

# Supporting Information

## Palladium-catalyzed hydrocarbonylative cross-coupling with two different alkenes

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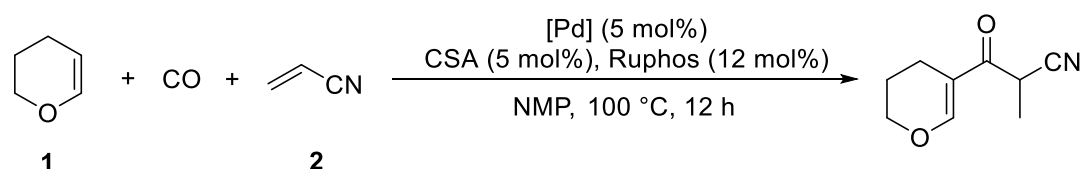
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## 1. General information

All non-aqueous reactions and manipulations were performed in a N<sub>2</sub> atmosphere glove box. All solvents before used were dried and degassed by standard methods and stored under nitrogen atmosphere. Purification of products was performed by flash chromatography (FC) using silica gel. NMR spectra were recorded on BRUKER Avence III 400 MHz or 500 MHz NMR spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). GC-MS analyses were performed on Agilent 7890B/5975B GC-MS system. All commercially available compounds were purchased from Alfa Aesar, J&K, Adamas and Energy Chemical. Enol ethers such as **1a**, **1b**, **1c**, **1e**, **1l**, **1s** and enamides such as **1h**, **1i**, **1j** were purchased from commercial sources and used as received. **1d**<sup>[1]</sup>, **1f**<sup>[1]</sup>, **1g**<sup>[1]</sup>, **1k**<sup>[2]</sup>, **1m**<sup>[3]</sup>, **1n**<sup>[4]</sup>, **1o**<sup>[5]</sup>, **1p**<sup>[6]</sup>, **1q**<sup>[7]</sup>, **1r**<sup>[7]</sup> were prepared according to the literature methods.

## 2. Optimization of the reaction conditions

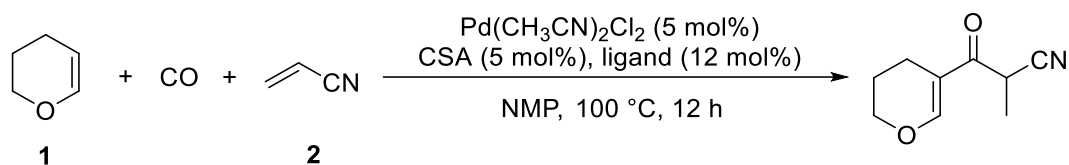
### 2.1 Screening of catalysts<sup>a</sup>



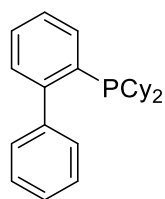
Entry	[Pd]	Yield
1	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	87%
2	PdBr <sub>2</sub>	61%
3	PdI <sub>2</sub>	23%
4	Pd(OAc) <sub>2</sub>	trace
5	Pd( <sup>t</sup> Bu <sub>3</sub> P) <sub>2</sub>	trace
6	Pd <sub>2</sub> (dba) <sub>3</sub> <sup>b</sup>	trace
7	Pd(acac) <sub>2</sub>	trace

<sup>a</sup>Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), CO (40 atm), [Pd] (5 mol%), CSA (camphorsulfonic acid, 5 mol%), Ruphos (12 mol%), NMP (1 mL), 100 °C, 12 h. <sup>b</sup>Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%).

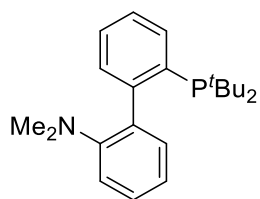
## 2.2 Screening of ligands<sup>a</sup>



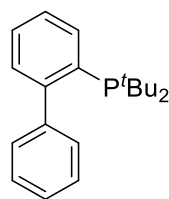
Entry	Ligand	Yield
1	RuPhos	87%
2	SPhos	84%
3	Davephos	81%
4	XPhos	82%
5	BnPAD <sub>2</sub>	67%
6	<sup>n</sup> BuPAD <sub>2</sub>	63%
7	L <sub>1</sub>	47%
8	L <sub>2</sub>	53%
9	L <sub>3</sub>	56%
10	L <sub>4</sub>	69%
11	Xantphos <sup>b</sup>	21%



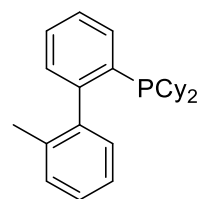
L<sub>1</sub>



L<sub>2</sub>



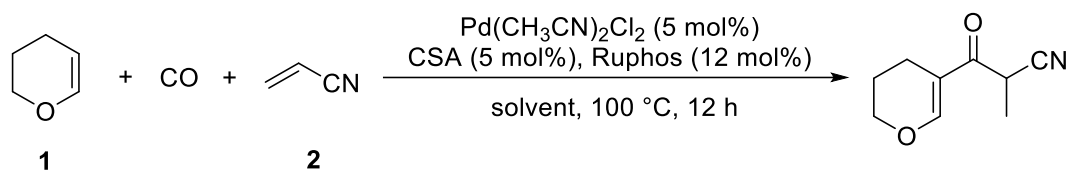
L<sub>3</sub>



L<sub>4</sub>

<sup>a</sup>Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), CO (40 atm), Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (5 mol%), CSA (5 mol%), ligand (12 mol%), NMP (1 mL), 100 °C, 12 h. <sup>b</sup>Xantphos (6 mol%).

### 2.3 Screening of solvents<sup>a</sup>



Entry	Solvent	Yield
1	NMP	87%
2	THF	15%
3	dioxane	8%
4	toluene	trace
5	PhOMe	25%
6	CpME	11%
7	PhCl	13%

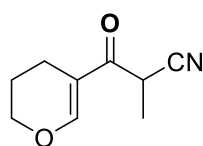
<sup>a</sup>Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), CO (40 atm), Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (5 mol%), CSA (5 mol%), Ruphos (12 mol%), solvent (1 mL), 100 °C, 12 h.

### 3. General procedure for the carbonylation reactions

In a N<sub>2</sub> atmosphere glove box, Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (6.4 mg, 0.025 mmol), CSA (5.8 mg, 0.025 mmol), Ruphos (28.0 mg, 0.06 mmol), enol ethers (0.5 mmol), acrylonitrile (0.6 mmol), and NMP (1 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO (40 atm). The reaction mixture was stirred at 100 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the hood. The d.r. and *Z/E* values were measured by H NMR. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 30/1 - 3/1) to give the desired product **3**.

### 4. Experimental characterization data for products.

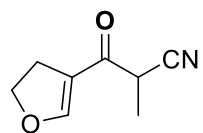
**3-(3,4-dihydro-2H-pyran-5-yl)-2-methyl-3-oxopropanenitrile (3a)**: (colorless oil, 72.6 mg, yield: 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 (s, 1H), 4.19 – 4.12 (m, 2H),



**3a**

3.93 (q,  $J = 7.1$  Hz, 1H), 2.33 – 2.30 (m, 2H), 1.95 – 1.90 (m, 2H), 1.53 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  188.9, 158.8, 119.0, 114.5, 67.6, 31.8, 20.7, 18.6, 15.4. **HRMS** (ESI) calcd. for  $\text{C}_9\text{H}_{11}\text{NNaO}_2$   $[\text{M}+\text{Na}]^+$ : 188.0682, found: 188.0692.

**3-(4,5-dihydrofuran-3-yl)-2-methyl-3-oxopropanenitrile (3b)**: (colorless oil, 50.3

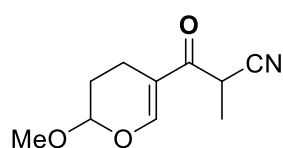


**3b**

mg, yield: 66%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (t,  $J = 1.6$  Hz, 1H), 4.66 – 4.61 (m, 2H), 3.77 (q,  $J = 7.2$  Hz, 1H), 2.94 – 2.89 (m, 2H), 1.55 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.4, 160.2, 119.0, 117.8, 74.0, 34.4, 27.6, 15.4. **HRMS** (ESI) calcd. for

$\text{C}_8\text{H}_{10}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 152.0706, found: 152.0712.

**3-(2-methoxy-3,4-dihydro-2H-pyran-5-yl)-2-methyl-3-oxopropanenitrile (3c)**:

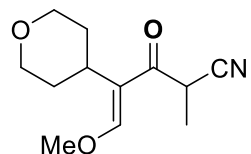


**3c**

(colorless oil, 50.3 mg, yield: 51%, d.r. = 1.1:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (s, 0.53H), 7.61 (s, 0.47H), 5.12 – 5.09 (m, 1H), 3.92 (qd,  $J = 7.2, 2.6$  Hz, 1H), 3.52 (s, 3H), 2.41 – 2.28 (m, 2H), 2.04 – 1.98 (dt,  $J = 13.9, 6.0, 4.0$  Hz, 1H), 1.85

– 1.71 (m, 1H), 1.53 (d,  $J = 3.5$  Hz, 1.65H), 1.52 (d,  $J = 3.5$  Hz, 1.41H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  188.9, 188.6, 155.63, 155.57, 118.9, 118.8, 115.4, 115.2, 100.0, 99.9, 56.6, 56.5, 32.1, 31.7, 25.33, 25.30, 15.5, 15.2, 14.93, 14.91. **HRMS** (ESI) calcd. for  $\text{C}_{10}\text{H}_{13}\text{NNaO}_3$   $[\text{M}+\text{Na}]^+$ : 218.0788, found: 218.0793.

**(E)-5-methoxy-2-methyl-3-oxo-4-(tetrahydro-2H-pyran-4-yl)pent-4-enenitrile**

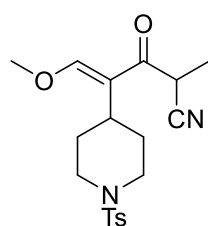


**3d**

(**3d**): (colorless oil, 75.1 mg, yield: 67%,  $E/Z=12:1$ ).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (s, 0.92H), 6.66 (s, 0.08H), 4.26 (q,  $J = 7.2$  Hz, 0.07H), 3.99 – 3.97 (m, 2H), 3.96 (s, 2.84H), 3.94 (s,

0.23H), 3.91 (q,  $J = 7.1$  Hz, 0.97H), 3.48 – 3.36 (m, 2H), 3.00 – 2.91 (m, 0.97H), 2.76 – 2.70 (m, 0.11H), 2.19 – 2.11 (m, 2H), 1.51 (d,  $J = 7.1$  Hz, 2.84H), 1.46 (d,  $J = 7.2$  Hz, 0.28H), 1.37 – 1.33 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 189.1, 162.7, 158.6, 122.3, 119.8, 119.3, 119.2, 68.65, 68.64, 68.44, 68.41, 62.6, 62.4, 38.3, 34.2, 33.1, 32.8, 32.7, 32.4, 29.4, 15.4, 14.4. **HRMS** (ESI) calcd. for  $\text{C}_{12}\text{H}_{17}\text{NNaO}_3$   $[\text{M}+\text{Na}]^+$ : 246.1101, found: 246.1106.

**(E)-5-methoxy-2-methyl-3-oxo-4-(1-tosylpiperidin-4-yl)pent-4-enitrile (3e):**

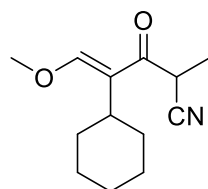


**3e**

(colorless oil, 133.8 mg, yield: 71%, *E/Z*>20:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 8.4$  Hz, 2H), 7.36 – 7.29 (m, 3H), 3.94 (s, 3H), 3.88 (q,  $J = 7.1$  Hz, 1H), 3.83 – 3.77 (m, 2H), 2.61 – 2.55 (m, 1H), 2.44 (s, 3H), 2.22 – 2.08 (m, 4H), 1.49 – 1.44 (m, 5H).  $^{13}\text{C NMR}$

(126 MHz,  $\text{CDCl}_3$ )  $\delta$  188.9, 163.1, 143.6, 133.0, 129.7, 127.8, 121.6, 119.1, 62.8, 47.18, 47.16, 32.8, 32.3, 28.0, 27.9, 21.6, 15.4. **HRMS** (ESI) calcd. for  $\text{C}_{19}\text{H}_{24}\text{N}_2\text{NaO}_4\text{S}$   $[\text{M}+\text{Na}]^+$ : 399.1349, found: 399.1356.

**(E)-4-cyclohexyl-5-methoxy-2-methyl-3-oxopent-4-enitrile (3f):** (colorless oil,

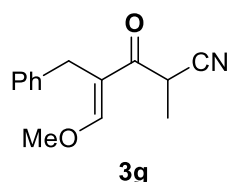


**3f**

67.4 mg, yield: 61%, *E/Z*>20:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (s, 1H), 3.93 (s, 3H), 3.91 (q,  $J = 7.2$  Hz, 1H), 2.64 (tt,  $J = 12.1, 3.4$  Hz, 1H), 1.80 – 1.71 (m, 4H), 1.67 – 1.62 (m, 1H), 1.50 (d,  $J = 7.2$  Hz, 3H), 1.47 – 1.44 (m, 2H), 1.31 – 1.15 (m, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  189.6, 162.1, 124.1, 119.3, 62.4, 35.6, 32.6, 29.64,

29.62, 27.0, 26.0, 15.6. **HRMS** (ESI) calcd. for  $\text{C}_{13}\text{H}_{19}\text{NNaO}_2$   $[\text{M}+\text{Na}]^+$ : 244.1308, found: 244.1313.

**(E)-4-benzyl-5-methoxy-2-methyl-3-oxopent-4-enitrile (3g):** (colorless oil, 75.9

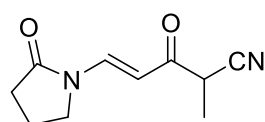


**3g**

mg, yield: 66%, *E/Z*>20:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (s, 1H), 7.28 – 7.19 (m, 4H), 7.18 – 7.14 (m, 1H), 3.98 (s, 3H), 3.82 (q,  $J = 7.1$  Hz, 1H), 3.68 – 3.61 (m, 2H), 1.45 (d,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  189.1, 162.3, 139.8, 128.5, 126.2,

119.1, 119.0, 62.5, 32.4, 29.2, 15.2. **HRMS** (ESI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 230.1176, found: 230.1174.

**(E)-2-methyl-3-oxo-5-(2-oxopyrrolidin-1-yl)pent-4-enitrile (3h):** (colorless oil,

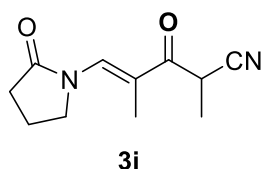


**3h**

53.4 mg, yield: 55%, *E/Z*>20:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J = 13.9$ , 1H), 5.81 (d,  $J = 13.9$  Hz, 1H), 3.70 – 3.64 (m, 3H), 2.62 – 2.58 (m, 2H), 2.28 – 2.20 (m, 2H), 1.54 (d,  $J = 7.3$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.5, 174.9, 139.0,

118.9, 103.9, 45.1, 36.7, 30.9, 17.4, 14.8. **HRMS** (ESI) calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 215.0791, found: 215.0795.

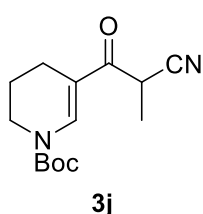
**(E)-2,4-dimethyl-3-oxo-5-(2-oxopyrrolidin-1-yl)pent-4-enitrile (3i)**: (colorless oil,



54.7 mg, yield: 53%, *E/Z*>20:1). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.87 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 1H), 4.11 – 4.03 (m, 2H), 2.54 (t, *J* = 8.2 Hz, 2H), 2.20 (p, *J* = 7.9 Hz, 2H), 2.04 (d, *J* = 1.2 Hz, 3H), 1.55 (d, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ

192.0, 175.9, 135.9, 118.8, 115.7, 48.0, 32.4, 29.8, 18.6, 16.0, 11.3. **HRMS** (ESI) calcd. for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 229.0947, found: 229.0954.

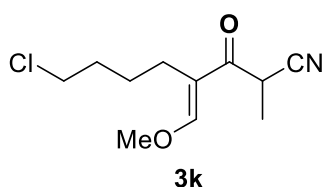
**tert-butyl 5-(2-cyanopropanoyl)-3,4-dihydropyridine-1(2H)-carboxylate (3j)**:



(colorless oil, 82.4 mg, yield: 62%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 4.07 (q, *J* = 7.2 Hz, 1H), 3.63 – 3.59 (m, 2H), 2.35 – 2.31 (m, 2H), 1.88 – 1.84 (m, 2H), 1.55 – 1.53 (m, 12H). **<sup>13</sup>C NMR**

(101 MHz, CDCl<sub>3</sub>) δ 188.7, 151.5, 139.1, 119.0, 114.8, 83.4, 42.6, 31.5, 28.0, 20.2, 20.0, 15.6. **HRMS** (ESI) calcd. for C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup>: 287.1366, found: 287.1370.

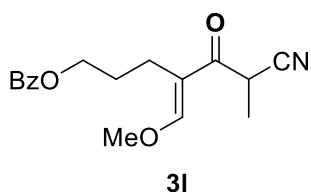
**(E)-8-chloro-4-(methoxymethylene)-2-methyl-3-oxooctanenitrile (3k)**: (colorless



oil, 95.6 mg, yield: 83%, *E/Z*>20:1). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.38 (s, 1H), 3.96 (s, 3H), 3.87 (q, *J* = 7.1 Hz, 1H), 3.54 (t, *J* = 6.8 Hz, 2H), 2.32 – 2.29 (m, 2H), 1.75 (dq, *J* = 8.4, 6.8 Hz, 2H), 1.53 (s, 3H), 1.52 – 1.46 (m, 2H). **<sup>13</sup>C**

**NMR** (126 MHz, CDCl<sub>3</sub>) δ 189.1, 162.1, 119.7, 119.2, 62.4, 45.0, 32.3, 32.2, 25.6, 22.6, 15.3. **HRMS** (ESI) calcd. for C<sub>11</sub>H<sub>16</sub>ClNNaO<sub>2</sub> [M+Na]<sup>+</sup>: 252.0762, found: 252.0761.

**(E)-6-cyano-4-(methoxymethylene)-5-oxoheptyl benzoate (3l)**: (colorless oil, 94.6

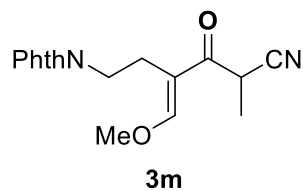


mg, yield: 62%, *E/Z*>20:1). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.10 – 8.01 (m, 2H), 7.59 – 7.55 (m, 1H), 7.47 – 7.43 (m, 2H), 7.39 (s, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.89 (s, 3H), 3.87 (q, *J* = 7.2 Hz, 1H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.90 – 1.83 (m,

2H), 1.52 (d, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 166.8, 162.4, 133.0,

130.5, 129.7, 128.5, 119.1, 119.0, 64.5, 62.4, 32.2, 27.3, 20.0, 15.3. **HRMS** (ESI) calcd. for  $C_{17}H_{19}NNaO_4$   $[M+Na]^+$ : 324.1207, found: 324.1212.

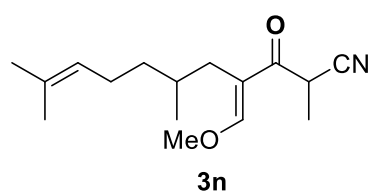
**(E)-6-(1,3-dioxoisindolin-2-yl)-4-(methoxymethylene)-2-methyl-3-**



**oxohexanenitrile (3m)**: (colorless oil, 108.5 mg, yield: 69%,  $E/Z > 20:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.84 – 7.79 (m, 2H), 7.74 – 7.68 (m, 2H), 7.34 (s, 1H), 3.86 (q,  $J = 7.1$  Hz, 1H), 3.80 – 3.75 (m, 2H), 3.68 (s, 3H), 2.71 – 2.66 (m, 2H),

1.50 (d,  $J = 7.2$  Hz, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  189.1, 168.5, 163.1, 133.9, 132.2, 123.2, 119.0, 117.1, 62.3, 36.5, 32.2, 22.6, 15.5. **HRMS** (ESI) calcd. for  $C_{17}H_{16}N_2NaO_4$   $[M+Na]^+$ : 335.1002, found: 335.1007.

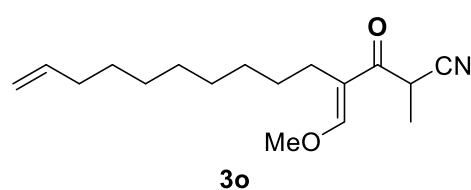
**(E)-4-(methoxymethylene)-2,6,10-trimethyl-3-oxoundec-9-enenitrile (3n)**:



(colorless oil, 96.9 mg, yield: 73%,  $E/Z > 20:1$ ; d.r.=1.1:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.394 (s, 0.48H), 7.392 (s, 0.52H), 5.08 (tdt,  $J = 7.1, 3.0, 1.4$  Hz, 1H), 3.93 (s, 3H), 3.92 (q,  $J = 7.3, 1.0$  Hz, 1H), 2.28 (dt,

$J = 13.1, 5.8$  Hz, 1H), 2.13 (ddd,  $J = 13.1, 8.4, 3.7$  Hz, 1H), 2.08 – 1.90 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.58 – 1.55 (m, 1H), 1.51 (d,  $J = 7.1$  Hz, 3H), 1.33 – 1.25 (m, 1H), 1.17 – 1.10 (m, 1H), 0.81 (d,  $J = 1.9$  Hz, 1.56H), 0.80 (d,  $J = 1.9$  Hz, 1.48H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  189.68, 189.67, 162.20, 162.19, 131.17, 131.15, 124.9, 119.24, 119.23, 119.22, 62.16, 62.15, 37.1, 37.0, 32.3, 32.1, 32.0, 30.6, 25.8, 25.7, 19.3, 17.7, 15.5. **HRMS** (ESI) calcd. for  $C_{16}H_{25}NNaO_2$   $[M+Na]^+$ : 286.1778, found: 286.1786.

**(E)-4-(methoxymethylene)-2-methyl-3-oxooct-7-enenitrile (3o)**: (colorless oil,



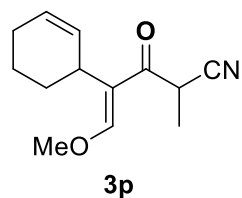
114.1 mg, yield: 82%,  $E/Z > 20:1$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35 (s, 1H), 5.86 – 5.76 (m, 1H), 4.99 (dq,  $J = 17.2, 1.8$  Hz, 1H), 4.94 – 4.90 (m, 1H), 3.94 (s, 3H), 3.90 (q,  $J = 7.2$  Hz, 1H), 2.27

– 2.24 (m, 2H), 2.06 – 2.00 (m, 2H), 1.51 (d,  $J = 7.1$  Hz, 3H), 1.38 – 1.30 (m, 4H), 1.27 – 1.25 (m, 8H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  189.5, 161.8, 139.3, 120.3, 119.3, 114.2,



62.2, 33.9, 32.2, 29.6, 29.5, 29.4, 29.2, 29.0, 28.4, 23.4, 15.5. **HRMS** (ESI) calcd. for  $C_{17}H_{27}NNaO_2$   $[M+Na]^+$ : 300.1934, found: 300.1938.

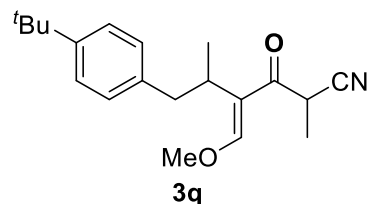
**(E)-4-(cyclohex-2-en-1-yl)-5-methoxy-2-methyl-3-oxopent-4-enitrile (3p):**



(colorless oil, 65.6 mg, yield: 59%,  $E/Z > 20:1$ ; d.r.=1.0:1).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.32 (s, 1H), 5.70 – 5.64 (m, 2H), 3.97 (td,  $J = 7.1, 1.3$  Hz, 1H), 3.94 (s, 3H), 2.97 – 2.89 (m, 1H), 2.44 – 2.34 (m, 1H), 2.14 – 2.02 (m, 3H), 1.92 – 1.83 (m, 1H), 1.57 – 1.52

(m, 1H), 1.52 (d,  $J = 7.3$  Hz, 1.49H), 1.50 (d,  $J = 7.2$  Hz, 1.50H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  189.61, 189.57, 162.5, 126.81, 126.78, 126.63, 126.59, 123.3, 119.3, 62.4, 32.6, 32.6, 31.4, 28.50, 28.49, 26.0, 25.9, 15.7, 15.6. **HRMS** (ESI) calcd. for  $C_{13}H_{17}NNaO_2$   $[M+Na]^+$ : 242.1151, found: 242.1158.

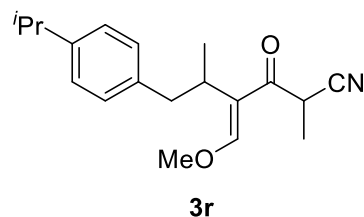
**(E)-6-(4-(tert-butyl)phenyl)-4-(methoxymethylene)-2,5-dimethyl-3-**



oxohexanenitrile (3q): (colorless oil, 101.7 mg, yield: 65%,  $E/Z > 20:1$ ; d.r.=1.1:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.26 – 7.22 (m, 2H), 7.16 (s, 0.45H), 7.12 (s, 0.58H), 7.04 – 7.02 (m, 2H), 3.85 (s, 1.76H), 3.84 (s, 1.24H), 3.75 (q,  $J = 7.2$  Hz, 0.58H), 3.70 (q,  $J = 7.1$  Hz, 0.46H),

3.26 – 3.15 (m, 1H), 2.87 – 2.76 (m, 2H), 1.32 (d,  $J = 7.2$  Hz, 1.53H), 1.28 (s, 4.28H), 1.27 (s, 4.71H), 1.25 (d,  $J = 7.2$  Hz, 1.65H), 1.18 (d,  $J = 7.0$  Hz, 1.46H), 1.17 (d,  $J = 7.0$  Hz, 1.58H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  189.8, 189.5, 162.1, 161.9, 148.62, 148.59, 138.19, 138.16, 128.7, 128.6, 124.9, 123.1, 123.0, 119.13, 119.06, 62.31, 62.28, 39.8, 39.7, 34.4, 32.8, 32.7, 32.4, 32.3, 31.5, 18.1, 17.9, 15.9, 15.4. **HRMS** (ESI) calcd. for  $C_{20}H_{27}NNaO_2$   $[M+Na]^+$ : 336.1934, found: 336.1939.

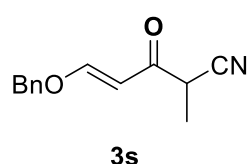
**(E)-6-(4-isopropylphenyl)-4-(methoxymethylene)-2,5-dimethyl-3-**



oxohexanenitrile (3r): (colorless oil, 114.4 mg, yield: 76%,  $E/Z > 20:1$ ; d.r.=1.2:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.16 (s, 0.46H), 7.12 (s, 0.54H), 7.08 (dd,  $J = 8.1, 1.6$  Hz, 2H), 7.02 (dd,  $J = 8.3, 2.4$  Hz, 2H), 3.86 (s, 1.49H), 3.85 (s, 1.41H), 3.73 (q,  $J = 7.2$  Hz, 0.55H), 3.67 (q,  $J =$

7.1 Hz, 0.45H), 3.28 – 3.15 (m, 1H), 2.87 – 2.78 (m, 3H), 1.33 (d,  $J = 7.2$  Hz, 1.43H), 1.29 (d,  $J = 7.2$  Hz, 1.61H), 1.21 – 1.16 (m, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  189.6, 189.3, 162.0, 161.9, 146.4, 146.4, 138.6, 138.6, 129.0, 129.0, 126.1, 123.3, 123.1, 119.1, 119.1, 62.4, 62.3, 39.9, 39.9, 33.8, 32.7, 32.6, 32.5, 32.4, 24.2, 24.2, 18.1, 18.0, 15.8, 15.4. HRMS (ESI) calcd. for  $\text{C}_{19}\text{H}_{25}\text{NNaO}_2$   $[\text{M}+\text{Na}]^+$ : 322.1778, found: 322.1782.

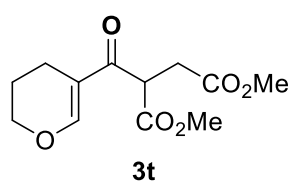
**(E)-5-(benzyloxy)-2-methyl-3-oxopent-4-enitrile (3s)**: (colorless oil, 59.9 mg,



yield: 55%,  $E/Z > 20:1$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 12.2$  Hz, 1H), 7.44 – 7.38 (m, 3H), 7.36 – 7.33 (m, 2H), 6.01 (d,  $J = 12.2$  Hz, 1H), 5.01 (s, 2H), 3.48 (q,  $J = 7.3$  Hz, 1H), 1.51 (d,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  189.7, 164.9,

134.6, 129.1, 129.0, 128.0, 119.0, 102.2, 74.4, 37.4, 14.7. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{13}\text{NNaO}_2$   $[\text{M}+\text{Na}]^+$ : 238.0838, found: 238.0845.

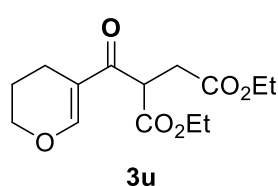
**dimethyl 2-(3,4-dihydro-2H-pyran-5-carbonyl)succinate (3t)**: (colorless oil, 49.7



mg, yield: 39%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (s, 1H), 4.34 (t,  $J = 7.2$  Hz, 1H), 4.12 (dd,  $J = 5.8, 4.7$  Hz, 2H), 3.72 (s, 3H), 3.68 (s, 3H), 3.02 – 2.88 (m, 2H), 2.30 (t,  $J = 6.4$  Hz, 2H), 1.90 (qd,  $J = 6.2, 4.5$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$

191.7, 172.1, 169.7, 159.3, 116.1, 67.4, 52.9, 52.1, 47.9, 33.1, 20.9, 18.6. HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_{16}\text{NaO}_6$   $[\text{M}+\text{Na}]^+$ : 279.0839, found: 279.0847.

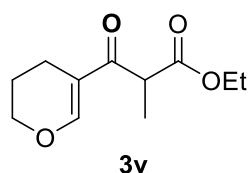
**diethyl 2-(3,4-dihydro-2H-pyran-5-carbonyl)succinate (3u)**: (colorless oil, 57.4 mg,



yield: 40%).  $^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.85 (s, 1H), 4.32 (t,  $J = 7.2$  Hz, 1H), 4.21 – 4.07 (m, 6H), 2.93 (dd,  $J = 7.2, 1.2$  Hz, 2H), 2.30 (tdd,  $J = 6.3, 3.2, 1.2$  Hz, 2H), 1.94 – 1.84 (m, 2H), 1.26 – 1.23 (m, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  191.8,

171.6, 169.1, 159.1, 116.0, 67.3, 61.6, 60.9, 48.2, 33.2, 20.9, 18.5, 14.1, 14.0. HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{20}\text{NaO}_6$   $[\text{M}+\text{Na}]^+$ : 307.1152, found: 307.1158.

**ethyl 3-(3,4-dihydro-2H-pyran-5-yl)-2-methyl-3-oxopropanoate (3v):** (colorless oil,



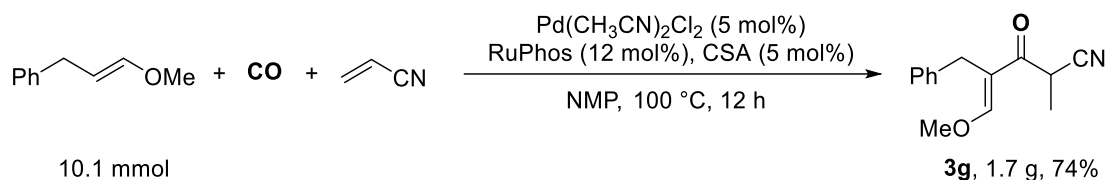
**3v**

33.2 mg, yield: 31%). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 1.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.11 – 4.08 (m, 2H), 3.88 (q, *J* = 7.1 Hz, 1H), 2.31 – 2.28 (m, 2H), 1.88 (qd, *J* = 6.0, 4.0 Hz, 2H), 1.37 (d, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR**

(126 MHz, CDCl<sub>3</sub>) δ 194.3, 171.3, 158.0, 116.1, 77.4, 77.2, 76.9, 67.3, 61.3, 46.8, 21.1, 18.7, 14.24, 14.22. **HRMS** (ESI) calcd. for C<sub>11</sub>H<sub>16</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 235.0941, found: 235.0943.

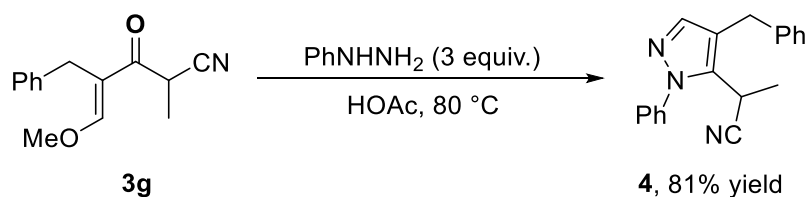
## 5. Gram-scale reaction and synthetic applications

### 5.1 Gram-scale reaction

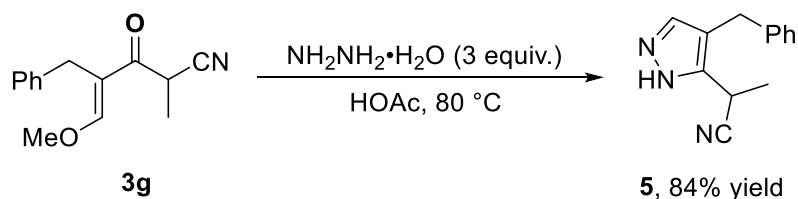


In a N<sub>2</sub> atmosphere glove box, Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (131.0 mg, 0.505 mmol), CSA (117.3 mg, 0.505 mmol), Ruphos (565.5 mg, 1.21 mmol), enol ethers (1.5 g, 10.1 mmol), acrylonitrile (1.3 mL, 20.2 mmol), and NMP (20 mL) were added into a teflon reaction tube which was placed in an autoclave. Then the autoclave was purged and charged with CO (40 atm). The reaction mixture was stirred at 100 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the hood. Then NMP was removed under reduced pressure and the residual reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 30/1 - 3/1) to give the desired product **3g** (1.7 g, 74% yield).

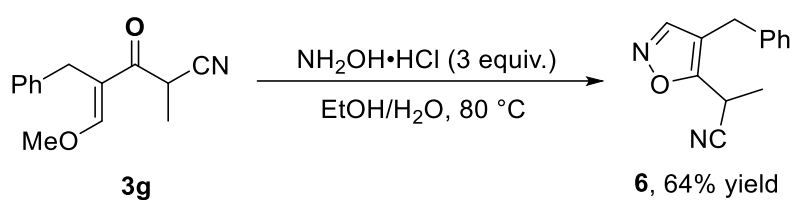
### 5.2 Synthetic applications



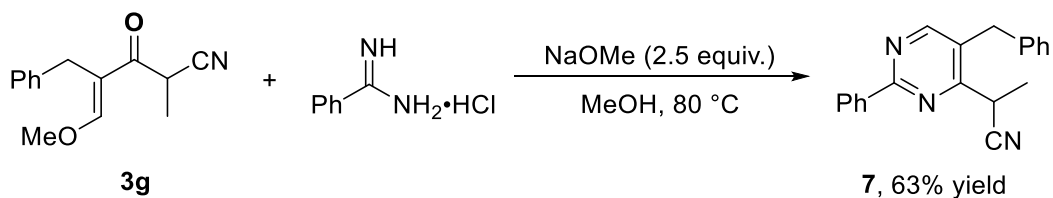
To a 25 mL dry Schlenk tube were added **3g** (229.3 mg, 1.0 mmol), PhNHNH<sub>2</sub> (295 uL, 3.0 mmol) and HOAc (3 mL), then the mixture was stirred and heated to 80 °C for 16 h. The reaction mixture was then cooled down to room temperature and quenched by 15 mL saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution carefully and extracted by EtOAc (10 mL×3). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 10/1 - 3/1 as the eluent to give the desired product **4** as colorless oil (233.3 mg, 81% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.45 (m, 3H), 7.44 (s, 1H), 7.41 – 7.37 (m, 2H), 7.35 – 7.32 (m, 2H), 7.31 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 4.10 – 4.00 (m, 3H), 1.39 (d, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 141.5, 139.8, 138.9, 133.8, 129.7, 129.2, 128.8, 128.7, 126.5, 126.2, 119.8, 119.1, 30.1, 22.3, 18.9. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>Na [M+Na]<sup>+</sup>: 310.1315, found: 310.1306.



To a 25 mL dry Schlenk tube were added **3g** (229.3 mg, 1.0 mmol), NH<sub>2</sub>NH<sub>2</sub> H<sub>2</sub>O (156 uL, 3.0 mmol) and HOAc (3 mL), then the mixture was stirred and heated to 80 °C for 16 h. The reaction mixture was then cooled down to room temperature and quenched by 15 mL saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution carefully and extracted by EtOAc (10 mL×3). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 3/1 - 1/1 as the eluent to give the desired product **5** as colorless oil (177.6 mg, 84% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 12.12 (s, 1H), 7.45 (s, 1H), 7.28 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 3.87 – 3.83 (m, 3H), 1.50 (d, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 139.8, 128.7, 128.5, 126.5, 120.9, 117.0, 29.6, 23.9, 18.9. HRMS (ESI) calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>Na [M+Na]<sup>+</sup>: 234.1002, found: 234.0987.



To a 25 mL dry Schlenk tube were added **3g** (229.3 mg, 1.0 mmol),  $\text{NH}_2\text{OH HCl}$  (208.5 mg, 3.0 mmol), EtOH (2 mL) and  $\text{H}_2\text{O}$  (1 mL), then the mixture was stirred and heated to 80 °C for 16 h. The reaction mixture was then cooled down to room temperature and quenched by 15 mL saturated  $\text{Na}_2\text{CO}_3$  aqueous solution carefully and extracted by EtOAc (10 mL $\times$ 3). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 15/1 - 5/1 as the eluent to give the desired product **6** as colorless oil (135.8 mg, 64% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 1H), 7.37 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 7.20 – 7.16 (m, 2H), 4.04 (q,  $J = 7.3$  Hz, 1H), 3.87 (s, 2H), 1.65 (d,  $J = 7.4$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 152.4, 137.8, 129.1, 128.4, 127.2, 117.7, 115.1, 28.4, 23.1, 17.5. **HRMS** (ESI) calcd. for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 213.1022, found: 213.1030.



To a 25 mL dry Schlenk tube were added **3g** (229.3 mg, 1.0 mmol), benzamidine hydrochloride (313.2 mg, 2.0 mmol), MeOH (3 mL) and NaOMe (135 mg, 2.5 mmol), then the mixture was stirred and heated to 80 °C for 16 h. The reaction mixture was then cooled down to room temperature and quenched by 15 mL  $\text{H}_2\text{O}$  carefully and extracted by EtOAc (10 mL $\times$ 3). The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 15/1 - 5/1 as the eluent to give the desired product **7** as colorless oil (188.9 mg, 63% yield).  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  8.62 (s, 1H), 8.53 – 8.49 (m, 2H), 7.52 – 7.48

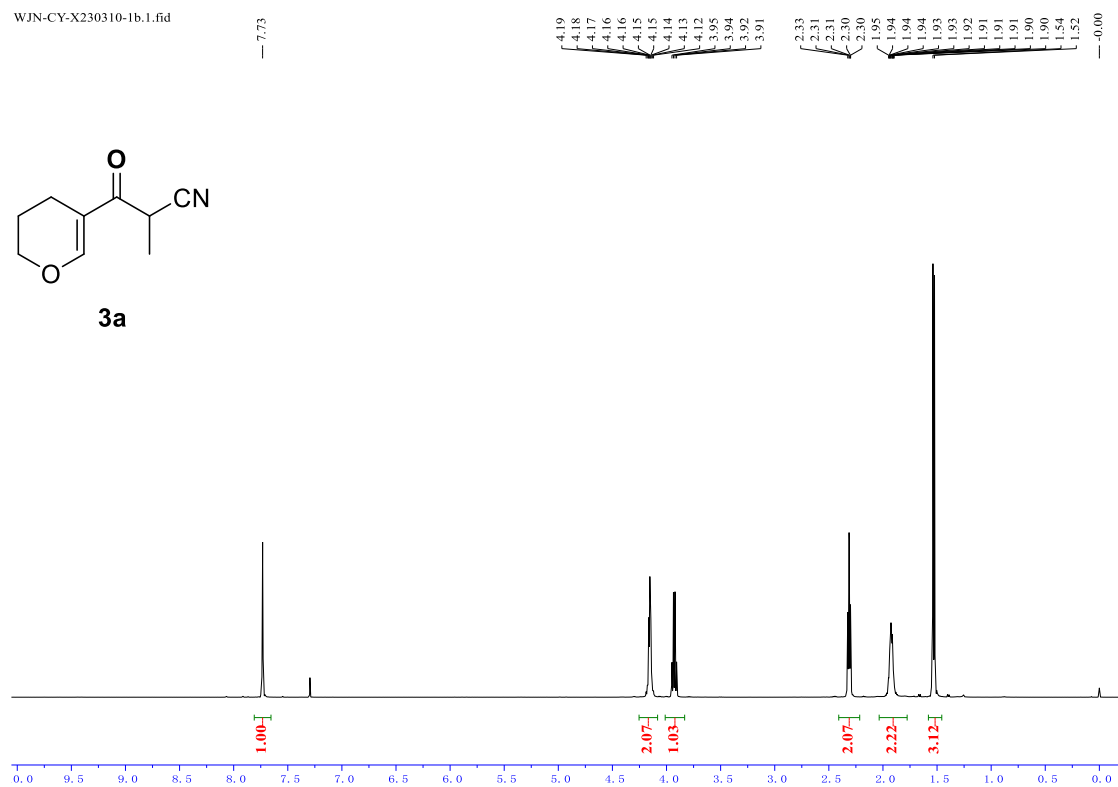
(m, 3H), 7.35 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.13 (dt,  $J = 6.4, 1.3$  Hz, 2H), 4.10 – 4.04 (m, 3H), 1.57 (d,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 162.4, 159.5, 137.5, 136.8, 131.1, 129.3, 128.8, 128.6, 128.3, 127.4, 119.8, 35.3, 30.4, 17.9. HRMS (ESI) calcd. for  $\text{C}_{20}\text{H}_{18}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 300.1495, found: 300.1494.

## 6. References

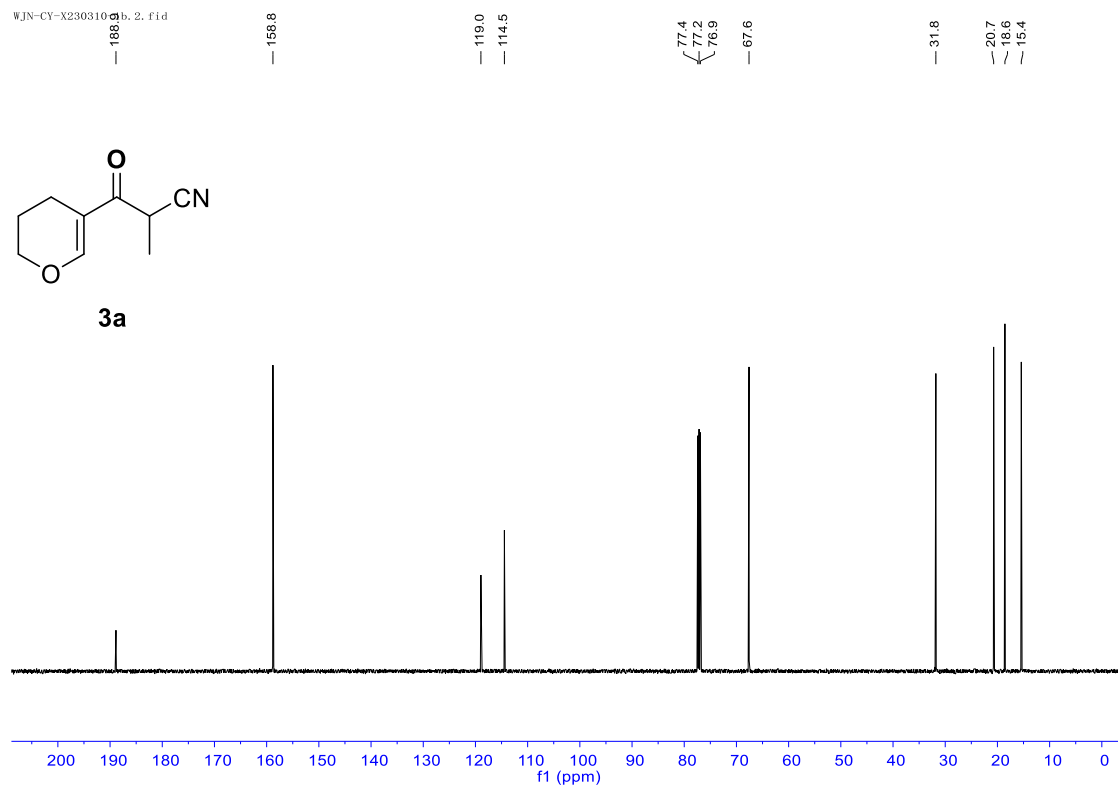
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## 7. Spectra of products.

### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3a



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3a



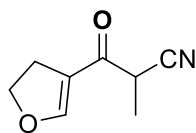
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3b

dyz-x210726-5-iso. 1. f1.d  
7.60  
7.59  
7.59

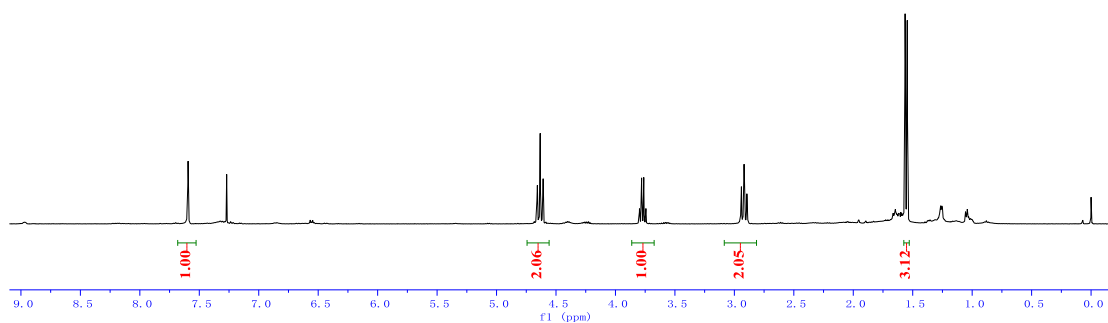
4.66  
4.66  
4.63  
4.61  
3.80  
3.78  
3.76  
3.74  
2.94  
2.92  
2.92  
2.92  
2.91  
2.90  
2.89

1.56  
1.55

0.00



**3b**



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3b

dyz-x210726-5-iso. 2. f1.d  
185.4

160.2

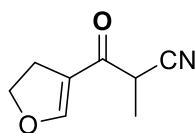
119.0  
117.8

77.5  
77.2  
76.8  
74.0

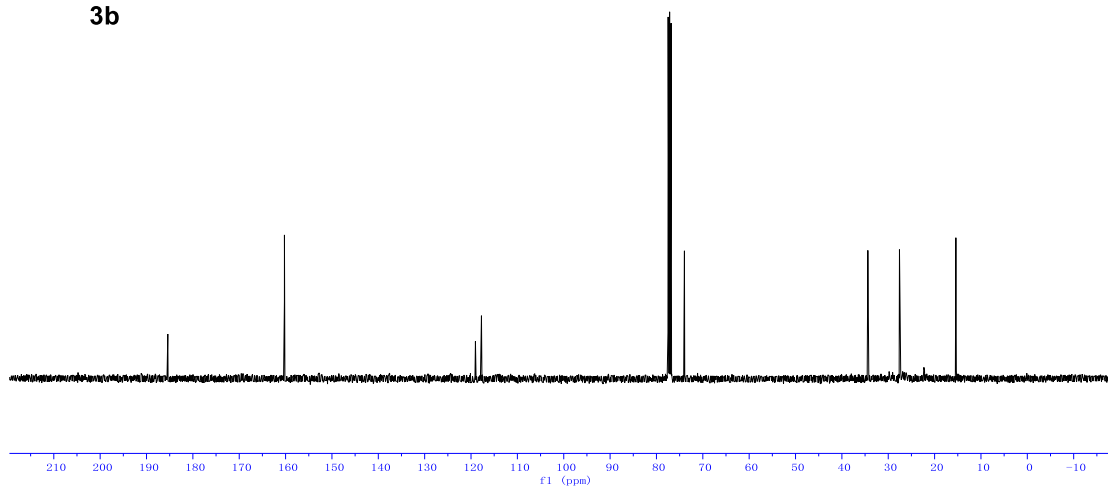
34.4

27.6

15.4

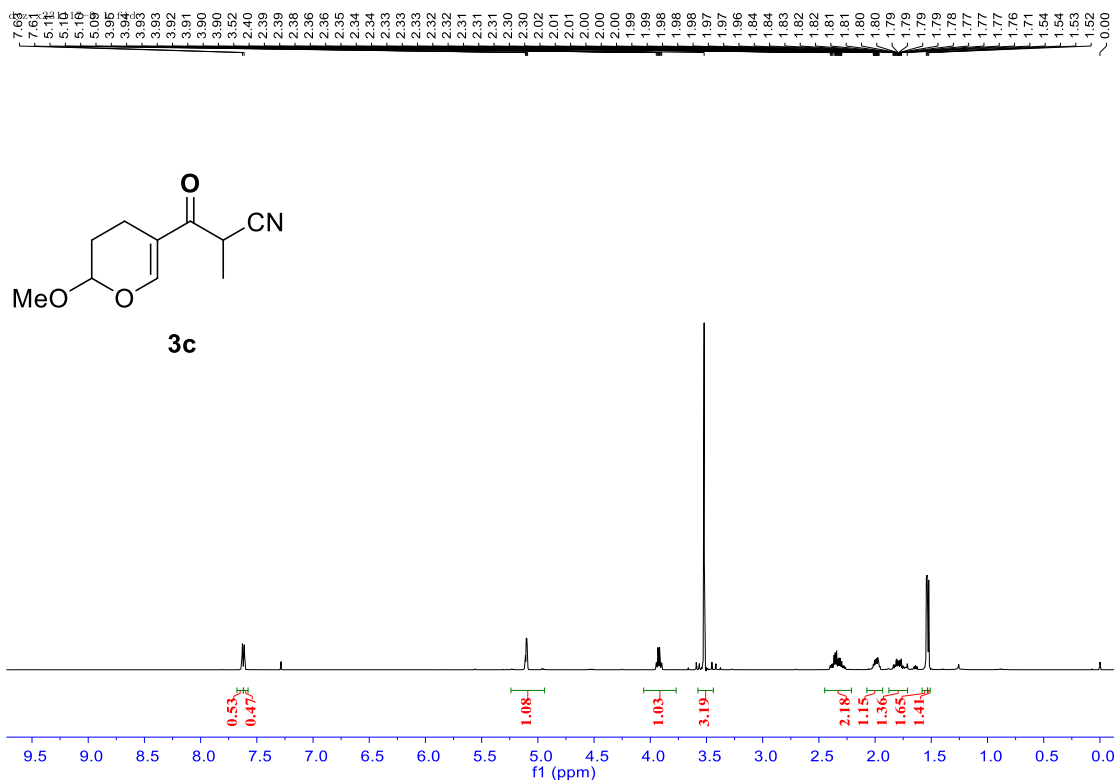


**3b**

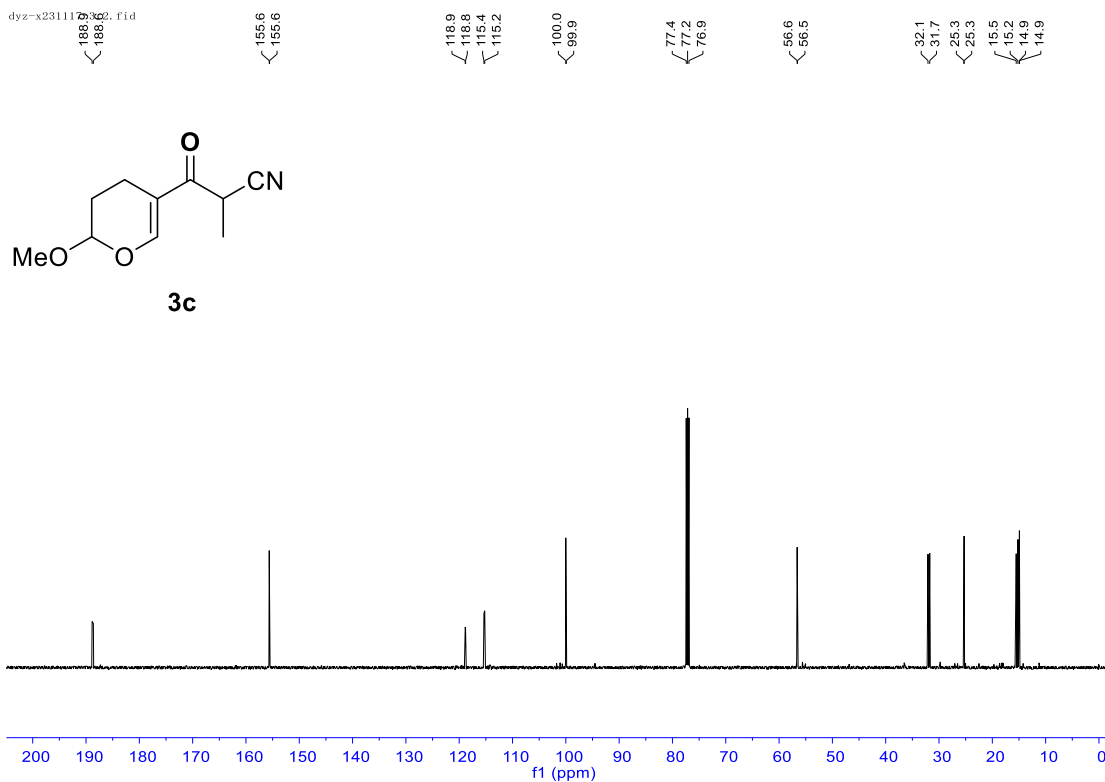




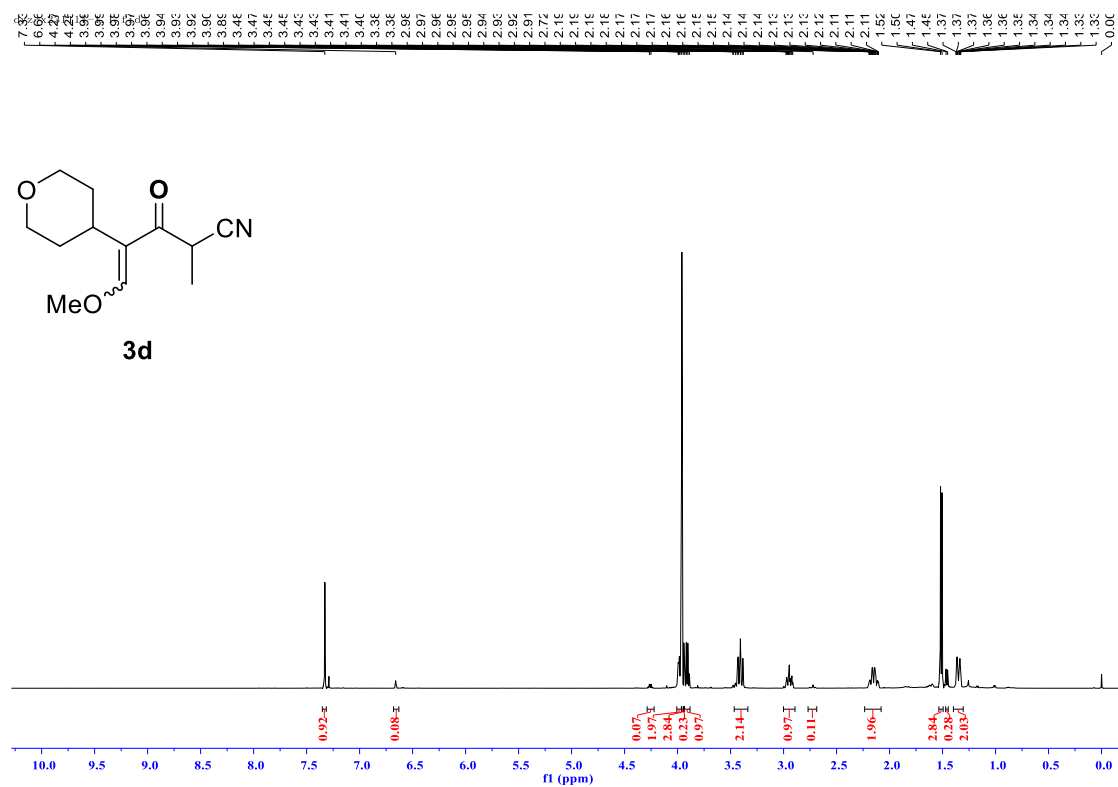
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3c



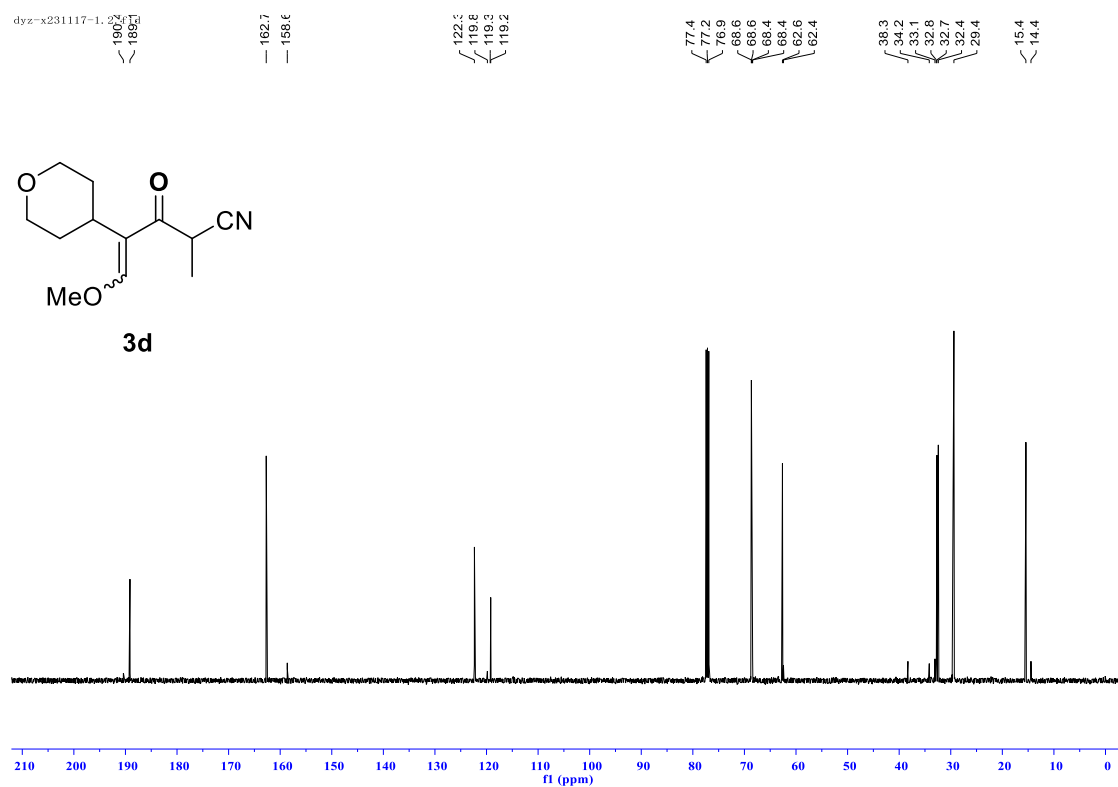
### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3c



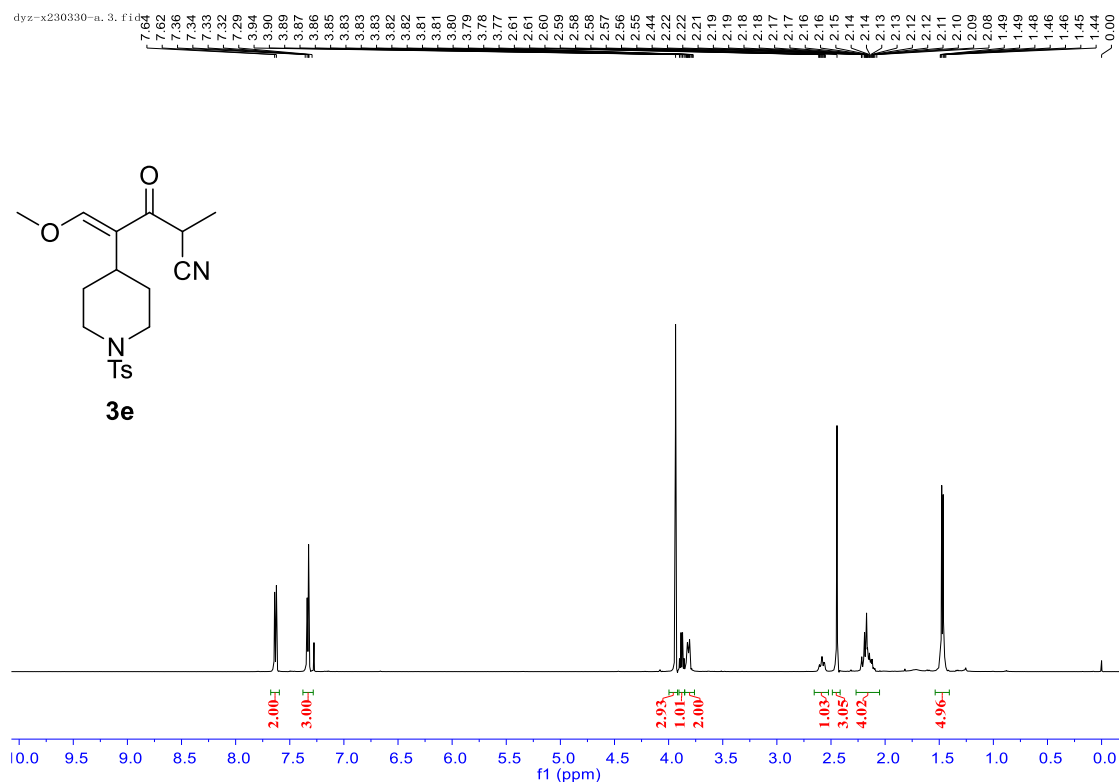
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3d**



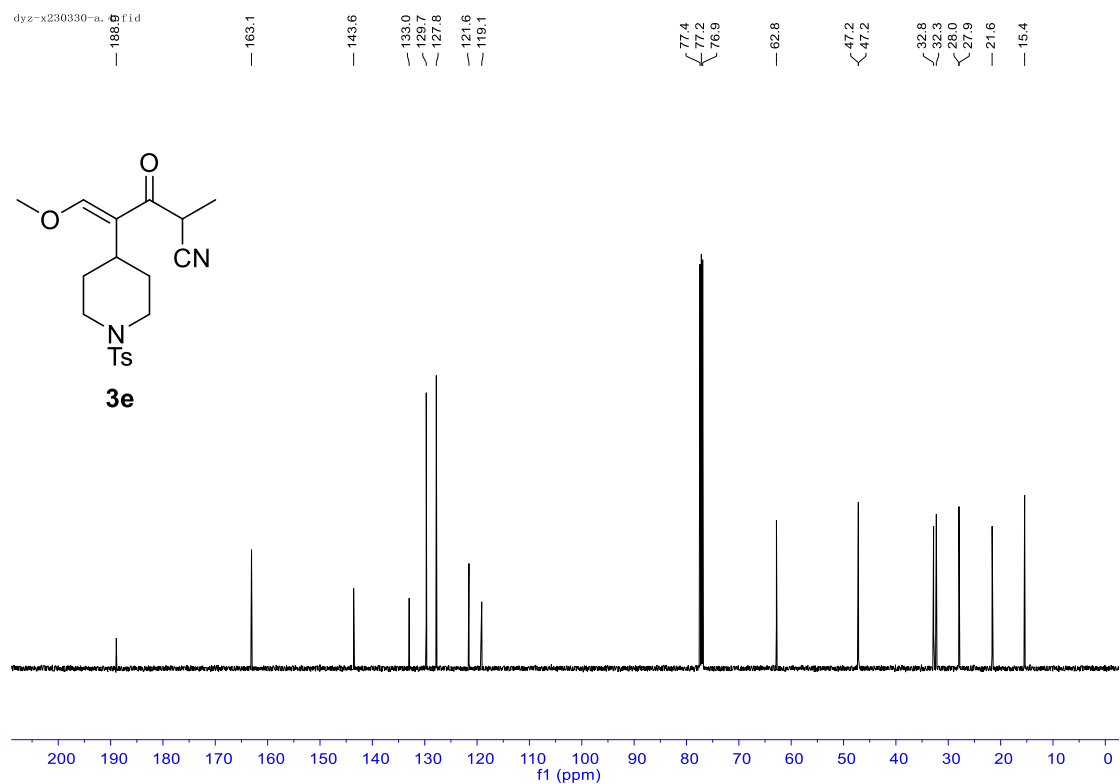
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3d**



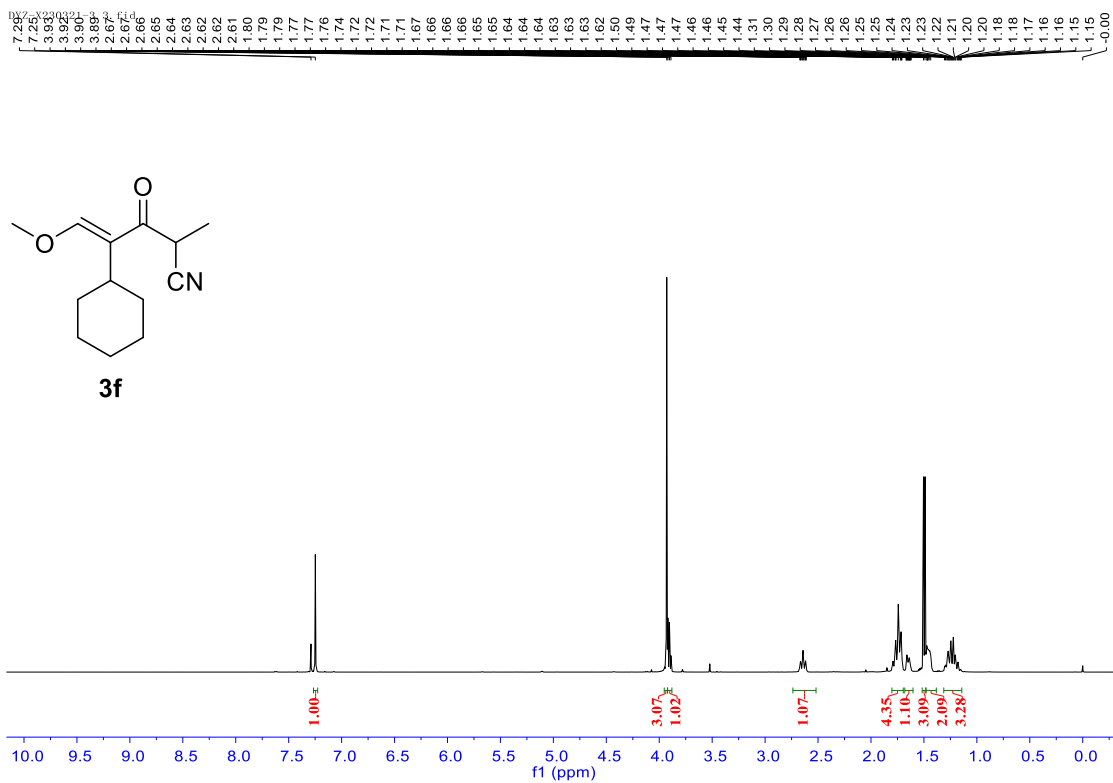
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3e



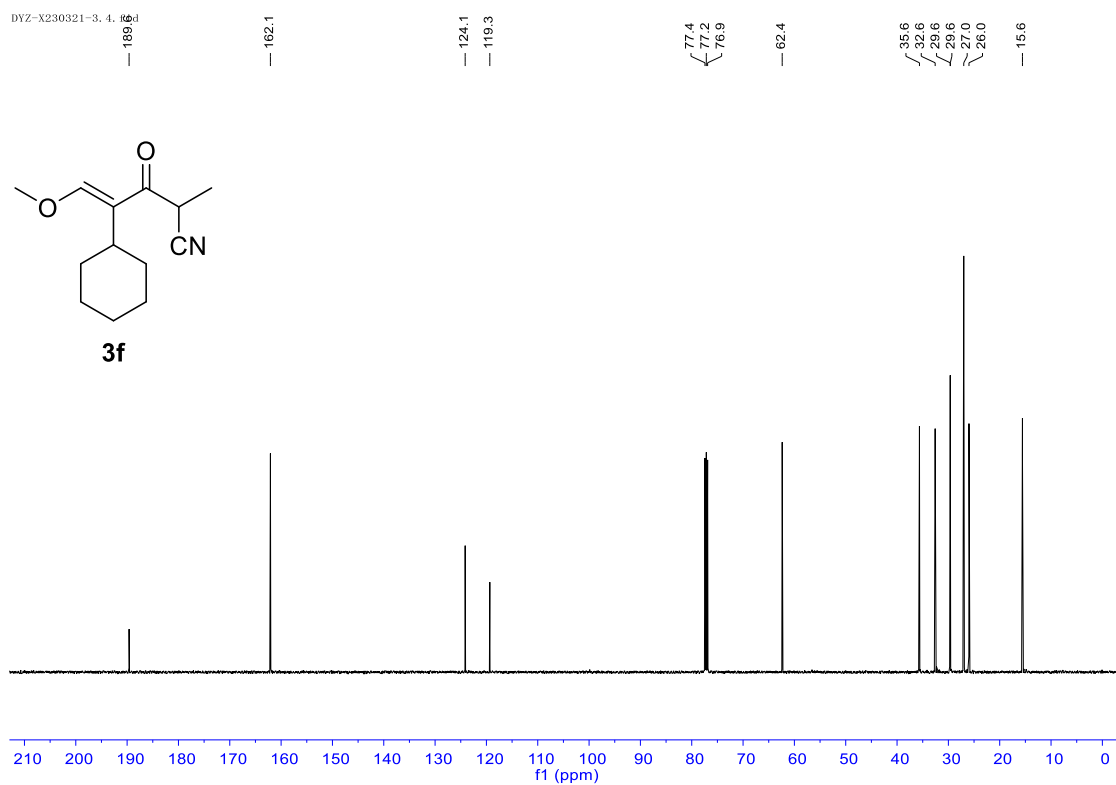
### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3e



### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3f

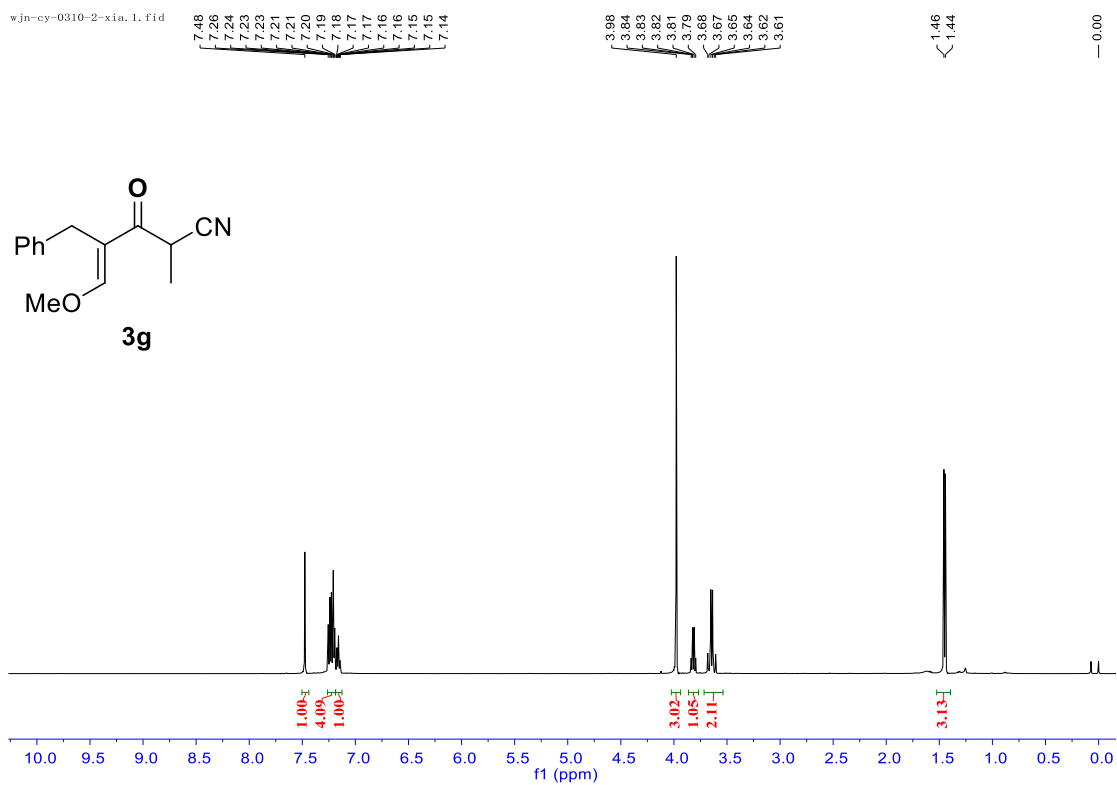


### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3f



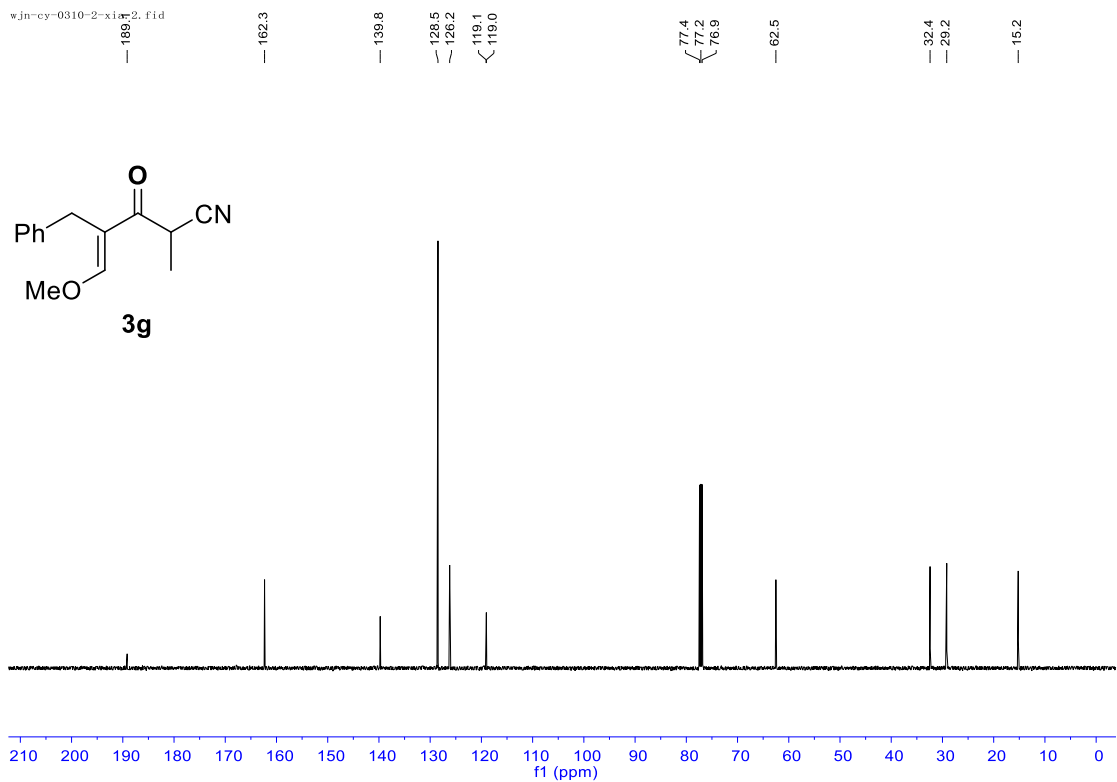
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3g

wjn-cy-0310-2-xia.1.fid



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3g

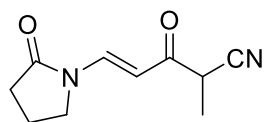
wjn-cy-0310-2-xia.2.fid



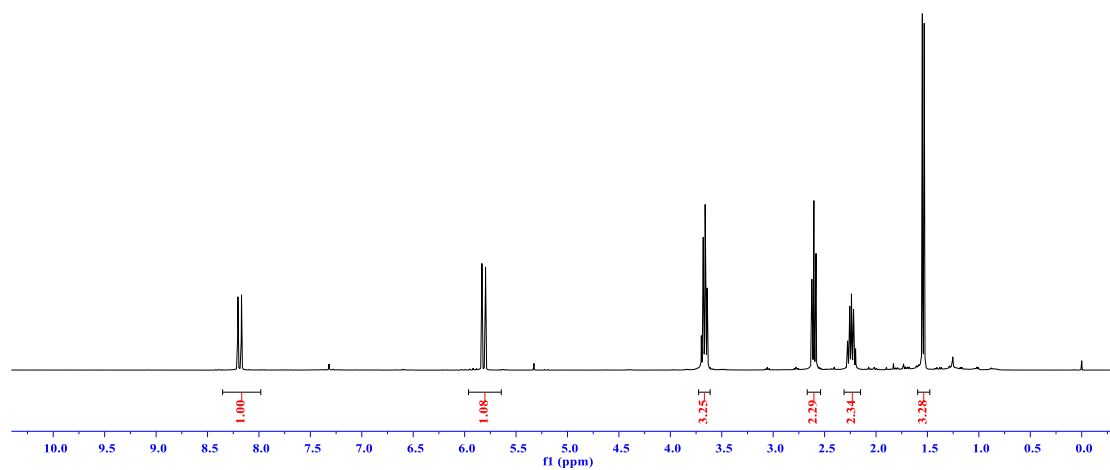
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum for 3h

dyz-x231205-1-iso. 1. fid

8.20  
8.17  
5.88  
5.80  
3.70  
3.66  
3.66  
3.66  
3.66  
3.64  
3.64  
2.62  
2.60  
2.58  
2.28  
2.28  
2.22  
2.24  
2.24  
2.22  
2.22  
2.22  
2.22  
1.55  
1.55  
0.00



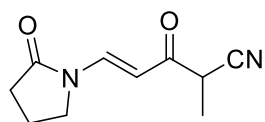
3h



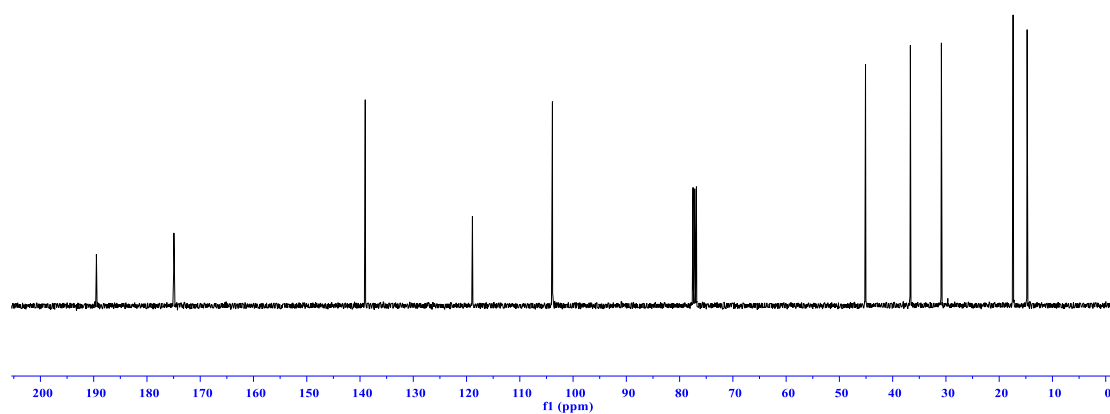
### <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum for 3h

dyz-x231205-1-2. fid

189.48  
174.98  
139.02  
116.90  
103.88  
77.48  
77.16  
76.84  
45.10  
36.67  
30.85  
17.99  
14.75

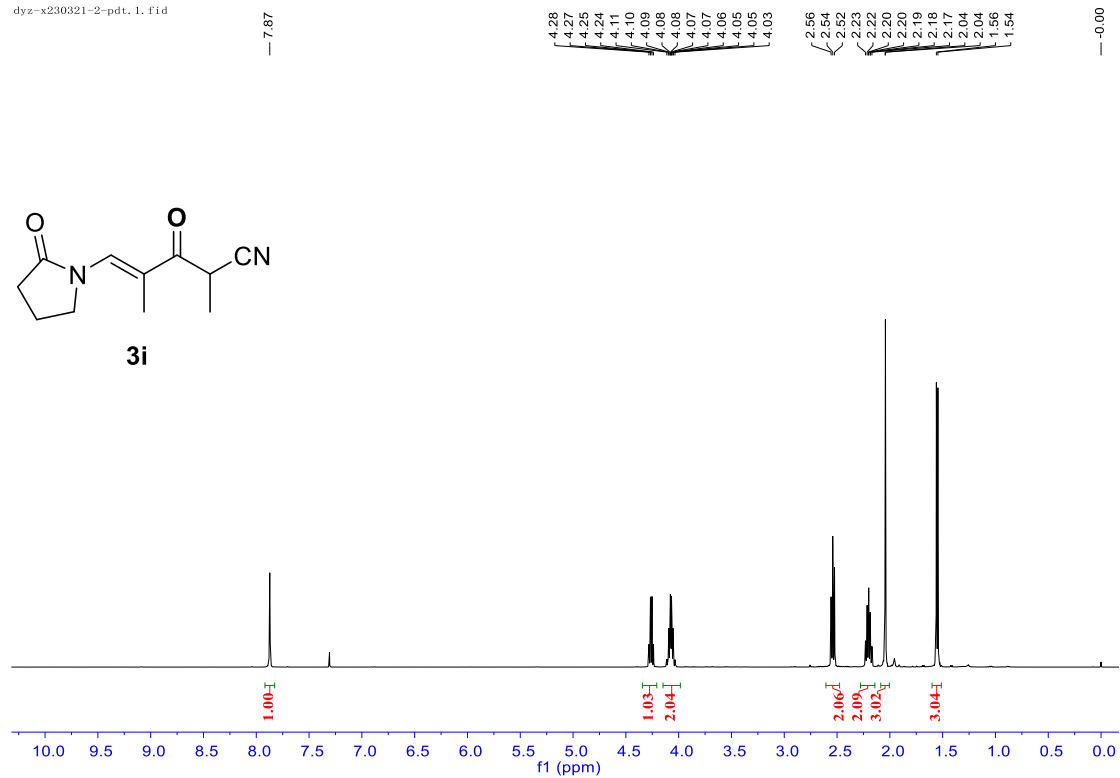


3h



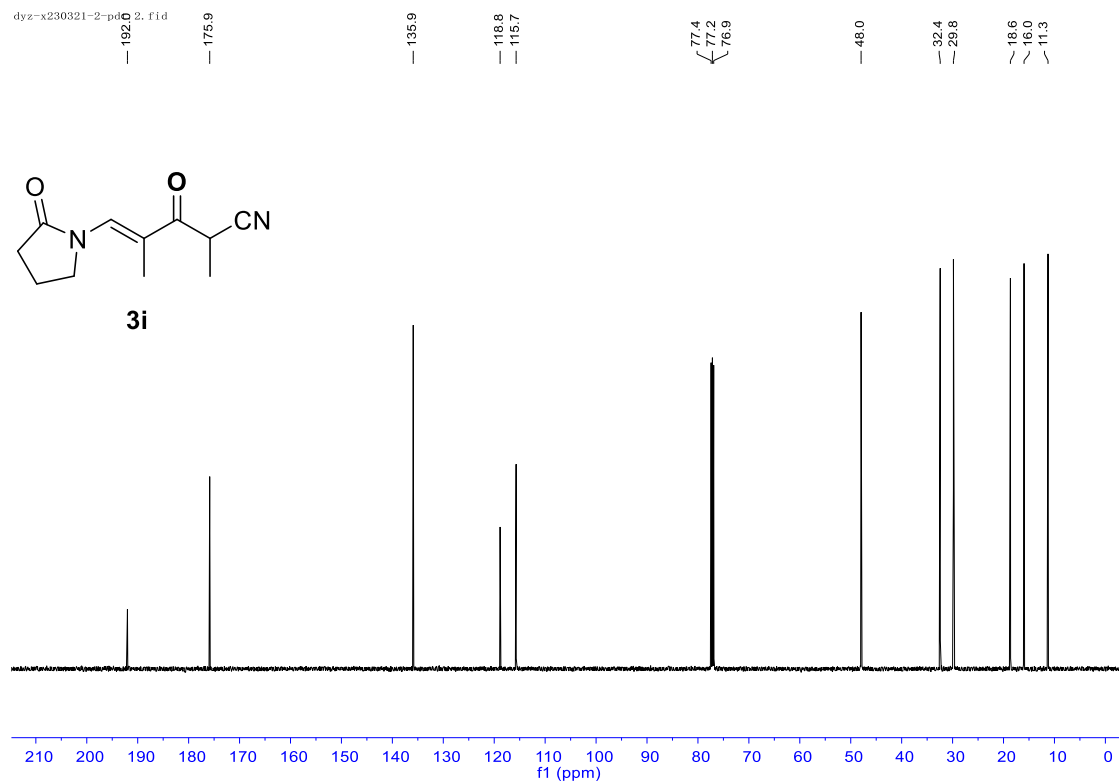
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3i

dyz-x230321-2-pdt. 1. f.id



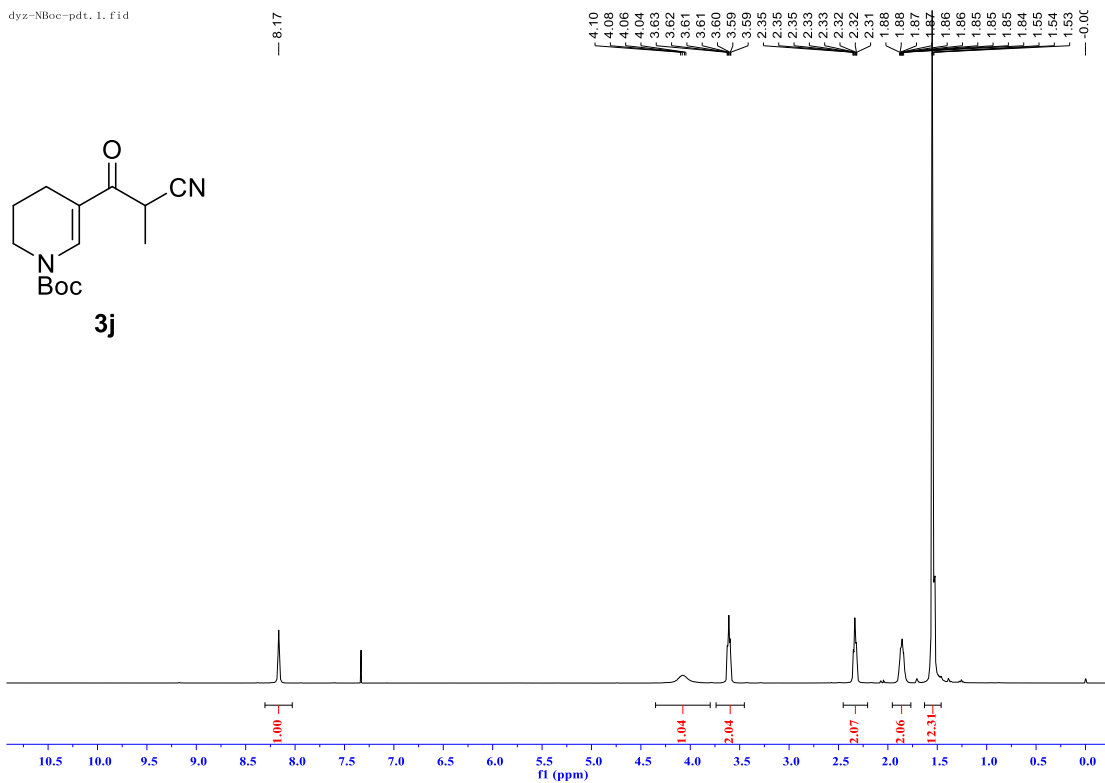
### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3i

dyz-x230321-2-pdt. 2. f.id



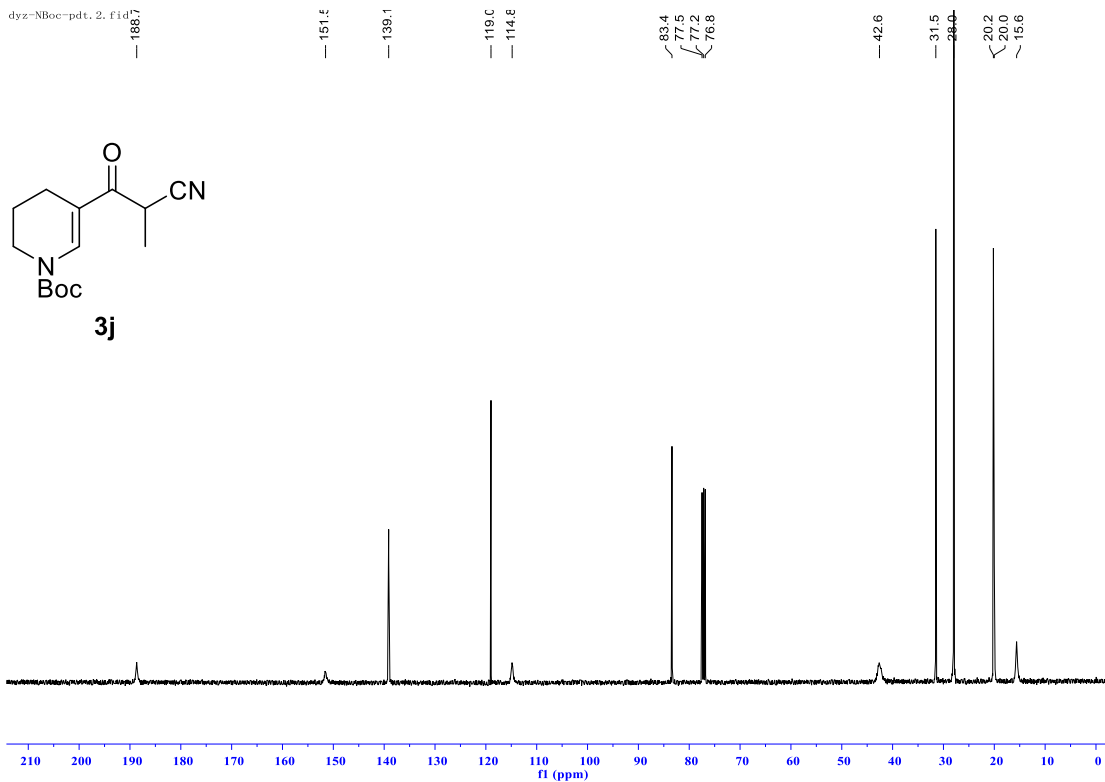
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum for 3j

dyz-NBoc-pdt, 1, fid



### <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum for 3j

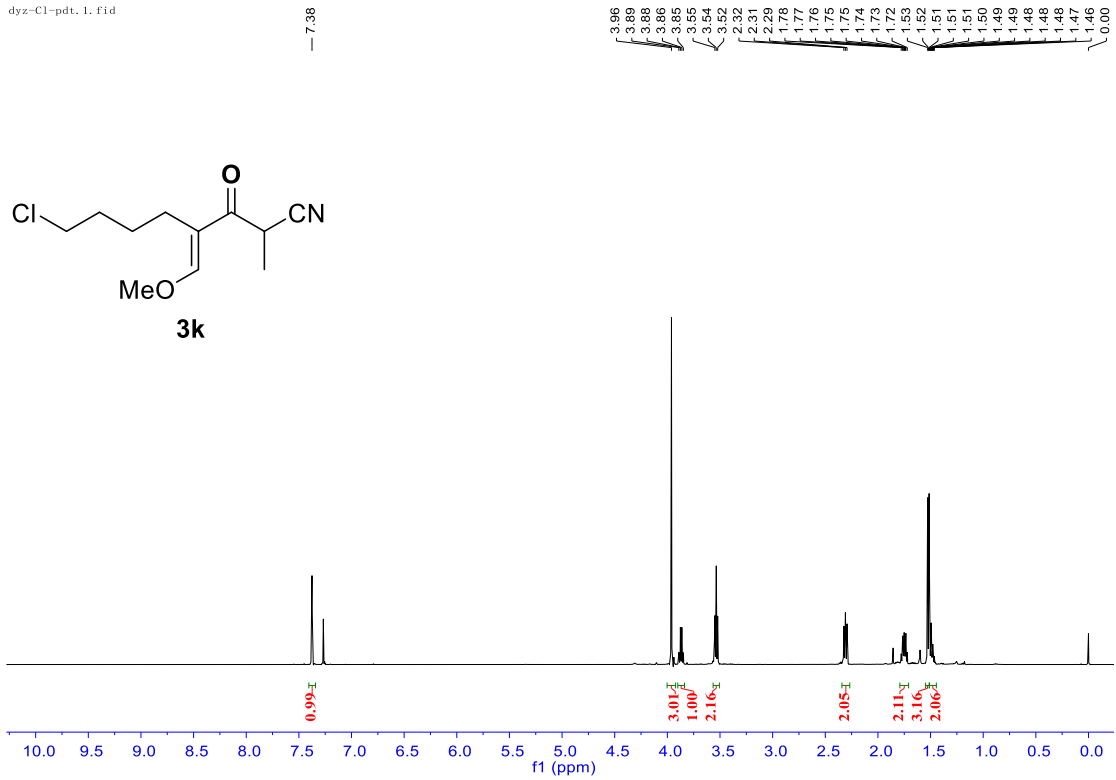
dyz-NBoc-pdt, 2, fid





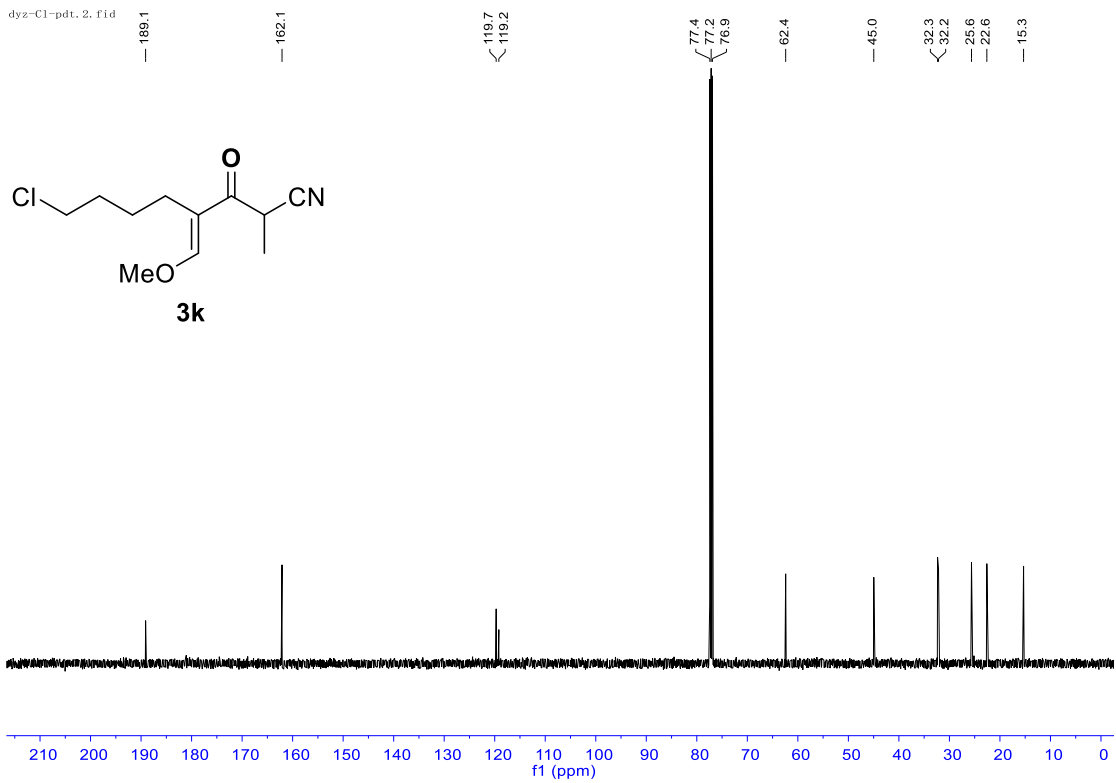
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3k

dyz-cl-pdt. 1. fid

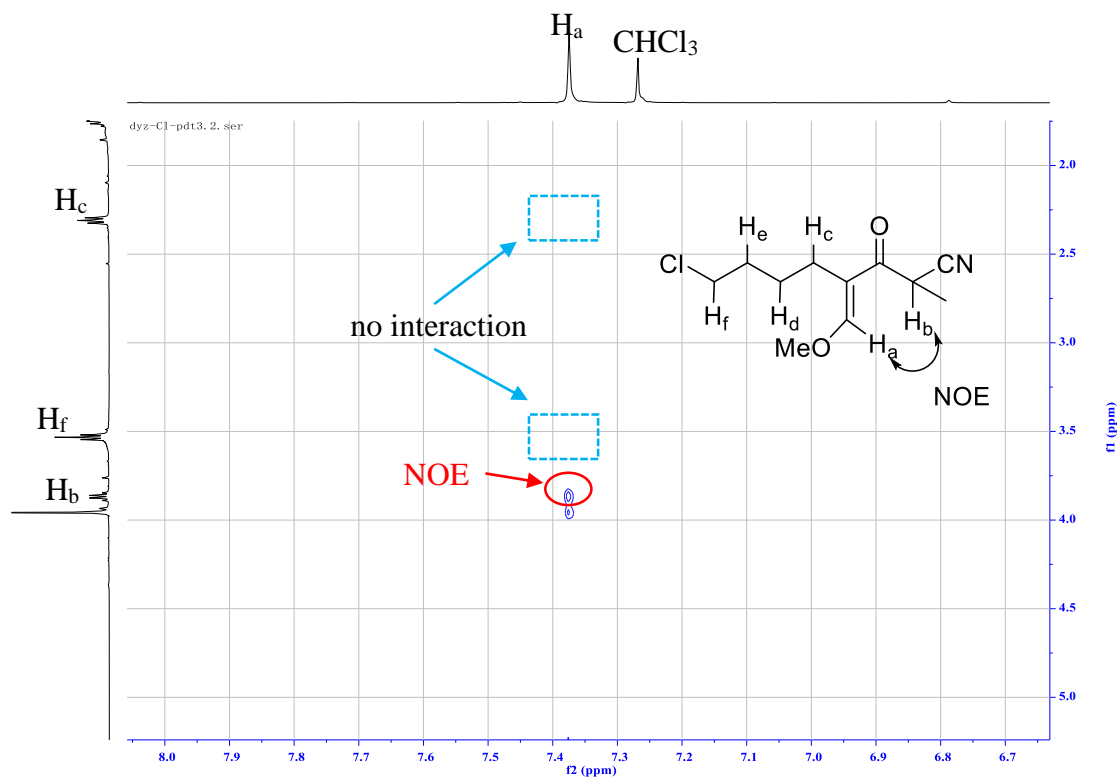


### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3k

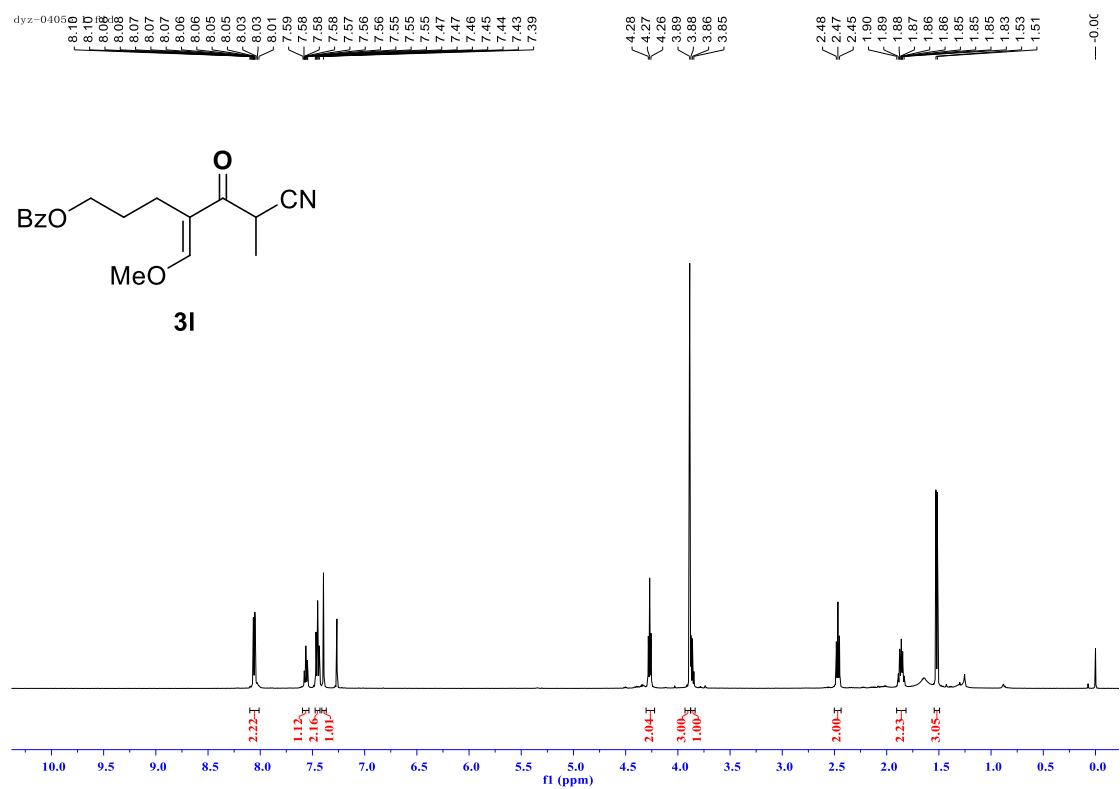
dyz-cl-pdt. 2. fid



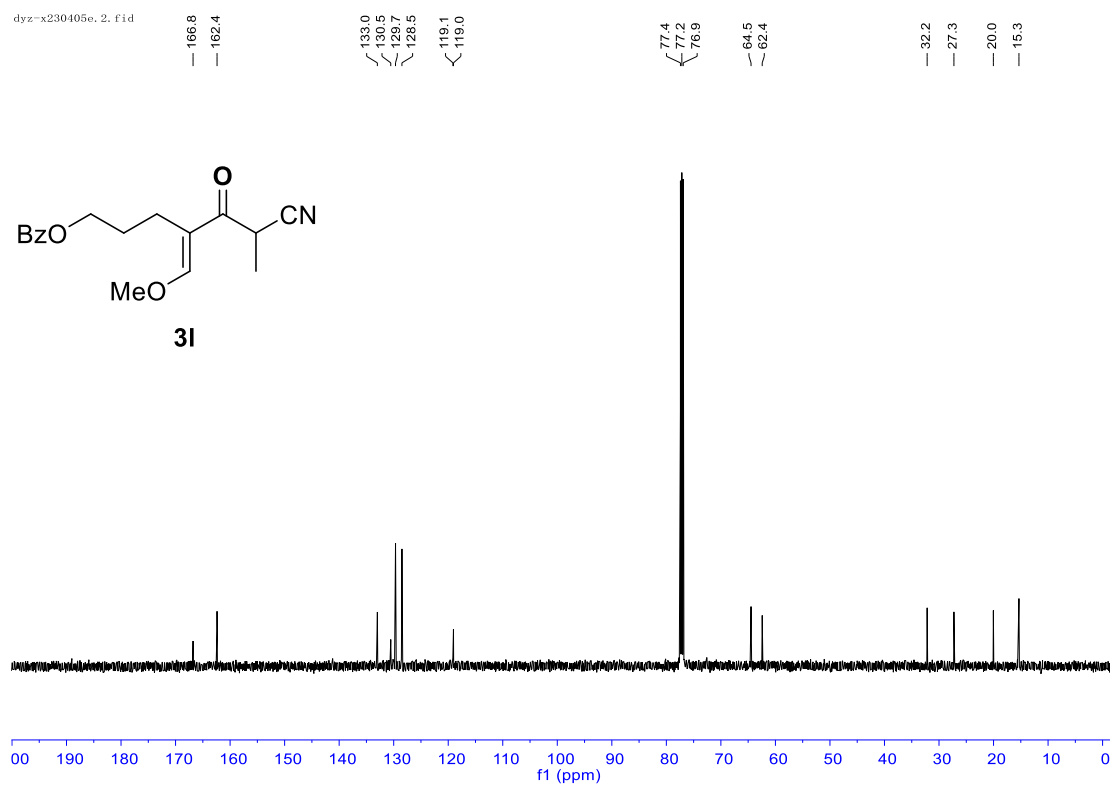
### NOESY (500 MHz, CDCl<sub>3</sub>) spectrum for 3k



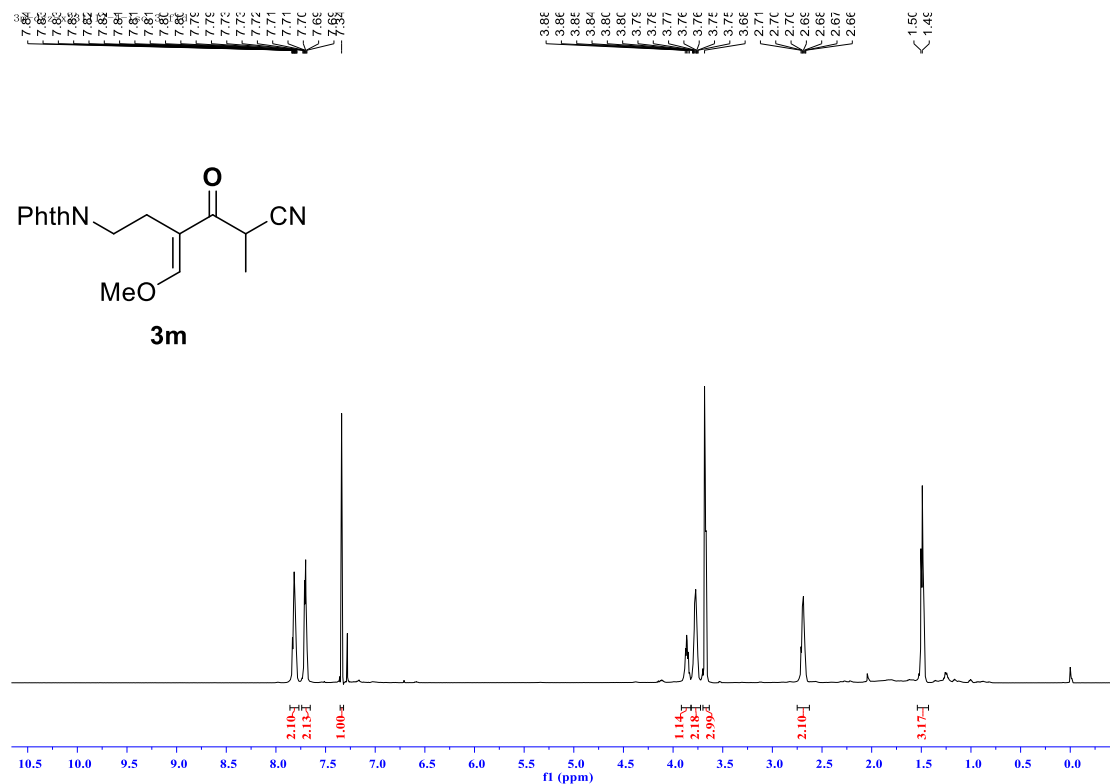
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3l



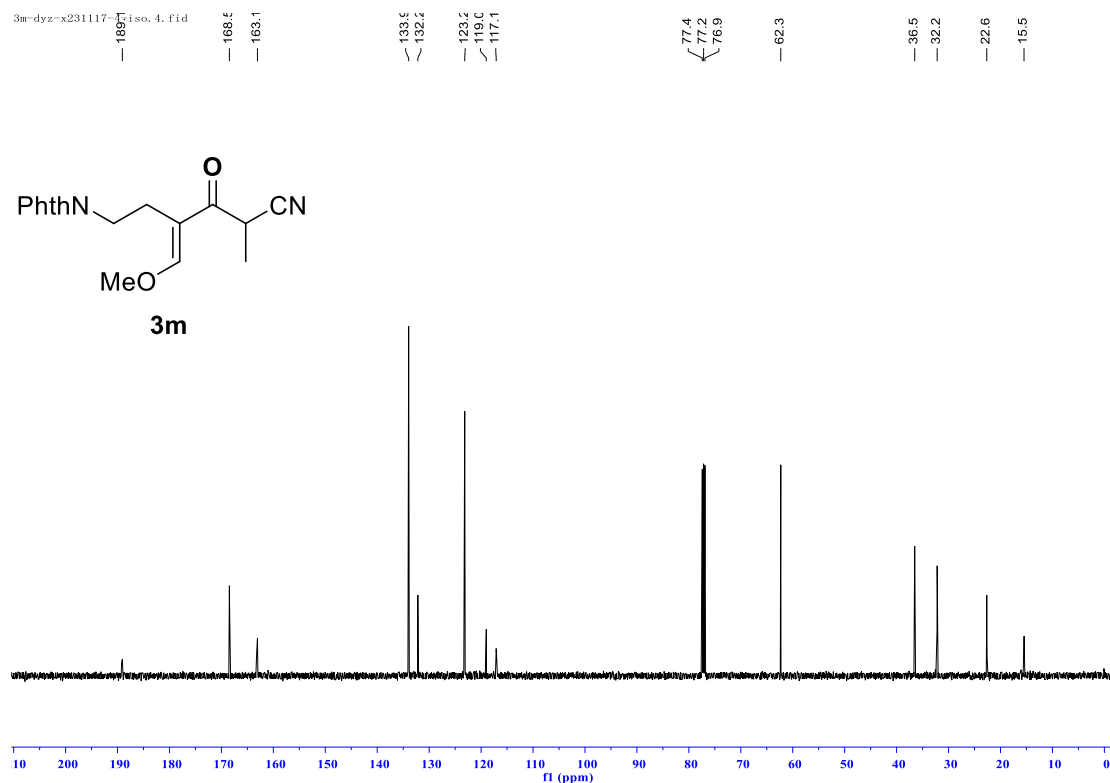
### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3l



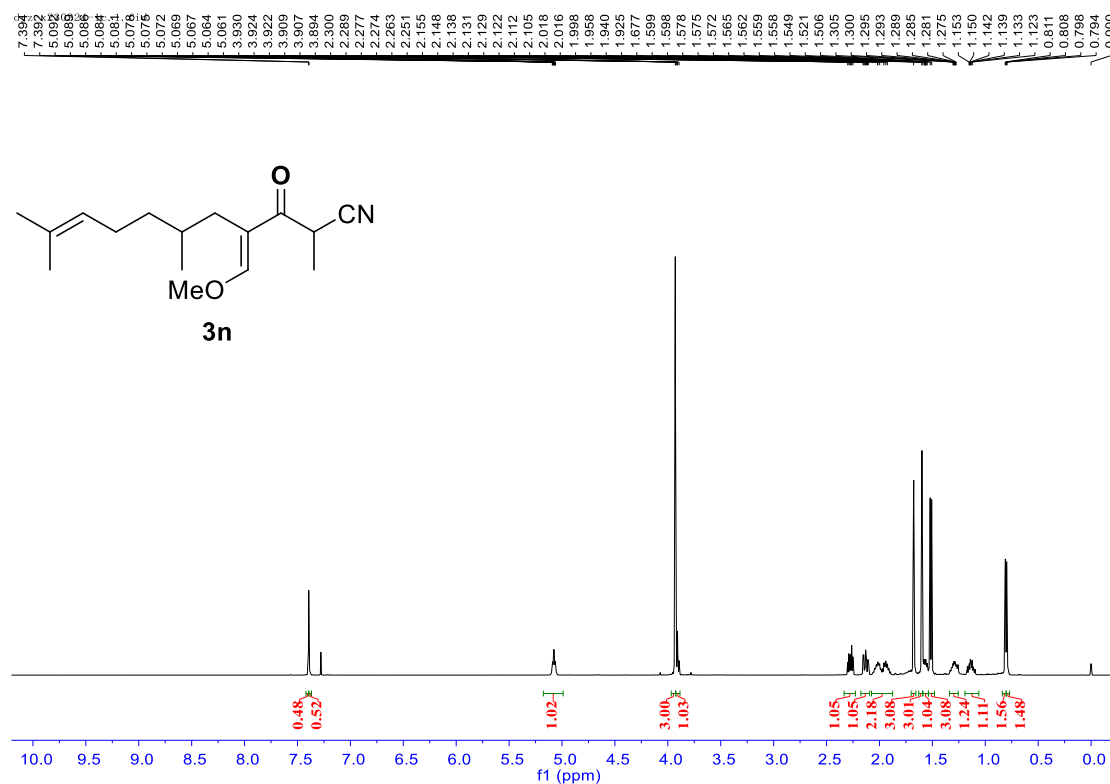
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3m



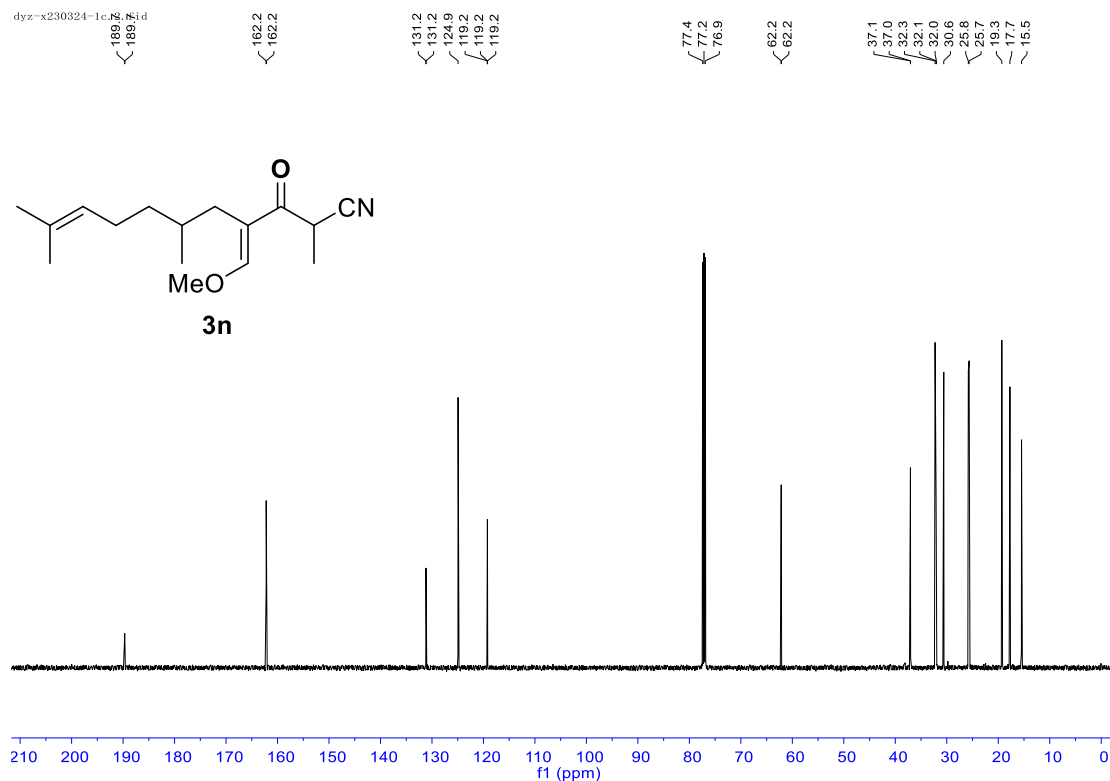
### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3m



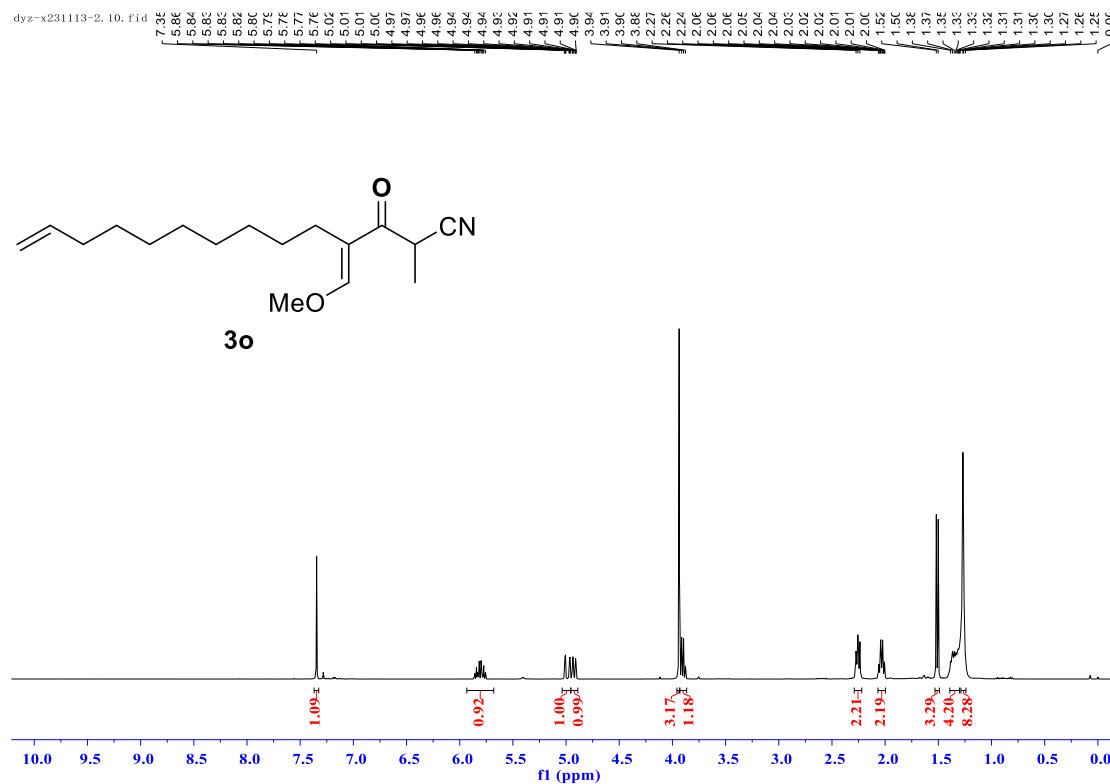
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3n



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3n



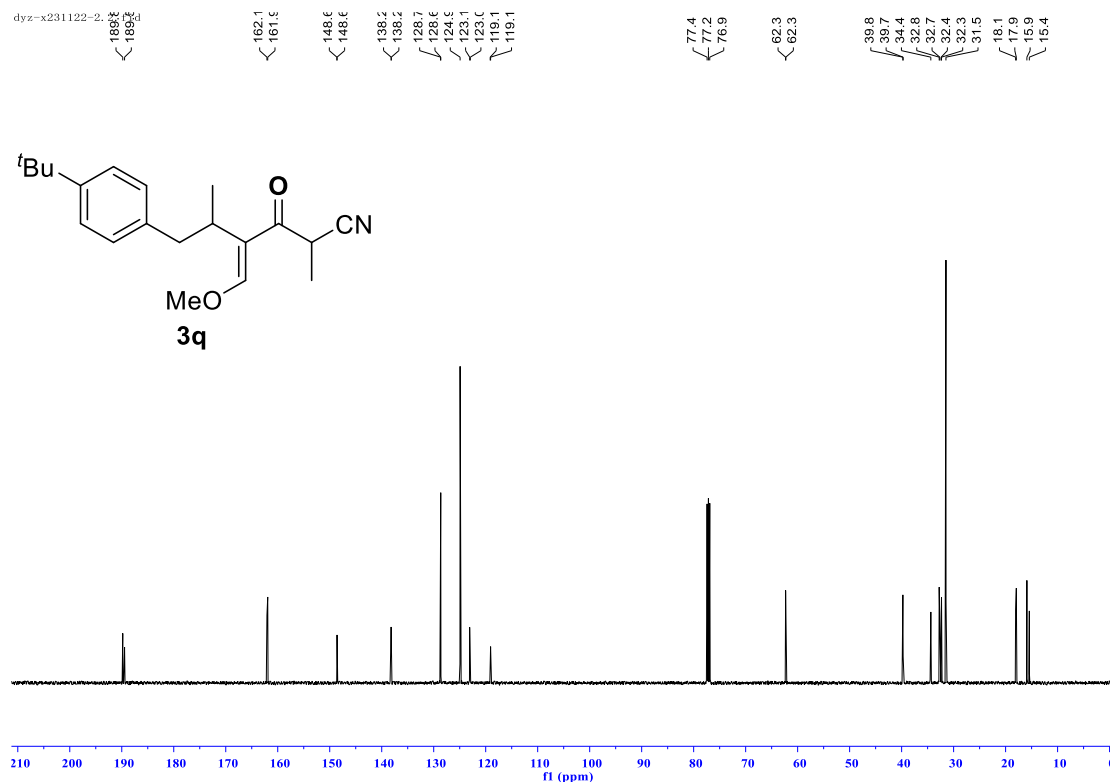
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum for 3o



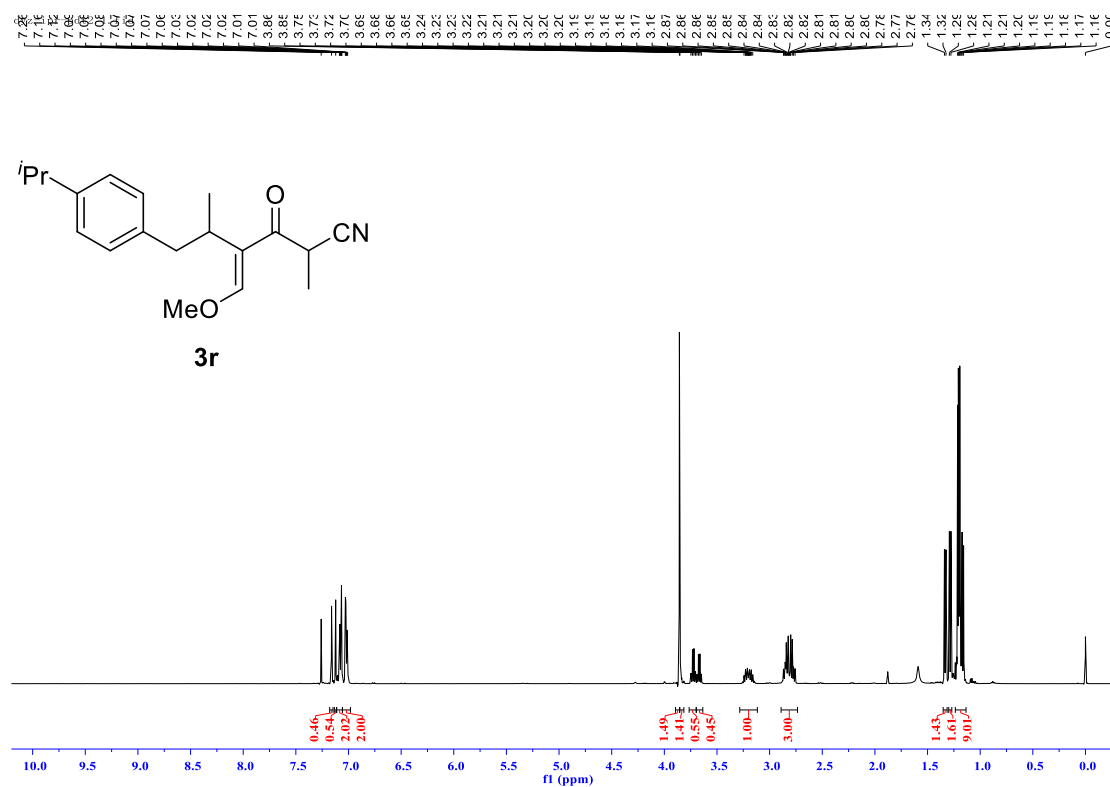




**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3q**

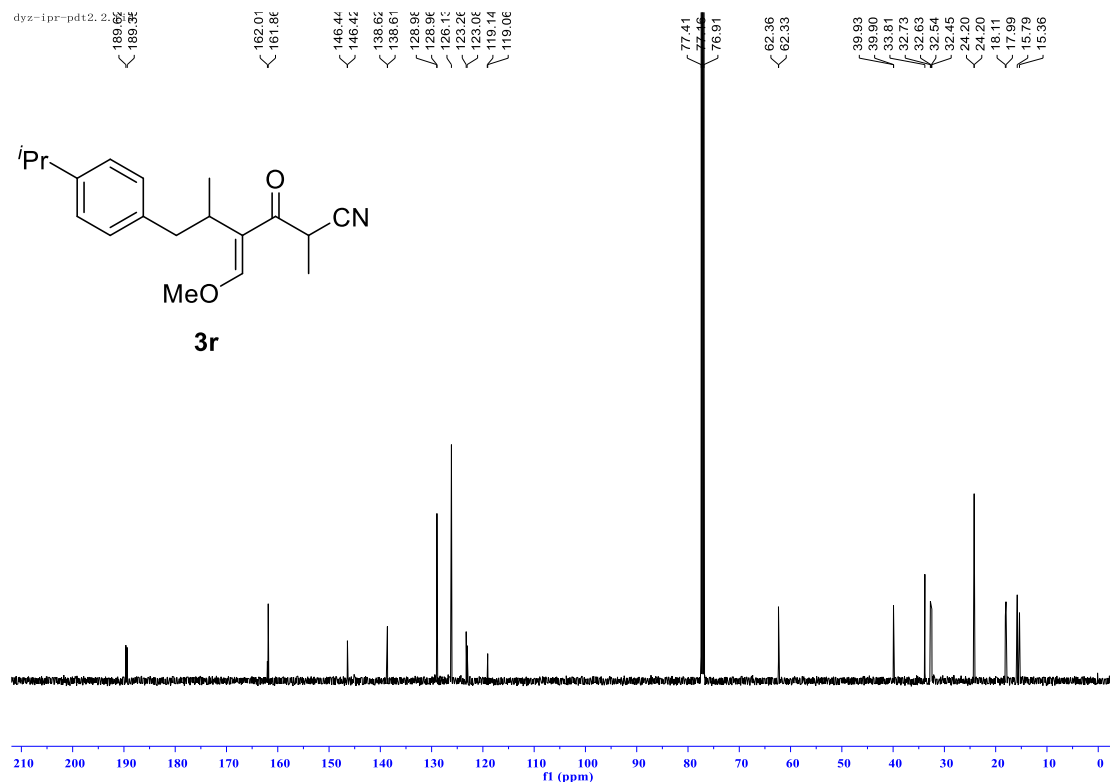


**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3r**

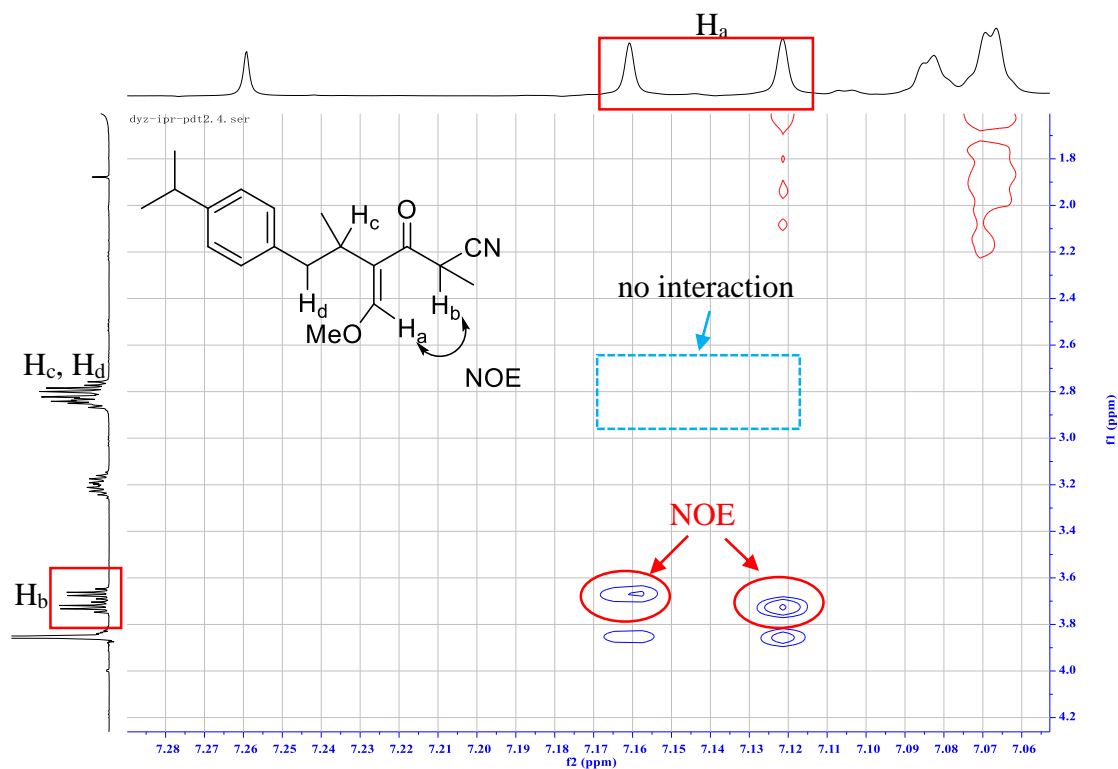




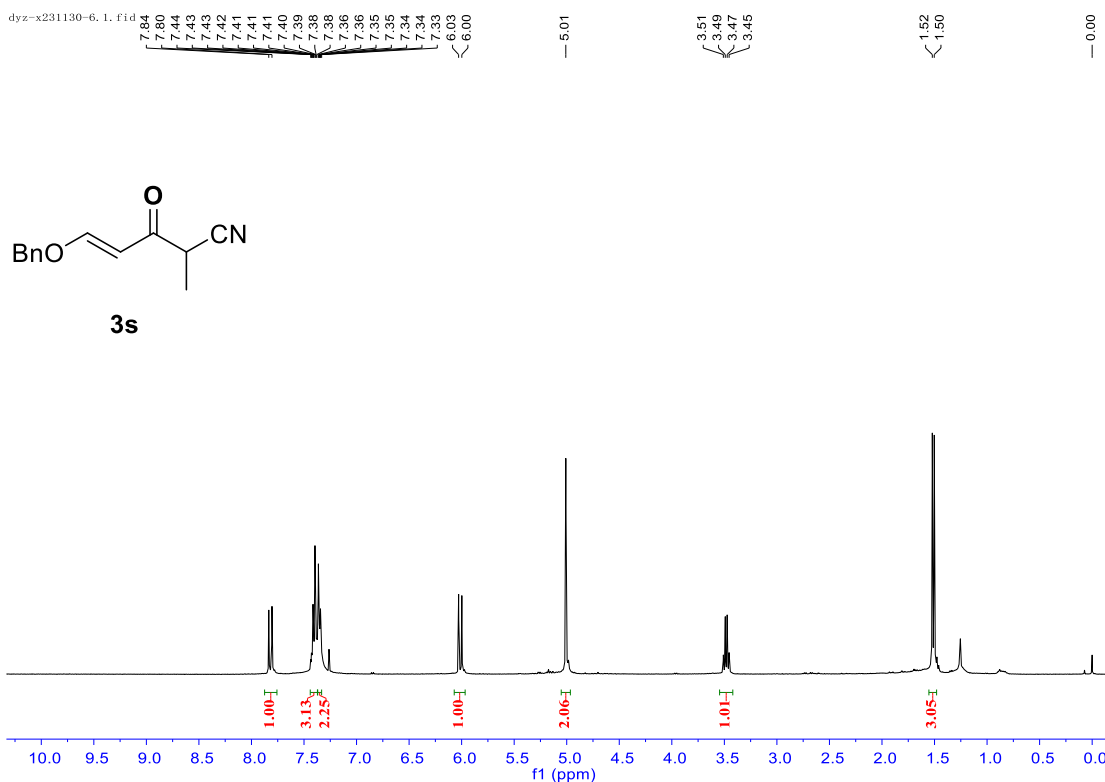
### $^{13}\text{C}$ NMR (126 MHz, $\text{CDCl}_3$ ) spectrum for 3r



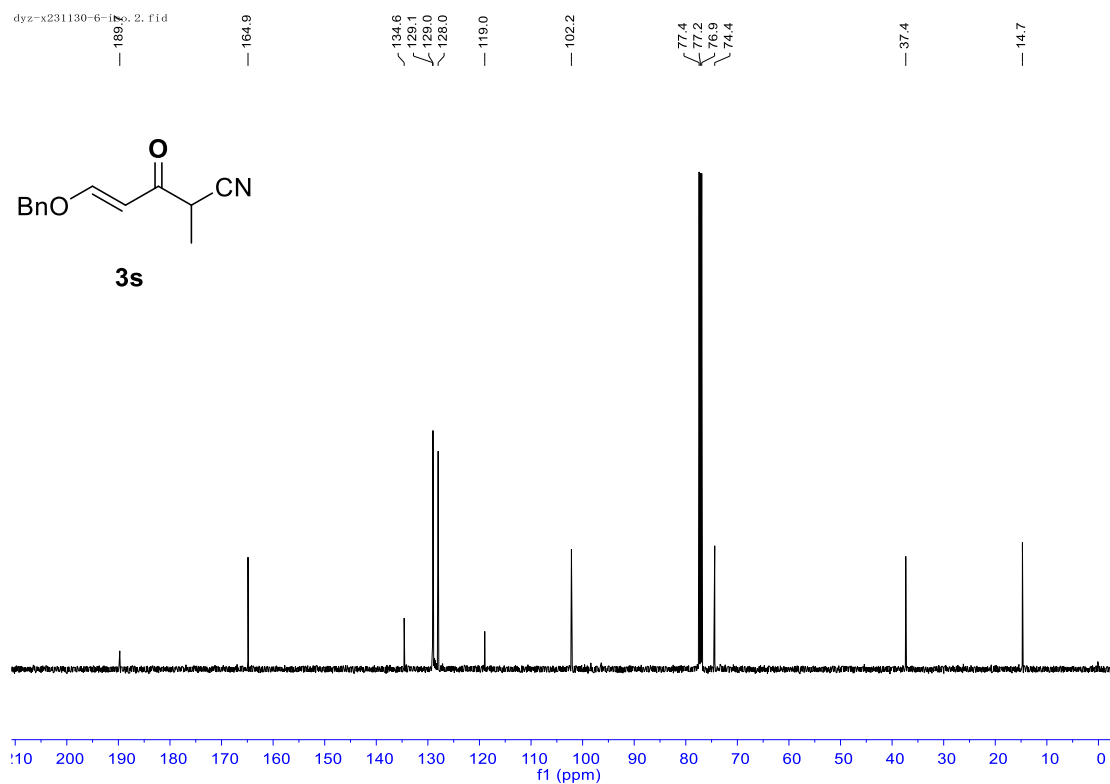
### NOESY (500 MHz, $\text{CDCl}_3$ ) spectrum for 3r



### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum for 3s



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3s



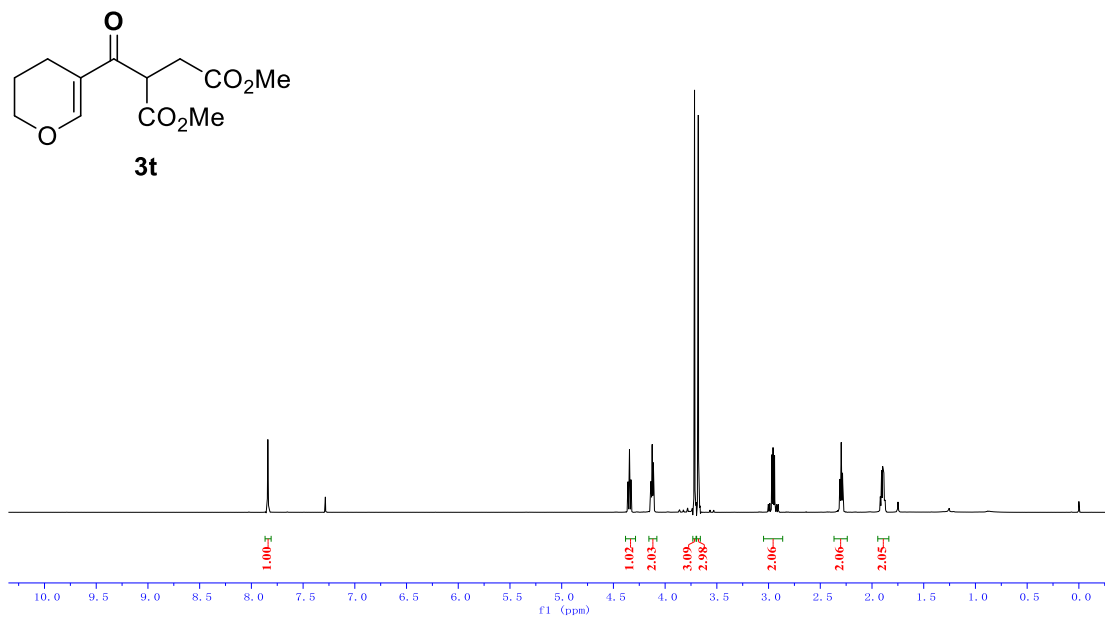
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3t

dyz-co2me-二甲酯. 1. f1d

7.84

4.36  
4.34  
4.33  
4.14  
4.13  
4.12  
4.11  
3.72  
3.68  
3.00  
2.99  
2.97  
2.96  
2.95  
2.94  
2.92  
2.91  
2.31  
2.30  
2.28  
1.92  
1.91  
1.90  
1.89  
1.88  
1.87

0.00



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3t

dyz-co2me-二甲酯. 2. f1d

191.1

172.1

169.7

159.3

116.1

77.4

77.2

76.9

67.4

52.9

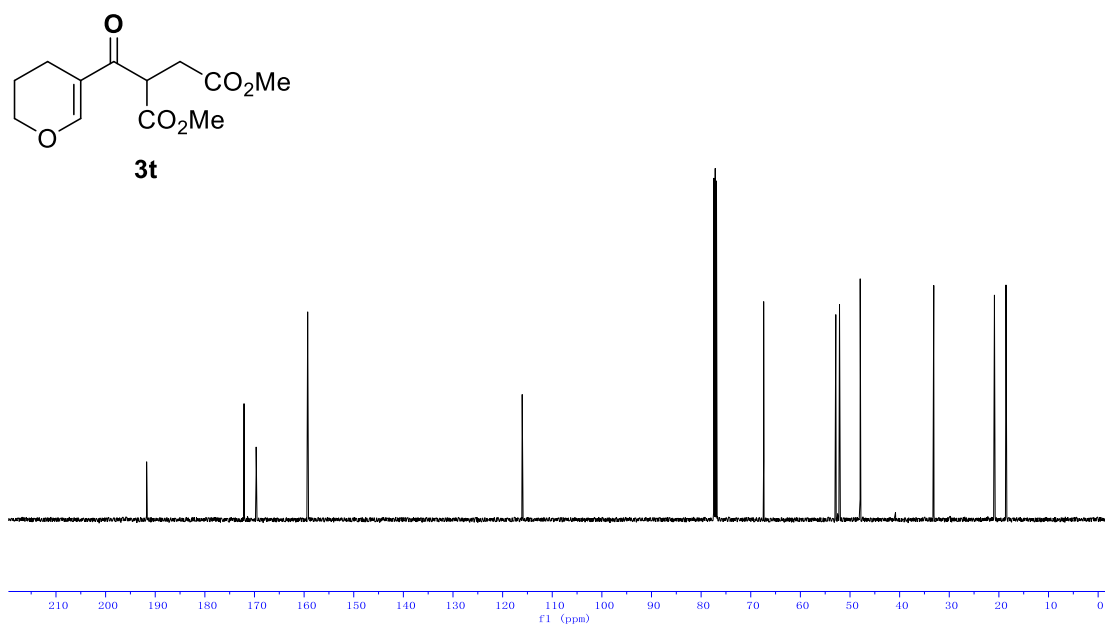
52.1

47.9

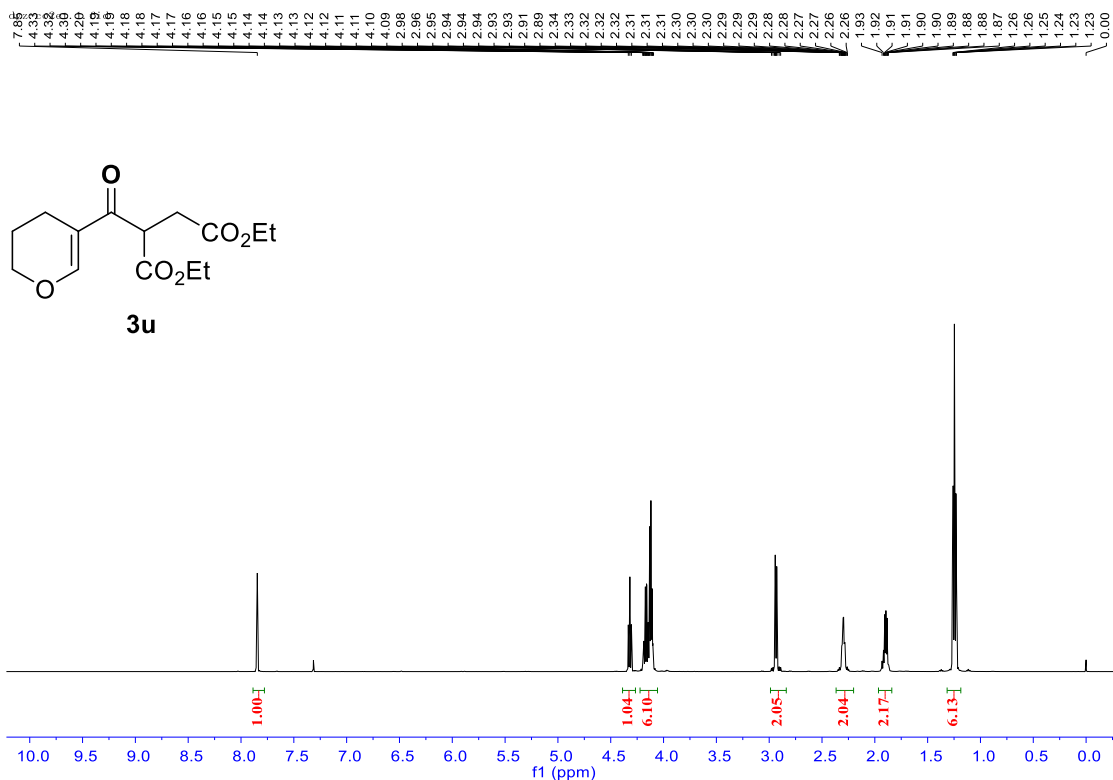
33.1

20.9

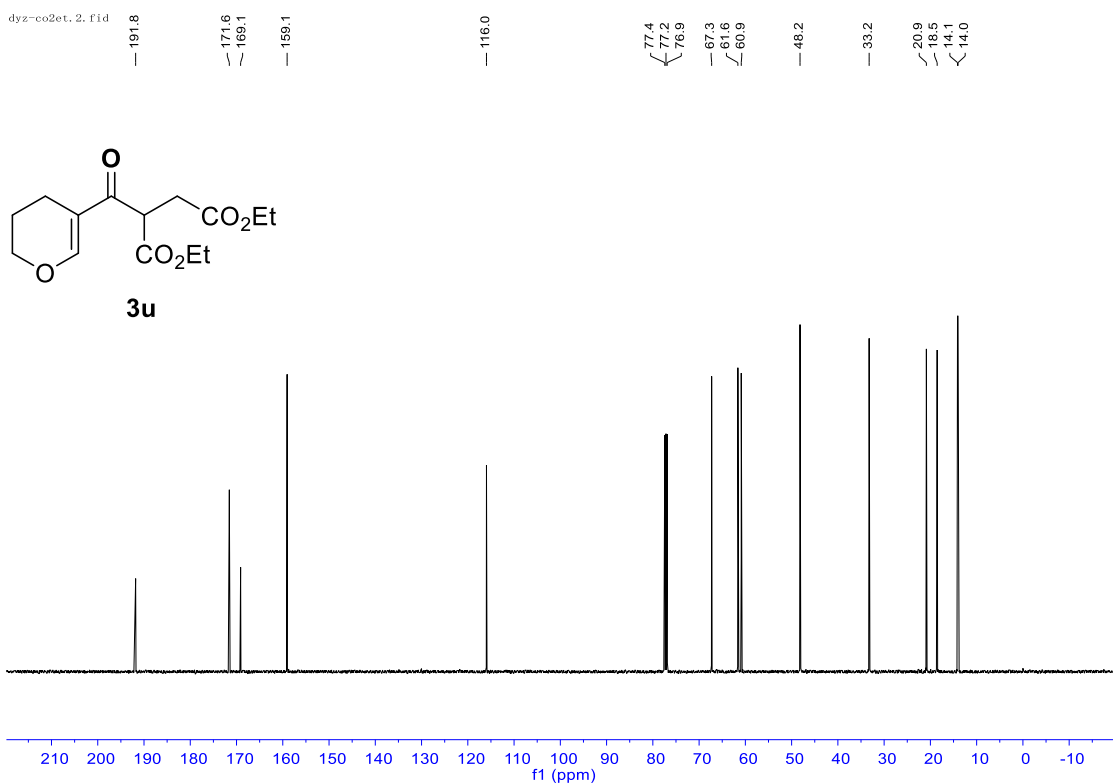
18.6



### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3u

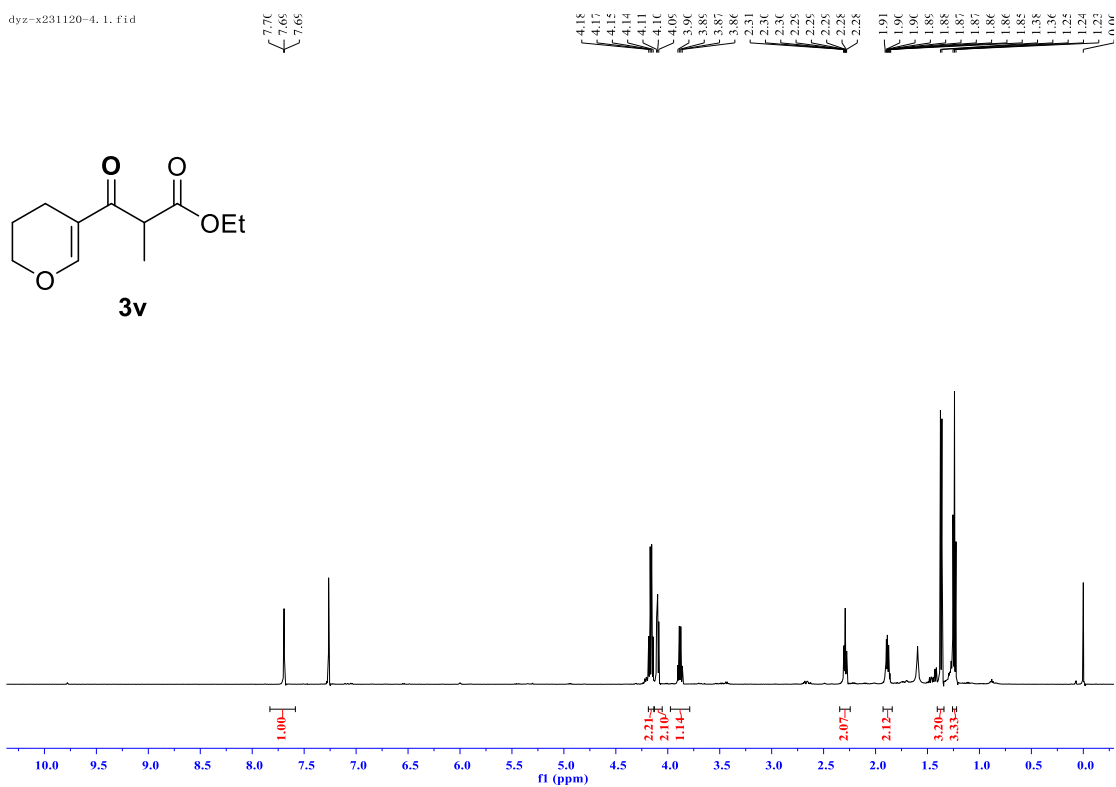


### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3u



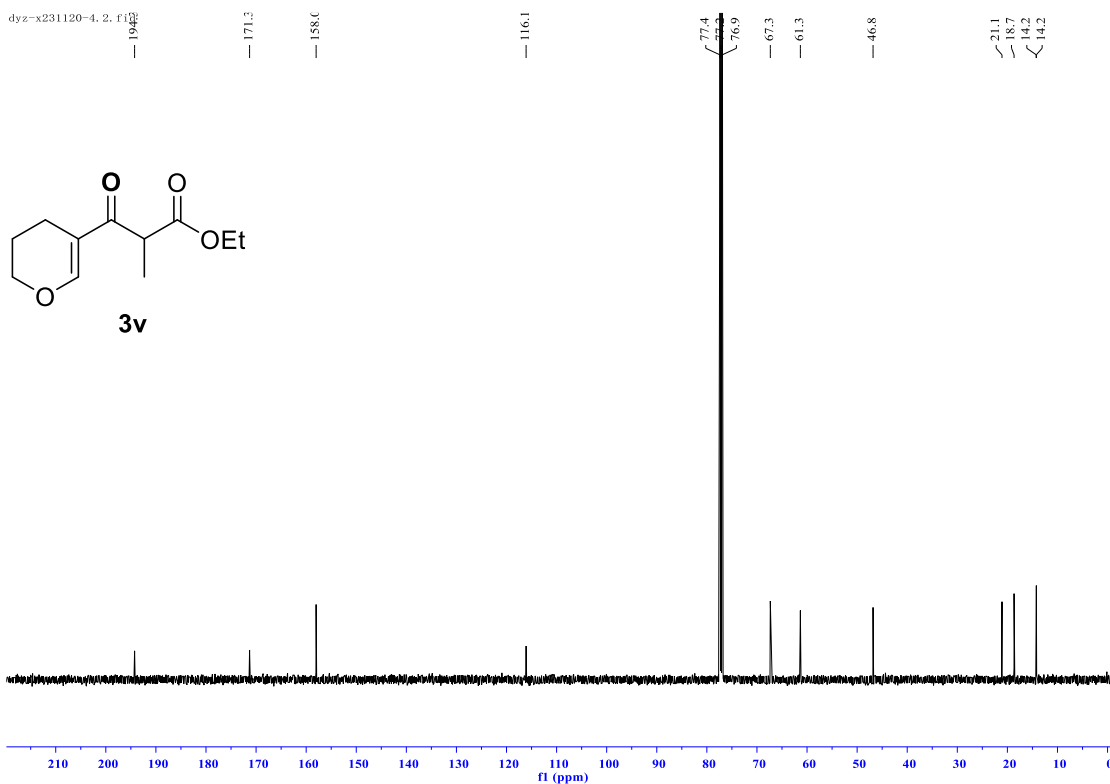
# <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 3v

dyz-x231120-4.1.fid



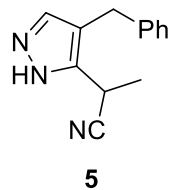
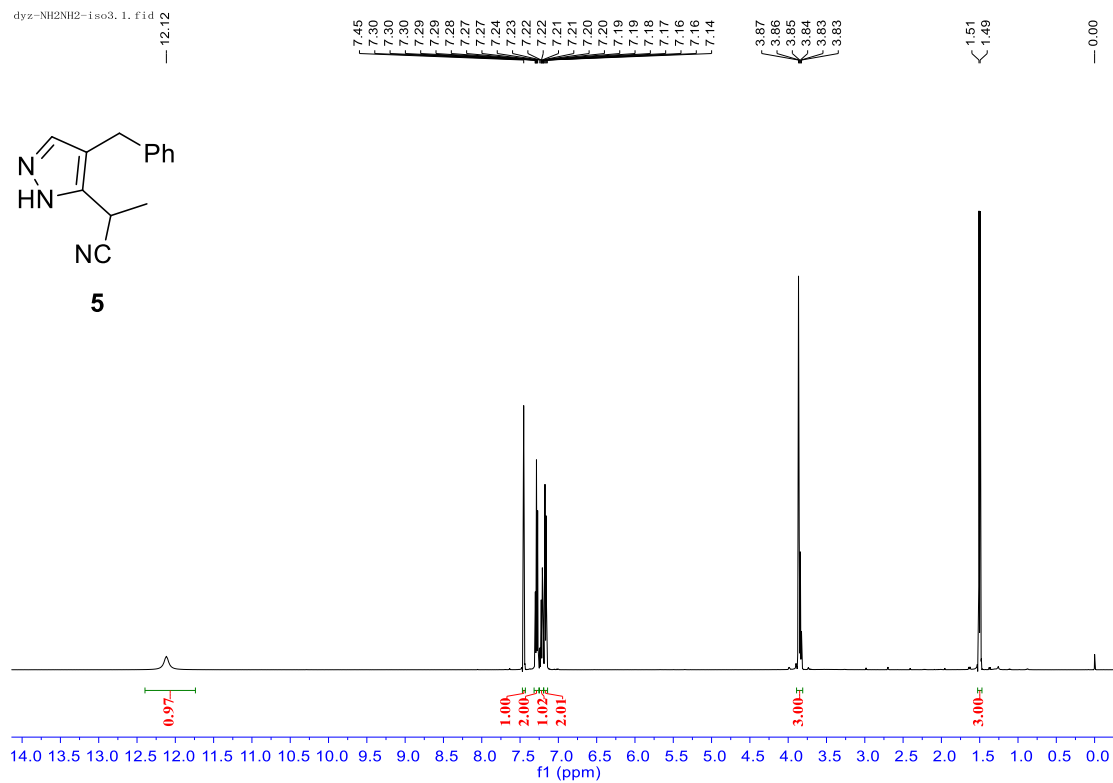
# <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 3v

dyz-x231120-4.2.fid

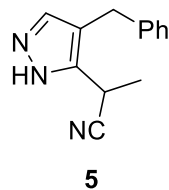
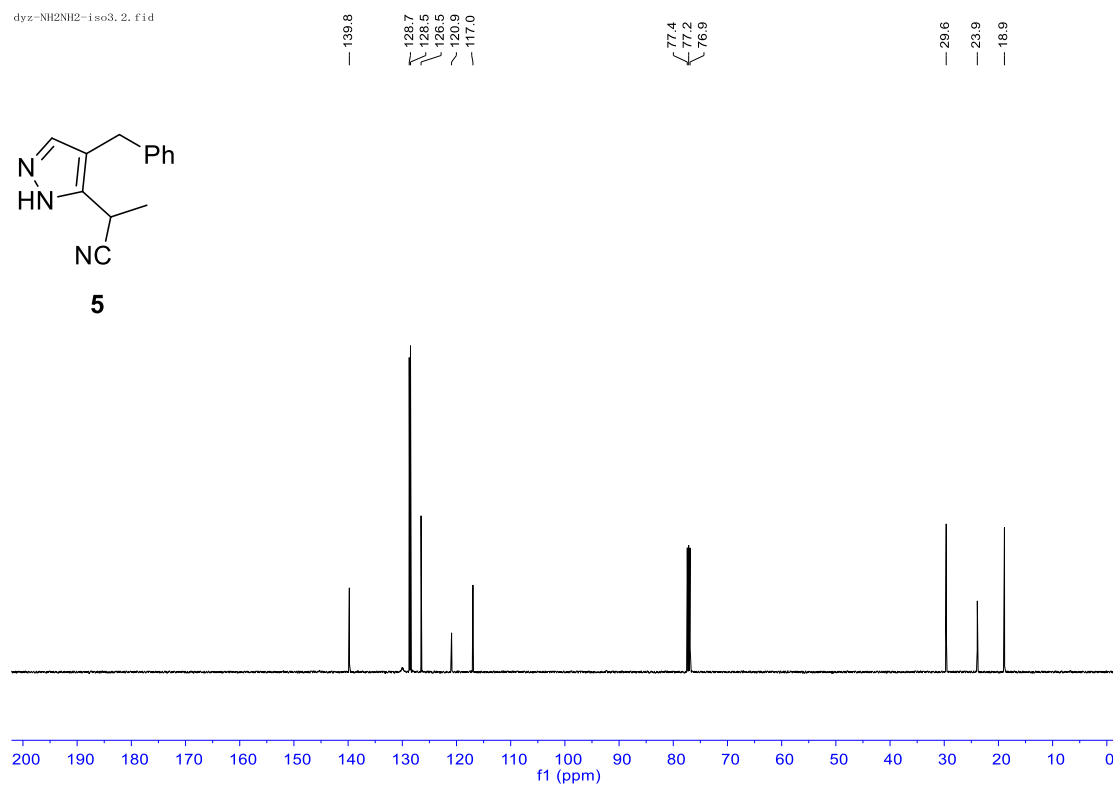




# <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 5

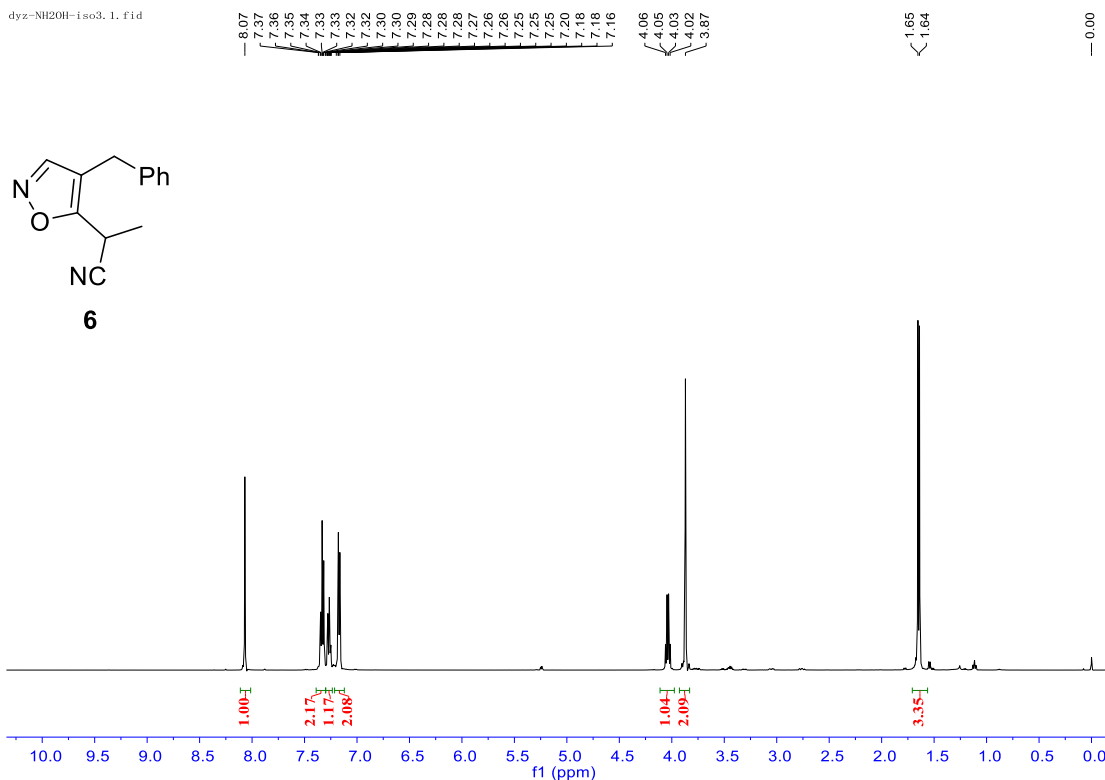


# <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 5



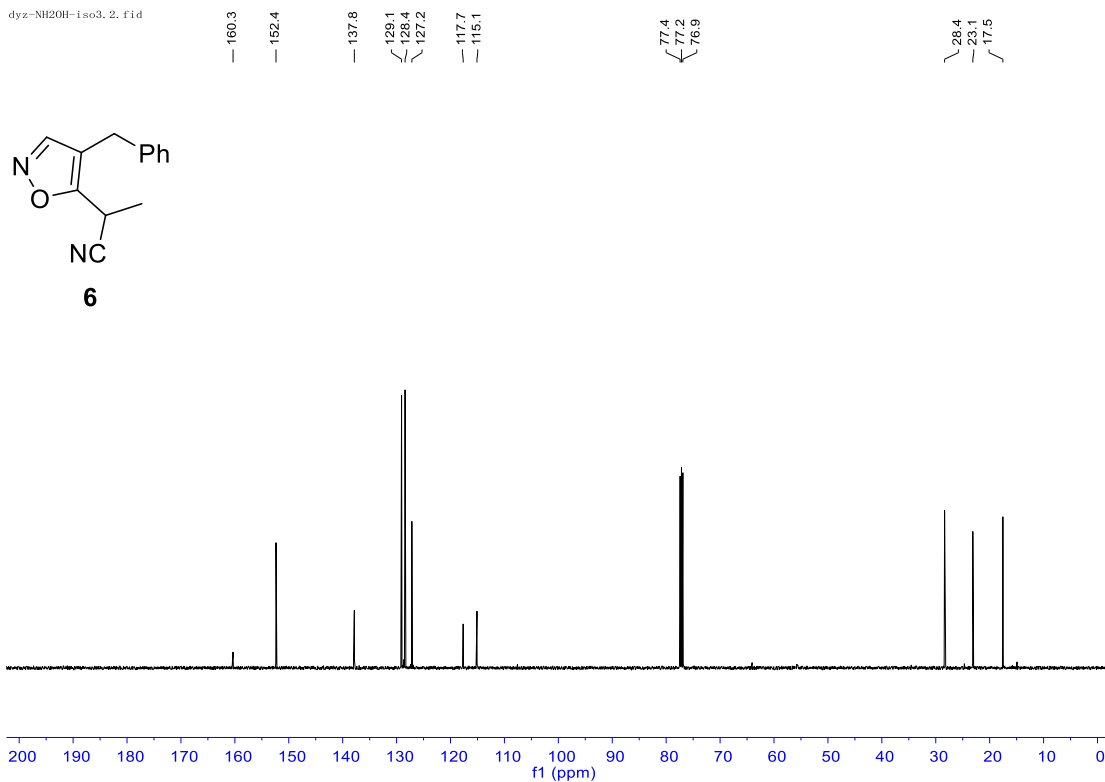
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 6

dyz-NH20H-iso3.1.fid



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 6

dyz-NH20H-iso3.2.fid

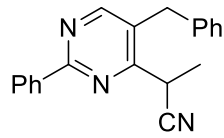




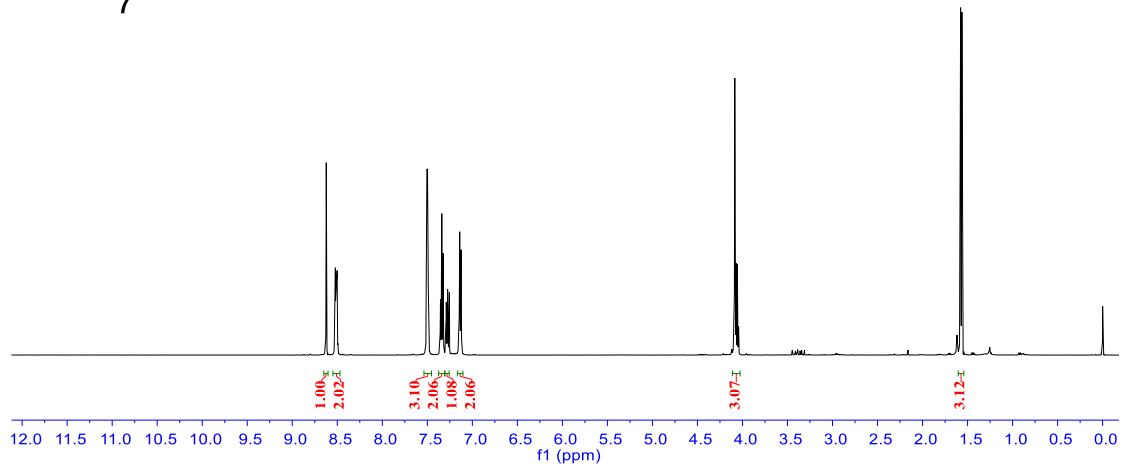
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum for 7

dyz-bianmi-iso3.1.fid

8.62 8.63 8.63 8.63 8.62 8.62 8.62 8.61 8.61 8.61 8.60 8.60 8.49 8.49 7.52 7.51 7.51 7.51 7.50 7.50 7.50 7.49 7.49 7.48 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.14 7.14 7.14 7.13 7.13 7.12 7.12 4.10 4.09 4.07 4.06 4.05 4.04 1.58 1.56



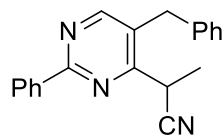
7



### <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum for 7

dyz-bianmi-iso3.2.fid

163.6 162.4 159.5 137.5 136.8 131.1 129.3 128.8 128.6 128.3 127.4 119.8 77.4 77.2 76.9 35.3 30.4 17.9



7

