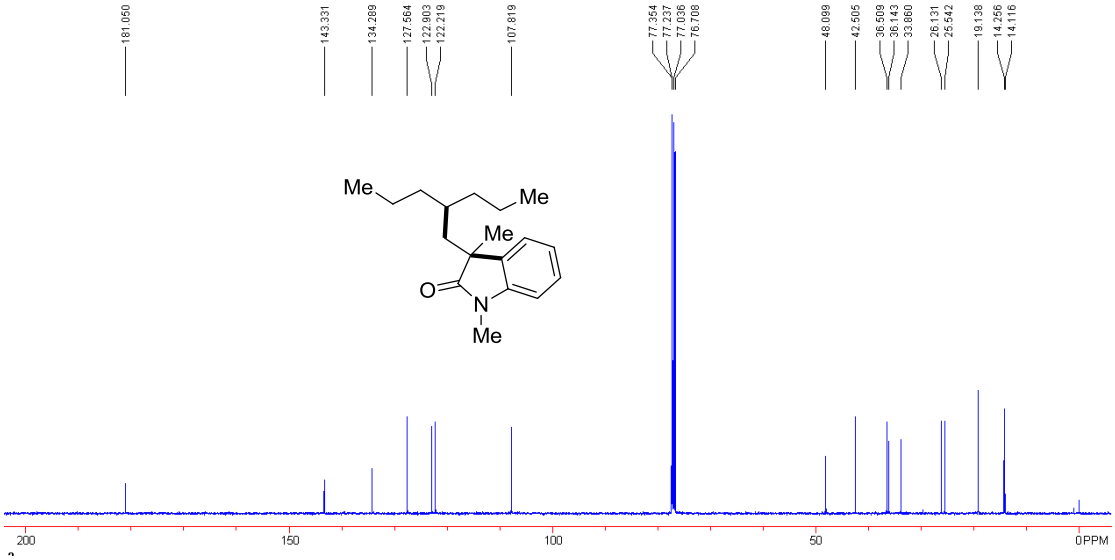
The ^{13}C NMR spectrum of 4m



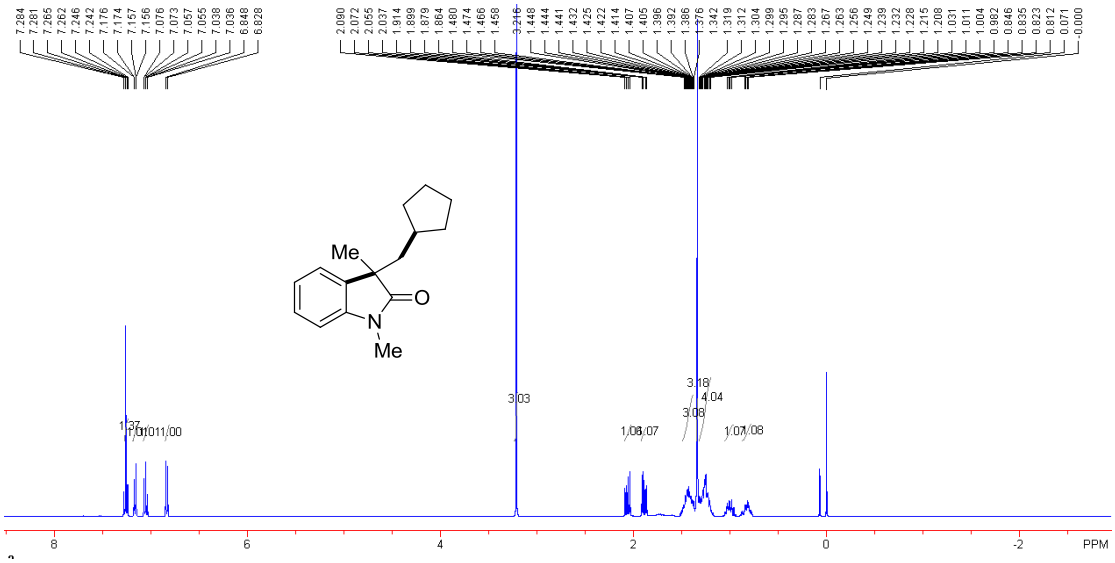
The ^{1}H NMR spectrum of 4n



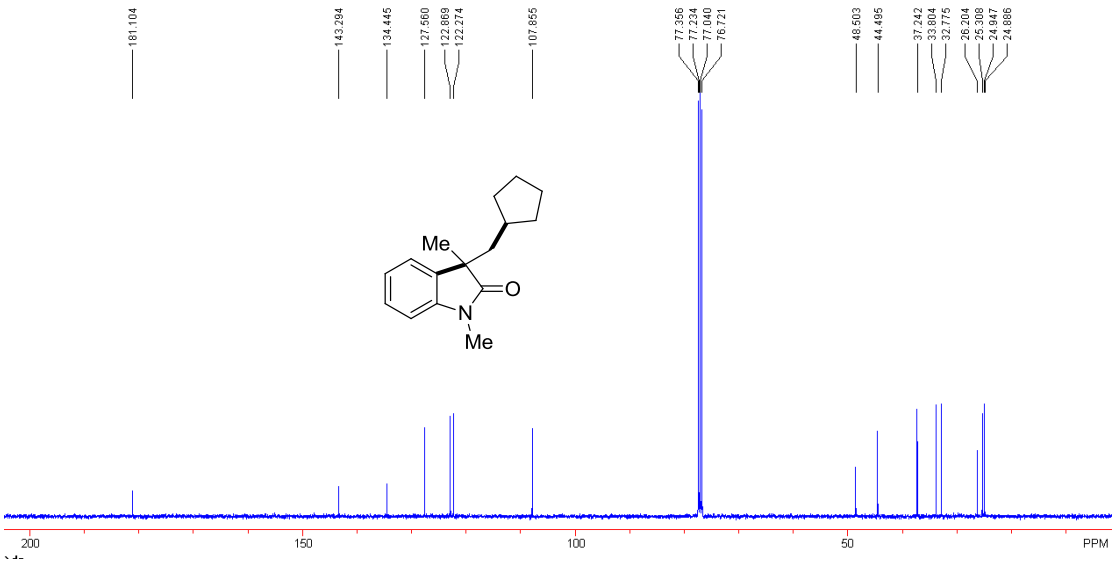
The ^{13}C NMR spectrum of 4n



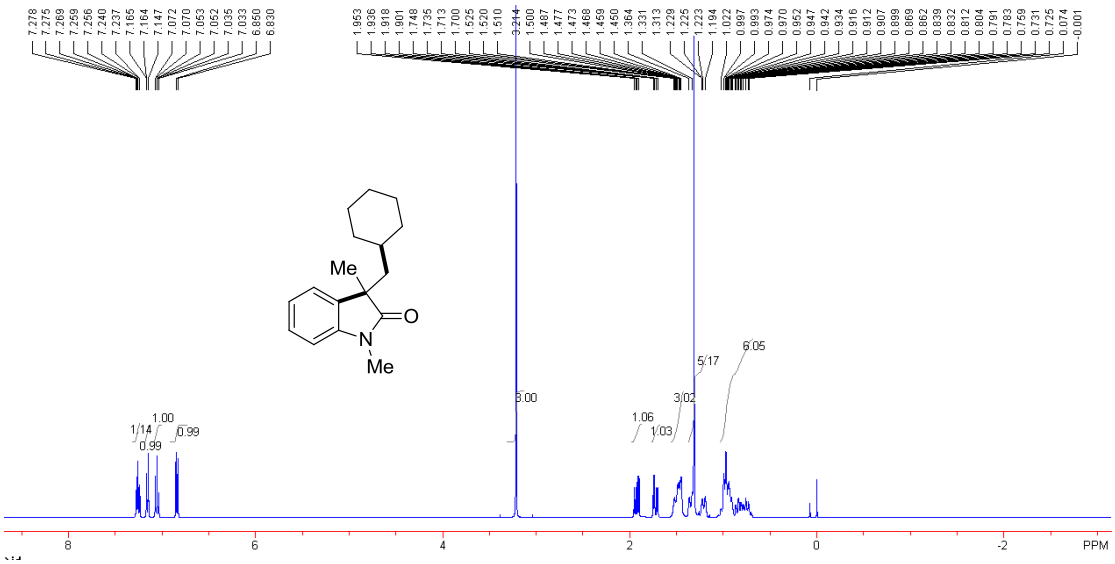
The ^{1}H NMR spectrum of 4o



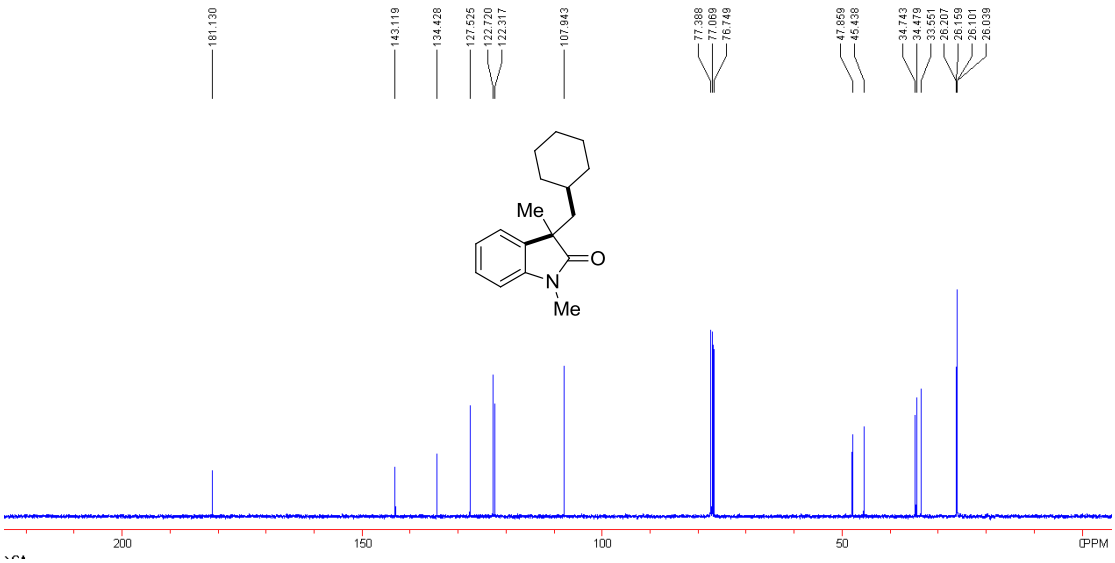
The ^{13}C NMR spectrum of 4o



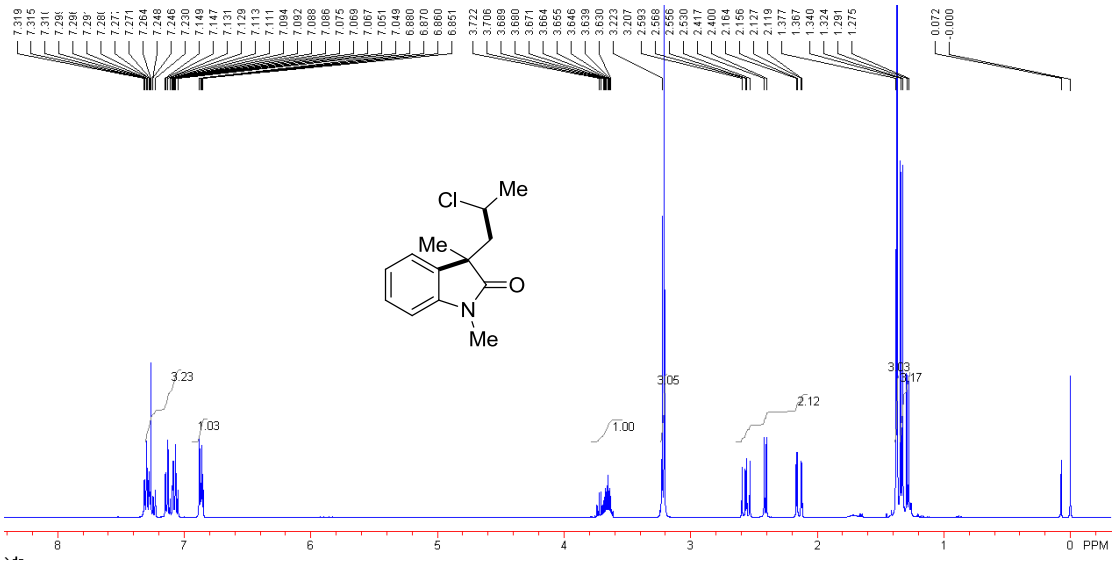
The ^{1}H NMR spectrum of 4p



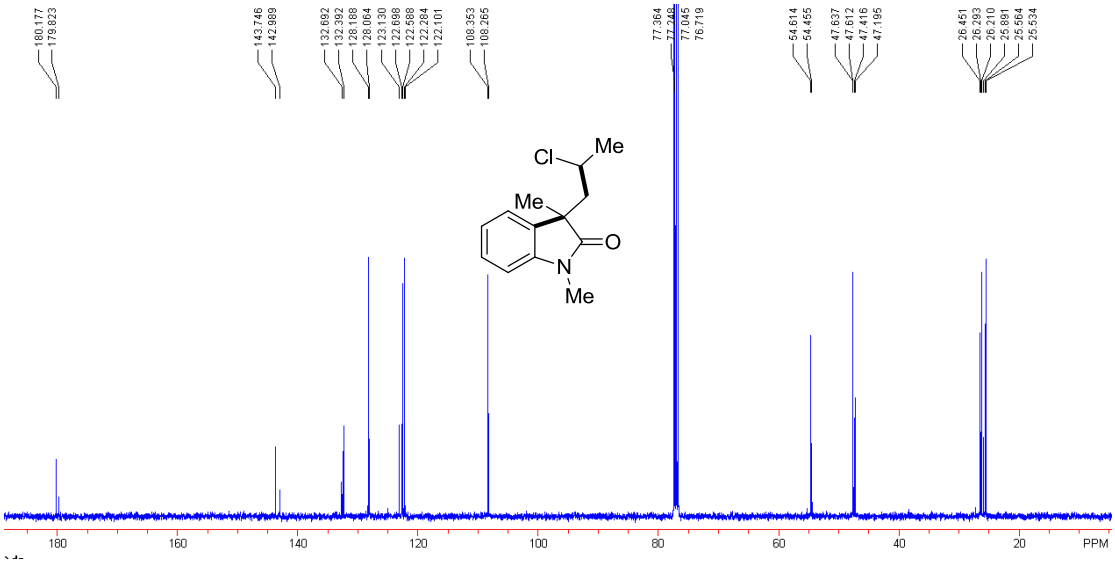
The ^{13}C NMR spectrum of 4p



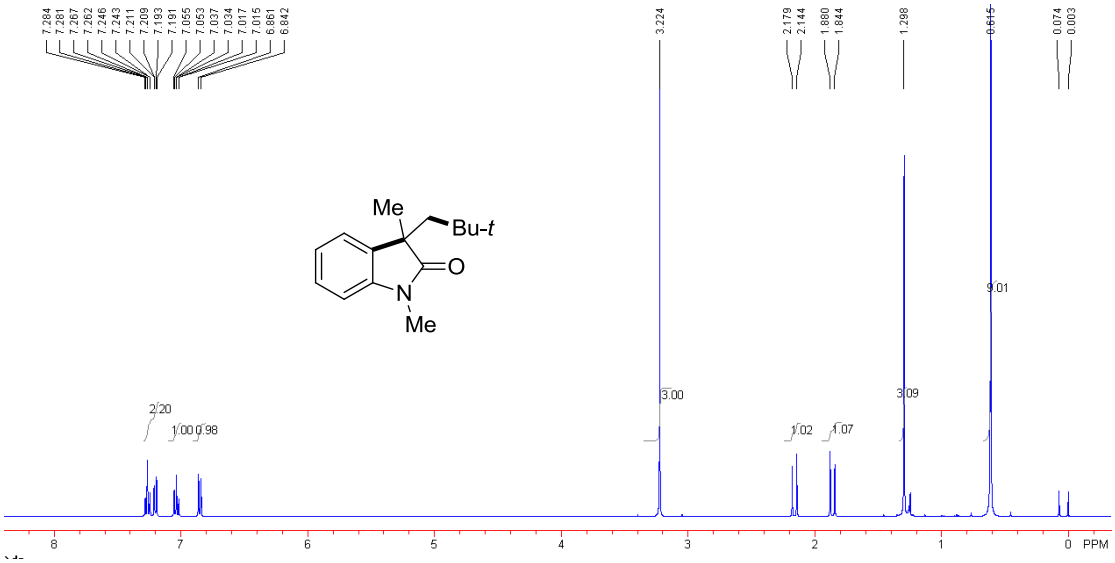
The ^{1}H NMR spectrum of 4q



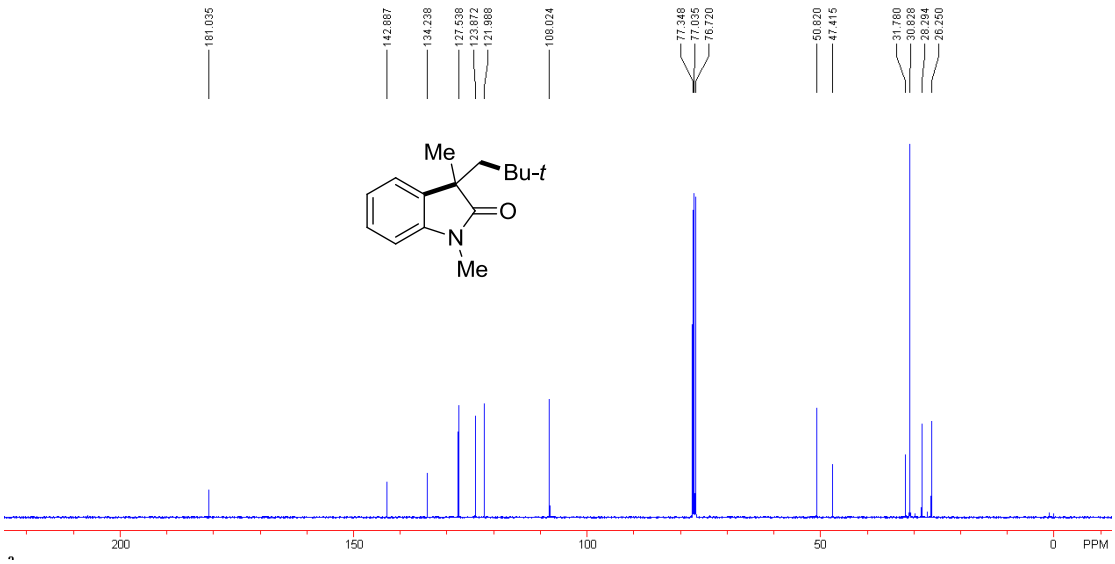
The ^{13}C NMR spectrum of 4q



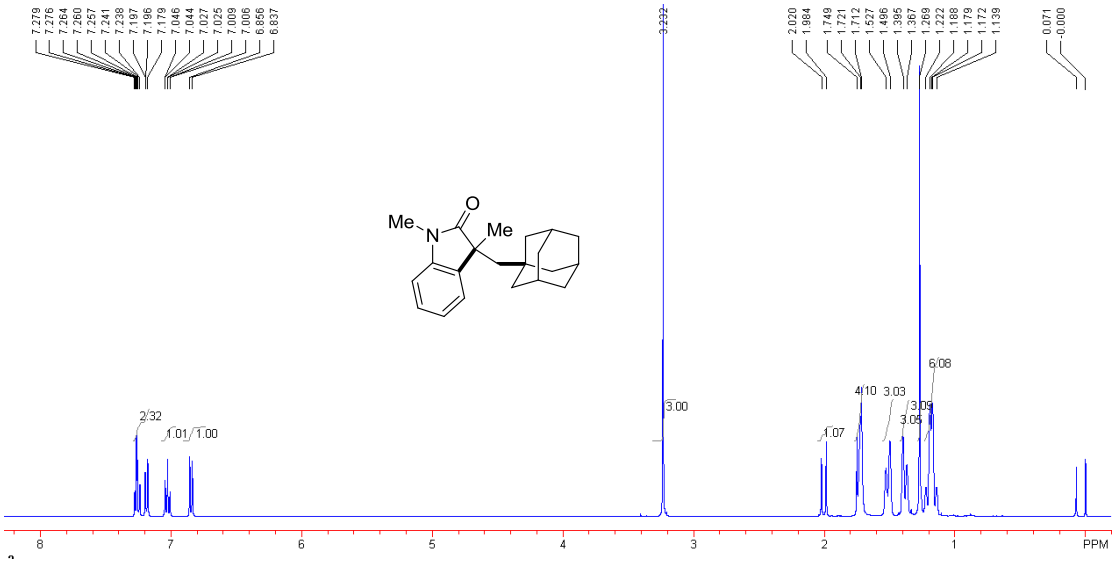
The ^{1}H NMR spectrum of 4s



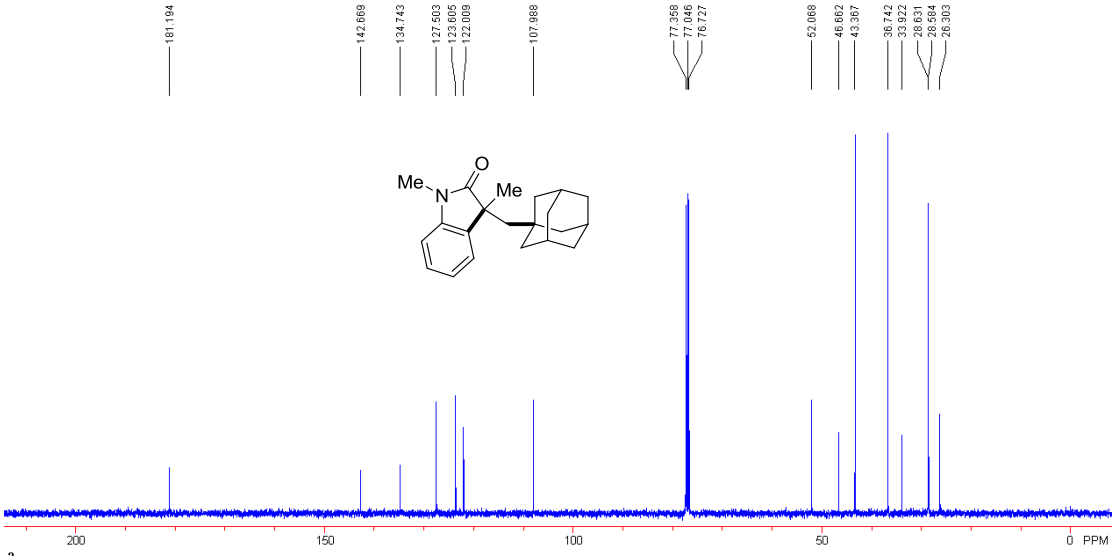
The ^{13}C NMR spectrum of 4s



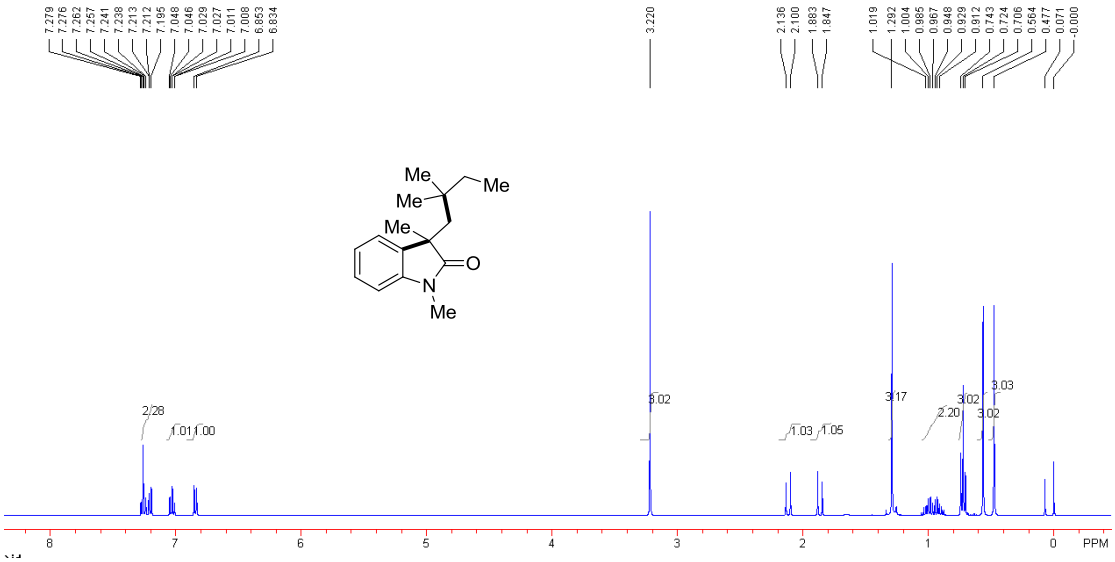
The ^{1}H NMR spectrum of 4t



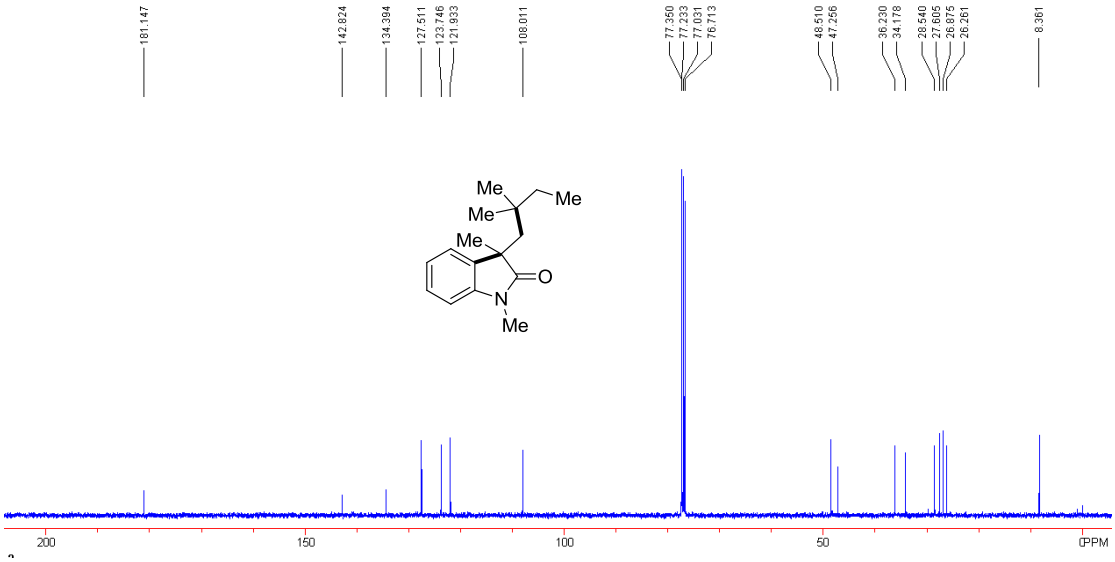
The ^{13}C NMR spectrum of 4t



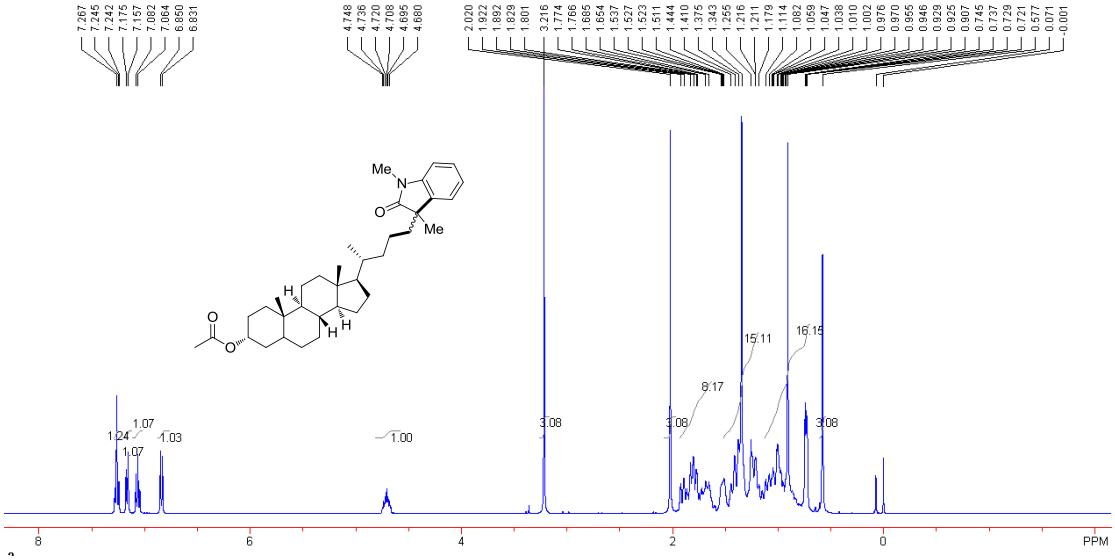
The ^{1}H NMR spectrum of 4u



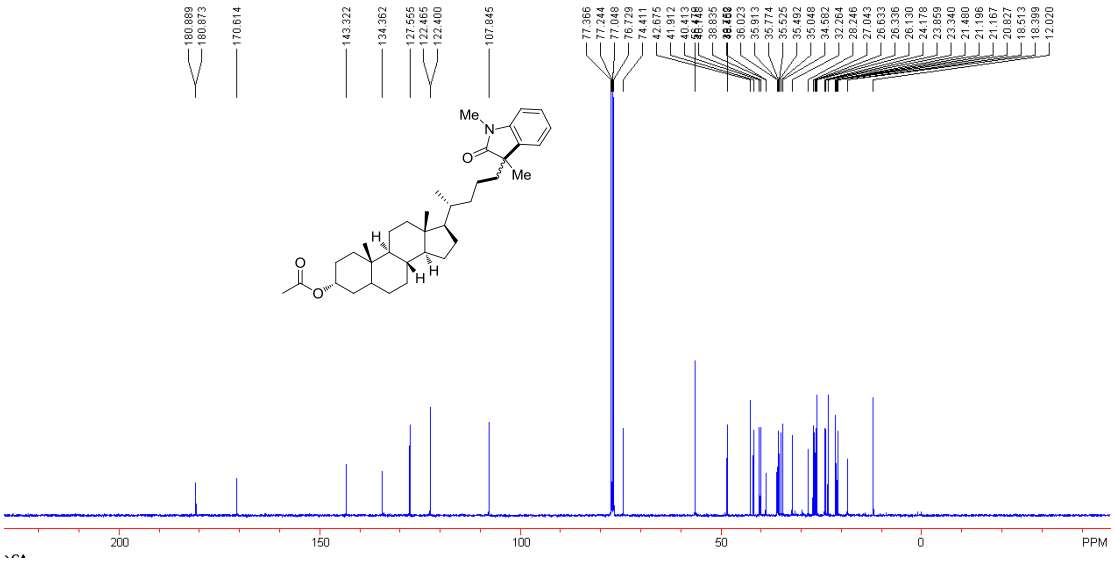
The ^{13}C NMR spectrum of 4u



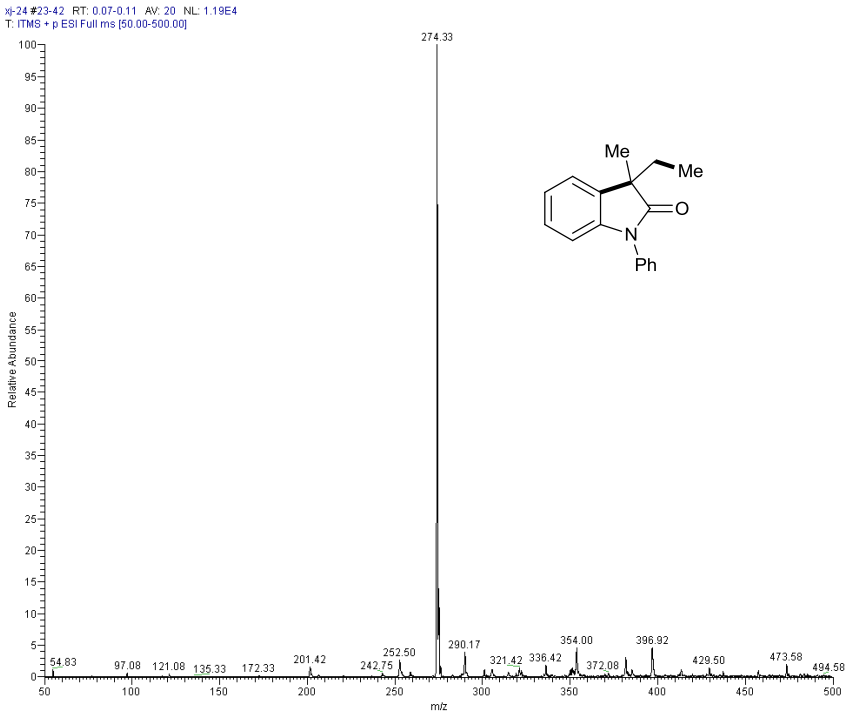
The ^{1}H NMR spectrum of 4v



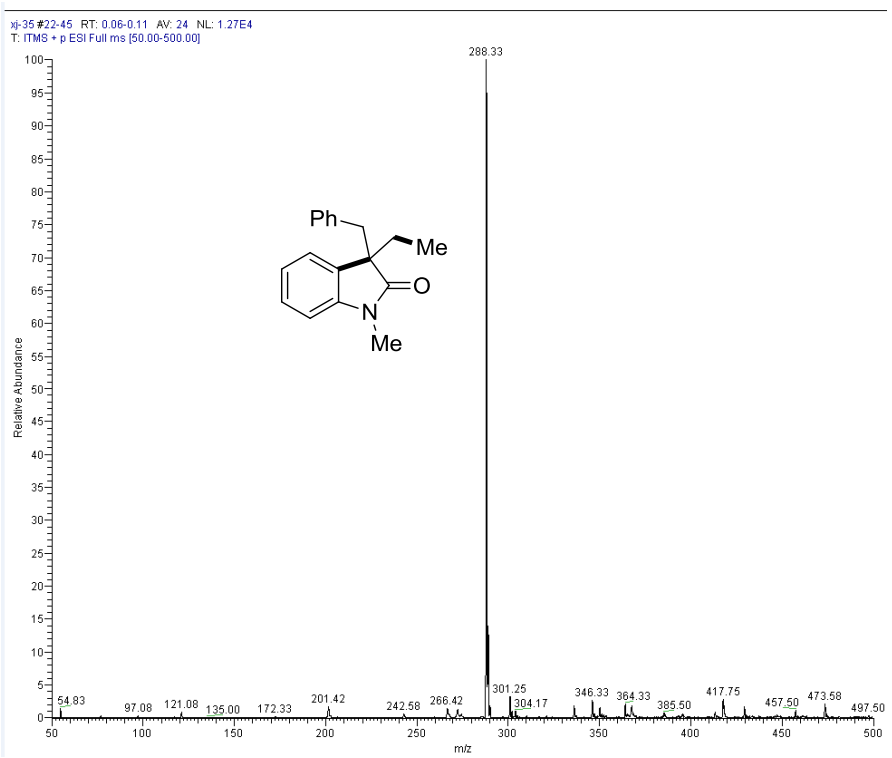
The ^{13}C NMR spectrum of 4v



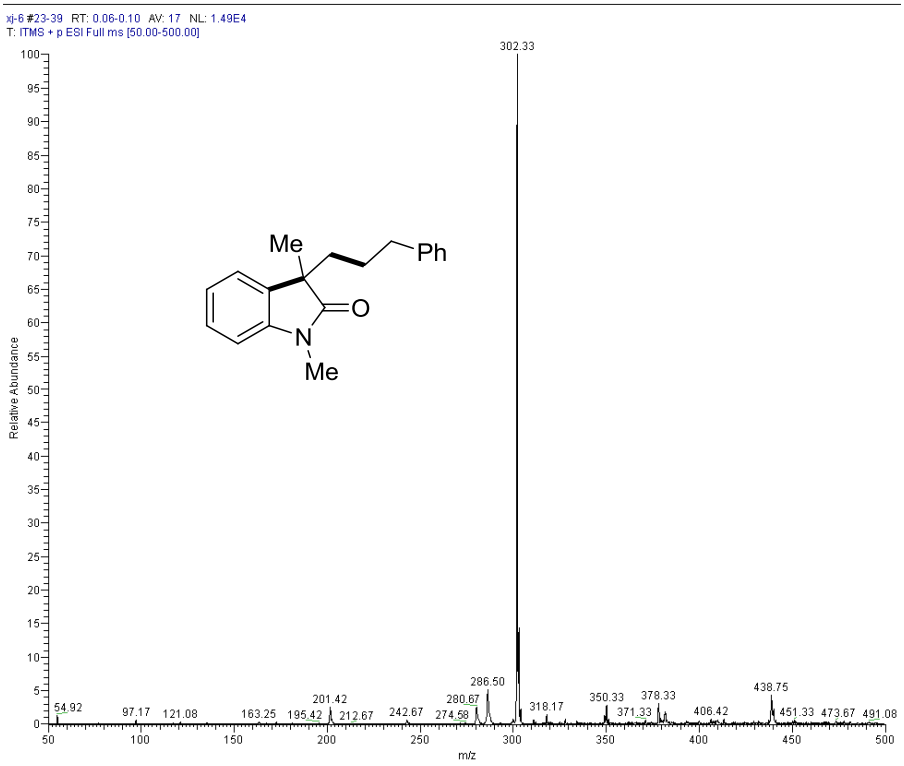
The MS(ESI) spectrum of **3e**



The MS(ESI) spectrum of **3m**



The MS(ESI) spectrum of **4f**



The MS(ESI) spectrum of **4v**