

## ***Supporting Information***

### **Microwave-accelerated and benzoyl peroxide (BPO) initiated cyclization of 1,5-enynes having cyano groups with cyclic alkanes under metal-free conditions**

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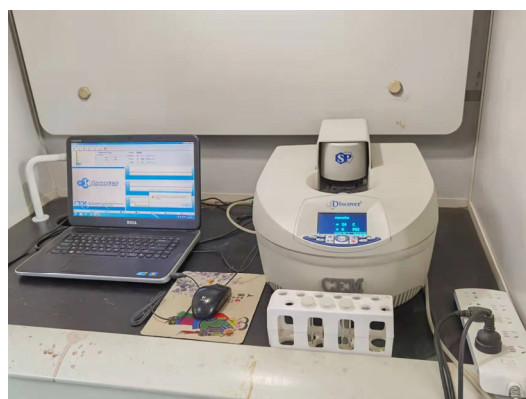
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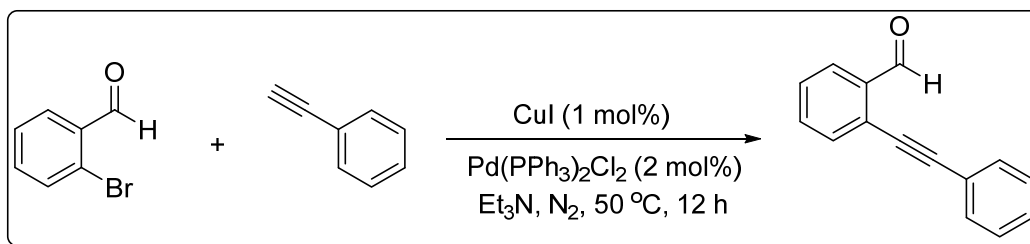
## 1. General information

The following starting materials 1,5-enynes having cyano groups were synthesized according to previously described procedures (Zou, L.; Wang, L.; Sun, L.; Xie, X.; Li, P. *Chem. Commun.* **2020**, *56*, 7933–7936). Other starting materials were purchased from commercial suppliers. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F<sub>254</sub> plates. Compounds were visualized by exposure to UV light. Flash column chromatography was performed with silica gel (300 – 400 meshes). NMR spectra were recorded on a 600 MHz spectrometer at ambient temperature, and chemical shifts were given in dimensionless  $\delta$  values and were frequency referenced relative to TMS in <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The peak patterns are indicated as follows: **s**, singlet; **d**, doublet; **t**, triplet; **q**, quartet; **m**, multiplet; **td**, triplet of doublet; **dd**, doublet of doublet; **qd**, quartet of doublet; **qt** quartet of triplet. The coupling constant, *J*, was reported in Hertz (Hz). HRMS data were recorded on an Agilent Technologies 6540 UHD ESI-TOF mass spectrometer. All MW reactions were carried out under microwave irradiation conditions and air atmosphere in a Discover SP (CEM) microwave reactor.

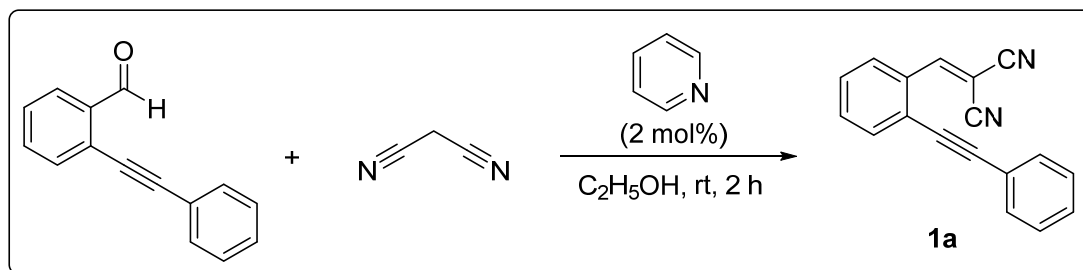


## 2. Experimental procedure

### 2.1 General procedure for the preparation of 1a



To a solution of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (70 mg, 2 mol%) and CuI (10 mg, 1 mol%) were dissolved in Et<sub>3</sub>N (10.0 mL) was added 2-bromobenzaldehyde (0.93 g, 5.0 mmol) and ethynylbenzene (0.61 g, 6.0 mmol). The resulting mixture was stirred at 50 °C for 12 h under nitrogen atmosphere. Then, the aqueous phase was extracted with EtOAc (10 mL×3). The combined organic layer were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 100:1) to give the product as a yellow liquid (75% yield).



2-(Phenylethynyl)benzaldehyde (2.06 g, 10.0 mmol) and malononitrile (0.99 g, 15.0 mmol) were dissolved in EtOH (20 mL). Pyridine (1.5 mL, 0.2 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 2 h. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 50:1) to give the product **1a** in 95% yield as a yellow solid.

## 2.2 Further optimization of reaction conditions

**Table S1. Screening solvents**<sup>[a]</sup>

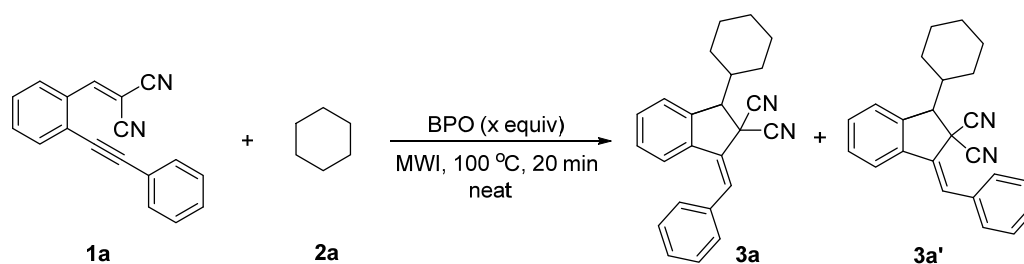
Entry	Solvent	Yield of <b>3a</b> (%) <sup>[b]</sup>	Yield of <b>3a'</b> (%) <sup>[b]</sup>
1	MeCN	15	trace
2	DMSO	21	trace
3	H <sub>2</sub> O	0	0
4	DCE	0	0
5	DCM	12	0
6	DMF	12	trace
7	Acetone	0	0
8	Cyclohexane	75	15

<sup>[a]</sup>All reactions were carried out with **1a** (0.3 mmol), **2a** (1.0 mL), solvent (1.0 mL) and BPO (0.045 mmol) at 100 °C under microwave irradiation for 20 min; 2.0 mL of **2a** was added when the reaction was conducted in neat conditions. <sup>[b]</sup>Isolated yield.

**Table S2. Screening Initiator**<sup>[a]</sup>

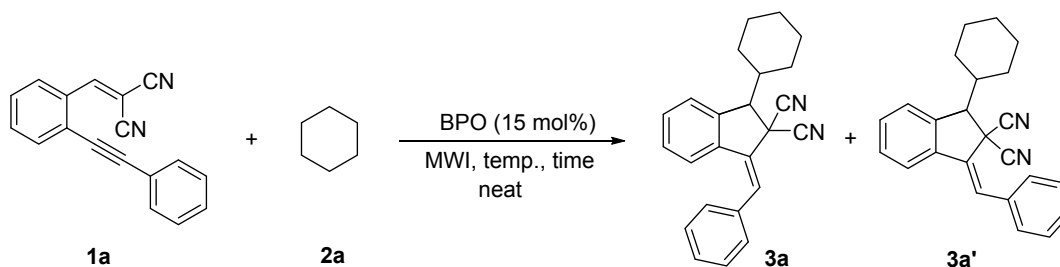
Entry	Initiator	Yield <b>3a</b> of (%) <sup>[b]</sup>	Yield of <b>3a'</b> (%) <sup>[b]</sup>
1	BPO	75	15
2	TBHP	55	12
3	<i>m</i> -CPBA	43	8
4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	45	7
5	H <sub>2</sub> O <sub>2</sub>	22	trace
6	Selectfluor	13	0

<sup>[a]</sup>All reactions were carried out with **1a** (0.3 mmol), **2a** (2.0 mL) and initiator (0.045 mmol) at 100 °C under microwave irradiation for 20 min. <sup>[b]</sup>Isolated yield.

**Table S3. Screening the loading of BPO<sup>[a]</sup>**

Entry	BPO (x equiv.)	Yield of <b>3a</b> (%) <sup>[b]</sup>	Yield of <b>3a'</b> (%) <sup>[b]</sup>
1	1.5	36	trace
2	1.0	35	trace
3	0.5	40	trace
4	0.25	40	trace
5	0.20	55	12
6	0.15	75	15
7	0.10	43	trace
8	0.05	21	trace

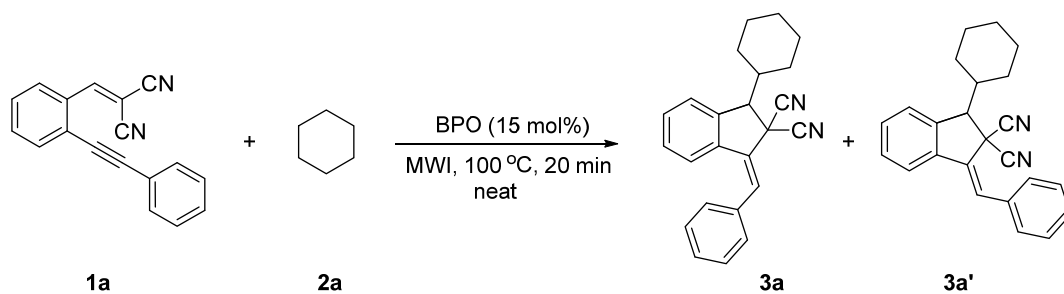
<sup>[a]</sup>All reactions were carried out with **1a** (0.3 mmol), **2a** (2.0 mL) and BPO (x equiv.) at 100 °C under microwave irradiation for 20 min. <sup>[b]</sup>Isolated yield.

**Table S4. Screening reaction time and temperature<sup>[a]</sup>**

Entry	Temp. (°C)	Time	Yield of <b>3a</b> (%) <sup>[b]</sup>	Yield of <b>3a'</b> (%) <sup>[b]</sup>
1	100	30 min	75	7
2	100	20 min	75	15
3	100	15 min	55	12
4 <sup>[c]</sup>	100	12 h	39	trace
4	90	20 min	43	trace
5	90	15 min	45	8
6	80	20 min	22	trace
7	80	10 min	13	0

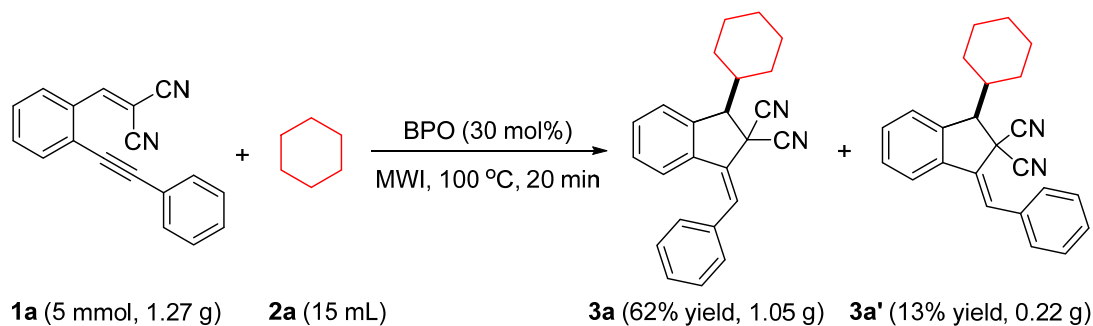
<sup>[a]</sup>All reactions were carried out with **1a** (0.3 mmol), **2a** (2.0 mL) and BPO (0.045 mmol) under microwave irradiation. <sup>[b]</sup>Isolated yield. <sup>[c]</sup>In an oil bath.

### 2.3 Typical procedure for the cyclization of **1a** and **2a**



In a 10 mL of sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 0.3 mmol), BPO (15 mol%) and cyclohexane (**2a**, 2 mL). The reaction vessel was placed in a Discover SP (CEM) microwave reactor, and the reaction mixture was irradiated at 150 W and 100 °C for 20 min. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (petroleum ether) to give the product **3a** (white solid, 76.1 mg, 75% yield) and **3a'** (white solid, 15.2 mg, 15% yield).

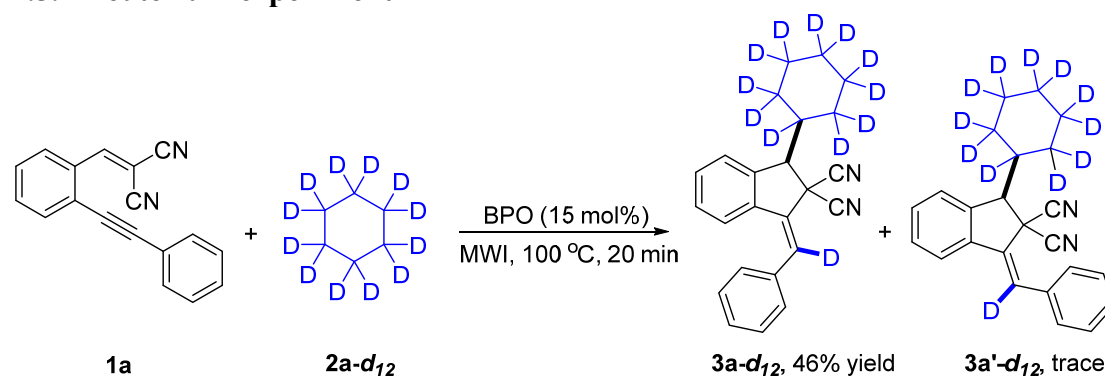
### 2.4 Gram-scale synthesis of **3a** and **3a'**



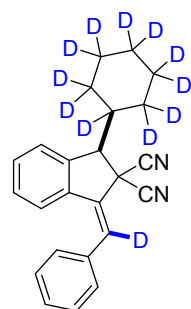
In a 35 mL of sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile **1a** (1.27 g, 5.0 mmol), BPO (484.5 mg, 1.5 mmol) and cyclohexane **2a** (15 mL). The reaction vessel was placed in a Discover SP (CEM) microwave reactor, and the reaction mixture was irradiated at 150 W and 100 °C for 20 min. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (petroleum ether) to give the desired product **3a** in 62% yield as a white solid and **3a'** in 13% yield as a white solid.

## 2.5 Mechanistic studies

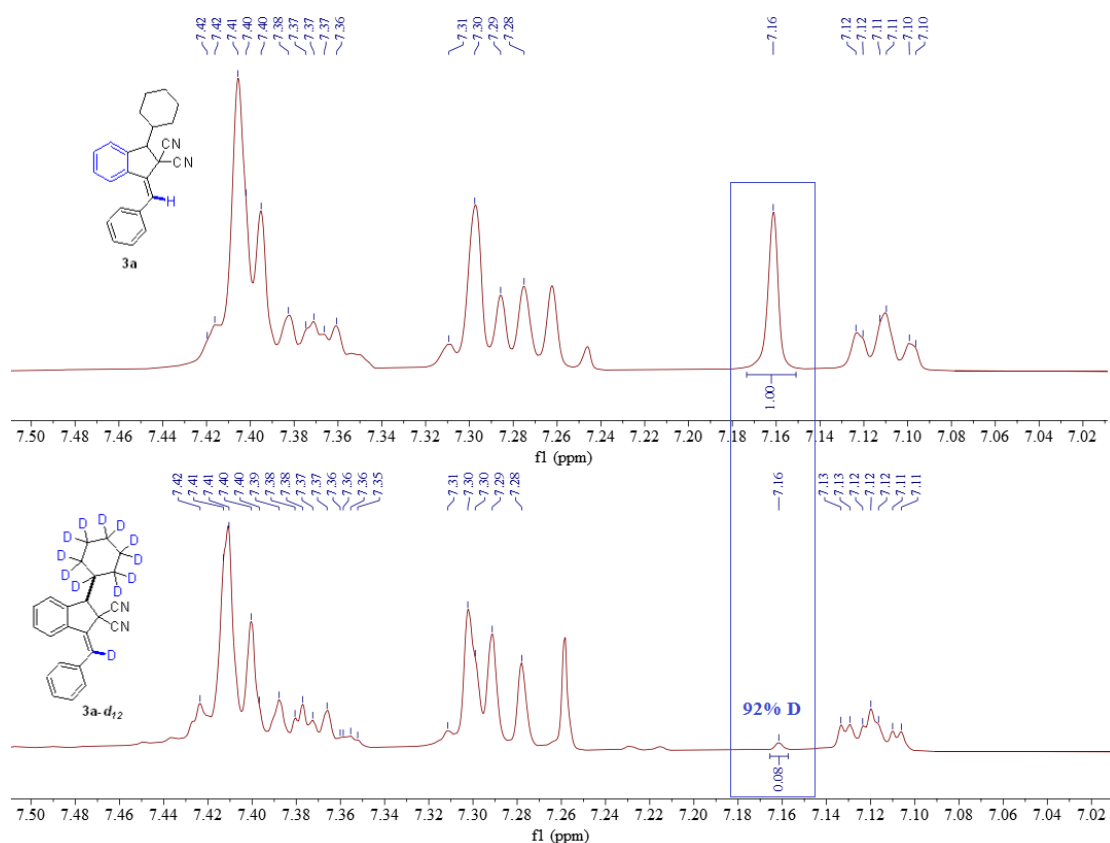
### 2.5.1 Deuterium experiment



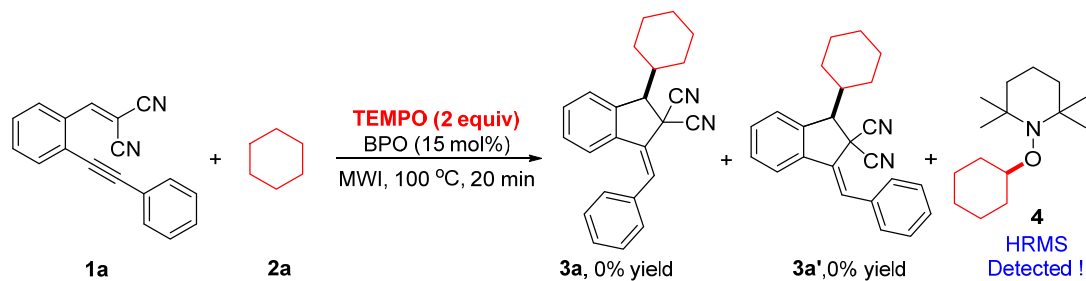
In a 10 mL of sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 0.3 mmol), BPO (15 mol%) and cyclohexane-*d*<sub>12</sub> (**2a-d**<sub>12</sub>, 2 mL). The reaction vessel was placed in a Discover SP (CEM) microwave reactor, and the reaction mixture was irradiated at 150 W and 100 °C for 20 min. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (petroleum ether) to give the desired product **3a-d**<sub>12</sub> in 46% yield as a white solid, and only trace amount of **3a'-d**<sub>12</sub> was obtained.



**(E)-1-(Cyclohexyl-*d*<sub>11</sub>)-3-(phenylmethylene-*d*)-1,3-dihydro-2H-indene-2,2-dicarbonitrile (**3a-d**<sub>12</sub>)**. White solid; 48.3 mg, 46% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.42–7.35 (m, 5H), 7.31–7.28 (m, 3H), 7.13–7.11 (m, 1H), 3.66 (s, 1H).



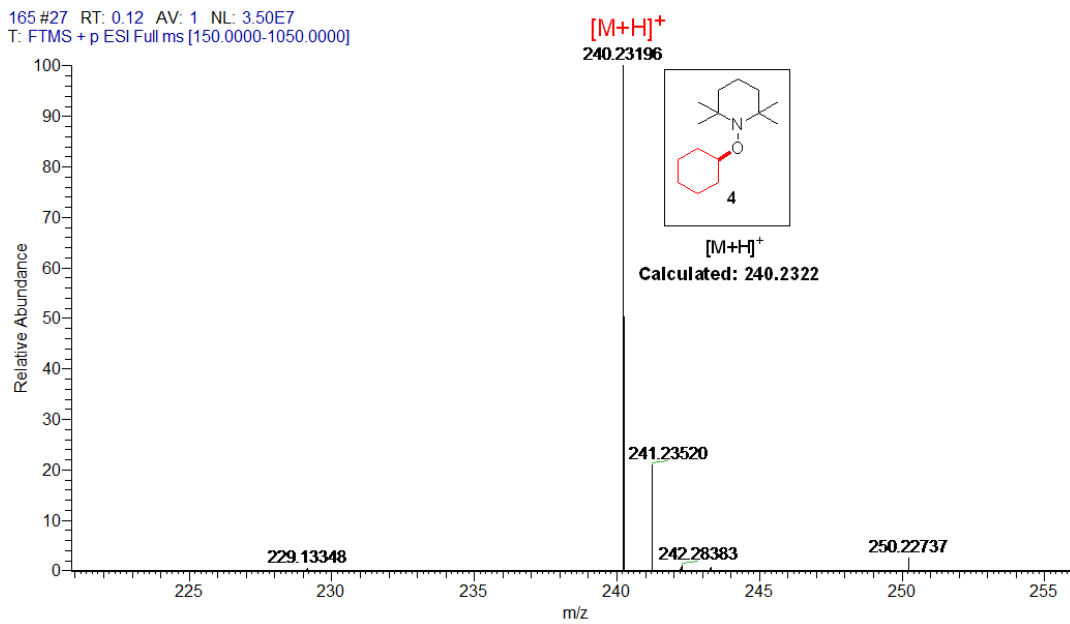
## 2.5.2 Radical inhibiting experiments



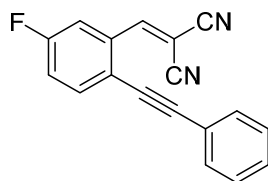
In a 10 mL of sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 0.3 mmol), TEMPO (93.8 mg, 0.6 mmol), BPO (15 mol%) and cyclohexane (**2a**, 2 mL). The reaction vessel was placed in a Discover SP (CEM) microwave reactor, and the reaction mixture was irradiated at 150 W and 100 °C for 20 min. In the reaction mixture, no desired product **3a** and **3a'** was detected, while an adduct of TEMPO with a cyclohexyl radical was formed, which was detected by HPLC/HRMS.



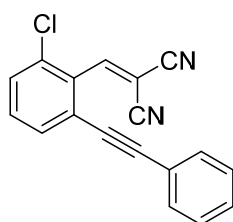
165 #27 RT: 0.12 AV: 1 NL: 3.50E7  
T: FTMS + p ESI Full ms [150.0000-1050.0000]



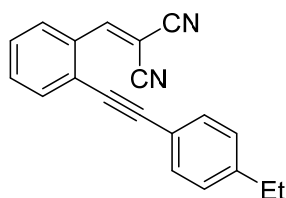
### 3. Characterization data for the products



**2-(5-Fluoro-2-(phenylethynyl)benzylidene)malononitrile (1h).** Yellow solid, 76% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.40 (s, 1H), 8.00 (dd,  $J = 9.2, 2.6$  Hz, 1H), 7.69 (dd,  $J = 8.7, 5.4$  Hz, 1H), 7.56–7.53 (m, 2H), 7.43–7.39 (m, 3H), 7.31 (td,  $J = 8.1, 2.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 161.9 (d,  $J = 253.4$  Hz), 156.5 (d,  $J = 2.7$  Hz), 135.2 (d,  $J = 8.2$  Hz), 133.3 (d,  $J = 8.2$  Hz), 131.7, 129.6, 128.7, 123.0 (d,  $J = 3.3$  Hz), 121.5 (d,  $J = 22.4$  Hz), 121.5, 114.8 (d,  $J = 24.6$  Hz), 113.3, 111.8, 98.4 (d,  $J = 1.75$  Hz), 85.4, 84.2;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : -107.0. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{18}\text{H}_{10}\text{FN}_2^+$ : 273.0823, Found: 273.0821.

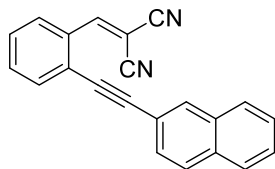


**2-(2-Chloro-6-(phenylethynyl)benzylidene)malononitrile (1i).** Yellow solid, 67% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.12 (s, 1H), 7.61–7.59 (m, 1H), 7.55–7.54 (m, 2H), 7.48–7.45 (m, 2H), 7.42–7.39 (m, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 157.7, 133.7, 132.2, 131.8, 131.6, 131.2, 129.8, 129.5, 128.6, 124.8, 121.6, 112.5, 111.0, 97.7, 92.7, 85.5. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{18}\text{H}_{10}\text{ClN}_2^+$ : 289.0527, Found: 289.0521.

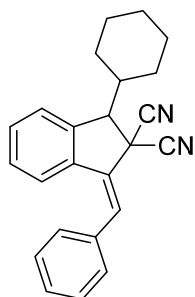


**2-(2-((4-Ethylphenyl)ethynyl)benzylidene)malononitrile (1n).** Yellow solid, 62% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.46 (s, 1H), 8.30 (d,  $J = 8.0$  Hz, 1H), 7.68–7.67 (m, 1H), 7.59–7.57 (m, 1H), 7.49–7.47 (m, 3H), 7.24–7.23 (m, 2H), 2.70 (q,  $J = 7.6$

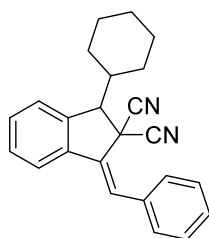
Hz, 2H), 1.26 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 158.0, 146.2, 133.8, 133.3, 131.8, 131.6, 128.8, 128.2, 127.9, 127.0, 118.8, 113.8, 112.4, 99.0, 84.6, 83.8, 28.9, 15.3. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{20}\text{H}_{15}\text{N}_2^+$ : 283.1230, Found: 283.1227.



**2-(2-(Naphthalen-2-ylethynyl)benzylidene)malononitrile (1w).** Yellow solid, 78% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.46 (s, 1H), 8.29 (d,  $J = 8.1$  Hz, 1H), 8.08–8.07 (m, 1H), 7.85–7.82 (m, 3H), 7.71–7.70 (m, 1H), 7.59–7.55 (m, 2H), 7.54–7.52 (m, 2H), 7.47 (t,  $J = 7.7$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 151.6, 127.6, 127.2, 127.1, 126.6, 125.9, 125.5, 122.8, 122.2, 121.8, 121.7, 121.7, 121.7, 121.2, 120.7, 120.6, 112.7, 107.6, 106.2, 92.8, 79.3, 77.7. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{22}\text{H}_{12}\text{N}_2\text{Na}^+$ : 327.0893, Found: 327.0891.

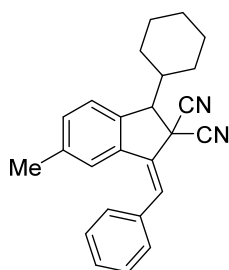


**(E)-1-Benzylidene-3-cyclohexyl-1H-indene-2,2(3H)-dicyanonitrile (3a).** White solid, 76.1 mg, 75% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.42–7.36 (m, 5H), 7.31–7.25 (m, 3H), 7.16 (s, 1H), 7.12–7.10 (m, 1H), 3.66 (d,  $J = 3.4$  Hz, 1H), 2.20 (td,  $J = 11.7, 3.1$  Hz, 1H), 1.88–1.82 (m, 2H), 1.77–1.75 (m, 1H), 1.67–1.65 (m, 2H), 1.48–1.38 (m, 2H), 1.32–1.29 (m, 1H), 1.05–0.98 (m, 1H), 0.66 (qd,  $J = 12.7, 3.4$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.1, 136.3, 135.0, 134.8, 129.8, 128.8, 128.6, 128.2, 128.1, 127.3, 126.5, 124.9, 116.5, 114.3, 57.9, 46.1, 41.8, 31.1, 27.4, 26.5, 25.8, 25.7. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{23}\text{N}_2^+$ : 339.1856, Found: 339.1852.



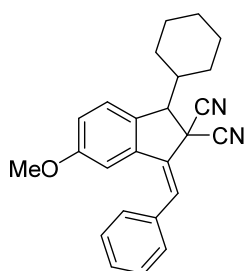
**(Z)-1-Benzylidene-3-cyclohexyl-1,3-dihydro-2H-indene-2,2-dicarbonitrile (3a').**

White solid, 15.2 mg, 15% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60–7.57 (m, 3H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.42–7.39 (m, 2H), 7.38–7.35 (m, 2H), 7.33 (s, 1H), 3.81 (d,  $J = 3.3$  Hz, 1H), 2.15–2.10 (m, 1H), 1.84–1.77 (m, 2H), 1.59 (d,  $J = 13.6$  Hz, 1H), 1.55–1.52 (m, 1H), 1.47–1.40 (m, 2H), 1.37–1.31 (m, 1H), 1.18 (dddd,  $J = 16.9, 13.3, 8.4, 3.7$  Hz, 1H), 0.94 (qt,  $J = 12.8, 3.7$  Hz, 1H), 0.36 (qd,  $J = 12.7, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 139.7, 137.9, 134.6, 133.8, 129.6, 129.3, 129.0, 128.9, 128.6, 126.1, 125.7, 121.4, 116.5, 112.3, 60.0, 42.2, 41.8, 31.2, 27.1, 26.5, 25.7, 25.5. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{Na}^+$ : 361.1675, Found: 361.1672.



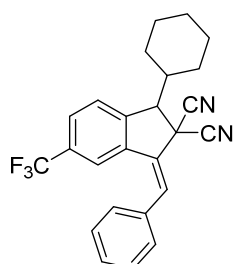
**(E)-3-Benzylidene-1-cyclohexyl-5-methyl-1H-indene-2,2(3H)-dicarbonitrile (3b).**

White solid, 73.1 mg, 69% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43–7.35 (m, 5H), 7.19–7.18 (m, 1H), 7.12–7.08 (m, 3H), 3.62 (d,  $J = 3.3$  Hz, 1H), 2.20–2.17 (m, 1H), 2.17 (s, 3H), 1.85–1.82 (m, 2H), 1.75 (d,  $J = 13.1$  Hz, 1H), 1.66–1.64 (m, 2H), 1.47–1.35 (m, 2H), 1.33–1.26 (m, 1H), 1.05–0.98 (m, 1H), 0.66 (qd,  $J = 12.7, 3.3$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 139.3, 138.0, 136.3, 135.1, 134.8, 130.9, 128.7, 128.6, 128.1, 126.9, 126.2, 125.3, 116.6, 114.3, 57.6, 46.3, 41.7, 31.1, 27.2, 26.5, 25.8, 25.6, 21.3. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{25}\text{N}_2^+$ : 353.2012, Found: 353.2014.



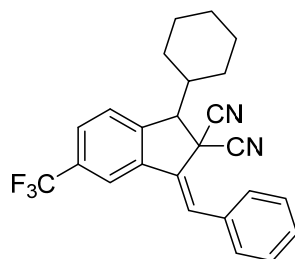
**(E)-3-Benzylidene-1-cyclohexyl-5-methoxy-1H-indene-2,2(3H)-dicyanonitrile (3c).**

White solid, 64.1 mg, 58% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43–7.39 (m, 4H), 7.37–7.35 (m, 1H), 7.19 (d,  $J = 8.5$  Hz, 1H), 7.17 (s, 1H), 6.85 (dd,  $J = 8.5, 2.5$  Hz, 1H), 6.71 (d,  $J = 2.4$  Hz, 1H), 3.61 (d,  $J = 3.3$  Hz, 1H), 3.52 (s, 3H), 2.19–2.14 (m, 1H), 1.83 (d,  $J = 8.9$  Hz, 2H), 1.74 (d,  $J = 13.0$  Hz, 1H), 1.67–1.65 (m, 2H), 1.44–1.36 (m, 2H), 1.33–1.24 (m, 1H), 1.05–0.97 (m, 1H), 0.65 (qd,  $J = 12.6, 3.4$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.4, 136.5, 136.2, 134.7, 134.2, 128.7, 128.6, 128.3, 127.2, 127.1, 117.4, 116.6, 114.2, 108.7, 57.2, 55.1, 46.4, 41.8, 31.1, 27.2, 26.5, 25.8, 25.6. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}^+$ : 369.1961, Found: 369.1958.



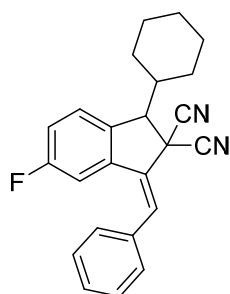
**(E)-3-Benzylidene-1-cyclohexyl-5-(trifluoromethyl)-1H-indene-2,2(3H)-dicyanonitrile (3d).**

White solid, 89.0 mg, 73% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.54 (s, 1H), 7.44–7.42 (m, 3H), 7.40–7.38 (m, 3H), 7.36–7.35 (m, 1H), 7.31 (s, 1H), 3.72 (d,  $J = 3.4$  Hz, 1H), 2.27–2.22 (m, 1H), 1.90–1.86 (m, 2H), 1.78 (d,  $J = 12.9$  Hz, 1H), 1.70–1.66 (m, 2H), 1.45–1.38 (m, 2H), 1.36–1.29 (m, 1H), 1.07–1.00 (m, 1H), 0.66 (qd,  $J = 12.6, 3.5$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.6, 138.5, 134.9, 134.1, 131.6 (q,  $J = 32.6$  Hz), 130.1, 129.2, 129.0, 128.0, 125.4 (q,  $J = 3.8$  Hz), 125.23, 123.5 (q,  $J = 272.6$  Hz), 123.3 (q,  $J = 3.9$  Hz), 115.9, 113.7, 57.7, 46.0, 41.8, 31.0, 27.3, 26.4, 25.6, 25.6;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : -62.7. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{22}\text{F}_3\text{N}_2^+$ : 407.1730, Found: 407.1725.



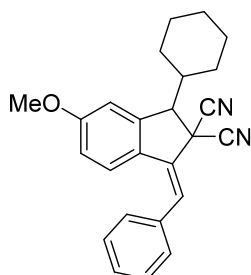
**(Z)-3-Benzylidene-1-cyclohexyl-5-(trifluoromethyl)-1,3-dihydro-2H-indene-2,2-dicyanonitrile (3d').** White solid, 11.0 mg, 9% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ :

7.69 (q,  $J = 8.2$  Hz, 2H), 7.59–7.58 (m, 3H), 7.53–7.50 (m, 2H), 7.46–7.44 (m, 2H), 3.86 (d,  $J = 3.3$  Hz, 1H), 2.18–2.14 (m, 1H), 1.85–1.82 (m, 2H), 1.62 (d,  $J = 13.6$  Hz, 1H), 1.57–1.55 (m, 1H), 1.43–1.41 (m, 1H), 1.39–1.32 (m, 2H), 1.23–1.16 (m, 1H), 1.00–0.94 (m, 1H), 0.35 (qd,  $J = 12.7, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.3, 140.2, 133.2, 133.2, 131.4 (q,  $J = 32.6$  Hz), 129.6, 129.4, 128.7, 128.5, 126.2 (q,  $J = 3.7$  Hz), 123.7 (q,  $J = 272.4$  Hz), 123.1 (q,  $J = 3.9$  Hz), 121.8, 116.0, 111.8, 59.8, 42.1, 42.0, 31.1, 27.1, 26.4, 25.6, 25.4;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : -62.3. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{22}\text{F}_3\text{N}_2^+$ : 407.1730, Found: 407.1725.



**(E)-3-Benzylidene-1-cyclohexyl-5-fluoro-1H-indene-2,2(3H)-dicyanonitrile (3e).**

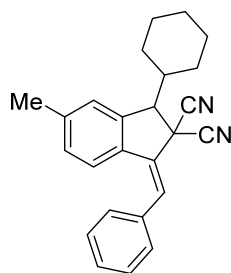
White solid, 68.4 mg, 64% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.42–7.36 (m, 5H), 7.25 (dd,  $J = 8.5, 5.0$  Hz, 1H), 7.22 (s, 1H), 6.99 (td,  $J = 8.5, 2.5$  Hz, 1H), 6.92 (dd,  $J = 9.3, 2.5$  Hz, 1H), 3.63 (d,  $J = 3.4$  Hz, 1H), 2.21–2.16 (m, 1H), 1.84–1.82 (m, 2H), 1.77–1.73 (m, 1H), 1.68–1.64 (m, 2H), 1.42–1.36 (m, 2H), 1.32–1.26 (m, 1H), 1.05–0.95 (m, 1H), 0.64 (qd,  $J = 12.7, 3.5$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.2 (d,  $J = 246.9$  Hz), 137.5 (d,  $J = 2.5$  Hz), 136.7 (d,  $J = 9.3$  Hz), 135.3 (d,  $J = 3.5$  Hz), 134.0, 128.9, 128.8, 128.6, 127.9, 127.6 (d,  $J = 8.8$  Hz), 117.2 (d,  $J = 23.1$  Hz), 116.1, 113.8, 111.5 (d,  $J = 24.7$  Hz), 57.0, 46.3, 41.6, 30.9, 27.1, 26.3, 25.6, 25.5;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : -112.2. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{21}\text{FN}_2\text{Na}^+$ : 379.1581, Found: 379.1582.



**(E)-1-Benzylidene-3-cyclohexyl-5-methoxy-1H-indene-2,2(3H)-dicyanonitrile (3f).**

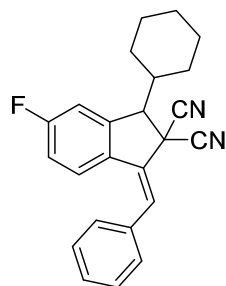
White solid, 65.2 mg, 59% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.41–7.37 (m, 4H),

7.35–7.32 (m, 1H), 7.20 (d,  $J = 8.7$  Hz, 1H), 7.00 (s, 1H), 6.79 (d,  $J = 2.4$  Hz, 1H), 6.66 (dd,  $J = 8.7, 2.4$  Hz, 1H), 3.81 (s, 3H), 3.61 (d,  $J = 3.3$  Hz, 1H), 2.19 (tq,  $J = 11.9, 3.0$  Hz, 1H), 1.86–1.83 (m, 2H), 1.77–1.74 (m, 1H), 1.68–1.65 (m, 2H), 1.47–1.37 (m, 2H), 1.32–1.27 (m, 1H), 1.03 (qt,  $J = 12.8, 3.8$  Hz, 1H), 0.69 (qd,  $J = 12.7, 3.5$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 160.9, 144.1, 135.7, 135.1, 128.7, 128.3, 128.1, 127.6, 125.9, 124.5, 116.6, 114.2, 114.2, 111.5, 57.8, 55.5, 46.4, 41.8, 31.1, 27.2, 26.5, 25.7, 25.6. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}^+$ : 369.1961, Found: 369.1957.



**(*E*)-1-Benzylidene-3-cyclohexyl-5-methyl-1*H*-indene-2,2(3*H*)-dicyanitrile (3g).**

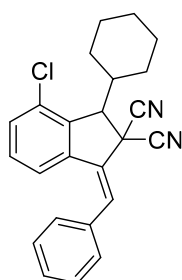
White solid, 66.6 mg, 63% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.41–7.37 (m, 4H), 7.36–7.33 (m, 1H), 7.16 (d,  $J = 8.1$  Hz, 1H), 7.10–7.09 (m, 1H), 7.08 (s, 1H), 6.93–6.92 (m, 1H), 3.61 (d,  $J = 3.3$  Hz, 1H), 2.36 (s, 3H), 2.22–2.16 (m, 1H), 1.85–1.83 (m, 2H), 1.78–1.74 (m, 1H), 1.68–1.65 (m, 2H), 1.48–1.37 (m, 2H), 1.34–1.27 (m, 1H), 1.07–1.00 (m, 1H), 0.68 (qd,  $J = 12.8, 3.4$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.3, 140.3, 136.2, 135.0, 132.4, 129.2, 128.7, 128.4, 128.1, 127.0, 126.1, 124.6, 116.6, 114.3, 57.8, 46.3, 41.8, 31.1, 27.2, 26.5, 25.8, 25.7, 21.7. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{25}\text{N}_2^+$ : 353.2012, Found: 353.2016.



**(*E*)-1-Benzylidene-3-cyclohexyl-5-fluoro-1*H*-indene-2,2(3*H*)-dicyanitrile (3h).**

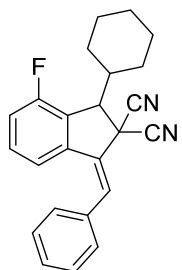
White solid, 78.0 mg, 73% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.42–7.35 (m, 5H), 7.25–7.21 (m, 1H), 7.13 (s, 1H), 7.01–6.99 (m, 1H), 6.84–6.81 (m, 1H), 3.64 (d,  $J = 3.4$  Hz, 1H), 2.23–2.19 (m, 1H), 1.86–1.84 (m, 2H), 1.78–1.75 (m, 1H), 1.69–1.66 (m,

2H), 1.46–1.37 (m, 2H), 1.36–1.28 (m, 1H), 1.08–1.01 (m, 1H), 0.67 (qd,  $J = 12.6$ , 3.5 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 163.2 (d,  $J = 252.0$  Hz), 144.4 (d,  $J = 8.6$  Hz), 135.0, 134.5, 131.1 (d,  $J = 3.0$  Hz), 128.9, 128.7, 128.0, 126.8 (d,  $J = 2.3$  Hz), 126.5 (d,  $J = 8.9$  Hz), 116.2, 115.8 (d,  $J = 22.9$  Hz), 113.9, 113.6 (d,  $J = 23.3$  Hz), 57.6 (d,  $J = 2.1$  Hz), 46.3, 41.7, 31.0, 27.2, 26.4, 25.7, 25.6;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : -108.9. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{22}\text{FN}_2^+$ : 357.1762, Found: 357.1758.



**(E)-1-Benzylidene-4-chloro-3-cyclohexyl-1H-indene-2,2(3H)-dicyanitrile (3i).**

White solid, 78.1 mg, 70% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.42–7.38 (m, 5H), 7.29 (d,  $J = 7.9$  Hz, 1H), 7.21 (s, 1H), 7.18–7.16 (m, 1H), 7.08–7.05 (m, 1H), 3.88 (d,  $J = 3.2$  Hz, 1H), 2.22–2.17 (m, 1H), 1.84–1.78 (m, 2H), 1.77–1.75 (m, 2H), 1.66 (d,  $J = 13.3$  Hz, 1H), 1.50–1.44 (m, 1H), 1.36–1.24 (m, 3H), 1.16–1.09 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.8, 136.9, 135.5, 134.2, 132.0, 130.9, 129.6, 129.0, 128.9, 128.7, 128.1, 123.1, 116.1, 114.2, 57.1, 45.5, 42.8, 30.6, 29.1, 26.7, 26.4, 25.7. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{22}^{35}\text{ClN}_2^+$ : 373.1466, Found: 373.1461

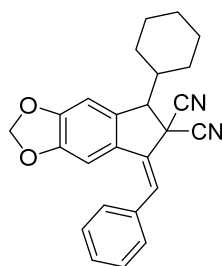


**(E)-1-Benzylidene-3-cyclohexyl-4-fluoro-1H-indene-2,2(3H)-dicyanitrile (3j).**

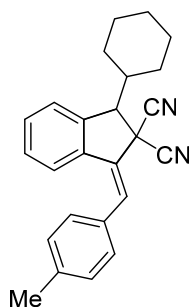
White solid, 79.1 mg, 74% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.41–7.38 (m, 5H), 7.21 (s, 1H), 7.13–7.09 (m, 1H), 7.07–7.06 (m, 1H), 7.03–7.00 (m, 1H), 3.91 (d,  $J = 3.3$  Hz, 1H), 2.25–2.21 (m, 1H), 1.91–1.90 (m, 1H), 1.83–1.82 (m, 1H), 1.77 (d,  $J = 13.1$  Hz, 1H), 1.67 (t,  $J = 15.4$  Hz, 2H), 1.37–1.29 (m, 3H), 1.08–1.01 (m, 1H), 0.84–0.77 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.4 (d,  $J = 249.6$  Hz), 138.0 (d,



$J = 4.9$  Hz), 135.4 (d,  $J = 2.6$  Hz), 134.3, 130.2 (d,  $J = 7.4$  Hz), 128.9, 128.9, 128.5, 128.4 (d,  $J = 17.9$  Hz), 128.1, 120.8 (d,  $J = 3.5$  Hz), 117.1 (d,  $J = 21.1$  Hz), 116.0, 113.9, 54.9 (d,  $J = 2.3$  Hz), 46.5, 42.5, 31.6 (d,  $J = 4.3$  Hz), 27.5, 26.6, 25.8, 25.7;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : -112.4. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{22}\text{FN}_2^+$ : 357.1762, Found: 357.1763.

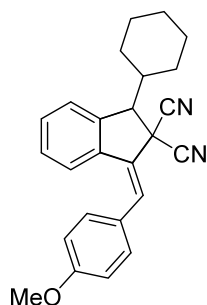


**(E)-5-Benzylidene-7-cyclohexyl-5,7-dihydro-6H-indeno[5,6-*d*][1,3]dioxole-6,6-dicarbonitrile (3k).** White solid, 71.1 mg, 62% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.41–7.33 (m, 5H), 7.00 (s, 1H), 6.72 (s, 1H), 6.63 (s, 1H), 5.98–5.96 (m, 2H), 3.54 (d,  $J = 3.2$  Hz, 1H), 2.19–2.13 (m, 1H), 1.85–1.81 (m, 2H), 1.75–1.72 (m, 1H), 1.70–1.66 (m, 2H), 1.45–1.36 (m, 2H), 1.35–1.29 (m, 1H), 1.08–1.00 (m, 1H), 0.71 (qd,  $J = 12.7$ , 3.4 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 149.5, 148.0, 136.9, 135.8, 134.8, 128.8, 128.4, 128.2, 124.8, 116.6, 114.1, 106.4, 104.6, 101.9, 57.5, 46.6, 41.9, 31.2, 27.2, 26.5, 25.8, 25.7. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2\text{Na}^+$ : 405.1573, Found: 405.1577.



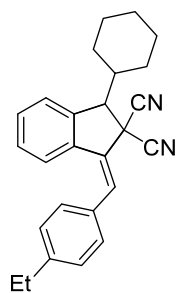
**(E)-1-Cyclohexyl-3-(4-methylbenzylidene)-1H-indene-2,2(3H)-dicarbonitrile (3l).** White solid, 64.5 mg, 61% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.35 (d,  $J = 7.9$  Hz, 1H), 7.31–7.27 (m, 4H), 7.20–7.19 (m, 2H), 7.14–7.12 (m, 2H), 3.65 (d,  $J = 3.3$  Hz, 1H), 2.40 (s, 3H), 2.20 (td,  $J = 11.9$ , 3.1 Hz, 1H), 1.87–1.82 (m, 2H), 1.76 (d,  $J = 13.1$  Hz, 1H), 1.67–1.64 (m, 2H), 1.48–1.37 (m, 2H), 1.34–1.27 (m, 1H), 1.05–0.98 (m, 1H), 0.66 (qd,  $J = 12.7$ , 3.3 Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.9, 138.7, 135.5, 135.2, 131.8, 129.7, 129.5, 128.1, 128.1, 127.5, 126.5, 124.9, 116.6, 114.3,

57.9, 46.1, 41.8, 31.1, 27.3, 26.5, 25.8, 25.7, 21.4. HRMS (ESI) ( $[M+Na]^+$ ) Calcd For  $C_{25}H_{24}N_2Na^+$ : 375.1832, Found: 375.1827.



**(E)-1-Cyclohexyl-3-(4-methoxybenzylidene)-1H-indene-2,2(3H)-dicyanitrile**

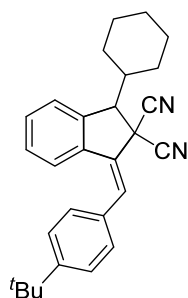
**(3m).** White solid, 66.3 mg, 60% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 7.56–7.52 (m, 3H), 7.40–7.36 (m, 1H), 7.35–7.32 (m, 2H), 7.25 (s, 1H), 7.02–6.99 (m, 2H), 3.86 (s, 3H), 3.81 (d,  $J = 3.3$  Hz, 1H), 2.14 (td,  $J = 11.9, 3.1$  Hz, 1H), 1.84–1.78 (m, 2H), 1.61–1.53 (m, 2H), 1.48–1.41 (m, 2H), 1.38–1.31 (m, 1H), 1.19 (qt,  $J = 13.2, 3.6$  Hz, 1H), 0.95 (qt,  $J = 13.0, 3.7$  Hz, 1H), 0.37 (qd,  $J = 12.7, 3.6$  Hz, 1H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$ : 160.0, 139.4, 138.3, 132.6, 131.0, 129.1, 128.9, 126.2, 126.1, 125.4, 121.1, 116.5, 114.0, 112.5, 60.1, 55.3, 42.3, 41.8, 31.2, 27.1, 26.5, 25.8, 25.5. HRMS (ESI) ( $[M+Na]^+$ ) Calcd For  $C_{25}H_{24}N_2ONa^+$ : 391.1781, Found: 391.1776.



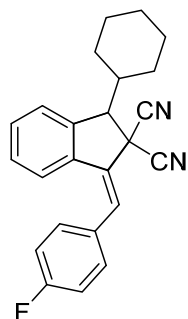
**(E)-1-Cyclohexyl-3-(4-ethylbenzylidene)-1H-indene-2,2(3H)-dicyanitrile (3n).**

White solid, 60.4 mg, 55% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 7.38 (d,  $J = 7.9$  Hz, 1H), 7.35–7.34 (m, 2H), 7.31–7.27 (m, 2H), 7.23–7.22 (m, 2H), 7.15–7.12 (m, 2H), 3.65 (d,  $J = 3.3$  Hz, 1H), 2.70 (q,  $J = 7.7$  Hz, 2H), 2.20 (td,  $J = 11.9, 3.2$  Hz, 1H), 1.87–1.82 (m, 2H), 1.76 (d,  $J = 13.1$  Hz, 1H), 1.65 (d,  $J = 12.7$  Hz, 2H), 1.48–1.37 (m, 2H), 1.36–1.31 (m, 1H), 1.28 (t,  $J = 7.6$  Hz, 3H), 1.05–0.98 (m, 1H), 0.69–0.62 (m, 1H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$ : 145.0, 141.9, 135.4, 135.2, 132.0, 129.7, 128.2, 128.1, 128.1, 127.5, 126.5, 124.9, 116.6, 114.3, 57.9, 46.2, 41.8, 31.1, 28.7, 27.3, 26.5, 25.8, 25.7, 15.4. HRMS (ESI) ( $[M+H]^+$ ) Calcd For  $C_{26}H_{27}N_2^+$ : 367.2169, Found:

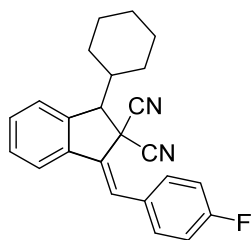
367.2165.



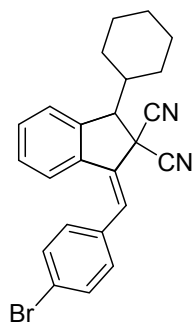
**(E)-1-(4-(*tert*-Butyl)benzylidene)-3-cyclohexyl-1*H*-indene-2,2(3*H*)-dicyanonitrile (3o).** White solid, 79.2 mg, 67% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.44–7.40 (m, 2H), 7.40–7.36 (m, 3H), 7.31–7.29 (m, 2H), 7.16–7.14 (m, 1H), 7.11 (s, 1H), 3.65 (d,  $J = 3.4$  Hz, 1H), 2.22–2.17 (m, 1H), 1.87–1.81 (m, 2H), 1.77–1.74 (m, 1H), 1.67–1.63 (m, 2H), 1.46–1.39 (m, 2H), 1.35 (s, 9H), 1.31–1.26 (m, 1H), 1.05–0.98 (m, 1H), 0.66 (qd,  $J = 12.7, 3.4$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.0, 142.0, 135.4, 135.2, 131.7, 129.7, 128.1, 127.9, 127.4, 126.4, 125.6, 124.9, 116.6, 114.3, 57.8, 46.3, 41.8, 34.8, 31.2, 31.1, 27.2, 26.5, 25.8, 25.6. HRMS (ESI) ( $[\text{M} + \text{Na}]^+$ ) Calcd For  $\text{C}_{28}\text{H}_{30}\text{N}_2\text{Na}^+$ : 417.2301, Found: 417.2300.



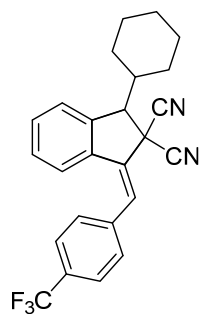
**(E)-1-Cyclohexyl-3-(4-fluorobenzylidene)-1*H*-indene-2,2(3*H*)-dicyanonitrile (3p).** White solid, 93 mg, 87% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40–7.38 (m, 2H), 7.32–7.29 (m, 2H), 7.25–7.24 (m, 1H), 7.15–7.12 (m, 1H), 7.11–7.08 (m, 3H), 3.67 (d,  $J = 3.3$  Hz, 1H), 2.23–2.18 (m, 1H), 1.88–1.82 (m, 2H), 1.74 (d,  $J = 13.0$  Hz, 1H), 1.67–1.65 (m, 2H), 1.46–1.37 (m, 2H), 1.34–1.27 (m, 1H), 1.05–0.98 (m, 1H), 0.65 (qd,  $J = 12.7, 2.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.6 (d,  $J = 249.0$  Hz), 142.1, 136.5, 134.8, 130.7 (d,  $J = 3.4$  Hz), 130.0, 130.0, 128.2, 126.6, 126.1, 124.7, 116.3, 115.9 (d,  $J = 21.6$  Hz), 114.2, 57.8, 46.0, 41.7, 31.1, 27.2, 26.5, 25.7, 25.6;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : –111.9. HRMS (ESI) ( $[\text{M} + \text{Na}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{21}\text{FN}_2\text{Na}^+$ : 379.1581, Found: 379.1583.



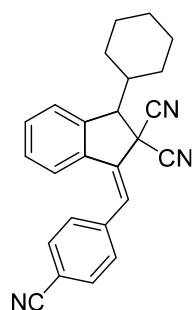
**(Z)-1-Cyclohexyl-3-(4-fluorobenzylidene)-1,3-dihydro-2H-indene-2,2-dicarbonitrile (3p')**. White solid, 9.6 mg, 9% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.58 (d,  $J = 7.7$  Hz, 1H), 7.56–7.54 (m, 2H), 7.42–7.38 (m, 2H), 7.37–7.34 (m, 1H), 7.28 (s, 1H), 7.18 (t,  $J = 8.6$  Hz, 2H), 3.82 (d,  $J = 3.3$  Hz, 1H), 2.15–2.10 (m, 1H), 1.84–1.78 (m, 2H), 1.61–1.54 (m, 2H), 1.48–1.39 (m, 2H), 1.38–1.31 (m, 1H), 1.19 (qt,  $J = 13.1, 3.6$  Hz, 1H), 0.98–0.93 (m, 1H), 0.37 (qd,  $J = 12.7, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.8 (d,  $J = 249.7$  Hz), 139.8, 137.7, 134.8, 131.2 (d,  $J = 8.2$  Hz), 130.0 (d,  $J = 3.7$  Hz), 129.7, 129.0, 126.2, 124.5, 121.4, 116.4, 115.8 (d,  $J = 21.8$  Hz), 112.3, 60.0, 42.2, 41.7, 31.2, 27.2, 26.5, 25.8, 25.5;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : -111.3. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{21}\text{FN}_2\text{Na}^+$ : 379.1581, Found: 379.1583.



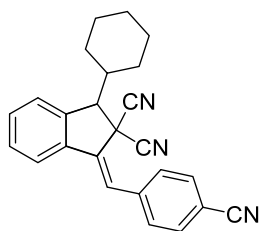
**(E)-1-Cyclohexyl-3-(4-(trifluoromethyl)benzylidene)-1H-indene-2,2(3H)-dicyanonitrile (3q)**. White solid, 78.6 mg, 63% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.54–7.52 (m, 2H), 7.32–7.31 (m, 2H), 7.30–7.28 (m, 2H), 7.26–7.25 (m, 1H), 7.16–7.12 (m, 1H), 7.06 (s, 1H), 3.67 (d,  $J = 3.4$  Hz, 1H), 2.22–2.18 (m, 1H), 1.88–1.82 (m, 2H), 1.74–1.71 (m, 1H), 1.67–1.64 (m, 2H), 1.48–1.37 (m, 2H), 1.32–1.25 (m, 1H), 1.05–0.98 (m, 1H), 0.65 (qd,  $J = 12.7, 3.3$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.2, 136.9, 134.6, 133.6, 132.0, 130.1, 129.7, 128.3, 126.6, 125.8, 124.8, 122.6, 116.2, 114.1, 57.8, 46.1, 41.7, 31.0, 27.3, 26.4, 25.7, 25.6. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{24}\text{H}_{22}^{79}\text{BrN}_2^+$ : 417.0961, Found: 417.0966.



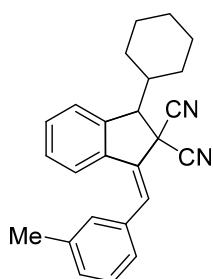
**(E)-1-Cyclohexyl-3-(4-(trifluoromethyl)benzylidene)-1H-indene-2,2(3H)-dicyanonitrile (3r).** White solid, 93.8 mg, 77% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.75–7.73 (m, 2H), 7.69–7.68 (m, 2H), 7.62–7.61 (m, 1H), 7.45–7.40 (m, 2H), 7.38–7.36 (m, 1H), 7.33 (s, 1H), 3.84 (d,  $J = 3.3$  Hz, 1H), 2.15–2.10 (m, 1H), 1.85–1.78 (m, 2H), 1.62–1.59 (m, 1H), 1.56–1.54 (m, 1H), 1.47–1.43 (m, 1H), 1.40–1.30 (m, 2H), 1.18 (qt,  $J = 13.2, 3.6$  Hz, 1H), 0.95 (qt,  $J = 12.9, 3.7$  Hz, 1H), 0.36 (qd,  $J = 12.7, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.2, 137.4, 137.3, 136.7, 130.6 (q,  $J = 32.7$  Hz), 130.2, 129.6, 129.1, 126.3, 125.6 (q,  $J = 3.7$  Hz), 123.9 (q,  $J = 272.3$  Hz), 123.9, 121.6, 116.2, 112.2, 60.0, 42.2, 41.6, 31.2, 27.2, 26.5, 25.7, 25.4;  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$ : –62.7. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{22}\text{F}_3\text{N}_2^+$ : 407.1730, Found: 407.1730.



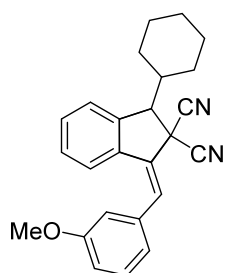
**(E)-1-(4-Cyanobenzylidene)-3-cyclohexyl-1H-indene-2,2(3H)-dicyanonitrile (3s).** White solid, 79.5 mg, 73% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.72–7.70 (m, 2H), 7.55–7.53 (m, 2H), 7.37–7.34 (m, 2H), 7.18–7.16 (m, 2H), 7.12 (s, 1H), 3.71 (d,  $J = 3.4$  Hz, 1H), 2.24–2.19 (m, 1H), 1.89–1.84 (m, 2H), 1.73–1.66 (m, 3H), 1.49–1.40 (m, 2H), 1.33–1.30 (m, 1H), 1.05–0.99 (m, 1H), 0.65 (qd,  $J = 12.6, 3.2$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.6, 139.6, 138.8, 134.1, 132.6, 130.7, 129.0, 128.4, 126.8, 124.8, 124.8, 118.4, 116.0, 113.8, 112.2, 57.9, 46.2, 41.7, 31.1, 27.3, 26.4, 25.7, 25.6. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{22}\text{N}_3^+$ : 364.1808, Found: 364.1808.



**(Z)-1-(4-Cyanobenzylidene)-3-cyclohexyl-1,3-dihydro-2H-indene-2,2-dicarbonitrile (3s').** White solid, 17.4 mg, 16% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.78–7.77 (m, 2H), 7.68–7.67 (m, 2H), 7.63–7.61 (m, 1H), 7.46–7.42 (m, 2H), 7.39–7.36 (m, 1H), 7.30 (s, 1H), 3.85 (d,  $J = 3.3$  Hz, 1H), 2.12 (td,  $J = 11.9, 3.1$  Hz, 1H), 1.82 (t,  $J = 14.7$  Hz, 2H), 1.62–1.60 (m, 1H), 1.56–1.54 (m, 1H), 1.47–1.40 (m, 1H), 1.38–1.33 (m, 2H), 1.20–1.15 (m, 1H), 0.99–0.92 (m, 1H), 0.35 (qd,  $J = 12.7, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.4, 138.3, 137.5, 137.1, 132.4, 130.5, 129.9, 129.2, 126.3, 123.4, 121.7, 118.5, 116.1, 112.4, 112.1, 60.0, 42.2, 41.6, 31.2, 27.2, 26.5, 25.7, 25.4. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{22}\text{N}_3^+$ : 364.1808, Found: 364.1808.

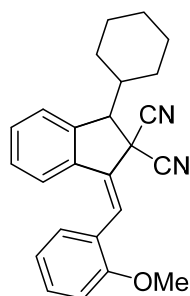


**(E)-1-cyclohexyl-3-(3-methylbenzylidene)-1H-indene-2,2(3H)-dicyanitrile (3t).** White solid, 65.5 mg, 62% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.31–7.26 (m, 4H), 7.22–7.21 (m, 2H), 7.18–7.17 (m, 1H), 7.13–7.08 (m, 2H), 3.66–3.66 (m, 1H), 2.37 (s, 3H), 2.22–2.18 (m, 1H), 1.85 (t,  $J = 13.2$  Hz, 2H), 1.76 (d,  $J = 13.2$  Hz, 1H), 1.68–1.64 (m, 2H), 1.49–1.38 (m, 2H), 1.35–1.26 (m, 1H), 1.06–0.98 (m, 1H), 0.66 (qd,  $J = 12.6, 3.4$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.0, 138.5, 136.0, 135.1, 134.6, 129.7, 129.3, 128.7, 128.6, 128.1, 127.5, 126.4, 125.0, 124.9, 116.5, 114.3, 57.8, 46.1, 41.8, 31.1, 27.2, 26.5, 25.8, 25.6, 21.3. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{25}\text{N}_2^+$ : 353.2012, Found: 353.2013.



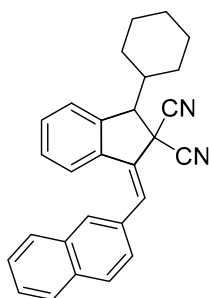
**(E)-1-Cyclohexyl-3-(3-methoxybenzylidene)-1H-indene-2,2(3H)-dicyanitrile**

**(3u).** White solid, 71.8 mg, 65% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.33–7.27 (m, 4H), 7.14–7.11 (m, 2H), 6.99 (d,  $J = 7.6$  Hz, 1H), 6.94–6.93 (m, 1H), 6.92–6.90 (m, 1H), 3.81 (s, 3H), 3.66 (d,  $J = 3.4$  Hz, 1H), 2.22–2.17 (m, 1H), 1.87–1.82 (m, 2H), 1.75 (d,  $J = 13.0$  Hz, 1H), 1.67–1.64 (m, 2H), 1.48–1.37 (m, 2H), 1.32–1.29 (m, 1H), 1.05–0.97 (m, 1H), 0.64 (qd,  $J = 12.7, 3.3$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.9, 142.0, 136.5, 136.0, 134.9, 129.9, 129.8, 128.2, 127.1, 126.4, 125.1, 120.4, 116.5, 114.3, 114.2, 113.4, 57.9, 55.3, 46.1, 41.8, 31.1, 27.3, 26.5, 25.8, 25.7. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}\text{Na}^+$ : 391.1781, Found: 391.1780.

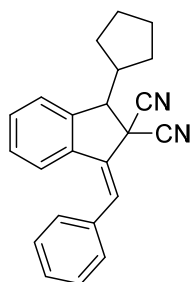


**(E)-1-Cyclohexyl-3-(2-methoxybenzylidene)-1H-indene-2,2(3H)-dicyanitrile**

**(3v).** White solid, 72.9 mg, 66% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.39–7.38 (m, 1H), 7.37–7.34 (m, 1H), 7.30–7.27 (m, 3H), 7.17 (s, 1H), 7.13–7.10 (m, 1H), 6.96–6.91 (m, 2H), 3.82 (s, 3H), 3.66 (d,  $J = 3.3$  Hz, 1H), 2.22–2.18 (m, 1H), 1.86–1.82 (m, 2H), 1.78 (d,  $J = 13.2$  Hz, 1H), 1.65 (d,  $J = 11.6$  Hz, 2H), 1.48–1.38 (m, 2H), 1.33–1.26 (m, 1H), 1.05–0.97 (m, 1H), 0.62 (qd,  $J = 12.7, 3.4$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 157.2, 141.8, 135.5, 135.5, 130.3, 129.5, 129.0, 128.1, 126.3, 124.8, 123.8, 123.5, 120.3, 116.6, 114.4, 111.0, 58.0, 55.4, 46.1, 41.8, 31.1, 27.2, 26.5, 25.8, 25.7. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}^+$ : 369.1961, Found: 369.1958.

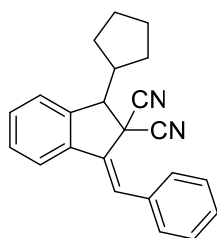


**(E)-1-Cyclohexyl-3-(naphthalen-2-ylmethylene)-1H-indene-2,2(3H)-dicarbonitrile (3w).** White solid, 66.4 mg, 57% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.89–7.85 (m, 3H), 7.83–7.82 (m, 1H), 7.55–7.49 (m, 3H), 7.34–7.28 (m, 4H), 7.07 (t,  $J = 7.5$  Hz, 1H), 3.70 (d,  $J = 3.4$  Hz, 1H), 2.26–2.21 (m, 1H), 1.90–1.81 (m, 3H), 1.72–1.66 (m, 2H), 1.51–1.39 (m, 2H), 1.37–1.29 (m, 1H), 1.08–1.00 (m, 1H), 0.72 (qd,  $J = 12.6, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.1, 136.4, 135.1, 133.3, 133.2, 132.2, 129.9, 128.4, 128.2, 128.1, 127.8, 127.6, 127.3, 126.7, 126.6, 126.5, 125.6, 124.9, 116.5, 114.3, 57.9, 46.2, 41.8, 31.1, 27.3, 26.5, 25.8, 25.7. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{28}\text{H}_{25}\text{N}_2^+$ : 389.2012, Found: 389.2009.



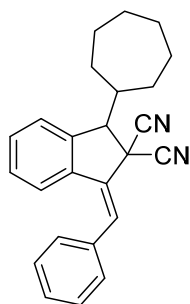
**(E)-1-Benzylidene-3-cyclopentyl-1H-indene-2,2(3H)-dicarbonitrile (3x).** White solid, 68.1 mg, 70% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43–7.40 (m, 4H), 7.38–7.35 (m, 2H), 7.30–7.27 (m, 2H), 7.20 (s, 1H), 7.12–7.10 (m, 1H), 3.82 (d,  $J = 7.3$  Hz, 1H), 2.55–2.48 (m, 1H), 2.21–2.16 (m, 1H), 2.09–2.04 (m, 1H), 1.73–1.59 (m, 5H), 1.33–1.27 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.8, 135.5, 134.9, 134.7, 130.0, 128.8, 128.6, 128.1, 128.1, 128.1, 126.0, 124.9, 116.3, 114.4, 57.2, 46.6, 42.8, 31.3, 29.4, 25.1, 24.6. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{23}\text{H}_{21}\text{N}_2^+$ : 325.1699, Found: 325.1701.





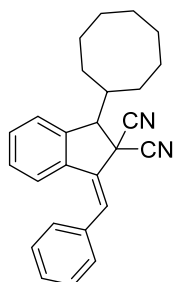
**(Z)-1-Benzylidene-3-cyclopentyl-1,3-dihydro-2H-indene-2,2-dicarbonitrile (3x').**

White solid, 14.6 mg, 15% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60–7.58 (m, 3H), 7.50–7.45 (m, 3H), 7.42–7.38 (m, 2H), 7.37–7.35 (m, 2H), 3.91 (d,  $J = 8.0$  Hz, 1H), 2.58–2.51 (m, 1H), 2.22–2.16 (m, 1H), 2.12–2.06 (m, 1H), 1.71–1.63 (m, 3H), 1.61–1.55 (m, 2H), 1.33–1.26 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.8, 138.0, 134.1, 133.9, 129.9, 129.3, 129.0, 129.0, 128.6, 126.7, 125.6, 121.4, 115.3, 113.7, 60.0, 43.1, 42.3, 31.6, 29.8, 25.2, 24.7. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{Na}^+$ : 347.1519, Found: 347.1515.

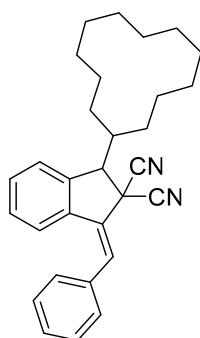


**(E)-1-Benzylidene-3-cycloheptyl-1H-indene-2,2(3H)-dicarbonitrile (3y).**

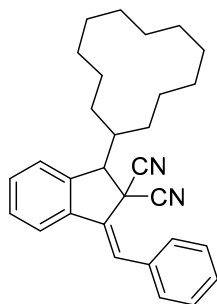
White solid, 66.6 mg, 63% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.42–7.36 (m, 5H), 7.34–7.33 (m, 1H), 7.30–7.26 (m, 2H), 7.18 (s, 1H), 7.12–7.10 (m, 1H), 3.82 (d,  $J = 3.3$  Hz, 1H), 2.37–2.33 (m, 1H), 1.95–1.91 (m, 1H), 1.84–1.74 (m, 2H), 1.71–1.59 (m, 4H), 1.56–1.42 (m, 4H), 1.08–1.01 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.4, 136.5, 135.1, 134.8, 130.0, 128.8, 128.1, 128.6, 128.2, 127.6, 126.1, 124.9, 116.5, 114.6, 59.0, 45.6, 43.0, 33.4, 29.3, 27.3, 27.3, 27.2, 26.5. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{25}\text{H}_{24}\text{N}_2\text{Na}^+$ : 375.1832, Found: 375.1837.



**(E)-1-Benzylidene-3-cyclooctyl-1H-indene-2,2(3H)-dicyanonitrile (3z).** White solid, 95.6 mg, 87% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.41–7.40 (m, 4H), 7.38–7.36 (m, 1H), 7.34–7.33 (m, 1H), 7.29–7.24 (m, 2H), 7.18 (s, 1H), 7.11–7.09 (m, 1H), 3.82 (d,  $J = 3.4$  Hz, 1H), 2.50–2.46 (m, 1H), 1.82–1.73 (m, 3H), 1.70–1.66 (m, 1H), 1.64–1.48 (m, 9H), 1.27–1.21 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.6, 136.4, 135.1, 134.7, 130.0, 128.8, 128.6, 128.1, 128.1, 127.6, 125.8, 124.9, 116.6, 114.7, 59.9, 45.3, 40.5, 32.0, 28.9, 26.7, 26.4, 26.0, 25.8, 25.2. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{Na}^+$ : 389.1988, Found: 389.1988.

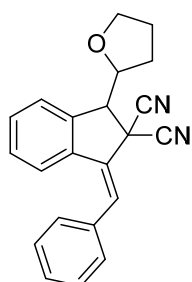


**(E)-1-Benzylidene-3-cyclododecyl-1H-indene-2,2(3H)-dicyanonitrile (3aa).** White solid, 83.6 mg, 66% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.41–7.39 (m, 4H), 7.38–7.36 (m, 1H), 7.33–7.32 (m, 1H), 7.30–7.27 (m, 2H), 7.19 (s, 1H), 7.11 (t,  $J = 7.6$  Hz, 1H), 3.87–3.86 (m, 1H), 2.42–2.38 (m, 1H), 1.77–1.73 (m, 1H), 1.62–1.55 (m, 2H), 1.54–1.43 (m, 6H), 1.41–1.29 (m, 11H), 1.27–1.20 (m, 1H), 1.07–1.03 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.6, 136.4, 135.1, 134.8, 130.0, 128.8, 128.6, 128.1, 128.1, 127.5, 126.2, 125.0, 116.6, 114.5, 55.1, 45.9, 36.5, 26.9, 26.0, 25.1, 25.0, 23.4, 23.2, 23.0, 22.9, 22.5, 22.2. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{30}\text{H}_{34}\text{N}_2\text{Na}^+$ : 445.2614, Found: 445.2610.



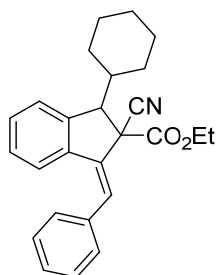
**(Z)-1-Benzylidene-3-cyclododecyl-1,3-dihydro-2H-indene-2,2-dicyanonitrile (3aa').** White solid, 16.5 mg, 13% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60–7.59 (m,

3H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.41–7.39 (m, 2H), 7.36–7.35 (m, 3H), 4.01 (d,  $J = 2.8$  Hz, 1H), 2.36–2.31 (m, 1H), 1.73–1.69 (m, 1H), 1.60–1.54 (m, 2H), 1.51–1.40 (m, 6H), 1.37–1.24 (m, 11H), 1.18–1.14 (m, 1H), 0.93–0.89 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.3, 138.1, 134.6, 133.8, 129.7, 129.3, 129.0, 128.9, 128.6, 126.1, 125.8, 121.4, 116.3, 112.8, 57.4, 41.7, 36.6, 27.0, 26.1, 25.2, 25.1, 23.5, 23.2, 23.1, 22.7, 22.5, 22.0. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{30}\text{H}_{34}\text{N}_2\text{Na}^+$ : 445.2614, Found: 445.2610.



**(E)-1-Benzylidene-3-(tetrahydrofuran-2-yl)-1H-indene-2,2(3H)-dicyanitrile**

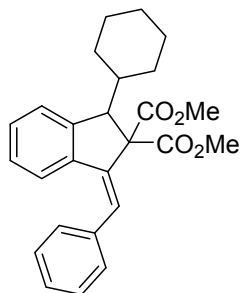
**(3ab).** White solid, 56.7 mg, 58% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.69–7.67 (m, 1H), 7.43–7.40 (m, 3H), 7.39–7.36 (m, 2H), 7.32–7.29 (m, 1H), 7.25 (s, 1H), 7.20 (s, 1H), 7.13–7.10 (m, 1H), 4.36–4.32 (m, 1H), 3.91–3.87 (m, 3H), 2.37–2.32 (m, 1H), 2.07–1.98 (m, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.0, 135.8, 134.7, 134.6, 130.3, 128.8, 128.6, 128.4, 128.2, 128.0, 126.7, 124.7, 116.0, 114.0, 79.8, 68.5, 56.3, 43.7, 29.6, 25.6. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}^+$ : 327.1492, Found: 327.1492.



**(E)-Ethyl 1-benzylidene-2-cyano-3-cyclohexyl-2,3-dihydro-1H-indene-2-**

**carboxylate (3ac).** White solid, 65.9 mg, 57% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40–7.36 (m, 4H), 7.34–7.31 (m, 1H), 7.28–7.26 (m, 1H), 7.21 (td,  $J = 7.4, 1.1$  Hz, 1H), 7.17 (d,  $J = 7.9$  Hz, 1H), 7.09 (s, 1H), 7.02–7.00 (m, 1H), 4.25–4.19 (m, 2H), 3.63 (d,  $J = 3.1$  Hz, 1H), 2.21–2.15 (m, 1H), 1.86–1.81 (m, 3H), 1.66–1.63 (m, 2H), 1.53–1.46 (m, 1H), 1.43–1.31 (m, 2H), 1.27 (t,  $J = 7.1$  Hz, 3H), 1.04–0.97 (m, 1H),

0.64–0.57 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.3, 145.1, 139.4, 136.2, 136.1, 129.0, 128.6, 128.2, 127.9, 127.1, 126.1, 125.9, 124.3, 118.1, 63.2, 59.4, 54.9, 42.0, 31.5, 27.6, 26.8, 26.0, 25.9, 13.8. HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd For  $\text{C}_{26}\text{H}_{28}\text{NO}_2^+$ : 386.2115, Found: 386.2118.



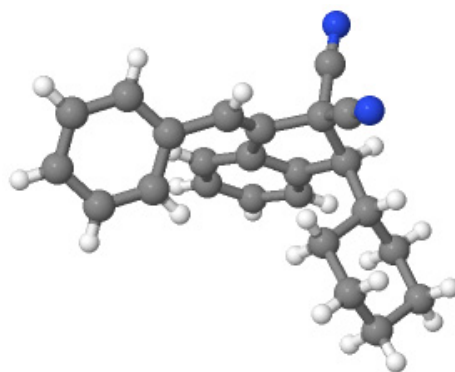
**(E)-Dimethyl 1-benzylidene-3-cyclohexyl-1H-indene-2,2(3H)-dicarboxylate (3ad).**

White solid, 77.6 mg, 64% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.41–7.39 (m, 2H), 7.35–7.32 (m, 2H), 7.28–7.25 (m, 2H), 7.15–7.12 (m, 1H), 7.10–7.07 (m, 2H), 6.93–6.91 (m, 1H), 3.83 (s, 3H), 3.79–3.78 (m, 1H), 3.68 (s, 3H), 1.80–1.76 (m, 3H), 1.58–1.56 (m, 2H), 1.48–1.45 (m, 2H), 1.29–1.25 (m, 1H), 1.11–1.03 (m, 1H), 0.98–0.91 (m, 1H), 0.42–0.36 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.5, 169.7, 145.2, 138.1, 137.9, 137.5, 128.4, 128.3, 128.3, 128.1, 127.2, 126.4, 125.6, 124.2, 70.1, 55.2, 53.1, 52.2, 41.1, 32.2, 27.6, 27.2, 26.3, 26.1. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd For  $\text{C}_{26}\text{H}_{28}\text{O}_4\text{Na}^+$ : 427.1880, Found: 427.1875.

## 4. X-Ray crystallographic data for 3a and 3a'

### 4.1 X-Ray crystallographic data for 3a

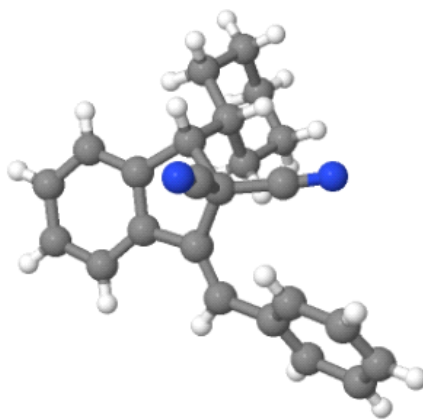
Single crystals of **3a** were obtained from slow evaporation of dichloromethane solution at room temperature. The data of the crystal structure **3a** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC: 2132227.



Bond precision:	C-C = 0.0022 Å	Wavelength=0.71073	
Cell:	a=10.1427 (17) alpha=90	b=14.521 (3) beta=103.529 (6)	c=13.705 (2) gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1962.5 (6)	1962.6 (6)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C24 H22 N2	C24 H22 N2	
Sum formula	C24 H22 N2	C24 H22 N2	
Mr	338.44	338.43	
Dx, g cm <sup>-3</sup>	1.145	1.145	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.067	0.067	
F000	720.0	720.0	
F000'	720.24		
h, k, lmax	12, 17, 16	12, 17, 16	
Nref	3492	3476	
Tmin, Tmax	0.983, 0.987	0.983, 0.987	
Tmin'	0.983		
Correction method=	# Reported T Limits: Tmin=0.983 Tmax=0.987		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.995	Theta(max) =	25.099
R(reflections)=	0.0446 ( 3209)	wR2(reflections)=	0.1119 ( 3476)
S =	1.079	Npar=	235

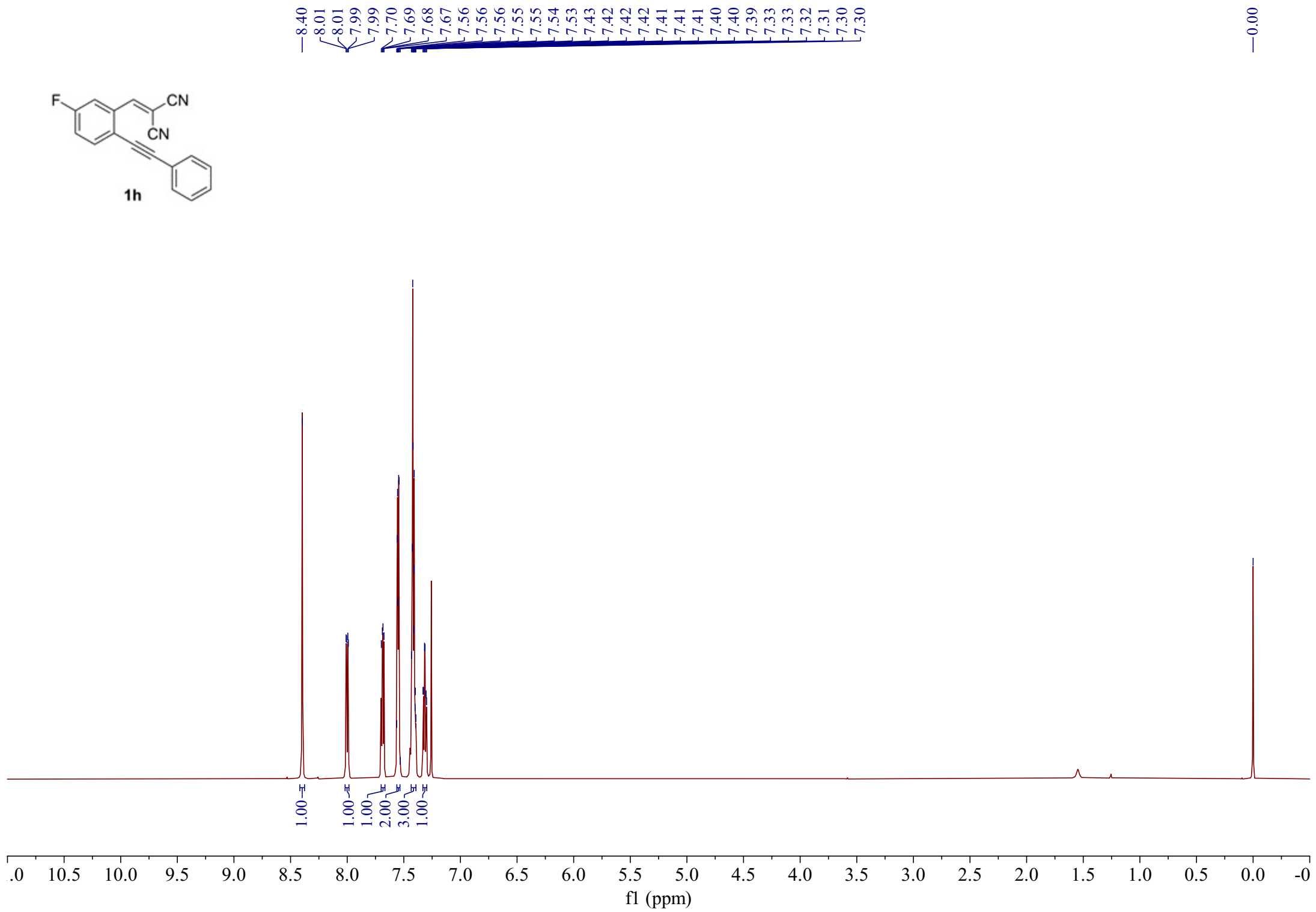
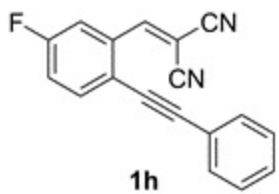
## 4.2 X-Ray crystallographic data for 3a'

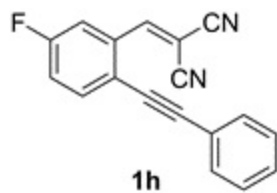
Single crystals of **3a'** were obtained from slow evaporation of dichloromethane solution at room temperature. The data of the crystal structure **3a'** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2132228.



Bond precision:	C-C = 0.0025 Å	Wavelength=0.71073	
Cell:	a=12.796(2) alpha=90	b=13.651(3) beta=117.073(6)	c=12.334(2) gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1918.4(6)	1918.3(6)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C24 H22 N2	C24 H22 N2	
Sum formula	C24 H22 N2	C24 H22 N2	
Mr	338.44	338.43	
Dx, g cm <sup>-3</sup>	1.172	1.172	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.069	0.069	
F000	720.0	720.0	
F000'	720.24		
h, k, lmax	15, 16, 14	15, 16, 14	
Nref	3417	3403	
Tmin, Tmax	0.983, 0.986	0.981, 0.985	
Tmin'	0.983		
Correction method=	# Reported T Limits: Tmin=0.981 Tmax=0.985		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.996	Theta(max)=	25.093
R(reflections)=	0.0421( 2832)	wR2(reflections)=	0.1090( 3403)
s =	1.037	Npar=	235

## 5. Copies of <sup>1</sup>H, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra



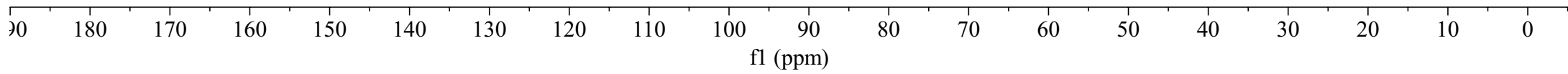


162.70  
161.02  
156.52  
156.51

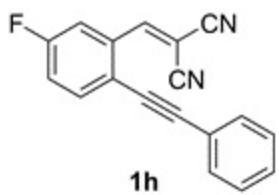
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129.63  
128.68  
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121.47  
121.40  
114.87  
114.71  
113.32  
111.83

98.35

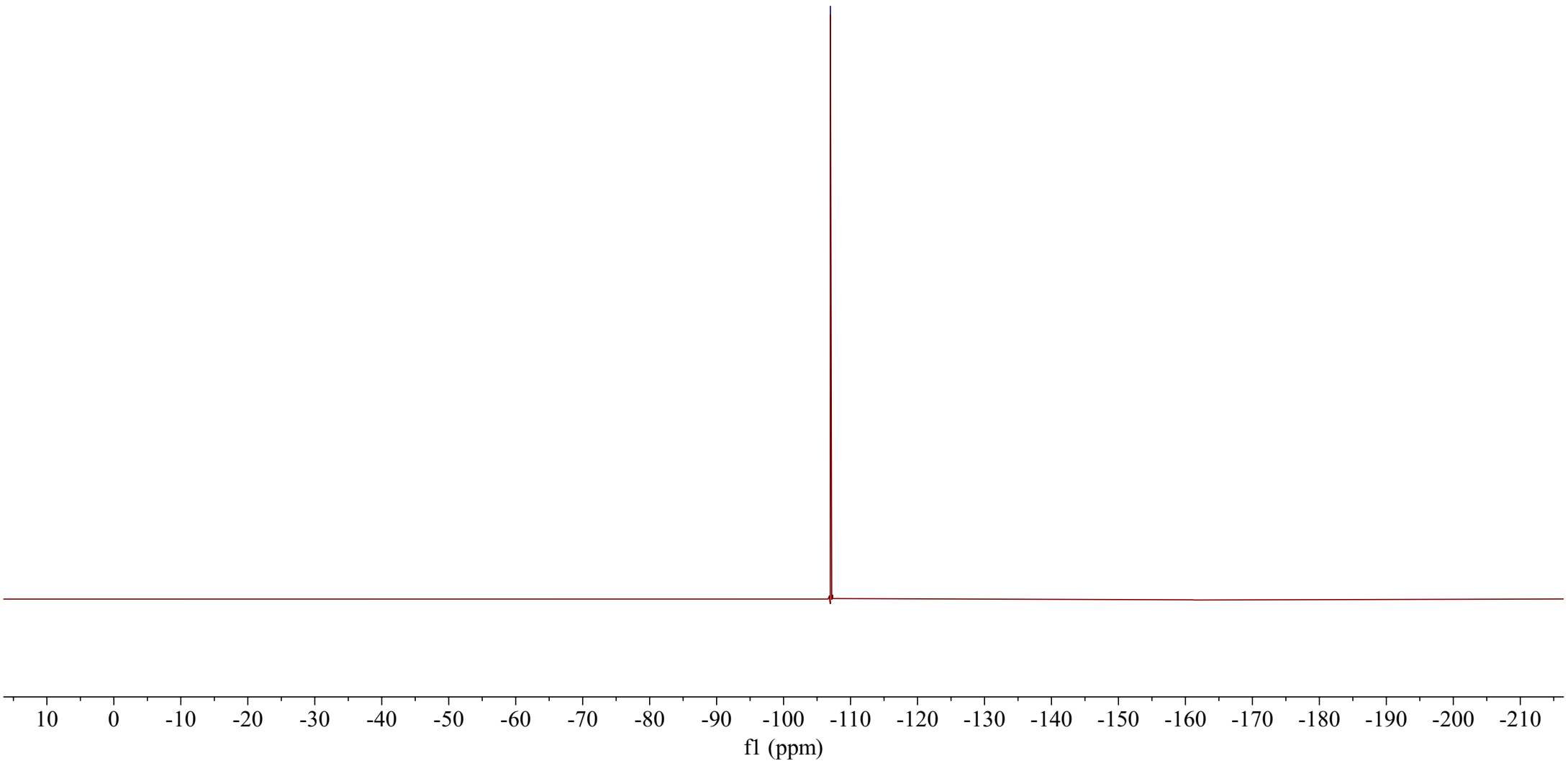
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77.21  
77.00  
76.79

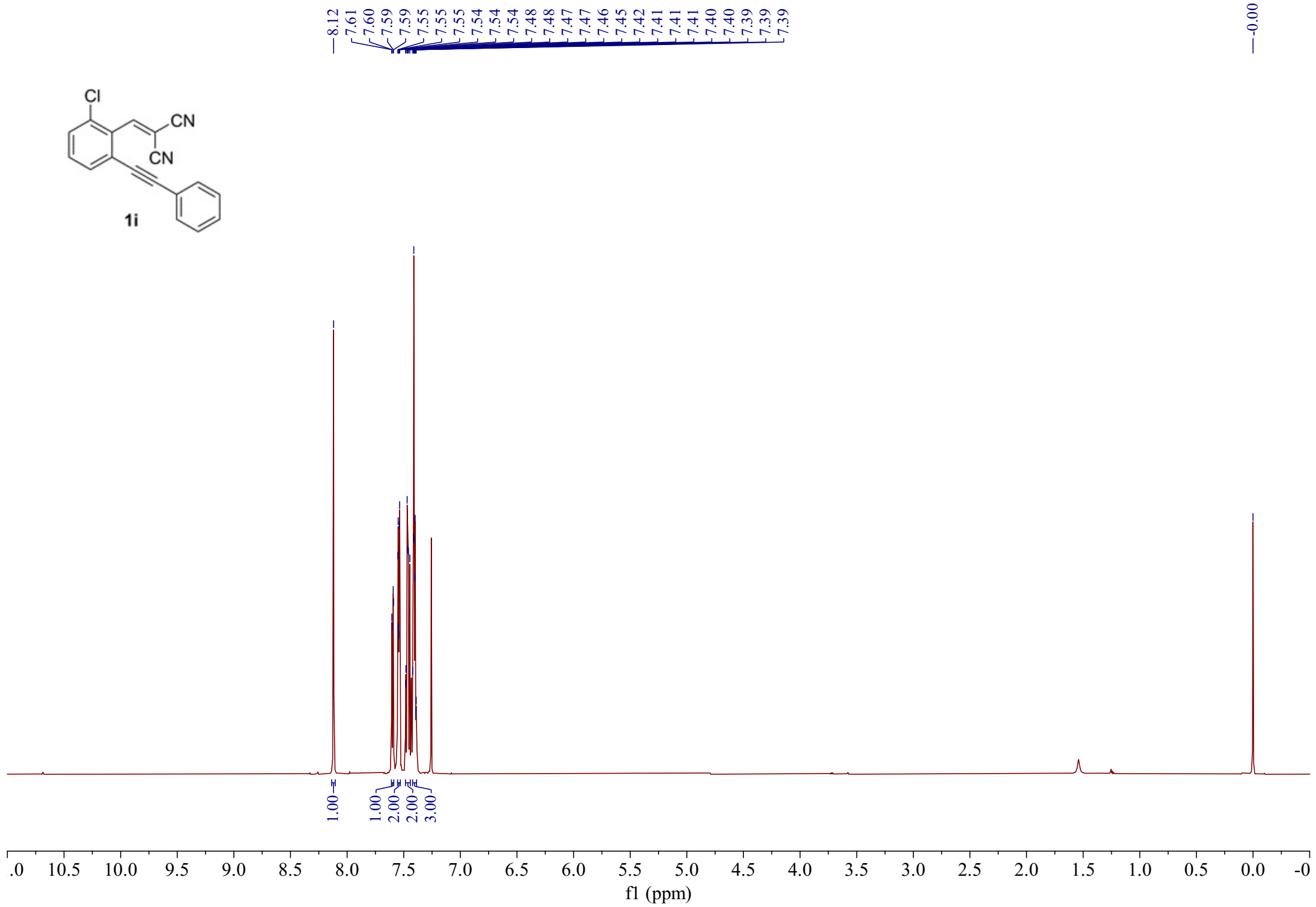
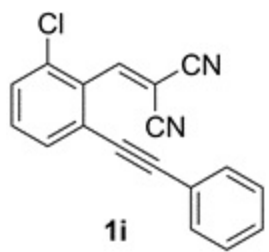


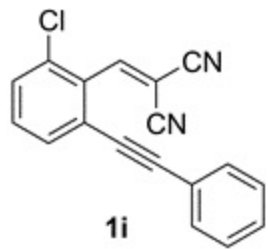




--106.99







— 157.73

133.66  
132.16  
131.76  
131.56  
131.20  
129.77  
129.55  
128.64  
124.81  
121.57  
~ 112.46  
~ 110.98

— 97.66

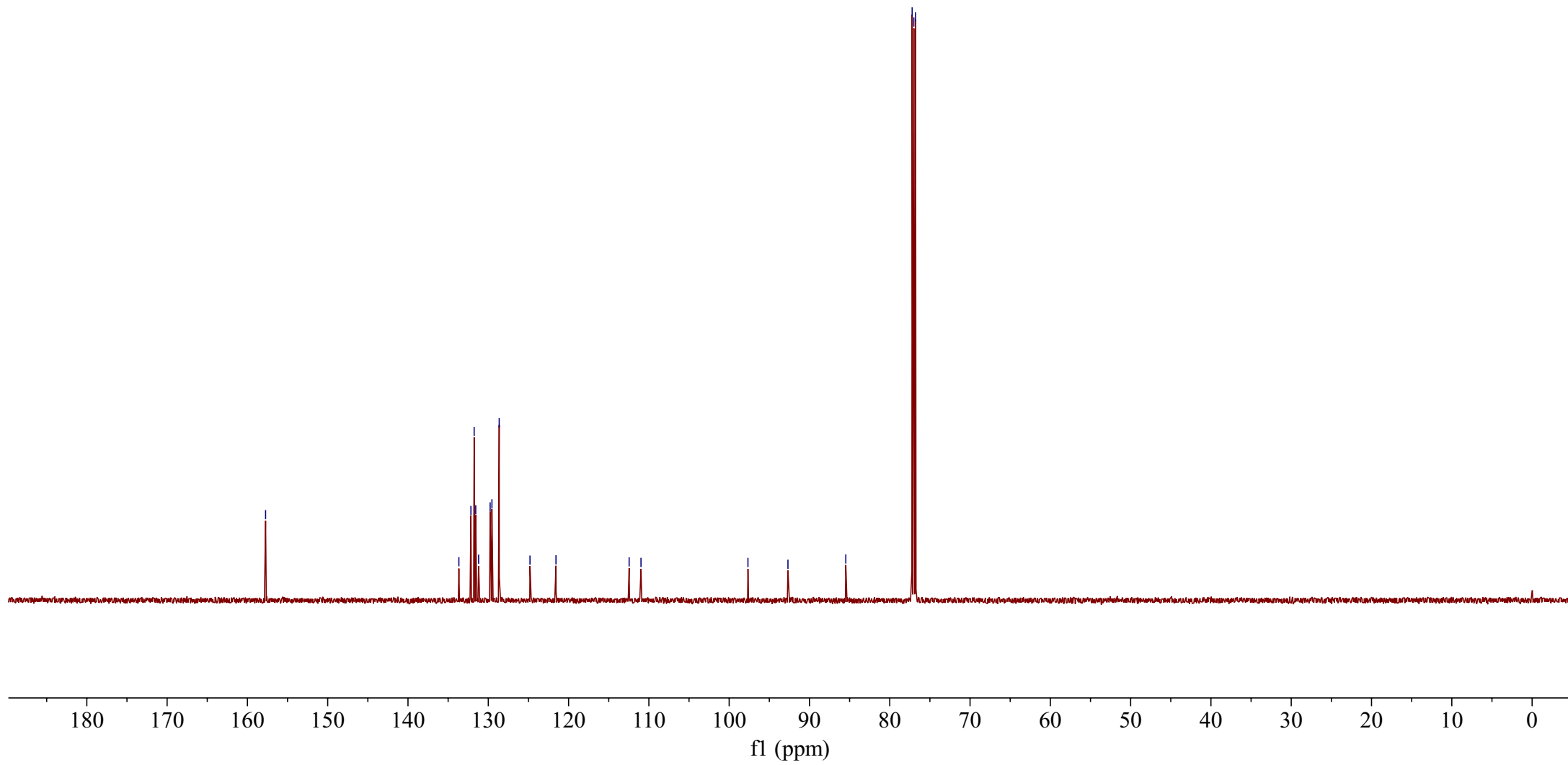
— 92.68

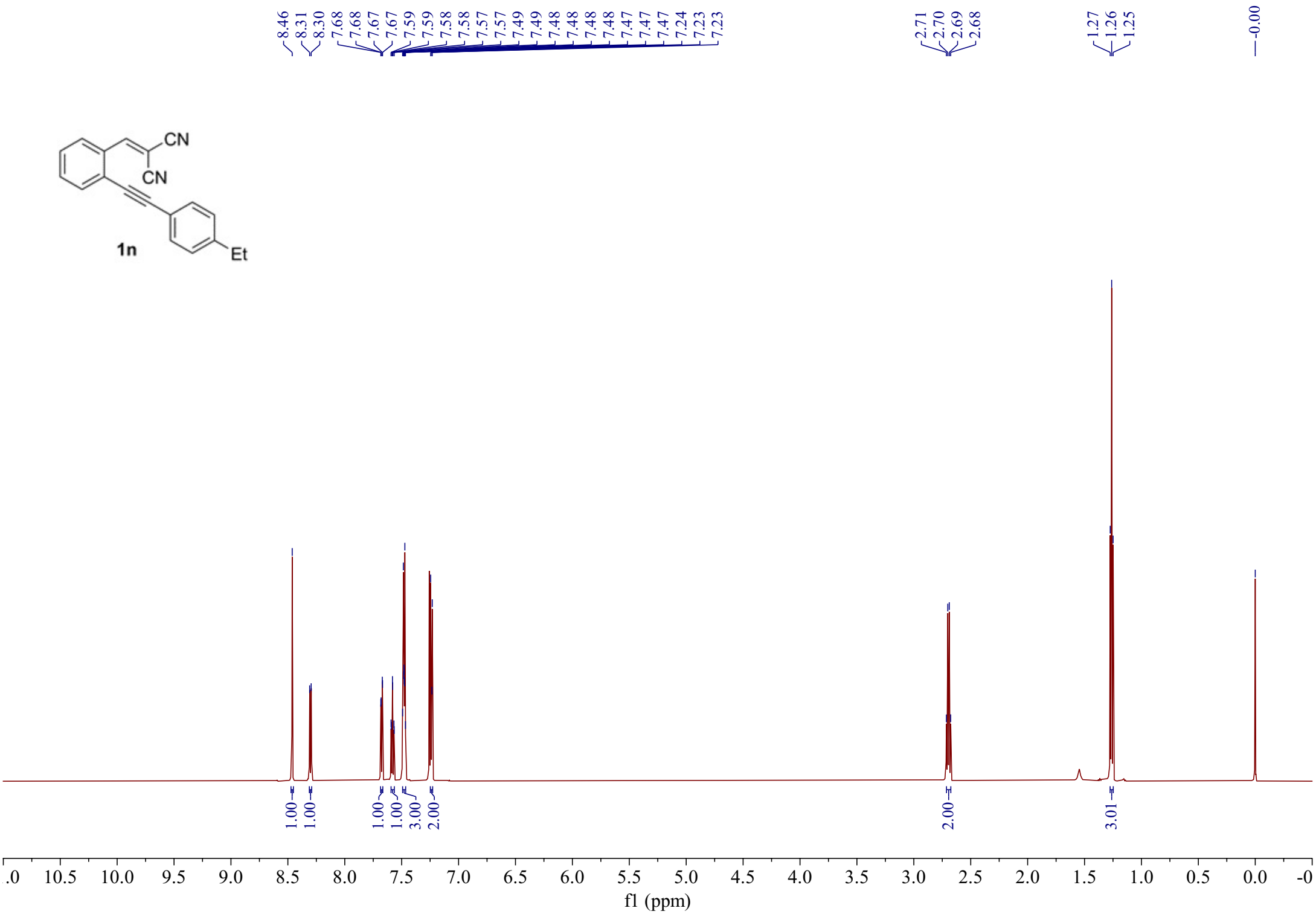
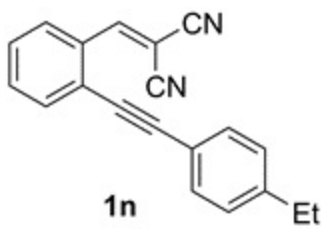
— 85.47

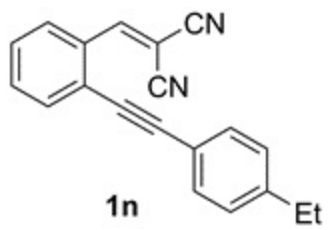
77.21

77.00

76.79







— 157.97

— 146.25

133.82

133.28

131.75

131.65

128.79

128.23

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127.03

118.80

113.82

112.45

— 98.96

84.61

83.82

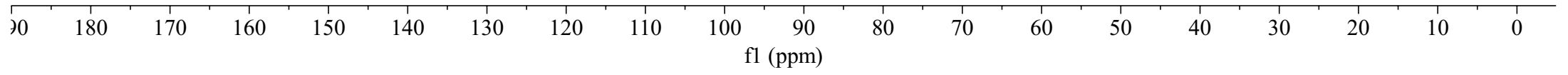
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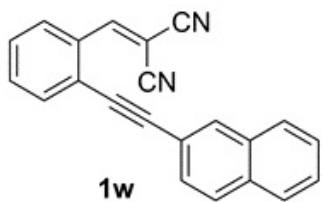
77.00

76.79

— 28.92

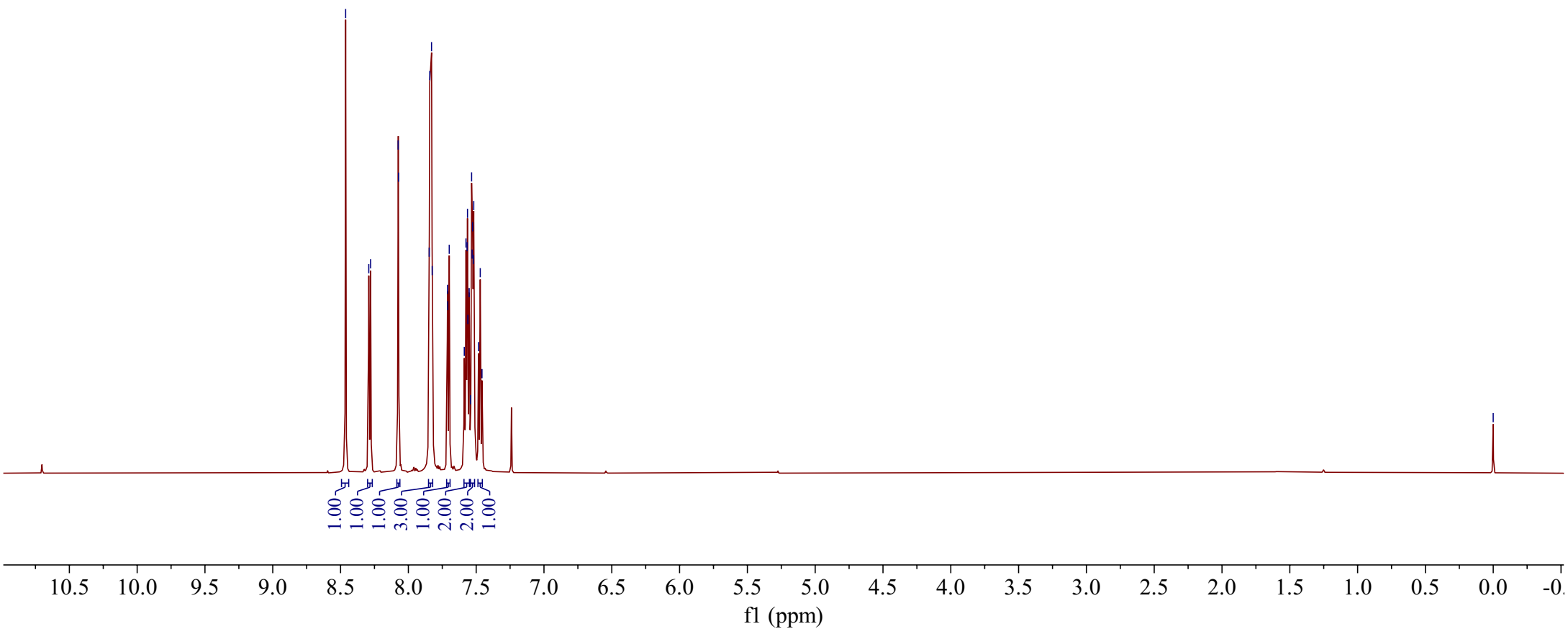
— 15.28

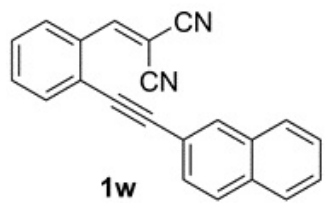




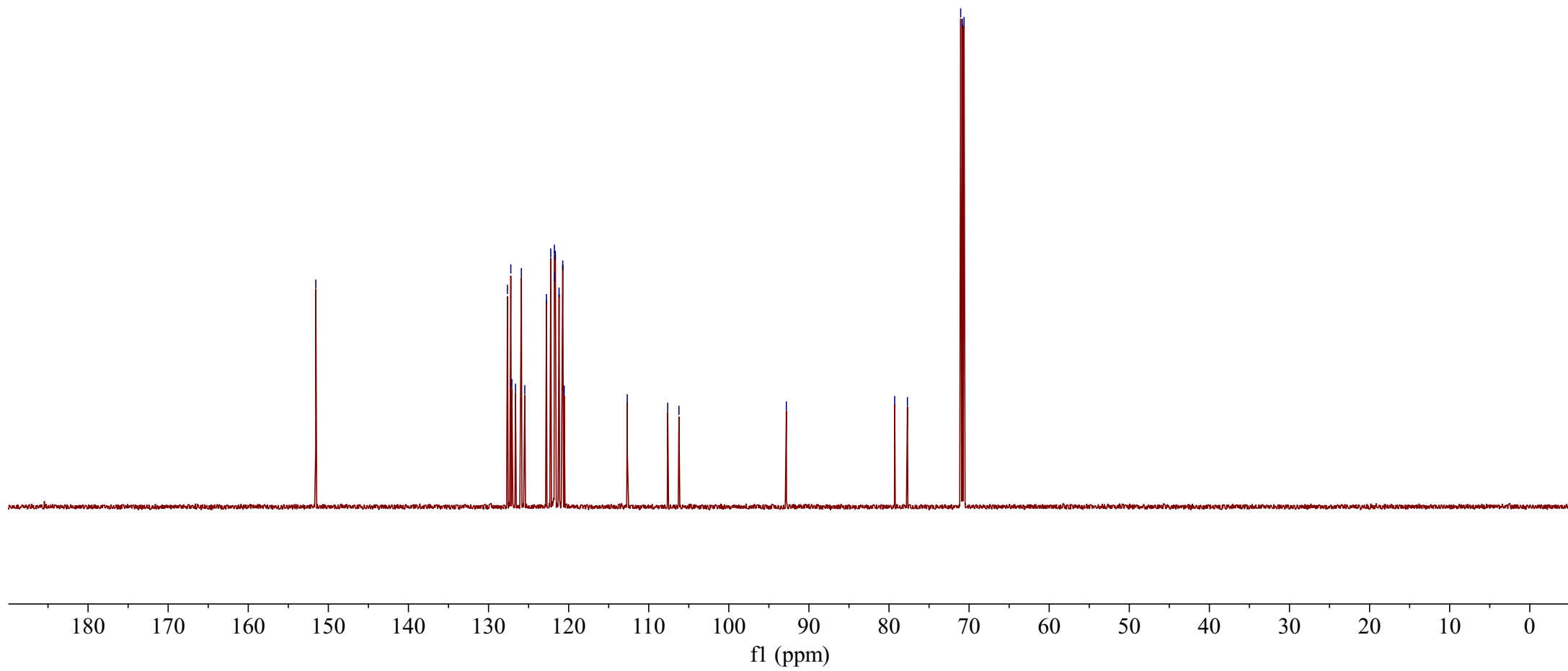
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7.46

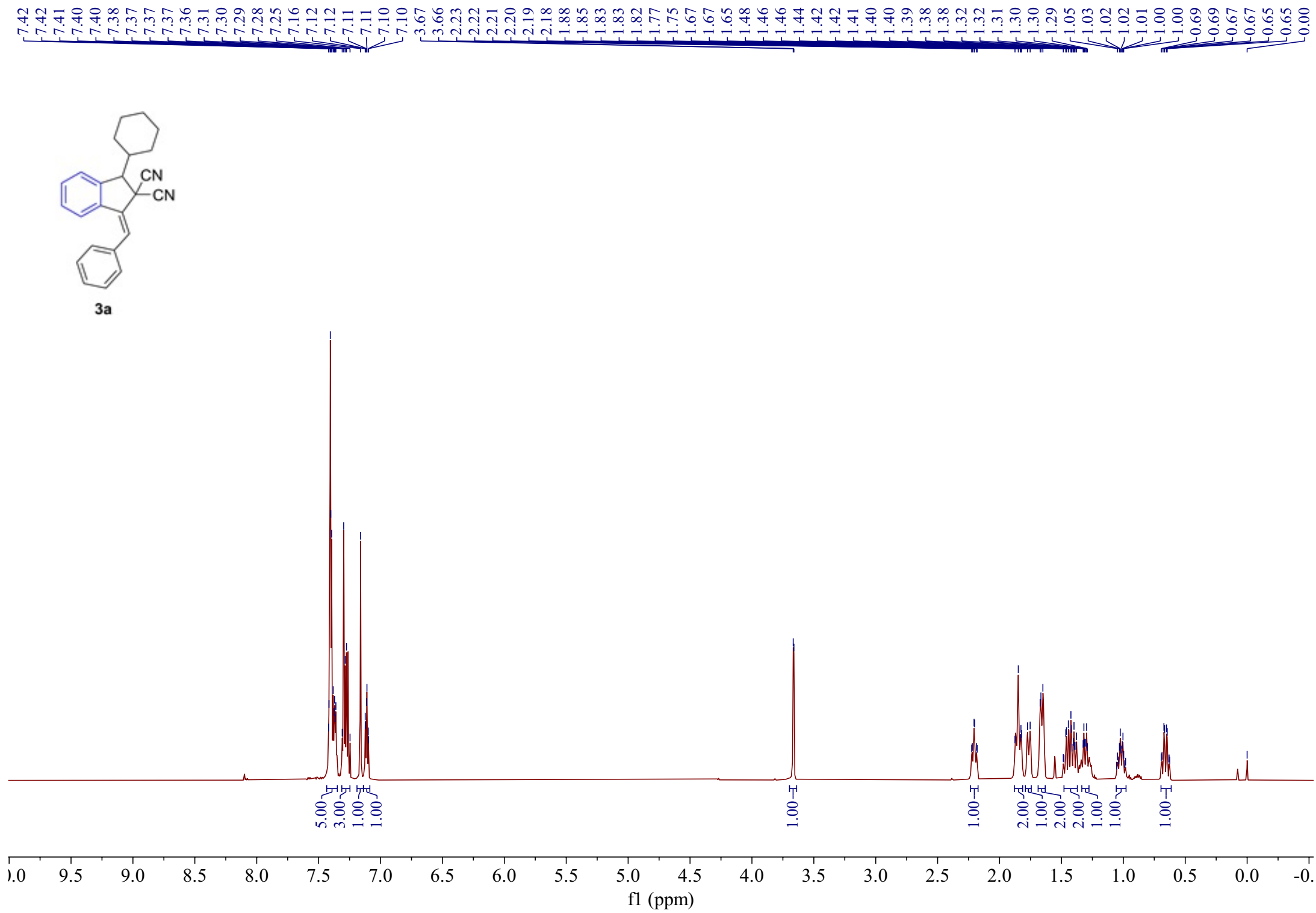
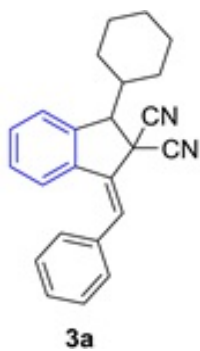
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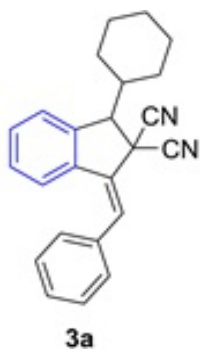


151.57  
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126.63  
125.90  
125.47  
122.77  
122.23  
121.78  
121.75  
121.69  
121.66  
121.19  
120.73  
120.55  
112.68  
107.63  
106.23  
92.82  
79.29  
77.70  
71.05  
70.84  
70.63









142.07  
136.32  
135.02  
134.79  
129.82  
128.79  
128.60  
128.16  
128.11  
127.30  
126.46  
124.93  
— 116.49  
— 114.26

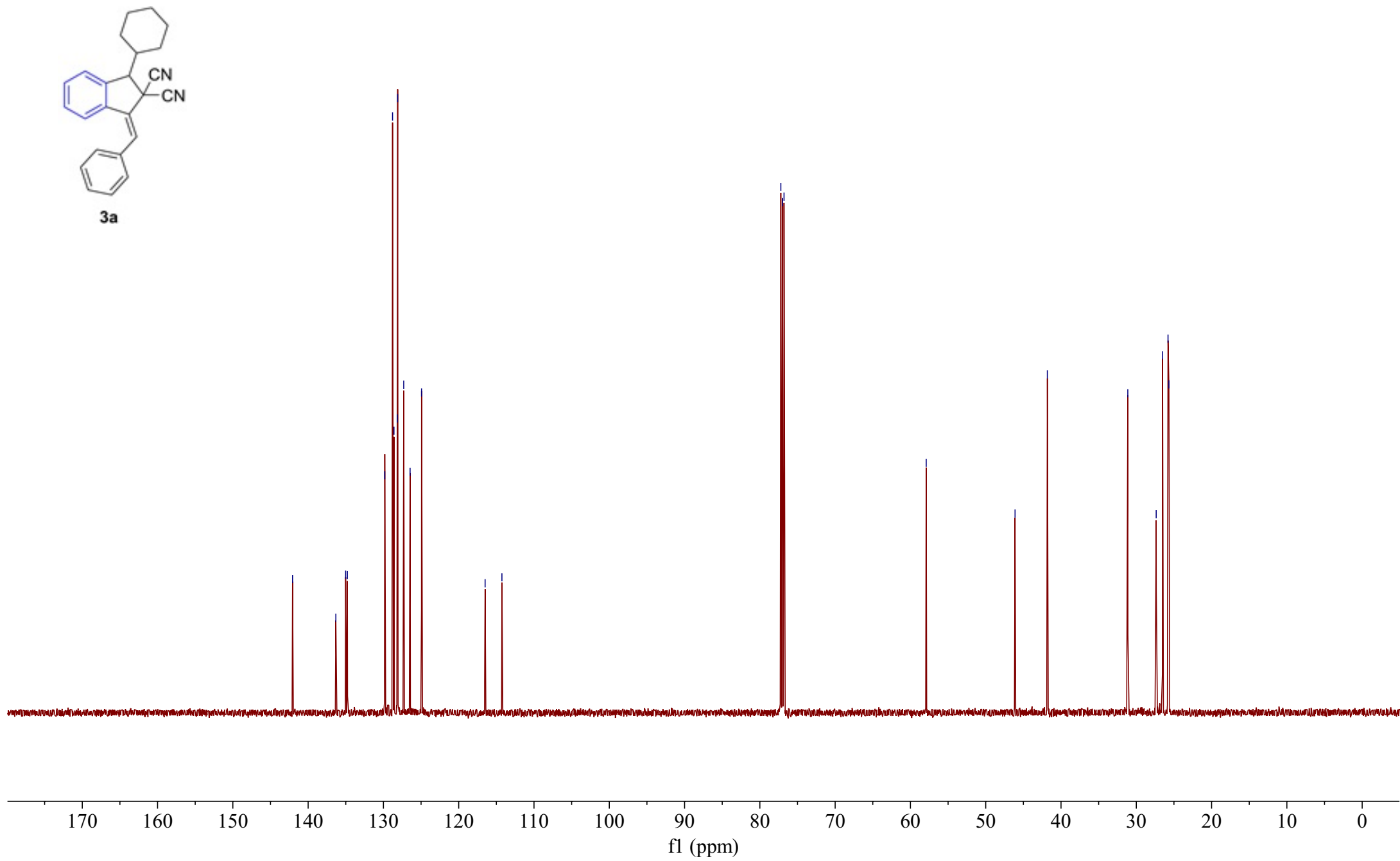
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77.00  
76.79

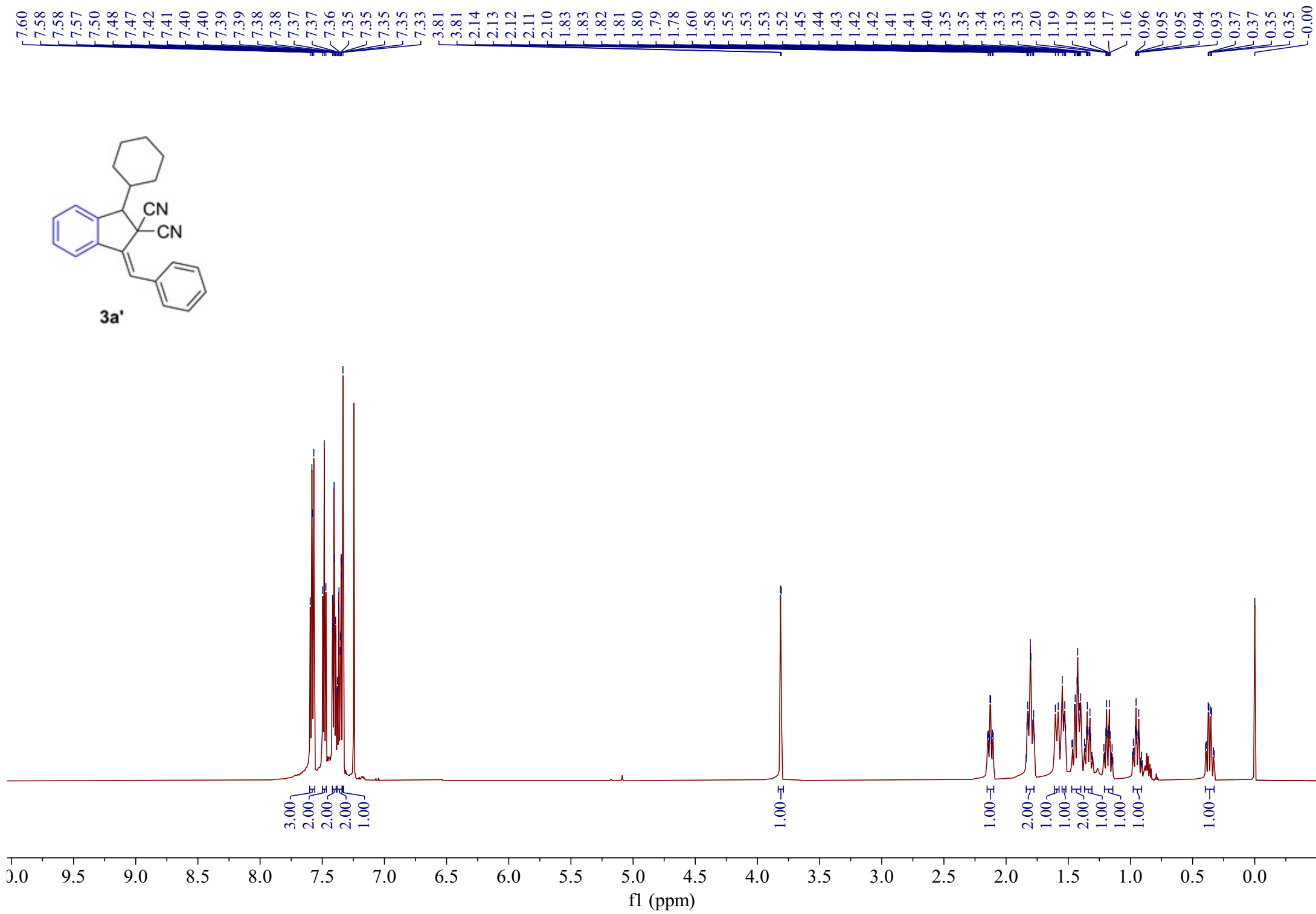
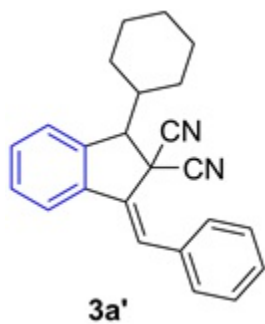
— 57.90

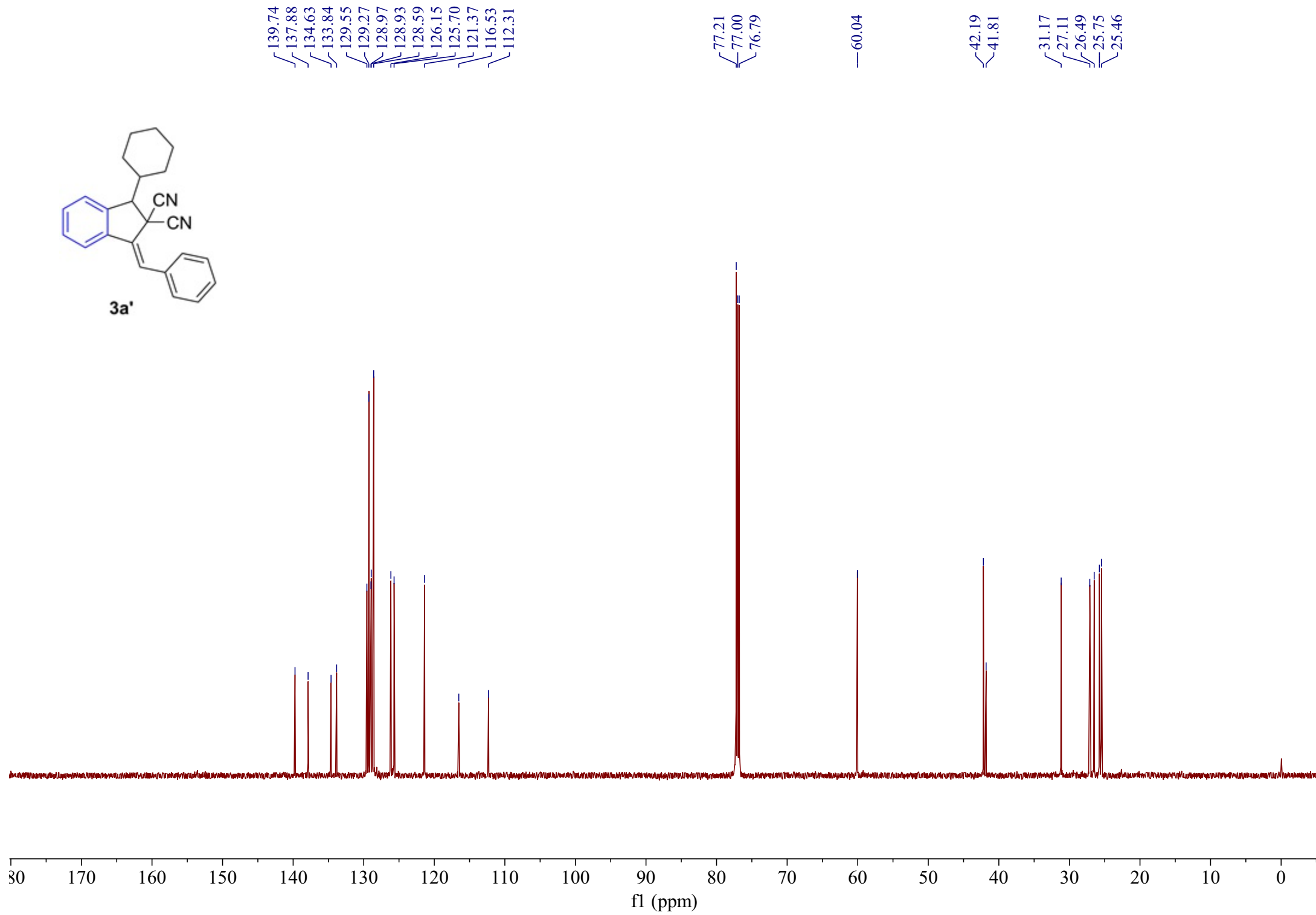
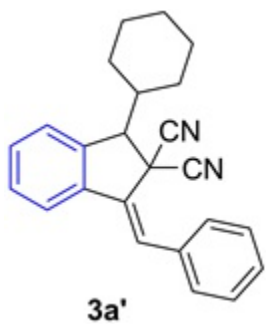
— 46.10

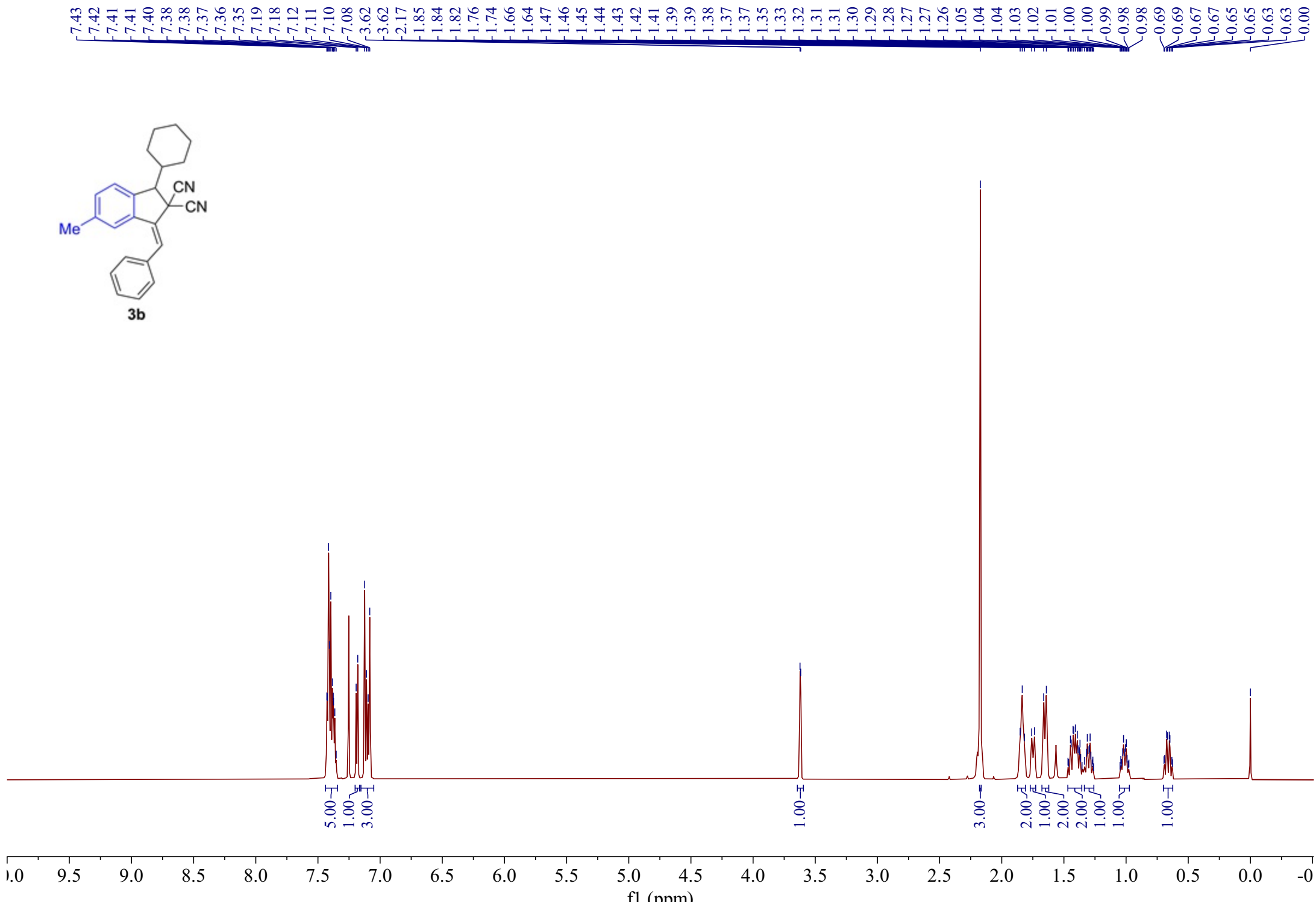
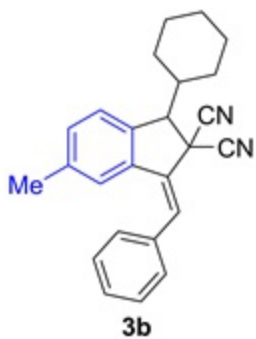
— 41.81

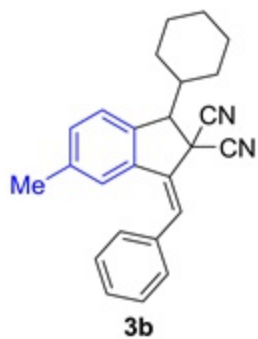
31.13  
27.36  
26.52  
25.79  
25.67











139.26  
138.04  
136.31  
135.09  
134.83  
130.91  
128.68  
128.58  
128.15  
126.90  
126.17  
125.29  
— 116.60  
— 114.32

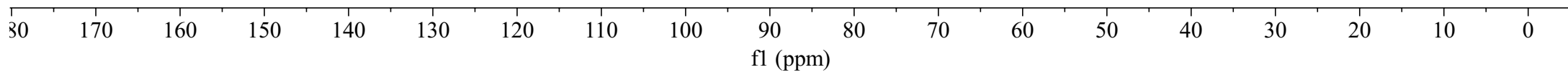
77.21  
77.00  
76.79

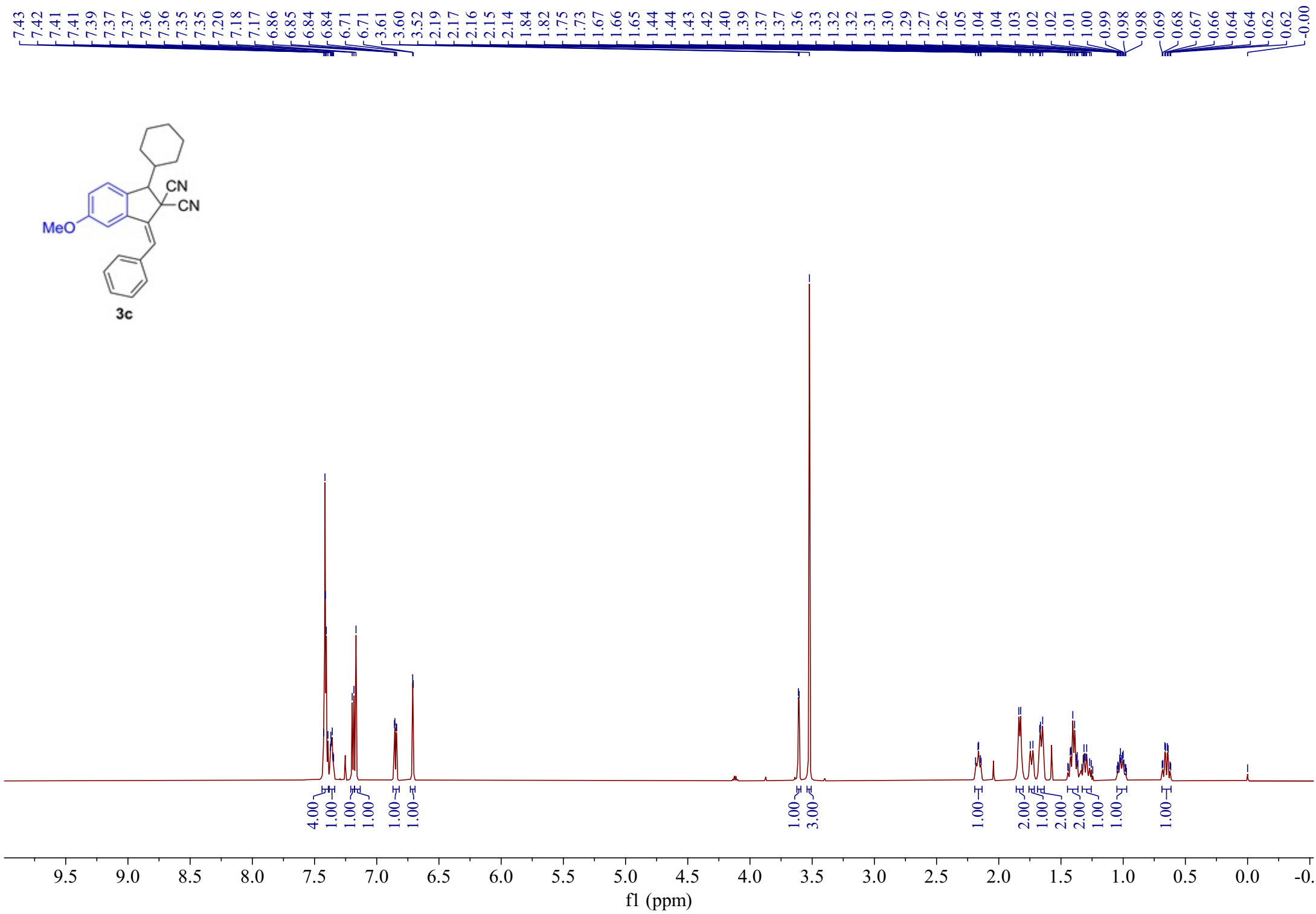
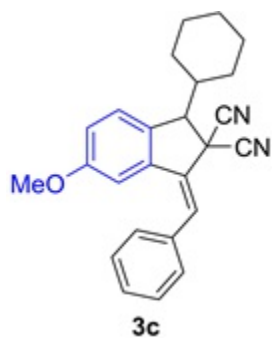
— 57.57

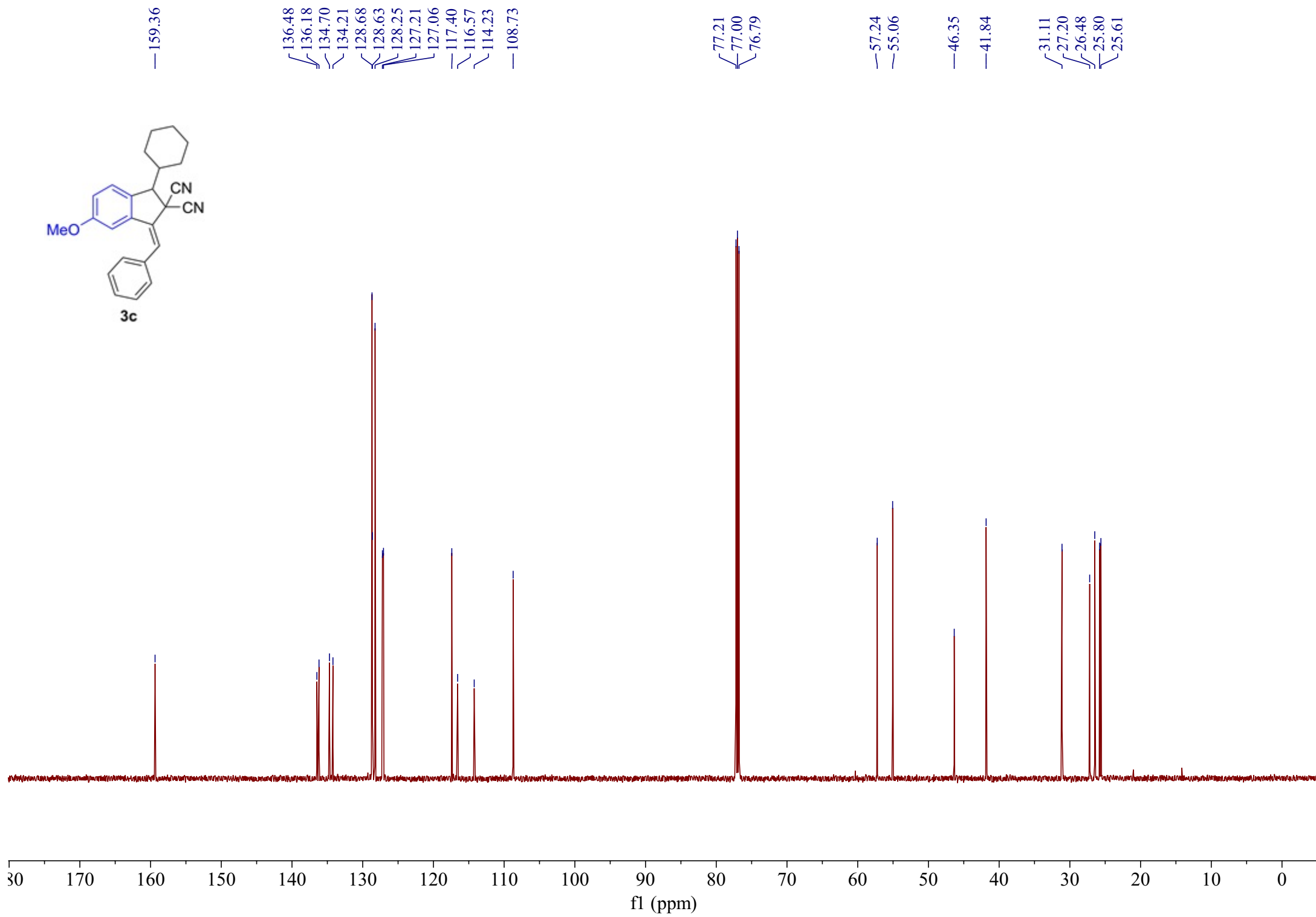
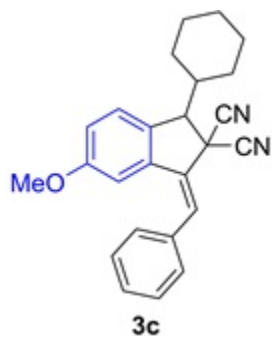
— 46.34

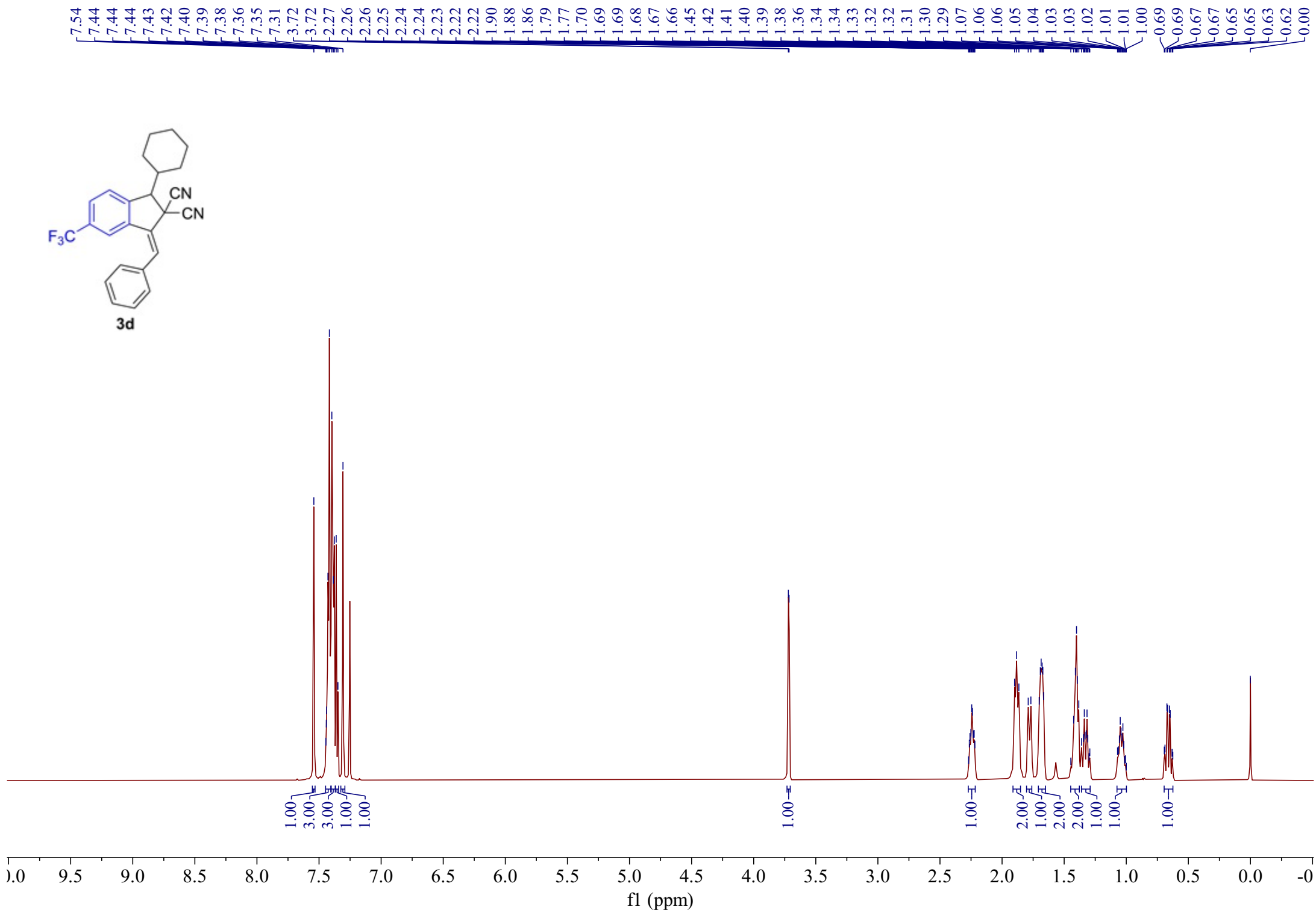
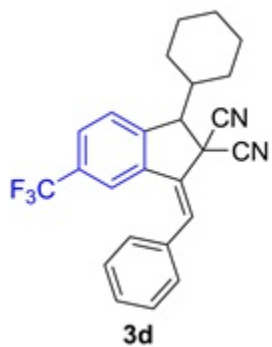
— 41.75

31.13  
27.21  
26.50  
25.80  
25.63  
21.28

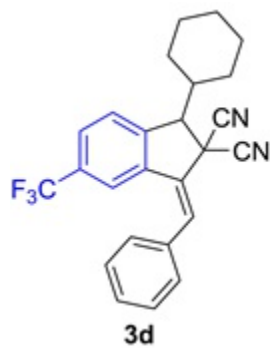












142.55  
138.46  
134.91  
134.06  
131.90  
131.68  
131.47  
131.25  
130.11  
129.18  
129.03  
127.98  
126.23  
125.47  
125.45  
125.42  
125.40  
125.27  
124.42  
123.31  
123.29  
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123.24  
122.61  
120.81  
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113.71

77.21  
77.00  
76.79

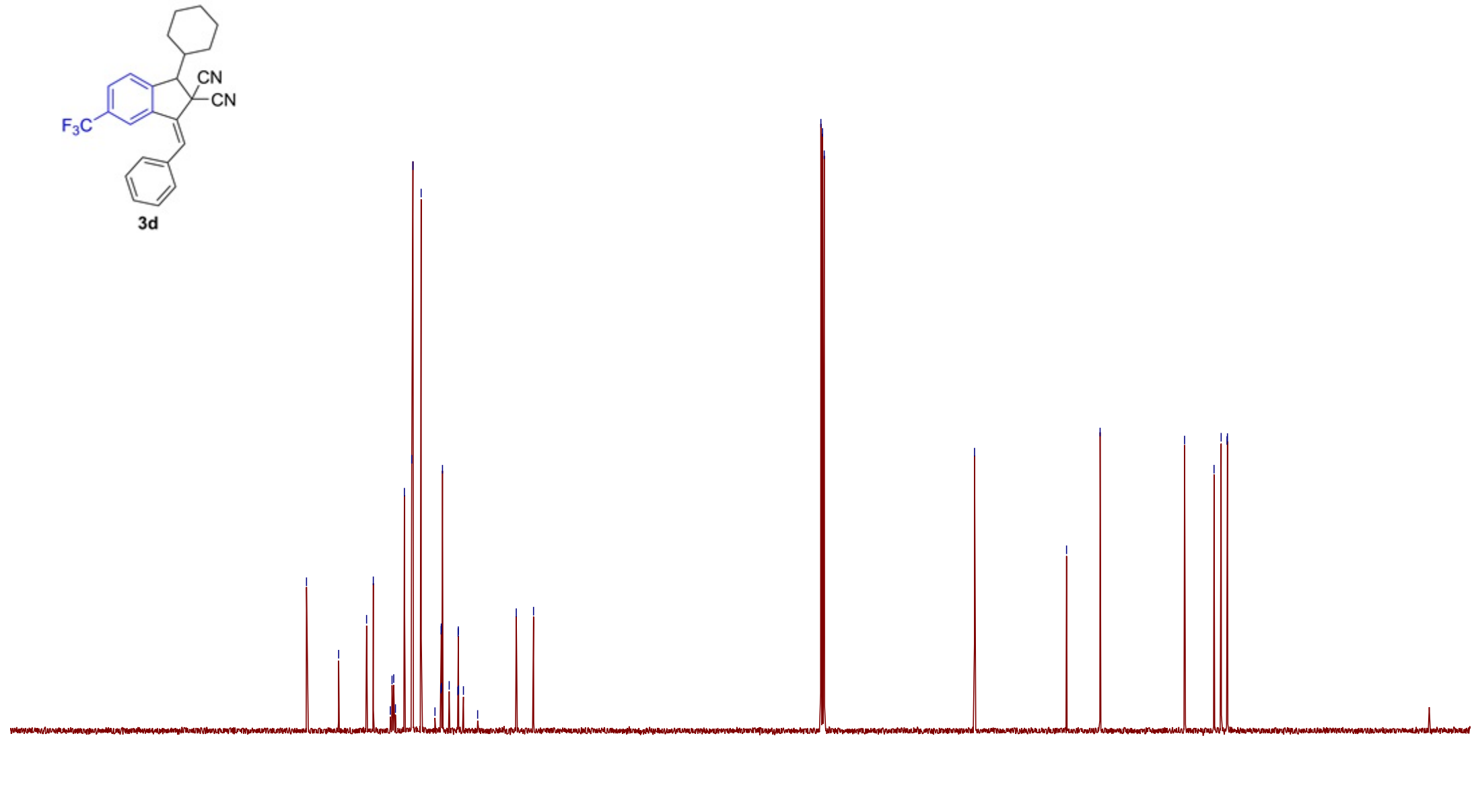
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41.75

31.02  
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25.57

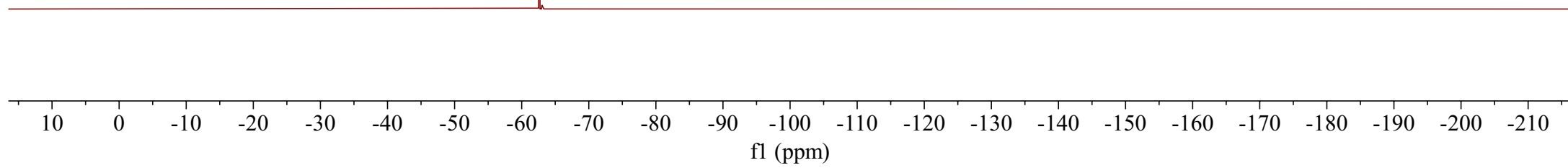
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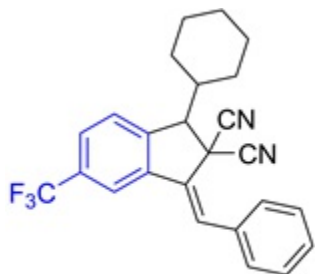
f1 (ppm)



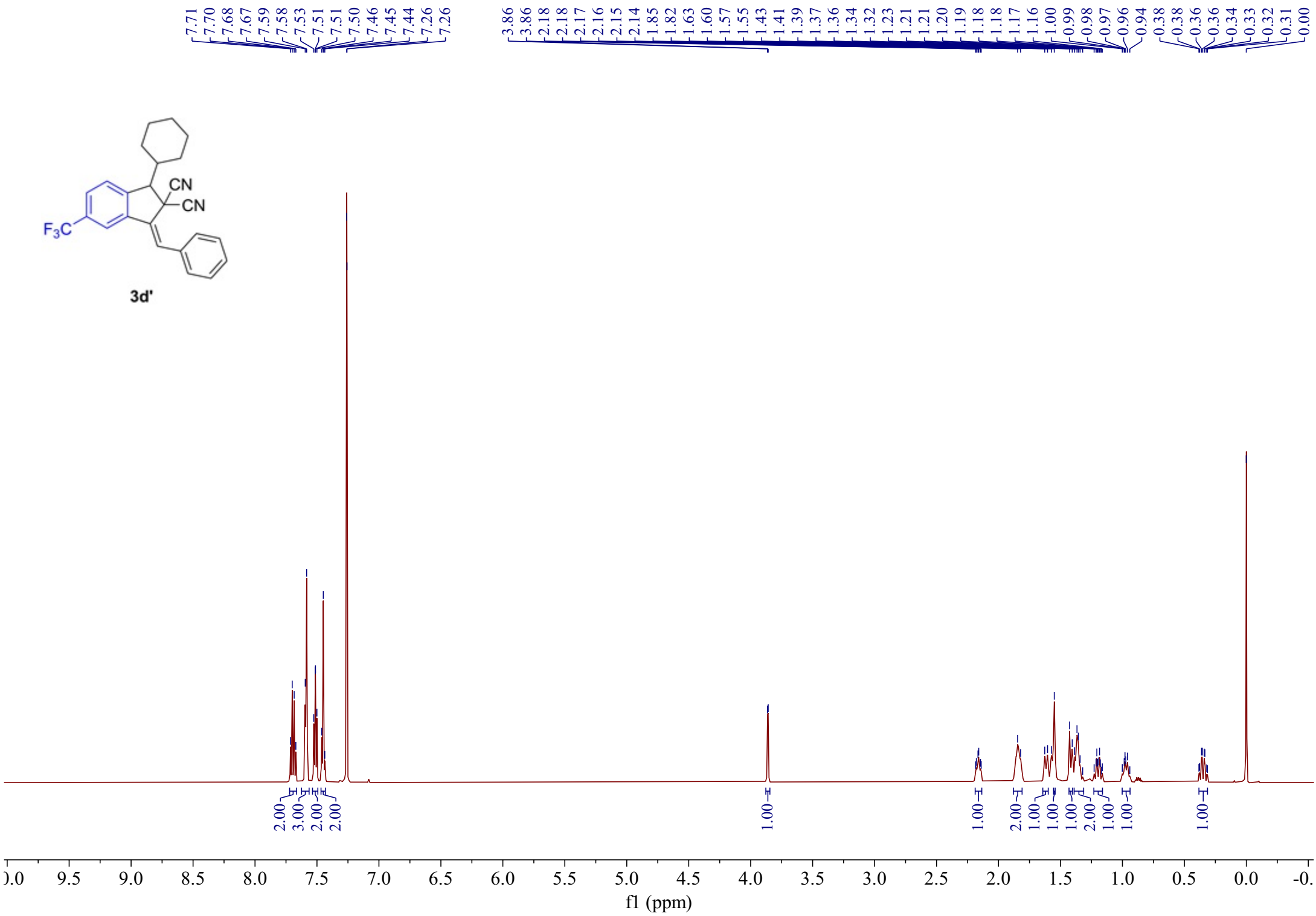


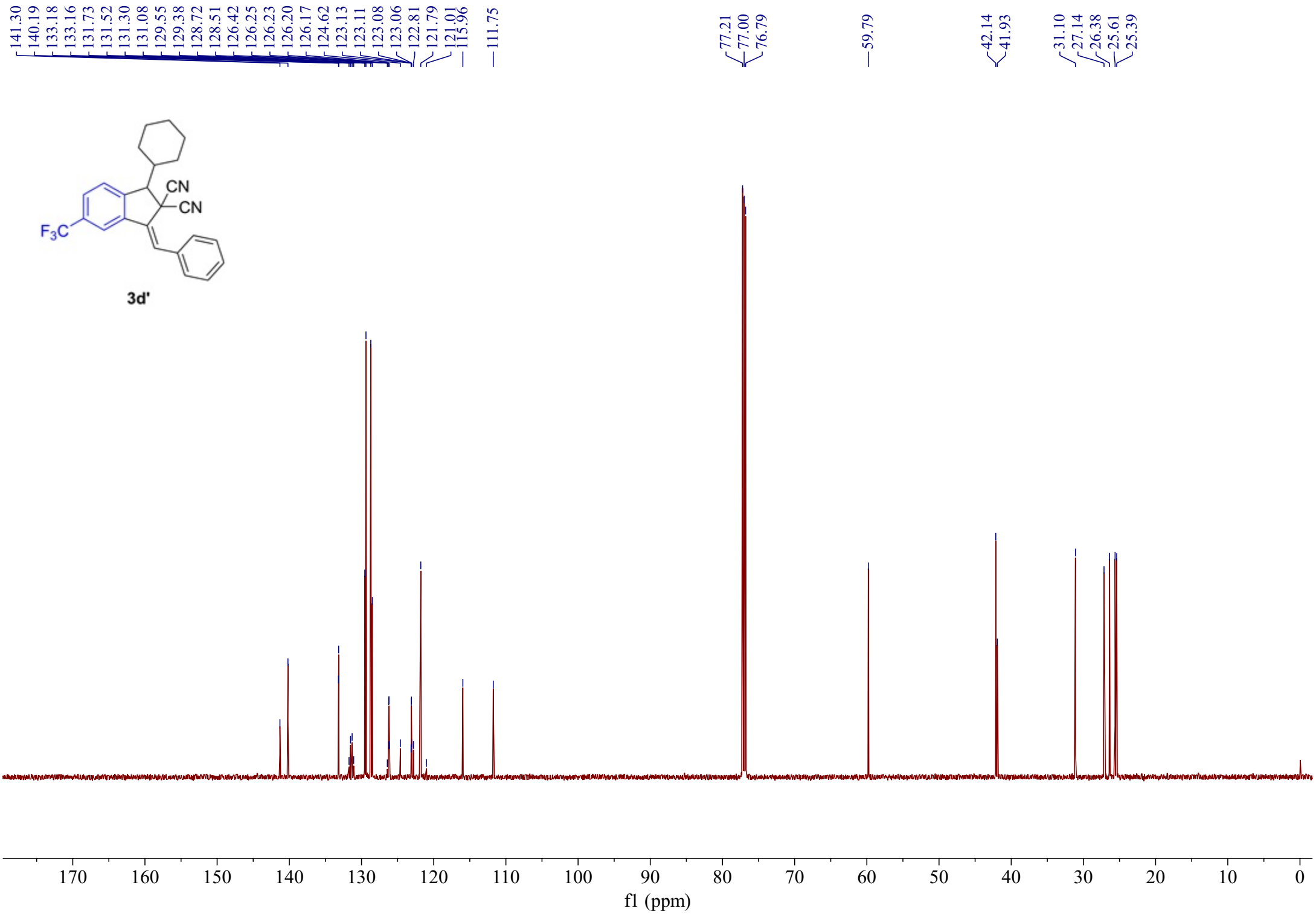
— -62.65





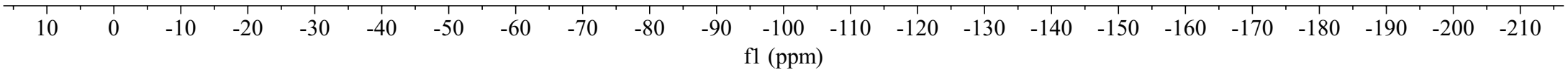
**3d'**

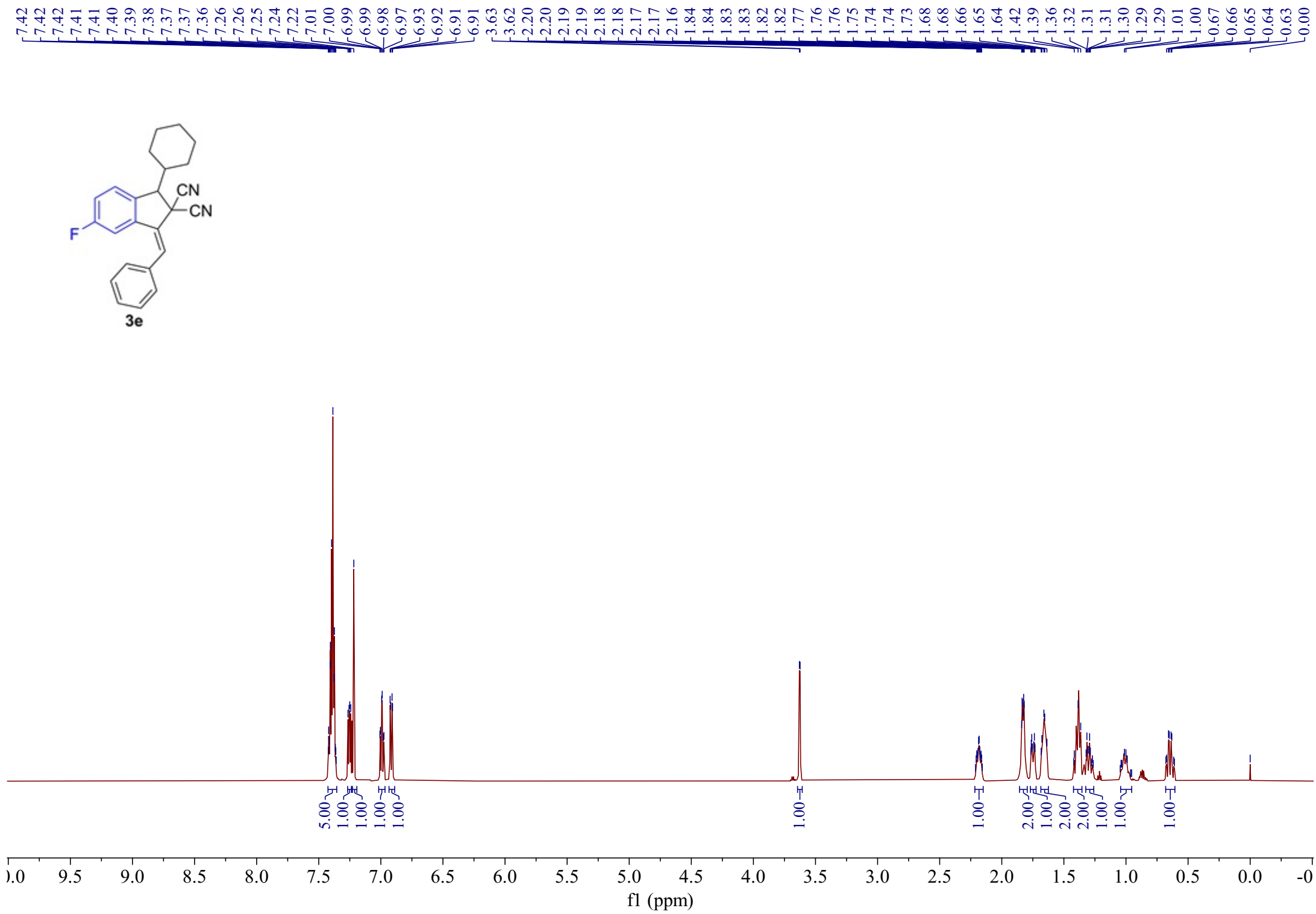
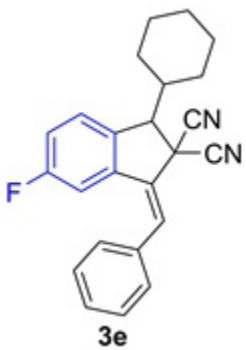


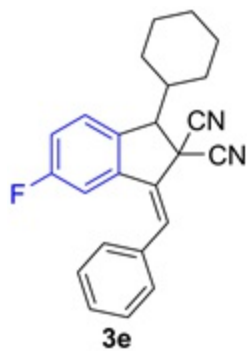




—-62.32







162.98  
161.34  
137.51  
137.49  
136.76  
136.70  
135.33  
135.31  
134.01  
128.89  
128.84  
128.63  
127.86  
127.59  
127.53  
117.23  
117.07  
116.13  
113.82  
111.62  
111.46

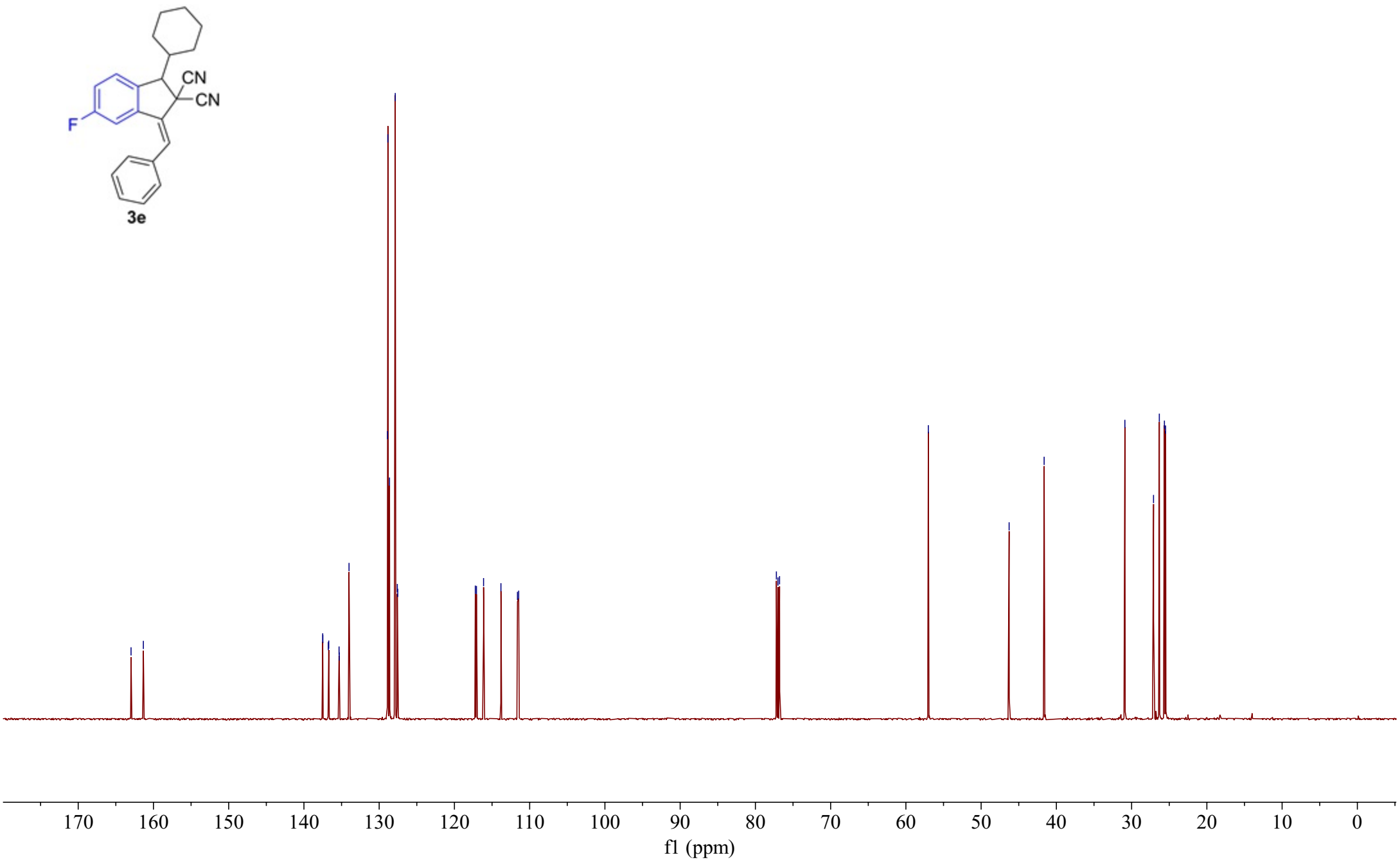
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76.79

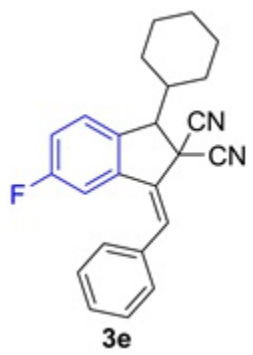
57.02

46.28

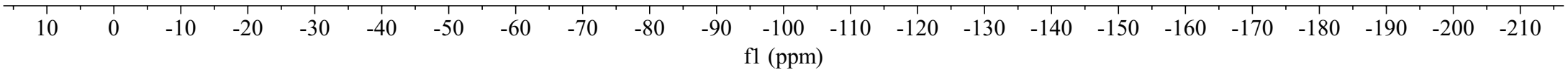
41.63

30.90  
27.09  
26.32  
25.64  
25.48

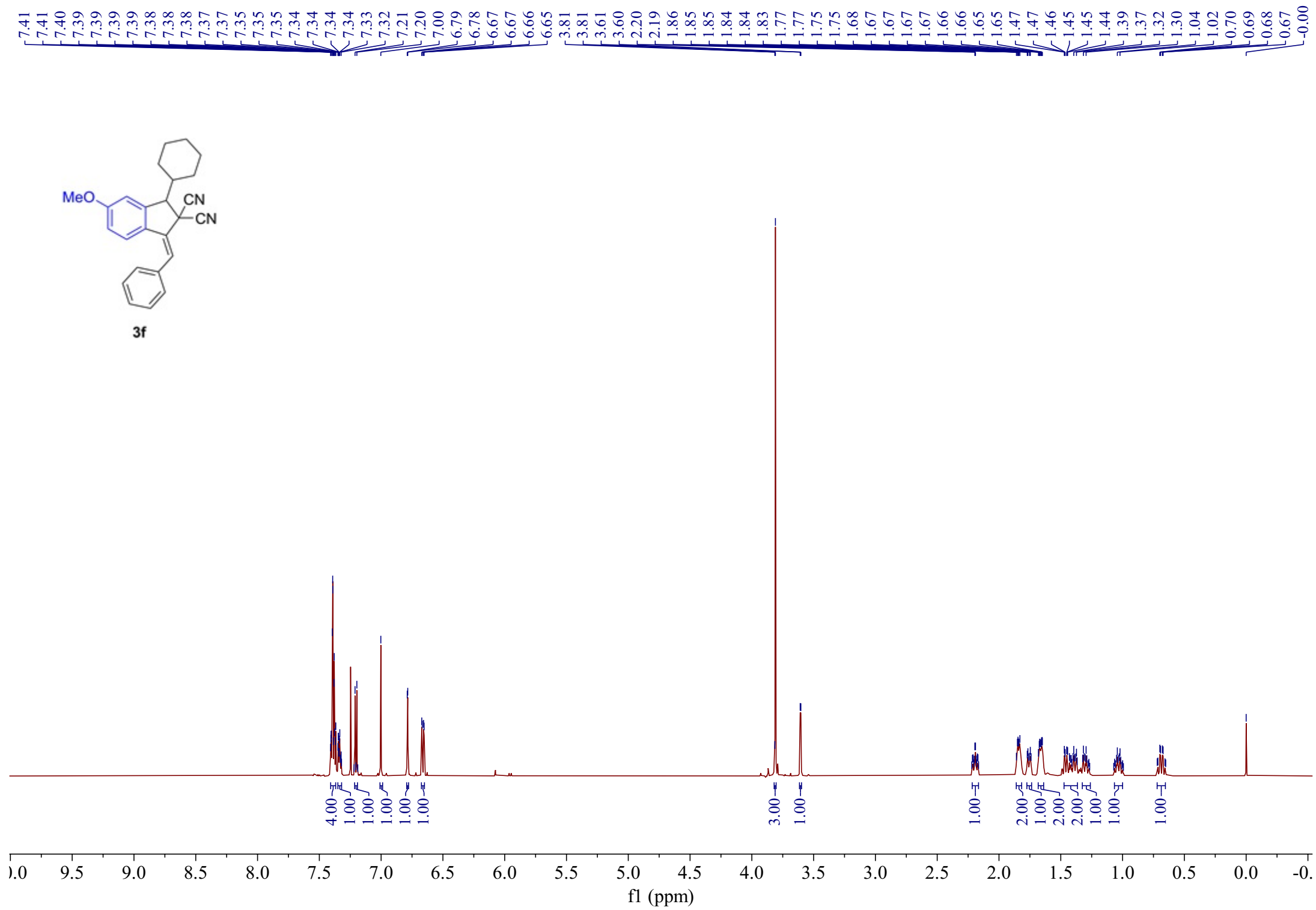
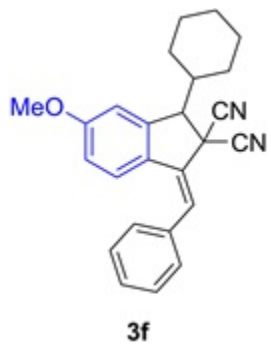


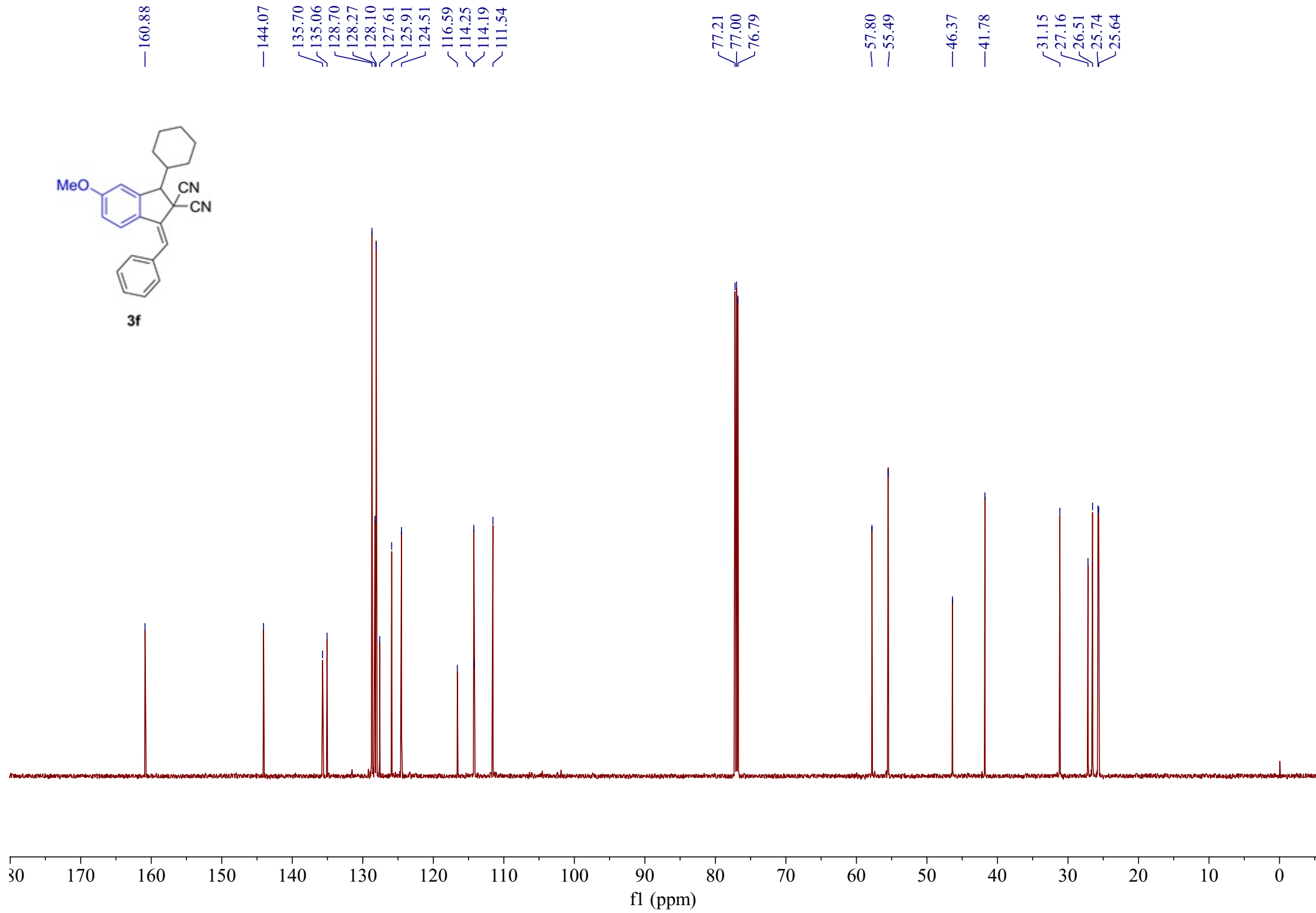
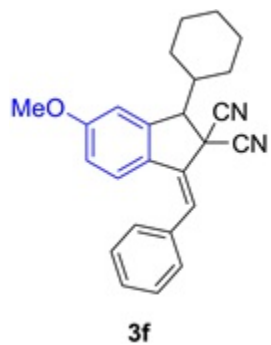


--112.15

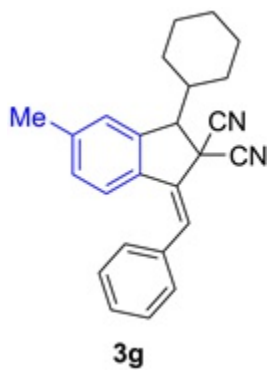












142.31  
 140.34  
 136.18  
 134.97  
 132.38  
 129.17  
 128.72  
 128.44  
 128.14  
 126.95  
 126.05  
 124.62  
 116.60  
 114.30

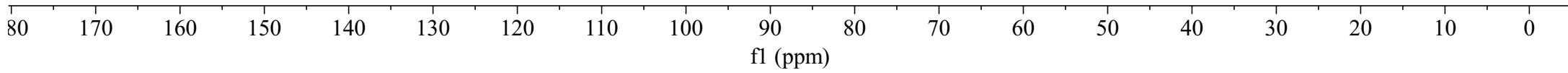
77.21  
 77.00  
 76.79

57.82

46.28

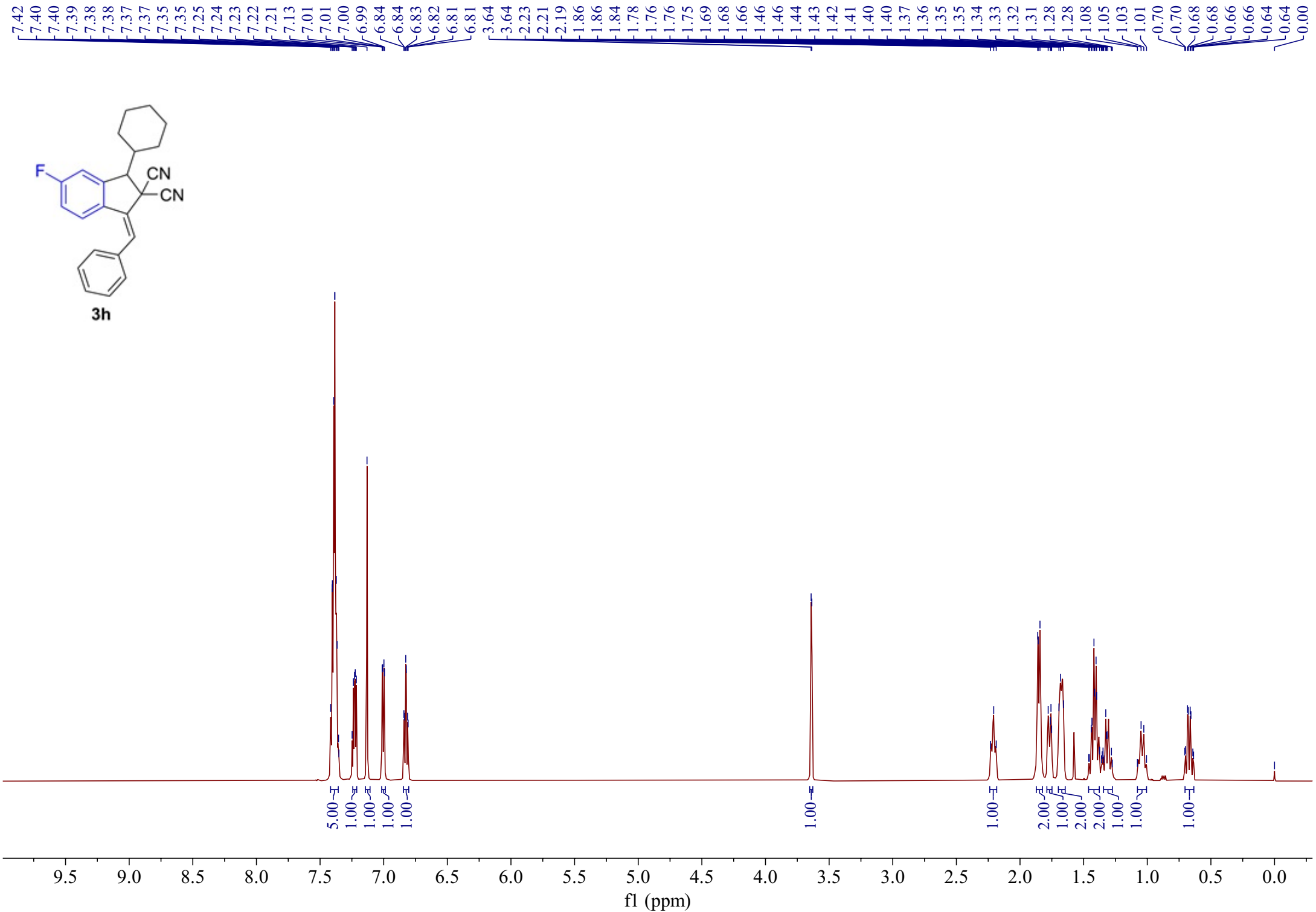
41.78

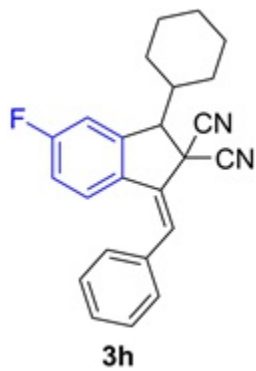
31.12  
 27.24  
 26.52  
 25.77  
 25.67  
 21.65





3h





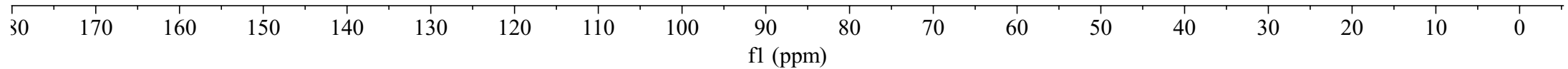
164.0  
162.4  
144.5  
144.4  
134.9  
134.5  
131.1  
131.1  
128.9  
128.7  
128.0  
126.8  
126.8  
126.5  
126.4  
116.2  
115.9  
115.7  
113.8  
113.6  
113.5

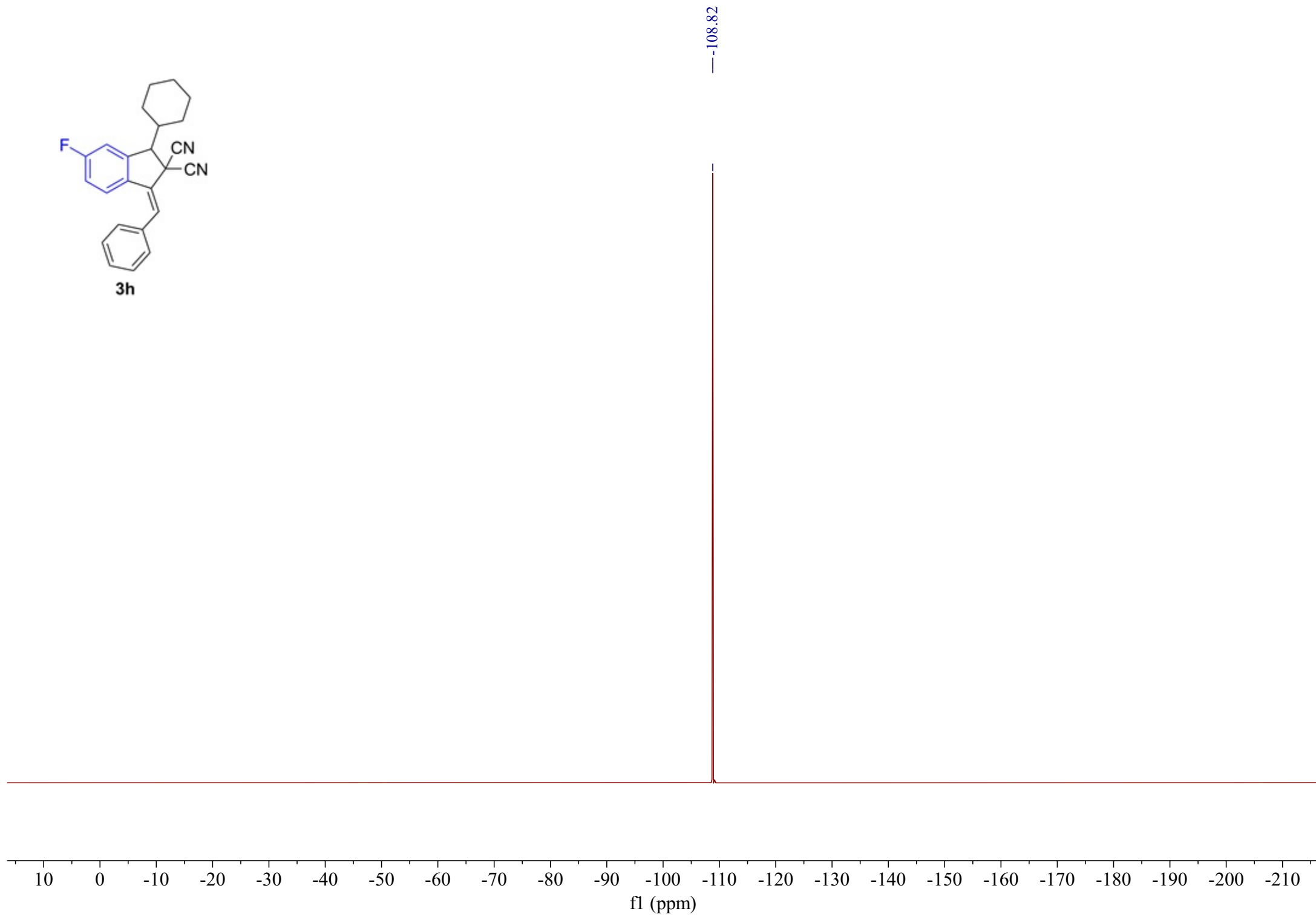
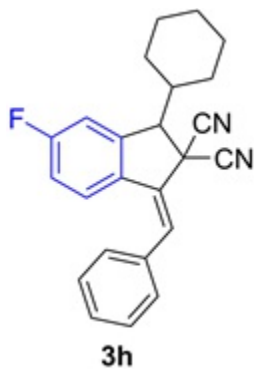
77.2  
77.0  
76.8

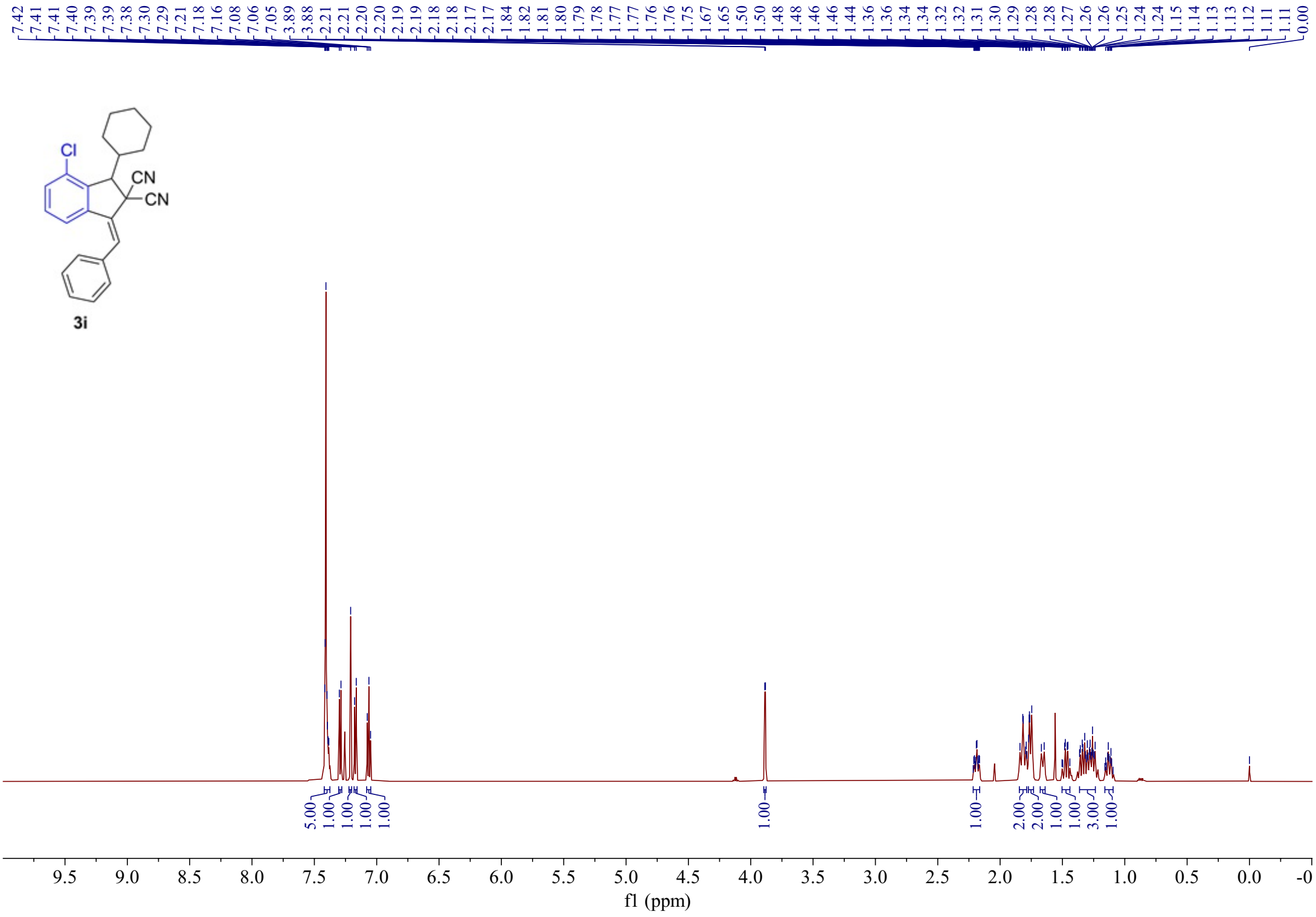
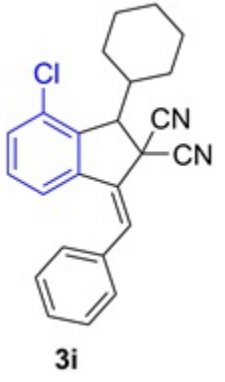
57.6  
57.6

46.3  
41.7

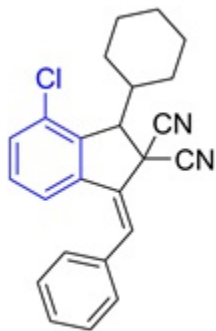
31.0  
27.2  
26.4  
25.7  
25.6











**3i**

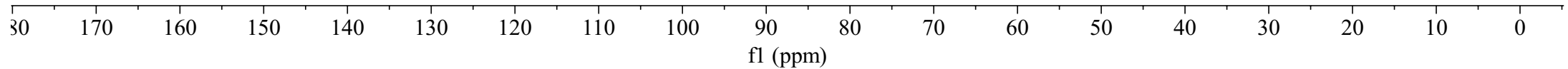
140.77  
136.91  
135.48  
134.24  
132.03  
130.87  
129.61  
128.95  
128.91  
128.73  
128.10  
123.12  
116.10  
114.17

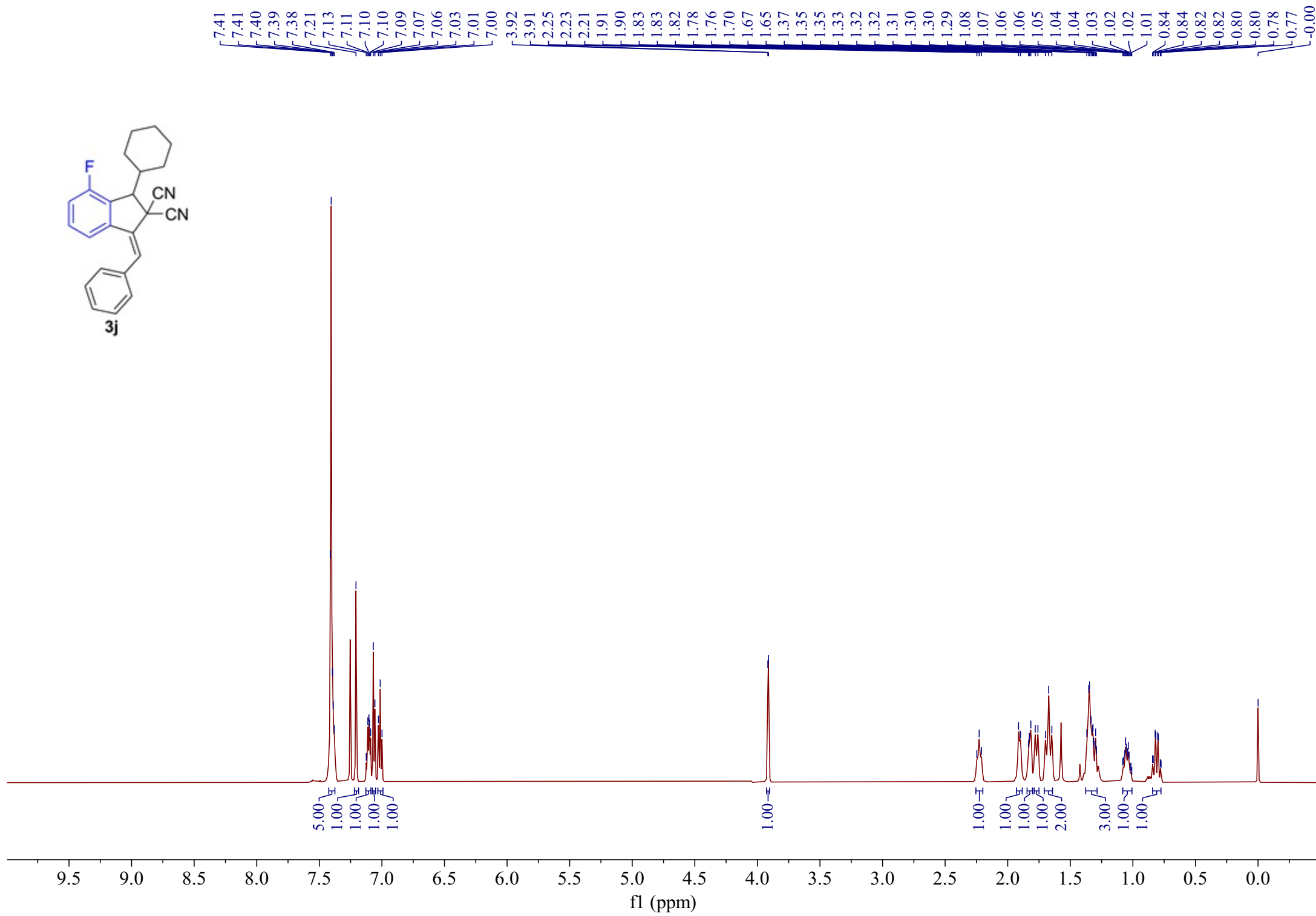
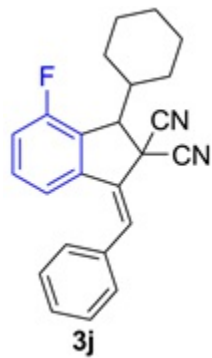
77.21  
77.00  
76.79

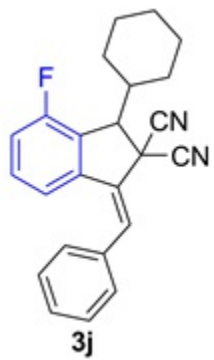
57.08

45.48  
42.80

30.64  
29.06  
26.70  
26.38  
25.72







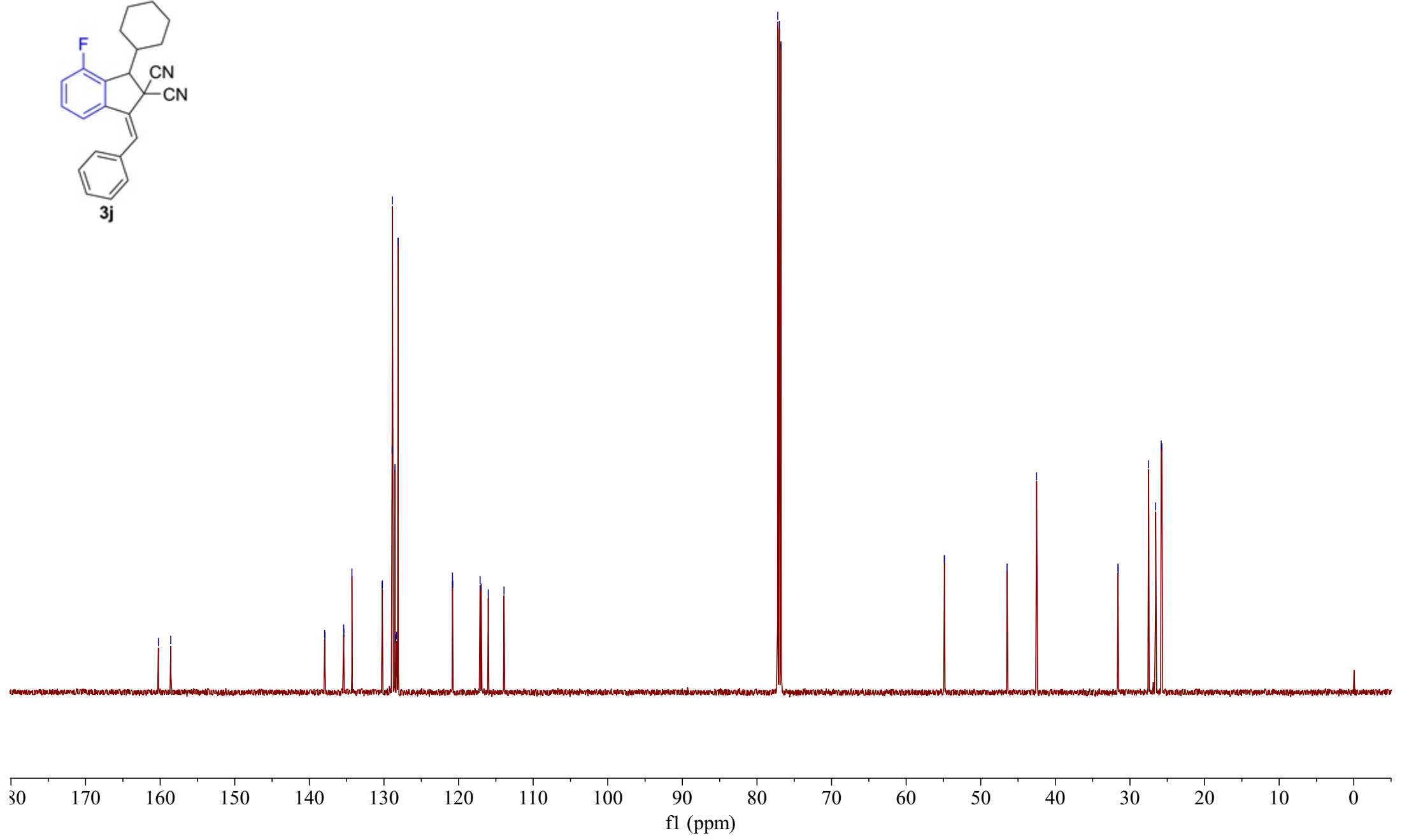
160.24  
158.58  
137.95  
137.92  
135.40  
135.39  
134.30  
130.26  
130.21  
128.91  
128.87  
128.53  
128.43  
128.31  
128.10  
120.81  
120.79  
117.12  
116.98  
116.02  
113.90

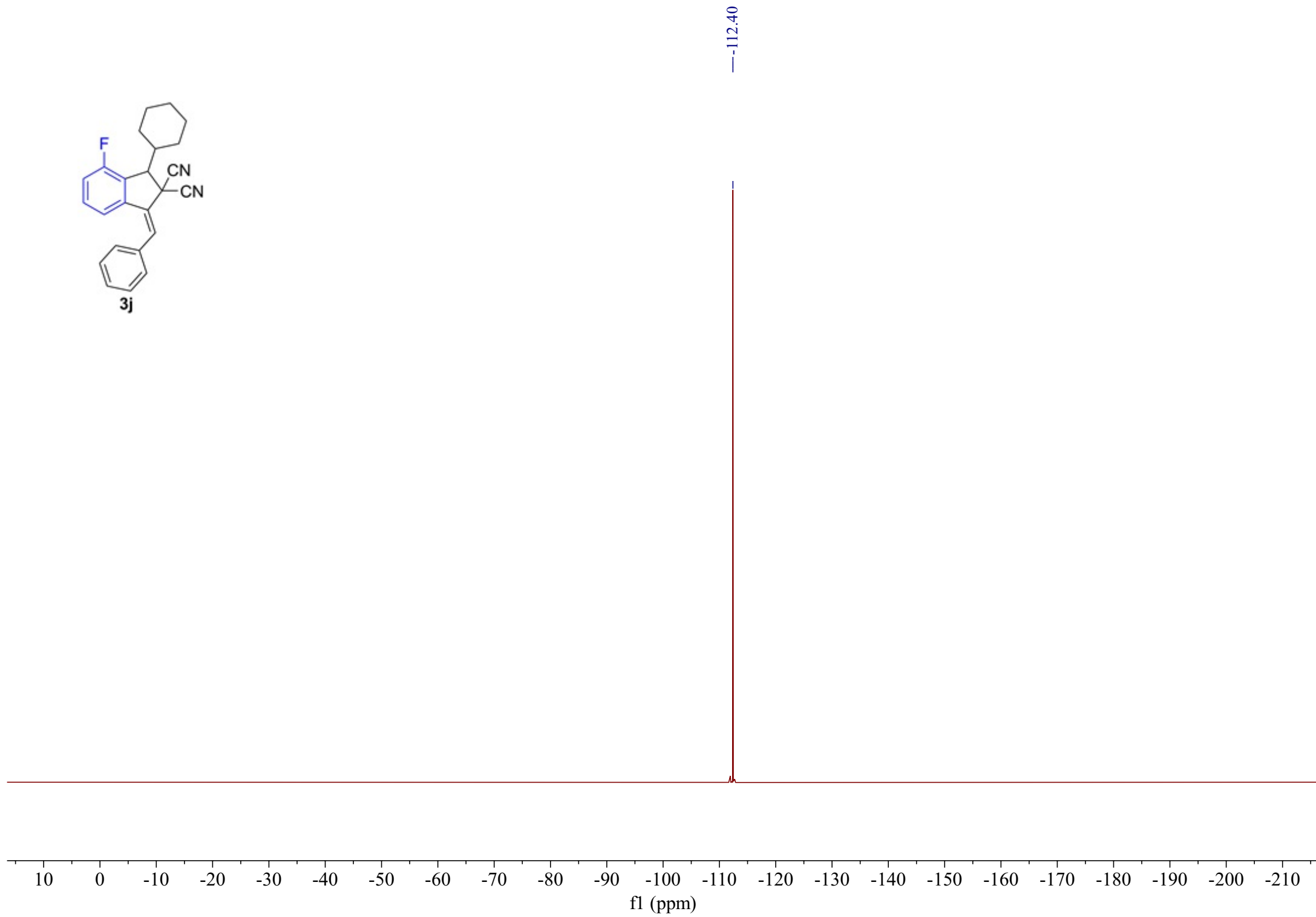
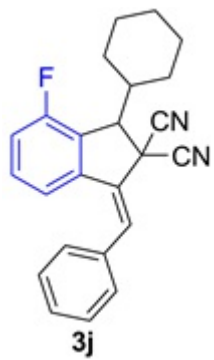
77.21  
77.00  
76.79

54.88  
54.87

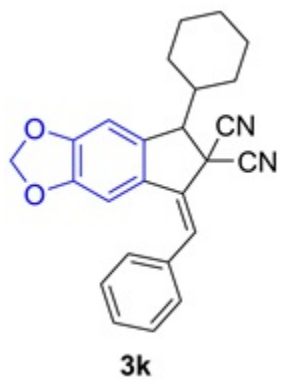
46.47  
42.51

31.61  
31.58  
27.50  
26.55  
25.81  
25.72









~149.53  
~147.96

~136.93  
~135.78  
~134.79  
~128.81  
~128.43  
~128.16  
~124.79

—116.64  
—114.11

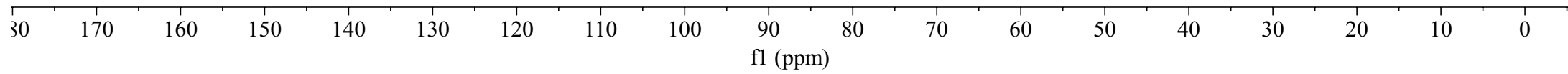
~106.37  
~104.59  
~101.93

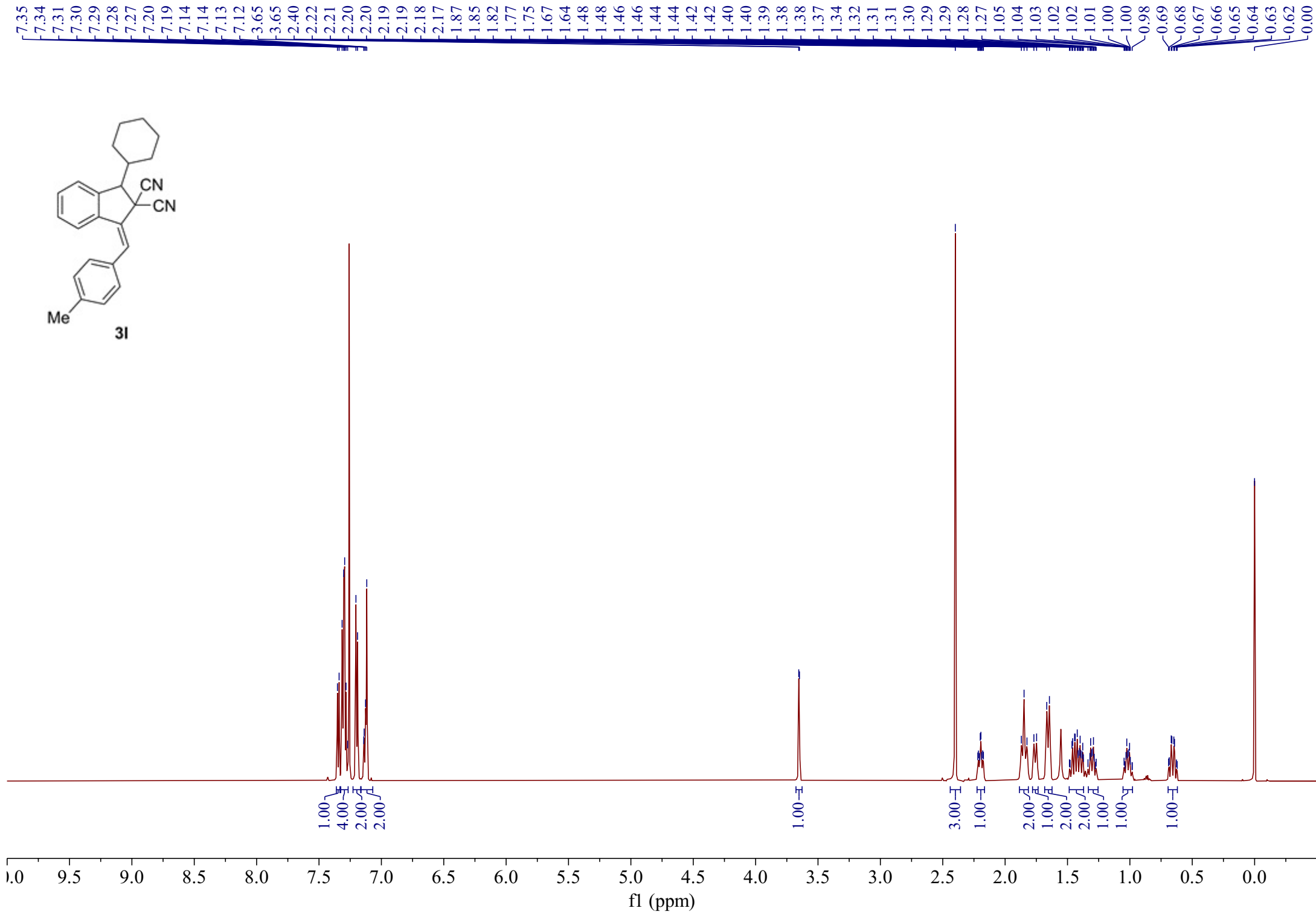
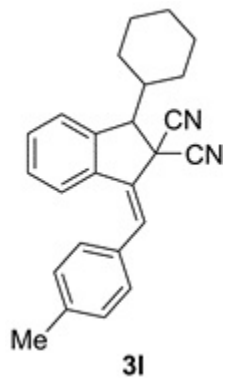
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~77.00  
~76.79

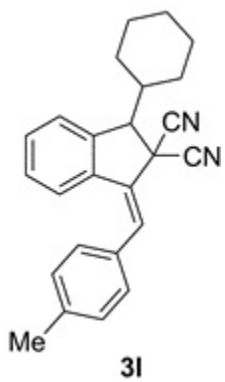
—57.46

—46.56  
—41.91

~31.19  
~27.19  
~26.55  
~25.82  
~25.65







141.94  
138.66  
135.49  
135.20  
131.77  
129.68  
129.45  
128.12  
128.05  
127.47  
126.46  
124.89  
116.58  
114.34

77.21  
77.00  
76.79

57.86

46.14

41.77

31.13

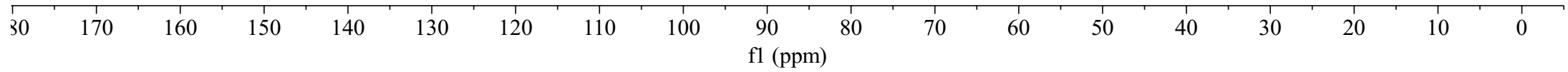
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26.52

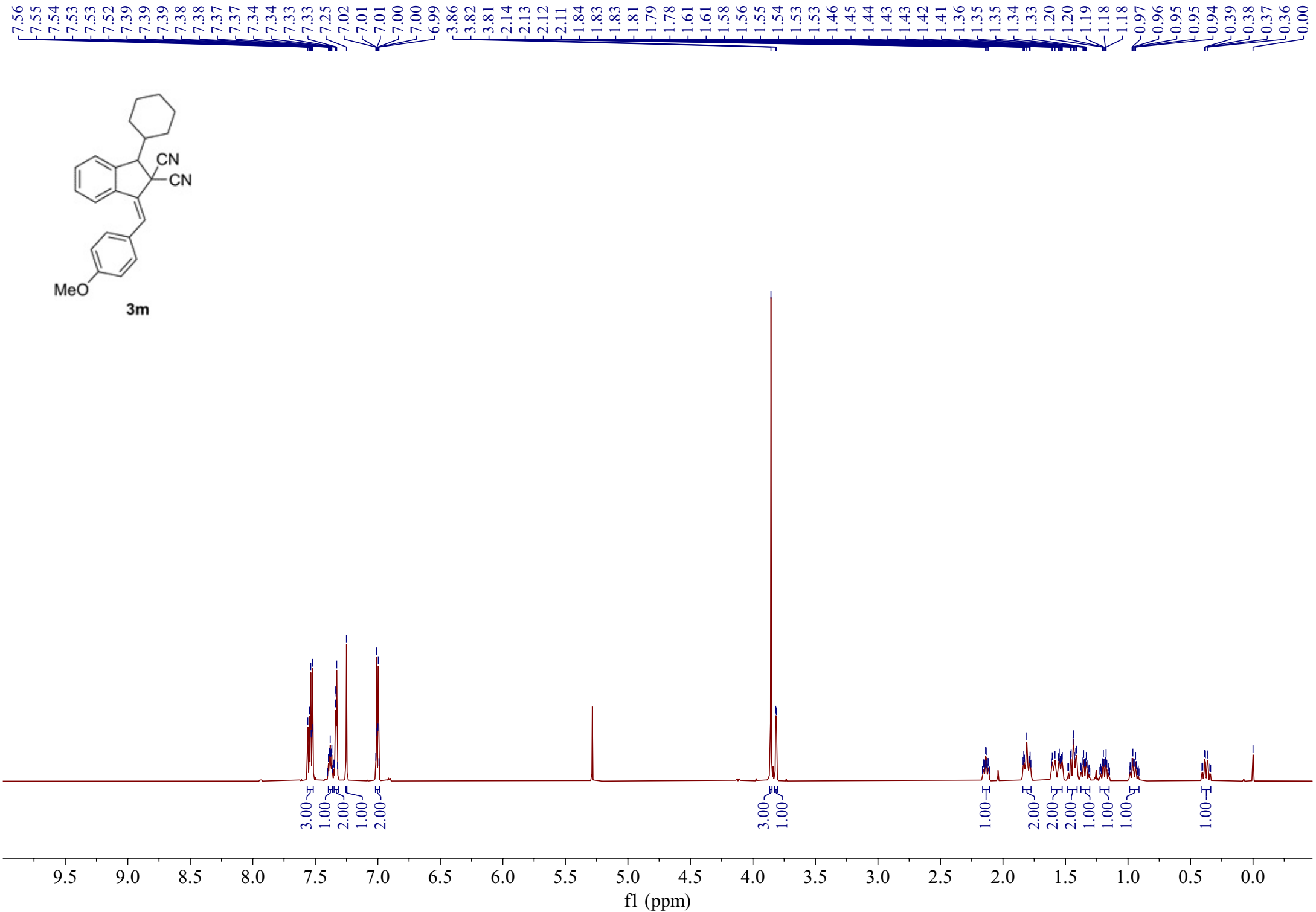
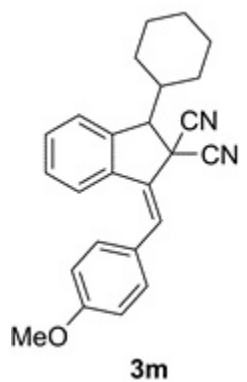
25.80

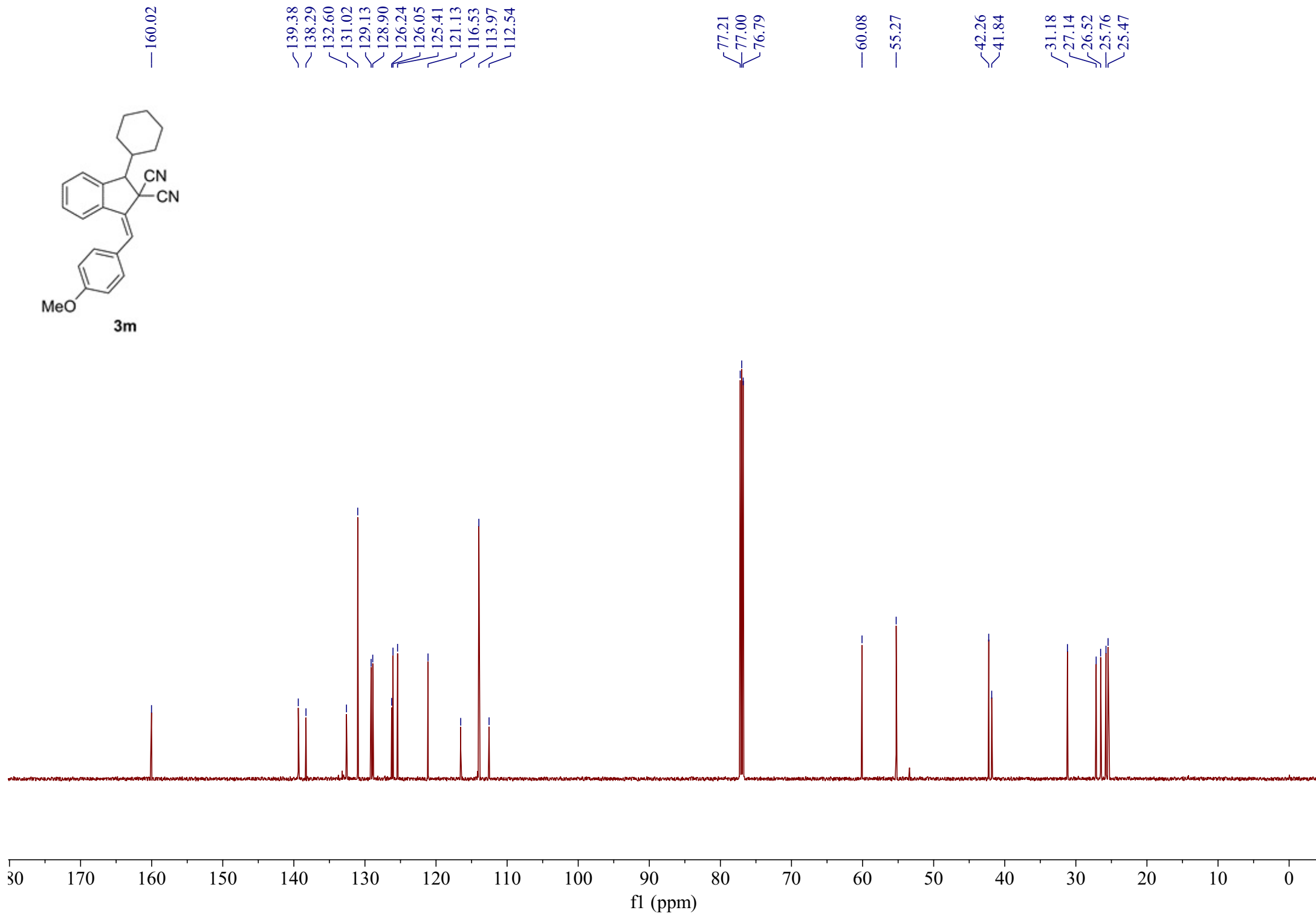
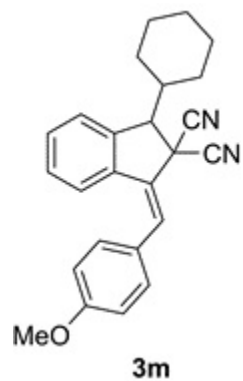
25.67

21.40

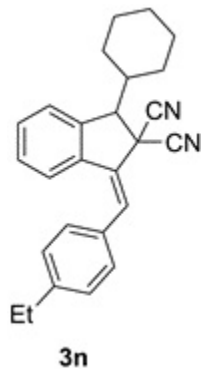












145.02  
141.95  
135.42  
135.21  
131.98  
129.68  
128.23  
128.14  
128.13  
127.48  
126.46  
124.88  
— 116.58  
— 114.33

77.21  
77.00  
76.79

— 57.86

— 46.19

— 41.77

31.12

28.72

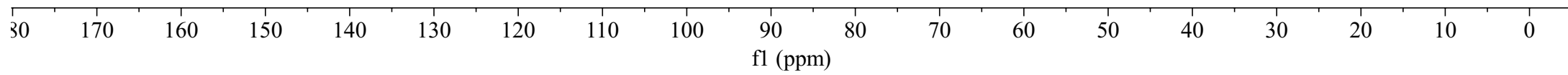
27.25

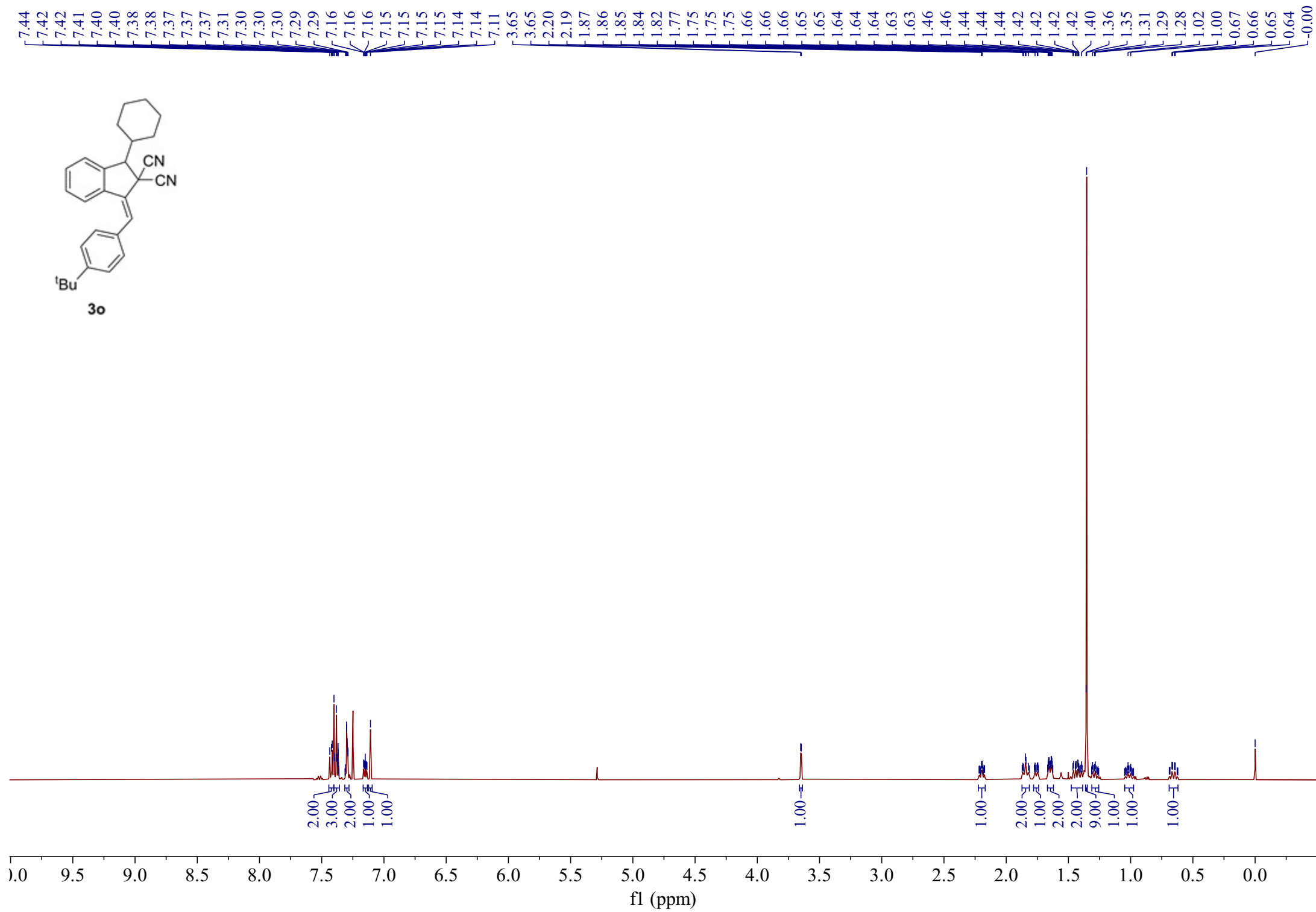
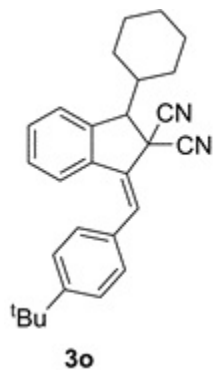
26.52

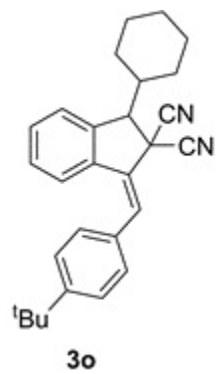
25.79

25.66

— 15.39







— 151.99  
— 141.96  
— 135.36  
— 135.20  
— 131.71  
— 129.68  
— 128.13  
— 127.92  
— 127.35  
— 126.44  
— 125.62  
— 124.86  
— 116.57  
— 114.32

— 77.21  
— 77.00  
— 76.79

— 57.84

— 46.28

— 41.75

— 34.76

— 31.23

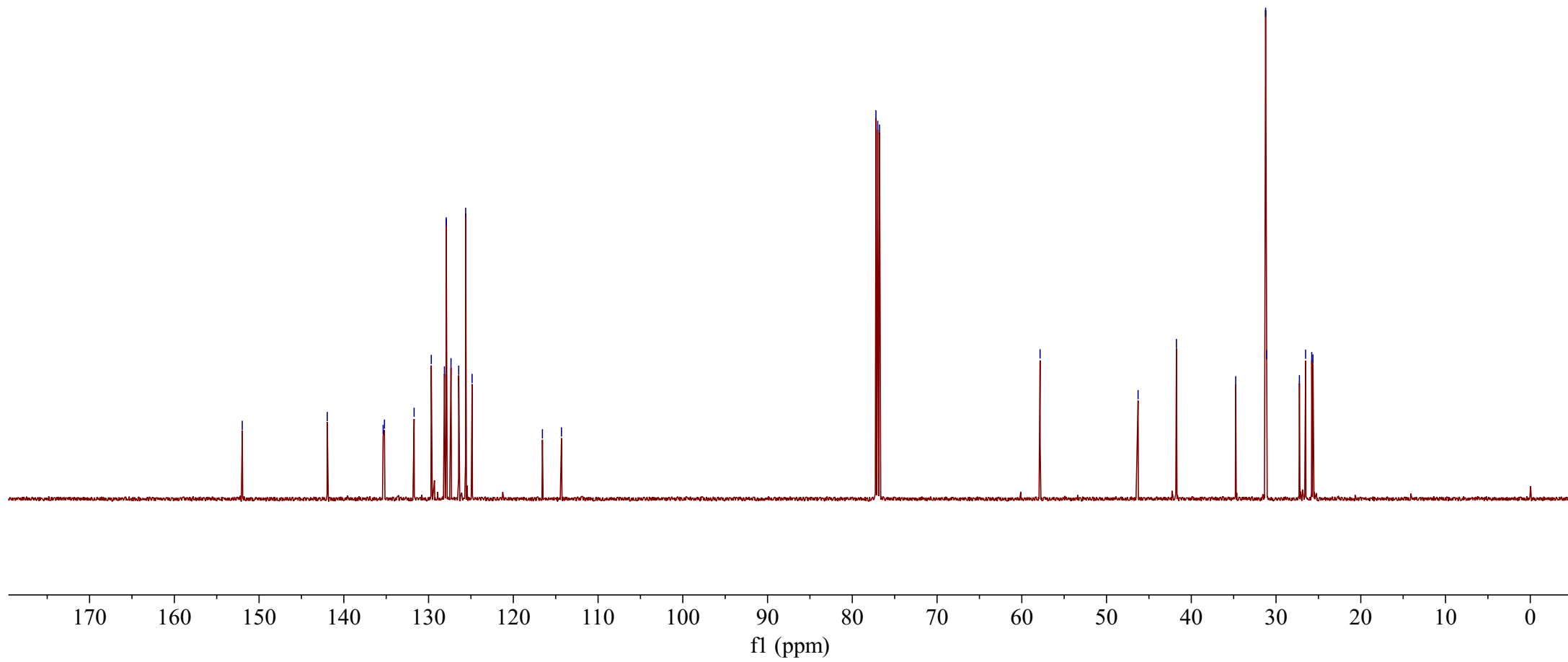
— 31.10

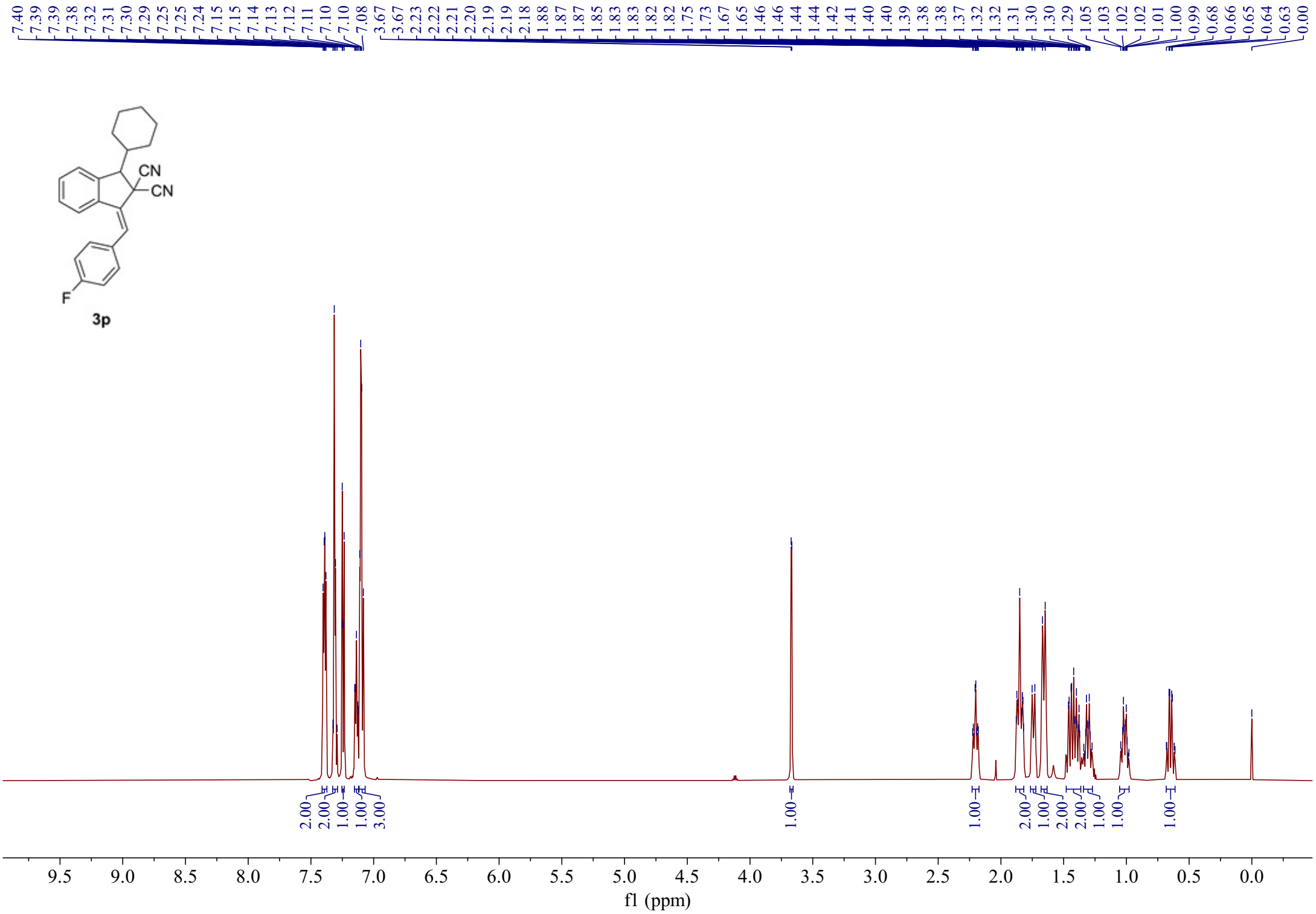
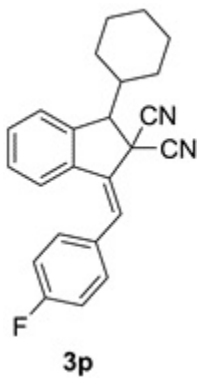
— 27.24

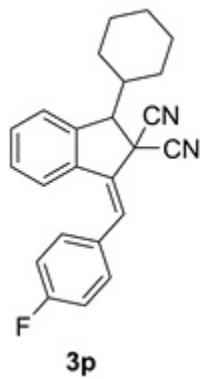
— 26.51

— 25.79

— 25.64







163.5  
161.8

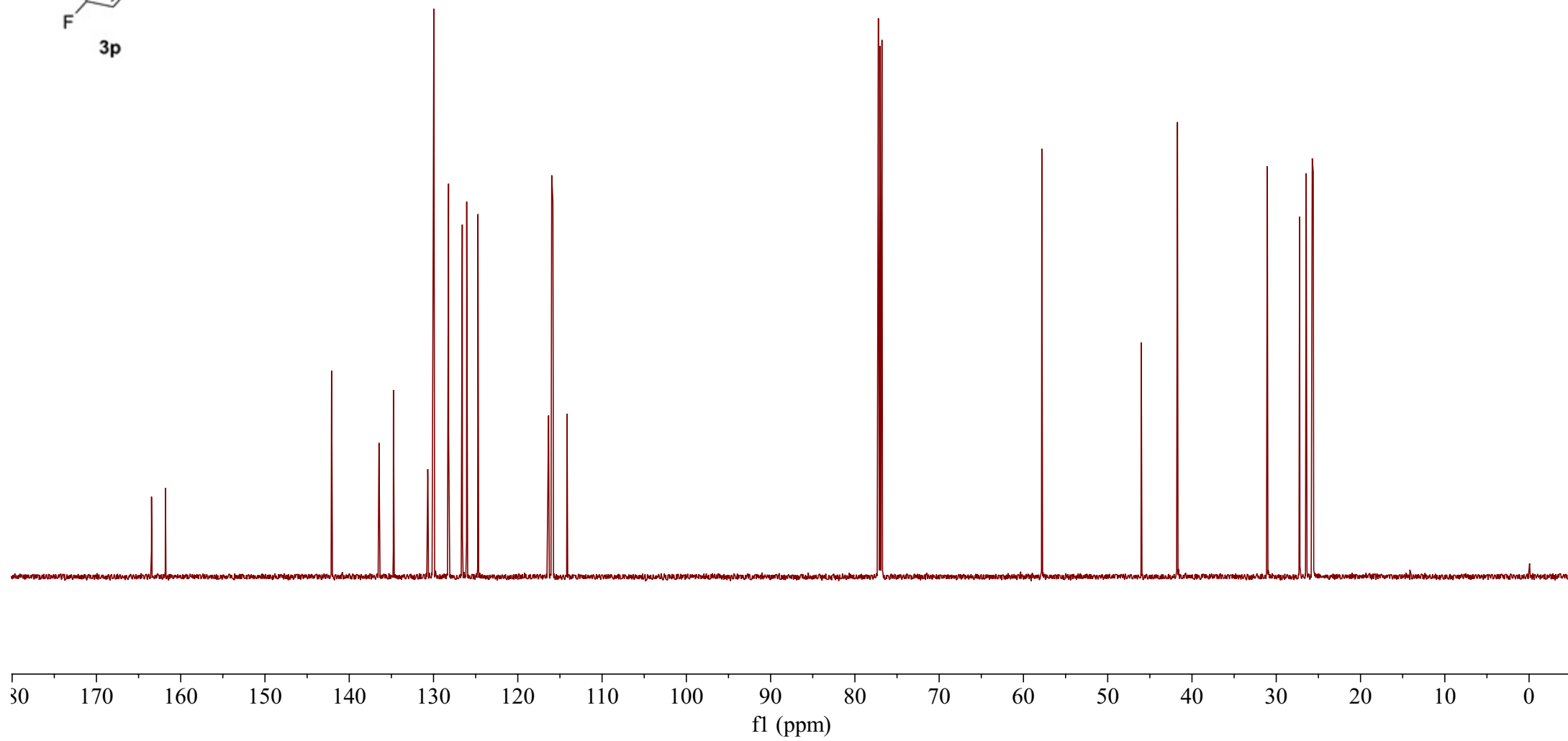
142.1  
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134.8  
130.7  
130.7  
130.0  
130.0  
128.2  
126.6  
126.1  
124.7  
116.3  
116.0  
115.8  
114.2

77.2  
77.0  
76.8

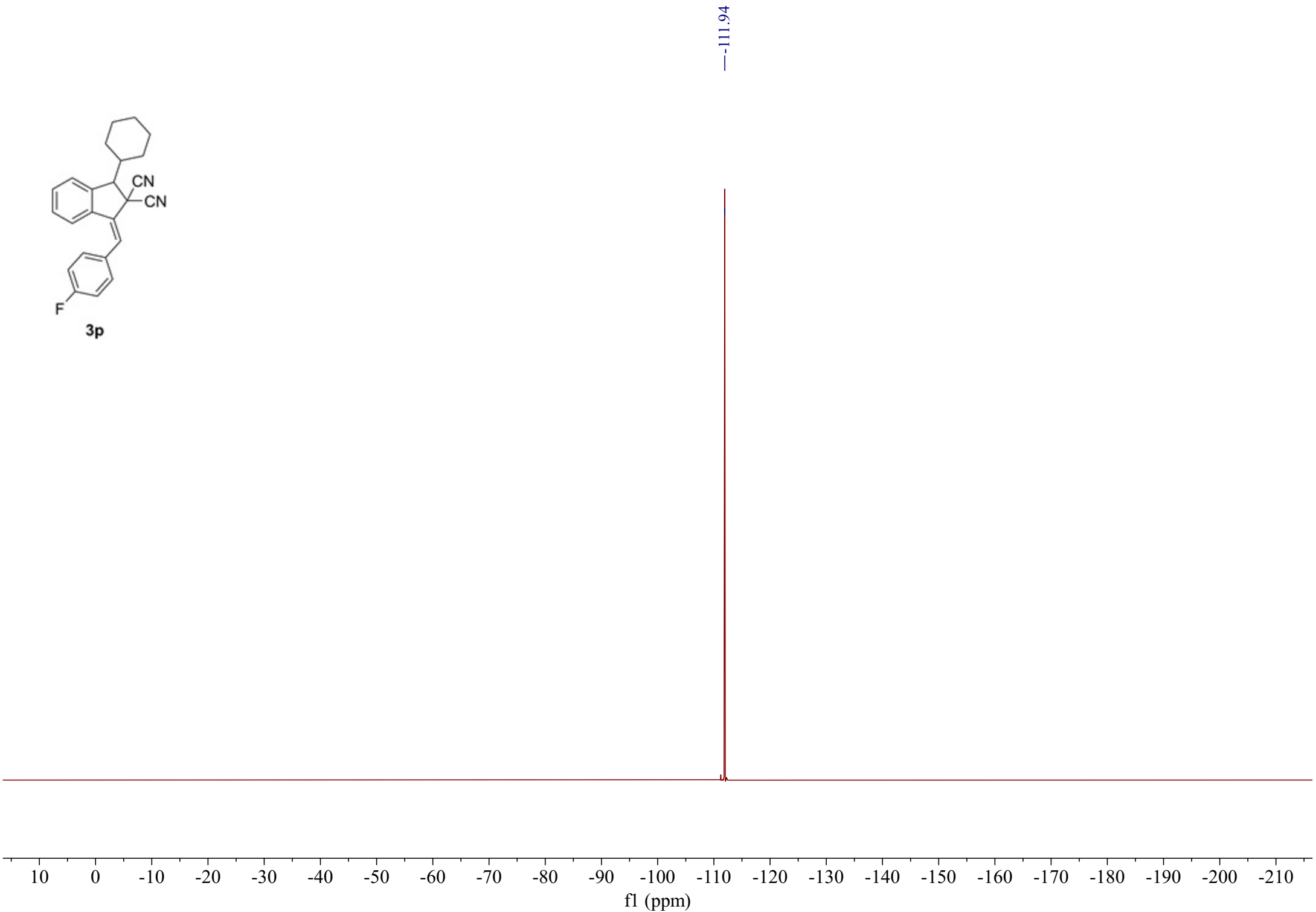
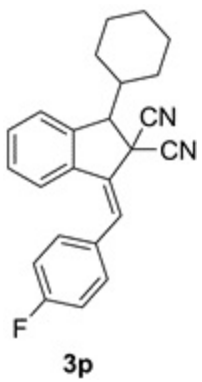
57.8

46.0  
41.7

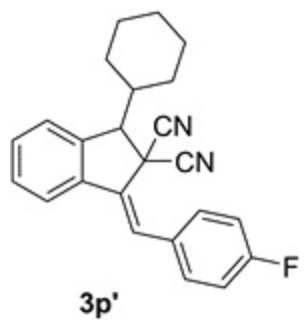
31.1  
27.2  
26.5  
25.7  
25.6











163.64  
161.98

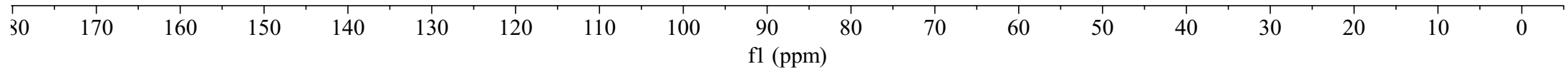
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131.17  
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129.03  
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124.50  
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115.72  
112.33

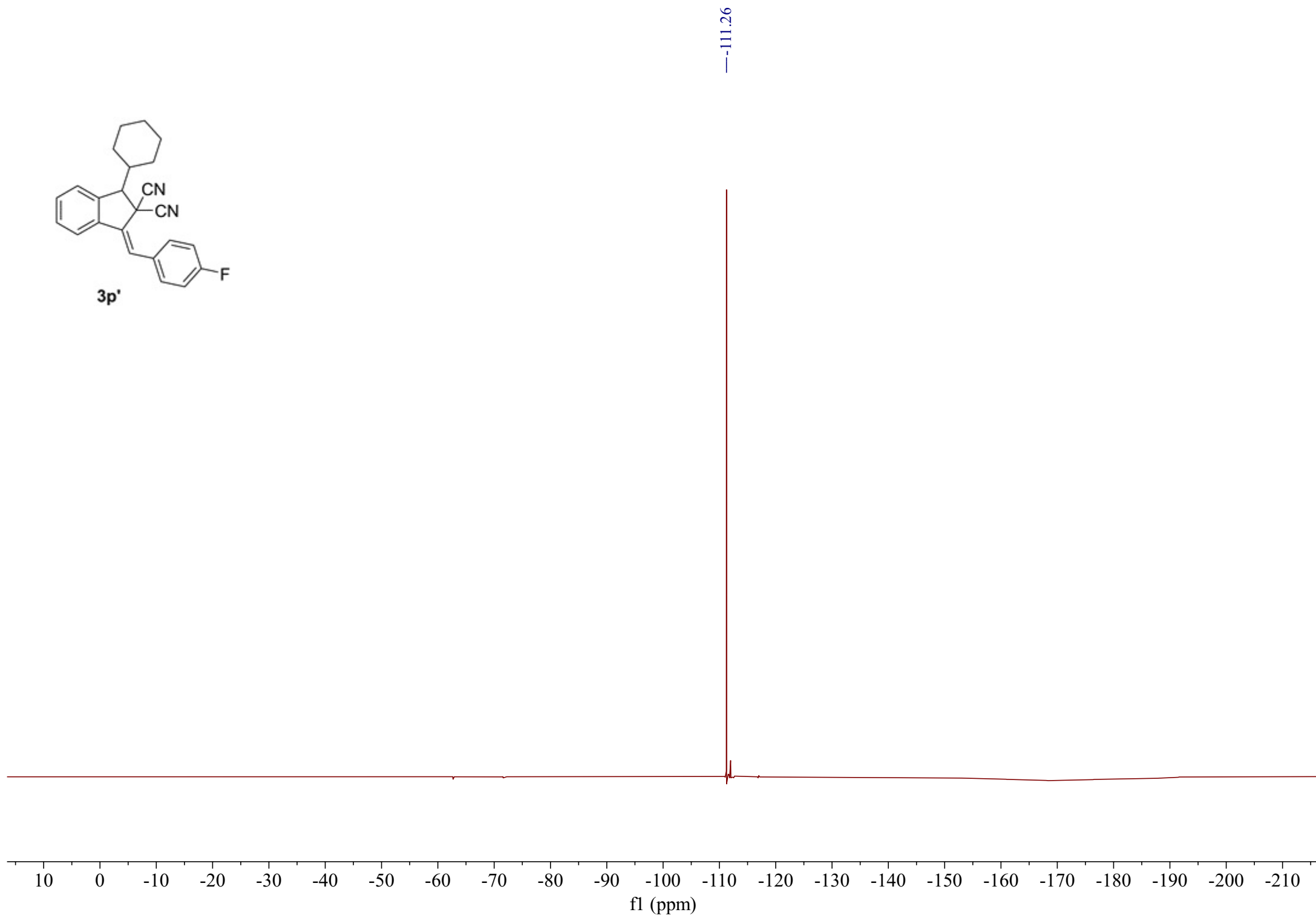
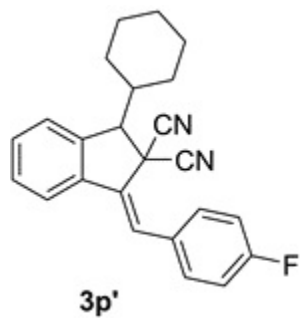
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76.79

59.98

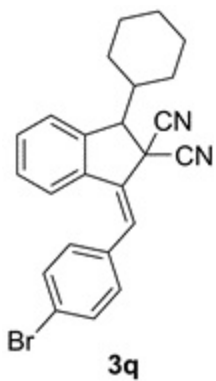
42.22  
41.70

31.17  
27.15  
26.49  
25.75  
25.46









142.19  
136.92  
134.59  
133.60  
131.99  
130.09  
129.75  
128.25  
126.59  
125.79  
124.79  
122.60  
116.20  
114.05

57.81

46.05

41.69

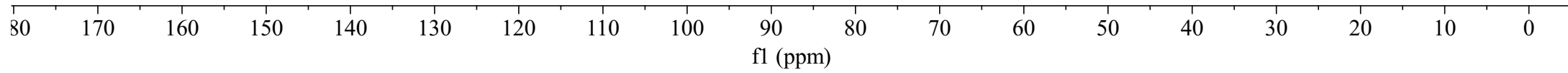
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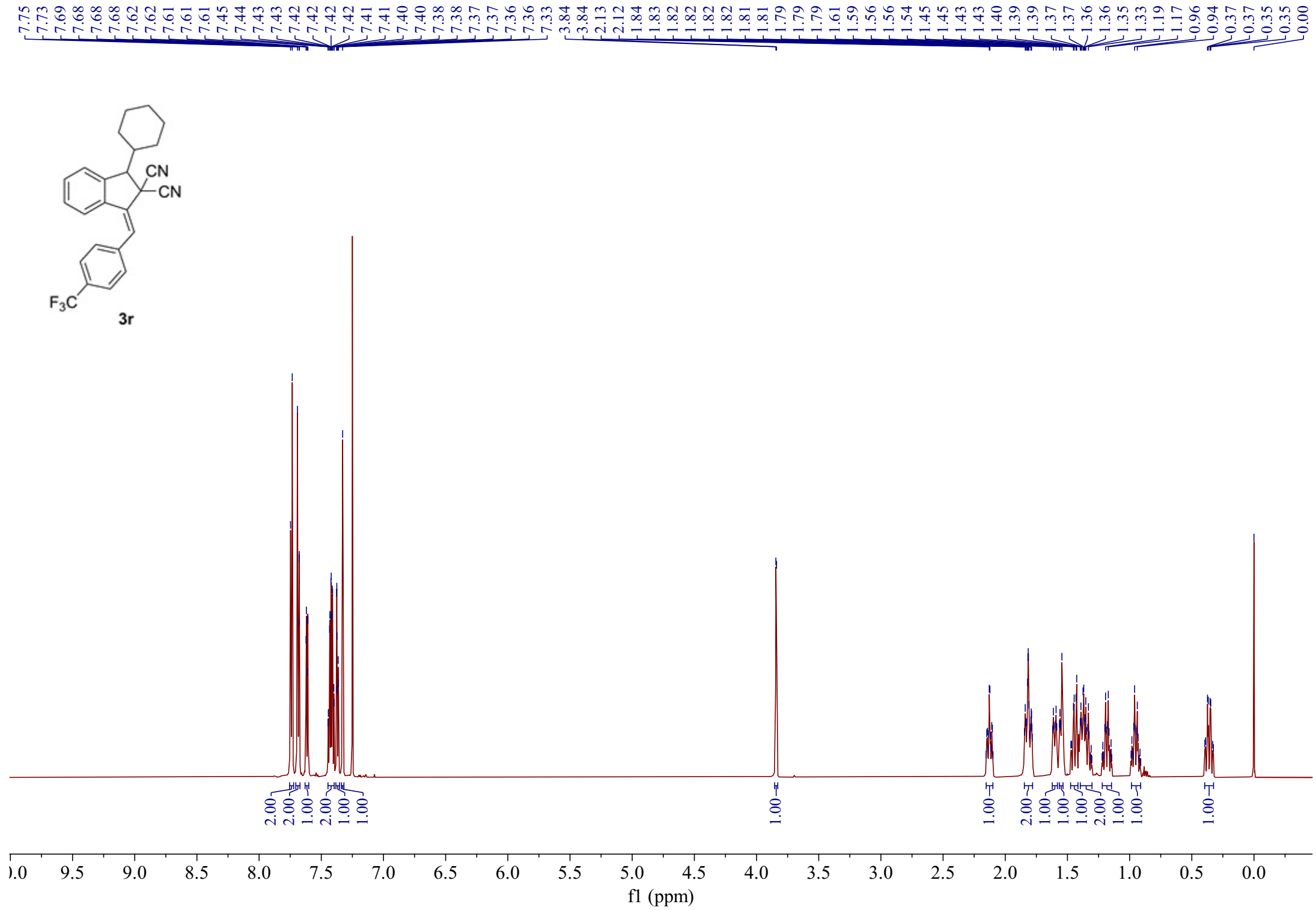
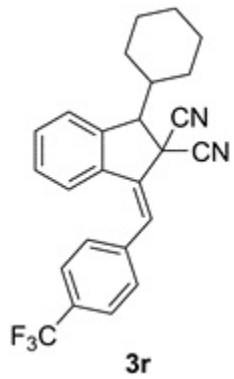
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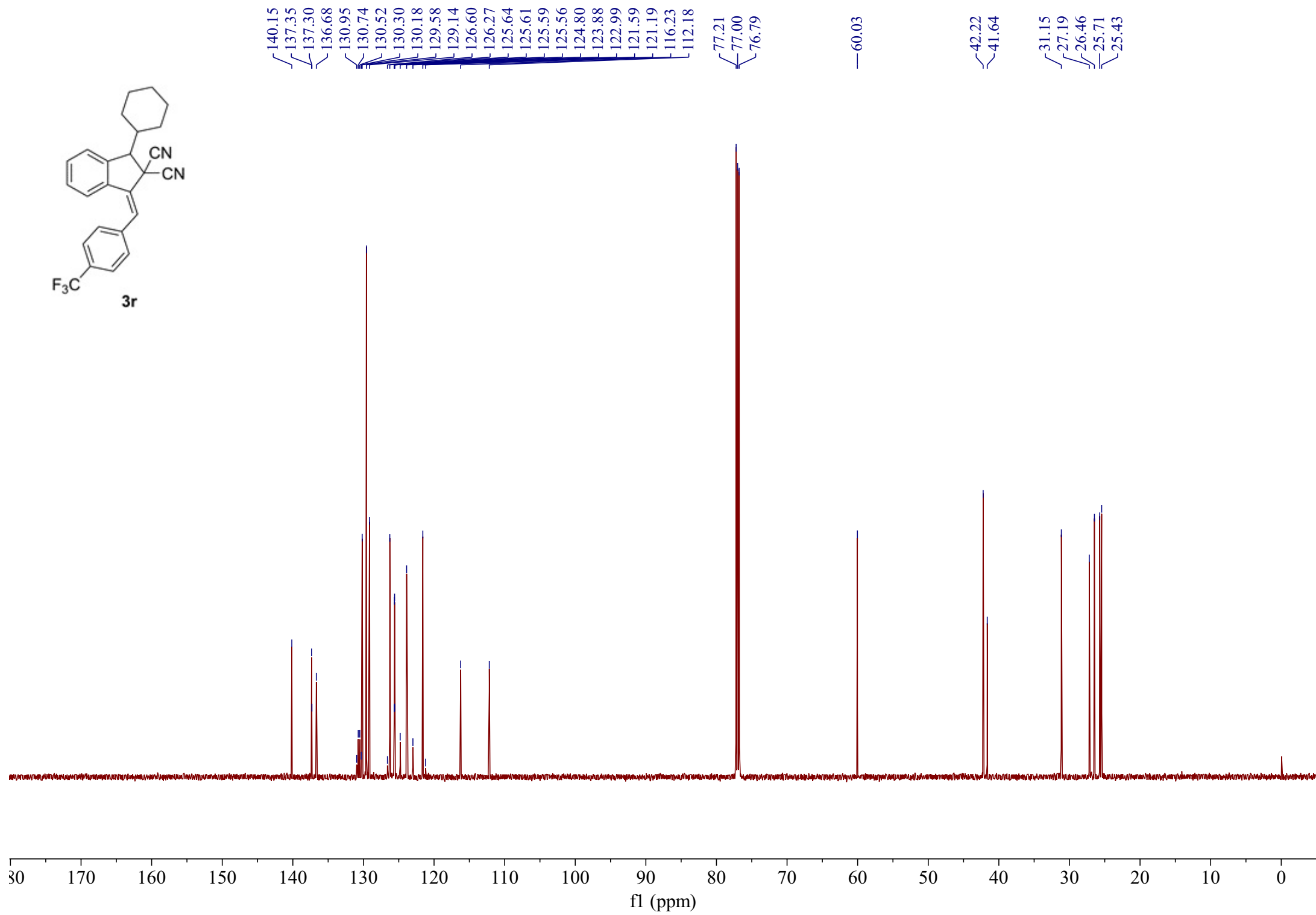
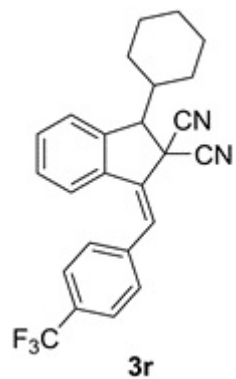
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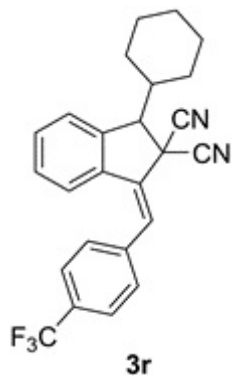
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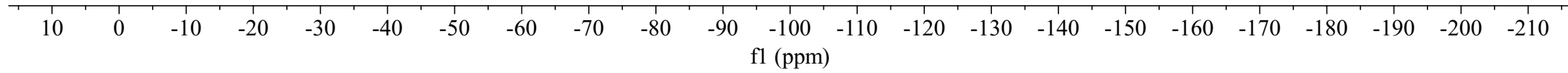


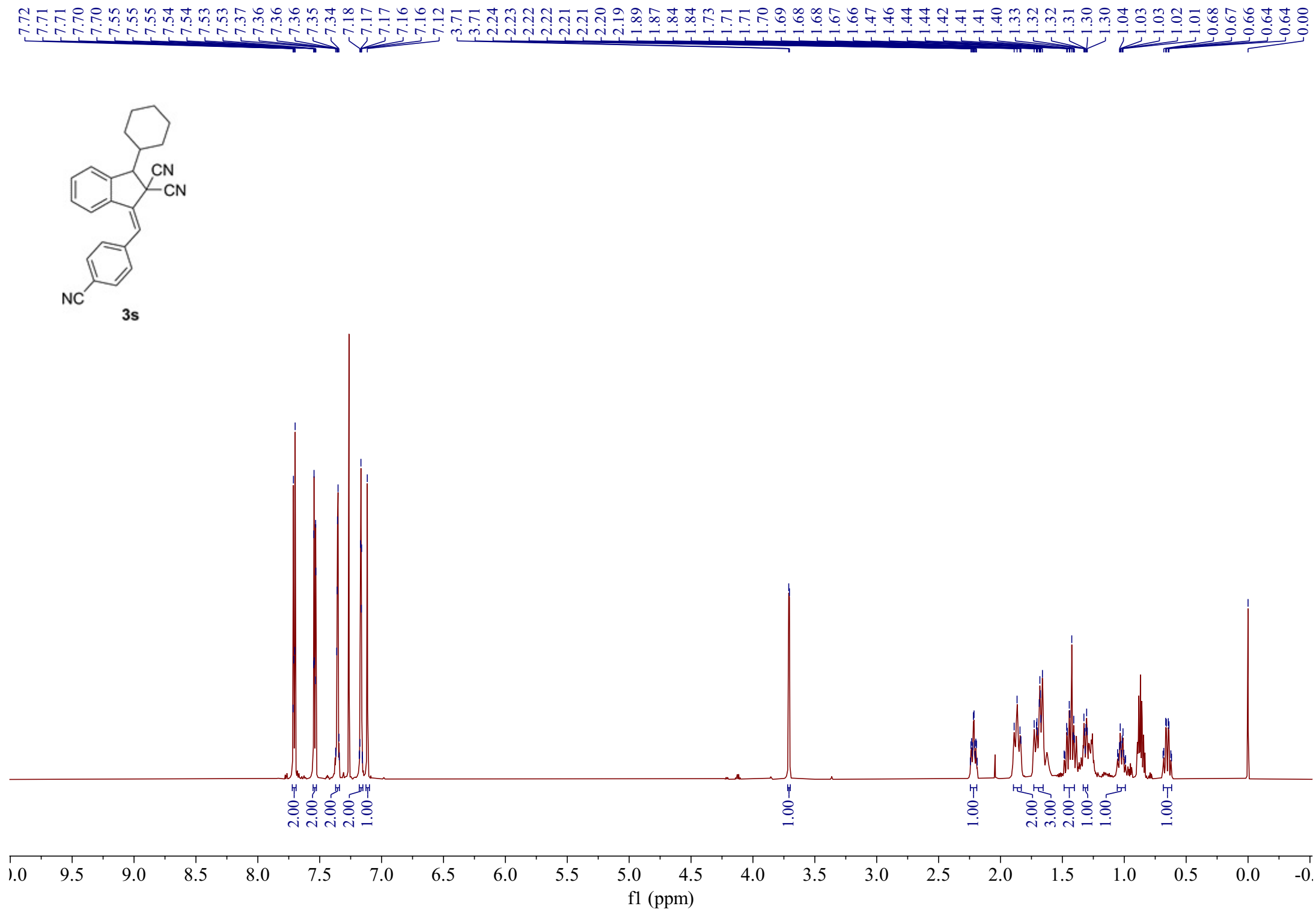
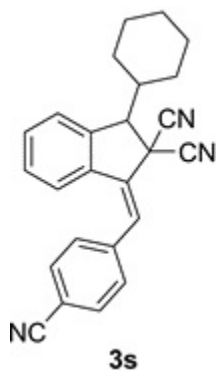


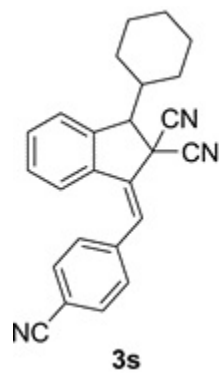




— -62.66







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138.83  
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126.83  
124.82  
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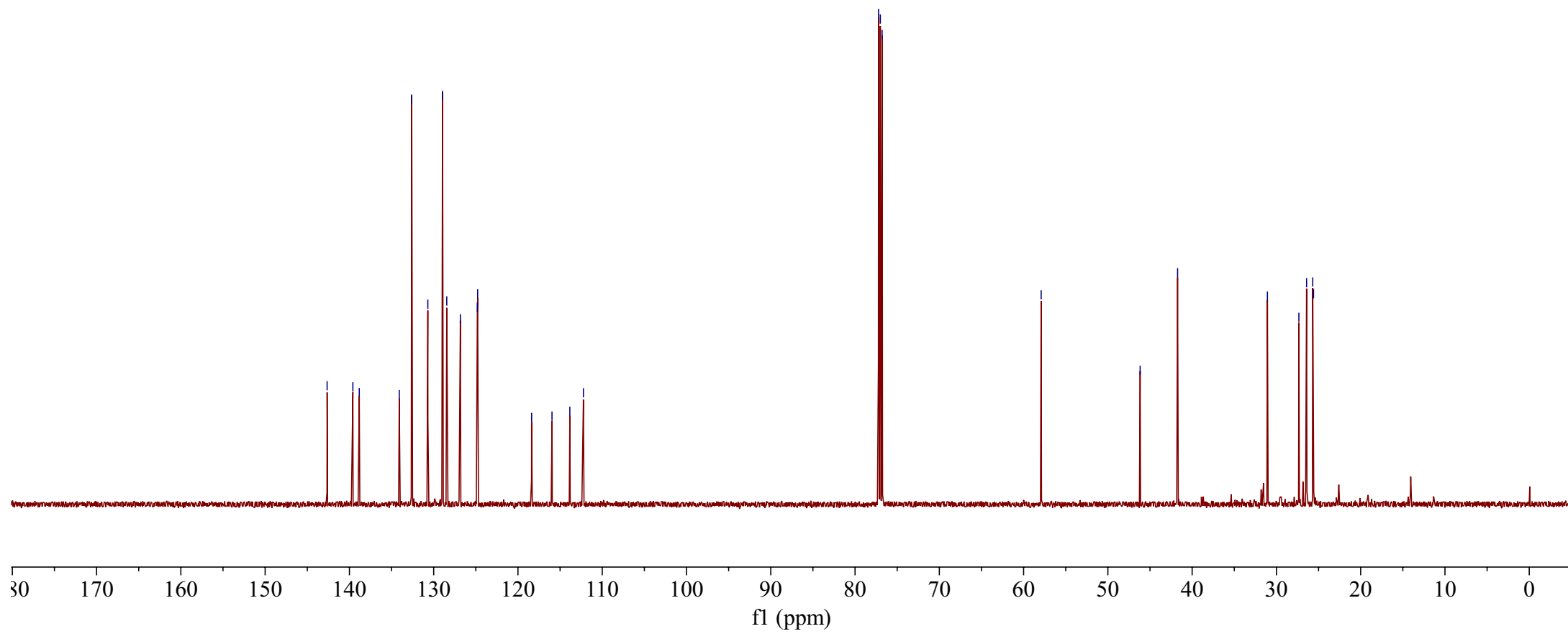
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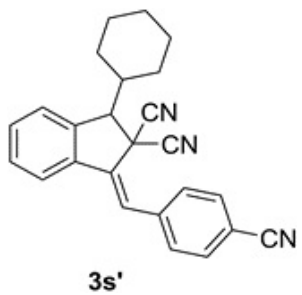
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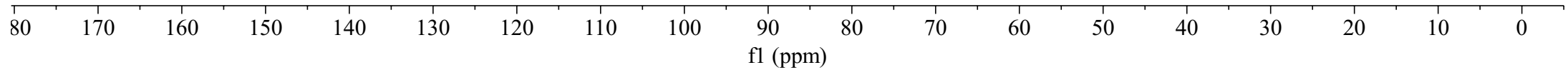
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112.14

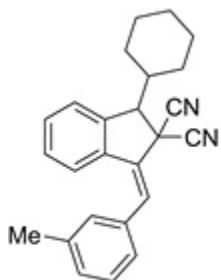
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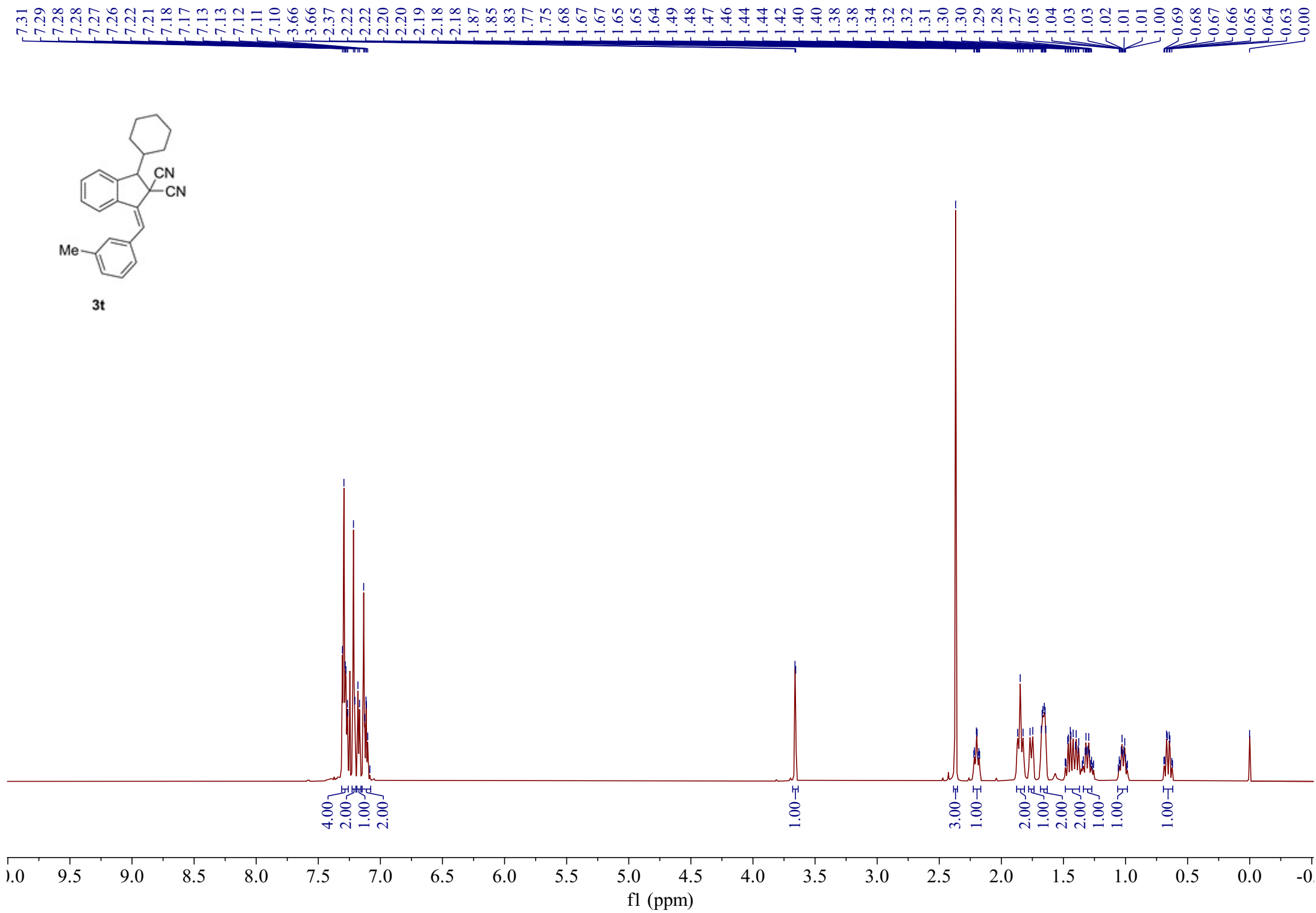
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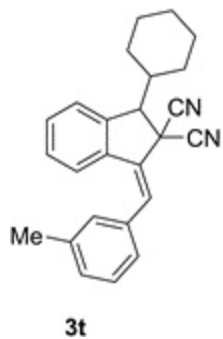
31.15  
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25.42





3t





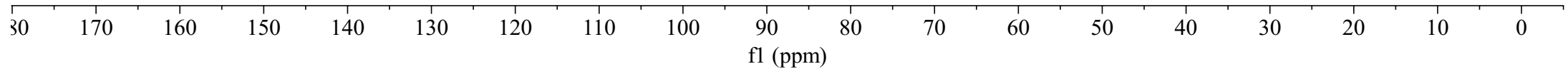
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— 116.5  
— 114.3

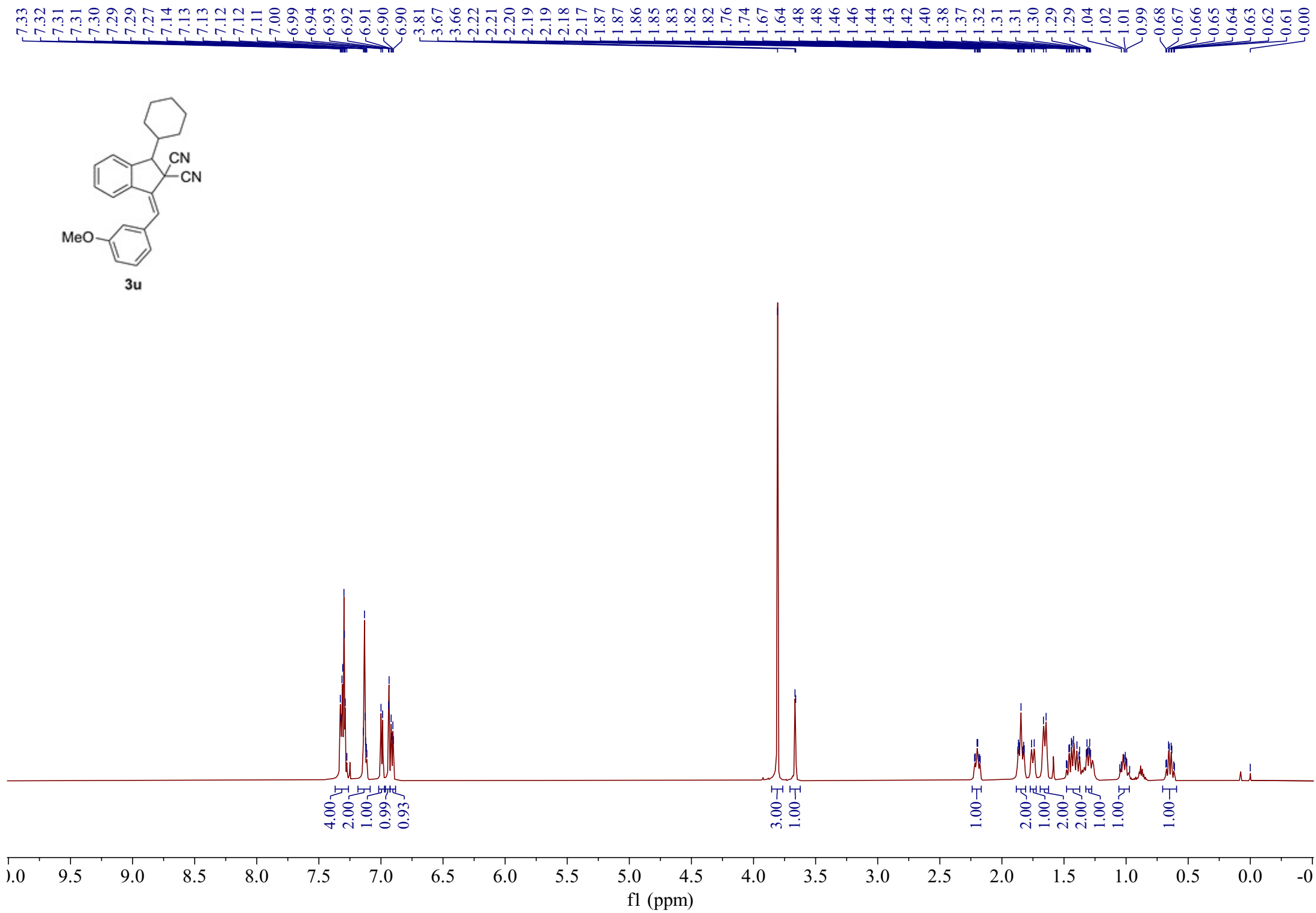
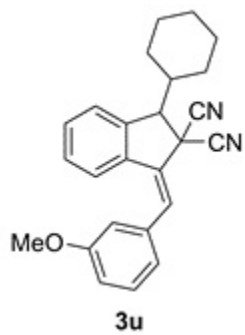
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76.8

— 57.8

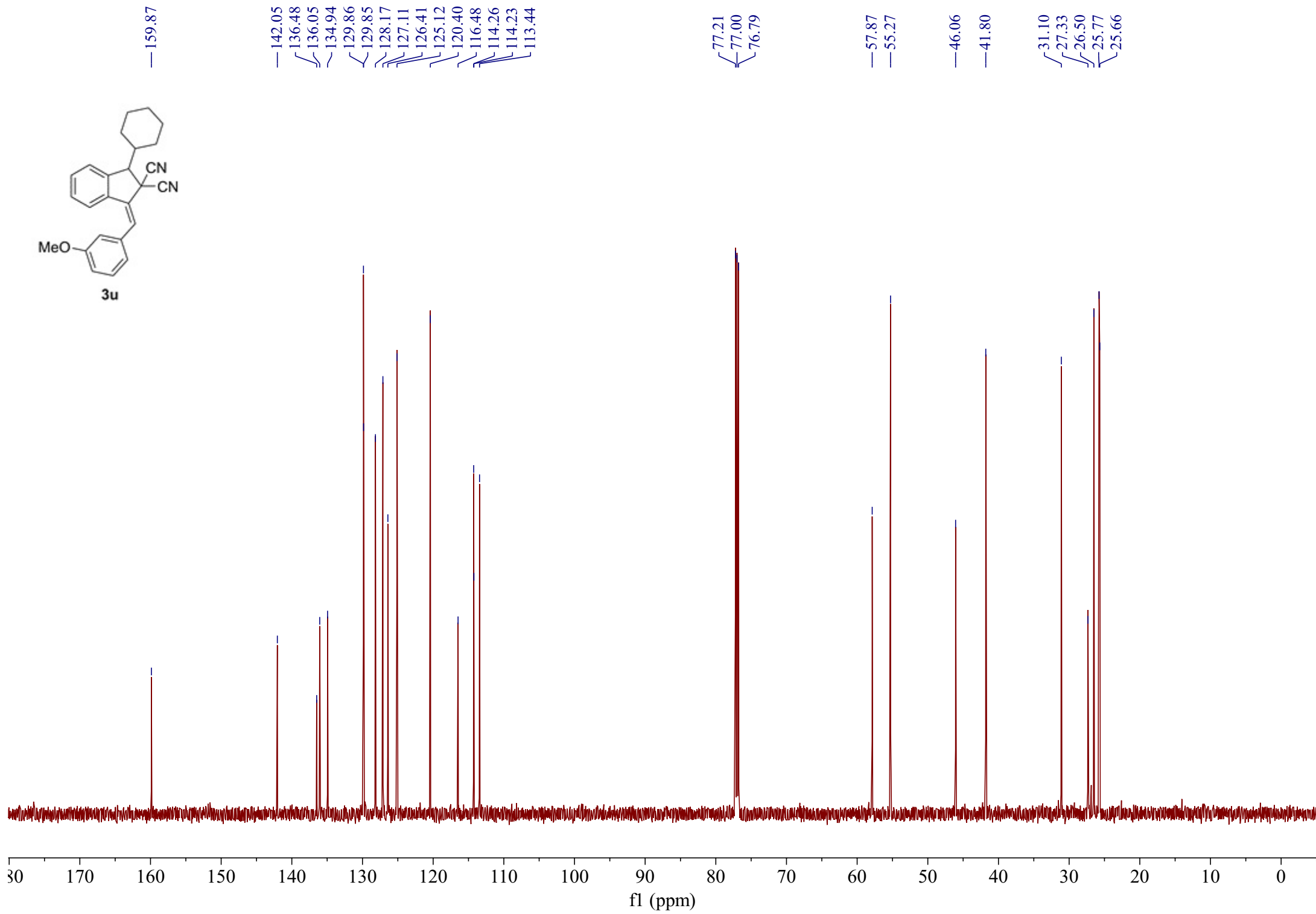
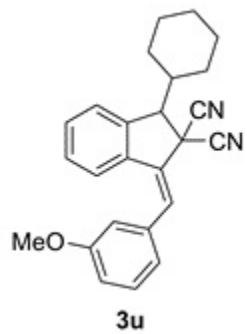
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— 41.8

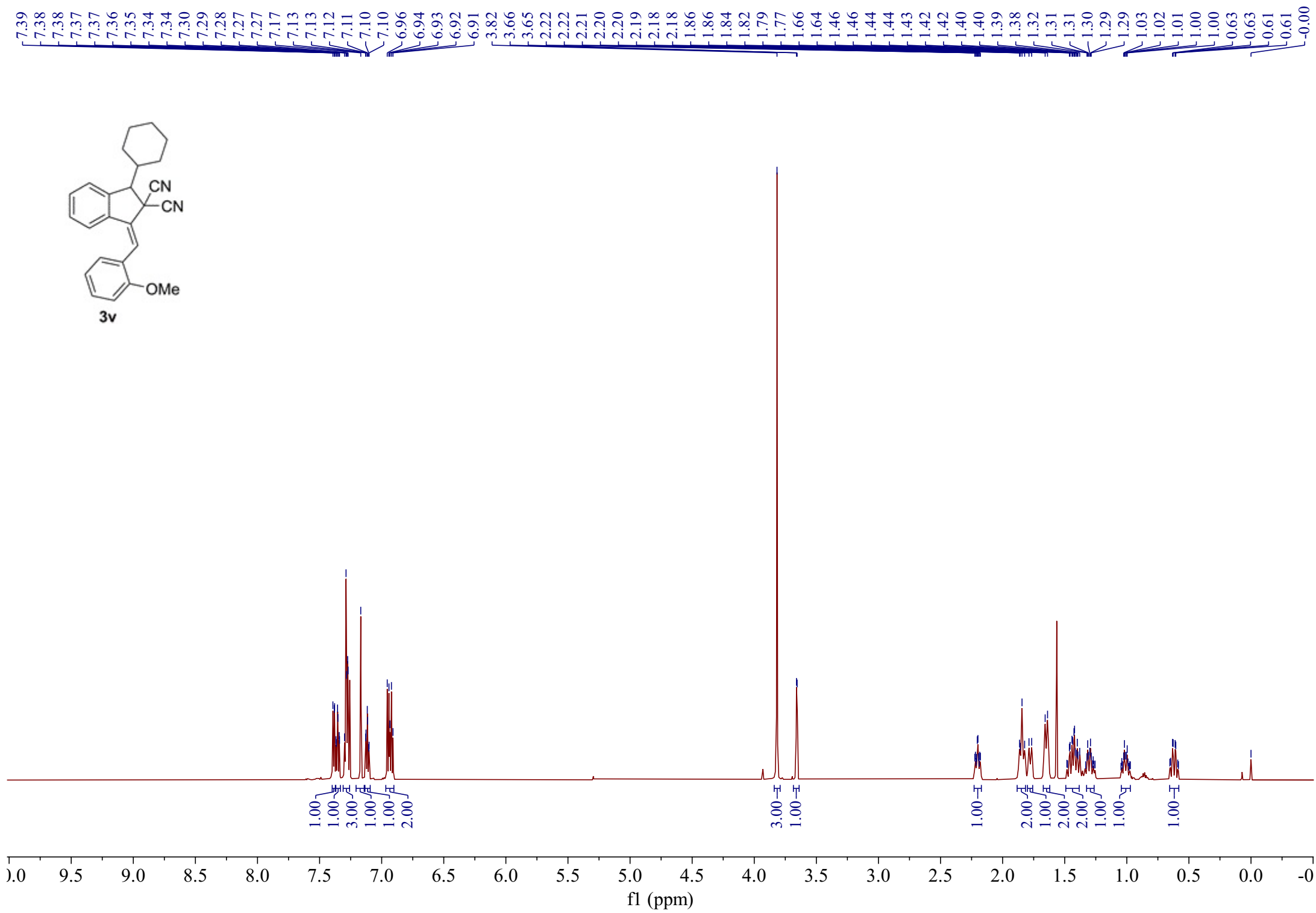
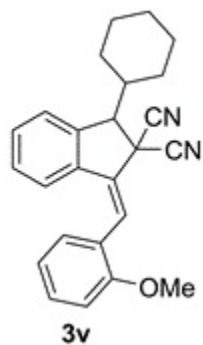
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25.6  
21.3

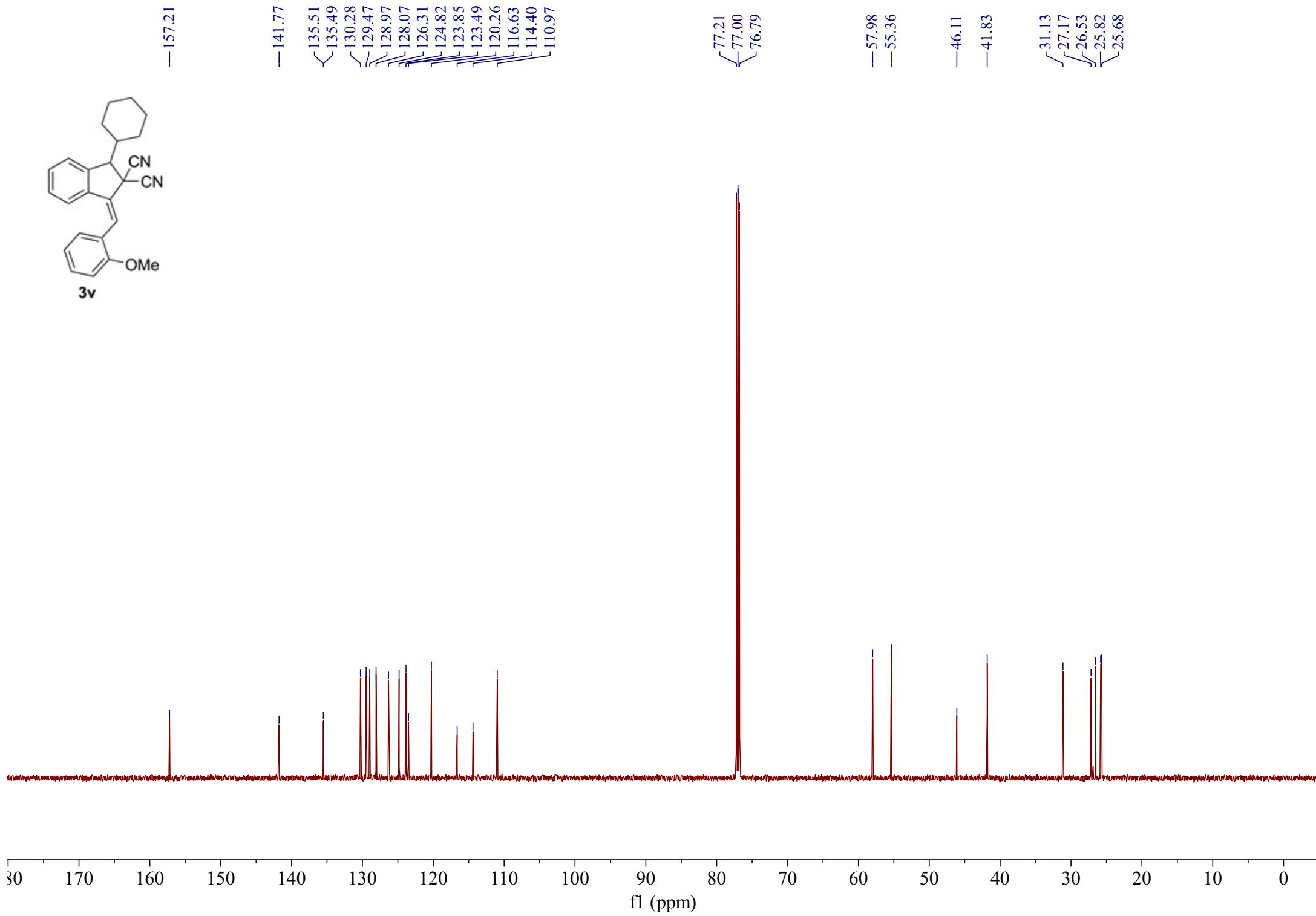
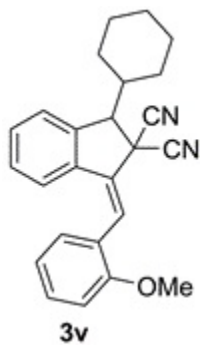


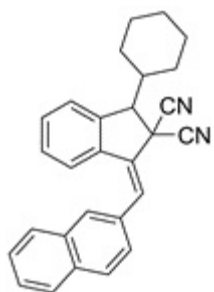




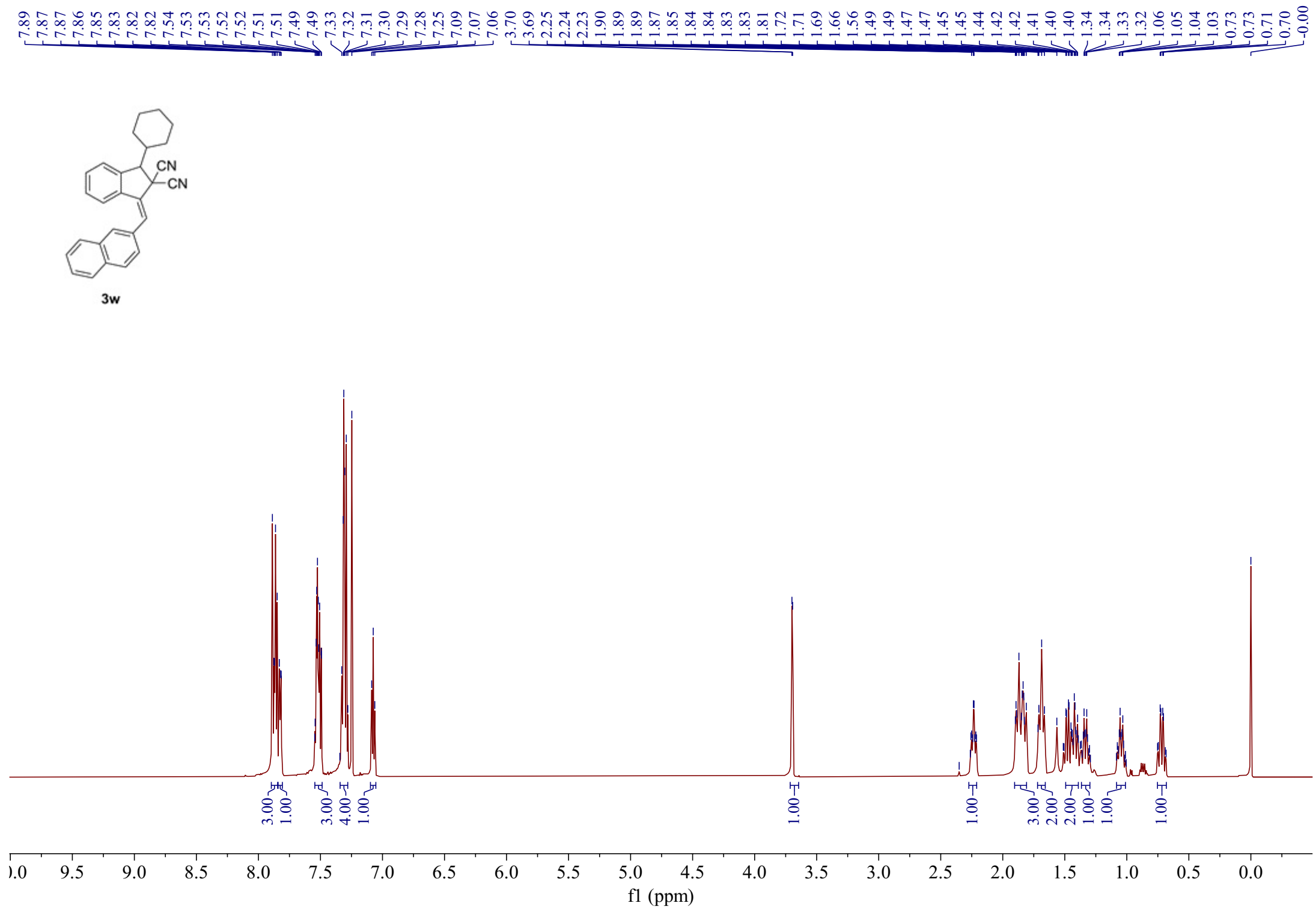


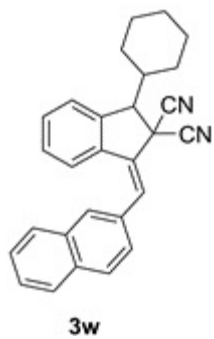






3w





142.14  
136.41  
135.05  
133.28  
133.15  
132.17  
129.92  
128.42  
128.22  
128.14  
127.79  
127.61  
127.27  
126.70  
126.56  
126.51  
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124.94  
— 116.52  
— 114.31

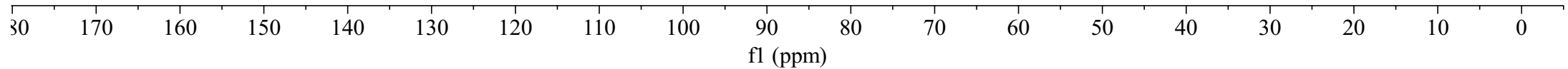
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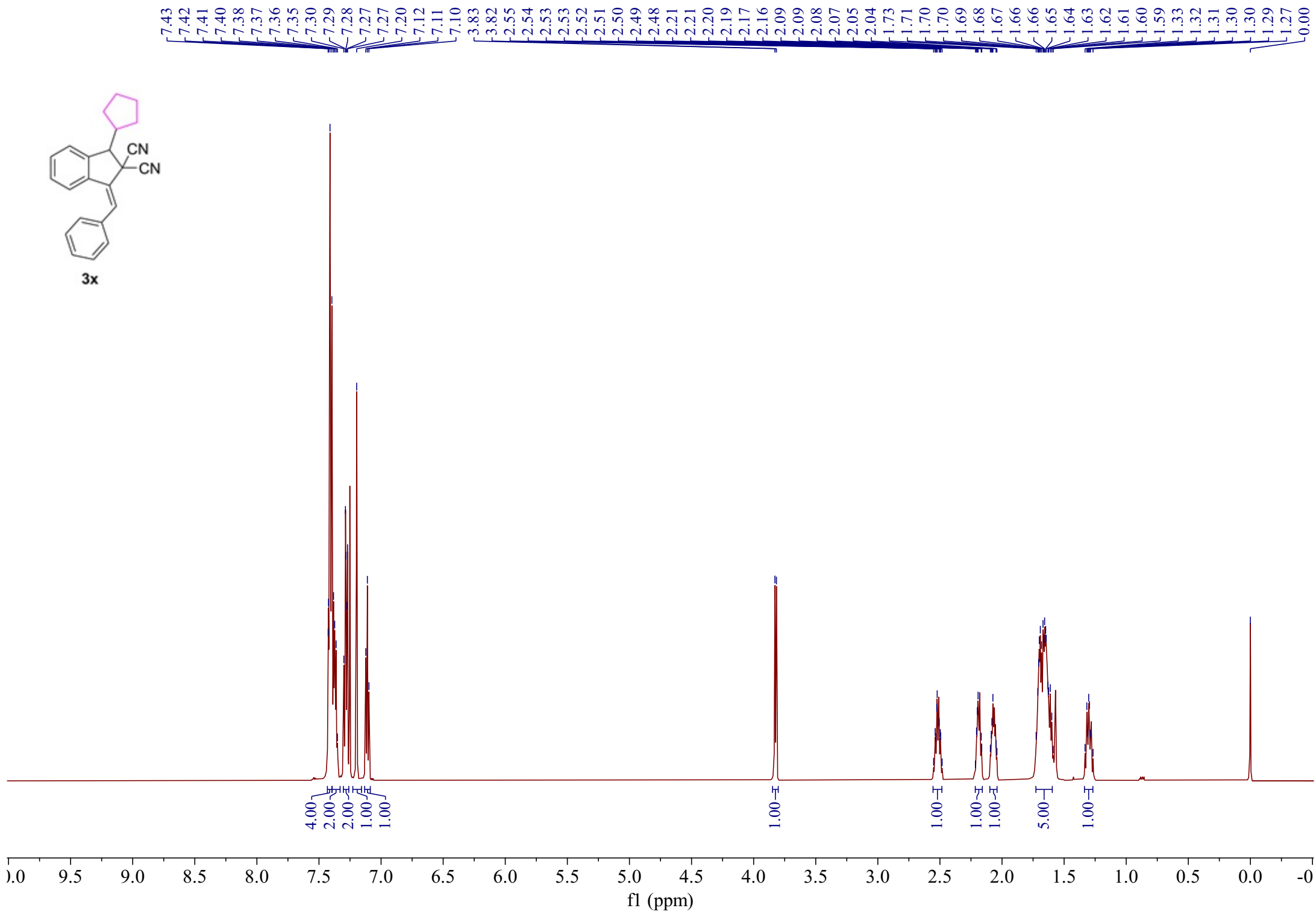
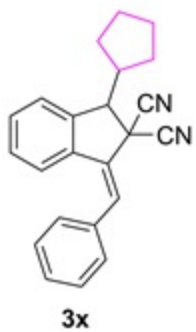
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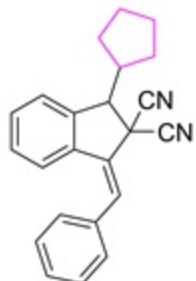
— 46.19

— 41.81

31.14  
27.35  
26.52  
25.79  
25.68







**3x**

142.82  
135.46  
134.91  
134.65  
130.00  
128.77  
128.62  
128.13  
128.11  
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124.95  
116.30  
114.42

77.21  
77.00  
76.79

57.16

46.60

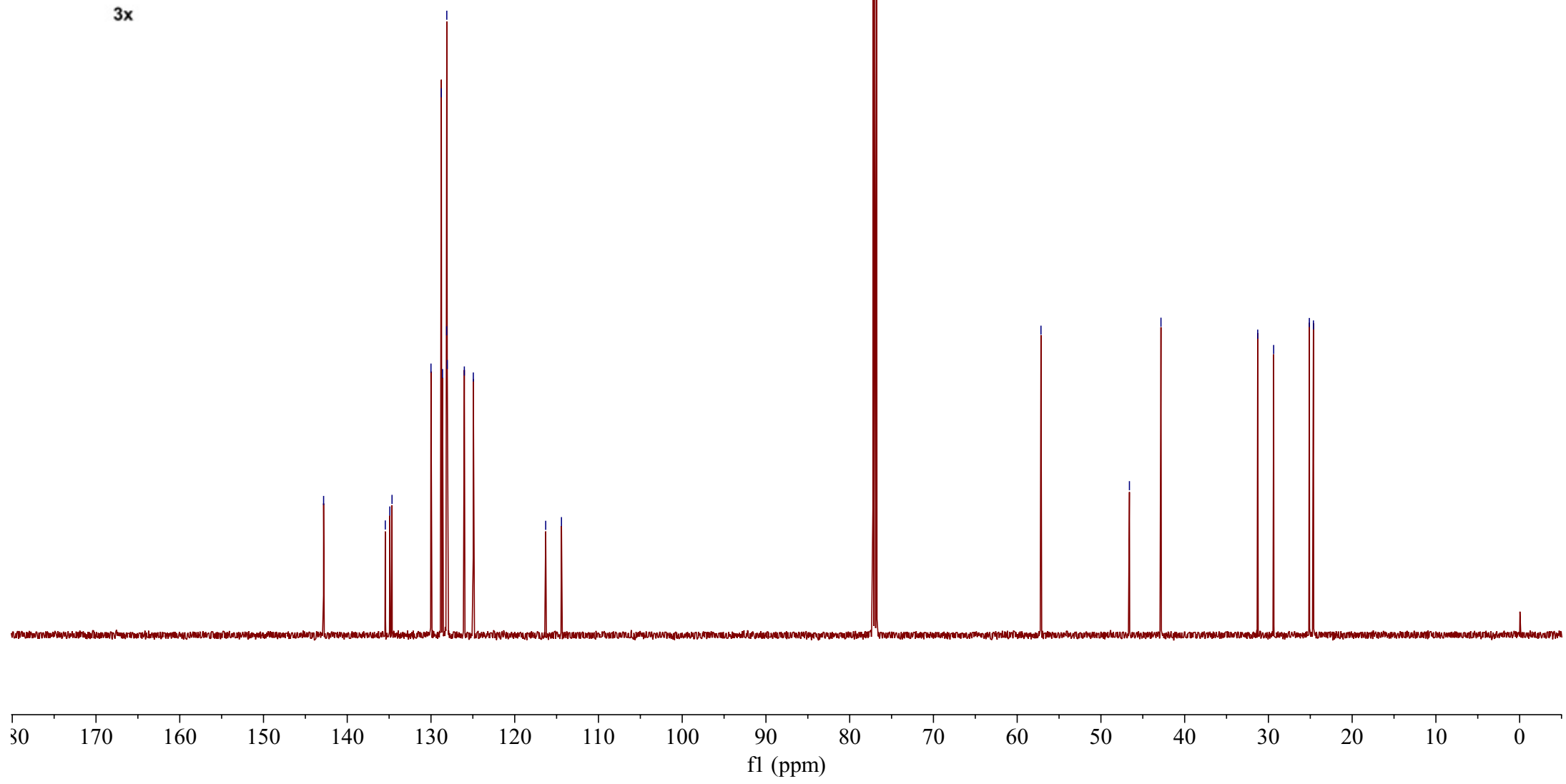
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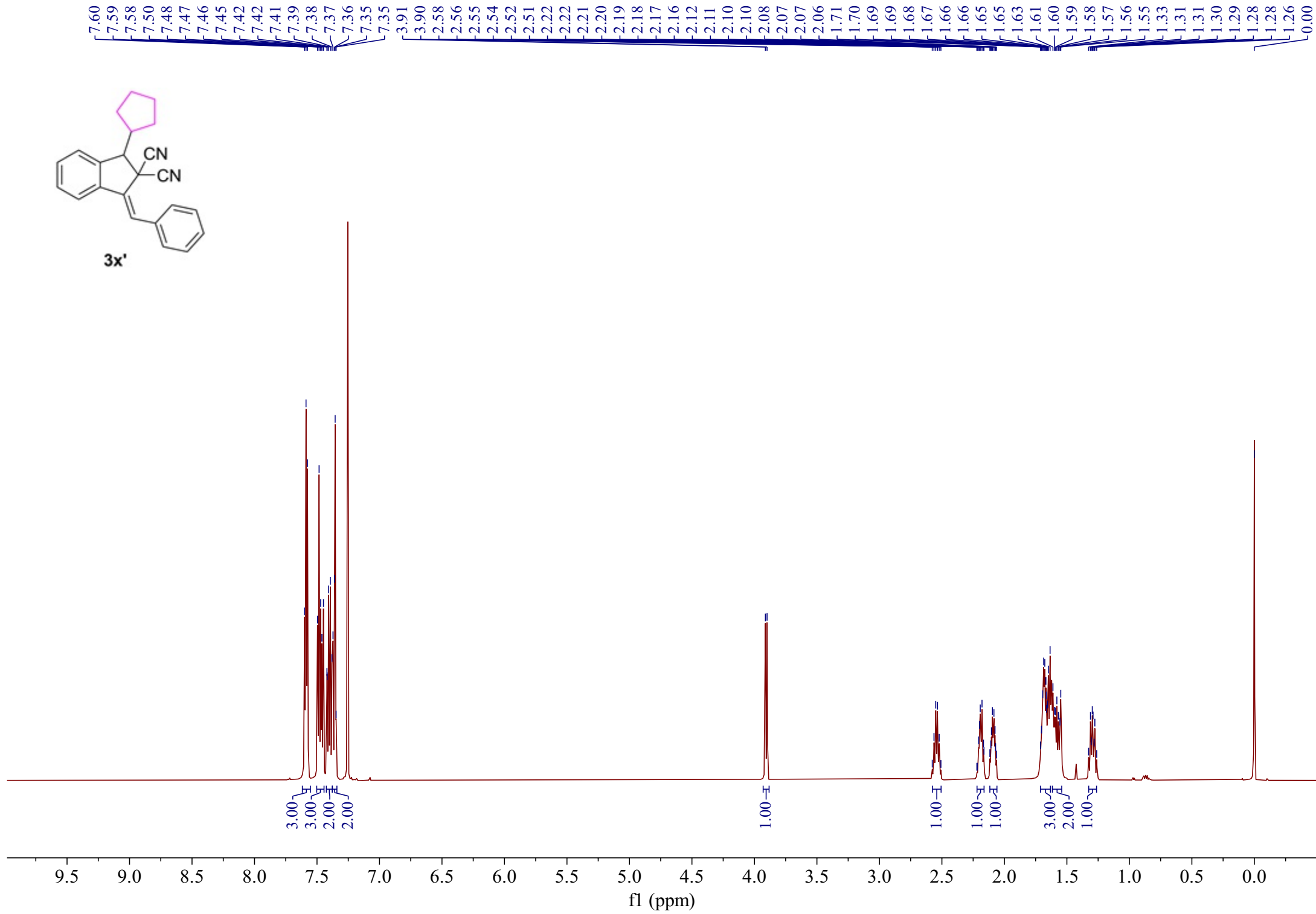
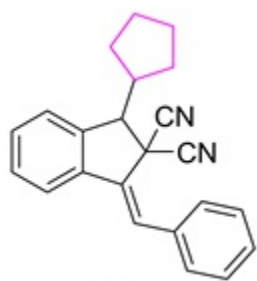
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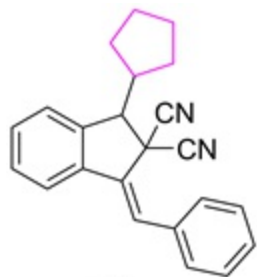
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24.63









3x'

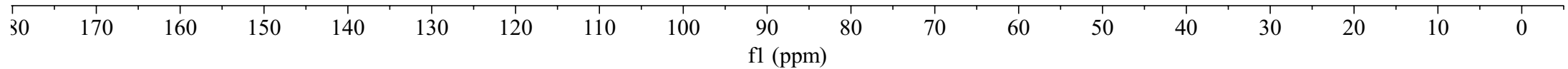
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115.25  
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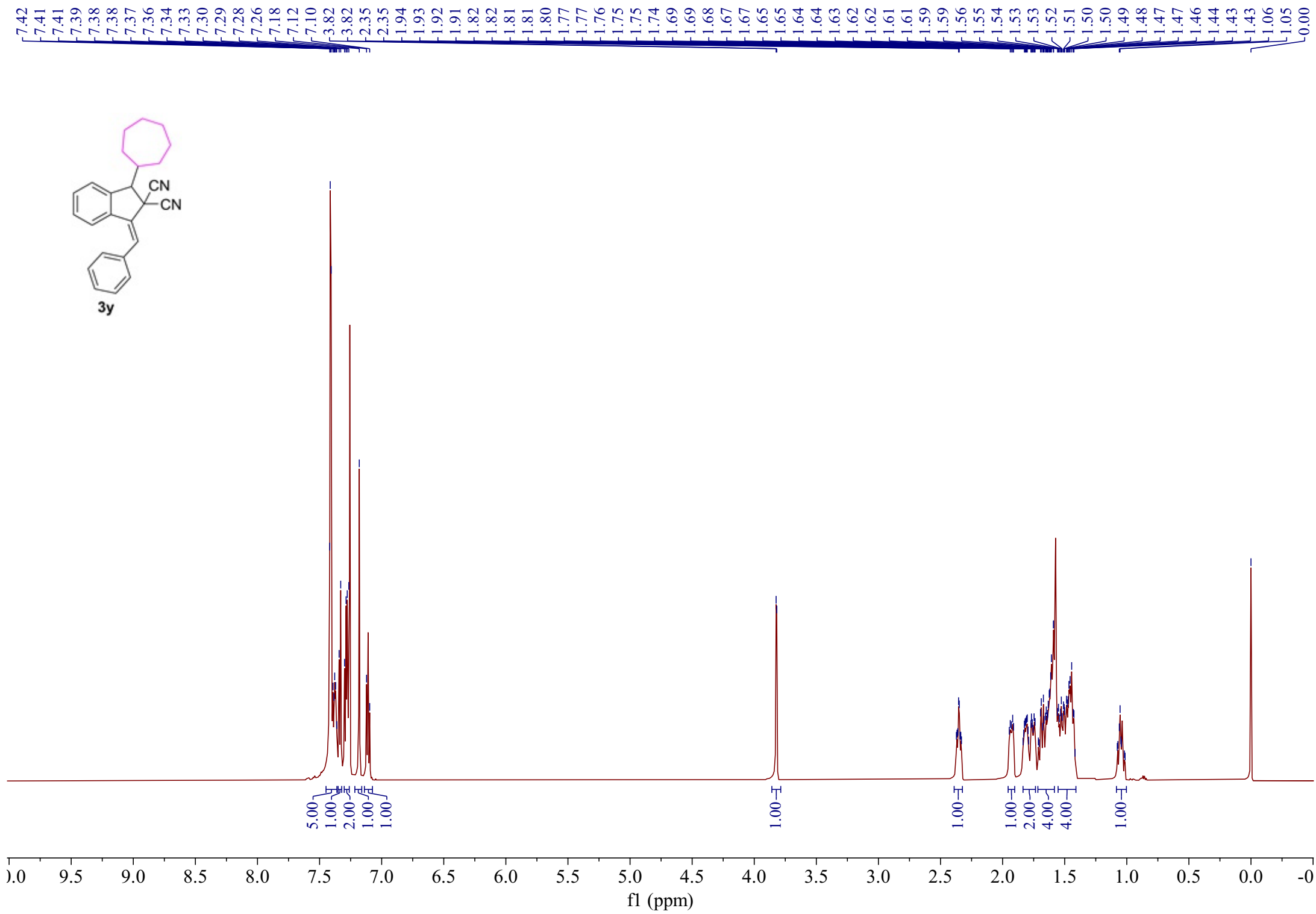
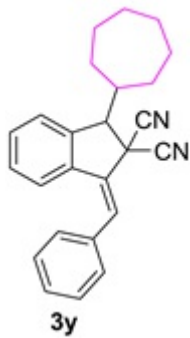
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76.79

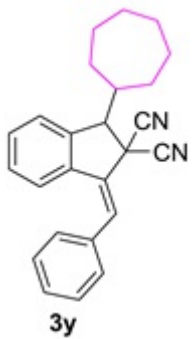
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24.72







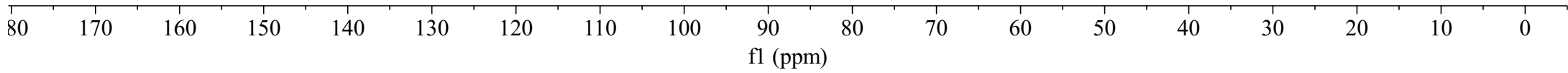
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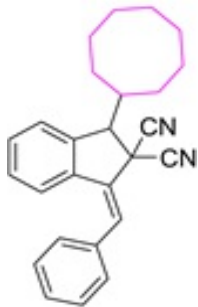
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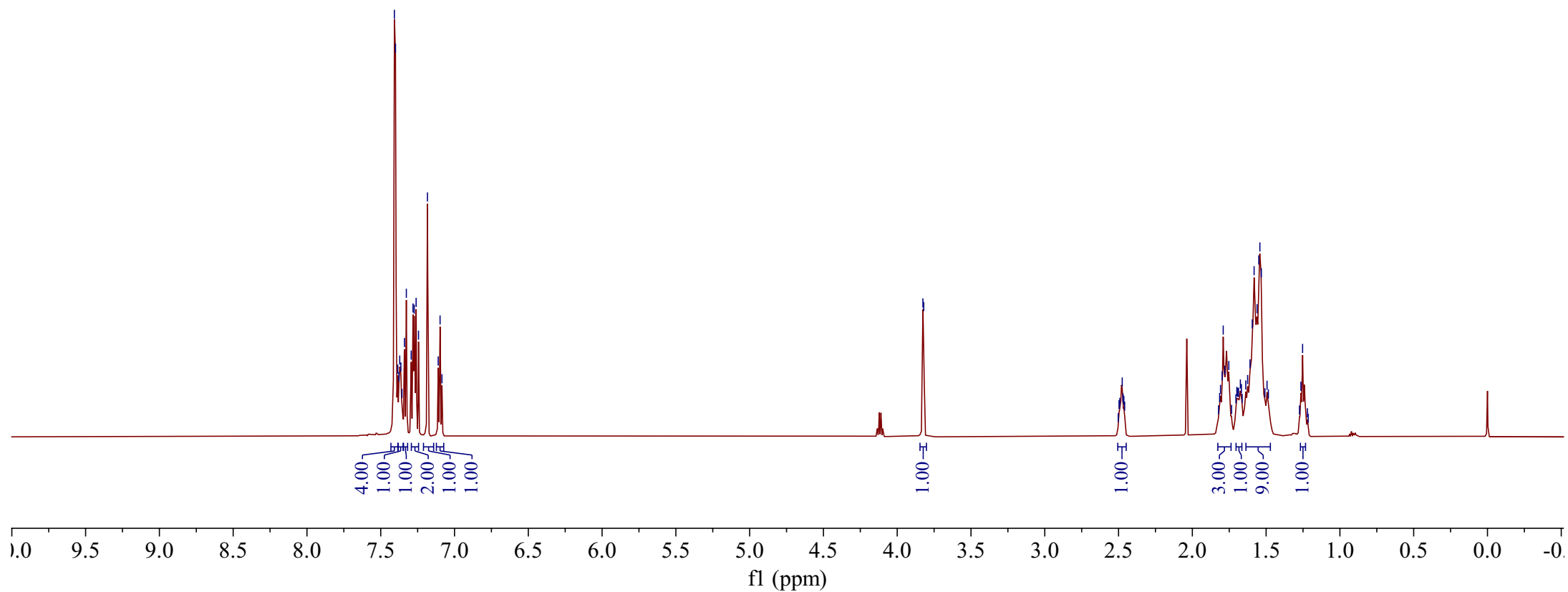


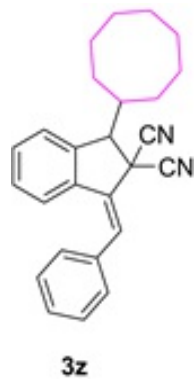


3z

7.41  
7.40  
7.38  
7.38  
7.37  
7.36  
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7.34  
7.33  
7.29  
7.28  
7.27  
7.26  
7.24  
7.18  
7.11  
7.10  
7.09

3.83  
3.82  
2.50  
2.50  
2.49  
2.48  
2.47  
2.46  
2.46  
1.82  
1.82  
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1.79  
1.78  
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1.69  
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1.67  
1.67  
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1.63  
1.61  
1.59  
1.58  
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1.55  
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1.22  
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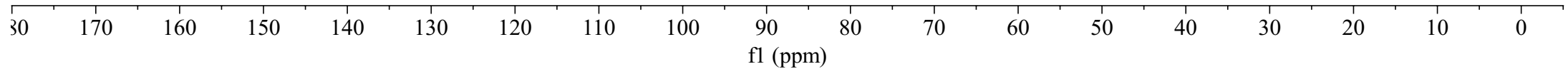
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76.79

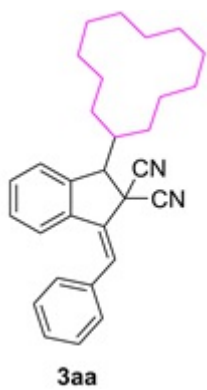
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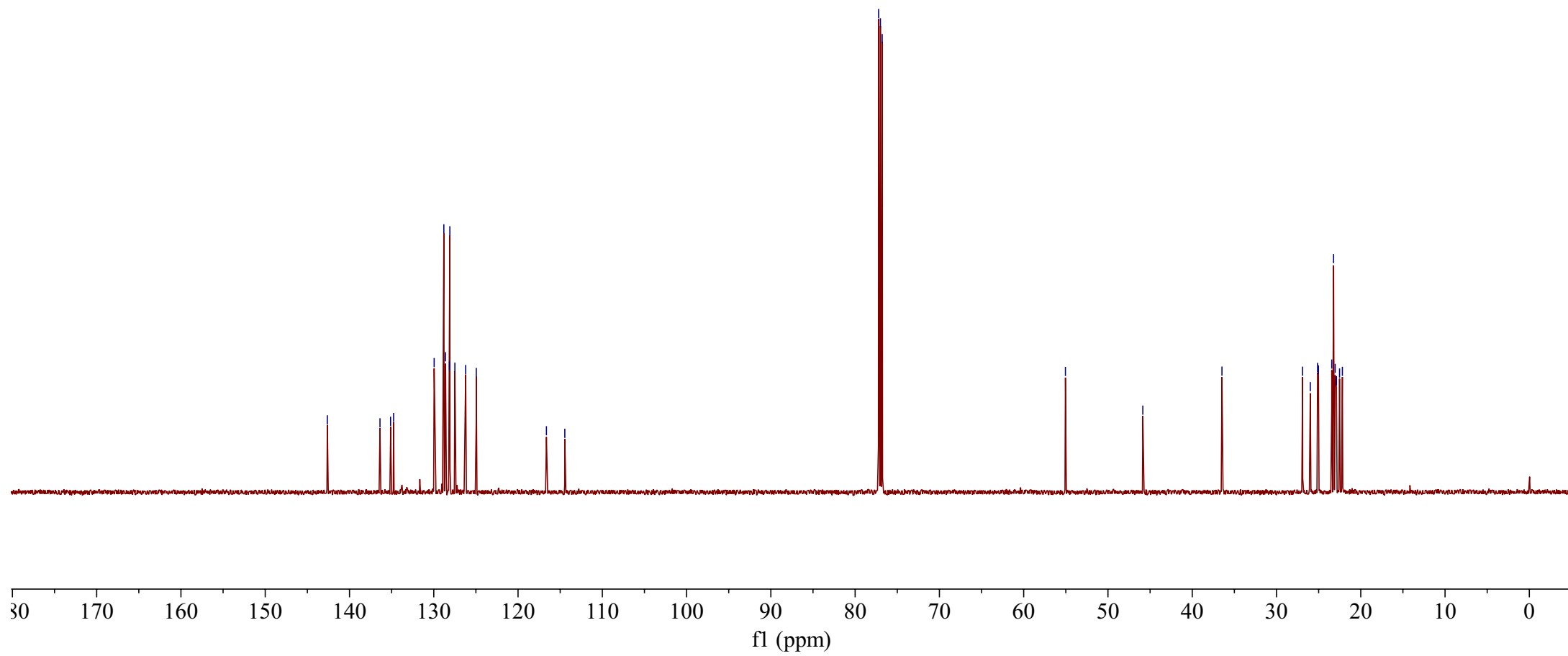
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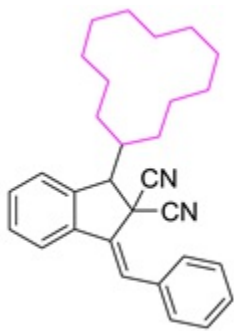
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55.05

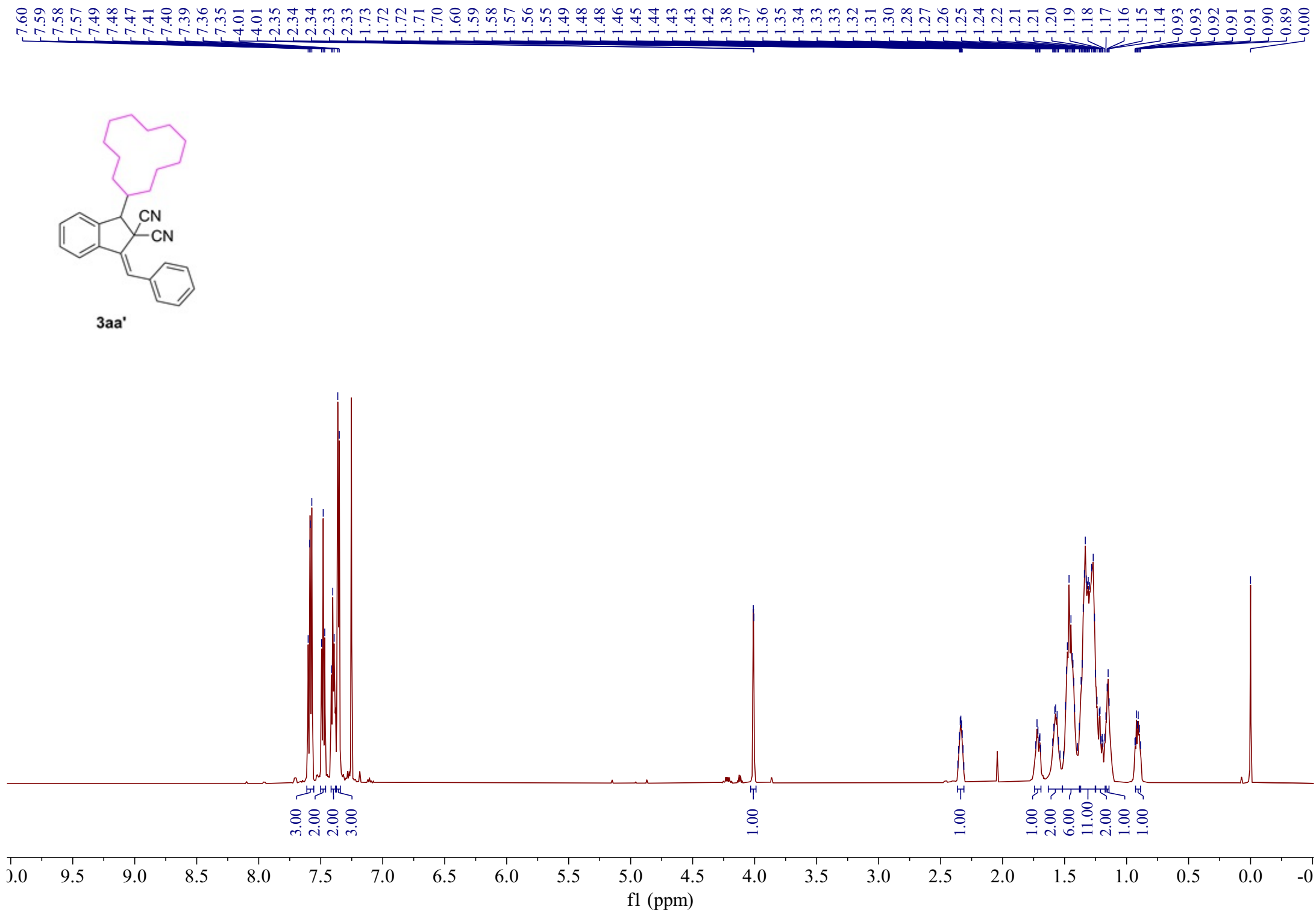
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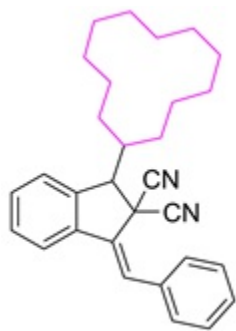




3aa'







3aa'

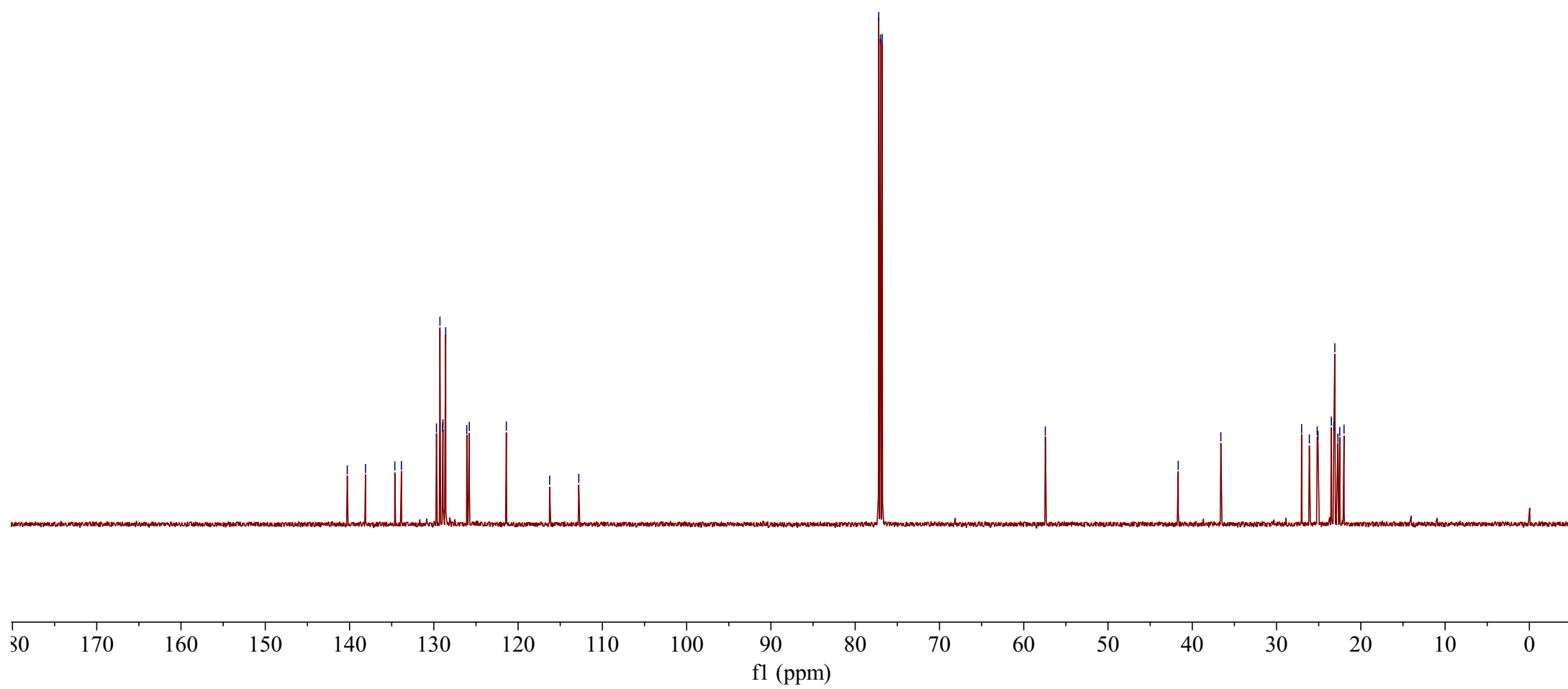
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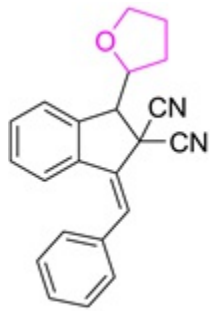
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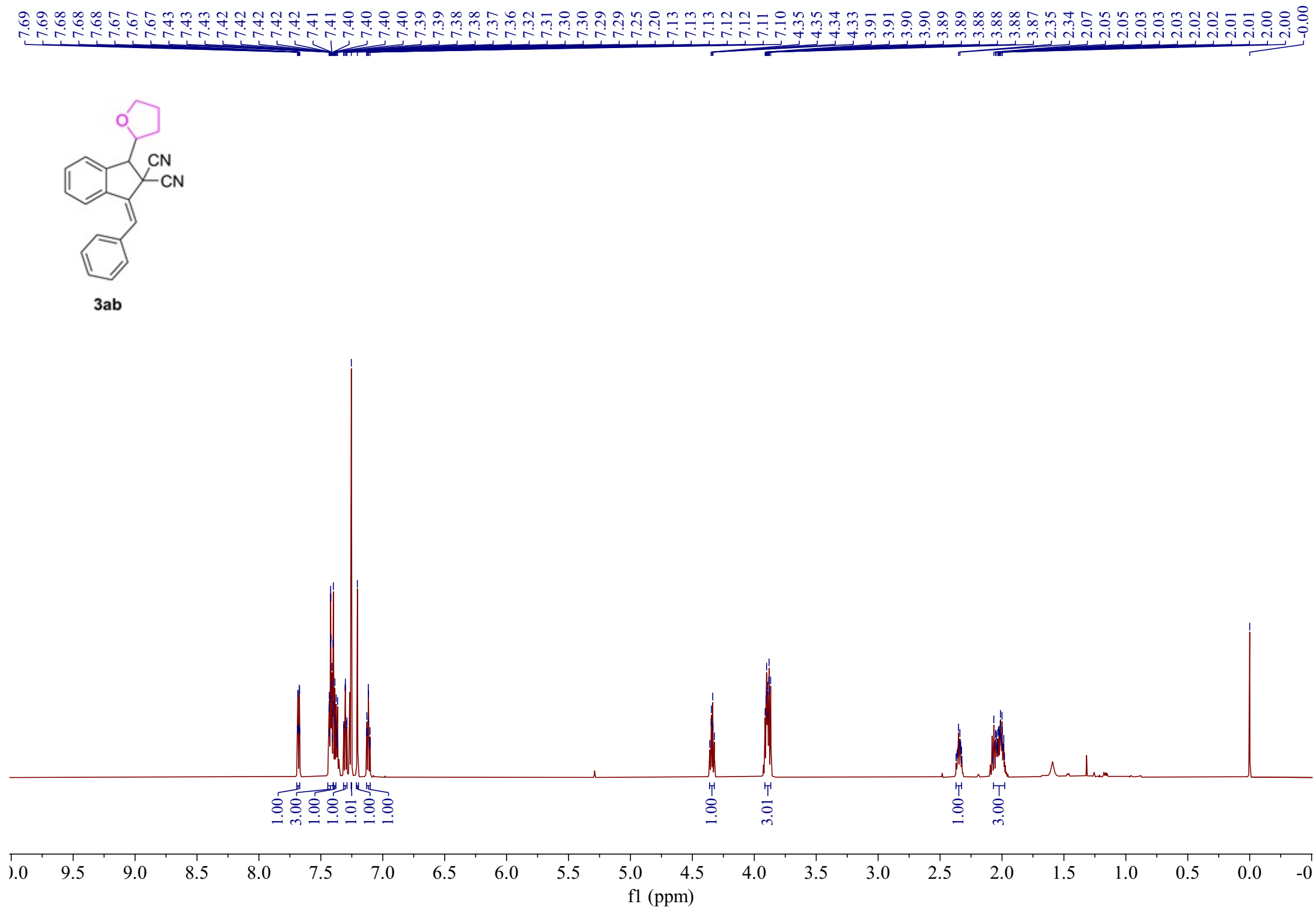
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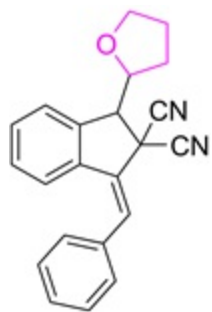
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22.72  
22.50  
21.99





3ab





3ab

141.98  
135.75  
134.68  
134.62  
130.28  
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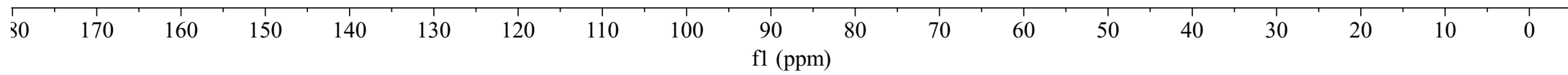
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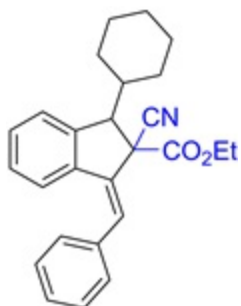
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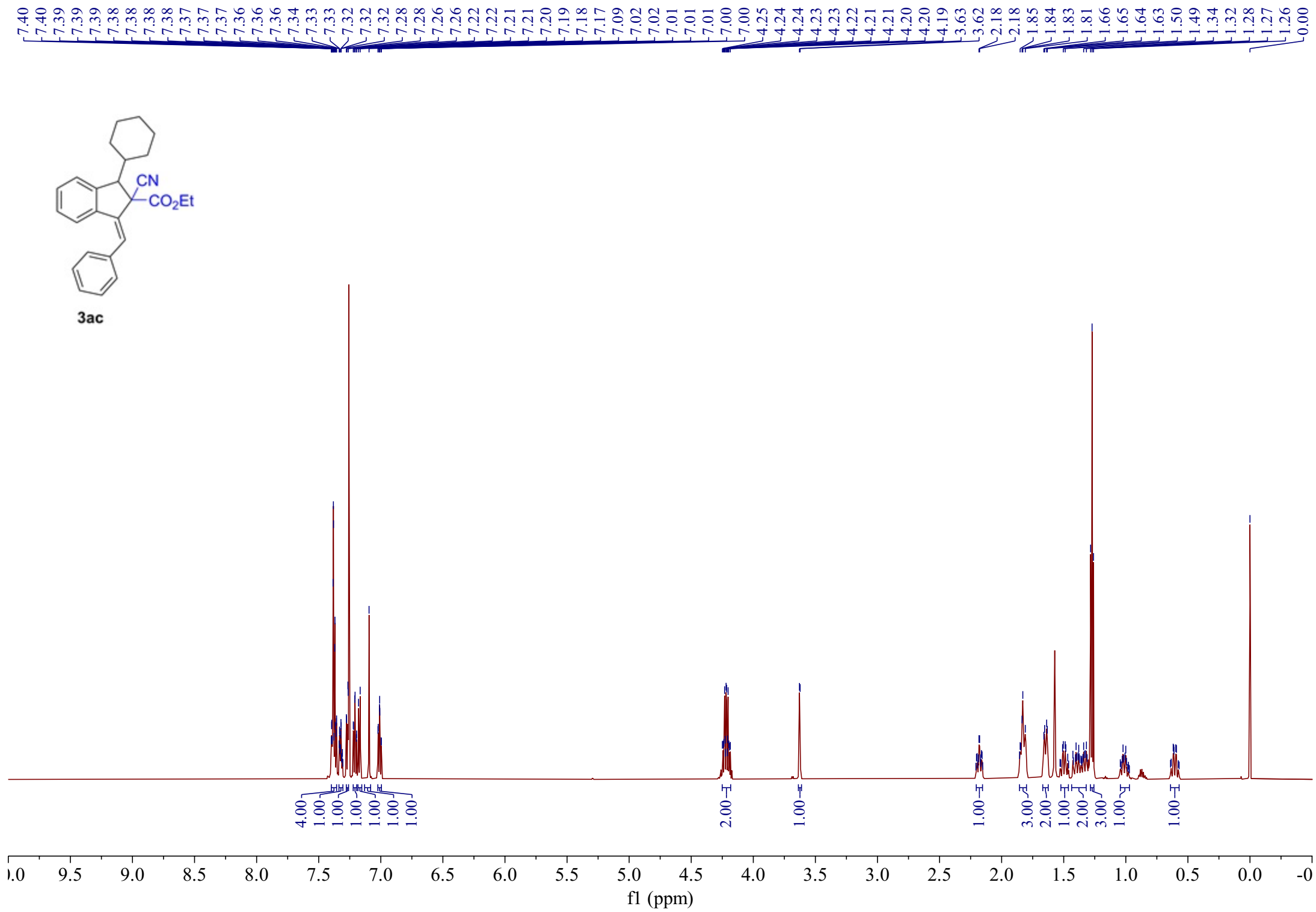
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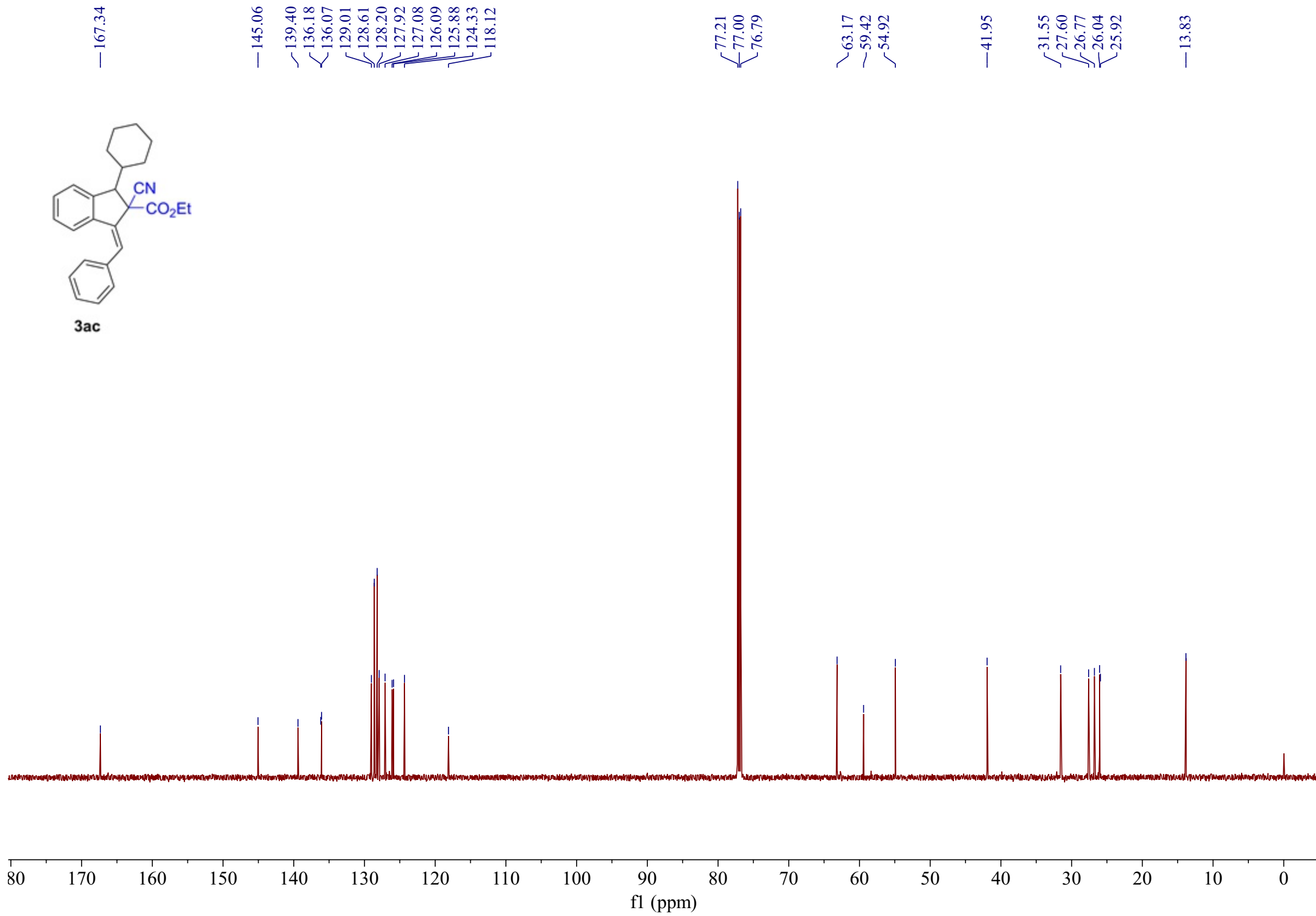
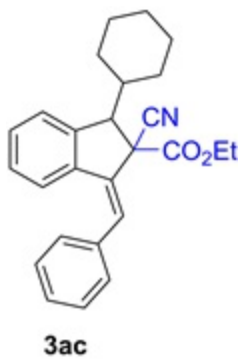
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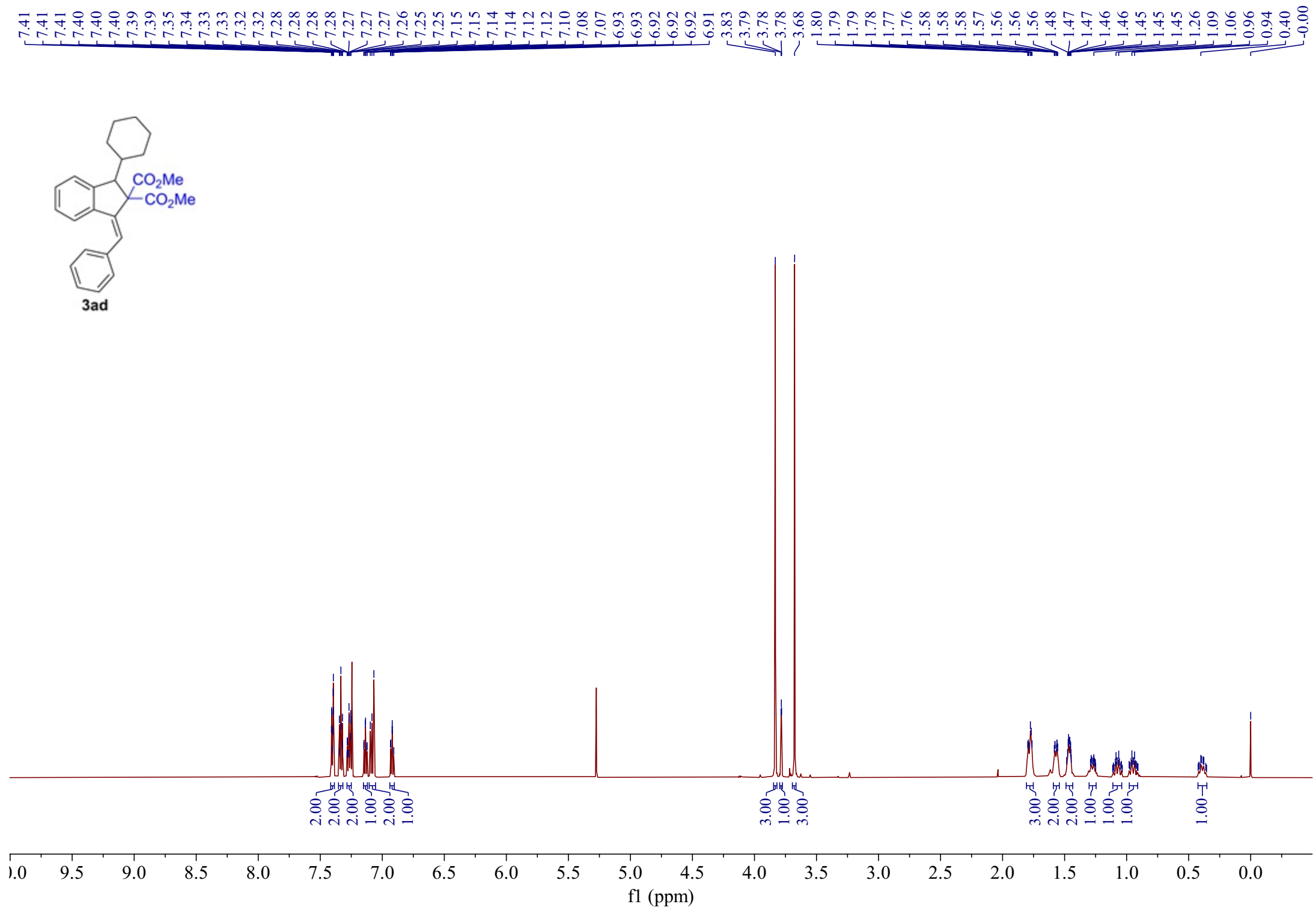
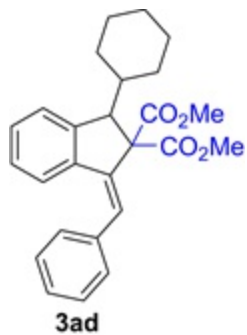


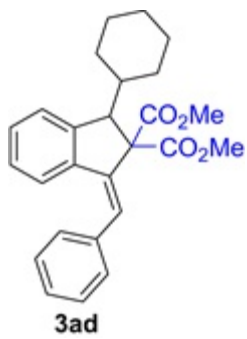


3ac









170.47  
169.68

145.20  
138.05  
137.88  
137.52  
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128.30  
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127.24  
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125.65  
124.16

77.21  
77.00  
76.79  
70.15

55.19  
53.08  
52.23

41.15

32.24  
27.63  
27.15  
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26.10

