SUPPLEMENTARY INFORMATION

Iron-catalyzed cross-dehydrogenative coupling of indolin-2-ones with active methylenes for direct carbon-carbon double bonds formation

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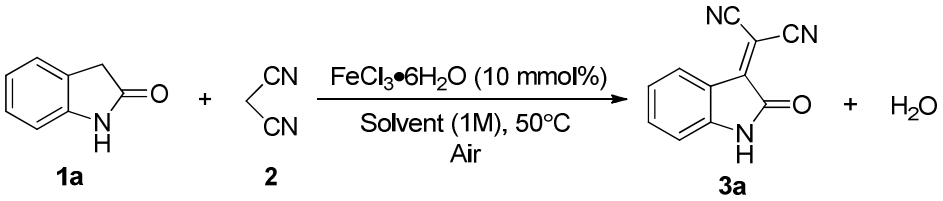
Table of contents

1. General Information

All chemicals were purchased from commercial suppliers and were used without further purification. Melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-d_6 as the solvent. Chemical shifts are reported relative to TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant in hertz, and number of protons.

2. Optimization details

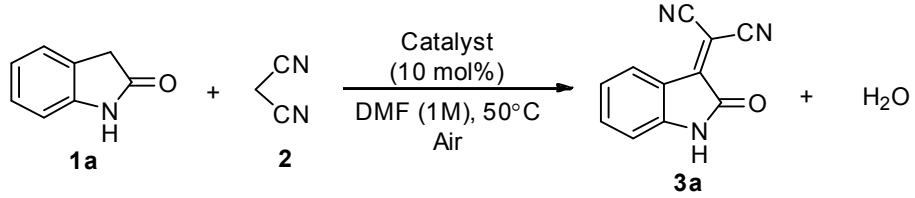
Table S1. Optimization of the iron-catalyzed oxidative coupling reaction in different solvents.[a]



Entry	Solvent	T(ºC)	Time (h)	Yield (%)[b]	TON	TOF(h^{-1})
1	DMSO	50	5	78	7.8	1.56
2	DMF	50	5	91	9.1	1.82
3	Dioxane	50	5	81	8.1	1.62
4	H_2O	50	5	<5	<0.5	<0.1
5	DCE	50	5	---	---	---
6	CH_3CN	50	5	---	---	---
7	C_2H_5OH	50	5	84	8.4	1.68
8	CH_3OH	50	5	63	6.3	1.26
9	DMF	rt	12	trace	---	---
10	DMF	80	5	85	8.5	1.7

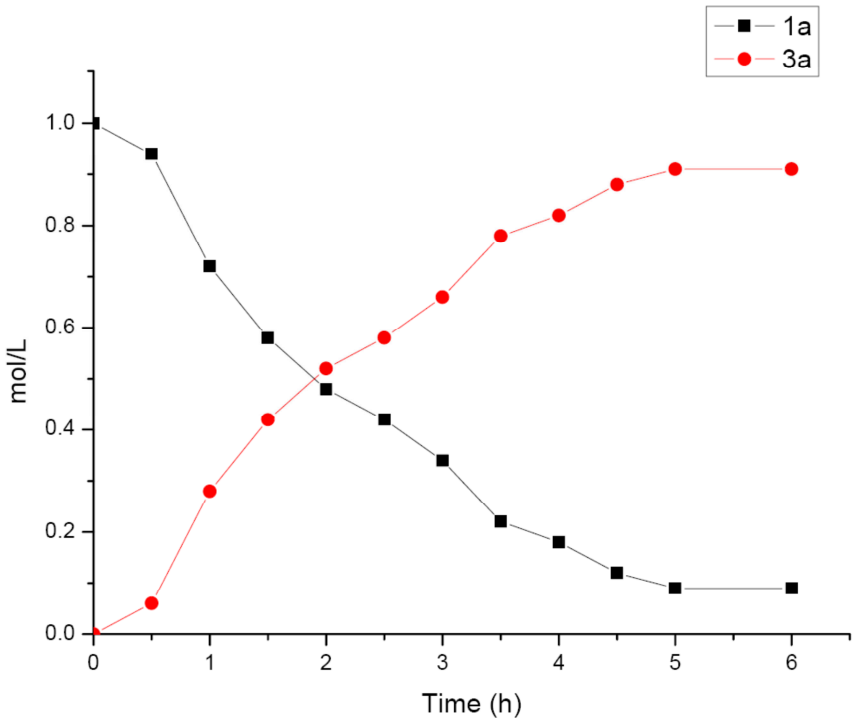
[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv), **2** (0.6 mmol, 1.2 equiv), $FeCl_3$•$6H_2O$ (10 mol%), solvent (0.5 mL), under open air. [b] Isolated yield.

Table S2. Optimization of the iron-catalyzed oxidative coupling reaction.[a]



Entry	Cat. (10 mol%)	Solvent	Yield (%)[b]	TON	TOF(h^{-1})
1	$FeCl_3$•$6H_2O$	DMSO	78	7.8	1.56
2	$FeCl_3$•$6H_2O$	DCE	---	---	---
3	$FeCl_3$•$6H_2O$	DMF	91	9.1	1.82
4	$InCl_3$	DMF	---	---	---
5	$In(OTf)_3$	DMF	---	---	---
6	$Yb(OTf)_3$	DMF	---	---	---
7	$Sc(OTf)_3$	DMF	---	---	---
8[c]	$FeCl_3$•$6H_2O$	DMF	91	18.2	3.64
9[d]	$FeCl_3$•$6H_2O$	DMF	91	30.33	6.06
10[d]	$FeBr_3$	DMF	90	30	6
11[d]	$Fe(NO_3)_3$•$9H_2O$	DMF	82	27.33	5.46
12[d]	$Fe_2(SO_4)_3$•xH_2O	DMF	77	25.66	5.13
13[d]	$FeCl_2$•$4H_2O$	DMF	---	---	---
14[d]	$Fe(OAc)_2$	DMF	37	12.33	2.46
15	---	DMF	---	---	---

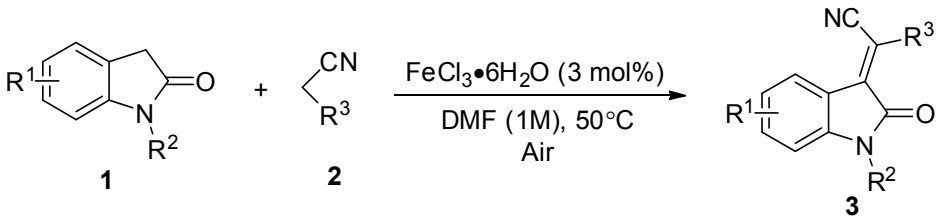
[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv), **2** (0.6 mmol, 1.2 equiv), catalyst (10 mol%), DMF (0.5 mL), 50 ºC, under open air, 5 h. [b] Isolated yield. [c] With 5 mol% catalyst. [d] With 3 mol% catalyst.



Scheme 1. The kinetic profiles of the reaction (**1a:** indolin-2-one, **3a**: 2-(2-oxoindolin-3-ylidene)malononitrile)

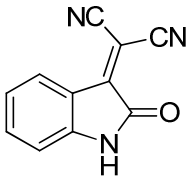
3. General Procedure

General procedure for the oxidative coupling reaction



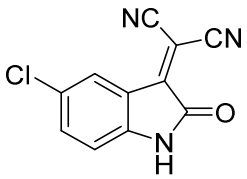
Indolin-2-ones (0.5 mmol), nitriles (0.6 mmol), and $FeCl_3$•$6H_2O$ (3 mmol%) were added to DMF (0.5 mL). Then the mixture was stirred at 50 ºC in the presence of ambient air. The progress of the reaction was monitored by TLC. After completion of the reaction, cold water (5 mL) was added. The mixture was extracted with ethyl acetate (3×5 mL). The organic layer was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:3) as eluent to afford the pure product.

4. Characterization Data of Compounds 3



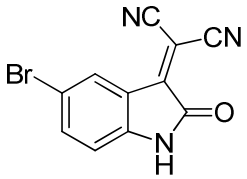
2-(2-oxoindolin-3-ylidene)malononitrile (3a)

Red solid, mp 195-197°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.93 (d, 1H, J = 7.6Hz, ArH), 7.13 (t, 1H, J = 8.4Hz, ArH), 7.57 (s, 1H, J = 7.6Hz, ArH), 7.89 (d, 1H, J = 7.6Hz, ArH), 11.22 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ 81.06, 112.11, 113.53, 119.10, 123.38, 126.29, 138.28, 146.94, 151.10, 164.22.



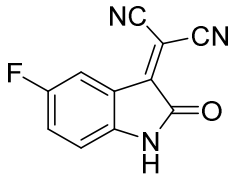
2-(5-Chloro-2-oxoindolin-3-ylidene)malononitrile (3b)

Purple solid, mp = 234-236°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.97 (d, 1H, J = 8.4 Hz, ArH), 7.64 (d, 1H, J = 7.6 Hz, ArH), 7.77 (s, 1H, ArH), 11.37 (s, 1H, NH), ^{13}C NMR (100MHz, DMSO-d_6): δ 82.3, 111.1, 112.7, 113.2, 119.9, 124.7, 126.4, 136.9, 145.1, 149.6, 163.4.



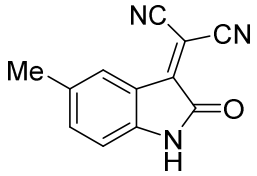
2-(5-bromo-2-oxoindolin-3-ylidene)malononitrile (3c)

Purple solid, mp 228-230°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.92 (d, 1H, J = 8.4 Hz, ArH), 7.74-7.77 (m, 1H, ArH), 7.90-7.91 (m, 1H, ArH), 11.37 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-d_6): δ 82.7, 111.7, 113.7, 114.1, 114.4, 121.0, 128.0, 140.1, 146.0, 150.0, 163.8.



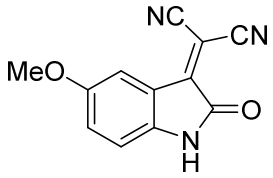
2-(5-Fluoro-2-oxoindolin-3-ylidene)malononitrile (3d)

Purple solid, mp 243-245 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.95-6.98 (m, 1H, ArH), 7.48-7.57 (m, 2H, ArH), 11.25 (s, 1H, NH), ^{13}C NMR (100MHz, DMSO-d_6): δ 82.7, 82.8, 111.7, 112.3, 112.5, 113.1, 113.4, 113.5, 119.6, 119.7, 124.8, 125.0, 143.4, 150.6, 150.7, 156.8, 159.1, 164.2.



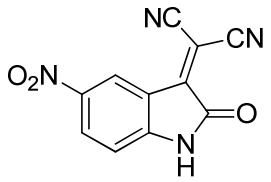
2-(5-methyl-2-oxoindolin-3-ylidene)malononitrile (3e)

Dark purple solid, mp. 179-183°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 2.78 (s, 3H, CH_3), 6.83 (d, 1H, ArH, J = 8.0 Hz), 7.39 (d, 1H, ArH, J = 8.0 Hz), 7.64 (s, 1H, ArH), 11.10 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 163.7, 150.5, 144.4, 138.5, 131.8, 125.6, 118.6, 113.0, 111.5, 111.5, 80.2, 20.4.



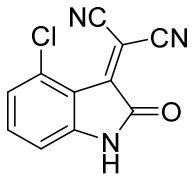
2-(5-methoxy-2-oxoindolin-3-ylidene)malononitrile (3f)

Black solid, mp. 213-215°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 3.35 (s, 3H, CH_3), 6.85 (d, 1H, ArH, J = 8.6 Hz), 7.20 (d, 1H, ArH, J = 7.5 Hz), 7.35 (s, 1H, ArH), 11.01 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 164.1, 155.3, 151.1, 141.0, 124.6, 119.4, 113.4, 112.9, 111.9, 110.6, 81.2, 56.1.



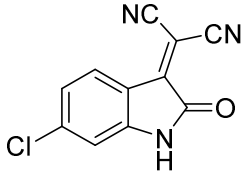
2-(5-nitro-2-oxoindolin-3-ylidene)malononitrile (3g)

Brown solid, mp 258-260°C; ^{1}H NMR (400MHz, DCl+D_2O+DMSO-d_6): δ 7.11 (d, 1H, J = 8.8 Hz, ArH), 8.33 (d, 1H, J = 8.4 Hz, ArH), 8.50 (s, 1H, ArH); ^{13}C NMR (100MHz, DCl+D_2O+DMSO-d_6): δ 84.7, 111.9, 113.1, 113.3, 119.5, 121.9, 133.8, 143.5, 150.1, 151.9, 164.8.



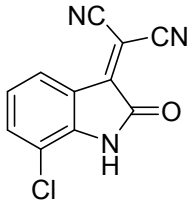
2-(4-Chloro-2-oxoindolin-3-ylidene)malononitrile (3h)

Brown solid, mp 240-242°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.87 (d, 2H, ArH, J = 7.6 Hz), 7.12 (d, 1H, ArH, J = 8.0 Hz), 7.54 (t, 1H, ArH, J = 8.2 Hz), 11.47 (s, 1H, NH), ^{13}C NMR (100MHz, DMSO-d_6): δ 83.8, 110.2, 112.9, 114.1, 116.7, 124.4, 132.7, 138.5, 148.1, 148.2, 163.6.



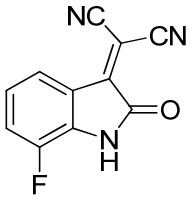
2-(6-Chloro-2-oxoindolin-3-ylidene)malononitrile (3i)

Purple solid, mp 238-240°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.99 (s, 1H, ArH), 7.23 (d, 1H, J = 7.6 Hz, ArH), 7.87 (d, 1H, J = 7.6 Hz, ArH), 11.40 (s, 1H, NH), ^{13}C NMR (100MHz, DMSO-d_6): δ 80.9, 111.4, 111.6, 112.9, 117.6, 122.9, 127.1, 141.9, 147.5, 149.5, 163.8.



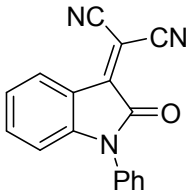
2-(7-Chloro-2-oxoindolin-3-ylidene)malononitrile (3j)

Purple solid, mp 245-247°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 7.17 (t, 1H, J = 7.6 Hz, ArH), 7.67 (d, 1H, J = 8.0 Hz, ArH), 7.86 (d, 1H, J = 7.6 Hz, ArH), 11.70 (s, 1H, NH), ^{13}C NMR (100MHz, DMSO-d_6): δ 82.1, 111.3, 112.7, 115.7, 120.4, 124.0, 124.3, 136.6, 143.7, 150.2, 163.7.



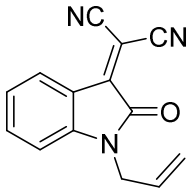
2-(7-fluoro-2-oxoindolin-3-ylidene)malononitrile (3k)

Purple solid, mp 258-260°C; ^{1}H NMR (400MHz, DCl+D_2O+DMSO-d_6): δ 7.17-7.22 (m, 1H, ArH), 7.54 (t, 1H, J = 9.2 Hz, ArH), 7.56 (d, 1H, J = 8.0 Hz, ArH); ^{13}C NMR (100MHz, DCl+D_2O+DMSO-d_6): δ 82.2, 111.1, 112.5, 120.9, 121.8, 123.9, 124.1, 132.8, 146.5 (d, J_{CF} = 244 Hz), 149.8, 163.3.



2-(2-Oxo-1-phenylindolin-3-ylidene)malononitrile (3l)

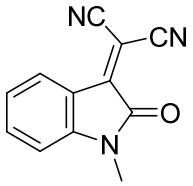
Brown solid, mp 228-230°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 6.82-6.83 (m, 1H, ArH), 7.27-7.28 (m, 1H, ArH), 7.49 (m, 3H, ArH), 7.61 (m, 3H, ArH), 8.04-8.05 (m, 1H, ArH), ^{13}C NMR (100MHz, DMSO-d_6): δ 81.7, 111.2, 111.9, 113.5, 118.7, 124.5, 126.3, 127.2, 129.4, 130.3, 133.1, 138.2, 147.5, 150.4, 162.5.



2-(1-Allyl-2-oxoindolin-3-ylidene)malononitrile (3m)

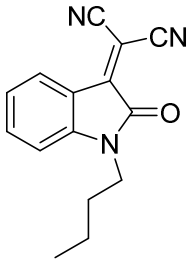
Purple solid, mp 154-156°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 4.34 (d, 2H, CH_2, J = 4.8 Hz), 5.19-5.29 (m, 2H, CH_2), 5.80-5.89 (m, 1H, CH), 7.10 (d, 1H, ArH, J = 7.6 Hz), 7.21 (t, 1H, ArH, J = 7.8 Hz), 7.64 (t, 1H, ArH, J = 7.8 Hz), 7.95 (d, 1H, ArH, J = 7.6 Hz) , ^{13}C NMR (100MHz,

DMSO-d_6): δ 41.8, 81.3, 111.0, 111.4, 112.9, 117.6, 118.1, 123.5, 125.6, 130.9, 137.6, 146.2, 149.5, 162.1.



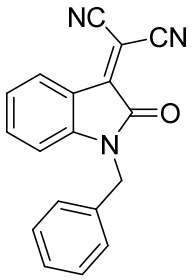
2-(1-Methyl-2-oxoindolin-3-ylidene)malononitrile (3n)

Purple solid, mp 215-217°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 3.15 (s, 3H, CH_3), 7.15-7.22 (m, 2H, ArH), 7.67 (s, 1H, ArH), 7.91 (d, 1H, ArH, J = 8.0 Hz), ^{13}C NMR (100MHz, DMSO-d_6): δ 26.2, 81.2, 110.5, 111.4, 112.9, 118.0, 123.4, 125.4, 137.7, 147.2, 149.8, 162.4.



2-(1-Butyl-2-oxoindolin-3-ylidene)malononitrile (3o)

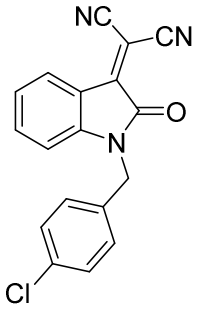
Brown solid, mp 145-146°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 0.90 (t, 3H, CH_3, J = 7.4 Hz), 1.28-1.37 (m, 2H, CH_2), 1.54-1.61 (m, 2H, CH_2), 3.69 (t, 2H, CH_2, J = 7.2 Hz), 7.18-7.22 (m, 2H, ArH), 7.65 (t, 1H, ArH, J = 7.8 Hz), 7.92 (d, 1H, ArH, J = 7.6 Hz), ^{13}C NMR (100MHz, DMSO-d_6): δ 13.4, 19.3, 28.7, 39.4, 81.1, 110.5, 111.3, 112.8, 117.9, 123.2, 125.5, 137.6, 146.4, 149.5, 162.2.



2-(1-Benzyl-2-oxoindolin-3-ylidene)malononitrile (3p)

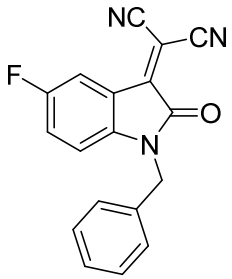
Purple solid, mp 202-204°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 4.94 (s, 2H, CH_2), 7.06 (d, 1H,

ArH, *J* = 8.0 Hz), 7.20 (t, 1H, ArH, *J* = 7.6 Hz), 7.29 (t, 1H, ArH, *J* = 6.8 Hz), 7.33-7.40 (m, 4H, ArH), 7.59 (t, 1H, ArH, *J* = 7.8 Hz), 7.96 (d, 1H, ArH, *J* = 7.6 Hz) , ^{13}C NMR (100MHz, DMSO-d_6): δ 43.4, 82.1, 111.4, 111.9, 113.4, 118.7, 124.0, 126.1, 127.8, 128.2, 129.1, 135.6, 137.9, 146.5, 150.0, 163.1.



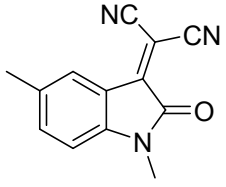
2-(1-(4-Chlorobenzyl)-2-oxoindolin-3-ylidene)malononitrile (3q)

Purple solid, mp 235-237°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 4.95 (s, 2H, CH_2), 7.05 (d, 1H, ArH, *J* = 8.0 Hz), 7.21 (t, 1H, ArH, *J* = 7.6 Hz), 7.42-7.43 (m, 4H, ArH), 7.60 (t, 1H, ArH, *J* = 7.6 Hz), 7.97 (d, 1H, ArH, *J* = 7.6 Hz), ^{13}C NMR (100MHz, DMSO-d_6): δ 42.9, 82.1, 111.5, 112.0, 113.5, 118.8, 124.2, 126.3, 129.2, 129.9, 132.9, 134.8, 138.1, 146.5, 150.2, 163.2.



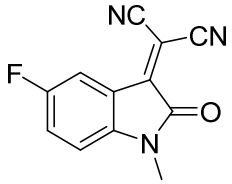
2-(1-Benzyl-5-fluoro-2-oxoindolin-3-ylidene)malononitrile (3r)

Purple solid, mp 220-222°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 4.94 (d, 2H, CH_2, *J* = 7.2 Hz), 7.09 (s, 1H, ArH), 7.30-7.38 (m, 5H, ArH), 7.50-7.51 (m, 1H, ArH), 7.64 (s, 1H, ArH), ^{13}C NMR (100MHz, DMSO-d_6): δ 43.6, 83.7, 111.6, 112.5, 112.7, 112.8, 113.1, 119.4, 119.5, 124.3, 124.5, 127.9, 128.2, 129.2, 135.5, 143.1, 149.6, 157.2, 159.6, 163.0.



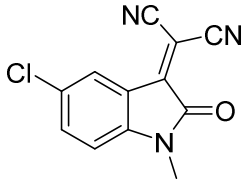
2-(1,5-Dimethyl-2-oxoindolin-3-ylidene)malononitrile (3s)

Brown solid, mp 241-243°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 2.31 (s, 3H, CH_3), 3.13 (s, 3H, CH_3), 7.06 (d, 1H, ArH, J = 8.4 Hz), 7.49 (d, 1H, ArH, J = 8.0 Hz), 7.69 (s, 1H, ArH), ^{13}C NMR (100MHz, DMSO-d_6): δ 20.9, 26.7, 81.4, 110.9, 111.9, 113.4, 118.5, 126.0, 133.0, 138.7, 145.7, 150.3, 162.9.



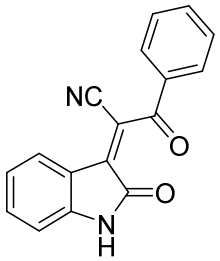
2-(5-Fluoro-1-methyl-2-oxoindolin-3-ylidene)malononitrile (3t)

Black solid, mp 174-175°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 3.26 (s, 3H, CH_3), 7.22 (s, 1H, ArH), 7.60-7.61 (m, 2H, ArH), ^{13}C NMR (100MHz, DMSO-d_6): δ 26.4, 82.8, 111.0, 111.7, 111.9, 112.4, 118.4, 118.5, 124.0, 124.3, 143.6, 149.1, 156.7, 159.1, 162.1.



2-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene)malononitrile (3u)

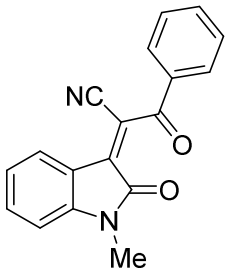
Purple solid, mp 149-150°C; ^{1}H NMR (400MHz, DMSO-d_6): δ 3.16 (s, 3H, CH_3), 7.23 (d, 1H, ArH, J = 8.4 Hz), 7.76 (d, 1H, ArH, J = 8.4 Hz), 7.80 (s, 1H, ArH), ^{13}C NMR (100MHz, DMSO-d_6): δ 26.4, 82.9, 111.0, 112.2 112.6, 119.3, 124.4, 127.0, 136.7, 145.9, 148.7, 162.1.



(Z)-3-oxo-2-(2-oxoindolin-3-ylidene)-3-phenylpropanenitrile (3v)

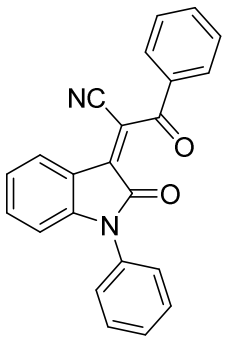
Orange solid, mp 201-202°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.81* (t, 1H, ArH, J = 7.6 Hz),

6.82* (t, 1H, ArH, *J* = 8.4 Hz), 6.89* (d, 1H, ArH, *J* = 8.0 Hz), 6.94 (d, 1H, ArH, *J* = 8.0 Hz), 7.18 (t, 1H, ArH, *J* = 7.6 Hz), 7.37* (t, 1H, ArH, *J* = 8.4 Hz), 7.50 (t, 1H, ArH, *J* = 7.6 Hz), 7.60 (t, 2H, ArH, *J* = 7.6 Hz), 7.67* (t, 2H, ArH, *J* = 8.0 Hz), 7.77 (t, 1H, ArH, *J* = 7.2 Hz), 7.85* (t, 1H, ArH, *J* = 7.2 Hz), 7.98 (d, 1H, ArH, *J* = 7.6 Hz), 8.06 (d, 2H, ArH, *J* = 7.2 Hz), 8.16* (d, 2H, ArH, *J* = 7.6 Hz), 11.00 (s, 1H, NH), 11.11* (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 187.4*, 187.7, 165.1, 164.7*, 145.5, 144.9*, 142.4*, 141.9, 136.2*, 135.0, 134.9*, 134.8, 134.0, 132.9*, 130.0*, 129.8, 129.3, 129.2*, 125.4*, 124.4, 122.6, 122.1*, 119.0, 118.5*, 114.7, 114.2*, 111.2, 111.1*, 110.6, 110.5*.



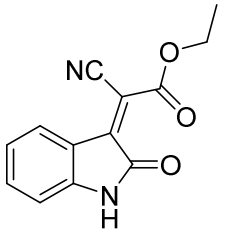
(Z)-2-(1-methyl-2-oxoindolin-3-ylidene)-3-oxo-3-phenylpropanenitrile (3w)

Red solid, mp 185-188°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 3.10 (s, 3H, CH_3), 3.22* (s, 3H, CH_3), 6.86-6.91* (m, 1H, ArH), 7.11* (d, 1H, ArH, *J* = 8.0 Hz), 7.15 (d, 1H, ArH, *J* = 8.0 Hz), 7.26 (t, 1H, ArH, *J* = 7.6 Hz), 7.47* (t, 1H, ArH, *J* = 8.4 Hz), 7.61 (t, 3H, ArH, *J* = 8.0 Hz), 7.67* (t, 1H, ArH, *J* = 8.0 Hz), 7.78 (t, 1H, ArH, *J* = 7.6 Hz), 7.86* (t, 1H, ArH, *J* = 7.6 Hz), 8.02* (d, 2H, ArH, *J* = 7.6 Hz), 8.06 (d, 2H, ArH, *J* = 7.6 Hz), 8.17*(d, 2H, ArH, *J* = 7.2 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 188.2*, 187.5, 163.6, 163.3*, 146.4, 145.8*, 141.5*, 140.9, 136.3*, 135.1, 134.8*, 134.7, 133.9, 132.8*, 130.0*, 129.8*, 129.3, 129.2, 125.1*, 124.0, 123.1, 122.6*, 118.3, 117.8*, 114.6, 114.1*, 111.1, 110.9*, 110.1, 110.0*, 26.2*, 26.0.



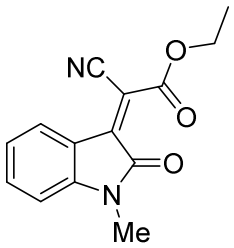
(Z)-3-oxo-2-(2-oxo-1-phenylindolin-3-ylidene)-3-phenylpropanenitrile (3x)

Dark purple, mp. 191-193°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.75* (d, 1H, ArH , J = 8.0 Hz), 6.84 (d, 1H, ArH , J = 8.0 Hz), 6.94* (t, 1H, ArH, J = 8.0 Hz), 6.99* (t, 1H, ArH, J = 7.2 Hz), 7.32 (t, 1H, ArH, J = 7.2 Hz), 7.39-7.47 (m, 3H, ArH), 7.52-7.57 (m, 3H, ArH), 7.60 (t, 2H, ArH, J = 7.6 Hz), 7.63* (t, 3H, ArH, J = 8.4 Hz), 7.70* (t, 2H, ArH, J = 8.0 Hz), 7.77 (t, 1H, ArH, J = 7.6 Hz), 7.88* (t, 1H, ArH, J = 7.2 Hz), 8.10 (d, 2H, ArH, J = 7.2 Hz), 8.13 (d, 1H, ArH, J = 7.6 Hz), 8.24* (t, 2H, ArH, J = 7.2 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 188.4, 163.7, 146.7, 141.3, 135.7, 135.2, 134.3, 133.3, 130.1, 129.8, 129.1, 127.1, 124.9, 124.2, 119.0, 115.2, 112.0, 110.9.



Ethyl (Z)-2-cyano-2-(2-oxoindolin-3-ylidene)acetate (3y)

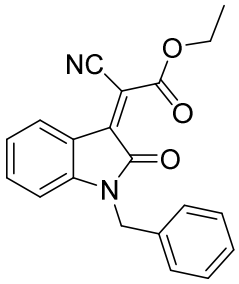
Rred solid, mp 195-197°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 1.31* (t, 3H, CH_3, J = 7.2 Hz), 1.34 (t, 3H, CH_3, J = 7.2 Hz), 4.36* (m, 2H, CH_2, J = 7.2 Hz), 4.42 (m, 2H, CH_2, J = 7.2 Hz), 6.88 (d, 1H, ArH, J = 7.6 Hz), 6.93* (d, 1H, ArH, J = 7.6 Hz), 7.01 (t, 1H, ArH, J =7.6 Hz), 7.13* (t, 1H, ArH, J =7.6 Hz), 7.47 (t, 1H, ArH, J = 7.6 Hz), 7.49* (t, 1H, ArH, J = 7.6 Hz), 7.86* (d, 1H, ArH, J = 7.6 Hz), 8.11 (d, 1H, ArH, J = 8.0 Hz), 11.09 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 165.7, 165.0*, 161.8, 161.0*, 146.3, 145.8*, 136.5, 135.8*, 129.7, 125.0, 123.1*, 122.6, 119.2, 119.0*, 114.7*, 114.6, 111.8*, 111.3, 105.0, 63.7*, 63.6, 14.3, 14.0*.



Ethyl (Z)-2-cyano-2-(1-methyl-2-oxoindolin-3-ylidene)acetate (3z)

Dark red solid, mp 172-173°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 1.31* (t, 3H, CH_3, J = 7.2 Hz), 1.34 (t, 3H, CH_3, J = 7.2 Hz), 3.14* (s, 3H, CH_3), 3.16 (s, 3H, CH_3), 4.37* (m, 2H, CH_2, J = 7.2 Hz), 4.42 (m, 2H, CH_2, J = 7.2 Hz), 7.08 (m, 2H, ArH), 7.13* (d, 1H, ArH, J = 8.0 Hz), 7.19* (t, 1H, ArH, J = 7.6 Hz), 7.56 (t, 1H, ArH, J = 8.0 Hz), 7.59* (t, 1H, ArH, J = 7.2 Hz), 7.90* (d, 1H, ArH, J = 7.2 Hz), 8.13 (d, 1H, ArH, J = 8.0 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 164.4*, 164.3,

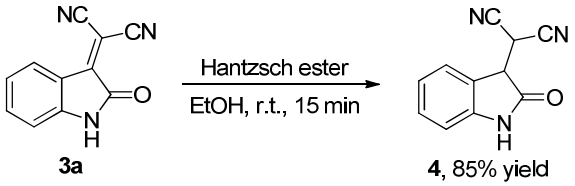
161.7*, 161.6, 147.1, 144.9*, 136.4, 135.7*, 129.3, 124.6*, 123.7*, 123.2, 118.6, 118.3*, 114.6*, 114.6, 110.7*, 110.2, 105.5, 104.8*, 100.0, 98.7*, 63.9*, 63.7, 26.7, 26.6*, 14.3, 14.0*.



Ethyl (Z)-2-(1-benzyl-2-oxoindolin-3-ylidene)-2-cyanoacetate (3aa)

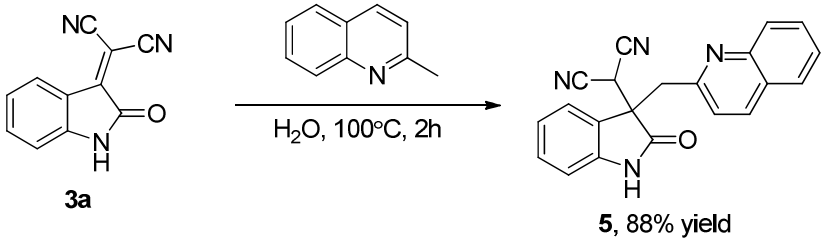
Dark purple solid, mp 174-176°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 1.32* (t, 3H, CH_3, J = 7.2 Hz), 1.35 (t, 3H, CH_3, J = 7.2 Hz), 4.36-4.14* (m, 2H, CH_2), 4.14-4.46 (m, 2H, CH_2), 4.92* (s, 2H, CH_2), 4.95 (s, 2H, CH_2), 6.99 (d, 1H, ArH, J = 8.0 Hz), 7.05* (d, 1H, ArH, J = 8.0 Hz), 7.08 (t, 1H, ArH, J = 7.6 Hz), 7.19* (t, 1H, ArH, J = 7.6 Hz), 7.29-7.30* (m, 1H, ArH), 7.33-7.36 (m, 4H, ArH), 7.48 (t, 1H, ArH, J = 8.0 Hz), 7.93* (d, 1H, ArH, J = 7.6 Hz), 8.16 (d, 1H, ArH, J = 7.6 Hz). ^{13}C NMR (100MHz, DMSO-d_6): δ 164.6, 161.7, 146.0, 145.7*, 144.5, 136.3, 136.1, 136.0*, 135.6*, 129.6, 129.2*, 129.2, 128.1*, 127.8, 124.9*, 123.9*, 123.4, 118.8, 118.5*, 114.6, 111.2*, 110.7, 106.0, 63.9*, 63.8, 43.5, 14.3, 14.1*.

5. Product transformations processes for compounds 4-9



2-(2-oxoindolin-3-yl)malononitrile (4)

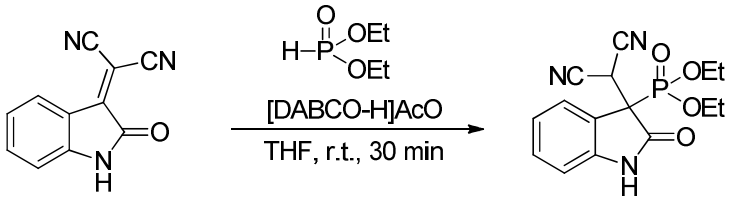
To a solution of **3a** (195.2 mg, 1.0 mmol) in EtOH (10.0 mL) was added Hantzsch ester (266.0 mg, 1.05 mmol). After stirring at room temperature for 15 min, the mixture was concentrated, taking up the residue in ethyl acetate, and extracting with aqueous HCl (1.0 mol L^{-1}). After drying over Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using ethyl acetate /petroleum (1:2) as eluent to afford the pure product **4** as a white solid (167.6 mg, 85% yield). Mp. 176-179°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 4.44 (d, 1H, CH, J = 3.0 Hz), 5.65 (d, 1H, CH, J = 4.0 Hz), 6.93 (d, 1H, ArH, J = 7.7 Hz), 7.01 (t, 1H, ArH, J = 7.6 Hz), 7.33 (t, 1H, ArH, J = 7.6 Hz), 7.45 (d, 1H, ArH, J = 7.2 Hz), 10.91 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 174.2, 143.5, 130.3, 125.0, 122.6, 113.2, 112.8, 110.6, 44.4, 24.3.



2-(2-oxo-3-(quinolin-2-ylmethyl)indolin-3-yl)malononitrile (5)

A 10-mL round bottomed flask was charged with **3a** (195.2 mg, 1.0 mmol), 2-methylquinoline (150.4 mg, 1.05 mmol) and H_2O (2.0 mL). Then the mixture was heated to 100°C and stirred for 2 h. The formation of the products was monitored by TLC. After completion of the reaction, cool the mixture to room temperature, and the insoluble crude product was isolated by filtration, washed with H_2O (2×10 mL). The crude product was diluted with H_2O and extracted with EtOAc. The combined EtOAc extracts were washed with brine (10 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent under vacuum, the residue was purified by flash column chromatography using ethyl acetate /petroleum (1:6) as eluent to afford the pure product **5** as a

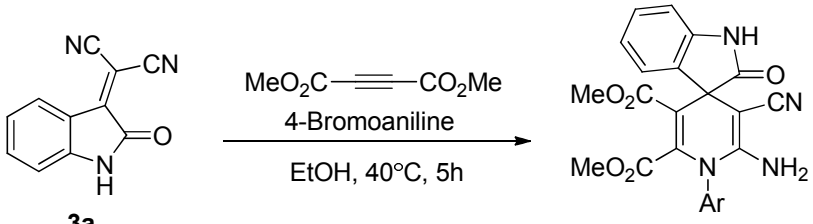
dark green solid (297.8 mg, 88% yield). Mp. 163-165°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 3.67-3.79 (m, 2H, CH_2), 5.94 (s, 1H, CH), 6.83 (t, 1H, ArH, J = 6.3 Hz), 6.93 (m, 1H, ArH, J = 6.7 Hz), 7.20 (m, 1H, ArH, J = 7.2 Hz), 7.23-7.29 (m, 1H, ArH), 7.31 (d, 1H, ArH, J = 6.8 Hz), 7.53 (m, 1H, ArH, J = 6.4 Hz), 7.70 (m, 1H, ArH, J = 6.8 Hz), 7.79 (d, 1H, ArH, J = 7.6 Hz), 7.86 (d, 1H, ArH, J = 7.6 Hz), 8.17(d, 1H, ArH, J = 8.4Hz), 10.99 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 176.0, 156.0, 147.1, 143.3, 136.7, 130.3, 130.0, 128.9, 128.2, 126.9, 126.8, 124.6, 122.5, 122.3, 112.7, 112.3, 110.5, 100.0, 51.6, 41.1, 30.4.



3a **6,** 97% yield

Diethyl (3-(dicyanomethyl)-2-oxoindolin-3-yl)phosphonate(6)

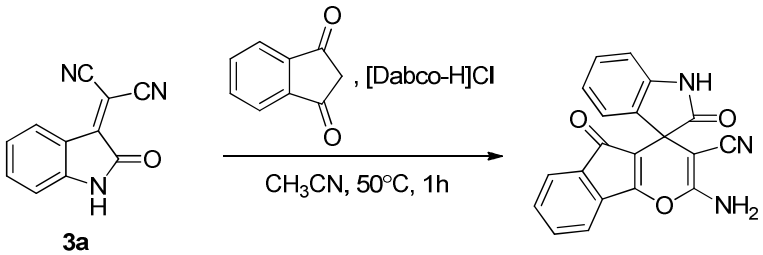
A 10-mL round bottomed flask was charged with **3a** (195.2 mg, 1.0 mmol), diethyl phosphate (145.0 mg, 1.05 mmol), [DABCO-H]AcO (17.2 mg, 0.1 mmol) and THF (0.3 mL). Then the reaction mixture was vigorously stirred at room temperature. The formation of the products was monitored by TLC. After completion of the reaction, water (2.0 mL) was added and the insoluble crude product was isolated by simple filtration. The crude product was recrystallized from EtOH to afford pure product **6** as a white solid (323.3 mg, 97% yield). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.24-1.30 (m, 3H, CH_3), 1.32-1.37 (m, 3H, CH_3), 4.14-4.20 (m, 4H, OCH_2), 4.87(t, 1H, J = 6.8 Hz, CH), 6.99 (t, 1H, J = 7.6 Hz, ArH), 7.11-7.16 (m, 1H, ArH), 7.33-7.39 (m, 1H, ArH), 7.68 (t, 1H, J = 6.8 Hz, ArH), 10.85 (s, 1H, NH); ^{13}C NMR (100MHz, $CDCl_3$): δ 15.8, 26.9, 53.1 (d, $^1J_{CP}$ = 139 Hz, C-P), 64.4, 65.0, 109.7, 110.3, 110.70, 120.6, 122.5, 125.7, 130.6, 142.8, 170.4.



3a **7,** 85% yield (Ar = 4-BrC_6H_4)

2'-Amino-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate (7)

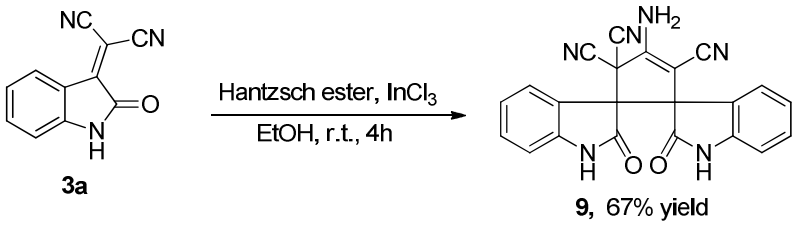
To a solution of 4-bromoaniline (172.0 mg, 1.0 mmol) in EtOH (1.0 mL) was added dimethyl acetylenedicarboxylate (149.2 mg, 1.05 mmol) and [DABCO-H]AcO (17.2 mg, 0.1 mmol). After stirring at 40°C for 10 min, **3a** (195.2 mg, 1 mmol) was added to the reaction mixture and the reaction was continued for 5h. The formation of the products was monitored by TLC. After completion of the reaction, cold water (5 mL) was added, filtered and washed with cold water. The crude product was purified by recrystallization from ethanol to provid pure product **7** as a yellow solid (432.8 mg, 85% yield). Mp 147-148°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.80 (t, 3H, CH_3, J = 7.2 Hz), 0.90 (t, 3H, CH_3, J = 7.2 Hz), 3.79 (m, 4H, CH_2), 5.94 (s, 2H, NH_2), 6.81 (d, 1H, ArH, J = 7.6 Hz), 7.00 (t, 1H, ArH, J = 7.6 Hz), 7.21 (t, 1H, ArH, J = 7.6 Hz), 7.27 (d, 1H, ArH, J = 7.2 Hz), 7.37 (d, 1H, ArH, J = 8.4 Hz), 7.73 (d, 1H, ArH, J = 8.4 Hz), 10.44 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 179.3, 164.1, 162.4, 151.8, 143.6, 142.0, 136.2, 135.3, 133.2, 133.1, 129.1, 124.3, 124.0, 122.4, 119.0, 109.7, 104.3, 62.2, 61.0, 50.1, 13.6, 13.5.



8, 91% yield

2-Amino-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (8)

To a stirred mixture of **3a** (195.2 mg, 1 mmol) and 1,3-indanedione (153.4 mg, 1.05 mmol) in CH_3CN (1.0 mL), a catalytic amount of [DABCO-H]Cl (10 mol %) was added. Then the mixture was heated to 50°C and stirred about for 1 h. The formation of the products was monitored by TLC. After completion of the reaction, insoluble crude product was isolated by filtration. The crude product was recrystallized from EtOH to afford pure product **8** as a white solid (310.6 mg, 91% yield). Mp 207-208℃. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.90 (d, 1H, ArH, J = 7.6 Hz), 6.97 (t, 1H, ArH, J = 7.2 Hz), 7.24 (t, 2H, ArH, J = 7.6 Hz), 7.31 (d, 1H, ArH, J = 7.2 Hz), 7.37 (d, 1H, ArH, J = 7.2 Hz), 7.44 (t, 1H, ArH, J = 7.6 Hz), 7.57 (t, 1H, ArH, J = 7.2 Hz), 7.71 (s, 2H, NH_2), 10.70 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 189.3, 176.8, 167.5, 160.4, 141.8, 135.1, 133.6, 132.0, 131.3, 130.5, 129.1, 124.6, 122.1, 122.2, 118.8, 117.3, 109.7, 107.2, 57.2, 46.4.

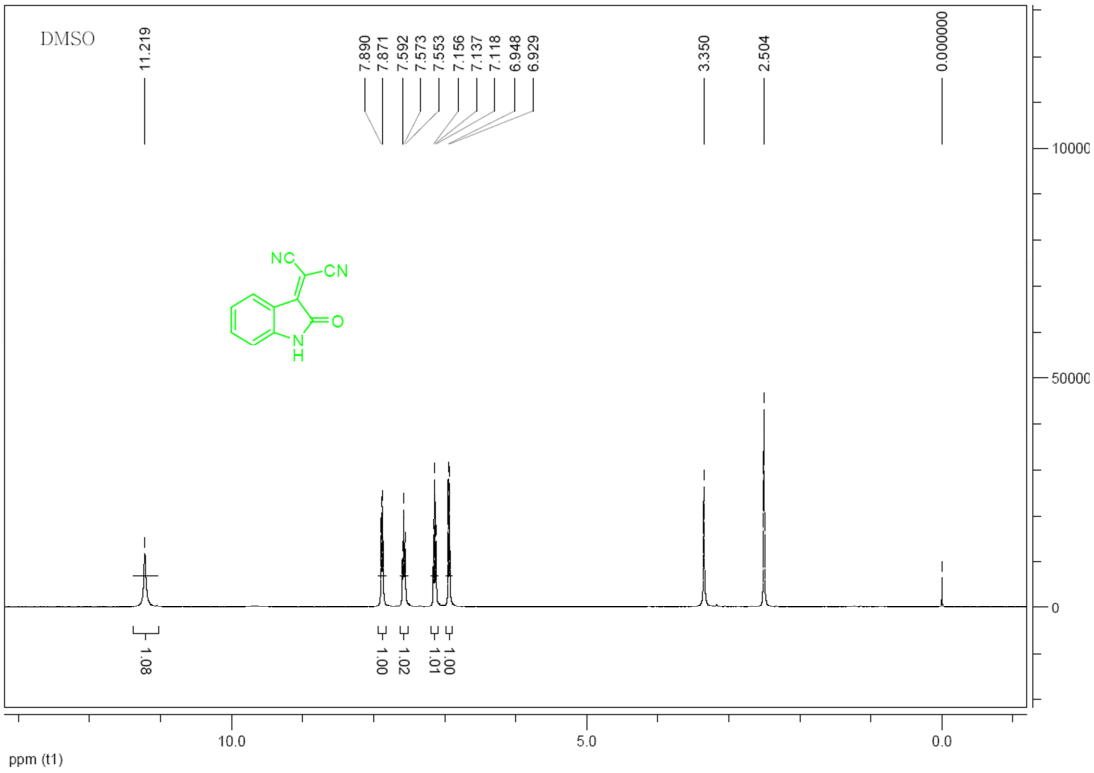


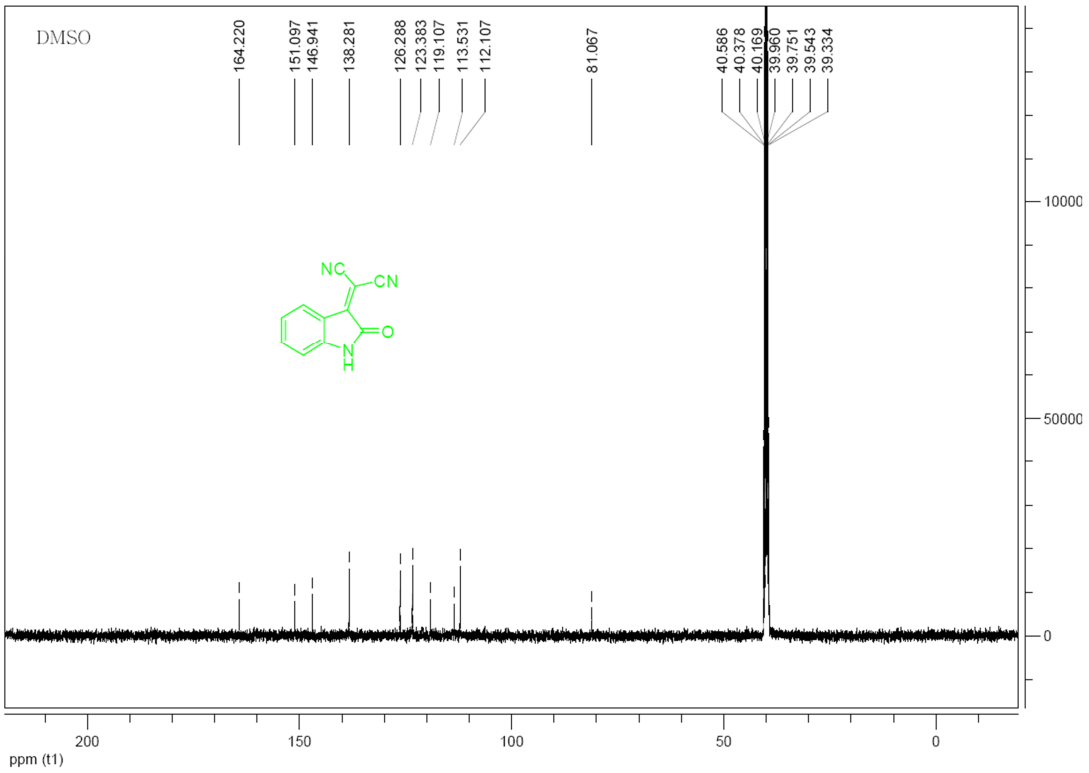
4'-Amino-2,2',3,3"-tetrahydro-1H-indole-3-spiro-1'-cyclopent-3'-ene-2'-spiro-3"-1H-indole-3',5',5'-tricarbonitrile (9)

To a stirred mixture of **3a** (195.2 mg, 1 mmol) and Hantzsch ester (126.7 mg, 0.5 mmol) in ethanol (5 mL), a catalytic amount of $InCl_3$ (20 mol %) was added. Then the resulting mixture was stirred at room temperature for about 4h. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was diluted with water (20 mL) and extracted with ethyl acetate (2×30 mL). The combined extract was washed with brine (10 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent under vacuum, the residue was purified by flash column chromatography using ethyl acetate /petroleum (1:2) as eluent to afford the pure product **9** as white solid (131.4 mg, 67% yield). Mp 221-224°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 6.67 (d, 1H, ArH, J = 7.6 Hz), 6.78 (d, 1H, ArH, J = 7.6 Hz), 7.00 (t, 1H, ArH, J = 7.5 Hz), 7.12 (t, 1H, ArH, J = 7.6 Hz), 7.21 (t, 1H, ArH, J = 7.2 Hz), 7.34 (m, 2H, ArH, J = 7.6 Hz), 7.70 (d, 1H, ArH, J = 7.6 Hz), 8.39 (s, 2H, NH_2), 10.78 (s, 1H, NH), 11.22 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 175.2, 172.5, 153.4, 142.9, 142.7, 131.6, 130.6, 126.5, 126.4, 122.9, 122.6, 122.4, 119.4, 114.9, 112.2, 111.4, 110.5, 110.1, 75.9, 62.3, 62.0, 46.4.

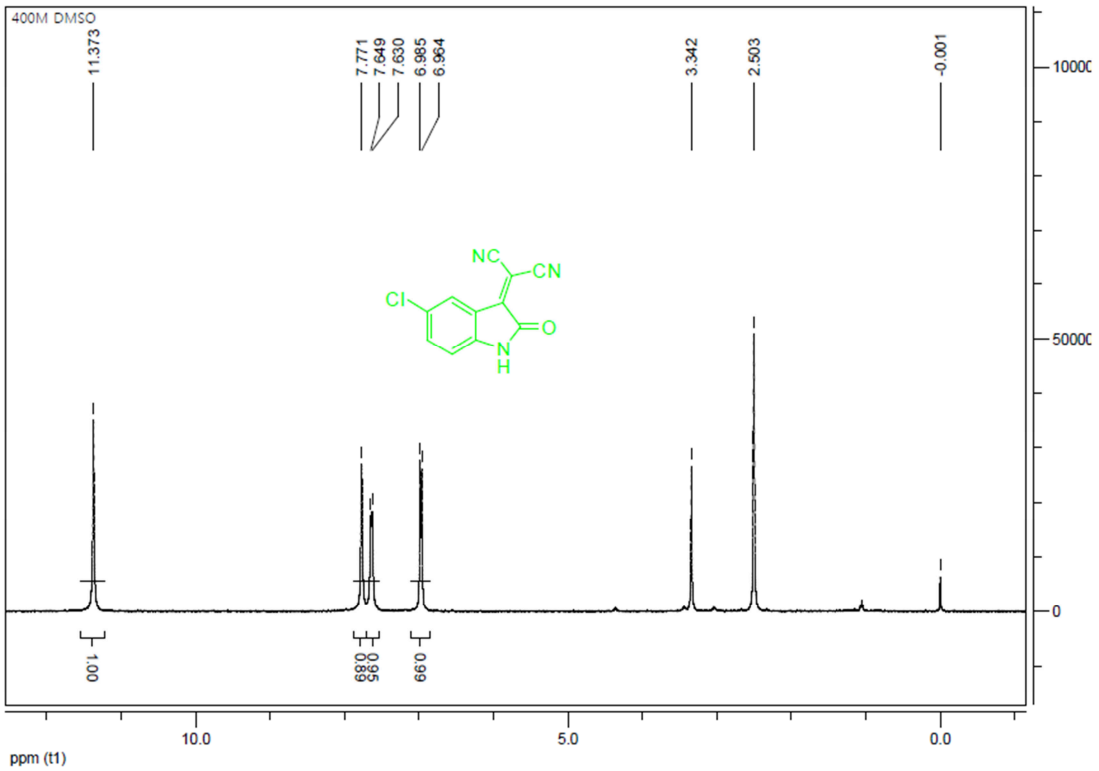
6. Spectroscopic Data for Compounds 3

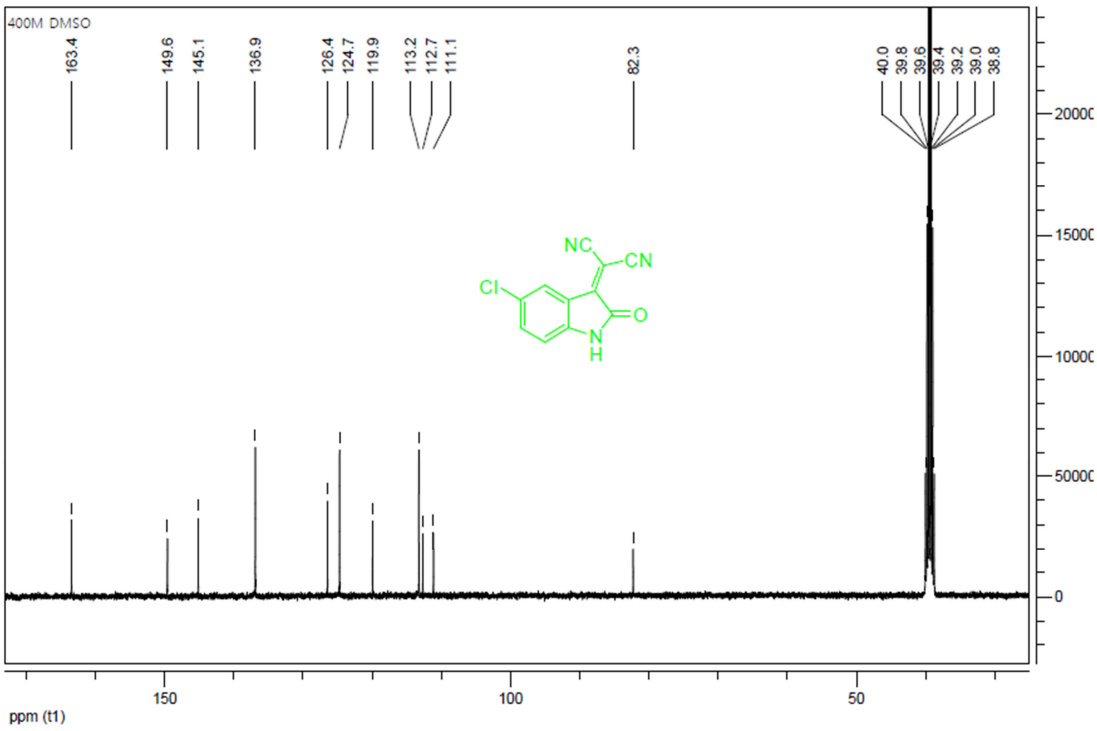
2-(2-oxoindolin-3-ylidene)malononitrile (3a)



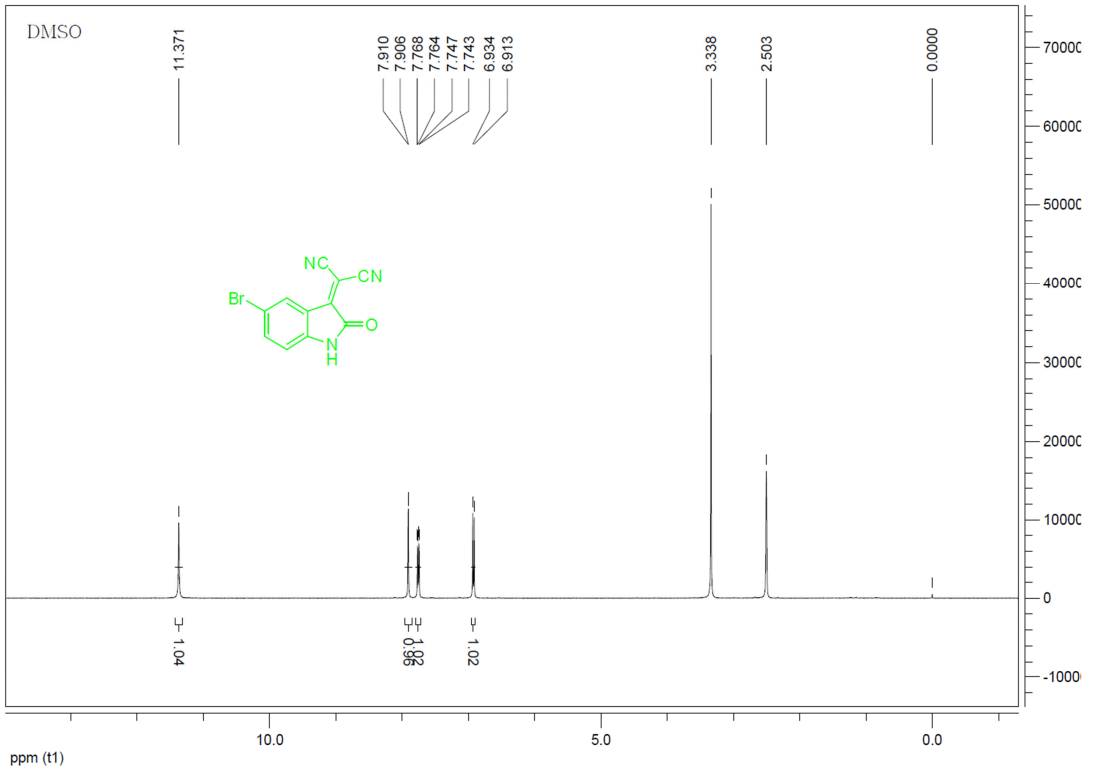


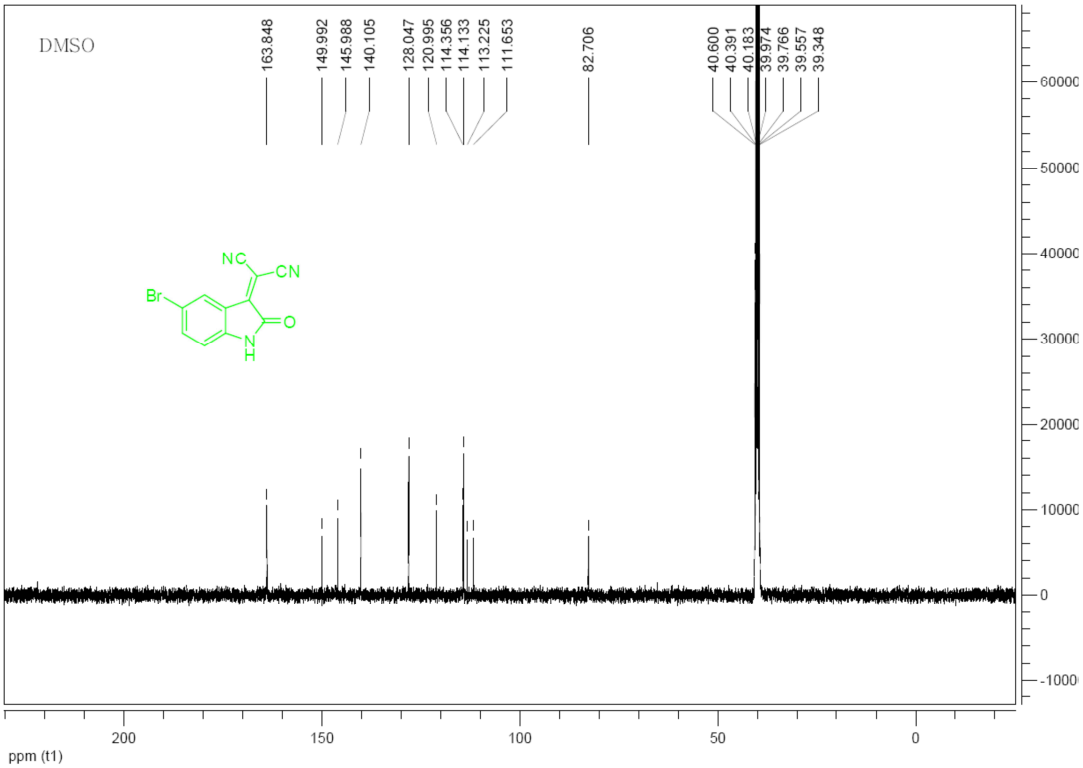
2-(5-Chloro-2-oxoindolin-3-ylidene)malononitrile (3b)



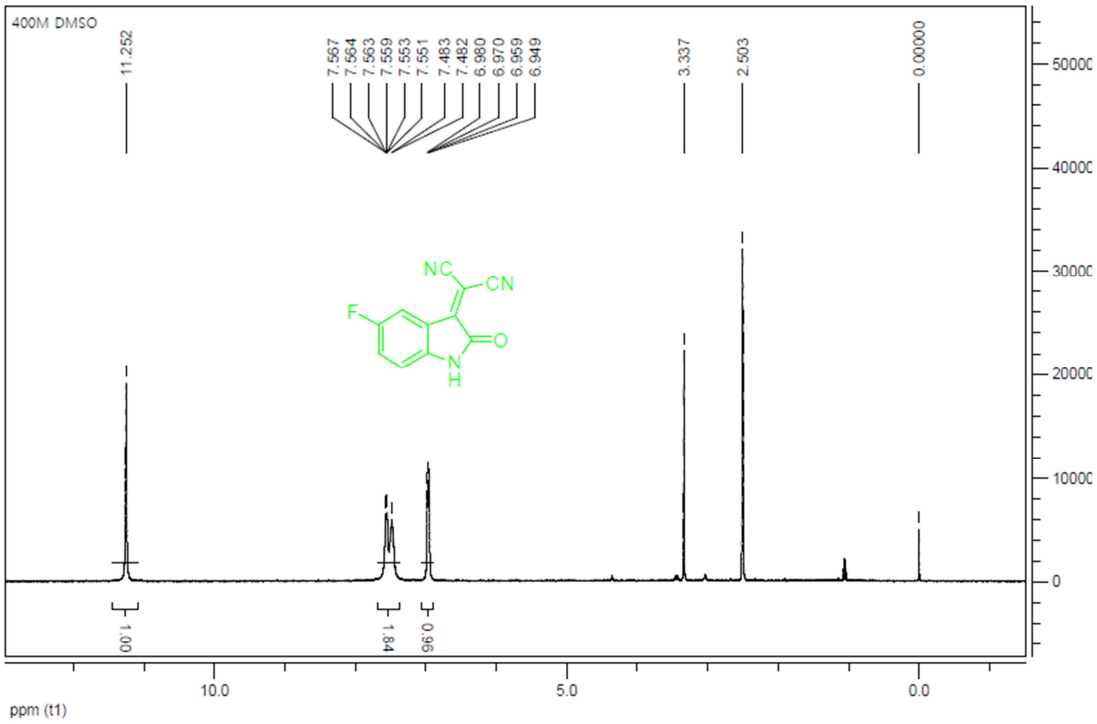


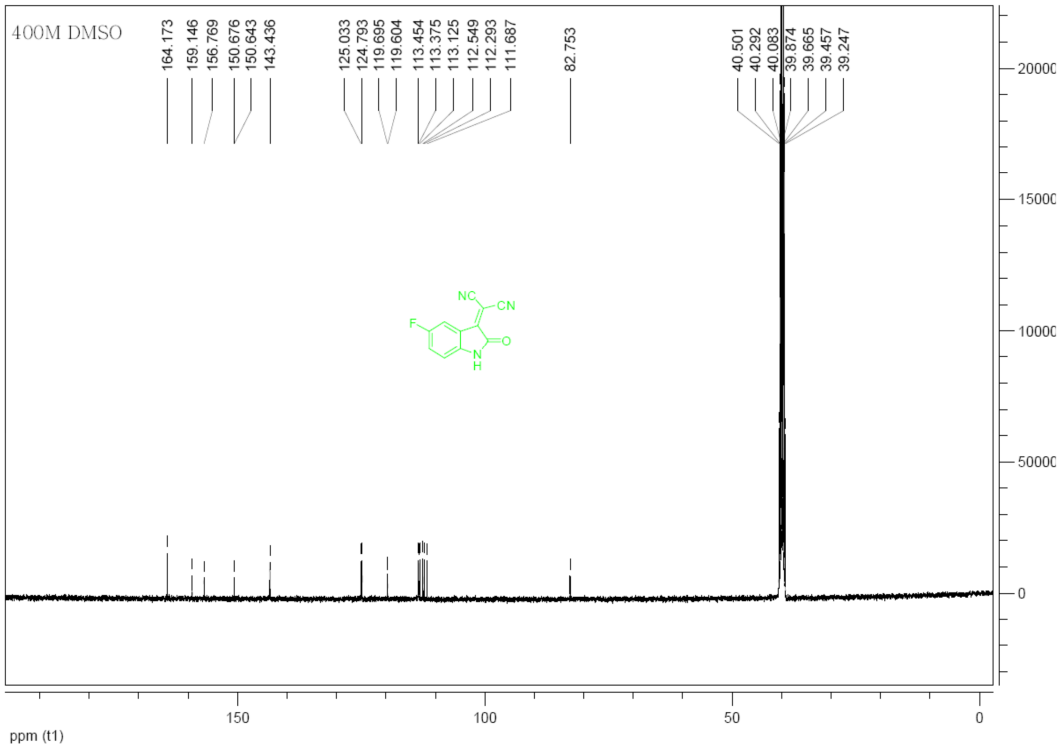
2-(5-bromo-2-oxoindolin-3-ylidene)malononitrile (3c)



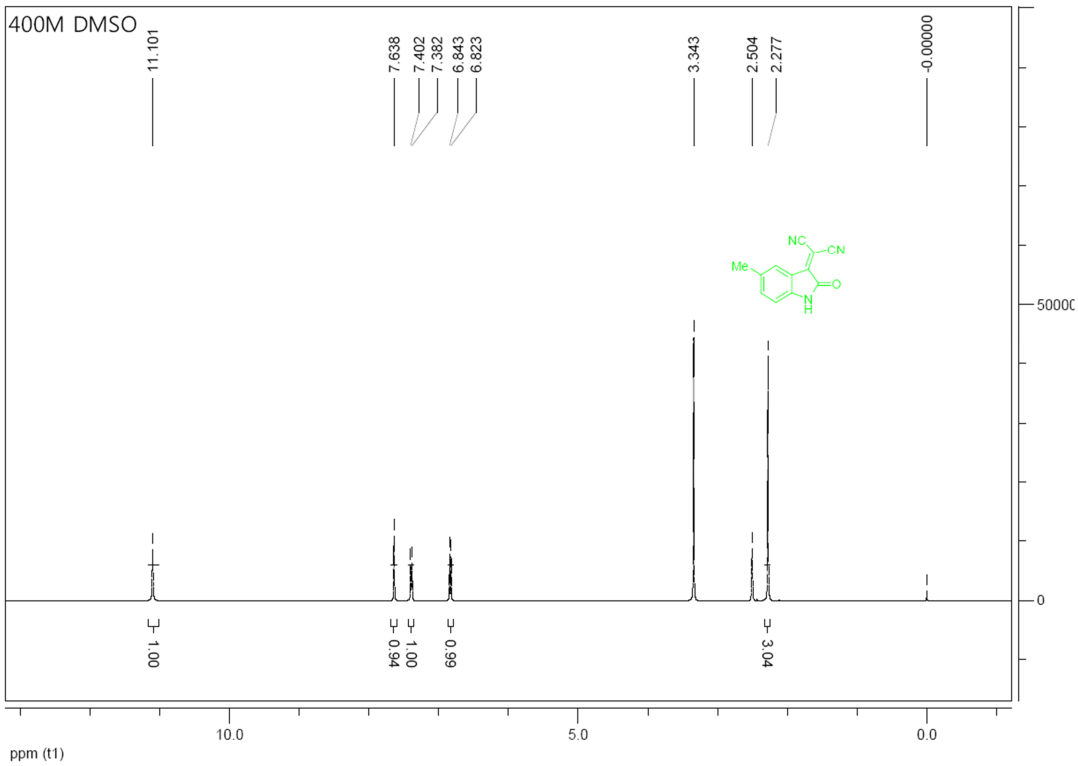


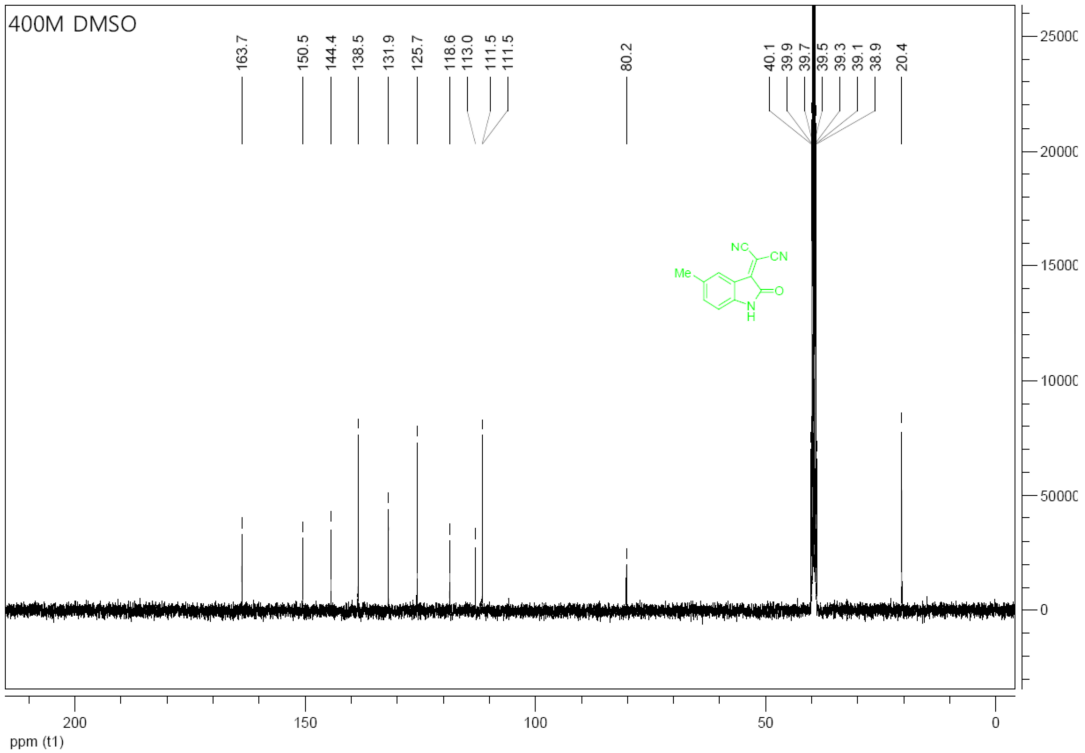
2-(5-Fluoro-2-oxoindolin-3-ylidene)malononitrile (3d)



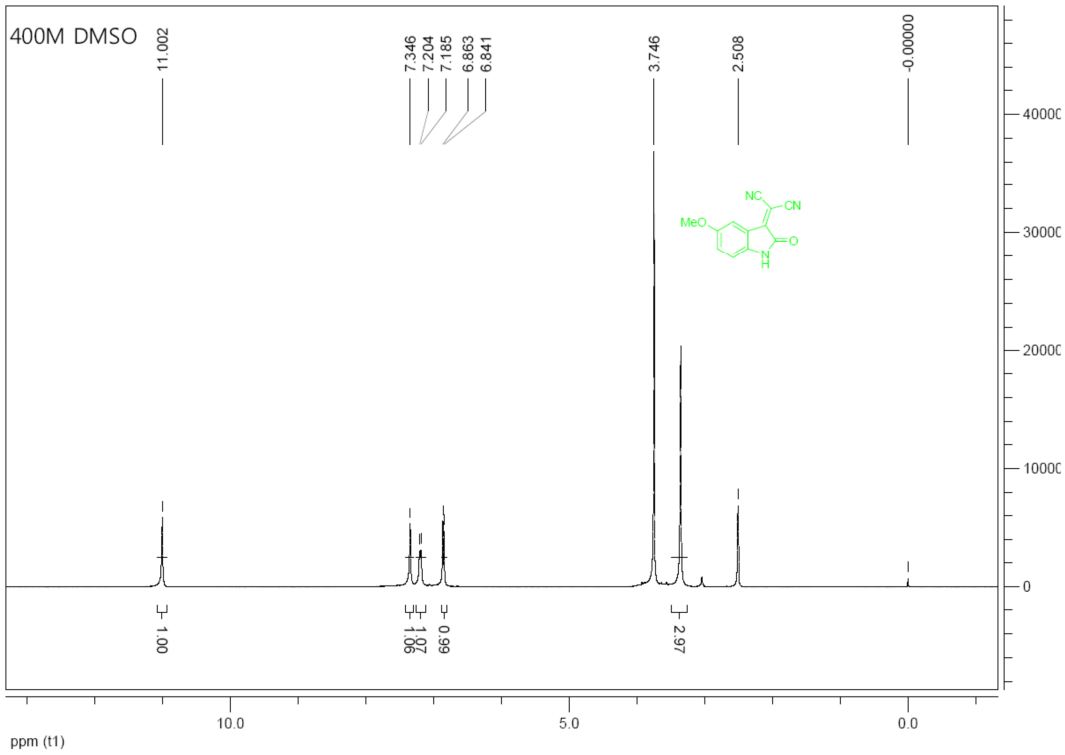


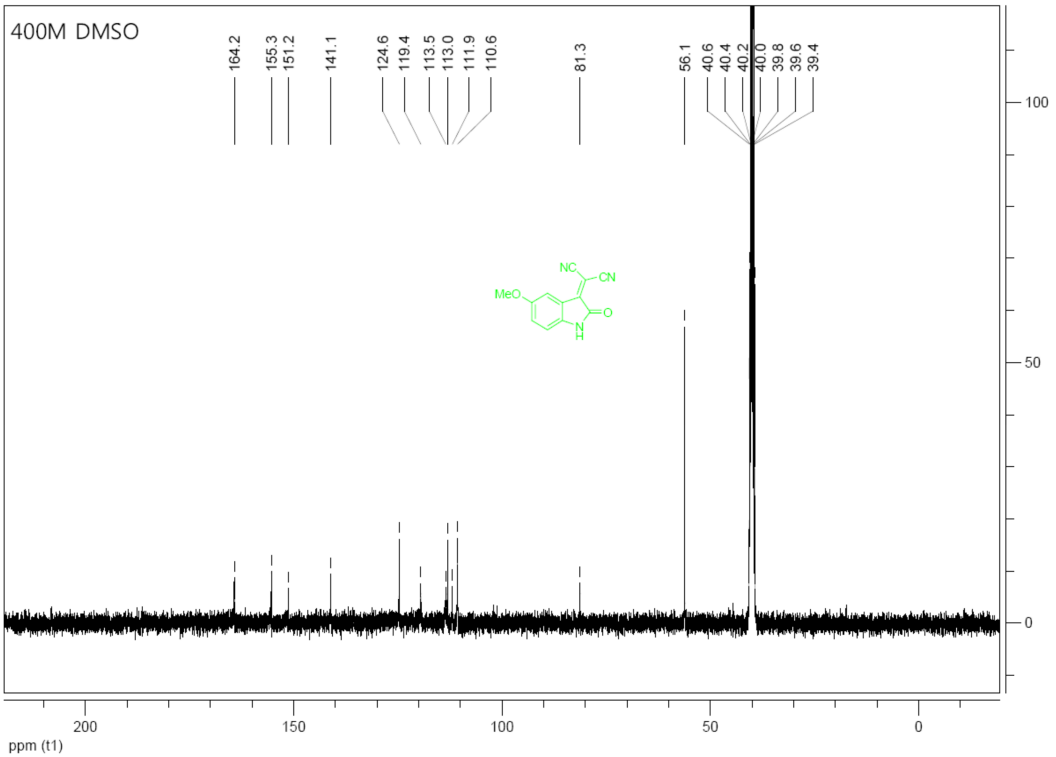
2-(5-methyl-2-oxoindolin-3-ylidene)malononitrile (3e)



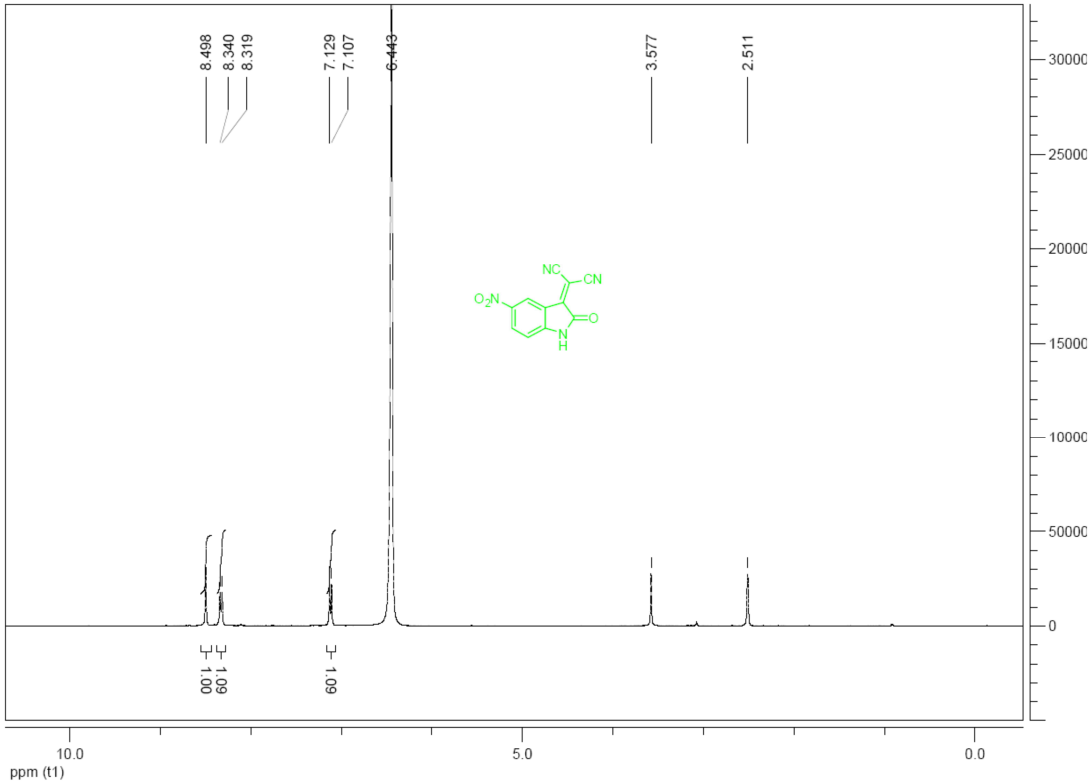


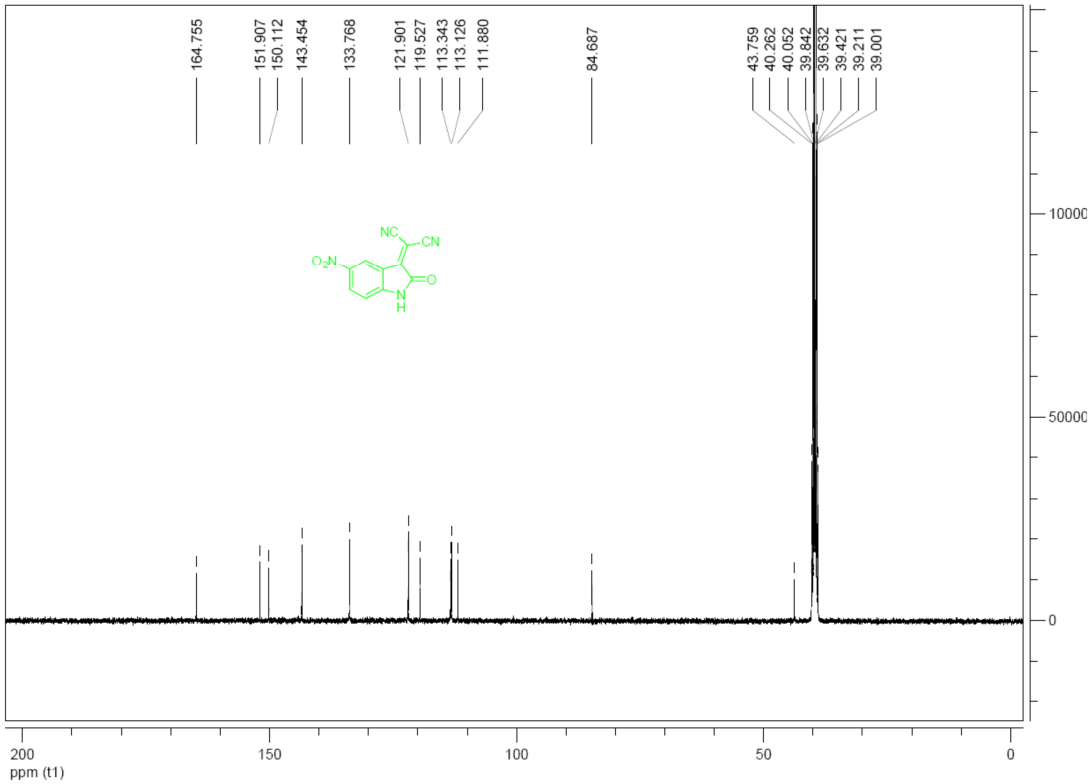
2-(5-methoxy-2-oxoindolin-3-ylidene)malononitrile (3f)



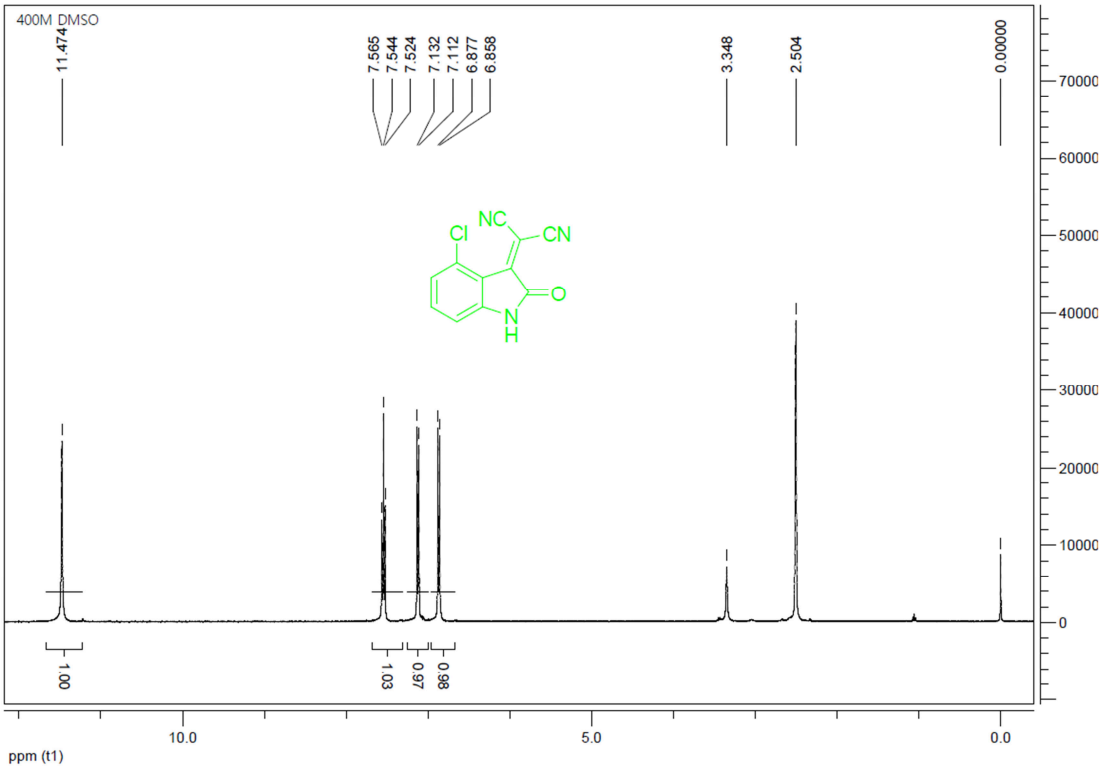


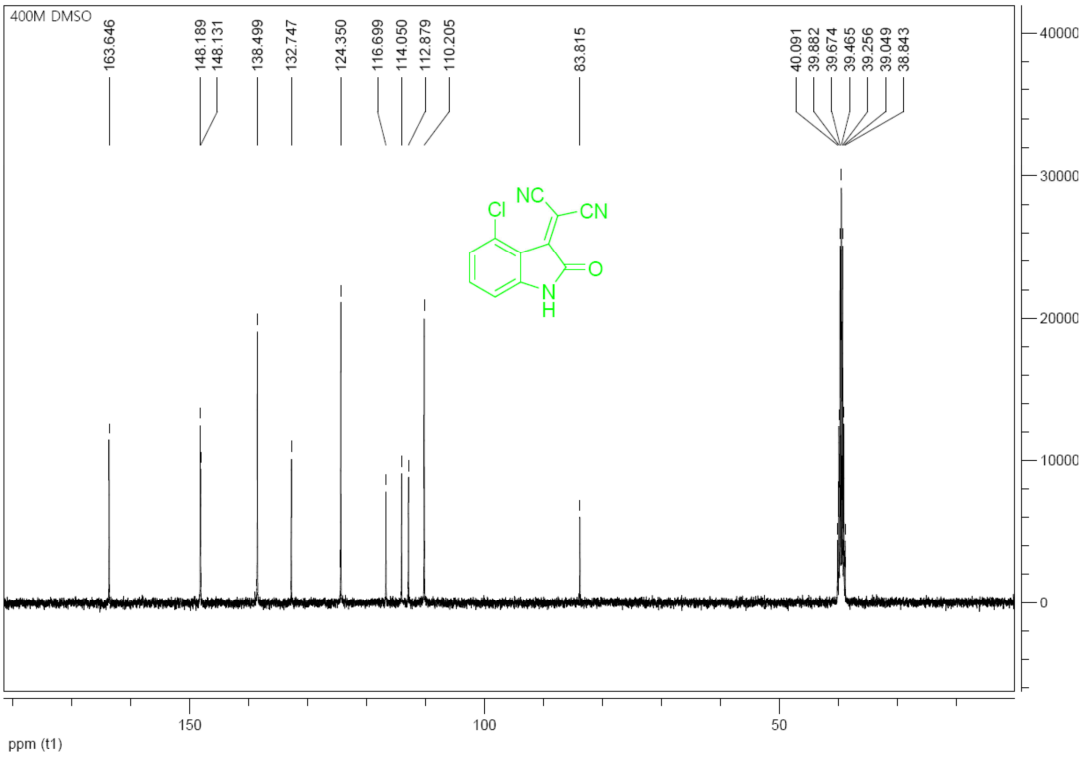
2-(5-nitro-2-oxoindolin-3-ylidene)malononitrile (3g)



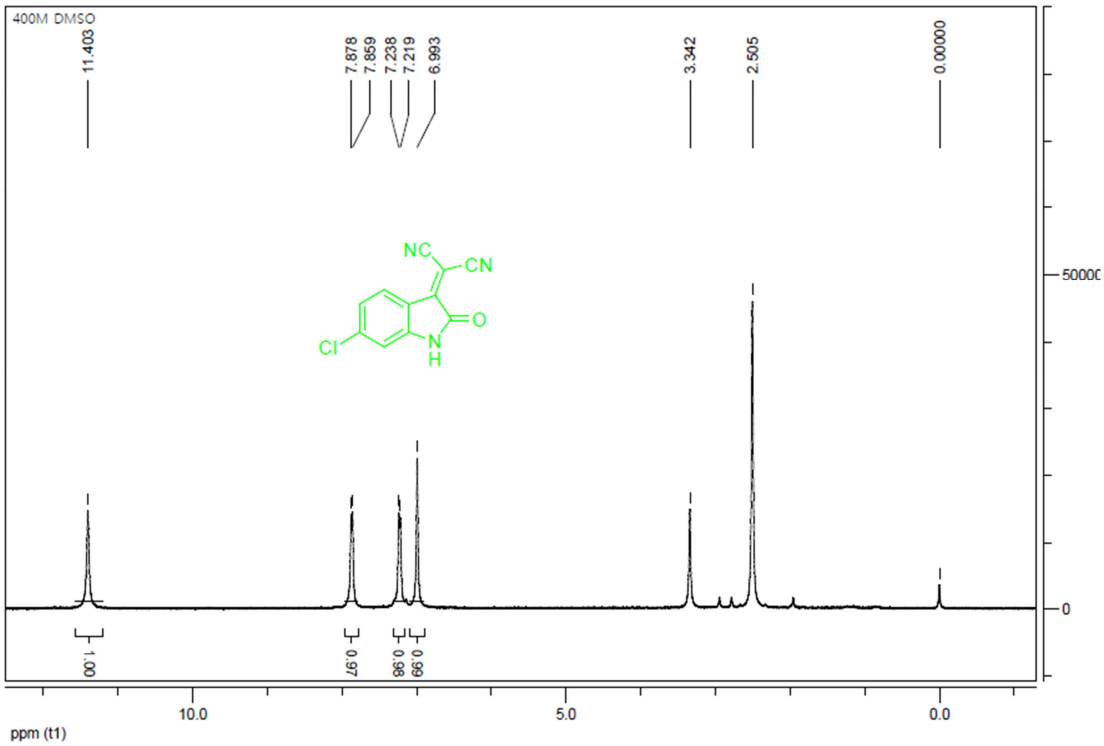


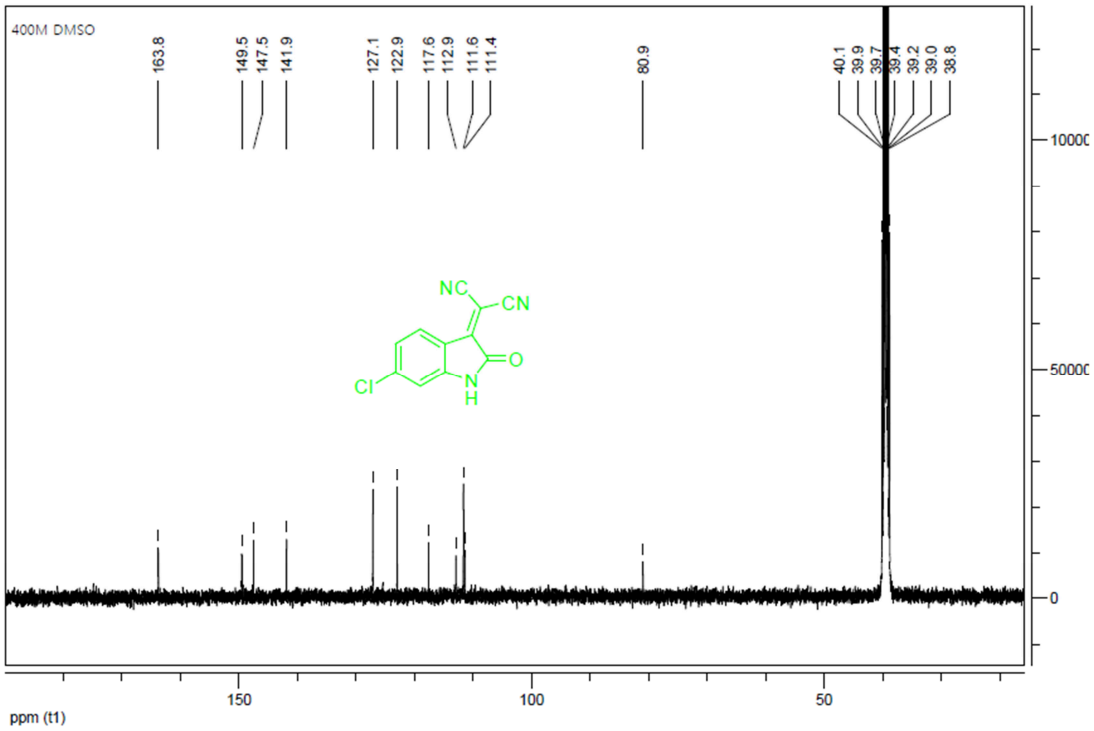
2-(4-Chloro-2-oxoindolin-3-ylidene)malononitrile (3h)



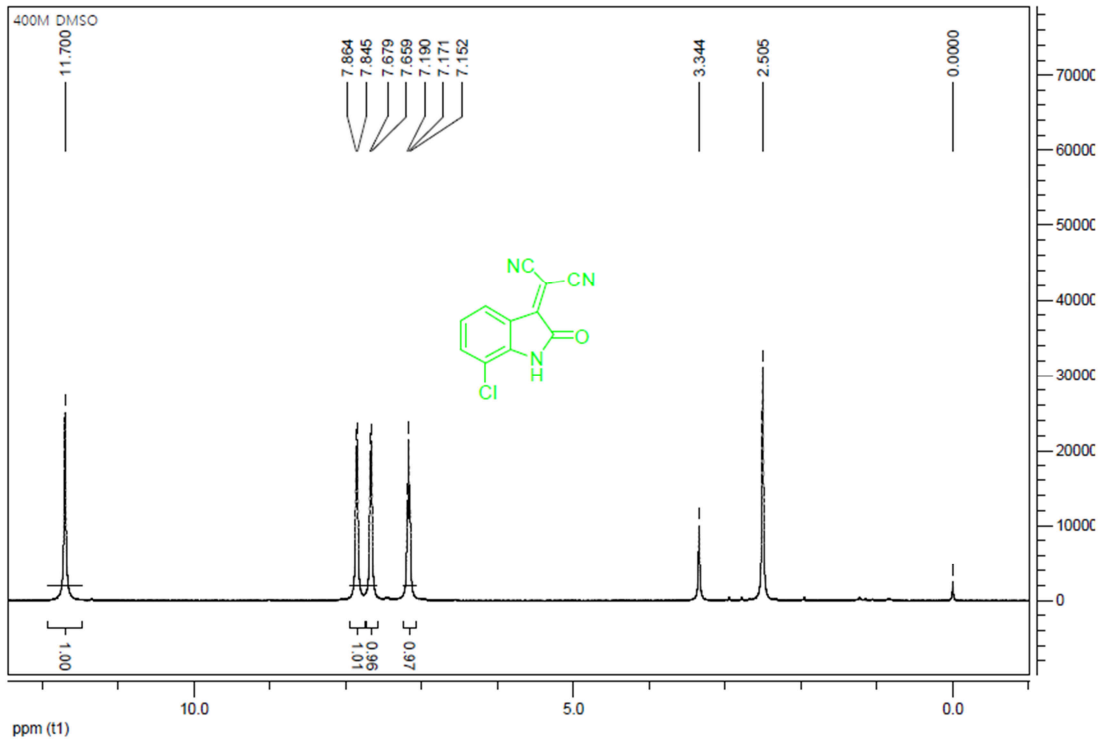


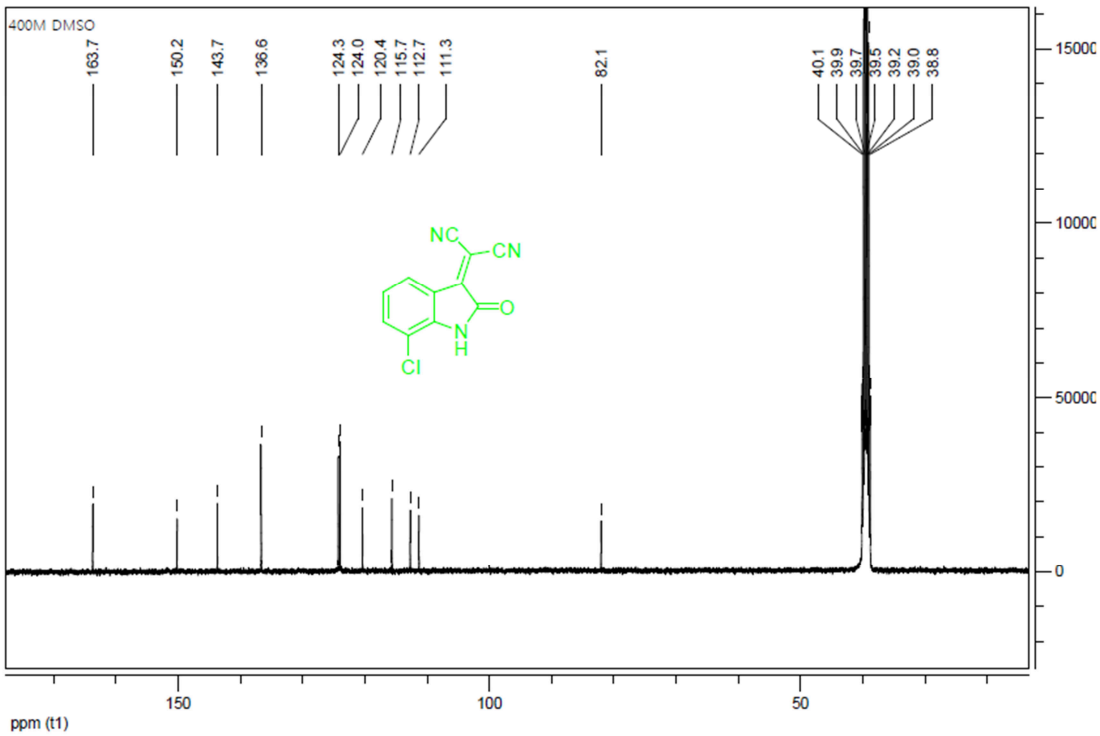
2-(6-Chloro-2-oxoindolin-3-ylidene)malononitrile (3i)



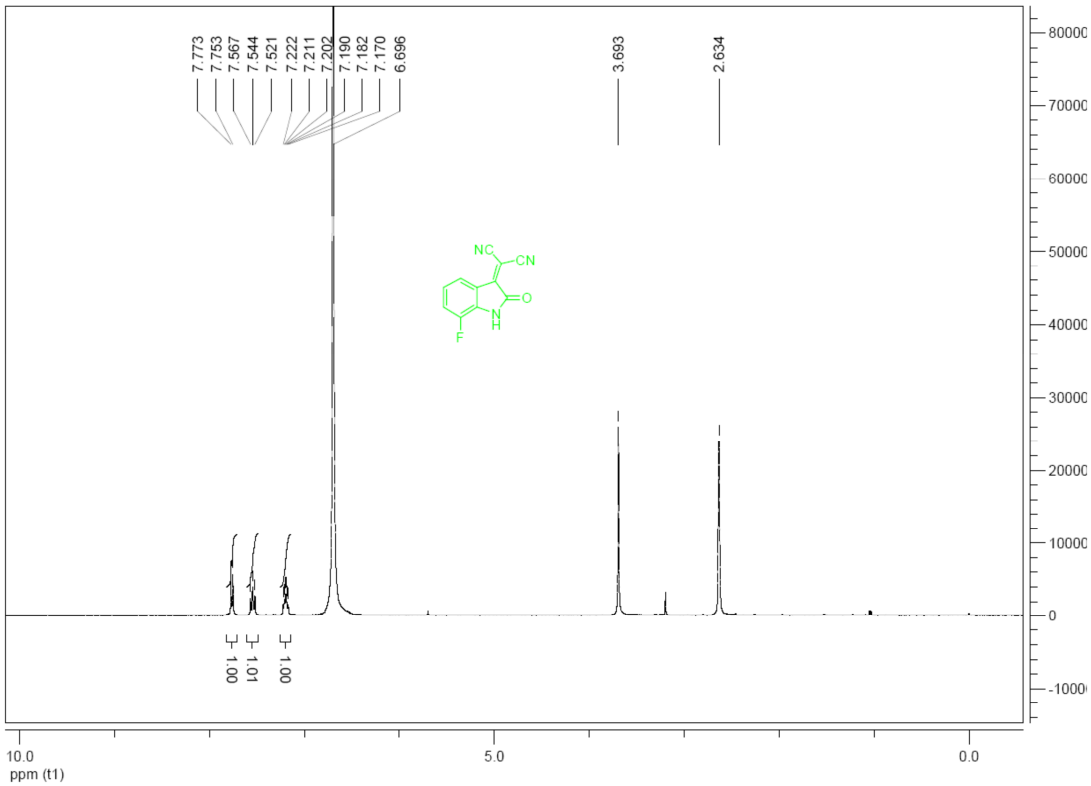


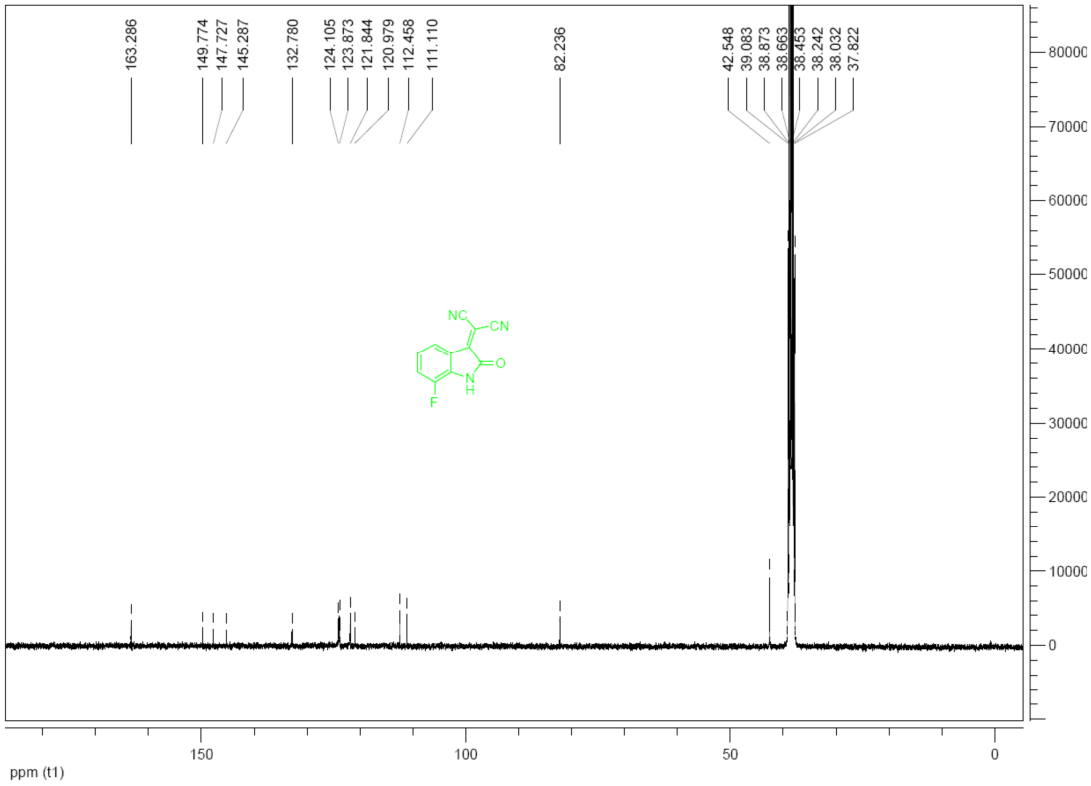
2-(7-Chloro-2-oxoindolin-3-ylidene)malononitrile (3j)



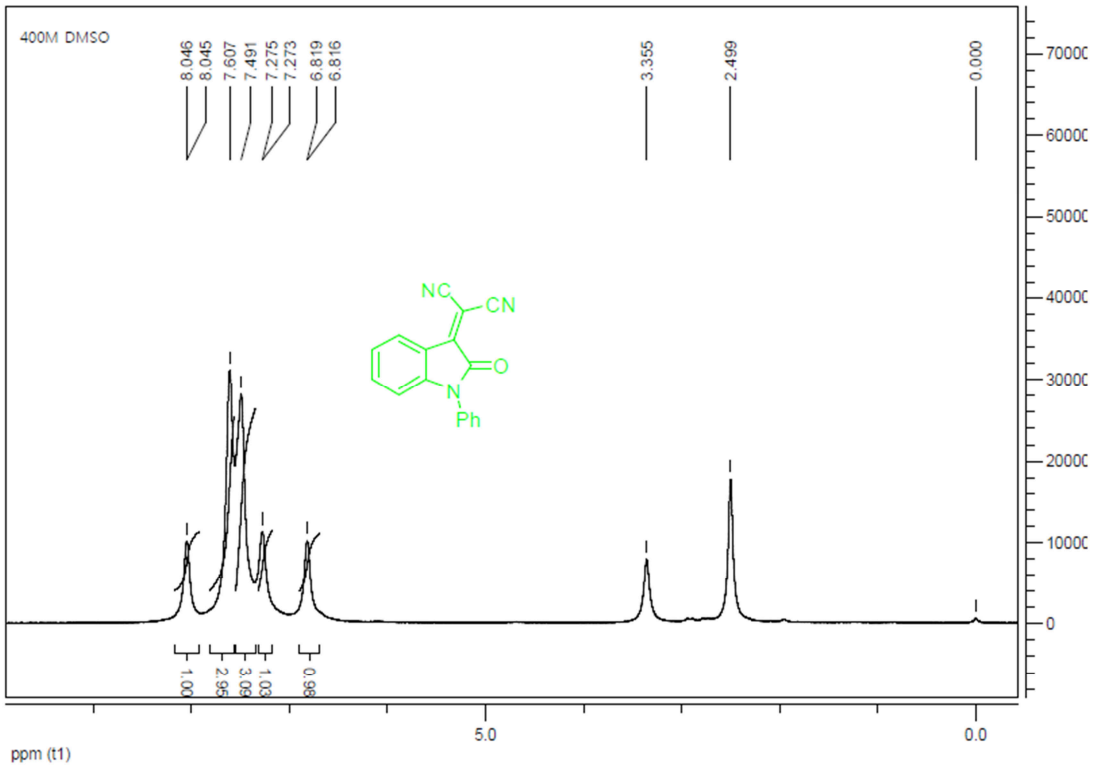


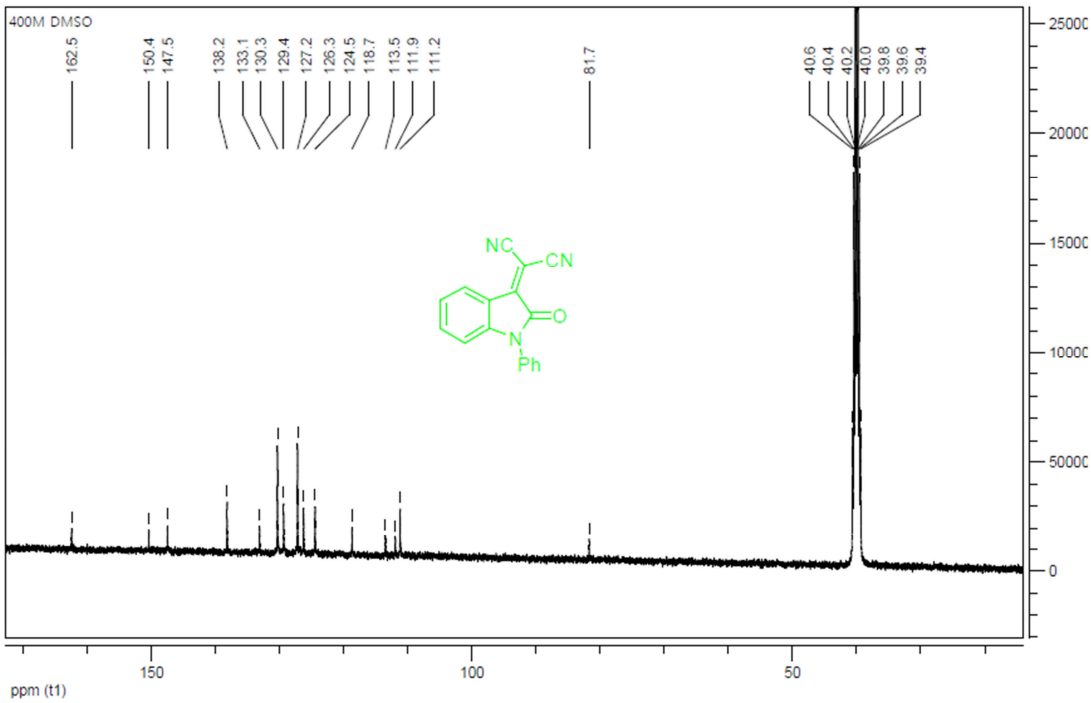
2-(7-fluoro-2-oxoindolin-3-ylidene)malononitrile (3k)



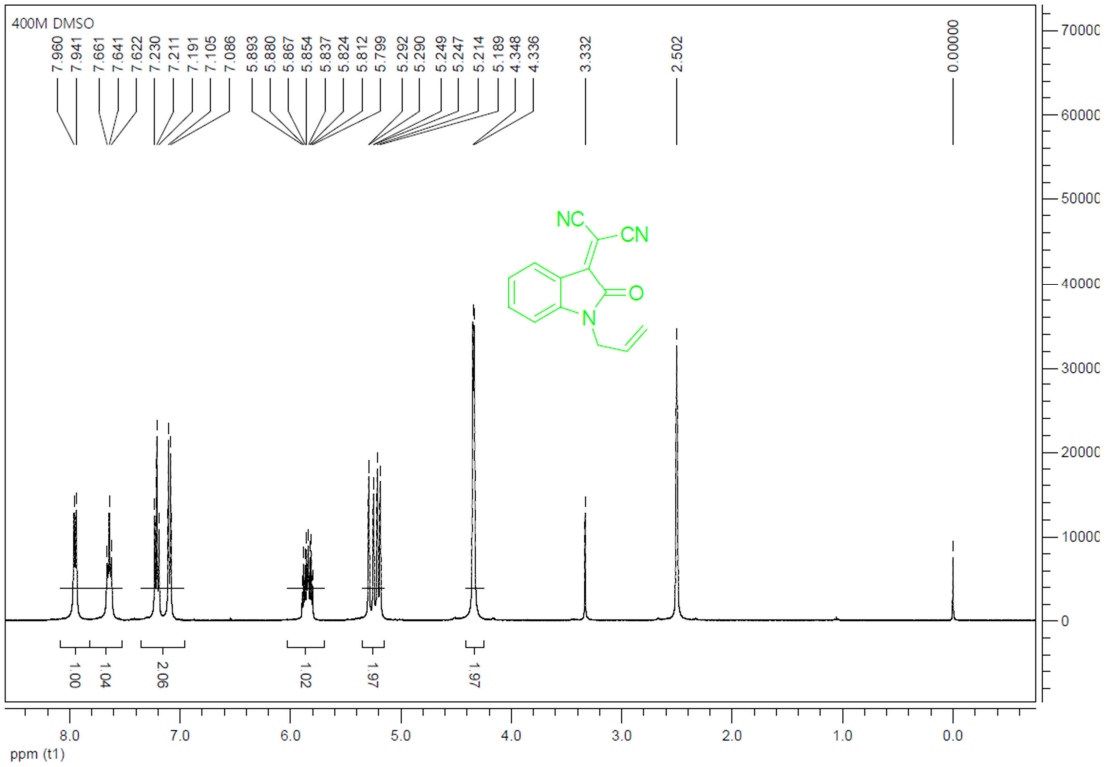


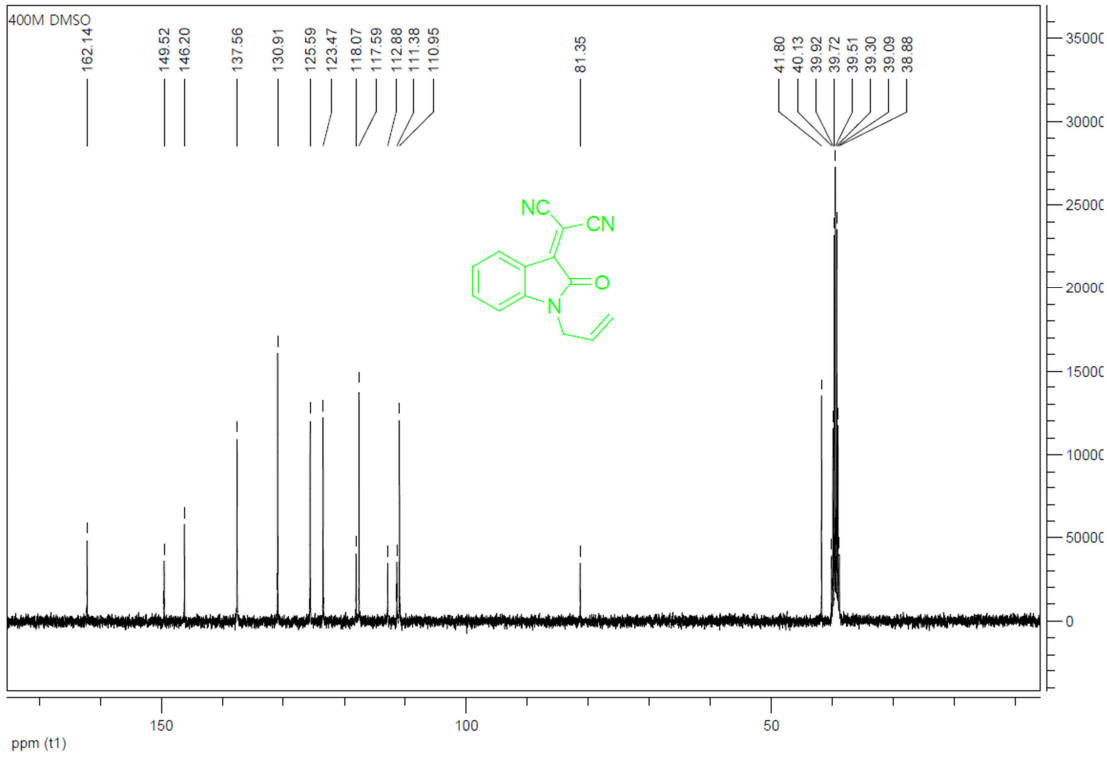
2-(2-Oxo-1-phenylindolin-3-ylidene)malononitrile (3l)



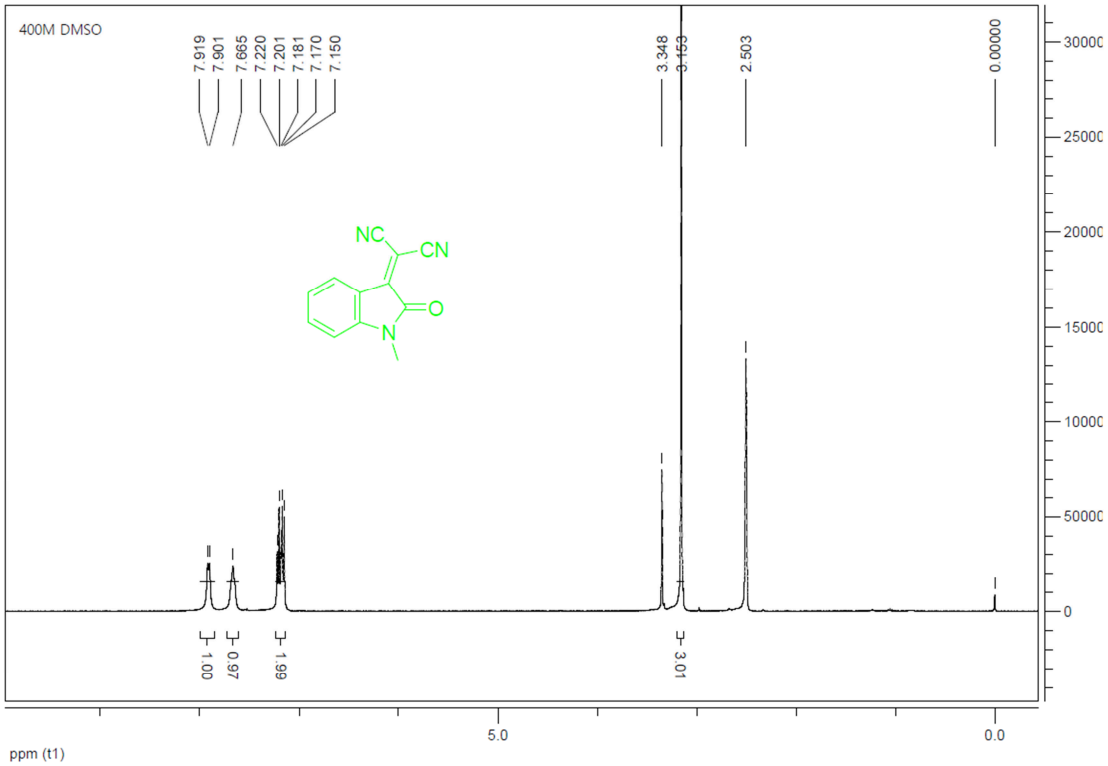


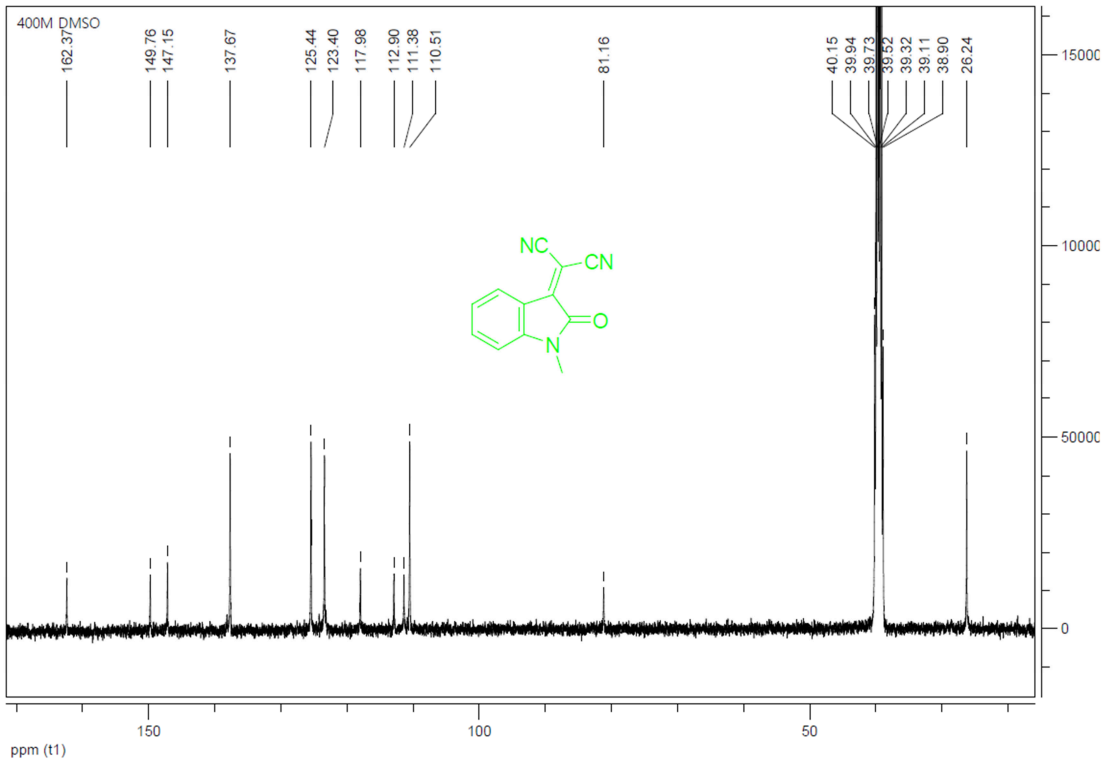
2-(1-Allyl-2-oxoindolin-3-ylidene)malononitrile (3m)



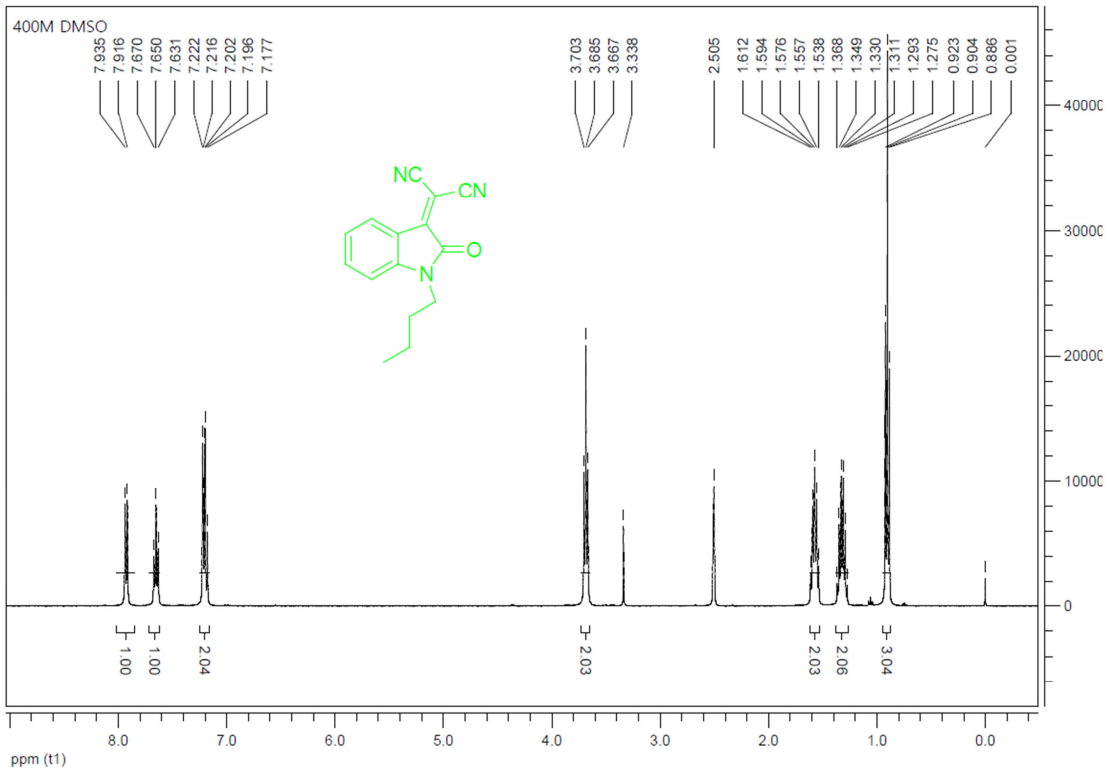


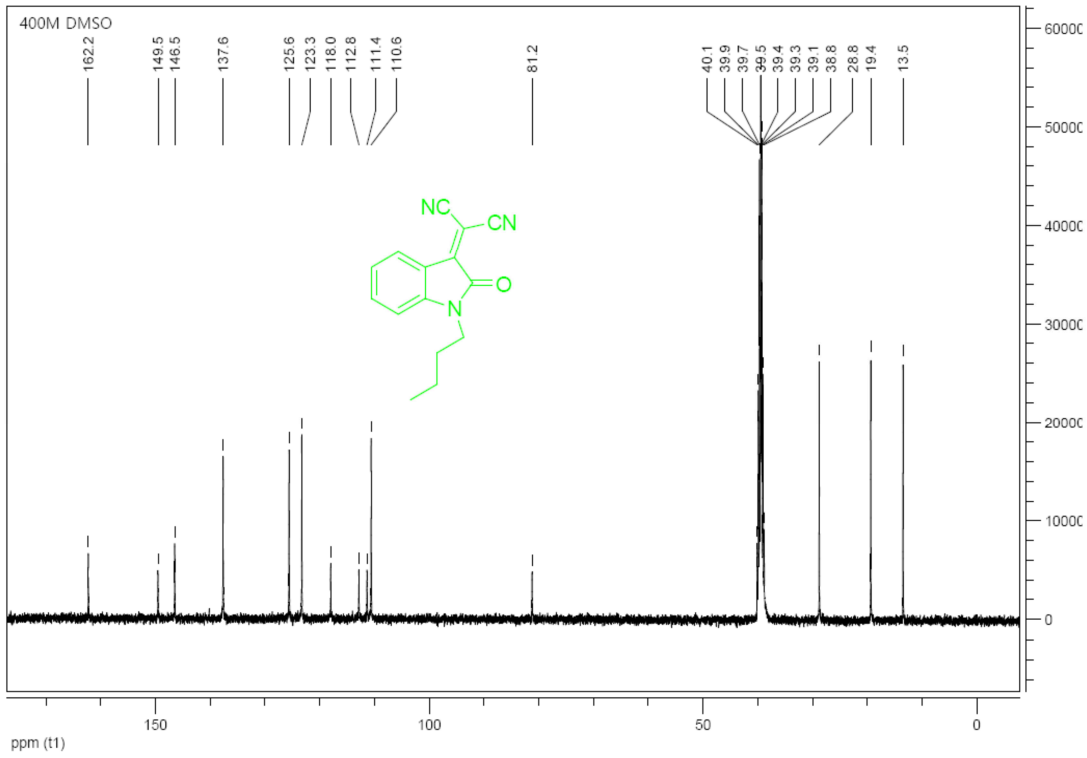
2-(1-Methyl-2-oxoindolin-3-ylidene)malononitrile (3n)



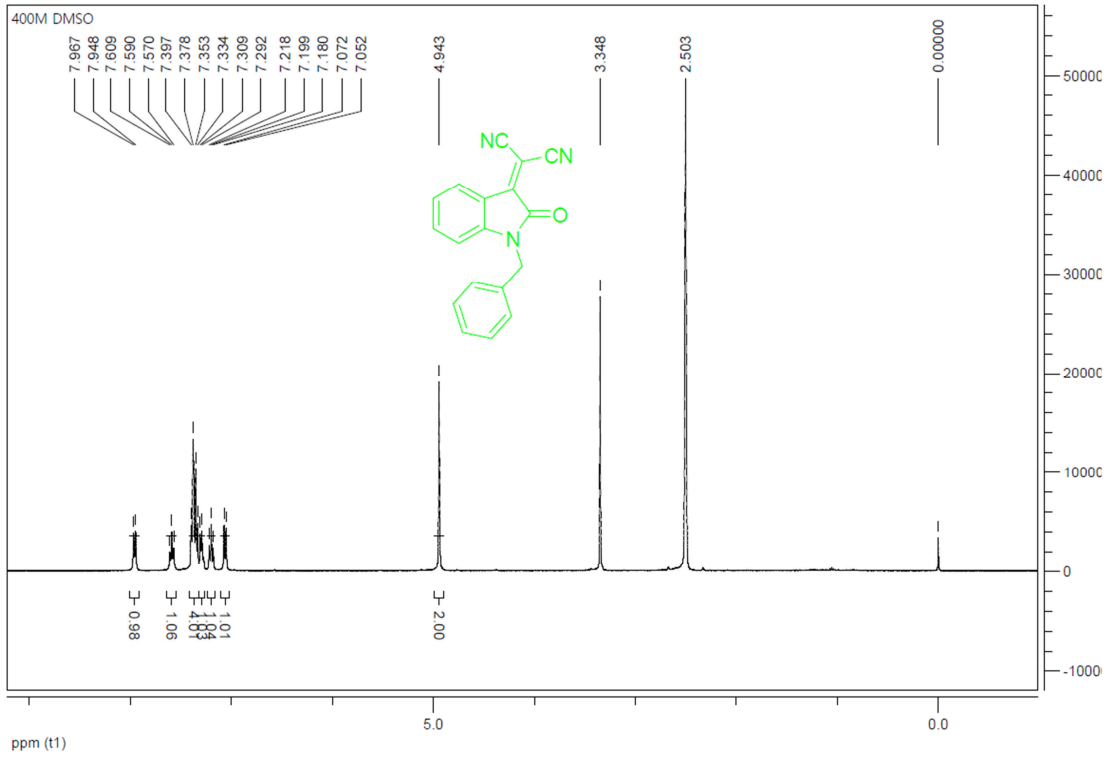


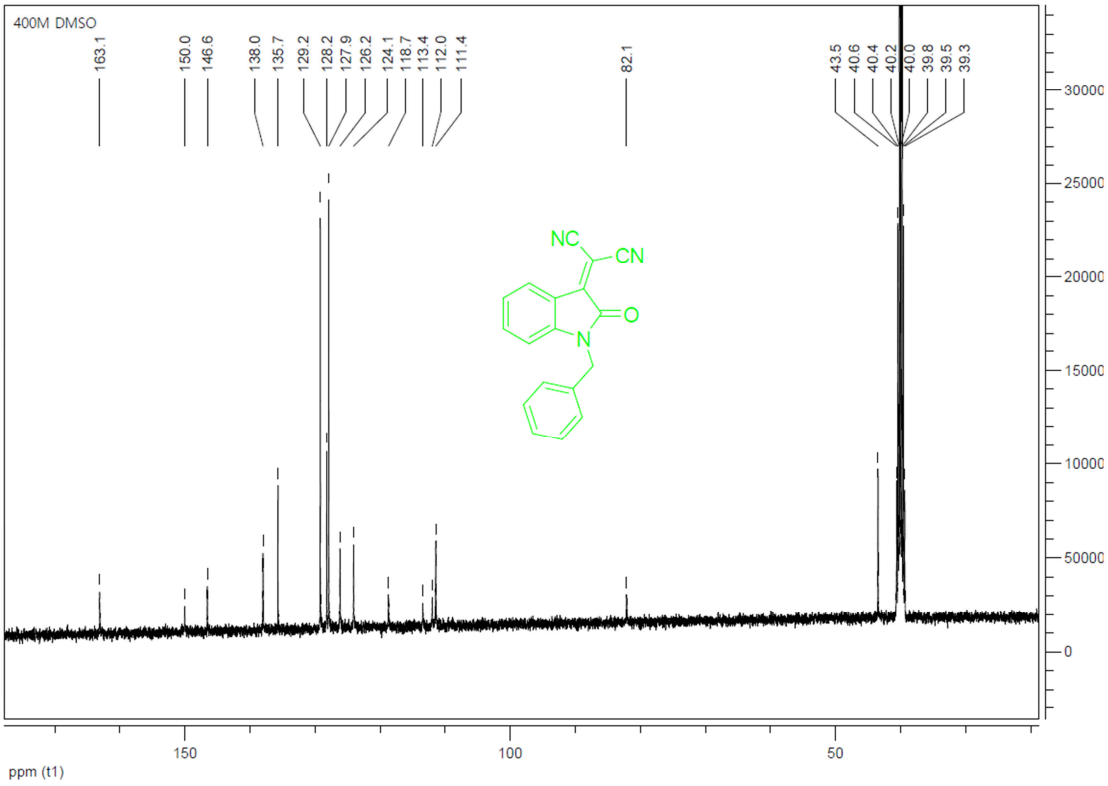
2-(1-Butyl-2-oxoindolin-3-ylidene)malononitrile (3o)



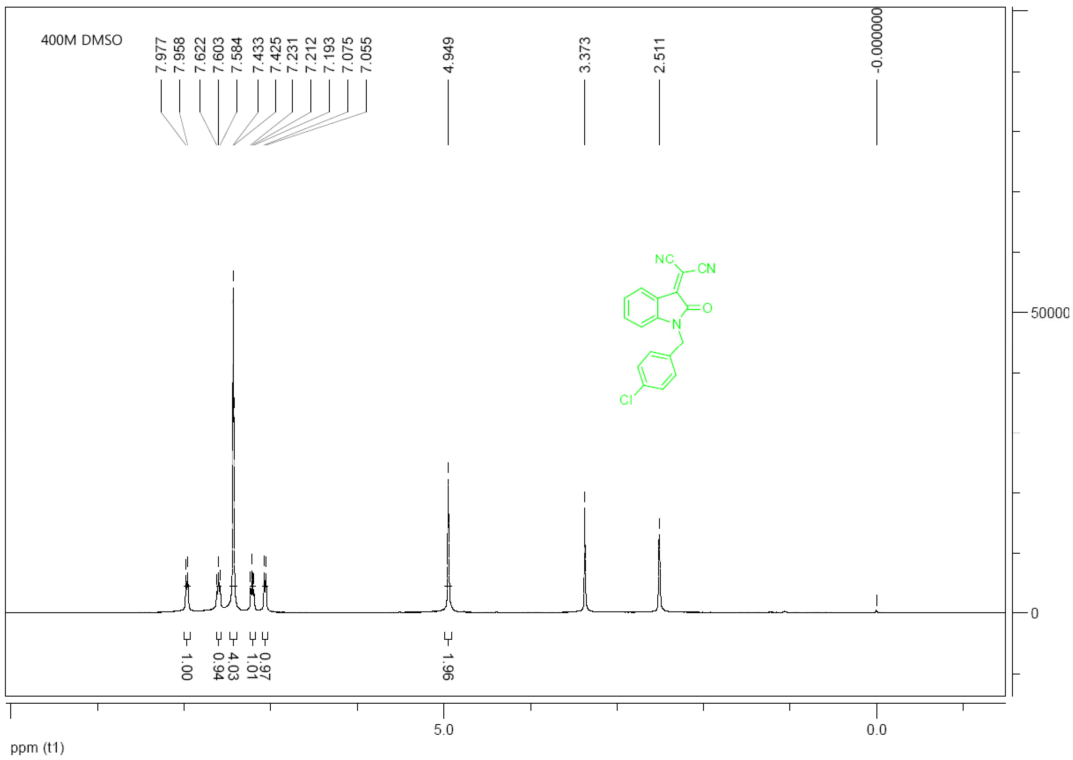


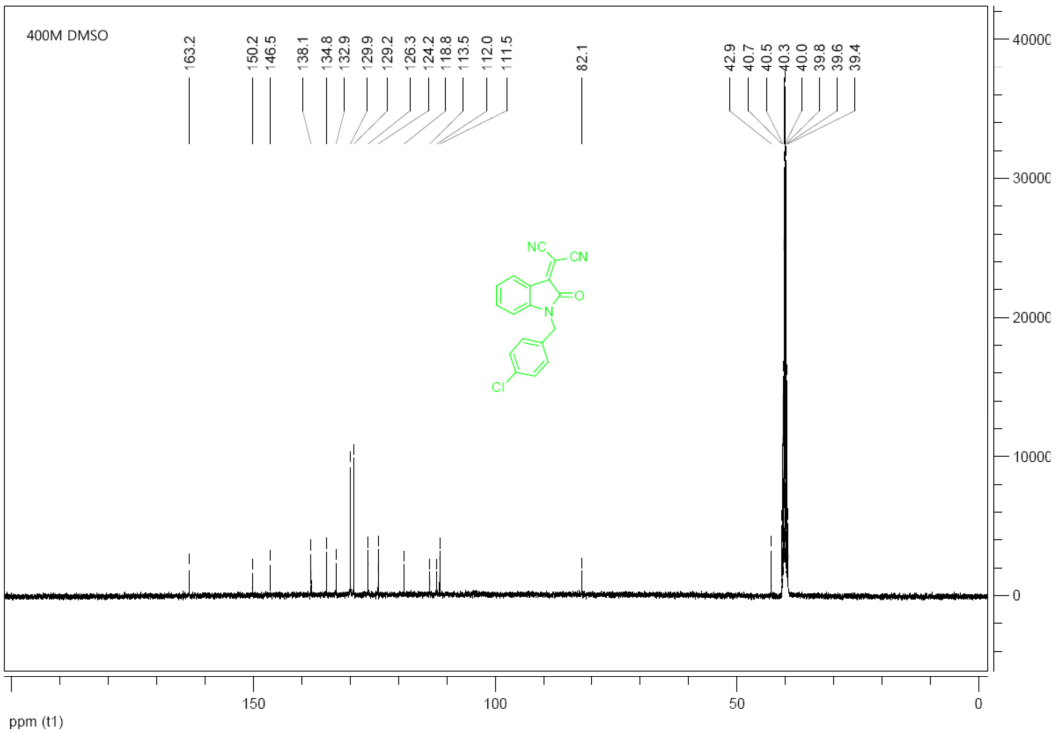
2-(1-Benzyl-2-oxoindolin-3-ylidene)malononitrile (3p)



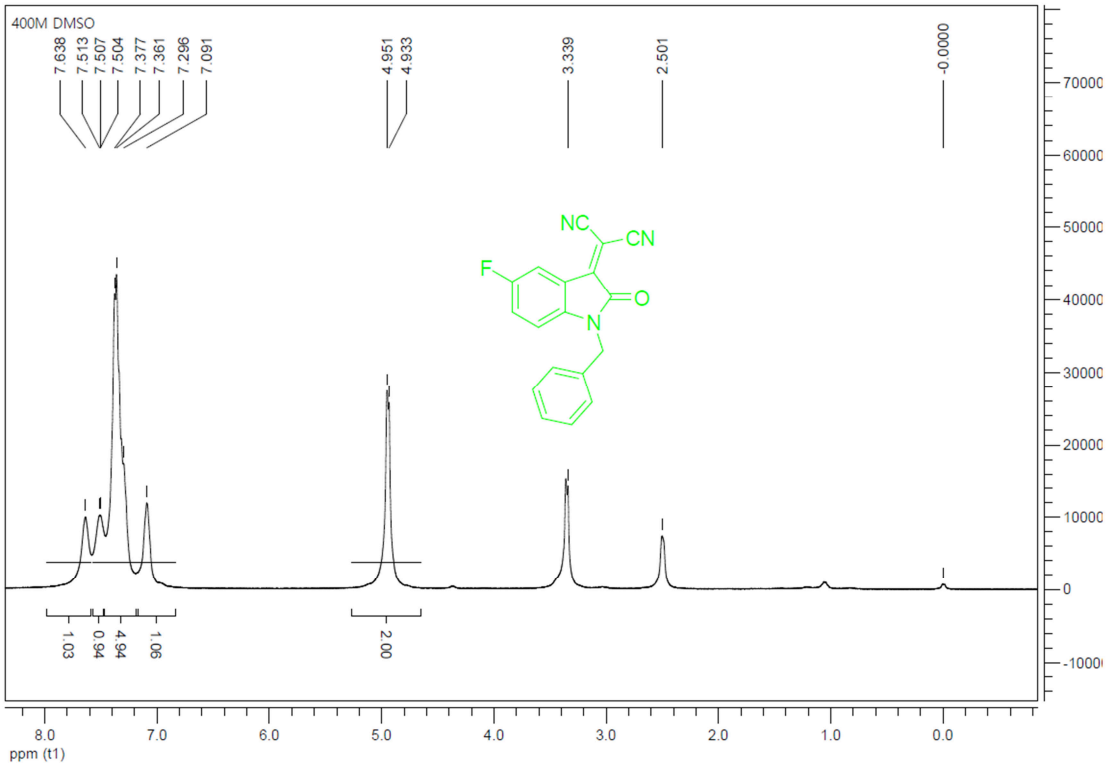


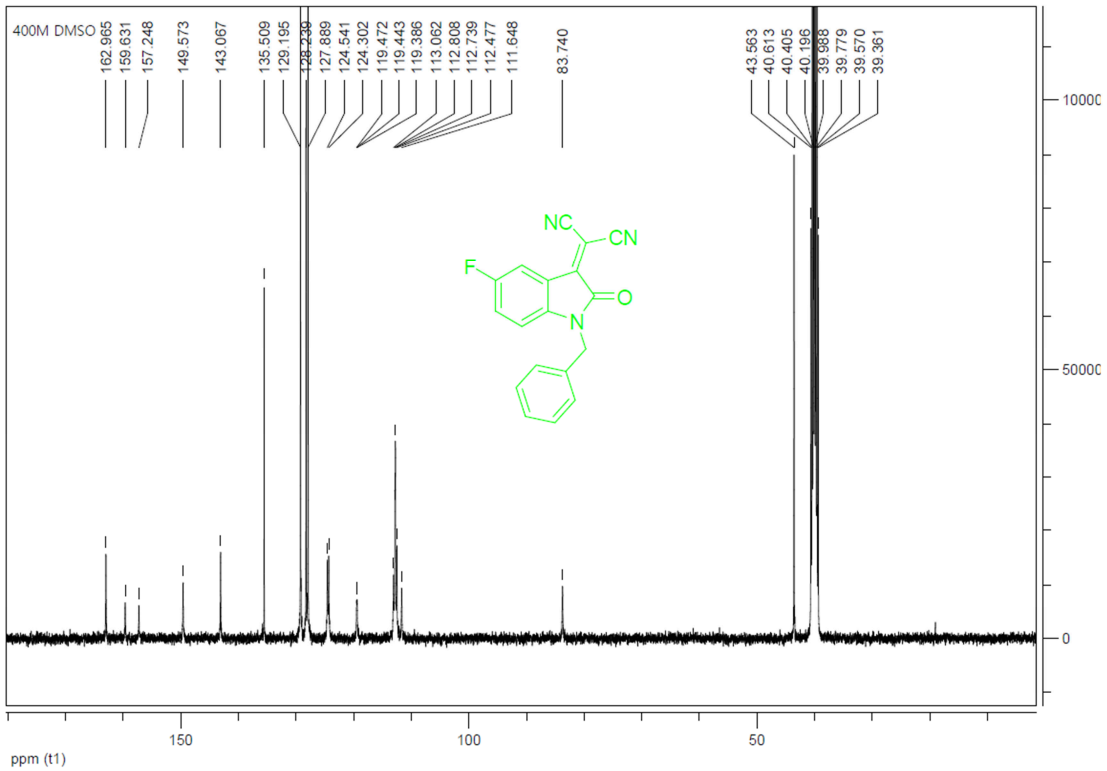
2-(1-(4-Chlorobenzyl)-2-oxoindolin-3-ylidene)malononitrile (3q)



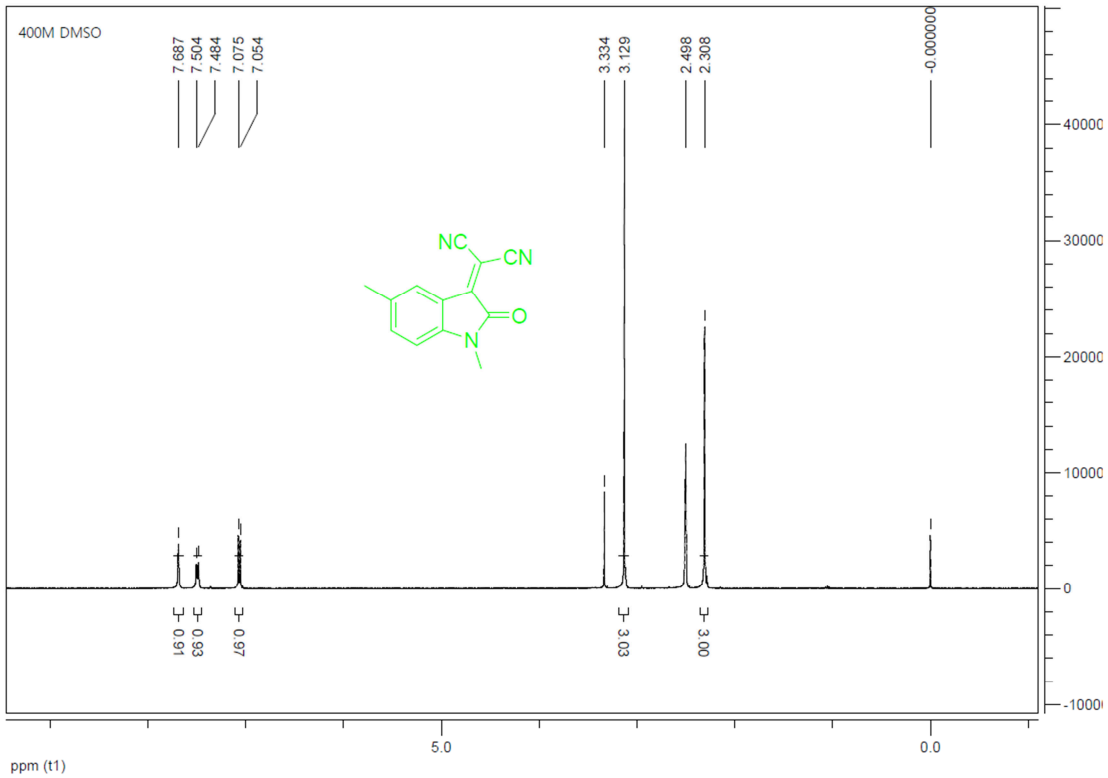


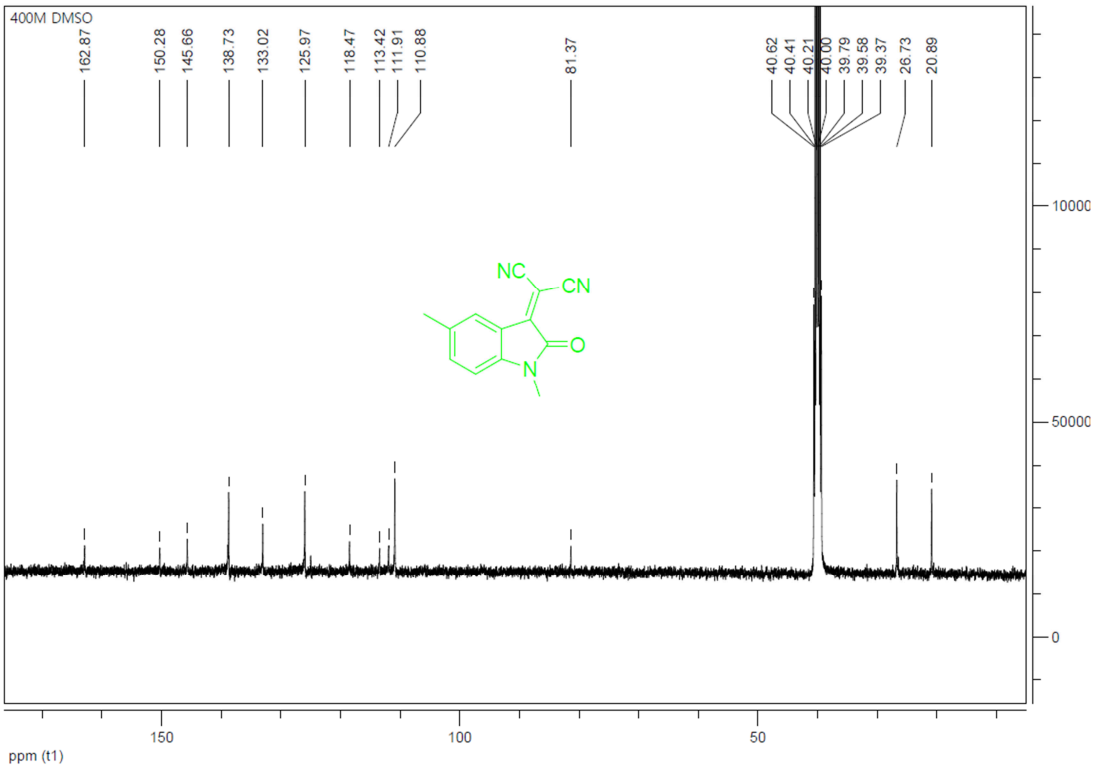
2-(1-Benzyl-5-fluoro-2-oxoindolin-3-ylidene)malononitrile (3r)



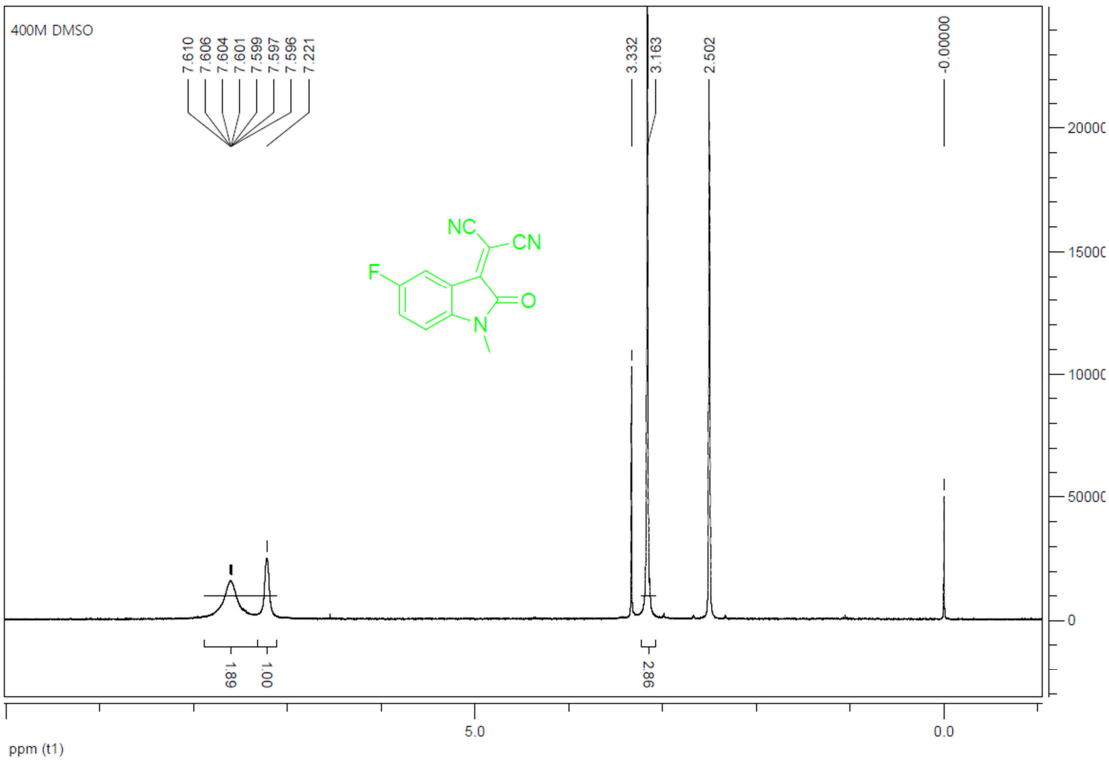


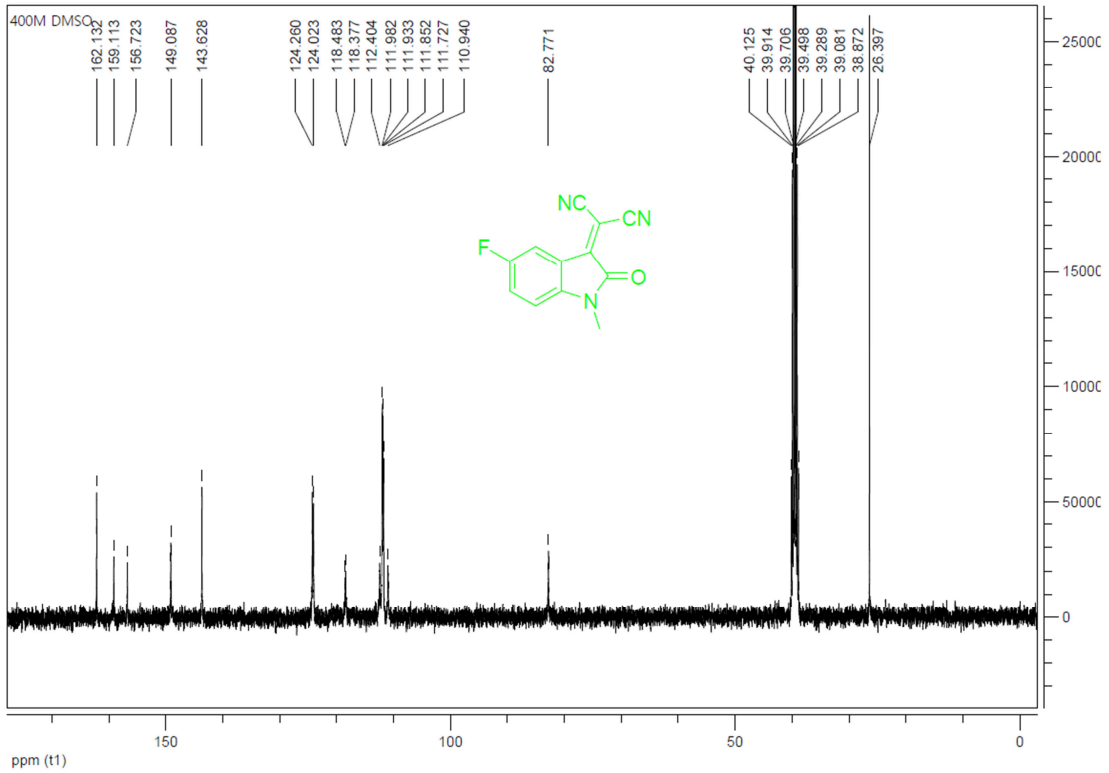
2-(1,5-Dimethyl-2-oxoindolin-3-ylidene)malononitrile (3s)



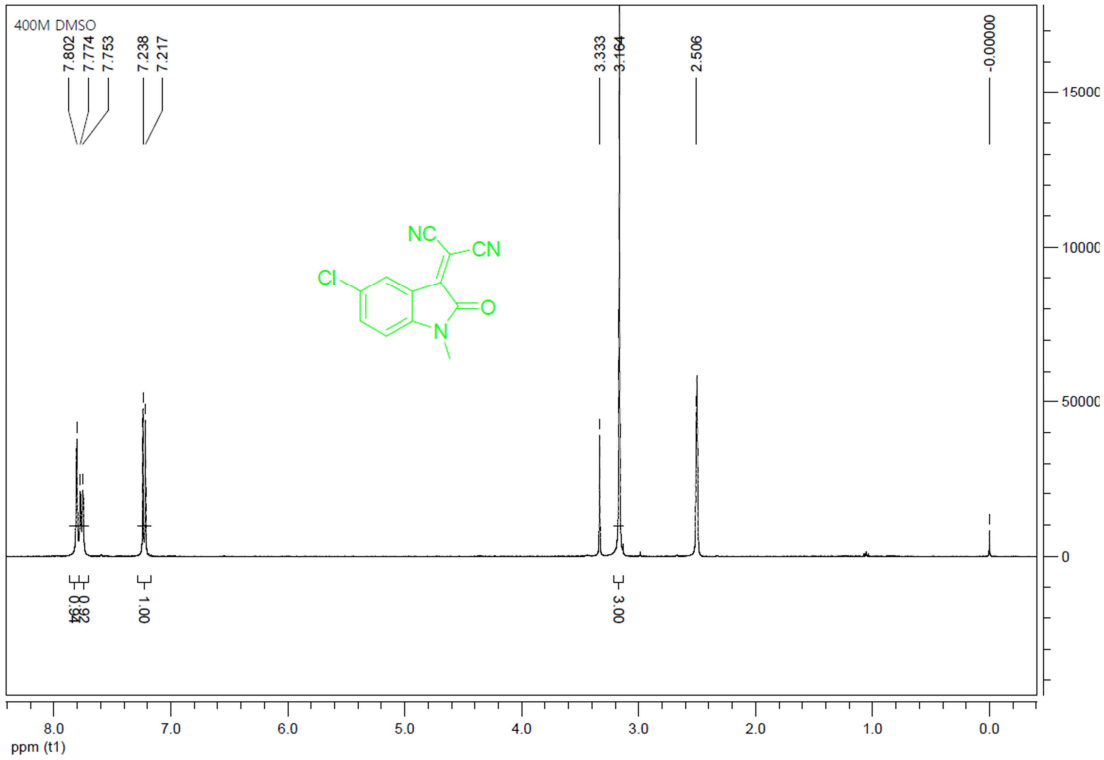


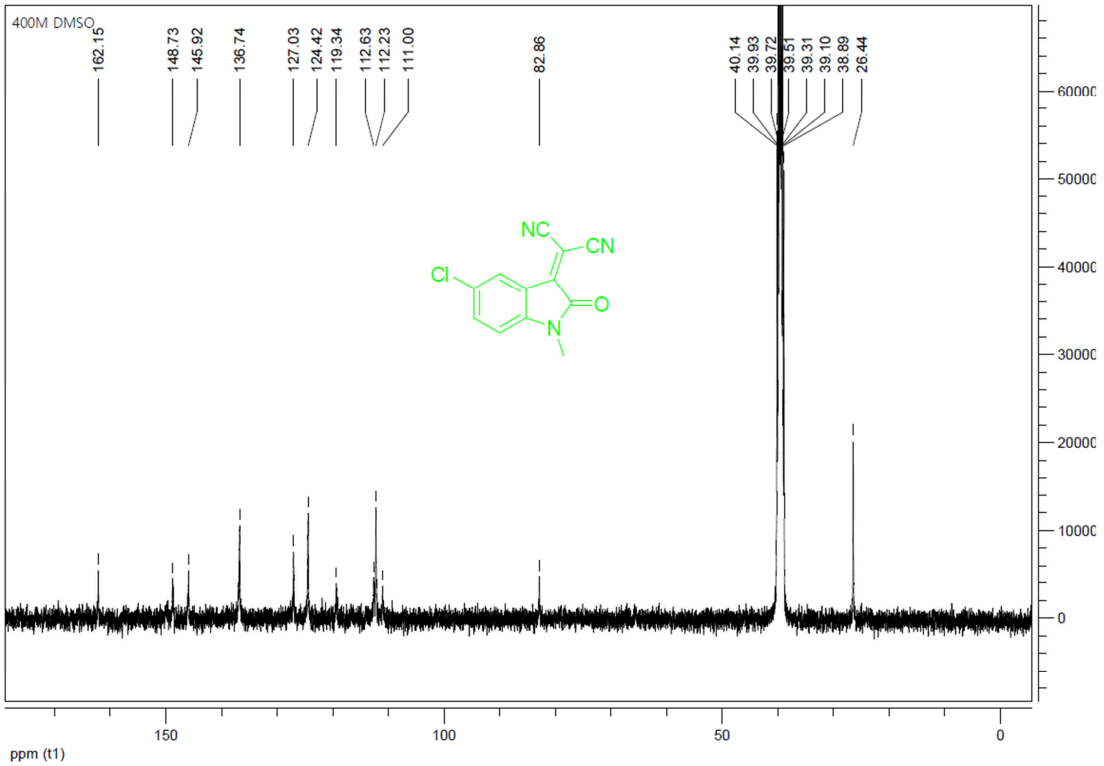
2-(5-Fluoro-1-methyl-2-oxoindolin-3-ylidene)malononitrile (3t)



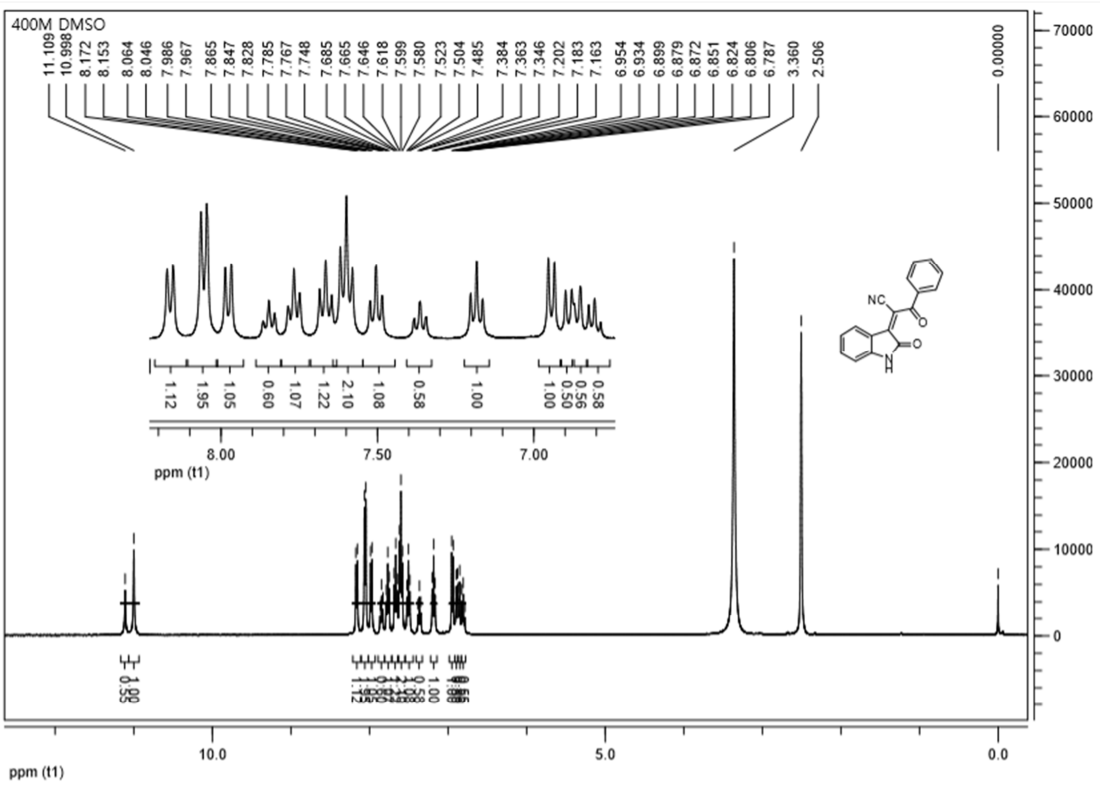


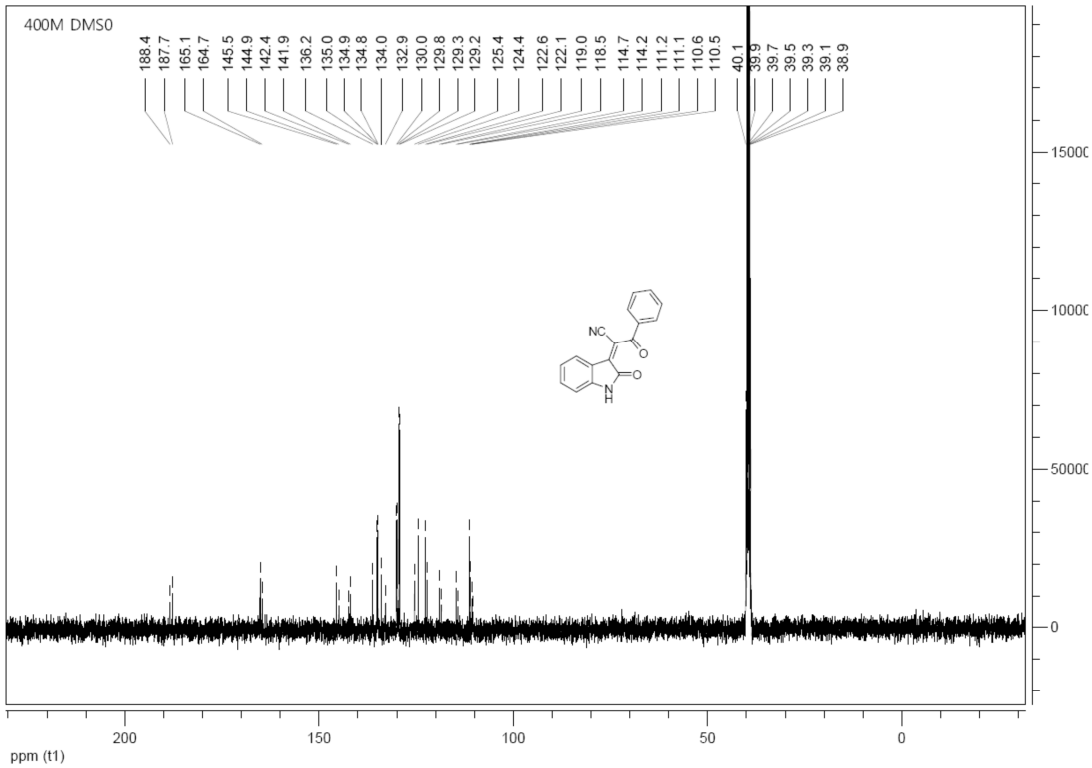
2-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene)malononitrile (3u)



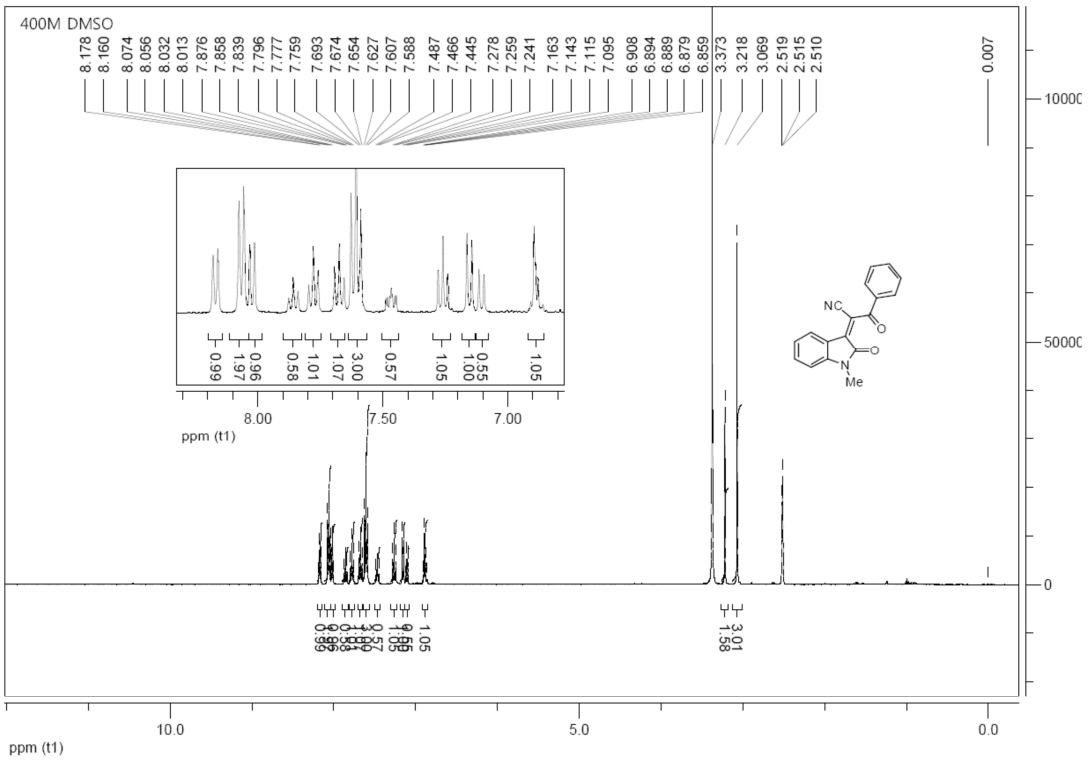


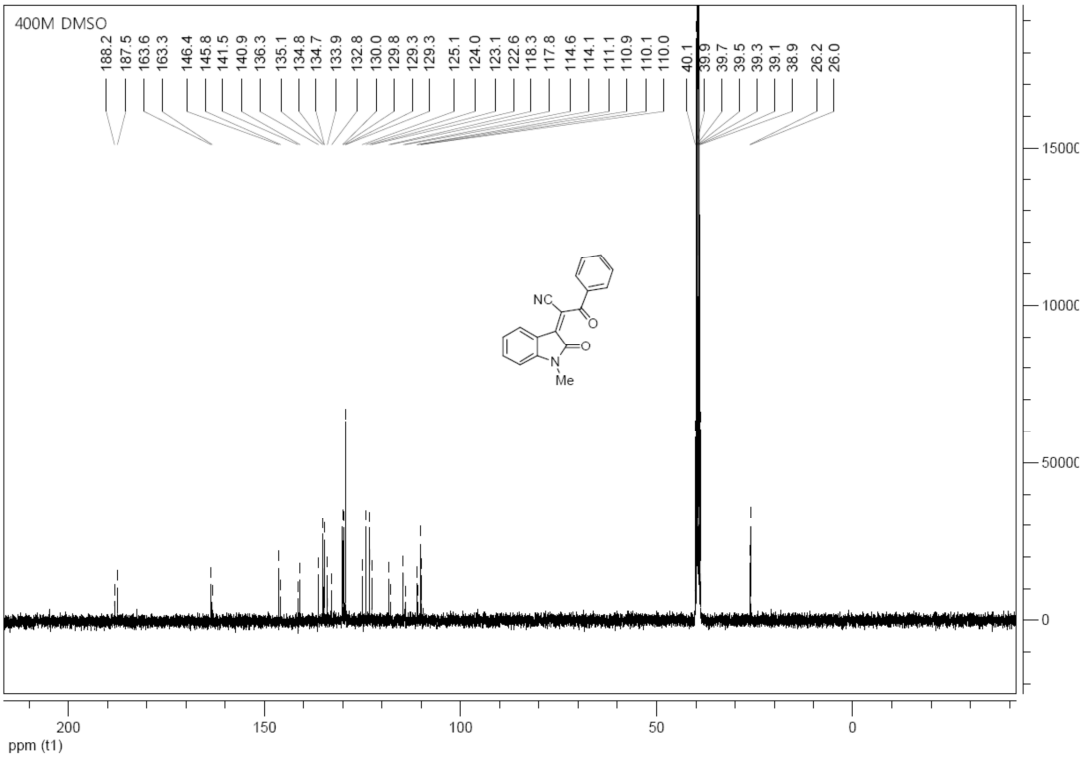
(Z)-3-oxo-2-(2-oxoindolin-3-ylidene)-3-phenylpropanenitrile (3v)



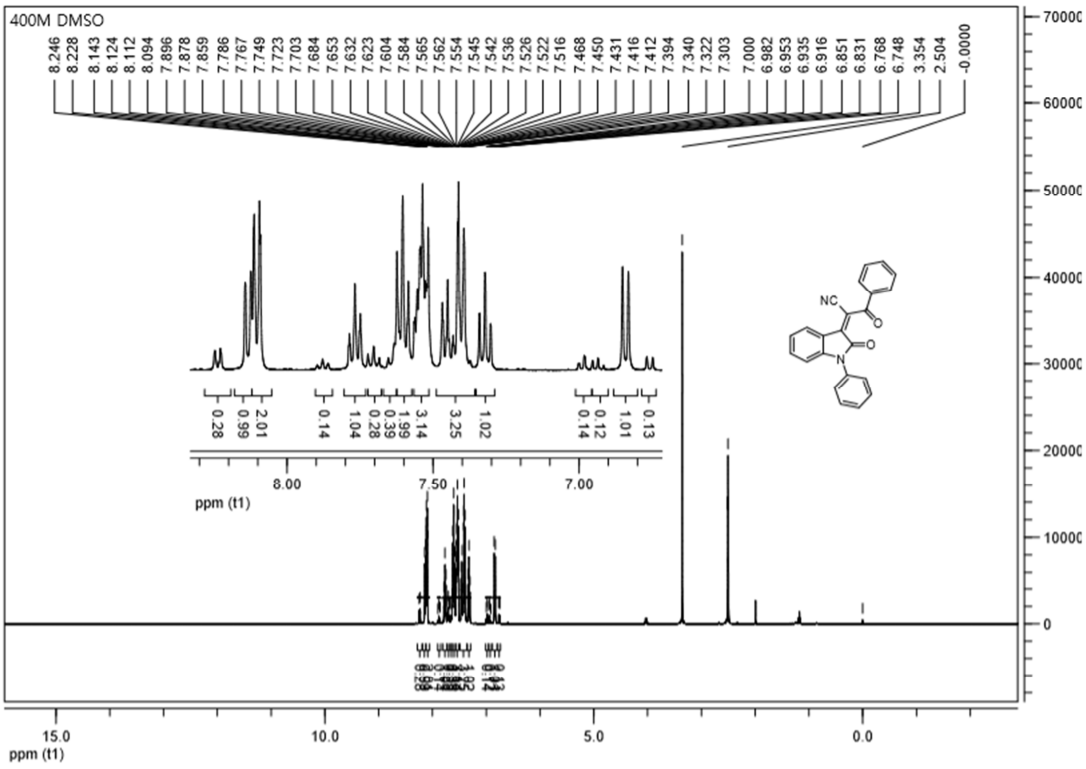


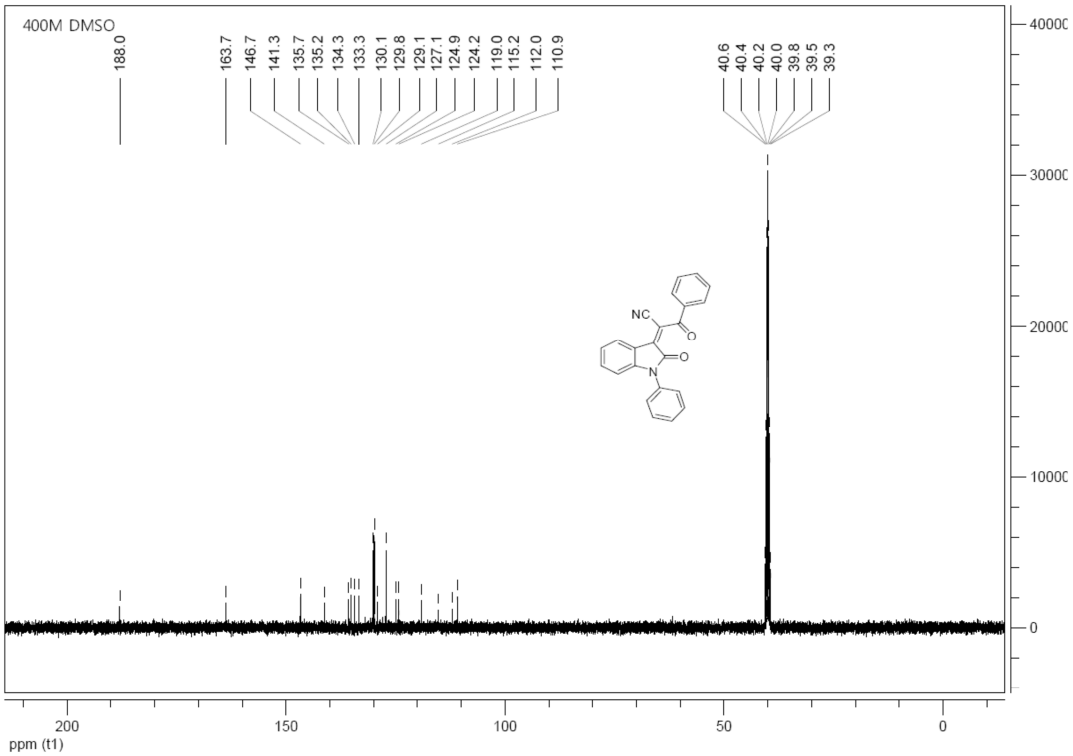
(Z)-2-(1-methyl-2-oxoindolin-3-ylidene)-3-oxo-3-phenylpropanenitrile (3w)



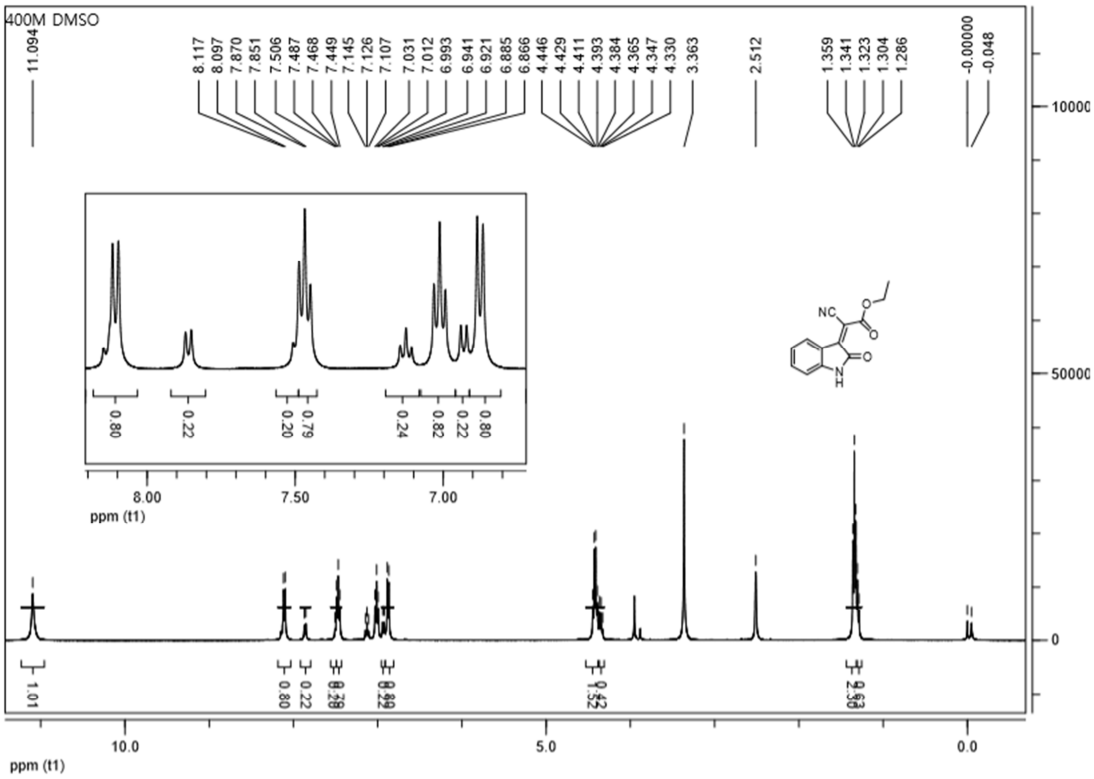


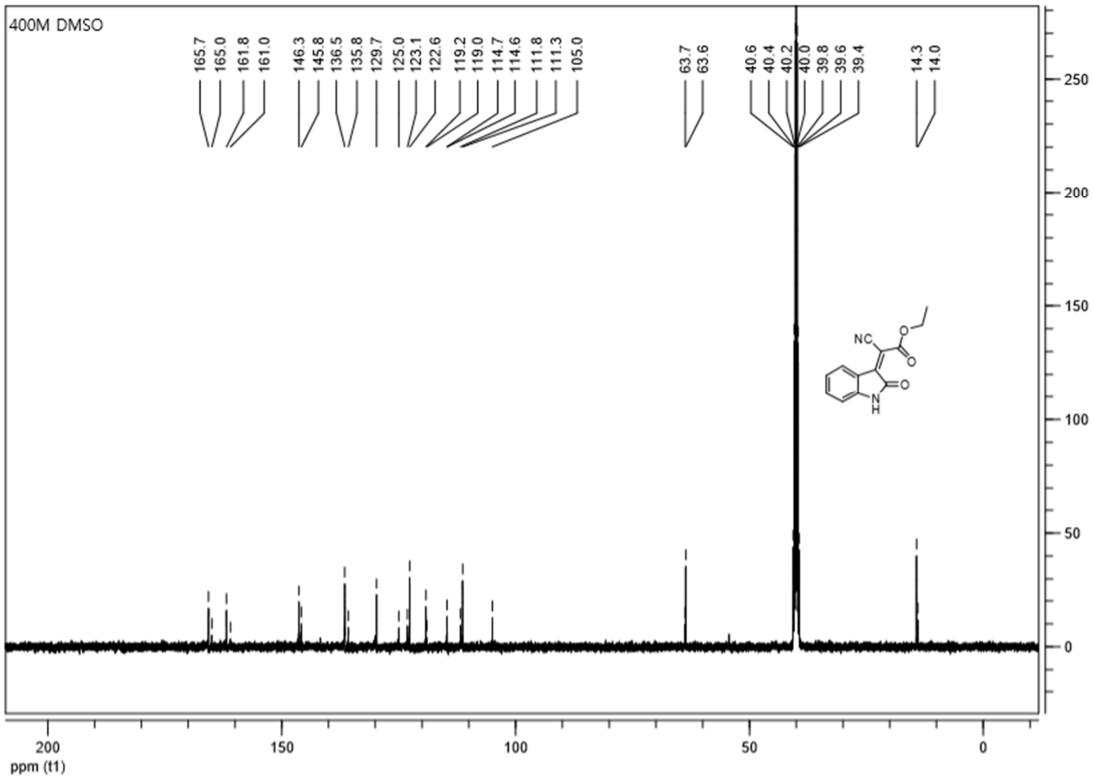
(Z)-3-oxo-2-(2-oxo-1-phenylindolin-3-ylidene)-3-phenylpropanenitrile (3x)



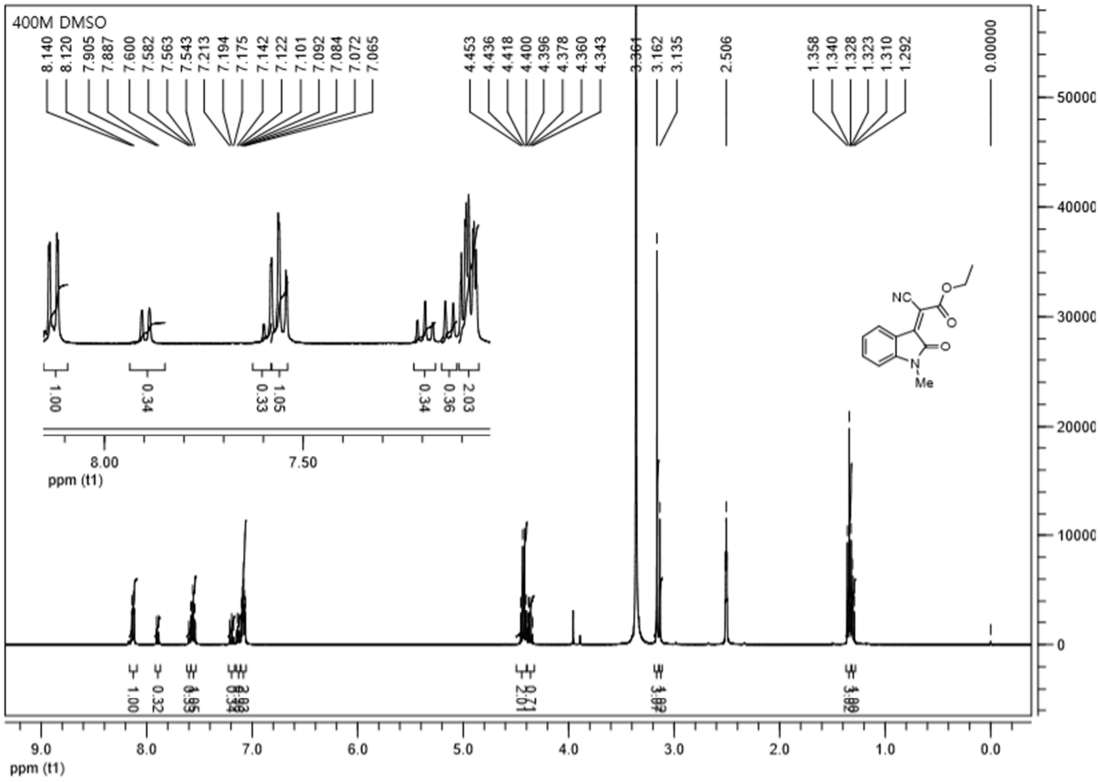


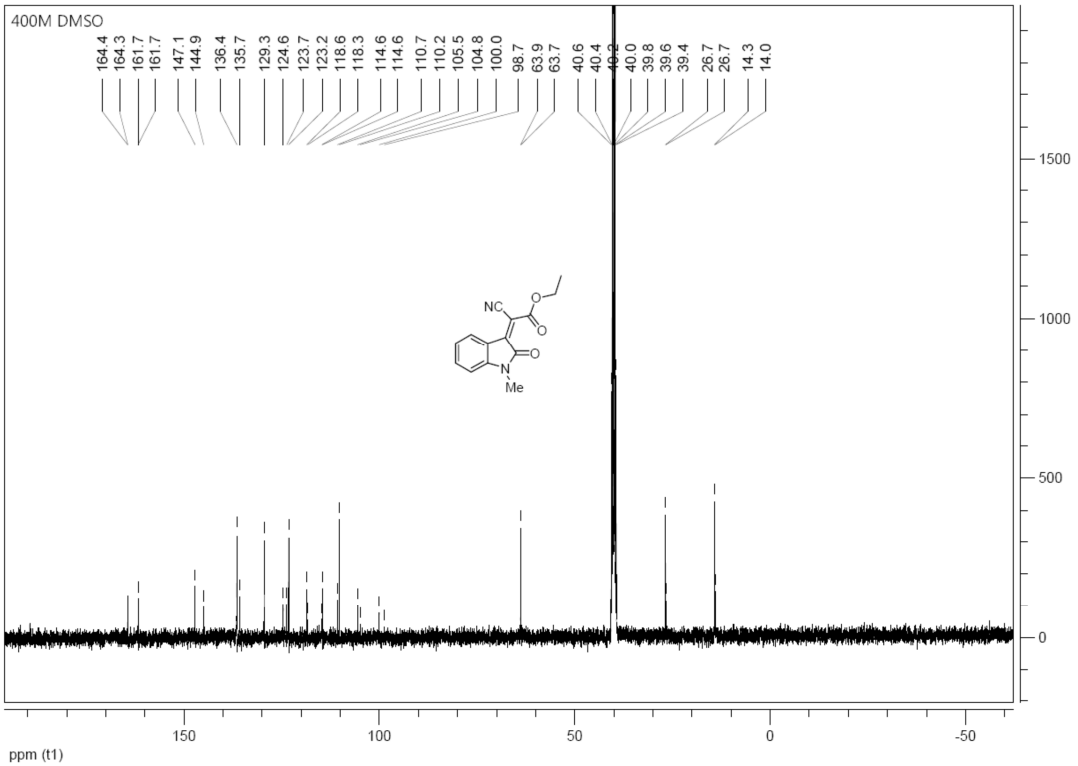
Ethyl (Z)-2-cyano-2-(2-oxoindolin-3-ylidene)acetate (3y)



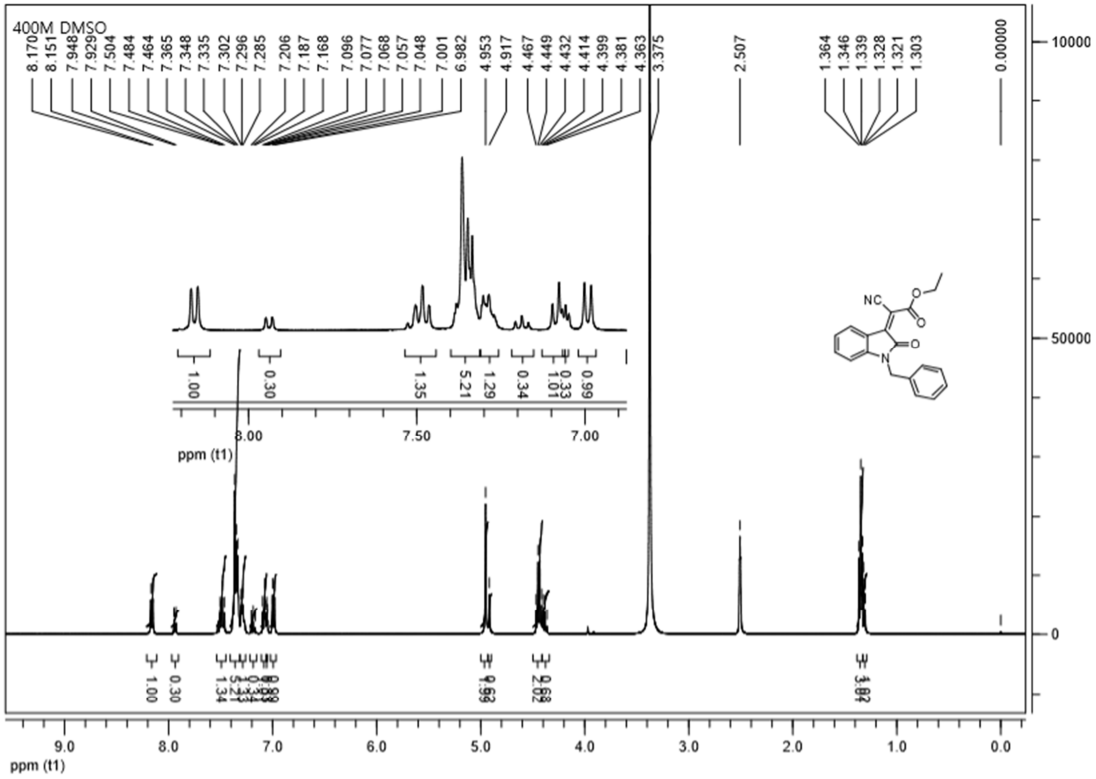


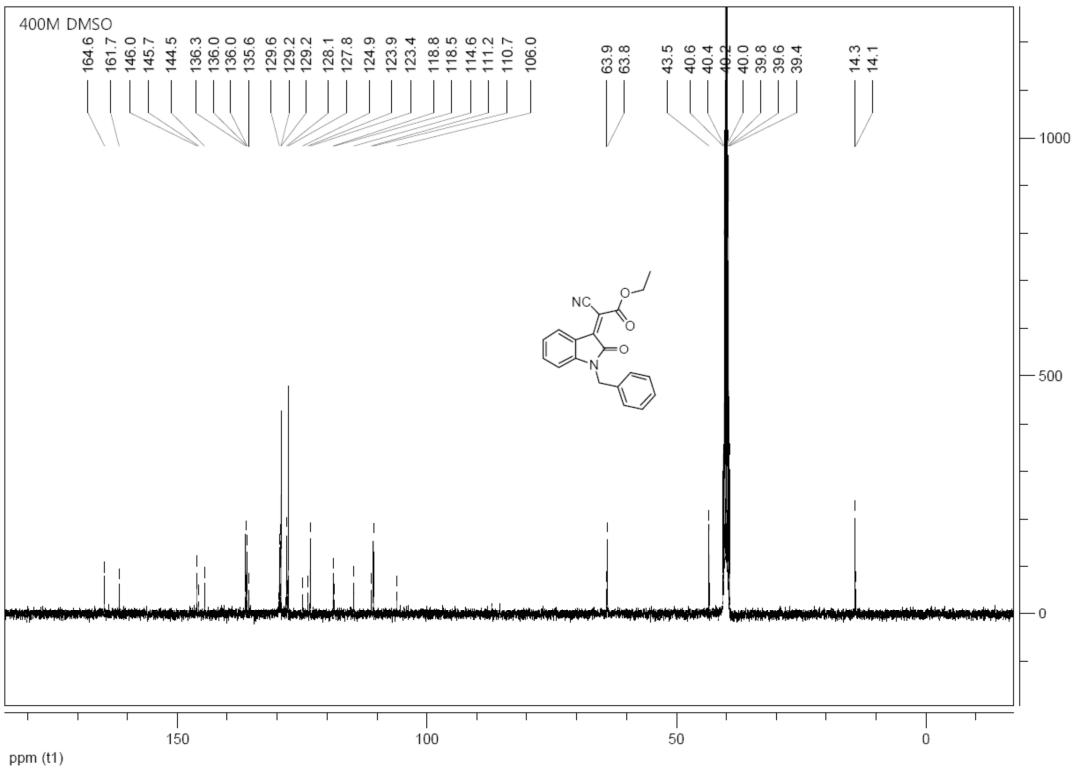
Ethyl (Z)-2-cyano-2-(1-methyl-2-oxoindolin-3-ylidene)acetate (3z)





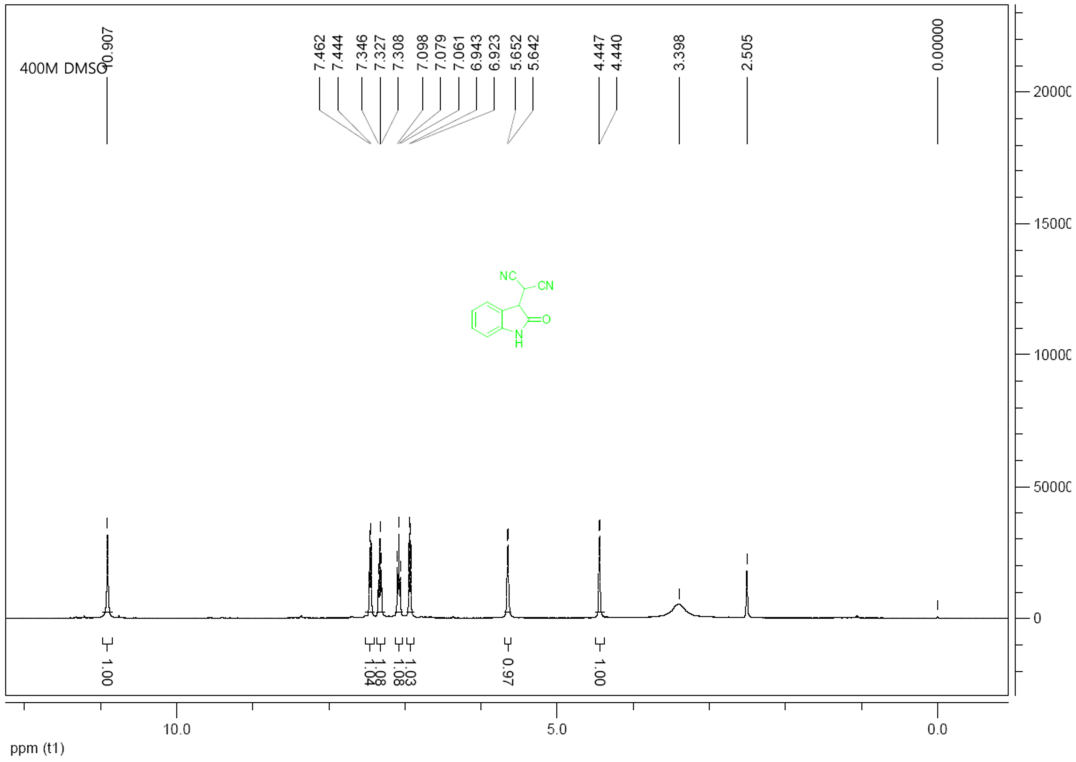
Ethyl (Z)-2-(1-benzyl-2-oxoindolin-3-ylidene)-2-cyanoacetate (3aa)

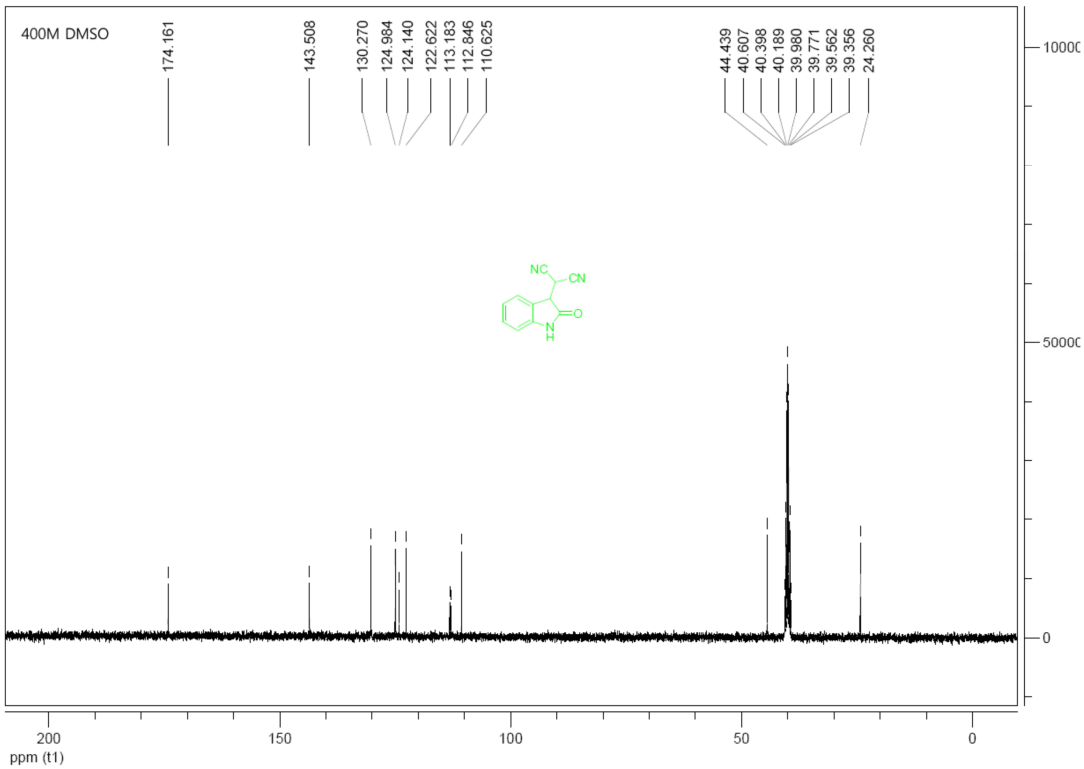




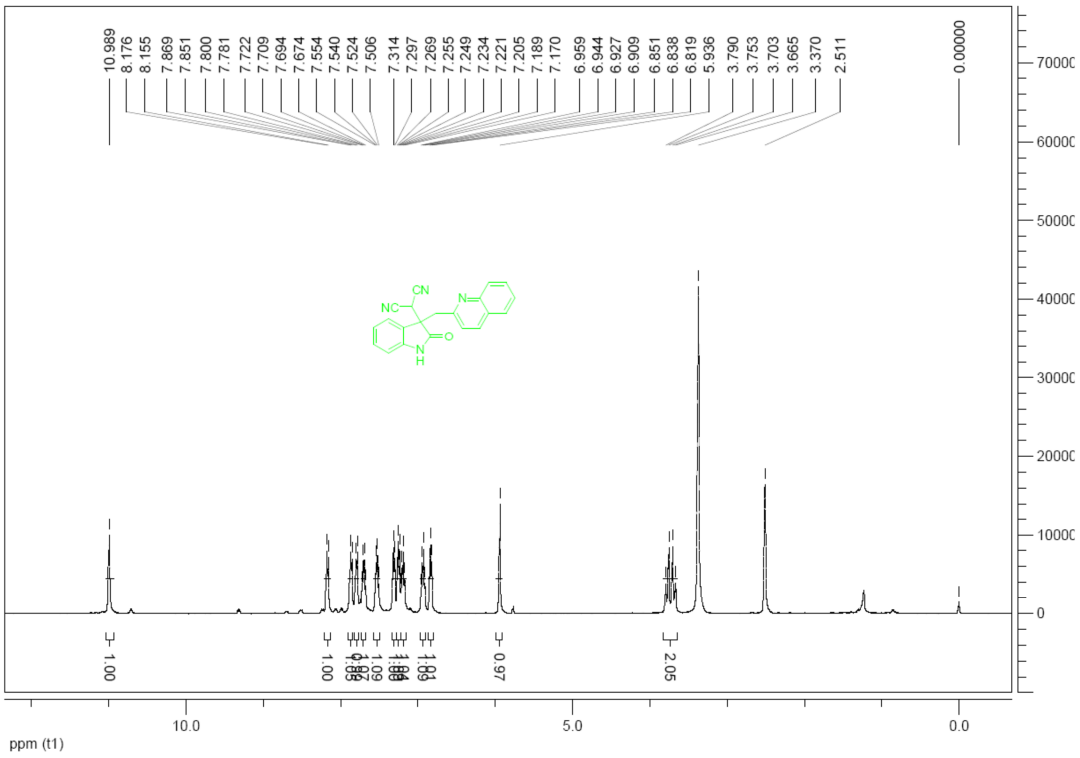
7. Spectroscopic Data for Compounds 4-9

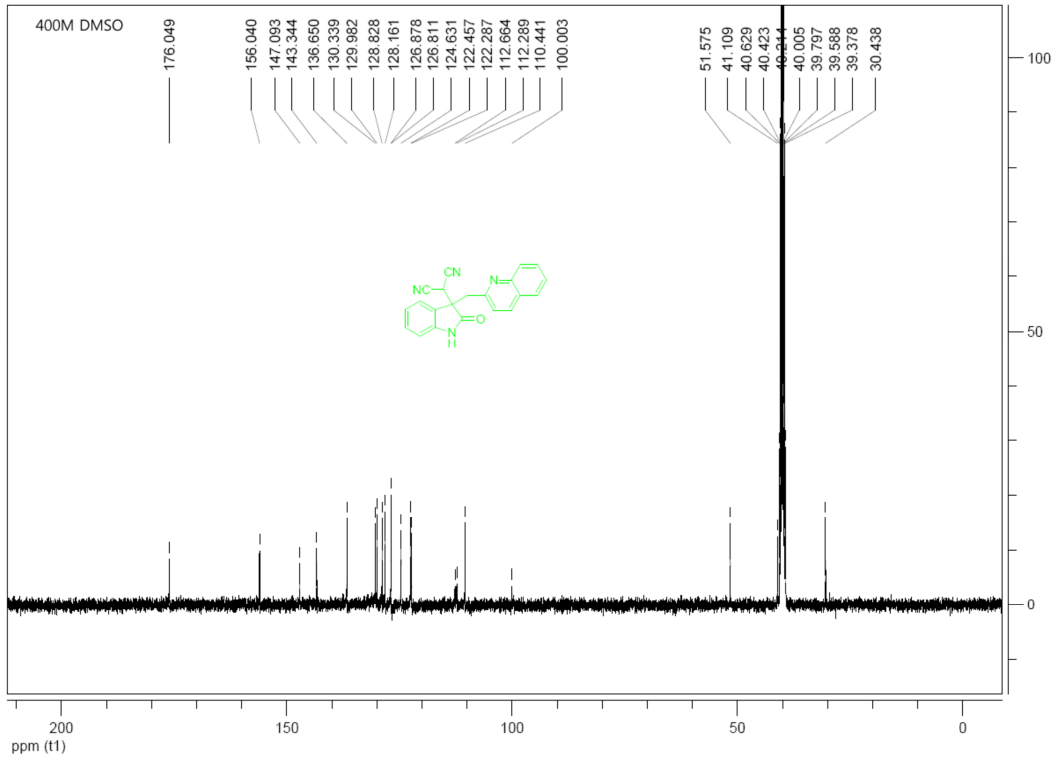
2-(2-oxoindolin-3-yl)malononitrile (4)



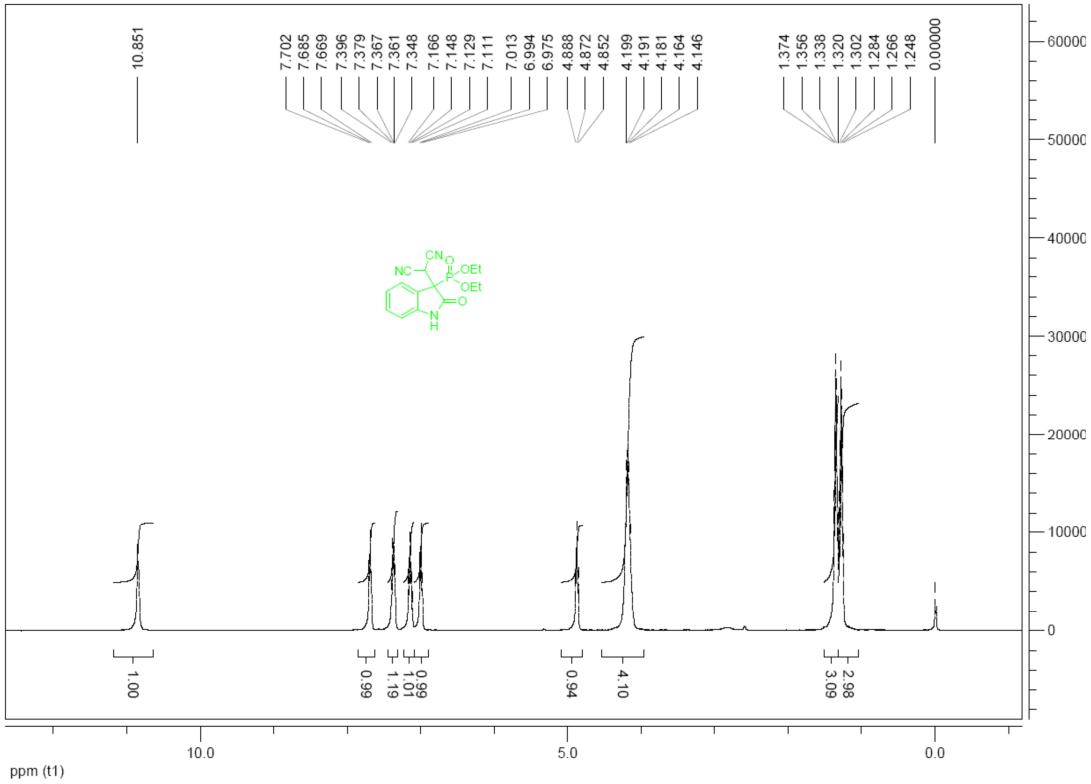


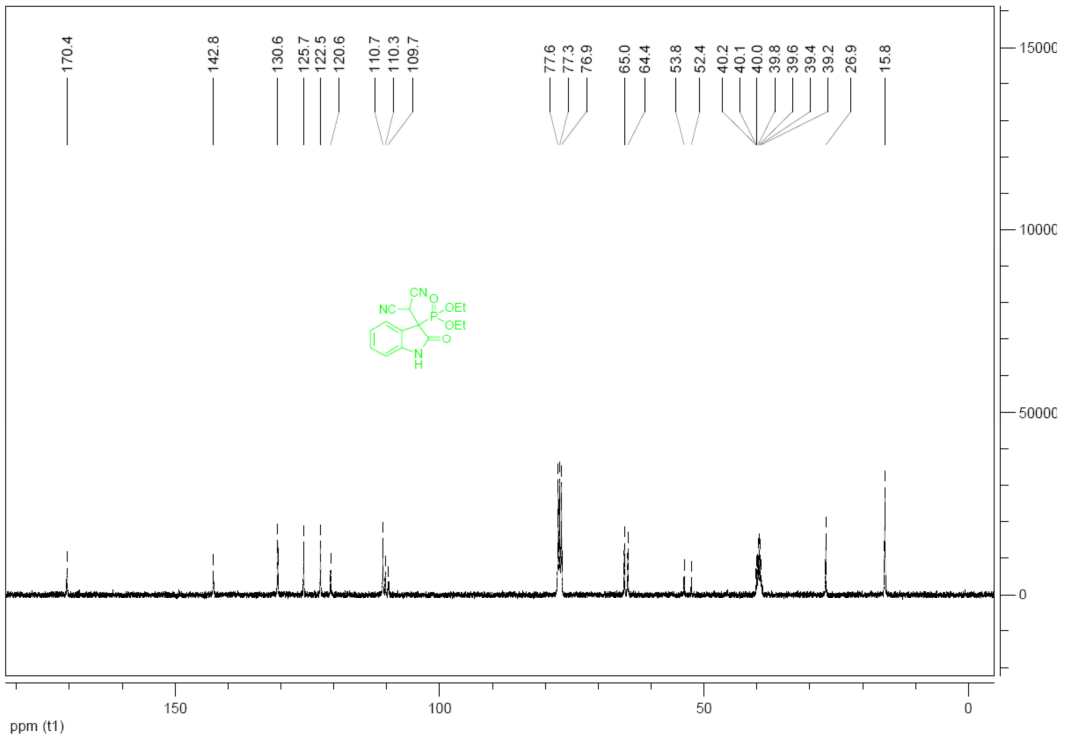
2-(2-oxo-3-(quinolin-2-ylmethyl)indolin-3-yl)malononitrile (5)



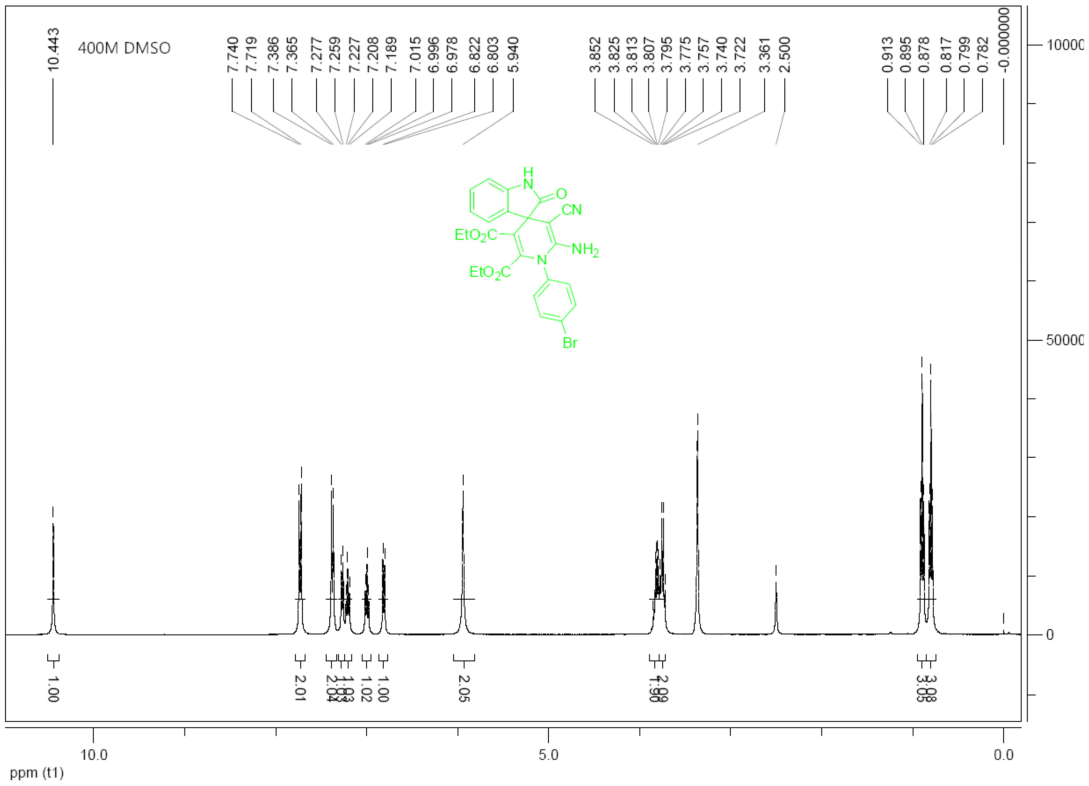


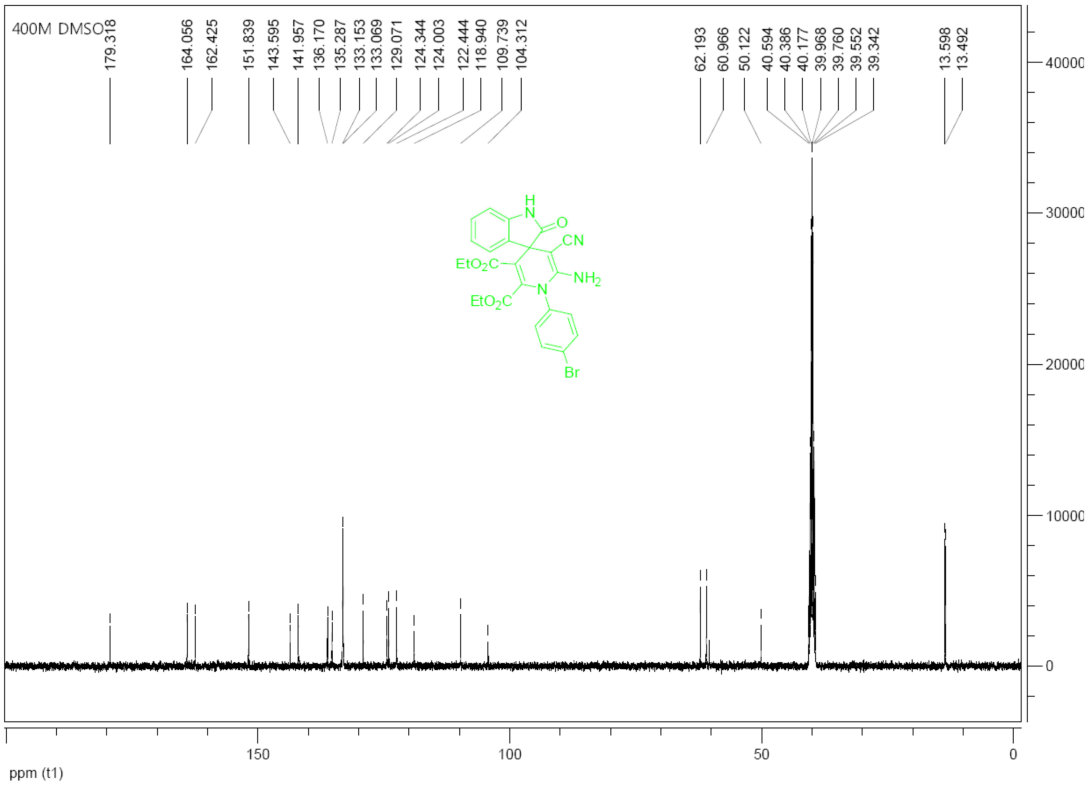
Diethyl (3-(dicyanomethyl)-2-oxoindolin-3-yl)phosphonate(6)



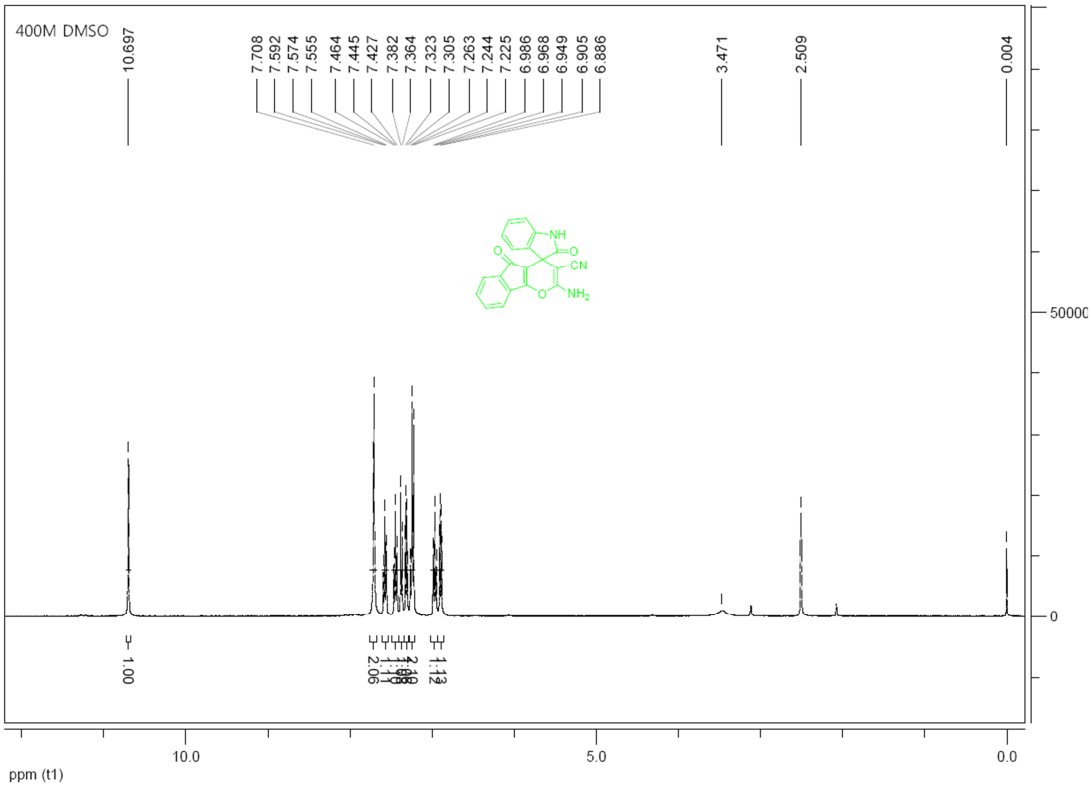


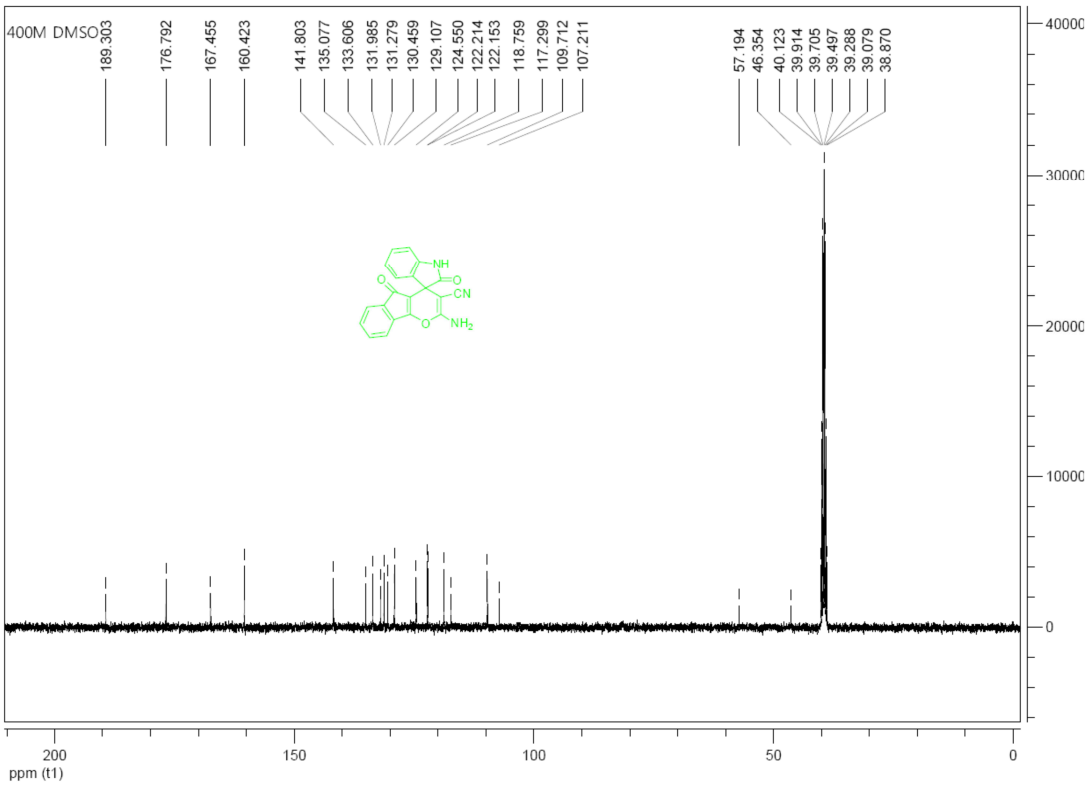
2'-Amino-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarbo xylate (7)





2-Amino-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (8)





4’-Amino-2,2’,3,3”-tetrahydro-1H-indole-3-spiro-1’-cyclopent-3’-ene-2’-spiro-3”-1H-indole-3’,5’,5’-tricarbonitrile (9)