Supplementary Information for

Atom Economical Synthesis of Oxindoles by Metal-Catalyzed Intramolecular C-C Bond Formation under Solvent-Free and Aerobic Conditions

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General Information:

All reactions were carried out with magnetic stirring. tetrahydrofuran (THF) was distilled from sodium/benzophenone. Dichloromethane was distilled from calcium hydride. Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates (60 F254). Visualization was accomplished with either UV light, or by immersion in solutions of Ninhydrin followed by heating on a hot plate for about 10 sec. Purification of starting materials was carried out by flash chromatography using Kieselgel 60 Art 9385 (230-400 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Varian Vnmr-400 (400 MHz for ^{1}H, and 100 MHz for ^{13}C) spectrometer. Chemical shifts are reported relative to chloroform (δ = 7.26) for ^{1}H NMR and chloroform (δ = 77.2) for ^{13}C NMR. Data are reported as (*br* = broad, *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet.) Coupling constants are given in Hz. Ambiguous assignments were resolved on the basis of standard one dimensional proton decoupling experiments. Elemental analyses were performed by the Organic Chemistry Research Center at Sogang University using a Carlo Erba EA 1180 elemental analyzer. Metal catalyst was purchased from Aldrich. N-methylaniline and ethyl malonyl chloride were obtained from TCI. Cyanoacetic acid and oxalyl chloride were purchased from Aldrich. All other commercially available compounds were used as received unless stated otherwise.

General experimental procedures:

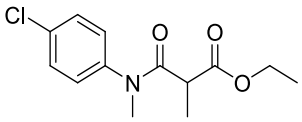
The starting material (**1a**) (500 mg, 2.69 mmol) and the copper oxide nanoparticle (10 mg, 5 mol %) were placed in a reaction vial. The mixture was heated to 150℃ and then the mixture was melted for stirring. The mixture was stirred for 6 h in a heating block. After the reaction was completed the mixture was cooled and ethyl acetate (10.0 mL) was added and the mixture was filtered through a glass filter with a little amount of celite and silica gel. The organic solvent was removed under vacuo. This crude product was purified by column chromatography to provide 460 mg of the analytically cyclized product (**2a**) (95 %).

Spectroscopic data for compounds :

Known compounds:

The preparation of following starting substrates referred to in this article has been reported in the literature: **1a-1e**[1], **1h-1j**[1], **1m**[2].

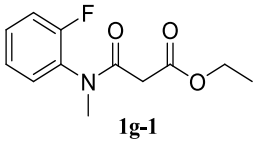
***Ethyl 3-((4-chlorophenyl)(methyl)amino)-2-methyl-3-oxopropanoate* (*1f*)**



1f

Yellow oil; R_f= 0.37 (n-Hexane/Ethyl acetate 6:4 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48-7.43 (dd, *J* =4.4Hz, *J*=4.8 Hz, 2H) 7.28-7.24 (dd, *J*=4.8 Hz, *J*=4.8 Hz, 2H) 4.17-4.10 (q, *J*=1.6 Hz, 2H), 3.44-3.40 (t, *J*=7.2 Hz, 1H), 3.32 (s, 3H), 1.36-1.30(m, *J*=13.2 Hz, 3H) 1.25-1.21(t, *J*=12.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 170 43 (C) 169.83 (C) 142.01 (C) 133.96 (C) 130.05 (CH) 128.93 (CH) 61.15 (CH2) 43.47 (CH) 37.47 (CH_3) 14.09 (CH_3) 13.88 (CH_3) ; MS (EI^+) m/z = 269, 224, 168, 141, 129, 111, 101, 90, 77, 57, 41; GC-MS retention time R_t = 8.31 min; Anal. Calcd for $C_{13}H_{16}ClNO_3$: C, 57.89; H, 5.98; N, 5.19. Found: C, 57.81; H, 5.94; N, 5.19.

***Ethyl 3-((2-fluorophenyl)(methyl)amino)-3-oxopropanoate* (*1g-1*)**

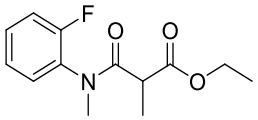


1g-1

Brown oil; R_f = 0.29 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40-7.37 (q, *J*= 6.0 Hz, 1H), 7.37-7.34 (t, *J*= 9.6 Hz, 1H), 7.32-7.19 (*m*, *J*=3.2 Hz, 2H), 4.15-4.09 (q, *J*=5.2 Hz, 2H), 3.28 (s, 3H), 3.21 (s, 3H), 1.25-1.21 (t, *J*=2.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 167.32 (C) 166.25 (C) 159.10 (C) 156.61 (CH) 130.39 (C) 129.69 (CH) 125.24 (CH) 117.10 (CH) 61.30 (CH_2) 41.29 (CH_3) 36.61 (CH_2) 14.01 (CH_3); MS (EI^+) m/z =239, 220, 221, 194, 182, 174, 166, 152, 144, 137, 125, 118, 109, 102, 95, 84, 77, 69, 57, 50, 43;

GC-M S retention time R_t = 10.35 min; Anal. Calcd for $C_{12}H_{14}FNO_3$: C, 60.24; H, 5.90; N, 5.85. Found: C 60.34; H 5.79; N 5.72.

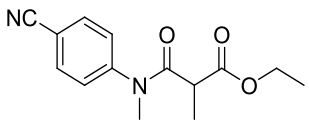
***Ethyl 3-((2-fluorophenyl)(methyl)amino)-2-methyl-3-oxopropanoate* (*1g-2*)**



1g-2

Brown oil; R_f = 0.31 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46-7.42 (t, *J*= 7.6 Hz, 2H), 7.39-7.37 (q, *J*= 12.0 Hz, 1H), 7.27-7.24 (m, J=8.0 Hz, 2H) 4.13-4.09 (q, *J*=1.0 Hz, 2H), 3.41-3.39 (q, *J*=7.2 Hz, 1H) 3.32 (s, 3H), 1.31-1.26 (d, *J*=7.2 Hz, 3H), 1.25-1.21 (t, *J*=7.2 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) 170.39 (C) 170.18 (C) 130.32 (C) 129.92 (CH) 125.14 (C) 117.32 (CH) 117.09 (CH) 116.85 (CH) 61.19 (CH2) 43.54 (CH) 36.74 (CH_3) 14.12 (CH_3) 13.88 (CH_3) ; MS (EI^+) m/z =253, 233, 225, 208, 197, 187, 180, 168, 160, 152, 144, 137, 125, 117, 109, 102, 95, 84, 77, 69, 57, 45, 38; GC-M S retention time R_t = 6.38 min; Anal. Calcd for $C_{13}H_{16}FNO_3$: C, 61.65; H, 6.37; N, 5.53. Found: C 61.65; H 6.43; N 5.42.

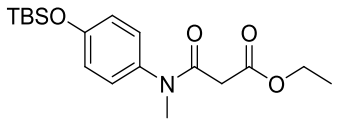
***Ethyl 3-((4-cyanophenyl)(methyl)amino)-2-methyl-3-oxopropanoate* (*1k*)**



1k

White solid; R_f = 0.25 (n-Hexane/Ethyl acetate 5:5 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.45 – 7.39 (m, 2H), 4.21 – 4.06 (m, 2H), 3.37 (d, *J* = 26.9 Hz, 4H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 170.08(C), 169.48(C), 147.50(C), 133.70(CH), 128.23(CH), 117.77(CN), 111.81(C), 61.35(CH_2), 43.73(CH), 37.56(CH_3), 14.05(CH_3), 13.99(CH_3);

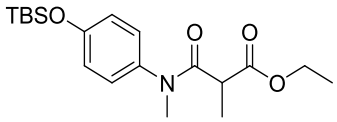
***Ethyl 3-((4-(tert-butyldimethylsilyloxy)phenyl)(methyl)amino)-3-oxopropanoate* (*1l-1*)**



1l-1

Brown oil; R_f = 0.20 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.09 – 7.05 (m, 2H), 6.86 – 6.81 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.26 (s, 3H), 3.19 (s, 2H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.00 – 0.96 (m, 9H), 0.22 – 0.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.08(C), 169.48(C), 147.50(C), 133.70(CH), 128.23(CH), 117.77(CN), 111.81(C), 61.35(CH_2), 43.73(CH), 37.56(CH_3), 14.05(CH_3), 13.99(CH_3);

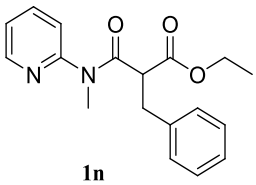
***Ethyl 3-((4-(tert-butyldimethylsilyloxy)phenyl)(methyl)amino)-2-methyl-3-oxopropanoate* (*1l-2*)**



1l-2

Yellow oil; R_f = 0.25 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.11 – 7.05 (m, 2H), 6.85 (m, 2H), 4.17 – 4.01 (m, 2H), 3.40 (q, *J* = 7.1 Hz, 1H), 3.25 (s, 3H), 1.28 (d, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.01 – 0.96 (m, 9H), 0.23 – 0.20 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 170.84(C), 170.38(C), 155.40(C), 136.81(C), 128.53(CH), 121.02(CH), 61.05(CH_2), 43.41(CH), 37.71(CH_3), 25.55(CH_3), 18.13(C), 14.11(CH_3), 14.04(CH_3), -4.47(CH_3);

***Ethyl 2-benzyl-3-(methyl(pyridin-2-yl)amino)-3-oxopropanoate* (*1n*)**

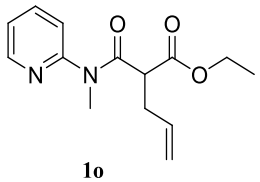


1n

Brown oil; R_f=0.30 (n-Hexane/Ethyl acetate 3:7 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.46-8.44 (dd, *J*=1.2, 1.0 Hz, 1H) 7.70-7.65 (t, *J*=2.0 Hz, 1H) 7.24-7.17 (m, *J*=2.0 Hz, 3H) 7.09-7.08(m, *J*=3.2 Hz, 2H) 4.14-4.10 (q, *J*=3.2 Hz, 2H), 3.93 (t, *J*=3.2 Hz, 1H), 3.33 (s, 3H)

3.25-3.20 (m, *J*=8.0 Hz, 2H) 1.26-1.17(t, *J*=6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 173.48 (C) 169.25 (C) 144.01 (CH) 134.39 (C) 129.66 (C) 128.14 (CH) 127.34 (CH) 126.82 (CH) 123.80 (CH) 122.48 (CH) 108.18 (CH) 62.16 (C) 61.34 (CH_2) 40.00 (CH_2) 26.10 (CH_3) 13.98 (CH_3); MS (EI^+) m/z = 312, 269, 157, 101, 88, 73, 55, 43; GC-MS retention time R_t = 9.83 min; Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.17; H, 6.52; N, 8.95.

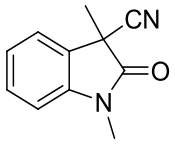
***Ethyl 2-(methyl(pyridin-2-yl)carbamoyl)pent-4-enoate* (*1o*)**



1o

Red solid; Rf= 0.37 (n-Hexane/Ethyl acetate 3:7 (v/v)); 1H-NMR (400 MHz, CDCl3) δ (ppm) 8.49-8.48 (dd, *J*=1.1 Hz, *J*=1.1 Hz, 1H) 7.79-7.75 (td, *J*=15.2 Hz, 1H) 7.29 (br, 1H) 7.27-7.21 (t, *J*=7.2 Hz, 1H) 5.74-5.73 (q, *J*=10 Hz, 1H) 5.31-4.99 (m, *J*=10 Hz, 2H) 4.16-4.10 (m, *J*=7.2 Hz, 2H), 3.71-3.69 (t, *J*=6.8 Hz, 1H), 3.41 (s, 3H), 2.71-2.62 (m, *J*=7.6 Hz, 2H) 1.25-1.21(t, *J*=5.6 Hz, 3H); 13C-NMR (100 MHz, CDCl3) 169.41 (C) 168.53 (C) 143.14 (CH) 138.42 (C) 129.51 (CH) 129.23 (CH) 128.17 (CH) 127.58 (CH) 126.58 (CH2) 61.24 (CH2) 50.97 (CH) 37.41 (CH3) 35.27 (CH2) 14.09 (CH3); MS (EI+) m/z = 262, 221, 189, 154, 108, 79, 67, 53, 40; GC-MS retention time Rt = 9.37 min; Anal. Calcd for C14H18N2O3: C, 64.10; H, 6.92; N, 10.68. Found: C, 64.16; H, 6.94; N, 10.72.

***1,3-dimethyl-2-oxoindoline-3-carbonitrile*[1] (*2a*)**

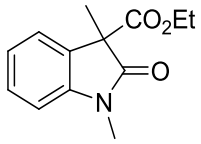


2a

Brown oil; R_f = 0.40 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41-7.44 (m, *J*=33.2 Hz, 1H), 7.40 (td, *J*=1.0 Hz, *J*=8.0 Hz, 1H), 7.17 (td, *J*=1.0 Hz, *J*=7.5 Hz, 1H), 6.90 (t, *J*=1.0 Hz, *J*=8.0 Hz, 1H), 3.26 (s, 3H), 1.81 (s, 3H); ^{13}C-NMR (100 MHz,

$CDCl_3$) δ (ppm)165.52 (C) 142.27 (C) 130.45 (CH) 129.12 (CH) 129.05 (C) 127.29 (CH) 118.44 (CH) 38.21 (C) 29.47 (CH_3) 15.87 (CH_3); MS (EI^+) m/z = 186, 171, 159, 153, 143, 130, 116, 102, 89, 77, 63, 51, 40; GC-MS retention time R_t = 9.94 min; HRMS (ESI):calcd for $[(C_{11}H_{10}N_2O_1) + Na]^+$ 209.0685; found 209.0684

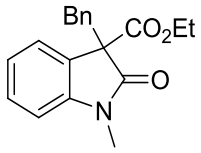
***Ethyl 1,3-dimethyl-2-oxoindoline-3-carboxylate[1]* (*2b*)**



2b

Brown oil; R_f = 0.58 (n-Hexane/Ethyl acetate 5:5 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34-7.31 (td, *J*=1.0 Hz, *J*=8.0 Hz, 1H) 7.28-7.26 (m, *J*=1.2 Hz, 1H) 7.09-7.07 (td, *J*=1.0 Hz, *J*=7.5 Hz, 1H) 6.90-6.69 (d, *J*=8.0 Hz, 1H) 4.16-4.10 (m, *J*=1.6 Hz, 2H), 3.27-3.26 (s, 3H), 1.68-1.66 (s, 3H), 1.18-1.13 (t, *J*=7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 175.18 (C) 169.70 (C) 143.56 (C) 130.12 (CH) 128.95 (CH) 122.87 (CH) 108.45 (CH) 61.87 (C) 55.01 (CH_2) 26.16 (CH_3) 20.10 (CH_3) 13.89 (CH_3) ; MS (EI^+) m/z = 233, 160, 145, 130, 117, 103, 77; GC-MS retention time R_t = 10.25 min; Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.98; H, 6.45; N, 6.01.

***Ethyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate[1]* (*2c*)**

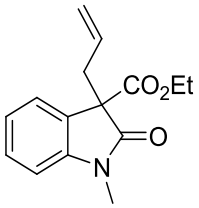


2c

Pale yellow solid; R_f = 0.56 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ(ppm) 7.33 (dd, *J*=1.0 Hz, *J*= 7.5 Hz, 1H), 7.22 (td, *J*=1.5 Hz, *J*=7.5 Hz, 1H), 7.06 (td, *J*= 1.0 Hz, *J*=7.5 Hz, 1H), 6.97-7.04 (m, *J*=1.6 Hz, 3H), 6.82-6.86 (m, *J*=7.6 Hz, 2H), 6.57 (d, *J* = 7.5 Hz, 1H), 4.11-4.25 (m, *J*=4.0 Hz, 2H), 3.54 (s, 2H), 2.94 (s, 3H), 1.19 (t, *J*=7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 170.78 (C) 170.08 (C) 141.81 (C) 137.24 (C) 129.80 (CH) 129.53 (CH) 128.75 (CH) 128.27 (CH) 128.39 (CH) 128.22 (CH) 127.60 (CH) 127.26 (C) 61.18 (C) 53.28 (CH_2) 53.00 (CH_2) 43.78 (CH_3) 14.10 (CH_3); MS (EI^+) m/z = 309, 91, 77,

65, 51, 39; GC-MS retention time R_t = 10.18 min; Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.79; H, 6.26; N, 4.41.

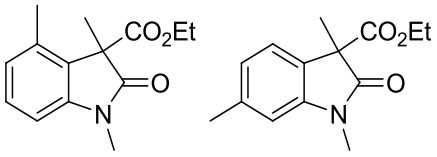
Ethyl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate[1] (2d)



2d

Brown oil; R_f = 0.54 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31 (td, *J*=1.0 Hz, *J*=7.5 Hz, 1H), 7.25-7.28 (m, 1H), 7.06 (td, *J*=1.0 Hz, *J*=7.5 Hz, 1H), 6.84 (d, *J*=8.0 Hz, 1H), 5.31-5.41 (m, *J*=1.2 Hz, 1H), 5.02 (t, *J*=1.5 Hz, *J*= 17.0 Hz, 1H), 4.89-4.93 (m, *J*=1.2 Hz, 1H),4.07-4.19 (m, *J*=4.0 Hz, 2H), 3.22 (s, 3H), 2.91-3.04 (m, *J*=1.2 Hz, 2H), 1.16 (t, *J*=7.0 Hz, 3H); ^{13}C-NMR (100MHz, $CDCl_3$) δ (ppm) 173.66 (C), 168.98 (C), 144.09 (C), 131.03(CH), 129.00 (CH), 127.63(CH), 123.56(CH), 122.57 (CH), 119.72(CH), 108.12 (CH), 61.94 (C) 59.22 (CH_2) 38.36 (CH_2) 26.39 (CH_3) 13.92 (CH_3); MS (EI^+) m/z = 259, 218, 186, 162, 146, 130, 117, 103, 91, 77, 63, 51, 39; GC-MS retention time R_t = 7.72 min; Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.51; H, 6.77; N, 5.27.

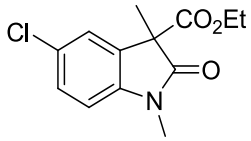
Ethyl 1,3-dimethyl-2-oxoindoline-3-carboxylate[1] (2e + 2e')



2e + 2e'

Brown oil; R_f = 0.58 (n-Hexane/Ethyl acetate 5:5 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26-6.69 (m, 6H), 4.14 (m, 4H), 3.24 (s, 3H) 3.23 (s, 3H), 2.37 (d, *J* = 17.2 Hz, 3H), 2.26(s, 3H), 1.69(s, 3H), 1.62, (s, *J* = 14.0 Hz, 3H) 1.57 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 149.38 (C) 139.86 (C) 129.66 (C) 128.94 (CH) 127.87 (CH) 124.24 (CH) 60.94 (C) 43.37 (CH_2) 37.44 (CH_3) 21.14 (CH_3) 14.01 (CH_3);

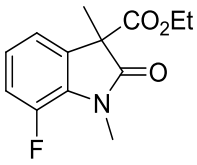
***Ethyl 5-chloro-1,3-dimethyl-2-oxoindoline-3-carboxylate* (*2f*)**



2f

Brown oil; R_f = 0.45 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, CDCl3) δ(ppm) 7.31 (dd, *J*=1.0 Hz, 1H), 7.27 (td, *J*=1. Hz, 1H), 6.79 (dd, *J*= 1.0 Hz, 1H), 4.17-4.12 (m, 2H), 3.24 (s, 2H), 1.66 (s, 3H), 1.18 (t, *J*=7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 174.64 (C) 169.06 (C) 142.17 (C) 131.63 (C) 128.88 (CH) 123.57 (C) 109.34 (CH) 62.18 (CH_2) 55.12 (C) 26.64 (CH_3) 20.09 (CH_3)13.88 (CH_3); MS (EI^+) m/z = 267, 194, 179, 164, 151, 130, 102, 89, 75, 63, 51, 44; GC-MS retention time R_t = 8.97 min; Anal. Calcd for $C_{13}H_{14}ClNO_3$: C, 58.32; H, 5.27; N, 5.23. Found: C, 58.32; H, 5.26; N, 5.27.

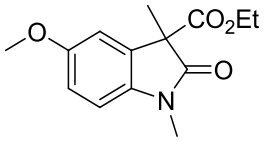
***Ethyl 7-fluoro-1,3-dimethyl-2-oxoindoline-3-carboxylate* (*2g*)**



2g

Pale yellow oil; R_f = 0.37 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26-6.98 (m, *J*=1.0 Hz, 3H), 4.15-4.11 (q, *J*=0.4 Hz, 2H), 3.46 (s, 3H), 1.65 (s, 3H), 1.18-1.14 (t, *J*=1.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 174.74 (C) 169.24 (C) 123.42 (C) 123.36 (C) 118.83 (C) 118.80 (CH) 117.06 (CH) 116.87 (CH) 62.12 (C) 55.24 (CH_2) 28.98 (CH_3) 20.27 (CH_3) 13.88 (CH_3) ; MS (EI^+) m/z = 251, 236, 222, 206, 192, 178, 163, 156, 148, 135, 128, 121, 109, 101, 94, 83, 75, 63, 51, 43; GC-M S retention time R_t = 5.82 min; Anal. Calcd for $C_{13}H_{14}FNO_3$: C, 62.14; H, 5.62; N, 5.57. Found: C 62.52; H 5.53; N 5.21.

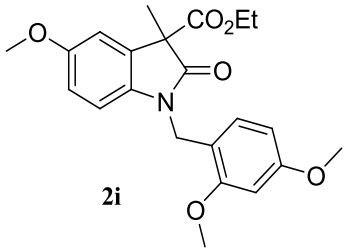
***Ethyl 5-methoxy-1,3-dimethyl-2-oxoindoline-3-carboxylate*[1] (*2h*)**



2h

Brown oil; R_f = 0.38 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.07 (d, *J*= 1.0 Hz, 1H), 7.01 (d, *J*= 1.0 Hz, 2H), 6.82 (dd, *J*=1.0 Hz, *J*=1.2 Hz, 1H), 4.13-4.08 (m, 2H), 3.79 (s, 3H), 3.21 (s, 3H), 1.63 (s, 3H), 1.14 (t, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 174.84 (C) 169.68 (C) 156.13 (C) 137.01 (C) 131.34 (C) 113.20 (CH) 110.29 (CH) 108.76 (CH) 61.90 (C) 55.79 (CH_2) 55.44 (CH_3) 26.57 (CH_3) 20.19 (CH_3) 13.82 (CH_3); MS (EI^+) m/z = 263, 190, 175, 159, 147, 132, 118, 104, 91, 77, 65, 51, 39; GC-MS retention time R_t = 8.63 min; Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.71; H, 6.48; N, 5.46.

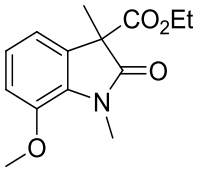
***Ethyl 3-allyl-1-(2,4-dimethoxybenzyl)-5-methoxy-2-oxoindoline-3-carboxylate* (*2i*)**



2i

Brown oil; R_f = 0.25 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.06 (d, *J*=8.5 Hz, 1H), 6.86 (d, *J*=2.5 Hz, 1H), 6.72 (dd, *J*=.5 Hz, *J*=8.5 Hz, 1H), 6.66 (d, *J*= 8.5 Hz, 1H), 6.46 (d, *J*=2.5 Hz, 1H), 6.34 (dd, *J*=2.5 Hz, *J*=8.5 Hz, 1H), 5.35-5.46 (m, 1H), 5.07 (dq, *J*=1.5 Hz, *J*=17.0 Hz, 1H), 4.79-4.95 (m, 3H), 4.05-4.23 (m, 2H), 3.86 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 2.96-3.06 (m, 2H), 1.18 (t, *J*=7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 173.61 (C) 169.14 (C) 160.26 (C) 157.94 (C) 155.85 (C) 137.037 (C) 131.27 (CH) 128.99 (CH) 128.79 (C) 119.72 (C) 115.99 (CH) 113.36 (CH_2) 110.57 (CH) 110.15 (CH) 104.25 (CH) 98.25 (CH) 61.87 (CH_2) 59.65 (CH_3) 55.73 (CH_3) 55.43 (CH_3) 55.26 (CH_2) 37.96 (CH_2) 13.90 (CH_3); MS (EI^+) m/z = 425, 151, 121, 106, 91, 77, 65, 44; GC-MS retention time R_t = 12.67 min; Anal. Calcd for $C_{24}H_{27}NO_6$: C, 67.75; H, 6.40; N, 3.29. Found: C, 67.75; H, 6.38; N, 3.31.

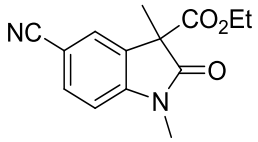
***Ethyl 7-methoxy-1,3-dimethyl-2-oxoindoline-3-carboxylate*[1] (*2j*)**



2j

Brown oil; R_f = 0.35 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 6.99 (t, *J*=1.0 Hz, 1H), 6.88 (t, *J*=1.0 Hz, 2H), 4.14-4.10 (m, *J*=4.12 Hz, 2H), 3.87 (s, 3H), 3.52 (s, 3H), 1.64 (s, 3H), 1.16 (t, *J*=6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) 175.39 (C) 169.78 (C) 145.32 (C) 131.63 (C) 131.43 (C) 123.34 (CH) 115.55 (CH) 112.66 (CH) 61.87 (C) 55.94 (CH_2) 55.17 (CH_3) 29.81 (CH_3) 20.36 (CH_3) 13.90 (CH_3); MS (EI^+) m/z =249, 176, 162, 148, 133, 120, 104, 92, 77, 65, 52, 43; GC-M S retention time R_t = 11.25 min; Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C 63.82; H 6.52; N 5.34.

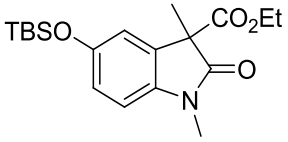
***Ethyl 5-cyano-1,3-dimethyl-2-oxoindoline-3-carboxylate* (*2k*)**



2k

White solid; R_f = 0.31 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.54 – 7.51 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 4.24 – 4.08 (m, 2H), 3.29 (s, 3H), 1.69 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 174.66(C), 168.40(C), 147.38(C), 134.25(C), 131.00(CH), 126.50(CH), 118.77(CN), 108.86(CH), 106.08(C), 62.49(CH_2), 54.65(C), 26.78(CH_3), 20.06(CH_3), 13.88(CH_3);

***Ethyl 5-(tert-butyldimethylsilyloxy)-1,3-dimethyl-2-oxoindoline-3-carboxylate* (*2l*)**

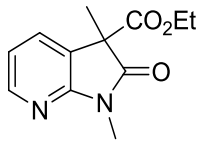


2l

Yellow oil; R_f = 0.26 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm)

6.79 (dd, *J* = 6.2, 3.8 Hz, 1H), 6.78 (s, 1H), 6.72 – 6.69 (m, 1H), 4.13 (qd, *J* = 7.1, 0.4 Hz, 2H), 3.22 (s, 3H), 1.64 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.97 (s, 9H), 0.17 (d, *J* = 1.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 175.12(C), 169.85(C), 151.87(C), 137.65(C), 131.38(C), 119.91(CH), 116.03(CH), 108.89(CH), 62.03(CH_2), 55.51(C), 26.74(CH_3), 25.82(CH_3), 20.29(C), 18.34(CH_3), 14.08(CH_3), -4.38(CH_3).

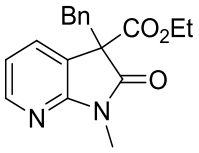
***Ethyl 1,3-dimethyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine-3-carboxylate* (*2m*)**



2m

Brown oil, R_f = 0.24 (n-Hexane/Ethyl acetate 8:2 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.23-8.21 (d, *J*=1.0 Hz, 1H) 7.49-7.47 (dd, *J*=1.0 Hz, 1H) 6.98-6.95 (dd, *J*=1.0 Hz, 1H) 4.15-4.11 (m, 2H), 3.32 (s, 3H) 1.67(s, 3H) 1.18-1.13 (t, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) *δ* (ppm) 170.76 (C), 170.06 (C), 155.60 (C), 148.78(CH), 138.57 (CH), 122.06(C), 120.08(CH), 60.95 (CH_2), 44.64(C), 35.65 (CH_3), 14.06 (CH_3); MS (EI^+) m/z = 234, 161, 145, 131, 118, 104, 91, 77, 65, 51, 40; GC-MS retention time R_t = 9.95 min; Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.02; N, 11.96. Found: C, 61.58; H, 5.87; N, 11.82.

***Ethyl 3-benzyl-1-methyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine-3-carboxylate* (*2n*)**

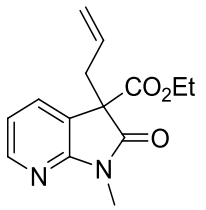


2n

Pale yellow solid; R_f = 0.30 (n-Hexane/Ethyl acetate 3:7 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.12-8.10 (t, *J*=1.6 Hz, 1H) 7.49-7.47 (d, *J*=1.6 Hz, 1H) 7.07-7.05 (t, *J*=2.4 Hz, 3H) 6.96-6.94 (dd, *J*=1.2 Hz, *J*=1.2 Hz, 1H) 6.88-6.86 (t, *J*=1.6 Hz, 1H) 4.22-4.19 (m, *J*=3.6 Hz, 2H), 3.55 (s, 2H) 3.07 (s, 3H) 1.25-1.19(t, *J*=7.2 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) *δ* (ppm) 169.45 (C) 168.75 (C) 155.50 (C) 148.82 (CH) 138.54 (C) 128.92 (CH) 128.30 (CH) 126.45 (C) 122.04 (CH) 120.27 (CH) 61.20 (C) 52.18 (CH_2) 35.71 (CH_3) 35.28 (CH_2) 14.01 (CH_3); MS (EI^+) m/z =310, 91, 77, 65, 44; GC-MS retention time R_t = 10.71 min; HRMS

(ESI):calcd for $[(C_{18}H_{18}N_2O_3) + Na]^+$ 333.1210; found 333.1209

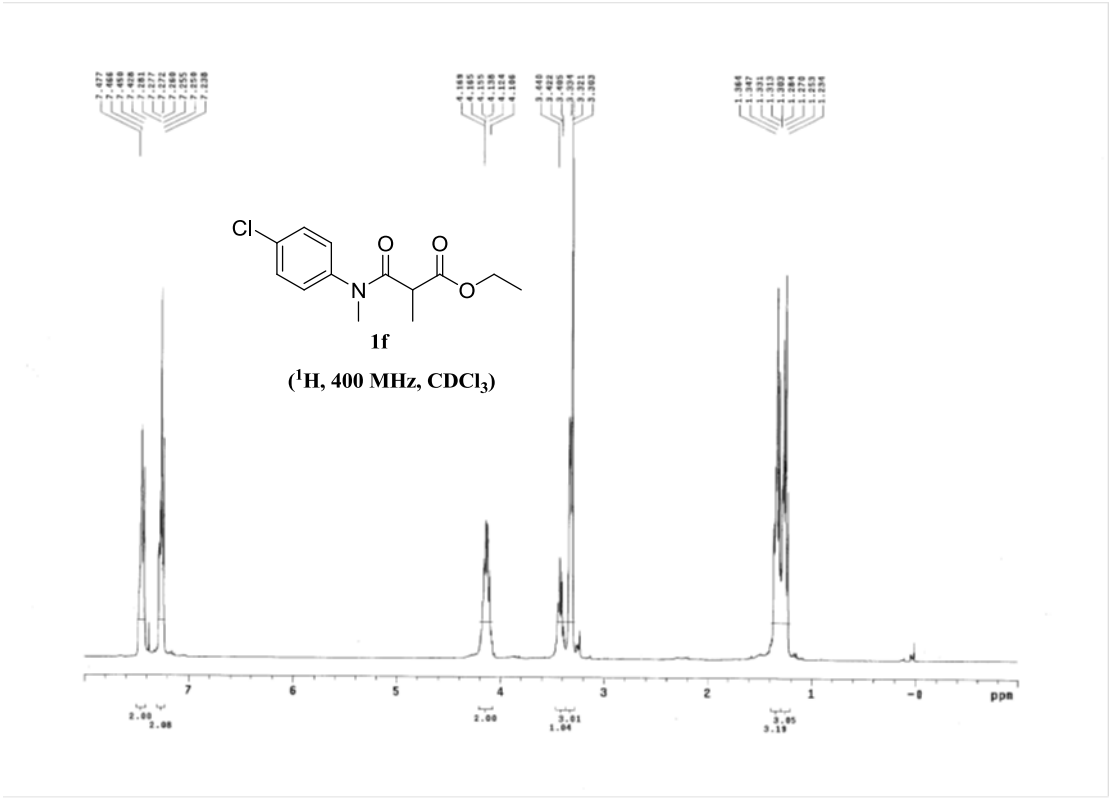
***Ethyl 3-allyl-1-methyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine-3-carboxylate* (*2o*)**

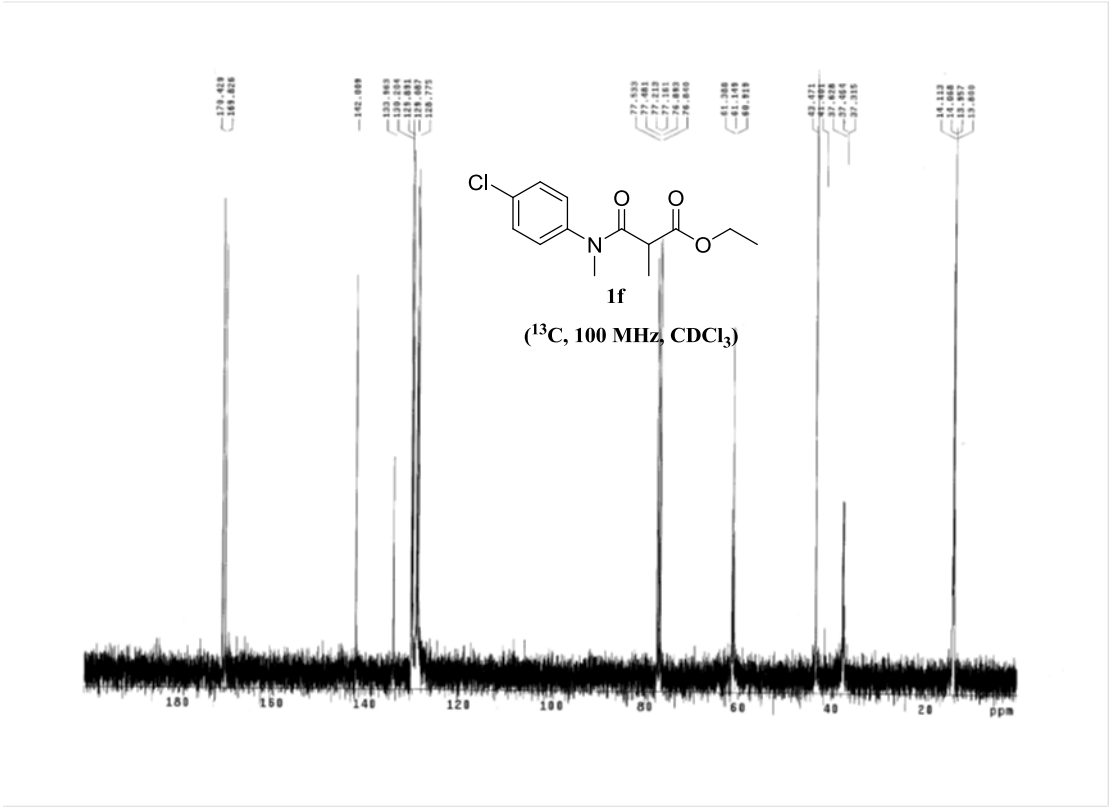


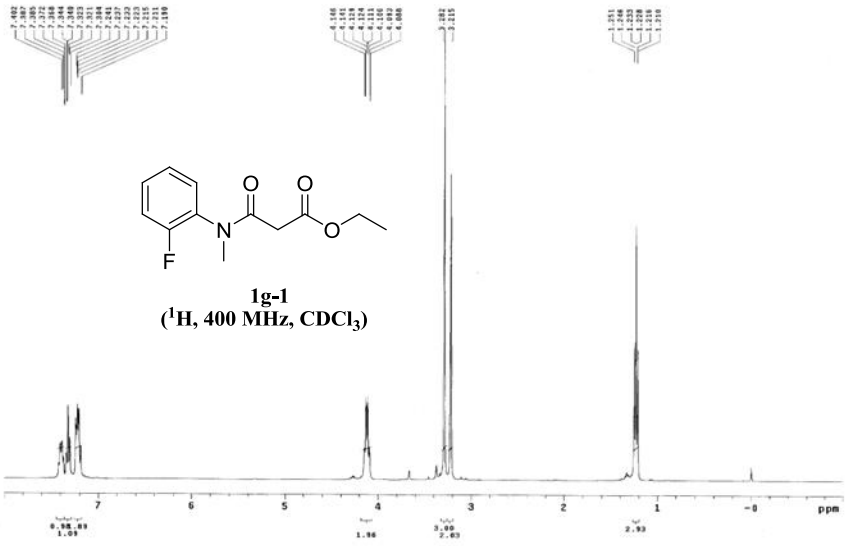
2o

Red solid; R_f = 0.37 (n-Hexane/Ethyl acetate 7:3 (v/v)); ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24-8.22 (d, *J*=1.6 Hz, *J*=1.6 Hz, 1H) 7.52-7.50 (dd, *J*= 1.0 Hz, *J*=1.2 Hz, 1H) 7.00-6.97 (dd, *J*=1.0 Hz, *J*=7.2 Hz, 1H) 5.46-5.38 (m, *J*=7.6 Hz, 1H), 5.07-4.97 (m, *J*=1.2 Hz, 2H), 4.21-4.12 (m, *J*=3.6 Hz, 2H), 3.04-2.89 (m, *J*=6.8 Hz, 2H) 1.25-1.17(t, *J*=6.8 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 169.41 (C) 168.53 (C) 143.14 (C) 138.42 (CH) 129.60 (CH) 129.30 (CH) 128.30 (C) 127.70 (CH) 126.56 (CH2) 61.24 (C) 50.97 (CH_2) 37.41 (CH_2) 35.27 (CH_3) 14.09 (CH_3); MS (EI^+) m/z =260, 187, 174, 159, 147, 131, 118, 103, 77; GC-MS retention time R_t = 10.62 min; Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.65; H, 6.17; N, 10.61.

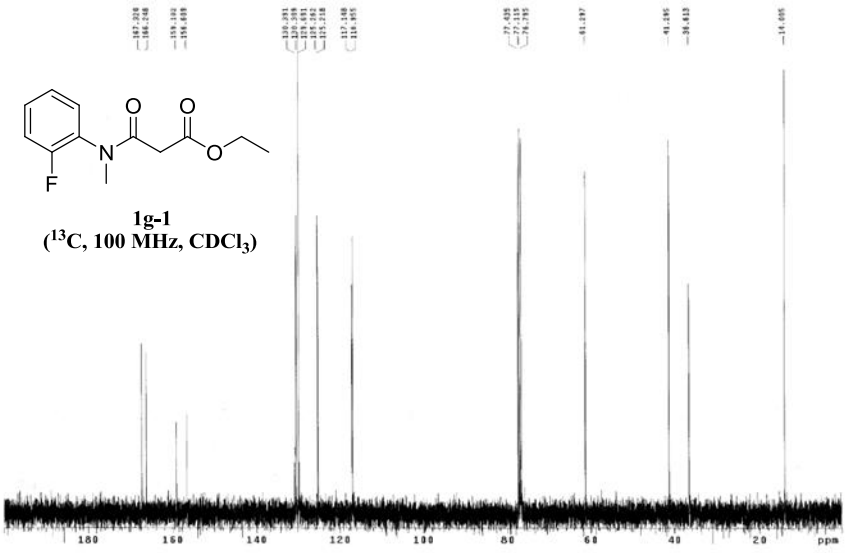
^{1}H NMR and ^{13}C NMR Spectra :



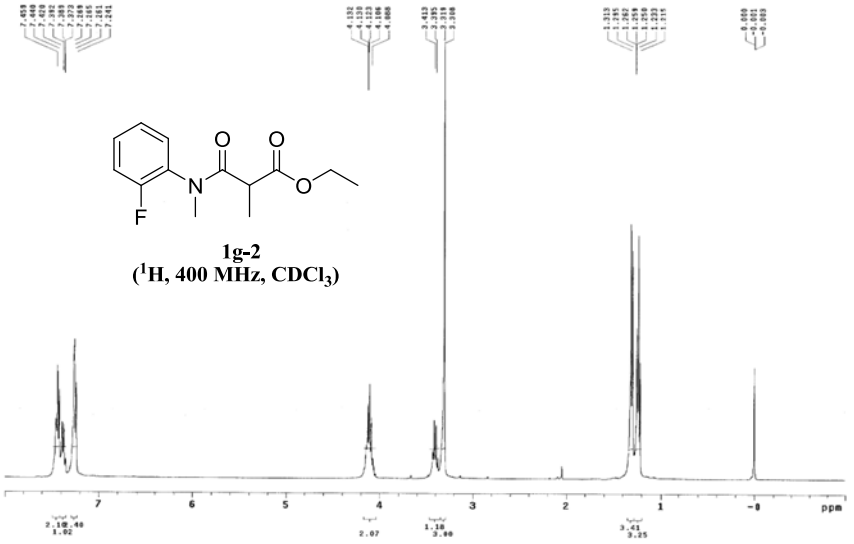




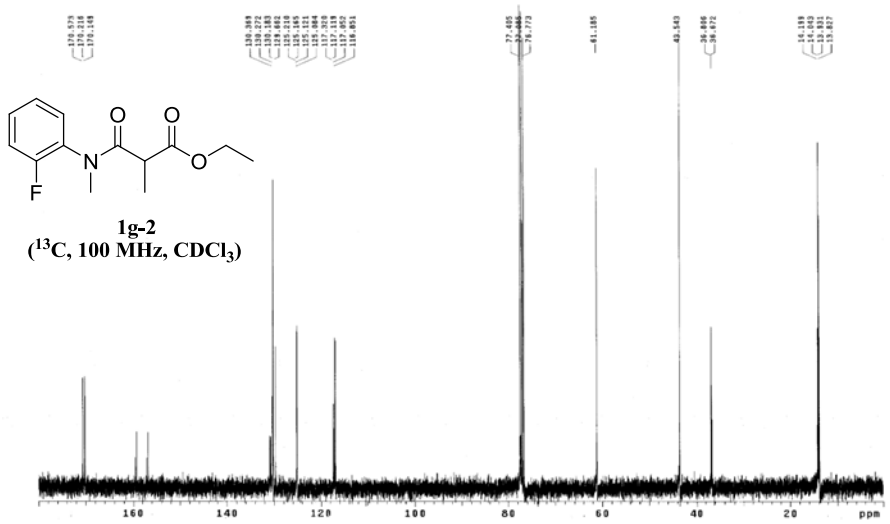
1g-1
(^{1}H, 400 MHz, $CDCl_3$)



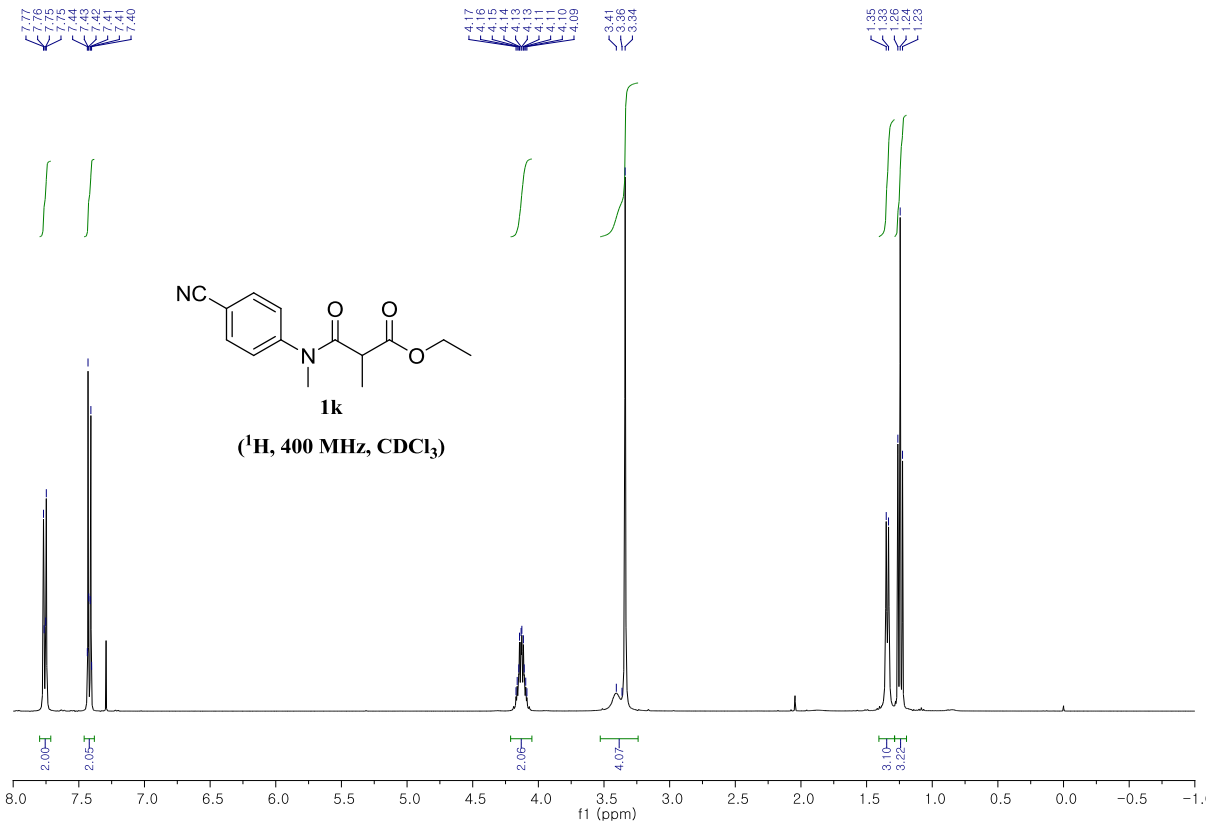
1g-1
(^{13}C, 100 MHz, $CDCl_3$)



1g-2
(^{1}H, 400 MHz, $CDCl_3$)

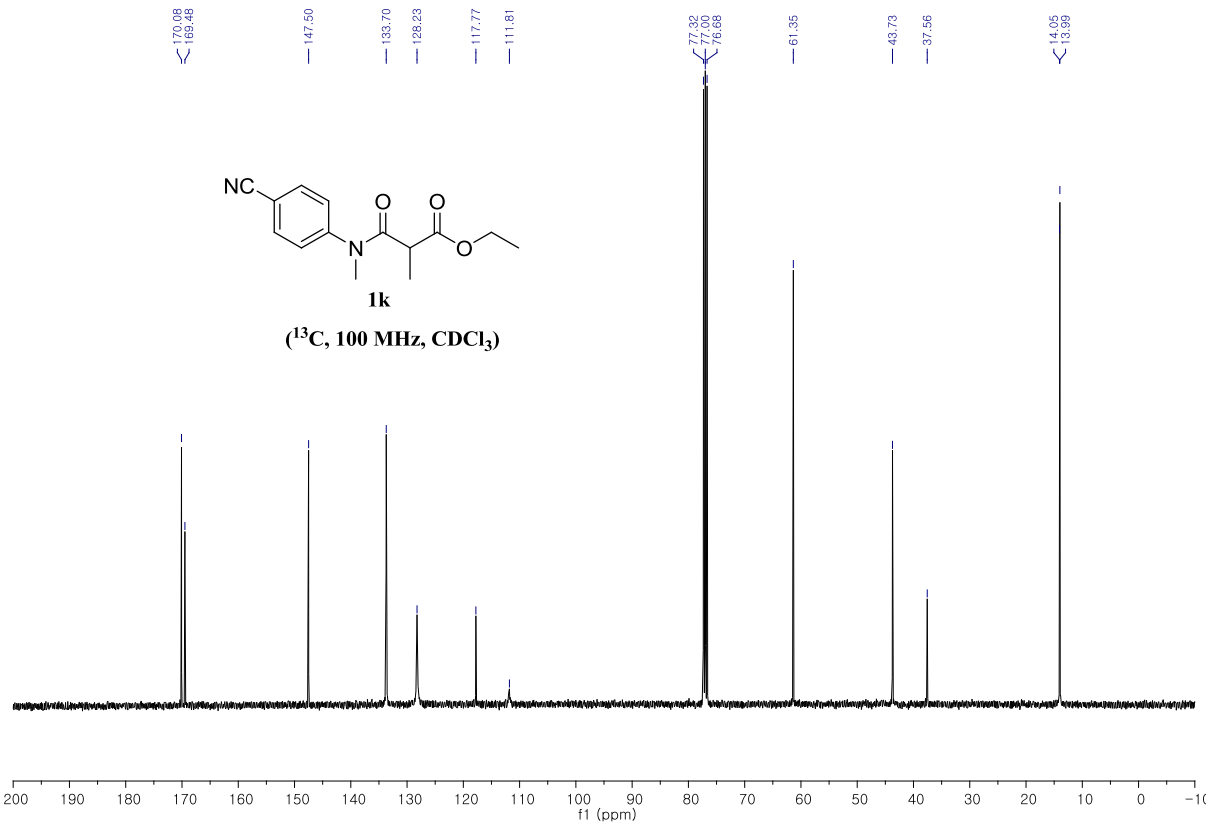


1g-2
(^{13}C, 100 MHz, $CDCl_3$)



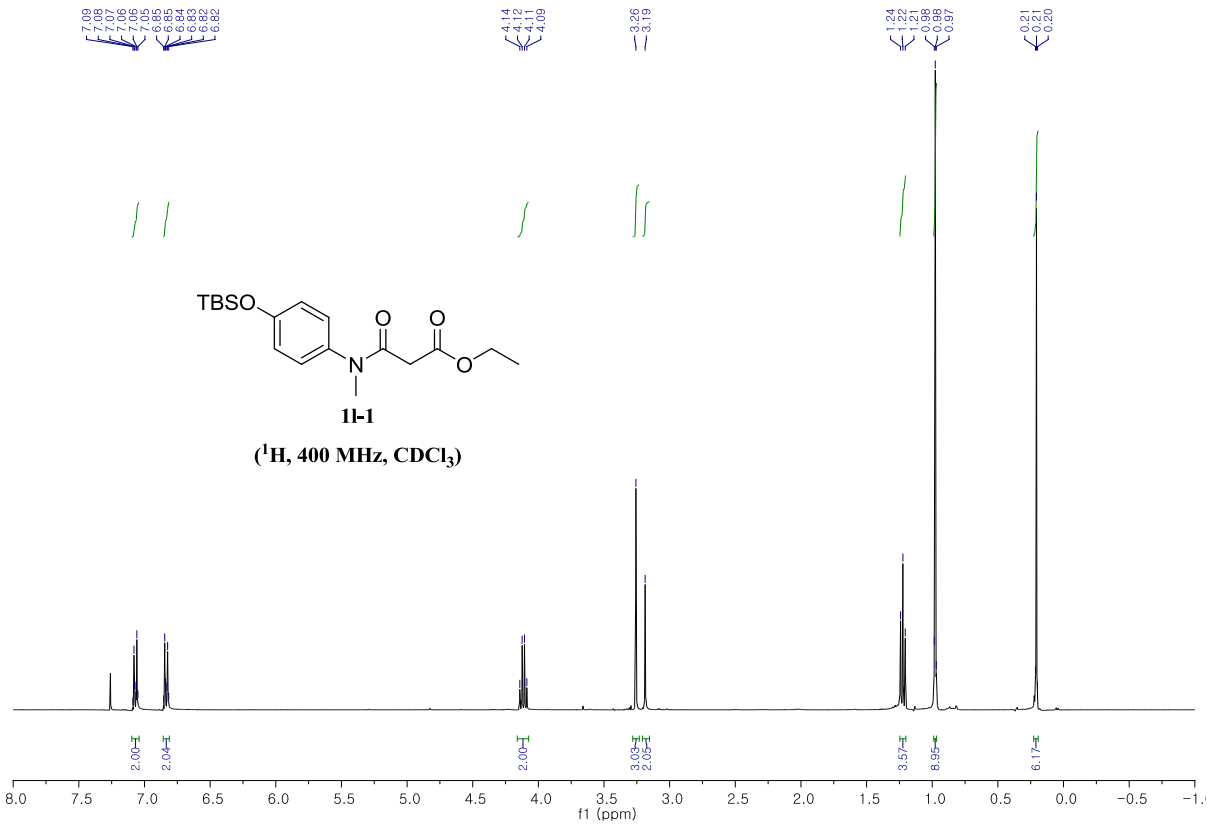
1k

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



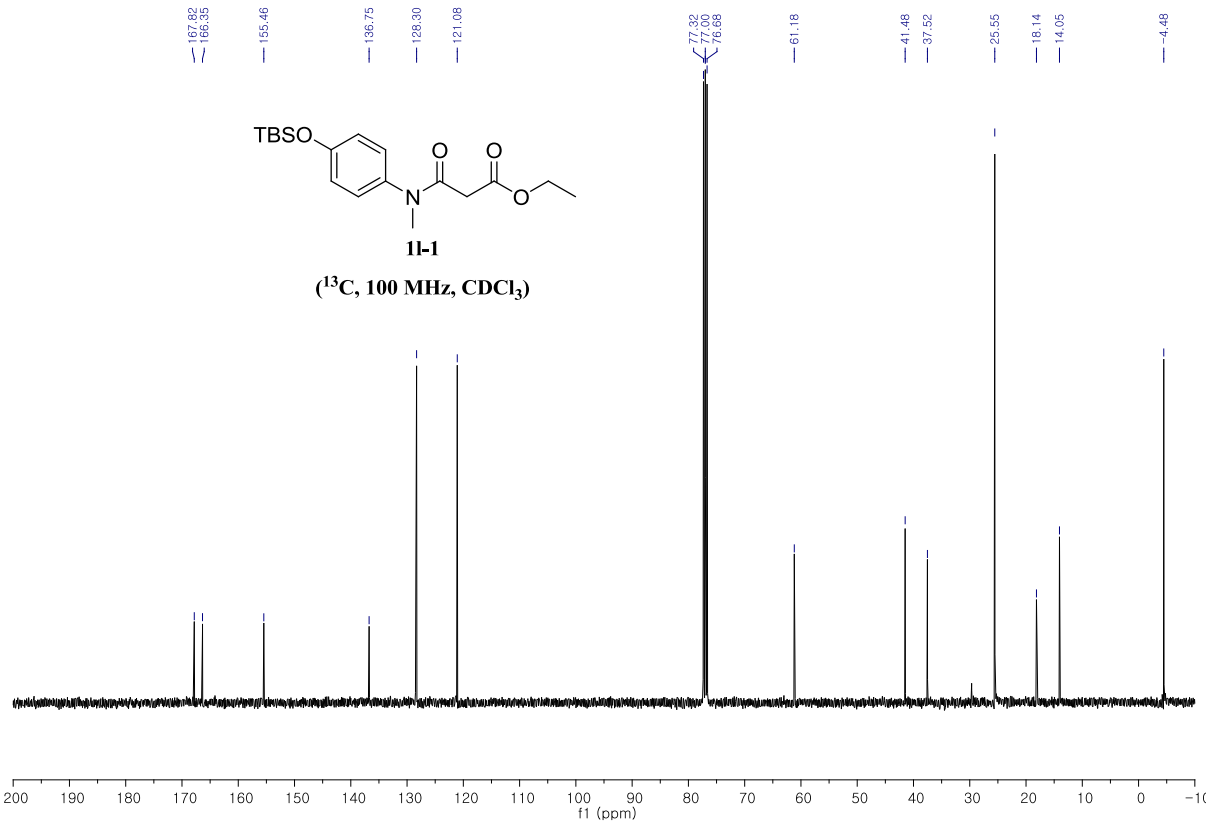
1k

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



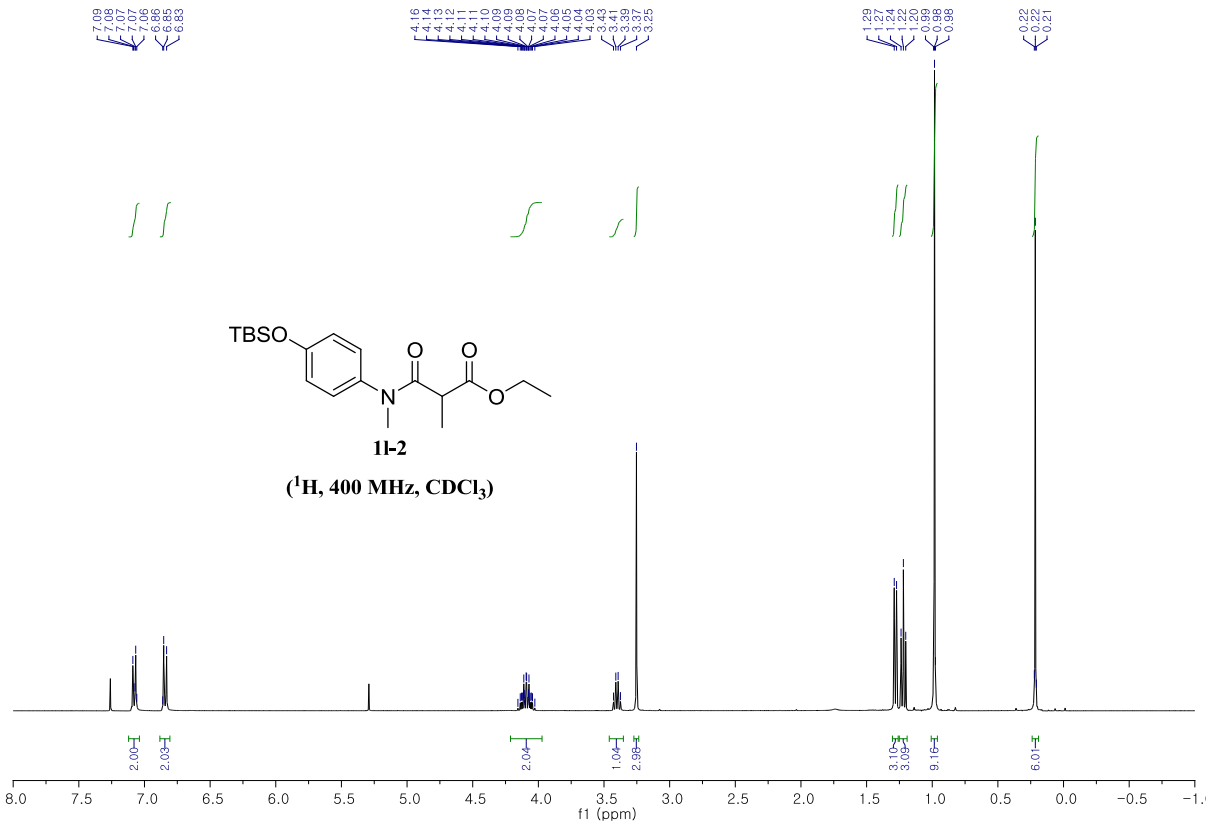
1l-1

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



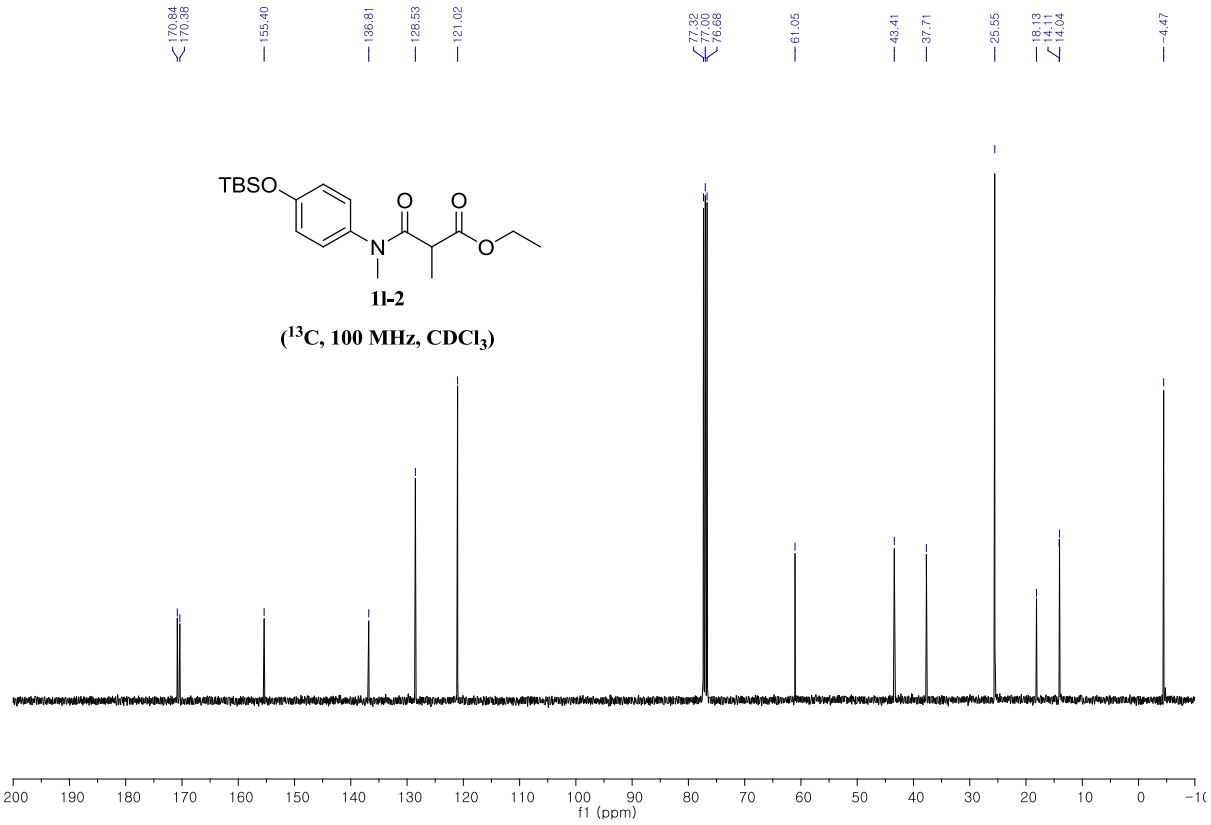
1l-1

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



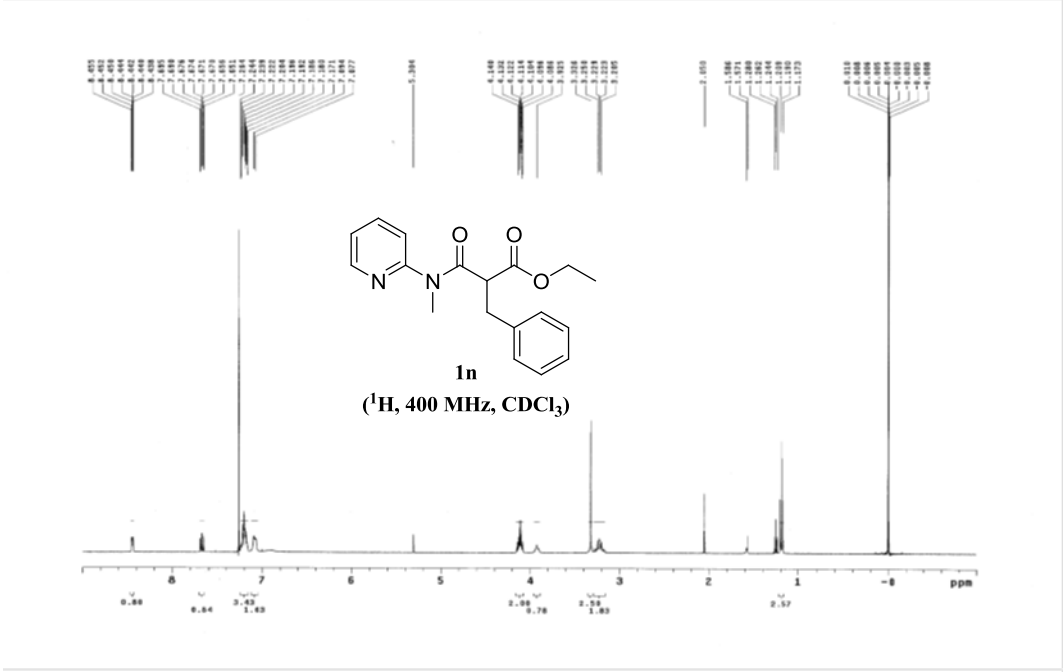
1l-2

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



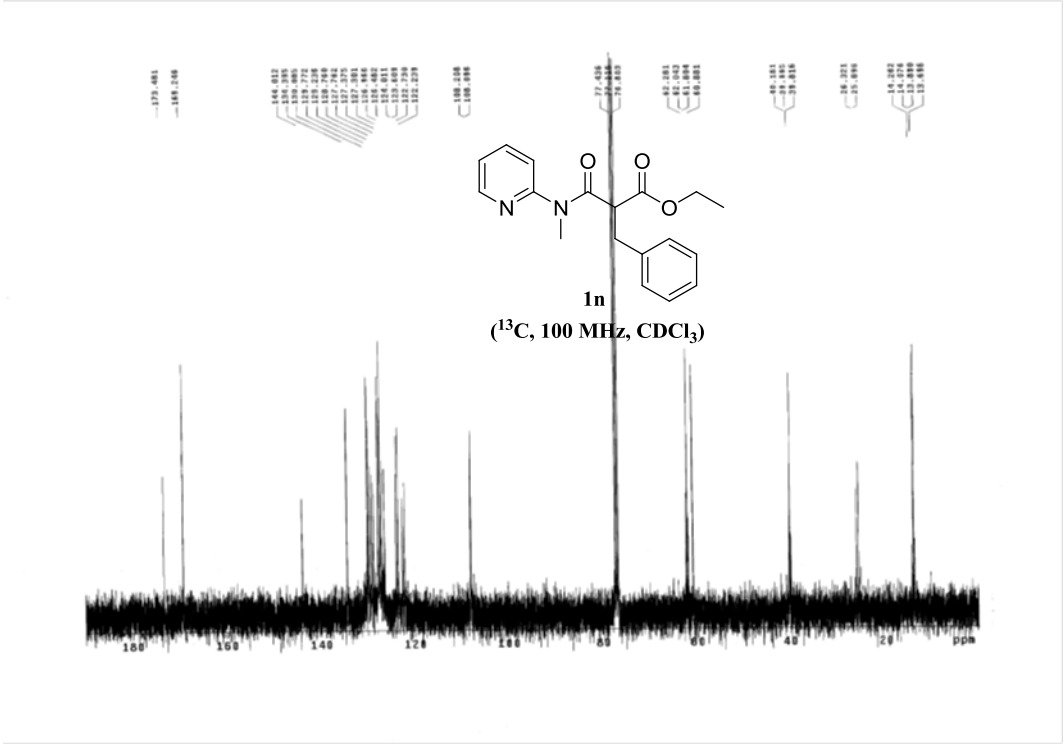
1l-2

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



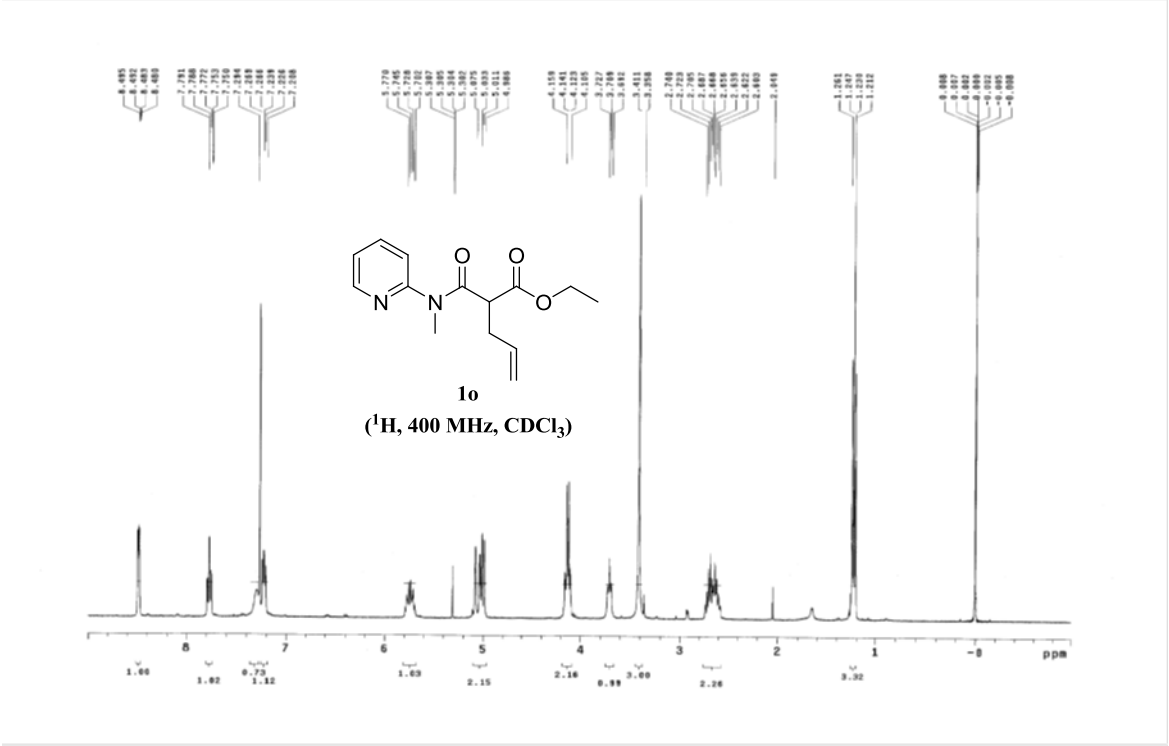
1n

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



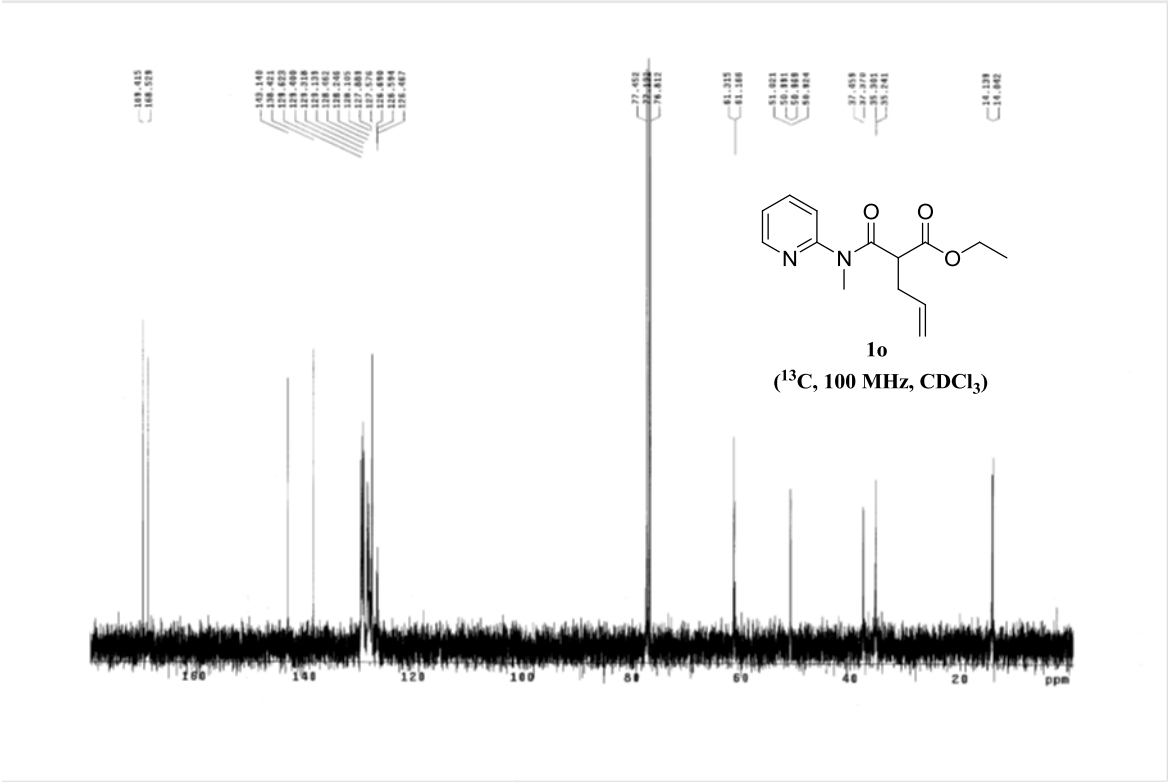
1n

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



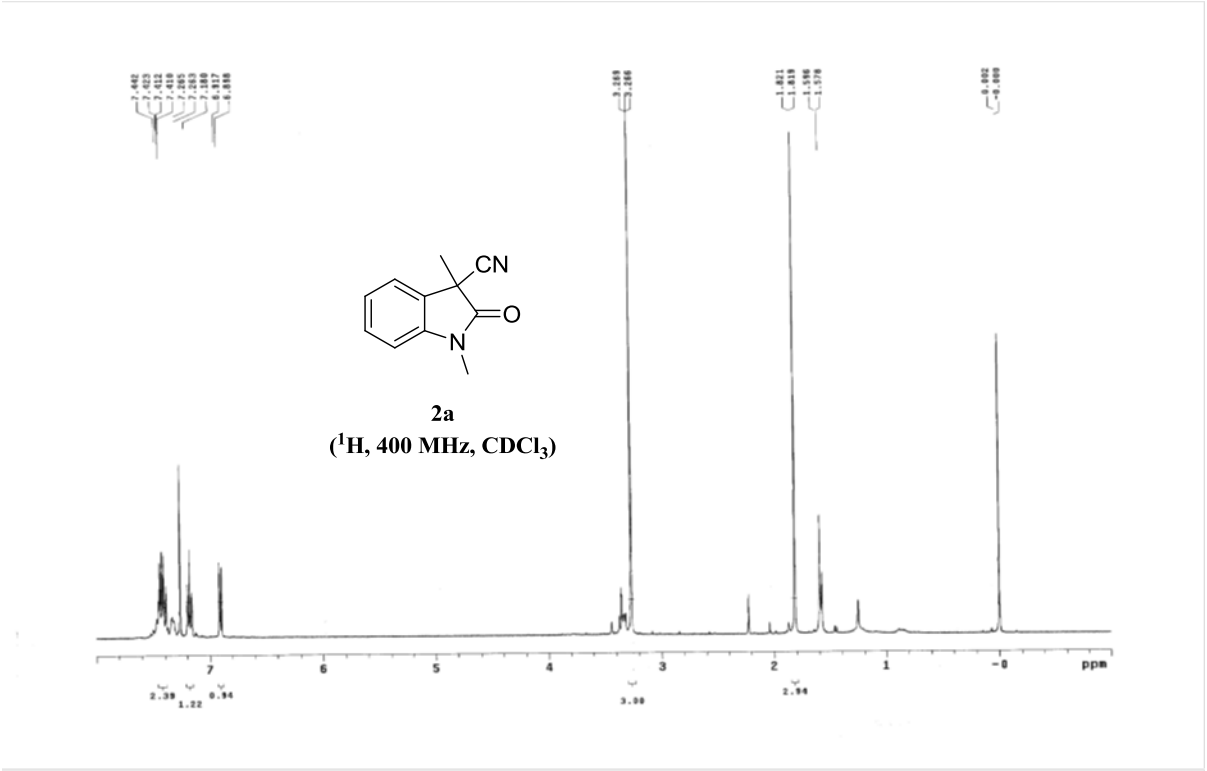
1o

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

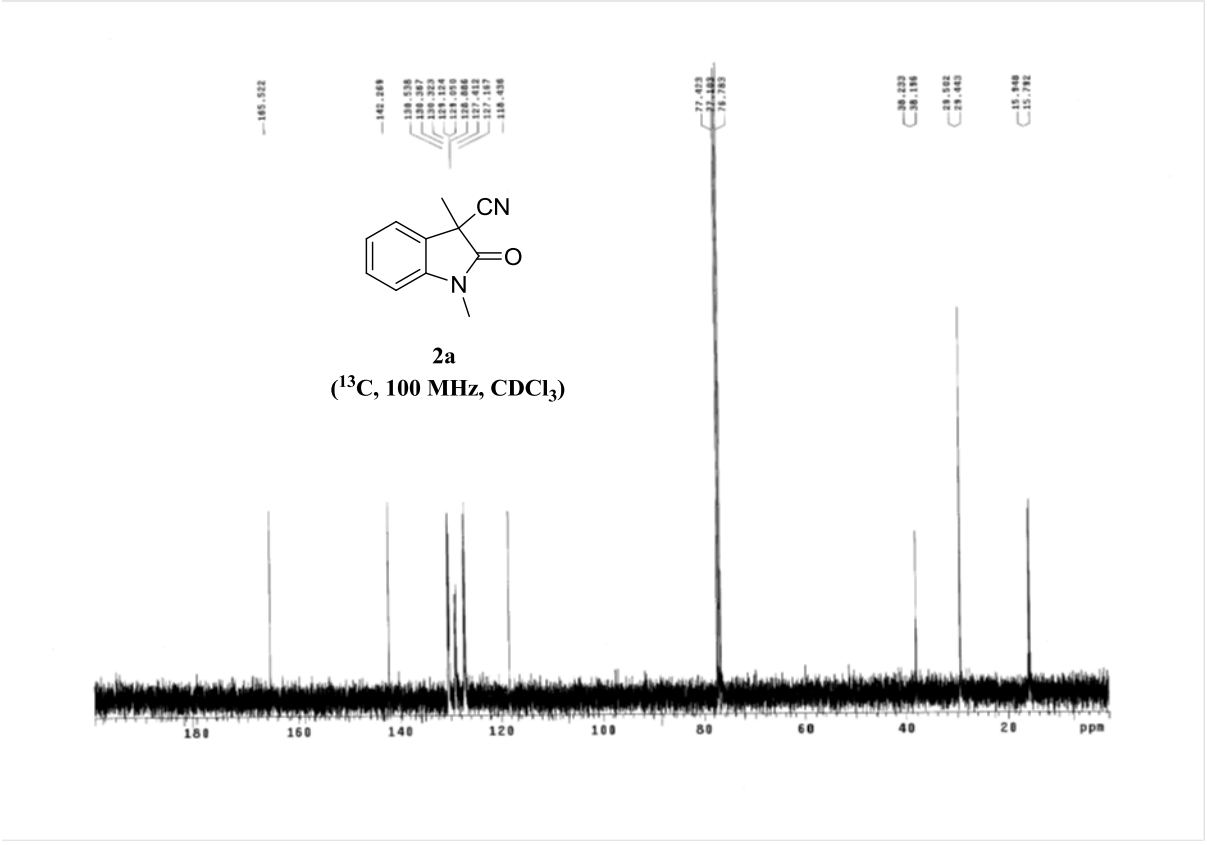


1o

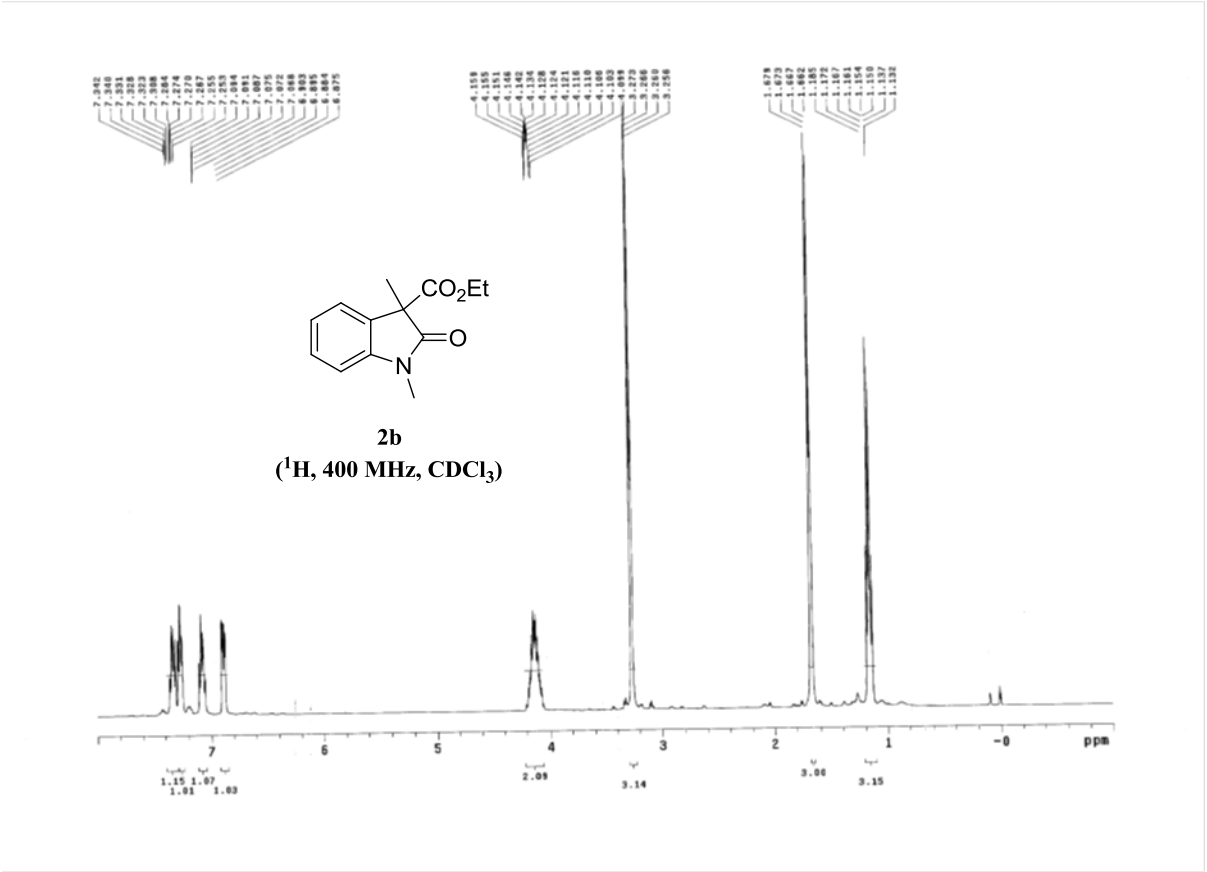
(^{13}C, 100 MHz, $CDCl_3$)



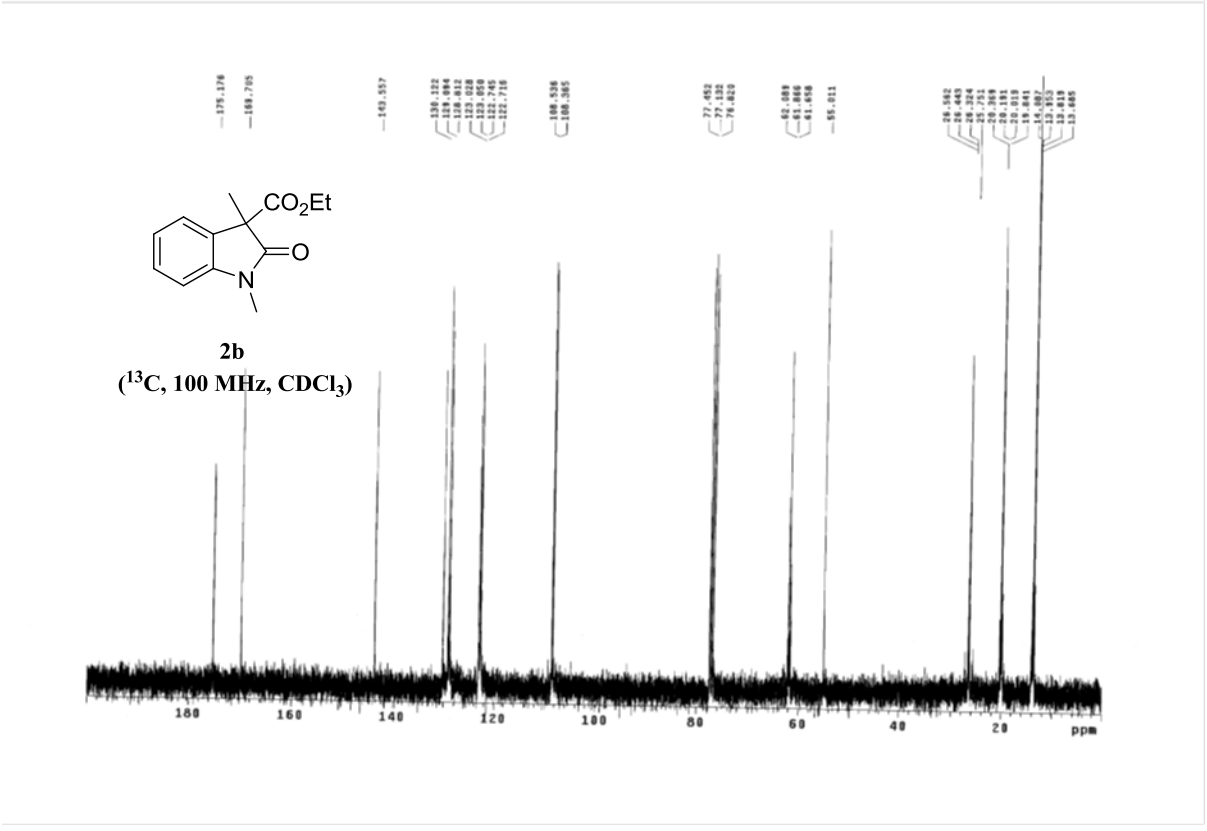
2a
(^{1}H, 400 MHz, $CDCl_3$)



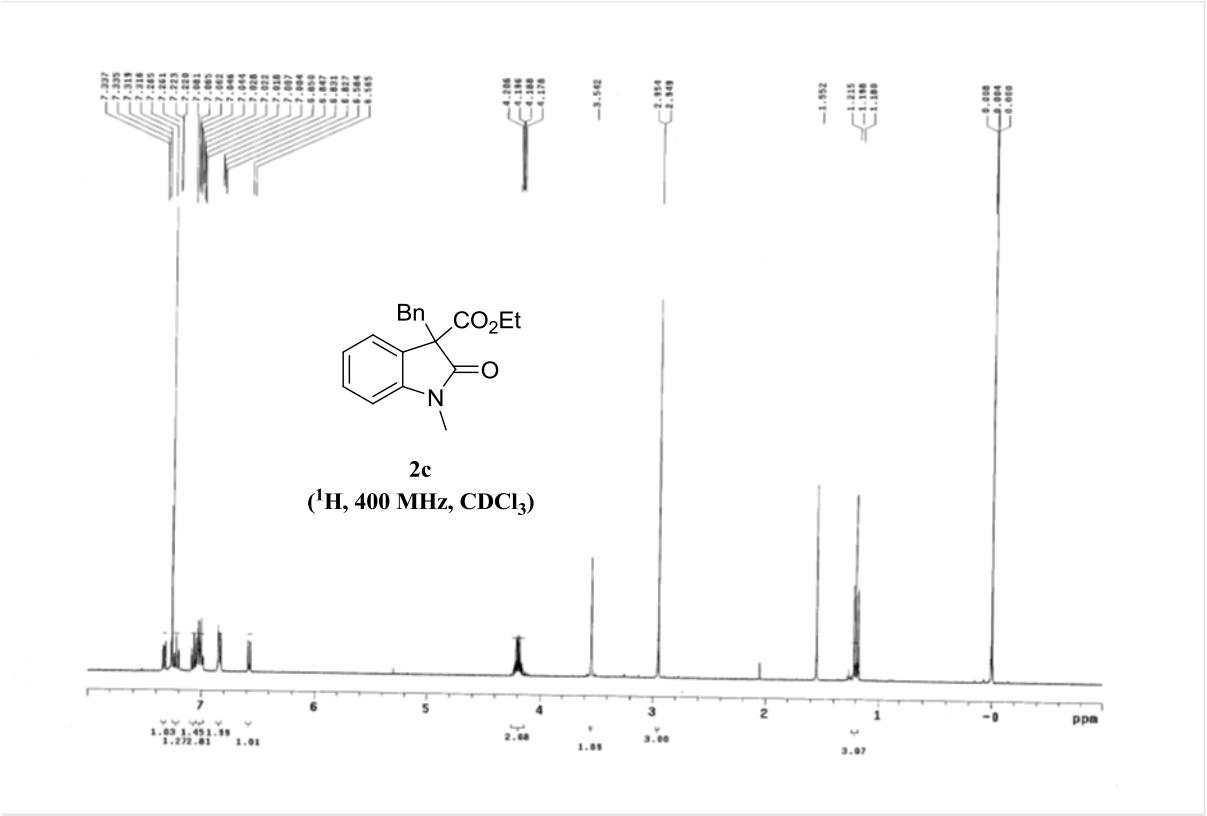
2a
(^{13}C, 100 MHz, $CDCl_3$)



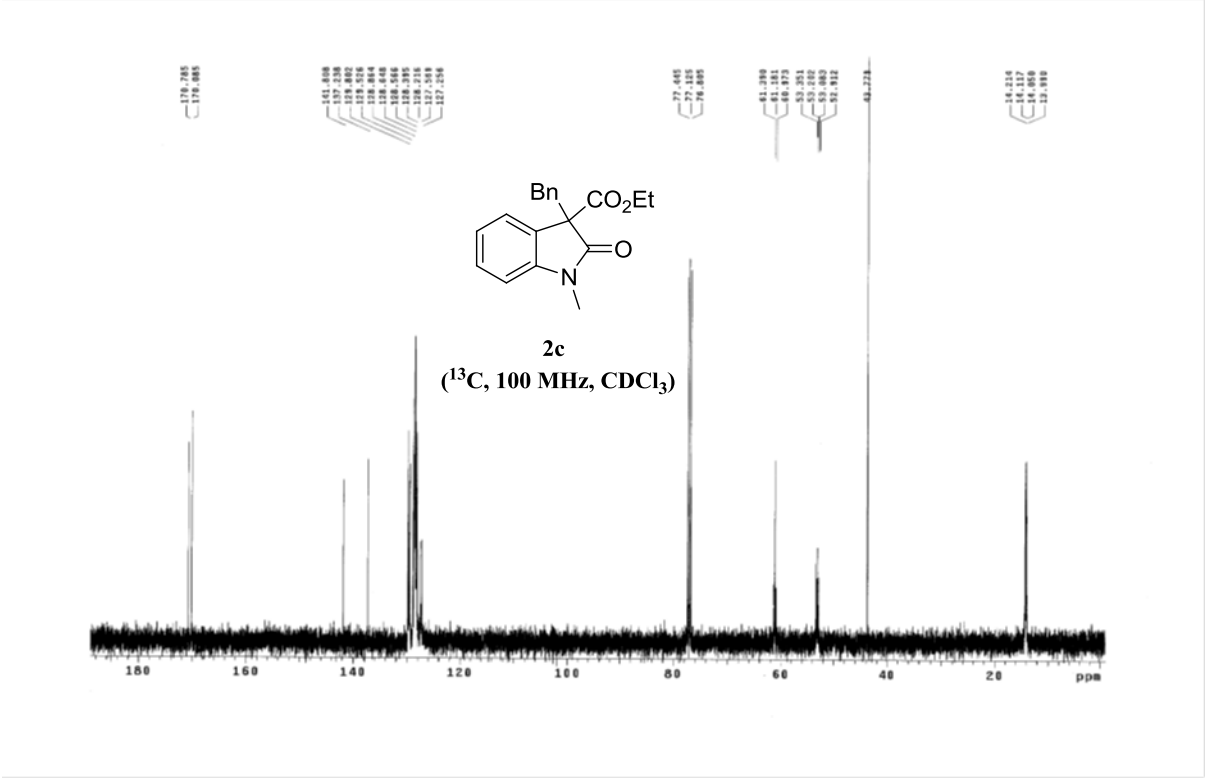
2b
(^{1}H, 400 MHz, $CDCl_3$)



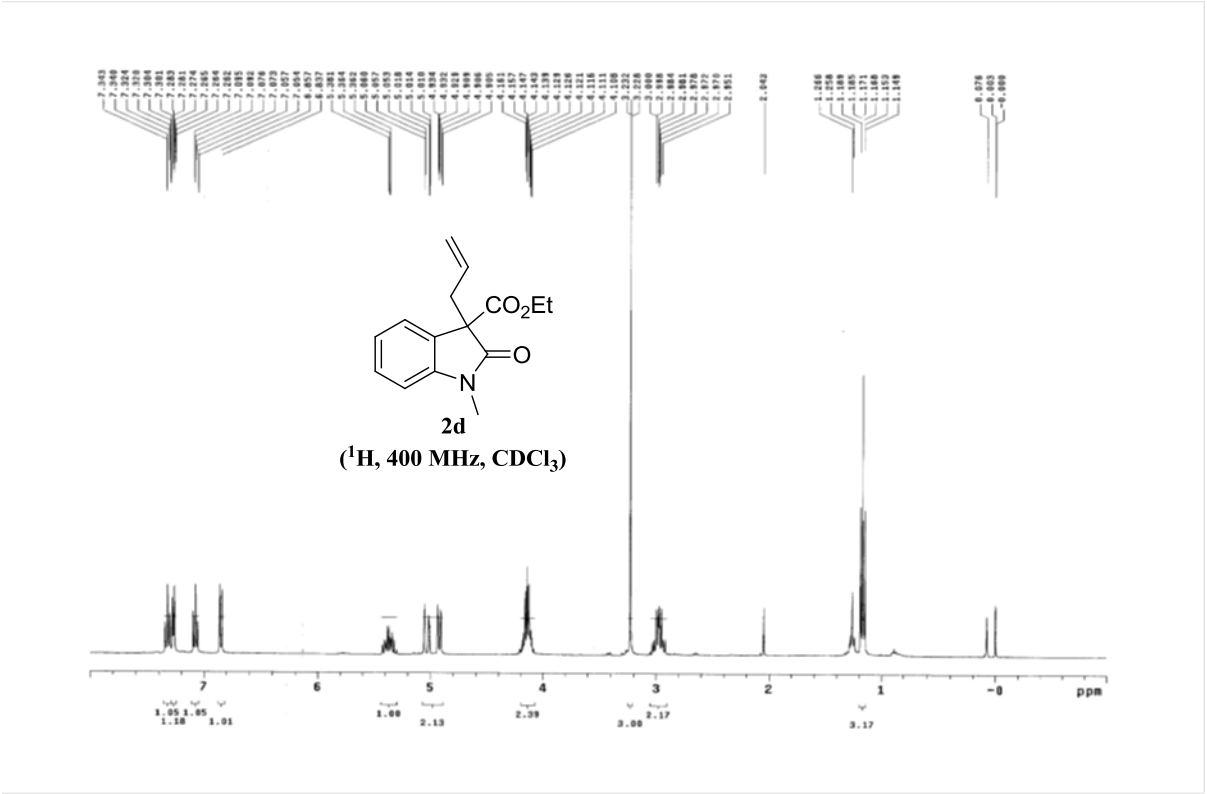
2b
(^{13}C, 100 MHz, $CDCl_3$)



2c
(^{1}H, 400 MHz, $CDCl_3$)

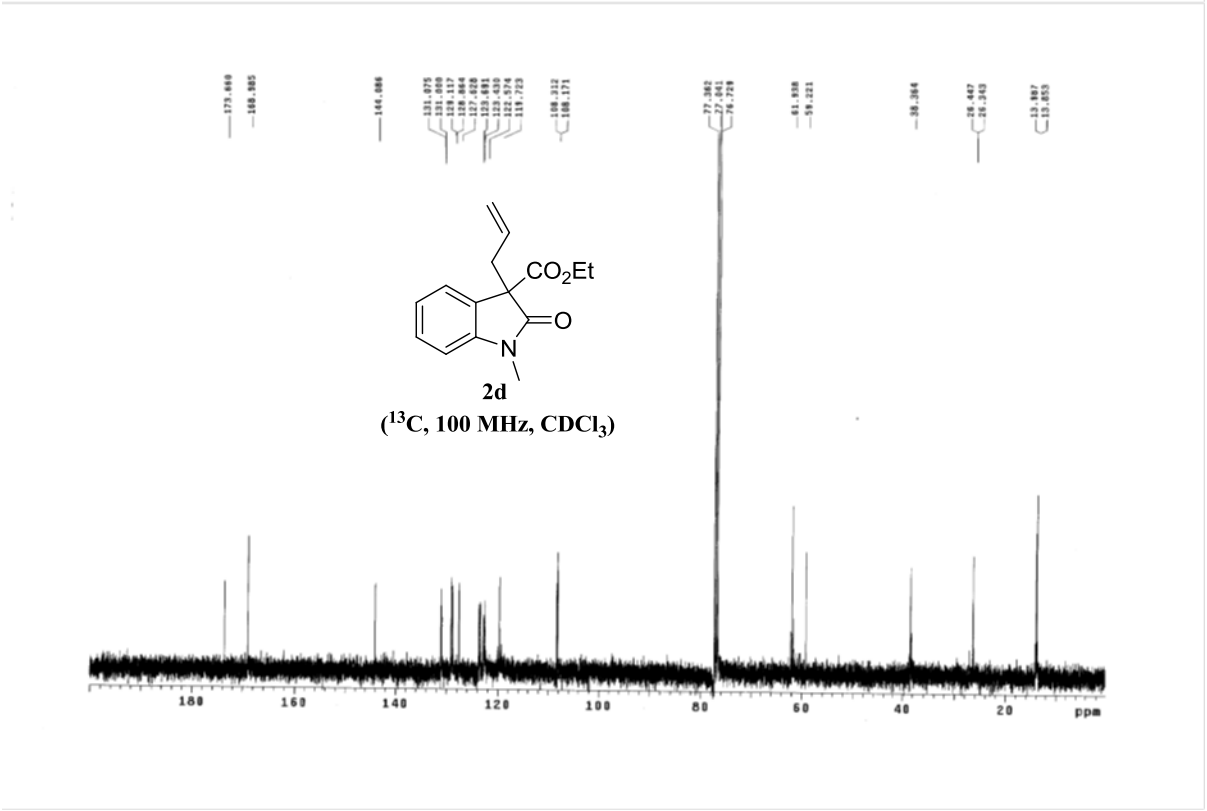


2c
(^{13}C, 100 MHz, $CDCl_3$)



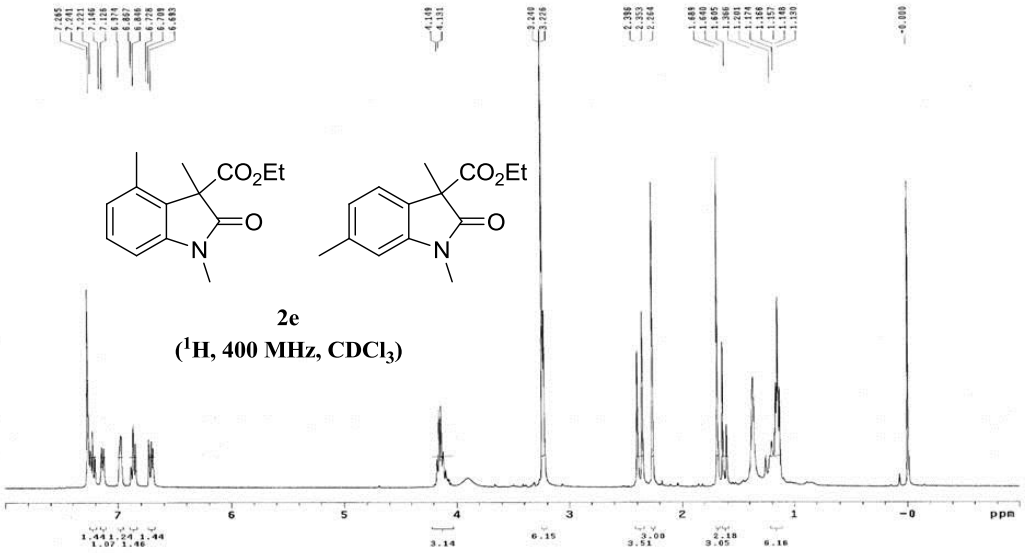
2d

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

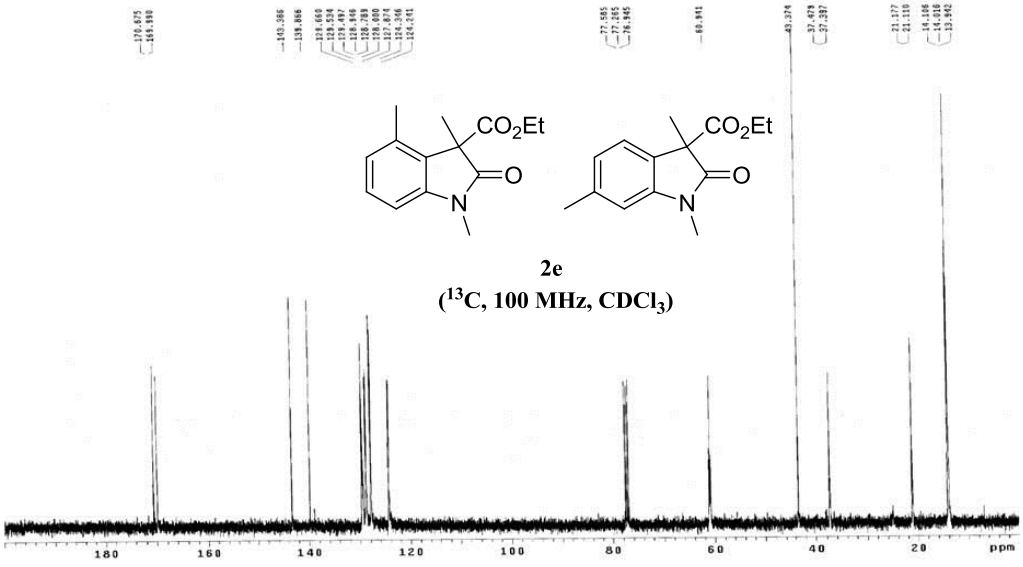


2d

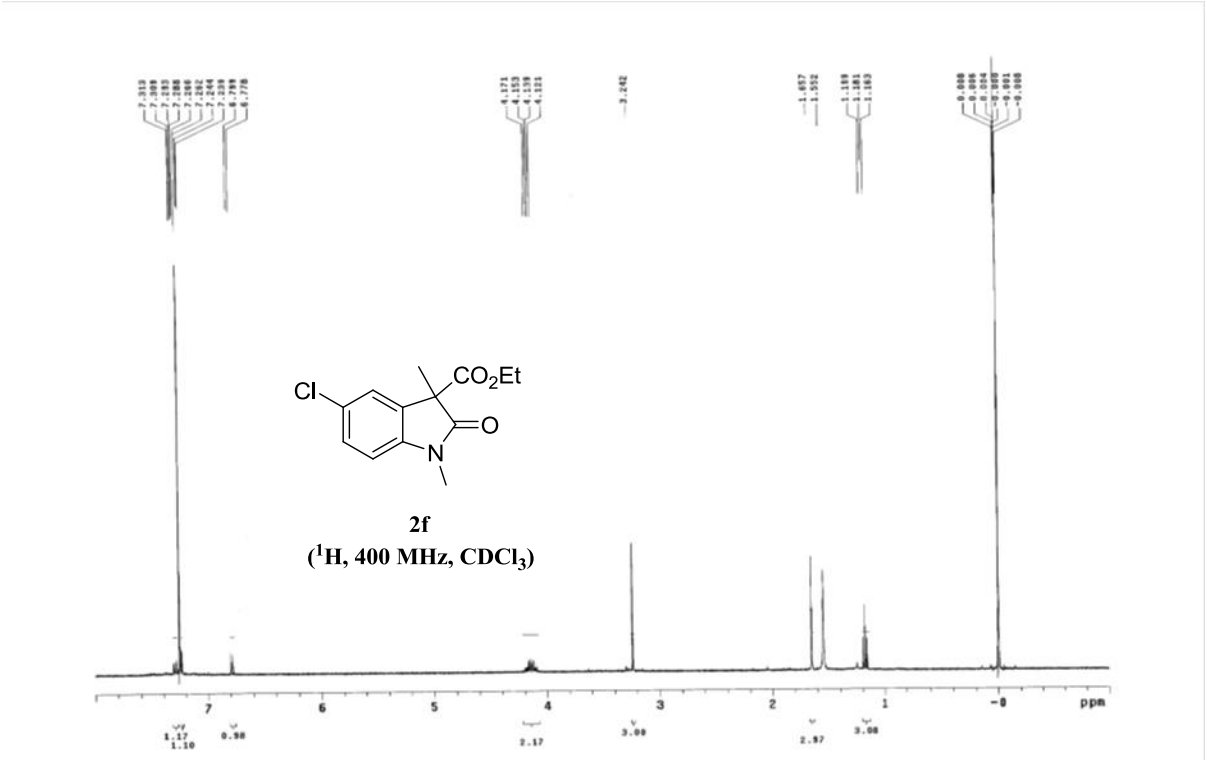
(^{13}C, 100 MHz, $CDCl_3$)



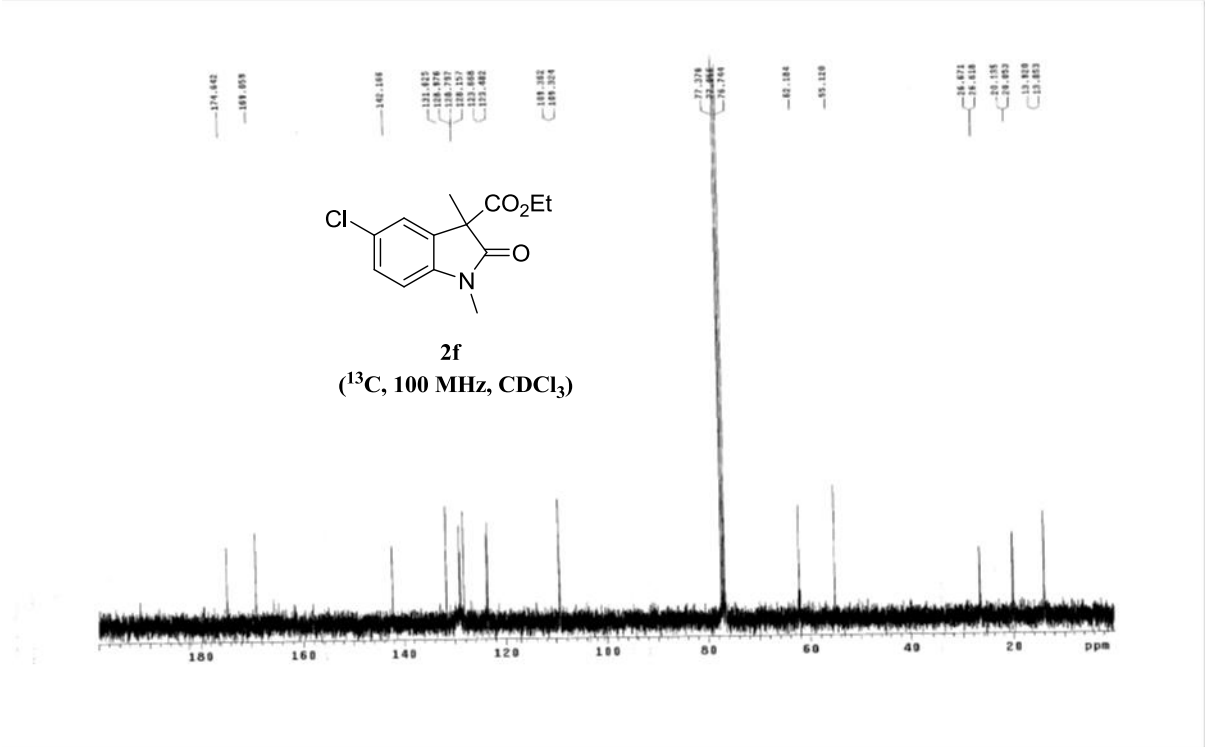
2e
(^{1}H, 400 MHz, $CDCl_3$)



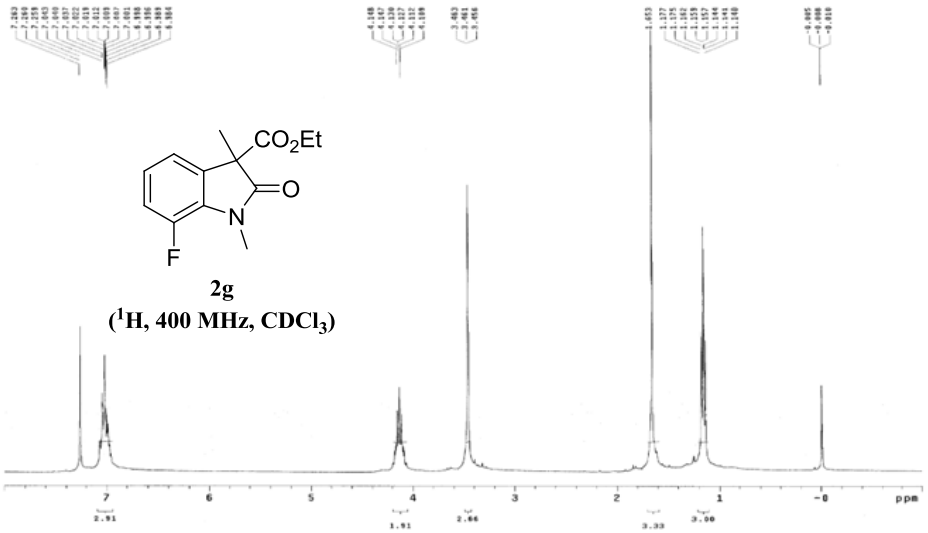
2e
(^{13}C, 100 MHz, $CDCl_3$)



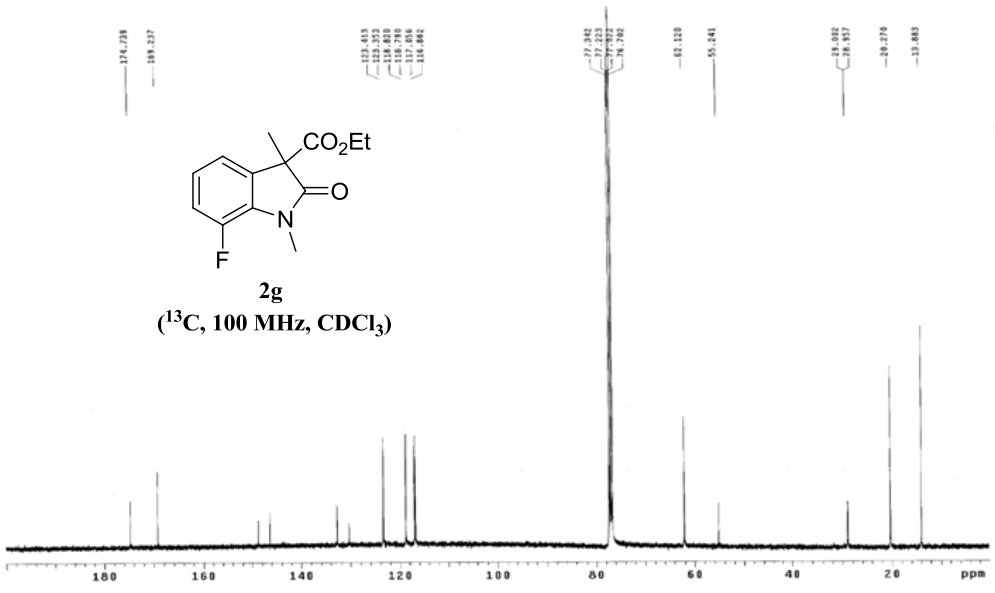
2f
(^{1}H, 400 MHz, $CDCl_3$)



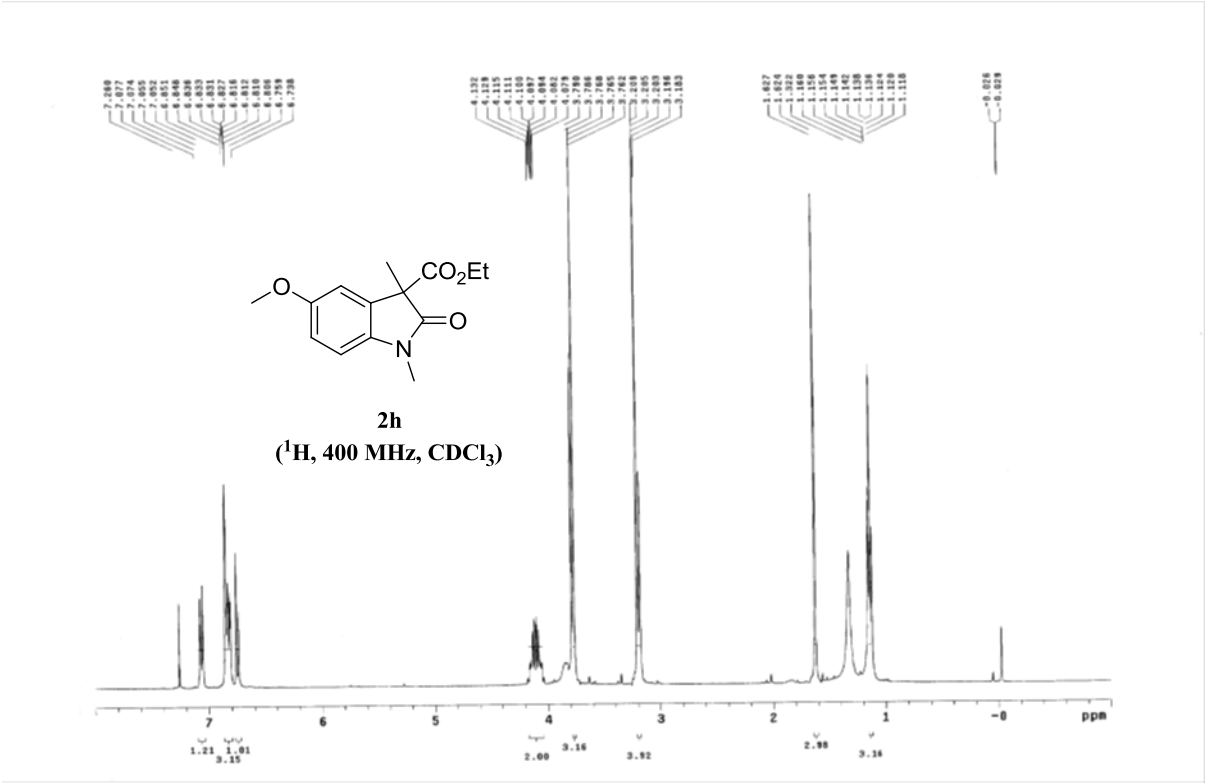
2f
(^{13}C, 100 MHz, $CDCl_3$)



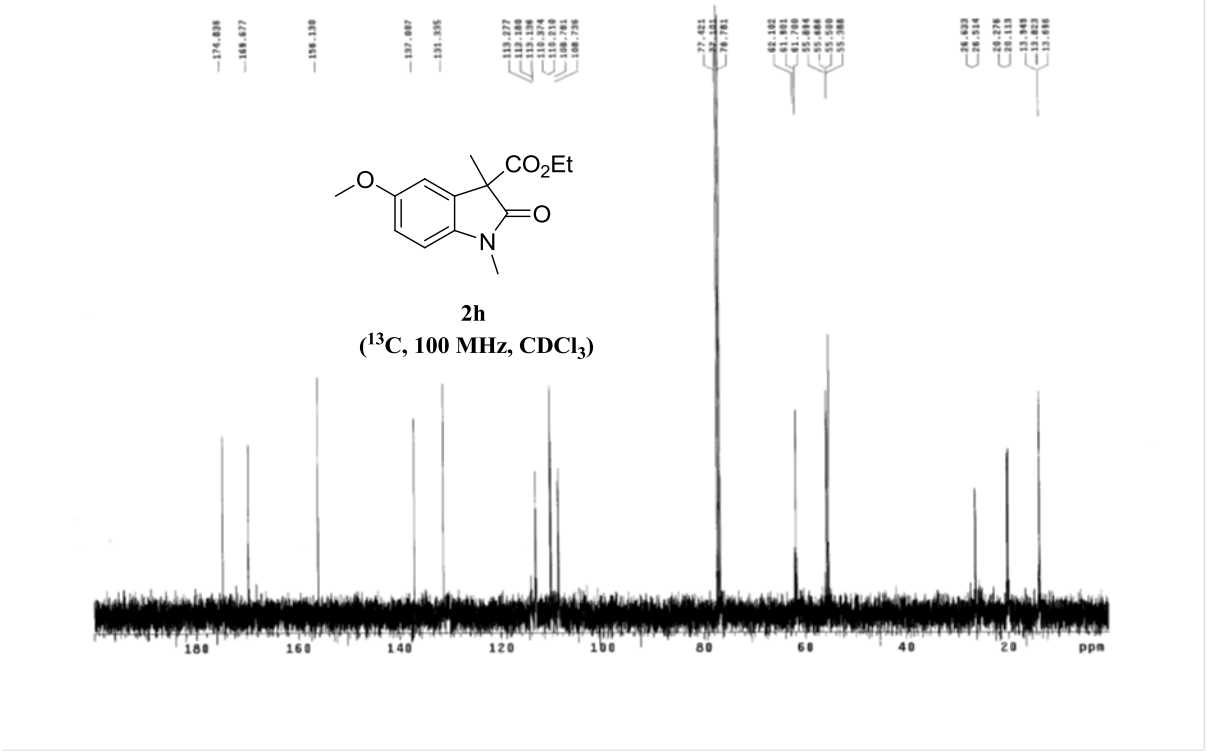
2g
(^{1}H, 400 MHz, $CDCl_3$)



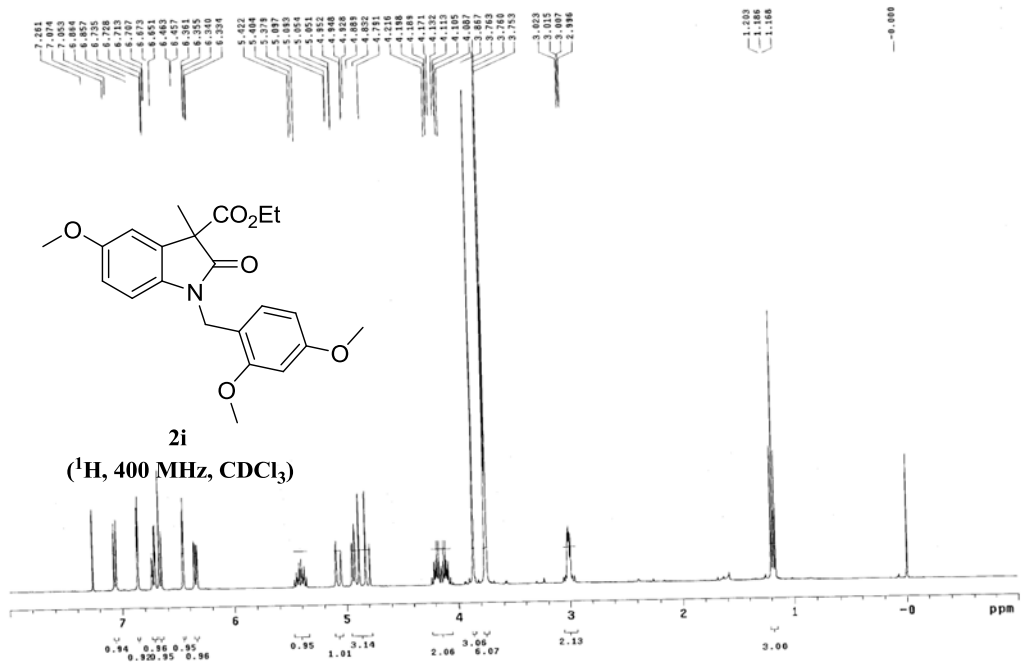
2g
(^{13}C, 100 MHz, $CDCl_3$)



2h
(^{1}H, 400 MHz, $CDCl_3$)

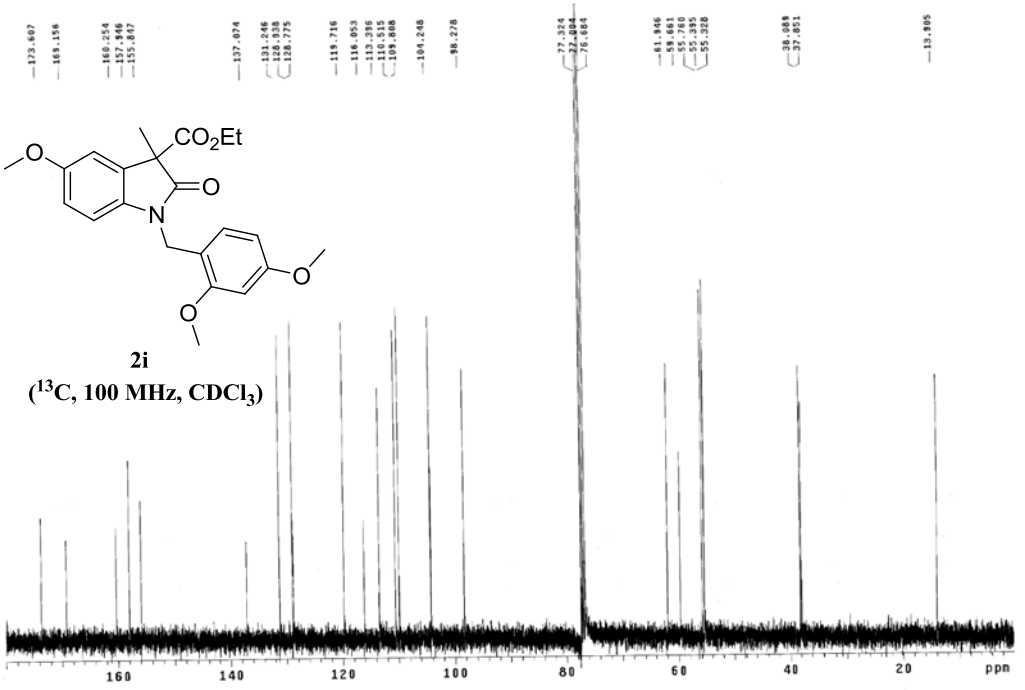


2h
(^{13}C, 100 MHz, $CDCl_3$)



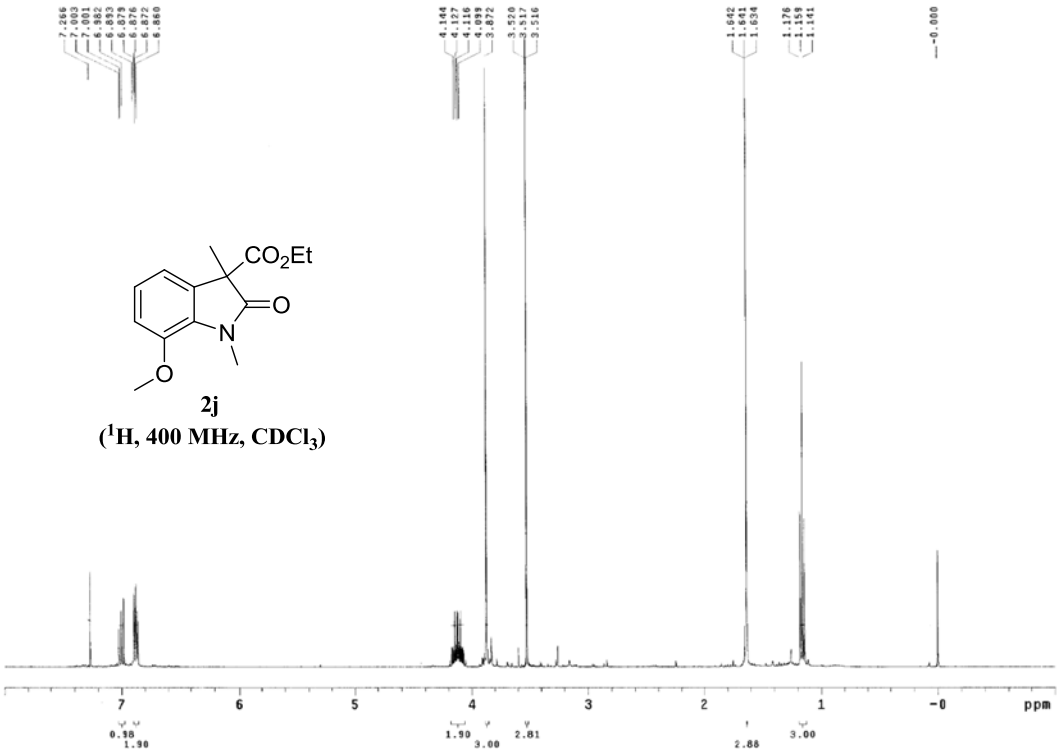
2i

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

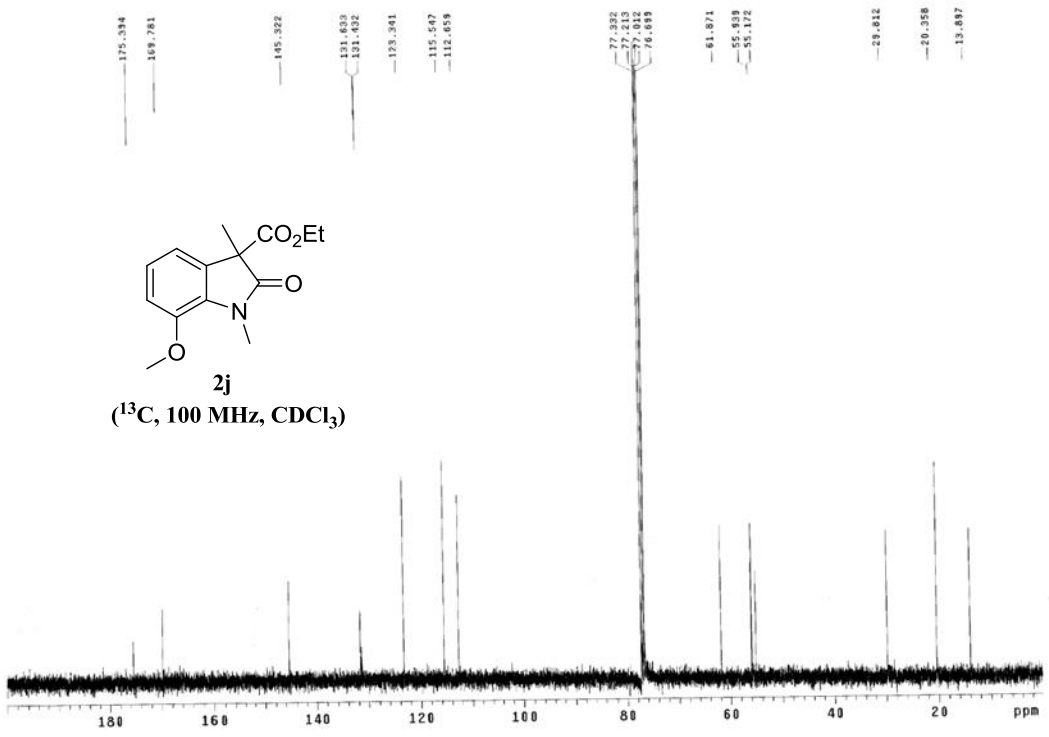


2i

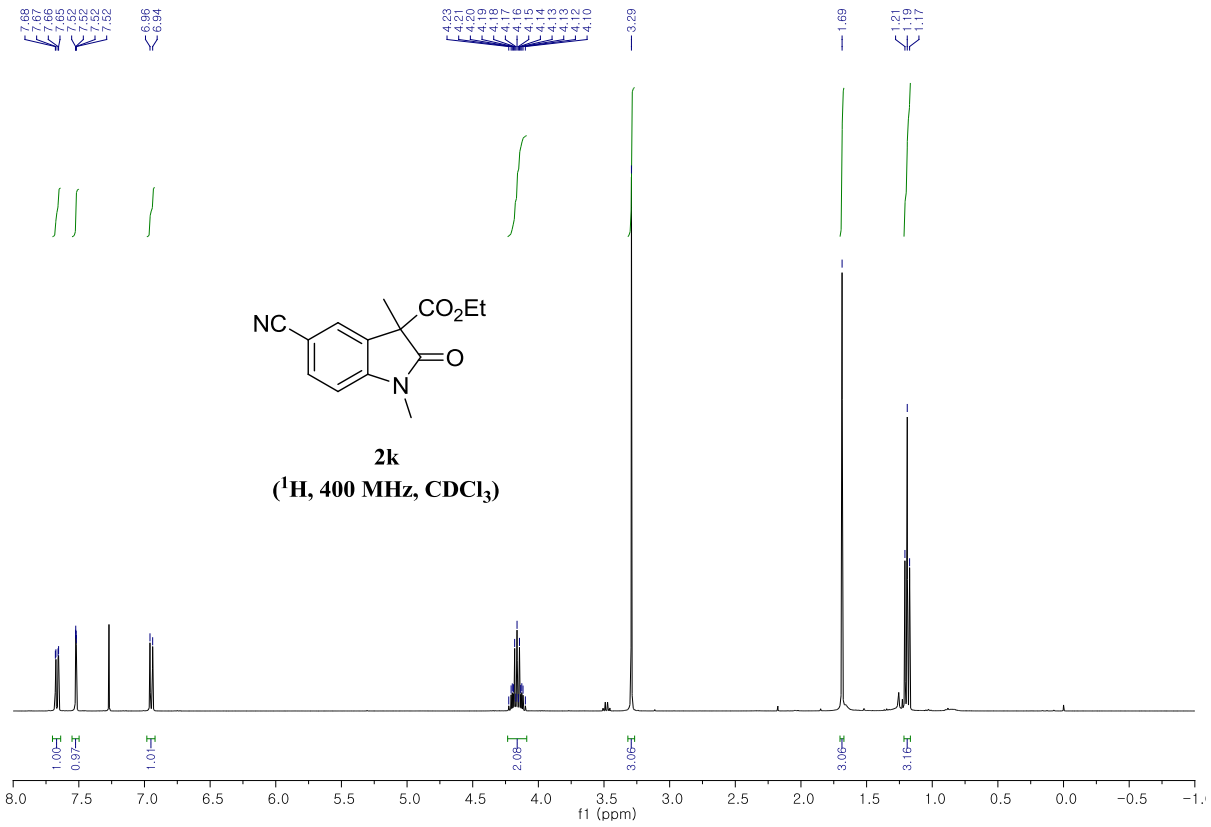
(^{13}C, 100 MHz, $CDCl_3$)



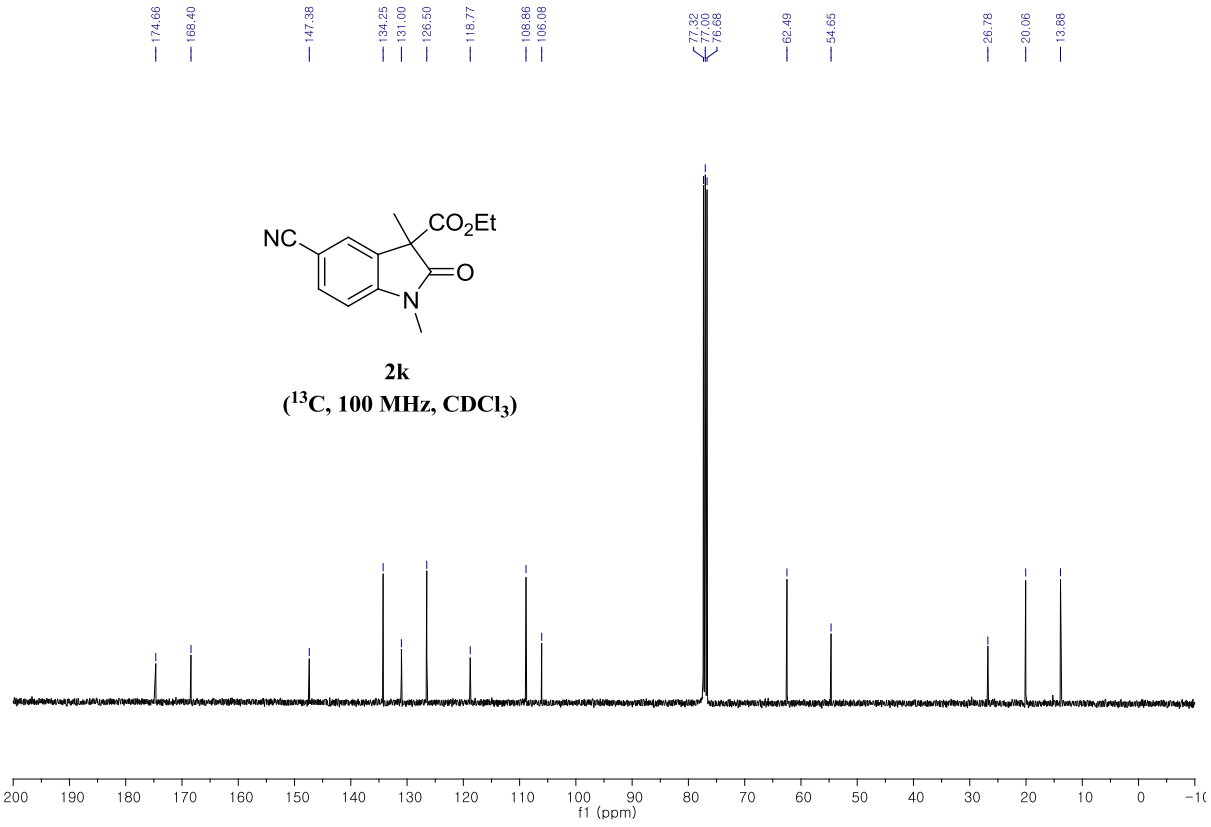
2j
(^{1}H, 400 MHz, $CDCl_3$)



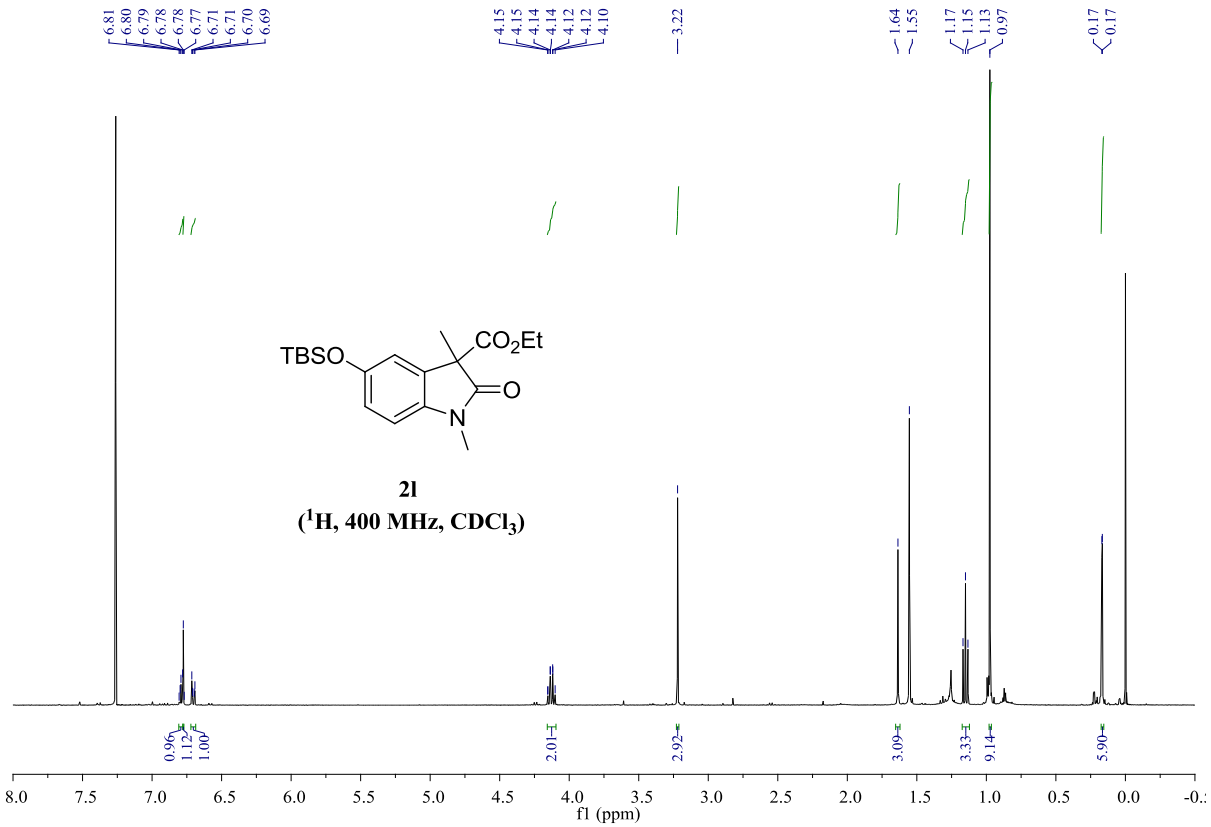
2j
(^{13}C, 100 MHz, $CDCl_3$)



2k
(^{1}H, 400 MHz, $CDCl_3$)

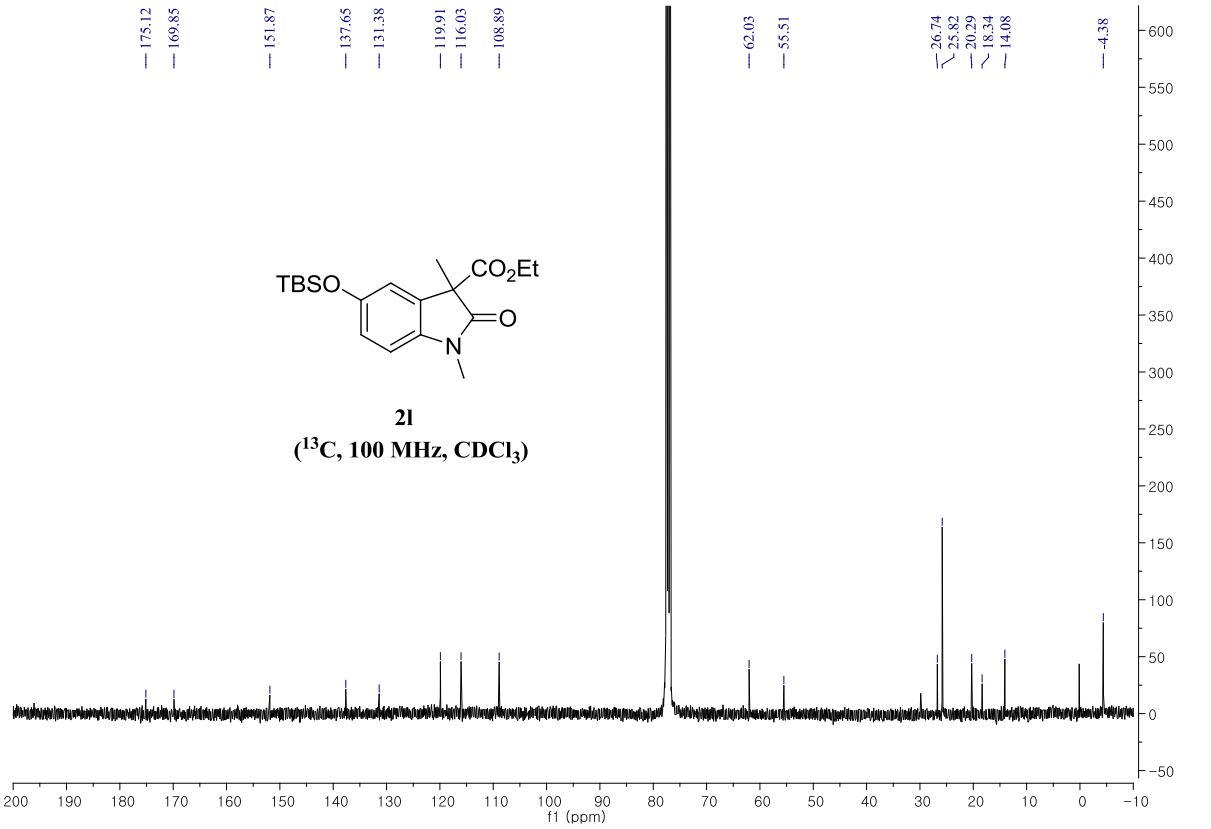


2k
(^{13}C, 100 MHz, $CDCl_3$)



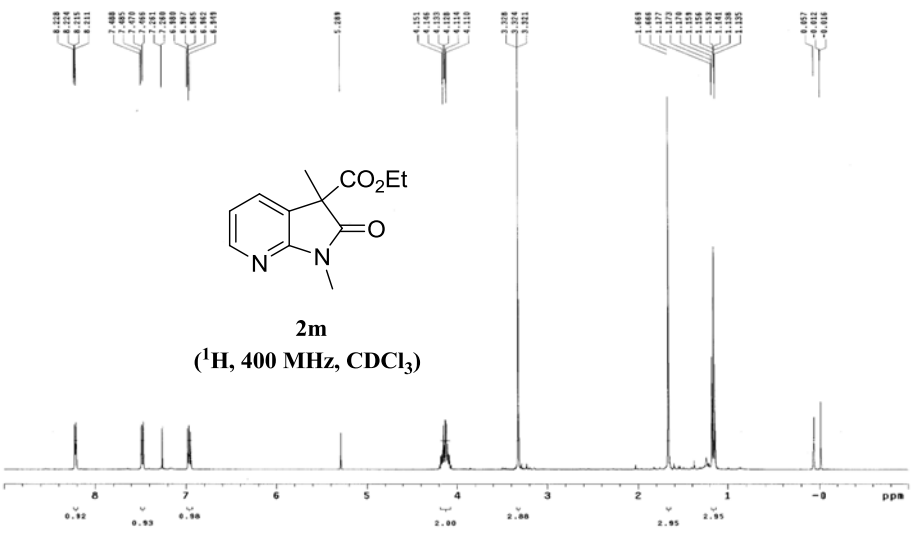
2l

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

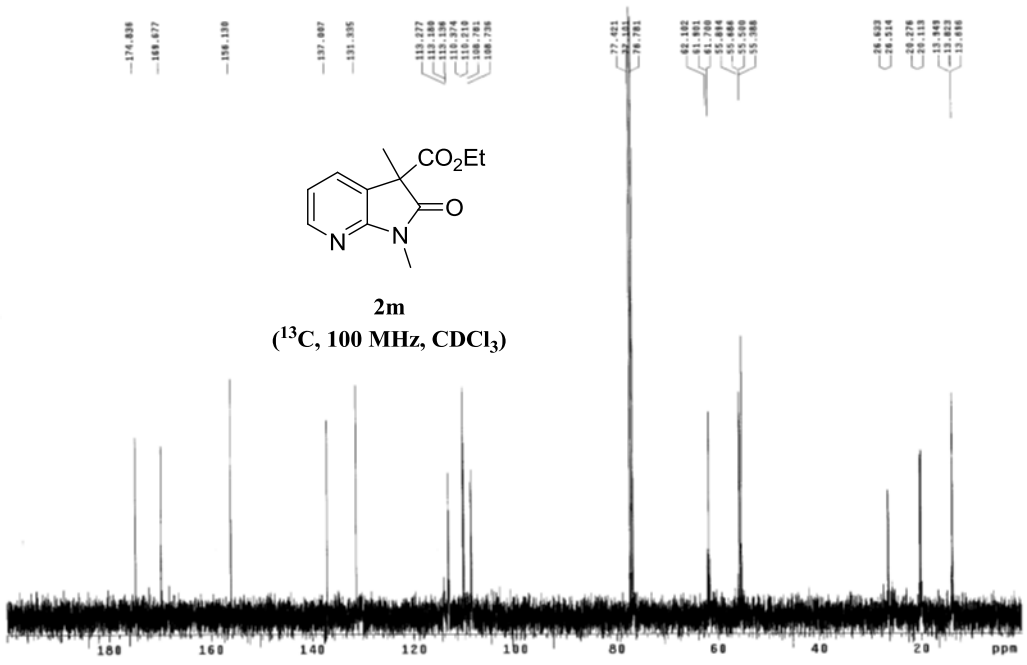


2l

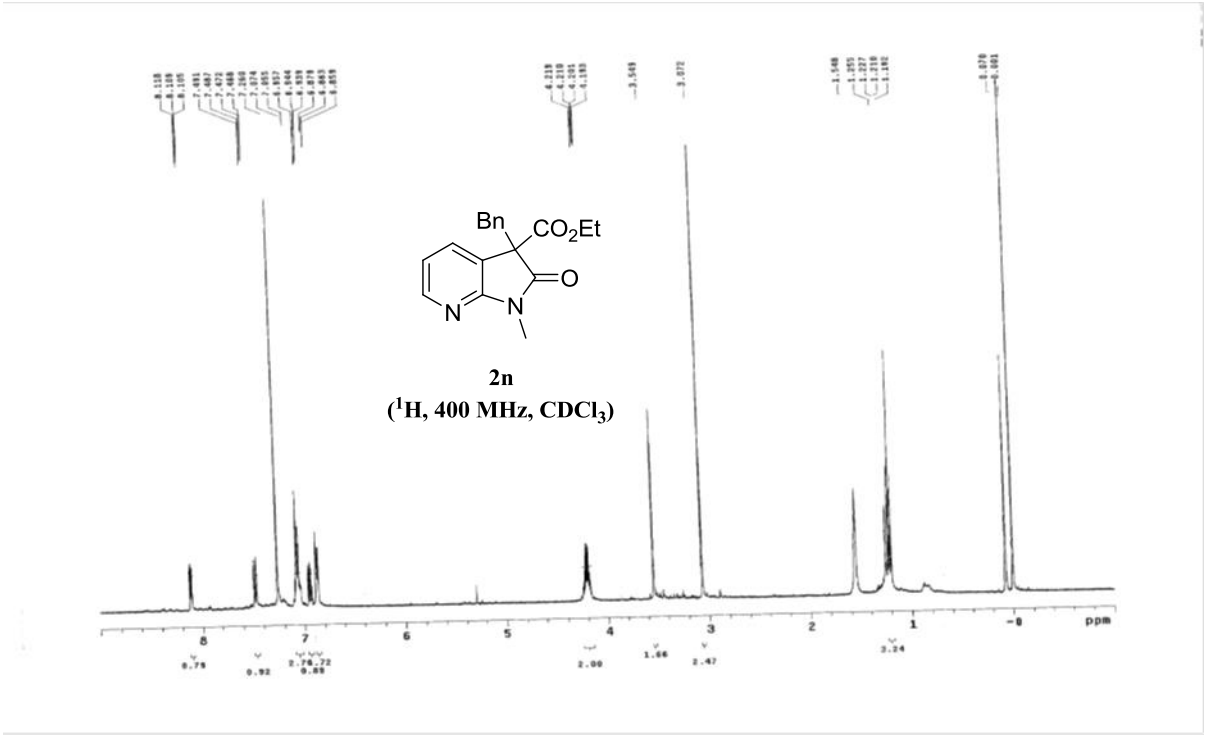
(^{13}C, 100 MHz, $CDCl_3$)



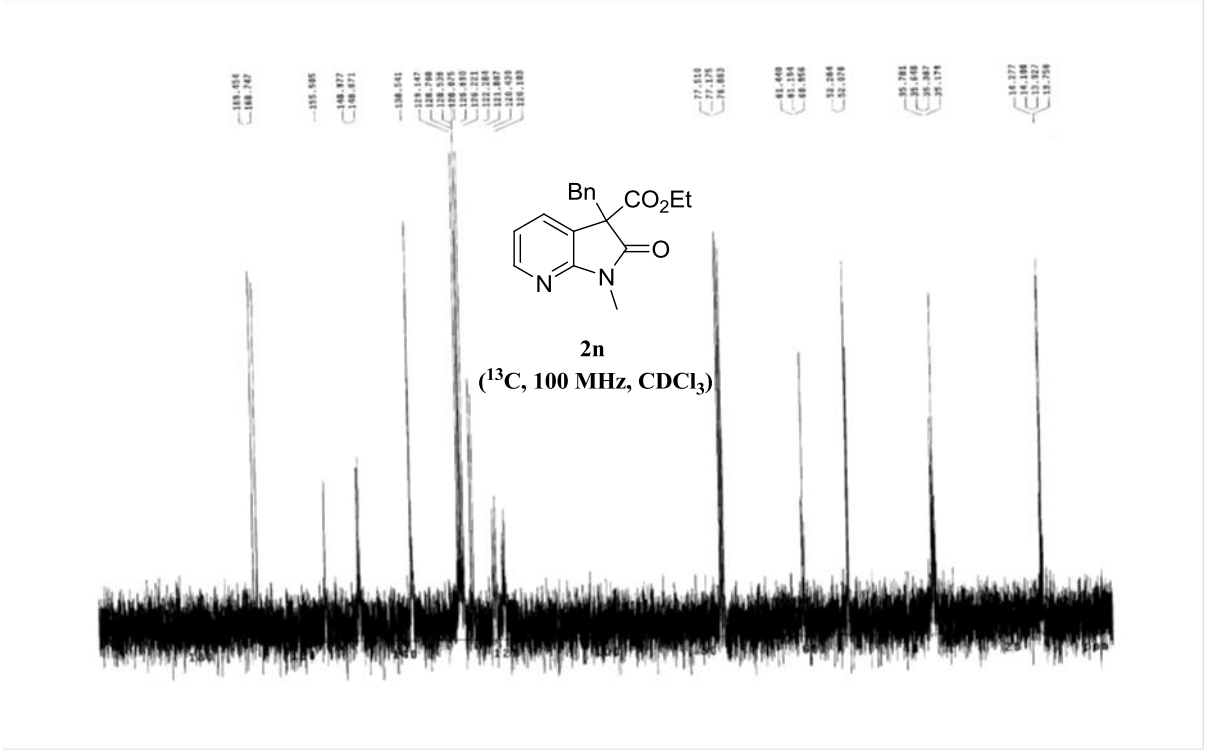
2m
(^{1}H, 400 MHz, $CDCl_3$)



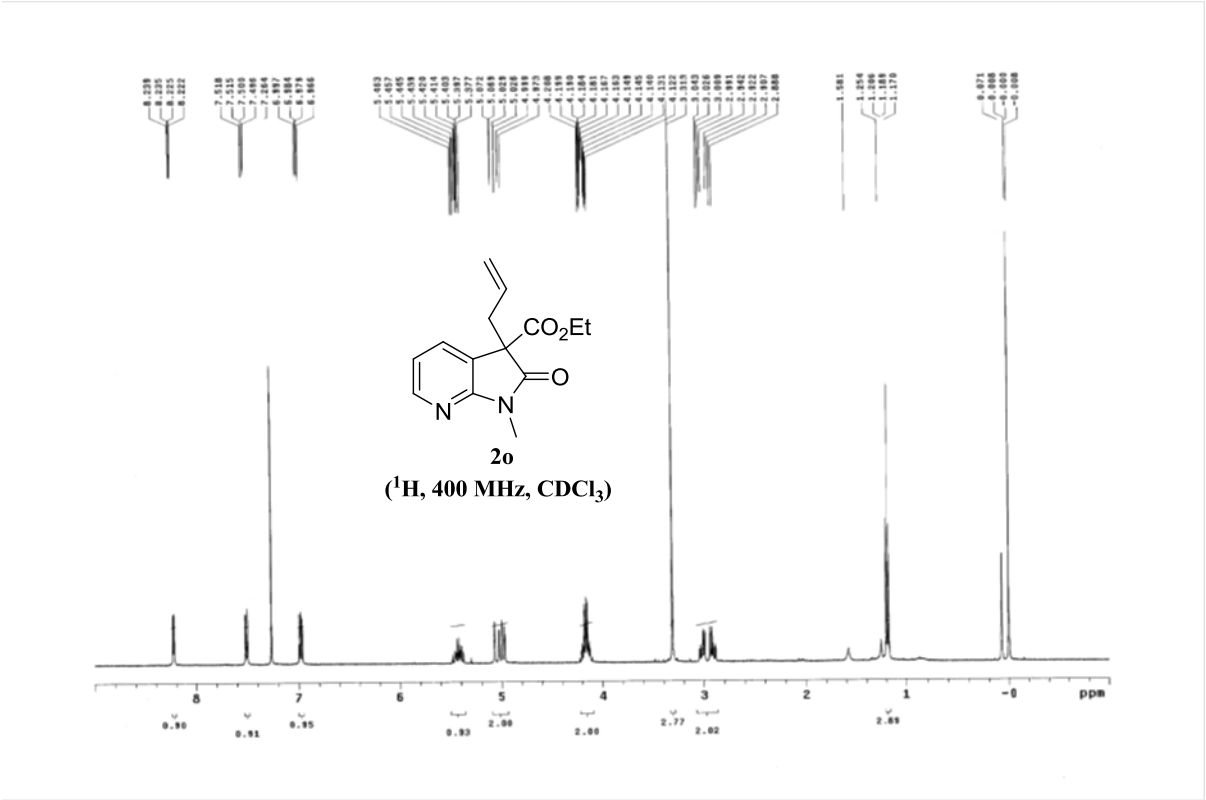
2m
(^{13}C, 100 MHz, $CDCl_3$)



2n
(^{1}H, 400 MHz, $CDCl_3$)

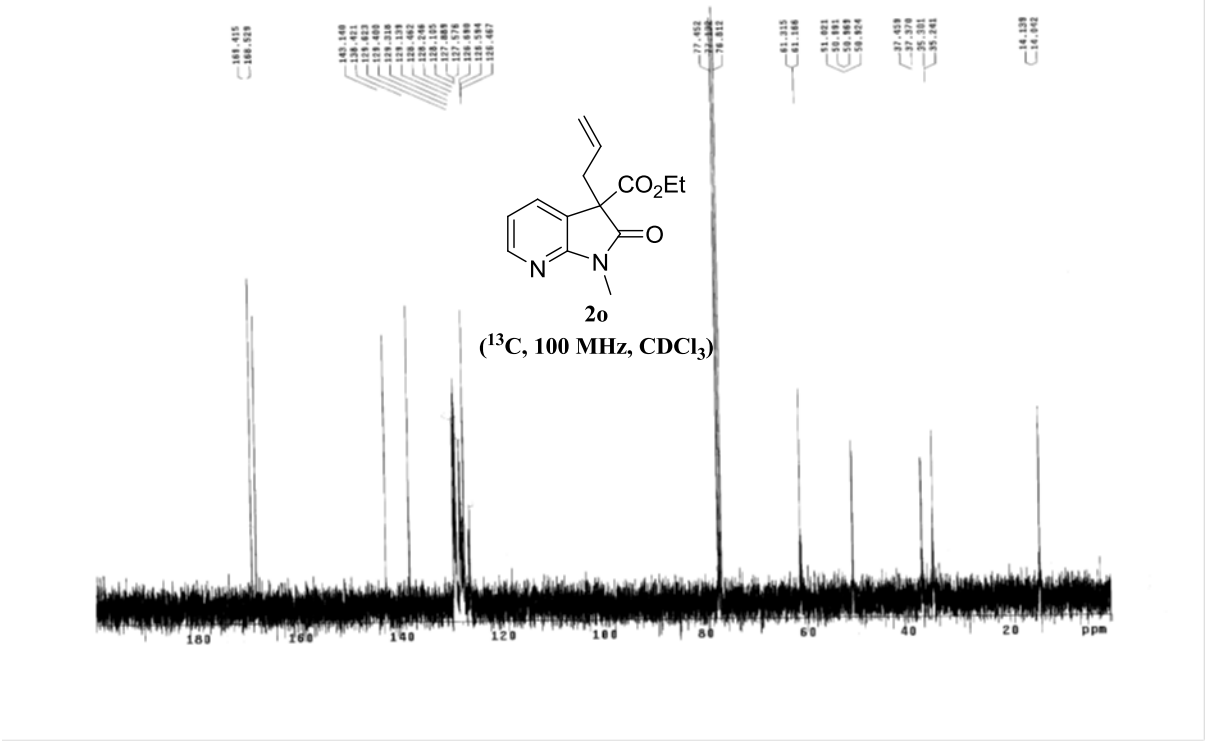


2n
(^{13}C, 100 MHz, $CDCl_3$)



2o

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



2o

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

References :

[1] Klein, J. E. M. N.; Perry, A.; Pugh, D. S.; Taylor, R. J. K. *Org. Lett.* **2010**, *12*, 3446-3449.

[2] Kiriazis, L.; Kalatzis, E.; Alexandrou, N. E., *J. Heterocyclc. Chem.* **1989**, *26*, 155-160.