Supporting Information

Vinylogous Propargylation of α,α-dicyanoalkenes Construction of an All-carbon Quaternary Center

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I General Information

All reactions were performed in Schlenk tubes at room temperature using oven-dried glassware. Commercially obtained reagents were used without further purification, unless otherwise noted. THF was obtained from solvent distillation machine (Vigor VSPS-5) and stored under argon over 4 Å molecular sieves. Toluene was freshly distilled before use over sodium and benzophenone. Dichloromethane (DCM) was distilled over CaH_2. Methanol and Ethyl Alcohol were used without further purification. Reactions were monitored by TLC analysis and plates were visualized with short-wave UV light (254 nm). The ^{1}H NMR、^{13}C NMR and ^{19}F NMR spectra were obtained in $CDCl_3$ using a Bruker-BioSpin AVANCE III HD NMR spectrometer at 400 MHz, 100 MHz and 376 MHz respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. HPLC analyses of the compounds were done using chiralcel IA-IF columns and chiralcel AD-H, AS-H, OJ-H and OD-H columns using hexane and isopropanol as eluent. High-resolution mass spectra were recorded on a Bruker Impact II UHR TOF LC/MS Mass Spectrometry.

II Optimization of Reaction Conditions

Table 1. Optimization of the Reaction Conditions[a]

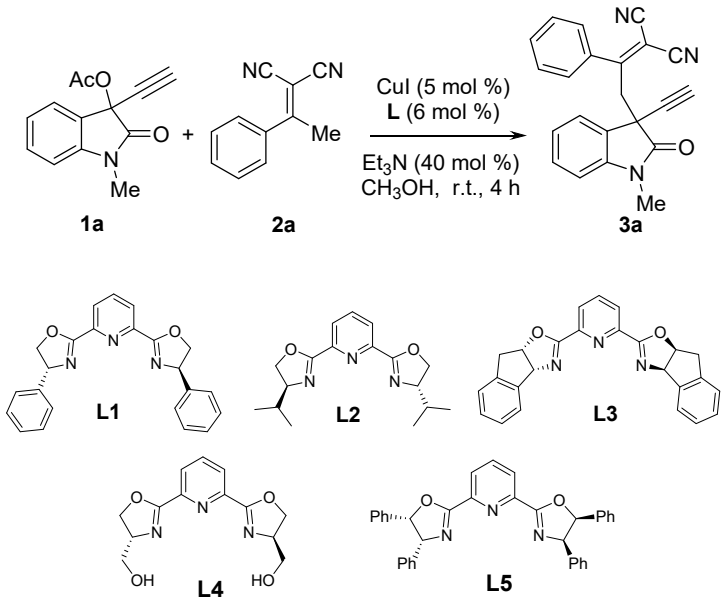


Table S1: Ligand screening

entry	Cat.	Base	M	Solvent	T(℃)	t(h)	Yield(%)[b]	Ee(%)[c]
1	/	Et_3N	L1	CH_3OH	rt	4	n.r.	/
2	CuI	Et_3N	/	CH_3OH	rt	4	n.r.	/
3	**CuI**	**Et_3N**	**L1**	**CH_3OH**	**rt**	**4**	**74%**	**0**
4	CuI	Et_3N	L2	CH_3OH	rt	4	36%	0
5	CuI	Et_3N	L3	CH_3OH	rt	4	27%	0
6	CuI	Et_3N	L4	CH_3OH	0	12	26%	10%
7	CuI	Et_3N	L5	CH_3OH	-20	12	54%	20%

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), N_2 atmosphere, CuI (5 mol%), L (6 mol%), Et_3N (0.08 mmol), CH_3OH (1 mL), rt = room temperature. [b]isolated yield. n.r. = no reaction.[c] Determined by chiral HPLC analysis.

Table S2: Lewis acid screening

entry	Cat.	Base	M	Solvent	t (h)	Yield(%)[b]
1	**CuI**	**Et_3N**	**L1**	**CH_3OH**	**4**	**74%**
2	Cu $(CH_3CN)_4PF_6$	Et_3N	L1	CH_3OH	4	72%
3	Cu $(OTf)_2$	Et_3N	L1	CH_3OH	4	37%
4	Cu $(OAc)_2$	Et_3N	L1	CH_3OH	4	20%
5	Cu $(CH_3CN)_4BF_4$	Et_3N	L1	CH_3OH	4	27%
6	$C_5H_3CuO_2S$	Et_3N	L1	CH_3OH	4	73%

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), N_2 atmosphere, M (5 mol%), L1 (6 mol%), base (0.08 mmol), CH_3OH (1 mL), T = rt. [b]isolated yield.

Table S3: Solvent screening

entry	Cat.	Base	M	Solvent	t (h)	Yield(%)[b]
1	**CuI**	**Et_3N**	**L1**	**CH_3OH**	**4**	**74%**
2	CuI	Et_3N	L1	CH_3CH_2OH	4	72%
3	CuI	Et_3N	L1	CH_3Cl_2	4	8%
4	CuI	Et_3N	L1	Toluene	4	trace
5	CuI	Et_3N	L1	THF	4	trace

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), N_2 atmosphere, CuI (5 mol%), L1 (6 mol%), Et_3N (0.08 mmol), Solvent (1 mL), T = rt. [b]isolated yield.

Table S4: base screening

entry	Cat.	Base	M	Solvent	t (h)	Yield(%)[b]
1	**CuI**	**Et_3N**	**L1**	**CH_3OH**	**4**	**74%**
2	CuI	DIPEA	L1	CH_3OH	4	74%
3	CuI	Na_2CO_3	L1	CH_3OH	4	50%
4	CuI	K_2CO_3	L1	CH_3OH	4	71%
5	CuI	Cs_2CO_3	L1	CH_3OH	4	33%
6	CuI	/	L1	CH_3OH	4	/

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), N_2 atmosphere, CuI (5 mol%), L1 (6 mol%), base (0.08 mmol), CH_3OH (1 mL), T = rt. [b]isolated yield.

Table S5: base screening and **1a**:**2a**

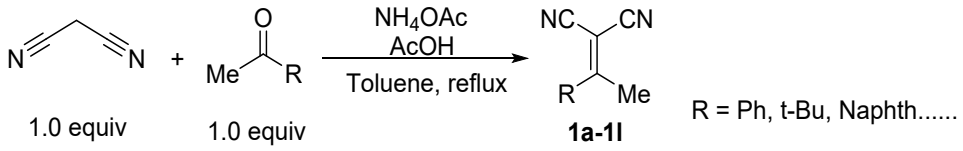
entry	Cat.	Base	M	Solvent	1a:2a (mol)	t (h)	Yield(%)[b]
1	CuI	Et_3N (0.2 equiv)	L1	CH_3OH	1:1.2	4	74%
2	CuI	Et_3N (0.4 equiv)	L1	CH_3OH	1:1.2	4	75%
3	CuI	Et_3N (1.0 equiv)	L1	CH_3OH	1:1.2	4	78%
4	CuI	Et_3N (1.5 equiv)	L1	CH_3OH	1:1.2	4	82%
5	CuI	Et_3N (2.0 equiv)	L1	CH_3OH	1:1.2	4	63%
6	CuI	Et_3N (1.5 equiv)	L1	CH_3OH	1:1.0	4	71%
7	CuI	Et_3N (1.5 equiv)	L1	CH_3OH	1.5:1	4	83%
8	**CuI**	**Et_3N (1.5 equiv)**	L1	**CH_3OH**	**1:1.5**	**4**	**89%**

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (x mmol), N_2 atmosphere, CuI (5 mol%), L1 (6 mol%), Et_3N (x mmol), CH_3OH (1 mL), T = rt. [b]isolated yield.

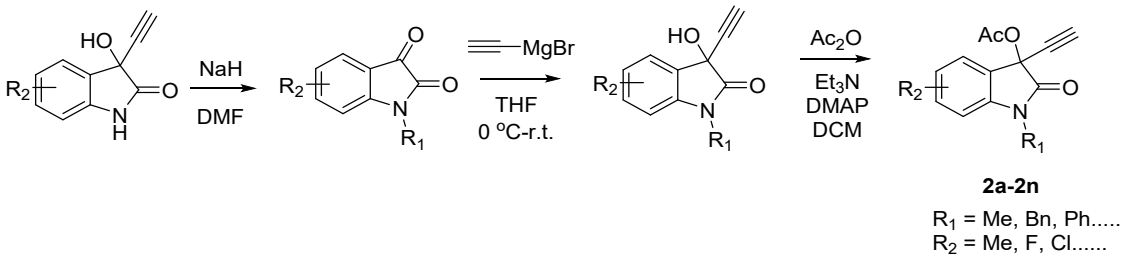
III Experimental Section

Tertiary Propargylic Esters and *α, α*-dicyanoalkenes were synthesized according to reported procedures.[1-8]

General procedure for the two raw materials of the template reaction



Malonitrile(48.0 mmol), ethylketone (48.0 mmol) acetate and NH_4OAc(48.0 mmol) were added to 250 mL round bottled flask, and then 30 mL toluene was added as solvent to dissolve them completely. Then, 3 mL of anhydrous acetic acid was added to the dissolved mixture at room temperature and then connect the reflux water distributor. The reaction mixture is reflux for 12 hours until the water separator stops producing water, or the raw malonitrile is detected by thin layer chromatography. After the reaction is complete, the mixture is transferred and cooled to room temperature. The resulting reaction solution was diluted with 50 mL toluene. The reaction mixture was washed with 350 mL saturated sodium bicarbonate solution, and then washed twice with 50 mL saturated NaCl. The treated organic phase was further dried with anhydrous magnesium sulfate, and **1a** was obtained by concentrating under reduced pressure and evaporating the solvent. The crude product was recrystallized in ethanol solution to obtain pure target product. Following the same steps and selecting different substituents of ethylketone, the crude products **1a-1l** of dicyanolefin substrates with different substituents can be obtained.[1]



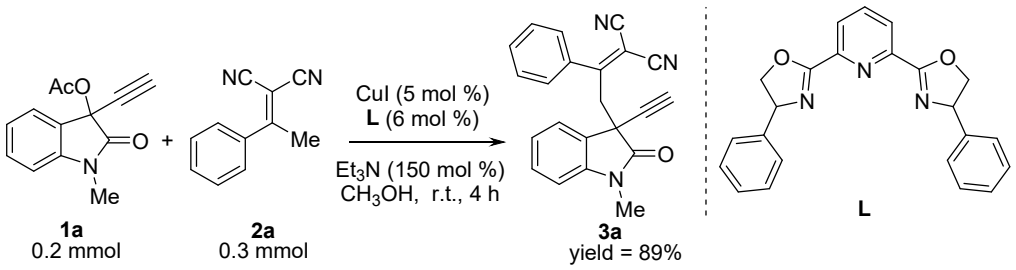
Sodium hydride (60% dispersed in mineral oil, 0.84 g, 21 mmo1) was dissolved in isatin (2.94 g, 20 mmo1) solution of 100 mL anhydrous DMF at 0 °C and stirred for 15 minutes. Add benzyl bromide (2.61 mL, 22 mmo1) or other halide within 20 minutes,

reaction and stir for 30 minutes. Add 100 mL of water, filter the orange sediment, and wash with 200 mL of water. Then, the resulting orange precipitate is dissolved with 100 mL dichloromethane and washed with 100 mL salt water to remove the impurities dissolved in the water phase. The organic layer was separated and the resulting organic phase was dried with anhydrous magnesium sulfate and concentrated under vacuum to obtain an orange-yellow solid (4.55 g, 19.2 mmol) with yield of 96%.

Dissolved 10 mmol 1-benzyl indole in 10 mL tetrahydrofuran, cooled to 0 °C in nitrogen atmosphere and ice water bath, then slowly added 40 mL acetylidene magnesium bromide (20 mmo1, 0.5 M THF), stirring at 0 °C for 10 min. Bring to room temperature and stir in nitrogen overnight. 10 mL NH_4Cl_2 saturated solution was added to quench the reaction mixture. Extracted with ethyl acetate, the combined organic phase was washed with 20 mL saturated NaCl and water. Dry with anhydrous sodium sulfate and concentrate under reduced pressure. The crude product is used directly for further production without further purification [2].

Dissolve the crude product obtained in the previous step, Et_3N (2.7 mL, 20 mmol.) and DMAP (12.1 mg, 0.1 mmol) in DCM (20 mL). The mixture was then cooled to 0 °C and slowly added Ac_2O (2.0 mL, 20 mmol). The mixture was then heated to room temperature and stirred for 1 hour, after which the reaction was quenched with 5 mL saturated NH_4Cl_2 solution. The organic phase in the reaction mixture is extracted by dichloromethane (2×10 mL), and anhydrous Na_2SO_4 can be used for the organic phase after dry extraction and concentration under reduced pressure. The concentrated mixture was purified by silica gel column (PE/EA = 5/1) to obtain a relatively clean tertiary propargyl ester solid compound **2a-2n** with different substituents.

General procedure for propargyl substitution reaction catalyzed by copper based on oxindoles

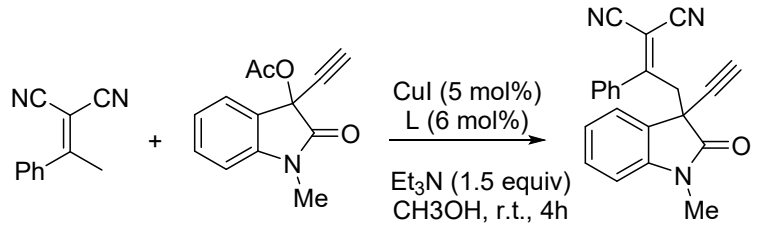


1a 0.2 mmol **2a** 0.3 mmol **3a** yield = 89%

CuI (1.9 mg, 0.010 mmol) and L (4.4 mg, 0.012 mmol) were stirred at room temperature in 1 mL of anhydrous methanol under nitrogen atmosphere for 0.5 h. Then,a solution of 3-ethynyl-2-oxoindolin-3-yl acetate (**1a**, 0.2 mmol) and *α, α*-dicyanoalkene (**2a**, 0.3

mmol) and Et_3N (30.3 mg, 0.3 mmol) in 1 mL of anhydrous methanol was added dropwisely. The mixture was stirred at room temperature for 4 h, concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc = 5/1-2:1) to afford **3a** (Brown solid, 89% yield).

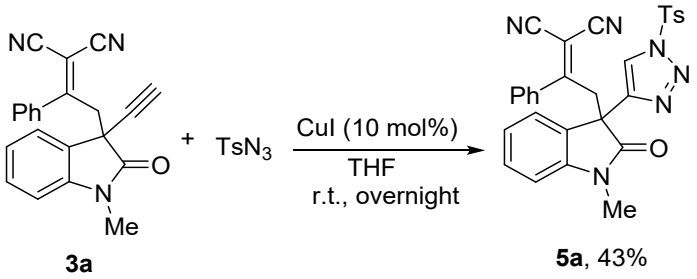
General procedure for gram-scale experiment



1a, 1.260 g **2a**, 1.145 g **3a,** 1.499g, 89%

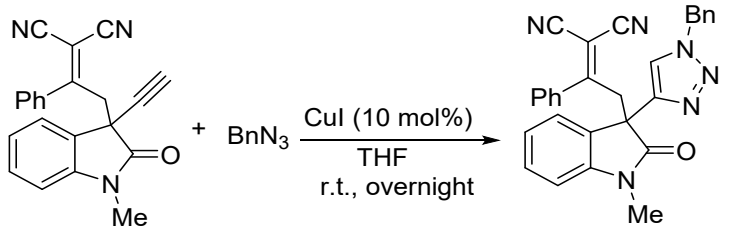
CuI (47.6 mg, 0.25 mmol) and **L** (110.7 mg, 0.30 mmol) were stirred at room temperature in 20 mL of anhydrous methanol under nitrogen atmosphere for 0.5 h. Then,a solution of 3-ethynyl-2-oxoindolin-3-yl acetate (**1a**, 1.145 g, 5.0 mmol) and *α, α*-dicyanoalkene (**2a**, 1.260 g, 7.5 mmol) and Et_3N (0.76 g, 7.5 mmol) in 30 mL of anhydrous methanol was added dropwisely. The mixture was stirred at room temperature for 4 h, concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc = 5/1-2:1) to afford **3a** (Brown solid, 1.499 g, 89% yield).

General procedure for synthetic transformation of the Alkyne propylation product 3a



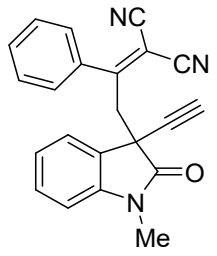
3a **5a**, 43%

A 25 mL Pressure tube was charged with **3a** (0.2 mmol), benzylazide (0.3 mmol), and CuI (0.3 mmol) in ethanol (2 mL, 1.0 M solution). The reaction was stirred at room temperature for 12 h, concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc = 5/1-2:1) to afford **5a** (Brown oil, 51% yield).



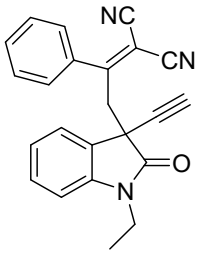
3a **6a**, 43%

A 25 mL Pressure tube was charged with **3a** (0.2 mmol),tosylazide (0.3 mmol), and CuI (0.3 mmol) in ethanol (2 mL, 1.0 M solution). The reaction was stirred at room temperature for 12 h, concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc = 5/1-2:1) to afford **6a** (Brown oil, 43% yield).



3a

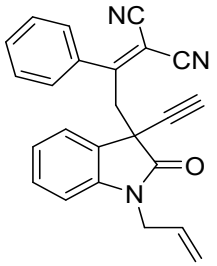
2-(2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)-1-phenylethylidene)malononitrile: Brown solid, 60 mg, 89% yield, mp = 135-137 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.43-7.35 (m, 2H), 7.34-7.27 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 1H), 3.79 (d, *J* = 2.4 Hz, 2H), 2.57 (s, 3H), 2.23 (s, 1H).**^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 173.4, 172.2, 142.7, 132.6, 132.4, 130.1, 128.5, 128.2, 127.0, 124.2, 123.7, 112.4, 112.1, 108.8, 88.4, 79.7, 73.2, 46.2, 43.9, 26.3. **HRMS (ESI, m/z)** calcd for $C_{22}H_{15}N_3OH^+$ [M+H]+ : 338.1284, found: 338.1288.



3b

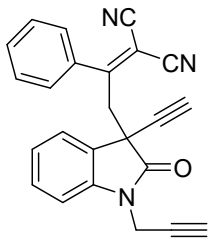
2-(2-(1-ethyl-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene)malononitrile: Brown oil, 62 mg, 89% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.44-7.37 (m, 1H),

7.35 (d, *J* = 7.2 Hz, 1H), 7.33-7.25 (m, 3H), 7.13-7.03 (m, 3H), 3.74 (s, 2H), 3.23 (dt, *J* = 14.2, 7.0 Hz, 1H), 3.05 (dt, *J* = 14.2, 7.0 Hz, 1H), 2.17 (s, 1H), 0.95 (t, *J* = 6.8 Hz, 3H).**^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 173.5, 171.8, 141.8, 132.9, 132.4, 130.0, 128.5, 128.3, 127.4, 124.3, 123.4, 112.4, 112.2, 109.0, 88.4, 79.7, 73.3, 46.3, 43.9, 35.2, 26.9, 12.3. **HRMS (ESI, m/z)** calcd for $C_{23}H_{17}N_3OH^+$ $[M+H]^+$: 352.1439, found: 352.1444.



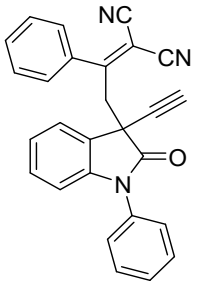
3c

2-(2-(1-allyl-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene)malononitrile: Brown oil, 66 mg, 91% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.55-7.48 (m, 1H), 7.46-7.32 (m, 4H), 7.22-7.13 (m, 3H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.24-5.10 (m, 2H), 4.01-3.91 (m, 1H), 3.85 (s, 2H), 3.77 (d, *J* = 33.6 Hz, 1H), 3.58 (dd, *J* = 16.2, 5.0 Hz, 1H), 2.27 (d, *J* = 1.2 Hz, 1H).**^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 173.4, 171.9, 141.9, 132.9, 132.4, 130.5, 129.9, 128.5, 128.3, 127.2, 124.2, 123.6, 118.1, 112.4, 112.1, 109.7, 88.5, 79.6, 73.4, 46.2, 43.9, 42.6, 26.9. **HRMS (ESI, m/z)** calcd for $C_{24}H_{17}N_3OH^+$ $[M+H]^+$: 364.1437, found: 364.1444.



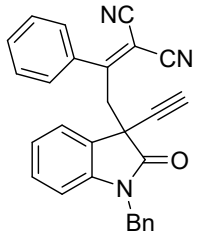
3d

2-(2-(3-ethynyl-2-oxo-1-(prop-2-yn-1-yl)indolin-3-yl)-1-phenylethylidene) malononitrile: Brown solid, 64 mg, 89% yield, mp = 66-68 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 (dt, *J* = 15.9, 7.8 Hz, 4H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.09 (d, *J* = 17.8 Hz, 1H), 3.77 (s, 2H), 3.57 (d, *J* = 17.8 Hz, 1H), 2.19 (d, *J* = 35.2 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.9, 171.2, 140.8, 132.8, 132.4, 130.1, 128.6, 128.2, 126.8, 124.3, 124.0, 112.3, 112.1, 109.9, 88.6, 79.3, 75.8, 73.7, 73.2, 46.3, 44.0, 29.6. **HRMS (ESI, m/z)** calcd for $C_{24}H_{15}N_3OH^+$ $[M+H]^+$: 362.1281, found: 362.1288.



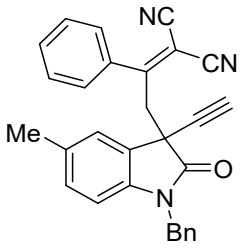
3e

2-(2-(3-ethynyl-2-oxo-1-phenylindolin-3-yl)-1-phenylethylidene)malononitrile: White solid, 71 mg, 89% yield, mp = 140-143 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**:δ = 7.46-7.39 (m, 2H), 7.37-7.27 (m, 5H), 7.25-7.19 (m, 5H), 7.18-7.12 (m, 3H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 3.85 (dd, *J* = 14.0 Hz, 26.4Hz, 2H), 2.19 (s, 1H).**^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 173.4, 171.5, 142.6, 133.3, 133.2, 132.5, 129.9, 129.4, 128.9, 128.4, 127.2, 126.0, 124.4, 124.1, 112.6, 112.2, 110.3, 88.8, 79.7, 73.7, 46.6, 44.1. **HRMS (ESI, m/z)** calcd for $C_{27}H_{17}N_3OH^+$ $[M+H]^+$: 400.1441, found: 400.1444.



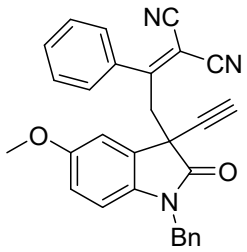
3f

2-(2-(1-benzyl-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene)malononitrile: Brown oil, 74 mg, 90% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.47-7.40 (m, 1H), 7.32 (t, *J* = 8.0 Hz, 3H), 7.24-7.19 (m, 2H), 7.18-7.13 (m, 2H), 7.11-7.02 (m, 5H), 4.56 (d, *J* = 16.0 Hz, 1H), 3.88 (d, *J* = 15.6 Hz, 1H), 3.78 (s, 2H), 2.20 (s, 1H).**^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.4, 172.4, 141.8, 134.7, 133.0, 132.4, 129.9, 128.9, 128.5, 128.4, 127.9, 127.2, 127.1, 124.2, 123.6, 112.4, 112.2, 109.9, 88.5, 79.5, 73.6, 46.2, 44.0, 43.9, 26.9. **HRMS (ESI, m/z)** calcd for $C_{28}H_{19}N_3OH^+$ $[M+H]^+$: 414.1595, found: 414.1601.



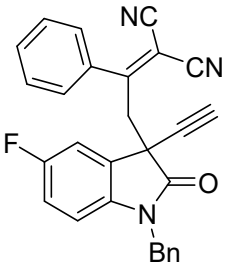
3g

3-(2-(1-benzyl-3-ethynyl-5-methyl-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: Brown oil, 77 mg, 90% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.43 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.23-7.18 (m, 2H), 7.17-7.13 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 5H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 16.0 Hz, 1H), 3.90 (d, *J* = 16.0 Hz, 1H), 3.81-3.69 (m, 2H), 2.26 (s, 3H), 2.22 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.4, 172.2, 139.3, 134.9, 133.4, 133.2, 132.3, 130.2, 128.9, 128.5, 128.3, 127.8, 127.2, 127.2, 125.0, 112.4, 112.2, 109.6, 88.5, 79.7, 73.5, 46.4, 44.2, 43.9, 21.1. **HRMS (ESI, m/z)** calcd for $C_{29}H_{21}N_3OH^+$ $[M+H]^+$: 428.1754, found: 428.1757.



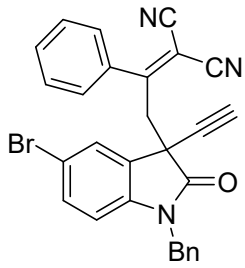
3h

2-(2-(1-benzyl-3-ethynyl-5-methoxy-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: Yellow solid, 73 mg, 83% yield, mp = 47-49 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**:δ = 7.44 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.22-7.16(m, 3H), 7.11-7.03 (m, 4H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.40 (d, *J* = 8.4 Hz, 1H), 4.51 (d, *J* = 15.6 Hz, 1H), 3.85-3.76 (m, 3H), 3.74 (s, 3H), 2.24 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.4, 172.0, 156.5, 134.9, 134.8, 133.0, 132.4, 128.9, 128.5, 128.3, 128.2, 127.9, 127.1, 115.3, 112.5, 112.2, 110.5, 110.5, 88.5, 79.6, 73.7, 55.9, 46.7, 44.0, 43.9. **HRMS (ESI, m/z)** calcd for $C_{29}H_{21}N_3O_2H^+$ $[M+H]^+$: 444.1700, found: 444.1706.



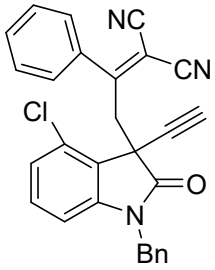
3i

2-(2-(1-benzyl-3-ethynyl-5-fluoro-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: Yellow oil, 74 mg, 86% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.44 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26-7.19 (m, 3H), 7.14-7.07 (m, 4H), 6.99 (dd, *J* = 7.4, 2.4 Hz, 1H), 6.85 (td, *J* = 8.8, 2.4 Hz, 1H), 6.44 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.60 (d, *J* = 15.6 Hz, 1H), 4.02 (d, *J* = 15.6 Hz, 1H), 3.76-3.70 (m, 2H), 2.21 (s, 1H).**^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.7, 172.1, 160.6, 158.1, 134.5, 133.1, 132.5, 129.0, 128.6, 128.3, 128.1, 127.2, 116.6, 116.3, 112.5, 112.3, 112.2, 112.1, 110.6, 110.6, 88.8, 78.7, 74.2, 54.9, 46.5, 44.2, 44.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -117.95. **HRMS (ESI, m/z)** calcd for $C_{28}H_{18}FN_3OH^+$ $[M+H]^+$: 432.1500, found: 432.1506.



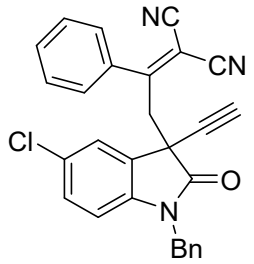
3j

2-(2-(1-benzyl-5-bromo-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: Yellow solid, 83 mg, 85% yield, mp = 134-136 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.44 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.29-7.19 (m, 5H), 7.11 (t, *J* = 7.2 Hz, 4H), 6.41 (d, *J* = 8.4 Hz, 1H), 4.60 (d, *J* = 15.6 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 3.78-3.64 (m, 2H), 2.22 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.5, 171.8, 140.7, 134.3, 133.3, 132.7, 132.5, 129.3, 129.0, 128.7, 128.3, 128.2, 127.5, 127.2, 116.1, 112.2, 112.1, 111.2, 88.8, 78.5, 74.4, 46.3, 44.2, 44.1. **HRMS (ESI, m/z)** calcd for $C_{28}H_{18}BrN_3O$ $[M+H]^+$: 492.0700, found: 492.0706.



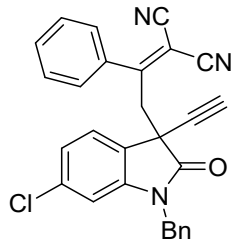
3k

3-(2-(1-benzyl-4-chloro-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: Brown oil, 83 mg, 93% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.42 (t, *J* = 7.2 Hz, 1H), 7.38-7.29 (m, 4H), 7.28-7.22 (m, 3H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.04 (m, J = 7.2 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 4.77 (d, *J* = 15.6 Hz, 1H), 4.23-3.98 (m, 3H), 2.31 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.0, 171.9, 143.5, 134.5, 132.9, 131.8, 131.4, 130.8, 129.1, 128.3, 128.2, 127.9, 127.4, 124.2, 124.1, 112.2, 112.1, 108.1, 88.8, 73.7, 46.2, 44.4, 41.4. **HRMS (ESI, m/z)** calcd for $C_{28}H_{18}ClN_3OH^+$ $[M+H]^+$: 448.1206, found: 448.1211.



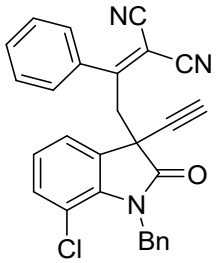
3l

2-(2-(1-benzyl-5-chloro-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: White solid, 78 mg, 87% yield, mp = 160-162 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.54 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37-7.25 (m, 5H), 7.24-7.21 (m, 2H), 7.20-7.17 (m, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 4.70 (d, *J* = 15.6 Hz, 1H), 4.21 (d, *J* = 15.6 Hz, 1H), 3.88-3.78 (m, 2H), 2.31 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.5, 171.9, 140.2, 134.4, 133.3, 132.5, 129.8, 129.0, 128.9, 128.6, 128.3, 128.1, 127.2, 124.8, 112.2, 112.1, 110.8, 88.8, 78.6, 74.4, 46.3, 44.2, 44.1. **HRMS (ESI, m/z)** calcd for $C_{28}H_{18}ClN_3OH^+$ $[M+H]^+$: 448.1205, found: 448.1211.



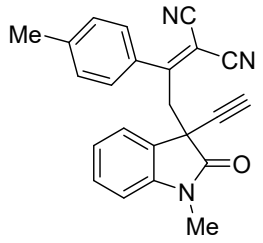
3m

2-(2-(1-benzyl-6-chloro-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: Brown oil, 81 mg, 91% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.55 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36-7.30 (m, 3H), 7.29-7.27 (m, 1H), 7.18 (d, *J* = 7.2 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.61 (s, 1H), 4.63 (d, *J* = 15.6 Hz, 1H), 3.99 (d, *J* = 15.6 Hz, 1H), 3.89-3.82 (m, 2H), 2.33 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.9, 172.3, 143.0, 135.9, 134.2, 132.9, 132.5, 129.1, 128.7, 128.3, 128.2, 127.1, 125.6, 125.2, 123.6, 112.3, 112.0, 110.4, 88.7, 78.9, 74.0, 54.9, 45.9, 44.1, 43.9. **HRMS (ESI, m/z)** calcd for $C_{28}H_{18}ClN_3OH^+$ $[M+H]^+$: 448.1204, found: 448.1211.



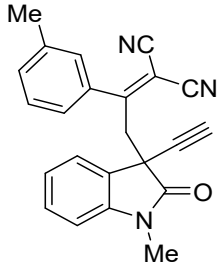
3n

2-(2-(1-benzyl-7-chloro-3-ethynyl-2-oxoindolin-3-yl)-1-phenylethylidene) malononitrile: Brown oil, 77 mg, 86% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.48 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.19-7.12 (m, 4H), 7.08 – 6.98 (m, 5H), 4.61 (dd, *J* = 16.0, 43.6 Hz, 2H), 3.79 (s, 2H), 2.27 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.1, 173.0, 137.9, 136.4, 132.6, 132.6, 132.5, 129.9, 128.6, 128.3, 127.4, 126.3, 124.5, 122.9, 116.2, 112.3, 112.0, 88.6, 79.1, 74.1, 45.9, 44.9, 44.2. **HRMS (ESI, m/z)** calcd for $C_{28}H_{18}ClN_3OH^+$ $[M+H]^+$: 448.1204, found: 448.1211.



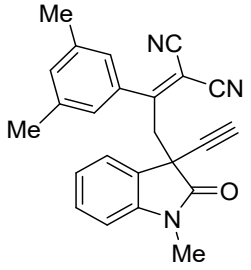
4b

2-(2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)-1-(p-tolyl)ethylidene)malononitrile: Brown solid, 62 mg, 88% yield, mp = 66-69 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.47 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.24-7.15 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 3.87 (dd, *J* = 14.0, 16.8 Hz, 2H), 2.65 (s, 3H), 2.39 (s, 3H), 2.34 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.5, 172.2, 143.4, 142.6, 130.0, 129.7, 129.1, 128.3, 127.0, 124.3, 123.6, 112.6, 112.4, 108.7, 87.5, 79.8, 73.2, 46.3, 43.8, 26.2, 21.5. **HRMS (ESI, m/z)** calcd for $C_{23}H_{17}N_3OH^+$ $[M+H]^+$: 352.1436, found: 352.1444.



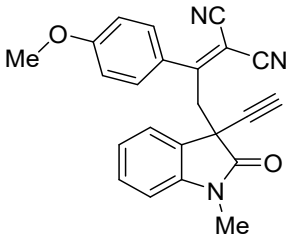
4c

2-(2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)-1-(m-tolyl)ethylidene)malononitrile: Orange solid, 63 mg, 90% yield, mp = 64-66 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.45 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.30-7.18 (m, 3H), 6.85 (d, *J* = 6.8 Hz, 1H), 6.81 (s, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 2H), 2.65 (s, 3H), 2.35 (s, 3H), 2.33 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.8, 172.3, 142.8, 138.4, 133.1, 132.4, 130.0, 128.7, 128.3, 127.0, 125.3, 124.2, 123.6, 112.5, 112.1, 108.6, 88.0, 79.9, 73.1, 46.2, 43.9, 26.2, 21.2. **HRMS (ESI, m/z)** calcd for $C_{23}H_{17}N_3OH^+$ $[M+H]^+$: 352.1440, found: 352.1444.



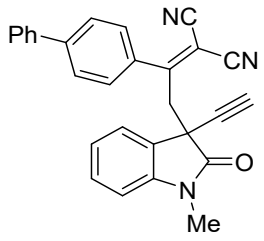
4d

2-(1-(3,5-dimethylphenyl)-2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)ethylidene) malononi-trile: Yellow solid, 62 mg, 85% yield, mp = 99-101 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.46 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 3.87 (dd, *J* = 14.0, 16.4 Hz, 2H), 2.62 (s, 3H), 2.34 (s, 1H), 2.29 (s, 3H), 2.25 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.7, 172.3, 142.8, 142.0, 136.9, 130.0, 129.9, 129.6, 129.3, 127.0, 125.8, 124.3, 123.6, 112.7, 112.4, 108.5, 87.2, 79.9, 73.1, 46.2, 43.8, 26.1, 19.9, 19.6. **HRMS (ESI, m/z)** calcd for $C_{24}H_{19}N_3O$ $H^+[M+H]^+$: 366.1598, found: 366.1601.



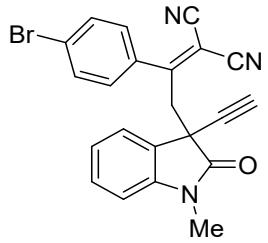
4e

2-(2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)-1-(4-methoxyphenyl)ethylidene) malononi-trile: Orange solid, 64 mg, 87% yield, mp = 72-74 ^{o}C.**^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.38 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 3.80-3.71 (m, 5H), 2.61 (s, 3H), 2.25 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.6, 172.4, 163.1, 142.6, 130.5, 130.0, 127.0, 124.7, 124.3, 123.6, 113.9, 112.9, 112.7, 108.7, 86.3, 79.8, 73.2, 55.6, 46.4, 43.7, 26.3. **HRMS (ESI, m/z)** calcd for $C_{23}H_{17}N_3O_2$ $H^+[M+H]^+$: 368.1389, found: 368.1393.



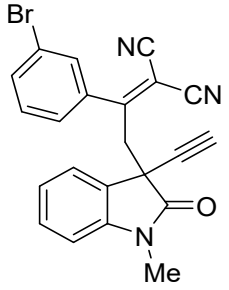
4f

2-(1-([1,1'-biphenyl]-4-yl)-2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)ethylidene) malononi-trile: Brown oil, 19 mg, 23% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.51 (d, *J* = 8.0 Hz, 4H), 7.43-7.36 (m, 3H), 7.34-7.28 (m, 1H), 7.19 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 3.84 (s, 2H), 2.56 (s, 3H), 2.25 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.7, 172.3, 142.8, 142.0, 136.9, 130.0, 129.9, 129.6, 129.3, 127.0, 125.8, 124.3, 123.6, 112.7, 112.4, 108.5, 87.2, 79.9, 73.1, 46.2, 43.8, 26.1, 19.9, 19.6. **HRMS (ESI, m/z)** calcd for $C_{28}H_{19}N_3OH^+$ $[M+H]^+$: 414.1595, found: 414.1601.



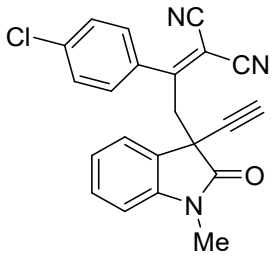
4g

2-(1-(4-bromophenyl)-2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)ethylidene) malononi-trile：Yellow solid, 76 mg, 92% yield, mp = 147-150 °C.**^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.53 (d, *J* = 8.0 Hz, 2H), 7.47-7.37 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 2H), 2.75 (s, 3H), 2.33 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.1, 172.1, 142.6, 131.8, 131.4, 130.2, 129.8, 127.2, 127.0, 124.1, 123.8, 112.1, 111.9, 108.9, 88.8, 79.5, 73.6, 46.2, 43.9, 26.4. **HRMS (ESI, m/z)** calcd for $C_{22}H_{14}BrN_3OH^+$ $[M+H]^+$: 416.0388, found: 416.0393.



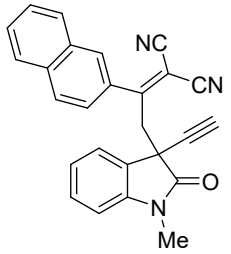
4h

2-(1-(3-bromophenyl)-2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)ethylidene) malononi-trile： White solid, 59 mg, 71% yield, mp = 174-176 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.53 (d, *J* = 8.0 Hz, 1H), 7.38-7.30 (m, 2H), 7.24-7.18 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 6.69 (s, 1H), 3.78-3.66 (m, 2H), 2.70 (s, 3H), 2.23 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.0, 171.7, 142.6, 135.0, 134.6, 130.8, 130.3, 130.1, 126.9, 126.9, 124.1, 123.8, 122.4, 111.9, 111.5, 108.9, 89.6, 79.5, 73.5, 46.1, 44.0, 26.4. **HRMS (ESI, m/z)** calcd for $C_{22}H_{14}BrN_3OH^+$ $[M+H]^+$: 416.0386, found: 416.0393.



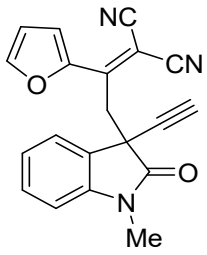
4i

2-(1-(4-chlorophenyl)-2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)ethylidene) malononitrile： White solid, 68 mg, 92% yield, mp = 121-123 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.47-7.35 (m, 4H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.85-3.80 (m, 2H), 2.75 (s, 3H), 2.33 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.1, 142.6, 138.8, 131.0, 130.2, 129.7, 128.8, 127.0, 124.1, 123.8, 112.1, 111.9, 108.9, 88.8, 79.5, 77.4, 77.1, 76.8, 73.5, 46.2, 43.9, 26.3. **HRMS (ESI, m/z)** calcd for $C_{22}H_{14}ClN_3OH^+$ $[M+H]^+$: 372.0894, found: 372.0898.



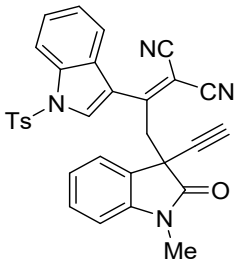
4j

2-(2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)-1-(naphthalen-2-yl)ethylidene) malononitrile： Yellow solid, 60 mg, 78% yield, mp = 63-65 °C.**^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.79-7.68 (m, 3H), 7.51-7.45 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.36 (s, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.19-7.11 (m, 1H), 7.02 (dd, *J* = 1.2, 8.4 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 3.90 (dd, *J* = 14.4, 17.6 Hz, 2H), 2.20 (s, 1H), 2.16 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 173.6, 172.2, 142.7, 134.7, 131.9, 130.0, 129.7, 129.3, 129.0, 128.8, 128.3, 127.7, 127.4, 127.0, 124.2, 124.2, 123.7, 112.5, 112.2, 108.7, 88.2, 79.9, 73.2, 46.2, 43.9, 25.9. **HRMS (ESI, m/z)** calcd for $C_{26}H_{14}N_3OH^+$ $[M+H]^+$: 388.1439, found: 388.1444.



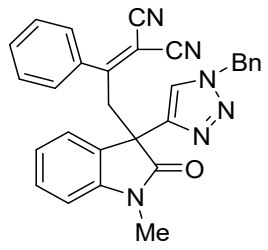
4k

2-(2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)-1-(furan-2-yl)ethylidene) malononitrile: Brown solid, 38 mg, 59% yield, mp = 127-129 °C. **^{1}H NMR (400 MHz, $CDCl_3$)**:δ = 7.63 (s, 1H), 7.46 (d, *J* = 3.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23-7.17 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 3.57 (d, *J* = 13.2 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 3.09 (s, 3H), 2.24 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 172.8, 153.5, 148.4, 148.0, 142.4, 130.0, 127.8, 124.5, 123.5, 121.6, 114.1, 113.3, 113.0, 109.0, 80.8, 79.1, 74.0, 47.0, 41.2, 26.9. **HRMS (ESI, m/z)** calcd for $_{20}H_{13}N_3O_2H^+$ $[M+H]^+$: 328.1077, found: 328.1080.



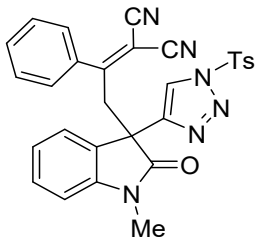
4l

2-(2-(3-ethynyl-1-methyl-2-oxoindolin-3-yl)-1-(1-tosyl-1H-indol-3-yl)ethylidene) malon-onitrile: Yellow solid, 34 mg, 32% yield, mp = 74-76 ^{o}C.**^{1}H NMR (400 MHz, $CDCl_3$)**:δ = 8.02 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.43-7.30 (m, 4H), 7.27-7.18 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 4.04-3.83 (m, 2H), 2.41 (s, 3H), 2.34 (s, 1H), 1.90 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 172.2, 164.7, 146.2, 142.1, 134.0, 130.2, 130.0, 129.5, 128.0, 126.8, 125.8, 124.4, 123.7, 121.0, 114.0, 113.3, 112.6, 109.2, 87.7, 79.7, 73.3, 46.9, 45.4, 31.5, 30.2, 25.2, 21.7 **HRMS (ESI, m/z)** calcd for $C_{31}H_{22}N_4O_3SH^+$ $[M+H]^+$: 531.1478, found: 531.1485.



5a

2-(2-(3-(1-benzyl-1H-1,2,3-triazol-4-yl)-1-methyl-2-oxoindolin-3-yl)-1-phenylethylidene)-malononitrile: Brown oil, 48 mg, 51% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.68 (d, *J* = 7.4 Hz, 1H), 7.35-7.26 (m, 3H), 7.25-7.18 (m, 4H), 7.16-7.07 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.57 (dd, *J* = 14.4, 24.0 Hz, 2H) , 4.00-3.87 (m, 2H), 2.59 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 174.7, 145.5, 142.6, 134.0, 132.9, 131.9, 129.5, 129.1, 128.9, 128.3, 128.2, 128.1, 125.8, 123.5, 121.3, 112.5, 112.3, 108.5, 88.2, 54.3, 50.7, 44.5, 26.0. **HRMS (ESI, m/z)** calcd for $C_{29}H_{22}N_6OH^+$ $[M+H]^+$:471.1921, found:471.1928.



6a

2-(2-(1-methyl-2-oxo-3-(1-tosyl-1H-1,2,3-triazol-4-yl)indolin-3-yl)-1-phenylethylidene)-malononitrile: Brown oil, 45 mg, 43% yield. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.86 (d, *J* = 7.2 Hz, 2H), 7.75 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.34-7.26 (m, 4H), 7.25-7.19 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.89 (dd, *J* = 14.0, 28.4 Hz, 2H), 2.65 (s, 3H), 2.37 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 174.1, 173.8, 147.6, 144.7, 142.7, 132.7, 132.6, 132.2, 130.5, 129.9, 129.7, 128.9, 128.4, 128.1, 127.6, 126.5, 125.7, 123.6, 121.3, 112.4, 112.2, 108.7, 88.3, 54.9, 50.3, 44.2, 26.2, 21.9. **HRMS (ESI, m/z)** calcd for $C_{29}H_{22}N_6O_3SH^+$ $[M+H]^+$: 535.1540, found: 535.1547.

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IV NMR Spectrum

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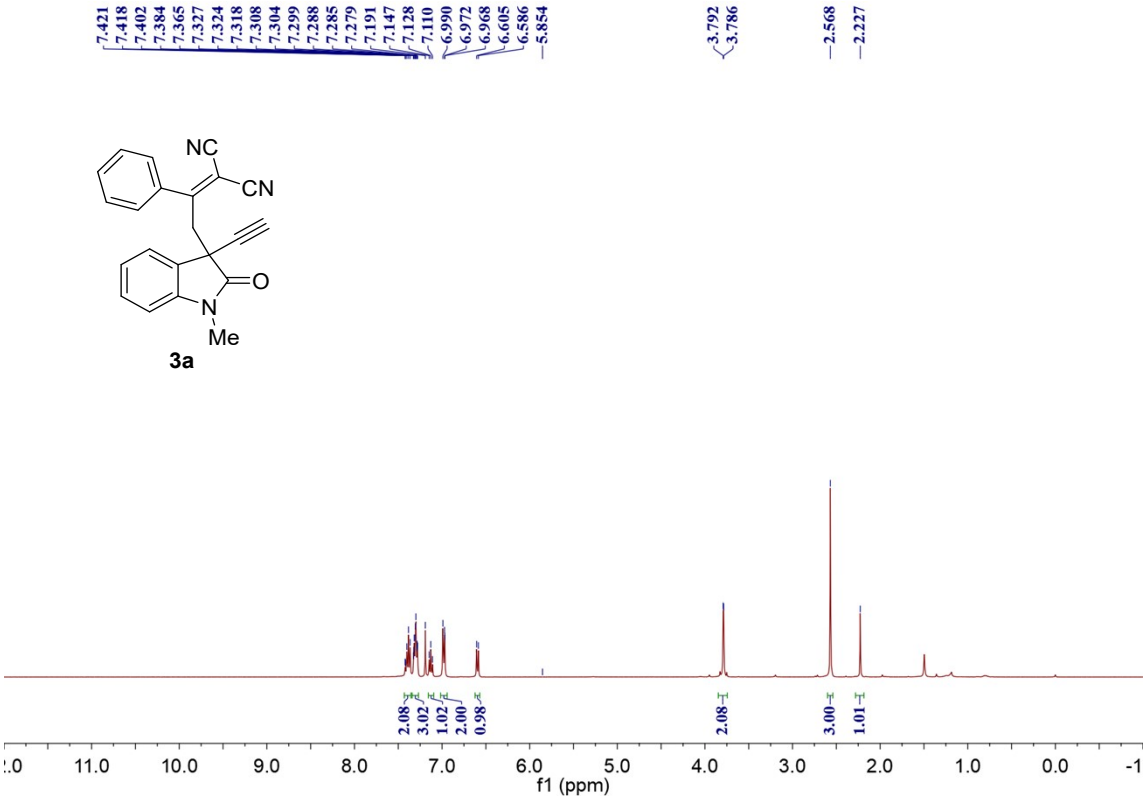

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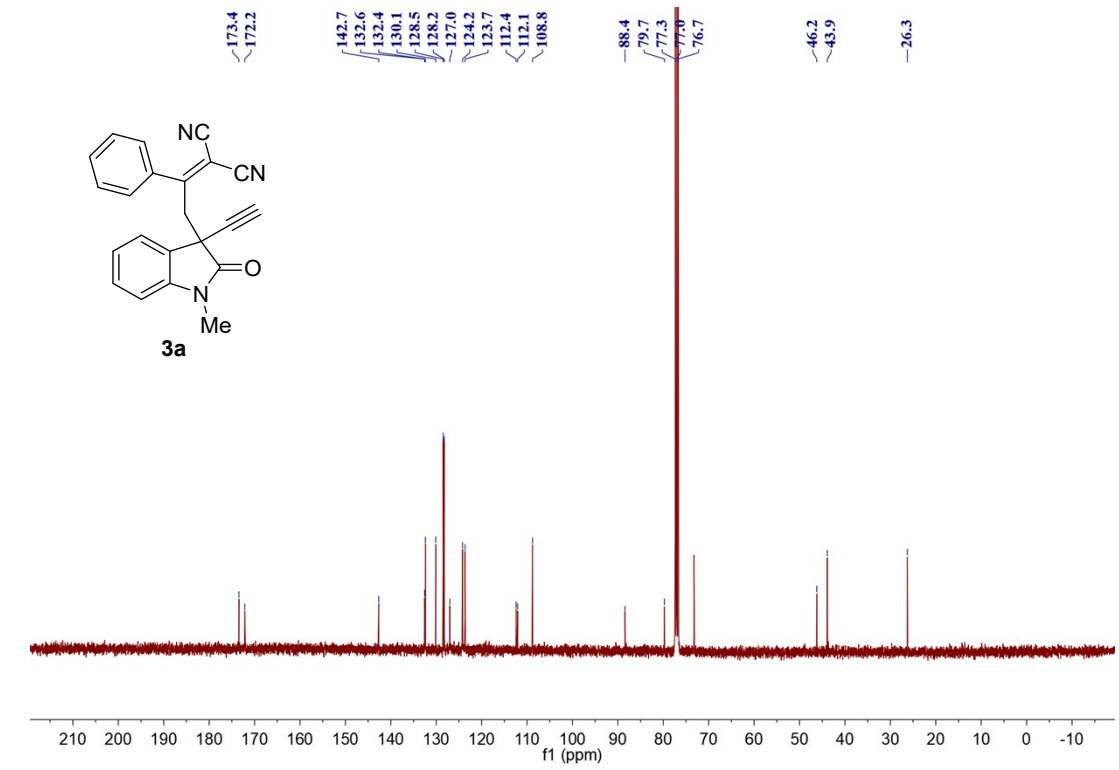

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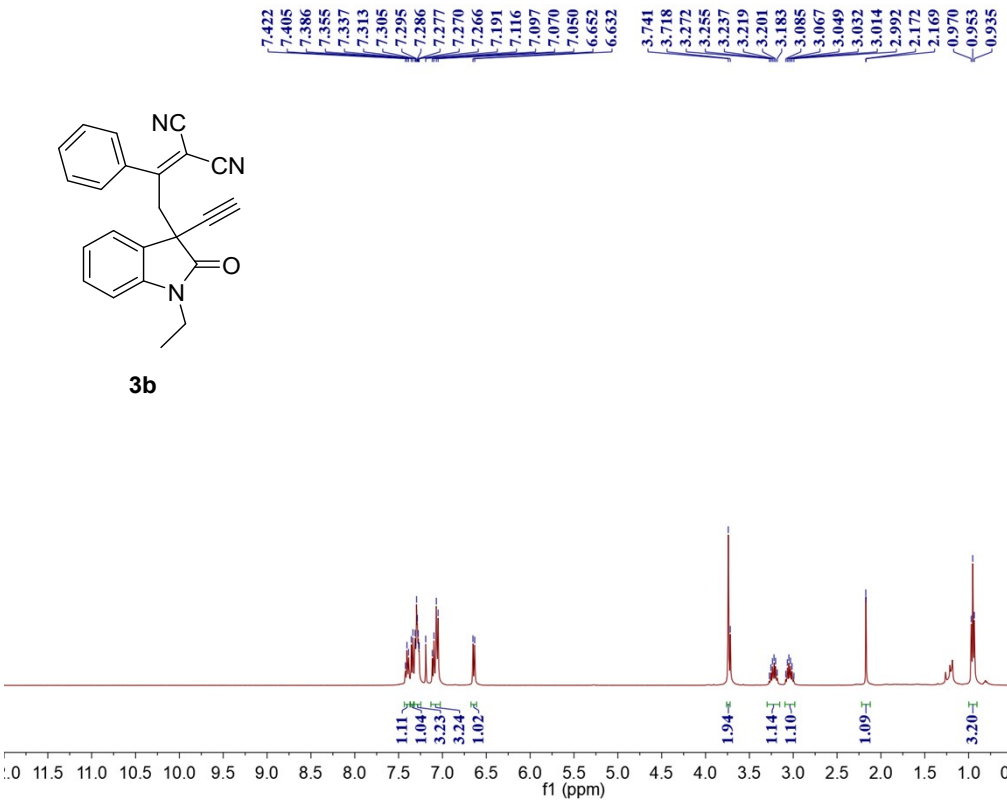
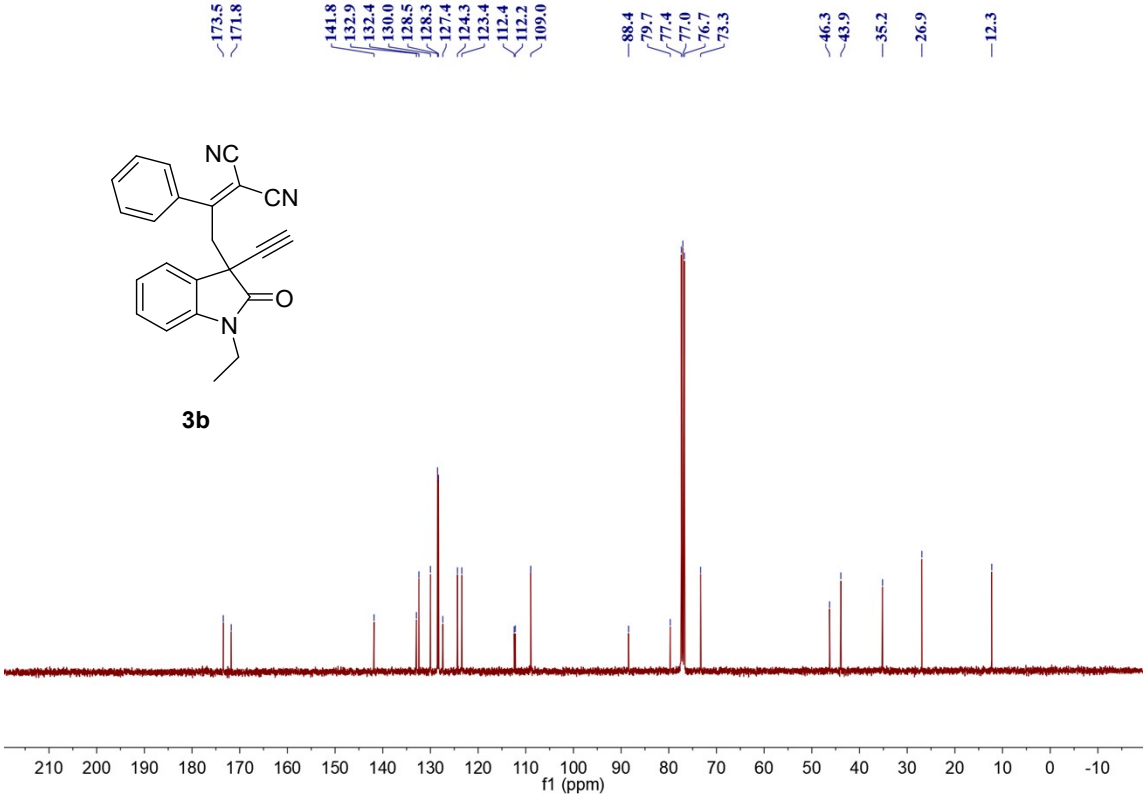


3b

^{13}C-NMR-3b



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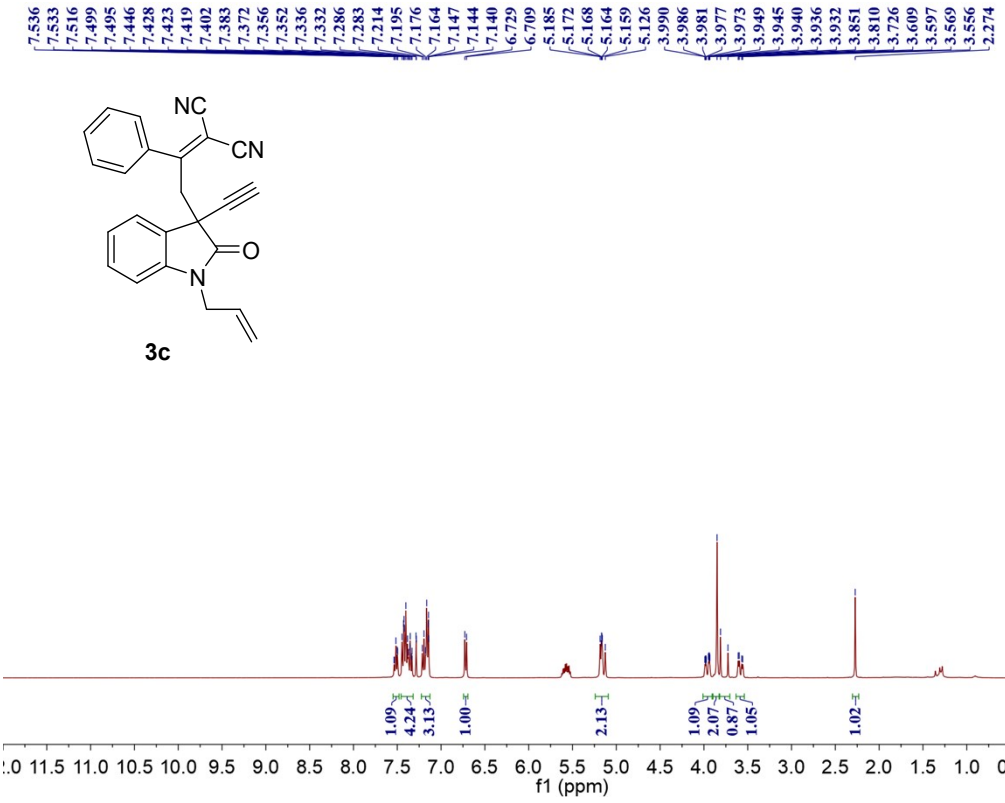

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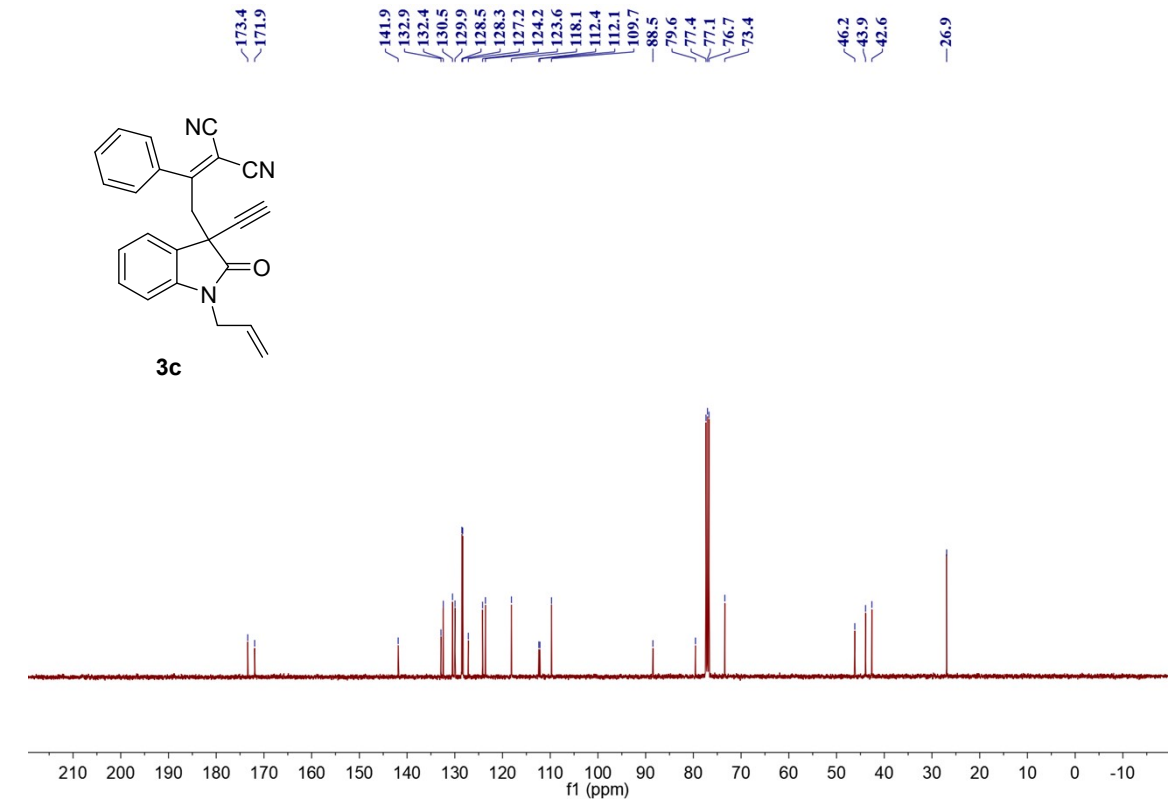

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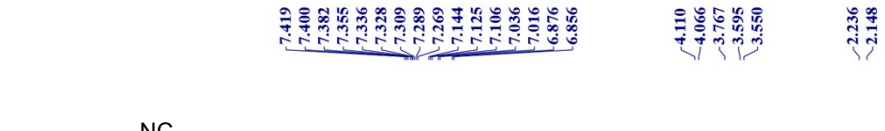

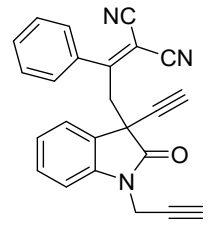

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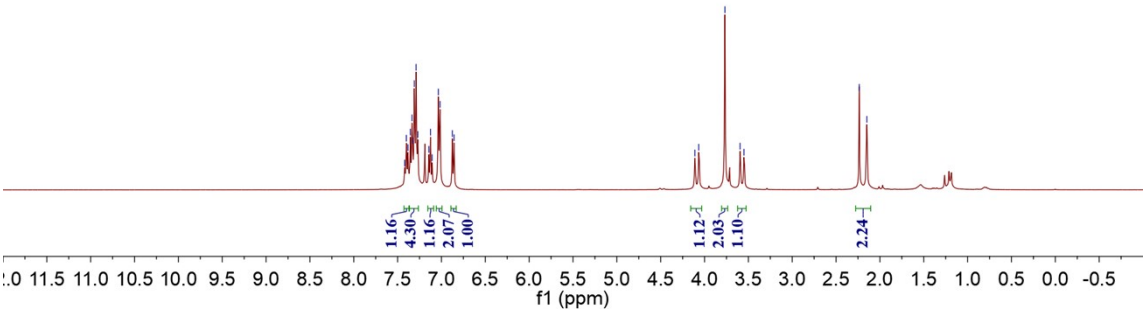

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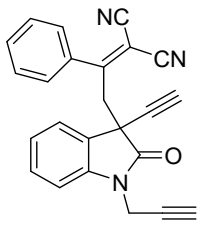

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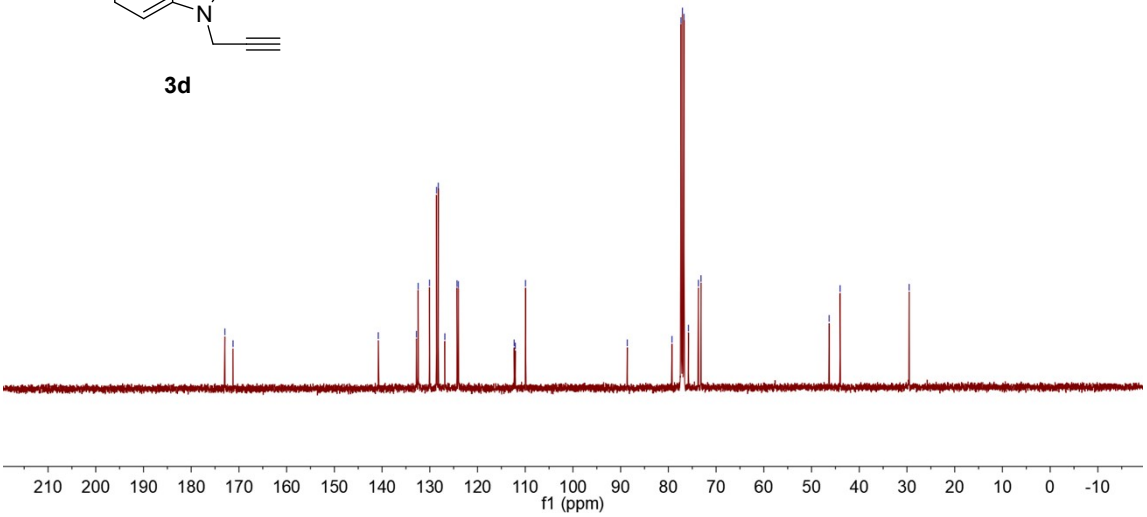

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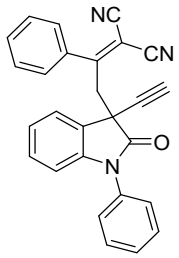

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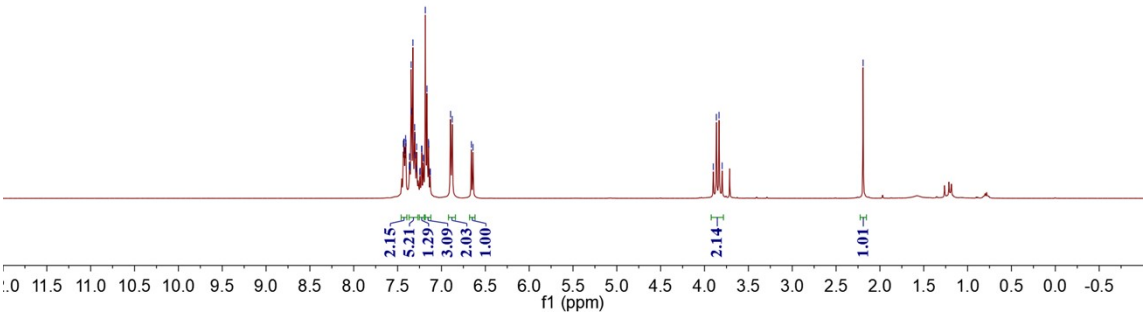

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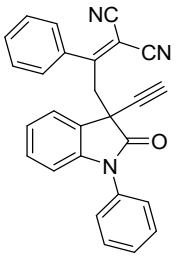

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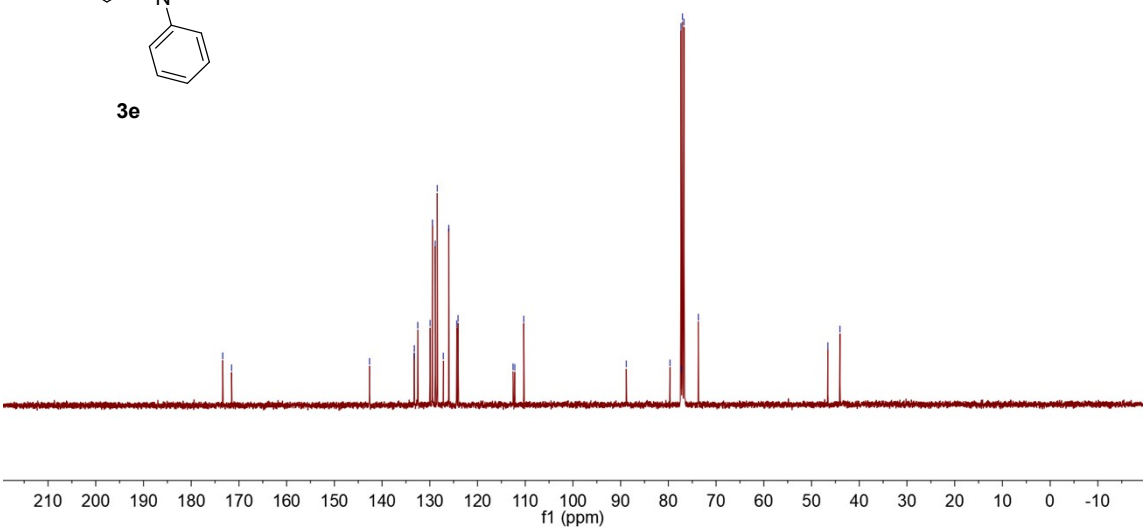

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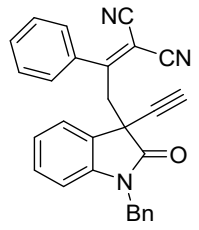

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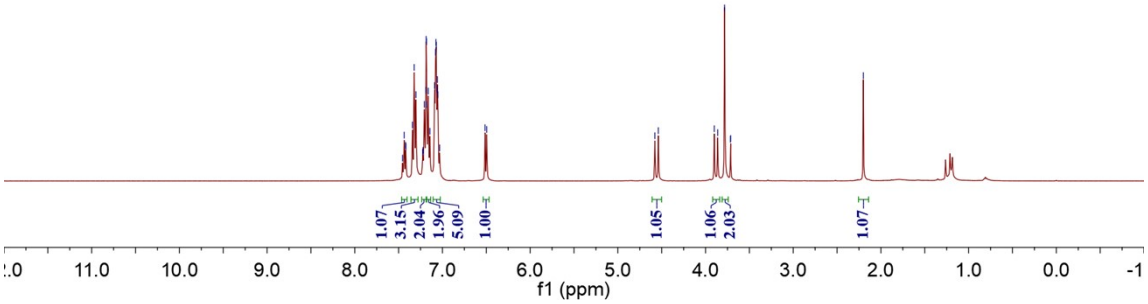

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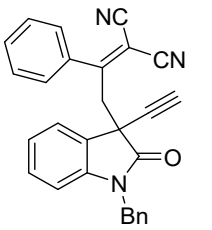

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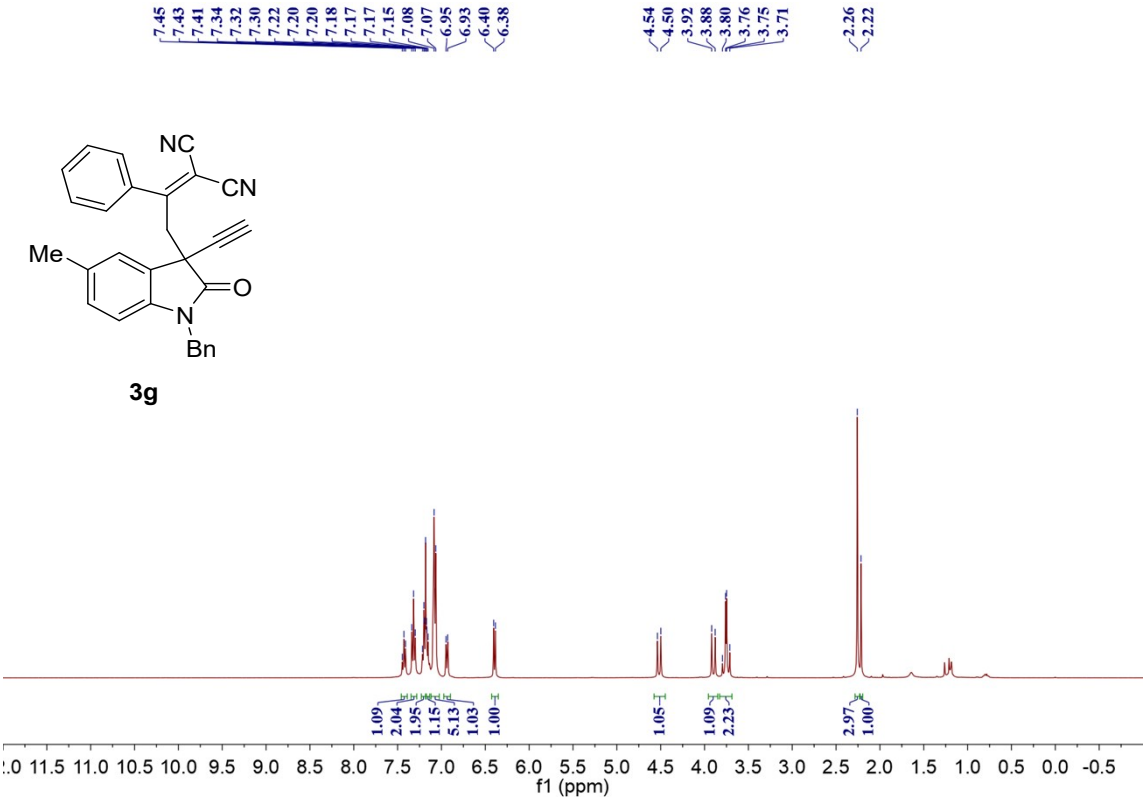
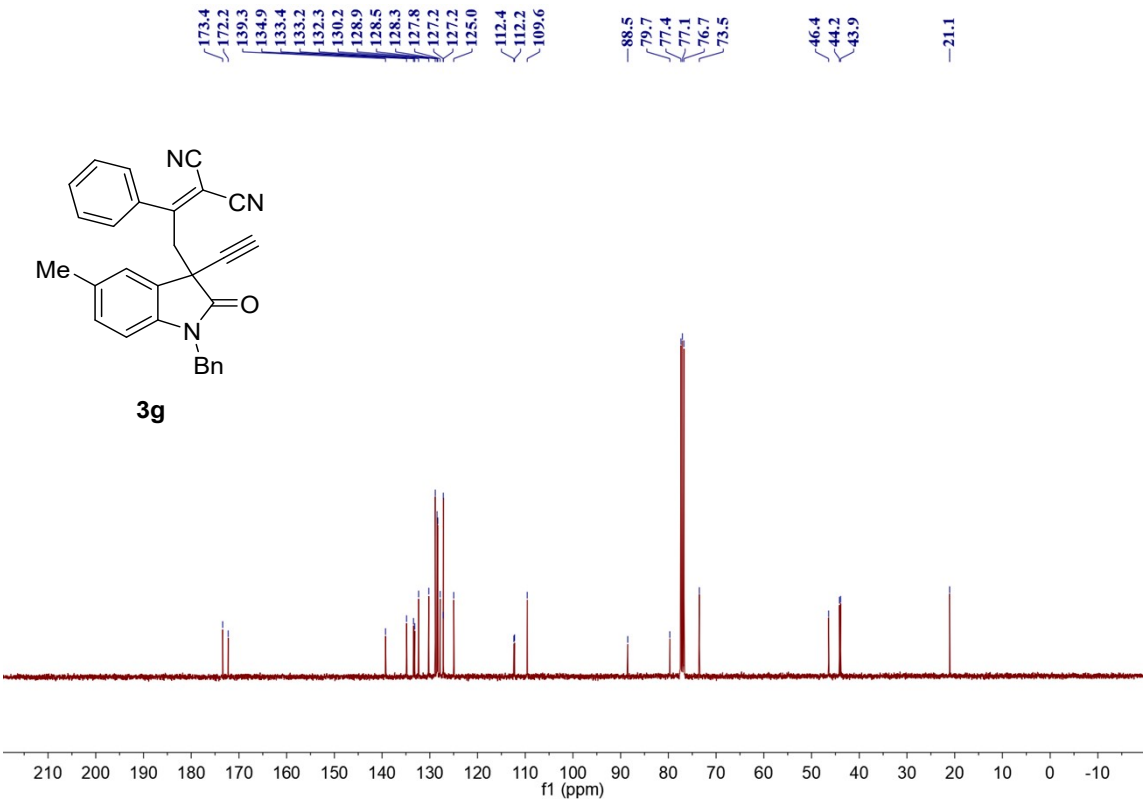
^{1}H-NMR-3g



3g

^{13}C NMR-3g



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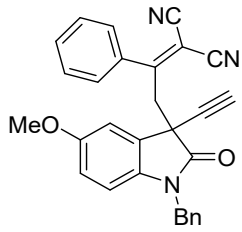

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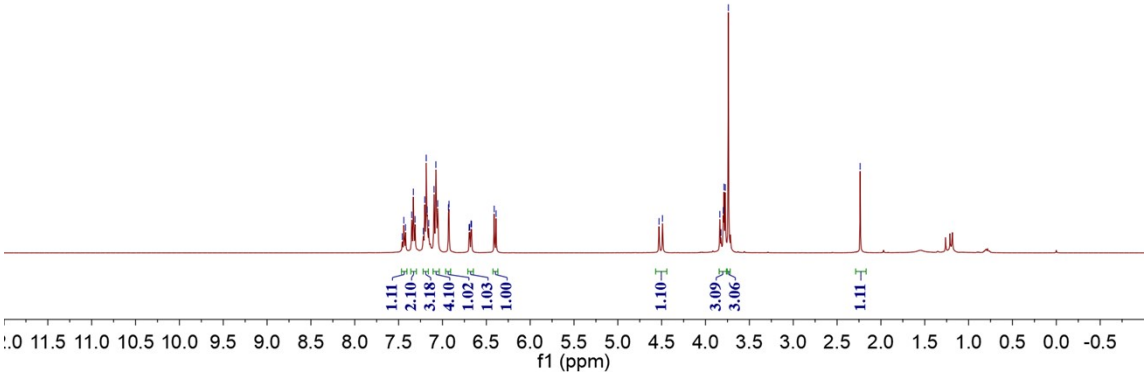

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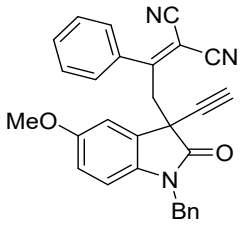
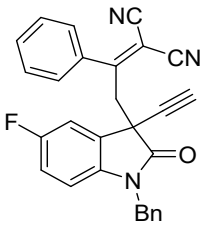


3h

^{1}H-NMR-3i



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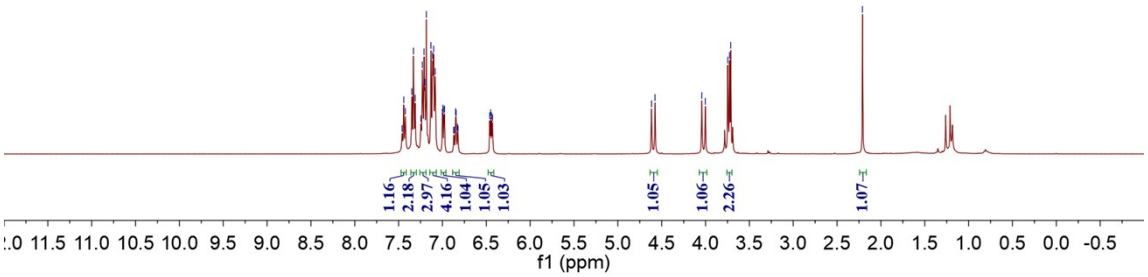

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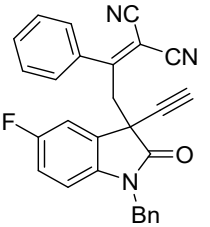

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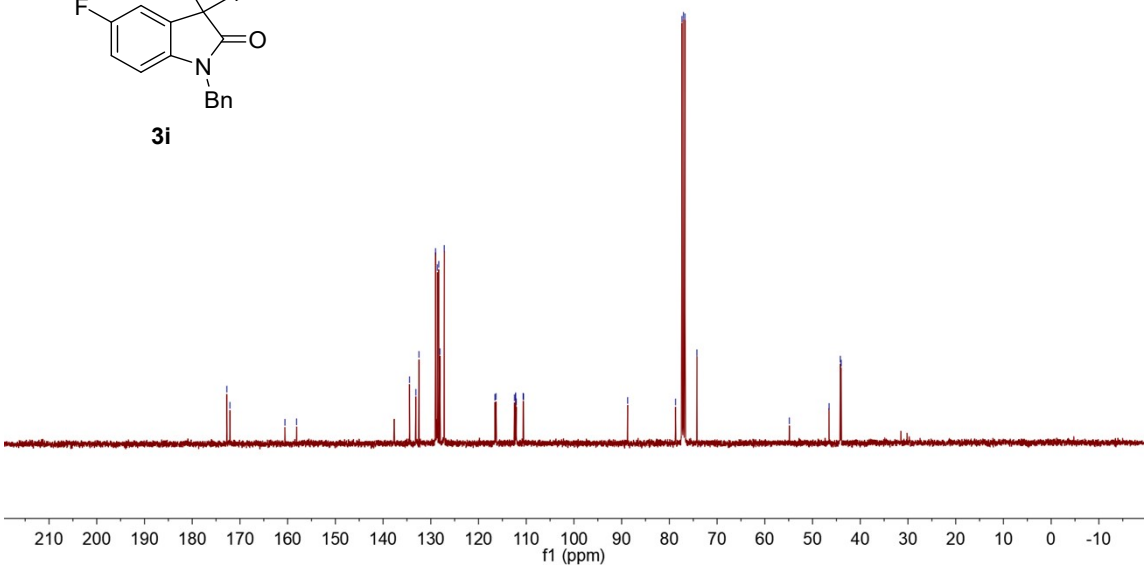

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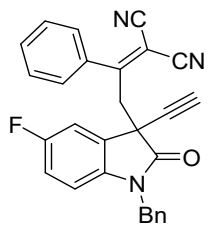

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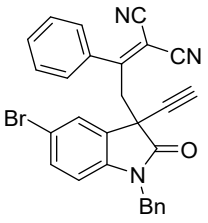

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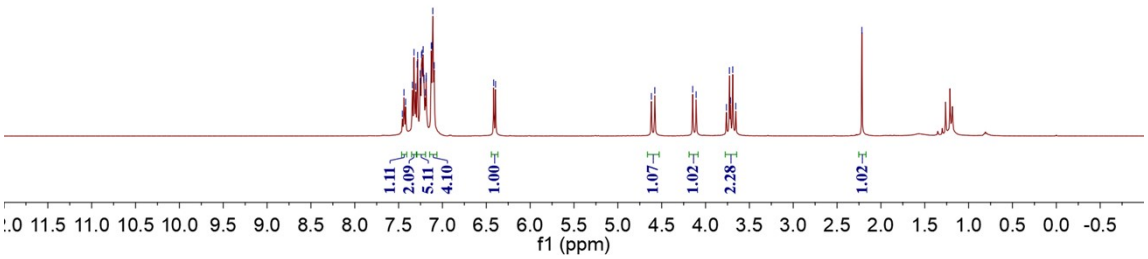

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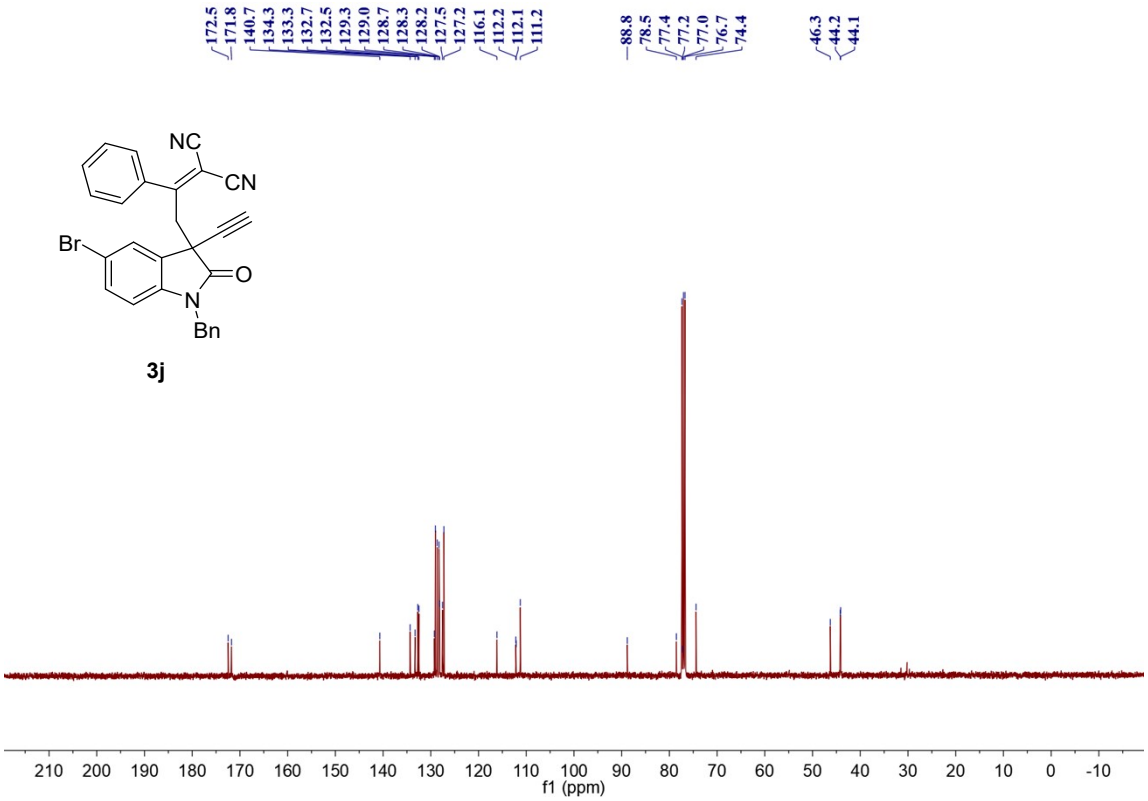

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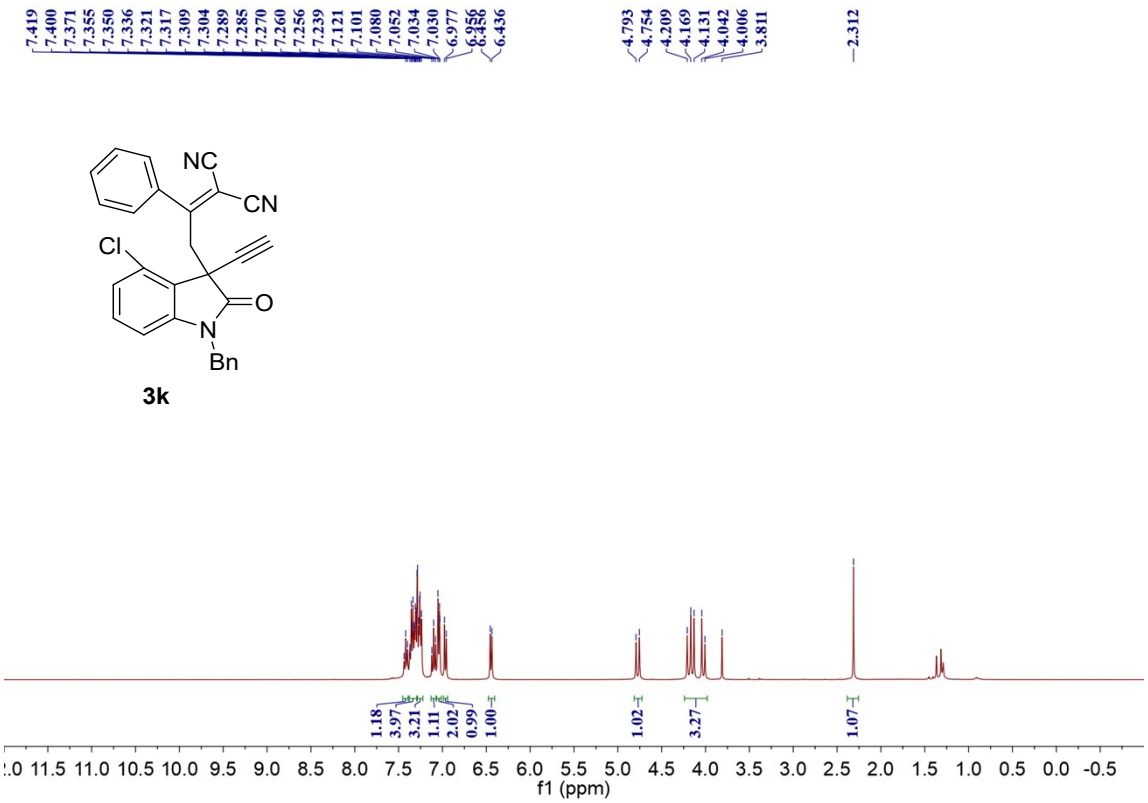

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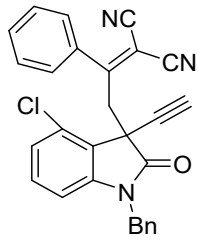

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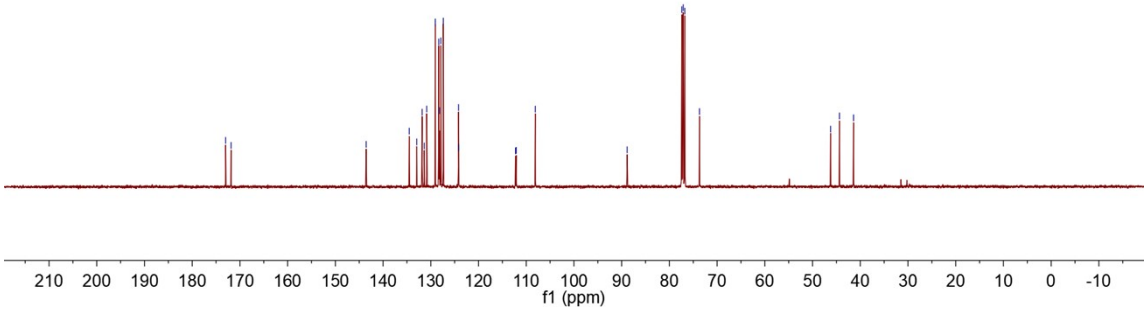

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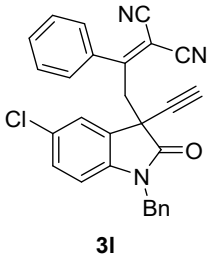
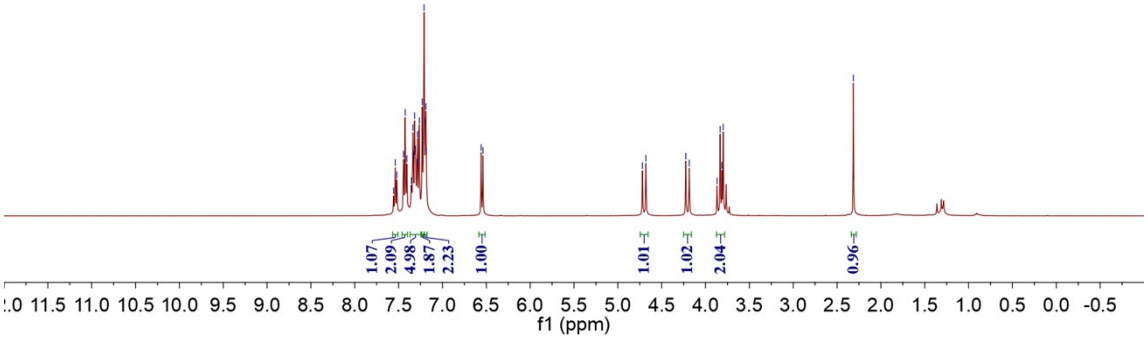
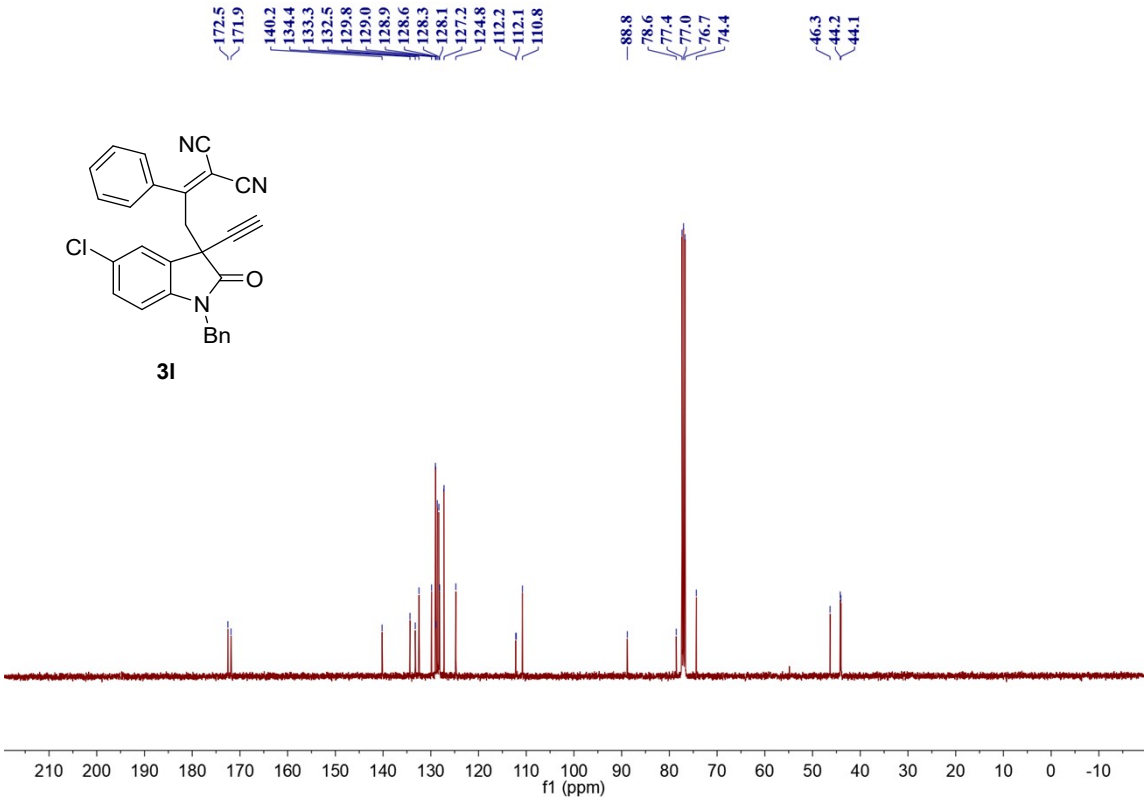


3l

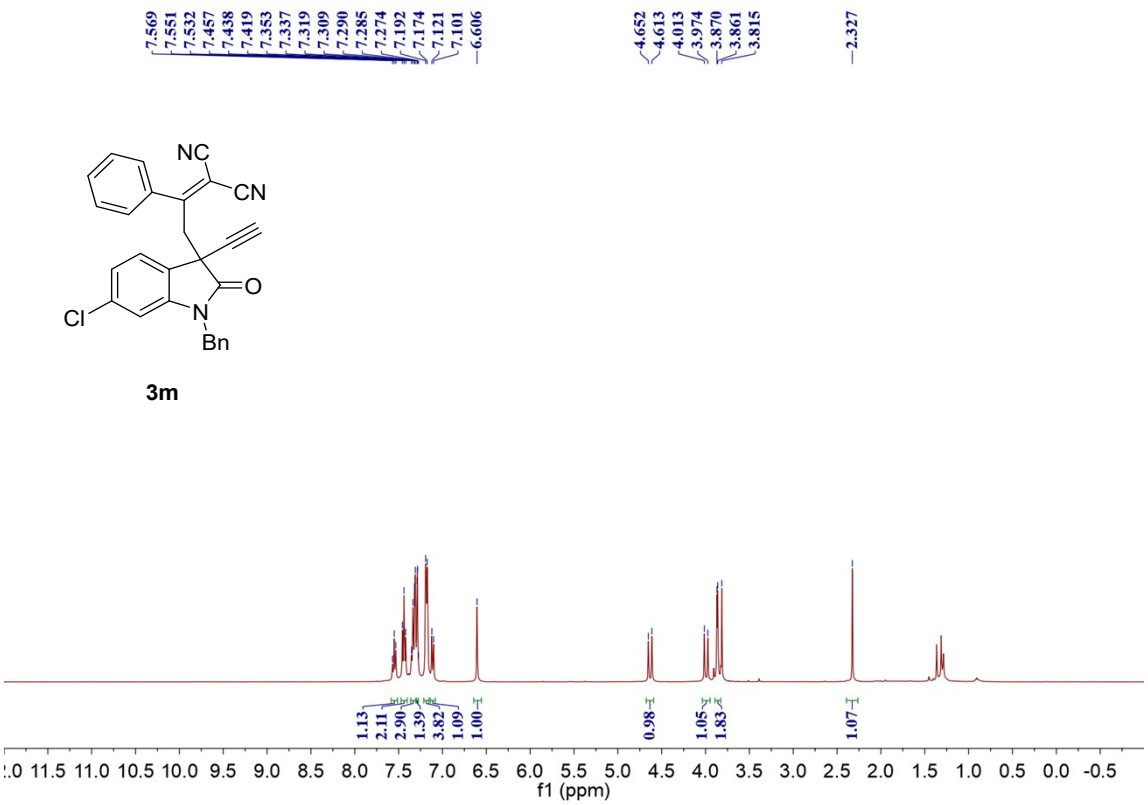


^{13}C NMR-3l



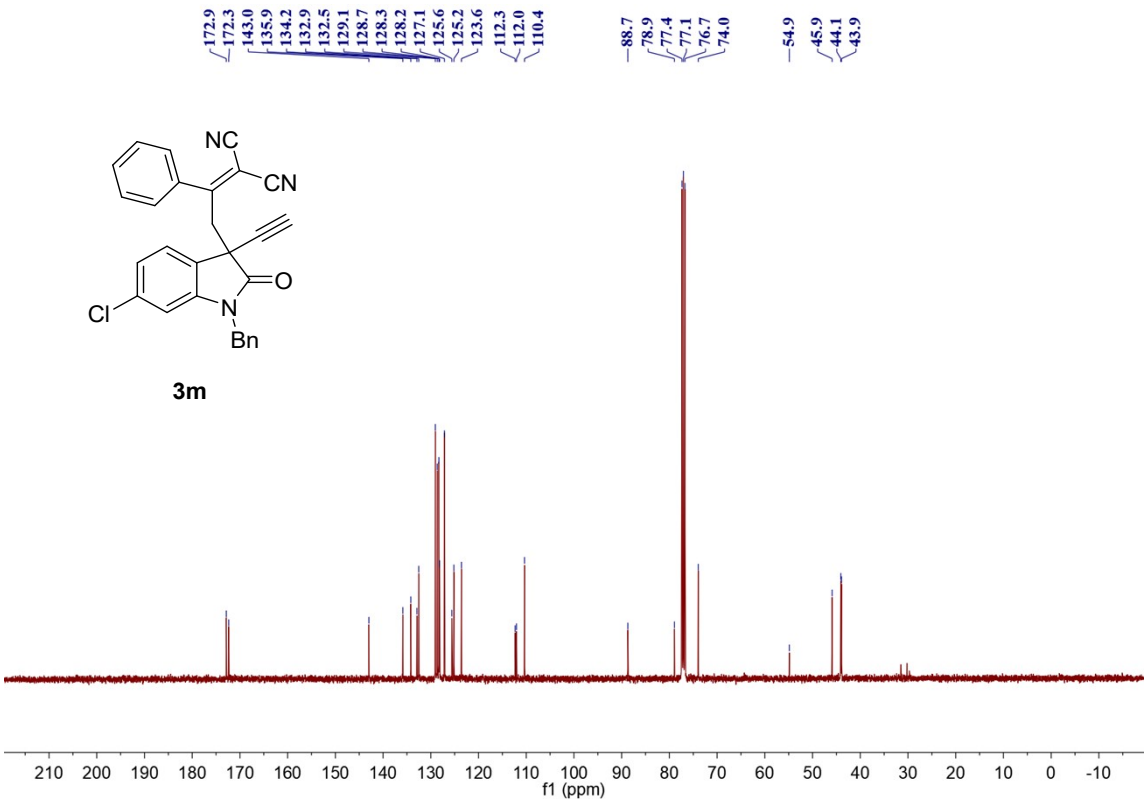
3l

^{1}H-NMR-3m



3m

^{13}C NMR-3m



3m

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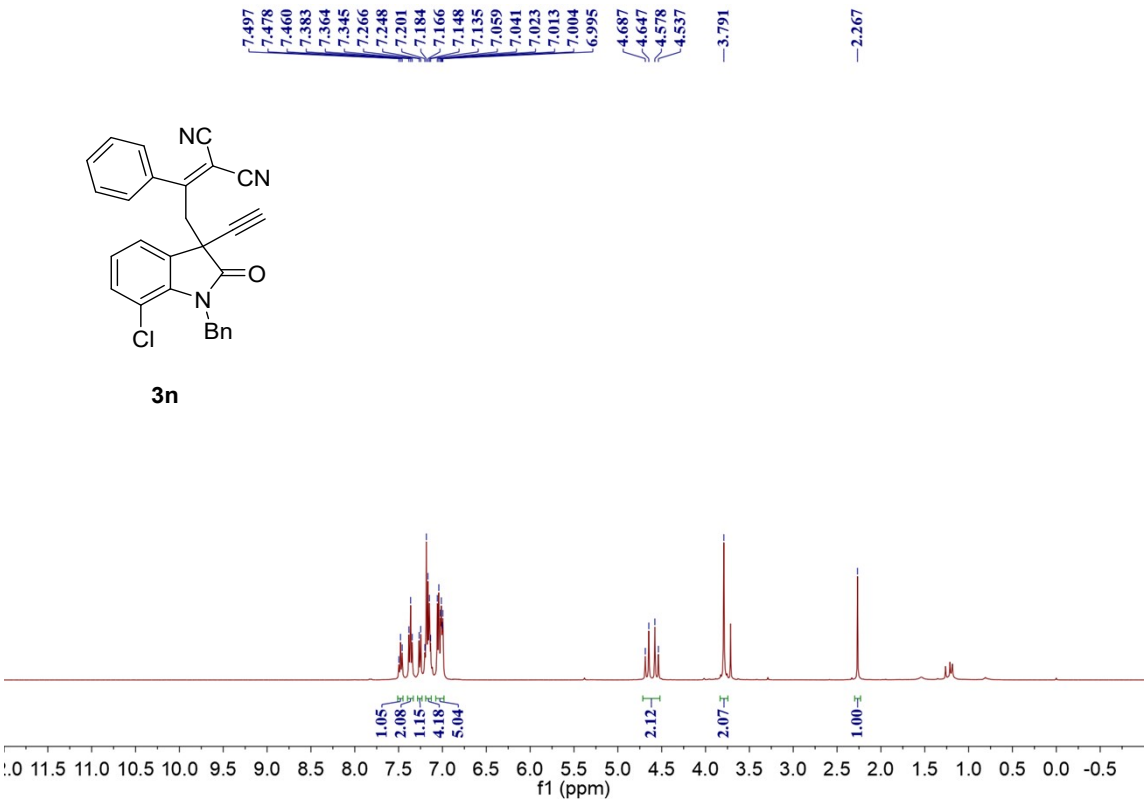

3n

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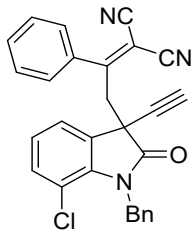

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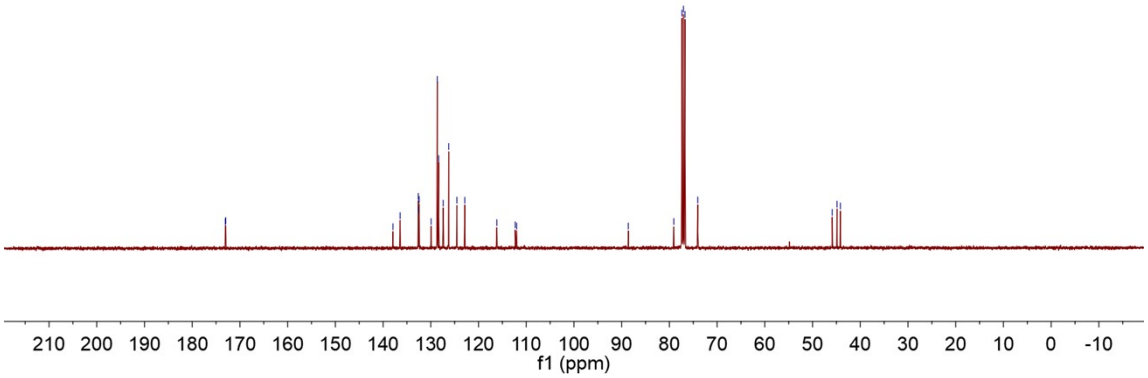

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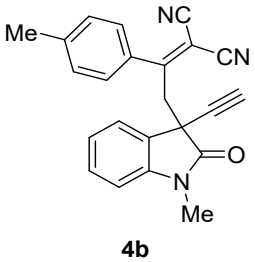
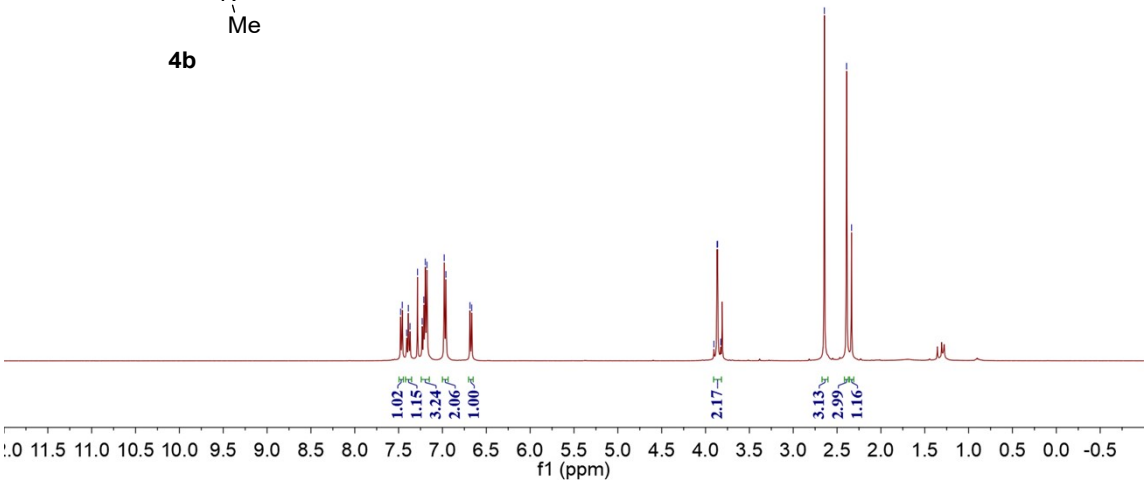


4b



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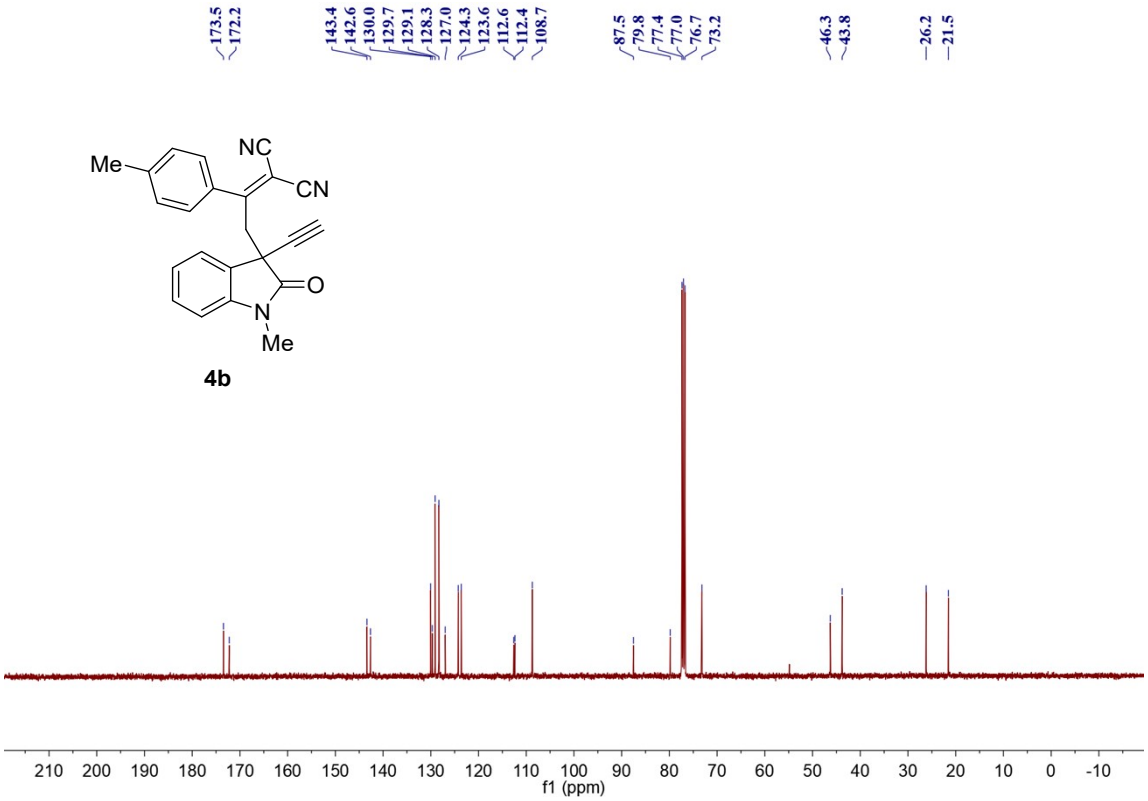

4b

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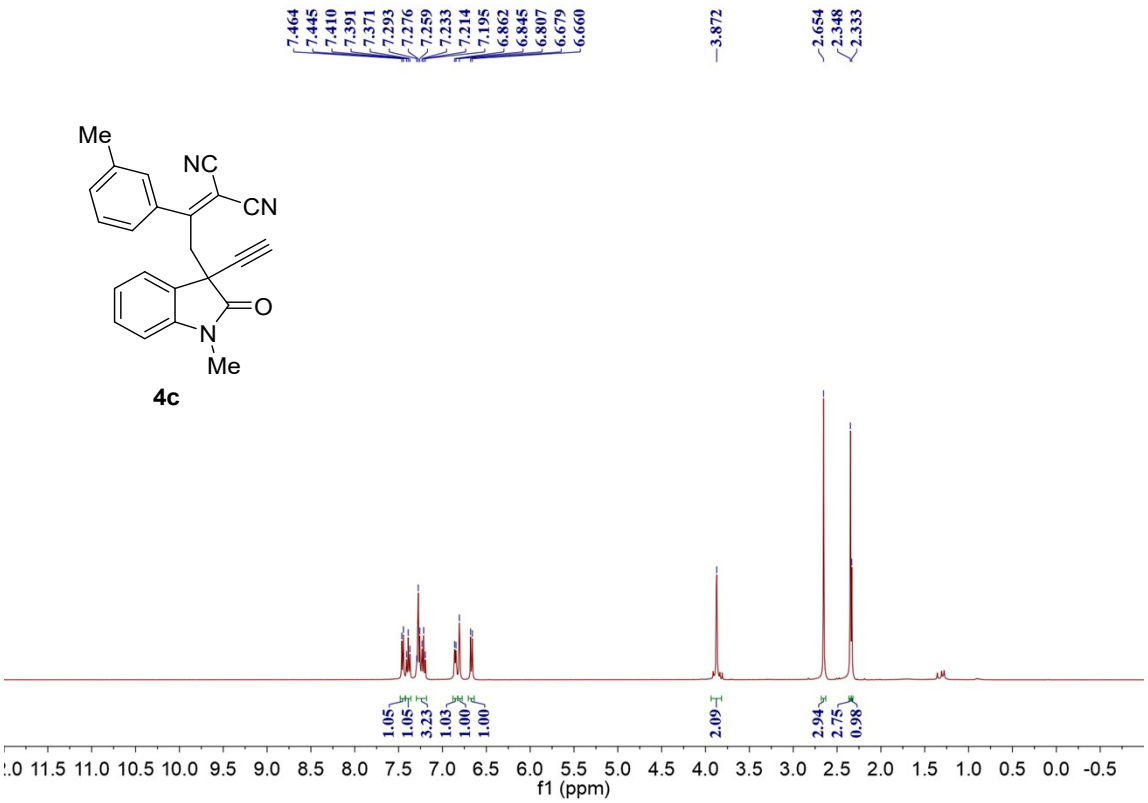

4c

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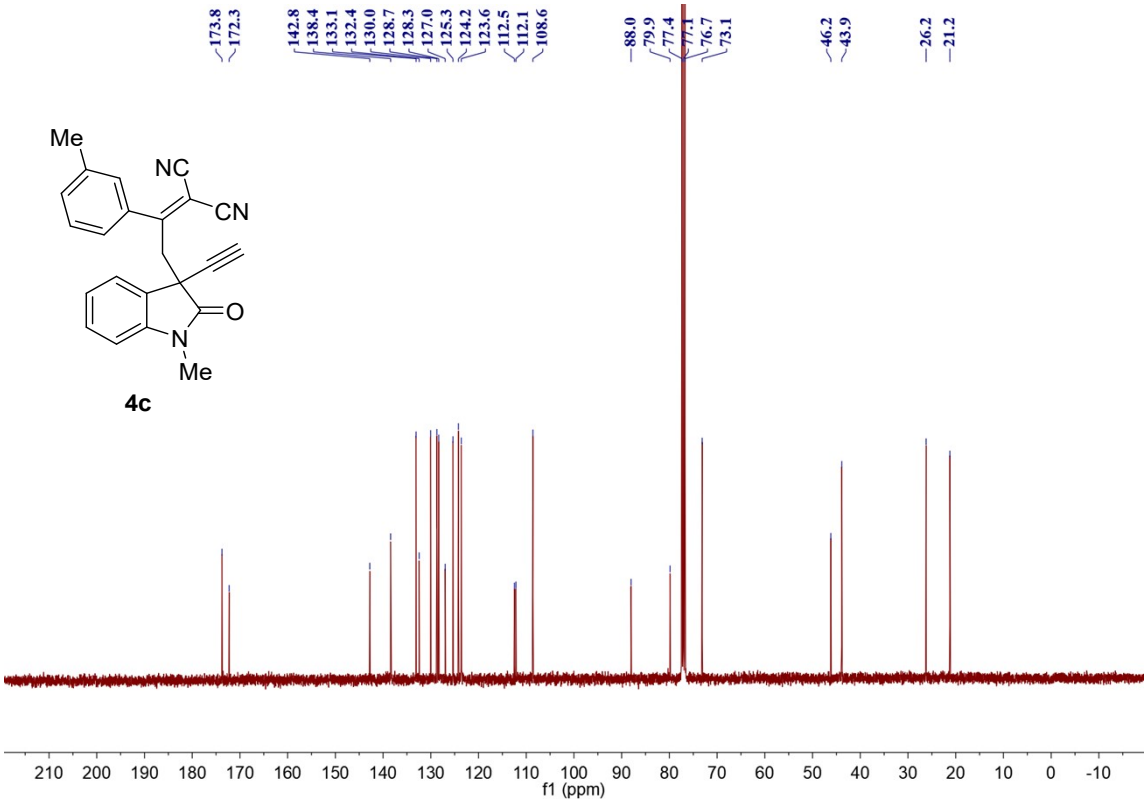

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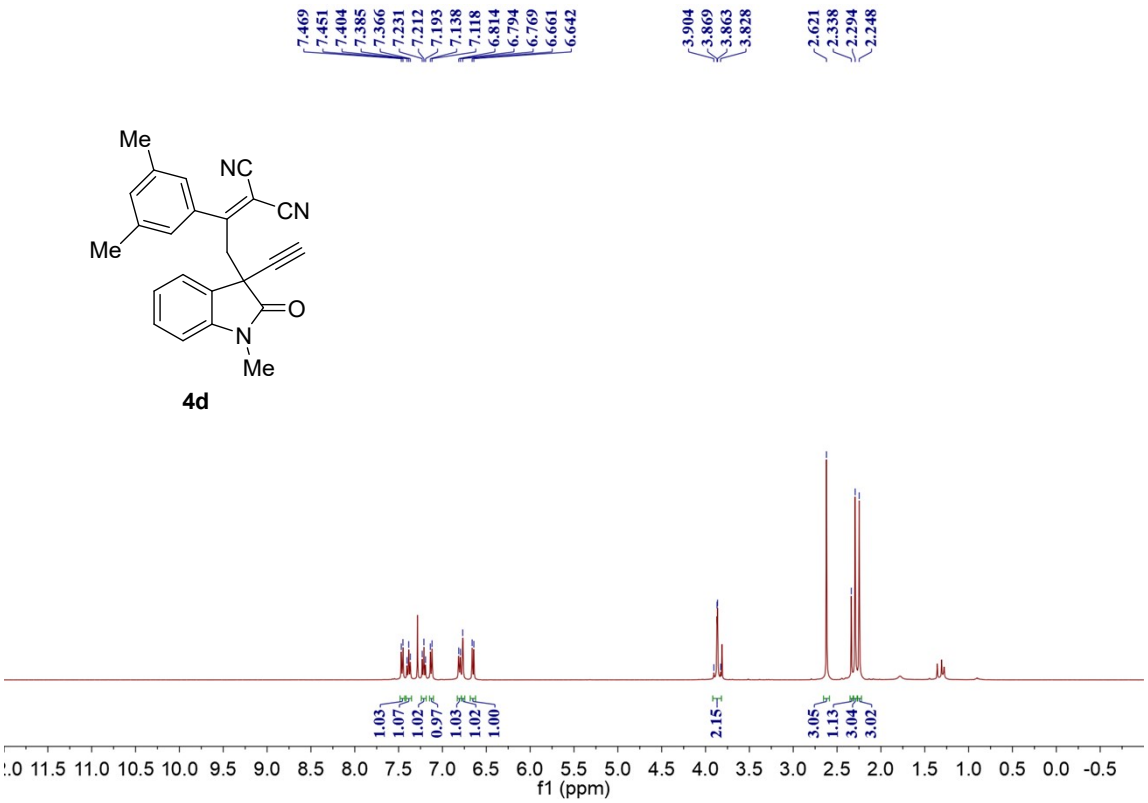

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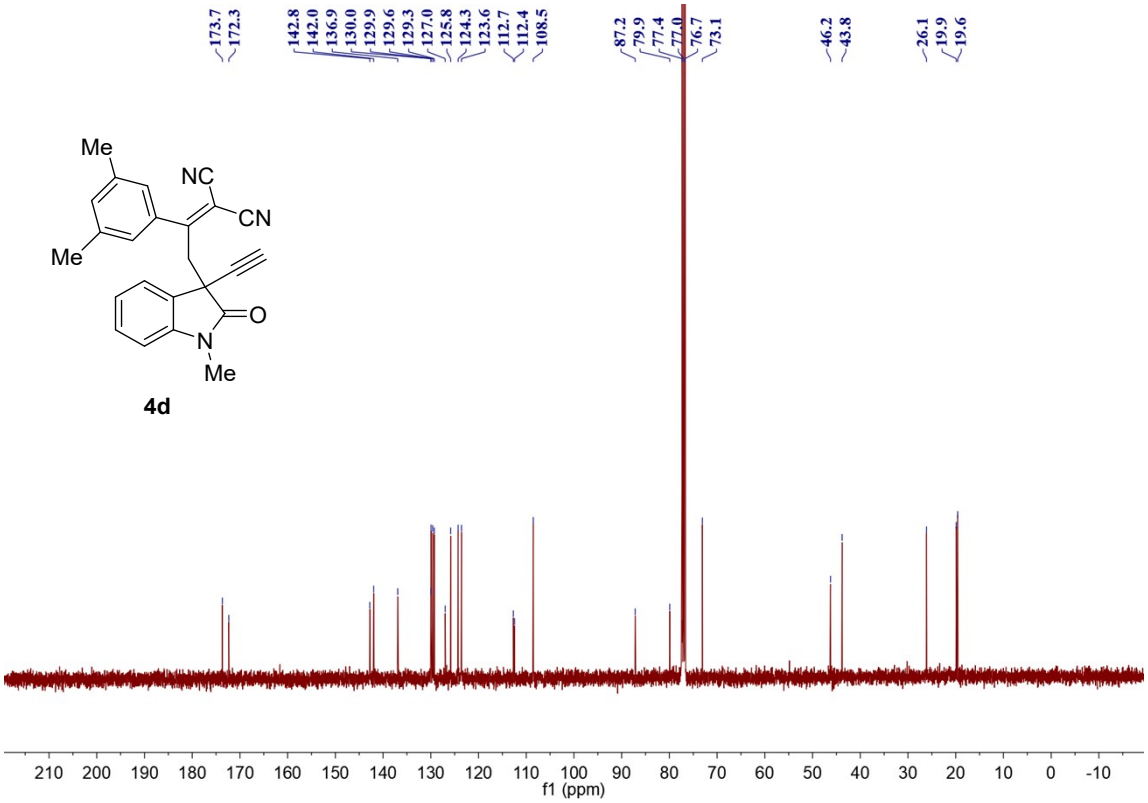

4d

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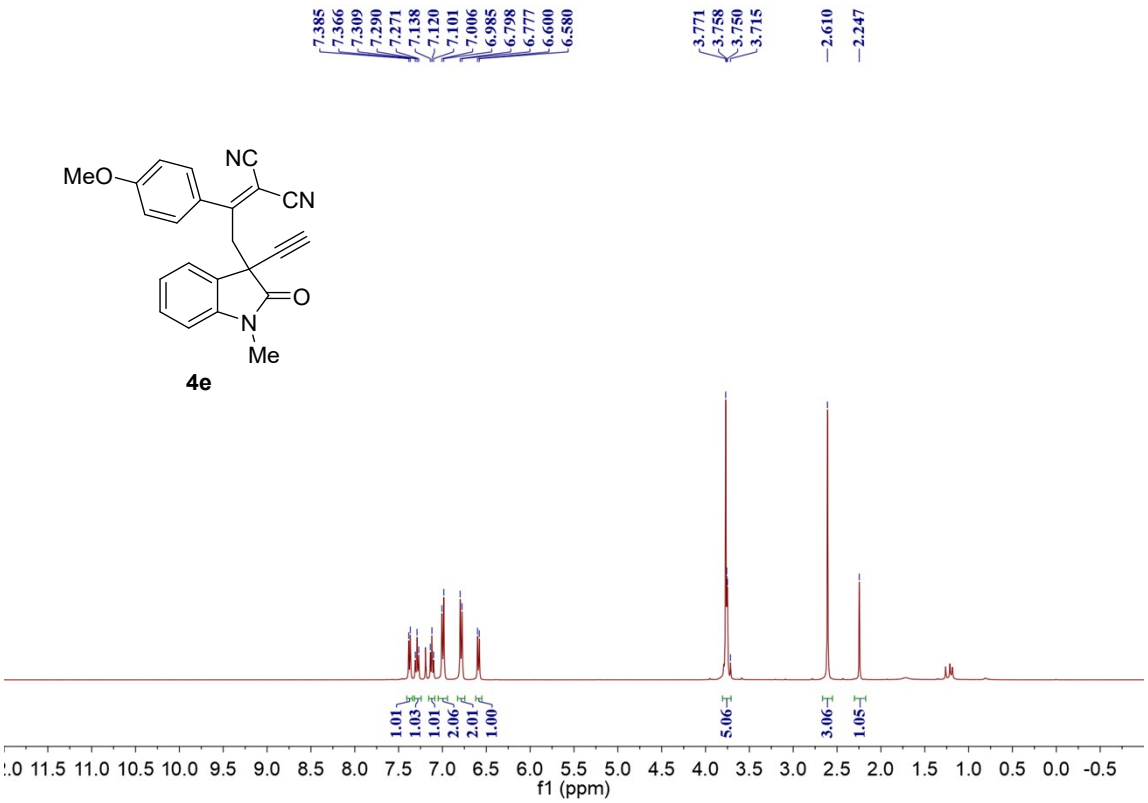

4e

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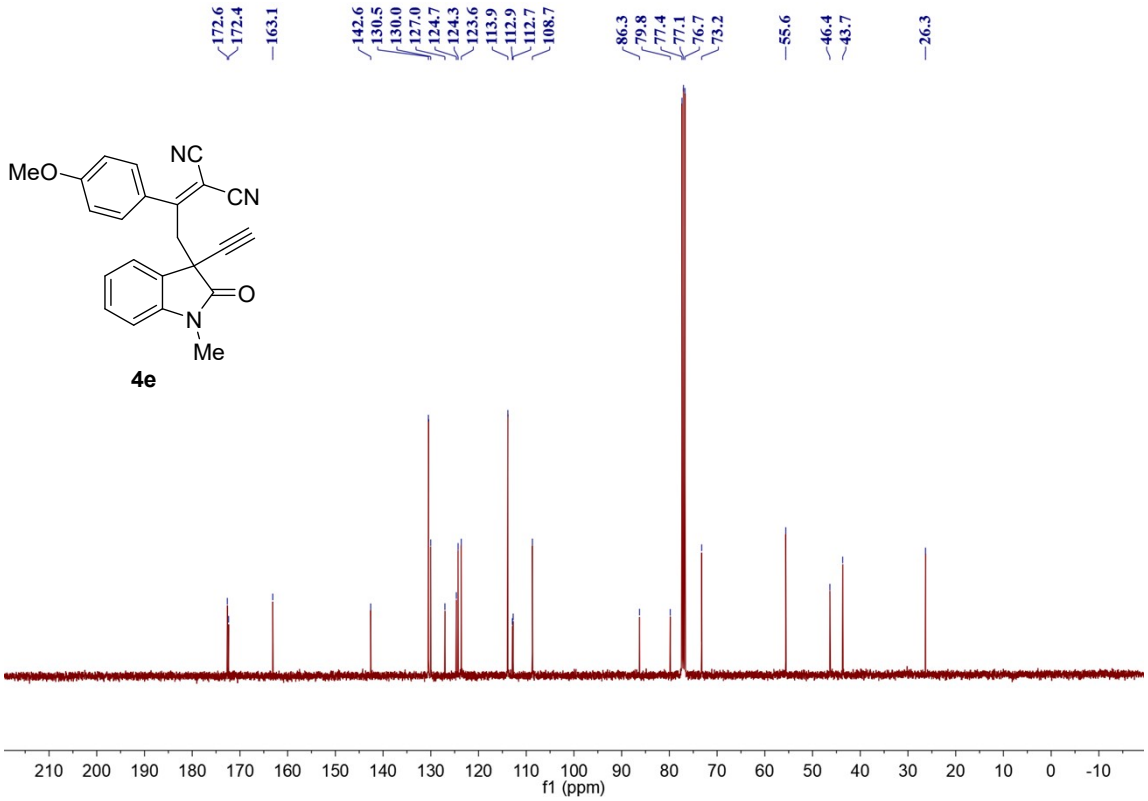
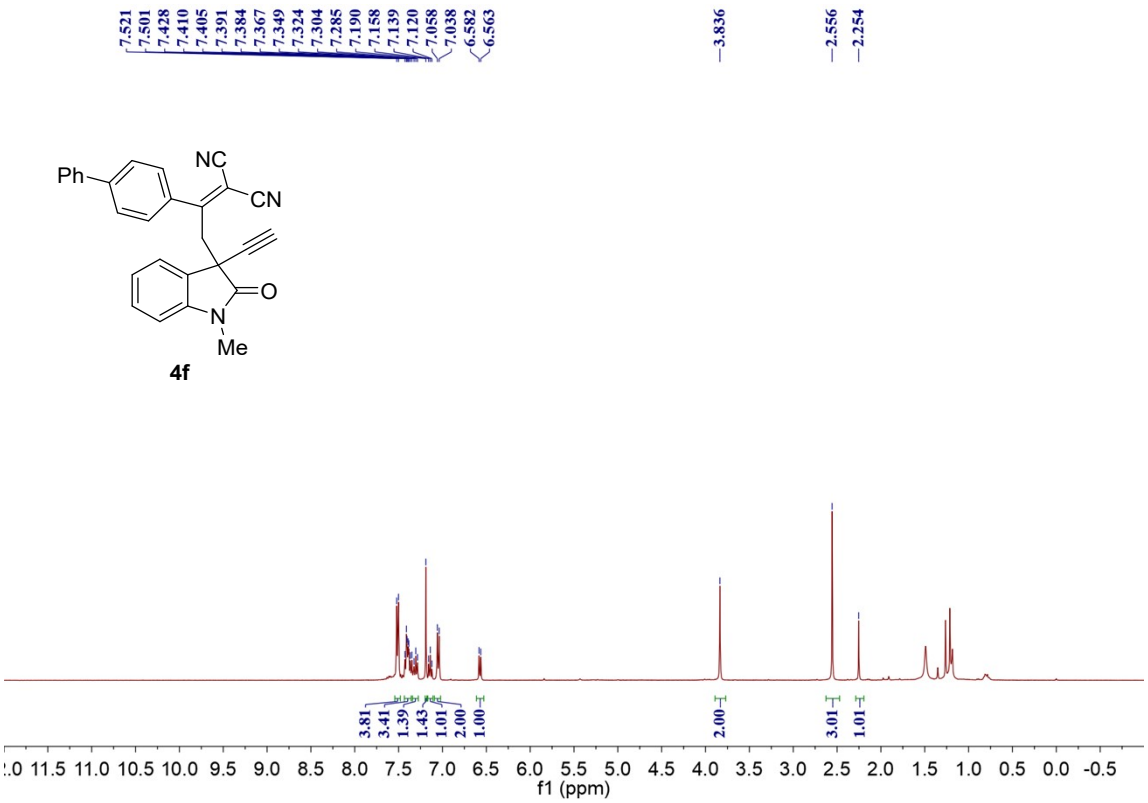


4e

^{1}H-NMR-4f



4f

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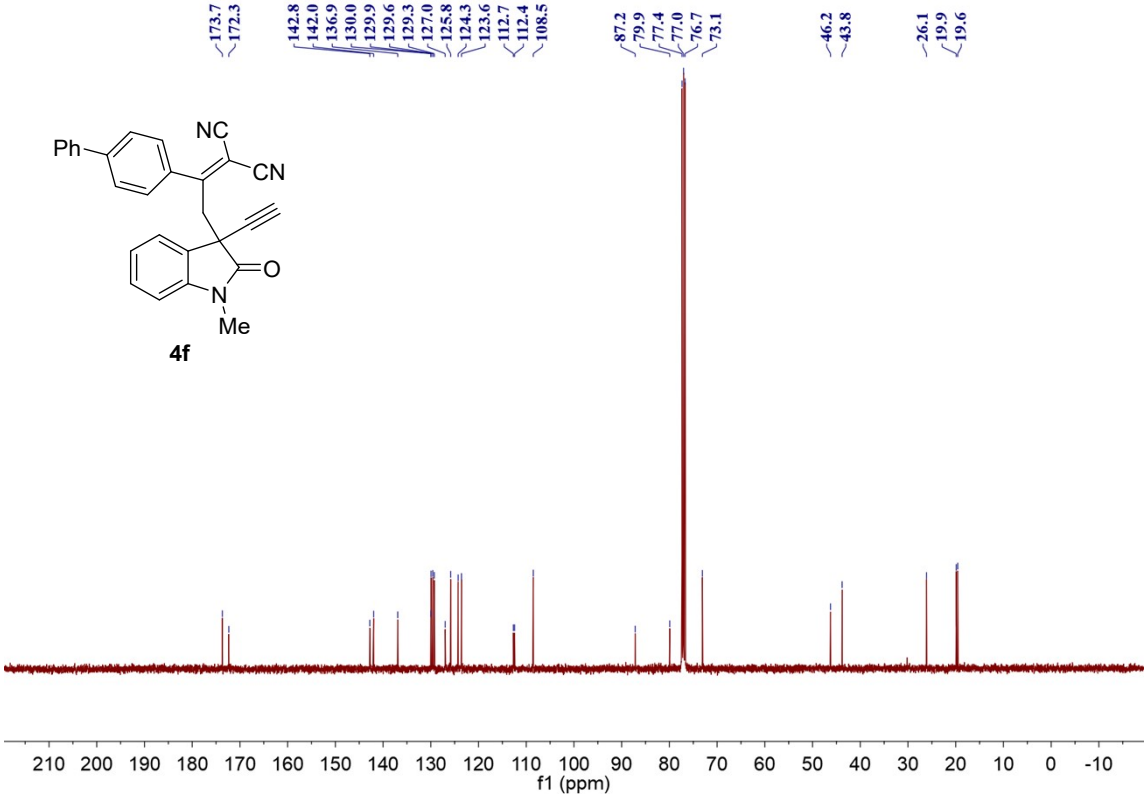

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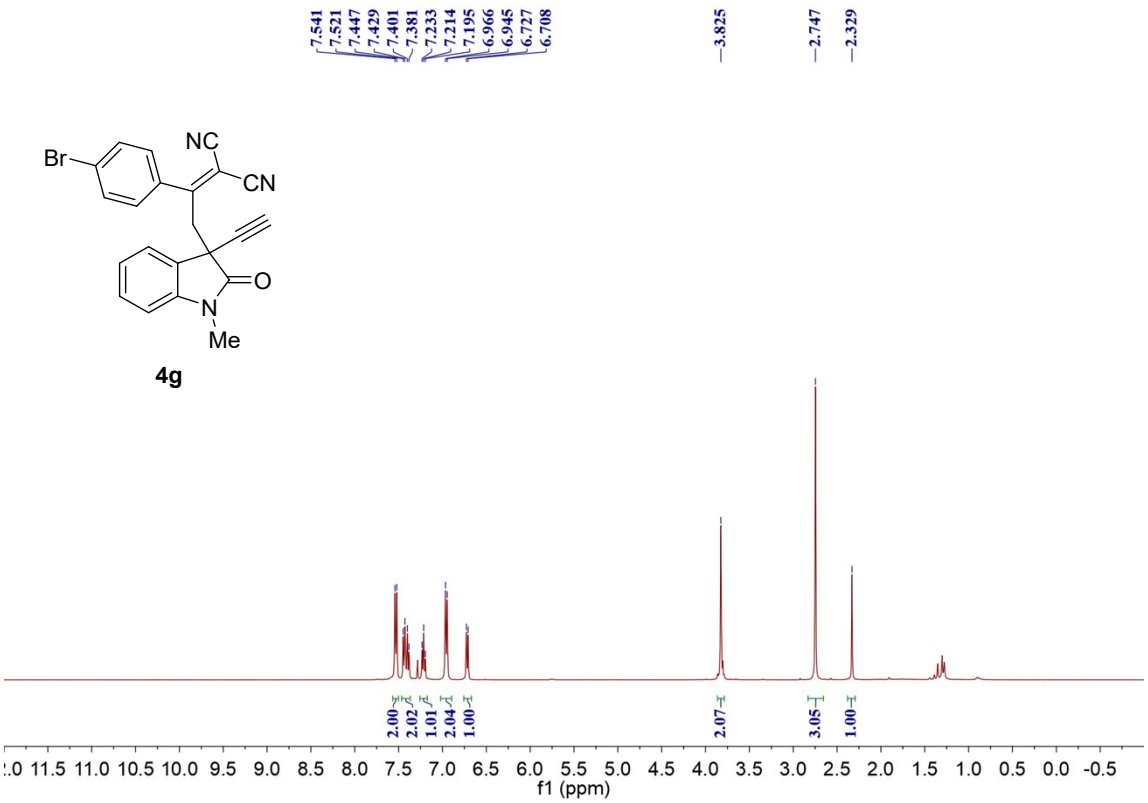

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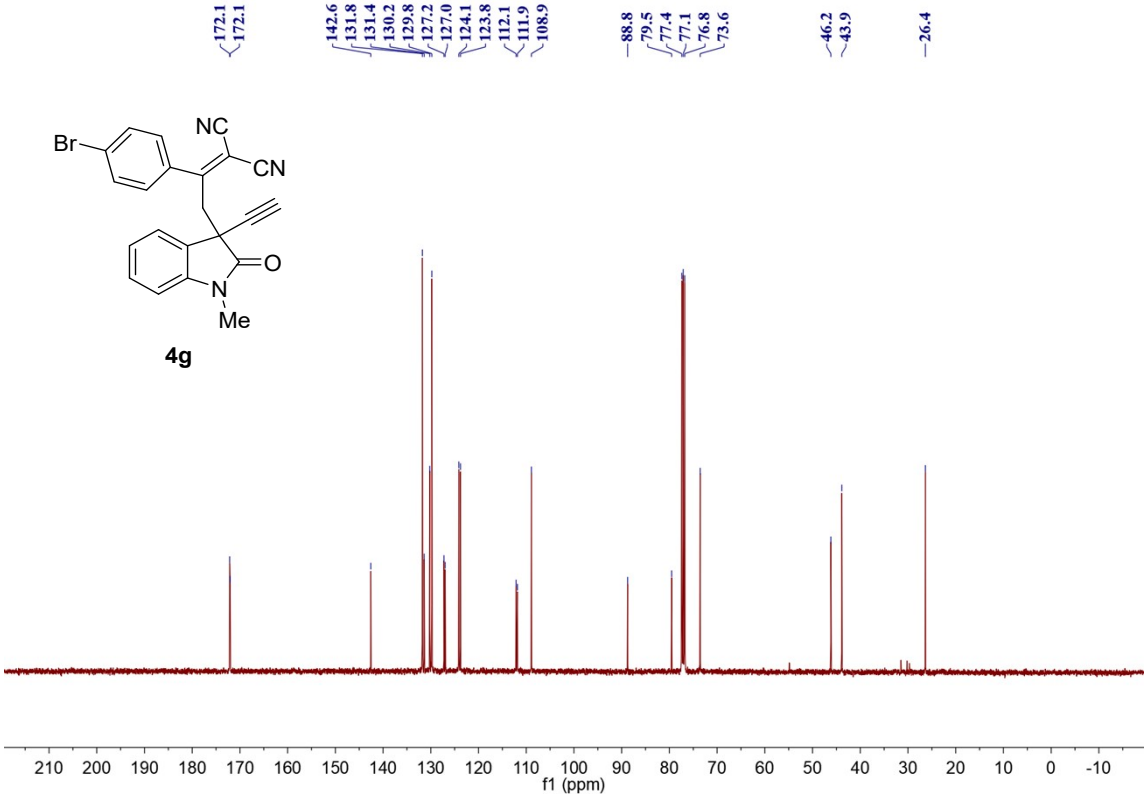

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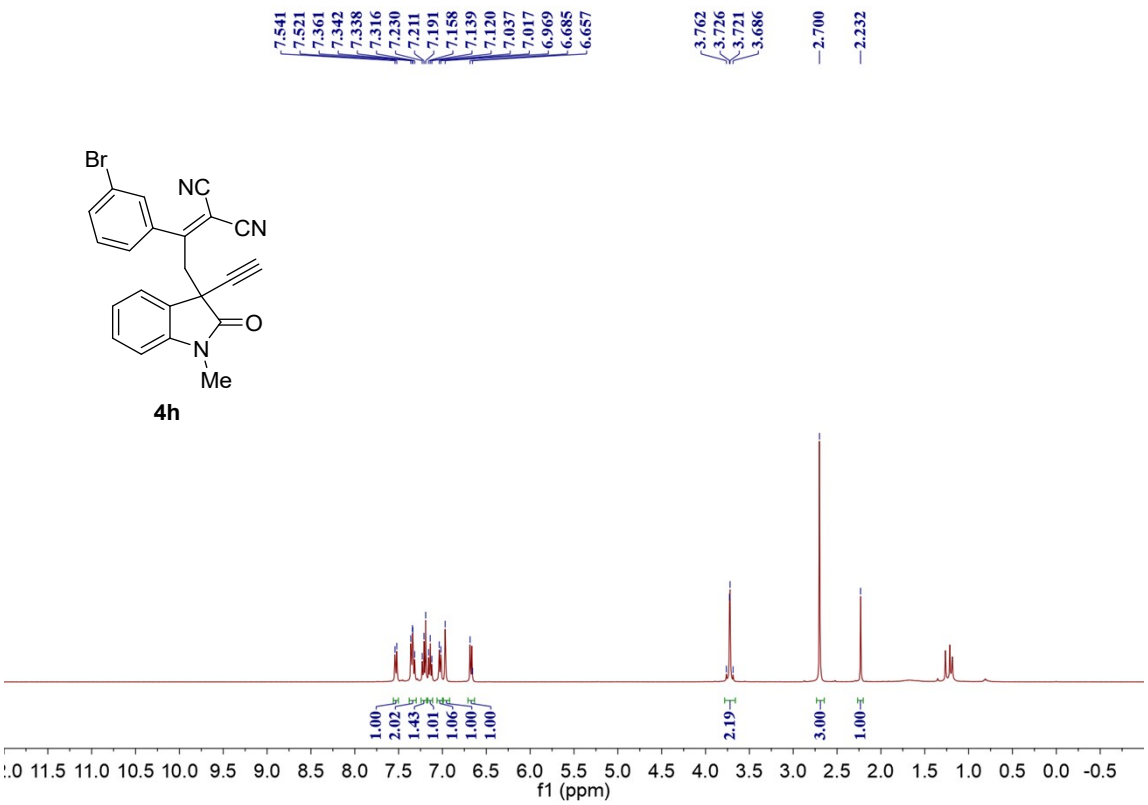
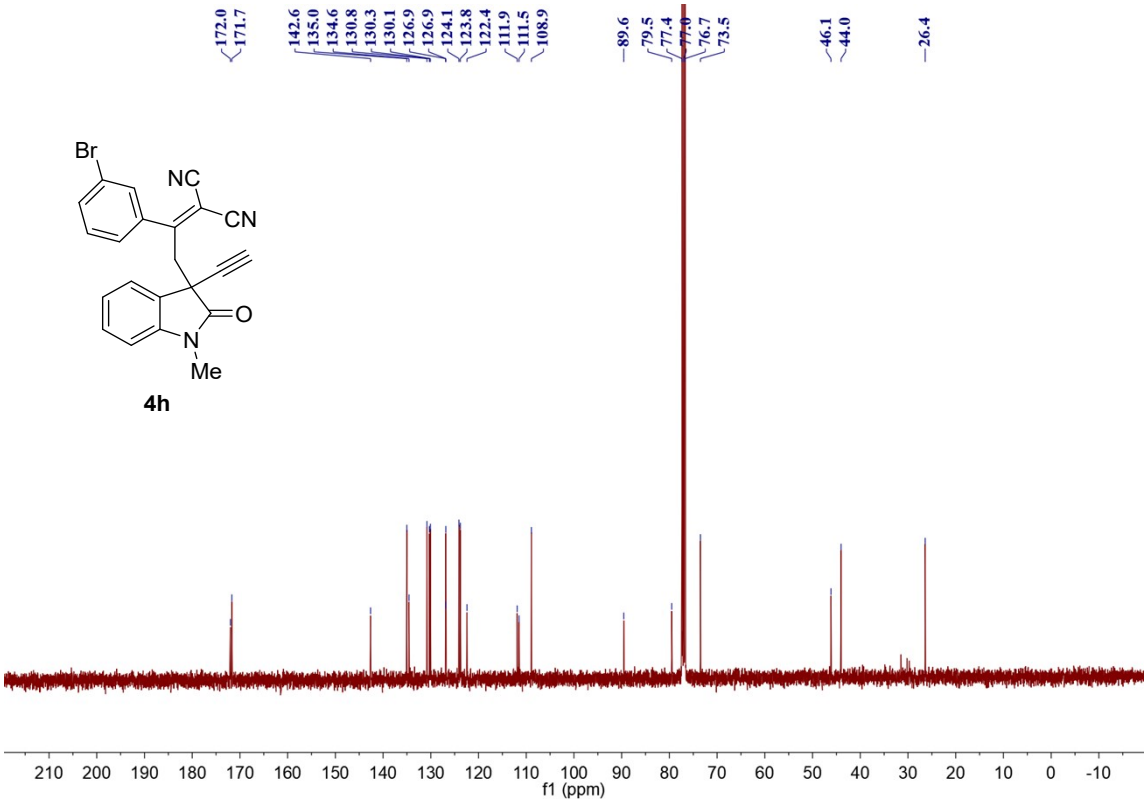
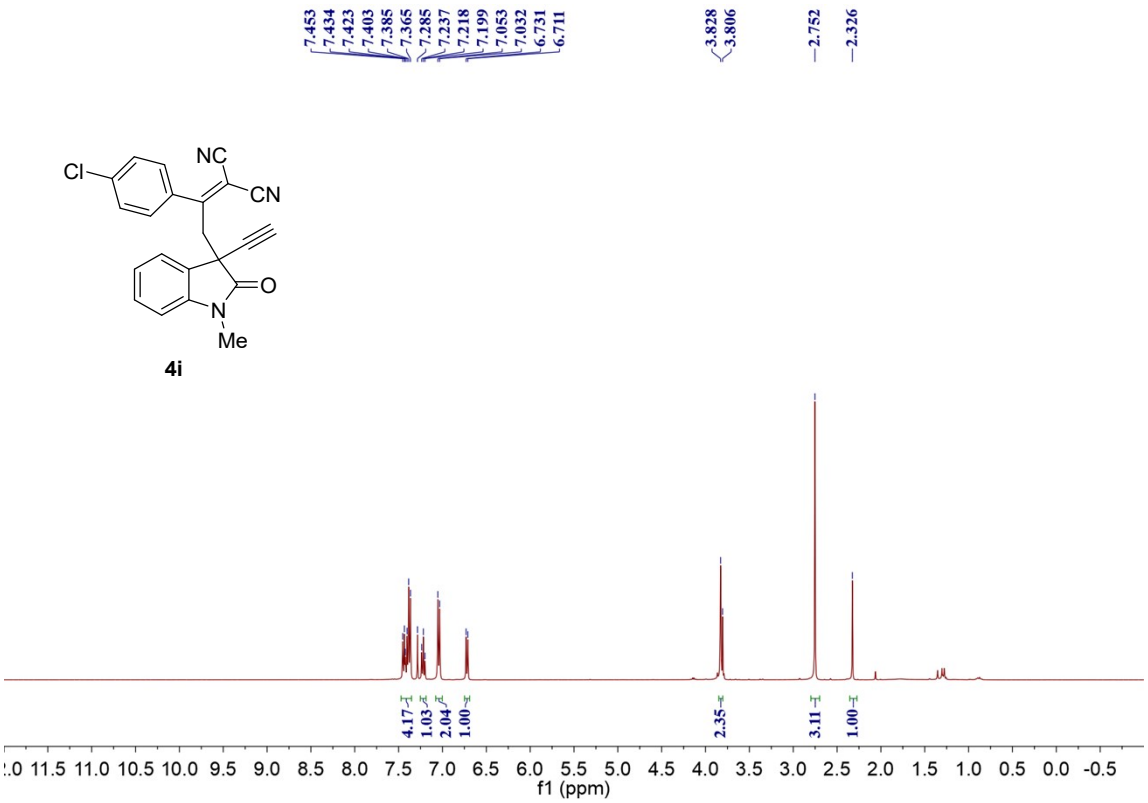


^{13}C NMR-4h



^{1}H-NMR-4i



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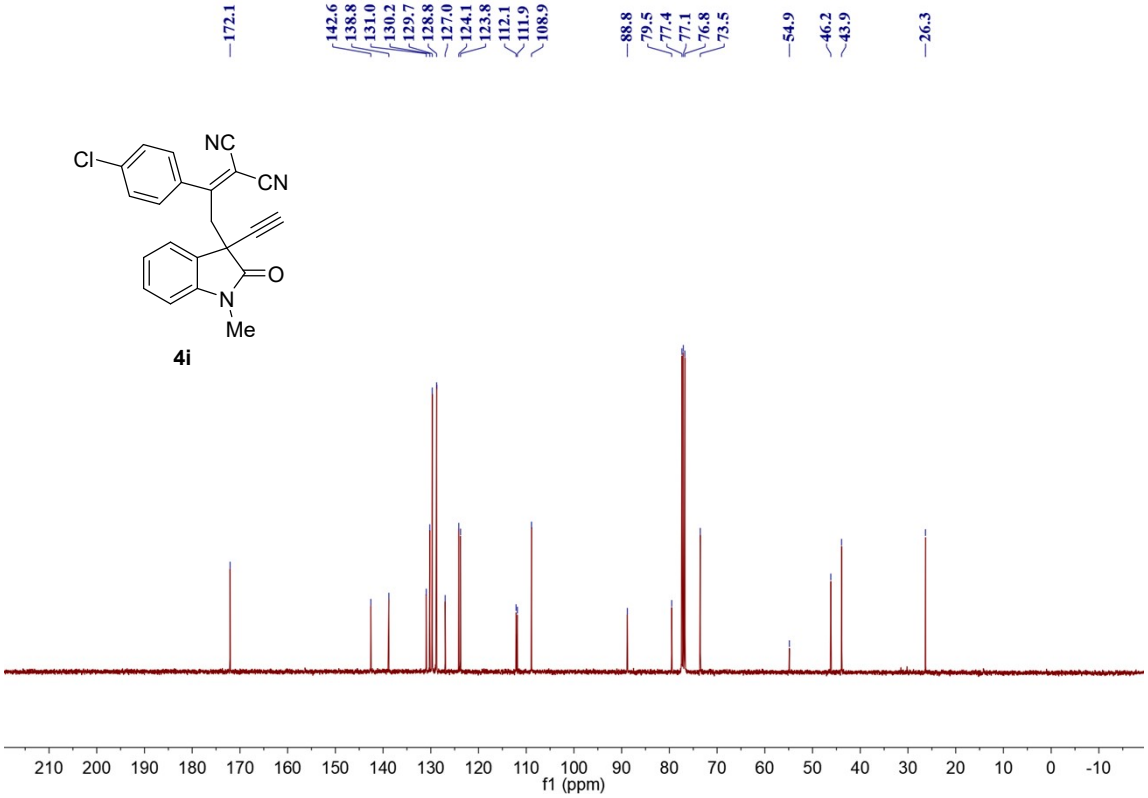

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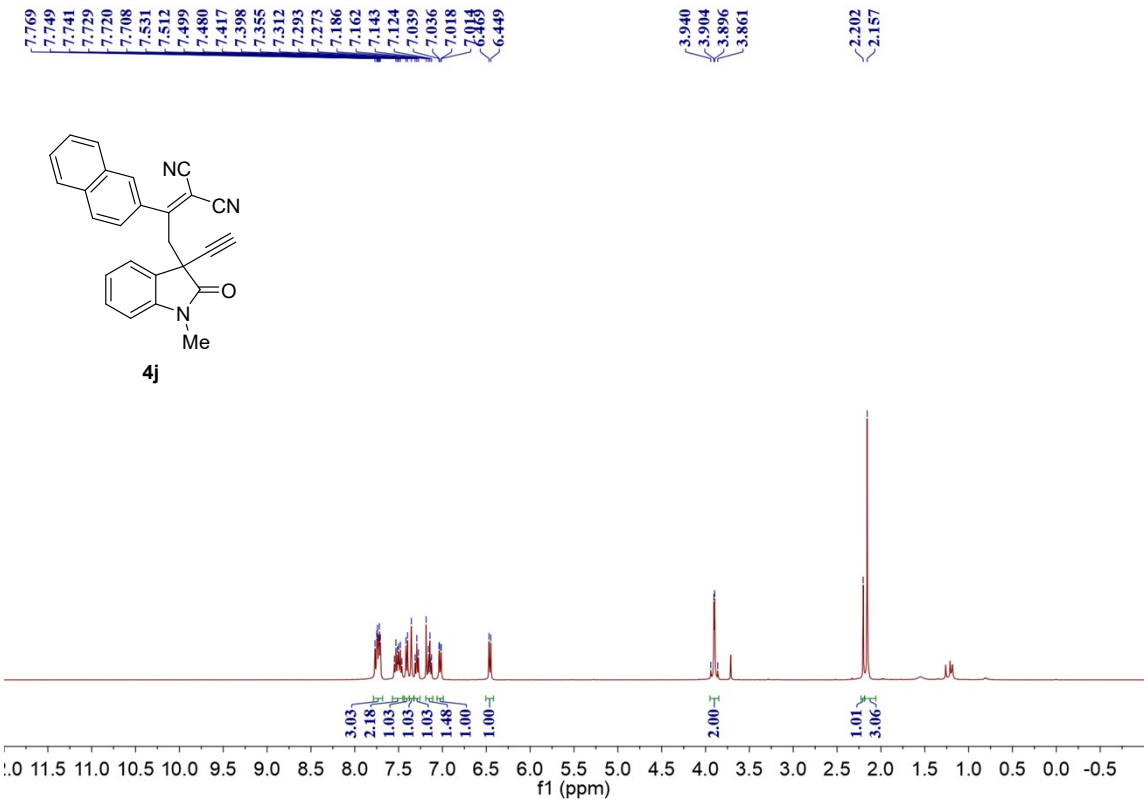

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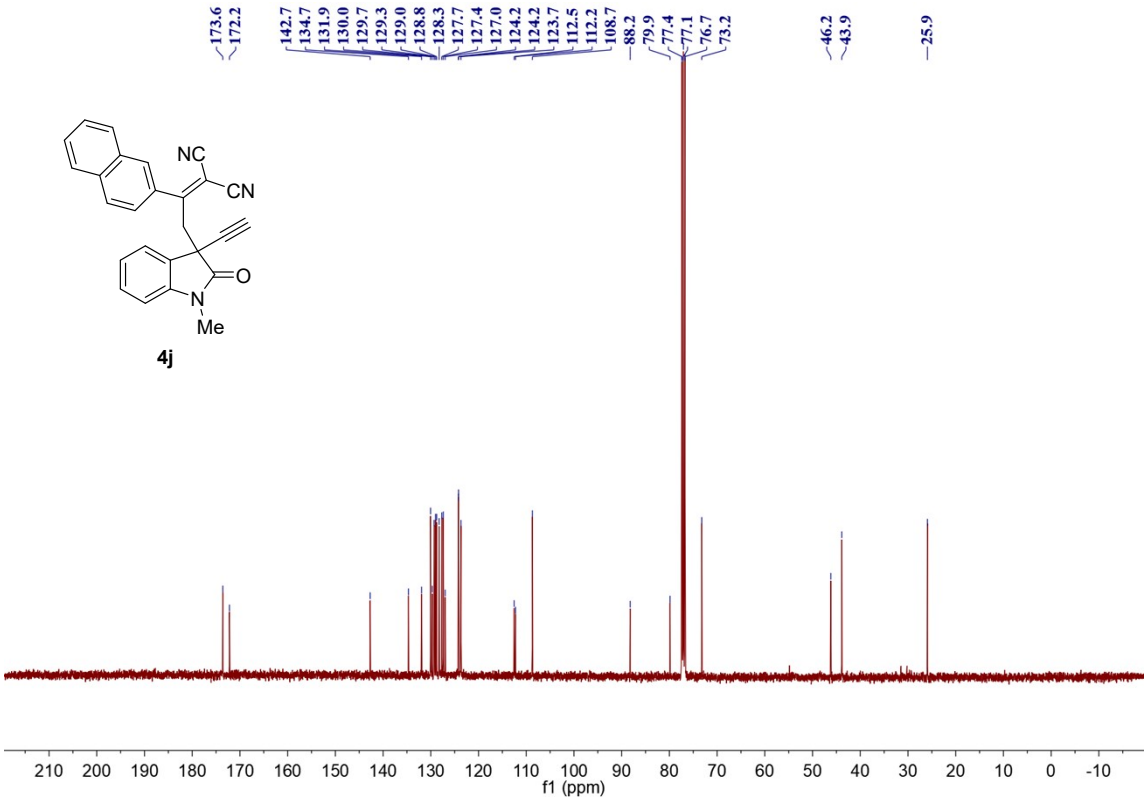

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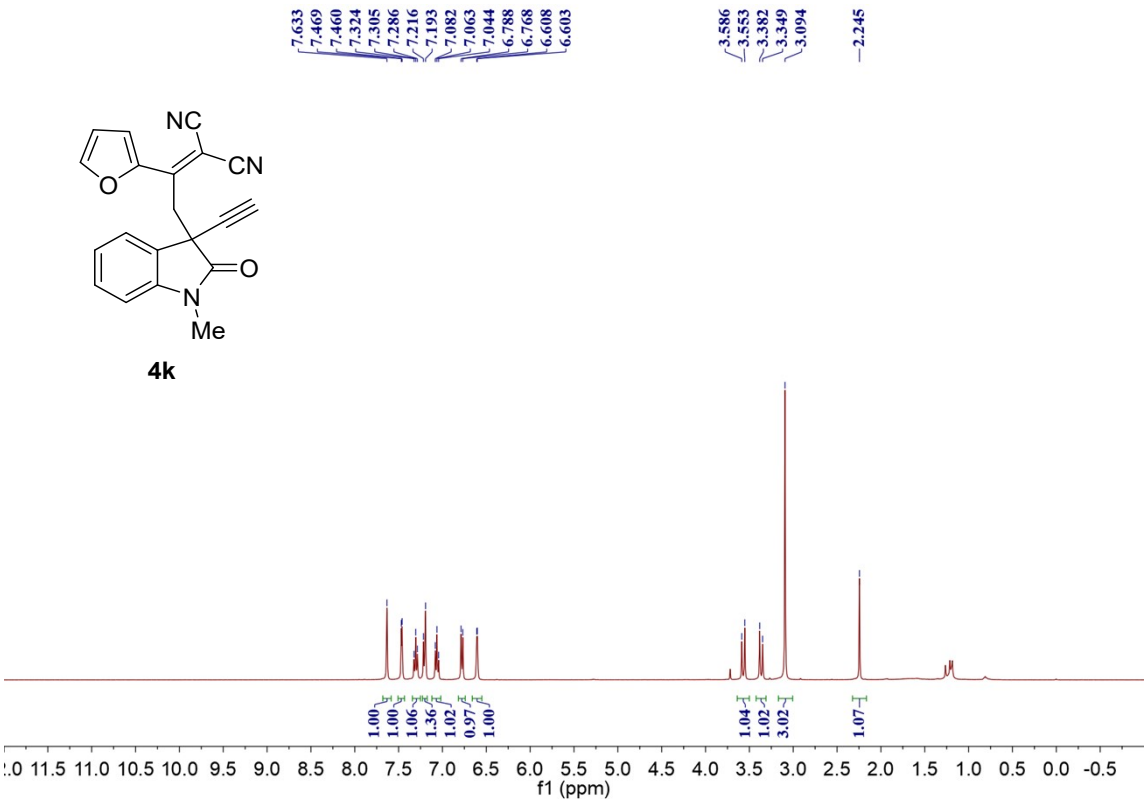
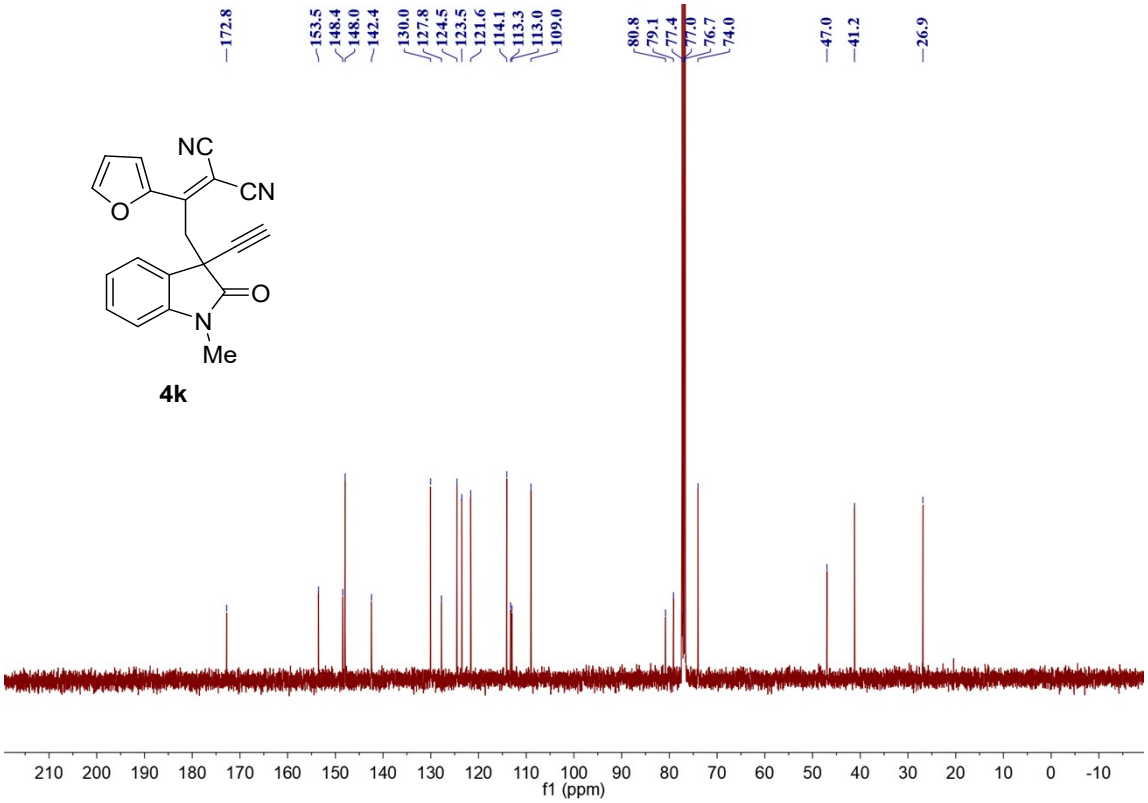
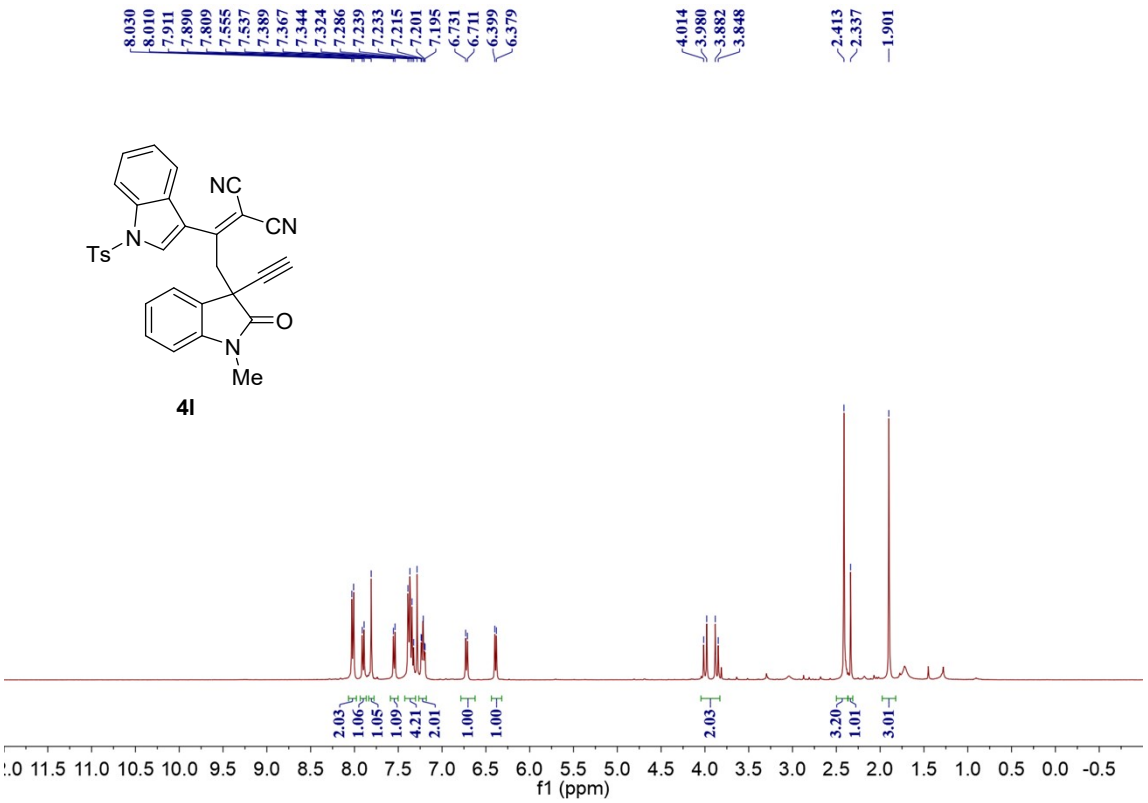


^{13}C NMR-4k



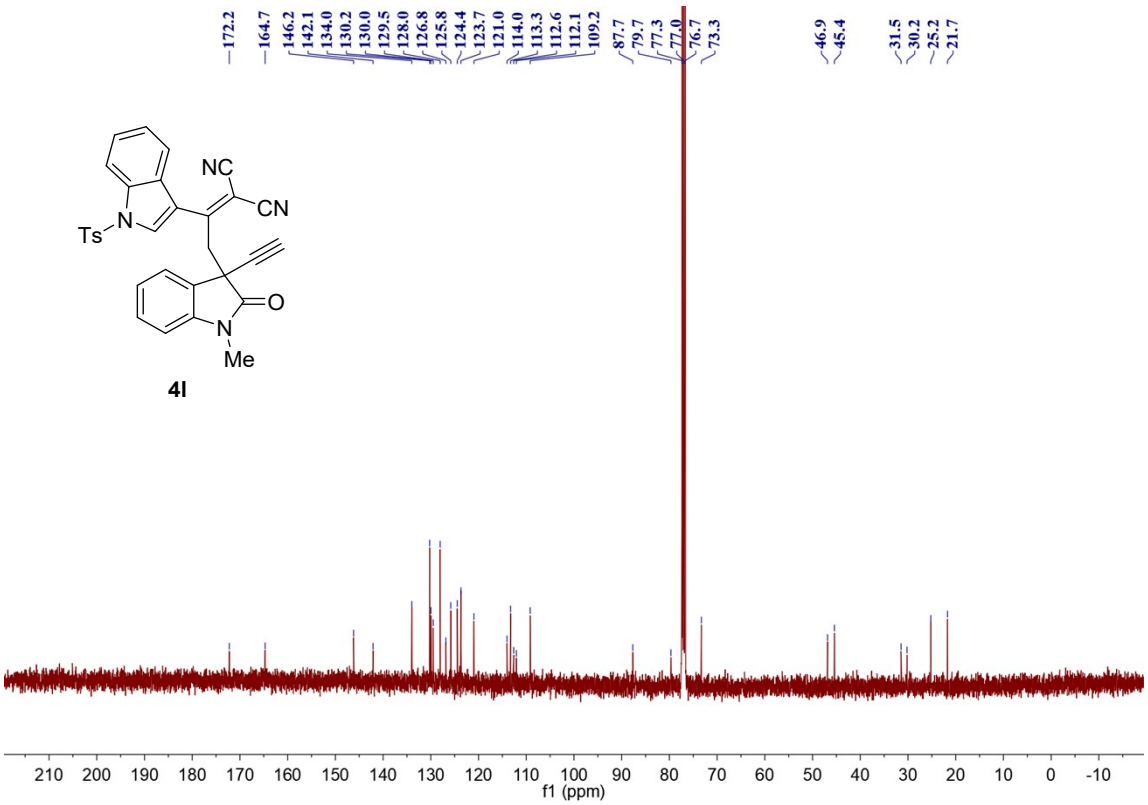
4k

^{1}H-NMR-4l



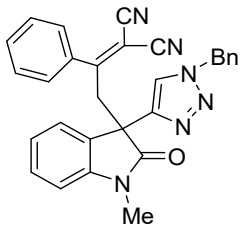
4l

^{13}C NMR-4l

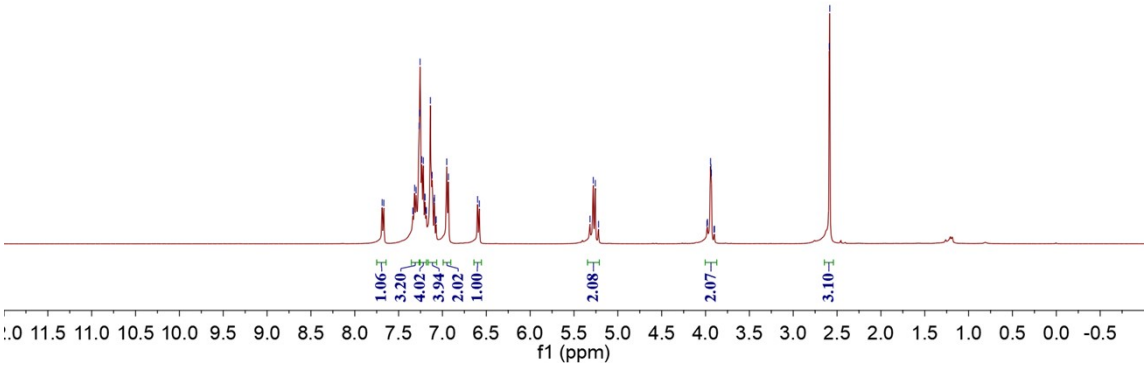


4l

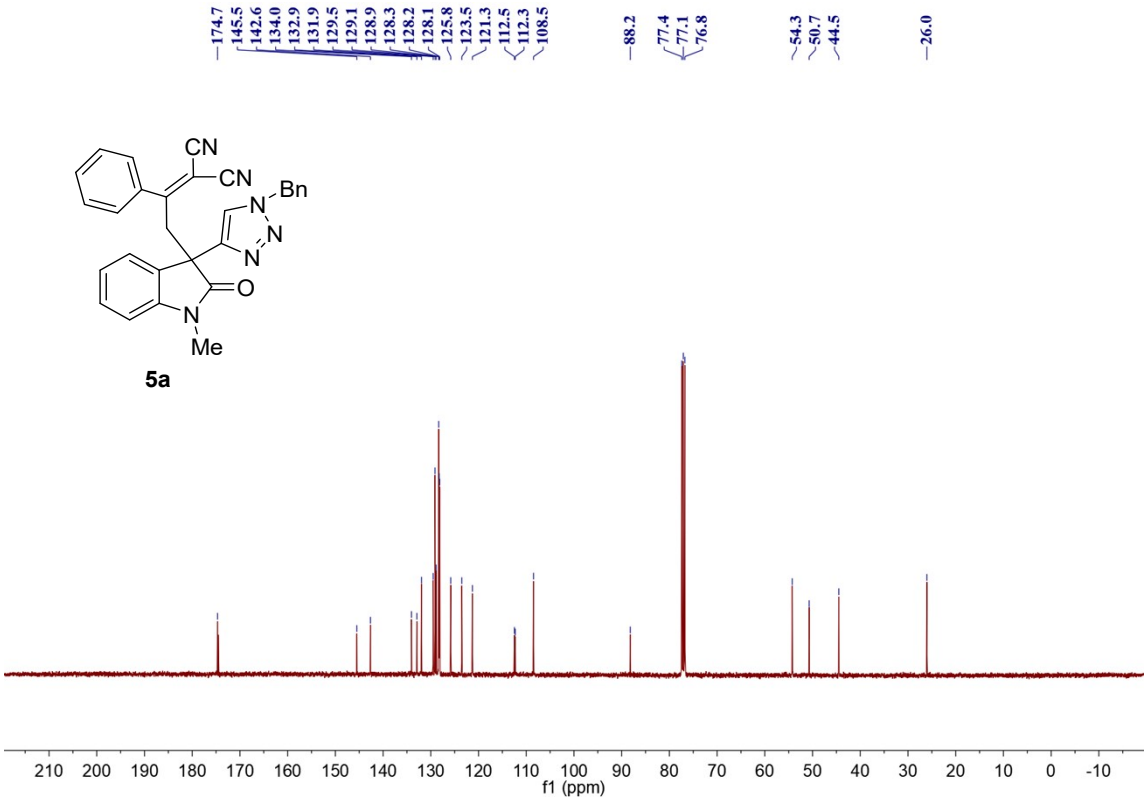
^{1}H-NMR-5a



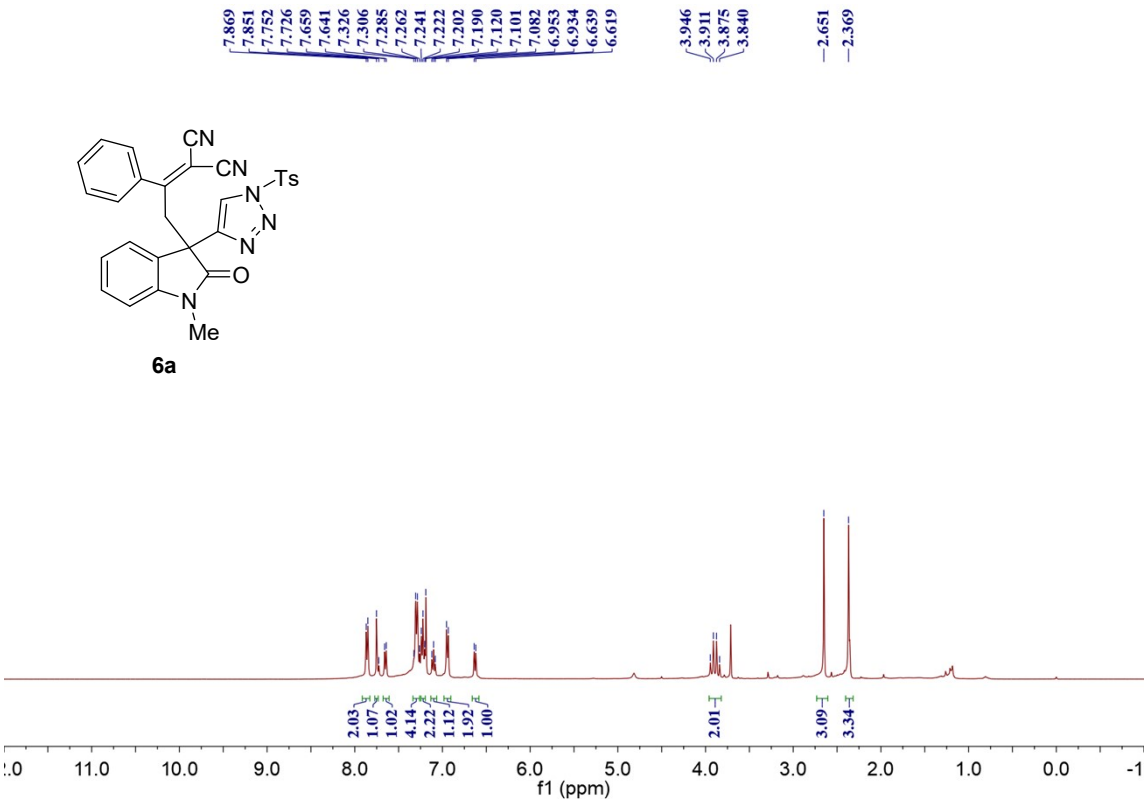
5a



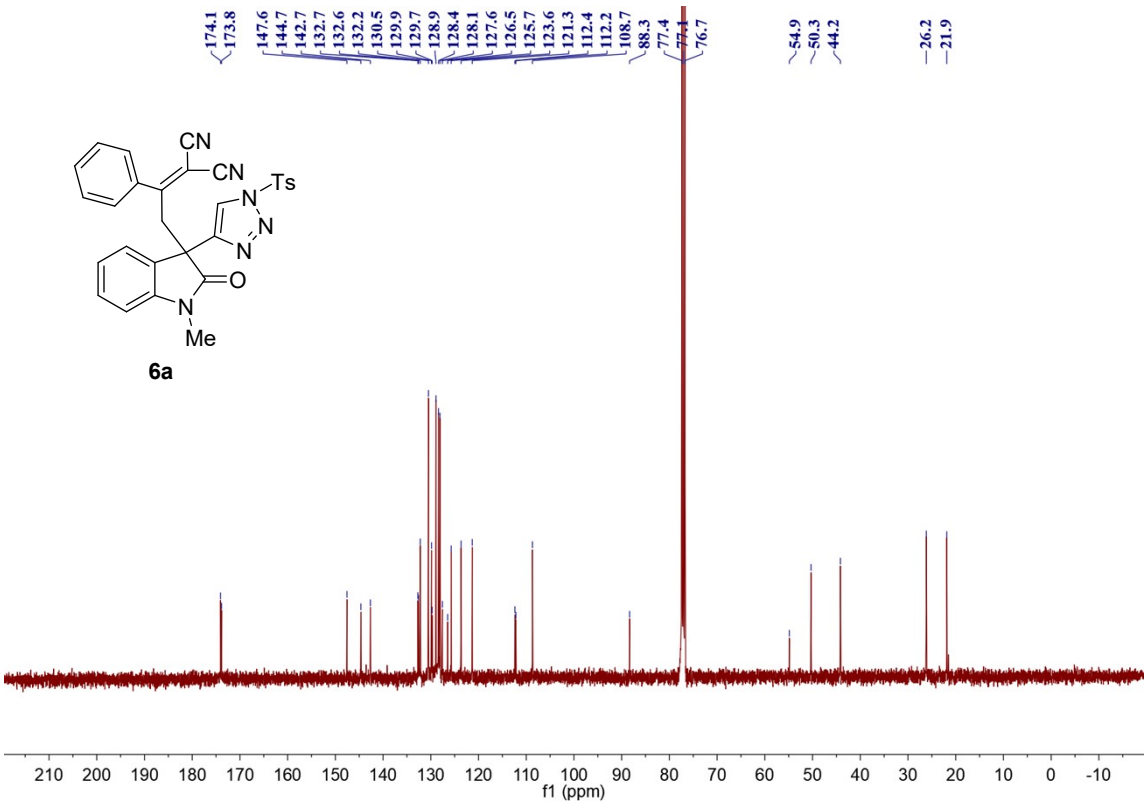
^{13}C NMR-5a



^{1}H-NMR-6a



^{13}C NMR-6a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50.3
44.2
26.2
21.9
CN
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Me
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)